Gallium(III)- and Calcium(II)-Catalyzed Meyer-Schuster Rearrangements Followed by Intramolecular Aldol Condensation or *endo*-Michael Addition

Supporting Information

Marc Presset, Bastien Michelet, Régis Guillot, Christophe Bour, Sophie Bezzenine-Lafollée and Vincent Gandon*

vincent.gandon@u-psud.fr

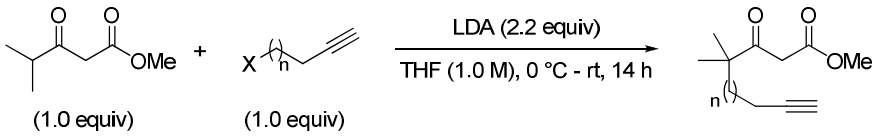
Table of Contents:

1. General experimental information

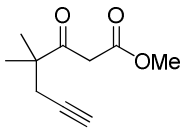
All commercially available reagents were used as received. In particular, $Ca(NTf_2)_2$ and $[JohnPhosAu(CH_3CN)]SbF_6$ were purchased from Aldrich; JohnPhosAuCl from Strem Chemicals; $Cu(OTf)_2$ from Acros; KPF_6 from Alfa-Aesar. $[IPrGaCl_2]SbF_6$ was prepared following our reported procedure.[1] Tetrahydrofuran (THF) was distilled over Na in the presence of benzophenone prior to use. Reactions in overheated solvent were performed in 10 mL reaction tubes sealed with a teflon-coated rodaviss stopper and immersed in a pre-heated oil bath. Analytical thin-layer chromatography (TLC) was performed on TLC silica gel plates (0.25 mm) precoated with a fluorescent indicator. Flash chromatography (FC) was performed on 40-63 μm silica gel with mixtures of ethyl acetate (EA) and cyclohexane (Cy). Visualization was effected with ultraviolet light and/or *p*-anisaldehyde stain. NMR spectra were recorded on AM250, AV300, AV360, DRX400 MHz Bruker spectrometers. ^{1}H NMR chemical shifts were referenced to the residual solvent signal; ^{13}C NMR chemical shifts were referenced to the deuterated solvent signal. Multiplicity was defined by DEPT 135 analysis. Data are presented as follows: chemical shift δ (ppm), multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *br* = broad), coupling constant *J* (Hz), integration. High-resolution mass spectra were obtained by electrospray ionization on a TOF instrument (MicrOTOFq Bruker spectrometer).

2. Starting materials

2.1. Preparation of yne-β-ketoesters SM1[2] and SM2[3]



General procedure for the y-alkylation of methyl isobutyrylacetate: An oven-dried round bottom flask equipped with a stir bar and closed with a septum was evacuated and placed under Ar (balloon). THF (c = 1 M) and di*iso*propylamine (2.2 equiv) were added (by syringes) and the mixture was cooled to 0 °C (ice-water bath). *n*-BuLi (2.2 equiv) was added by syringe and the resulting solution was stirred at 0 °C for 15 min. Methyl isobutyrylacetate (1.0 equiv) was added by syringe and the resulting solution was stirred at 0 °C for 15 min. The alkylating reagent (1.0 equiv) was added by syringe. The reaction was allowed to warm to rt and stirred for 14 h. Then, the reaction mixture was poured into sat aq NH_4Cl and this solution was extracted twice with EtOAc. The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated. Purification by FC afforded the desired product.

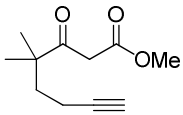


SM1, 54%
$C_{10}H_{14}O_3$
MW=182.22

Following the general procedure, the reaction performed with methyl isobutyrylacetate (4.0 mL, 28.0 mmol, 1.0 equiv) and propargyl bromide (3.1 mL, purity = 80%, 28.0 mmol, 1.0 equiv) afforded, after purification by FC (250 mL SiO_2, EA/Cy:0.5/9.5 then 1/9), the desired product (3.266 g, purity = 84%, 54% yield) as a yellow oil. On different runs, this product has been obtained in 72 – 84% purity.

Rf (EA/Cy:1/9, UV+pAnis): 0.30. **^{1}H NMR (250 MHz, $CDCl_3$):** (major keto form) δ 3.64 (s, 3H), 3.54 (s, 2H), 2.32 (d, *J* = 2.6 Hz, 2H), 1.99 (t, *J* = 2.6 Hz, 1H), 1.18 (s, 6H). **^{13}C NMR**

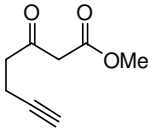
(63 MHz, $CDCl_3$): (major keto form) δ 206.1 (C), 167.8 (C), 80.5 (C), 71.2 (CH), 52.2 (CH_3), 47.5 (C), 44.3 (CH_2), 28.3 (CH_2), 23.5 (2 CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{10}H_{15}O_3$ $(M + H)^+$ 183.1016, found 183.1019.



SM2, 58%
$C_{11}H_{16}O_3$
MW=196.24

Following the general procedure, the reaction performed with methyl isobutyrylacetate (2.0 mL, 14.0 mmol, 1.0 equiv) and 4-bromobutyne (1.3 mL, 14.0 mmol, 1.0 equiv) afforded, after purification by FC (250 mL SiO_2, EA/Cy:0.5/9.5 then 1/9), the desired product (1.945 g, purity = 82%, 58% yield) as a yellow oil. On different runs, this product has been obtained in 77 – 84% purity.

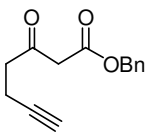
Rf (EA/Cy:1/9, UV+pAnis): 0.31. **^{1}H NMR (250 MHz, $CDCl_3$):** δ 3.64 (s, 3H), 3.49 (s, 2H), 2.10 – 1.98 (m, 2H), 1.90 (t, *J* = 4 Hz, 1H), 1.74 (dd, *J* = 11, 4 Hz, 2H), 1.09 (s, 6H). **^{13}C NMR (63 MHz, $CDCl_3$):** (keto/enol forms) δ 207.0 (C), 183.4 (C), 173.3 (C), 168.0 (C), 87.1 (CH), 84.3 (C), 83.6 (C), 69.0 (C), 68.3 (C), 52.2 (CH_3), 51.1 (CH_3), 47.7 (C), 46.7 (C), 44.0 (CH_2), 39.1 (CH_2), 37.9 (CH_2), 25.2 (2 CH_3), 23.8 (2 CH_3), 14.1 (2 CH_2). **HRMS (ESI+):** *m/z* calcd. for $C_{11}H_{16}NaO_3$ $(M + Na)^+$ 219.0992, found 219.0981.



SM3, 44%
$C_8H_{10}O_3$
MW=154.16

Following the general procedure, the reaction performed with the methyl acetoacetate (2.0 mL, 18.5 mmol, 1.0 equiv) and propargyl bromide (2.1 mL, purity = 80%, 18.5 mmol, 1.0 equiv) afforded, after purification by FC (250 mL SiO_2, EA/Cy:0.5/9.5 then 1/9), the desired product (1.26 g, 44%) as a yellow oil.

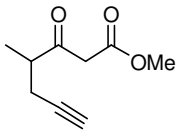
Rf (EA/Cy:1/9, UV+pAnis): 0.14. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 3.67 (s, 3H), 3.43 (s, 2H), 2.75 (t, *J* = 7.2 Hz, 2H), 2.39 (td, *J* = 7.2, 2.7 Hz, 2H), 1.92 (t, *J* = 2.7 Hz, 1H). **^{13}C NMR (90 MHz, $CDCl_3$):** (major keto form) δ 200.5 (C), 167.3 (C), 82.5 (C), 69.0 (CH), 52.4 (CH_3), 48.8 (CH_2), 41.5 (CH_2), 12.7 (CH_2). **HRMS (ESI+):** *m/z* calcd. for $C_8H_{10}NaO_3$ $(M + Na)^+$ 177.0522, found 177.0524.



SM4, 41%
$C_{14}H_{14}O_3$
MW=230.26

Following the general procedure, the reaction performed with the benzyl acetoacetate (2.0 mL, 11.5 mmol, 1.0 equiv) and propargyl bromide (1.3 mL, purity = 80%, 11.5 mmol, 1.0 equiv) afforded, after purification by FC (250 mL SiO_2, EA/Cy:0.5/9.5 then 1/9), the desired product (1.100 g, 41%) as a yellow oil.

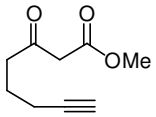
Rf (EA/Cy:1/9, UV+pAnis): 0.28. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.35 (s, 5H), 5.16 (s, 2H), 3.49 (s, 2H), 2.75 (t, *J* = 7.2 Hz, 2H), 2.43 (td, *J* = 7.2, 2.6 Hz, 2H), 1.98 (t, *J* = 2.6 Hz, 1H). **^{13}C NMR (90 MHz, $CDCl_3$):** (major keto form) δ 200.3 (C), 166.6 (C), 135.2 (C), 128.5 (2 CH), 128.3 (CH), 128.2 (2 CH), 82.5 (C), 69.0 (CH), 66.9 (CH_2), 48.8 (CH_2), 41.4 (CH_2), 12.6 (CH_2). **HRMS (ESI+):** *m/z* calcd. for $C_{14}H_{14}NaO_3$ $(M + Na)^+$ 253.0835, found 253.0832.



SM5, 66%
$C_9H_{12}O_3$
MW=168.19

Following the general procedure, the reaction performed with the methyl 3-oxovalerate (2.0 mL, 15.9 mmol, 1.0 equiv) and propargyl bromide (1.8 mL, purity = 80%, 15.9 mmol, 1.0 equiv) afforded, after purification by FC (250 mL SiO_2, EA/Cy:0.5/9.5 then 1/9), the desired product (1.78 g, 66%) as a yellow oil.

Rf (EA/Cy:1/9, UV+pAnis): 0.24. **^{1}H NMR (360 MHz, $CDCl_3$):** δ 3.64 (s, 3H), 3.48 (s, 2H), 2.78 (dq, J = 16.9, 7.1 Hz, 1H), 2.40 (ddd, J = 16.9, 6.8, 2.7 Hz, 1H), 2.24 (ddd, J = 16.9, 6.8, 2.7 Hz, 1H), 1.95 (t, J = 2.7 Hz, 1H), 1.15 (d, J = 7.1 Hz, 3H). **^{13}C NMR (90 MHz, $CDCl_3$):** (major keto form) δ 204.2 (C), 167.4 (C), 81.3 (C), 70.2 (CH), 52.2 (CH_3), 47.6 (CH_2), 45.3 (CH), 21.5 (CH_2), 15.6 (CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_9H_{12}NaO_3$ $(M + Na)^+$ 191.0679, found 191.0682.

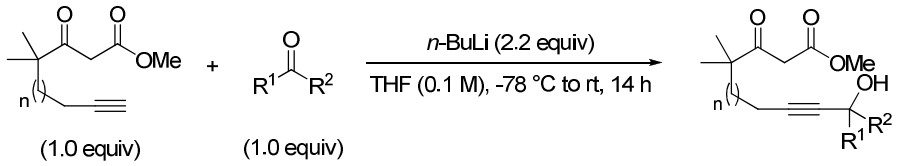


SM6, 42%
$C_9H_{12}O_3$
MW=168.19

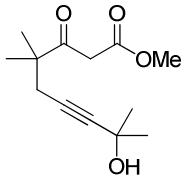
Following the general procedure, the reaction performed with the methyl acetoacetate (0.6 mL, 5.33 mmol, 1.0 equiv) and 4-bromobutyne (0.5 mL, 5.33 mmol, 1.0 equiv) afforded, after purification by FC (100 mL SiO_2, EA/Cy:0.5/9.5 then 1/9), the desired product (378 mg, 42%) as a yellow oil.

Rf (EA/Cy:1/9, UV+pAnis): 0.20. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 3.65 (s, 3H), 3.40 (s, 2H), 2.62 (t, J = 7.1 Hz, 2H), 2.16 (td, J = 6.8, 2.6 Hz, 2H), 1.92 (t, J = 2.6 Hz, 1H), 1.75 – 1.70 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$):** (major keto form) δ 202.1 (C), 167.5 (C), 83.3 (C), 69.3 (CH), 52.3 (CH_3), 49.0 (CH_2), 41.3 (CH_2), 21.9 (CH_2), 17.5 (CH_2). **HRMS (ESI+):** *m/z* calcd. for $C_9H_{12}NaO_3$ $(M + Na)^+$ 191.0679, found 191.0680.

2.2. Preparation of the propargylic alcohols derived from β-ketoesters



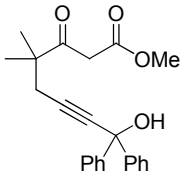
General procedure: A round bottom flask equipped with a stir bar was charged with the alkyne (1.0 equiv), closed with septum, evacuated and backfilled with Ar (balloon). THF (c = 0.1 M) was added by syringe and the solution was cooled to -78 °C (dry ice-acetone bath). *n*-BuLi (2.2 equiv) was added by syringe and the resulting solution was stirred at -78 °C for 5 min. The carbonylated compound (1.0 equiv) was added (by syringe for liquids or by quick removal of the septum for solids). The reaction was allowed to warm to rt and stirred for 14 h. Then, the reaction mixture was poured into sat aq NH_4Cl and this solution was extracted twice with EtOAc. The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated. Purification by FC afforded the desired product.



1a, 77%
$C_{13}H_{20}O_4$
MW=240.30

Following the general procedure, the reaction performed with **SM1** (482 mg, purity = 72%, 1.90 mmol, 1.0 equiv) and acetone (0.14 mL, 1.90 mmol, 1.0 equiv) in THF (20 mL) afforded, after purification by FC (50 mL SiO_2, EA/Cy:2/8 then 4/6), the desired product **1a** (351 mg, 77%) as a yellow oil.

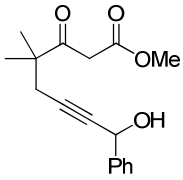
Rf (EA/Cy:2/8, UV+pAnis): 0.14. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 3.59 (s, 3H), 3.51 (s, 2H), 3.15 (br, 1H), 2.24 (s, 2H), 1.33 (s, 6H), 1.09 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** (major keto form) δ 206.5 (C), 168.1 (C), 88.4 (C), 77.9 (C), 64.6 (C), 52.1 (CH_3), 47.8 (C), 44.5 (CH_2), 31.3 (2 CH_3), 28.9 (CH_2), 23.5 (2 CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{13}H_{20}NaO_4$ $(M + Na)^+$ 263.1254, found 263.1255.



1b, 70%
$C_{23}H_{24}O_4$
MW=364.43

Following the general procedure, the reaction performed with **SM1** (506 mg, purity = 83%, 2.30 mmol, 1.0 equiv) and benzophenone (420 mg, 2.30 mmol, 1.0 equiv) in THF (10 mL) afforded, after purification by FC (100 mL SiO_2, EA/Cy:1/9 then 2/8), the desired product **1b** (591 mg, 70%) as a pale yellow paste.

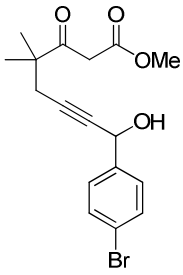
Rf (EA/Cy:2/8, UV+pAnis): 0.42. **^{1}H NMR (360 MHz, $CDCl_3$):** δ 7.60 (d, J = 7.5 Hz, 4H), 7.33 (dd, J = 7.5, 7.5 Hz, 4H), 7.29 – 7.24 (m, 2H), 3.68 (s, 3H), 3.59 (s, 2H), 2.55 (s, 2H), 2.03 (br, 1H), 1.27 (s, 6H). **^{13}C NMR (90 MHz, $CDCl_3$):** (major keto form) δ 206.4 (C), 168.1 (C), 145.3 (2 C), 128.1 (4 CH), 127.5 (2 CH), 125.9 (4 CH), 86.3 (C), 83.9 (C), 74.3 (C), 52.3 (CH_3), 48.0 (C), 44.6 (CH_2), 29.4 (CH_2), 23.9 (2 CH_3). **HRMS (ESI+):** *m*/*z* calcd. for $C_{23}H_{24}NaO_4$ $(M + Na)^+$ 387.1567, found 387.1559.



1c, 58%
$C_{17}H_{20}O_4$
MW=288.34

Following the general procedure, the reaction performed with **SM1** (521 mg, purity = 83%, 2.37 mmol, 1.0 equiv) and benzaldehyde (0.24 mL, 2.37 mmol, 1.0 equiv) in THF (12 mL) afforded, after purification by FC (100 mL SiO_2, EA/Cy:2/8 then 4/6), the desired product **1c** (398 mg, 58%) as a yellow oil.

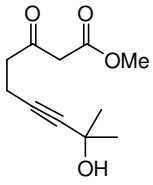
Rf (EA/Cy:4/6, UV+pAnis): 0.48. **^{1}H NMR (360 MHz, $CDCl_3$):** δ 7.48 – 7.46 (m, 2H), 7.35 – 7.25 (m, 3H), 5.38 (br s, 1H), 3.66 (s, 3H), 3.56 (s, 2H), 3.49 (br, 1H), 2.43 (d, J = 2.0 Hz, 2H), 1.21 (s, 6H). **^{13}C NMR (90 MHz, $CDCl_3$):** (major keto form) δ 206.5 (C), 168.1 (C), 141.1 (C), 128.4 (2 CH), 128.0 (CH), 126.4 (2 CH), 83.3 (C), 82.9 (C), 64.2 (CH), 52.2 (CH_3), 47.8 (C), 44.4 (CH_2), 29.0 (CH_2), 23.7 (2 CH_3). **HRMS (ESI+):** *m*/*z* calcd. for $C_{17}H_{20}NaO_4$ $(M + Na)^+$ 311.1254, found 311.1250.



1d, 60%
$C_{17}H_{19}BrO_4$
MW=367.23

Following the general procedure, the reaction performed with **SM1** (587 mg, purity = 83%, 2.67 mmol, 1.0 equiv) and 4-bromobenzaldehyde (495 mg, 2.67 mmol, 1.0 equiv) in THF (14 mL) afforded, after purification by FC (100 mL SiO_2, EA/Cy:2/8 then 4/6), the desired product **1d** (588 mg, 60%) as a yellow oil.

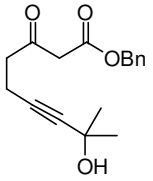
Rf (EA/Cy:4/6, UV+pAnis): 0.42. **^{1}H NMR (250 MHz, $CDCl_3$):** δ 7.44 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 5.31 (br s, 1H), 3.82 (br, 1H), 3.67 (s, 3H), 3.56 (s, 2H), 2.42 (s, 2H), 1.20 (s, 6H). **^{13}C NMR (63 MHz, $CDCl_3$):** (major keto form) δ 206.5 (C), 168.1 (C), 140.1 (C), 131.4 (2 CH), 128.2 (2 CH), 121.8 (C), 83.2 (C), 82.8 (C), 63.5 (CH), 52.3 (CH_3), 47.9 (C), 44.4 (CH_2), 29.0 (CH_2), 23.7 (2 CH_3). **HRMS (ESI+):** *m*/*z* calcd. for $C_{17}H_{19}BrNaO_4$ $(M + Na)^+$ 389.0359, found 389.0349.



1e, 41%
$C_{11}H_{16}O_4$
MW=212.24

Following the general procedure, the reaction performed with **SM3** (508 mg, 3.29 mmol, 1.0 equiv) and acetone (0.24 mL, 3.29 mmol, 1.0 equiv) in THF (30 mL) afforded, after purification by FC (50 mL SiO_2, EA/Cy:4/6 then 6/4), **1e** (286 mg, 41%) as a yellow oil.

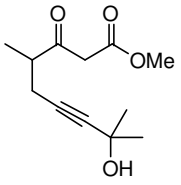
Rf (EA/Cy:4/6, UV+pAnis): 0.26. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 3.67 (s, 3H), 3.43 (s, 2H), 2.82 (br, 1H), 2.69 (t, J = 7.2 Hz, 2H), 2.38 (t, J = 7.2 Hz, 2H), 1.38 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** (major keto form) δ 201.1 (C), 167.5 (C), 86.1 (C), 80.1 (C), 64.9 (C), 52.4 (CH_3), 49.0 (CH_2), 41.2 (CH_2), 31.5 (2 CH_3), 13.1 (CH_2). **HRMS (ESI+):** m/z calcd. for $C_{11}H_{16}NaO_4$ $(M + Na)^+$ 235.0941, found 235.0940.



1f, 42%
$C_{17}H_{20}O_4$
MW=288.34

Following the general procedure, the reaction performed with **SM4** (555 mg, 2.41 mmol, 1.0 equiv) and acetone (0.18 mL, 2.41 mmol, 1.0 equiv) in THF (10 mL) afforded, after purification by FC (100 mL SiO_2, EA/Cy:2/8 then 4/6), **1f** (292 mg, 42%) as a yellow oil.

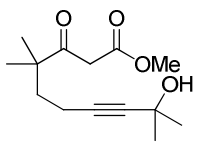
Rf (EA/Cy:4/6, UV+pAnis): 0.29. **^{1}H NMR (250 MHz, $CDCl_3$):** δ 7.33 (s, 5H), 5.14 (s, 2H), 3.49 (s, 2H), 2.84 (br, 1H), 2.70 (t, J = 7.2 Hz, 2H), 2.41 (t, J = 7.2 Hz, 2H), 1.43 (s, 6H). **^{13}C NMR (63 MHz, $CDCl_3$):** (major keto form) δ 200.9 (C), 166.9 (C), 135.1 (C), 128.5 (2 CH), 128.4 (CH), 128.3 (2 CH), 86.1 (C), 80.0 (C), 67.1 (CH_2), 64.8 (C), 49.1 (CH_2), 41.7 (C), 31.5 (2 CH_3), 13.1 (CH_2). **HRMS (ESI+):** m/z calcd. for $C_{17}H_{20}NaO_4$ $(M + Na)^+$ 311.1254, found 311.1244.



1g, 55%
$C_{12}H_{18}O_4$
MW=226.27

Following the general procedure, the reaction performed with **SM5** (515 mg, 3.06 mmol, 1.0 equiv) and acetone (0.22 mL, 3.06 mmol, 1.0 equiv) in THF (15 mL) afforded, after purification by FC (50 mL SiO_2, EA/Cy:2/8 then 4/6), **1g** (384 mg, 55%) as a pale yellow oil.

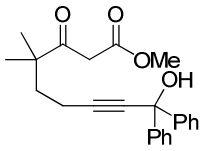
Rf (EA/Cy:4/6, UV+pAnis): 0.37. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 3.63 (s, 3H), 3.49 (s, 2H), 3.00 (br, 1H), 2.80 – 2.68 (m, 1H), 2.38 – 2.19 (m, 2H), 1.36 (s, 6H), 1.09 (d, J = 7.0 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** (major keto form) δ 204.9 (C), 167.7 (C), 87.5 (C), 78.7 (C), 64.7 (C), 52.3 (CH_3), 47.9 (CH_2), 45.4 (CH), 31.4 (CH_3), 31.4 (CH_3), 21.9 (CH_2), 15.7 (CH_3). **HRMS (ESI+):** m/z calcd. for $C_{12}H_{18}NaO_4$ $(M + Na)^+$ 249.1097, found 249.1097.



5a, 84%
$C_{14}H_{22}O_4$
MW=254.32

Following the general procedure, the reaction performed with **SM2** (347 mg, purity = 80%, 1.41 mmol, 1.0 equiv) and acetone (0.1 mL, 1.41 mmol, 1.0 equiv) in THF (15 mL) afforded, after purification by FC (20 mL SiO_2, EA/Cy:2/8 then 4/6), the desired product **5a** (303 mg, 84%) as a yellow oil.

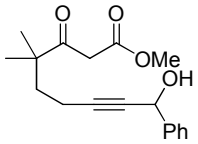
Rf (EA/Cy:2/8, UV+pAnis): 0.16. **^{1}H NMR (360 MHz, $CDCl_3$):** δ 3.62 (s, 3H), 3.55 (s, 2H), 3.12 (br, 1H), 2.06 (t, J = 7.5 Hz, 2H), 1.68 (t, J = 7.5 Hz, 2H), 1.34 (s, 6H), 1.05 (s, 6H). **^{13}C NMR (90 MHz, $CDCl_3$):** (major keto form) δ 207.2 (C), 168.6 (C), 86.3 (C), 80.6 (C), 64.7 (C), 52.2 (CH_3), 47.5 (C), 44.2 (CH_2), 37.7 (CH_2), 31.3 (2 CH_3), 24.0 (2 CH_3), 14.3 (CH_2). **HRMS (ESI+):** m/z calcd. for $C_{14}H_{22}NaO_4$ $(M + Na)^+$ 277.1410, found 277.1414.



5b, 65%
$C_{24}H_{26}O_4$
MW=378.46

Following the general procedure, the reaction performed with **SM2** (513 mg, purity = 77%, 2.61 mmol, 1.0 equiv) and benzophenone (476 mg, 2.61 mmol, 1.0 equiv) in THF (20 mL) afforded, after purification by FC (50 mL SiO_2, EA/Cy:1/9 then 2/8), the desired product **5b** (648 mg, 65%) as a pale yellow oil.

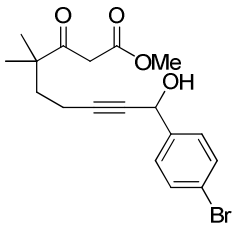
Rf (EA/Cy:1/9, UV+pAnis): 0.22. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.62 – 7.59 (m, 4H), 7.35 – 7.23 (m, 6H), 3.67 (s, 3H), 3.60 (s, 2H), 3.08 (br, 1H), 2.35 (t, J = 7.6 Hz, 2H), 1.89 (t, J = 7.6 Hz, 2H), 1.19 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** (major keto form) δ 207.2 (C), 168.5 (C), 145.5 (2 C), 128.1 (4 CH), 127.4 (2 CH), 126.0 (4 CH), 86.5 (C), 84.1 (C), 74.2 (C), 52.4 (CH_3), 47.6 (C), 44.3 (CH_2), 37.8 (CH_2), 24.1 (2 CH_3), 14.8 (CH_2). **HRMS (ESI+):** m/z calcd. for $C_{24}H_{26}NaO_4$ $(M + Na)^+$ 401.1723, found 401.1733.



5c, 57%
$C_{18}H_{22}O_4$
MW=302.36

Following the general procedure, the reaction performed with **SM2** (550 mg, purity = 82%, 2.16 mmol, 1.0 equiv) and benzaldehyde (0.22 mL, 2.16 mmol, 1.0 equiv) in THF (10 mL) afforded, after purification by FC (50 mL SiO_2, EA/Cy:2/8 then 4/6), the desired product **5c** (371 mg, 57%) as a yellow oil.

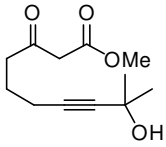
Rf (EA/Cy:2/8, UV+pAnis): 0.17. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.48 (d, J = 7.2 Hz, 2H), 7.35 – 7.24 (m, 3H), 5.38 (s, 1H), 3.67 (s, 3H), 3.59 (s, 2H), 3.13 (br, 1H), 2.21 (t, J = 7.1 Hz, 2H), 1.80 (t, J = 7.1 Hz, 2H), 1.13 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** (major keto form) δ 207.4 (C), 168.6 (C), 141.1 (C), 128.3 (2 CH), 127.9 (CH), 126.5 (2 CH), 85.5 (C), 81.5 (C), 64.2 (CH), 52.3 (CH_3), 47.5 (C), 44.2 (CH_2), 37.6 (CH_2), 24.0 (CH_3), 23.9 (CH_3), 14.5 (CH_2). **HRMS (ESI+):** m/z calcd. for $C_{18}H_{22}NaO_4$ $(M + Na)^+$ 325.1410, found 325.1403.



5d, 78%
$C_{18}H_{21}BrO_4$
MW=381.26

Following the general procedure, the reaction performed with **SM2** (667 mg, purity = 82%, 2.79 mmol, 1.0 equiv) and 4-bromobenzaldehyde (516 mg, 2.79 mmol, 1.0 equiv) in THF (10 mL) afforded, after purification by FC (50 mL SiO_2, EA/Cy:1/9 then 2/8), the desired product **5d** (833 mg, 78%) as a yellow oil.

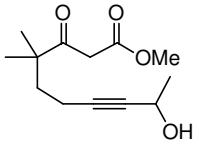
Rf (EA/Cy:2/8, UV+pAnis): 0.17. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 7.40 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 5.29 (d, J = 1.6 Hz, 1H), 4.00 (br, 1H), 3.64 (s, 3H), 3.57 (s, 2H), 2.17 (td, J = 7.5, 1.6 Hz, 2H), 1.75 (t, J = 7.5 Hz, 2H), 1.09 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** (major keto form) δ 207.4 (C), 168.7 (C), 140.2 (C), 131.3 (2 CH), 128.3 (2 CH), 121.6 (C), 85.7 (C), 81.1 (C), 63.4 (CH), 52.3 (CH_3), 47.4 (C), 44.2 (CH_2), 37.4 (CH_2), 24.0 (CH_3), 23.9 (CH_3), 14.5 (CH_2). **HRMS (ESI+):** m/z calcd. for $C_{18}H_{21}BrNaO_4$ $(M + Na)^+$ 403.0515, found 403.0502.



5e, 46%
$C_{12}H_{18}O_4$
MW=226.27

Following the general procedure, the reaction performed with **SM6** (218 mg, 1.30 mmol, 1.0 equiv) and acetone (0.10 mL, 1.30 mmol, 1.0 equiv) in THF (10 mL) afforded, after purification by FC (20 mL SiO_2, EA/Cy:4/6), **5e** (134 mg, 46%) as a colorless oil.

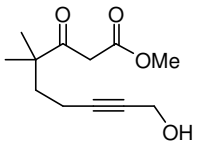
Rf (EA/Cy:4/6, UV+pAnis): 0.29. **^{1}H NMR (360 MHz, $CDCl_3$):** δ 3.65 (s, 3H), 3.41 (s, 2H), 2.69 (br, 1H), 2.58 (t, J = 7.0 Hz, 2H), 2.14 (t, J = 7.0 Hz, 2H), 1.70 (pent, J = 7.0 Hz, 2H), 1.39 (s, 6H). **^{13}C NMR (90 MHz, $CDCl_3$):** (major keto form) δ 202.2 (C), 167.7 (C), 86.5 (C), 80.8 (C), 64.9 (C), 52.3 (CH_3), 49.1 (CH_2), 41.4 (CH_2), 31.6 (2 CH_3), 22.1 (CH_2), 17.7 (CH_2). **HRMS (ESI+):** m/z calcd. for $C_{12}H_{18}NaO_4$ $(M + Na)^+$ 249.1097, found 249.1098.



5i, 8%
$C_{13}H_{20}O_4$
MW=240.30

Following the general procedure, the reaction performed with **SM2** (524 mg, 2.67 mmol, 1.0 equiv) and acetaldehyde (0.15 mL, 2.67 mmol, 1.0 equiv) in THF (20 mL) afforded, after purification by FC (50 mL SiO_2, EA/Cy:2/8 then 4/6), **5i** (49 mg, 8%) as a yellow oil.

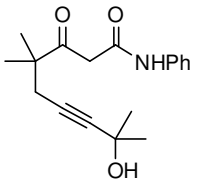
Rf (EA/Cy:4/6, UV+pAnis): 0.32. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 4.45 – 4.39 (m, 1H), 3.71 (s, 3H), 3.63 (s, 2H), 2.90 (br, 1H), 2.19 – 2.14 (m, 2H), 1.77 (t, J = 7.4 Hz, 2H), 1.35 (d, J = 6.6 Hz, 3H), 1.13 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** (major keto form) δ 207.4 (C), 168.8 (C), 83.9 (C), 82.8 (C), 58.2 (CH), 52.5 (CH_3), 47.6 (C), 44.5 (CH_2), 37.8 (CH_2), 24.3 (2 CH_3), 24.2 (CH_3), 14.6 (CH_2).



5j, 71%
$C_{12}H_{18}O_4$
MW=226.27

Following the general procedure, the reaction performed with **SM2** (428 mg, 2.18 mmol, 1.0 equiv) and para-formaldehyde (65 mg, 2.18 mmol, 1.0 equiv) in THF (20 mL) afforded, after purification by FC (100 mL SiO_2, EA/Cy:3/7 then 4/6), **5j** (350 mg, 71%) as a pale yellow oil.

Rf (EA/Cy:4/6, UV+pAnis): 0.30. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 4.12 (t, J = 2.1 Hz, 2H), 3.68 (s, 3H), 3.61 (s, 2H), 2.76 (br, 1H), 2.17 – 2.12 (m, 2H), 1.76 (t, J = 7.4 Hz, 2H), 1.11 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** (major keto form) δ 207.6 (C), 168.9 (C), 84.4 (C), 80.2 (C), 52.4 (CH_3), 50.8 (CH_2), 47.6 (C), 44.4 (CH_2), 37.7 (CH_2), 24.1 (2 CH_3), 14.6 (CH_2). **HRMS (ESI+):** m/z calcd. for $C_{12}H_{19}O_4$ $(M + H)^+$ 227.1278, found 227.1279.



1h, 53%
$C_{18}H_{23}NO_3$
MW=301.38

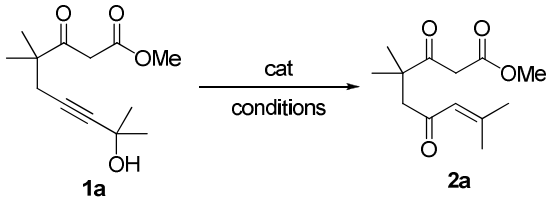
In air, a sealed tube equipped with a stir bar was charged with **1a** (351 mg, 1.46 mmol, 1.0 equiv), aniline (0.13 mL, 1.46 mmol, 1.0 equiv) and DMAP (53 mg, 0.44 mmol, 0.3 equiv) in toluene (1.5 mL) and the tube was sealed. The reaction was stirred at 120 °C for 16 h. Then, the reaction mixture was poured into 1 M aq HCl and this solution was extracted twice with EtOAc. The combined organic layers were washed with brine, dried ($MgSO_4$) and evaporated. Purification by FC (50 mL SiO_2, EA/Cy:4/6 then 5/5) afforded **1h** (233 mg, 53%) as an orange oil.

Rf (EA/Cy:4/6, UV+pAnis): 0.23. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 9.17 (br, 1H), 7.54 (d, J = 7.9 Hz, 2H), 7.27 (dd, J = 7.9, 7.9 Hz, 2H), 7.08 (t, J =7.9 Hz, 1H), 3.67 (s, 2H), 3.64 (s, 1H), 2.34 (s, 2H), 1.42 (s, 6H), 1.20 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 210.6 (C), 164.6 (C), 137.6 (C), 128.9 (2 CH), 124.4 (CH), 120.1 (2 CH), 88.7 (C), 78.0 (C), 64.9 (C), 48.3 (C), 45.6 (CH_2), 31.4 (2 CH_3), 29.3 (CH_2), 23.6 (2 CH_3).

3. Catalytic reactions

3.1. Initial findings (related to Scheme 4)

Table S1. Catalyst screening.



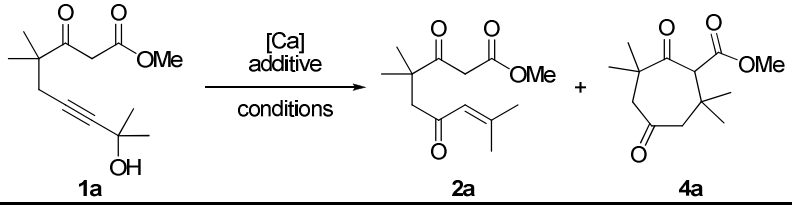
1a 2a

Entry	cat	Conditions	^{1}H Yield
1	JohnPhosAu(CH_3CN)SbF_6 (5 mol%)	CH_2Cl_2/amylene (0.1 M), 50 °C, 18 h	41%
2	[IPrGaCl_2]SbF_6 (5 mol%)	DCE, 80 °C, 4 h	60%
3	Ca(NTf_2)$_2$ (5 mol%) KPF_6 (5 mol%)	CH_2Cl_2/amylene (0.1 M), 50 °C, 18 h	73%

In air, **1a** (24 mg, 0.1 mmol, 1.0 equiv) and cat were charged in a 10 mL screw-cap vial equipped with a stir bar. The solvent (1 mL, c = 0.1 M) was added and the tube was sealed. The reaction was stirred at the indicated temperature for the indicated time. Then, the reaction mixture was filtered through a short pad of SiO_2 (thoroughly rinsed with EtOAc) and evaporated. Conversion and ^{1}H NMR yields were determined by ^{1}H NMR analysis of this material, using 4-methoxybenzaldehyde (1.0 equiv) as an internal standard.

3.2. Optimization of the cyclization of 1a (related to Table 1)

Table S2. Optimization of the calcium-catalyzed reactions.



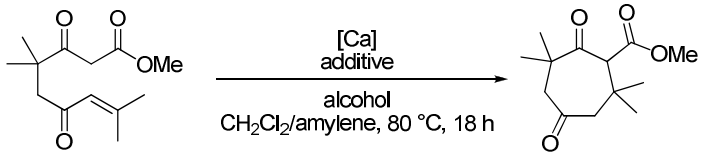
1a 2a 4a

Entry	[Ca]	Additive	Conditions [d]	^{1}H Conv [c]	Ratio [b,c] 2a	4a
1	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%)	CH_2Cl_2/amylene (0.1 M), 50 °C, 18 h	0% (NR)	-	-
2	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%)	CH_2Cl_2/amylene (0.1 M), **80 °C**, 18 h	100%	100	0
3	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%)	**CH_2Cl_2/0.1% EtOH** (0.1 M), **80 °C**, 18 h	100%	25	75
4	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%)	**CH_2Cl_2/0.1% EtOH** (0.1 M), **100 °C**, 18 h	100%	47	53
5	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%)	**wet DCM** (0.1 M), 80 °C, 18 h	100%	44	56
6	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%) **CaH_2 (5 mol%)**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	0%	-	-
7	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%) **4 Å MS (100 mg/mmol)**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	0%	-	-
8	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%) ***t*-BuOK (1 mol%)**	CH_2Cl_2/amylene (0.1 M),80 °C, 18 h	0%	-	-
9	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%) **IPr (5 mol%)**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	0%	-	-
10	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%) **TEA (5 mol%)**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	0%	-	-
11	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%) **K_2CO_3(5 mol%)**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	0%	-	-
12	Ca(NTf_2)$_2$ (5 mol%)	KPF_6 (5 mol%)	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	0%	-	-

13	$Ca(NTf_2)_2$ (5 mol%)	**PPh_3 (3 mol%)** KPF_6 (5 mol%) **DMAP (3 mol%)**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	0%	-	-
14	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **1 equiv EtOH**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	100%	11	89
15	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **2 equiv EtOH**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	100%	8	92
16	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **5 equiv EtOH**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	100% [e]	3	97
17	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **10 equiv EtOH**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	100% [e]	2	98
18	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%)	**EtOH** (0.1 M), 80 °C, 18 h	CM	-	-
19	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **5 equiv MeOH**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	100%	17	83
20	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **5 equiv *i*-PrOH**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	100%	3	97
21	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **10 equiv *i*-PrOH**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	100%	23	77
22	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **5 equiv (L)-Menthol**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	100%	0	100
23	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **5 equiv t-BuOH**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	100%	96	4
24	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **5 equiv PhOH**	CH_2Cl_2/amylene (0.1 M), 80 °C, 18 h	100%	100	0

[a] Reactions set up in air using 0.1 mmol of **1a** in bulk solvents in 10 mL sealed tubes; [b] Abbreviations: NR = no reaction; CM = complex mixture; [c] Determined by ^{1}H NMR analysis; [d] CH_2Cl_2/0.1% EtOH is CH_2Cl_2 stabilized on EtOH; [e] Transesterification product detected in the crude mixture.

