

Supporting Information

A sodium trifluoromethanesulfinate-mediated photocatalytic strategy for aerobic oxidation of alcohols

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1. General Information

A. Materials and general procedures

Sodium trifluoromethanesulfinate was purchased from Xiya Reagent (purity $\geq 99\%$). Other reagents and solvents were purchased from commercial suppliers Adamas, Bide, TCI, J&K Chemical, Energy Chemical and Meryer, and they were used directly without further purification. All reactions were conducted in oven-dried reaction vessels under O₂ atmosphere (purity $\geq 99.99\%$) unless otherwise mentioned. The reaction solutions were concentrated under reduced pressure on Shanghai YaRong rotary evaporator.

B. Analytical methods

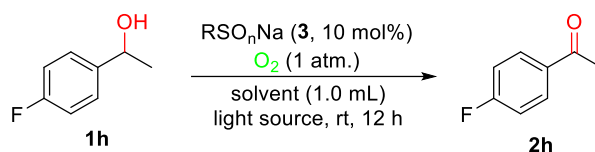
Analysis of gas chromatography-mass spectrometry (GC-MS) was acquired on a JEOL JMS-Q1050GC system equipped with a flame-ionization detector. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker Avance 400 spectrometer or JEOL ECS-400 or JNM-ECA 600 spectrometers at ambient temperature. Chemical shifts were reported in parts per million (ppm), ¹H NMR chemical shifts were internally referenced to tetramethylsilane (TMS) (¹H NMR: TMS references at 0.00 ppm) and residual proton signals of solvents (¹H NMR: CDCl₃ at 7.26 ppm, and DMSO-*d*₆ at 2.50 ppm), and ¹³C NMR chemical shifts were internally referenced to carbon signals of solvents (¹³C NMR: CDCl₃ at 77.00 ppm, DMSO-*d*₆ at 39.50 ppm). Coupling constants (*J*) were reported in Hz with the following splitting abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, and br = broad. Purification of products was accomplished by column chromatography on silica gel (Qingdao Haiyang, 200-300 mesh).

2. Investigations of the Key Reaction Parameters

Investigations on reaction conditions.

To verify our hypothesis in **Figure 1**, we attempted oxidation of 1-(4-fluorophenyl)ethanol (**1h**) to 1-(4-fluorophenyl)ethanone (**2h**) using oxygen (1 atm.) as the oxidant in the presence of 10 mol% sodium trifluoromethanesulfinate (**3a**) under irradiation of 3 W LED (400-405 nm) at room temperature for 12 h. As shown in Table 1, the reaction provided a quantitative conversion to **2h** (entry 1). Other light sources were tried (entries 2-6), and we found that the 3 W LEDs (380-385 nm and 360-365 nm) also were suitable (entries 5 and 6). No reaction occurred in the absence of light (entry 7). The effect of solvents was investigated (entries 8-12), and DMF was proved to be adoptable (entry 12). Other sulfide reagents were screened (entries 13-18), and they were inferior to sodium trifluoromethanesulfinate (**3a**). The reaction did not work without addition of a sulfide agent (entry 19). A quantitative conversion was also observed when air replaced oxygen as the oxidant (entry 20). The reaction was not performed under an argon atmosphere (entry 21). We changed reaction time to 6 h (entry 22), and yield slightly decreased (compare entries 1 and 22). Different amounts of **3a** were used as the precursor of photocatalyst (entries 23-25), and a quantitative conversion yield was provided in the presence of 25 mol% or 5 mol% of **3a**. Therefore, optimal conditions for the photoredox aerobic oxidation of secondary alcohols to ketones are as follows: 5-25 mol% of sodium trifluoromethanesulfinate (**3a**) as the precursor of photocatalyst, MeCN or DMF as the solvent, 3 W LED (400-405 nm) as the light source under oxygen or air atmosphere (1 atm.) at room temperature for 12 h.

Table S1 Optimization of conditions for photocatalytic aerobic oxidation of 1-(4-fluorophenyl)ethanol (**1h**) to 1-(4-fluorophenyl)ethanone (**2h**)^a

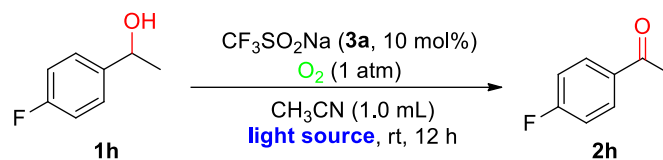


Entry	RSO _n Na (3)	Light source	Solvent	Yield (%) ^b
1	CF ₃ SO ₂ Na (3a)	3 W LED (400-405 nm)	MeCN	100 (96 ^c)
2	3a	3 W LED (530-535 nm)	MeCN	nr
3	3a	3 W LED (450-455 nm)	MeCN	trace
4	3a	3 W LED (420-425 nm)	MeCN	3
5	3a	3 W LED (380-385 nm)	MeCN	100
6	3a	3 W LED (360-365 nm)	MeCN	95
7	3a	dark	MeCN	nr
8	3a	3 W LED (400-405 nm)	CH ₂ Cl ₂	nr
9	3a	3 W LED (400-405 nm)	THF	9
10	3a	3 W LED (400-405 nm)	EtOAc	trace
11	3a	3 W LED (400-405 nm)	acetone	78
12	3a	3 W LED (400-405 nm)	DMF	98
13	EtSO ₂ Na (3b)	3 W LED (400-405 nm)	MeCN	trace
14	PhSO ₂ Na (3c)	3 W LED (400-405 nm)	MeCN	nr
15	CF ₃ SOCi (3d)	3 W LED (400-405 nm)	MeCN	46
16	^t BuSOCi (3e)	3 W LED (400-405 nm)	MeCN	61
17	TfOH (3f)	3 W LED (400-405 nm)	MeCN	nr
18	Tf ₂ O (3g)	3 W LED (400-405 nm)	MeCN	trace
19		3 W LED (400-405 nm)	MeCN	nr
20 ^d	3a	3 W LED (400-405 nm)	MeCN	100
21 ^e	3a	3 W LED (400-405 nm)	MeCN	nr
22 ^f	3a	3 W LED (400-405 nm)	MeCN	94
23 ^g	3a	3 W LED (400-405 nm)	MeCN	100
24 ^h	3a	3 W LED (400-405 nm)	MeCN	100
25 ⁱ	3a	3 W LED (400-405 nm)	MeCN	61

^aReaction conditions: **1a** (0.1 mmol), catalyst (**3**) (10 mol%), solvent (1.0 mL), under O₂ atmosphere (1 atm.) and light irradiation (3 W) at room temperature (~25 °C) for 12 h. ^bThe conversion yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard.

^cIsolated yield. ^dUnder air. ^eAr atmosphere. ^f6 h. ^gCF₃SO₂Na (25 mol %). ^hCF₃SO₂Na (5 mol%). ⁱCF₃SO₂Na (2 mol%). nr = no reaction.

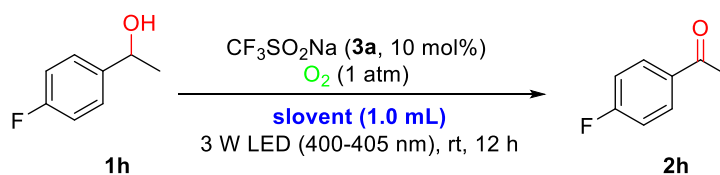
Table S2 Effect of different light source in the aerobic oxidation of alcohol^a



Entry	Light source	Yield (%)
1	3 W LED (400-405 nm)	100
2	dark	nr
3	CFL (34 W)	nr
4	3 W LED (530-535 nm)	nr
5	3 W LED (450-455 nm)	trace
6	3 W LED (420-425 nm)	3
7	3 W LED (380-385 nm)	100
8	3 W LED (360-365 nm)	95

^aReaction conditions: **1h** (0.1 mmol), CF₃SO₂Na (**3a**, 10 mol%), CH₃CN (1.0 mL) under O₂ atmosphere and light irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard. nr = no reaction.

Table S3 Effect of different solvents in the aerobic oxidation of alcohol^a

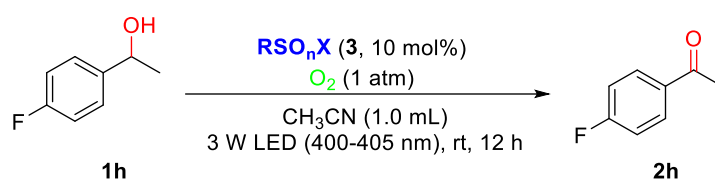


Entry	Solvent	Yield (%)
1	CH ₃ CN	100
2	DCM	nr
3	DCE	nr
4	THF	9
5	DMF	98
6	DMSO	14
7	dioxane	11
8	MeOH	nr

9	EtOH	nr
10	EtOAc	trace
11	acetone	78

^aReaction conditions: **1h** (0.1 mmol), CF₃SO₂Na (**3a**, 10 mol%), solvent (1.0 mL) under O₂ atmosphere and 3 W LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard. nr = no reaction.

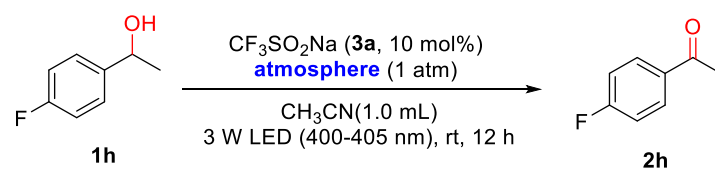
Table S4 Effect of different RSO_nX in the aerobic oxidation of alcohol^a



Entry	RSO _n X	Yield (%)
1	CF ₃ SO ₂ Na	100
2	CF ₃ SO ₃ Na	nr
3	CH ₃ SO ₂ Na	trace
4	CH ₃ CH ₂ SO ₂ Na	trace
5	^t BuSOCl	61
6	CF ₃ SOC1	46
7	TfOH	nr
8	(TfO) ₂ O	trace
9	PhSO ₂ Na	nr
10	-	nr

^aReaction conditions: **1h** (0.1 mmol), RSO_nX (**3**, 10 mol%), CH₃CN (1.0 mL) under O₂ atmosphere and 3 W LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard. nr = no reaction.

Table S5 Effect of different atmospheres in the aerobic oxidation of alcohol^a

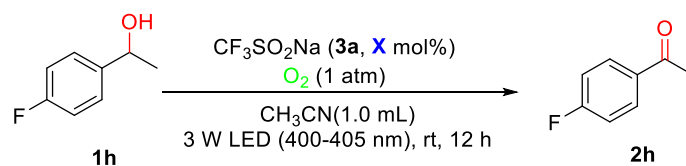


Entry	Atmosphere	Yield (%)
1	O ₂	100

2	air	100
3	Ar	nr

^aReaction conditions: **1h** (0.1 mmol), CF₃SO₂Na (**3a**, 10 mol%), CH₃CN (1.0 mL) under different atmosphere and 3 W LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard. nr = no reaction.

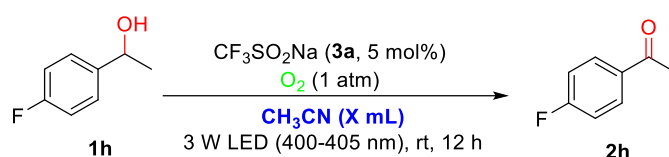
Table S6 Effect of different CF₃SO₂Na loadings in the aerobic oxidation of alcohol^a



Entry	X	Yield (%)
1	50	100
2	25	100
3	10	100
4	5	100
5	2	61
6	0	nr

^aReaction conditions: **1h** (0.1 mmol), CF₃SO₂Na (**3a**, x mol%), CH₃CN (1.0 mL) under O₂ atmosphere and 3 W LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard. nr = no reaction.

Table S7 Effect of different amounts of CH₃CN in the aerobic oxidation of alcohol^a



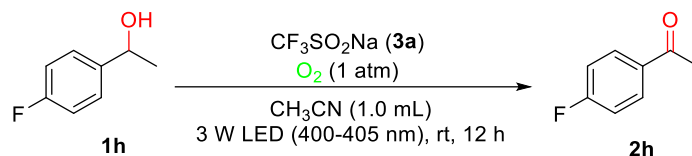
Entry	X	Yield (%)
1	1.5	100
2	1.0	100
3	0.5	100

^aReaction conditions: **1h** (0.1 mmol), CF₃SO₂Na (**3a**, 5 mol%), CH₃CN (x mL) under O₂ atmosphere and 3 W LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard. nr = no reaction.

3. General Experimental Procedures

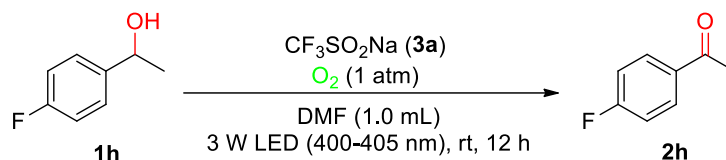
3.1 Experimental procedures

General procedure A



1-(4-Fluorophenyl)ethanol (**1h**, 1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (**3a**, 5 mol%, 10 mol% or 25 mol%) and CH_3CN (1.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O_2 atmosphere. After the reaction was completed, the mixture was analyzed by GC-MS, and the yield was determined using dodecane as the internal standard. The reaction solution was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2h**.

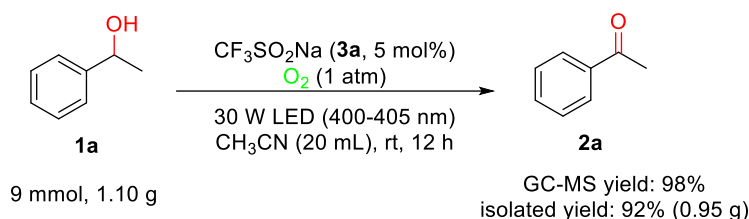
General procedure B



1-(4-Fluorophenyl)ethanol (**1h**, 1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (**3a**, 5 mol%, 10 mol% or 25 mol%) and DMF (1.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O_2 atmosphere. After the reaction was completed, the mixture was analyzed by GC-MS, and the yield was determined using dodecane as the internal standard. The reaction solution was concentrated under reduced pressure, and the residue was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2h**.

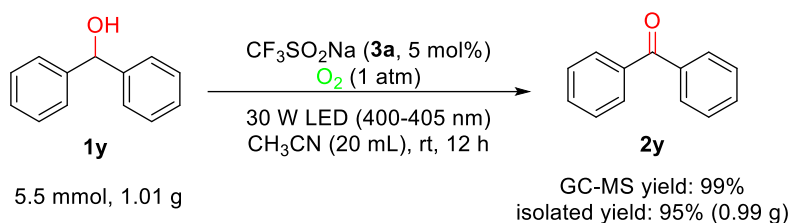
4. Scale-up Reactions

4.1 Scale-up reaction for the oxidation of 1-phenylethan-1-ol



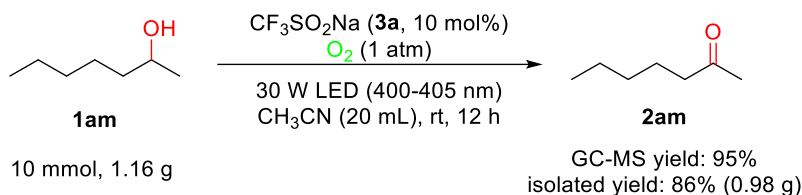
Phenylethan-1-ol (**1a**, 1.0 equiv, 9 mmol, 1.10 g), sodium trifluoromethanesulfinate (**3a**, 5 mol%) and CH_3CN (20 mL) were added to an oven-dried reaction vessel (50 mL) equipped with magnetic stirring bar, and the reaction vessel was irradiated with 30 W LED (400-405 nm) for 12 h under O_2 atmosphere. After the reaction was completed, the yield was determined by GC-MS using dodecane as the internal standard to give acetophenone (**2a**) in 98% conversion yield. And the reaction solution was concentrated under reduced pressure to provide a crude product, that was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2a** in 92% isolated yield (0.95 g).

4.2 Scale-up reaction for the oxidation of diphenylmethanol



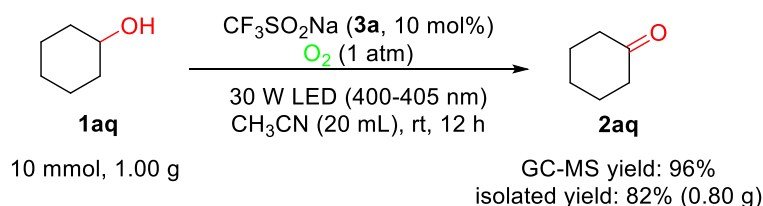
Diphenylmethanol (**1y**, 1.0 equiv, 5.5 mmol, 1.01 g), sodium trifluoromethanesulfinate (**3a**, 5 mol%) and CH_3CN (20 mL) were added to an oven-dried reaction vessel (50 mL) equipped with magnetic stirring bar, and the reaction vessel was irradiated with 30 W LED (400-405 nm) for 12 h under O_2 atmosphere. After the reaction was completed, the yield was determined by GC-MS using dodecane as the internal standard to give benzophenone (**2y**) in 99% conversion yield. And the reaction solution was concentrated under reduced pressure to provide crude product, that was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2y** in 95% isolated yield (0.99 g).

4.3 Scale-up reaction for the oxidation of heptan-2-ol



Heptan-2-ol (**1am**, 1.0 equiv, 10 mmol, 1.16 g), sodium trifluoromethanesulfinate (**3a**, 10 mol%) and CH_3CN (20 mL) were added to an oven-dried reaction vessel (50 mL) equipped with magnetic stirring bar, and the reaction vessel was irradiated with 30 W LED (400-405 nm) for 12 h under O_2 atmosphere. After the reaction was completed, the yield was determined by GC-MS using dodecane as the internal standard to give heptan-2-one (**2am**) in 95% conversion yield. And the reaction solution was concentrated under reduced pressure to provide a crude product, that was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2am** in 86% isolated yield (0.98 g).

4.4 Scale-up reaction for the oxidation of cyclohexanol

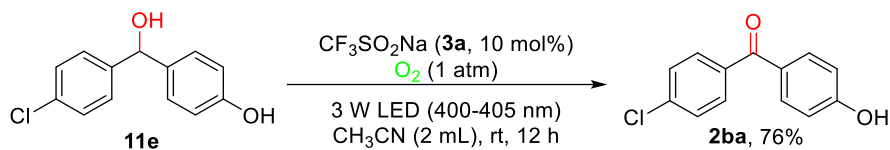


Cyclohexanol (**1aq**, 1.0 equiv, 10 mmol, 1.00 g), sodium trifluoromethanesulfinate (**3a**, 10 mol%) and CH_3CN (20 mL) were added to an oven-dried reaction vessel (50 mL) equipped with magnetic stirring bar, and the reaction vessel was irradiated with 30 W LED (400-405 nm) for 12 h under O_2 atmosphere. After the reaction was completed, the yield was determined by GC-MS using dodecane as the internal standard to give cyclohexanone (**2aq**) in 96% conversion yield. And the reaction solution was concentrated under reduced pressure to provide a crude product, that was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2aq** in 82% isolated yield (0.80 g).

