Electronic Supplementary Information

Title: An efficient ligand free chemoselective transfer hydrogenation of the olefinic bonds by palladium nanoparticles in aqueous reaction medium

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A) General Information:

All chemicals and reagents were procured from M/s Sigma Aldrich, M/s Lancaster (Alfa-Aesar), M/s S. D. fine chemical and commercial suppliers. Palladium (II) chloride was purchased from M/s Parekh Platinum Ltd., Mumbai ($PdCl_2$, 99%). All reactions were carried out in 10 mL round bottom flask connected with reflux condenser. All products are well known in literature and were characterised by appropriate technique such as ^{1}H NMR, ^{13}C NMR, GC-MS and were compared with previously reported data. The ^{1}H NMR spectra were recorded with Varian Mercury, 400 MHz NMR Spectrometer) in $CDCl_3$ and ^{13}C NMR spectra were recorded with Varian Mercury, 101 MHz NMR Spectrometer in $CDCl_3$ solvent. Chemical shifts are reported in parts per million (δ) relative to tetamethylsilane as internal standard. Mass spectra were obtained on Shimadzu GC-MS (QP 2010) (Rtx-17, 30 m × 25mmID, film thickness 0.25 μm df) (column flow- 2 mL/min, 80 °C to 240 °C at 10°/min. rise) instrument. GC analysis was carried out on a Perkin Elmer (Clarus-400) gas chromatograph equipped with flame ionization detector with a capillary column (Elite-1, 30 m x 0.32 mm x 0.25 μm).

B) Experimental set up and procedure for the synthesis of palladium nanoparticles

The synthesis of palladium nanoparticles were carried out in the 25 mL round bottom flask fitted with a water condenser (Fig. 1). In a typical procedure for the synthesis of PdNPs, PVP (126 mg) and citric acid (161 mg) were dissolved in deionized water (10 mL) followed by addition of palladium (II) chloride (31 mg). The resulting mixture was then exposed under solar radiations concentrated by 'Fresnel lens (1×1 ft)' at noon in summer for 6 h (temperature range was 85-95 ^{o}C). As the solar energy effect is special and temporal, the experiment was carried out at a specific location at the time from 10:00 am to 4:00 pm. To check the complete reduction of $PdCl_2$, the UV of reaction mixture was measured and it

shows complete reduction of palladium(II) to palladium(0). The characterization of prepared Pd (0) nanoparticles was carried out by using various analytical techniques such as field emission gun-scanning electron microscopy (FEG-SEM), transmission electron microscopy (TEM), and electron dispersive X-ray spectral (EDAX) analysis. The size and morphology of synthesized PdNPs were determined by FEG-SEM (Fig. 2 A and B) and TEM analysis (Fig. 2 C). The Transmission electron microscopy (TEM) image confirmed that the obtained particles are in the nano region with uniform size ranging from 25 nm to 40 nm. The EDS spectrum shows that the prepared PdNPs contains palladium metal only (Fig. 2 D). Finally the nanoparticle solution was diluted with deionized water to make proper concentration of 1 mol % and used as a stock solution for the hydrogenation reaction.

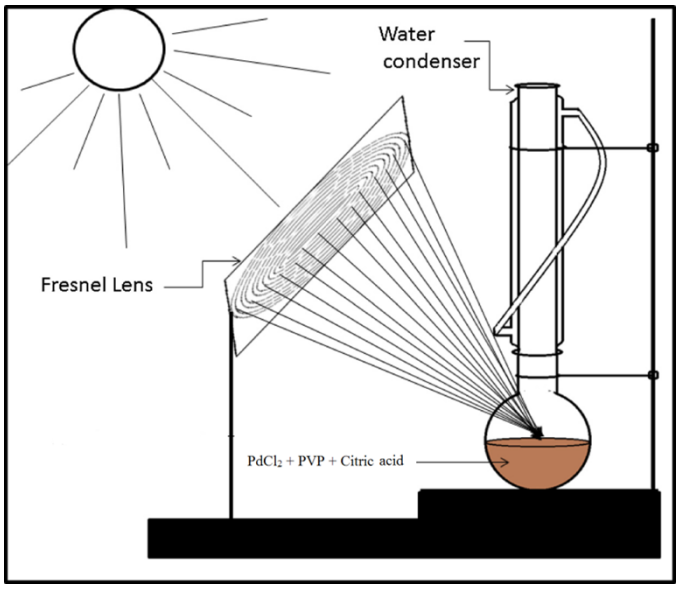


Fig. 1. Schematic representation of reaction setup for the synthesis of PdNPs.

Characterization of palladium nanoparticles

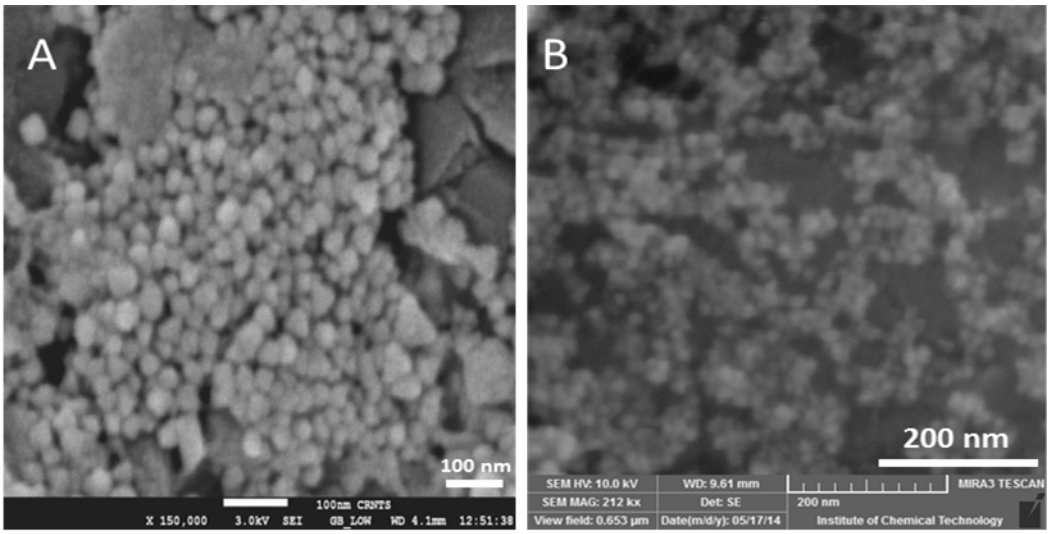


Figure 2. FEG-SEM, image (A) Fresh PdNPs. (B) after 4 recycle runs

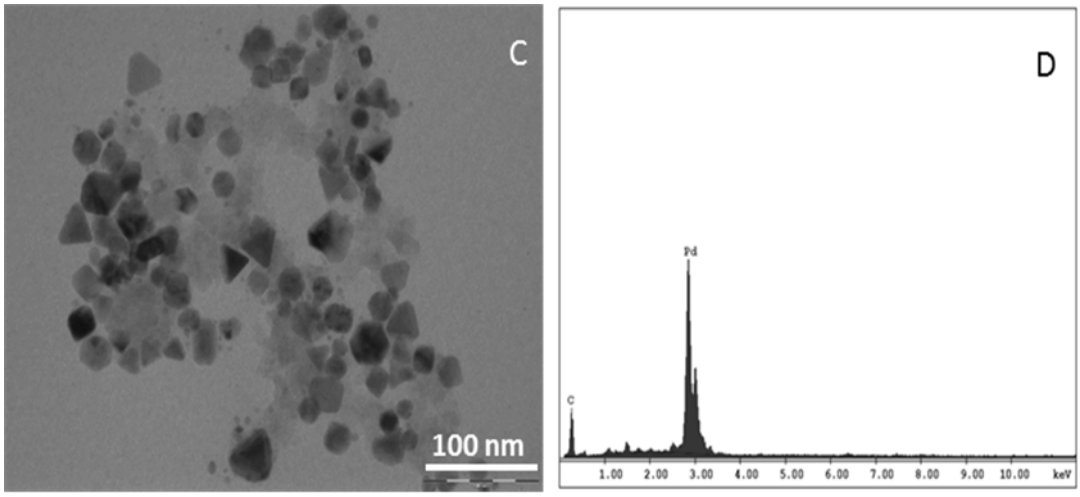


Figure 2. Image (C) TEM image of PdNPs, (D) EDS pattern of Palladium nanoparticles