Table S3. Blank tests.



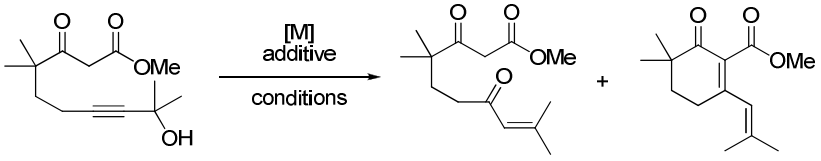
2a **4a**

Entry	[Ca]	Additive	Alcohol	^{1}H Conv [b,c]
1	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%)	*i*-PrOH (5.0 equiv)	100%
2	-	KPF_6 (5 mol%)	*i*-PrOH (5.0 equiv)	0% (NR)
3	-	-	*i*-PrOH (5.0 equiv)	0% (NR)
4	$Ca(NTf_2)_2$ (5 mol%)	-	*i*-PrOH (5.0 equiv)	0% (NR)
5	-	SiO_2 (1.0 equiv)	-	0% (NR)
6	-	$Ca(OH)_2$ (25 mol%)	-	0% (NR)
7	-	K_2CO_3 (20 mol%)	-	0% (NR)
8	-	pTSA (30 mol%)	-	0% (NR)

[a] Reactions set up in air using 0.1 mmol of **2a** in bulk CH_2Cl_2 in 10 mL sealed tubes; [b] Abbreviations: NR = no reaction; [c] Determined by ^{1}H NMR analysis.

3.3. Optimization of the cyclization of 5a (related to Table 2)

Table S4. Optimization of the calcium-catalyzed reactions.



5a **6a** **7a**

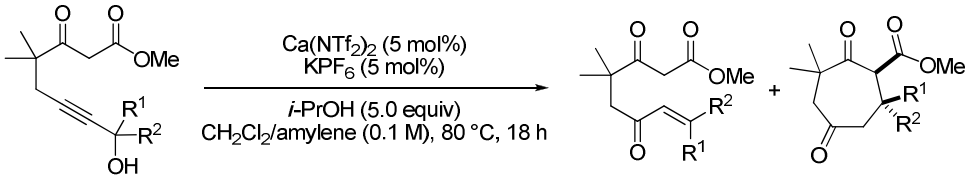
Entry	[M]	Additive	Conditions	^{1}H Conv [c]	^{1}H Yield [d] 6a	27a
1	$Ca(NTf_2)_2$ (5 mol%)	**Bu_4NPF_6** (5 mol%)	CH_2Cl_2/amylene (0.1 M), 50 °C, 18 h	100%	62%	12%
2	$Ca(NTf_2)_2$ (5 mol%)	**KPF_6** (5 mol%)	CH_2Cl_2/amylene (0.1 M), 50 °C, 18 h	100%	1%	67%
3	$Ca(NTf_2)_2$ (5 mol%)	**Bu_4NCl** (5 mol%)	CH_2Cl_2/amylene (0.1 M), 50 °C, 18 h	0% (NR)	-	-
4	$Ca(NTf_2)_2$ (5 mol%)	**Bu_4NBF_4** (5 mol%)	CH_2Cl_2/amylene (0.1 M), 50 °C, 18 h	100%	1%	64%
5	**-**	KPF_6 (5 mol%)	CH_2Cl_2/amylene (0.1 M), 50 °C, 18 h	0% (NR)	-	-
6	$Ca(NTf_2)_2$ (5 mol%)	**-**	CH_2Cl_2/amylene (0.1 M), 50 °C, 18 h	0% (NR)	-	-
7	**JohnPhosAu(CH_3CN)SbF_6** (5 mol%)		CH_2Cl_2/amylene (0.1 M), 50 °C, 18 h	100%	5%	90%
8	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%)	CH_2Cl_2/amylene (0.1 M), **80 °C**, 18 h	100%	-	85%

9	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%)	CH_2Cl_2/amylene (0.1 M), **100 °C**, 18 h	100%	33%	60%
10	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%)	CH_2Cl_2/amylene (**0.05 M**), 80 °C, 18 h	100%	25%	50%
11	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%)	**CH_3CN** (0.1 M), **60 °C**, 18 h	100%	-	86%
12	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%)	**DCE** (0.1 M), **80 °C**, 18 h	100%	-	46%
13	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%)	**PhMe** (0.1 M), **100 °C**, 18 h	100%	8%	39%
14	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **CaH_2 (100mg/mmol)**	CH_2Cl_2/amylene (0.1 M), **80 °C**, 18 h	0% (NR)	-	-
15	$Ca(NTf_2)_2$ (5 mol%)	KPF_6 (5 mol%) **4 Å MS (100mg/mmol)**	CH_2Cl_2/amylene (0.1 M), **80 °C**, 18 h	0% (NR)	-	-

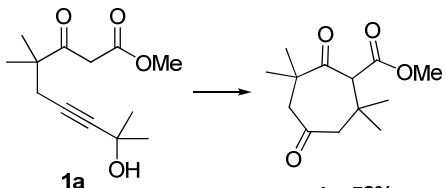
[a] Reactions set up in air on 0.1 mmol of **5a** in bulk solvents in 10 mL sealed tubes; [b] Abbreviations: NR = no reaction; [c] Determined by ^{1}H NMR analysis; [d] Yields determined using 1.0 equiv of 4-methoxybenzaldehyde as an internal standard.

4. Scope of the reactions

4.1. Type 1 substrates (related to Scheme 6)

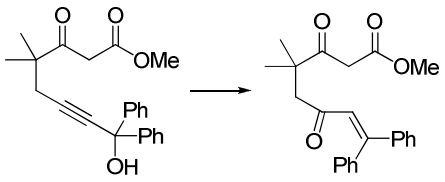


General procedure: In air, the substrate (1.0 equiv), $Ca(NTf_2)_2$ (5 mol%) and KPF_6 (5 mol%) were charged in a 10 mL screw-cap vial equipped with a stir bar. Bulk CH_2Cl_2 stabilized on amylene (c = 0.1 M) and *i*-PrOH (5.0 equiv) were added and the tube was sealed. The reaction was stirred at 80 °C for 18 h. Then, the reaction mixture was filtered through a short pad of SiO_2 (thoroughly rinsed with EtOAc) and evaporated. Purification by FC afforded the desired product.



Following the general procedure, the reaction performed with **1a** (104 mg, 0.43 mmol, 1.0 equiv) in bulk CH_2Cl_2 stabilized on amylene (4 mL, c = 0.1 M) with *i*-PrOH (0.17 mL, 2.16 mmol, 5.0 equiv) at 80 °C for 18 h afforded, after purification by FC (20 mL SiO_2, EA/Cy:1/9 then 2/8), **4a** (55 mg, 53%) as a yellow solid.

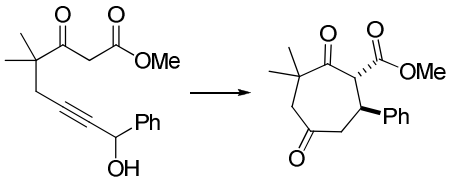
Rf (EA/Cy:2/8, UV+pAnis): 0.23. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 4.01 (s, 1H), 3.67 (s, 3H), 2.72 (d, J = 13.0 Hz, 1H), 2.58 (d, J = 12.4 Hz, 1H), 2.54 (d, J = 12.4 Hz, 1H), 2.44 (d, J = 13.0 Hz, 1H), 1.18 (s, 3H), 1.15 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 208.4 (C), 207.6 (C), 168.4 (C), 63.3 (CH), 58.5 (CH_2), 52.1 (CH_2), 52.0 (CH_3), 46.4 (C), 36.1 (C), 29.0 (CH_3), 28.0 (CH_3), 25.0 (CH_3), 24.8 (CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{13}H_{21}O_4$ $(M + H)^+$ 241.1434, found 241.1434.



1b **2b, 48%**
$C_{23}H_{24}O_4$
MW=364.43

Following the general procedure, the reaction performed with **1b** (192 mg, 0.53 mmol, 1.0 equiv) in bulk CH_2Cl_2 stabilized on amylene (5 mL, c = 0.1 M) with *i*-PrOH (0.20 mL, 2.63 mmol, 5.0 equiv) at 80 °C for 18 h afforded, after purification by FC (20 mL SiO_2, EA/Cy: 2/8), **2b** (92 mg, 48%) as a yellow oil.

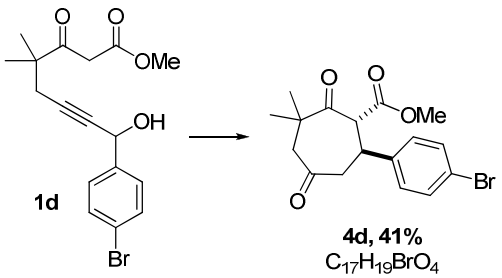
Rf (EA/Cy:2/8, UV+pAnis): 0.21. **^{1}H NMR (360 MHz, $CDCl_3$):** δ 7.42 – 7.41 (m, 3H), 7.36 – 7.27 (m, 5H), 7.21 – 7.18 (m, 2H), 6.53 (s, 1H), 3.71 (s, 3H), 3.61 (s, 2H), 2.59 (s, 2H), 1.08 (s, 6H). **^{13}C NMR (90 MHz, $CDCl_3$):** δ 207.3 (C), 199.5 (C), 168.3 (C), 153.8 (C), 140.8 (C), 138.8 (C), 129.7 (2 CH), 129.5 (CH), 128.8 (CH), 128.4 (2 CH), 128.4 (4 CH), 126.6 (CH), 53.9 (CH_2), 52.1 (CH_3), 45.8 (C), 44.9 (CH_2), 24.8 (2 CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{13}H_{24}NaO_4$ $(M + Na)^+$ 387.1567, found 387.1557.



1c **4c, 69%**
$C_{17}H_{20}O_4$
MW=288.34

Following the general procedure, the reaction performed with **1c** (86 mg, 0.3 mmol, 1.0 equiv) in bulk CH_2Cl_2 stabilized on amylene (3 mL, c = 0.1 M) with *i*-PrOH (0.11 mL, 1.5 mmol, 5.0 equiv) at 80 °C for 18 h afforded, after purification by FC (20 mL SiO_2, EA/Cy: 1/9 then 2/8), **4c** (60 mg, 69%) as a white solid.

Rf (EA/Cy:2/8, UV+pAnis): 0.32. **^{1}H NMR (360 MHz, $CDCl_3$):** δ 7.32 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.18 (d, J = 7.0 Hz, 2H), 4.49 (d, J = 9.8 Hz, 1H), 3.94 – 3.88 (m, 1H), 3.65 (s, 3H), 2.96 (d, J = 15.7 Hz, 1H), 2.75 (dd, J = 12.2, 5.8 Hz, 2H), 2.68 (d, J = 15.7 Hz, 1H), 1.29 (s, 3H), 1.23 (s, 3H). **^{13}C NMR (90 MHz, $CDCl_3$):** δ 208.2 (C), 207.6 (C), 169.1 (C), 142.2 (C), 129.1 (2 CH), 127.5 (CH), 126.8 (2 CH), 59.7 (CH), 52.9 (CH_2), 52.6 (CH_3), 47.4 (CH_2), 46.9 (C), 40.2 (CH), 27.2 (CH_3), 23.2 (CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{17}H_{20}NaO_4$ $(M + Na)^+$ 311.1254, found 311.1242.

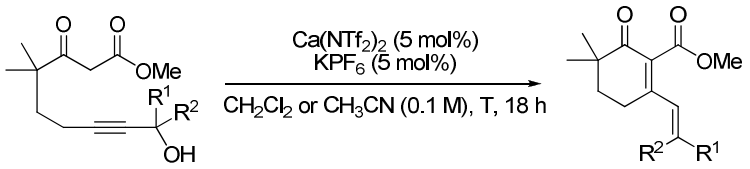


1d **4d, 41%**
$C_{17}H_{19}BrO_4$
MW=367.23

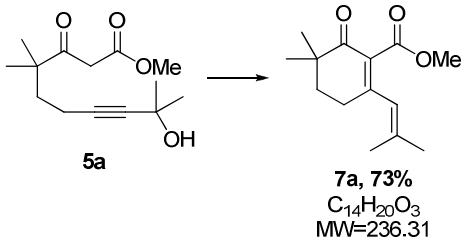
Following the general procedure, the reaction performed with **1d** (110 mg, 0.3 mmol, 1.0 equiv) in bulk CH_3CN (3 mL, c = 0.1 M) at 80 °C for 18 h afforded, after purification by FC (20 mL SiO_2, EA/Cy:2/8 then 4/6), **4d** (56 mg, purity = 80%, 41%) as a yellow oil.
Rf (EA/Cy:2/8, UV+pAnis): 0.33.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 (d, J = 8.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 4.39 (d, J = 10.0 Hz, 1H), 3.85 – 3.80 (m, 1H), 3.64 (s, 3H), 3.03 – 2.63 (m, 4H), 1.27 (s, 3H), 1.18 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 207.9 (C), 207.3 (C), 168.8 (C), 141.2 (C), 132.2 (2 CH), 128.6 (2 CH), 123.5 (C), 59.3 (CH), 52.8 (CH_2), 52.7 (CH_3), 47.3 (CH_2), 46.9 (C), 39.8 (CH), 27.2 (CH_3), 23.2 (CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{17}H_{19}BrNaO_4$ $(M + Na)^+$ 389.0359, found 389.0328.

4.2. Type 5 substrates (related to Scheme 7)

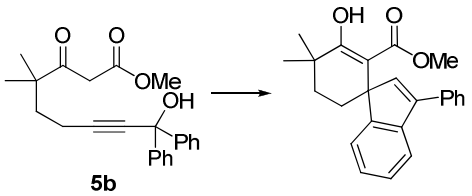


General procedure: In air, the substrate (1.0 equiv), $Ca(NTf_2)_2$ (5 mol%) and KPF_6 (5 mol%) were charged in a 10 mL screw-cap vial equipped with a stir bar. Bulk solvent (CH_2Cl_2 or CH_3CN) was added and the tube was sealed. The reaction was stirred at the indicated temperature for 18 h. Then, the reaction mixture was filtered through a short pad of SiO_2 (thoroughly rinsed with EtOAc) and evaporated. Purification by FC afforded the desired product.



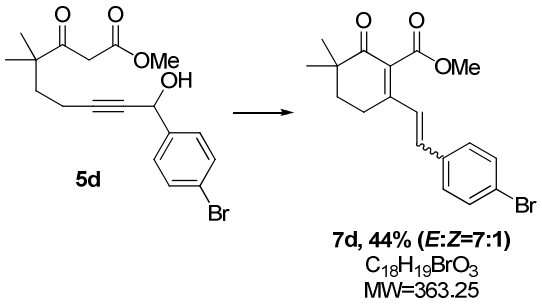
Following the general procedure, the reaction performed with **5a** (76 mg, 0.3 mmol, 1.0 equiv) in bulk CH_3CN (3 mL, c = 0.1 M) at 80 °C for 18 h afforded, after purification by FC (20 mL SiO_2, EA/Cy:1/9 then 2/8), **7a** (52 mg, 73%) as a colorless oil.

Rf (EA/Cy:2/8, UV+pAnis): 0.43. **^{1}H NMR (300 MHz, $CDCl_3$):** δ 5.82 (s, 1H), 3.74 (s, 3H), 2.51 (t, J = 6.0 Hz, 2H), 1.81 (t, J = 6.0 Hz, 2H), 1.80 (s, 3H), 1.77 (s, 3H), 1.11 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 200.5 (C), 168.0 (C), 156.1 (C), 142.7 (C), 131.2 (C), 122.9 (CH), 52.1 (CH_3), 40.3 (C), 35.8 (CH_2), 27.6 (CH_3), 27.3 (CH_2), 24.0 (2 CH_3), 20.8 (CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{14}H_{21}O_3$ $(M + H)^+$ 237.1485, found 237.1485.



Following the general procedure, the reaction performed with **5b** (189 mg, 0.5 mmol, 1.0 equiv) in bulk CH_2Cl_2 (5 mL, c = 0.1 M) at 50 °C for 18 h afforded, after purification by FC (20 mL SiO_2, EA/Cy:0.5/9.5 then 1/9), **8b** (94 mg, 52%) as a yellow oil.

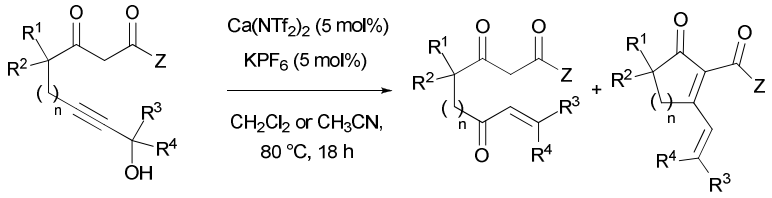
Rf (EA/Cy:1/9, UV+pAnis): 0.74. **^{1}H NMR (360 MHz, $CDCl_3$):** δ 13.25 (s, 1H), 7.64 – 7.61 (m, 2H), 7.53 – 7.46 (m, 3H), 7.42 – 7.40 (m, 1H), 7.30 – 7.22 (m, 3H), 6.49 (s, 1H), 3.25 (s, 3H), 1.92 – 1.77 (m, 4H), 1.45 (s, 3H), 1.38 (s, 3H). **^{13}C NMR (90 MHz, $CDCl_3$):** δ 181.3 (C), 173.3 (C), 154.3 (C), 142.5 (C), 142.2 (CH), 141.7 (C), 136.3 (C), 128.7 (2 CH), 127.7 (2 CH), 127.6 (CH), 126.3 (CH), 125.3 (CH), 121.7 (CH), 120.5 (CH), 97.9 (C), 53.0 (C), 50.9 (CH_3), 36.4 (C), 36.0 (CH_2), 31.5 (CH_2), 27.5 (CH_3), 27.4 (CH_3). **HRMS (ESI+):** *m*/*z* calcd. for $C_{24}H_{25}O_3$ $(M + H)^+$ 361.1798, found 361.1783.



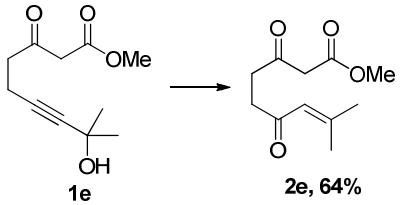
Following the general procedure, the reaction performed with **5d** (191 mg, 0.5 mmol, 1.0 equiv) in bulk CH_2Cl_2 (1 mL, c = 0.5 M) at 80 °C for 18 h afforded, after purification by FC (50 mL SiO_2, EA/Cy:1/9 then 2/8), the two diastereomers of **7d** (80 mg, 44%, *E*:*Z*=7:1) as a pale yellow oil.

Rf (EA/Cy:2/8, UV+pAnis): 0.37. **^{1}H NMR (300 MHz, $CDCl_3$):** (major E-diastereomer) δ 7.46 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 16.0 Hz, 1H), 6.88 (d, J = 16.0 Hz, 1H), 3.87 (s, 3H), 2.69 (t, J = 5.9 Hz, 2H), 1.90 (t, J = 5.9 Hz, 2H), 1.15 (s, 6H); (minor Z-diastereomer) δ 7.46 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 6.62 (d, J = 12.2 Hz, 1H), 6.35 (d, J = 12.2 Hz, 1H), 3.73 (s, 3H), 2.27 (t, J = 5.8 Hz, 2H), 1.72 (t, J = 5.8 Hz, 2H), 1.11 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$):** (major E-diastereomer) δ 200.8 (C), 167.8 (C), 151.1 (C), 136.3 (CH), 134.6 (C), 132.1 (2 CH), 131.4 (C), 129.0 (2 CH), 125.9 (CH), 123.7 (C), 52.5 (CH_3), 40.7 (C), 35.0 (CH_2), 24.1 (2 CH_3), 22.2 (CH_2); (minor Z-diastereomer) δ 199.7 (C), 167.8 (C), 155.8 (C), 135.3 (C), 133.8 (CH), 131.7 (2 CH), 131.0 (C), 130.1 (2 CH), 127.6 (CH), 124.6 (C), 52.3 (CH_3), 40.5 (C), 35.9 (CH_2), 26.0 (CH_2), 24.0 (2 CH_3). **HRMS (ESI+):** *m*/*z* calcd. for $C_{18}H_{20}BrO_3$ $(M + H)^+$ 363.0590, found 363.0582.

4.3. Influence of the substitution of the substrate (relative to Scheme 8)

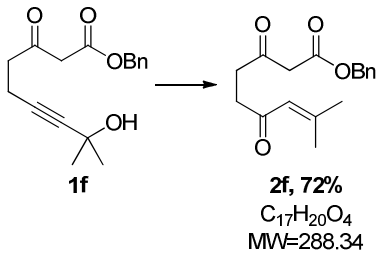


General procedure: In air, the substrate (1.0 equiv), $Ca(NTf_2)_2$ (5 mol%) and KPF_6 (5 mol%) were charged in a 10 mL screw-cap vial equipped with a stir bar. Bulk solvent (CH_2Cl_2 or CH_3CN) was added and the tube was sealed. The reaction was stirred at 80 °C for 18 h. Then, the reaction mixture was filtered through a short pad of SiO_2 (thoroughly rinsed with EtOAc) and evaporated. Purification by FC afforded the desired product.



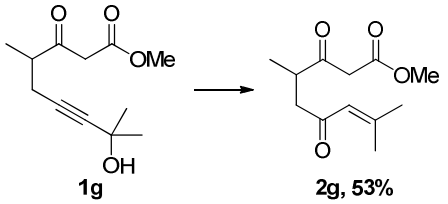
Following the general procedure, the reaction performed with **1e** (53 mg, 0.25 mmol, 1.0 equiv) in bulk CH_3CN (2.5 mL, c = 0.1 M) at 80 °C for 18 h afforded, after purification by FC (20 mL SiO_2, EA/Cy:1/9 then 4/6), **2e** (34 mg, 64%) as a yellow oil.

Rf (EA/Cy:2/8, UV+pAnis): 0.20. **^{1}H NMR (250 MHz, $CDCl_3$):** δ 6.06 (dd, J = 1.1, 0.9 Hz, 1H), 3.70 (s, 3H), 3.52 (s, 2H), 2.77 – 2.72 (m, 4H), 2.09 (d, J = 0.9 Hz, 3H), 1.85 (d, J = 1.1 Hz, 3H). **^{13}C NMR (63 MHz, $CDCl_3$):** δ 201.8 (C), 198.3 (C), 167.7 (C), 156.0 (C), 123.3 (CH), 52.4 (CH_3), 49.3 (CH_2), 37.7 (CH_2), 36.5 (CH_2), 27.7 (CH_3), 20.9 (CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{11}H_{16}NaO_4$ $(M + Na)^+$ 235.0941, found 235.0937.



Following the general procedure, the reaction performed with **1f** (86 mg, 0.3 mmol, 1.0 equiv) in bulk CH_3CN (3 mL, c = 0.1 M) at 80 °C for 18 h afforded, after purification by FC (20 mL SiO_2, EA/Cy:1/9 then 2/8), **2f** (62 mg, 72%) as a yellow oil.

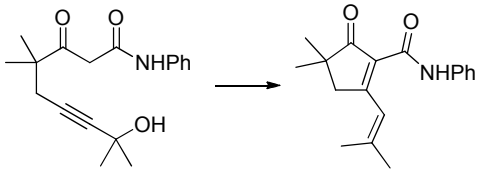
Rf (EA/Cy:2/8, UV+pAnis): 0.21. **^{1}H NMR (360 MHz, $CDCl_3$):** δ 7.35 – 7.28 (m, 5H), 6.07 (s, 1H), 5.16 (s, 2H), 3.57 (s, 2H), 2.79 – 2.71 (m, 4H), 2.11 (s, 3H), 1.87 (s, 3H). **^{13}C NMR (90 MHz, $CDCl_3$):** δ 201.7 (C), 198.2 (C), 167.1 (C), 155.9 (C), 135.4 (C), 128.6 (2 CH), 128.4 (CH), 128.4 (2 CH), 123.3 (CH), 67.1 (CH_2), 49.4 (CH_2), 37.7 (CH_2), 36.5 (CH_2), 27.7 (CH_3), 20.8 (CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{17}H_{20}NaO_4$ $(M + Na)^+$ 311.1254, found 311.1246.



1g **2g, 53%**
$C_{12}H_{18}O_4$
MW=226.27

Following the general procedure, the reaction performed with **1g** (68 mg, 0.3 mmol, 1.0 equiv) in bulk CH_3CN (3 mL, c = 0.1 M) at 80 °C for 18 h afforded, after purification by FC (20 mL SiO_2, EA/Cy:1/9 then 2/8), **2g** (36 mg, 53%) as a pale yellow oil.

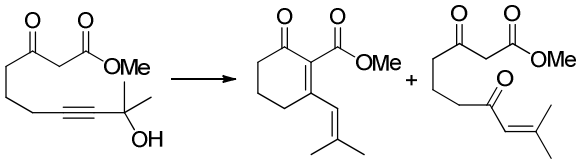
Rf (EA/Cy:2/8, UV+pAnis): 0.28. **^{1}H NMR (250 MHz, $CDCl_3$):** δ 6.01 (dd, J = 0.9, 0.8 Hz, 1H), 3.70 (s, 3H), 3.63 (d, J = 2.4 Hz, 2H), 3.16 – 3.06 (m, 1H), 2.94 (dd, J = 17.7, 8.8 Hz, 1H), 2.46 (dd, J = 17.7, 4.5 Hz, 1H), 2.08 (d, J = 0.8 Hz, 3H), 1.84 (d, J = 0.9 Hz, 3H), 1.10 (d, J = 7.1 Hz, 3H). **^{13}C NMR (63 MHz, $CDCl_3$):** δ 205.9 (C), 198.3 (C), 167.8 (C), 156.2 (C), 123.2 (CH), 52.3 (CH_3), 48.2 (CH_2), 47.6 (CH_2), 41.4 (CH), 27.7 (CH_3), 20.9 (CH_3), 16.4 (CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{12}H_{19}O_4$ $(M + H)^+$ 227.1278, found 227.1278.



1h **3h, 71%**
$C_{18}H_{21}NO_2$
MW=283.36

Following the general procedure, the reaction performed with **1h** (90 mg, 0.3 mmol, 1.0 equiv) in bulk CH_3CN (3 mL, c = 0.1 M) at 80 °C for 18 h afforded, after purification by FC (20 mL SiO_2, EA/Cy:1/9 then 2/8), **3h** (60 mg, 70%) as a yellow solid.

Rf (EA/Cy:2/8, UV+pAnis): 0.45. **^{1}H NMR (250 MHz, $CDCl_3$):** δ 10.76 (br, 1H), 7.98 (s, 1H), 7.66 (d, J = 7.8 Hz, 2H), 7.31 (dd, J = 7.8, 7.8 Hz, 2H), 7.07 (t, J = 7.8 Hz, 1H), 2.89 (s, 2H), 2.09 (s, 6H), 1.19 (s, 6H). **^{13}C NMR (63 MHz, $CDCl_3$):** δ 213.2 (C), 177.8 (C), 161.4 (C), 154.7 (C), 138.3 (C), 128.9 (2 CH), 124.2 (C), 124.1 (CH), 123.1 (CH), 120.3 (2 CH), 47.4 (CH_2), 44.1 (C), 30.3 (CH_3), 25.5 (2 CH_3), 22.3 (CH_3). **HRMS (ESI+):** *m/z* calcd. for $C_{18}H_{21}NNaO_2$ $(M + Na)^+$ 306.1465, found 306.1462.



5e **6e:7e=1.4:1, 55%**

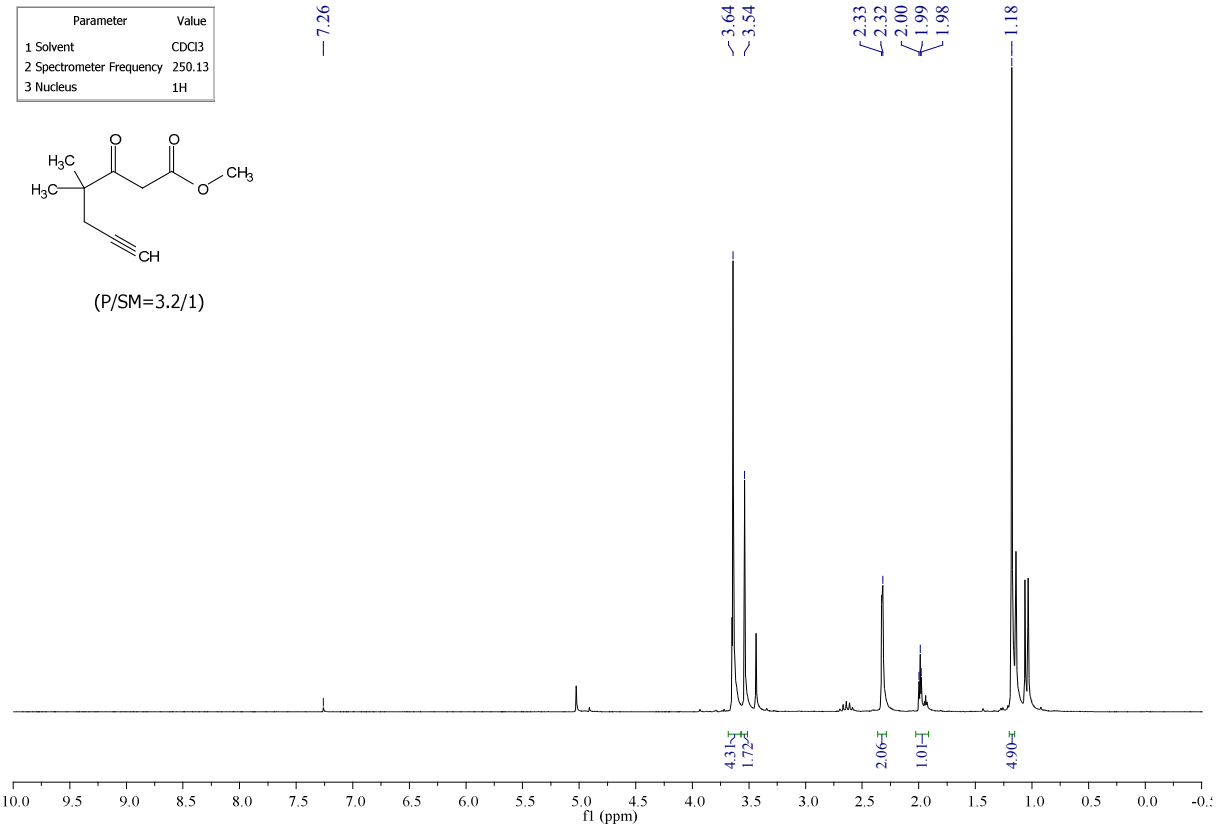
$C_{12}H_{16}O_3$ MW=208.25 $C_{12}H_{18}O_4$ MW=226.27

Following the general procedure, the reaction performed with **5e** (113 mg, 0.5 mmol, 1.0 equiv) in bulk CH_2Cl_2 (1 mL, c = 0.5 M) at 80 °C for 18 h afforded, after purification by FC

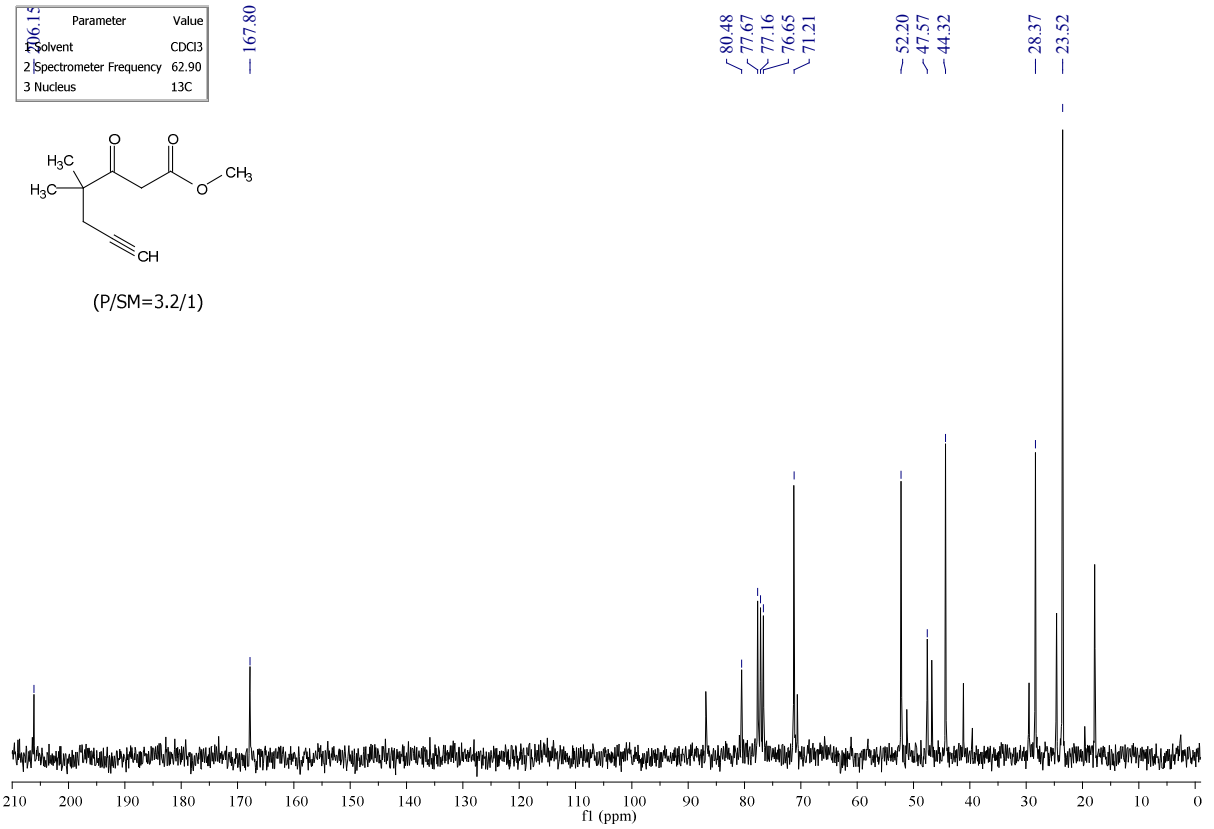
(50 mL SiO_2, EA/Cy:1/9 then 2/8), a mixture of **6e** and **7e** (59 mg, 55%, 1.4:1) as a colorless oil.

Rf (EA/Cy:2/8, UV+pAnis): 0.20. **6e: ^{1}H NMR (300 MHz, $CDCl_3$):** δ .5.99 (s, 1H), 3.73 (s, 3H), 2.56 (t, J = 7.1 Hz, 2H), 2.42 (t, J = 6.9 Hz, 2H), 2.10 (s, 3H), 1.87 – 1.82 (m, 2H), 1.84 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 195.5 (C), 167.5 (C), 158.1 (C), 143.3 (C), 132.5 (C), 123.1 (CH), 52.1 (CH_3), 37.2 (CH_2), 30.3 (CH_2), 27.6 (CH_3), 22.3 (CH_2), 20.8 (CH_3). **HRMS (ESI+):** m/z calcd. for $C_{12}H_{17}O_3$ $(M + H)^+$ 209.1172, found 209.1170. **7e: ^{1}H NMR (300 MHz, $CDCl_3$):** δ 5.83 (s, 1H), 3.67 (s, 3H), 3.40 (s, 2H), 2.52 – 2.48 (m, 2H), 2.42 (t, J = 6.7 Hz, 2H), 1.97 (dt, J = 11.9, 6.0 Hz, 2H), 1.79 (s, 3H), 1.75 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 202.4 (C), 200.0 (C), 167.6 (C), 155.5 (C), 123.5 (CH), 52.3 (CH_3), 48.9 (CH_2), 42.6 (CH_2), 42.0 (CH_2), 27.7 (CH_3), 20.7 (CH_3), 17.7 (CH_2). **HRMS (ESI+):** m/z calcd. for $C_{12}H_{18}NaO_4$ $(M + Na)^+$ 249.1097, found 249.1096.

