Supporting information for:

Decatungstate-Mediated Solar Photooxidative Cleavage of C=C Bonds Using Air as Oxidant in Water

Pan Xie,*[a] Cheng Xue,[a] Junfei Luo,[b] Sanshan Shi[a] and Dongdong Du[a]

[a] College of Chemistry and Chemistry Engineering, Shaanxi Key Laboratory of Chemistry Additives for Industry, Shaanxi University of Science & Technology, Xi'an, China 710021

[b] Materials Science and Chemical Engineering, Ningbo University, Ningbo, P. R. China, 315211

* Corresponding author: pan.xie@sust.edu.cn

Supporting Information

List of Contents

1. General Information 3

2. Optimization of the reaction conditions 4

3. General procedure for TBADT-catalyzed photooxidative cleavage of olefins 5

4. Experimental characterization data for products 6

References 28

5. The reaction practicability examination 29

5.1 Gram-scale reaction of 1,1-diphenylethylene 29

5.2 *Reusability test of the catalytic system* 30

5.3 The testing of stability of TBADT 31

5.4 "Window ledge" experiment 32

6. Mechanistic studies 33

6.1 Control experiments 33

6.2 Radical scavenger effect studies 33

6.3 Quenching experiments 34

6.4 On/off light experiments of 1,1-diphenylethylene 35

6.5 ^{18}*O labeling experiment* 35

6.6 The testing of HCHO 36

7. NMR spectra 38

1. General Information

Unless otherwise indicated, all reactions and manipulations were performed under air. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020SL). All starting materials and solvents were purchased from Adamas-beta, Alfa Aesar, Chempur, Merck as well as Sigma Aldrich, and used without further purification, unless otherwise stated. Tetrabutylammonium decatungstate (TBADT) is synthesized according to the previous literature.[1] All reactions were monitored by TLC with silica gel-coated plates. Column chromatography was carried out on silica gel, particle size 37-48 μm, using flash techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Ascend 400 (400 MHz) spectrometer. ^{1}H NMR are referenced to the residual solvent peak at 7.26 ppm ($CDCl_3$), and quoted in ppm to 2 decimal places with coupling constants (*J*) to the nearest 0.1 Hz. ^{13}C NMR spectra, recorded at 101 MHz, are referenced to the solvent peak at 77.16 ppm ($CDCl_3$), and quoted in ppm to 2 decimal places.

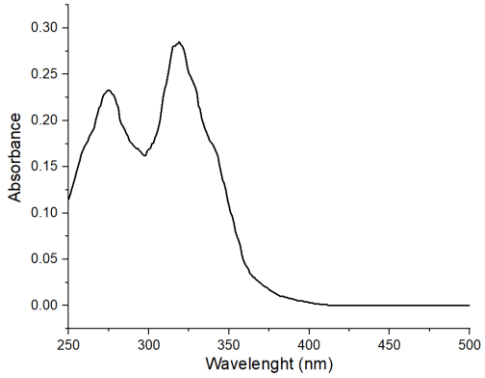
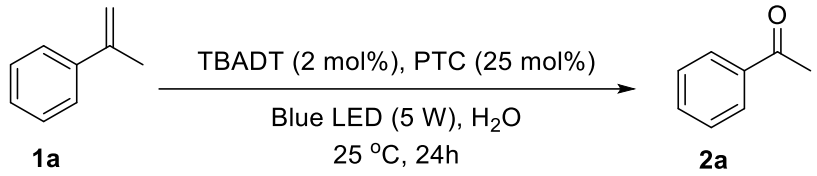


Fig S1. Absorption spectrum of TBADT (0.001 M in CH_3CN)

2. Optimization of the reaction conditions

A mixture of styrene, catalyst, additive and H_2O was added into a quartz tube which was placed in a photochemical reactor. The reaction mixture was stirred at the designed temperature under air. After the reaction, 2 ml of ethyl acetate and 1 drop of triethylamine were added, and the mixture was stirred at room temperature for 15 minutes, which was extracted with ethyl acetate (2 x 10 ml), dichloromethane (2 x 10 ml). The organic phase was dried with anhydrous magnesium sulfate. After concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel and eluted with EtOAc/petroleum ether to afford the desired product.

Table 1. Screening of phase transfer catalysts [a]

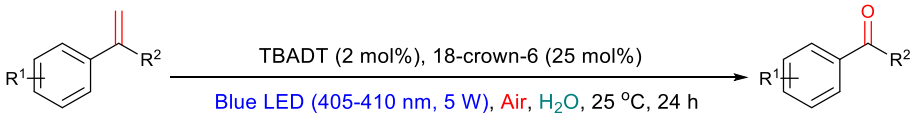


1a **2a**

Entry	PTC (25 mol%)	Yeild (%)
1	-	70
2	18-crown-6	91
3	TBAB	79
4	TBAC	78
5	CTAB	75

[a] **1a** (0.2mmol), TBADT (2 mol%), PTC (25 mol%), H_2O (1.0 mL) at room temperature (25°C), Blue LED (405-410 nm, 5 W) for 24 h, yields were determined by GC analysis with *n*-dodecane as internal standard.

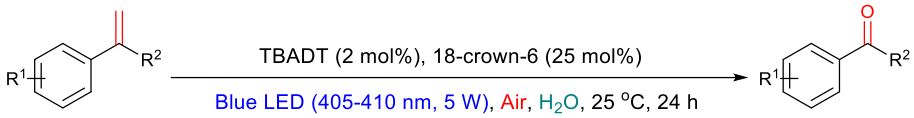
Table 2. Screening of the light sources and photocatalysts[a]



Entry	Light source	photocatalyst (2 mol%)	Yield (%)
1	Blue light	TBADT	91
2	White light	TBADT	58
3	Blue light	Eosin Y	55
4	White light	Eosin Y	Trace
5	Blue light	Rhodamine B	50
6	White light	Rhodamine B	Trace
7	Blue light	$CeCl_3$	37
8	White light	$CeCl_3$	Trace

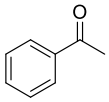
[a] **1a** (0.2mmol), photocatalyst (2 mol%), 18-crown-6 (25 mol%), H_2O (1.0 mL) at room temperature (25℃), blue light is from blue LED (405-410 nm, 5 W), white light from white LED (6500 K, 5 W), yields were determined by GC analysis with *n*-dodecane as internal standard.

3. General procedure for TBADT-catalyzed photooxidative cleavage of olefins



A mixture of olefin (0.2 mmol), TBADT (2 mol%, 10.4 mg), 18-crown-6 (25 mol%, 13.2 mg) and H_2O (1.0 mL) was added into a quartz tube which was placed in a photochemical reactor (Blue LED, 405-410 nm, 5 W). The reaction mixture was stirred at 25 ^oC under air for 24 h. After the reaction, 2 ml of ethyl acetate and 1 drop of triethylamine were added, and the mixture was stirred at room temperature for 15 min, which was extracted with ethyl acetate (2 x 10 ml), dichloromethane (2 x 10 ml). The organic phase was dried with anhydrous magnesium sulfate. After concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel and eluted with EtOAc/petroleum ether to afford the desired product.

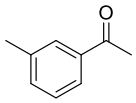
4. Experimental characterization data for products



Acetophenone (2a). The product **2a** was obtained via the *general procedure* using prop-1-en-2-ylbenzene **1a** (23.6 mg, 0.2 mmol) and isolated by flash column chromatography as colorless oil.

Known compound, spectroscopic data matched those previously reported.[2]

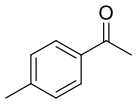
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 - 7.91 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.90, 137.14, 132.99, 128.49, 128.22, 26.42.



3'-Methylacetophenone (2b). The product **2b** was obtained via the *general procedure* using 1-methyl-3-(prop-1-en-2-yl) benzene **1b** (26.4 mg, 0.2 mmol) and isolated by flash column chromatography as colorless oil.

Known compound, spectroscopic data matched those previously reported.[3]

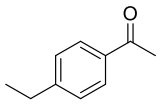
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.37 (p, *J* = 7.5 Hz, 2H), 2.60 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.16, 138.24, 137.10, 133.78, 128.71, 128.38, 125.52, 26.52, 21.22.



4’-Methylacetophenone (2c). The product **2c** was obtained via the *general procedure* using 1-methyl-4-(prop-1-en-2-yl) benzene **1c** (26.4 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[4]

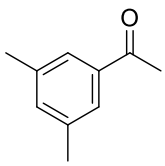
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.46 (s, 3H), 2.30 (s, 3H)； ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.37, 143.61, 134.60, 129.09, 128.29, 26.24, 21.38.



4-Ethylacetophenone (2d). The product **2d** was obtained via the general procedure using 1-ethyl-4-(prop-1-en-2-yl) benzene **1d** (29.2 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[3]

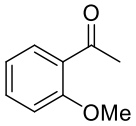
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 2.64 (q, J = 7.6 Hz, 2H), 2.50 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.41, 149.82, 134.89, 128.43, 127.93, 28.80, 26.29, 15.05.



3,5-DiMethylacetoph (2e). The product **2e** was obtained via the *general procedure* using 1,3-dimethyl-5-(prop-1-en-2-yl) benzene **1e** (29.2 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[5]

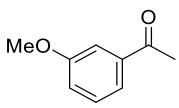
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2H), 7.21 (s, 1H), 2.59 (s, 3H), 2.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.37, 138.13, 137.31, 134.63, 126.08, 26.57, 21.12.



2-Methoxyacetophenone (2f). The product **2f** was obtained via the *general procedure* using 1-methoxy-2-(prop-1-en-2-yl) benzene **1f** (29.6 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

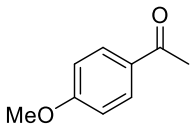
Known compound, spectroscopic data matched those previously reported.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.32 - 7.25 (m, 1H), 6.82 (t, *J* = 8.9 Hz, 2H), 3.72 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.15, 158.82, 133.53, 130.01, 128.04, 120.29, 111.60, 55.24, 31.54.



3-Methoxyacetophenone (2g). The product **2g** was obtained via the *general procedure* using 1-methoxy-3-(prop-1-en-2-yl) benzene **1g** (29.6 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil. Known compound, spectroscopic data matched those previously reported.[6]

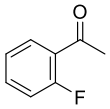
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 16.0, 9.3 Hz, 2H), 7.33 (dd, *J* = 14.8, 8.6 Hz, 1H), 7.08 (t, *J* = 5.4 Hz, 1H), 3.82 (d, *J* = 6.0 Hz, 3H), 2.56 (d, *J* = 5.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.68, 159.79, 138.49, 129.48, 120.98, 119.39, 112.43, 55.28, 26.52.



4-Methoxyacetophenone (2h). The product **2h** was obtained in MeCN: H_2O (2:3) via the *general procedure* using 1-methoxy-4-(prop-1-en-2-yl) benzene **1h** (29.6 mg, 0.2 mmol) and isolated by flash column chromatography as a yellow solid.

Known compound, mp 36-38 ^{o}C, spectroscopic data matched those previously reported.[4]

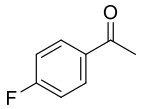
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, *J* = 7.0 Hz, 2H), 6.95 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.58, 163.47, 130.50,130.38, 113.65, 55.37, 26.17.



2-Fluoroacetophenone (2i). The product 2**i** was obtained via the general *procedure* using 1-fluoro-2-(prop-1-en-2-yl) benzene **1i** (27.2 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[3]

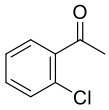
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 5.1, 2.5 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.44, 163.34, 160.71, 134.53, 130.42, 125.57, 124.23, 116.61, 116.37, 31.08.



4-Fluoroacetophenone (2j). The product **2j** was obtained via the general procedure using 1-fluoro-4-(prop-1-en-2-yl) benzene **1j** (27.2mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[7]

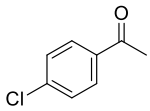
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.83 (m, 2H), 7.05 - 6.96 (m, 2H), 2.46 (s, 3H)； ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.12, 166.81, 164.28, 133.48, 130.78, 115.50, 115.28, 26.18.



2’-Chloroacetophenone (2k). The product **2k** was obtained via the general procedure using 1-chloro-2-(prop-1-en-2-yl) benzene **1k** (30.4 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[7]

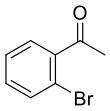
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.39 (m, 1H), 7.28 (t, *J* = 10.7 Hz, 2H), 7.20 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.81, 138.92, 131.87, 130.99, 130.47, 129.27, 126.85, 30.41.



4’-Chloroacetophenone (2l). The product **2l** was obtained via the general procedure using 1-chloro-4-(prop-1-en-2-yl) benzene **1l** (30.4 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[8]

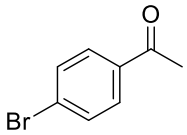
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.26, 139.12, 135.25, 129.54, 128.59, 26.21.



2’-Bromoacetophenone (2m). The product **2m** was obtained via the general procedure using 1-bromo-2-(prop-1-en-2-yl) benzene **1m** (39.2 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[4]

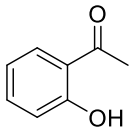
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 1H), 7.44 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.34 (td, J = 7.5, 1.0 Hz, 1H), 7.26 (td, J = 7.7, 1.7 Hz, 1H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.00, 141.43, 133.77, 131.73, 128.86, 127.42, 118.79, 30.19.



4'-Bromoacetophenone (2n). The product **2n** was obtained via the *general procedure* using 1-bromo-4-(prop-1-en-2-yl) benzene **1n** (39.2 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 48-51 ^{o}C, spectroscopic data matched those previously reported.[9]

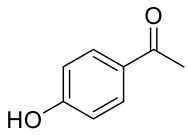
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 - 7.79 (m, 2H), 7.63 - 7.58 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.84, 135.88, 131.85, 129.79, 128.22, 26.42.



2'-Hydroxyacetophenone (2o). The product **3o** was obtained via using 2-(prop-1-en-2-yl) phenol **1o** (26.8 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 132-135 ºC, spectroscopic data matched those previously reported [8].

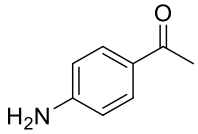
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1H), 7.68 (dd, J = 8.0, 1.5 Hz, 1H), 7.44 - 7.40 (m, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.85 (t, J = 8.1 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.50 (s), 162.34 (s), 136.33 (s), 130.73 (s), 119.68 (s), 118.87 (s), 118.24 (s), 26.39 (s).



4'-Hydroxyacetophenone (2p). The product **2p** was obtained via using 4-(prop-1-en-2-yl) phenol **1p** (26.8 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 132-135 ºC, spectroscopic data matched those previously reported [2].

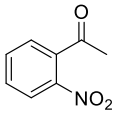
^{1}H NMR (400 MHz, DMSO) δ 10.35 (s, 1H), 7.84 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 2.47 (s, 3H)； ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.99, 161.70, 131.29, 129.46, 115.65, 26.23.



4-Aminoacetophenone (2q). The product was obtained **2q** via using 4-(prop-1-en-2-yl) aniline **1q** (26.6 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 103-107 °C, spectroscopic data matched those previously reported [5].

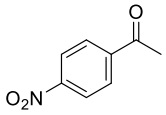
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 6.69 (d, J = 8.0 Hz, 2H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.61, 151.21, 130.81, 127.71, 113.69, 26.11.



2-Nitroacetophenone (2r). The product **2r** was obtained via the general procedure using 1-nitro-2-(prop-1-en-2-yl) benzene **1r** (32.6 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[3]

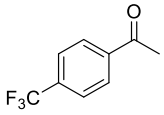
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.68, 145.83, 137.72, 134.17, 130.70, 127.35, 124.26, 29.95.



4-Nitroacetophenone (2s). The product **2s** was obtained via the general procedure using 1-nitro-4-(prop-1-en-2-yl) benzene **1s** (32.6 mg, 0.2 mmol) and isolated by flash column chromatography as a light-yellow solid.

Known compound, mp 75-78 °C, spectroscopic data matched those previously reported.[7]

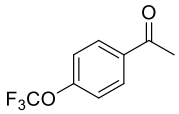
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 2.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.24, 150.34, 141.42, 129.26, 123.78, 26.86.



4'-(Trifluoromethyl) acetophenone (2t). The product **2t** was obtained via the *general procedure* using 1-(prop-1-en-2-yl)-4-(trifluoromethyl) benzene **1t** (37.2 mg, 0.2 mmol) and isolated by flash column chromatography as a yellow solid.

Known compound, mp 30-33 ^{o}C, spectroscopic data matched those previously reported.[3]

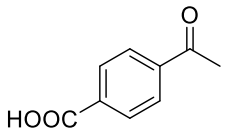
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 2.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.45, 139.60, 128.36, 125.26, 122.17, 26.10.



4'-(Trifluoromethoxy) acetophenone (2u). The product **2u** was obtained via the general procedure using 1-(prop-1-en-2-yl)-4-(trifluoromethoxy) benzene **1u** (40.4 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[3]

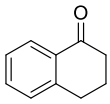
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 - 7.98 (m, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.33, 152.56, 135.32, 130.24, 120.28, 26.38.



4-Acetylbenzoic acid (2v). The product **2v** was obtained via using 4-(prop-1-en-2-yl) benzoic acid **1v** (32.4 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 208-210 °C, spectroscopic data matched those previously reported [2].

^{1}H NMR (400 MHz, DMSO) δ 13.33 (s, 1H), 8.08 (s, 4H), 2.65 (s, 3H);^{13}C NMR (101 MHz, DMSO) δ 198.16, 167.08, 140.25, 134.92, 129.98, 128.75, 27.42.

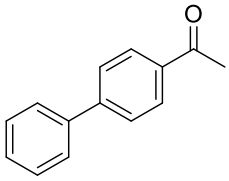


1-Tetralone (2w). The product **2w** was obtained via the general procedure using 1-methylene-1,2,3,4-tetrahydronaphthalene **1w** (28.8 mg, 0.2 mmol) and isolated by flash column chromatography as brown oil.

Known compound, spectroscopic data matched those previously reported.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.32 - 7.28 (m, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 2.96 (t, *J* = 6.1 Hz, 2H), 2.66 - 2.63 (m, 2H), 2.16 - 2.10 (m, 2H); ^{13}C NMR (101 MHz,

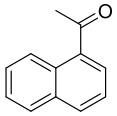
$CDCl_3$) δ 198.13 (s), 144.44, 133.25, 132.62, 128.73, 127.08, 126.55, 39.11, 29.65, 23.26.



4-Acetylbiphenyl (2x). The product **2x** was obtained in MeCN: H_2O (2:3) via the *general procedure* using 4-(prop-1-en-2-yl)-1,1'-biphenyl **1x** (38.8 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 116-118 ^oC, spectroscopic data matched those previously reported.[10]

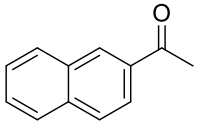
^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.3, 2.0 Hz, 2H), 7.72 (dd, *J* = 8.0, 3.2 Hz, 2H), 7.69 - 7.64 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 2.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.59, 145.70, 139.84, 135.91, 128.94, 128.25, 127.22, 26.59.



1'-Acetonaphthone (2y). The product **2y** was obtained via the general procedure using 1-(prop-1-en-2-yl) naphthalene **1y** (33.6 mg, 0.2 mmol) and isolated by flash column chromatography as light-yellow oil.

Known compound, spectroscopic data matched those previously reported.[9]

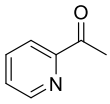
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 8.6 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.92 (dd, *J* = 16.9, 7.7 Hz, 2H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.52 - 7.47 (m, 1H), 2.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.72, 135.44, 134.01, 133.01, 130.19, 128.70, 128.43, 128.04, 126.43, 126.06, 124.35, 29.91.



2-Acetonaphthone (2z). The product **2z** was obtained via the *general procedure* using 2-(prop-1-en-2-yl) naphthalene **1z** (33.6 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 55-57 ^{o}C, spectroscopic data matched those previously reported.[4]

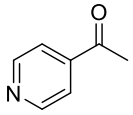
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.07 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.92 (dd, *J* = 8.2, 5.3 Hz, 2H), 7.66 - 7.57 (m, 2H), 2.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.98, 135.60, 134.55, 132.54, 130.13, 129.53, 128.41, 127.76, 126.75, 123.90, 26.60.



2-Acetylpyridine (2α). The product **2α** was obtained via the general procedure using 2-(prop-1-en-2-yl)-3,4-dihydropyridine **1α** (24.2 mg, 0.2 mmol) and isolated by flash column chromatography as brown oil.

Known compound, spectroscopic data matched those previously reported.[11]

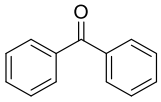
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 2.9 Hz, 1H), 7.87 (dd, *J* = 9.1, 2.2 Hz, 1H), 7.68 (dd, J = 8.6, 6.8 Hz, 1H), 7.32 (dd, *J* = 8.7, 4.7 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.67, 153.43, 148.81, 136.59, 126.86, 121.33, 25.46.



4-Acetylpyridine (2β). The product **2β** was obtained via the *general procedure* using 4-(prop-1-en-2-yl) pyridine **1β** (24.2 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[12]

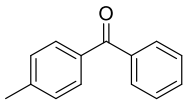
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 4.5, 1.6 Hz, 2H), 7.71 (dd, *J* = 4.4, 1.6 Hz, 2H), 2.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.15, 150.62, 142.55, 121.03, 26.34.



Benzophenone (4a). The product **4a** was obtained via the *general procedure* using ethene-1,1-diyldibenzene **3a** (36.0 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 48-49 ^{o}C, spectroscopic data matched those previously reported.[18]

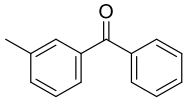
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.62 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.67, 137.63, 132.40, 130.04, 128.28.



4-Methylbenzophenone (4b). The product **4b** was obtained via the *general procedure* using 1-methyl-4-(1-phenylvinyl) benzene **3b** (38.8 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 59-61 ºC, spectroscopic data matched those previously reported.[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.81 (m, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.49 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 196.49, 143.23, 137.97, 134.90, 132.15, 130.30, 129.93, 128.97, 128.21, 21.65.

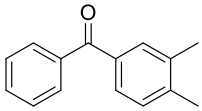


3-Methylbenzophenone (4c). The product **4c** was obtained via the *general procedure* using 1-methyl-3-(1-phenylvinyl) benzene **3c** (38.8 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[20]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.67 (s, 1H), 7.58 (dd, *J* = 15.2, 7.3 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.37 (q, *J* = 7.5 Hz,

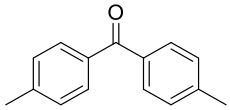
2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.67, 138.09, 137.73, 133.16, 132.30, 130.41, 129.98, 128.17, 127.32, 21.30.



3,4-Dimethylbenzophenone (4d). The product **4e** was obtained via the *general procedure* using 1,2-dimethyl-4-(1-phenylvinyl) benzene **3e** (41.6 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 46-48 ^{o}C, spectroscopic data matched those previously reported.[22]

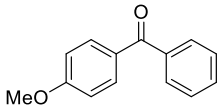
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.67 (s, 1H), 7.60 (dd, *J* = 15.1, 7.8 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.62, 141.91, 138.11, 136.71, 135.33, 132.05, 131.17, 129.90, 129.43, 128.08 , 19.96, 19.71.



4,4'-Dimethylbenzophenone (4e). The product **4e** was obtained in MeCN: H_2O (2:3) via the *general procedure* using 4,4'-(ethene-1,1-diyl) bis(methylbenzene) **3e** (41.6 mg, 0.2 mmol) and isolated by flash column chromatography as a brown solid.

Known compound, mp 95-97 ^{o}C, spectroscopic data matched those previously reported.[21]

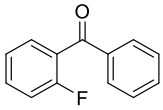
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.18, 142.88, 135.26, 130.16, 128.89, 21.59.



4-Methoxybenzophenone (4f). The product **4f** was obtained in MeCN: H_2O (2:3) via the *general procedure* using 1-methoxy-4-(1-phenylvinyl) benzene **3f** (42 mg, 0.2 mmol) and isolated by flash column chromatography as a yellow solid.

Known compound, mp 60-62 ^{o}C, spectroscopic data matched those previously reported.[18]

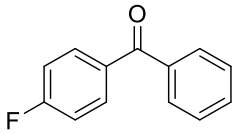
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.45, 163.24, 138.33, 132.51, 131.84, 130.19, 129.68, 128.17, 113.57, 55.46.



2-Fluorobenzophenone (4g). The product **4g** was obtained via the *general procedure* using 1-fluoro-2-(1-phenylvinyl) benzene **3g** (39.6 mg, 0.2 mmol) and isolated by flash column chromatography as colorless oil.

Known compound, spectroscopic data matched those previously reported**.**[23]

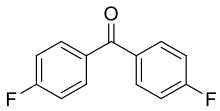
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.81 (m, 2H), 7.50 (dd, *J* = 34.7, 5.9 Hz, 5H), 7.24 (t, *J* = 9.7 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.22, 161.30, 158.79, 137.40, 133.38, 133.04, 130.64, 129.73, 128.46, 127.05, 124.27, 116.31, 116.09.



4-Fluoroacetophenone (4h). The product **4h** was obtained via the *general procedure* using 1-fluoro-4-(1-phenylvinyl) benzene **3h** (39.6 mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[24]

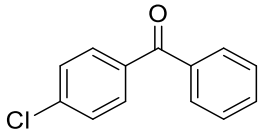
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.16, 166.65, 164.12, 137.55, 133.84, 132.86, 132.30, 129.83, 128.33, 115.46.



Bis (4-fluorophenyl)-methanone (4i). The product **4i** was obtained via the *general procedure* using 4,4'-(ethene-1,1-diyl) bis(fluorobenzene) **3i** (43.2 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 107-109 ^{o}C, spectroscopic data matched those previously reported.[20]

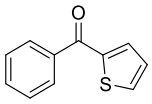
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.21 (t, *J* = 8.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.71, 166.65, 164.12, 133.72, 132.45, 115.63, 115.41.



4-Chlorobenzophenone (4j). The product **4j** was obtained via the *general procedure* using 1-chloro-4-(1-phenylvinyl) benzene **3j** (42.8 mg, 0.2 mmol) and isolated by flash column chromatography as a yellow solid.

Known compound, mp 75-77 ^{o}C, spectroscopic data matched those previously reported.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.79 (m, 4H), 7.65 (t, J = 7.4 Hz, 1H), 7.57 - 7.49 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.38, 138.87, 137.28, 135.91, 132.59, 131.42, 129.89, 128.61, 128.38.

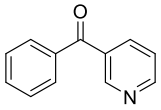


2-benzoylthiophene (4k). The product **4k** was obtained via the *general procedure* using 2-(1-phenylvinyl) thiophene **3k** (37.2mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 -7.89 (m, 2H), 7.77 (d, *J* = 4.9 Hz, 1H), 7.72 - 7.68 (m, 1H), 7.64 (t, J = 6.9 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.22

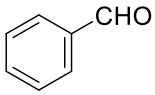
(dd, *J* = 6.6, 3.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.21, 143.63, 138.15, 134.84, 134.20, 132.26, 129.16, 128.41, 127.96.



3-benzoyl pyridine (4l). The product **4l** was obtained via the *general procedure* using 3-(1-phenylvinyl) pyridine **3l** (36.2mg, 0.2 mmol) and isolated by flash column chromatography as yellow oil.

Known compound, spectroscopic data matched those previously reported.[24]

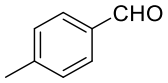
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 - 8.80 (m, 1H), 8.63 (d, *J* = 3.8 Hz, 1H), 8.01 - 7.87 (m, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 5.9 Hz, 1H), 7.38 - 7.22 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.44, 152.63, 150.69, 136.92, 136.56, 132.94, 129.80, 128.43, 123.15.



Benzaldehyde (6a). The product **6a** was obtained in MeCN: H_2O (2:3) via the *general procedure* using styrene **5a** (20.8 mg, 0.2 mmol) and isolated by flash column chromatography as colorless oil.

Known compound, spectroscopic data matched those previously reported.[14]

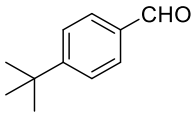
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.84 - 7.80 (m, 2H), 7.58 - 7.52 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H);^{13}C NMR (101 MHz, $CDCl_3$) δ 192.09, 136.39, 134.27, 129.54, 128.88.



p-Tolualdehyde (6b). The product **6b** was obtained in MeCN: H_2O (2:3) via the *general procedure* using 1-methyl-4-vinylbenzene **5b** (23.6 mg, 0.2 mmol) and isolated by flash column chromatography as colorless oil.

Known compound, spectroscopic data matched those previously reported.[15]

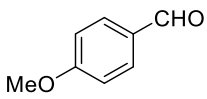
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.77, 145.40, 134.21, 129.67, 21.68.



4-tert-Butylbenzaldehyde (6c). The product **6c** was in MeCN: H_2O (2:3) obtained via the *general procedure* using 1-(tert-butyl)-4-vinylbenzene **5c** (32 mg, 0.2 mmol) and isolated by flash column chromatography as colorless oil.

Known compound, spectroscopic data matched those previously reported**.**[16.]

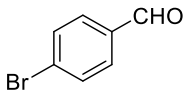
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.81 (d, *J* = 6.2 Hz, 2H), 7.54 (d, *J* = 6.0 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.90, 158.38, 134.13, 129.66, 125.95, 35.30, 31.04.



***p*-Anisaldehyde (6d).** The product **6d** was obtained in MeCN: H_2O (2:3) via the *general procedure* using 1-methoxy-4-vinylbenzene **5d** (26.8 mg, 0.2 mmol) and isolated by flash column chromatography as colorless oil.

Known compound, spectroscopic data matched those previously reported.[16]

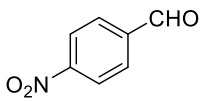
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.72 (d, *J* = 6.2 Hz, 2H), 6.89 (d, *J* = 6.2 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.60, 164.50, 131.79, 129.85, 114.21, 55.40.



4-Bromobenzaldehyde (6e). The product **6e** was obtained in MeCN: H_2O (2:3) via the *general procedure* using 1-bromo-4-vinylbenzene **5e** (36.4 mg, 0.2 mmol) and isolated by flash column chromatography as a white solid.

Known compound, mp 65-68 ^{o}C, spectroscopic data matched those previously reported**.**[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.03, 135.09, 132.43, 130.96, 129.75.



4-Nitrobenzaldehyde (6f). The product **6f** was obtained in MeCN: H_2O (2:3) via the *general procedure* using 1-nitro-4-vinylbenzene **5f** (29.8 mg, 0.2 mmol) and isolated by flash column chromatography as a yellow solid. Known compound, mp 104-106 ^oC, spectroscopic data matched those previously reported.[16]

^1H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.43 (d, J = 8.6 Hz, 2H), 8.11 (d, J = 8.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.25, 151.14, 140.05, 130.47, 124.30.

References

[1] T. Yamase, N. Takabayashi, M. Kaji. *J. Chem. Soc., Dalton Trans*. 1984, **1**, 793.

[2] Y. Yuan, X. Shi, W. Liu. *SynLett*. 2011,**4**, 559.

[3] J. W. Ruan. *J. Am. Chem. Soc*. 2008, **130**, 2424.

[4] A. Cunningham, V. Mokal-Parekh, C. Wilson, S. Woodward. *Org. Biomol. Chem*. 2004, **2**, 741.

[5] D. E. Pearson, J. D. Bruton. *J. Org. Chem.* 1954, **19**, 957.

[6] M. Jun. *J. Am. Chem. Soc*. 2005, **127**, 751.

[7] V. Michael, *Org. Biomol. Chem*. 2011, **9**, 5863.

[8] A. G. Babu. *J. Cryst. Growth*, **15**, 3561.

[9] B. Scheiper, M. Bonnekessel, H. Krause, A. Fürstner. *J. Org. Chem.* 2004, **69**, 3943.

[10] I. J. S. Fairlamb. *Org. Lett*. 2004, **6**, 4435.

[11] N. Tomoya. *Org. Lett*. 2011, **13**, 2576.

[12] W. Pei, J. Mo, J. Xiao. *J. Organomet. Chem*. 2005, **690**, 3546.

[13] J. O. Kyu, H. J. Jung, S. Y. Ji, K. L. Chang. *J. Heterocyclic. Chem*. 2003, **40**, 763.

[14] S. W. Lee, K. Lee, D. Seomoon, S. Kim, H. Kim, E. Shim, M. Lee, S. Lee, M. Kim, P. H. Lee. *J. Org. Chem.* 2004, **69**, 4852.

[15] M. L. N. Rao, V. Venkatesh, D. Banerjee. *Tetrahedron* 2007, **63**, 12917.

[16] G. A. Babu, P. Ramasamy. *J. Cryst. Growth*. 2008, **15**, 3561.

[17] S. K. Murari, S. N. Sriharsha, S. Shashikanth, B. S. Vishwanath. *Bioorg. Med. Chem. Lett.* 2004, **14**, 2423.

[18] M. Li, C. Wang, H. Ge. *Org. Lett.* 2011, **13**, 2062.

[19] O. Chuzel, A. Roesch, J.-P. Genet, S. Darses. *J. Org. Chem.* 2008, **73**, 7800.

[20] L. J. Gooßen, F. Rudolphi, C. Oppel, N. Rodríguez. *Angew. Chem. Int. Ed*. 2008, **47**, 3043.

[21] K. Hayamizu, O. Yamamoto. *J. Mol. Spectrosc*. 1968, **28**, 89.

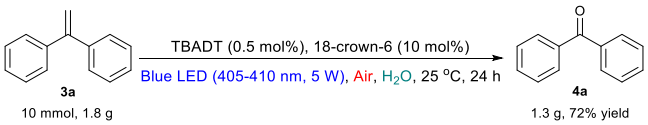
[22] B.C. Hong, H.-C. Tseng, S.-H. Chen. *Tetrahedron* 2007, **63**, 2840.

[23] M. Iinuma, K. Moriyama, H. Togo. *Tetrahedron* 2013, **69**, 2961.

[24] C. Jin, J. P. Burgess, J. A. Kepler, C. E. Cook. *Org. Lett.* 2007, **9**, 1887.

5. The reaction practicability examination.

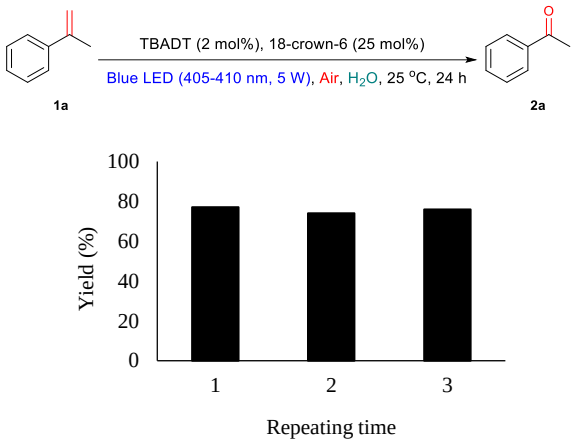
5.1 Gram-scale reaction of 1,1-diphenylethylene



A mixture of 1,1-diphenylethylene (10 mmol， 1.8 g), TBADT (0.5 mol%, 130 mg), 18-crown-6 (10 mol%, 264 mg) and H_2O (20 mL) was added into a round-bottomed flask which was illuminate by blue light (Blue LED, 405-410 nm, 5 W). The reaction mixture was stirred at 25 °C under air for 24 h. After the reaction, 20 ml of ethyl acetate and 2 mL of triethylamine were added, and the mixture was stirred at room temperature for 15 minutes. Extract with 2 x 50 ml ethyl acetate, 2 x 50 ml dichloromethane and dry

with anhydrous magnesium sulfate. After concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel and eluted with EtOAc/petroleum ether to afford benzophenone in 72% yield.

