Support Information

Decarboxylative Oxygenation of Carboxylic Acids with O_2 via a Non-Heme Manganese Catalyst

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Content

1. General information

All manipulations were carried out using standard Schlenk techniques. All glassware was dried at 120 °C for more than one hour before use. $Mn(OTf)_2$, substituted 2,2'-bipyridines, substituted-phenylacetic acids, naproxen, ibuprofen, flubiprofen, ketoprofen, ioxoprofen, isoxepac, indomethacin, Vitamin E, (*3E*)-4-phenyl-3-butenoic acid, (*1R*,*2S*,*5R*)-5-methyl-2-(1 methylethyl)cyclohexanecarboxylic acid, *L*-proline, 2-butyloctanoic acid, 2-methyloctadecanoic acid, stearic acid, oleic acid, ethyl 2-phenylacetate and 1-phenylethan-1-ol 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 visualized under UV irradiation, potassium permanganate, or phosphomolybdic acid 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 given as volume/volume. All 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). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift. The chemical shifts (δ) were given in parts per million relative to internal tetramethylsilane (0 ppm for ^{1}H), $CDCl_3$ (7.26 ppm for ^{1}H, 77.00 ppm for ^{13}C), DMSO-d_6 (2.5 ppm for ^{1}H, 39.52 ppm for ^{13}C). The Mass spectra were obtained by electrospray ionization (ESI) or chemical ionization (CI) at the Analytical Services of the Chemistry Department or Materials Innovation Factory, University of Liverpool. Melting points were determined on a Gallenkamp MF370 melting-point apparatus.

2. Information for photoreactors

Information for the blue LEDs: 2.95 V blue LED SMD, Lumileds LUXEON Rebel LXML-PB01-0040; dominant wavelength or Peak Wavelength (minimum: 460 nm, typical: 465 nm, maximum: 485 nm); typical spectral half-width (20 nm); typical temperature coefficient of dominant or Peak Wavelength (0.05 nm/°C); typical total included angle (160°); typical view angle (125°). Each hole on the photoreactor is fitted with three LEDs, giving a total power for each reaction tube as 9 W. Reactor temperature after 12 h irradiation is 45 °C.

Figure S1. Blue light photoreactor.

Information for LEDs with various wavelengths:

UV LEDs (365 nm): 3.0 V UV LED SMD, LUMINUS SST-10-UV-E365-00; dominant wavelength or peak wavelength (minimum: 365 nm, typical: 365 nm, maximum: 370 nm); typical spectral half-width (10 nm); typical total included angle (160°); typical view angle (130°). Each hole on the photoreactor is fitted with three LEDs, giving a total power for each reaction tube as 9 W. Reactor temperature after 12 h irradiation is around 20 °C.

UV LEDs (405 nm): 3.0 V UV LED SMD, LUMINUS SST-10-UV-F405-00; dominant wavelength or peak wavelength (minimum: 405 nm, typical: 405 nm, maximum: 410 nm); typical spectral half-width (10 nm); typical total included angle (160°); typical view angle (130°). Each hole on the photoreactor is fitted with three LEDs, giving a total power for each reaction tube as 9 W.

Cyan LEDs (505 nm): 2.90 V cyan LED SMD, Lumileds LUXEON Rebel LXML-PE01-0080; dominant wavelength or peak wavelength (minimum: 495 nm, typical: 505 nm, maximum: 515 nm); typical spectral half-width (30 nm); typical temperature coefficient of dominant or Peak Wavelength (0.04 nm/°C); typical total included angle (160°); typical view angle (125°). Each hole on the photoreactor is fitted with three LEDs, giving a total power for each reaction tube as 9 W.

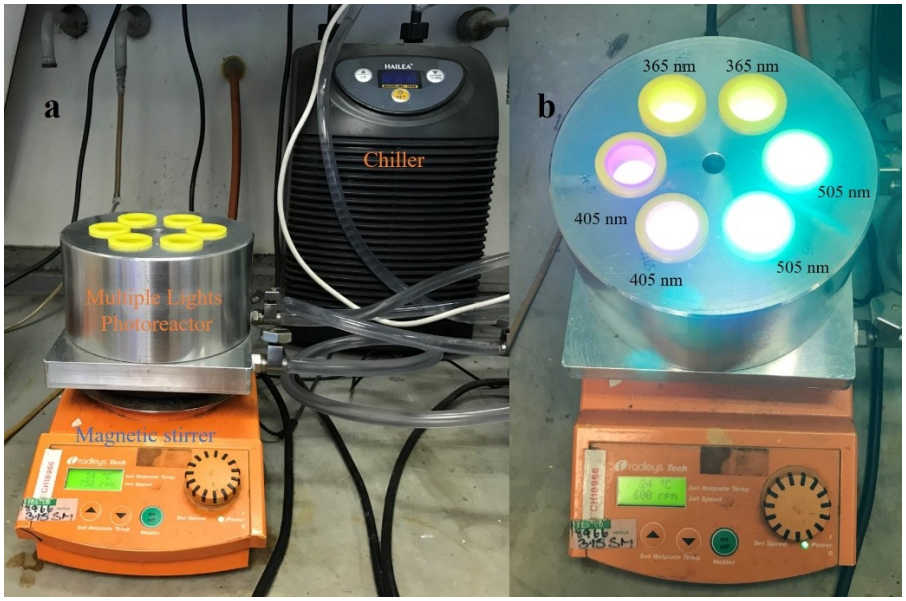
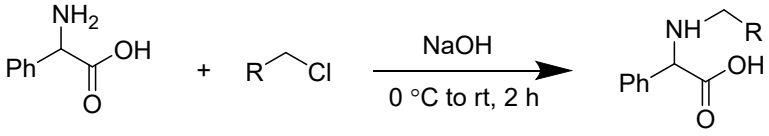


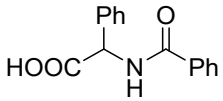
Figure S2. Multi-wavelength photoreactor.

3 Preparation of substrates

3.1 Synthesis of 1v and 1x



2-(Benzylamino)-2-phenylacetic acid (**1v**) and 2-([[(9*H*-Fluoren-9-yl)methoxy]carbonyl]amino)-2-phenylacetic acid (**1x**) were synthesized according to the literature.[1] A mixture of 2.0 M NaOH (50 mL) and phenyl glycine (3.0 g, 19.85 mmol) were added to a 250 mL round-bottom flask equipped with a magnetic stirrer. Then, the solution was cooled to 0 °C in an ice bath. After that, benzoyl chloride or 9-fluorenylmethoxycarbonyl chloride (1.1 equiv., 21.83 mmol) was added to the mixture over the course of 20 mins. In the next step, the reaction was warmed to room temperature and stirred for 2 h. After completion of the reaction, 2.0 M HCl was added dropwise to make the solution slightly acidic (pH 5-6), and the mixture was extracted with ethyl acetate (75 mL × 5). The combined organic phase was dried over magnesium sulfate and concentrated to obtain **1v** or **1x**.



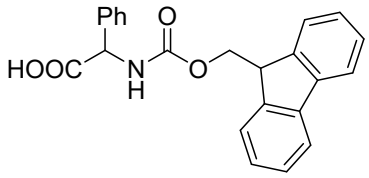
2-(Benzylamino)-2-phenylacetic acid (1v)[1]

^{1}H NMR (400 MHz, DMSO-d6) δ 12.94 (s, 1H), 9.05 (d, J = 7.5 Hz, 1H), 7.94 (dd, J = 7.2, 1.8 Hz, 2H), 7.56 – 7.32 (m, 8H), 5.64 (d, J = 7.5 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 171.98, 166.37, 137.16, 131.51, 128.44, 128.23, 128.20, 127.94, 127.75, 56.88.

HRMS (ESI) calcd for $C_{15}H_{13}NO_3$ $[M+Na]^+$: 278.0788; found: 278.0787.

Melting point: 170-172 ℃.



2-([[(*9H*-Fluoren-9-yl)methoxy]carbonyl]amino)-2-phenylacetic acid (**1x**)[2]

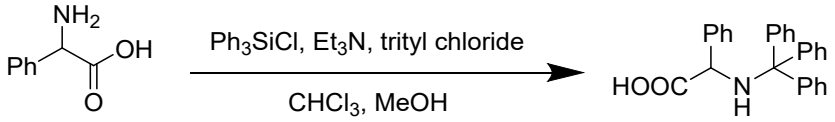
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.89 (s, 1H), 8.23 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.76 (d, J = 7.5 Hz, 2H), 7.48 – 7.21 (m, 9H), 5.18 (d, J = 8.1 Hz, 1H), 4.31 – 4.17 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 172.14, 155.88, 143.89, 143.79, 140.75, 137.39, 128.45, 127.90, 127.81, 127.69, 127.12, 127.10, 125.46, 125.42, 120.12, 65.99, 58.20, 46.65.

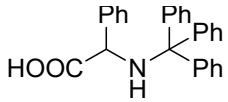
HRMS (ESI) calcd for $C_{23}H_{19}NO_4$ [M+Na]$^+$: 396.1207; found: 396.1198.

Melting point: 187-189 ℃.

3.2 Synthesis of 1w



2-(Triphenylmethylthio)acetic acid (**1w**) was synthesized according to the literature.[3] A mixture of 2-phenylglycine (1.81 g, 12 mmol) and triphenylmethyl chloride (Ph_3SiCl, 2.17g, 20 mmol) in 25 mL of $CHCl_3$ was heated under reflux for 2 h. After cooling to room temperature, triethylamine (Et_3N, 3.34 g, 33 mmol) and trityl chloride (2.79 g, 10 mmol) were added, and the mixture was stirred at room temperature for 20 h. Then, MeOH (1.60g, 50 mmol) was added and stirred for 0.5 h. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in ethyl acetate (50 mL). The organic layer was washed with 10% aqueous citric acid (50 mL × 3), and brine (50 mL) and dried over $MgSO_4$. The solvent was evaporated, and the oily crude product was recrystallized from $CHCl_3$/hexane to give **1w** as a colourless solid.



2-(Triphenylmethylthio)acetic acid (**1w**)

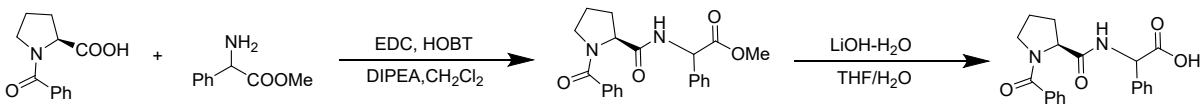
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.1 Hz, 2H), 7.44 – 7.37 (m, 8H), 7.36 – 7.28 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 6H), 7.06 (t, *J* = 7.3 Hz, 3H), 4.36 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.26, 145.34, 139.26, 129.67, 128.86, 128.71, 127.91, 127.13, 126.74, 72.09, 60.22.

HRMS (ESI) calcd for $C_{27}H_{23}NO_2$ [M+Na]$^+$: 416.1621; found: 416.1623.

Melting point: 195-197 ℃.

3.3 Synthesis of 1y



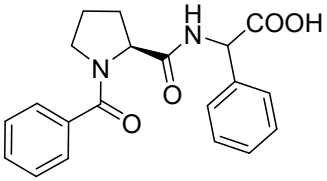
2-((*S*)-1-Benzoylpyrrolidine-2-carboxamido)-2-phenylacetic acid (**1y**) was synthesized according to the literature.[4] Methyl 2-amino-2-phenylacetate hydrochloride (2.01 g, 1.0 equiv., 10 mmol) was weighed into a round-bottom flask with a stirrer bar, diluted with CH_2Cl_2 (108 mL), and cooled to 0 °C in an ice bath. To this solution, diisopropyl ethylamine (1.74 mL, 1.0 equiv., 10 mmol) was added dropwise. Next, reagents were added in the following order: 1) *N*-benzoyl-*l*-proline (**4e**) (2.19 g, 1.0 equiv., 10 mmol), 2) hydroxybenzotriazole (HOBt, 20% by weight H_2O, 1.49 g, 1.1 equiv.), and 3) 1-ethyl-3-(3-

dimethylaminopropyl)carbodiimide hydrochloride (EDC, 1.92 g, 1.0 equiv., 10 mmol), and the reaction was warmed to room temperature. The reaction was then stirred overnight or until complete consumption of the carboxylic acid coupling partner was observed by TLC (typically: 1% acetic acid in ethyl acetate eluent).

The reaction contents were added to an appropriately sized separatory funnel and washed with a 1:1 volume each of saturated $NaHCO_3$ solution, 10 wt% aqueous citric acid, and brine. Following each of the first two washes, the aqueous layer was extracted with CH_2Cl_2 (× 2), and the combined organic layers were combined for the next wash. The combined organic layers were then dried over Na_2SO_4, filtered, and concentrated *in vacuo* to provide crude ester product (assumed quantitative yield) which was taken on without further purification to the next step. (Note 1: in order to achieve a dry solid after purification, it may be necessary to dry the pure oil *in vacuo* from hexane several times to completely remove residual CH_2Cl_2, followed by placement on a high vacuum line for 24 h. Note 2: in the case of using a free amine methyl ester in place of a hydrochloride salt, DIPEA (0.1 equiv.) was used).

Then the ester product underwent hydrolysis to afford the final acid product (**1y**). To a glass round-bottom flask with Teflon stir bar was added crude ester product in 3:1 of THF: H_2O (30 mL, 0.5 M). The solution was cooled to 0 °C in an ice bath, and LiOH (2.1 g, 5.0 equiv., 50 mmol) was added in 1 portion. The reaction was held at 0 °C for 10 mins, and then warmed to room temperature and stirred for 24 h, or until complete conversion of the ester was observed by TLC.

Upon complete conversion, the reaction was cooled back down to 0 °C, and acidified to a pH of < 2 via dropwise addition of 10 wt% aqueous $KHSO_4$. The solution was then diluted with ethyl acetate (~1:1 v/v) and the two layers were separated via a separatory funnel. The pH of the aqueous layer was then taken. If it was found to be > 4/5, the aqueous layer was re-acidified with 10 wt% aqueous $KHSO_4$ to pH < 2. It was then extracted with ethyl acetate (× 2), making sure to retain an acidic pH before each extraction. The organic layers were combined and washed with water (× 1) and brine (× 1), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford the crude acid product (**1y**), which was purified via flash chromatography on silica gel.



2-((*S*)-1-Benzoylpyrrolidine-2-carboxamido)-2-phenylacetic acid (**1y**)

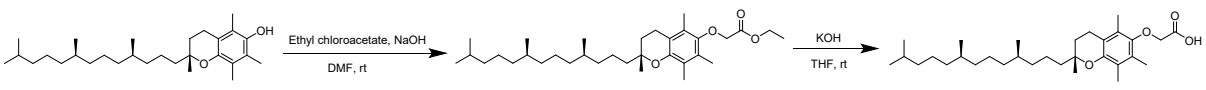
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.05 (s, 1H), 8.13 (dd, *J* = 45.1, 6.8 Hz, 1H), 7.56-7.28 (m, 10H), 5.61 (dd, *J* = 15.4, 6.8 Hz, 1H), 4.92 (dt, *J* = 45.3, 6.8 Hz, 1H), 3.59-3.4 (m, 2H), 2.23-1.68 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.52, 172.26, 170.97, 136.40, 135.36, 130.34, 128.65, 128.60, 128.23, 127.05, 127.01, 59.94, 56.60, 50.47, 28.51, 25.01.

HRMS (ESI) calcd for $C_{20}H_{20}N_2O_4$ $[M+Na]^+$: 375.1315; found: 375.1311.

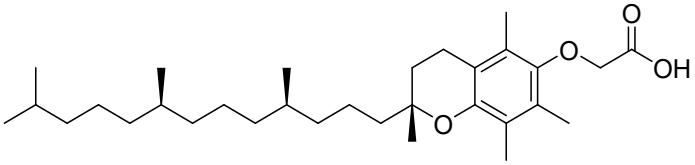
Melting point: 157-158 °C.

3.4 Synthesis of 2-((*R*)-2,5,7,8-tetramethyl-2-((*4R*,*8R*)-4,8,12-trimethyltridecyl)chroman-6-yloxy)acetic acid



2-((*R*)-2,5,7,8-Tetramethyl-2-((*4R,8R*)-4,8,12-trimethyltridecyl)chroman-6-yloxy)acetic acid was synthesized according to the literature.[5] To a mixture of (2*R*)-2,5,7,8-tetramethyl-2-[(*4R*,*8R*)-(4,8,12-trimethyltridecyl)]-6-chromanol (1.7 g, 4.25 mmol) in DMF (50 mL), ethyl chloroacetate (0.6 g, 4.85 mmol) and powdered NaOH (240 mg, 6 mmol) were added, and the mixture was stirred at room

temperature and monitored by TLC until there was no starting material remaining. Then, the aqueous was extracted with ethyl acetate (75 mL × 2), and the combined ethyl acetate fractions were washed with brine (100 mL × 2) and water (100 mL × 1), and dried over $MgSO_4$. After removal of the solvent, the ester product was obtained as a colourless oil compound, and it was used in the next step without purification. A mixture of ester compound (1 g, 1.92 mmol) in THF (10 mL) and 10% KOH (30 mL) was stirred at room temperature for 5 h, and then the THF was evaporated, and the residue was neutralized with HCl and extracted with CH_2Cl_2. Afterwards, it was washed with water, and dried over $MgSO_4$. The solvent was evaporated to give the acid product as pale yellow oil without purification.



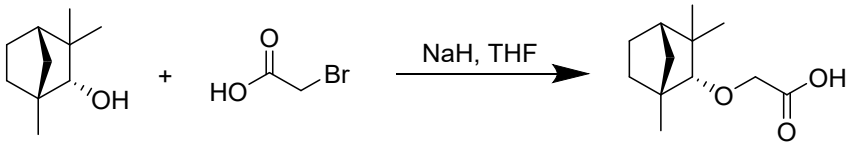
2-((*R*)-2,5,7,8-tetramethyl-2-((*4R,8R*)-4,8,12-trimethyltridecyl)chroman-6-yloxy)acetic acid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.32 (m, *J* = 25.6 Hz, 2H), 2.57 (q, *J* = 5.8, 4.9 Hz, 2H), 2.17 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 1.79 (qt, *J* = 13.3, 6.8 Hz, 2H), 1.61 – 1.48 (m, 3H), 1.42 – 1.20 (m, 15H), 1.16 – 1.02 (m, 6H), 0.86 (m, 12H).

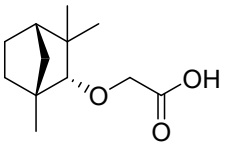
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.41, 148.59, 146.80, 127.28, 125.41, 123.31, 117.83, 75.03, 69.12, 39.99, 39.36, 37.44, 37.39, 37.37, 37.27, 32.78, 32.68, 31.14, 27.96, 24.79, 24.42, 23.83, 22.71, 22.61, 21.01, 20.60, 19.73, 19.67, 12.72, 11.86, 11.77.

HRMS (CI) calcd for $C_{31}H_{52}O_4$ $[M+H]^+$: 489.3938; found: 489.3941.

3.5 Synthesis of 4c



(*1R-endo*)-[(1,3,3-Trimethylbicyclo[2.2.1]hept-2-yl)oxy]-acetic acid (**4c**) was synthesized according to the literature.[6] To a suspension of NaH (1 g, 60% dispersion in mineral oil, 25.0 mmol) in dry THF (35 mL) under Ar at 0 °C, was added a solution of (1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol(11.3 mmol) in THF (5 mL). After the mixture was stirred for 1 h, a solution of 2-bromo-acetic acid (0.99 g, 7.1 mmol) in THF (20 mL) was added and the mixture was heated to reflux overnight. The mixture was then quenched with methanol (20 mL), diluted with water, and washed with ether. The aqueous layer was then acidified with concentrated HCl to pH 4, and extracted with ethyl acetate. The combined ethyl acetate extracts were dried (Na_2SO_4) and filtered, and the solvent was evaporated to give **4c**.



2-(((*1R,2R,4S*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl)oxy)acetic acid

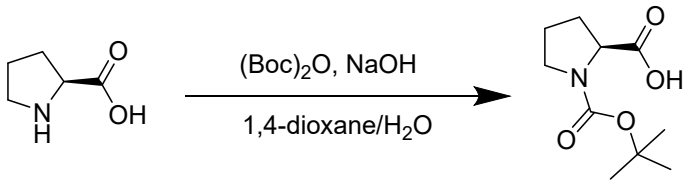
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.22 – 4.00 (m, 2H), 3.04 (s, 1H), 1.74 – 1.66 (m, 3H), 1.49 – 1.40 (m, 2H), 1.14 – 1.01 (m, 8H), 0.94 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.48, 95.08, 68.75, 49.22, 48.47, 41.35, 39.60, 31.42, 25.96, 25.85, 20.57, 20.00.

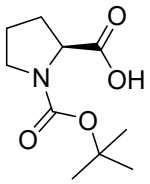
HRMS (CI) calcd for $C_{12}H_{20}O_3$ $[M+H]^+$: 213.1486; found: 213.1495.

Melting point: 89-90 °C.

3.6 Synthesis of 4d



(*Tert*-Butoxycarbonyl)proline (**4d**) was synthesized according to the literature.[7] To a solution of *L*-proline (1.15 g, 10 mmol) in 1,4-dioxane (15 mL) was added NaOH (0.48 g, 12 mmol), H_2O (10 mL) at 0 °C. After stirring for 20 mins, di-*tert*-butyl dicarbonate (Boc_2O, 2.76 mL, 12 mmol) was added. Then, the reaction was stirred at room temperature and detected by TLC until the reaction was finished. The mixture was diluted with H_2O and washed with Et_2O (× 1). The aqueous layer was acidified with 10% HCl to pH 1 and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and evaporated, affording **4e** as colourless crystals.



(*Tert*-Butoxycarbonyl)proline (4d)

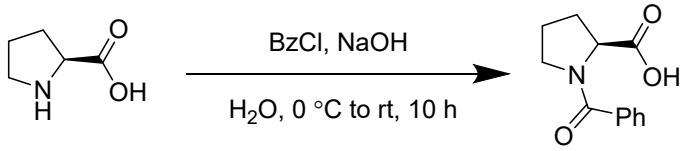
^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.40 (s, 1H), 4.37 – 4.11 (m, 1H), 3.54 – 3.25 (m, 2H), 2.27 – 1.72 (m, 4H), 1.38 (m, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.14, 176.44, 155.34, 153.91, 80.56, 80.25, 58.82, 58.72, 46.63, 46.19, 30.65, 29.16, 28.23, 28.09, 24.11, 23.48.

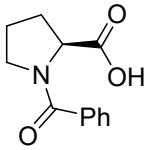
HRMS (ESI) calcd for $C_{10}H_{17}NO_4$ $[M+Na]^+$: 238.1050; found: 238.1053.

Melting point: 130-132 ℃.

3.7 Synthesis of 4e



N-Benzoyl-*l*-proline (**4e**) was synthesized according to the literature.[8] To a solution of *L*-proline (4.00 g, 34.7 mmol) and NaOH (2.78 g, 69.5 mmol) in H_2O (64 mL) was added benzoyl chloride (BzCl, 4.0 mL, 34.7 mmol) dropwise at 0 °C. The mixture was stirred for 10 h at room temperature. The mixture was diluted with H_2O and washed with Et_2O (× 1). The aqueous layer was acidified with 10% HCl to pH = 1 and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and evaporated to afford **4e** as colourless crystals.



***N*-Benzoyl-*l*-proline (4e)**

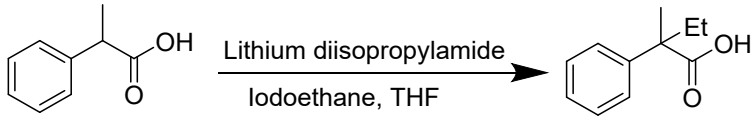
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.09 (s, 1H), 7.59 – 7.53 (m, 2H), 7.48 – 7.38 (m, 3H), 4.74 (t, J = 6.0 Hz, 1H), 3.62-3.52 (m, 2H), 2.34 – 2.22 (m, 2H), 2.06-1.98 (m, 1H), 1.94-1.84 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.35, 171.20, 135.30, 130.56, 128.36, 127.22, 59.75, 50.37, 28.55, 25.16.

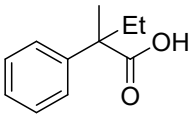
HRMS (ESI) calcd for $C_{12}H_{13}NO_3$ $[M+Na]^+$: 242.0788; found: 242.0784.

Melting point: 150-152 ℃.

3.8 Synthesis of 6c

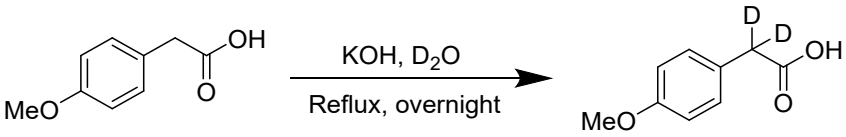


Acid **6c** was synthesized according to the literature.[9] A solution containing 2-phenylpropanoic acid (10.0 mmol) in dry tetrahydrofuran (5 mL) was added to lithium diisopropylamide (25.0 mmol) in dry tetrahydrofuran (20 mL) at 0 °C. The suspension was stirred for 1 hour at 25 °C and then for 30 minutes at 60 °C. The mixture was then cooled to 0 °C and iodoethane (25.0 mmol) was added dropwise and the reaction stirred at 25 °C for 21 hours. The mixture was quenched with saturated ammonium chloride (aq), acidified with concentrated sulfuric acid and the layers separated. The aqueous layer was then extracted with diethyl ether (50 mL × 2). The ether layers were combined and washed with 20% K_2CO_3 (50 mL), dried over magnesium sulfate, filtered and concentrated in *vacuo*. The acid **6c** was then used without further purification.

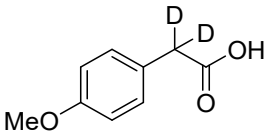


2-Methyl-2-phenylbutanoic acid (6c)[10]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.20 (m, 5H), 2.05 (m, 2H), 1.57 (s, 3H), 0.86 (t, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.68, 142.80, 128.37, 126.86, 126.25, 50.35, 31.59, 21.67, 9.02.
Melting point: 135-136 °C.

3.9 Synthesis of 1a-d^2

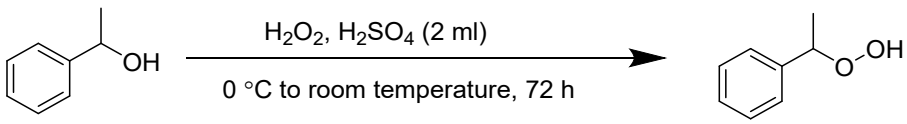


Acid **1a-d^2** was synthesized according to the literature.[11] A mixture of 2-(4-methoxyphenyl)acetic acid (1.83 g), anhydrous potassium hydroxide (2.24 g, 40.0 mmol) and deuterium oxide (7.5 mL) was heated to reflux overnight. After the reaction, the mixture was cooled to room temperature. The reaction mixture was acidified to pH = 2 with 6 N HCl. The solution was then extracted with diethyl ether (50 mL × 3). The combined organic layers were washed with brine, and dried over Na_2SO_4. After evaporating the combined organic layers *in vacuo*, **1h-d^2** was afforded as a colourless powder.

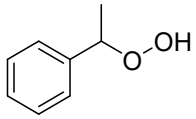


2-(4-Methoxyphenyl)acetic-2,2-d^2 acid (1h-d^2)[12]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.23, 158.83, 130.34, 125.21, 114.05, 55.22, 39.81 (m).
Melting point: 78-80 °C.

3.10 Synthesis of 1-phenylethyl hydroperoxide (9)



1-Phenylethyl hydroperoxide (**9**) was *in situ* synthesized according to the literature.[13] To a cooled (0 °C) solution of H_2O_2 (25.05 ml, 0.25 mol, 30 wt% in H_2O) and H_2SO_4 (0.25 mL, 4.5 mmol) was added 1-phenylethanol (1.15 g, 9 mmol). The reaction mixture was stirred vigorously for 72 h at ambient temperature and partitioned between Et_2O (20 mL) and water (30 mL). The aqueous layer was extracted with Et_2O (2 × 20 mL). The combined fractions were dried over $MgSO_4$, concentrated *in vacuo* and purified by flash chromatography (hexane/ethyl acetate 9:1) to yield the hydroperoxide.



1-Phenylethyl hydroperoxide (9)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (b, 1H), 7.43 – 7.30 (m, 5H), 5.09 (q, *J* = 6.6 Hz, 1H), 1.48 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.37, 128.68, 128.28, 126.51, 83.79, 20.08.

4 General procedure for decarboxylative oxygenation of carboxylic acids

4.1 *In situ* synthesis of $[Mn(dtbpy)_2(OTf)_2]$[14]

To an oven dried Schlenk tube, $Mn(OTf)_2$ (8.8 mg, 5 mol%) and 4,4'-di-*tert*-butyl-2,2'- bipyridine (13.4 mg, 10 mol%) were added. Then the reaction tube was placed under vacuum and purged with nitrogen at least three times. Then 1 mL of CH_3CN was added via syringe under N_2. The Schlenk tube was allowed to stir at 80 °C for 1 h to obtain $[Mn(dtbpy)_2(OTf)_2]$ to be used in subsequent oxidation.

4.2 General procedure for decarboxylative oxygenation of 2-(4-methoxyphenyl)acetic acid (1a) under various conditions

To an oven dried Schlenk tube, $Mn(OTf)_2$, $Cu(OTf)_2$, $Fe(OTf)_2$, $CoCl_2$, or $MnCl_2$ (5 mol%) and ligand (L1-L9, 10 mol%) were added. Then the reaction tube was placed under vacuum and purged with nitrogen at least three times, and 1 mL of solvent was injected through a syringe under N_2. The reaction mixture was then heated at 80 °C for 1 h to *in situ* prepare the catalyst. The reaction tube was cooled to room temperature and connected to an oxygen balloon. Finally, after the addition of **1a** (0.25 mmol), the reaction tube was allowed to stir under blue light for 12 h. After the reaction, water (2 mL), chloroform-*d* (1 mL), and mesitylene (17.3 mg) were added. The product yield of **2a** was obtained by ^{1}H NMR analysis of the organic layer.

4.3 Standard procedure for decarboxylative oxygenation of carboxylic acids

To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. Then, acid (0.5 mmol) and CH_3CN (1 mL) were added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature under blue light for 12 h. After the crude mixture was concentrated under vacuum, the pure product was obtained by flash chromatography on silica gel with hexane/ethyl acetate.

Decarboxylative oxygenation of **1d**, **1e**, and **1q**: To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. Then, acid (0.5 mmol), CH_3COONa (30 mol%), and CH_3CN (1 mL) were added under N_2. The reaction tube was then fitted with an oxygen balloon, and allowed to stir at room temperature under blue light for 12 h. After the crude mixture was concentrated under vacuum, the pure product was obtained by flash chromatography on silica gel with hexane/ethyl acetate.

Decarboxylative oxygenation of **4c**-**4h**: To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. Then, acid (0.5 mmol), CH_3COONa (30 mol%), and CH_3CN (1 mL) were added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature under UV light (365 nm) for 12 h. After the crude mixture was concentrated under vacuum,

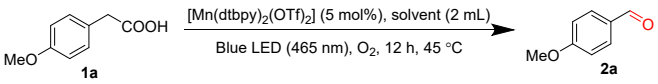
unless otherwise noted, the pure product was obtained by flash chromatography on silica gel with hexane/ethyl acetate.

5. Optimization of experimental conditions

5.1 Selection of solvent

To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. Then, acid (0.5 mmol) and CH_3CN (1 mL) were added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature under blue light for 12 h. After reaction, 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 Oxidative decarboxylation/oxidation of acid **1a** in different solvents. [a, b]



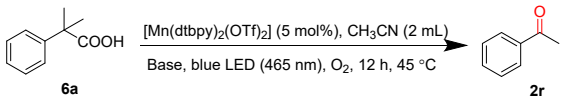
Entry	Catalyst	Solvent	Time (h)	Yield (%)
1	$[Mn(dtbpy)_2(OTf)_2]$	DCE	12	59
2	$[Mn(dtbpy)_2(OTf)_2]$	EtOH	12	28
3	$[Mn(dtbpy)_2(OTf)_2]$	THF	12	14
4	$[Mn(dtbpy)_2(OTf)_2]$	MeOH	12	29
5	$[Mn(dtbpy)_2(OTf)_2]$	Acetone	12	41
6	$[Mn(dtbpy)_2(OTf)_2]$	Ethyl acetate	12	37
7	$[Mn(dtbpy)_2(OTf)_2]$	Hexane	12	35
8	$[Mn(dtbpy)_2(OTf)_2]$	Trifluoroethanol	12	50
9	$[Mn(dtbpy)_2(OTf)_2]$	TFE	12	23
10[c]	$[Mn(dtbpy)_2(OTf)_2]$	Acetonitrile	12	72
11	$[Mn(dtbpy)_2(OTf)_2]$	Acetonitrile	6	67
12	$[Mn(dtbpy)_2(OTf)_2]$	Acetonitrile	9	79

[a] Reaction conditions: **1a** (0.5 mmol), $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%), solvent (2 mL), under blue LED light (465 nm, 9 W) at 45 °C under O_2 atmosphere (1 atm) for 12 h. [b] NMR yields are given. [c] 20 °C.

5.2 Selection of base

To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. Then, acid (0.5 mmol), base and CH_3CN (1 mL) were added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature under blue light for 12 h. After the reaction, mesitylene (17.3 mg) as internal standard, water (2 mL) and $CDCl_3$ (2 mL) were added. Finally, the product yield of **2r** was obtained by ^1H NMR analysis of the organic layer.

Table S2 Oxidative decarboxylation/oxidation of acid **6a** with different bases. [a, b]



6a **2r**

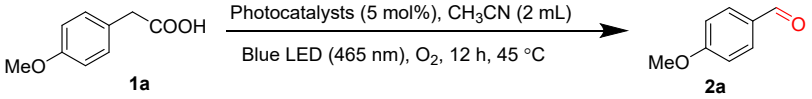
Entry	Base	Content	Yield (%)
1	KOH	10 mol%	48
2	NaOH	10 mol%	49
3	LiOH	10 mol%	50
4	K_2CO_3	10 mol%	44
5	Na_2CO_3	10 mol%	39
6	NaOAc	10 mol%	53
7	NaOAc	30 mol%	79
8	NaOAc	90 mol%	79
9	KOAc	30 mol%	46
10	LiOAc	30 mol%	73

[a] Reaction conditions: **6a** (0.5 mmol), $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%), base, solvent (2 mL), under blue LED light (465 nm, 9 W) at 45 °C under O_2 atmosphere (1 atm) for 12 h. [b] NMR yields are given.

6. Mechanistic investigations

6.1 Control experiments

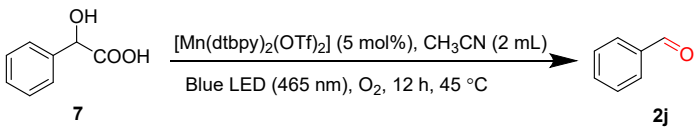
6.1.1 Decarboxylative oxygenation of 2-(4-methoxyphenyl)acetic acid (1a) with well-known photosensitizers capable of producing singlet oxygen



1a **2a**

To an oven dried Schlenk tube, a photocatalyst (5 mol%) and **1a** (0.5 mmol) were added. Then the reaction tube was placed under vacuum and purged with nitrogen at least three times. The reaction tube was the fitted with an oxygen balloon, and CH_3CN (2 mL) was added under N_2. The reaction tube was allowed to stir at room temperature under blue light (465 nm) for 12 h. After the reaction, 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. The photocatalysts tested were Eosin Y disodium salt, $[Ru(bpy)_3 \cdot 6H_2O]$, $[Ir(dFppy)_3]$ and rose Bengal.

6.1.2 Decarboxylative oxygenation of 2-hydroxy-2-phenylacetic acid (7)

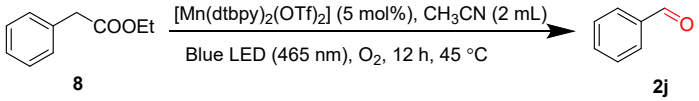


7 **2j**

To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. Then, 2-hydroxy-2-phenylacetic acid (**7**, 0.5 mmol) and CH_3CN (1 mL) were added under N_2. The reaction tube was then

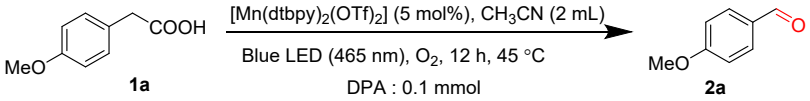
fitted with an oxygen balloon, and was allowed to stir at room temperature under blue light (465 nm) for 12 h. After the reaction, mesitylene (17.3 mg) as internal standard, water (2 mL) and $CDCl_3$ (2 mL) were added. Finally, the product yield of **2j** was obtained by ^1H NMR analysis of the organic layer.

6.1.3 Decarboxylative oxygenation of ethyl 2-phenylacetate (8)



To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. Then, ethyl 2-phenylacetate (**8**, 0.5 mmol) and CH_3CN (1 ml) were added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature under blue light (465 nm) for 12 h. After reaction, mesitylene (17.3 mg) as internal standard, water (2 mL) and $CDCl_3$ (2 mL) were added. Finally, the product yield of **2j** was obtained by ^1H NMR analysis of the organic layer.

6.2 Singlet oxygen trap experiment



To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. Then, **1a** (0.5 mmol), 9,10-diphenylanthracene (33 mg, 0.1 mmol, singlet oxygen trap) and CH_3CN (2 ml) were added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature under blue light (465 nm) for 12 h. The product yield of **2a** (70%) was obtained by ^1H NMR analysis with mesitylene (17.3 mg) as internal standard. In the meantime, no 9,10-diphenyl-4a,9,9a,10-tetrahydro-9,10-epidioxyanthracene was observed by ^1H NMR analysis. These results indicated that singlet oxygen was not involved as the key intermediate during the decarboxylative oxygenation.

6.3 Light on/off experiments

To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized and 1,3,5-tribromobenzene (62.4 mg) as internal standard were added. CH_3CN (2 mL) was injected through a syringe, and **1a** (0.5 mmol) was added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature under blue light. After 1 h, 0.1 mL of the reaction mixture was taken out for ^1H NMR analysis; in the meantime, the reaction tube was further stirred in the dark. After 1 h, 0.1 mL of the reaction mixture was taken out for ^1H NMR analysis, and the reaction tube was exposed to blue light again for another 1 h, followed by ^1H NMR analysis. This on/off process was further repeated.

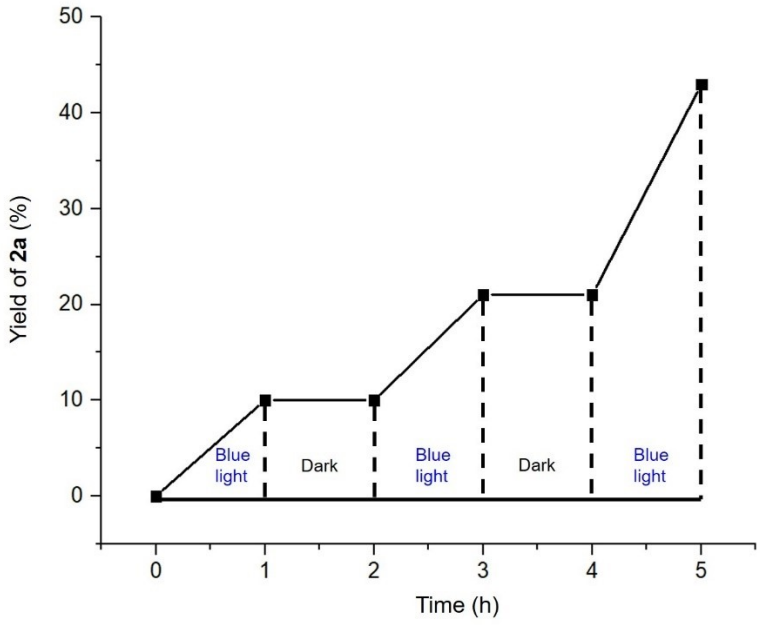


Figure. S3 Decarboxylative oxidation of **1a** under light on/off conditions.

6.4 UV-Vis experiment

$[Mn(dtbpy)_2(OTf)_2]$: To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%, 0.5 mmol) was *in situ* synthesized, and then CH_3CN (1 mL) was added under N_2. 0.1 mL of the solution was then taken out and diluted to 10 mL for UV-Vis analysis.

1a: **1a** (0.5 mmol) was dissolved in CH_3CN (2 mL). 0.1 mL of the solution was then taken out and diluted to 10 mL for UV-Vis analysis.

The mixture of $[Mn(dtbpy)_2(OTf)_2]$ and **1a** in the absence of blue light: To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. Then **1a** (0.5 mmol) and CH_3CN (1 mL) was added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature in dark for 1 h. Then, 0.1 mL of the solution was taken out and diluted to 10 mL for UV-Vis analysis.

The mixture of $[Mn(dtbpy)_2(OTf)_2]$ and **1a** in the presence of blue light: To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. Then **1a** (0.5 mmol) and CH_3CN (1 mL) were added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature under blue light (465 nm) for 1 h. 0.1 mL of the solution was then taken out and diluted to 10 mL for UV-Vis analysis.

In situ UV-Vis monitoring of the mixture of $[Mn(dtbpy)_2(OTf)_2]$ and **9**: To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized, and then CH_3CN (1 mL) was added under N_2. 0.1 mL of the solution was then taken out and diluted to 10 mL. After the addition of 2 mL of the solution to a cuvette, **9** (50 25 μmol) was added to the cuvette and UV-Vis monitoring was started immediately. The mixture was monitored by UV-Vis again at 10 mins and 30 mins.

The mixture of $[Mn(dtbpy)_2(OTf)_2]$ and **9**: To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized, and then **9** (0.5 mmol) and CH_3CN (1 mL) were added under N_2. It was then allowed to stir at room temperature in the dark. 0.1 mL of the solution was taken out every 10 mins, and it was diluted to 10 mL for UV-Vis analysis.

