Supporting Information

Non-Heme Manganese(II) Complex-Catalysed Oxidative Cleavage of 1,2-Diols via Alcohol-Assisted O2 Activation

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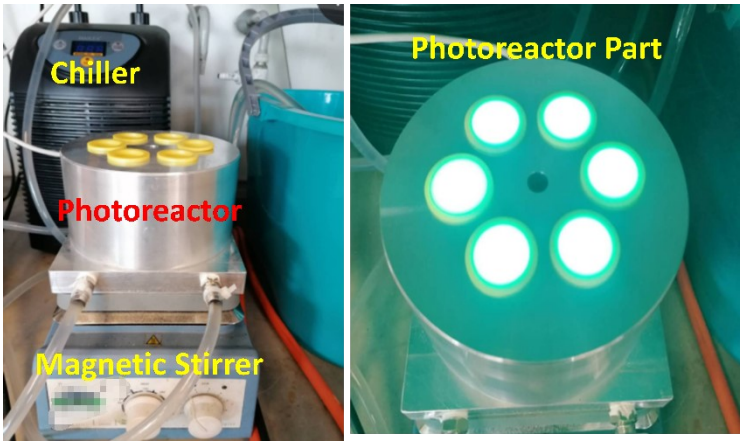
1. General information

All manipulations were carried out using standard Schlenk techniques unless otherwise indicated. All glassware was oven dried at 120 °C for more than 1 hour prior to use. $Mn(OTf)_2$, 1,2-dichloroethane (DCE), *tert*-butanol, anhydrous methanol, 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy), methyl 9,10-dihydroxyoctadecanoate, 1-phenyl-1,2-ethanediol, 1-phenylpropane-1,2-diol, (*S,S*)-(-)-hydrobenzoin, (*R,R*)-(+)-hydrobenzoin, *meso*-hydrobenzoin and 2,3-diphenyl-2,3-buthanediol were purchased from commercial suppliers and used without further purification. Unless otherwise noted, analytical grade solvents and commercially available reagents were used as received. Analytical thin-layer chromatography (TLC) was conducted with TLC Silica gel 60 F254 (Merck) and plates were revealed under UV irradiation, iodine, potassium permanganate, phosphomolybdic acid or vanillin staining. Flash column chromatography was performed using Aldrich Silica Gel 60 and columns were packed according to the dry method and equilibrated with the appropriate eluent prior to use. HPLC grade solvents were used and the solvent mixtures used as eluent are understood as

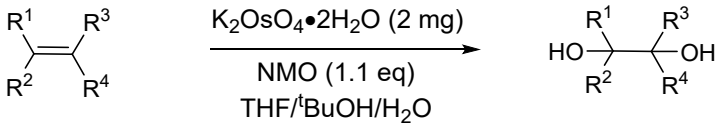
volume/volume. New compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^{1}H NMR, and ^{13}C NMR. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 NMR spectrometer at 400 MHz (^{1}H NMR), and 101 MHz (^{13}C NMR). The chemical shifts (δ) were given in part per million relative to internal tetramethylsilane (0 ppm for ^{1}H) and $CDCl_3$ (77.00 ppm for ^{13}C) or DMSO-d^{6} (2.50 ppm for ^{1}H NMR spectra, and 39.52 ppm for ^{13}C NMR spectra). Mass spectra were obtained by electrospray ionization (ESI) or chemical ionization (CI) at the Analytical Services of the Chemistry Department, University of Liverpool. UV-Vis spectra were measured on the Agilent Cary 5000 at Materials Innovation Factory, University of Liverpool.

2. Information of the blue light photoreactor



Information of the blue LEDs: 2.95 V Blue LED SMD, Lumileds LUXEON Rebel LXML-PB01-0040; dominant wavelength or Peak Wavelength (minimum: 460 nm, typical: 470 nm, maximum: 485 nm); typical spectral half-width (20 nm); typical temperature coefficient of dominant or Peak Wavelength (0.05 nm/^{o}C); typical total included angle (160^{o}); typical view angle (125^{o}). Each hole/chamber in the photoreactor has three LEDs, giving a total power for a reaction tube of 9 W.

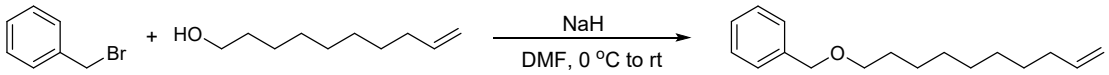
3. Preparation of substrates[1]



To a solution of alkenes (5 mmol) (unless otherwise noted, all alkenes were commercially available, or synthesized with the methods reported in our previous work,[2] or obtained via methylenation of the corresponding ketones or aldehydes according to the literature[3]), and *N*-methylmorpholine-*N*-oxide (NMO, 5.1 mmol) in THF-^{t}BuOH-H_2O (5:1:1, 6 mL) was added

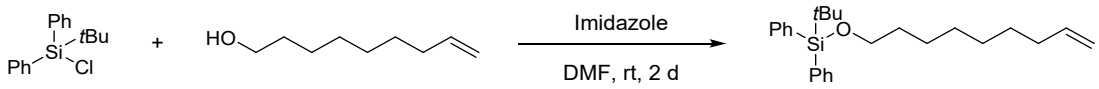
potassium osmate(VI) dihydrate (2 mg) at room temperature under stirring. After stirring for 12 h, the reaction mixture was quenched with 10% aqueous Na_2SO_3 (10 mL), and extracted with EtOAc (20 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a crude oil. The pure product of 1,2-diols was obtained by flash chromatography on silica gel with petroleum ether/ethyl acetate or ethyl acetate/methanol.

Synthesis of ((dec-9-en-1-yloxy)methyl)benzene[4]



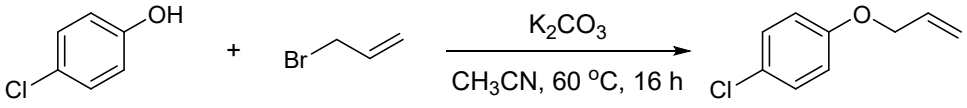
To an oven dried flask with 9-decen-1-ol (1 mL, 5.6 mmol) in anhydrous DMF (8 mL) at 0 °C, NaH (60 % w/w in oil, 246 mg, 6.16 mmol) was added. The mixture was stirred for 25 mins, and then at room temperature for 90 mins. Thereafter, the mixture was cooled to 0 °C again and treated with BnBr (732 uL, 6.16 mmol). After 15 mins, the reaction solution was allowed to warm to room temperature and then stirred for an additional 2 h. The reaction mixture was then diluted with Et_2O (40 mL), washed with sat. NH_4Cl (20 mL), and brine (20 mL), and then dried (Na_2SO_4) and concentrated. The crude product was purified by silica gel column chromatography to afford the desired product, which was then used to synthesize the 10-(benzyloxy)decane-1,2-diol.

Synthesis of tert-butyl(non-8-en-1-yloxy)diphenylsilane[5]



To a solution of the non-8-en-1-ol (512 mg, 3.6 mmol) in DMF (10 mL) were added imidazole (735 mg, 10.8 mmol) and then tertbutylchlorodiphenylsilane (0.95 mL, 3.6 mmol) at room temperature. After 2 days the reaction was complete (monitored by TLC). Then, an aqueous solution of HCl (10%, 30 mL) was added and the mixture was extracted with Et_2O (3 x 20 mL). The organic portion was dried over Na_2SO_4, filtered and evaporated. The crude product was purified by silica gel column chromatography to afford the desired product, which was then used to synthesize the 9-((tert-butyldiphenylsilyl)oxy)nonane-1,2-diol.

Synthesis of 4-(allyloxy)-chlorobenzene[6]



To an oven dried flask with a mixture of 4-chlorophenol (643 mg, 5 mmol) and potassium carbonate (1.04 g, 1.5 eq) in anhydrous MeCN (20 mL), allyl bromide (908 mg, 1.5 eq) was added dropwise. The reaction mixture was then allowed to heat to 60 °C and stirred for 16 h before being cooled to room temperature. The MeCN was then removed under vacuum and the crude product was washed with water and brine and extracted with DCM (3 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum to give 4-(allyloxy)-chlorobenzene, which was used to synthesize Chlorphenesin without further purification.

Synthesis of pent-4-en-1-yl phenylcarbamate, 1-allyl-1,3-diphenylurea and 2-methylallyl phenylcarbamate[7]

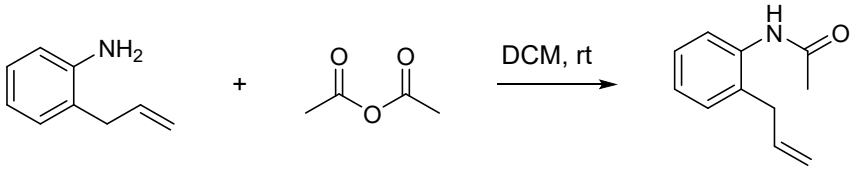
An oven dried roundbottomed flask was degassed, flushed with nitrogen, and charged with phenyl isocyanate (10 mmol, 1 equiv), DCM (10 mL), Et_3N (30 mmol, 3.0 equiv) and alcohol/amine (10 mmol, 1 equiv). The reaction mixture was stirred at room temperature until the alcohol/amine was fully consumed by TLC. The reaction mixture was then diluted with DCM (20 mL), washed with 1 M HCl (3 x 20 mL), water (20 mL), and brine (20 mL), and then dried (Na_2SO_4) and concentrated. The crude product was purified by either silica gel column chromatography or recrystallization to afford the desired product, which was then used to synthesize the corresponding diols.

Synthesis of N-substituted 4-pentenamide[7]

An oven dried round-bottomed flask was degassed, flushed with nitrogen, and charged with DCM (25 mL), EDC-HCl (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, 13 mmol, 1.3 equiv), and DMAP (14 mmol, 1.4 eqiuv). The reaction flask was cooled to zero degrees in an ice bath and the carboxylic acid (10 mmol, 1.0 equiv) was added. After five minutes of stirring, the amine (12 mmol, 1.2 equiv) was added. The ice bath was then removed and the reaction allowed to stir for 24 hours at RT or until starting material was consumed by TLC. The reaction was quenched with 1 M HCl (25 mL) and the organics separated. The aqueous layer was then extracted with DCM (2 x 25 mL). The organic layers were combined

and dried over Na_2SO_4 and concentrated. The crude product was purified by either silica gel column chormatography or recrystallization to afford the desired product, which was then used to synthesize the corresponding diols.

Synthesis of N-(2-allylphenyl)acetamide[8]



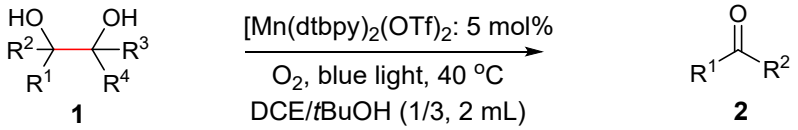
To an oven dried Schlenk tube, o-allylanline (666 mg, 5 mmol) was added. The reaction tube was vacuumed and purged with nitrogen for three times. Dry DCM (15 mL) was injected through a syringe. Then, acetic anhydride (0.57 mL, 6 mmol) was added, and the reaction was stirred at room temperature and monitored by TLC. After the completion of the reaction, the reaction mixture was washed with a saturated solution of sodium carbonate (20 mL). The aqueous layer was then extracted with DCM (2 x 20 mL). The organic layers were combined and dried over Na_2SO_4 and concentrated to obtained the product in quantitative yield, which was used to synthesize *N*-(2-(2,3-dihydroxypropyl)phenyl)acetamide without further purification.

4. General procedure for the aerobic oxidative cleavage of diols

4.1 General procedure for the aerobic oxidative cleavage of 1a under varied conditions in the presence of blue light

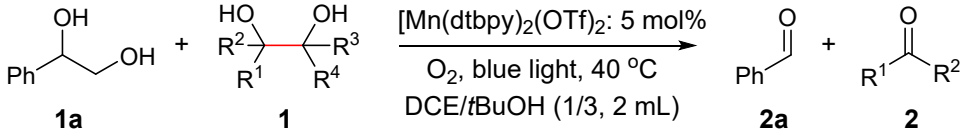
To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) or $Mn(OTf)_2$ (5 mol%) and ligand (10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. 0.25 mL of solvent was injected through a syringe under N_2. Then, the reaction mixture was heated at 60 ^oC for 1 h to *in situ* prepare the Mn(II) catalyst. The reaction tube was then cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of **1a** (0.5 mmol), the corresponding solvent (0.75 mL), the reaction tube was allowed to stir under blue light for 7 h. The product yield of **2a** was obtained by ^1H NMR analysis with mesitylene as internal standard.

4.2 Standard procedures for aerobic oxidative cleavage of diols in DCE/tBuOH (1:3)



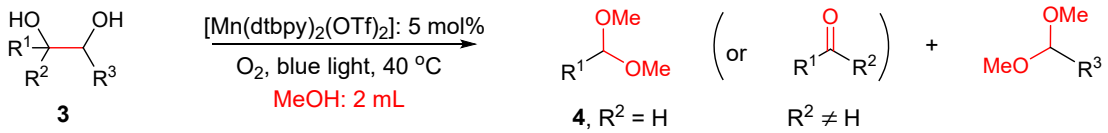
To an oven dried Schlenk tube, $Mn(OTf)_2$ (8.8 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 13.4 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. DCE (0.5 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of diol **1** (0.5 mmol), and *t*BuOH (1.5 mL), the reaction tube was allowed to stir under blue light until the diol was consumed by TLC analysis. After the crude mixture was concentrated under vacuum, the pure product **2** was obtained by flash chromatography on silica gel with hexane/ethyl acetate.

4.3 Standard procedures for aerobic oxidative cleavage of two diols in one-pot



To an oven dried Schlenk tube, $Mn(OTf)_2$ (8.8 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 13.4 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. DCE (0.5 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of diol **1** (0.5 mmol), 1-phenylethane-1,2-diol **1a** (0.5 mmol) and *t*BuOH (1.5 mL), the reaction tube was allowed to stir under blue light until diol was consumed by TLC analysis. The product yield of **2a** was obtained by ^1H NMR analysis with mesitylene as internal standard. Meanwhile, after the crude mixture was concentrated under vacuum, the pure product **2** was obtained by flash chromatography on silica gel with hexane/ethyl acetate.

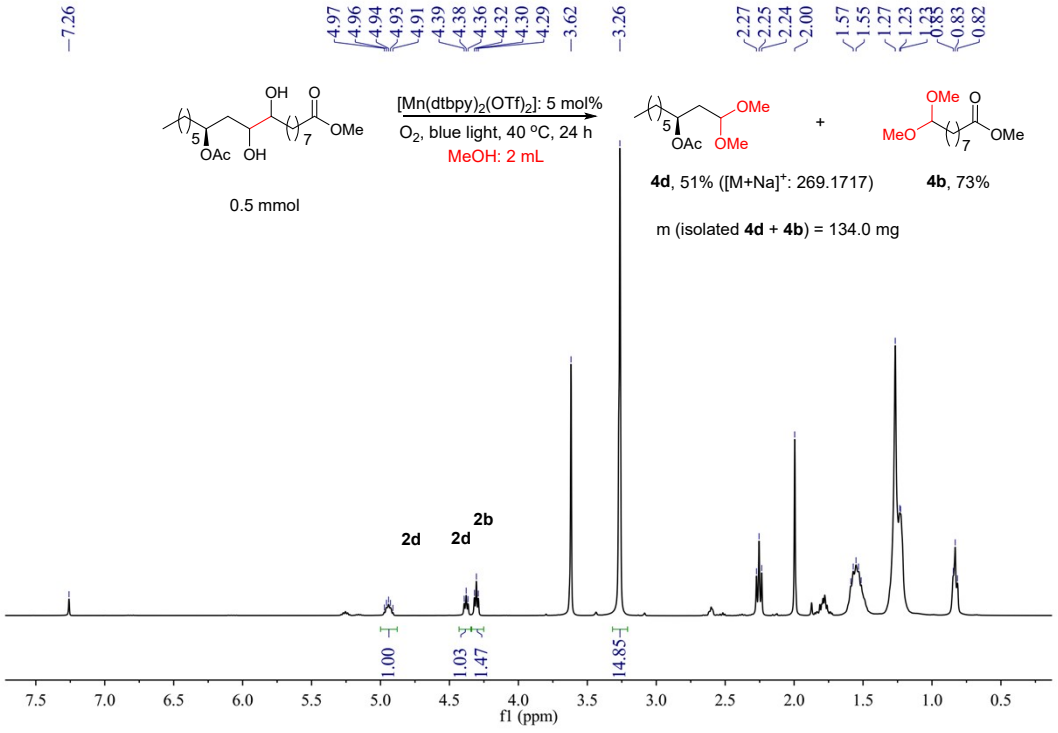
4.4 Standard procedures for aerobic oxidative cleavage of 1,2-diols in MeOH



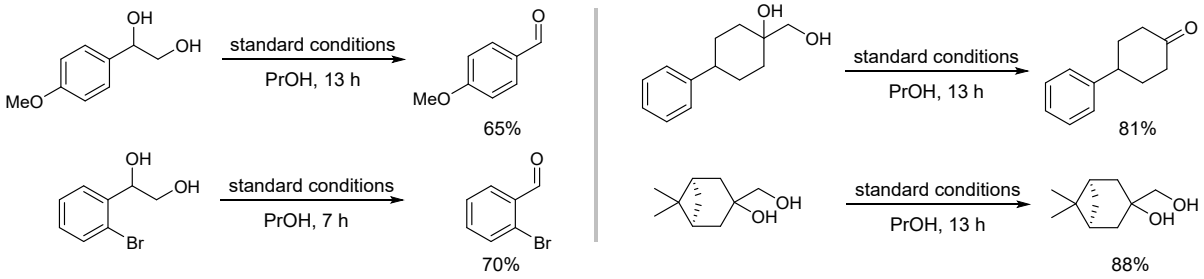
To an oven dried Schlenk tube, $Mn(OTf)_2$ (5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. MeOH (2 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of diol **3**

(0.5 mmol), the reaction tube was allowed to stir under blue light until the diol was consumed by TLC analysis. After the crude mixture was concentrated under vacuum, the pure product **4** was obtained by flash chromatography on silica gel with hexane/ethyl acetate.

Note: The product yield of the oxidation of methyl 12-acetoxy-9,10-dihydroxyoctadecanoate was determined by ^{1}H NMR after isolation. See the following spectrum for more details.



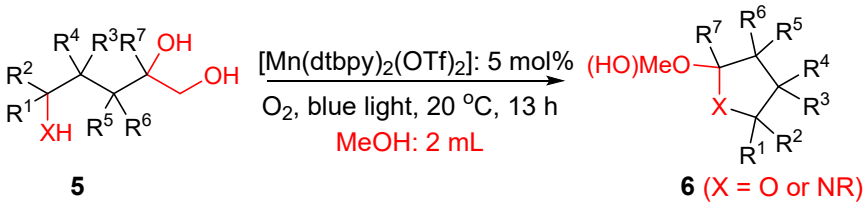
4.5 Standard procedures for aerobic oxidative cleavage of 1,2-diols in PrOH



To an oven dried Schlenk tube, $Mn(OTf)_2$ (5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. PrOH (2 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of diol (0.5 mmol), the reaction tube was allowed to stir under blue light until the diol was consumed

by TLC analysis. After the crude mixture was concentrated under vacuum, the pure product **4** was obtained by flash chromatography on silica gel with hexane/ethyl acetate.

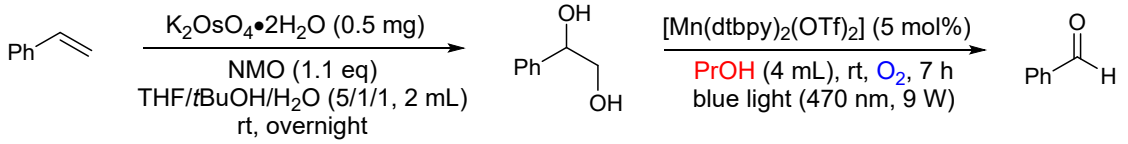
4.6 Standard procedures for aerobic oxidative cleavage of diols towards the synthesis of five-membered-ring heterocycles



5 **6** (X = O or NR)

To an oven dried Schlenk tube, $Mn(OTf)_2$ (5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. MeOH (2 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of diol **5** (0.5 mmol), the reaction tube was allowed to stir under blue light for 13 h until the diol was consumed by TLC analysis. After the crude mixture was concentrated under vacuum, the pure product **6** was obtained by flash chromatography on silica gel with hexane/ethyl acetate.

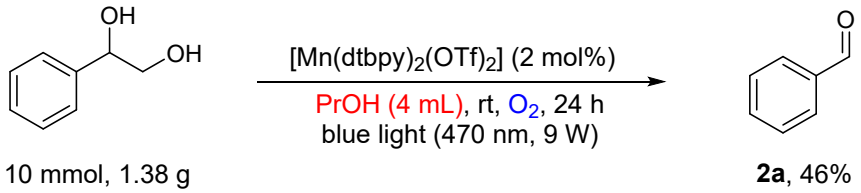
4.7 Standard procedures for aerobic oxidative cleavage of styrene in two steps



1 mmol without purification **2a**, 75%

To a solution of styrene (1 mmol) and *N*-methylmorpholine-N-oxide (NMO, 1.05 mmol) in THF-*t*BuOH-H_2O (5:1:1, 2 mL) was added potassium osmate(VI) dihydrate (0.5 mg) at room temperature under stirring. After stirring for 12 h, the reaction mixture was quenched with water (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a crude oil. The crude oil product was then subjected to the solution of $[Mn(dtbpy)(OTf)_2]$ (5 mol%) in 1-propanol (4 mL) in a Schlenk tube. After connecting to an oxygen balloon, the mixture was allowed to stir at room temperature under blue light for 7 h. Finally, the product yield of **2a** was obtained by ^1H NMR analysis with mesitylene (17.3 mg) as internal standard.

4.8 Standard procedures for the scale-up aerobic oxidative cleavage of 1a



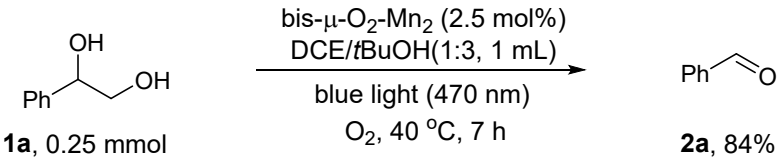
10 mmol, 1.38 g **2a**, 46%

To an oven dried Schlenk tube, $Mn(OTf)_2$ (71.0 mg, 2 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 107.2 mg, 4 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. PrOH (4 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of 1-phenylethane-1,2-diol **1a** (1.38 g, 10 mmol), the reaction tube was allowed to stir under blue light for 24 h. After the compeletion of the reaction, **2a** was isolated in 46% yield.

5. Mechanistic investigation

5.1 Control experiments

5.1.1 Aerobic oxidative cleavage of 1-phenylethane-1,2-diol (1a) with bis-μ-O_2-Mn_2 complex



1a, 0.25 mmol **2a**, 84%

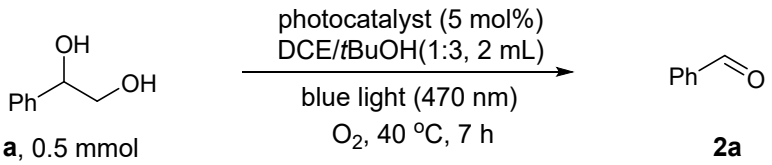
To an oven dried Schlenk tube, **bis-μ-O_2-Mn_2** complex (9.2 mg, 2.5 mol%, prepared according to our previous work[2]) and **1a** (34.5 mg, 0.25 mmol) were added. The reaction tube was vacuumed and purged with oxygen via an oxygen balloon. Then, DCE (0.25 mL) and *t*BuOH (0.75 mL) was injected through a syringe. Finally, the reaction tube was allowed to stir at 40 °C under blue light for 7 h. Then, mesitylene (17.3 mg) as internal standard, water (2 mL) and $CDCl_3$ (2 mL) were added. Finally, the product yield of **2a** was obtained by ^1H NMR analysis of the organic layer.

5.1.2 Aerobic oxidative cleavage of 1-phenylethane-1,2-diol (1a) with well-known photosensitizers capable of producing singlet oxygen

To an oven dried Schlenk tube, a photocatalyst (5 mol%) was added. The reaction tube was vacuumed and purged with dioxygen three times. Then, 1-phenylethane-1,2-diol **1a** (0.5 mmol), DCE (0.5 mL) and *t*BuOH (1.5 mL) were added. The reaction tube was allowed to stir

under blue light for 7 h. Then, mesitylene (17.3 mg) as internal standard, water (2 mL) and $CDCl_3$ (2 mL) were added. Finally, the product yield of **2a** was obtained by ^1H NMR analysis of the organic layer.

Table S1. Oxidation of 1a in the presence of well-kown photosensitizers



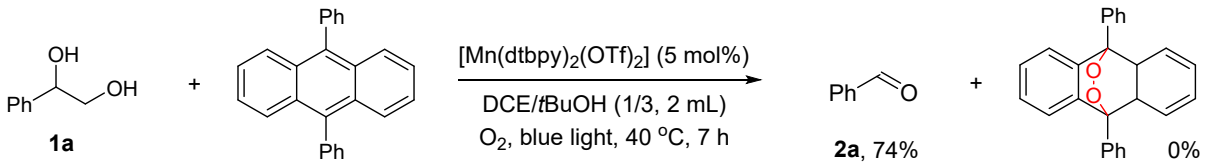
1a, 0.5 mmol **2a**

Entry	Photocatalyst	yield of **2a**[a]
1	Eosin Y disodium salt	0%
2	$[Ru(bpy)_3 \bullet 6H_2O]$	0%
3	$[Ir(dFppy)_3]$	0%

[a] Yield determined by ^1H NMR with mesitylene as internel standard.

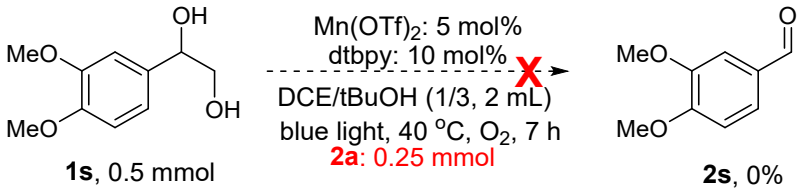
Three well-known photosensitizers capable of producing singlet oxygen with blue light were used as replacement catalysts for the oxidative cleavage of **1a**. No desired oxidative cleavage product **2a** was observed when eosin Y disodium salt, $Ru(bpy)_3 \bullet 6H_2O$, or $Ir(dFppy)_3$ was employed (Table S1). The poor selectivity toward **2a** with these $^1O_2$-generating photocatalysts indicates that the formation of **2a** under the catalysis of $[Mn(dtbpy)_2(OTf)_2]$ and blue light irradiation involves no singlet oxygen as a key oxidizing intermediate.

5.1.3 Singlet oxygen trap experiment



To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (22.2 mg, 5 mol%) was added. Then the reaction tube was vacuumed and purged with oxygen via an oxygen balloon. DCE (0.5 mL) and *t*BuOH (1.5 mL) was injected through a syringe. Finally, after the addition of **1a** (69.1 mg, 0.5 mmol) and 9,10-diphenylanthracene (DPA, 33 mg, 0.1 mmol, singlet oxygen trap), the reaction tube was allowed to stir at 40 °C under blue light for 7 h. No 9,10-diphenyl-4a,9,9a,10-tetrahydro-9,10-epidioxyanthracene was observed by TLC/GC-MS/^1H NMR analysis. The product yield of **2a** (74%) was obtained by ^1H NMR analysis with mesitylene as internal standard. These results indicate that singlet oxygen is not involved as the key intermediate during the oxidative cleavage of diol.

5.1.4 Aerobic oxidative cleavage of 1-(3,4-dimethoxyphenyl)ethane-1,2-diol (1s) in the presence of benzaldehyde (2a)



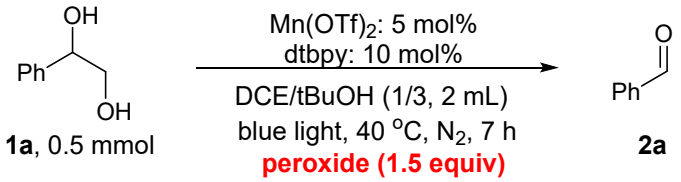
1s, 0.5 mmol **2s**, 0%

To an oven dried Schlenk tube, $Mn(OTf)_2$ (8.8 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 13.4 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen for three times. DCE (0.5 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of **1s** (99.2 mg, 0.5 mmol), **2a** (53 mg, 0.5 mmol) and *t*BuOH (1.5 mL), the reaction tube was allowed to stir under blue light for 7 h. Then, mesitylene (17.3 mg) as internal standard, water (2 mL) and $CDCl_3$ (2 mL) were added. Finally, the product yield of **2s** was obtained by ^{1}H NMR analysis of the organic layer.

5.1.5 Aerobic oxidative cleavage of 1a with peroxides as oxidant in the presence of blue light

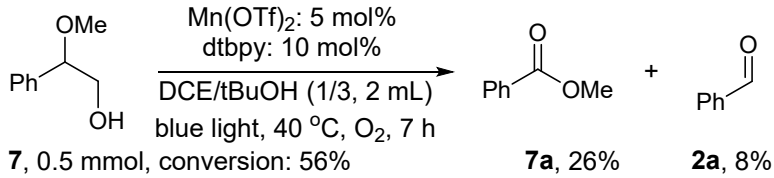
To an oven dried Schlenk tube, $Mn(OTf)_2$ (8.8 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 13.4 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. DCE (0.5 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, after that, diol **1a** (0.5 mmol), a peroxide (0.75 mmol) and *t*BuOH (1.5 mL) were added under nitrogen. Finally, the reaction tube was allowed to stir under blue light for 7 h. The product yield of **2a** was obtained by ^{1}H NMR analysis with mesitylene as internal standard.

Table S2. Oxidative cleavage of 1a with peroxides



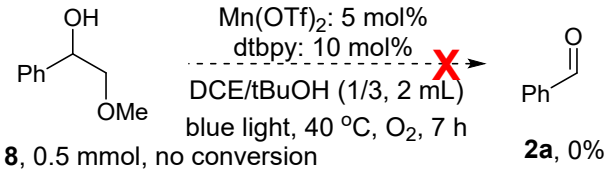
Entry	peroxide	yield of **2a**
1	H_2O_2 (30% in water)	<1%
2	TBHP (5.5 M in decane)	17%
3	DTBP	13%
4	benzoyl peroxide	6%
5	*m*CPBA	<1%

5.1.6 Aerobic oxidative cleavage of 2-methoxy-2-phenylethan-1-ol (7)



To an oven dried Schlenk tube, $Mn(OTf)_2$ (8.8 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 13.4 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. DCE (0.5 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of **7** (76.2 mg, 0.5 mmol) and *t*BuOH (1.5 mL), the reaction tube was allowed to stir under blue light for 7 h. Then, mesitylene (17.3 mg) as internal standard, water (2 mL) and $CDCl_3$ (2 mL) were added. Finally, the conversion of **7** and the product yield of **7a** and **2a** were obtained by ^1H NMR analysis of the organic layer.

5.1.7 Aerobic oxidative cleavage of 2-methoxy-1-phenylethan-1-ol (8)

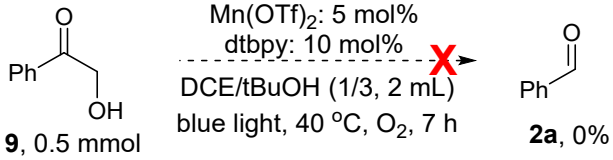


To an oven dried Schlenk tube, $Mn(OTf)_2$ (8.8 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 13.4 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. DCE (0.5 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally,

after the addition of **8** (76.2 mg, 0.5 mmol) and *t*BuOH (1.5 mL), the reaction tube was allowed to stir under blue light for 7 h. Then, mesitylene (17.3 mg) as internal standard, water (2 mL) and $CDCl_3$ (2 mL) were added. Finally, the conversion of **8** and the product yield of **2a** were obtained by ^1H NMR analysis of the organic layer.

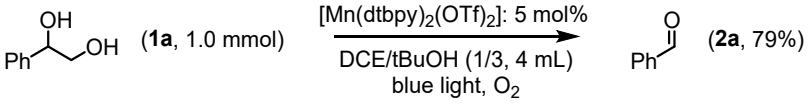
5.1.8 Aerobic oxidative cleavage of 2-hydroxy-1-phenylethan-1-one (9)

To an oven dried Schlenk tube, $Mn(OTf)_2$ (8.8 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 13.4 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. DCE (0.5 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of **9** (68.2 mg, 0.5 mmol) and *t*BuOH (1.5 mL), the reaction tube was allowed to stir under blue light for 7 h. Then, mesitylene (17.3 mg) as internal standard, water (2 mL) and $CDCl_3$ (2 mL) were added. Finally, the product yield of **2a** were obtained by ^1H NMR analysis of the organic layer.



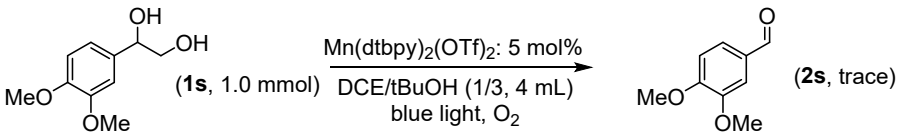
5.2 Kinetic investigation

5.2.1 Kinetics of oxidative cleavage of 1a



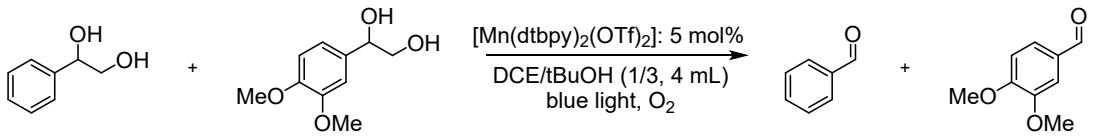
To an oven dried Schlenk tube, $Mn(OTf)_2$ (17.6 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 26.8 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. DCE (1 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of **1a** (138 mg, 1 mmol), 3,5-bis(trifluoromethyl)bromobenzene (80.7 mg, internal standard) and *t*BuOH (3 mL), the reaction tube was allowed to stir under blue light at 40 °C. Then, 0.2 mL of the reaction mixture was taken out for ^1H NMR analysis every 2 or 10 mins. [Note: the reaction mixture was first washed by water (1 mL), and then extracted by $CDCl_3$ (1 mL). Finaly, the organic layer was dried for ^1H NMR analysis.]

5.2.2 Kinetics of oxidative cleavage of 1s



To an oven dried Schlenk tube, $Mn(OTf)_2$ (17.6 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 26.8 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. DCE (1 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of **1s** (198.2 mg, 1 mmol), 3,5-bis(trifluoromethyl)bromobenzene (80.7 mg, internal standard) and *t*BuOH (3 mL), the reaction tube was allowed to stir under blue light at 40 °C. Then, 0.2 mL of the reaction mixture was taken out for ^{1}H NMR analysis every 2 or 10 mins. [Note: the reaction mixture was first washed by water (1 mL), and then extracted by $CDCl_3$ (1 mL). Finaly, the organic layer was dried for ^{1}H NMR analysis.]

5.2.3 Kinetics of oxidative cleavage of the mixture of 1a and 1s



1a, 1.0 mmol **1s**, 1.0 mmol **2a**, 76% **2s**, 76%

To an oven dried Schlenk tube, $Mn(OTf)_2$ (17.6 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 26.8 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. DCE (1 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of **1a** (138 mg, 1 mmol), **1s** (198.2 mg, 1 mmol), 3,5-bis(trifluoromethyl)bromobenzene (80.7 mg, internal standard) and *t*BuOH (3 mL), the reaction tube was allowed to stir under blue light at 40 °C. Then, 0.2 mL of the reaction mixture was taken out for ^{1}H NMR analysis every 2 or 10 mins. [Note: the reaction mixture was first washed by water (1 mL), and then extracted by $CDCl_3$ (1 mL). Finaly, the organic layer was dried for ^{1}H NMR analysis.]

5.3 UV-Vis experiments

[Mn(dtbpy)$_2$(OTf)$_2$]: To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (8.9 mg, 0.01 mmol) was dissolved in DCE/*t*BuOH (1/3 volume, 40 mL) or MeOH (40 mL). The solution was then

directly used for UV-Vis analysis.

bis-μ-O_2-Mn_2 complex: To an oven dried Schlenk tube, **bis-μ-O_2-Mn_2** complex (1.1 mg, 0.00075 mmol) was dissolved in DCE/*t*BuOH (1/3 volume, 3 mL) or MeOH (3 mL). The solution was then directly used for UV-Vis analysis.

The mixture of [Mn(dtbpy)$_2$(OTf)$_2$] with 1a in the absence of blue light: To an oven dried Schlenk tube, [Mn(dtbpy)$_2$(OTf)$_2$] (22.2 mg, 0.025 mmol) and **1a** (69.1 mg, 0.5 mmol) were added. The reaction tube was vacuumed and purged with oxygen via an oxygen balloon. Then, DCE/*t*BuOH (1/3 volume, 2 mL) was injected through a syringe, and the reaction mixture was stirred for 1 h at 40 °C in dark. After that, 0.1 mL of the reaction solution was taken out and diluted to 5 mL for UV-Vis analysis.

The mixture of [Mn(dtbpy)$_2$(OTf)$_2$] with 1a or 1b or 1f in the presence of blue light: To an oven dried Schlenk tube, [Mn(dtbpy)$_2$(OTf)$_2$] (22.2 mg, 0.025 mmol) and **1a** (69.1 mg, 0.5 mmol) or **1b** (86.3 mg, 0.5 mmol) or **1f** (84.1 mg, 0.5 mmol) were added. The reaction tube was vacuumed and purged with oxygen via an oxygen balloon. Then, DCE/*t*BuOH (1/3 volume, 2 mL) was injected through a syringe, and the reaction mixture was stirred for 1 h at 40 °C in the presence of blue light. After that, 0.1 mL of the reaction solution was taken out and diluted to 5 mL for UV-Vis analysis.

The mixture of bis-μ-O_2-Mn_2 complex with 1a or 1s in the presence of blue light: To an oven dried Schlenk tube, **bis-μ-O_2-Mn_2** complex (3.6 mg, 0.0025 mmol) and **1a** (13.8 mg, 0.1 mmol) or **1s** (19.8 mg, 0.1 mmol) were added. The reaction tube was vacuumed and purged with N_2. Then, DCE/*t*BuOH (1/3 volume, 1 mL) was injected through a syringe, and the reaction mixture was stirred for 1 min at 40 °C in the presence of blue light. After that, 0.3 mL of the reaction solution was taken out and diluted to 3 mL for UV-Vis analysis.

The mixture of [Mn(dtbpy)$_2$(OTf)$_2$] with 3e or 3o in the absence of blue light: To an oven dried Schlenk tube, [Mn(dtbpy)$_2$(OTf)$_2$] (22.2 mg, 0.025 mmol) and **3e** (102.1 mg, 0.5 mmol) or **3o** (76.1 mg, 0.5 mmol) were added. The reaction tube was vacuumed and purged with oxygen via an oxygen balloon. Then, MeOH (2 mL) was injected through a syringe, and the reaction mixture was stirred for 13 h at 40 °C in the absence of blue light. After that, 0.1 mL of the reaction solution was taken out and diluted to 5 mL for UV-Vis analysis.

The mixture of [Mn(dtbpy)$_2$(OTf)$_2$] with 3e or 3f or 3o in the absence of blue light: To an oven dried Schlenk tube, [Mn(dtbpy)$_2$(OTf)$_2$] (22.2 mg, 0.025 mmol) and **3e** (102.1 mg, 0.5 mmol) or **3f** (95.1 mg, 0.5 mmol) or **3o** (76.1 mg, 0.5 mmol) were added. The reaction tube was vacuumed and purged with oxygen via an oxygen balloon. Then, MeOH (2 mL) was injected through a syringe, and the reaction mixture was stirred for 4 h or 13 h at 40 °C in the

presence of blue light. After that, 0.1 mL of the reaction solution was taken out and diluted to 5 mL for UV-Vis analysis.

The mixture of bis-μ-O_2-Mn_2 complex with 3o in the presence of blue light: To an oven dried Schlenk tube, **bis-μ-O_2-Mn_2** complex (3.6 mg, 0.0025 mmol) and **3o** (15.2, 0.1 mmol) were added. The reaction tube was vacuumed and purged with N_2. Then, MeOH (1 mL) was injected through a syringe, and the reaction mixture was stirred for 1 min at 40 °C in the presence of blue light. After that, 0.3 mL of the reaction solution was taken out and diluted to 3 mL for UV-Vis analysis.

Dioxygen activation by [Mn(dtbpy)$_2$(OTf)$_2$]: To an oven dried Schlenk tube, [Mn(dtbpy)$_2$(OTf)$_2$] (22.2 mg, 0.025 mmol) was added. The reaction tube was vacuumed and purged with oxygen via an oxygen balloon. Then, MeOH (2 mL) was injected through a syringe, and the reaction mixture was stirred for 1 h at 40 °C in the presence of blue light. After that, 0.1 mL of the reaction solution was taken out and diluted to 5 mL for UV-Vis analysis.

Results and discussion: As shown in Figure S1(A), no obvious absorption for the possible Mn(IV)-oxo species or the corresponding Mn-oxo dimer was seen via UV-Vis spectroscopy, and only the signal of [Mn(dtbpy)$_2$(OTf)$_2$] was observed during the oxidation of **1a** or **1b** or **1f**. These results support that those Mn-oxygen species are too active to be observed during the oxidation of diols. Indeed, when **bis-μ-O_2-Mn_2** complex was mixed with **1a** or **1s** under blue light, the greenish brown solution of **bis-μ-O_2-Mn_2** immediately changed to colorless, and the UV-Vis absorption of **bis-μ-O_2-Mn_2** disappeared accordingly (Figure S1(B)).

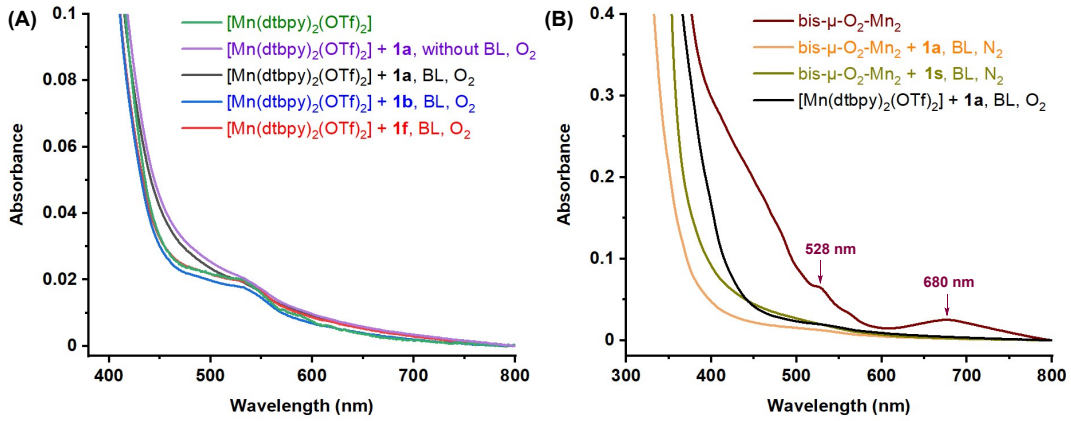


Figure S1. (A) UV-Vis spectra of [Mn(dtbpy)$_2$(OTf)$_2$], and of the mixture of [Mn(dtbpy)$_2$(OTf)$_2$] and 1,2-diol (**1a**, **1b**, **1f**) with or without blue light irradiation for 1 h; (B) UV-Vis spectra of **bis-μ-O_2-Mn_2** complex, the mixture of **bis-μ-O_2-Mn_2** complex with **1a or 1s** under N_2 after BL irradiation for 1 min, and the mixture of [Mn(dtbpy)$_2$(OTf)$_2$] and **1a** with BL irradiation for 1 h. (The concentration of [Mn] for UV-Vis measurement was 0.25 mM in DCE/tBuOH (1/3 in volume))

The oxidation of **3e**, **3f**, **3o** in MeOH were also studied by UV-Vis spectroscopy. Similar to the oxidation of **1a** or **1b** or **1f** in DCE/*t*BuOH, no color change was observed during the reaction. As shown in Figure S2(C), no obvious absorption for the possible Mn(IV)-oxo species or the corresponding Mn-oxo dimer was observed. However, after the completion of the oxidation of **3e**, **3f**, or **3o**, an identical color change to greenish brown were found, and all of those greenish brown solutions showed a UV-Vis absorption at around 537 nm, which could be assigned to the **bis-μ-O_2-Mn_2** complex from MeOH-promoted O_2 activation by [Mn(dtbpy)$_2$(OTf)$_2$] (Figure S1(A)).[2] In the meantime, when **bis-μ-O_2-Mn_2** complex was mixed with **3o** under blue light, the greenish brown solution immediately changed to colorless, and the absorption at 537 nm disappeared accordingly (Figure S1(B)). These observations again implied that the active Mn-oxygen species might not survive during the oxidation of 1,2-diol.

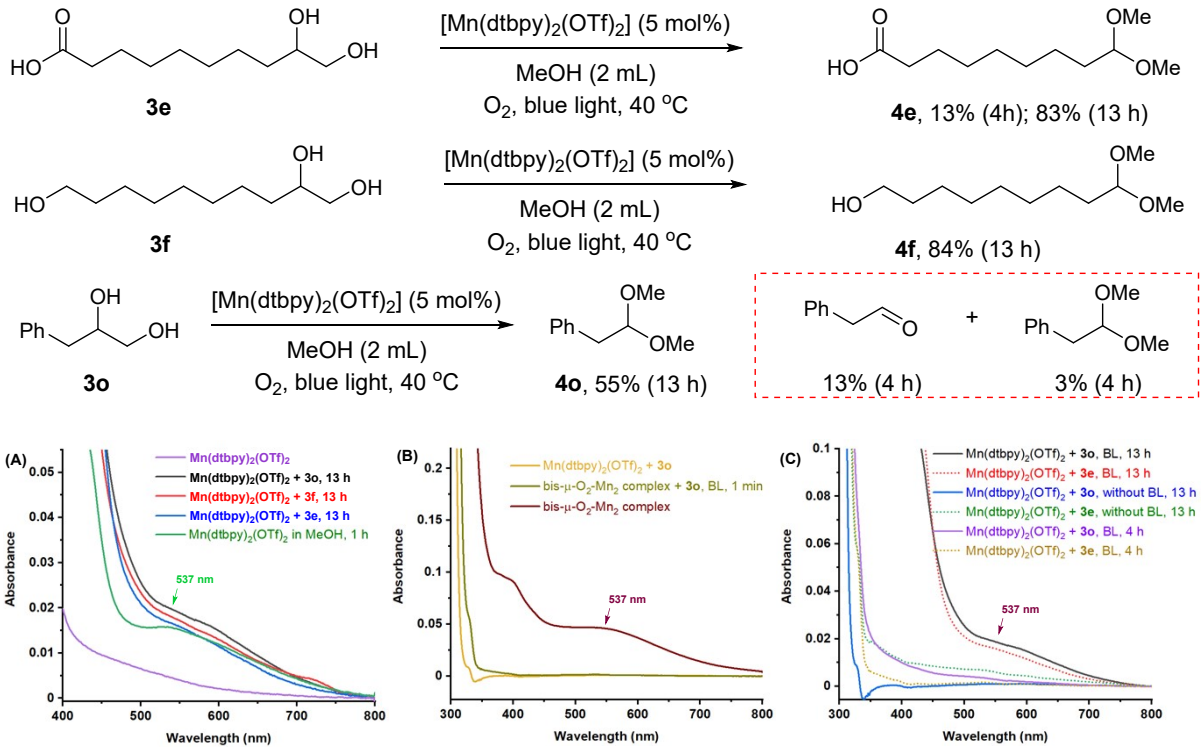


Figure S2. (A) UV-Vis spectra of [Mn(dtbpy)$_2$(OTf)$_2$], the reaction mixture of [Mn(dtbpy)$_2$(OTf)$_2$] with **3e/3f/3o** in MeOH under O_2 after blue light (BL) irradiation for 13 h, and MeOH solution of [Mn(dtbpy)$_2$(OTf)$_2$] under O_2 after BL irradiation for 1 h; (B) UV-Vis spectra of **bis-μ-O_2-Mn_2** complex, the mixture of **bis-μ-O_2-Mn_2** complex with **3o** under N_2 after BL irradiation for 1 min, and the mixture of [Mn(dtbpy)$_2$(OTf)$_2$] and **3o** in the absence of BL; (C) UV-Vis spectra of the reaction mixture of [Mn(dtbpy)$_2$(OTf)$_2$] with **3e/3o** in MeOH under O_2 without or with blue light (BL) irradiation for 4 or 13 h (The concentration of [Mn] for UV-Vis measurement is 0.25 mM in MeOH)

5.4 Light on/off experiment

To an oven dried Schlenk tube, $Mn(OTf)_2$ (8.8 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy, 13.4 mg, 10 mol%) were added. The reaction tube was vacuumed and purged with nitrogen three times. DCE (0.5 mL) was injected through a syringe. Then, the reaction mixture was heated at 60 °C for 1 h to *in situ* prepare the $[Mn(dtbpy)_2(OTf)_2]$ catalyst. The reaction tube was cooled to room temperature, and connected to an oxygen balloon. Finally, after the addition of **1a** (69.1 mg, 0.5 mmol), 3,5-bis(trifluoromethyl)bromobenzene (80.7 mg, internal standard) and *t*BuOH (1.5 mL), the reaction tube was allowed to stir under blue light at 40 °C. After 10 mins, 0.2 mL of the reaction mixture was taken out for ^{1}H NMR analysis, and in the meantime, the light was switched off and the reaction tube was further stirred in the dark. After another 10 mins, 0.2 mL of the reaction mixture was taken out for ^{1}H NMR analysis, and the reaction tube was exposed to blue light again for another 10 mins. Then, 0.2 mL of the reaction mixture was taken out for ^{1}H NMR analysis. The light was switched off and the reaction tube was further stirred in the dark; another 10 mins later, 0.2 mL of the reaction mixture was taken out for ^{1}H NMR analysis. Finally, the reaction tube was exposed to blue light again for another 10 mins, and 0.2 mL of the reaction mixture was taken out for ^{1}H NMR analysis. [Note: the reaction mixtures were first washed by water (1 mL), and then extracted by $CDCl_3$ (1 mL). Finaly, the organic layers were dried for ^{1}H NMR analysis.]

As shown in Figure S3, compared to the reaction under our standard conditions, the reaction in the absence of blue light totally stalled, which highlights the importance of light irradiation.

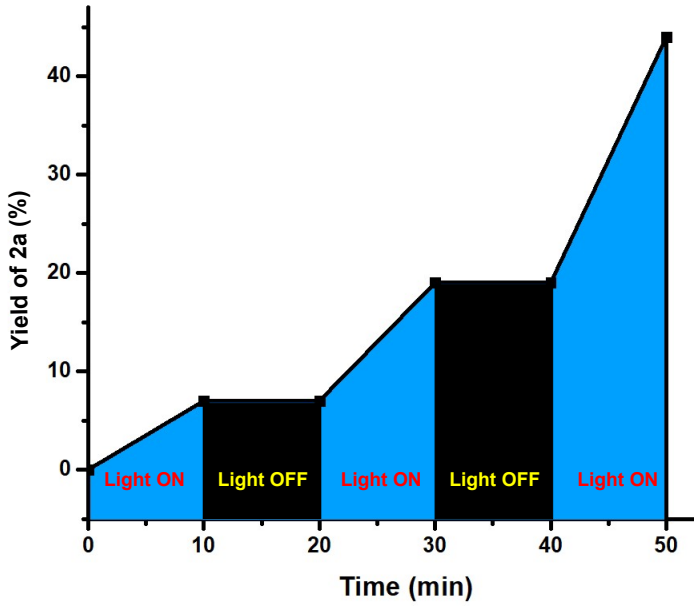
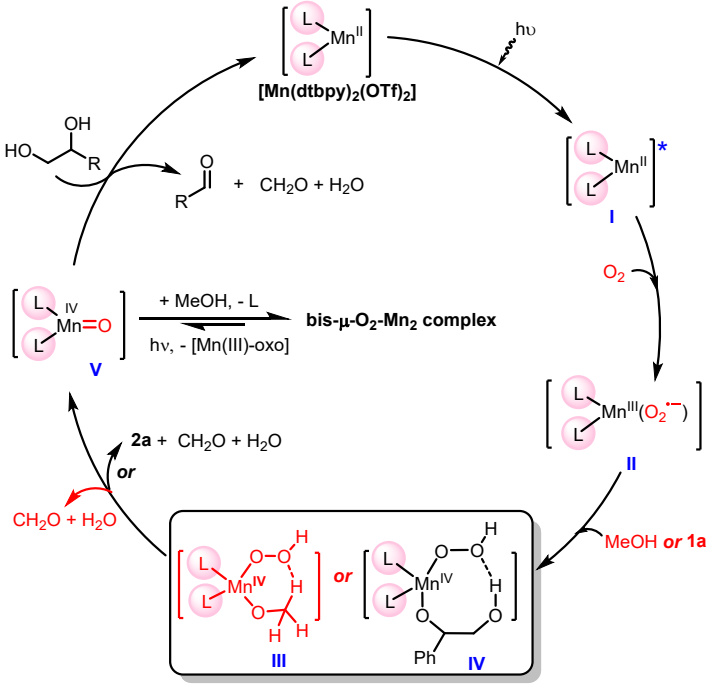


Figure S3. Oxidation of **1a** under light on/off conditions

5.5 Proposed mechanism

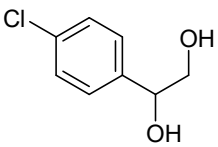
Based on the preliminary mechanistic investigation, and our previous work as well as literature

precedents, a putative and simplified reaction pathway was proposed for understanding this Mn-catalyzed aerobic oxidative cleavage of 1,2-diols (Scheme S1). Initially, $[Mn(dtbpy)_2(OTf)_2]$ is excited by blue light to afford a more active Mn(II) intermediate **I**, which reacts with O_2 to form a Mn^{III}(superoxo) complex **II**. As a nucleophilic radical speices, the radical **II** will abstract the hydrogen from methanol or less nucleophilic diols, like **1a** to form intermediate **III** or **IV**. However, the species **III** and **IV** are unstable**,** and they will further decompose to the Mn(IV)-oxo **V** with release of water, benzaldehyde and/or formaldehyde. Whilst catalytically active, **V** may easily transfer to the more stable μ-oxo dimer, the **bis-μ-O_2-Mn_2** complex. Under the blue light irradiation, the oxo dimer dissociates, presumably reversibly, to **V** and a Mn(III) species. With a higher activity, **V** is able to oxidize the 1,2-diols of lower reactivities to afford the desired carbonyls while regenerating the Mn(II) catalyst.



Scheme S1. A putative mechanism for the photo-Mn promoted oxidative cleavage of diol by O_2.

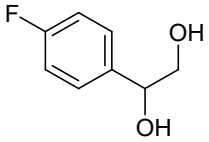
6. Analytical Data of products



1-(4-Chlorophenyl)ethane-1,2-diol (1b)[9]

^{1}H NMR (400 MHz, DMSO) δ 7.40-7.29 (m, 4H), 5.32 (d, J = 4.3 Hz, 1H), 4.73 (t, J = 5.8 Hz, 1H), 4.59 – 4.45 (m, 1H), 3.46 – 3.37 (m, 2H).

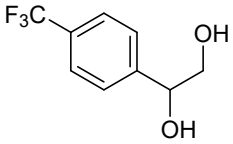
^{13}C NMR (101 MHz, DMSO) δ 142.54, 131.24, 128.18, 127.74, 73.03, 67.18.



1-(4-Fluorophenyl)ethane-1,2-diol (1c)[10]

^{1}H NMR (400 MHz, DMSO) δ 7.43 – 7.29 (m, 2H), 7.12 (t, *J* = 8.9 Hz, 2H), 5.28 (d, *J* = 4.3 Hz, 1H), 4.72 (t, *J* = 5.8 Hz, 1H), 4.59 – 4.46 (m, 1H), 3.47 – 3.38 (m, 2H).

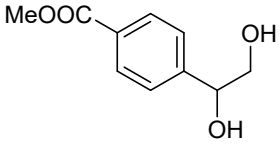
^{13}C NMR (101 MHz, DMSO) δ 161.24 (d, *J* = 240.0 Hz), 139.67 (d, *J* = 2.9 Hz), 128.17 (d, *J* = 8.0 Hz), 114.50 (d, *J* = 21.0 Hz), 73.11, 67.36.



1-(4-(Trifluoromethyl)phenyl)ethane-1,2-diol (1d)[11]

^{1}H NMR (400 MHz, DMSO) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 5.46 (d, *J* = 4.4 Hz, 1H), 4.79 (t, *J* = 5.8 Hz, 1H), 4.67 – 4.56 (m, 1H), 3.52 – 3.38 (m, 2H).

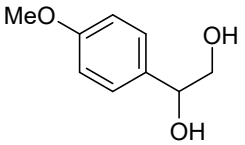
^{13}C NMR (101 MHz, DMSO) δ 148.38, 127.45 (q, *J* = 31.4 Hz), 127.09, 124.64 (q, *J* = 272.8 Hz), 124.45 (q, *J* = 3.8 Hz),73.17, 67.06.



Methyl 4-(1,2-dihydroxyethyl)benzoate (1e)[12]

^{1}H NMR (400 MHz, DMSO) δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 5.42 (d, *J* = 4.4 Hz, 1H), 4.78 (t, *J* = 5.8 Hz, 1H), 4.66 – 4.56 (m, 1H), 3.84 (s, 3H), 3.51 – 3.39 (m, 2H).

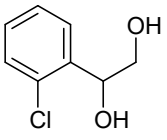
^{13}C NMR (101 MHz, DMSO) δ 166.24, 149.17, 128.77, 128.13, 126.61, 73.41, 67.12, 52.02.



1-(4-Methoxyphenyl)ethane-1,2-diol (1f)[9]

^{1}H NMR (400 MHz, DMSO) δ 7.24 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.10 (d, *J* = 4.2 Hz, 1H), 4.65 (t, *J* = 5.8 Hz, 1H), 4.47 (dd, *J* = 10.5, 5.7 Hz, 1H), 3.72 (s, 3H), 3.42 – 3.36 (m, 2H).

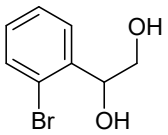
^{13}C NMR (101 MHz, DMSO) δ 158.23, 135.45, 127.38, 113.26, 73.39, 67.56, 55.01.



1-(2-Chlorophenyl)ethane-1,2-diol (1g)[9]

^{1}H NMR (400 MHz, DMSO) δ 7.57 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.40 – 7.27 (m, 2H), 7.29 – 7.20 (m, 1H), 5.44 (d, *J* = 4.5 Hz, 1H), 4.92 (dt, *J* = 7.7, 4.0 Hz, 1H), 4.83 (t, *J* = 5.9 Hz, 1H), 3.58 – 3.44 (m, 1H), 3.34 – 3.27 (m, 1H).

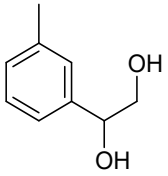
^{13}C NMR (101 MHz, DMSO) δ 140.38, 131.07, 128.78, 128.49, 128.33, 127.01, 70.68, 65.80.



1-(2-Bromophenyl)ethane-1,2-diol (1h)[13]

^{1}H NMR (400 MHz, DMSO) δ 7.55 (td, *J* = 7.9, 1.4 Hz, 2H), 7.38 (td, *J* = 7.5, 1.0 Hz, 1H), 7.18 (td, *J* = 7.7, 1.8 Hz, 1H), 5.48 (d, *J* = 4.4 Hz, 1H), 4.89 – 4.78 (m, 2H), 3.56 – 3.45 (m, 1H), 3.33 – 3.24 (m, 1H).

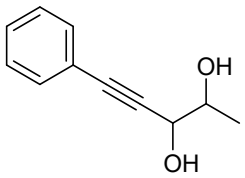
^{13}C NMR (101 MHz, DMSO) δ 141.90, 132.04, 128.90, 128.62, 127.56, 121.59, 72.96, 65.83.



1-(*m*-Tolyl)ethane-1,2-diol (1i)[9]

^{1}H NMR (400 MHz, DMSO) δ 7.15 (dt, *J* = 16.6, 7.5 Hz, 3H), 7.03 (d, *J* = 7.4 Hz, 1H), 5.15 (d, *J* = 4.2 Hz, 1H), 4.67 (t, *J* = 5.8 Hz, 1H), 4.49 (dd, *J* = 10.3, 5.7 Hz, 1H), 3.41 (t, *J* = 5.9 Hz, 2H), 2.29 (s, 3H).

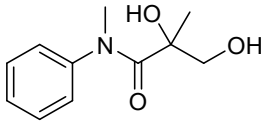
^{13}C NMR (101 MHz, DMSO) δ 143.36, 136.75, 127.71, 127.39, 126.88, 123.40, 73.86, 67.53, 21.12.



5-Phenylpent-4-yne-2,3-diol (1j)[14]

^{1}H NMR (400 MHz, DMSO) δ 7.49 – 7.26 (m, 5H), 5.61 – 5.31 (m, 1H), 4.95 – 4.65 (m, 1H), 4.31 – 4.14 (m, 1H), 3.74 – 3.56 (m, 1H), 1.20 – 1.07 (m, 3H).