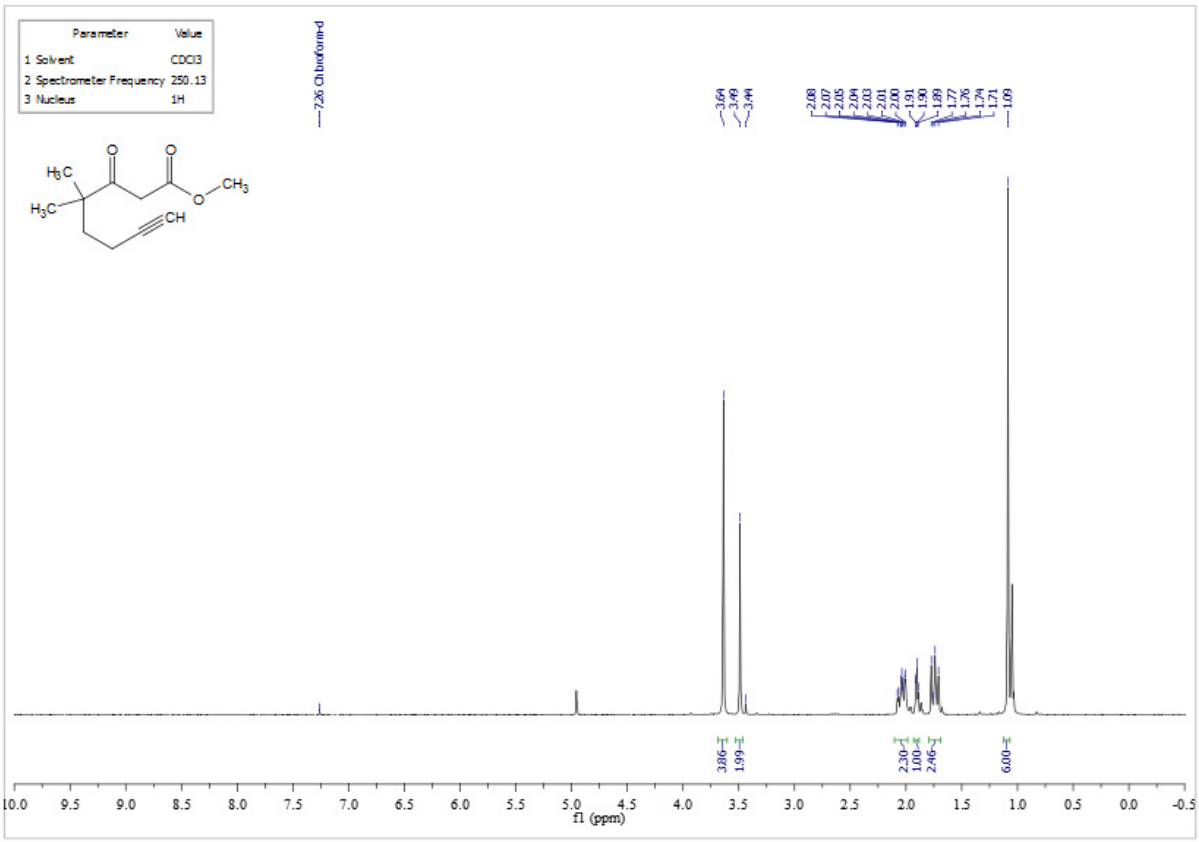
5. Copies of ^{1}H and ^{13}C NMR spectra

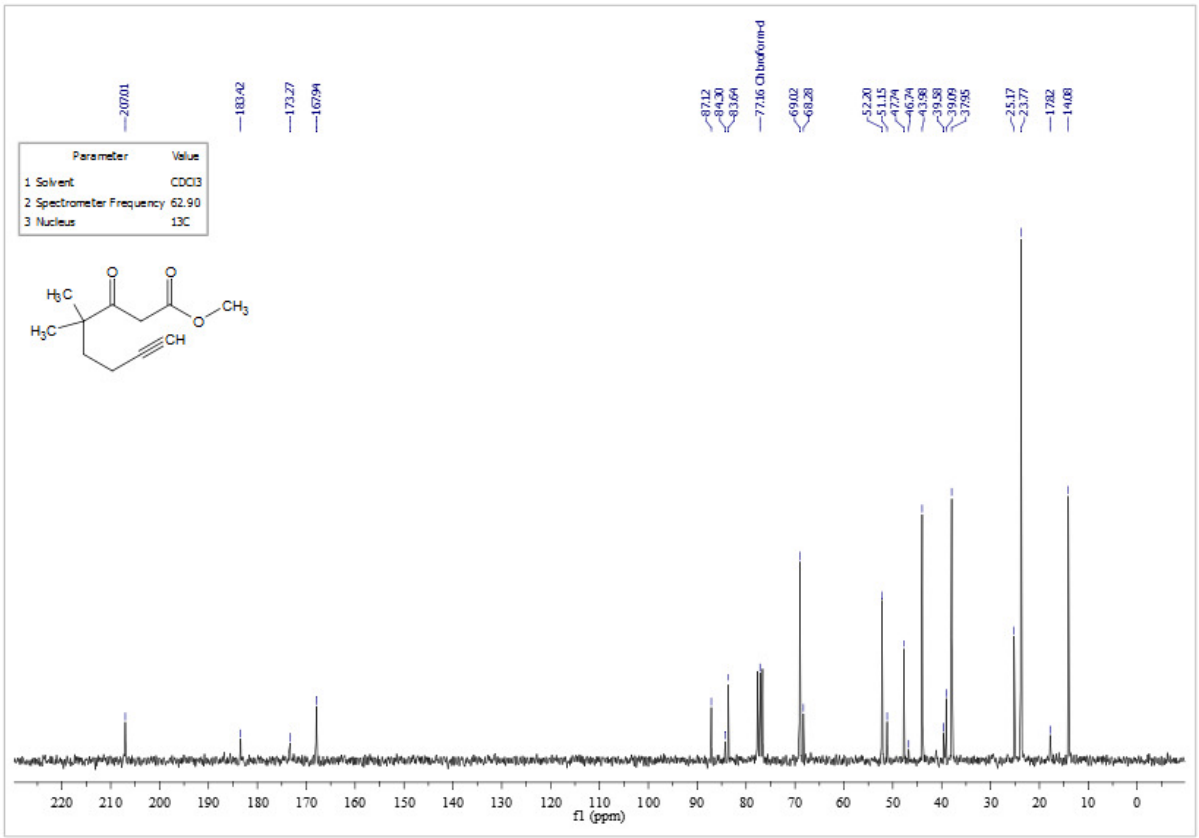


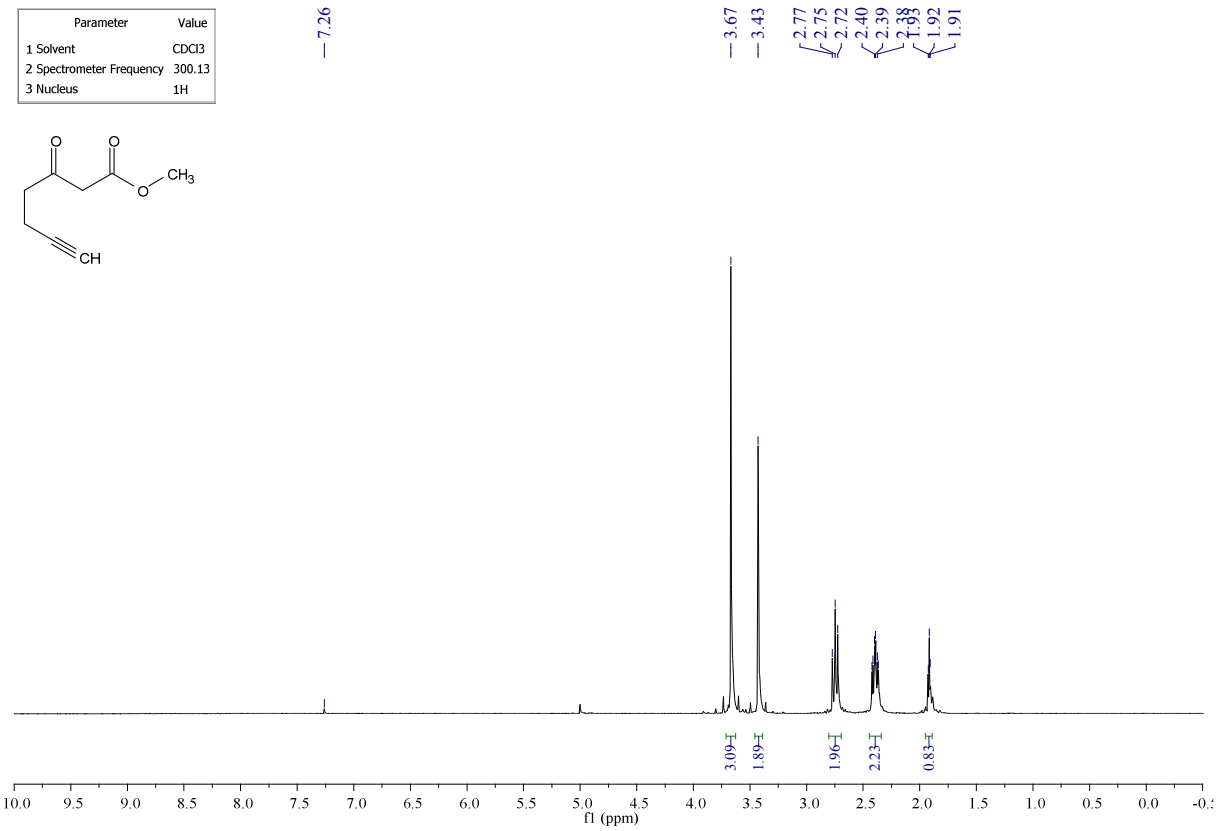
(P/SM=3.2/1)

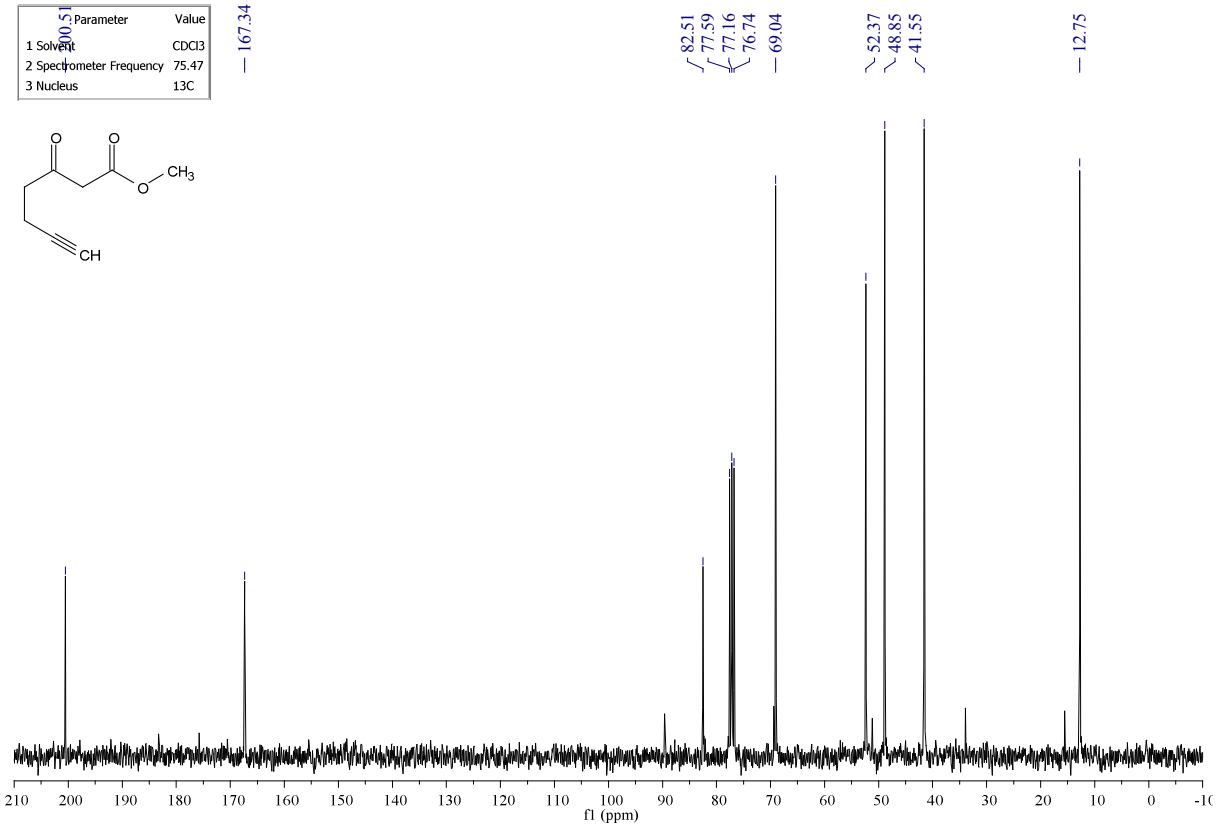


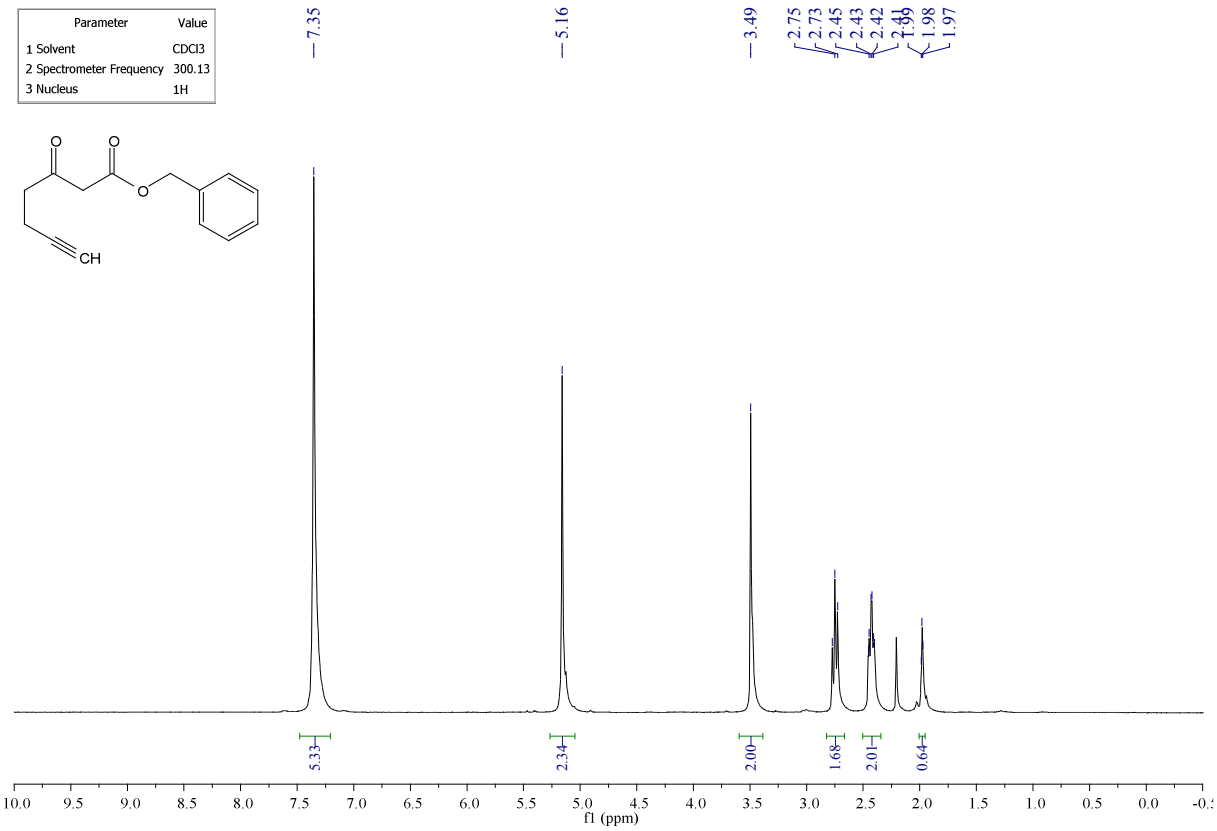
(P/SM=3.2/1)

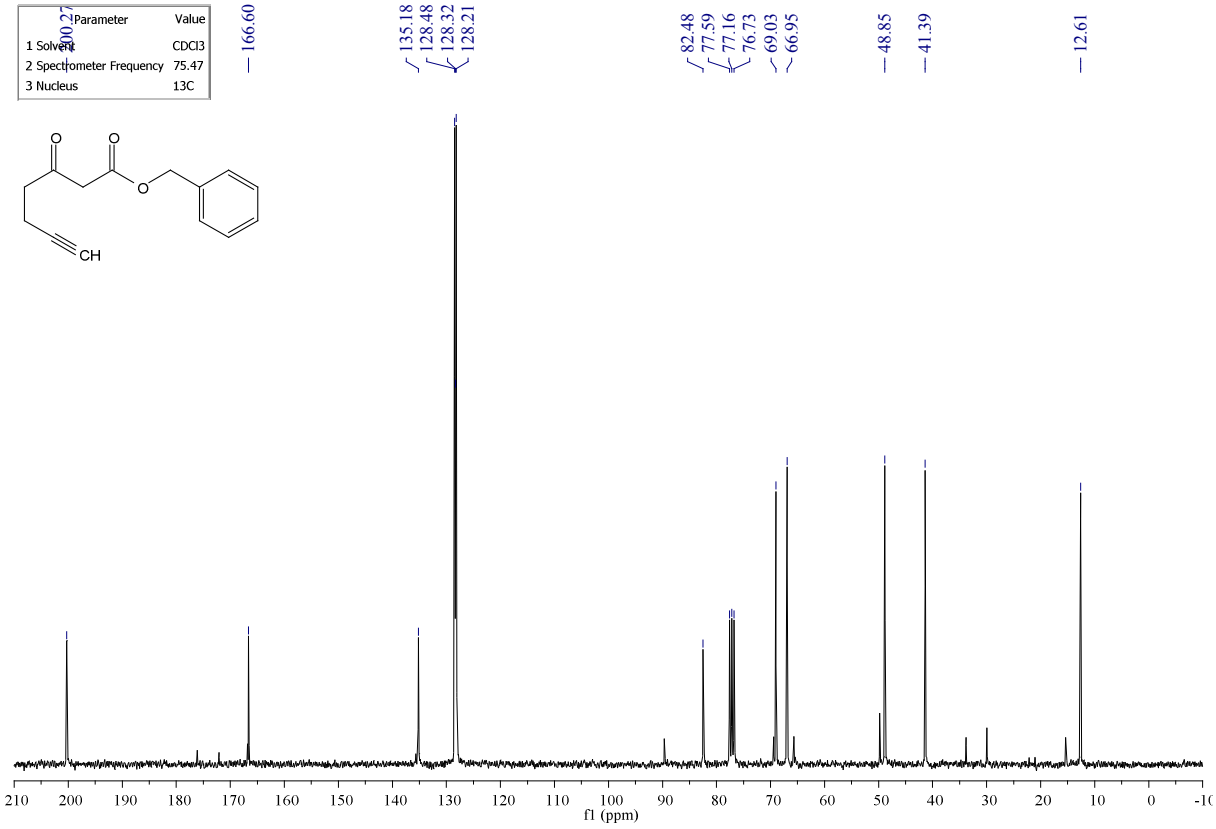

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 250.13
3 Nucleus 1H
7.26 Chloroform-d
3.64
3.49
3.44
2.08
2.07
2.05
2.04
2.03
2.01
2.00
1.91
1.90
1.89
1.77
1.76
1.74
1.71
1.09
3.86
1.99
2.30
1.00
2.46
6.00
f1 (ppm)

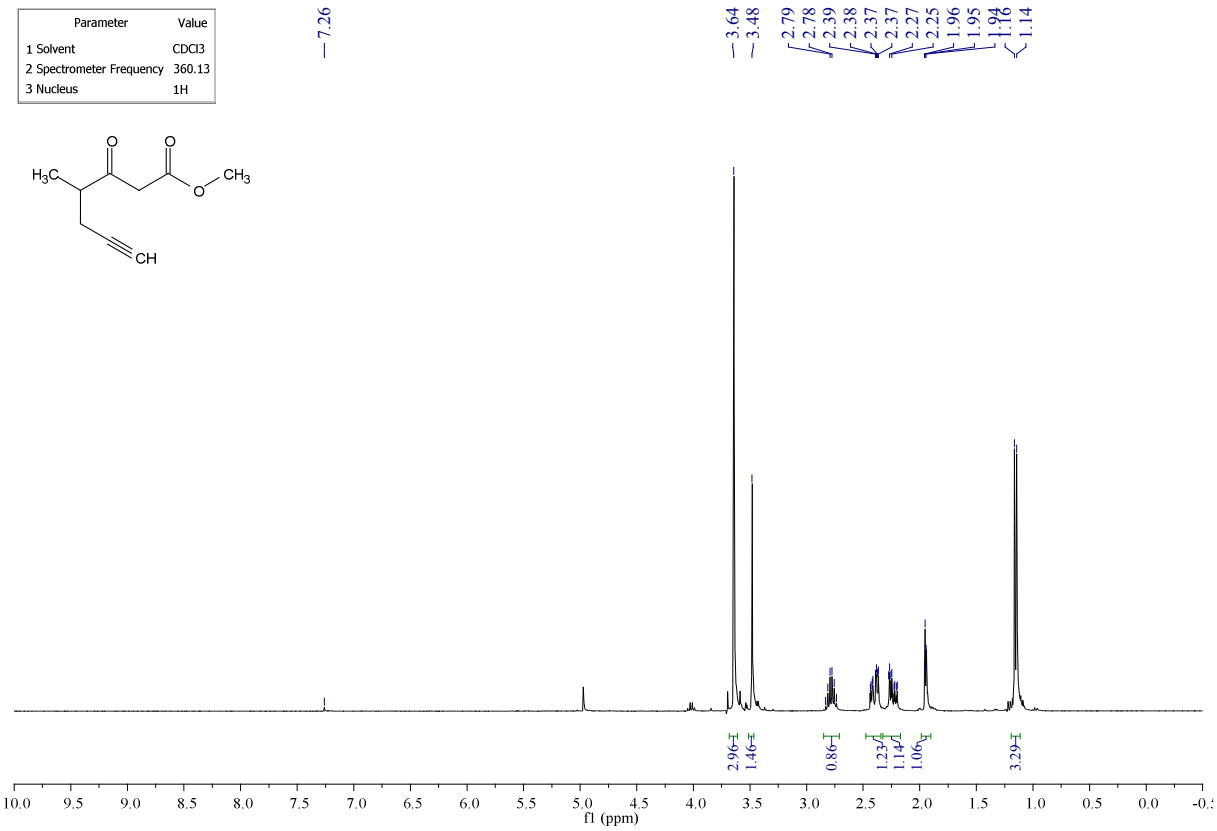

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 62.90
3 Nucleus 13C
207.01
183.42
173.27
167.94
87.12
84.30
83.64
77.16 Chloroform-d
69.02
68.28
52.20
51.15
47.74
46.74
43.98
39.58
39.09
37.95
25.17
23.77
17.82
14.08
f1 (ppm)

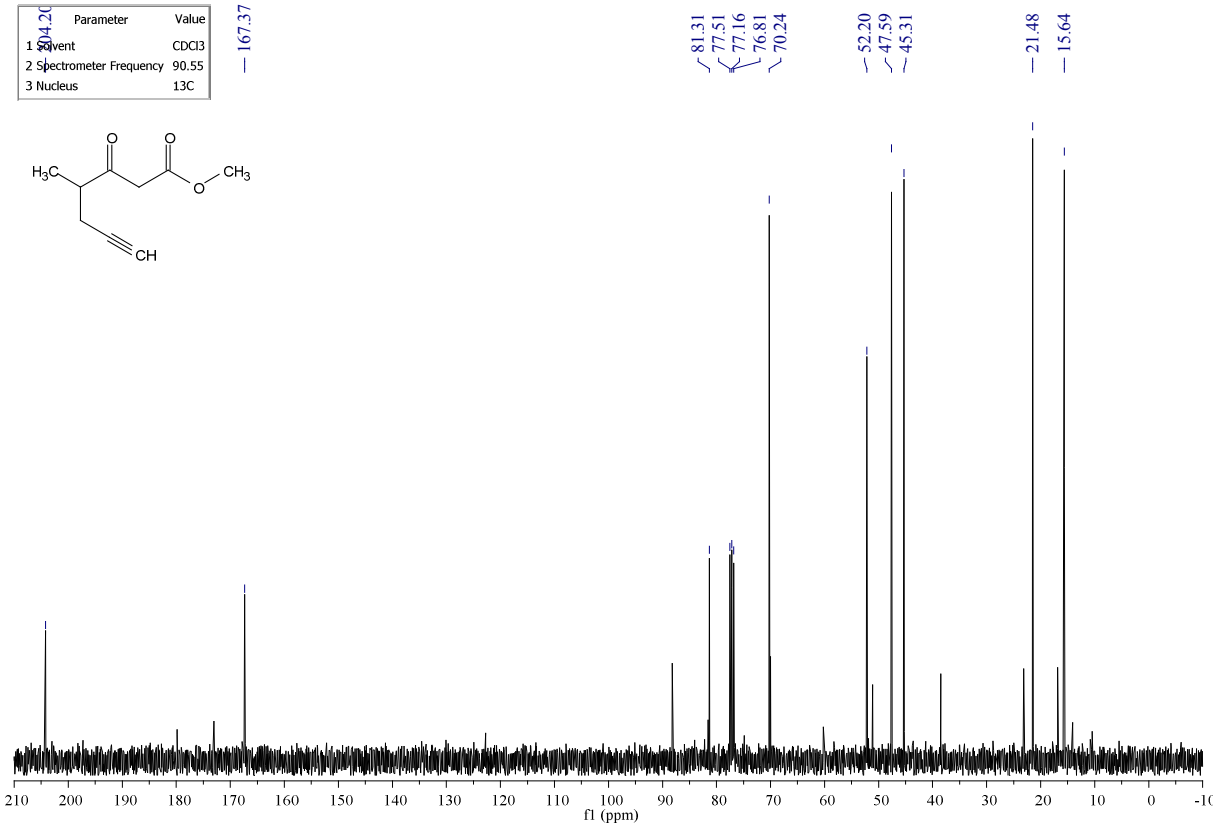

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.26
3.67
3.43
2.77
2.75
2.72
2.40
2.39
1.92
1.91
3.09
1.89
1.96
2.23
0.83
f1 (ppm)

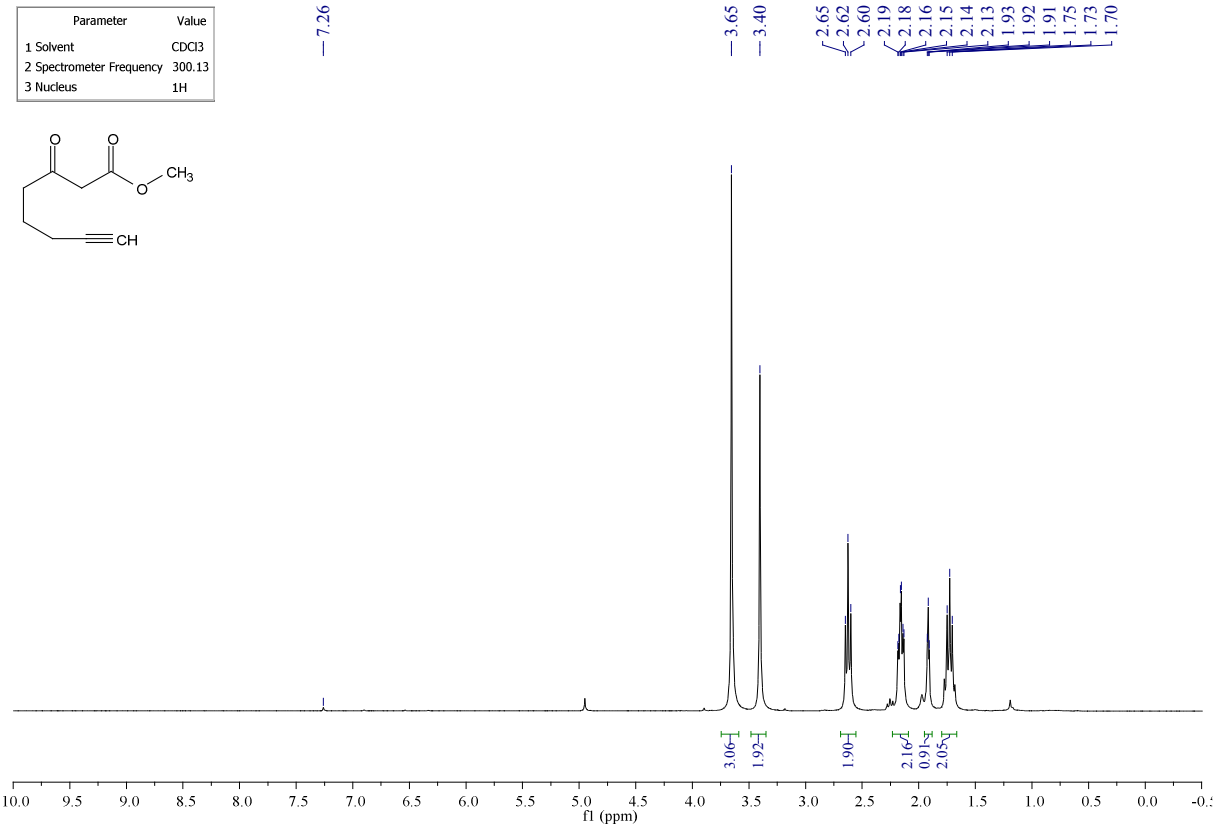

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
167.34
82.51
77.59
77.16
76.74
69.04
52.37
48.85
41.55
12.75
f1 (ppm)

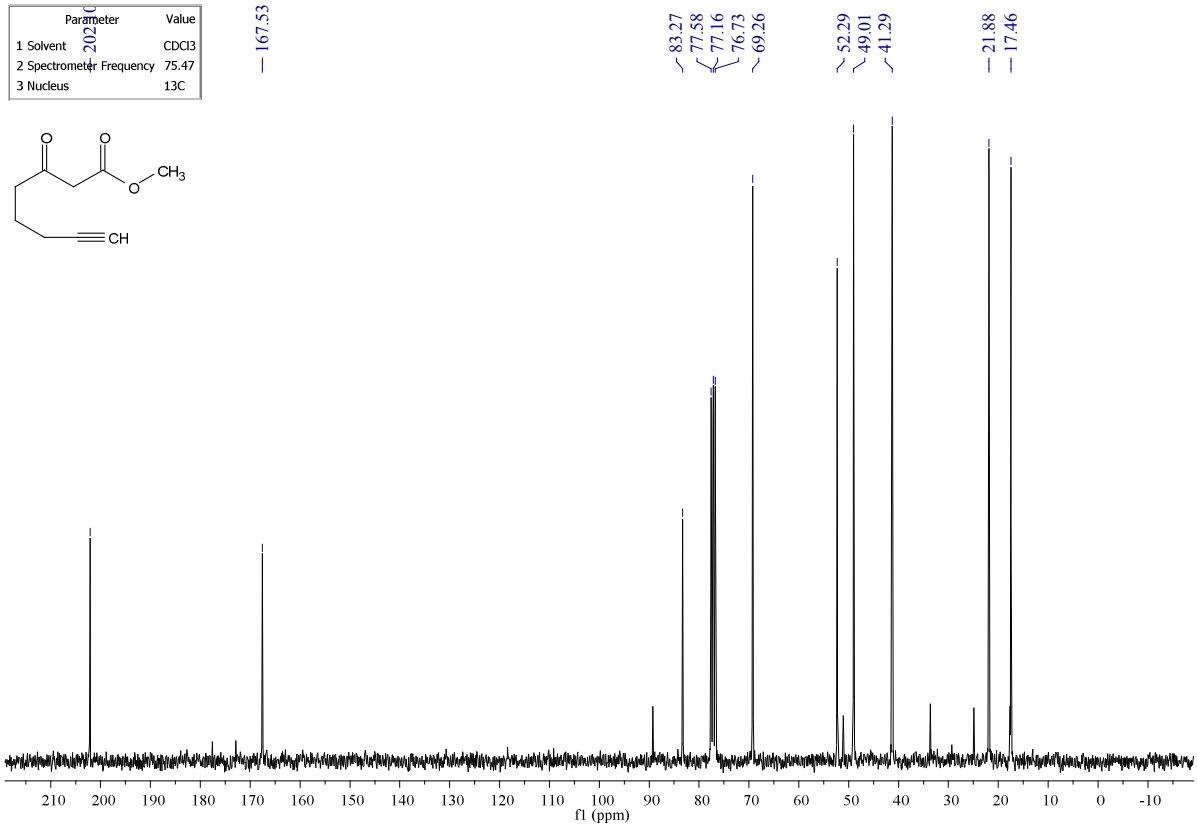

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.35
5.16
3.49
2.75
2.73
2.45
2.43
2.42
2.41
1.99
1.98
1.97
5.33
2.34
2.00
1.68
2.01
0.64
f1 (ppm)

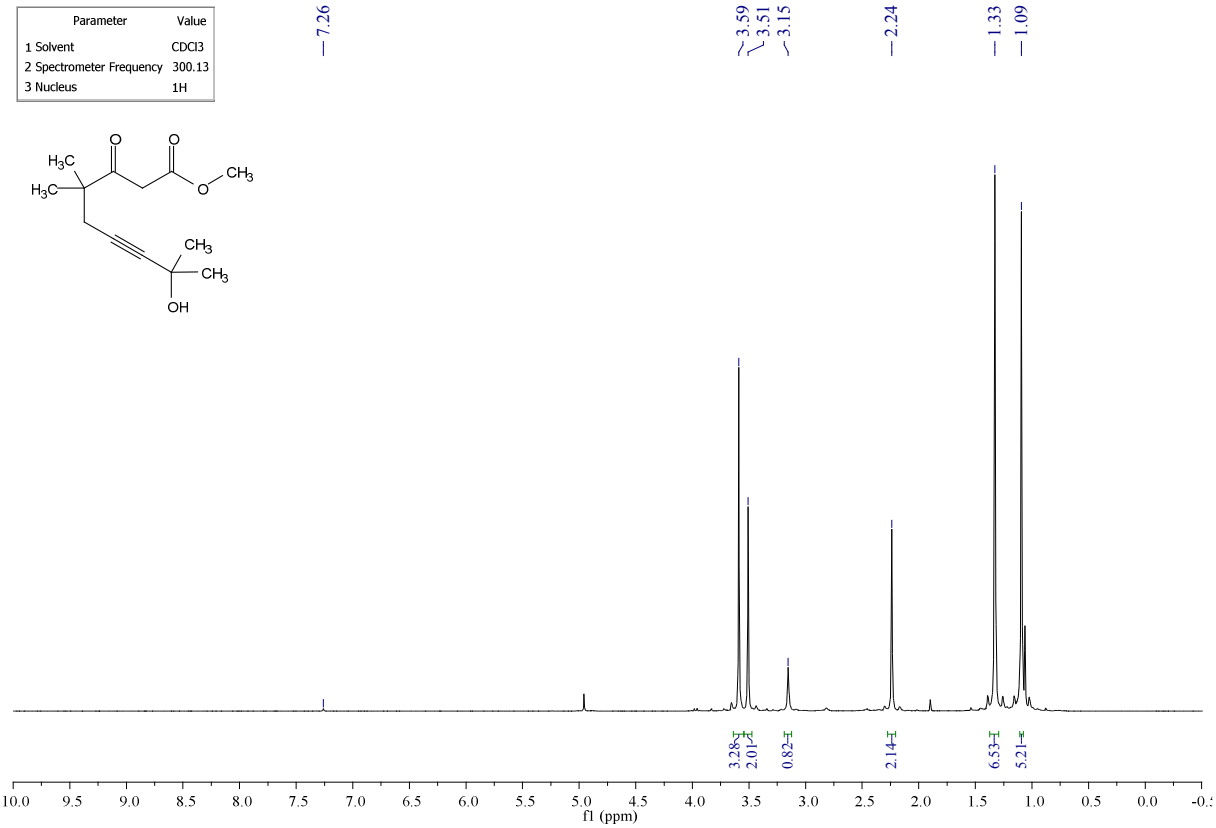

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
166.60
135.18
128.48
128.32
128.21
82.48
77.59
77.16
76.73
69.03
66.95
48.85
41.39
12.61
f1 (ppm)

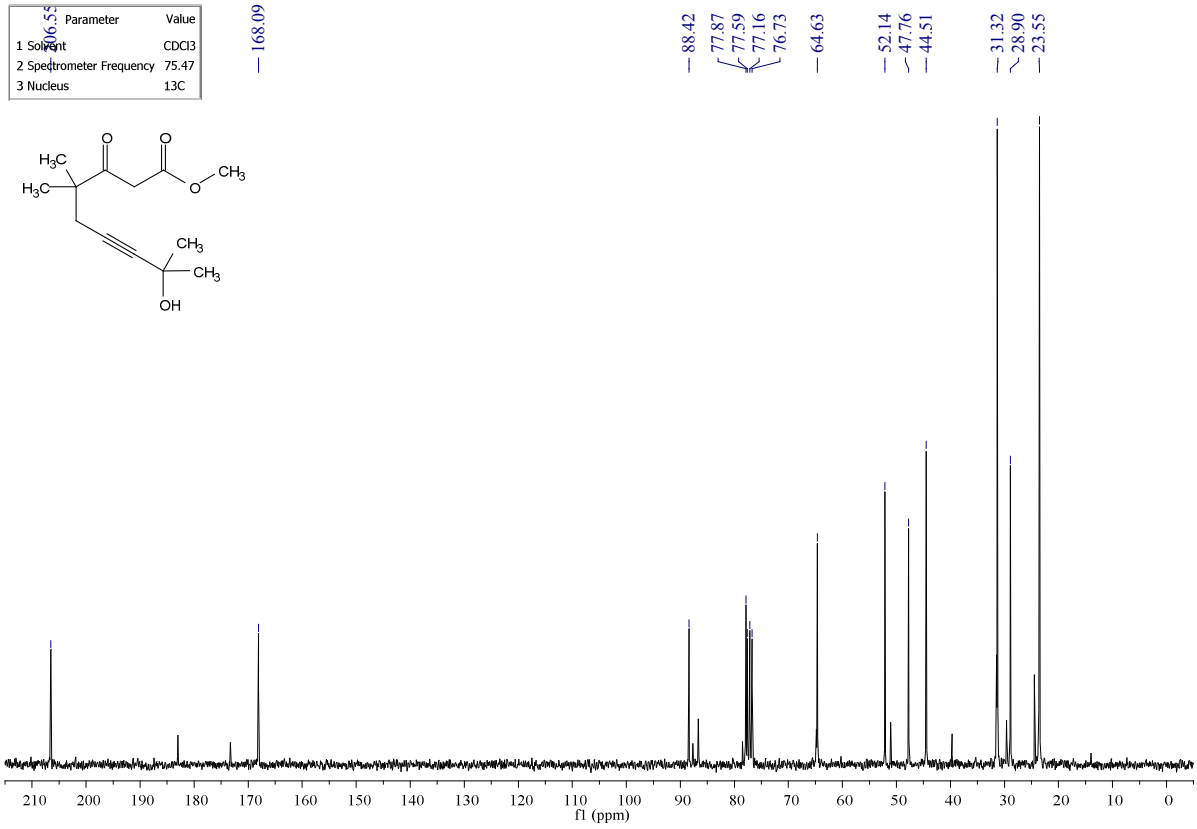

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 360.13
3 Nucleus 1H
7.26
3.64
3.48
2.79
2.78
2.39
2.38
2.37
2.37
2.27
2.25
1.96
1.95
1.94
1.16
1.14
2.96
1.46
0.86
1.23
1.14
1.06
3.29
f1 (ppm)

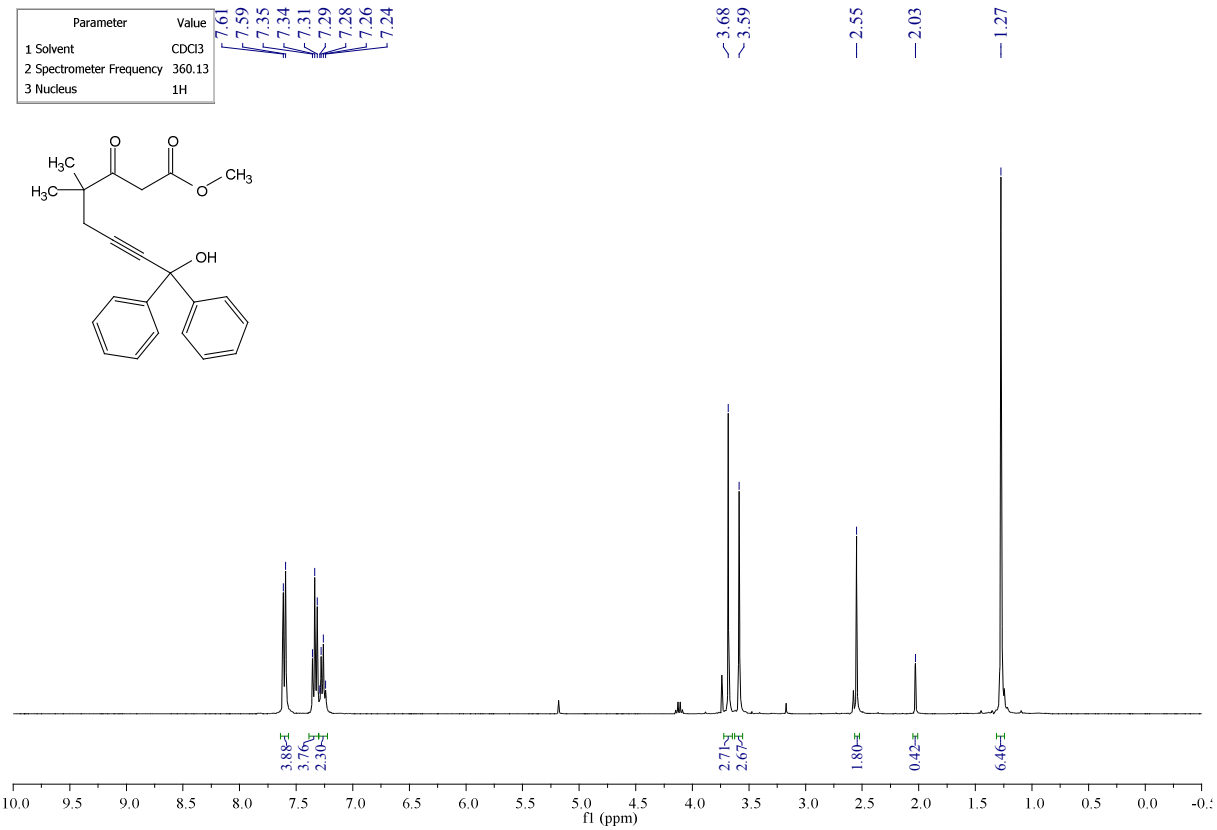

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 90.55
3 Nucleus 13C
167.37
81.31
77.51
77.16
76.81
70.24
52.20
47.59
45.31
21.48
15.64
f1 (ppm)