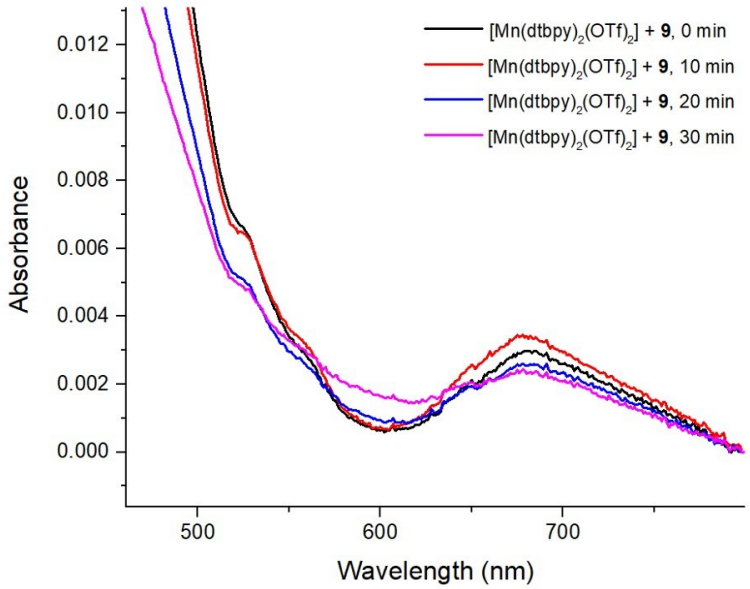


Figure S4 UV-Vis analysis of the mixture of $[Mn(dtbpy)_2(OTf)_2]$ and **9**.

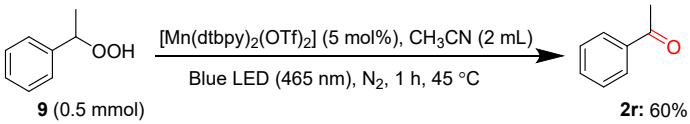
6.5 Kinetic behaviours of decarboxylative oxygenation of acid 1r and 1-phenylethyl hydroperoxide (9)

Decarboxylative oxygenation of **1r**: To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized and 1,3,5-tribromobenzene (62.4 mg) as internal standard was added. CH_3CN (1 mL) was injected through a syringe, and acid **1r** (0.5 mmol) was added under N_2. The reaction tube was then allowed to stir under blue light. Every 20 min, 0.1 mL of the reaction mixture was taken out for ^1H NMR analysis.

Decarboxylative oxygenation of **9**: To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized and 1,3,5-tribromobenzene (62.4 mg) as internal standard was added. CH_3CN (1 mL) was injected through a syringe, and 1-phenylethyl hydroperoxide (**9**) (0.5 mmol) was added under N_2. The reaction tube was then allowed to stir under blue light. Every 20 min, 0.1 mL of the reaction mixture was taken out for ^1H NMR analysis.

6.6 Reaction of 1-phenylethyl hydroperoxide (9) without blue light irradiation under N_2.

Scheme S1. Decomposition of 9 by $[Mn(dtbpy)_2(OTf)_2]$ in the absence of blue light and O_2.



To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized. CH_3CN (1 mL) was injected through a syringe, and **9** (0.5 mmol) was added under N_2. The reaction tube was allowed to stir at room temperature for 1 h. After the reaction, mesitylene (17.3 mg) as internal standard, water (2 mL) and $CDCl_3$ (2 mL) were added. Finally, the product yield of **2r** was obtained by ^1H NMR analysis of the organic layer.

6.7 Kinetic isotope effect (KIE) experiment

To an oven dried Schlenk tube, $[Mn(dtbpy)_2(OTf)_2]$ (5 mol%) was *in situ* synthesized and 1,3,5-tribromobenzene (62.4 mg) as internal standard was added. CH_3CN (1 mL) was injected through a syringe, and **1a** (0.5 mmol) was added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature under blue light. Every 15 mins, 0.1 mL of the

reaction mixture was taken out for ^{1}H NMR analysis. Meanwhile, the deuterated acid **1a-*d*^{2}** was tested in the experiment using the same procedures. The yields of **2a** and **2a-*d*** between 1 h and 3h were collected and analysed by Origin 2016 to get corresponding k_{obs}^{H} and k_{obs}^{D} values.

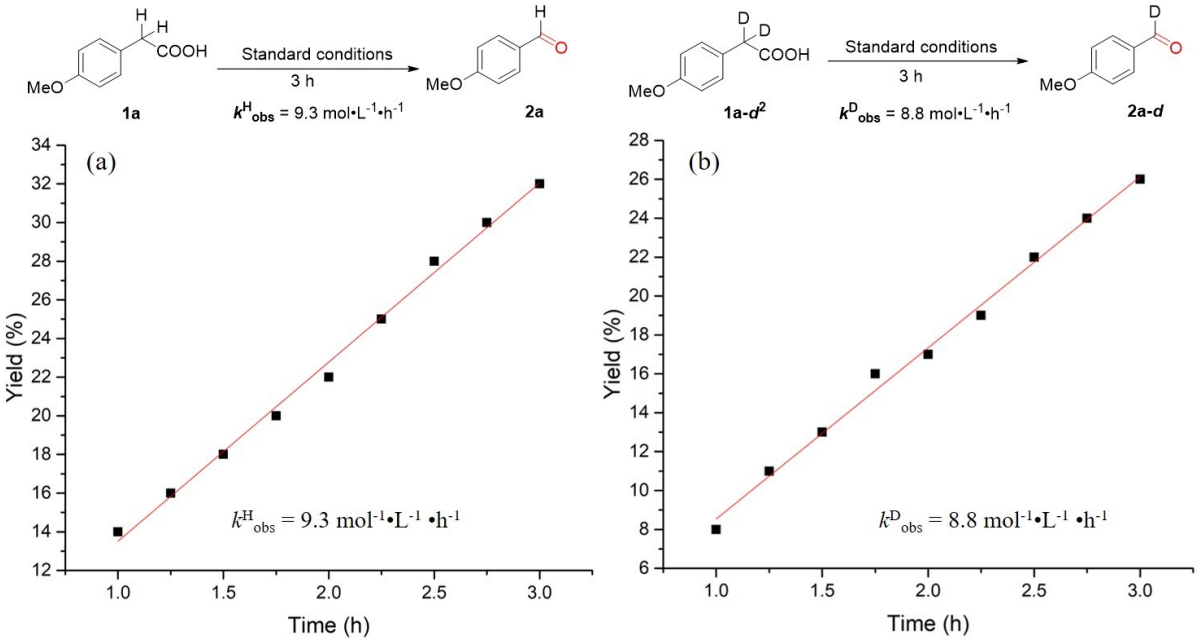
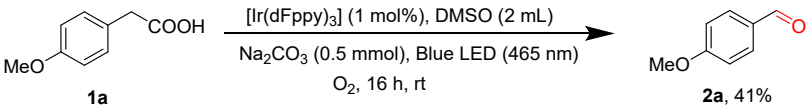


Figure S5 Kinetic behaviors of **1a** (a) and **1a-*d*** (b).

6.8 HRMS analysis of [Mn(dtbpy)$_2$(1a-H)(OTf)] complex

To an oven dried Schlenk tube, [Mn(dtbpy)$_2$(OTf)$_2$] (5 mol%) was *in situ* synthesized. CH_3CN (1 mL) was injected through a syringe, and **1a** (0.5 mmol) was added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir in the dark for 2 h. Then, the solution was analysed by HRMS.

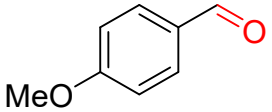
6.9 [Ir(dFppy)$_3$]-catalysed decarboxylative oxygenation of 1a



Scheme S2. Decomposition of 1a by [Ir(dFppy)$_3$] under Macmillan's conidtions.

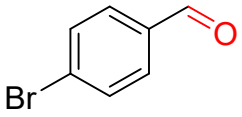
The dose of [Ir(dFppy)$_3$], solvent and base was chosen according to Macmillan's work.[15] To an oven dried Schlenk tube, [Ir(dFppy)$_3$] (1 mol%), **1a** (0.5 mmol), Na_2CO_3 (0.5 mmol) and DMSO (2 mL) were added under N_2. The reaction tube was then fitted with an oxygen balloon, and was allowed to stir at room temperature under blue light for 16 h. After the reaction, 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 ^{1}H NMR analysis of the organic layer.

7 Analytical data of products

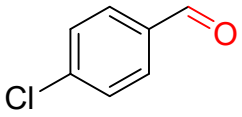


4-Methoxybenzaldehyde (2a)[16]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.87 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H).

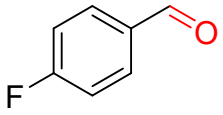
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.72, 164.54, 131.91, 129.90, 114.25, 55.52.



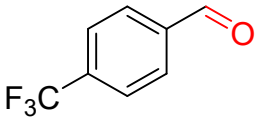
4-Bromobenzaldehyde (2b)[17]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.00, 135.04, 132.41, 130.93, 129.74.



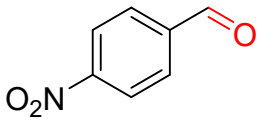
4-Chlorobenzaldehyde (2c)[17]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.83, 140.95, 134.70, 130.89, 129.45.



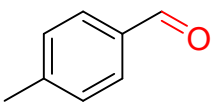
4-Fluorobenzaldehyde (2d)[18]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 7.90-7.86 (m, 2H), 7.20-7.16 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.42, 166.43 (d, *J* = 256.7 Hz), 132.90 (d, *J* = 2.7 Hz), 132.14 (d, *J* = 9.7 Hz), 116.25 (d, *J* = 22.3 Hz).



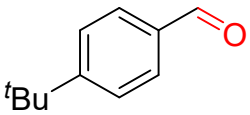
4-(Trifluoromethyl)benzaldehyde (2e)[19]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 7.93 – 7.83 (m, 2H), 7.21-7.15 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.08, 138.65, 135.62 (q, *J* = 32.7 Hz), 129.91, 126.11 (q, *J* = 3.7 Hz), 123.42 (d, J = 272.8 Hz).



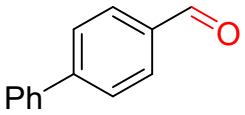
4-Nitrobenzaldehyde (2f)[17]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.16 (s, 1H), 8.39 (d, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 8.7 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.25, 151.08, 140.01, 130.44, 124.26.



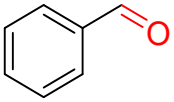
4-Methylbenzaldehyde (2g)[17]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.91, 145.48, 134.16, 129.78, 129.65, 21.82.



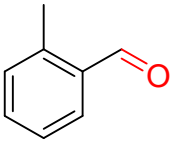
4-(*Tert*-butyl)benzaldehyde (2h)[17]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 1.35 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.96, 158.38, 134.04, 129.64, 125.94, 35.30, 31.03.



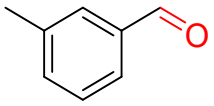
4-Phenylbenzaldehyde (2i)[19]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.06 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.71 – 7.58 (m, 2H), 7.51-7.40 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.88, 147.15, 139.67, 135.16, 130.23, 128.98, 128.43, 127.64, 127.32.



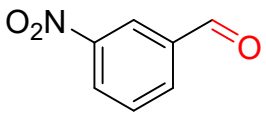
Benzaldehyde (2j)[16]
1H NMR (400 MHz, Chloroform-d) δ 10.02 (s, 1H), 7.91 – 7.85 (m, 2H), 7.66 – 7.60 (m, 1H), 7.53 (t, J = 7.5 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.40, 136.37, 134.44, 129.72, 128.97.



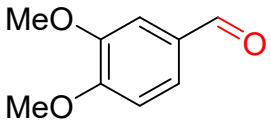
2-Methylbenzaldehyde (2k)[20]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.27 (s, 1H), 7.80 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.48 (td, *J* = 7.5, 1.6 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 2.68 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.77, 140.59, 134.14, 133.61, 132.02, 131.74, 126.30, 19.56.



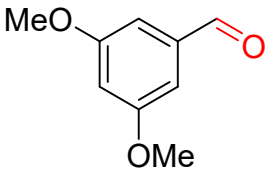
3-Methylbenzaldehyde (2l)[21]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.68 (m, 2H), 7.43 (m, 2H), 2.44 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.59, 138.90, 136.47, 135.27, 130.00, 128.86, 127.21, 21.17.



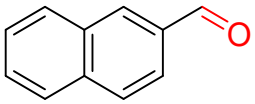
3-Nitrobenzaldehyde (2m)[22]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.13 (s, 1H), 8.72 (s, 1H), 8.50 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.24 (d, *J* = 7.6 Hz, 1H), 7.77 (t, *J* = 7.9 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.73, 148.76, 137.36, 134.63, 130.36, 128.55, 124.42.



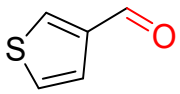
3,4-Dimethoxybenzaldehyde (2n)[23]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 7.43 (dd, J = 8.2, 1.9 Hz, 1H), 7.38 (d, J = 1.9 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 3.92 (d, J = 10.2 Hz, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.77, 154.37, 149.51, 130.03, 126.75, 110.29, 108.84, 56.07, 55.89.



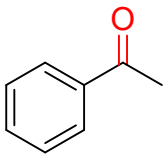
3,5-Dimethoxybenzaldehyde (2o)[24]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.91 (s, 1H), 7.02 (d, *J* = 2.4 Hz, 2H), 6.71 (t, *J* = 2.3 Hz, 1H), 3.85 (s, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.90, 161.23, 138.38, 107.10, 55.62.



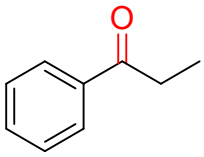
2-Naphthaldehyde (2p)[25]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.16 (s, 1H), 8.33 (s, 1H), 8.02 – 7.89 (m, 4H), 7.66 – 7.57 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.20, 136.41, 134.50, 134.08, 132.60, 129.49, 129.07, 129.06, 128.04, 127.05, 122.73.



Thiophene-3-carbaldehyde (2q)[26]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 8.13 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.56 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.38 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.95, 143.03, 136.68, 127.38, 125.37.

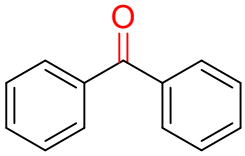


Acetophenone (2r)[17]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 2.61 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.12, 137.10, 133.07, 128.54, 128.27, 26.59.

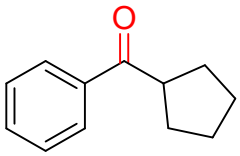


Propiophenone (2s)[21]

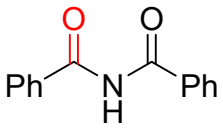
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 3.01 (q, *J* = 7.3 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.78, 136.90, 132.83, 128.51, 127.93, 31.75, 8.21.



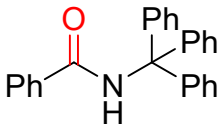
Benzophenone (2t)[20]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 6.9 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.64, 137.52, 132.34, 129.97, 128.20.



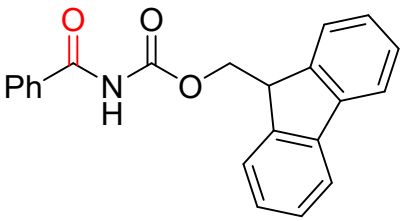
Cyclopentyl(phenyl)methanone (2u)[27]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.0 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 3.72 (p, *J* = 7.9 Hz, 1H), 1.92 (q, *J* = 6.2, 5.5 Hz, 4H), 1.77 – 1.62 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.76, 136.92, 132.65, 128.46, 128.42, 46.34, 29.96, 26.29.



***N*-benzoylbenzamide (2v)**[28]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.09 (s, 1H), 7.86 (dd, *J* = 8.3, 1.3 Hz, 4H), 7.68 – 7.55 (m, 2H), 7.49 (t, *J* = 7.7 Hz, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.46, 133.31, 133.03, 128.80, 127.93.

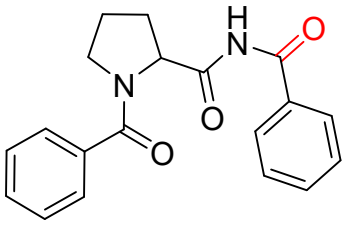


***N*-tritylbenzamide (2w)**[29]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.82 (m, 3H), 7.41 – 7.40 (m, 3H), 7.29-7.23 (m, 15H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.60, 145.79, 136.71, 130.71, 129.78, 128.58, 128.53, 127.73, 126.75, 78.26.

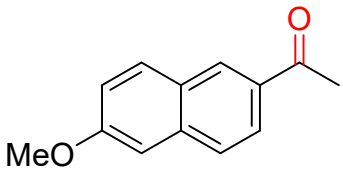


(9*H*-fluoren-9-yl)methyl benzoylcarbamate (2x)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 4.58 (d, *J* = 6.8 Hz, 2H), 4.31 (t, *J* = 6.8 Hz, 1H).

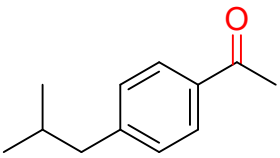
^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.84, 151.31, 143.28, 141.29, 133.03, 132.90, 128.83, 127.89, 127.68, 127.21, 125.04, 120.04, 67.97, 46.68.
HRMS (ESI) calcd for $C_{22}H_{17}NO_3$ [M+Na]$^+$: 366.1101; found: 366.1097.



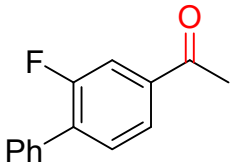
***N*,1-Dibenzoylpyrrolidine-2-carboxamide (2y)**
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.57 (s, 1H), 7.97 (d, *J* = 7.7 Hz, 2H), 7.53 (m, 3H), 7.48 – 7.38 (m, 5H), 5.21 (dd, *J* = 8.1, 4.3 Hz, 1H), 3.61 – 3.50 (m, 2H), 2.54-2.48 (m, 1H), 2.22-2.17 (m, 1H), 2.11-2.04 (m, 1H), 1.94-1.86 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.34, 170.79, 165.42, 135.64, 132.97, 132.65, 130.36, 128.80, 128.40, 127.89, 126.94, 61.02, 50.51, 26.75, 25.07.
HRMS (ESI) calcd for $C_{19}H_{18}N_2O_3$ [M+Na]$^+$: 345.1210; found: 345.1214.



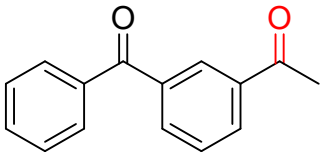
1-(6-Methoxynaphthalen-2-yl)ethan-1-one (3a)[30]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 8.00 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.23 – 7.12 (m, 2H), 3.94 (s, 3H), 2.69 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.80, 159.71, 137.23, 132.58, 131.06, 130.00, 127.77, 127.04, 124.61, 119.67, 105.71, 55.37, 26.51.



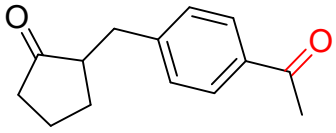
1-(4-Isobutylphenyl)ethan-1-one (3b)[30]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.58 – 2.52 (m, 5H), 1.93-1.87 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.84, 147.53, 134.92, 129.23, 128.26, 45.33, 30.07, 26.49, 22.28.



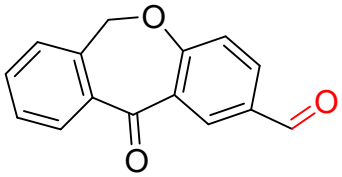
1-(2-Fluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (3c)[31]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.74 (dd, *J* = 11.2, 1.7 Hz, 1H), 7.61 – 7.51 (m, 3H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 2.63 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.43, 159.63 (d, *J* = 249.8 Hz), 137.77 (d, *J* = 6.3 Hz), 134.63, 133.75 (d, *J* = 13.7 Hz), 130.89 (d, *J* = 3.4 Hz), 128.96 (d, *J* = 3.1 Hz), 128.47, 124.30 (d, *J* = 3.4 Hz), 115.86 (d, *J* = 24.0 Hz), 26.61.



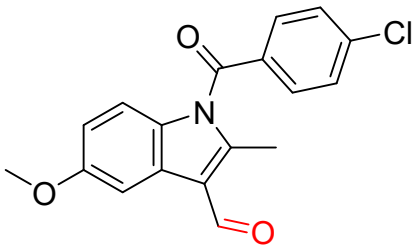
1-(3-Benzoylphenyl)ethan-1-one (3d)[30]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.60 (q, *J* = 7.9 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 2.64 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.23, 195.79, 138.02, 137.13, 136.95, 134.19, 132.83, 131.71, 129.98, 129.64, 128.69, 128.46, 26.70.



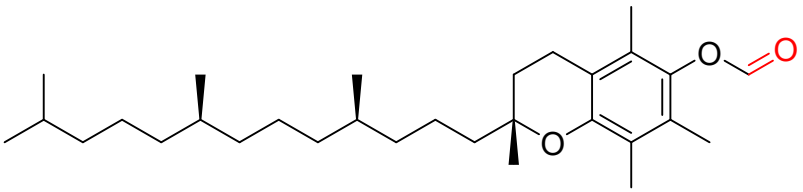
2-(4-Acetylbenzyl)cyclopentan-1-one (3e)
1H NMR (400 MHz, Chloroform-d) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.12 (dd, *J* = 13.9, 4.3 Hz, 1H), 2.61 – 2.53 (m, 1H), 2.51 (s, 3H), 2.34 – 2.25 (m, 2H), 2.08 – 1.94 (m, 2H), 1.92 – 1.87 (m, 1H), 1.71 – 1.62 (m, 1H), 1.52-1.41 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 219.45, 197.67, 145.76, 135.30, 129.05, 128.51, 50.58, 37.97, 35.48, 29.05, 26.49, 20.45.
HRMS (ESI) calcd for $C_{14}H_{16}O_2$ $[M+Na]^+$: 239.1043; found: 239.1046.



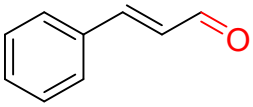
11-Oxo-6,11-dihydrodibenzo[*b*,*e*]oxepine-2-carbaldehyde (3f)[32]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 8.73 (d, *J* = 2.2 Hz, 1H), 8.02 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 5.28 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.34, 190.13, 165.51, 140.28, 137.41, 134.49, 133.39, 133.18, 130.90, 129.70, 129.37, 128.12, 124.98, 122.13, 73.59.
HRMS (CI) calcd for $C_{15}H_{10}O_3$ $[M+H]^+$: 239.0703; found: 239.0692.



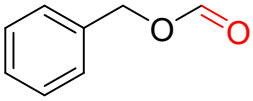
1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1H-indole-3-carbaldehyde (3g)[30]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.32 (s, 1H), 7.80 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.73 (s, 2H), 3.87 (s, 3H), 2.76 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 185.71, 168.20, 157.16, 148.46, 140.88, 132.04, 131.65, 130.59, 129.46, 126.93, 118.34, 114.25, 113.84, 103.27, 55.72, 12.62.
HRMS (CI) calcd for $C_{18}H_{14}ClNO_3$ $[M+H]^+$: 328.0735; found: 328.0734.



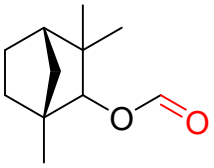
(*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl formate (3h)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 2.60 (t, *J* = 6.8 Hz, 2H), 2.10 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.86-1.72 (m, 2H), 1.54 – 1.51 (m, 2H), 1.43-1.35 (m, 4H), 1.28 – 1.24 (m, 11H), 1.16 – 1.03 (m, 7H), 0.88 – 0.84 (m, 12H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.02, 149.77, 139.73, 126.56, 124.85, 123.32, 117.61, 75.20, 40.02, 39.37, 37.45, 37.40, 37.38, 37.28, 32.77, 32.69, 31.03, 27.97, 24.80, 24.43, 23.90, 22.71, 22.62, 21.02, 20.62, 19.74, 19.68, 13.09, 12.24, 11.84.
HRMS (ESI) calcd for $C_{30}H_{50}O_3$ $[M+Na]^+$: 481.3653; found: 481.3649



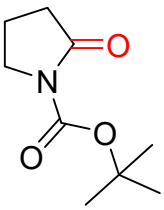
Cinnamaldehyde (5a)[17]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.71 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.51 – 7.39 (m, 4H), 6.72 (dd, *J* = 16.0, 7.7 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.68, 152.76, 133.97, 131.24, 129.07, 128.56, 128.46.



Benzyl formate (5b)[33]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.39 – 7.33 (m, 5H), 5.21 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.76, 135.17, 128.64, 128.49, 128.35, 65.68.

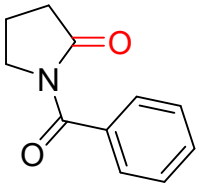


(*1R*,*4S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl formate (5c)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 4.47 (s, 1H), 1.71 (dd, *J* = 20.4, 9.0 Hz, 3H), 1.60 (d, *J* = 10.5 Hz, 1H), 1.51 – 1.40 (m, 1H), 1.21 (d, *J* = 8.9 Hz, 1H), 1.11-1.04 (m, 7H), 0.80 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.53, 86.37, 48.26, 48.23, 41.36, 39.20, 29.68, 26.52, 25.77, 20.31, 19.24.
HRMS (CI) calcd for $C_{11}H_{18}O_2$ $[M+H]^+$: 183.1380; found: 183.1381.

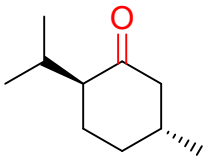


***Tert*-butyl 2-oxopyrrolidine-1-carboxylate (5d)**[34]

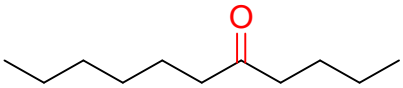
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.74 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 8.1 Hz, 2H), 2.00 (q, *J* = 9.2, 7.7 Hz, 2H), 1.52 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.27, 150.24, 82.75, 46.45, 32.95, 28.01, 17.38.



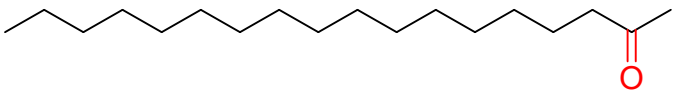
1-Benzoylpyrrolidin-2-one (5e)[35]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 3.95 (t, *J* = 7.1 Hz, 2H), 2.59 (t, *J* = 8.0 Hz, 2H), 2.17-2.09 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.45, 170.61, 134.28, 131.82, 128.83, 127.70, 46.46, 33.23, 17.59.



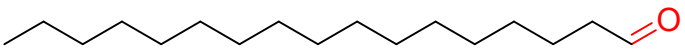
(2*S*,5*R*)-2-Isopropyl-5-methylcyclohexan-1-one (5f)[36]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.37 – 2.29 (m, 1H), 2.16 – 1.81 (m, 6H), 1.43-1.31 (m, 2H), 1.00 (d, *J* = 6.3 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.42, 55.89, 50.86, 35.46, 33.92, 27.86, 25.89, 22.27, 21.20, 18.69.



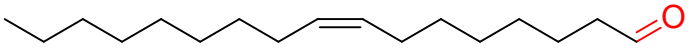
Undecan-5-one (5g)[37]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.39 (t, *J* = 7.5 Hz, 4H), 1.57-1.51 (m, 4H), 1.35 – 1.26 (m, 8H), 0.92 – 0.86 (m, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 211.73, 42.83, 42.52, 31.61, 28.94, 25.99, 23.86, 22.49, 22.38, 14.02, 13.86.



Octadecan-2-one (5h)[38]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.40 (t, *J* = 7.5 Hz, 2H), 2.12 (s, 3H), 1.61 – 1.50 (m, 2H), 1.30-1.24 (m, 26H), 0.87 (t, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 209.32, 43.81, 31.91, 29.81, 29.67, 29.65, 29.64, 29.59, 29.46, 29.39, 29.34, 29.17, 23.86, 22.67, 14.09.



Heptadecanal (5i)[39]
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.76 (s, 1H), 2.42 (t, *J* = 7.4, 1.9 Hz, 2H), 1.63 (t, *J* = 7.1 Hz, 2H), 1.30-1.26 (m, 26H), 0.88 (t, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.98, 43.92, 31.92, 29.69, 29.65, 29.63, 29.57, 29.42, 29.35, 29.16, 22.68, 22.09, 14.11.

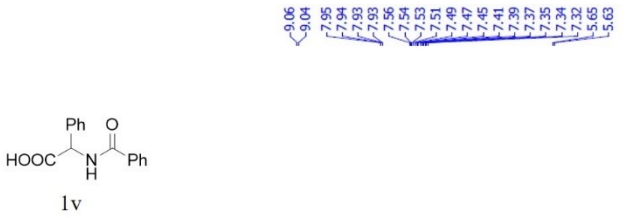


(*Z*)-heptadec-8-enal (5j)[40]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.76 (s, 1H), 5.39-5.30 (m, 2H), 2.42 (td, *J* = 7.4, 1.9 Hz, 2H), 2.03-2.00 (m, 4H), 1.65-1.61 (m, 2H), 1.36 – 1.25 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.87, 130.31, 130.14, 129.55, 129.33, 43.88, 31.89, 29.75, 29.50, 29.31, 29.05, 28.97, 27.21, 27.08, 22.67, 22.05, 14.10.

8 NMR spectra of substrates



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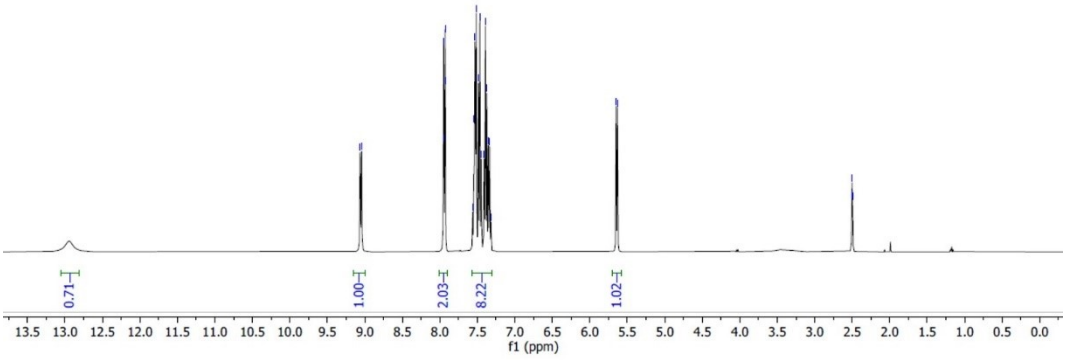
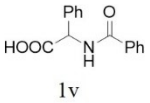


^{1}H NMR



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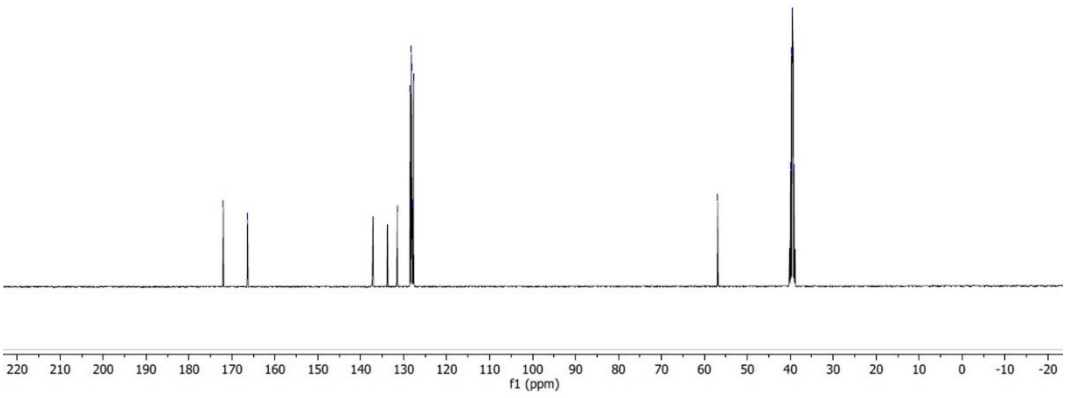

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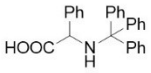

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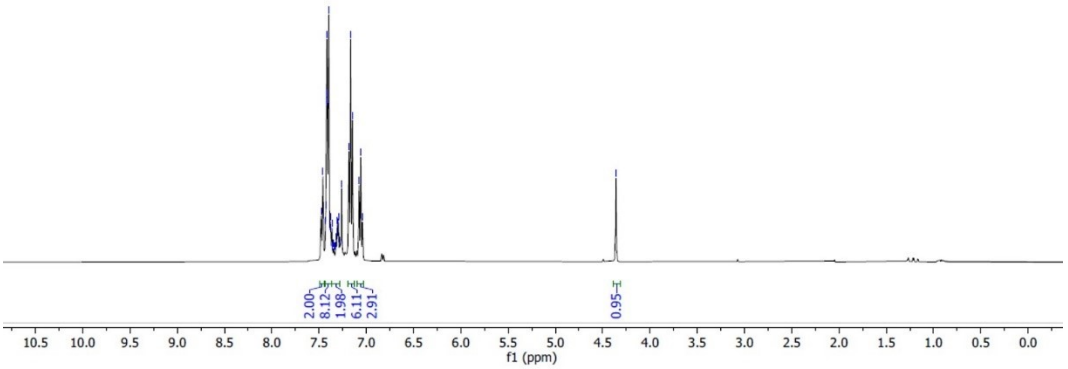

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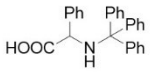

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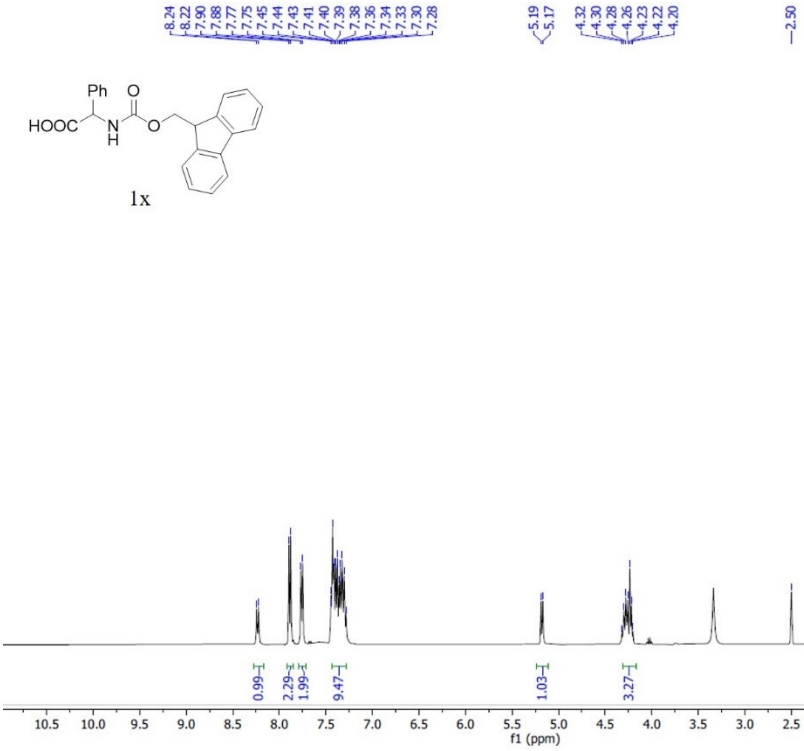

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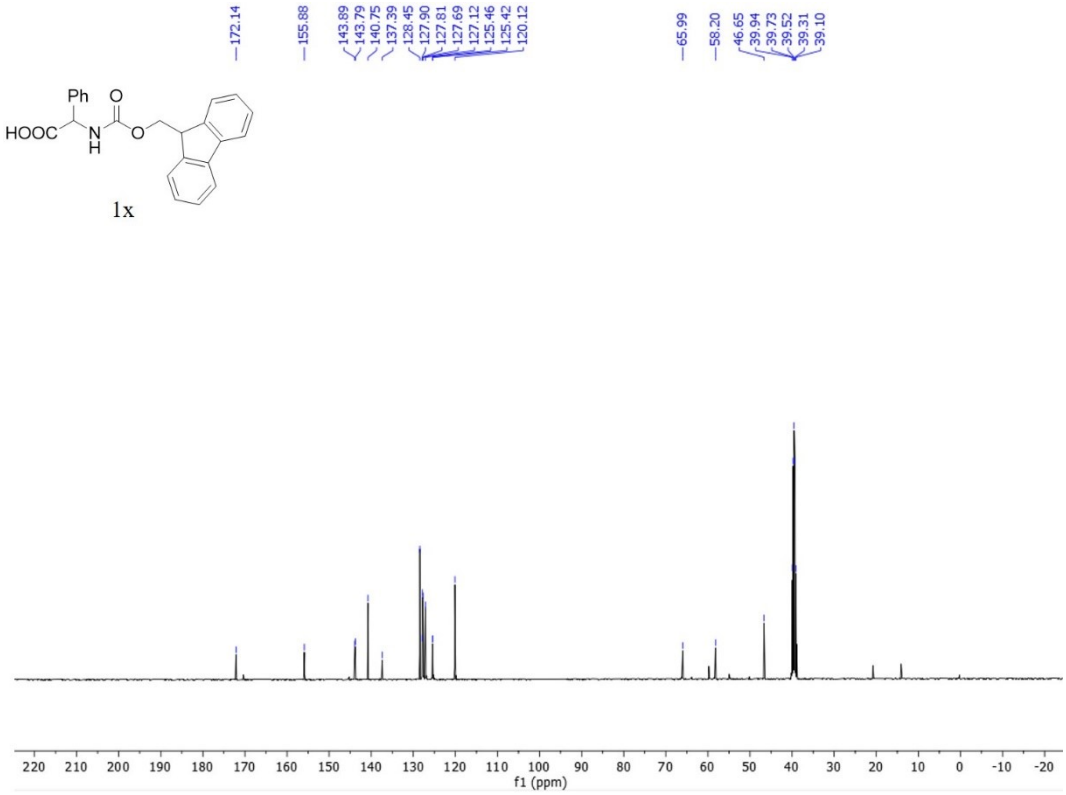

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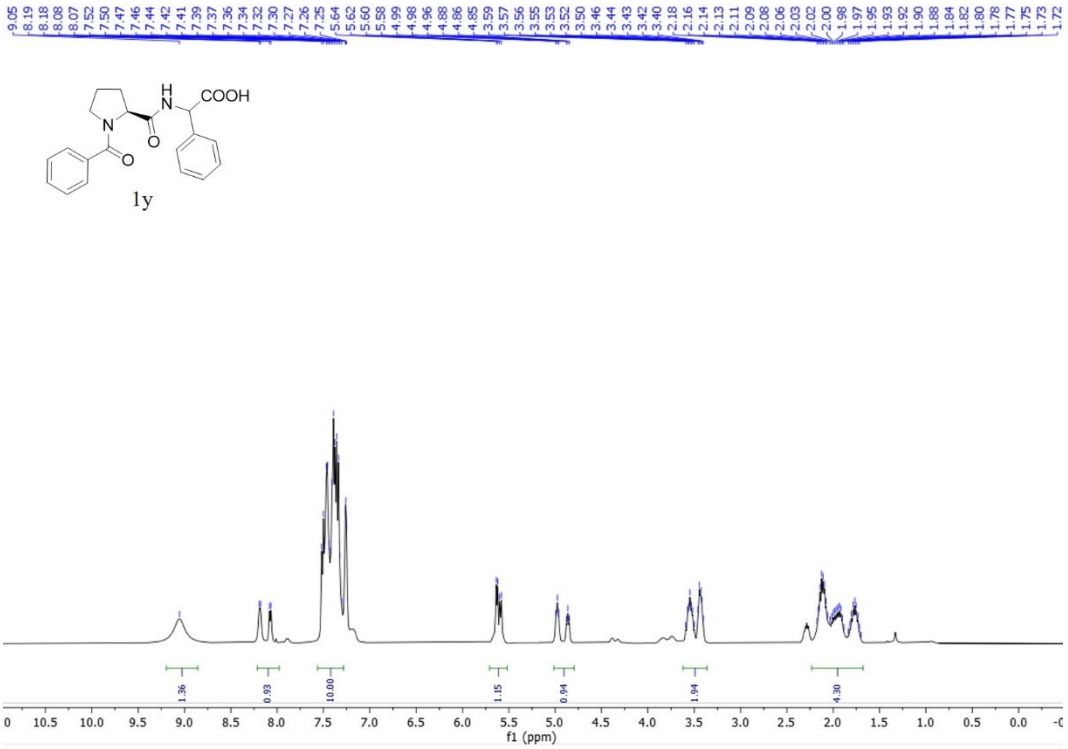

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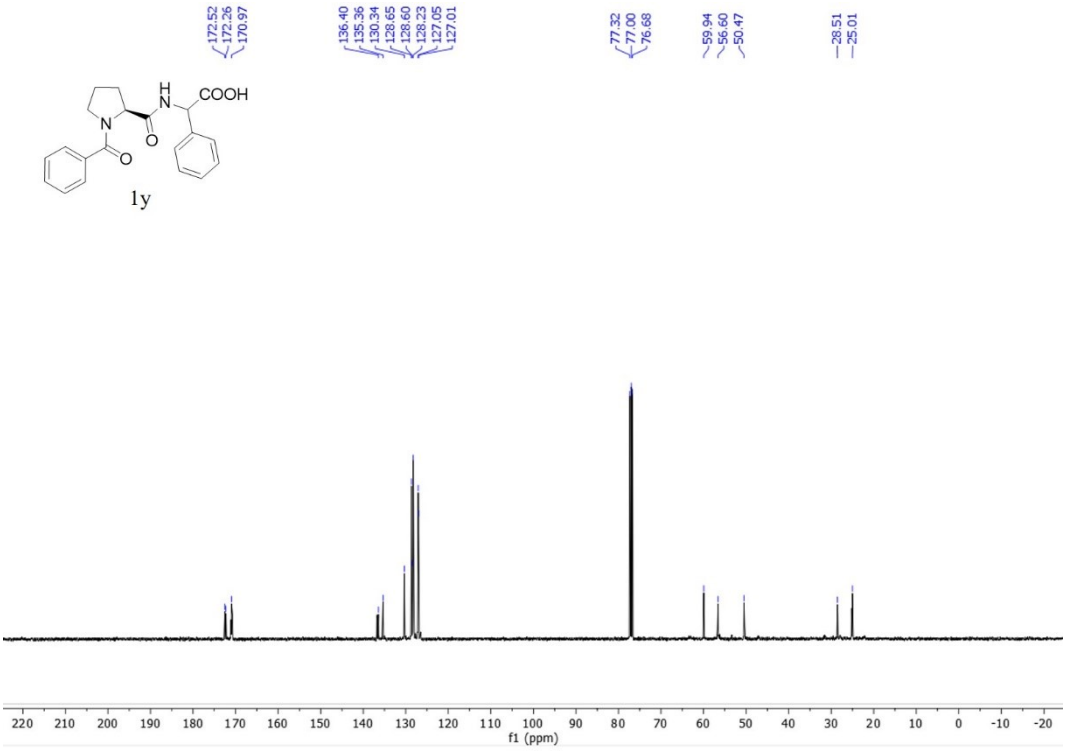