C) Typical experimental procedure for chemoselective conjugates reduction of α,β-unsaturated carbonyls

In a 5 mL stock solution of 1 mol % PdNPs suspended in water, 1 mmol of corresponding α,β-unsaturated carbonyl compound and 3 mmol of HCOONa were added and the reaction mixture was stirred at 100 °C for 8 h. The progress of the reaction was monitored using thin layer chromatography (TLC) and GC analysis (Perkin Elmer, Clarus 400) (BP-10

GC column, 30 m × 0.32 mm ID, film thickness 0.25 mm). On completion of reaction, the products were extracted with ethyl acetate, dried over Na_2SO_4 and the solvent was evaporated under vacuum. The obtained crude product was then purified by column chromatography using silica gel, (100-200 mesh size,) with petroleum ether/ethyl acetate (PE-EtOAc, 95:05) as eluent to afford pure product. All products are well known, which were confirmed by GC-MS analysis. Some of the selected compounds were characterized by different spectroscopic techniques such as ^{1}H NMR (Varian Mercury, 400 MHz NMR Spectrometer), ^{13}C NMR spectra (101 MHz), GC-MS (Shimadzu GC-MS QP 2010) (Rtx-17, 30 m × 25mmID, film thickness 0.25 µm df) (column flow- 2 mL/min, 80 °C to 240 °C at 10°/min. rise.).

D) Recyclability study

The reaction was carried out as mentioned above in typical experimental procedure. After completion of reaction, the reaction mixture was cooled to room temperature and the product was extracted in ethyl acetate. The aqueous layer containing PdNPs was then used for further catalyst recyclability experiment and it was observed that the PdNPs could be reused for five consecutive cycles affording good conversion with appreciable chemoselectivity. Further we have checked the morphology of reused (4th run) palladium nanoparticles by FEG-SEM analysis and we observed that the morphology of PdNPs remains same (Fig. 2 B).

E) Characterisation of some selected compounds:

1) 1, 3-Diphenyl-propan-1-one (Table 2, entry 1)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, J = 8.3, 1.2 Hz, 2H, Ar), 7.54 (t, 1H, Ar), 7.44 (t, 2H, Ar), 7.25 (m, J = 13.0, 8.6, 7.2 Hz, 5H, Ar), 3.29 (t, J=7.78 Hz, 2H, -CH_2-CO), 3.06 (t, J=7.78 Hz, 2H, -CH_2-Ar); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 199.27, 141.33, 136.86, 133.11, 128.65, 128.57, 128.47, 128.07, 126.18, 39.49, 30.15; **GC-MS** (EI) *m/z* (%) = 210(38) $[M]^+$, 106(9), 105(100), 91(12), 77(42), 51(11).

2) 3-phenyl-1-(p-tolyl)propan-1-one (Table 2, entry 2)

^{1}H NMR (400 MHz, CDCl3) δ = 7.86 (d, J = 8.2 Hz, 2H, Ar), 7.28 (d, J = 7.1 Hz, 2H, Ar), 7.28 (m, 5H, Ar), 3.27 (t, J = 8Hz, 2H, -CH_2-CO), 3.05 (t, J = 7.8Hz, 2H, -CH_2-Ar), 2.40 (s, 3H, CH_3-Ar); **^{13}C NMR** (101 MHz, CDCl3) δ = 198.94, 143.87, 141.43, 134.39, 129.31, 128.54, 128.46, 128.20, 126.13, 40.38, 30.23, 21.67; **GC-MS** (EI) *m/z* (%) = 224 $[M]^+$, 209, 119, 105, 91, 65, 51.

3) 3-(4-Methoxy-phenyl)-1-phenyl-propan-1-one (Table 2, entry 3)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, J = 9.0 Hz, 2H, Ar), 7.25 (m, 5H, Ar), 6.92 (d, J = 9.0 Hz, 2H, Ar), 3.85 (s, 3H, -OCH_3), 3.24 (t, J = 7.9 Hz, 2H, -CH_2-CO), 3.05 (t, 2H, -CH_2-Ar); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 197.86, 163.46, 141.49, 130.33, 129.96, 128.53, 128.45, 126.11, 113.74, 55.48, 40.14, 30.34; **GC-MS** (EI) *m/z* (%) =240(40) $[M]^+$, 135(12), 122(9), 121(100), 108(18), 105(47), 77(41), 78(8), 51(8).

4) 1-Phenyl-3-thiophen-2-yl-propan-1-one (Table 2, entry 8)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, J = 7.1 Hz, 2H, Ar), 7.56 (t, 1H, Ar), 7.46 (t, J = 8.2, 7.0 Hz, 2H, Ar), 7.13 (dd, J = 5.1, 1.2 Hz, 1H, =CH-S), 6.92 (dd, J = 5.1, 3.4 Hz, 1H, =<u>CH</u>=CH), 6.86 (dd, J = 3.4, 1.0 Hz, 1H, -<u>CH</u>-CH_2), 3.37 (m, 2H, -CH_2), 3.29 (m, 2H, -CH_2-CO); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 198.62, 143.90, 136.73, 133.21, 128.66, 128.05, 126.88, 124.71, 123.41, 40.57, 24.21; **GC-MS** (EI) *m/z* (%) =216(51) $[M]^+$, 111(56), 110(14), 105(100), 97(64), 84(10), 77(75), 51(21), 45(13).

5) 3-Furan-2-yl-1-phenyl-propan-1-one (Table 2, entry 9)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.0(d, 2H, J=8 Hz, Ar), 7.64 (t, 1 H, J = 7.6 Hz, Ar), 7.53(d, 2H, J = 7.6 Hz, Ar), 7.5(d, 1H, J=7.6 Hz), 6.34 (d, 1H, J = 8 Hz), 6.13 (d, 1H, J = 2.8 Hz,), 3.38 (t, 2H, J = 7.2, -CH_2-CO), 3.09 (t, 2H, J = 7.2, -CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ

= 198.5, 154.6, 141.2, 136.44, 133.19, 128.7, 127.9, 105, 36.1, 22.11; **GC-MS** (EI) *m/z* (%) = 200(45) $[M]^+$, 144(6), 106(9), 105(100), 95(35), 94(11), 91(14), 77(65), 53(12), 51(20).

6) 3,3,5-trimethylcyclohexanone (Table 2, entry 10)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.12 - 1.94 (m, 1H), 1.89 (t, J = 13.0 Hz, 1H), 1.68 - 1.51 (m, 2H), 1.25 (s, 3H), 1.03 (dd, J = 12.6, 6.9 Hz, 3H, $-CH_3$), 0.88 (s, 6H, $-CH_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 212.17, 54.23, 49.29, 47.32, 35.42, 32.14, 29.72, 25.84, 22.51.