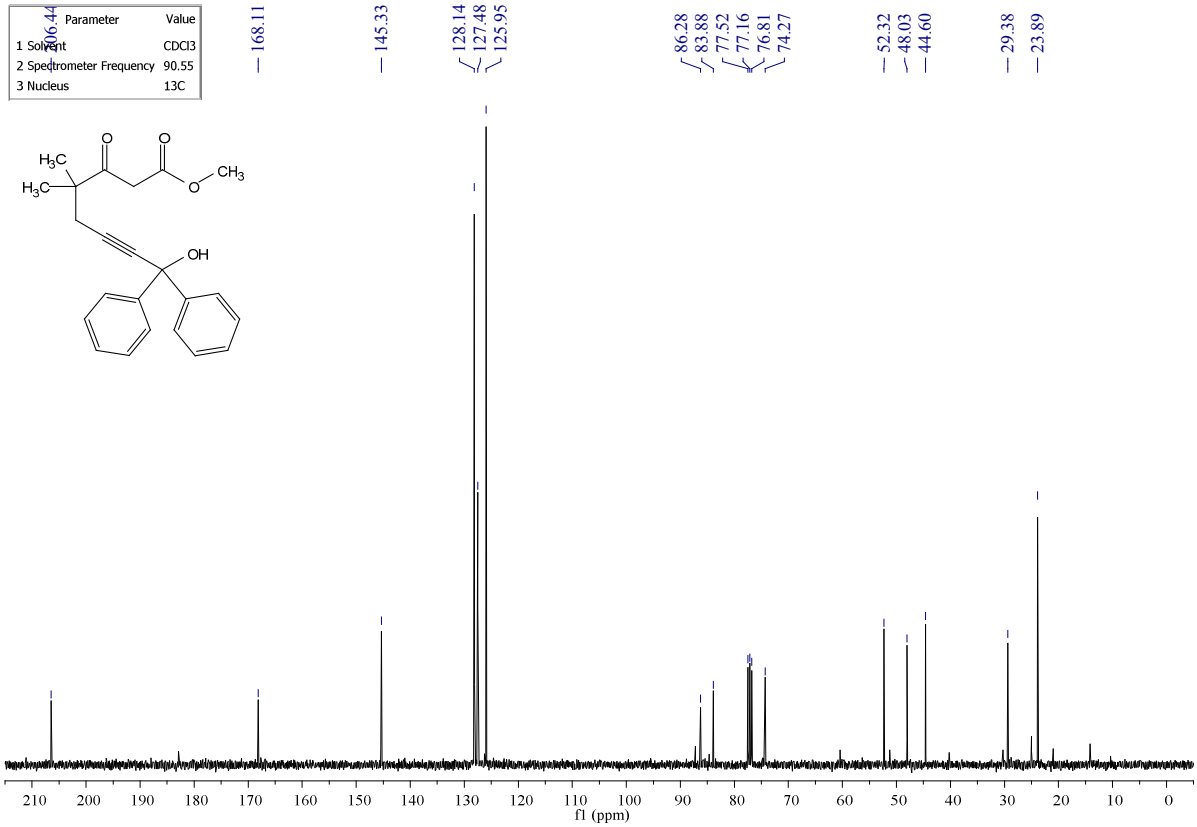

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.26
3.65
3.40
2.65
2.62
2.60
2.19
2.18
2.16
2.15
2.14
2.13
1.93
1.92
1.91
1.75
1.73
1.70
O
O
CH3
O
CH
3.06
1.92
1.90
2.16
0.91
2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

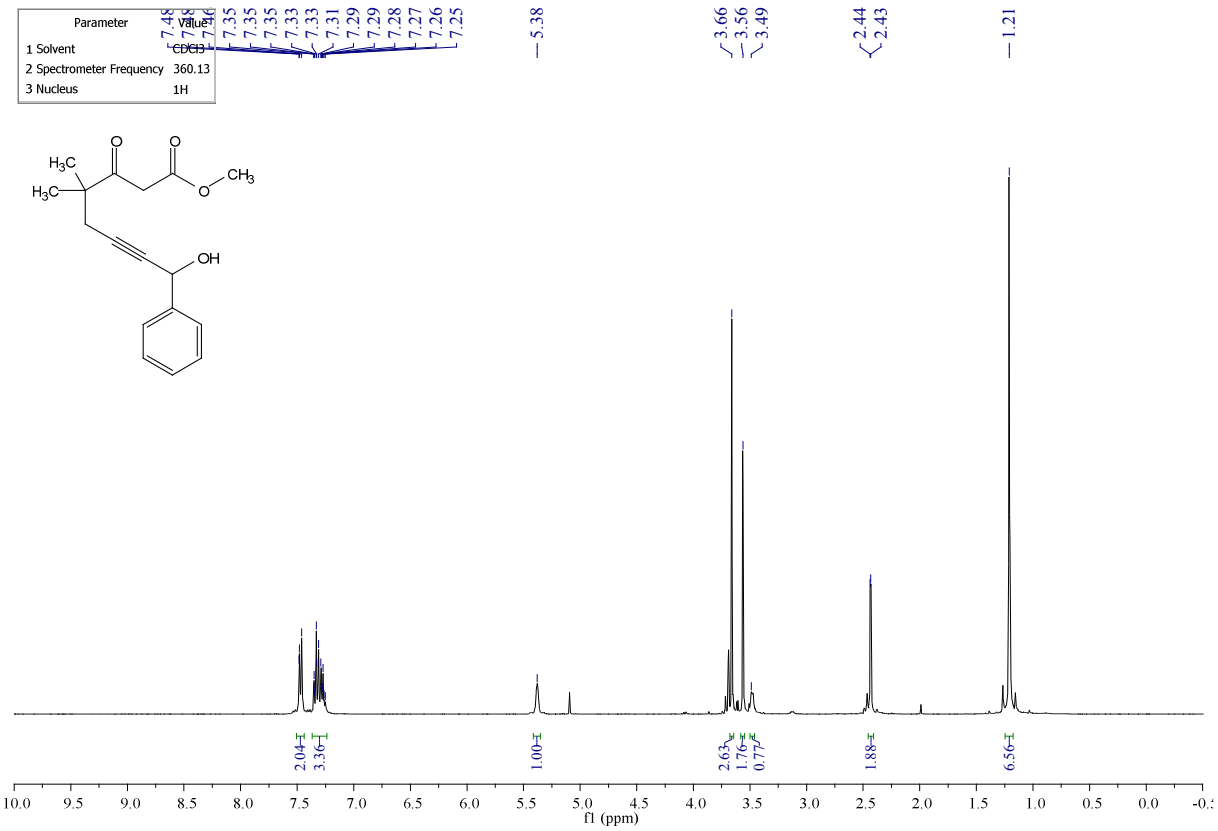

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
167.53
83.27
77.58
77.16
76.73
69.26
52.29
49.01
41.29
21.88
17.46
O
O
CH3
O
CH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

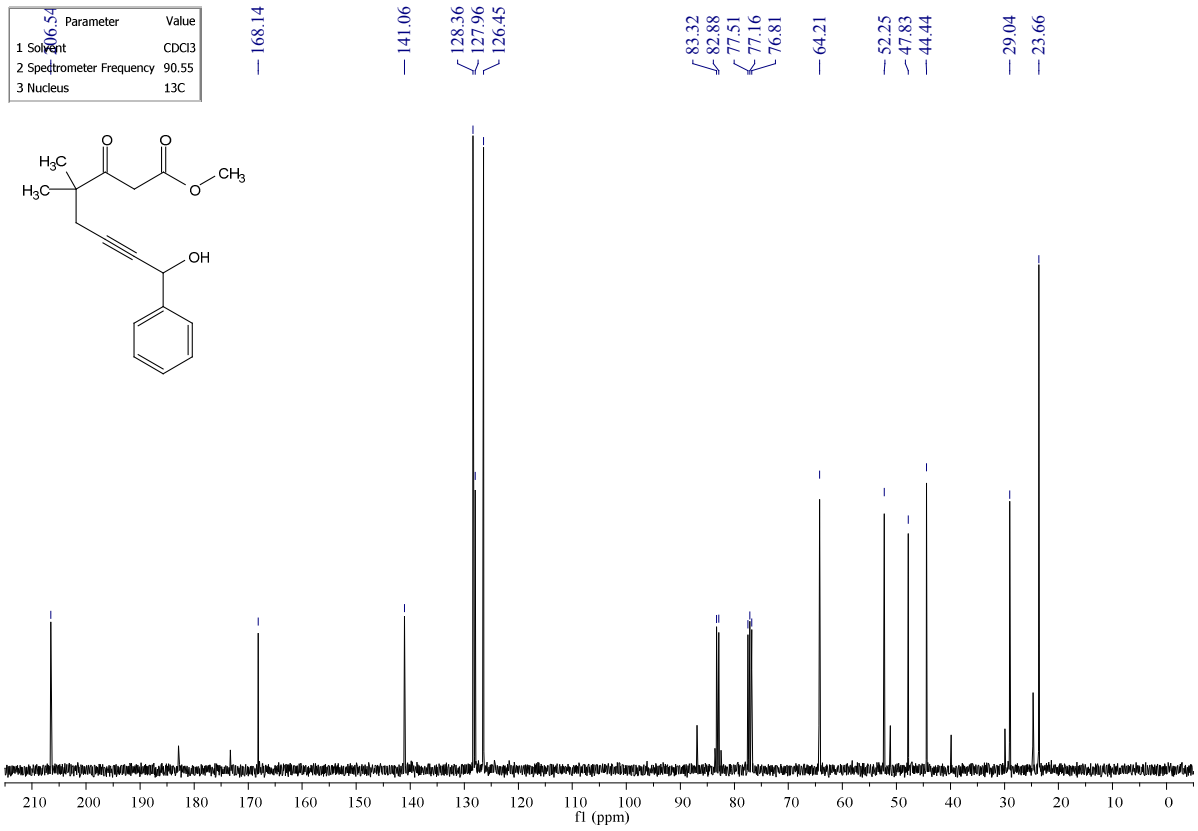

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.26
3.59
3.51
3.15
2.24
1.33
1.09
3.28
2.01
0.82
2.14
6.53
5.21
f1 (ppm)

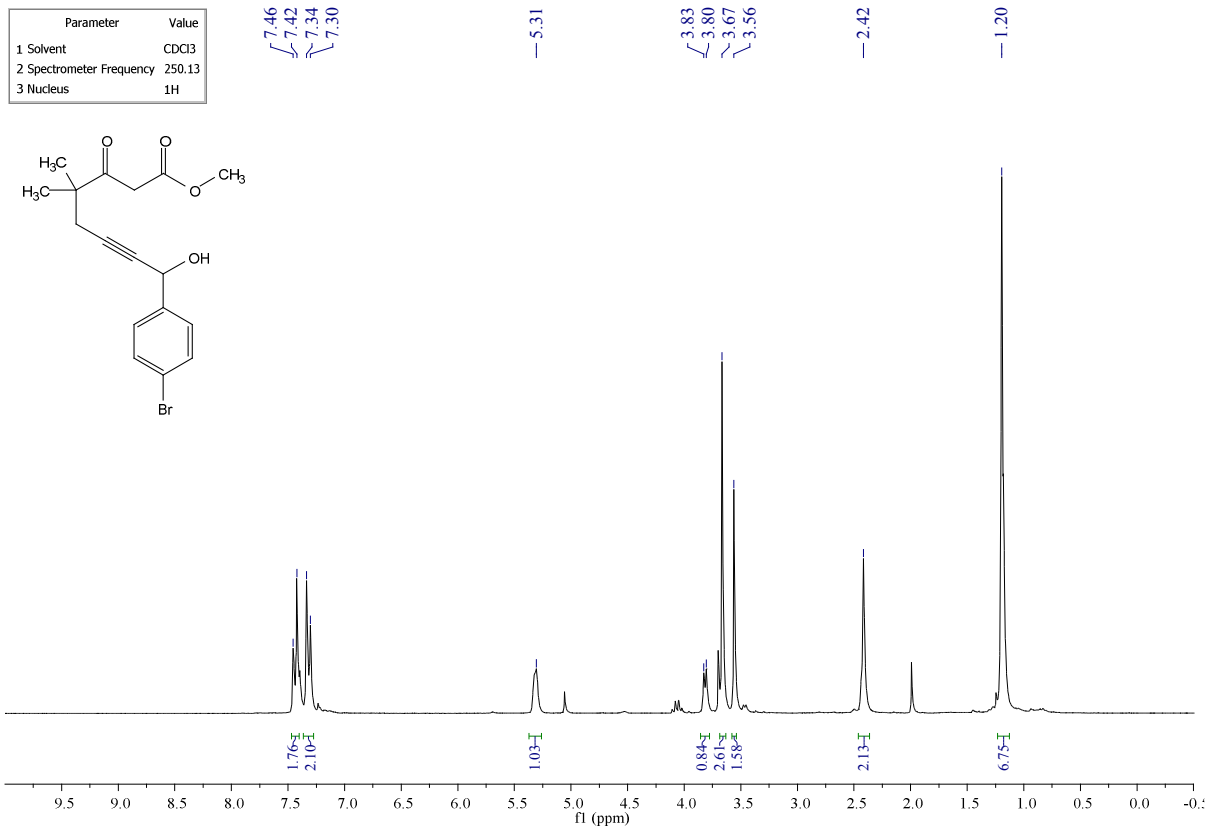

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
168.09
88.42
77.87
77.59
77.16
76.73
64.63
52.14
47.76
44.51
31.32
28.90
23.55
f1 (ppm)

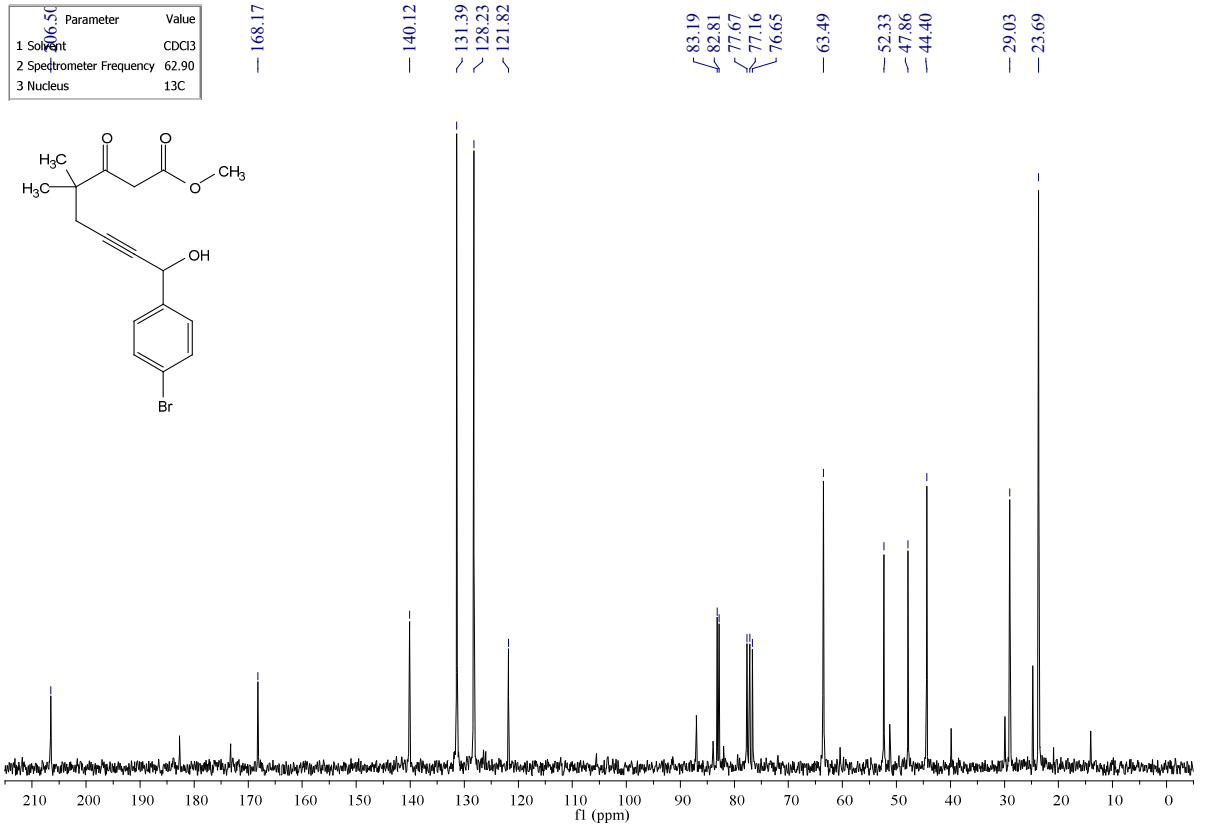

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 360.13
3 Nucleus 1H
7.61
7.59
7.35
7.34
7.31
7.29
7.28
7.26
7.24
3.68
3.59
2.55
2.03
1.27
3.88
3.76
2.30
2.71
2.67
1.80
0.42
6.46
f1 (ppm)

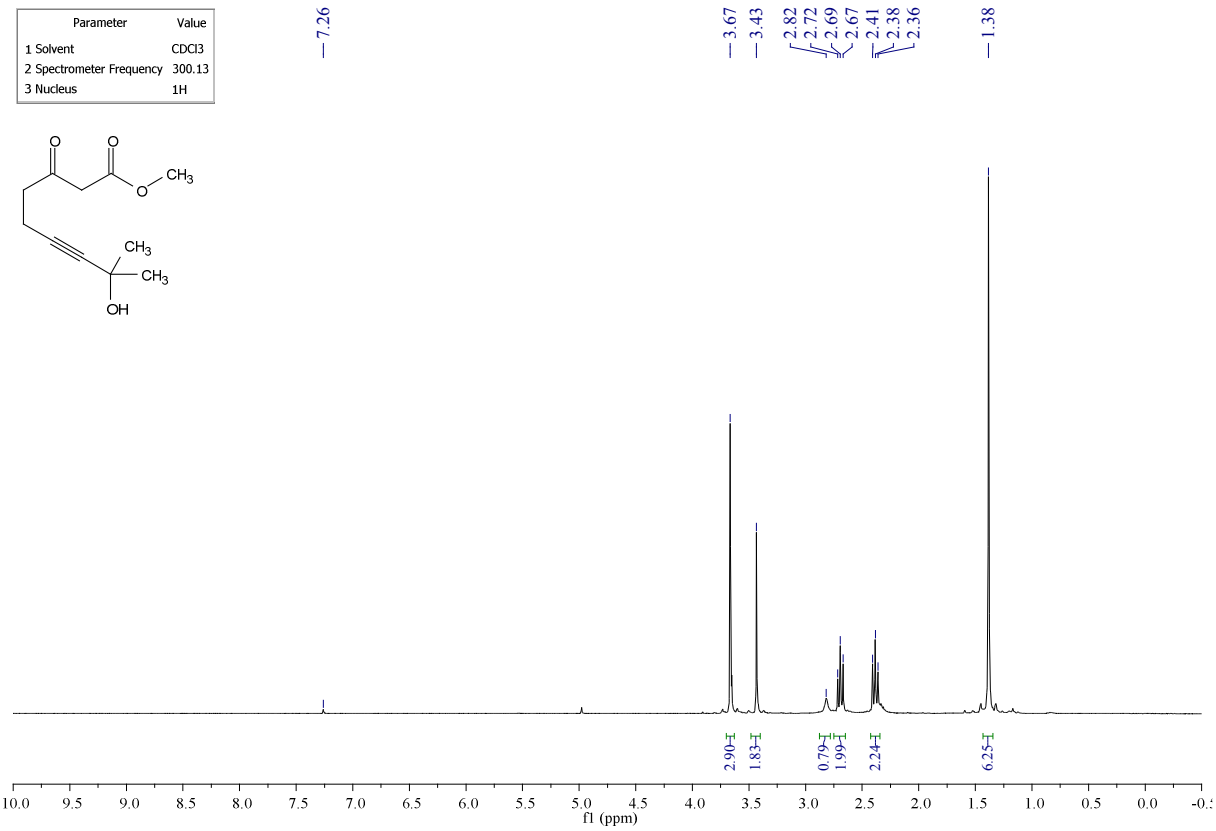

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 90.55
3 Nucleus 13C
168.11
145.33
128.14
127.48
125.95
86.28
83.88
77.52
77.16
76.81
74.27
52.32
48.03
44.60
29.38
23.89
f1 (ppm)

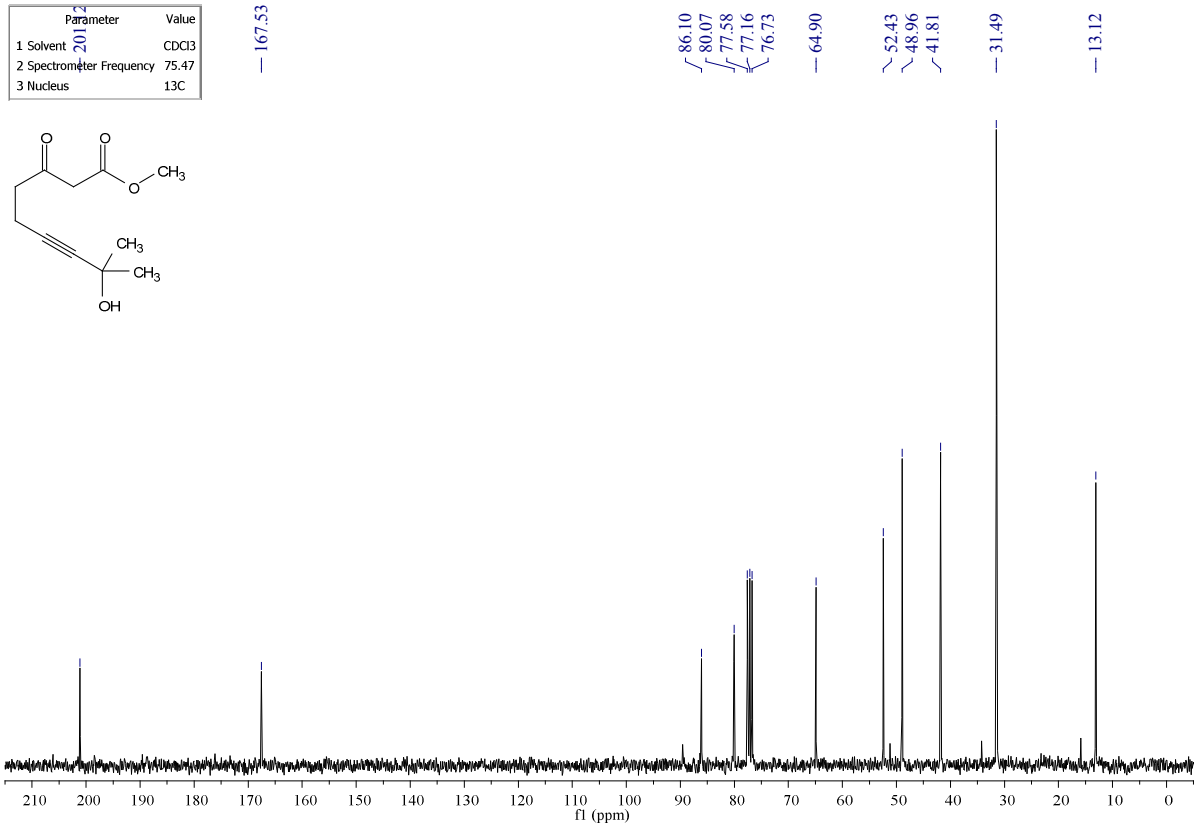

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 360.13
3 Nucleus 1H
7.48 7.46 7.35 7.35 7.35 7.33 7.33 7.31 7.29 7.29 7.28 7.27 7.26 7.25
5.38
3.66 3.56 3.49
2.44 2.43
1.21
2.04 3.36 1.00 2.63 1.76 0.77 1.88 6.56
f1 (ppm)

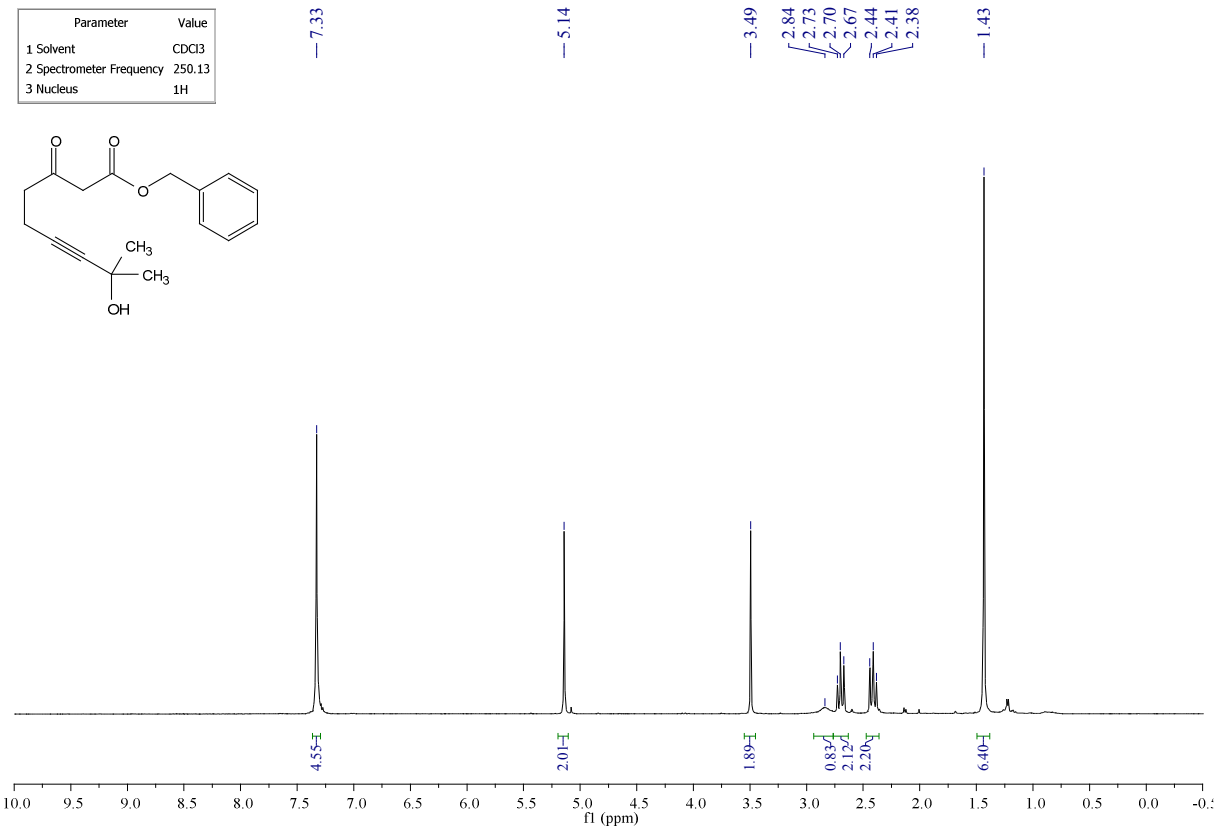

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 90.55
3 Nucleus 13C
168.14
141.06
128.36 127.96 126.45
83.32 82.88 77.51 77.16 76.81
64.21
52.25 47.83 44.44
29.04 23.66
f1 (ppm)

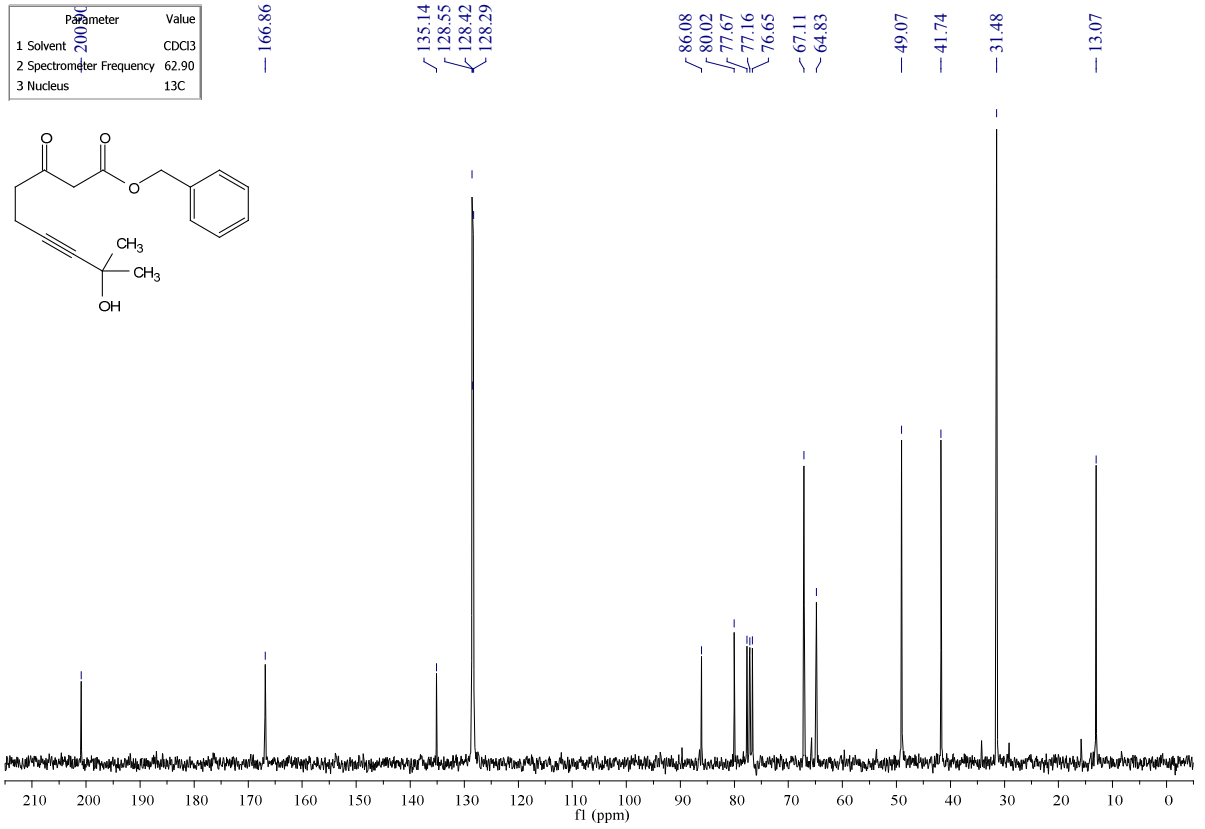

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 250.13
3 Nucleus 1H
7.46
7.42
7.34
7.30
5.31
3.83
3.80
3.67
3.56
2.42
1.20
1.76
2.10
1.03
0.84
2.61
1.58
2.13
6.75
f1 (ppm)

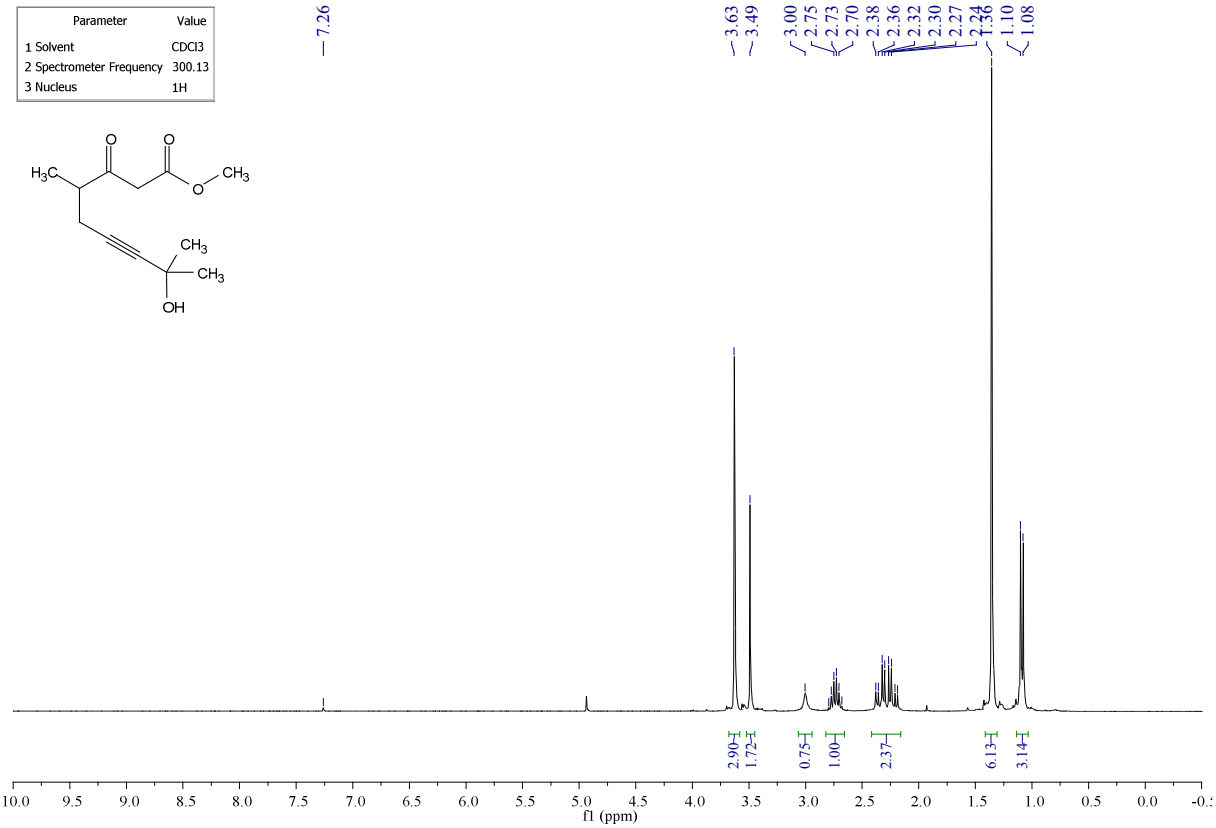

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 62.90
3 Nucleus 13C
168.17
140.12
131.39
128.23
121.82
83.19
82.81
77.67
77.16
76.65
63.49
52.33
47.86
44.40
29.03
23.69
f1 (ppm)

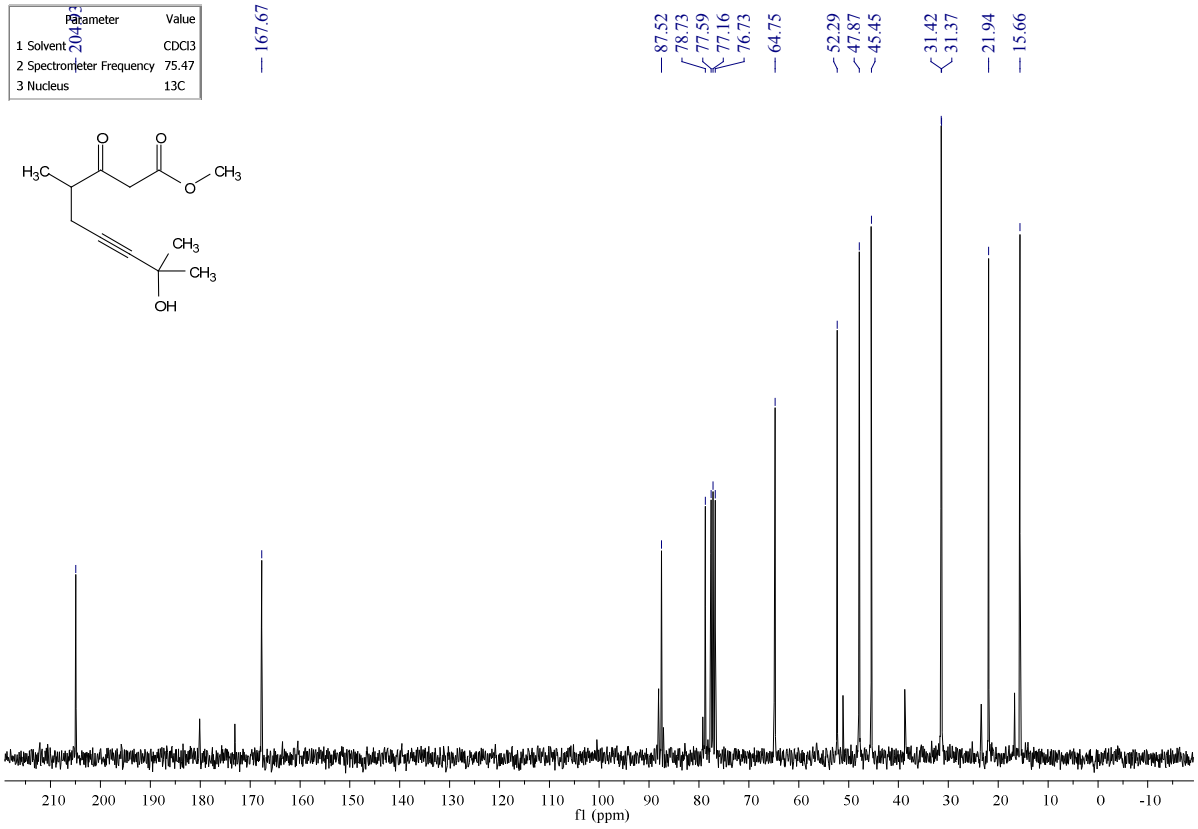

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.26
3.67
3.43
2.82
2.72
2.69
2.67
2.41
2.38
2.36
1.38
2.90
1.83
0.79
1.99
2.24
6.25
f1 (ppm)