5.2 *Reusability test of the catalytic system*



The reaction was performed according to the general procedure. After 24 h, 1.0 mL of petroleum ether was added. After stirring for another 1 min, the organic layer was removed. After repeating this operation for three times, the organic phase was combined. The yield was determined by GC analysis with *n*-dodecane as internal standard. Then, another 0.2 mmol of *α*-methyl styrene was added to the remaining aqueous solution. The reusability of this process would be tested by repeating the above operations.

5.3 The testing of stability of TBADT

The photoelectrochemical performance of TBADT before and after the reaction was first examined by Cyclic Voltammetry. The results demonstrated that there was no significant decrease of the photoelectrochemical properties of TBADT before and after the reaction.

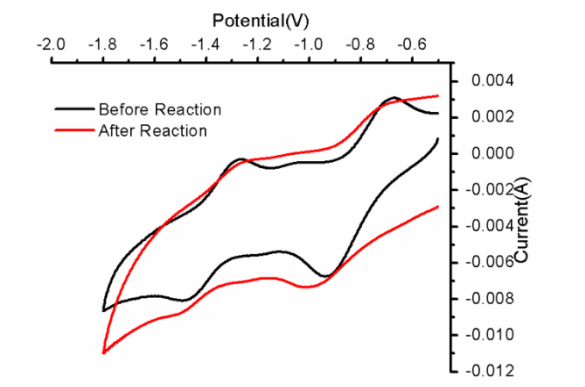


Fig S2. Cyclic voltammograms of TBADT (10 mM) in 0.5 M *n*-Bu_4NPF_6/MeCN at a scan rate of 0.05 Vs^{-1}.

Then, the absorbances of TBADT were also examined. After the reaction, the absorbance of the catalyst decreased slightly, which suggested a slight decomposition of TBADT would take place during the reaction.

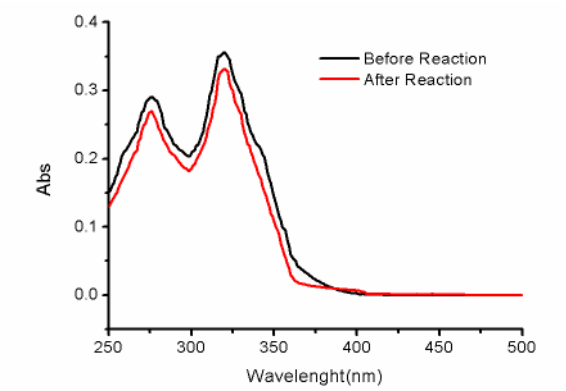
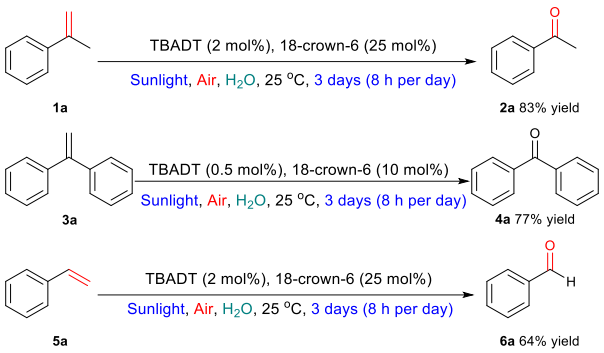


Fig S3. Absorption spectra of TBADT before and after the reaction (0.125 mM in H_2O/CH_3CN)

Both examinations revealed that a slight decomposition happened during the reaction, but it did not affect the photocatalytic activity of TBADT obviously.

5.4 "Window ledge" experiment

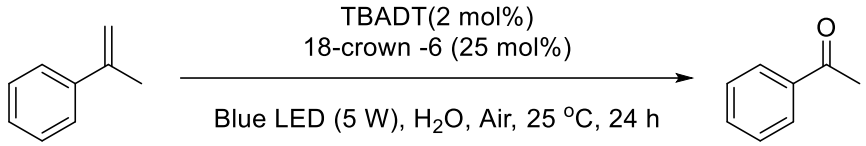


On the sunny day, all reagents were added into a flask and then the mixture was took outside. After stirring for 3 days (8 h per day) under sunlight, the product was generated by flash column chromatography.

6. Mechanistic studies

6.1 Control experiments

To explore the reaction mechanism for our oxidative process, some control experiments were first carried out.



1a **2a**

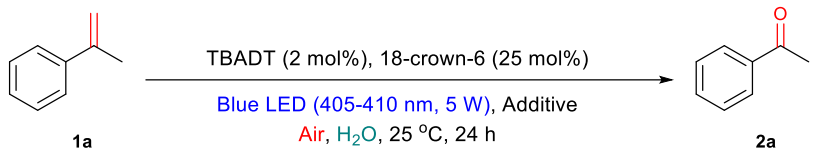
Entry	Additive	Yield (%)
1	No catalyst	No reaction
2	No light	No reaction
3	N_2-atmosphere	No reaction

Reaction condition: **1a** (0.2mmol), TBADT (2 mol%), 18-crown-6 (25 mol%), H_2O (1.0 mL) under air at room temperature (25°C), Blue LED (5 W) for 24 h.

The results demonstrated that light, TBADT catalyst and air, none of these three can be excluded. The absence of anyone lead to the complete inhibition of this oxidative process.

6.2 Radical scavenger effect studies

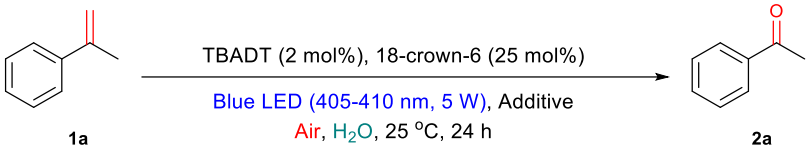
To further investigate the reaction mechanism for this photocatalytic reaction, radical scavengers, such as TEMPO and BHT, were employed in the standard reaction, and the reaction was inhibited obviously. This result suggested that a free radical process might be involved in the present oxidative reaction.



Additive	Yield	Conclusion
BHT (1.0 equiv.)	Trace	Radical process
TEMPO (1.0 equiv,)	Trace	Radical process

6.3 Quenching experiments

Finally, some quenching reagents were subjected to the reaction.



Entry	Quenchers	Equivalent	Yield (%)	Conclusions
1	BHT	1.0	Trace	Radical
2	TEMPO	1.0	Trace	Radical
3	Benzoquinone	1.0	23	superoxide
4	Benzoquinone	2.0	Trace	superoxide
5	DABCO	1.0	41	singlet oxygen
6	DABCO	2.0	36	singlet oxygen
7	DABCO	3.0	Trace	singlet oxygen
8	Soduim azide	1.0	44	singlet oxygen
9	Soduim azide	2.0	42	singlet oxygen
10	Soduim azide	3.0	Trace	singlet oxygen
11	Salicylic acid	1.0	83	No hydroxyl radical involved
12	Salicylic acid	2.0	85	No hydroxyl radical involved
13	*tert*-Butanol	1.0	74	No hydroxyl radical involved
14	*tert*-Butanol	2.0	75	No hydroxyl radical involved

Reaction condition: **1a** (0.2 mmol), TBADT (2 mol%), 18-crown-6 (25 mol%), H_2O (1.0 mL) at room temperature (25 °C), Blue LED (405-410 nm, 5 W) for 24 h.

6.4 On/off light experiments of 1,1-diphenylethylene

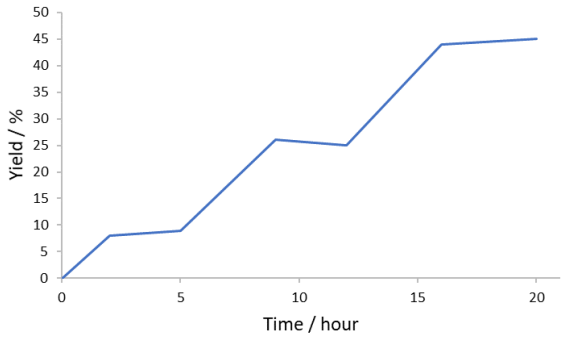
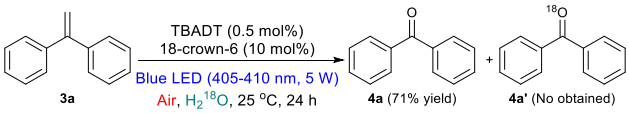


Fig S4. On/off light experiments of 1,1-diphenylethylene

The reaction was performed according to the general procedure. After stirring for 2 hours, the blue LED was turned off. The reaction mixture was keep stirring for 3 hours in the dark. Then turn on the light, continue stirring for 4 hours under the light illumination. Repeating the operations above make the reaction proceeded under light or in dark. The yields were determined by GC analysis with *n*-dodecane as internal standard.

6.5 ^{18}O labeling experiment



The reaction was carried out according to the general procedure, except that $H_2{}^{18}O$ was served as the solvent. After 24 h, no ^{18}O-labelled product was observed by GC-MS.

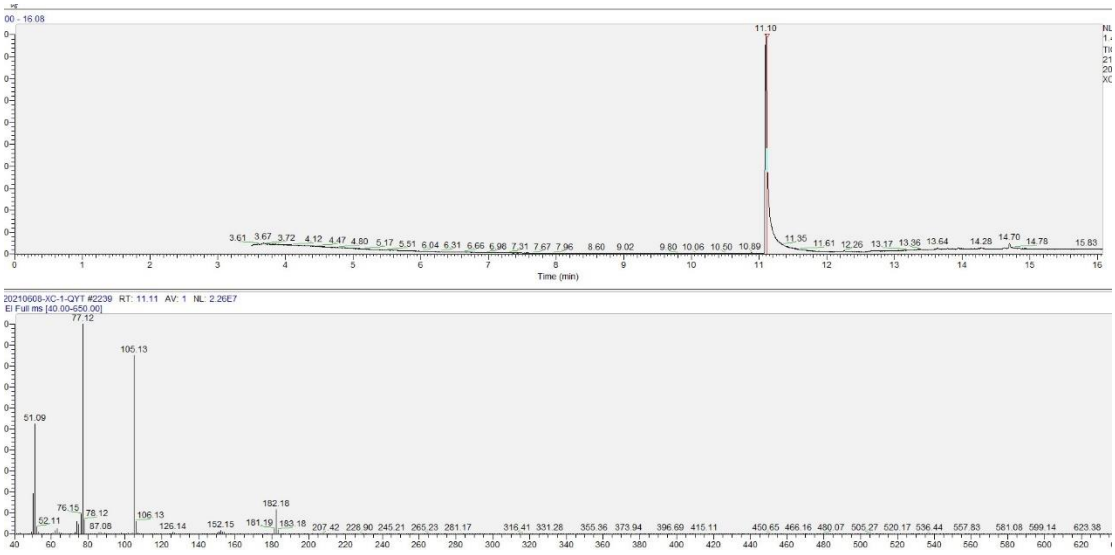


Fig S5. GC-MS spectrum of the product of 3a with $H_2{}^{18}O$ as the solvent

6.6 The testing of HCHO

Firstly, the MBTH method (*Anal. Chem.* 1961, **33**, 93-96) was applied for the testing of HCHO. The testing reagent was produced by mixing 3-methyl-2-benzothiazolone and ammonium ferric sulfate solution. Then one drop of the resulting reaction solution was added to the testing reagent, and the color turned blue very quickly, which, to some extent, demonstrated the presence of HCHO.

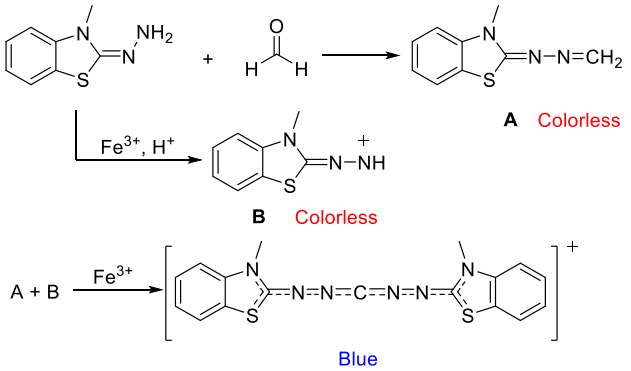


Fig S6. Before adding reaction solution

Fig S7. After adding reaction solution

To further confirm the generation of HCHO in the reaction, one equivalent of 2,4-dinitrophenylhydrazine was added to the reaction system after the reaction finished. Through the column chromatography separation and ^{1}H NMR analysis, we found the generation of formaldehyde hydrazone, which could prove the HCHO was generated in the oxidation reaction process.

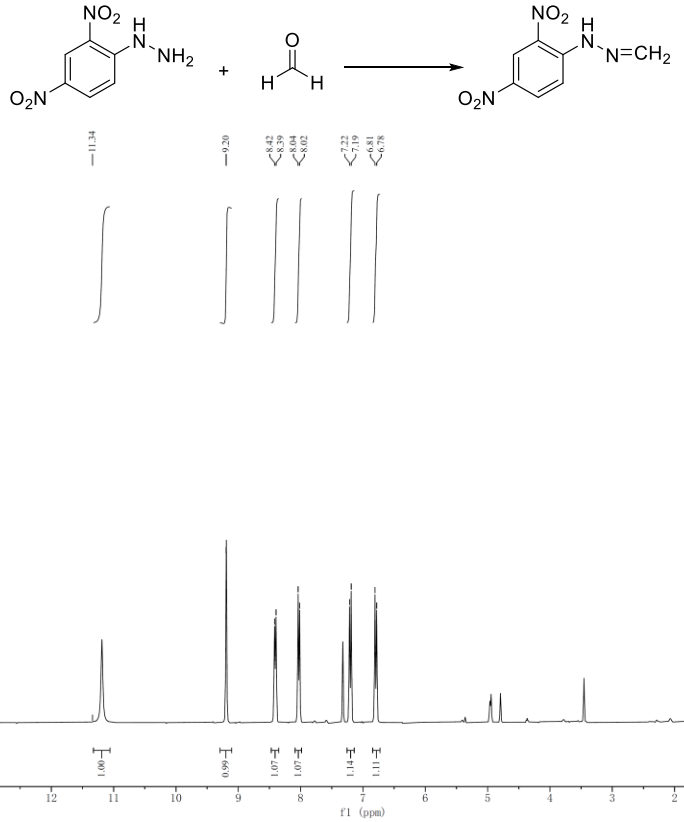
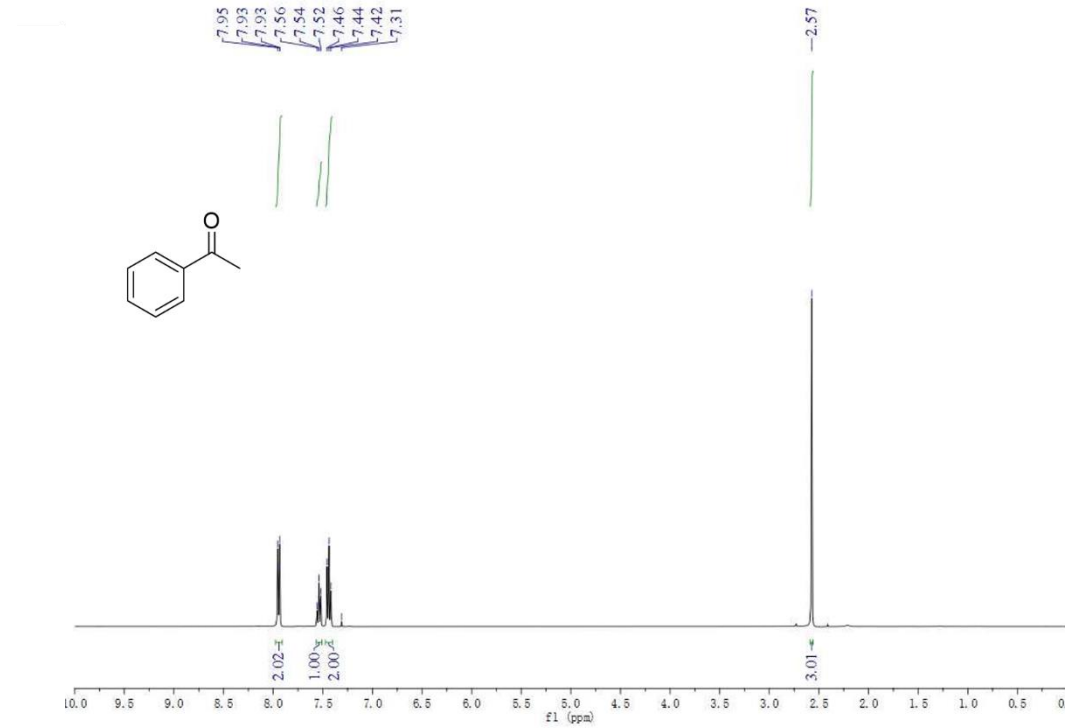


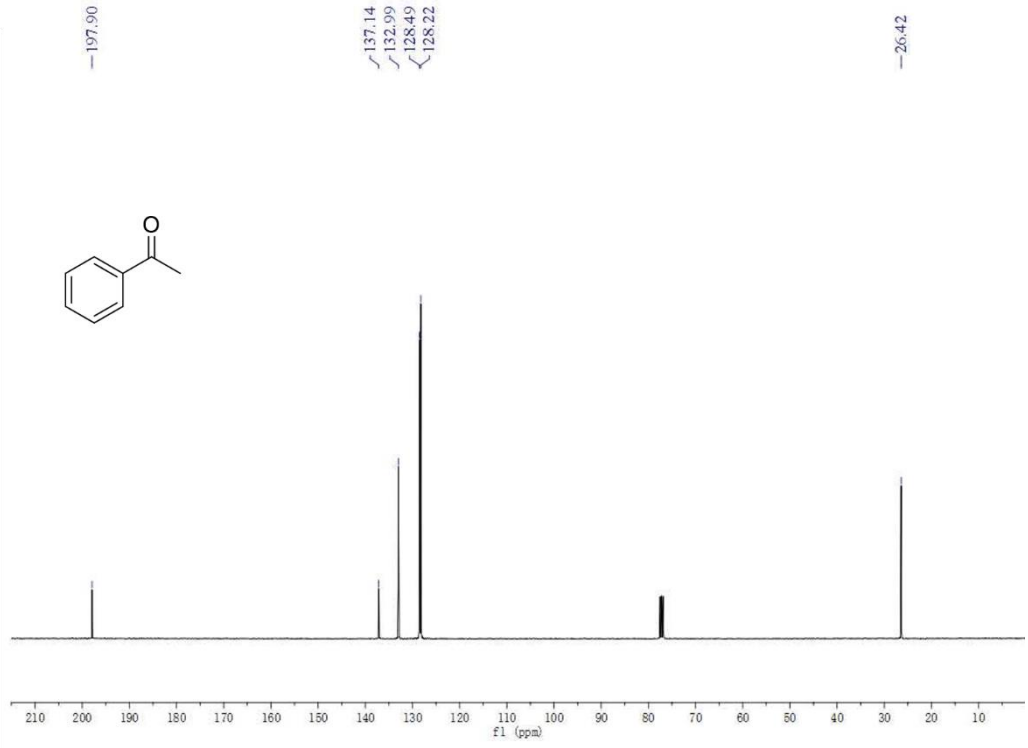
Fig S8. ^{1}H NMR of formaldehyde hydrazone

7. NMR spectra

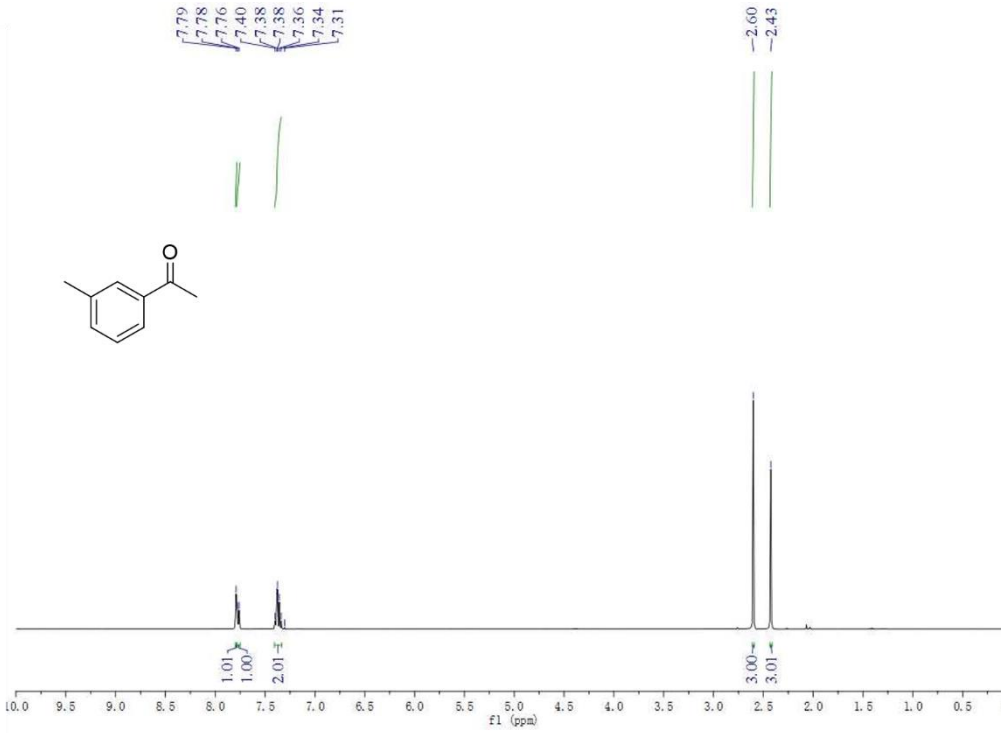
^{1}H NMR spectrum of **2a** in $CDCl_3$ at 400 MHz



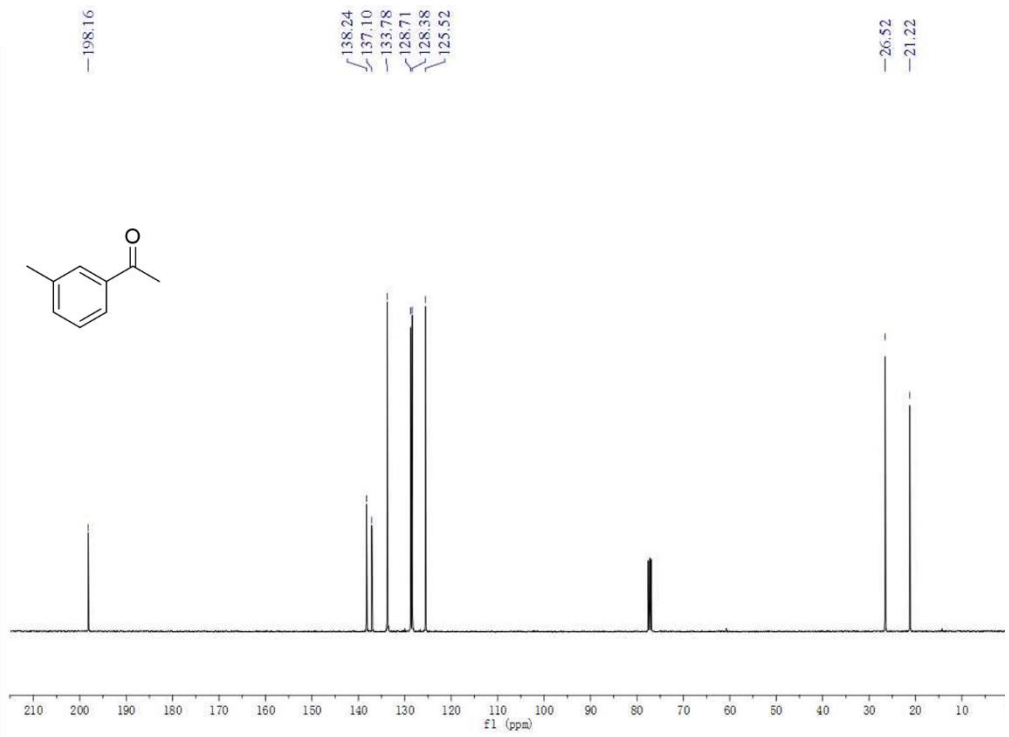
^{13}C NMR spectrum of **2a** in $CDCl_3$ at 101 MHz



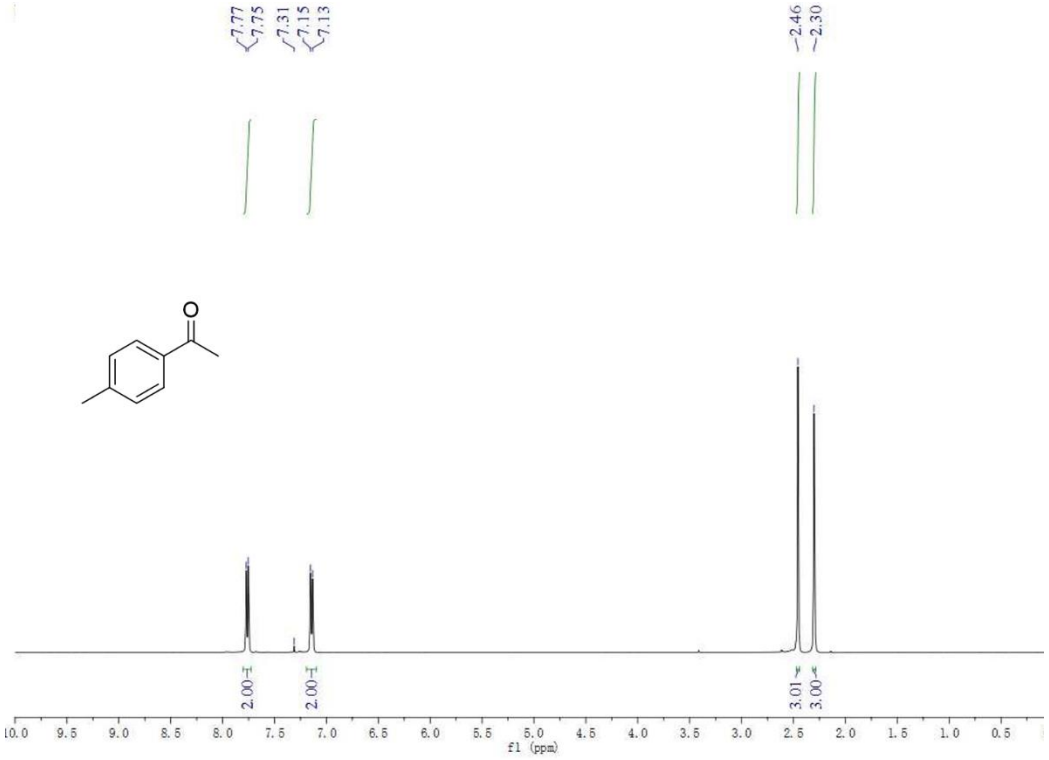
^{1}H NMR spectrum of **2b** in $CDCl_3$ at 400 MHz



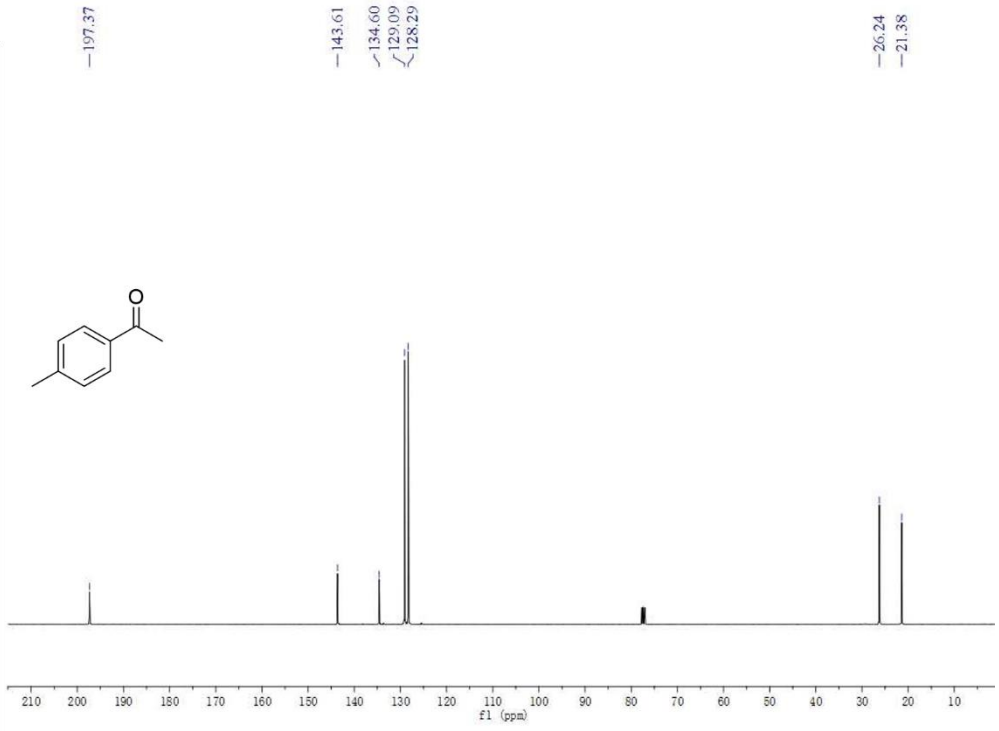
^{13}C NMR spectrum of **2b** in $CDCl_3$ at 101 MHz



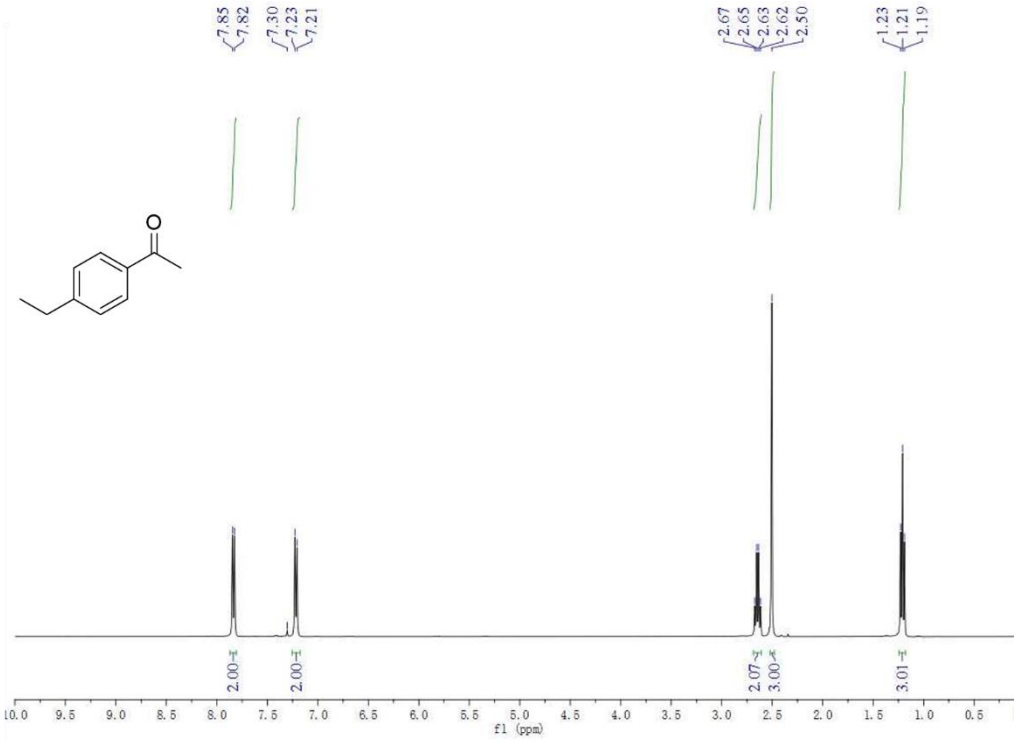
^{1}H NMR spectrum of **2c** in $CDCl_3$ at 400 MHz



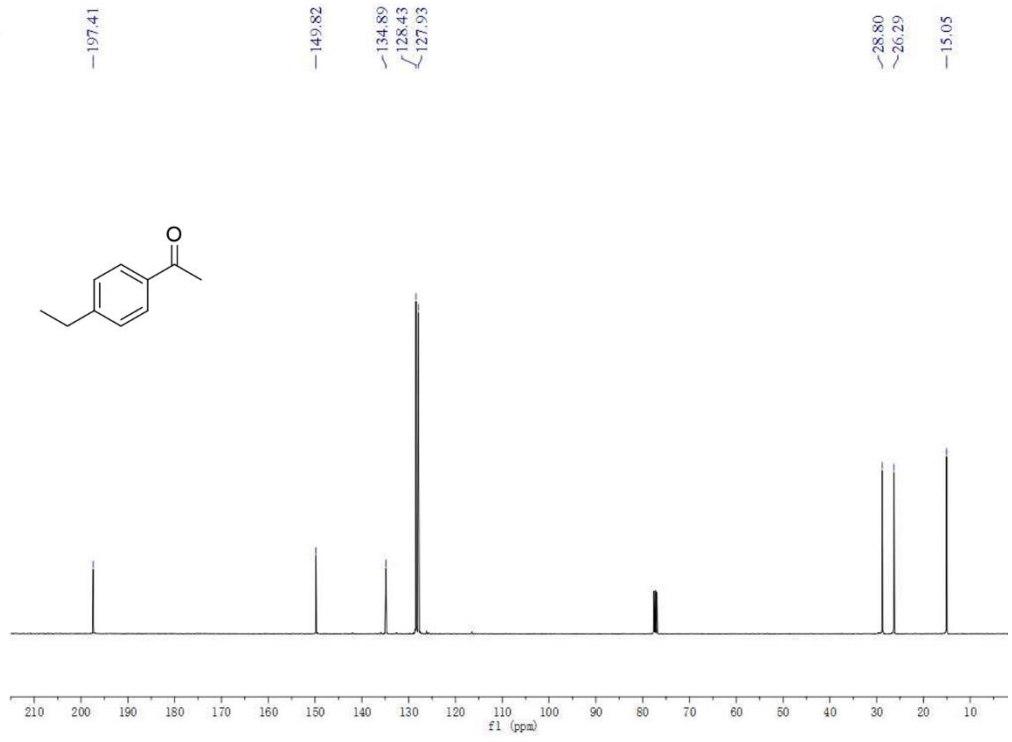
^{13}C NMR spectrum of **2c** in $CDCl_3$ at 101 MHz



