Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Triphenylphosphine Oxide Promoting Visible-Light-Driven C-C Coupling via Desulfurization

Shea Stewart, Robert Maloney, and Yugang Sun*

Department of Chemistry, Temple University, 1901 North 13th Street, Philadelphia, Pennsylvania 19122, USA

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Experimental Information

Chemicals and Instrumentation

All commercial chemicals were purchased from ThermoFisher Scientific and Sigma-Aldrich and used without purification unless otherwise noted. Optical absorption spectra were recorded using a Thermo Scientific Evolution 220 spectrophotometer. NMR spectra were obtained using a Bruker Advance 500 MHz spectrometer. ^{1}H NMR chemical shifts were reported in parts per million (ppm) referenced from the solvent peak ($CDCl_3$). The NMR signals were reported in the following manner: chemical shift, multiplicity number of protons (no. H), (s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, se=sexted, sep=septet, dd=doublet of doublets, m=multiplet), and coupling constant (Hz) where applicable. ^{13}C NMR chemical shifts were reported in ppm in reference to solvent peak ($CDCl_3$). The light sources used for driving reactions were Dolan-Jenner Fiber-Lite MI-LED B1 High Intensity LED Illuminators. Light intensity measurements were done with a ThorLabs PM100D digital handheld optical power and energy console equipped with an S305C thermal power sensor head. The gas chromatography (GC) combined with flame ionization detector (FID) was performed using an Agilent Technologies 7820A GC System. The liquid chromatography (LC) combined with mass spectrometry (MS) was performed using a G6125 single quadrupole ESI MS with an Infinity 1260 HPLC system (Agilent). The LC-MS was equipped with a reverse-phase Zorbax 300SB-C8 analytical column (4.6 × 50 mm, particle size of 5 μm) (Agilent). Mobile phase A was 0.1% formic acid in water and mobile phase B was 0.1% formic acid in acetonitrile. Each run of separation was obtained using a 1mL/min flow rate with initial mobile phase conditions set at 95% A and 5% B for the first 0.5 min followed by linear increase of B for a total run time of 6 min until the mobile phase A was 5% and B was 95%.

Light-Driven Reactions and Product Analysis

All solvents for the reactions were taken directly from the original bottles without drying. In a typical reaction, 72 μL of methyl thioglycolate (**2**)**,** 157 mg of triphenylphosphine (TPP), and 46 μL of styrene (**1**) were added to 2 mL solvent before capping and sonicating until TPP was fully dissolved prior to photoillumination. Note: The chemicals directly taken from the original bottles are denoted with the prefix, b-, while the chemicals purified prior to use are denoted with the prefix, p-. For example, TPP taken from the original bottle is labelled as b-TPP and purified TPP with removal of triphenylphosphine oxide (TPPO) is labelled as p-TPP. TPP was purified by eluting it with pure hexanes through a glass pipette packed with silica gel for column chromatography purchased from Sigma Aldrich. Hexanes was removed by rotoevaporation at 25 °C**. 2** was purified via acid base extraction, using 10% sodium carbonate to pull the mercaptan into an aqueous layer while leaving behind the disulfide in ethyl acetate. The aqueous layers were then neutralized with HCl before extracting the purified **2** with DCM. DCM was removed via rotoevaporation at 25 °C. When the atmosphere was controlled with an argon balloon, the solvent and reagents were added to a 4-mL glass vial that was equipped with a screw cap and a rubber septum. Then an outlet needle and a needle equipped with an argon balloon were inserted. The reaction mixture was purged this way with argon for five minutes while sonicating. The outlet needle was then removed, and the argon balloon needle was kept in place for the entire reaction. The reactants and reaction products were analysed and quantitated with NMR. In a typical analysis,

the crude reaction solution was directly spiked with 20 μL of cinnamaldehyde. Several drops of the thoroughly mixed solution were added to an NMR tube containing 700 μL of $CDCl_3$. The purity of cinnamaldehyde was ensured by frequently passing it through a silica plug and storing it at -20 °C after flushing with argon. Multiple batches of crude reaction mixtures were combined for isolation of C-C product. A few tiny crystals of triphenylphosphine sulfide (TPPS) were added to the solution as seeds to aid in precipitation of TPPS when the solution was placed in a freezer set at -20 °C overnight. Filtration removed the TPPS precipitate, giving the solution containing C-C product. The solvent (i.e., acetonitrile) of the solution was removed in a rotary evaporator set at 25 °C. The leftover crude oil was then directly loaded onto the silica column and eluted without flashing, ramping slowly from 100% hexanes to 5% ethyl acetate in hexanes. TLC (10% ethyl acetate in hexanes) was used to confirm which fractions contained the C-C coupling product.

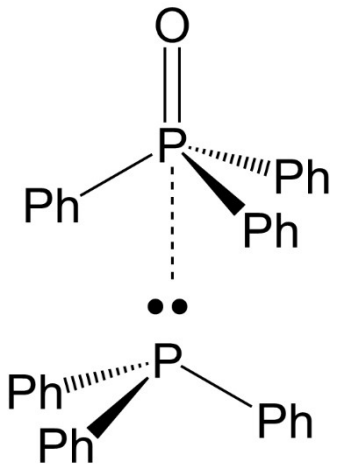
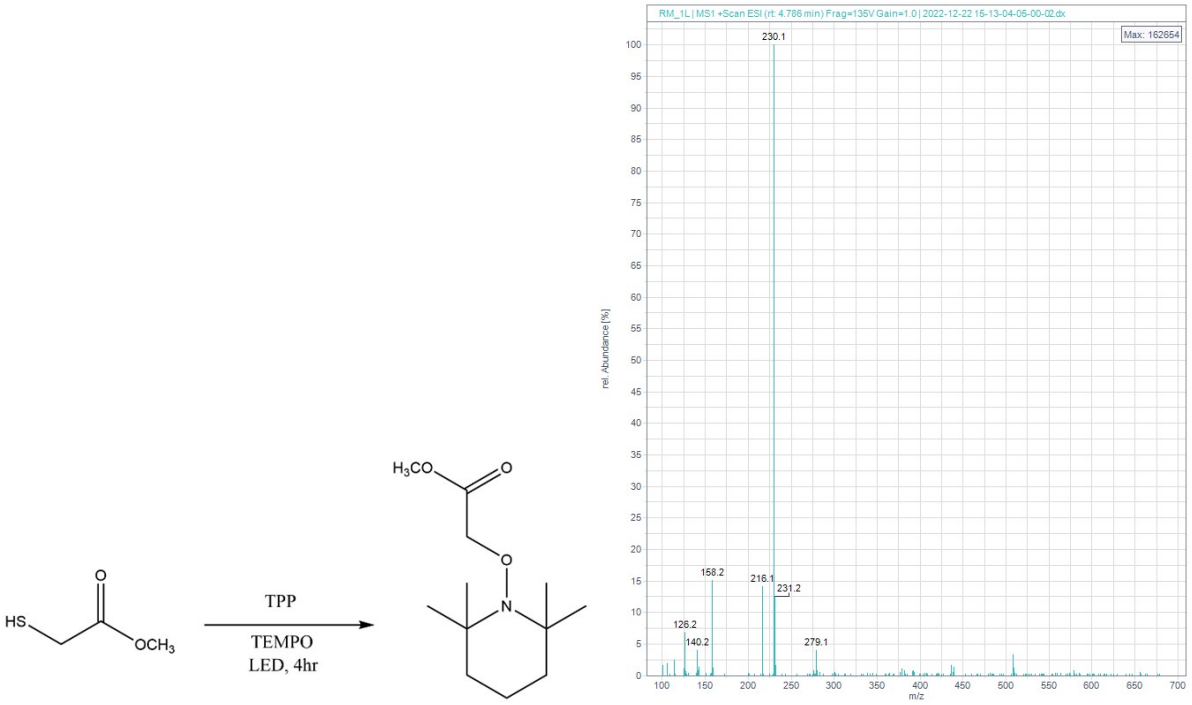


Figure S1 Proposed structure of the TPPO-TPP EDA complex.



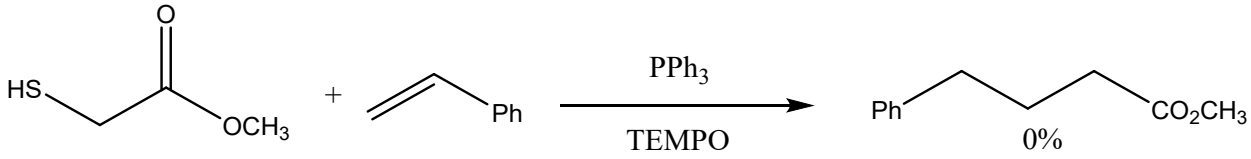


Figure S2 (top left) TEMPO radical trapping experiment for **2** desulfurization. 36 µL of **2**, 78 mg of TPP, 62 mg of TEMPO, and 2 mL of acetonitrile were added to a 4-mL vial before capping and sonicating to form a homogeneous solution. The solution was illuminated for 4 hours, then 5 µL of the final solution were dissolved into 2 mL of acetonitrile for analysis by LC-MS. (top right right) ESI MS spectrum of the eluent at 4.786 minutes. The major peak corresponding to an m/z of 230.1 represents the TEMPO-methyl acetate adduct (cald. [$M^{\cdot+}$], 229.17) expected to form due to **2** desulfurization. (bottom) Scheme of TEMPO radical quenching experiment, conditions: 0.8 mmol of methyl thioglycolate, 0.4 mmol of **1**, 0.6 mmol of triphenylphosphine, 2.4 mmol of TEMPO, no stir bar, 60 °C, 0.8 W/cm^2 white LED, 18 hours, in air. No C-C coupling product was observed, and 80% of the **1** remained in the final solution.