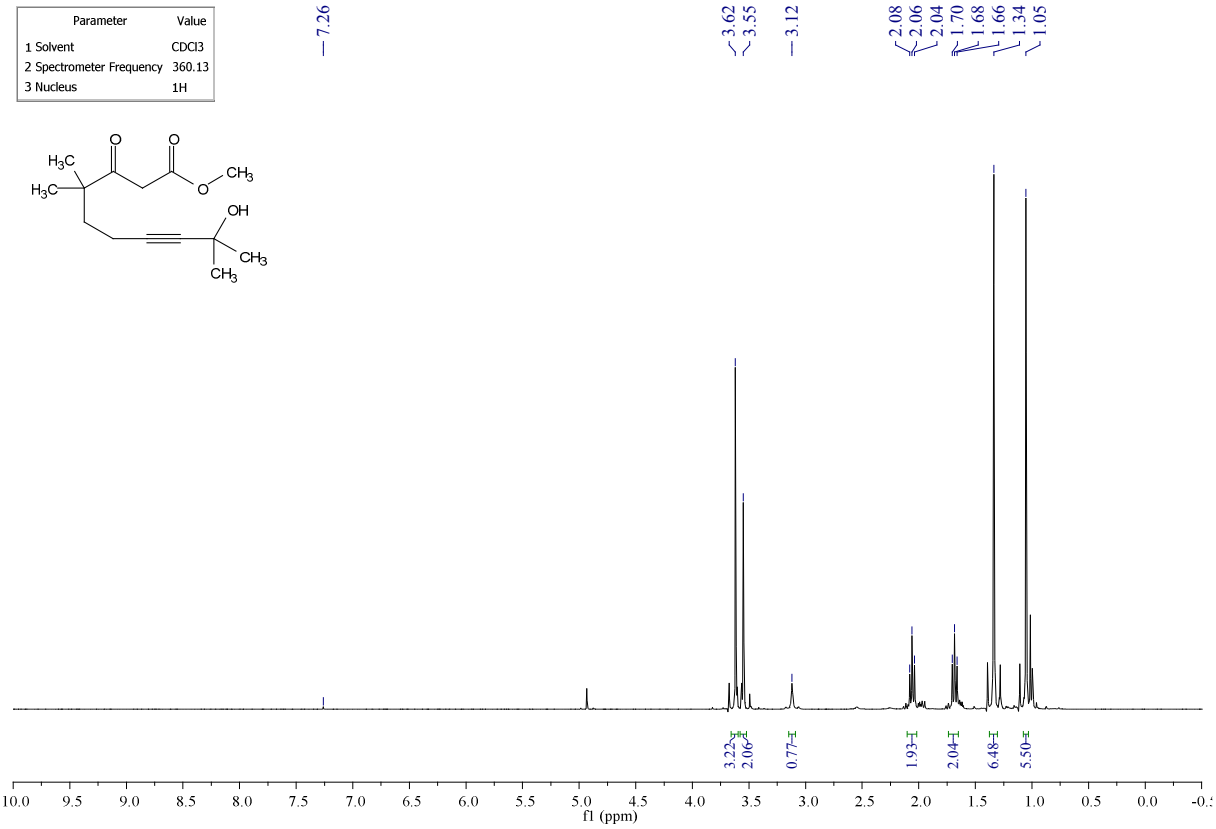

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
167.53
86.10
80.07
77.58
77.16
76.73
64.90
52.43
48.96
41.81
31.49
13.12
f1 (ppm)

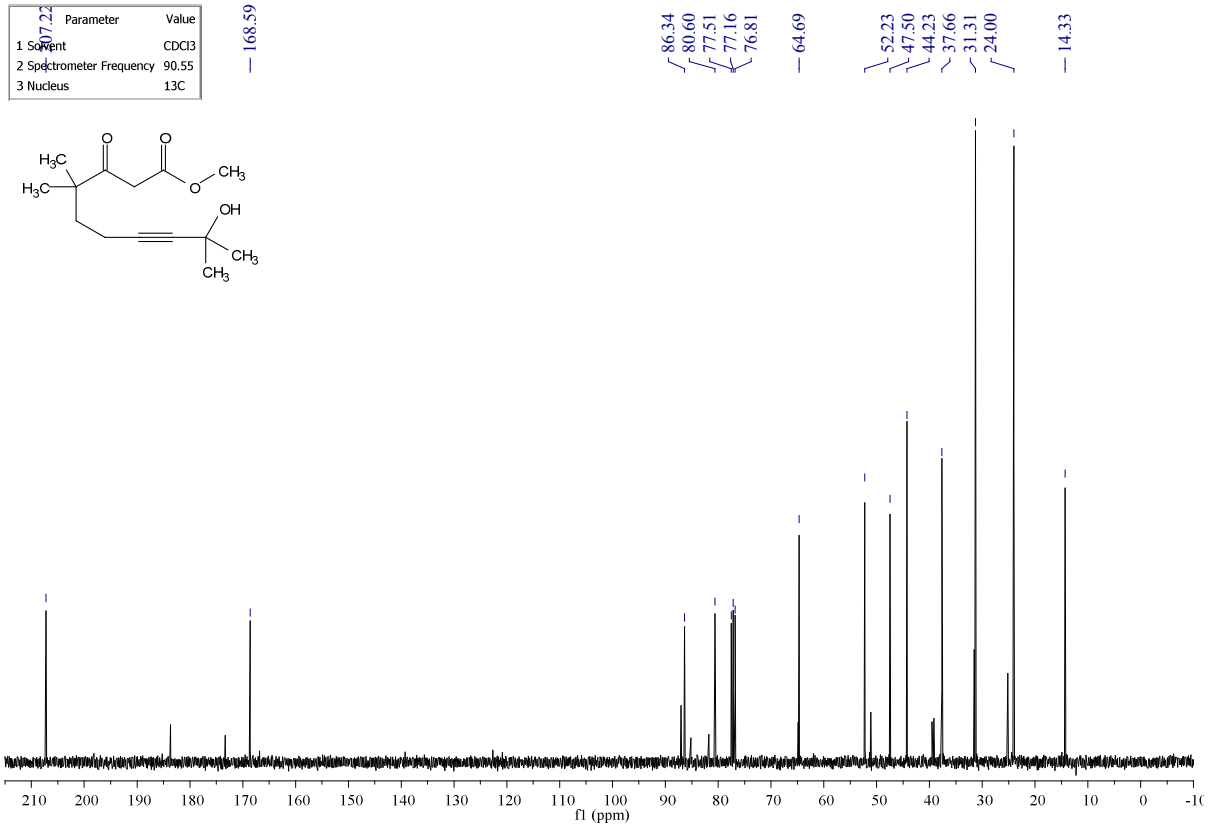

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 250.13
3 Nucleus 1H
7.33
5.14
3.49
2.84
2.73
2.70
2.67
2.44
2.41
2.38
1.43
4.55
2.01
1.89
0.83
2.12
2.20
6.40
f1 (ppm)

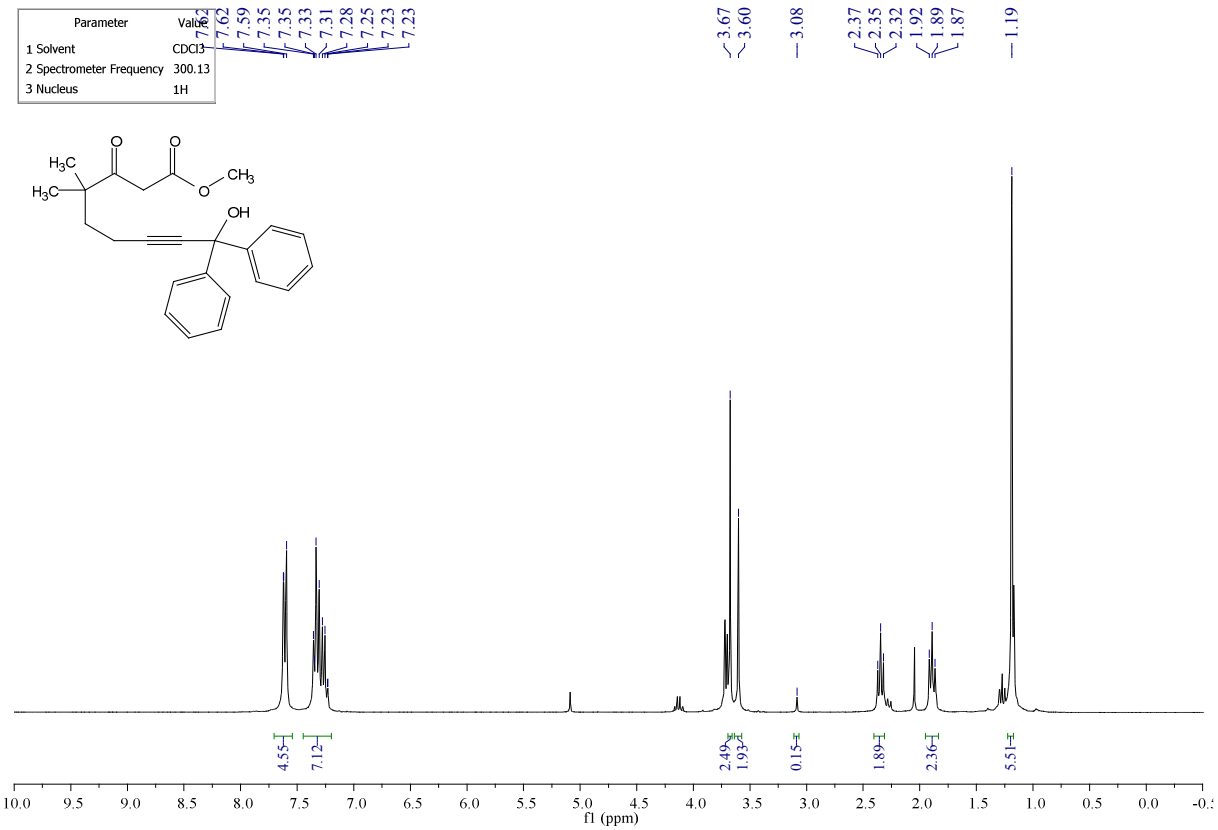

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 62.90
3 Nucleus 13C
166.86
135.14
128.55
128.42
128.29
86.08
80.02
77.67
77.16
76.65
67.11
64.83
49.07
41.74
31.48
13.07
f1 (ppm)

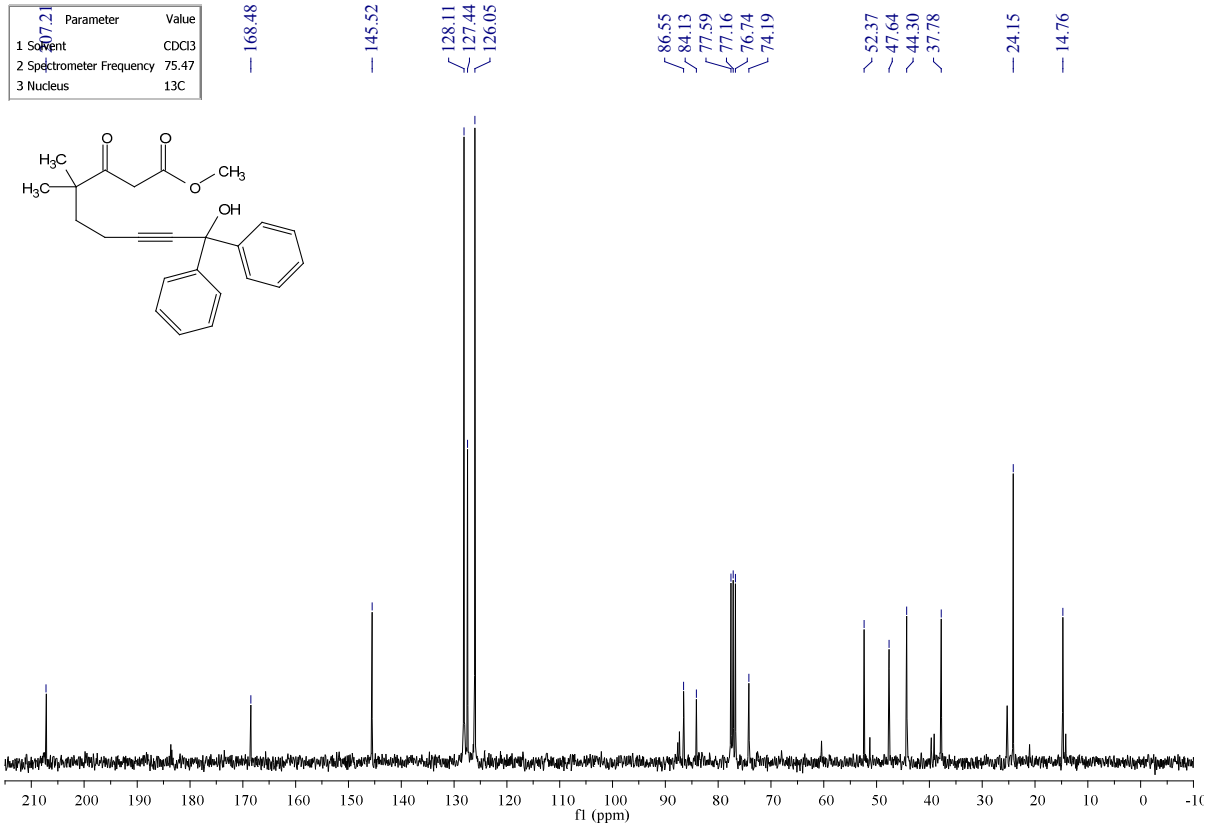

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.26
3.63
3.49
3.00
2.75
2.73
2.70
2.38
2.36
2.32
2.30
2.27
1.38
1.10
1.08
2.90
1.72
0.75
1.00
2.37
6.13
3.14
f1 (ppm)

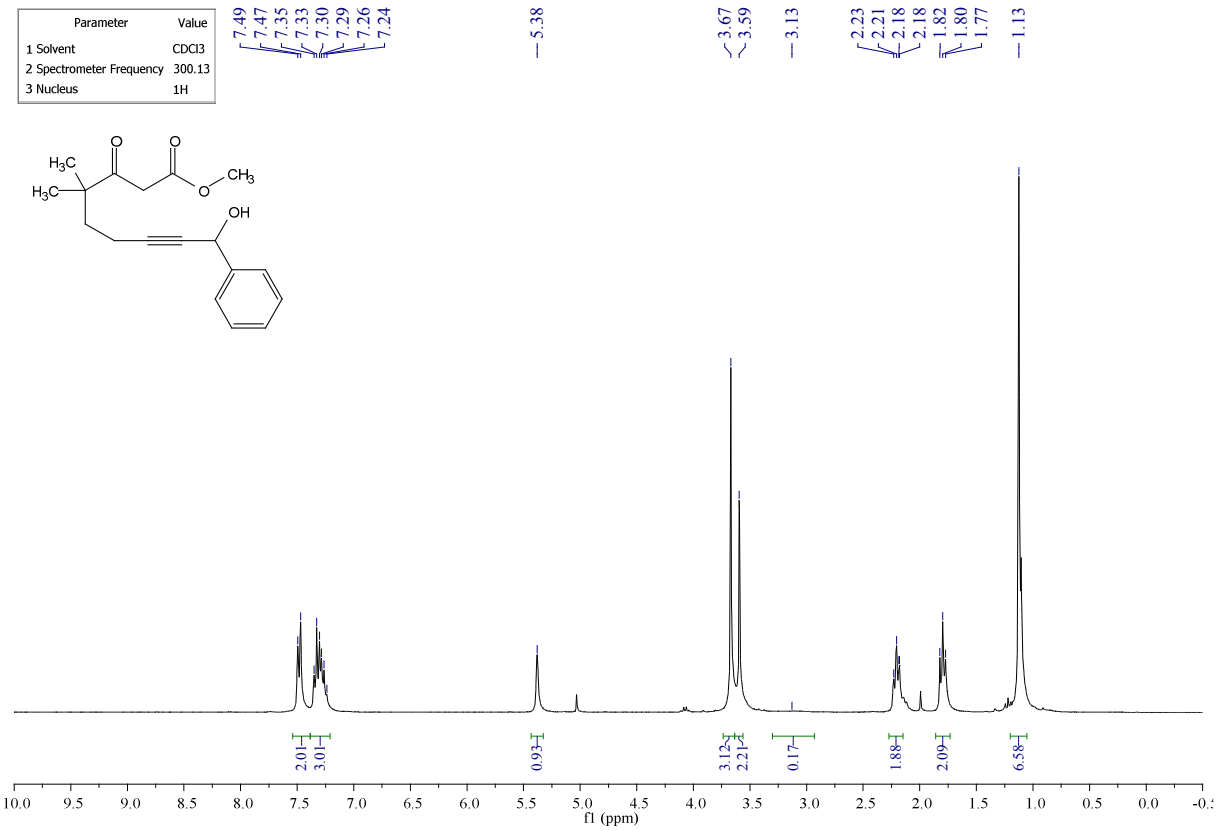

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
204.13
167.67
87.52
78.73
77.59
77.16
76.73
64.75
52.29
47.87
45.45
31.42
31.37
21.94
15.66
f1 (ppm)

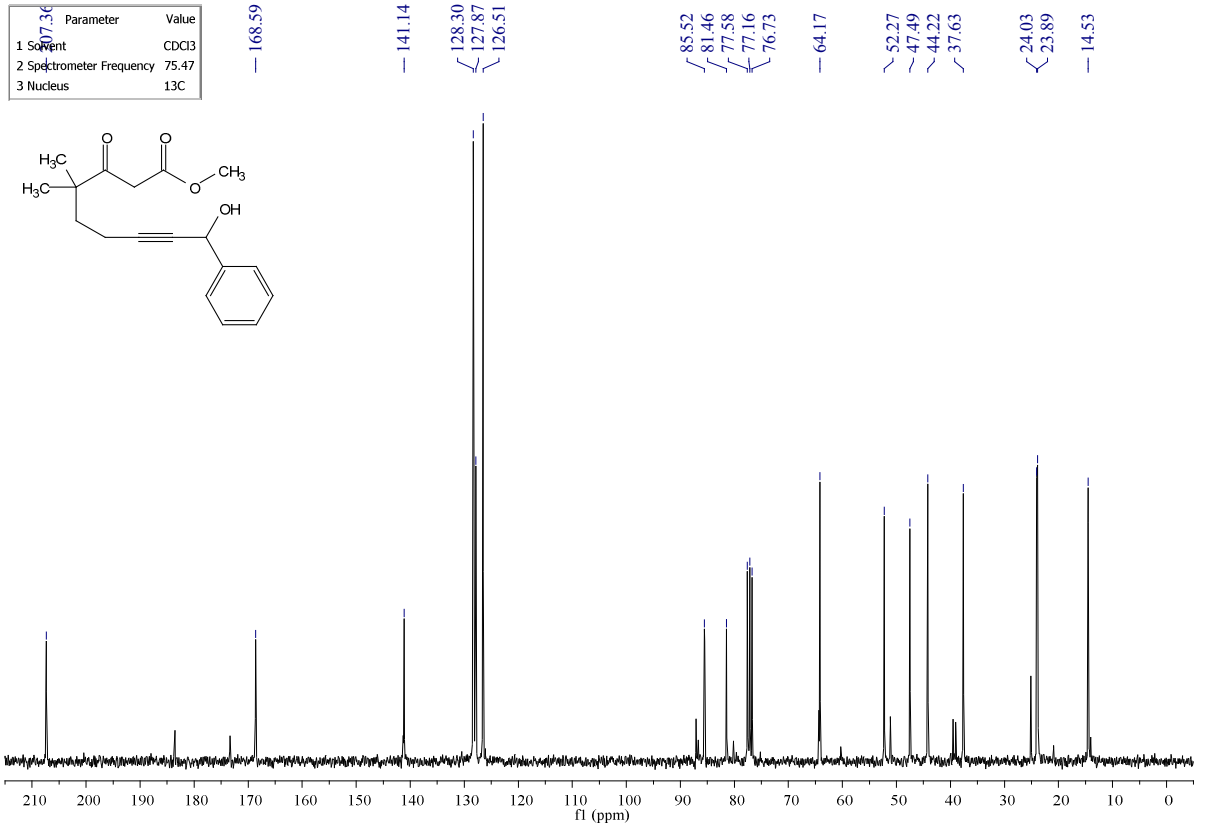

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 360.13
3 Nucleus 1H
7.26
3.62
3.55
3.12
2.08
2.06
2.04
1.70
1.68
1.66
1.34
1.05
3.22
2.06
0.77
1.93
2.04
6.48
5.50
f1 (ppm)

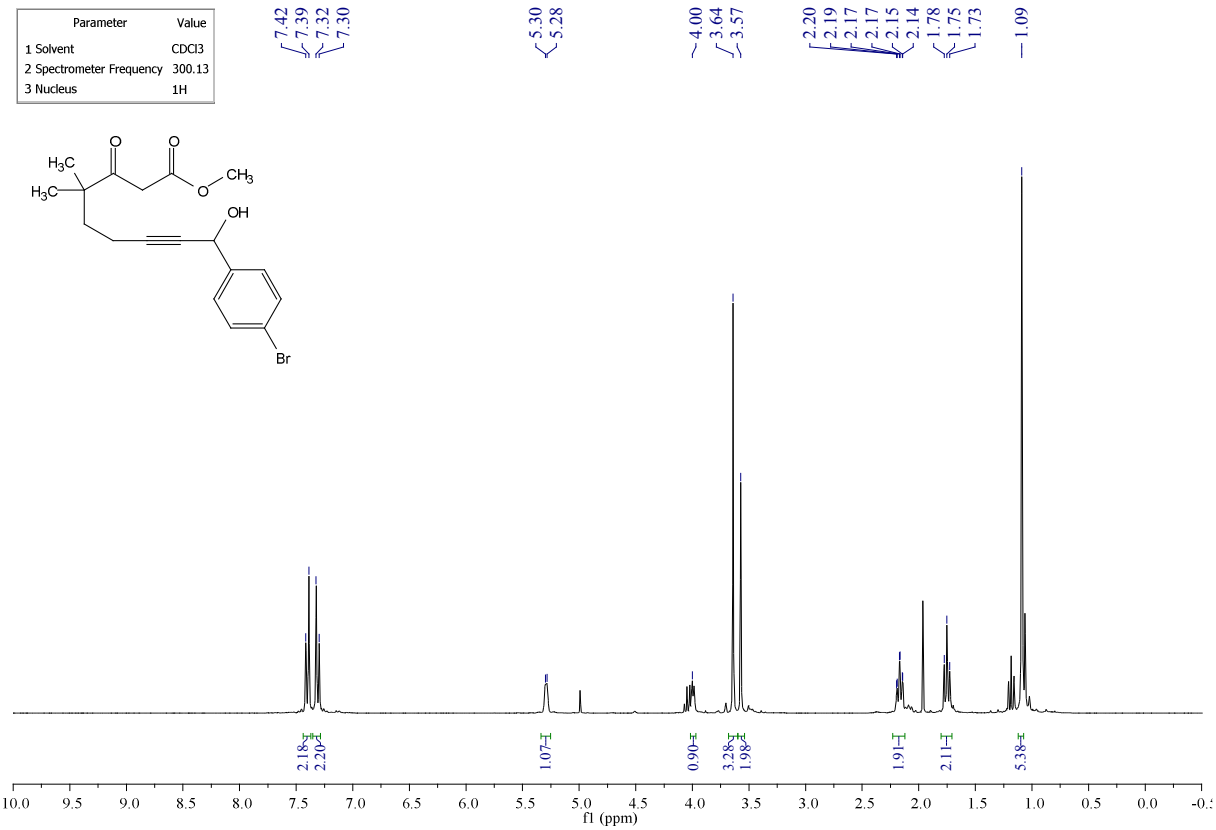

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 90.55
3 Nucleus 13C
77.22
168.59
86.34
80.60
77.51
77.16
76.81
64.69
52.23
47.50
44.23
37.66
31.31
24.00
14.33
f1 (ppm)

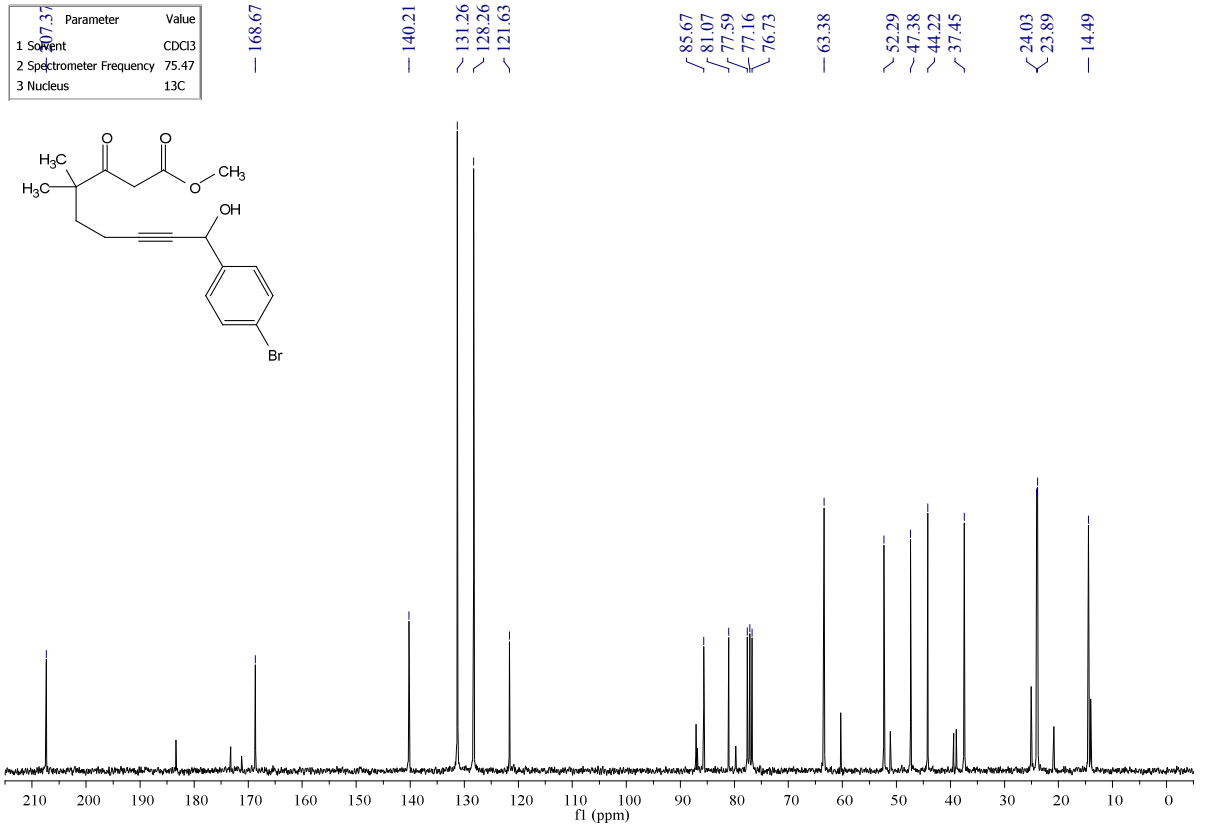

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.62
7.59
7.35
7.35
7.33
7.31
7.28
7.25
7.23
7.23
3.67
3.60
3.08
2.37
2.35
2.32
1.92
1.89
1.87
1.19
4.55
7.12
2.49
1.93
0.15
1.89
2.36
5.51
f1 (ppm)

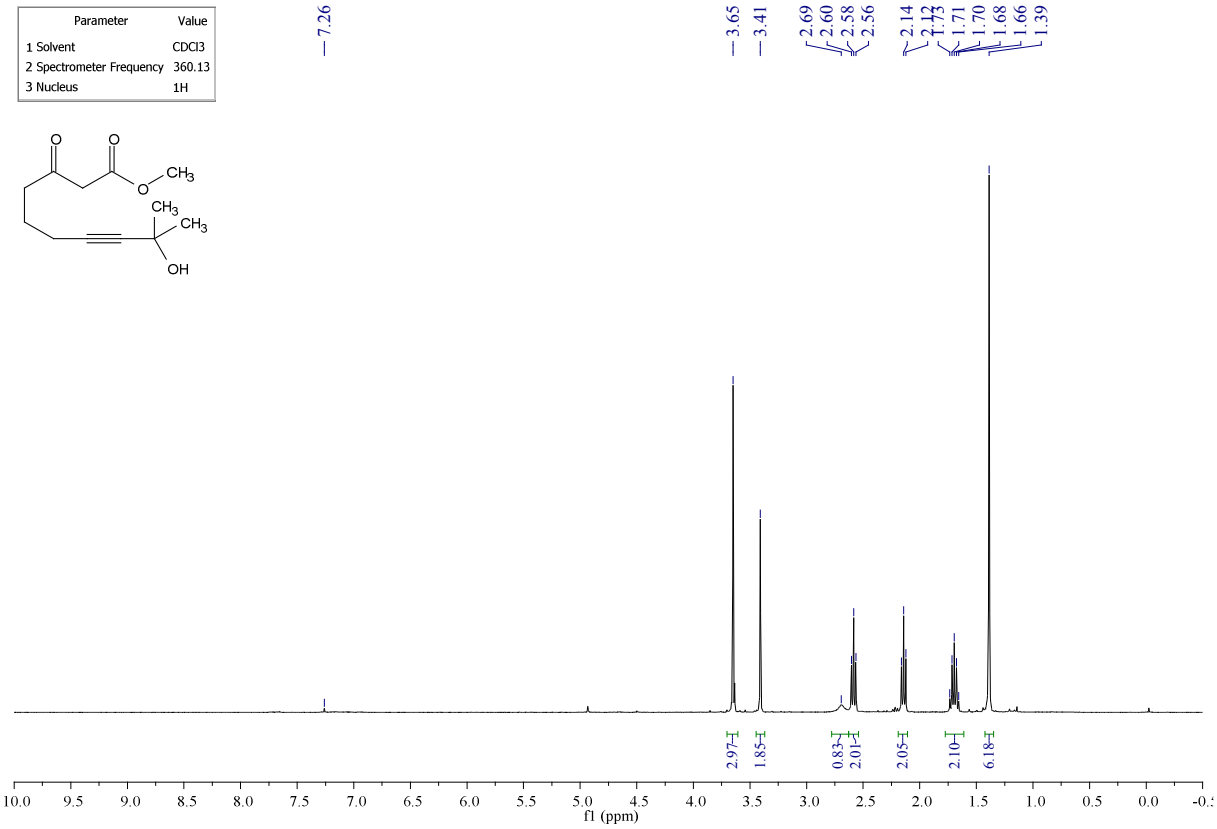

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
168.48
145.52
128.11
127.44
126.05
86.55
84.13
77.59
77.16
76.74
74.19
52.37
47.64
44.30
37.78
24.15
14.76
f1 (ppm)

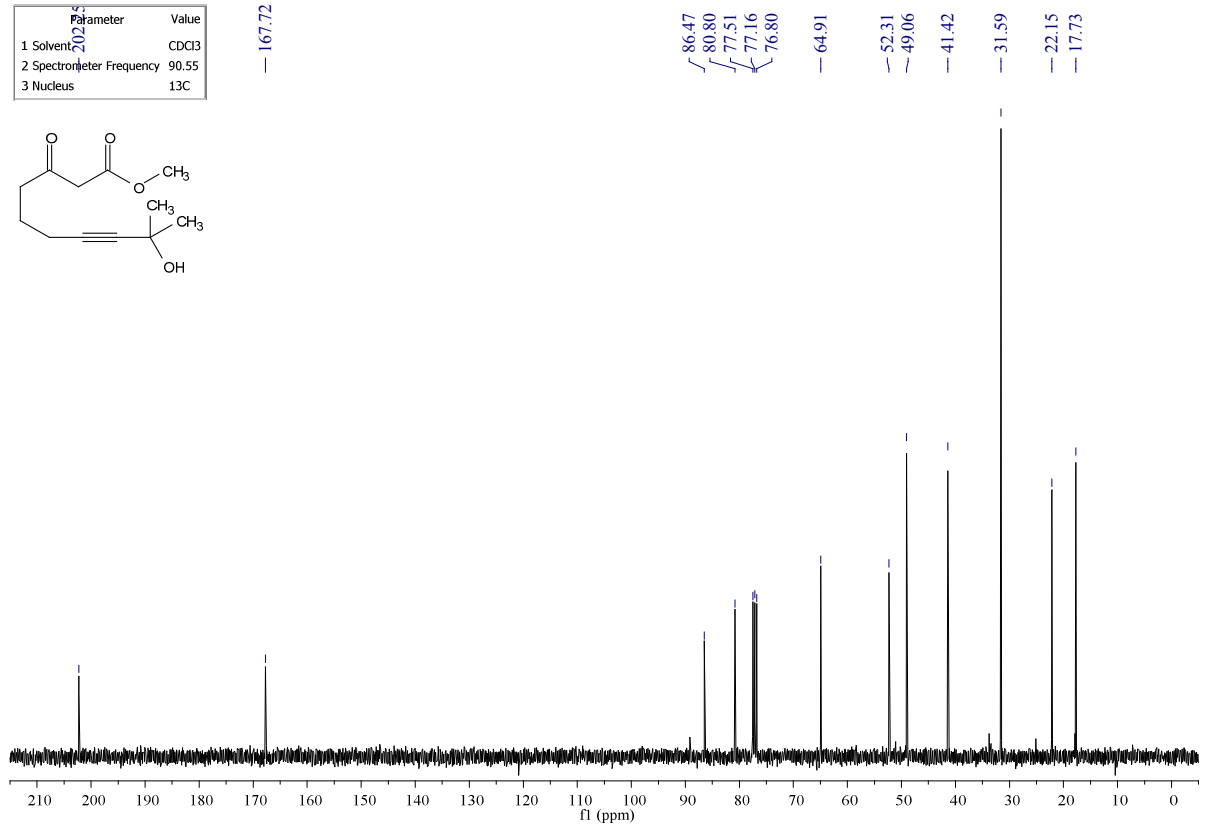

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.49
7.47
7.35
7.33
7.30
7.29
7.26
7.24
5.38
3.67
3.59
3.13
2.23
2.21
2.18
2.18
1.82
1.80
1.77
1.13
O
O
H3C
H3C
CH3
O
OH
2.01
3.01
0.93
3.12
2.21
0.17
1.88
2.09
6.58
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

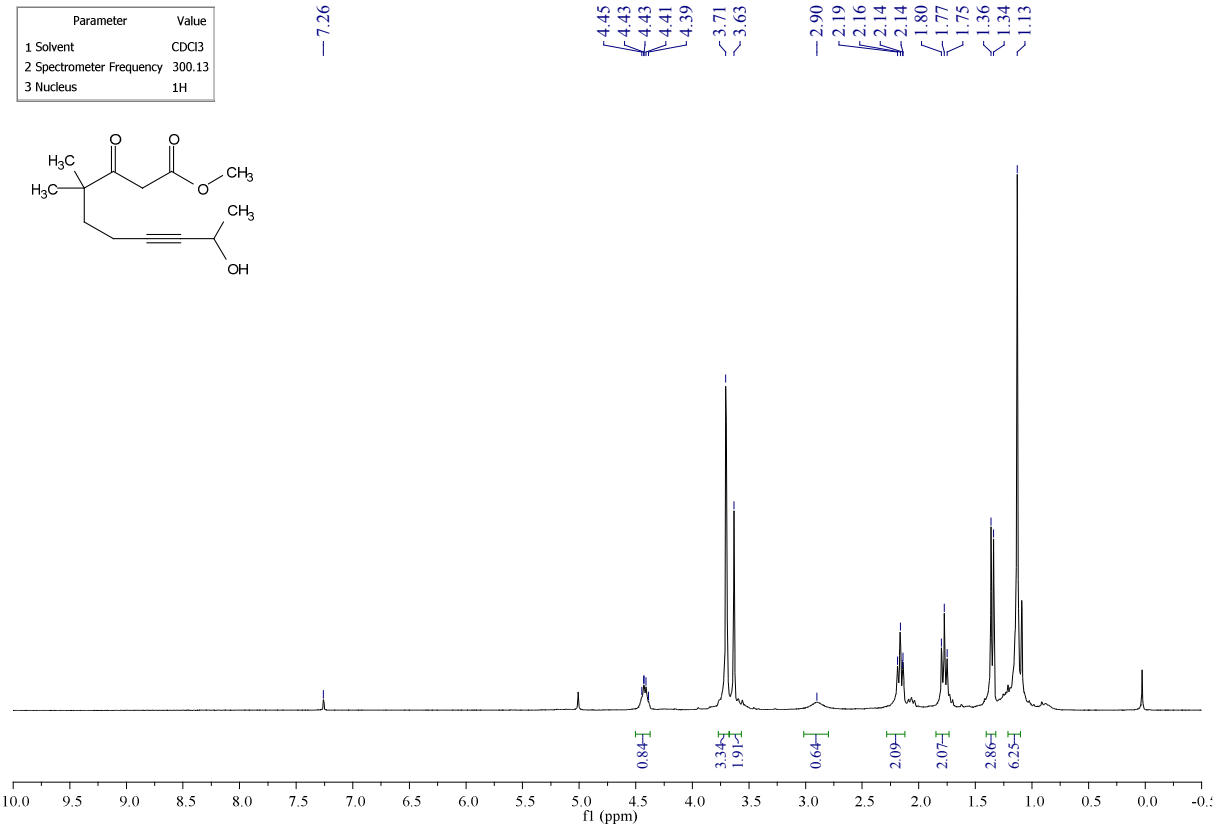

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
77.36
168.59
141.14
128.30
127.87
126.51
85.52
81.46
77.58
77.16
76.73
64.17
52.27
47.49
44.22
37.63
24.03
23.89
14.53
O
O
H3C
H3C
CH3
O
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

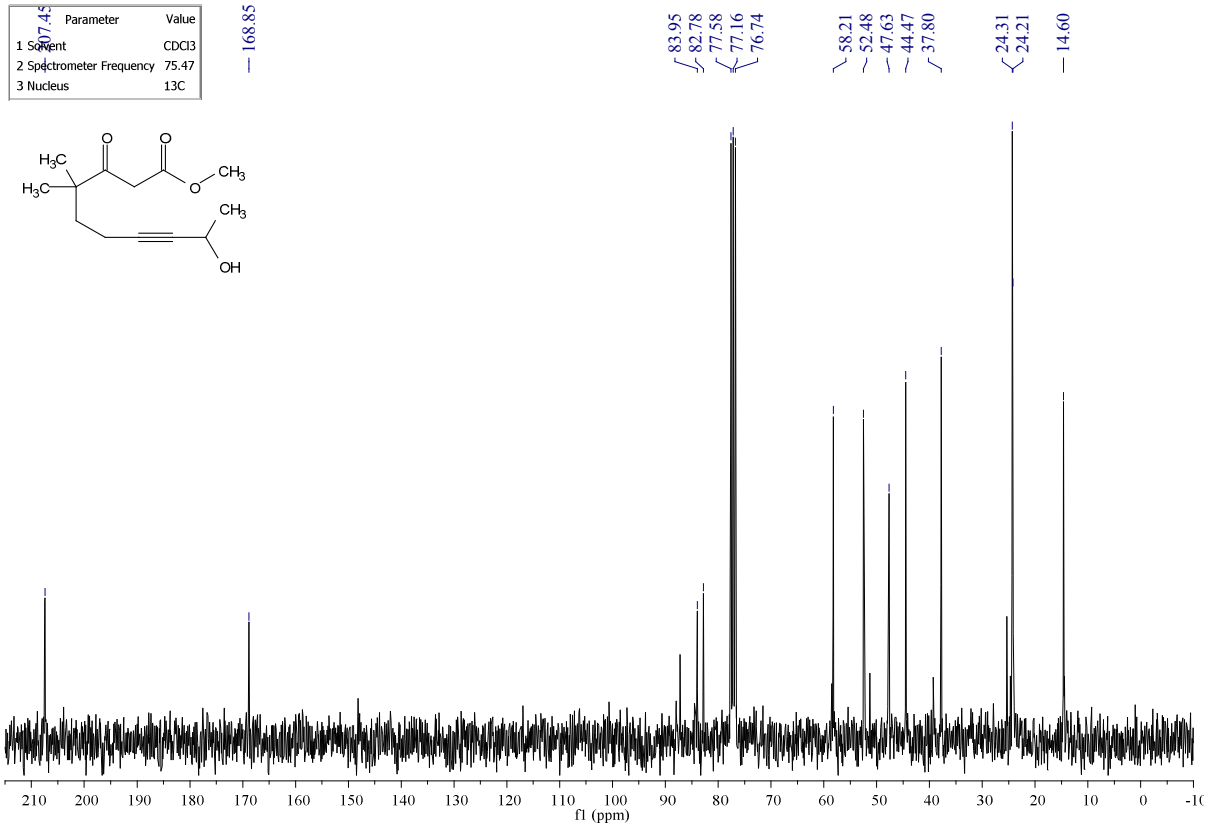

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.42
7.39
7.32
7.30
5.30
5.28
4.00
3.64
3.57
2.20
2.19
2.17
2.17
2.15
2.14
1.78
1.75
1.73
1.09
H3C
H3C
O
O
O
CH3
OH
Br
2.18
2.20
1.07
0.90
3.28
1.98
1.91
2.11
5.38
f1 (ppm)