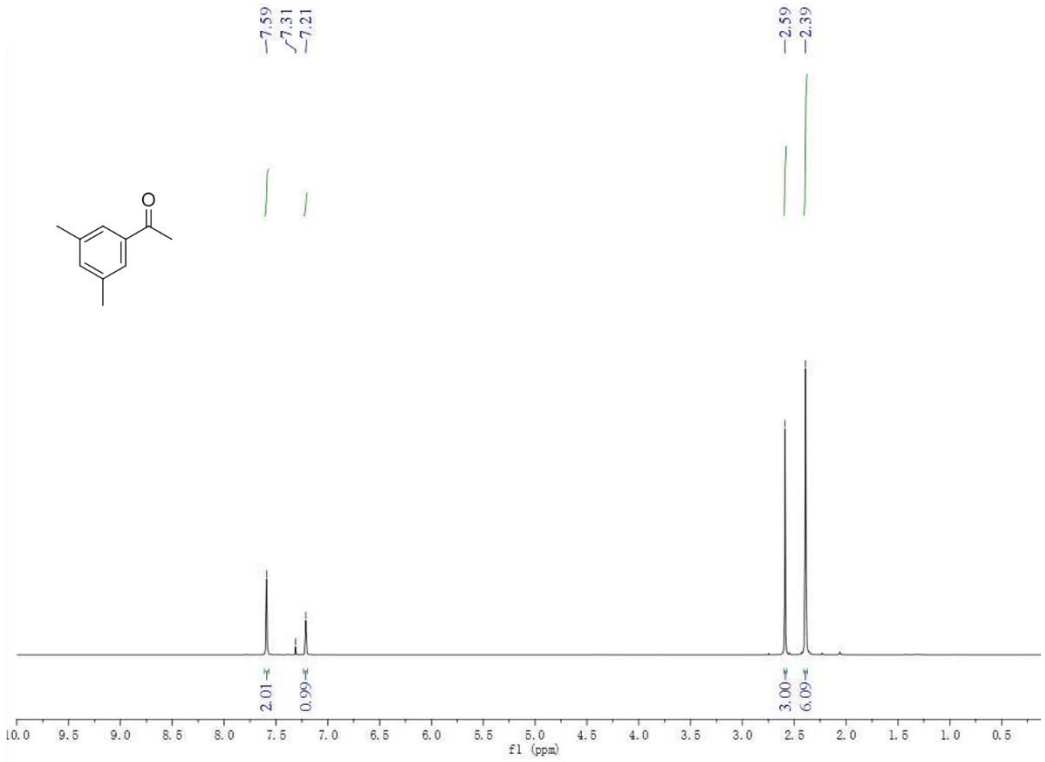
^{1}H NMR spectrum of **2d** in $CDCl_3$ at 400 MHz



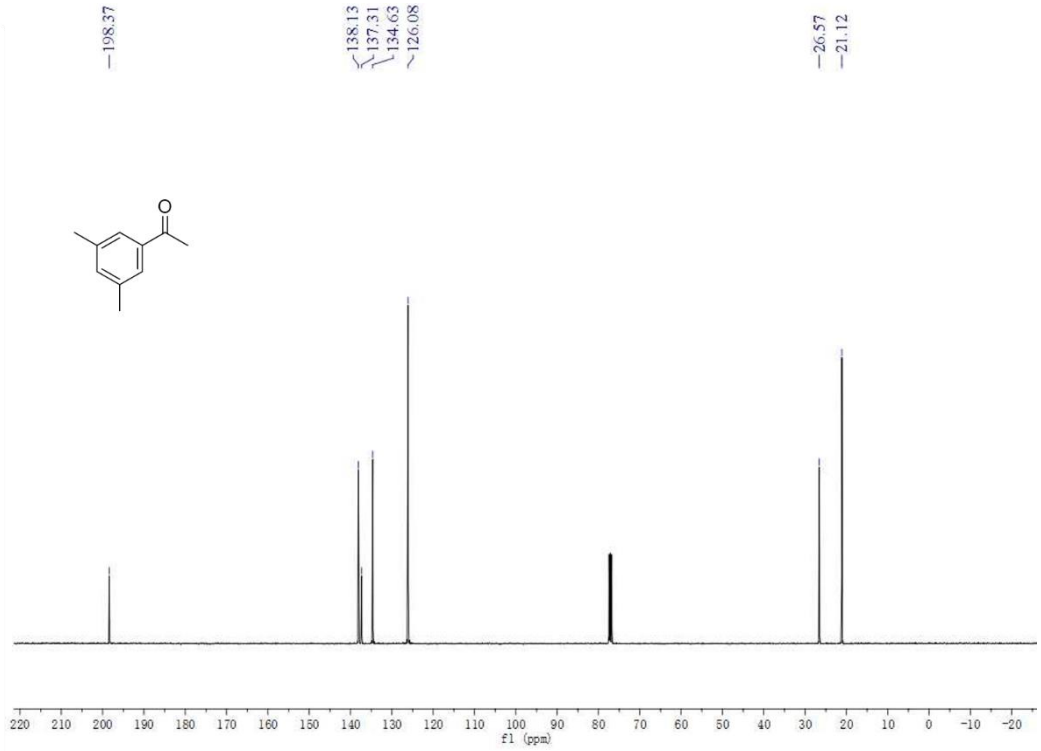
^{13}C NMR spectrum of **2d** in $CDCl_3$ at 101 MHz



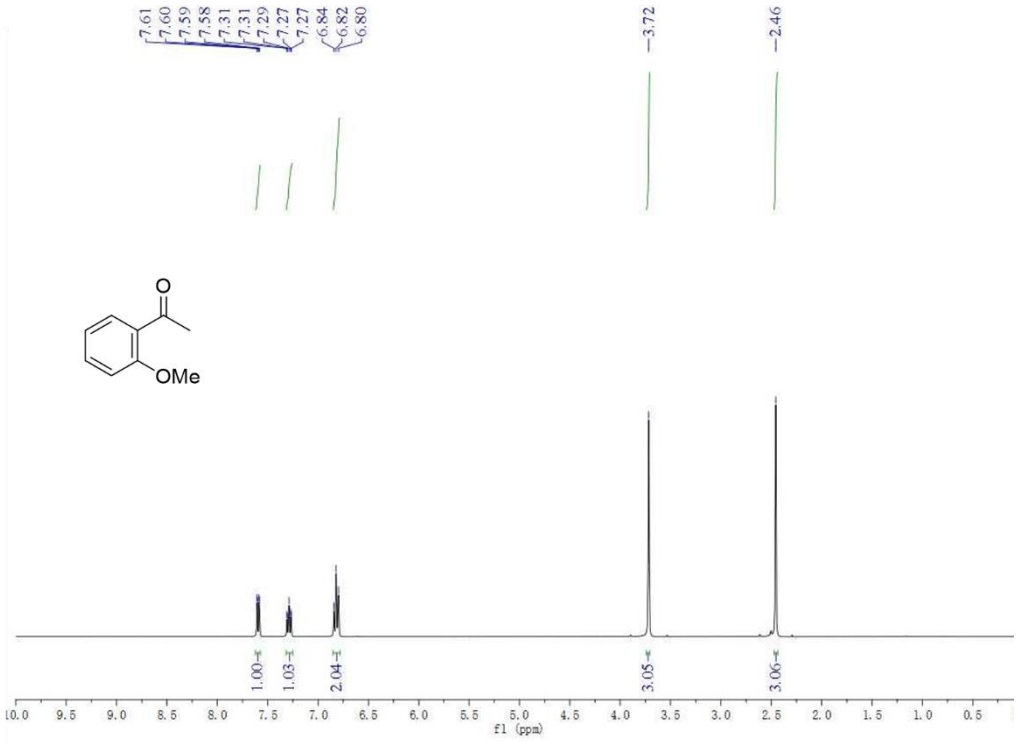
^{1}H NMR spectrum of **2e** in $CDCl_3$ at 400 MHz



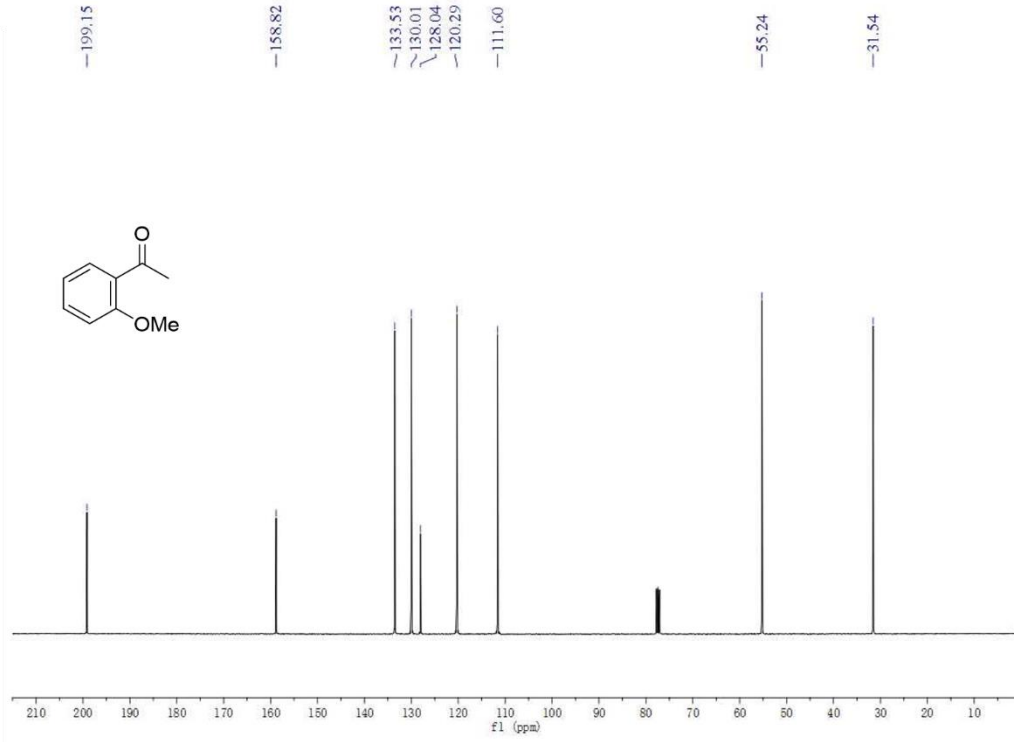
^{13}C NMR spectrum of **2e** in $CDCl_3$ at 101 MHz



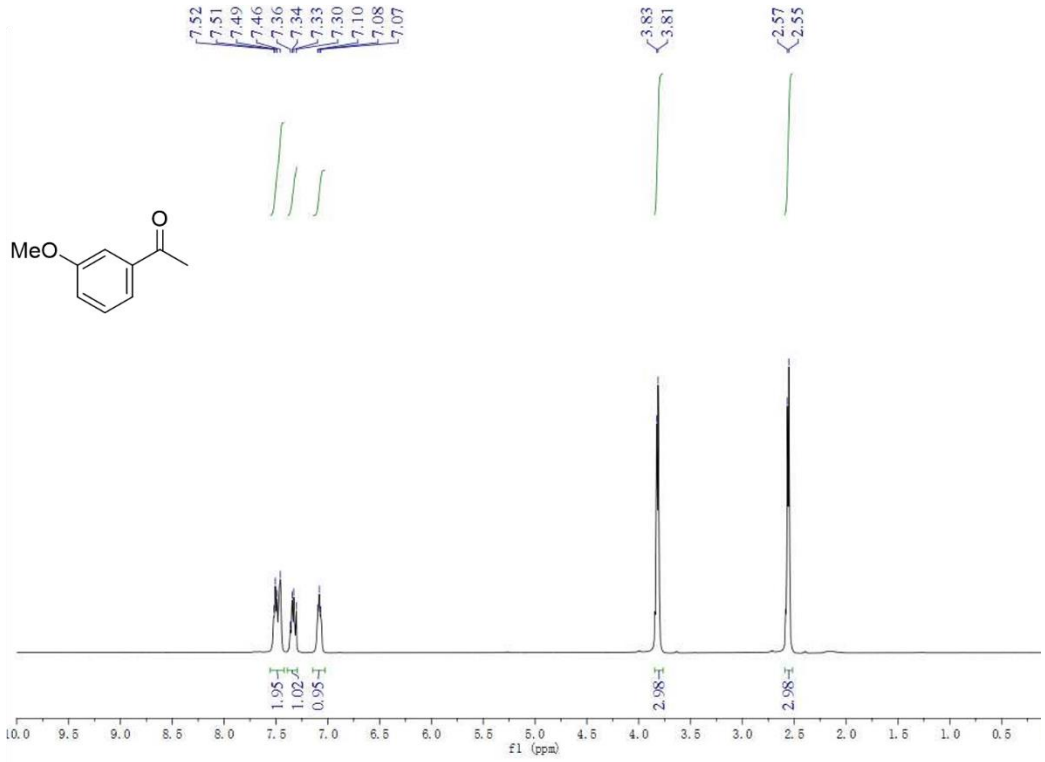
^{1}H NMR spectrum of **2f** in $CDCl_3$ at 400 MHz



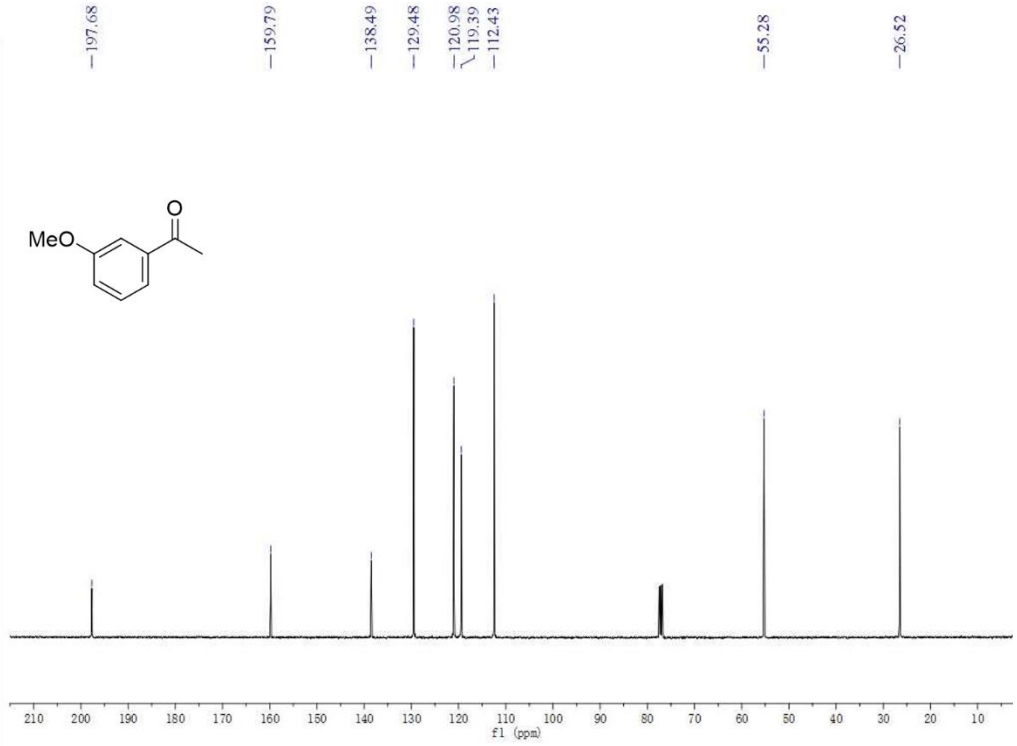
^{13}C NMR spectrum of **2f** in $CDCl_3$ at 101 MHz



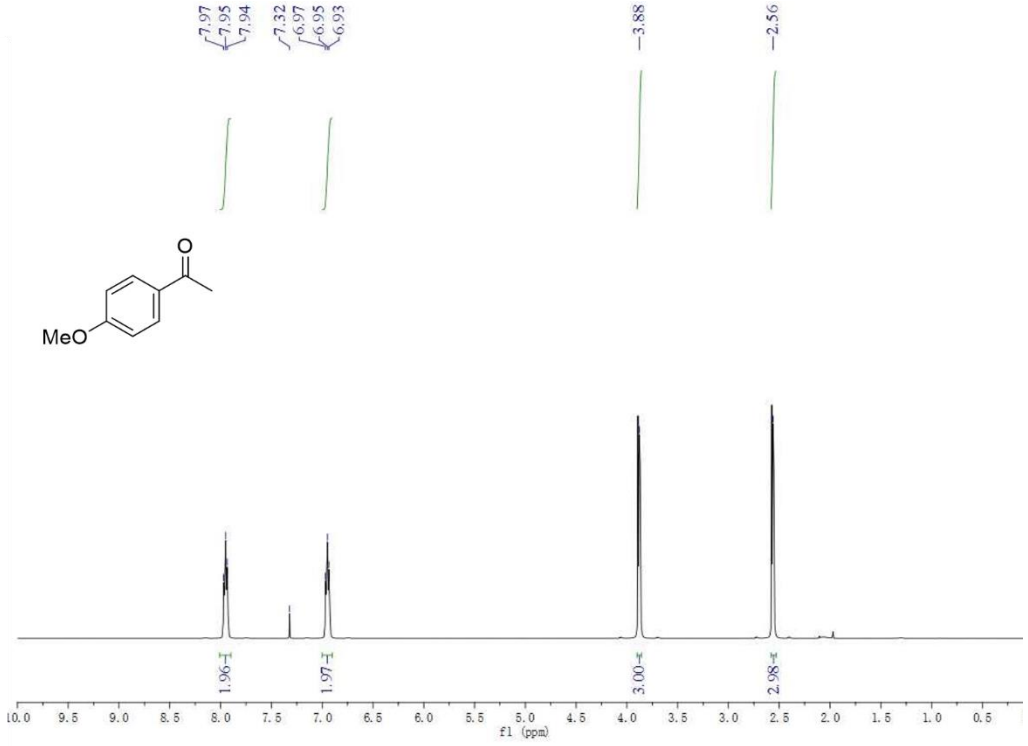
^{1}H NMR spectrum of **2g** in $CDCl_3$ at 400 MHz



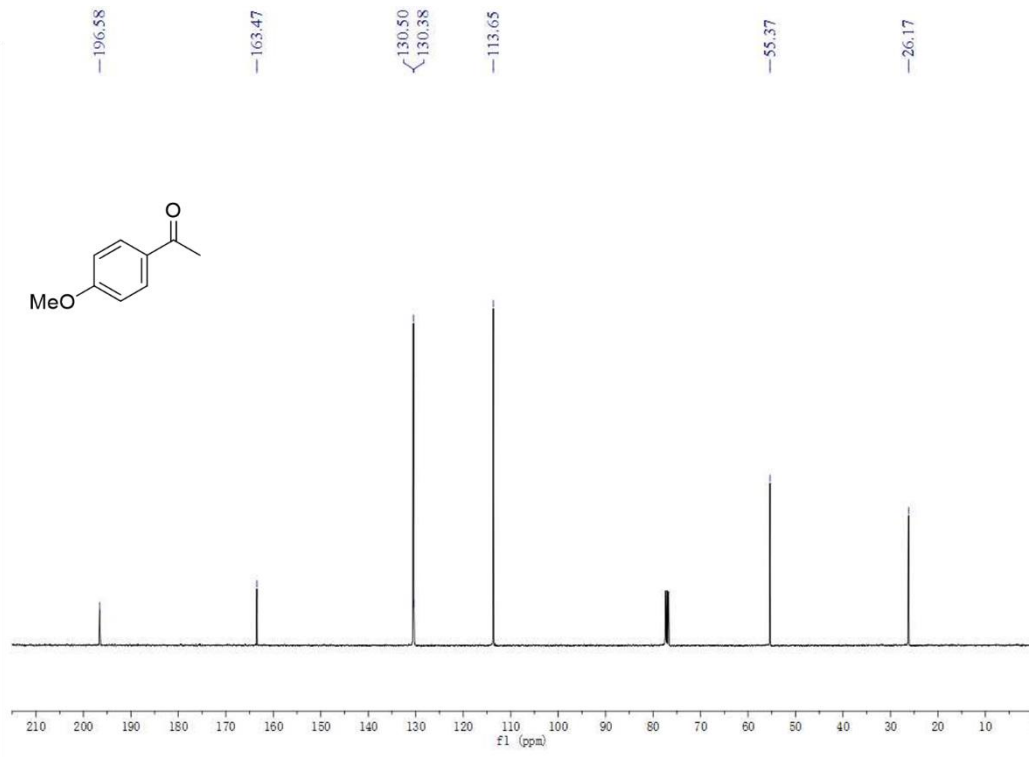
^{13}C NMR spectrum of **2g** in $CDCl_3$ at 101 MHz



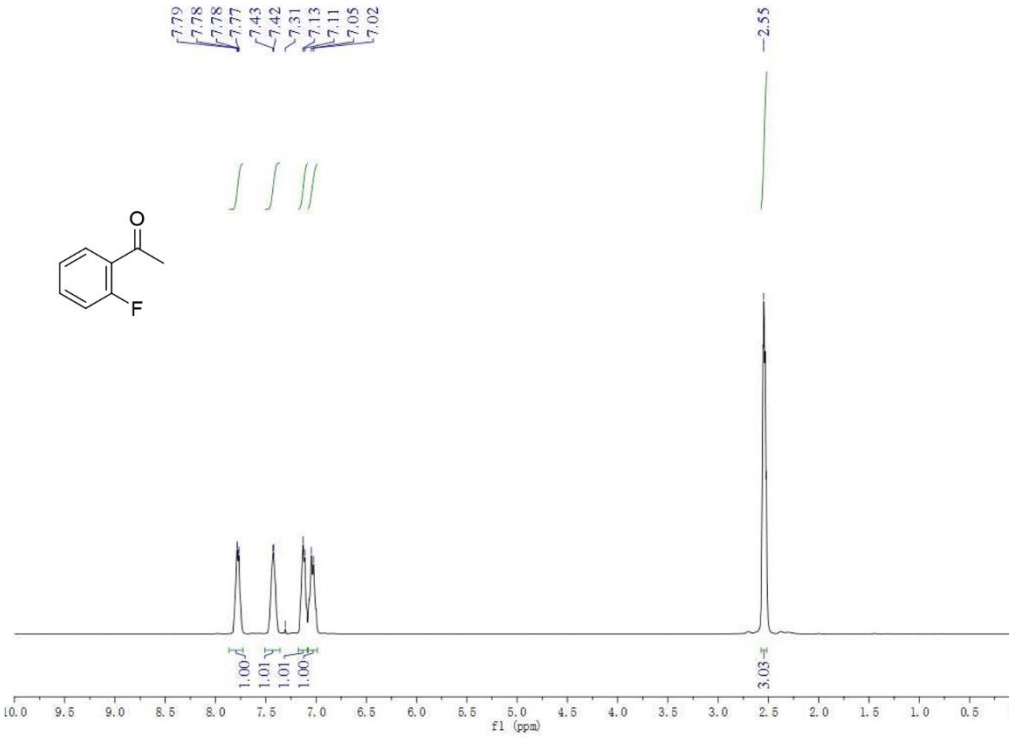
^{1}H NMR spectrum of **2h** in $CDCl_3$ at 400 MHz



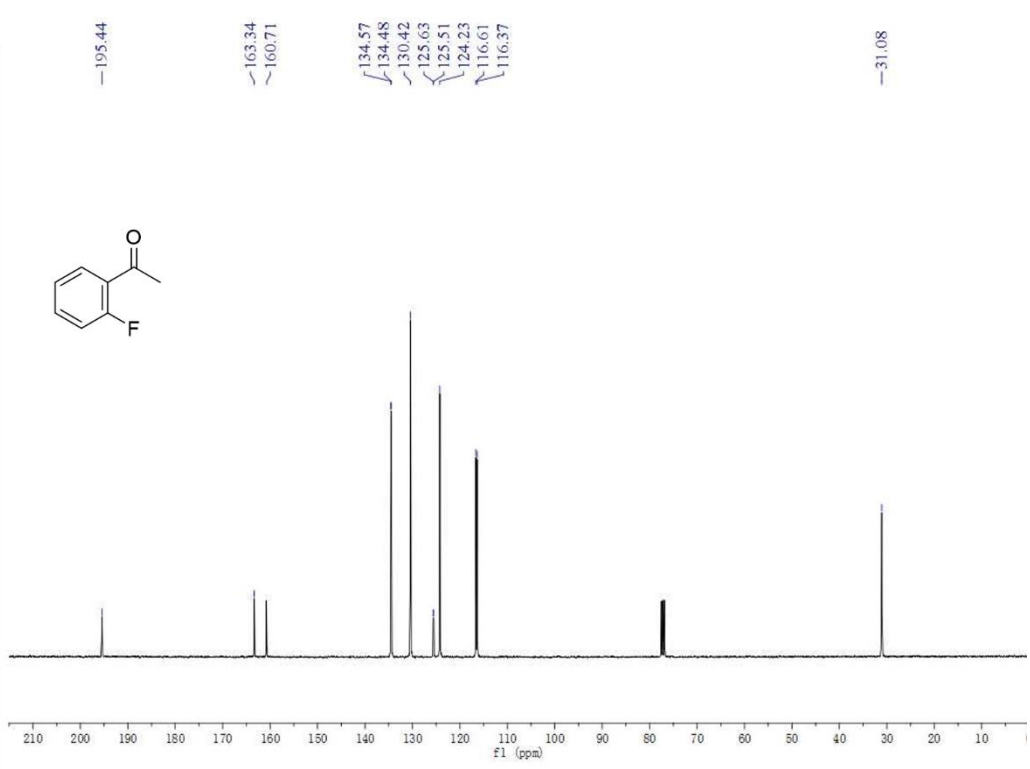
^{13}C NMR spectrum of **2h** in $CDCl_3$ at 101 MHz



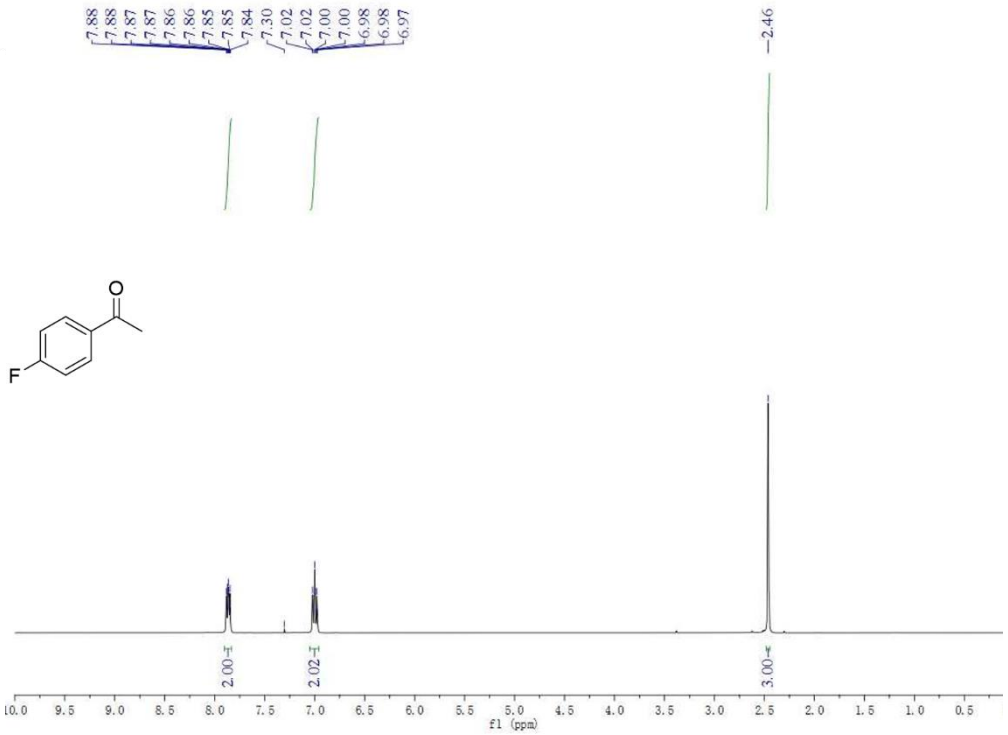
^{1}H NMR spectrum of **2i** in $CDCl_3$ at 400 MHz



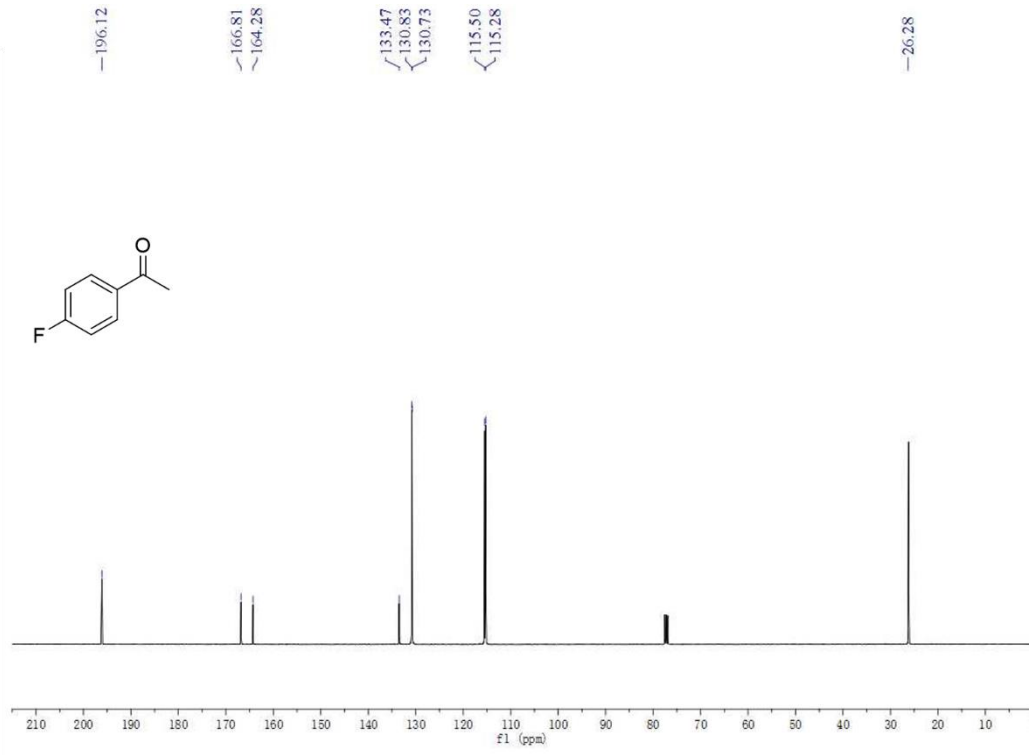
^{13}C NMR spectrum of **2i** in $CDCl_3$ at 101 MHz



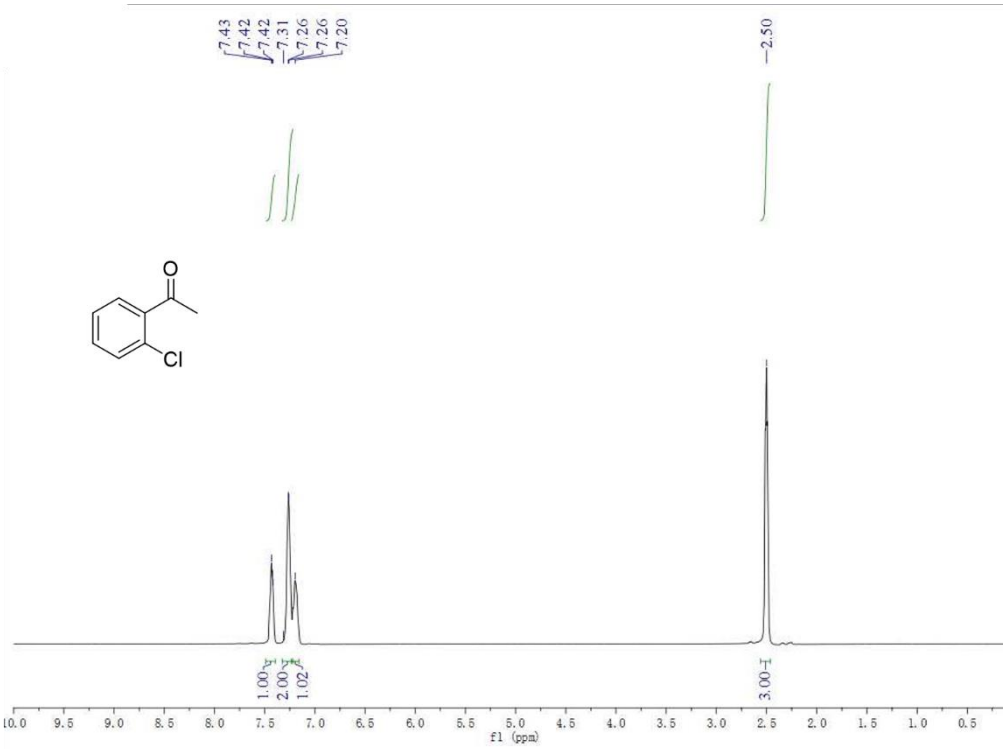
^{1}H NMR spectrum of **2j** in $CDCl_3$ at 400 MHz



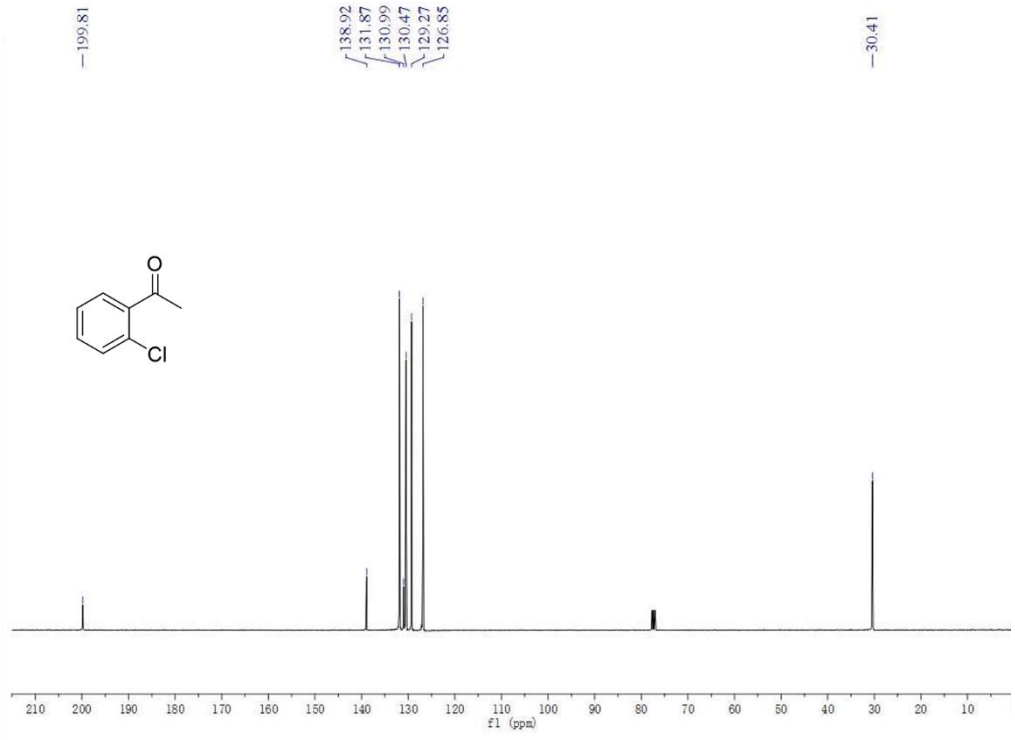
^{13}C NMR spectrum of **2j** in $CDCl_3$ at 101 MHz



