Supplemental Information

Photocatalytic Oxidative Cleavage of Styrenes Using Water and Chlorides for Application in Rubber Degradation

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1. General information

All reactions were conducted under inert atmospheres using standard techniques, unless specified otherwise. All reagents and materials were obtained commercially and utilized without further purification, unless stated otherwise. Solvents were maintained in super-dry, anhydrous conditions with a minimum purity of 99.9%. Column chromatography was performed using silica gel (Merck, 200-300 mesh), and thin-layer chromatography (TLC) was carried out on silica gel GF254 plates, employing a mixture of petroleum ether (PE) and ethyl acetate (EA) as the developing solvent. The plates were visualized under ultraviolet light. The Mooney viscosity of the isoprene rubber, sourced from Xinjiang Tianli Petrochemical Co., Ltd., was 80. Products were purified via column chromatography using silica gel (200–300 mesh). Thin-layer chromatography (TLC) separations were conducted on silica gel GF254 plates with a solvent mixture of petroleum ether (PE) and ethyl acetate (EA), and the plates were visualized using UV light. Nuclear magnetic resonance (NMR) spectra, including ^{1}H (400 MHz), ^{13}C (101 MHz), and ^{19}F (376 MHz), were recorded on a Bruker AMX 400 NMR spectrometer, with tetramethylsilane (TMS) as the internal standard in $CDCl_3$ or DMSO$_{-d6}$ solutions. Chemical shifts for ^{1}H NMR were reported relative to TMS at 0.00 ppm, residual $CHCl_3$ at 7.26 ppm, or residual DMSO$_{-d6}$ at 2.50 ppm (δ ppm). The following abbreviations were used to denote signal characteristics: δ = chemical shift, J = coupling constant, s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet. High-resolution mass spectra (HRMS) were obtained via an Agilent LC/MSD TOF 6500 series mass spectrometer. Shimadzu Co., Ltd. utilized a gas chromatograph-mass spectrometer (GC-MS) for the analysis of key intermediates.

2. Setup for photocatalytic reaction

A schematic diagram of the photochemical apparatus is shown in Figure S1. The blue light LED irradiation reaction setup utilized commercially available blue light LEDs (30 W, λ=455 nm) from Beijing Nuozhi Technology Co., Ltd., model RLH-18CF, as the reaction light source. All reactions were conducted in a 25 mL quartz tube equipped with a magnetic stirrer. The reactions were stirred at a speed ranging from 800 to 1000 rpm, and the reaction temperature was maintained at 25 °C using a commercially available DL-400 low-temperature cooling circulation pump.

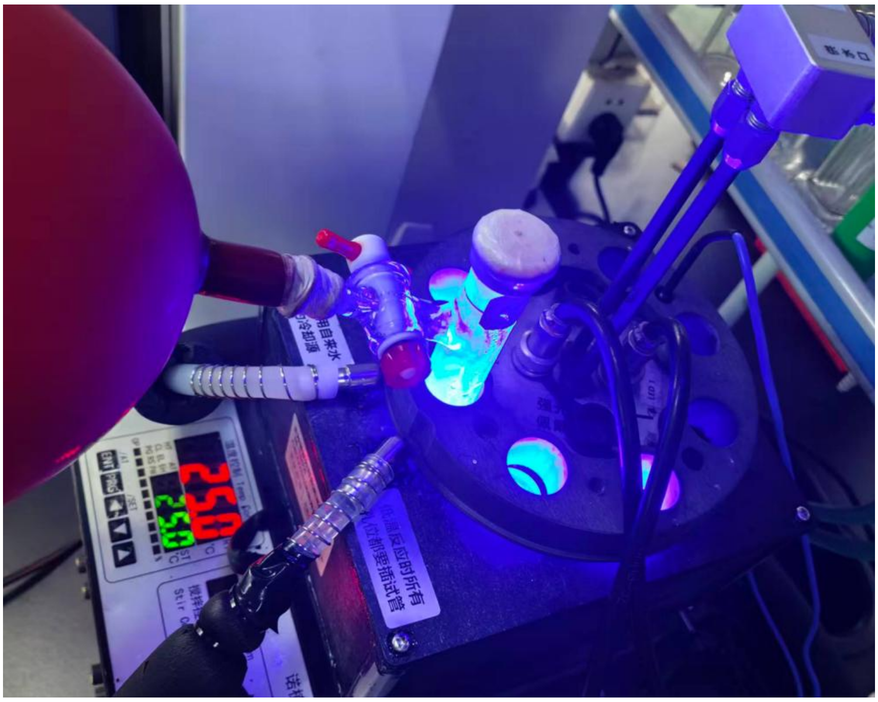
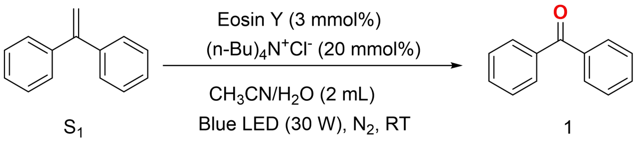


Figure S1. LED reaction setup for photocatalytic reactions.

3. Mechanistic investigation

Control experiments

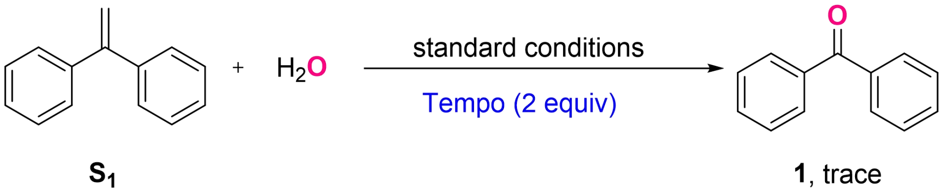
Table S1 Control experiments[a, b]



entry	conditions [a]	yield (%) [b]
1	No photocatalyst at 80 °C	N.D.
2	No $(n\text{-Bu})_4N^+Cl^-$	trace
3	No light	N.D.
4	No water	N.D.

[a] Reaction conditions: 1,1-diphenylethylene S1 (0.2 mmol, 35 uL), photocatalysts (3 mol%), $(n\text{-Bu})_4N^+Cl^-$ (20 mol%), DCM (2 mL), H_2O (200 uL), N_2, 30 W blue LED, rt, 72 h. [b] NMR yield.

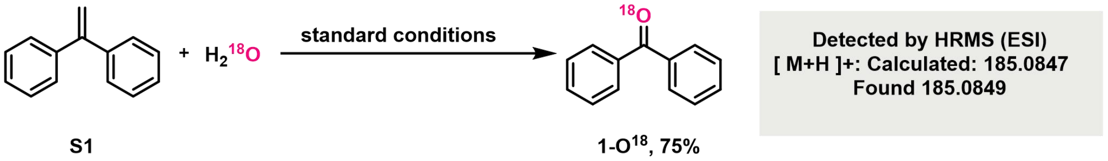
Radical trap experiments

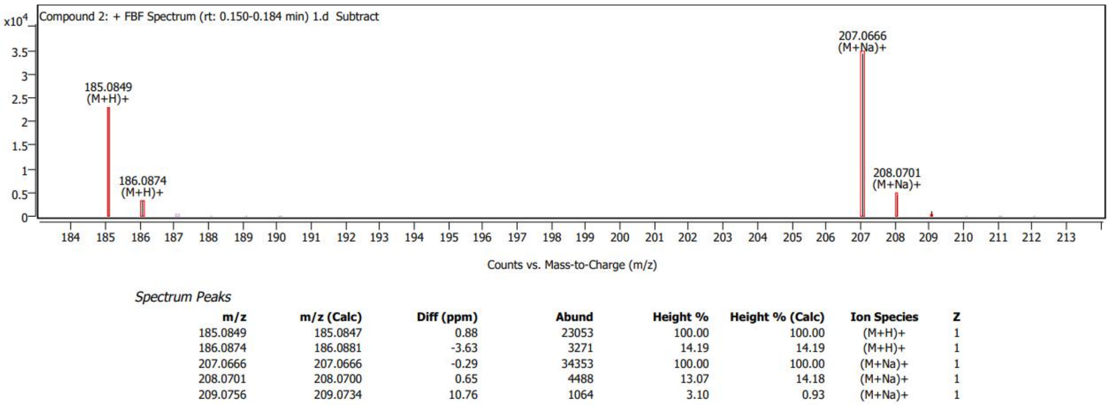


Following the standard procedure, a mixture consisting of Eosin Y ((3 mol%, 3.9 mg), 1,1-diphenylethylene (S1, 0.2 mmol, 35 μL), (n-$Bu_4N^+Cl^-$ ((20 mol%, 11 mg), CH_3CN (2 mL), H_2O (200 μL), and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 0.4 mmol) was added to a 25 mL quartz tube under a nitrogen atmosphere at room temperature. The contents were then stirred under 30 W blue LED irradiation for 72 hours. After cooling the reaction mixture to room temperature, it was isolated using preparative thin-layer chromatography. No product **1** was observed.

Isotope labeling experiments

Following the standard procedure, a mixture consisting of Eosin Y ((3 mol%, 3.9 mg), 1,1-diphenylethylene S1 (0.2 mmol, 35 µL), *n*-$Bu_4N^+Cl^-$ (20 mol%, 11 mg), CH_3CN (2 mL), and $H_2{}^{18}O$ (200 µL) was added to a 25 mL quartz tube under a nitrogen atmosphere at room temperature. The contents were then stirred under 30 W blue LED irradiation for 72 hours. After cooling the reaction mixture to room temperature, it was isolated using preparative thin-layer chromatography. Compound 1-O^{18} was obtained in 75% yield and detected by HRMS as well.





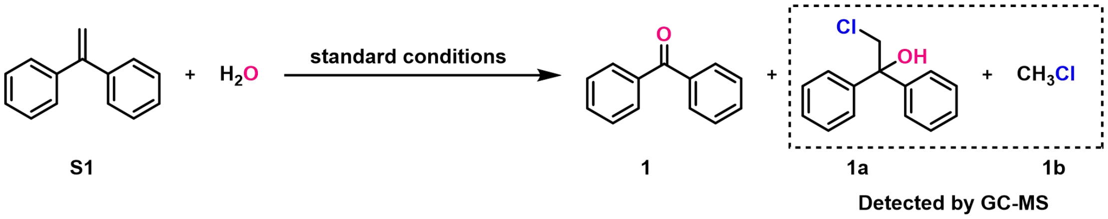
Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
185.0849	185.0847	0.88	23053	100.00	100.00	(M+H)+	1
186.0874	186.0881	-3.63	3271	14.19	14.19	(M+H)+	1
207.0666	207.0666	-0.29	34353	100.00	100.00	(M+Na)+	1
208.0701	208.0700	0.65	4488	13.07	14.18	(M+Na)+	1
209.0756	209.0734	10.76	1064	3.10	0.93	(M+Na)+	1

Figure S2. HRMS spectra of compound **1-O^{18}**

Detected experiments of key intermediates 1a and 1b

Following the standard procedure, the reaction mixture was analyzed by GCMS. Compounds 1a and 1b were detected successfully.



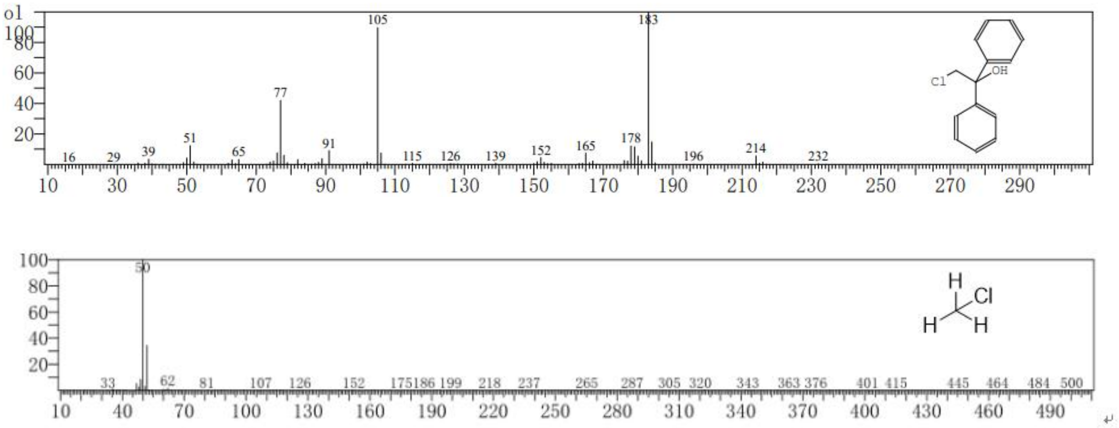


Figure S3. GCMS spectra of compound **1a** and **1b**

Stern-Volmer fluorescence quenching experiment

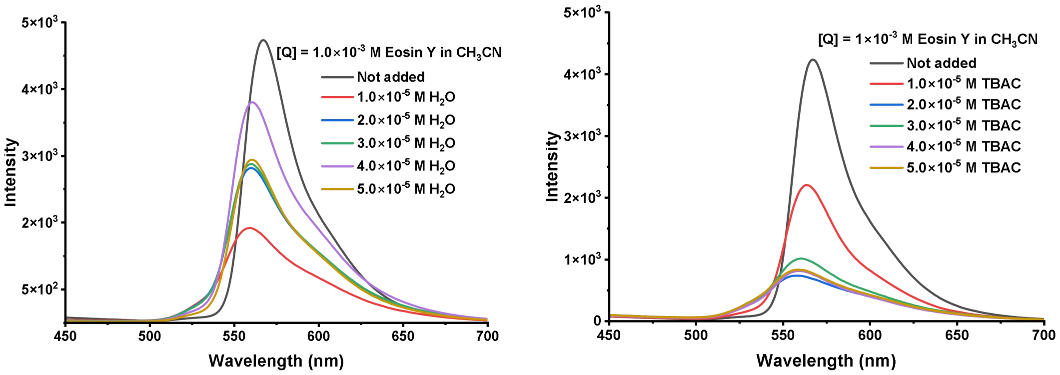
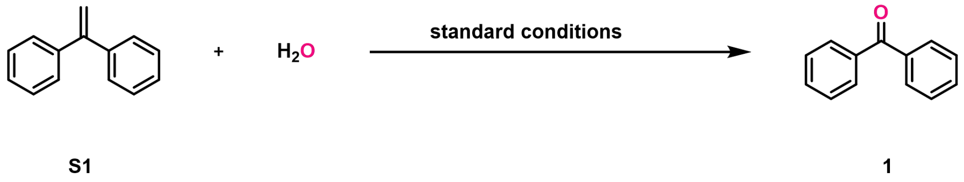


Figure S4. Stern-Volmer fluorescence quenching experiment

On/off Light Experiment

Following the standard procedure. Yield was determined by ^{1}H NMR of the crude mixture using 1,3,5- trimethoxybenzene (149.5 mg, 0.89 mmol) as internal standard. Turn off the light source and stir the reaction mixture in the dark for 6 hours. The subsequent reaction is carried out in an intermittent light irradiation mode, with cycles of stirring under light for 12 hours, stirring in the dark for 12 hours, stirring under light for 15 hours, and stirring in the dark for 15 hours.



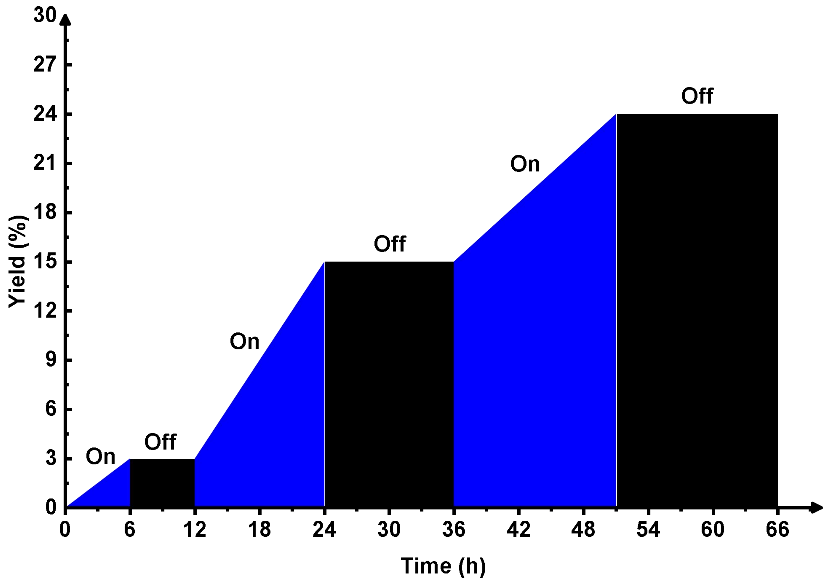


Figure S5. On/off experiment

4. Degradation experiment of isoprene rubber

Crush the isoprene rubber. In a 25 mL Schlenk tube equipped with a magnetic stir bar, combine polyisoprene rubber (143 mg), Eosin Y (39 mg, 0.06 mmol), and $(n\text{-Bu})_4N^+Cl^-$ (111 mg, 0.4 mmol). After backfilling the tube with nitrogen (a process repeated three times), add water (0.5 mL) and DCM (5.0 mL). Seal the tube and irradiate it with a blue LED lamp (30 W) at room temperature for 10 days. Once the degradation is complete, perform suction filtration. Spin-dry the filter residue and weigh it to obtain 5.4 mg of a pink solid (the undegraded rubber sample). Calculate the degradation rate using the formula: (total rubber sample - undegraded rubber sample) / total rubber sample = 96%.

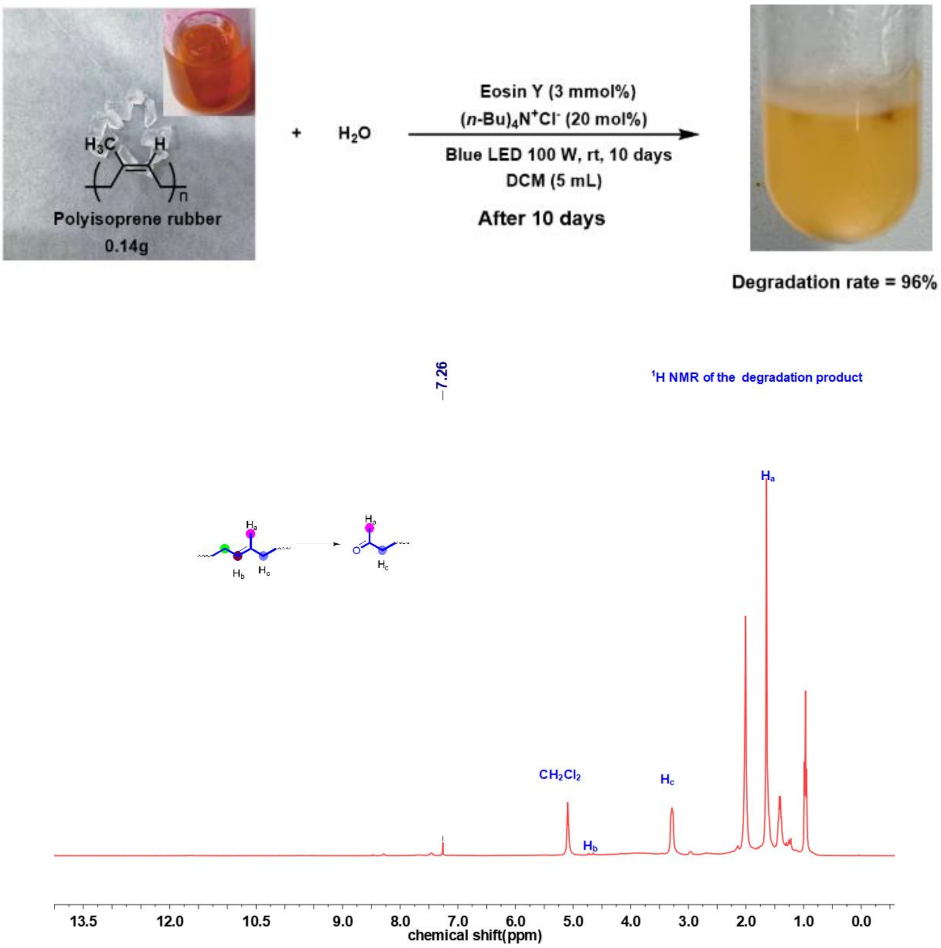


Figure S6. Photochemical degradation reaction of isoprene rubber

VCR.mp4

Figure S7. Video of the photochemical degradation reaction of isoprene rubber

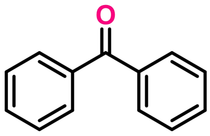
5. Standard procedure for 1-24

A mixture consisting of Eosin Y (3 mol%, 3.9 mg), styrenes S1-S24 (0.2 mmol), n-$Bu_4N^+Cl^-$ (20 mol%, 11 mg), CH_3CN (2 mL), and H_2O (200 μL) was added to a 25 mL quartz tube under a nitrogen atmosphere at room temperature. The contents were then stirred under 30 W blue LED irradiation for 72 hours. After cooling the reaction mixture to room temperature, the reaction mixture was diluted with H_2O (15 mL) and washed with dichloromethane (3 x 10 mL). The organic phase was dried over anhydrous sodium sulfate and then purified directly by column chromatography to afford product **1-24** using a PE:EA ratio of 200:1 (*v/v*).

6. Characterization data of compounds 1-24

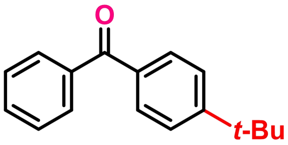
***Note**:* All compounds are known and reported in the following references: Shibata, S.; Kamata, K.; Hara, M. *Catal. Sci. Technol.* 2021, 11, 2369; Angela Gonzalez - de - Castro, a. J. X. *J. Am. Chem. Soc.* 2015, 137, 8206; Li, X. - X.; Hua, H. - Z.; Liu, Y. - H.; Yu, L. *Org. Lett.* 2023, 25, 6720; Amaya, T.; Fujimoto, H. *Tetrahedron Lett.* 2018, 59, 2657; Huang, Z. - L.; Guan, R. - P.; Shanmugam, M.; Bennett, E. L.; Robertson, C. M.; Brookfield, A.; McInnes, E. J. L.; Xiao, J. - L. *J. Am. Chem. Soc.* 2021, 143, 10005.

Benzophenone (1):



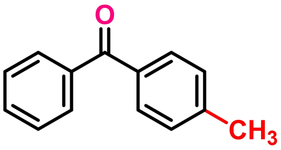
White solid (27.8 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.4 Hz, 4H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.9, 137.7, 132.6, 130.2, 128.4.

(4-(tert-butyl)phenyl)(phenyl)methanone (2):



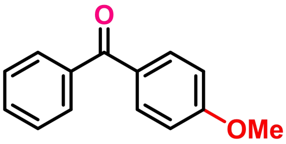
White solid (40.5 mg, 85%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.51-7.46 (m, 4H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 196.6, 156.3, 138.0, 134.9, 132.3, 130.2, 128.3, 125.4, 35.2, 31.3.

phenyl(*p*-tolyl)methanone (3):



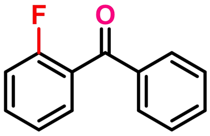
Colorless oil (20.7 mg, 53%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, *J* = 7.4 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 2.46 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 196.6, 143.3, 138.0, 135.0, 132.3, 130.4, 130.0, 129.1, 128.3, 21.8.

(4-methoxyphenyl)(phenyl)methanone (4):



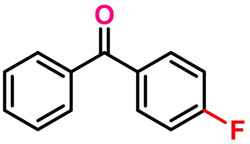
White solid (25.0 mg, 59%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H).^{13}C NMR (101 MHz, CDCl$_3$) δ 195.6, 163.3, 138.4, 132.7 132.0, 130.2, 129.8, 128.3, 113.7, 55.6.

(2-fluorophenyl)(phenyl)methanone (5):



Colorless (35.2 mg, 88%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.64 - 7.48 (m, 5H), 7.27 (dd, *J* = 9.2, 5.7 Hz, 1H), 7.16 (t, *J* = 9.1 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 193.6, 160.2 (d, $J_{F\text{-}C}$ = 252.4 Hz), 137.5, 133.5, 133.2 (d, $J_{F\text{-}C}$ = 8.4 Hz), 130.9 (d, $J_{F\text{-}C}$ = 2.8 Hz), 129.9, 128.6, 127.2 (d, $J_{F\text{-}C}$ = 14.8 Hz), 124.4 (d, $J_{F\text{-}C}$ = 3.6 Hz), 116.4 (d, $J_{F\text{-}C}$ = 21.7 Hz).

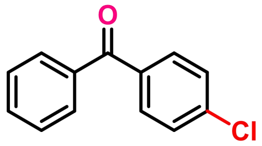
(4-fluorophenyl)(phenyl)methanone (6):



Colorless oil (27.7 mg, 69%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.80 (m, 2H), 7.81 – 7.73 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 8.6

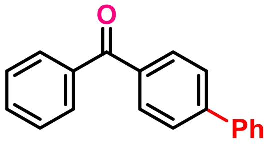
Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 165.5 (d, $J_{F\text{-}C}$ = 254.0 Hz), 137.6, 133.9 (d, $J_{F\text{-}C}$ = 3.0 Hz), 132.8 (d, $J_{F\text{-}C}$ = 9.3 Hz), 132.6, 130, 128.5, 115.6 (d, $J_{F\text{-}C}$ = 21.9 Hz).