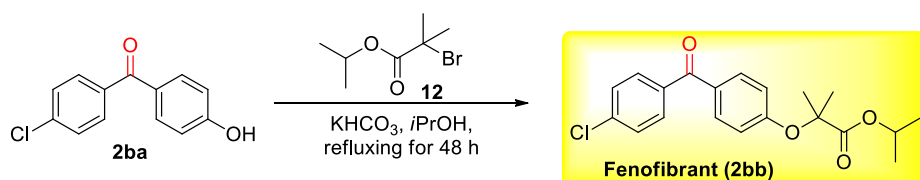
5. The Synthetic Applications

5.1 Synthesis of drug fenofibrate

5.1.1 Synthesis of fenofibrate from 4-((4-chlorophenyl)(hydroxy)methyl)phenol (11e)



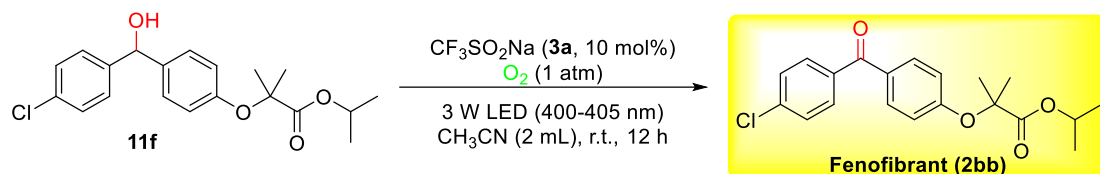
4-((4-Chlorophenyl)(hydroxy)methyl)phenol (**11e**, 1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfonate (**3a**, 10 mol%) and CH_3CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O_2 atmosphere. After the reaction was completed, the resulting solution was concentrated under reduced pressure to get a crude product, that was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give (4-chlorophenyl)(4-hydroxyphenyl)methanone (**2ba**) as a white solid in 76% yield (35.4 mg). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.49 (s, 1H), 7.67 (t, $J = 8.9$ Hz, 4H), 7.59 (d, $J = 8.4$ Hz, 2H), 6.90 (d, $J = 8.6$ Hz, 2H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 193.14, 162.18, 136.75, 136.67, 132.54, 131.04, 128.50, 127.55, 115.33.



2ba (0.1 mmol, 1 equiv) was dissolved in isopropylalcohol (2.0 mL), then KHCO_3 (0.2 mmol, 2 equiv) was added, and the resulting solution was stirred for 10 min at room temperature. Isopropyl 2-bromo-2-methylpropanoate (**12**) (0.2 mmol, 2 equiv) was added, and the reaction mixture was refluxed at 90 °C for 48 h. After completion of the reaction, the reaction solution was concentrated under reduced pressure to get a crude product, that was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give fenofibrate (**2bb**) as a white solid (32.4 mg, 90%). ^1H and ^{13}C NMR of **2bb** is identical with the spectra of the known compound.¹ ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.7$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 5.18 – 5.00 (m, 1H), 1.66 (s, 6H), 1.20 (d, $J = 6.2$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 194.24, 173.08, 159.71, 138.33, 136.40,

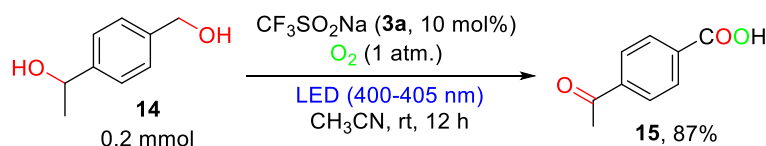
131.93, 131.14, 130.19, 128.52, 117.21, 79.40, 69.33, 25.35, 21.51.

5.1.2 Synthesis of fenofibrate from 4-((4-chlorophenyl)(hydroxy)methyl)phenol (11f)



4-((4-Chlorophenyl)(hydroxy)methyl)phenol (**11f**, 1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (**3a**, 10 mol%) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. After the reaction completed, the resulting solution was concentrated under reduced pressure to get a crude product, that was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give (4-chlorophenyl)(4-hydroxyphenyl)methanone (**2bb**) as a white solid in 83% yield (59.8 mg).

5.2 Photocatalytic aerobic oxidation of 1-(4-(hydroxymethyl)phenyl)ethan-1-ol containing two different kinds of hydroxyls.



1-(4-(Hydroxymethyl)phenyl)ethan-1-ol (**14**, 1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (**3a**, 10 mol%) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. After the reaction completed, the resulting solution was concentrated under reduced pressure to get a crude product. After this, the crude product was dissolved in H₂O (4 mL), and the solution was adjusted to pH = 12 with 0.1 M NaOH. The resulting solution was then washed with methylene chloride (DCM) three times with a total DCM volume of 20 mL. The aqueous phase was adjusted to pH = 2 with 0.1M HCl, and the desired product 4-acetylbenzoic acid (**15**) was precipitated as a white solid in 87% yield (28.6

mg). This result showed that our method was very practical for synthesis of multi-functional compounds.

6. Studies on Reaction Mechanism

6.1 UV-vis absorption spectroscopic measurements

6.1.1 UV-vis absorption spectroscopic measurement of $\text{CF}_3\text{SO}_2\text{Na}$

The UV-vis absorption spectrum of $\text{CF}_3\text{SO}_2\text{Na}$ was recorded on Beijing Purkinje TU-1901 UV-visible spectrophotometer. The sample was prepared by mixing $\text{CF}_3\text{SO}_2\text{Na}$ (0.2 mmol, 31.2 mg) in CH_3CN (total volume = 3.0 mL). The reaction mixture was stirred for 10 min, and the reaction mixture was filtered with a filter. The resulted solution was stored in a light path quartz fluorescence cuvette, and UV-vis absorption spectrum was recorded (**Figure S1**).

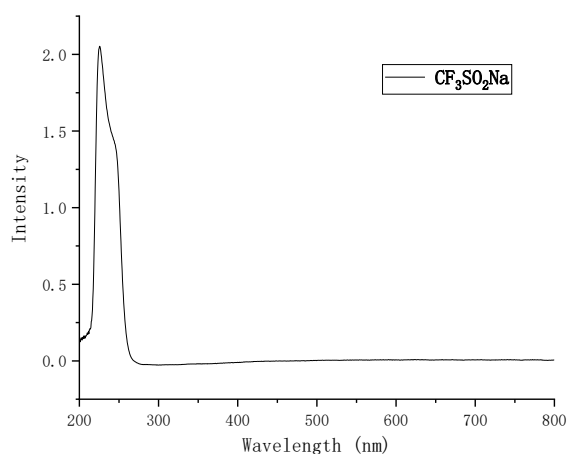


Figure S1. The UV-vis absorption spectrum of $\text{CF}_3\text{SO}_2\text{Na}$

6.1.2 UV-vis absorption spectroscopic measurement of $\text{CF}_3\text{SO}_4\text{Na}$

The UV-vis absorption spectrum of $\text{CF}_3\text{SO}_4\text{Na}$ was recorded on Beijing Purkinje TU-1901 UV-visible spectrophotometer. The sample was prepared by mixing $\text{CF}_3\text{SO}_2\text{Na}$ (0.2 mmol, 31.2 mg) in CH_3CN (total volume = 3.0 mL) to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under O_2 (1 atm.) atmosphere. After the reaction was completed, the reaction mixture was detected by ^{19}F NMR, which showed the $\text{CF}_3\text{SO}_2\text{Na}$ had converted into the corresponding pentacoordinate

sulfide. Then the reaction mixture was filtered with a filter. The resulted solution was stored in a light path quartz fluorescence cuvette, and UV-vis absorption spectrum was recorded. As shown in **Figure S2**, the absorption at 400 nm was observed.

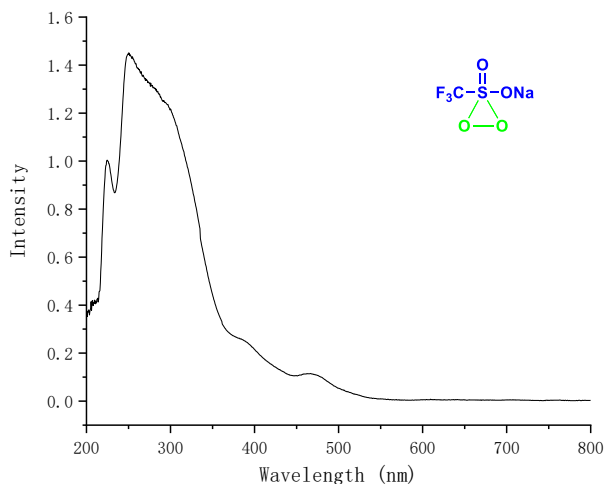
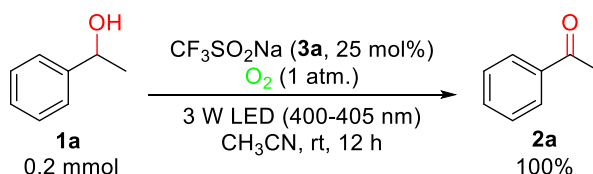


Figure S2. The UV-vis absorption spectrum of CF₃SO₄Na

On the basis of the above investigations, the UV-vis absorption spectrum of CF₃SO₄Na (**Figure S2**) is very distinct from the spectra of CF₃SO₂Na (**Figure S1**). Moreover, the absorption intensity of CF₃SO₄Na at 400 nm was bigger than that of CF₃SO₂Na (**Figure S1**).

6.1.3 UV-vis absorption spectroscopic measurement of the reaction solution

The UV-vis absorption spectrum of the reaction solution was recorded on Beijing Purkinje TU-1901 UV-visible spectrophotometer.



The sample was prepared by mixing CF₃SO₂Na (0.05 mmol, 7.8 mg) and 1-phenylethan-1-ol (0.1 mmol, 12.2 mg) in CH₃CN (total volume = 2.0 mL) to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under O₂ (1 atm.) atmosphere. After the reaction was completed, the reaction mixture was filtered with a filter. The resulted solution was stored in a light path quartz fluorescence cuvette, and

UV-vis absorption spectrum was recorded. As shown in **Figure S3**, the UV-Vis absorption patterns of the reaction solution was similar to $\text{CF}_3\text{SO}_4\text{Na}$ (**Figure S2**), and the additive peak in reaction solution could be attributed to the acetophenone.

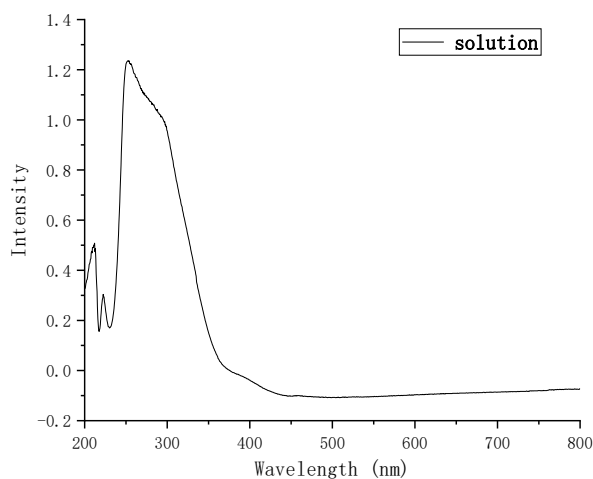


Figure S3. The UV-vis absorption spectrum of reaction solution

6.2 Oxygen type investigations determined by EPR

6.2.1 Determination of singlet oxygen in the reaction

In order to determine the active species of oxygen involved in the present reaction, 2,2,6,6-tetramethylpiperidin-4-one (TMPD) was employed to capture $^1\text{O}_2$. As shown in **Figure S4a**, no obvious signal was detected when the acetonitrile solution of TMPD and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) was not irradiated with light. However, when the same solution was irradiated with full wavelength light, a series of characteristic signal of $^1\text{O}_2$ adduct with TMPD was observed. Moreover, when the irradiation time was prolonged, a series of stronger characteristic signal of $^1\text{O}_2$ adduct with TMPD were collected (**Figure S4b-4g**).

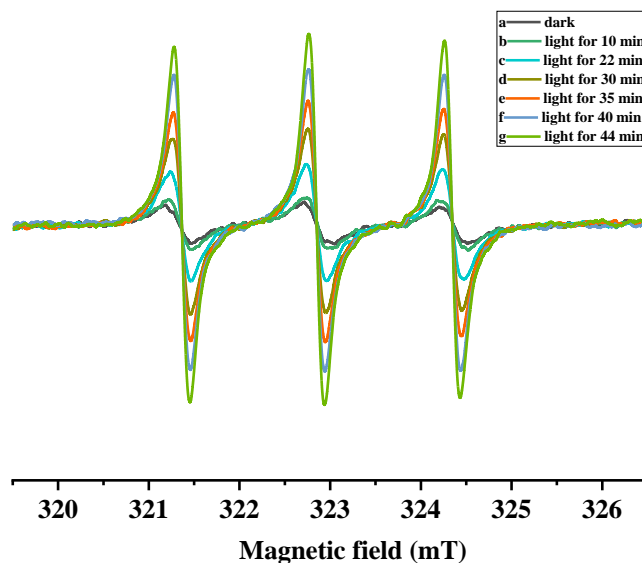


Figure S4 The X-band electron paramagnetic resonance (EPR) spectra of the singlet oxygen captured by TMPD. The g -value ($g = 2.0068$) is derived from the spectra. (a) Solution of TMPD, and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN without light irradiation. (b) solution of TMPD, and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 10 min. (c) Solution of TMPD, and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 22 min. (d) Solution of TMPD, and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 30 min. (e) Solution of TMPD, and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 35 min. (f) Solution of TMPD, and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 40 min. (g) Solution of TMPD, and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 44 min.

6.2.2 Determination of superoxide radical anion in the reaction

Superoxide radical anion ($\text{O}_2^{\bullet-}$) is generated from molecular oxygen by single electron transfer (SET).² 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was used as a probe to capture active species $\text{O}_2^{\bullet-}$. As shown in Figure S5, no signal was detected when the acetonitrile solution of DMPO and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) was not irradiated with light. However, when the same solution was irradiated with full wavelength light, a series of characteristic signal of $\text{O}_2^{\bullet-}$ adduct with DMPO was observed. In addition, when the irradiation time was prolonged, a series of stronger characteristic signal of $\text{O}_2^{\bullet-}$ were collected (Figure S5).

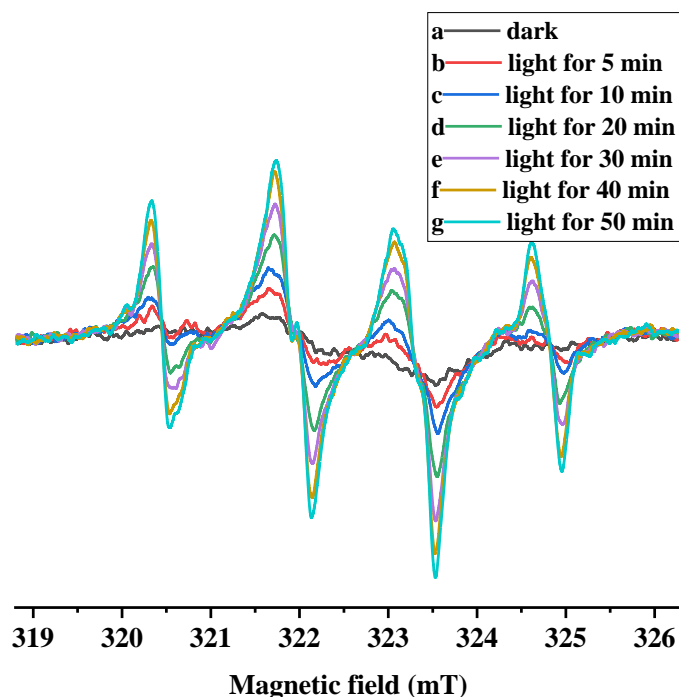
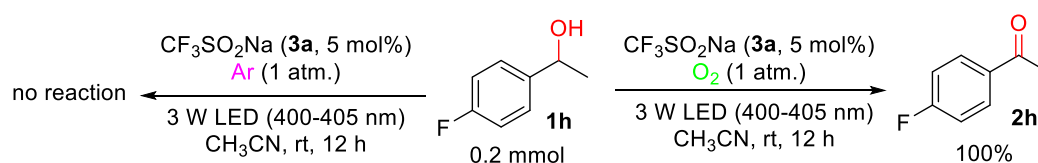


Figure S5 The X-band electron paramagnetic resonance (EPR) spectra of the superoxide radical anion captured by DMPO. (a) Solution of DMPO and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN without light irradiation. (b) Solution of DMPO and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 5 min. (c) Solution of DMPO and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 10 min. (d) Solution of DMPO and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 20 min. (e) Solution of DMPO and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 30 min. (f) Solution of DMPO and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 40 min. (g) Solution of DMPO and $\text{CF}_3\text{SO}_2\text{Na}$ (**3a**) in air-saturated CH_3CN with light irradiation for 50 min.

6.3 Controlled experiments

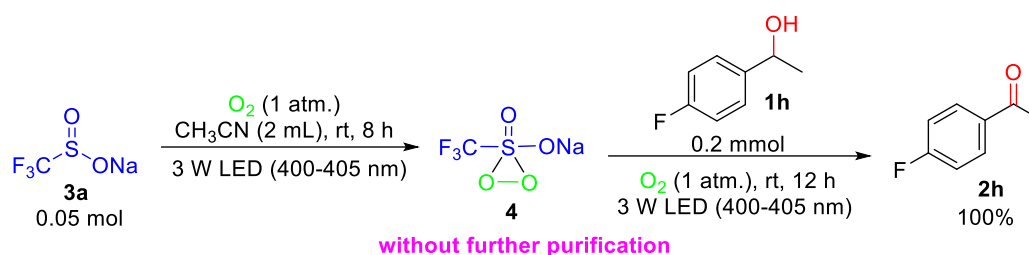
In order to explore the possible mechanism of the present transformation, various control experiments were conducted.

6.3.1 Controlled experiments of atmospheres



1-(4-Fluorophenyl)ethan-1-ol (**1h**, 1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (**3a**, 5 mol%) and CH₃CN (1.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under Ar atmosphere. TLC (PE/EA = 30:1) and GC-MS showed that no desired product **2h** was detected and **1h** was totally remained. The above reaction solution was further conducted with irradiation of 3 W LED (400-405 nm) under O₂ atmosphere, and the reaction was smoothly performed to get **2h** in 100% conversion yield (GC-MS and ¹⁹F NMR determination). These results indicated that O₂ played a crucial role in this transformation.

