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Supporting information

Solvent-free direct α-alkylation of ketones by alcohols catalyzed by nickel supported on silica-alumina

Aubin Charvieux[a], Javier B. Giorgi[b], Nicolas Duguet*[a], Estelle Métay*[a]

[a] Univ Lyon, Université Claude Bernard Lyon1, CNRS, INSA-Lyon, CPE-Lyon, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, ICBMS, UMR 5246, Equipe CAtalyse, SYnthèse et ENvironnement (CASYEN), Campus LyonTech La Doua, Bâtiment Lederer, 1 rue Victor Grignard, F-69622 Villeurbanne cedex, France. Phone: +33(0)-472-448-507; Fax: +33-(0)472-431-408, E-mails: nicolas.duguet@univ-lyon1.fr, estelle.metay@univ-lyon1.fr

[b] Centre for Catalysis Research and Innovation, Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Table of contents

1. General information 2
2. General procedure for the α-alkylation of ketones by alcohols catalyzed by nickel supported on silica alumina in the optimized conditions 2
3. General procedure for measurement of NMR yields 2
4. Procedure for catalyst recycling 3
5. Procedure for leaching test 3
6. Synthesis of 1,3,5-triphenylpentane-1,5-dione (4) 4
7. Study of the reversibility of 1,3,5-triphenylpentane-1,5-dione (4) formation 4
8. Characterization of the catalysts 4
9. Crystalline species by XRD 4
10. Determination of Ni species by XPS 5
11. Characterization of compounds 6
12. ^{1}H and ^{13}C NMR Spectra 11

1. General information

All chemicals were purchased from Sigma-Aldrich, Alfa Aesar and Strem chemicals. Unless otherwise noted, materials were obtained from commercial suppliers and used without purification.

Reactions were monitored by TLC using silica gel ($60F_{254}$) supported aluminium plate and NMR. Purification by flash chromatography was performed using silica gel 60H (40-63µm).

Nuclear magnetic resonance spectra were recorded on a Brüker DRX 300 or Brüker ALS 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{19}F: 282 MHz). Chemical shifts are given with reference to residual $CHCl_3$ central peak: 7.26 ppm for proton, 77.16 ppm for carbon, respectively. *J* values are given in Hertz (Hz). Abbreviations are defined as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quadruplet, qt = quintuplet, m = multiplet.

The HRMS-ESI mass spectra were recorded in a positive ion mode on a hybrid quadrupole time-of-flight mass spectrometer (MicroTOFQ-II, Bruker Daltonics, Bremen) with an Electrospray Ionization (ESI) ion source. The flow of spray gas is 0.6 bar and the capillary voltage is 4.5 kV. The solutions are infused at 180µL/h in a mixture of solvents (methanol / dichloromethane/water 45/40/15). The mass range of the analysis is 50-1000 m/z and the calibration was done with sodium formate. The mass HRMS-CI spectra were recorded on a double-focusing mass spectrometer (ThermoFinnigan MAT95XL, Bremen, Germany) equipped with a chemical ionization (CI) sources.

Melting points were measured using a Köfler bench.

2. General procedure for the α-alkylation of ketones by alcohols catalyzed by nickel supported on silica alumina in the optimized conditions

65wt% $Ni/SiO_2,Al_2O_3$ (174 mg, 0.2 equiv) and K_3PO_4 (204 mg, 0.1 equiv), alcohol (9.66 mmol, 1 equiv) and ketone (11.6 mmol, 1.2 equiv) were introduced in that order in a pressure tube, which was then sealed. The mixture was stirred at 175°C for 24h. After completion of the reaction, NMR internal standard (mesitylene) was added and NMR yield was measured. The mixture was then diluted with ethyl acetate and filtered. The filtrate was concentrated under reduced pressure and purified by flash chromatography (ethyl acetate/cyclohexane) to afford desired compounds.

3. General procedure for measurement of NMR yields

NMR yields were measured using mesitylene as an internal standard, added in known quantity to the reaction mixture after completion of the reaction. The mixture is then analyzed by ^{1}H NMR spectroscopy. NMR yields are calculated as follow:

$$NMR\ yield = \frac{n_{is} * N_{His}}{I_{is}} * \frac{I_p}{n_{pmax} * N_{Hp}} = \frac{m_{is} * N_{His}}{M_{is} * I_{is}} * \frac{M_{BnOH} * I_p}{m_{BnOH} * N_{Hp}}$$

where: “n” is the amount of substance, “N_H” the number of integrated protons, “I” the value of the integration, “m” the mass and “M” the molar mass. “is” refers to the internal standard, “p” the desired product when yield is 100% and “BnOH” benzyl alcohol.

Practical example: measurement of NMR yield of 1,3-diphenylpropan-1-one (**3a**)

208 mg of internal standard are added to the reaction mixture, dichloromethane (1 mL) is added to homogenize the mixture, which is then stirred vigorously. A sample of the mixture is taken and filtered through a cotton in a pipette directly in a NMR tube. Deuterated chloroform is added. The tube is then analyzed by $_{1}H$ NMR spectroscopy, giving spectrum shown in Figure 1. Aromatic protons of mesitylene and CH_2-Ph of **3a** are integrated. Yield is then calculated using previously described formula:

$$NMR\ yield\ of\ 3a = \frac{m_{is} * N_{His}}{M_{is} * I_{is}} * \frac{M_p * I_p}{m_p * N_{Hp}} = \frac{0.208 * 3}{120.2 * 1} * \frac{108.1 * 3.47}{1.045 * 2} = 93\%$$

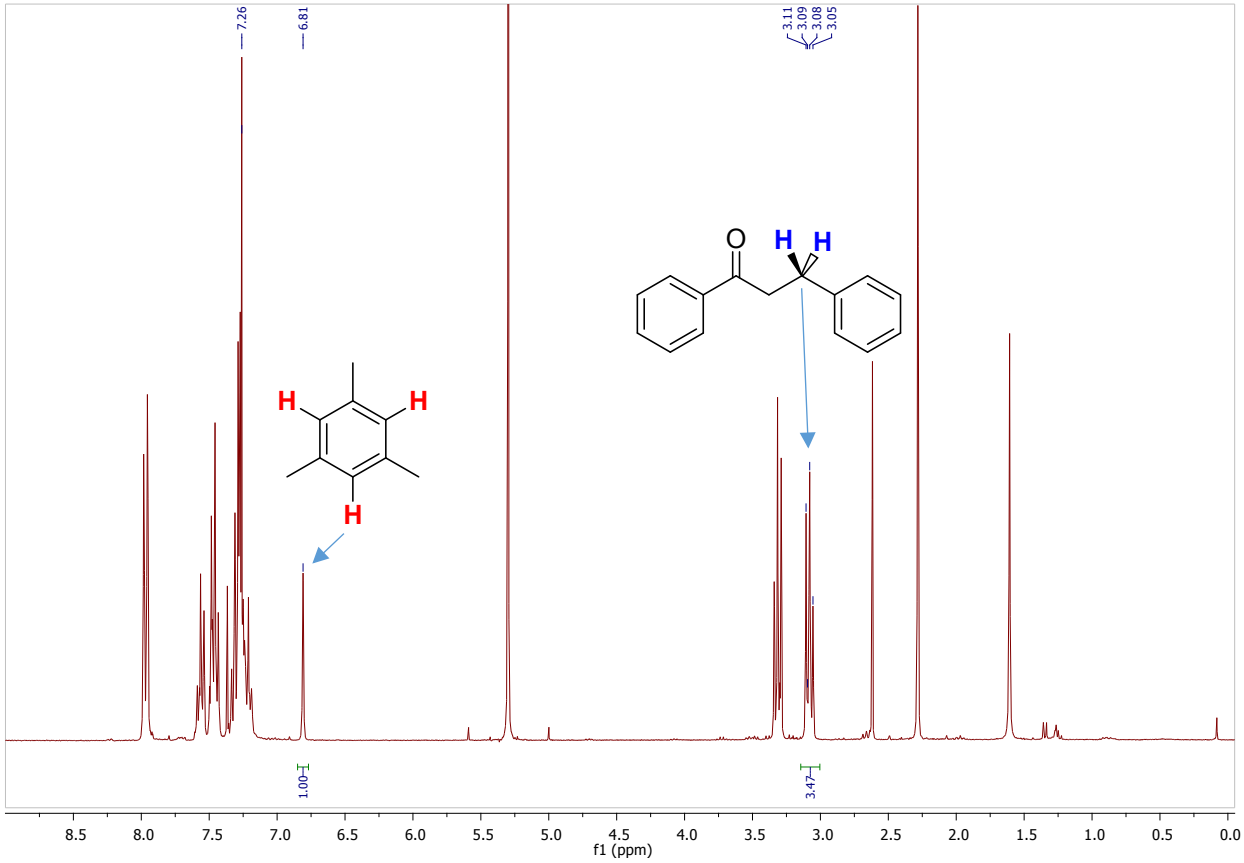


Figure SI 1: ^1H NMR spectrum of crude mixture from the reaction affording 3a

4. Procedure for catalyst recycling

After reaction (α-alkylation of acetophenone by benzyl alcohol, in optimized conditions), the catalyst is thoroughly washed with acetone (3x 10 mL), water (3x 10 mL) and acetone again (2x 5 mL). Washed catalyst is then dry under reduced pressure and reengaged in reaction following the procedure described in part 2 of this document (using acetophenone and benzyl alcohol).

5. Procedure for leaching test

In order to verify the potential leaching of the catalyst in solution, two reactions (α-alkylation of acetophenone by benzyl alcohol, in optimized conditions) were ran in parallel. First, they were stopped after one hour of heating. The first tube was used to determine the NMR yield of **3a** and conversion of benzyl alcohol after one hour of reaction, according to the procedure described in part 3 of this document. Hot reaction mixture from the other tube was filtered in order to remove the catalyst, then the filtrate was reengaged in reaction during 23h and the NMR yield and conversion were measured. As shown in Table 1, the yield of 3a did not evolve after removal of the catalyst, thus proving that no leaching of the catalyst occurs during the reaction.

Table 1: Leaching test

	NMR Conversion of benzyl alcohol	NMR Yield of **3a**
After 1 hour reaction	75%	61%
After 1 hour reaction +	76%	57%

filtration + 23 hours reaction		

6. Synthesis of 1,3,5-triphenylpentane-1,5-dione (4)

trans-Chalcone (**5**, 8.05 g, 38.6 mmol, 1 equiv.), acetophenone (**1a**, 9 mL, 77.2 mmol, 2 equiv.) and K_3PO_4 (820 mg, 3.86 mmol, 0.1 equiv.) were introduced in a 70 mL pressure-tube. The pressure-tube was sealed with a top and put under magnetic stirring at 175°C (oil bath) for 15h. The crude mixture was then dissolved in EtOAc and filtrated. The filtrate was evaporated under reduce pressure. The obtained solid was then recrystallized in EtOH and filtrated. Obtained solid was dried, giving 10 g of the desired compound **4** (79% yield).

7. Study of the reversibility of 1,3,5-triphenylpentane-1,5-dione (4) formation

65wt% $Ni/SiO_2,Al_2O_3$ (171 mg, 0.2 equiv) and K_3PO_4 (201 mg, 0.1 equiv), 1,3,5-triphenylpentane-1,5-dione (**4**, 1.56 g, 4.75 mmol, 1 equiv.), benzyl alcohol (**2a**, 0.99 mL, 9.50 mmol, 2 equiv.) were introduced in a 40 mL pressure tube, which was then sealed and put under magnetic stirring at 175°C (oil bath) for 15h. NMR internal standard (mesitylene) was then added and NMR yield was measured. Desired product **3a** was obtained in 85% yield, conversion was almost total (96% conversion with respect to product **4**).

8. Characterization of the catalysts

The crystal phases present in the catalysts were determined by powder X-Ray Diffraction using an Ultima IV X-ray diffractometer. The instrument used Cu Kα radiation (λ=1.54 Å) and the scattering angle, 2θ, was scanned between 10◦and 120◦at a rate of 0.02◦/s. The Rigaku PDXL Software (Version 1.8.0.3) was used for profile refinement and phase indexing to the Powder Diffraction File database (JCPDS, 2012).

A JEOL JSM-7500F field emission scanning electron microscope (FE-SEM) with an energy dispersive X-ray spectroscopy (EDS X-Sight) attachment was used to image the surface morphology of the catalysts and provide qualitative elemental composition. The BET surface areas of fresh and used catalysts were determined using a Quantachrome Autosorb 1-C instrument using nitrogen as the vector gas.

The surface chemical states and compositions of the catalysts were determined by X-ray photoelectron spectroscopy (XPS; Kratos AXIS UltraDLD 39-306l), using a monochromatic Al source. Survey spectra were obtained to identify elements present and high resolution spectra were measured for the relevant element regions. The Casa Software[1] was used for the analysis and quantification of the XP spectra. The binding energy of the C1s level (284.8 eV) was used to calibrate the energy scales of all spectra.

9. Crystalline species by XRD

Powder X-ray diffraction (pXRD) spectra of used Ni/SiO2-Al2O3 catalyst. Species are identified from their corresponding reference spectra: NiO (JCPDS# 01-089-3080), Ni (JCPDS# 01-071-3740) and quartz (JCPDS# 00-001-0649). Spectrum has been fitted and only strong peaks are shown.

[1] Fairley, N. CASA XPS Version 2.3.13 Dev73. 2007

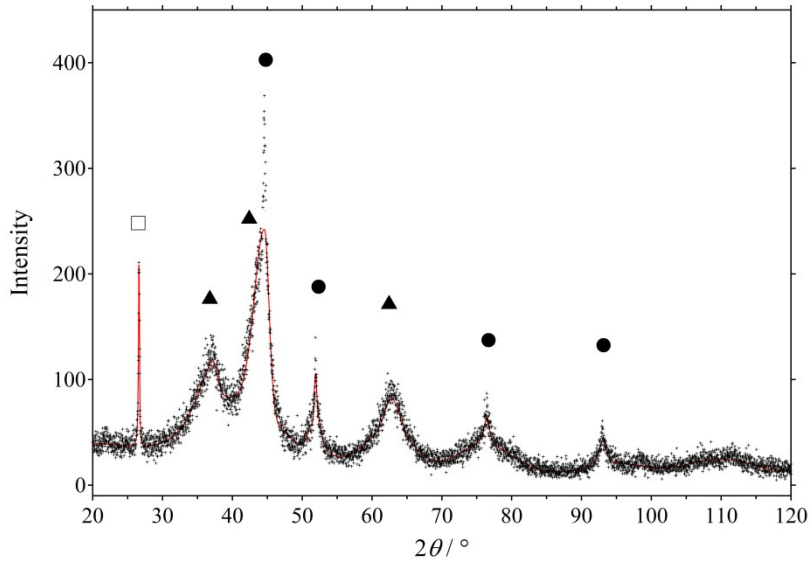


Figure SI-2 X-Ray Diffractogram of fresh Ni/SiO2-Al2O3 catalyst. Primary species are identified as ● Ni (JCPDS# 01-071-3740), ▲ NiO (JCPDS# 01-089-3080), and □ quartz (JCPDS# 00-001-0649).

10. Determination of Ni species by XPS

The fitting procedures proposed by Biesinger et al.[2],[3] were followed to determine the presence of nickel metal, nickel oxide and nickel hydroxide. Multiple peaks were fitted in accordance with the appropriate satellite scheme and respecting the relationship of peak position, intensities and widths between peaks.

[2] Biesinger, M. C. XPS fitting http://www.xpsfitting.com (accessed Oct 6, 2017).

[3] Biesinger, M. C.; Payne, B. P.; Lau, L. W. M.; Gerson, A.; Smart, R. S. C. X-Ray Photoelectron Spectroscopic Chemical State Quantification of Mixed Nickel Metal, Oxide and Hydroxide Systems. *Surf. Interface Anal.* **2009**, *41* (4), 324–332.

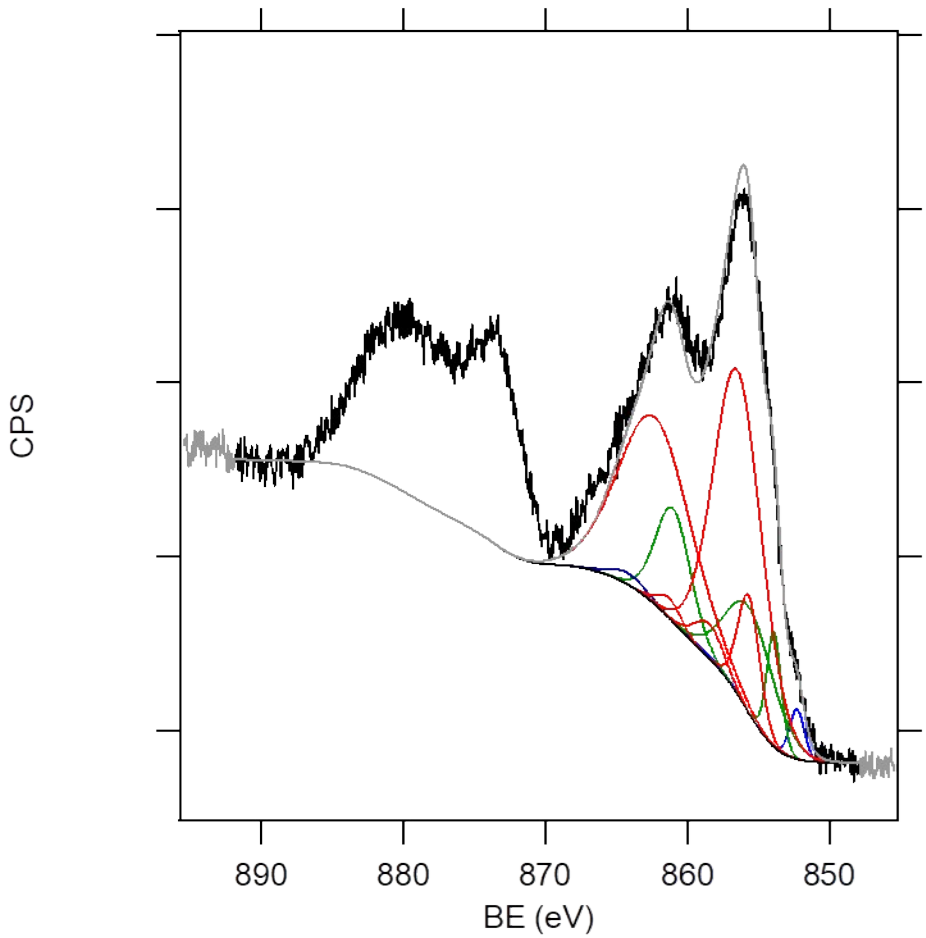
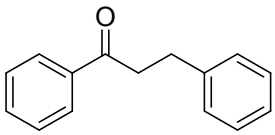


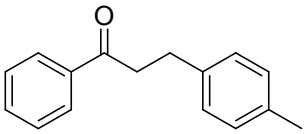
Figure SI-3 XP spectrum of the Ni 2p region for the fresh Ni/SiO2-Al2O3 catalyst. Blue curves correspond to Ni metal, green curves to NiO and red curves to Ni(OH)2.

11. Characterization of compounds

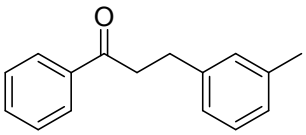
1,3-diphenylpropan-1-one (**3a**): 1.883 g, 98% GC purity, 93%, white solid, mp: 68°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.05-3.11 (m, 2H, CH_2), 3.29-3.34 (m, 2H, CH_2), 7.18-7.34 (m, 5H), 7.43-7.48 (m, 2H), 7.53-7.59 (m, 1H), 7.95-7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.1 (CH_2), 40.4 (CH_2), 126.1 (CH), 128.0 (2CH), 128.1 (2CH), 128.5 (2CH), 128.6 (2CH), 133.0 (CH), 136.9 (C), 141.3 (C), 199.1 (CO); HRMS (ESI$^+$) $[M+H]^+$ $C_{15}H_{15}O$: requires 211.1117, found 211.1116 (0.7 ppm).



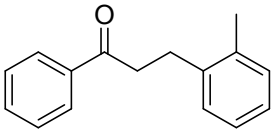
1-phenyl-3-(p-tolyl)propan-1-one (**3b**): 1.563 g, 98% GC purity, 71%, pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3H, CH_3), 3.02-3.07 (m, 2H, CH_2), 3.27-3.32 (m, 2H, CH_2), 7.11-7.18 (m, 4H), 7.43-7.49 (m, 2H), 7.54-7.59 (m, 1H), 7.96-7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (CH_3), 29.8 (CH_2), 40.7 (CH_2), 128.1 (2CH), 128.4 (2CH), 128.7 (2CH), 129.3 (2CH), 133.1 (CH), 135.7 (C), 137.0 (C), 138.3 (C), 199.4 (CO); HRMS (ESI$^+$) $[M+H]^+$ $C_{16}H_{17}O$: requires 225.1274, found 225.1271 (1.3 ppm) .



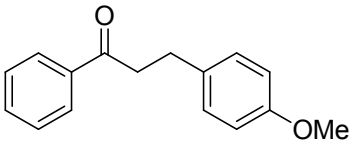
1-phenyl-3-(m-tolyl)propan-1-one (**3c**): 1.448 g, 99% GC purity, 67%, pale yellow solid, mp: 70°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3H, CH_3), 3.01-3.06 (m, 2H, CH_2), 3.28-3.33 (m, 2H, CH_2), 7.02-7.07 (m, 3H), 7.17-7.22 (m, 1H), 7.43-7.48 (m, 2H), 7.53-7.59 (m, 1H), 7.95-7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 30.2 (CH_2), 40.7 (CH_2), 125.5 (CH), 127.0 (CH), 128.2 (2CH), 128.6 (CH), 128.7 (2CH), 129.4 (CH), 133.2 (CH), 136.7 (C), 138.2 (C), 141.3 (C), 199.4 (CO); HRMS (ESI$^+$) $[M+H]^+$ $C_{16}H_{17}O$: requires 225.1274, found 225.1271 (1.1 ppm).



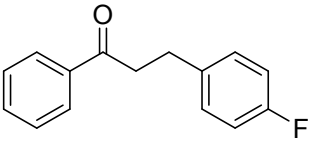
1-phenyl-3-(o-tolyl)propan-1-one (**3d**): 1.392 g, 97% GC purity, 62%, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H, CH_3), 3.03-3.09 (m, 2H, CH_2), 3.23-3.29 (m, 2H, CH_2), 7.12-7.21 (m, 4H), 7.43-7.49 (m, 2H), 7.54-7.60 (m, 1H), 7.96-8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5 (CH_3), 27.6 (CH_2), 39.2 (CH_2), 126.3 (CH), 126.4 (CH), 128.2 (2CH), 128.7 (2CH), 128.8 (CH), 130.5 (CH), 133.2 (CH), 136.1 (C), 136.9 (C), 139.5 (C), 199.5 (CO); HRMS (ESI^+) $[M+H]^+$ $C_{16}H_{17}O$: requires 225.1274, found 225.1268 (2.7 ppm).



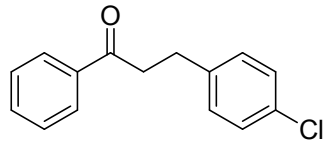
3-(4-methoxyphenyl)-1-phenylpropan-1-one (**3e**): 2.053 g, 97% GC purity, 86%, yellow solid, mp: 67°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.00-3.05 (m, 2H, CH_2), 3.25-3.30 (m, 2H, CH_2), 3.79 (s, 3H, OCH_3), 6.83-6.88 (m, 2H), 7.16-7.20 (m, 2H), 7.43-7.46 (m, 2H), 7.53-7.59 (m, 1H), 7.95-7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.4 (CH_2), 40.8 (CH_2), 55.4 (CH_3), 114.0 (2CH), 128.1 (2CH), 128.7 (2CH), 129.5 (2CH), 133.1 (CH), 133.4 (C), 137.0 (C), 158.1 (C), 199.5 (CO); HRMS (ESI^+) $[M+Na]^+$ $C_{16}H_{16}NaO_2$: requires 263.1043, found 263.1037 (2.0 ppm).



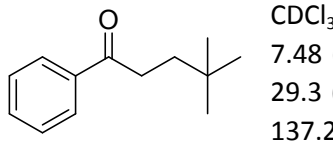
1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**3f**): 1.444 g, 97% GC purity, 52%, white solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.11-3.16 (m, 2H, CH_2), 3.31-3.36 (m, 2H, CH_2), 7.36-7.39 (m, 2H), 7.43-7.49 (m, 2H), 7.54-7.60 (m, 3H), 7.94-7.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.9 (CH_2), 39.9 (CH_2), 124.4 (q, $^{1}J_{C-F}$ = 271.7, CF_3), 125.5 (q, $^{3}J_{C-F}$ = 3.7, 2CH), 128.1 (2CH), 128.8 (2CH), 128.9 (2CH), 133.4 (CH), 136.8 (C), 145.6 (C), 198.7 (CO); ^{19}F NMR (282 MHz, CDCl3): δ = -62.4 (s, CF_3); HRMS (ESI^+) $[M+H]^+$ $C_{16}H_{14}F_3O$: requires 279.0991, found 279.0984 (2.5 ppm).



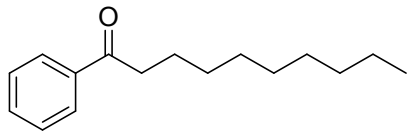
3-(4-fluorophenyl)-1-phenylpropan-1-one (**3g**): 1.279 g, 97% GC purity, 55%, orange solid, mp: 66°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.02-3.07 (m, 2H, CH_2), 3.26-3.31 (m, 2H, CH_2), 6.95-7.00 (m, 2H), 7.18-7.28 (m, 2H), 7.43-7.48 (m, 2H), 7.53-7.61 (m, 1H), 7.94-7.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.4 (CH_2), 40.5 (CH_2), 115.2 (CH), 115.5 (CH), 128.1 (2CH), 128.7 (2CH), 129.9 (CH), 130.0 (CH), 133.3 (CH), 136.9 (C), 137.0 (C), 161.5 (d, $^{1}J_{C-F}$ = 244, CF), 199.1 (CO); ^{19}F NMR (282 MHz, CDCl3): δ = -117.3- -117.23 (m, F); HRMS (ESI^+) $[M+H]^+$ $C_{15}H_{14}FO$: requires 229.1023, found 229.1017 (2.7 ppm).



3-(4-chlorophenyl)-1-phenylpropan-1-one (**3h**):0.439 g, 97% GC purity, 18%, white solid, mp: 62°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.02-3.07 (m, 2H, CH_2), 3.26-3.31 (m, 2H, CH_2), 7.17-7.28 (m, 4H), 7.41-7.48 (m, 2H), 7.54-7.59 (m, 1H), 7.93-7.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.5 (CH_2), 40.3 (CH_2), 128.1 (2CH), 128.7 (2CH), 128.8 (2CH), 130.0 (2CH), 132.0 (C), 133.3 (CH), 136.9 (C), 139.9 (C), 198.9 (CO); HRMS (ESI^+) $[M+H]^+$ $C_{15}H_{14}ClO$: requires 245.0728, found 245.0722 (2.5 ppm).



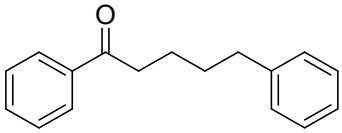
4,4-dimethyl-1-phenylpentan-1-one (**3i**): 0.446 g, 99% GC purity, 24%, pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (s, 9H, $3CH_3$), 1.62-1.67 (m, 2H, CH_2), 2.91-2.96 (m, 2H, CH_2), 7.43-7.48 (m, 2H), 7.52-7.58 (m, 1H), 7.95-7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.3 ($3CH_3$), 30.3 (C), 34.4 (CH_2), 38.3 (CH_2), 128.2 (2CH), 128.7 (2CH), 133.0 (CH), 137.2 (C), 201.2 (CO); HRMS (ESI^+) $[M+H]^+$ $C_{13}H_{19}O$: requires 191.1430, found 191.1422 (4 ppm).