(4-chlorophenyl)(phenyl)methanone (7):



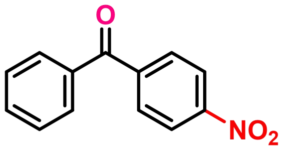
White solid (22.9 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 - 7.75 (m, 4H), 7.61 (t, J = 7.4 Hz, 1H), 7.51 - 7.45 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 139.0, 137.4, 136.0, 132.8, 131.6, 130.1, 128.8, 128.6.

[1,1'-biphenyl]-4-yl(phenyl)methanone (8):



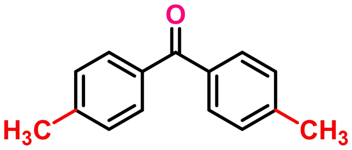
White solid (27.8 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.91 (d, J = 8.3 Hz, 2H), 7.85 (d, J = 7.7 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 7.2 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.50 (dd, J = 15.1, 7.7 Hz, 4H), 7.42 (t, J = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 145.3, 140.1, 137.9, 136.3, 132.5, 130.8, 130.1, 129.1, 128.4, 128.3, 127.4, 127.1.

(4-nitrophenyl)(phenyl)methanone (9):



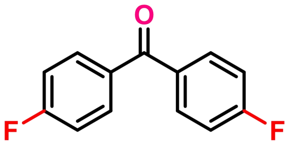
White solid (23.6 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 149.9, 143.0, 136.4, 133.6, 130.8, 130.2, 128.8, 123.6.

di-p-tolylmethanone (10):



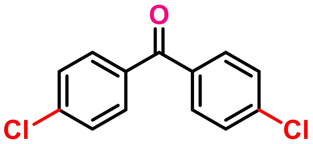
White solid (21.4 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1 Hz, 4H), 7.20 (d, J = 7.9 Hz, 4H), 2.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 143.0, 135.3, 130.3, 129.0, 21.8.

bis(4-fluorophenyl)methanone (11):



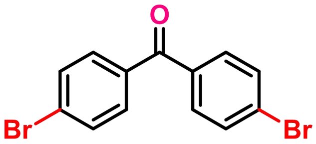
White solid (23.1 mg, 53%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 – 7.74 (m, 4H), 7.19 – 7.15 (m, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 194.0, 165.52 (d, $J_{F\text{-}C}$ = 254.4 Hz), 133.8 (d, $J_{F\text{-}C}$ = 3.0 Hz), 132.6 (d, $J_{F\text{-}C}$ = 9.2 Hz), 115.7 (d, $J_{F\text{-}C}$ = 21.9 Hz).

bis(4-chlorophenyl)methanone (12):



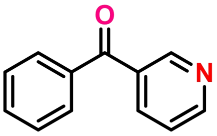
White solid (26.9 mg, 54%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, J = 8.5 Hz, 4H), 7.46 (d, J = 8.5 Hz, 4H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 194.4, 139.3, 135.6, 131.4, 128.9.

bis(4-bromophenyl)methanone (13):



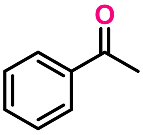
White solid (33.9 mg, 50%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66 - 7.64 (m, 8H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 194.7, 136.0, 131.9, 131.6, 128.0.

phenyl(pyridin-3-yl)methanone (14):



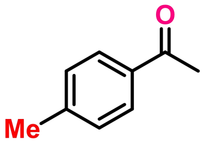
Colorless oil (6.9 mg, 19%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.98 (d, J = 1.7 Hz, 1H), 8.79 (dd, J = 4.8, 1.6 Hz, 1H), 8.10 (dt, J = 7.9, 1.9 Hz, 1H), 7.88 – 7.73 (m, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.56 – 7.40 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 195.0, 152.9, 151.0, 137.3, 136.8, 133.3, 131.1, 130.1, 128.7, 123.5.

Acetophenone (15):



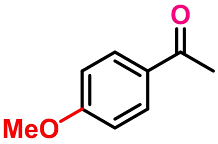
Colorless oil (16.3 mg, 68%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 198.3, 137.2, 133.2, 128.7, 128.4, 26.72.

1-(*p*-tolyl)ethan-1-one (16)



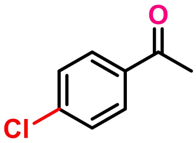
Colorless oil (16.0 mg, 60%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 2.59 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 198.0, 144.0, 134.8, 129.4, 128.6, 26.6, 21.7.

1-(4-methoxyphenyl)ethan-1-one (17):



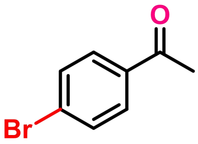
White solid (23.4 mg, 78%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 196.9, 163.6, 130.7, 130.4, 113.8, 55.6, 26.4.

1-(4-chlorophenyl)ethan-1-one (18):



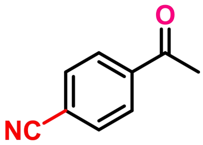
Colorless oil (15.4 mg, 50%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 196.9, 139.7, 135.6, 129.8, 129.0, 26.7.

1-(4-bromophenyl)ethan-1-one (19):



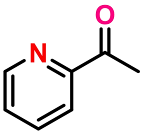
White solid (20.1 mg, 50%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 197.1, 135.9, 132.0, 129.9, 128.4, 26.6.

4-acetylbenzonitrile (20):



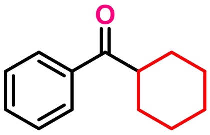
Colorless oil (15.2 mg, 53%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 196.6, 140.0, 132.6, 128.8, 118.0, 116.5, 26.8

1-(pyridin-2-yl)ethan-1-one (21):



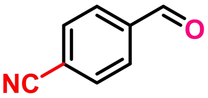
Colorless oil (9.9mg, 41%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.65 (d, *J* = 4.2 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.64 – 7.32 (m, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 200.2, 153.7, 149.1, 136.9, 127.2, 121.7, 25.9.

cyclohexyl(phenyl)methanone (22):



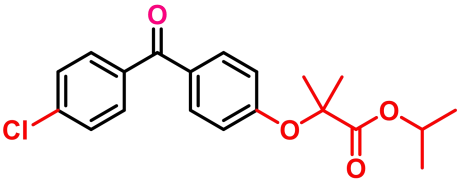
Colorless oil (16.5 mg, 44%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 3.39 – 3.17 (m, 1H), 1.87 (t, *J* = 15.3 Hz, 4H), 1.56 – 1.37 (m, 4H), 1.37 – 1.16 (m, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 204.0, 136.5, 132.8, 128.7, 128.4, 45.7, 29.5, 26.1, 26.0.

4-formylbenzonitrile (23):



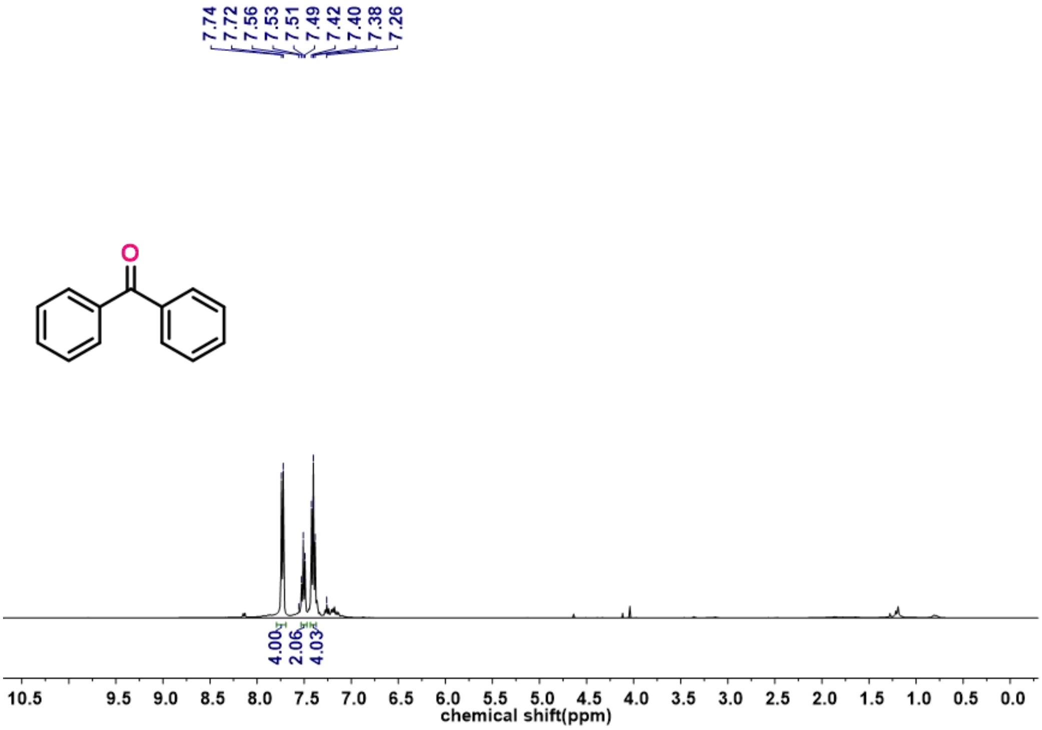
Colorless oil (12.3 mg, 47%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 10.09 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 2H), 7.85 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 190.7, 138.9, 133.0, 130.0, 117.8, 117.7.

isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (24):

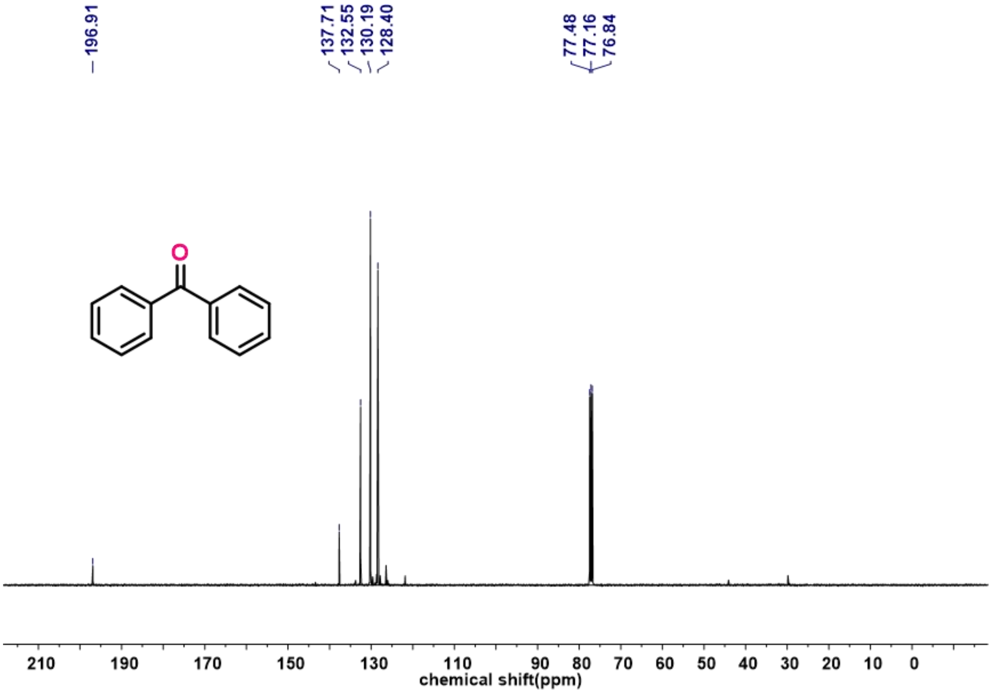


White solid (30.9 mg, 43%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.74 - 7.68 (m, 4H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.27 – 4.86 (m, 1H), 1.66 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 194.4, 173.2, 159.9, 138.5, 136.5, 132.1, 131.3, 130.3, 128.7, 117.4, 79.5, 69.5, 25.5, 21.6.

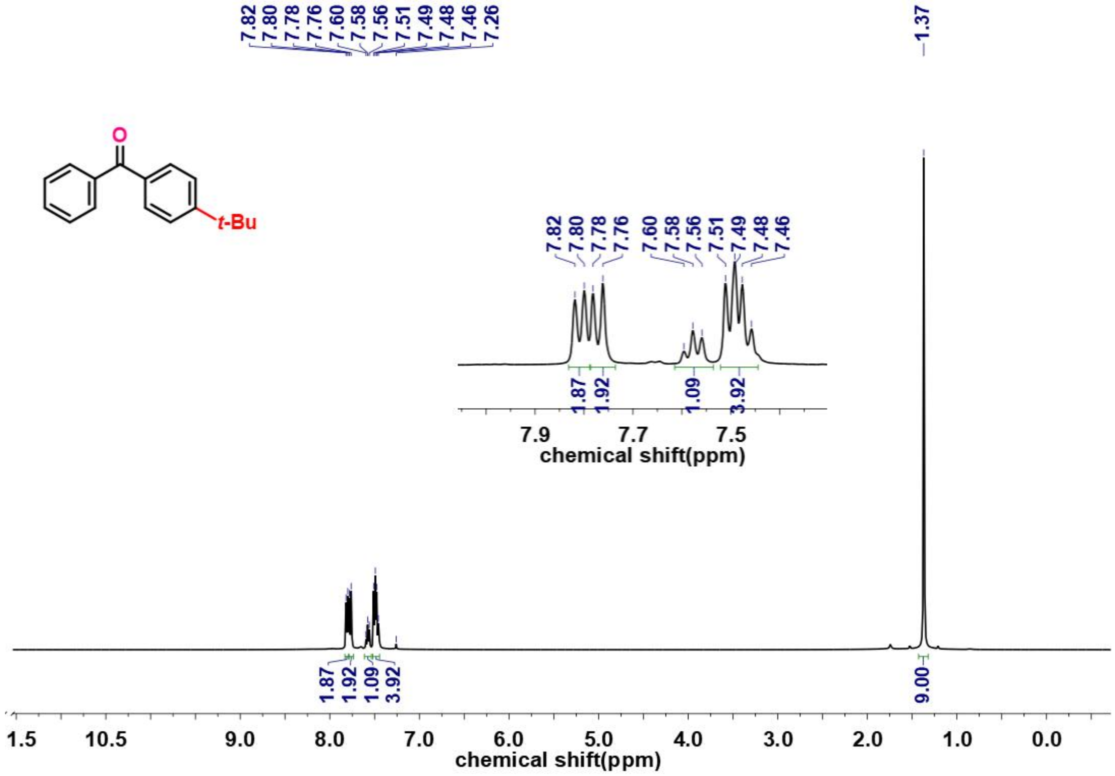
7. Copies of NMR Spectra of Compounds 1-24



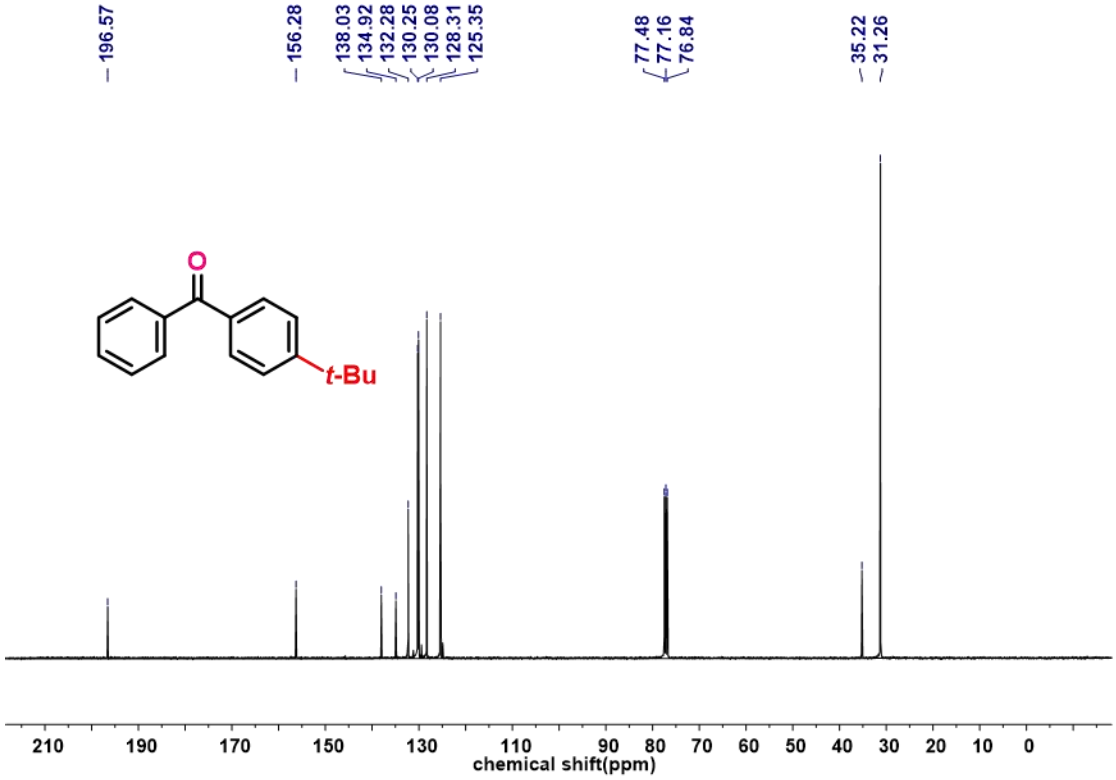
Benzophenone (1): ^{1}H NMR (400 MHz, CDCl$_3$)



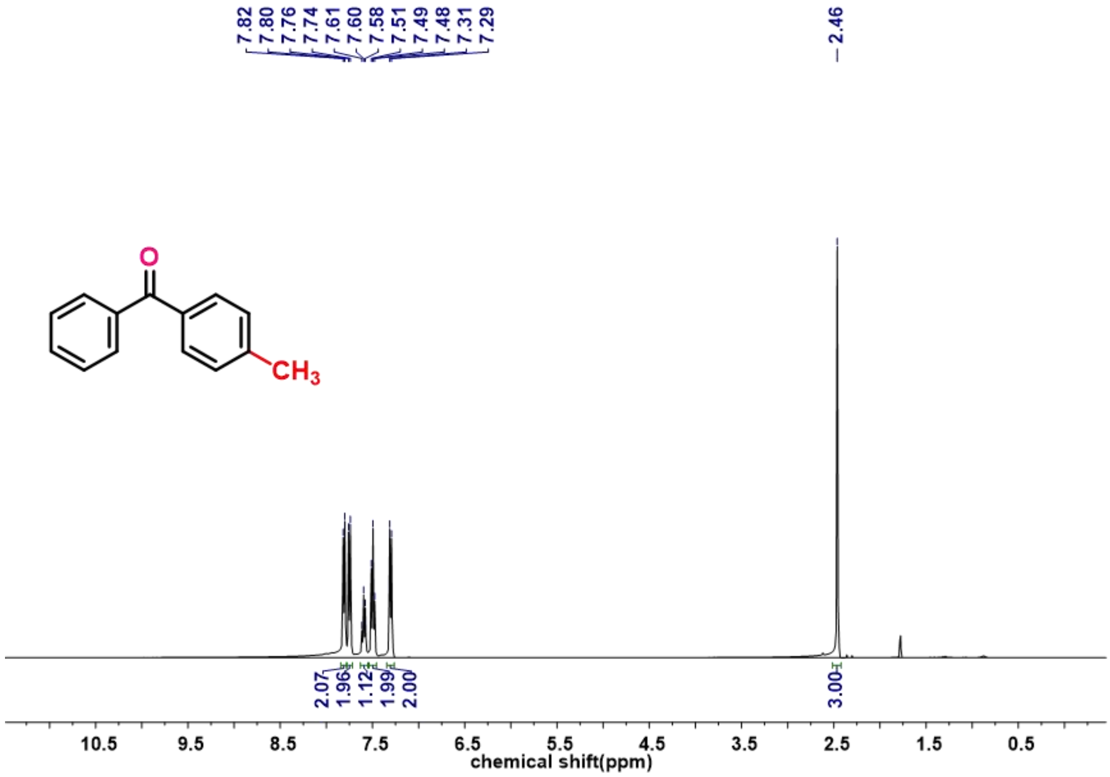
Benzophenone (1): ^{13}C NMR (101 MHz, CDCl$_3$)



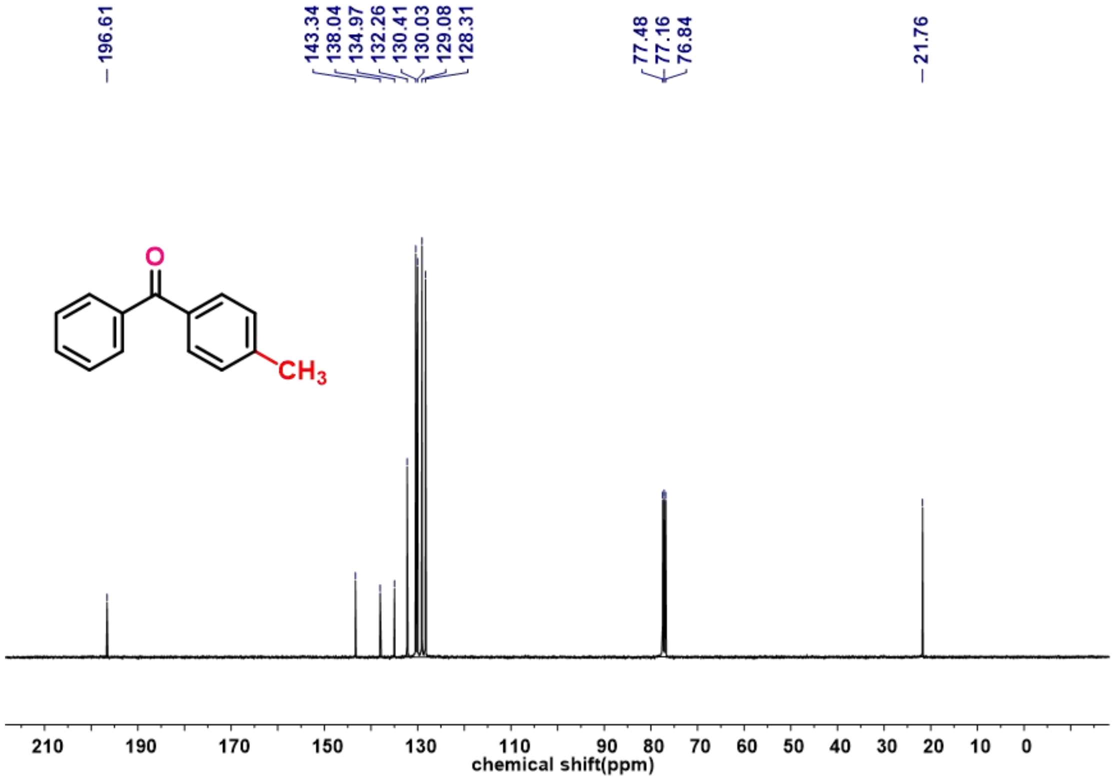
(4-(tert-butyl)phenyl)(phenyl)methanone (2): ^{1}H NMR (400 MHz, $CDCl_3$)



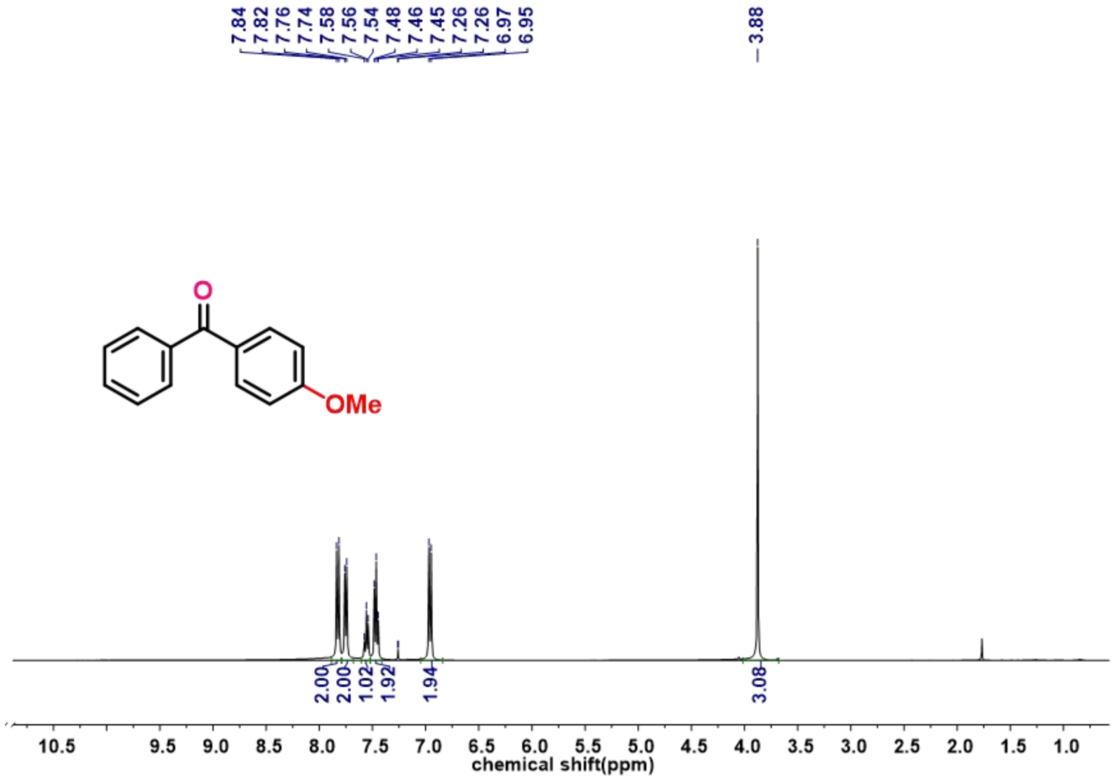
(4-(tert-butyl)phenyl)(phenyl)methanone (2): ^{13}C NMR (101 MHz, $CDCl_3$)