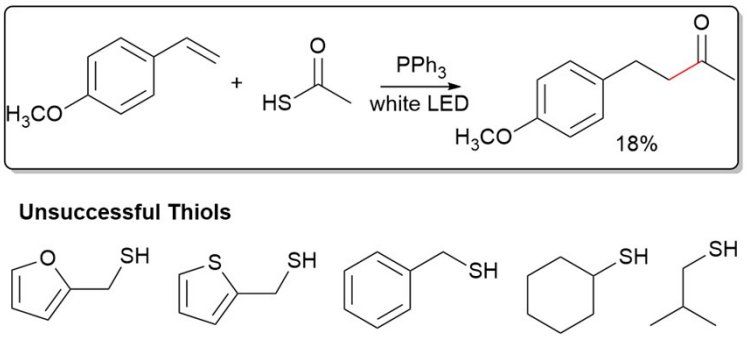


Figure S3 Testing of various mercaptans for the visible-light-driven reductive C-C coupling via desulfurization. For each trial, 0.8 mmol of mercaptan, 0.4 mmol of **1**, 157 mg of TPP, and 2 mL of acetonitrile were added to a 4 mL glass vial before capping and sonicating to form a homogeneous solution. Then, the solution was illuminated with 0.8 W/cm^2 white light while heating to 60 °C for 18 hours. Final crude reaction mixtures were analysed via ^{1}H NMR. Of the mercaptans tested, other than **2**, only thioacetic acid yielded C-C coupling product detectable by NMR. Other thiols shown in this figure with electron-rich groups adjacent to -S were not favourable for the C-C coupling reaction.

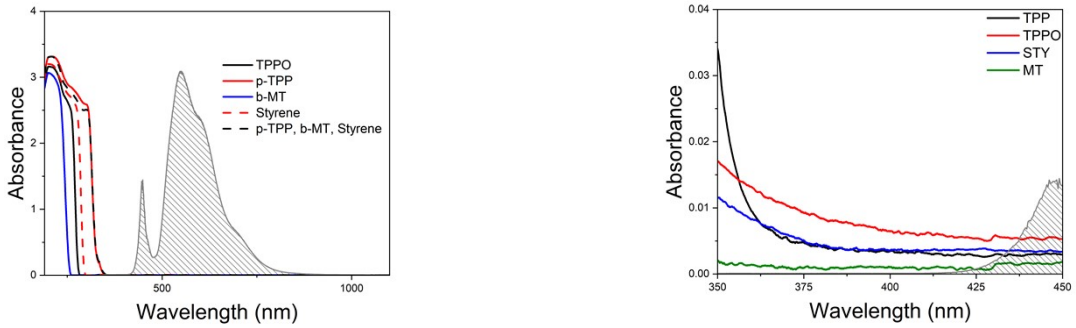


Figure S4 (left) Survey UV-Vis absorption spectra of individual reagents and their combination in the spectral range of 200-1100 nm and (right) UV-vis absorption of spectra of individual reagents in the focused range of 350-450 nm. For the wider spectral range scans, 0.057 mmol of each reagent were dissolved in 2 mL of acetonitrile by sonicating for a few minutes, and the total scan time was approximately 1 minute. Meanwhile, the narrow range scans took 30 minutes and solutions contained 0.27 mmol of each reagent to improve signal to noise ratio. These same long-time-scan procedures were followed for the spectra shown in Figure 1 of the main text. For the longer scans, solvent evaporation during measurement could not be completely avoided, resulting in concentration gradients of the solutions in the cuvette. The concentration gradients yielded heterogeneity in the refractive index throughout the solutions, which induced light scattering contributions to the absorption spectra. In contrast, such heterogeneity does not exist in the pure solvent used as a baseline. Therefore, the minor offsets of baselines are ascribed to the solvent-evaporation-induced heterogeneity in the solutions. It is reasonable to consider that any section of the absorption spectra being flat/parallel to the x-axis as corresponding to zero absorbance. In both panels, the grey shaded line represents the emission spectrum of the LED lamp.

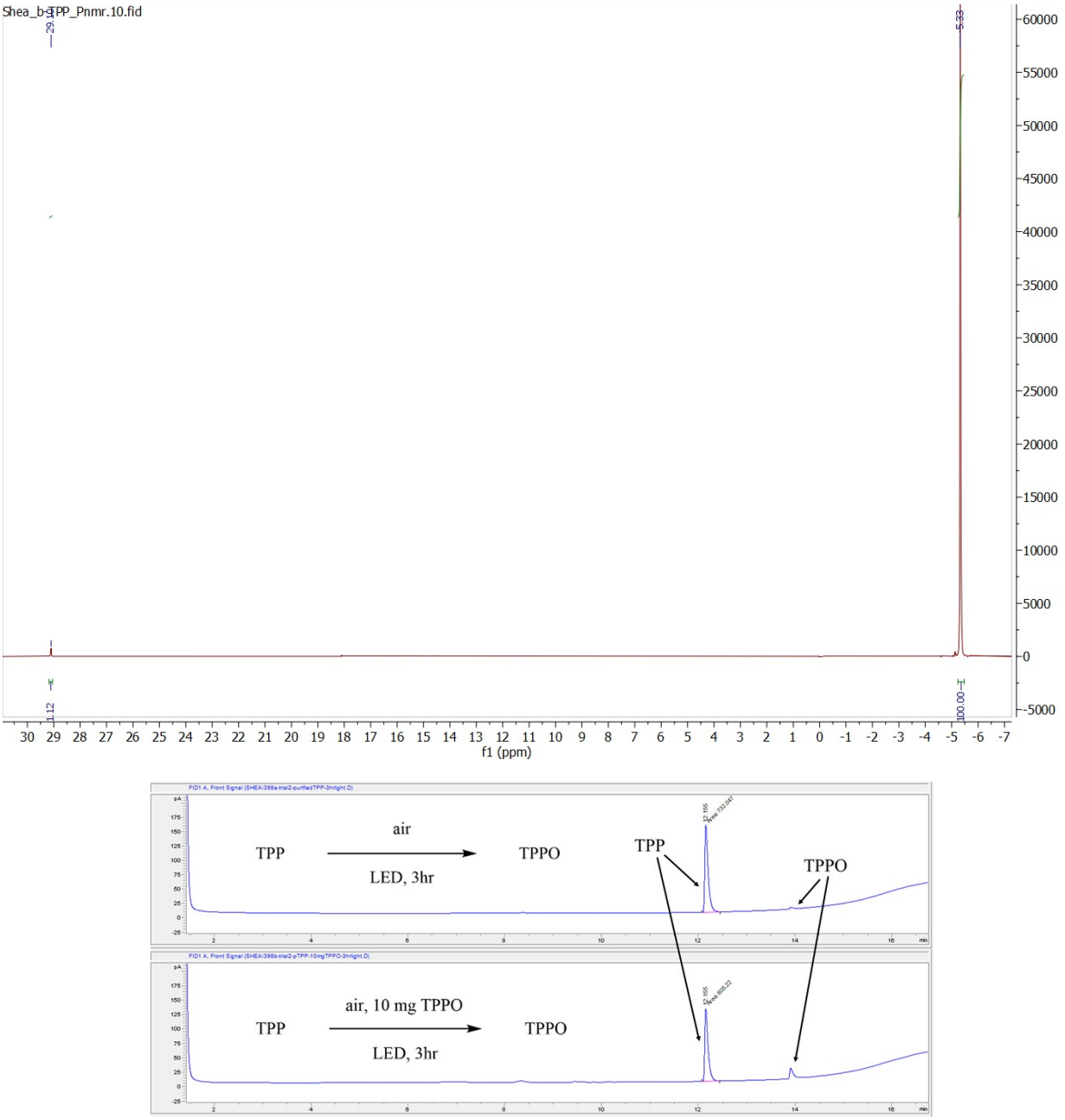


Figure S5 (top) ^{31}P-NMR spectrum of TPP taken from the original bottle (b-TPP) that were dissolved in $CDCl_3$. The delay between pulses was increased to 10 seconds and 64 scans were taken to increase the integrity of the data for use in relative quantification of the TPP:TPPO ratio, which was found to be roughly 99:1.