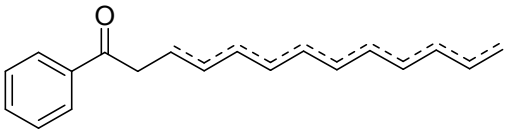
1-phenyldecan-1-one (**3j**): 1.207 g, 97% GC purity, 52%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, ^{3}J = 6.7, 3H, CH_3), 1.27-1.44 (m, 12H, $6CH_2$), 1.73 (qt, ^{3}J = 7.5, 2H, CH_2), 2.96 (t, ^{3}J = 7.4, 2H, CH_2), 7.43-7.48 (m, 2H), 7.52-7.58 (m, 1H), 7.94-7.98 (m, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (CH_3), 22.8

(CH_2), 24.5 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 32.0 (CH_2), 38.8 (CH_2), 128.2 (2CH), 128.7 (2CH), 133.0 (CH), 137.2 (C), 200.7 (CO); HRMS (ESI^+) $[M+H]^+$ $C_{16}H_{25}O$: requires 233.1900, found 233.1890 (4.3 ppm).

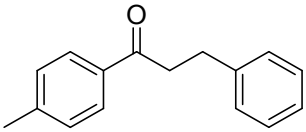
1,5-diphenylpentan-1-one (**3k**): 0.947 g, 95% GC purity, 39%, colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.68-1.87 (s, 4H, $2CH_2$), 2.66-2.71 (m, 2H, CH_2), 2.97-3.02 (m, 2H, CH_2), 7.16-7.21 (m, 3H), 7.26-7.32 (m, 2H), 7.44-7.49 (m, 2H), 7.54-7.59 (m, 1H), 7.94-7.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.1 (CH_2), 31.2 (CH_2), 35.9 (CH_2), 38.5 (CH_2), 125.9 (CH), 128.1 (2CH), 128.4 (2CH), 128.5 (2CH), 128.7 (2CH), 133.0 (CH), 137.1 (C), 142.4 (C), 200.4 (CO); HRMS (ESI^+) $[M+H]^+$ $C_{17}H_{19}O$: requires 239.1430, found 239.1427 (1.3 ppm).



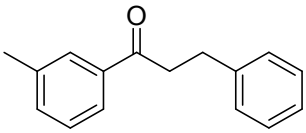
1-phenyltridec-12-en-1-one (**3m'**, 4%), (*E*)-1-phenyltridec-x-en-1-one (**3m''**, x<12, 36%) and 1-phenyltridecan-1-one (**3m'''**, 16%), obtained in a 1 : 9.2 : 4.3 (molar ratio) mixture, 1.485 g, colorless oil.



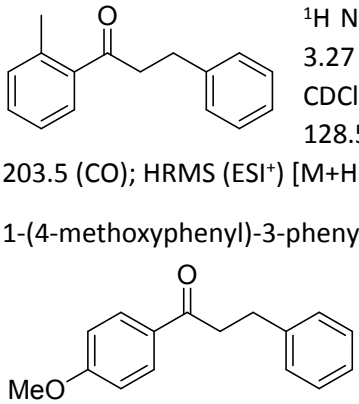
3-phenyl-1-(p-tolyl)propan-1-one (**3n**): 1.676 g, 98% GC purity, 76%, white solid, mp: 68°C; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3H, CH_3), 3.04-3.9 (m, 2H, CH_2), 3.25-3.31(m, 2H, CH_2), 7.18-7.33 (m, 7H), 7.85-7.88 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7 (CH_3), 30.3 (CH_2), 40.4 (CH_2), 126.2 (CH), 128.3 (2CH), 128.5 (2CH), 128.6 (2CH), 129.4 (2CH), 134.5 (C), 141.5 (C), 143.9 (C), 199.0 (CO); HRMS (ESI^+) $[M+H]^+$ $C_{16}H_{17}O$: requires 225.1274, found 225.1272 (0.9 ppm).



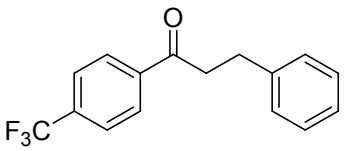
3-phenyl-1-(m-tolyl)propan-1-one (**3o**): 1.494 g, 99% GC purity, 67%, yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H, CH_3), 3.04-3.09 (m, 2H, CH_2), 3.27-3.32 (m, 2H, CH_2), 7.19-7.39 (m, 7H), 7.75-7.77 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 30.3 (CH_2), 40.6 (CH_2), 125.4 (CH), 126.2 (CH), 128.5 (2CH), 128.6 (CH), 128.6 (2CH), 128.7 (CH), 133.9 (CH), 137.0 (C), 138.5 (C), 141.5 (C), 199.5 (CO); HRMS (ESI^+) $[M+H]^+$ $C_{16}H_{17}O$: requires 225.1274, found 225.1270 (1.7 ppm).



3-phenyl-1-(o-tolyl)propan-1-one (**3p**): 1.256 g, 96% GC purity, 56%, yellow oil; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.49 (s, 3H, CH_3), 3.04-3.09 (m, 2H, CH_2), 3.24-3.27 (m, 2H, CH_2), 7.22-7.38 (m, 8H), 7.60-7.63 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 30.4 (CH_2), 43.3 (CH_2), 125.8 (CH), 126.2 (CH), 128.5 (CH), 128.5 (2CH), 128.6 (2CH), 131.3 (CH), 132.1 (CH), 138.0 (C), 138.2 (C), 141.3 (C), 203.5 (CO); HRMS (ESI^+) $[M+H]^+$ $C_{16}H_{17}O$: requires 225.1274, found 225.1267 (3 ppm).

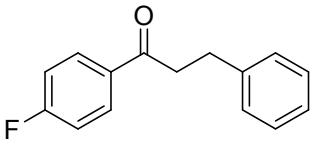


1-(4-methoxyphenyl)-3-phenylpropan-1-one (**3q**): 2.007 g, 97% GC purity, 81%, white solid, 90°C; ^1H NMR (300 MHz, $CDCl_3$): δ = 3.03-3.08 (m, 2H, CH_2), 3.23-3.28 (m, 2H, CH_2), 3.87 (s, 3H, OCH_3), 6.90-6.95 (m, 2H), 7.18-7.33 (m, 5H), 7.93-7.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.4 (CH_2), 40.2 (CH_2), 55.6 (CH_3), 113.8 (2CH), 126.2 (CH), 128.5 (2CH), 128.6 (2CH), 130.1 (C), 130.4 (2CH), 141.6 (C), 163.5 (C), 197.9 (CO); HRMS (ESI^+) $[M+H]^+$ $C_{16}H_{17}O_2$: requires 241.1223, found 241.1228 (1.9 ppm).

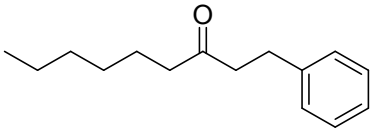


3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (**3r**): 1.088 g, 97% GC purity, 47%, white solid, mp: 44°C; ^1H NMR (300 MHz, $CDCl_3$): δ = 3.06-3.11 (m, 2H, CH_2), 3.31-3.36 (m, 2H, CH_2), 7.20-7.34 (m, 5H), 7.71-7.74 (m, 2H), 8.04-8.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.0 (CH_2), 40.9

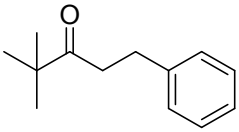
(CH_2), 123.7 (d, $^1J_{C\text{-}F}$ = 273, CF_3), 125.8 (q, $^3J_{C\text{-}F}$ = 3.7, 2CH), 126.4 (CH), 128.5 (2CH), 128.5 (2CH), 128.7 (2CH), 134.5 (d, $^2J_{C\text{-}F}$ =33, C), 139.6 (C), 141.0 (C), 198.3 (CO); ^{19}F NMR (282 MHz, CDCl3): δ = -63.1 (s, CF_3); HRMS (ESI$^+$) $[M+H]^+$ $C_{16}H_{14}F_3O$: requires 279.0991, found 279.0996 (1.8 ppm).



1-(4-fluorophenyl)-3-phenylpropan-1-one (**3s**): 1.060 g, 99% GC purity, 48%, white solid, mp: 42°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.04-3.09 (m, 2H, CH_2), 3.25-3.31 (m, 2H, CH_2), 7.08-7.16 (m, 2H), 7.18-7.34 (m, 5H), 7.96-8.02 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.2 (CH_2), 40.5 (CH_2), 115.6 (CH), 115.9 (CH), 126.3 (CH), 128.5 (2CH), 128.7 (2CH), 130.7 (CH), 130.8 (CH), 133.4 (C), 141.2 (C), 165.8 (d, $^1J_{C\text{-}F}$ = 254, CF), 197.7 (CO); ^{19}F NMR (282 MHz, CDCl3): δ = -105.3- -105.25 (m, F); HRMS (ESI$^+$) $[M+H]^+$ $C_{15}H_{14}FO$: requires 229.1023, found 229.1030 (2.8 ppm).

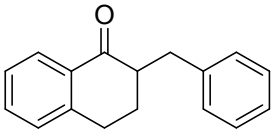


1-phenylnonan-3-one (**3u**): 1.352 g, 97% GC purity, 62%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.7, 3H, CH_3), 1.25-1.33 (m, 6H, 3CH_2), 1.51-1.61 (m, 2H, CH_2), 2.38 (t, J = 7.4, 2H, CH_2), 2.70-2.75 (m, 2H, CH_2), 2.88-2.93 (m, 2H, CH_2), 7.17-7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH_2), 23.9 (CH_2), 29.0 (CH_2), 29.9 (CH_2), 31.7 (CH_2), 43.2 (CH_2), 44.3 (CH_2), 126.2 (CH), 128.4 (2CH), 128.6 (2CH), 141.3 (C), 210.5 (CO); HRMS (ESI$^+$) $[M+H]^+$ $C_{15}H_{23}O$: requires 213.1743, found 213.1743 (0.2 ppm).



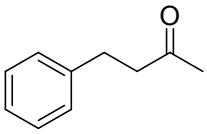
4,4-dimethyl-1-phenylpentan-3-one (**3v**): 0.803 g, 99% GC purity, 44%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (s, 9H, 3CH_3), 2.77-2.83 (m, 2H, CH_2), 2.86-2.92 (m, 2H, CH_2), 7.17-7.21 (m, 3H), 7.28-7.31 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.4 (3CH_3), 30.2 (CH_2), 38.6 (CH_2), 44.2 (C), 126.1 (CH), 128.5 (2CH), 128.5 (2CH), 141.7 (C), 215.0 (CO); HRMS (ESI$^+$) $[M+Na]^+$ $C_{13}H_{18}NaO$: requires 213.1250, found 213.1242 (3.5 ppm).

2-benzyl-3,4-dihydronaphthalen-1(2H)-one (**3x**): 0.894 g, 97% GC purity, 38%, yellow solid, mp: 52°C; ^{1}H



NMR (300 MHz, $CDCl_3$): δ = 1.73-1.86 (m, 1H), 2.07-2.16 (m, 1H), 2.61-2.80 (m, 2H, CH_2), 2.91-3.00 (m, 2H, CH_2), 3.50 (dd, J = 13.3, 3.6, 1H, CH), 7.20-7.34 (m, 7H), 7.44-7.49 (m, 1H), 8.06-8.09 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.8 (CH_2), 28.7 (CH_2), 35.8 (CH_2), 49.6 (CH), 126.2 (CH), 126.7 (CH), 127.6 (CH), 128.5 (2CH), 128.8 (CH), 129.4 (2CH), 132.6 (C), 133.4 (CH), 140.1 (C), 144.1 (C), 199.5 (CO); HRMS (ESI$^+$) $[M+H]^+$ $C_{17}H_{17}O$: requires 237.1274, found 237.1274 (0.1 ppm).

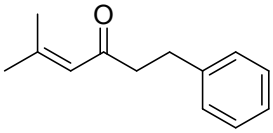
4-phenylbutan-2-one (**3z**): 0.272 g, 98% GC purity, 19%, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21



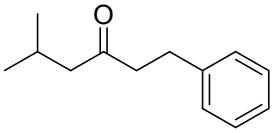
(s, 3H, CH_3), 2.83 (t, ^3J = 8.3, 2H, CH_2), 2.98 (t, ^3J = 8.3, 3H, CH_2), 7.23-7.30 (m, 3H), 7.35-7.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.6 (CH_3), 29.9 (CH_2), 45.0 (CH_2), 126.0 (CH), 128.2 (2CH), 128.4 (2CH), 140.9 (C), 207.7 (CO);

5-methyl-1-phenylhex-4-en-3-one (**3aa'**) and 5-methyl-1-phenylhexan-3-one (**3aa"**), obtained as a 26 : 74 (molar ratio) mixture after flash chromatography, 596 mg, yellow oil;

5-methyl-1-phenylhex-4-en-3-one (**3aa'**): 156 mg (calculated), 9%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.84 (d,

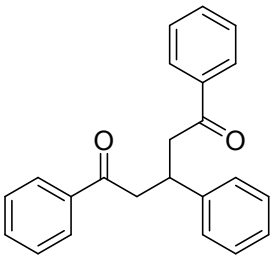


J = 1.2, 3H, CH_3), 2.12 (d, J = 1.2, 3H, CH_3), 2.64-2.72 (m, 2H, CH_2), 2.83-2.91 (m, 2H, CH_2), 6.02-6.04 (m, 1H, CH), 7.11-7.16 (m, 3H, 3CH), 7.21-7.26 (m, 2H, 2CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7 (CH_3), 27.6 (CH_3), 30.1 (CH_2), 45.7 (CH_2), 123.7 (CH), 125.9 (CH), 128.3 (2CH), 128.4 (2CH), 141.4 (C), 155.3 (C), 200.0 (CO);



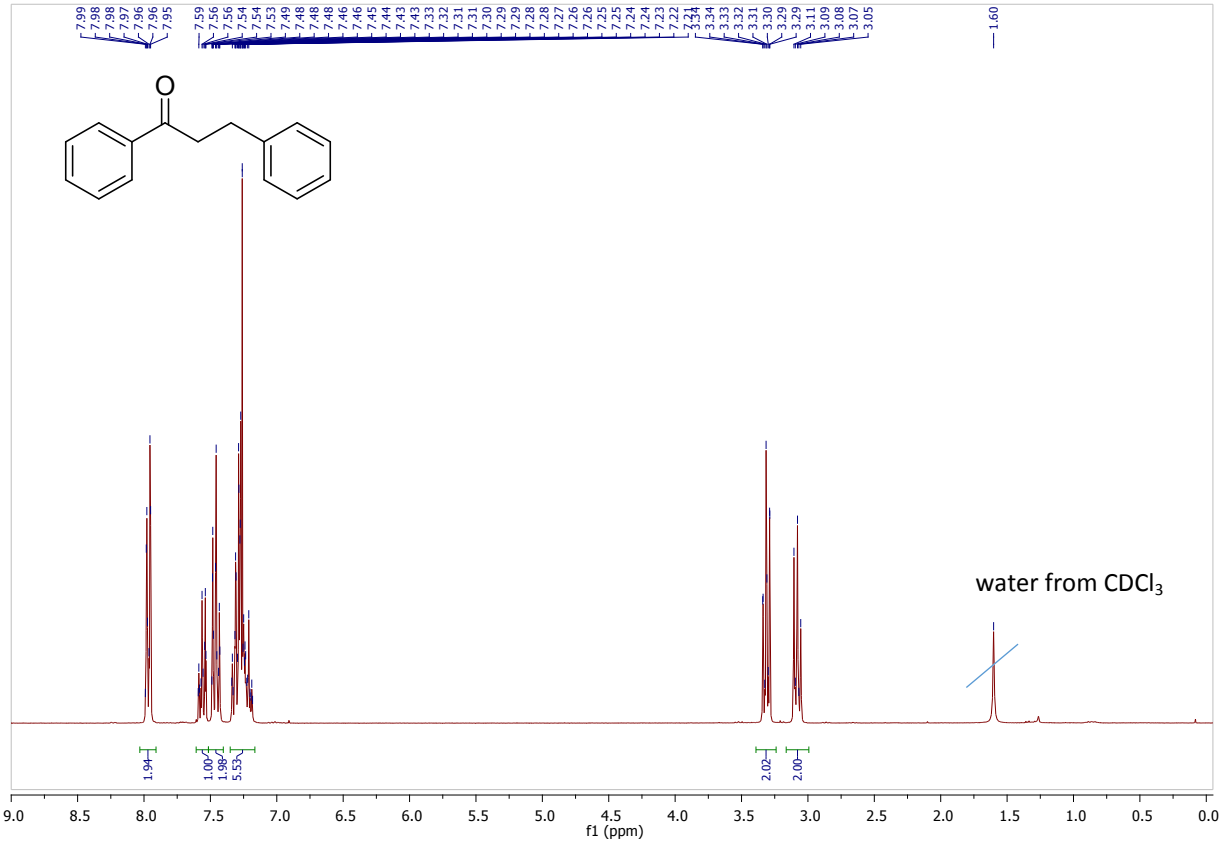
5-methyl-1-phenylhexan-3-one (**3aa”**): 440 mg (calculated), 24%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (d, ^{3}J = 6.6, 6H, $2CH_3$), 2.06-2.16 (m, 1H, CH), 2.22 (d, ^{3}J = 6.9, 2H, CH_2), 2.64-2.72 (m, 2H, CH_2), 2.83-2.91 (m, 2H, CH_2), 7.11-7.16 (m, 3H, 3CH), 7.21-7.26 (m, 2H, 2CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.6 ($2CH_3$), 24.6 (CH), 29.7 (CH_2), 44.7 (CH_2), 52.0 (CH_2), 126.0 (CH), 128.3 (2CH), 128.4 (CH), 141.2 (C), 209.8 (CO);

1,3,5-triphenylpentane-1,5-dione (**4**): white solid, mp: 82°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.36 (dd, *J* = 16.7, 7.1, 2H), 3.51 (dd, *J* = 16.7, 7.0, 2H), 4.08 (p, *J* = 7.0, 2H), 7.16-7.21 (m, 1H), 7.25-7.31 (m, 4H), 7.42-7.47 (m, 4H), 7.52-7.58 (m, 2H), 7.94-7.98 (m, 4H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.2 (CH), 44.9 ($2CH_2$), 126.7 (CH), 127.5 (2CH), 128.2 (4CH), 128.6 (4CH), 128.7 (2CH), 133.1 (2CH), 136.9 (2C), 143.9 (C), 198.6 (2CO);

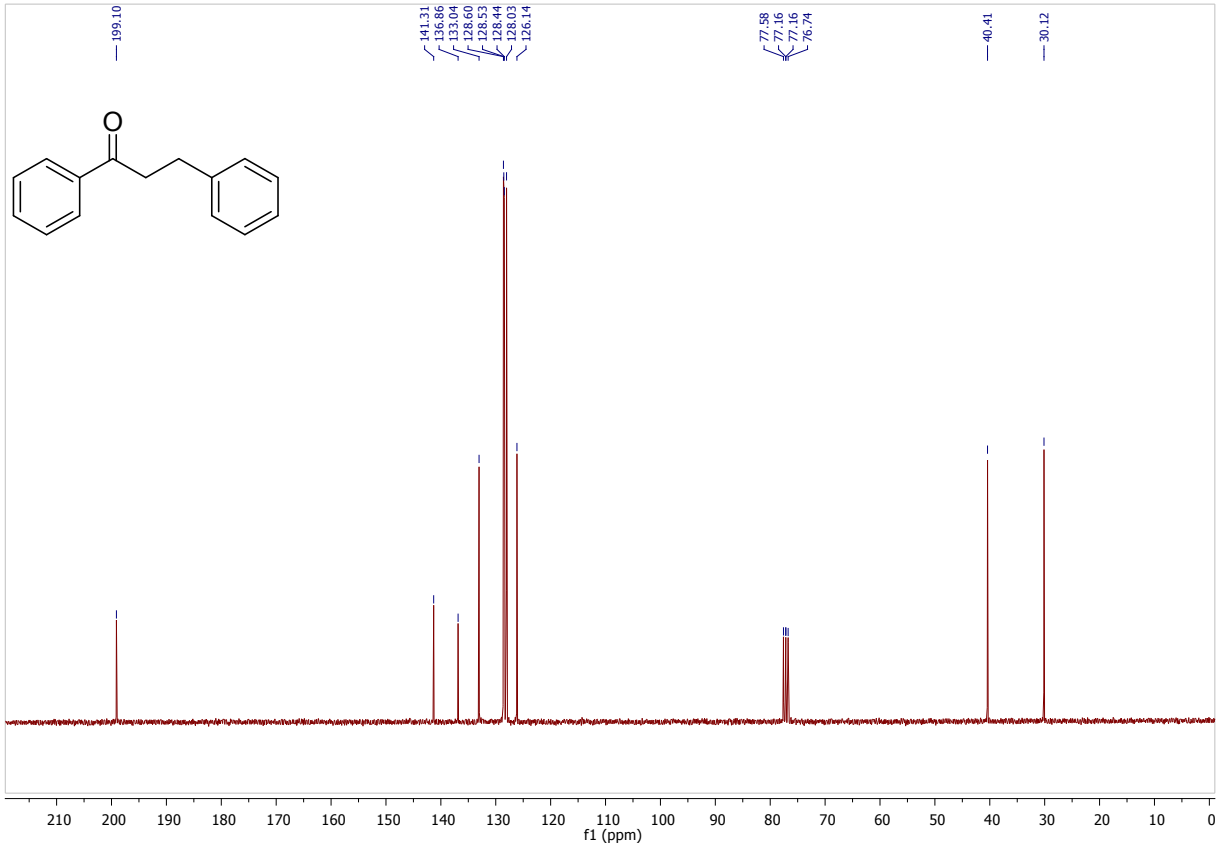


12. ^{1}H and ^{13}C NMR Spectra

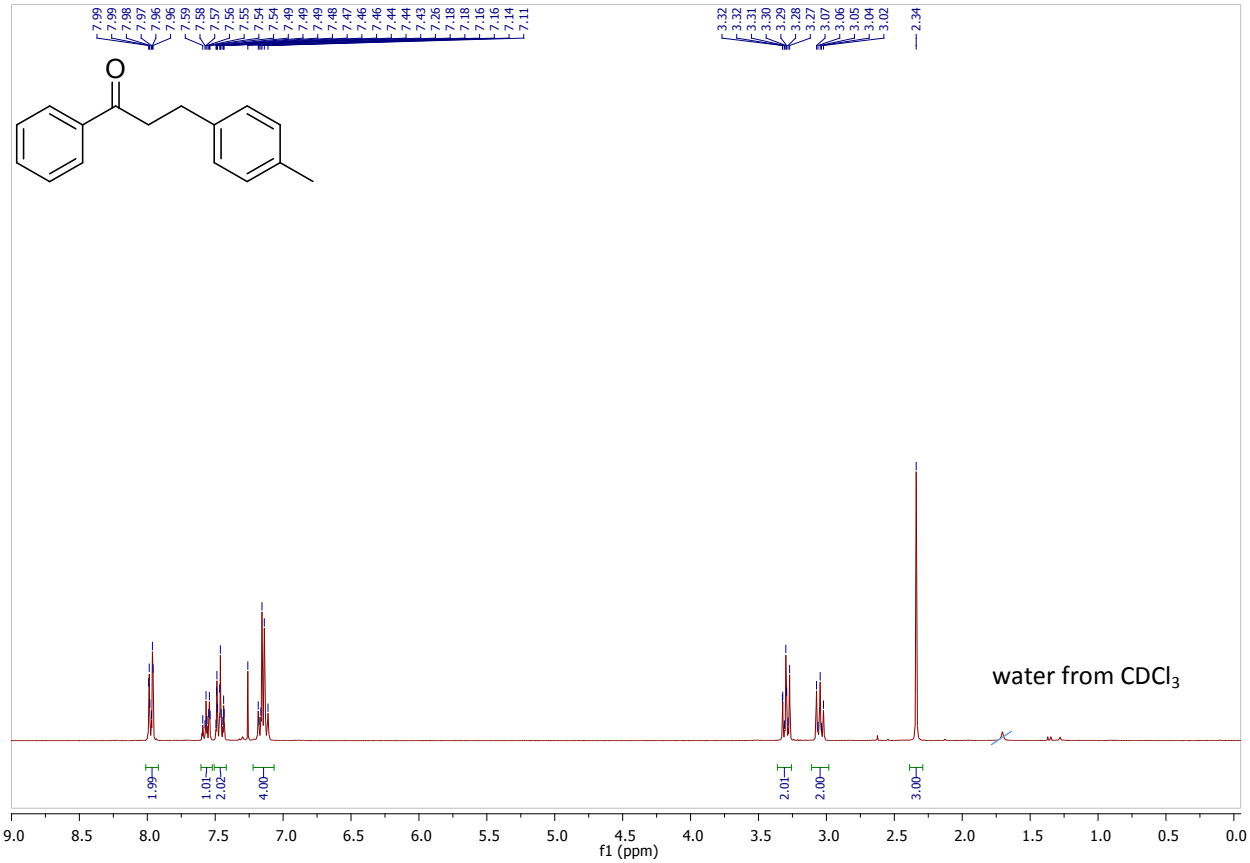
1,3-diphenylpropan-1-one (**3a**) ^{1}H NMR (300 MHz, $CDCl_3$)



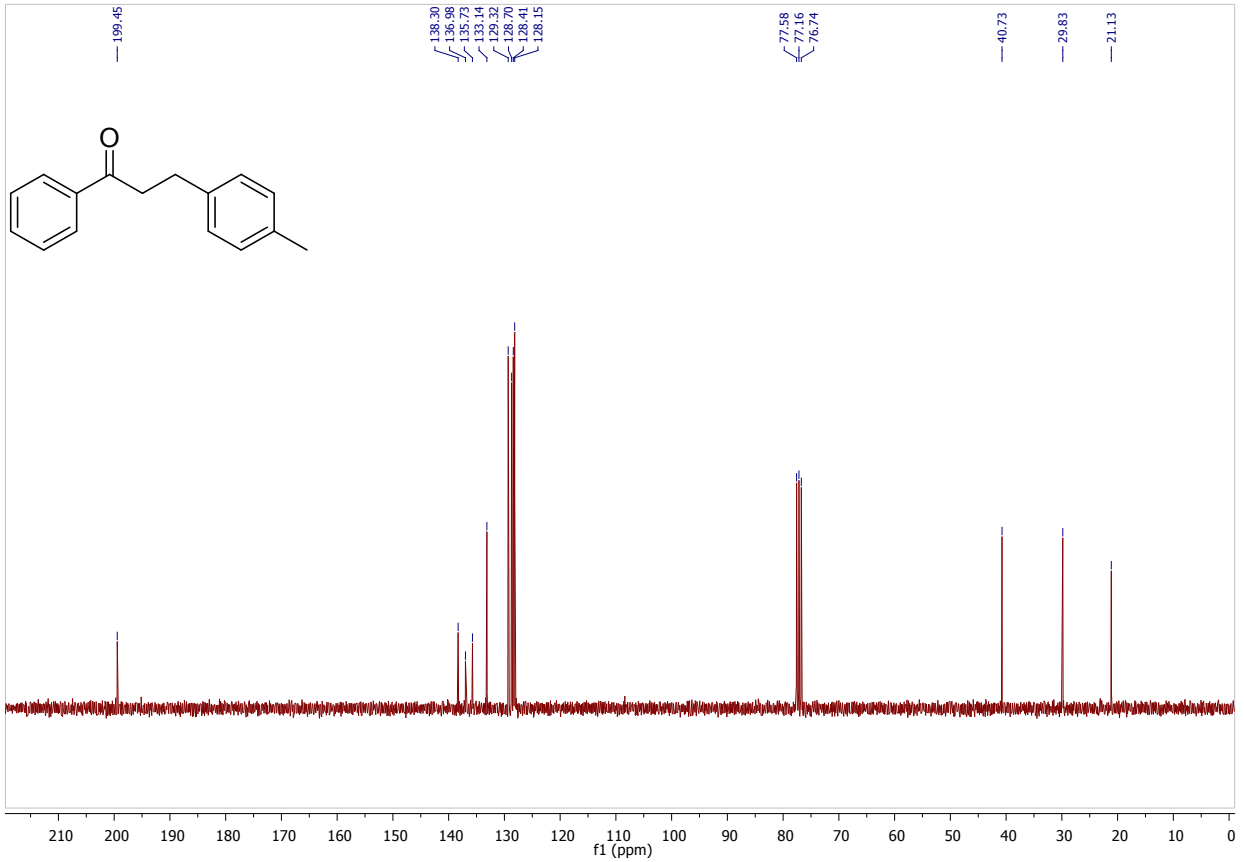
1,3-diphenylpropan-1-one (**3a**) ^{13}C NMR (75 MHz, $CDCl_3$)