7) Ethyl 3-phenylpropanoate (Table 2, entry 12)

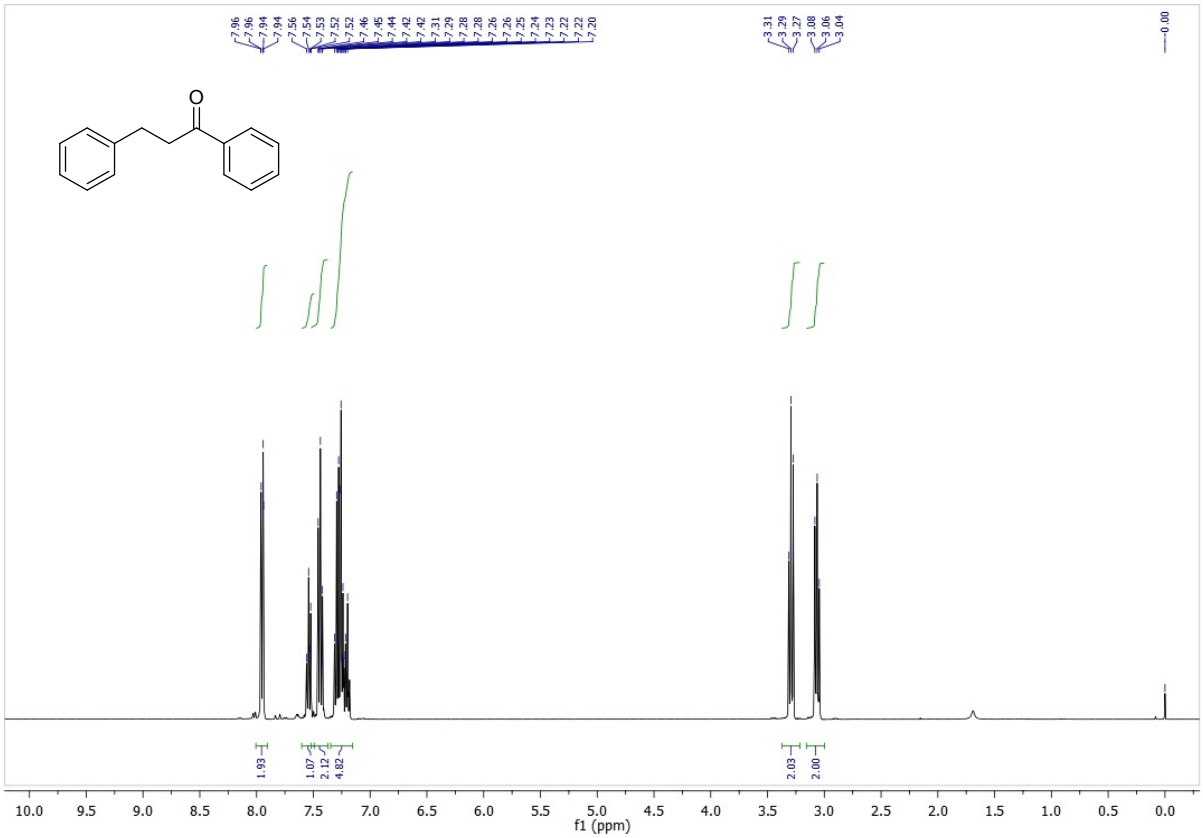
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32-7.10 (m, 5H, Ar), 4.13 (q, J = 7.1 Hz, 2H,$-CH_2$-O), 2.95 (t, 2H, $-CH_2$-Ar), 2.62 (t, J = 8.5, 7.3 Hz, 2H, $-CH_2$-CO), 1.23 (t, J = 7.1 Hz, 3H, $-CH_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 172.97, 140.59, 128.49, 128.32, 126.24, 60.45, 35.97, 30.99, 14.22. **GC-MS** (EI) *m/z* (%) = 178 $[M]^+$, 133, 104, 91, 77, 65, 51.

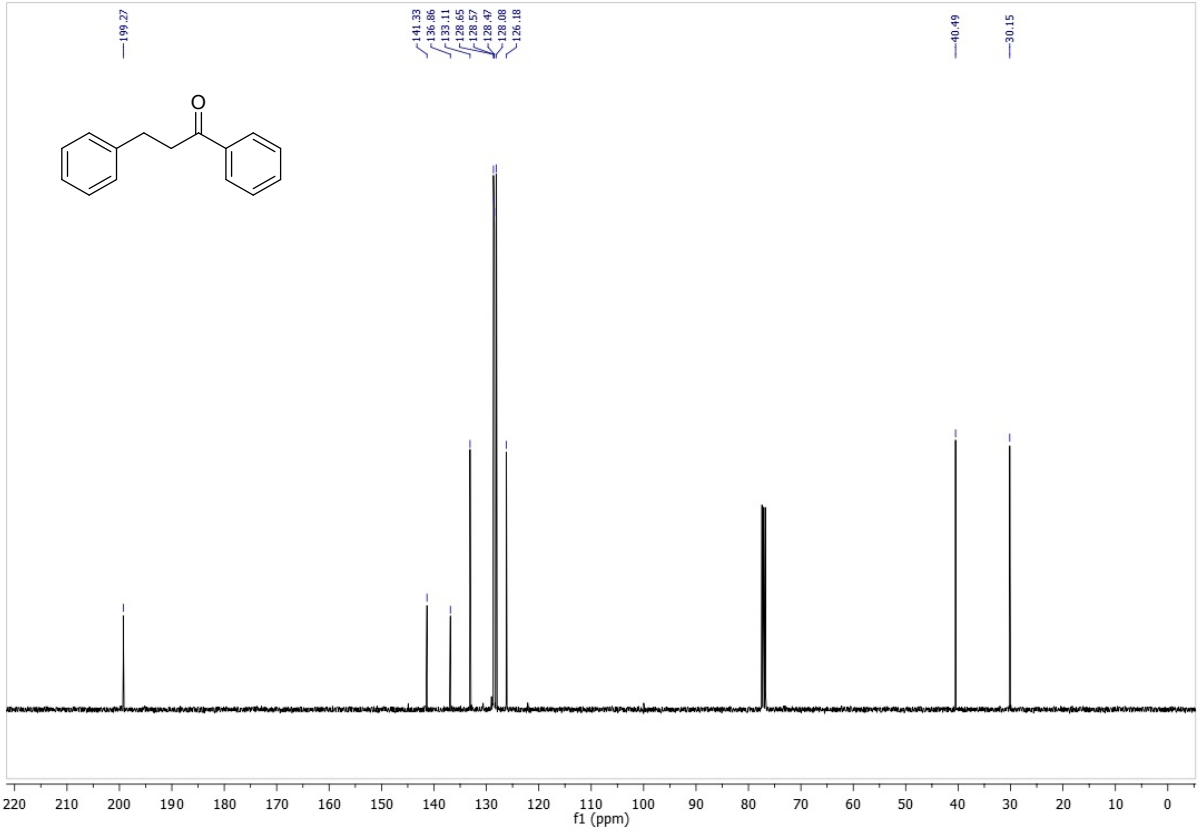
8) 3-phenylpropanamide (Table 2, entry 14)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 - 7.17 (m, 5H, Ar), 5.78 (bs, 1H, H_2N-CO), 5.48 (bs, 1H, H_2N-CO), 2.97 (t, 2H, $-CH_2$-Ar), 2.53 (t, 2H, $-CH_2$-CO); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 174.77, 140.67, 128.60, 128.33, 126.33, 37.56, 31.40. **MS** (EI) *m/z* (%) = 149 $[M]^+$, 132, 115, 104, 77, 65, 51.