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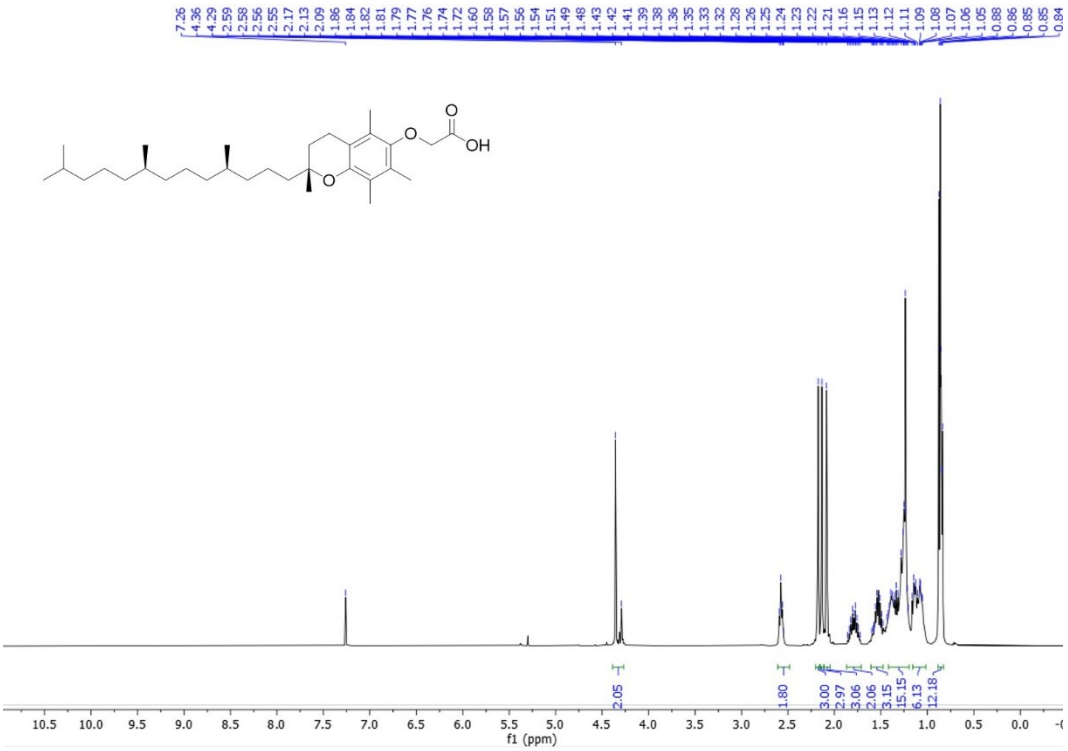

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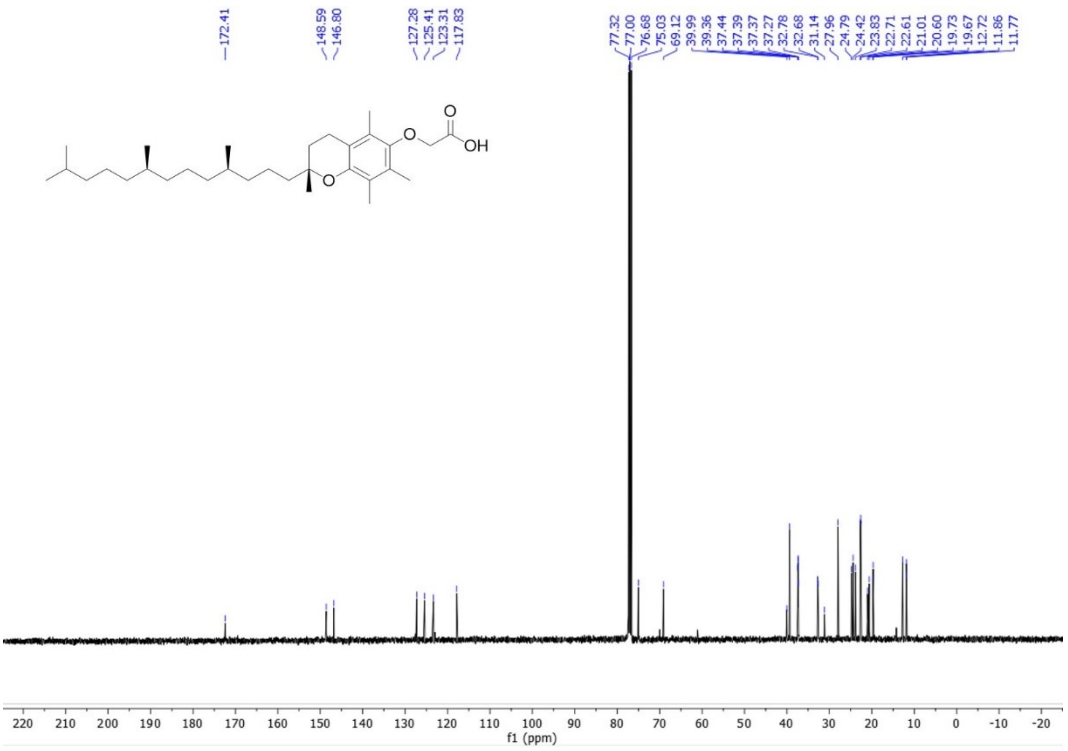

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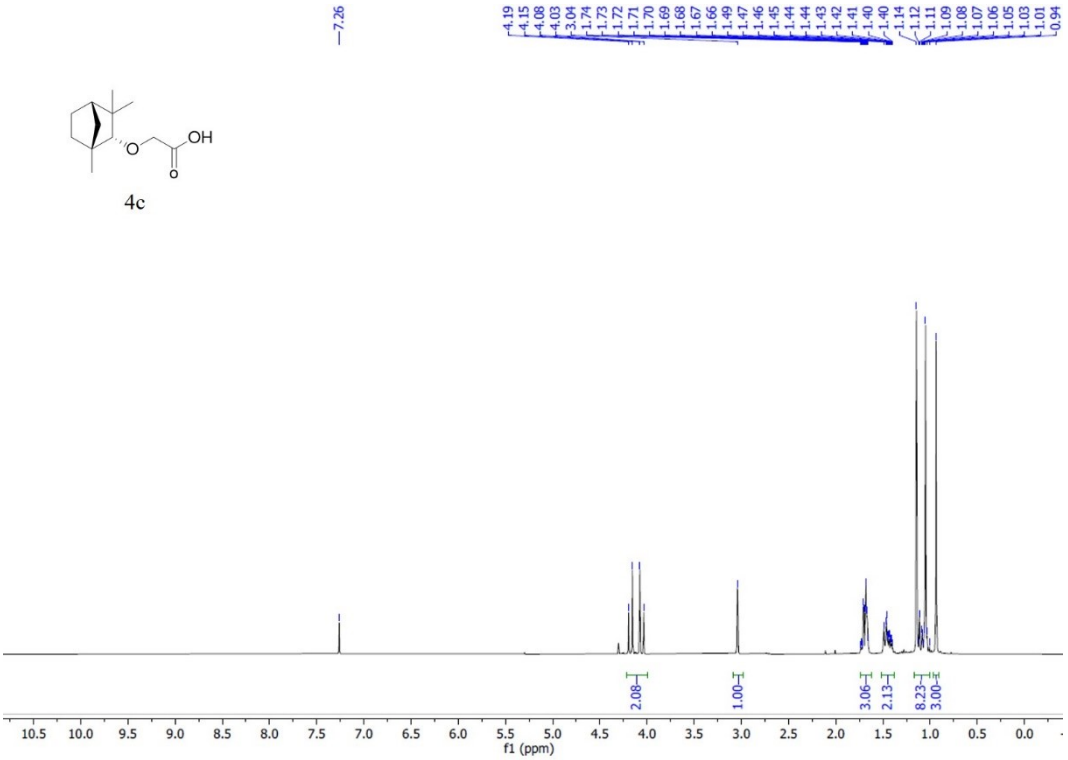

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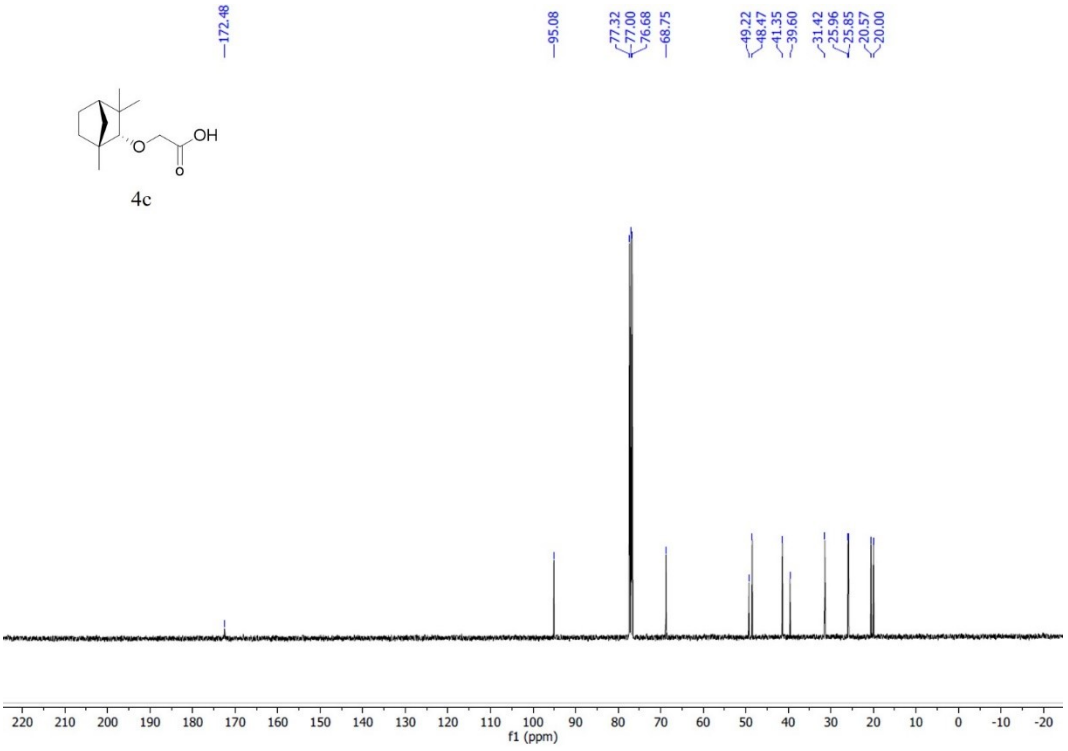

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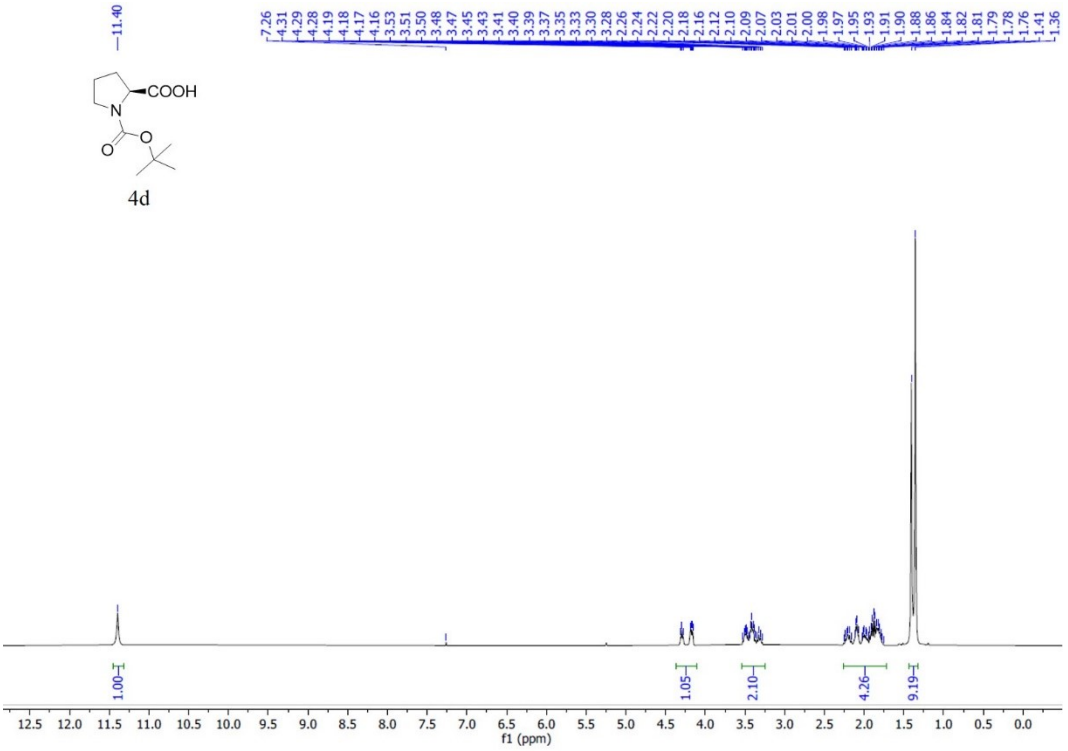
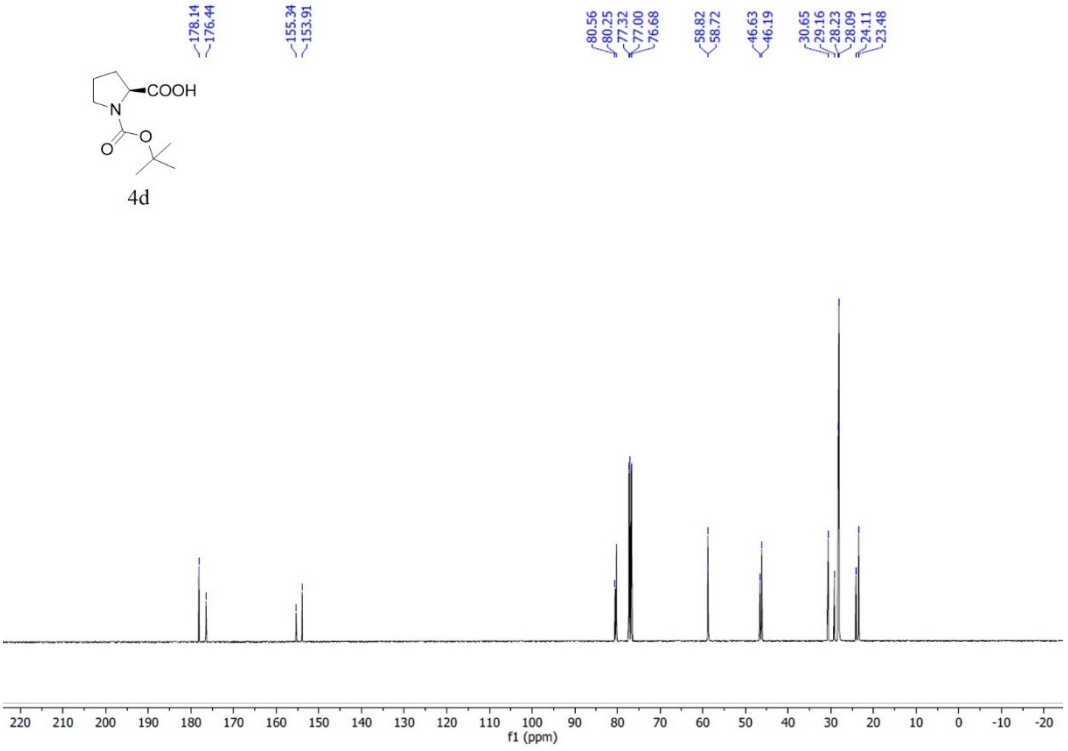


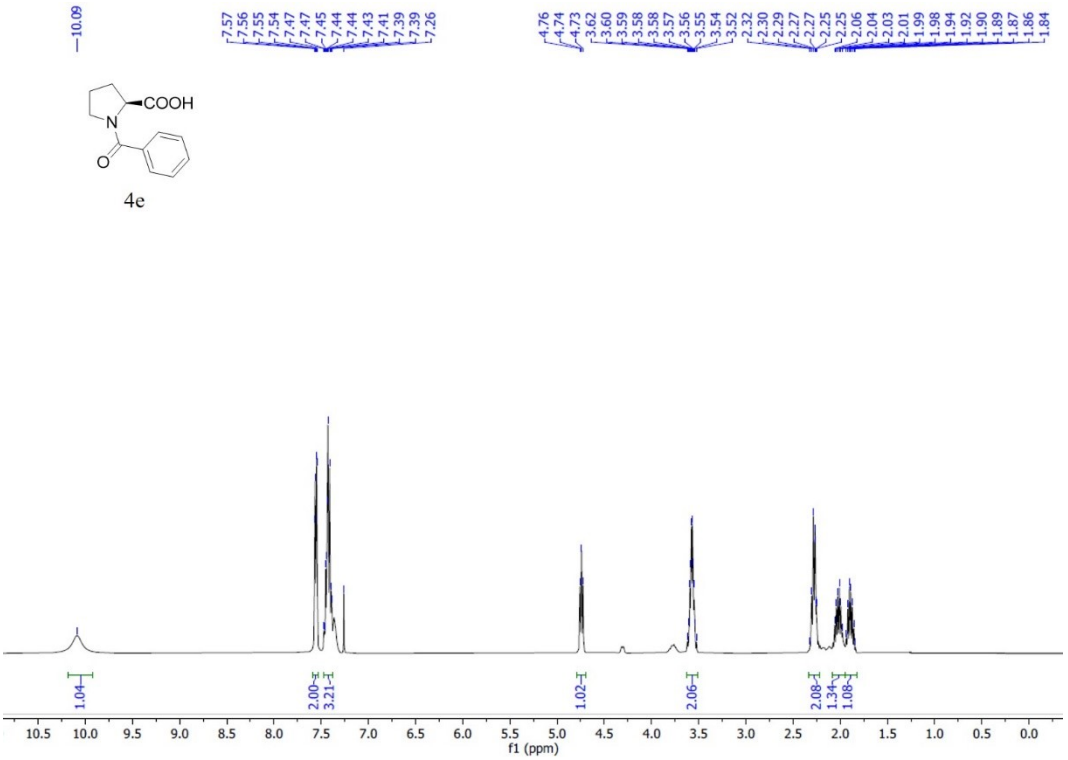
4d

^{1}H NMR

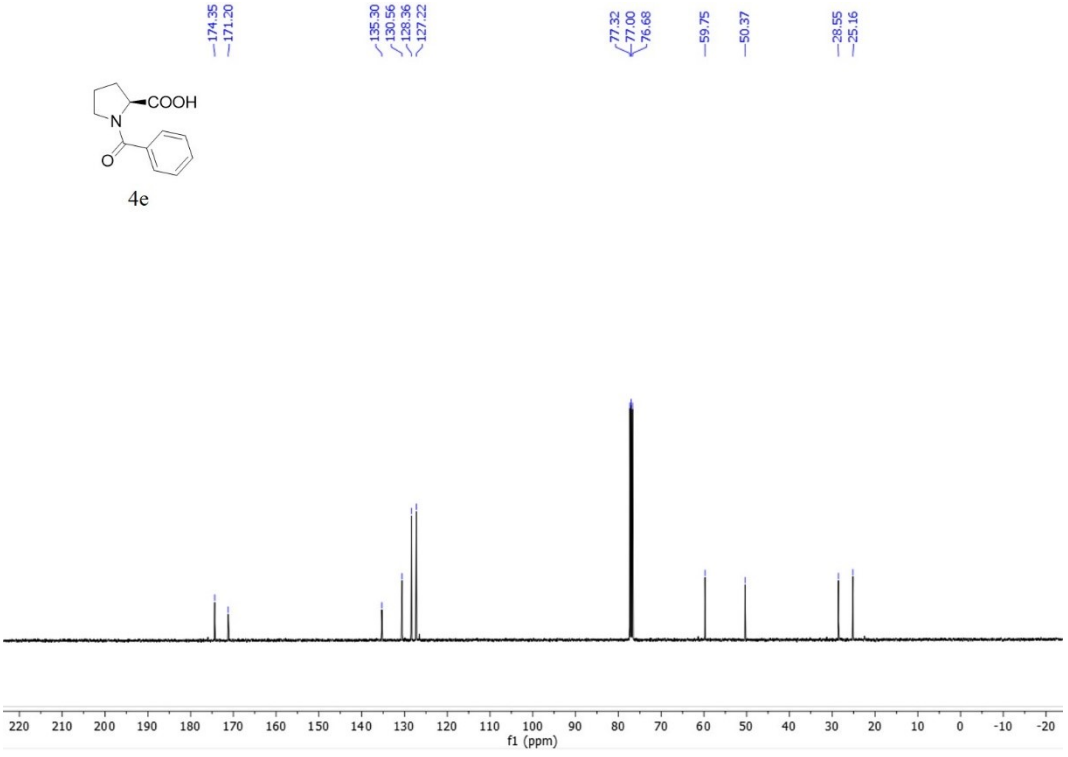


4d

^{13}C NMR



^{1}H NMR



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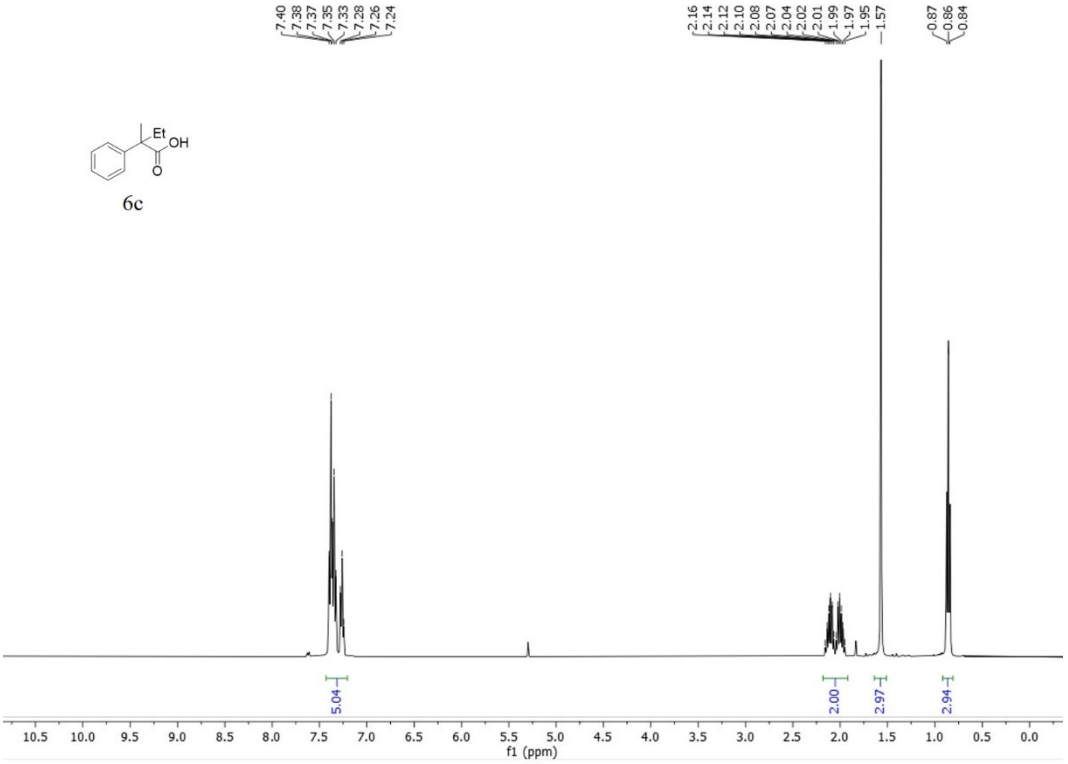

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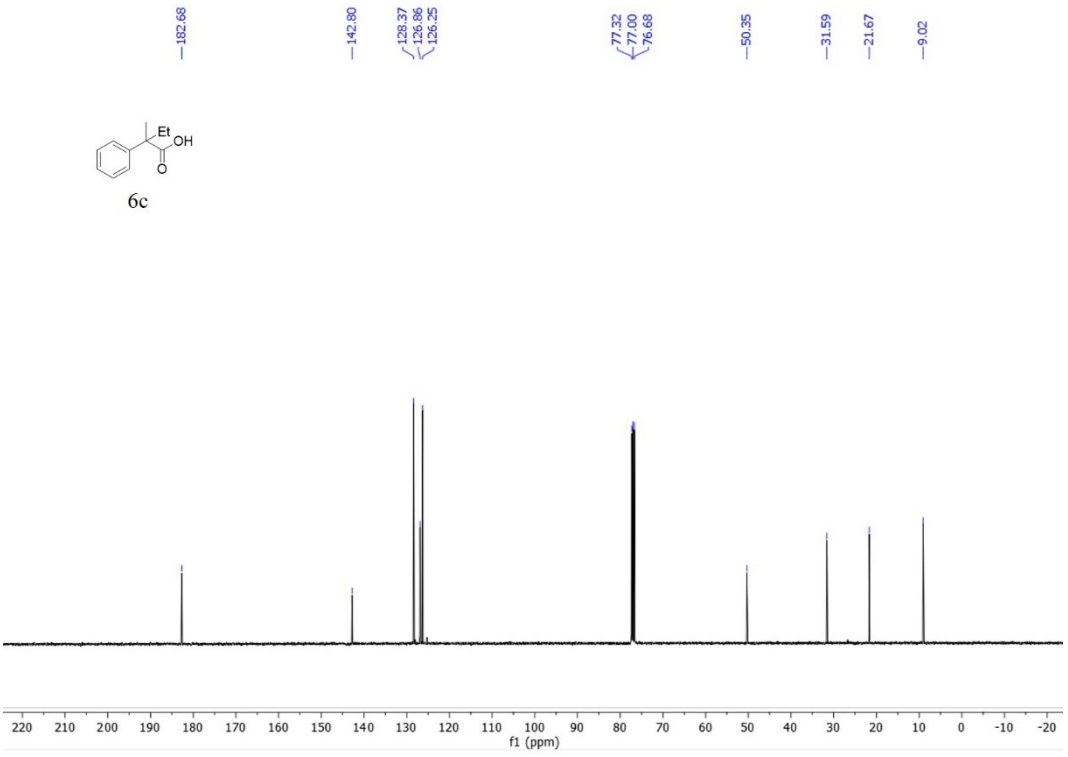

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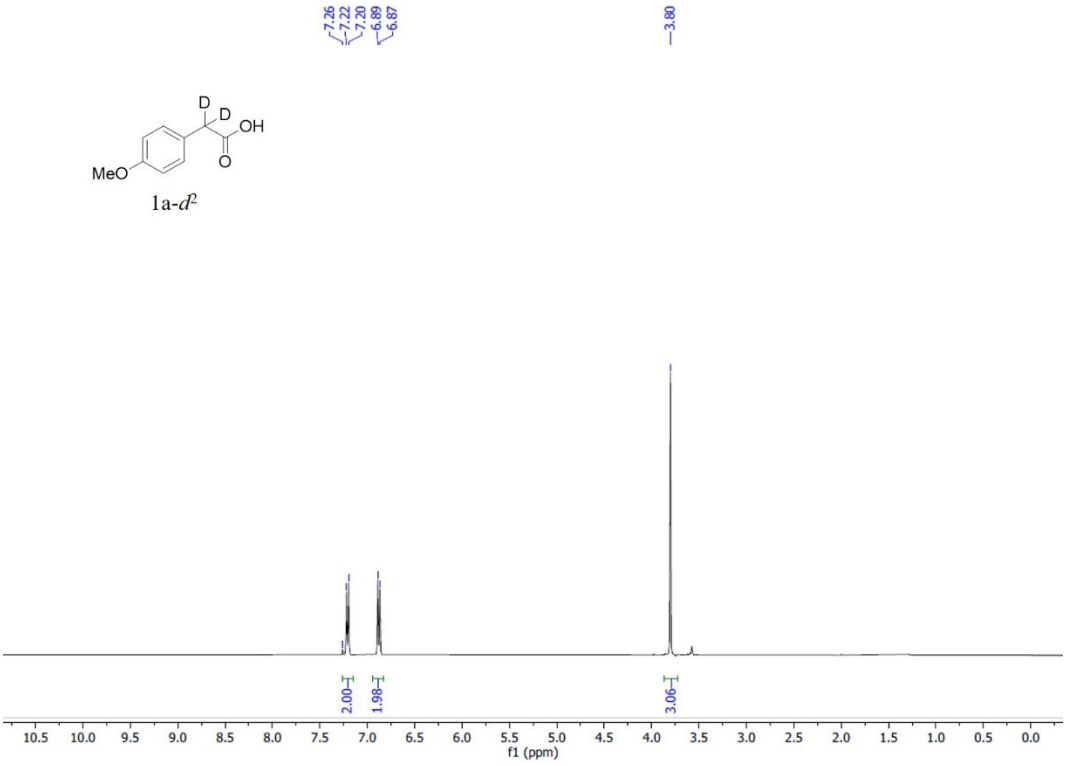

1a-d^2

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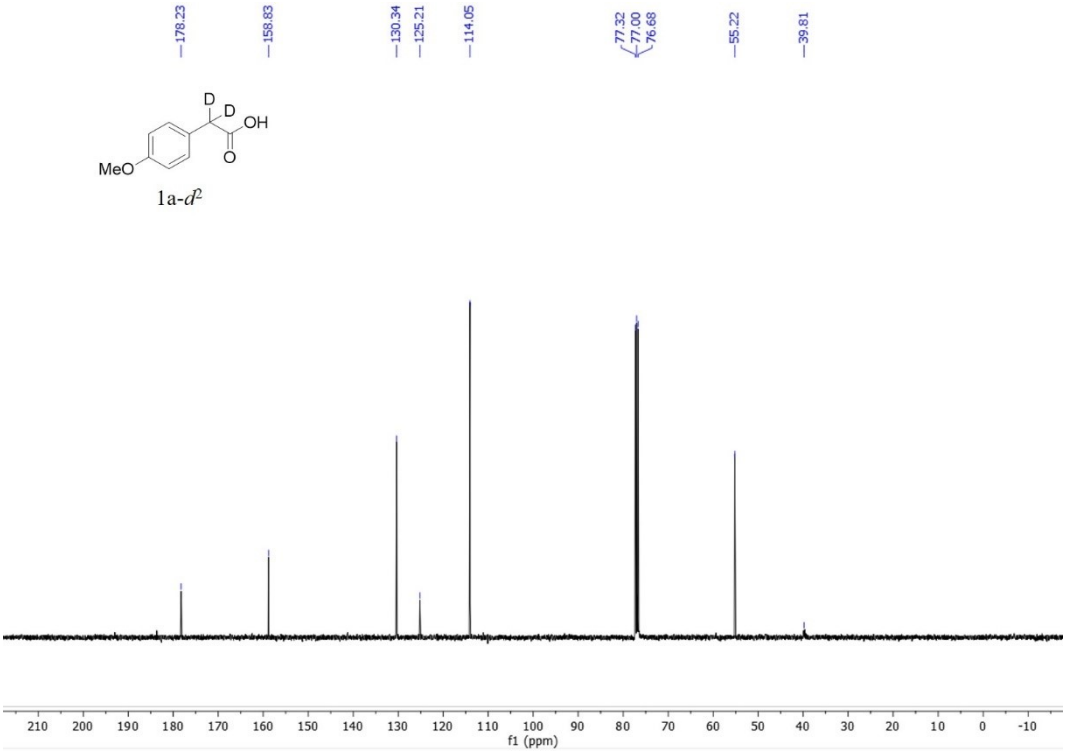

1a-d^2

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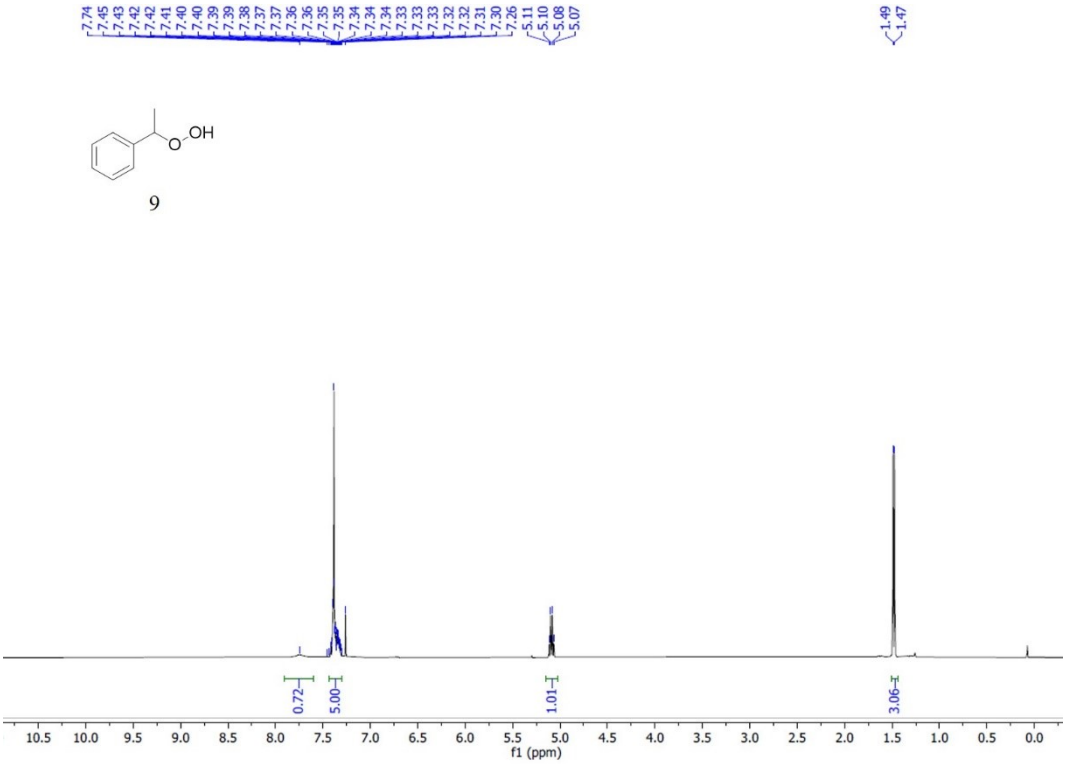

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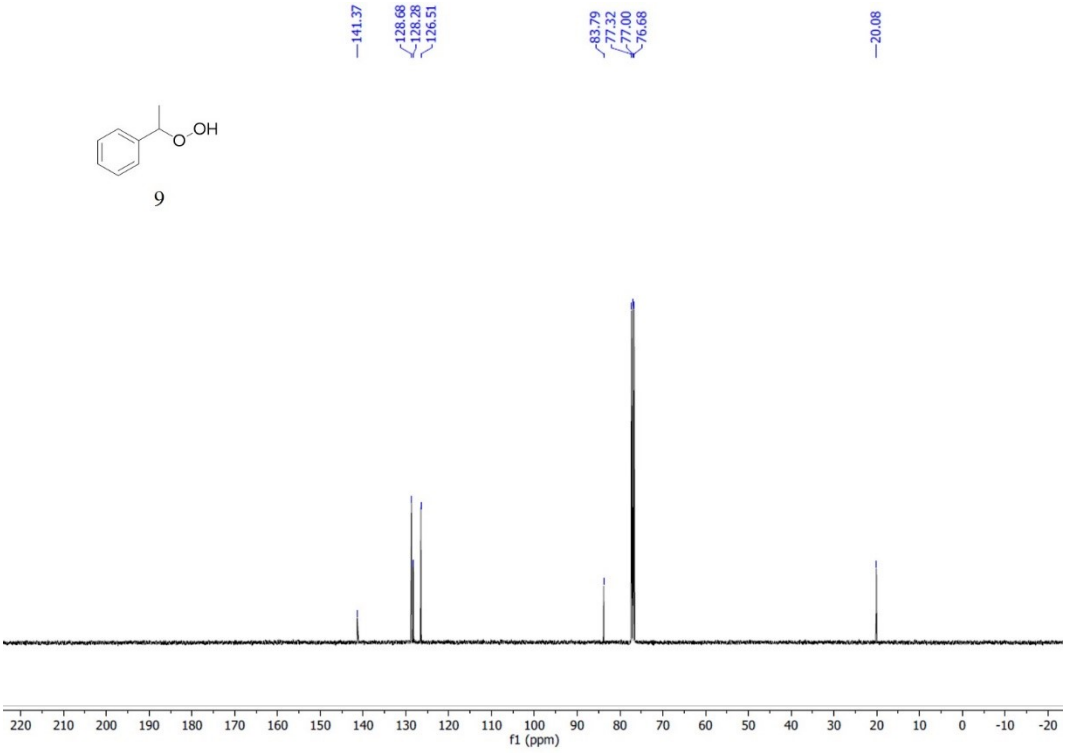
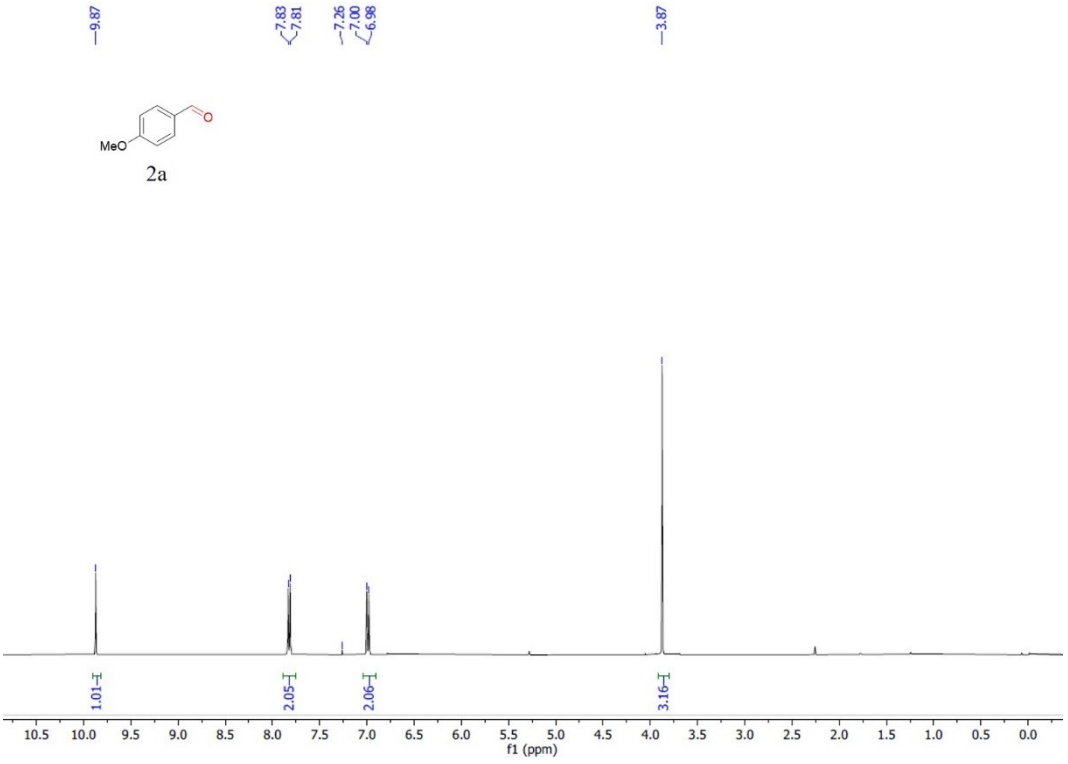


^{13}C NMR

9 NMR spectra of products



2a

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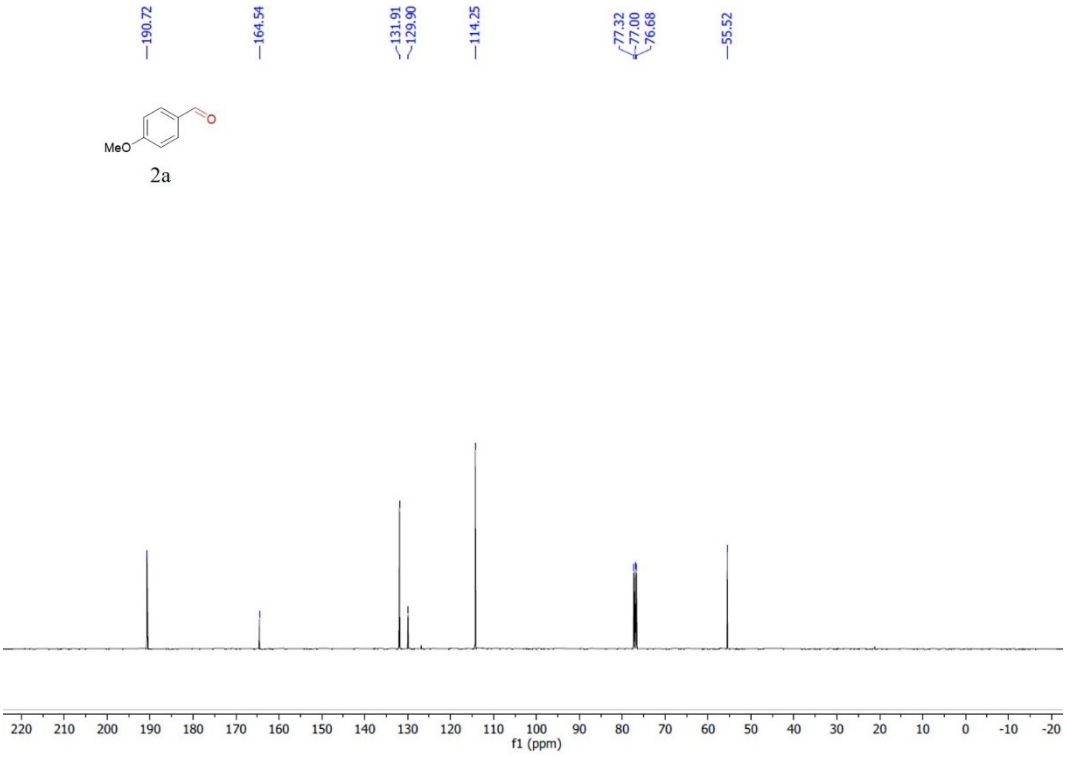