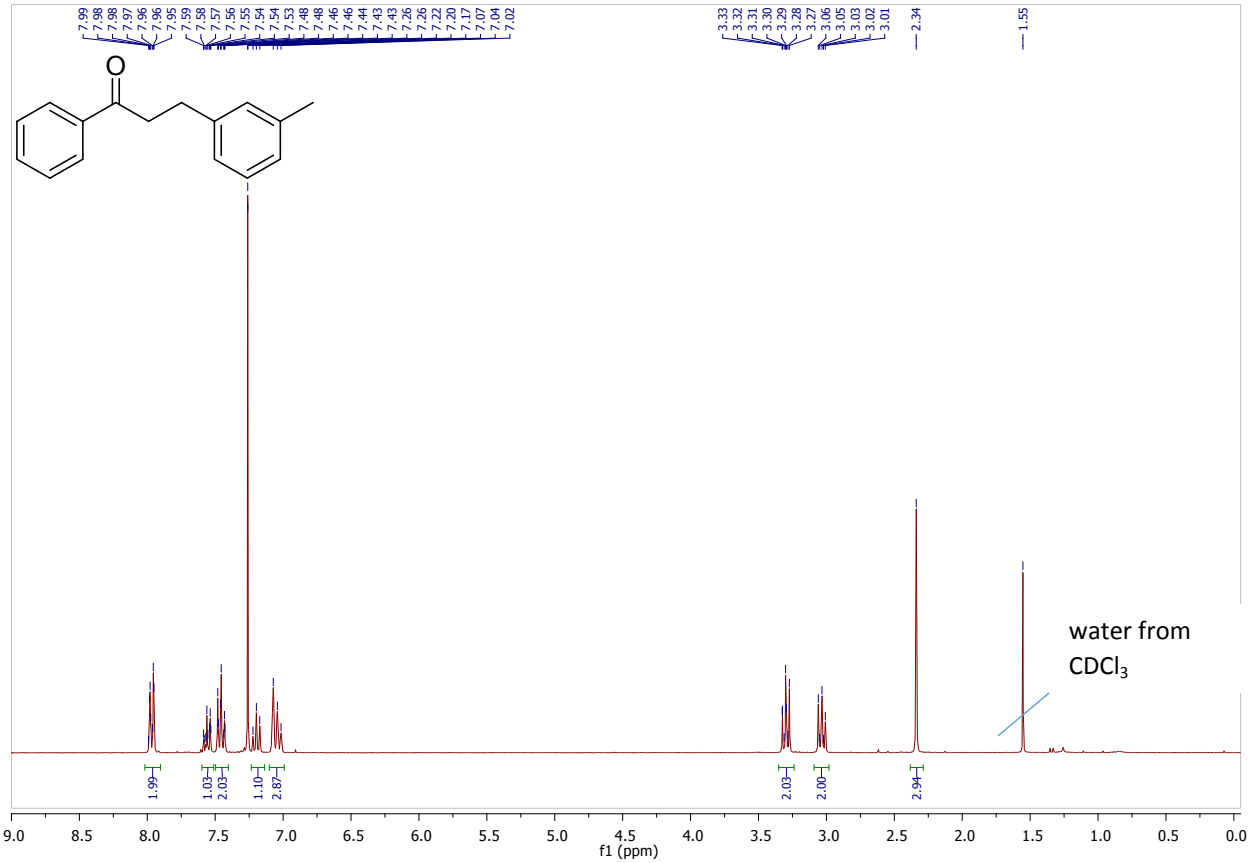
1-phenyl-3-(p-tolyl)propan-1-one (**3b**) ^{1}H NMR (300 MHz, $CDCl_3$)



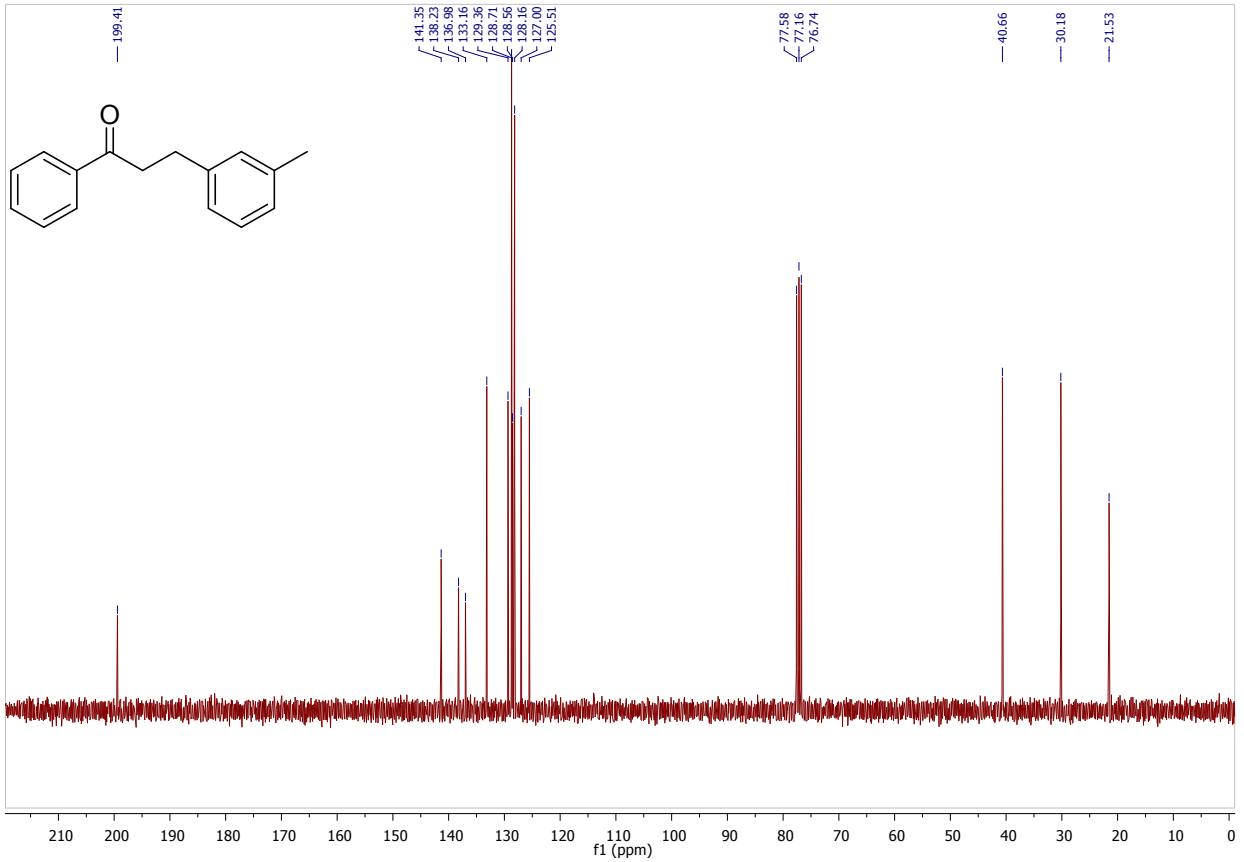
1-phenyl-3-(p-tolyl)propan-1-one (**3b**) ^{13}C NMR (75 MHz, $CDCl_3$)



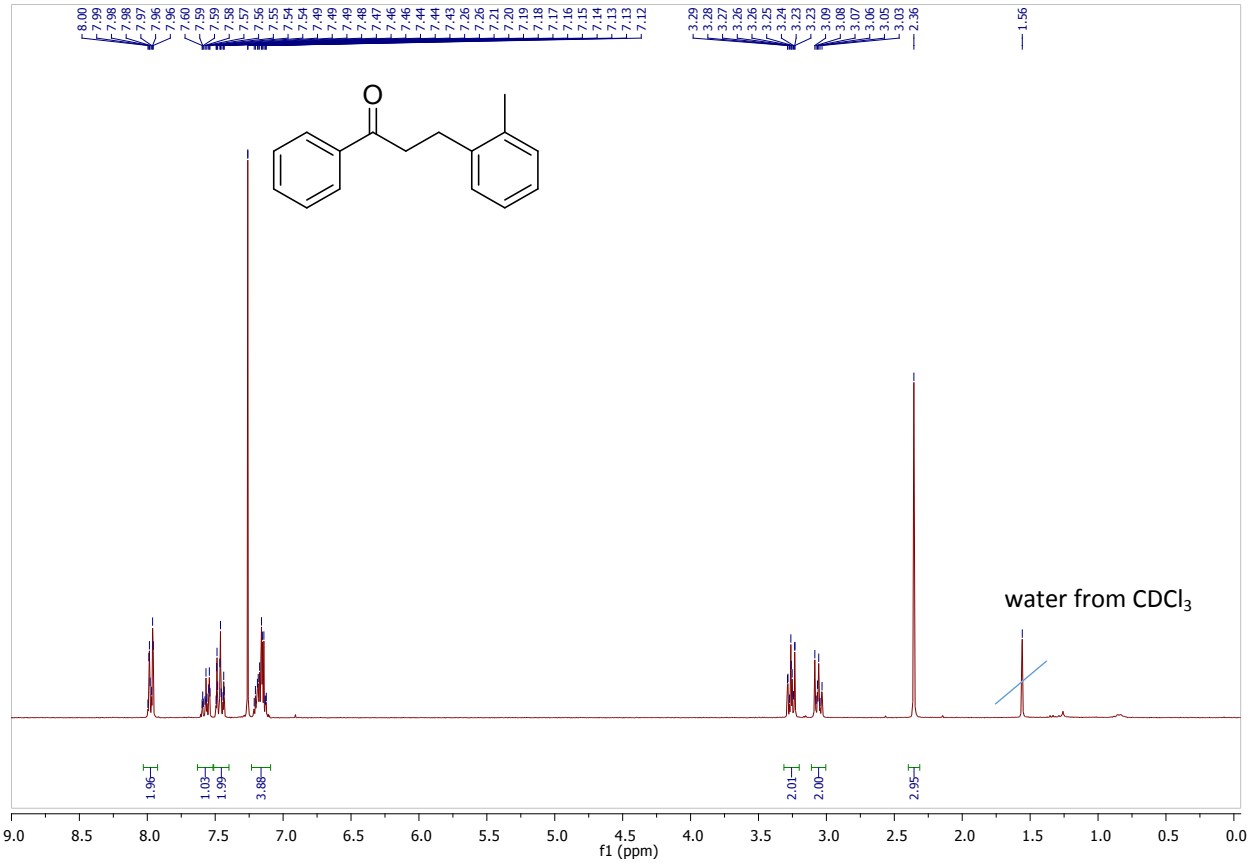
1-phenyl-3-(m-tolyl)propan-1-one (**3c**) ^{1}H NMR (300 MHz, $CDCl_3$)



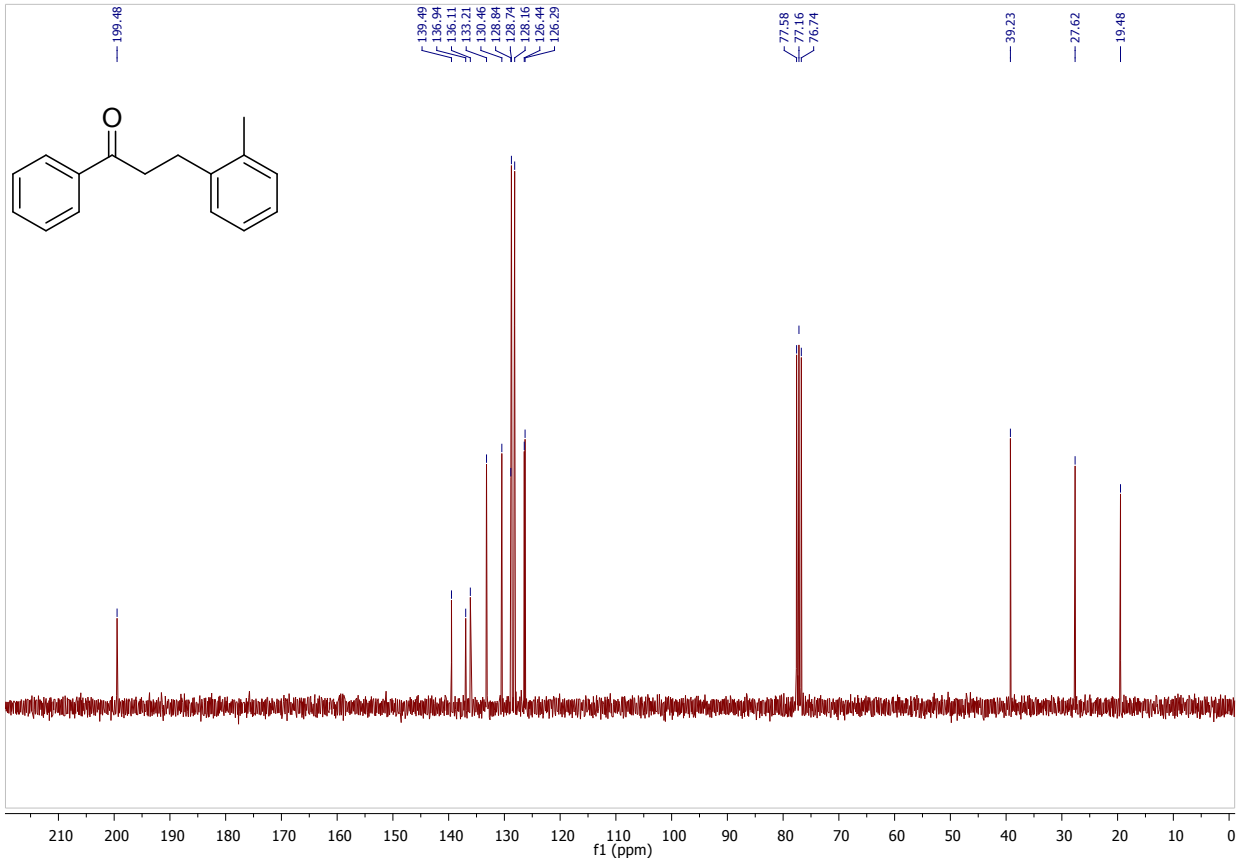
1-phenyl-3-(m-tolyl)propan-1-one (**3c**) ^{13}C NMR (75 MHz, $CDCl_3$)



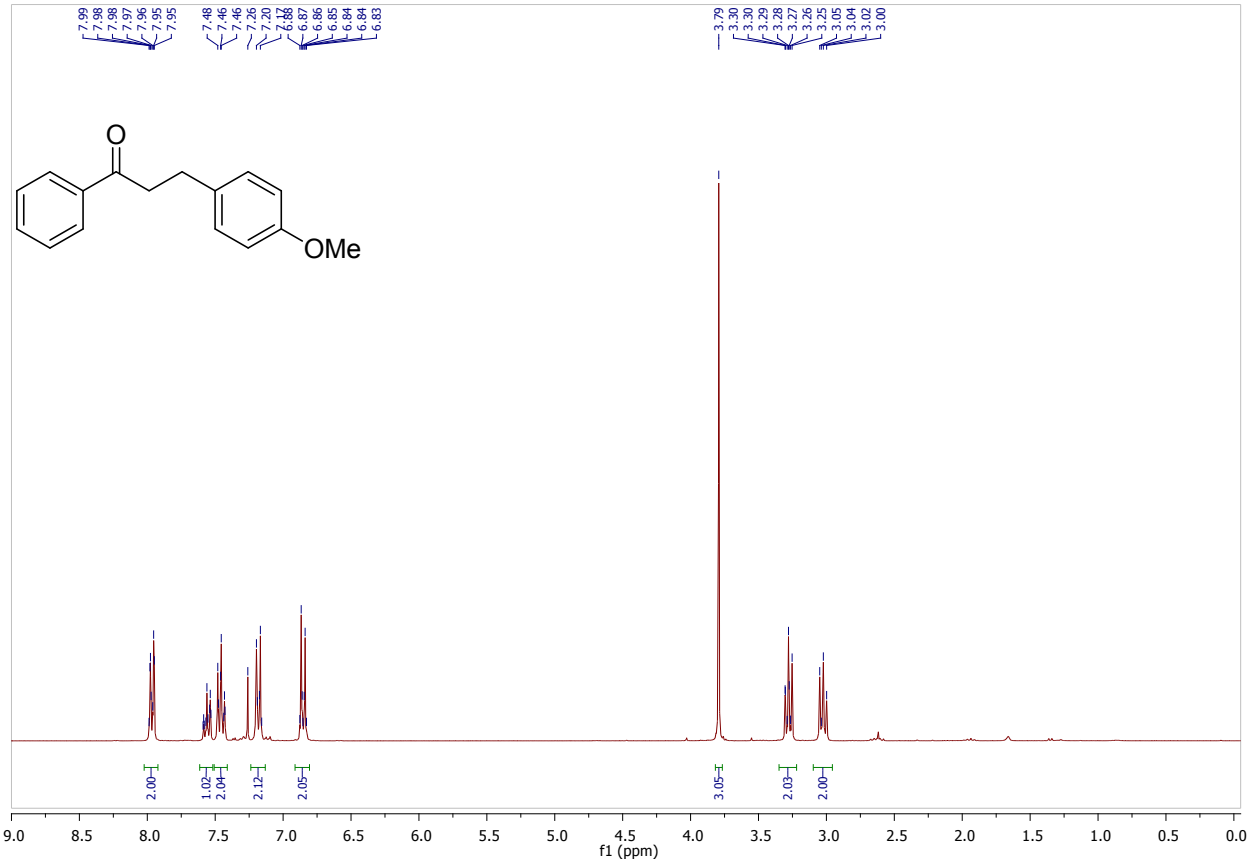
1-phenyl-3-(o-tolyl)propan-1-one (**3d**) ^{1}H NMR (300 MHz, $CDCl_3$)



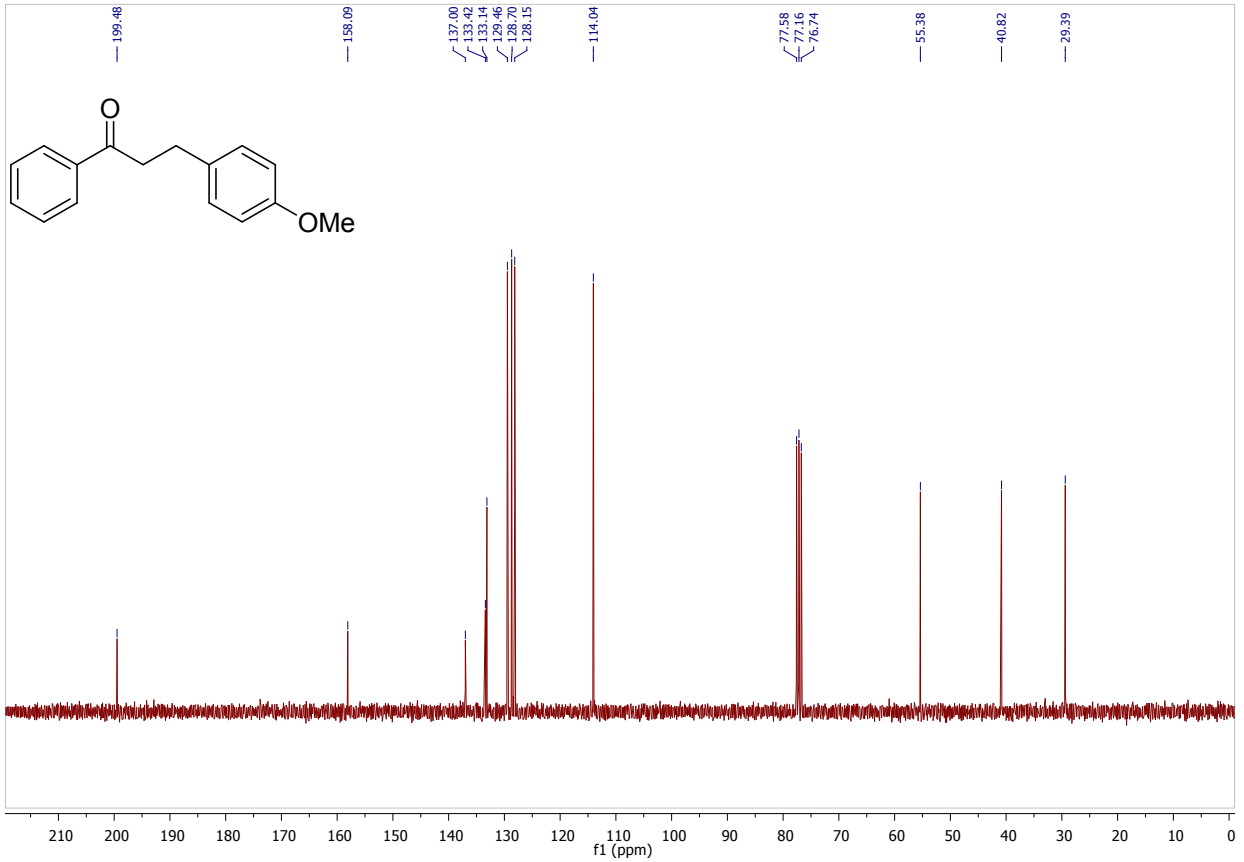
1-phenyl-3-(o-tolyl)propan-1-one (**3d**) ^{13}C NMR (75 MHz, $CDCl_3$)



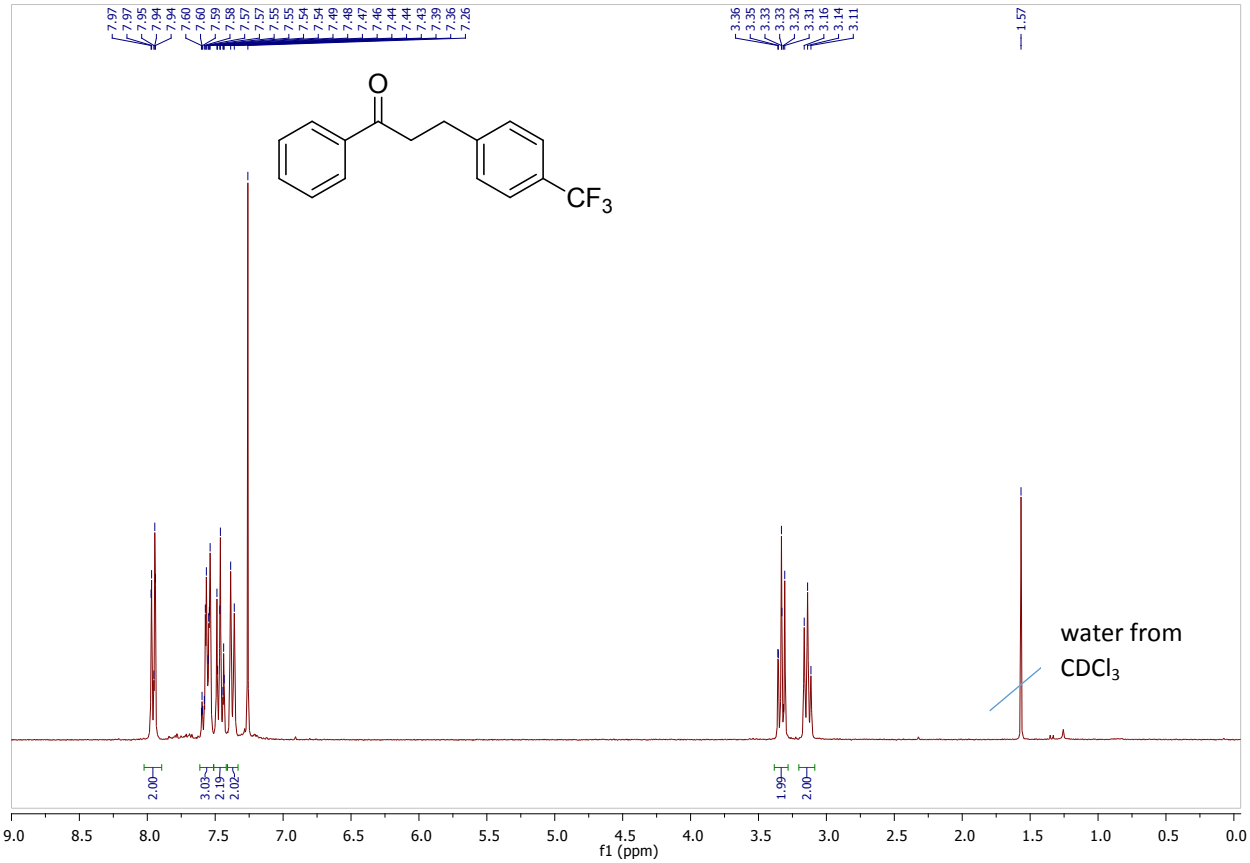
3-(4-methoxyphenyl)-1-phenylpropan-1-one (**3e**) ^{1}H NMR (300 MHz, $CDCl_3$)



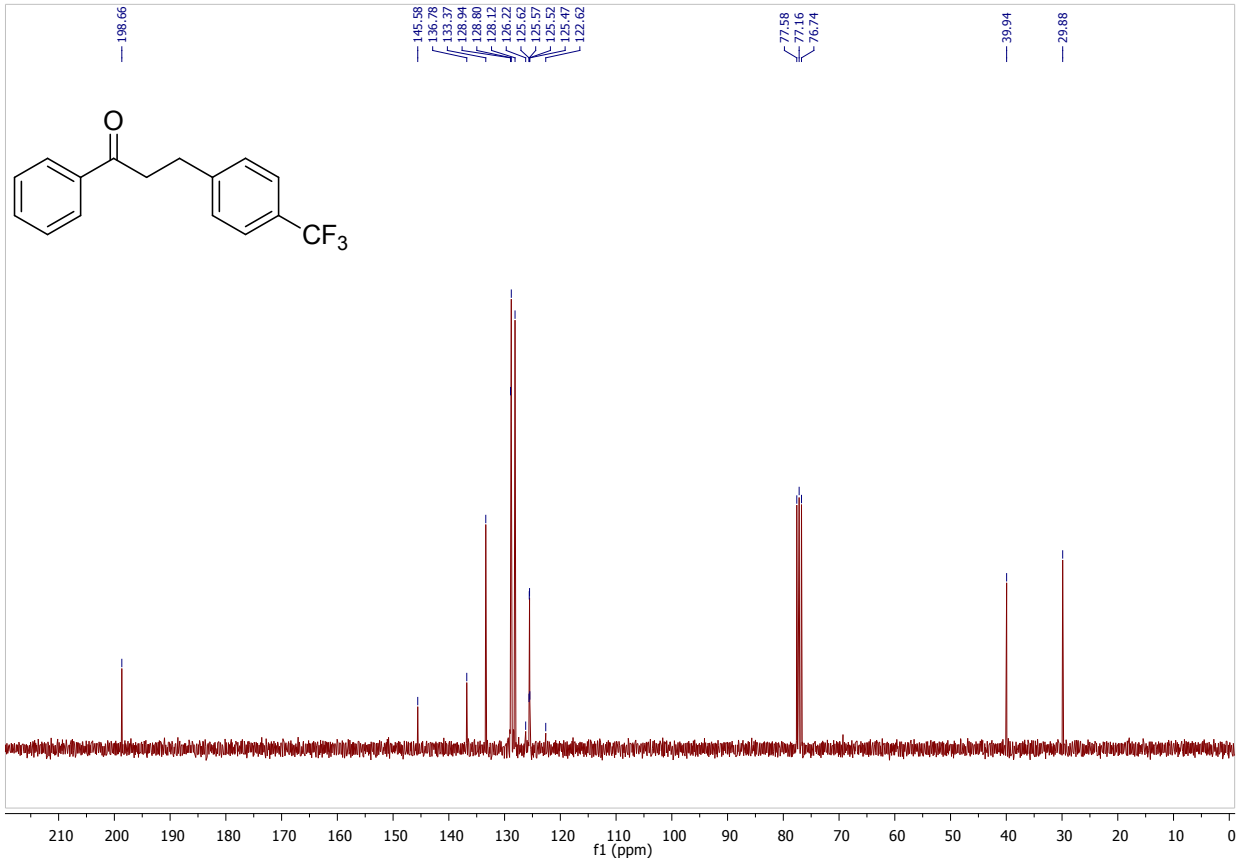
3-(4-methoxyphenyl)-1-phenylpropan-1-one (**3e**) ^{13}C NMR (75 MHz, $CDCl_3$)