6.3.2 Step by step experiments

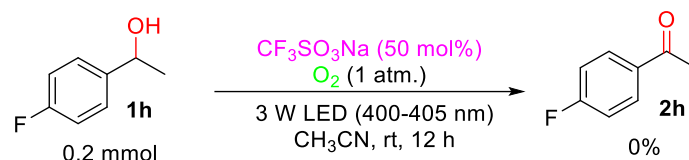


Sodium trifluoromethanesulfinate (**3a**, 0.05 mmol) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 8 h under O₂ atmosphere. After the reaction was completed, the resulting solution was detected by ¹⁹F NMR spectrometer. The result showed that the CF₃SO₂Na (**3a**) had converted into intermediate **4** (pentacoordinate sulfide). When 1-(4-fluorophenyl)ethan-1-ol (**1h**, 0.1 mmol) was added to the above resulting solution, and the solution was irradiated with 3 W LED (400-405 nm) for another 12 h under O₂ atmosphere, and the reaction was smoothly performed to get **2h** in 100% conversion yield determined by GC-MS using dodecane as the internal standard.

6.3.3 CF₃SO₃Na instead of **3a**

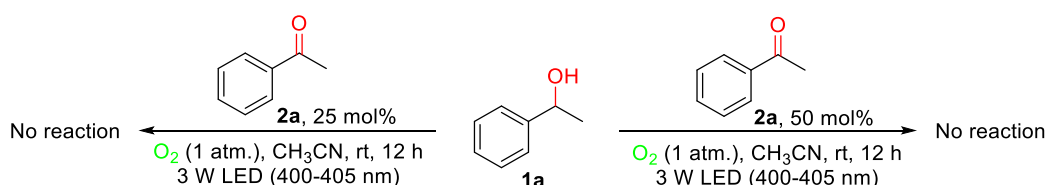
1-(4-Fluorophenyl)ethan-1-ol (**1h**, 0.2 mmol), sodium trifluoromethanesulfonate (CF₃SO₃Na, 0.1 mmol) and CH₃CN (2.0 mL) were added to an oven-dried reaction

vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. TLC (PE/EA =30 :1) and GC-MS showed that no desired product **2h** was detected, and **1h** was totally remained, which implied that CF₃SO₃Na was not a photocatalyst for this transformation.



These results certainly suggested that the pentacoordinate sulfide (**4**) (different with CF₃SO₃Na) could be a photocatalyst in this transformation.

6.3.4 The acetophenone instead of **3a** as photocatalyst



To exclude the possibility of ketone products act as photocatalyst, two control experiments was carried out. 1-phenylethan-1-ol (**1a**, 0.2 mmol, 24.4 mg), the ketone product acetophenone (**2a**, 0.05 or 0.1 mmol) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O₂ atmosphere. The yields were determined by GC-MS using dodecane as the internal standard, and the yields of desired product **2a** was remained. Based on the above observations, the ketone products act as photocatalyst could be ruled out.

6.4 Investigation of EDA complex in the reaction system

To exclude the possibility of EDA complex formed in the system, the UV-vis absorption spectrum of [CF₃SO₂Na], [1-phenylethan-1-ol (**1a**)] and [CF₃SO₂Na and **1a**] in DMF was recorded on DRS, Hitachi U-3010. The UV-vis absorption spectrum were recorded (**Figure S6**), which showed no additional peaks was observed in [CF₃SO₂Na and **1a**] vs [CF₃SO₂Na] and [1-phenylethan-1-ol (**1a**)] spectrums. The

above results suggested that no EDA complex was formed in the reaction system.

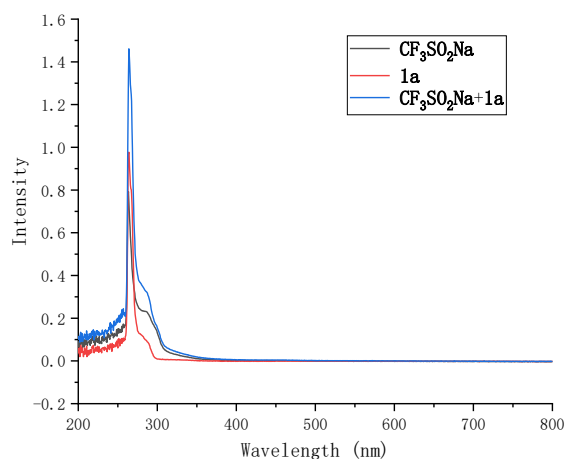
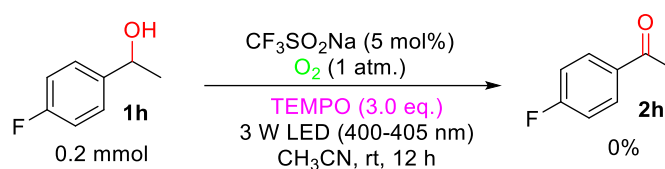


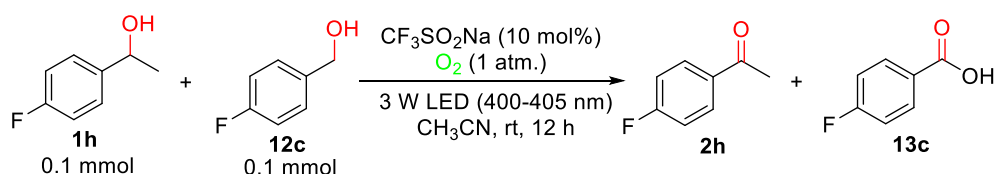
Figure S6. The UV-vis absorption spectrum of $\text{CF}_3\text{SO}_2\text{Na}$, **1a** and $[\text{CF}_3\text{SO}_2\text{Na}+\mathbf{1a}]$

6.5 Radical inhibited experiment



1-(4-Fluorophenyl)ethan-1-ol (**1h**, 1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (**3a**, 5 mol%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 3.0 equiv) and CH_3CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under O_2 atmosphere. No desired product **2h** was detected by TLC and GC-MS, indicating that the reaction was completely inhibited, and a radical process was involved in this transformation.

6.6 The kinetic investigation between secondary and primary alcohols



To verify the kinetic process between secondary and primary alcohols, we chose the 1-(4-fluorophenyl)ethanol (**1h**) and (4-fluorophenyl)methanol (**12c**) as model substrates to simplify the reaction system. 1-(4-fluorophenyl)ethanol (**1h**, 0.1 mmol,

14.0 mg), (4-fluorophenyl)methanol (**12c**, 0.1 mmol, 12.6 mg) sodium trifluoromethanesulfinate (**3a**, 10 mol%, 0.02 mmol, 3.2 mg) and CH₃CN (2 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 2h, 4h, 6h, 8h, 10h and 12h under O₂ atmosphere. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard and the yields of **2h** and **13c** under different reaction time was depicted in **Figure S7**. We found that (4-fluorophenyl)ethanol (**1h**) was relative kinetic favorable than (4-fluorophenyl)methanol (**12c**).

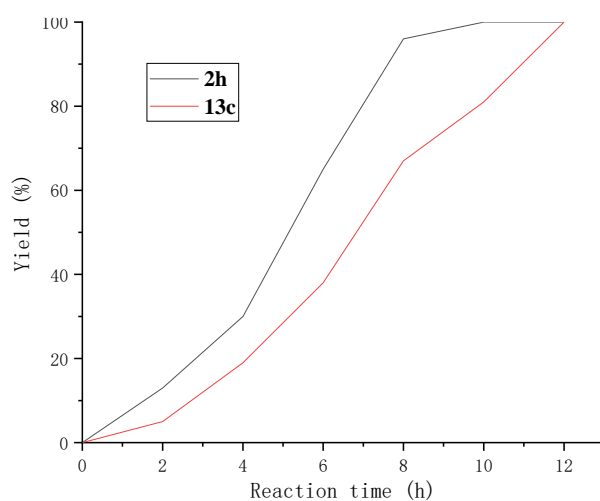
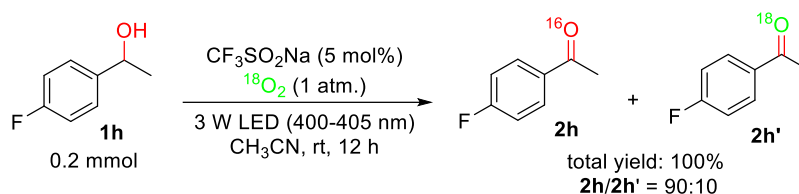


Figure S7 the yields of **2h** and **13c** under different reaction time

6.7 Isotopic labelling experiment



The ¹⁸O-labelling experiment was performed with ¹⁸O₂ (from Energy Chemical, ¹⁸O atom 99.7%). 1-(4-Fluorophenyl)ethan-1-ol (**1h**, 0.2 mmol), sodium trifluoromethanesulfinate (**3a**, 5 mol%) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W LED (400-405 nm) for 12 h under ¹⁸O₂ atmosphere. After the reaction was completed, products **2h** and **2h'** were confirmed by GC-MS as shown in

Figure S8. The dominated product was ^{16}O -carbonyl containing product. The results showed that origin of oxygen element in the desired product (**2h**) was from hydroxyl of **1h** rather than from O_2 .

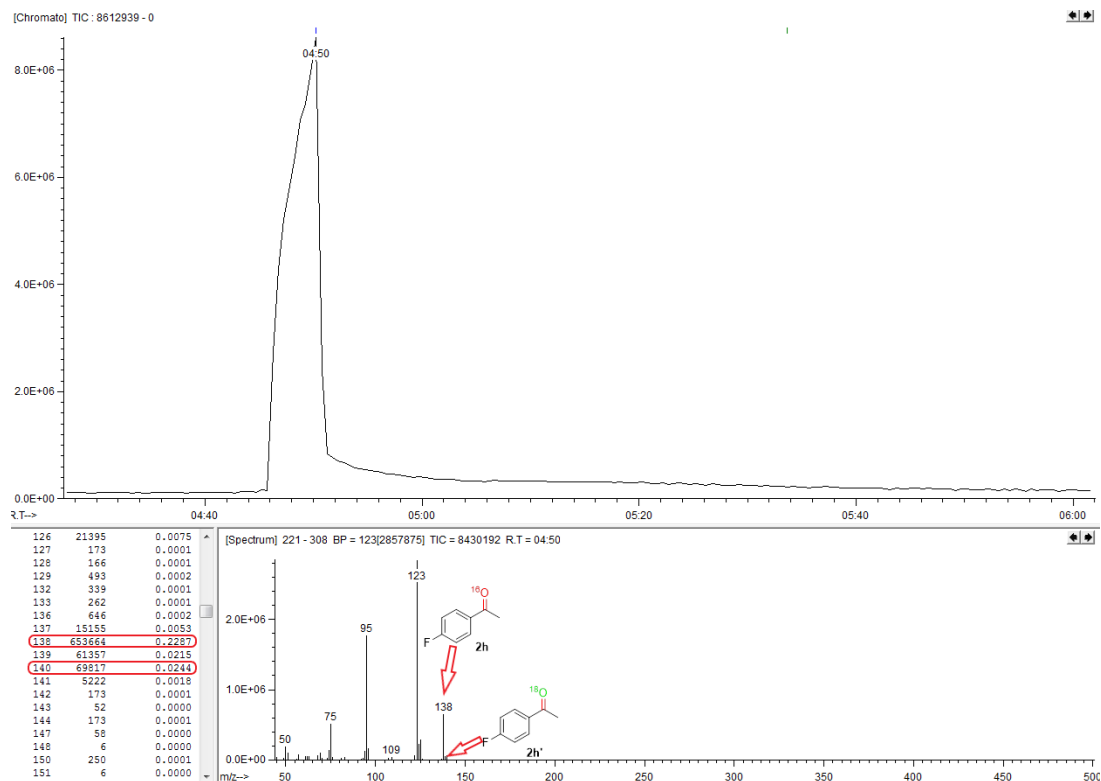
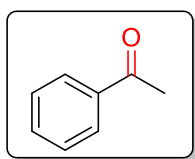
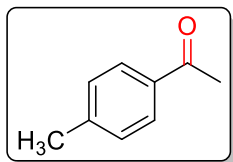


Figure S8 GC-MS of products **2h** and **2h'**.

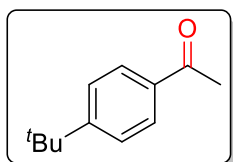
7. Characterization Data of the Synthesized Compounds



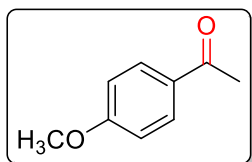
Acetophenone (2a): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2a** as a colorless liquid in 87% isolated yield (20.9 mg). ^1H and ^{13}C NMR of **2a** is identical with the spectra of the known compound.² ^1H NMR (600 MHz, CDCl_3) δ 7.97 (d, $J = 8.0$ Hz, 2H), 7.57 (t, $J = 7.8$ Hz, 1H), 7.47 (t, $J = 7.2$ Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 198.10, 137.05, 133.04, 128.50, 128.24, 26.55.



1-(p-Tolyl)ethan-1-one (2b): Yield was determined using dodecane as the internal standard (96% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2b** as a colorless liquid in 85% isolated yield (22.8 mg). ¹H and ¹³C NMR of **2b** is identical with the spectra of the known compound.³ ¹H NMR (600 MHz, CDCl₃) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.58 (s, 3H), 2.41 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 197.84, 143.85, 134.69, 129.22, 128.41, 26.52, 21.62.

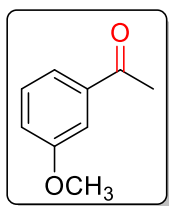


1-(4-(tert-Butyl)phenyl)ethan-1-one (2c): Yield was determined using dodecane as the internal standard (95% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2c** as a colorless liquid in 83% isolated yield (29.3 mg). ¹H and ¹³C NMR of **2c** is identical with the spectra of the known compound.⁴ ¹H NMR (600 MHz, CDCl₃) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 2.59 (s, 3H), 1.34 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 197.78, 156.73, 134.53, 128.21, 125.43, 35.02, 31.01, 26.47.

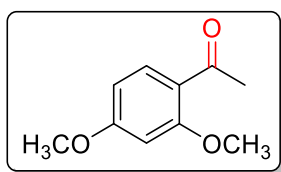


1-(4-Methoxyphenyl)ethan-1-one (2d): Yield was determined using dodecane as the internal standard (93% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2d** as a white solid in 85% isolated yield (25.6 mg). ¹H and ¹³C NMR of **2d** is identical with the spectra of the known compound.² ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.6 Hz,

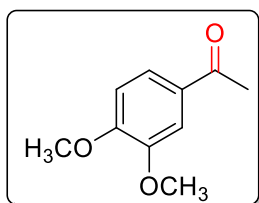
2H), 6.92 (d, $J = 8.7$ Hz, 2H), 3.86 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 196.71, 163.43, 130.54, 130.30, 113.63, 55.42, 26.29.



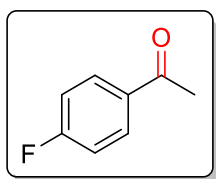
1-(3-Methoxyphenyl)ethan-1-one (2e): Yield was determined using dodecane as the internal standard (93% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2e** as a colorless liquid in 84% isolated yield (25.2 mg). ^1H and ^{13}C NMR of **2e** is identical with the spectra of the known compound.⁵ ^1H NMR (600 MHz, CDCl_3) δ 7.52 (d, $J = 7.6$ Hz, 1H), 7.49 – 7.46 (m, 1H), 7.36 (t, $J = 7.9$ Hz, 1H), 7.10 (dd, $J = 8.2, 2.6$ Hz, 1H), 3.84 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 197.63, 159.60, 138.27, 129.36, 120.88, 119.30, 112.18, 55.16, 26.46.



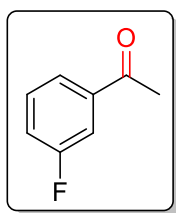
1-(2,4-Dimethoxyphenyl)ethan-1-one (2f): Yield was determined using dodecane as the internal standard (81% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2f** as a yellow solid in 75% isolated yield (27.0 mg). ^1H and ^{13}C NMR of **2f** is identical with the spectra of the known compound.⁶ ^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 8.8$ Hz, 1H), 6.52 (dd, $J = 8.8, 2.2$ Hz, 1H), 6.46 (d, $J = 2.2$ Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 197.64, 164.46, 161.02, 132.60, 121.09, 104.98, 98.24, 55.45, 55.37, 31.77.



1-(3,4-Dimethoxyphenyl)ethan-1-one (2g): Yield was determined using dodecane as the internal standard (72% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2g** as a white solid in 65% isolated yield (23.4 mg). ^1H and ^{13}C NMR of **2g** is identical with the spectra of the known compound.⁵ ^1H NMR (600 MHz, CDCl_3) δ 7.57 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.52 (d, $J = 2.0$ Hz, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 196.62, 153.14, 148.84, 130.34, 123.14, 109.91, 109.82, 55.92, 55.83, 26.06.

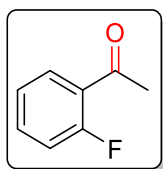


1-(4-Fluorophenyl)ethan-1-one (2h): Yield was determined using dodecane as the internal standard (100% GC-MS yield and 100% ^{19}F NMR yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2h** as a colorless liquid in 89% isolated yield (24.6 mg). ^1H and ^{13}C NMR of **2h** is identical with the spectra of the known compound.² ^1H NMR (600 MHz, CDCl_3) δ 7.98 (dd, $J = 8.3, 5.9$ Hz, 2H), 7.13 (t, $J = 8.6$ Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 196.18, 165.49 (d, $J = 254.6$ Hz), 133.37, 130.70 (d, $J = 9.4$ Hz), 115.36 (d, $J = 21.9$ Hz), 26.20. ^{19}F NMR (376 MHz, CDCl_3) δ -105.25 (s).

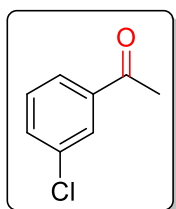


1-(3-Fluorophenyl)ethan-1-one (2i): Yield was determined using dodecane as the internal standard (100% GC-MS yield and 100% ^{19}F NMR yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2i** as a colorless liquid in 90% isolated yield (24.9 mg). ^1H and ^{13}C NMR of **2i** is identical with the spectra of the known compound.⁷ ^1H NMR (600 MHz, CDCl_3) δ 7.74 (d, $J = 7.1$ Hz, 1H), 7.64 (d, $J = 9.5$ Hz, 1H), 7.45 (dd, $J = 13.5,$

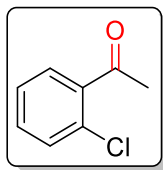
7.8 Hz, 1H), 7.28 (dd, $J = 8.3, 2.4$ Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 196.53, 162.65 (d, $J = 247.5$ Hz), 139.00 (d, $J = 5.8$ Hz), 130.10 (d, $J = 7.4$ Hz), 123.98, 119.89 (d, $J = 21.3$ Hz), 114.68 (d, $J = 22.5$ Hz), 26.42. ^{19}F NMR (376 MHz, CDCl_3) δ -111.82 – -111.88 (m).