(bottom) GC-FID results of experiments displaying the effect of TPPO on visible-light-driven aerobic TPP oxidation in the absence of photocatalyst. The TPP oxidation experiment conditions are included in the frame of their corresponding GC profiles. Both experiments were run with 100 mg of p-TPP in 2 mL of acetonitrile, and one vial also contained 10 mg of TPPO. The solutions were sonicated until all solids were fully dissolved, followed by bubbling air for a few minutes

before capping and shining LED light for 3 hours. GC samples were prepared by placing 100 μL of the final reaction mixture into 1 mL of acetonitrile, followed by vortexing and briefly sonicating. 1 μL of the solution was injected into the instrument for analysis. Peak area is directly proportional to analyte concentration. The final amount of TPP in the reaction with added TPPO was less than the reaction with only TPP added, indicating that the presence of TPPO favoured the visible-light-driven TPP oxidation due to the enhanced optical absorption of TPPO-TPP EDA complex.

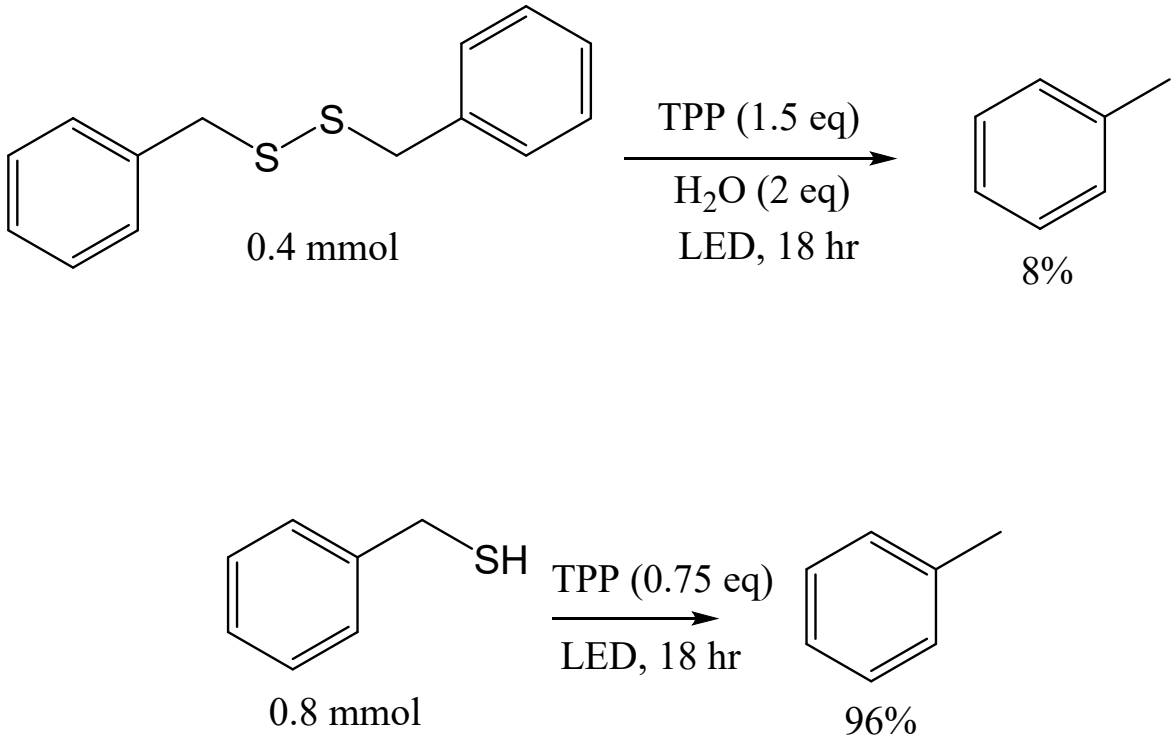
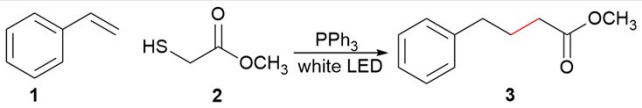


Figure S6 Visible-light-driven desulfurization of (top) dibenzyl disulfide and (bottom) benzyl mercaptan. Both reactions were run in 2 mL of acetonitrile and the final reaction mixtures were analysed by ^{1}H-NMR. Water was added as a hydrogen source for disulfide while the mercaptan acts as its own hydrogen source. The synthesis of dibenzyl disulfide was carried out according to a reported method described eslewhere.[S1]

Table S1 Effects of TPPO and atmospheric oxygen on visible-light-driven reductive C-C coupling via desulfurization



1 2 3

Entry	Conditions	Yield
1	p-TPP, Argon	4%
2	p-TPP, Air	9%
3	b-TPP, Argon	6%
4	b-TPP, Air	11%

Reaction conditions: 46 µL **1**, 157 mg TPP, 72 µL **2**, 2 mL acetonitrile (solvent), 0.8 W/cm^2 white LED, photoillumination of 6 hours, and temperature at 60 °C. For reactions run under argon, solutions were sonicated while bubbling argon for 5 minutes and an argon balloon was left in place for the entire reaction. All reactions were run without a stir bar to avoid contamination. The yield of product, methyl acetate, was determined using ^{1}H-NMR with t-cinnamaldehyde as an internal standard. b-TPP contained ~1% TPPO as determined by ^{31}P-NMR.

Synthesis and Characterization of Substrate Scope Compounds

All the following compounds were synthesized according to the procedure outlined in Table 2 of the main text, then isolated according to the procedure outlined in the Experimental Information. Briefly, 0.4 mmol of styrene derivative, 0.8 mmol of mercaptan, 0.6 mmol of TPP, and 2 mL of acetonitrile were added to a 4 mL glass vial before capping and sonicating to achieve a homogeneous solution. The vial was then placed into an in house designed aluminum reaction vial holder as shown in the photo below, at which point the solution was heated to 60 °C and the LED was shined at 0.8 W/cm^2 for 18 h

methyl 4-phenylbutyrate

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.04 (2H, p, J = 7.5Hz), 2.40 (2H, t, J = 7.5Hz), 2.72 (2H, t, J = 7.5Hz), 3.73 (3H, s), 7.26 (3H, m), 7.34 (2H, m) ppm

The ^{1}H NMR spectrum agrees with that previously reported[S2]

LCMS (ESI) calculated [$M^{\cdot+}$] for $C_{11}H_{14}O_2$: 178.10, found: 179.2

methyl 4-(4-methoxyphenyl)butanoate

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.92(2H, p, J = 7.5Hz), 2.32(2H, t, J = 7.5Hz), 2.59(2H, t, J = 7.5Hz), 3.66(3H, s), 3.78(3H, s), 6.83(2H, d, J = 9Hz), 7.09(2H, d, J = 9Hz), ppm

The ^{1}H NMR spectrum agrees with that previously reported[S2]

LCMS (ESI) calculated [$M^{\cdot+}$] for $C_{12}H_{16}O_3$: 208.11, found: 209.1

methyl 4-(4-fluorophenyl)butanoate

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.07(2H, p, J = 7.5Hz), 2.46(2H, t, J = 7.5Hz), 2.76(2H, t, J = 7.5Hz), 3.8(3H, s), 7.10(2H, m), 7.26(2H, m) ppm

The ^{1}H NMR spectrum agrees with that previously reported[S2]

LCMS (ESI) calculated [$M^{\cdot+}$] for $C_{11}H_{13}FO_2$: 196.09, found: 197.1

methyl 4-(2-bromophenyl)butanoate

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.97(2H, m, J = 7.5Hz), 2.37(2H, t, J = 7.5Hz), 2.78(2H, t, J = 7.5Hz), 3.67(3H, s), 7.05(1H, m), 7.22(2H, m), 7.52(1H, dd, J =8.0, 1.5Hz) ppm

The ^{1}H NMR spectrum agrees with that previously reported[S2]

LCMS (ESI) calculated [$M^{\cdot+}$] for $C_{11}H_{13}BrO_2$: 256.01, found: 257.9

methyl 4-phenylpentanoate

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.26(3H, d, J = 7.0Hz), 1.92(2H, m), 2.18(2H, m), 2.70(1H, dp, J = 8.0, 1.5Hz), 3.61(3H, s), 7.17(3H, m), 7.28(2H, dt, J = 7.0, 2.0Hz) ppm

The ^{1}H NMR spectrum agrees with that previously reported[S2]

LCMS (ESI) calculated [$M^{\cdot+}$] for $C_{12}H_{16}O_2$: 192.12, found: 193.2

methyl 3-methyl-4-phenylbutanoate

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94(3H, d, J = 6.5Hz), 2.16(1H, dd, J = 14.5, 8Hz), 2.28(1H, se, J = 6.5Hz), 2.35(1H, dd, J = 14.5, 6.0Hz), 2.51(1H, dd, J = 13.5, 7.0Hz), 2.60(1H, dd, J = 13.5, 7.0Hz), 3.65(3H, s), 7.16(3H, m), 7.28(2H, m) ppm

The ^{1}H NMR spectrum agrees with that previously reported[S2]

LCMS (ESI) calculated [$M^{\cdot+}$] for $C_{11}H_{16}O_2$: 192.12, found: 193.1

methyl 2-(2,3-dihydro-1H-inden-2-yl)acetate

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.49(2H, d, J = 7.0 Hz), 2.64(2H, dd, J = 15.5, 8.5Hz), 2.88(1H, hep, J = 7.5Hz), 3.13(2H, dd, J = 15.5, 8.0Hz), 3.68(3H, s), 7.12(2H, m), 7.17(1H, m) ppm