^{13}C NMR (101 MHz, DMSO) δ 131.29, 128.64, 128.61, 128.39, 128.32, 122.67, 122.58, 99.58, 90.88, 90.40, 84.04, 83.73, 69.56, 69.47, 66.74, 66.56, 18.82, 18.40.

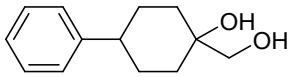


2,3-Dihydroxy-*N*,2-dimethyl-*N*-phenylpropanamide (1k)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.35 (m, 3H), 7.30 (d, *J* = 6.7 Hz, 2H), 4.65 (b, 1H), 3.30 (m, 5H), 2.65 (b, 1H), 1.13 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.37, 143.20, 129.45, 128.63, 128.27, 76.52, 68.49, 41.01, 23.19.

HRMS (ESI) calcd for $C_{11}H_{15}NO_3$ $[M+H]^+$: 210.1125; found: 210.1125.

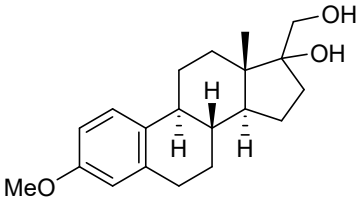


1-(Hydroxymethyl)-4-phenylcyclohexan-1-ol (1l)

^{1}H NMR (400 MHz, DMSO) δ 7.32 – 7.11 (m, 5H), 4.51 (t, *J* = 5.8 Hz, 0.2H), 4.35 (t, *J* = 6.0 Hz, 0.78H), 4.13 (s, 0.79H), 3.95 (s, 0.20H), 3.45 (d, *J* = 6.0 Hz, 1.55H), 3.19 (d, *J* = 5.8 Hz, 0.41H), 2.58 – 2.33 (m, 1H), 1.89 – 1.74 (m, 2H), 1.73 – 1.29 (m, 6H).

^{13}C NMR (101 MHz, DMSO) δ 147.55, 146.67, 128.22, 126.72, 126.65, 125.79, 125.70, 70.71, 70.62, 69.59, 65.20, 43.44, 42.94, 34.90, 33.50, 30.70, 28.74.

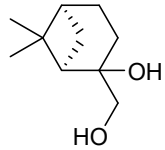
HRMS (ESI) calcd for $C_{13}H_{18}O_2$ $[M+Na]^+$: 229.1199; found: 229.1207.



(8R,9S,13S,14S)-17-(Hydroxymethyl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15, 16,17-decahydro-6H-cyclopenta[a]phenanthren-17-ol (1m)[1]

^{1}H NMR (400 MHz, DMSO) δ 7.15 (d, *J* = 8.6 Hz, 1H), 6.66 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.59 (d, *J* = 2.6 Hz, 1H), 4.30 (t, *J* = 5.5 Hz, 1H), 3.85 (s, 1H), 3.68 (s, 3H), 3.55 – 3.35 (m, 2H), 2.82 – 2.69 (m, 2H), 2.30 – 2.17 (m, 1H), 2.16 – 2.00 (m, 1H), 1.92 – 1.39 (m, 7H), 1.37 – 1.22 (m, 3H), 1.20 – 1.06 (m, 1H), 0.68 (s, 3H).

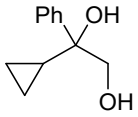
^{13}C NMR (101 MHz, DMSO) δ 156.98, 137.41, 132.35, 126.11, 113.40, 111.39, 82.74, 65.66, 54.84, 48.94, 45.99, 43.46, 38.48, 34.06, 31.25, 29.35, 27.61, 25.96, 23.26, 14.68.



(1R,5S)-2-(Hydroxymethyl)-6,6-dimethylbicyclo[3.1.1]heptan-2-ol (1n)[10]

^{1}H NMR (400 MHz, DMSO) δ 4.37 (t, *J* = 6.0 Hz, 1H), 3.84 (s, 1H), 3.30 – 3.18 (m, 2H), 2.11 – 1.99 (m, 1H), 1.91 (t, *J* = 5.5 Hz, 1H), 1.86 – 1.74 (m, 2H), 1.74 – 1.59 (m, 2H), 1.59 – 1.42 (m, 2H), 1.18 (s, 3H), 0.87 (s, 3H).

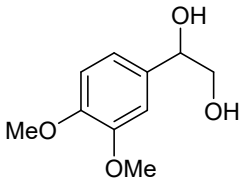
^{13}C NMR (101 MHz, DMSO) δ 75.55, 69.10, 48.27, 40.55, 37.60, 27.57, 26.99, 26.77, 24.65, 23.27.



1-Cyclopropyl-1-phenylethane-1,2-diol (1o)[15]

^{1}H NMR (400 MHz, DMSO) δ 7.53 – 7.46 (m, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 4.56 (t, *J* = 5.7 Hz, 1H), 4.42 (s, 1H), 3.70 – 3.51 (m, 2H), 1.32 – 1.22 (m, 1H), 0.55 – 0.43 (m, 1H), 0.37 – 0.11 (m, 3H).

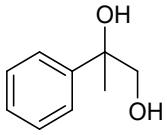
^{13}C NMR (101 MHz, DMSO) δ 146.66, 127.36, 126.11, 125.99, 73.59, 69.57, 18.28, 0.85.



1-(3,4-Dimethoxyphenyl)ethane-1,2-diol (1s)[1]

^{1}H NMR (400 MHz, DMSO) δ 6.92 (d, *J* = 1.7 Hz, 1H), 6.89 – 6.78 (m, 2H), 5.11 (d, *J* = 4.2 Hz, 1H), 4.63 (t, *J* = 5.8 Hz, 1H), 4.46 (dd, *J* = 10.3, 6.0 Hz, 1H), 3.76 – 3.69 (m, 6H), 3.39 (t, *J* = 5.9 Hz, 2H).

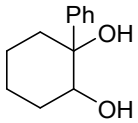
^{13}C NMR (101 MHz, DMSO) δ 148.37, 147.71, 136.00, 118.29, 111.43, 110.11, 73.61, 67.58, 55.56, 55.38.



2-Phenylpropane-1,2-diol (1q*)[1]

^{1}H NMR (400 MHz, DMSO) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 4.84 (s, 1H), 4.65 (t, *J* = 5.8 Hz, 1H), 3.40 (d, *J* = 5.8 Hz, 2H), 1.39 (s, 3H).

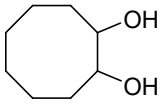
^{13}C NMR (101 MHz, DMSO) δ 147.43, 127.51, 126.02, 125.45, 73.63, 70.46, 26.09.



1-Phenylcyclohexane-1,2-diol (1t)[16]

^{1}H NMR (400 MHz, DMSO) δ 7.48 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 4.34 (s, 1H), 4.11 (d, *J* = 6.7 Hz, 1H), 3.82 – 3.64 (m, 1H), 1.73 – 1.48 (m, 6H), 1.46 – 1.25 (m, 2H).

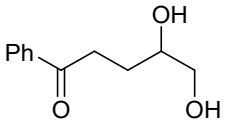
^{13}C NMR (101 MHz, DMSO) δ 148.75, 127.42, 125.66, 125.41, 75.14, 73.22, 39.14, 30.81, 24.33, 21.01.



Cyclooctane-1,2-diol (1u)[1]

^{1}H NMR (400 MHz, DMSO) δ 4.16 (d, *J* = 4.4 Hz, 2H), 3.69 – 3.58 (m, 2H), 1.80 – 1.66 (m, 2H), 1.65 – 1.52 (m, 2H), 1.52 – 1.29 (m, 8H).

^{13}C NMR (101 MHz, DMSO) δ 71.91, 30.35, 26.25, 23.11.

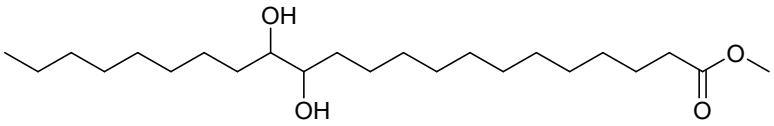


4,5-Dihydroxy-1-phenylpentan-1-one (1v)

^{1}H NMR (400 MHz, DMSO) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 4.60 – 4.42 (m, 2H), 3.57 – 3.41 (m, 1H), 3.32 – 3.24 (m, 2H), 3.15 – 2.96 (m, 2H), 1.88 – 1.73 (m, 1H), 1.64 – 1.42 (m, 1H).

^{13}C NMR (101 MHz, DMSO) δ 200.27, 136.77, 132.97, 128.69, 127.83, 70.40, 65.83, 34.36, 28.16.

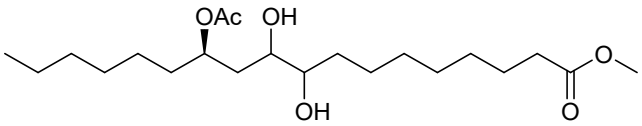
HRMS (ESI) calcd for $C_{11}H_{14}O_3$ $[M+Na]^+$: 217.0835; found: 217.0835.



Methyl 13,14-dihydroxydocosanoate (3c)[17]

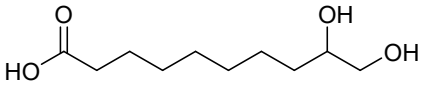
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.65 (s, 3H), 3.62 – 3.56 (m, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.68 – 1.55 (m, 2H), 1.54 – 1.36 (m, 6H), 1.35 – 1.20 (m, 26H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.35, 74.69, 51.41, 34.09, 31.85, 29.67, 29.64, 29.52, 29.50, 29.38, 29.25, 29.20, 29.11, 29.10, 26.00, 24.92, 22.64, 14.07.



Methyl (12R)-12-acetoxy-9,10-dihydroxyoctadecanoate (**3d**, was synthesized according to the literature)[17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 – 4.78 (m, 1H), 3.65 (s, 3H), 3.64 – 3.14 (m, 2H), 2.29 (t, *J* = 7.5 Hz, 2H), 2.08 and 2.05 and 2.03 and 2.00 (4s, 3H, $\underline{CH_3}$-C=O in 4 isomers), 1.84 – 1.13 (m, 24H), 0.83 (t, *J* = 6.6 Hz, 3H).

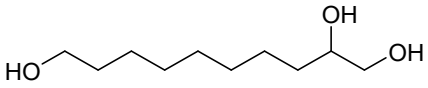


9,10-Dihydroxydecanoic acid (3e)

^{1}H NMR (400 MHz, DMSO) δ 4.38 (br, 2H), 3.28 – 3.18 (m, 3H), 2.18 (t, *J* = 6.9 Hz, 2H), 1.58 – 1.09 (m, 12H).

^{13}C NMR (101 MHz, DMSO) δ 174.77, 71.22, 66.09, 33.82, 33.49, 29.27, 28.92, 28.68, 25.23, 24.67.

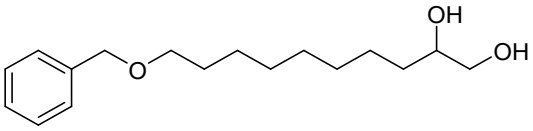
HRMS (ESI) calcd for $C_{10}H_{20}O_4$ [M+Na]$^+$: 227.1254; found: 227.1256.



Decane-1,2,10-triol (3f)[18]

^{1}H NMR (400 MHz, DMSO) δ 4.40 (t, *J* = 5.6 Hz, 1H), 4.35 – 4.26 (m, 2H), 3.39 – 3.34 (m, 3H), 3.28 – 3.14 (m, 2H), 1.39 (d, *J* = 6.4 Hz, 4H), 1.29 – 1.13 (m, 10H).

^{13}C NMR (101 MHz, DMSO) δ 71.10, 66.01, 60.75, 33.44, 32.57, 29.28, 29.18, 28.98, 25.54, 25.19.

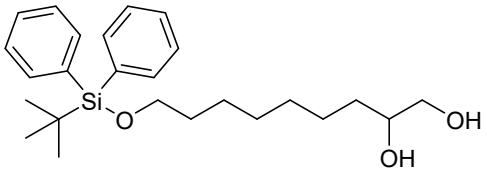


10-(Benzyloxy)decane-1,2-diol (3g)[19]

^{1}H NMR (400 MHz, DMSO) δ 7.43 – 7.09 (m, 5H), 4.48 (t, *J* = 5.4 Hz, 1H), 4.43 (s, 2H), 4.39 (d, *J* = 4.7 Hz, 1H), 3.42 – 3.32 (m, 3H), 3.31 – 3.16 (m, 2H), 1.60 – 1.47 (m, 2H), 1.45 – 1.34 (m, 2H), 1.33 – 1.17 (m, 10H).

^{13}C NMR (101 MHz, DMSO) δ 139.15, 128.67, 127.85, 127.77, 72.23, 71.54, 70.04, 66.39, 33.81, 29.66, 29.63, 29.49, 29.27, 26.15, 25.57.

HRMS (ESI) calcd for $C_{17}H_{28}O_3$ [M+Na]$^+$: 303.1931; found: 303.1927.

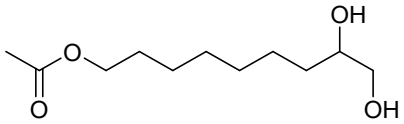


9-((*tert*-Butyldiphenylsilyl)oxy)nonane-1,2-diol (3h)

^{1}H NMR (400 MHz, DMSO) δ 7.63 – 7.51 (m, 4H), 7.46 – 7.31 (m, 6H), 4.47 (t, *J* = 5.5 Hz, 1H), 4.38 (d, *J* = 4.8 Hz, 1H), 3.61 (t, *J* = 6.2 Hz, 2H), 3.42 – 3.32 (m, 1H), 3.28 – 3.20 (m, 2H), 1.54 – 1.43 (m, 2H), 1.41 – 1.13 (m, 10H), 0.96 (s, 9H).

^{13}C NMR (101 MHz, DMSO) δ 135.13, 133.51, 129.91, 127.96, 71.28, 66.14, 63.55, 33.52, 32.11, 29.42, 28.91, 26.79, 25.36, 25.27, 18.91.

HRMS (ESI) calcd for $C_{25}H_{38}O_3Si$ [M+Na]$^+$: 437.2482; found: 437.2477.

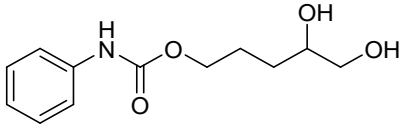


8,9-Dihydroxynonyl acetate (3i)

^{1}H NMR (400 MHz, DMSO) δ 4.56 – 4.27 (m, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 3.42 – 3.31 (m, 1H), 3.30 – 3.16 (m, 2H), 1.97 (s, 3H), 1.62 – 1.47 (m, 2H), 1.31 (d, *J* = 46.2 Hz, 10H).

^{13}C NMR (101 MHz, DMSO) δ 170.67, 71.34, 66.18, 64.07, 33.52, 29.39, 28.94, 28.35, 25.61, 25.31, 20.80.

HRMS (ESI) calcd for $C_{11}H_{22}O_4$ [M+Na]$^+$: 241.1410; found: 241.1418.

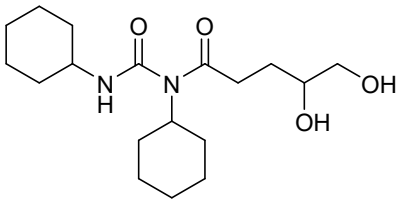


4,5-Dihydroxypentyl phenylcarbamate (3j)

^{1}H NMR (400 MHz, DMSO) δ 9.55 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.25 (t, *J* = 7.9 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 4.65 – 4.45 (m, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 3.47 – 3.39 (m, 1H), 3.34 – 3.19 (m, 2H), 1.84 – 1.69 (m, 1H), 1.68 – 1.48 (m, 2H), 1.36 – 1.23 (m, 1H).

^{13}C NMR (101 MHz, DMSO) δ 153.87, 139.34, 128.88, 122.48, 118.35, 70.94, 66.02, 64.64, 29.86, 25.16.

HRMS (ESI) calcd for $C_{12}H_{17}NO_4$ [M+Na]$^+$: 262.1050; found: 262.1052.

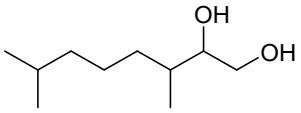


***N*-cyclohexyl-*N*-(cyclohexylcarbamoyl)-4,5-dihydroxypentanamide (3k)**

^{1}H NMR (400 MHz, DMSO) δ 8.21 (d, *J* = 7.8 Hz, 1H), 4.63 – 4.38 (m, 2H), 3.99 – 3.86 (m, 1H), 3.38 – 3.32 (m, 1H), 3.28 – 3.14 (m, 2H), 2.45 – 2.34 (m, 1H), 2.31 – 2.20 (m, 1H), 1.86 – 1.62 (m, 8H), 1.60 – 1.50 (m, 2H), 1.49 – 0.91 (m, 12H).

^{13}C NMR (101 MHz, DMSO) δ 170.27, 153.81, 70.76, 65.87, 52.77, 49.73, 31.84, 30.57, 30.52, 29.29, 25.61, 25.32, 25.24, 24.58.

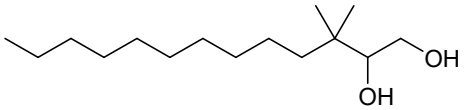
HRMS (ESI) calcd for $C_{18}H_{32}N_2O_4$ [M+Na]$^+$: 363.2254; found: 363.2266.



3,7-Dimethyloctane-1,2-diol (3m)[20]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 – 3.42 (m, 3H), 1.61 – 1.06 (m, 8H), 0.97 – 0.79 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 76.24, 75.76, 65.08, 64.53, 39.19, 39.13, 36.13, 35.71, 33.21, 32.59, 27.89, 27.73, 24.81, 24.68, 22.67, 22.65, 22.49, 22.48, 15.15, 14.54.

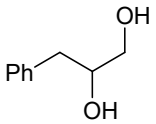


3,3-Dimethyltridecane-1,2-diol (3n)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.72 (dd, *J* = 10.3, 2.1 Hz, 1H), 3.56 – 3.41 (m, 2H), 1.40 – 1.10 (m, 18H), 0.94 – 0.82 (m, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 78.49, 62.98, 39.15, 35.99, 31.86, 30.58, 29.64, 29.59, 29.29, 23.58, 23.17, 22.89, 22.64, 14.07.

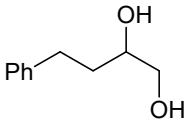
HRMS (ESI) calcd for $C_{15}H_{32}O_2$ $[M+H]^+$: 245.2475; found: 245.2477.



3-Phenylpropane-1,2-diol (3o)[10]

^{1}H NMR (400 MHz, DMSO) δ 7.31 – 7.09 (m, 5H), 4.62 – 4.48 (m, 2H), 3.67 – 3.52 (m, 1H), 3.32 – 3.19 (m, 2H), 2.82 – 2.68 (m, 1H), 2.57 – 2.51 (m, 1H).

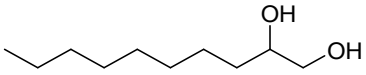
^{13}C NMR (101 MHz, DMSO) δ 139.69, 129.37, 127.95, 125.65, 72.52, 65.33, 39.80.



4-Phenylbutane-1,2-diol (3p)[1]

^{1}H NMR (400 MHz, DMSO) δ 7.31 – 7.08 (m, 5H), 4.56 – 4.38 (m, 2H), 3.45 – 3.36 (m, 1H), 3.33 – 3.18 (m, 2H), 2.78 – 2.51 (m, 2H), 1.80 – 1.62 (m, 1H), 1.59 – 1.39 (m, 1H).

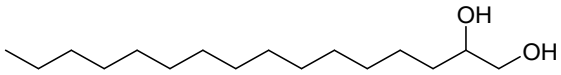
^{13}C NMR (101 MHz, DMSO) δ 142.54, 128.28, 128.21, 125.51, 70.43, 65.91, 35.42, 31.32.



Decane-1,2-diol (3a*)[21]

^{1}H NMR (400 MHz, DMSO) δ 4.40 (t, *J* = 5.6 Hz, 1H), 4.31 (d, *J* = 4.9 Hz, 1H), 3.29 – 3.14 (m, 2H), 1.46 – 1.32 (m, 2H), 1.31 – 1.10 (m, 12H), 0.85 (t, *J* = 6.7 Hz, 3H).

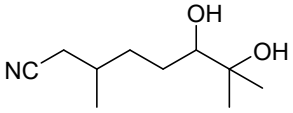
^{13}C NMR (101 MHz, DMSO) δ 71.11, 66.02, 33.44, 31.35, 29.33, 29.11, 28.75, 25.20, 22.14, 13.98.



Hexadecane-1,2-diol (3q)[22]

^{1}H NMR (400 MHz, DMSO) δ 4.39 (t, *J* = 5.6 Hz, 1H), 4.30 (d, *J* = 4.9 Hz, 1H), 3.39 – 3.33 (m, 1H), 3.29 – 3.15 (m, 2H), 1.44 – 1.31 (m, 2H), 1.30 – 1.01 (m, 24H), 0.85 (t, *J* = 6.8 Hz, 3H).

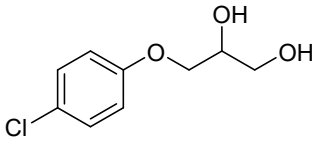
^{13}C NMR (101 MHz, DMSO) δ 71.08, 66.00, 33.42, 31.31, 29.32, 29.13, 29.08, 29.03, 28.73, 25.19, 22.11, 13.94.



6,7-Dihydroxy-3,7-dimethyloctanenitrile (3s)

^{1}H NMR (400 MHz, DMSO) δ 4.40 (t, *J* = 5.2 Hz, 1H), 4.13 (b, 1H), 3.12 – 2.97 (m, 1H), 2.48 – 2.32 (m, 2H), 1.84 – 1.68 (m, 1H), 1.65 – 1.25 (m, 2H), 1.22 – 1.07 (m, 2H), 1.04 (s, 3H), 1.01 – 0.92 (m, 6H).

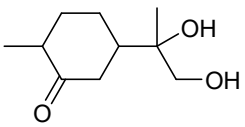
HRMS (ESI) calcd for $C_{10}H_{19}NO_2$ $[M+Na]^+$: 208.1308; found: 208.1312.



4-Chlorophenoxy)propane-1,2-diol (3t)[23]

^{1}H NMR (400 MHz, DMSO) δ 7.36 – 7.24 (m, 2H), 6.99 – 6.90 (m, 2H), 4.96 (d, *J* = 5.1 Hz, 1H), 4.67 (t, *J* = 5.7 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.89 – 3.72 (m, 2H), 3.44 (t, *J* = 5.7 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 157.66, 129.20, 124.09, 116.23, 69.97, 69.88, 62.63.

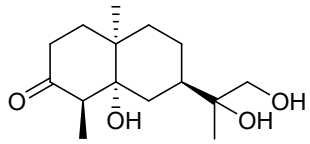


5-(1,2-Dihydroxypropan-2-yl)-2-methylcyclohexan-1-one (3u)

^{1}H NMR (400 MHz, DMSO) δ 4.58 – 4.46 (m, 0.47H), 4.41 – 4.29 (m, 0.24H), 4.18 – 4.08 (m, 0.46H), 3.90 – 3.52 (m, 0.87H), 3.30 – 3.09 (m, 1.38H), 2.47 – 1.94 (m, 3H), 1.92 – 0.69 (m, 12H).

^{13}C NMR (101 MHz, DMSO) δ 212.97, 212.71, 72.55, 72.52, 67.52, 67.45, 45.69, 45.39, 43.82, 43.77, 42.59, 41.97, 34.55, 34.45, 25.63, 25.01, 21.73, 21.64, 14.44, 14.42.

HRMS (ESI) calcd for $C_{10}H_{18}O_3$ [M+Na]$^+$: 209.1148; found: 209.1141.

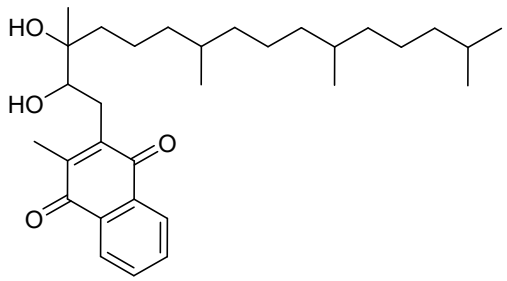


(1R,4aR,7R,8aR)-7-(1,2-dihydroxypropan-2-yl)-8a-hydroxy-1,4a-dimethyloctahydronaphthalen-2(1H)-one (3v)

^{1}H NMR (400 MHz, DMSO) δ 4.39 – 4.23 (m, 2H), 3.81 – 3.67 (m, 1H), 3.25 – 3.05 (m, 2H), 2.80 (q, *J* = 5.8 Hz, 1H), 2.59 (td, *J* = 14.0, 7.0 Hz, 1H), 2.13 – 1.86 (m, 2H), 1.81 – 1.64 (m, 2H), 1.55 – 1.15 (m, 5H), 1.10 (s, 3H), 0.96 – 0.81 (m, 6H), 0.76 (t, *J* = 13.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO) δ 210.76, 76.62, 76.61, 72.88, 72.78, 67.57, 67.52, 51.34, 37.43, 37.27, 37.23, 37.21, 35.09, 35.00, 30.87, 30.84, 28.23, 27.69, 22.31, 21.68, 21.65, 21.62, 20.80, 19.99, 6.83, 6.80.

HRMS (ESI) calcd for $C_{15}H_{26}O_4$ [M+Na]$^+$: 293.1723; found: 293.1730.

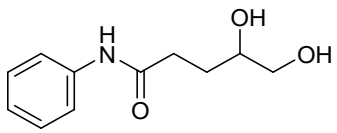


2-(2,3-Dihydroxy-3,7,11,15-tetramethylhexadecyl)-3-methylnaphthalene-1,4-dione (3w)

^{1}H NMR (400 MHz, DMSO) δ 8.02 – 7.89 (m, 2H), 7.87 – 7.71 (m, 2H), 4.50 – 4.37 (m, 1H), 4.14 – 3.98 (m, 1H), 2.88 – 2.73 (m, 1H), 2.68 – 2.55 (m, 1H), 2.11 (s, 3H), 1.55 – 0.96 (m, 25H), 0.87 – 0.75 (m, 12H).

^{13}C NMR (101 MHz, DMSO) δ 184.80, 184.44, 145.70, 144.41, 133.80, 131.92, 131.81, 125.89, 125.85, 75.92, 73.81, 38.16, 38.11, 37.64, 37.58, 37.55, 37.48, 36.92, 36.87, 36.76, 32.29, 32.26, 32.24, 32.21, 32.19, 29.39, 27.49, 24.28, 23.99, 23.95, 23.93, 22.83, 22.65, 22.56, 20.53, 20.49, 20.45, 19.85, 19.78, 19.73, 19.66, 13.10.

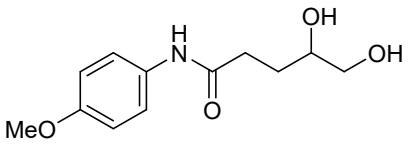
HRMS (ESI) calcd for $C_{31}H_{48}O_4$ [M+Na]$^+$: 507.3445; found: 507.3445.



4,5-Dihydroxy-*N*-phenylpentanamide (5a)[24]

^{1}H NMR (400 MHz, DMSO) δ 9.88 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 4.65 – 4.51 (m, 2H), 3.37 – 3.19 (m, 3H), 2.47 – 2.28 (m, 2H), 1.85 – 1.72 (m, 1H), 1.58 – 1.44 (m, 1H).

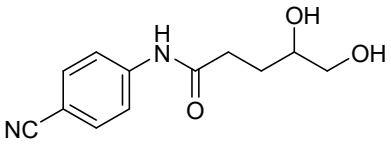
^{13}C NMR (101 MHz, DMSO) δ 171.83, 139.45, 128.80, 123.13, 119.23, 70.80, 65.92, 32.95, 29.40.



4,5-Dihydroxy-N-(4-methoxyphenyl)pentanamide (5b)[24]

^{1}H NMR (400 MHz, DMSO) δ 9.74 (s, 1H), 7.48 (d, *J* = 8.9 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 4.68 – 4.51 (m, 2H), 3.69 (s, 3H), 3.48 – 3.40 (m, 1H), 3.37 – 3.21 (m, 2H), 2.46 – 2.24 (m, 2H), 1.85 – 1.72 (m, 1H), 1.58 – 1.44 (m, 1H).

^{13}C NMR (101 MHz, DMSO) δ 171.36, 155.19, 132.65, 120.86, 113.92, 70.87, 65.94, 55.30, 32.83, 29.50.

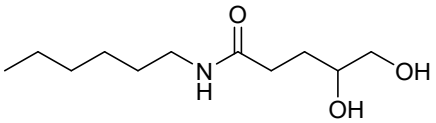


***N*-(4-cyanophenyl)-4,5-dihydroxypentanamide (5c)**

^{1}H NMR (400 MHz, DMSO) δ 10.33 (s, 1H), 7.92 – 7.65 (m, 4H), 4.82 – 4.49 (m, 2H), 3.38 – 3.19 (m, 3H), 2.49 – 2.30 (m, 2H), 1.87 – 1.72 (m, 1H), 1.59 – 1.44 (m, 1H).

^{13}C NMR (101 MHz, DMSO) δ 172.65, 143.64, 133.37, 119.15, 104.73, 70.64, 65.88, 33.04, 29.11.

HRMS (ESI) calcd for $C_{12}H_{14}N_2O_3$ $[M+Na]^+$: 257.0897; found: 257.0901.

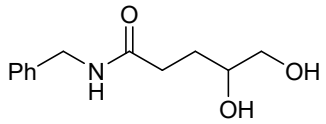


***N*-hexyl-4,5-dihydroxypentanamide (5d)**

^{1}H NMR (400 MHz, DMSO) δ 7.76 (t, *J* = 4.8 Hz, 1H), 4.74 – 4.43 (m, 2H), 3.43 – 3.31 (m, 1H), 3.31 – 3.19 (m, 2H), 3.08 – 2.93 (m, 2H), 2.27 – 2.01 (m, 2H), 1.75 – 1.59 (m, 1H), 1.49 – 1.12 (m, 9H), 0.84 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 172.97, 71.21, 66.11, 38.92, 32.29, 31.43, 29.95, 29.51, 26.50, 22.49, 14.32.

HRMS (ESI) calcd for $C_{11}H_{23}NO_3$ $[M+Na]^+$: 240.1570; found: 240.1576.

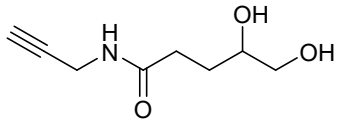


_N_-benzyl-4,5-dihydroxypentanamide (5e)

^{1}H NMR (400 MHz, DMSO) δ 8.32 (t, *J* = 5.7 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 4.64 – 4.50 (m, 2H), 4.25 (d, *J* = 5.9 Hz, 2H), 3.40 (tt, *J* = 9.8, 5.1 Hz, 1H), 3.26 (qt, *J* = 11.0, 5.6 Hz, 2H), 2.34 – 2.11 (m, 2H), 1.80 – 1.64 (m, 1H), 1.53 – 1.36 (m, 1H).

^{13}C NMR (101 MHz, DMSO) δ 172.87, 139.79, 128.43, 127.30, 126.87, 70.90, 65.85, 42.18, 31.95, 29.66.

HRMS (ESI) calcd for $C_{12}H_{17}NO_3$ $[M+H]^+$: 224.1281; found: 224.1276.

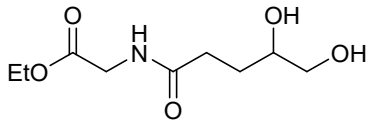


4,5-Dihydroxy-_N_-(prop-2-yn-1-yl)pentanamide (5f)

^{1}H NMR (400 MHz, DMSO) δ 8.24 (t, *J* = 5.0 Hz, 1H), 4.62 – 4.50 (m, 2H), 3.90 – 3.77 (m, 2H), 3.41 – 3.33 (m, 1H), 3.32 – 3.16 (m, 2H), 3.08 – 2.99 (m, 1H), 2.28 – 2.16 (m, 1H), 2.16 – 2.05 (m, 1H), 1.74 – 1.62 (m, 1H), 1.48 – 1.35 (m, 1H).

^{13}C NMR (101 MHz, DMSO) δ 172.59, 81.50, 72.88, 70.78, 65.82, 31.62, 29.43, 27.94.

HRMS (ESI) calcd for $C_8H_{13}NO_3$ $[M+Na]^+$: 194.0788; found: 194.0790.

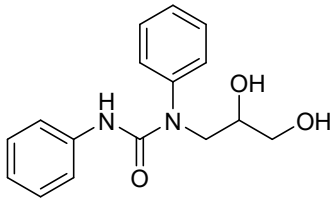


Ethyl (4,5-dihydroxypentanoyl)glycinate (5g)

^{1}H NMR (400 MHz, DMSO) δ 8.21 (t, *J* = 5.7 Hz, 1H), 4.63 – 4.48 (m, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.78 (d, *J* = 5.9 Hz, 2H), 3.46 – 3.34 (m, 1H), 3.33 – 3.20 (m, 2H), 2.32 – 2.10 (m, 2H), 1.77 – 1.62 (m, 1H), 1.52 – 1.37 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 173.76, 170.43, 71.02, 66.07, 60.84, 41.09, 31.84, 29.71, 14.45.

HRMS (ESI) calcd for $C_9H_{17}NO_5$ $[M+Na]^+$: 242.0999; found: 242.1006.

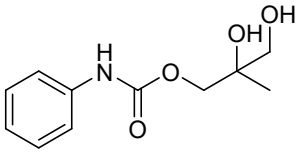


1-(2,3-Dihydroxypropyl)-1,3-diphenylurea (5h)

^{1}H NMR (400 MHz, DMSO) δ 8.35 (s, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.29 (m, 4H), 7.29 – 7.17 (m, 3H), 6.94 (t, *J* = 7.3 Hz, 1H), 5.29 (d, *J* = 3.4 Hz, 1H), 4.79 (t, *J* = 5.5 Hz, 1H), 3.82 – 3.73 (m, 1H), 3.68 – 3.62 (m, 2H), 3.43 – 3.30 (m, 2H).

^{13}C NMR (101 MHz, DMSO) δ 155.47, 143.24, 140.05, 129.40, 128.57, 127.68, 126.37, 122.20, 119.58, 70.17, 63.65, 53.24.

HRMS (ESI) calcd for $C_{16}H_{18}N_2O_3$ $[M+H]^+$: 287.1390; found: 287.1395.

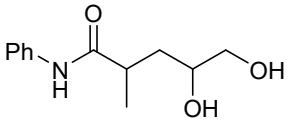


2,3-Dihydroxy-2-methylpropyl phenylcarbamate (5i)

^{1}H NMR (400 MHz, DMSO) δ 9.55 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 4.73 (t, *J* = 5.6 Hz, 1H), 4.57 (s, 1H), 4.06 – 3.87 (m, 2H), 3.39 – 3.23 (m, 2H), 1.09 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 153.97, 139.36, 128.91, 122.54, 118.44, 71.31, 68.40, 66.44, 21.80.

HRMS (ESI) calcd for $C_{11}H_{15}NO_4$ $[M+Na]^+$: 248.0893; found: 248.0899.

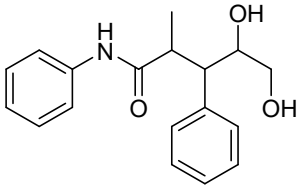


4,5-Dihydroxy-2-methyl-*N*-phenylpentanamide (5j)

^{1}H NMR (400 MHz, DMSO) δ 9.82 (s, 1H), 7.59 (t, *J* = 6.6 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.01 (t, *J* = 7.0 Hz, 1H), 4.66 – 4.41 (m, 2H), 3.34 – 3.11 (m, 3H), 2.82 – 2.56 (m, 1H), 1.86 – 1.71 (m, 0.52H), 1.64 – 1.42 (m, 1H), 1.27 – 1.15 (m, 0.59H), 1.15 – 0.98 (m, 3H).

^{13}C NMR (101 MHz, DMSO) δ 175.51, 175.07, 139.52, 139.46, 128.73, 123.15, 119.35, 119.31, 69.76, 68.97, 66.45, 66.21, 37.94, 37.52, 37.47, 37.19, 19.23, 17.51.

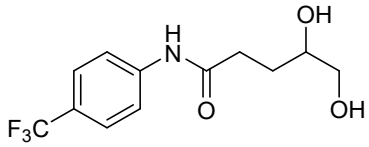
HRMS (ESI) calcd for $C_{12}H_{17}NO_3$ $[M+Na]^+$: 246.1101; found: 246.1103.



4,5-Dihydroxy-2-methyl-*N*,3-diphenylpentanamide (5k)

^{1}H NMR (400 MHz, DMSO) δ 9.72 – 9.50 (m, 1H), 7.48 – 6.82 (m, 10H), 4.97 (d, *J* = 4.6 Hz, 0.36H), 4.77 (d, *J* = 4.4 Hz, 0.62H), 4.58 – 4.43 (m, 1H), 3.96 – 3.82 (m, 1H), 3.27 – 3.01 (m, 2H), 2.98 – 2.88 (m, 2H), 1.26 (d, *J* = 6.6 Hz, 1.86H), 1.20 (d, *J* = 6.8 Hz, 1.2H).

HRMS (ESI) calcd for $C_{18}H_{21}NO_3$ $[M+Na]^+$: 322.1414; found: 322.1420.

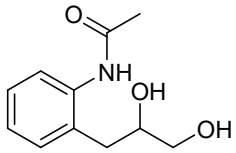


4,5-Dihydroxy-*N*-(4-(trifluoromethyl)phenyl)pentanamide (5l)

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.25 (s, 1H), 7.81 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 4.68 – 4.42 (m, 2H), 3.45 (dp, J = 9.6, 5.2 Hz, 1H), 3.37 – 3.22 (m, 2H), 2.56 – 2.32 (m, 2H), 1.93 – 1.70 (m, 1H), 1.66 – 1.38 (m, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 172.23, 142.93, 125.97 (q, J = 7.1 Hz), 124.42 (q, J = 514.1 Hz), 122.86 (q, J = 48.5 Hz), 70.54, 65.82, 32.88, 29.09.

HRMS (ESI) calcd for $C_{12}H_{14}F_3NO_3$ $[M+Na]^+$: 300.0818; found: 300.0826.

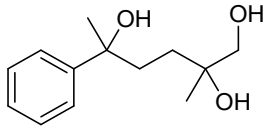


***N*-(2-(2,3-dihydroxypropyl)phenyl)acetamide (5m)**

^{1}H NMR (400 MHz, DMSO) δ 9.56 (s, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.30 – 7.11 (m, 2H), 7.05 (t, J = 7.4 Hz, 1H), 5.19 (d, J = 4.6 Hz, 1H), 4.87 (t, J = 5.4 Hz, 1H), 3.70 – 3.62 (m, 1H), 3.35 – 3.19 (m, 2H), 2.77 (dd, J = 14.1, 4.1 Hz, 1H), 2.59 (dd, J = 14.0, 7.6 Hz, 1H), 2.02 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 168.33, 136.95, 132.20, 131.03, 126.41, 124.65, 124.37, 72.51, 65.14, 35.59, 23.76.

HRMS (ESI) calcd for $C_{11}H_{15}NO_3$ $[M+Na]^+$: 232.0944; found: 232.0946.

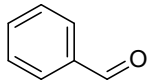


2-Methyl-5-phenylhexane-1,2,5-triol (5n)

^{1}H NMR (400 MHz, DMSO) δ 7.39 (d, J = 7.5 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 4.84 (s, 1H), 4.43 (t, J = 5.6 Hz, 1H), 3.97 (d, J = 4.9 Hz, 1H), 3.17 – 3.00 (m, 2H), 1.82 – 1.58 (m, 2H), 1.43 – 1.25 (m, 4H), 1.16 – 1.01 (m, 1H), 0.96 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, DMSO) δ 149.57, 149.51, 127.76, 125.82, 125.12, 125.09, 72.93, 71.51, 71.49, 69.33, 69.25, 37.87, 37.81, 32.71, 32.67, 30.57, 30.55, 24.21, 24.16.

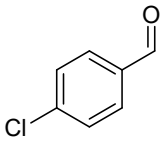
HRMS (ESI) calcd for $C_{13}H_{20}O_3$ $[M+Na]^+$: 247.1305; found: 247.1313.



Benzaldehyde (2a)[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.3 Hz, 2H).

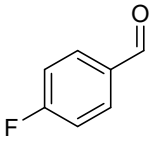
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.36, 136.35, 134.41, 129.69, 128.94.



4-Chlorobenzaldehyde (2b)[10]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H).

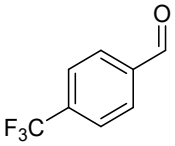
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.82, 140.94, 134.70, 130.88, 129.44.



4-Fluorobenzaldehyde (2c)[10]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 7.83 – 7.98 (m, 2H), 7.13 – 7.26 (m, 2H).

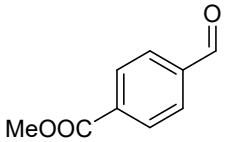
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.33, 166.34 (d, *J* = 255.0 Hz), 132.85 (d, *J* = 3 Hz), 132.06 (d, *J* = 9 Hz), 116.16 (d, *J* = 22 Hz).



4-(Trifluoromethyl)benzaldehyde (2d)[25]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 8.02 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H).

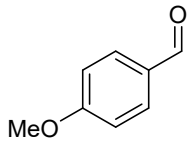
^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.05, 138.64, 135.61 (q, *J* = 65 Hz), 129.90, 126.10 (q, *J* = 8.0 Hz), 123.42 (q, *J* = 543.0 Hz).



Methyl 4-formylbenzoate (2e)[26]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.10 (s, 1H), 8.19 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 2H), 3.96 (s, 3H).

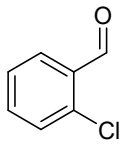
^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.52, 165.92, 139.04, 134.96, 130.07, 129.39, 52.46.



4-Methoxybenzaldehyde (2f)[10]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.88 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H).

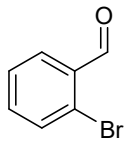
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.73, 164.53, 131.89, 129.86, 114.23, 55.49.



2-Chlorobenzaldehyde (2g)[25]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.48 (s, 1H), 7.92 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.56 – 7.43 (m, 2H), 7.42 – 7.36 (m, 1H).

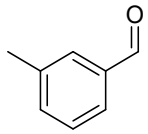
^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.75, 137.88, 135.07, 132.40, 130.55, 129.31, 127.23.



2-Bromobenzaldehyde (2h)[25]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.36 (s, 1H), 7.96 – 7.87 (m, 1H), 7.69 – 7.60 (m, 1H), 7.46 – 7.41 (m, 2H).

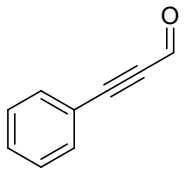
^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.77, 135.26, 133.81, 133.42, 129.78, 127.83, 127.03.



3-Methylbenzaldehyde (2i)[10]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.77 - 7.63 (m, 2H), 7.47 - 7.39 (m, 2H), 2.44 (s, 3H).

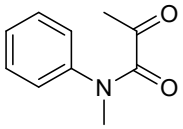
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.56, 138.90, 136.47, 135.26, 129.99, 128.85, 127.21, 21.18.



3-Phenylpropiolaldehyde (2j)[27]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.43 (s, 1H), 7.61 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.54 – 7.46 (m, 1H), 7.41 (t, *J* = 7.4 Hz, 2H).

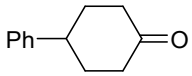
^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.76, 133.27, 131.28, 128.73, 119.43, 95.12, 88.42.



_N_-Methyl-2-oxo-_N_-phenylpropanamide (2k)[28]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.29 (m, 3H), 7.17 (d, *J* = 6.9 Hz, 2H), 3.35 (s, 3H), 2.22 (s, 3H).

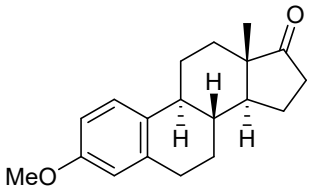
^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.81, 167.16, 141.50, 129.67, 128.15, 126.30, 36.35, 27.64.



4-Phenylcyclohexan-1-one (2l)[29]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.17 (m, 5H), 3.02 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.56 -2.44 (m, 4H), 2.27 - 2.17 (m, 2H), 2.01 - 1.84 (m, 2H).

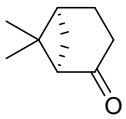
^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.00, 144.70, 128.51, 126.59, 126.49, 42.66, 41.28, 33.88.



(8R,9S,13S,14S)-3-Methoxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]ph-enanthren-17-one (2m)[1]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 3.78 (s, 3H), 2.95 – 2.78 (m, 2H), 2.59 – 2.35 (m, 2H), 2.31 – 1.88 (m, 5H), 1.70 – 1.36 (m, 6H), 0.91 (s, 3H).

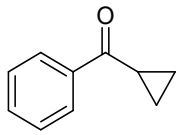
^{13}C NMR (101 MHz, Chloroform-*d*) δ 220.89, 157.56, 137.71, 131.99, 126.30, 113.85, 111.54, 55.18, 50.39, 47.99, 43.95, 38.36, 35.85, 31.56, 29.65, 26.53, 25.91, 21.56, 13.83.



(1R,5S)-6,6-Dimethylbicyclo[3.1.1]heptan-2-one (2n)[30]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.65 – 2.48 (m, 3H), 2.40 - 2.28 (m, 1H), 2.27 – 2.20 (m, 1H), 2.10 – 1.91 (m, 2H), 1.58 (d, *J* = 10.2 Hz, 1H), 1.33 (s, 3H), 0.86 (s, 3H).

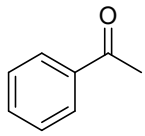
^{13}C NMR (101 MHz, Chloroform-*d*) δ 215.15, 57.97, 41.22, 40.39, 32.79, 25.89, 25.27, 22.12, 21.40.



Cyclopropyl(phenyl)methanone (2o)[25]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 2.73 – 2.60 (m, 1H), 1.27 – 1.21 (m, 2H), 1.07 – 1.00 (m, 2H).

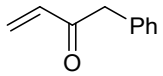
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.54, 137.91, 132.63, 128.40, 127.91, 17.05, 11.56.



Acetophenone (2p)[10]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 2.61 (s, 3H).

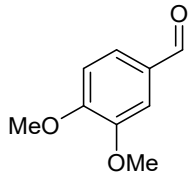
^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.11, 137.09, 133.06, 128.53, 128.26, 26.57.



1-phenylbut-3-en-2-one (2r)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.20 (m, 5H), 6.51 – 6.28 (m, 2H), 5.85 (dd, J = 10.2, 1.5 Hz, 1H), 3.90 (s, 2H).

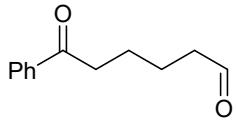
13C NMR (101 MHz, Chloroform-d) δ 197.72, 135.59, 134.03, 129.46, 129.03, 128.72, 127.00, 47.17.



3,4-Dimethoxybenzaldehyde (2s)[25]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.86 (s, 1H), 7.46 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.41 (d, *J* = 1.9 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H).

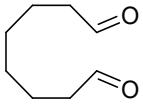
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.72, 154.33, 149.47, 129.99, 126.70, 110.27, 108.80, 56.03, 55.85.



6-Oxo-6-phenylhexanal (2t)[31]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.79 (t, *J* = 1.7 Hz, 1H), 7.96 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 3.01 (t, *J* = 6.9 Hz, 2H), 2.51 (td, *J* = 7.1, 1.6 Hz, 2H), 1.87 – 1.67 (m, 4H).

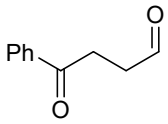
^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.23, 199.71, 136.88, 133.05, 128.60, 127.99, 43.76, 38.14, 23.61, 21.72.



Octanedial (2u)[32]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.77 (t, *J* = 1.8 Hz, 2H), 2.44 (td, *J* = 7.3, 1.8 Hz, 4H), 1.69 – 1.59 (m, 4H), 1.41 - 1.31 (m, 4H).

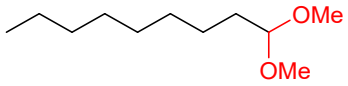
^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.56, 43.70, 28.80, 21.75.



4-Oxo-4-phenylbutanal (2v)[33]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.91 (s, 1H), 8.06 – 7.94 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 3.40 – 3.27 (m, 2H), 3.02 – 2.89 (m, 2H).

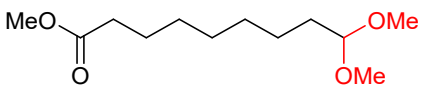
^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.60, 197.78, 136.39, 133.30, 128.63, 128.05, 37.59, 30.99.



1,1-Dimethoxynonane (4a)[34]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.36 (t, *J* = 5.8 Hz, 1H), 3.31 (s, 6H), 1.63 – 1.55 (m, 2H), 1.34 – 1.24 (m, 12H), 0.92 – 0.84 (m, 3H).

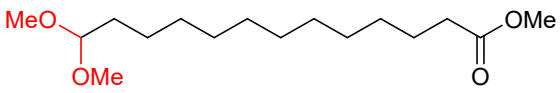
^{13}C NMR (101 MHz, Chloroform-*d*) δ 104.55, 52.51, 32.47, 31.84, 29.50, 29.47, 29.20, 24.58, 22.63, 14.06.



Methyl 9,9-dimethoxynonanoate (4b)[35]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.35 (t, *J* = 5.7 Hz, 1H), 3.66 (s, 3H), 3.31 (s, 6H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.65 – 1.55 (m, 4H), 1.35 – 1.28 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.19, 104.46, 52.53, 51.36, 34.00, 32.39, 29.20, 29.10, 28.97, 24.85, 24.46.

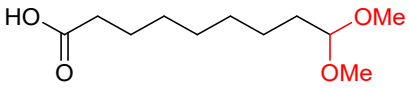


Methyl 13,13-dimethoxytridecanoate (4c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (t, *J* = 5.8 Hz, 1H), 3.64 (s, 3H), 3.29 (s, 6H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.50 (m, 4H), 1.34 – 1.20 (m, 16H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.24, 104.53, 52.52, 51.37, 34.06, 32.44, 29.49, 29.46, 29.42, 29.37, 29.19, 29.10, 24.91, 24.55.

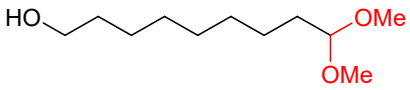
HRMS (ESI) calcd for $C_{16}H_{32}O_4$ $[M+Na]^+$: 311.2193; found: 311.2194.



9,9-Dimethoxynonanoic acid (4e)[35]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 (t, *J* = 5.8 Hz, 1H), 3.29 (s, 6H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.63 – 1.52 (m, 4H), 1.34 – 1.26 (m, 8H).

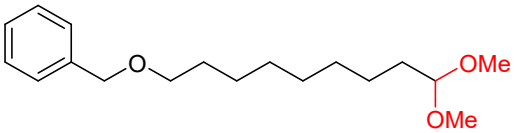
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.81, 104.45, 52.51, 33.99, 32.35, 29.18, 29.09, 28.89, 24.59, 24.46.



9,9-Dimethoxynonan-1-ol (4f)[36]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.36 (t, *J* = 5.7 Hz, 1H), 3.67 – 3.61 (m, 2H), 3.31 (s, 6H), 1.62 – 1.54 (m, 4H), 1.35 – 1.28 (m, 10H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 104.55, 63.05, 52.59, 32.77, 32.47, 29.48, 29.38, 29.29, 25.69, 24.56.

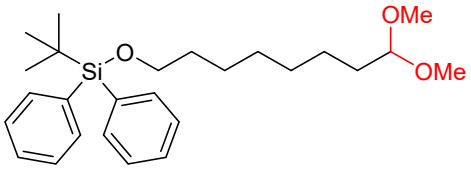


(((9,9-Dimethoxynonyl)oxy)methyl)benzene (4g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 5H), 4.52 (s, 2H), 4.38 (t, *J* = 5.7 Hz, 1H), 3.48 (t, *J* = 6.6 Hz, 2H), 3.33 (s, 6H), 1.71 – 1.54 (m, 4H), 1.40 – 1.28 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.66, 128.28, 127.56, 127.40, 104.52, 72.81, 70.45, 52.54, 32.44, 29.71, 29.45, 29.37, 29.33, 26.12, 24.54.

HRMS (ESI) calcd for $C_{18}H_{30}O_3$ $[M+Na]^+$: 317.2087; found: 317.2085.

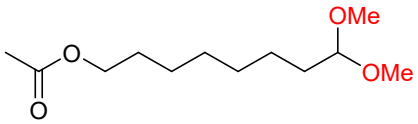


***tert*-Butyl((8,8-dimethoxyoctyl)oxy)diphenylsilane (4h)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 6.4 Hz, 4H), 7.53 – 7.37 (m, 6H), 4.41 (t, *J* = 5.7 Hz, 1H), 3.71 (t, *J* = 6.5 Hz, 2H), 3.36 (s, 6H), 1.73 – 1.55 (m, 4H), 1.45 – 1.28 (m, 8H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.51, 134.11, 129.42, 127.51, 104.50, 63.91, 52.50, 32.50, 32.43, 29.39, 29.24, 26.84, 25.64, 24.51, 19.17.

HRMS (ESI) calcd for $C_{26}H_{40}O_3Si$ $[M+Na]^+$: 451.2639; found: 451.2644.

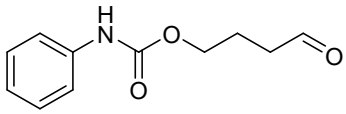


8,8-Dimethoxyoctyl acetate (4i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29 (t, *J* = 5.7 Hz, 1H), 3.99 (t, *J* = 6.7 Hz, 2H), 3.25 (s, 6H), 1.98 (s, 3H), 1.62 – 1.49 (m, 4H), 1.33 – 1.22 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.03, 104.38, 64.43, 52.44, 32.32, 29.20, 29.03, 28.44, 25.69, 24.36, 20.83.

HRMS (ESI) calcd for $C_{12}H_{24}O_4$ $[M+Na]^+$: 255.1567; found: 255.1571.

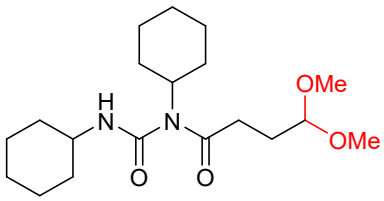


4-Oxobutyl phenylcarbamate (4j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.45 – 7.25 (m, 4H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.95 (br, 1H), 4.20 (t, *J* = 6.3 Hz, 2H), 2.57 (t, *J* = 7.1 Hz, 2H), 2.02 (p, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.41, 153.39, 137.72, 128.93, 123.39, 118.65, 64.03, 40.29, 21.54.

HRMS (ESI) calcd for $C_{11}H_{13}NO_3$ $[M+Na]^+$: 230.0788; found: 230.0780.

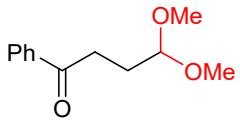


***N*-cyclohexyl-*N*-(cyclohexylcarbamoyl)-4,4-dimethoxybutanamide (4k)**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (br, 1H), 4.39 (t, *J* = 5.2 Hz, 1H), 4.05 – 3.88 (m, 1H), 3.71 – 3.59 (m, 1H), 3.30 (s, 6H), 2.45 (t, *J* = 7.0 Hz, 2H), 2.01 – 1.91 (m, 4H), 1.84 – 1.56 (m, 10H), 1.38 – 1.08 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.44, 154.03, 103.92, 55.53, 53.28, 49.87, 32.56, 30.77, 29.92, 28.03, 26.20, 25.48, 25.30, 24.73.

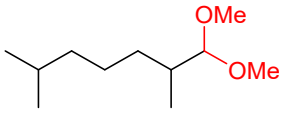
HRMS (ESI) calcd for $C_{19}H_{34}N_2O_4$ $[M+Na]^+$: 377.2411; found: 377.2420.



4,4-Dimethoxy-1-phenylbutan-1-one (4l)[37]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 4.48 (t, *J* = 5.5 Hz, 1H), 3.35 (s, 6H), 3.07 (t, *J* = 7.3 Hz, 2H), 2.11 - 2.03 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.55, 136.92, 133.01, 128.56, 128.02, 103.95, 53.30, 33.27, 26.96.

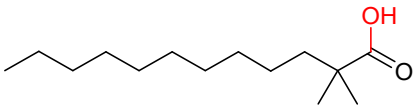


1,1-Dimethoxy-2,6-dimethylheptane (4m)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (d, *J* = 6.5 Hz, 1H), 3.34 (s, 6H), 1.78 – 1.61 (m, 1H), 1.55 – 1.33 (m, 3H), 1.24 – 1.05 (m, 4H), 0.90 – 0.83 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 108.96, 54.04, 53.85, 39.22, 35.67, 31.89, 27.90, 24.63, 22.73, 22.51, 14.30.

HRMS (ESI) calcd for $C_{11}H_{24}O_2$ $[M+H]^+$: 189.1849; found: 189.1853.

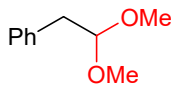


2,2-Dimethyldodecanoic acid (4n)

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.57 – 1.49 (m, 2H), 1.29 – 1.22 (m, 16H), 1.18 (s, 6H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.08, 42.14, 40.56, 31.91, 30.12, 29.64, 29.62, 29.50, 29.33, 24.91, 24.85, 22.68, 14.10.

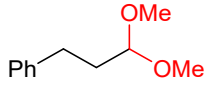
HRMS (ESI) calcd for $C_{14}H_{28}O_2$ $[M+H]^+$: 229.2162; found: 229.2162.



(2,2-Dimethoxyethyl)benzene (4o)[38]

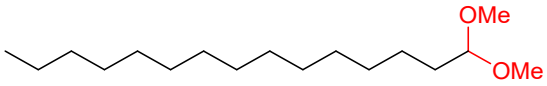
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.21 (m, 5H), 4.55 (t, *J* = 5.6 Hz, 1H), 3.34 (s, 6H), 2.91 (d, *J* = 5.7 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.01, 129.39, 128.29, 126.34, 105.32, 53.31, 39.65.



(3,3-Dimethoxypropyl)benzene (4p)[34]

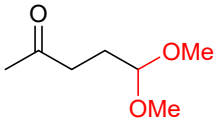
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.23 (m, 2H), 7.23 – 7.17 (m, 3H), 4.36 (t, *J* = 5.7 Hz, 1H), 3.32 (s, 6H), 2.73 – 2.62 (m, 2H), 1.97 – 1.84 (m, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.56, 128.33 (overlap x 2), 125.81, 103.69, 52.64, 34.04, 30.81.



1,1-Dimethoxypentadecane (4q)[39]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.36 (t, *J* = 5.8 Hz, 1H), 3.31 (s, 6H), 1.61 – 1.54 (m, 2H), 1.30 – 1.19 (m, 24H), 0.91 – 0.86 (m, 3H).

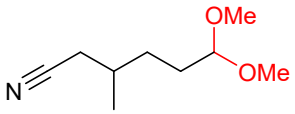
^{13}C NMR (101 MHz, Chloroform-*d*) δ 104.57, 52.56, 32.49, 31.92, 29.69, 29.68, 29.66, 29.65, 29.64, 29.56, 29.48, 29.35, 24.60, 22.69, 14.11.



5,5-Dimethoxypentan-2-one (4r)[40]

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (t, *J* = 5.5 Hz, 1H), 3.26 (s, 6H), 2.46 (t, *J* = 7.3 Hz, 2H), 2.10 (s, 3H), 1.82 (td, *J* = 7.3, 5.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.99, 103.68, 53.11, 38.17, 29.86, 26.50.

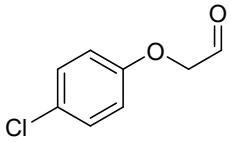


6,6-Dimethoxy-3-methylhexanenitrile (4s)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (t, *J* = 5.5 Hz, 1H), 3.30 (s, 6H), 2.27 (qd, *J* = 16.7, 6.3 Hz, 2H), 1.84 (dq, *J* = 13.2, 6.6 Hz, 1H), 1.67 – 1.40 (m, 3H), 1.38 – 1.27 (m, 1H), 1.06 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 118.60, 104.29, 52.87, 30.60, 30.29, 29.90, 24.40, 19.27.

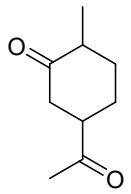
HRMS (ESI) calcd for $C_9H_{17}NO_2$ $[M+Na]^+$: 194.1151; found: 194.1148.



2-(4-Chlorophenoxy)acetaldehyde (4t*)[41]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.84 (d, *J* = 1.1 Hz, 1H), 7.27 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 4.56 (d, *J* = 1.0 Hz, 2H).

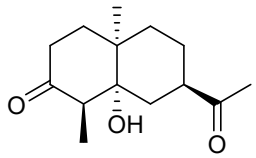
^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.53, 156.18, 129.62, 126.94, 115.86, 72.85.



5-Acetyl-2-methylcyclohexan-1-one (4u)[42]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 – 2.67 (m, 1H), 2.42 (d, *J* = 8.8 Hz, 2H), 2.32 (tt, *J* = 12.4, 6.2 Hz, 1H), 2.17 – 2.00 (m, 5H), 1.66 (ddd, *J* = 25.9, 13.1, 3.4 Hz, 1H), 1.36 (qd, *J* = 13.1, 3.3 Hz, 1H), 0.97 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.45, 208.20, 52.09, 44.54, 42.67, 34.50, 28.23, 27.76, 14.21.