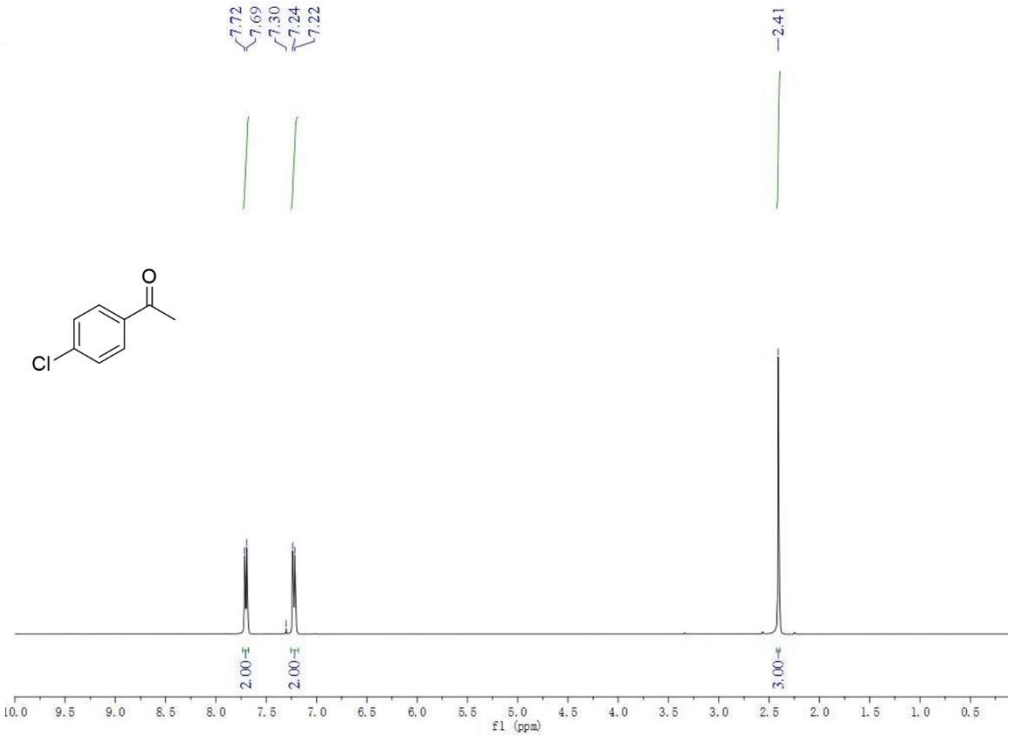
^{1}H NMR spectrum of **2k** in $CDCl_3$ at 400 MHz



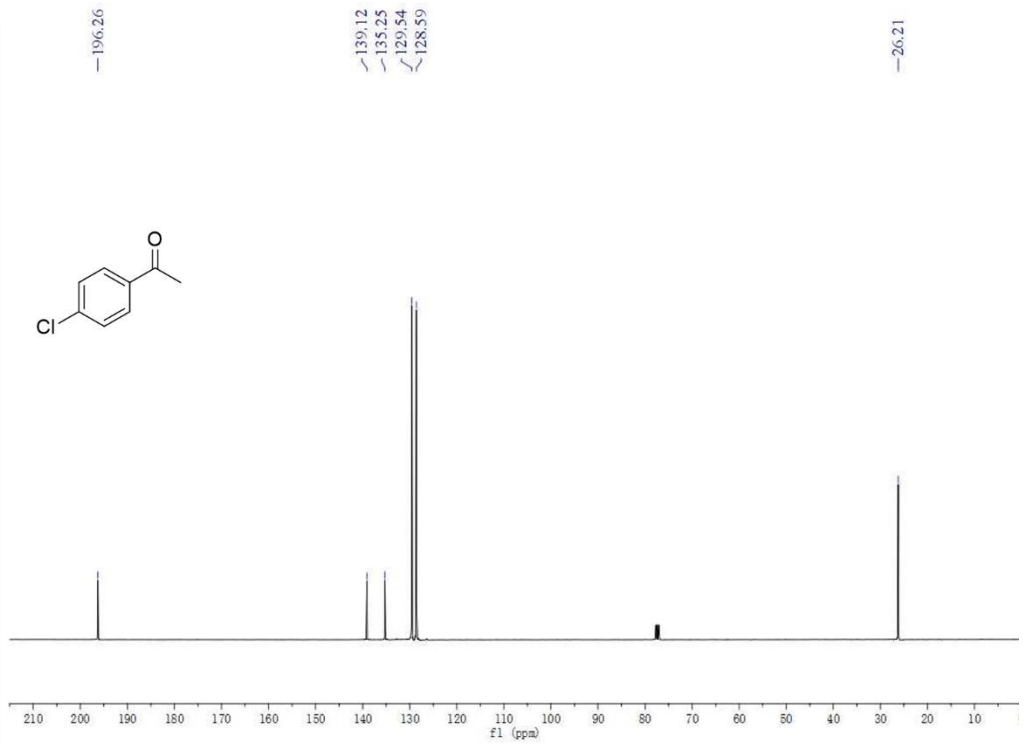
^{13}C NMR spectrum of **2k** in $CDCl_3$ at 101 MHz



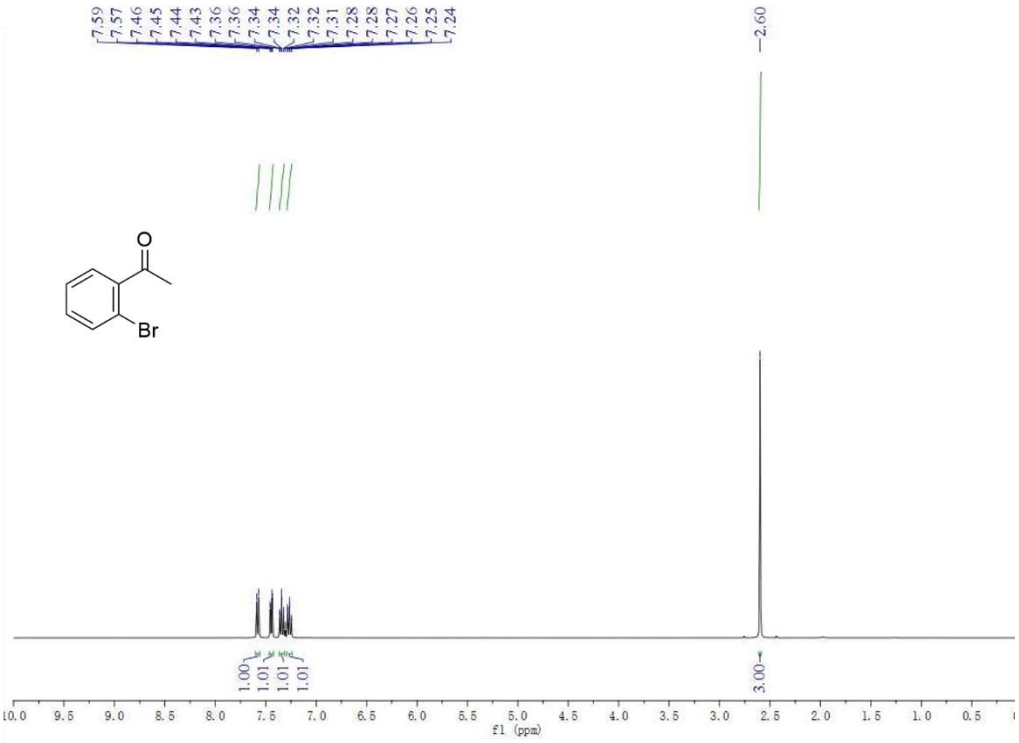
^{1}H NMR spectrum of **2l** in $CDCl_3$ at 400 MHz



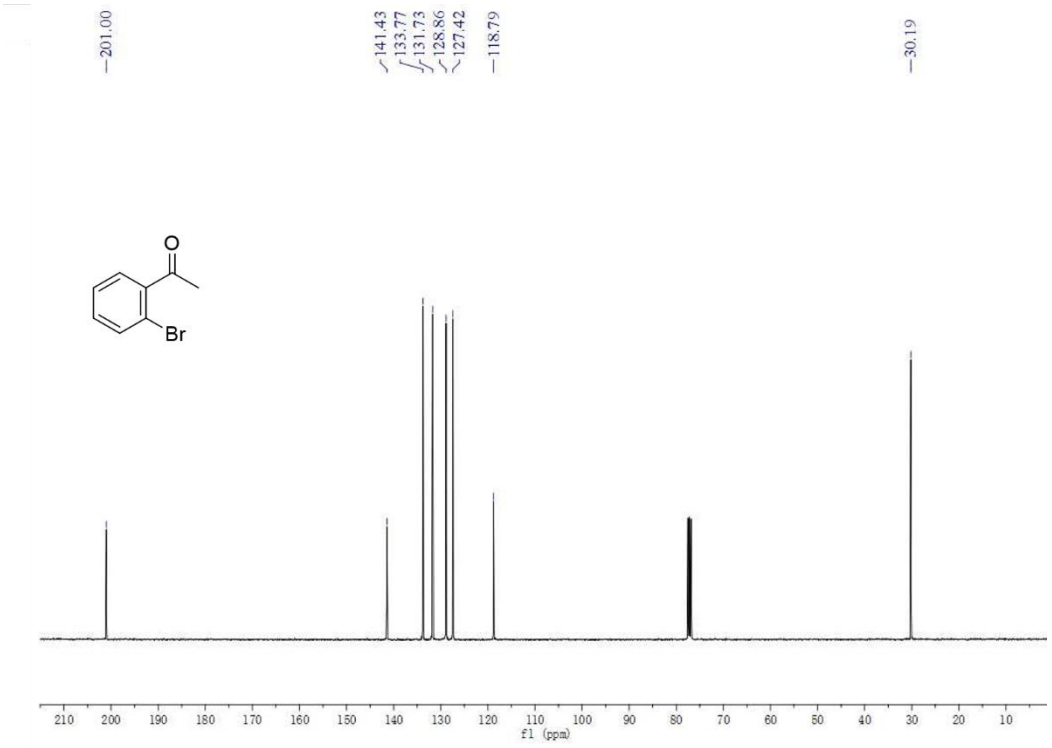
^{13}C NMR spectrum of **2l** in $CDCl_3$ at 101 MHz



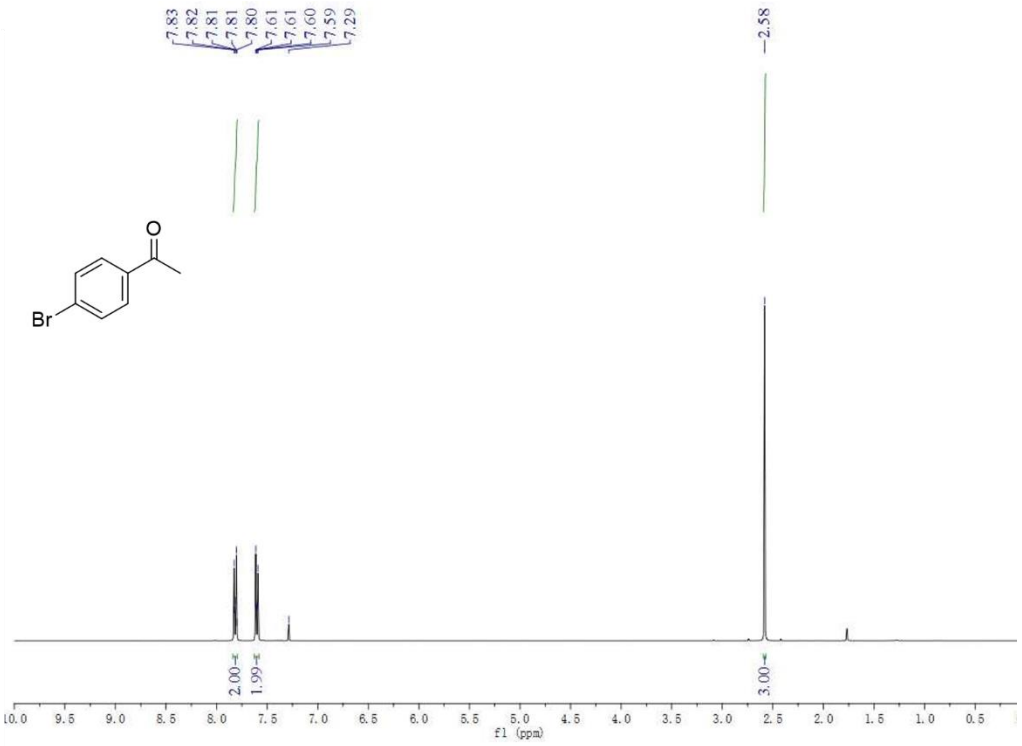
^{1}H NMR spectrum of **2m** in $CDCl_3$ at 400 MHz



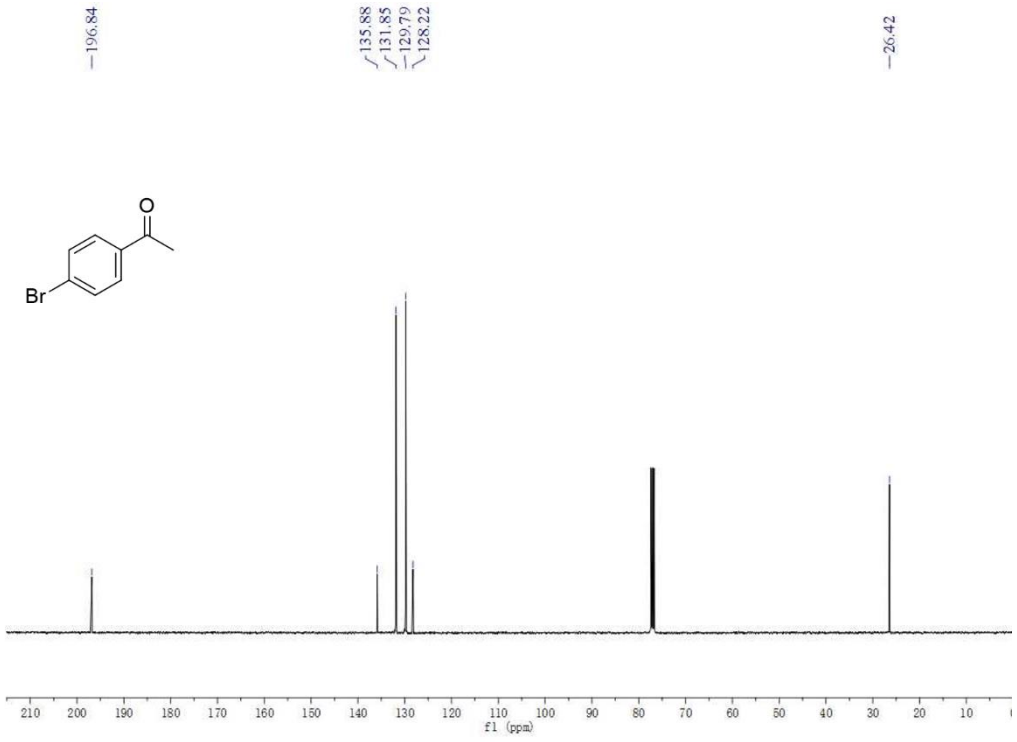
^{13}C NMR spectrum of **2m** in $CDCl_3$ at 101 MHz



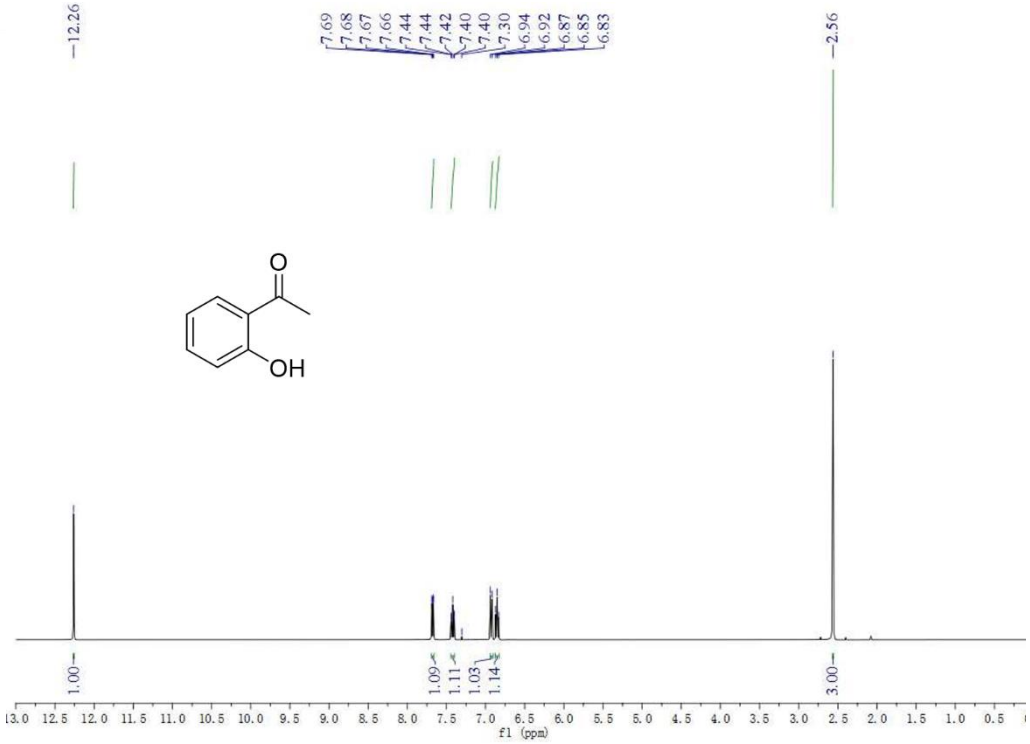
^{1}H NMR spectrum of **2n** in $CDCl_3$ at 400 MHz



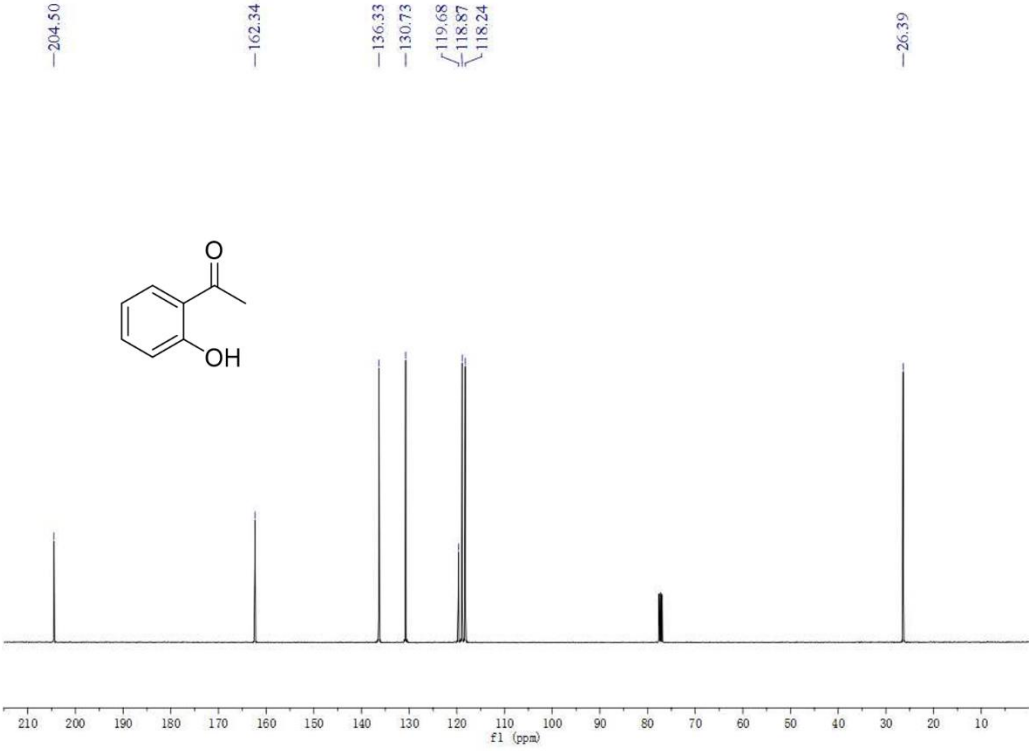
^{13}C NMR spectrum of **2n** in $CDCl_3$ at 101 MHz



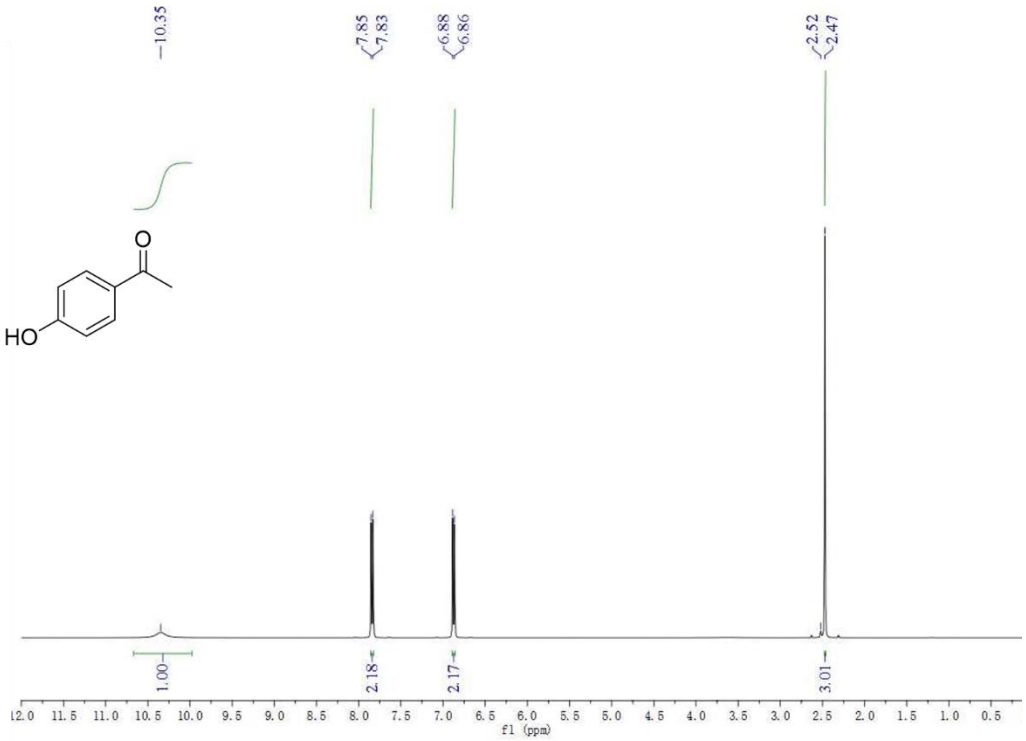
^{1}H NMR spectrum of **2o** in $CDCl_3$ at 400 MHz



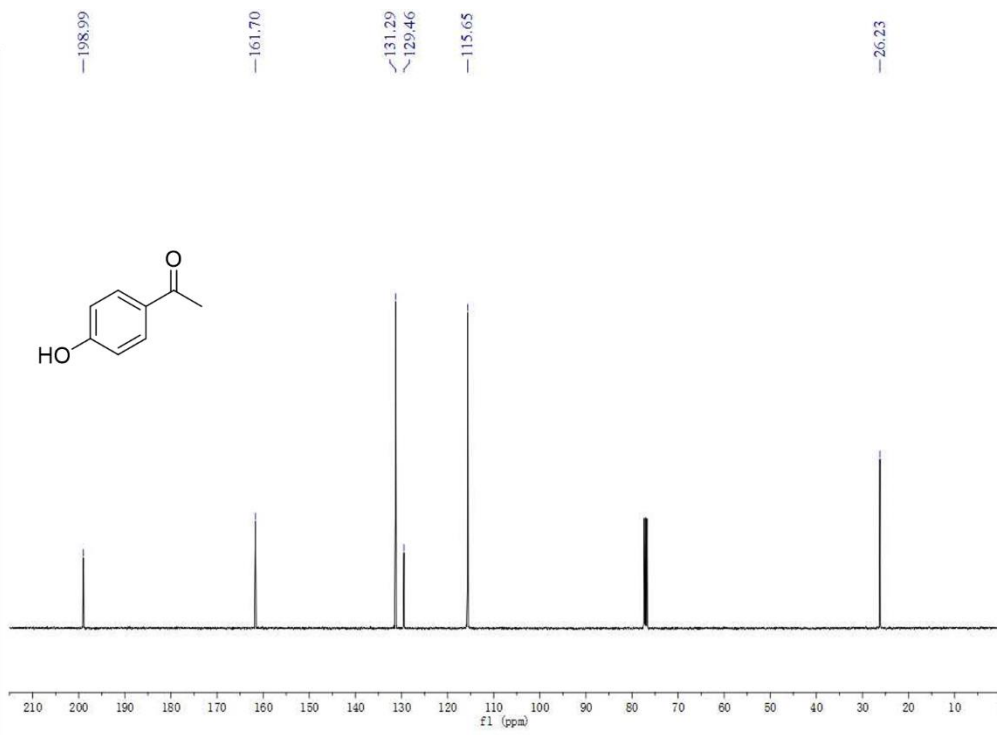
^{13}C NMR spectrum of **2o** in $CDCl_3$ at 101 MHz



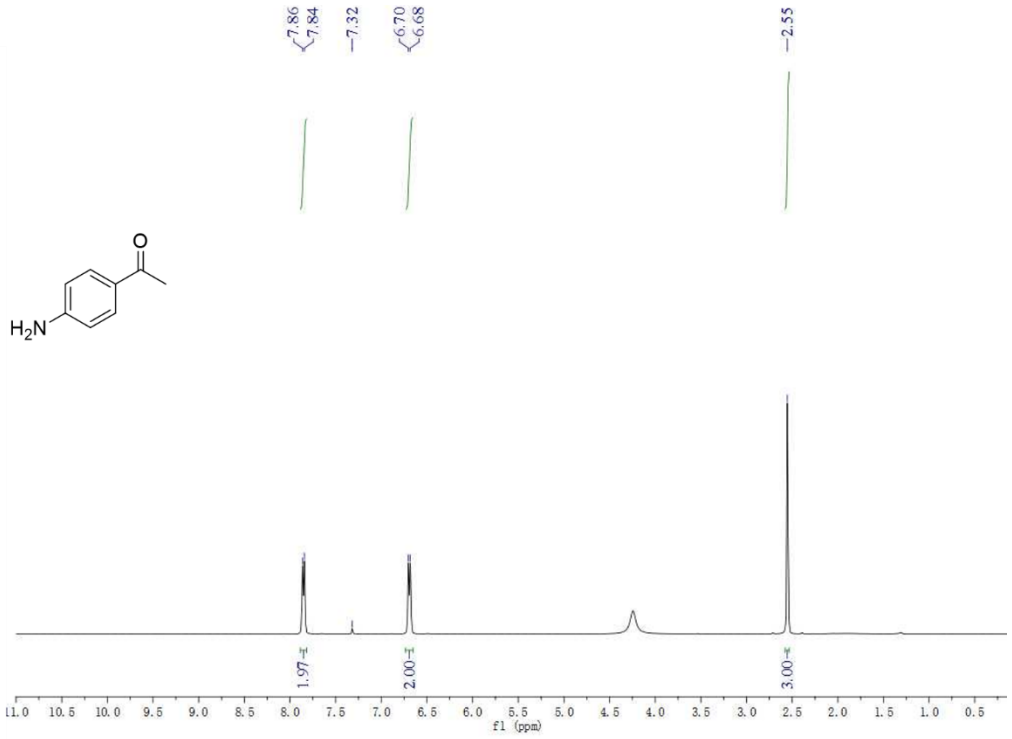
^{1}H NMR spectrum of **2p** in DMSO at 400 MHz



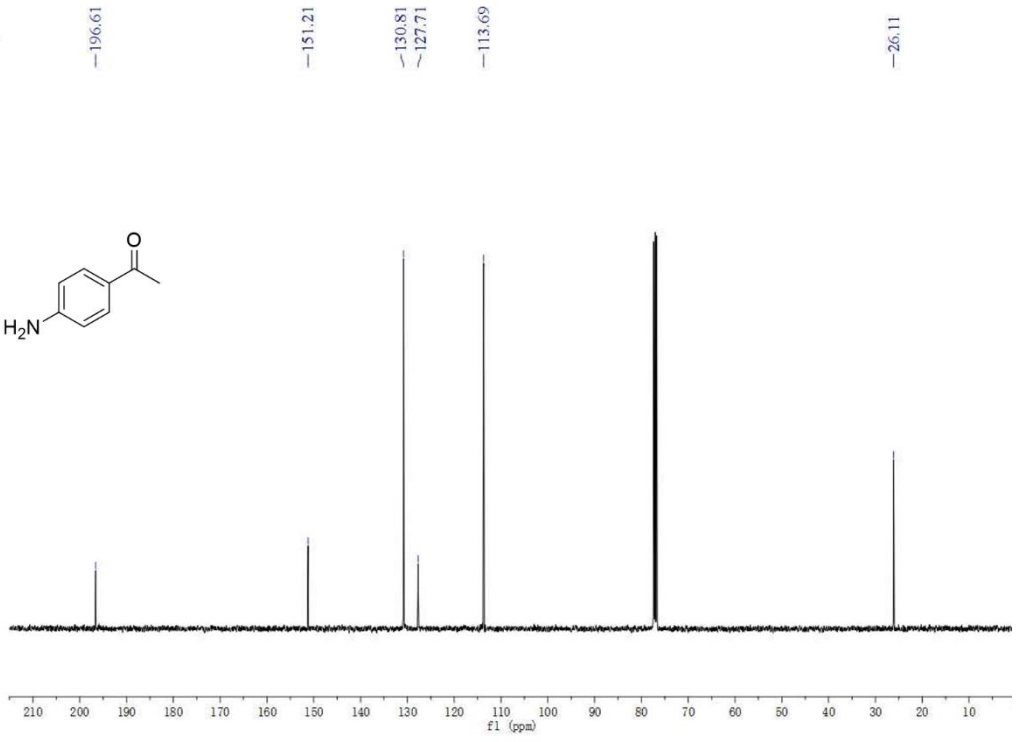
^{13}C NMR spectrum of **2p** in $CDCl_3$ at 101 MHz



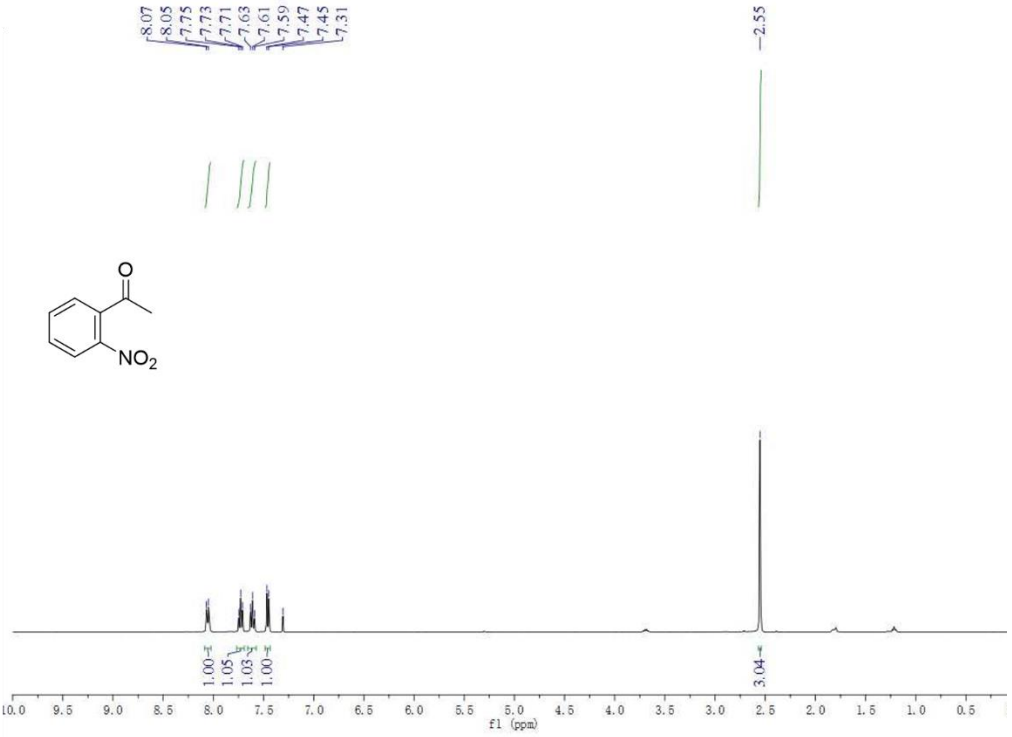
^{1}H NMR spectrum of **2q** in $CDCl_3$ at 400 MHz



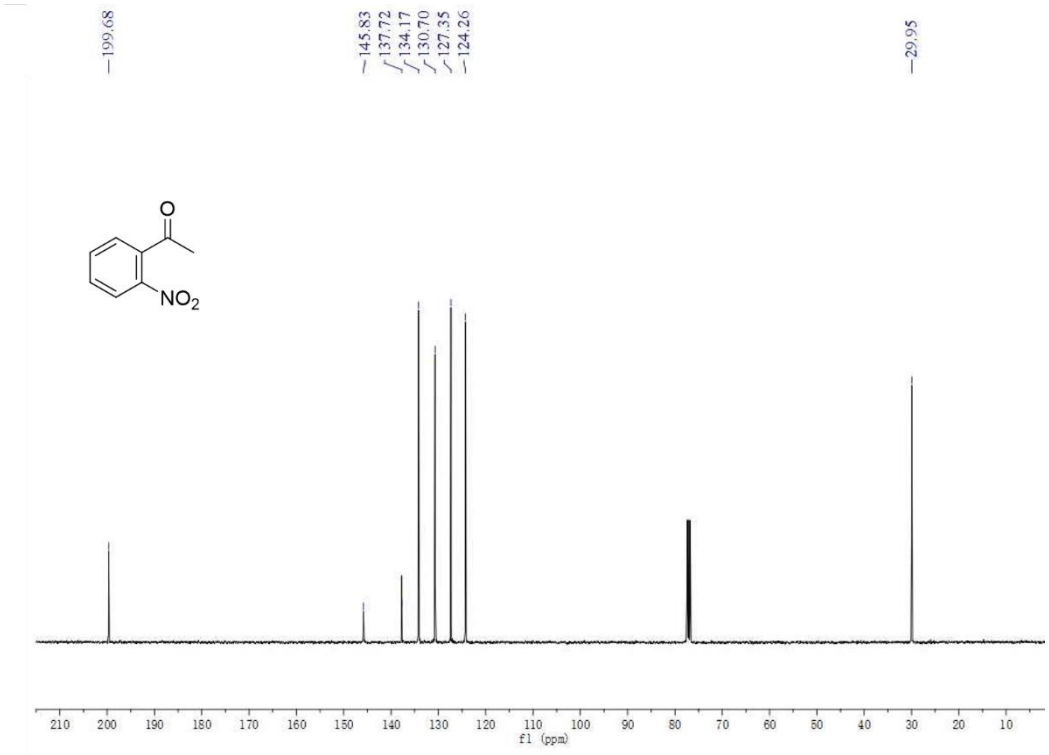
^{13}C NMR spectrum of **2q** in $CDCl_3$ at 101 MHz