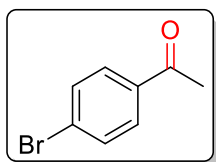
1-(2-Fluorophenyl)ethan-1-one (2j): Yield was determined using dodecane as the internal standard (100% GC-MS yield and 100% ^{19}F NMR yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2j** as a colorless liquid in 89% isolated yield (24.6 mg). ^1H and ^{13}C NMR of **2j** is identical with the spectra of the known compound.⁷ ^1H NMR (600 MHz, CDCl_3) δ 7.88 (td, $J = 7.7, 1.7$ Hz, 1H), 7.52 (ddd, $J = 7.3, 5.0, 1.8$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.14 (dd, $J = 11.2, 8.4$ Hz, 1H), 2.65 (d, $J = 4.9$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 195.84, 162.15 (d, $J = 255.2$ Hz), 134.61 (d, $J = 8.8$ Hz), 130.49 (d, $J = 2.0$ Hz), 125.60 (d, $J = 12.5$ Hz), 124.28 (d, $J = 3.1$ Hz), 116.57 (d, $J = 23.6$ Hz), 31.35 (d, $J = 7.5$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -109.11 – -109.50 (m).



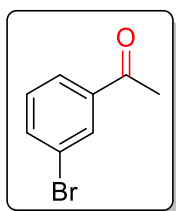
1-(3-Chlorophenyl)ethan-1-one (2k): Yield was determined using dodecane as the internal standard (98% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2k** as a colorless liquid in 86% isolated yield (26.6 mg). ^1H and ^{13}C NMR of **2k** is identical with the spectra of the known compound.⁷ ^1H NMR (600 MHz, CDCl_3) δ 7.91 (s, 1H), 7.82 (d, $J = 7.2$ Hz, 1H), 7.52 (dd, $J = 8.5, 1.6$ Hz, 1H), 7.40 (t, $J = 7.9$ Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 196.33, 138.32, 134.59, 132.71, 129.70, 128.04, 126.19, 26.33.



1-(2-Chlorophenyl)ethan-1-one (2l): Yield was determined using dodecane as the internal standard (99% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2l** as a colorless liquid in 88% isolated yield (27.2 mg). ^1H and ^{13}C NMR of **2l** is identical with the spectra of the known compound.⁷ ^1H NMR (600 MHz, CDCl_3) δ 7.55 (d, $J = 7.6$ Hz, 1H), 7.43 – 7.37 (m, 2H), 7.32 (t, $J = 7.5$ Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 200.07, 138.83, 131.77, 130.98, 130.38, 129.16, 126.71, 30.42.

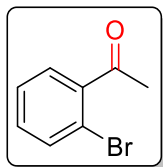


1-(4-Bromophenyl)ethan-1-one (2m): Yield was determined using dodecane as the internal standard (91% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2m** as a white solid in 80% isolated yield (31.9 mg). ^1H and ^{13}C NMR of **2m** is identical with the spectra of the known compound.² ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.5$ Hz, 2H), 7.59 (d, $J = 8.5$ Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 196.93, 135.77, 131.84, 129.79, 128.25, 26.49.

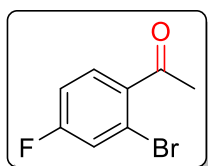


1-(3-Bromophenyl)ethan-1-one (2n): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2n** as a slightly yellow liquid in 91% isolated yield 36.2 mg). ^1H and ^{13}C NMR of **2n** is identical with the spectra of the known compound.² ^1H NMR (600 MHz, CDCl_3) δ

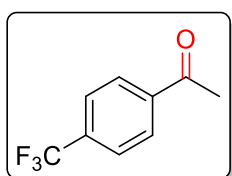
8.09 (s, 1H), 7.88 (d, $J = 7.8$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.35 (t, $J = 7.8$ Hz, 1H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.60, 138.80, 135.95, 131.38, 130.18, 126.83, 122.94, 26.60.



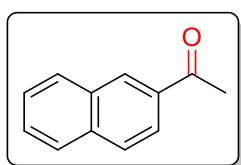
1-(2-Bromophenyl)ethan-1-one (2o): Yield was determined using dodecane as the internal standard (98% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2o** as a pale liquid isolated yield (35.4 mg). ^1H and ^{13}C NMR of **2o** is identical with the spectra of the known compound.² ^1H NMR (600 MHz, CDCl_3) δ 7.62 (d, $J = 8.0$ Hz, 1H), 7.50 – 7.44 (m, 1H), 7.37 (t, $J = 7.7$ Hz, 1H), 7.30 (dd, $J = 11.1, 4.2$ Hz, 1H), 2.64 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 201.36, 141.45, 133.82, 131.77, 128.89, 127.41, 118.89, 30.32.



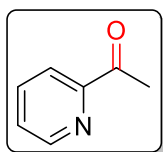
1-(2-Bromo-4-fluorophenyl)ethan-1-one (2p): Yield was determined using dodecane as the internal standard (95% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2p** as a pale solid in 83% isolated yield (36.0 mg). ^1H and ^{13}C NMR of **2p** is identical with the spectra of the known compound.⁸ ^1H NMR (400 MHz, CDCl_3) δ 7.52 (dd, $J = 8.3, 6.2$ Hz, 1H), 7.32 (dd, $J = 8.2, 0.8$ Hz, 1H), 7.09 – 7.01 (m, 1H), 2.59 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 199.40, 163.17 (d, $J = 256.1$ Hz), 137.14, 131.04 (d, $J = 8.9$ Hz), 121.23 (d, $J = 24.5$ Hz), 120.16 (d, $J = 10.0$ Hz), 114.63 (d, $J = 21.4$ Hz), 30.07. ^{19}F NMR (376 MHz, CDCl_3) δ -106.79 (dd, $J = 13.3, 8.1$ Hz).



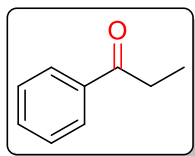
1-(4-(Trifluoromethyl)phenyl)ethan-1-one (2q): Yield was determined using dodecane as the internal standard (99% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2q** as a white solid in 90% isolated yield (33.9 mg). ¹H and ¹³C NMR of **2q** is identical with the spectra of the known compound.² ¹H NMR (600 MHz, CDCl₃) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 2.65 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 196.90, 139.62, 134.32 (q, *J* = 32.4 Hz), 128.55, 125.59 (q, *J* = 3.6 Hz), 123.55 (q, *J* = 272.5 Hz), 26.66. ¹⁹F NMR (376 MHz, CDCl₃) δ -63.03 (s).



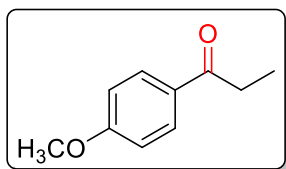
1-(Naphthalen-2-yl)ethan-1-one (2r): Yield was determined using dodecane as the internal standard (93% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2r** as a white solid in 84% isolated yield (28.6 mg). ¹H and ¹³C NMR of **2r** is identical with the spectra of the known compound.² ¹H NMR (400 MHz, CDCl₃) δ 8.47 (s, 1H), 8.04 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.85 (m, 2H), 7.62 – 7.54 (m, 2H), 2.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.05, 135.53, 134.43, 132.45, 130.14, 129.49, 128.42, 128.36, 127.73, 126.72, 123.83, 26.64.



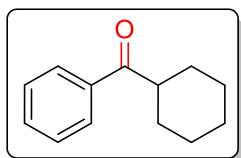
1-(Pyridin-2-yl)ethan-1-one (2s): Yield was determined using dodecane as the internal standard (98% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2s** as a colorless liquid in 93% isolated yield (22.5 mg). ¹H and ¹³C NMR of **2s** is identical with the spectra of the known compound.⁹ ¹H NMR (600 MHz, CDCl₃) δ 8.69 (d, *J* = 4.6 Hz, 1H), 8.05 (d, *J* = 7.3 Hz, 1H), 7.83 (td, *J* = 7.9, 1.9 Hz, 1H), 7.49 – 7.46 (m, 1H), 2.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 200.11, 153.57, 148.96, 136.80, 127.06, 121.62, 25.76.



Propiophenone (2t): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2t** as a colorless liquid in 89% isolated yield (23.9 mg). ^1H and ^{13}C NMR of **2t** is identical with the spectra of the known compound.² ^1H NMR (600 MHz, CDCl_3) δ 7.97 (d, $J = 7.5$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.46 (t, $J = 7.7$ Hz, 2H), 3.01 (q, $J = 7.3$ Hz, 2H), 1.23 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 200.73, 136.79, 132.78, 128.44, 127.86, 31.67, 8.13.

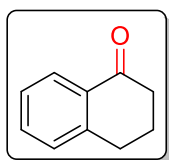


1-(4-Methoxyphenyl)propan-1-one (2u): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2u** as a white solid in 93% isolated yield (30.5 mg). ^1H and ^{13}C NMR of **2u** is identical with the spectra of the known compound.¹⁰ ^1H NMR (600 MHz, CDCl_3) δ 7.94 (d, $J = 8.9$ Hz, 2H), 6.92 (d, $J = 8.9$ Hz, 2H), 3.86 (s, 3H), 2.94 (q, $J = 7.4$ Hz, 2H), 1.20 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 199.11, 163.07, 129.93, 129.74, 113.41, 55.15, 31.12, 8.17.

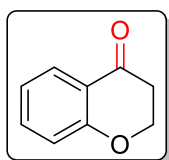


Cyclohexyl(phenyl)methanone (2v): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2v** as a white solid in 94% isolated yield (35.4 mg). ^1H and ^{13}C NMR of **2v** is identical with the

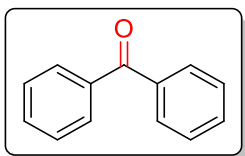
spectra of the known compound.² ¹H NMR (600 MHz, CDCl₃) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.29 – 3.24 (m, 1H), 1.90 – 1.83 (m, 4H), 1.75 – 1.72 (m, 1H), 1.53 – 1.46 (m, 2H), 1.42 – 1.35 (m, 2H), 1.31 – 1.23 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 203.89, 136.31, 132.69, 128.55, 128.22, 45.60, 29.39, 25.94, 25.83.



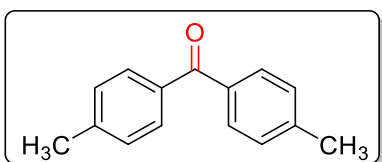
3,4-Dihydronaphthalen-1(2H)-one (2w): Yield was determined using dodecane as the internal standard (87% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2w** as a brown liquid in 79% isolated yield (23.0 mg). ¹H and ¹³C NMR of **2w** is identical with the spectra of the known compound.⁷ ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 2.96 (t, *J* = 6.1 Hz, 2H), 2.65 (t, *J* = 6.0 Hz, 2H), 2.16 – 2.10 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 198.20, 144.34, 133.23, 132.43, 128.63, 126.95, 126.44, 39.00, 29.52, 23.12.



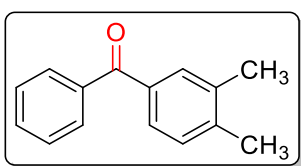
Chroman-4-one (2x): Yield was determined using dodecane as the internal standard (87% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give **2x** as a white solid in 82% isolated yield (24.3 mg). ¹H and ¹³C NMR of **2x** is identical with the spectra of the known compound.⁷ ¹H NMR (600 MHz, CDCl₃) δ 7.90 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.54 (t, *J* = 6.0 Hz, 2H), 2.83 (t, *J* = 6.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 191.78, 161.83, 135.94, 127.12, 121.34, 117.86, 66.99, 37.77.



Benzophenone (2y): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2y** as a white solid in 93% isolated yield (33.9 mg). ^1H and ^{13}C NMR of **2y** is identical with the spectra of the known compound.² ^1H NMR (600 MHz, CDCl_3) δ 7.81 (d, $J = 7.3$ Hz, 4H), 7.61 – 7.57 (m, 2H), 7.48 (t, $J = 7.7$ Hz, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.73, 137.55, 132.38, 130.02, 128.24.

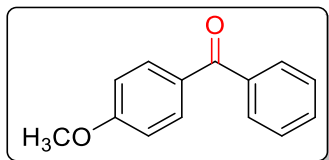


Di-*p*-tolylmethanone (2z): Yield was determined using dodecane as the internal standard (88% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2z** as a white solid in 85% isolated yield (35.7 mg). ^1H and ^{13}C NMR of **2z** is identical with the spectra of the known compound.¹¹ ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.1$ Hz, 4H), 7.27 (d, $J = 7.9$ Hz, 4H), 2.44 (s, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 196.28, 142.90, 135.17, 130.16, 128.87, 21.61.

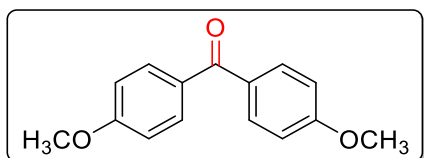


(3,4-Dimethylphenyl)(phenyl)methanone (2aa): Yield was determined using dodecane as the internal standard (86% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2aa** as a white solid in 81% isolated yield (34.0 mg). ^1H and ^{13}C NMR of **2aa** is identical with the spectra of the known compound.¹² ^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, $J = 7.2$ Hz, 2H), 7.62 (s, 1H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.53 (d, $J = 7.7$ Hz,

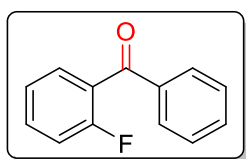
1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.23 (d, $J = 7.8$ Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 196.73, 141.96, 138.04, 136.73, 135.25, 132.06, 131.16, 129.92, 129.41, 128.15, 128.02, 20.00, 19.75.



(4-Methoxyphenyl)(phenyl)methanone (2ab): Yield was determined using dodecane as an internal standard (98% GC yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2ab** as a white solid in 91% isolated yield (41.2 mg). ^1H and ^{13}C NMR of **2ab** is identical with the spectra of the known compound.¹² ^1H NMR (600 MHz, CDCl_3) δ 7.83 (d, $J = 8.7$ Hz, 2H), 7.76 (d, $J = 7.4$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.48 (d, $J = 7.7$ Hz, 2H), 6.97 (d, $J = 8.7$ Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 195.57, 163.19, 138.25, 132.55, 131.87, 130.13, 129.71, 128.16, 113.53, 55.48.

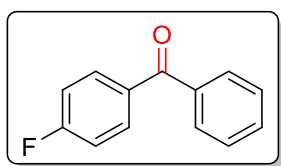


Bis(4-methoxyphenyl)methanone (2ac): Yield was determined using dodecane as the internal standard (98% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2ac** as a pale solid in 92% isolated yield (44.6 mg). ^1H and ^{13}C NMR of **2ac** is identical with the spectra of the known compound.¹³ ^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, $J = 8.7$ Hz, 4H), 6.96 (d, $J = 8.7$ Hz, 4H), 3.88 (s, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 194.46, 162.80, 132.20, 130.71, 113.42, 55.44.

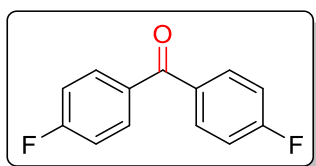


(2-Fluorophenyl)(phenyl)methanone (2ad): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by

flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2ad** as a white solid in 92% isolated yield (36.8 mg). ^1H and ^{13}C NMR of **2ad** is identical with the spectra of the known compound.¹⁴ ^1H NMR (600 MHz, CDCl_3) δ 7.84 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.48 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 7.1 Hz, 1H), 7.16 (t, J = 9.1 Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 193.37, 159.96 (d, J = 252.4 Hz), 137.25, 133.33, 132.98 (d, J = 8.4 Hz), 130.62 (d, J = 2.2 Hz), 129.69, 128.36, 126.89 (d, J = 14.7 Hz), 124.18 (d, J = 2.9 Hz), 116.15 (d, J = 21.7 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -110.87 – -110.98 (m).

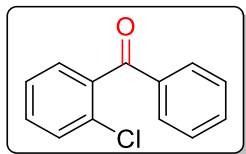


(4-Fluorophenyl)(phenyl)methanone (2ae): Yield was determined using dodecane as the internal standard (99% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2ae** as a white solid in 90% isolated yield (36.0 mg). ^1H and ^{13}C NMR of **2ae** is identical with the spectra of the known compound.¹² ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.83 (m, 2H), 7.77 (d, J = 7.2 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.24, 165.35 (d, J = 254.3 Hz), 137.46, 133.76 (d, J = 2.8 Hz), 132.63 (d, J = 9.0 Hz), 132.44, 129.84, 128.32, 115.42 (d, J = 21.7 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -105.80 – -105.98 (m).

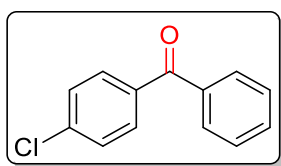


Bis(4-fluorophenyl)methanone (2af): Yield was determined using dodecane as the internal standard (98% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2af** as a white solid in 88% isolated yield (38.4 mg). ^1H and ^{13}C NMR of **2af** is identical with the spectra of the known compound.¹¹ ^1H NMR (600 MHz, CDCl_3) δ 7.87 – 7.78 (m, 4H), 7.17 (t, J = 8.6 Hz, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 193.81, 165.39 (d, J =

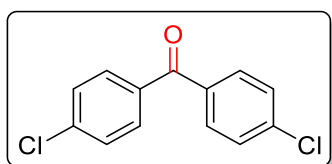
254.3 Hz), 133.68, 132.49 (d, $J = 9.3$ Hz), 115.55 (d, $J = 21.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -105.59 – -105.72 (m).



(2-Chlorophenyl)(phenyl)methanone (2ag): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2ag** as a white solid in 91% isolated yield (39.4 mg). ^1H and ^{13}C NMR of **2ag** is identical with the spectra of the known compound.¹² ^1H NMR (600 MHz, CDCl_3) δ 7.82 (d, $J = 7.9$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.50 – 7.42 (m, 4H), 7.41 – 7.35 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 195.28, 138.59, 136.45, 133.69, 131.30, 131.11, 130.07, 129.11, 128.60, 126.66.

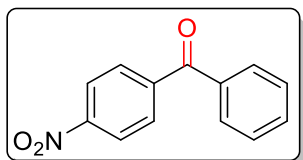


(4-Chlorophenyl)(phenyl)methanone (2ah): Yield was determined using dodecane as the internal standard (96% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2ah** as a white solid in 88% isolated yield (38.1 mg). ^1H and ^{13}C NMR of **2ah** is identical with the spectra of the known compound.¹² ^1H NMR (600 MHz, CDCl_3) δ 7.78 – 7.75 (m, 4H), 7.60 (t, $J = 7.3$ Hz, 1H), 7.50 – 7.46 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 195.49, 138.88, 137.22, 135.84, 132.63, 131.44, 129.91, 128.62, 128.38.