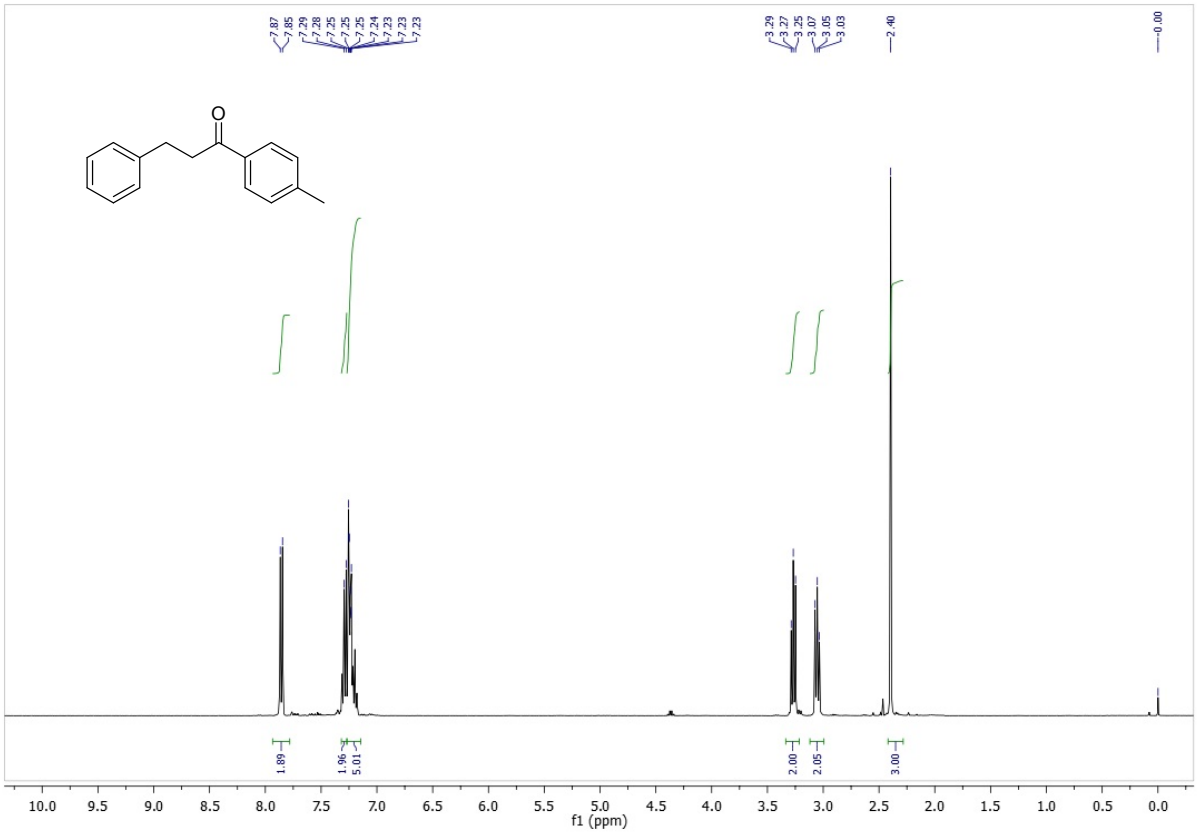
^{1}H and ^{13}C NMR spectra

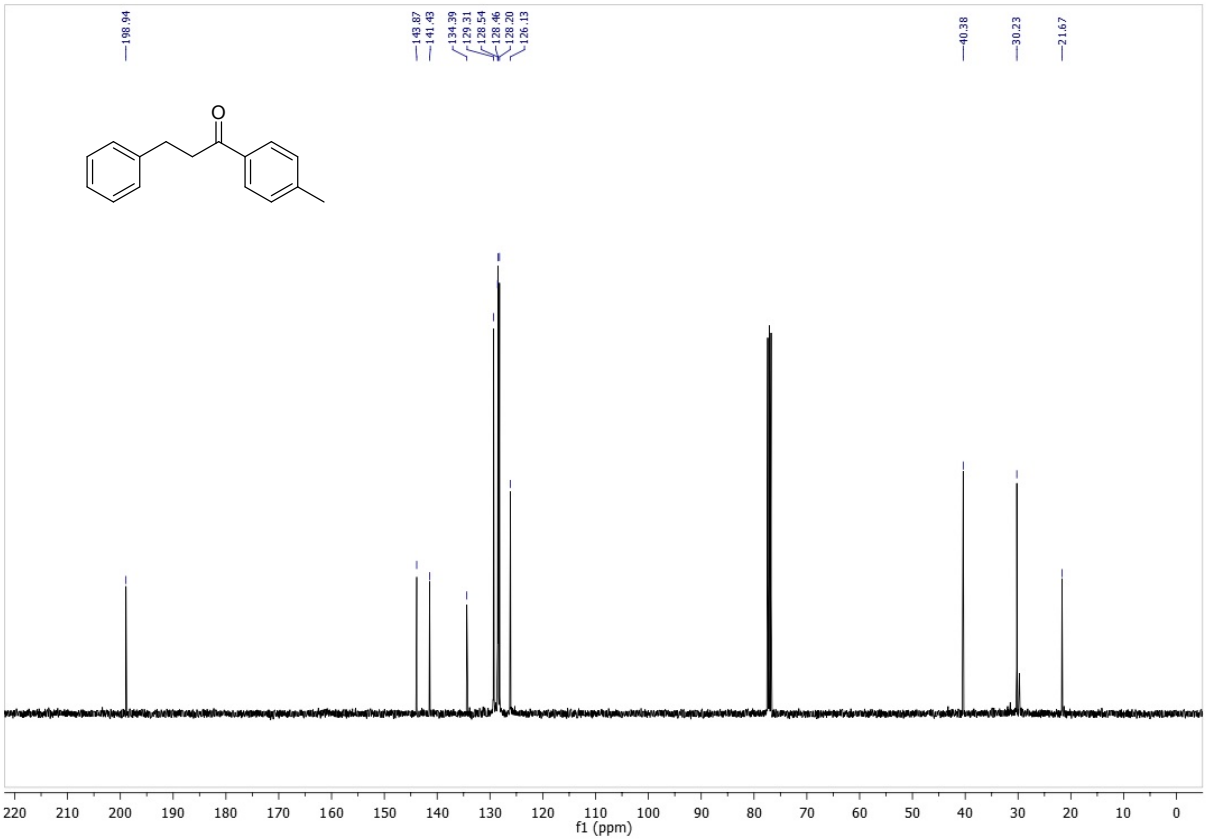
1, 3-Diphenyl-propan-1-one