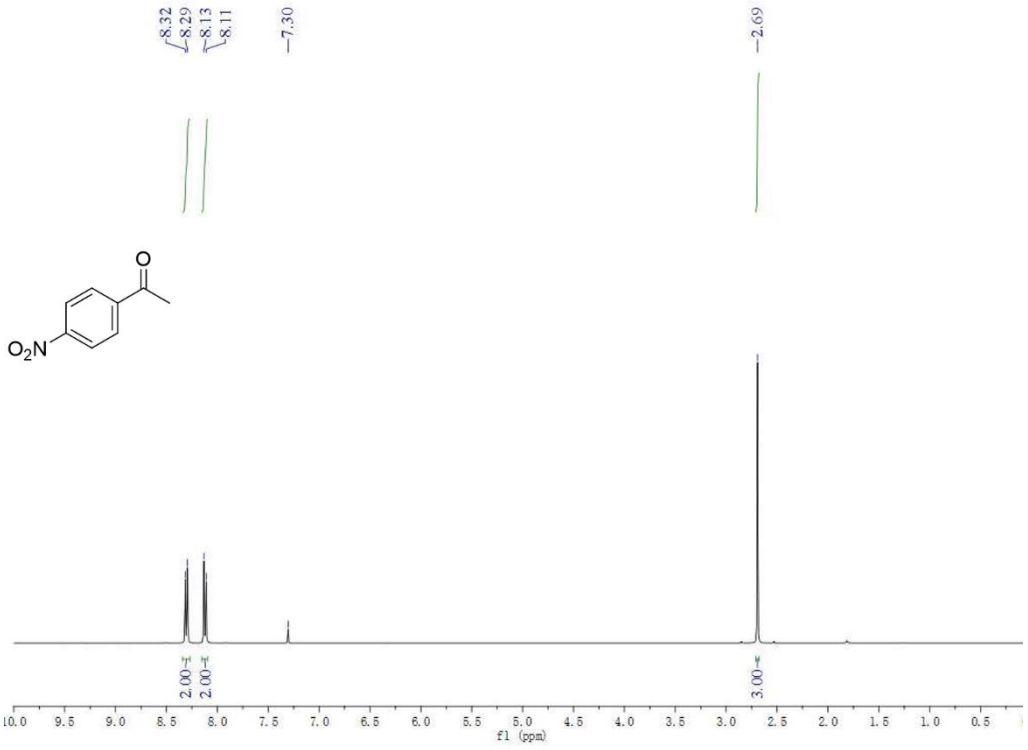
^{1}H NMR spectrum of **2r** in $CDCl_3$ at 400 MHz



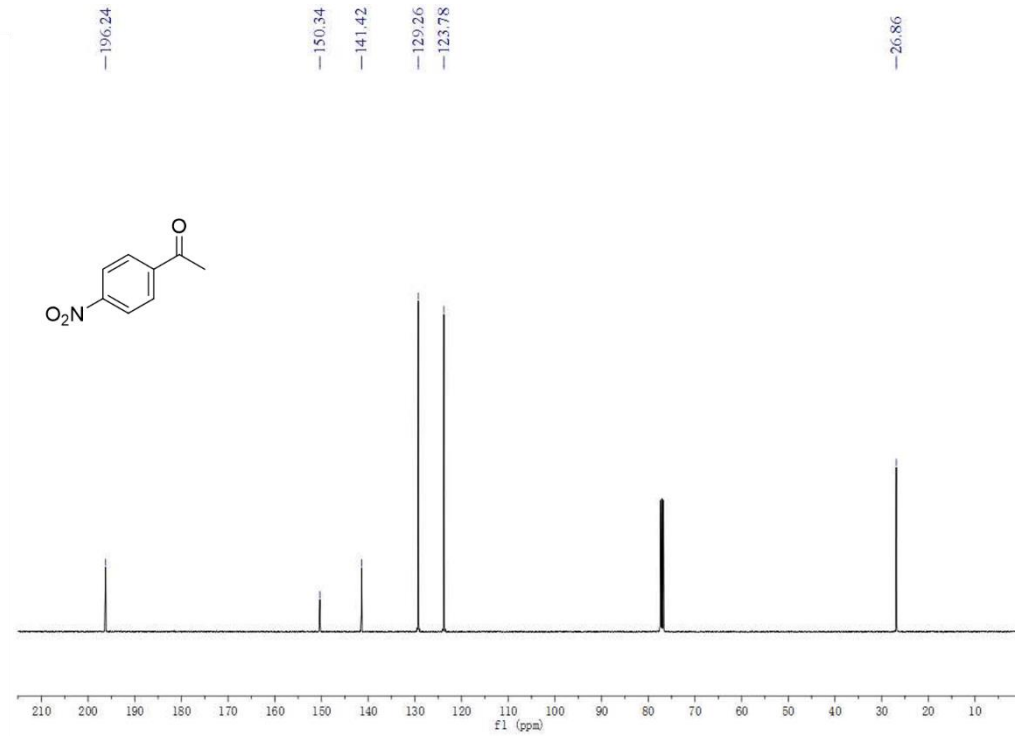
^{13}C NMR spectrum of **2r** in $CDCl_3$ at 101 MHz



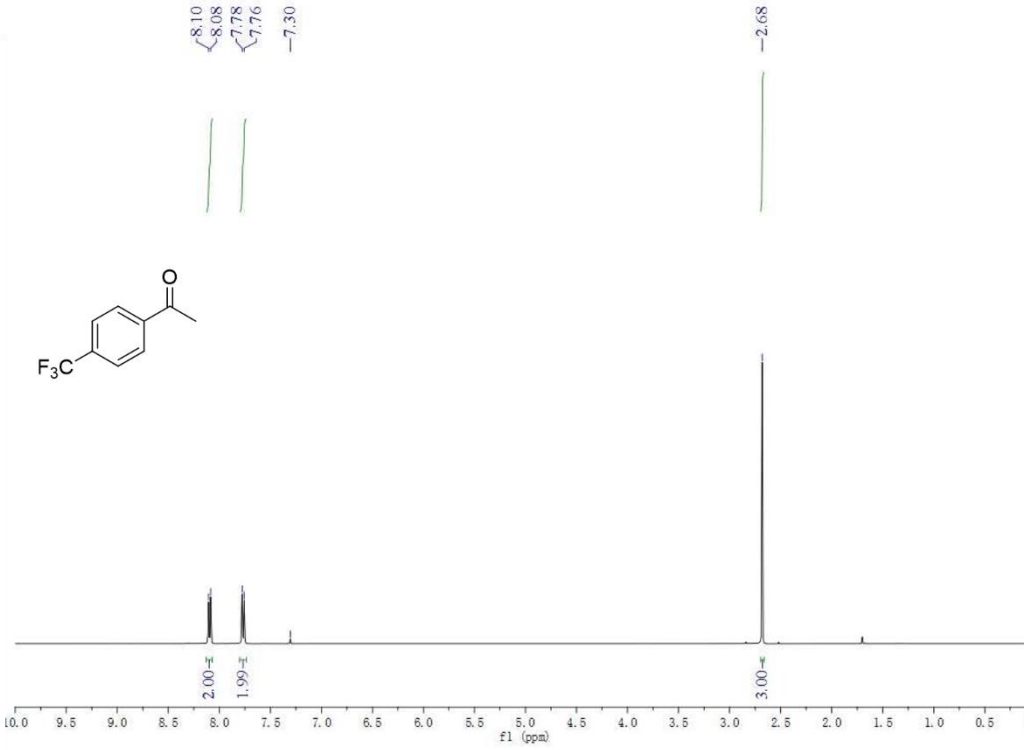
^{1}H NMR spectrum of **2s** in $CDCl_3$ at 400 MHz



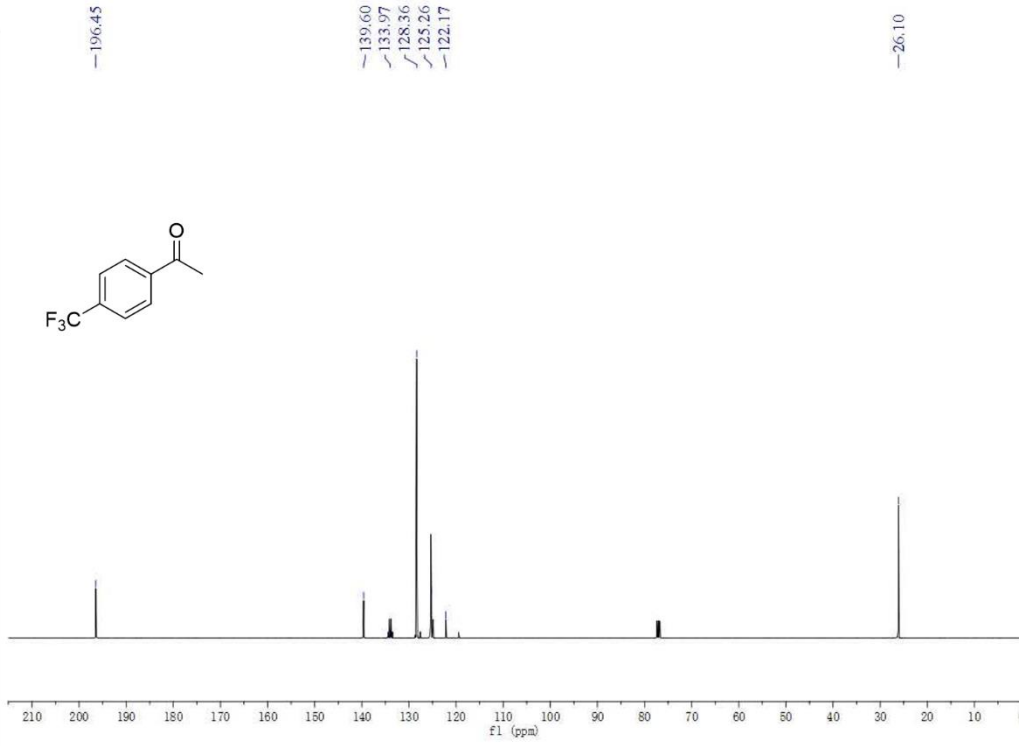
^{13}C NMR spectrum of **2s** in $CDCl_3$ at 101 MHz



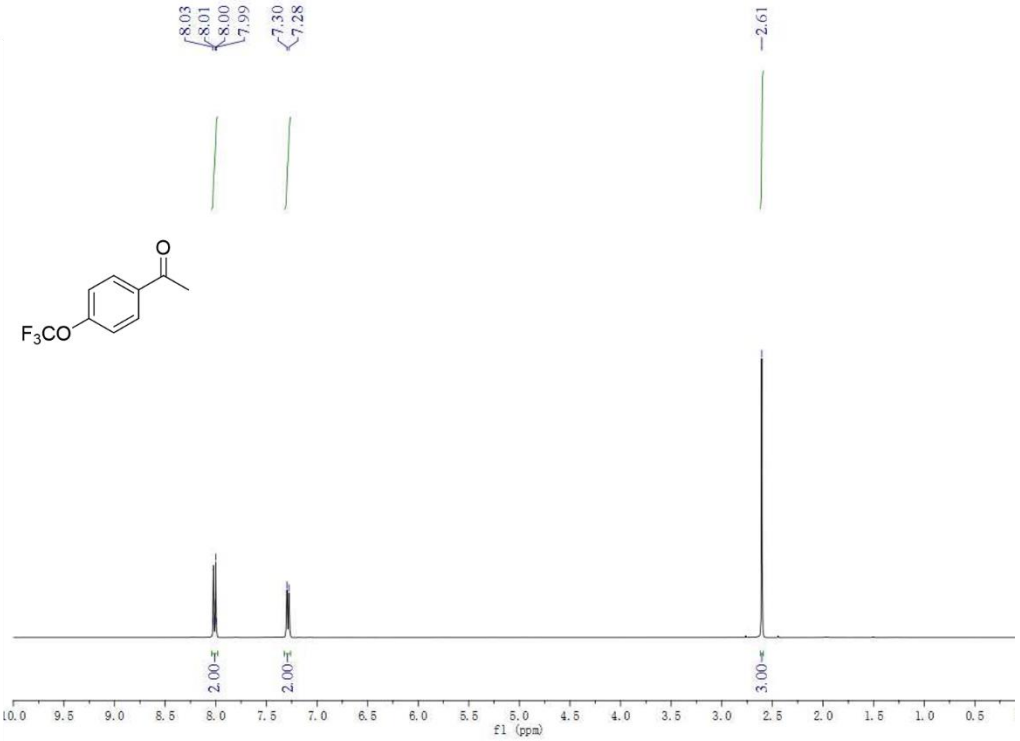
^{1}H NMR spectrum of **2t** in $CDCl_3$ at 400 MHz



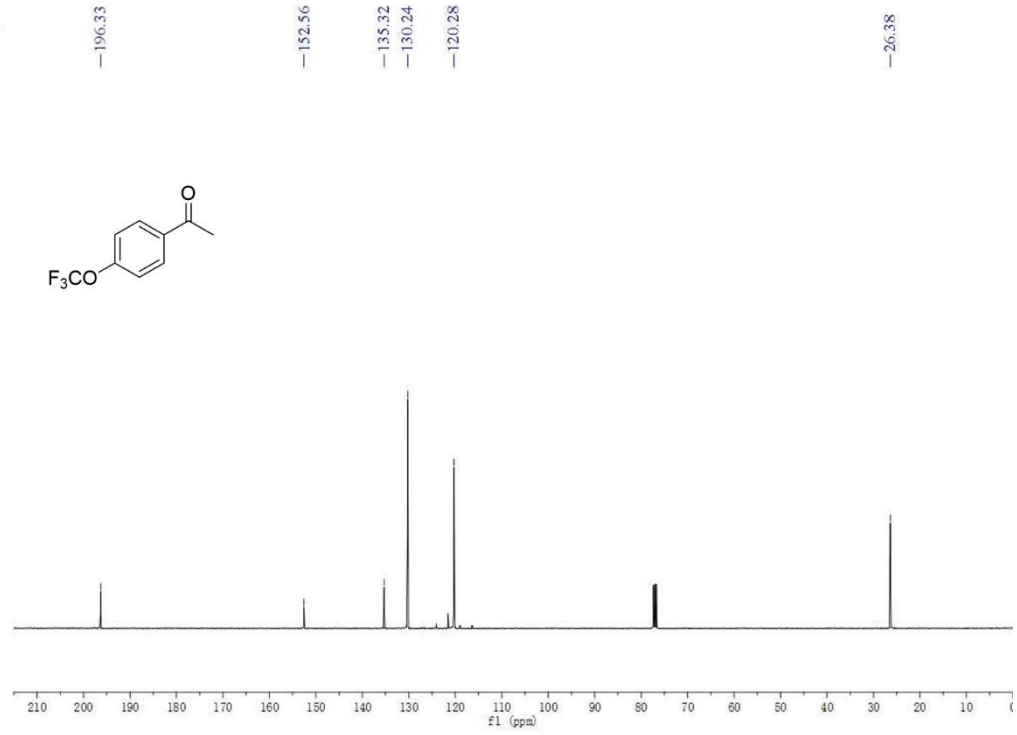
^{13}C NMR spectrum of **2t** in $CDCl_3$ at 101 MHz



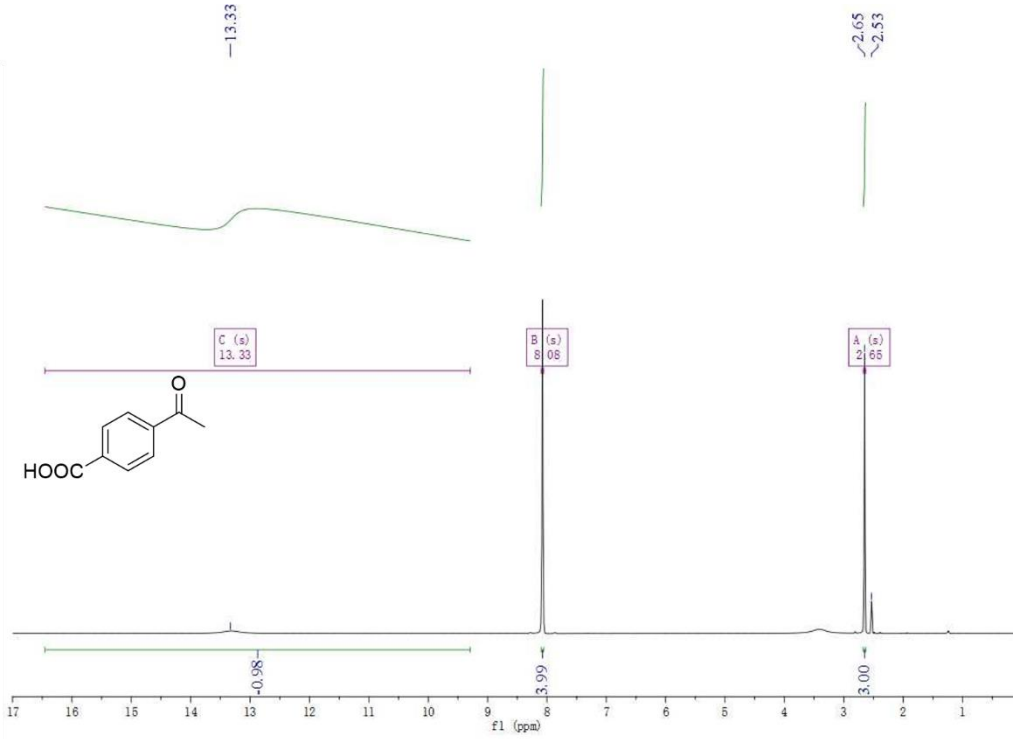
^{1}H NMR spectrum of **2u** in $CDCl_3$ at 400 MHz



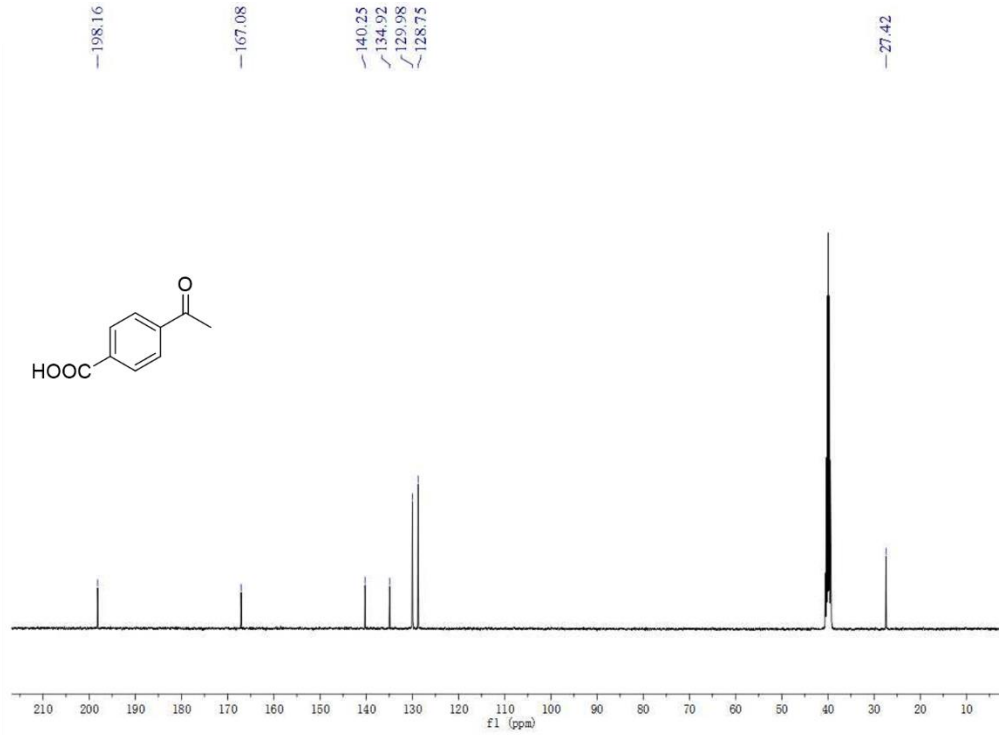
^{13}C NMR spectrum of **2u** in $CDCl_3$ at 101 MHz



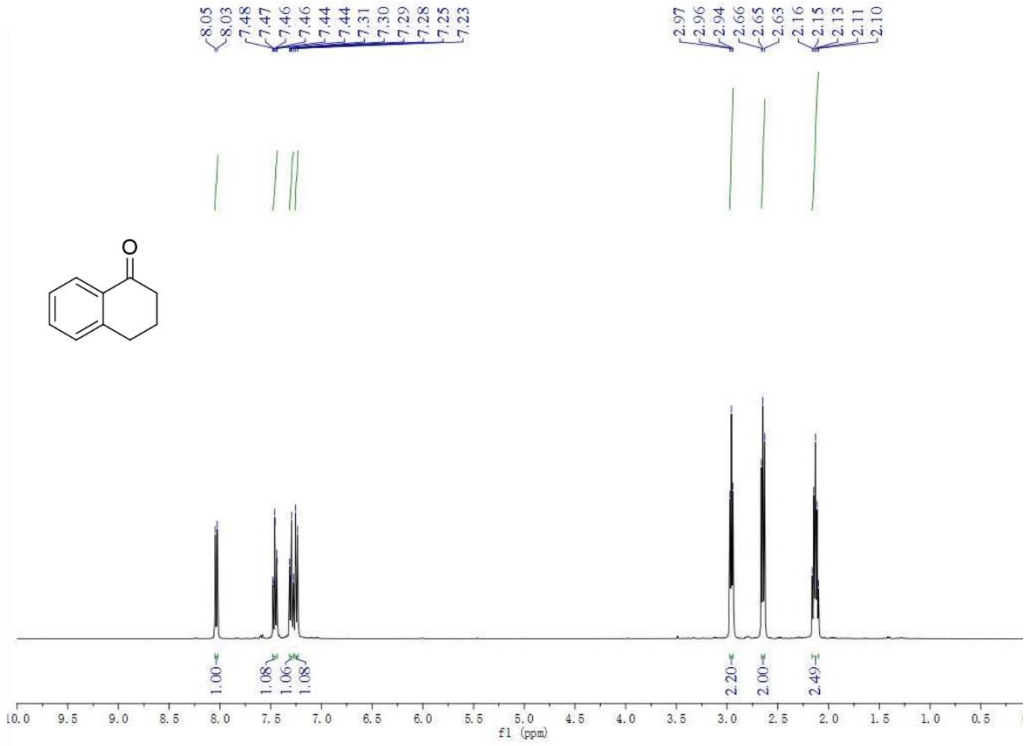
^{1}H NMR spectrum of **2v** in DMSO at 400 MHz



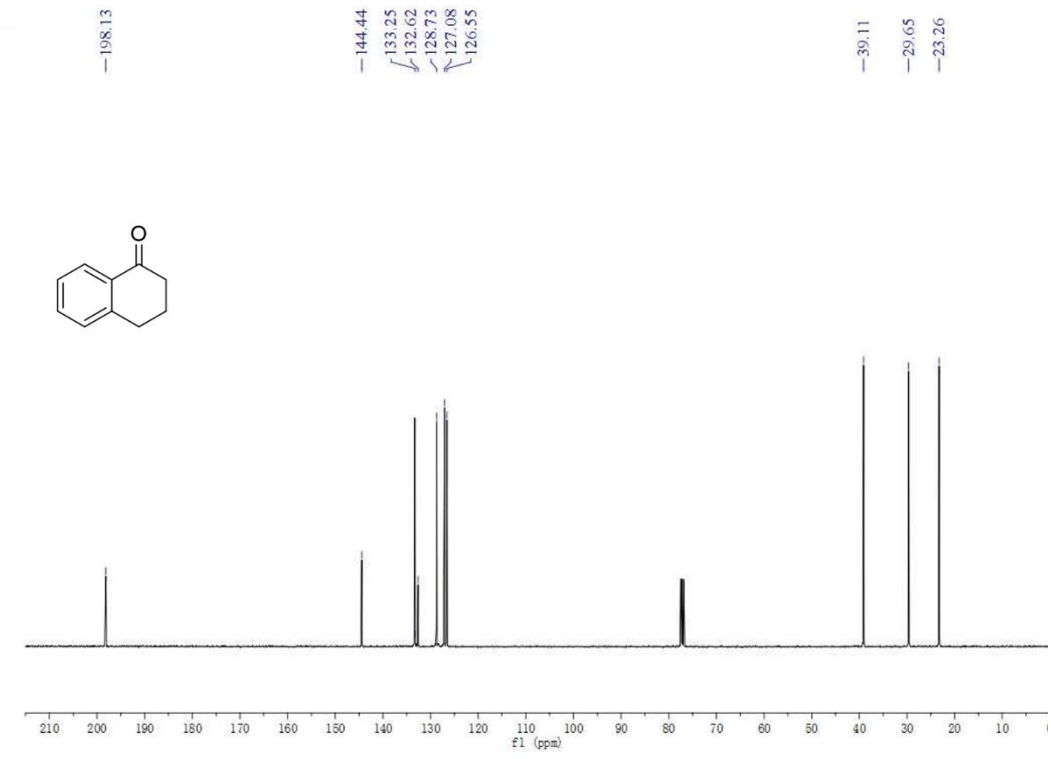
^{13}C NMR spectrum of **2v** in DMSO at 101 MHz



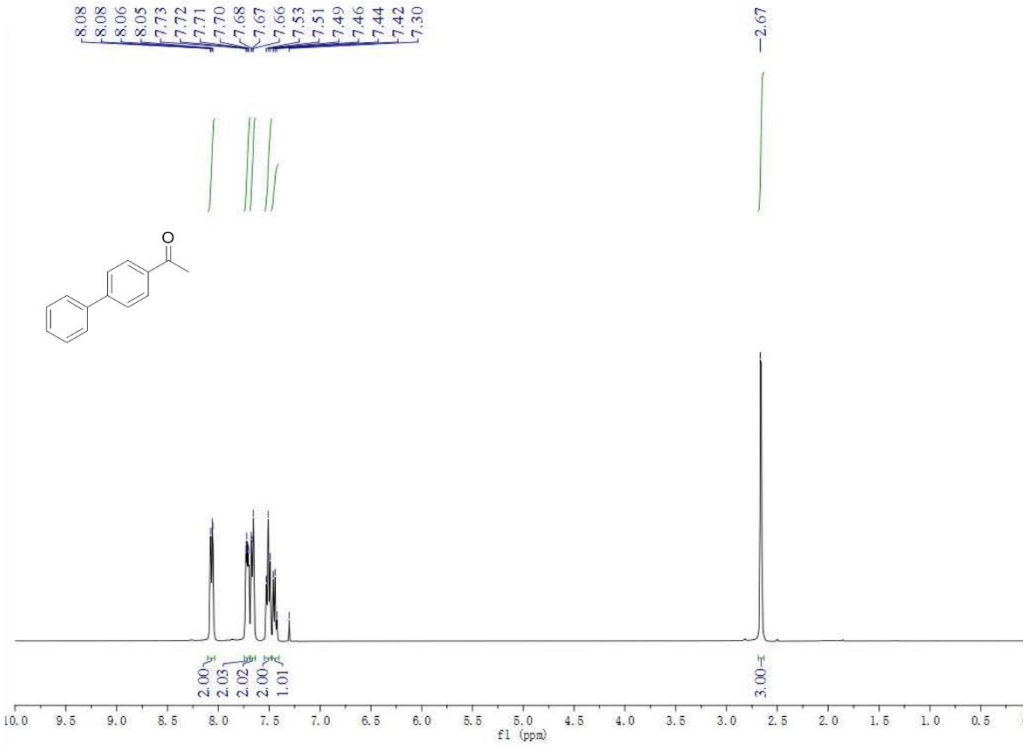
^{1}H NMR spectrum of **2w** in $CDCl_3$ at 400 MHz



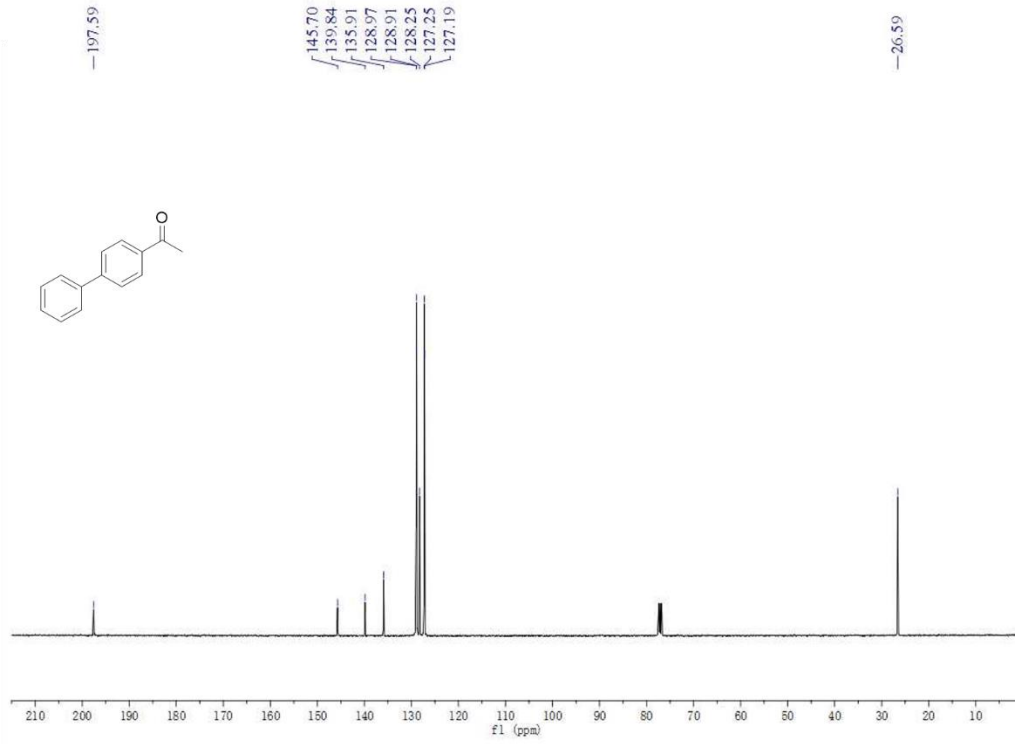
^{13}C NMR spectrum of **2w** in $CDCl_3$ at 101 MHz



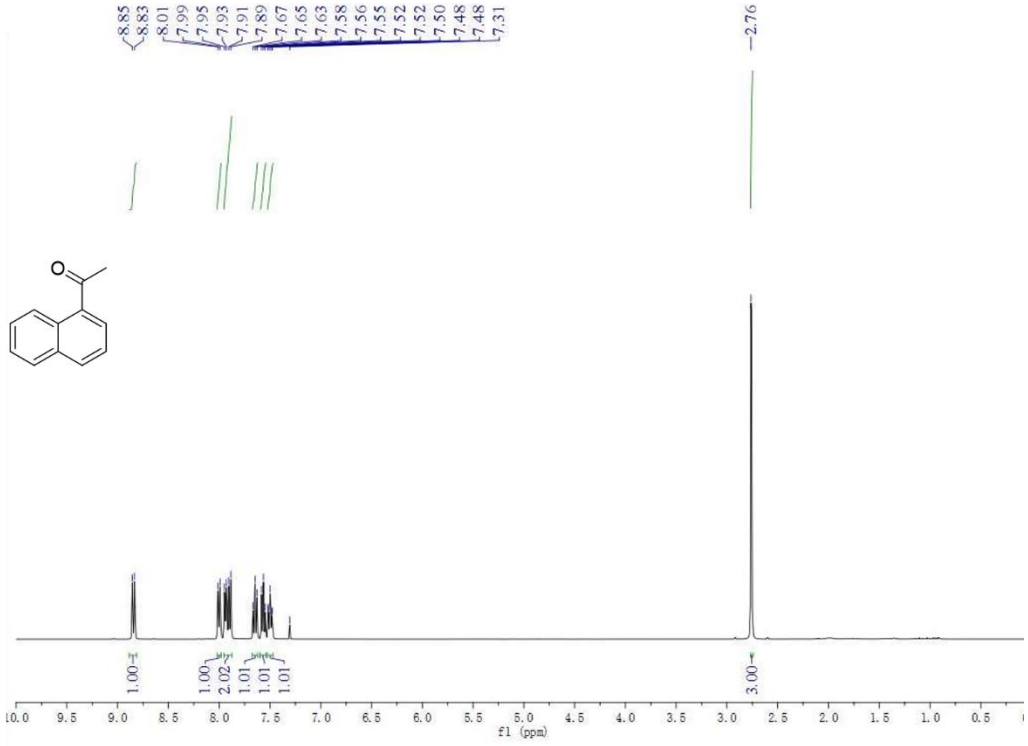
^{1}H NMR spectrum of **2x** in $CDCl_3$ at 400 MHz