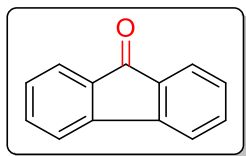


Bis(4-chlorophenyl)methanone (2ai): Yield was determined using dodecane as the internal standard (94% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2ai** as a

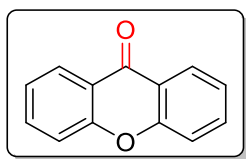
white solid in 86% isolated yield (43.2 mg). ^1H and ^{13}C NMR of **2ai** is identical with the spectra of the known compound.¹³ ^1H NMR (600 MHz, CDCl_3) δ 7.73 (d, $J = 8.4$ Hz, 4H), 7.47 (d, $J = 8.6$ Hz, 4H). ^{13}C NMR (151 MHz, CDCl_3) δ 194.25, 139.15, 135.48, 131.30, 128.76.



(4-Nitrophenyl)(phenyl)methanone (2aj): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give **2aj** as a yellow solid in 94% isolated yield (42.7 mg). ^1H and ^{13}C NMR of **2aj** is identical with the spectra of the known compound.¹² ^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, $J = 8.6$ Hz, 2H), 7.94 (d, $J = 8.6$ Hz, 2H), 7.80 (d, $J = 7.5$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.7$ Hz, 2H). ^{13}C NMR (151 MHz, CDCl_3) δ 194.76, 149.80, 142.85, 136.25, 133.44, 130.67, 130.07, 128.66, 123.51.

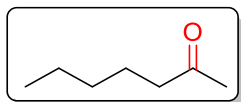


9H-Fluoren-9-one (2ak): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2ak** as a yellow solid in 91% isolated yield (32.8 mg). ^1H and ^{13}C NMR of **2ak** is identical with the spectra of the known compound.⁷ ^1H NMR (600 MHz, CDCl_3) δ 7.66 (d, $J = 7.4$ Hz, 2H), 7.52 – 7.47 (m, 4H) 7.30 – 7.28 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.84, 144.34, 134.61, 134.05, 128.99, 124.21, 120.24.

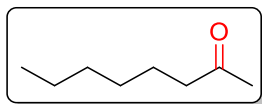


9H-Xanthen-9-one (2al): Yield was determined using dodecane as the internal standard (100% GC-MS yield). The reaction solution was purified by flash

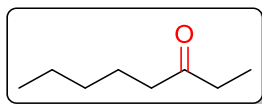
chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2al** as a white solid in 95% isolated yield (37.3 mg). ^1H and ^{13}C NMR of **2al** is identical with the spectra of the known compound.¹¹ ^1H NMR (400 MHz, CDCl_3) δ 8.35 (dd, $J = 8.0$, 1.5 Hz, 2H), 7.76 – 7.70 (m, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.39 (t, $J = 7.5$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 177.14, 156.10, 134.75, 126.66, 123.84, 121.78, 117.92.



Heptan-2-one (2am): Yield was determined using dodecane as the internal standard (99% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2am** as a colorless liquid in 75% isolated yield (17.1 mg). ^1H and ^{13}C NMR of **2am** is identical with the spectra of the known compound.¹⁵ ^1H NMR (600 MHz, CDCl_3) δ 2.41 (t, $J = 7.5$ Hz, 2H), 2.13 (s, 3H), 1.60 – 1.54 (m, 2H), 1.33 – 1.24 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 209.45, 43.77, 31.33, 29.84, 23.53, 22.43, 13.90.

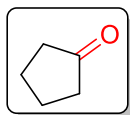


Octan-2-one (2an): Yield was determined using dodecane as the internal standard (97% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2an** as a colorless liquid in 71% isolated yield (18.2 mg). ^1H and ^{13}C NMR of **2an** is identical with the spectra of the known compound.⁷ ^1H NMR (600 MHz, CDCl_3) δ 2.41 (t, $J = 7.5$ Hz, 2H), 2.13 (s, 3H), 1.58 – 1.53 (m, 2H), 1.30 – 1.25 (m, 6H), 0.87 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 209.39, 43.81, 31.57, 29.83, 28.83, 23.81, 22.47, 14.01.

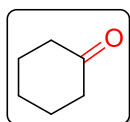


Octan-3-one (2ao): Yield was determined using dodecane as the internal standard (95% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2ao** as a colorless liquid in 73% isolated yield (18.7 mg). ^1H and ^{13}C NMR of **2ao** is identical with the spectra of

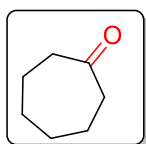
the known compound.¹⁰ ¹H NMR (600 MHz, CDCl₃) δ 2.43 – 2.38 (m, 4H), 1.59 – 1.54 (m, 2H), 1.34 – 1.23 (m, 4H), 1.05 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 212.02, 42.40, 35.84, 31.44, 23.63, 22.45, 13.92, 7.84.



Cyclopentanone (2ap): Yield was determined using dodecane as the internal standard (98% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give the desired product **2ap** as a colorless liquid in 68% isolated yield (11.5 mg). ¹H and ¹³C NMR of **2ap** is identical with the spectra of the known compound.⁷ ¹H NMR (600 MHz, CDCl₃) δ 2.07 (t, *J* = 7.6 Hz, 4H), 1.92 – 1.84 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 220.47, 38.11, 23.00.

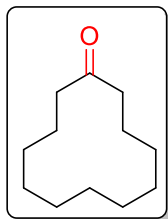


Cyclohexanone (2aq): Yield was determined using dodecane as the internal standard (99% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2aq** as a colorless liquid in 77% isolated yield (15.1 mg). ¹H and ¹³C NMR of **2aq** is identical with the spectra of the known compound.⁷ ¹H NMR (600 MHz, CDCl₃) δ 2.33 (t, *J* = 6.7 Hz, 4H), 1.90 – 1.82 (m, 4H), 1.73 – 1.70 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 212.25, 41.97, 27.00, 24.97.

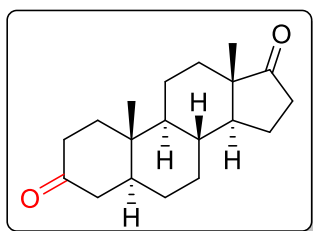


Cycloheptanone (2ar): Yield was determined using dodecane as the internal standard (99% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2ar** as a colorless liquid in 81% isolated yield (18.2 mg). ¹H and ¹³C NMR of **2ar** is identical with the spectra of

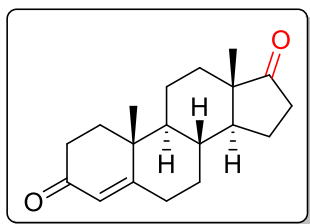
the known compound.¹⁶ ¹H NMR (600 MHz, CDCl₃) δ 2.55 – 2.45 (m, 4H), 1.73 – 1.65 (m, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 215.43, 43.69, 30.25, 24.16.



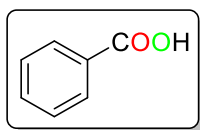
Cyclododecanone (2as): Yield was determined using dodecane as the internal standard (92% GC-MS yield). The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **2as** as a white solid in 86% isolated yield (31.4 mg). ¹H and ¹³C NMR of **2as** is identical with the spectra of the known compound.¹⁶ ¹H NMR (600 MHz, CDCl₃) δ 2.53 – 2.40 (m, 4H), 1.75 – 1.67 (m, 4H), 1.33 – 1.23 (m, 14H). ¹³C NMR (151 MHz, CDCl₃) δ 212.91, 40.37, 24.74, 24.60, 24.22, 22.55, 22.34.



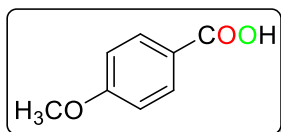
(5S,8R,9S,10S,13S,14S)-10,13-Dimethyltetradecahydro-3H-cyclopenta[*a*]phenanthrene-3,17(2H)-dione (2at): The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **2at** as a white solid in 87% (from **11a**), 85% (from **11b**) and 79% (from **11c**) isolated yield (50.2 mg, 49.0 mg and 45.6 mg), respectively. ¹H and ¹³C NMR of **2at** is identical with the spectra of the known compound.¹⁷ ¹H NMR (600 MHz, CDCl₃) δ 2.48 – 2.25 (m, 4H), 2.14 – 2.00 (m, 3H), 1.97 – 1.92 (m, 1H), 1.87 – 1.80 (m, 2H), 1.72 – 1.68 (m, 1H), 1.62 – 1.52 (m, 3H), 1.42 – 1.26 (m, 6H), 1.09 – 0.97 (m, 4H), 0.91 – 0.77 (m, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 220.94, 211.61, 53.86, 51.21, 47.72, 46.58, 44.57, 38.42, 38.06, 35.81, 34.94, 31.46, 30.52, 28.60, 21.77, 20.69, 13.79, 11.45.



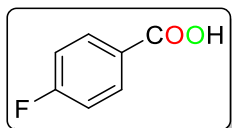
Androstenedione (2au): The reaction solution was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **2au** as a white solid in 82% isolated yield (47.0 mg). ^1H and ^{13}C NMR of **2au** is identical with the spectra of the known compound.¹⁸ ^1H NMR (600 MHz, CDCl_3) δ 5.72 (s, 1H), 2.47 – 2.37 (m, 3H), 2.36 – 2.29 (m, 2H), 2.11 – 2.00 (m, 2H), 1.98 – 1.93 (m, 2H), 1.86 – 1.82 (m, 1H), 1.74 – 1.65 (m, 3H), 1.58 – 1.51 (m, 1H), 1.47 – 1.40 (m, 1H), 1.30 – 1.25 (m, 2H), 1.19 (s, 3H), 1.13 – 1.06 (m, 1H), 0.99 – 0.94 (m, 1H), 0.89 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 220.27, 199.19, 170.23, 124.06, 53.74, 50.77, 47.42, 38.57, 35.67, 35.62, 35.07, 33.84, 32.49, 31.21, 30.68, 21.67, 20.24, 17.30, 13.63.



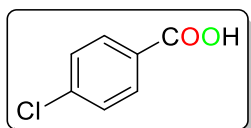
Benzoic acid (13a): **13a** was obtained as a white solid (23.4 mg, 96%), ^1H and ^{13}C NMR of **13a** is identical with the spectra of the known compound.² ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 7.94 (d, $J = 7.5$ Hz, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.7$ Hz, 2H). ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 167.46, 132.98, 130.82, 129.37, 128.67.



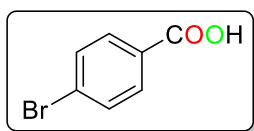
4-Methoxybenzoic acid (13b): **13b** was obtained as a white solid (28.0 mg, 92%). ^1H and ^{13}C NMR of **13b** is identical with the spectra of the known compound.² ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 7.89 (d, $J = 8.7$ Hz, 2H), 7.00 (d, $J = 8.6$ Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 167.13, 162.93, 131.45, 123.02, 113.90, 55.51.



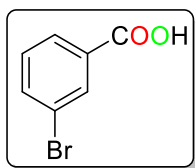
4-Fluorobenzoic acid (13c): **13c** was obtained as a white solid (26.6 mg, 95%) and is identical with the spectra of the known compound.² ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.99 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.30 (t, *J* = 8.8 Hz, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.50, 165.01 (d, *J* = 250.2 Hz), 132.20 (d, *J* = 9.1 Hz), 127.42, 115.70 (d, *J* = 21.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -103.95.



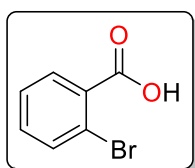
4-Chlorobenzoic acid (13d): **13d** was obtained as a pale solid (29.1 mg, 93%) and is identical with the spectra of the known compound.² ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.57, 137.90, 131.23, 129.70, 128.82.



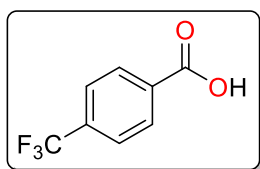
4-Bromobenzoic acid (13e): **13e** was obtained as a pale solid (38.2 mg, 95%) and is identical with the spectra of the known compound.² ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 7.7 Hz, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.71, 131.78, 131.37, 130.05, 126.97.



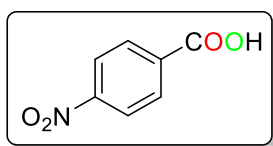
3-Bromobenzoic acid (13f): **13f** was obtained as a white solid (35.8 mg, 89%) and is identical with the spectra of the known compound.² ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.28 (s, 1H), 8.03 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 165.97, 135.60, 133.07, 131.73, 130.91, 128.28, 121.72.



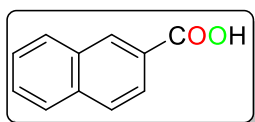
2-Bromobenzoic acid (13g): **13g** was obtained as a white solid (36.6 mg, 91%) and is identical with the spectra of the known compound.² ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.27 (s, 1H), 7.73 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.48 – 7.41 (m, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.35, 133.77, 133.73, 132.48, 130.55, 127.69, 119.89.



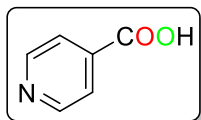
4-(Trifluoromethyl)benzoic acid (13h): **13h** was obtained as a white solid (34.6 mg, 91%) and is identical with the spectra of the known compound.² ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.40 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 166.17, 134.59, 132.47 (q, *J* = 31.8 Hz), 130.08, 125.57 (q, *J* = 7.0 Hz), 123.79 (q, *J* = 271.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -63.61 (s).



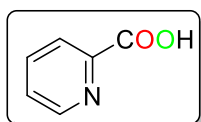
4-Nitrobenzoic acid (13i): **13i** was obtained as a yellow solid (30.7 mg, 92%) and is identical with the spectra of the known compound.¹⁹ ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.28 (d, *J* = 8.7 Hz, 2H), 8.13 (d, *J* = 8.7 Hz, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 165.92, 150.11, 136.46, 130.79, 123.79.



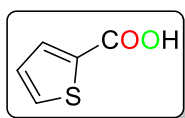
2-Naphthoic acid (13j): **13j** was obtained as a white solid (27.9 mg, 81%) and is identical with the spectra of the known compound.² ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 1H), 8.14 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.92 (t, *J* = 7.9 Hz, 2H), 7.65 – 7.56 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 172.28, 135.97, 132.43, 132.18, 129.55, 128.68, 128.33, 127.82, 126.78, 126.48, 125.37.



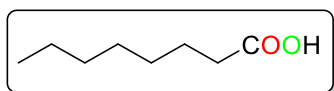
Isonicotinic acid (13k): **13k** was obtained as a brown solid (22.2 mg, 90%) and is identical with the spectra of the known compound.² ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.76 (d, *J* = 5.5 Hz, 2H), 7.80 (d, *J* = 5.7 Hz, 2H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.30, 150.69, 138.19, 122.87.



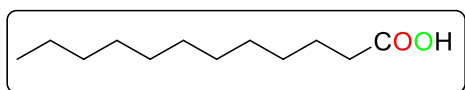
Picolinic acid (13l): **13l** was obtained as a white solid (24.1 mg, 98%) and is identical with the spectra of the known compound.² ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.69 (d, *J* = 4.4 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.97 (td, *J* = 7.7, 1.4 Hz, 1H), 7.61 (dd, *J* = 7.1, 5.2 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.31, 149.51, 148.45, 137.67, 127.21, 124.78.



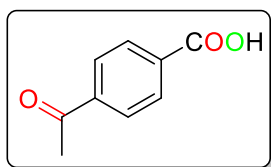
Thiophene-2-carboxylic acid (13m): **13m** was obtained as a white solid (14.3 mg, 56%) and is identical with the spectra of the known compound.² ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.91 (d, *J* = 3.6 Hz, 1H), 7.66 (d, *J* = 5.3 Hz, 1H), 7.17 – 7.13 (m, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 167.54, 135.03, 134.03, 132.79, 128.07.



Octanoic acid (13n): **13n** was obtained as a brown oil (17.9 mg, 62%) and is identical with the spectra of the known compound.²⁰ ¹H NMR (600 MHz, CDCl₃) δ 10.60 (s, 1H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.64 – 1.61 (m, 2H), 1.34 – 1.25 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 180.36, 34.06, 31.60, 28.99, 28.88, 24.64, 22.57, 14.04.



Dodecanoic acid (13o): **13o** was obtained as a white solid (28.8 mg, 72%) and is identical with the spectra of the known compound.²⁰ ¹H NMR (600 MHz, CDCl₃) δ 11.21 (s, 1H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.65 – 1.61 (m, 2H), 1.39 – 1.19 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 179.83, 33.98, 31.89, 29.58, 29.42, 29.32, 29.23, 29.04, 24.66, 22.67, 14.11.