The ^{1}H NMR spectrum agrees with that previously reported[S2]

LCMS (ESI) calculated [$M^{\cdot+}$] for $C_{12}H_{14}O_2$: 190.10, found: 191.1

4-(4-methoxyphenyl)butan-2-one

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.32(3H, s), 2.81(2H, t, J = 8.0Hz), 3.08(2H, t, J = 8.0Hz), 3.79(3H, s), 6.84(2H, dd, J = 10.0, 2.0Hz), 7.13(2H, dd, J = 10.0, 2.0Hz) ppm

The ^{1}H NMR spectrum agrees with that previously reported[S3]

LCMS (ESI) calculated [$M^{\cdot+}$] for $C_{11}H_{14}O_2$: 178.1, found: 179.2

methyl 4-(pyridin-2-yl)butanoate

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08(2H, p, J = 7.5Hz), 2.38(2H, t, J = 7.5Hz), 2.83(2H, t, J = 7.5Hz), 3.66(3H, s), 7.62(59H, m)** ppm

The ^{1}H NMR spectrum agrees with that previously reported (**aromatic signals buried under impurity)[S4]

LCMS (ESI) calculated [$M^{\cdot+}$] for $C_{10}H_{13}NO_2$: 179.09, found: 180.2

References

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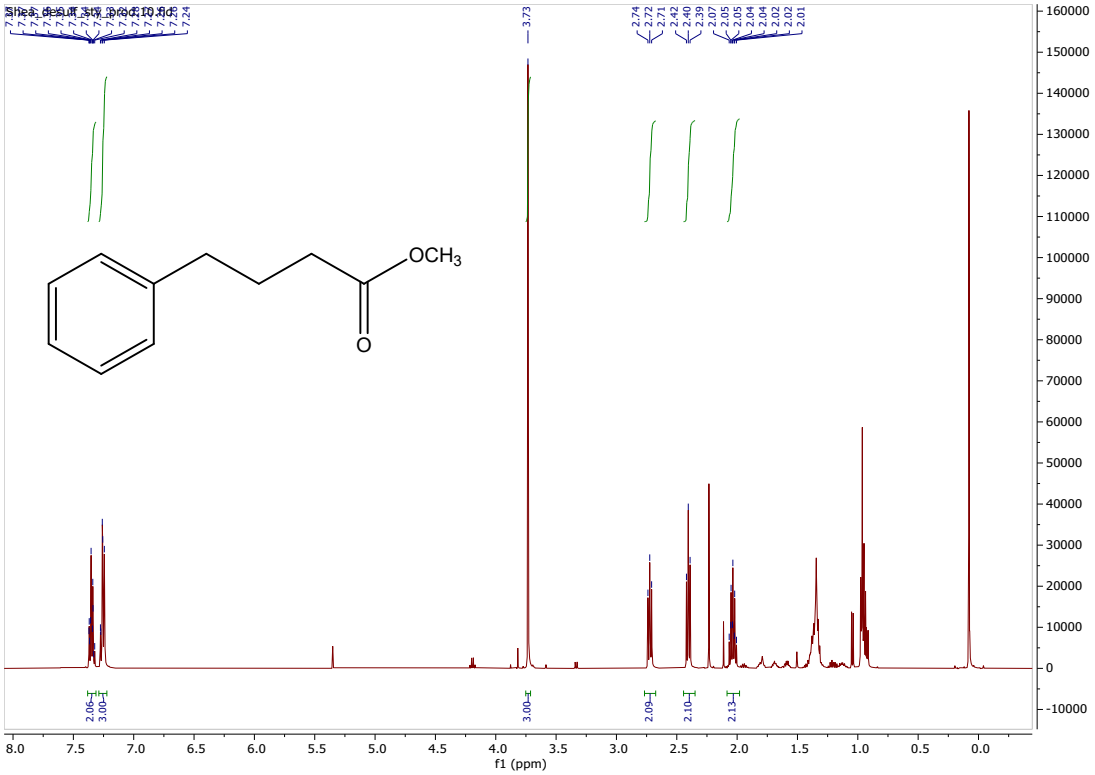
(S2) L. Zhang, X. Si, Y. Yang, S. Witzel, K. Sekine, M. Rudolph, F. Rominger, and A. S. K. Hashmi, *ACS Catal*., 2019, **9**, 6118-6123.

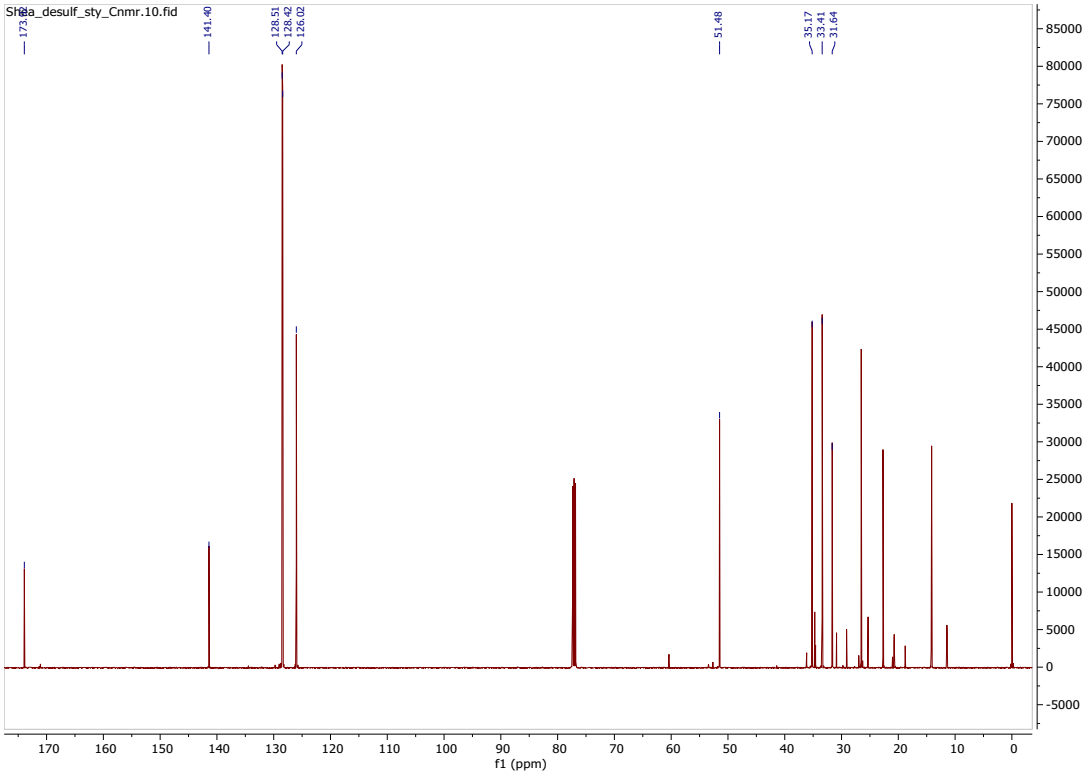
(S3) M. G. Lauer, M. K. Thompson, and K. H. Shaughnessy, *J. Org. Chem.*, 2014, **79**, 10837-10848

(S4) Q. Qin, W. Wang, C. Zhang, S. Song, and N. Jiao, *Chem. Commun.*, 2019, **55**, 10583-10586



^{1}H NMR spectrum of **methyl 4-phenylbutyrate** ($CDCl_3$, 500 MHz)

^{13}C NMR spectrum of **methyl 4-phenylbutyrate** ($CDCl_3$, 125 MHz)