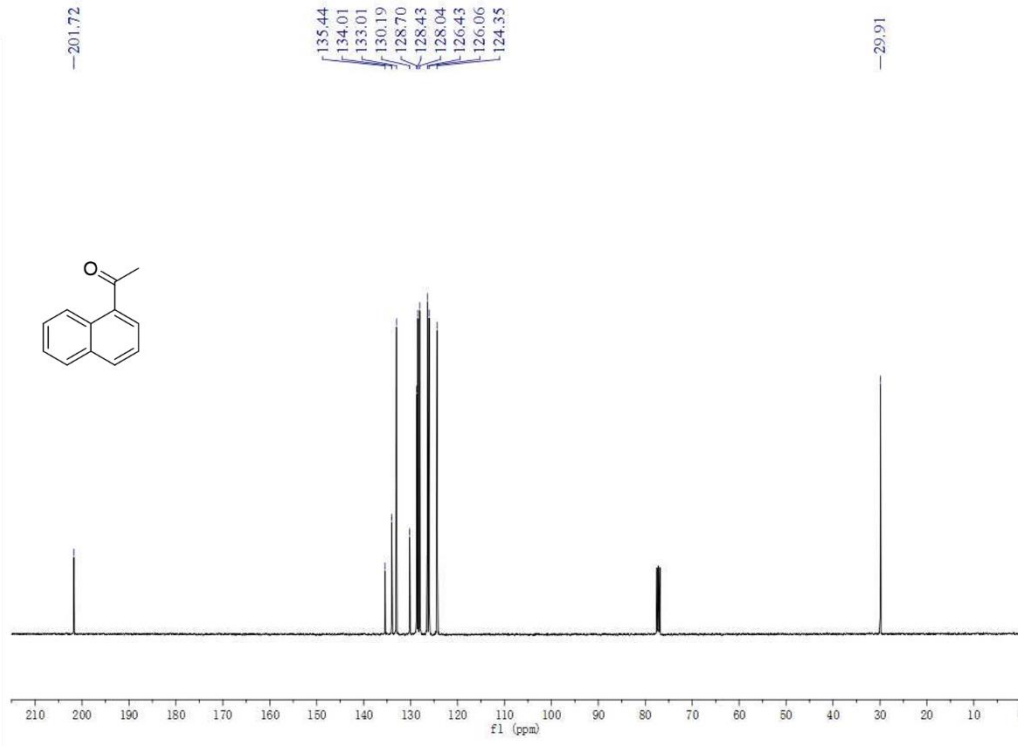
^{13}C NMR spectrum of **2x** in $CDCl_3$ at 101 MHz



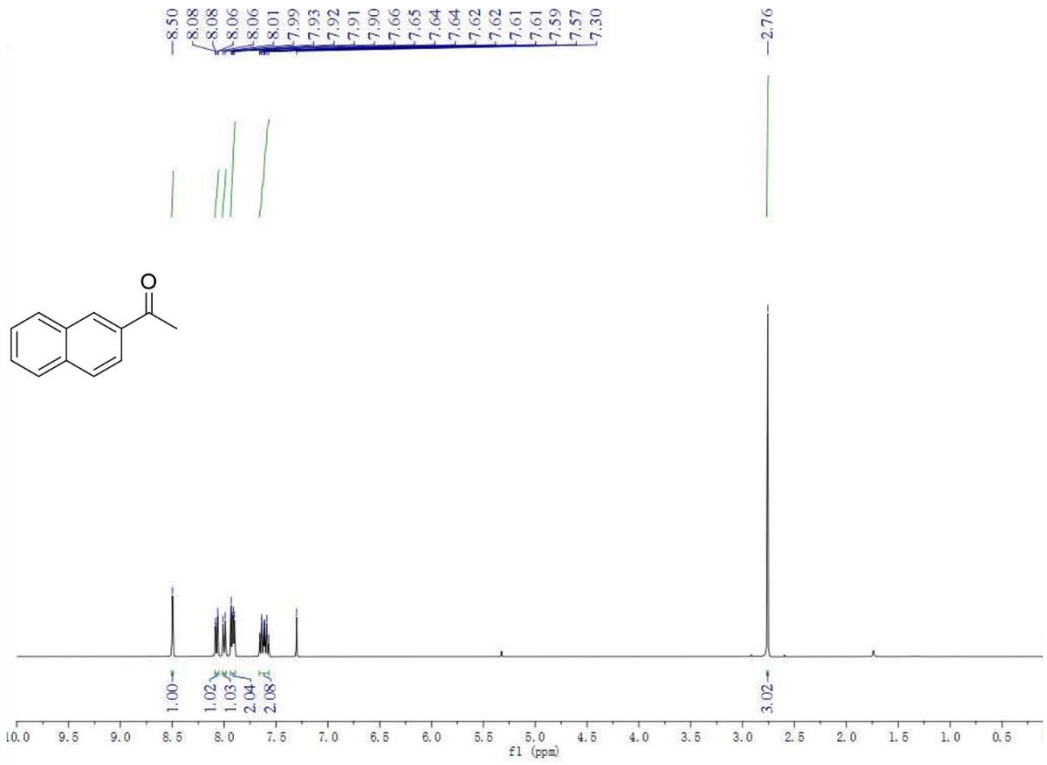
^{1}H NMR spectrum of **2y** in $CDCl_3$ at 400 MHz



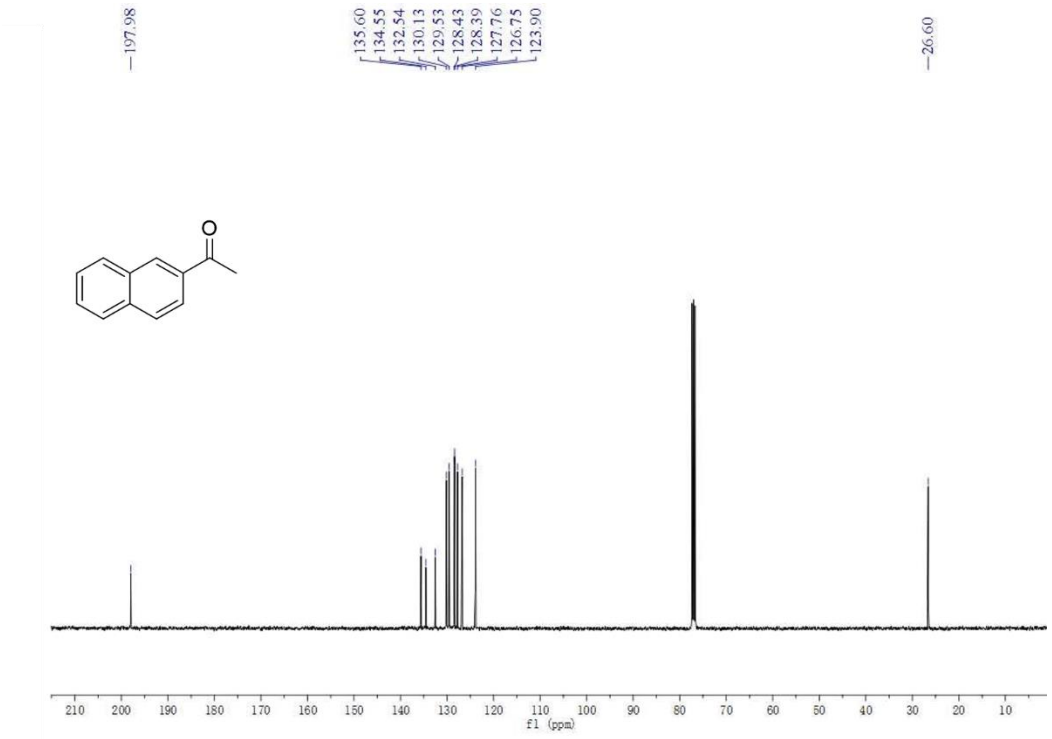
^{13}C NMR spectrum of **2y** in $CDCl_3$ at 101 MHz



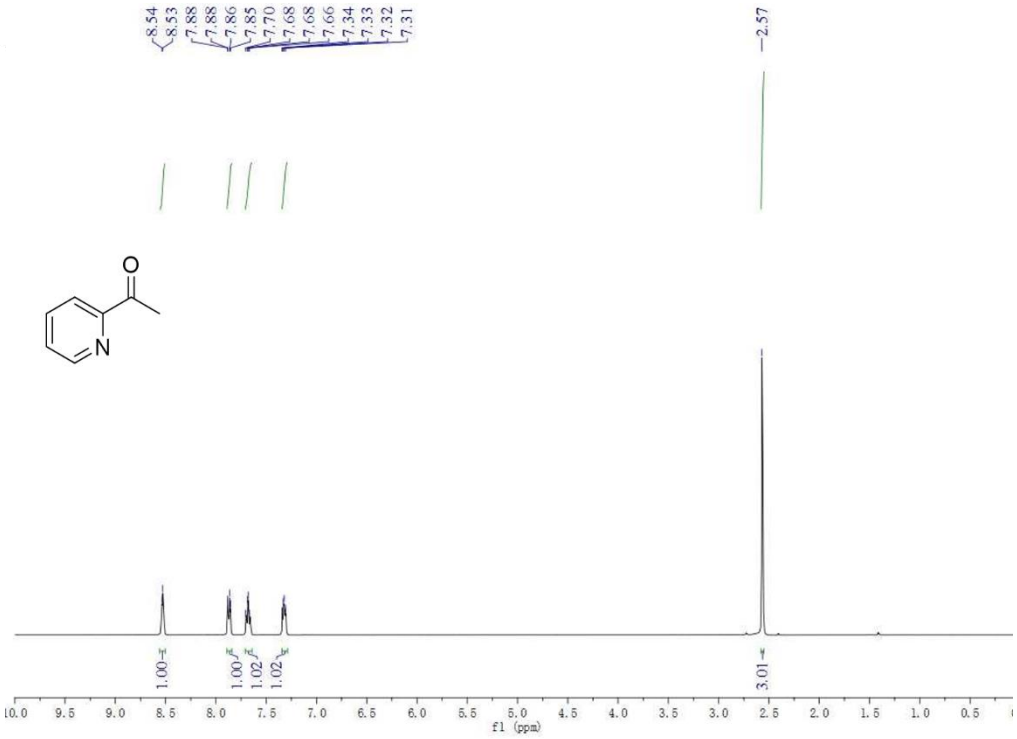
^{1}H NMR spectrum of **2z** in $CDCl_3$ at 400 MHz



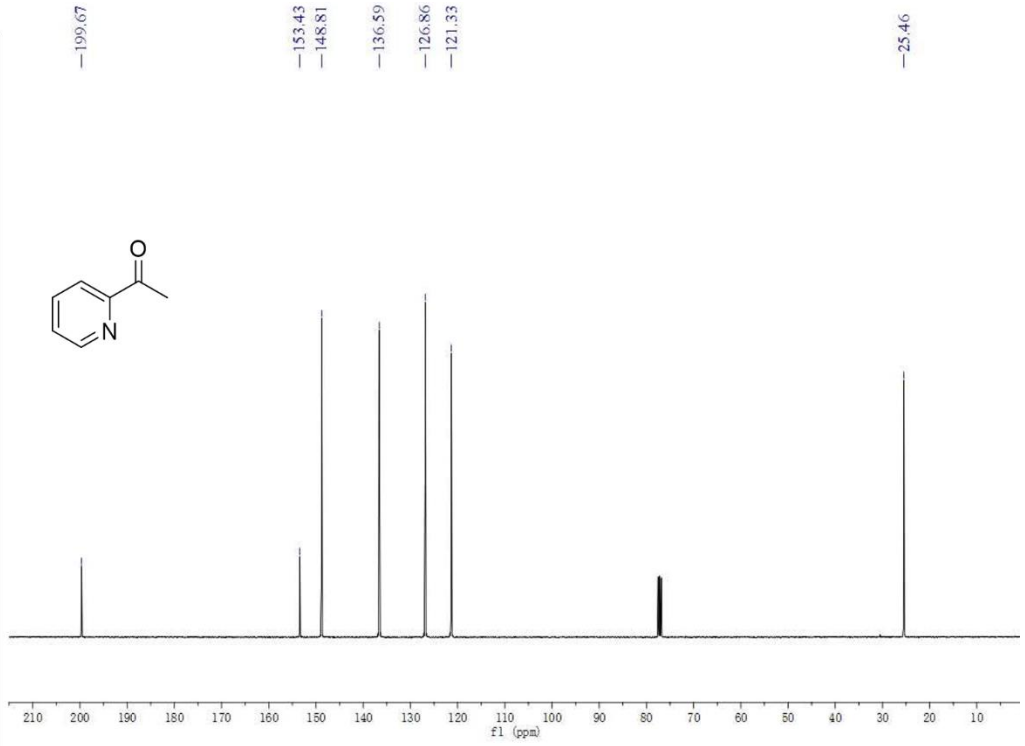
^{13}C NMR spectrum of **2z** in $CDCl_3$ at 101 MHz



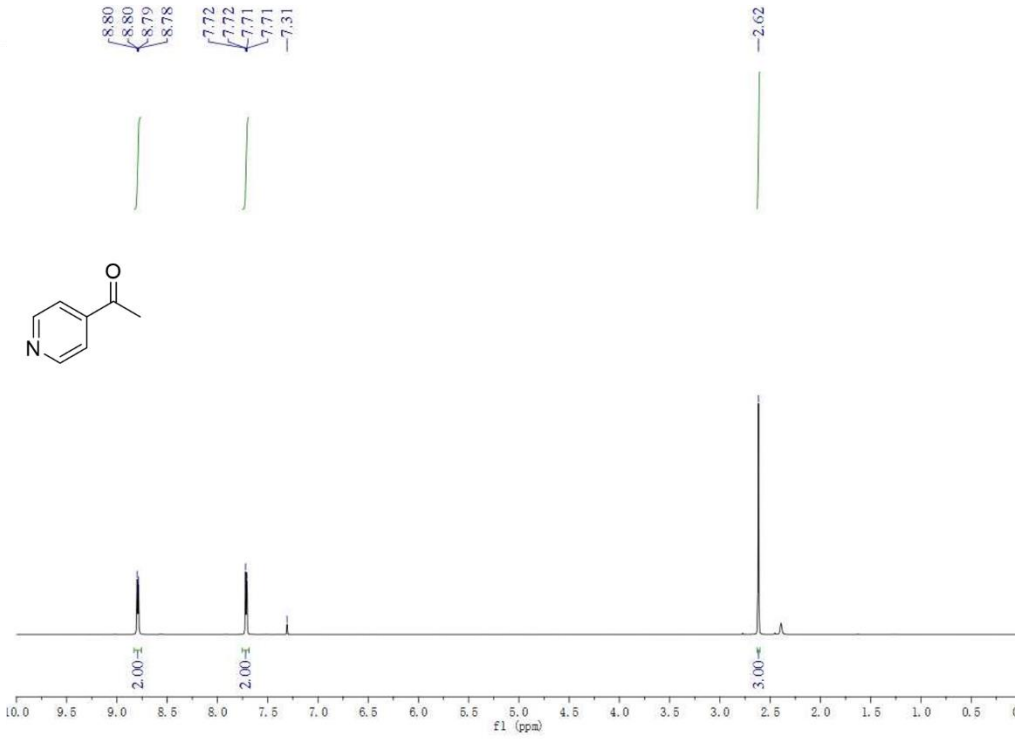
^{1}H NMR spectrum of **2α** in $CDCl_3$ at 400 MHz



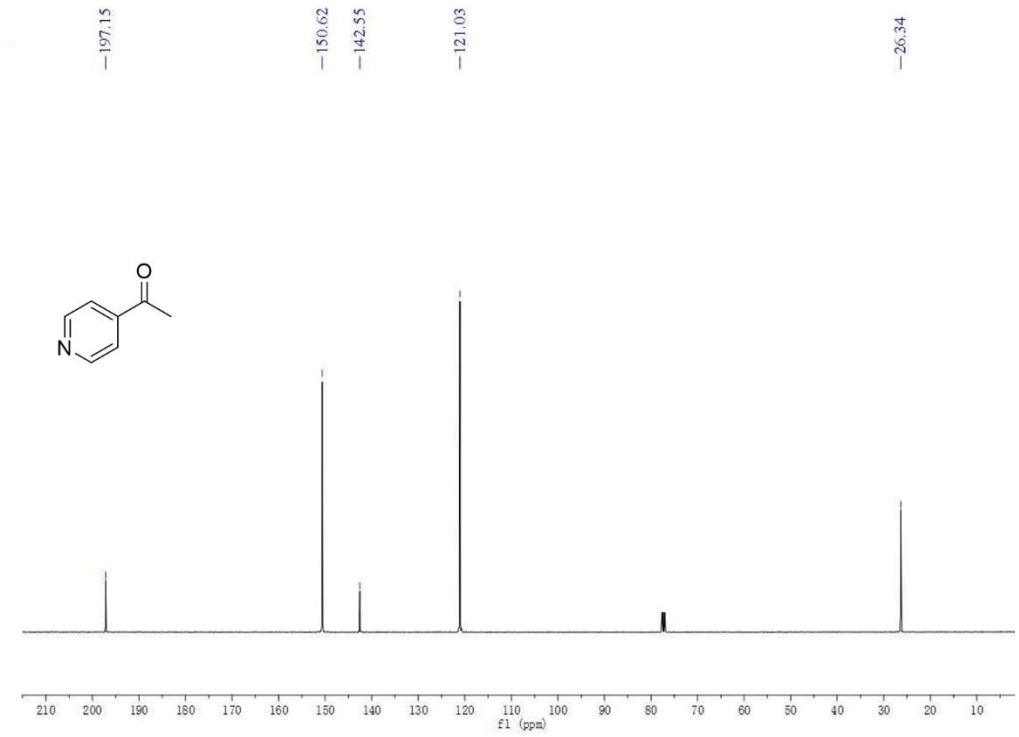
^{13}C NMR spectrum of **2α** in $CDCl_3$ at 101 MHz



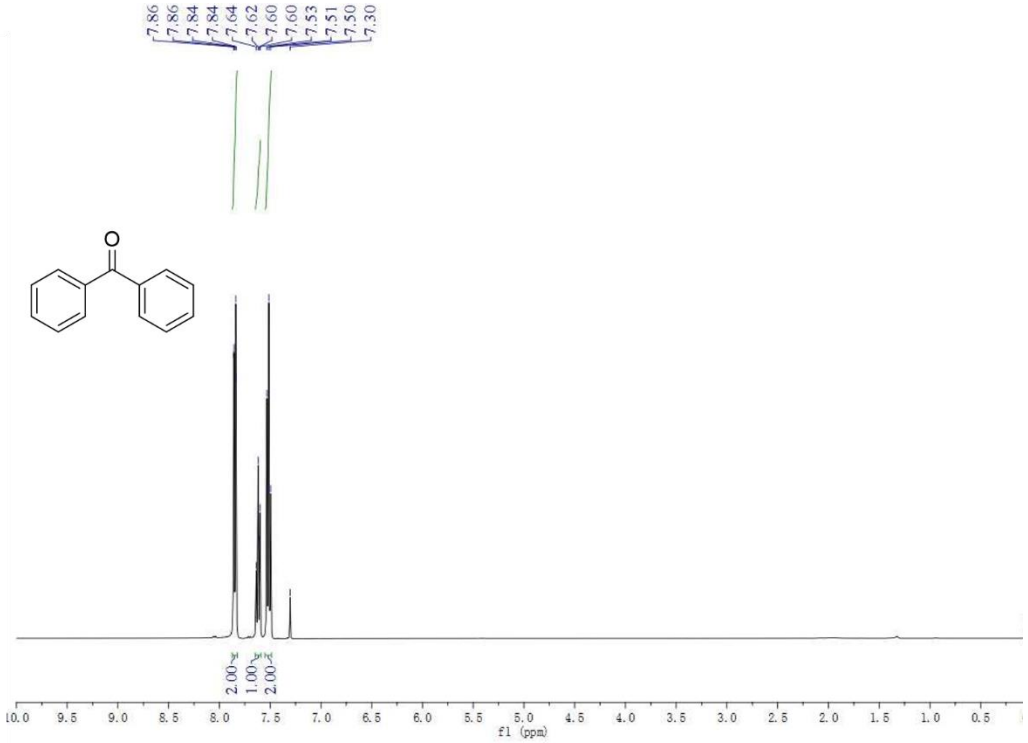
^{1}H NMR spectrum of **2β** in $CDCl_3$ at 400 MHz



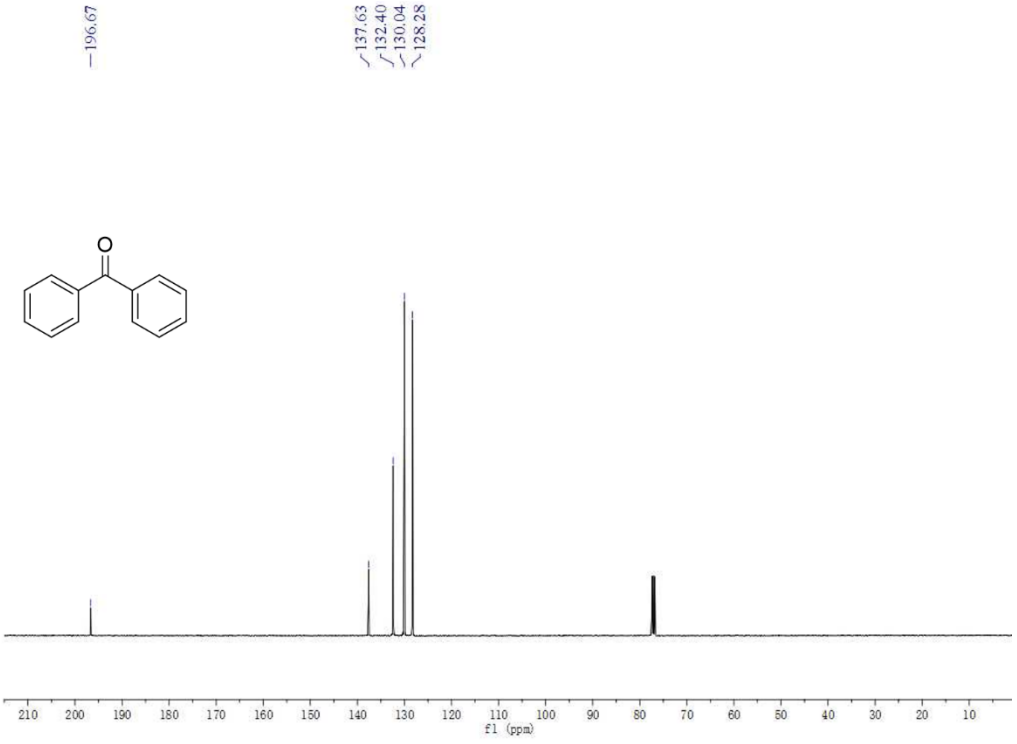
^{13}C NMR spectrum of **2β** in $CDCl_3$ at 101 MHz



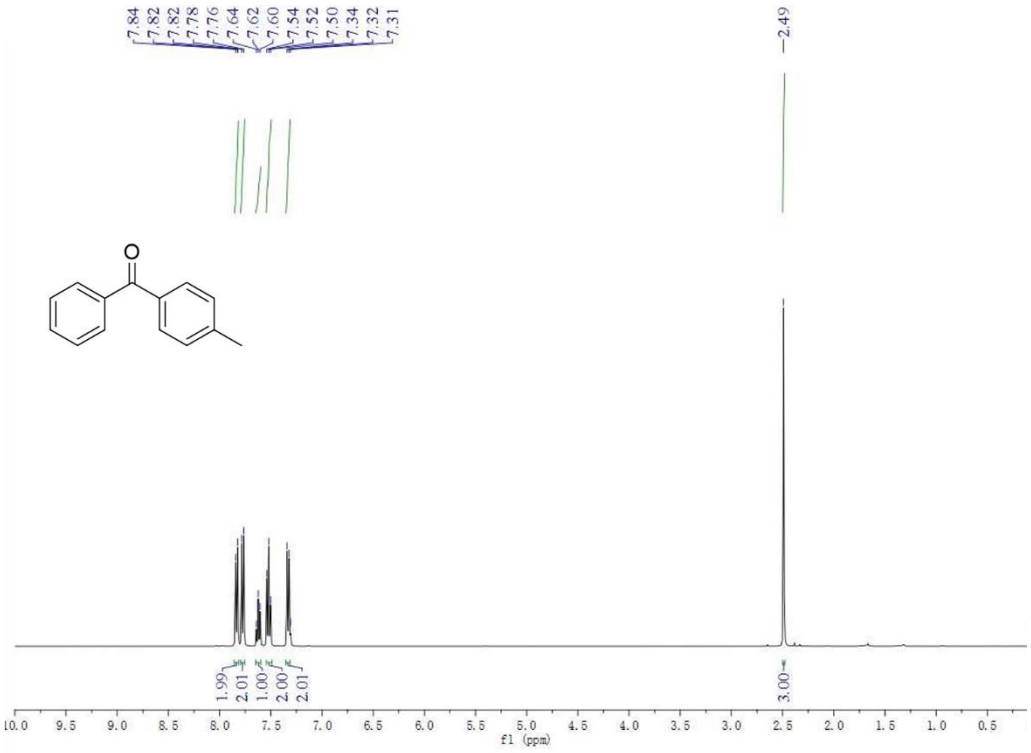
^{1}H NMR spectrum of **4a** in $CDCl_3$ at 400 MHz



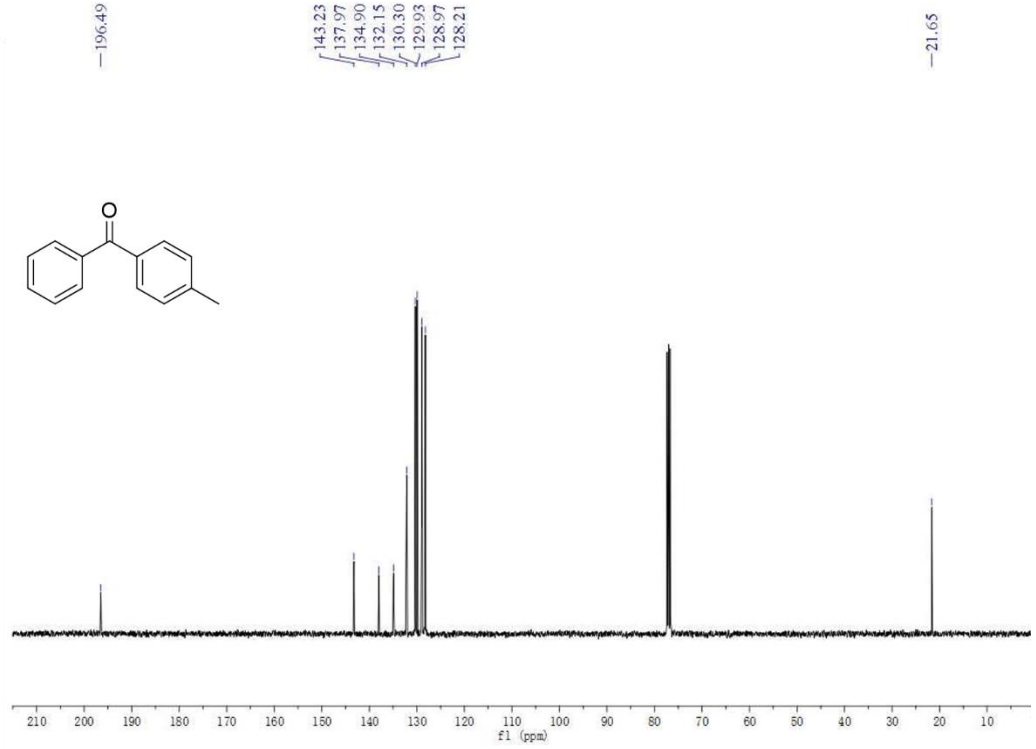
^{13}C NMR spectrum of **4a** in $CDCl_3$ at 101 MHz



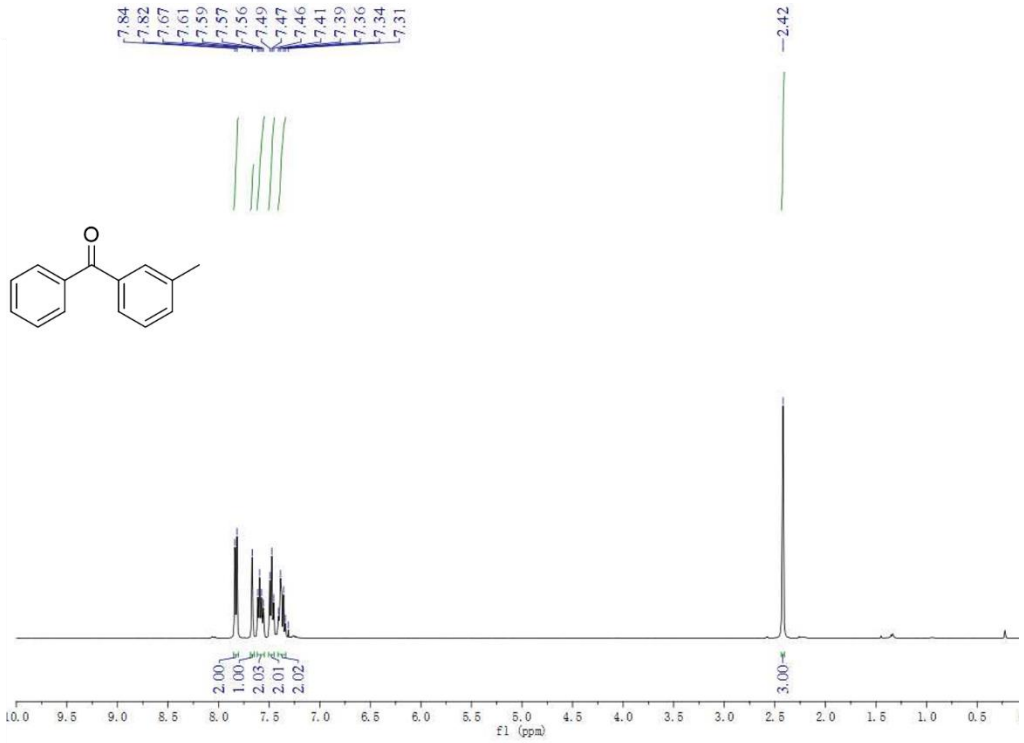
^{1}H NMR spectrum of **4b** in $CDCl_3$ at 400 MHz



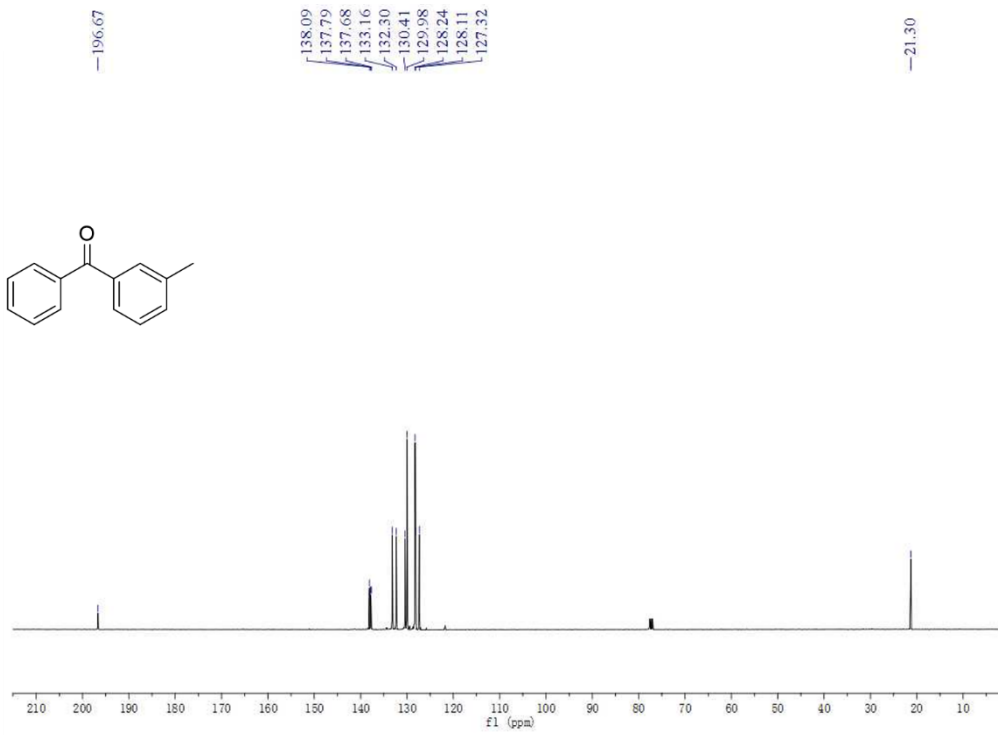
^{13}C NMR spectrum of **4b** in $CDCl_3$ at 101 MHz



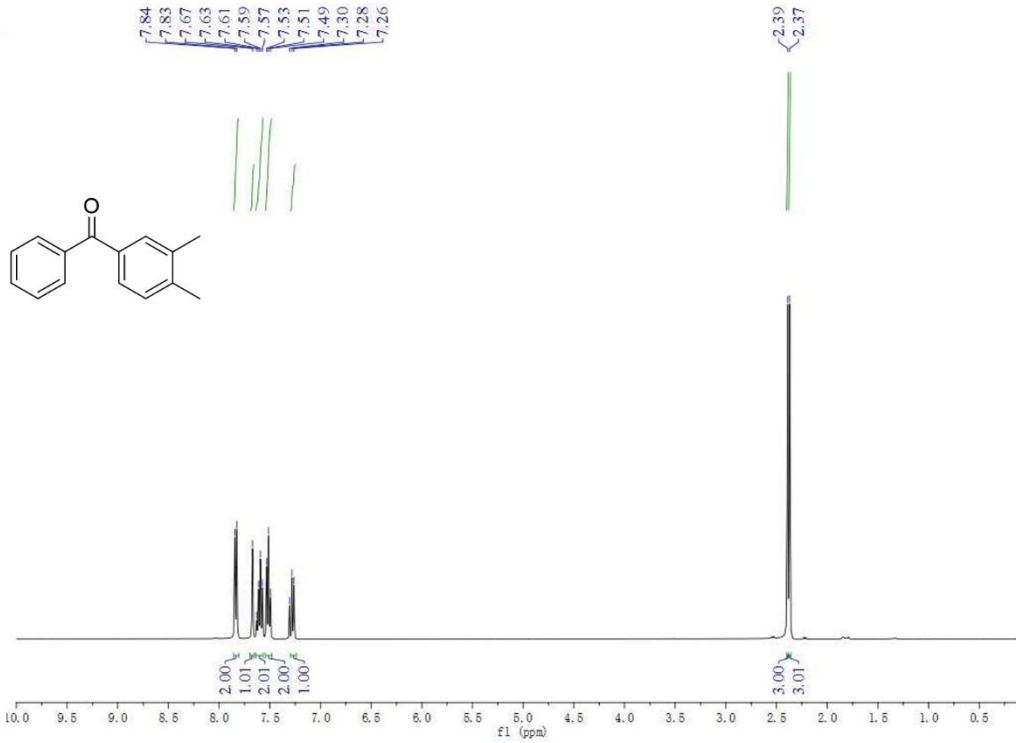
^{1}H NMR spectrum of **4c** in $CDCl_3$ at 400 MHz



