Electronic Supplementary Information (ESI)

Immobilizing a homogeneous manganese catalyst into MOF pores for α-alkylation of methylene ketones with alcohols

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Chemicals

All reagents and solvents were directly used without further purification. Zinc Acetate dihydrate $Zn(CH_3COO)_2.2H_2O$ (98%) was purchased from Molychem, 2-methylimidazole (98%) was purchased from Avra, 1,10-phenanthroline monohydrate (AR grade) was purchased from FINAR, Methanol (99%), Benzyl alcohol (99%) were purchased from RANKEM. Toluene HPLC grade (99.7%), K_2CO_3 (99.0%), Manganese Chloride tetrahydrate, Manganese acetate tetrahydrate, Hexane (>98%), Ethyl acetate (>98%) were purchased from SDFCL. Deoxybenzoin (97%), 4-chlorobenzyl alcohol (99%), α-Tetralone were acquired from Alfa Aesar. 4-isopropyl benzylalcohol (98%), Cyclohexanemethanol (>98%) and 4-ethyl benzylalcohol (>98%), 2-thiophenemethanol (98%), 4-methoxy benzylalcohol (98%), 4-fluorobenzyl alcohol (97%), Heptyl alcohol (>=97%), Octyl alcohol (98%), β-Citronellol (95%), Furfuryl alcohol (97%), Piperonyl alcohol (98%) were supplied by Sigma-Aldrich. Propiophenone (>98%) was purchased from TCI. Potassium-tert-butoxide t-BuOK (98%) was obtained from Spectrochem. KOH (85%) was acquired from Azytus. Chloroform-d (99.8% min.) was acquired from Merck.

Experimental Section

1. Synthesis

1.1 Synthesis of MnPhen@ZIF: In a typical synthesis and at room temperature, 1.0 mmol of $MnCl_2$ (197 mg) and 1.0 mmol of phenanthroline (198 mg) were dissolved in two separate 25 mL MeOH solvents. The manganese solution was added into phenanthroline solution with continuous stirring for 24 h at room temperature. A yellow-colored solution was obtained and was filtered. The filtrate was marked as solution '**A**'. In continuation, 3.46 mmol of $Zn(CH_3COO)_2.2H_2O$ (760 mg) was dissolved in 75 mL MeOH solvent, marked as solution '**B**'.

At the same time, 51.20 mmol of 2-methylimidazole (4.208 g) was also dissolved in 75 mL MeOH solvent and marked as solution '**C**'. Solution **C** was first added into solution **A** under vigorous stirring. The yellow-colored solution became colorless. To this solution, solution **B** was transferred quickly with continuous stirring. After 2 h continuous stirring, solution was kept as it for 24 h without any disturbance. A white color solid was precipitated. It was separated by centrifugation and washed with MeOH several times. Sample was dried in vacuum oven at 150 ^{o}C and named as MnPhen@ZIF.

1.2 Synthesis of ZIF-8: 3.46 mmol of $Zn(CH_3COO)_2 .2H_2O$ (760 mg) and 51.20 mmol of 2-methylimidazole (4.208 g) were dissolved in 75 mL MeOH solvents separately. Then the zinc solution was added into 2-methylimidazole solution under vigorous stirring. After 2 h continuous stirring, solution was kept as it for 24 h without any disturbance. A white color solid was precipitated. It was separated by centrifugation and washed with MeOH several times. Sample was dried in vacuum oven at 150 ^{o}C and stored for further use.

1.3 Synthesis of Mn-ZIF-8: 3.46 mmol of $Zn(CH_3COO)_2 .2H_2O$ and 0.7 mmol $MnCl_2$ was dissolved in 75 mL MeOH solvent. At the same time, 51.20 mmol of 2-methylimidazole was also dissolved in 75 mL MeOH solvent. Then the metal solution was added into 2-methylimidazole solution under vigorous stirring. After 2 h continuous stirring, solution was kept as it for 24 h without any disturbance. A white color solid was precipitated. It was separated by centrifugation and washed with MeOH several times. Sample was dried in vacuum oven at 150 ^{o}C and stored for further use.

1.4 Synthesis of MnPhen complex: To synthesize MnPhen complex, 1.0 mmol of $MnCl_2$ (197 mg) and 2.0 mmol of phenanthroline (396 mg) were dissolved in two separate 25 mL MeOH solvents. The manganese solution was added into phenanthroline solution with

continuous stirring for 24 h at room temperature. A yellow-colored precipitate was formed. Then we filter the solution and dried it at room temperature & named as "MnPhen".

2. Characterization:

PANalytical diffractometer using Cu Kα source (λ = 1.5405 Å) was utilized to measure Powder X-ray diffraction (PXRD) with 2°/min scan rate and 0.05 steps. Cary 5000 UV-Visible-NIR spectrophotometer used to record solid-state UV-VIS spectra with integrating spheres of 105 mm. For analyzing surface area and pore size distribution BELSORP Max sorption analyzer was used at liquid nitrogen temperature 77 K. Before sorption measurements, the samples were degassed 150 ^{o}C for 12 h. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific (K-Alpha) X-ray photoelectron spectrometer using an Al Kα source (10 kV, 10 mA) equipped with ion source (EX06). The Ar sputtering experiments were carried out under the conditions of background vacuum ~10^{-8} Pa, sputtering acceleration voltage of 2 kV and sputtering current of 10 mA. Micromeritics (AUTOCHEM) was used for temperature programmed desorption (TPD) measurements. Thermogravimetric analysis (TGA) was performed on TA Instrument Q500 thermogravimetric analyzer at under N_2 atmosphere with a heating rate of 10 ^{o}C /min from 25 to 700 ^{o}C. Scanning electron microscopy (SEM) images were acquired using JEOL (JXA-8230) at 20 KV. Transmission electron microscopy (TEM) images were acquired at 200 kV Talos F200S G2 transmission electron microscope combined with column energy dispersive X-ray spectrometer (EDS) and a CMOS Camera 4K x 4K detector. PERKIN ELMER OPTIMA 5300 DV ICP-OES was used for metals content determination. Nucon GC 5700 gas chromatography (model WINCHROM-1 Spartan) with TCD detector was used for the hydrogen gas analysis. GC-MS were recorded using Agilent Gas Chromatography Mass Spectrometry. ^{1}H NMR spectral data were collected at 400 MHz, and ^{13}C NMR were recorded at 100 MHz using JEOL-400 YH NMR spectrometer at 25 °C probe temperature.

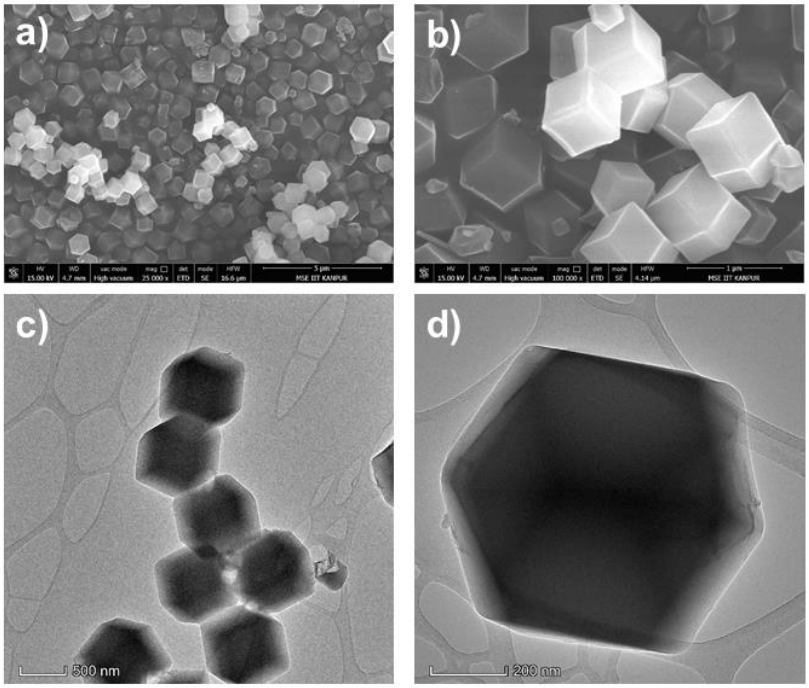


Figure S1 (a)-(b) SEM images, (c) & (d) TEM images of as-synthesized catalyst Mnphen@ZIF.

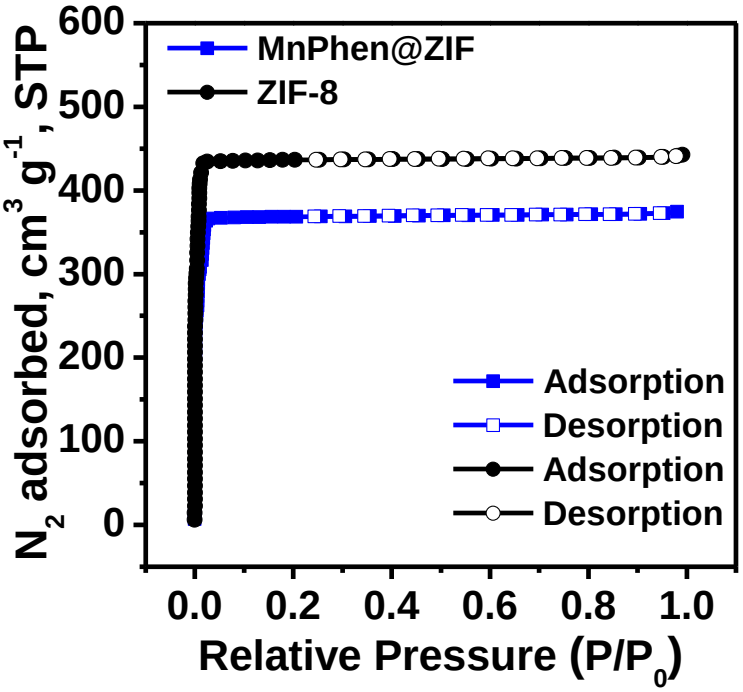


Figure S2 N_2 sorption isotherms of ZIF-8 (black) and Mnphen@ZIF (blue), recorded at 77 K. Filled and open circles represent adsorption and desorption, respectively.

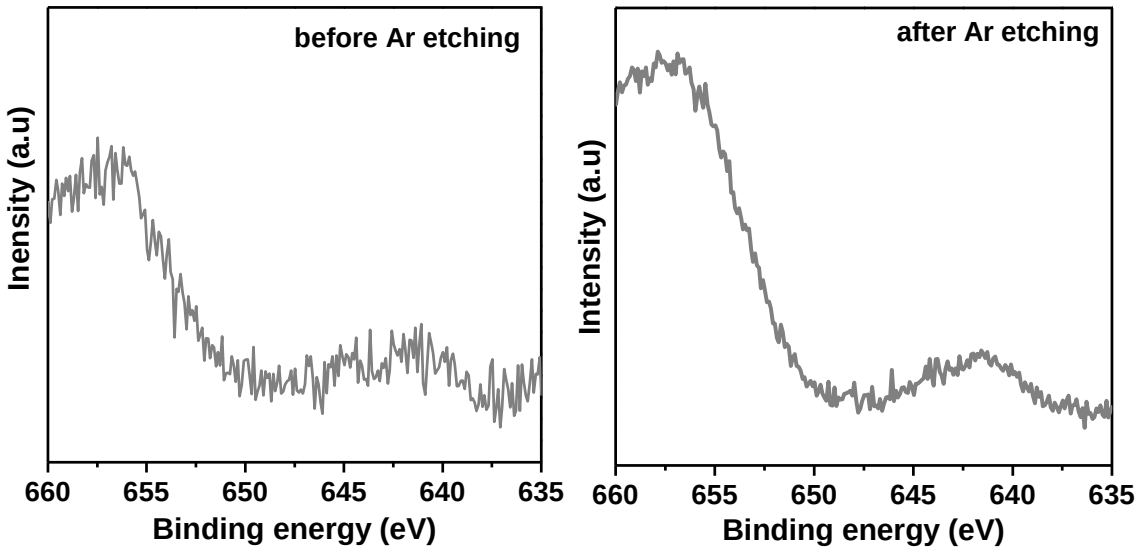


Figure S3 Mn 2p XPS spectra of MnPhen@ZIF before Ar-etching (left), and after Ar-etching (right). This Ar-sputtering suggests the presence of more Mn in the bulk of MnPhen@ZIF crystals.

Figure S4 Physical appearance of pure ZIF-8, manganese phenanthroline complex (MnPhen) and as-synthesized catalyst MnPhen@ZIF.

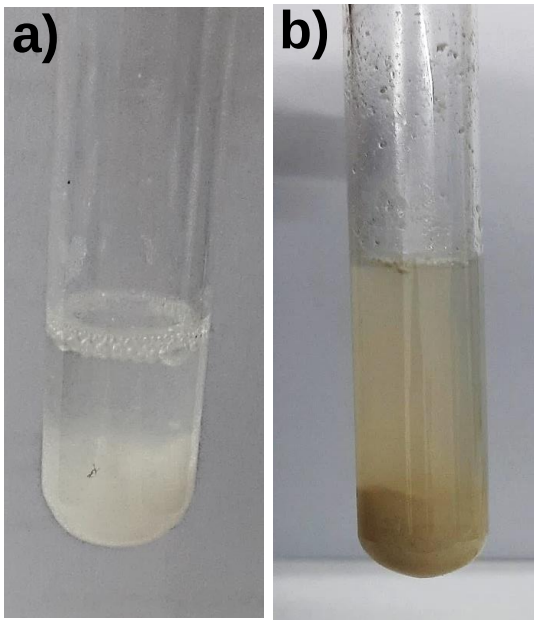


Figure S5 Physical appearances of Mn-NaOH test for MnPhen@ZIF a) without, and b) with acid.

3. Catalytic measurements

Silica Gel 60 F_{254} plates with the layer thickness of 0.25 mm were used for thin-layer chromatography. To afford pure product, column chromatography was performed. A gradient of ethyl acetate and hexane was used as a mobile phase and passed through the silica gel with mesh size of 100-200. All the reactions were carried out under Ar atmosphere.

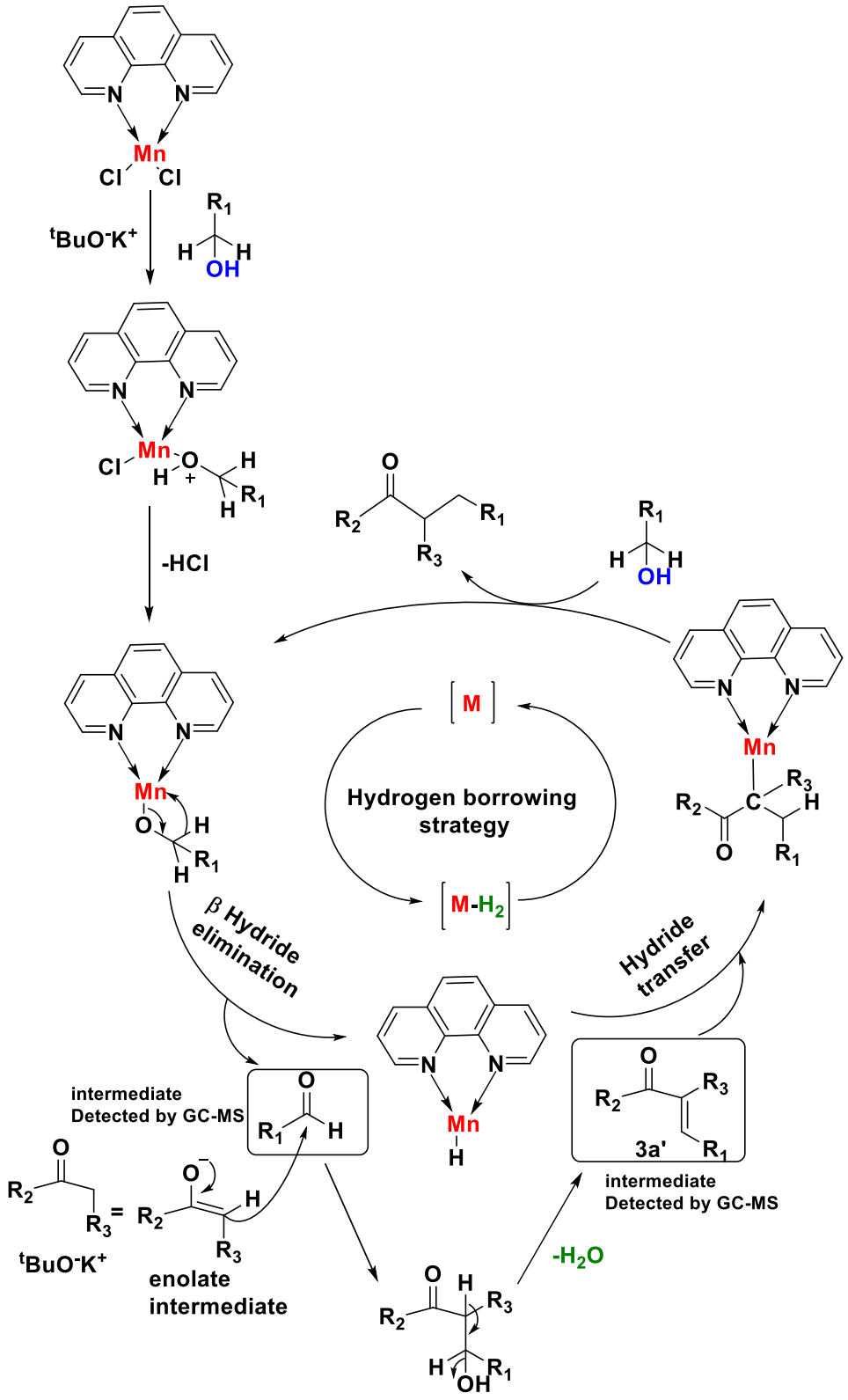
3.1 Synthetic method for the synthesis of α-substituted methylene ketones with alcohol:

0.25 mmol ketone, 0.3125 mmol alcohol, 0.25 mmol t-BuOK, 2 mL toluene, 50 mg catalyst were taken in a 25 ml round bottom flask. The reaction was performed in an oil bath under Ar atmosphere. It was heated at 140 ^{o}C for 24 h. After the completion of the reaction, the reaction mixture was left to cool down at room temperature. Then 3 mL ethyl acetate was added. The solid catalyst was easily recovered by filtration. The filtrated solution was then concentrated under reduced pressure to make a slurry for purification process by column chromatography. Hexane and ethyl acetate used as eluent for these purposes.

3.2 Synthesis of pure MnPhen Complex and its catalytic activity test:

0.007 mmols of manganese (corresponding to 0.8 wt% Mn in MnPhen@ZIF) and phenanthroline were taken into 25 mL round bottom flask using 2 mL toluene and Ar atmosphere. After stirring for 2 h, ketone (0.25 mmol), alcohol (0.3125 mmol), t-BuOK (0.25 mmol) were placed in that flask and heated at 140 ^{o}C for 24 h. When it cooled down to room temperature 3 mL ethyl acetate was added. The concentrated residue was further purified by column chromatography with the eluent system hexane and ethyl acetate.

4. Reaction Mechanism:



Scheme S1 Proposed mechanism for the Mn-catalyzed alkylation of ketones.

5. Determination of hydrogen gas produced in the reaction:

Figure S6 The set-up made for the measurement of generated H_2 gas in the reaction.

In a 15 mL oven dried Schlenk tube, propiophenone (0.25 mmol), benzylalcohol (0.3125 mmol), MnPhen@ZIF (50 mg), t-BuOK (0.25 mmol), toluene (2.0 mL) were mixed and flushed three times whole set up with Ar. Then gas burette was connected as mentioned in above Fig. S6. Then it was heated at 140 ^{o}C in an oil bath until the production of H_2 gas ceased. The procedure was repeated three times to get more accurate results.