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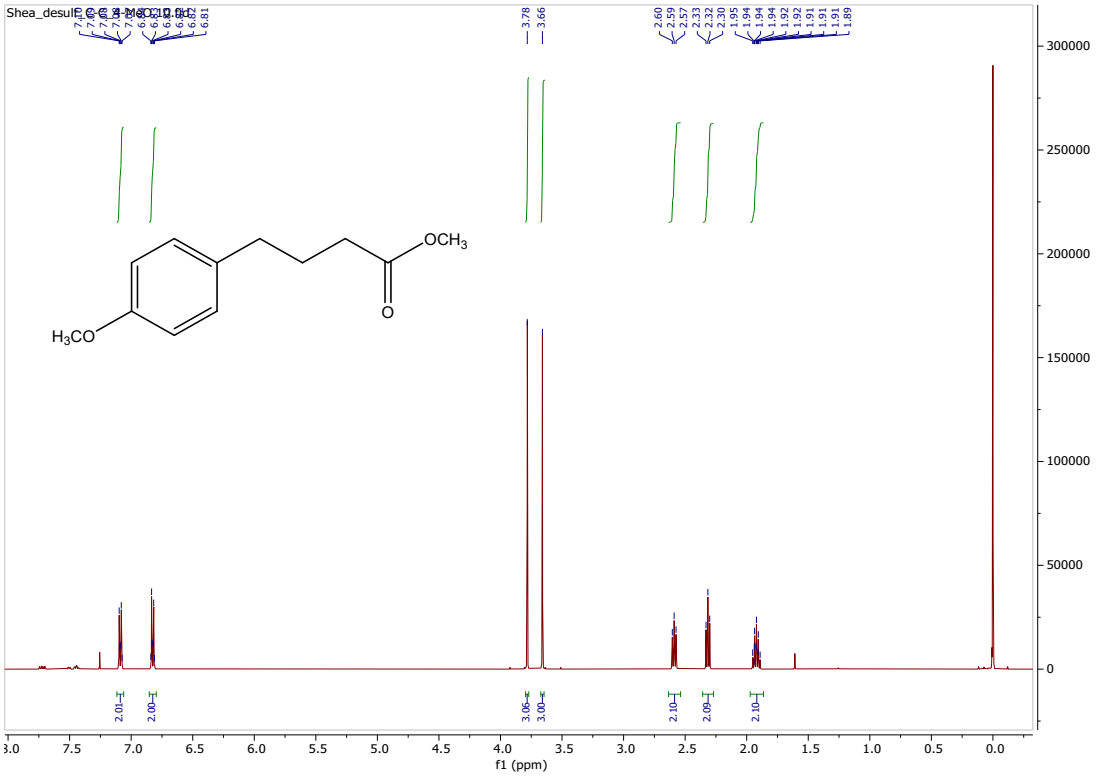
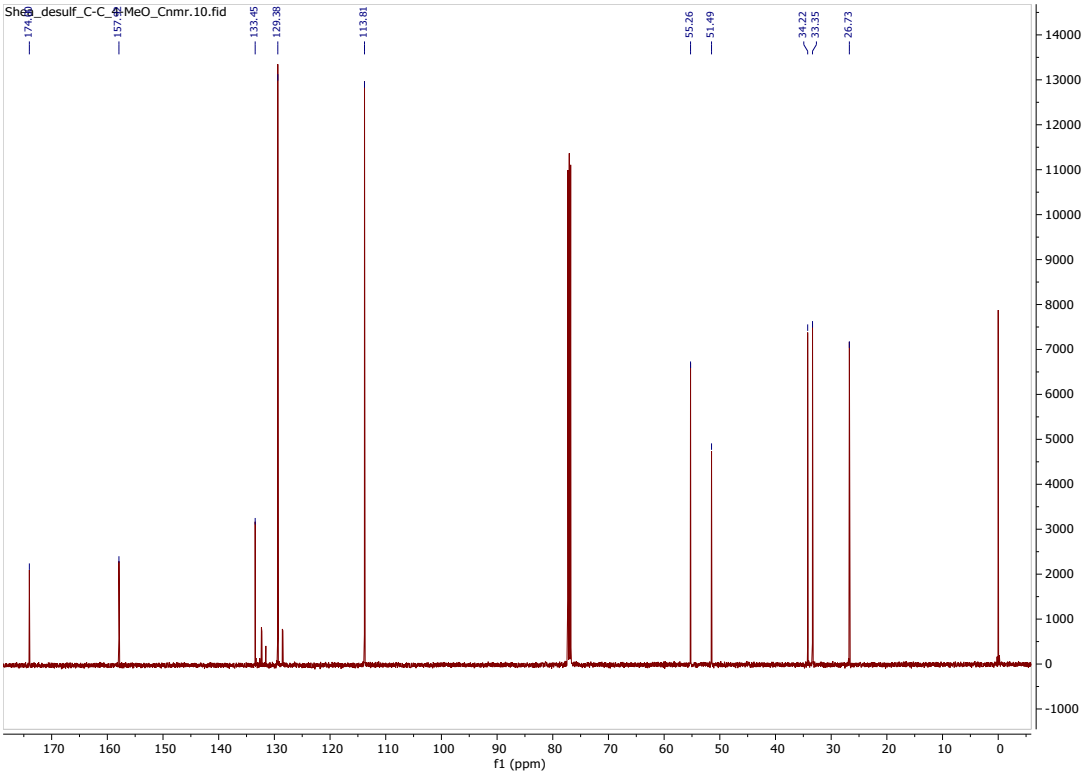
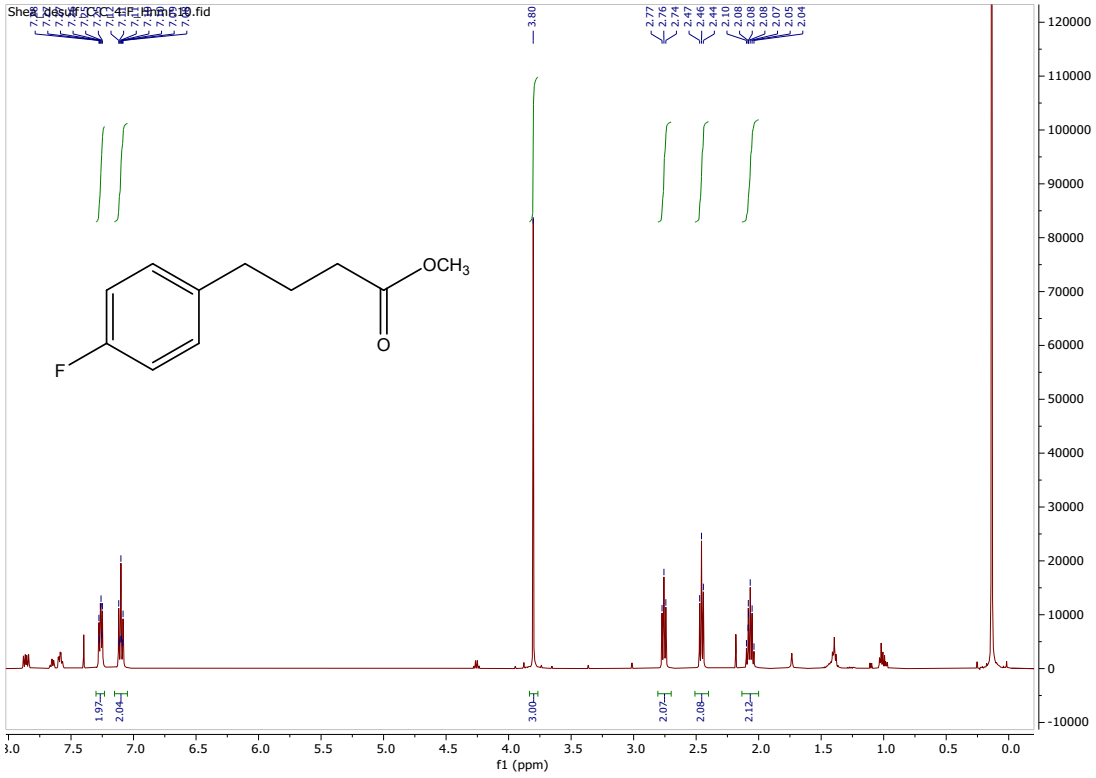