2a

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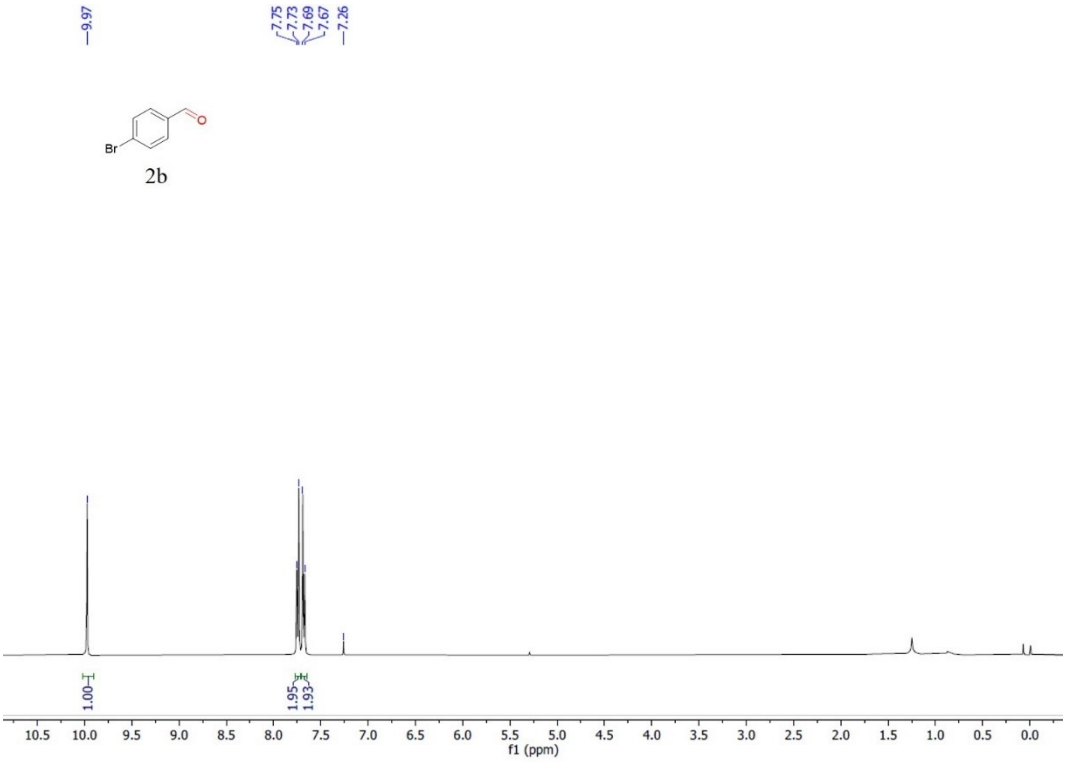

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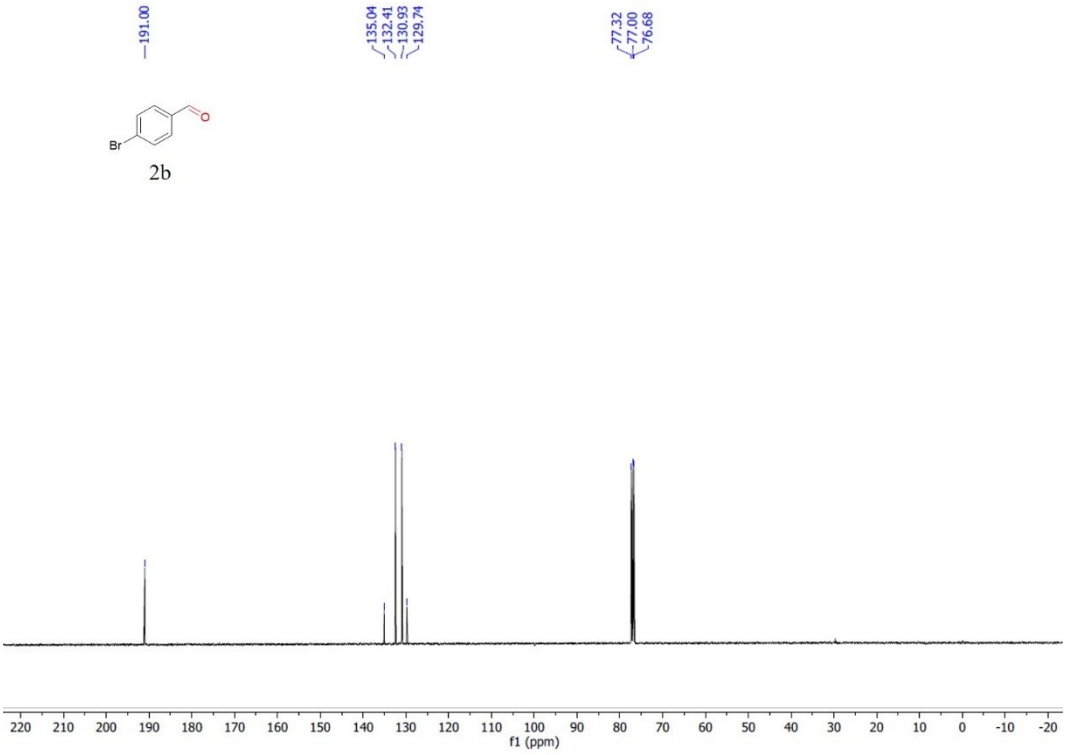

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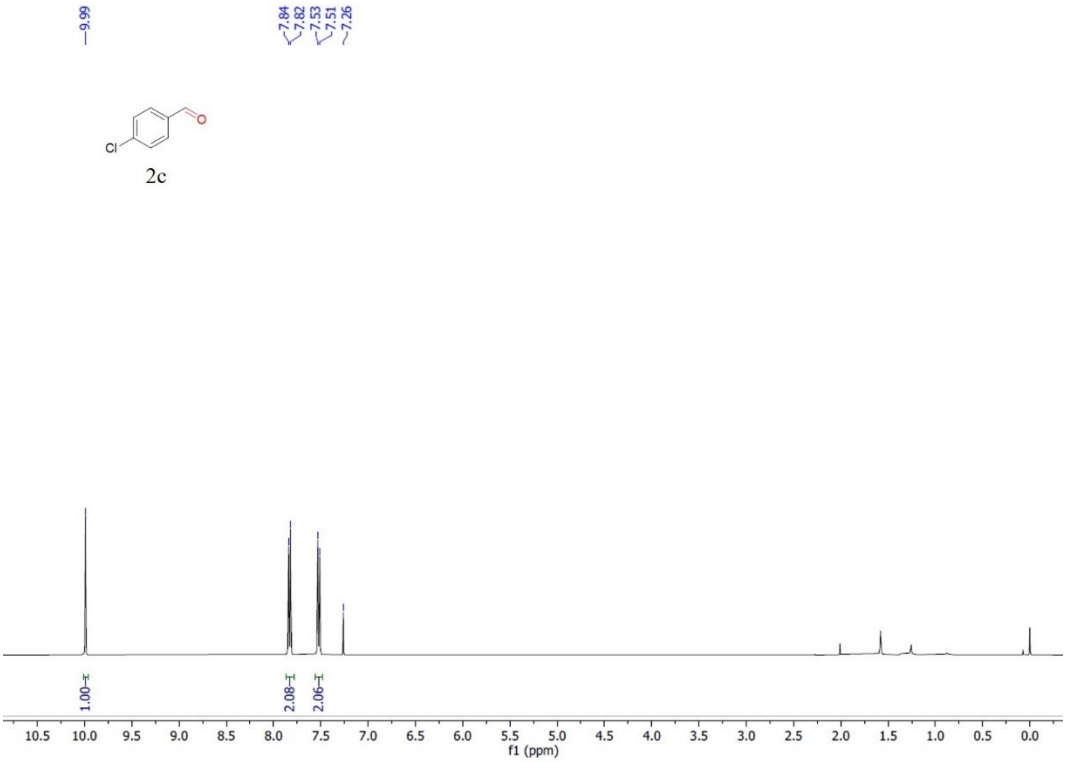

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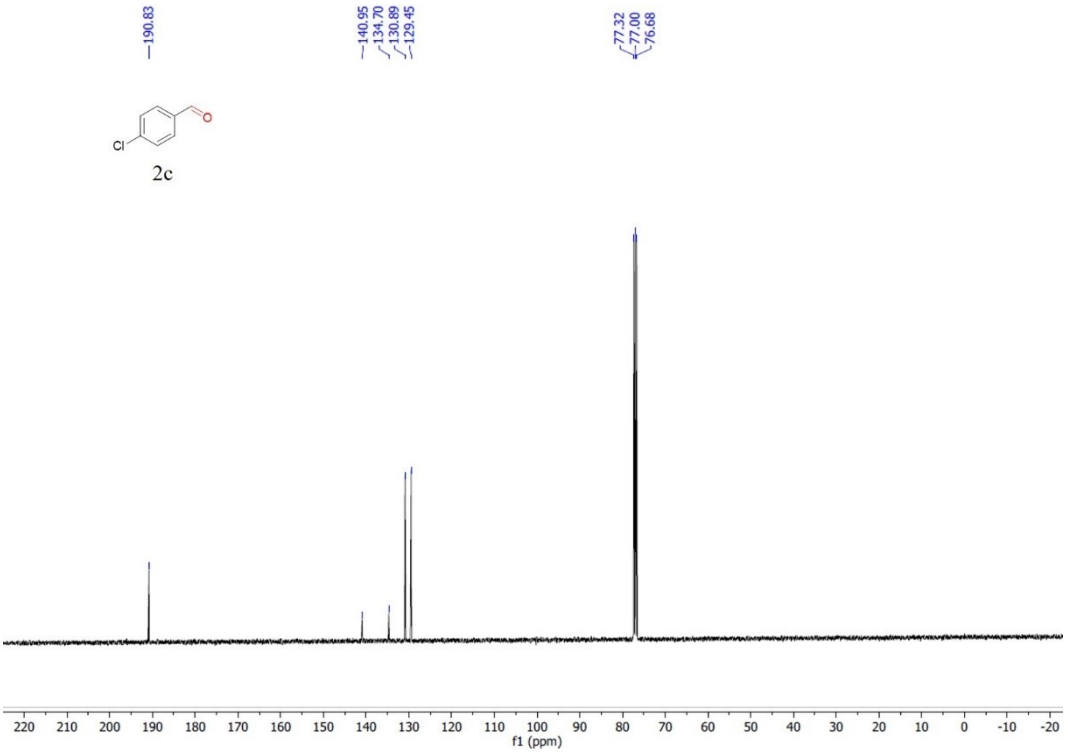

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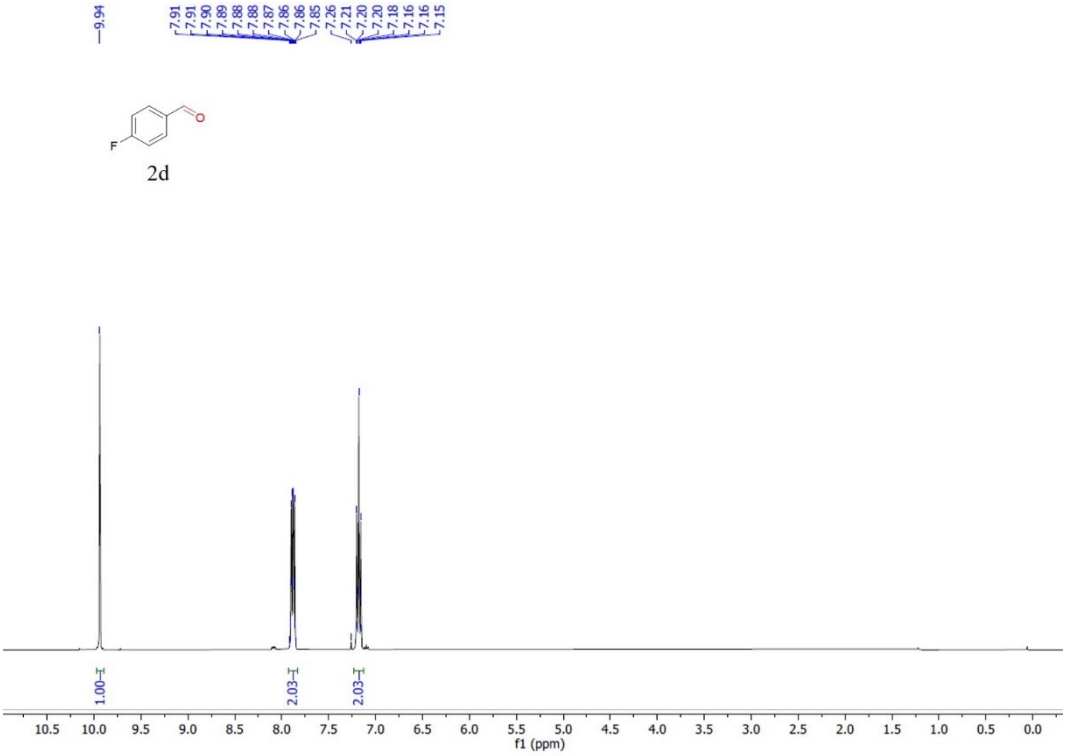

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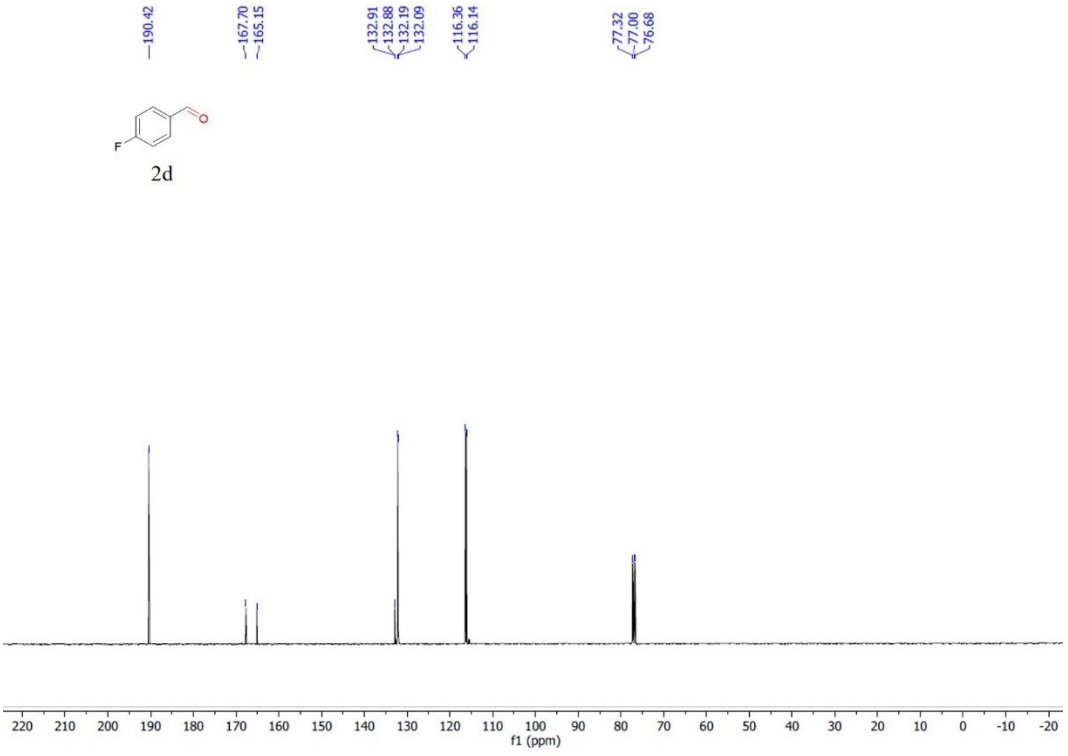

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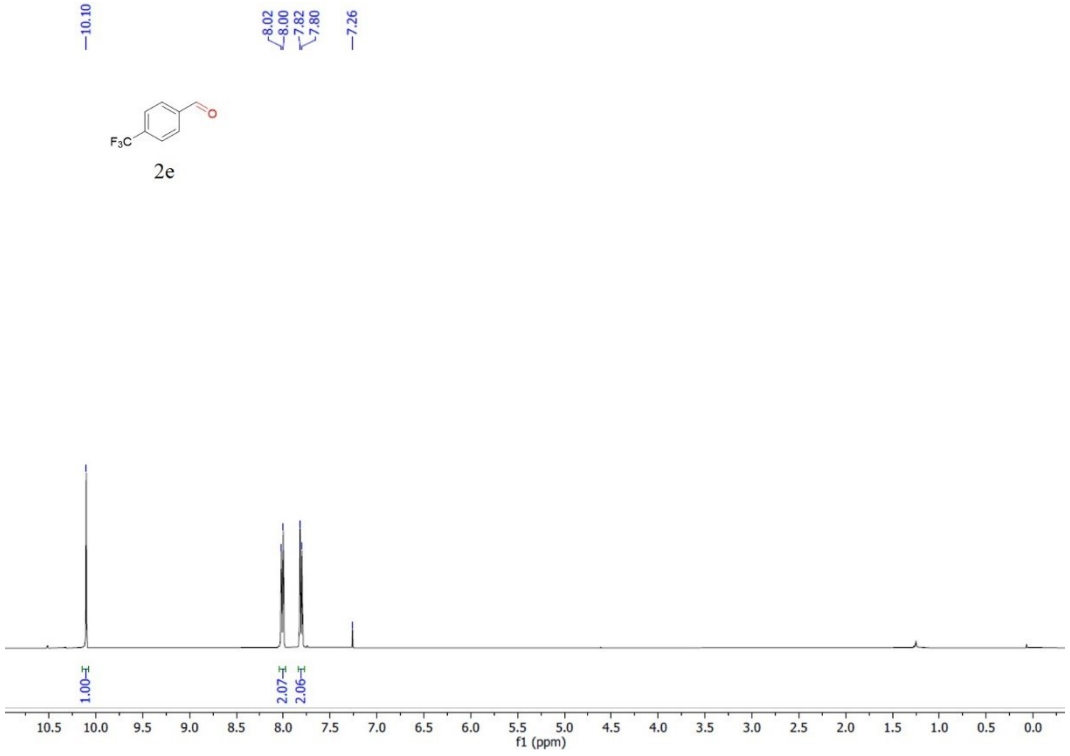

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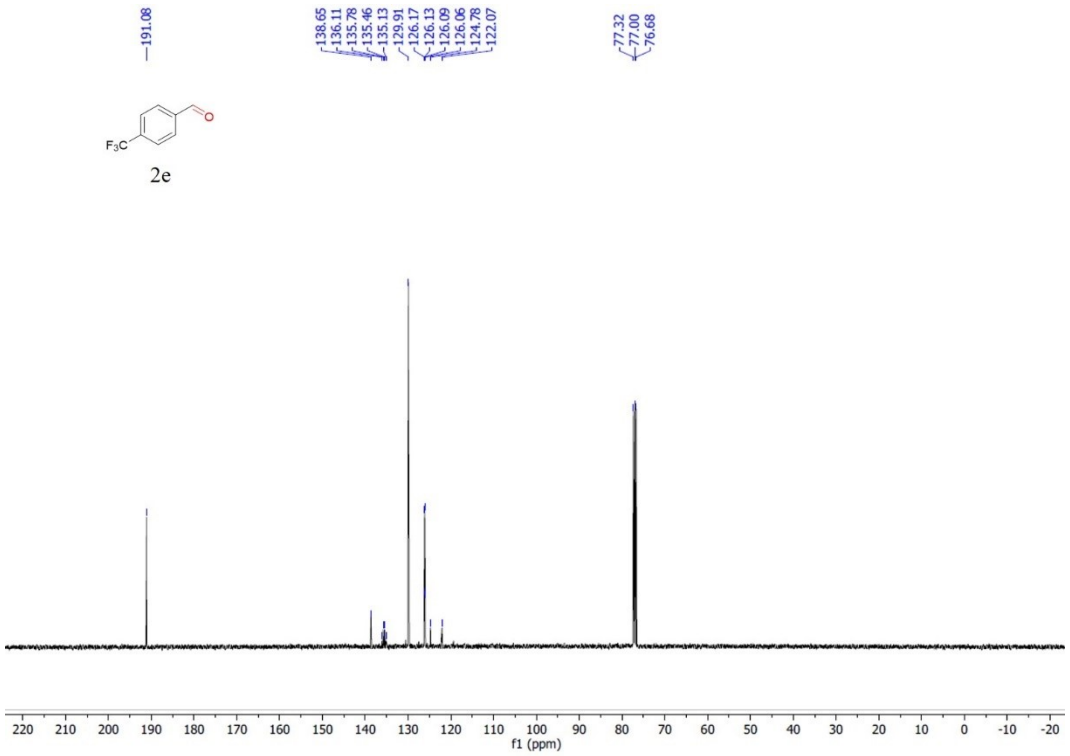

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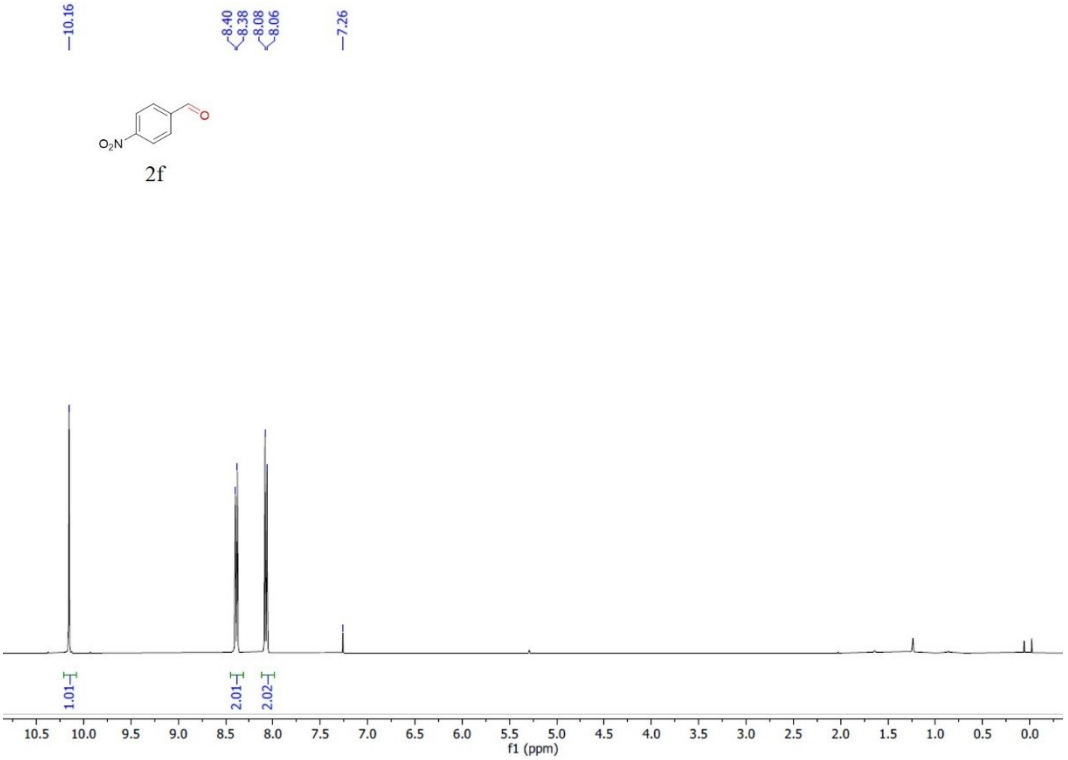

2f

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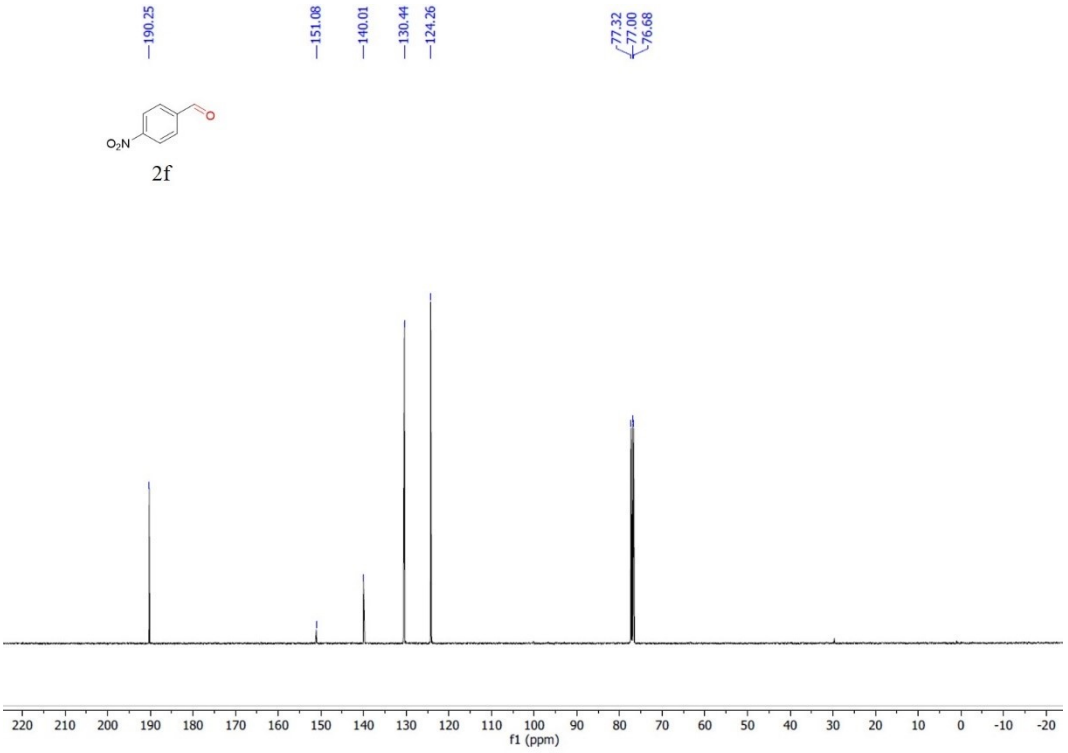

2f

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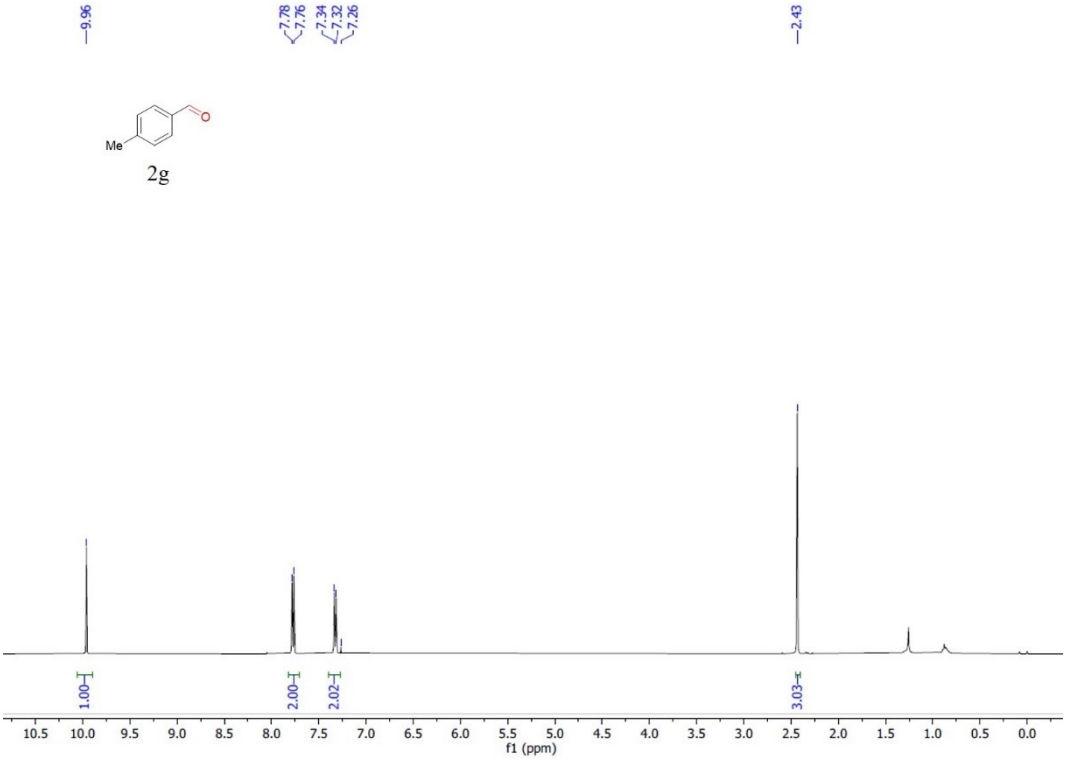
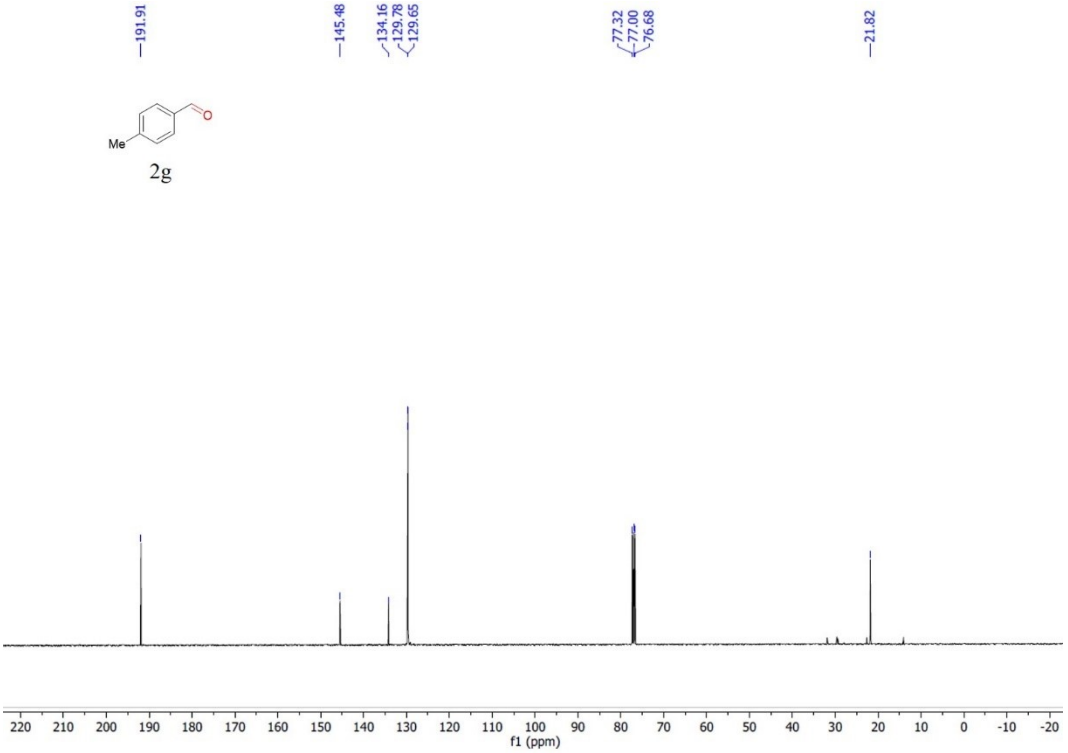


2g

^{1}H NMR



2g

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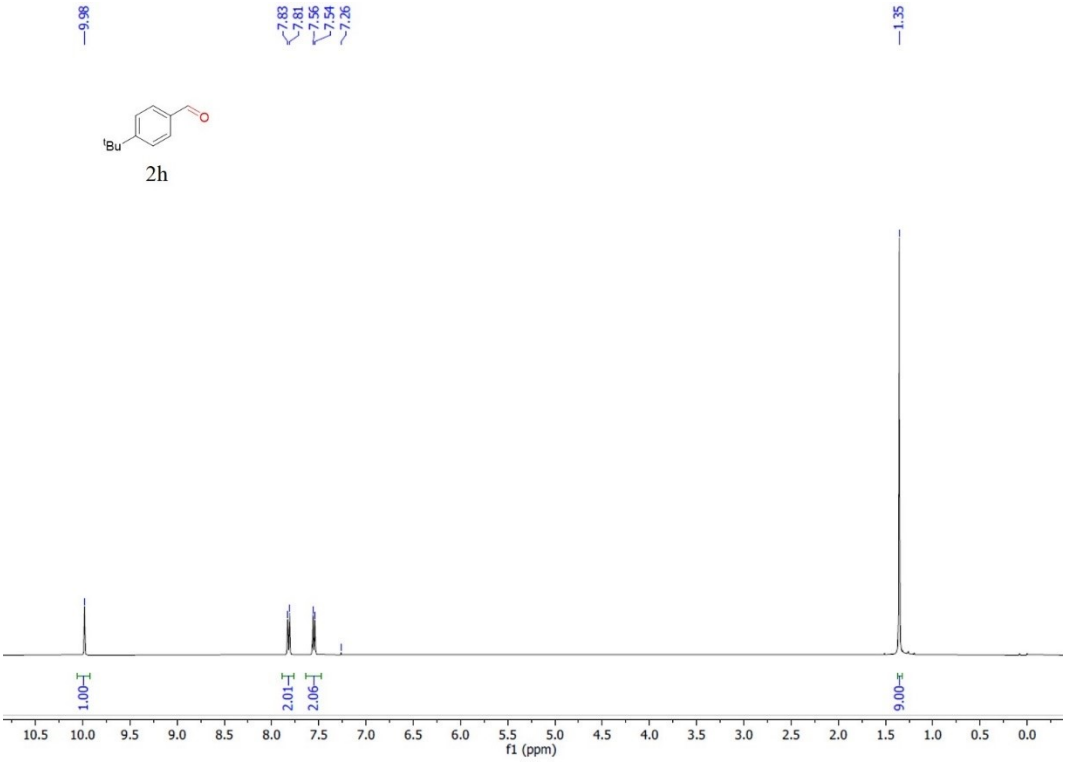

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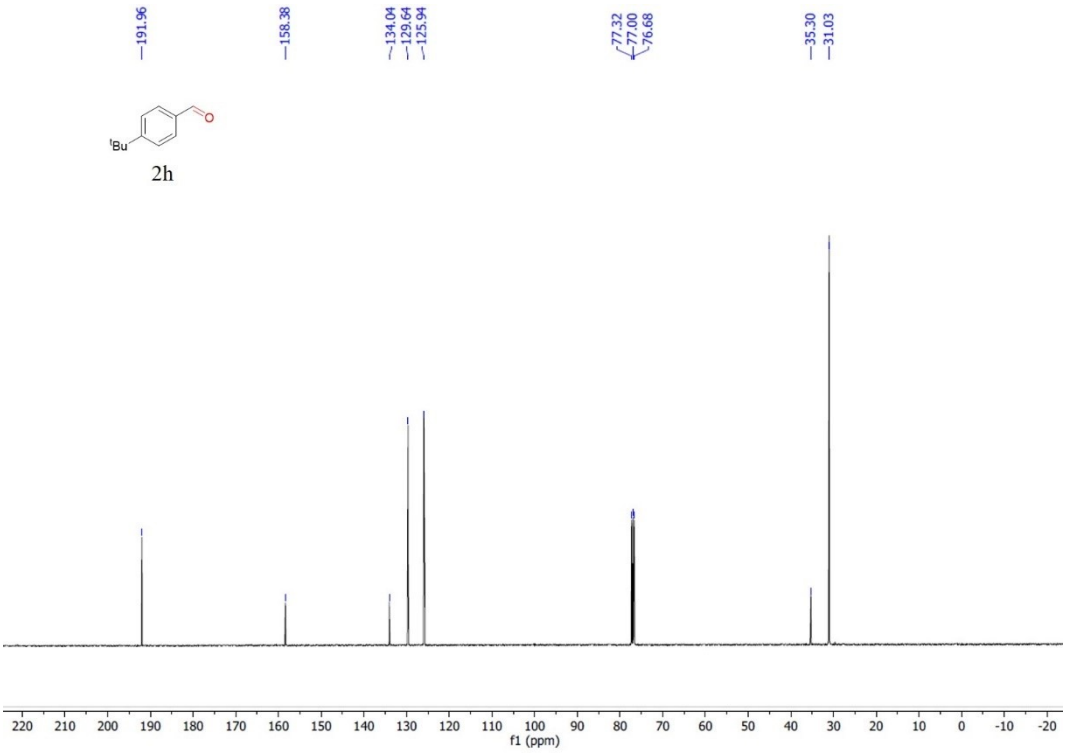

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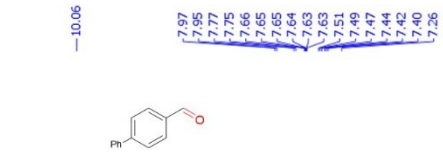

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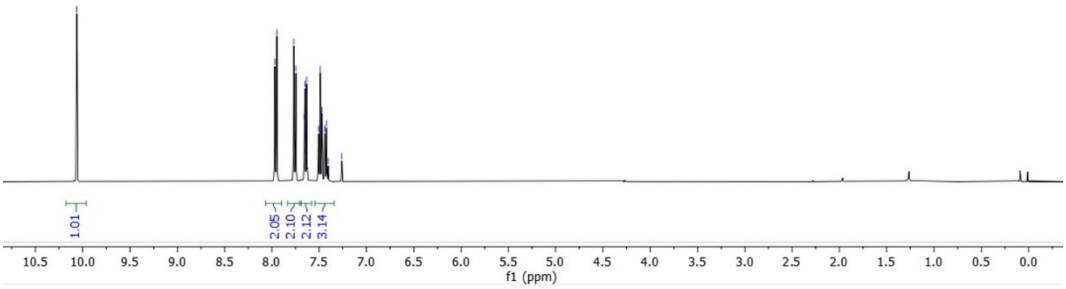

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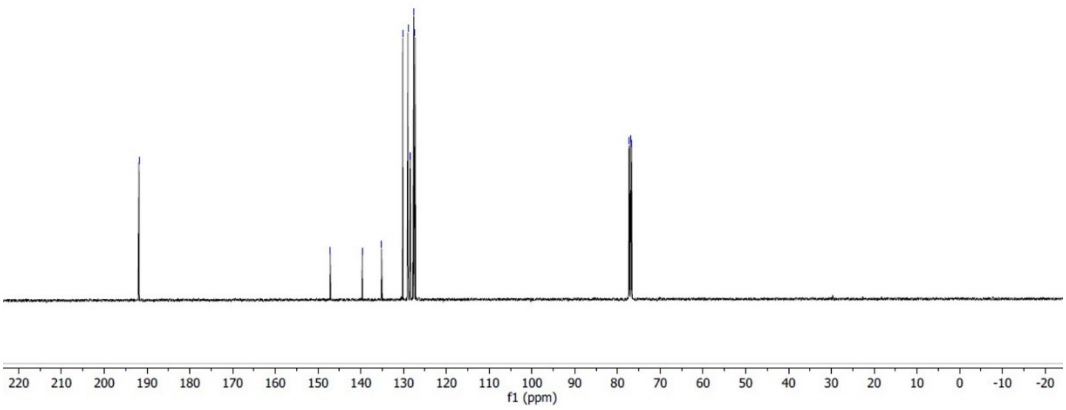
2h



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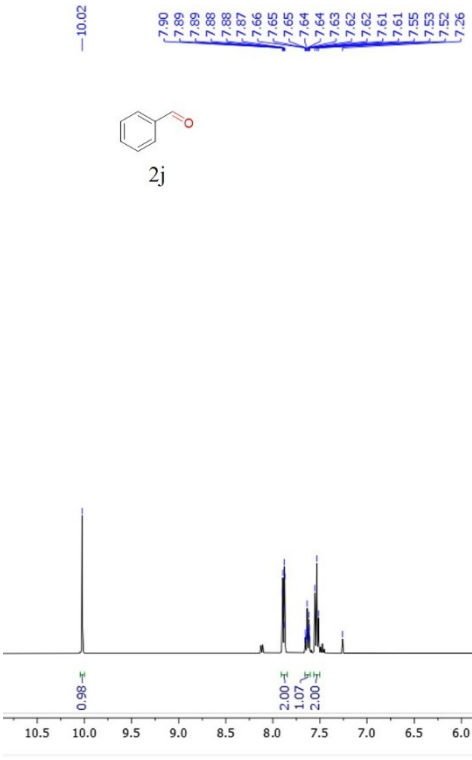

2j

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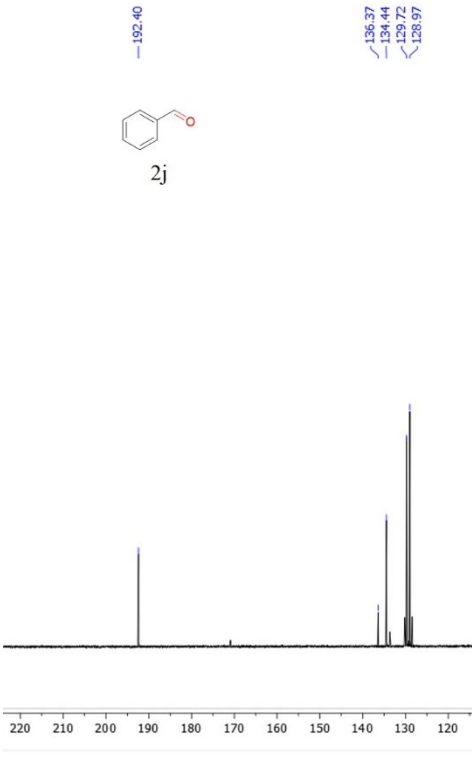

2j

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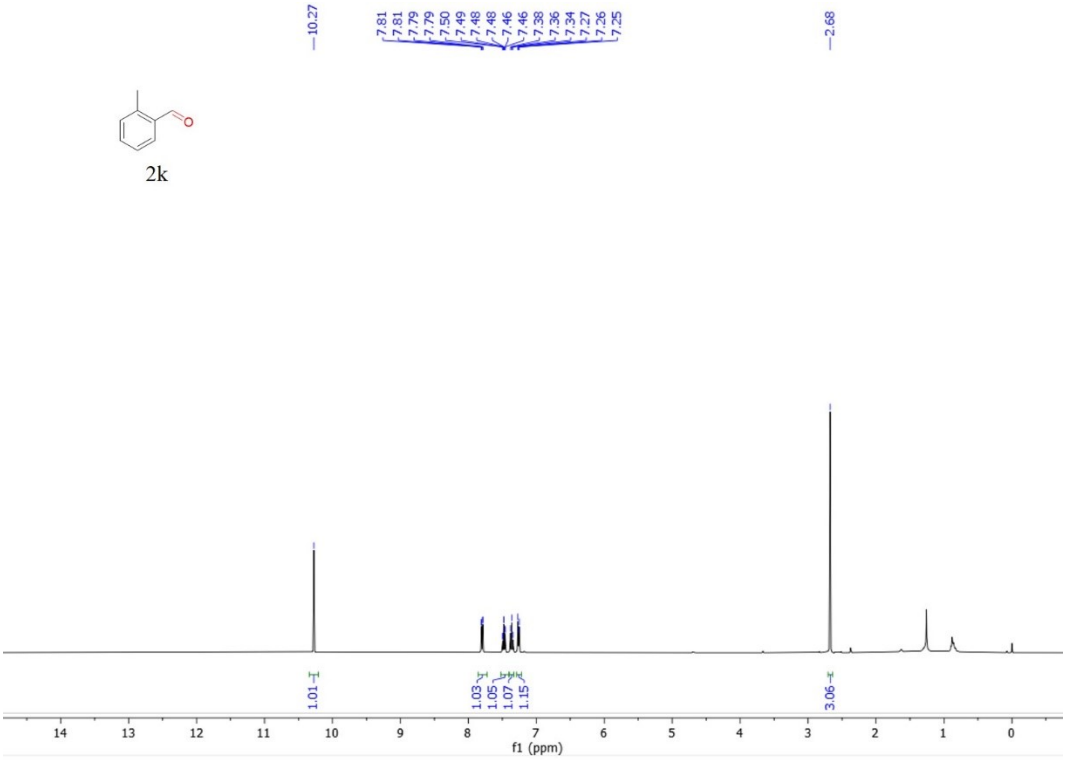