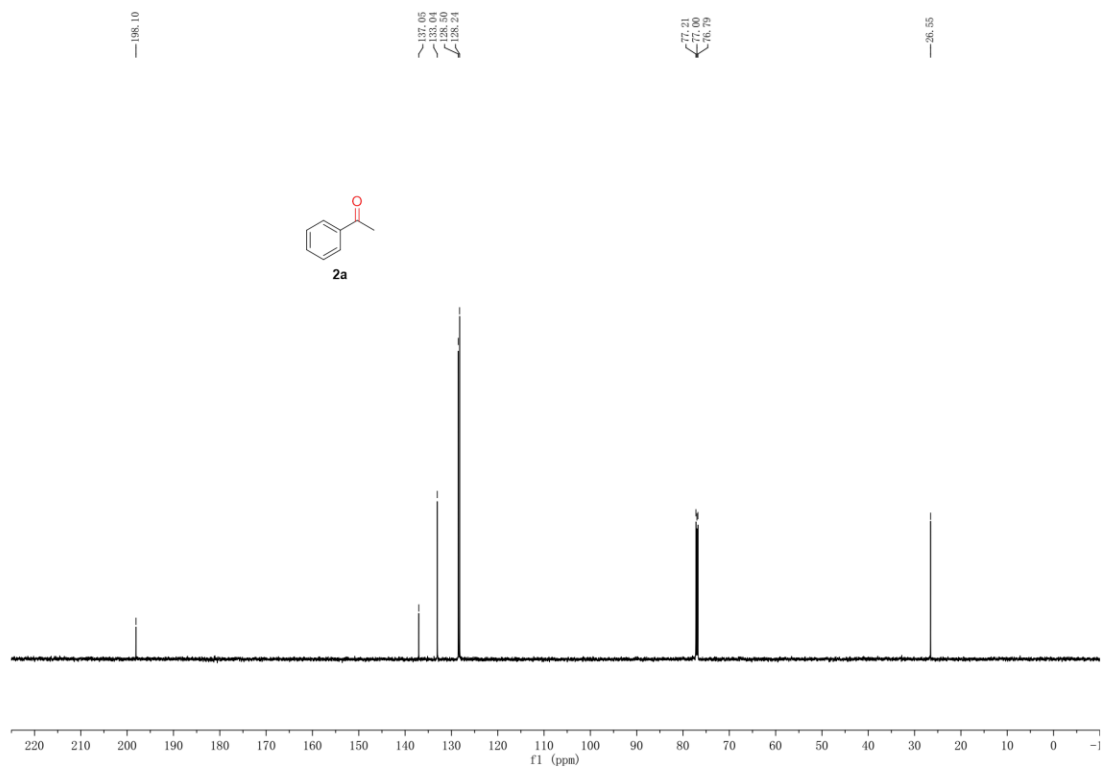
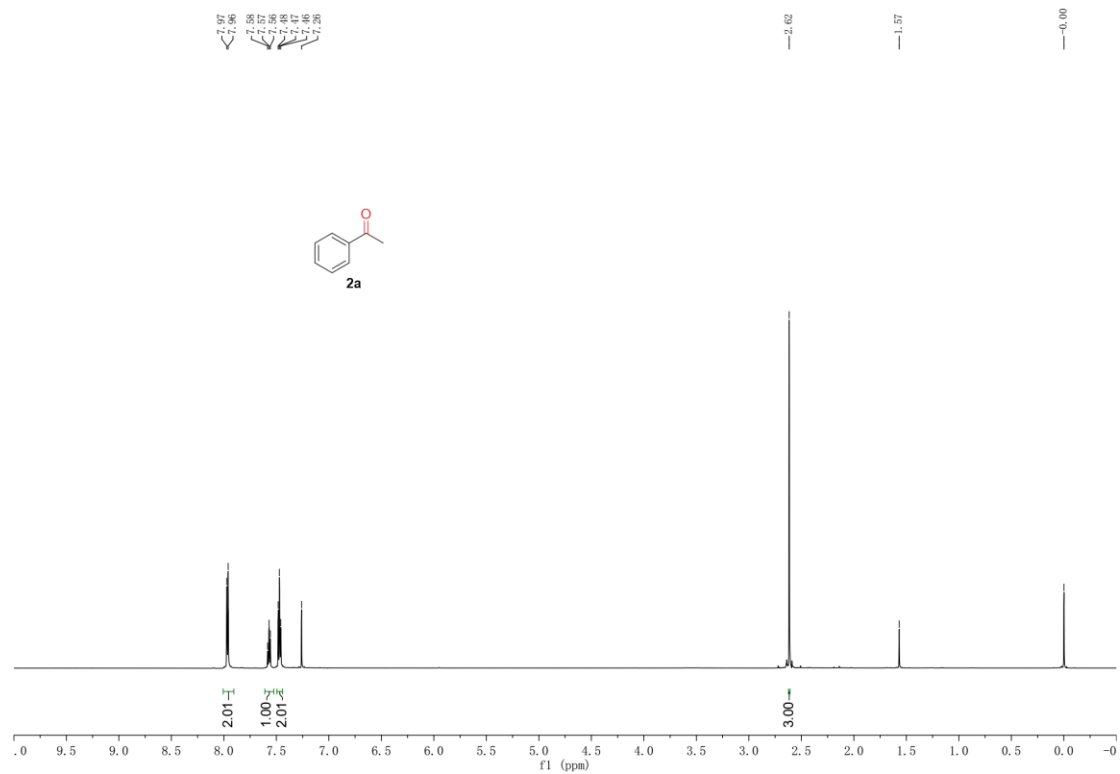


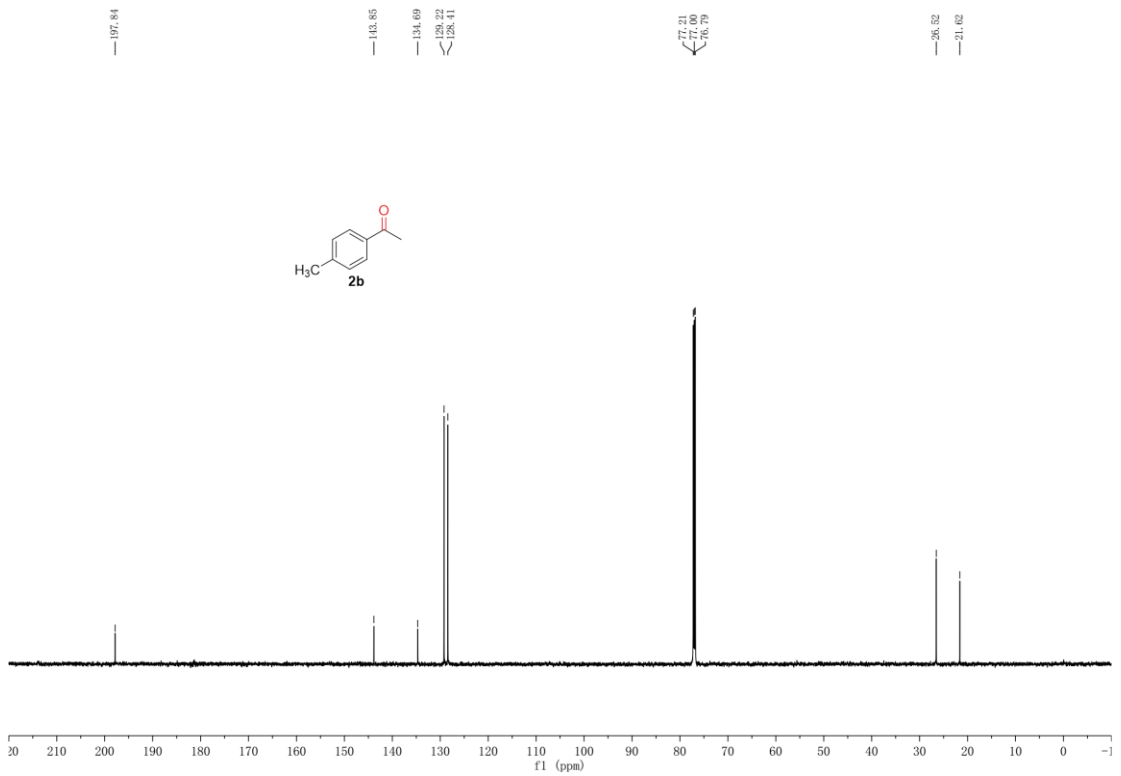
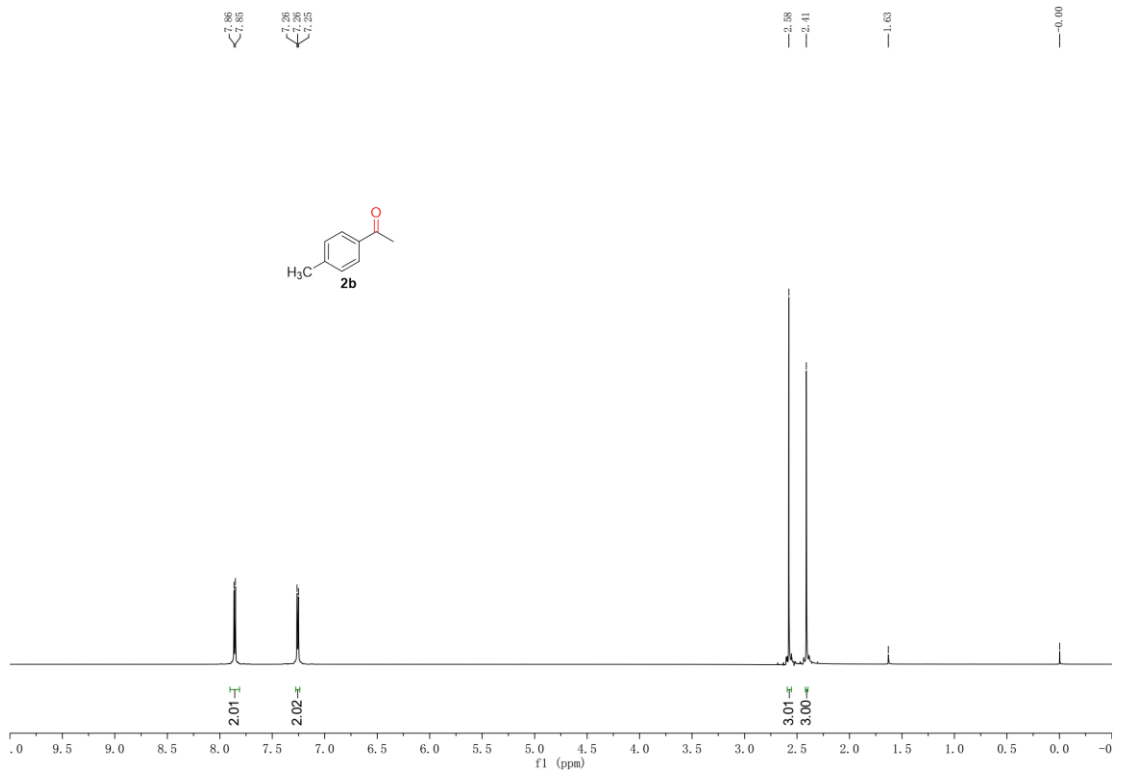
Dodecanoic acid (15): **15** was obtained as a white solid (28.6 mg, 87%) and is identical with the spectra of the known compound.² ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.13 (s), 8.05 (s, 4H), 2.50 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 197.73, 166.63, 139.83, 134.48, 129.54, 128.31, 27.00.

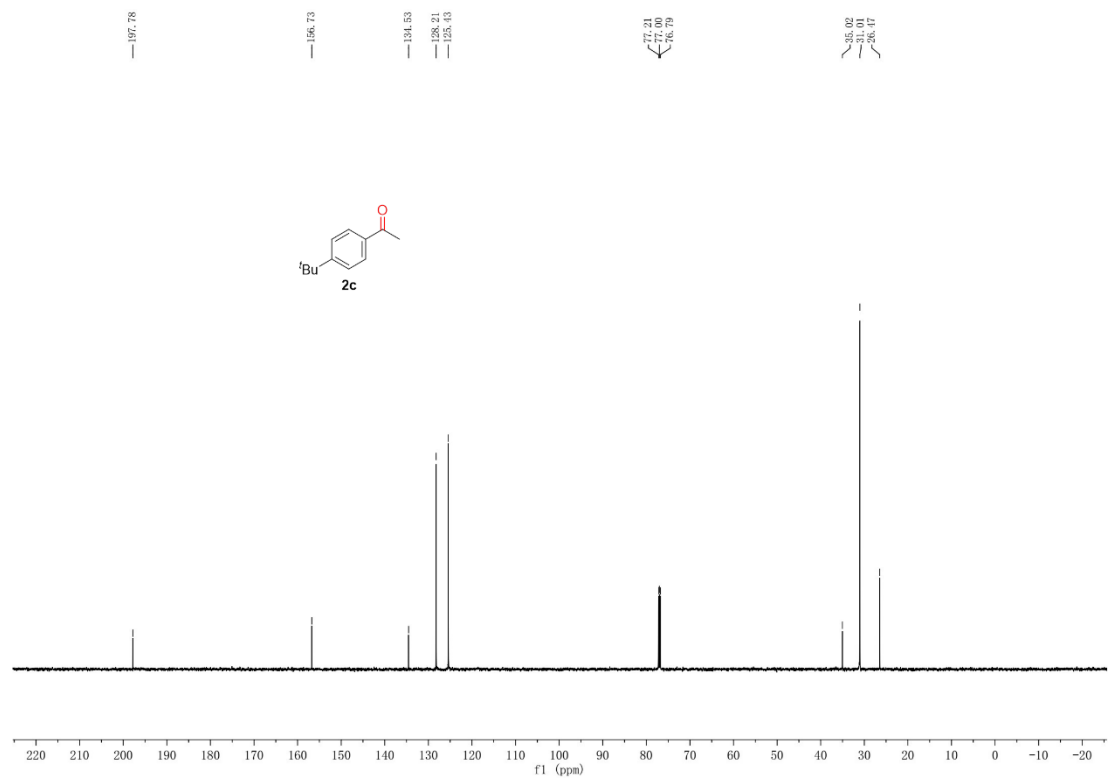
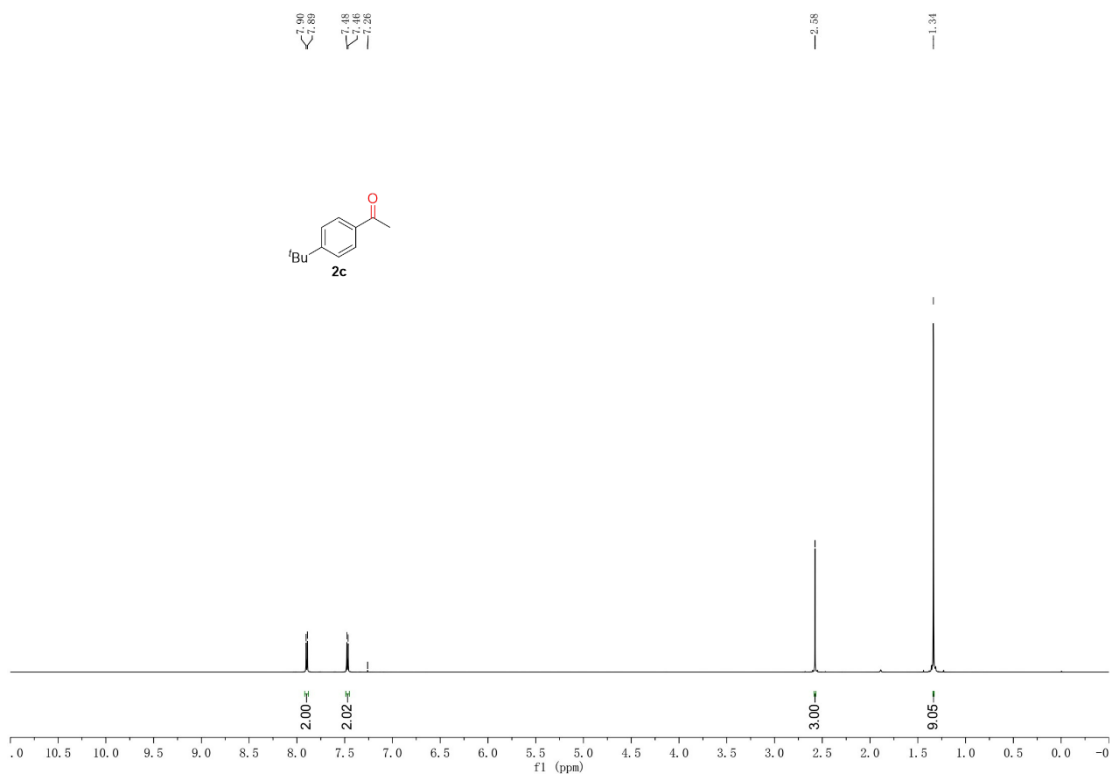
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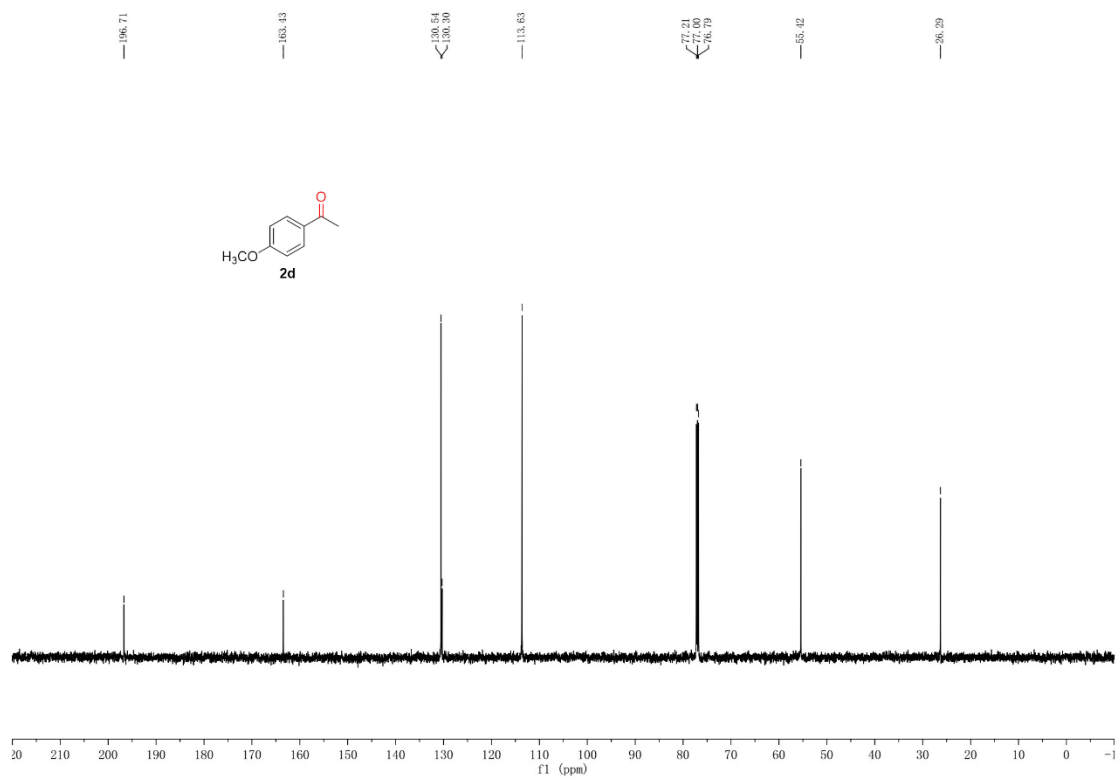
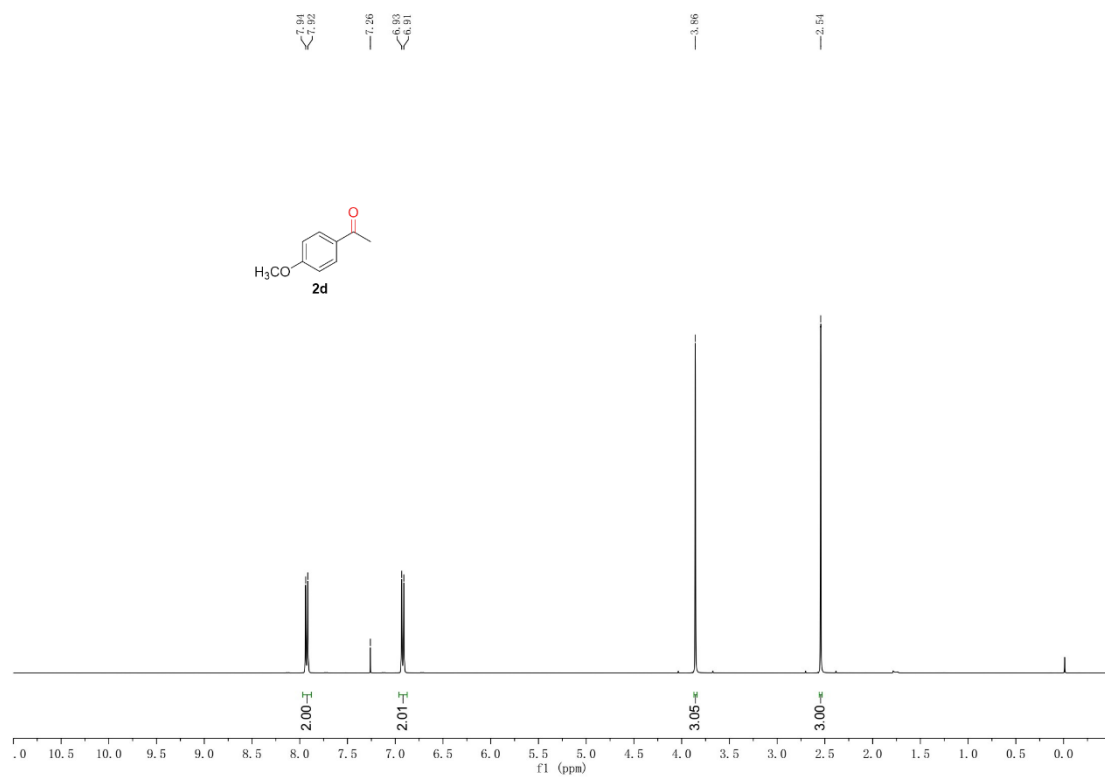
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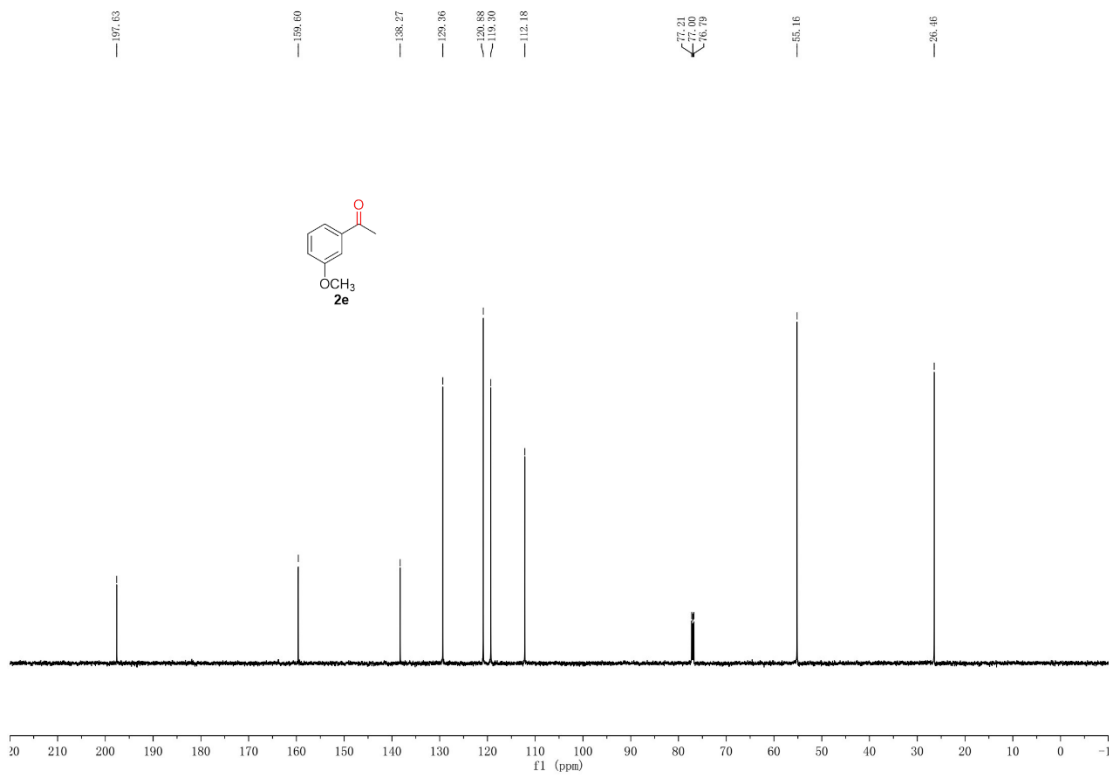
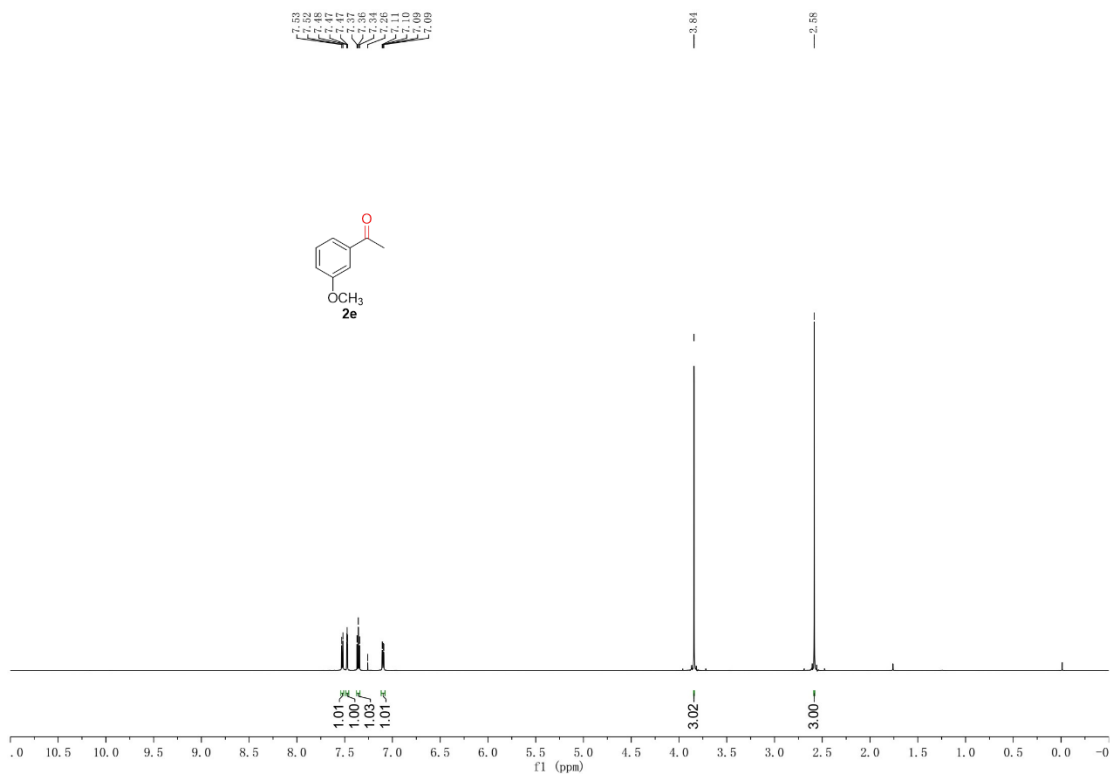
9. NMR Spectra