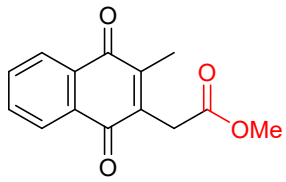


(*1R,4aR,7R,8aR*)-7-acetyl-8a-hydroxy-1,4a-dimethyloctahydronaphthalen-2(*1H*)-one (4v)

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.82 (q, *J* = 6.6 Hz, 1H), 2.71 (tt, *J* = 12.6, 3.7 Hz, 1H), 2.58 – 2.45 (m, 1H), 2.35 – 2.24 (m, 1H), 2.17 – 1.94 (m, 5H), 1.88 (td, *J* = 13.6, 4.2 Hz, 1H), 1.74 – 1.64 (m, 2H), 1.54 – 1.32 (m, 3H), 1.20 (s, 3H), 1.16 – 1.06 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.58, 210.02, 77.29, 51.61, 46.11, 37.43, 37.40, 34.49, 31.11, 29.92, 28.12, 22.71, 21.47, 6.43.

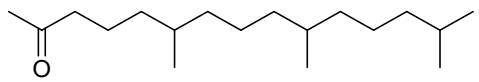
HRMS (ESI) calcd for $C_{14}H_{22}O_3$ $[M+Na]^+$: 261.1461; found: 261.1463.



Methyl 2-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)acetate (4w)[43]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.03 (m, 2H), 7.79 – 7.63 (m, 2H), 3.81 – 3.66 (m, 5H), 2.20 (s, 3H).

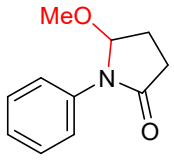
^{13}C NMR (101 MHz, $CDCl_3$) δ 184.79, 183.86, 169.96, 145.68, 139.62, 133.62, 133.60, 132.11, 131.77, 126.48, 126.43, 52.35, 32.35, 13.17.



6,10,14-Trimethylpentadecan-2-one (4x)[44]

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (t, *J* = 7.5 Hz, 2H), 2.13 (s, 3H), 1.64 – 1.45 (m, 3H), 1.43 – 1.01 (m, 17H), 0.91 – 0.77 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.25, 44.10, 39.34, 37.38, 37.36, 37.33, 37.26, 37.20, 37.16, 36.56, 36.47, 32.76, 32.74, 32.65, 32.62, 29.81, 27.95, 24.78, 24.77, 24.40, 24.39, 22.69, 22.60, 21.42, 21.41, 19.71, 19.64, 19.55, 19.49.

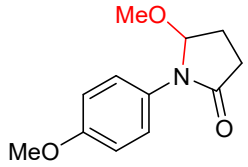


5-Methoxy-1-phenylpyrrolidin-2-one (6a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.43 (m, 2H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 5.32 (dd, *J* = 6.1, 1.2 Hz, 1H), 3.27 (s, 3H), 2.75 (dt, *J* = 17.4, 9.4 Hz, 1H), 2.49 (ddd, *J* = 17.4, 9.7, 2.4 Hz, 1H), 2.33 – 2.19 (m, 1H), 2.19 – 2.07 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.29, 137.81, 128.89, 125.95, 123.11, 91.92, 53.49, 29.82, 24.36.

HRMS (CI) calcd for $C_{11}H_{13}NO_2$ $[M+H]^+$: 192.1019; found: 192.1013.

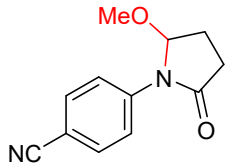


5-Methoxy-1-(4-methoxyphenyl)pyrrolidin-2-one (6b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.24 (d, *J* = 6.1 Hz, 1H), 3.79 (s, 3H), 3.27 (s, 3H), 2.73 (dt, *J* = 17.1, 9.3 Hz, 1H), 2.47 (ddd, *J* = 17.3, 9.8, 2.5 Hz, 1H), 2.36 – 2.20 (m, 1H), 2.20 – 2.06 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.39, 157.73, 130.53, 125.29, 114.14, 92.35, 55.30, 53.72, 29.51, 24.46.

HRMS (ESI) calcd for $C_{12}H_{15}NO_3$ $[M+Na]^+$: 244.0944; found: 244.0952.

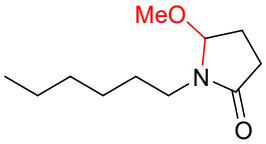


4-(2-Methoxy-5-oxopyrrolidin-1-yl)benzonitrile (6c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 5.38 (d, *J* = 5.6 Hz, 1H), 3.33 (s, 3H), 2.87 – 2.72 (m, 1H), 2.54 (ddd, *J* = 17.6, 9.2, 2.7 Hz, 1H), 2.32 – 2.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.38, 141.97, 132.89, 121.47, 118.64, 108.32, 90.87, 52.94, 30.03, 23.61.

HRMS (CI) calcd for $C_{12}H_{12}N_2O_2$ $[M+H]^+$: 217.0972; found: 217.0964.

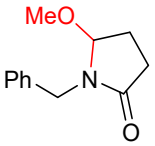


1-Hexyl-5-methoxypyrrolidin-2-one (6d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (d, J = 6.2 Hz, 1H), 3.50 – 3.43 (m, 1H), 3.22 (s, 3H), 3.09 – 2.97 (m, 1H), 2.52 – 2.41 (m, 1H), 2.32 – 2.22 (m, 1H), 2.14 – 1.90 (m, 2H), 1.60 – 1.41 (m, 2H), 1.28 – 1.21 (m, 6H), 0.85 (t, J = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.91, 89.84, 52.45, 40.49, 31.41, 29.02, 27.44, 26.59, 23.69, 22.46, 13.92.

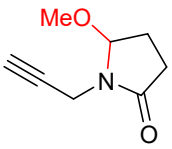
HRMS (ESI) calcd for $C_{11}H_{21}NO_2$ $[M+Na]^+$: 222.1465; found: 222.1464.



1-Benzyl-5-methoxypyrrolidin-2-one (6e)[45]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.14 (m, 5H), 4.87 (d, J = 14.7 Hz, 1H), 4.65 (d, J = 5.6 Hz, 1H), 3.94 (d, J = 14.7 Hz, 1H), 3.14 (s, 3H), 2.57 – 2.42 (m, 1H), 2.38 – 2.23 (m, 1H), 1.96 (dddd, J = 23.6, 15.6, 10.6, 4.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.75, 136.34, 128.55, 128.31, 127.48, 88.90, 52.84, 43.72, 28.92, 23.64.

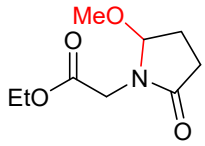


5-Methoxy-1-(prop-2-yn-1-yl)pyrrolidin-2-one (6f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (d, J = 6.3 Hz, 1H), 4.49 (dd, J = 17.5, 2.3 Hz, 1H), 3.73 (d, J = 17.5 Hz, 1H), 3.32 (s, 4H), 2.52 (dt, J = 17.6, 9.0 Hz, 1H), 2.39 – 2.28 (m, 1H), 2.26 – 2.11 (m, 2H), 2.04 – 1.96 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.09, 89.06, 77.67, 71.99, 53.62, 29.73, 28.78, 23.92.

HRMS (CI) calcd for $C_8H_{11}NO_2$ $[M+H]^+$: 154.0863; found: 154.0863.

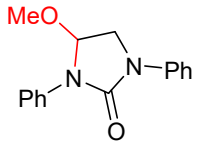


Ethyl 2-(2-methoxy-5-oxopyrrolidin-1-yl)acetate (6g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (d, *J* = 6.3 Hz, 1H), 4.34 (d, *J* = 17.6 Hz, 1H), 4.21 – 4.05 (m, 2H), 3.71 (d, *J* = 17.6 Hz, 1H), 3.22 (s, 3H), 2.49 (dt, *J* = 17.3, 8.7 Hz, 1H), 2.42 – 2.16 (m, 2H), 2.05 – 1.93 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.93, 168.67, 89.89, 61.21, 52.86, 41.33, 28.36, 23.67, 13.99.

HRMS (ESI) calcd for $C_9H_{15}NO_4$ $[M+Na]^+$: 244.0893; found: 244.0895.

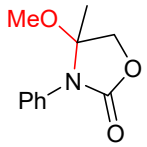


4-Methoxy-1,3-diphenylimidazolidin-2-one (6h)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.34 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.55 (d, *J* = 6.8 Hz, 1H), 4.07 (dd, *J* = 10.7, 6.9 Hz, 1H), 3.80 (d, *J* = 10.7 Hz, 1H), 3.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.15, 139.17, 138.27, 128.89, 124.61, 123.15, 121.04, 117.97, 83.23, 51.01, 47.77.

HRMS (ESI) calcd for $C_{16}H_{16}N_2O_2$ $[M+Na]^+$: 291.1104; found: 291.1104.

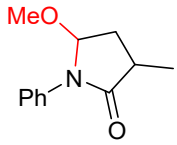


4-Methoxy-4-methyl-3-phenyloxazolidin-2-one (6i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 4H), 7.28 – 7.14 (m, 1H), 4.41 (d, *J* = 10.3 Hz, 1H), 4.14 (d, *J* = 10.3 Hz, 1H), 3.31 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.90, 134.74, 129.11, 126.80, 124.89, 91.39, 71.06, 49.79, 23.66.

HRMS (ESI) calcd for $C_{11}H_{13}NO_3$ $[M+Na]^+$: 230.0788; found: 230.0788.



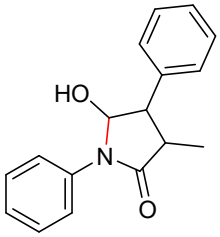
5-Methoxy-3-methyl-1-phenylpyrrolidin-2-one (6j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.45 (m, 2H), 7.42 – 7.32 (m, 2H), 7.27 – 7.15 (m, 1H), 5.31 – 5.16 (m, 1H), 3.41 – 3.18 (m, 3H), 2.95 – 2.80 (m, 0.77H), 2.69 – 2.57 (m, 0.2H), 2.55

– 2.45 (m, 0.24H), 2.44 – 2.32 (m, 0.77H), 1.91 – 1.73 (m, 1H), 1.40 (d, *J* = 7.4 Hz, 0.71H), 1.28 (d, *J* = 7.1 Hz, 2.34H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 138.25, 137.78, 128.85, 125.94, 125.63, 123.39, 122.57, 91.03, 89.97, 54.24, 53.81, 36.09, 35.13, 33.58, 32.17, 18.03, 16.06.

HRMS (CI) calcd for $C_{12}H_{15}NO_2$ $[M+H]^+$: 206.1176; found: 206.1171.

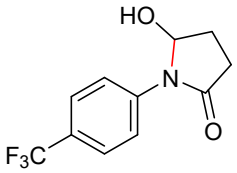


5-Hydroxy-3-methyl-1,4-diphenylpyrrolidin-2-one (6k)

^{1}H NMR (400 MHz, DMSO) δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.16 (m, 2H), 7.11 (d, *J* = 7.4 Hz, 2H), 6.71 (d, *J* = 3.0 Hz, 1H), 5.53 (s, 1H), 3.48 (d, *J* = 8.2 Hz, 1H), 3.35 – 3.27 (m, 1H), 0.72 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, DMSO) δ 175.43, 138.88, 138.16, 128.84, 128.70, 127.80, 127.06, 125.05, 121.94, 87.35, 51.55, 39.02, 11.48.

HRMS (CI) calcd for $C_{17}H_{17}NO_2$ $[M+H]^+$: 290.1151; found: 290.1158.

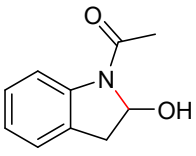


5-Hydroxy-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (6l)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.62 (d, *J* = 5.3 Hz, 1H), 4.45 (br, 1H), 2.80 – 2.60 (m, 1H), 2.48 – 2.27 (m, 2H), 2.06 – 1.92 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.94, 140.37, 127.43 (q, *J* = 33.3 Hz), 125.98 (q, *J* = 4.0 Hz), 123.87 (q, *J* = 272.7 Hz), 122.09, 85.02, 29.78, 28.22.

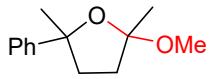
HRMS (ESI) calcd for $C_{11}H_{10}F_3NO_2$ $[M+H]^+$: 246.0736; found: 246.0736.



1-(2-Hydroxyindolin-1-yl)ethan-1-one (6m)

^{1}H NMR (400 MHz, DMSO) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.08 (m, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 6.6 Hz, 1H), 5.92 – 5.74 (m, 1H), 3.37 (dd, *J* = 16.9, 6.4 Hz, 1H), 2.86 (d, *J* = 17.0 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, DMSO) δ 169.92, 141.69, 129.77, 127.14, 125.11, 123.53, 116.03, 83.28, 38.16, 23.39. HRMS (CI) calcd for $C_{10}H_{11}NO_2$ $[M+H]^+$: 200.0682; found: 200.0680.



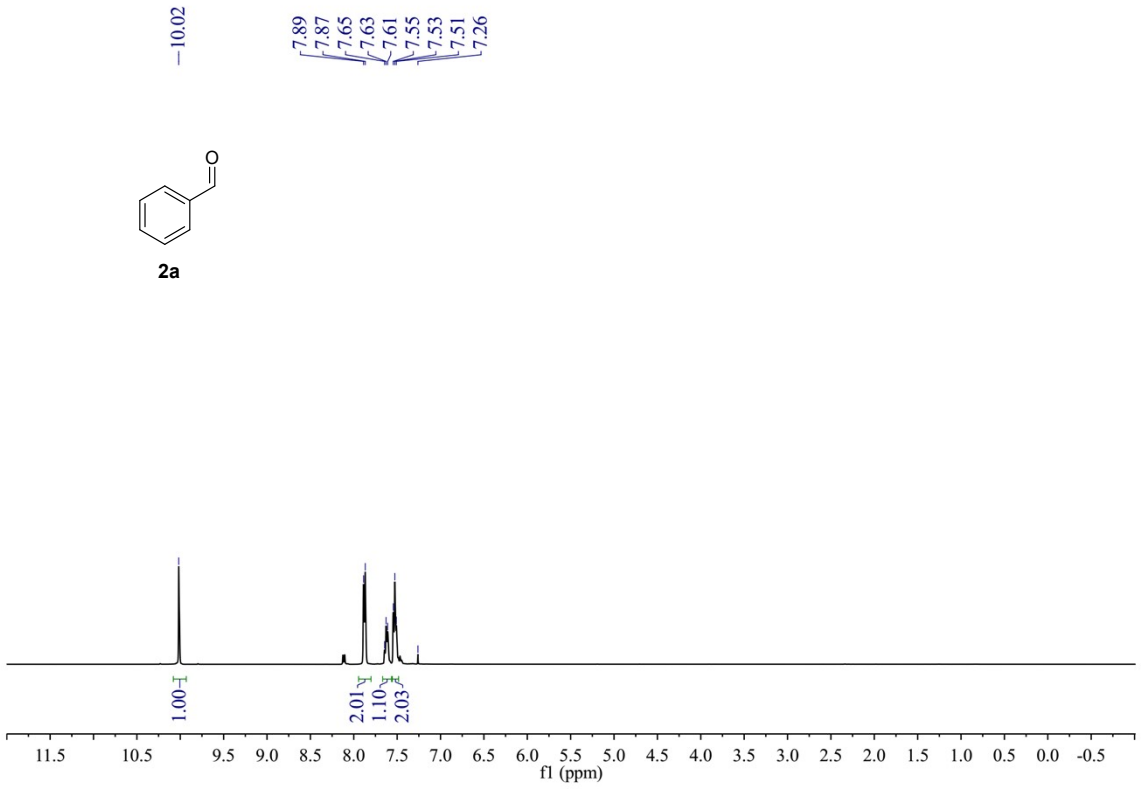
2-Methoxy-2,5-dimethyl-5-phenyltetrahydrofuran (6n, dr = 3:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.36 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.13 (m, 1H), 3.35 (s, 1.71H), 3.20 (s, 1.15H), 2.48 – 2.28 (m, 1H), 2.21 – 1.99 (m, 2.44H), 1.78 – 1.68 (m, 0.75H), 1.62 (s, 1.85H), 1.58 – 1.50 (m, 3H), 1.46 (s, 1.22H).

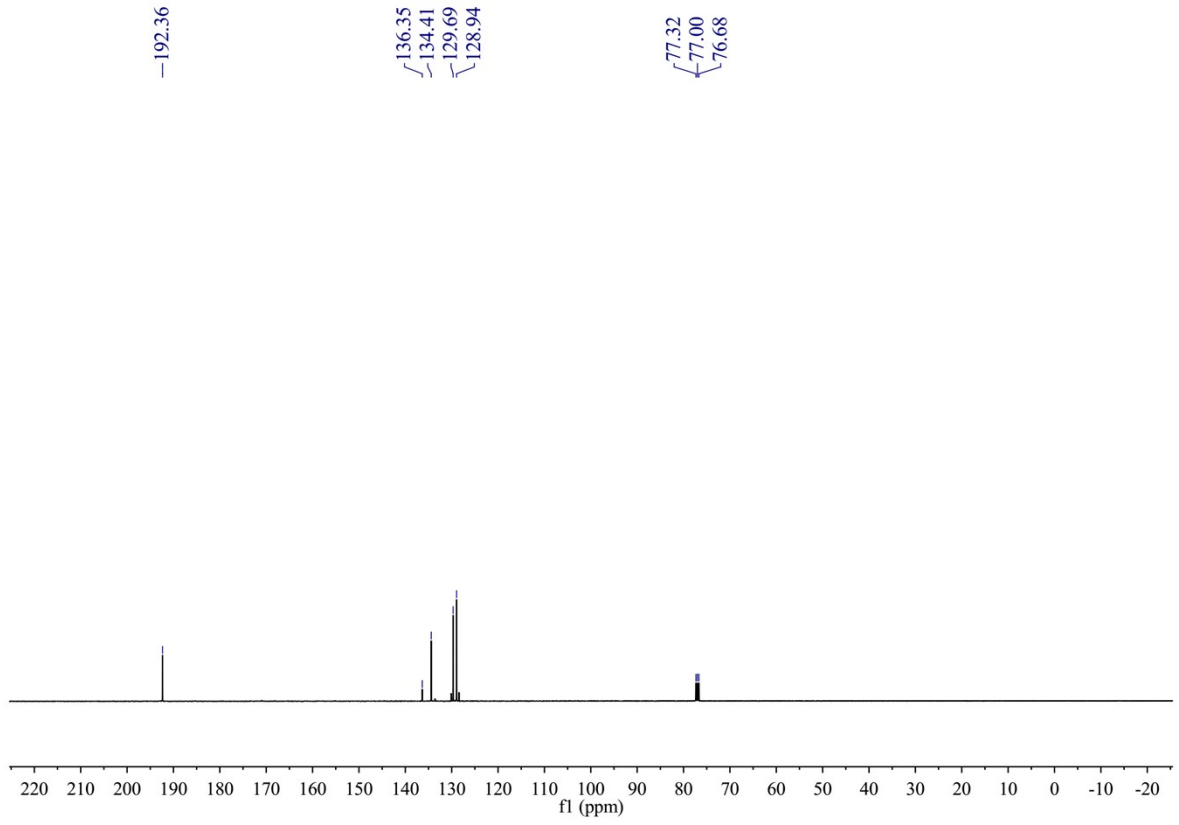
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.79, 148.53, 127.94, 127.88, 126.26, 126.21, 124.69, 124.55, 107.88, 85.88, 85.83, 49.04, 48.54, 39.60, 38.30, 38.05, 37.97, 30.91, 30.80, 22.97, 21.88.

HRMS (CI) calcd for $C_{13}H_{18}O_2$ $[M+H]^+$: 207.1380; found: 207.1382.

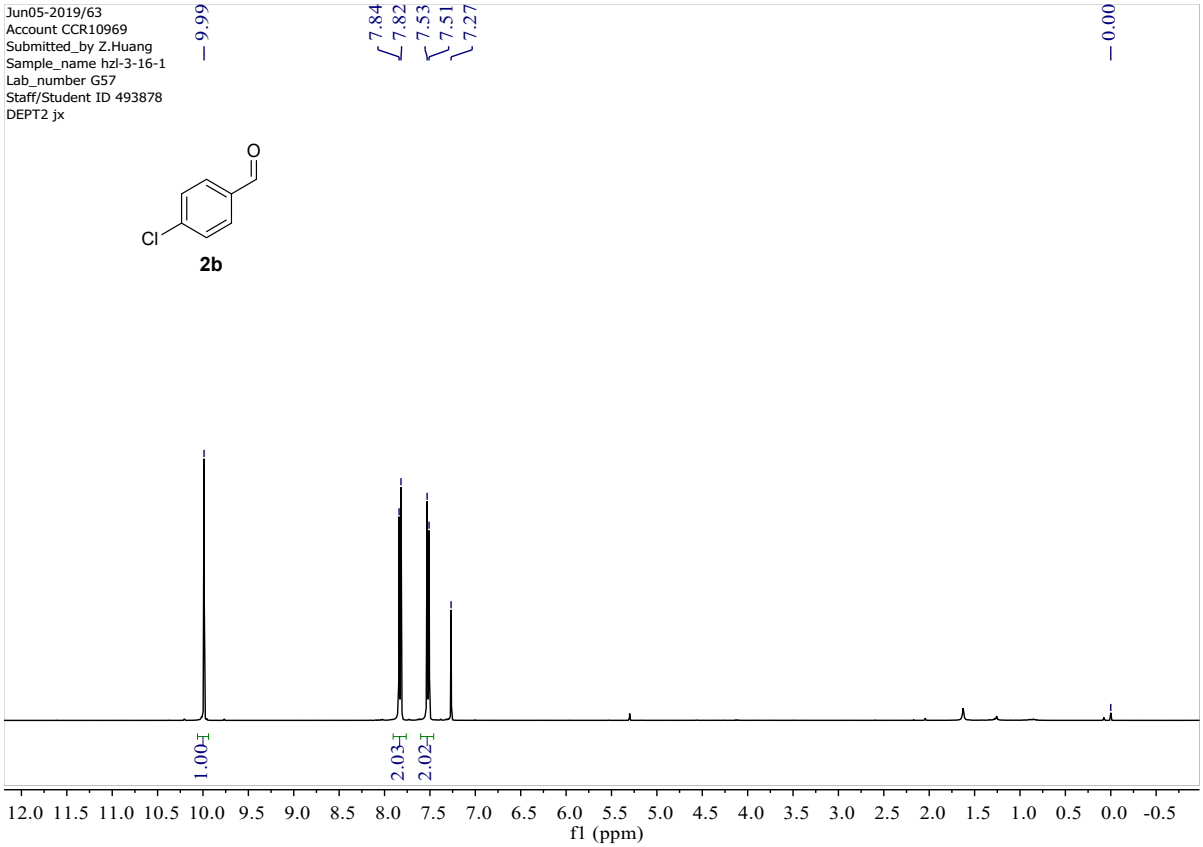
7. NMR spectra of products



^{1}H NMR



^{13}C NMR



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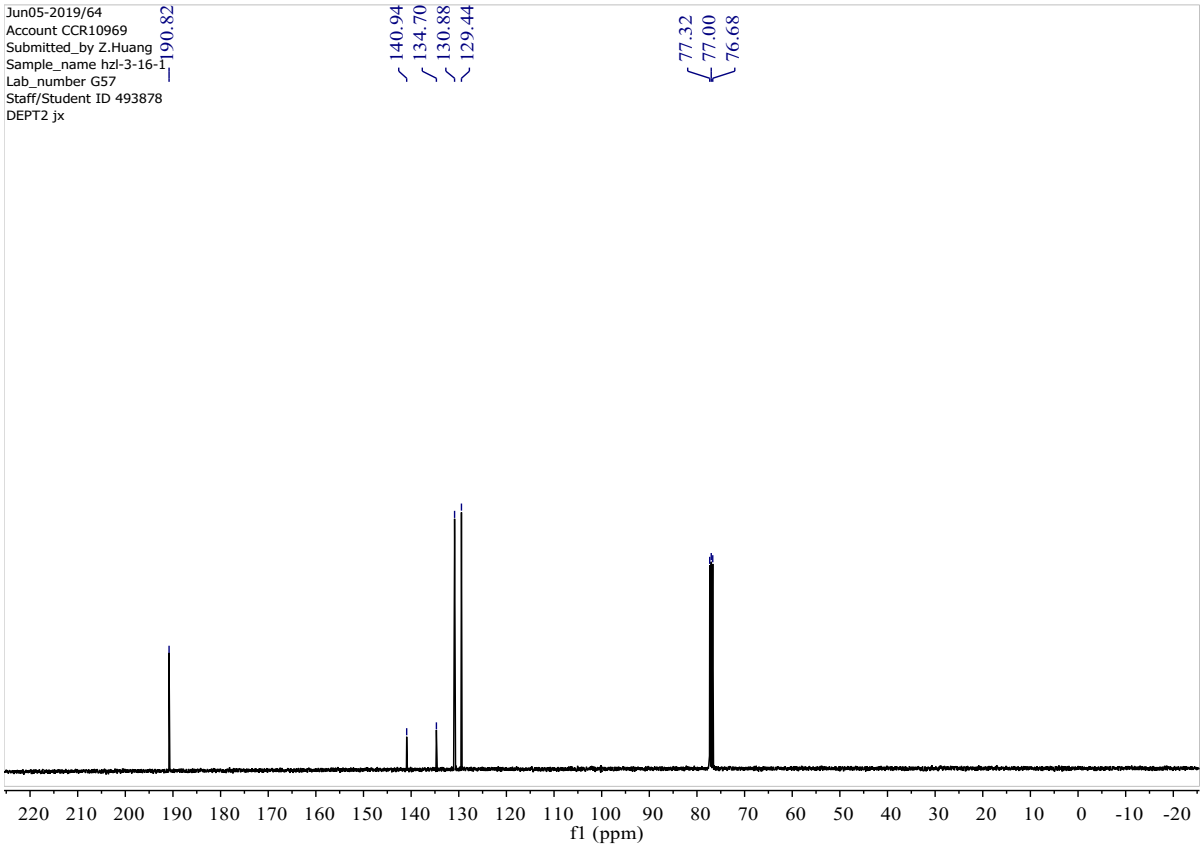
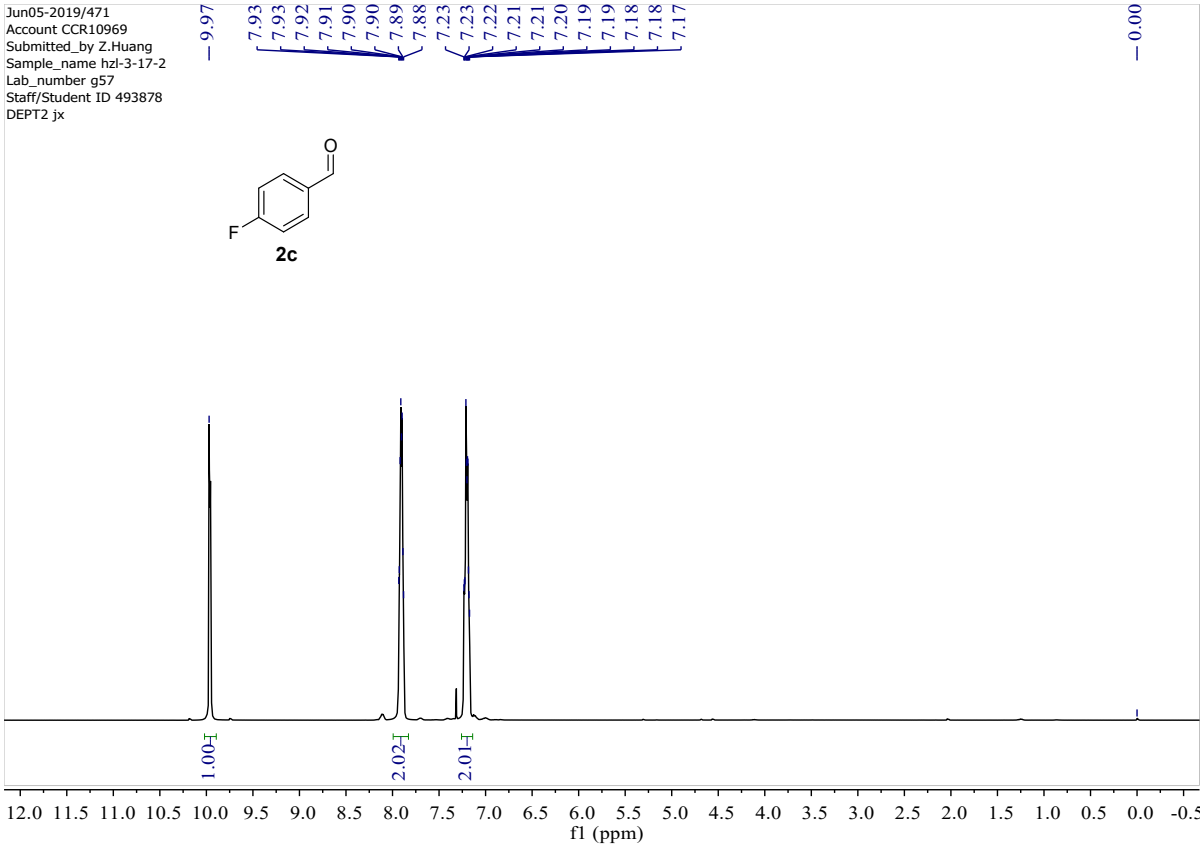
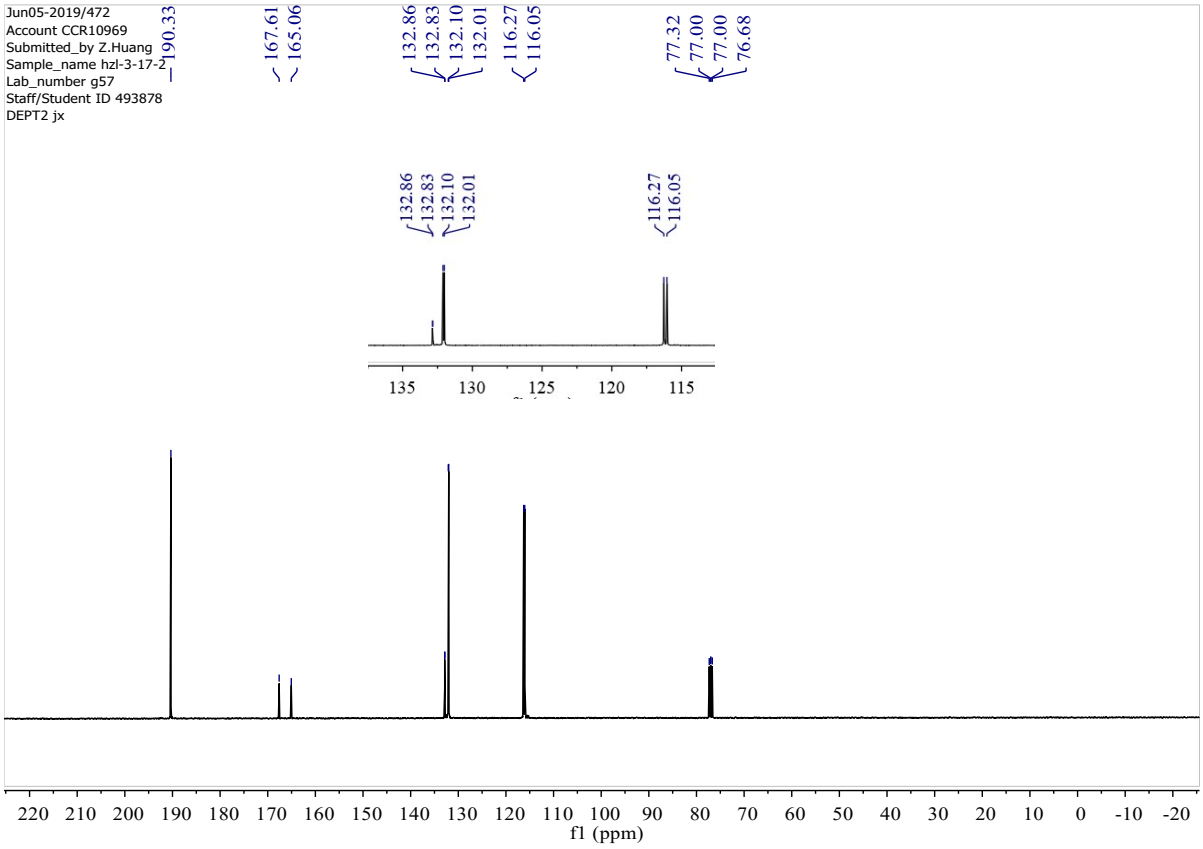


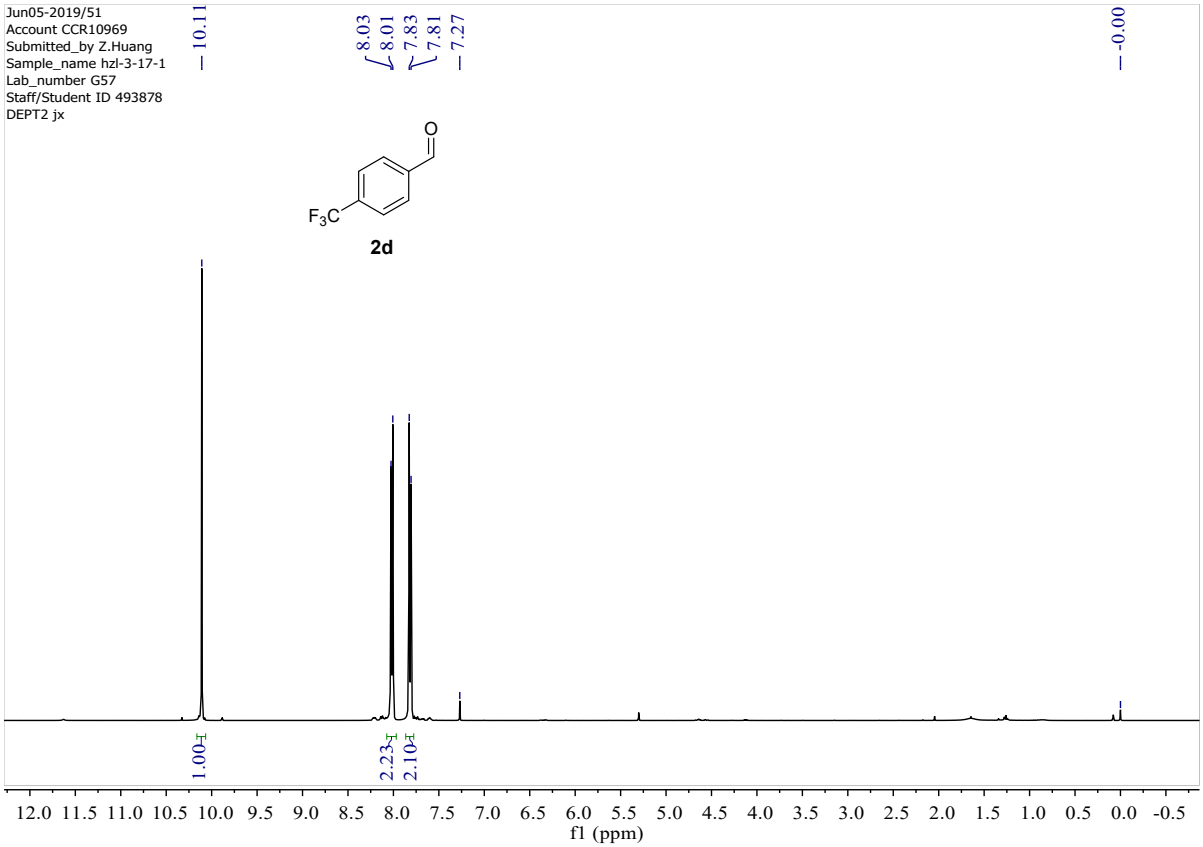
^{13}C NMR



^{1}H NMR



^{13}C NMR



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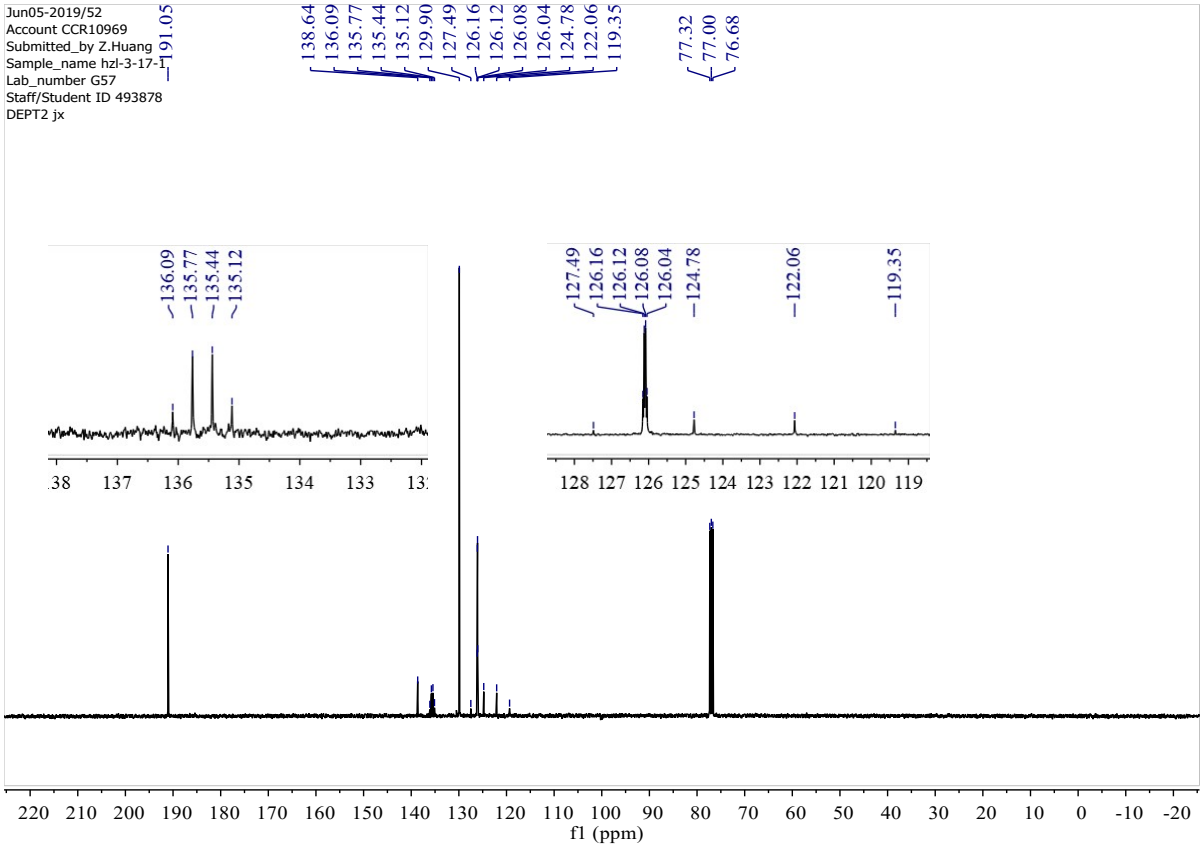
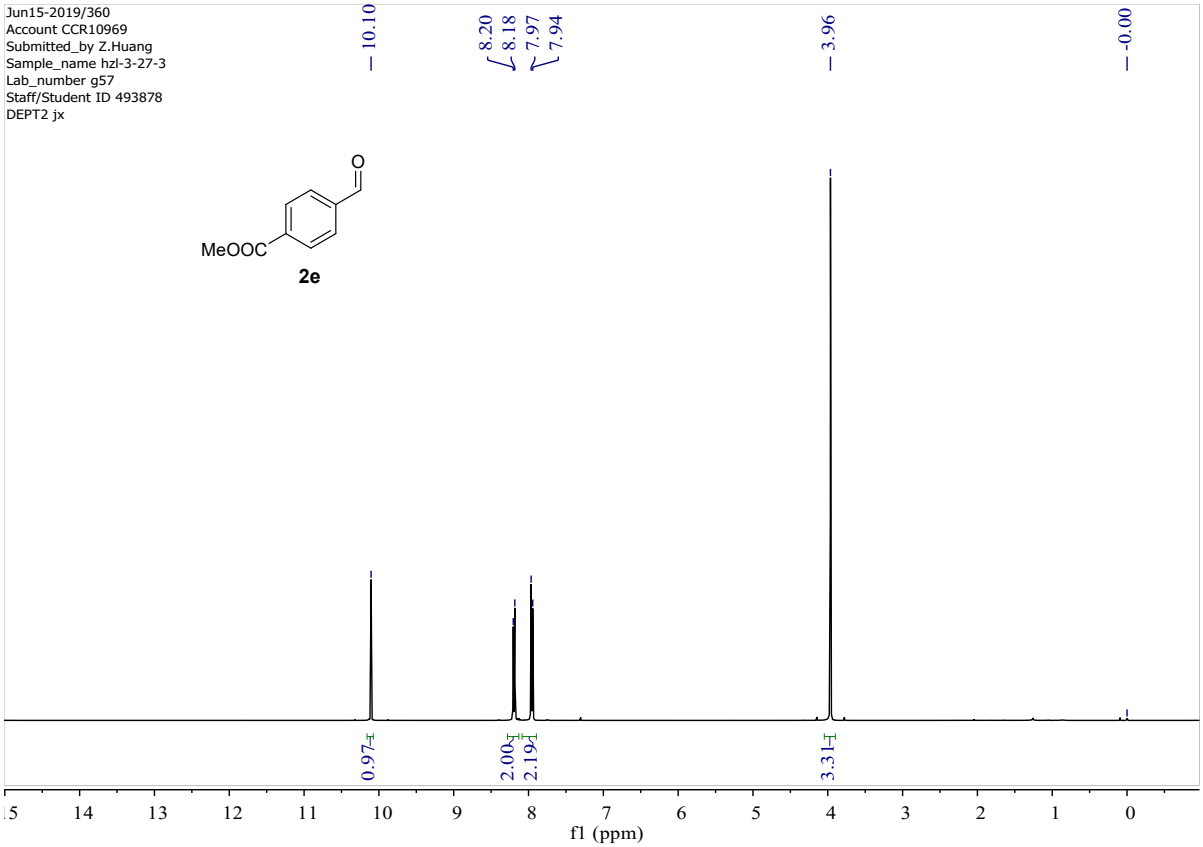
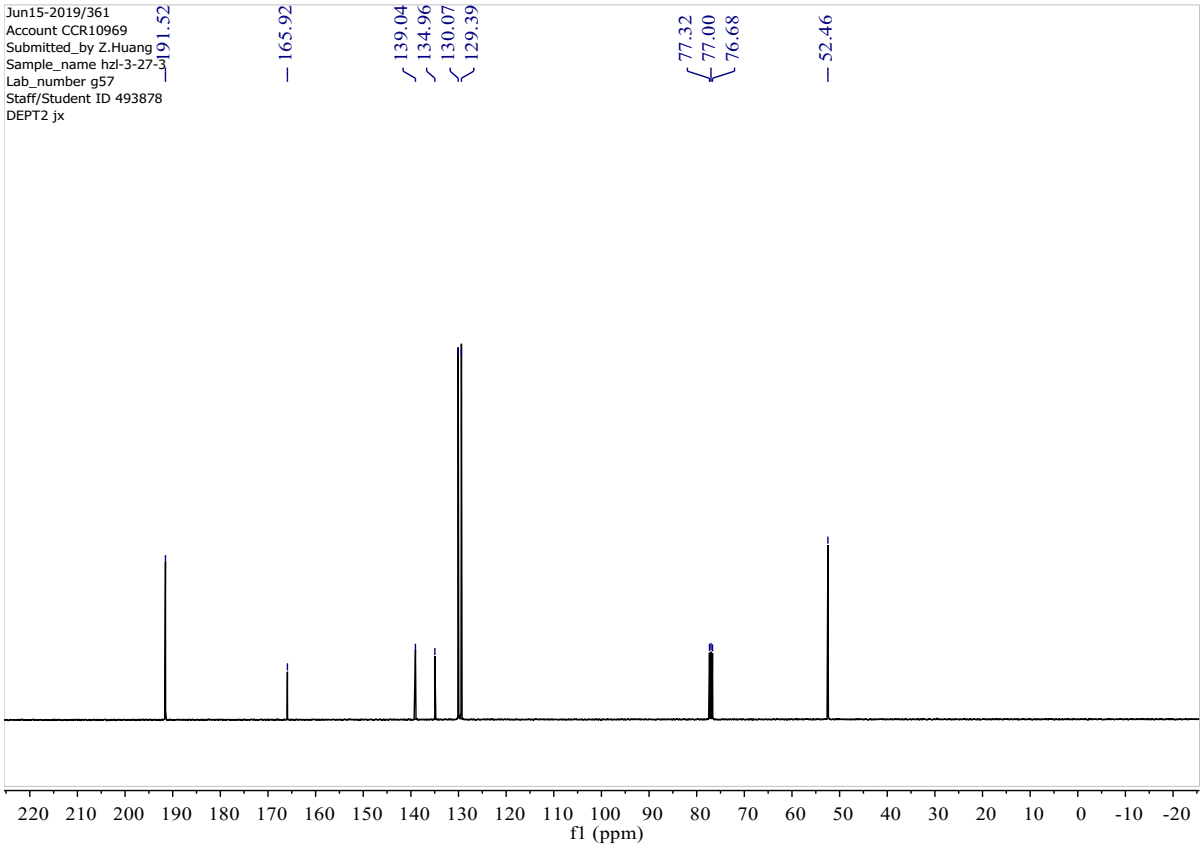


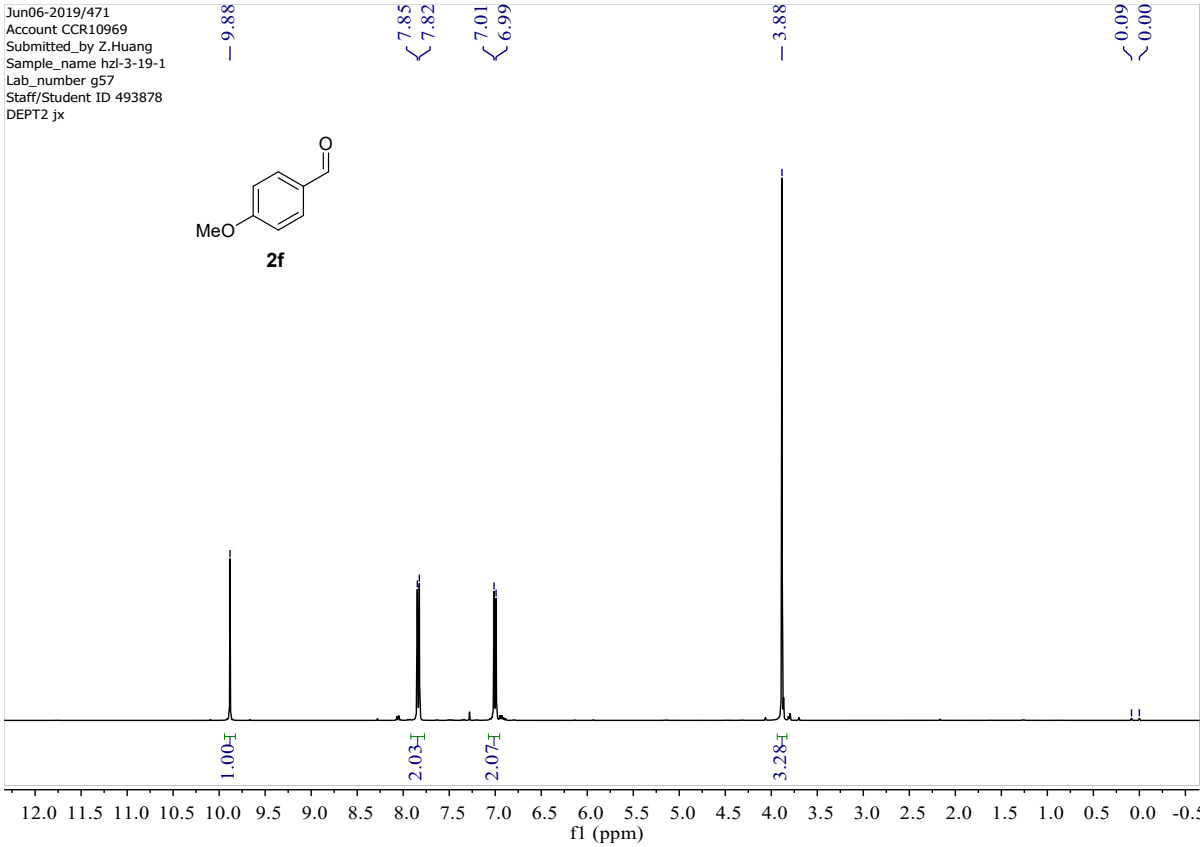
^{13}C NMR



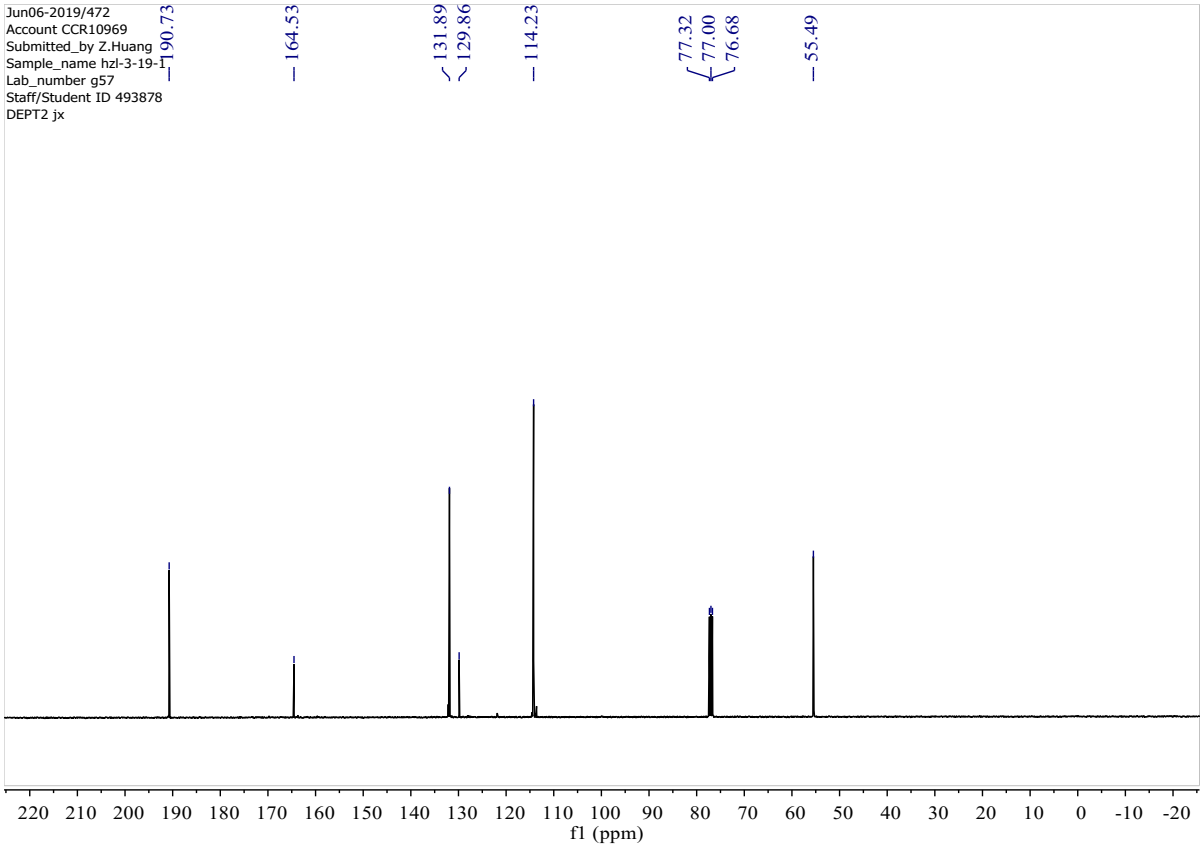
^{1}H NMR



^{13}C NMR



^{1}H NMR



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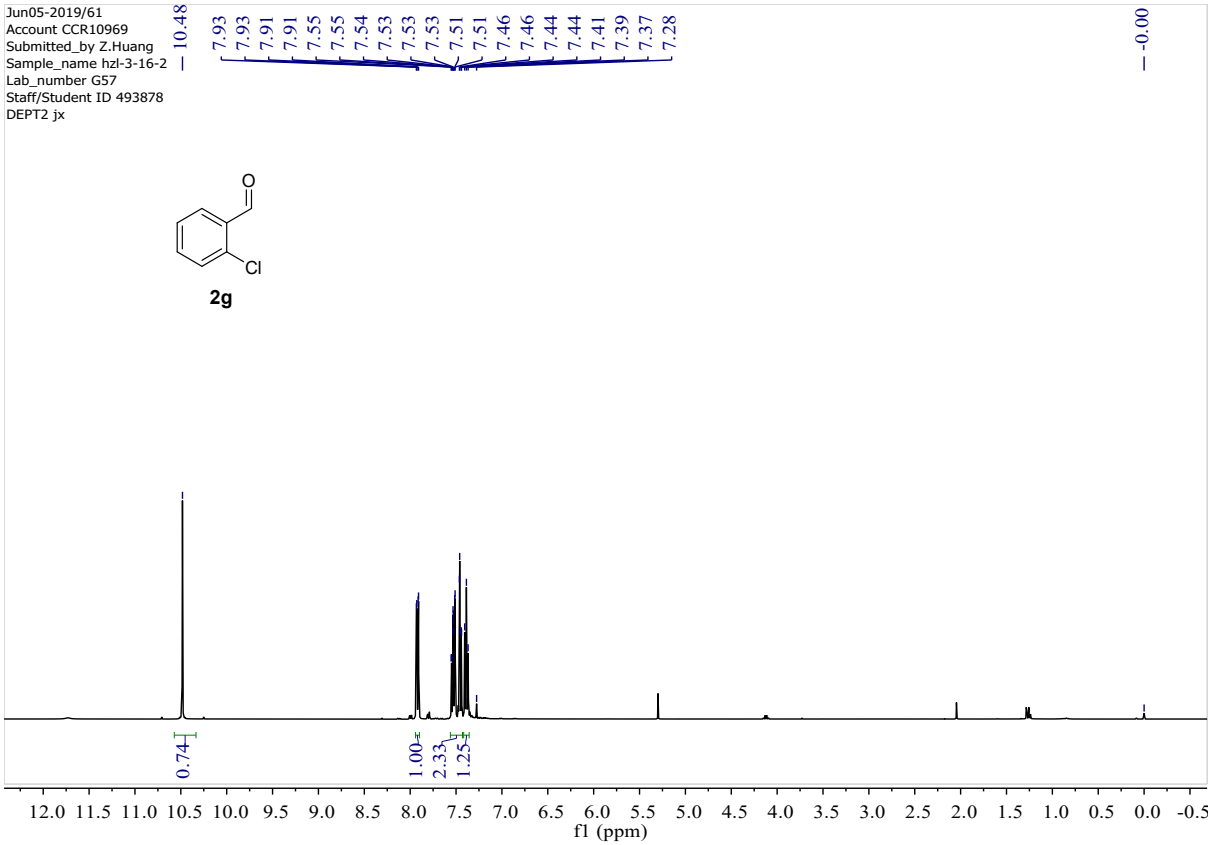

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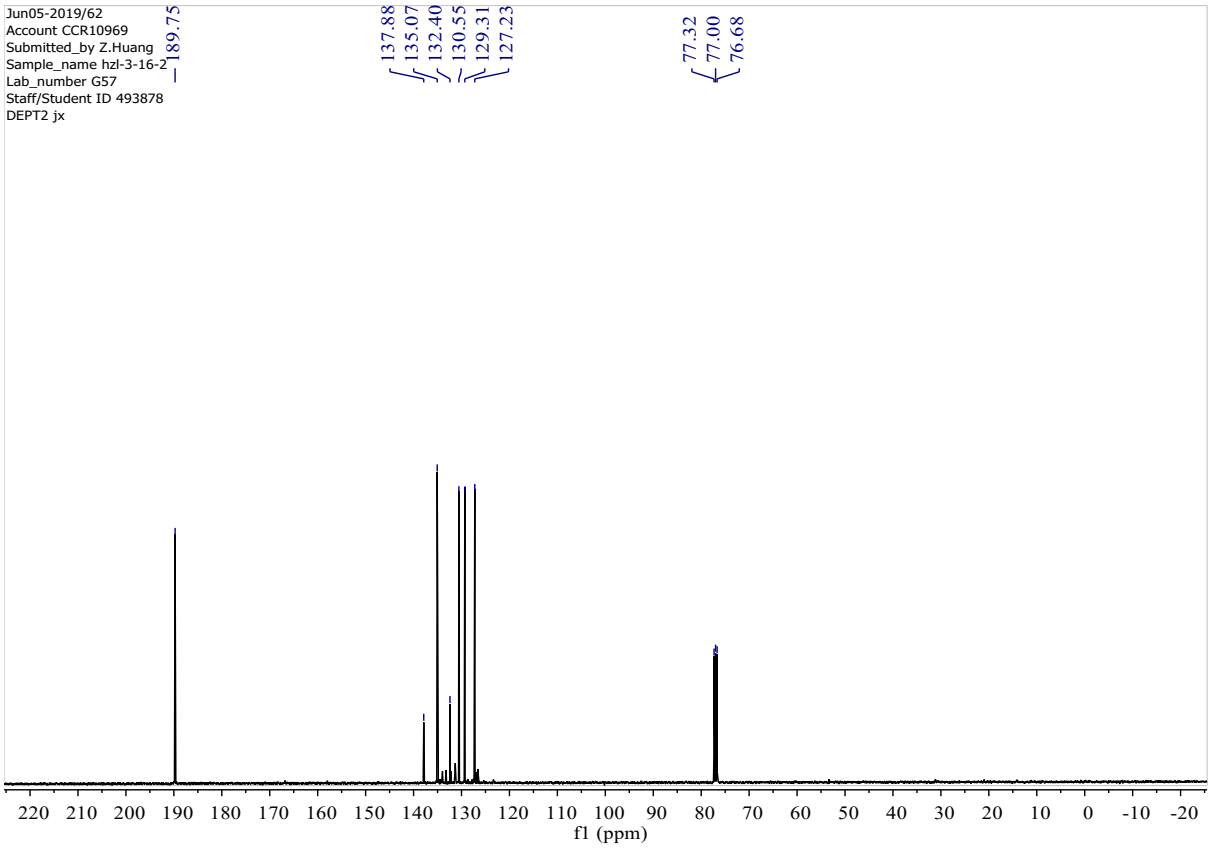

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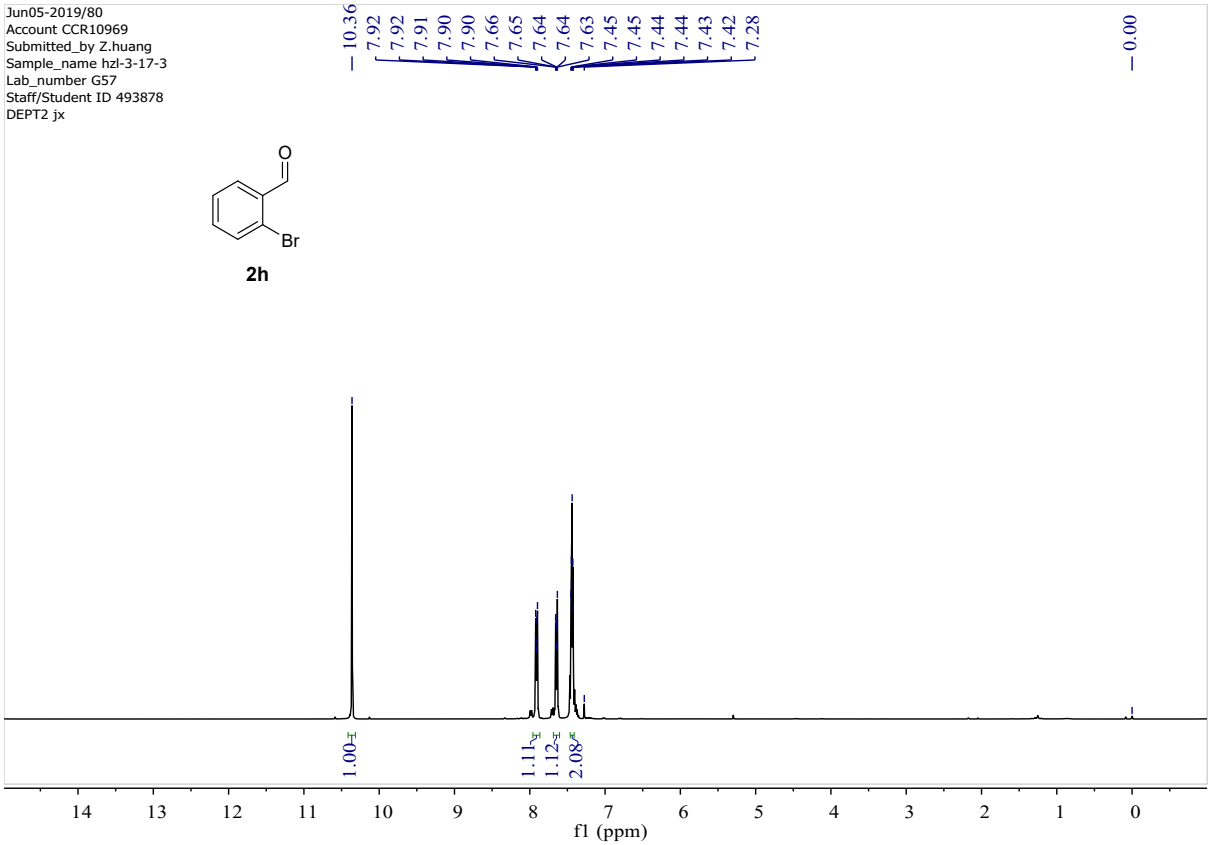