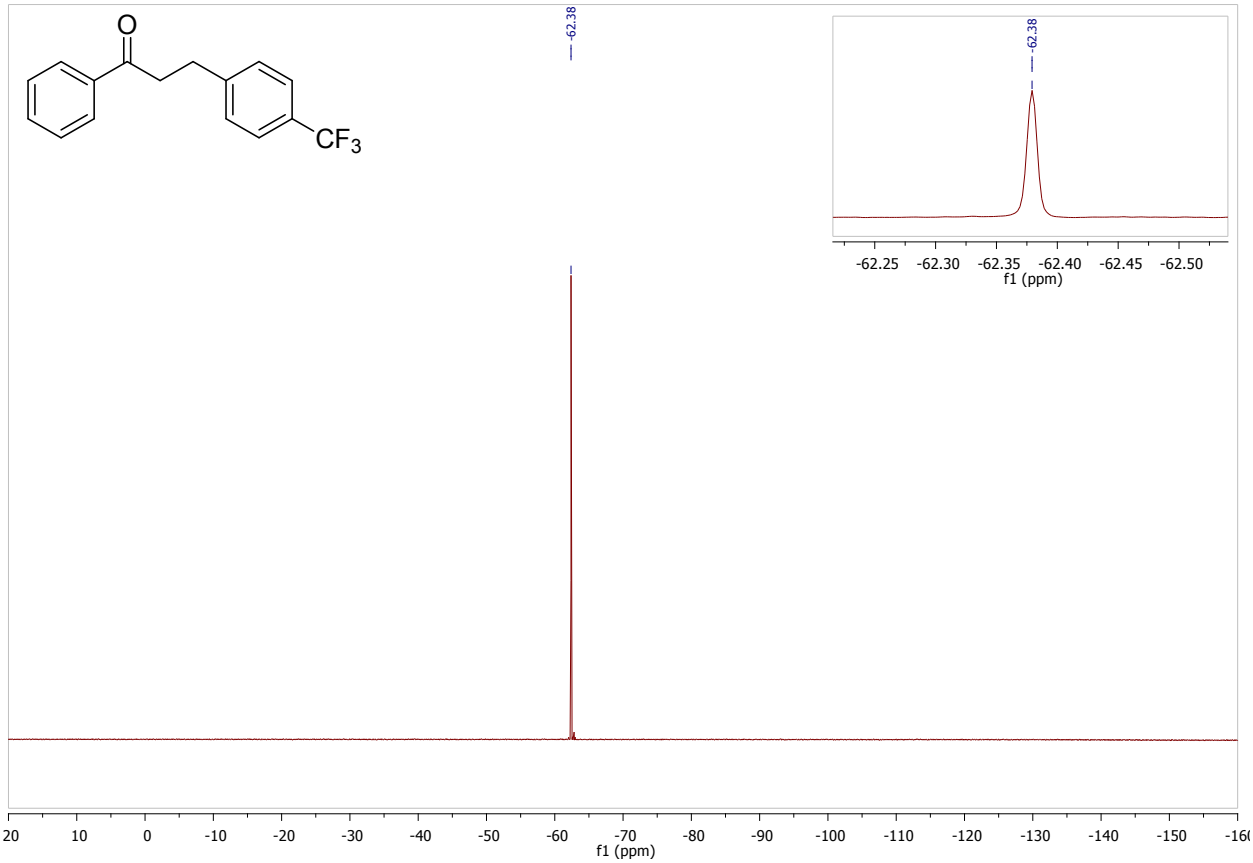
1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**3f**) ^{1}H NMR (300 MHz, $CDCl_3$)



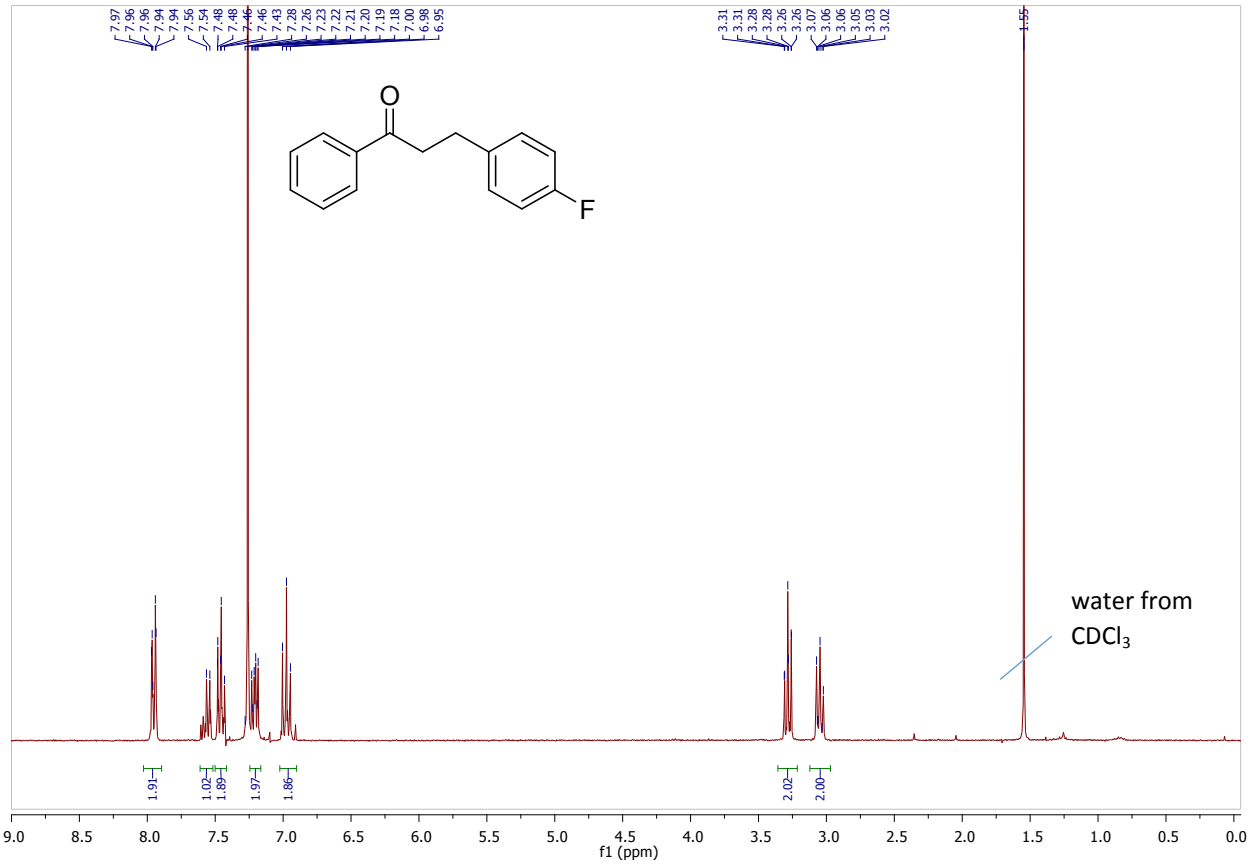
1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**3f**) ^{13}C NMR (75 MHz, $CDCl_3$)



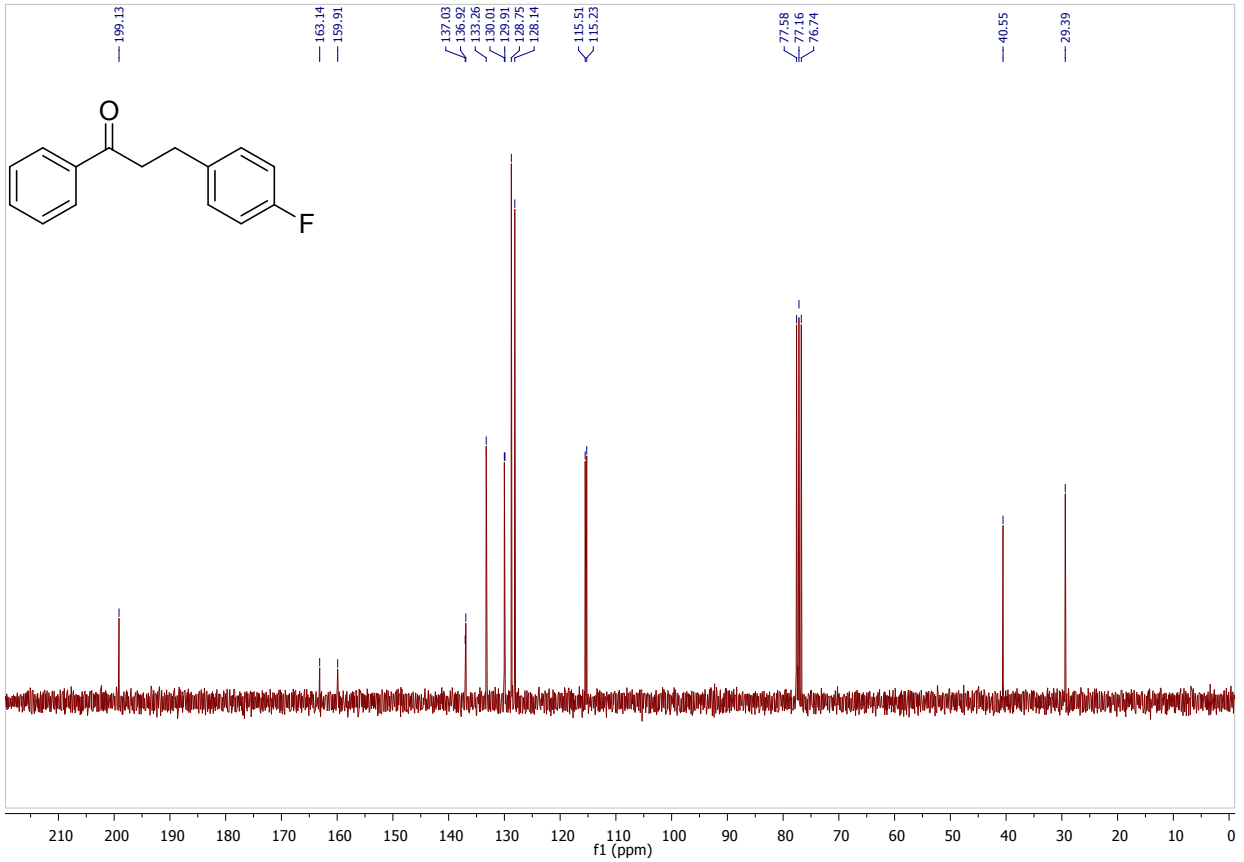
1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**3f**) ^{19}F NMR (282 MHz, $CDCl_3$)



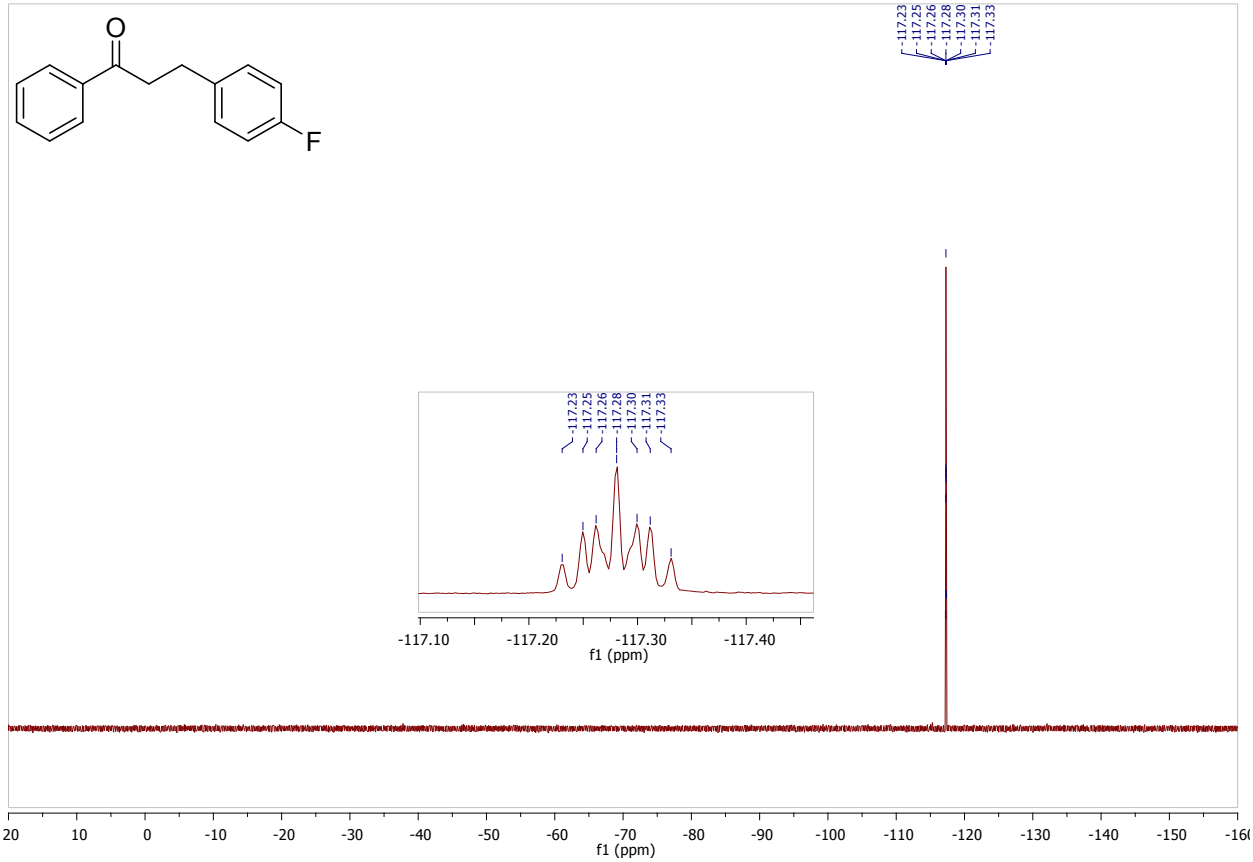
3-(4-fluorophenyl)-1-phenylpropan-1-one (**3g**) ^{1}H NMR (300 MHz, $CDCl_3$)



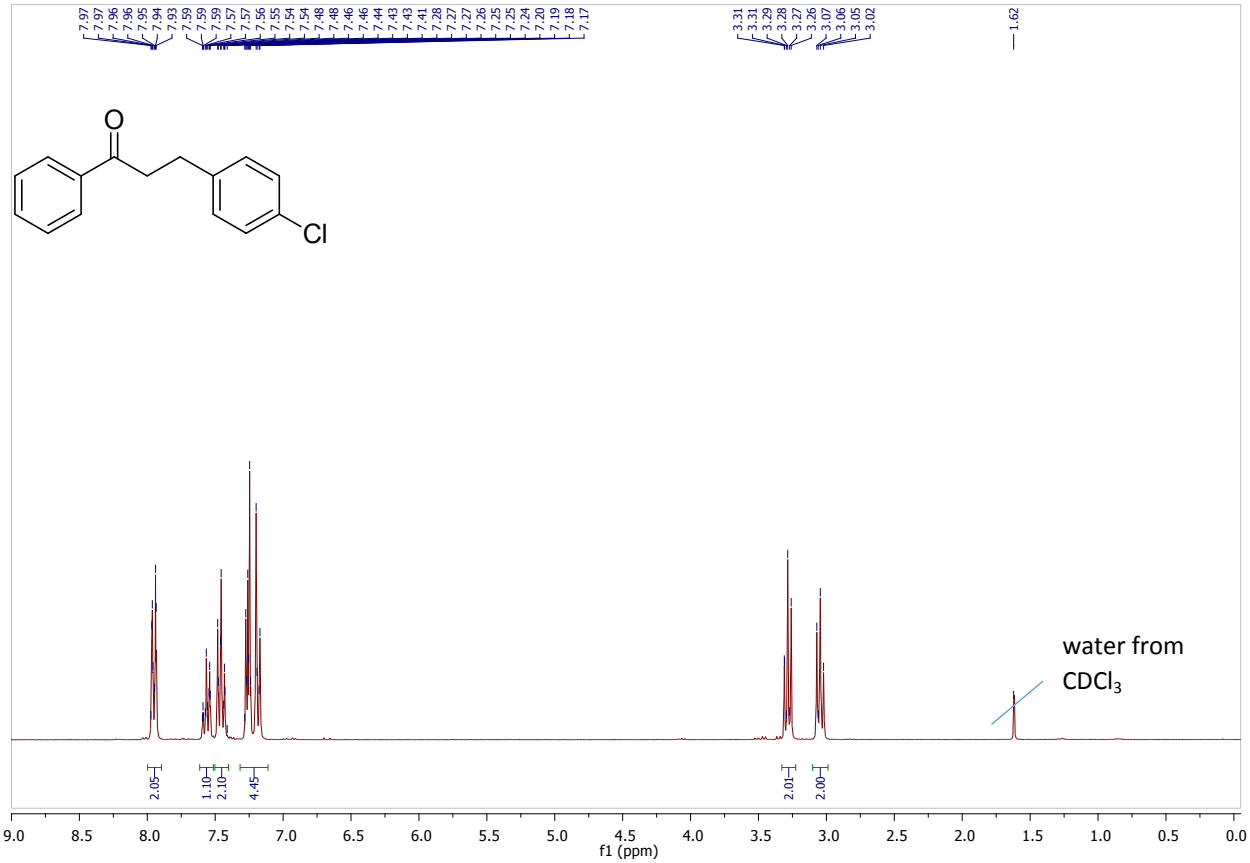
3-(4-fluorophenyl)-1-phenylpropan-1-one (**3g**) ^{13}C NMR (75 MHz, $CDCl_3$)



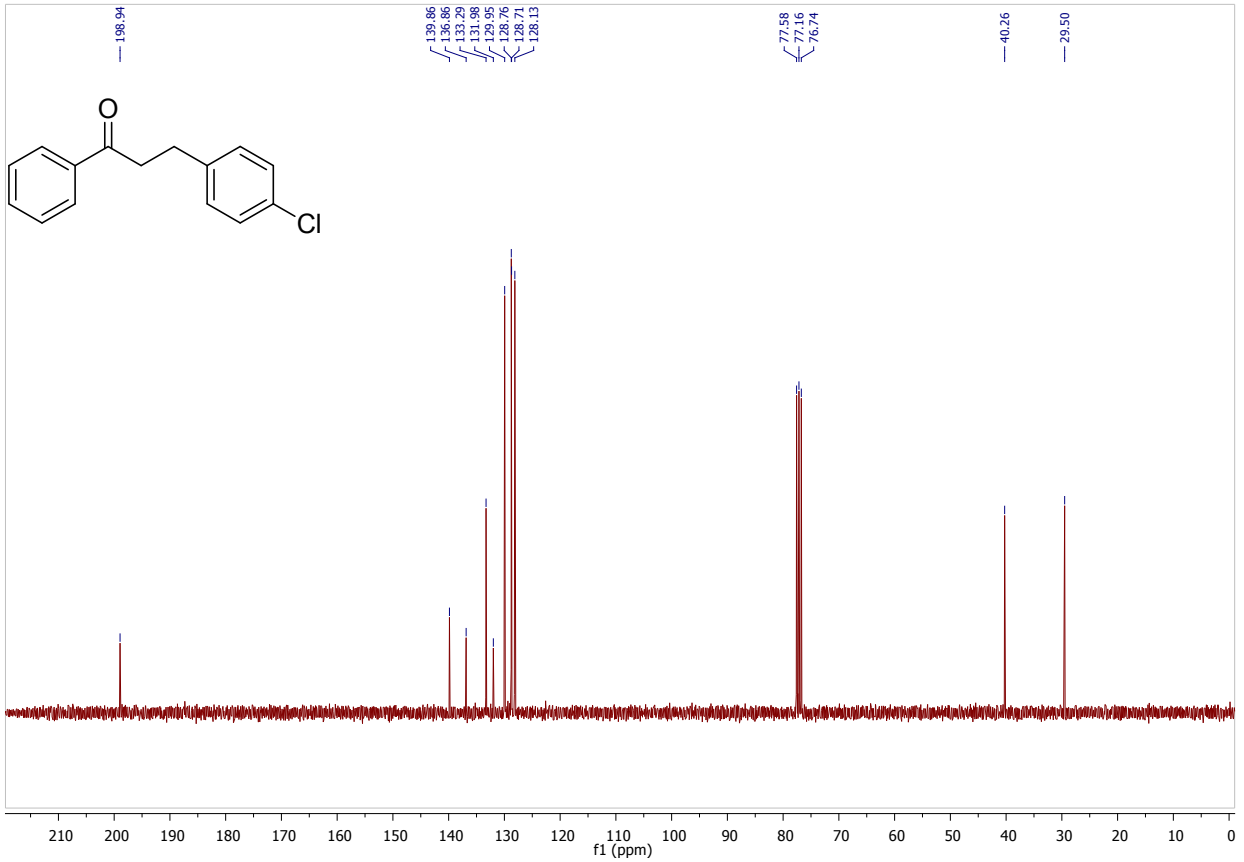
3-(4-fluorophenyl)-1-phenylpropan-1-one (**3g**) ^{19}C NMR (282 MHz, $CDCl_3$)



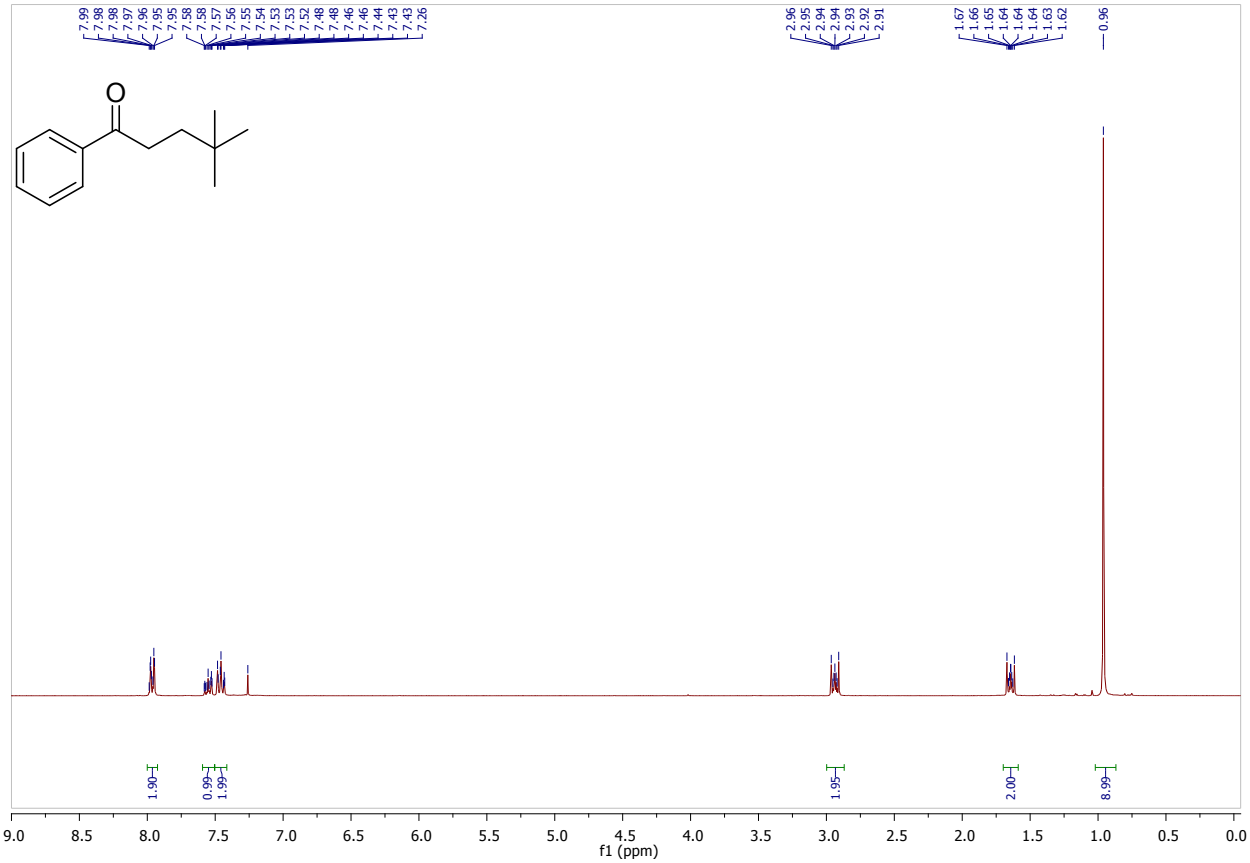
3-(4-chlorophenyl)-1-phenylpropan-1-one (**3h**) ^{1}H NMR (300 MHz, $CDCl_3$)