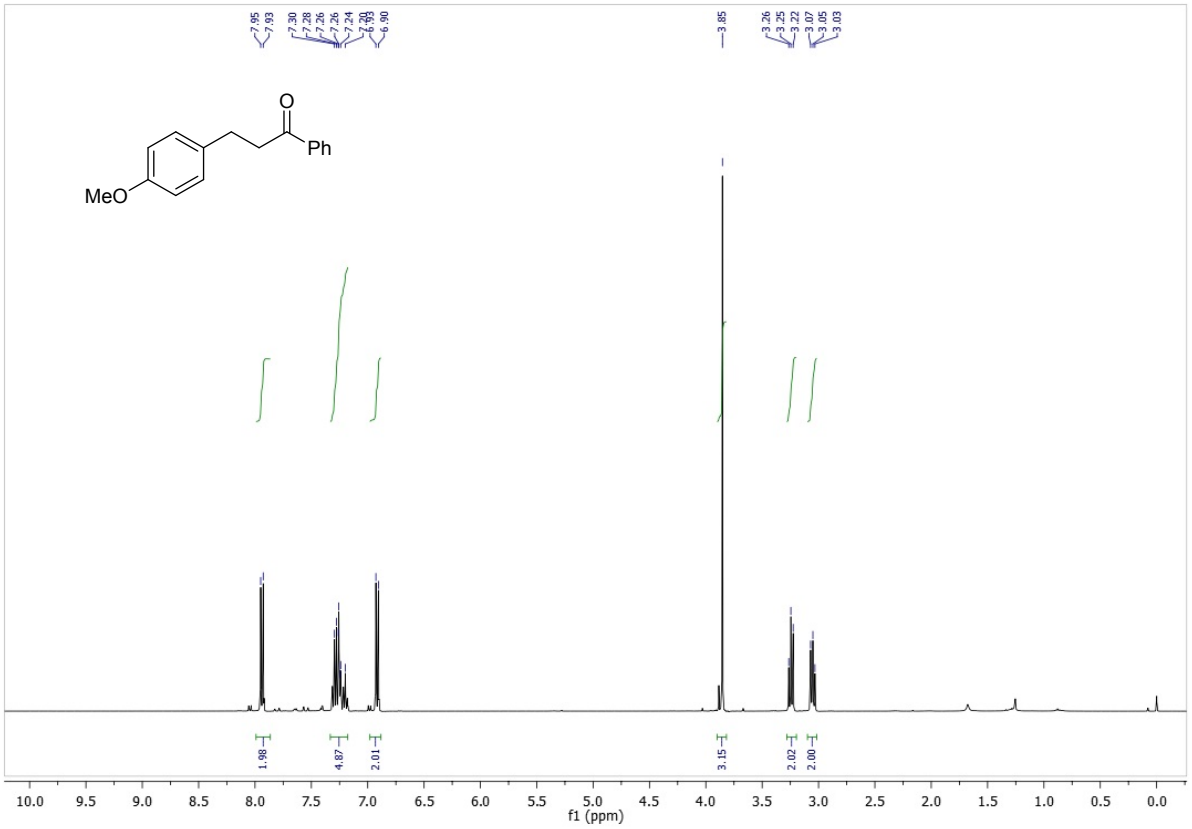


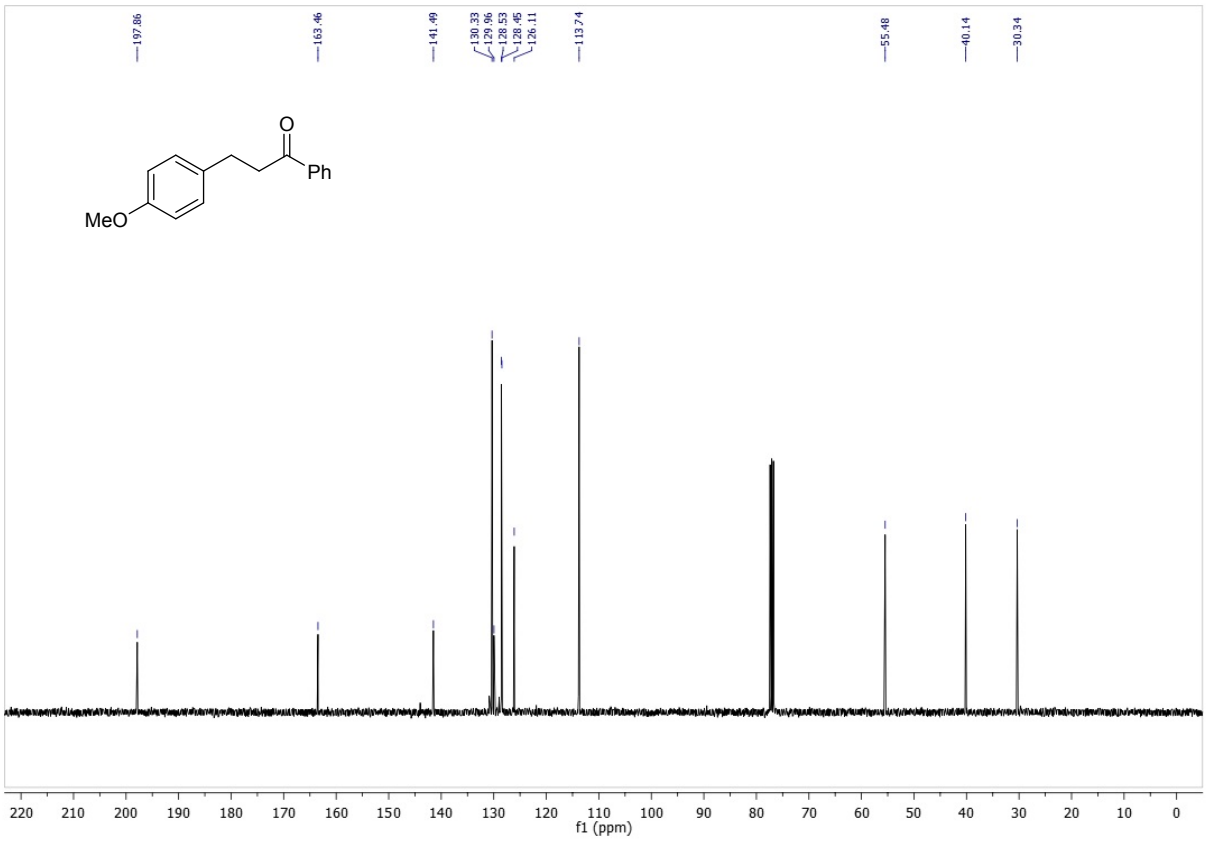
3-phenyl-1-(p-tolyl)propan-1-one