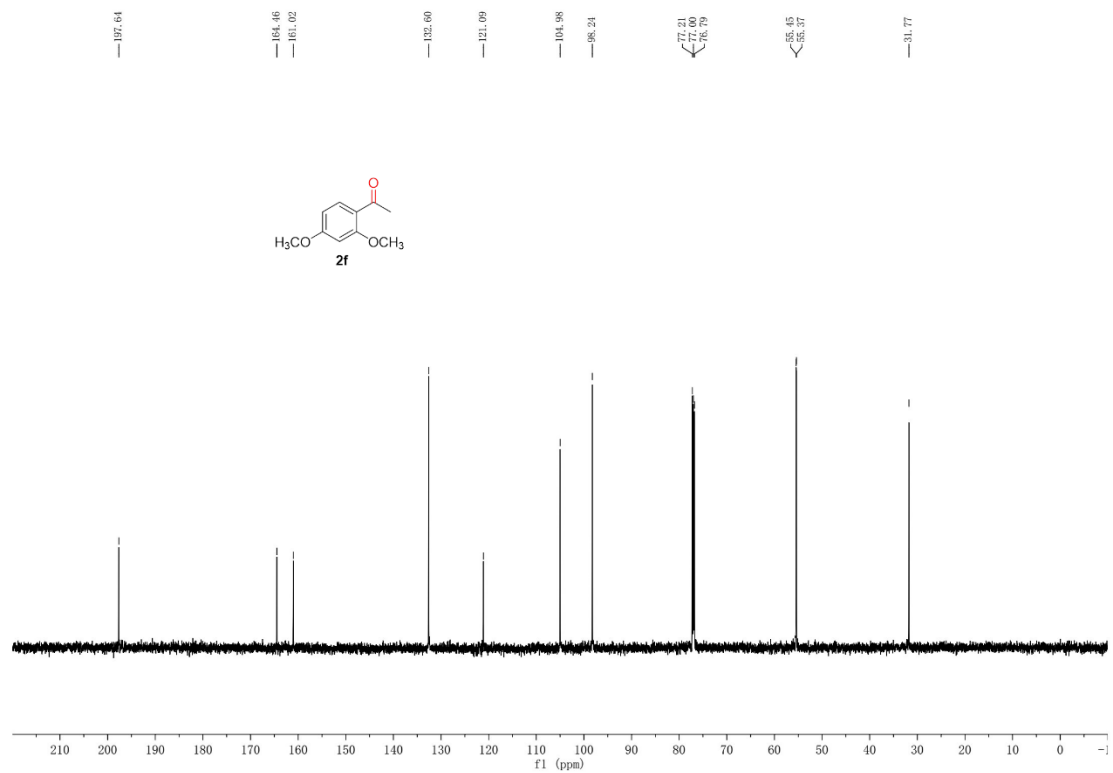
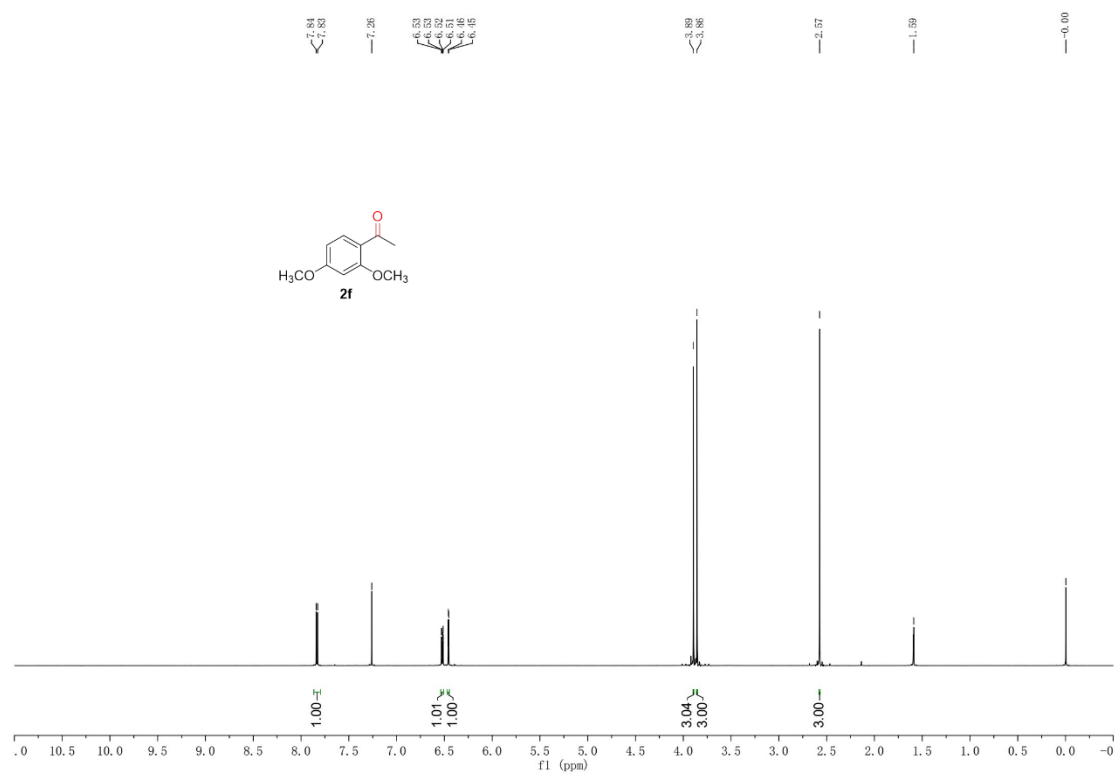


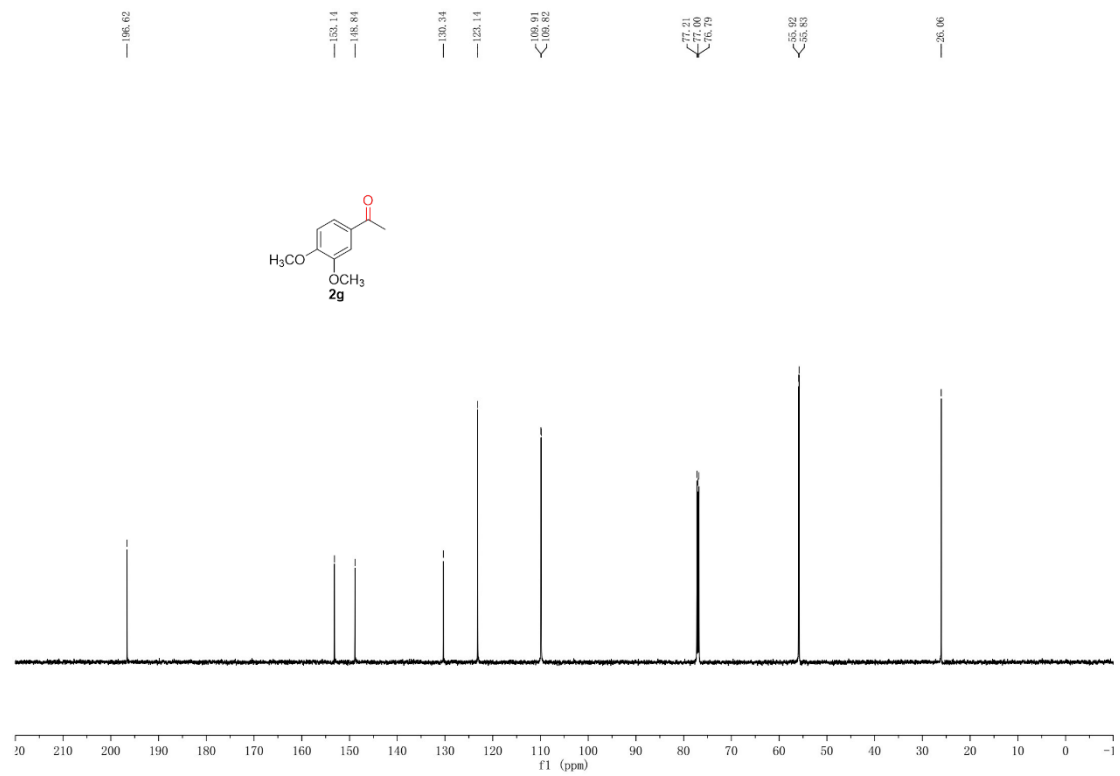
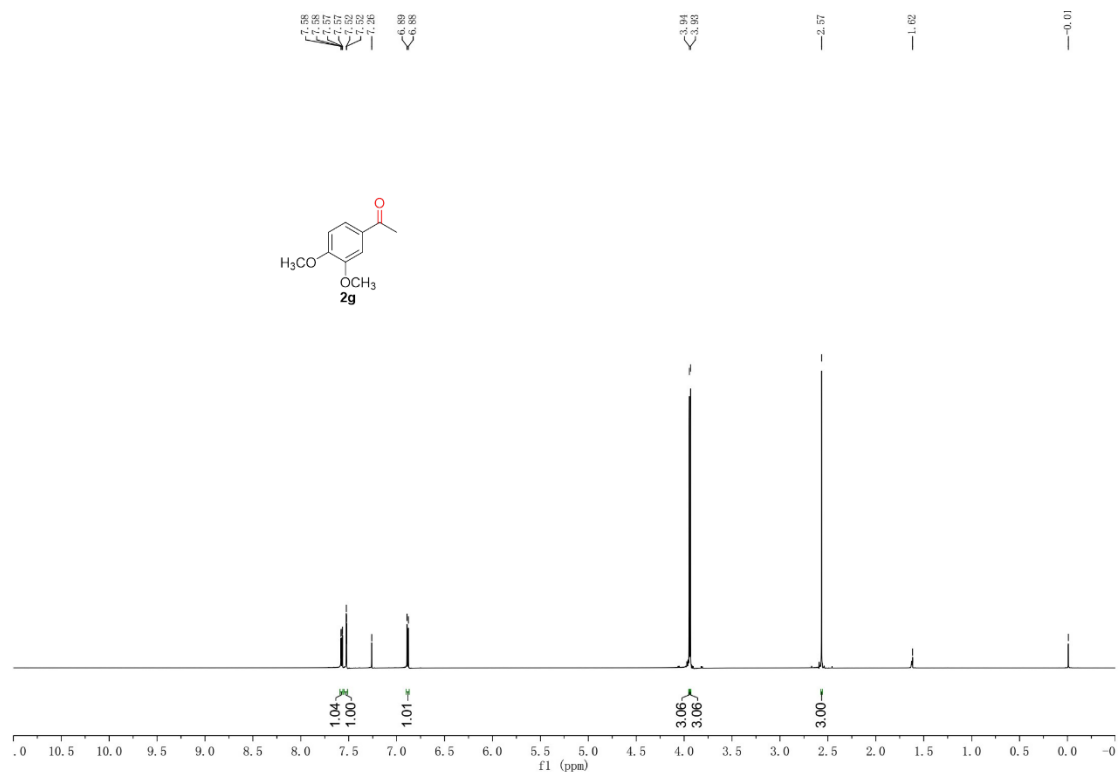