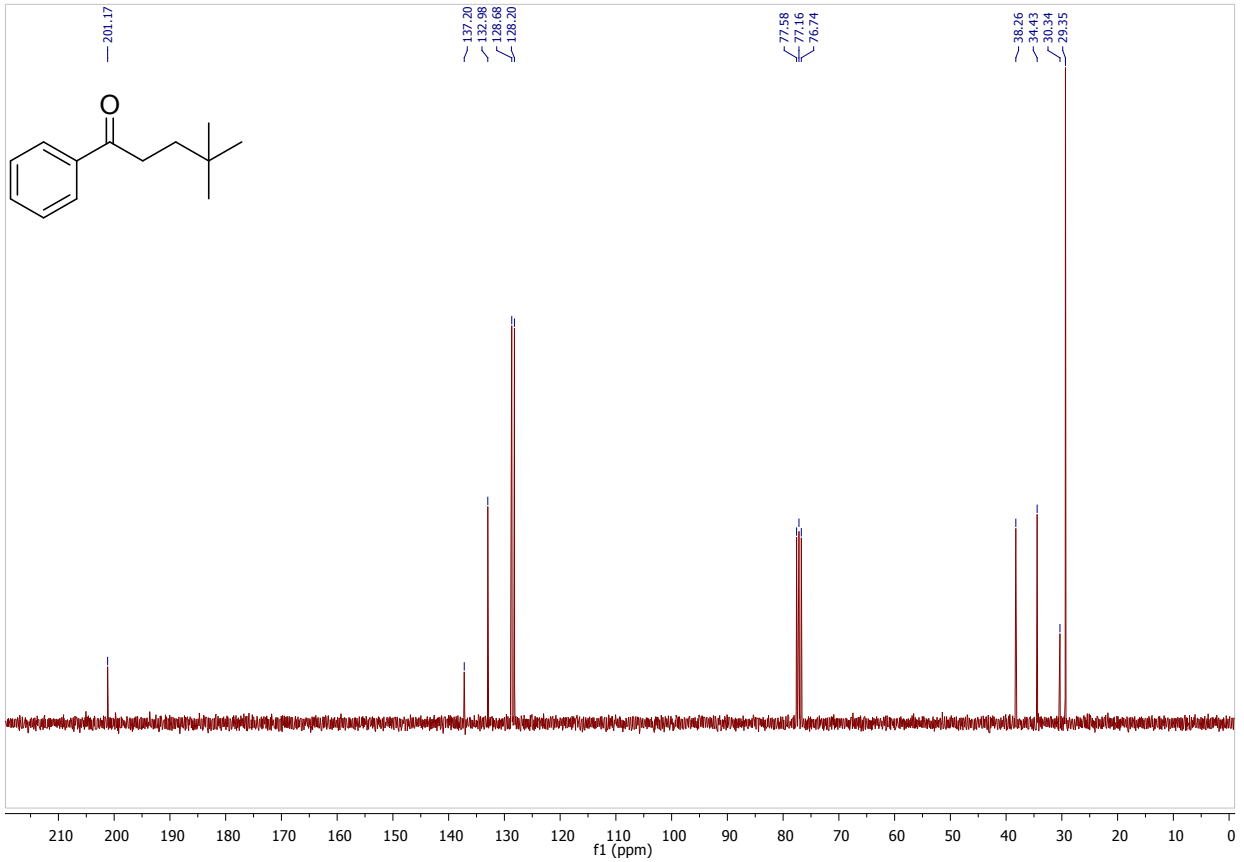
3-(4-chlorophenyl)-1-phenylpropan-1-one (**3h**) ^{13}C NMR (75 MHz, $CDCl_3$)



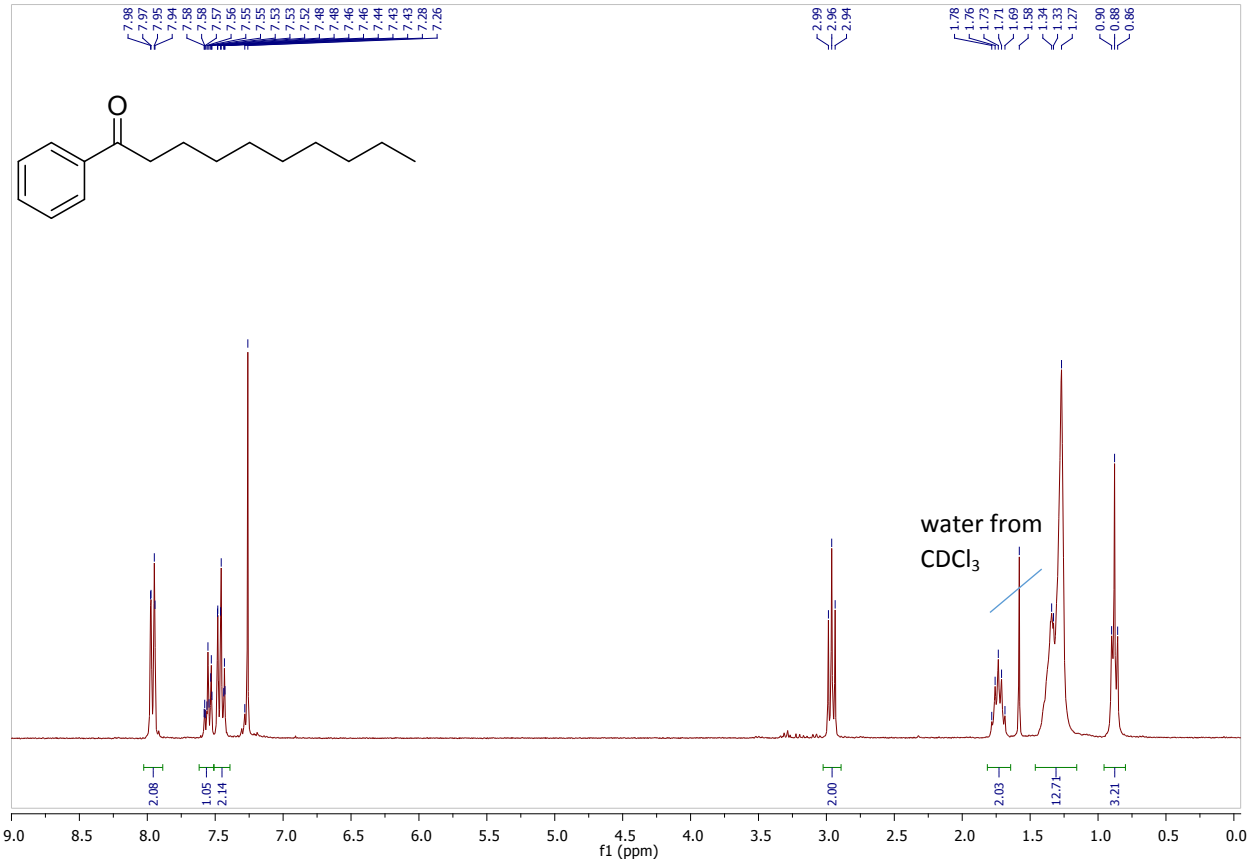
4,4-dimethyl-1-phenylpentan-1-one (**3i**) ^{1}H NMR (300 MHz, $CDCl_3$)



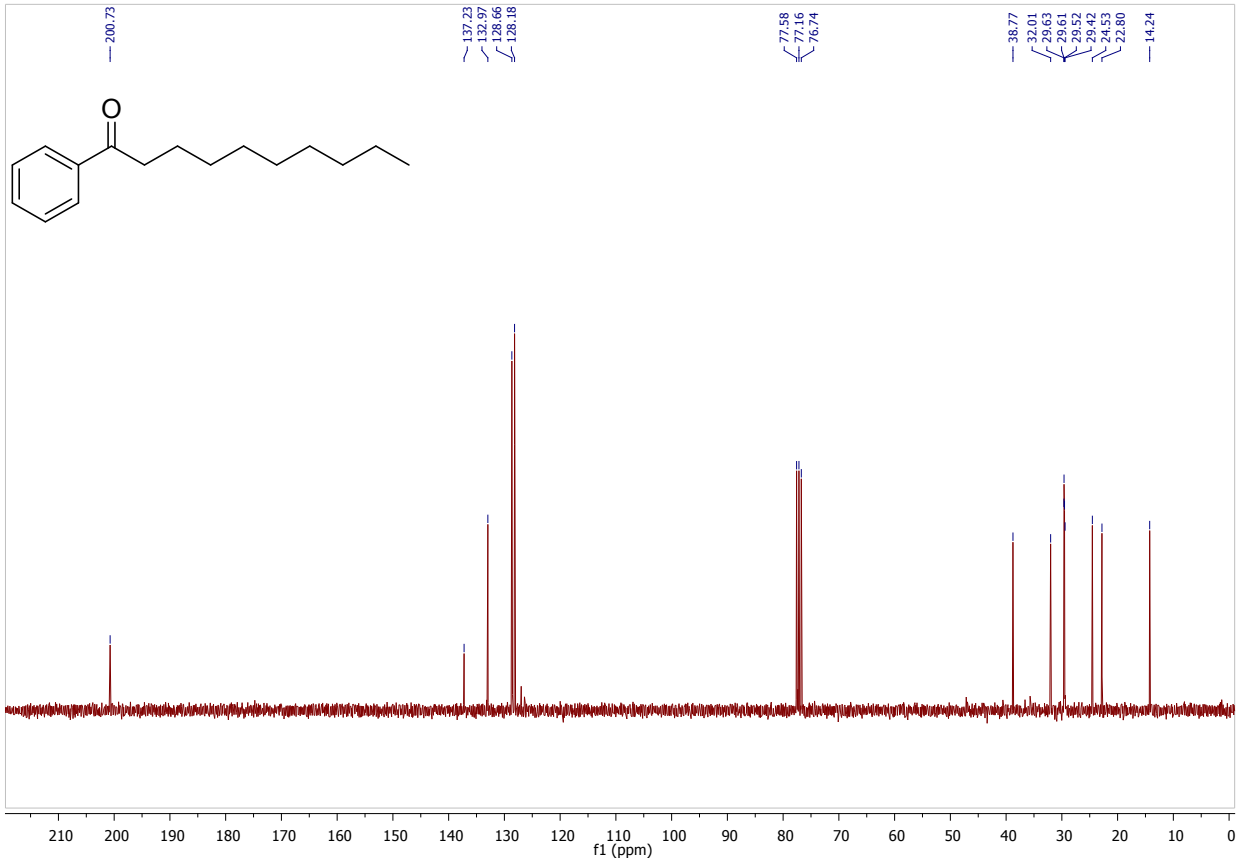
4,4-dimethyl-1-phenylpentan-1-one (**3i**) ^{13}C NMR (75 MHz, $CDCl_3$)



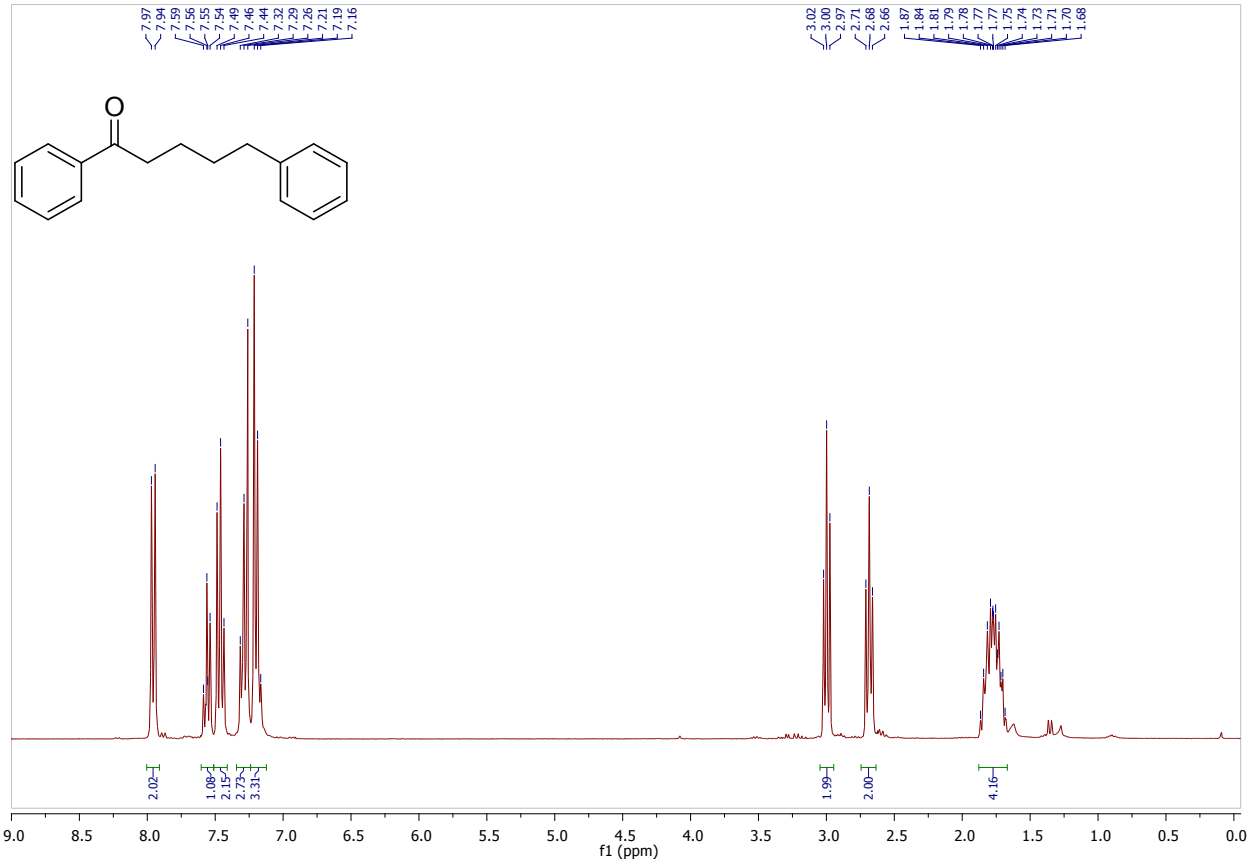
1-phenyldecan-1-one (**3j**) ^{1}H NMR (300 MHz, $CDCl_3$)



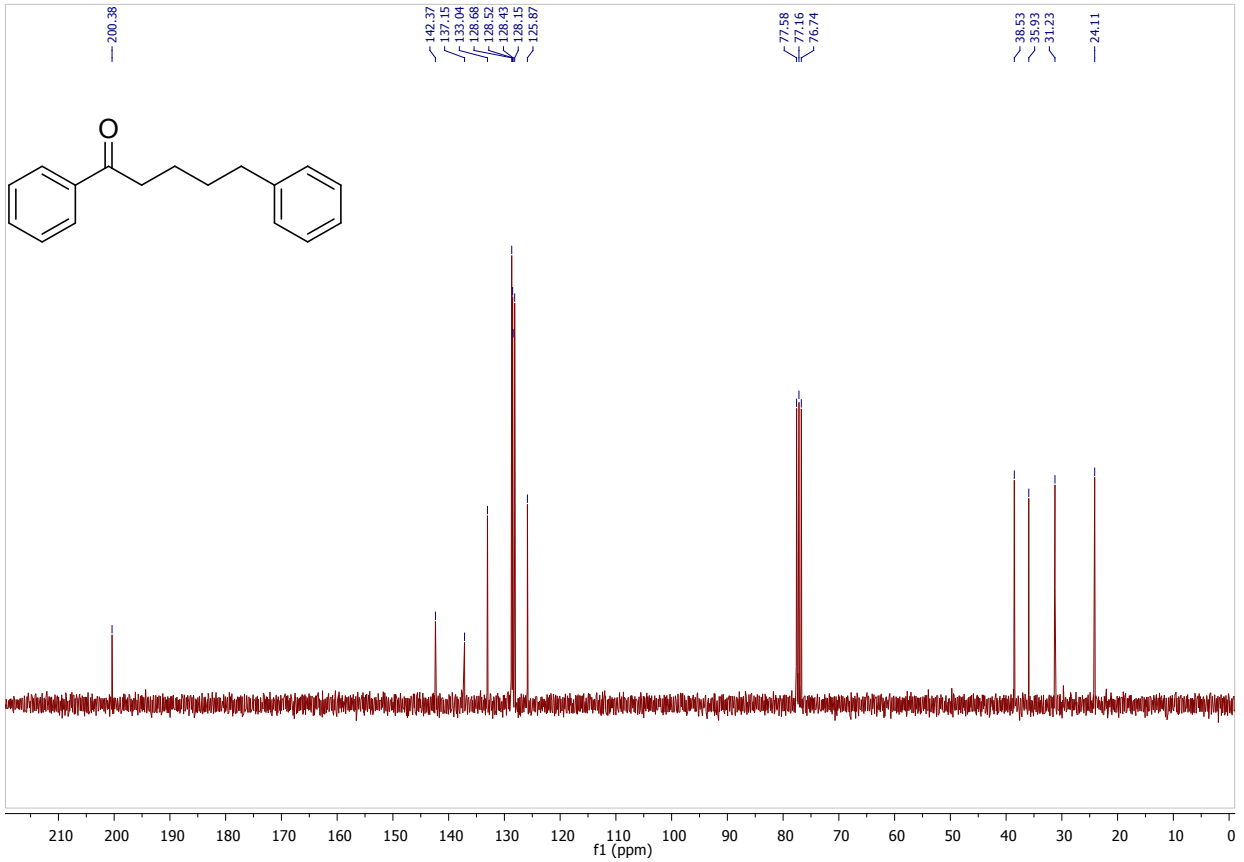
1-phenyldecan-1-one (**3j**) ^{13}C NMR (75 MHz, $CDCl_3$)



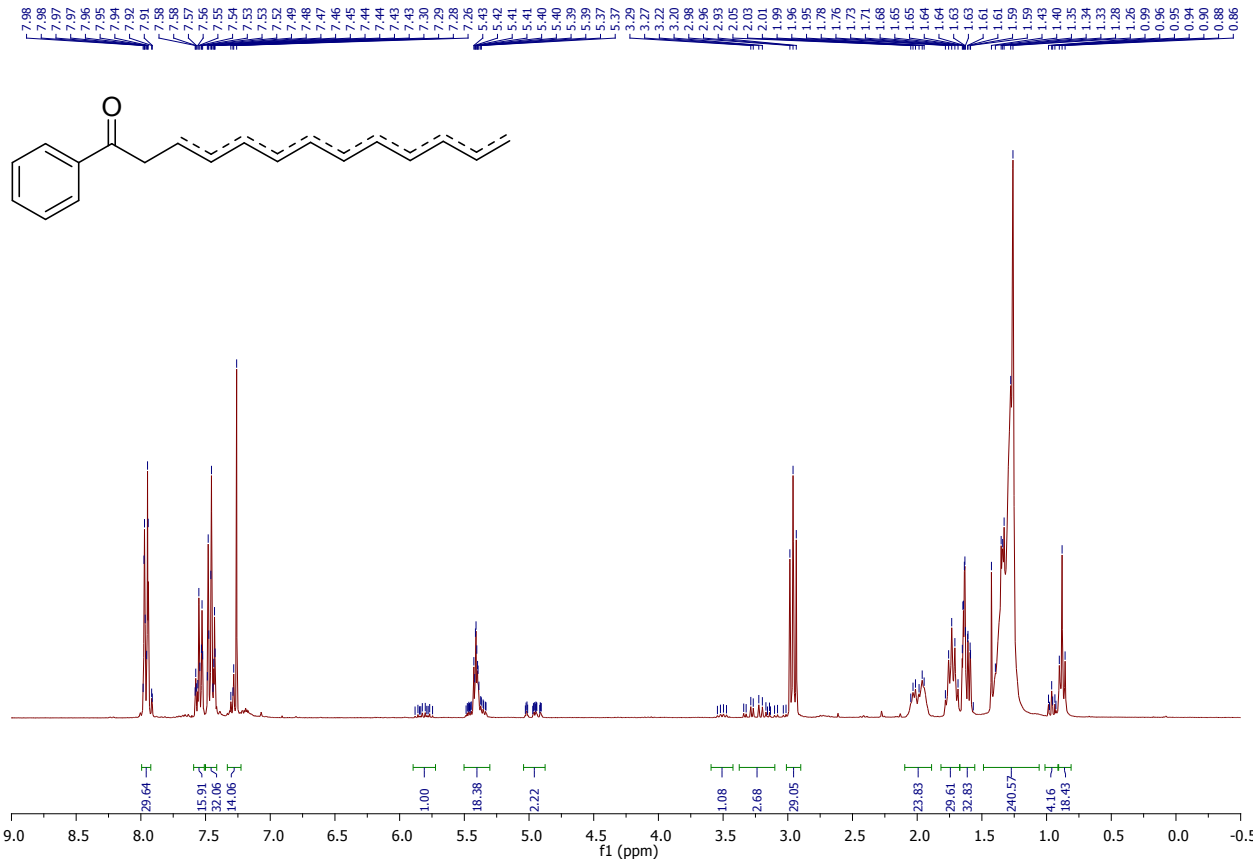
1,5-diphenylpentan-1-one (**3k**) ^{1}H NMR (300 MHz, $CDCl_3$)



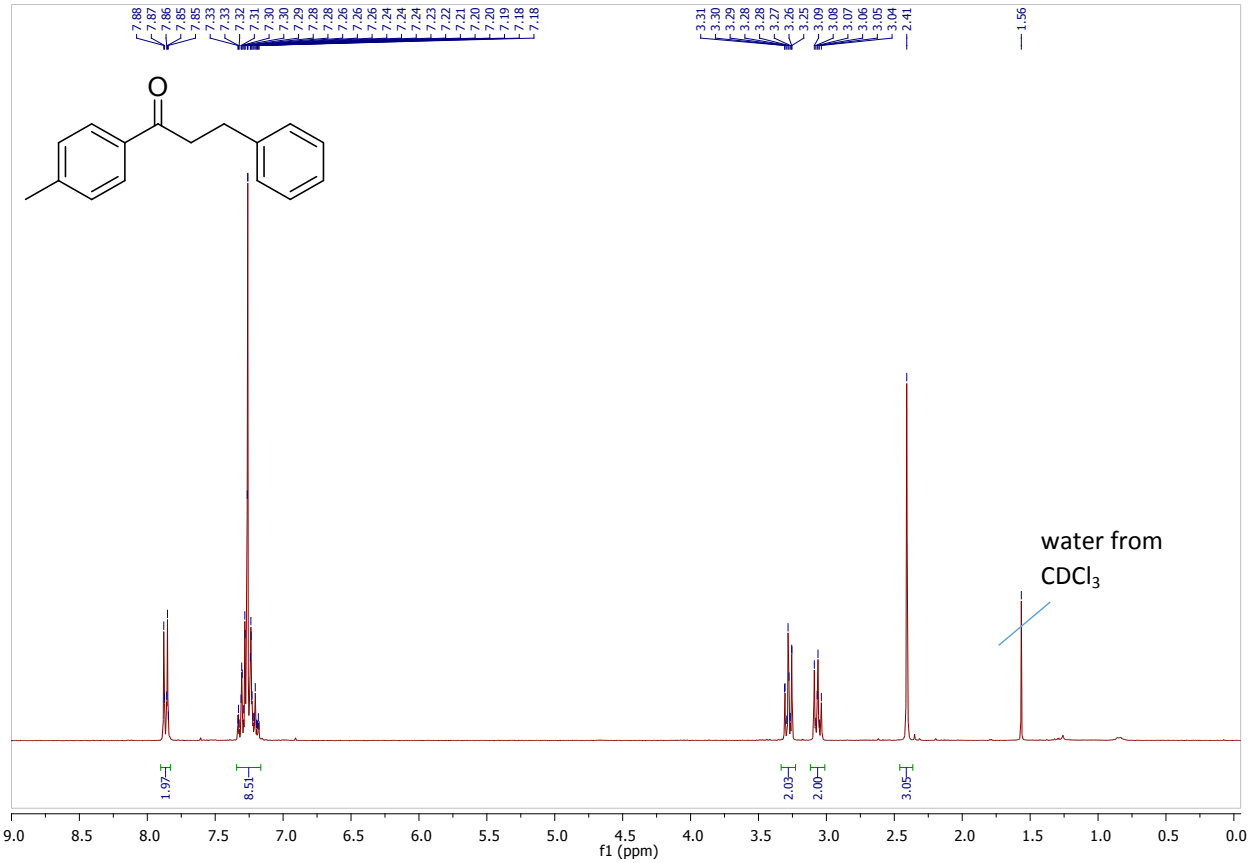
1,5-diphenylpentan-1-one (**3k**) ^{13}C NMR (75 MHz, $CDCl_3$)



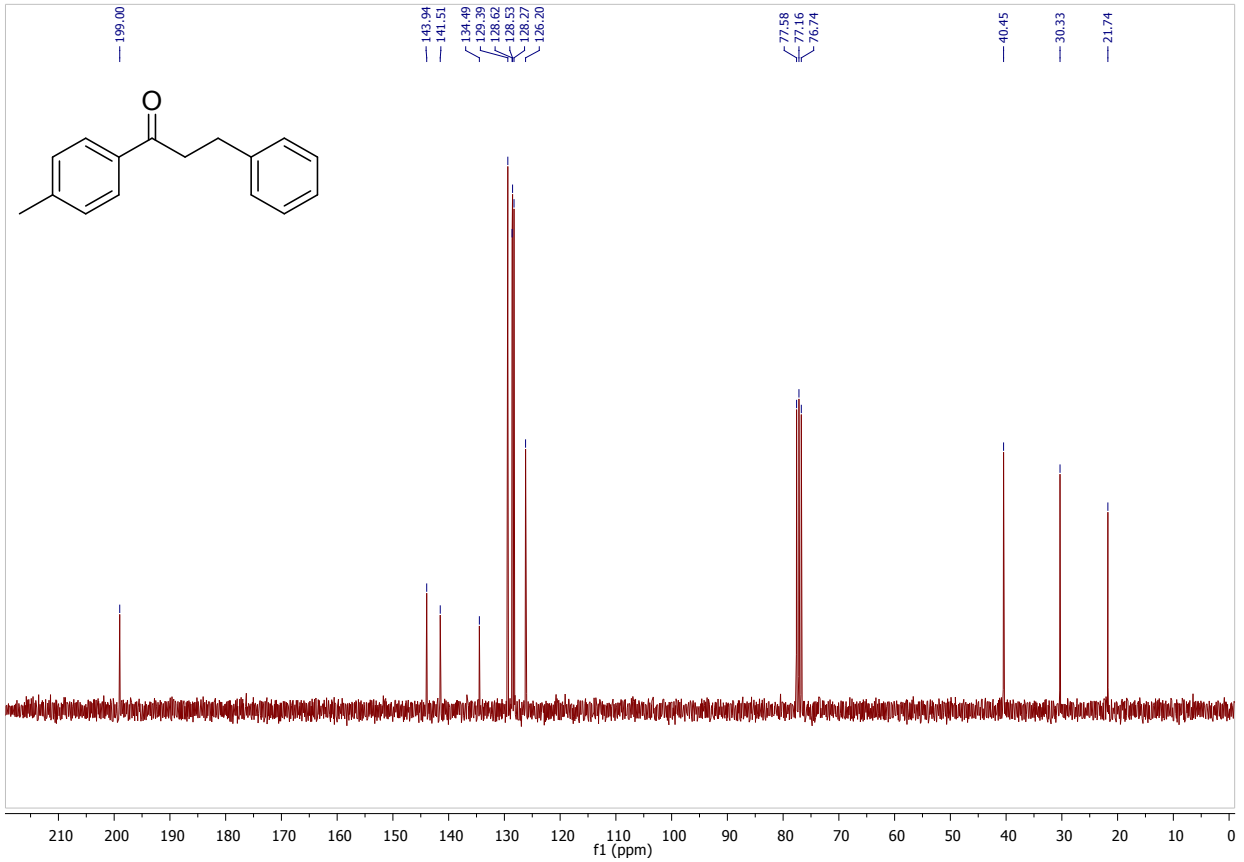
1-phenyltridec-12-en-1-one (**3m'**), (*E*)-1-phenyltridec-x-en-1-one (**3m'**, x<12) and 1-phenyltridecan-1-one (**3m"**) ^{1}H NMR (300 MHz, $CDCl_3$)