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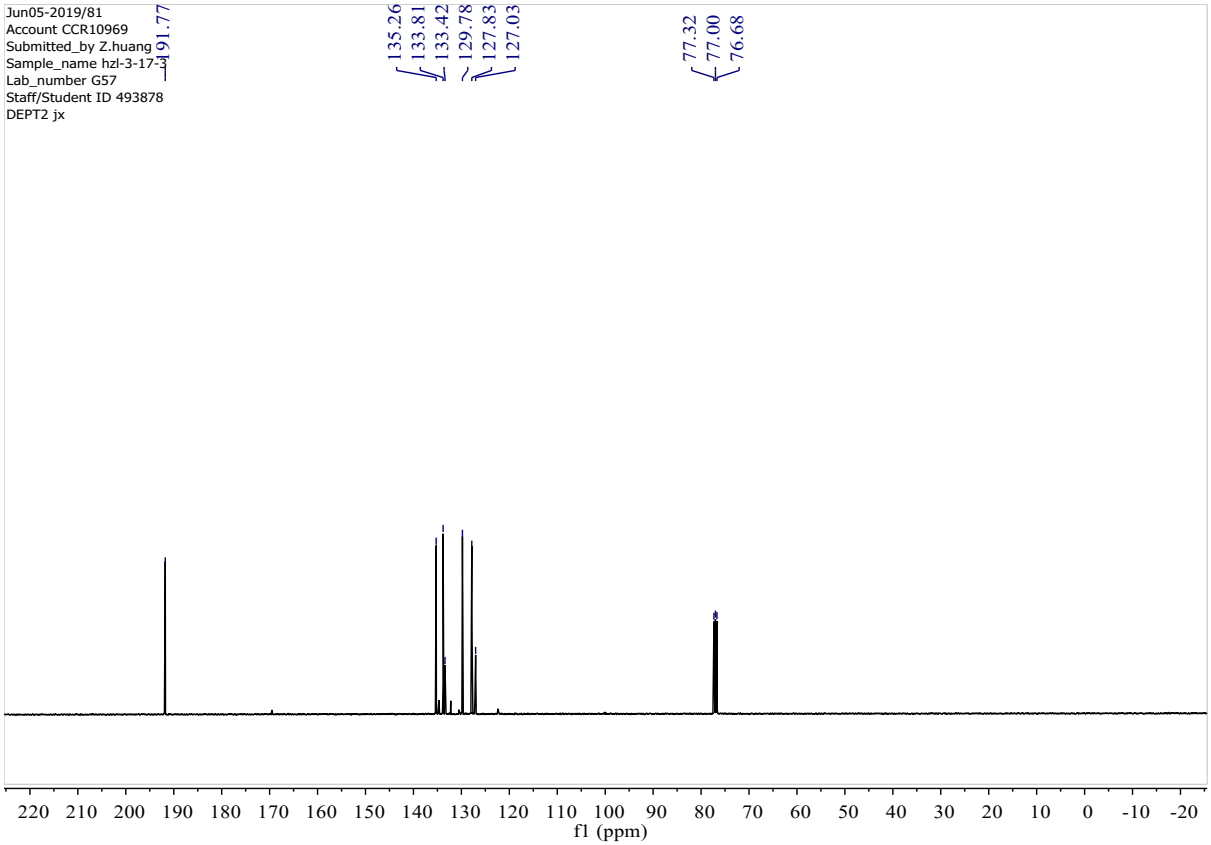

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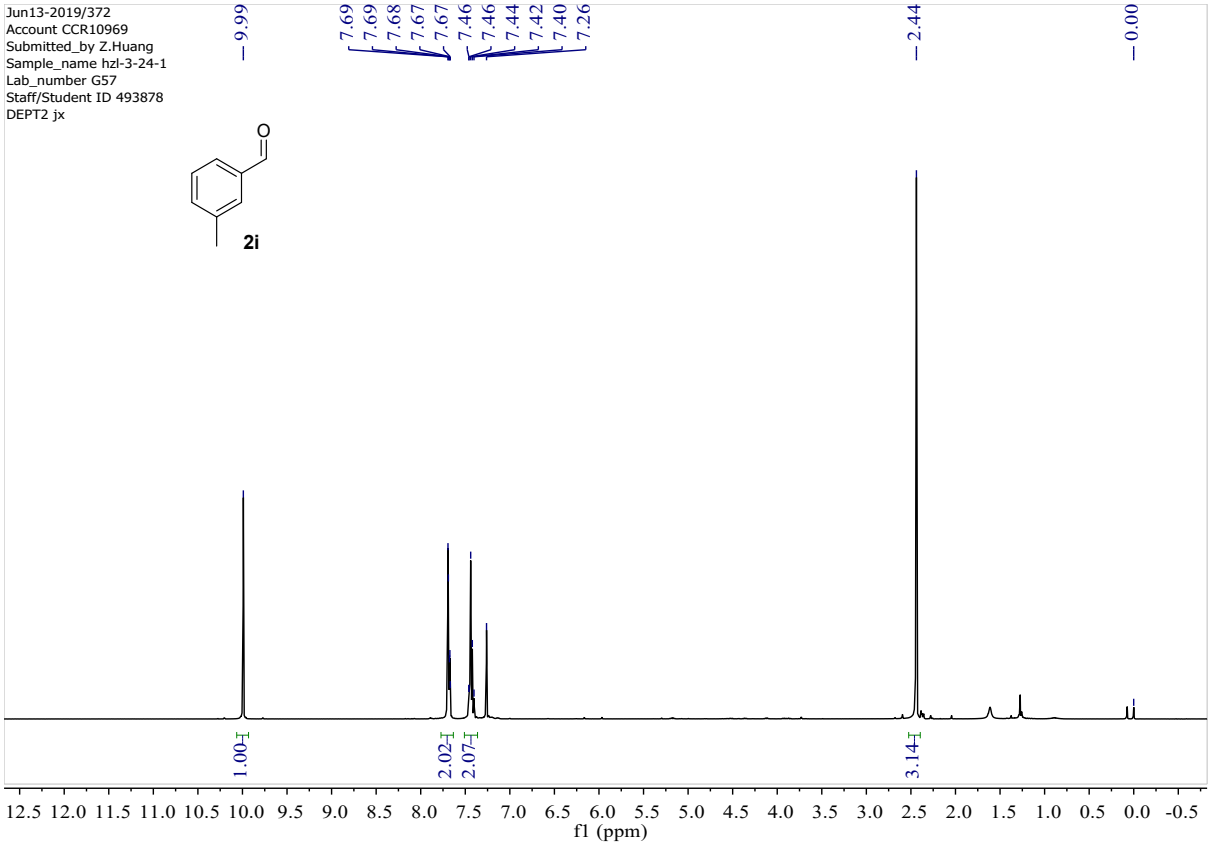

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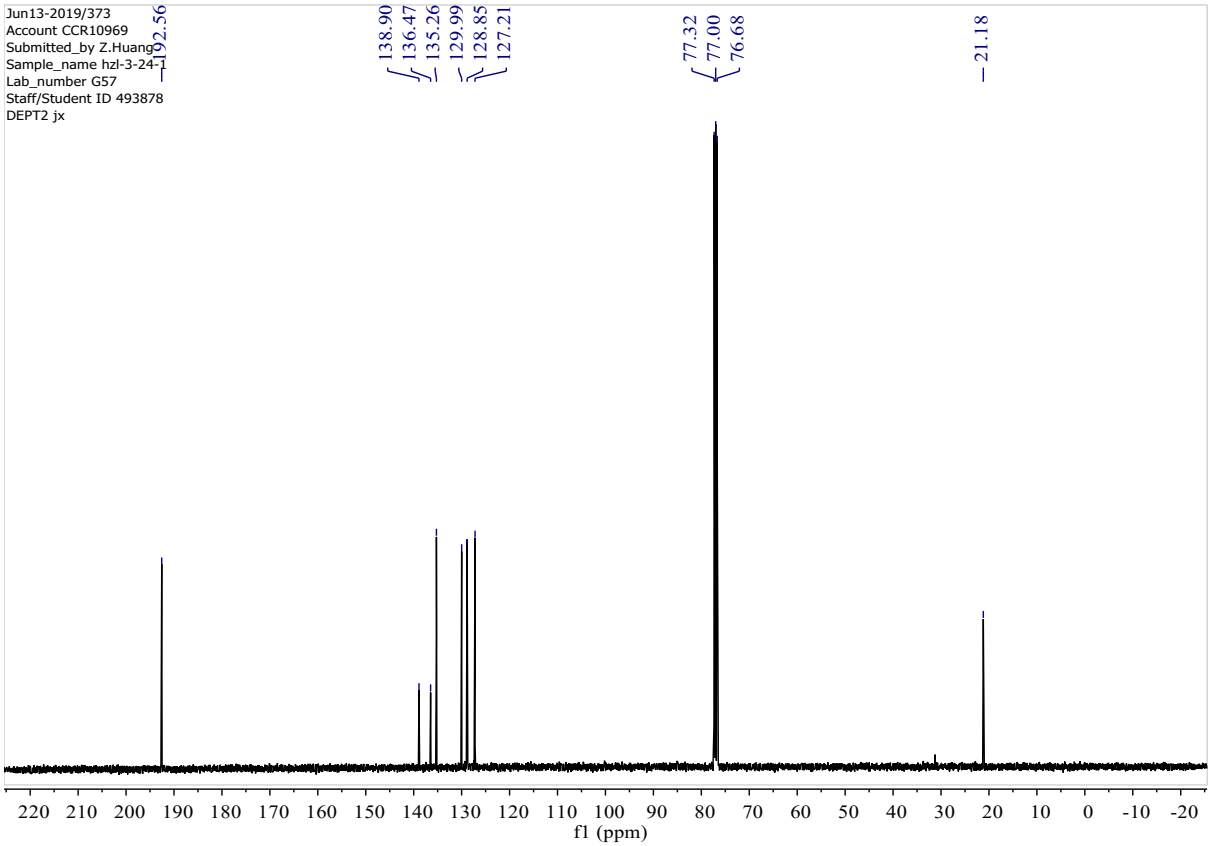

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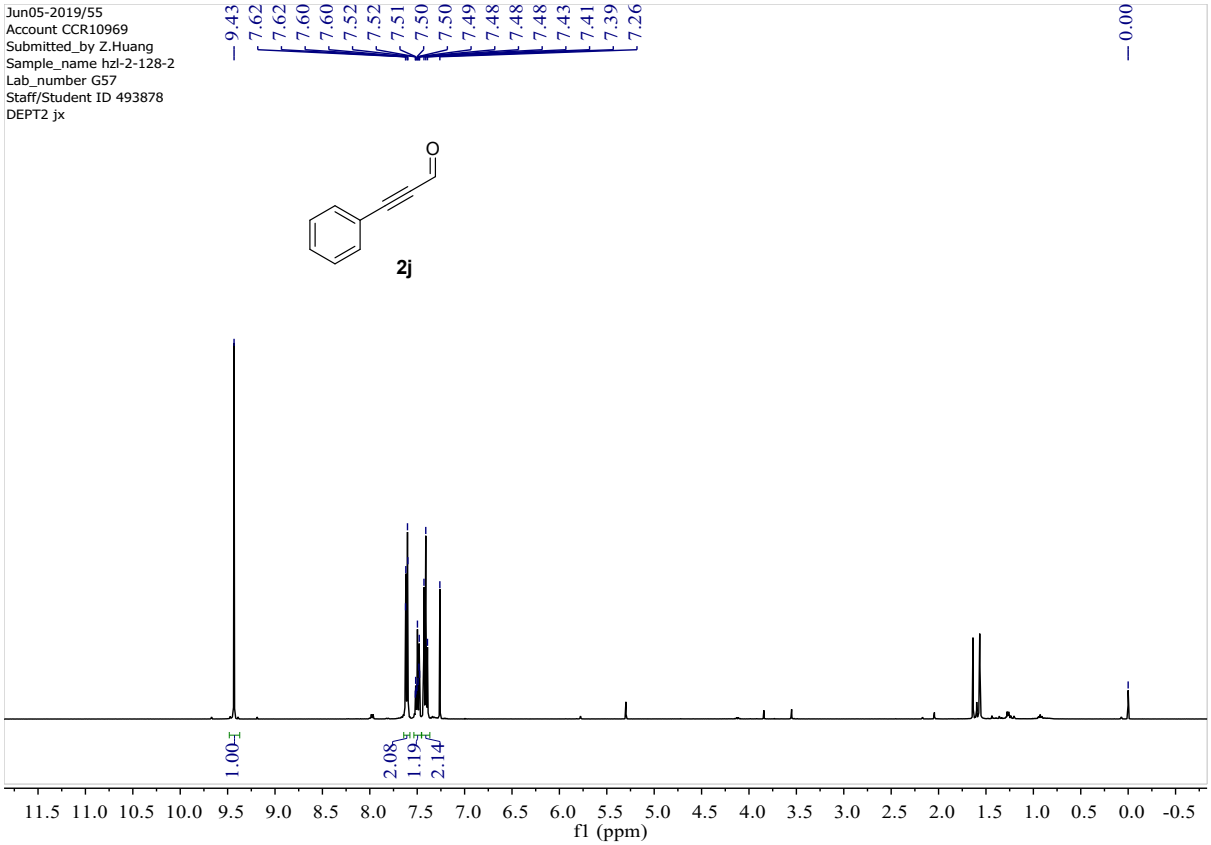

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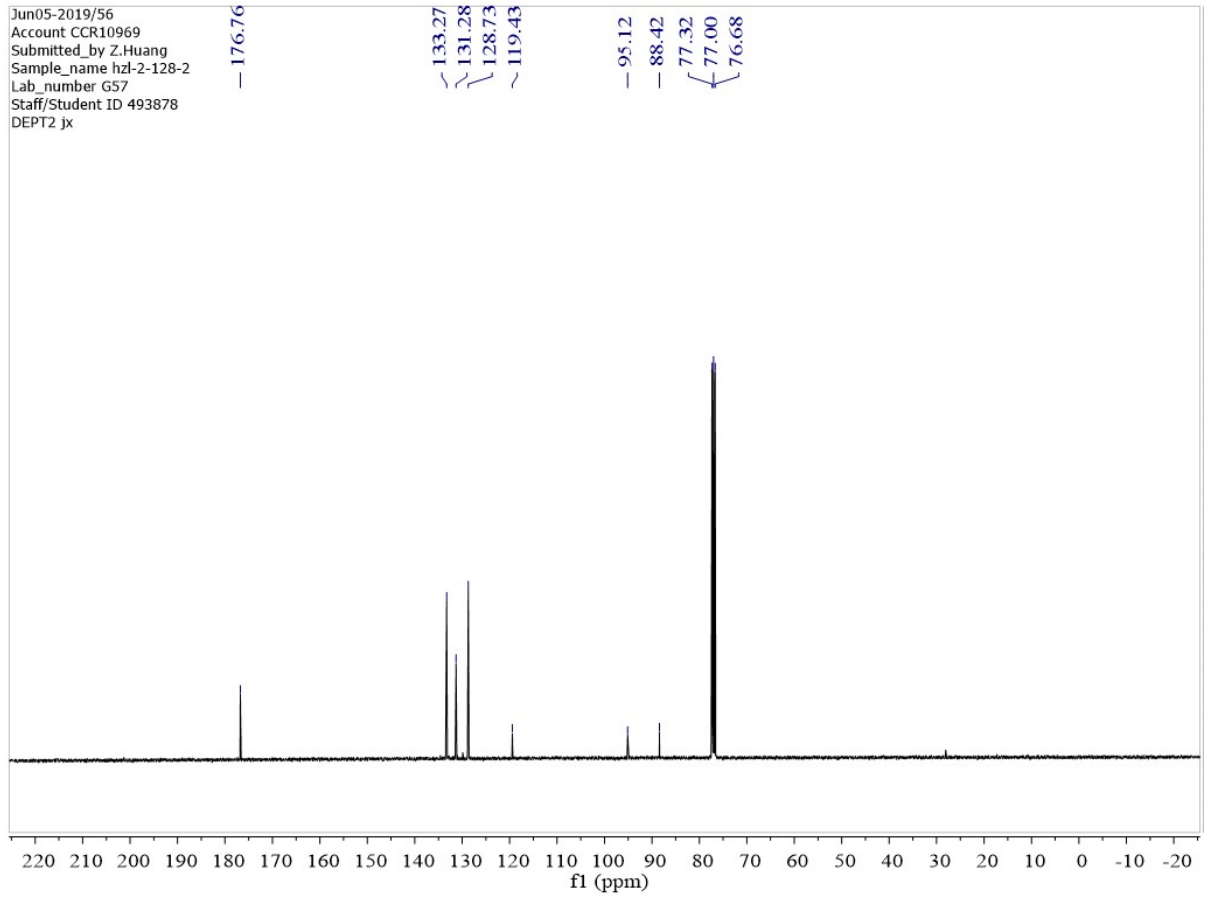

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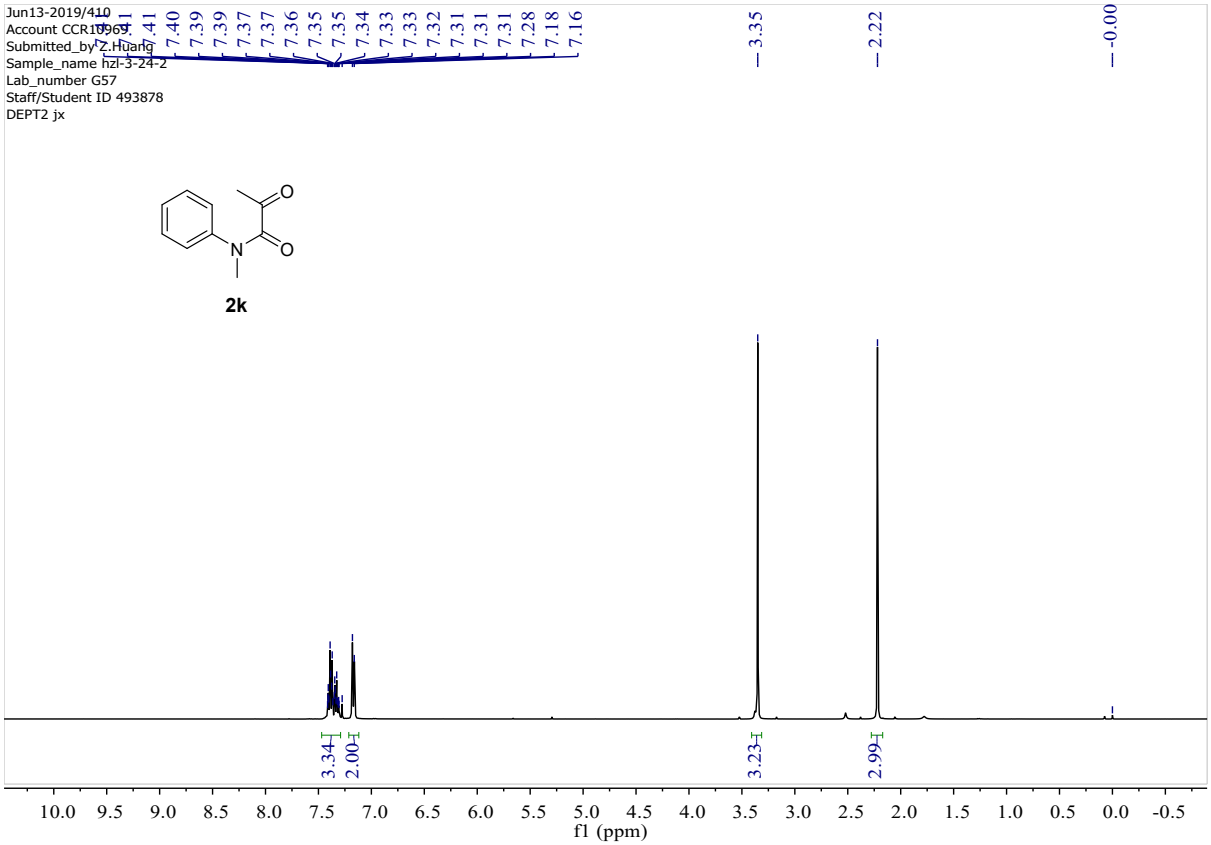

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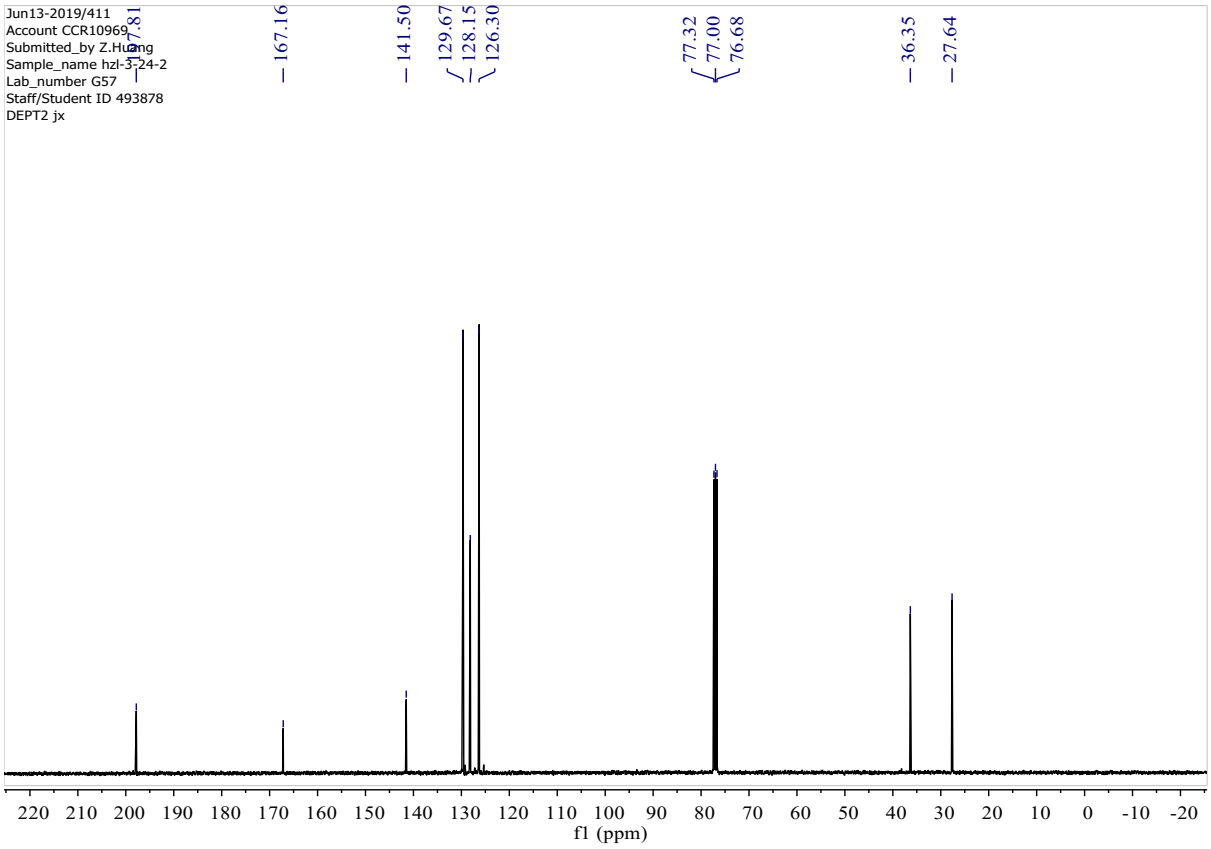

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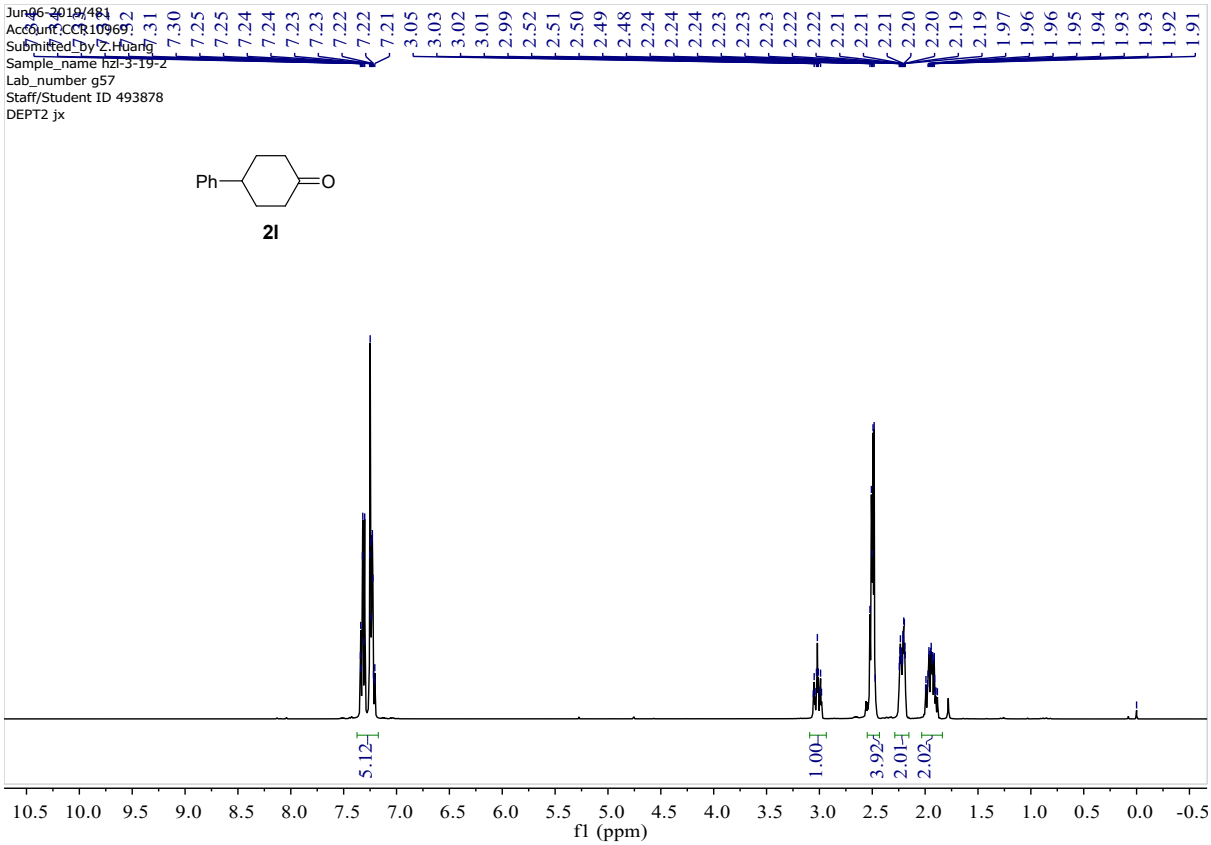

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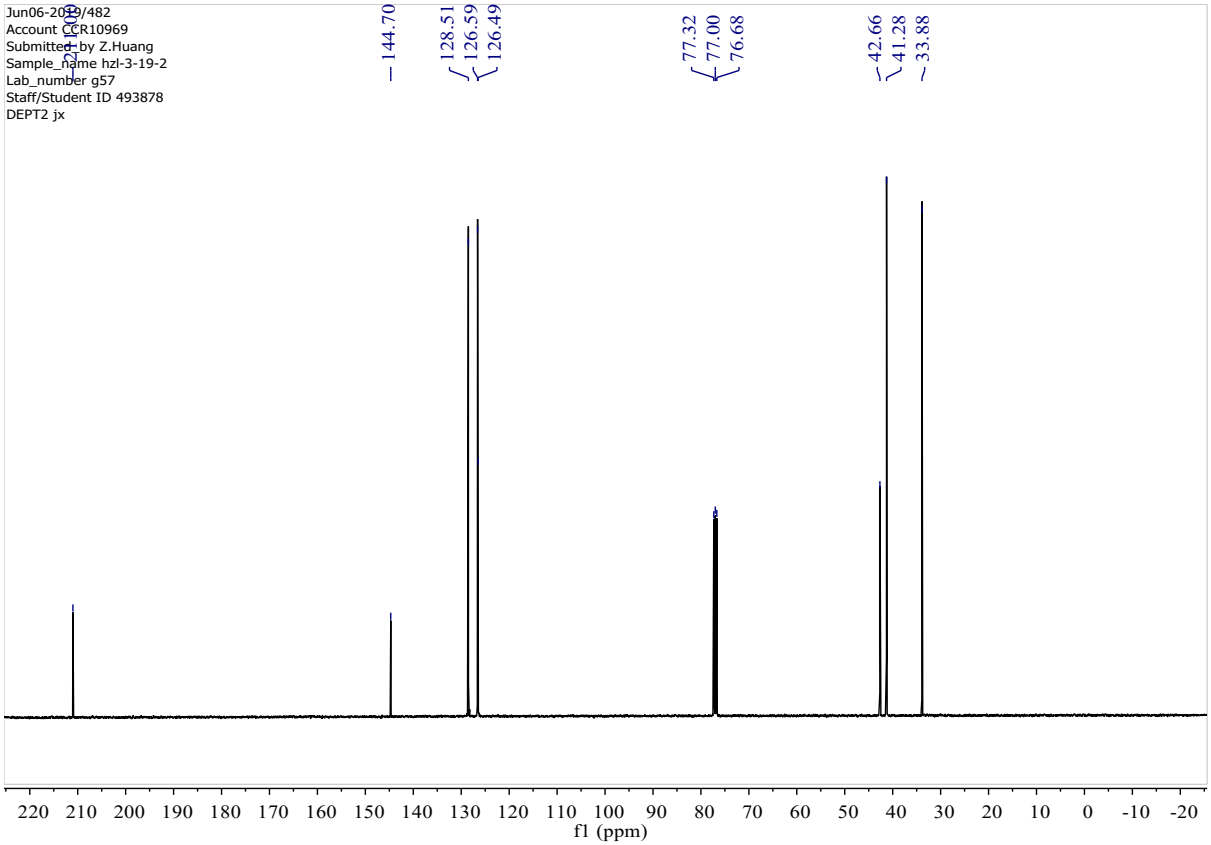

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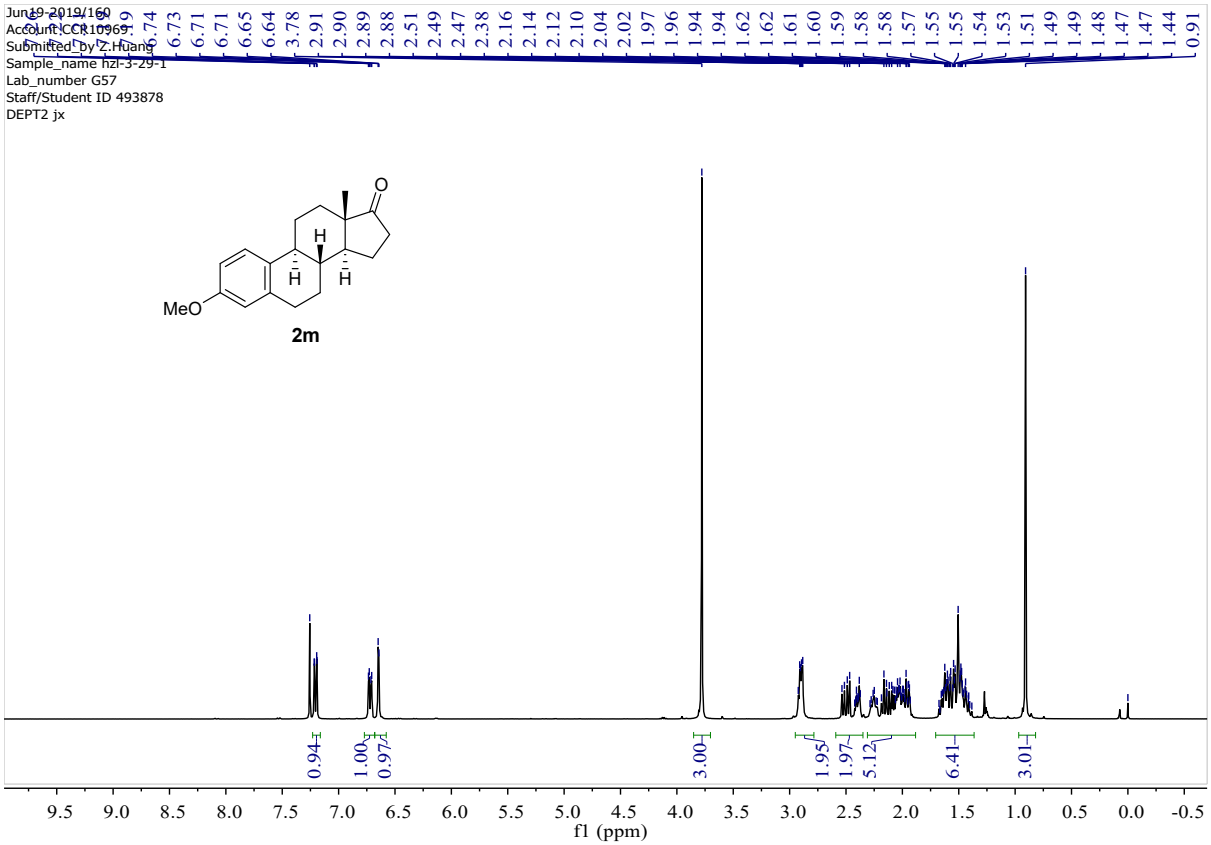

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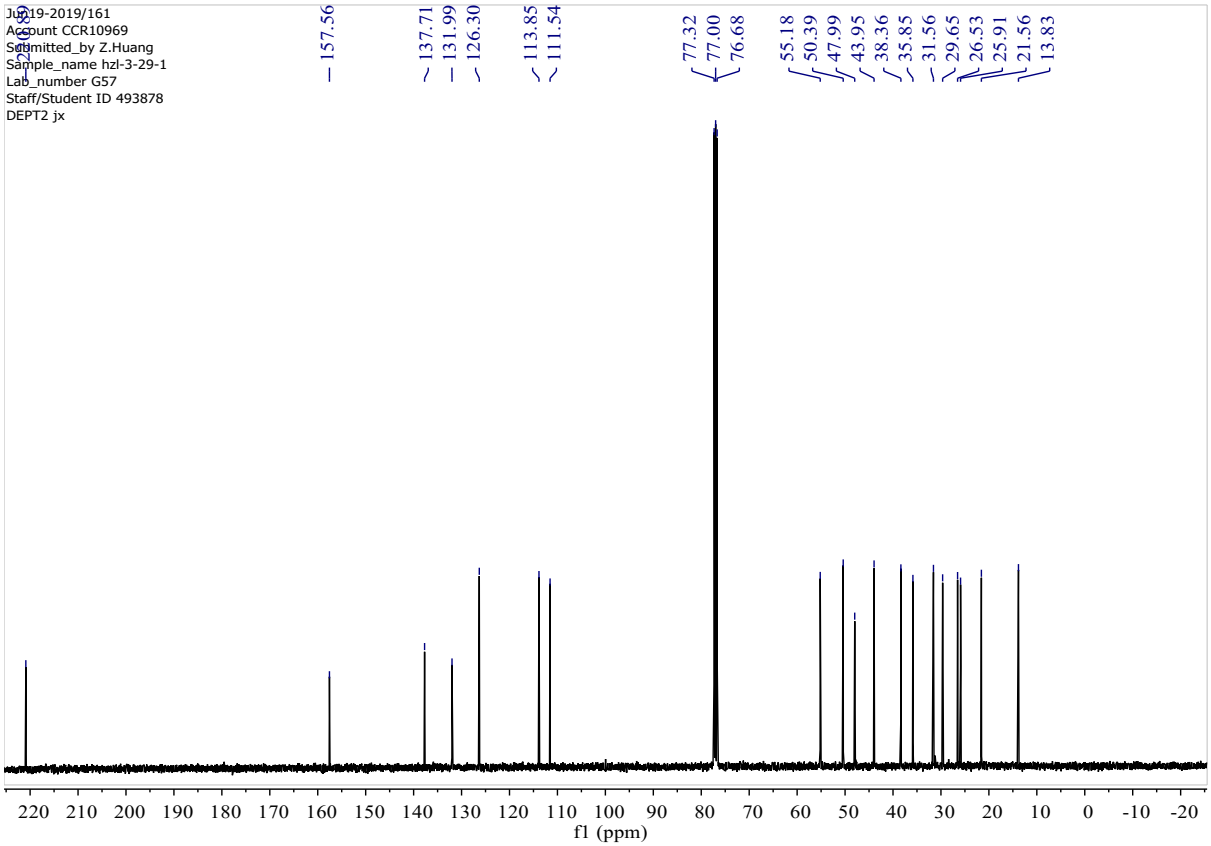

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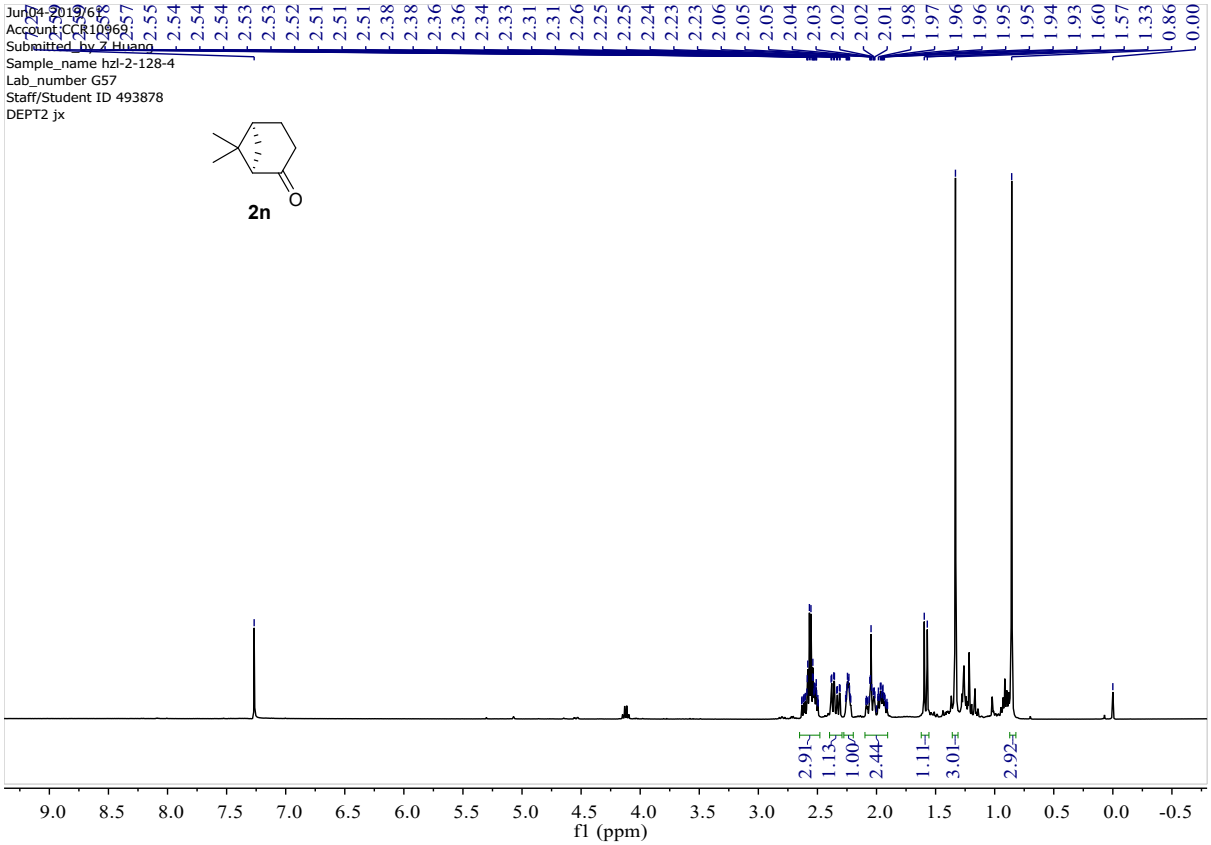

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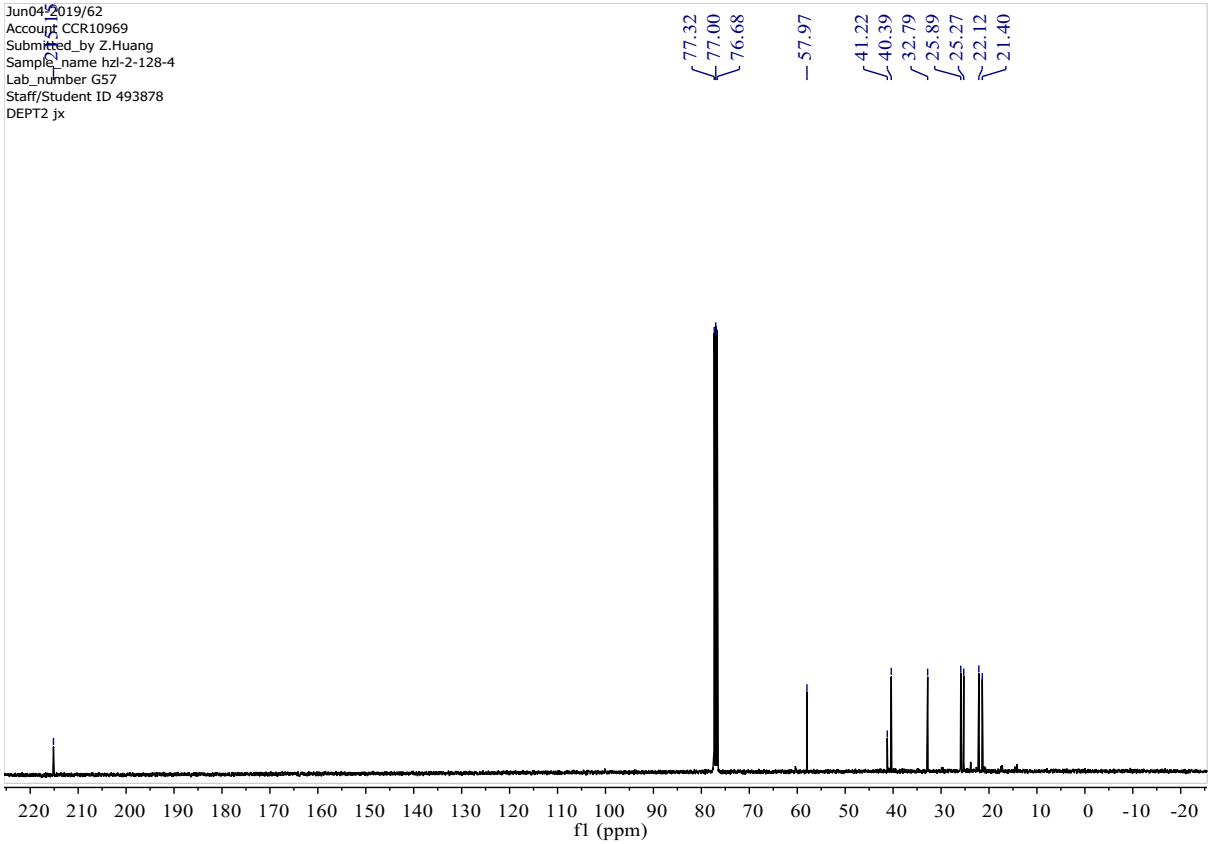

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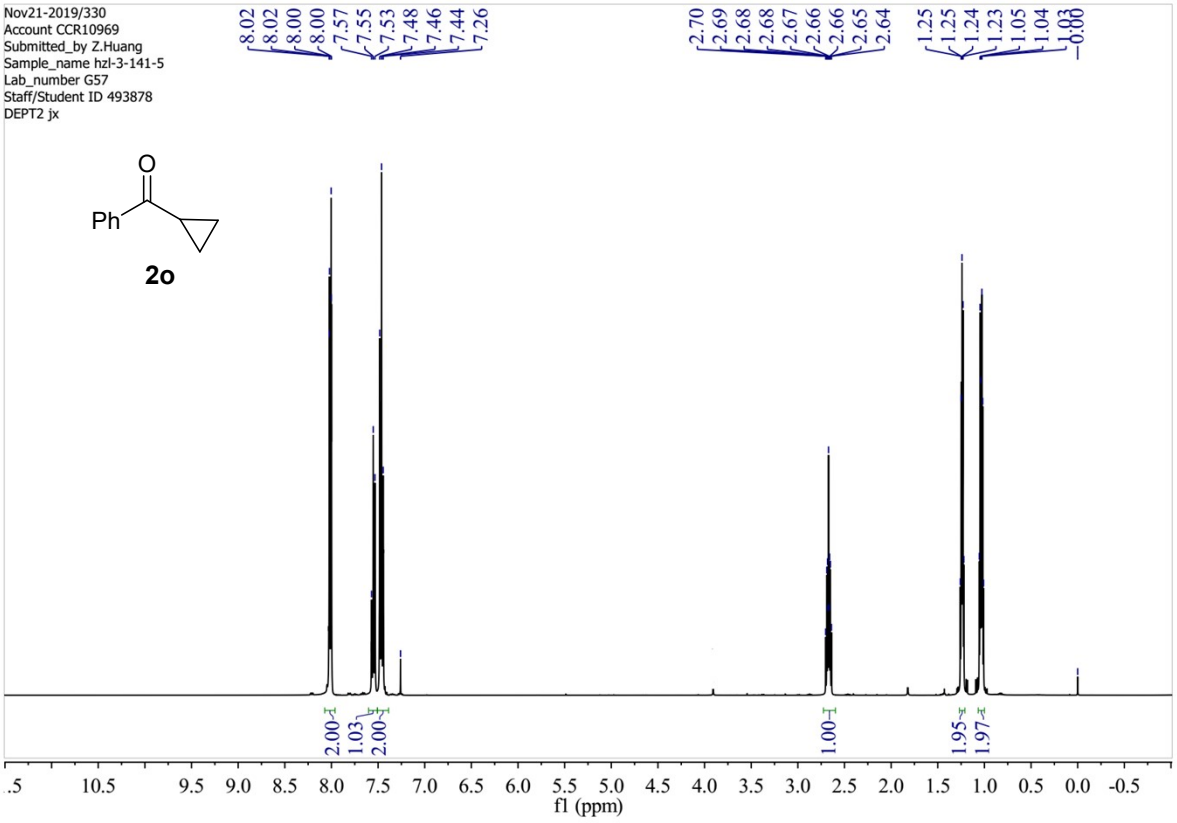

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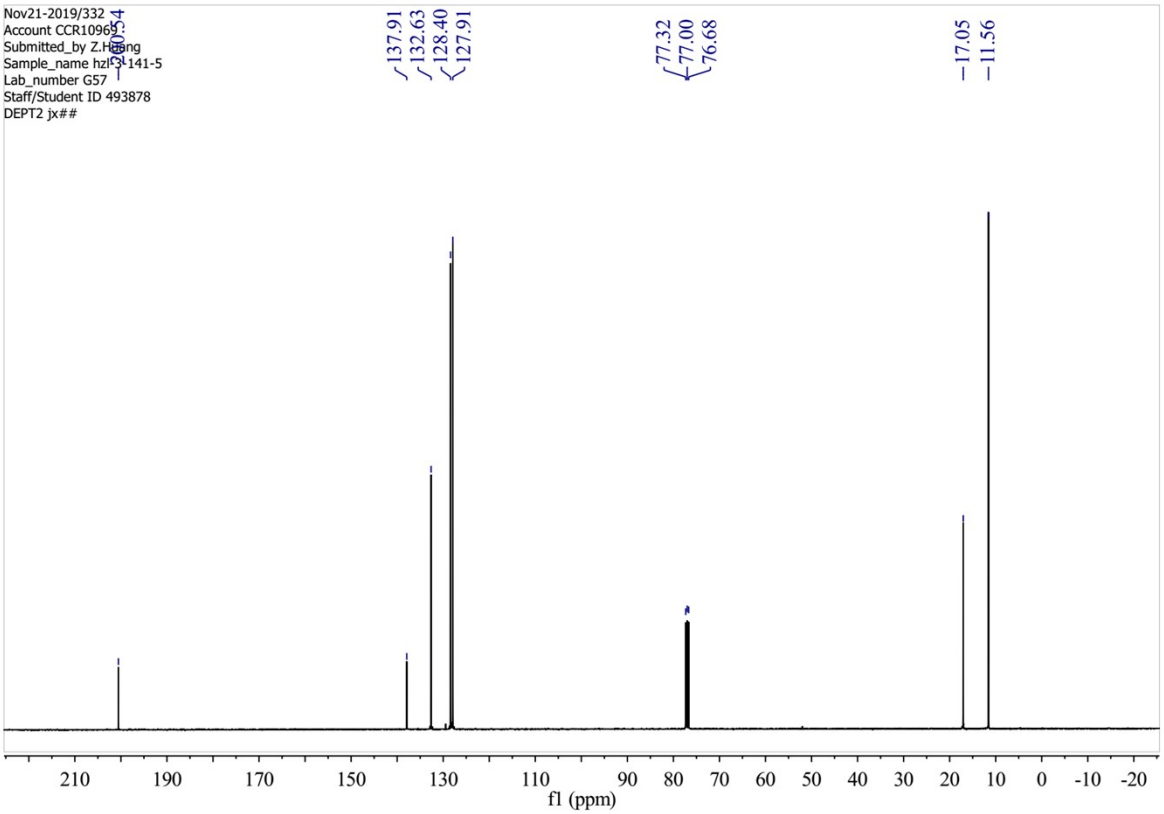

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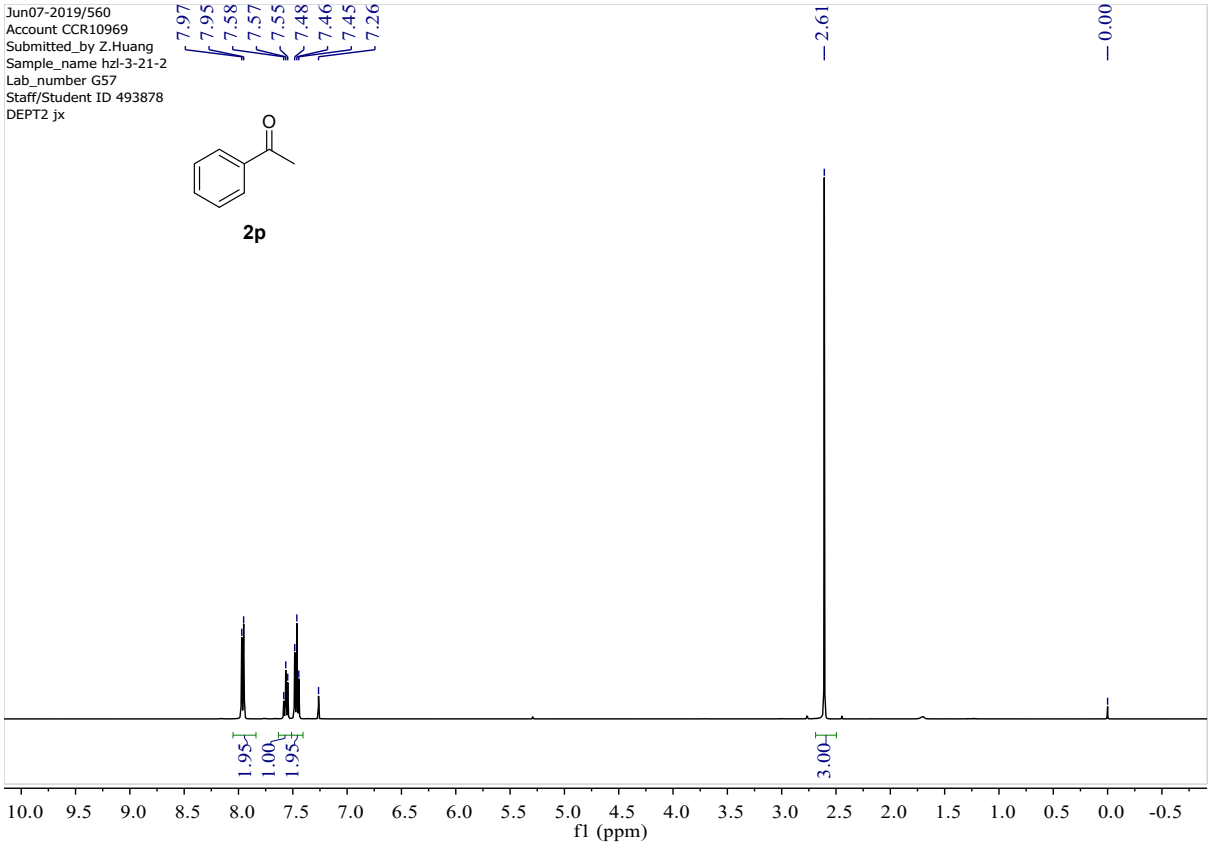

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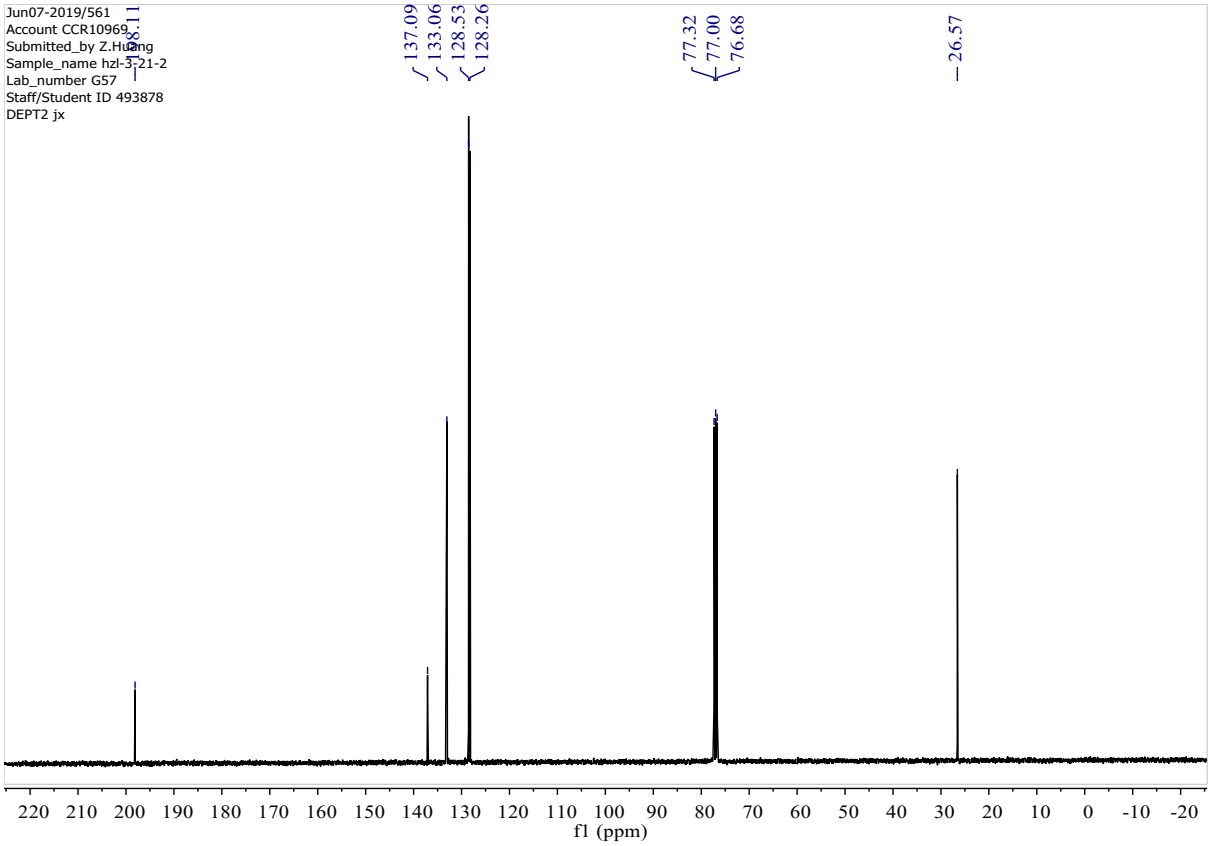

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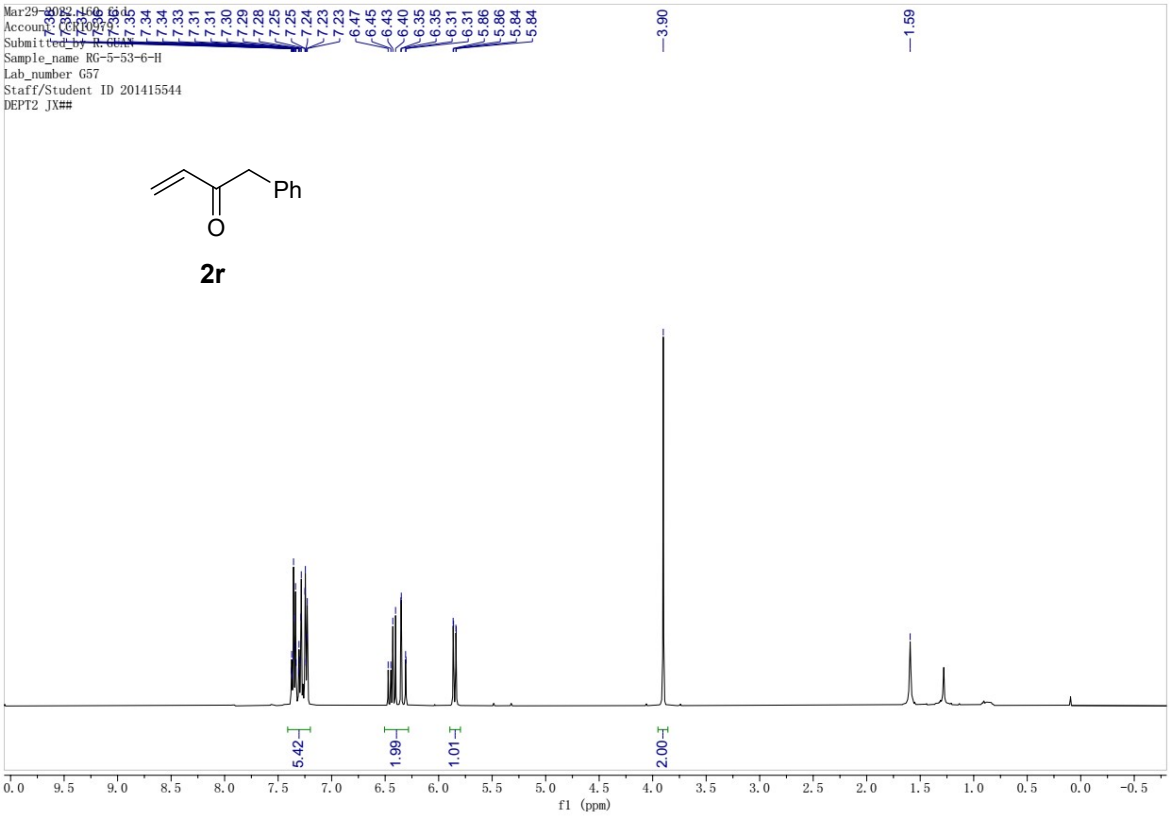

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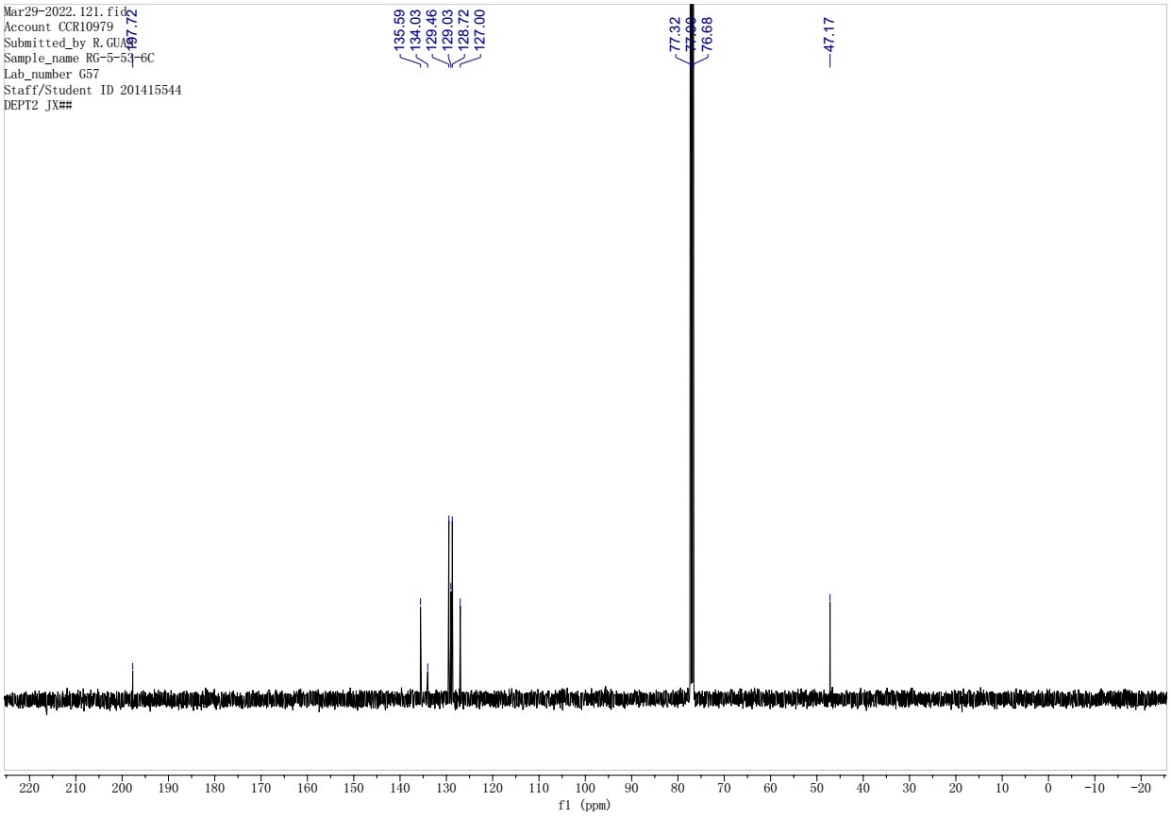