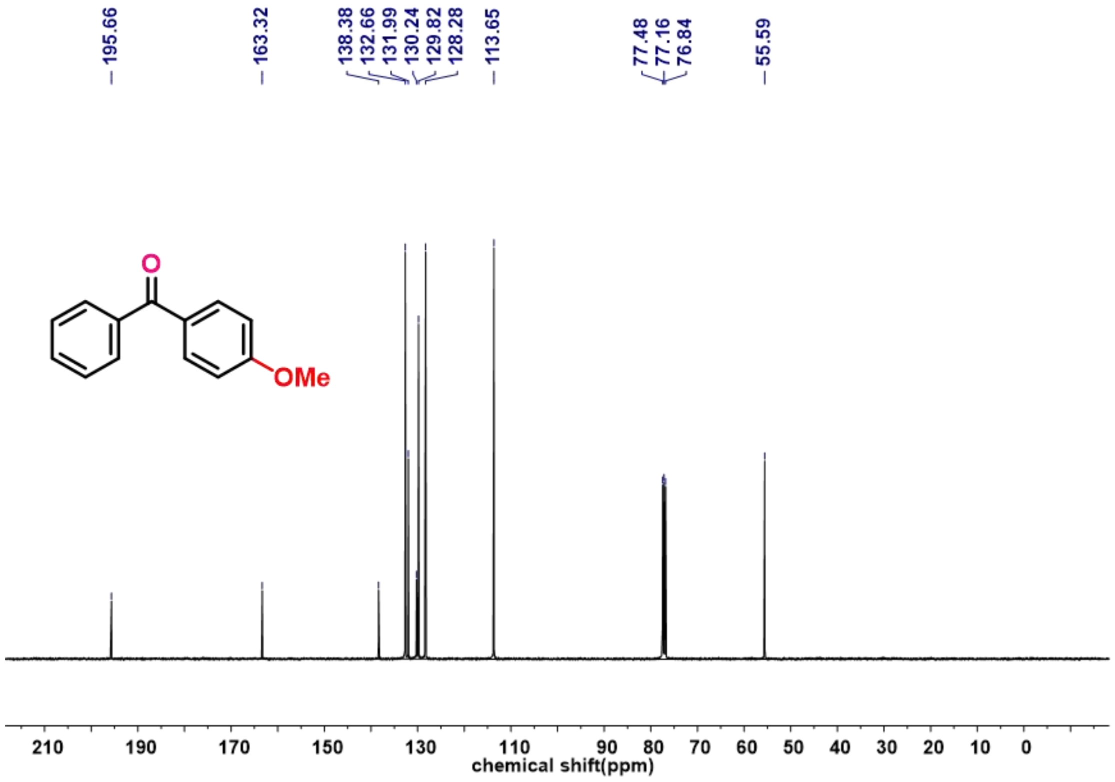
Phenyl(p-tolyl)methanone (3): ^{1}H NMR (400 MHz, $CDCl_3$)



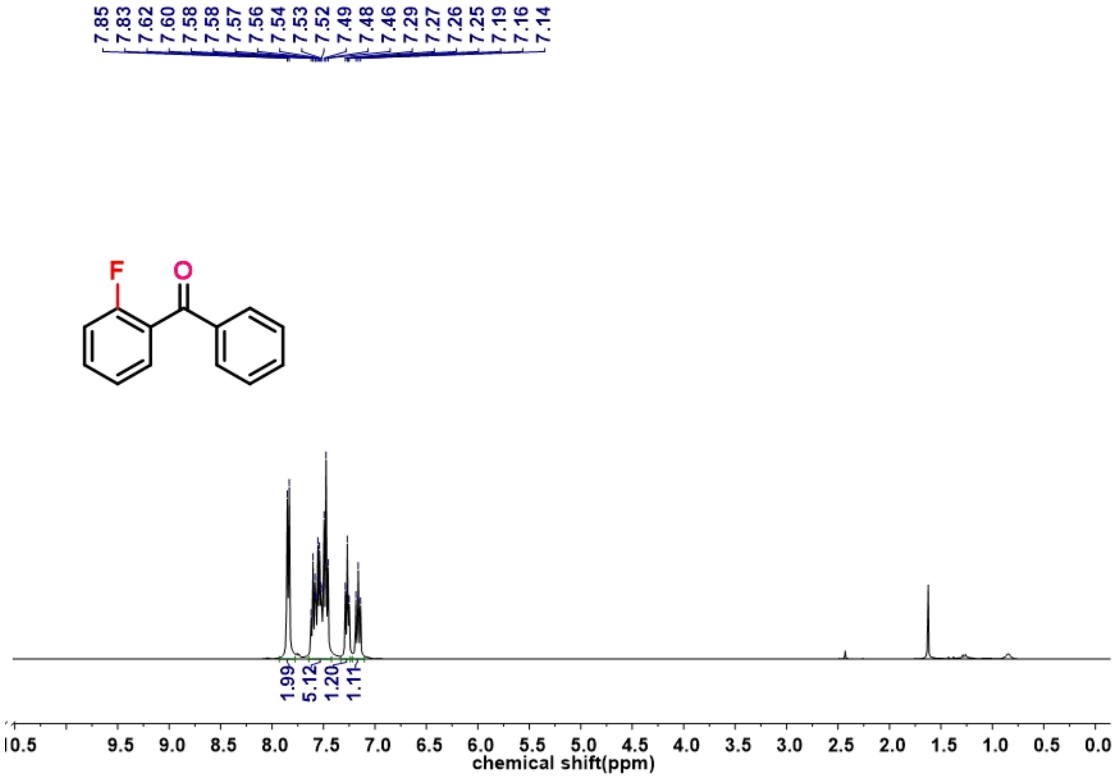
Phenyl(p-tolyl)methanone (3): ^{13}C NMR (101 MHz, $CDCl_3$)



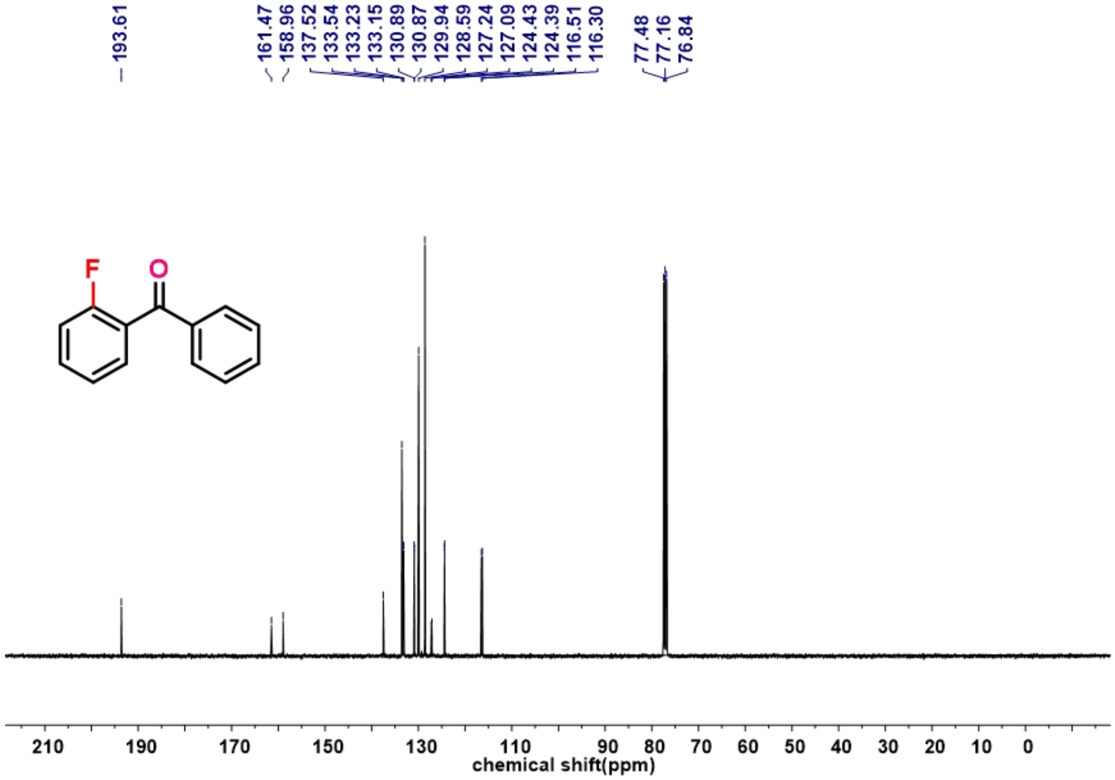
(4-methoxyphenyl)(phenyl)methanone (4): ^{1}H NMR (400 MHz, $CDCl_3$)



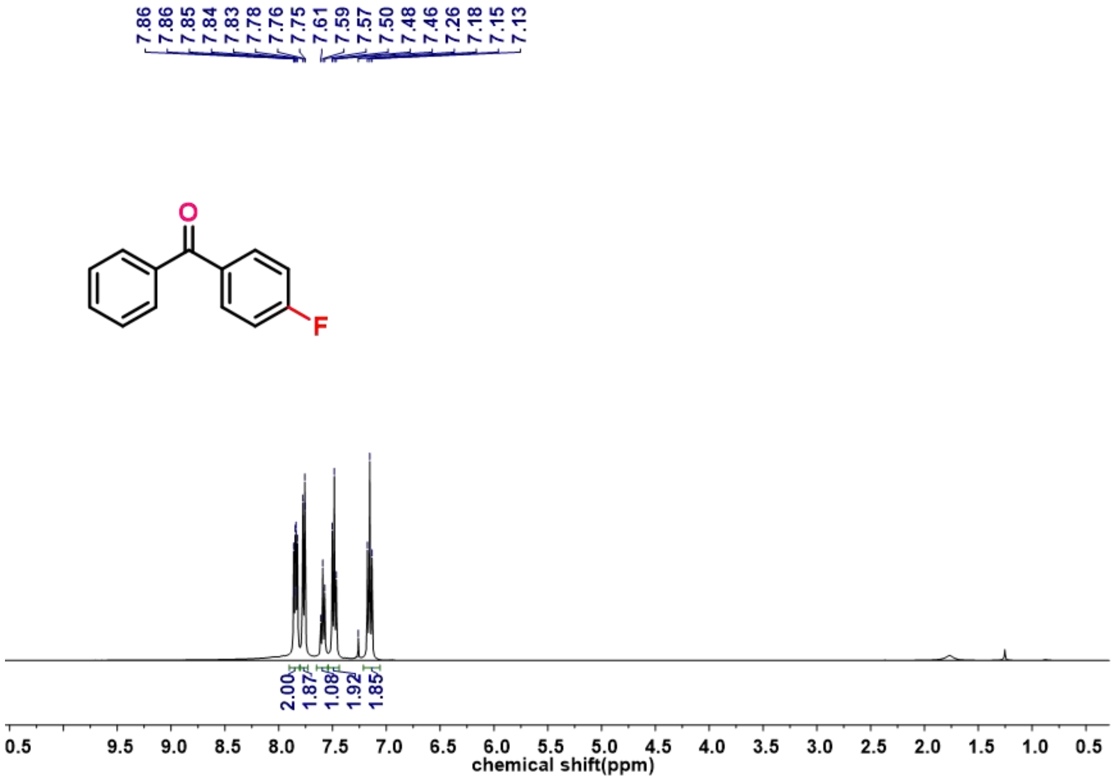
(4-methoxyphenyl)(phenyl)methanone (4):^{13}C NMR (101 MHz, $CDCl_3$)



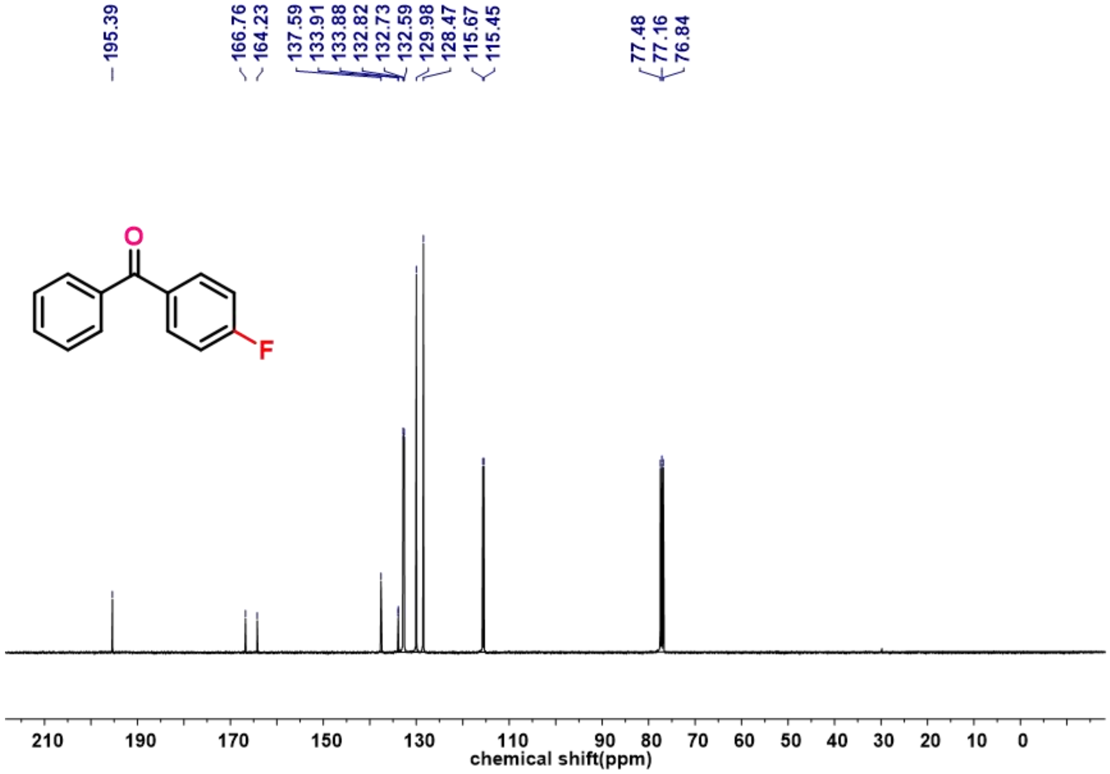
(2-fluorophenyl)(phenyl)methanone (5):^{1}H NMR (400 MHz, $CDCl_3$)



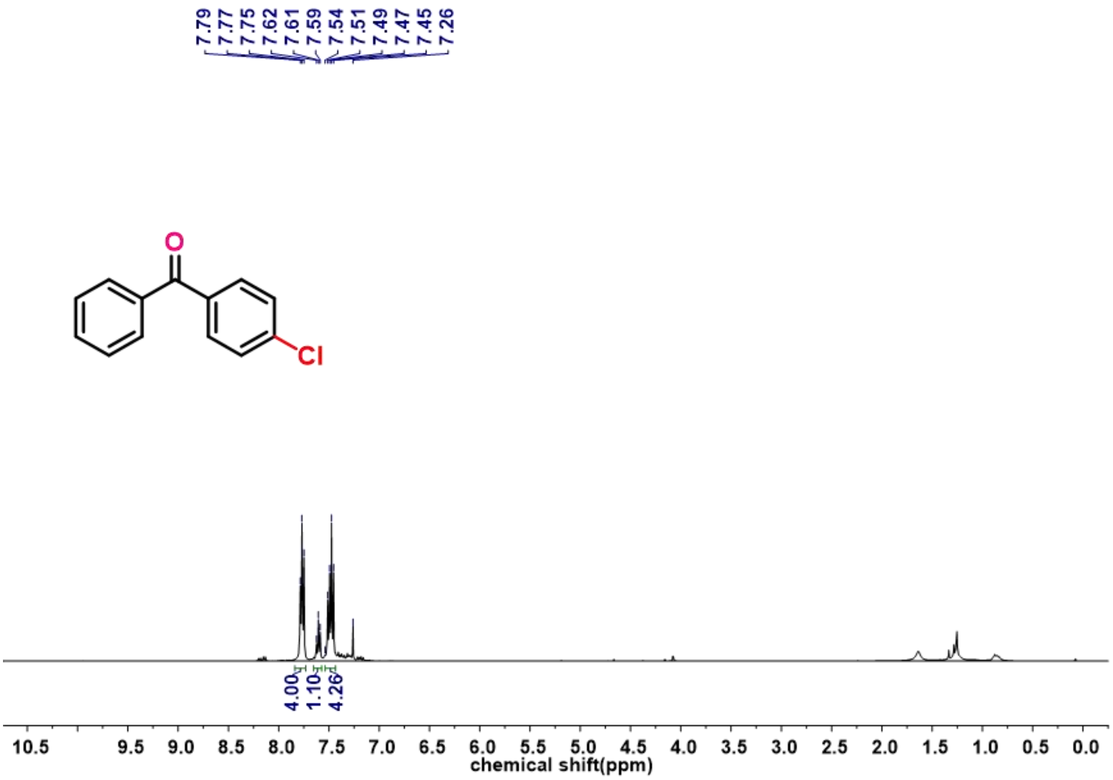
(2-fluorophenyl)(phenyl)methanone (5): ^{13}C NMR (101 MHz, $CDCl_3$)



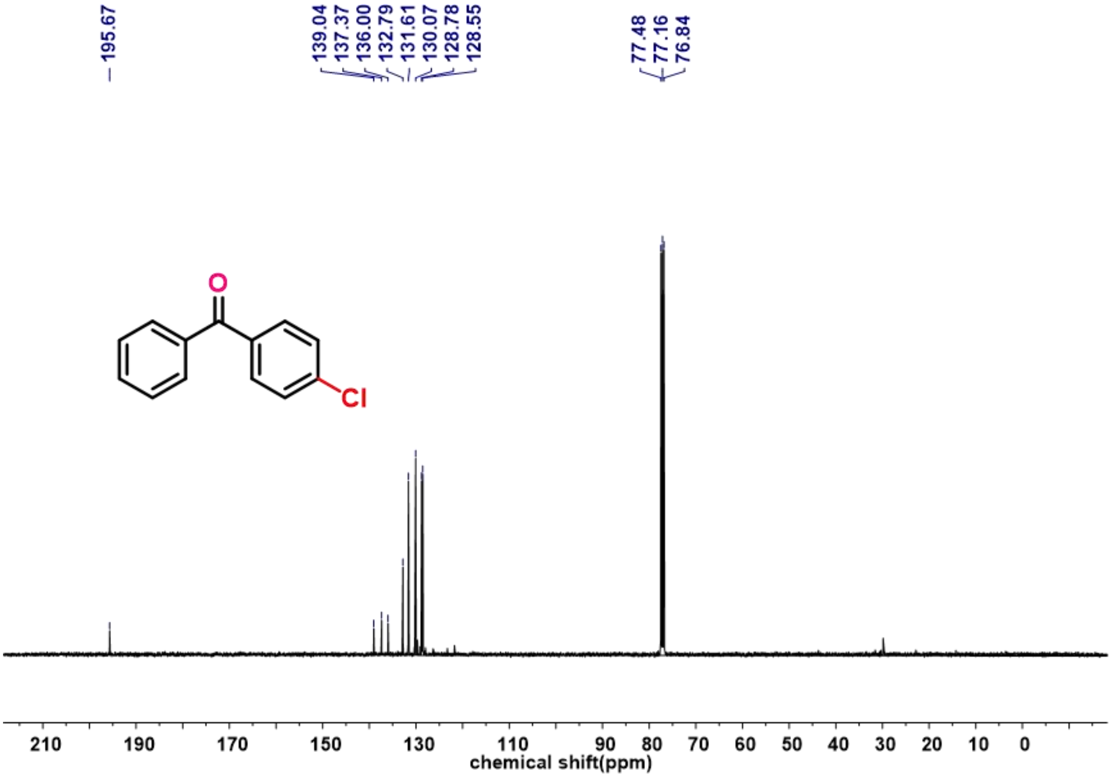
(4-fluorophenyl)(phenyl)methanone (6):^{1}H NMR (400 MHz, $CDCl_3$)



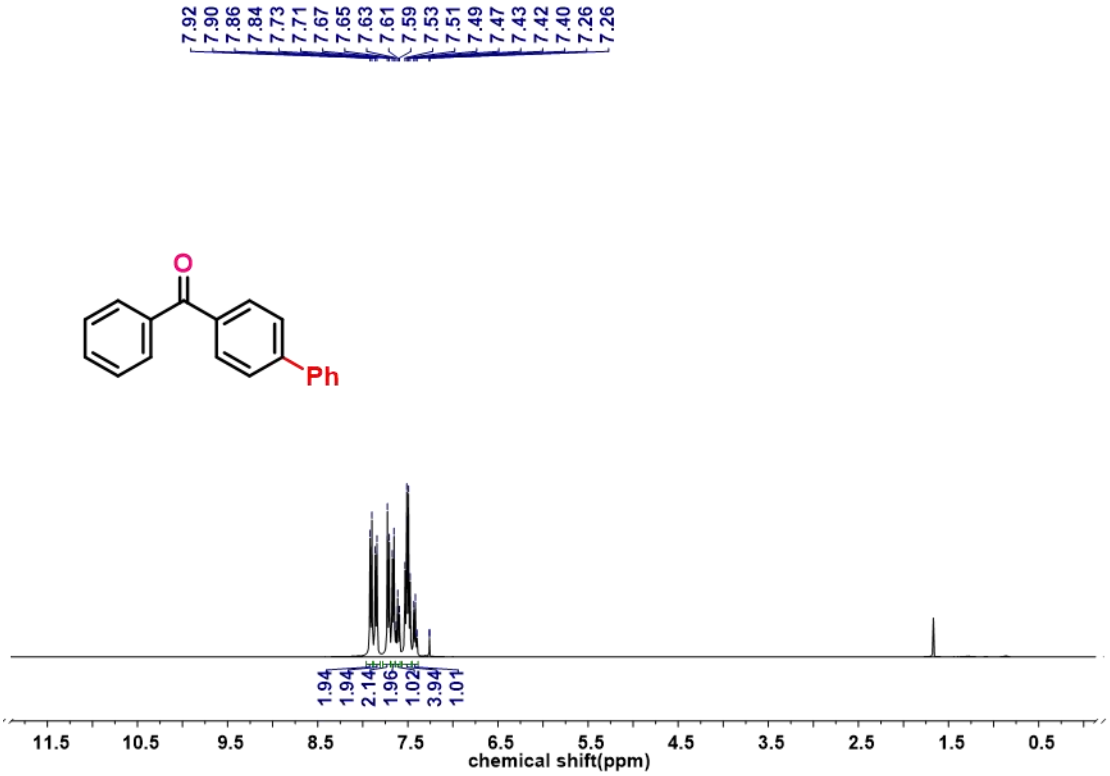
(4-fluorophenyl)(phenyl)methanone (6): ^{13}C NMR (101 MHz, $CDCl_3$)



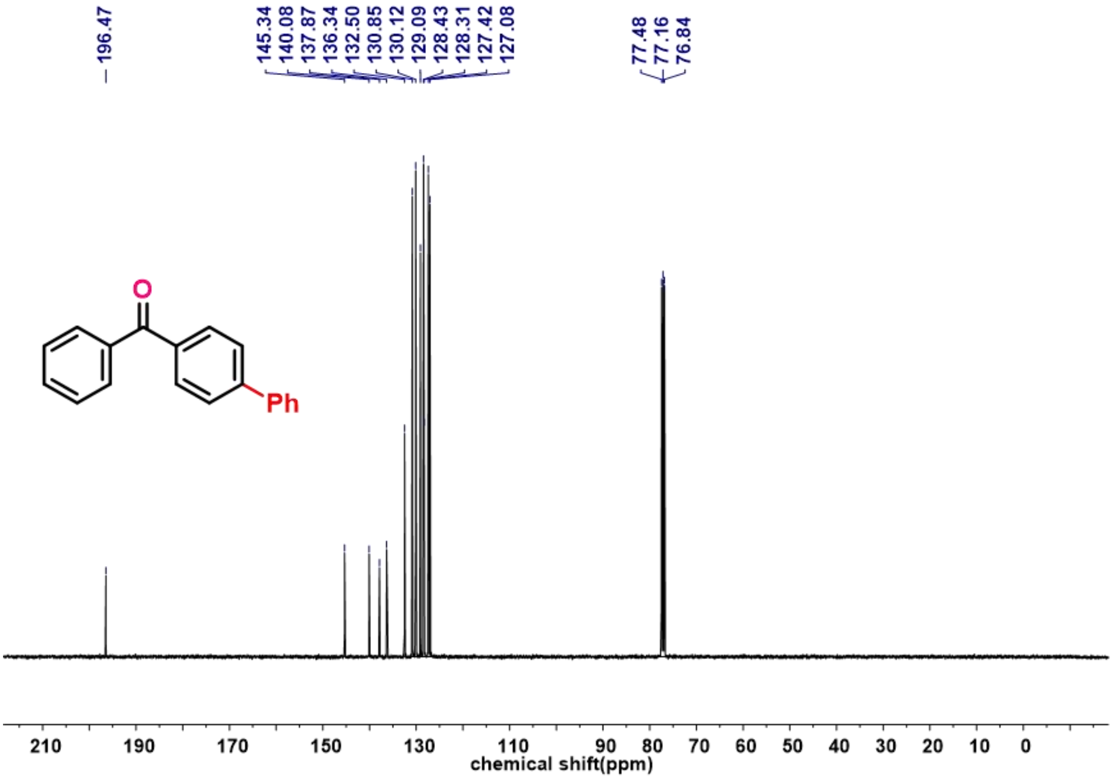
(4-chlorophenyl)(phenyl)methanone (7):^{1}H NMR (400 MHz, $CDCl_3$)