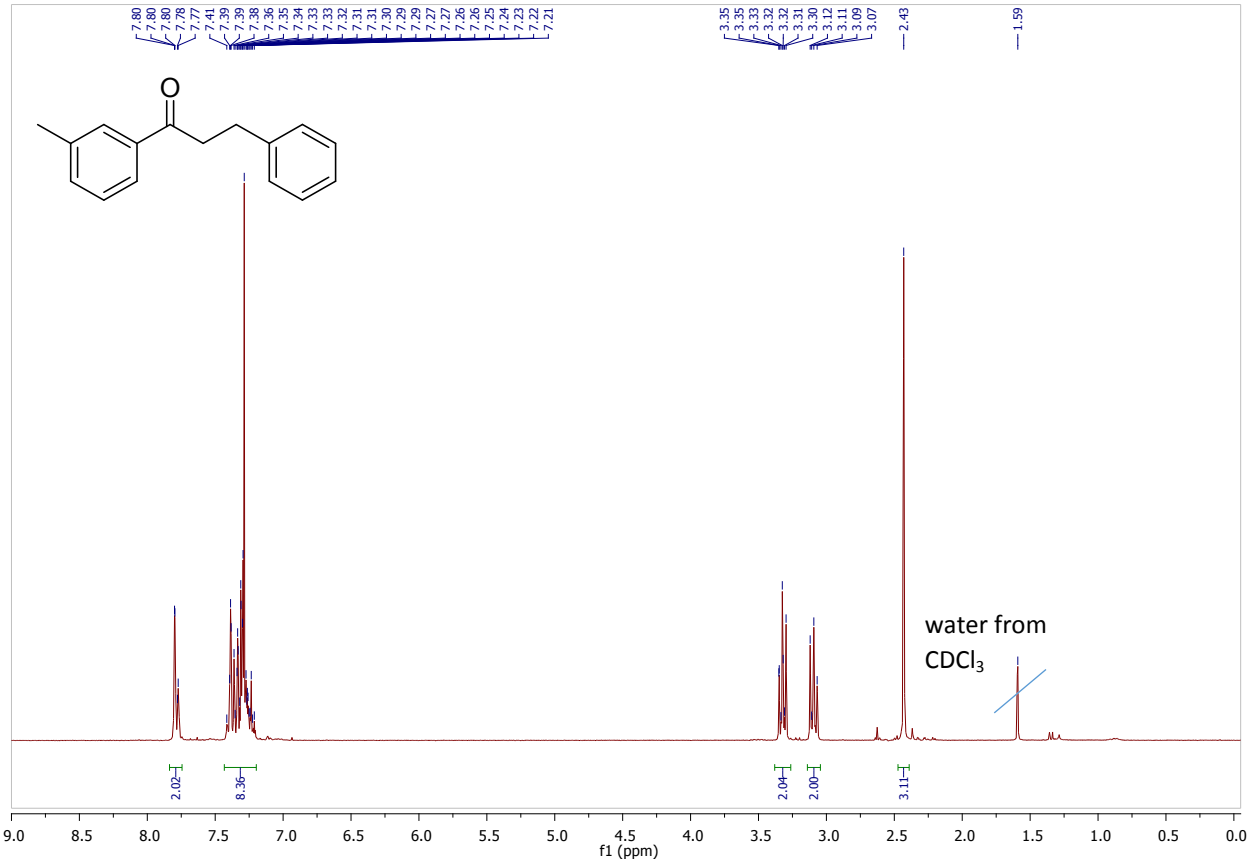
3-phenyl-1-(p-tolyl)propan-1-one (**3n**) ^{1}H NMR (300 MHz, $CDCl_3$)



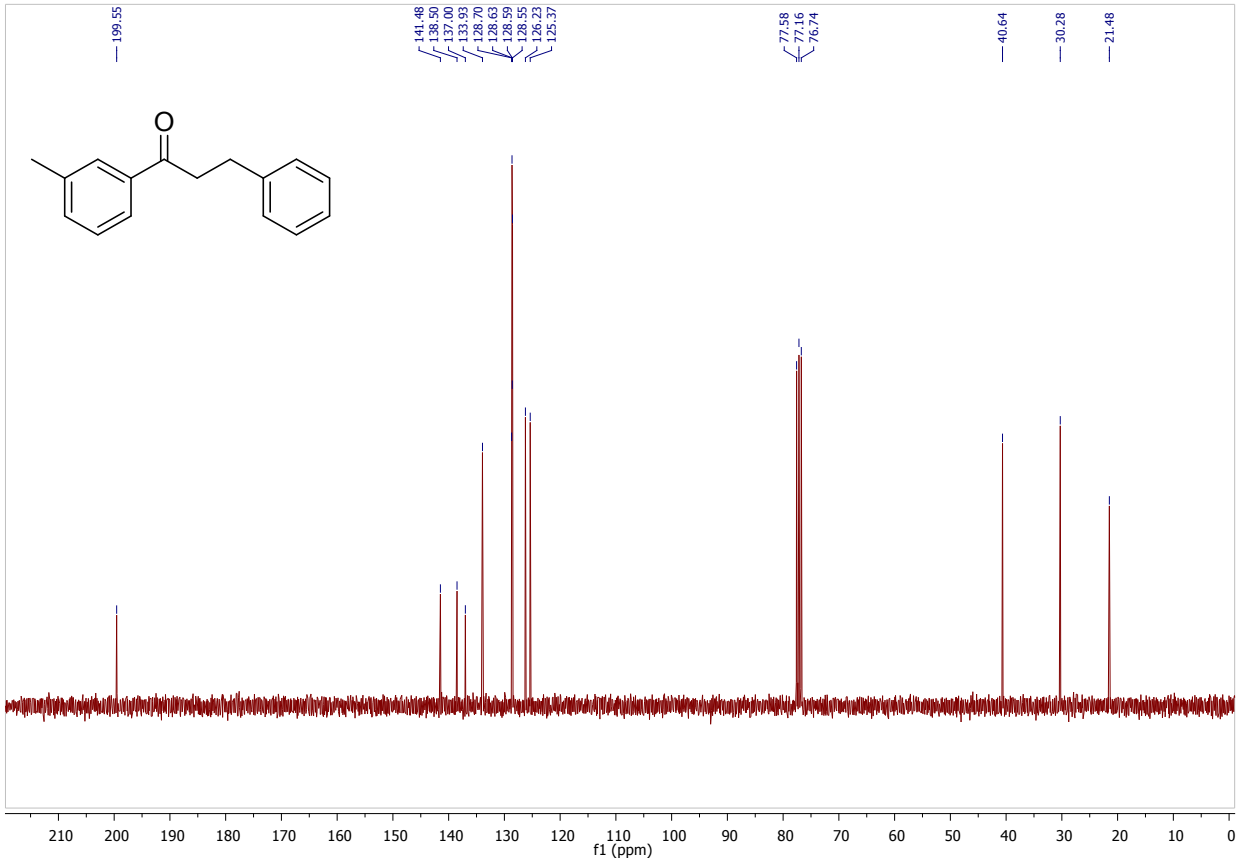
3-phenyl-1-(p-tolyl)propan-1-one (**3n**) ^{13}C NMR (75 MHz, $CDCl_3$)



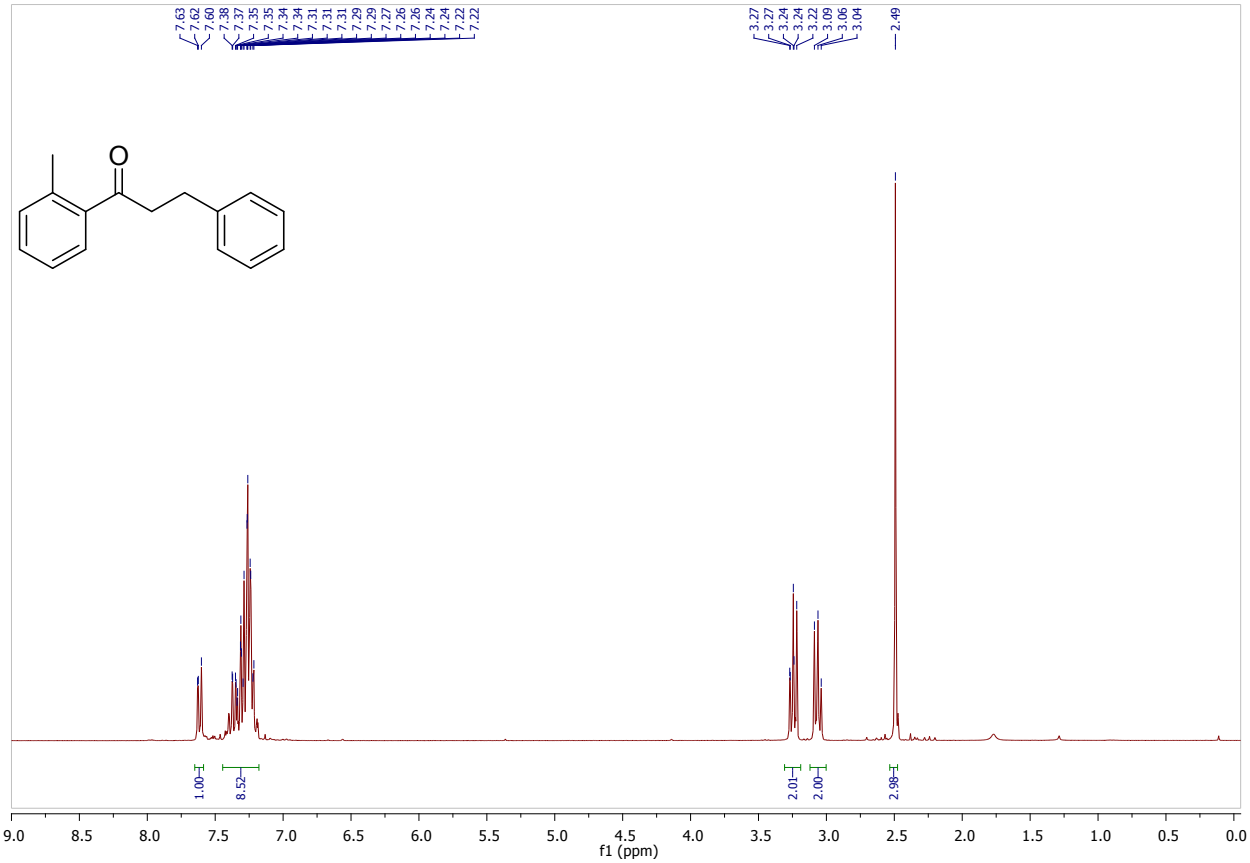
3-phenyl-1-(m-tolyl)propan-1-one (**3o**) ^{1}H NMR (300 MHz, $CDCl_3$)



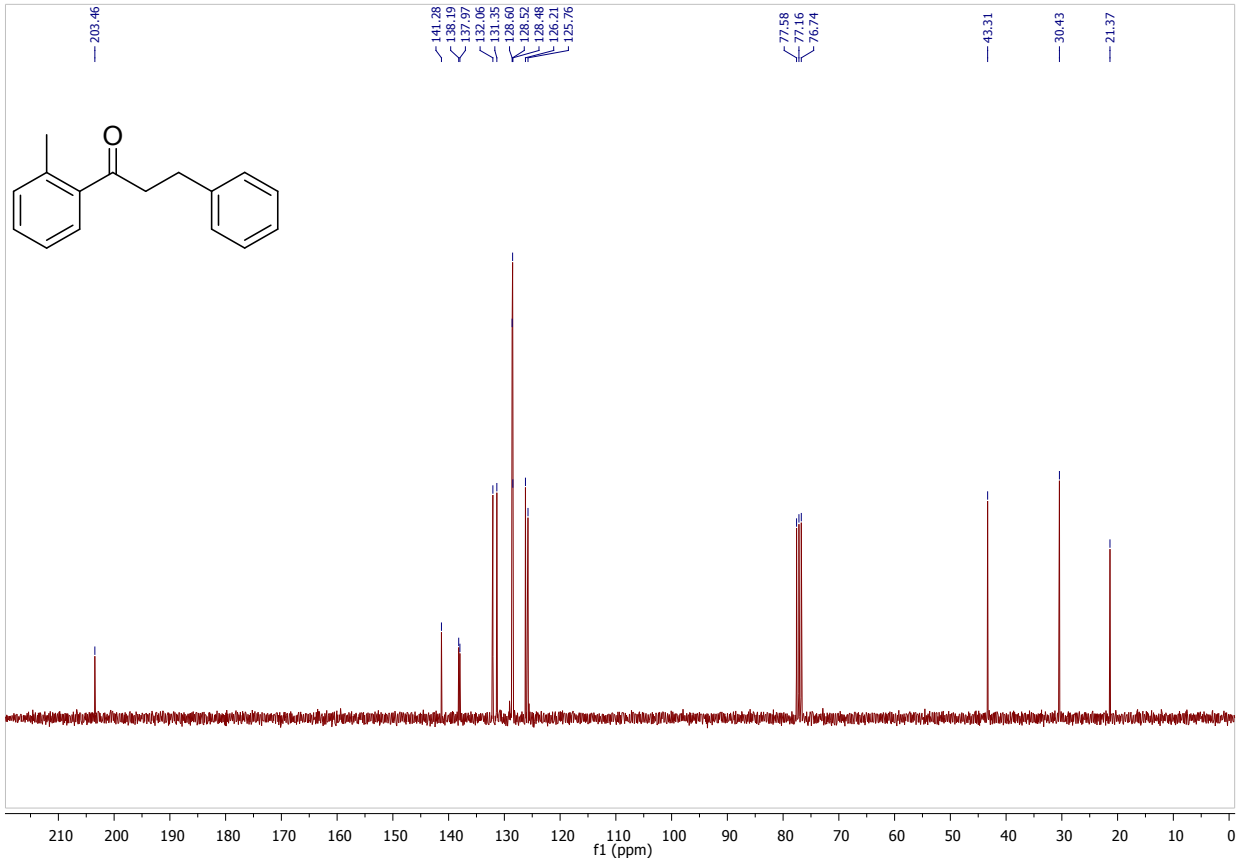
3-phenyl-1-(m-tolyl)propan-1-one (**3o**) ^{13}C NMR (75 MHz, $CDCl_3$)



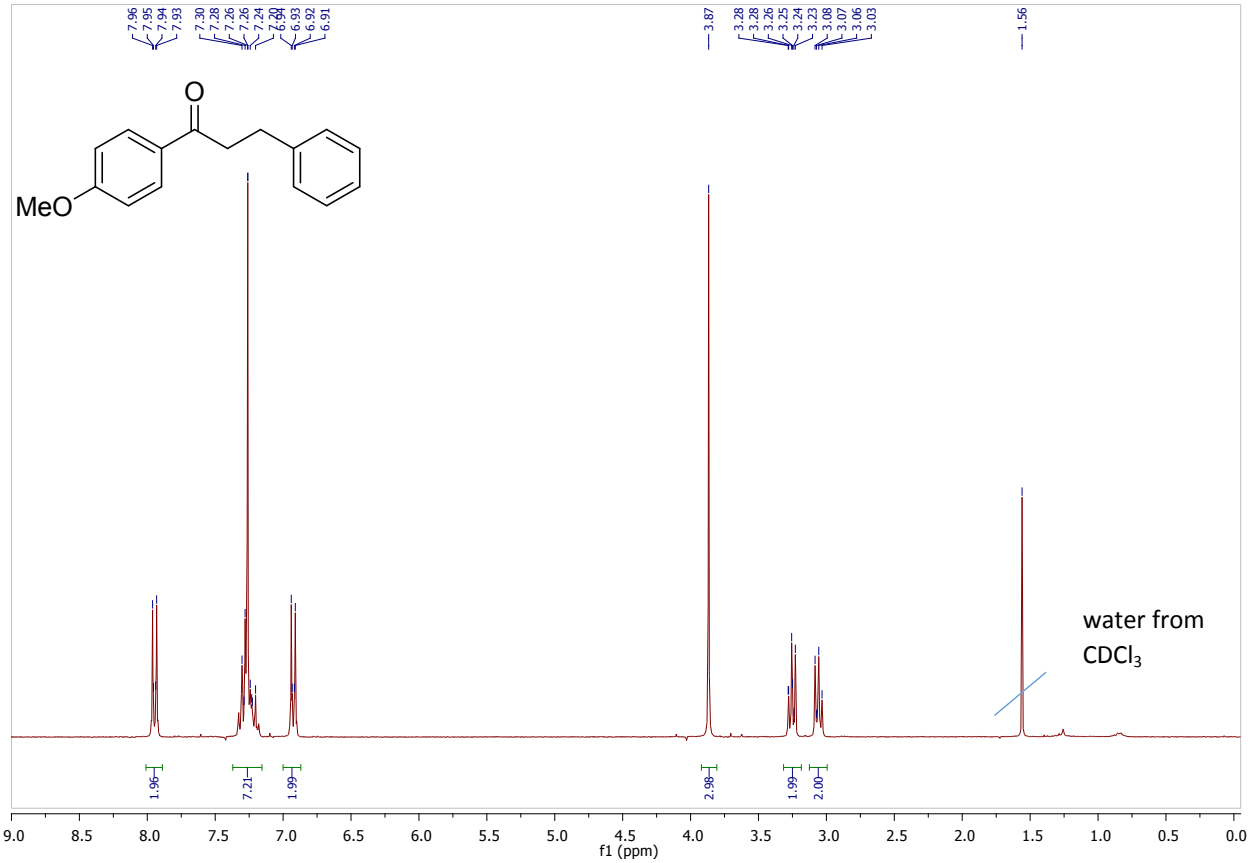
3-phenyl-1-(o-tolyl)propan-1-one (**3p**) ^{1}H NMR (300 MHz, $CDCl_3$)



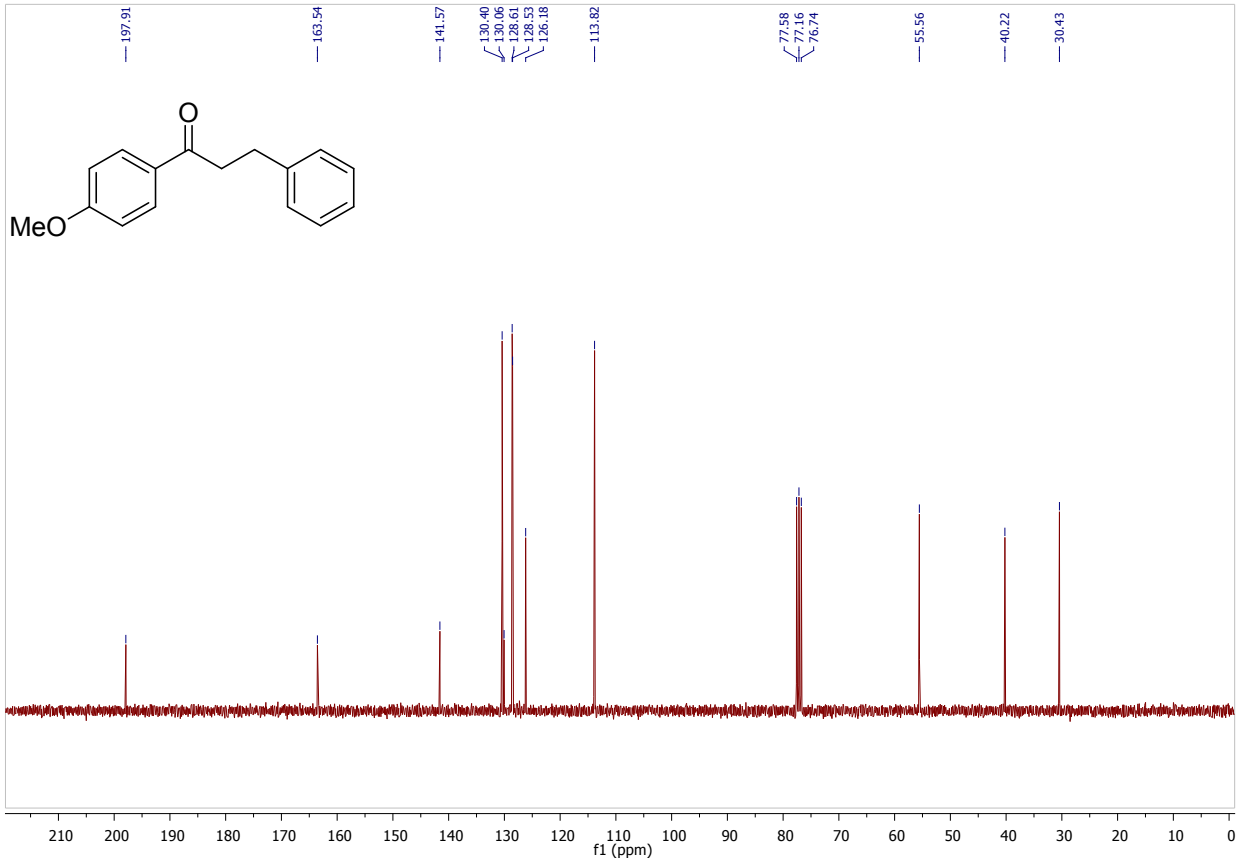
3-phenyl-1-(o-tolyl)propan-1-one (**3p**) ^{13}C NMR (75 MHz, $CDCl_3$)



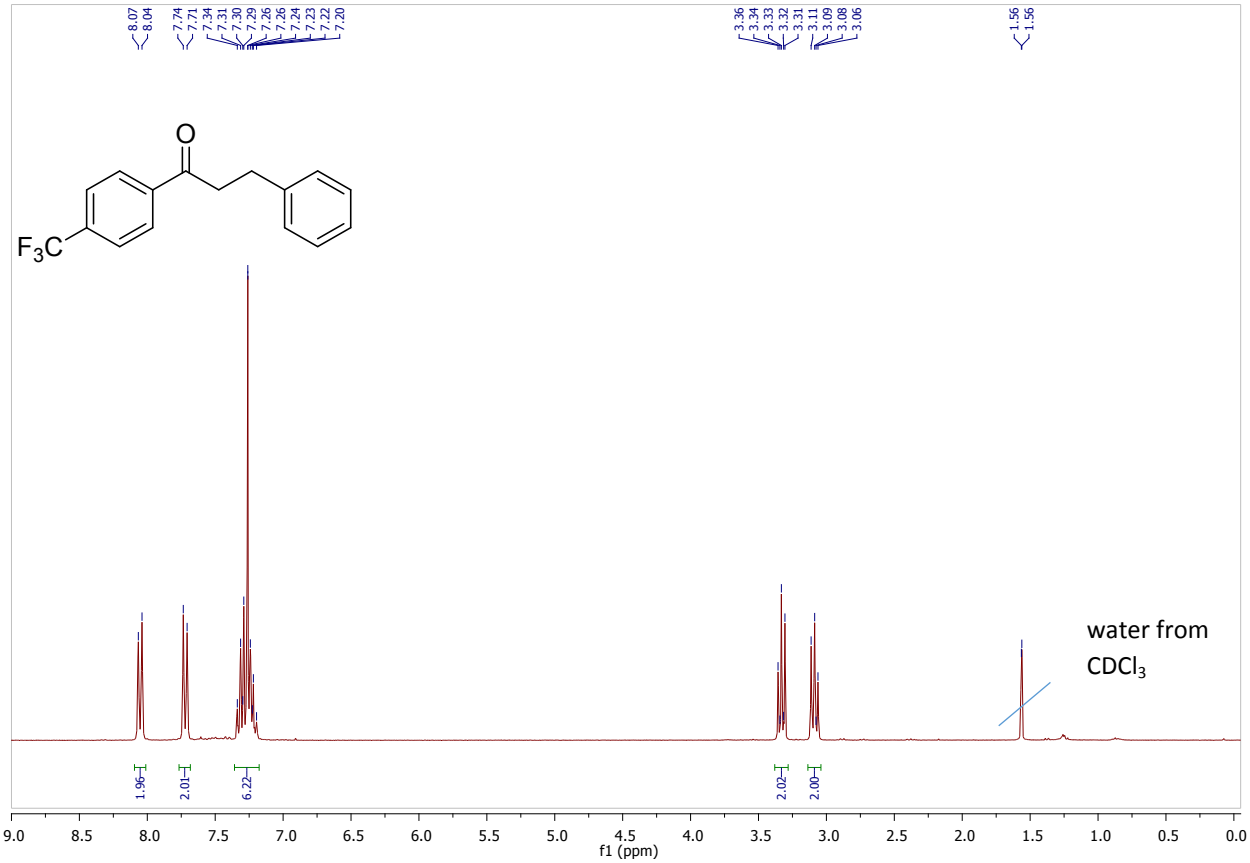
1-(4-methoxyphenyl)-3-phenylpropan-1-one (**3q**) ^{1}H NMR (300 MHz, $CDCl_3$)



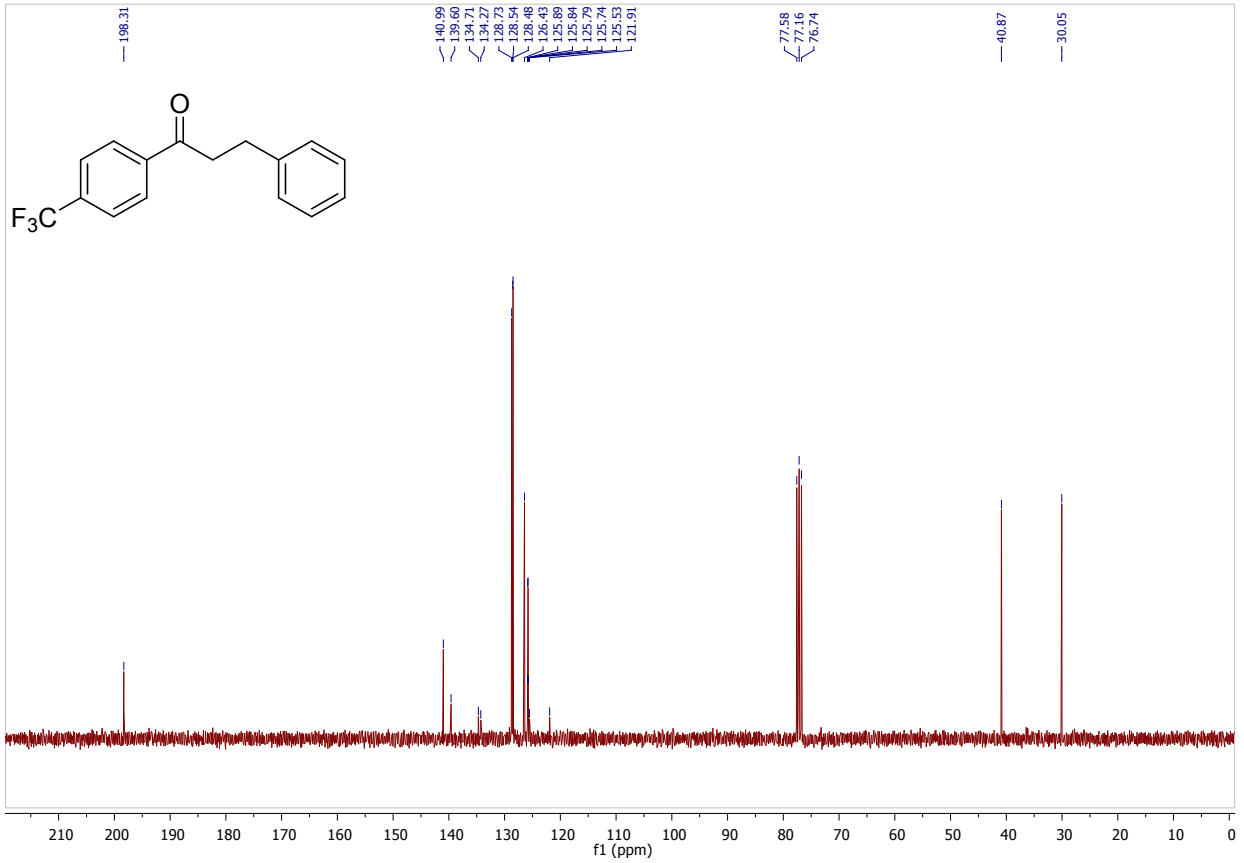
1-(4-methoxyphenyl)-3-phenylpropan-1-one (**3q**) ^{13}C NMR (75 MHz, $CDCl_3$)