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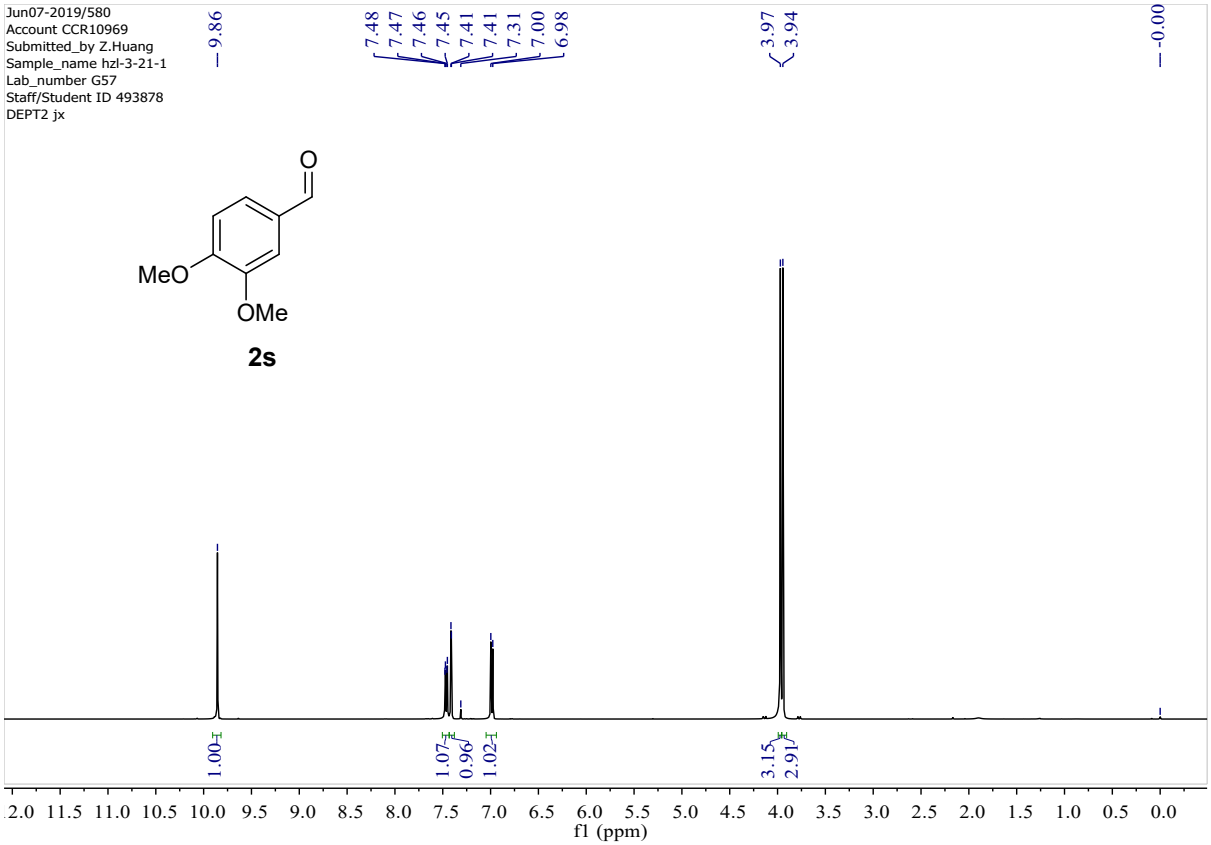

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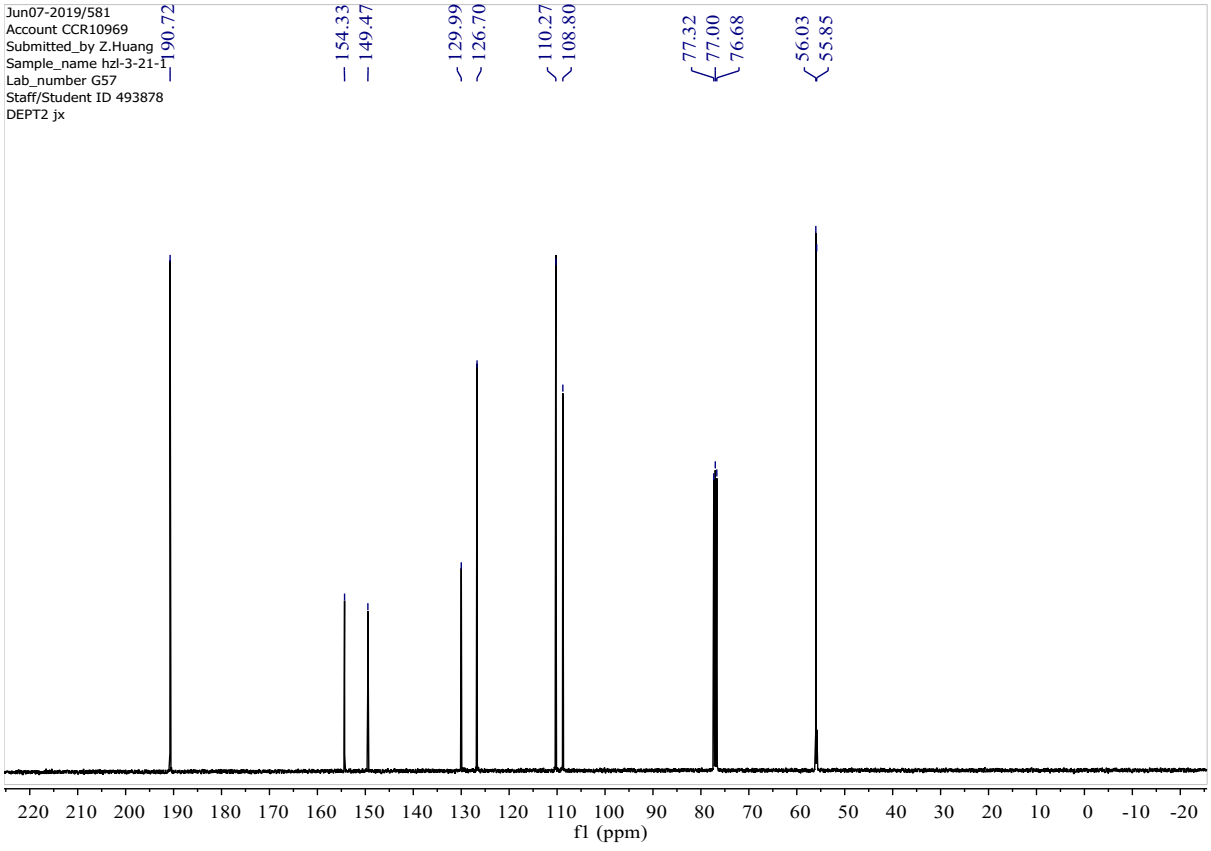

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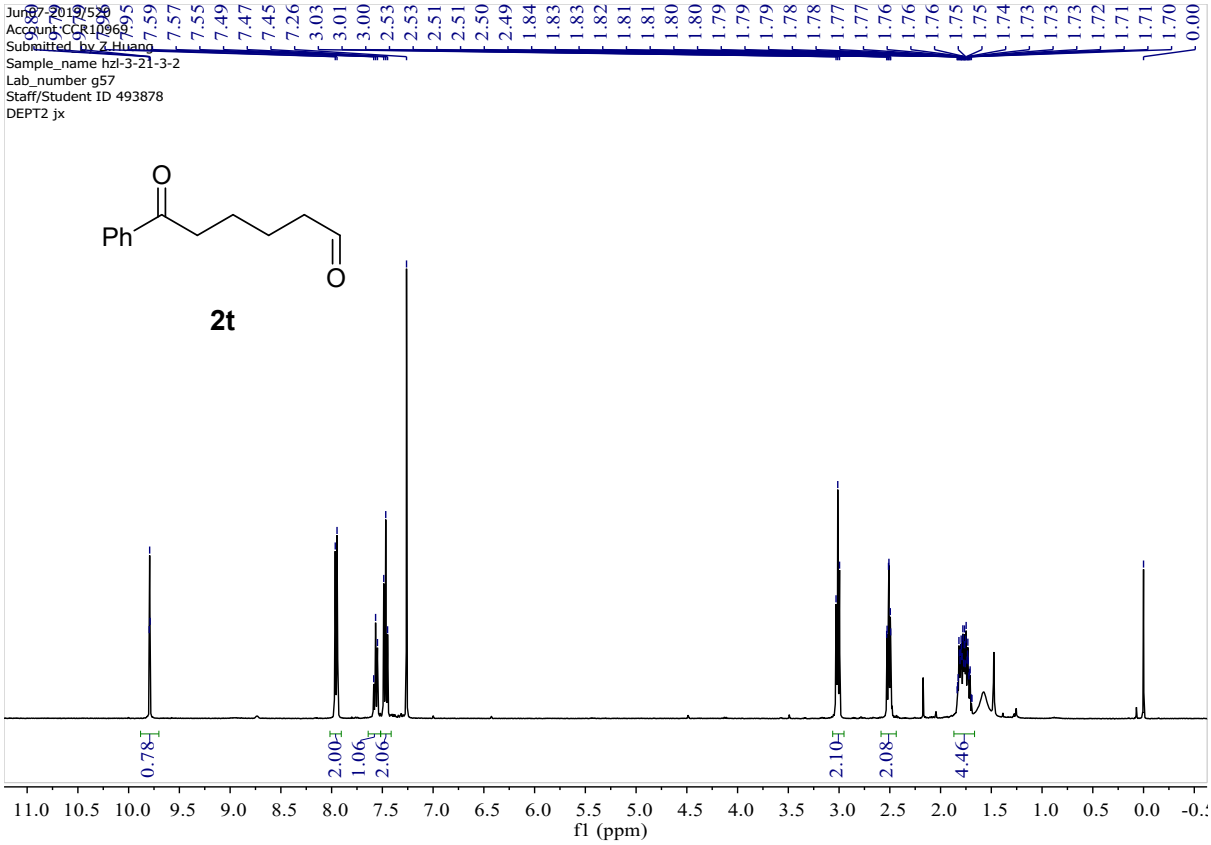

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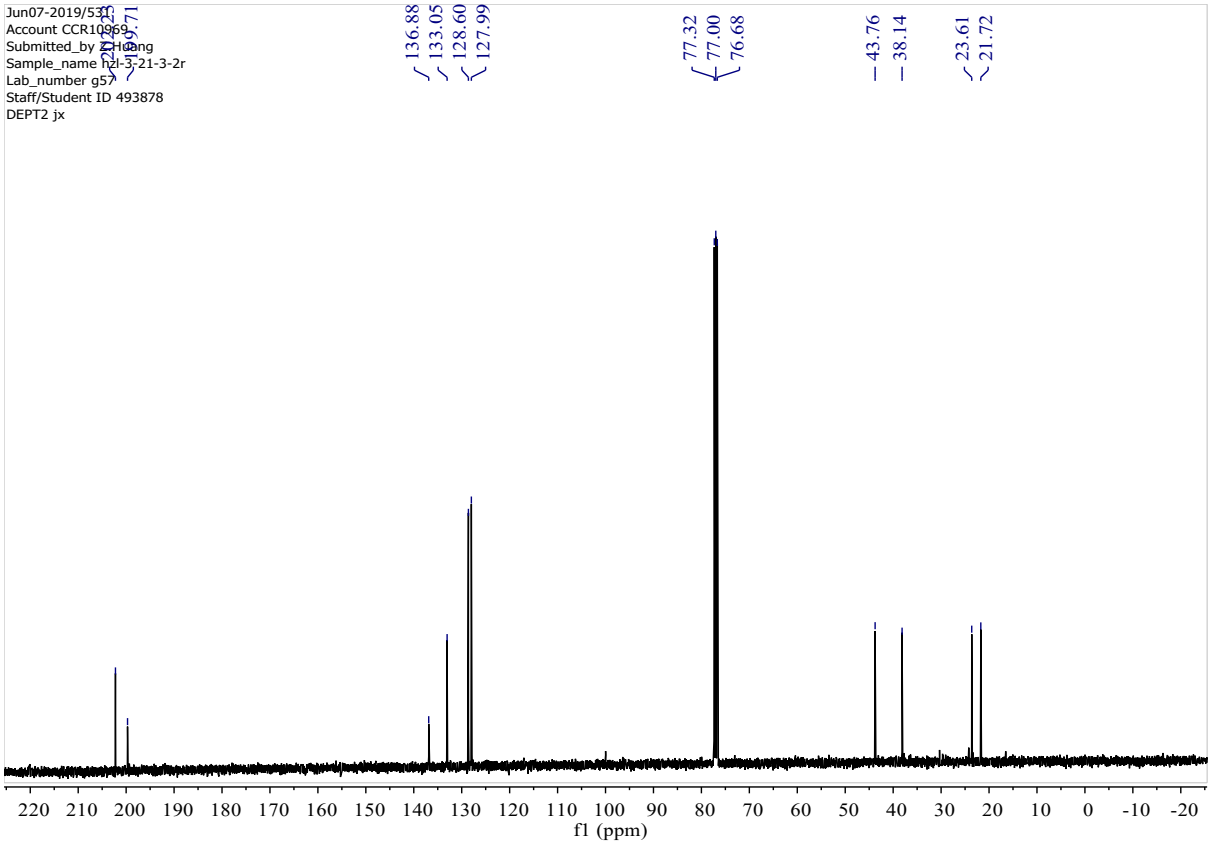

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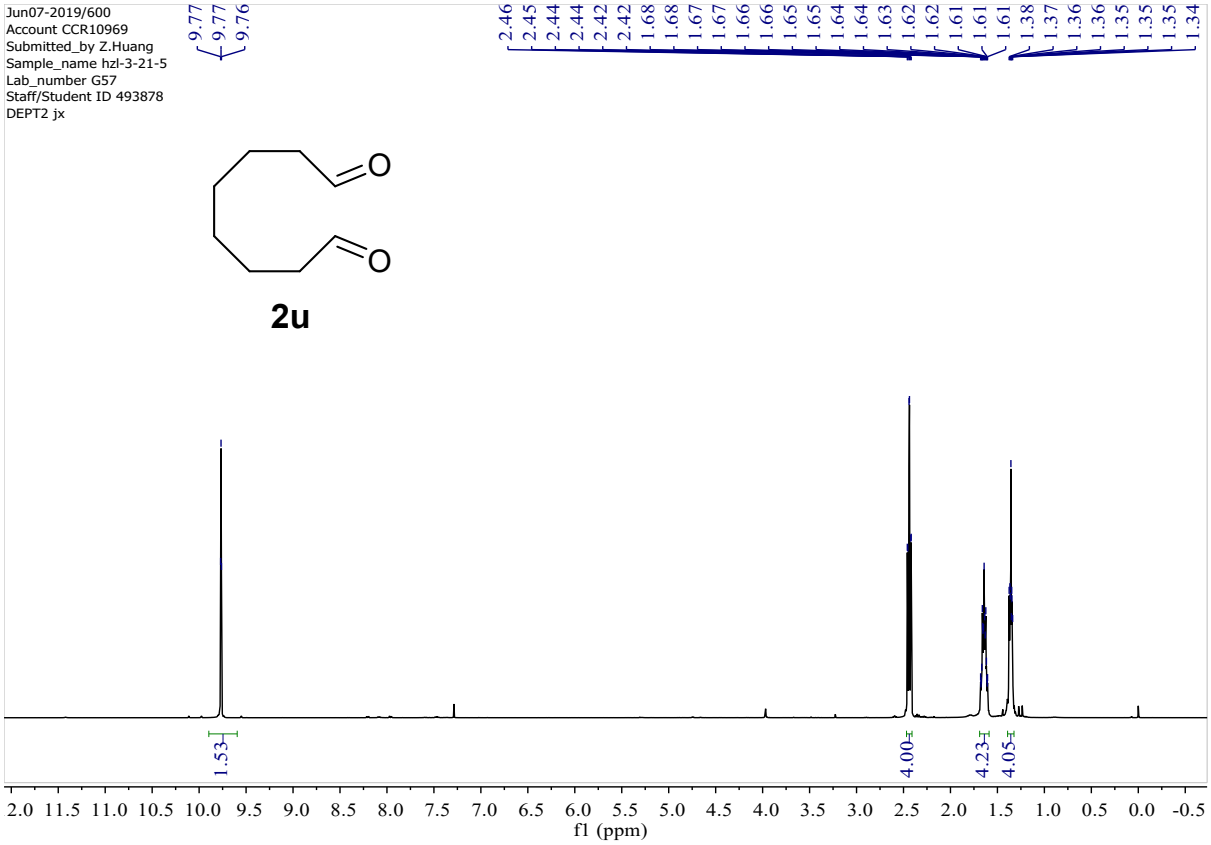

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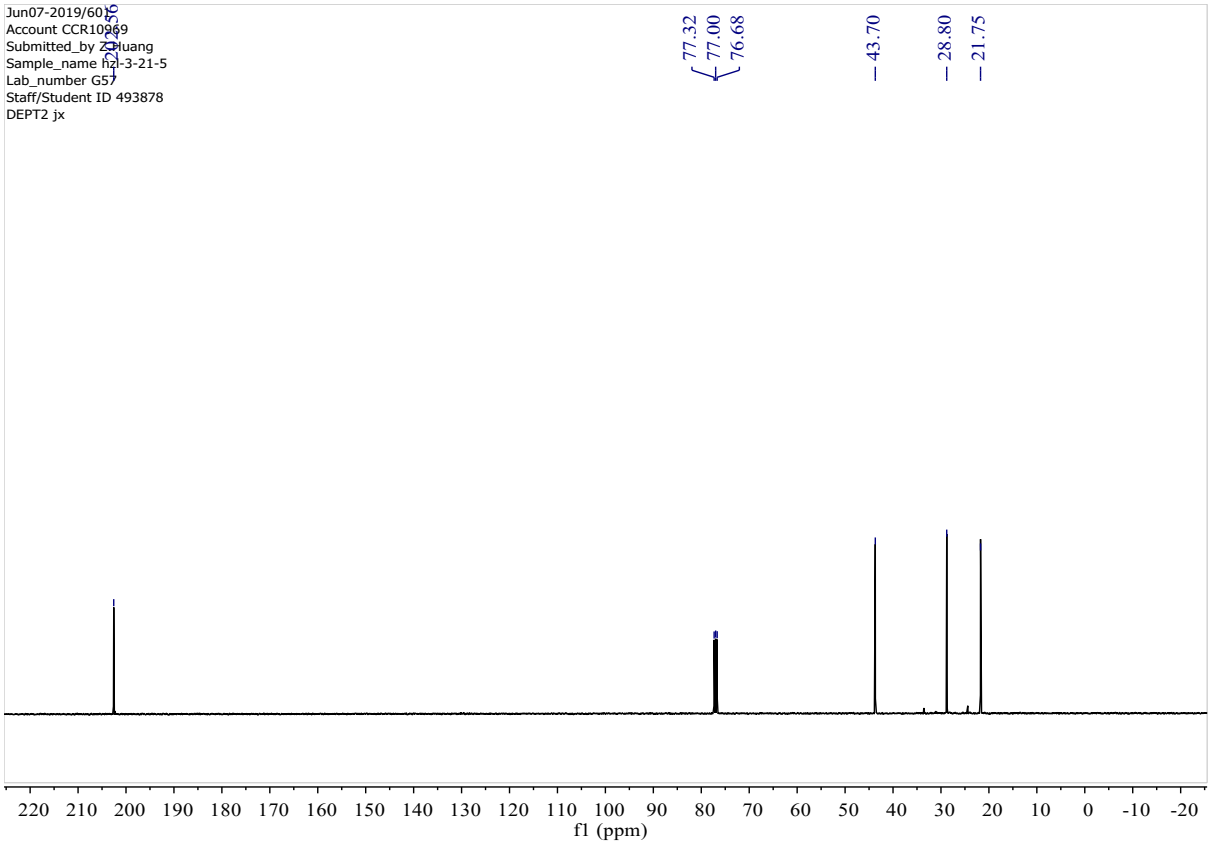

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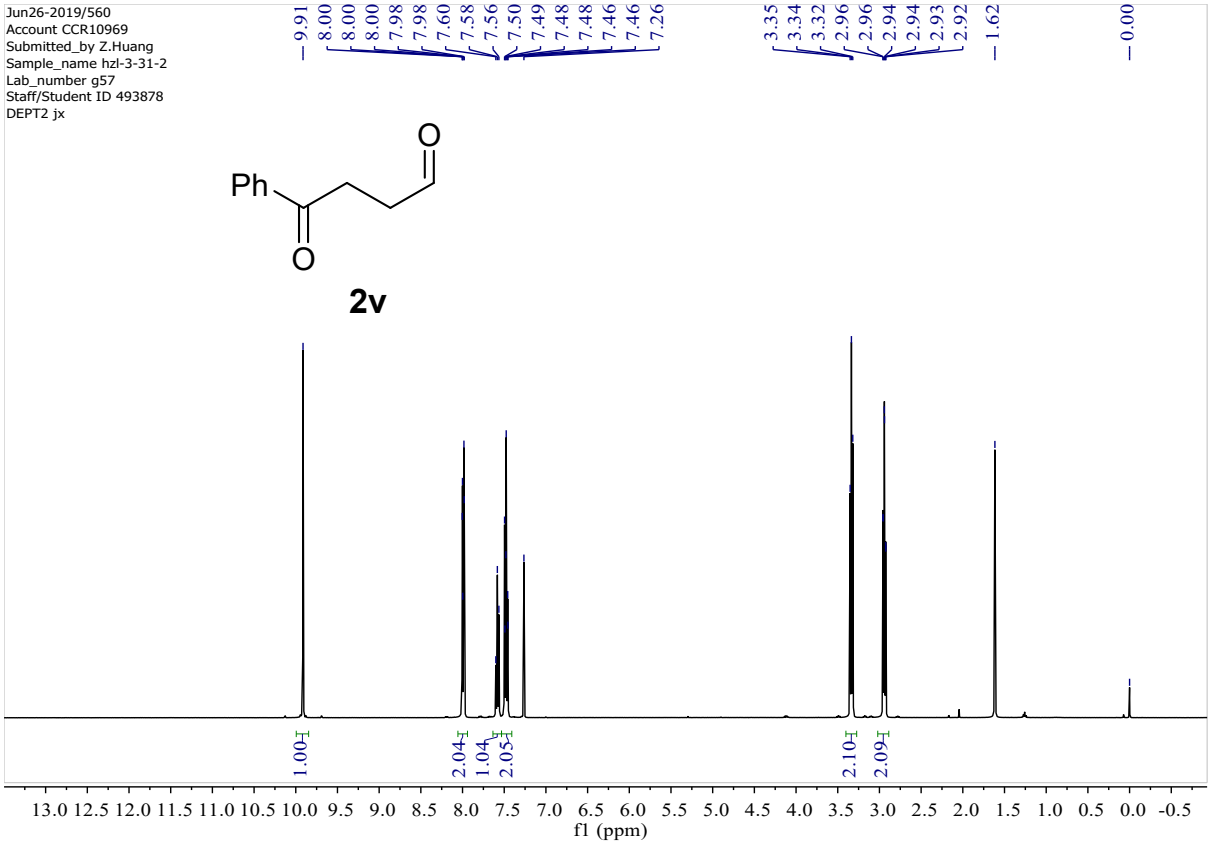

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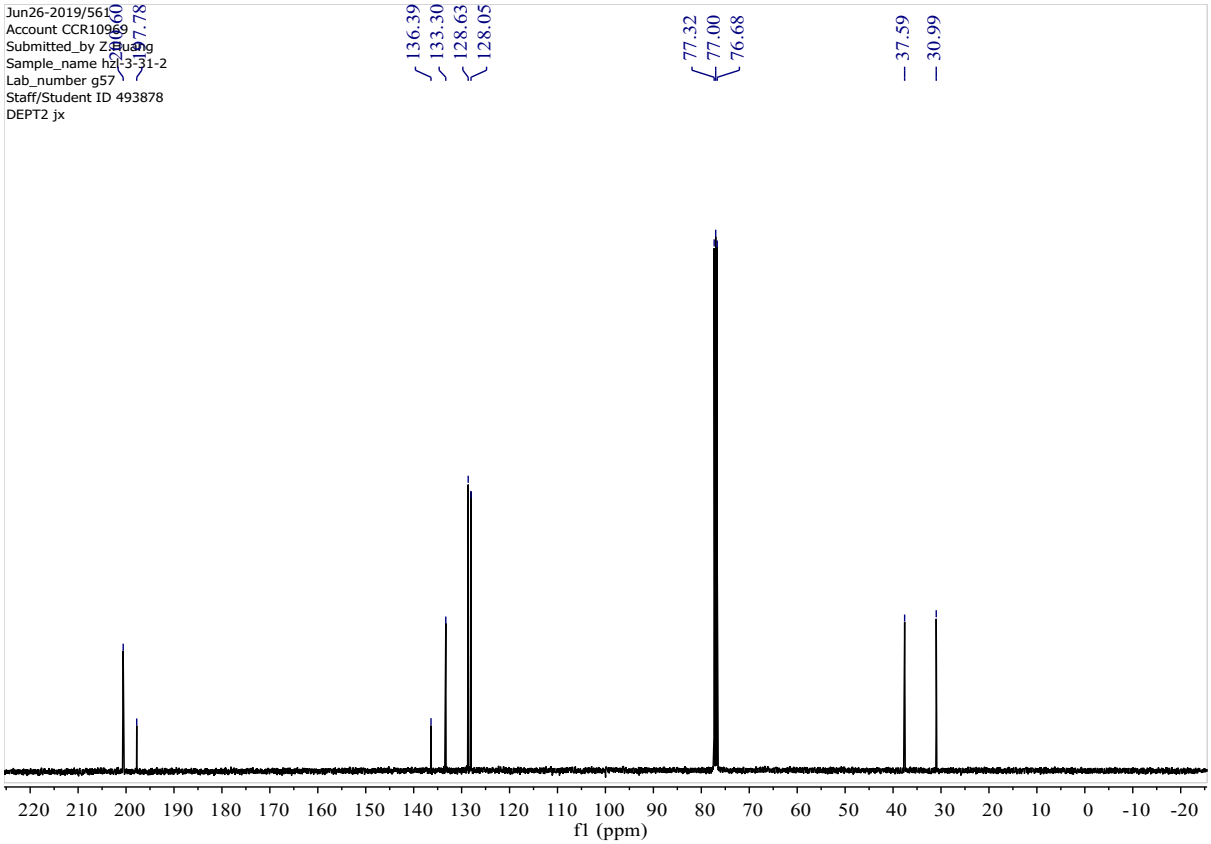

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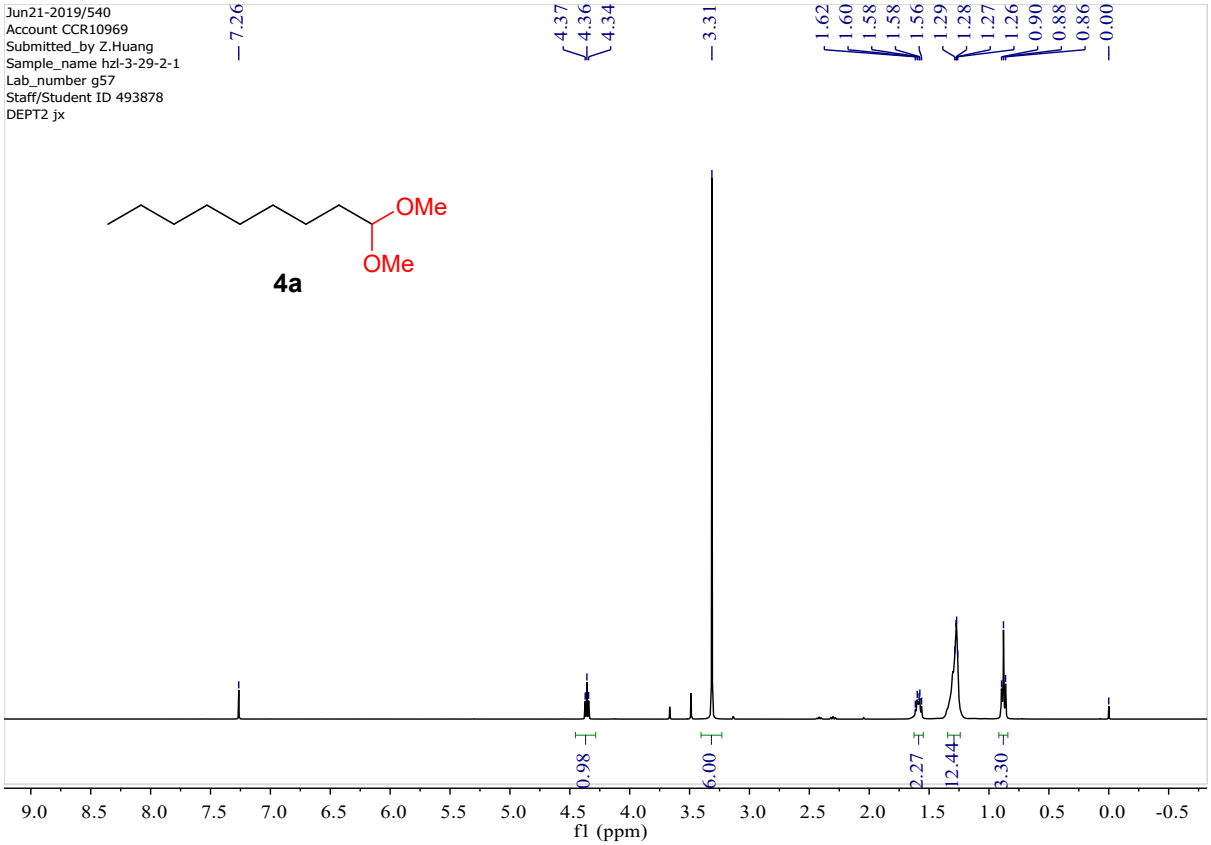

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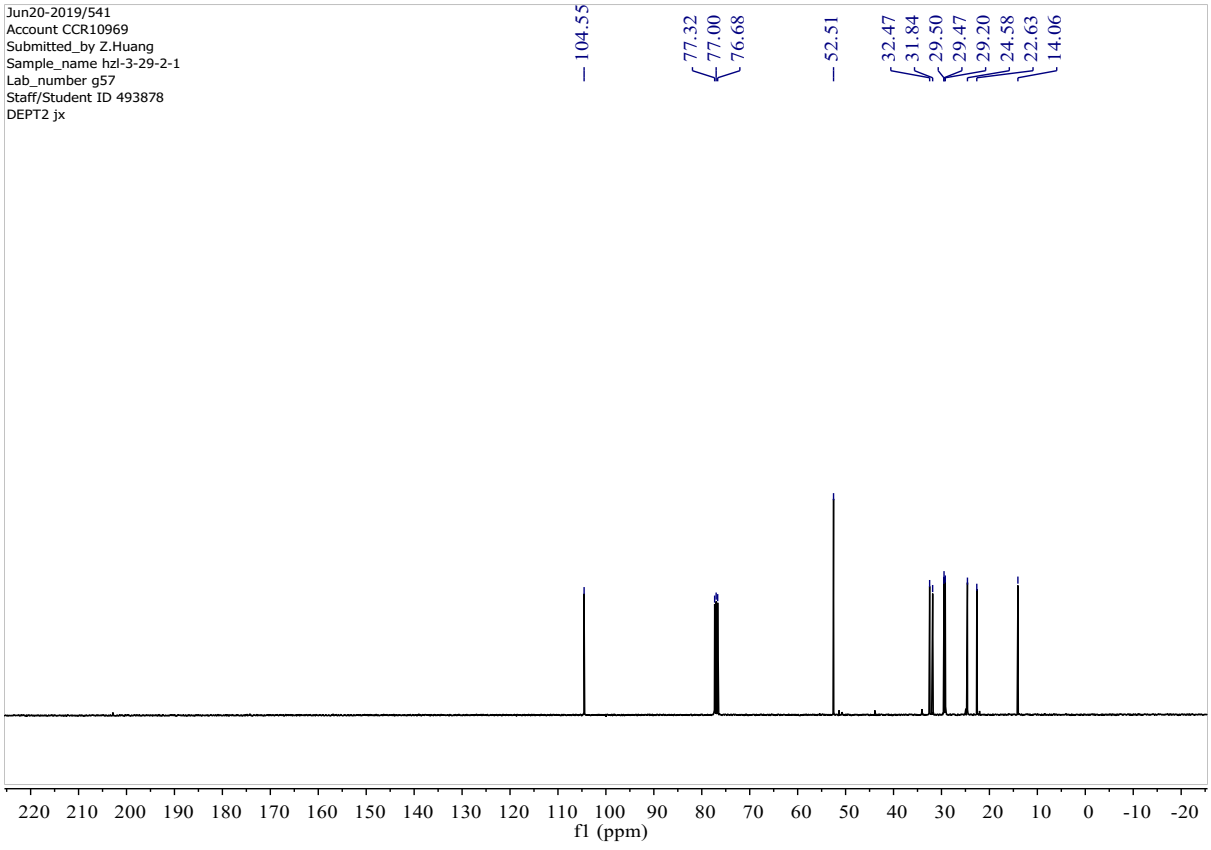

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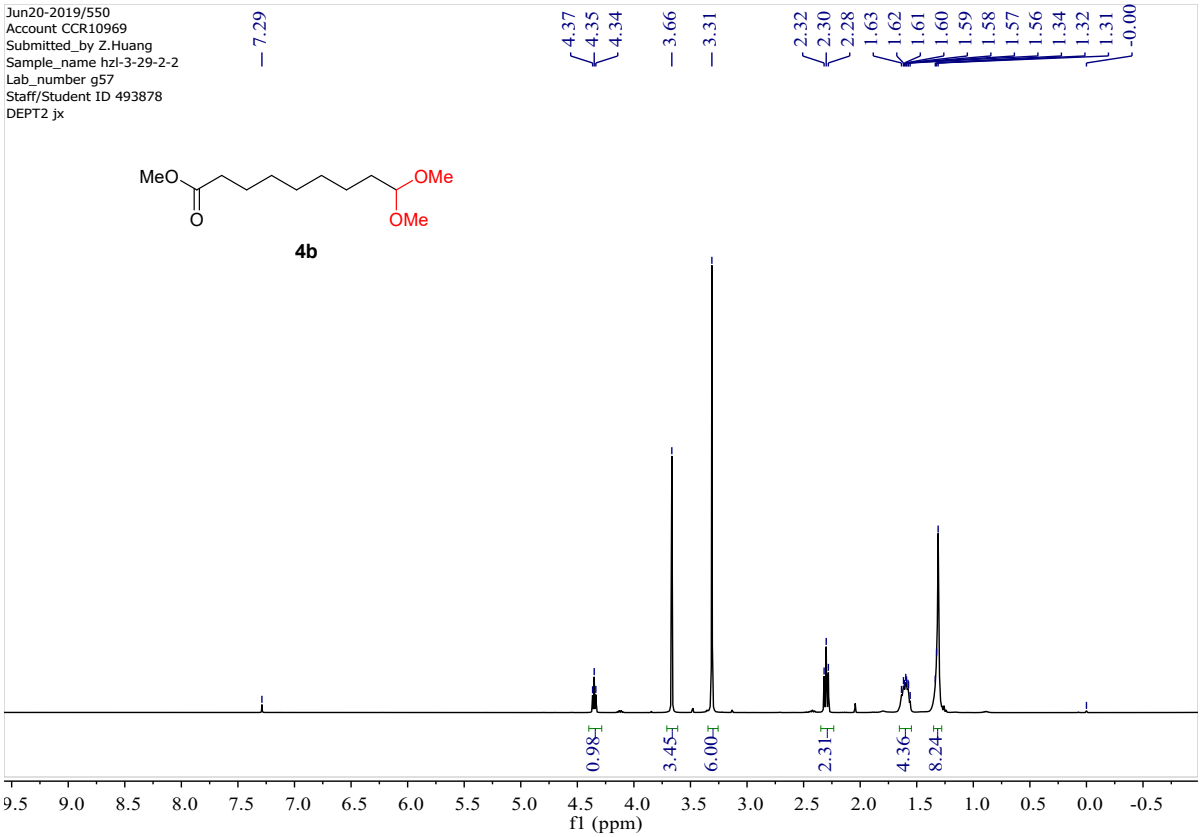

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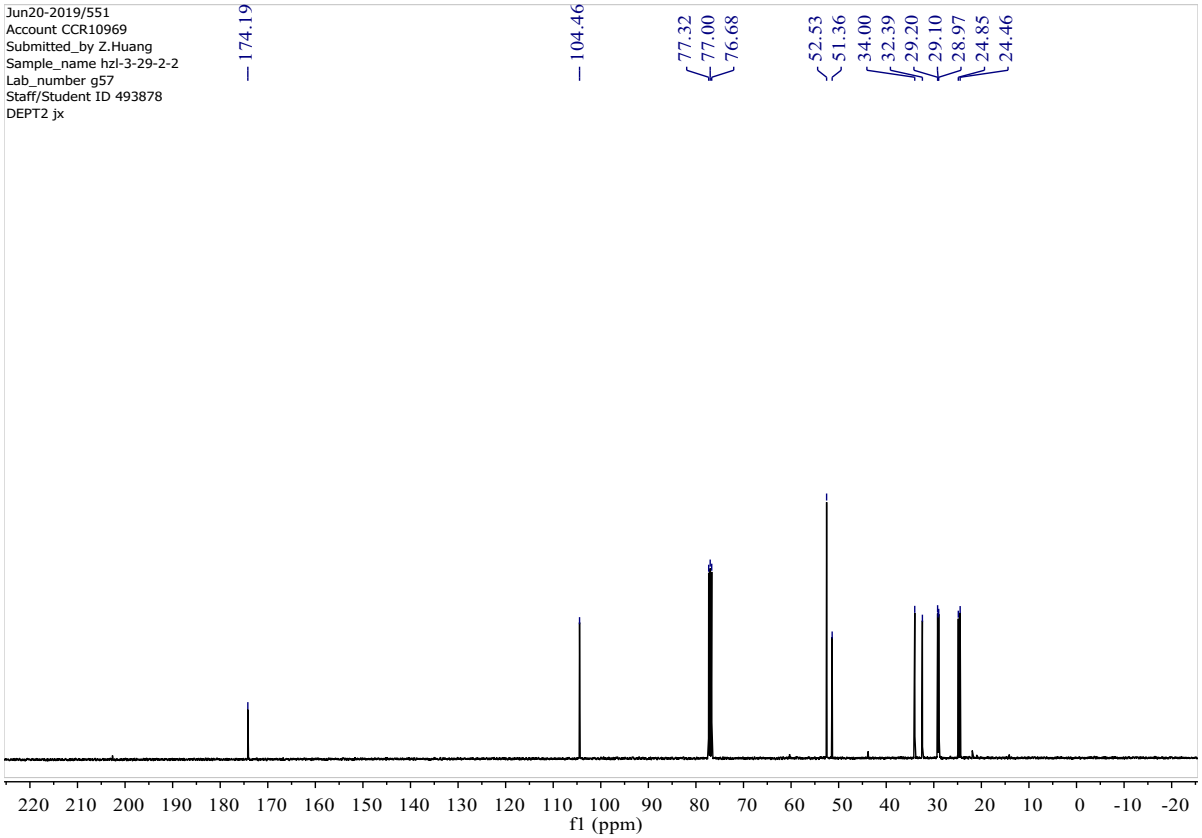

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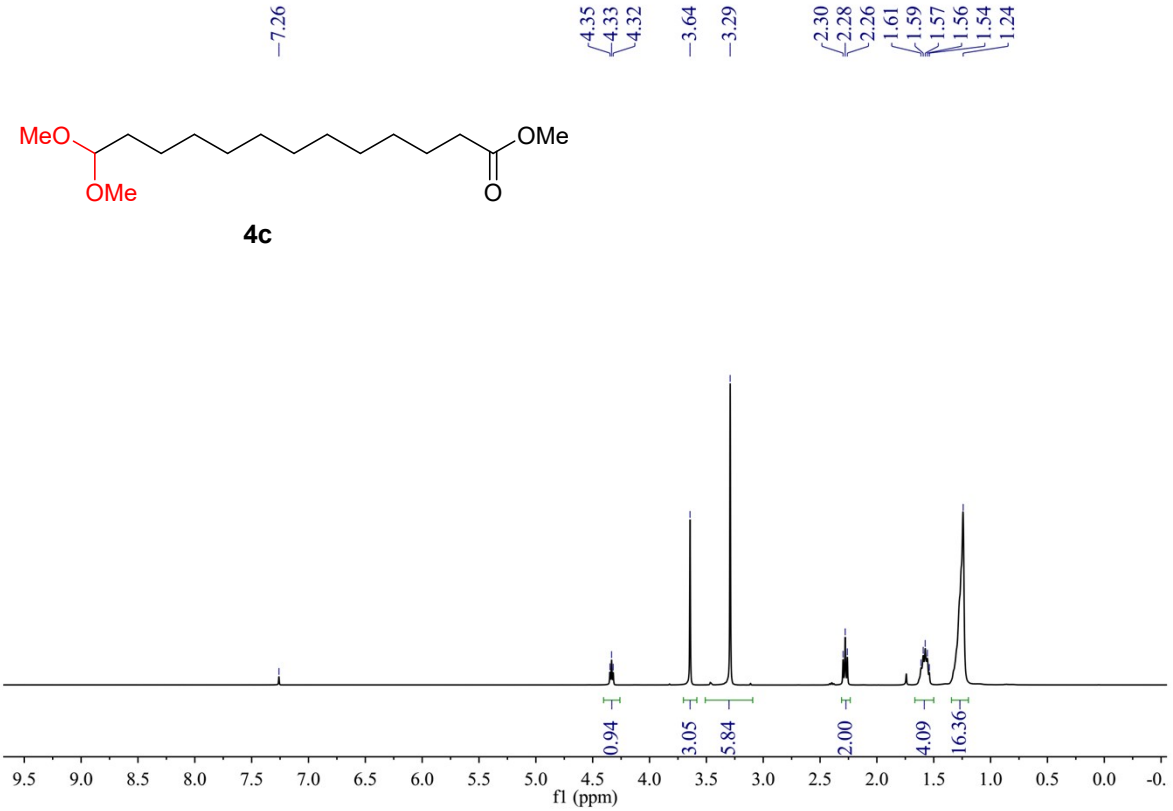

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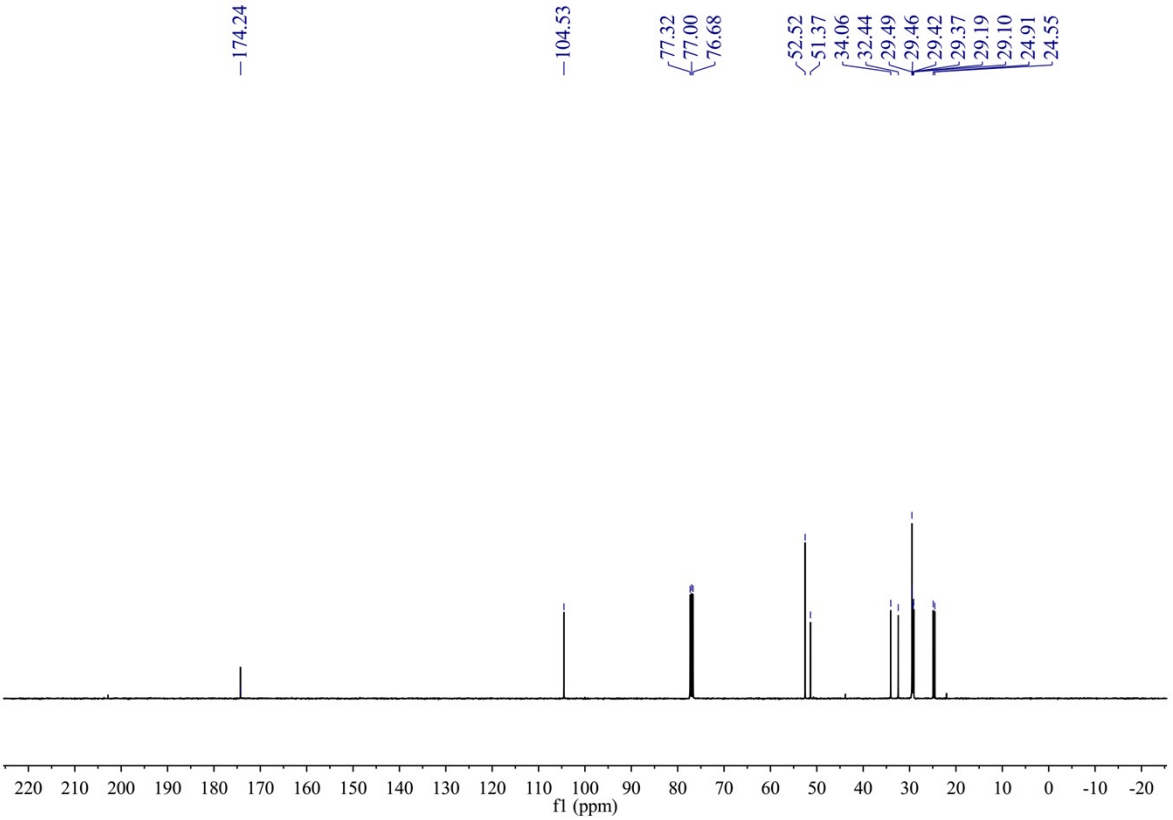

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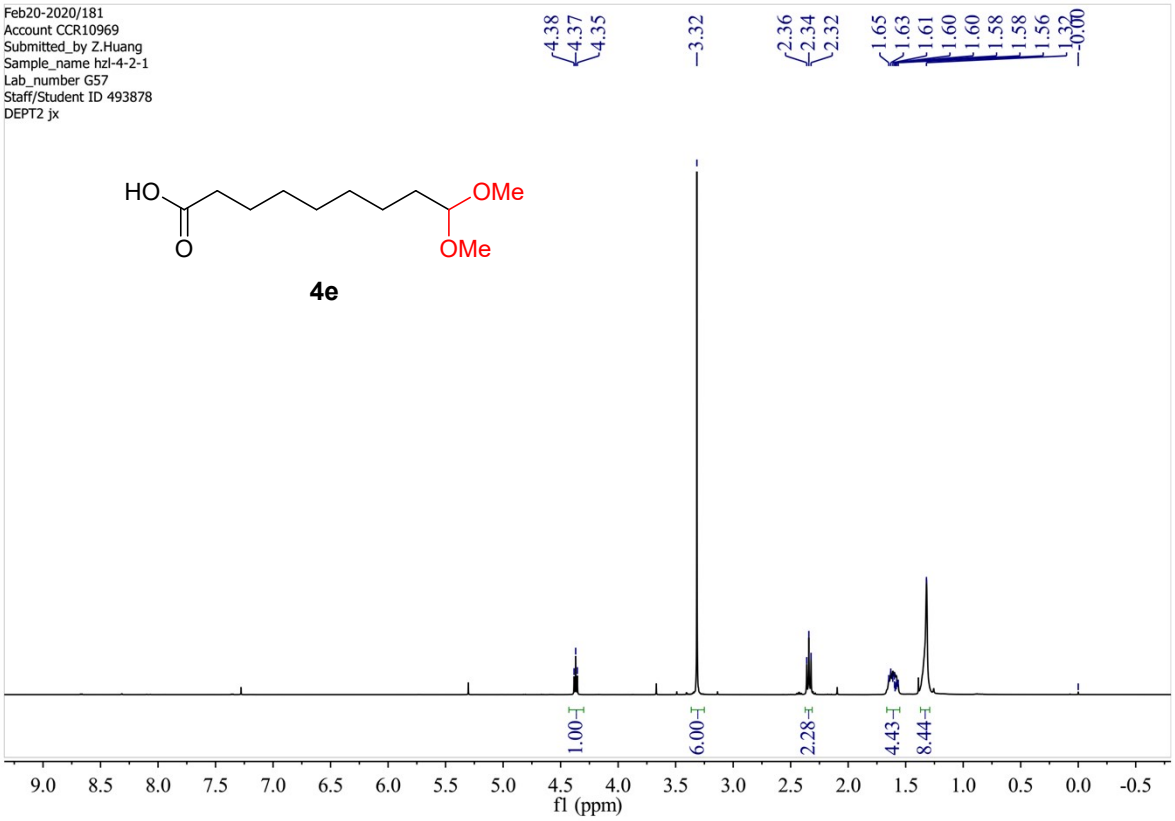

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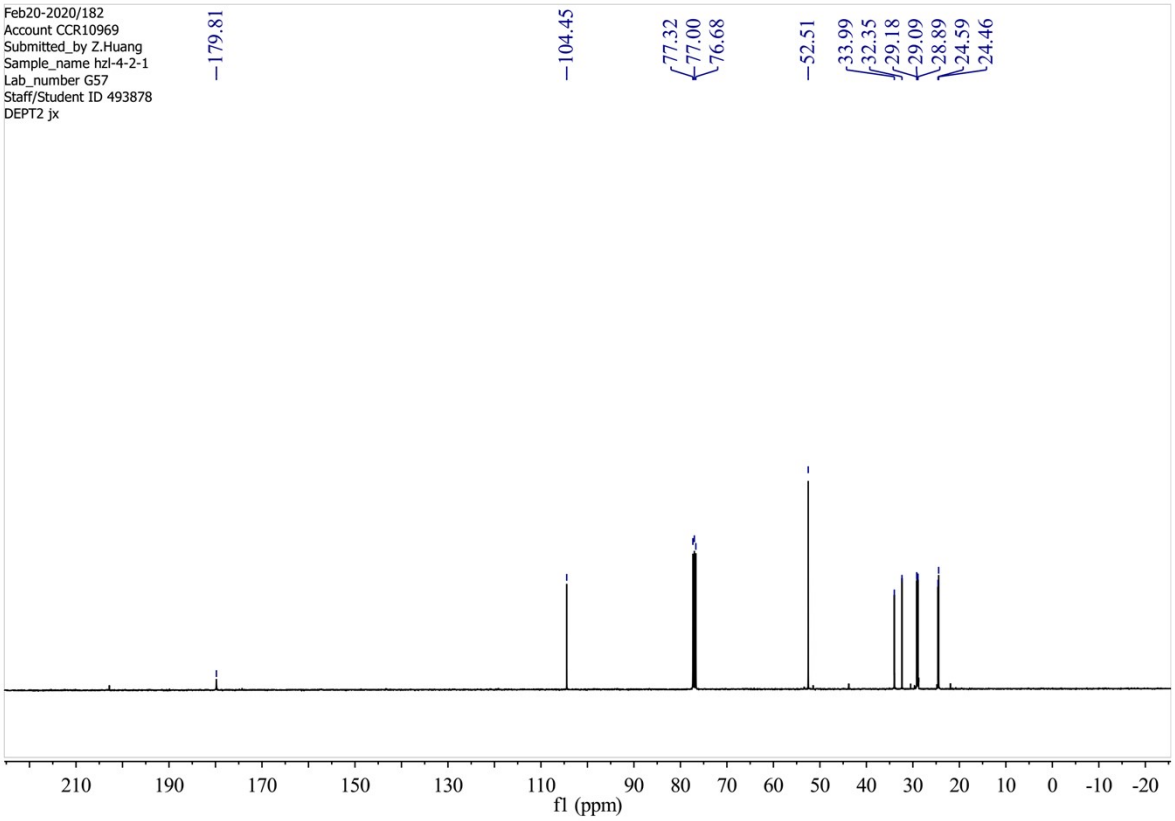

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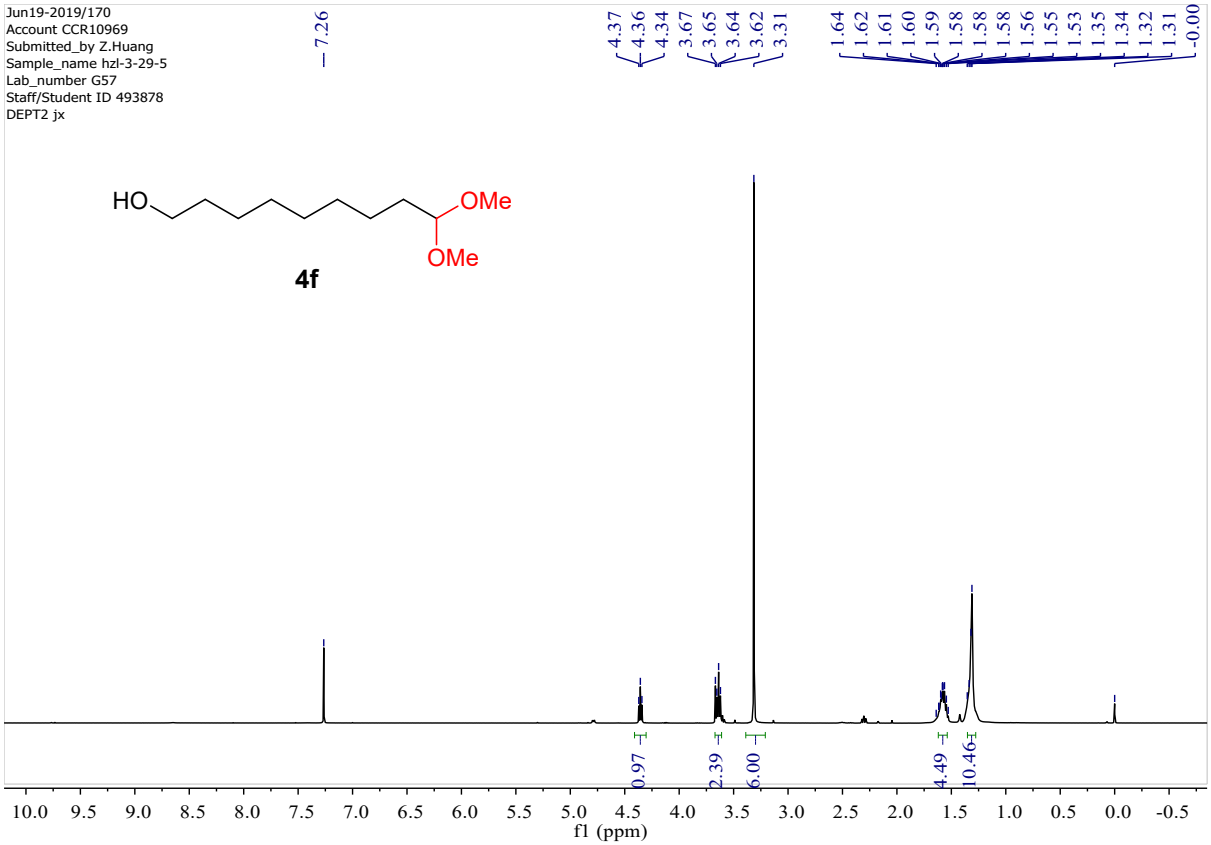

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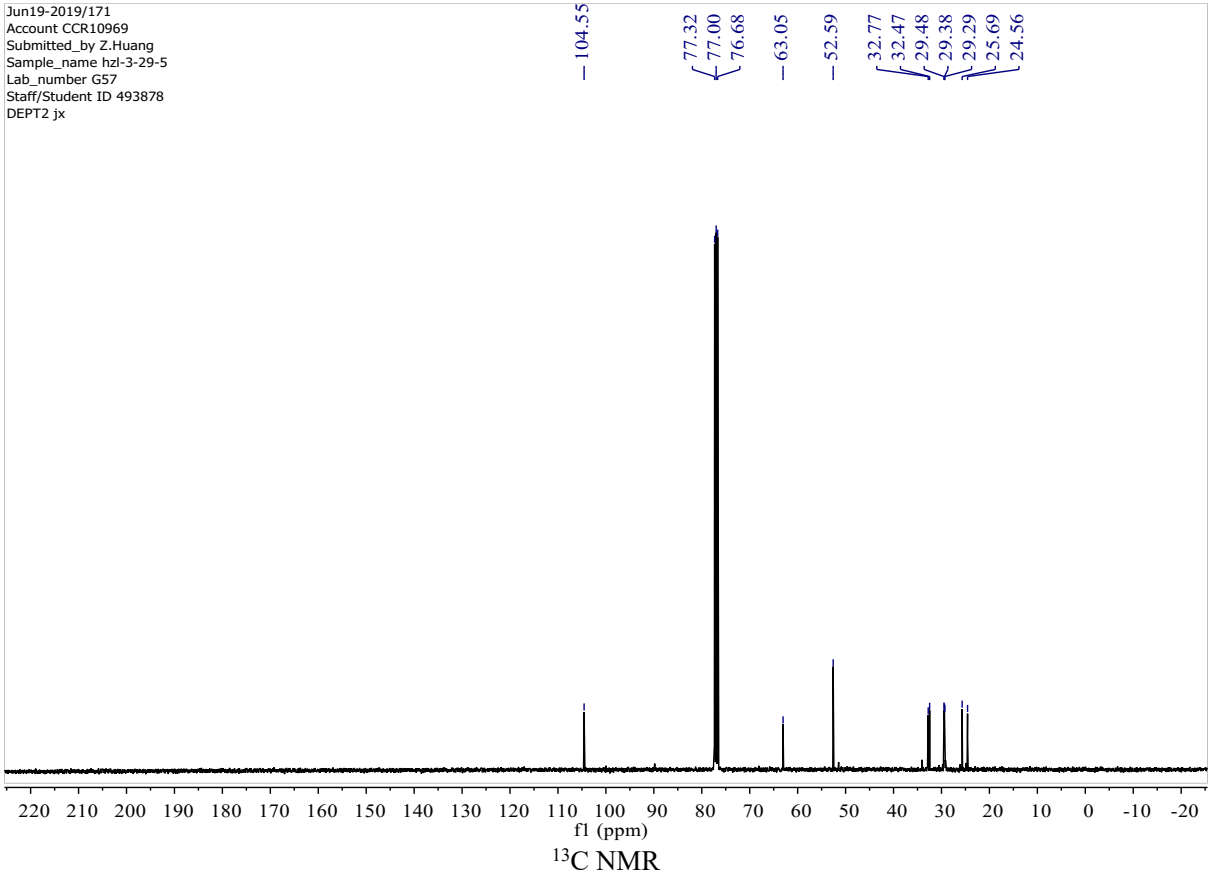

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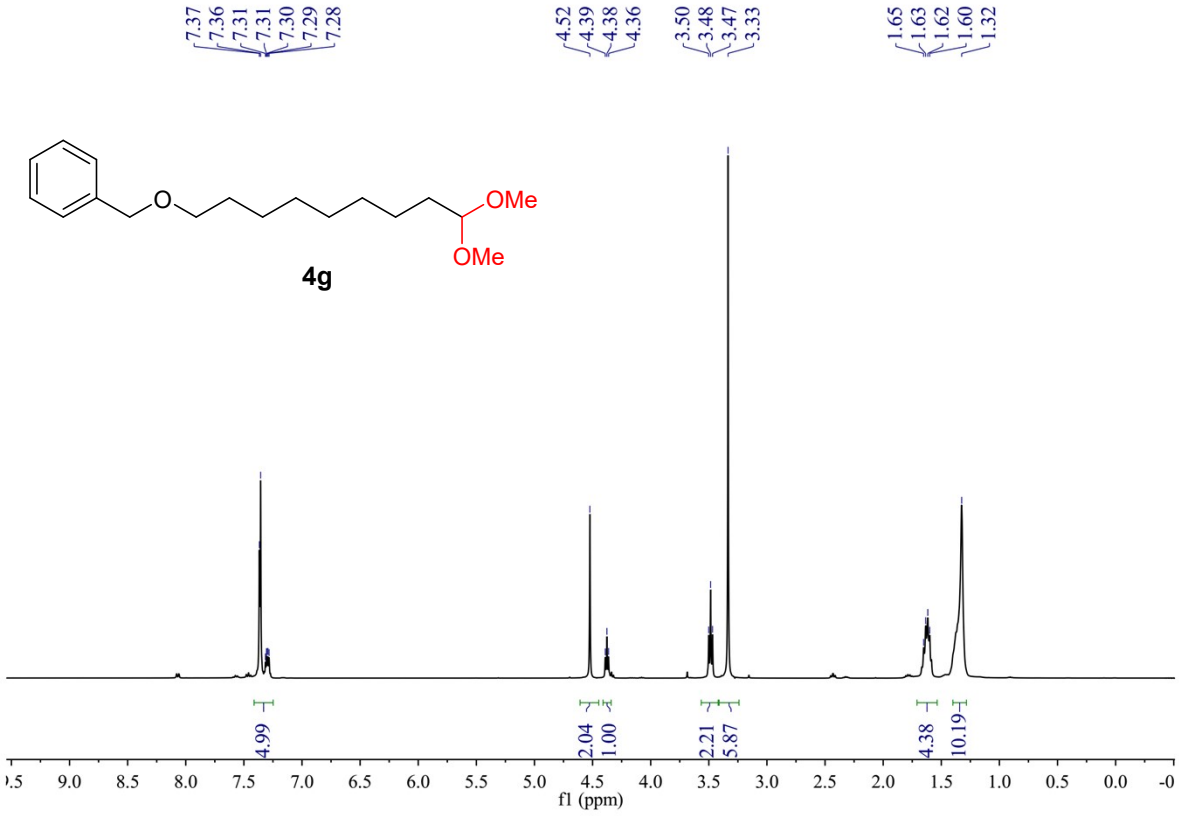