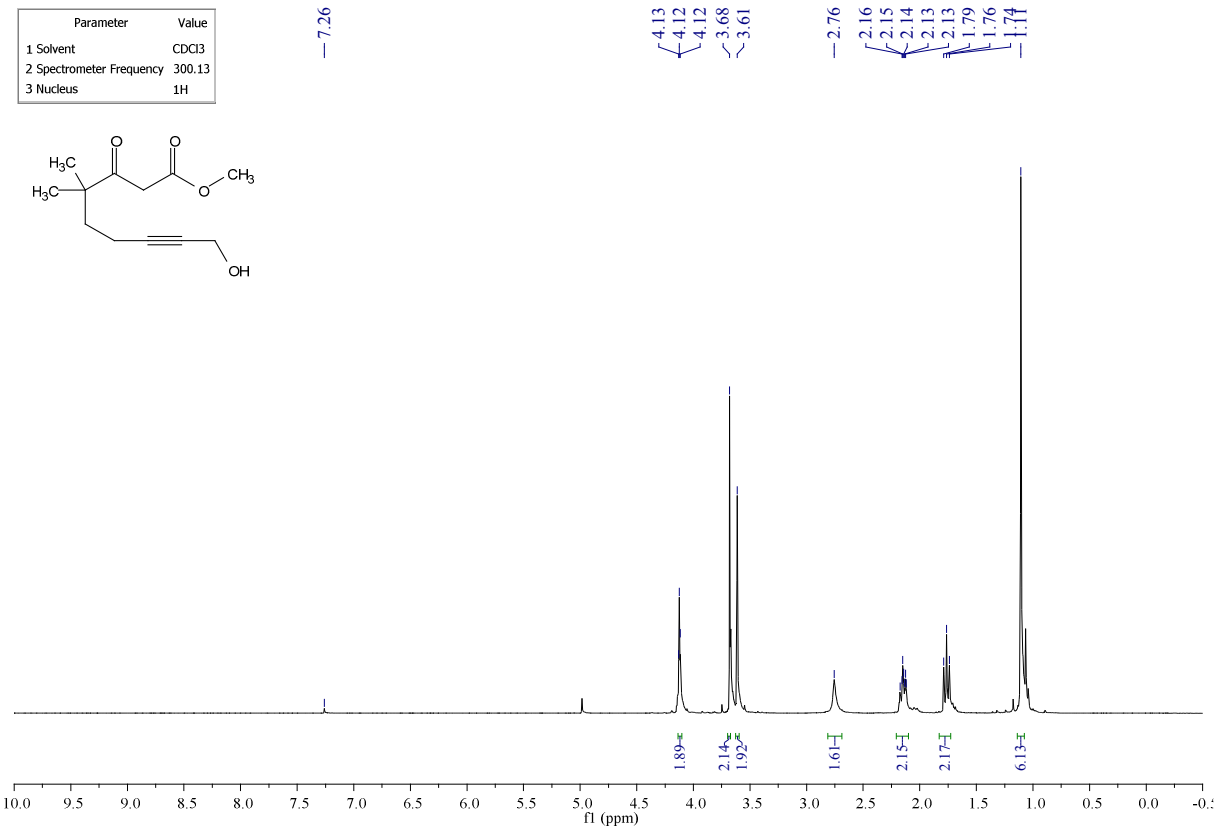

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
168.67
140.21
131.26
128.26
121.63
85.67
81.07
77.59
77.16
76.73
63.38
52.29
47.38
44.22
37.45
24.03
23.89
14.49
H3C
H3C
O
O
O
CH3
OH
Br
f1 (ppm)

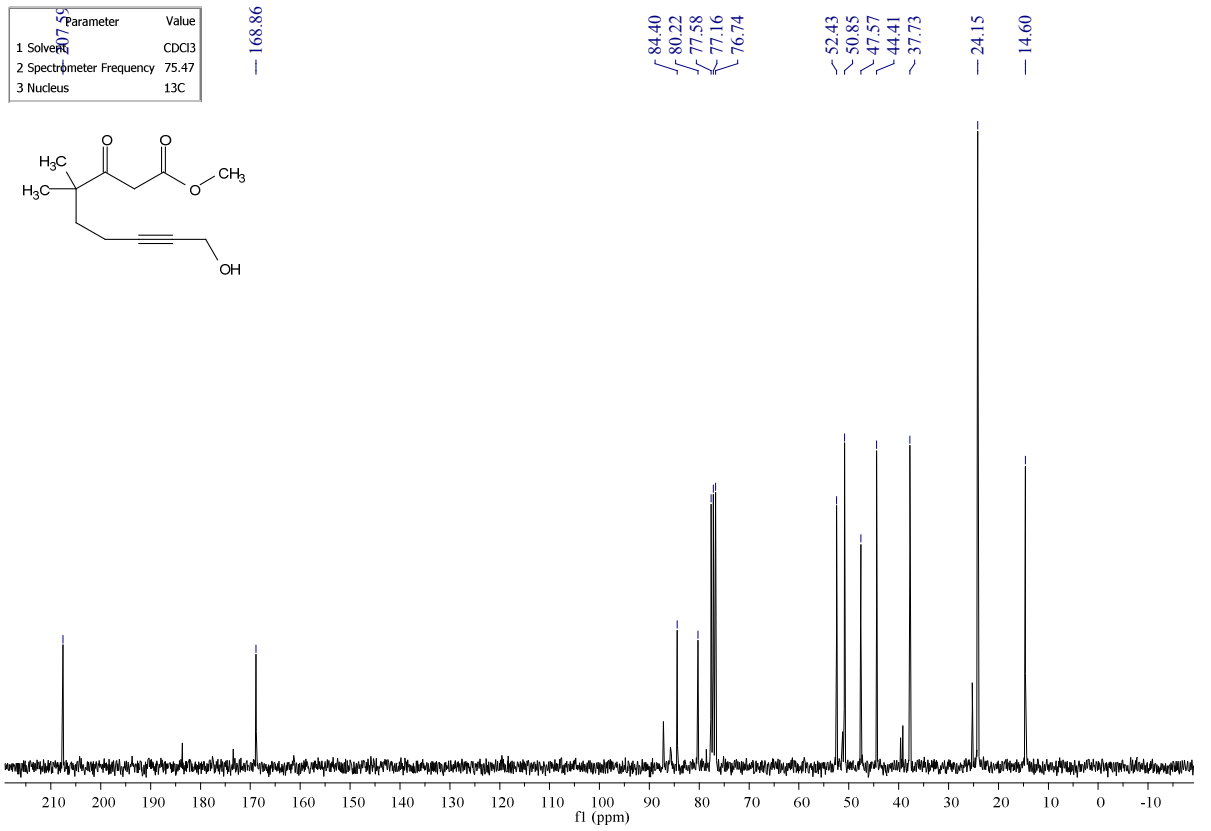

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 360.13
3 Nucleus 1H
7.26
3.65
3.41
2.69
2.60
2.58
2.56
2.14
2.12
2.11
1.71
1.70
1.68
1.66
1.39
2.97
1.85
0.83
2.01
2.05
2.10
6.18
f1 (ppm)

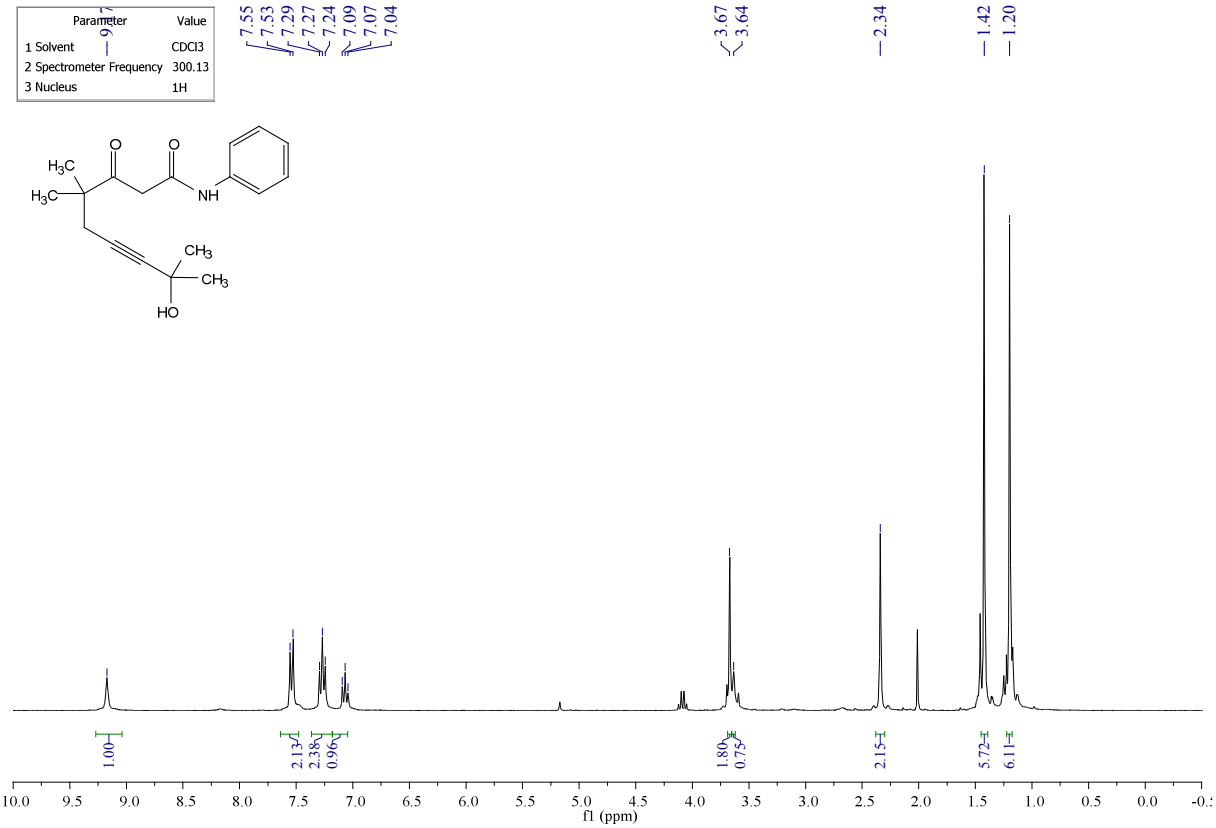

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 90.55
3 Nucleus 13C
167.72
86.47
80.80
77.51
77.16
76.80
64.91
52.31
49.06
41.42
31.59
22.15
17.73
f1 (ppm)

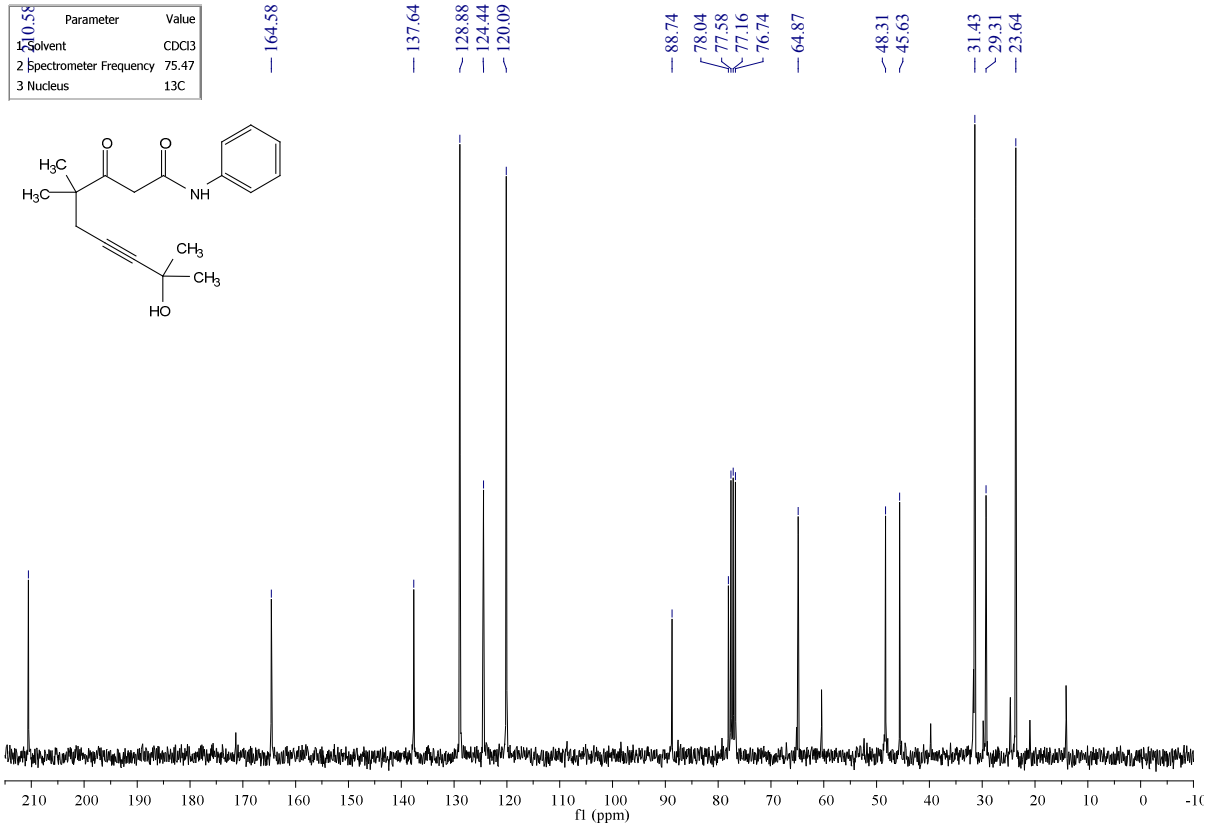

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.26
4.45
4.43
4.43
4.41
4.39
3.71
3.63
2.90
2.19
2.16
2.14
2.14
1.80
1.77
1.75
1.36
1.34
1.13
0.84
3.34
1.91
0.64
2.09
2.07
2.86
6.25
f1 (ppm)

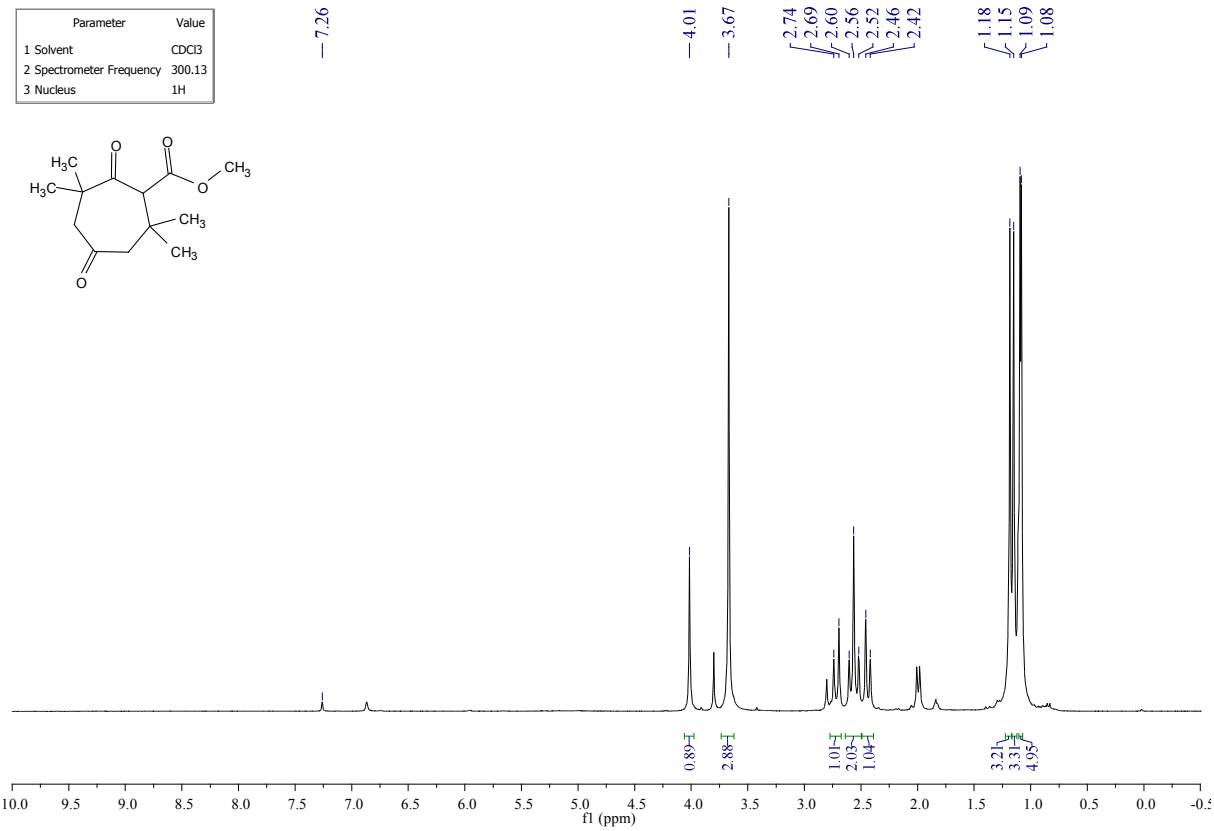

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
168.85
83.95
82.78
77.58
77.16
76.74
58.21
52.48
47.63
44.47
37.80
24.31
24.21
14.60
f1 (ppm)

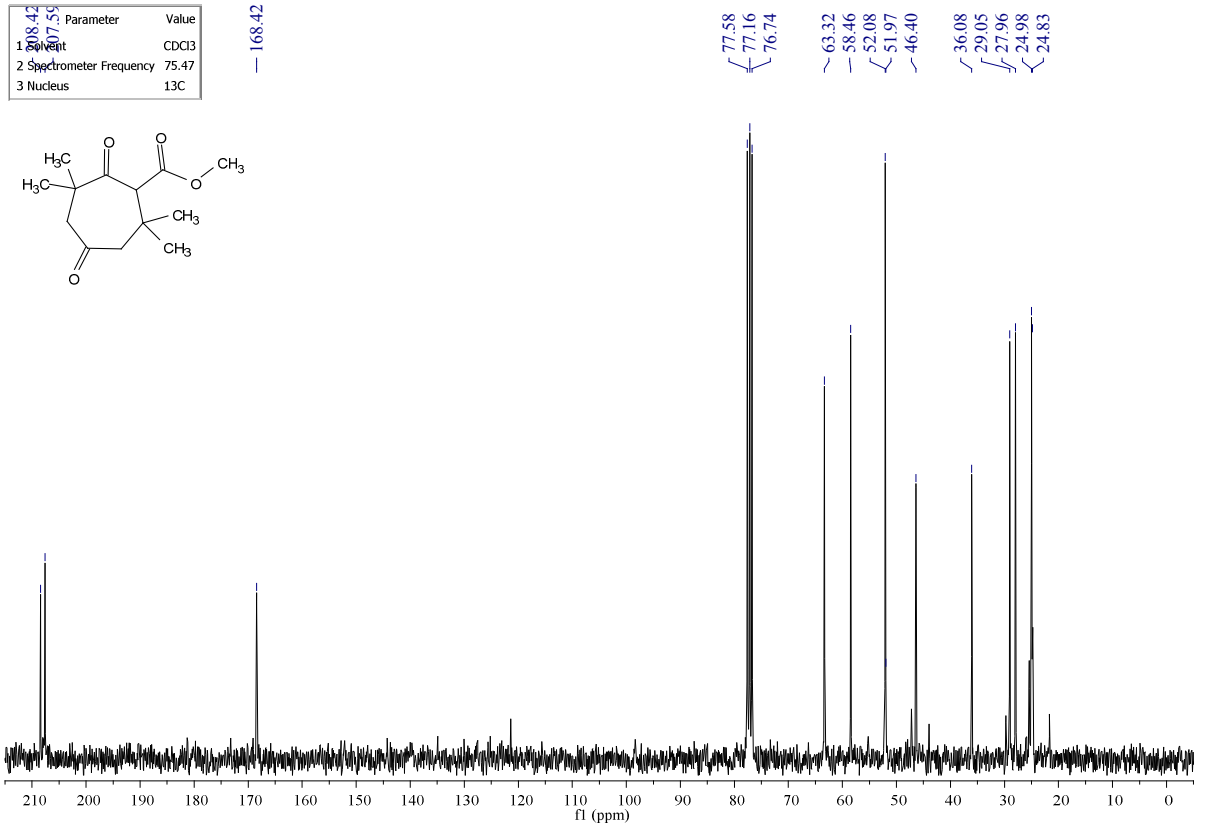

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.26
4.13
4.12
4.12
3.68
3.61
2.76
2.16
2.15
2.14
2.13
2.13
1.79
1.76
1.74
1.89
2.14
1.92
1.61
2.15
2.17
6.13
f1 (ppm)

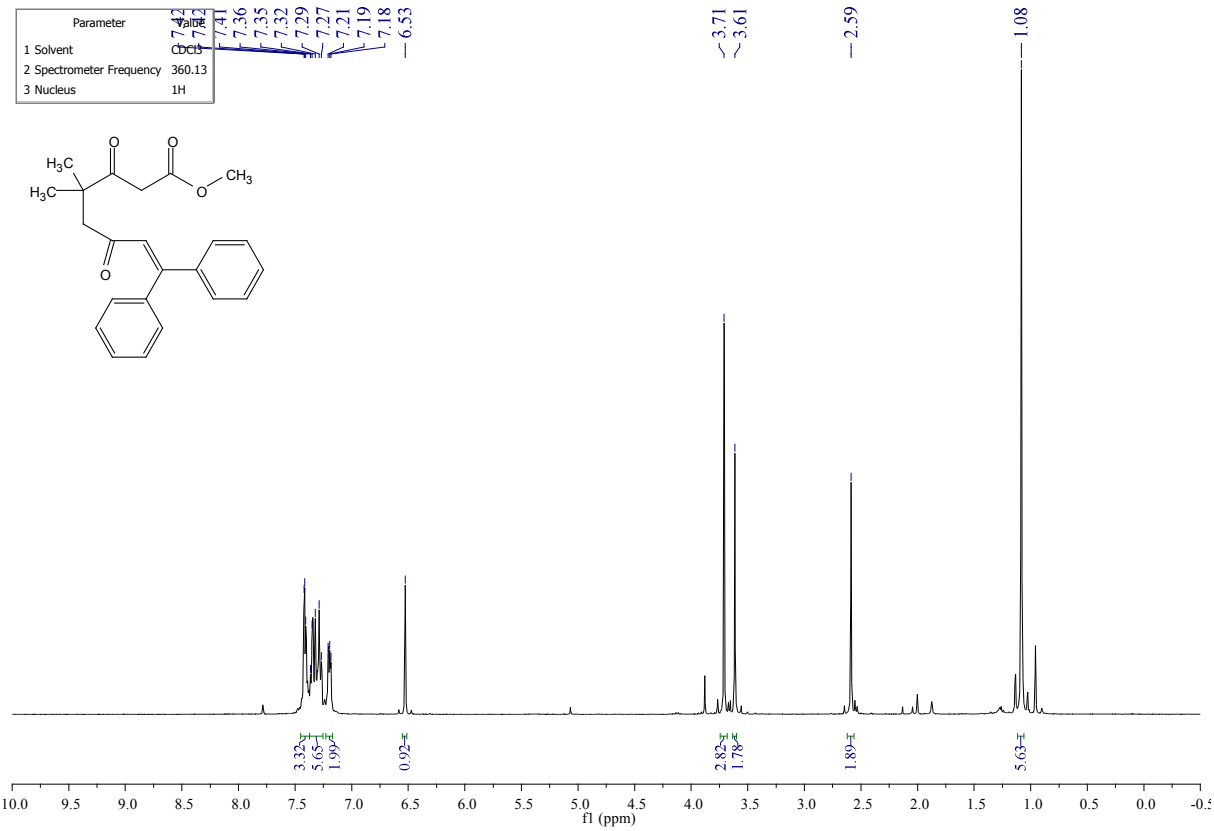

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
77.59
168.86
84.40
80.22
77.58
77.16
76.74
52.43
50.85
47.57
44.41
37.73
24.15
14.60
f1 (ppm)

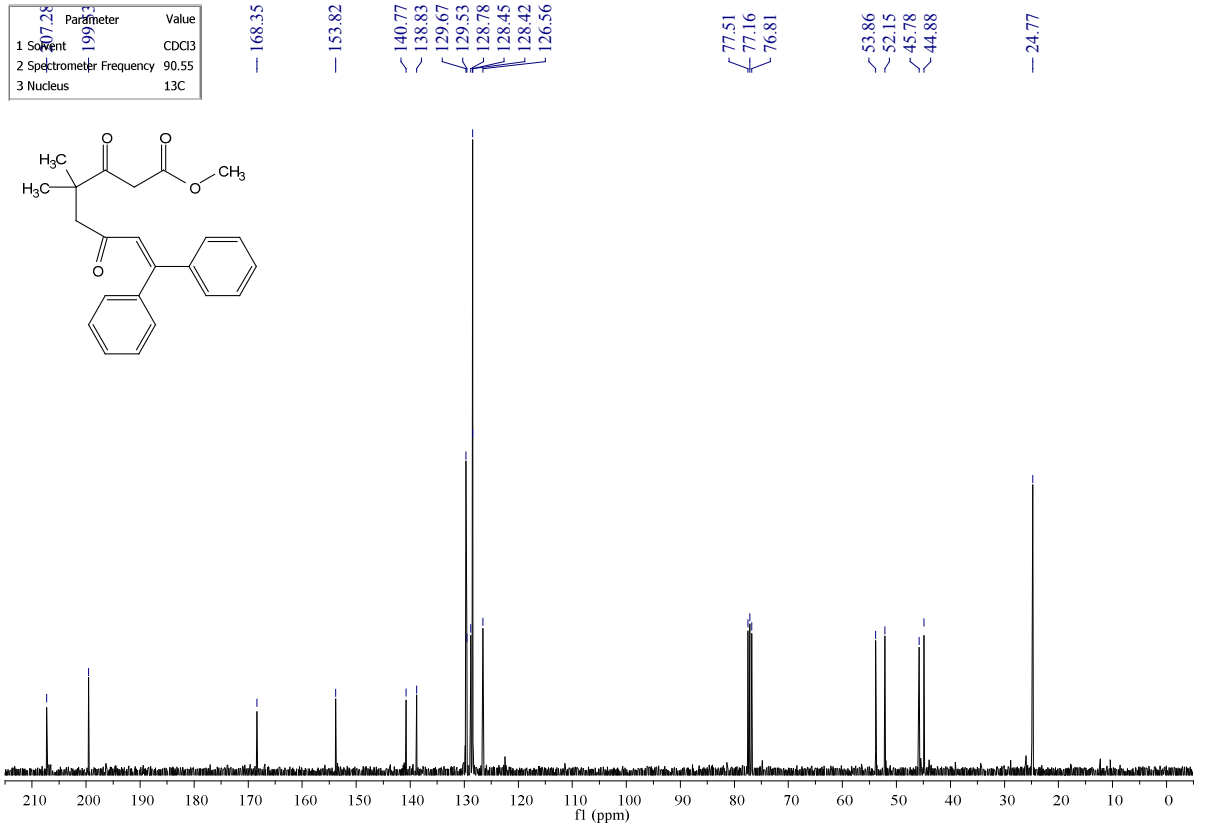

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.55
7.53
7.29
7.27
7.24
7.09
7.07
7.04
3.67
3.64
2.34
1.42
1.20
1.00
2.13
2.38
0.96
1.80
0.75
2.15
5.72
6.11
f1 (ppm)

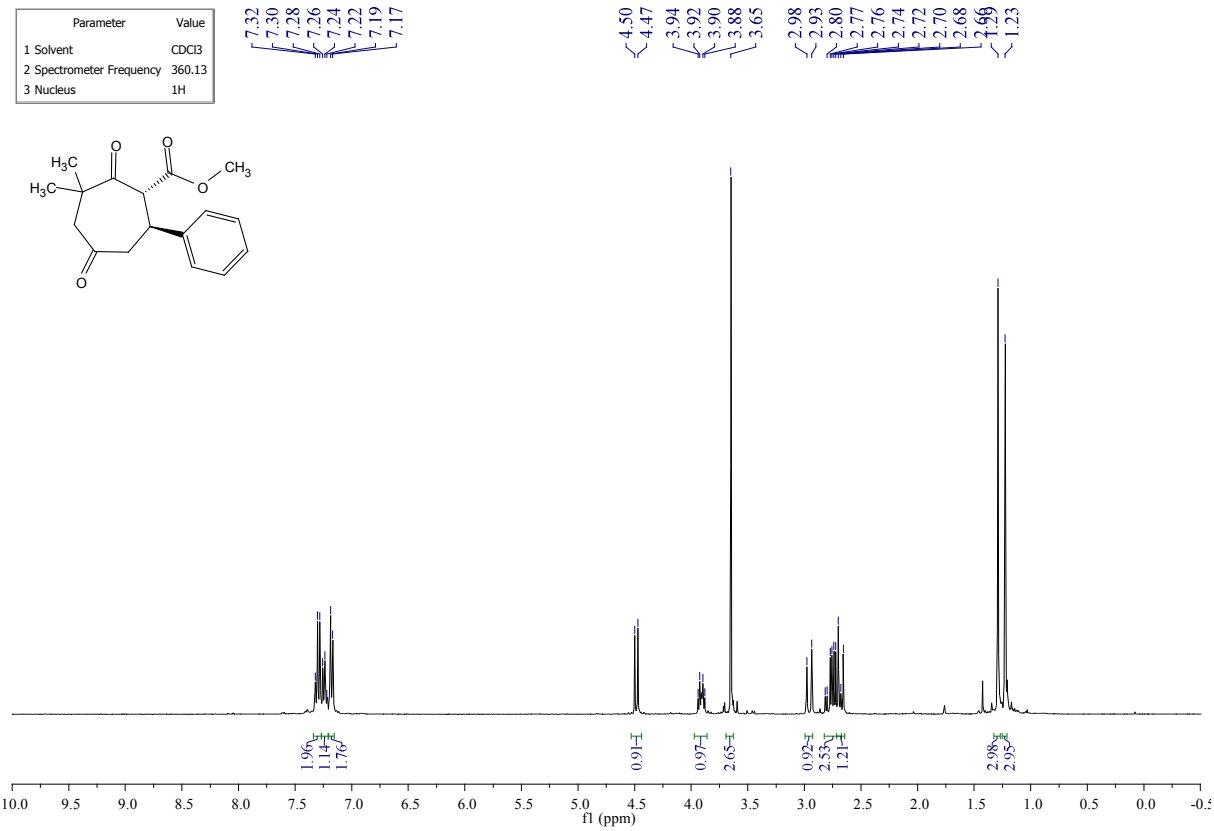

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
164.58
137.64
128.88
124.44
120.09
88.74
78.04
77.58
77.16
76.74
64.87
48.31
45.63
31.43
29.31
23.64
f1 (ppm)

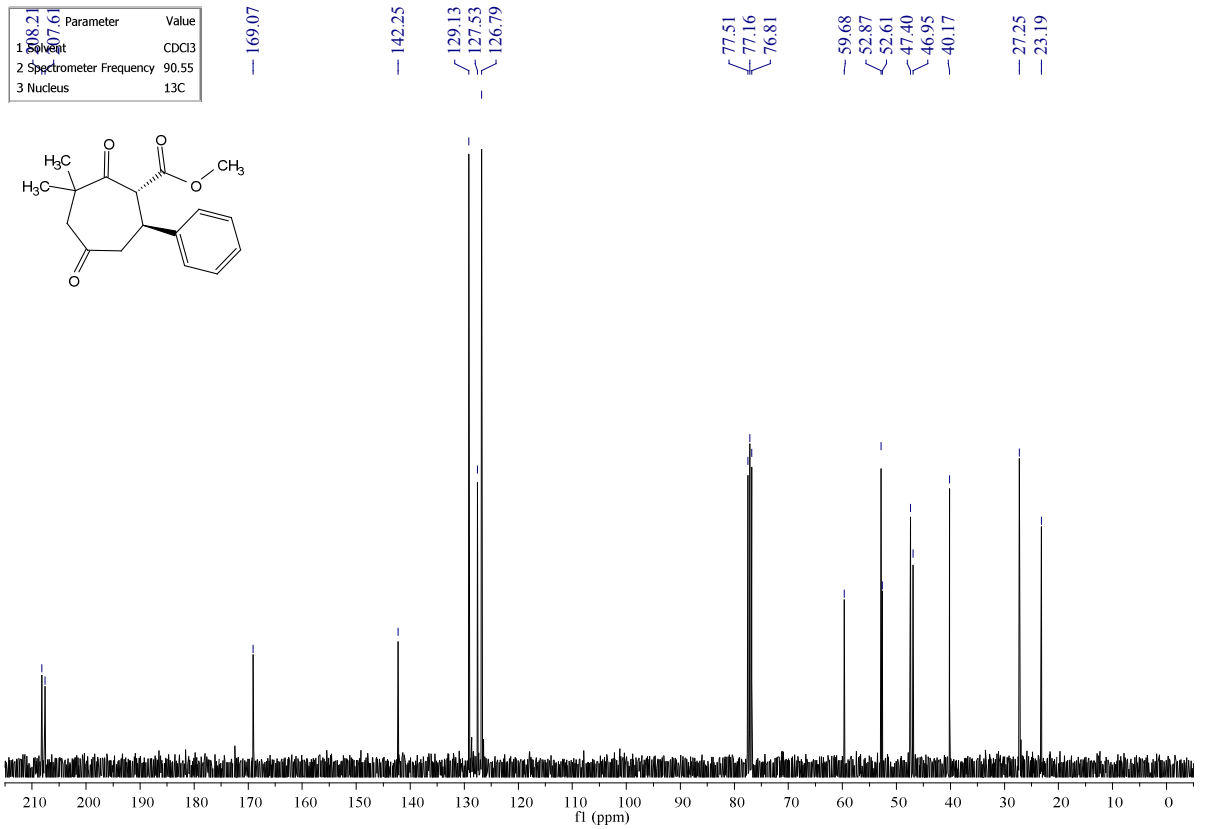

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.26
4.01
3.67
2.74
2.69
2.60
2.56
2.52
2.46
2.42
1.18
1.15
1.09
1.08
0.89
2.88
1.01
2.03
1.04
3.21
3.31
4.95
f1 (ppm)

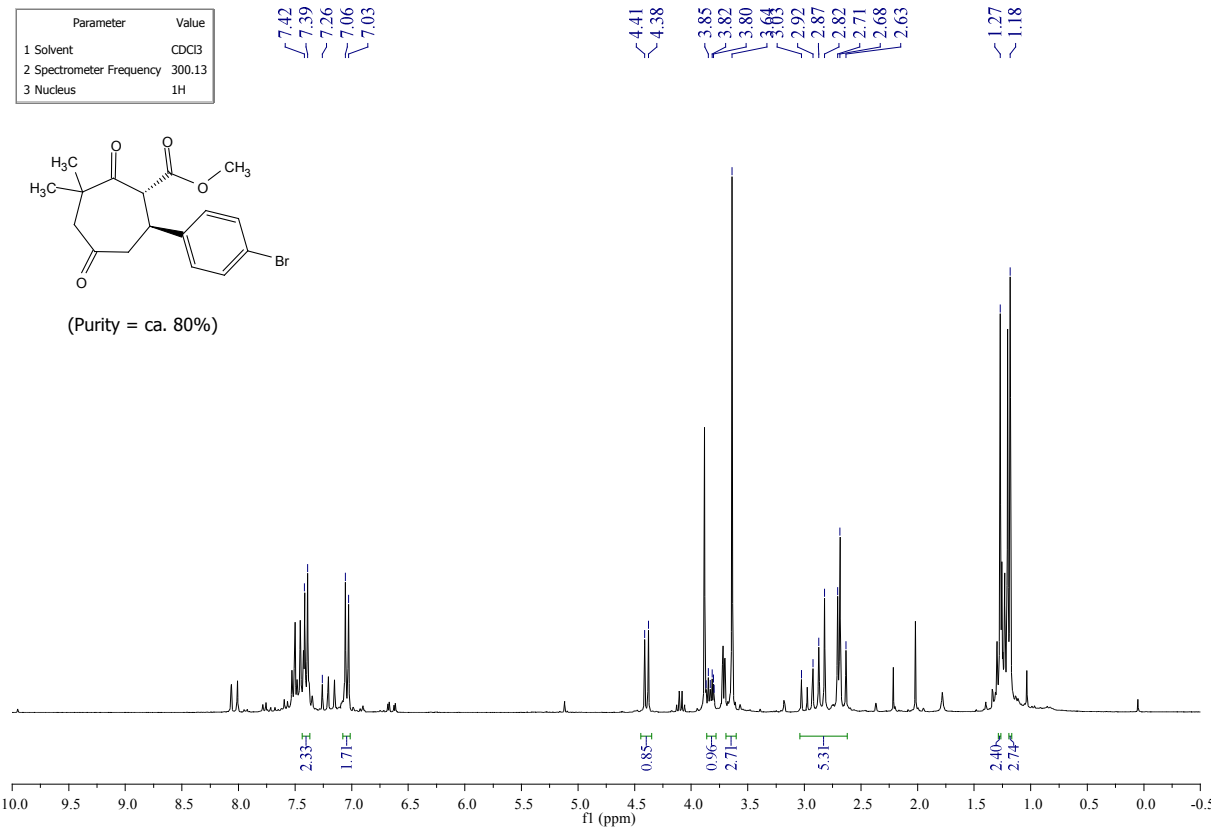

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
208.42
207.59
168.42
77.58
77.16
76.74
63.32
58.46
52.08
51.97
46.40
36.08
29.05
27.96
24.98
24.83
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 360.13
3 Nucleus 1H
7.42
7.41
7.36
7.35
7.32
7.29
7.27
7.21
7.19
7.18
6.53
3.71
3.61
2.59
1.08
3.32
5.65
1.99
0.92
2.82
1.78
1.89
5.63
f1 (ppm)