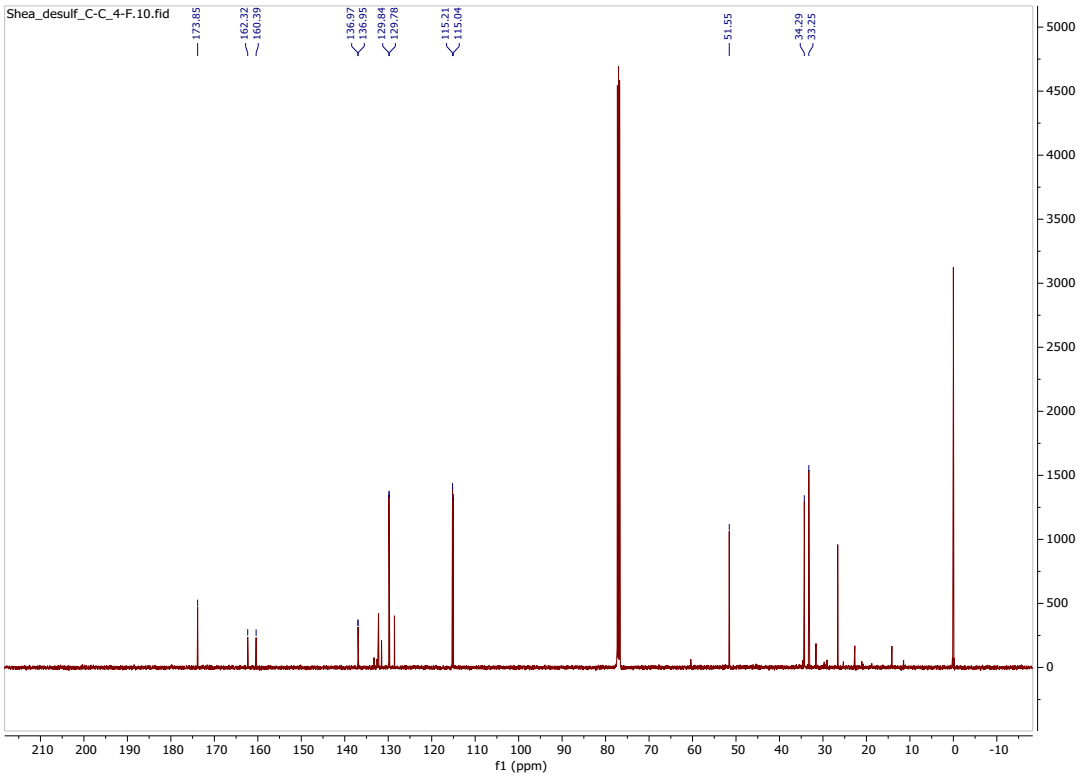


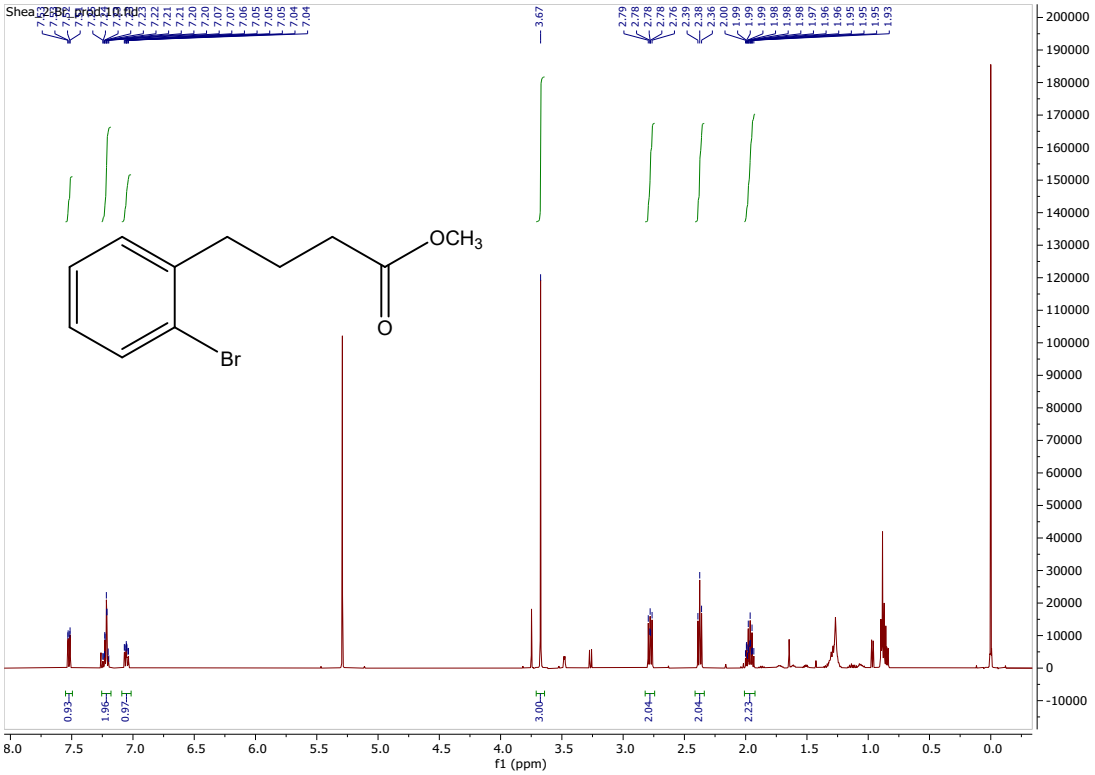
^{13}C NMR spectrum of **methyl 4-(4-methoxyphenyl)butanoate** ($CDCl_3$, 125 MHz)



^{1}H NMR spectrum of **methyl 4-(4-fluorophenyl)butanoate** ($CDCl_3$, 500 MHz)

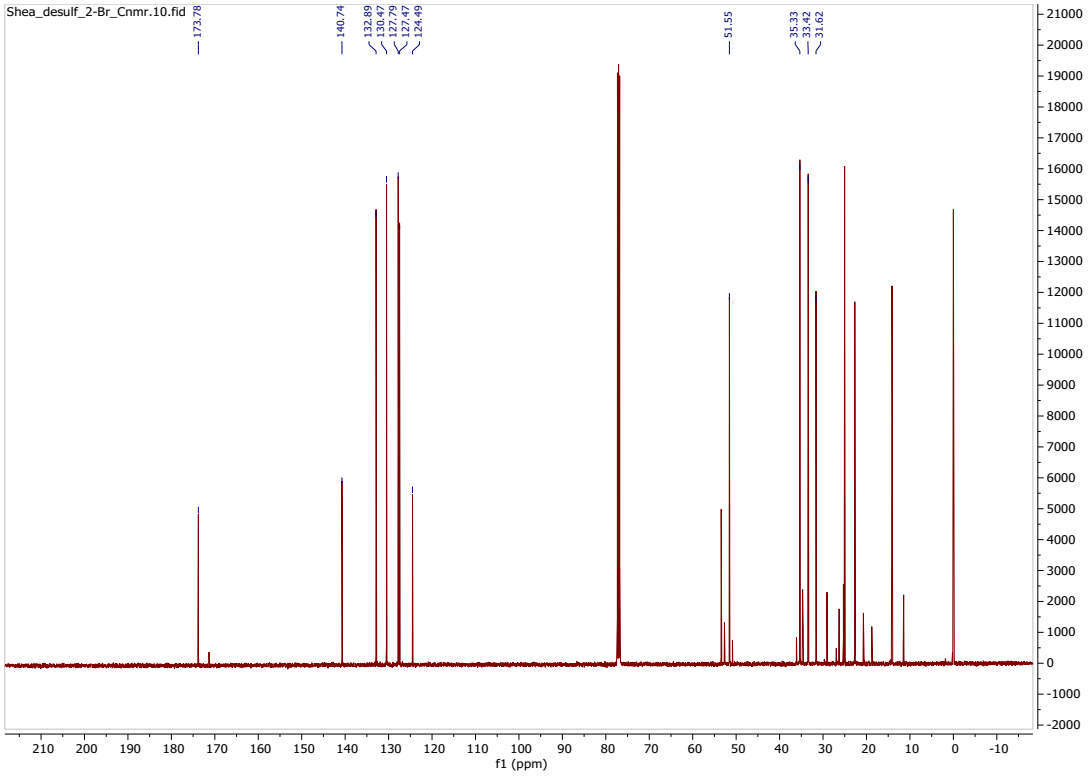
^{13}C NMR spectrum of **methyl 4-(4-fluorophenyl)butanoate** ($CDCl_3$, 125 MHz)

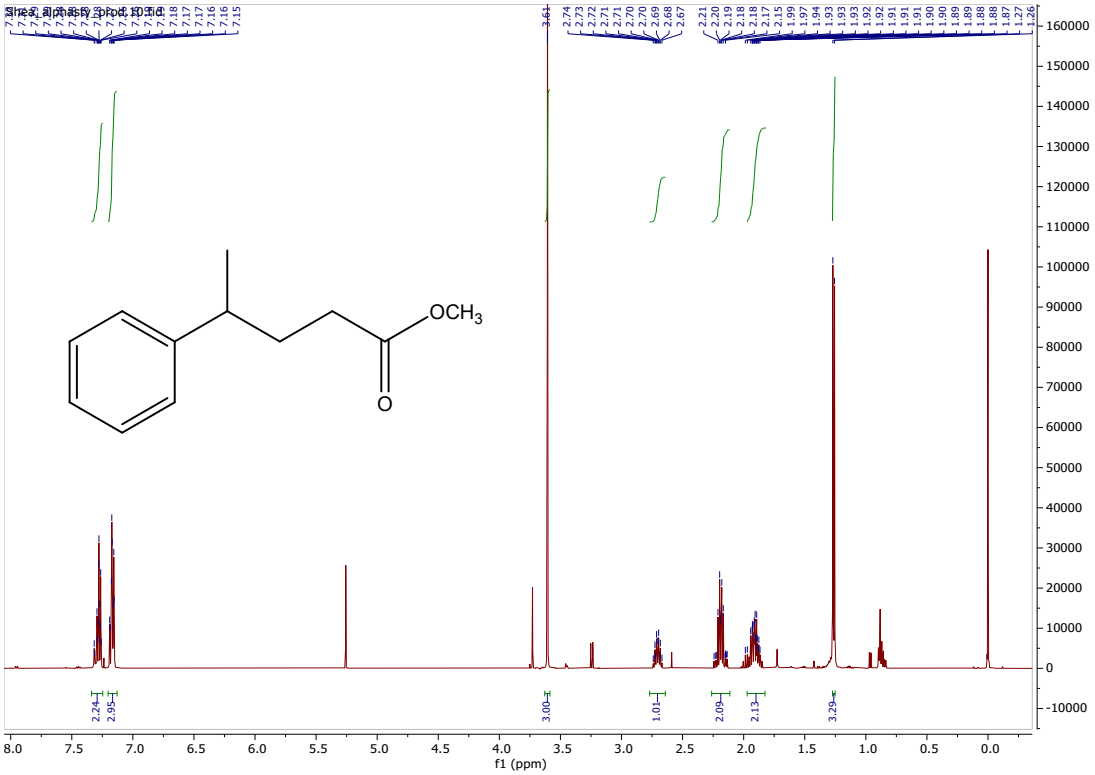




^{1}H NMR spectrum of **methyl 4-(2-bromophenyl)butanoate** ($CDCl_3$, 500 MHz)