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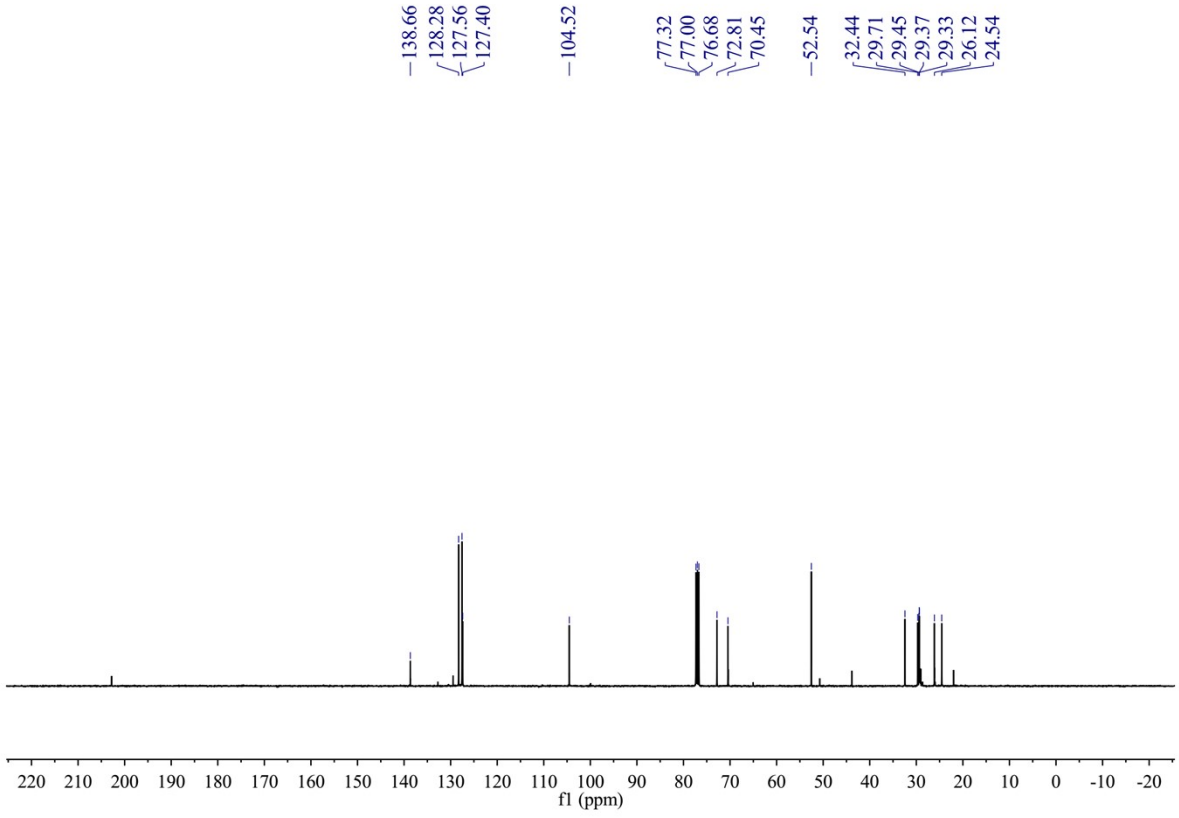

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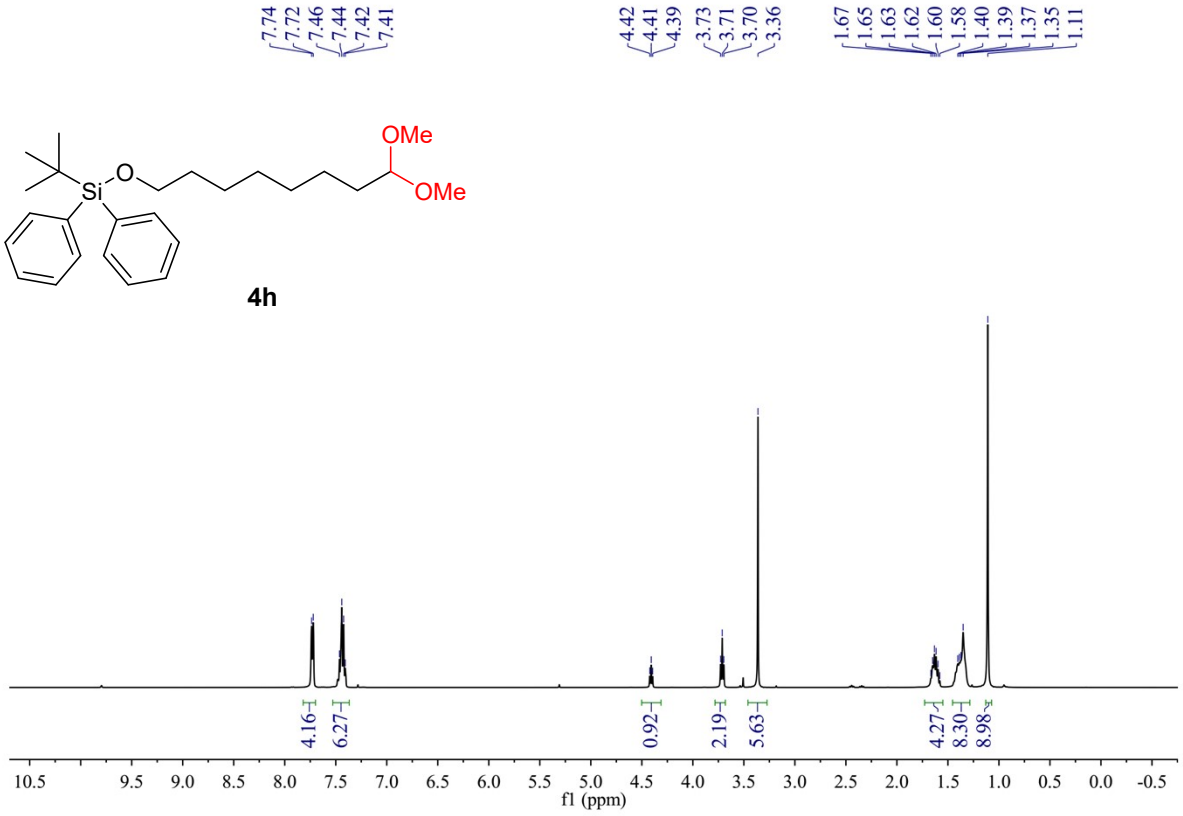

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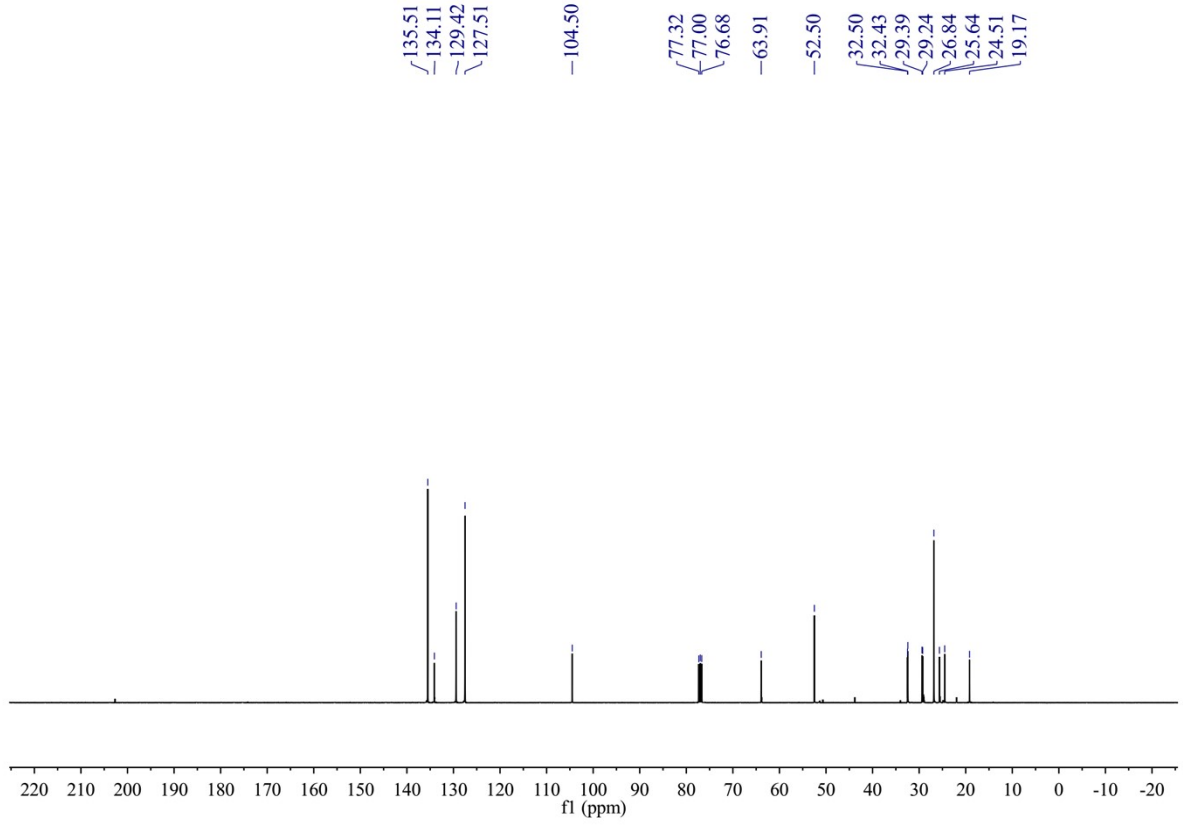

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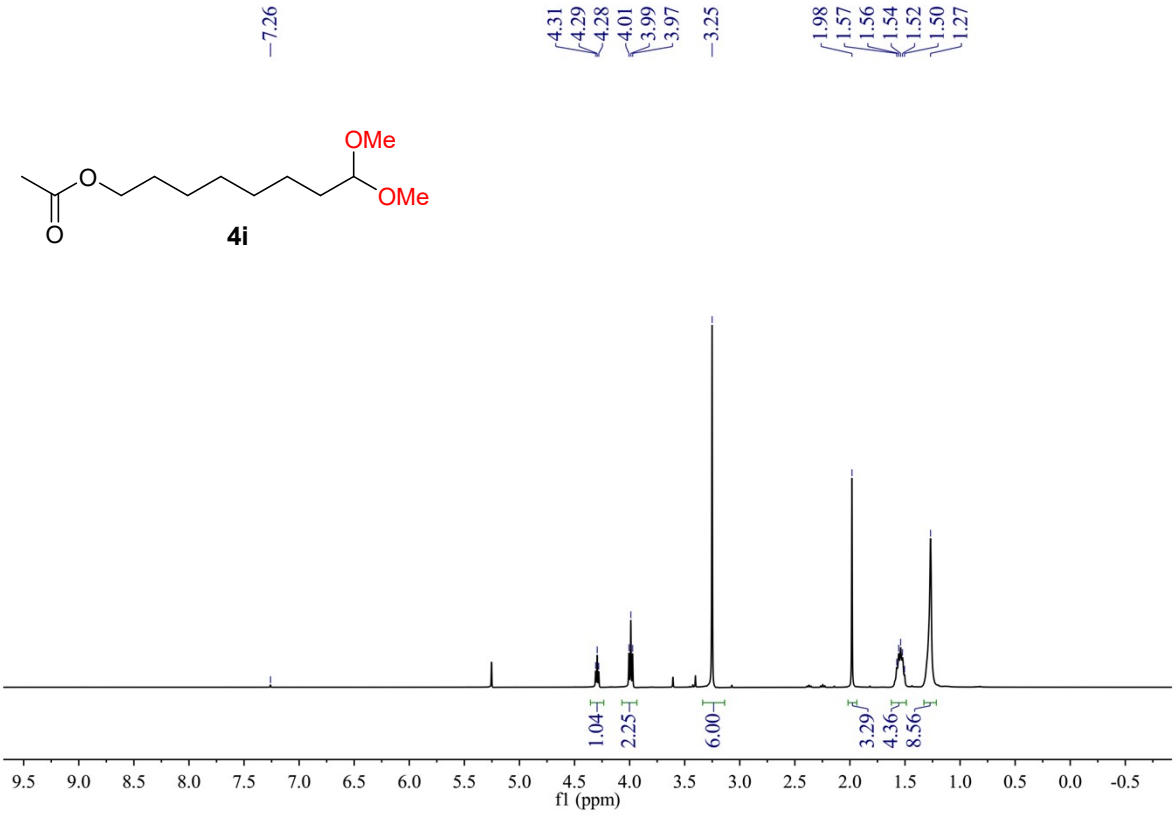

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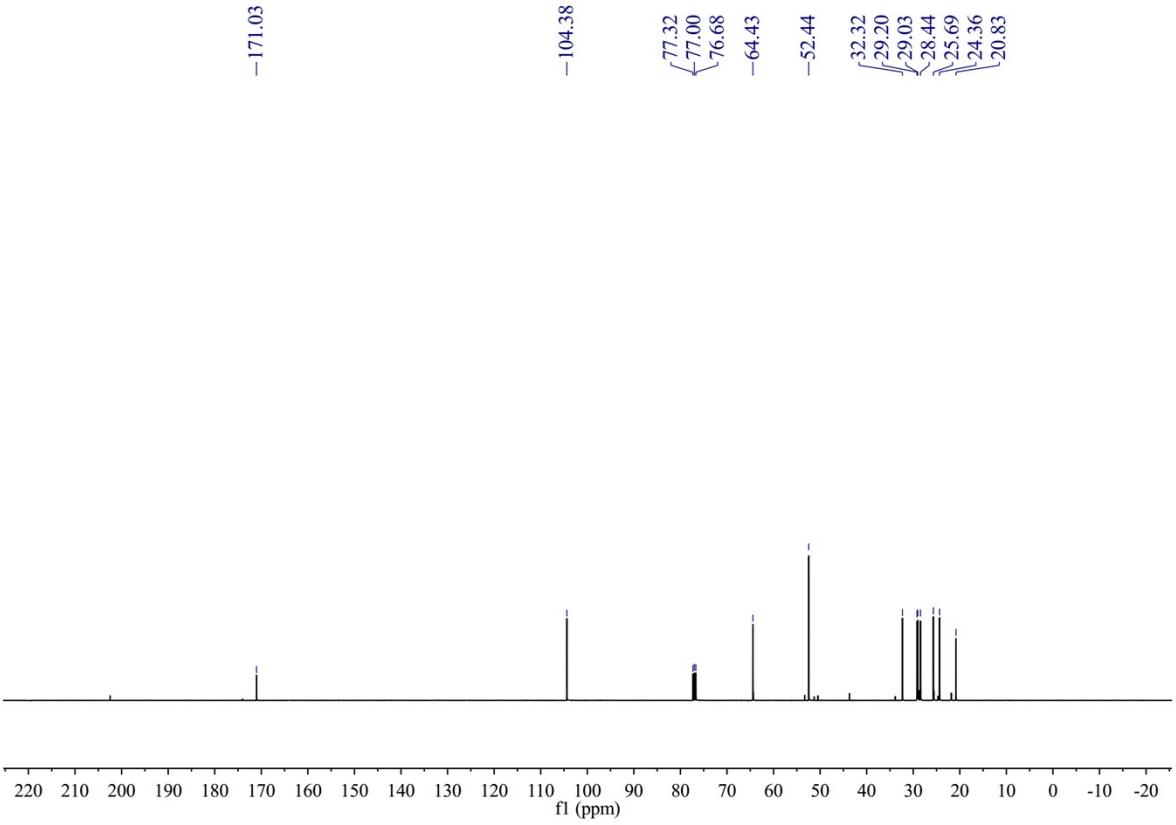

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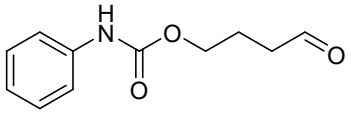

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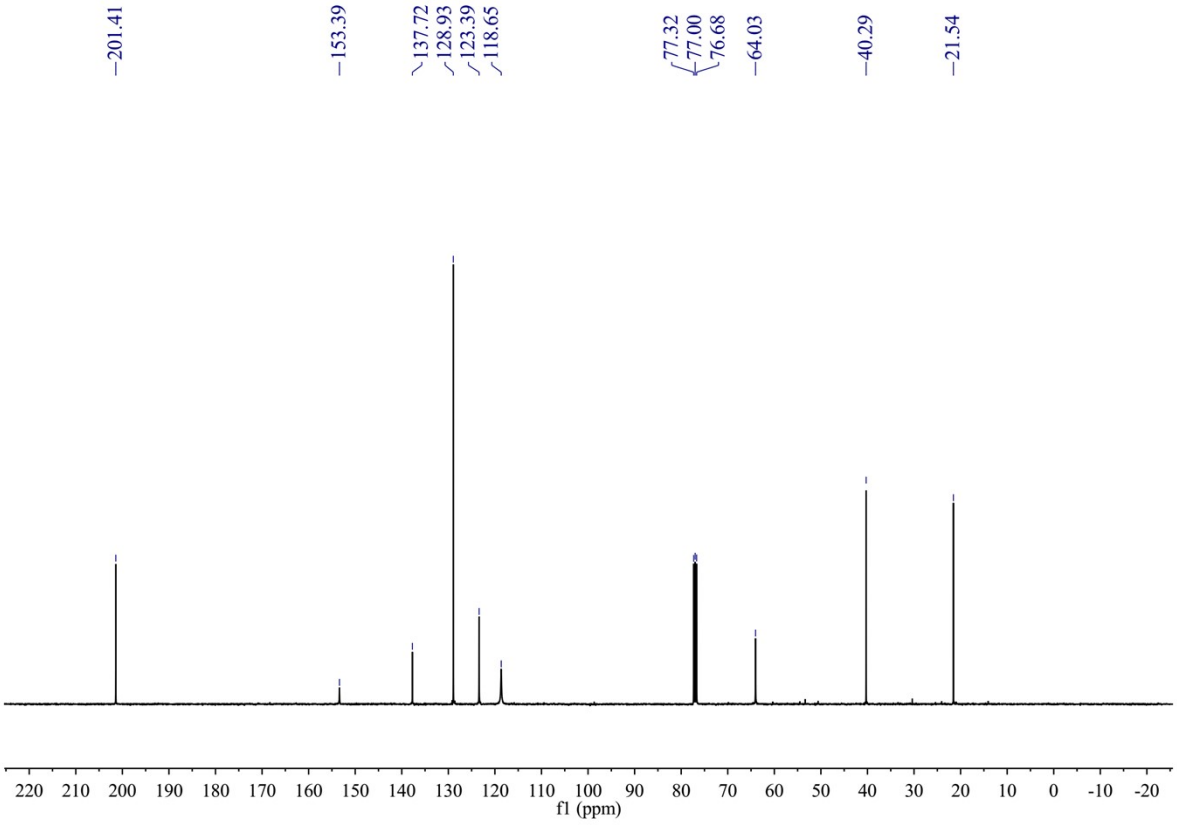
^{1}H NMR



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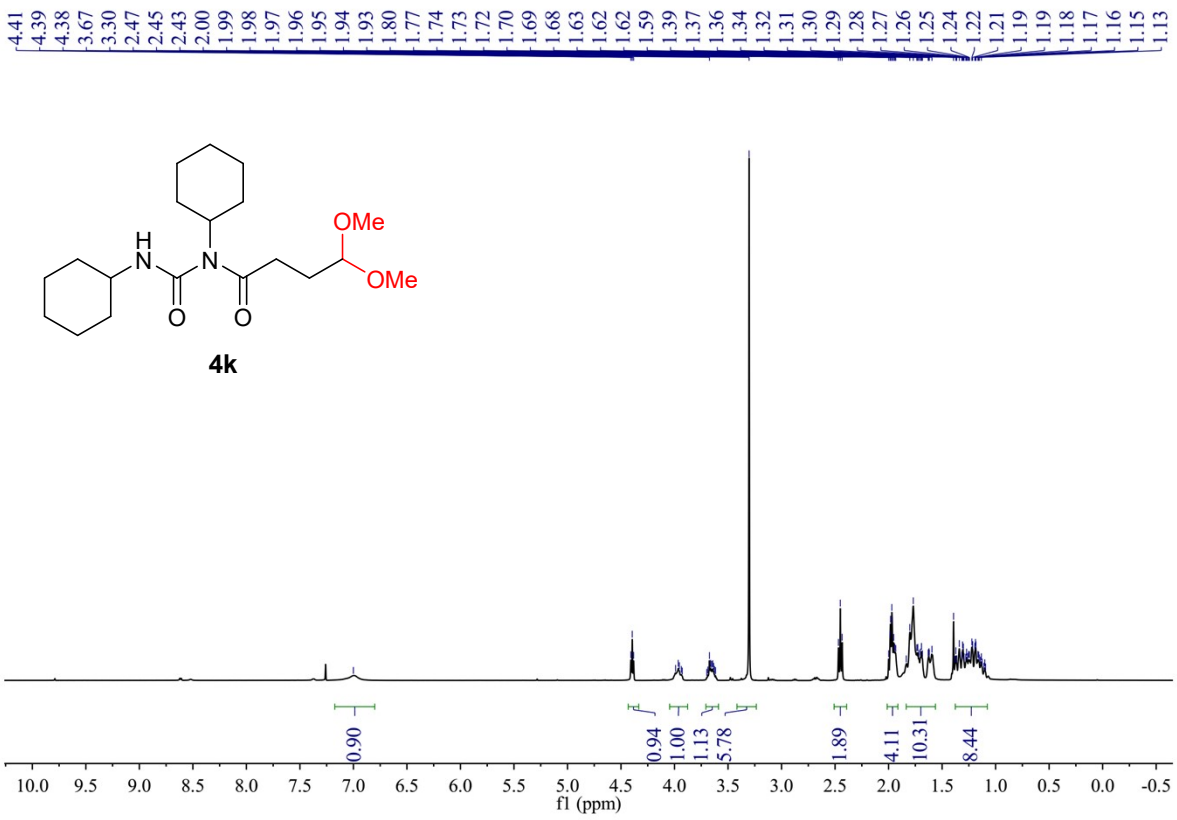

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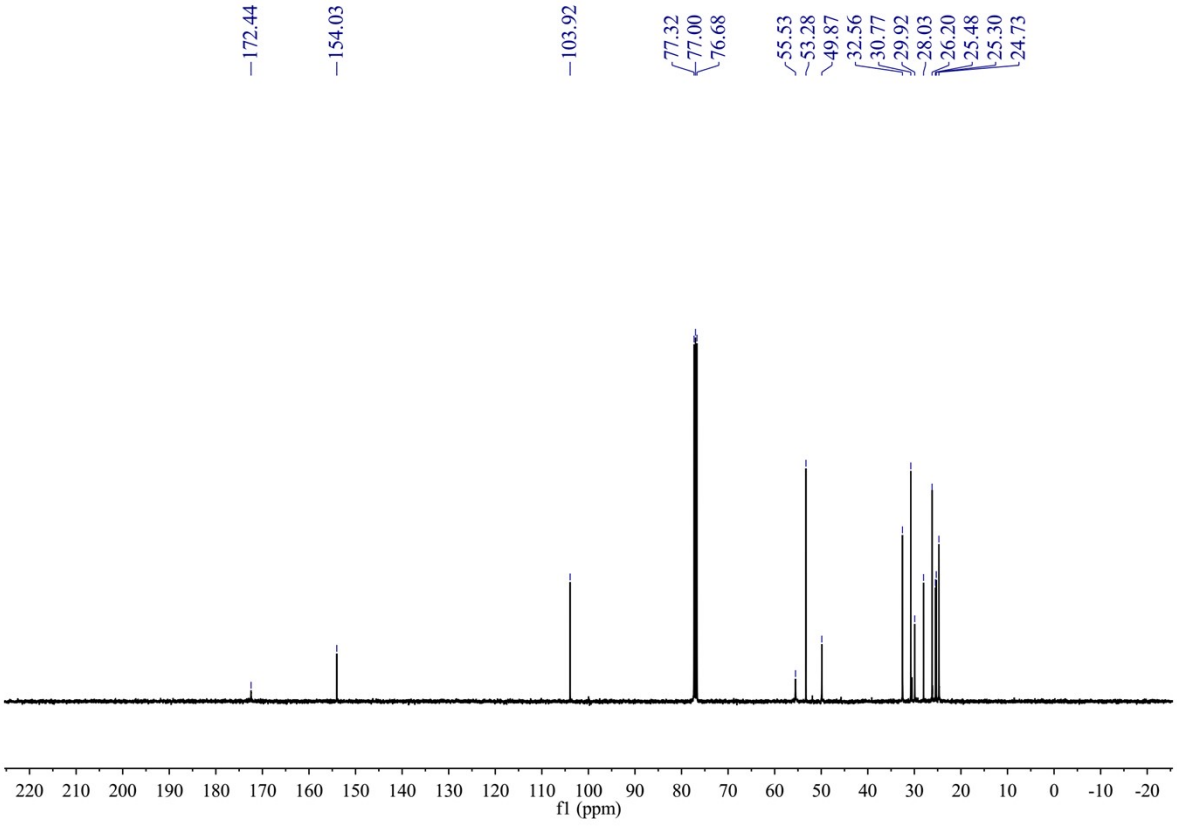

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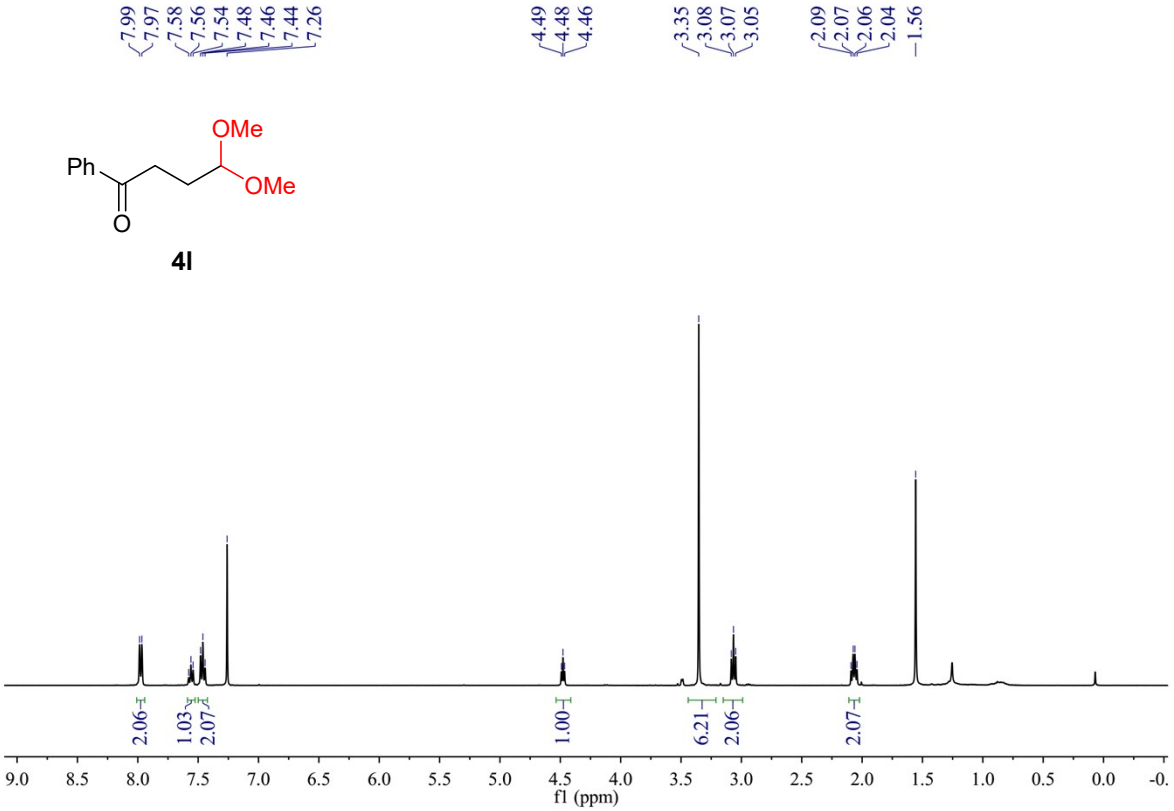

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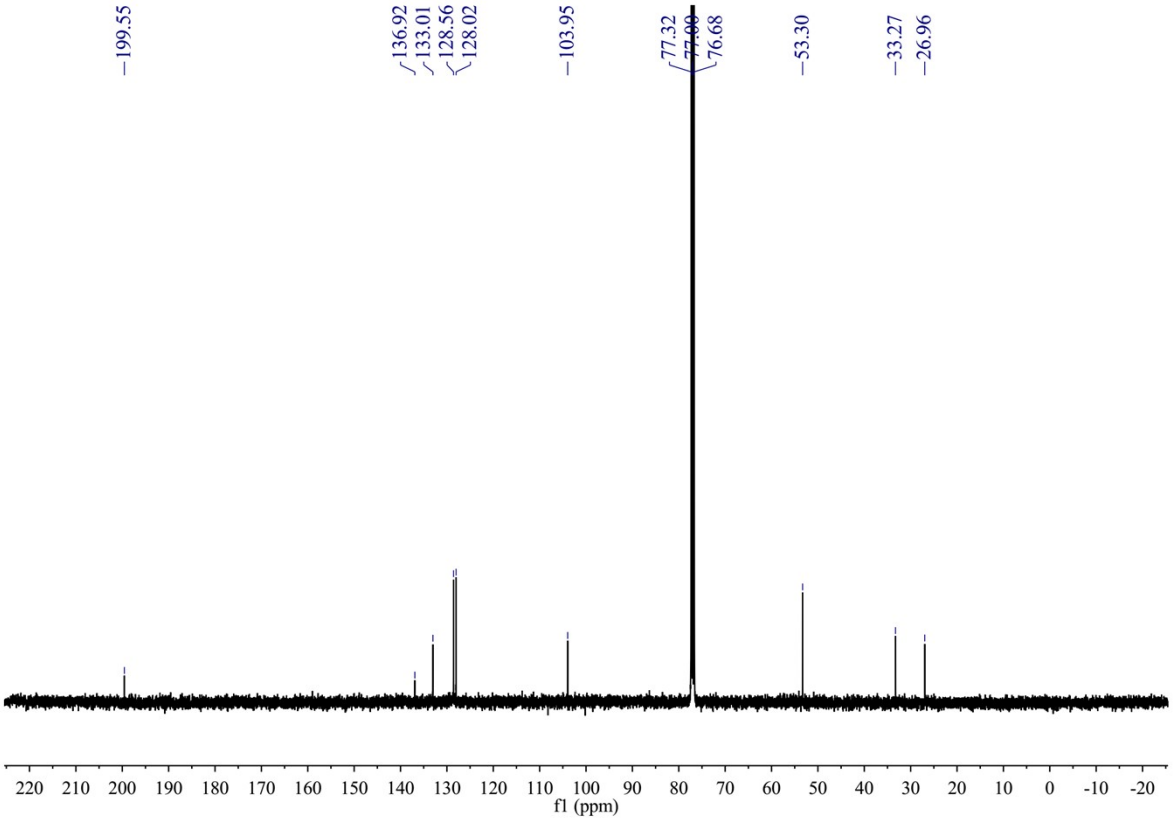

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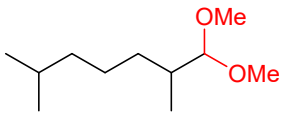

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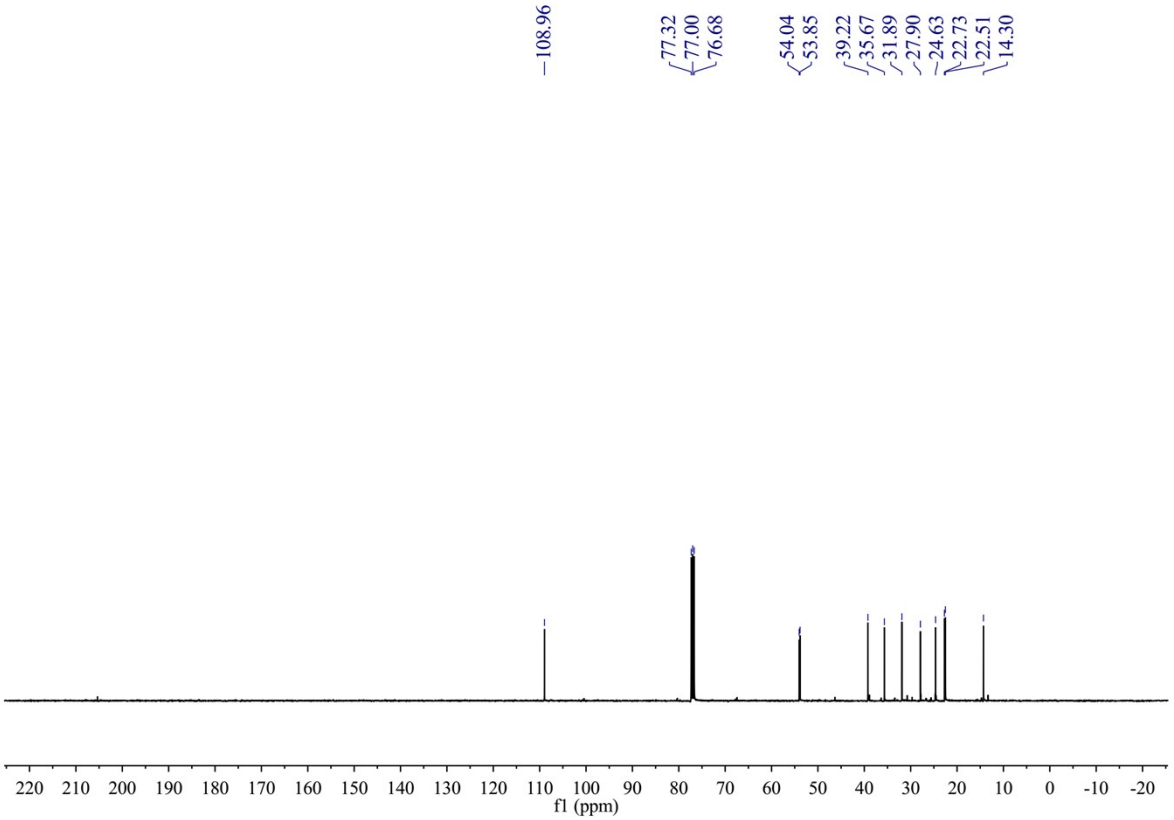

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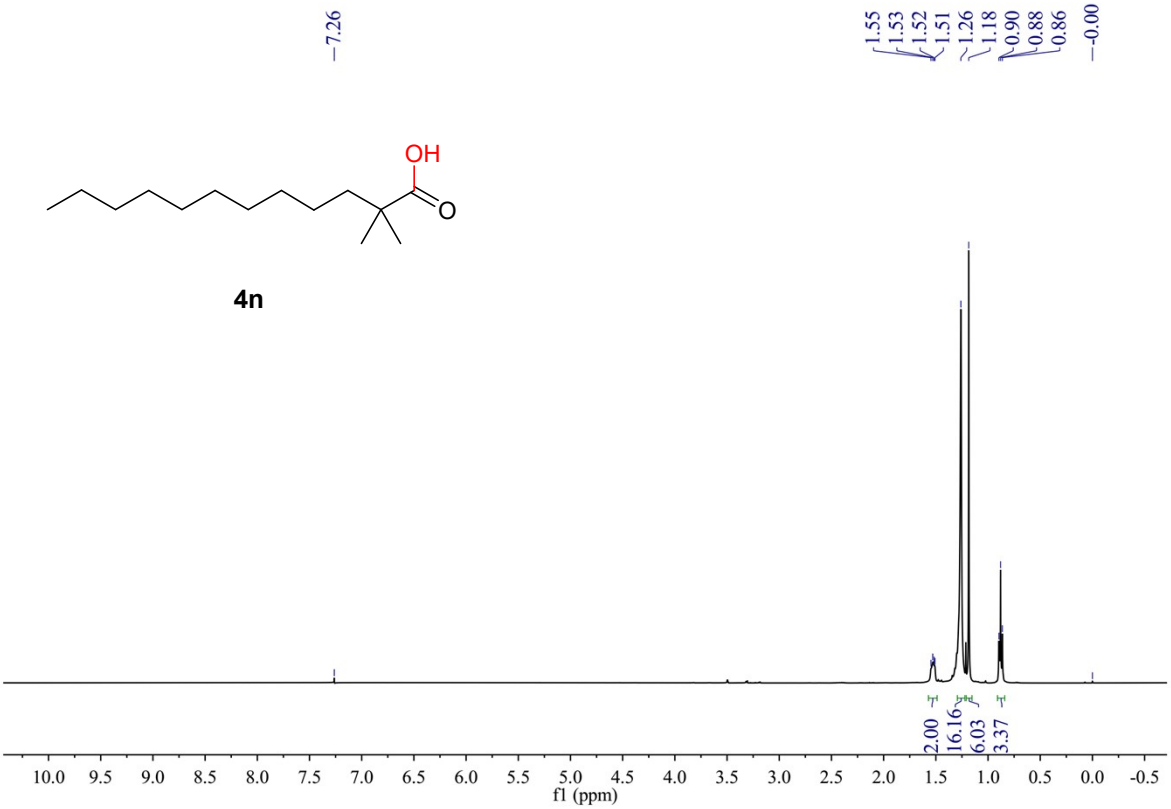

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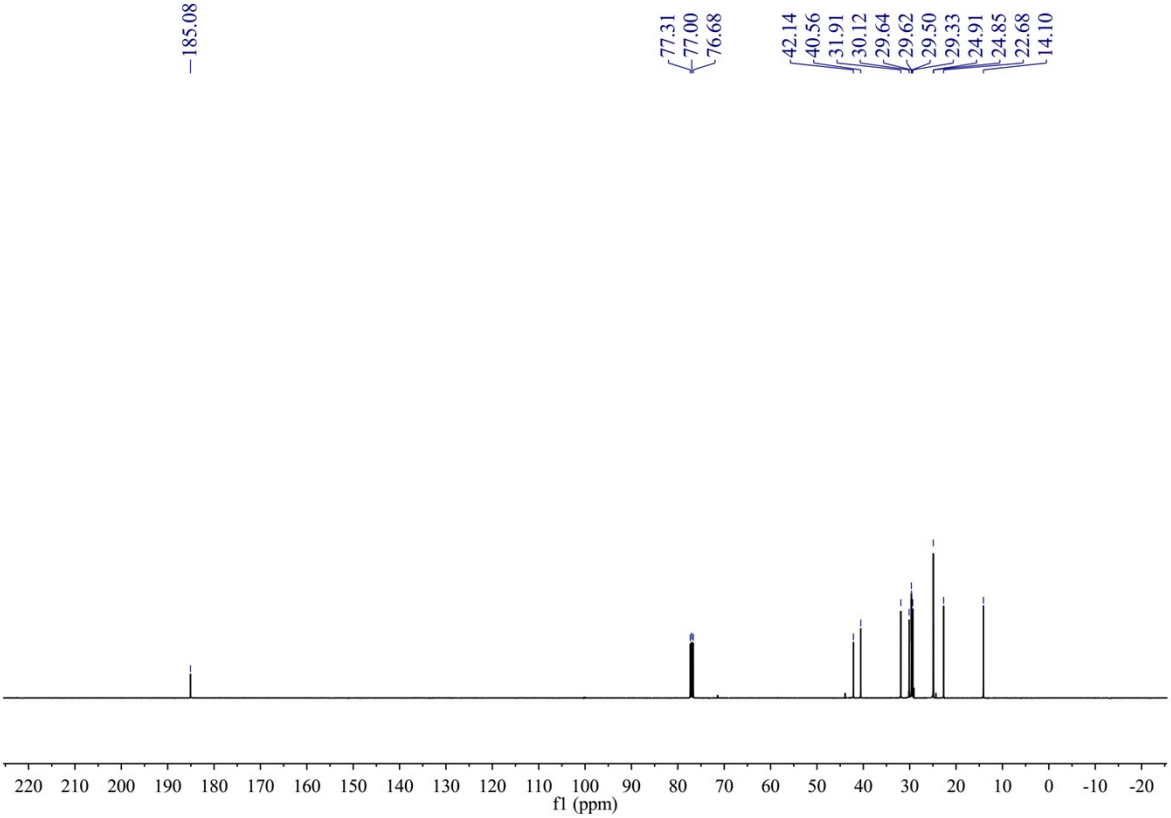

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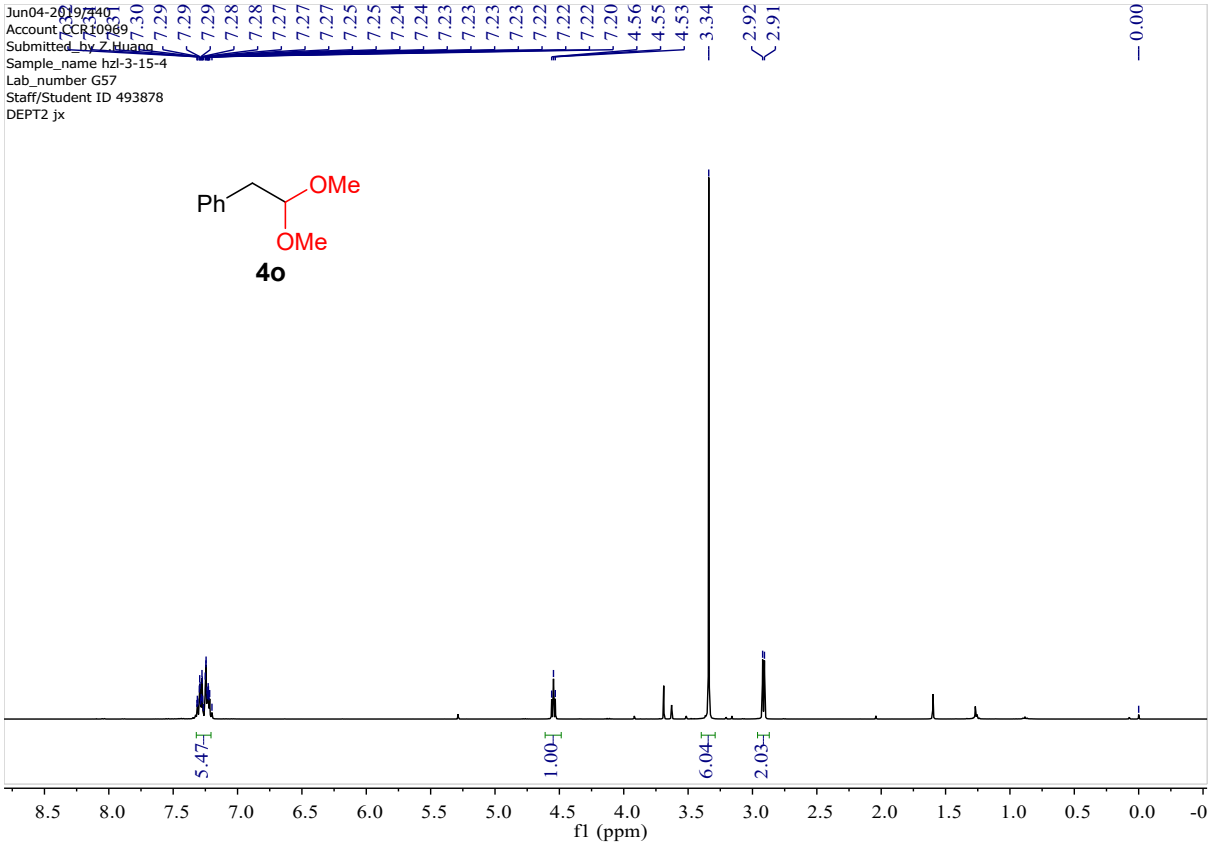

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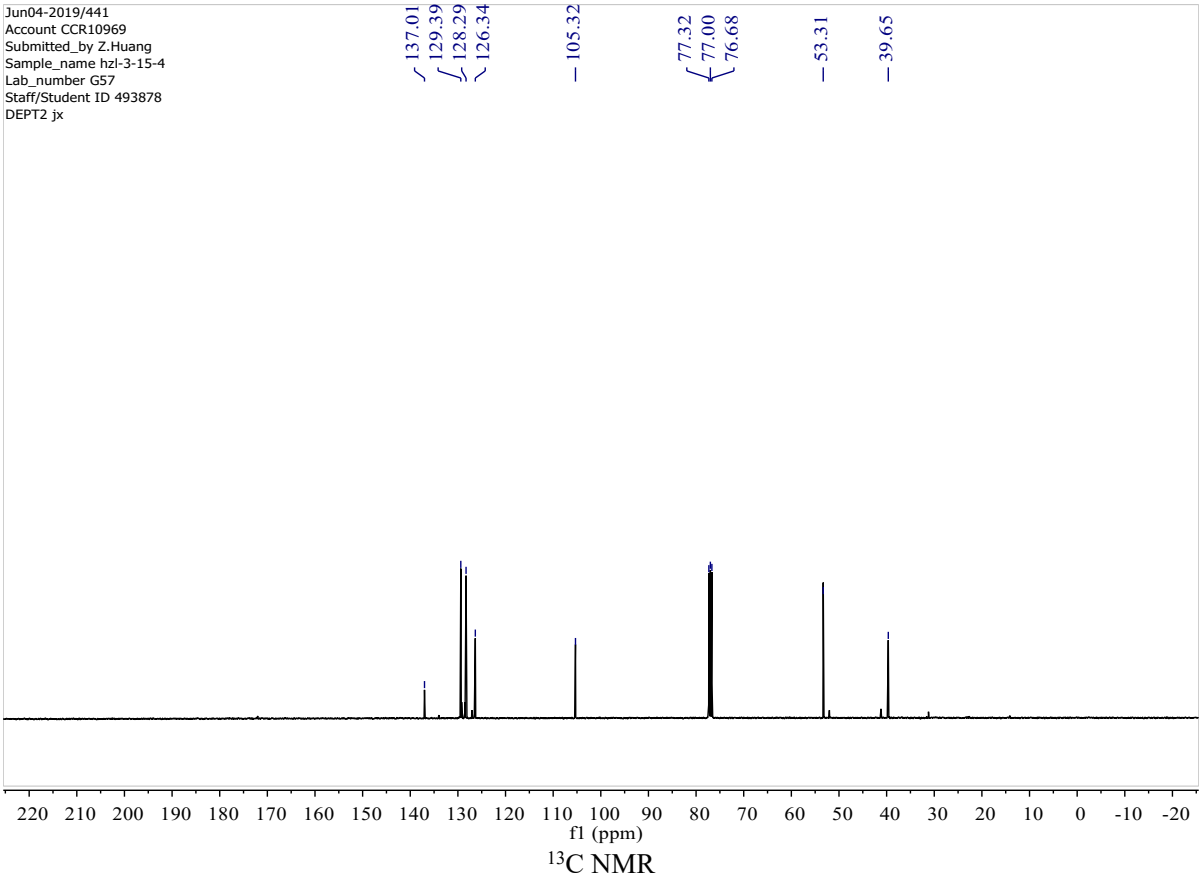

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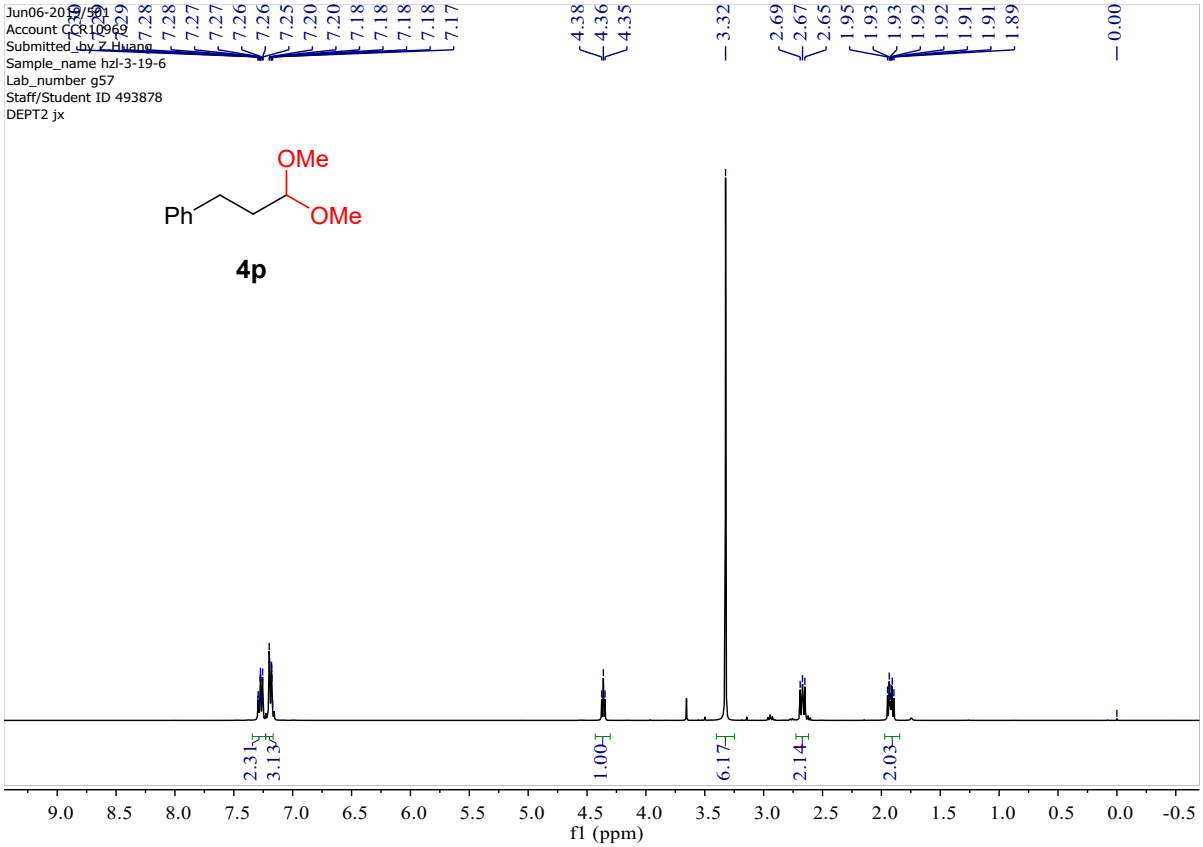

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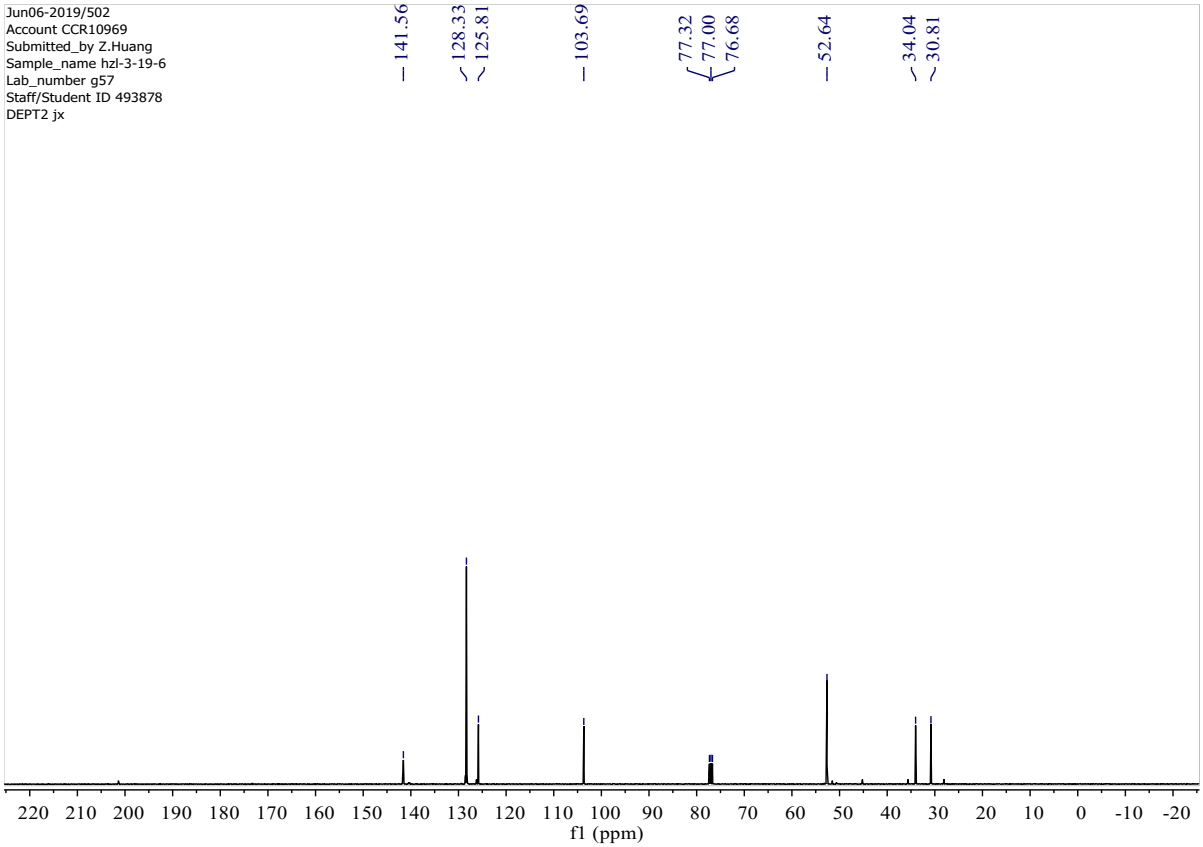

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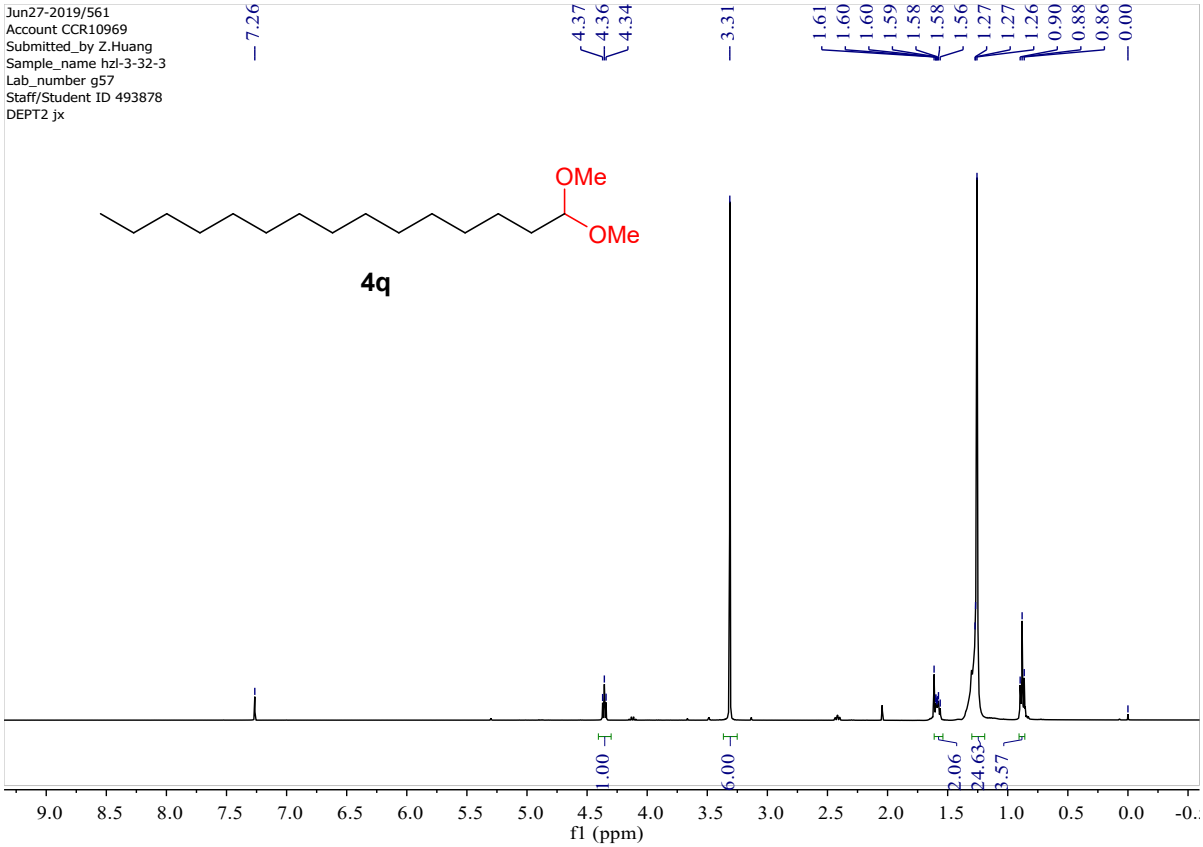

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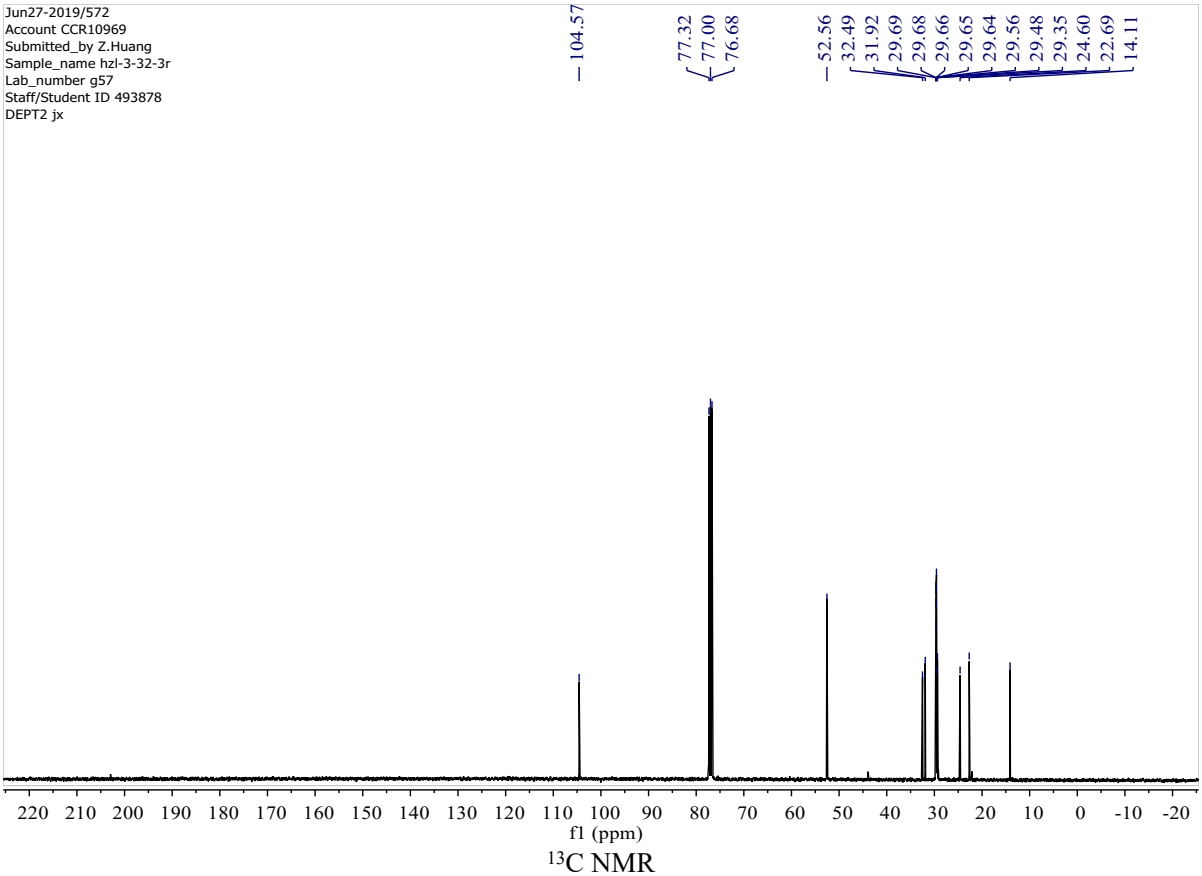