2k

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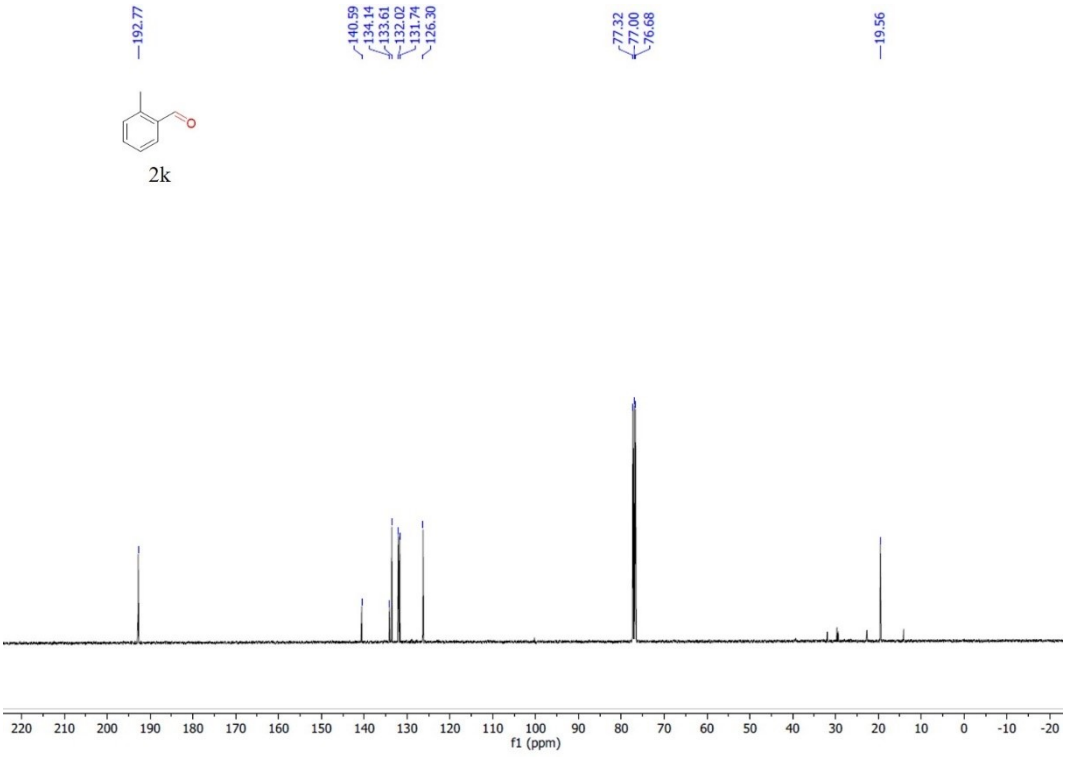

2k

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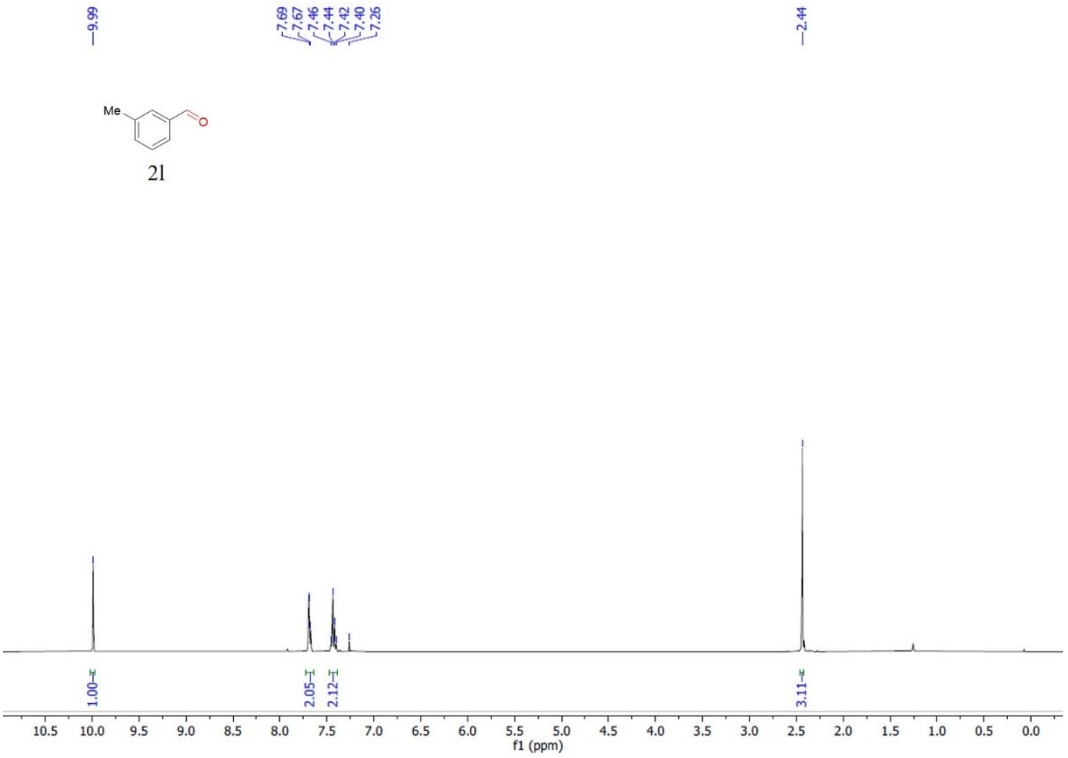

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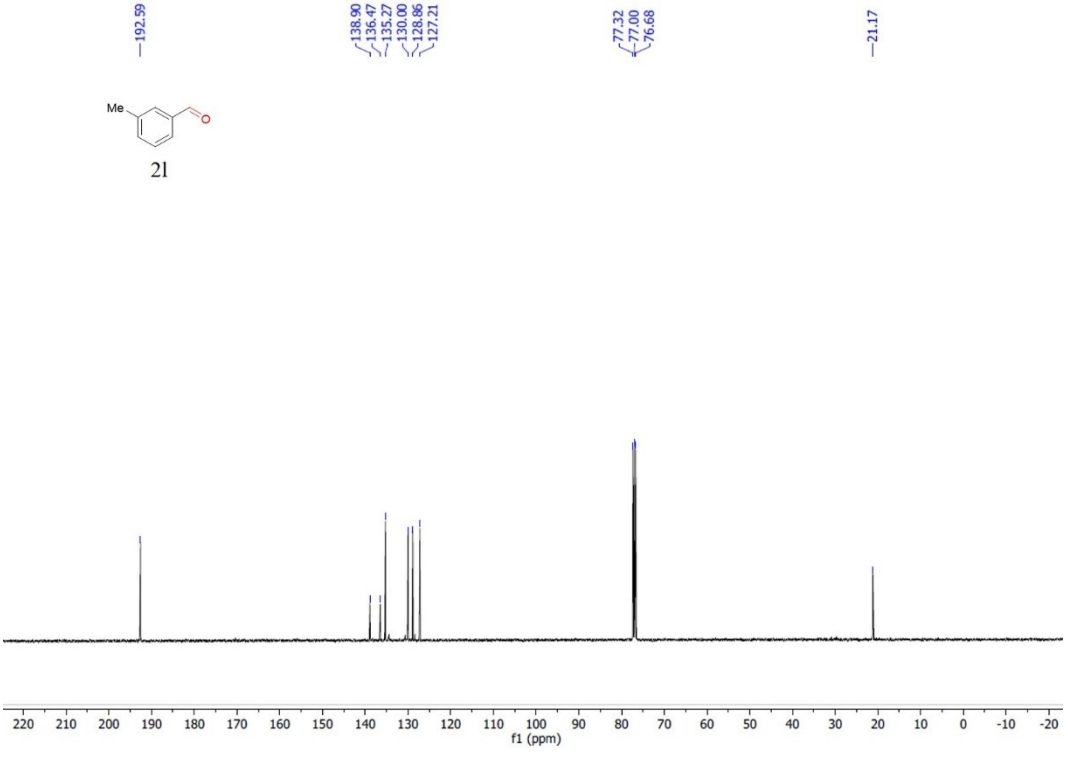

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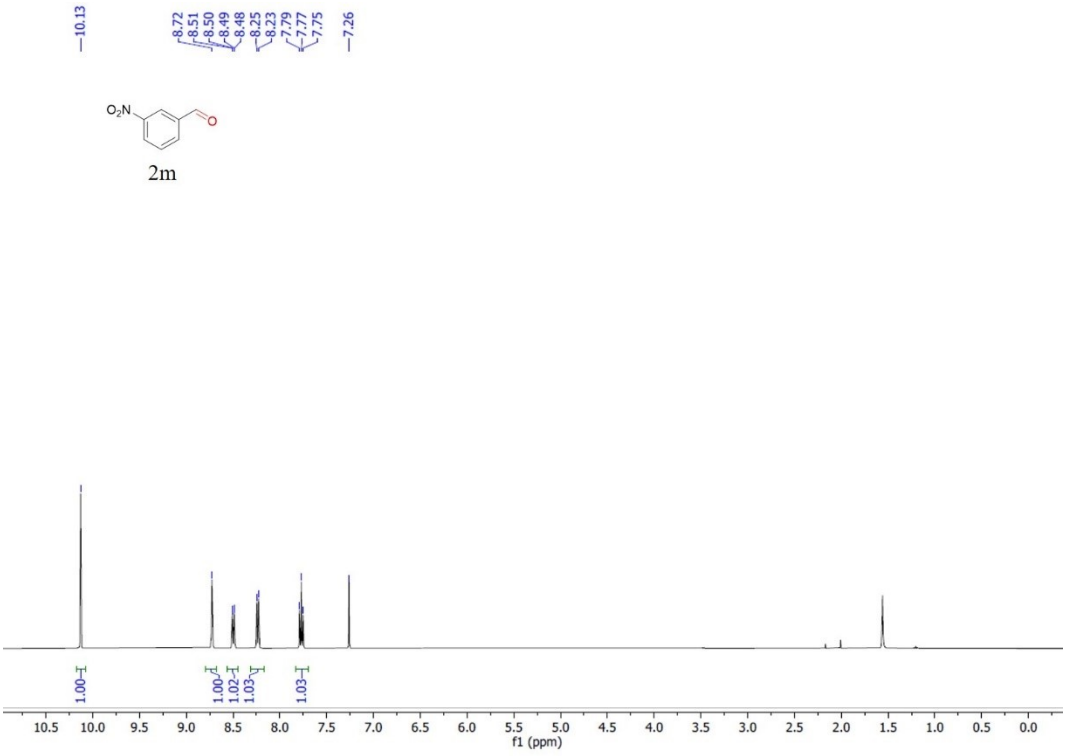

2m

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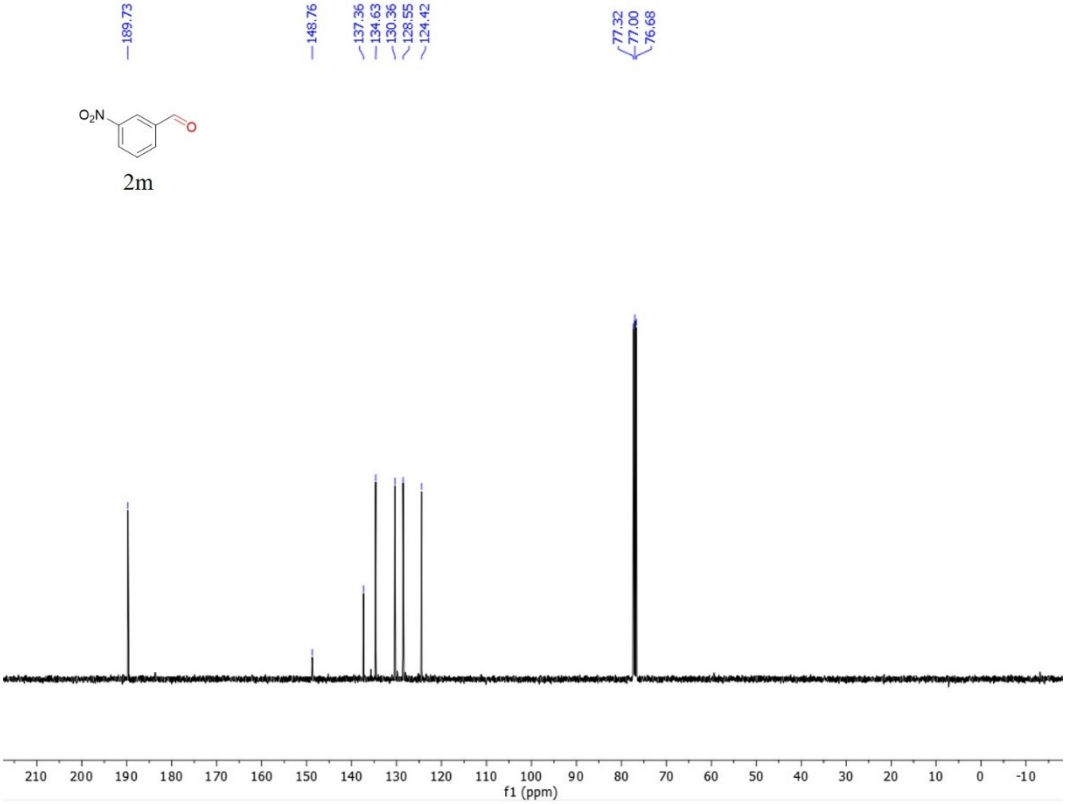

2m

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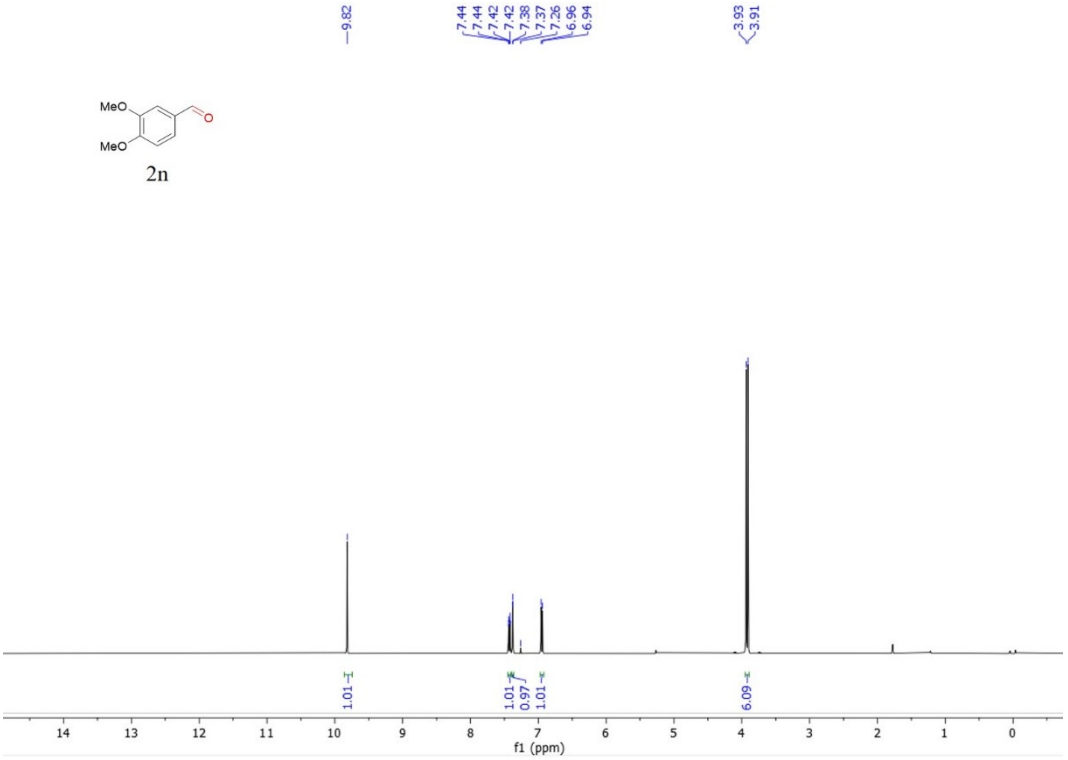

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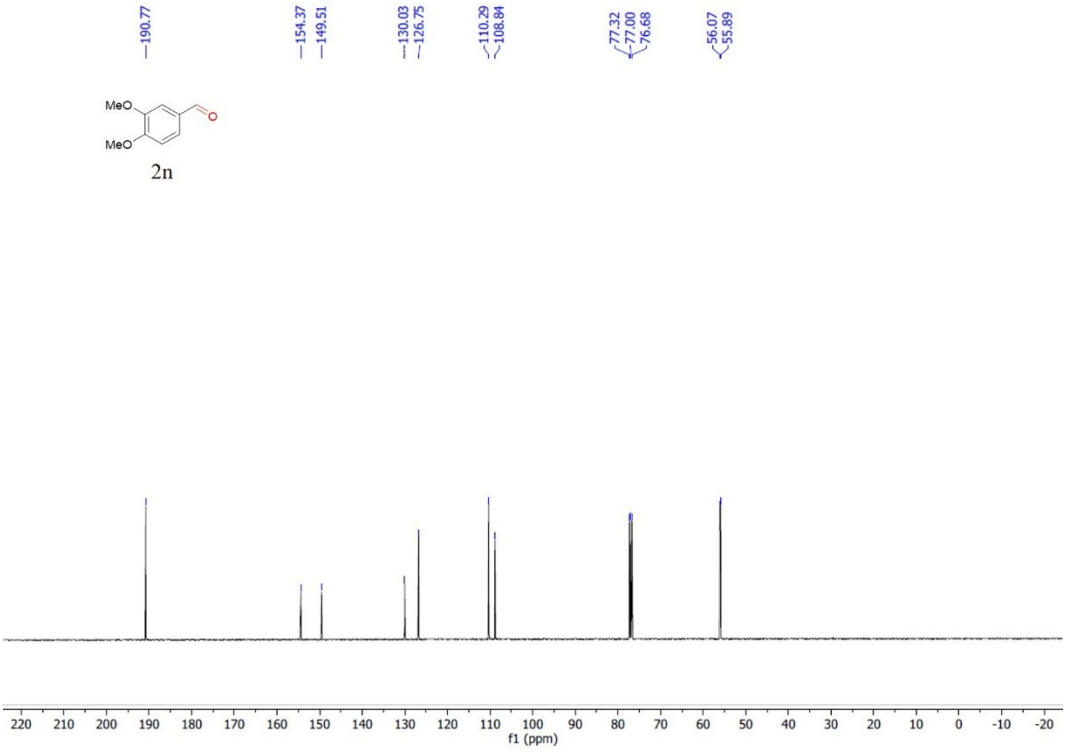

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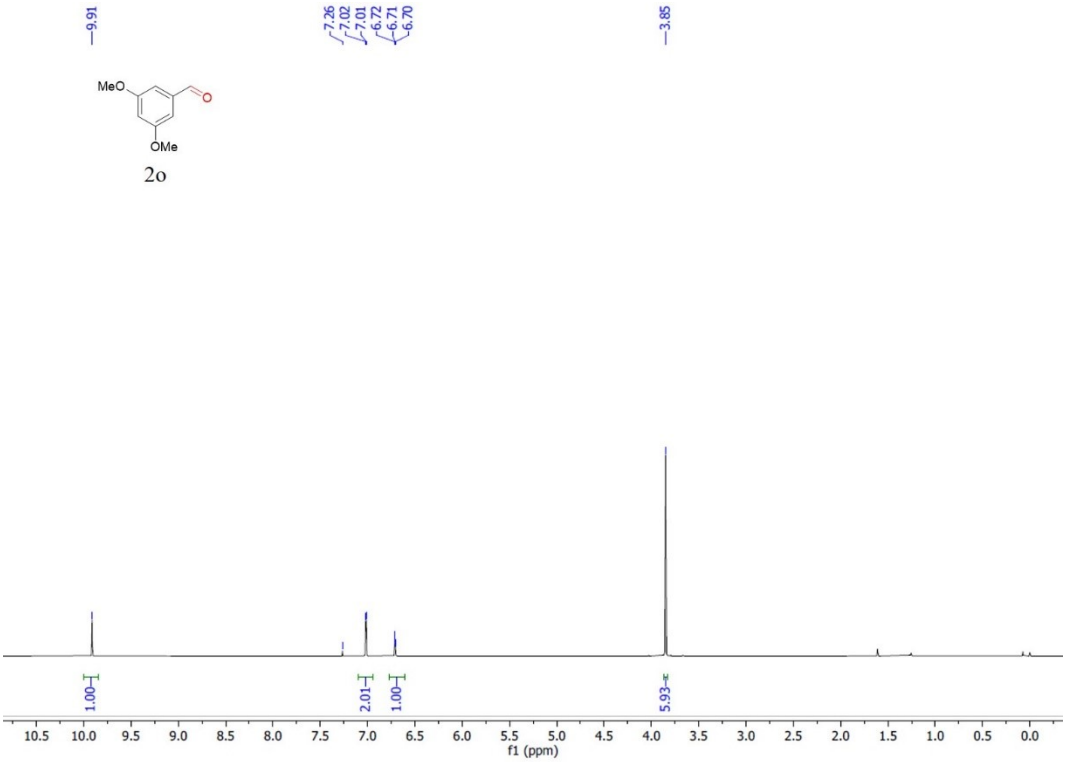

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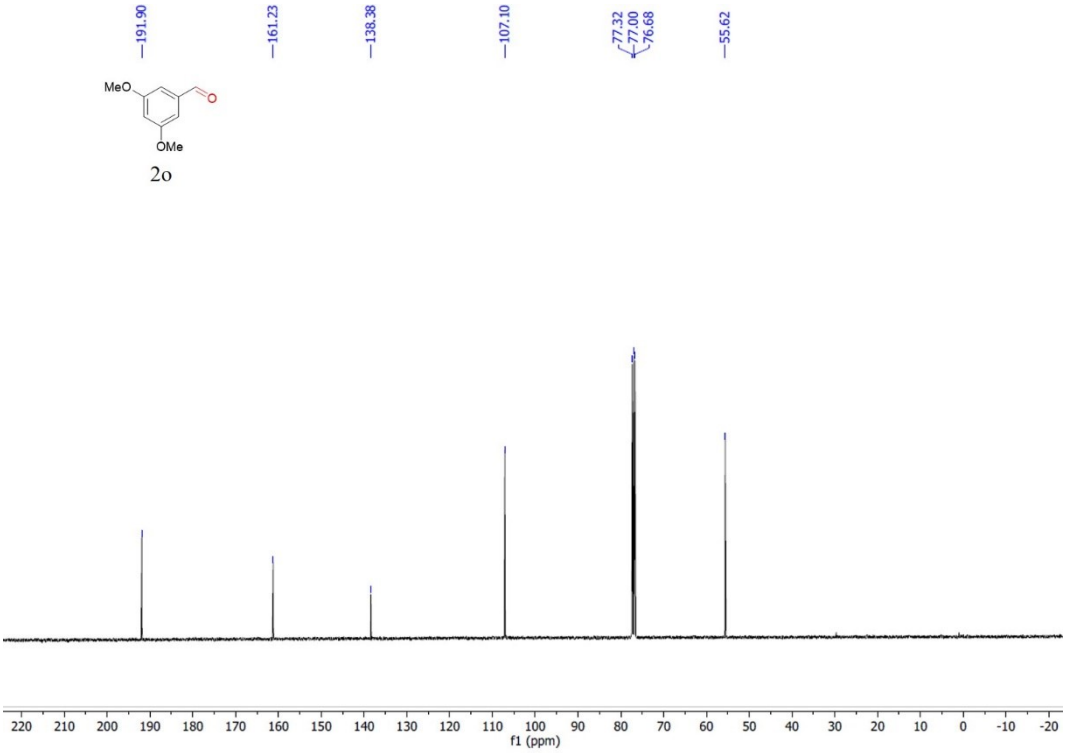

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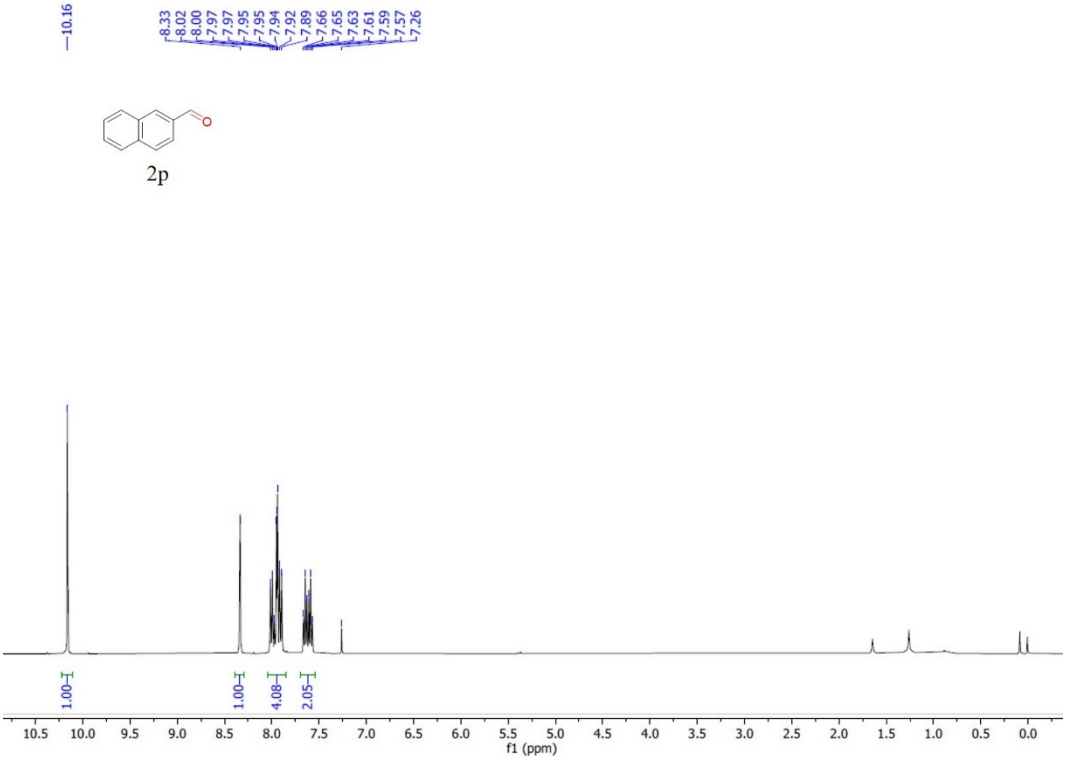

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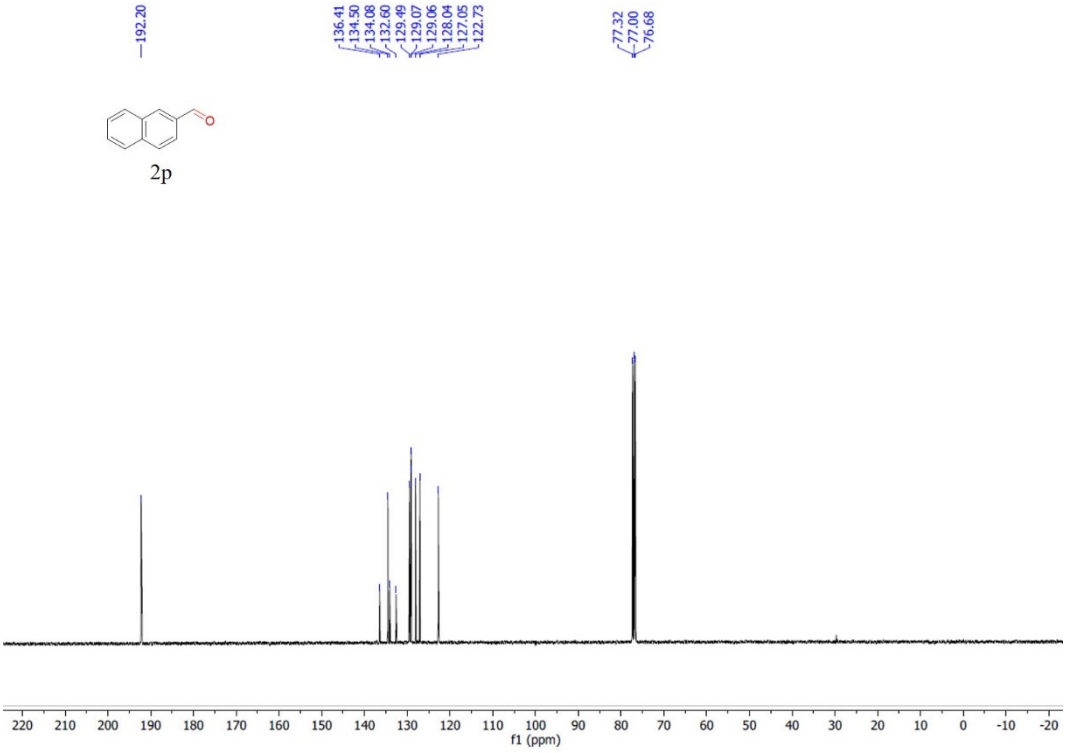

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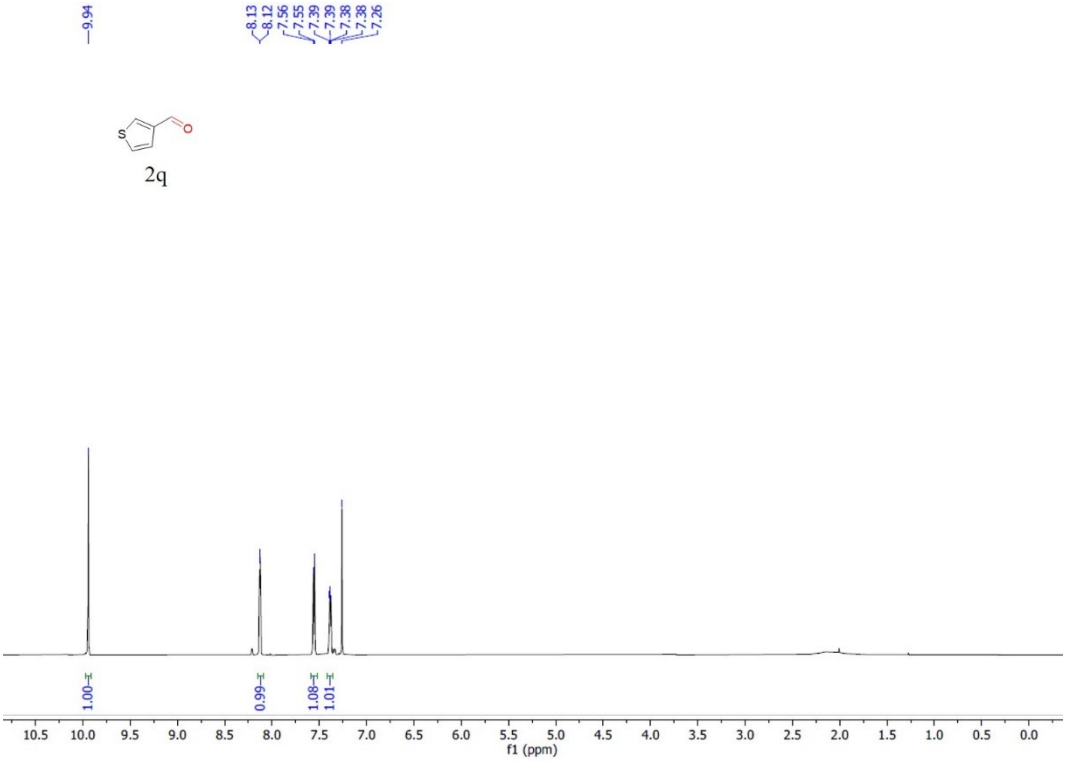

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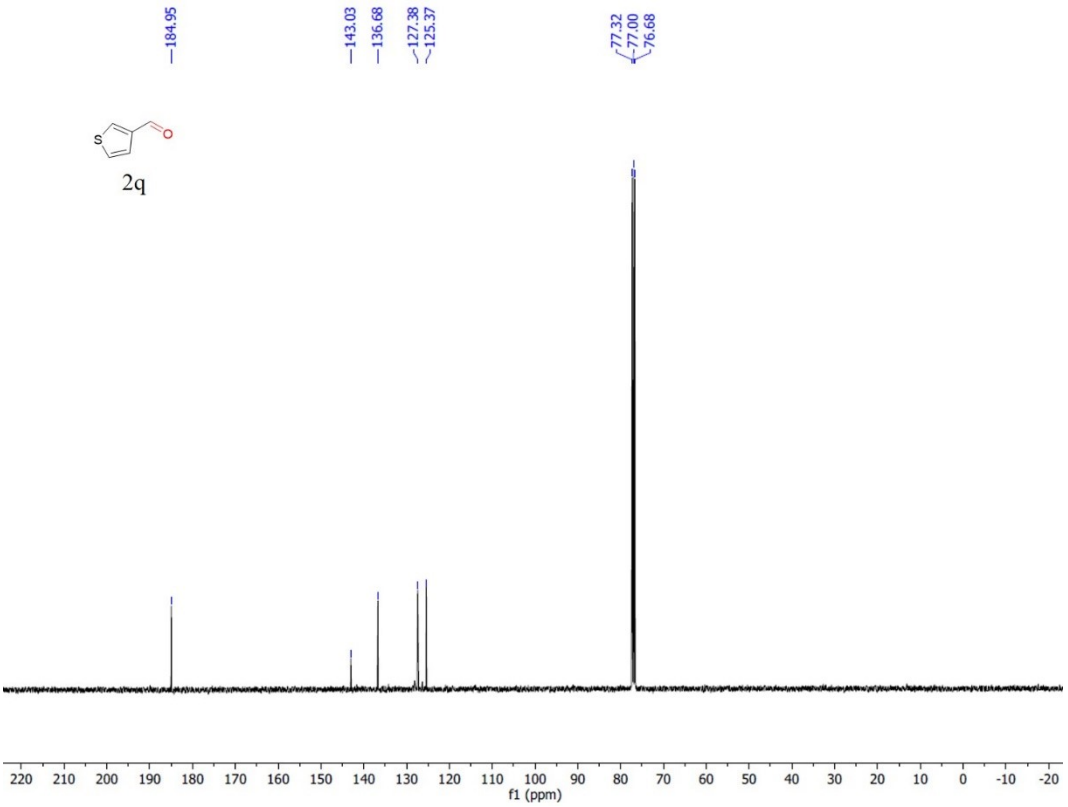

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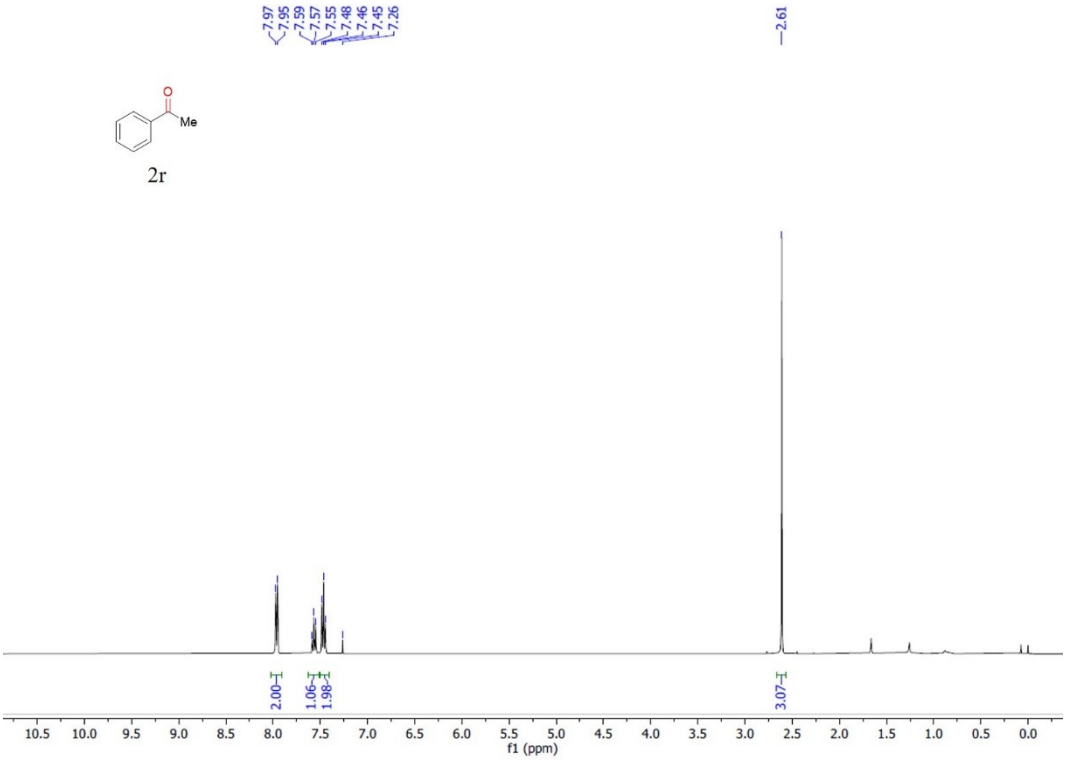

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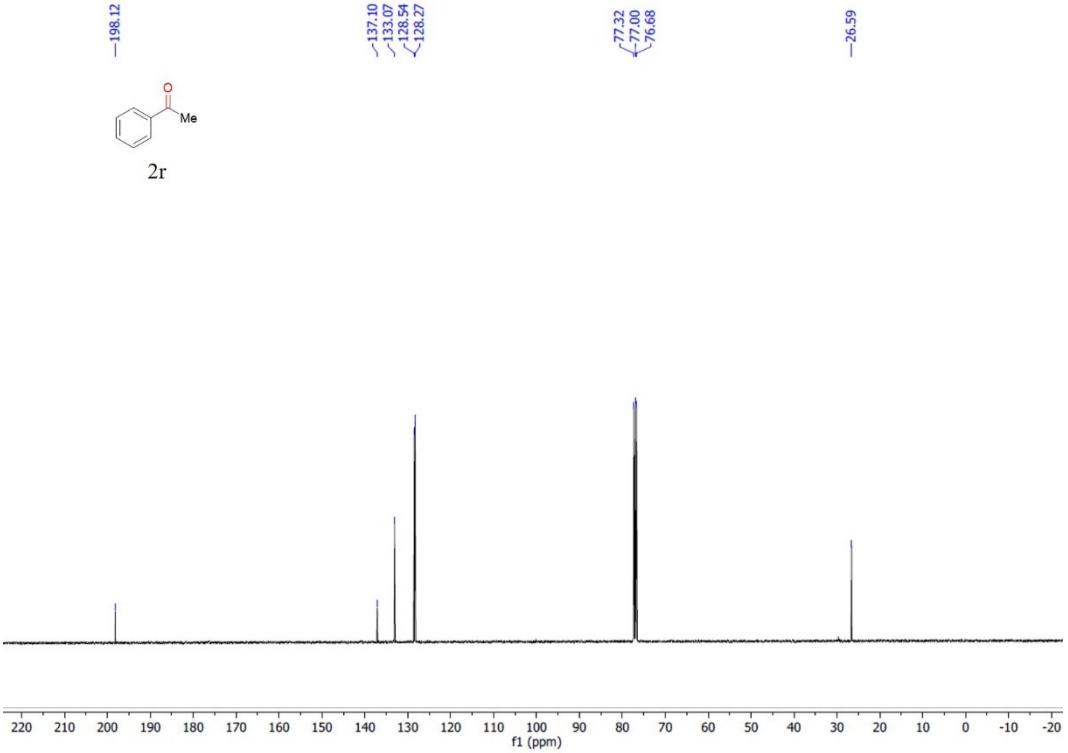

2r

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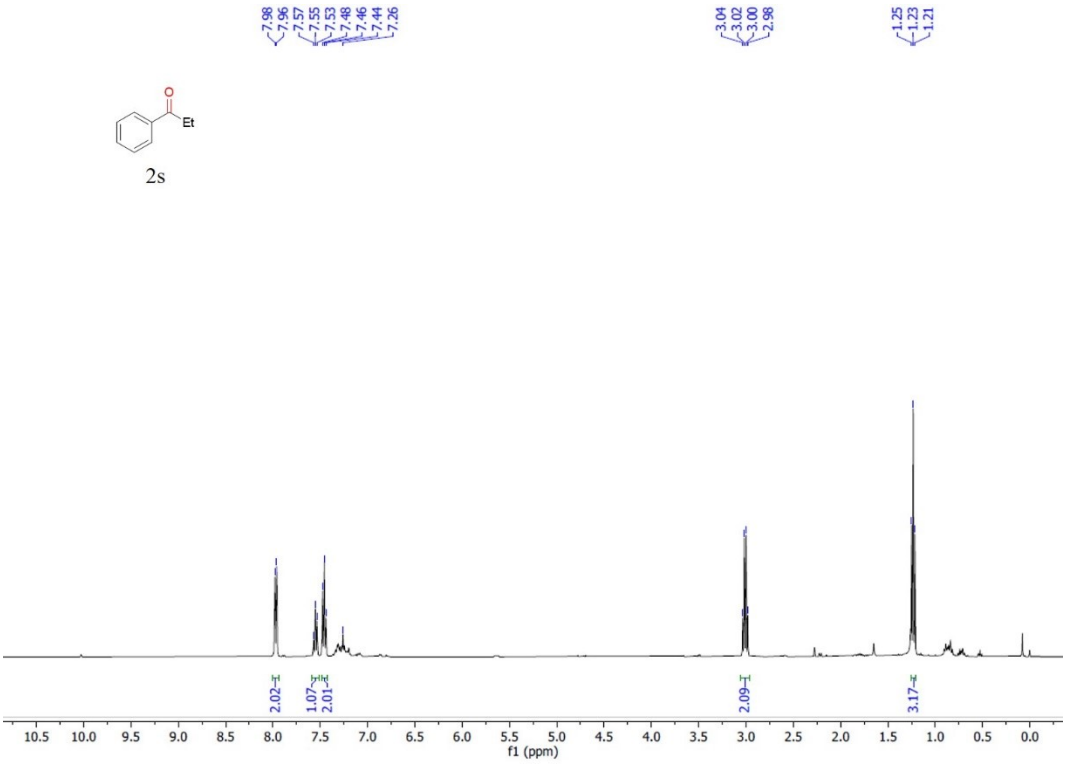