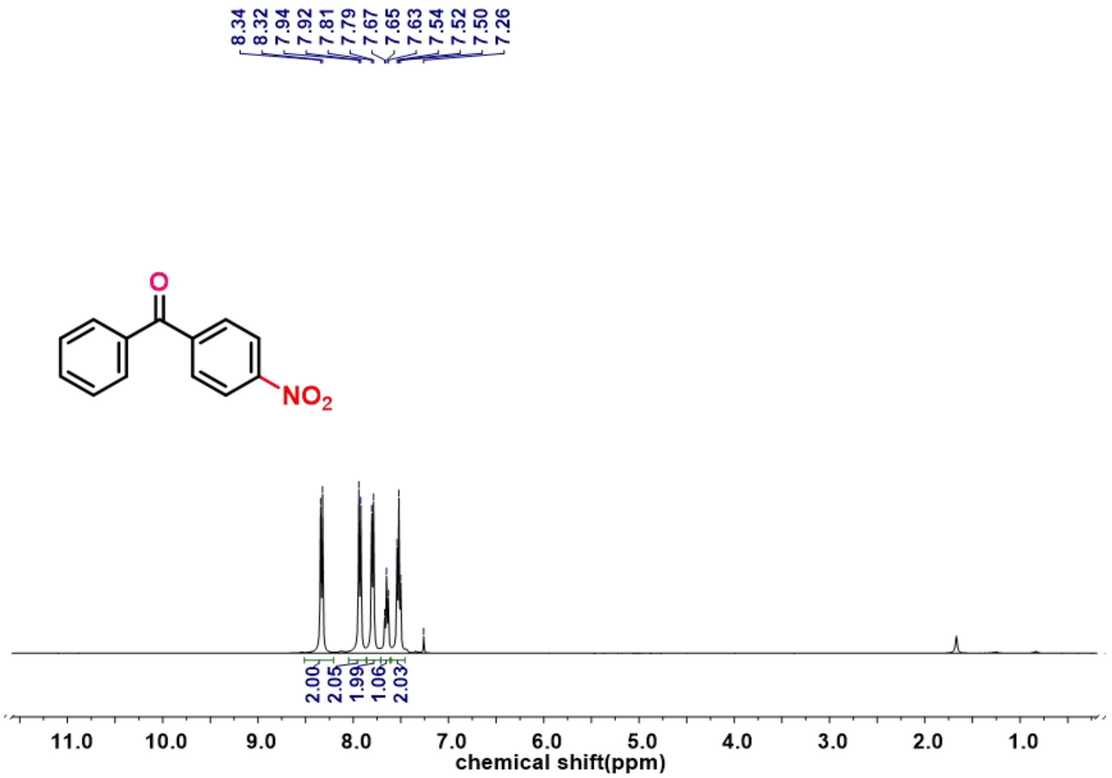
(4-chlorophenyl)(phenyl)methanone (7): ^{13}C NMR (101 MHz, $CDCl_3$)



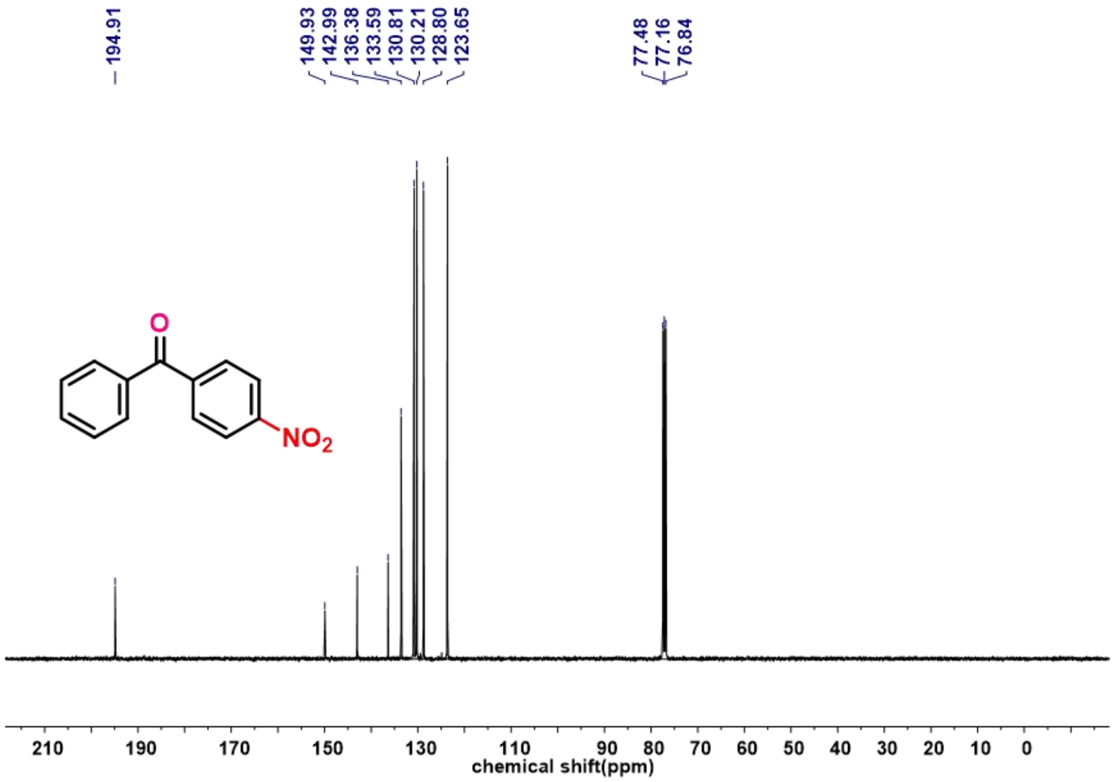
[1,1'-biphenyl]-4-yl(phenyl)methanone (8): ^{1}H NMR (400 MHz, CDCl$_3$)



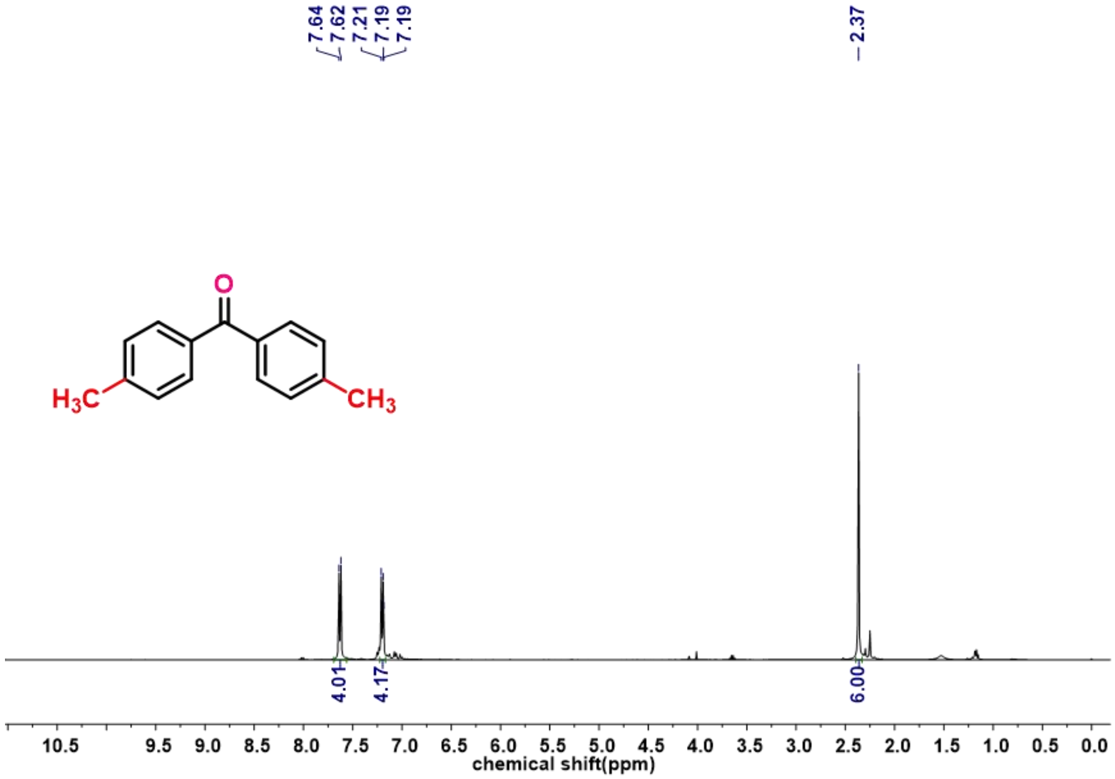
[1,1'-biphenyl]-4-yl(phenyl)methanone (8): ^{13}C NMR (101 MHz, CDCl$_3$)



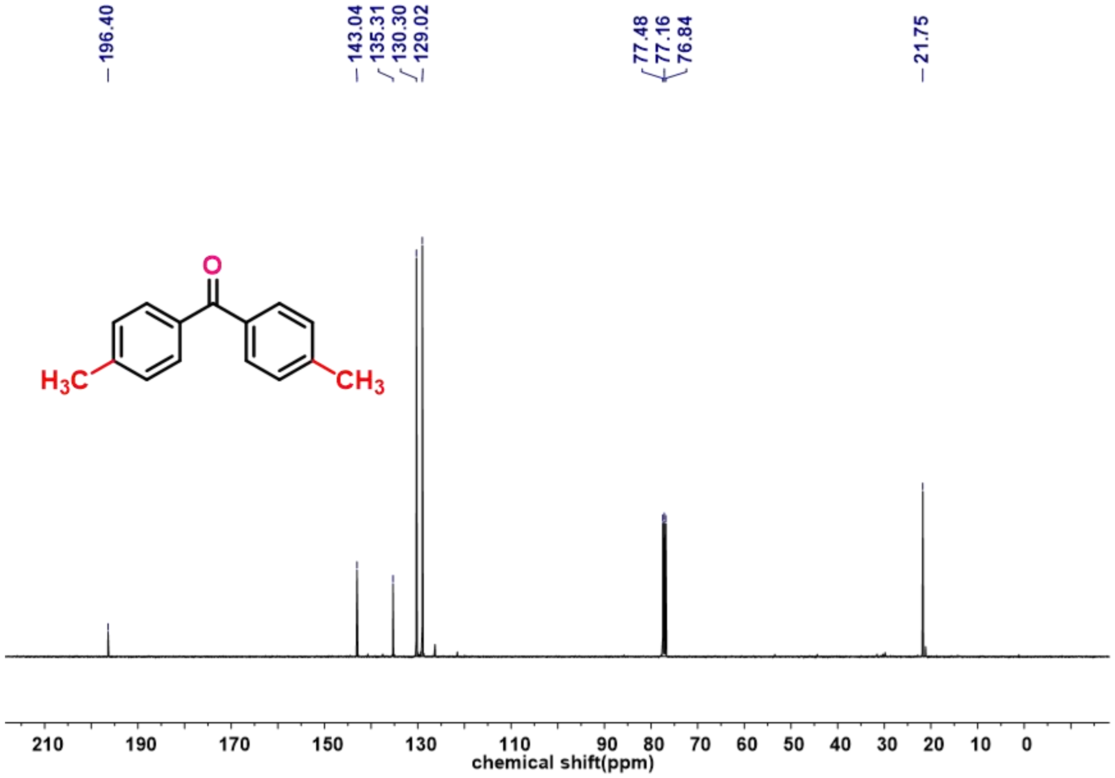
(4-nitrophenyl)(phenyl)methanone (9):^{1}H NMR (400 MHz, $CDCl_3$)



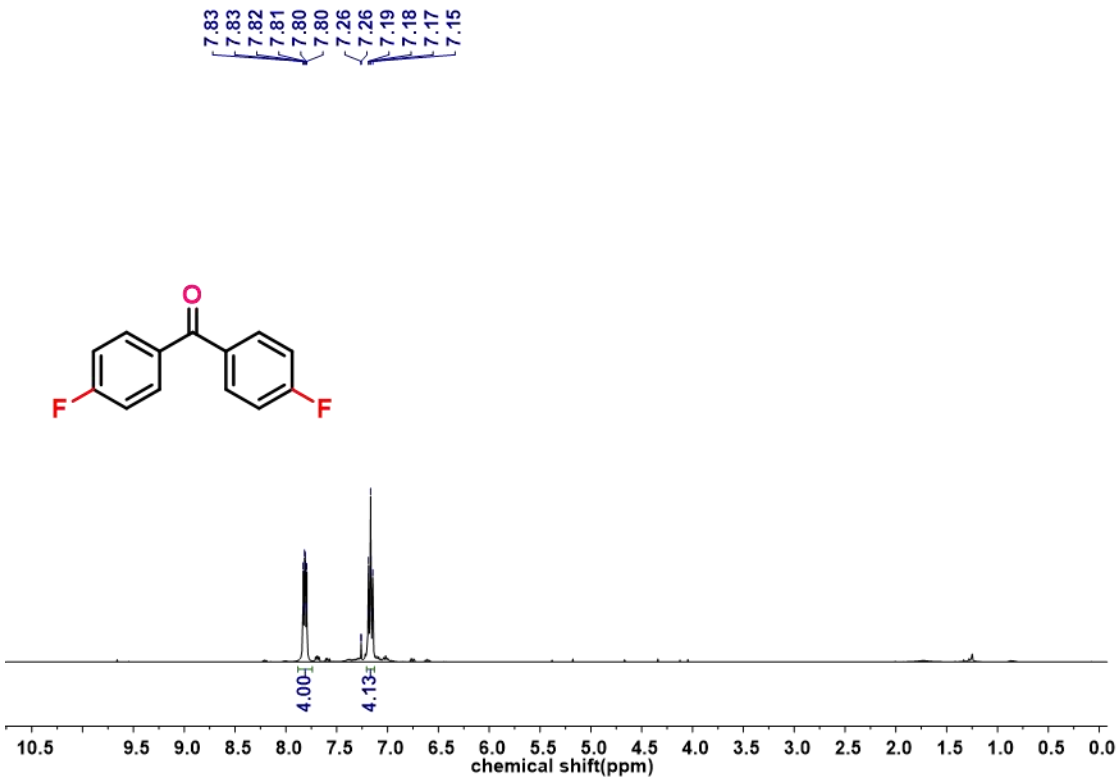
(4-nitrophenyl)(phenyl)methanone (9):^{13}C NMR (101 MHz, $CDCl_3$)



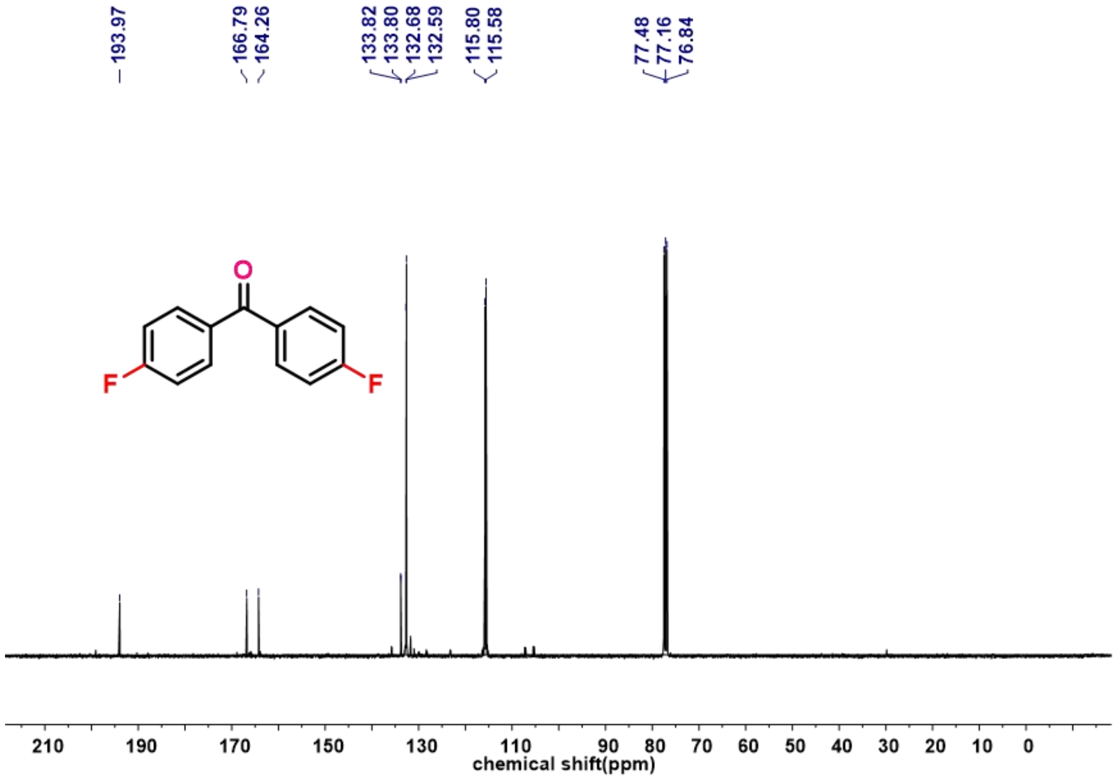
di-*p*-tolylmethanone (10):^{1}H NMR (400 MHz, $CDCl_3$)



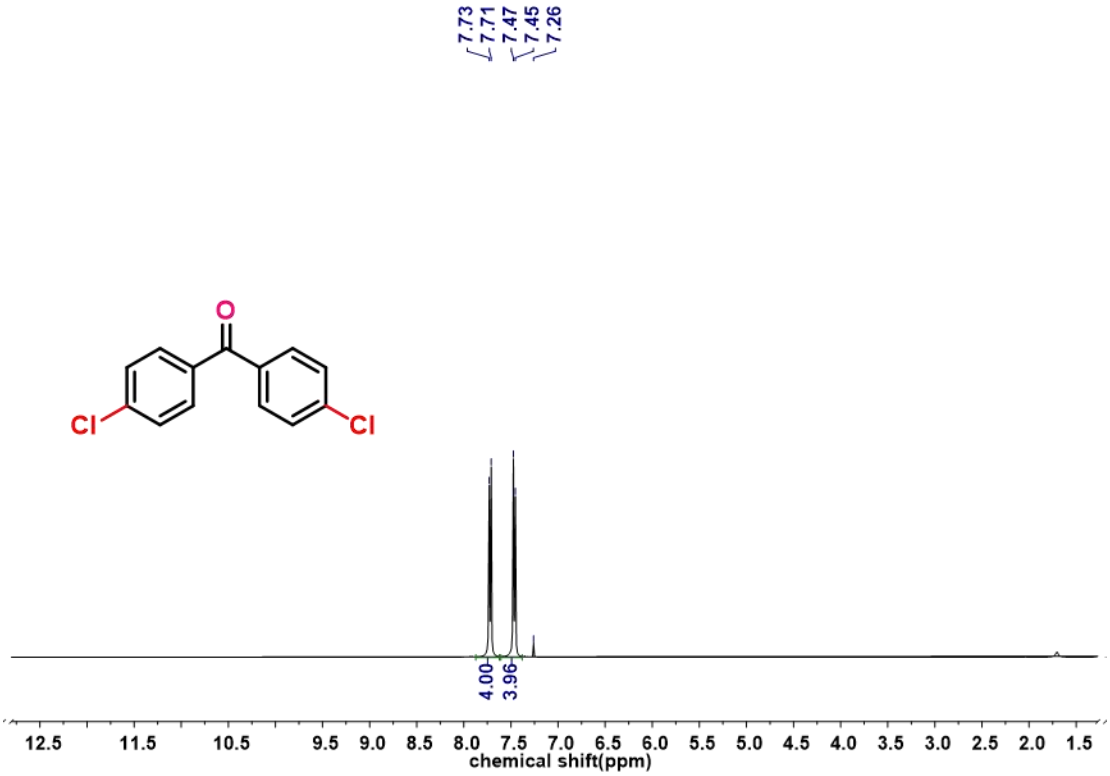
di-*p*-tolylmethanone (10):^{13}C NMR (101 MHz, $CDCl_3$)



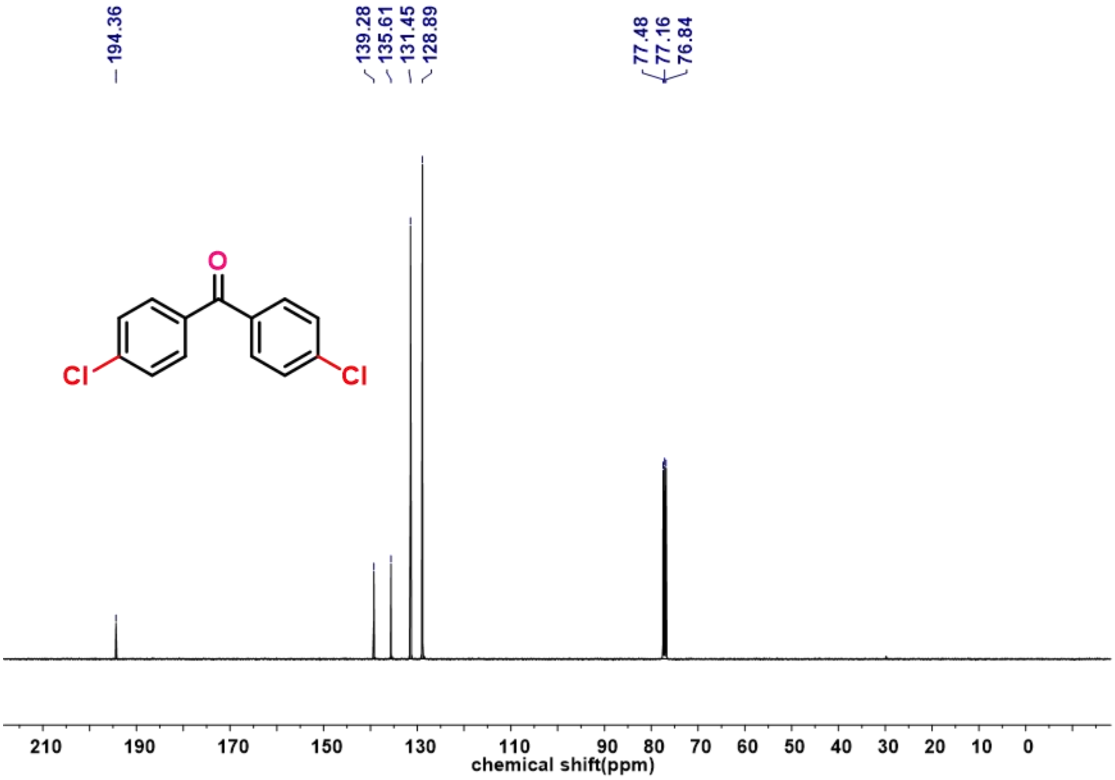
bis(4-fluorophenyl)methanone (11):^{1}H NMR (400 MHz, $CDCl_3$)