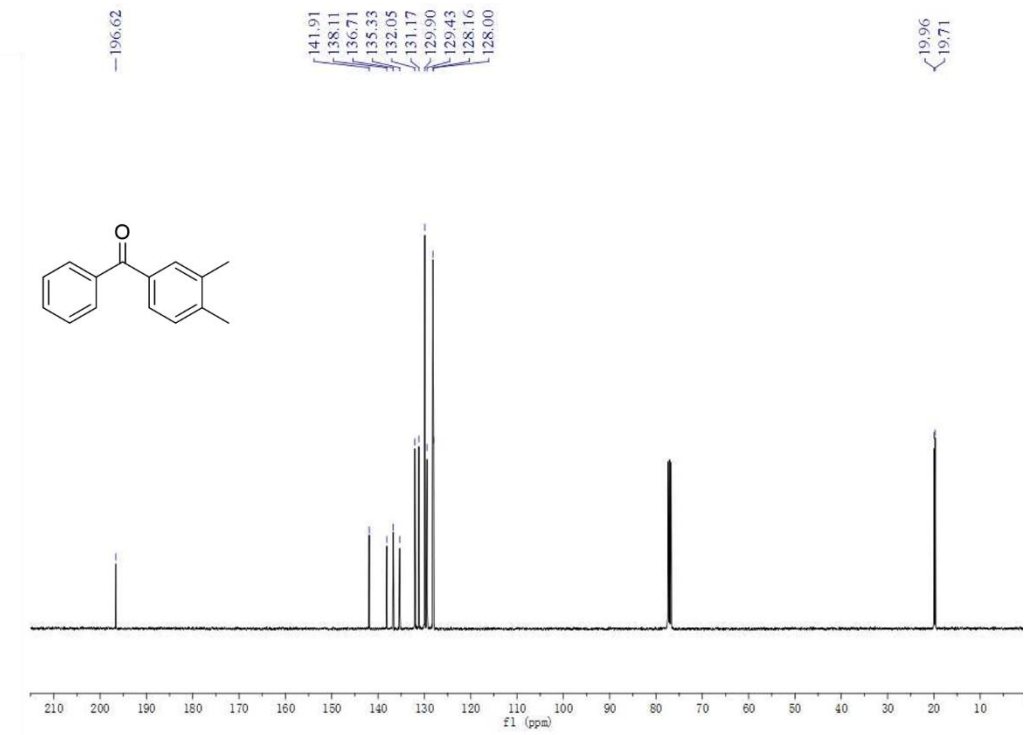
^{13}C NMR spectrum of **4c** in $CDCl_3$ at 101 MHz



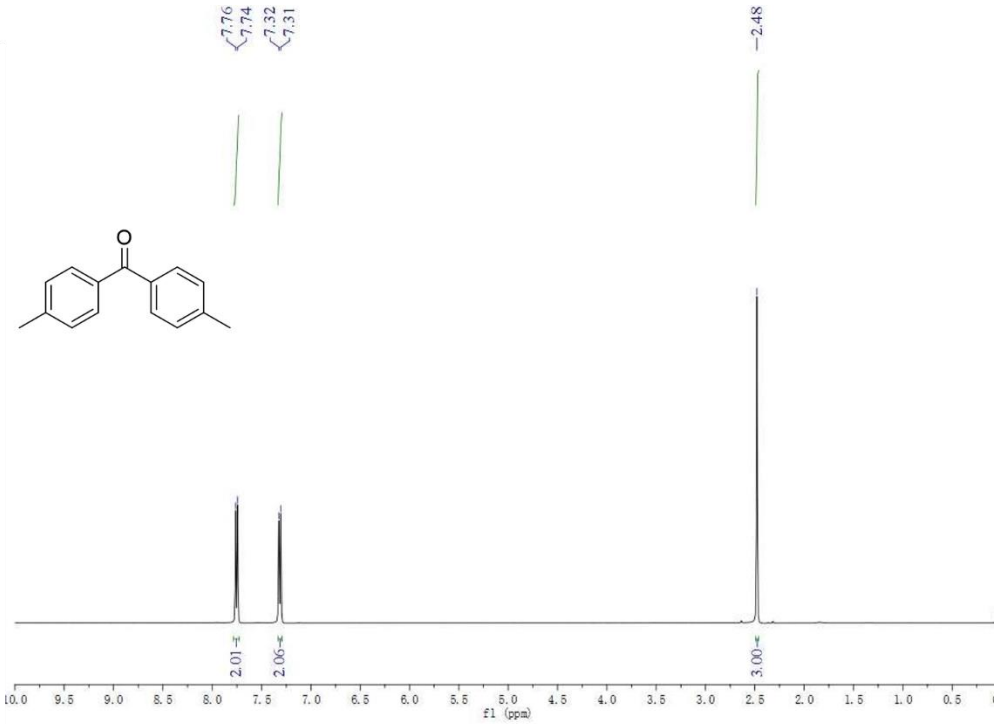
^{1}H NMR spectrum of **4d** in $CDCl_3$ at 400 MHz



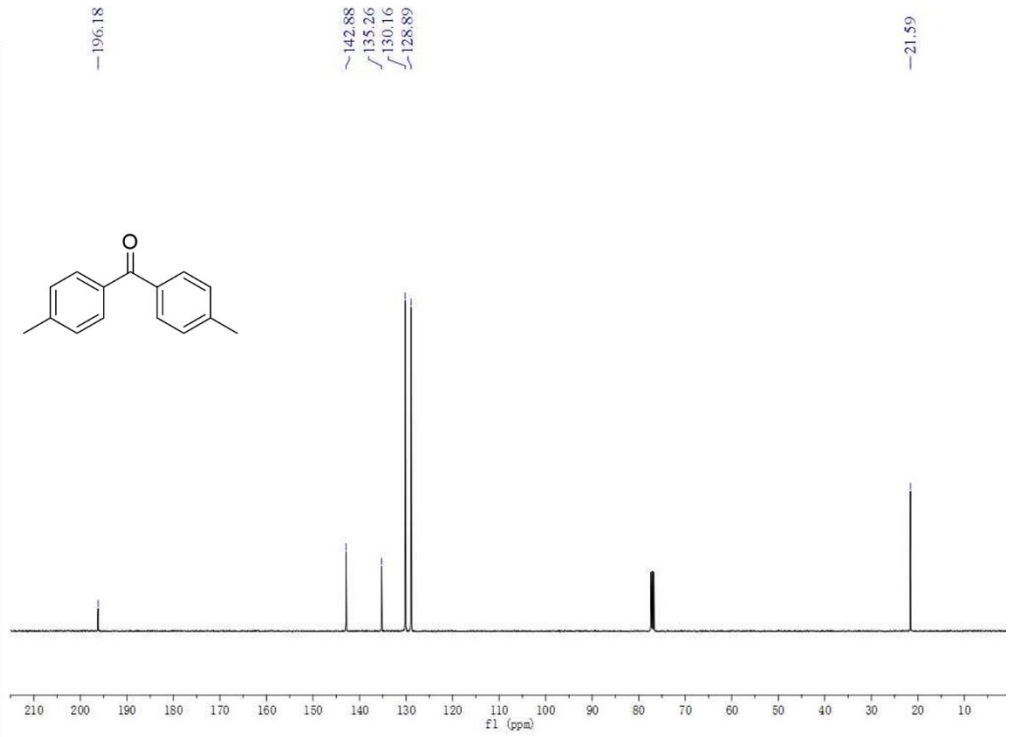
^{13}C NMR spectrum of **4d** in $CDCl_3$ at 101 MHz



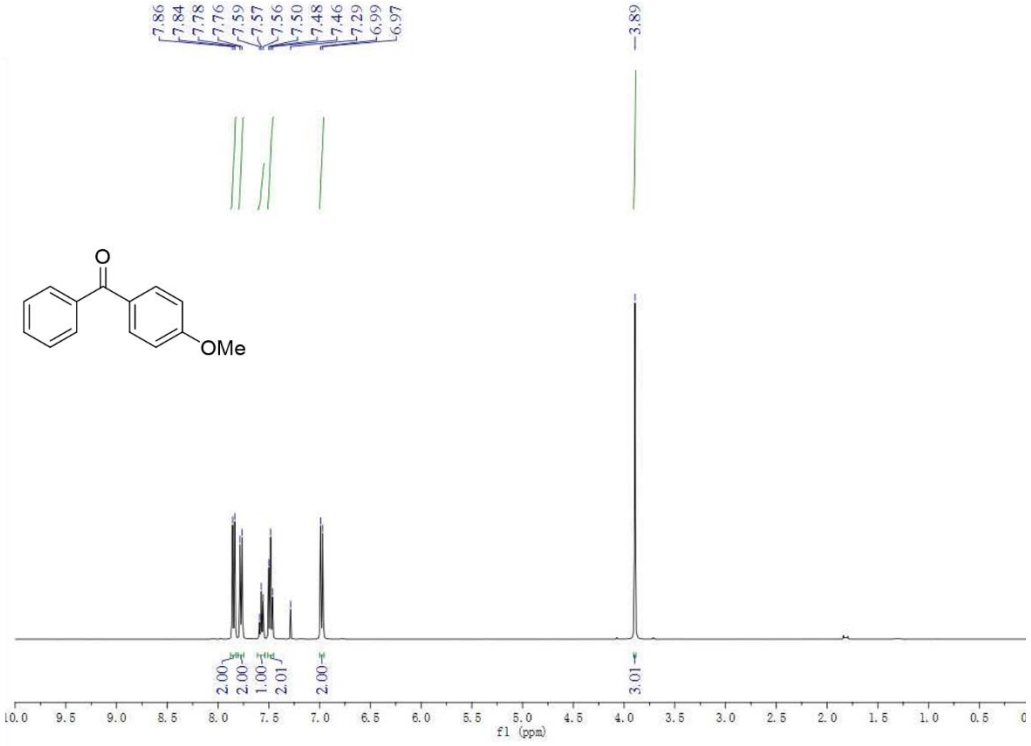
^{1}H NMR spectrum of **4e** in $CDCl_3$ at 400 MHz



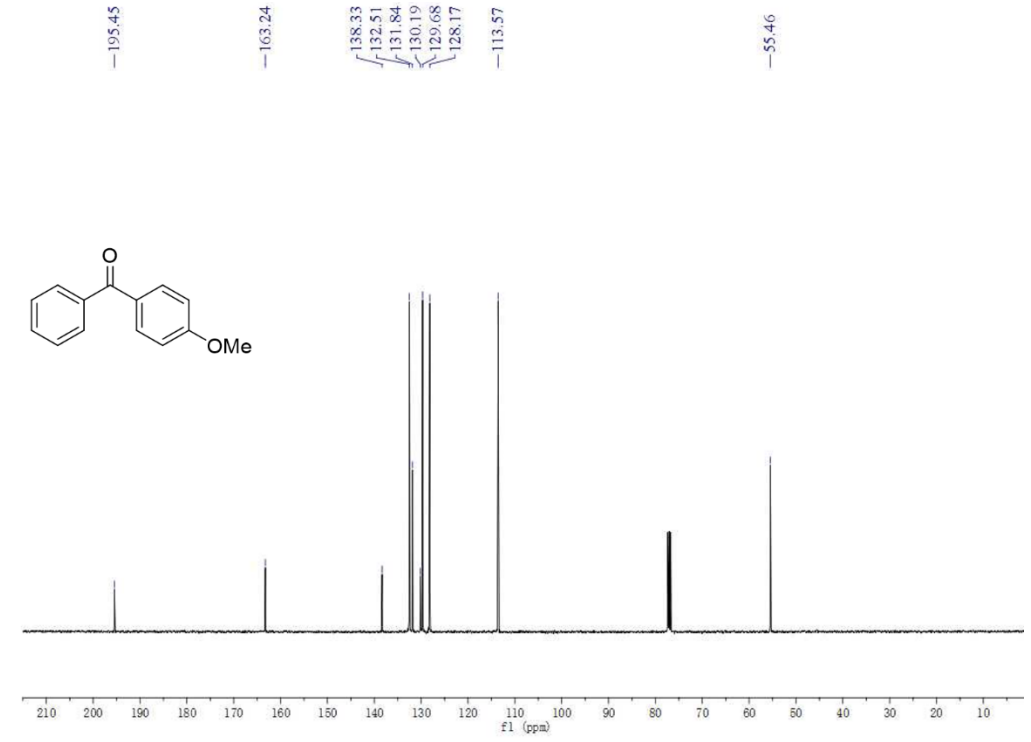
^{13}C NMR spectrum of **4e** in $CDCl_3$ at 101 MHz



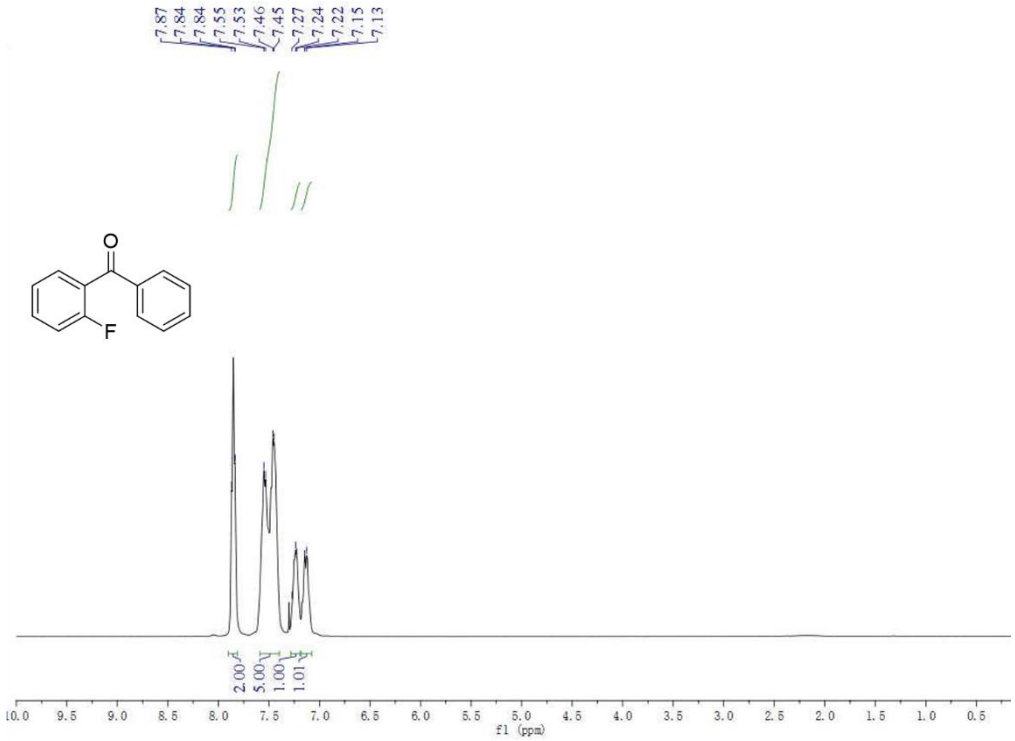
^{1}H NMR spectrum of **4f** in $CDCl_3$ at 400 MHz



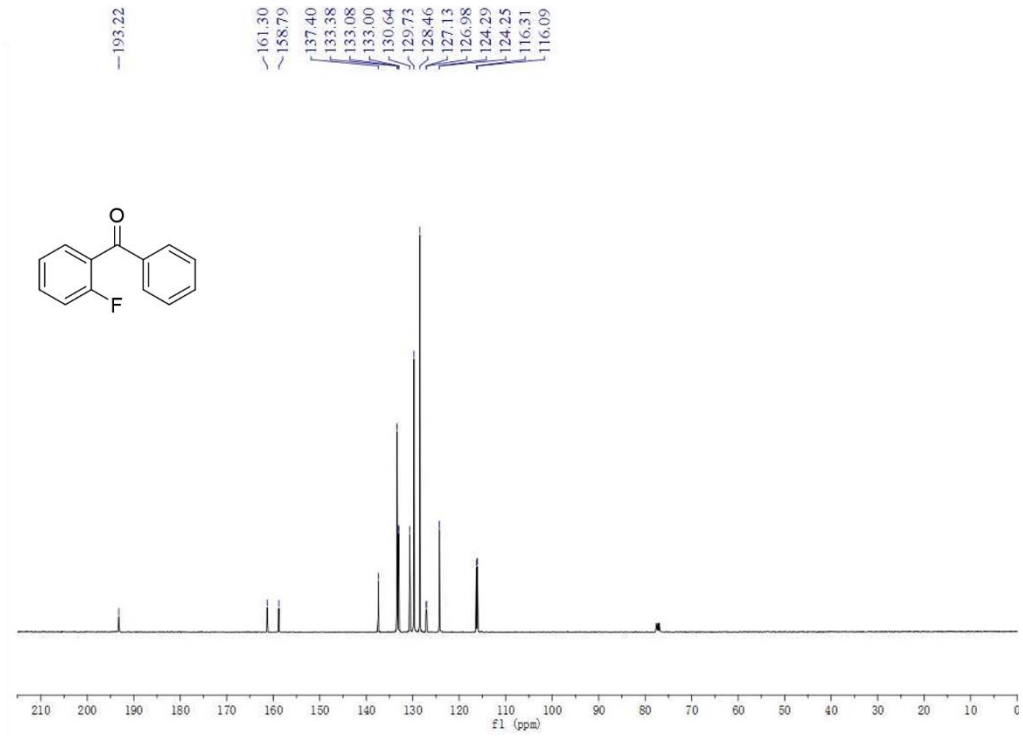
^{13}C NMR spectrum of **4f** in $CDCl_3$ at 101 MHz



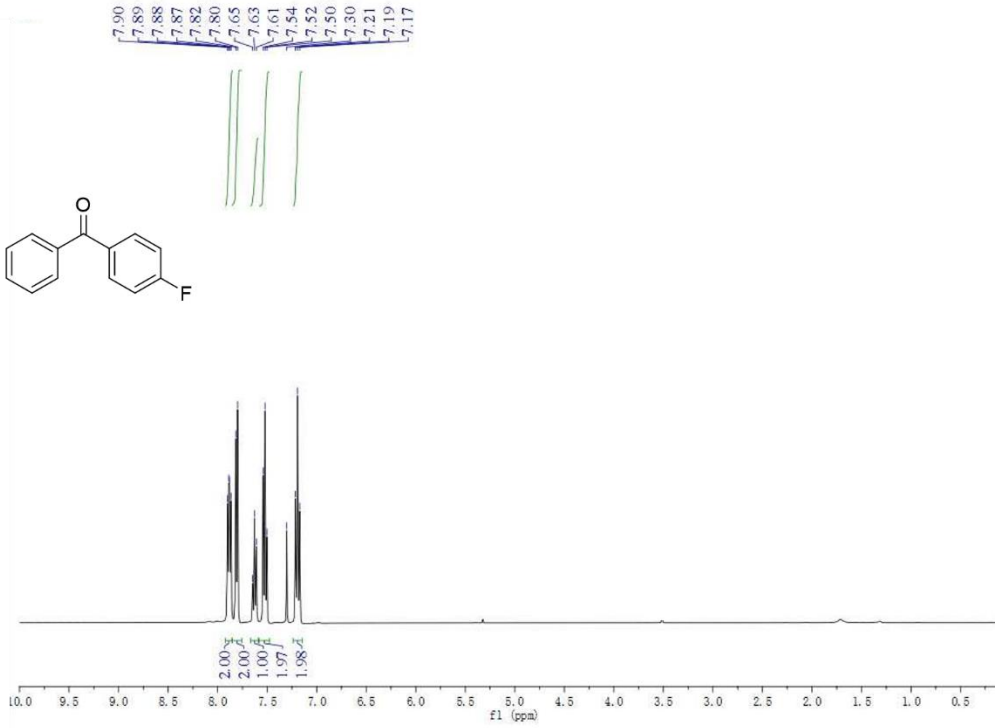
^{1}H NMR spectrum of **4g** in $CDCl_3$ at 400 MHz



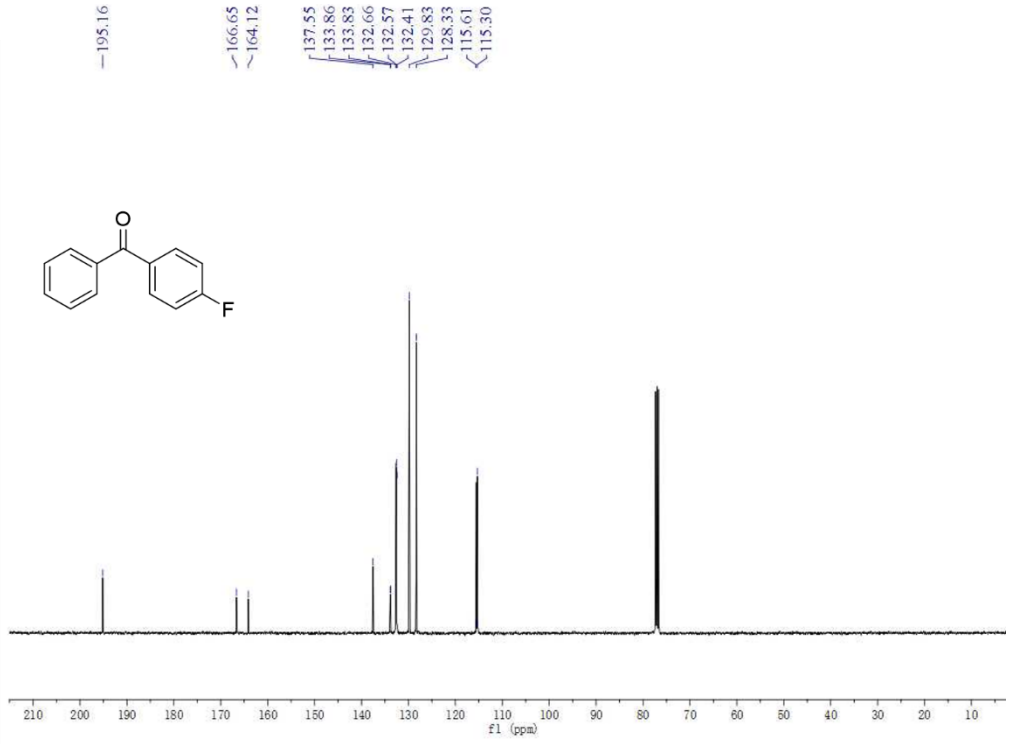
^{13}C NMR spectrum of **4g** in $CDCl_3$ at 101 MHz



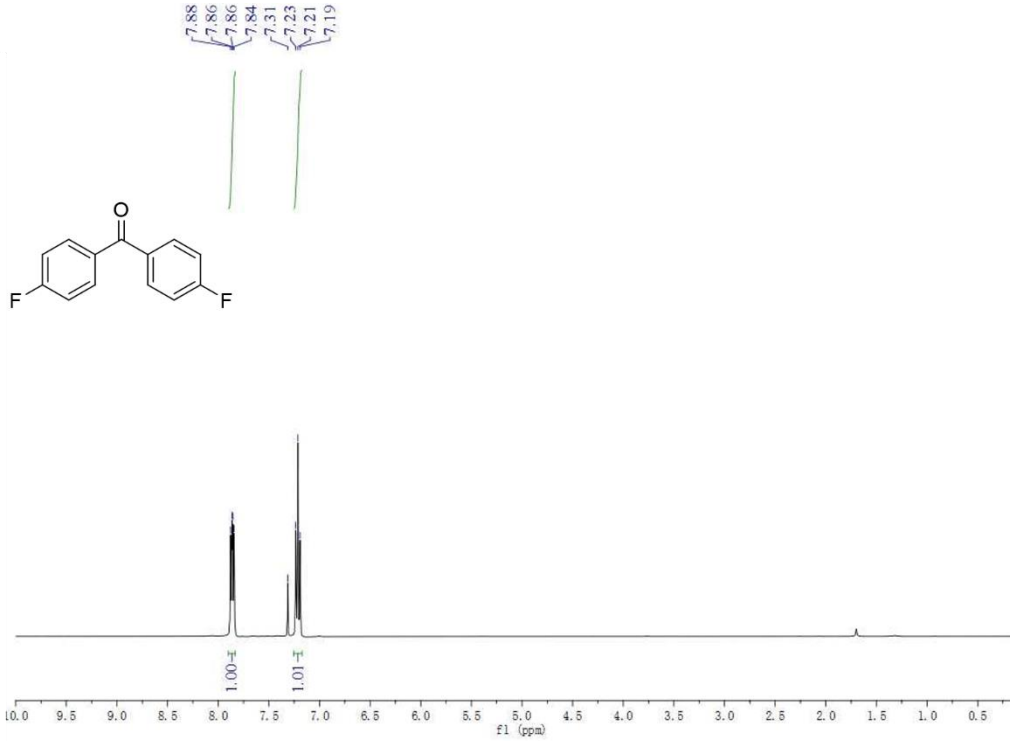
^{1}H NMR spectrum of **4h** in $CDCl_3$ at 400 MHz



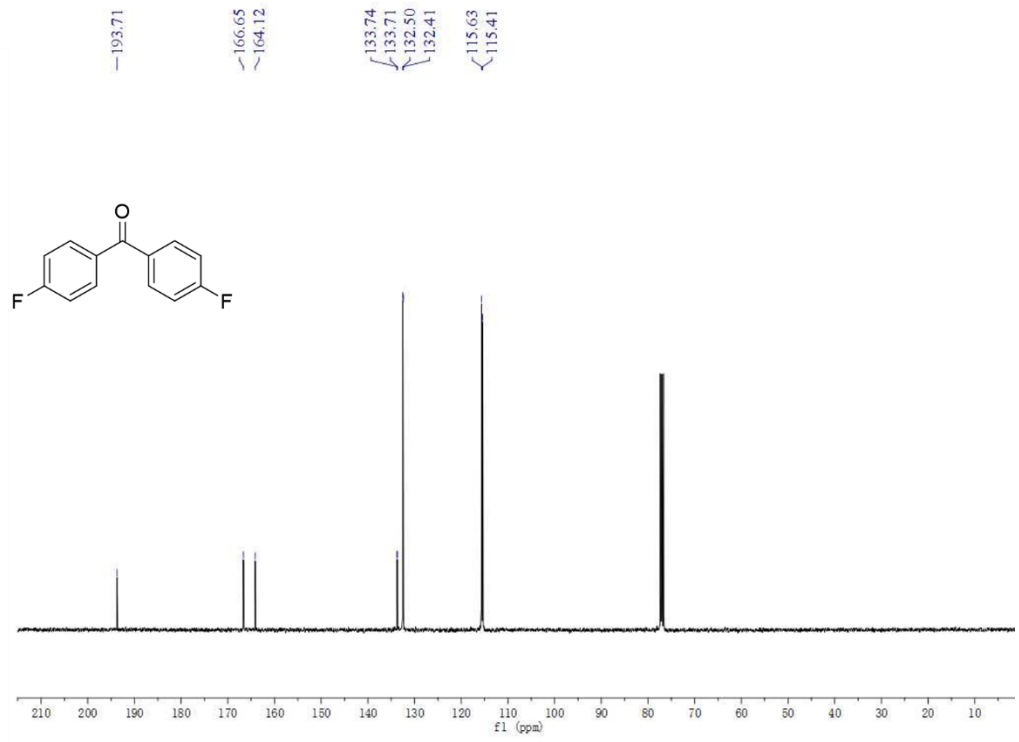
^{13}C NMR spectrum of **4h** in $CDCl_3$ at 101 MHz



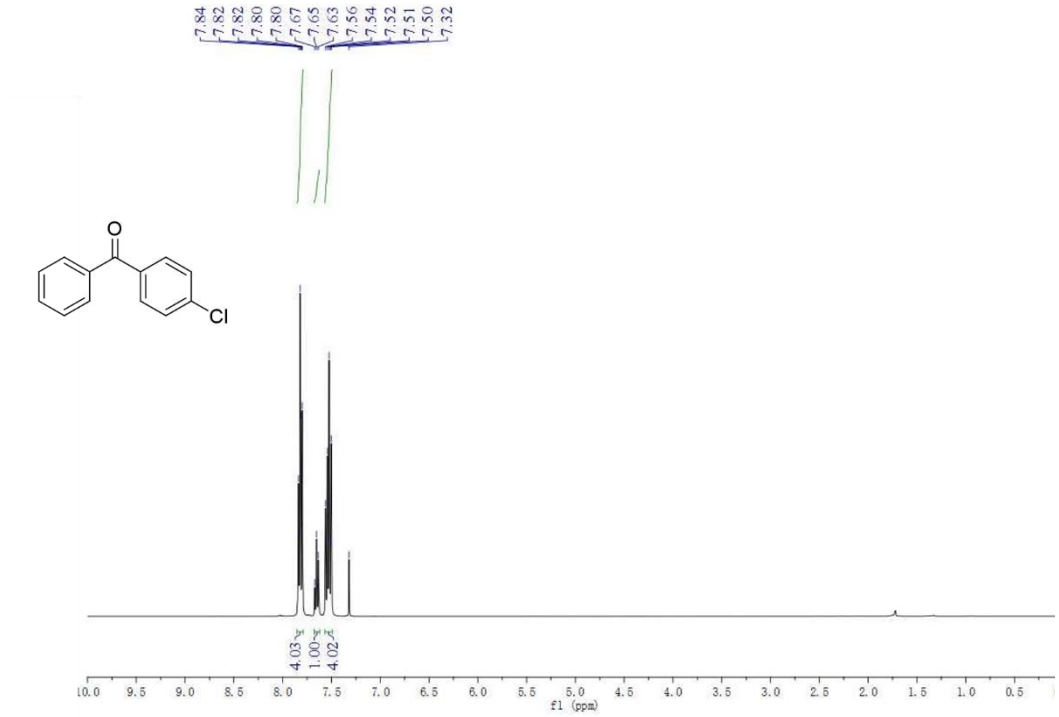
^{1}H NMR spectrum of **4i** in $CDCl_3$ at 400 MHz



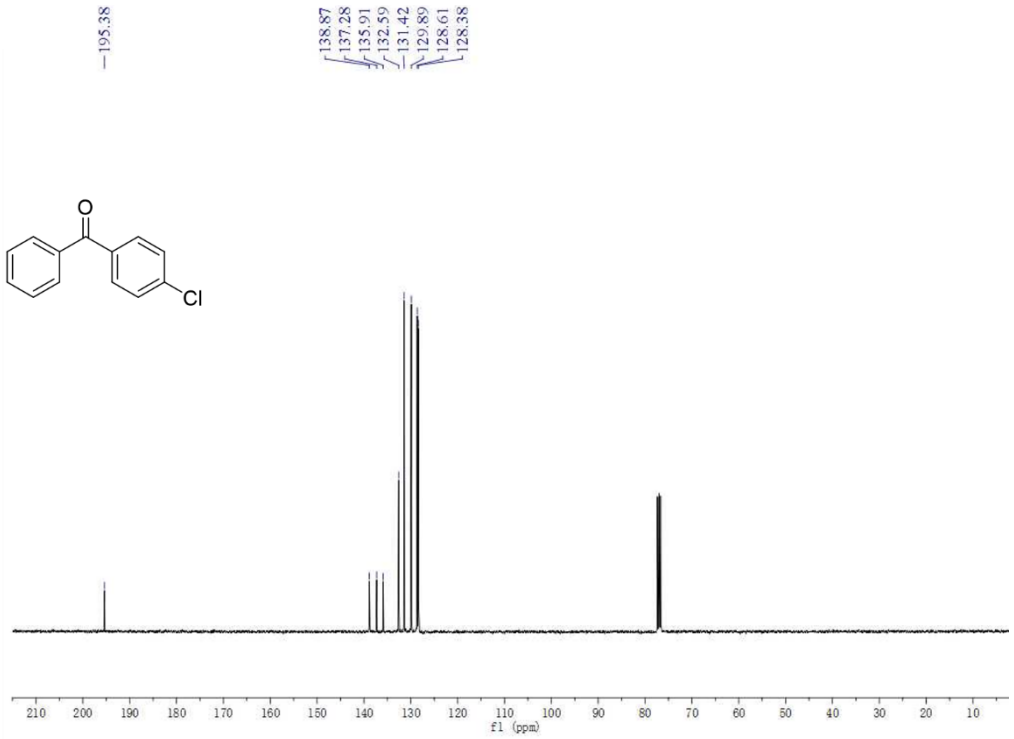
^{13}C NMR spectrum of **4i** in $CDCl_3$ at 101 MHz



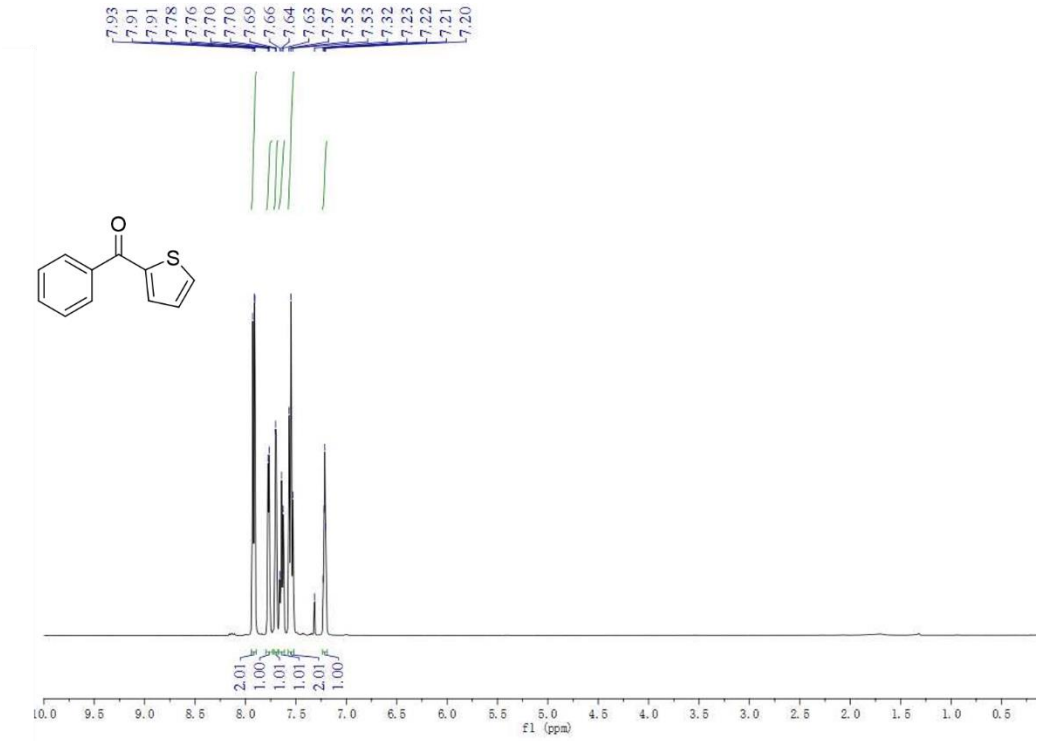
^{1}H NMR spectrum of **4j** in $CDCl_3$ at 400 MHz