Calculation:

Total volume of water displaced V = 17.1 ml/ 0.0171 L

Vapor pressure of water at 298K P_{H2O} = 23.7695 Torr

Atmospheric pressure at 298K P_{atm} = 758.3124 Torr

Pressure of H_2 gas,

$P_{H2} = P_{atm} - P_{H2O}$ = (758.3124 - 23.7695) Torr = 734.5429 Torr

Since $P_{H2} * V = n_{H2}*R*T$

or $n_{H2} = P_{H2} * V / R*T$ = 734.5429 Torr * 0.0171 L / 62.3635 L Torr K^{-1} mol^{-1} * 298K

= 0.0006758 mol

= 0.68 mmol

6. Collection of hydrogen gas produced in reaction for GC measurement

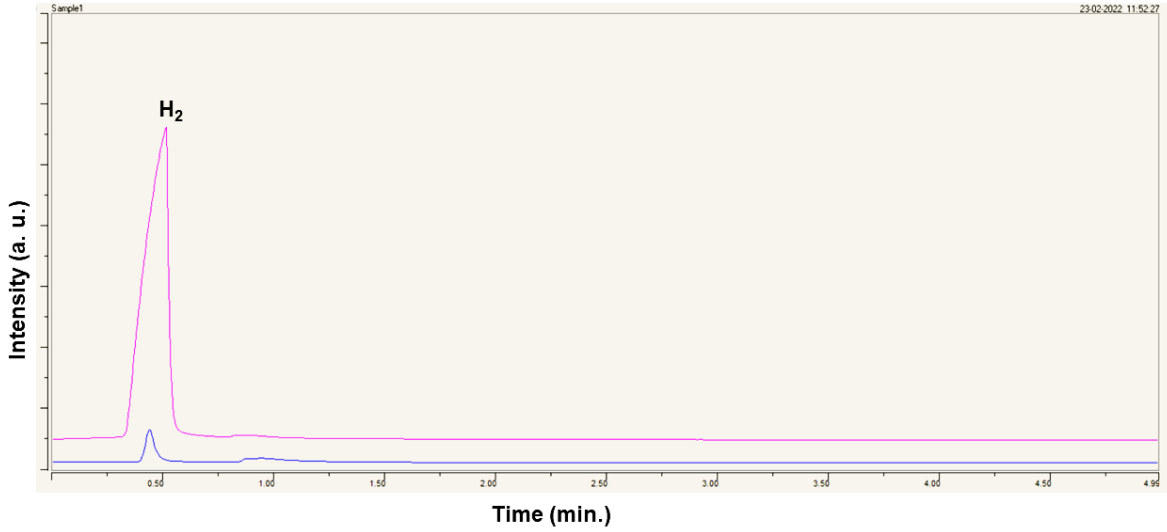
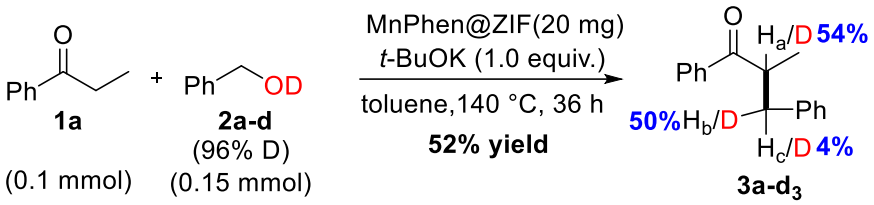
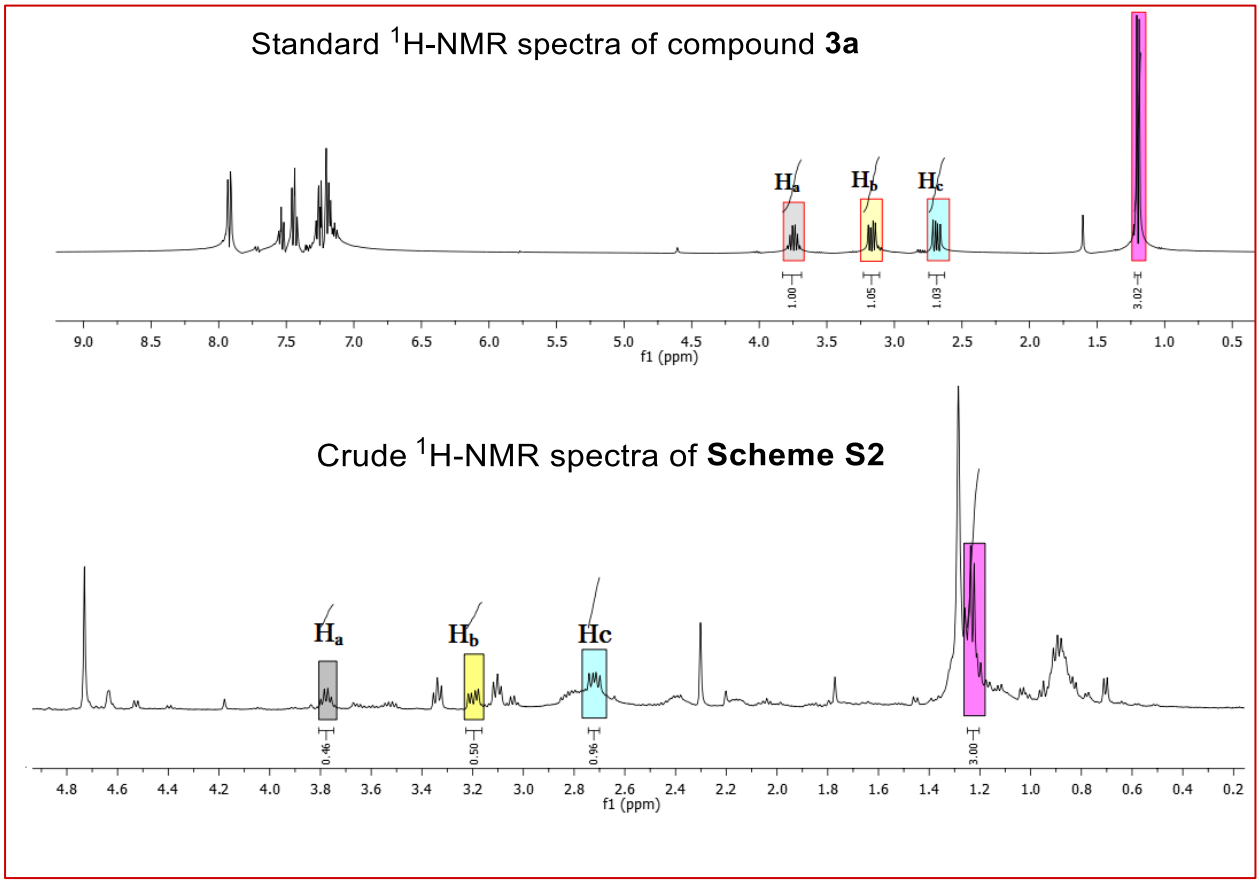


Figure S7 The set-up made for the collection of generated H_2 gas in the reaction (conditioned were same as mentioned in section 5) (above). Gas chromatographs of the collected gas in reaction mentioned as blue line, which has same retention time as pure H_2 shown in pink line (below).

7. Deuterium labelling experiments

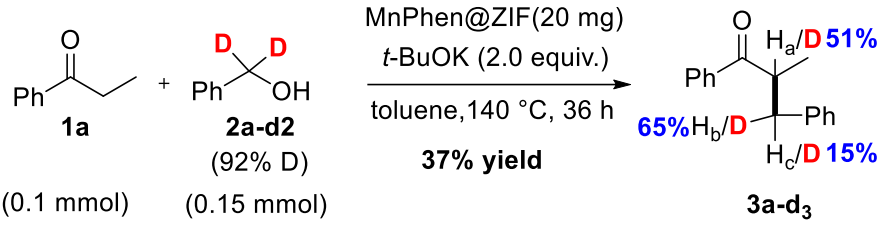
a) Scheme S2

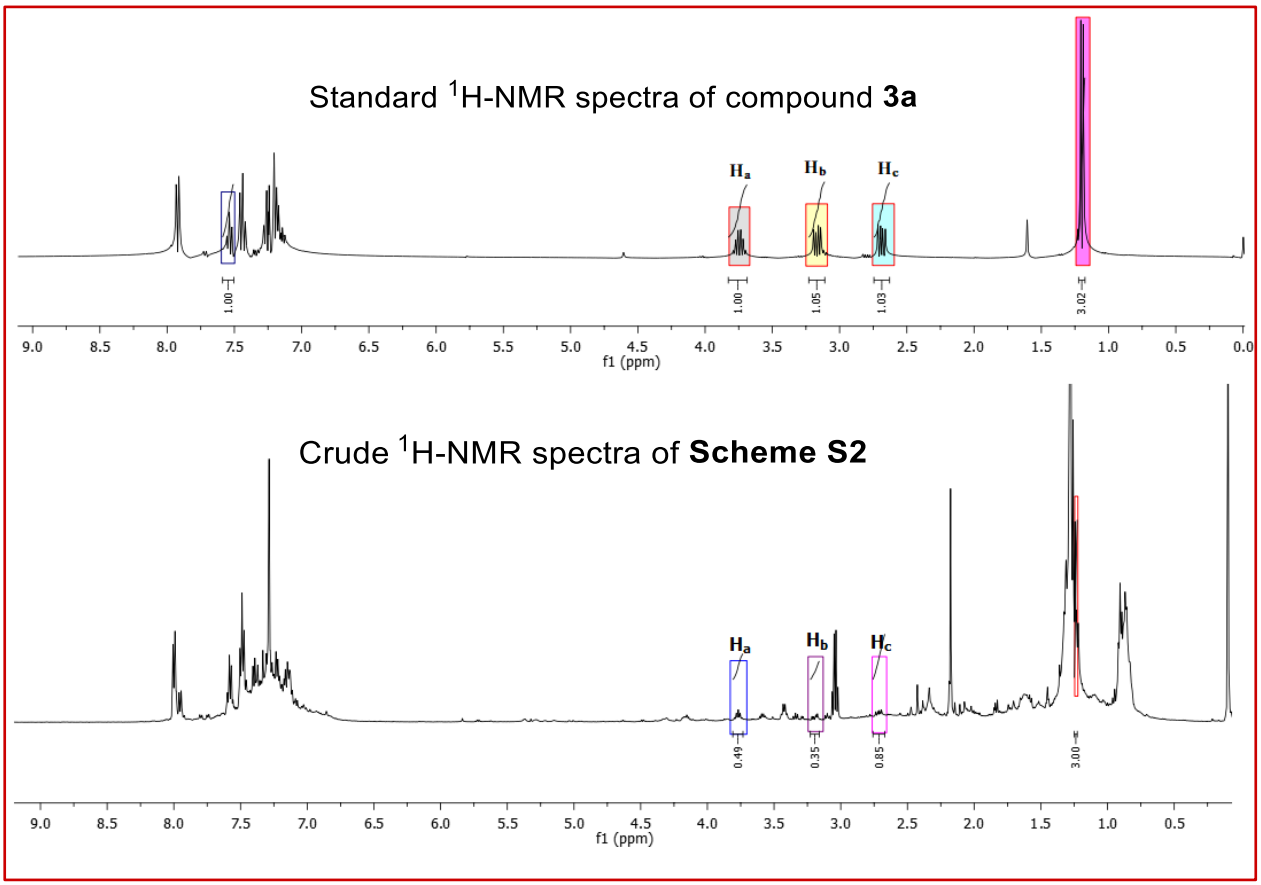




		Deuterium incorporation in **H_a** Position	Deuterium incorporation in **H_b** Position	Deuterium incorporation in **H_c** Position
Signal δ (ppm)	1.2 [d, CH_3, (3H)]	3.77 (1H)	3.19 (1H)	2.71 (1H)
Integral Value	3.0	0.46	0.50	0.96
Calculated ratio		(1-0.46)×100 = **54%**	(1-0.50)×100 = **50%**	(1-0.96)×100 = **4%**

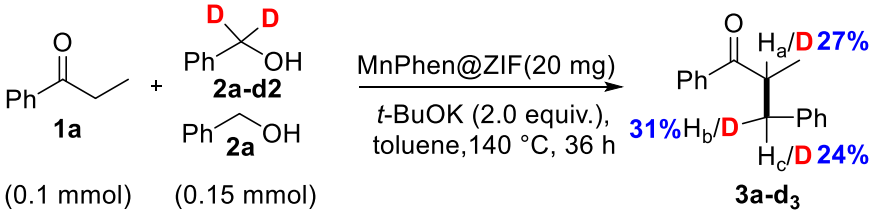
b) Scheme S3



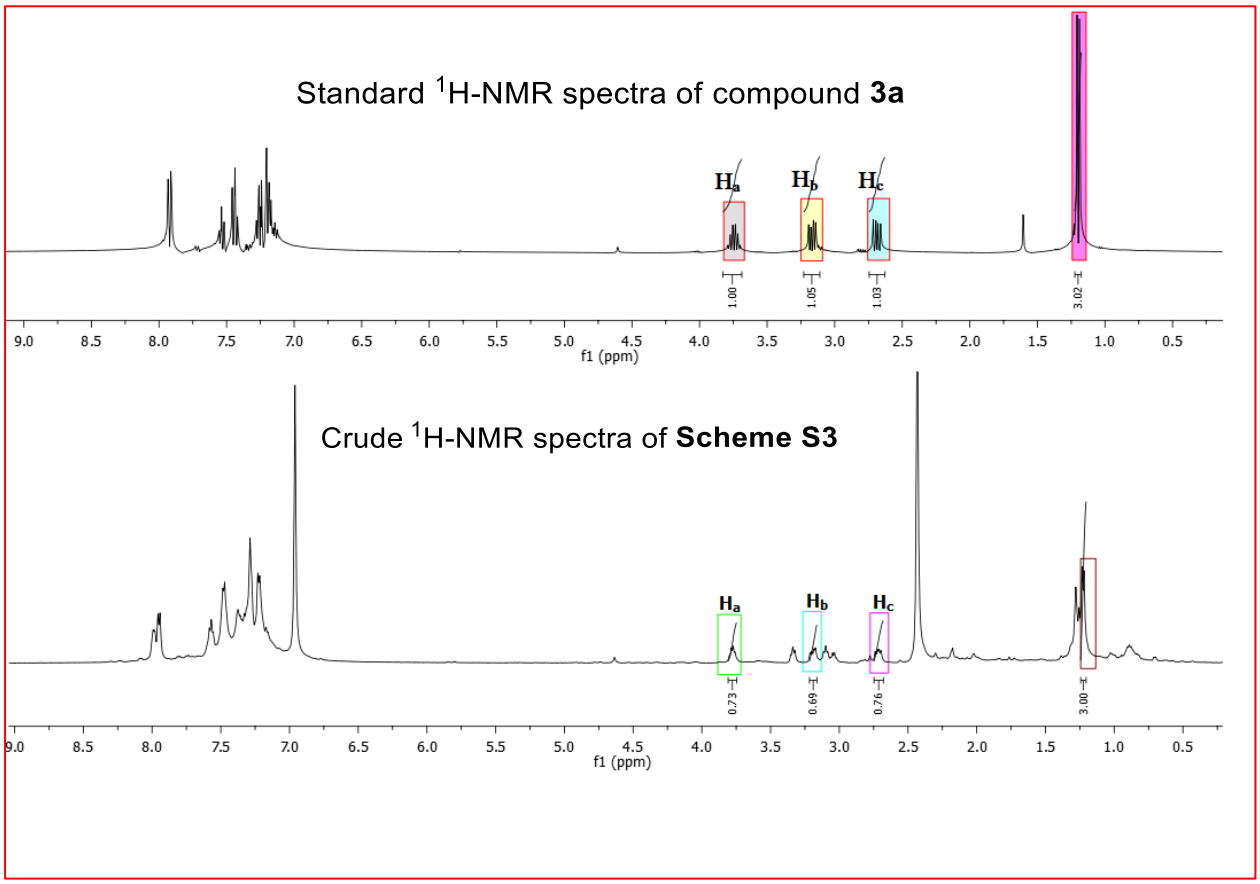


		Deuterium incorporation in **H_a** Position	Deuterium incorporation in **H_b** Position	Deuterium incorporation in **H_c** Position
Signal δ (ppm)	1.2 [d, CH_3, (3H)]	3.77 (1H)	3.19 (1H)	2.71 (1H)
Integral Value	3.0	0.49	0.35	0.85
Calculated ratio		(1-0.49)×100 = **51%**	(1-0.35)×100 = **65%**	(1-0.85)×100 = **15%**

c) Scheme S4

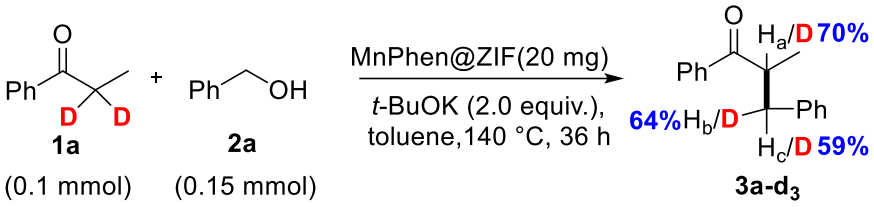


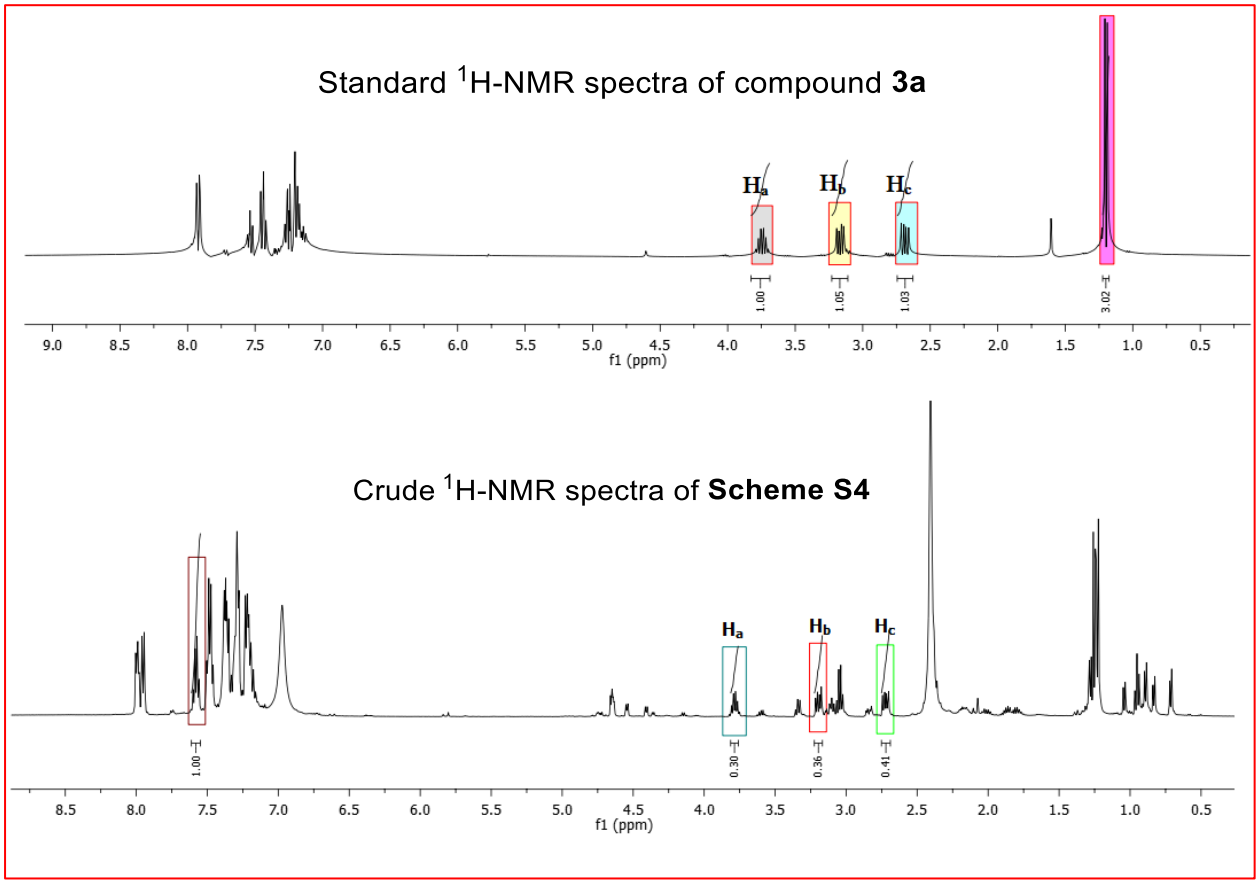
(0.1 mmol) (0.15 mmol)



		Deuterium incorporation in **H_a** Position	Deuterium incorporation in **H_b** Position	Deuterium incorporation in **H_c** Position
Signal δ (ppm)	1.2 [d, CH_3, (3H)]	3.77 (1H)	3.19 (1H)	2.71 (1H)
Integral Value	3.0	0.73	0.69	0.76
Calculated ratio		(1-0.73)×100 = **27%**	(1-0.69)×100 = **31%**	(1-0.76)×100 = **24%**

d) Scheme S5





		Deuterium incorporation in **H_a** Position	Deuterium incorporation in **H_b** Position	Deuterium incorporation in **H_c** Position
Signal δ (ppm)	7.54 [m, *p*-Ar-H, (1H)]	3.77 (1H)	3.19 (1H)	2.71 (1H)
Integral Value	1.0	0.30	0.36	0.41
Calculated ratio		(1-0.30)×100 = **70%**	(1-0.36)×100 = **64%**	(1-0.41)×100 = **59%**

8. Reusability test with MnPhen@ZIF

After completion of the reaction as mentioned in section 3.1, the solid product was separated out by filtration and washed with ethyl acetate and dried in oven at room temperature. In 2nd catalytic cycle, solid catalyst was further activated at 150 °C under vacuum and performed same as first cycle. Similarly, 3rd and 4th cycles were measured, and product conversion were determined by GC-MS.

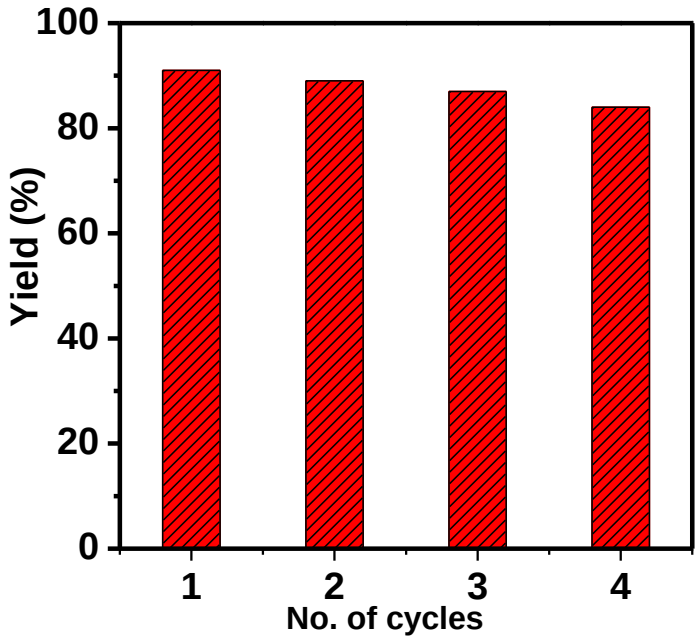


Figure S8 Recyclability test of MnPhen@ZIF for the synthesis of 2-Methyl-1,3-diphenylpropan-1-one (**3a**).