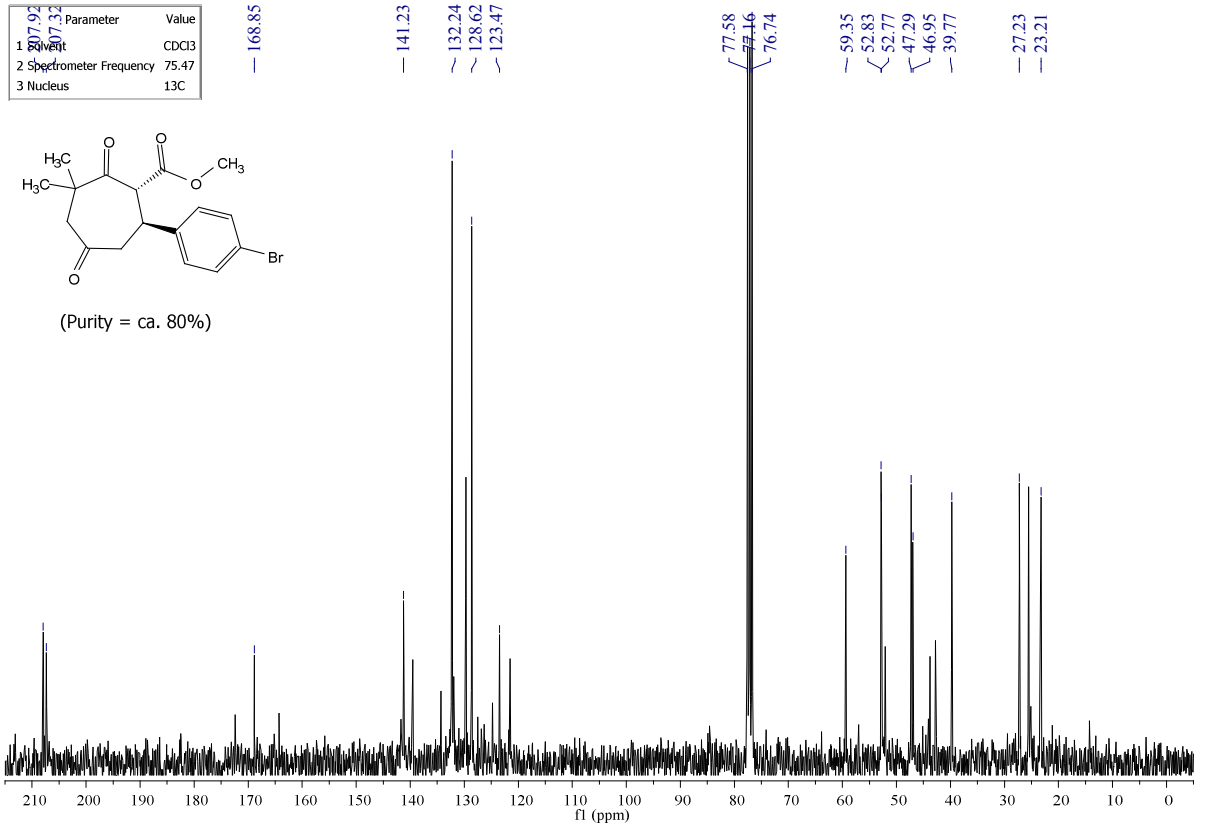

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 90.55
3 Nucleus 13C
77.28
199.93
168.35
153.82
140.77
138.83
129.67
129.53
128.78
128.45
128.42
126.56
77.51
77.16
76.81
53.86
52.15
45.78
44.88
24.77
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 360.13
3 Nucleus 1H
7.32
7.30
7.28
7.26
7.24
7.22
7.19
7.17
4.50
4.47
3.94
3.92
3.90
3.88
3.65
2.98
2.93
2.80
2.77
2.76
2.74
2.72
2.70
2.68
1.23
1.96
1.14
1.76
0.91
0.97
2.65
0.92
2.53
1.21
2.98
2.95
f1 (ppm)

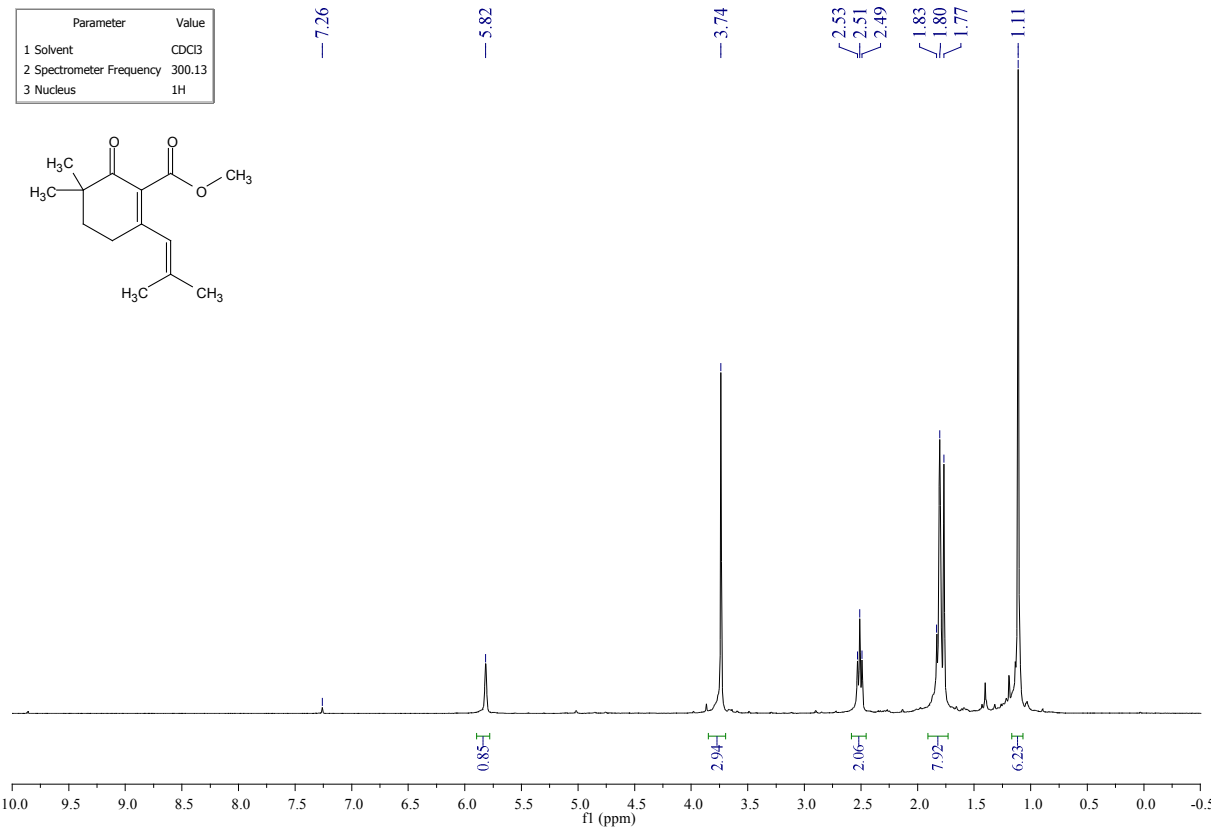

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 90.55
3 Nucleus 13C
169.07
142.25
129.13
127.53
126.79
77.51
77.16
76.81
59.68
52.87
52.61
47.40
46.95
40.17
27.25
23.19
f1 (ppm)

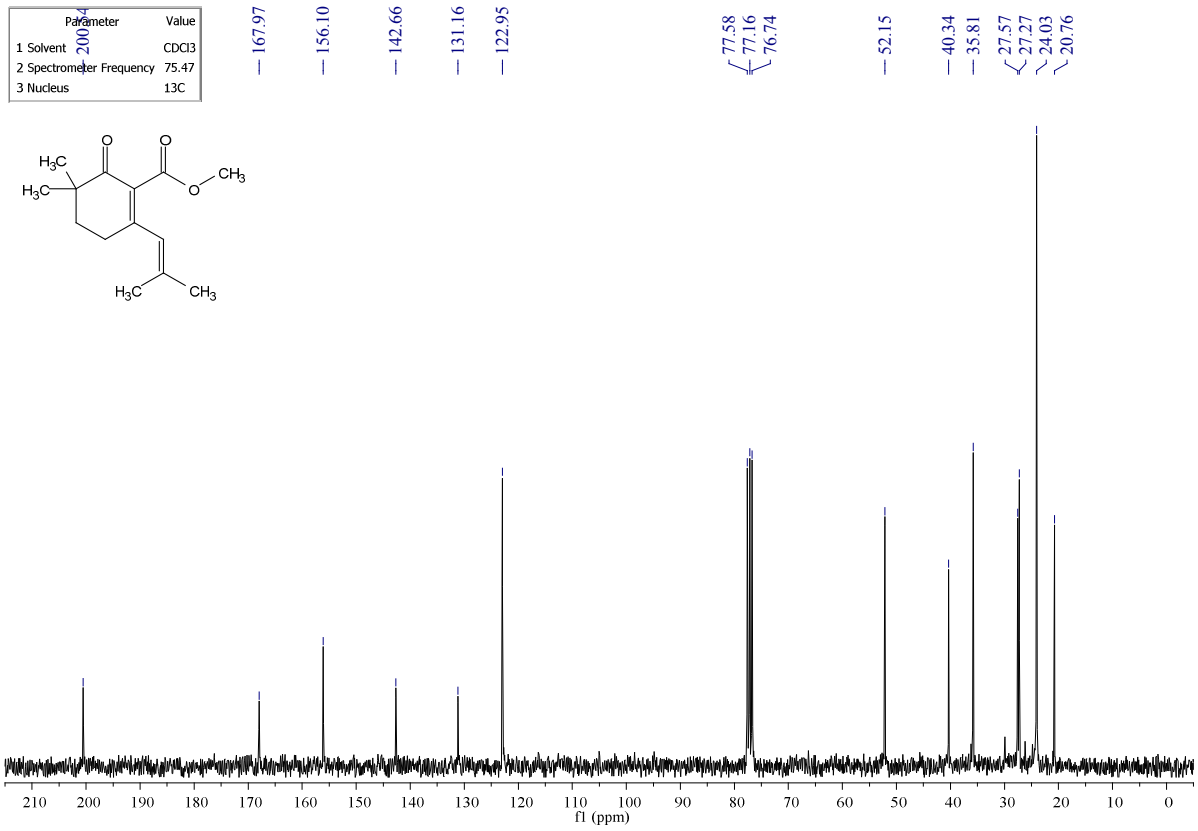


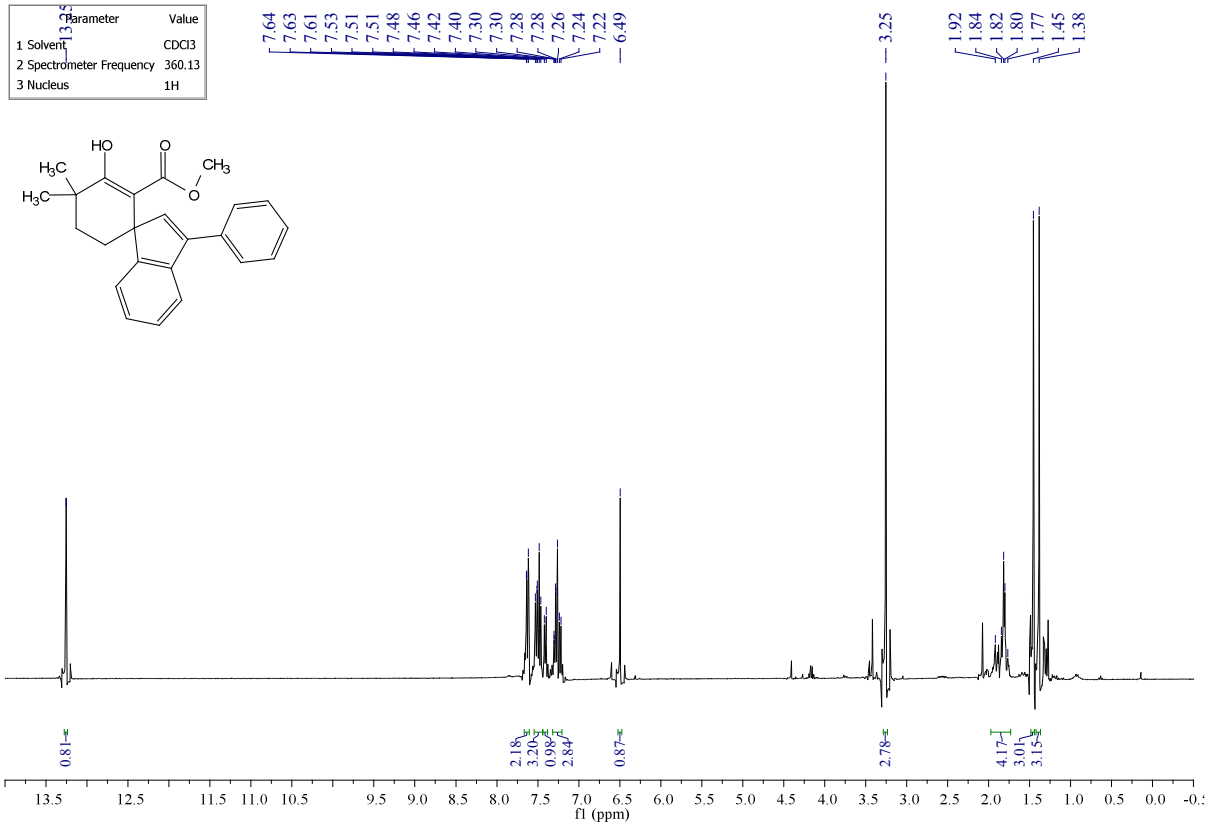
(Purity = ca. 80%)

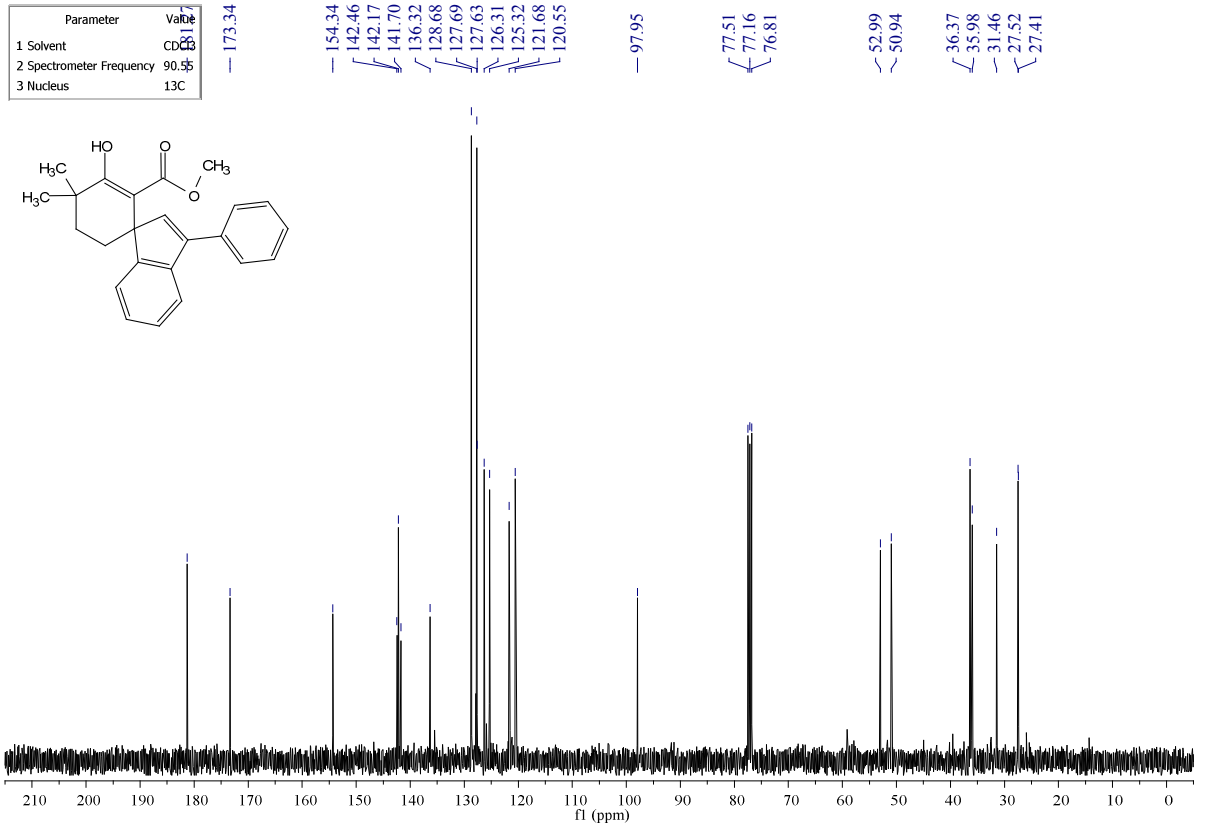


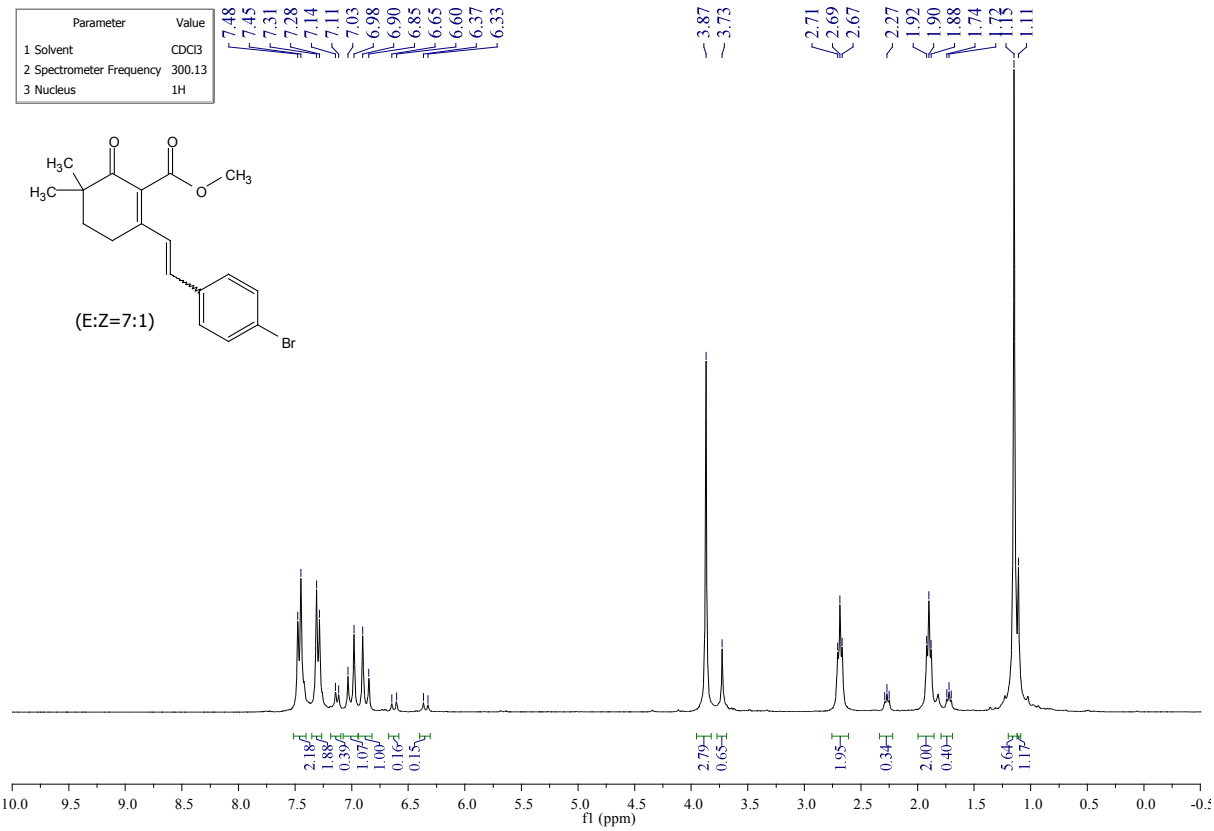
(Purity = ca. 80%)

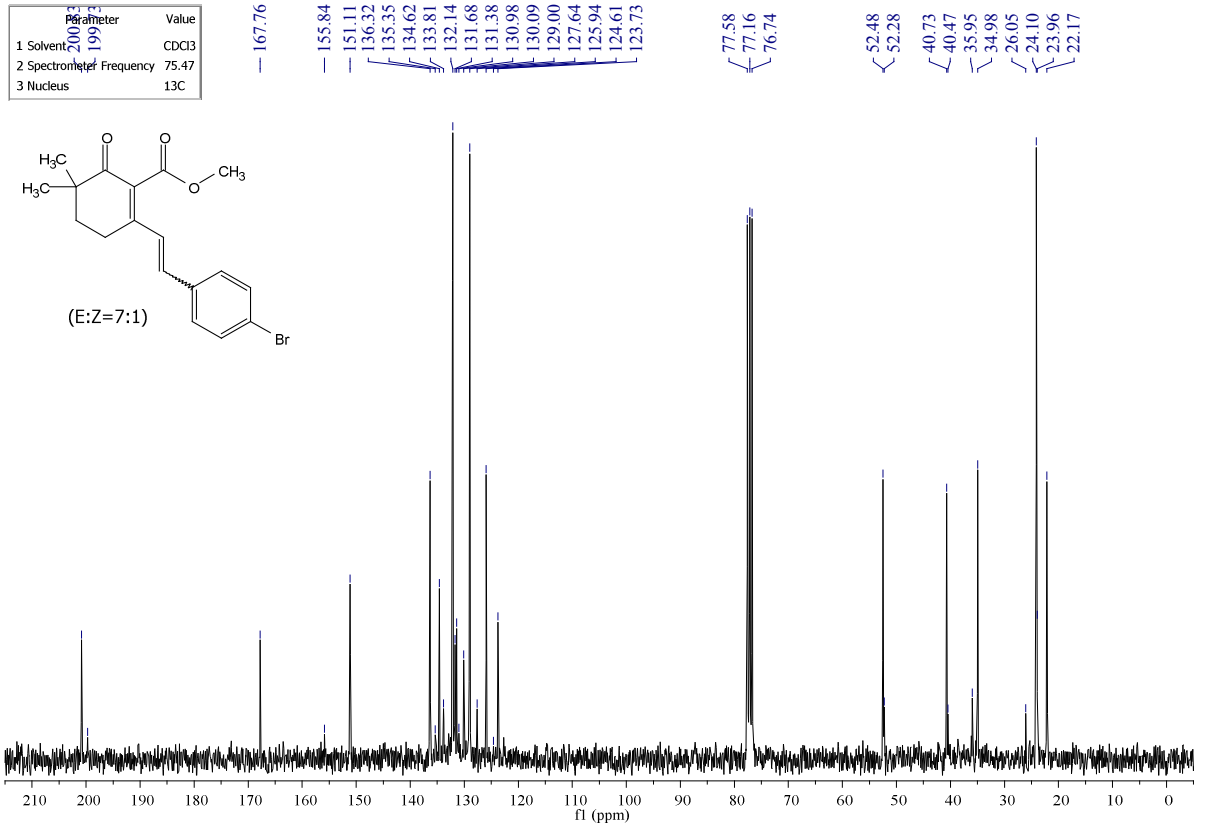

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.26
5.82
3.74
2.53
2.51
2.49
1.83
1.80
1.77
1.11
0.85
2.94
2.06
7.92
6.23
f1 (ppm)

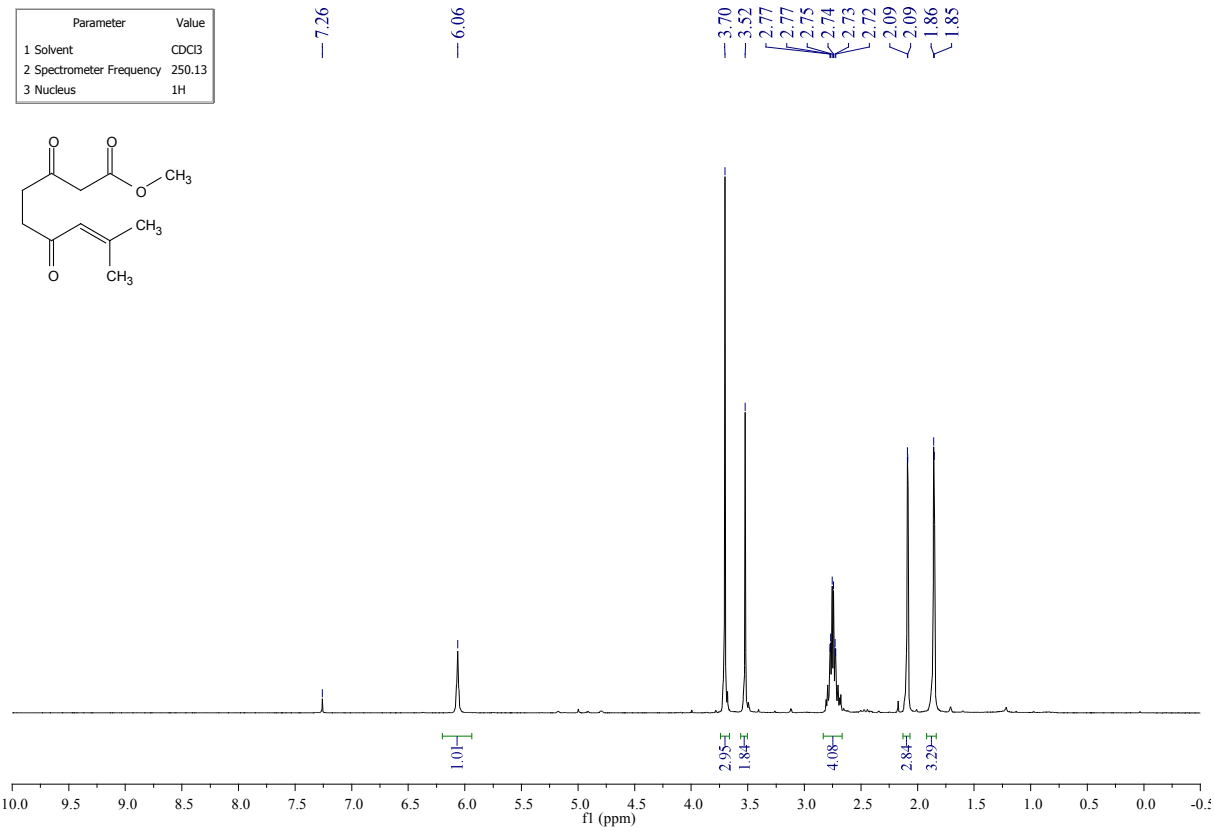

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
167.97
156.10
142.66
131.16
122.95
77.58
77.16
76.74
52.15
40.34
35.81
27.57
27.27
24.03
20.76
f1 (ppm)

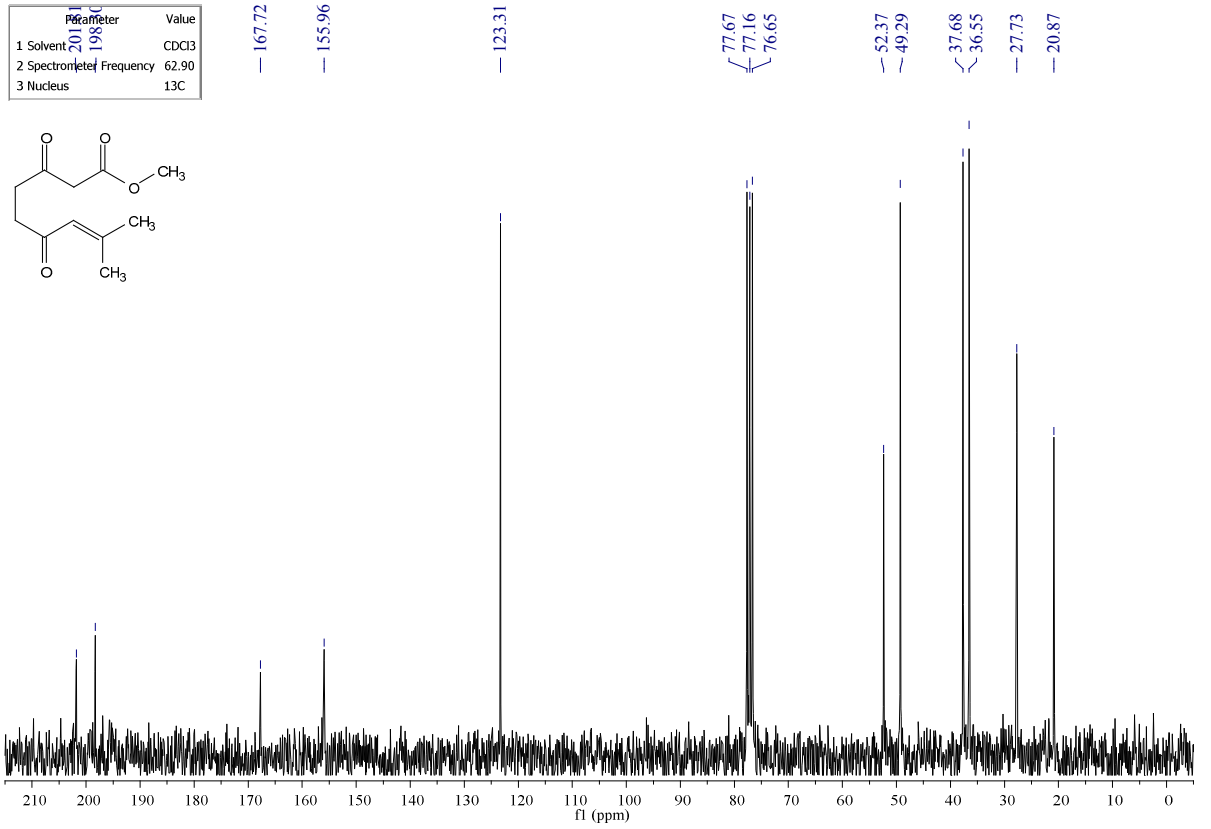

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 360.13
3 Nucleus 1H
HO
O
CH3
H3C
H3C
O
7.64
7.63
7.61
7.53
7.51
7.51
7.48
7.46
7.42
7.40
7.30
7.30
7.28
7.28
7.26
7.24
7.22
6.49
3.25
1.92
1.84
1.82
1.80
1.77
1.45
1.38
0.81
2.18
3.20
0.98
2.84
0.87
2.78
4.17
3.01
3.15
f1 (ppm)

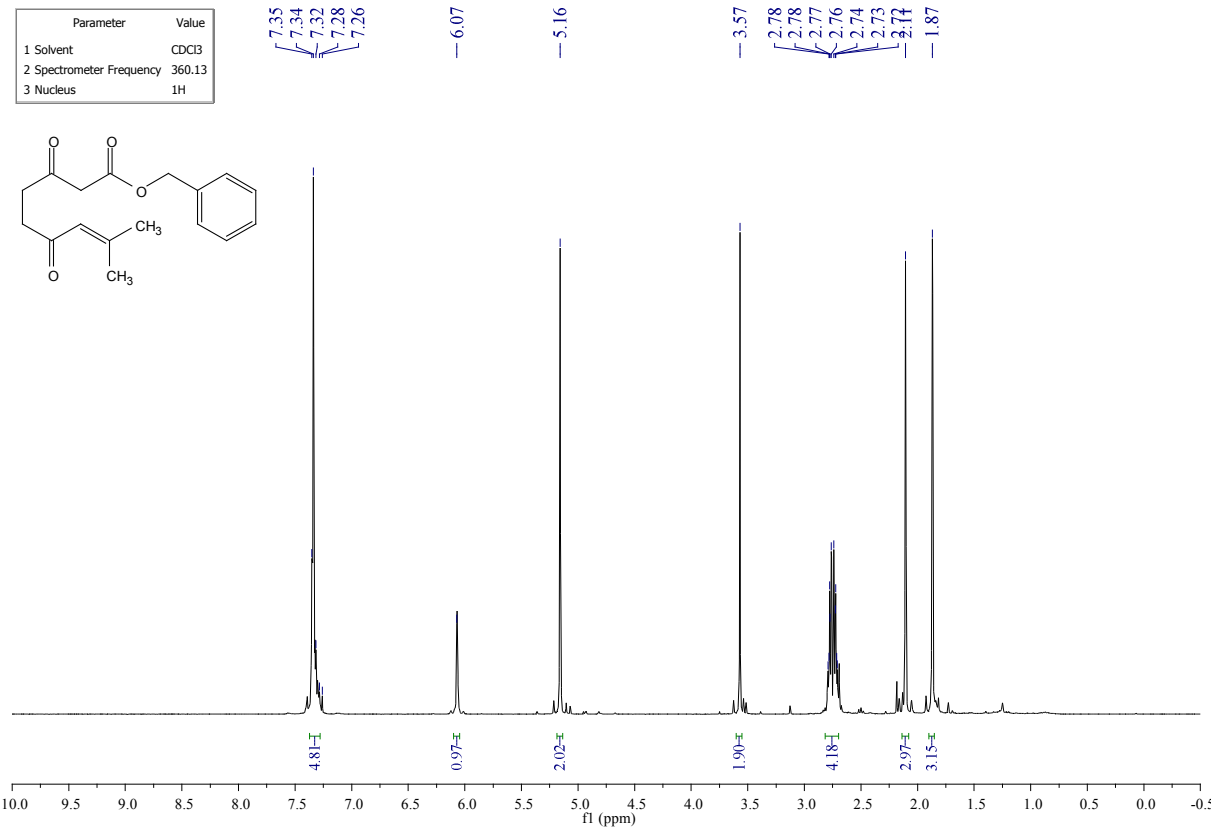

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 90.55
3 Nucleus 13C
HO
O
CH3
H3C
H3C
O
173.34
154.34
142.46
142.17
141.70
136.32
128.68
127.69
127.63
126.31
125.32
121.68
120.55
97.95
77.51
77.16
76.81
52.99
50.94
36.37
35.98
31.46
27.52
27.41
f1 (ppm)

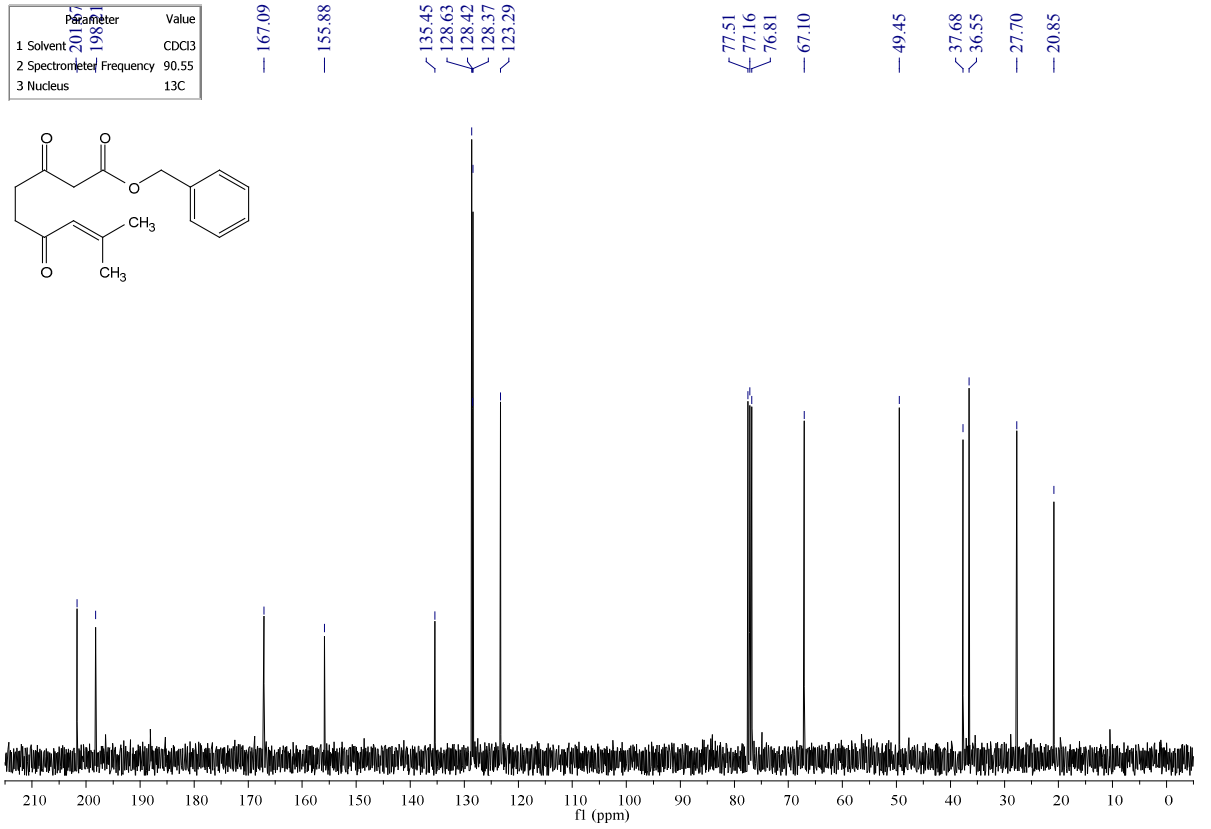

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
(E:Z=7:1)
Br
f1 (ppm)

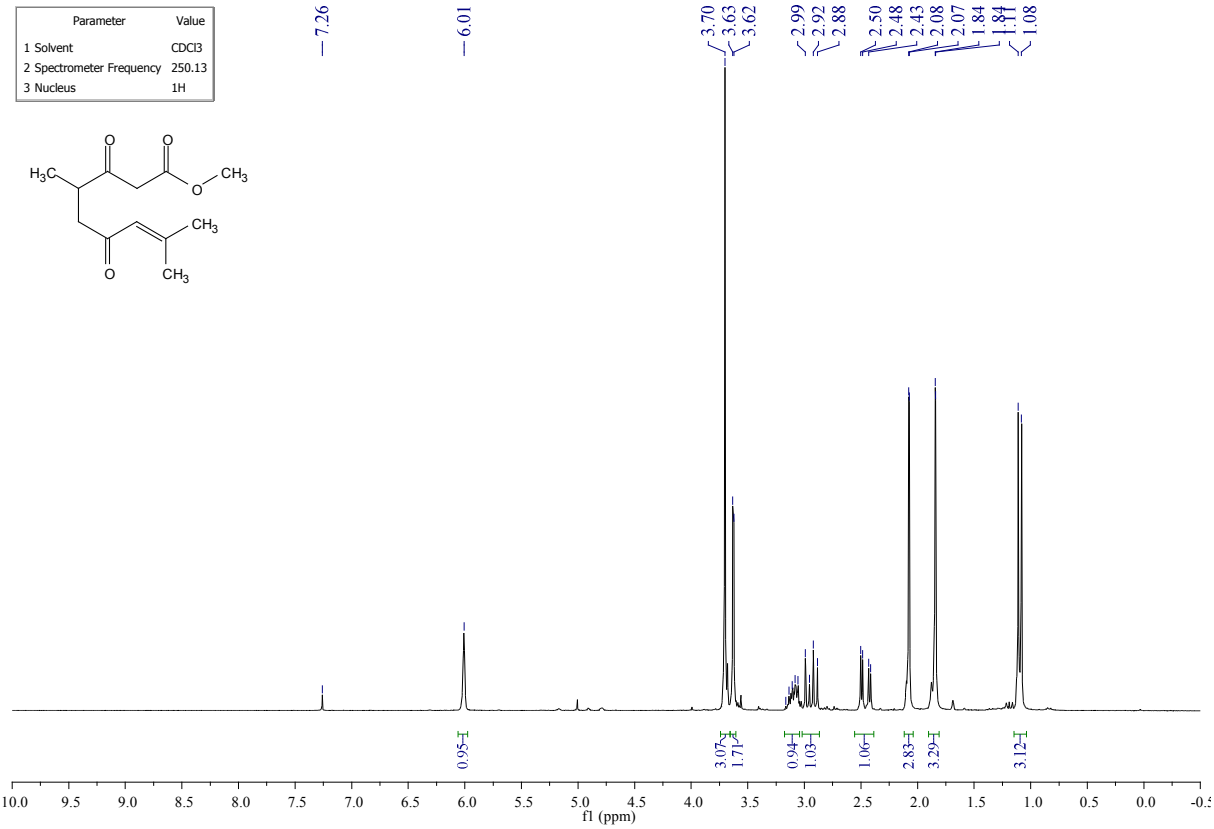

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
(E:Z=7:1)
Br
f1 (ppm)