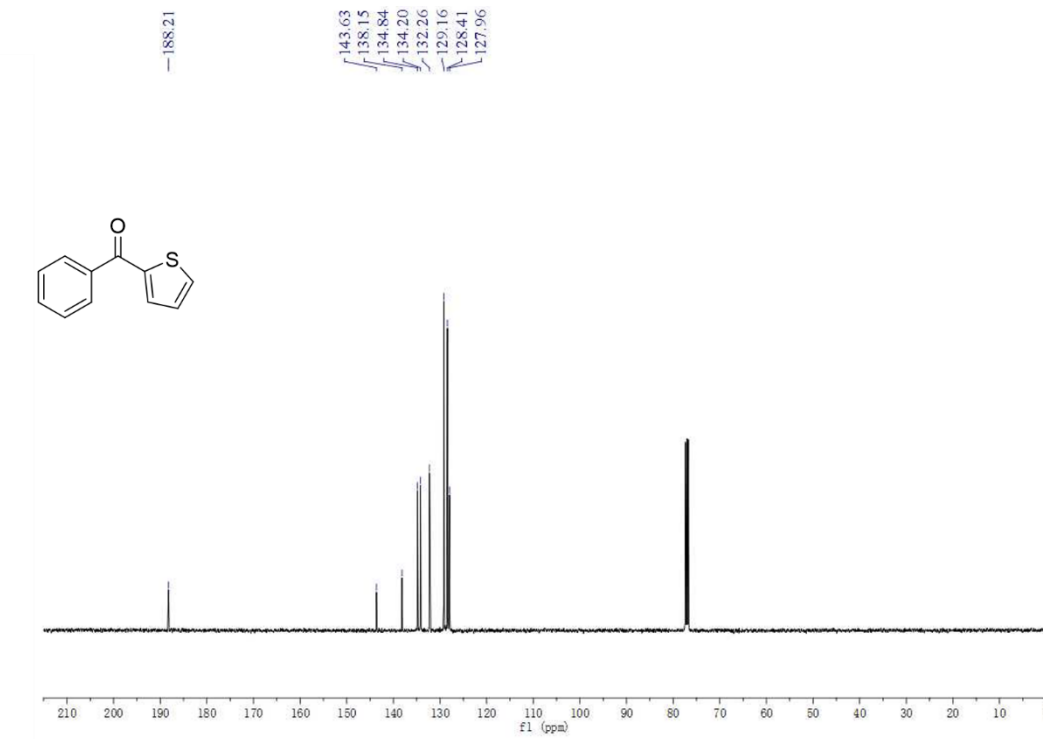
^{13}C NMR spectrum of **4j** in $CDCl_3$ at 101 MHz



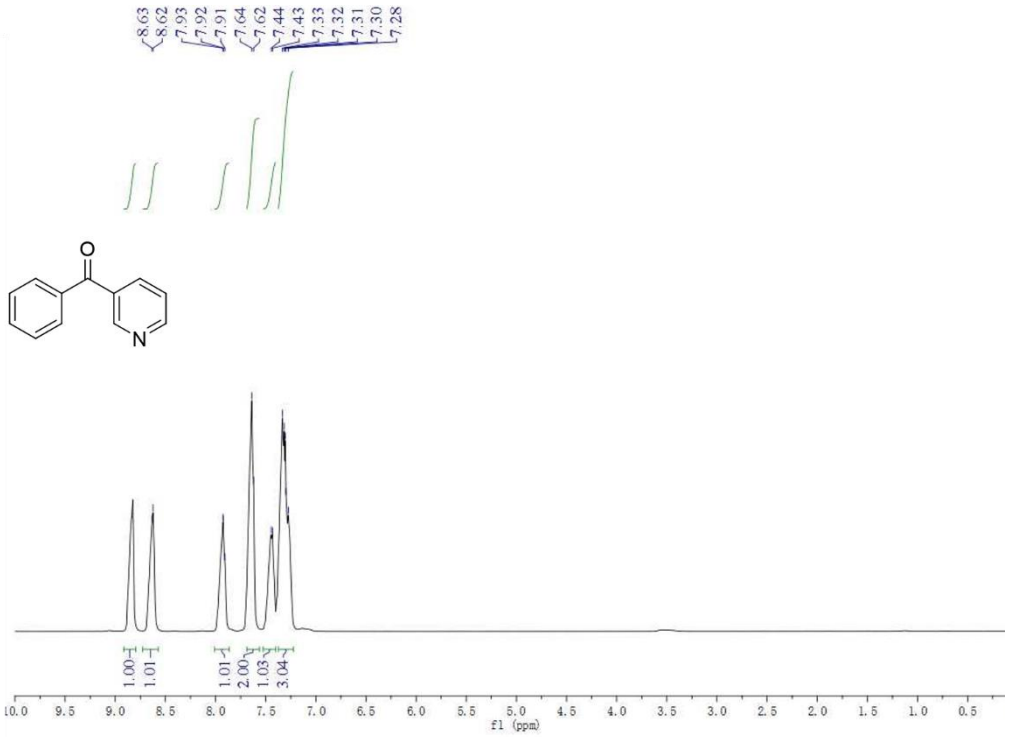
^{1}H NMR spectrum of **4k** in $CDCl_3$ at 400 MHz



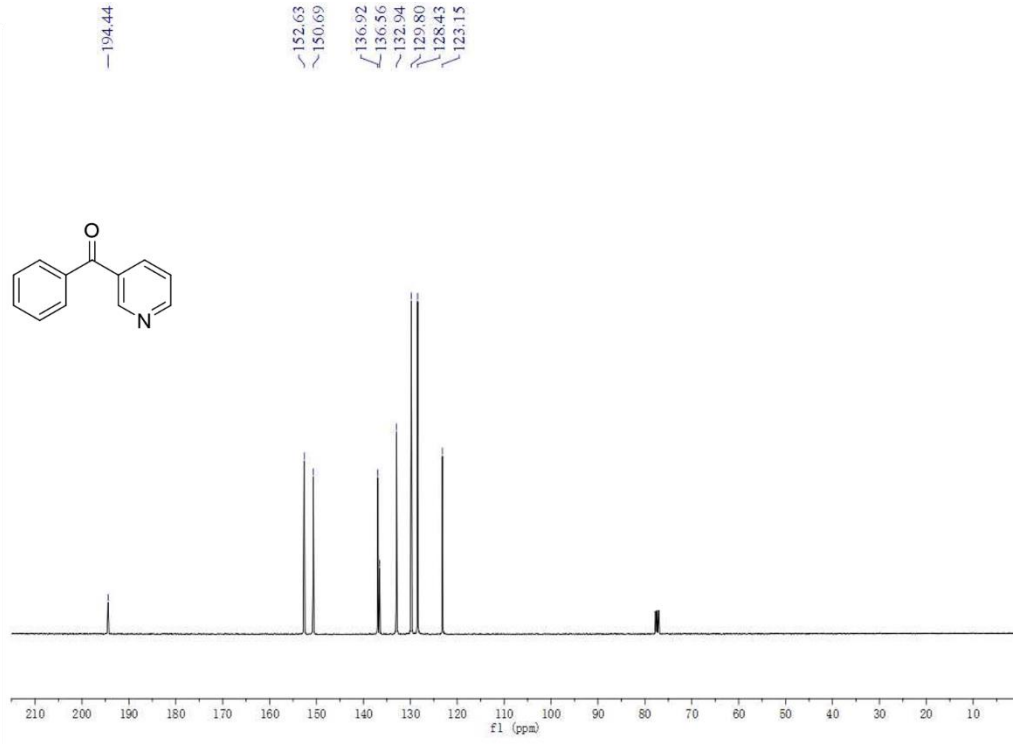
^{13}C NMR spectrum of **4k** in $CDCl_3$ at 101 MHz



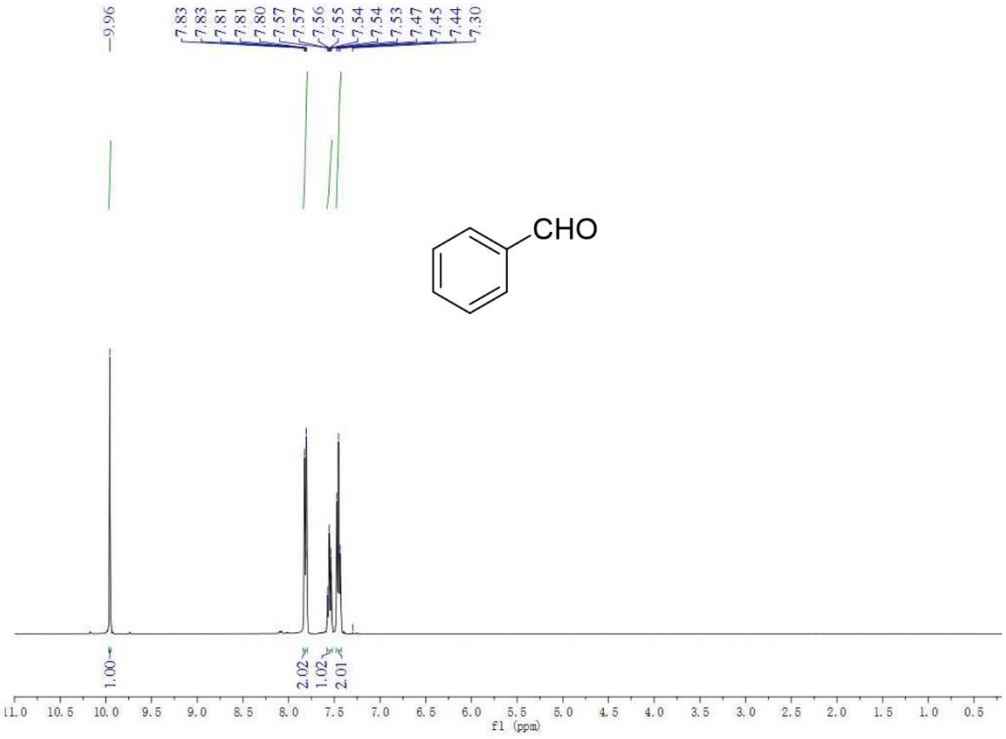
^{1}H NMR spectrum of **4l** in $CDCl_3$ at 400 MHz



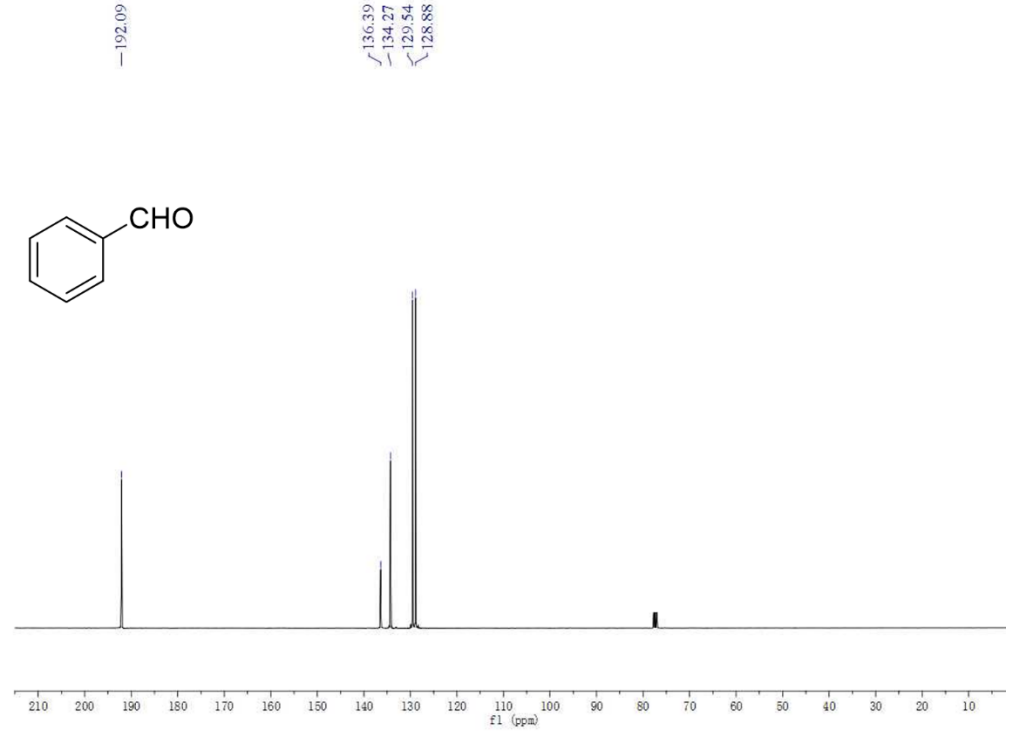
^{13}C NMR spectrum of **4l** in $CDCl_3$ at 101 MHz



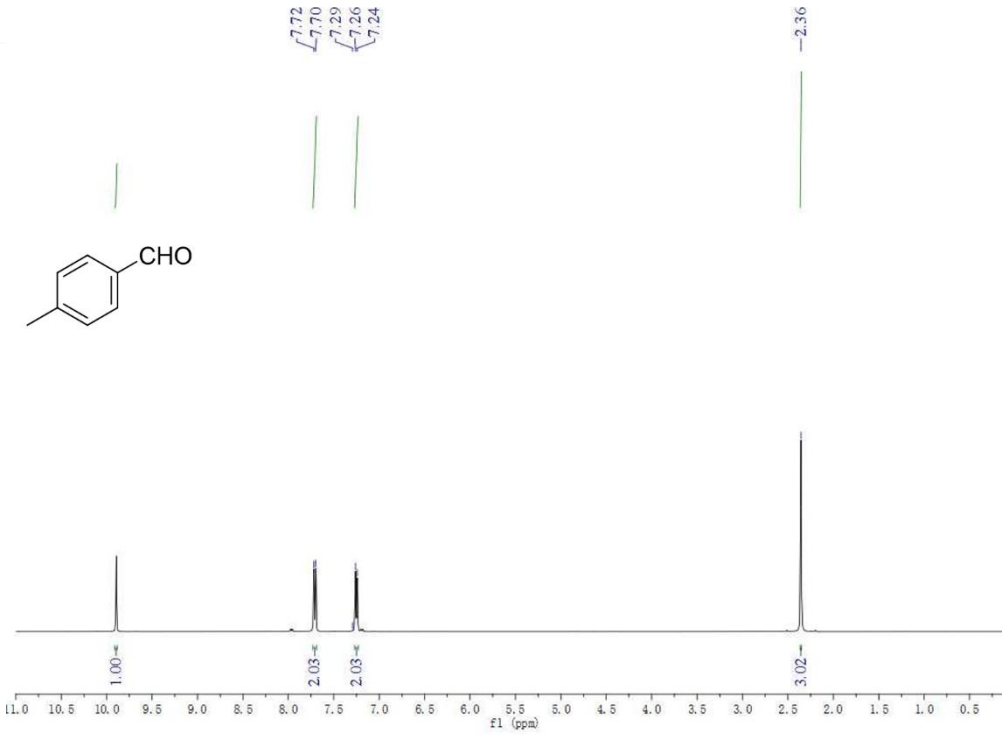
^{1}H NMR spectrum of **6a** in $CDCl_3$ at 400 MHz



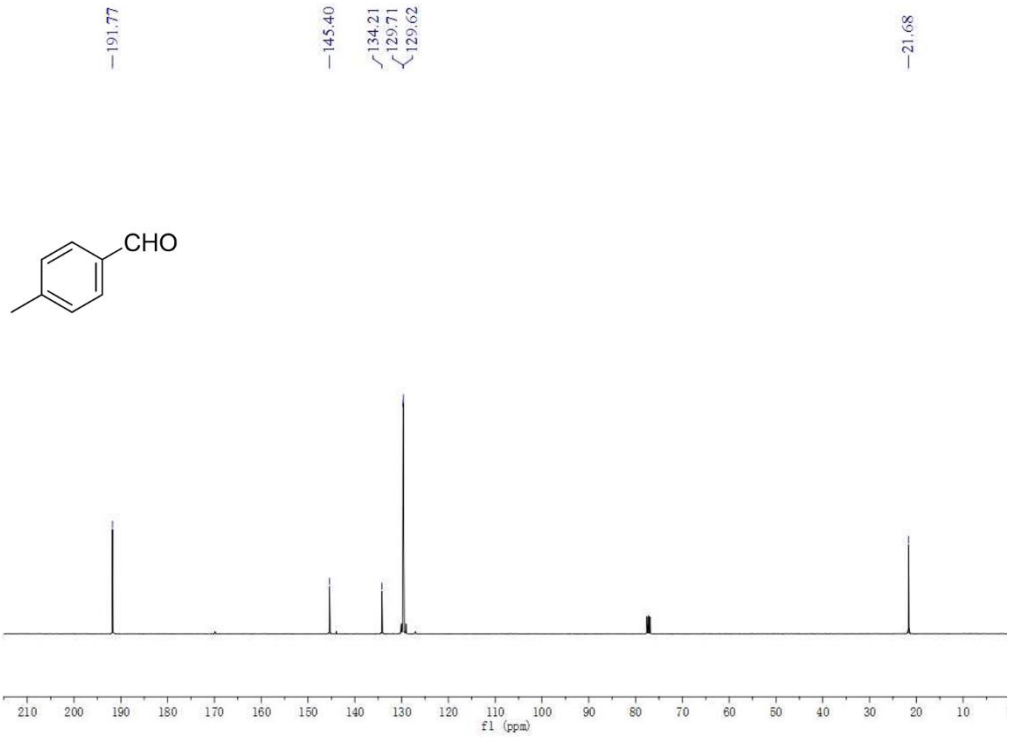
^{13}C NMR spectrum of **6a** in $CDCl_3$ at 101 MHz



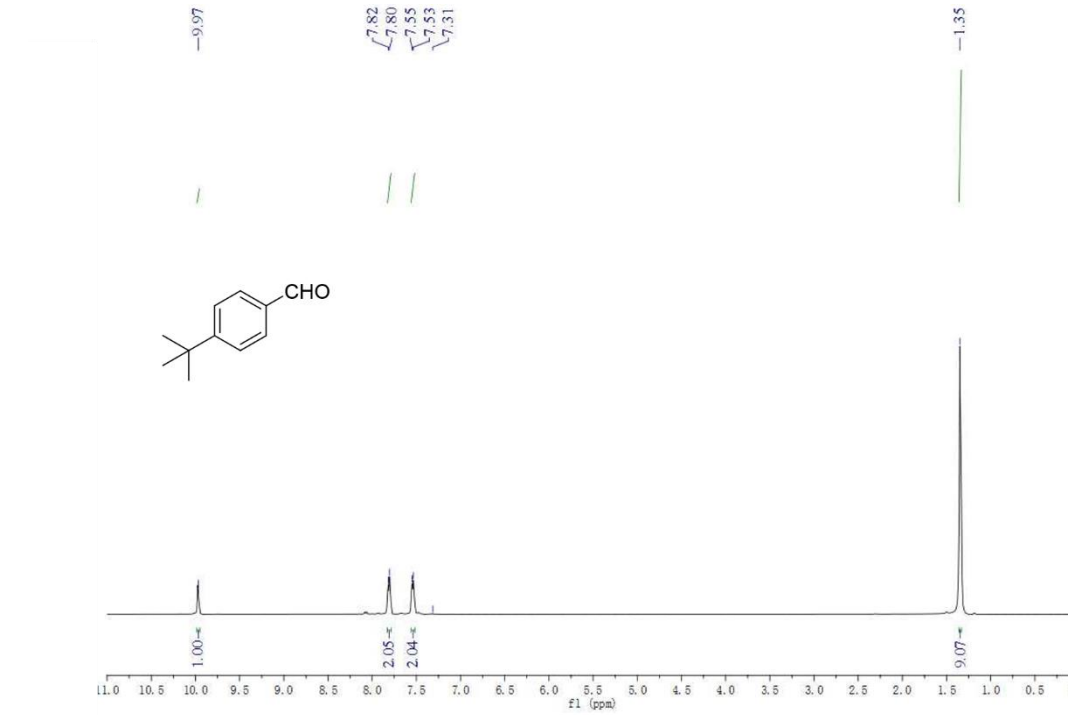
^{1}H NMR spectrum of **6b** in $CDCl_3$ at 400 MHz



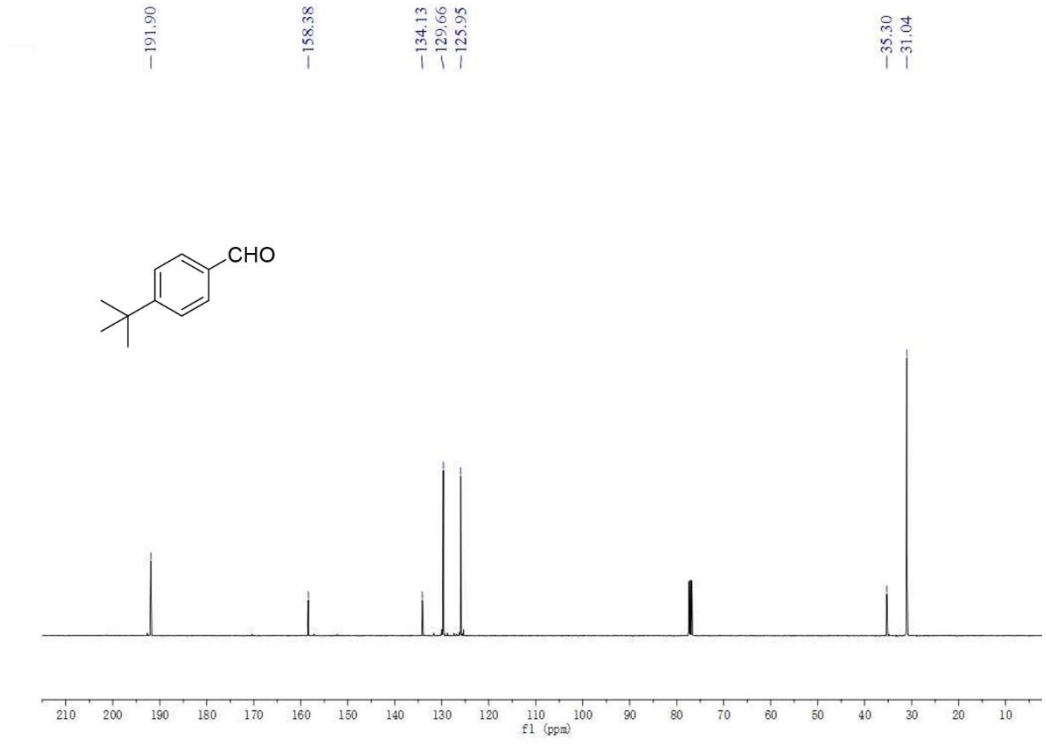
^{13}C NMR spectrum of **6b** in $CDCl_3$ at 101 MHz



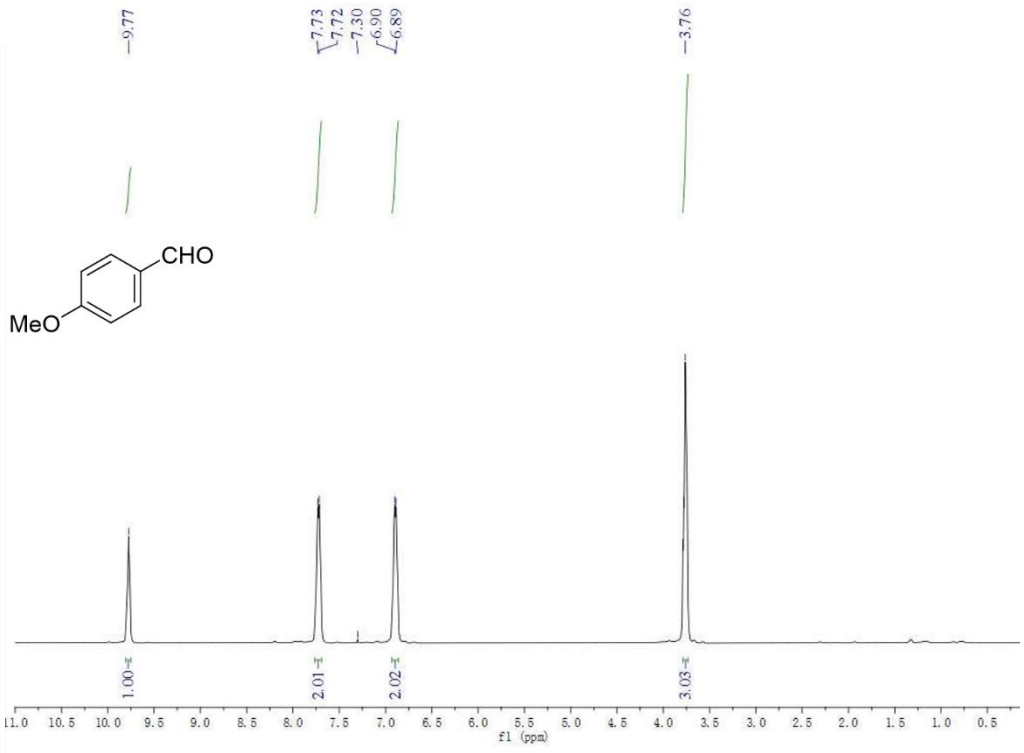
^{1}H NMR spectrum of **6c** in $CDCl_3$ at 400 MHz



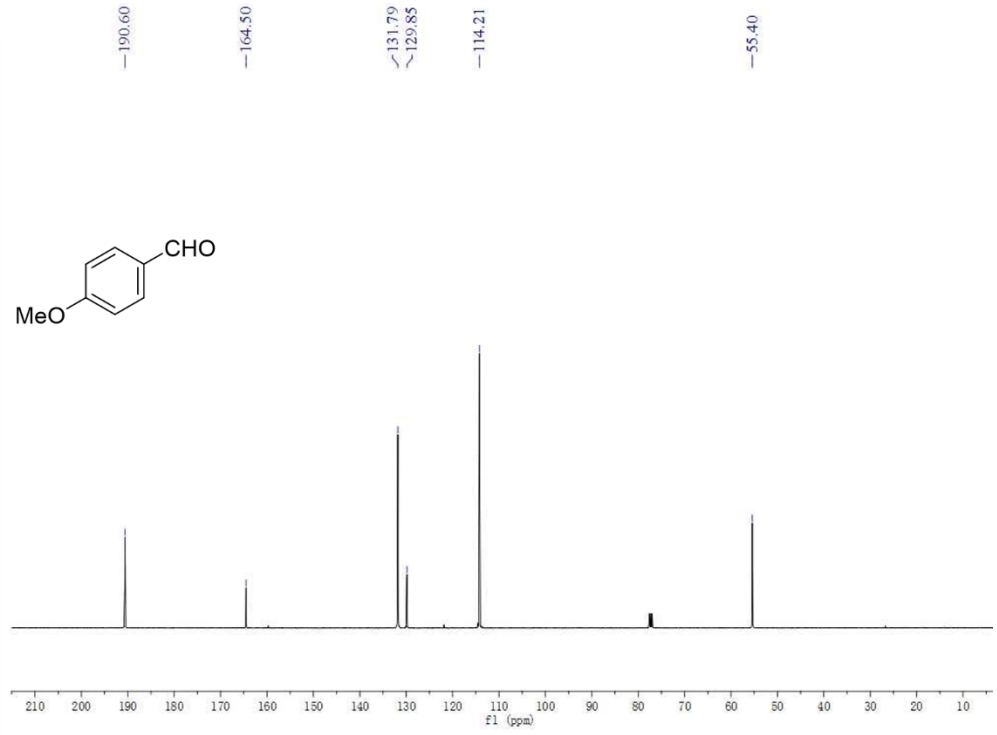
^{13}C NMR spectrum of **6c** in $CDCl_3$ at 101 MHz



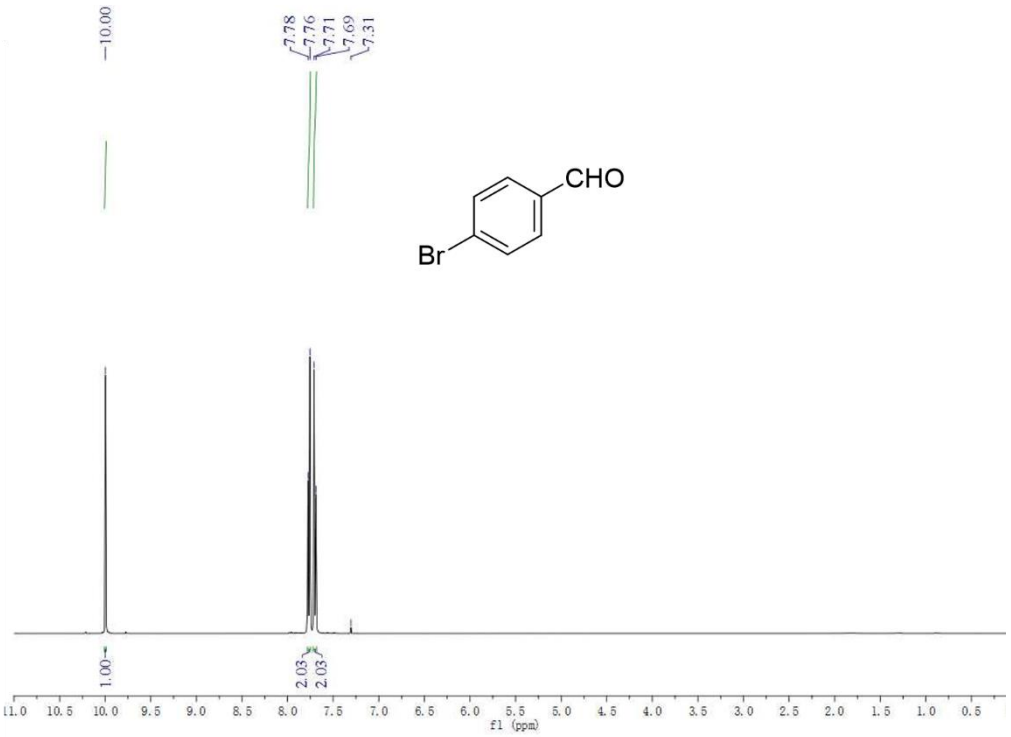
^{1}H NMR spectrum of **6d** in $CDCl_3$ at 400 MHz



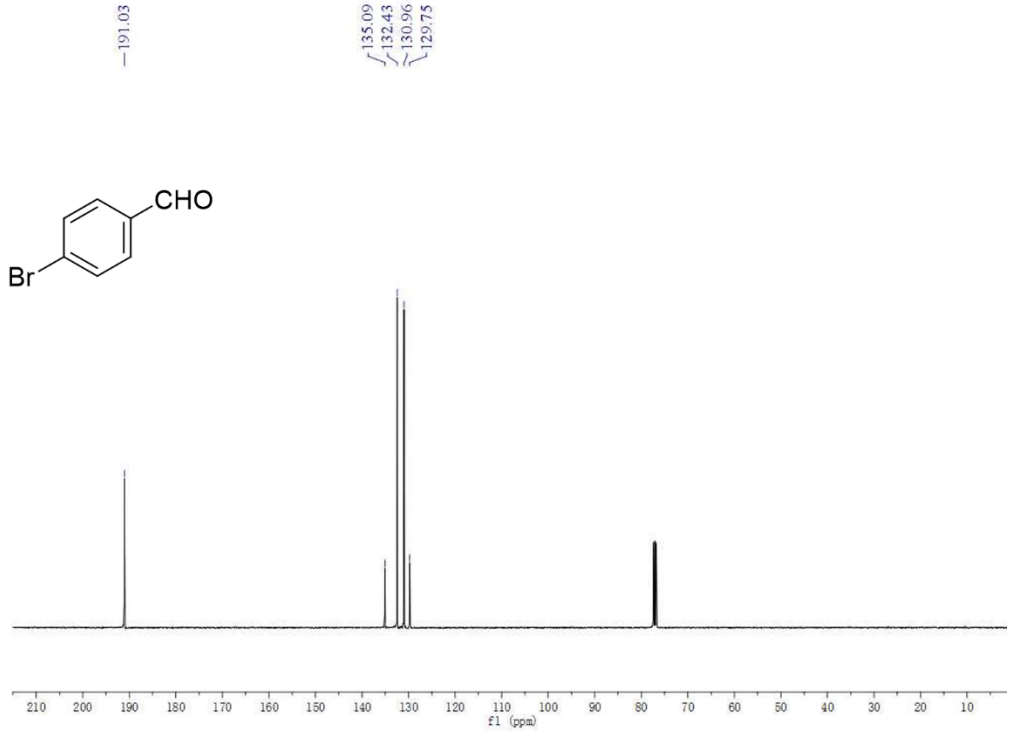
^{13}C NMR spectrum of **6d** in $CDCl_3$ at 101 MHz



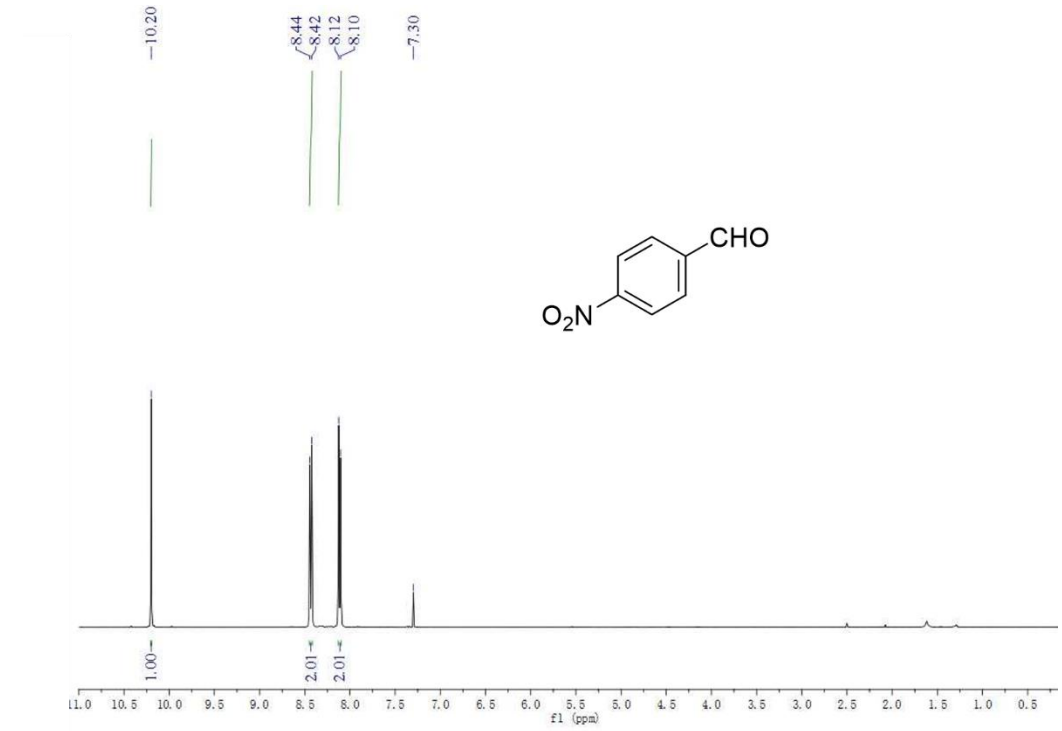
^{1}H NMR spectrum of **6e** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **6e** in $CDCl_3$ at 101 MHz



^{1}H NMR spectrum of **6f** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **6f** in $CDCl_3$ at 101 MHz