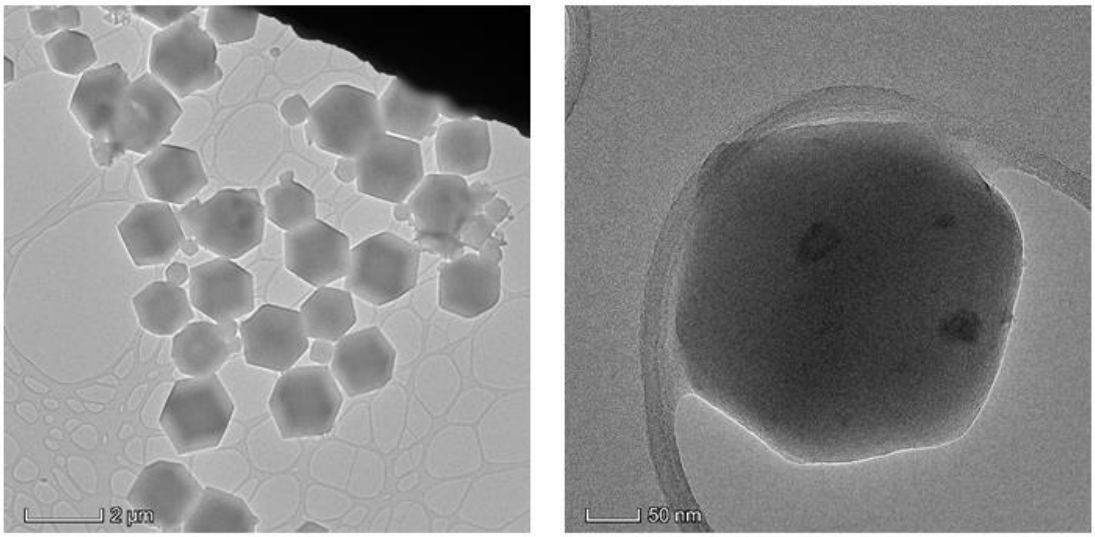


Figure S9 TEM images of MnPhen@ZIF after catalysis.

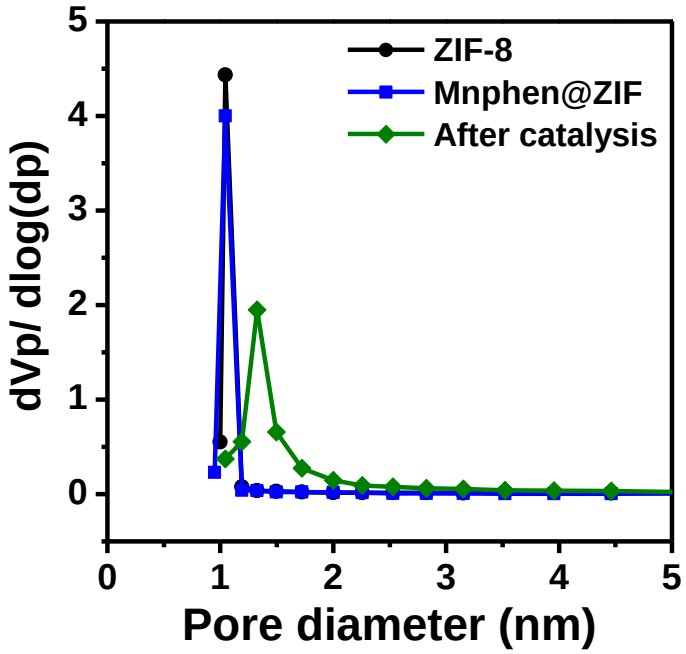


Figure S10 Pore size distribution of ZIF-8, MnPhen@ZIF (before catalysis), and MnPhen@ZIF (after catalysis).

Catalyst	Average pore size (nm)	Average pore volume ($cm^3 g^{-1}$)
ZIF-8	1.21	0.68
MnPhen@ZIF (before catalysis)	1.20	0.66
MnPhen@ZIF (after catalysis)	1.47	0.52

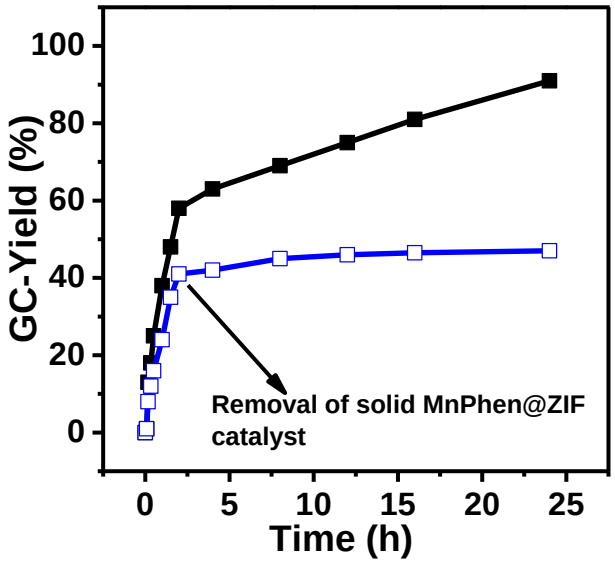


Figure S11 Hot filtration test indicating no further formation of branched ketone product 3a after removal of solid MnPhen@ZIF catalyst. Black line curve is product formation vs time plot till completion of the reaction (24 h), while blue curve is for second batch of reaction where catalyst was removed by hot filtration at the time of ~2 h.

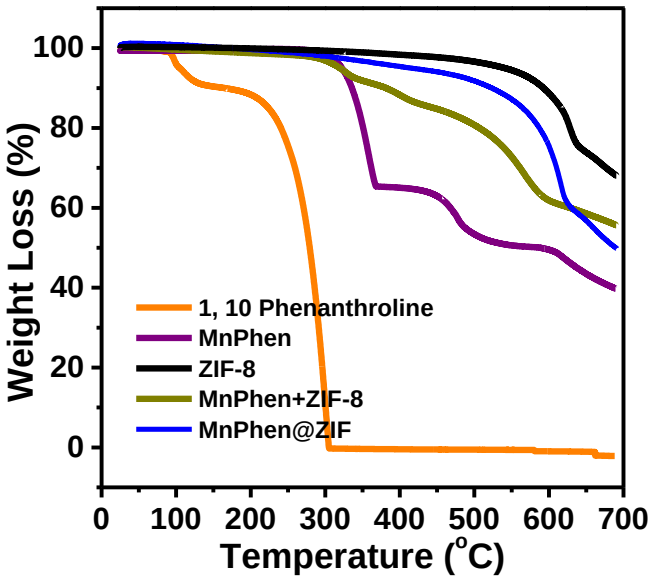


Figure S12 A comparison of TGA curves of as-synthesized catalyst MnPhen@ZIF, a mixture of MnPhen+ZIF-8 complex, pristine ZIF-8, MnPhen complex, and Phen ligand itself. This data suggests that MnPhen@ZIF and its encapsulated Mn-complex is stable under experimental catalytic reaction temperature ie; at 140 ^{o}C.

9. Calculations of Lewis acidity using NH_3-TPD measurements

Area under the NH_3-TPD profile of catalyst = A

Number of mmol of NH_3 = 0.294 × A

Catalyst mass = B g

Total acidity of catalyst = mmol of NH_3/Catalyst mass

= (0.294×A/B) mmol NH_3/g catalyst

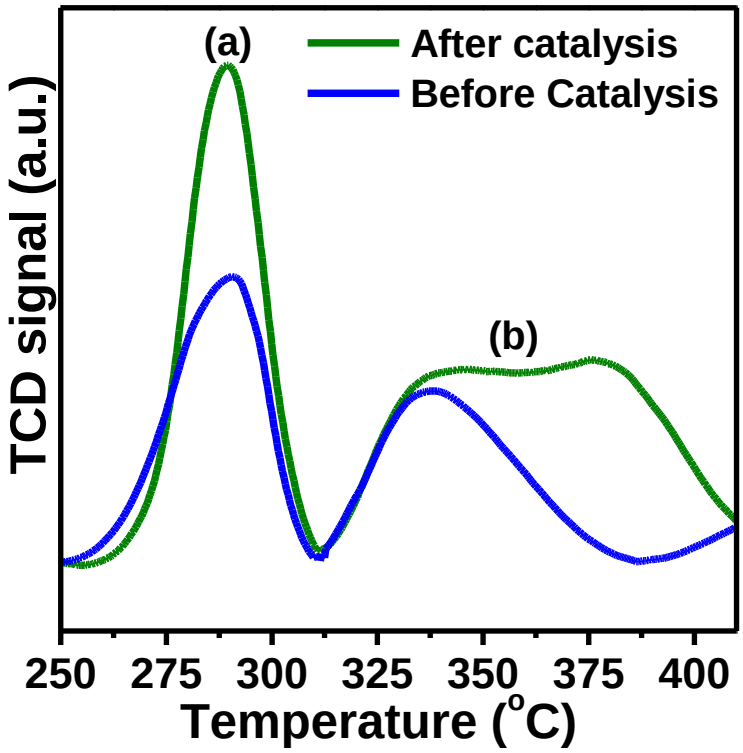


Figure S13 NH_3-TPD profiles for MnPhen@ZIF before and after catalysis.

MnPhen@ZIF	Acidity (mmol/g)
Before catalysis	a) 9.51 b) 8.17
After catalysis	a) 16.69 b) 21.92

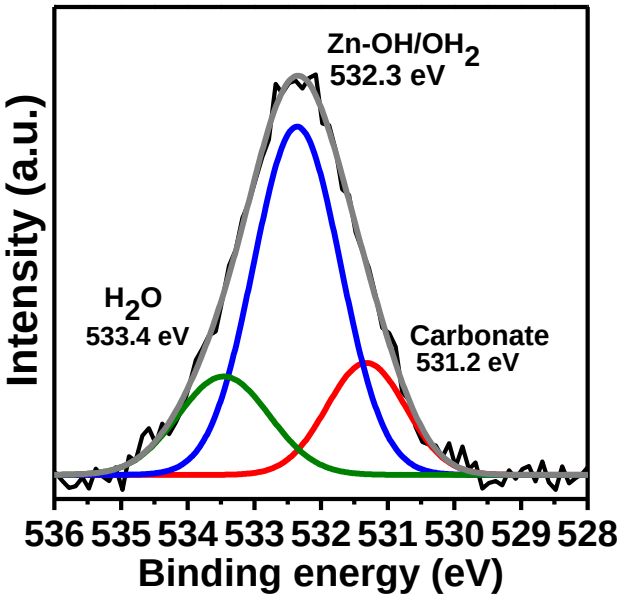


Figure S14 O 1s XPS spectrum of MnPhen@ZIF after catalysis

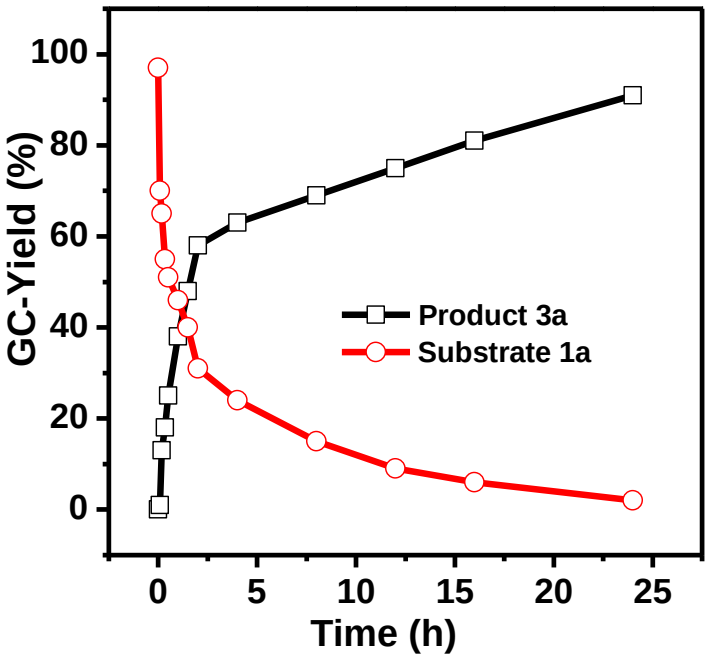


Figure S15 Formation of product 3a and decrease in concentration of 1a with reaction time in presence of catalyst MnPhen@ZIF.

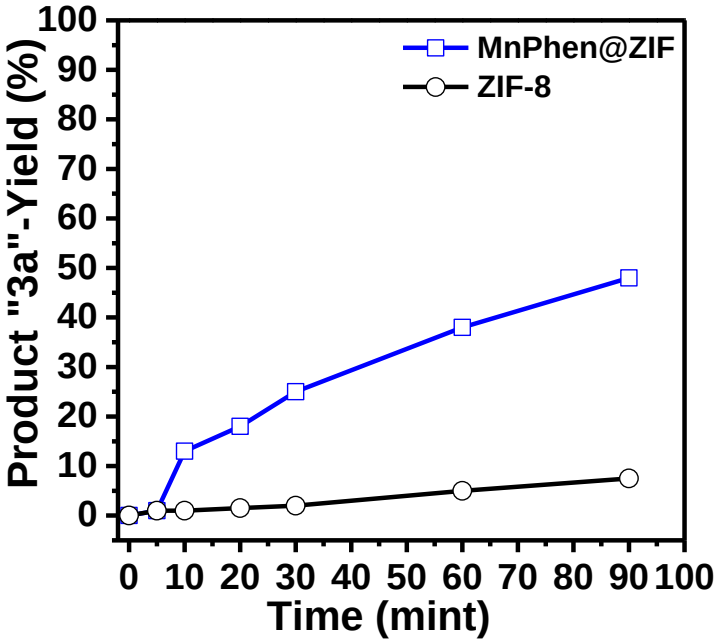
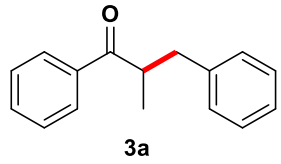


Figure S16 Comparison of product 3a formation with respect to initial period of time in presence of catalyst MnPhen@ZIF and ZIF-8.

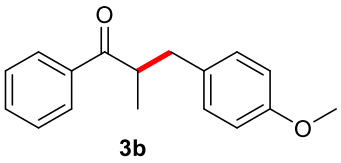
7. Analytical Data

2-Methyl-1,3-diphenylpropan-1-one (3a): According to the procedure described in section 3.1, the mentioned product obtained as colorless solid (46 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.4, 1.3 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.21 – 7.13 (m,3H), 3.74 (dq, J = 13.5, 6.7 Hz, 1H), 3.17 (dd, J = 13.9, 6.4 Hz, 1H), 2.69 (dd, J = 13.9, 8.0 Hz, 1H), 1.20 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.77, 139.92, 136.39, 132.92, 129.07, 128.62, 128.35, 128.27, 126.17, 42.74, 39.32, 17.38.



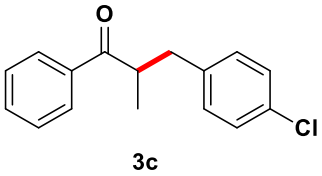
3a

3-(4-Methoxyphenyl)-2-methyl-1-phenylpropan-1-one (3b): According to the procedure described in section 3.1, the mentioned product obtained as colourless oil (41 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.3 Hz, 2H), 7.52 (m, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 3.76 (s, 3H), 3.73-3.65 (m, 1H), 3.10 (dd, J = 13.8, 6.4 Hz, 1H), 2.63 (dd, J = 13.8, 7.7 Hz, 1H), 1.18 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.4, 154.1, 133.0, 132.1, 130.1, 128.7, 128.3, 113.7, 109.5, 55.3, 43.0, 38.6, 17.4.



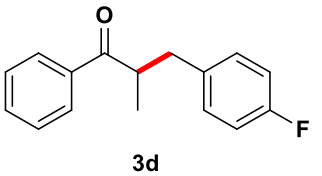
3b

3-(4-Chlorophenyl)-2-methyl-1-phenylpropan-1-one (3c): According to the procedure described in section 3.1, the mentioned product obtained as colorless liquid (34 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.7 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.3 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.9 Hz, 2H), 3.81 – 3.70 (m, 1H), 3.18 (dd, J = 14.4, 7.2 Hz, 1H), 2.72 (dd, J = 14.4, 7.6 Hz, 1H), 1.24 (d, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3, 138.4, 133.0, 132.0, 130.4, 128.7, 128.6, 128.5, 128.2, 42.7, 38.6, 17.6.



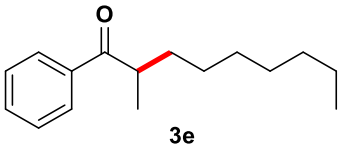
3c

3-(4-Fluorophenyl)-2-methyl-1-phenylpropan-1-one (3d): According to the procedure described in section 3.1, the mentioned product obtained as colorless liquid (29 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.9 Hz, 2H), 7.13 (dd, J = 9.0, 5.6 Hz, 2H), 6.92 (t, J = 8.9 Hz, 2H), 3.70 (dd, J = 14.2, 7.1 Hz, 1H), 3.12 (dd, J = 14.1, 7.0 Hz, 1H), 2.67 (dd, J = 14.0, 7.5 Hz, 1H), 1.19 (d, J = 7.1 Hz, 3H).



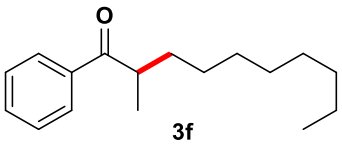
3d

2-methyl-1-phenylnonan-1-one (3e): According to the procedure described in section 3.1, the mentioned product obtained as colorless oil (29 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.3 Hz, 2H), 7.57 (d, J = 6.9 Hz, 1H), 7.49 (t, J = 6.8 Hz, 2H), 3.49 – 3.47 (m, 1H), 1.82 (dd, J = 12.8, 6.5 Hz, 1H), 1.45 (d, J = 5.8 Hz, 1H), 1.27 (s, 10H), 1.22 (d, J = 6.6 Hz, 3H), 0.89 (s, 3H).



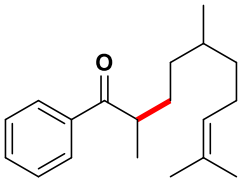
3e

2-methyl-1-phenyldecan-1-one (3e): According to the procedure described in section 3.1, the mentioned product obtained as colorless oil (28 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.3 Hz, 2H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 3.51 – 3.45 (m, 1H), 1.81 (dd, *J* = 24.3, 13.1 Hz, 1H), 1.47 (d, *J* = 17.6 Hz, 1H), 1.28 (d, *J* = 12.9 Hz, 12H), 1.22 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H).



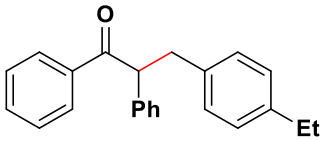
3f

2,5,9-Trimethyl-1-phenyldec-8-en-1-one (3g): According to the procedure described in section 3.1, the mentioned product obtained as a pale yellow oil (40 mg, 59% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 2H), 7.55 (dd, *J* = 8.2, 6.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.05 (ddd, *J* = 12.8, 5.8, 1.3 Hz, 1H), 3.41 (ddd, *J* = 13.5, 6.7, 2.2 Hz, 1H), 1.98 – 1.74 (m, 3H), 1.65 (d, *J* = 4.2 Hz, 3H), 1.57 (d, *J* = 5.0 Hz, 2H), 1.46 – 1.23 (m, 5H), 1.18 (d, *J* = 6.9 Hz, 3H), 1.15 – 1.08 (m, 2H), 0.84 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 133.3, 132.8, 131.2, 129.0, 128.7, 128.3, 40.9, 37.0, 36.8, 34.6, 32.57, 31.2, 25.5, 19.5, 17.2



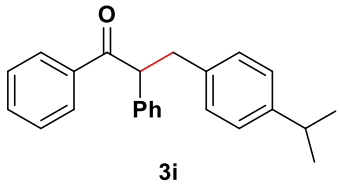
3g

3-(4-ethylphenyl)-1,2-diphenylpropan-1-one (3h): According to the procedure described in section 3.1, the mentioned product obtained as colorless solid (60 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.1 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.27 – 7.16 (m, 5H), 7.05 – 6.98 (m, 4H), 4.84 – 4.78 (m, 1H), 3.55 (dd, J = 13.8, 7.7 Hz, 1H), 3.02 (dd, J = 13.8, 6.7 Hz, 1H), 2.56 (q, J = 7.6 Hz, 2H), 1.18 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.29, 141.94, 139.22, 136.92, 136.72, 132.79, 128.99, 128.86, 128.66, 128.43, 128.26, 127.69, 127.07, 55.88, 39.68, 28.38, 15.55.