2s

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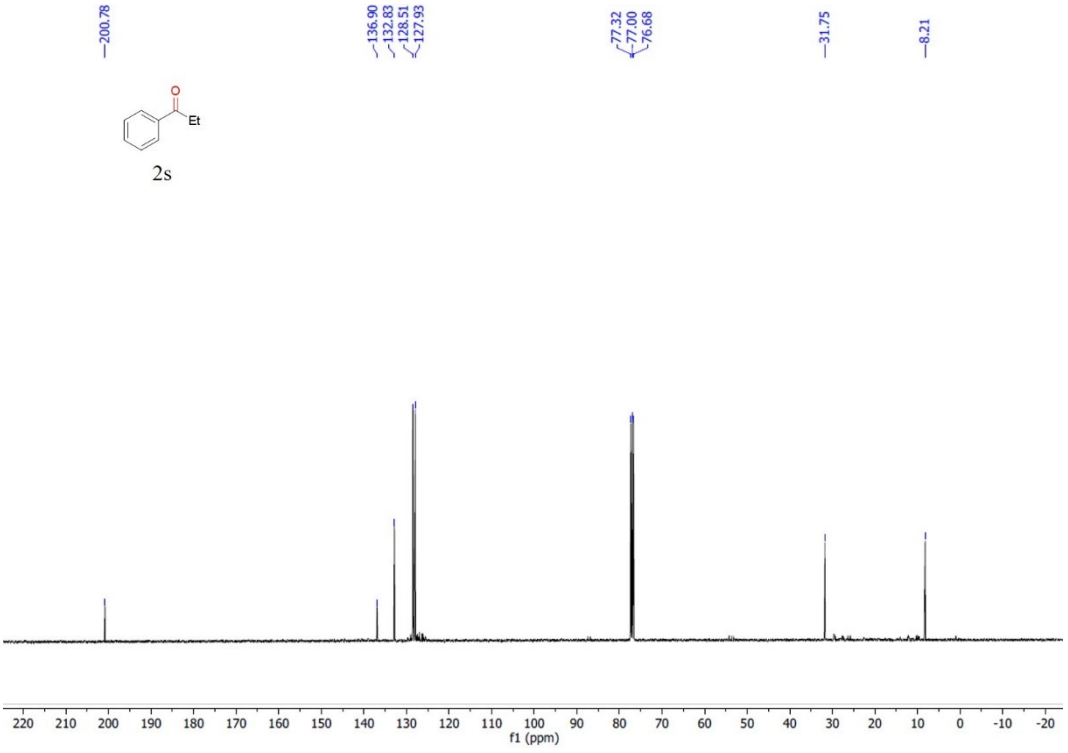

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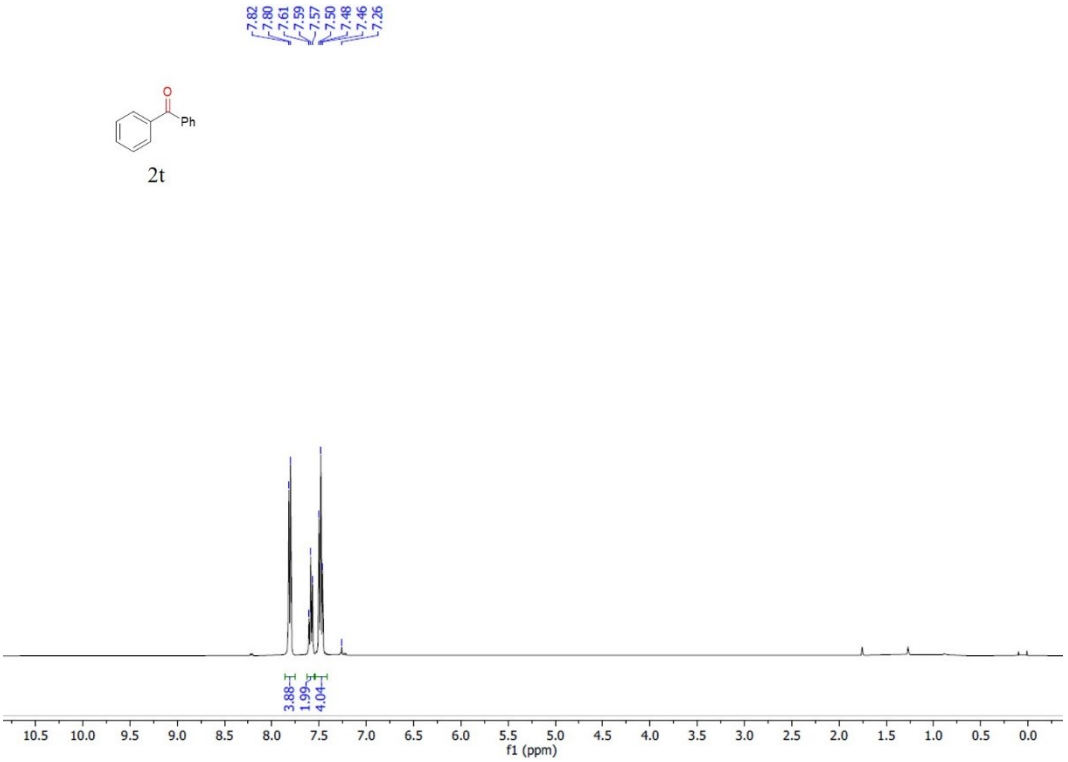

2t

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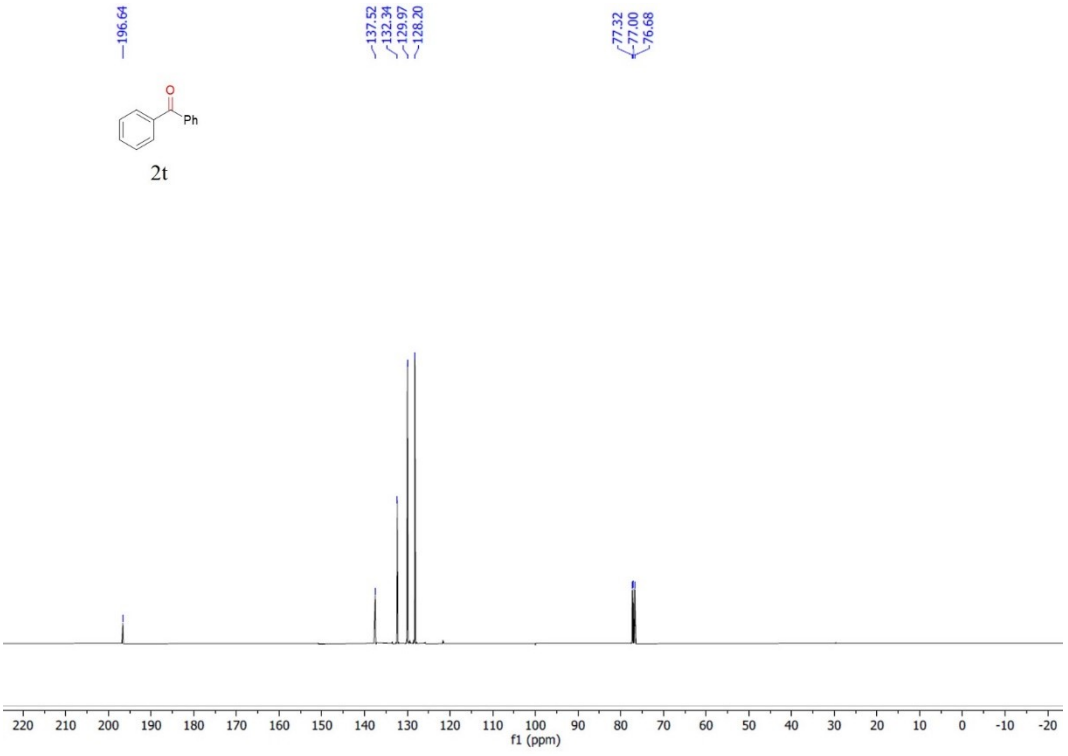

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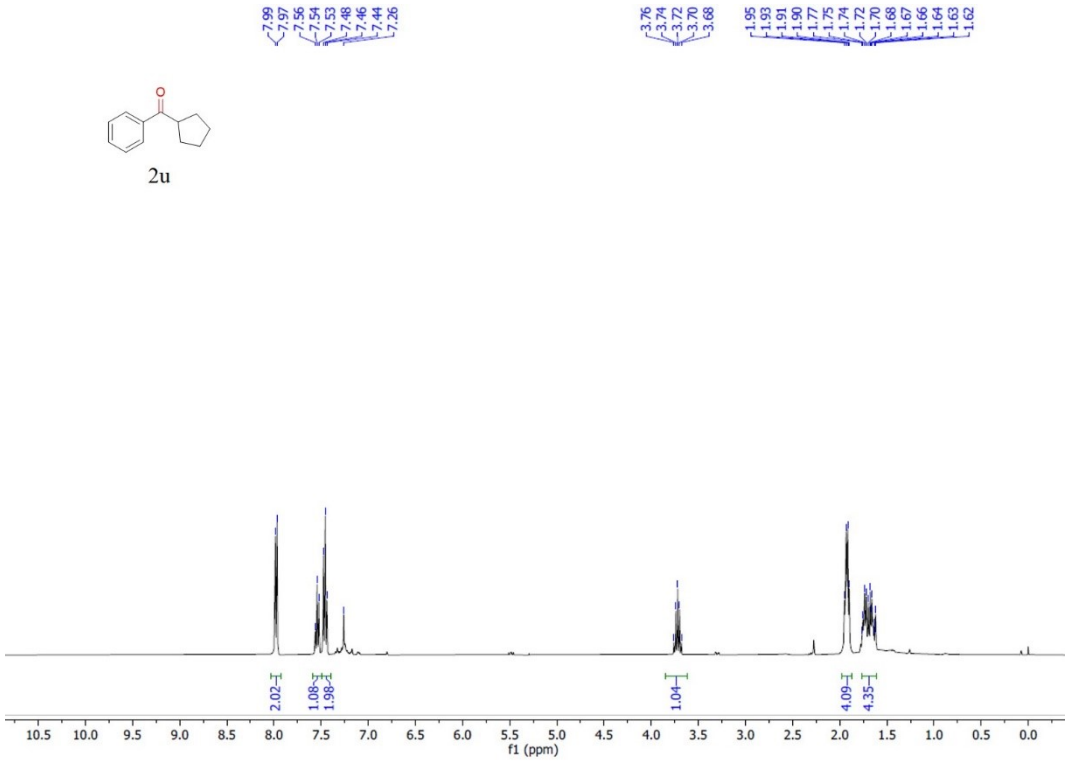
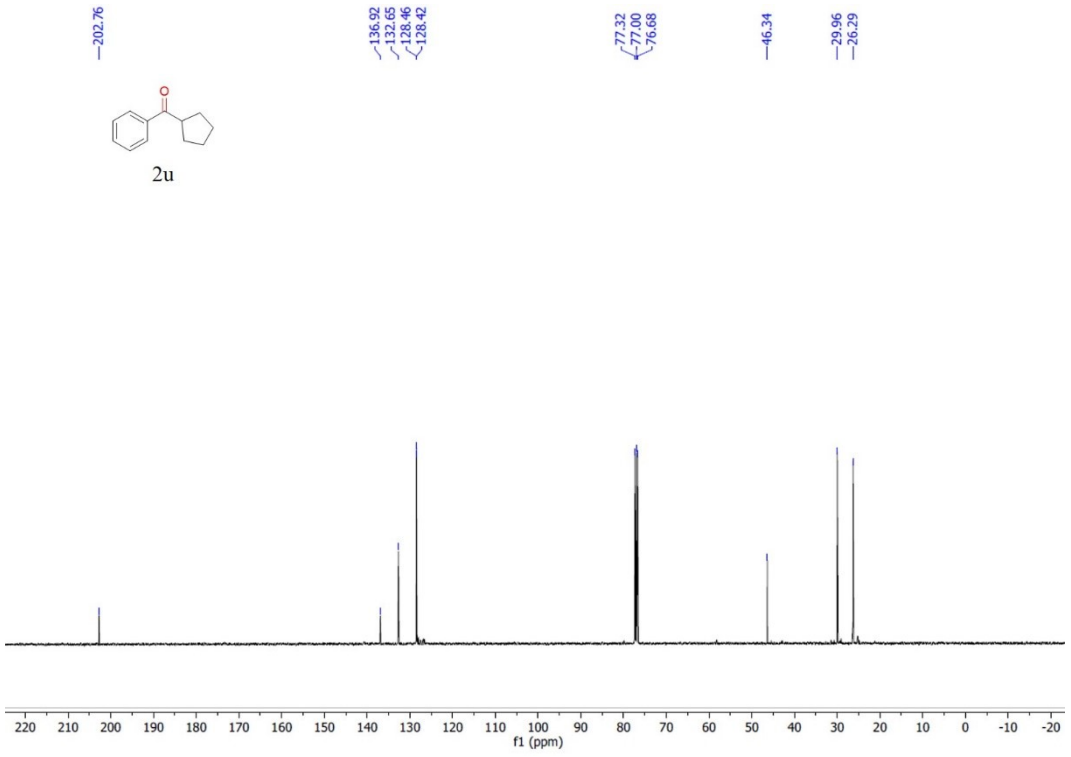


2u

^{1}H NMR



2u

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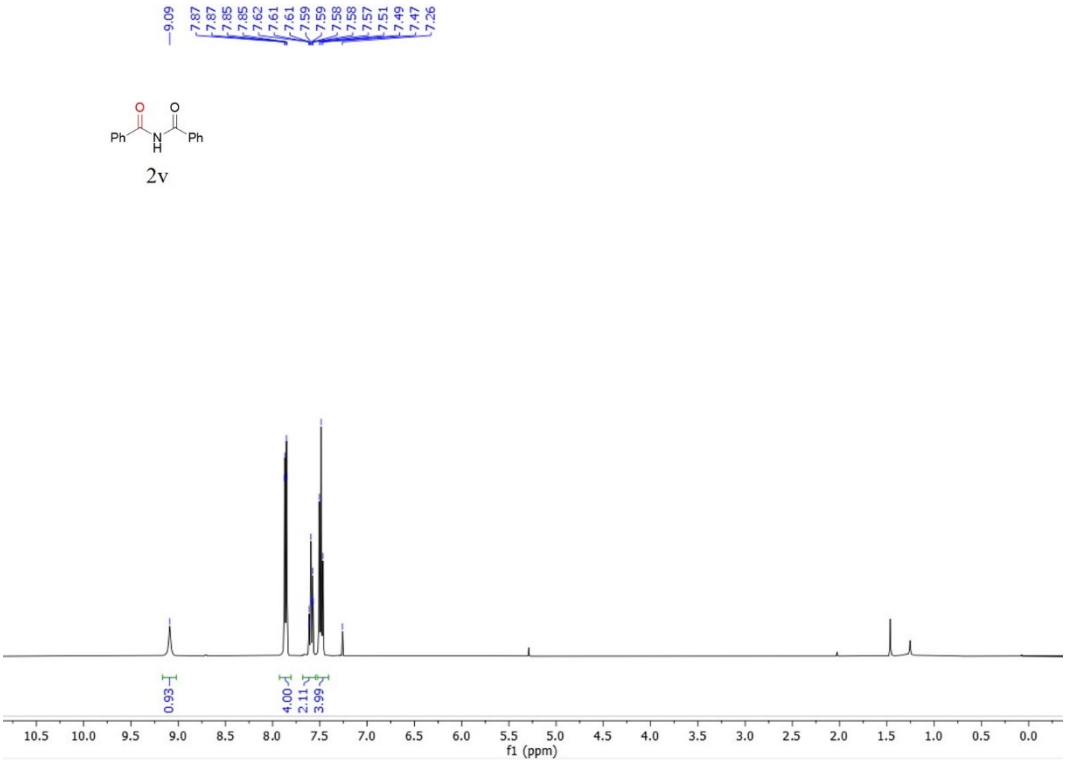

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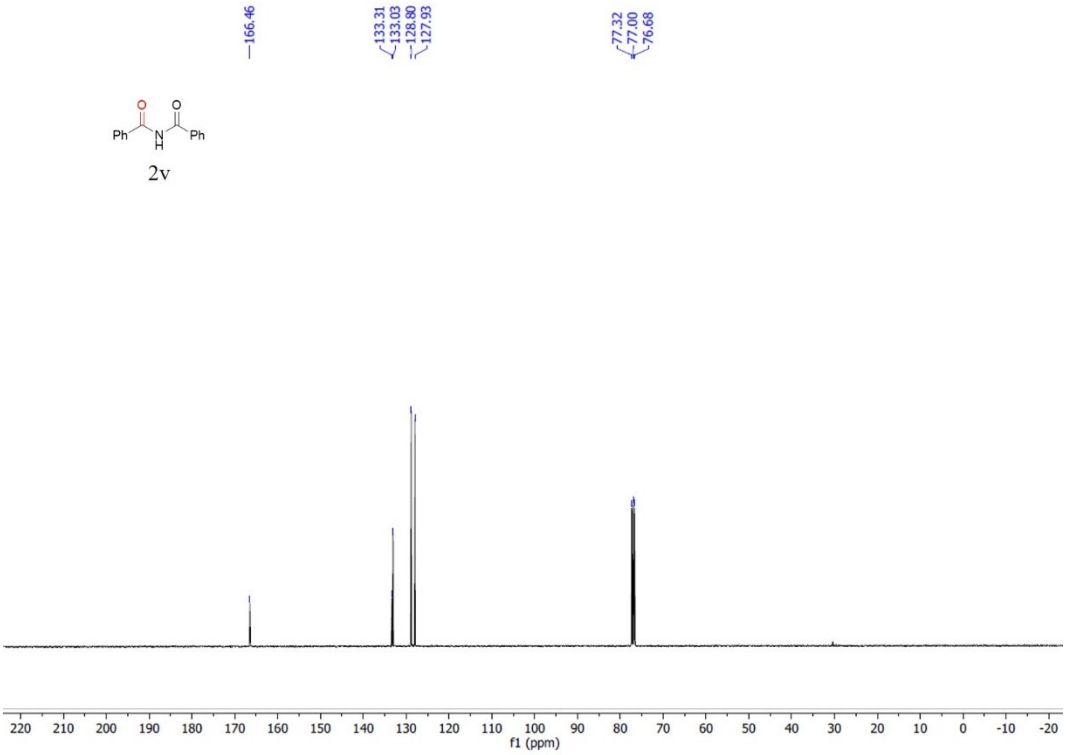
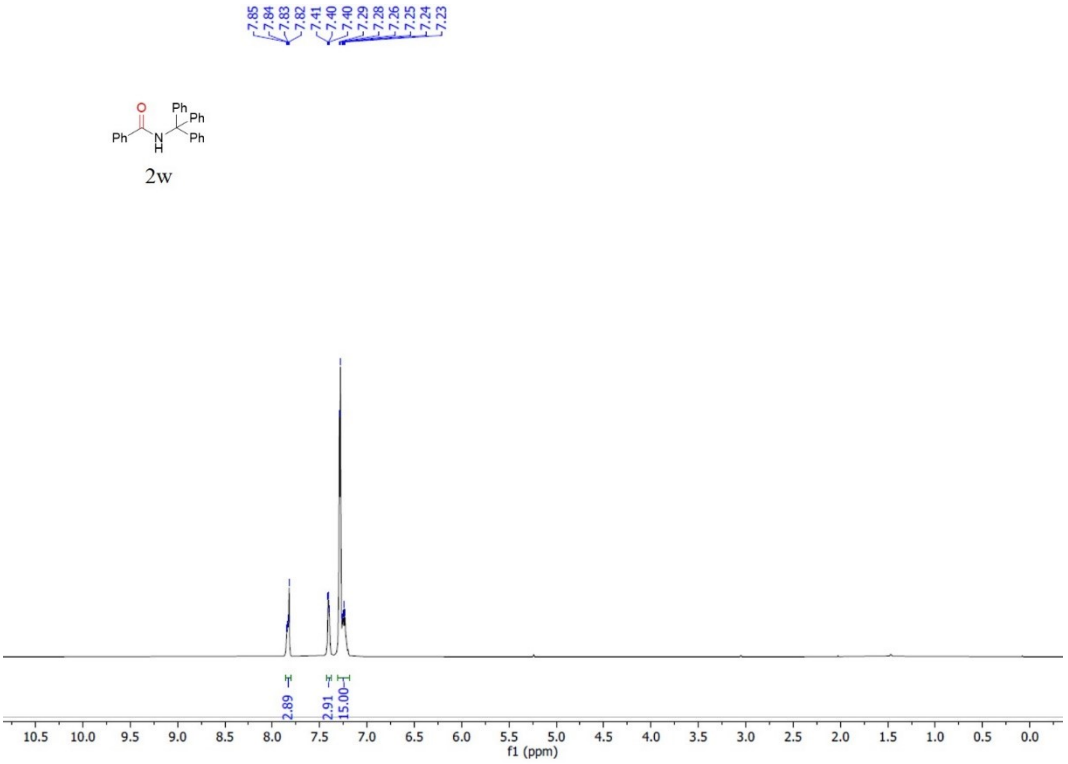
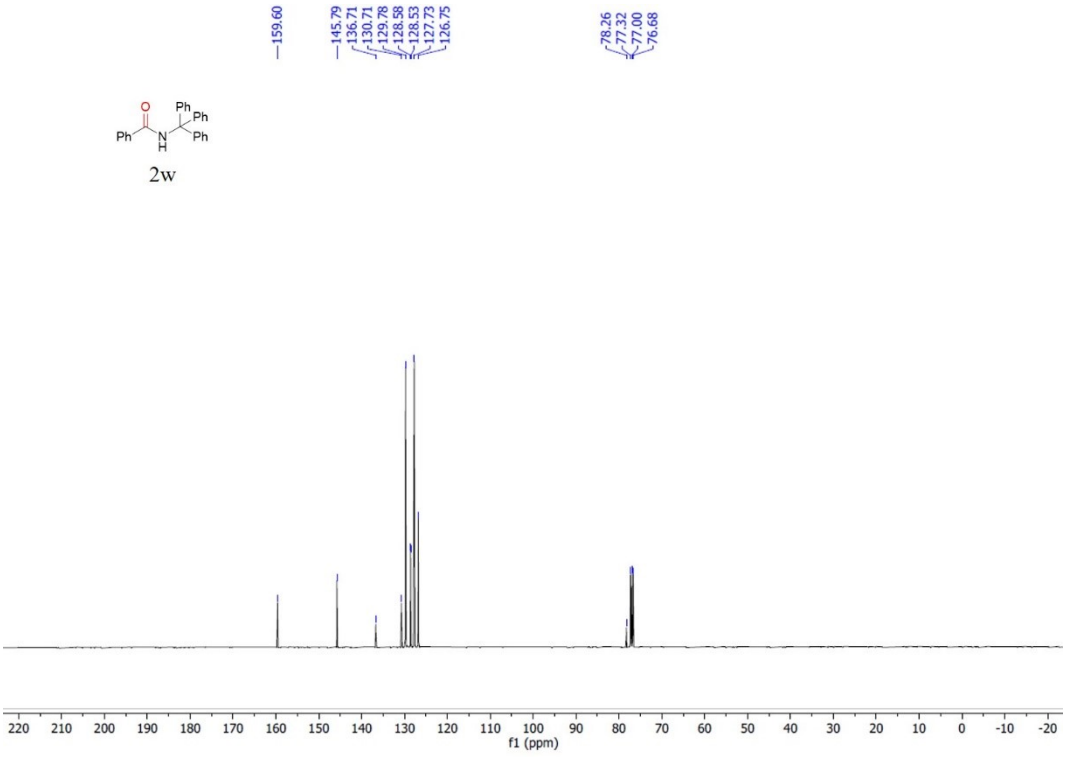


^{13}C NMR



^{1}H NMR



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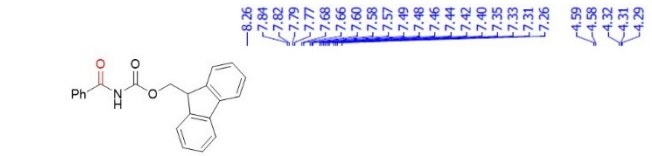
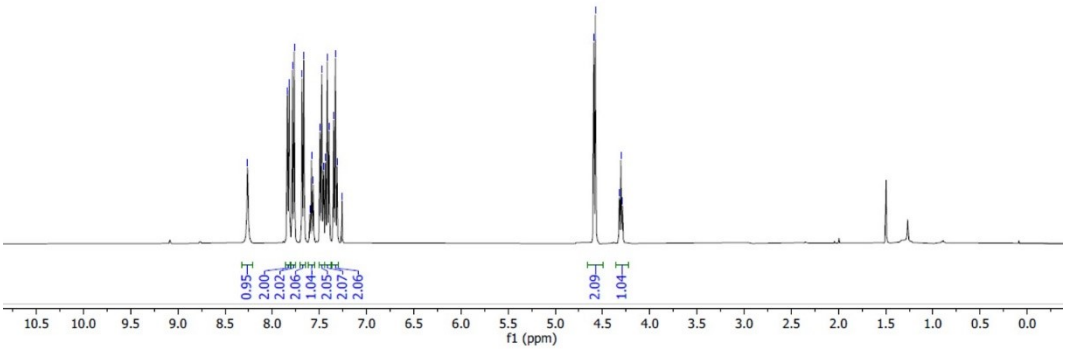


2x



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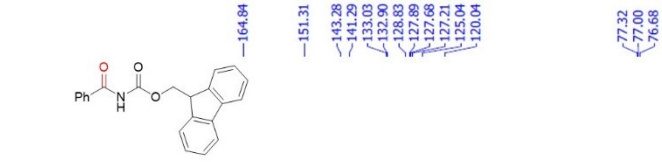

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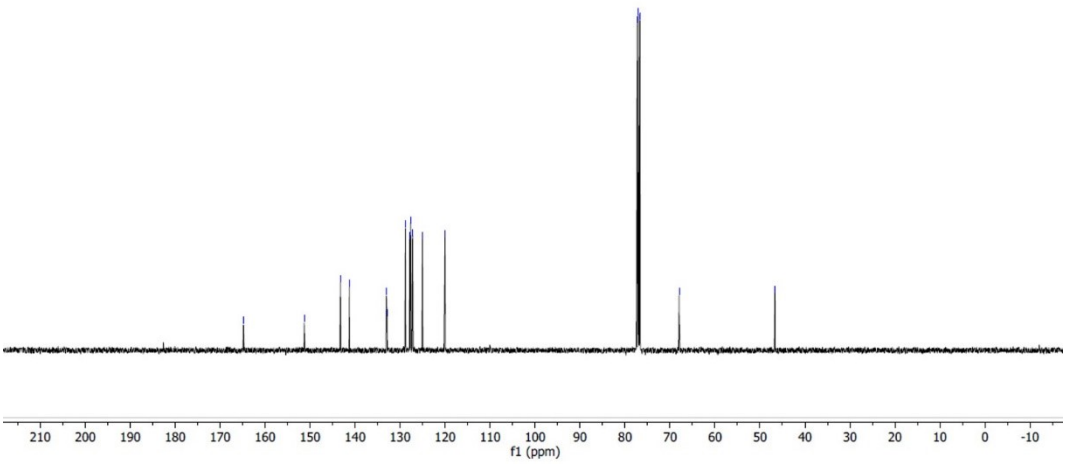

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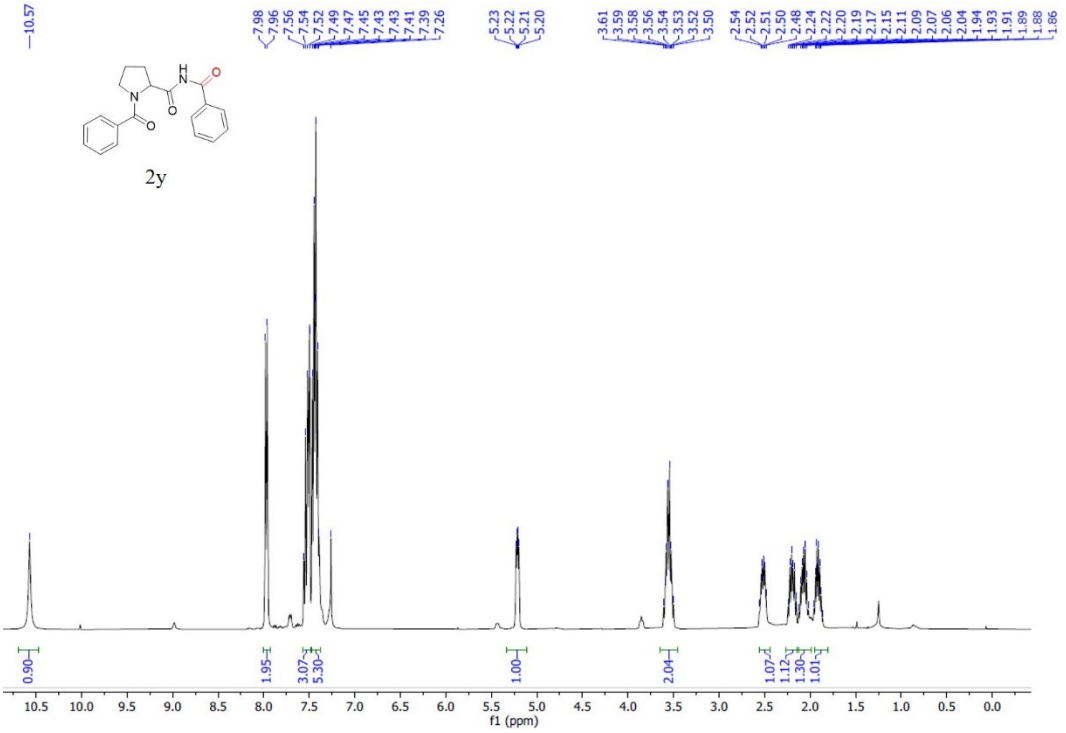

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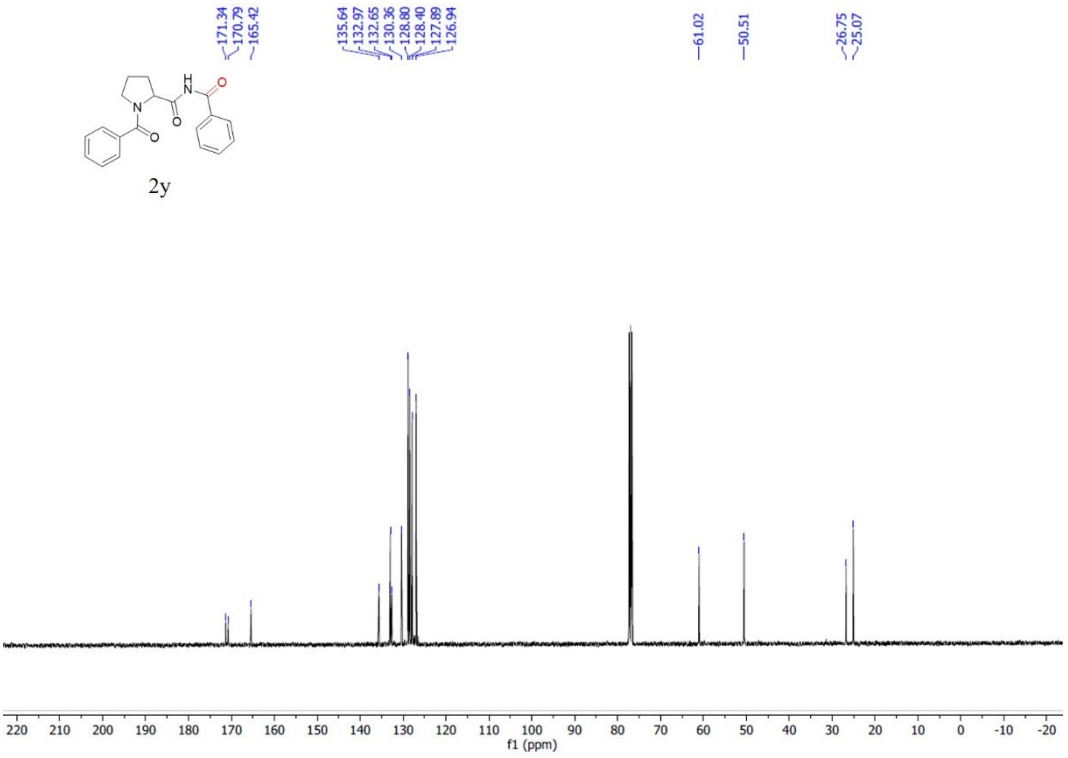

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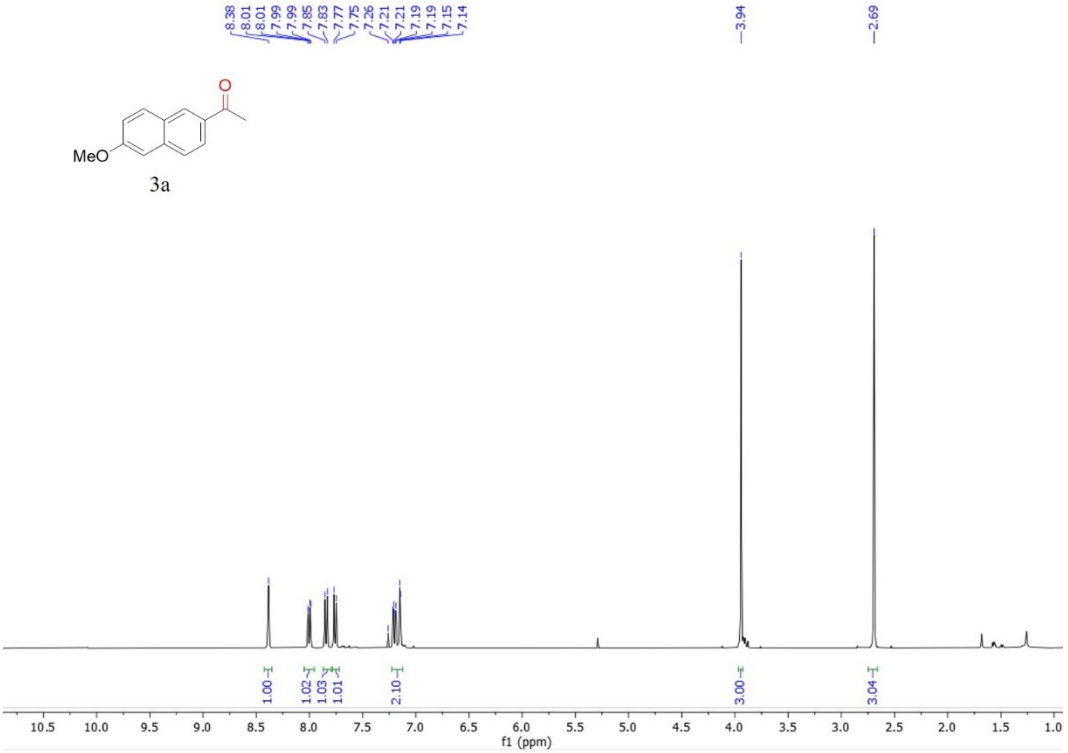

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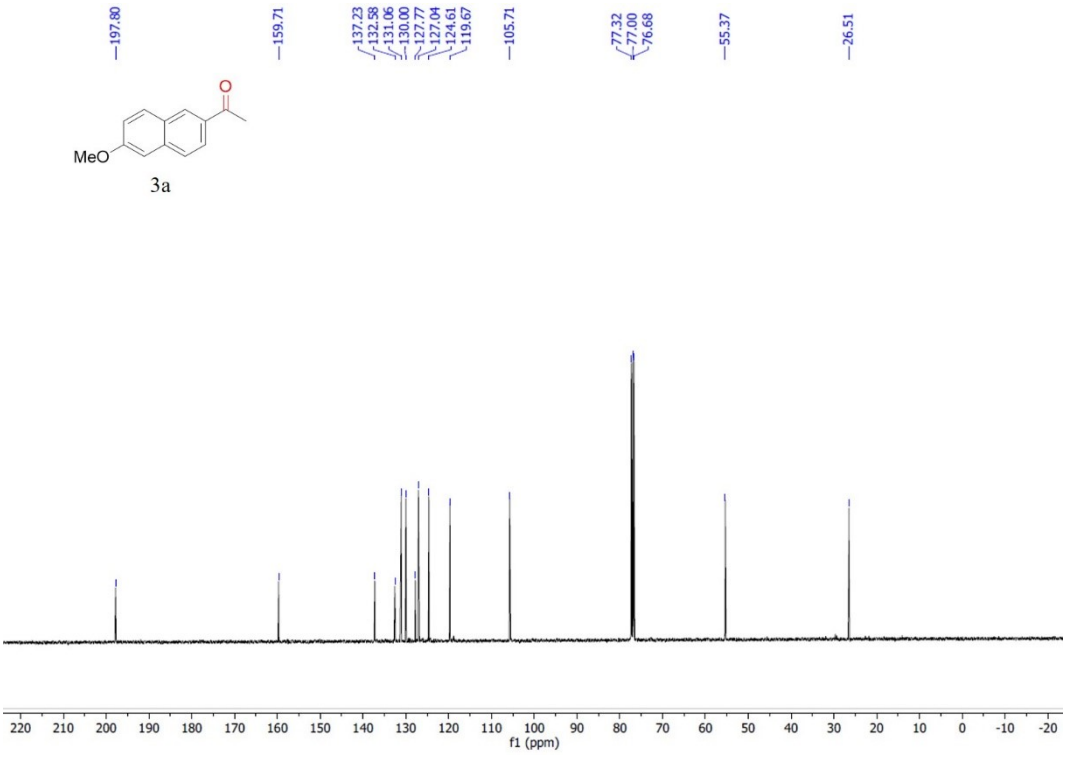

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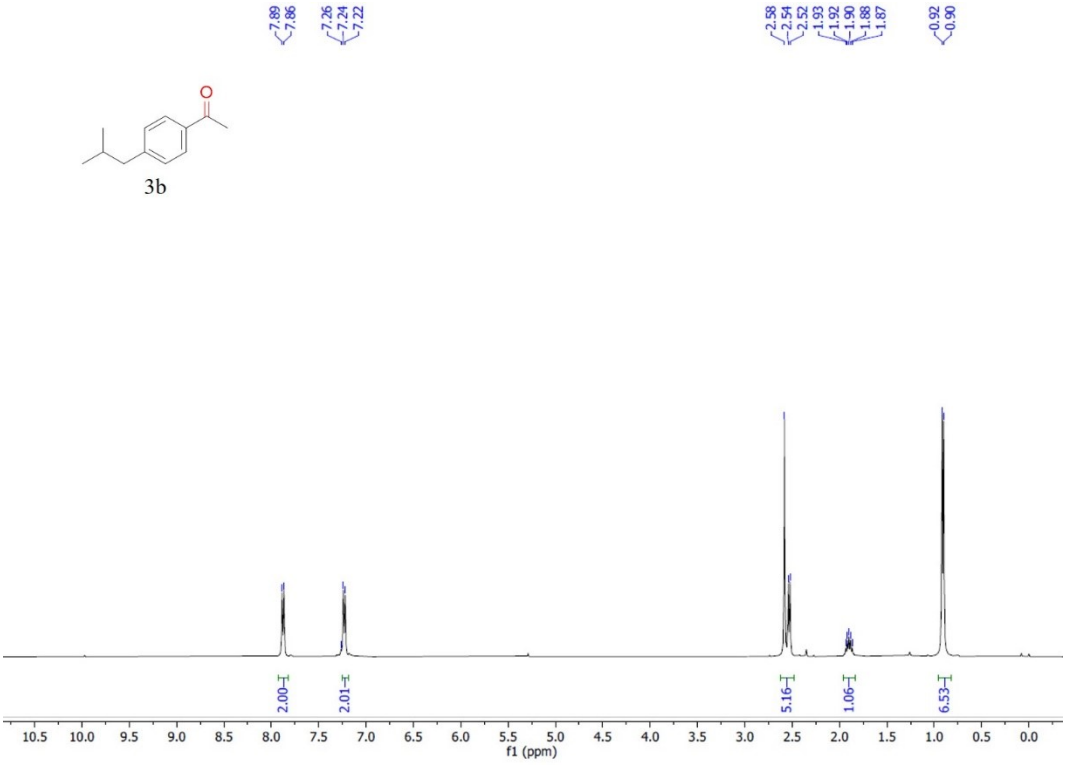