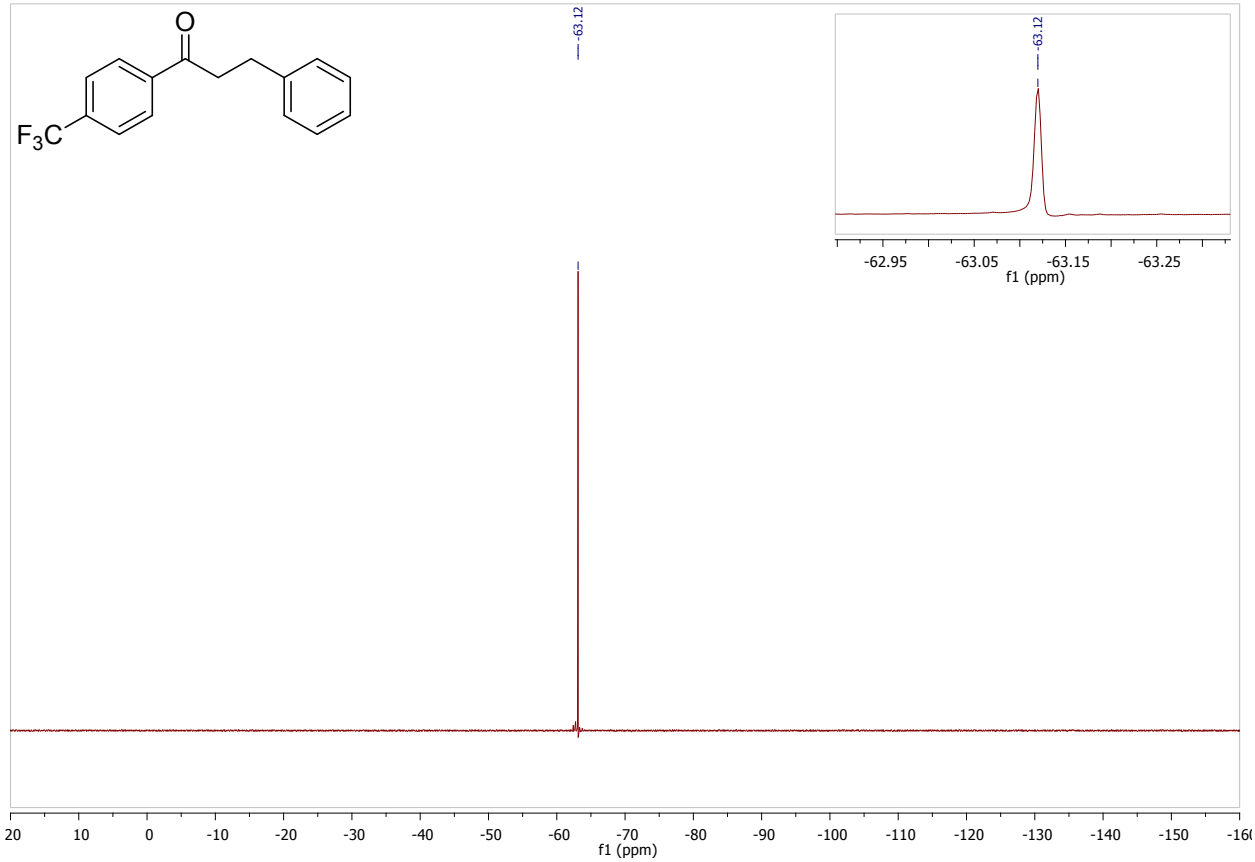
3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (**3r**) ^{1}H NMR (300 MHz, $CDCl_3$)



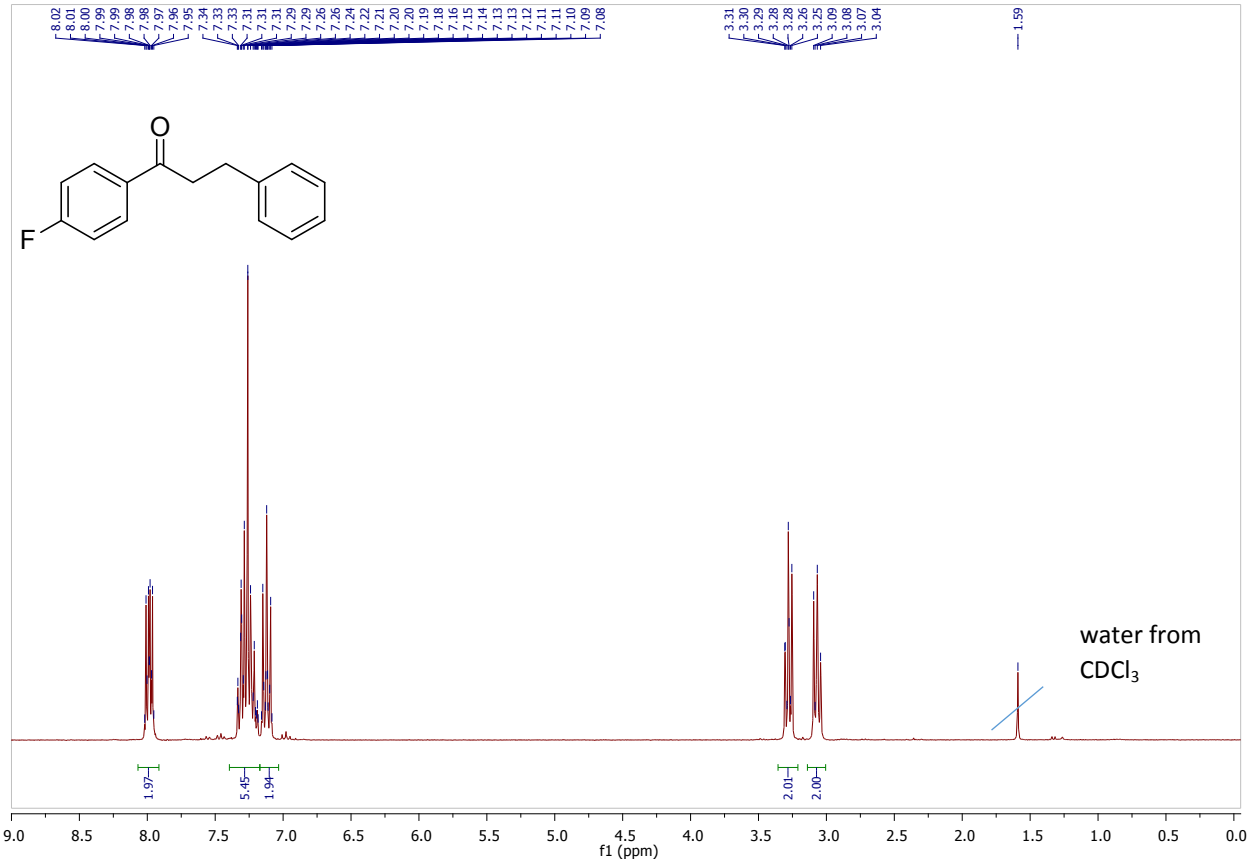
3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (**3r**) ^{13}C NMR (75 MHz, $CDCl_3$)



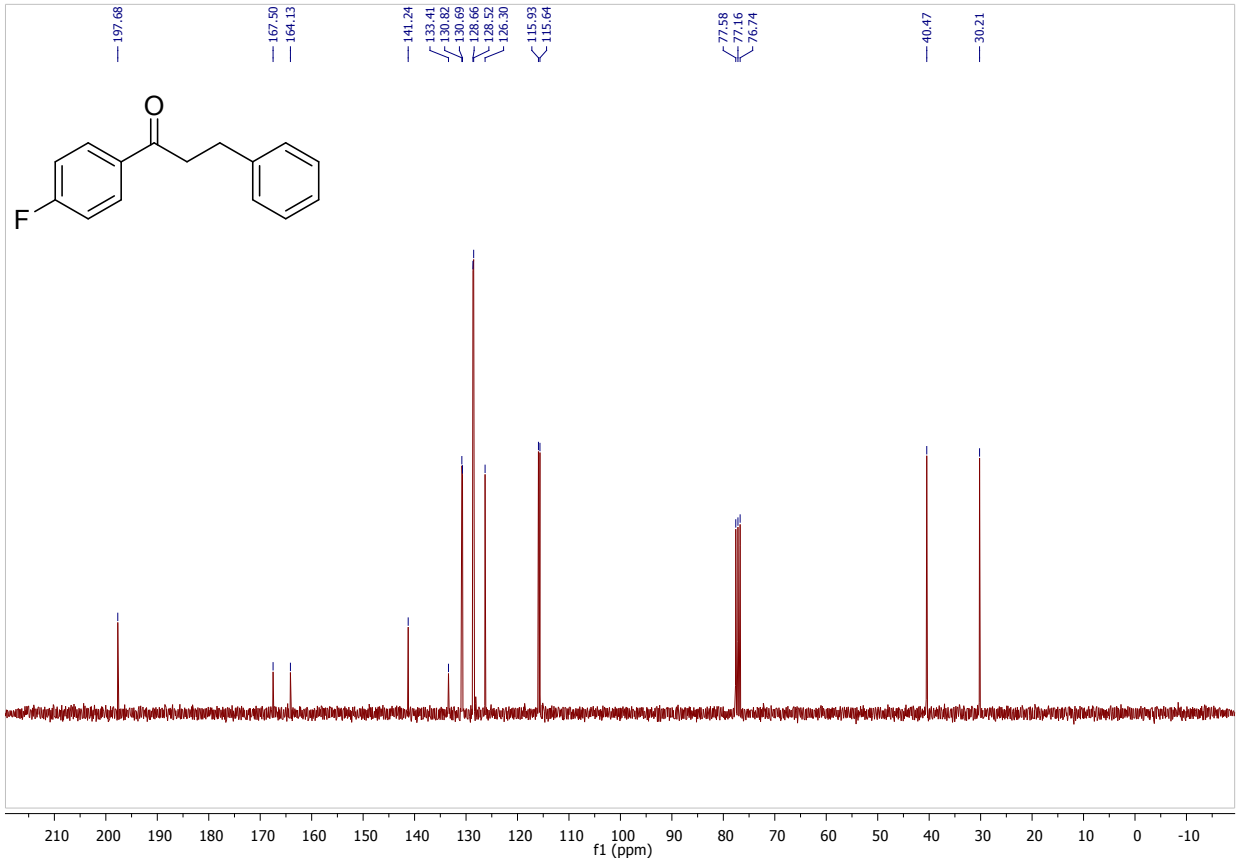
3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (**3r**) ^{19}F NMR (282 MHz, $CDCl_3$)



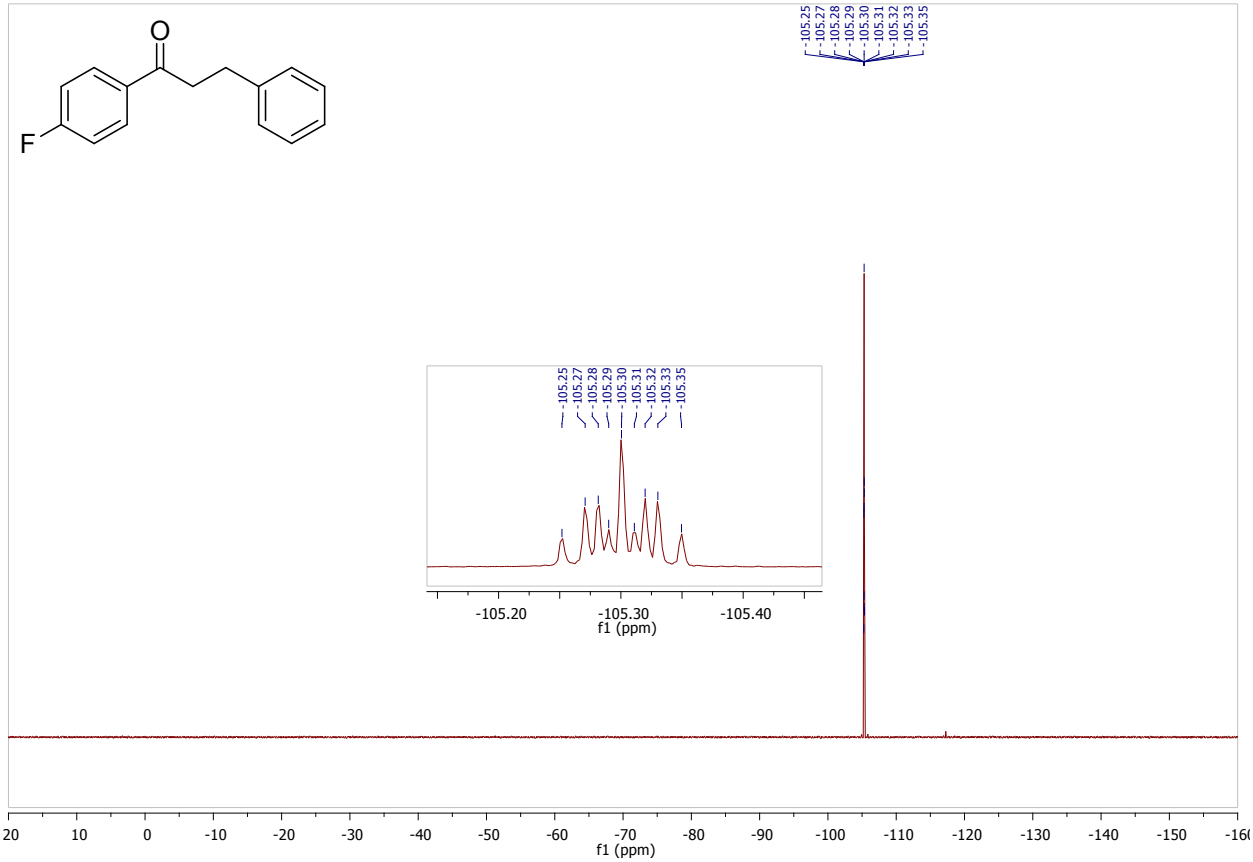
1-(4-fluorophenyl)-3-phenylpropan-1-one (**3s**) ^{1}H NMR (300 MHz, $CDCl_3$)



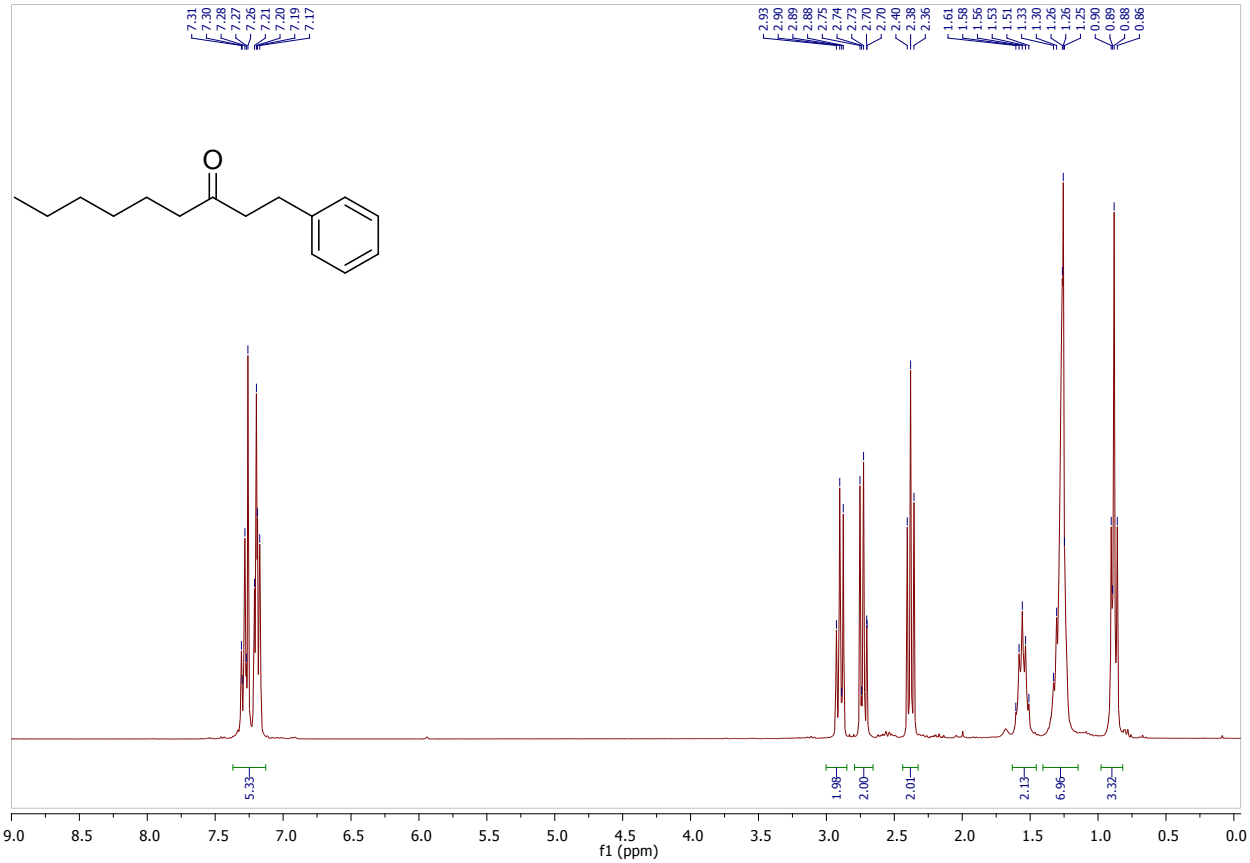
1-(4-fluorophenyl)-3-phenylpropan-1-one (**3s**) ^{13}C NMR (75 MHz, $CDCl_3$)



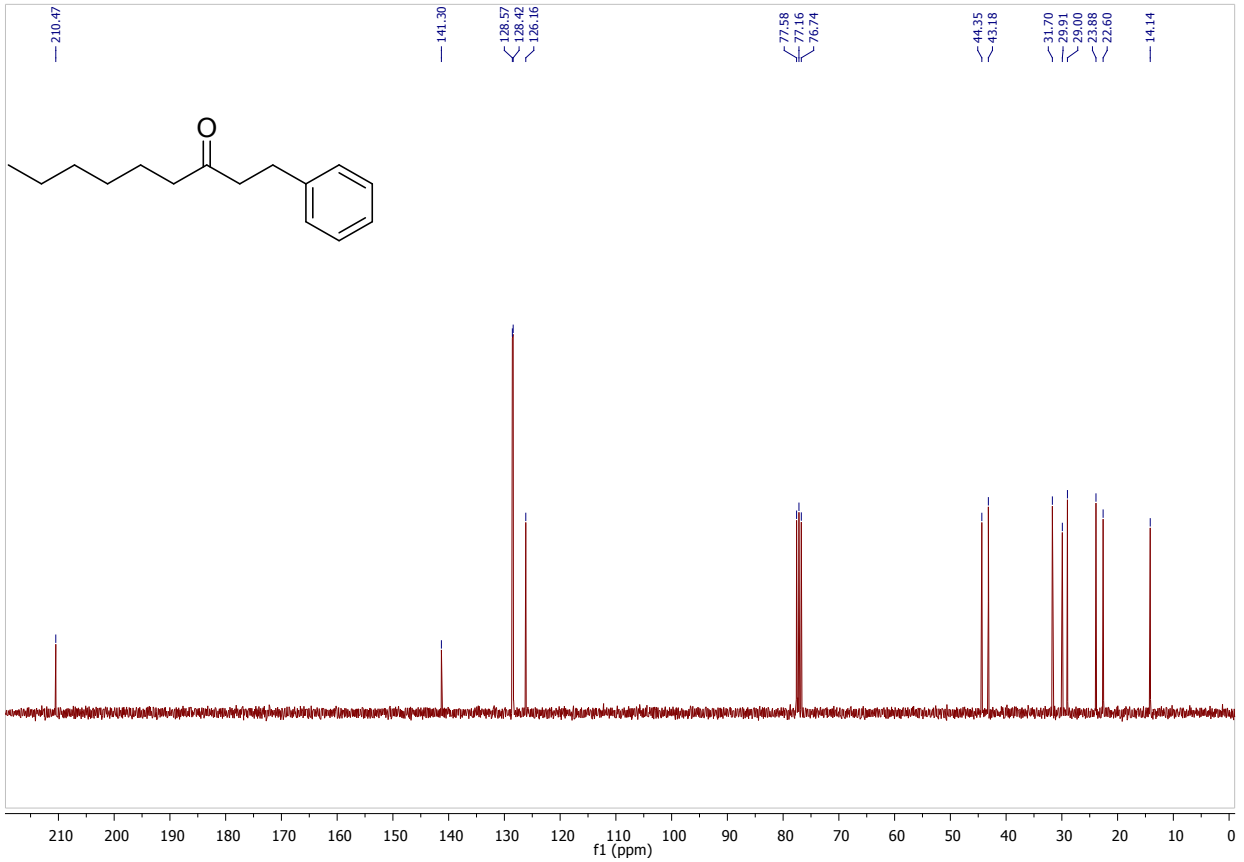
1-(4-fluorophenyl)-3-phenylpropan-1-one (**3s**) ^{19}F NMR (282 MHz, $CDCl_3$)



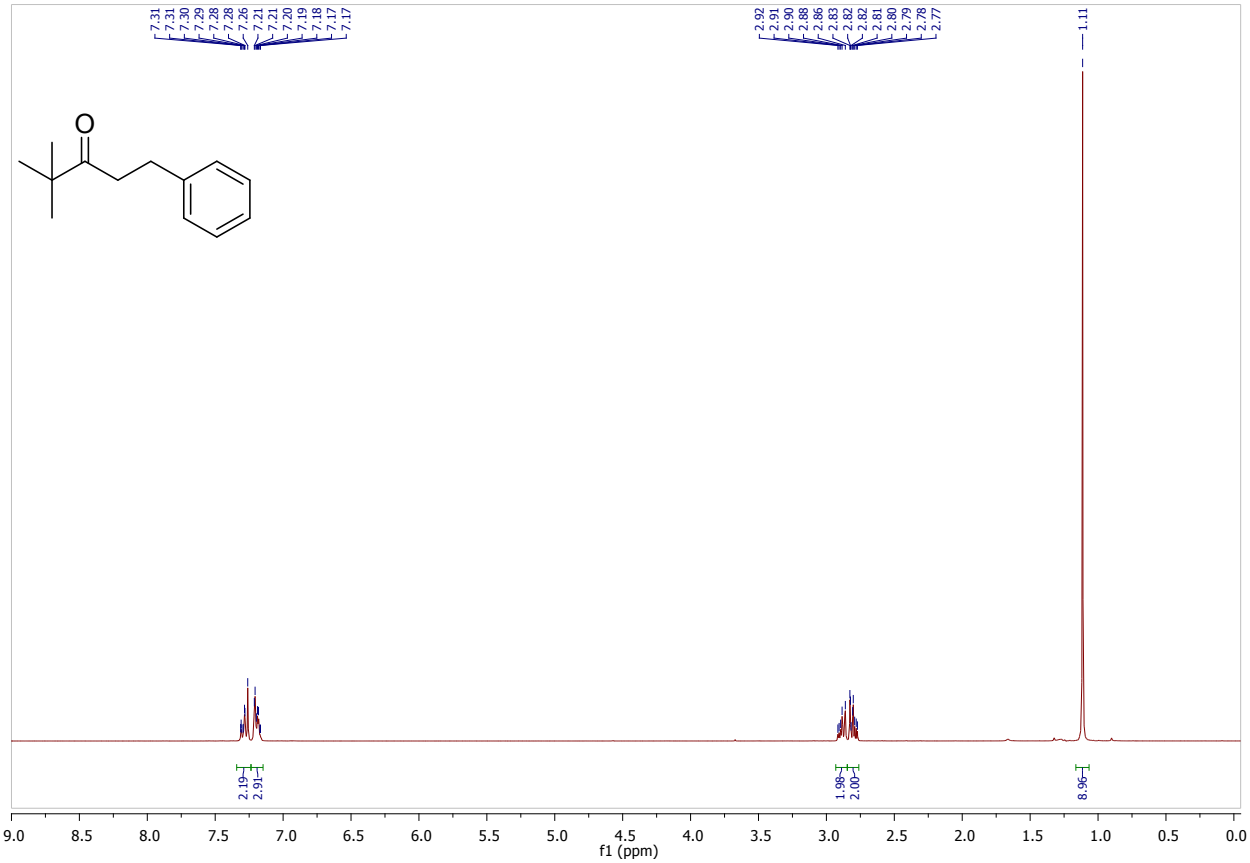
1-phenylnonan-3-one (**3u**) ^{1}H NMR (300 MHz, $CDCl_3$)



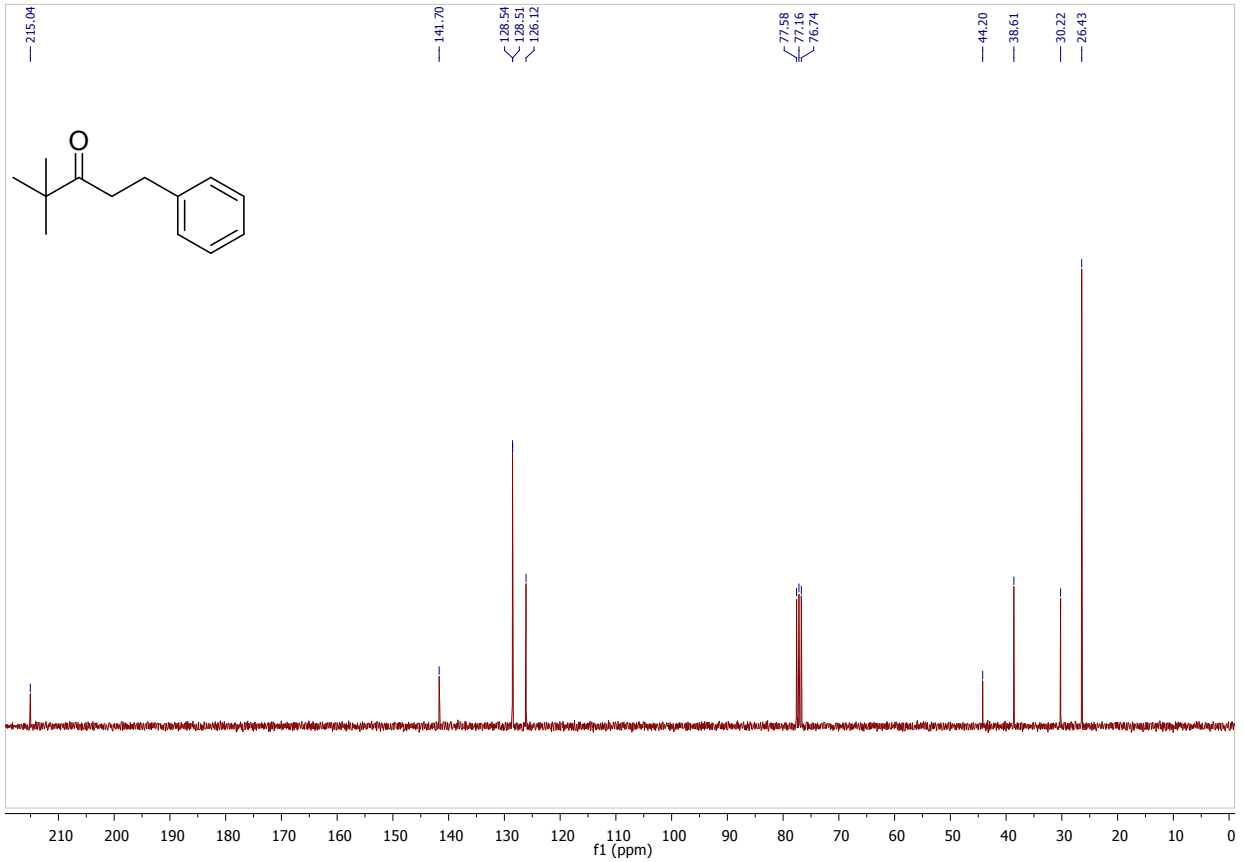
1-phenylnonan-3-one (**3u**) ^{13}C NMR (75 MHz, $CDCl_3$)