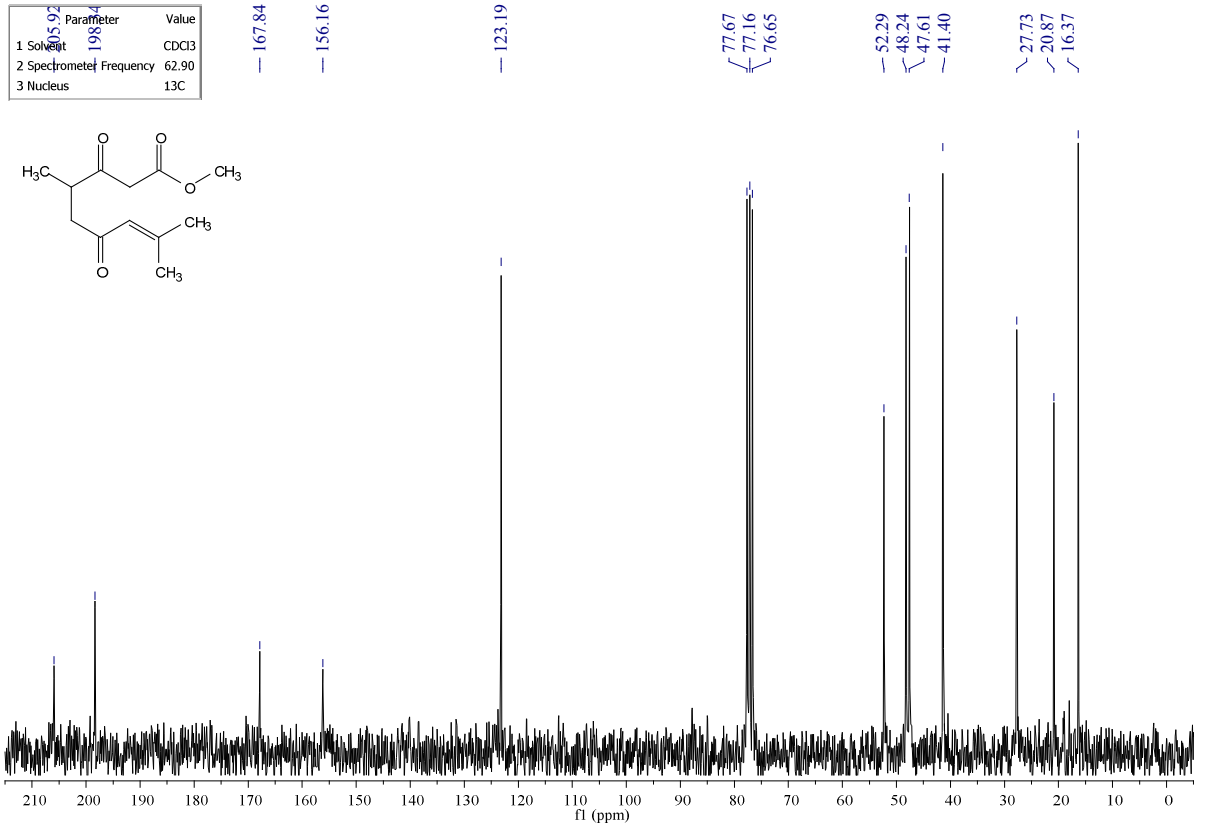

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 250.13
3 Nucleus 1H
7.26
6.06
3.70
3.52
2.77
2.77
2.75
2.74
2.73
2.72
2.09
2.09
1.86
1.85
1.01
2.95
1.84
4.08
2.84
3.29
f1 (ppm)

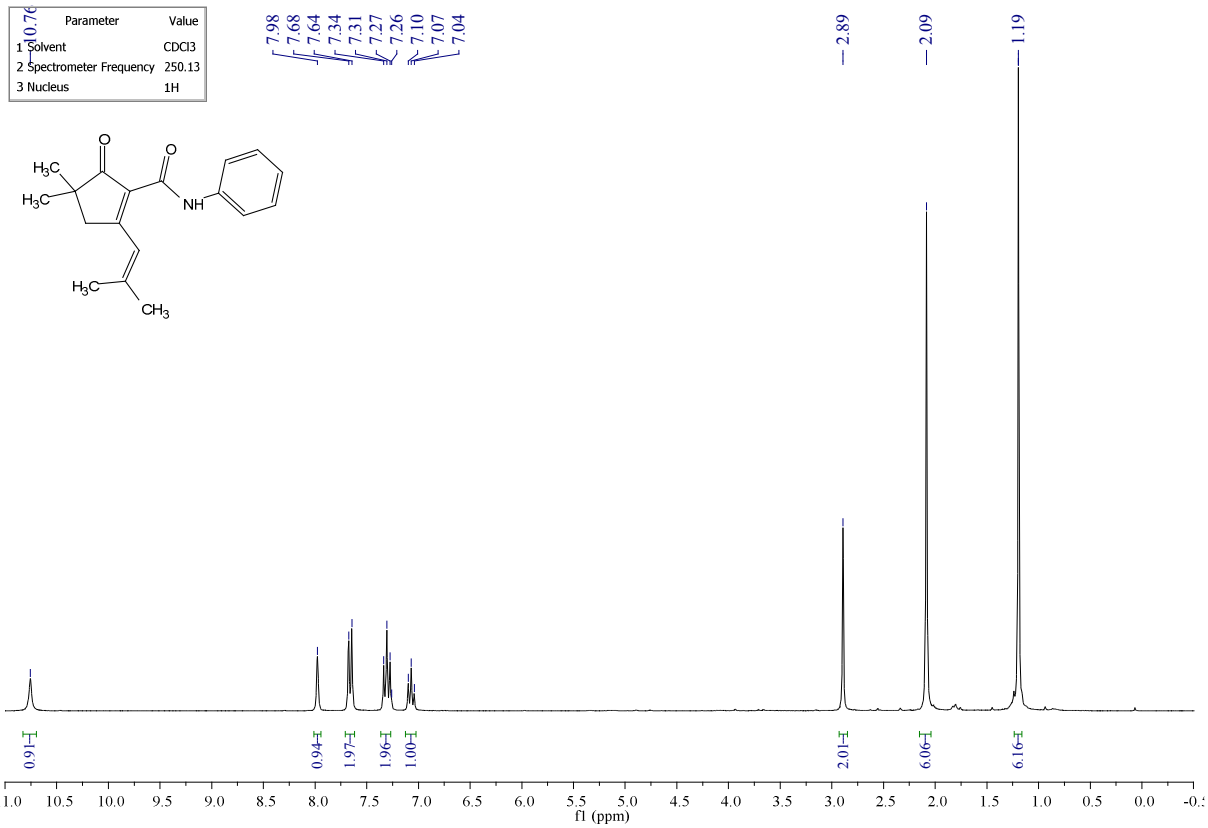

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 62.90
3 Nucleus 13C
167.72
155.96
123.31
77.67
77.16
76.65
52.37
49.29
37.68
36.55
27.73
20.87
f1 (ppm)

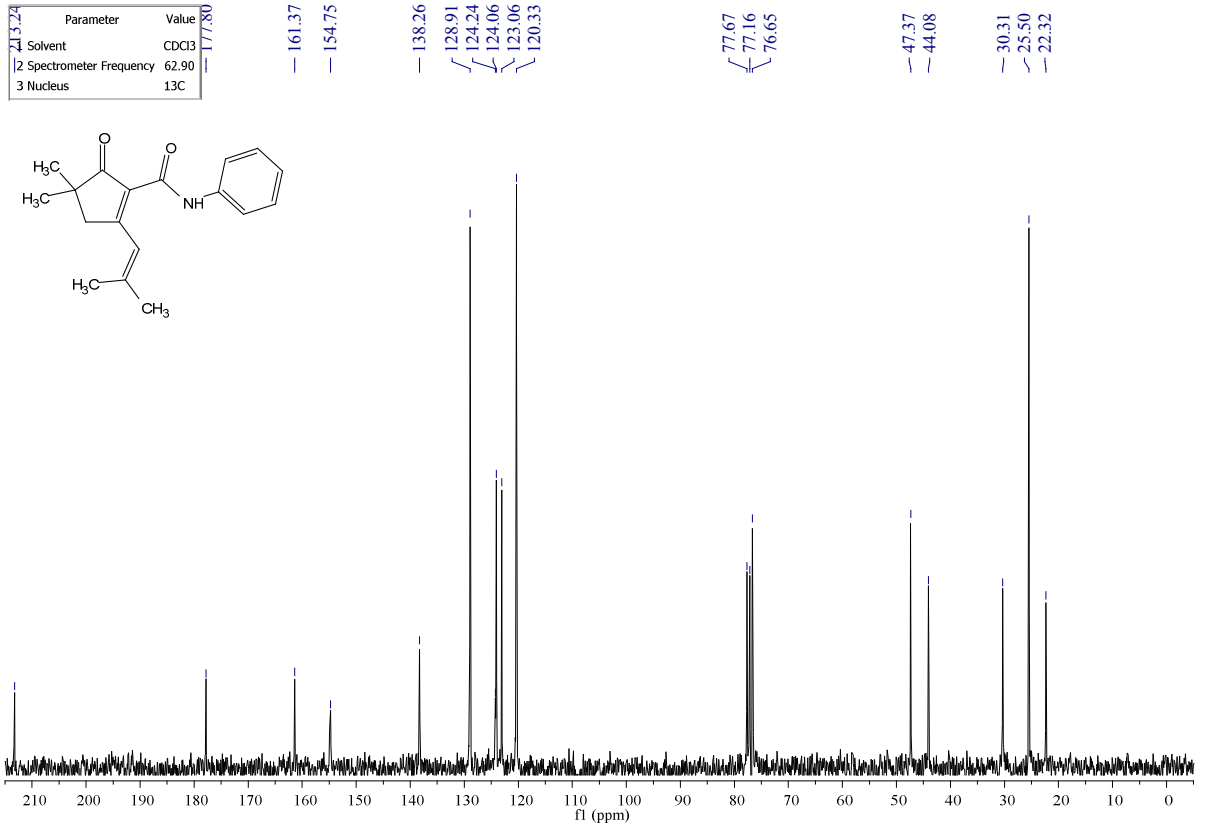

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 360.13
3 Nucleus 1H
7.35
7.34
7.32
7.28
7.26
6.07
5.16
3.57
2.78
2.78
2.77
2.76
2.74
2.73
2.72
2.71
1.87
4.81
0.97
2.02
1.90
4.18
2.97
3.15
f1 (ppm)

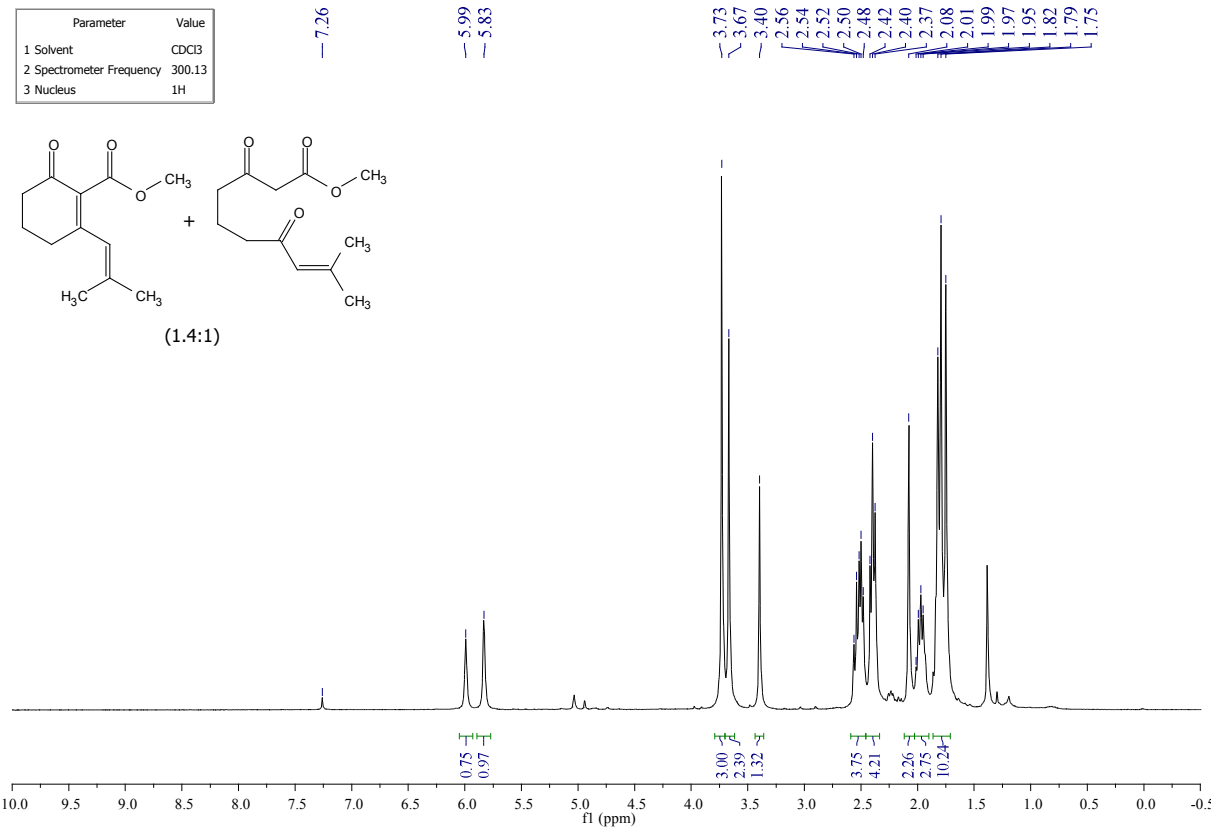

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 90.55
3 Nucleus 13C
167.09
155.88
135.45
128.63
128.42
128.37
123.29
77.51
77.16
76.81
67.10
49.45
37.68
36.55
27.70
20.85
f1 (ppm)

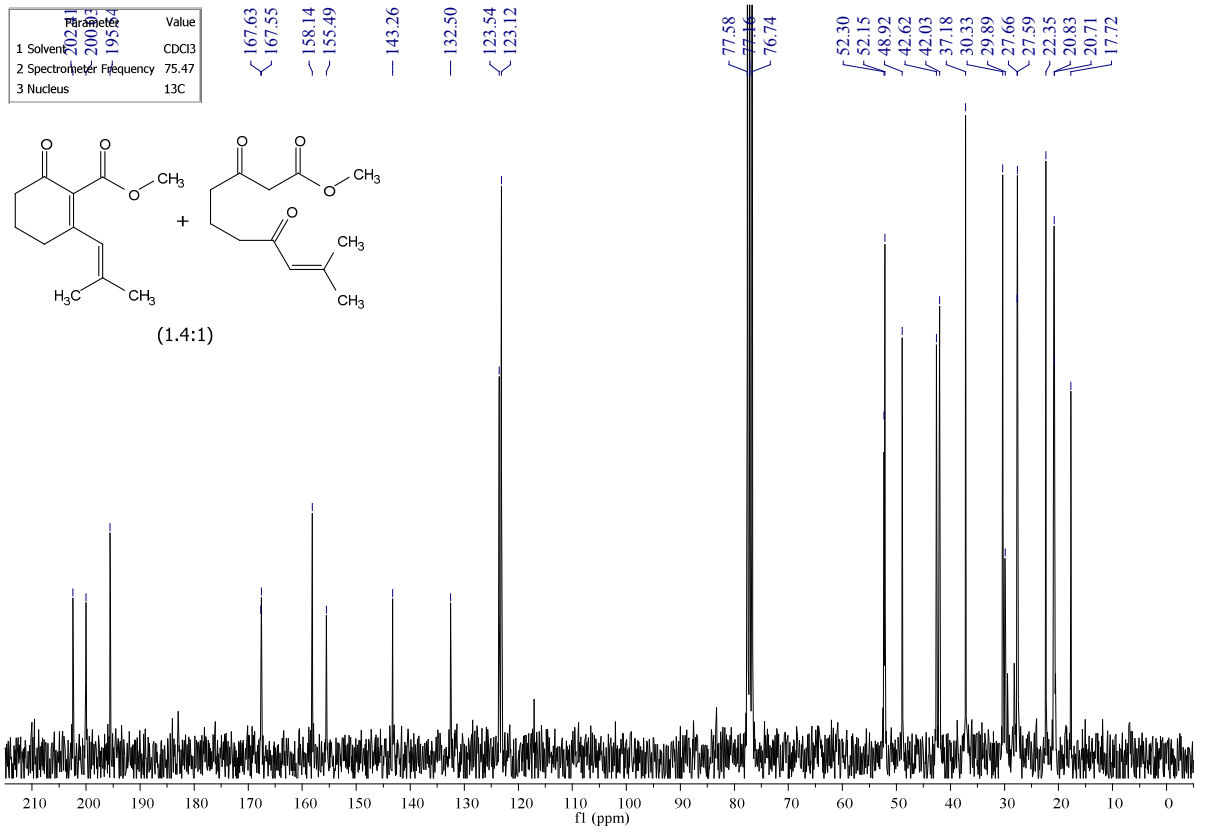

Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 250.13
3 Nucleus 1H
7.26
6.01
3.70
3.63
3.62
2.99
2.92
2.88
2.50
2.48
2.43
2.08
2.07
1.84
1.84
1.11
1.08
0.95
3.07
1.71
0.94
1.03
1.06
2.83
3.29
3.12
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 62.90
3 Nucleus 13C
205.92
198.44
167.84
156.16
123.19
77.67
77.16
76.65
52.29
48.24
47.61
41.40
27.73
20.87
16.37
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 250.13
3 Nucleus 1H
10.76
7.98
7.68
7.64
7.34
7.31
7.27
7.26
7.10
7.07
7.04
2.89
2.09
1.19
0.91
0.94
1.97
1.96
1.00
2.01
6.06
6.16
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 62.90
3 Nucleus 13C
213.24
177.80
161.37
154.75
138.26
128.91
124.24
124.06
123.06
120.33
77.67
77.16
76.65
47.37
44.08
30.31
25.50
22.32
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 300.13
3 Nucleus 1H
7.26
5.99
5.83
3.73
3.67
3.40
2.56
2.54
2.52
2.50
2.48
2.42
2.40
2.37
2.08
2.01
1.99
1.97
1.95
1.82
1.79
1.75
(1.4:1)
0.75
0.97
3.00
2.39
1.32
3.75
4.21
2.26
2.75
10.24
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Spectrometer Frequency 75.47
3 Nucleus 13C
202.1
200.3
195.4
167.63
167.55
158.14
155.49
143.26
132.50
123.54
123.12
77.58
77.16
76.74
52.30
52.15
48.92
42.62
42.03
37.18
30.33
29.89
27.66
27.59
22.35
20.83
20.71
17.72
(1.4:1)
f1 (ppm)

6. X-ray diffraction study of compound 4c

X-ray diffraction data was collected by using a Kappa X8 APEX II Bruker diffractometer with graphite-monochromated Mo$K\alpha$ radiation (= 0.71073 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SIR-97[4] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[5] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[6]

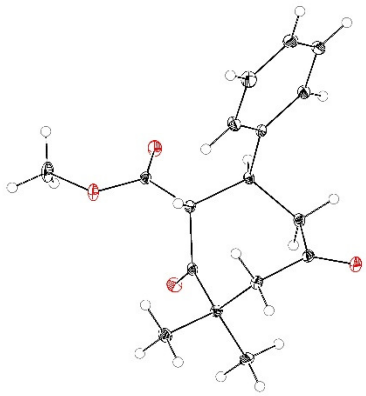
The crystal data collection and refinement parameters are given in Table S5.

CCDC 1001237 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

Table S5. Crystallographic data and structure refinement details for compound.

Compound 4c	
	CCDC 1001237
Empirical Formula	C_{17} H_{20} O_4
M_r	288.33
Crystal size, mm^3	0.24 x 0.19 x 0.05
Crystal system	monoclinic
Space group	*P* $2_1/n$
a, Å	8.3539(3)
b, Å	11.1450(3)
c, Å	16.1987(5)
α, °	90
β, °	101.7310(10)
γ, °	90
Cell volume, $Å^3$	1476.67(8)
Z	4
T, K	100(1)

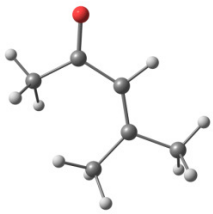
F_{000}	616
μ, mm^{-1}	0.092
θ range, °	2.23 – 30.55
Reflection collected	26 630
Reflections unique	4 434
R_{int}	0.0475
GOF	1.042
Refl. obs. (I>2σ(I))	3 431
Parameters	193
wR_2 (all data)	0.1080
R value (I>2σ(I))	0.0415
Largest diff. peak and hole (e-.$Å^{-3}$)	-0.220 ; 0.384



7. Calculations

Geometry optimizations were carried out using the Gaussian '09 software package[7] at the M06[8]/6-31+G(d,p)[9] level of theory. Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level of theory. Natural charges were obtained using the NBO 3.1 program as implemented in Gaussian.[10]

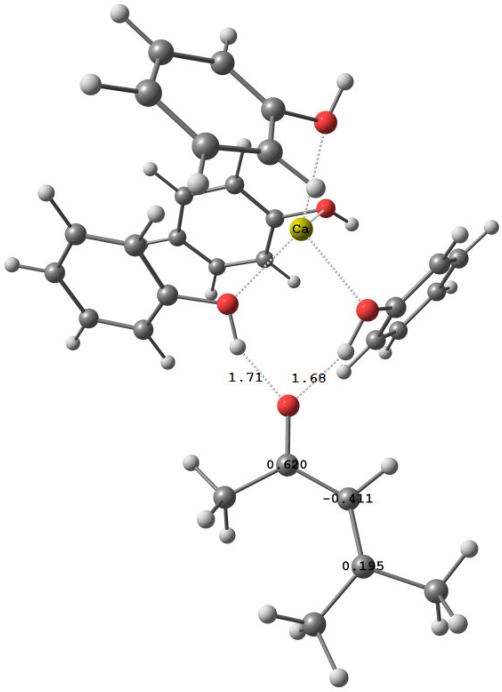
Table S6. Structure, selected bond distances (Å) and natural charges, coordinates (x,y,z) and electronic energy.



A

E(RM06) = -309.665920020

O	-2.286592000	-1.114797000	-0.089124000
C	-1.397678000	-0.278646000	-0.004212000
C	-1.762290000	1.181139000	0.105566000
H	-1.554459000	1.700169000	-0.838474000
H	-2.834294000	1.250223000	0.304365000
H	-1.204049000	1.691756000	0.897608000
C	0.002258000	-0.746683000	0.015167000
H	0.044030000	-1.835851000	0.060187000
C	1.173270000	-0.078912000	-0.011878000
C	2.457686000	-0.846688000	0.058470000
H	3.084787000	-0.469158000	0.878177000
H	2.297970000	-1.918087000	0.208762000
H	3.039327000	-0.707378000	-0.863056000
C	1.372008000	1.404836000	-0.097857000
H	0.554075000	1.936918000	-0.584275000
H	1.500565000	1.831422000	0.907210000
H	2.293260000	1.628081000	-0.649052000

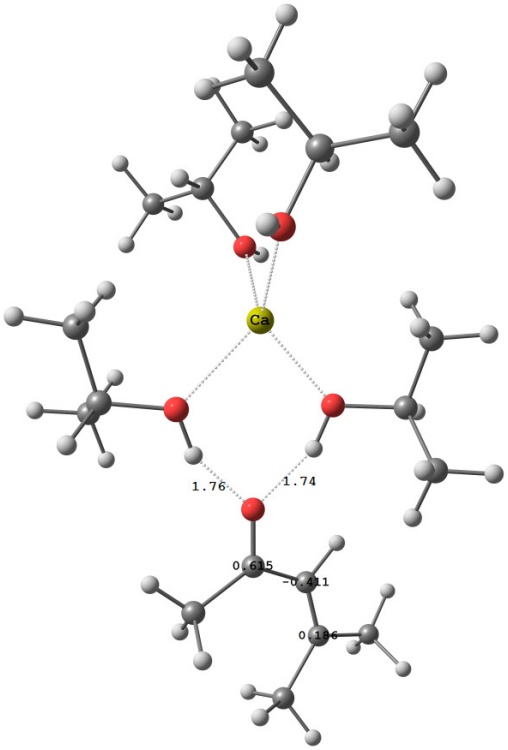


$[Ca(PhOH)_4]^{2+}\cdot A$ (I, R = Ph)

E(RM06) = -2216.00065957

O	-0.087658000	-0.987447000	-0.339258000
H	0.872047000	-1.232105000	-0.395129000
Ca	-0.814488000	0.968609000	0.710616000
O	1.510490000	1.024885000	1.354537000
O	2.522784000	-0.995120000	-0.012167000
C	3.619114000	-1.601376000	-0.137683000
C	3.612824000	-2.903764000	-0.867198000
H	3.774959000	-3.731300000	-0.165392000
H	2.641595000	-3.053455000	-1.346145000
H	4.403157000	-2.958437000	-1.621514000
C	4.797062000	-0.984400000	0.412541000
H	4.603152000	0.006375000	0.829327000
H	2.080065000	0.314531000	0.944791000
O	-1.435955000	2.870704000	-0.626814000
H	-0.892363000	3.605884000	-0.954102000
O	-2.294681000	1.530719000	2.482822000
H	-2.882833000	2.217366000	2.827047000
C	6.079878000	-1.441692000	0.481061000
C	7.122589000	-0.563117000	1.077657000
H	7.969282000	-0.464486000	0.385337000
H	6.754997000	0.432730000	1.335791000
H	7.532640000	-1.034258000	1.981191000
C	6.586178000	-2.763711000	0.005119000
H	5.892831000	-3.590723000	0.169303000
H	6.800043000	-2.717433000	-1.072154000
H	7.531477000	-3.008960000	0.497763000

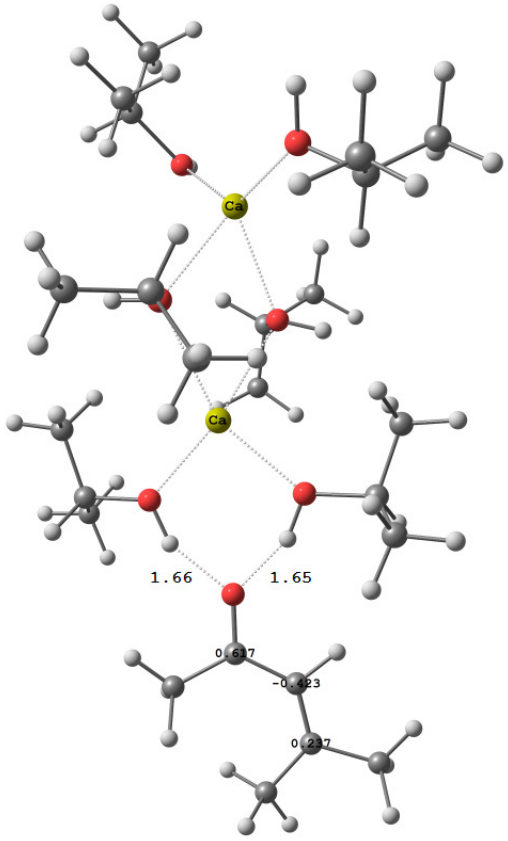
	C	-2.716900000	0.234194000	2.830691000
	C	-4.033598000	-0.167848000	2.642168000
	C	-1.727797000	-0.641056000	3.267551000
	C	-4.366066000	-1.490822000	2.923408000
	C	-2.075387000	-1.968057000	3.526542000
	C	-3.390912000	-2.389348000	3.356981000
	H	-4.785322000	0.539008000	2.295398000
	H	-0.721915000	-0.271714000	3.477527000
	H	-5.394599000	-1.819791000	2.802828000
	H	-1.320720000	-2.661053000	3.887661000
	H	-3.662494000	-3.417716000	3.577800000
	C	-1.938559000	2.070329000	-1.653482000
	C	-1.333422000	1.995895000	-2.902051000
	C	-3.013055000	1.253764000	-1.307626000
	C	-1.840645000	1.089593000	-3.830008000
	C	-3.491374000	0.334148000	-2.242521000
	C	-2.906289000	0.252745000	-3.500941000
	H	-0.495110000	2.643875000	-3.152133000
	H	-3.525015000	1.405352000	-0.354400000
	H	-1.392766000	1.034915000	-4.818632000
	H	-4.334748000	-0.301670000	-1.986510000
	H	-3.286785000	-0.455868000	-4.230979000
	C	-0.928788000	-1.892510000	-0.991514000
	C	-0.671967000	-2.278502000	-2.299890000
	C	-2.045391000	-2.345047000	-0.302765000
	C	-1.557995000	-3.153979000	-2.924131000
	C	-2.934359000	-3.205390000	-0.943406000
	C	-2.691177000	-3.610746000	-2.253458000
	H	0.201542000	-1.891592000	-2.822591000
	H	-2.192444000	-2.062663000	0.740873000
	H	-1.363699000	-3.475255000	-3.944170000
	H	-3.806058000	-3.573640000	-0.407646000
	H	-3.375977000	-4.294122000	-2.747564000
	C	1.661694000	2.237935000	0.703442000
	C	2.064887000	2.299206000	-0.631286000
	C	1.250745000	3.379544000	1.390431000
	C	2.067280000	3.535887000	-1.275543000
	C	1.246827000	4.606002000	0.726835000
	C	1.647047000	4.686097000	-0.607124000
	H	2.387528000	1.395358000	-1.147279000
	H	0.985703000	3.304441000	2.444523000
	H	2.404321000	3.599275000	-2.307438000
	H	0.949128000	5.503840000	1.262200000
	H	1.663617000	5.647328000	-1.113661000



$[Ca(iPrOH)_4]^{2+}\cdot A$ (I, R = *i*Pr)

E(RM06) = -1763.88921630

C	-0.035285000	2.865608000	-1.333610000
H	0.462824000	3.077865000	-2.290182000
O	0.238729000	1.482099000	-0.998341000
H	1.206864000	1.316948000	-0.880672000
C	0.488937000	3.773282000	-0.245606000
H	0.316500000	4.824083000	-0.500553000
H	-0.018214000	3.563986000	0.706227000
H	1.565897000	3.640021000	-0.093584000
C	-1.533262000	2.965469000	-1.509038000
H	-1.899513000	2.282300000	-2.287307000
H	-2.046255000	2.763385000	-0.551583000
H	-1.830242000	3.975772000	-1.806050000
Ca	-1.233188000	-0.114558000	-0.195679000
O	0.683200000	-1.224998000	0.473022000
C	0.843300000	-2.646251000	0.706120000
H	1.250077000	-2.771729000	1.719851000
C	-0.548136000	-3.233558000	0.636562000
H	-0.965530000	-3.107985000	-0.377444000
H	-0.538600000	-4.308752000	0.838767000
H	-1.218924000	-2.779939000	1.382133000
C	1.784715000	-3.235810000	-0.317620000
H	2.767033000	-2.750265000	-0.282067000



$[Ca_2(iPrOH)_6]^{2+}\cdot A$ (II, R = *i*Pr)

E(RM06) = -2829.17734788

C	-2.279970000	2.526214000	0.696857000
H	-3.017823000	2.643999000	1.502212000
O	-2.188940000	1.105132000	0.402901000
H	-3.105207000	0.708686000	0.262369000
C	-2.716025000	3.279083000	-0.537157000
H	-2.849295000	4.344223000	-0.321520000
H	-1.966206000	3.186744000	-1.336217000
H	-3.669498000	2.897526000	-0.918977000
C	-0.920230000	2.953907000	1.204655000
H	-0.656599000	2.418731000	2.131434000
H	-0.151048000	2.794381000	0.422287000
H	-0.901758000	4.022961000	1.439155000
Ca	-0.558770000	-0.344025000	-0.275067000
O	-2.134691000	-1.920530000	-0.674411000
C	-2.038052000	-3.344068000	-0.959481000
H	-2.549247000	-3.521970000	-1.915688000
C	-0.558176000	-3.617832000	-1.120361000
H	-0.025815000	-3.402625000	-0.173335000
H	-0.364465000	-4.670483000	-1.349695000
H	-0.134343000	-3.028674000	-1.952447000
C	-2.679392000	-4.146684000	0.145141000
H	-3.731436000	-3.871967000	0.277823000

H	1.936603000	-4.304155000	-0.132251000
H	1.379210000	-3.118278000	-1.330555000
O	2.612119000	0.459200000	-0.274196000
C	3.859178000	0.584070000	-0.334010000
C	4.417704000	1.631976000	-1.242084000
H	4.866736000	1.165650000	-2.127949000
H	3.614670000	2.290136000	-1.583790000
H	5.195904000	2.228495000	-0.757558000
C	4.671609000	-0.274968000	0.493878000
H	4.077940000	-0.881420000	1.181383000
H	1.555953000	-0.771105000	0.357482000
H	-2.768505000	3.280668000	1.610898000
C	-3.574245000	2.750251000	2.130737000
H	-4.491341000	3.338995000	2.027110000
H	-3.331894000	2.712608000	3.200900000
C	-3.780600000	1.360504000	1.581400000
H	-3.988792000	1.402359000	0.499204000
O	-2.511054000	0.612936000	1.647303000
H	-2.252358000	0.554183000	2.578976000
C	-4.861034000	0.584858000	2.292934000
H	-5.827937000	1.084621000	2.172210000
H	-4.655847000	0.529819000	3.369847000
H	-4.954787000	-0.435774000	1.905676000
H	-5.307952000	0.166909000	-0.957693000
C	-5.398107000	-0.882560000	-1.261007000
H	-5.578938000	-0.916368000	-2.343157000
H	-6.283138000	-1.303508000	-0.772073000
C	-4.171819000	-1.683365000	-0.898646000
H	-3.980871000	-1.623235000	0.185946000
O	-2.977433000	-1.041912000	-1.482653000
H	-3.064714000	-1.086169000	-2.446317000
C	-4.239587000	-3.123407000	-1.341277000
H	-5.092059000	-3.623007000	-0.869865000
H	-3.333633000	-3.678064000	-1.076800000
H	-4.386864000	-3.189111000	-2.427381000
C	6.025308000	-0.414157000	0.557103000
C	6.605944000	-1.348652000	1.561202000
H	7.379827000	-0.835021000	2.146733000
H	5.862932000	-1.765877000	2.245134000
H	7.120046000	-2.173517000	1.049656000
C	7.040533000	0.288544000	-0.283325000
H	6.719727000	0.481765000	-1.308145000
H	7.298038000	1.254325000	0.174705000
H	7.968487000	-0.290063000	-0.319655000

H	-2.650490000	-5.215836000	-0.088690000
H	-2.160644000	-3.992492000	1.100452000
O	-4.212278000	-0.421448000	-0.196781000
C	-5.481737000	-0.466768000	-0.254846000
C	-6.230968000	0.628547000	0.272922000
H	-5.604954000	1.439144000	0.651715000
C	-6.090899000	-1.671795000	-0.890824000
H	-6.865073000	-1.409223000	-1.617680000
H	-6.566077000	-2.310034000	-0.134762000
H	-3.079012000	-1.596921000	-0.572285000
H	-5.320263000	-2.256711000	-1.401523000
O	1.917953000	-0.835359000	-1.235640000
O	1.294693000	0.326868000	1.439251000
H	1.998378000	-1.788969000	-1.414815000
H	0.999379000	1.209384000	1.738361000
Ca	3.621670000	0.072282000	0.445135000
H	5.314799000	4.514256000	0.030653000
C	4.264709000	4.275727000	0.243626000
H	3.709106000	5.216188000	0.164361000
H	4.190719000	3.926176000	1.279187000
C	3.733980000	3.273758000	-0.747555000
H	2.690982000	2.990092000	-0.504566000
O	4.460791000	1.978911000	-0.580270000
H	5.380684000	2.142698000	-0.847332000
C	3.838663000	3.717536000	-2.183193000
H	3.259284000	4.633653000	-2.337760000
H	3.472817000	2.958641000	-2.884090000
H	4.878336000	3.957472000	-2.440548000
H	7.120901000	-2.671434000	2.419405000
C	7.153012000	-2.174761000	1.443511000
H	7.950174000	-2.664592000	0.873822000
H	7.435933000	-1.124917000	1.587435000
C	5.846005000	-2.301425000	0.709032000
H	5.559129000	-3.352699000	0.585267000
O	4.751278000	-1.665399000	1.501025000
H	4.818673000	-1.998746000	2.408911000
C	5.830080000	-1.592793000	-0.626342000
H	6.575751000	-2.023272000	-1.302816000
H	6.117209000	-0.531000000	-0.521890000
H	4.866209000	-1.705782000	-1.158052000
C	2.073135000	-0.145155000	-2.579863000
H	2.990167000	0.459906000	-2.480615000
C	0.875403000	0.754627000	-2.759309000
H	0.757437000	1.481378000	-1.935661000
H	0.990065000	1.366616000	-3.661829000
H	-0.047185000	0.173681000	-2.930983000

	C	2.230919000	-1.181904000	-3.658224000
	H	1.328334000	-1.800302000	-3.756706000
	H	2.388260000	-0.693141000	-4.626177000
	H	3.099942000	-1.828703000	-3.490515000
	C	1.183073000	-0.569359000	2.661101000
	H	1.802604000	-1.438874000	2.381493000
	C	-0.256595000	-0.985939000	2.837486000
	H	-0.922614000	-0.115708000	2.919042000
	H	-0.618449000	-1.668658000	2.050637000
	H	-0.370667000	-1.554397000	3.767407000
	C	1.761269000	0.160487000	3.844255000
	H	2.796276000	0.487821000	3.677062000
	H	1.155137000	1.038024000	4.109142000
	H	1.770435000	-0.490918000	4.724897000
	C	-7.588553000	0.804928000	0.374498000
	C	-8.650658000	-0.157874000	-0.033172000
	H	-8.817900000	-0.093165000	-1.118369000
	H	-8.424954000	-1.198910000	0.206077000
	H	-9.602828000	0.099866000	0.438586000
	C	-8.099364000	2.079577000	0.938667000
	H	-8.840740000	2.518079000	0.256894000
	H	-8.649747000	1.875988000	1.867908000
	H	-7.318993000	2.816069000	1.143035000

8. References

1 C. Bour, J. Monot, S. Tang, R. Guillot, J. Farjon and V. Gandon, *Organometallics*, 2014, **33**, 594.

2 Y. Liu, R.-J. Song, J.-H. Li, *Synthesis*, 2010, 3663.

3 W. Fang, M. Presset, A. Guérinot, C. Bour, S. Bezzenine-Lafollée and V. Gandon, *Chem. Eur. J.*, 2014, **20**, 5439.

4 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.

5 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.

6 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

7 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

8 Y. Zhao and D. G. Truhlar, *Theor. Chem. Account*, 2008, **120**, 215.

9 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297; V. A. Rassolov, J. A. Pople, M. A. Ratner and T. L. Windus, *J. Chem. Phys*., 1998, **109**, 1223.

10 Foster J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211; Weinhold F.; Carpenter, J. E. in *The Structure of Small Molecules and Ions*, Naaman R.; Vager Z. Eds. Plenum, 1988, 227.