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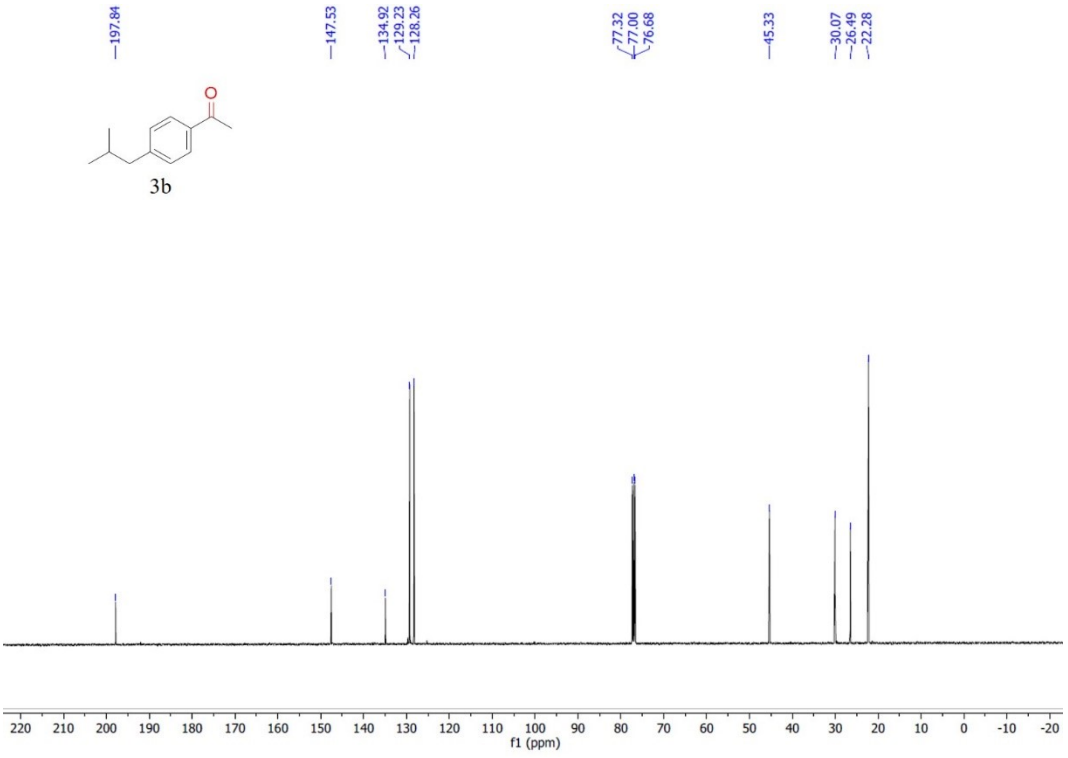

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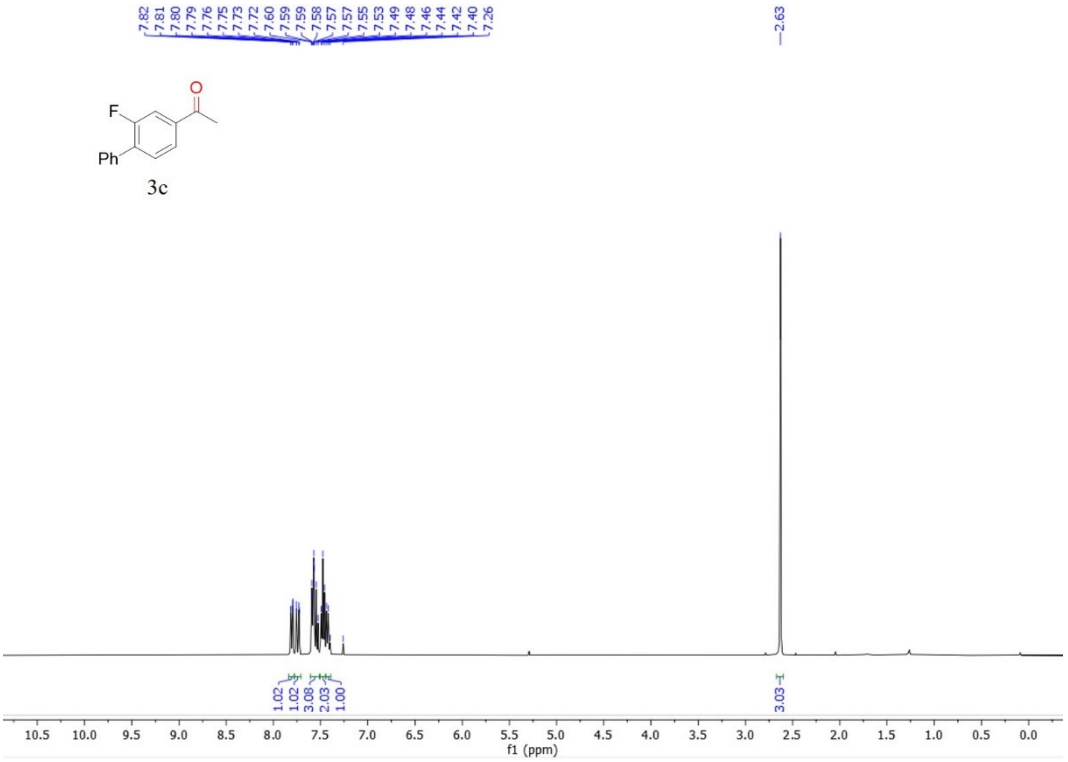

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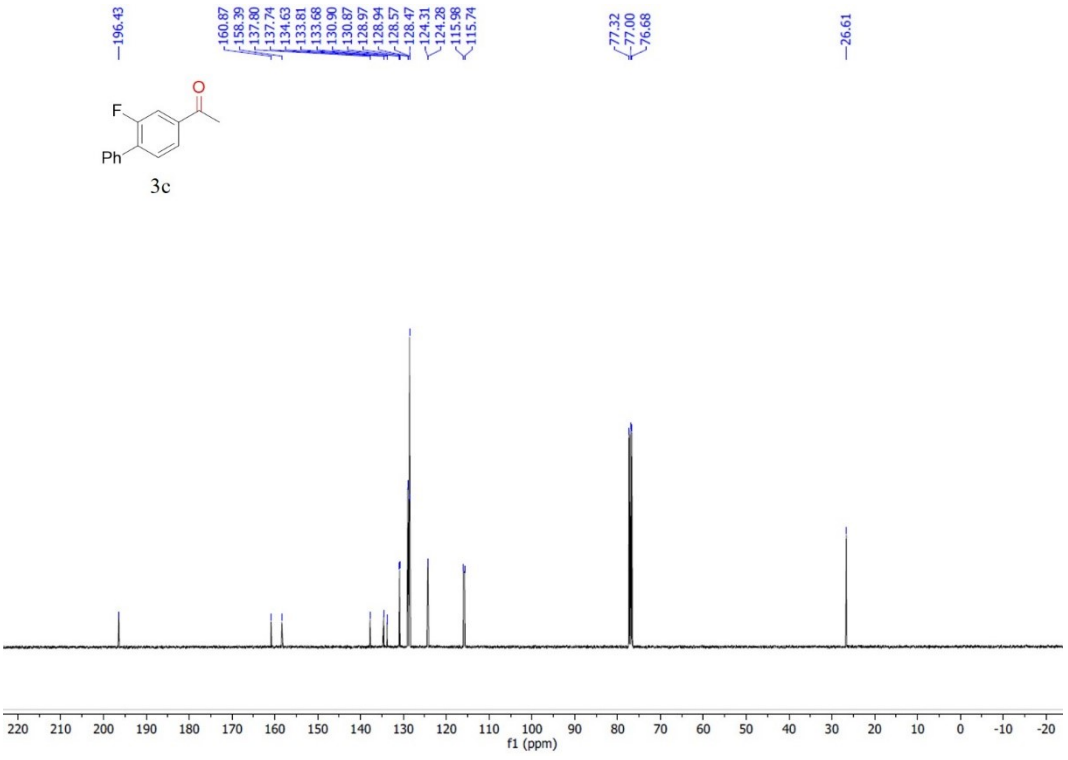

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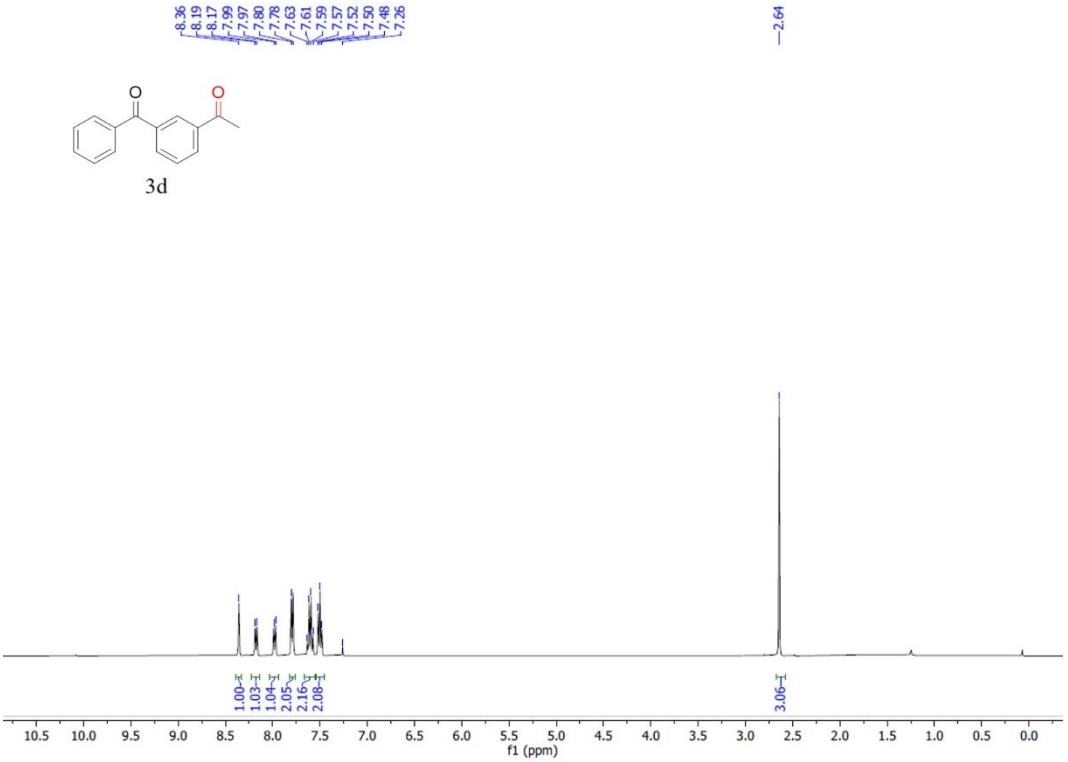

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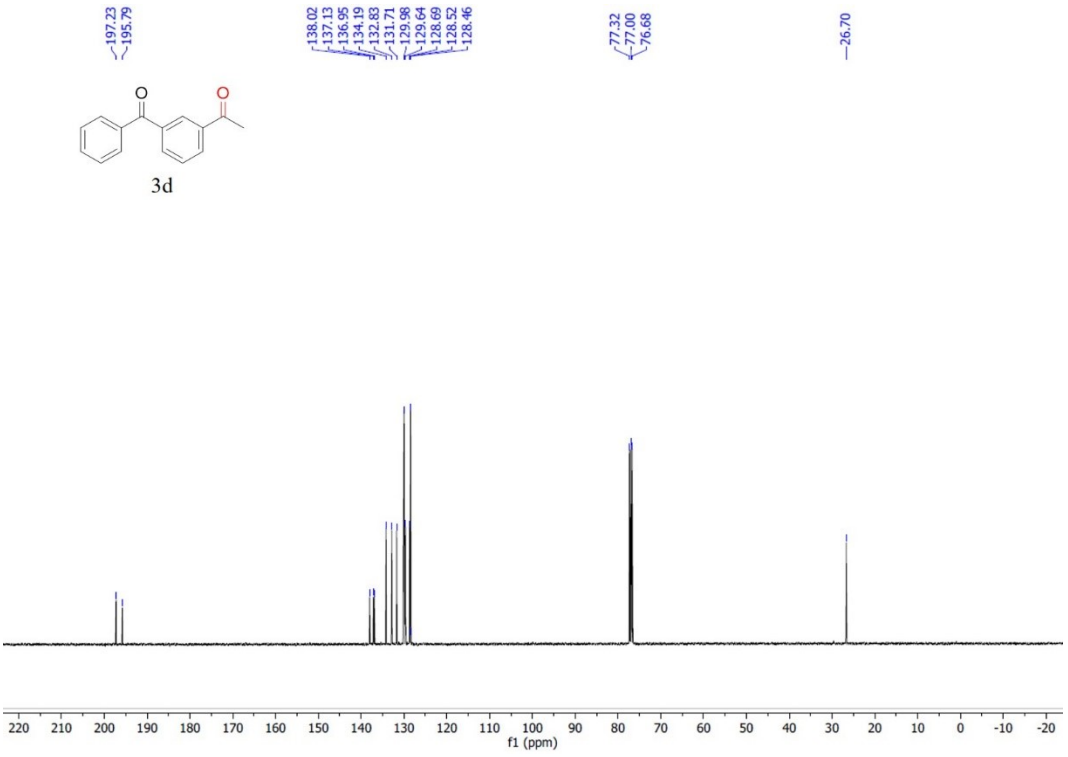

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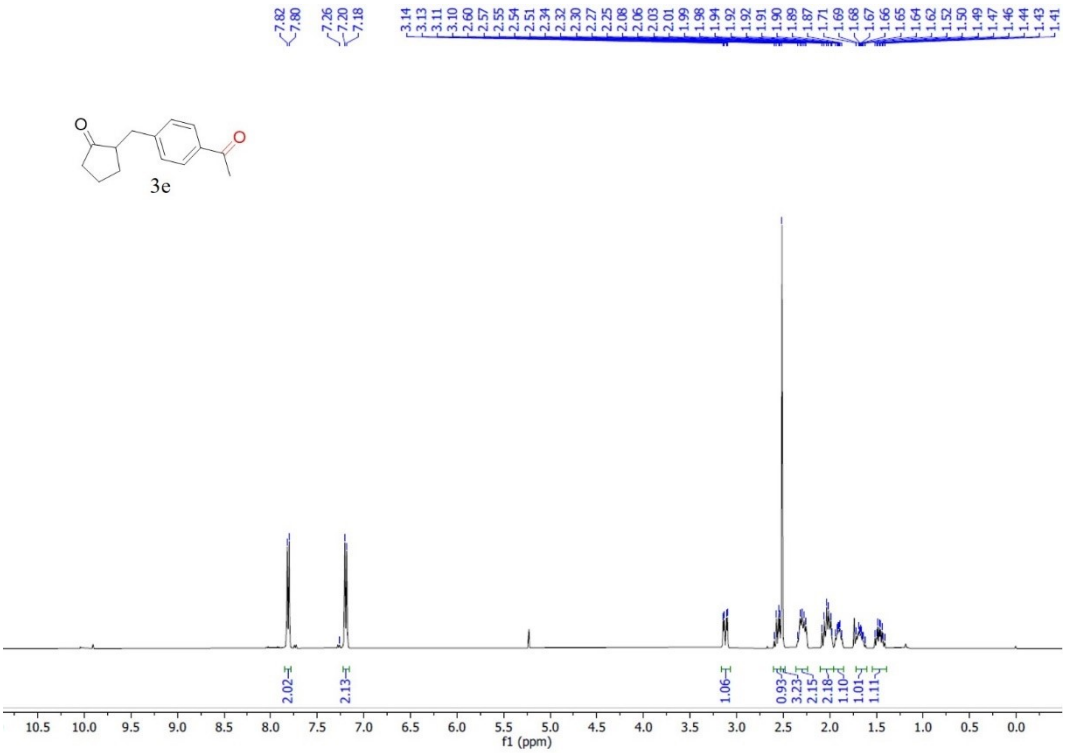

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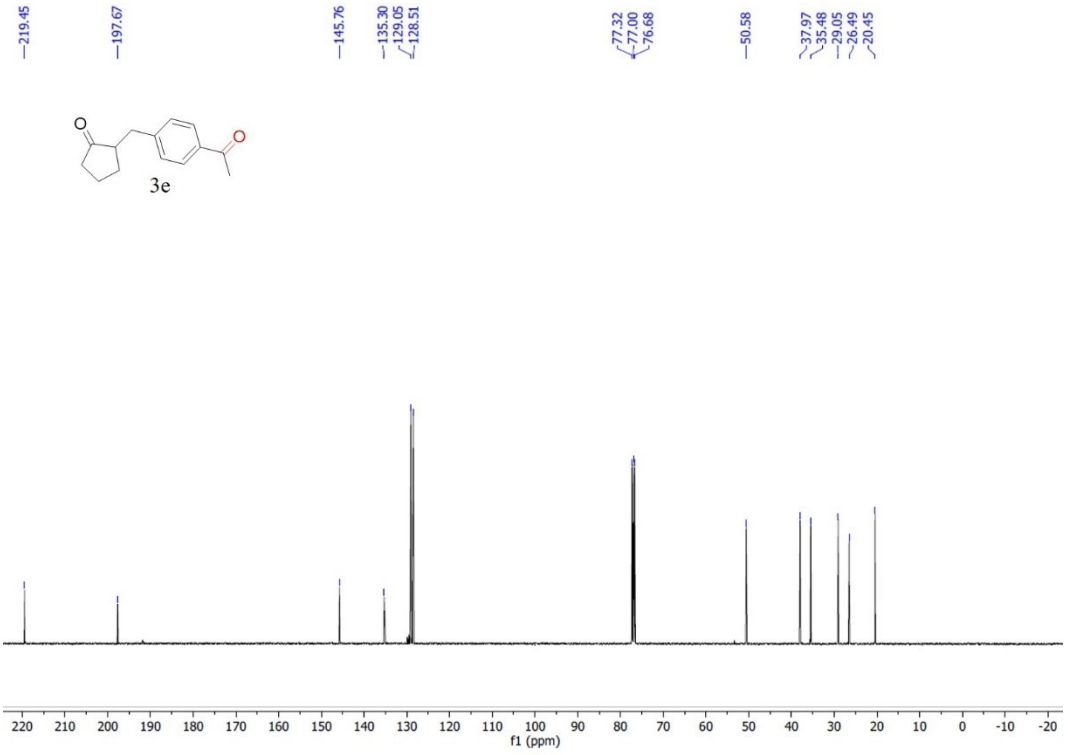

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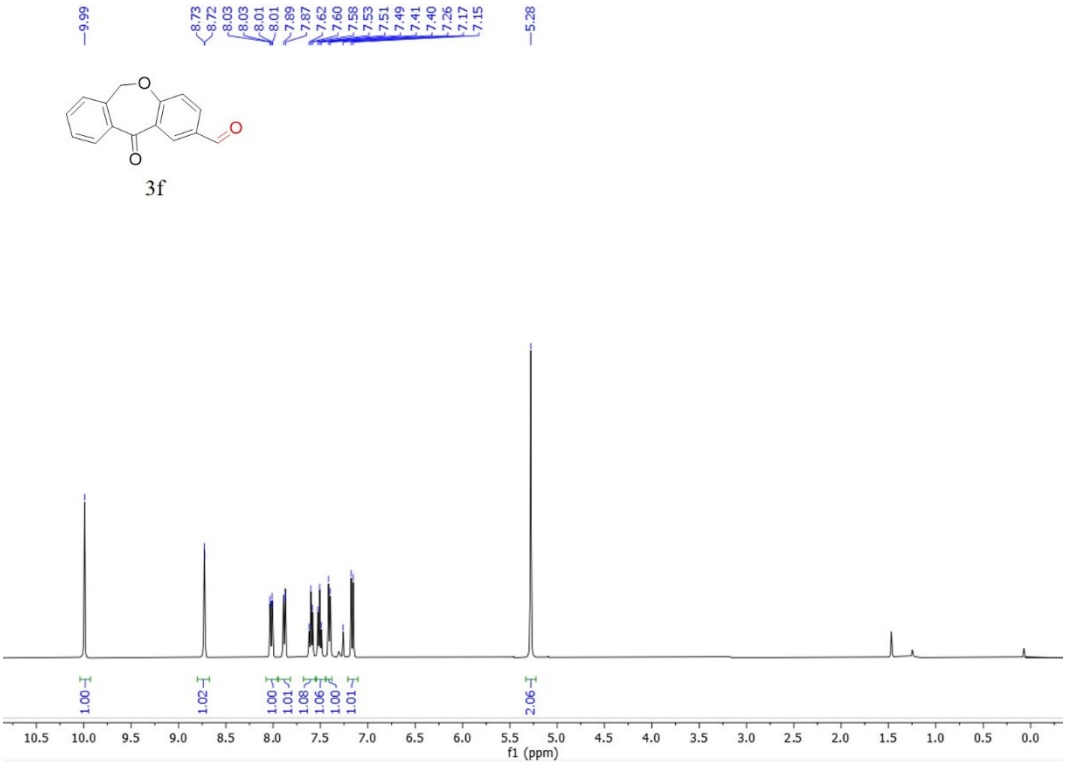

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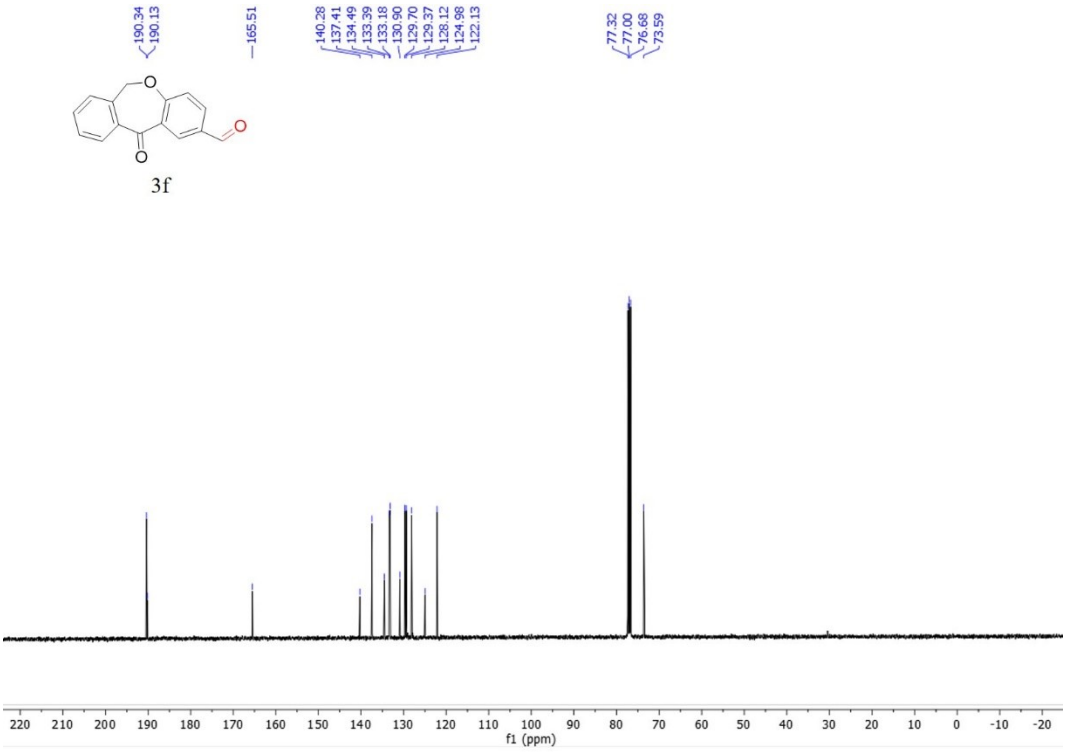

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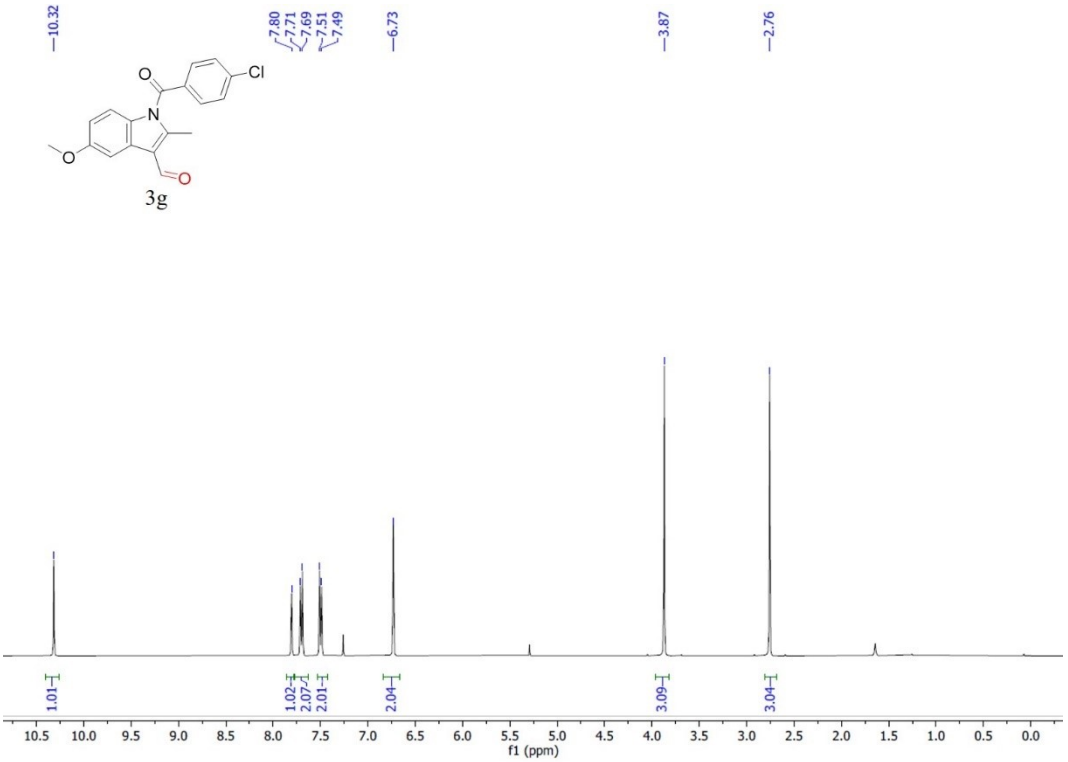

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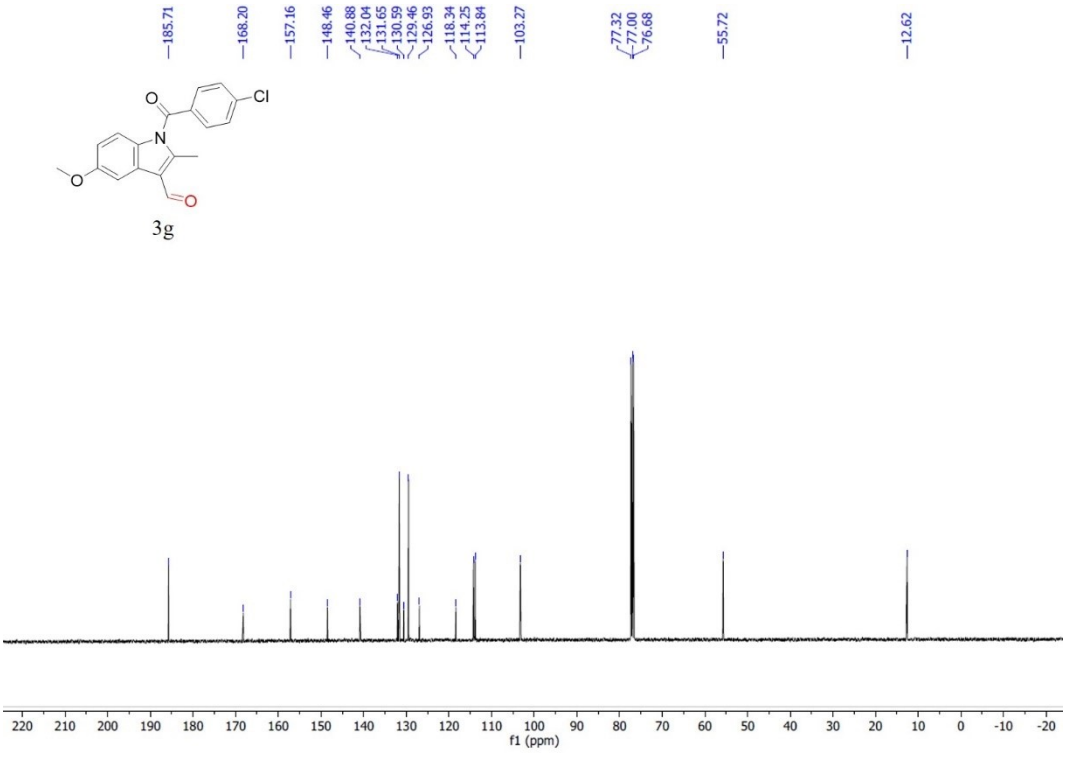

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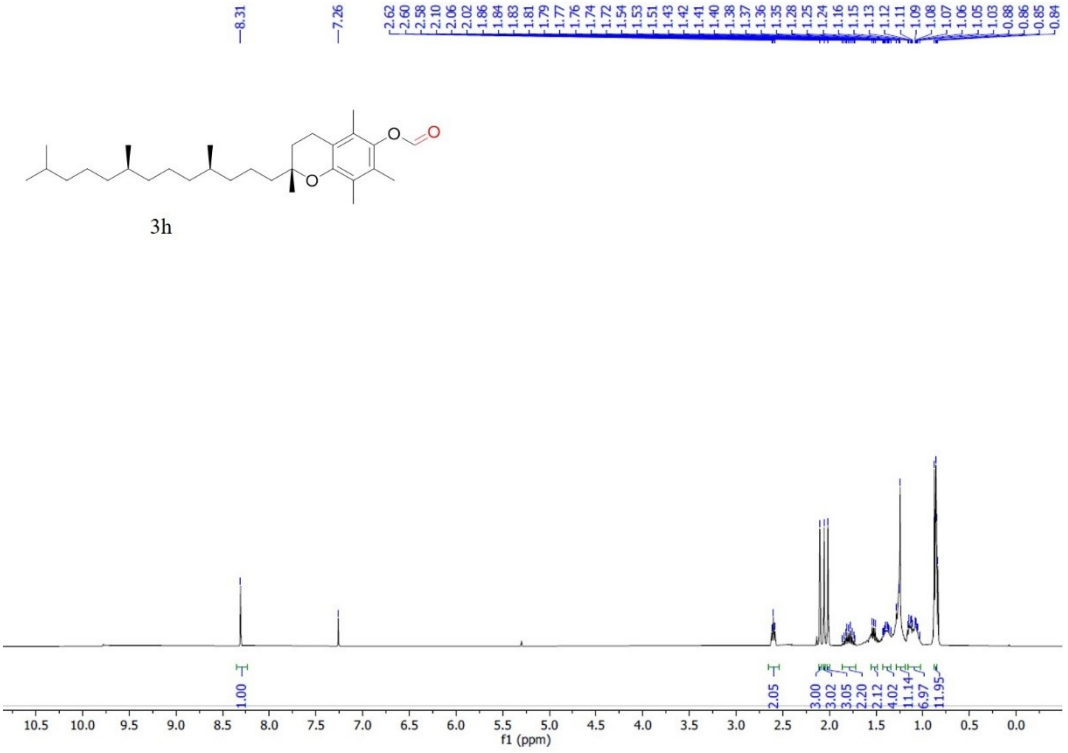

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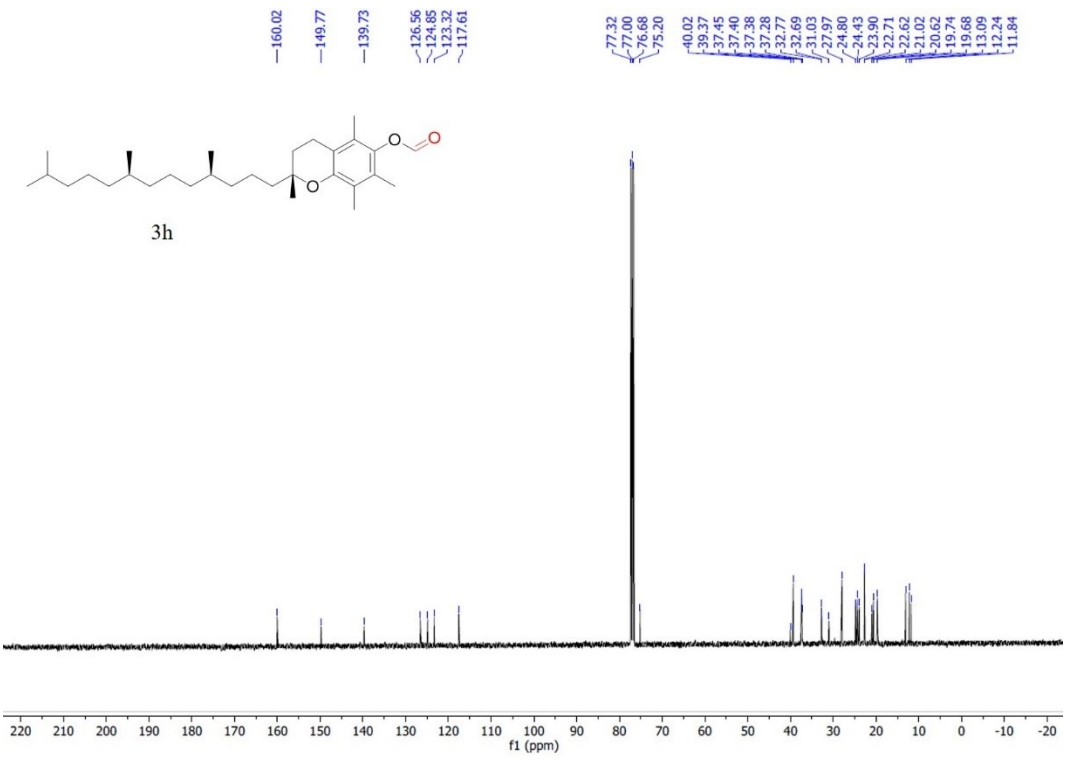

3h

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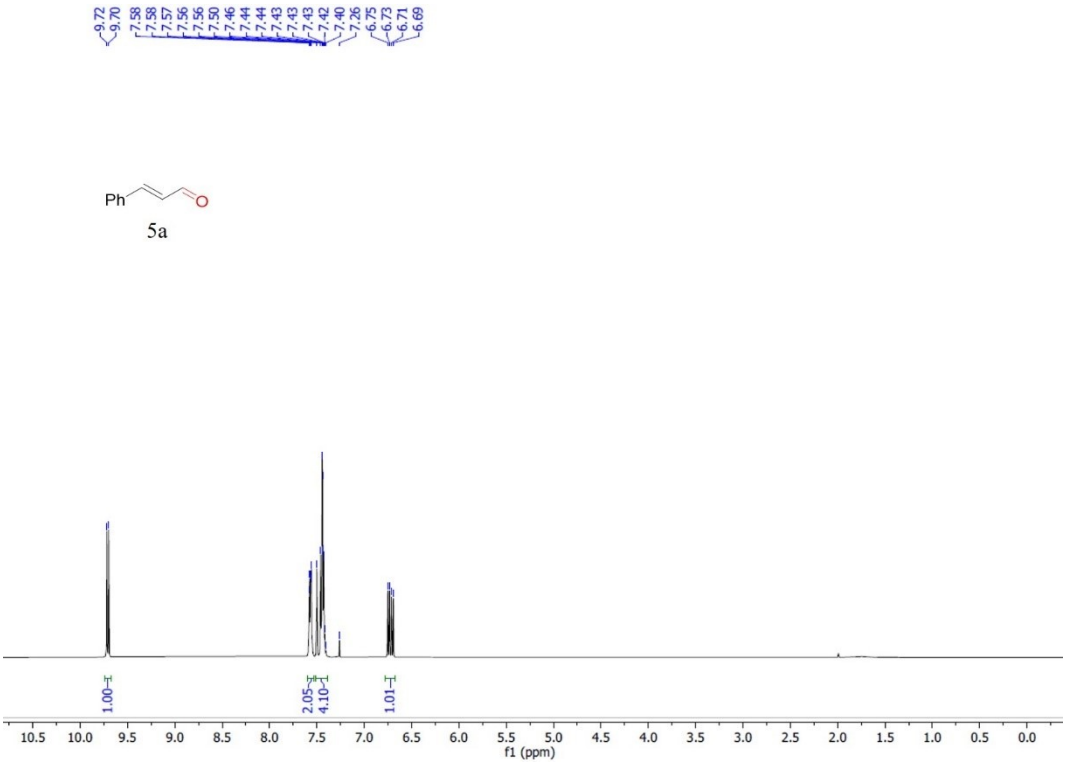

5a

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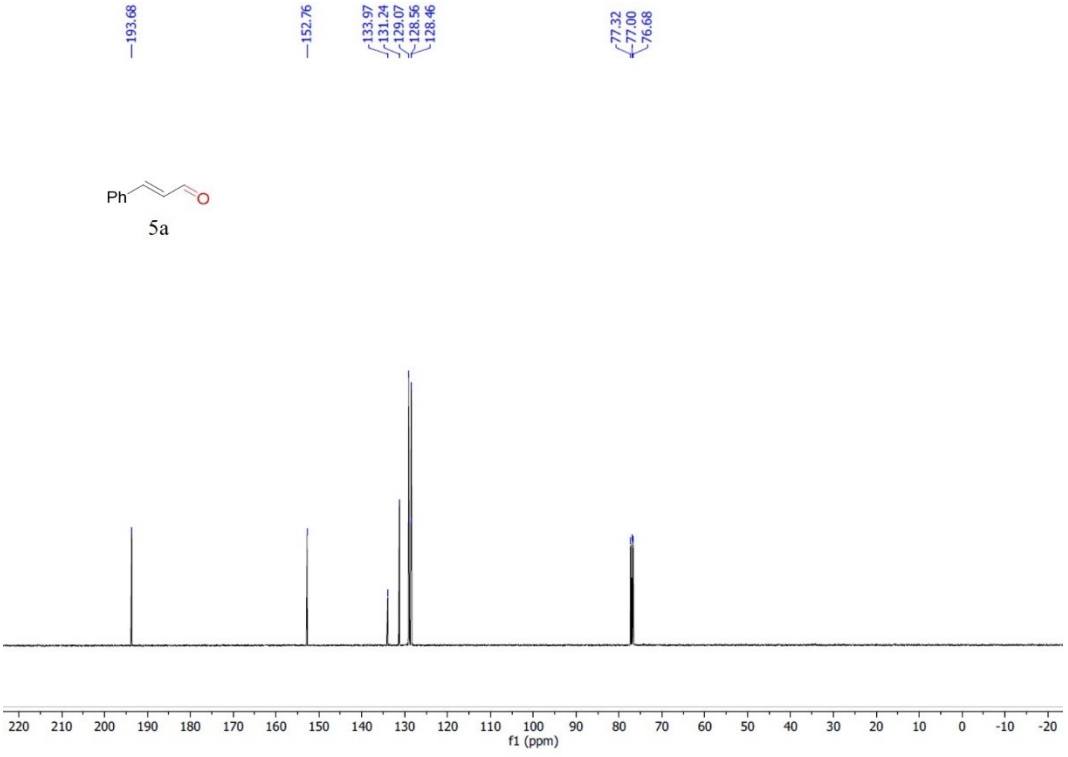

5a

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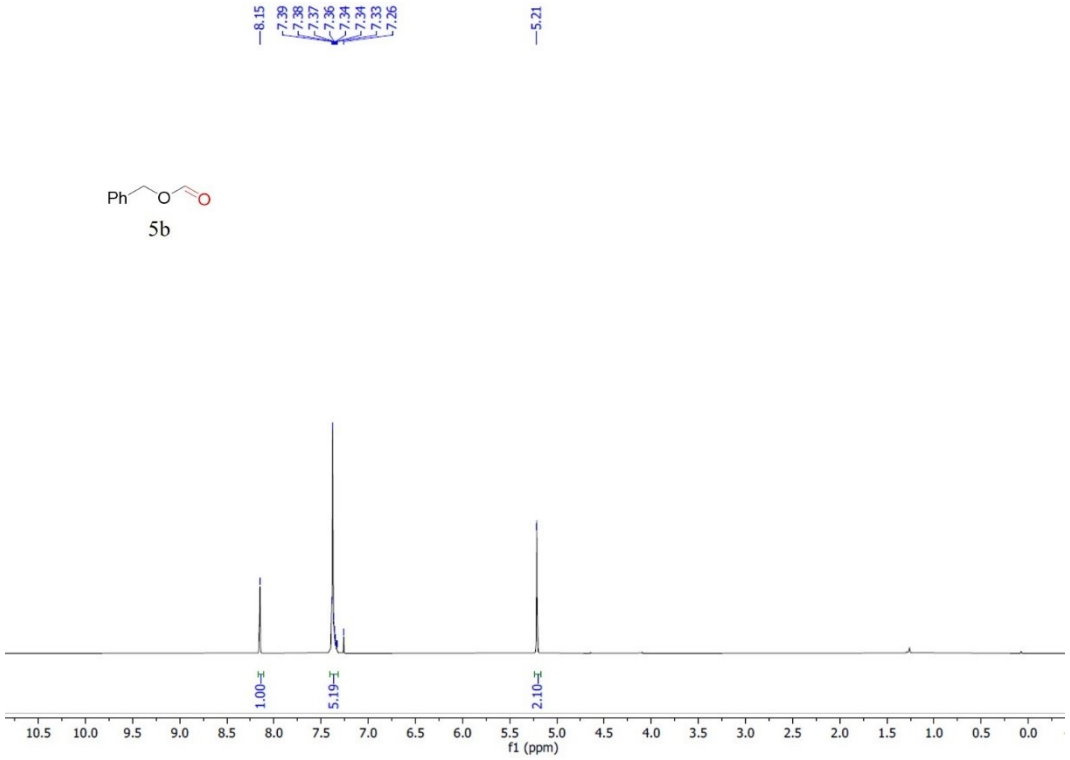

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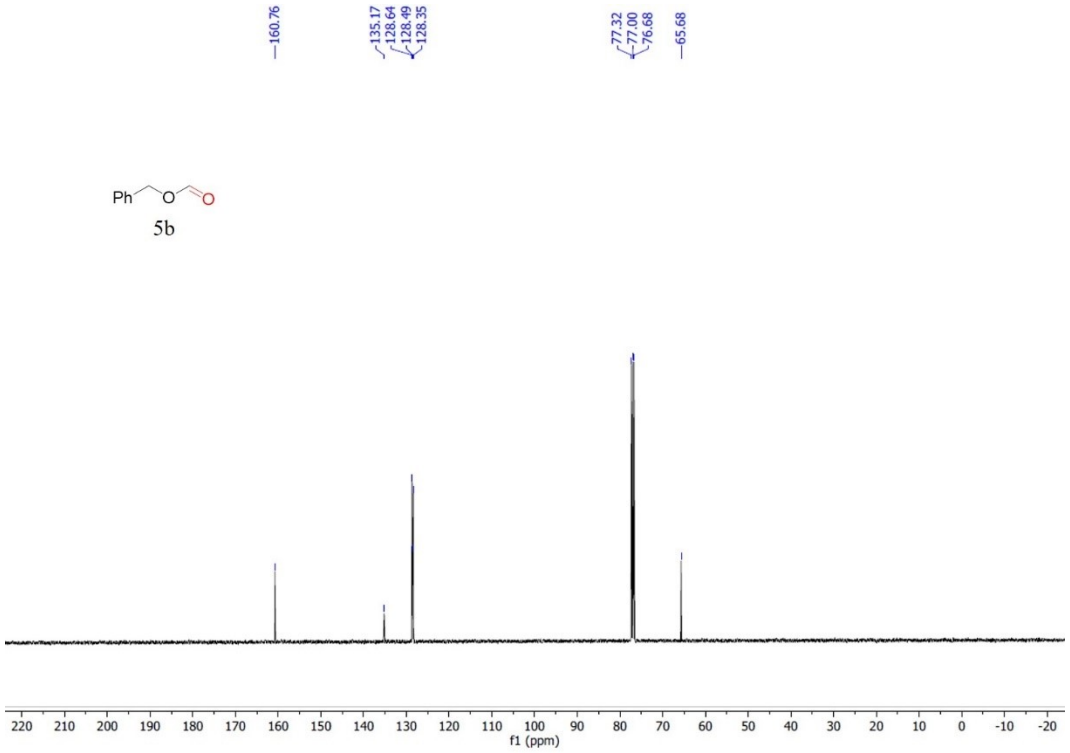