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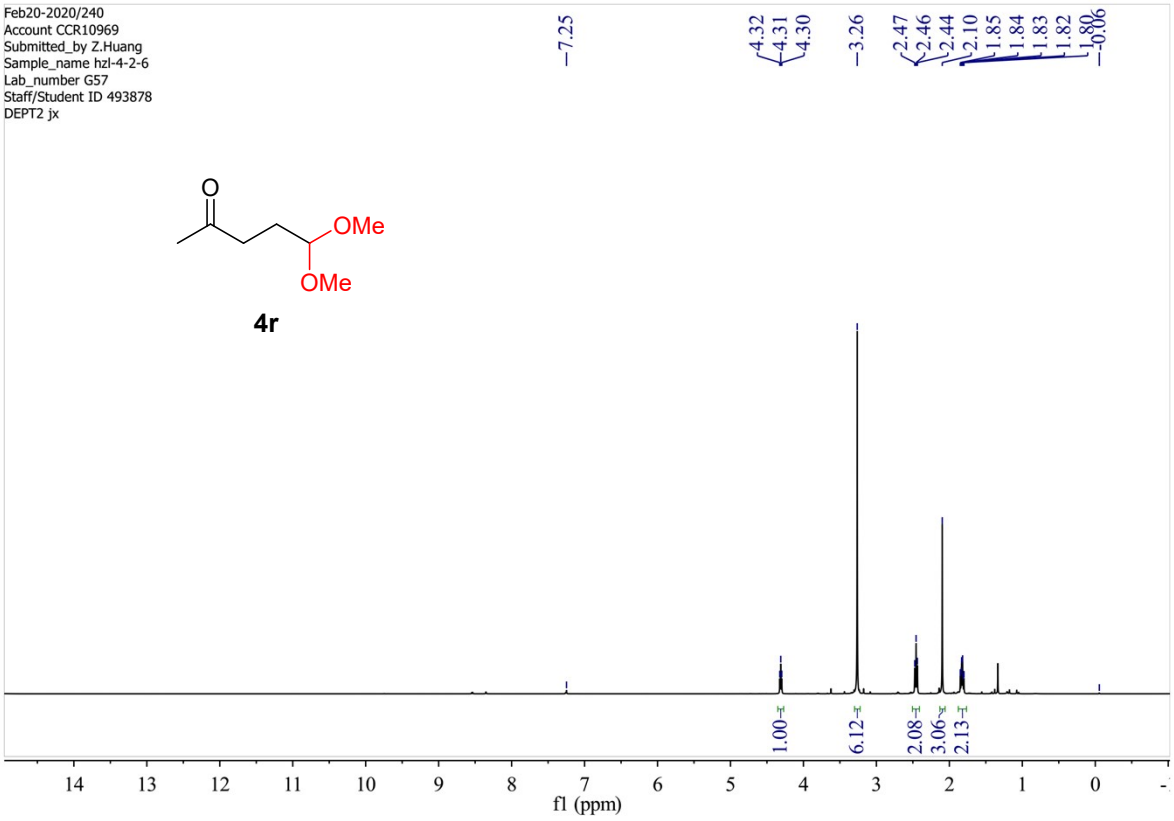

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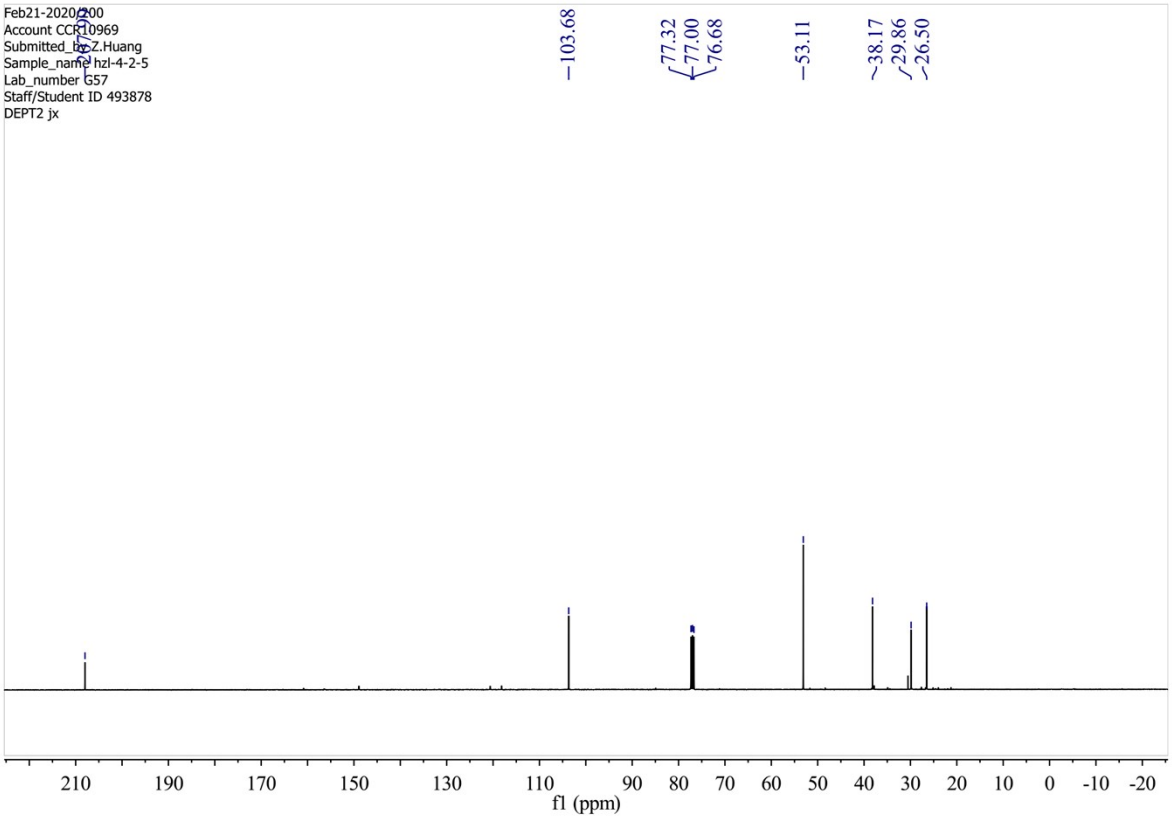

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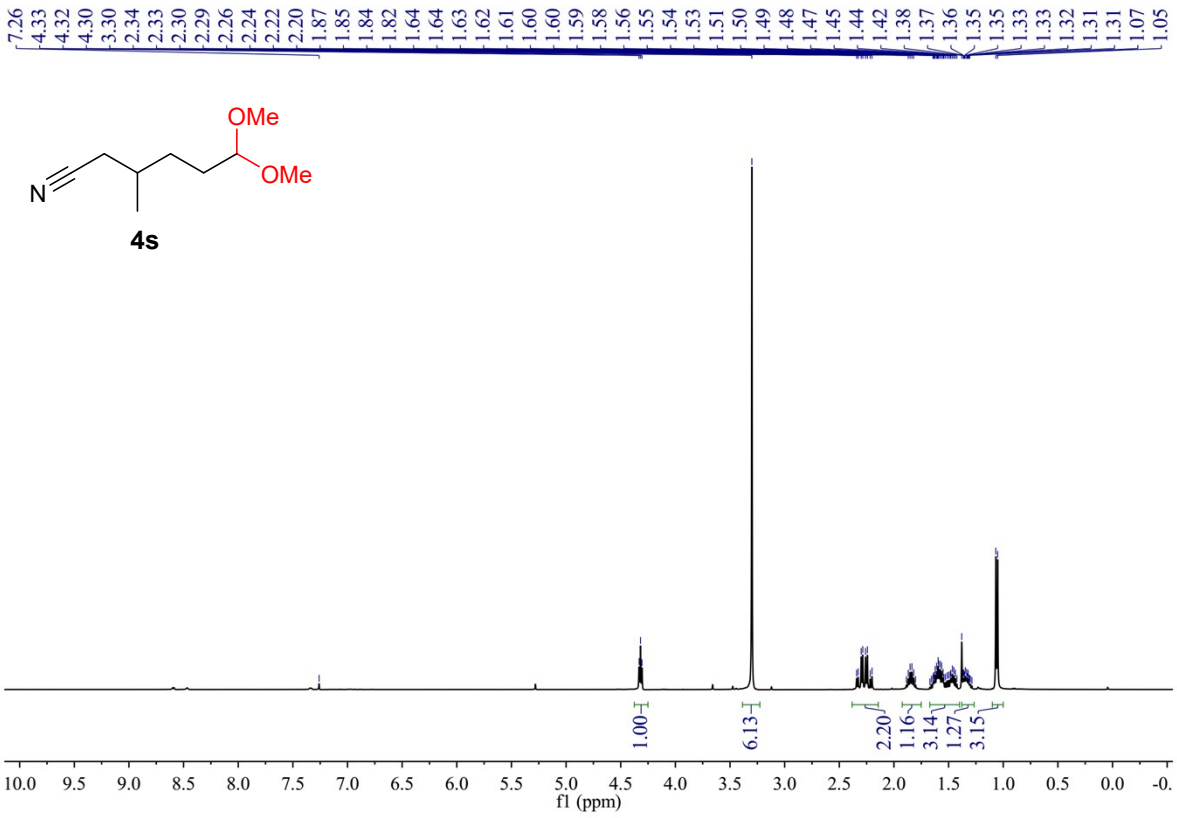

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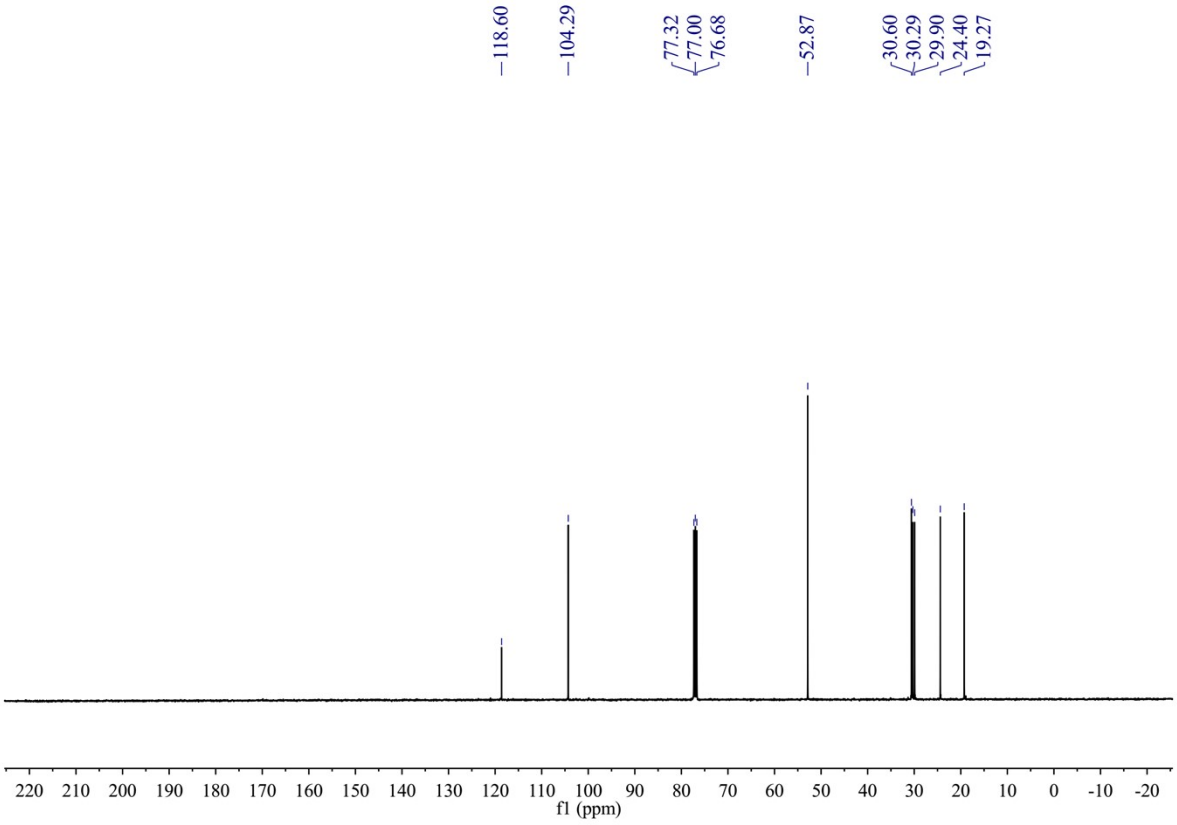

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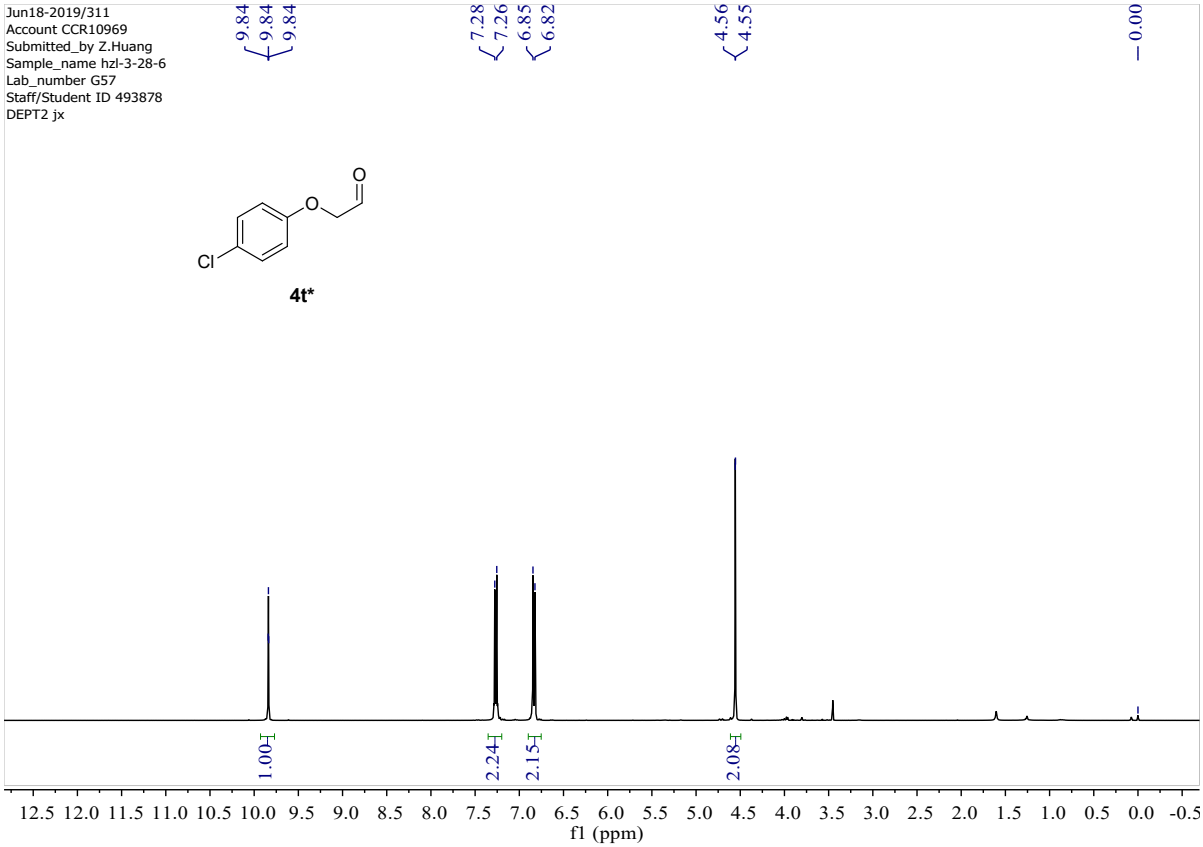

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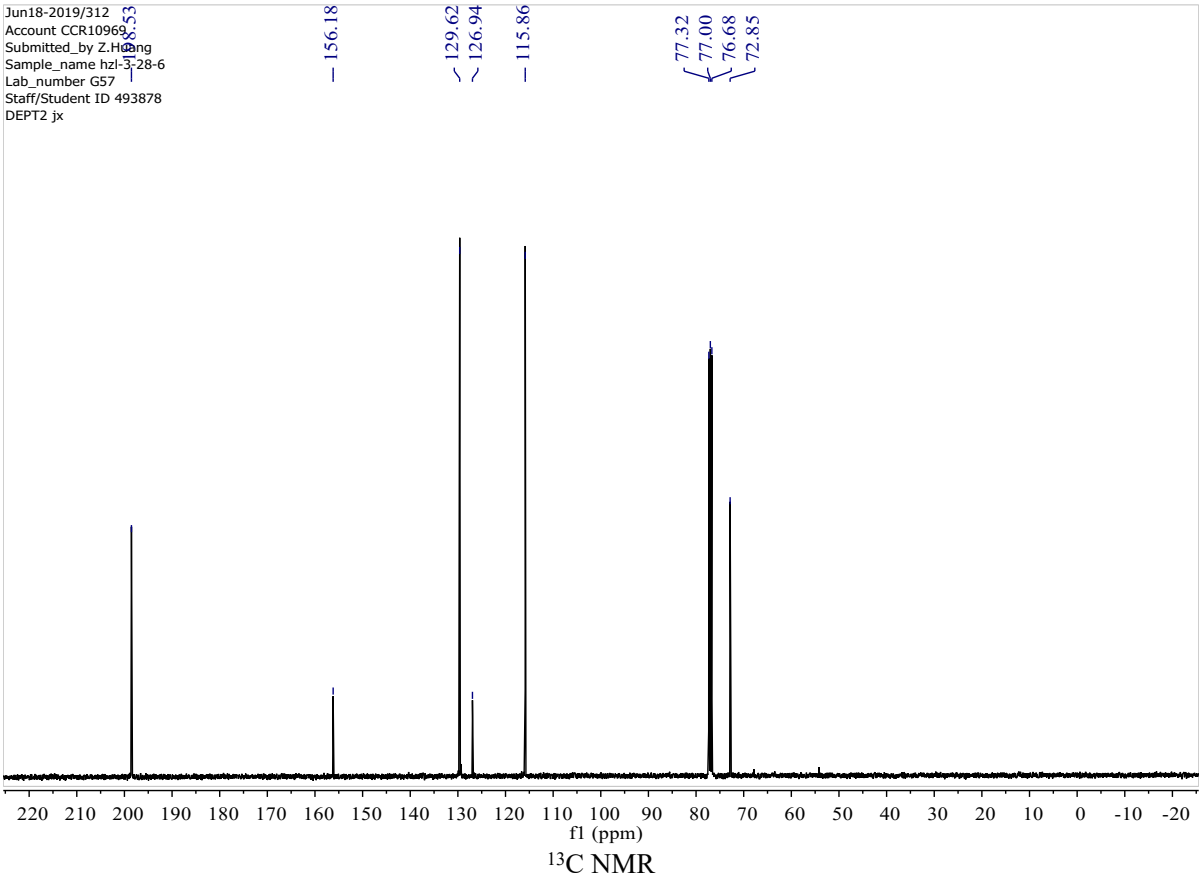

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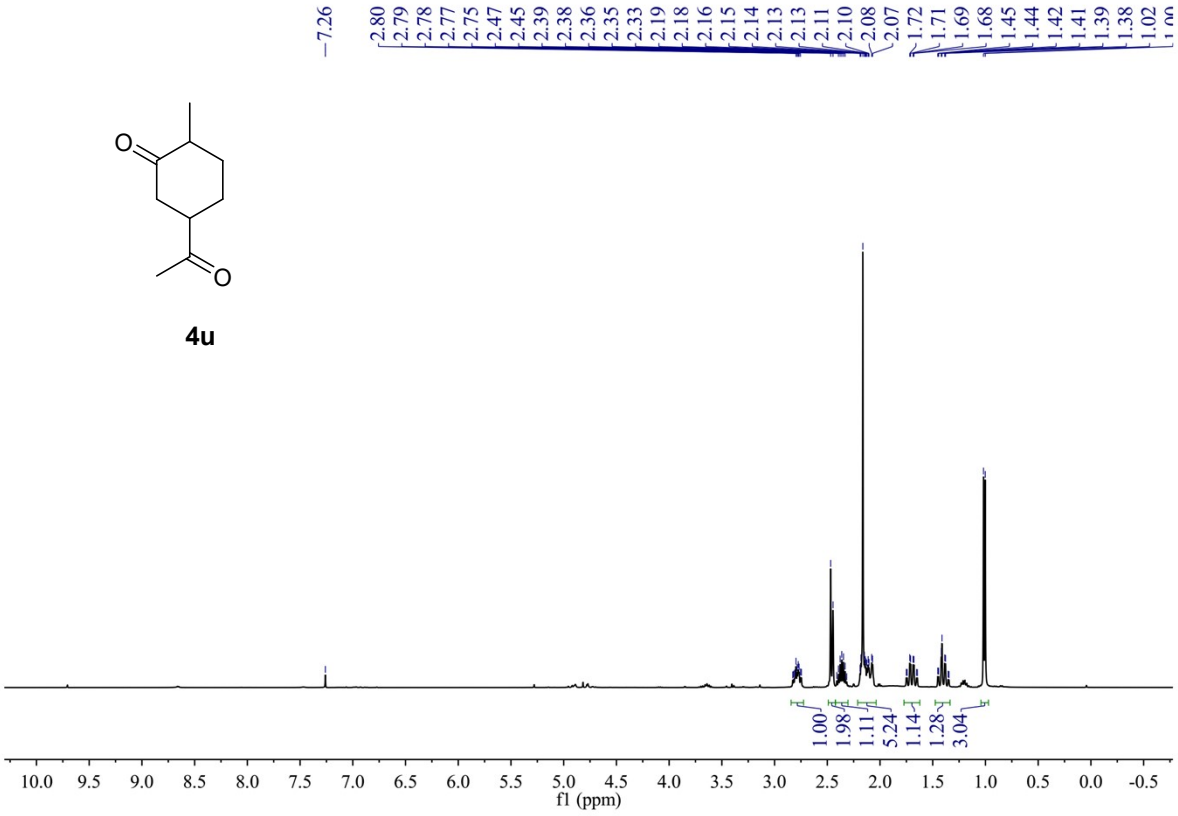

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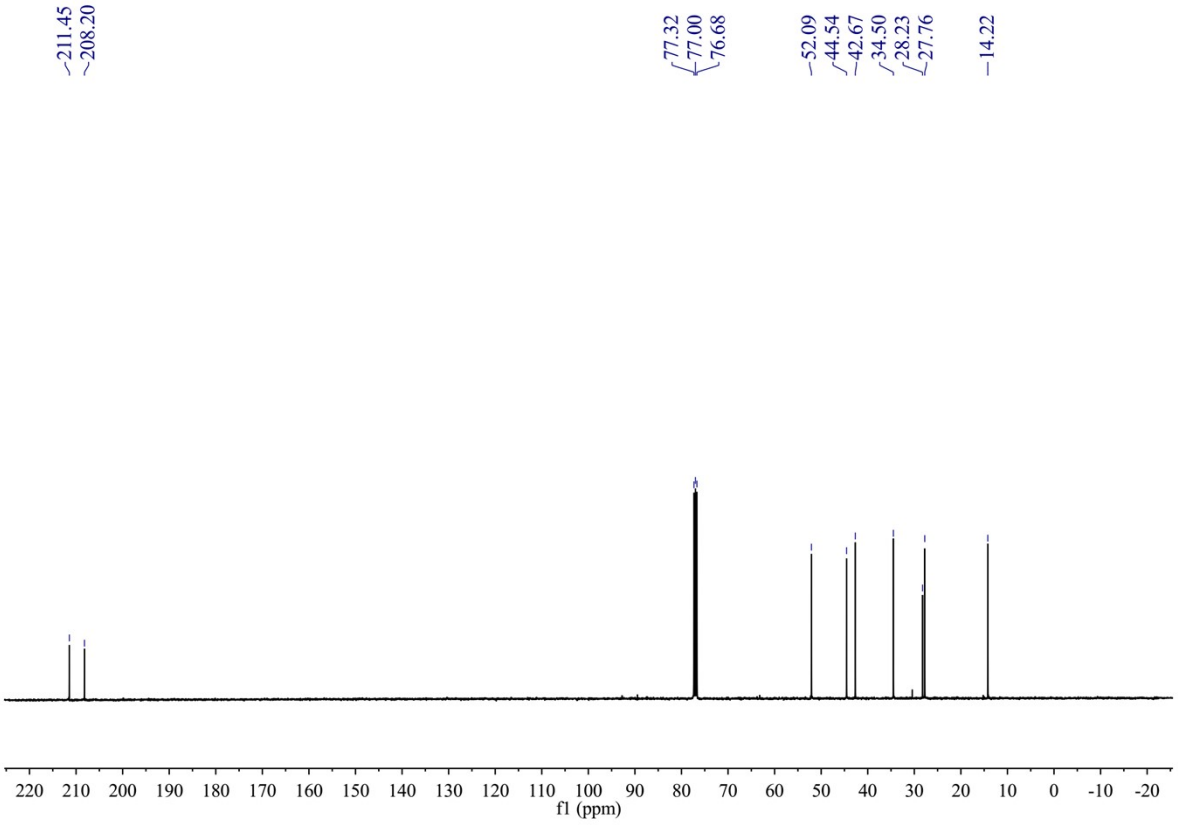

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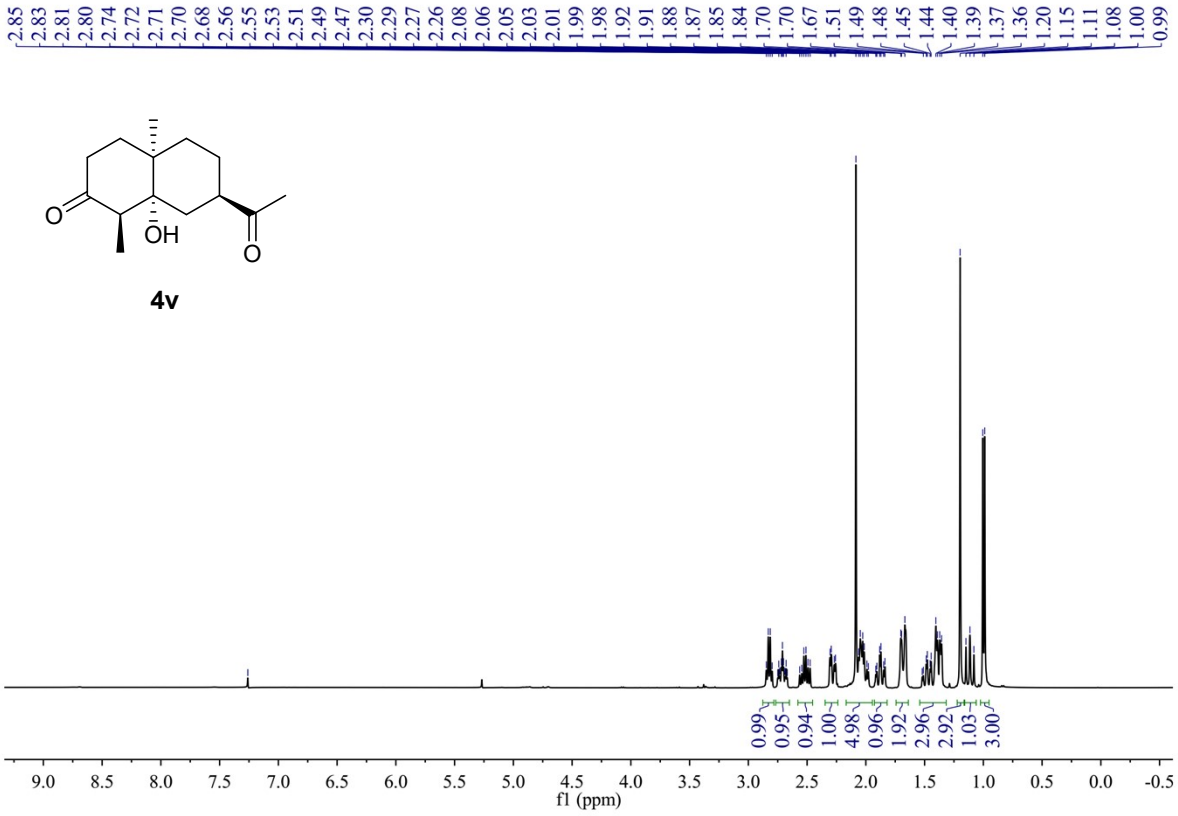

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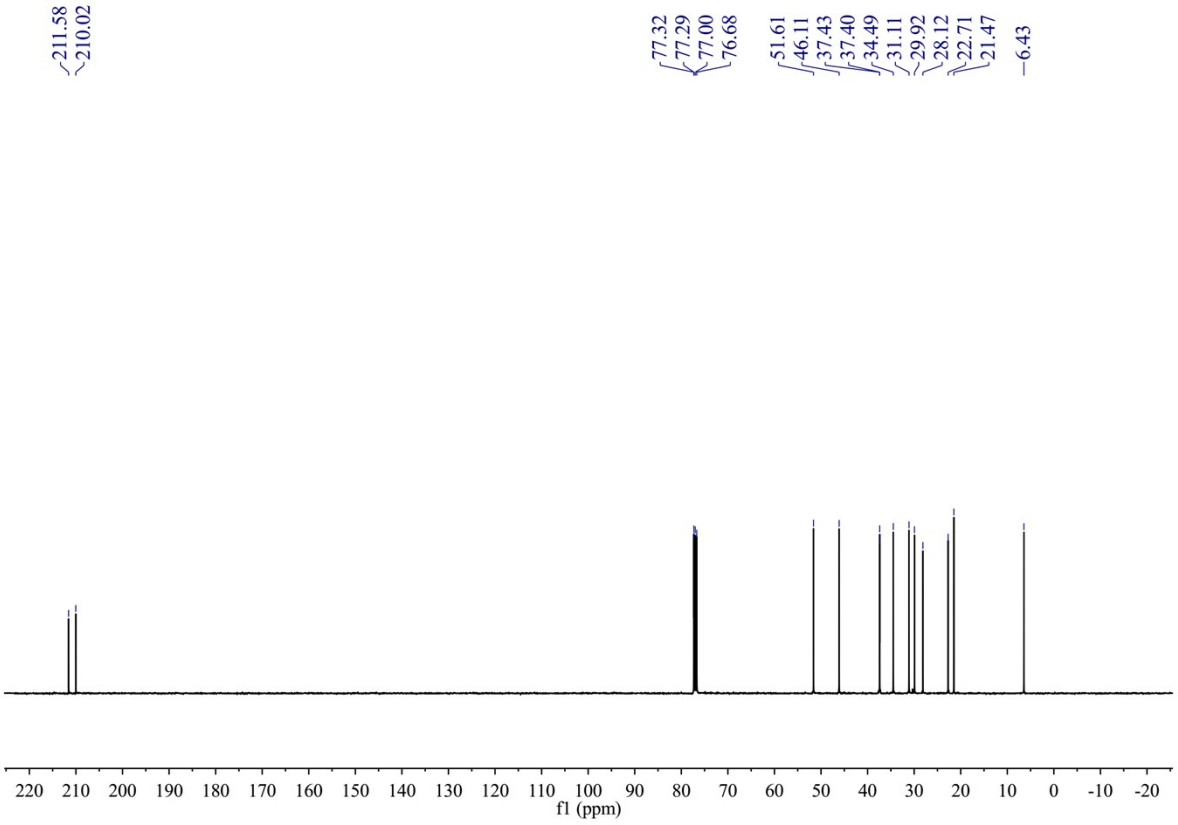

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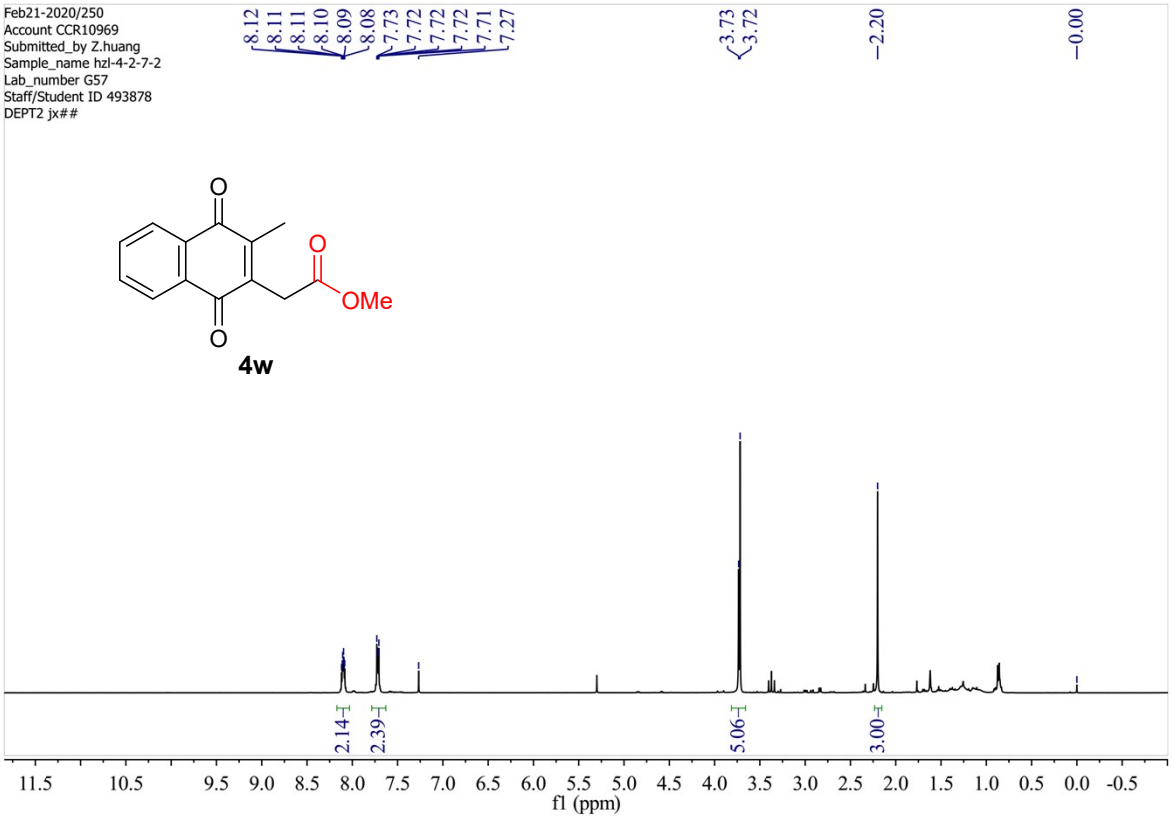

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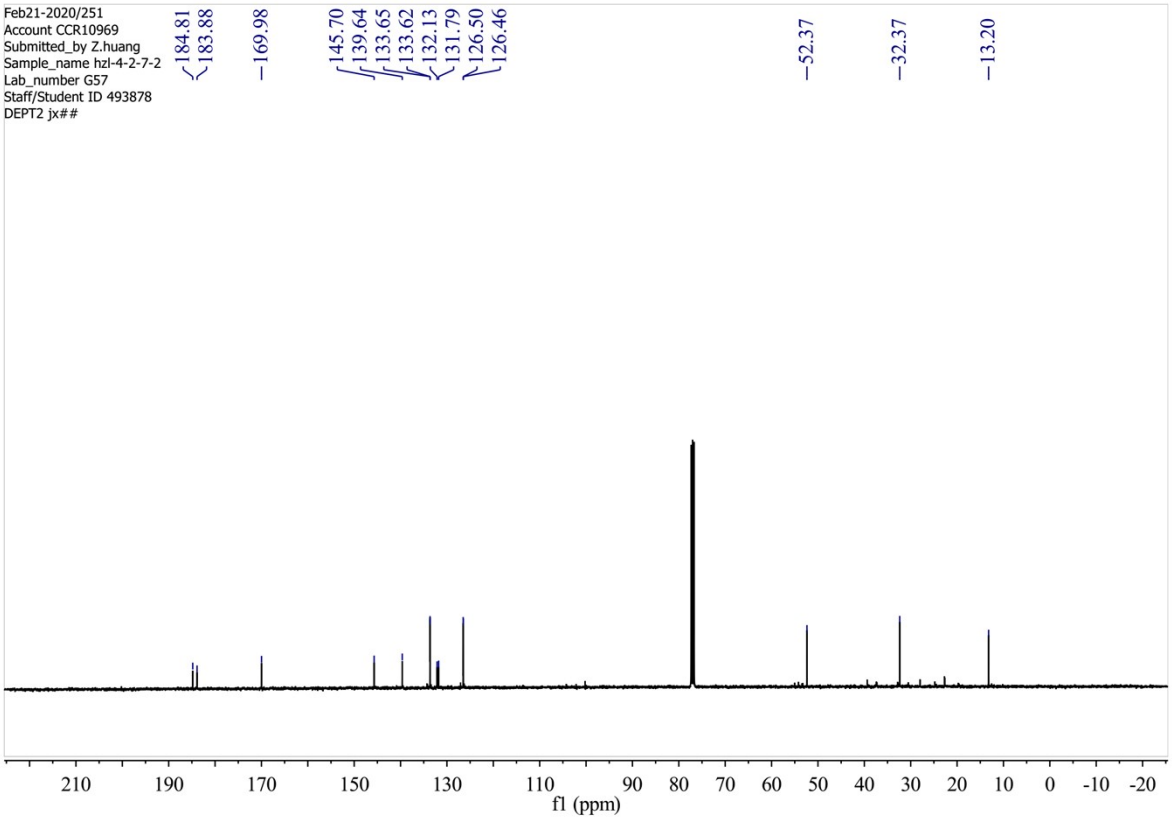

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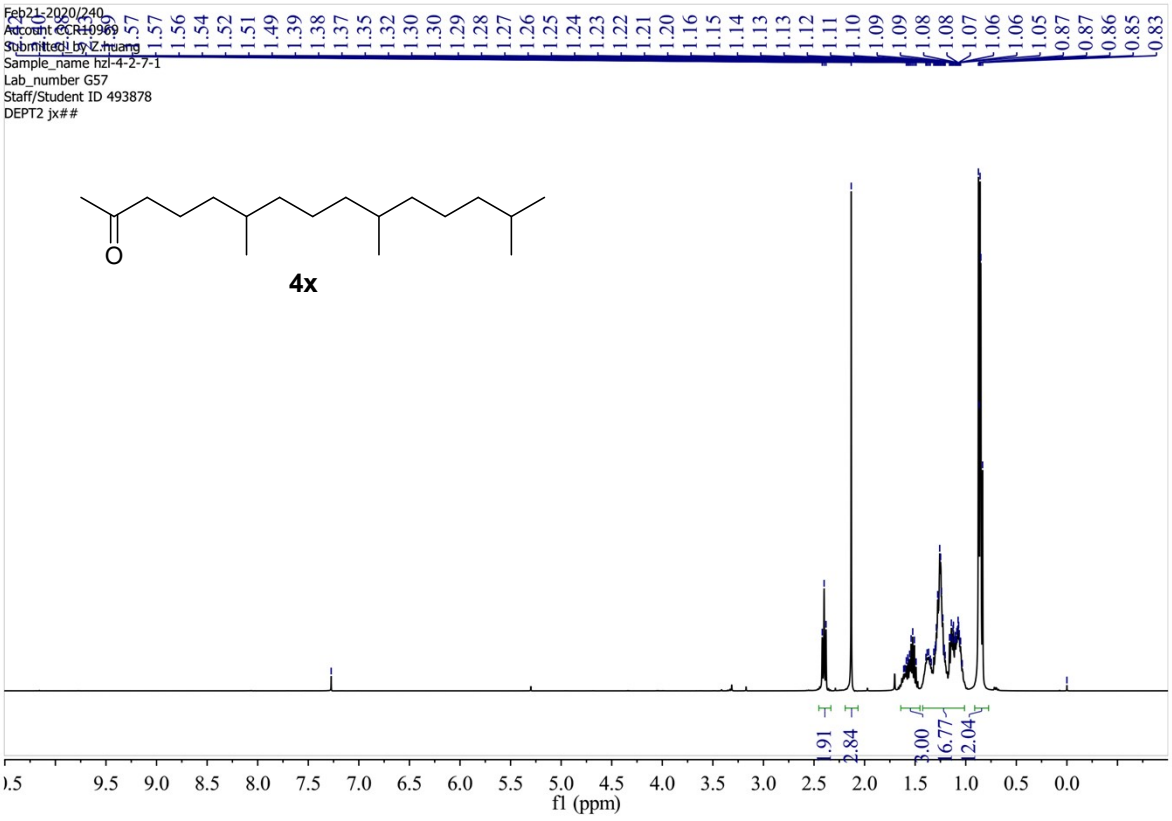

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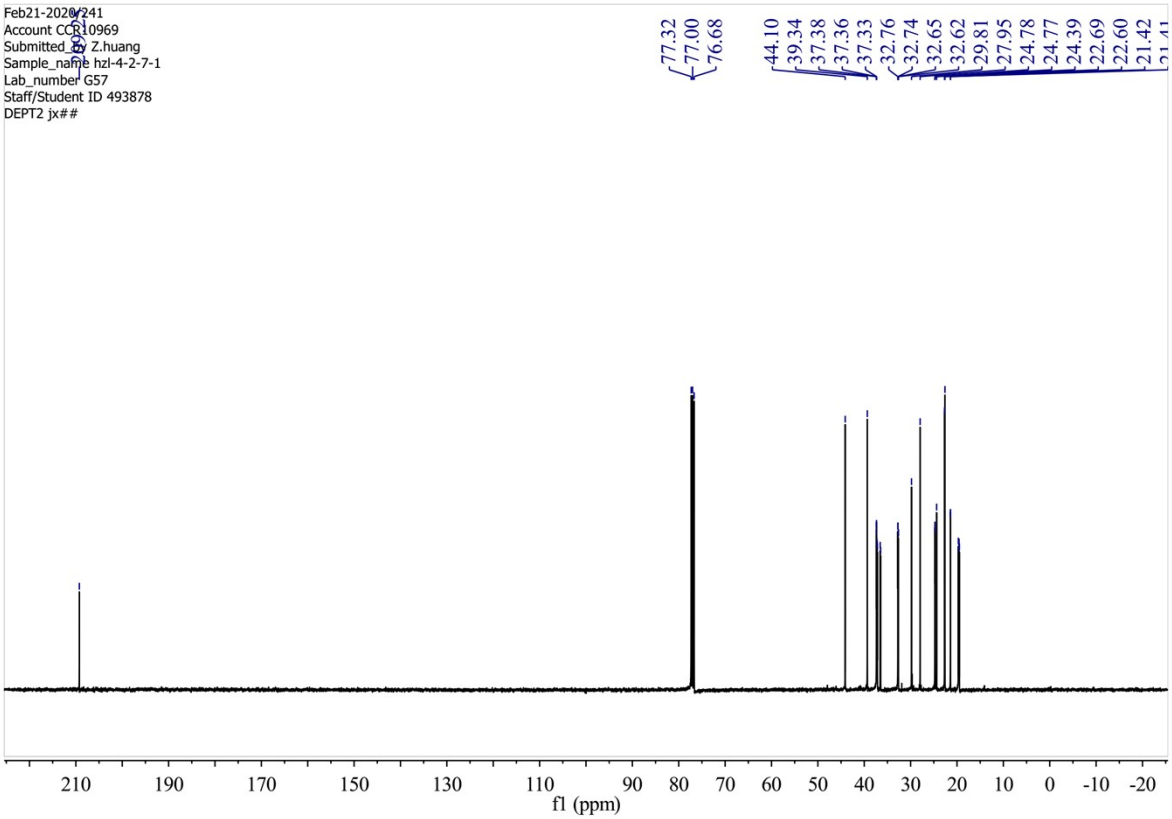

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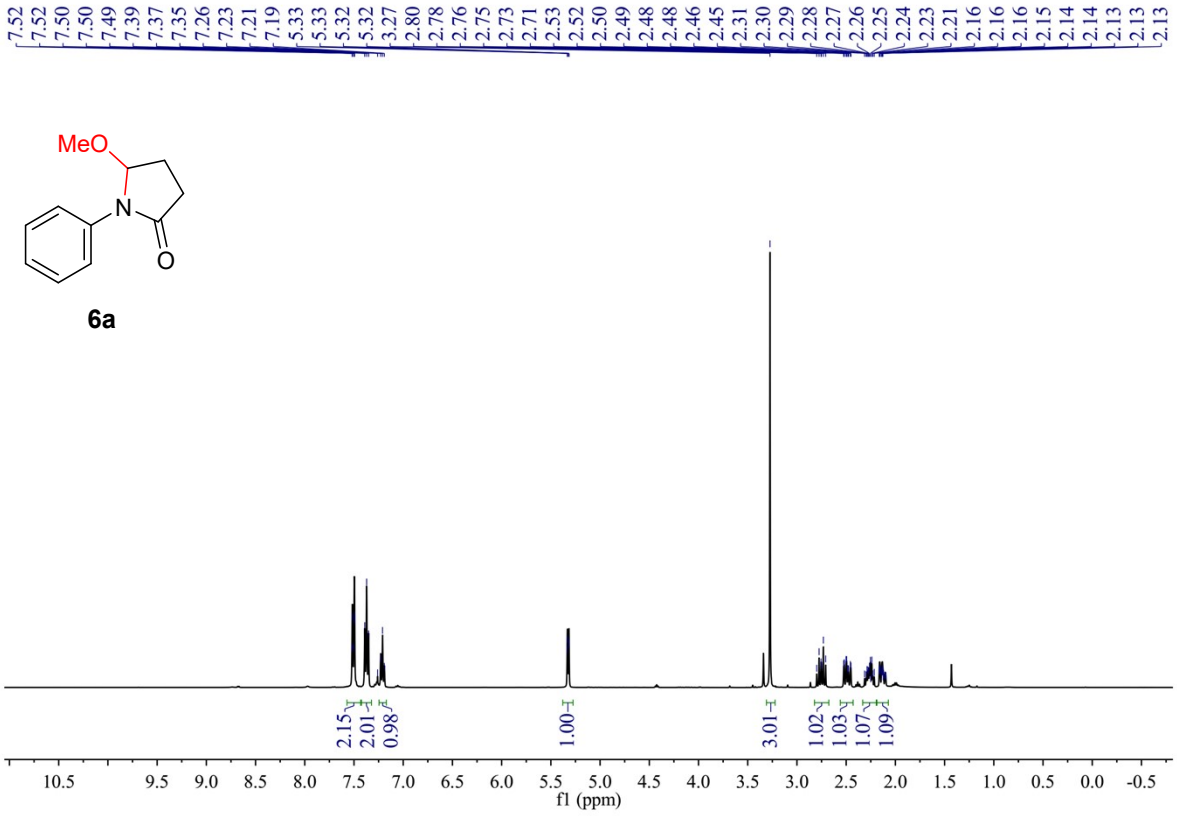

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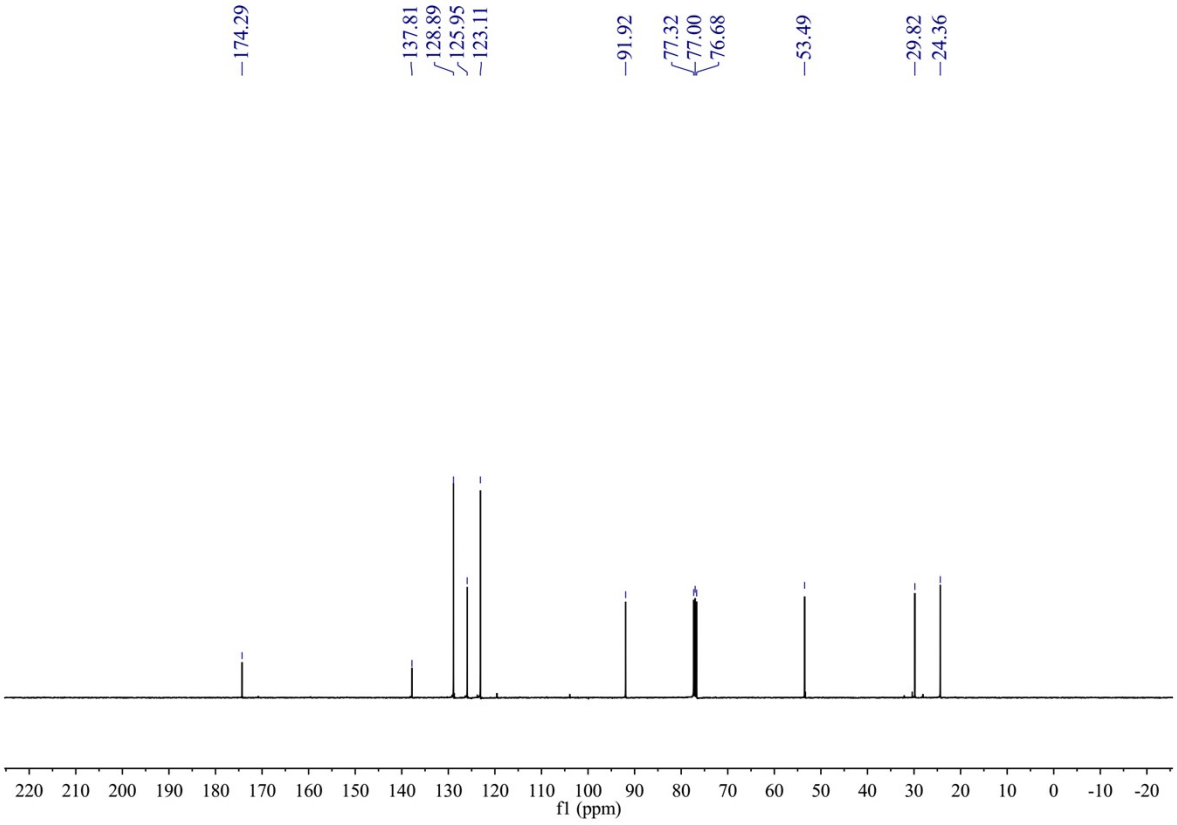

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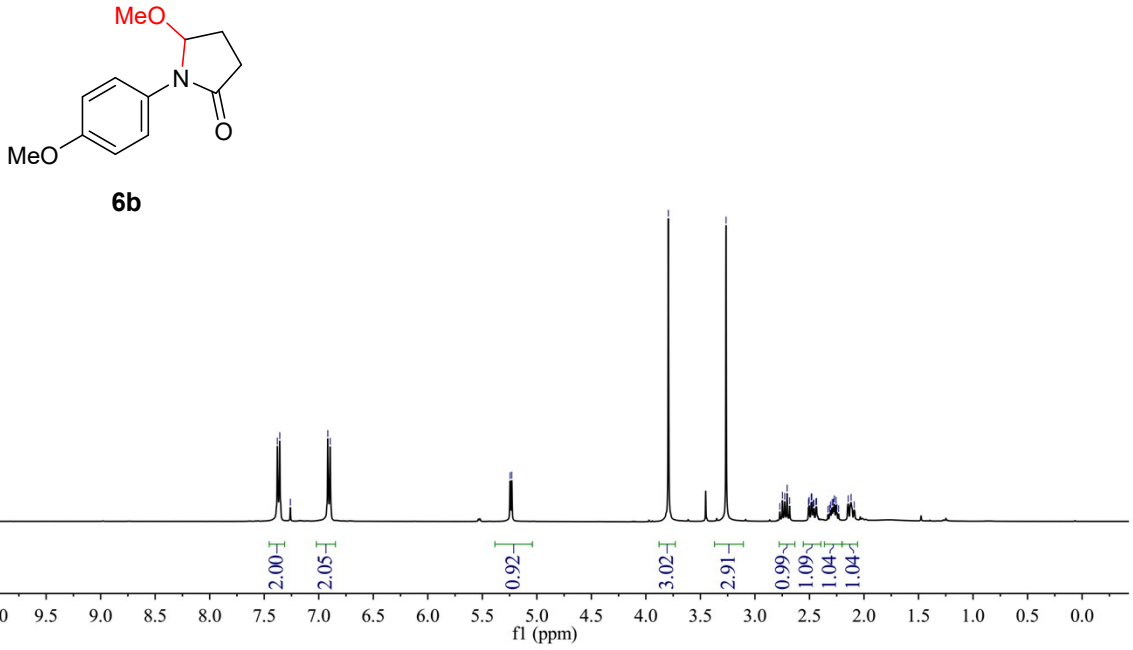

6b

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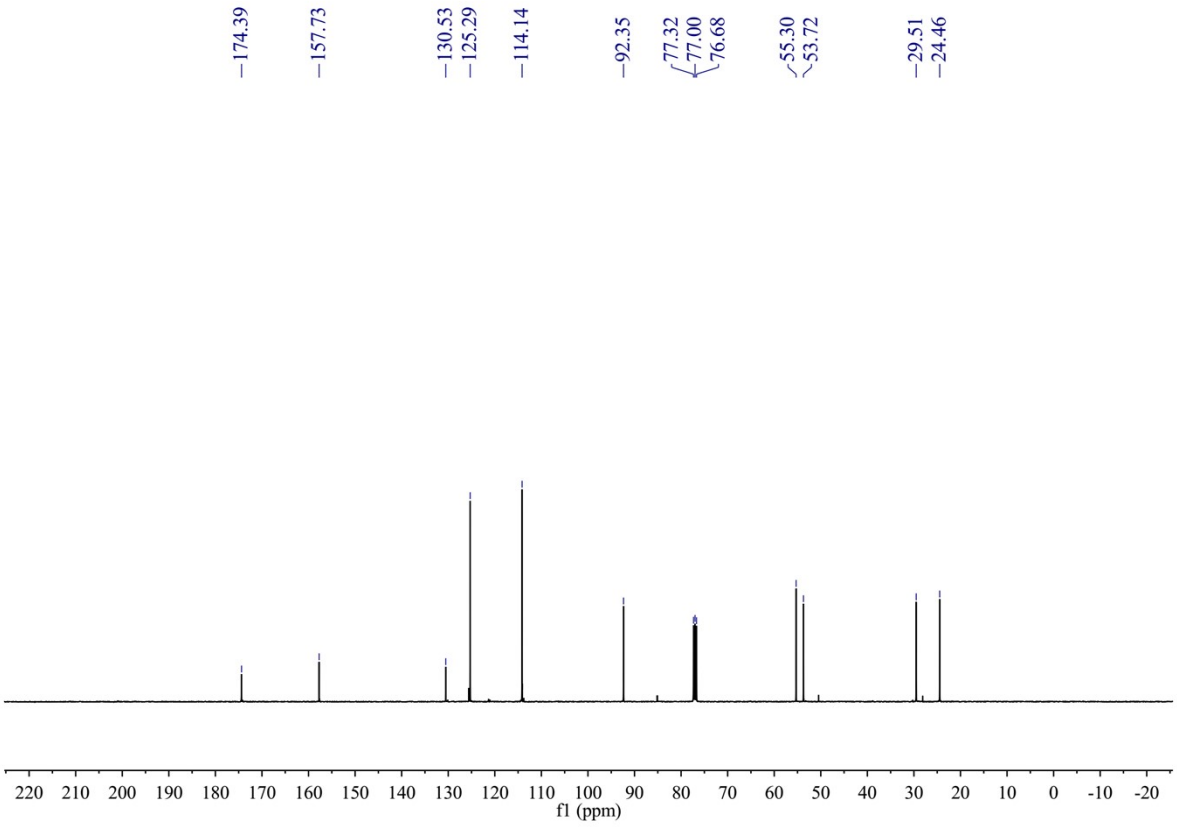

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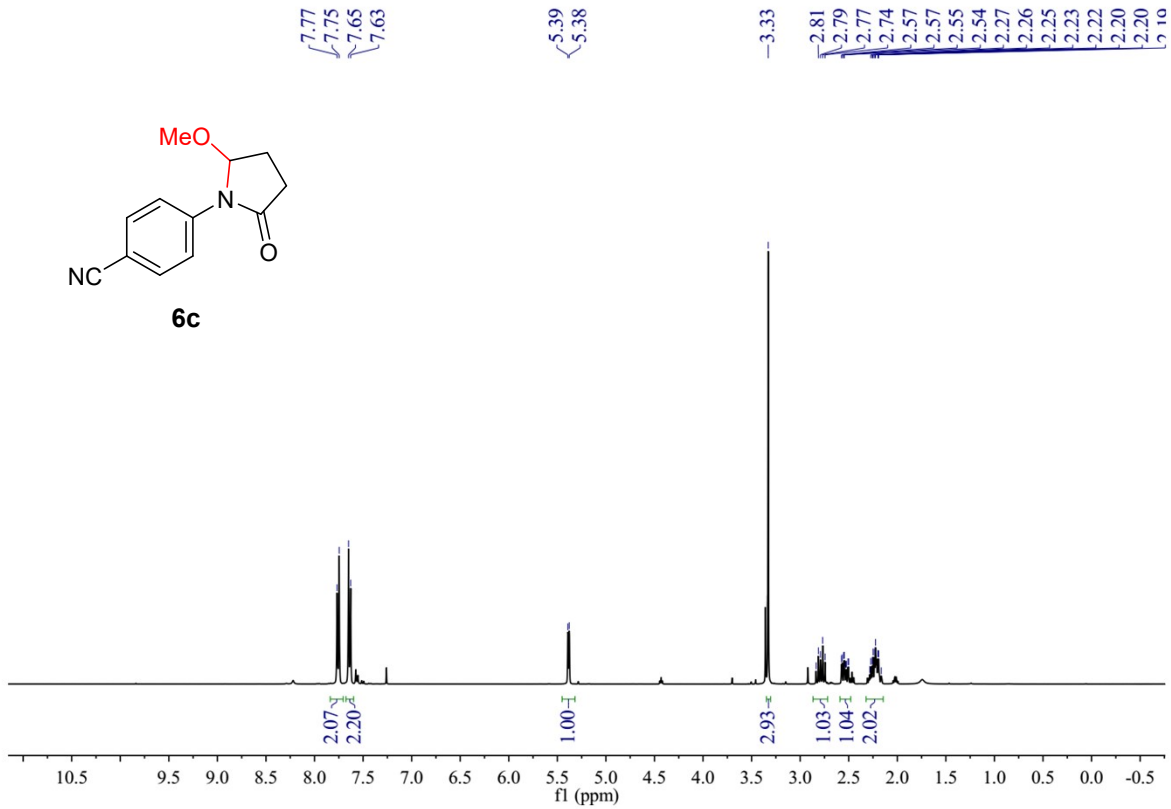

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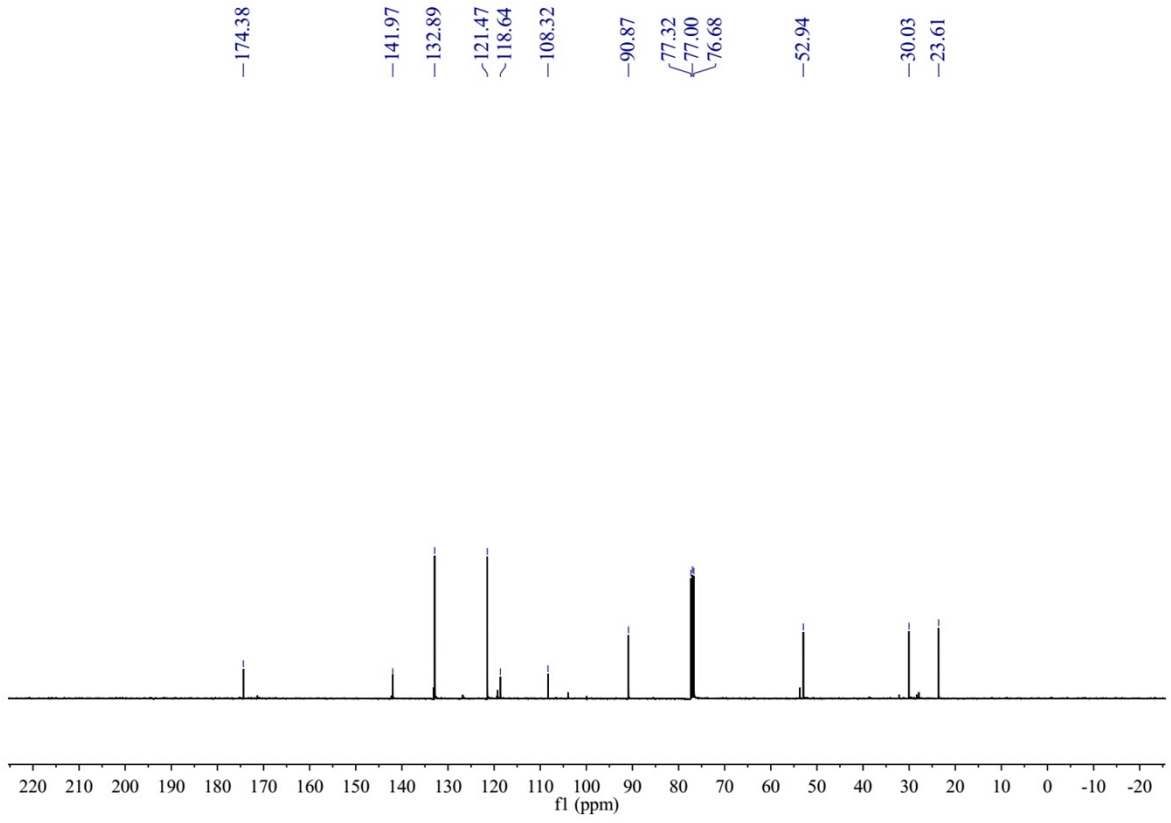