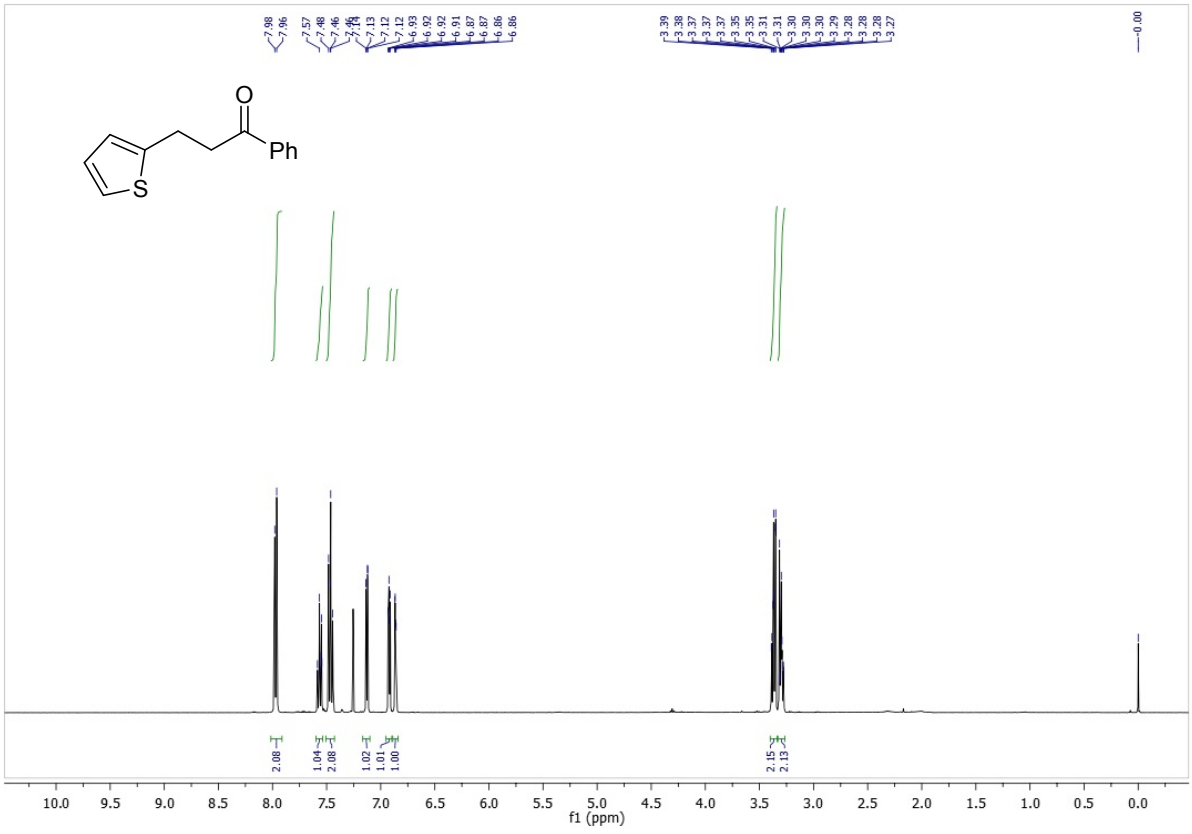


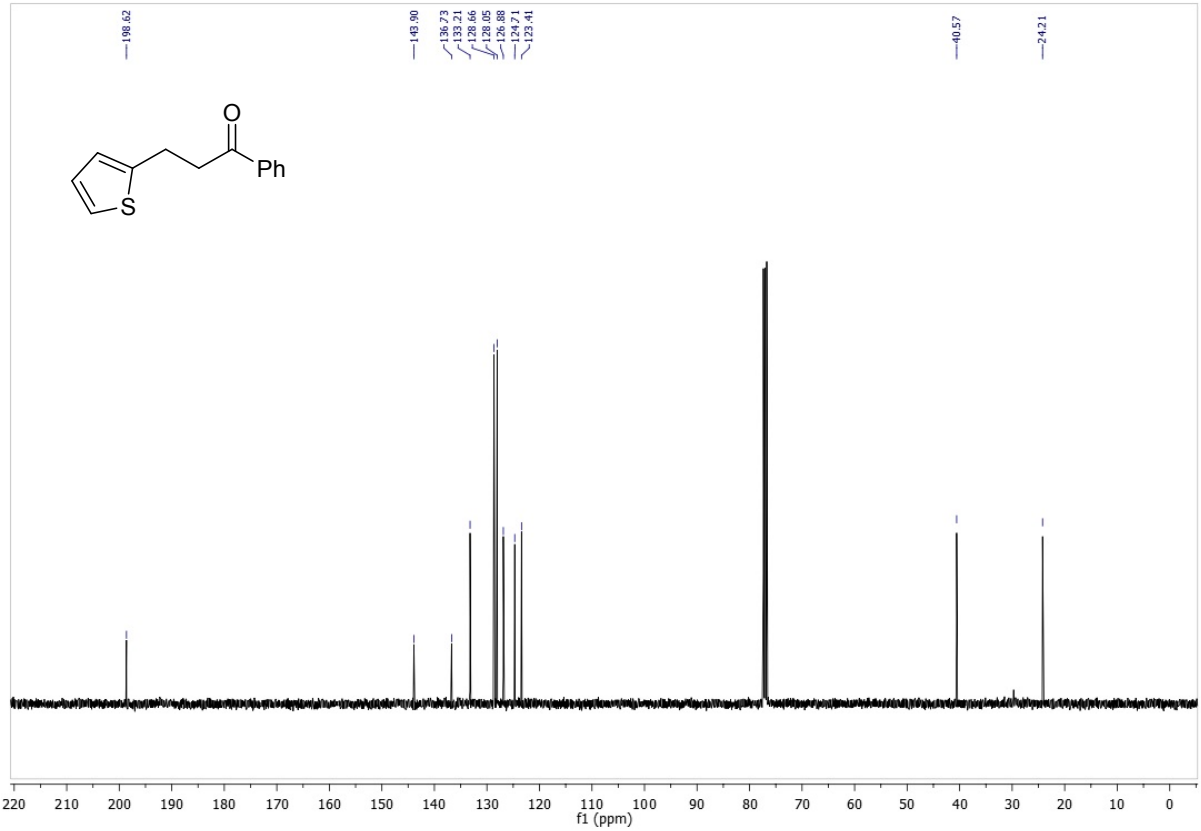
3-(4-Methoxy-phenyl)-1-phenyl-propan-1-one