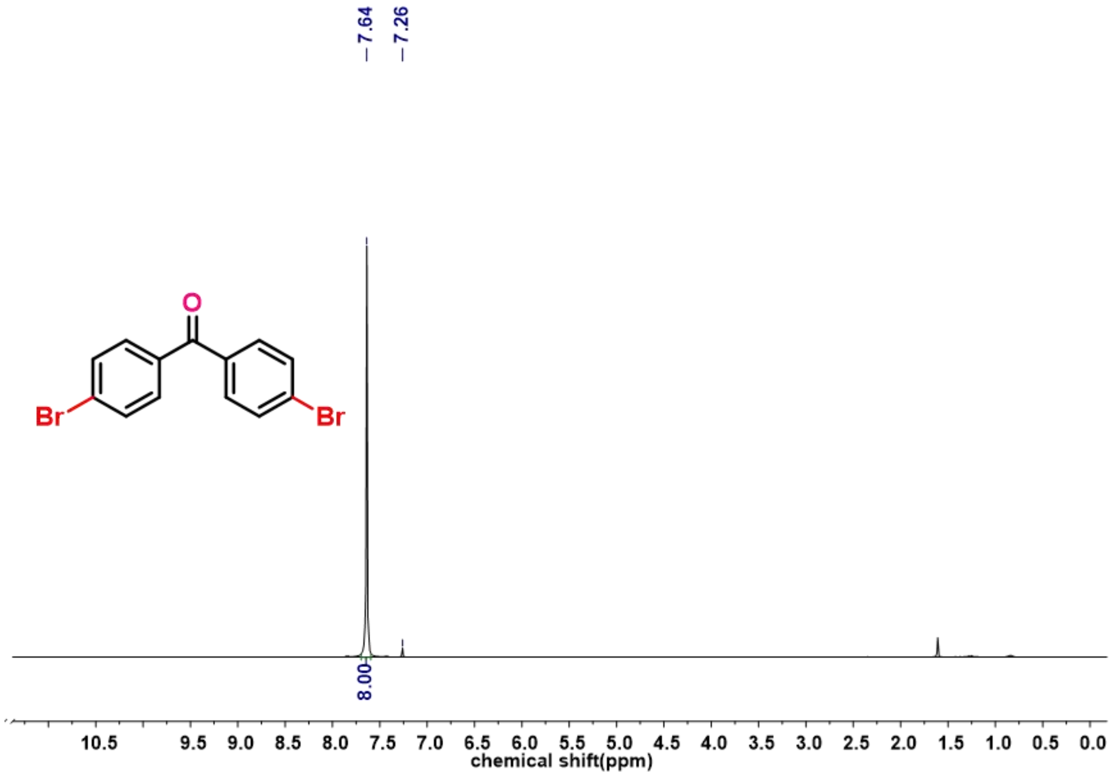
bis(4-fluorophenyl)methanone (11):^{13}C NMR (101 MHz, $CDCl_3$)



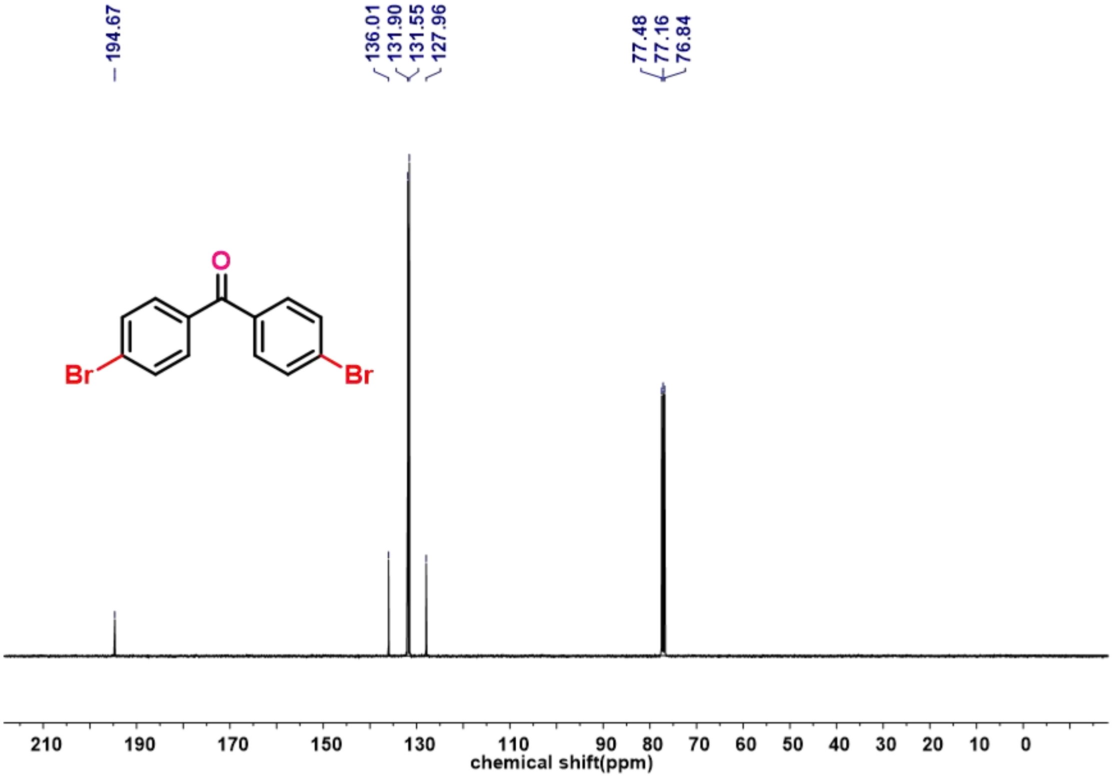
bis(4-chlorophenyl)methanone (12): ^{1}H NMR (400 MHz, $CDCl_3$)



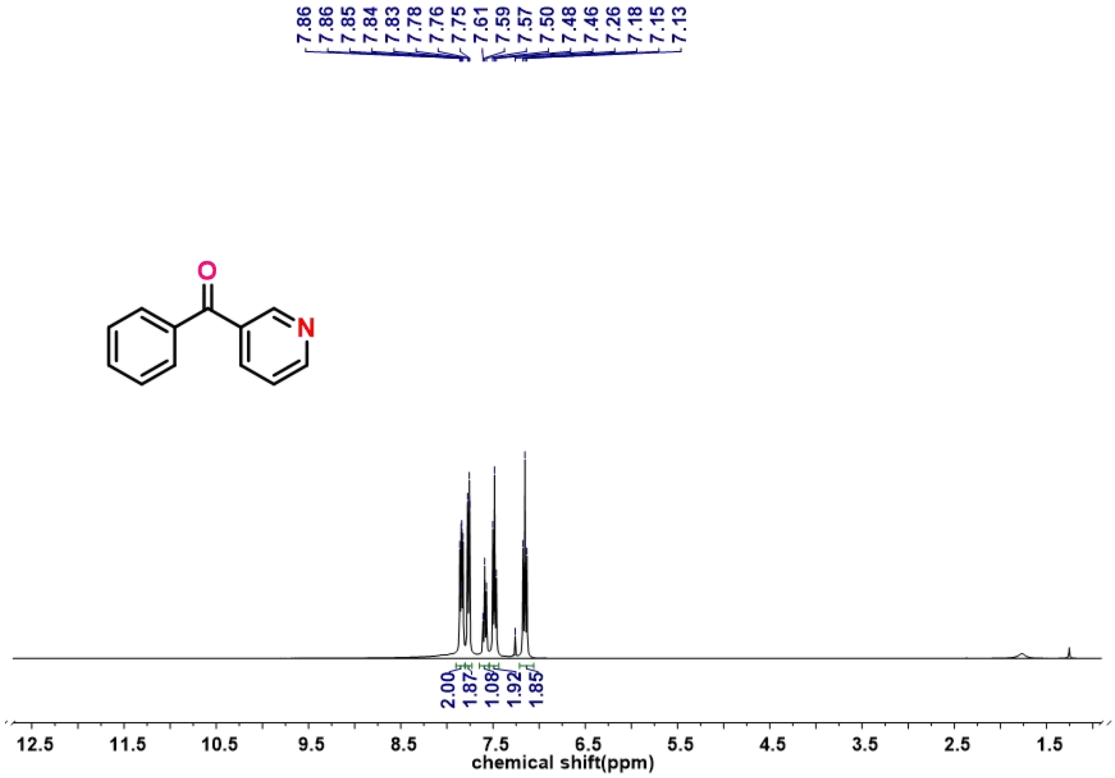
bis(4-chlorophenyl)methanone (12): ^{13}C NMR (101 MHz, $CDCl_3$)



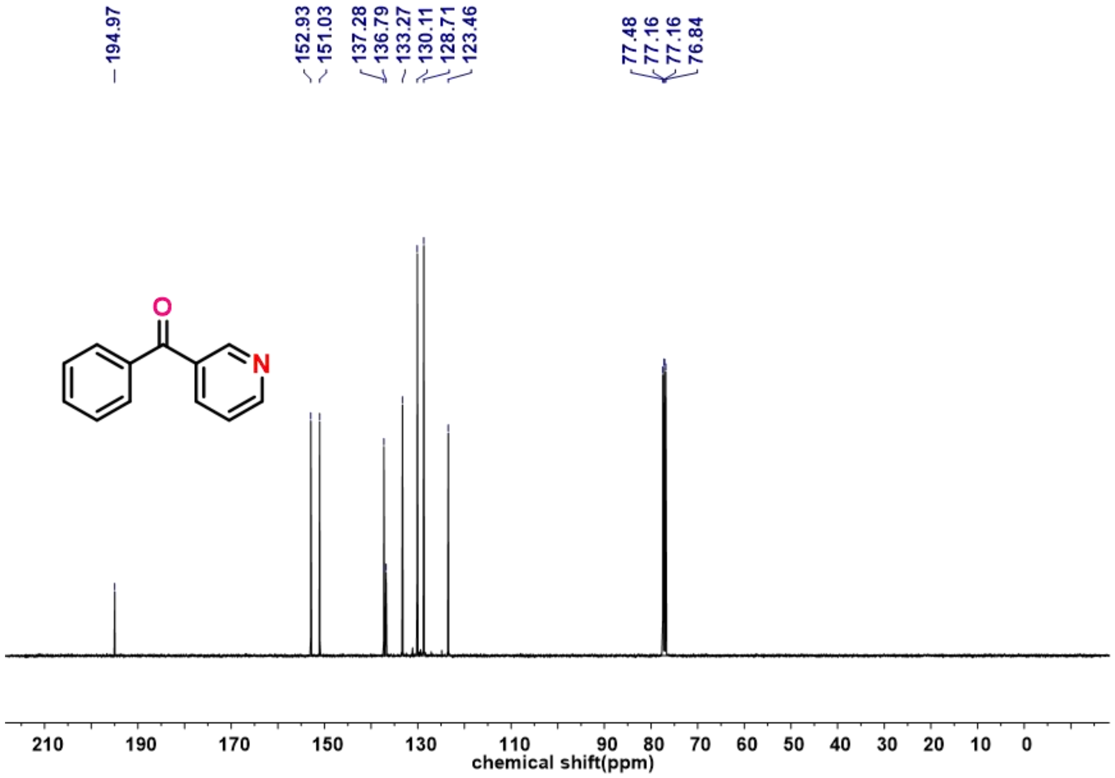
bis(4-bromophenyl)methanone (13):^{1}H NMR (400 MHz, CDCl$_3$)



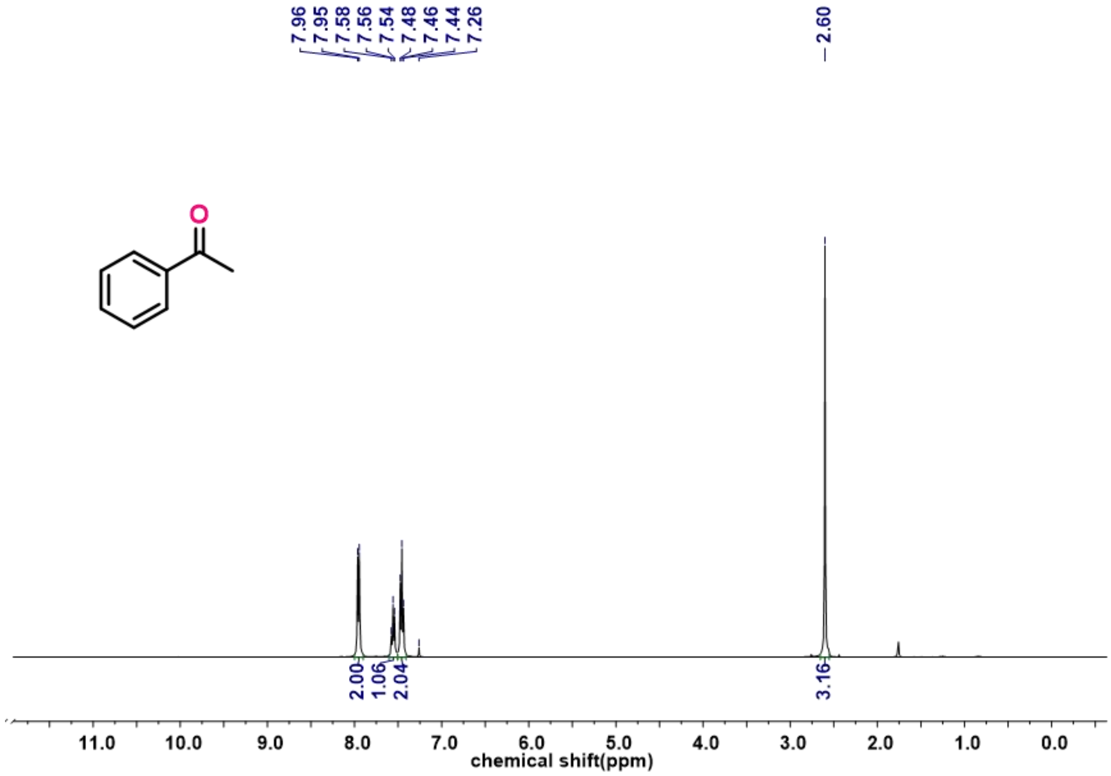
bis(4-bromophenyl)methanone (13): ^{13}C NMR (101MHz, CDCl$_3$)



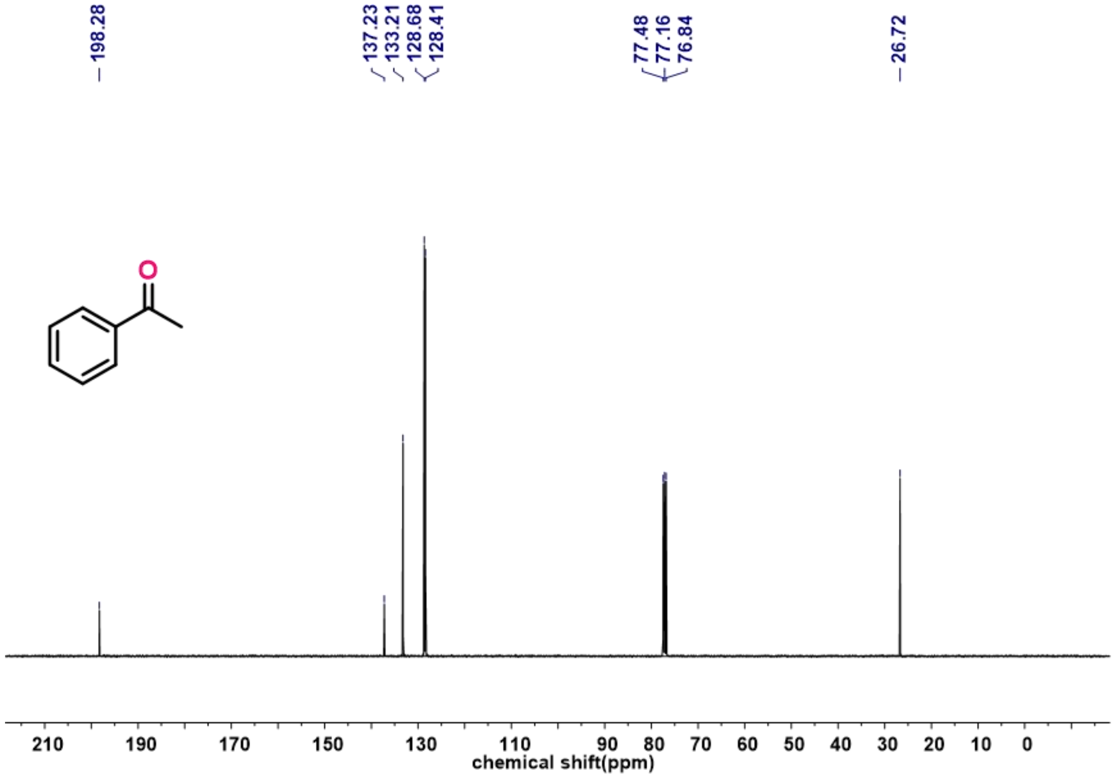
phenyl(pyridin-3-yl)methanone (14): ^{1}H NMR (400 MHz, CDCl$_3$)



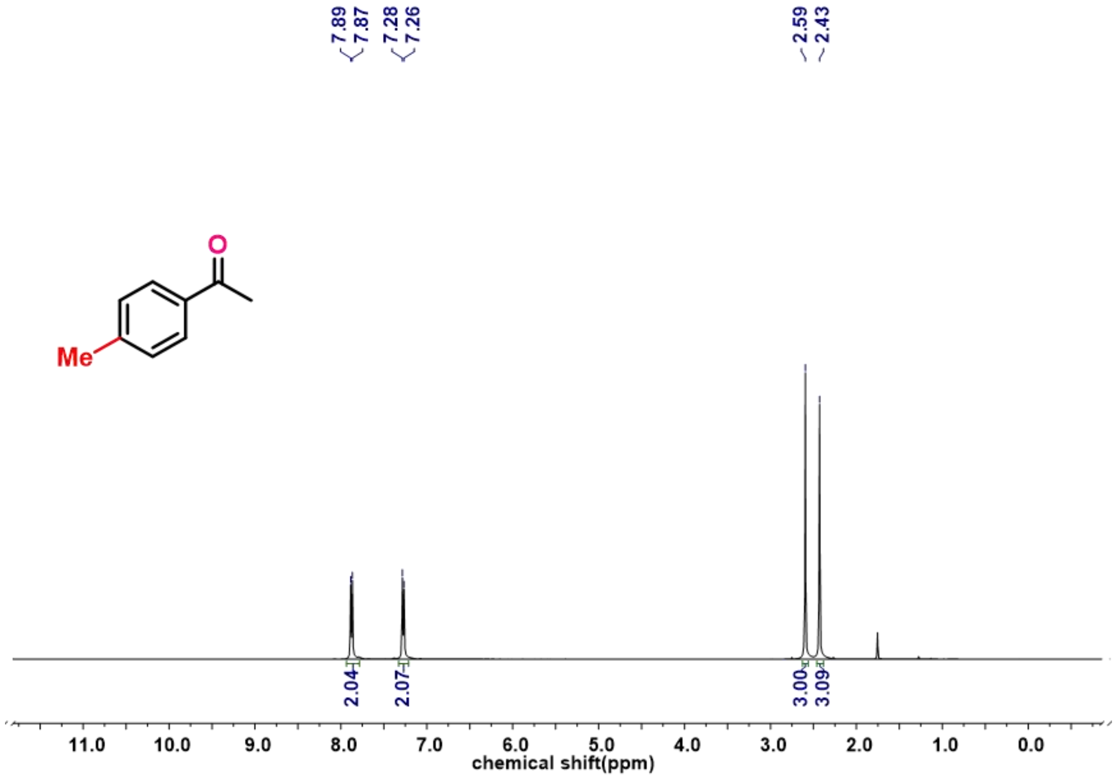
Phenyl(pyridin-3-yl)methanone (14): ^{13}C NMR (101 MHz, CDCl$_3$)



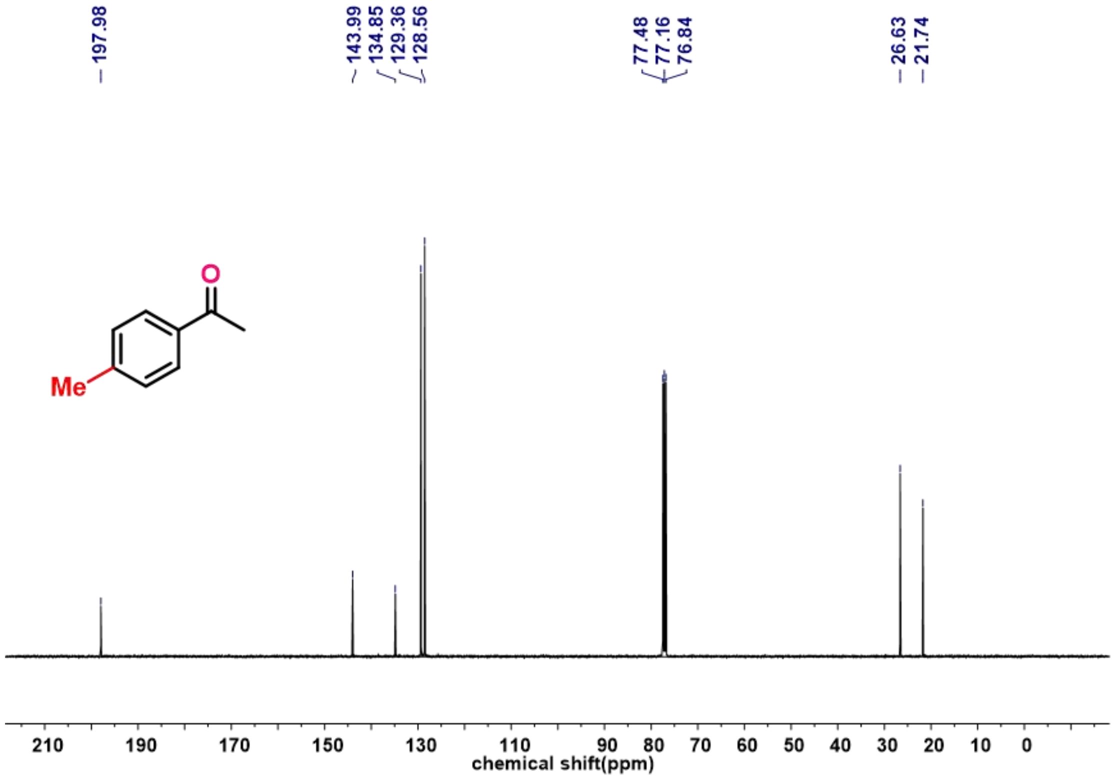
Acetophenone (15):^{1}H NMR (400 MHz, $CDCl_3$)



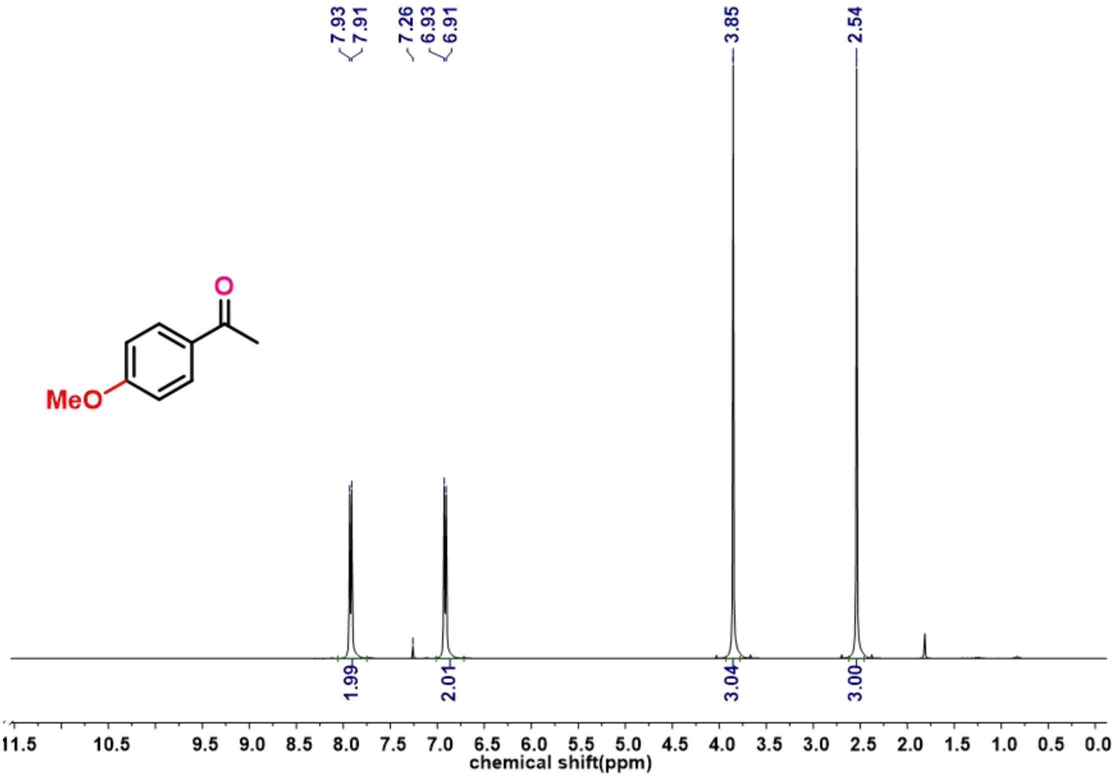
Acetophenone (15):^{13}C NMR (101 MHz, $CDCl_3$)