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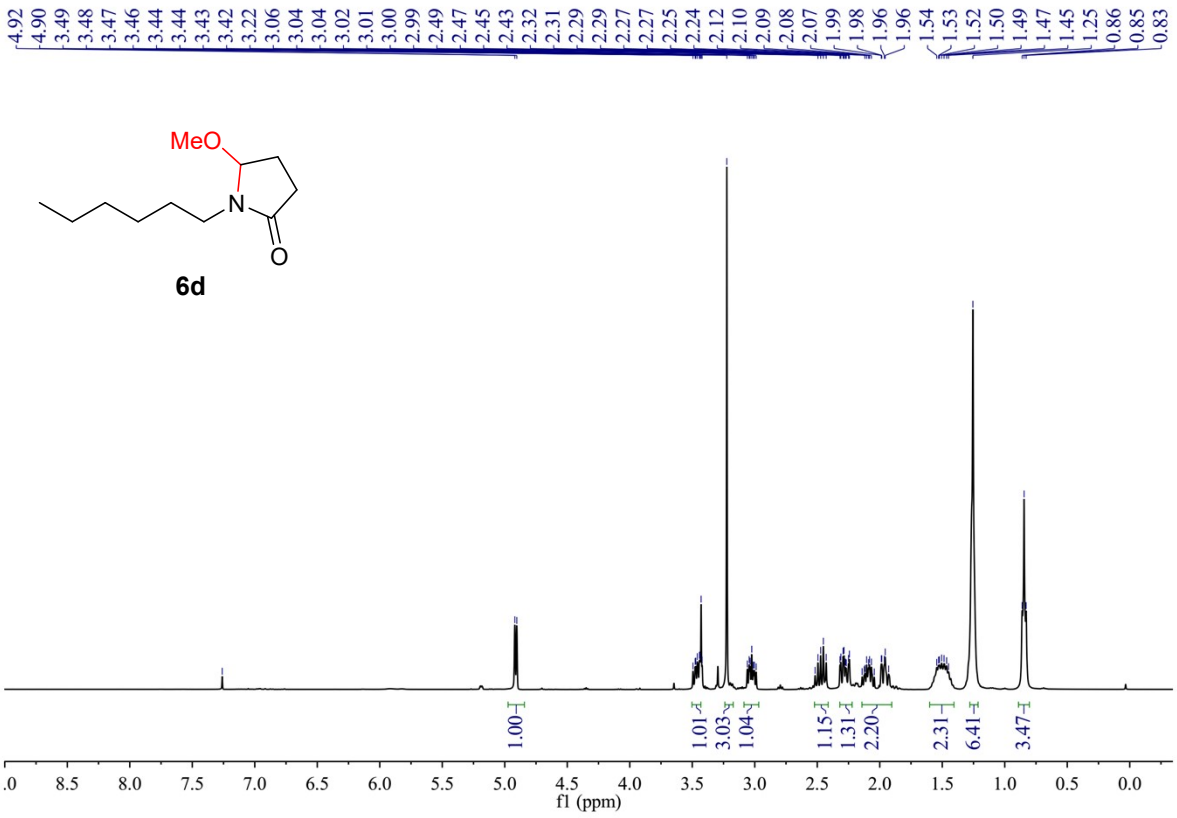

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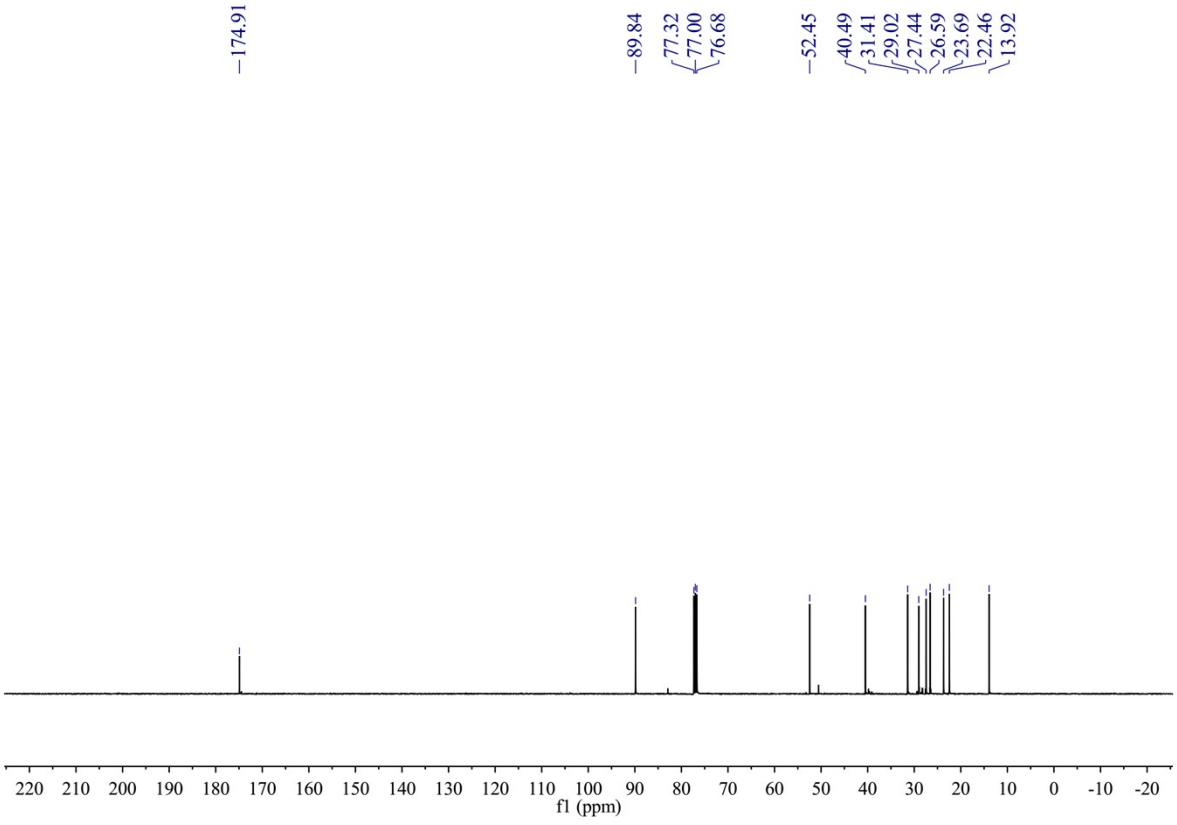

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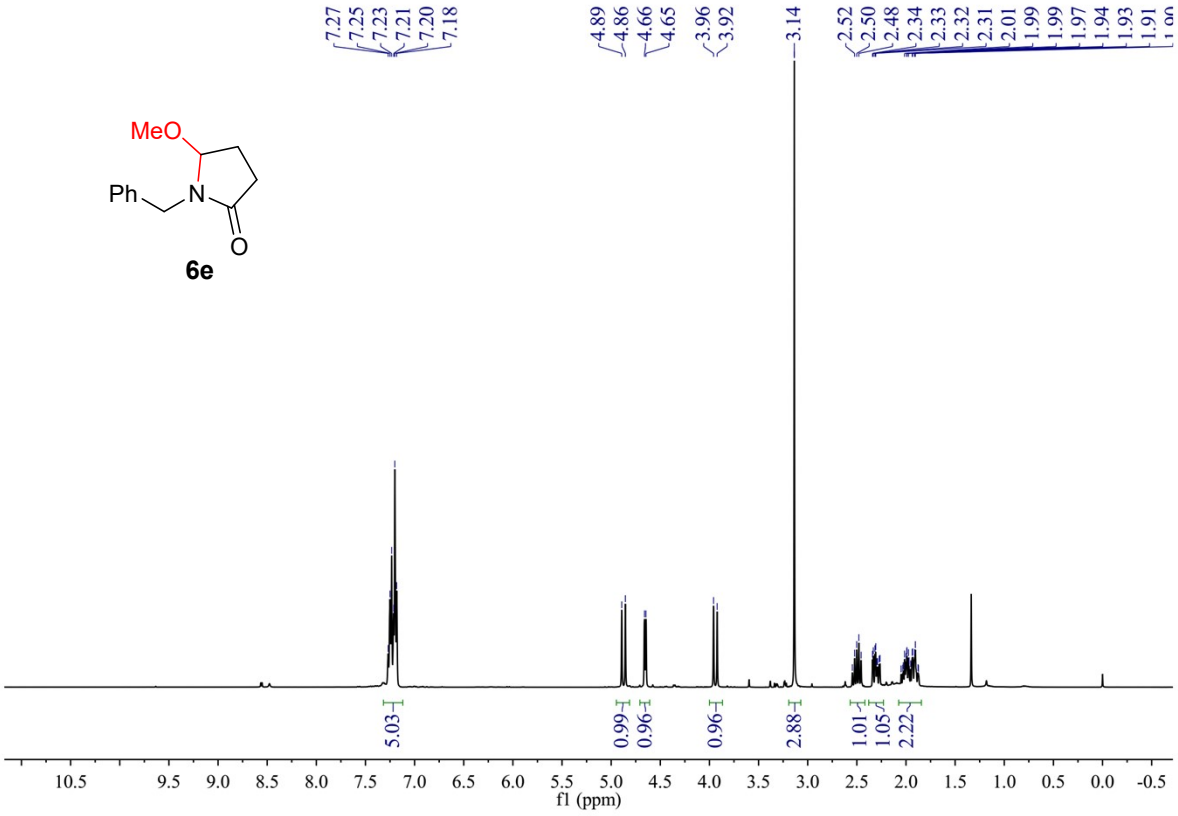

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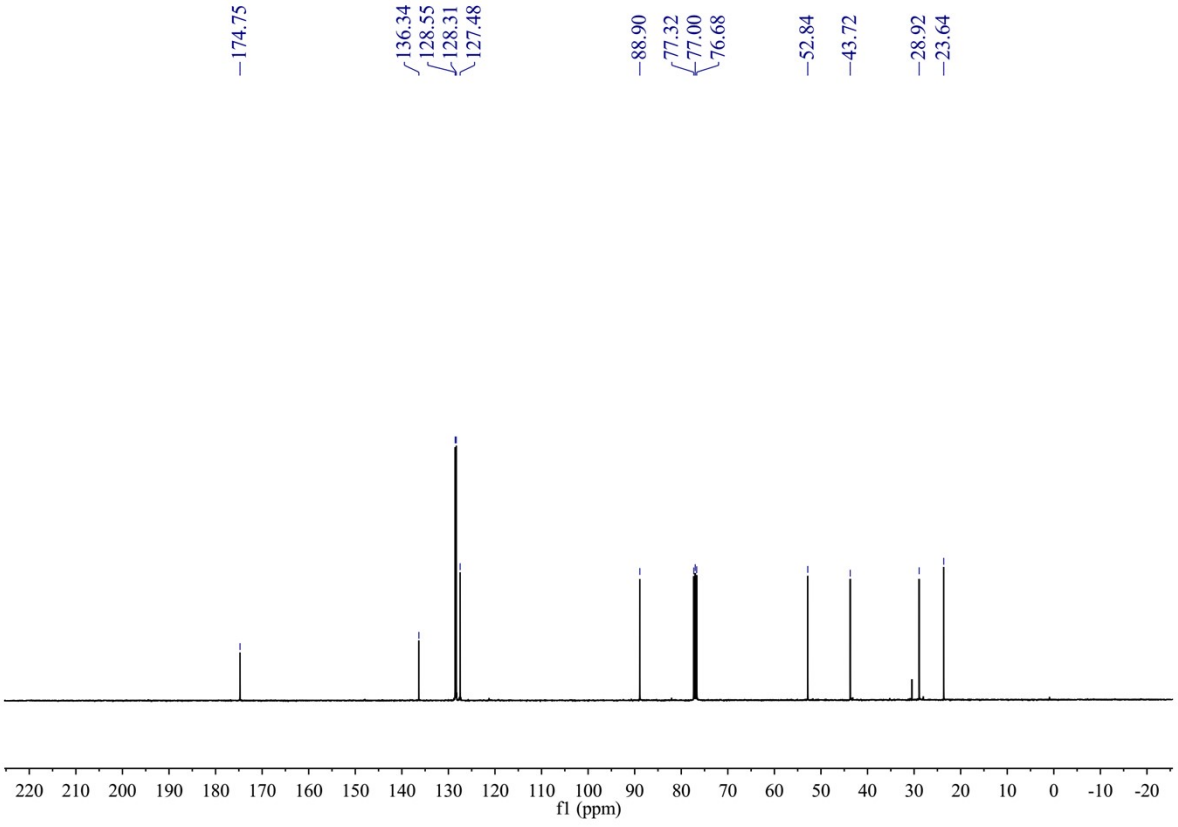

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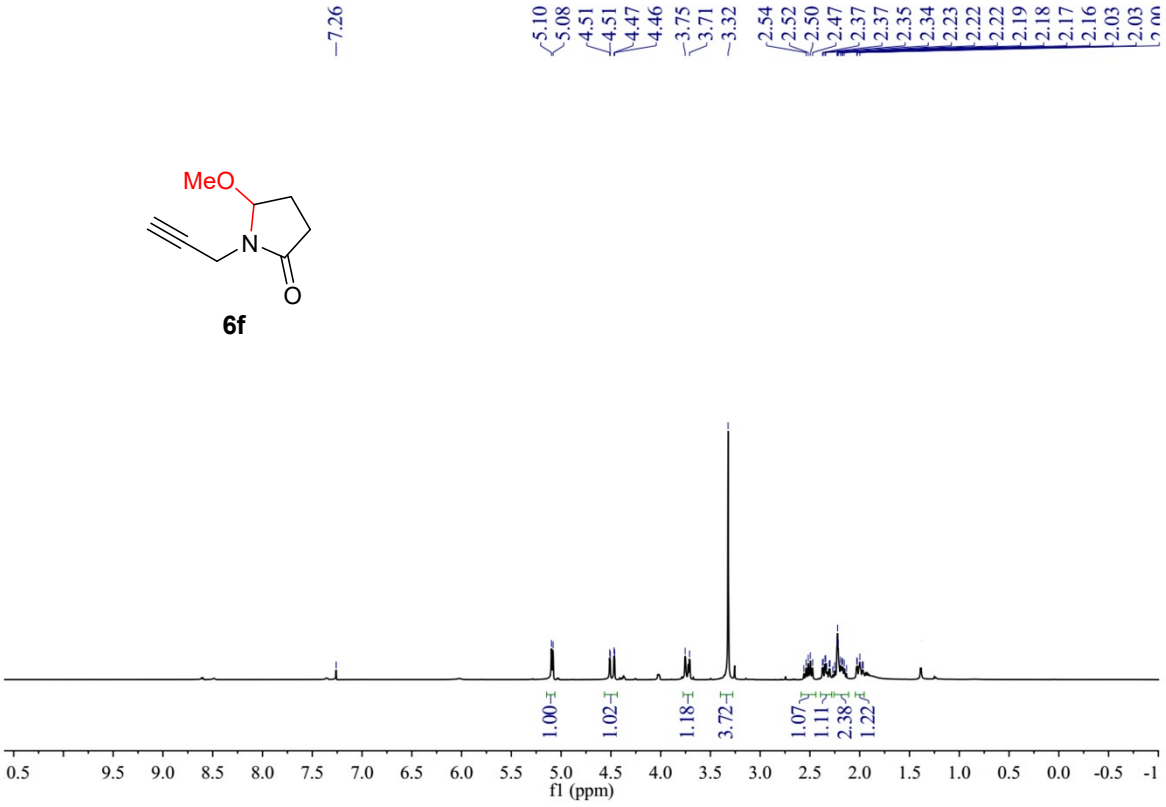

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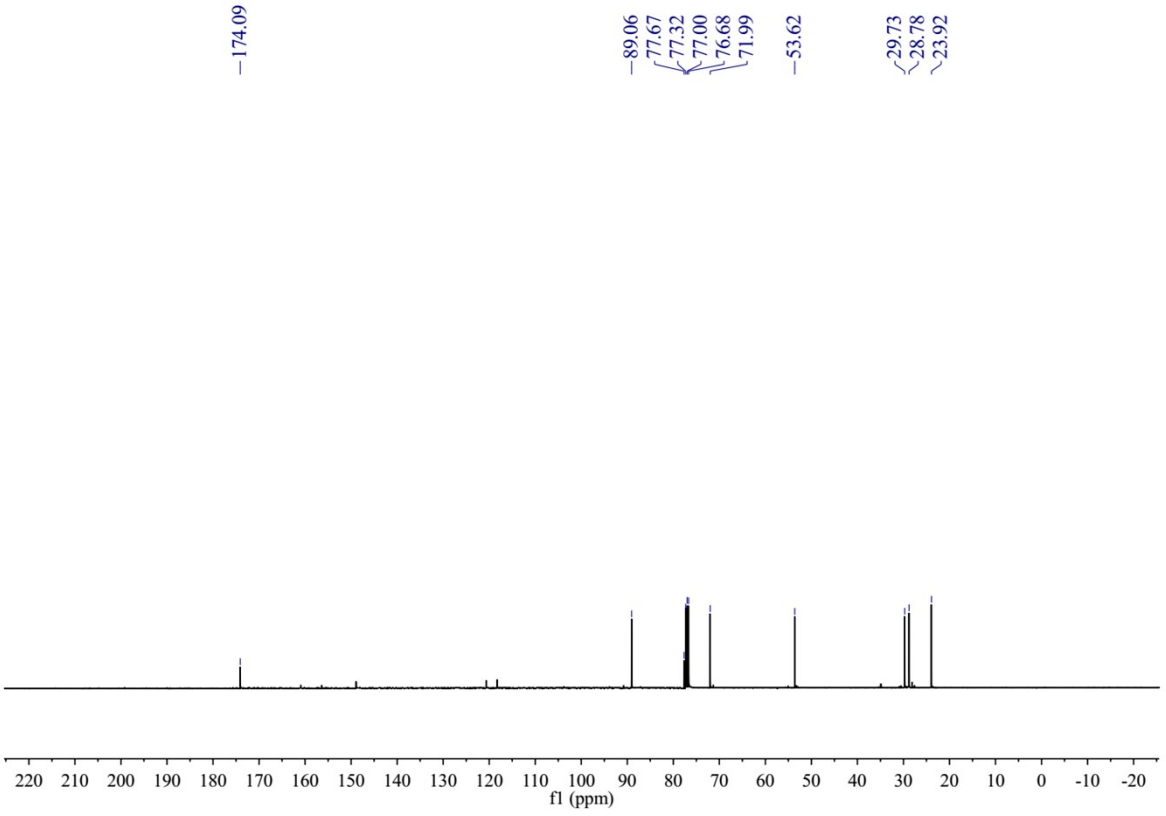

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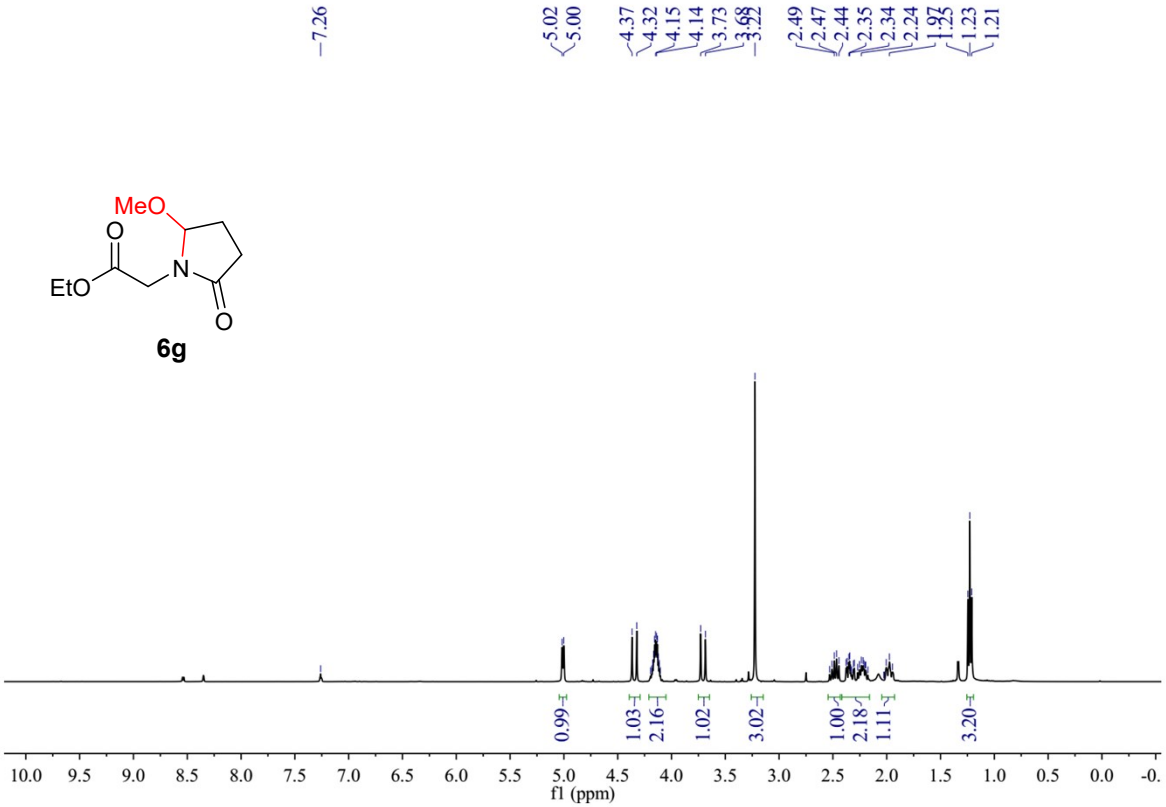

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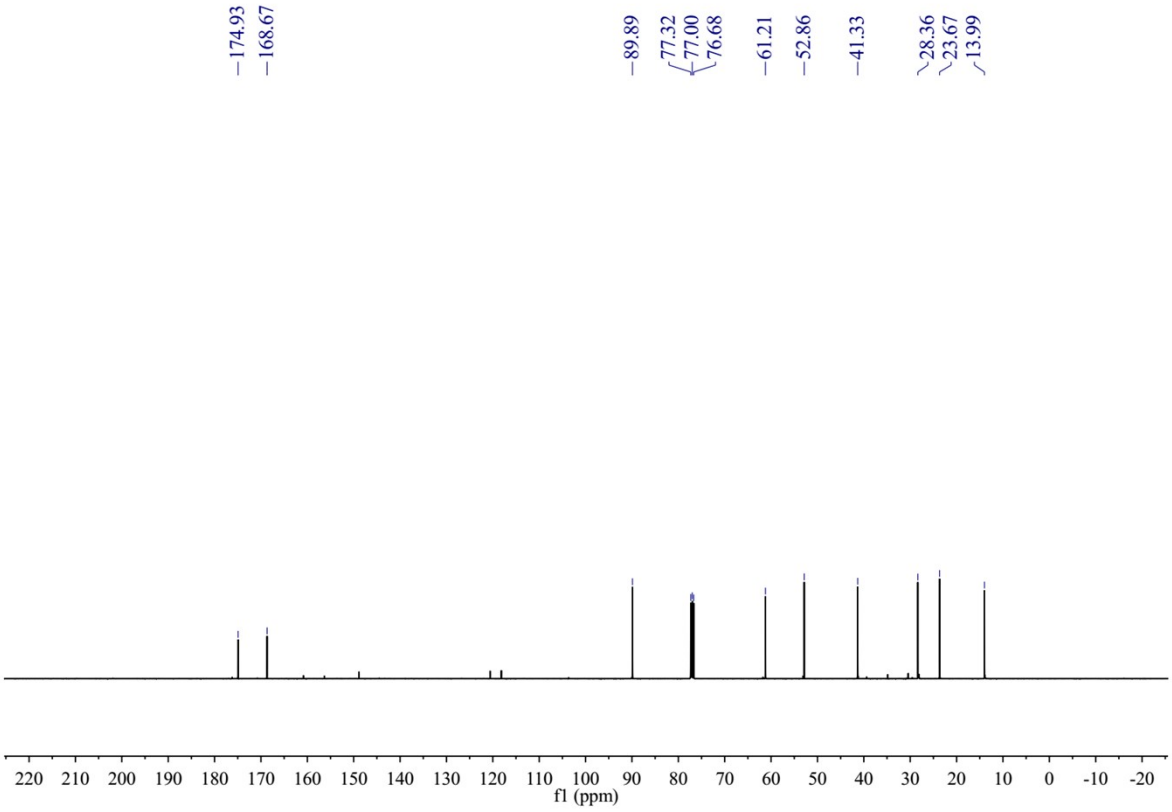

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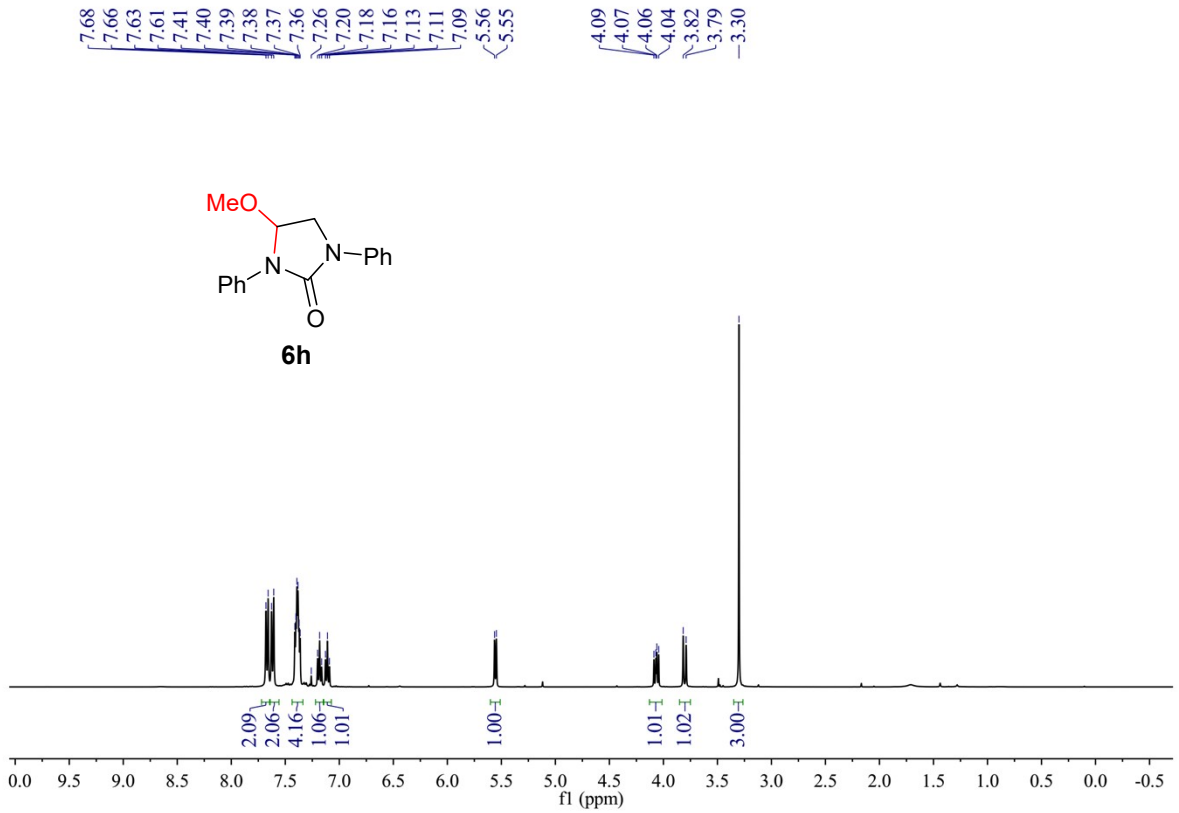
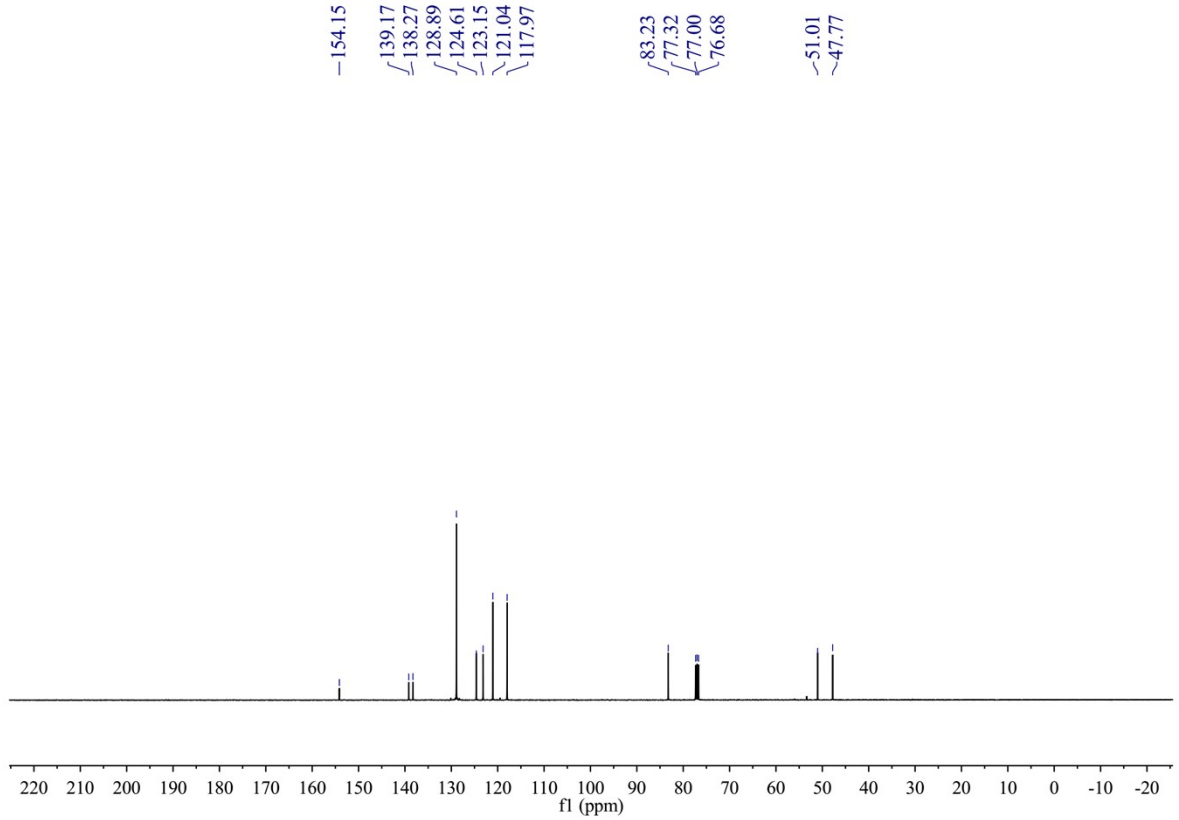


6h

^{1}H NMR



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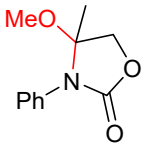

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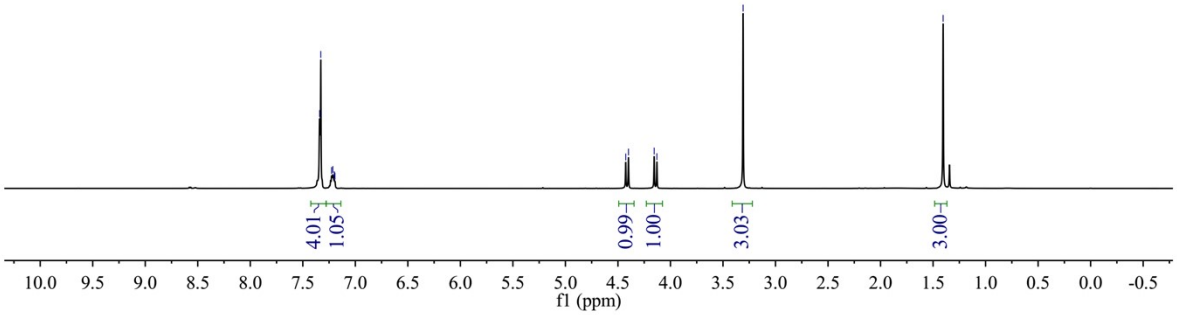

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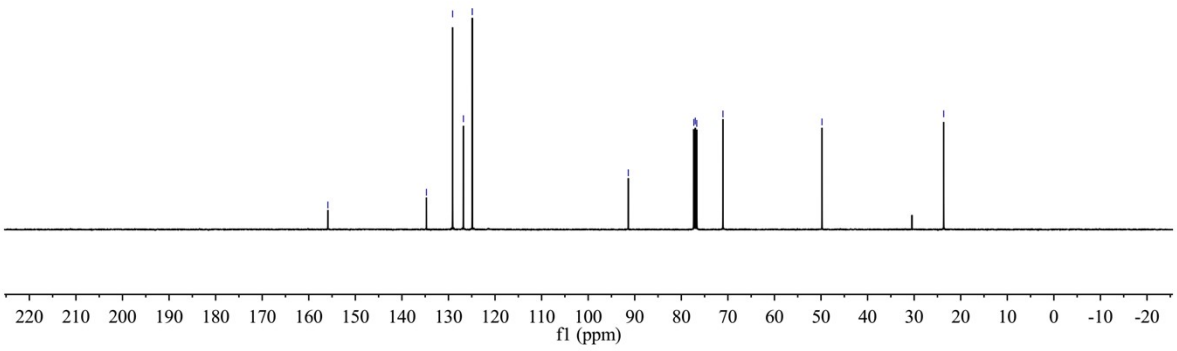

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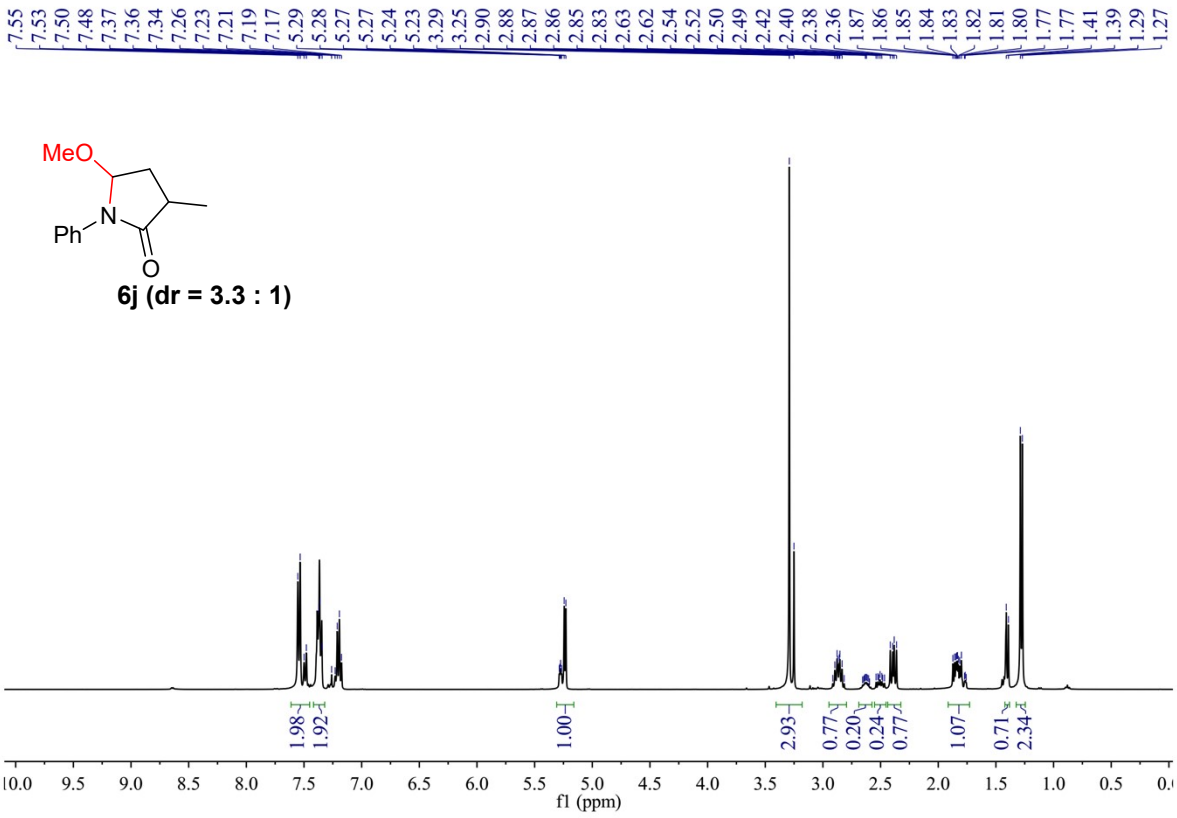

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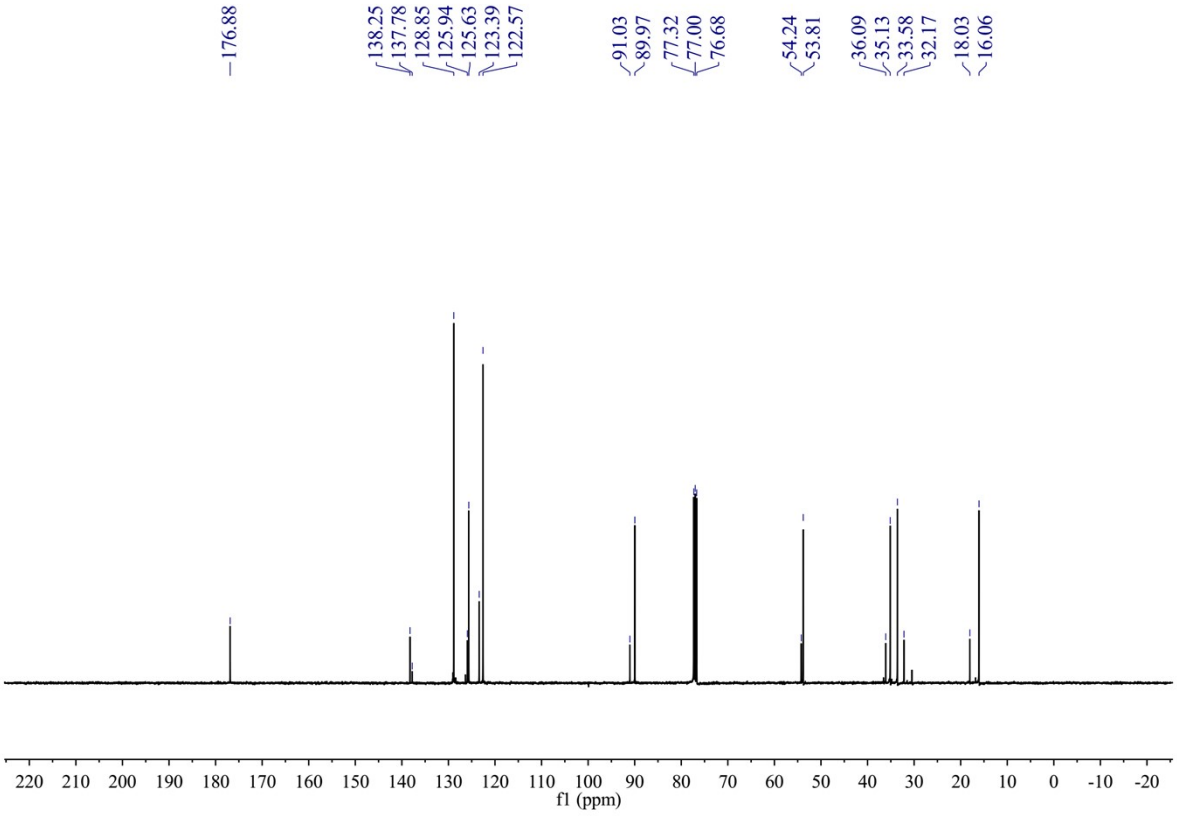

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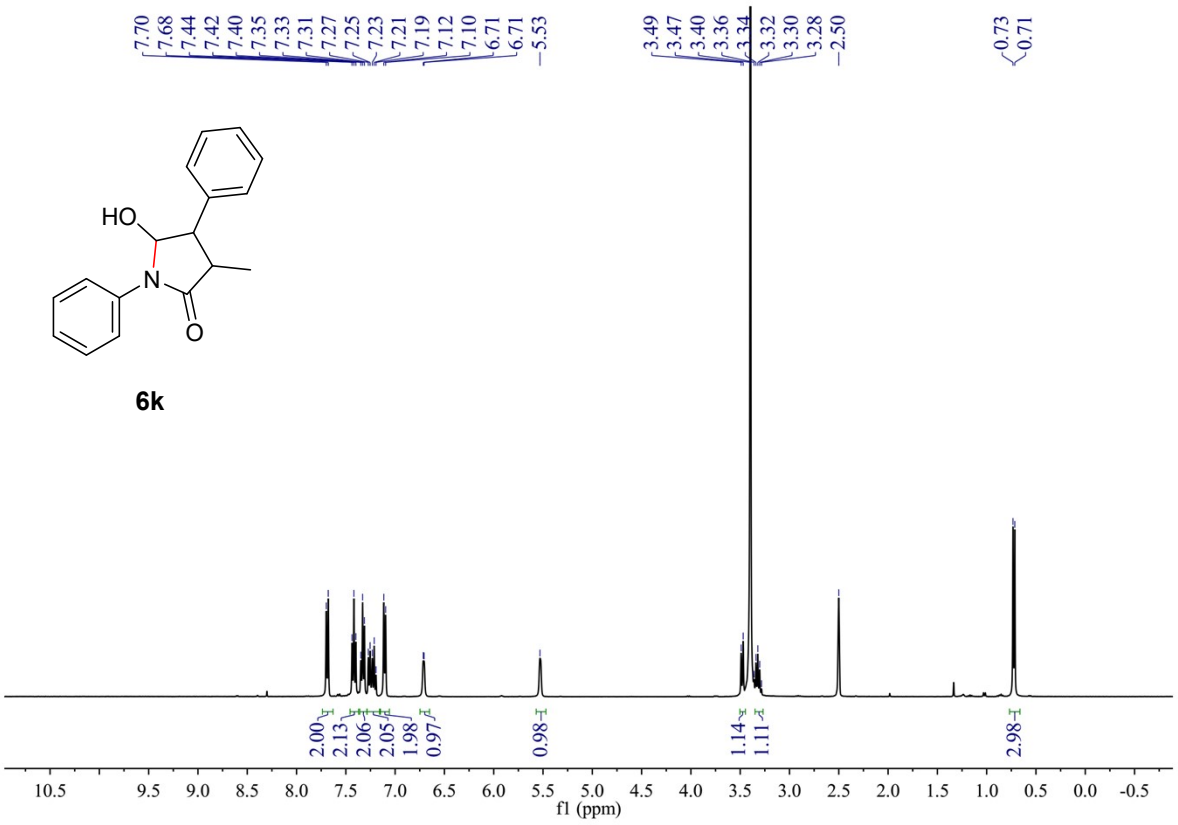
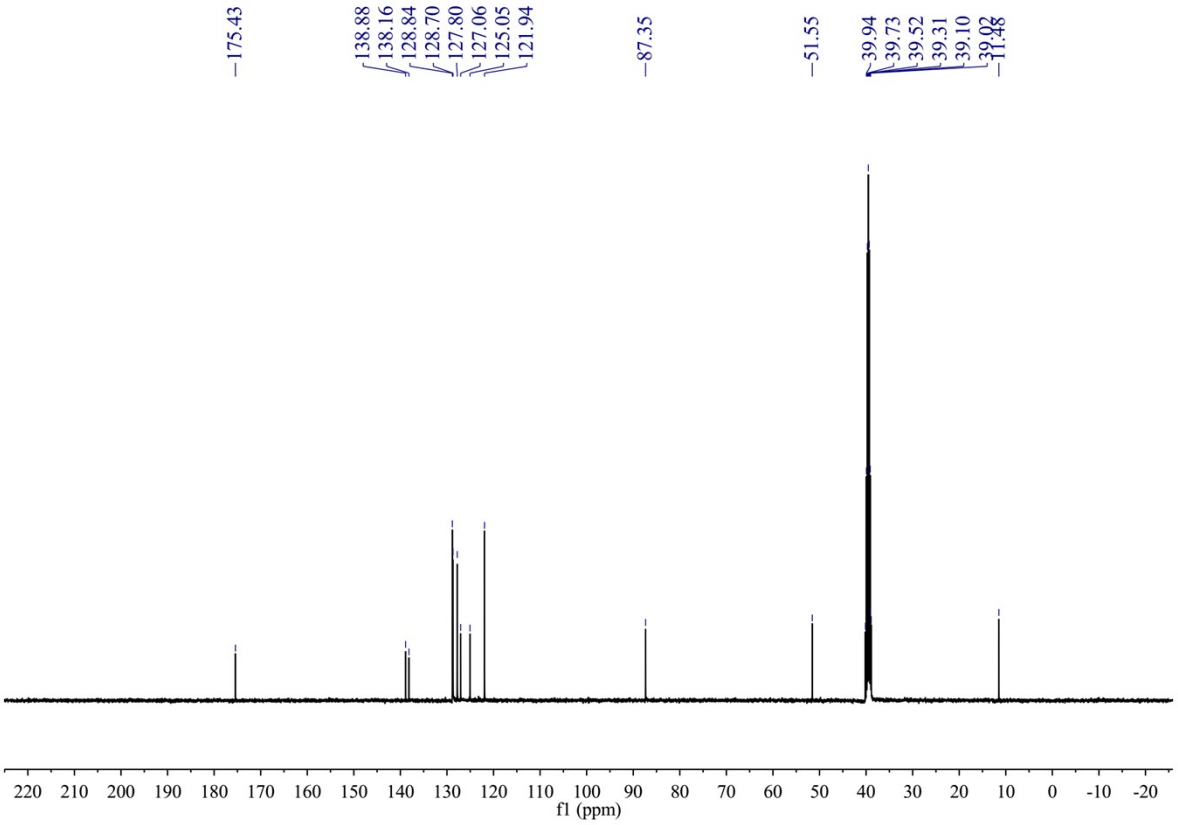


6k

^{1}H NMR



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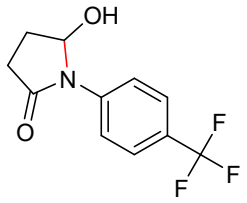

6l

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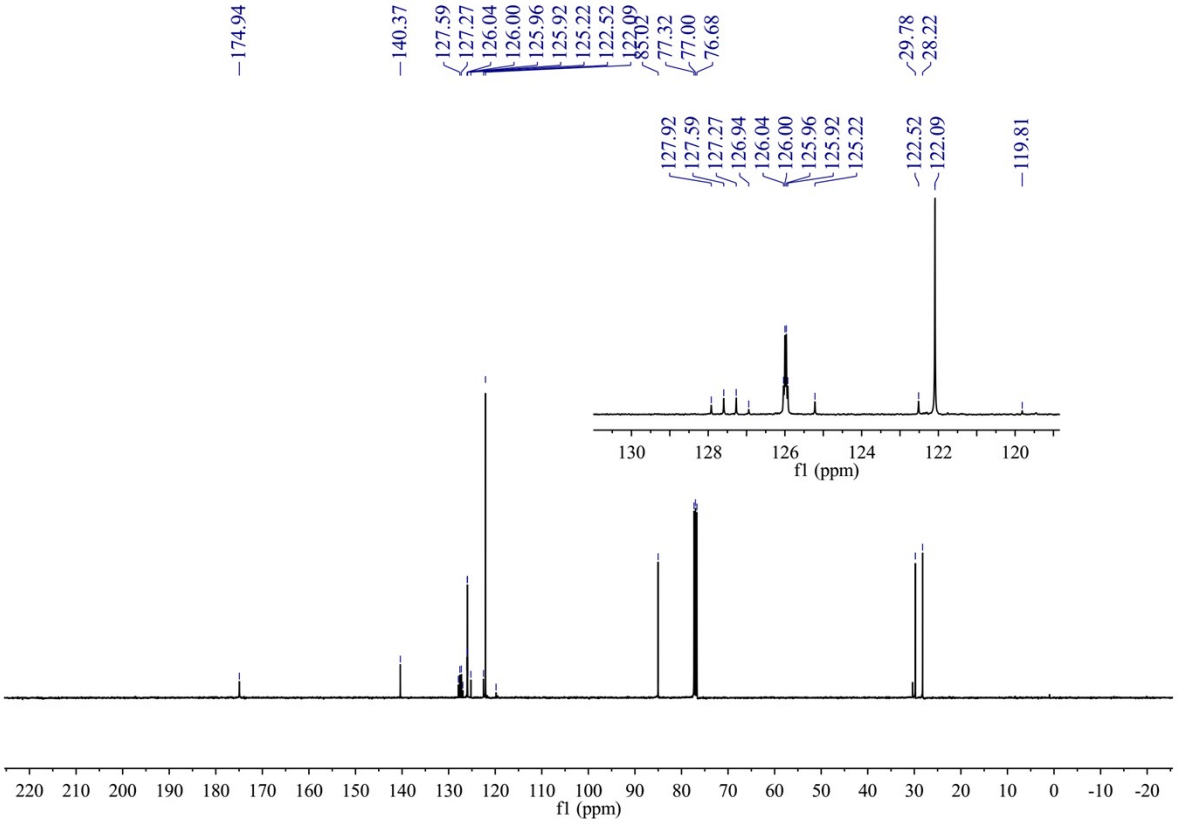

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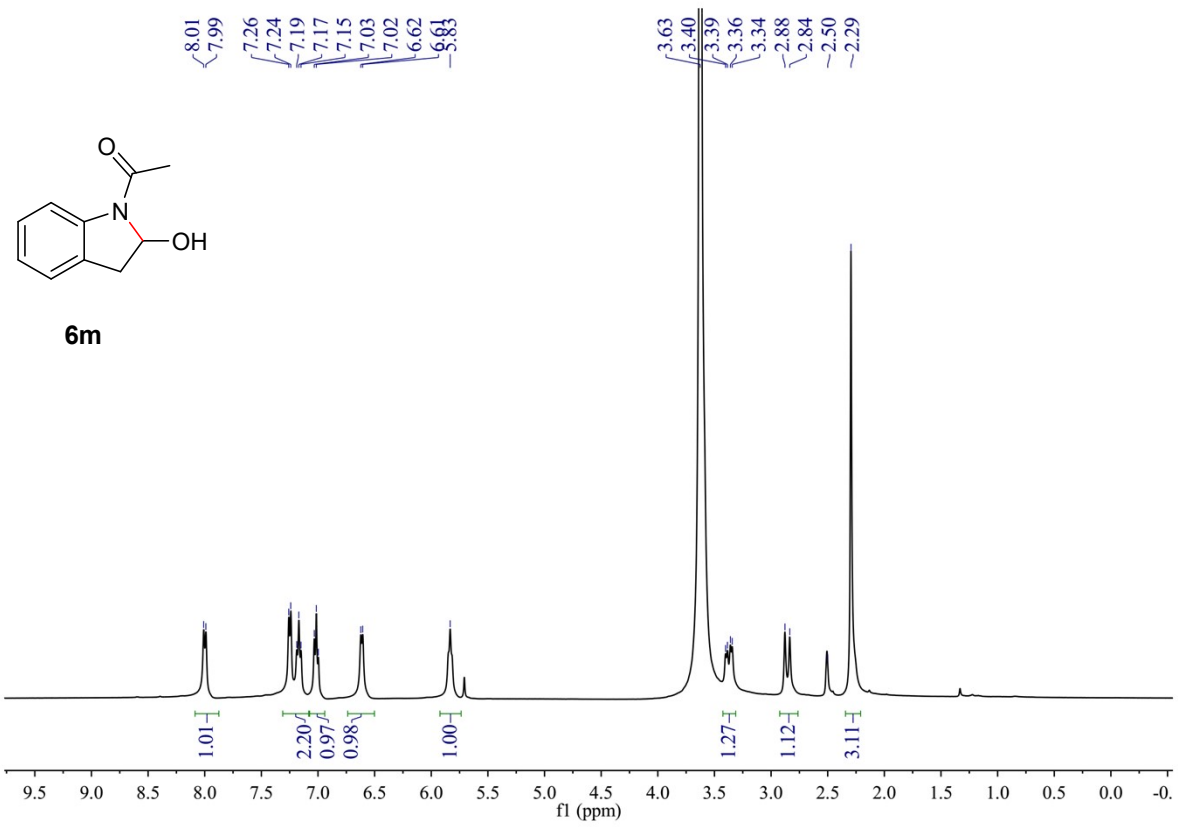

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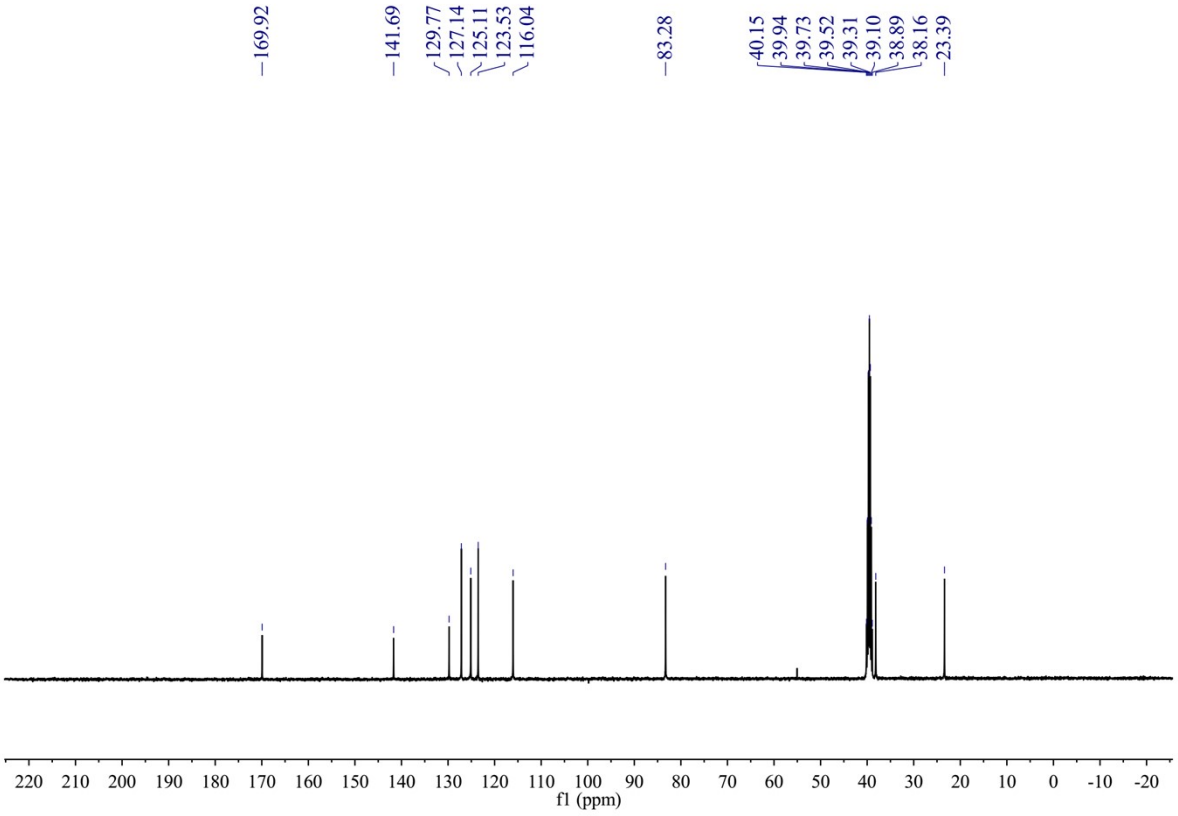

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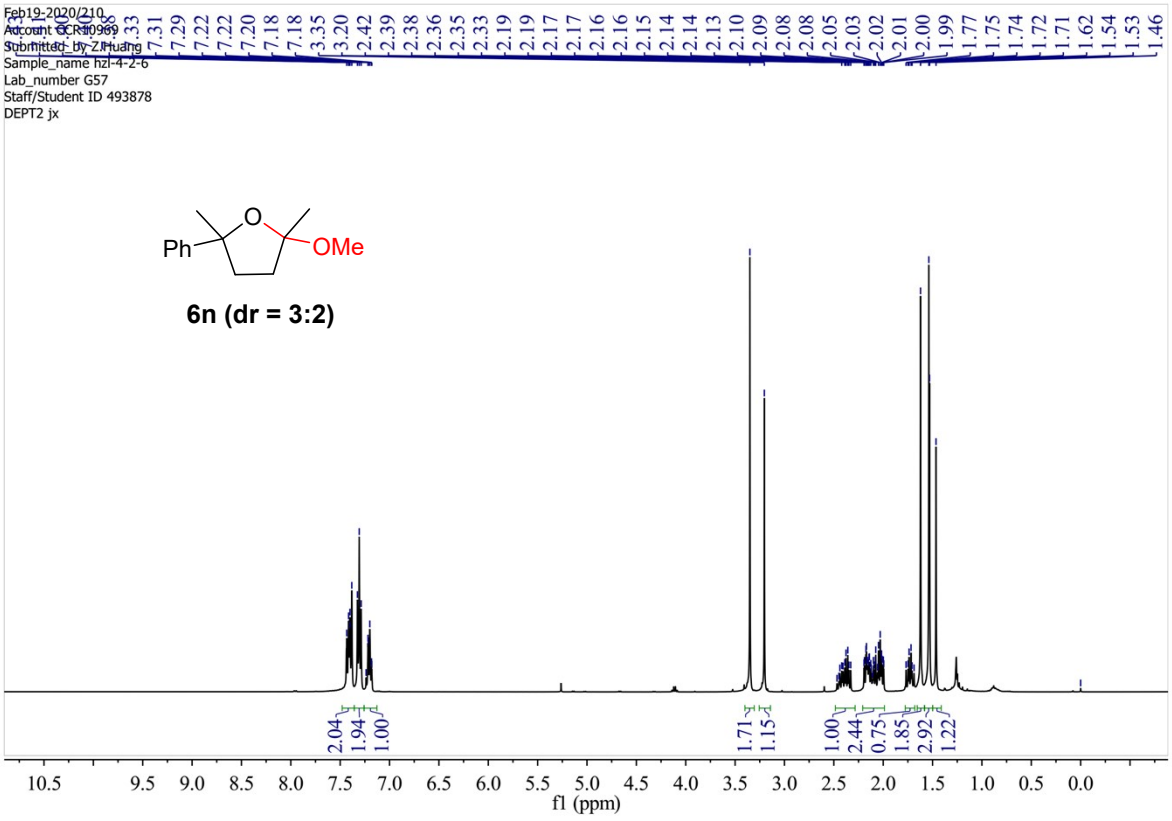

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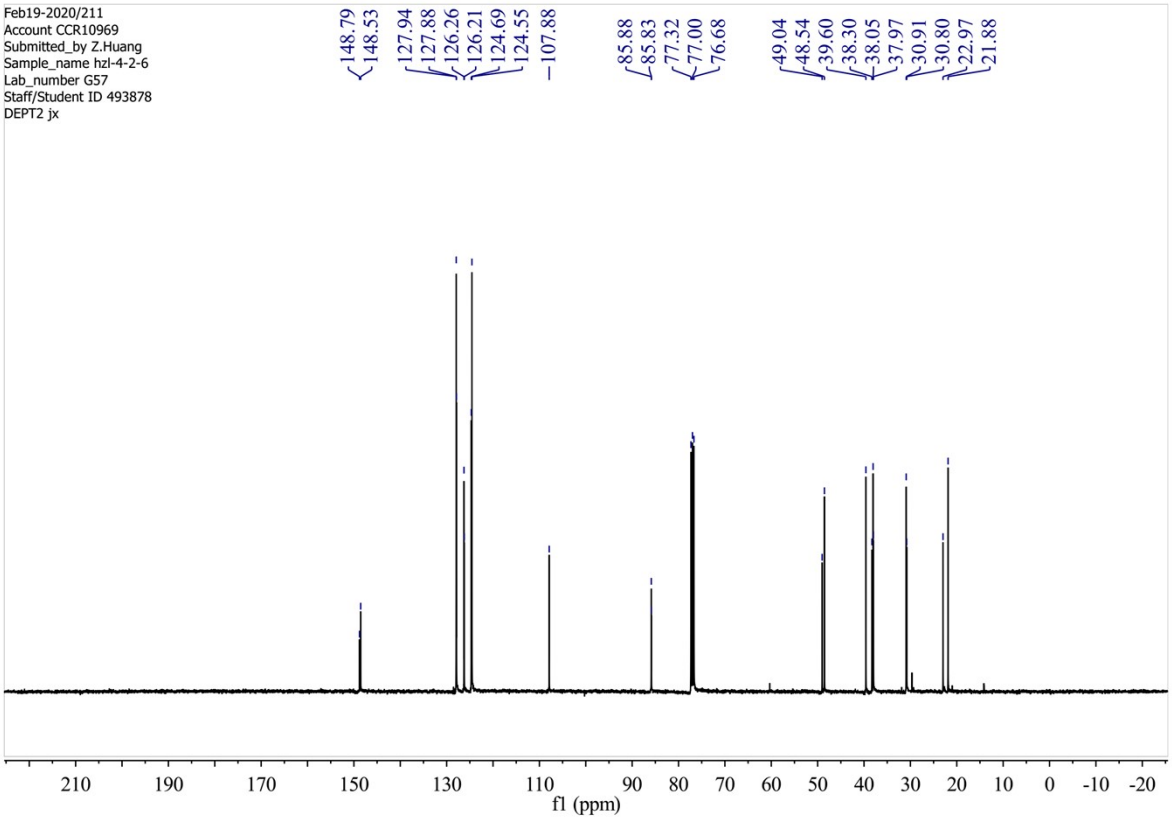

^{13}C NMR

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