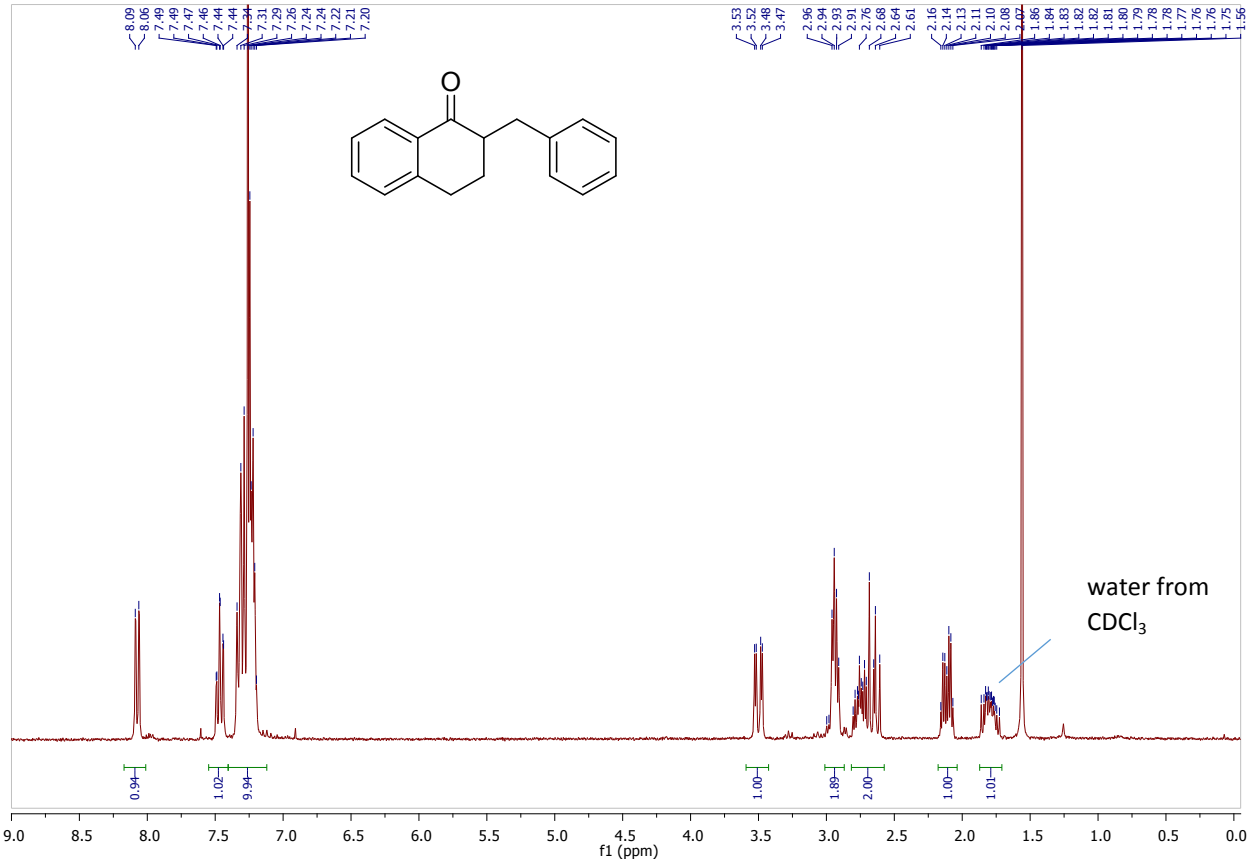
4,4-dimethyl-1-phenylpentan-3-one (**3v**) ^{1}H NMR (300 MHz, $CDCl_3$)



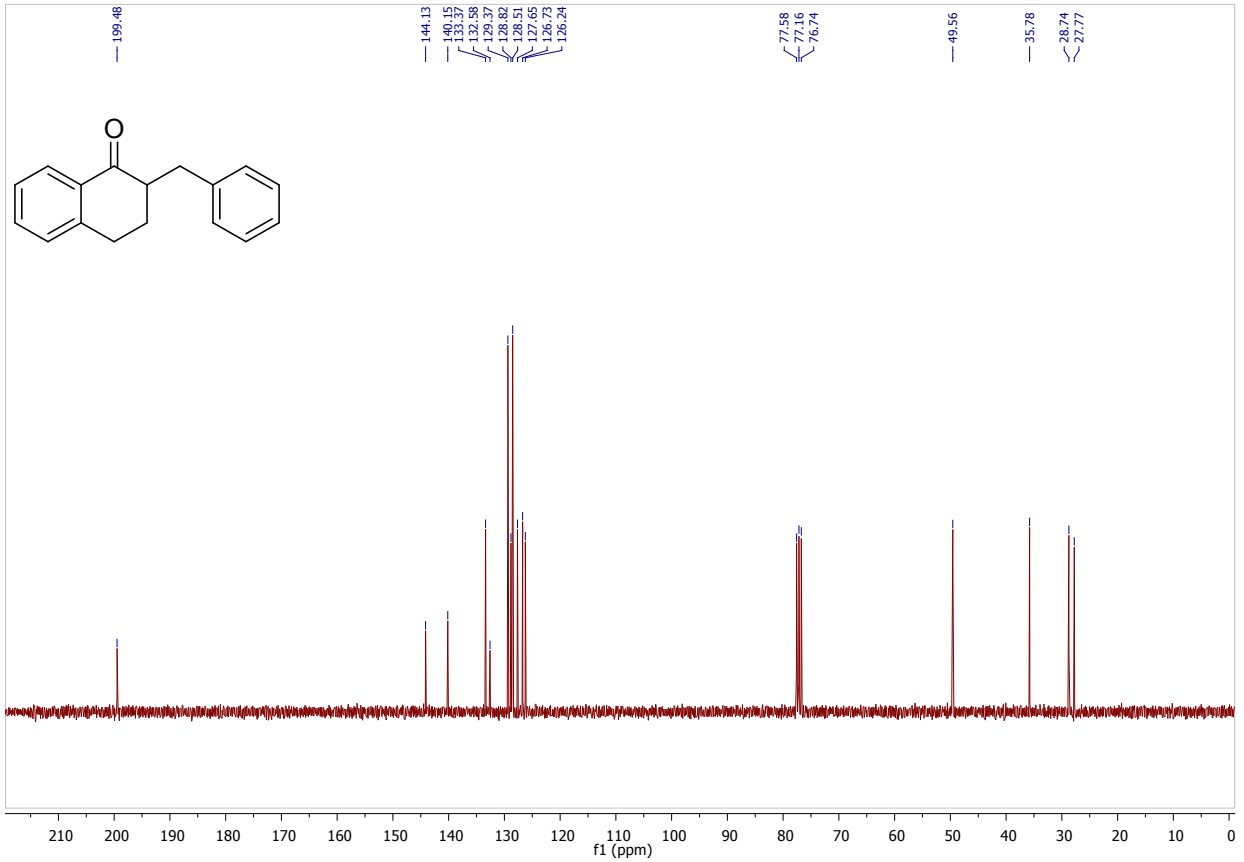
4,4-dimethyl-1-phenylpentan-3-one (**3v**) ^{13}C NMR (75 MHz, $CDCl_3$)



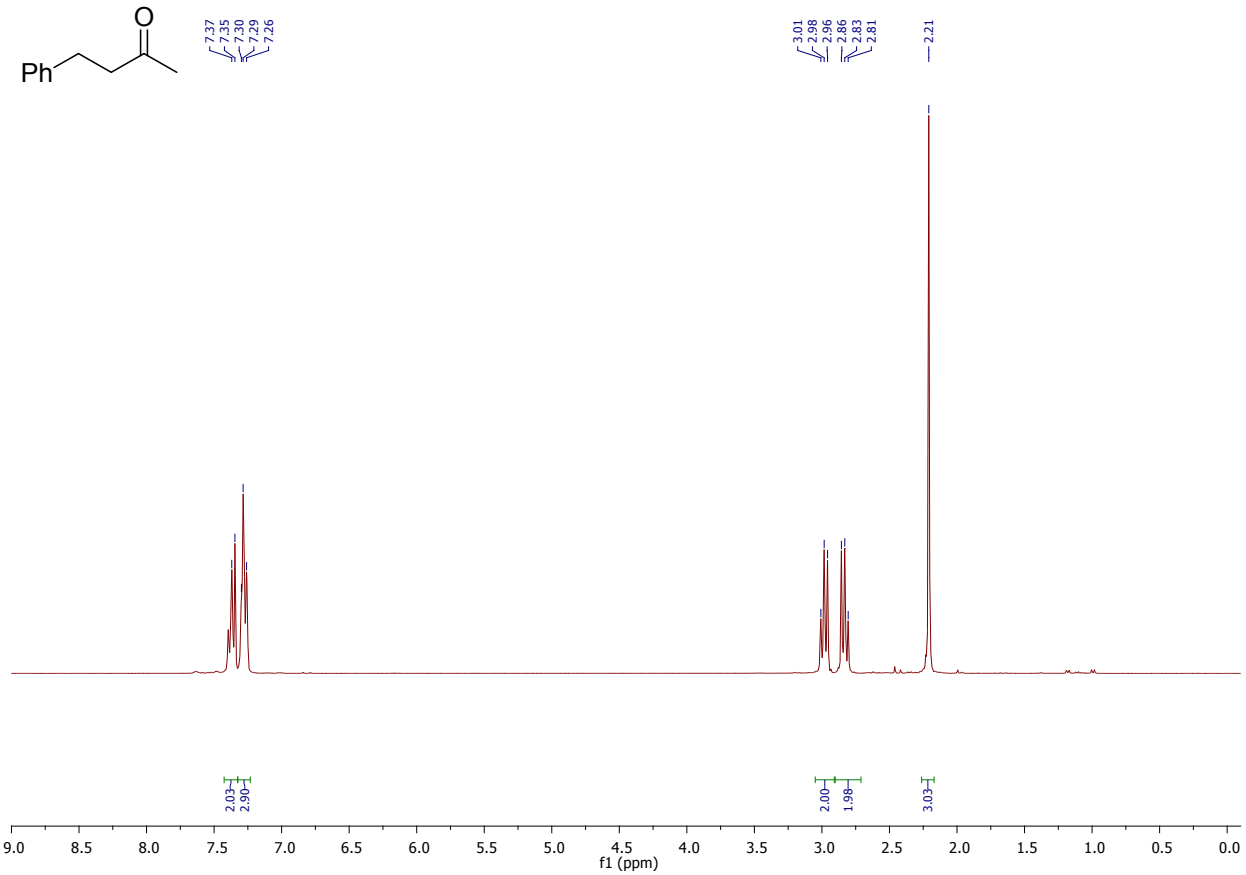
2-benzyl-3,4-dihydronaphthalen-1(2H)-one (**3x**) ^{1}H NMR (300 MHz, $CDCl_3$)



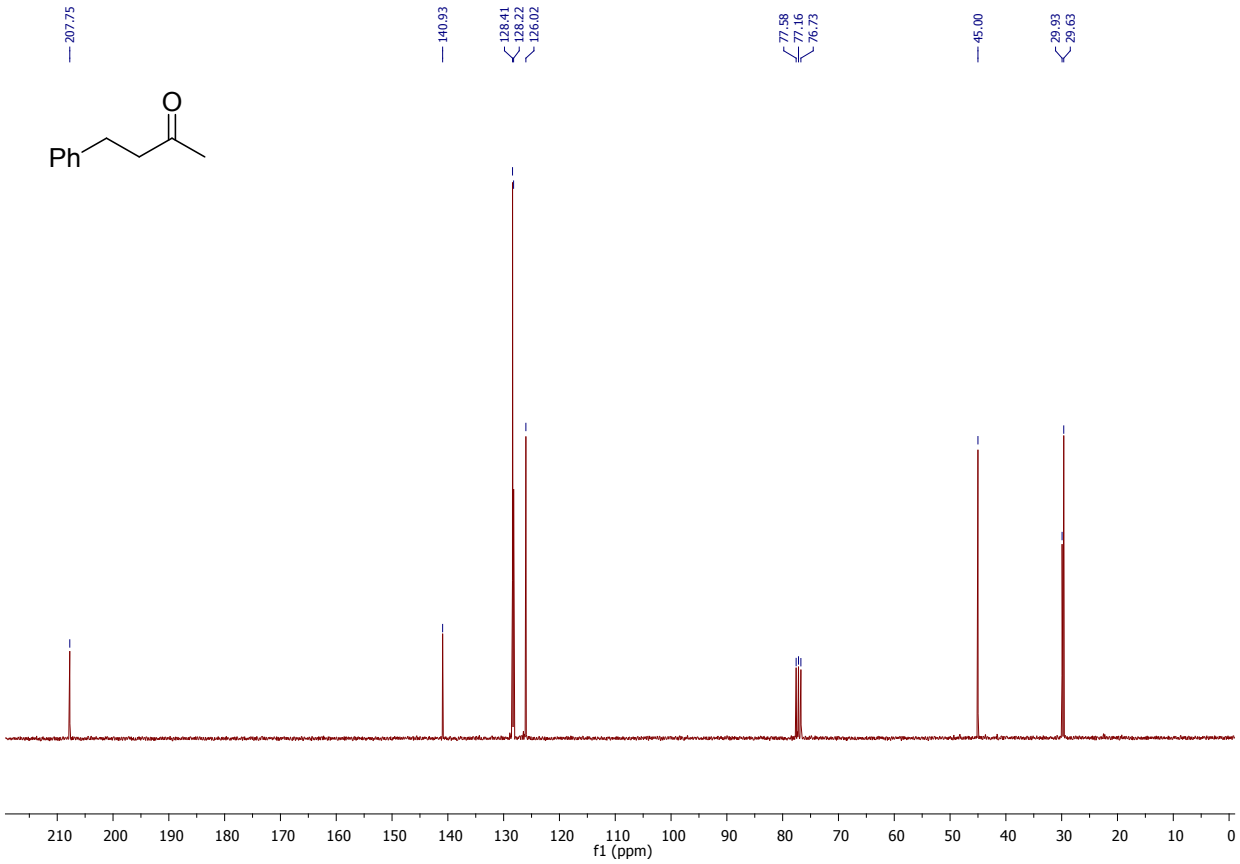
2-benzyl-3,4-dihydronaphthalen-1(2H)-one (**3x**) ^{13}C NMR (75 MHz, $CDCl_3$)



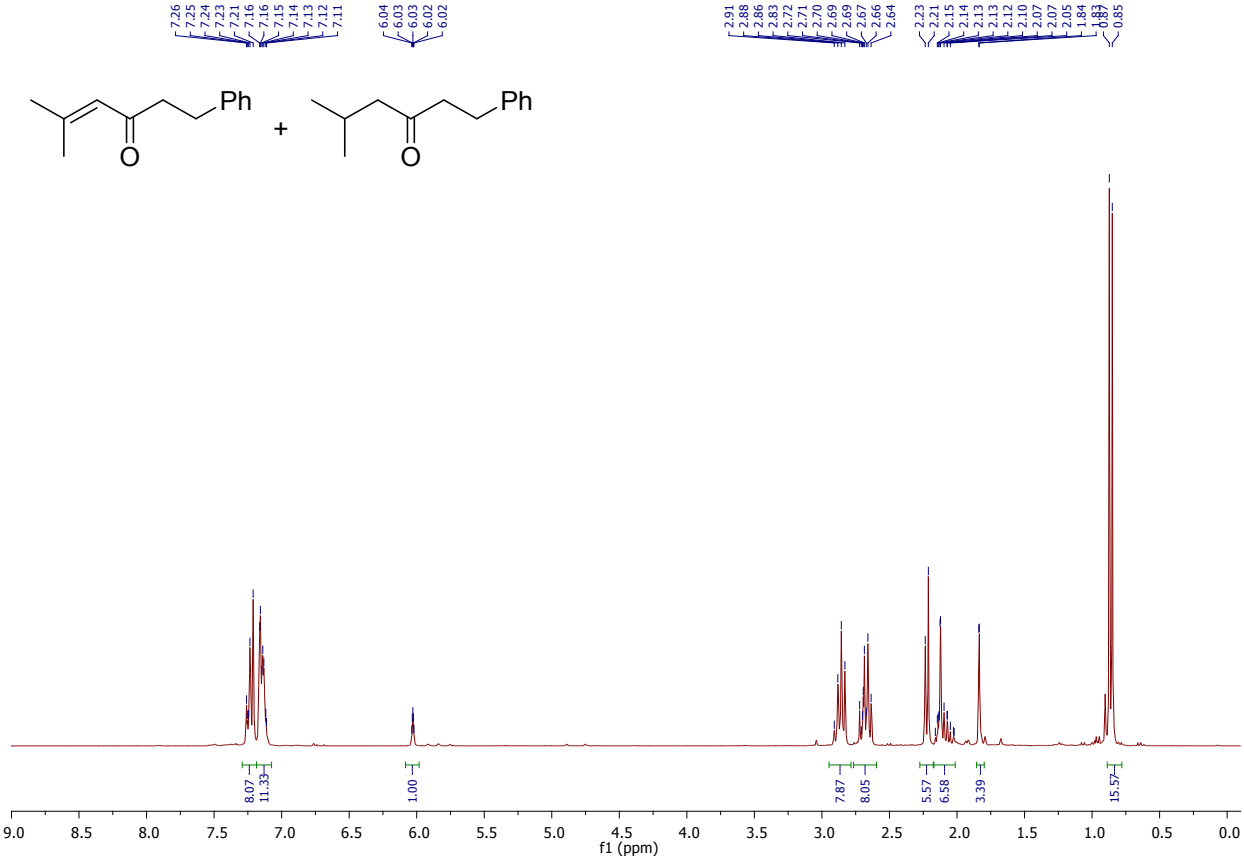
4-phenylbutan-2-one (**3z**) ^{1}H NMR (300 MHz, $CDCl_3$)



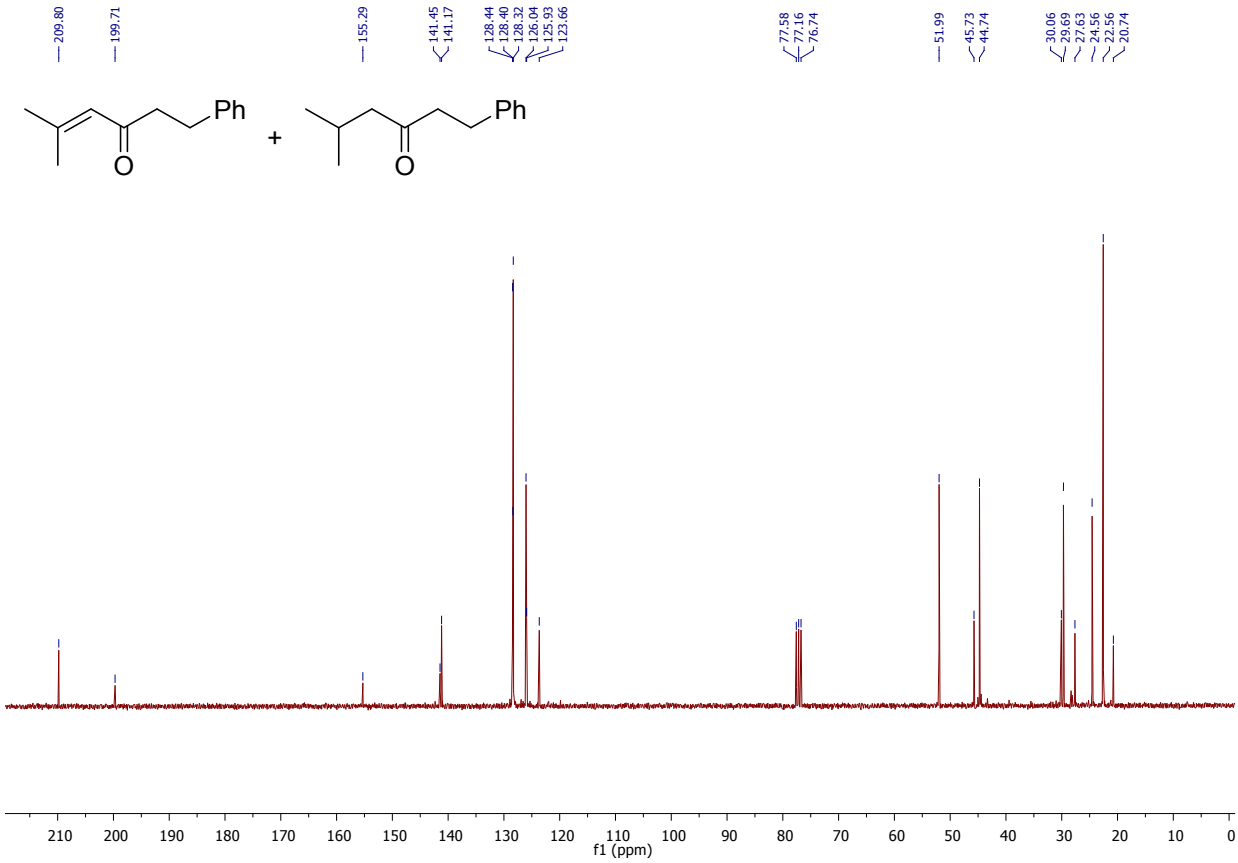
4-phenylbutan-2-one (**3z**) ^{13}C NMR (75 MHz, $CDCl_3$)



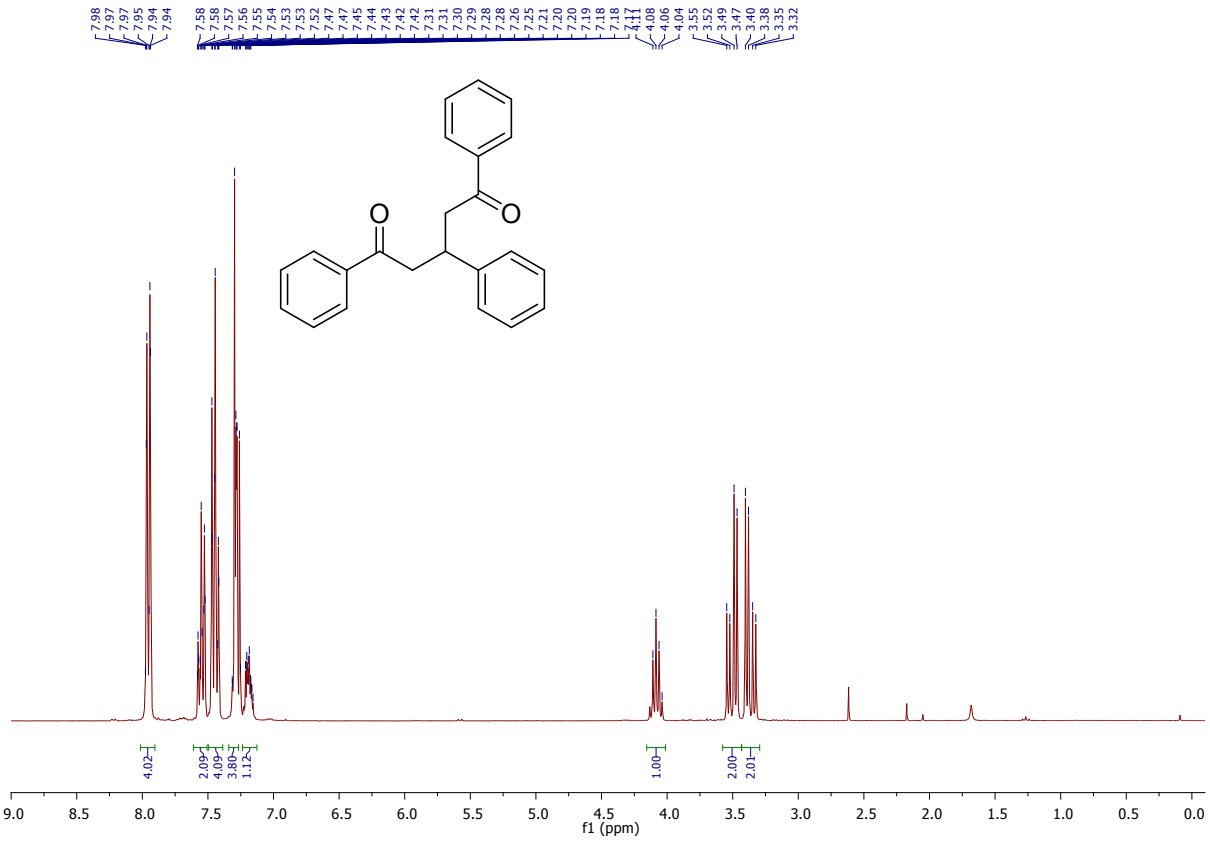
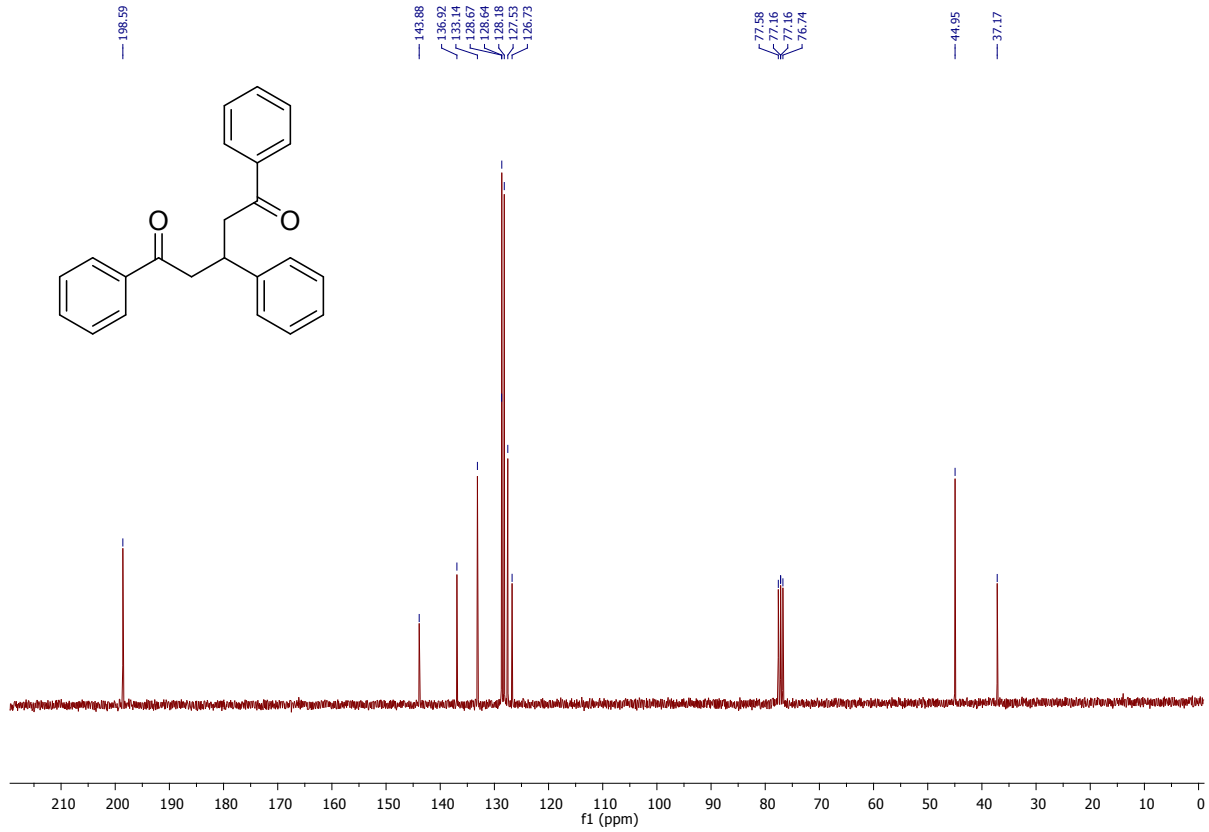
5-methyl-1-phenylhex-4-en-3-one (**3aa'**) and 5-methyl-1-phenylhexan-3-one (**3aa"**) ^{1}H NMR (300 MHz, $CDCl_3$)



5-methyl-1-phenylhex-4-en-3-one (**3aa'**) and 5-methyl-1-phenylhexan-3-one (**3aa"**) ^{13}C NMR (75 MHz, $CDCl_3$)



1,3,5-triphenylpentane-1,5-dione (**4**) ^{1}H NMR (300 MHz, $CDCl_3$)



1,3,5-triphenylpentane-1,5-dione (**4**) ^{13}C NMR (75 MHz, $CDCl_3$)