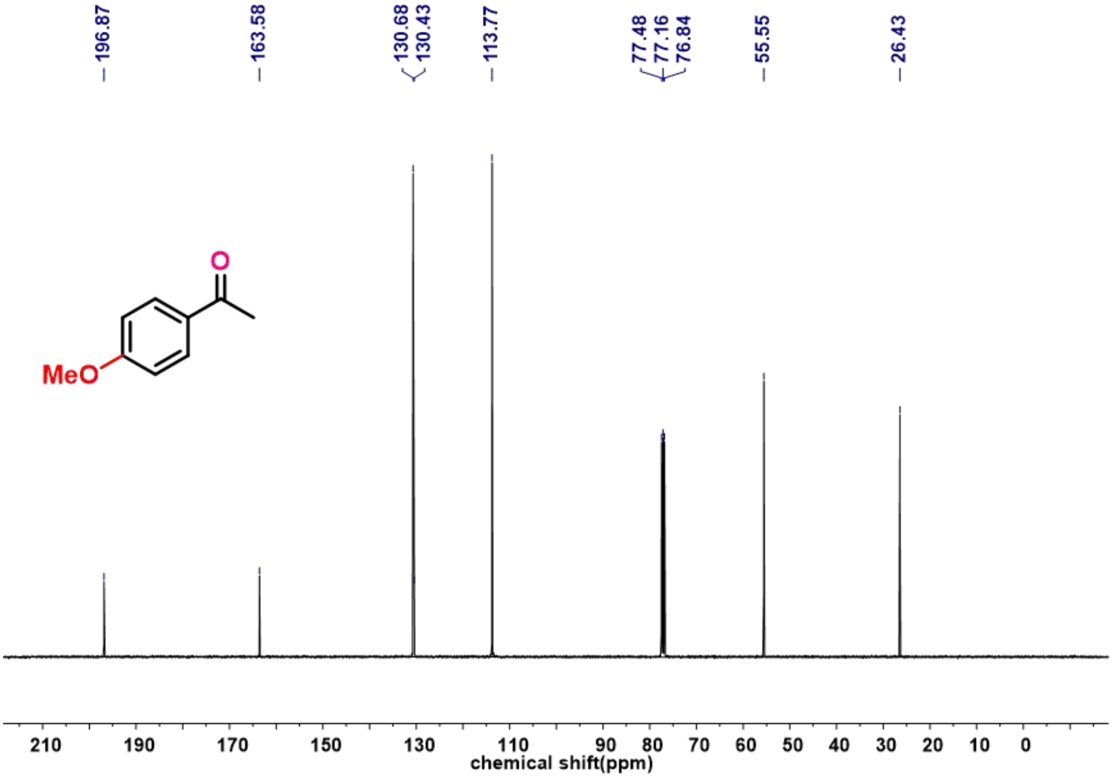
1-(*p*-tolyl)ethan-1-one (16):^{1}H NMR (400 MHz, $CDCl_3$)



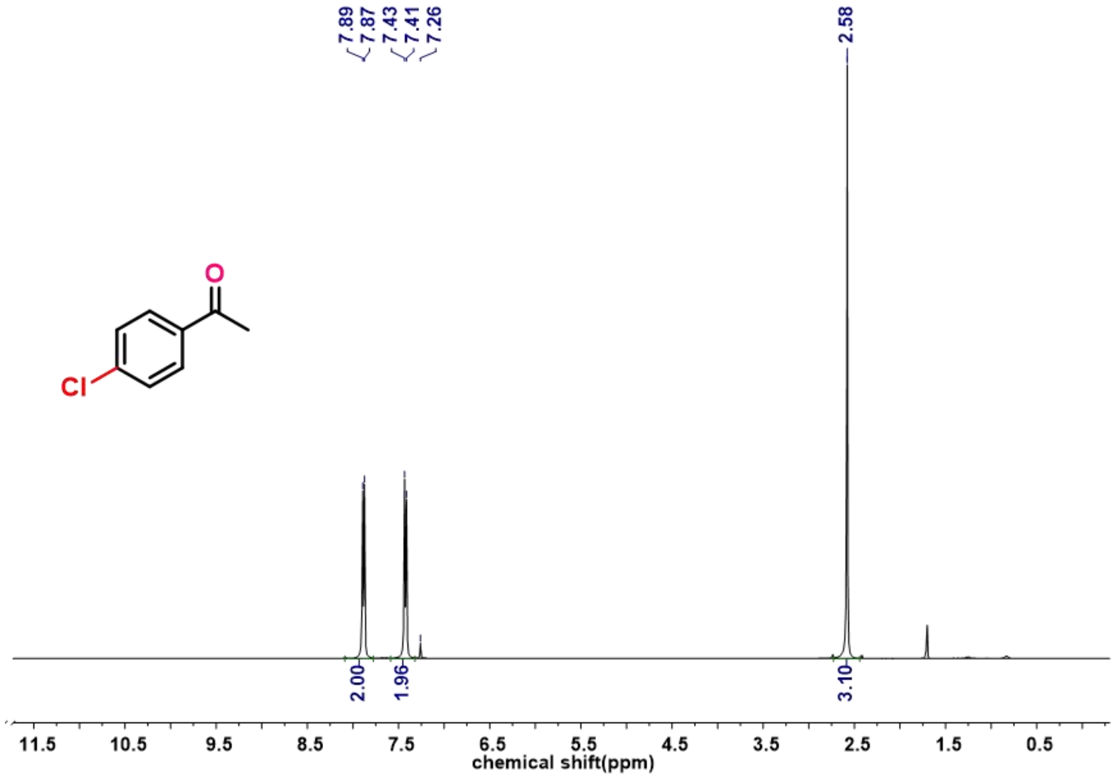
1-(*p*-tolyl)ethan-1-one (16):^{13}C NMR (101 MHz, $CDCl_3$)



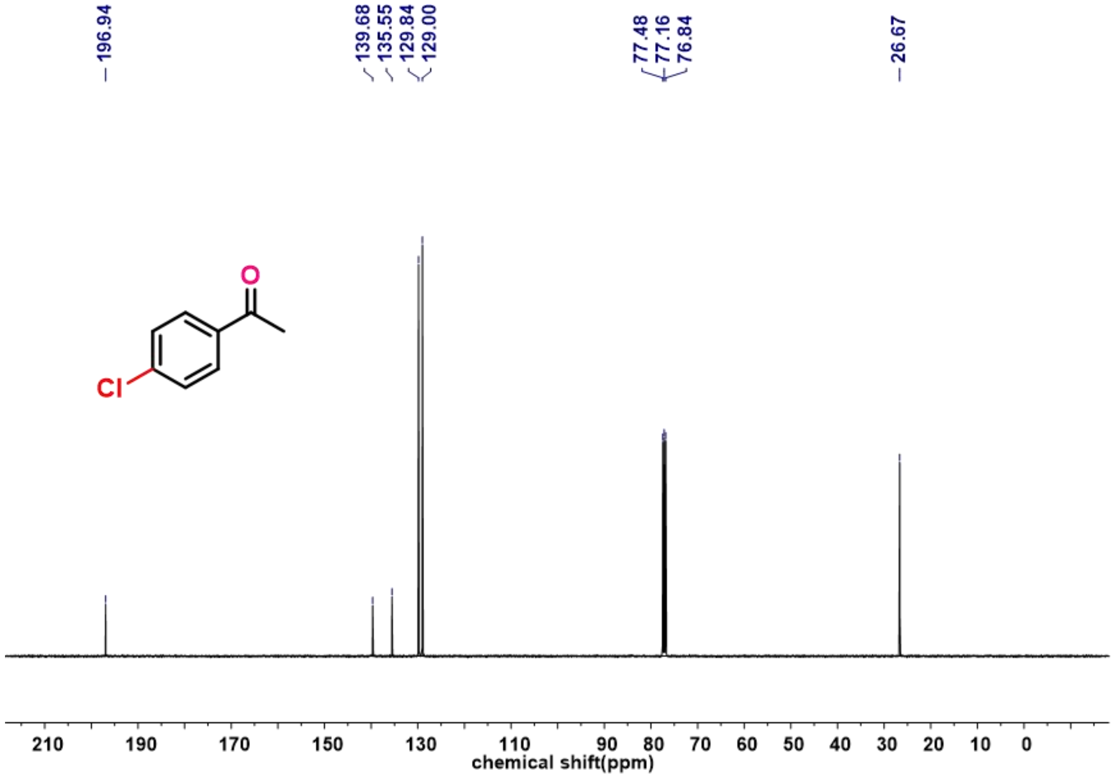
1-(4-methoxyphenyl)ethan-1-one (17):^{1}H NMR (400 MHz, CDCl$_3$)



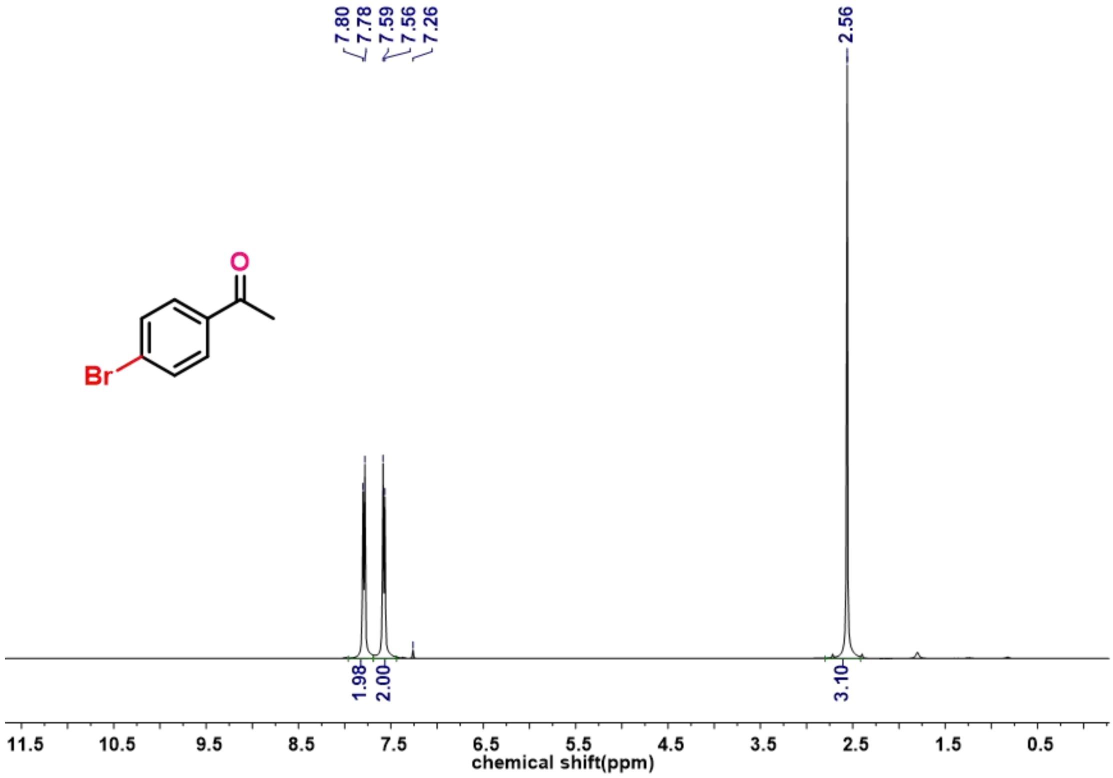
1-(4-methoxyphenyl)ethan-1-one (17):^{13}C NMR (101 MHz, CDCl$_3$)



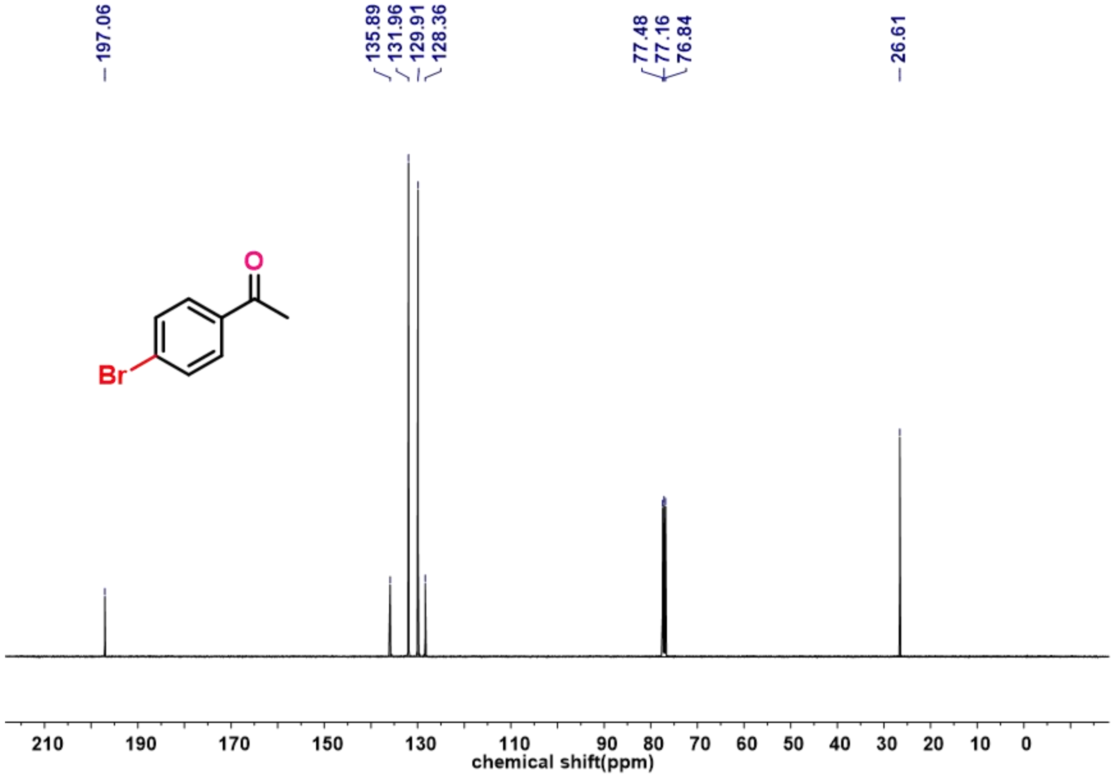
1-(4-chlorophenyl)ethan-1-one (18):^{1}H NMR (400 MHz, $CDCl_3$)



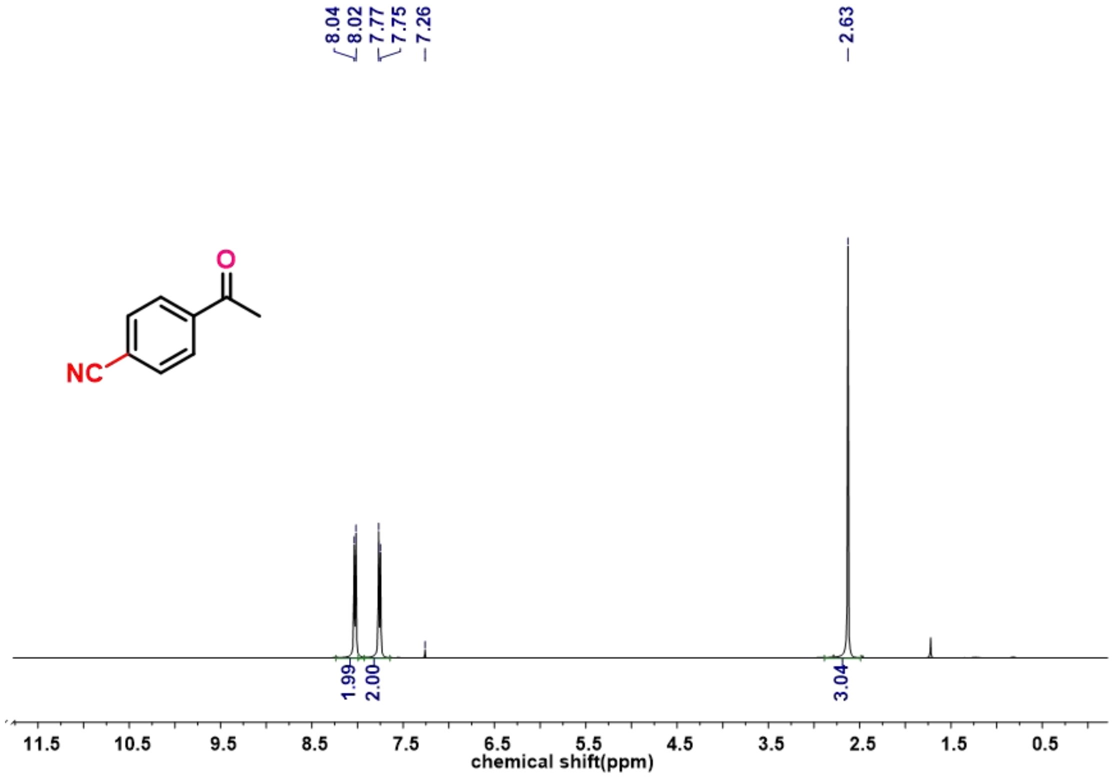
1-(4-chlorophenyl)ethan-1-one (18): ^{13}C NMR (101 MHz, $CDCl_3$)



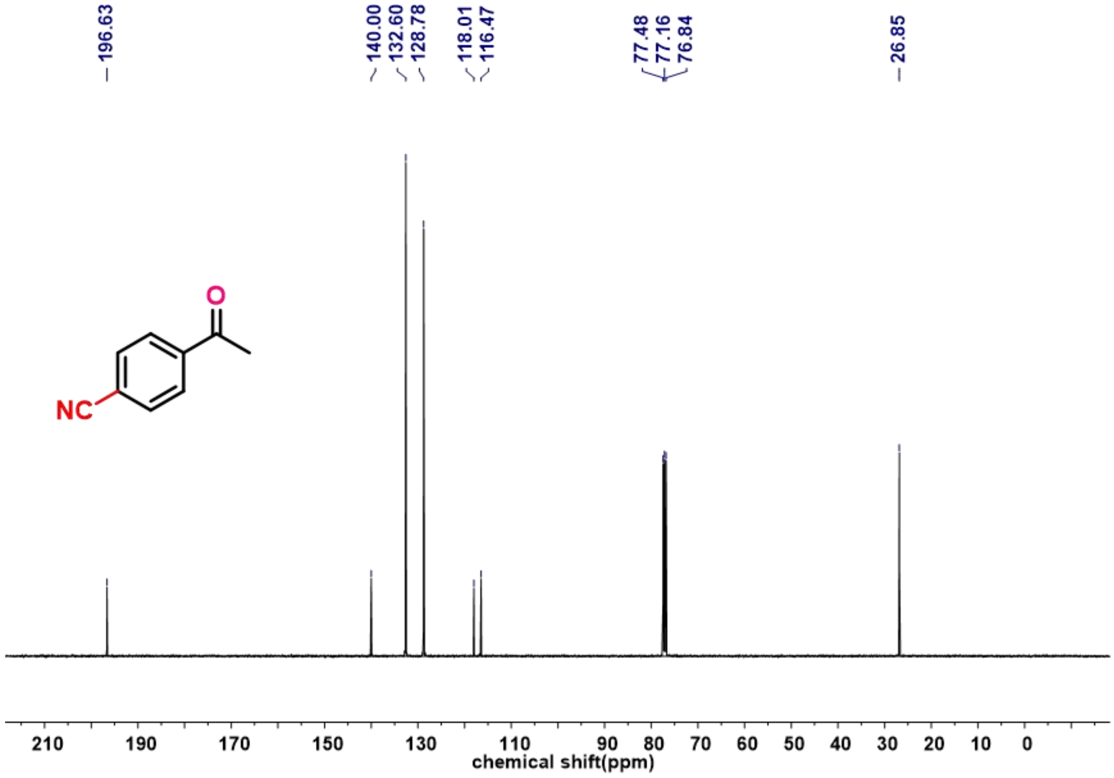
1-(4-bromophenyl)ethan-1-one (19):^{1}H NMR (400 MHz, CDCl$_3$)



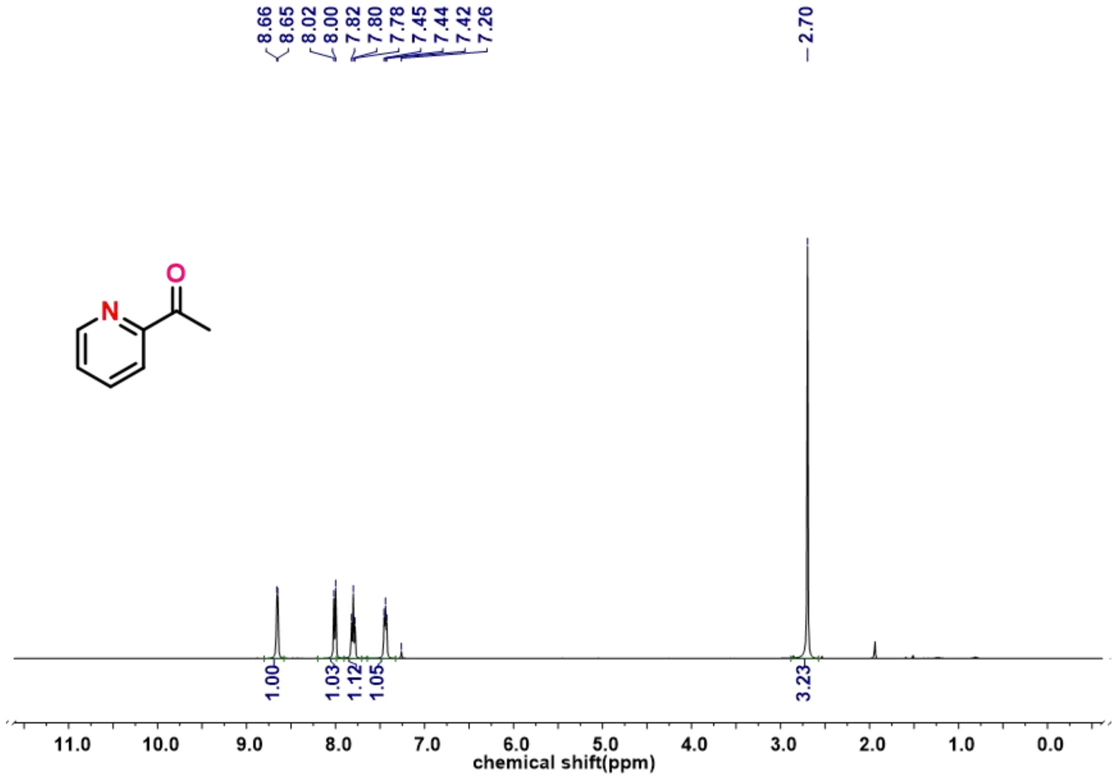
1-(4-bromophenyl)ethan-1-one (19):^{13}C NMR (101 MHz, CDCl$_3$)



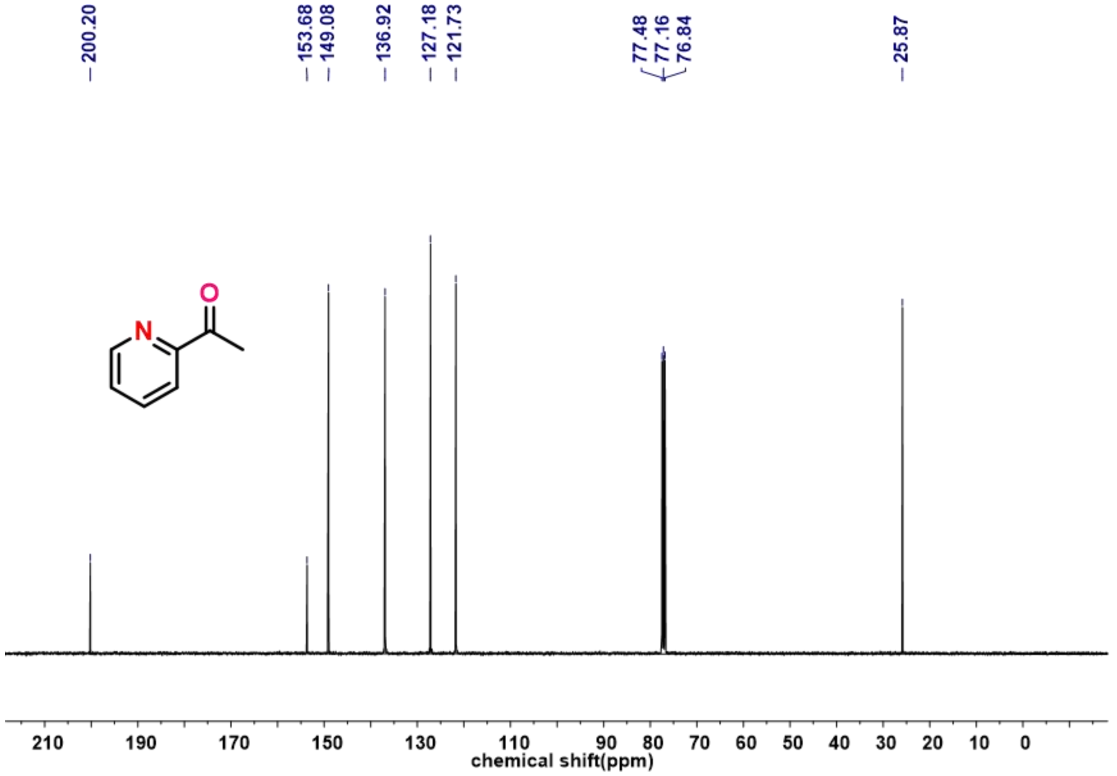
4-acetylbenzonitrile (20):^{1}H NMR (400 MHz, $CDCl_3$)