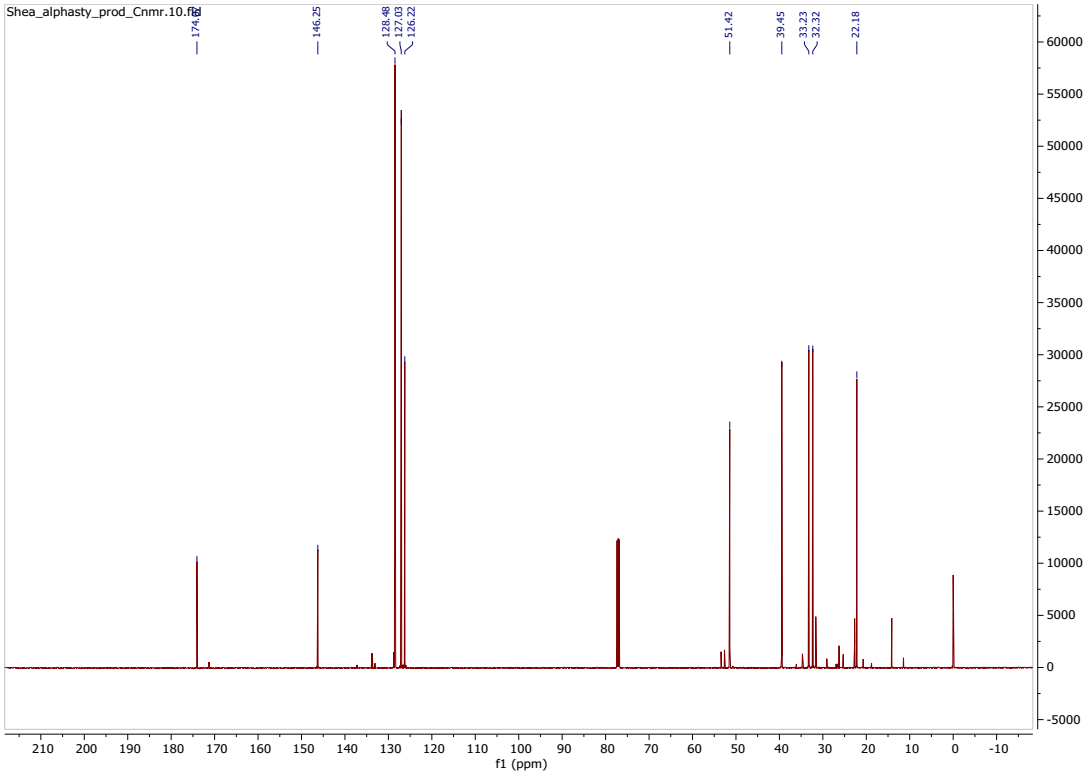
^{13}C NMR spectrum of **methyl 4-(2-bromophenyl)butanoate** ($CDCl_3$, 125 MHz)

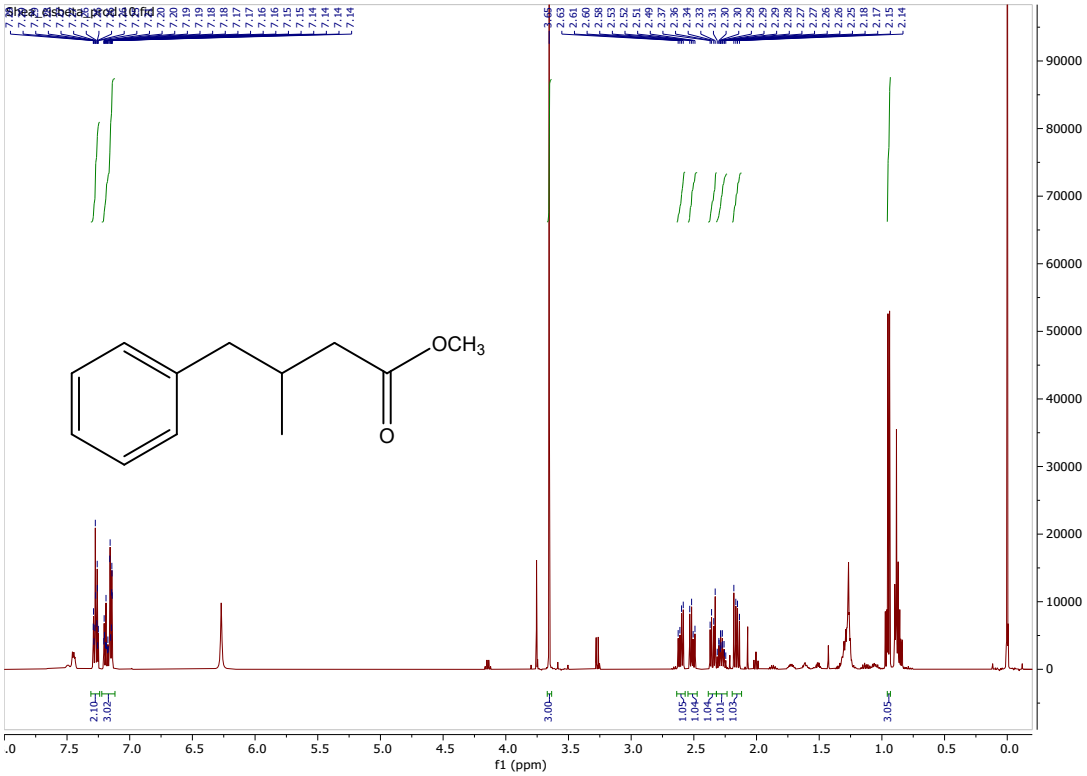




^{1}H NMR spectrum of **methyl 4-phenylpentanoate** ($CDCl_3$, 500 MHz)

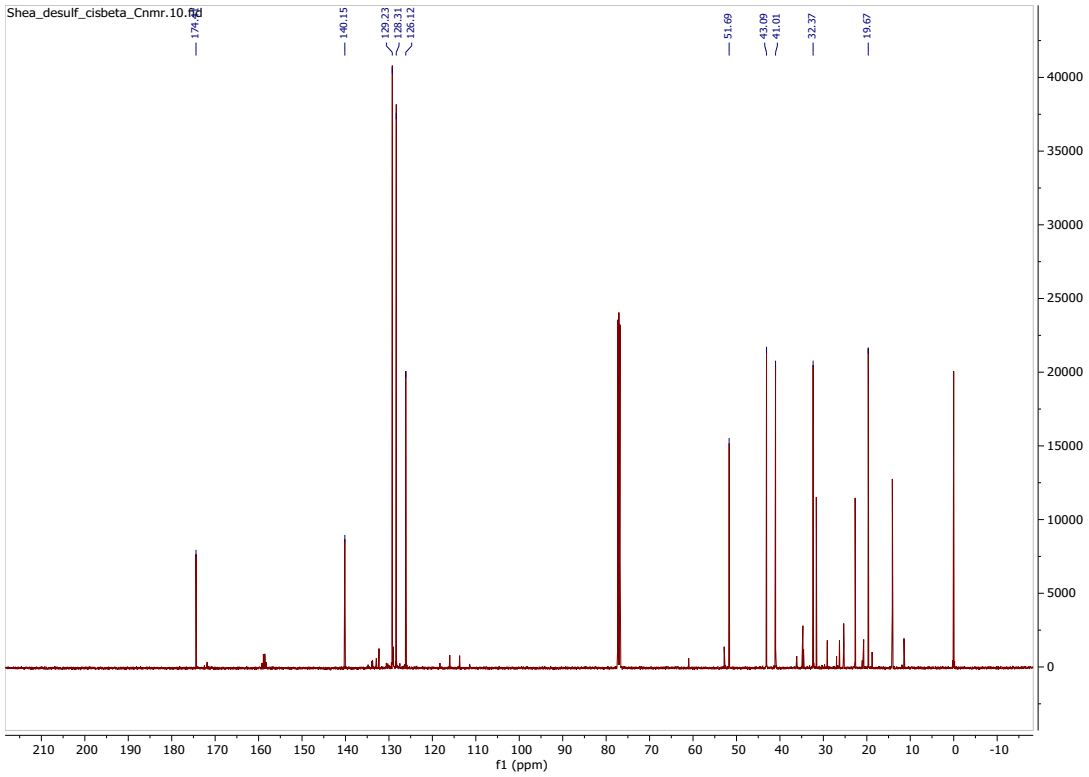
^{13}C NMR spectrum of **methyl 4-phenylpentanoate** ($CDCl_3$, 125 MHz)