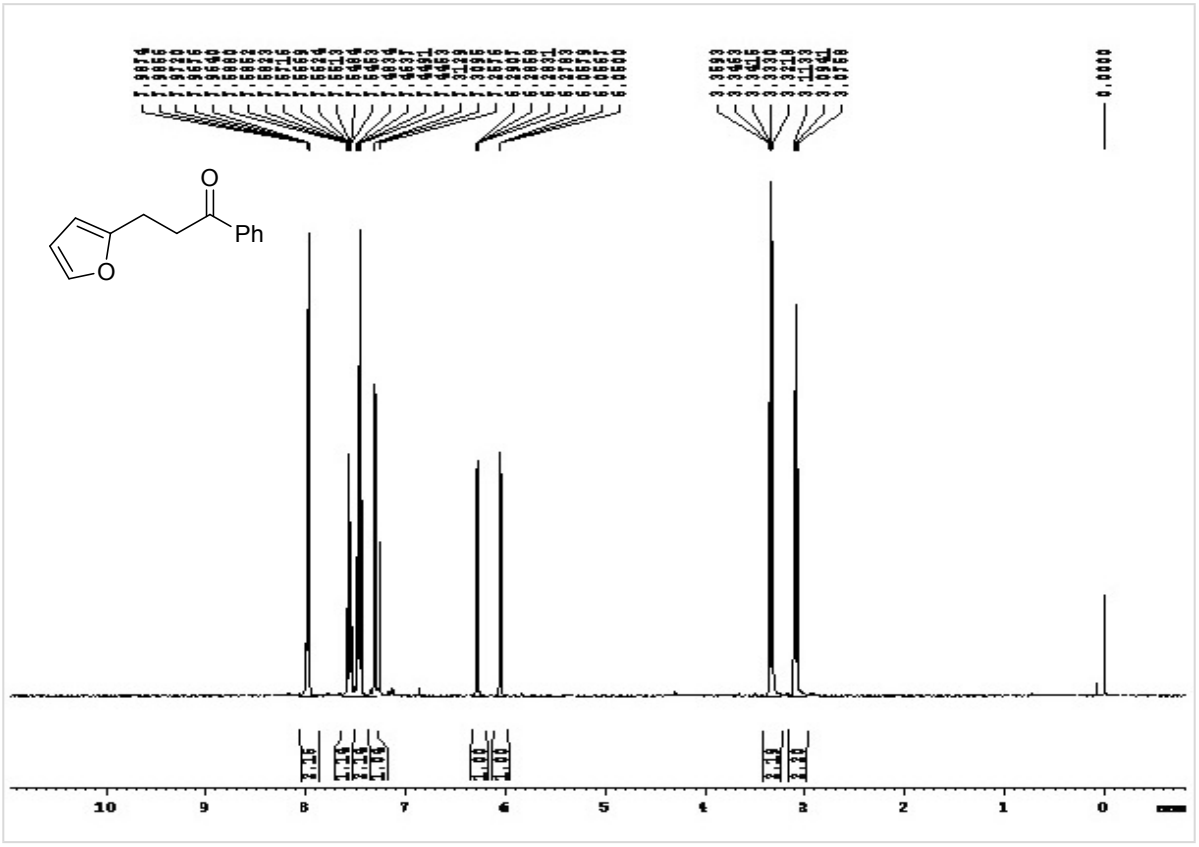


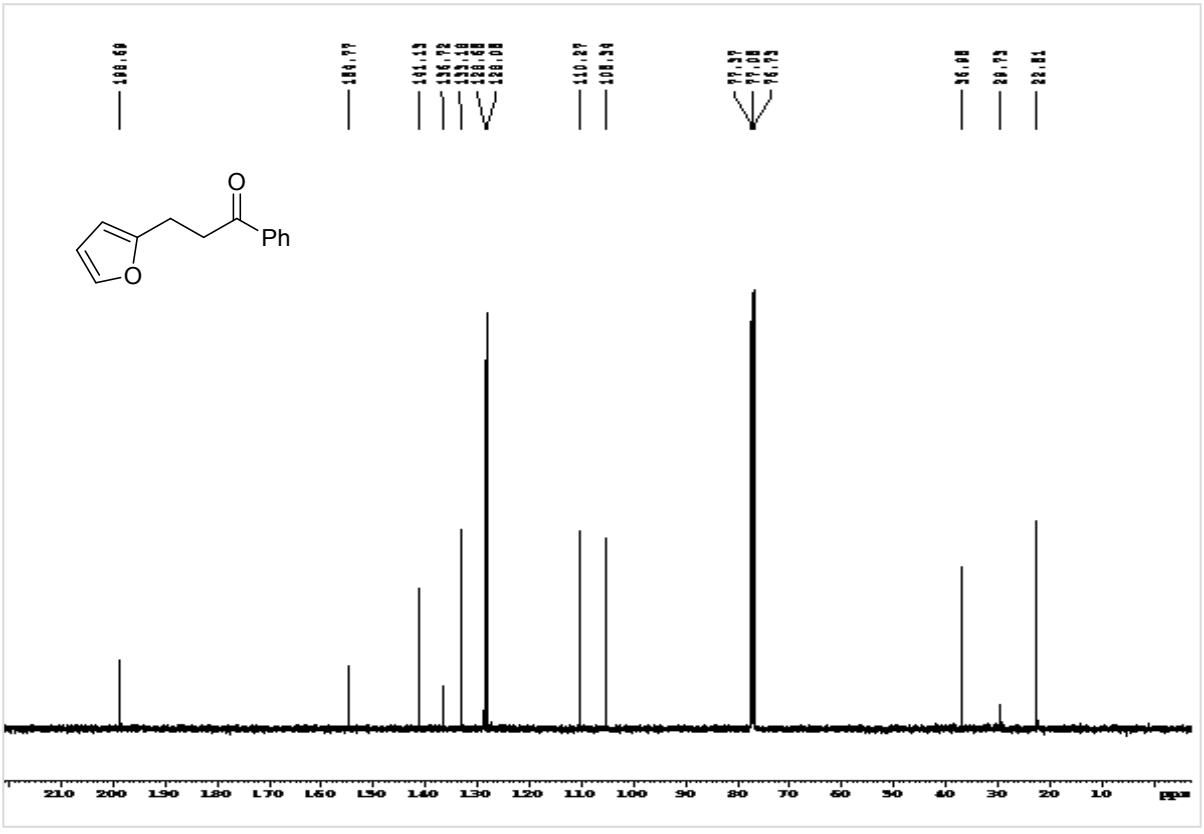
1-Phenyl-3-thiophen-2-yl-propan-1-one



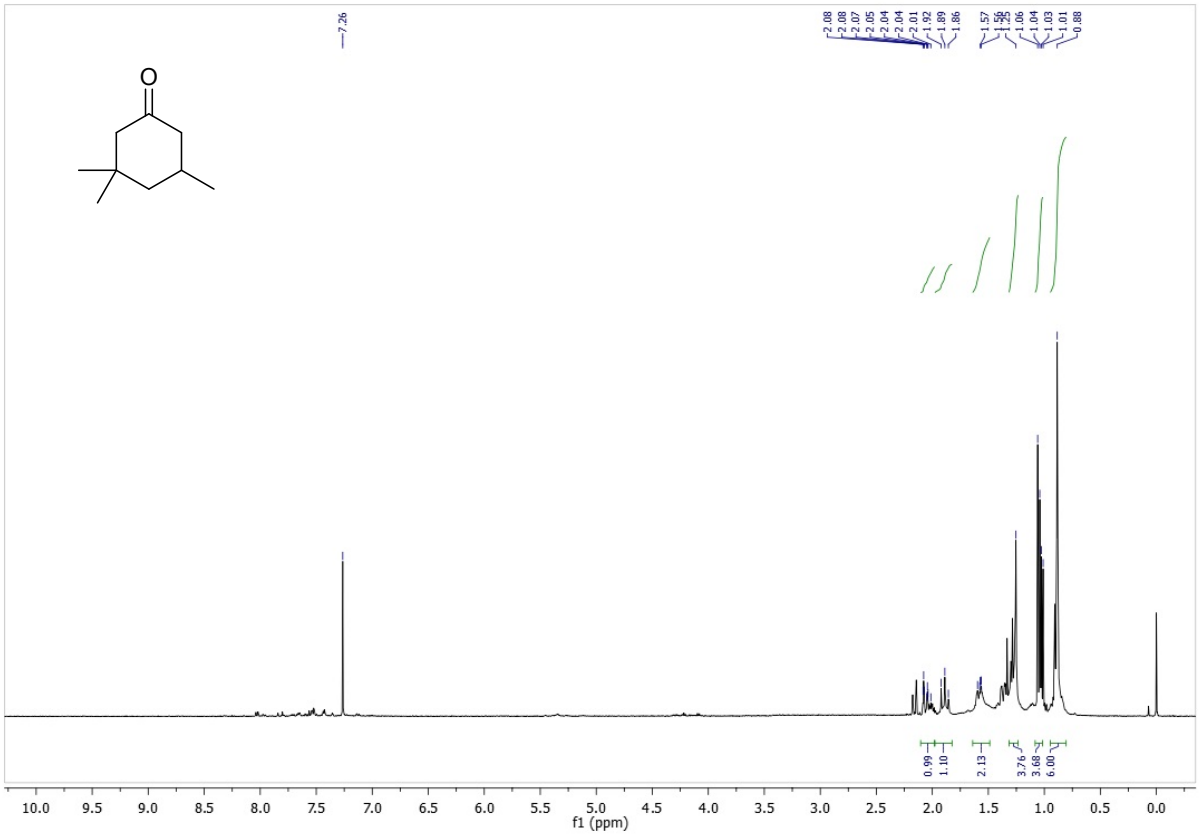


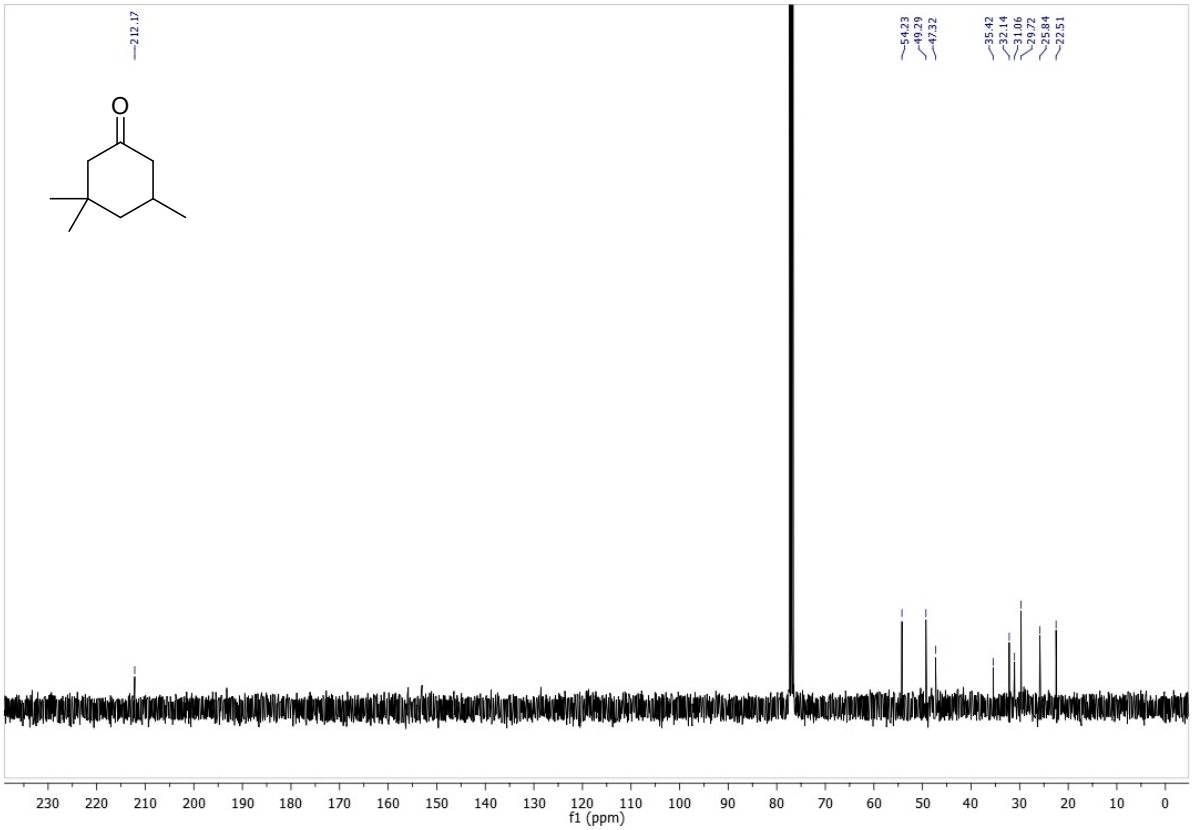