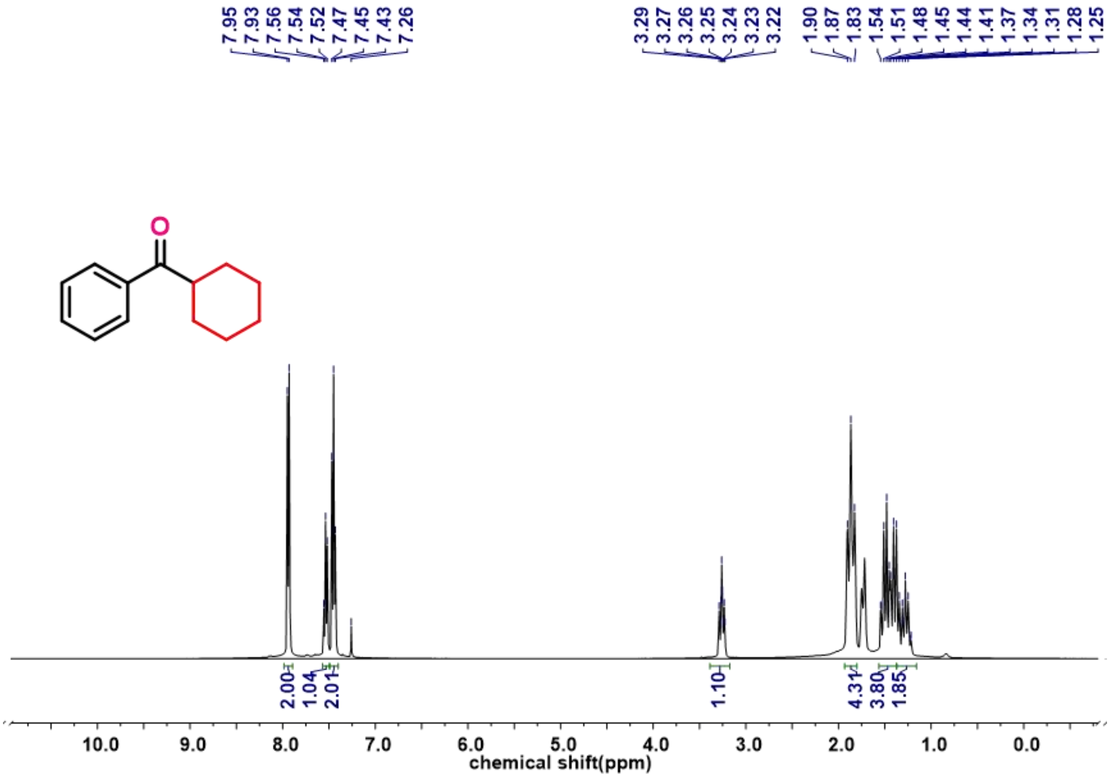
4-acetylbenzonitrile (20):^{13}C NMR (101 MHz, $CDCl_3$)



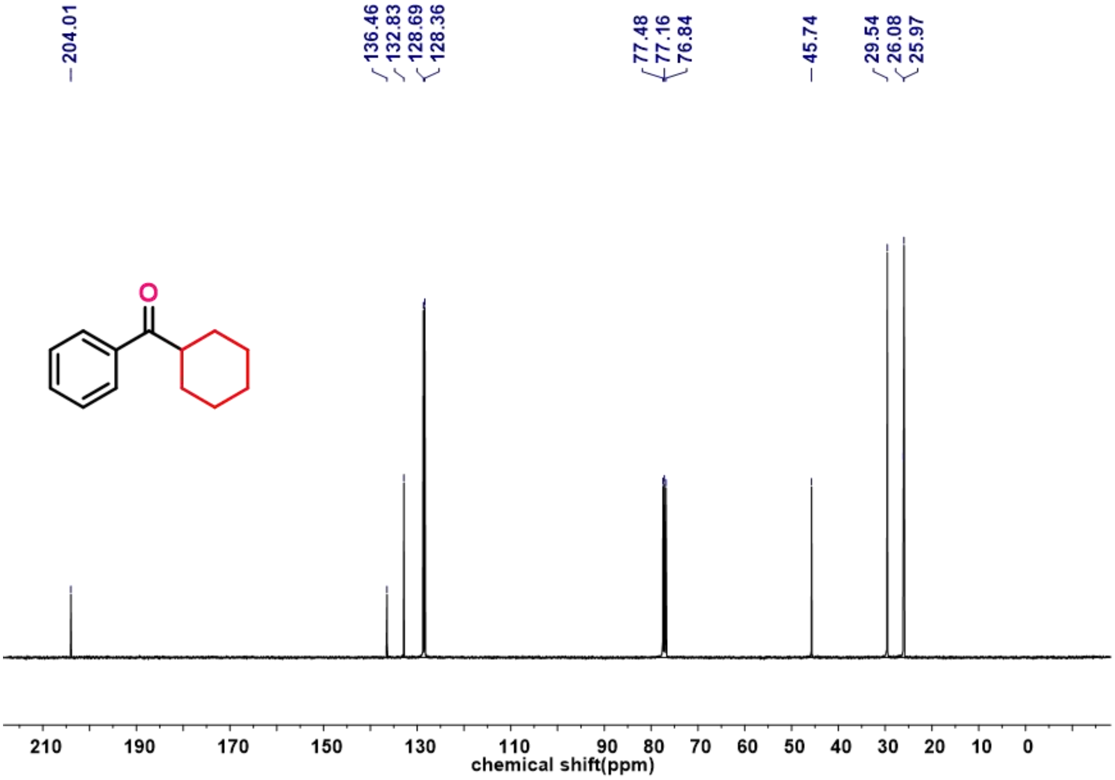
1-(pyridin-2-yl)ethan-1-one (21): ^{1}H NMR (400 MHz, CDCl$_3$)



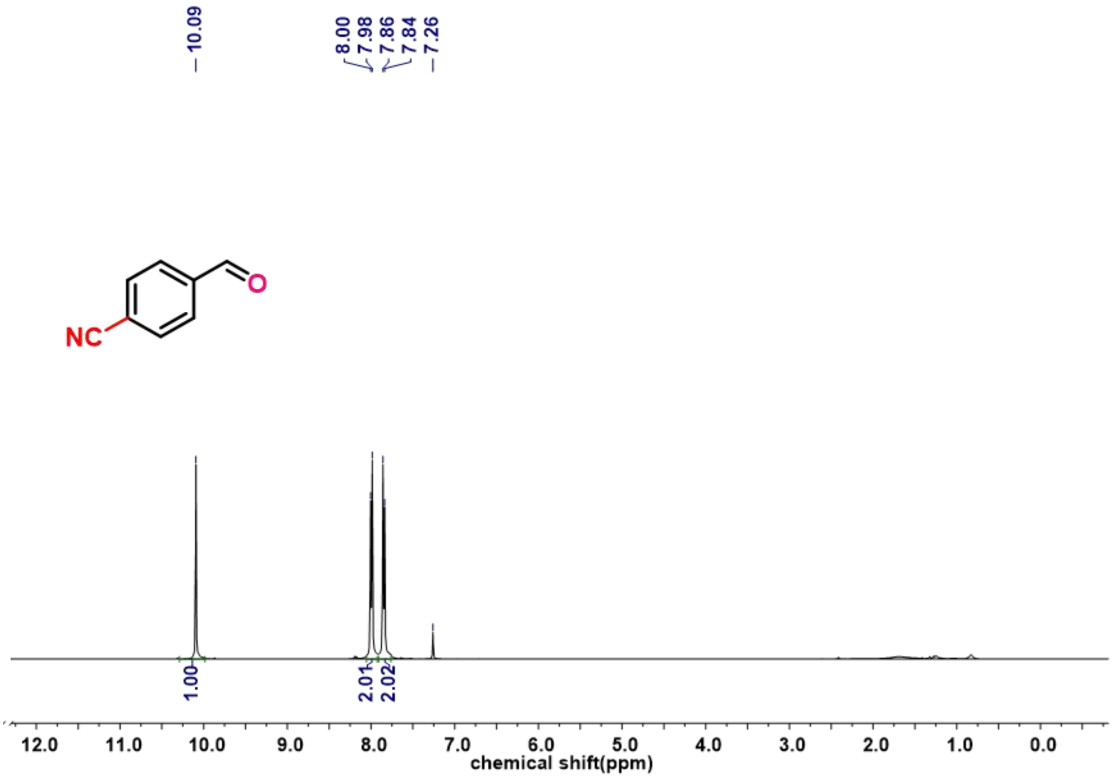
1-(pyridin-2-yl)ethan-1-one (21): ^{13}C NMR (101 MHz, CDCl$_3$)



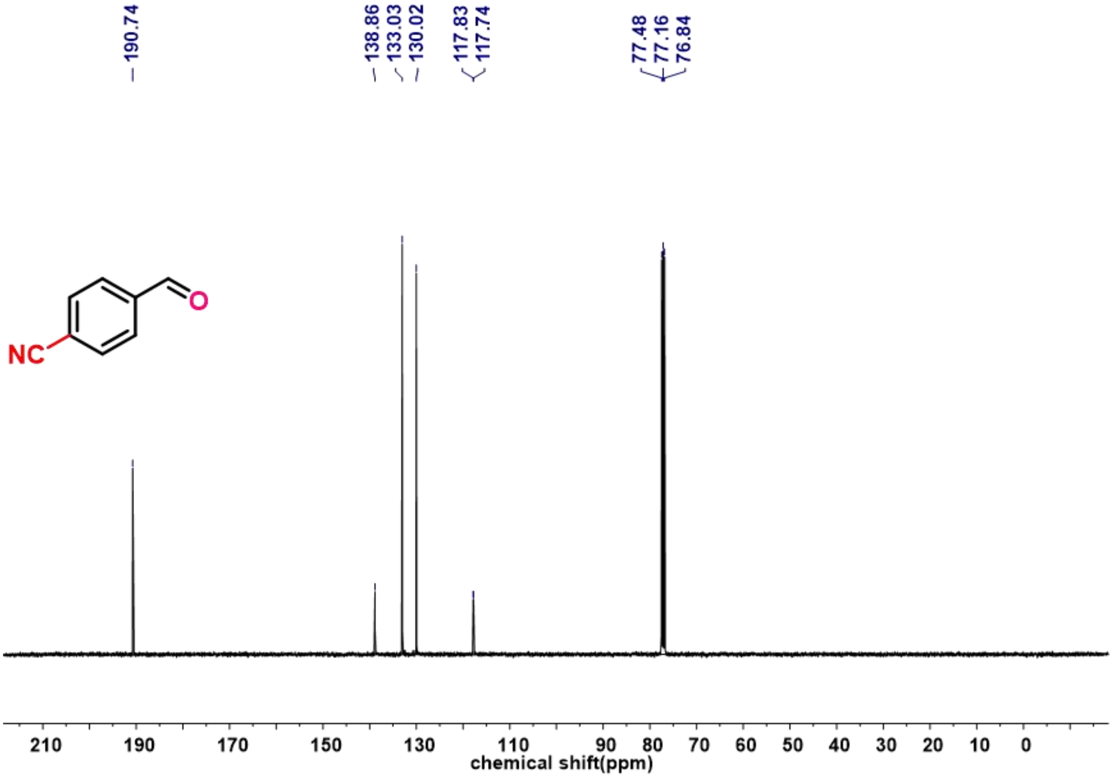
Cyclohexyl(phenyl)methanone (22): ^{1}H NMR (400 MHz, CDCl$_3$)



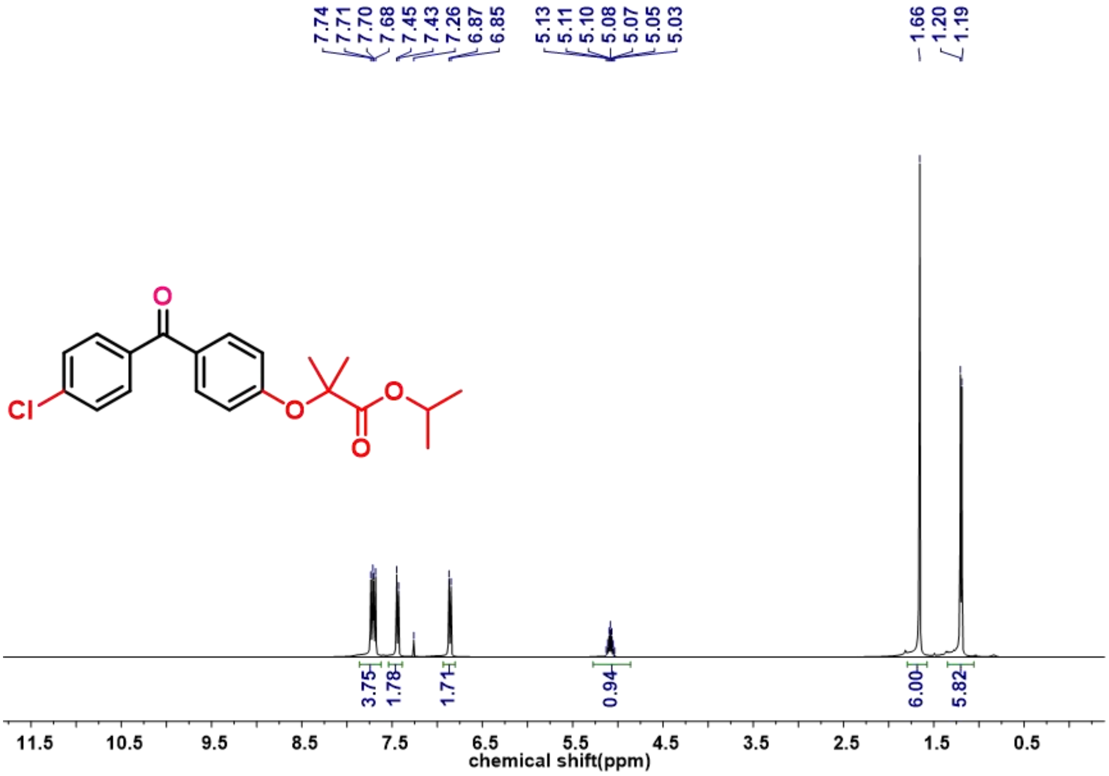
Cyclohexyl(phenyl)methanone (22): ^{13}C NMR (101 MHz, CDCl$_3$)



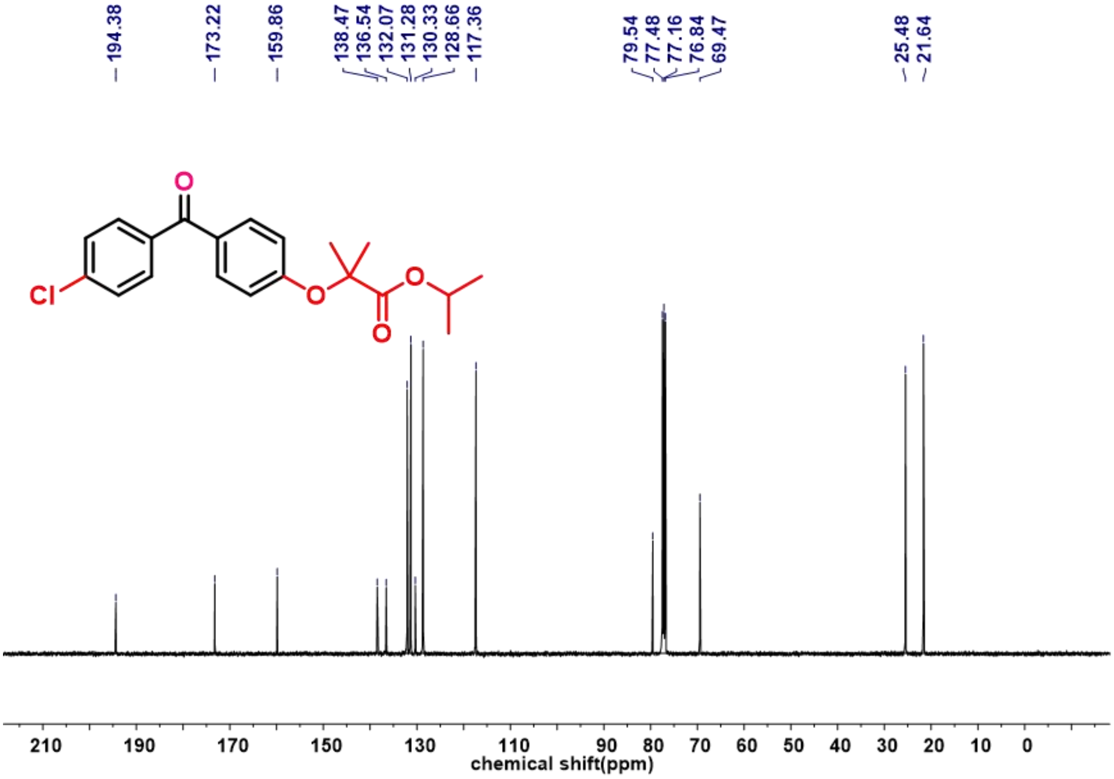
4-formylbenzonitrile (23):^{1}H NMR (400 MHz, $CDCl_3$)



4-formylbenzonitrile (23):^{13}C NMR (101 MHz, $CDCl_3$)

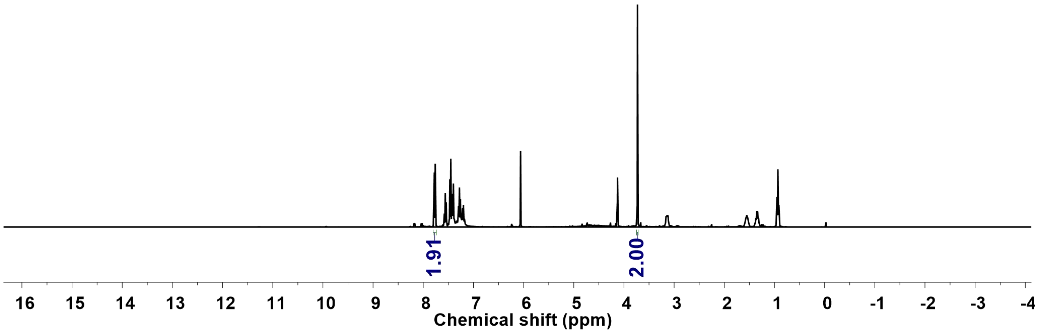


isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (24):^{1}H NMR (400 MHz, $CDCl_3$)

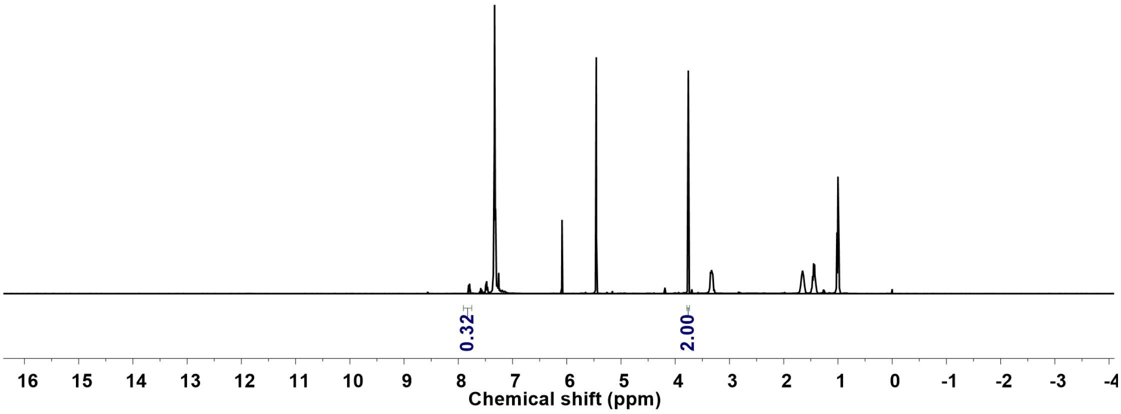


Isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (24): ^{13}C NMR (101 MHz, $CDCl_3$)

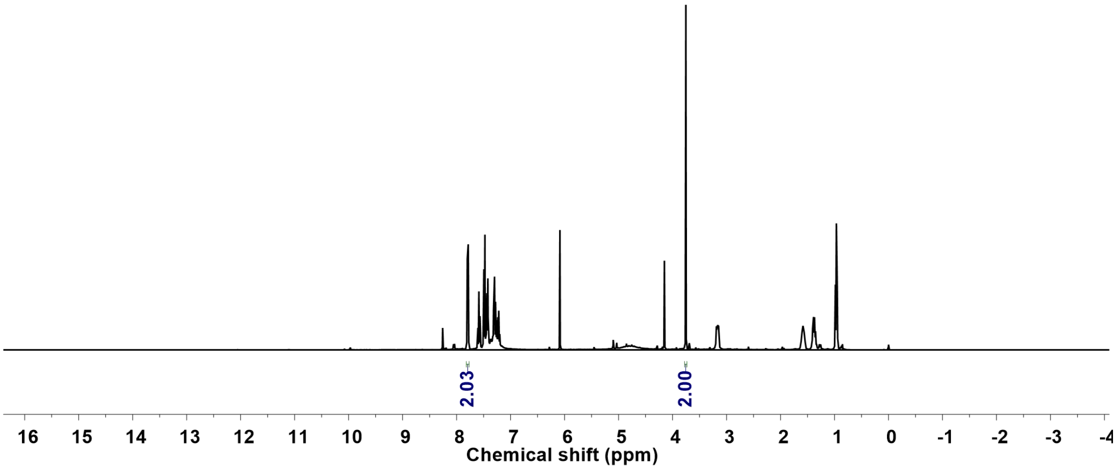
8. Copies of ^{1}H (400 MHz) in CDCl$_3$ of the optimization conditions



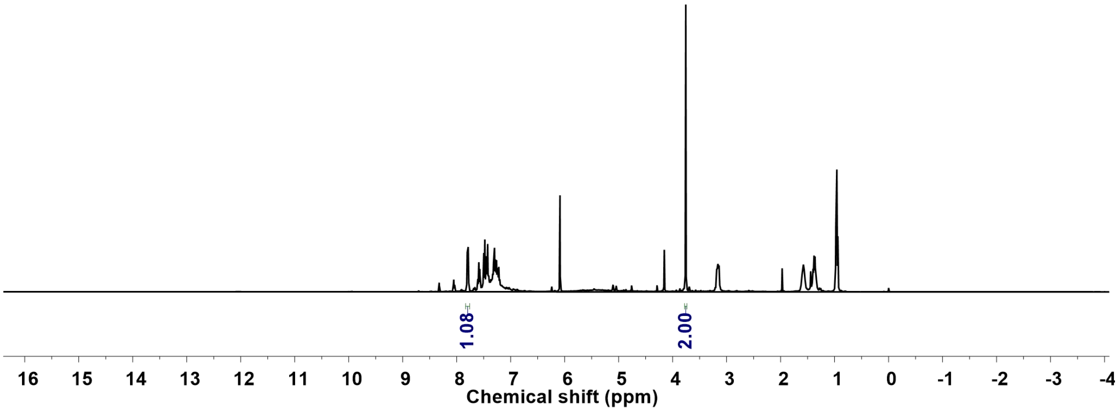
Entry 1: 4CzIPN as a photocatalyst (**^{1}H NMR 400 MHz, CDCl$_3$**)



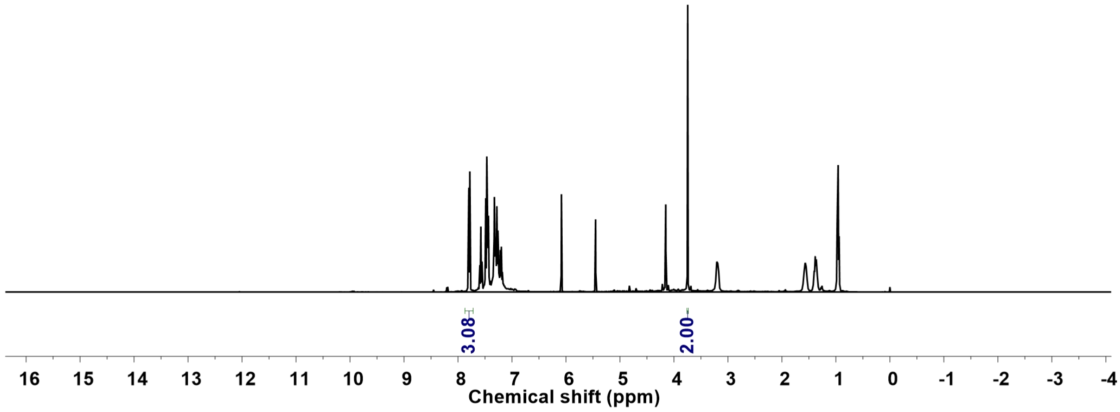
Entry 2 : 4CzTPN as a photocatalyst (**^{1}H NMR 400 MHz, CDCl$_3$**)



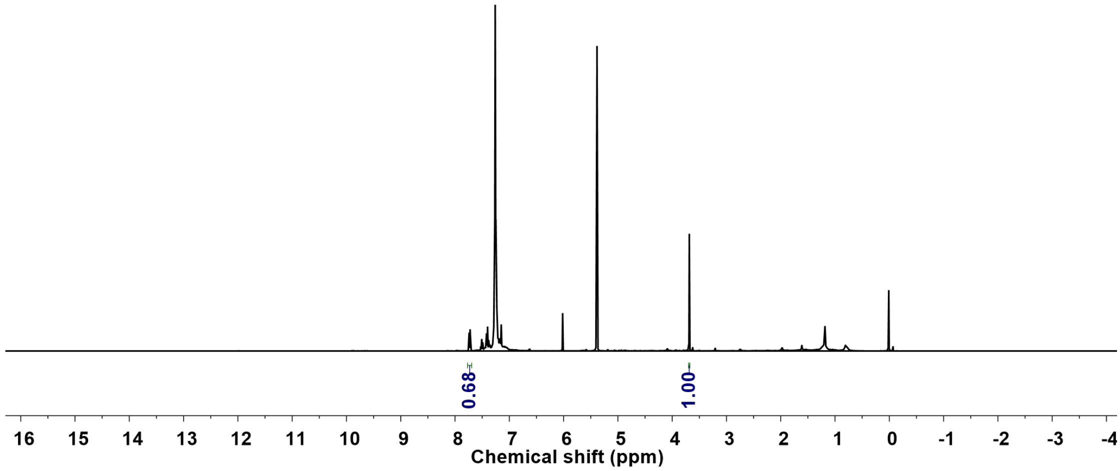
Entry 3: Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 as a photocatalyst (**^{1}H NMR 400 MHz, $CDCl_3$**)