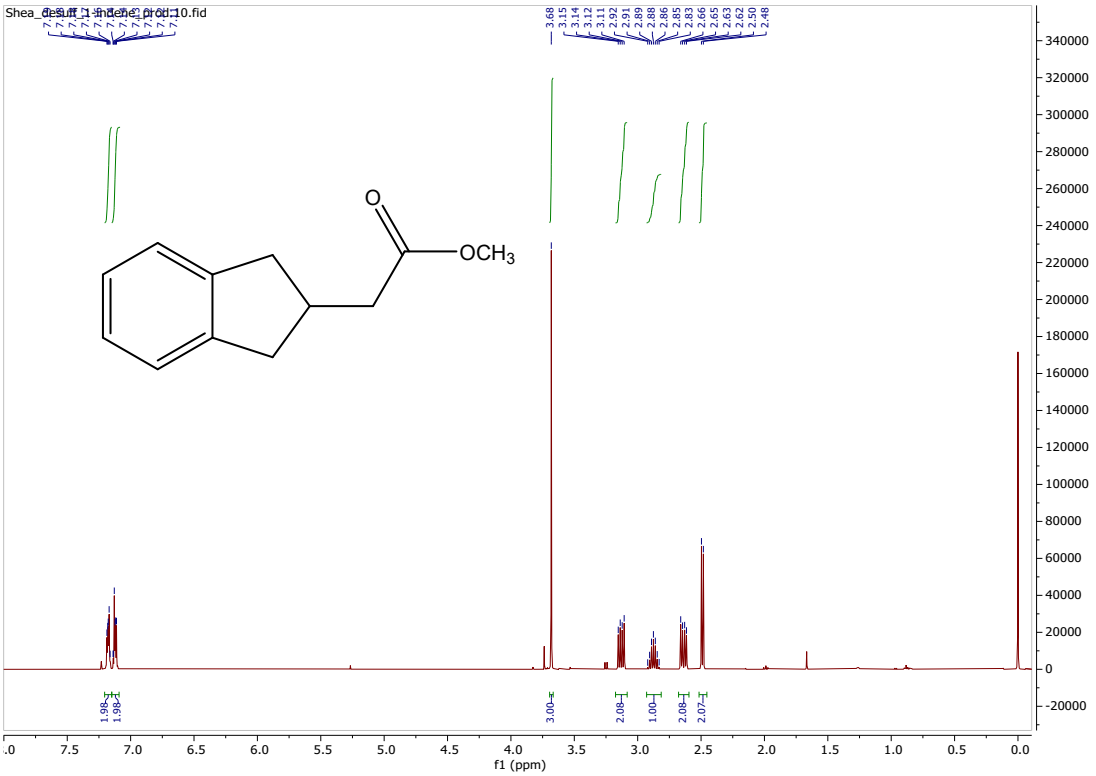


^{1}H NMR spectrum of **methyl 3-methyl-4-phenylbutanoate** ($CDCl_3$, 500 MHz)

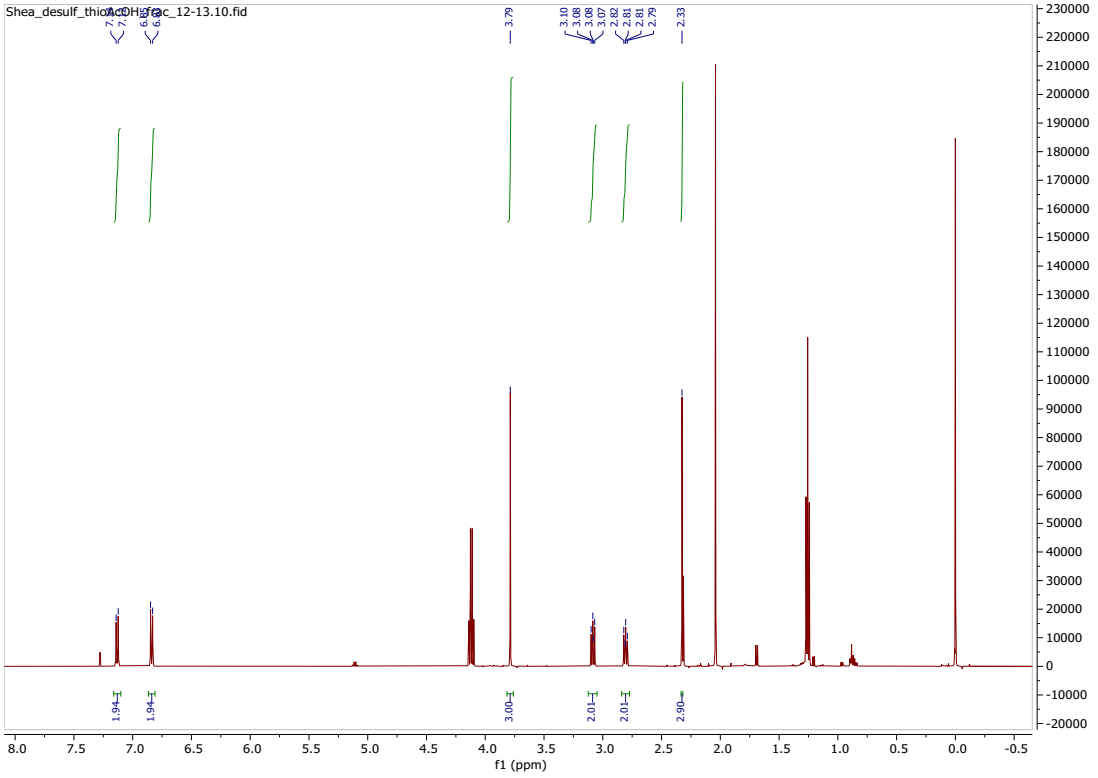
^{13}C NMR spectrum of **methyl 3-methyl-4-phenylbutanoate** ($CDCl_3$, 125 MHz)

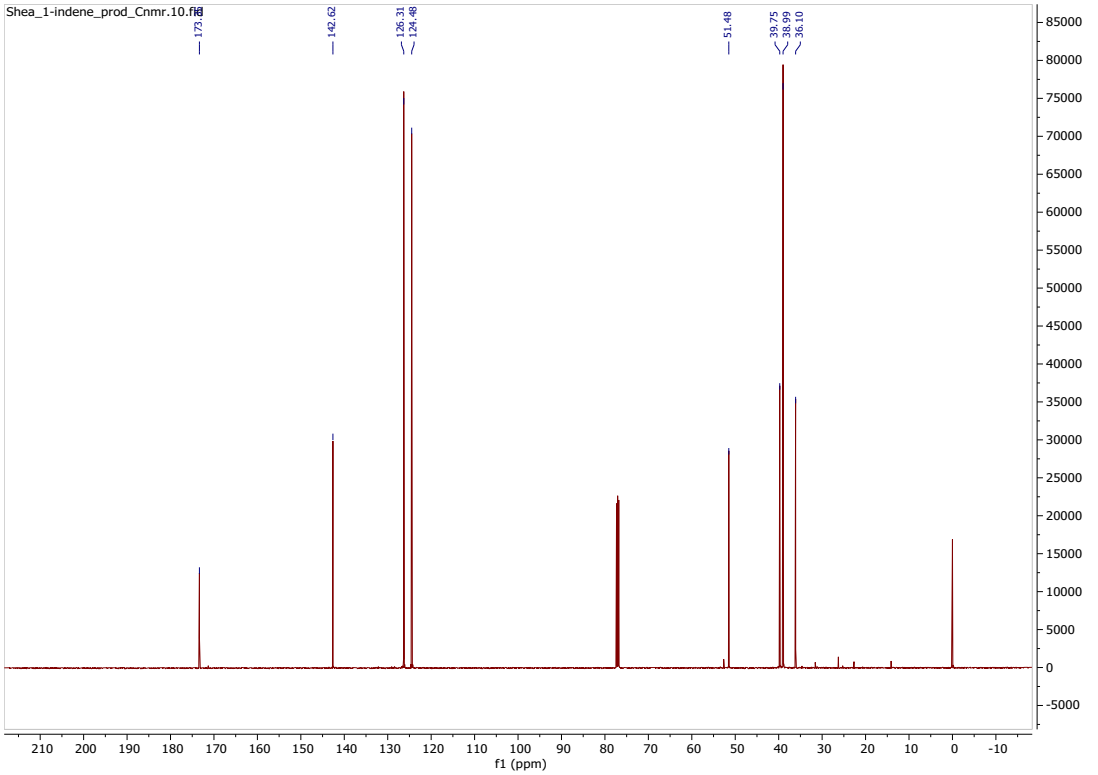


^{1}H NMR spectrum of **methyl 2-(2,3-dihydro-1H-inden-2-yl)acetate** ($CDCl_3$, 500 MHz)



^{13}C NMR spectrum of **methyl 2-(2,3-dihydro-1H-inden-2-yl)acetate** ($CDCl_3$, 125 MHz)

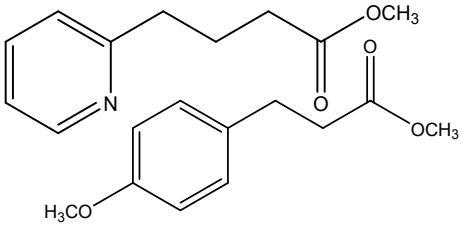




^{1}H NMR spectrum of **4-(4-methoxyphenyl)butan-2-one** ($CDCl_3$, 500 MHz)

^{13}C NMR spectrum of **4-(4-methoxyphenyl)butan-2- one** ($CDCl_3$, 125 MHz)

^{1}H NMR spectrum of **methyl 4-(pyridin-2-yl)butanoate** ($CDCl_3$, 400 MHz)



DEPT-135 ^{13}C NMR spectrum of **methyl 4-(pyridin-2-yl)butanoate** ($CDCl_3$, 100 MHz)