3-Furan-2-yl-1-phenyl-propan-1-one



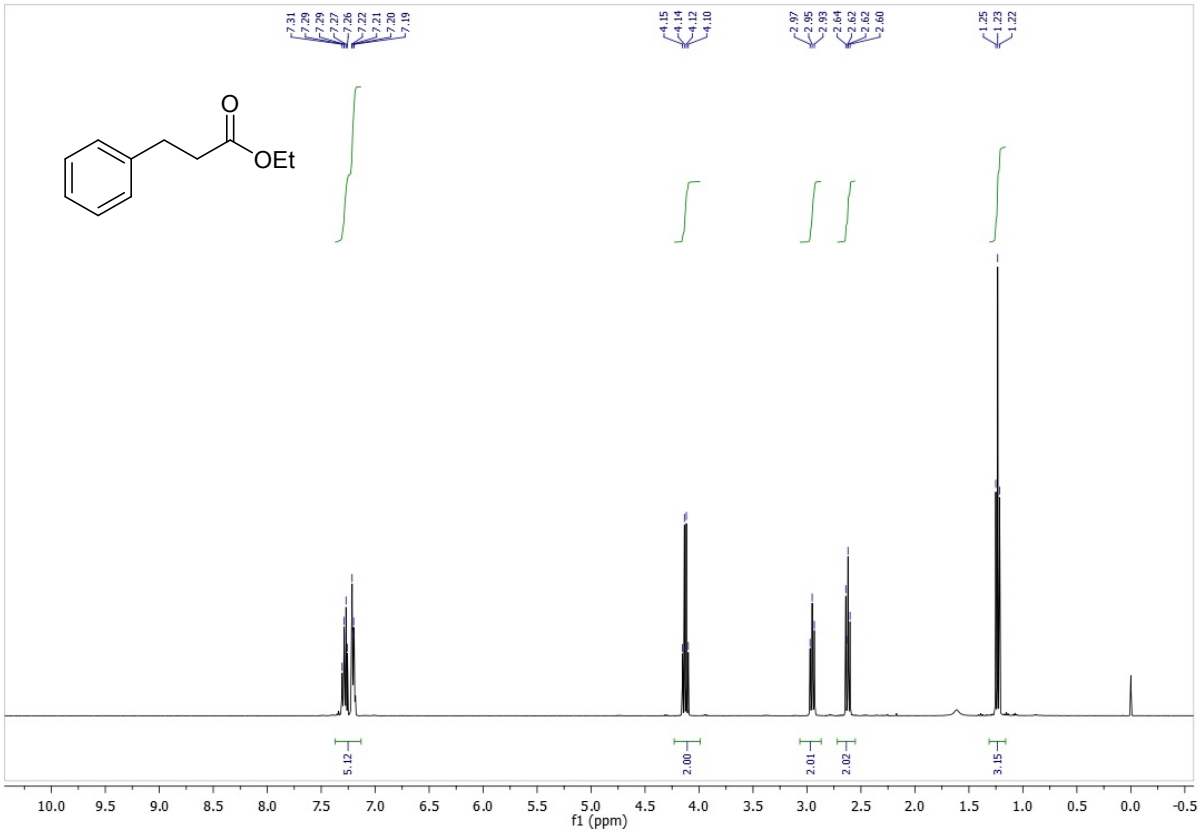


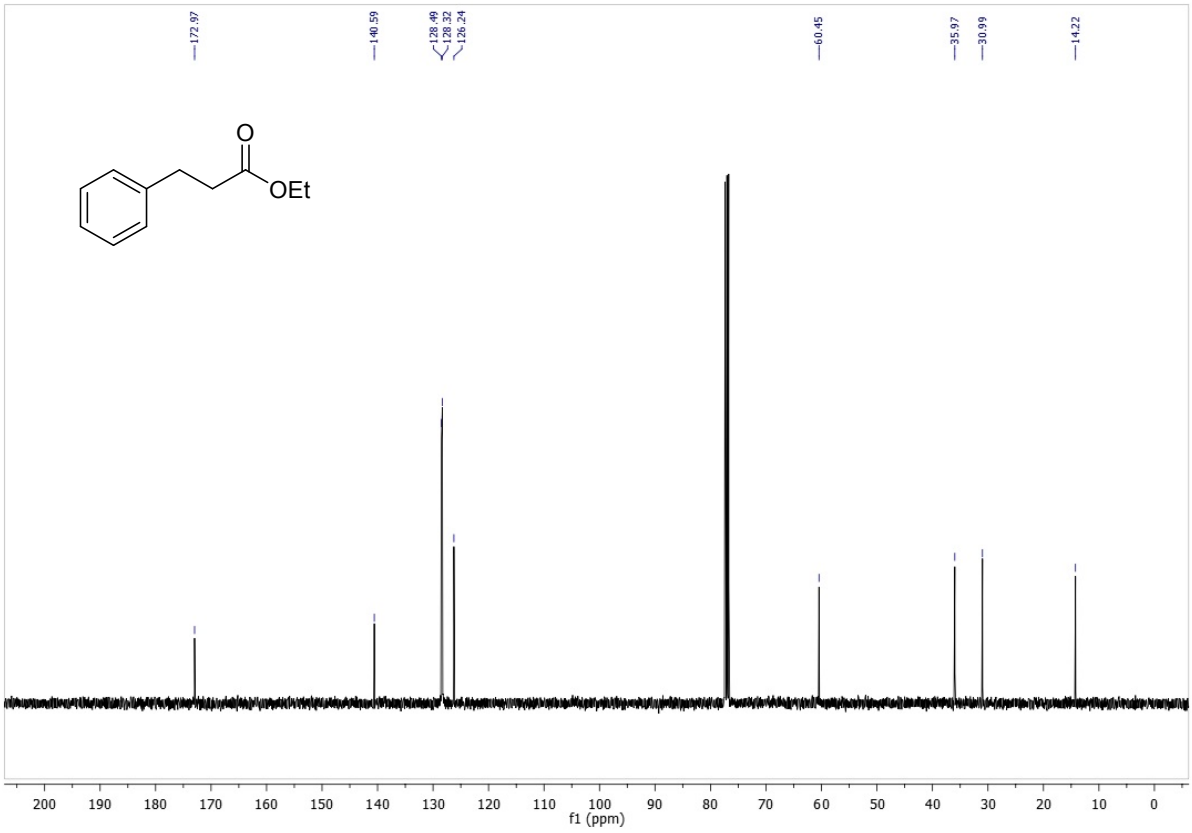
3,3,5-trimethylcyclohexanone





Ethyl 3-phenylpropanoate





3-phenylpropanamide