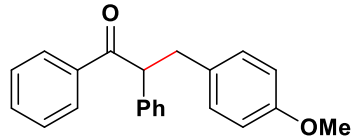
3h

3-(4-isopropylphenyl)-1,2-diphenylpropan-1-one (3i): According to the procedure described in section 3.1, the mentioned product obtained as colorless solid (65 mg, 79%); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.1 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.6 Hz 2H), 7.28 – 7.18 (m, 5H), 7.04 (q, J = 8.3 Hz, 4H), 4.82 (t, J = 7.9, 1H), 3.57 (dd, J = 13.8, 7.9 Hz, 1H), 3.02 (dd, J = 13.8, 6.5 Hz, 1H), 2.88 – 2.75 (m, 1H), 1.19 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.27, 146.57, 139.29, 137.08, 136.73, 132.77, 128.95, 128.86, 128.66, 128.41, 128.25, 127.06, 126.25, 55.82, 39.66, 33.60, 23.97.



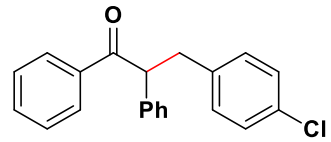
3i

3-(4-methoxyphenyl)-1,2-diphenylpropan-1-one (3j): According to the procedure described in section 3.1, the mentioned product obtained as colorless solid (48 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.1 Hz), 7.44 (t, J = 8.0 Hz), 7.34 (t, J = 7.6 Hz), 7.24 – 7.22 (m), 6.99 (d, J = 8.7 Hz), 6.73 (d, J = 8.7 Hz), 4.77 (t, J = 7.3 Hz), 3.73 (s), 3.50 (dd, J = 13.8, 7.5 Hz), 3.00 (dd, J = 13.8, 7.0 Hz). ^{13}C NMR (101 MHz,) δ 199.37, 157.86, 139.09, 136.70, 132.80, 131.79, 130.04, 128.84, 128.63, 128.43, 128.26, 127.06, 113.57, 56.12, 55.12, 39.22.



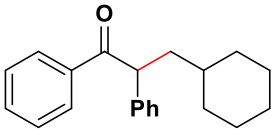
3j

3-(4-chlorophenyl)-1,2-diphenylpropan-1-one (3k): According to the procedure described in section 3.1, the mentioned product obtained as colorless solid (71 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.1 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.5 Hz, 3H), 7.21 (d, J = 6.9 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.01 – 6.98 (m, 2H), 4.75 (t, J = 7.3 Hz, 1H), 3.50 (dd, J = 13.8, 7.4 Hz, 1H), 3.03 (dd, J = 13.8, 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.89, 138.66, 138.18, 136.47, 132.98, 130.49, 128.98, 128.66, 128.51, 128.31, 128.22, 127.38, 127.28, 55.83, 39.39.



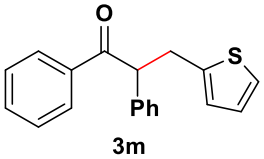
3k

3-Cyclohexyl-1,2-diphenylpropan-1-one (3l): According to the procedure described in section 3.1, the mentioned product obtained as colorless solid (31 mg, 42%); ^{1}H NMR (400 MHz,) δ 7.98 (d, J = 8.5 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.40 – 7.36 (m, 2H), 7.32 – 7.24 (m, 4H), 7.20 – 7.17 (m, 1H), 4.72 (t, J = 7.5 Hz, 1H), 2.15 – 2.04 (m, 1H), 1.74 – 1.69 (m, 6H), 1.20 – 1.08 (m, 4H), 0.96 – 0.90 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.95, 139.93, 136.83, 132.73, 128.78, 128.56, 128.45, 128.14, 126.79, 50.39, 41.63, 35.20, 33.49, 33.20, 26.43, 26.28, 26.08.



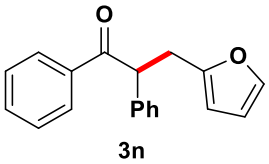
3l

1,2-diphenyl-3-(thiophen-2-yl)propan-1-one (3m): According to the procedure described in section 3.1, the mentioned product obtained as colorless solid (34 mg, 47%); ^{1}H NMR (400 MHz,) δ 7.94 (d, J = 8.3 Hz, 2H), 7.47 – 7.45 (m, J = 7.4 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.29 (dd, J = 3.8, 3.3 Hz ,4H), 7.25 – 7.19 (m, 1H), 7.06 (d, J = 5.1 Hz, 1H), 6.83 (dd, J = 5.1, 3.4 Hz, 1H), 6.69 (d, J = 4.5 Hz, 1H), 4.85 (dd, J = 7.9 Hz, 6.6 Hz, 1H), 3.79 (dd, J = 15.5, 7.9 Hz, 1H), 3.28 (dd, J = 14.8, 6.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.79, 142.03, 138.58, 136.44, 132.99, 128.98, 128.72, 128.50, 128.20, 127.35, 126.64, 125.68, 123.62, 56.03, 34.10, 22.34, 14.08.



3m

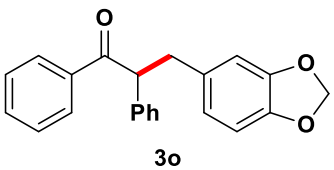
((S)-3-(furan-2-yl)-1,2-diphenylpropan-1-one (3n): According to the procedure described in section 3.1, the mentioned product obtained as a pale yellow solid (20 mg, 28% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.93 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.5 (m, 1H), 7.4 (m, 2H), 7.3 (m, 5H), 7.2 (m, 1H), 6.2 (dd, J = 3.1, 1.9 Hz, 1H), 5.9 (dd, J = 3.1, 0.5 Hz, 1H), 4.98 (dd, *J* = 7.7, 6.9 Hz, 1H), 3.60 – 3.53 (m, 1H), 3.09 (dd, *J* = 15.1, 6.8 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) *δ* 198.8, 153.3, 141.1, 138.7, 136.4, 132.9, 128.9, 128.7, 128.5, 128.0, 110.2, 106.5, 52.5, 32.4.



3n

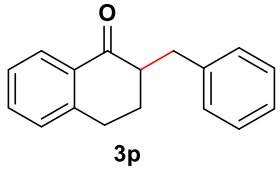
(S)-3-(benzo[d][1,3]dioxol-5-yl)-1,2-diphenylpropan-1-one (3o):

Following the general procedure B, the title product was obtained as a colorless solid (48 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.73 – 7.71 (m, 2H), 7.46 (t, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.22 – 7.12 (m, 5H), 6.60 (ddd, J = 20.1, 12.1, 8.0 Hz, 3H), 5.86 (dd, *J* = 3.3, 1.5 Hz, 2H), 3.98 – 3.91 (m, 1H), 3.06 (ddd, *J* = 24.3, 13.9, 8.0 Hz, 2H), 2.74 (ddd, *J* = 27.1, 13.9, 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 203.3, 147.5, 145.9, 139.5, 137.5, 137.4, 133.3, 132.8, 129.0, 128.5, 128.4, 128.1, 126.3, 122.0, 109.4, 108.2, 100.8, 50.7, 38.2, 37.9.



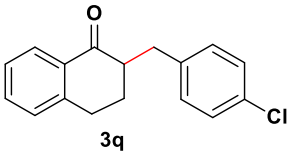
3o

2-Benzyl-3,4-dihydronaphthalen-1(2H)-one (3p): According to the procedure described in section 3.1, the mentioned product obtained as colorless liquid (50.2 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.25 – 7.21 (m, 4H), 3.50 (dd, *J* = 13.7, 3.9 Hz, 1H), 2.96-2.91 (m, 2H), 2.79 – 2.72 (m, 1H), 2.65 (dd, *J* = 13.7, 9.6 Hz, 1H), 2.13 – 2.08 (m, 1H), 1.84 – 1.74 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.38, 144.02, 139.99, 133.26, 132.42, 129.25, 128.70, 128.38, 127.52, 126.60, 126.10, 49.43, 35.63, 28.60, 27.62.



3p

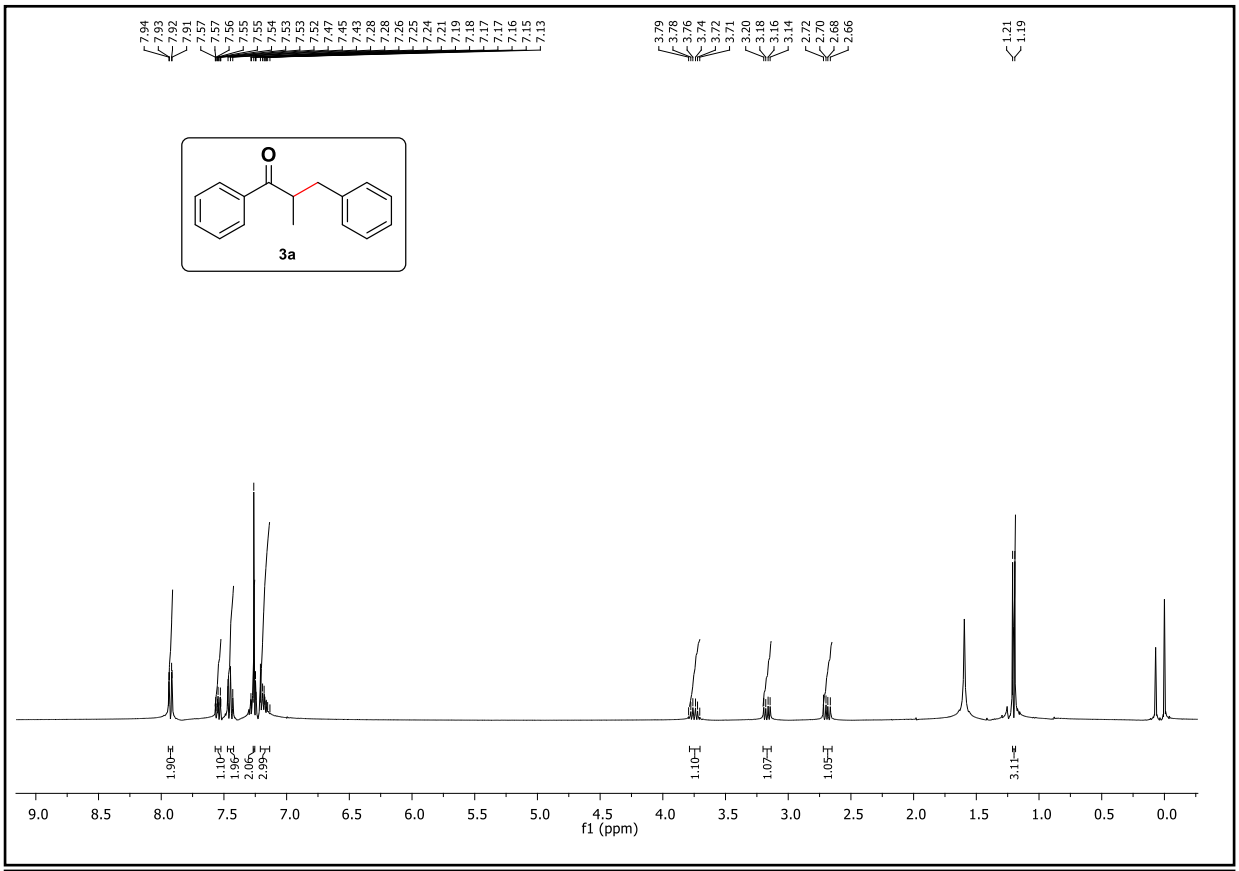
2-(4-chlorobenzyl)-3,4-dihydronaphthalen-1(2H)-one (3q): According to the procedure described in section 3.1, the mentioned product obtained as colorless liquid (61.6 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 1H), 7.47- 7.43 (m, 1H), 7.32- 7.26 (m, 3H), 7.24- 7.14 (m, 3H), 3.43- 3.39 (m, 1H), 2.97- 2.90 (m, 2H), 2.73- 2.61(m, 2H) , 2.11-2.02 (m, 1H), 1.81 - 1.71 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.09, 143.93, 138.63, 133.25, 132.40, 130.59, 128.69, 127.40, 126.59, 49.23, 35.20, 28.83, 27.72.

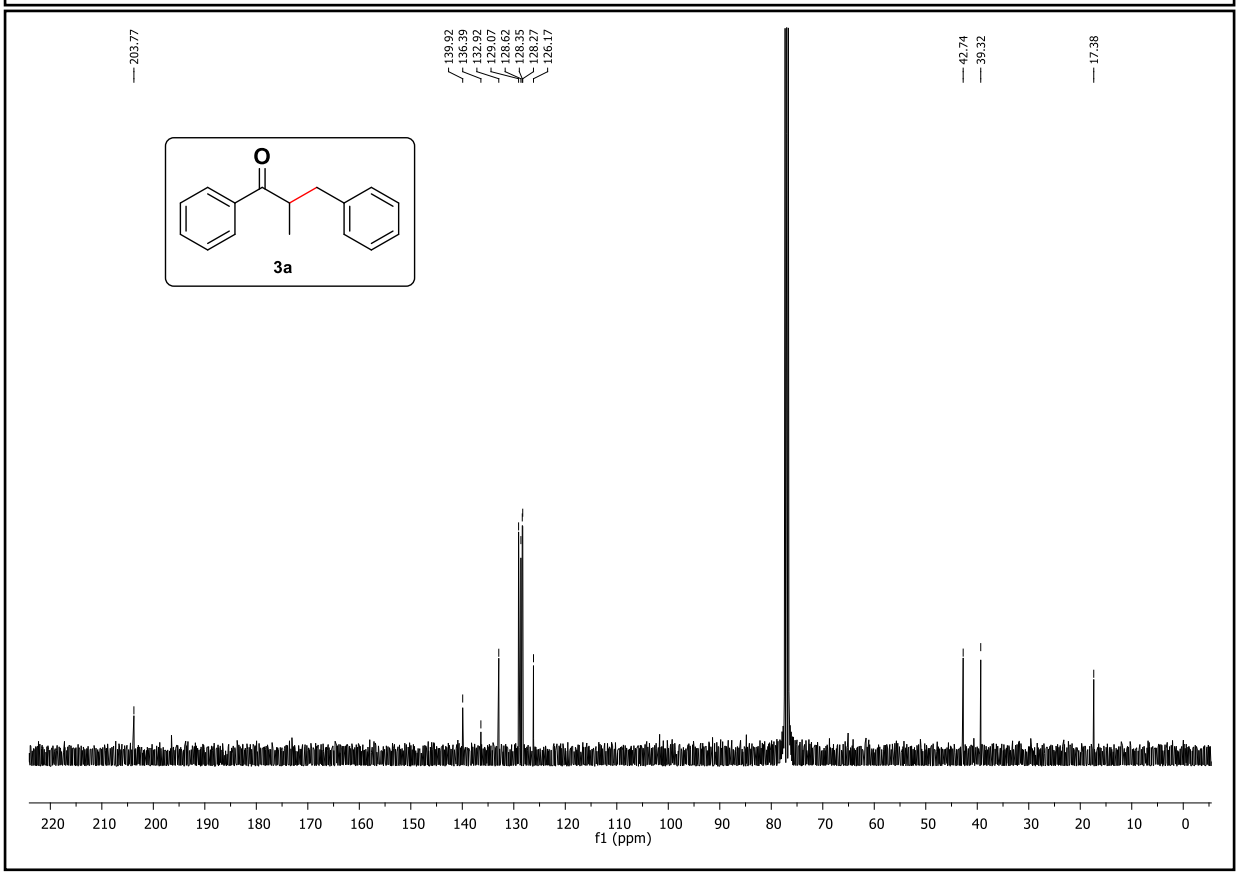


3q

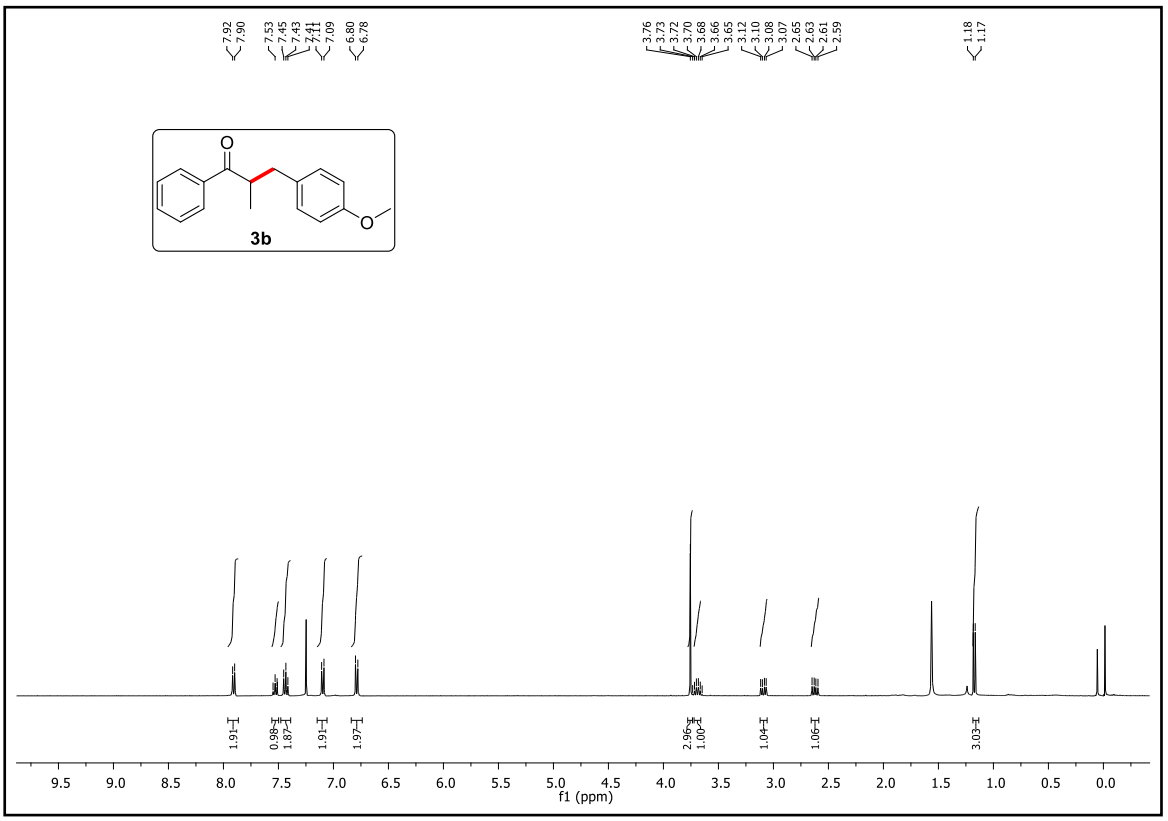
All ^{1}H & ^{13}C NMR data:

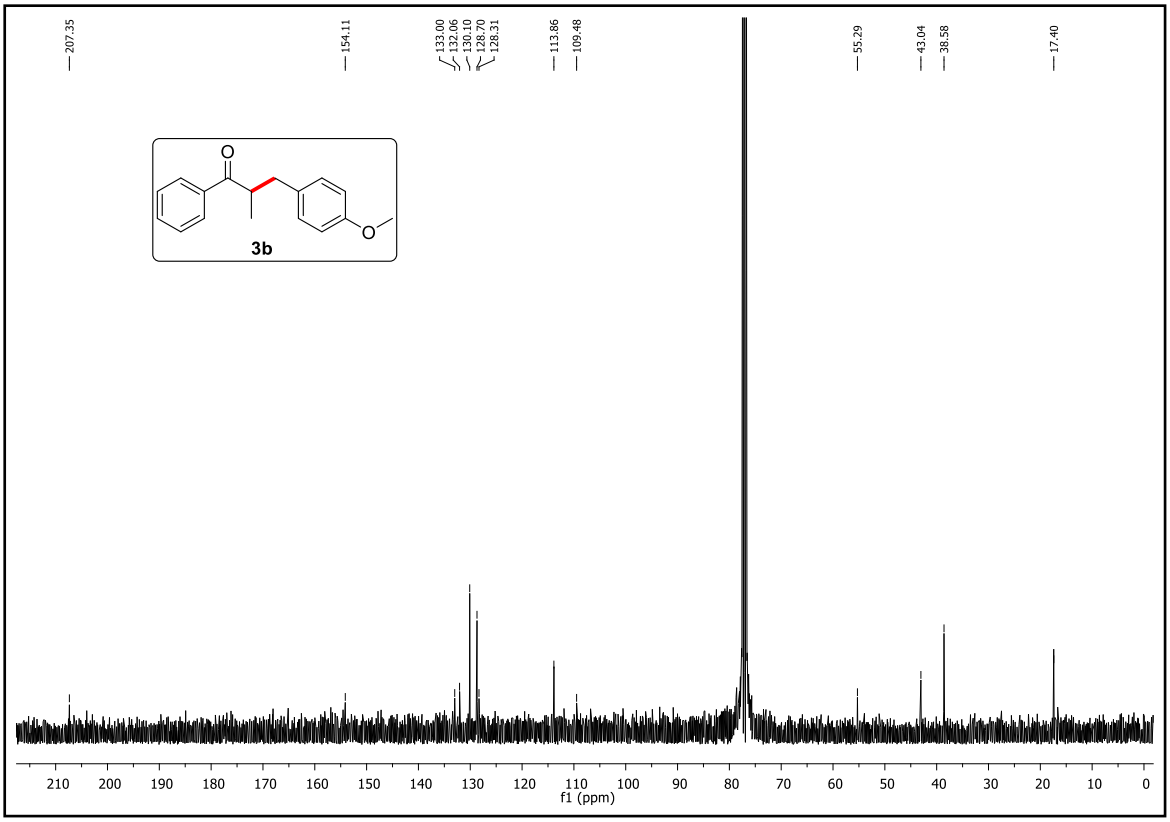
2-Methyl-1,3-diphenylpropan-1-one:



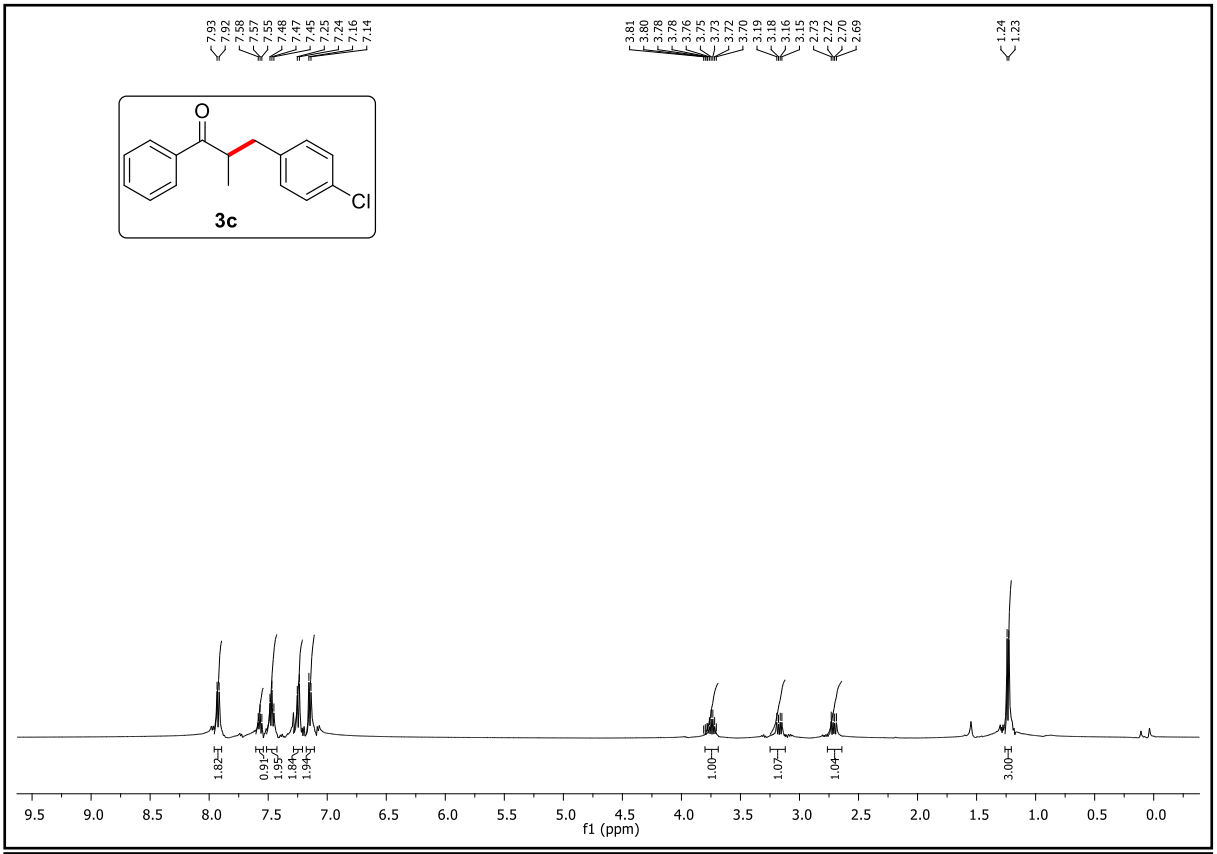


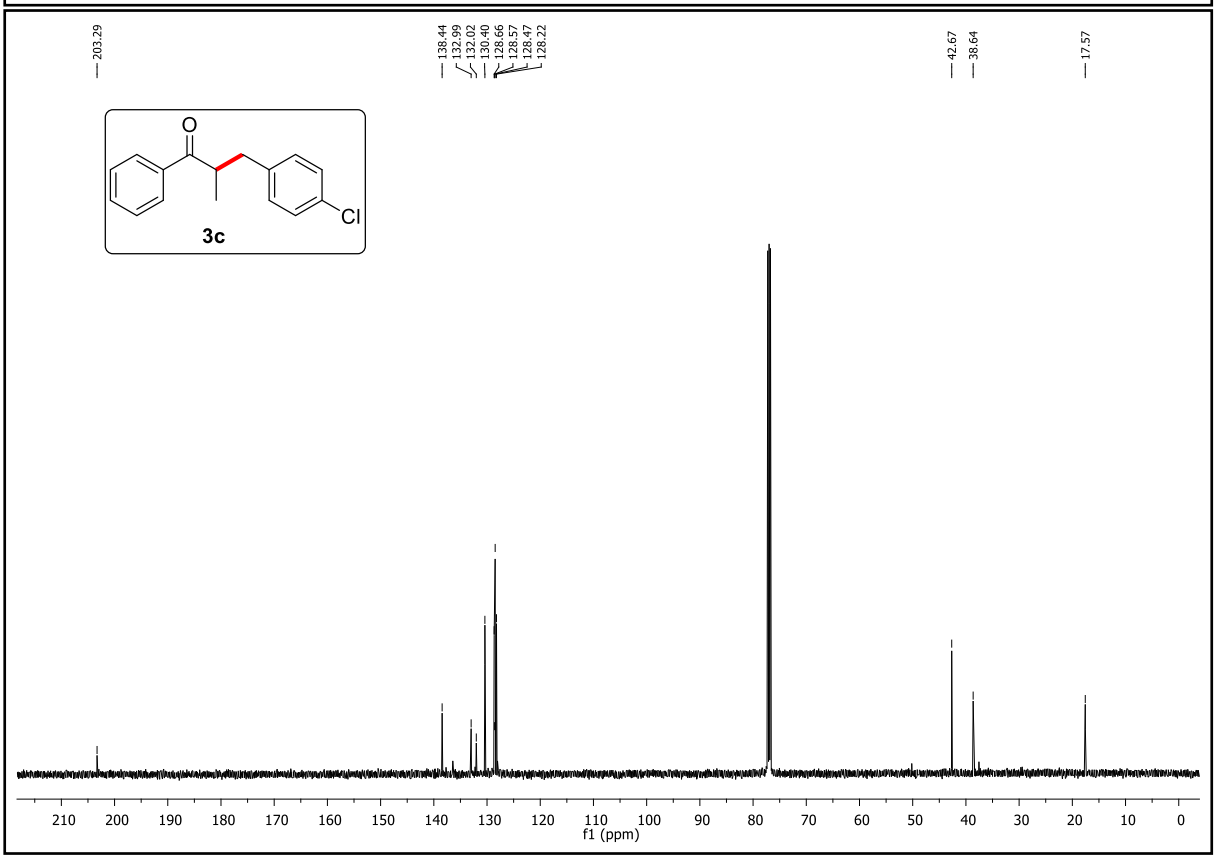
3-(4-Methoxyphenyl)-2-methyl-1-phenylpropan-1-one:



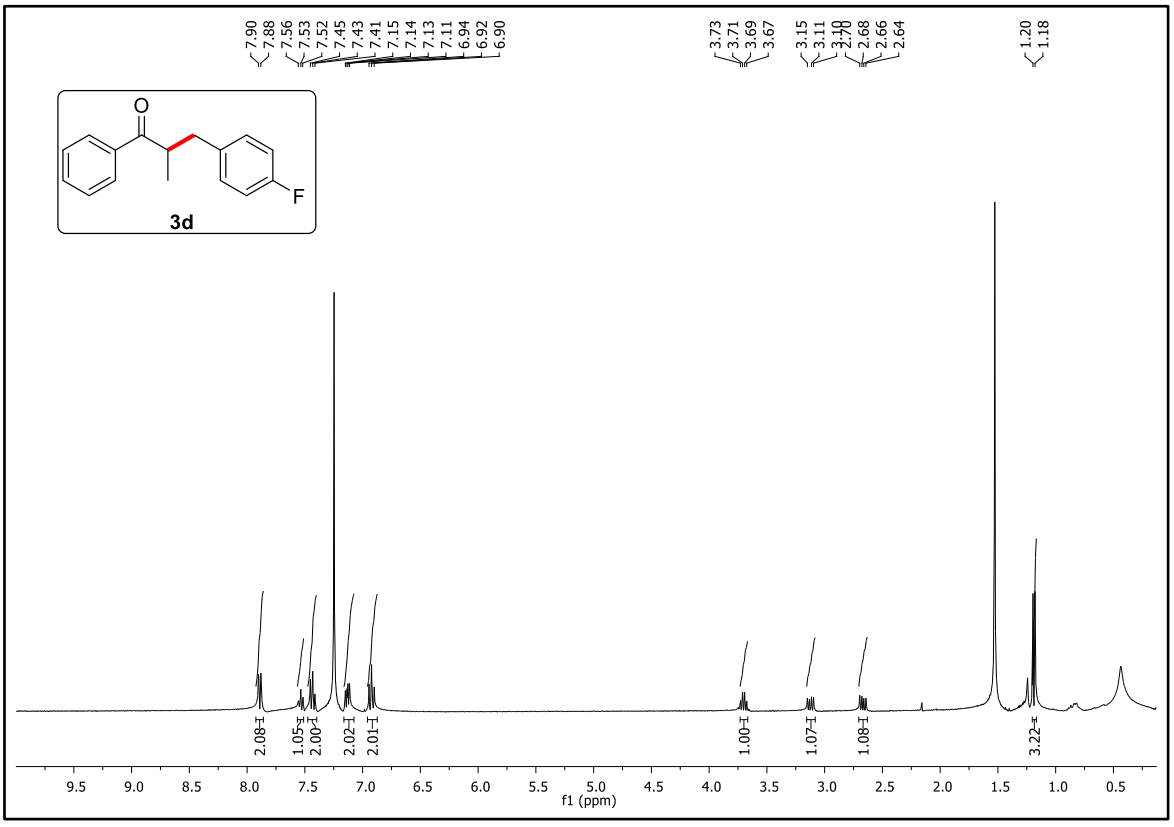


3-(4-Chlorophenyl)-2-methyl-1-phenylpropan-1-one:

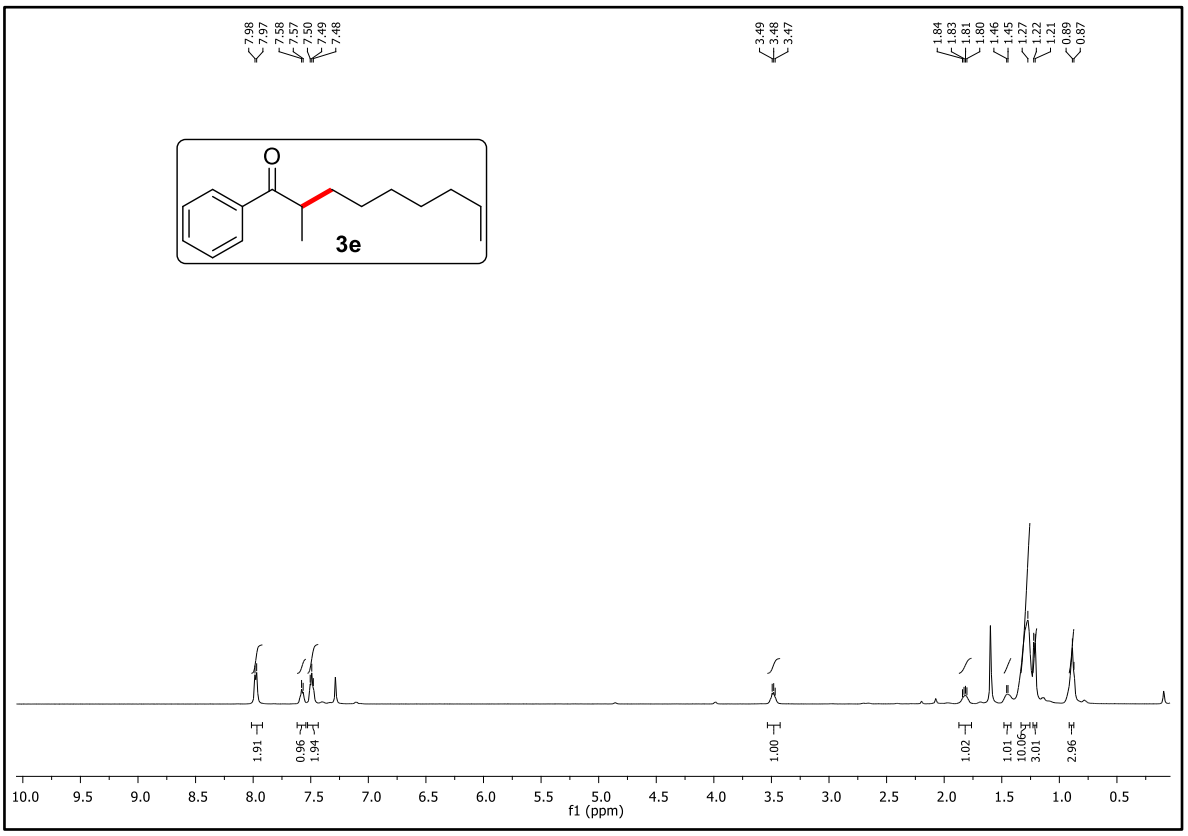




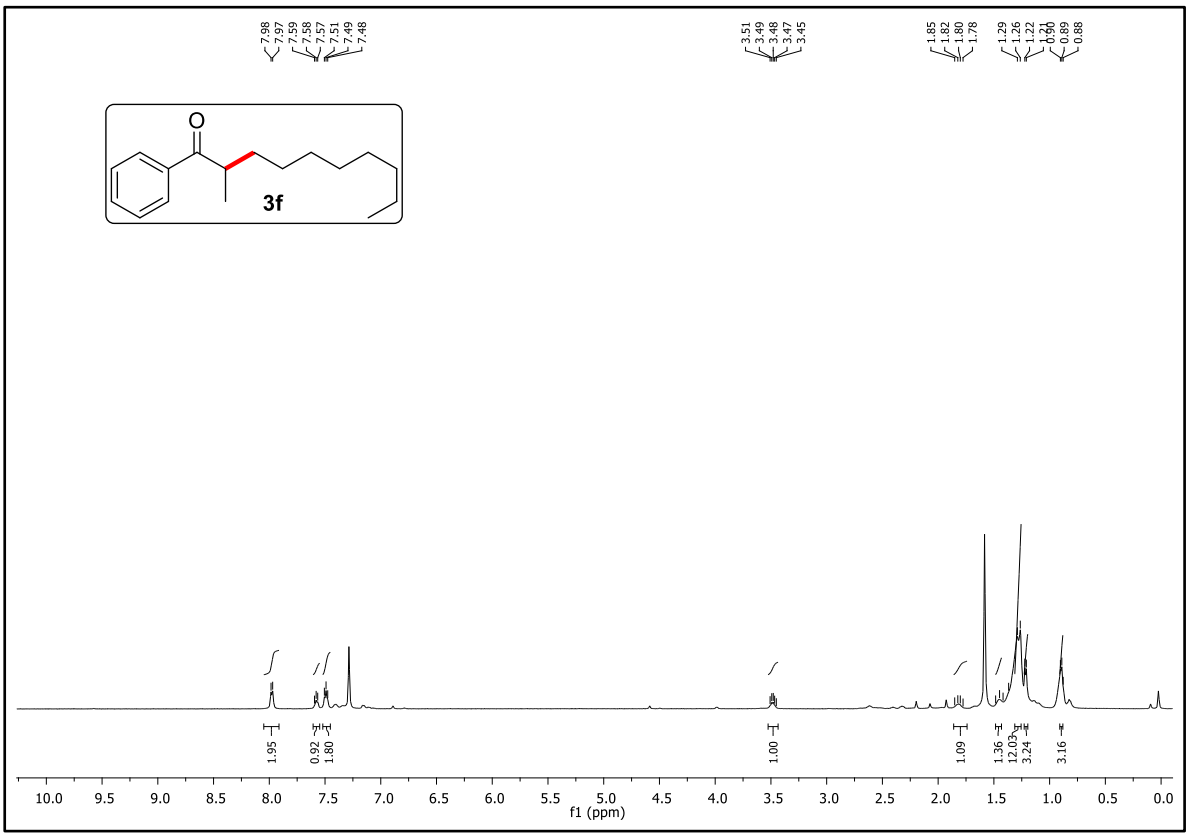
3-(4-Fluorophenyl)-2-methyl-1-phenylpropan-1-one:



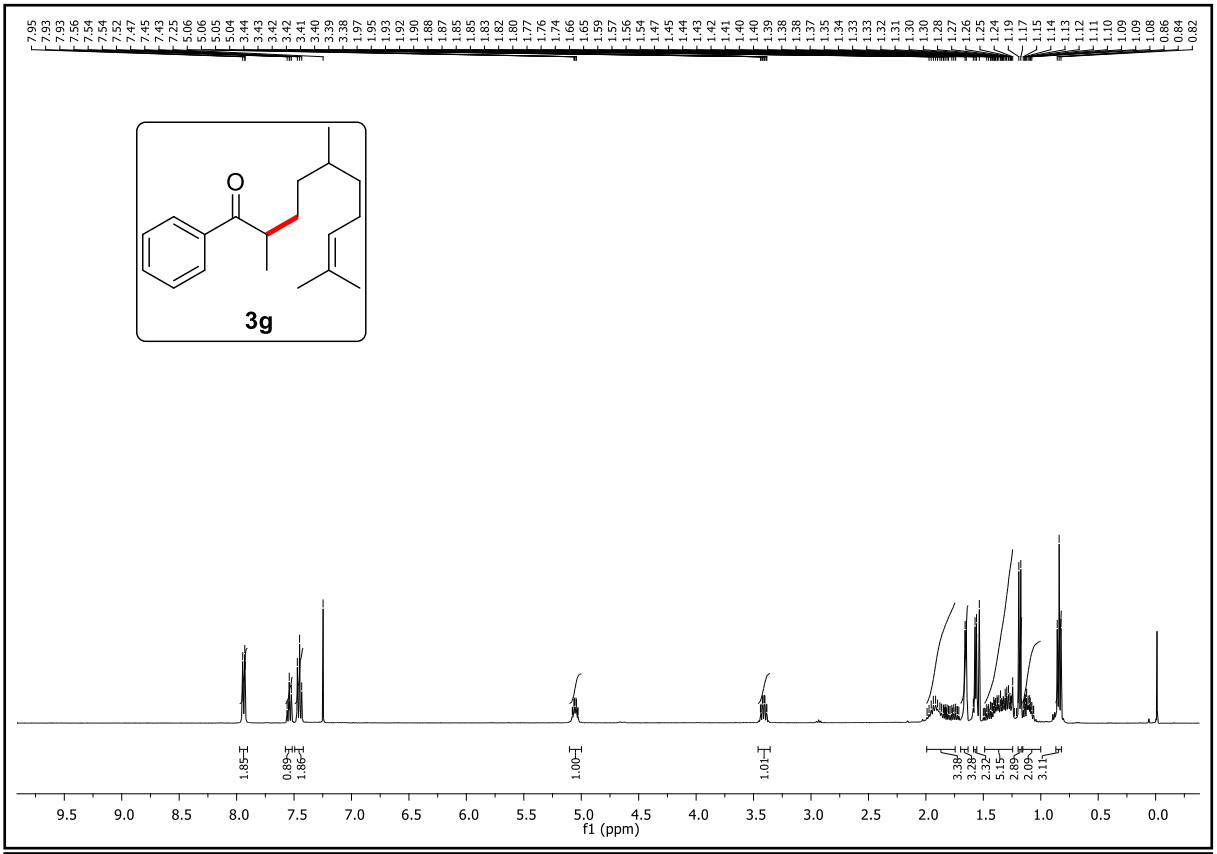
2-methyl-1-phenylnonan-1-one:

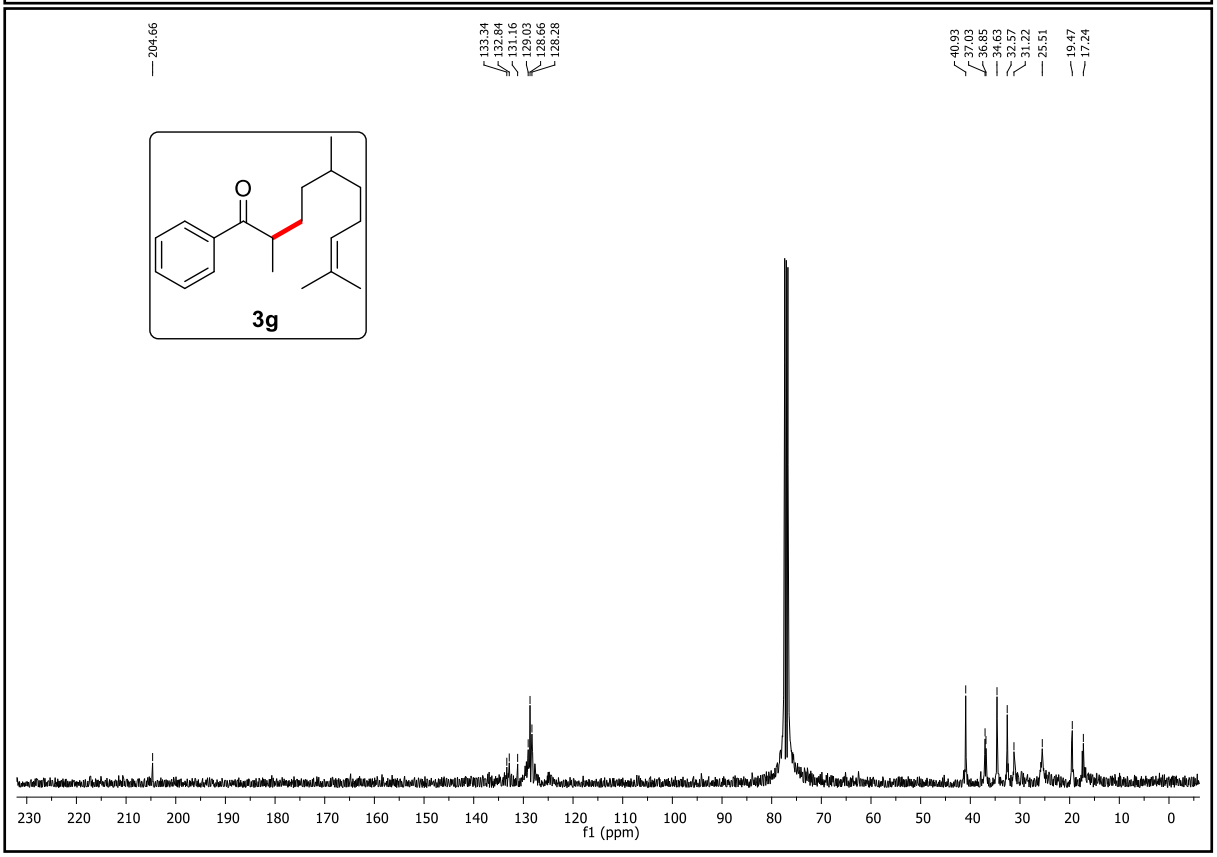


2-methyl-1-phenyldecan-1-one:

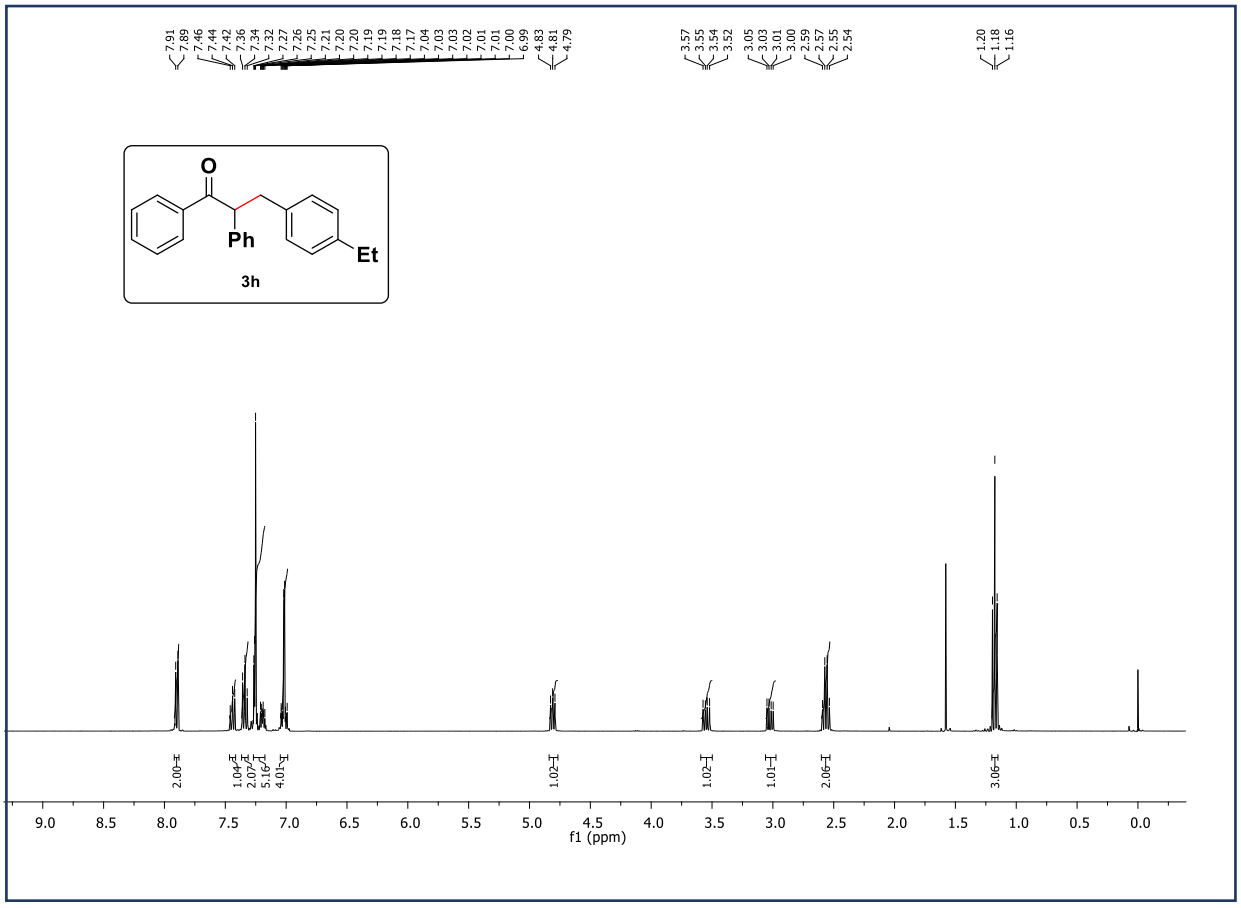


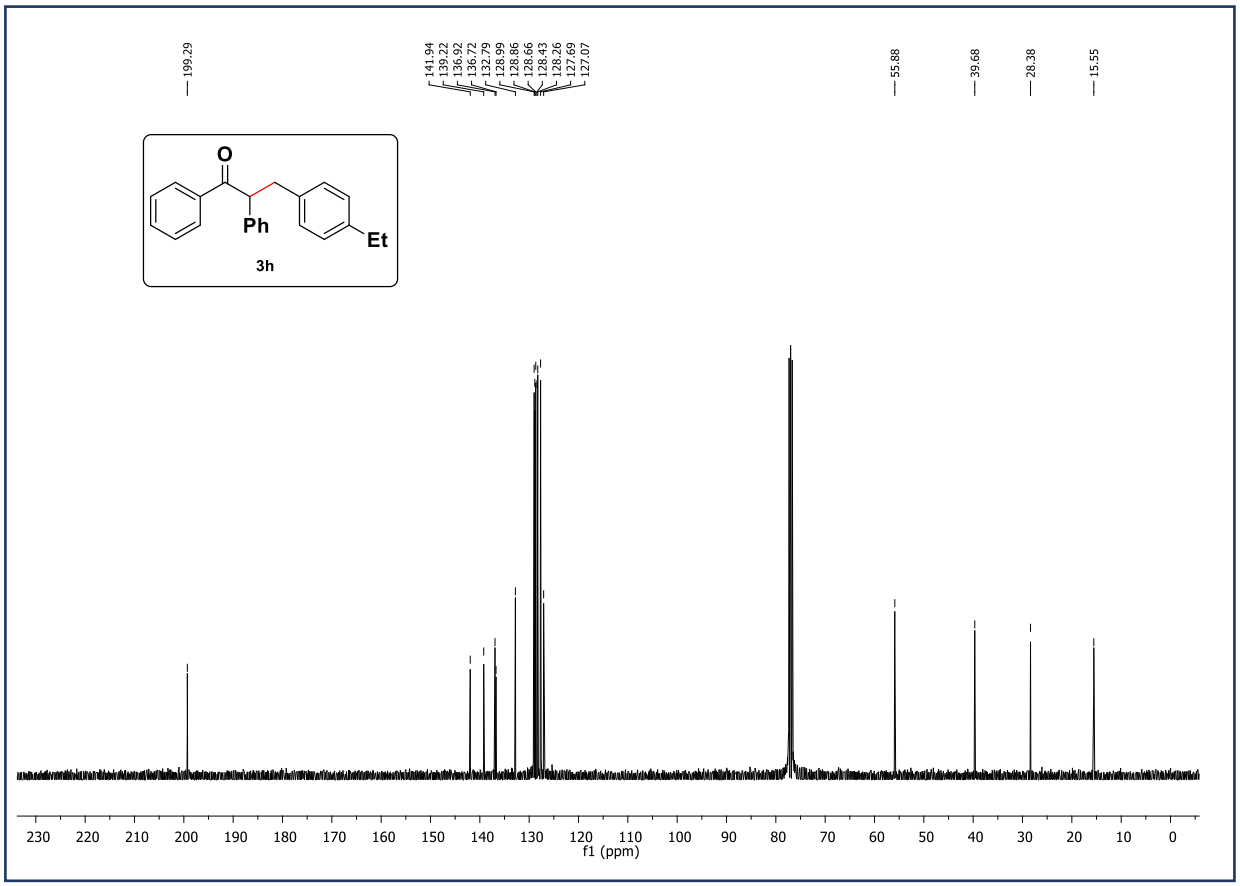
2,5,9-Trimethyl-1-phenyldec-8-en-1-one:



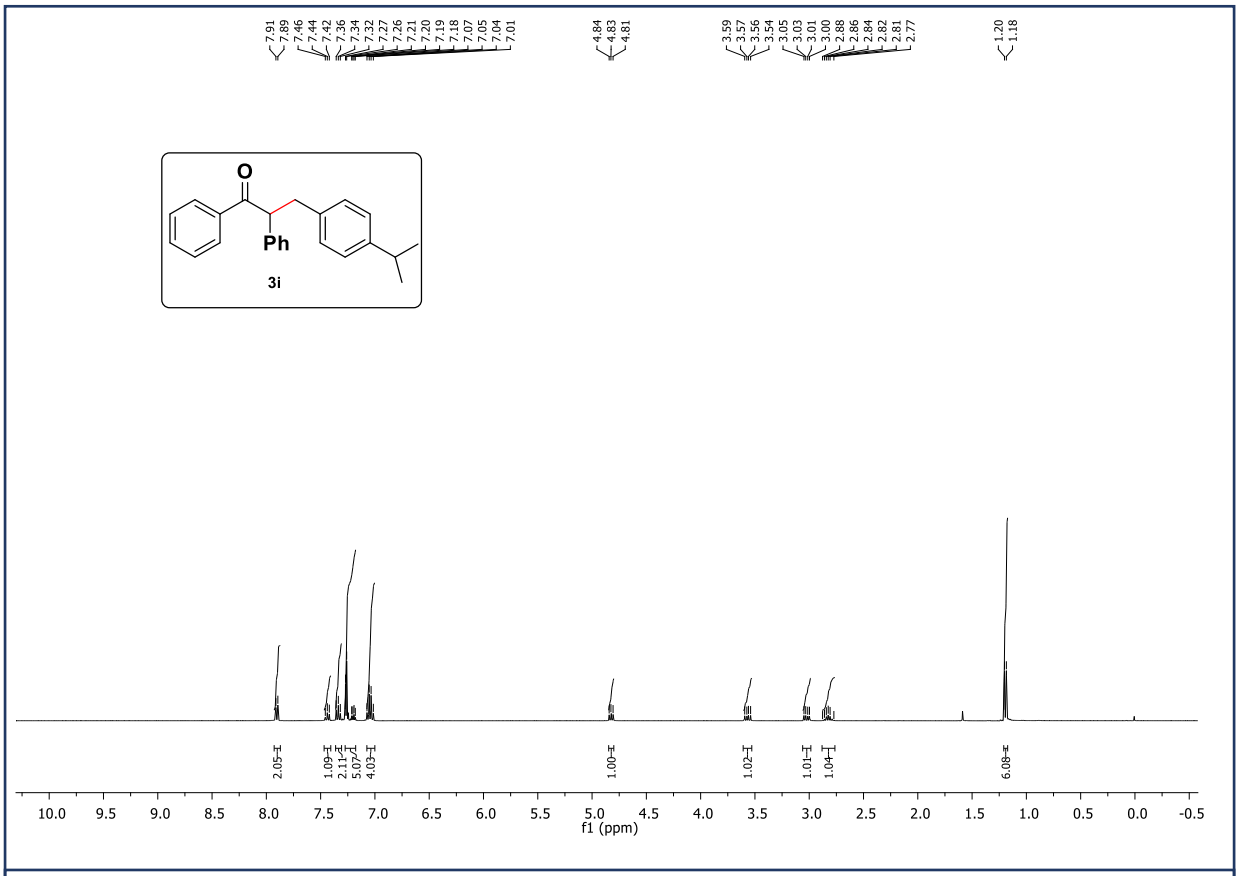


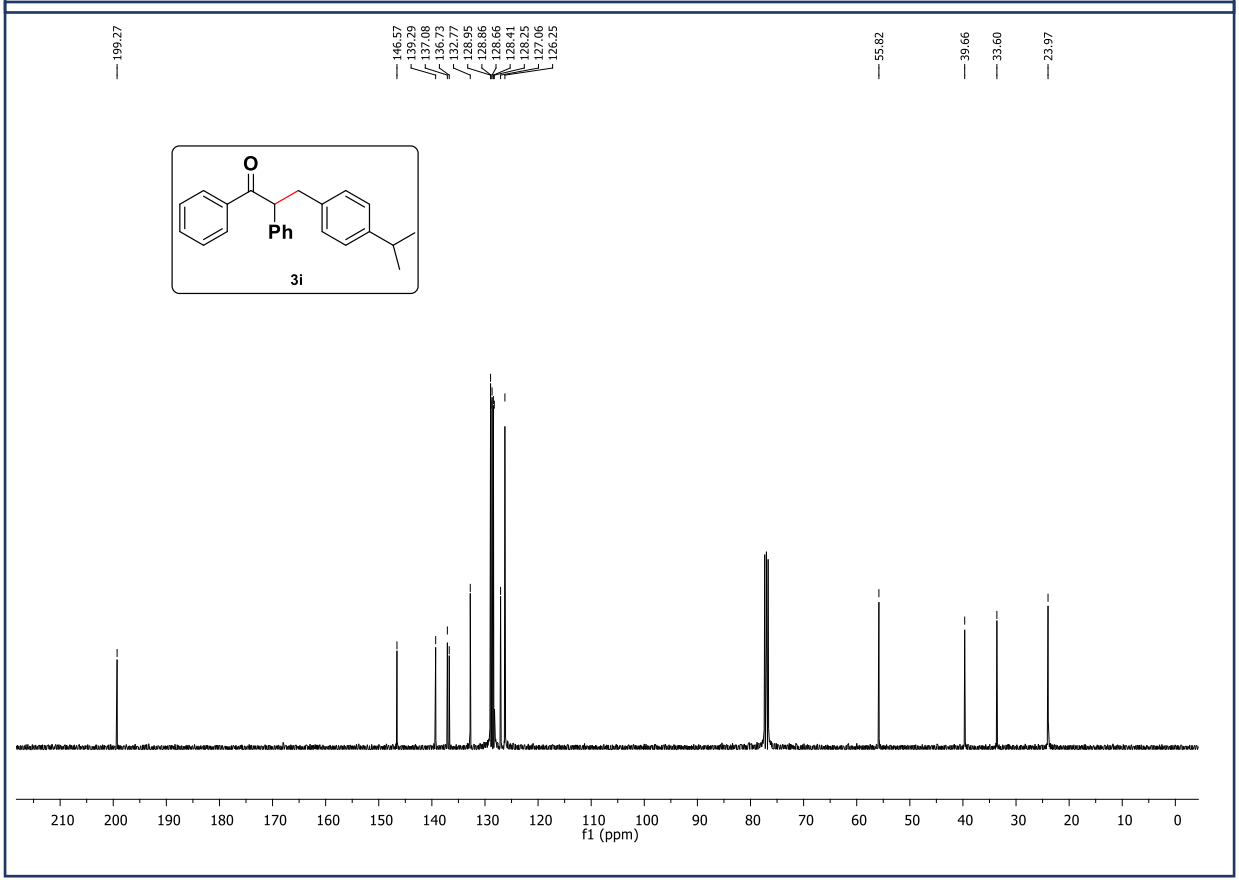
4-ethylphenyl)-1,2-diphenylpropan-1-one:



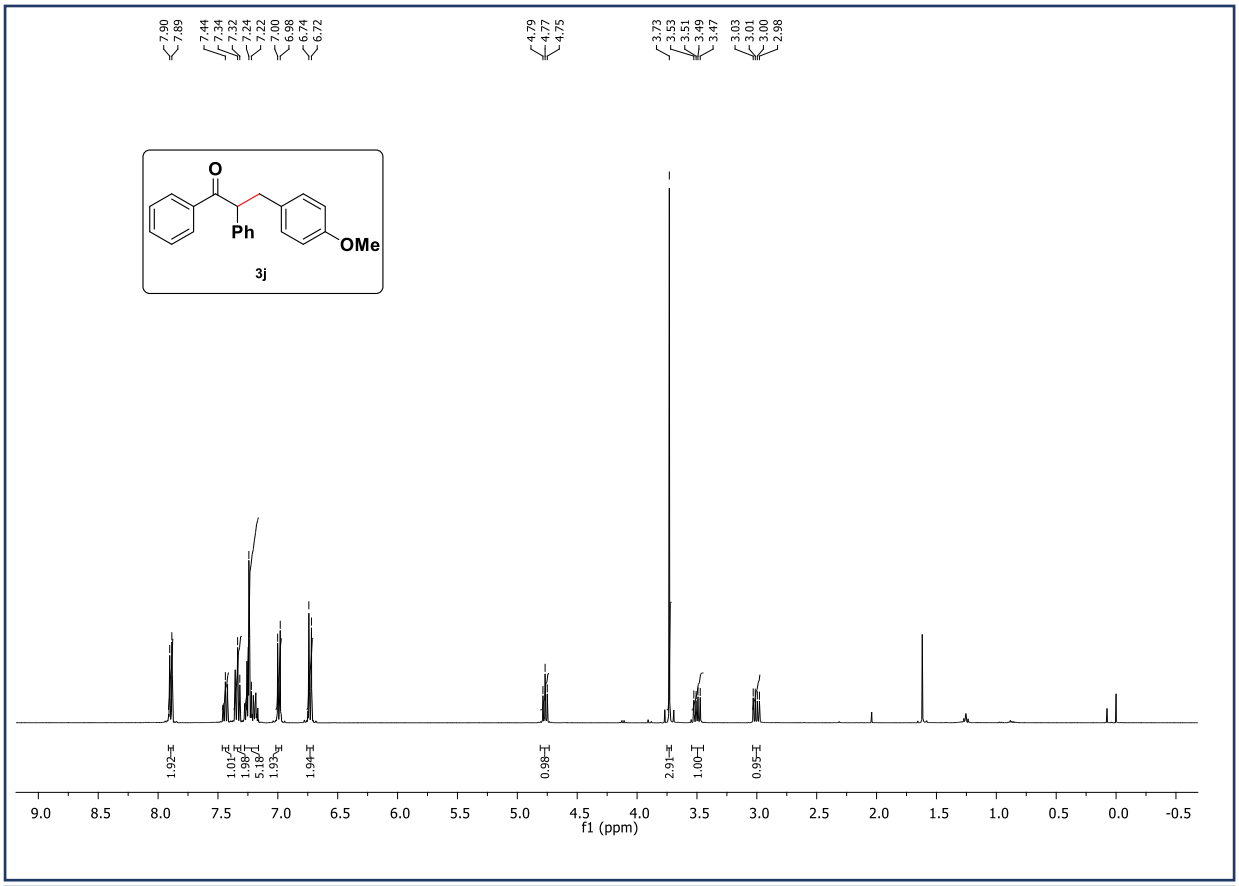


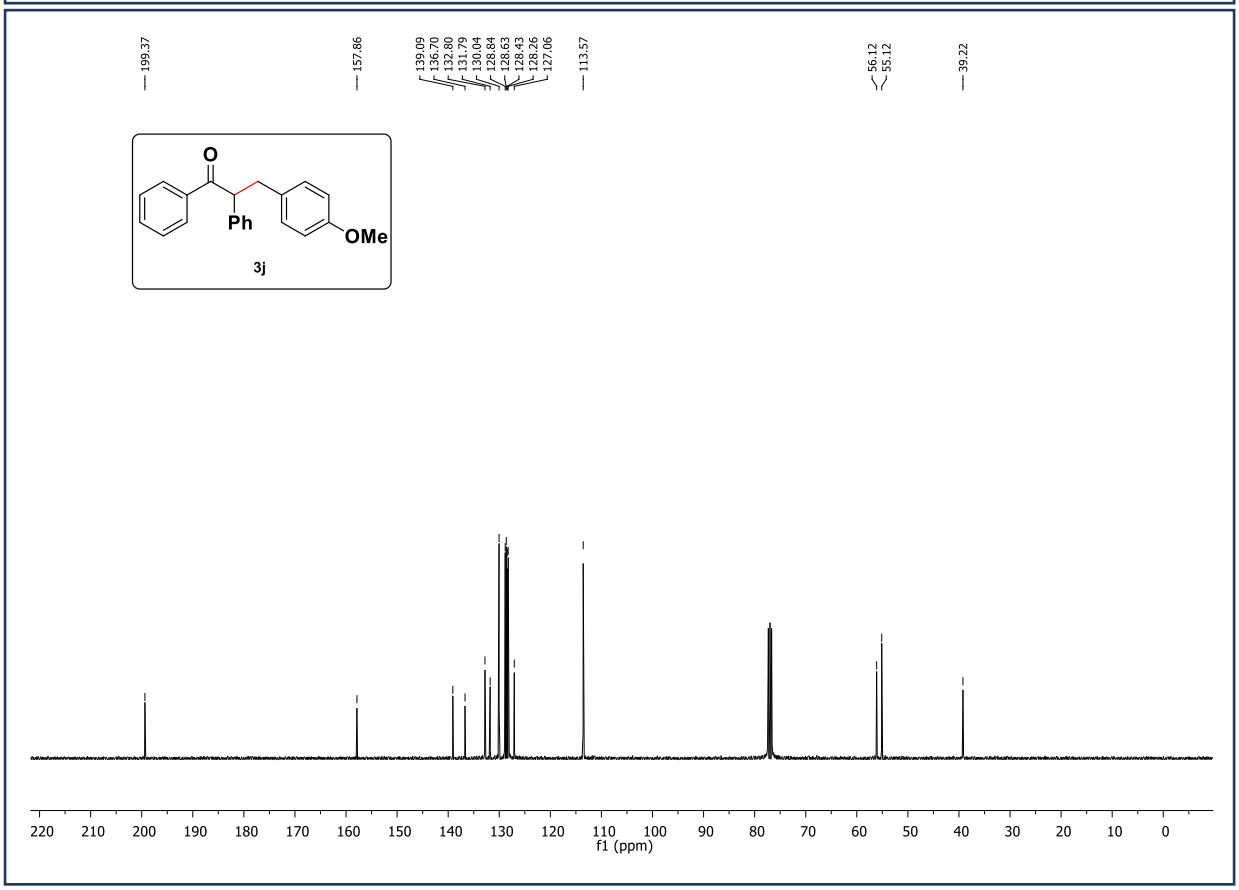
3-(4-isopropylphenyl)-1,2-diphenylpropan-1-one:



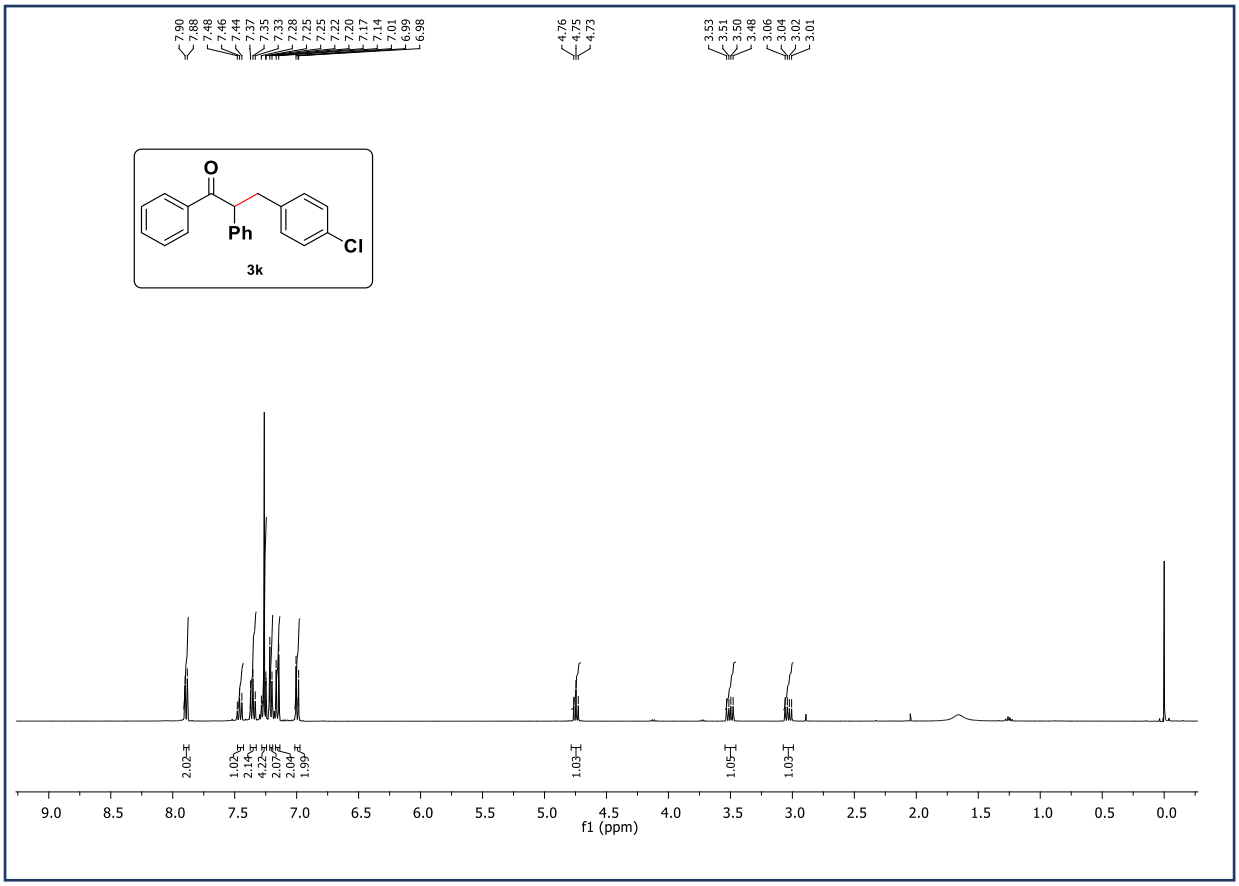


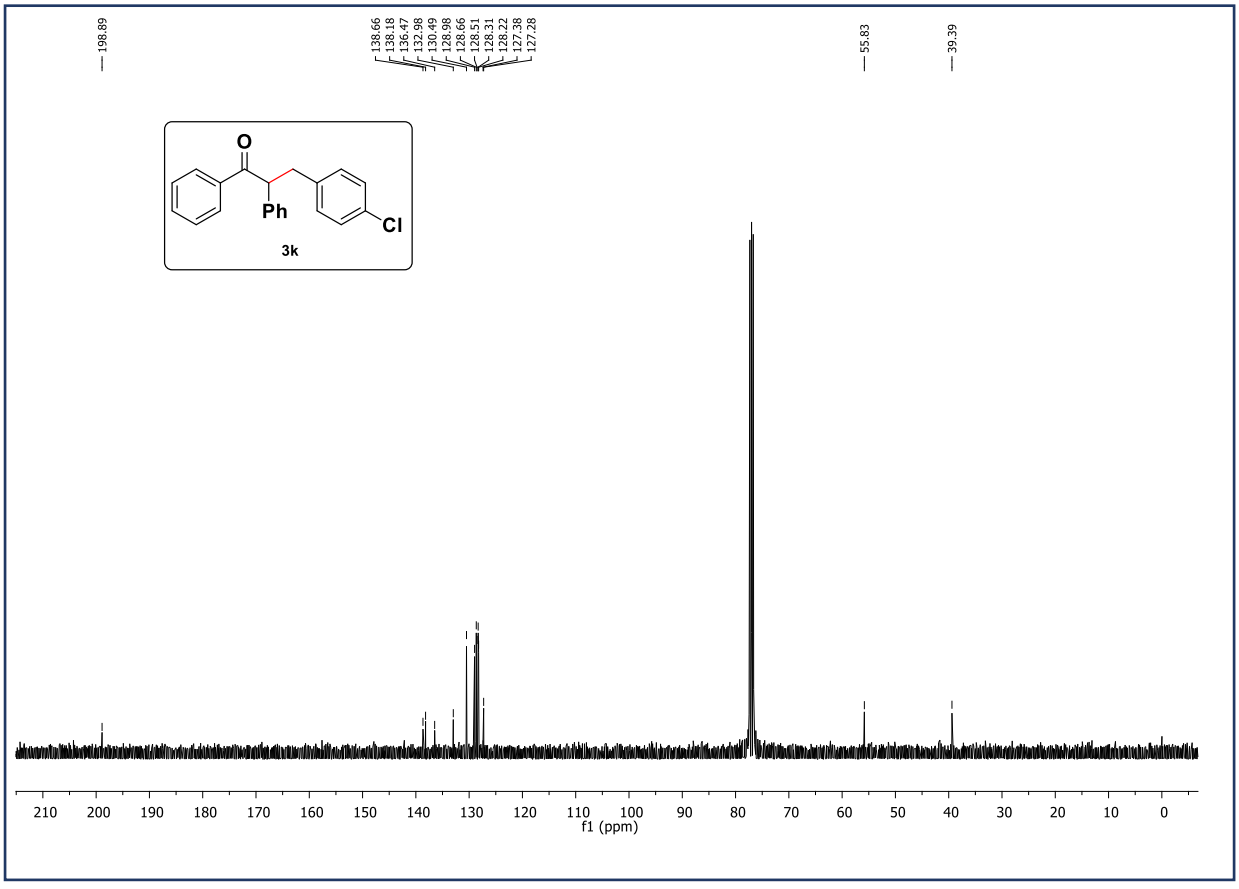
3-(4-methoxyphenyl)-1,2-diphenylpropan-1-one:



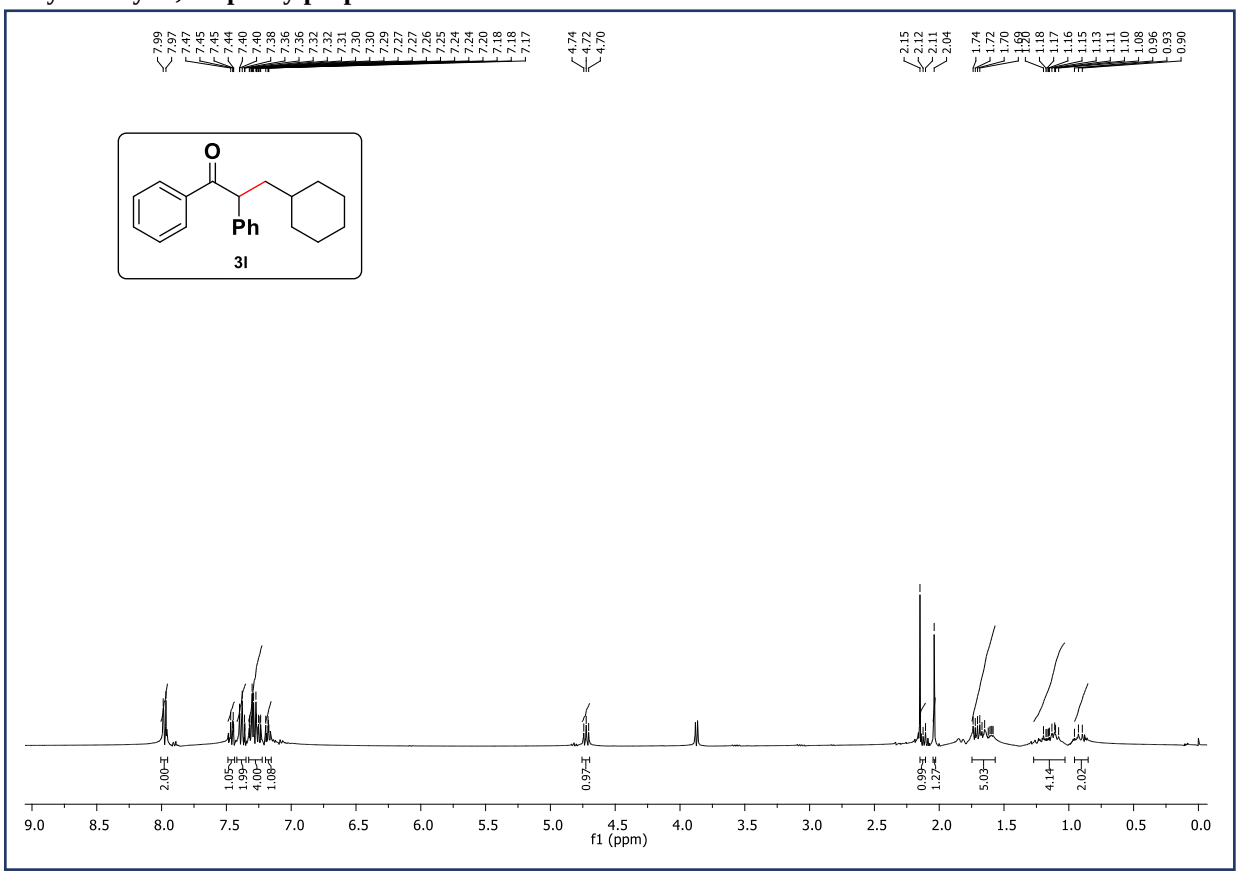


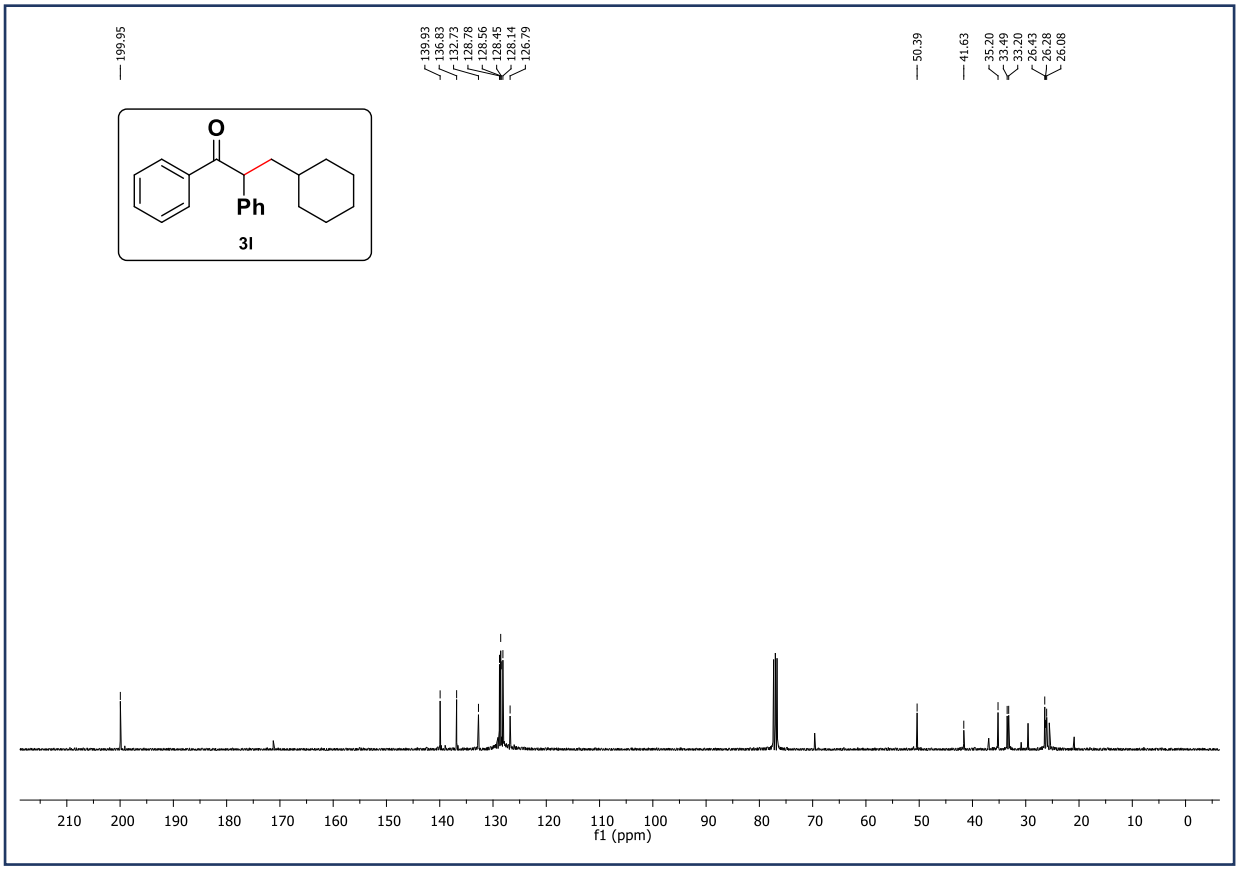
3-(4-chlorophenyl)-1,2-diphenylpropan-1-one:



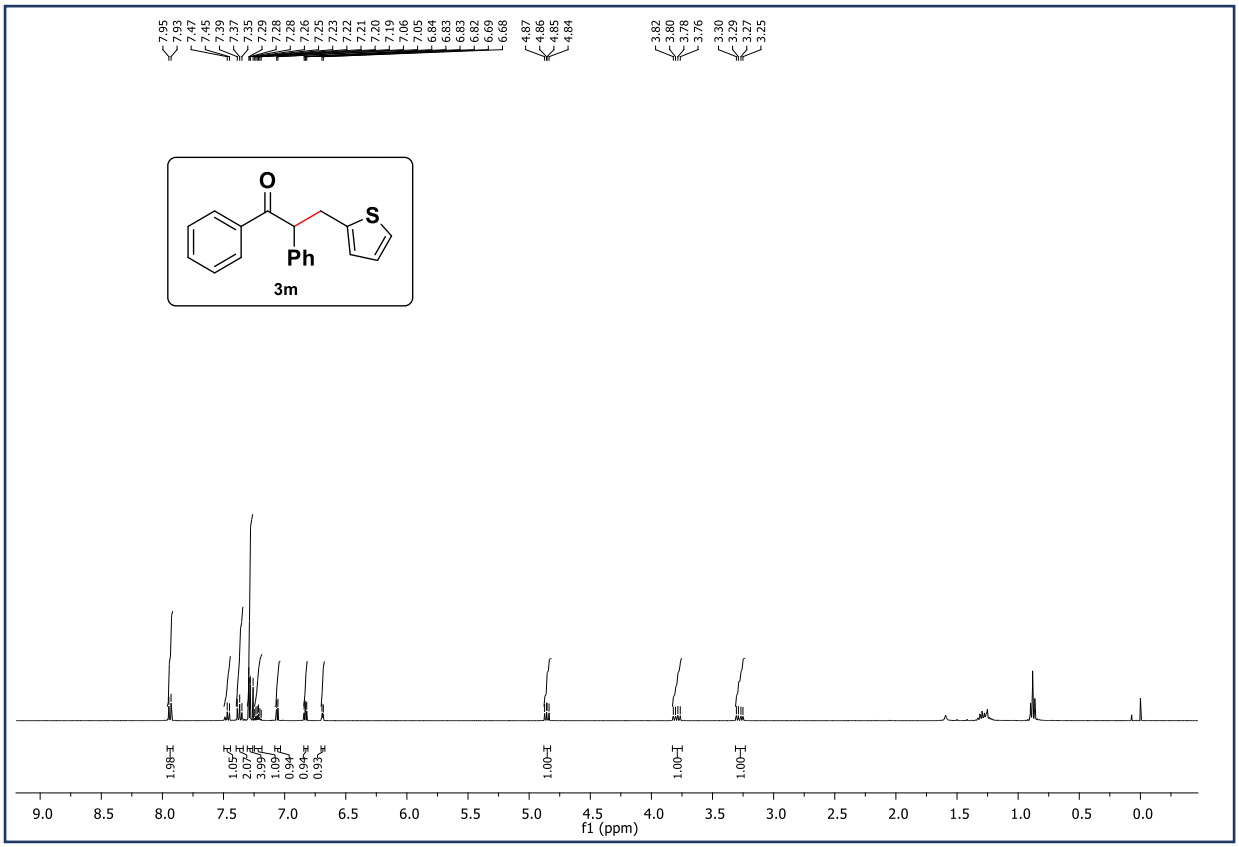


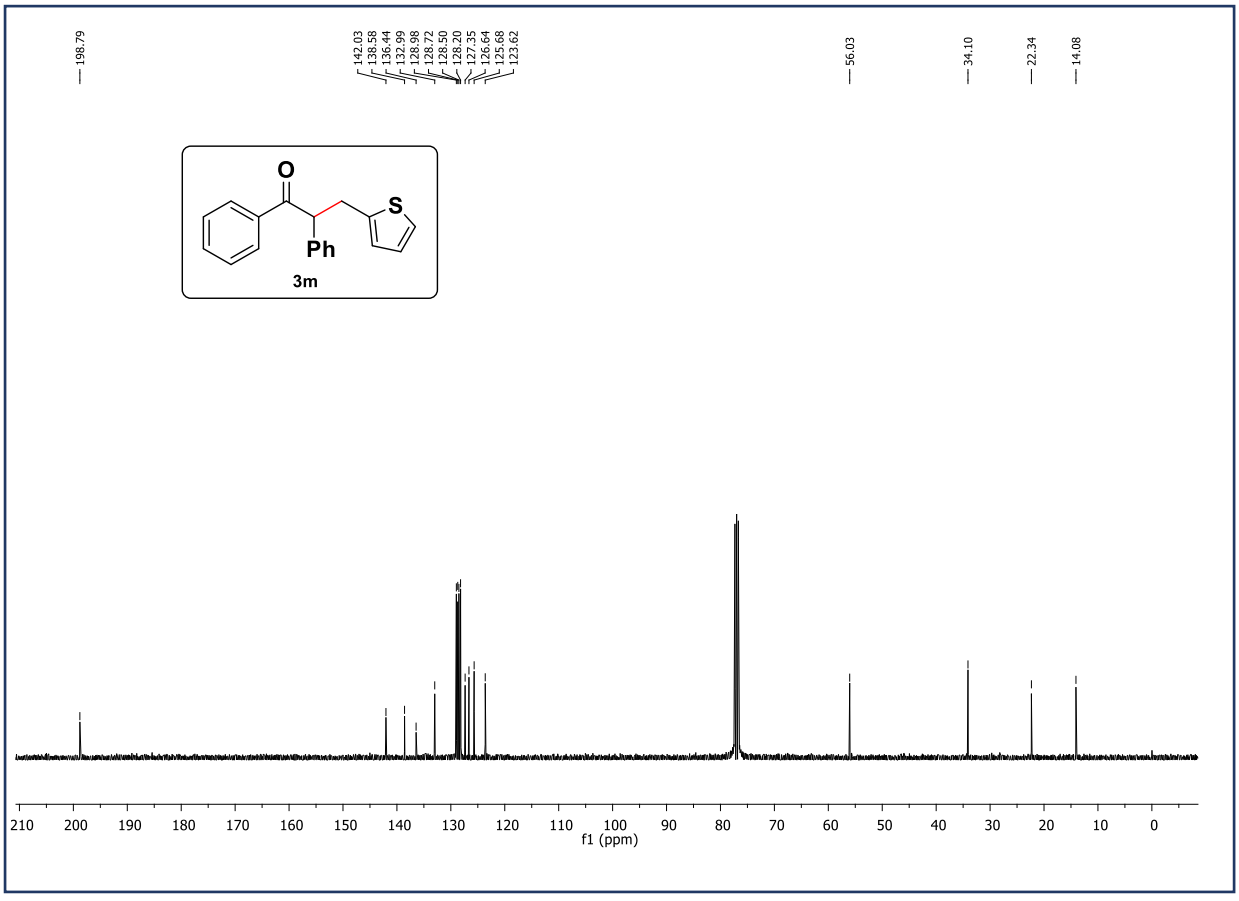
3-Cyclohexyl-1,2-diphenylpropan-1-one:



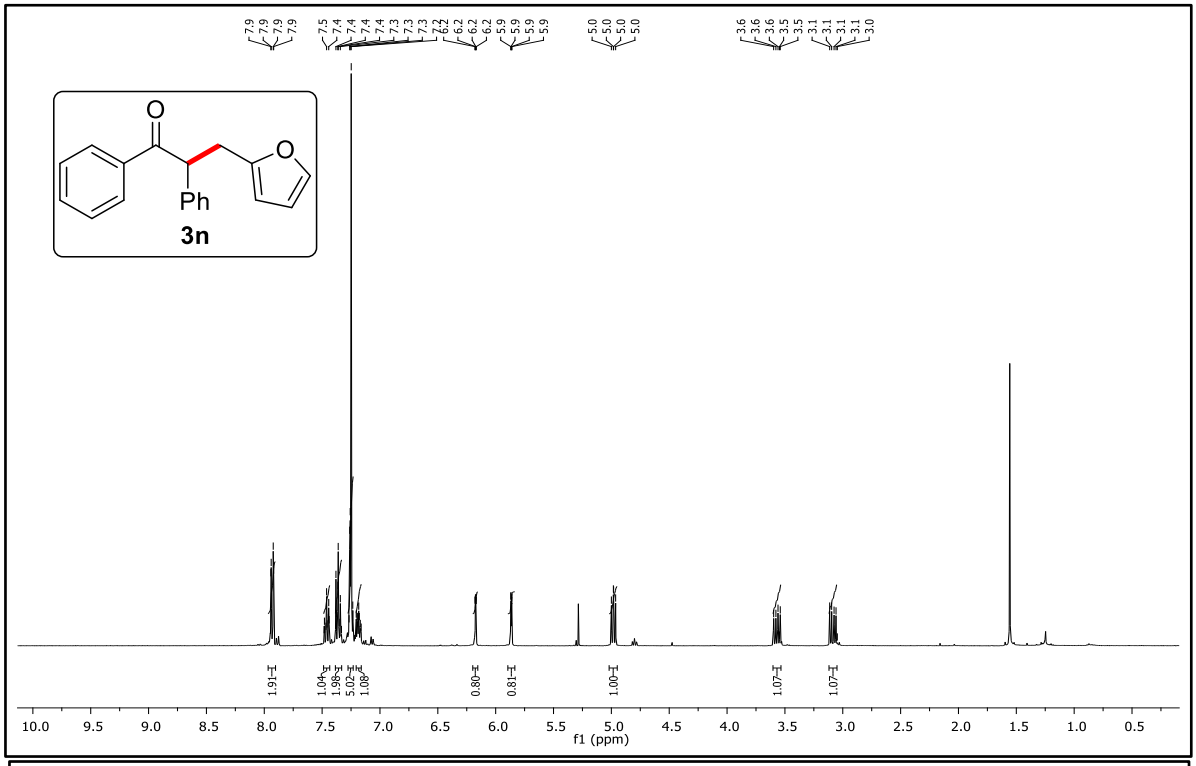


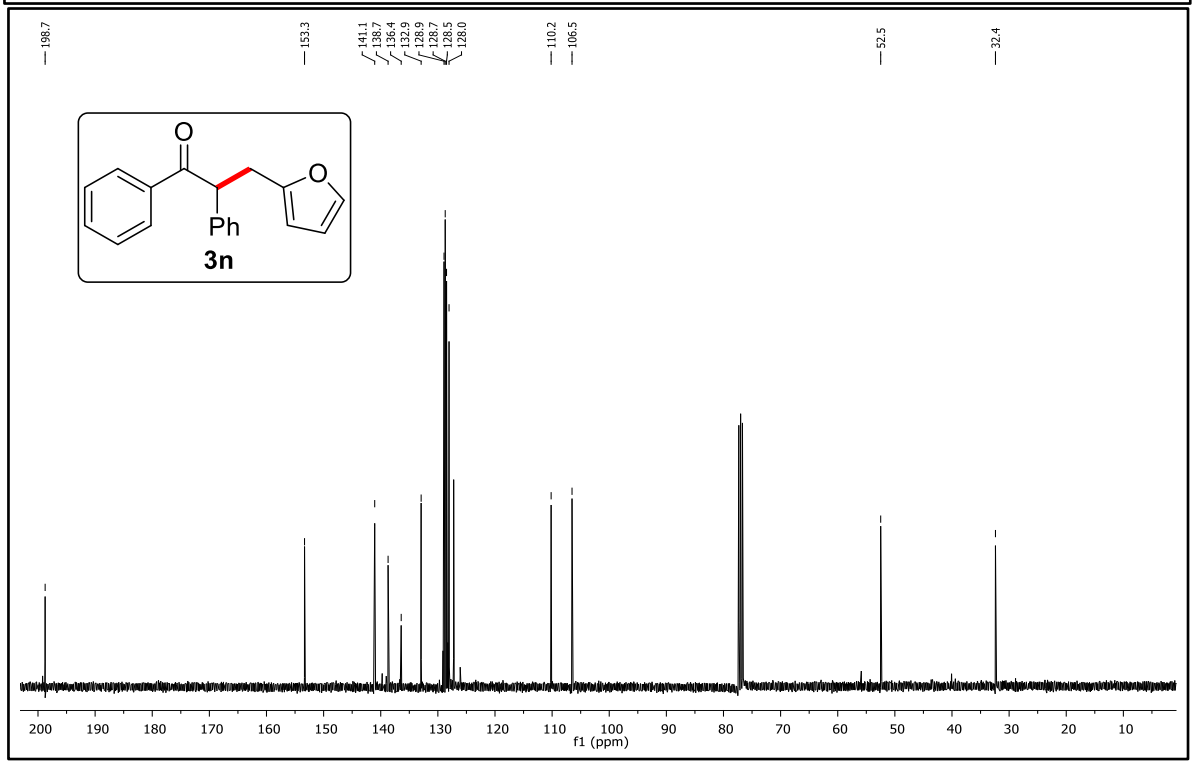
1,2-diphenyl-3-(thiophen-2-yl)propan-1-one:



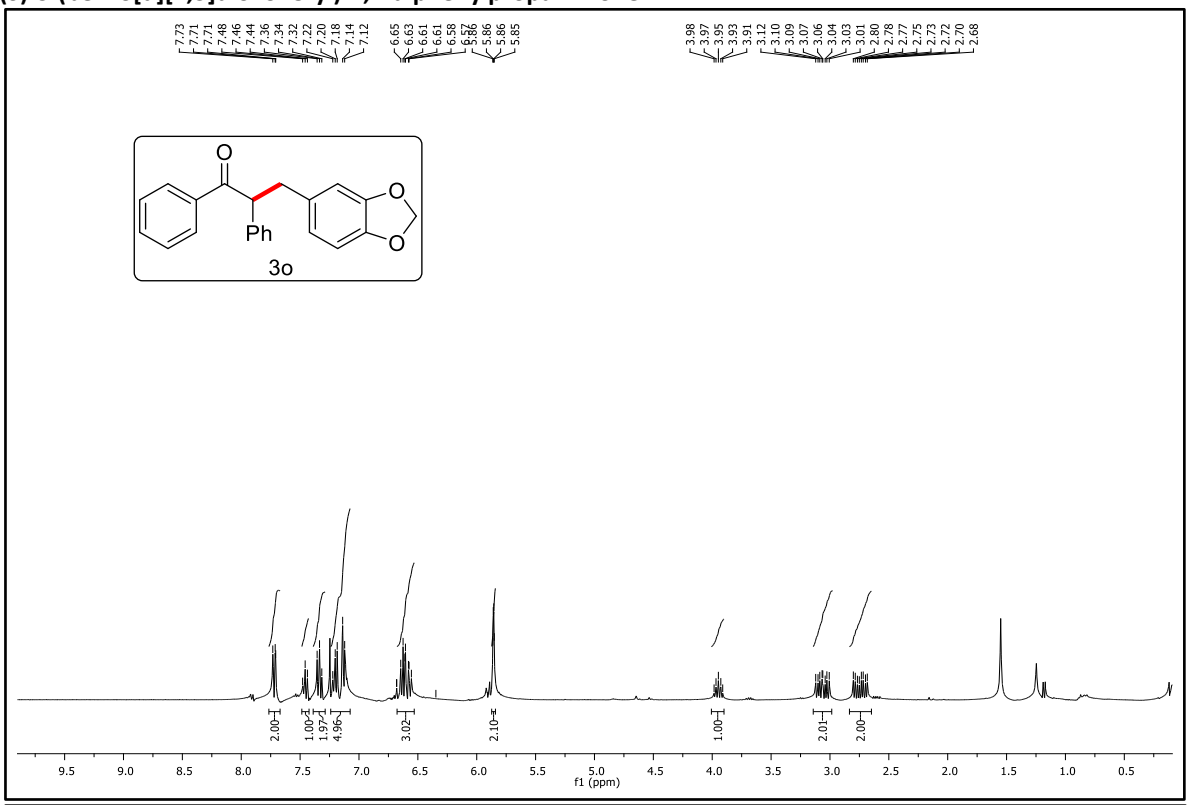


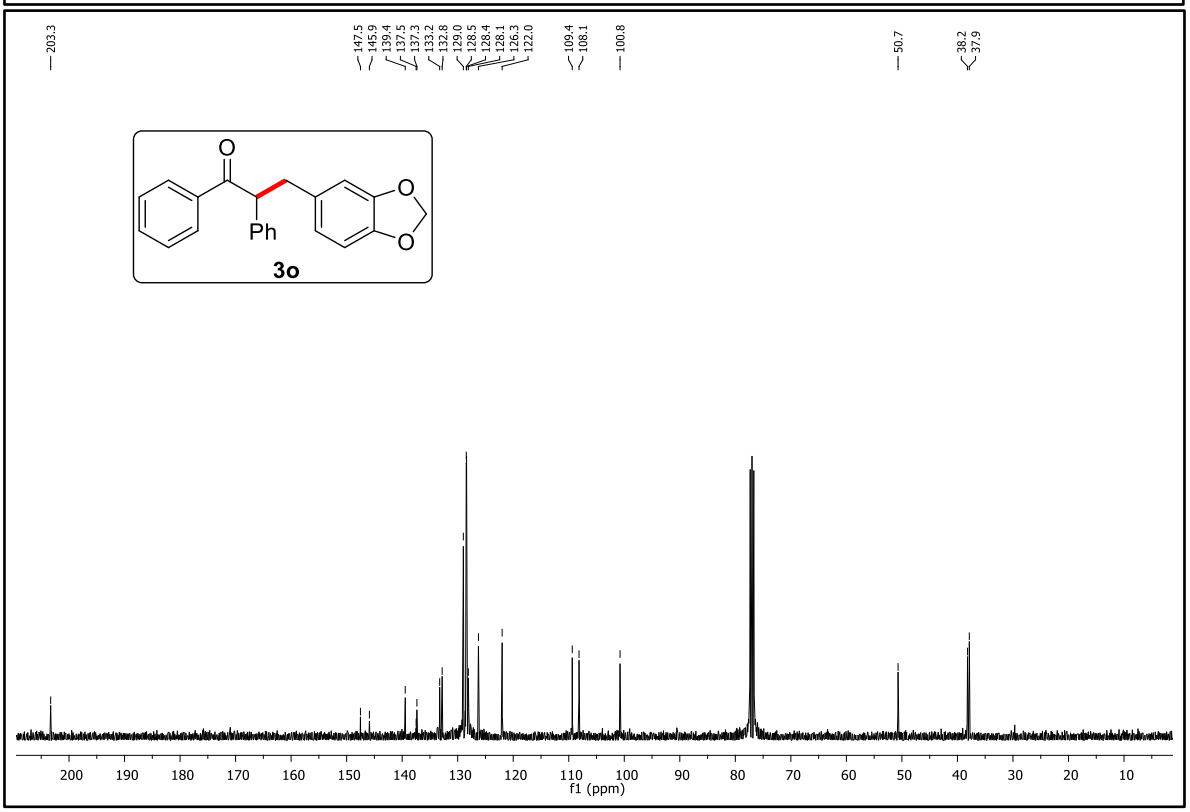
((S)-3-(furan-2-yl)-1,2-diphenylpropan-1-one:



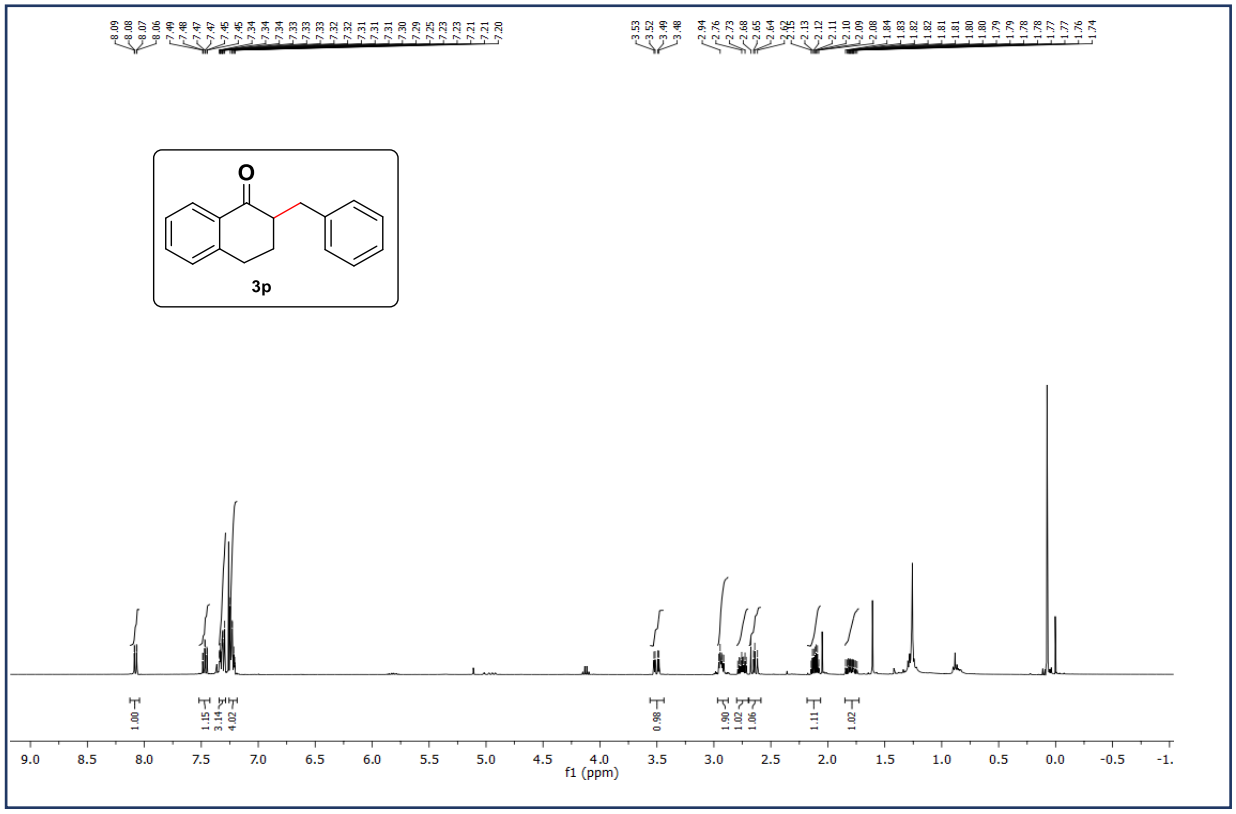


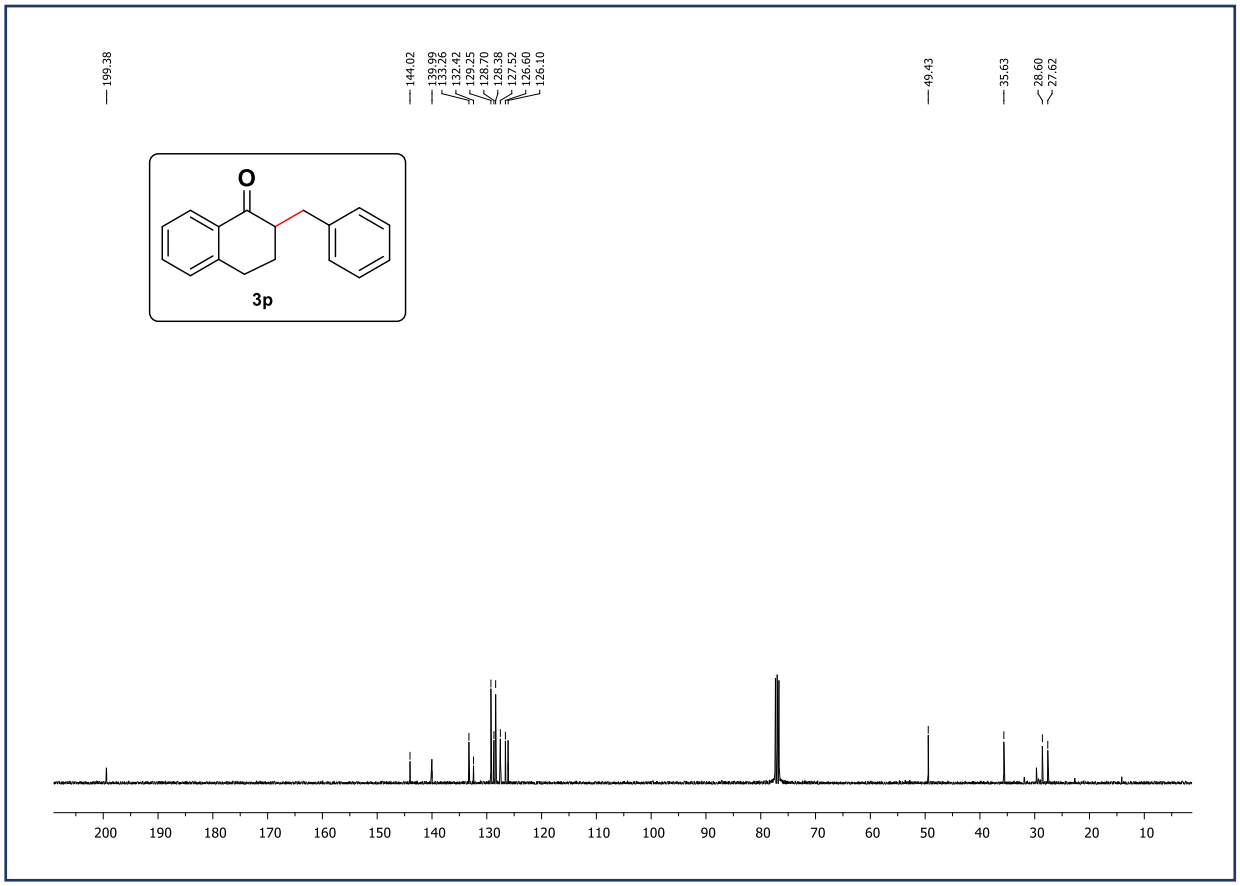
(S)-3-(benzo[d][1,3]dioxol-5-yl)-1,2-diphenylpropan-1-one :





2-Benzyl-3,4-dihydronaphthalen-1(2H)-one:





2-(4-chlorobenzyl)-3,4-dihydronaphthalen-1(2H)-one (3q)