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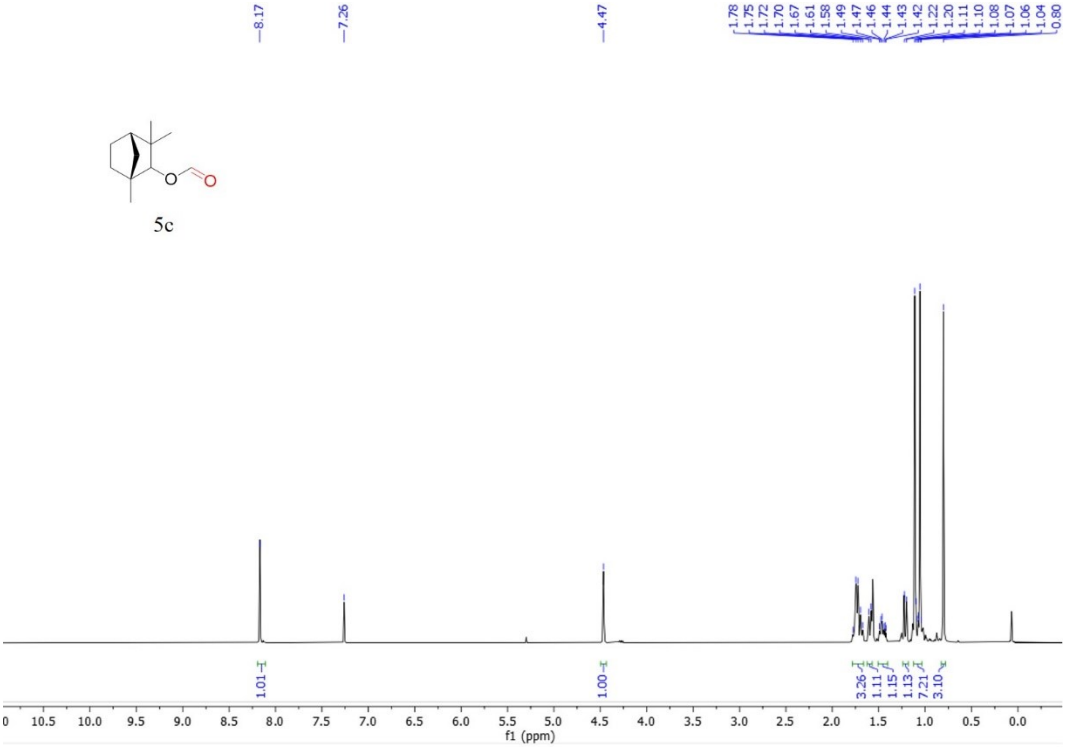

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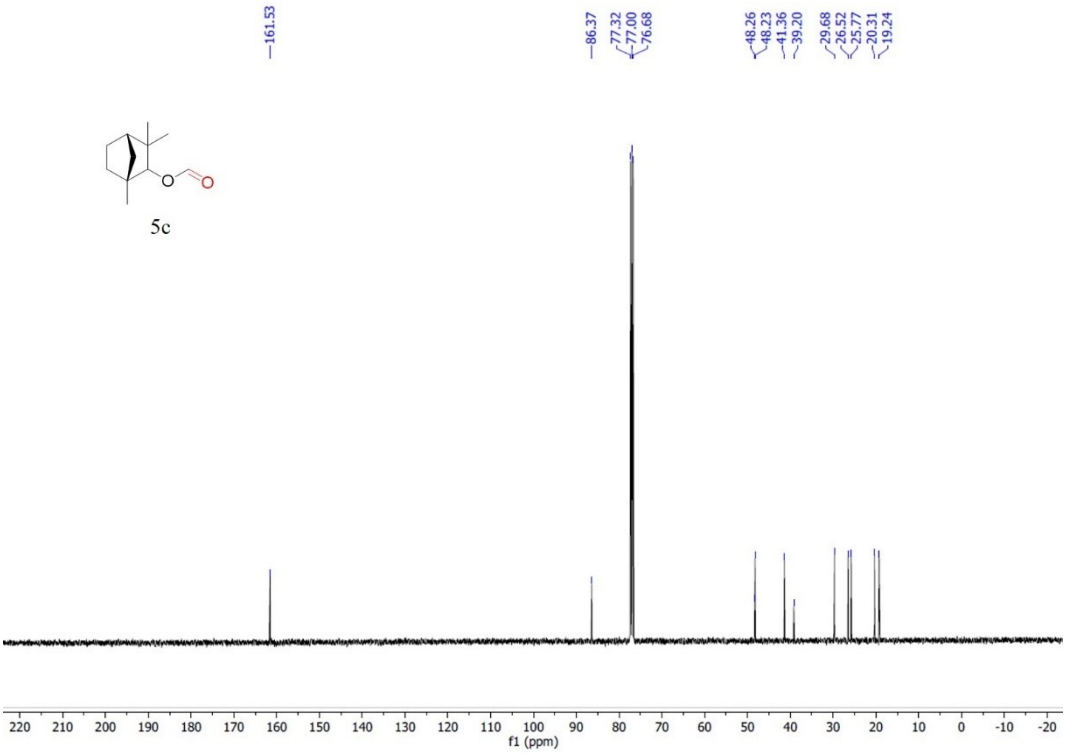

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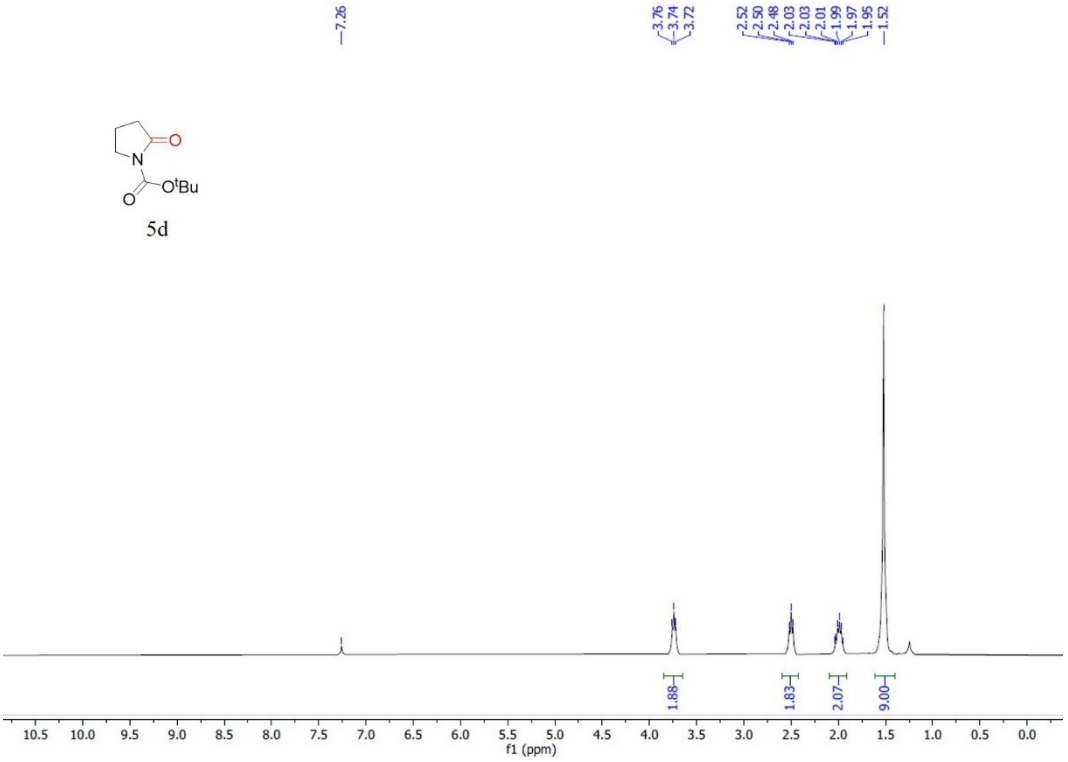

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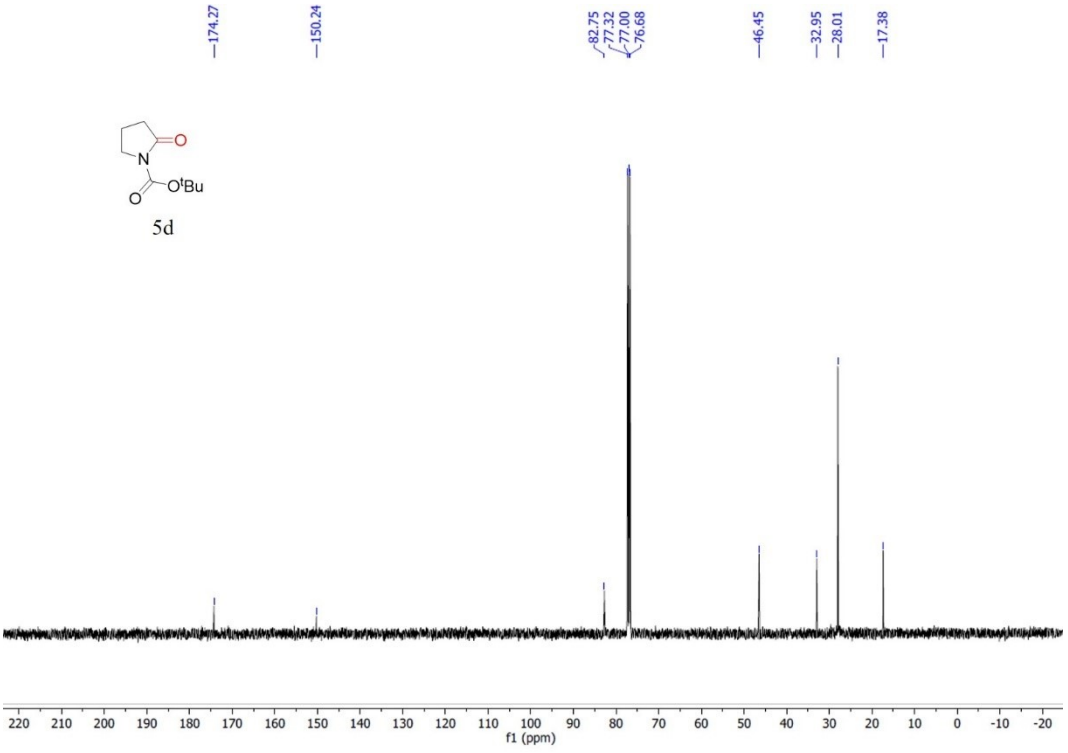

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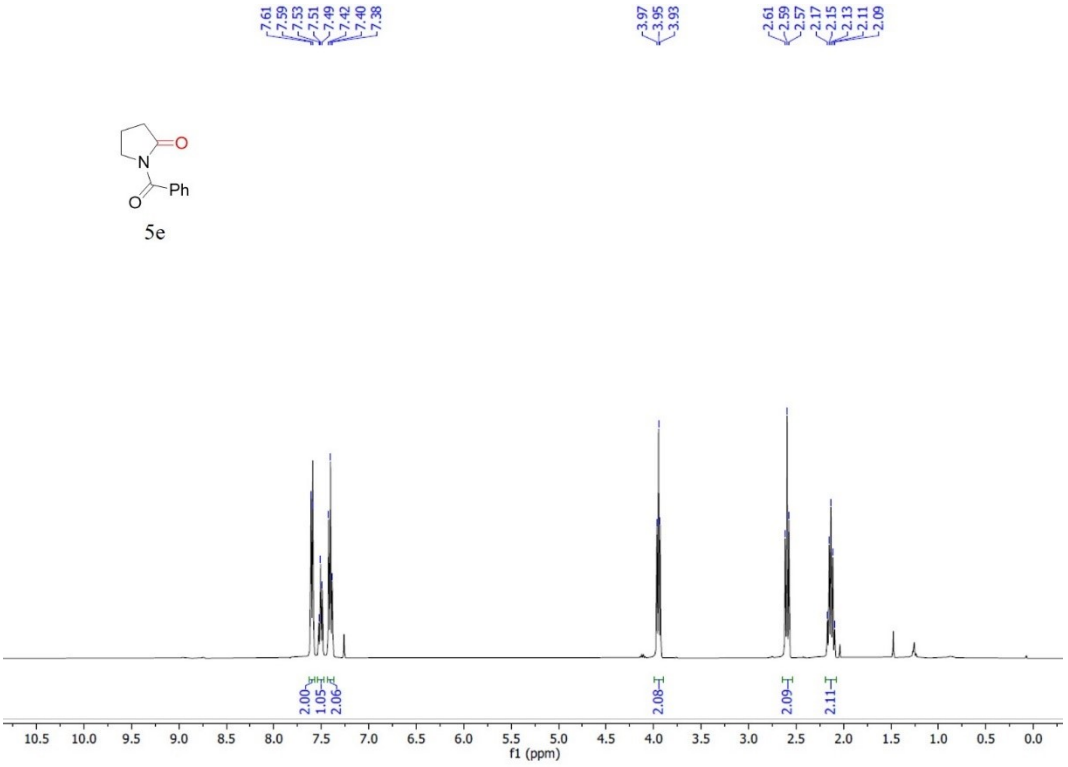

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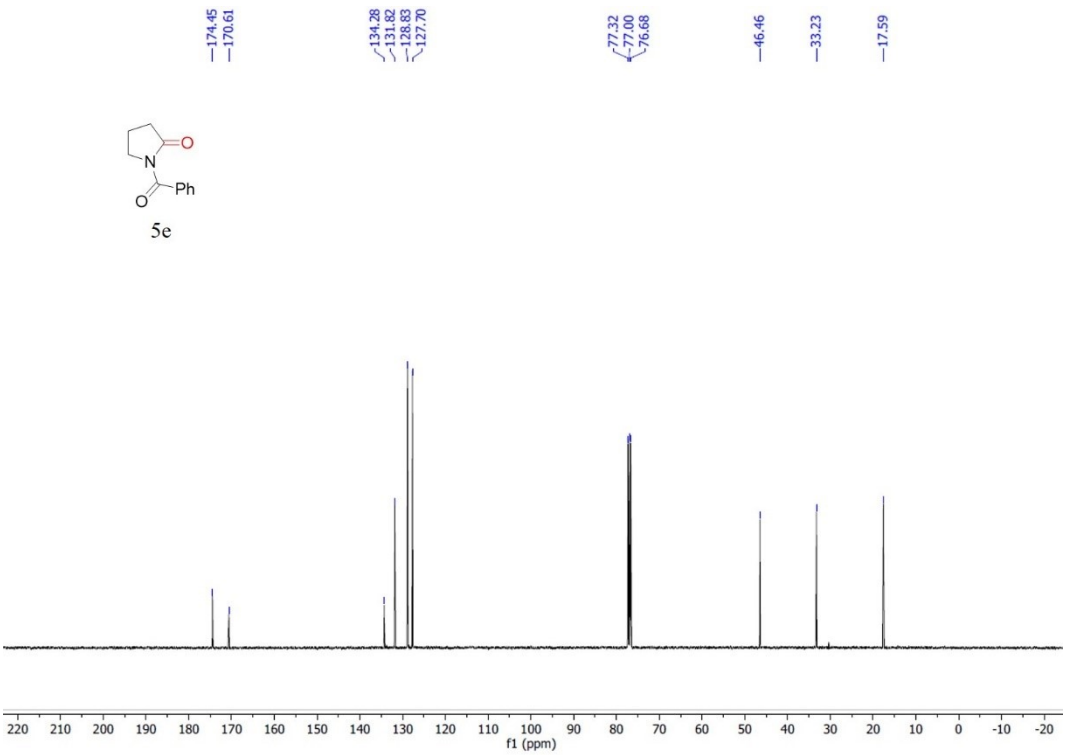

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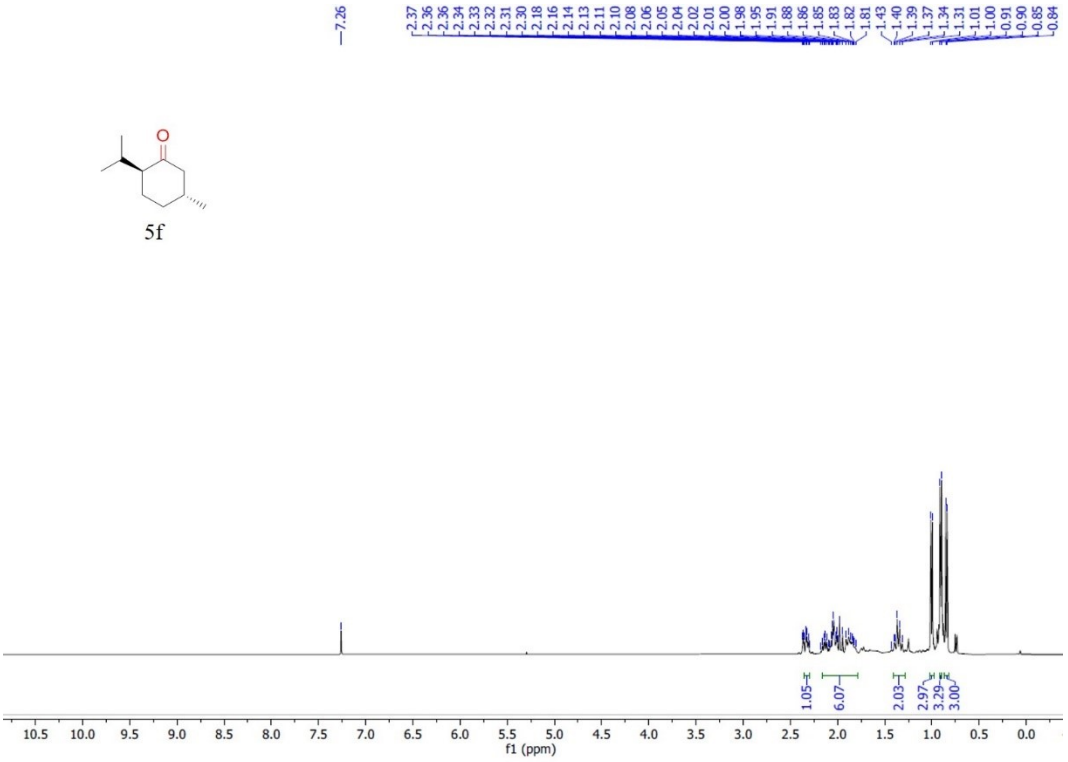

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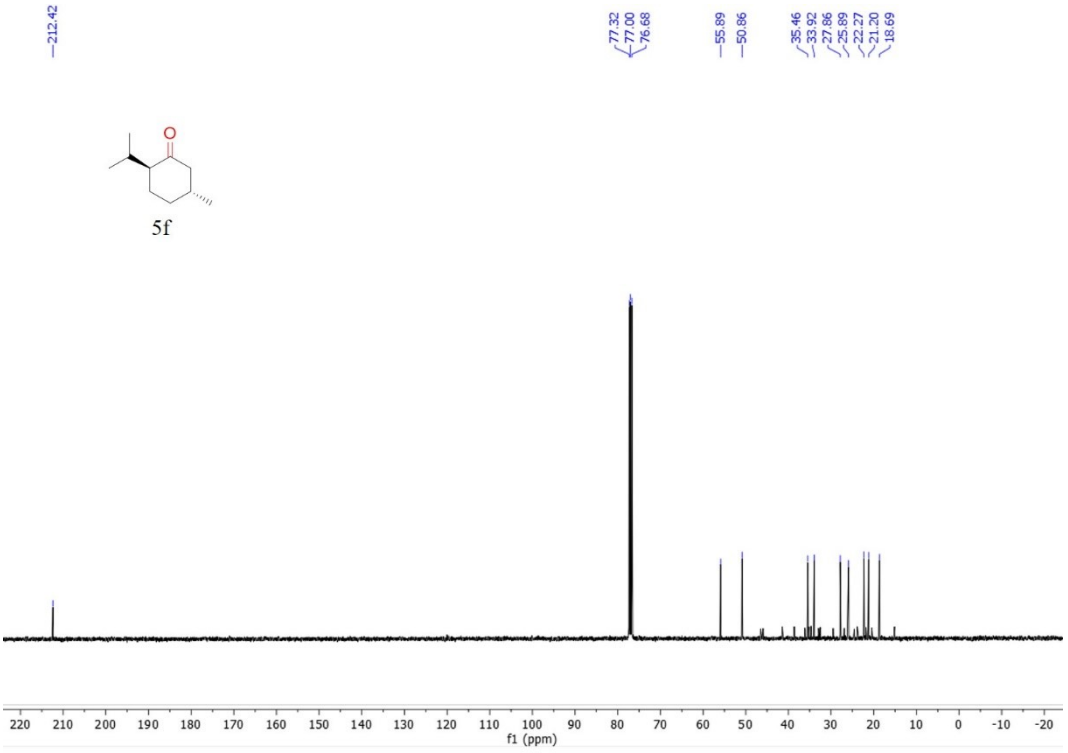

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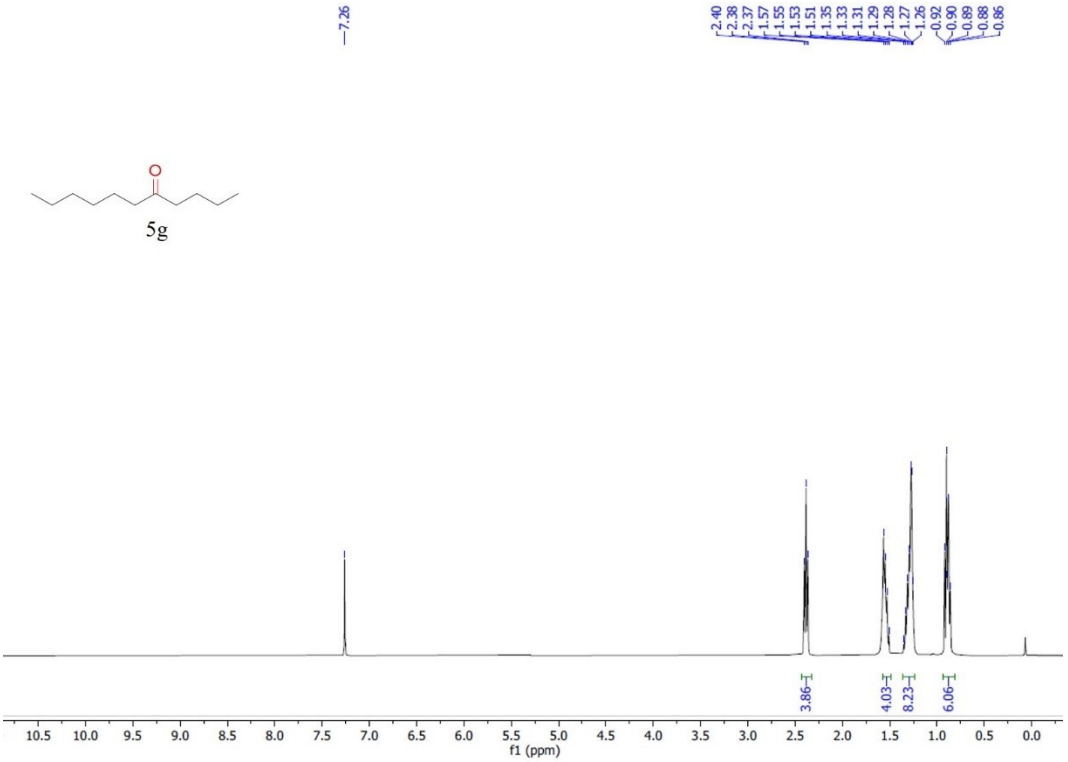

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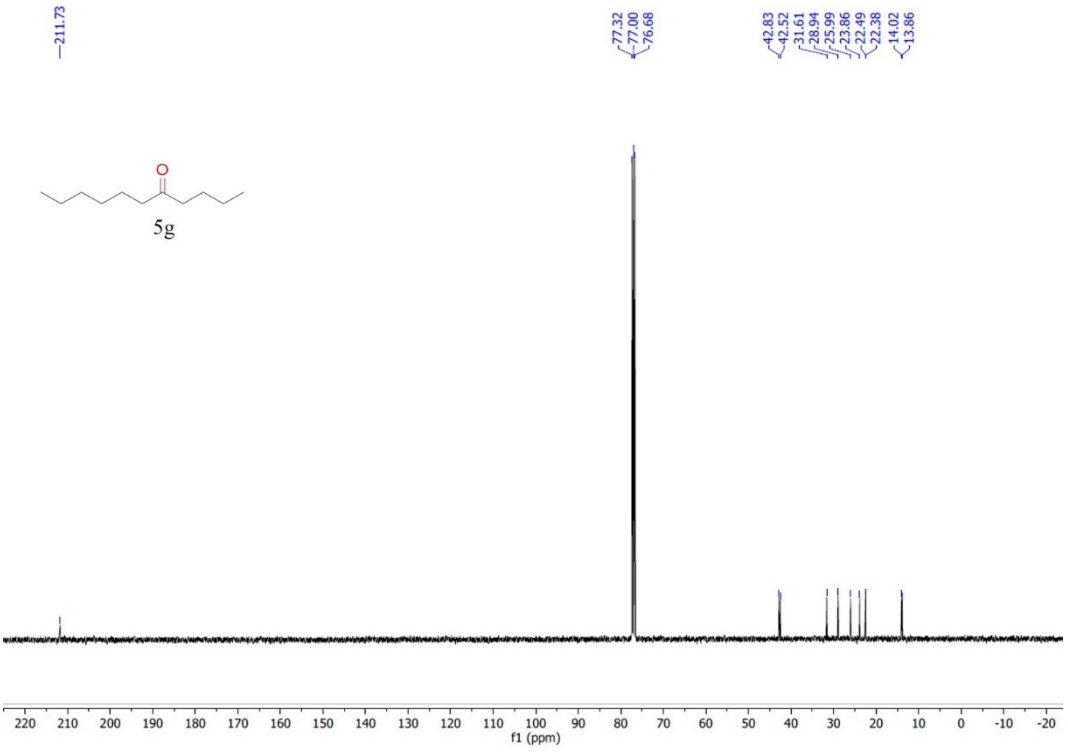

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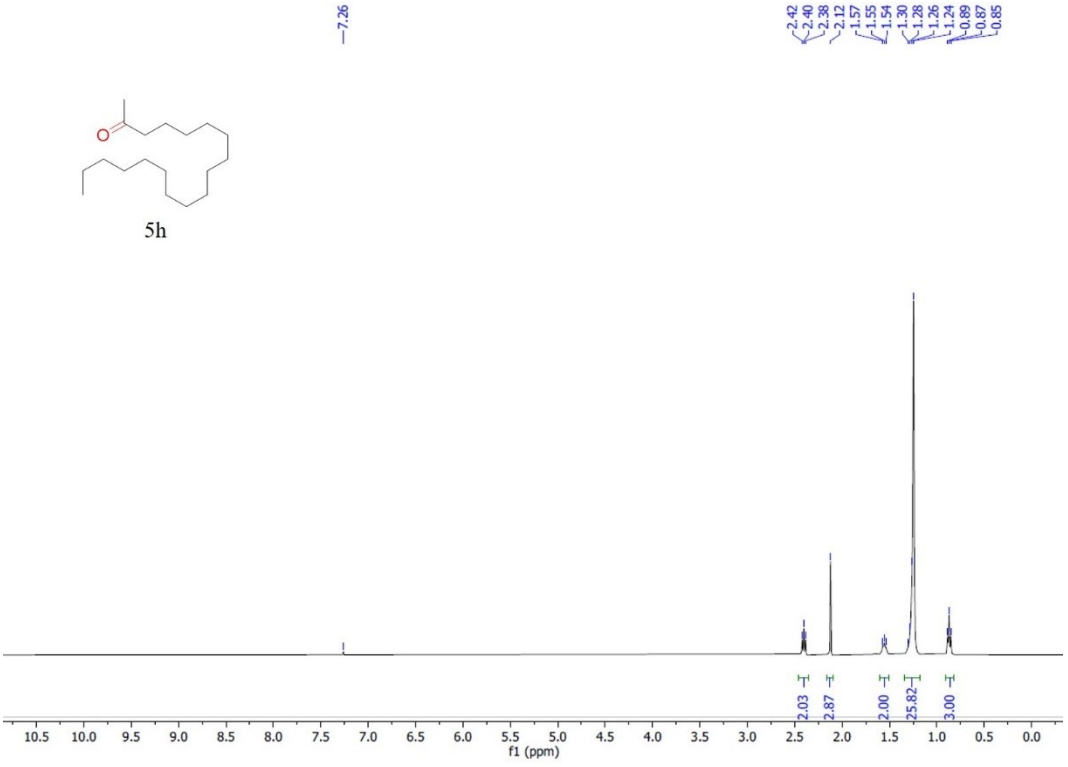

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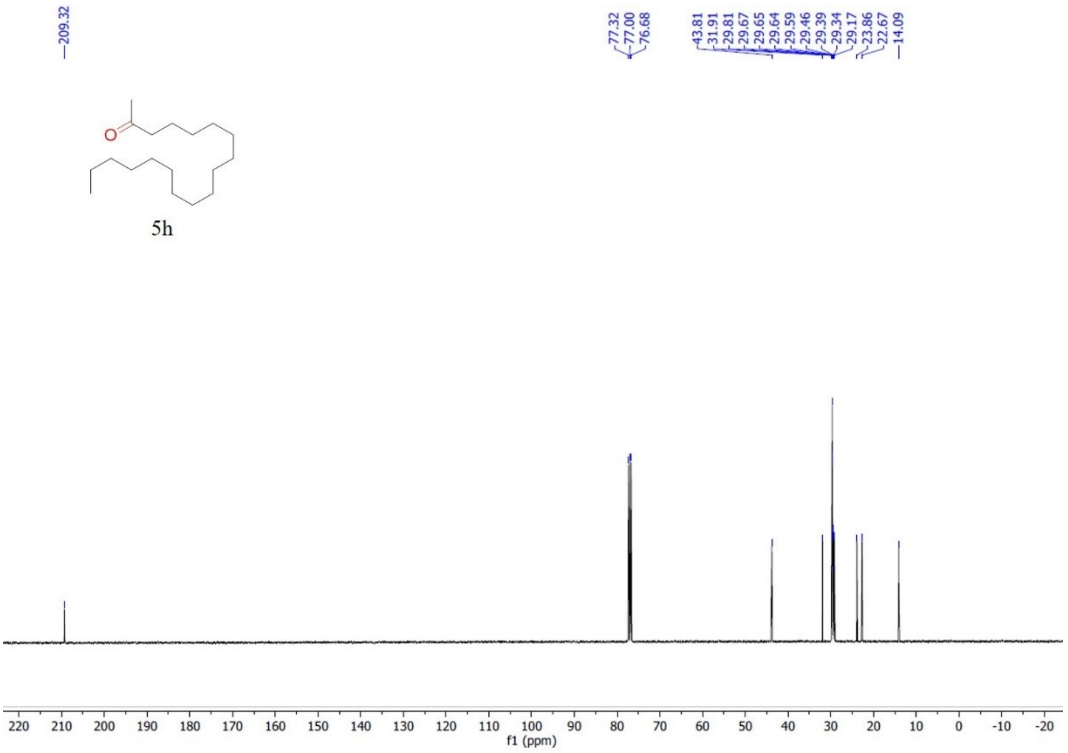

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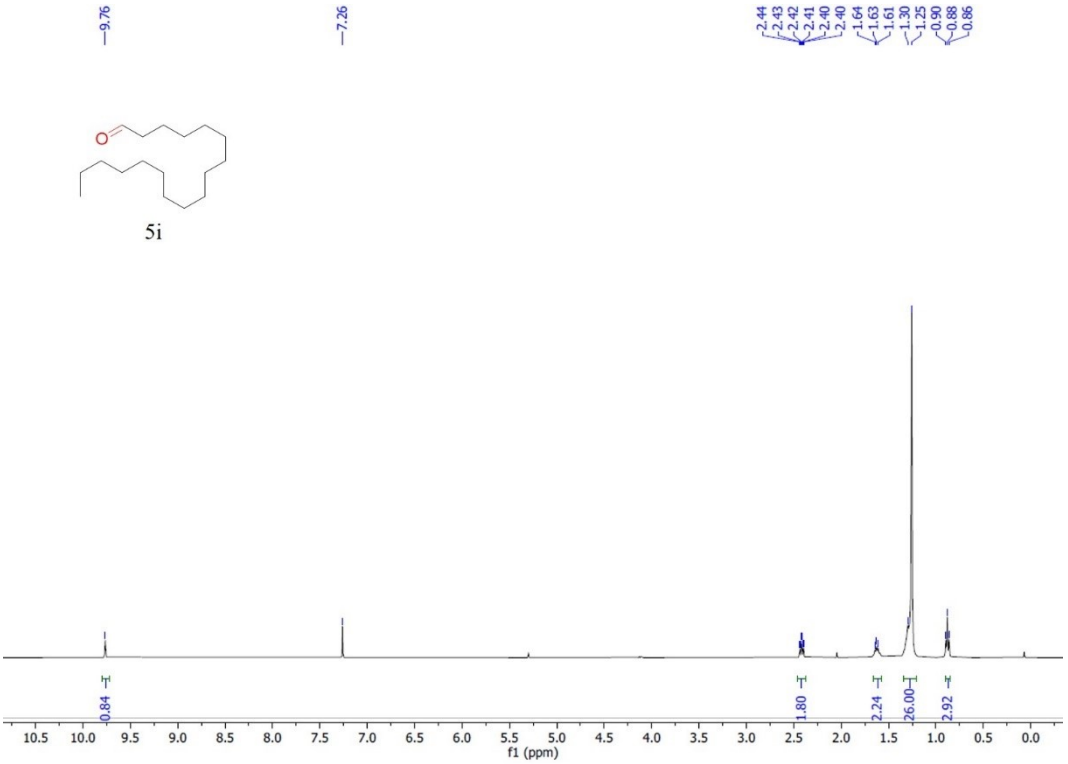

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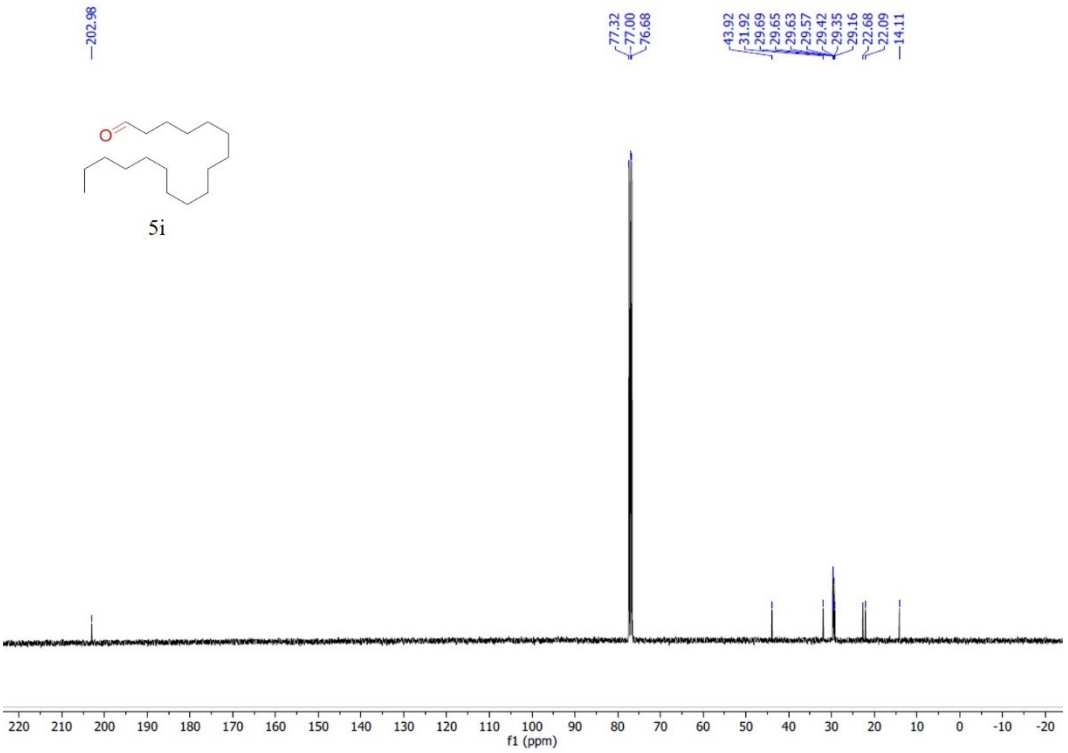

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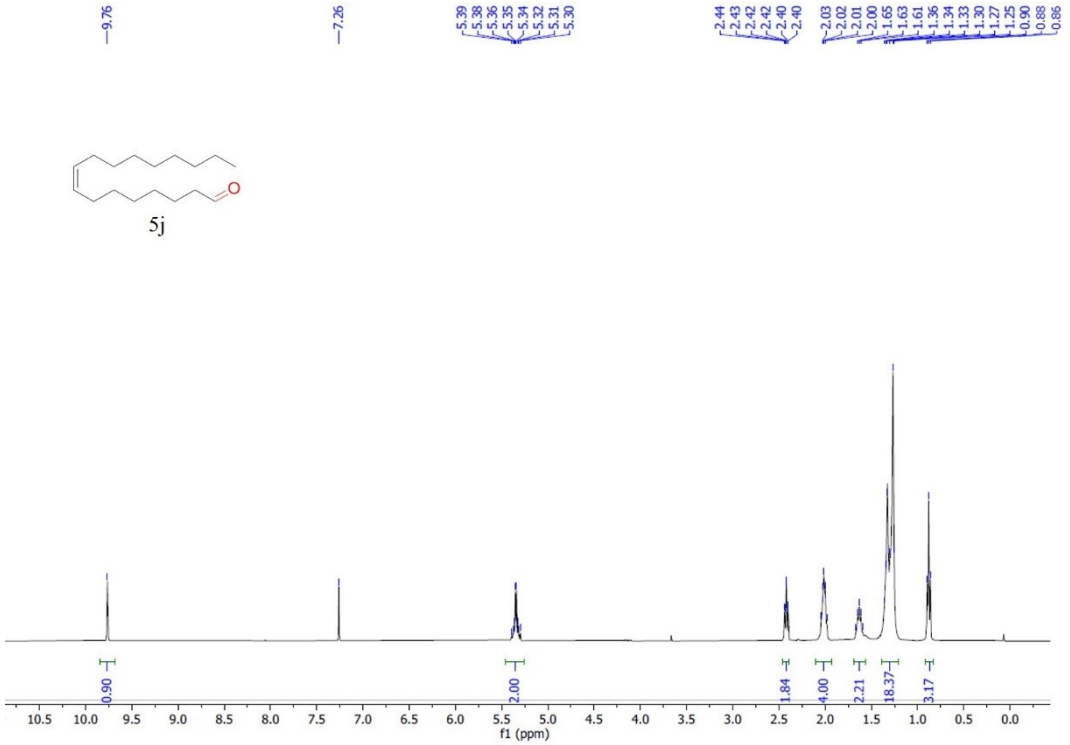

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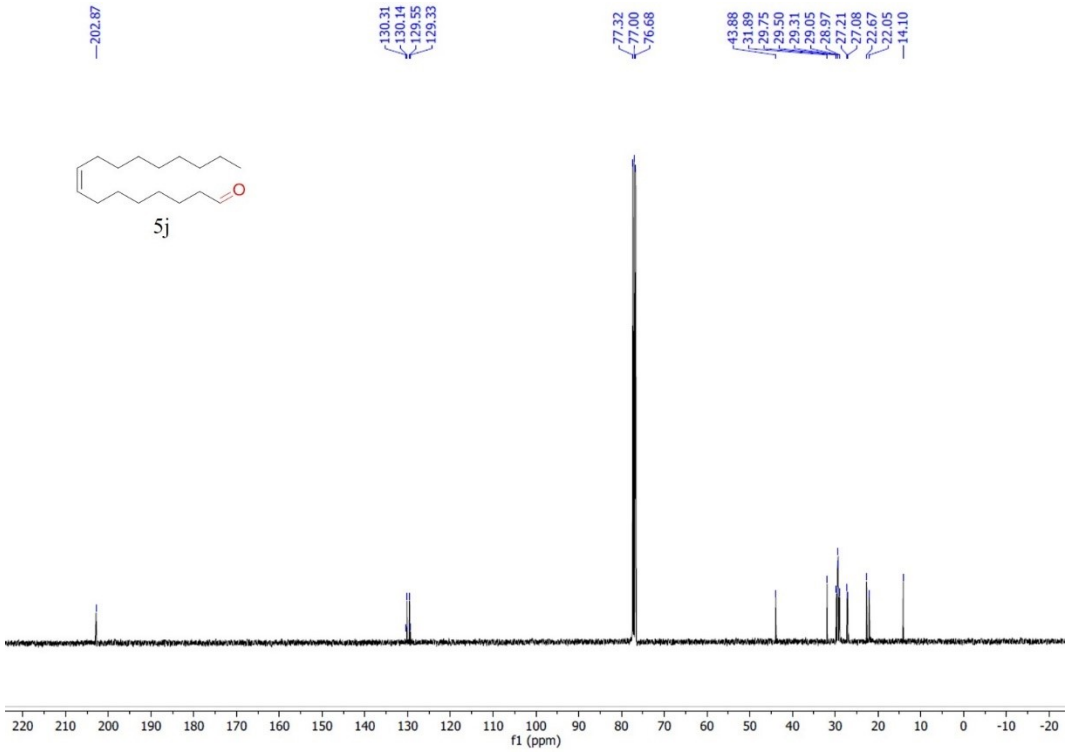

^{13}C NMR

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