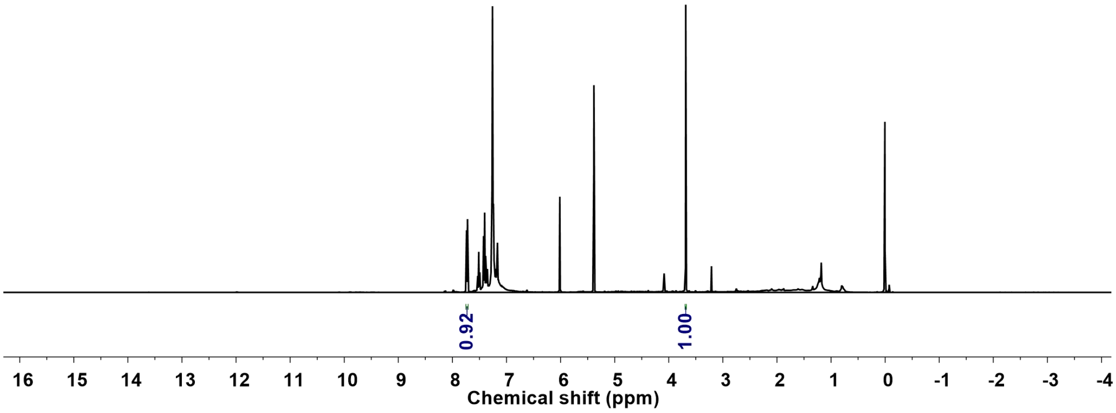
Entry 4: [Ir(ppy)$_2$(bpy)]PF_6 as a photocatalyst (**^{1}H NMR 400 MHz, $CDCl_3$**)



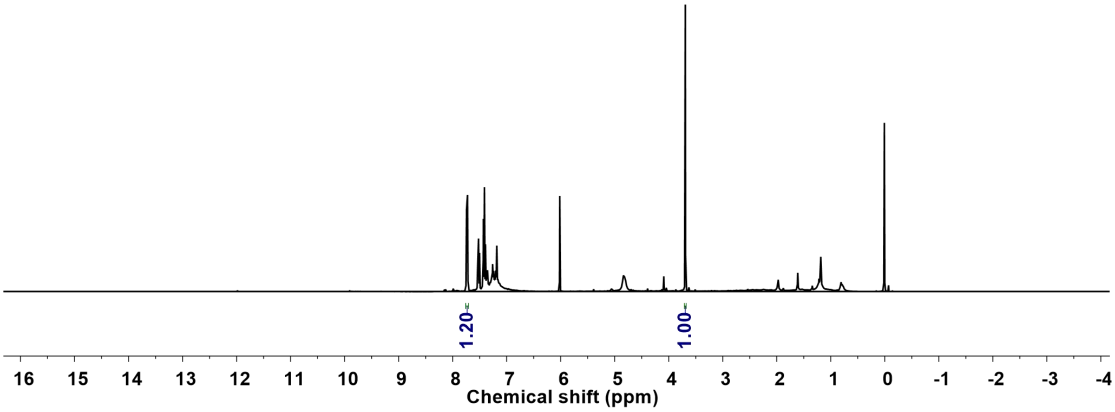
Entry 5 : Eosin Y as a photocatalyst (^{1}H NMR 400 MHz, $CDCl_3$)



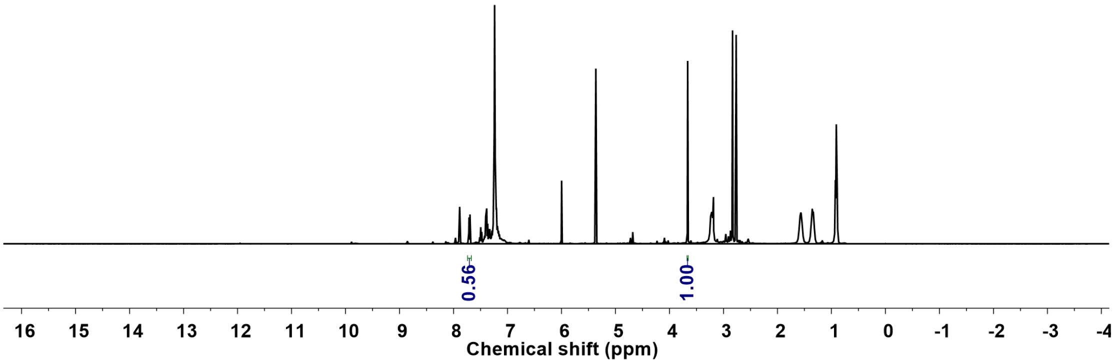
Entry 6: NaCl as a chloride salt (^{1}H NMR 400 MHz, $CDCl_3$)



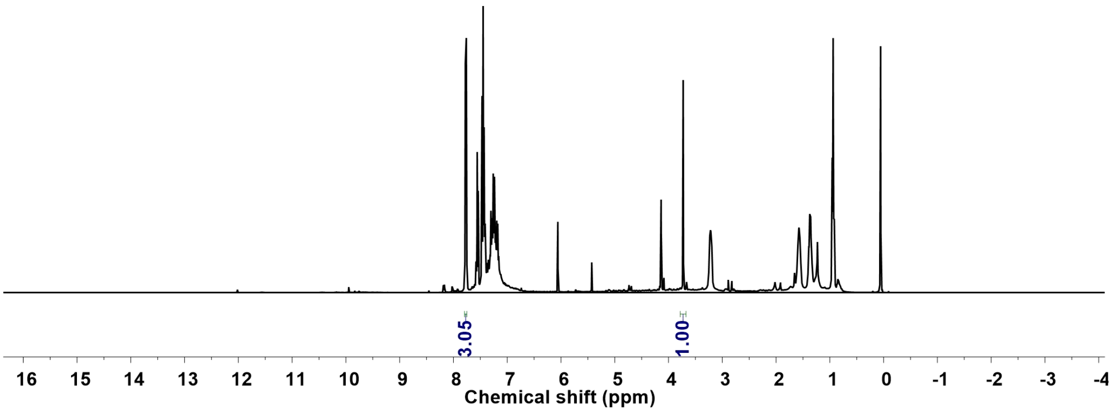
Entry 7 : KCl as a chloride salt (^{1}H NMR 400 MHz, $CDCl_3$)



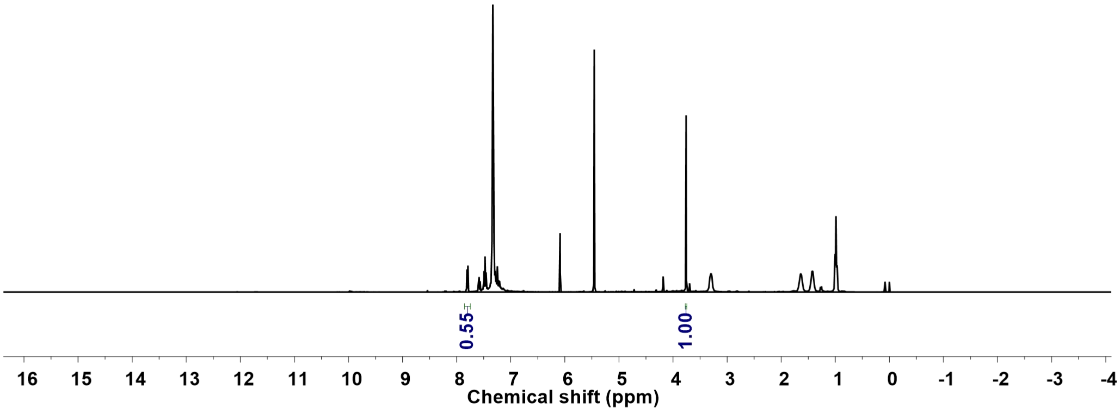
Entry 8 : $MgCl_2$ as a chloride salt (^{1}H NMR 400 MHz, $CDCl_3$)



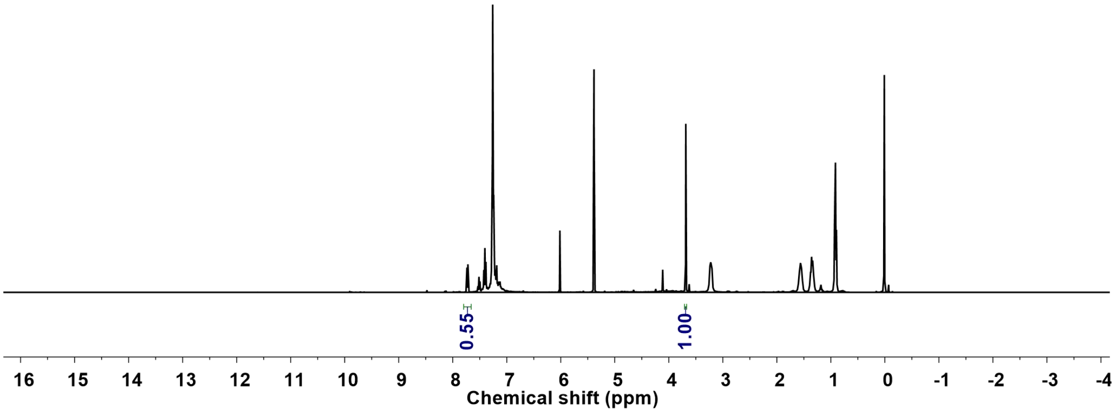
Entry 9 : DMF as a solvent (**^{1}H NMR 400 MHz, CDCl$_3$**)



Entry 10 : DCM as a solvent (**^{1}H NMR 400 MHz, CDCl$_3$**)

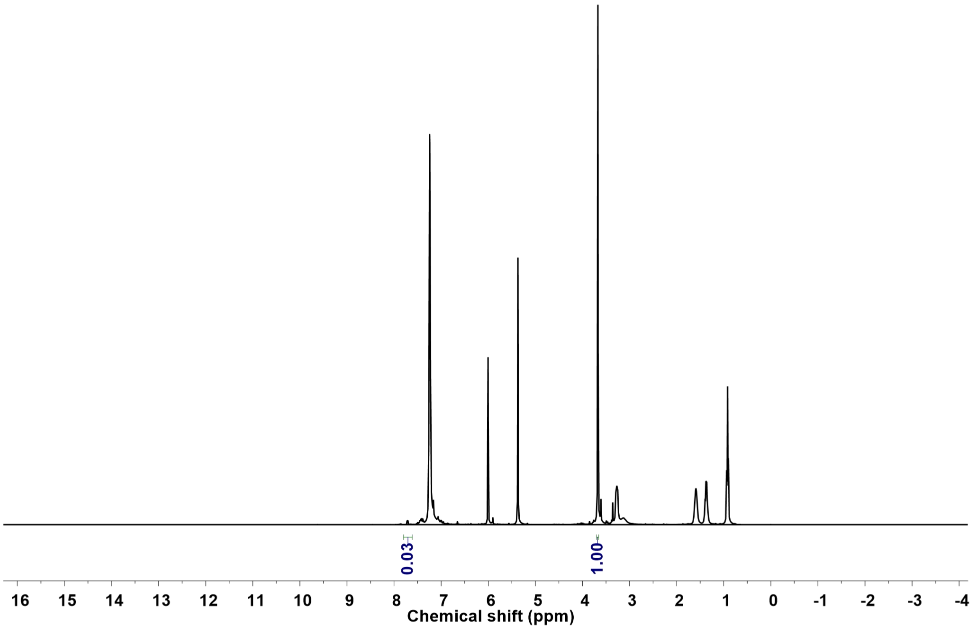


Entry 12 : The reaction time is 36 hours. (^{1}H NMR 400 MHz, $CDCl_3$)

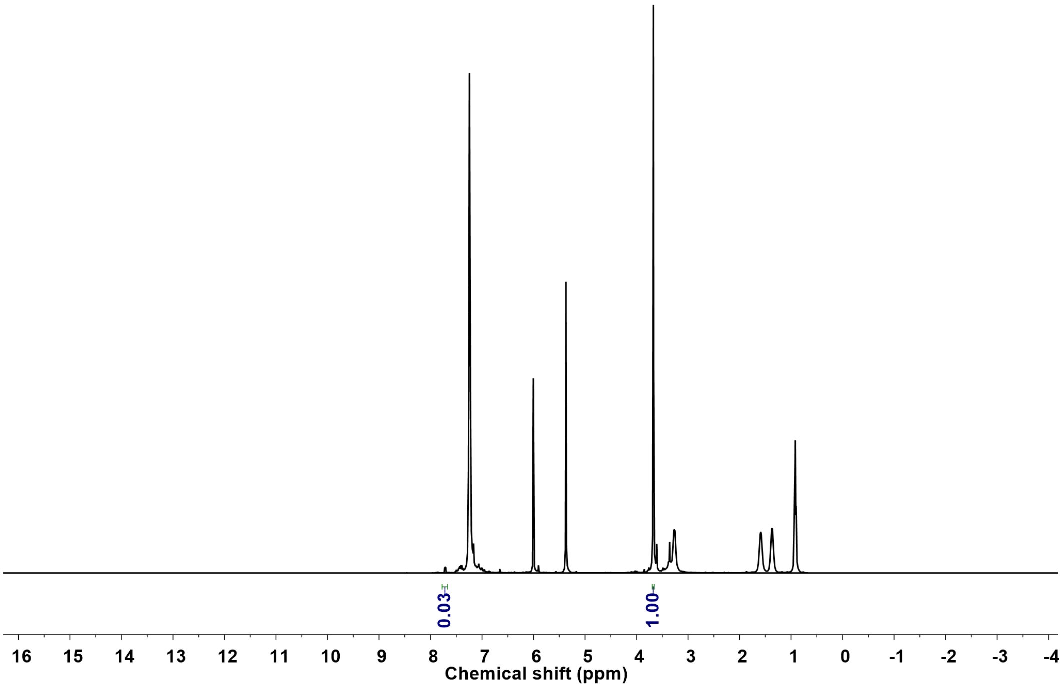


Entry 13 : The reaction time is 48 hours. (^{1}H NMR 400 MHz, $CDCl_3$)

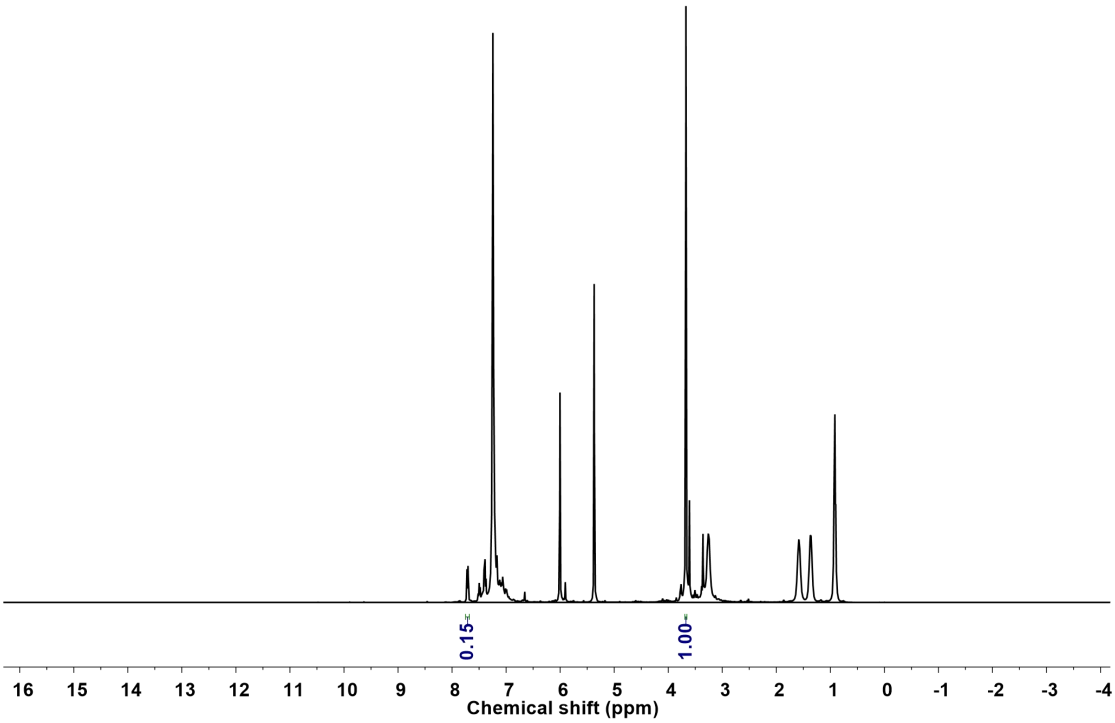
9. Copies of ^{1}H (400 MHz) in CDCl$_3$ of the light on-off experiments



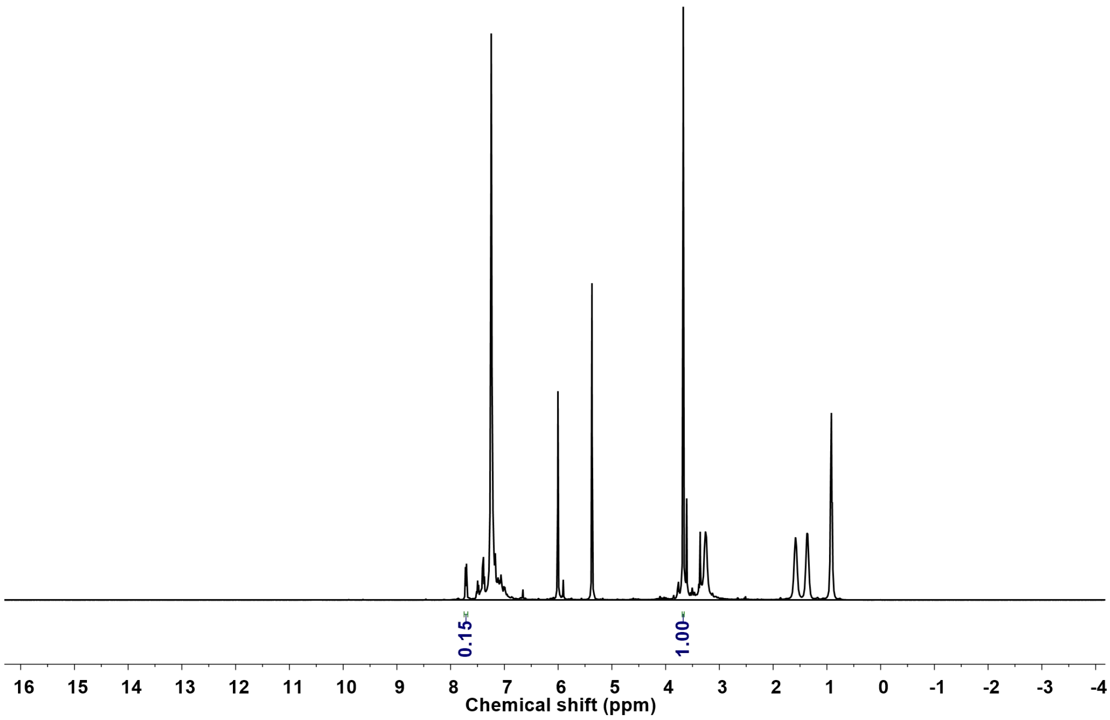
^{1}H NMR Spectrum of 6h



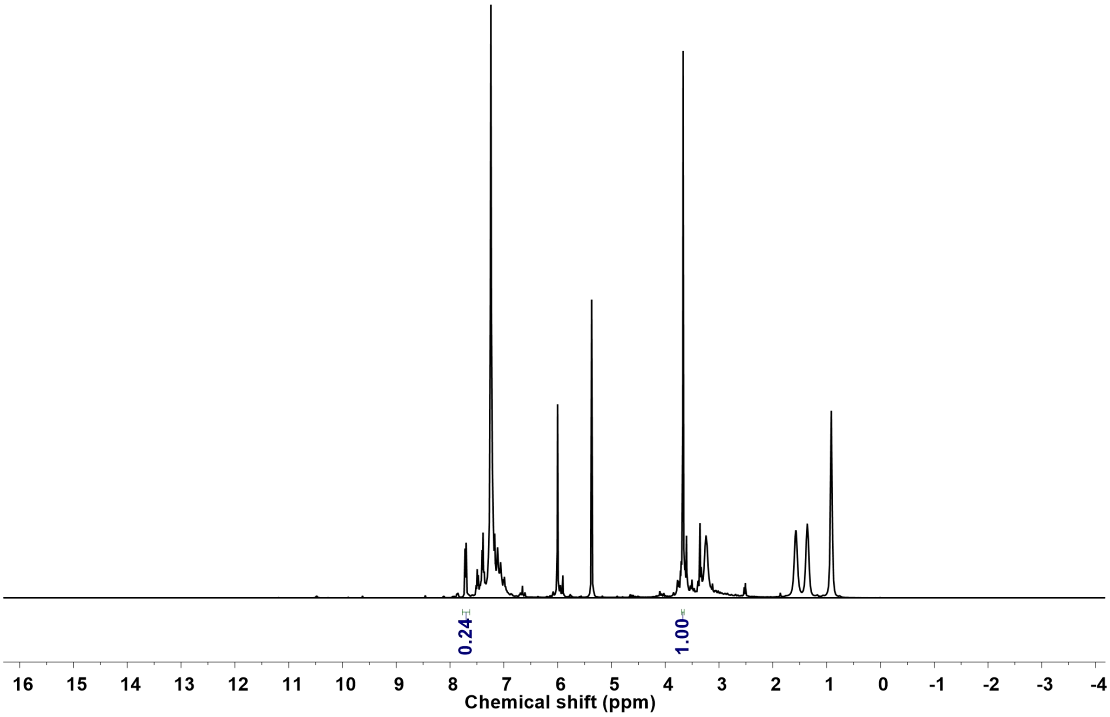
^{1}H NMR Spectrum of 12h



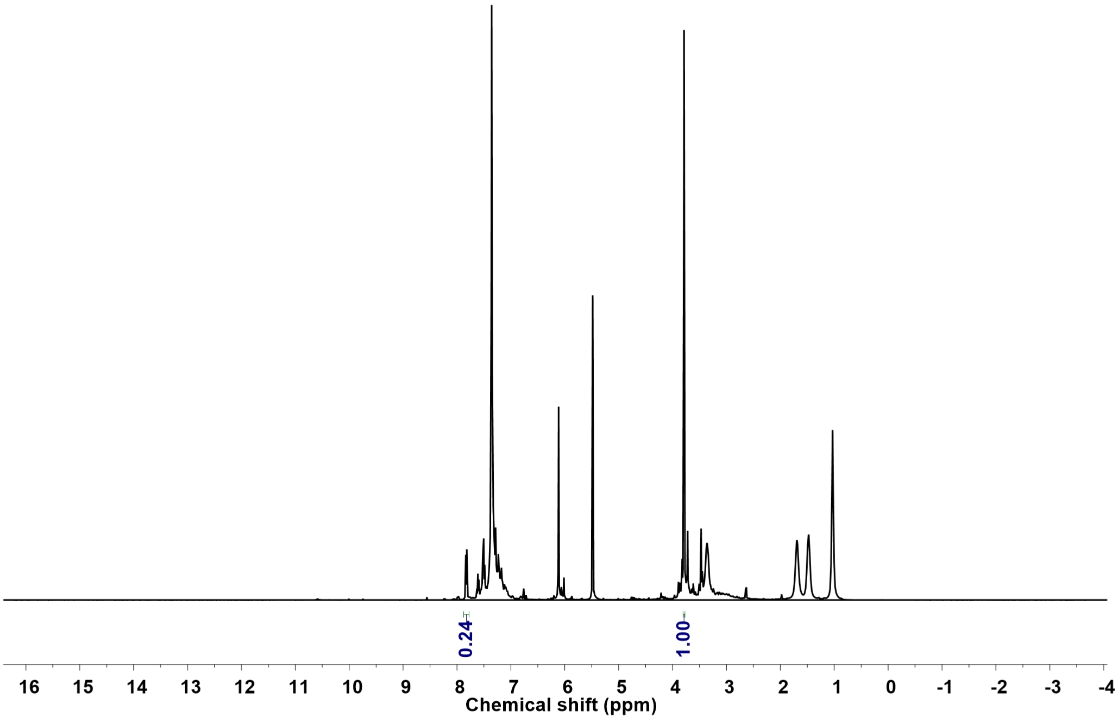
^{1}**H NMR** Spectrum of 24h



^{1}**H NMR** Spectrum of 36h



^{1}H NMR Spectrum of 50h



^{1}H NMR Spectrum of 66h