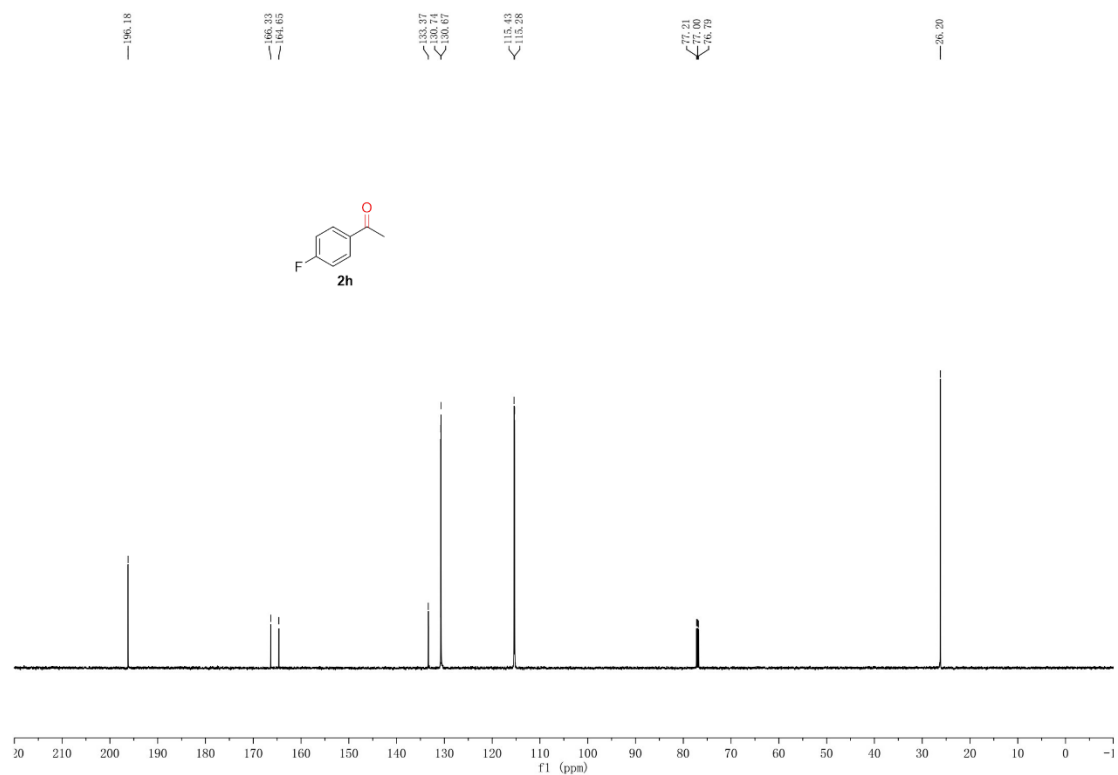
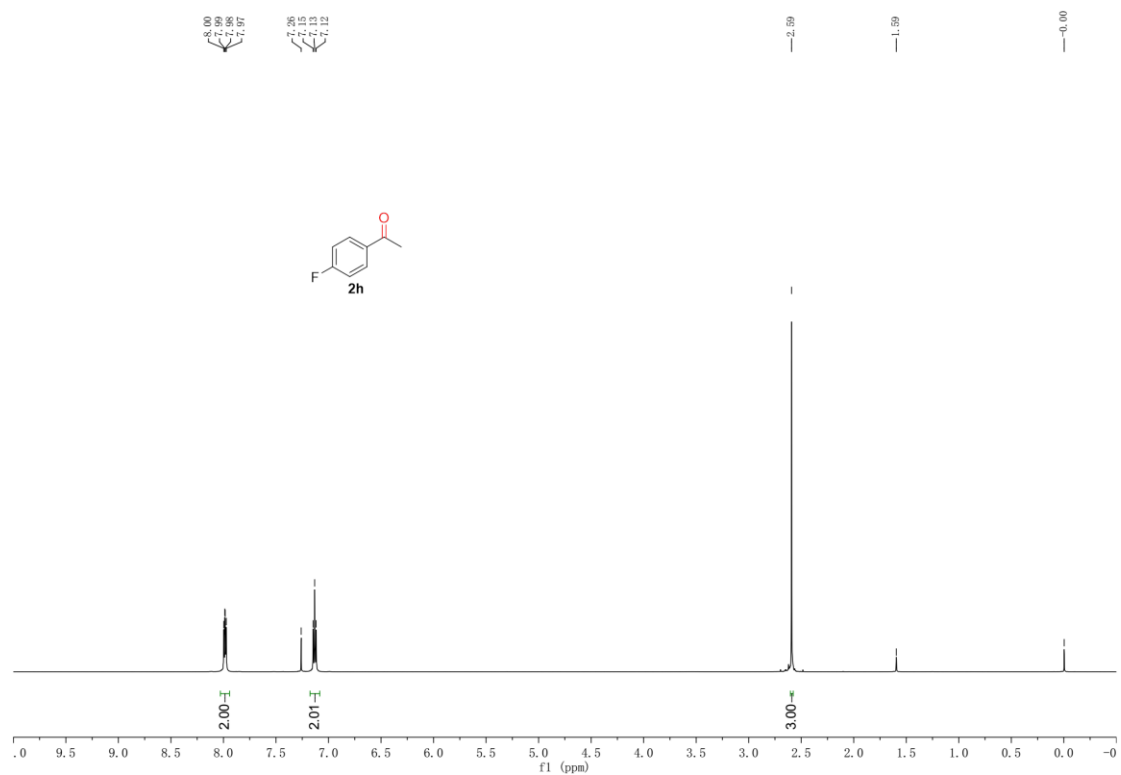


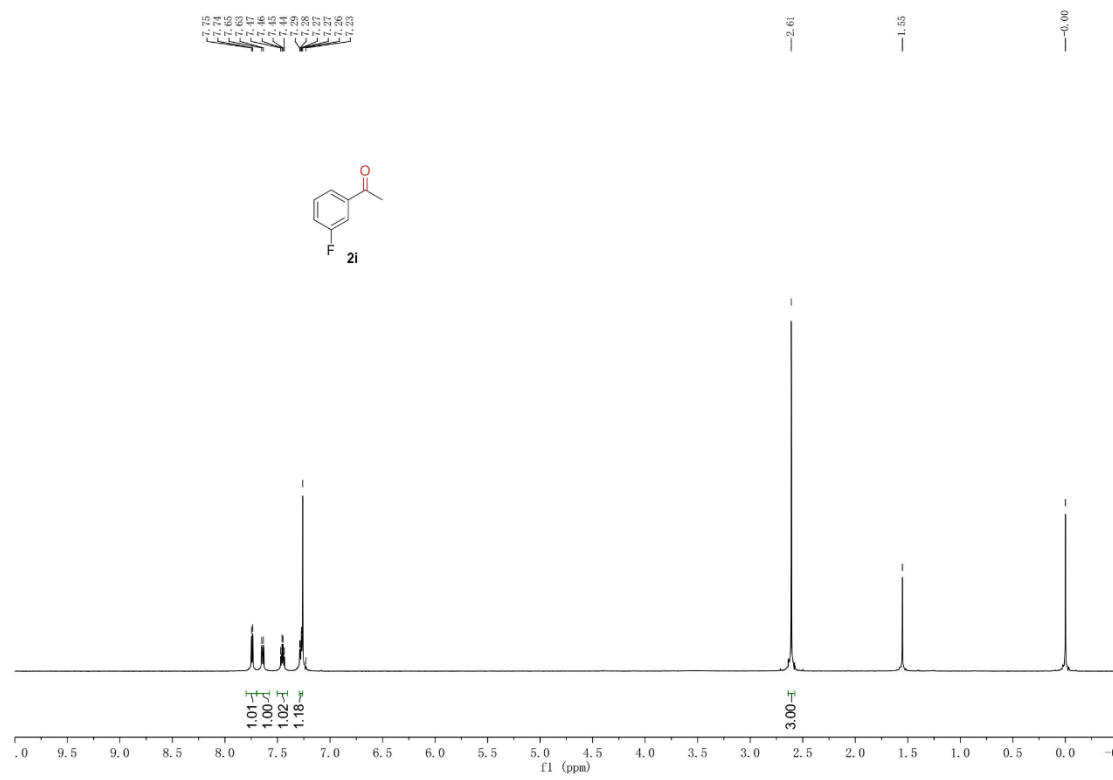
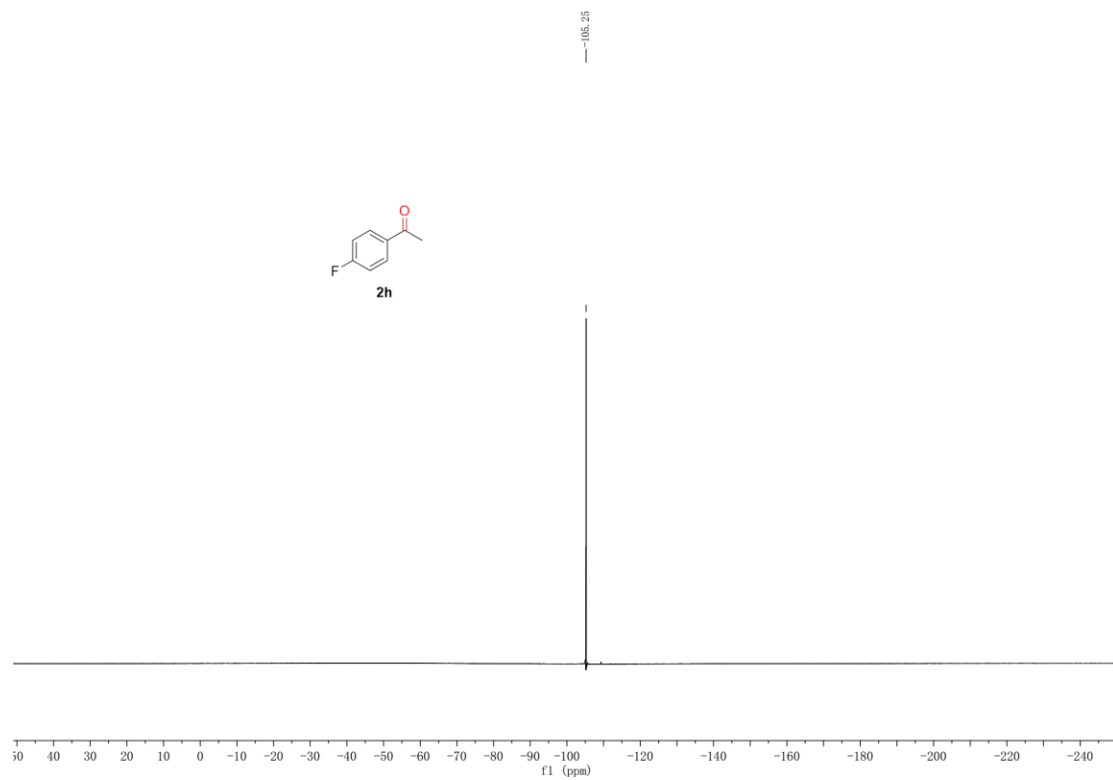


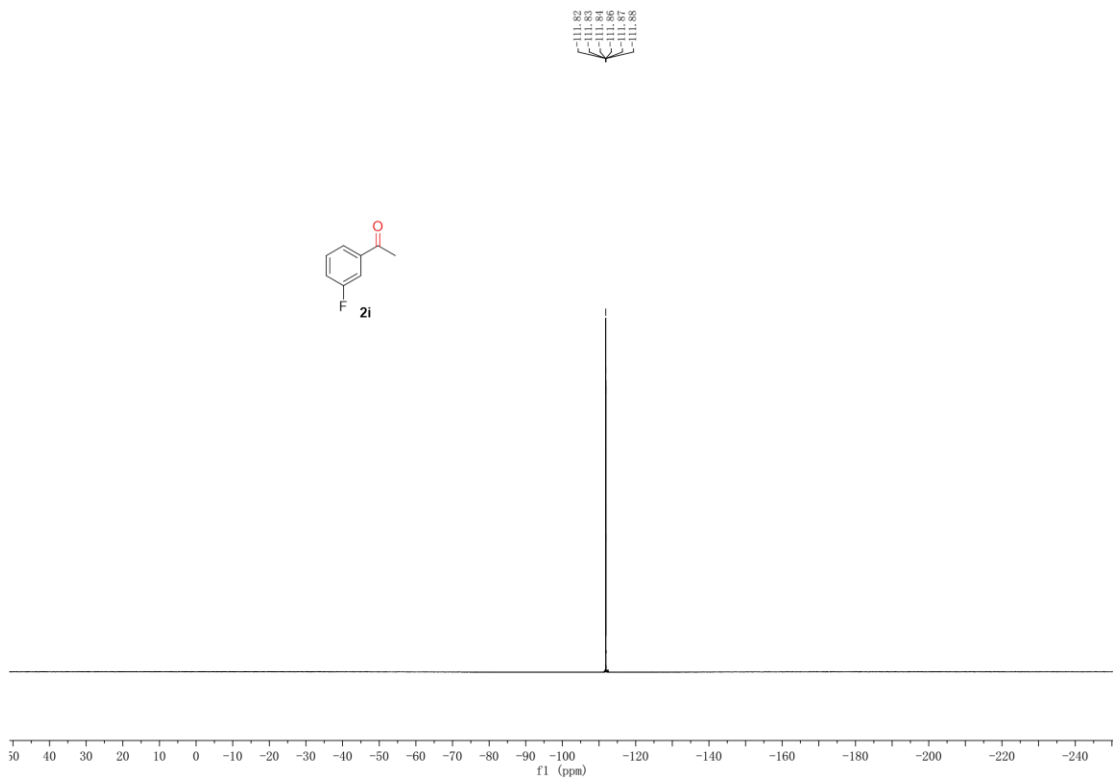
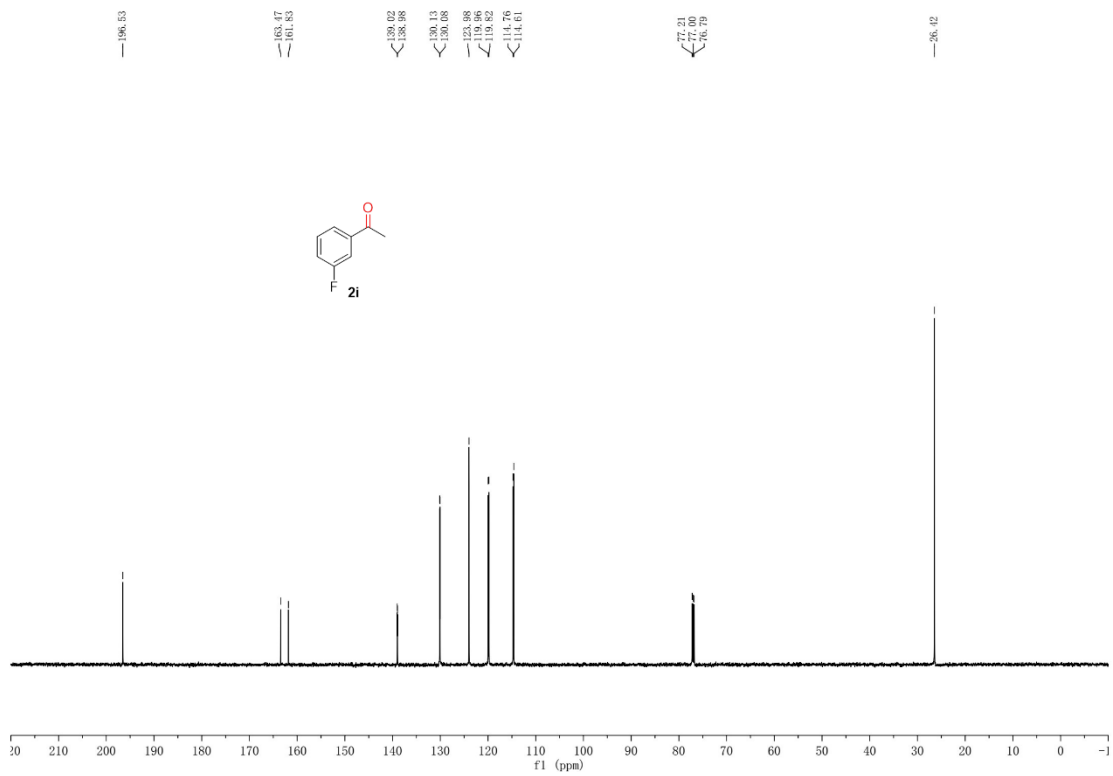


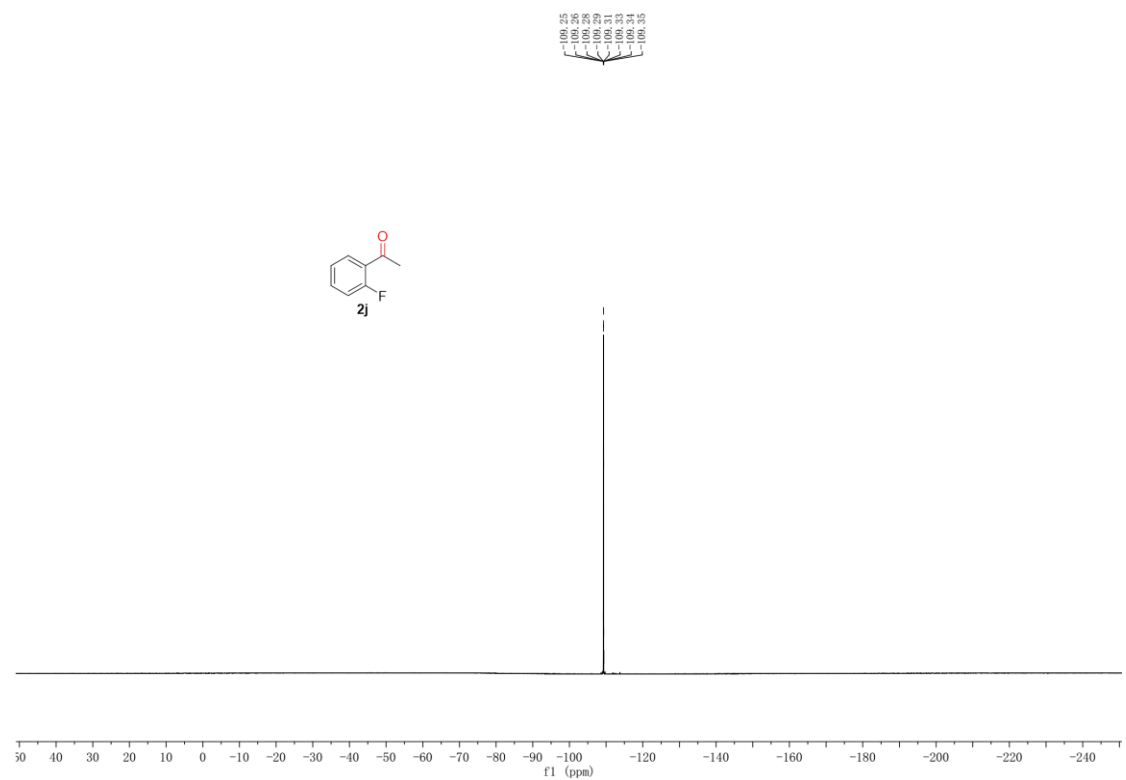
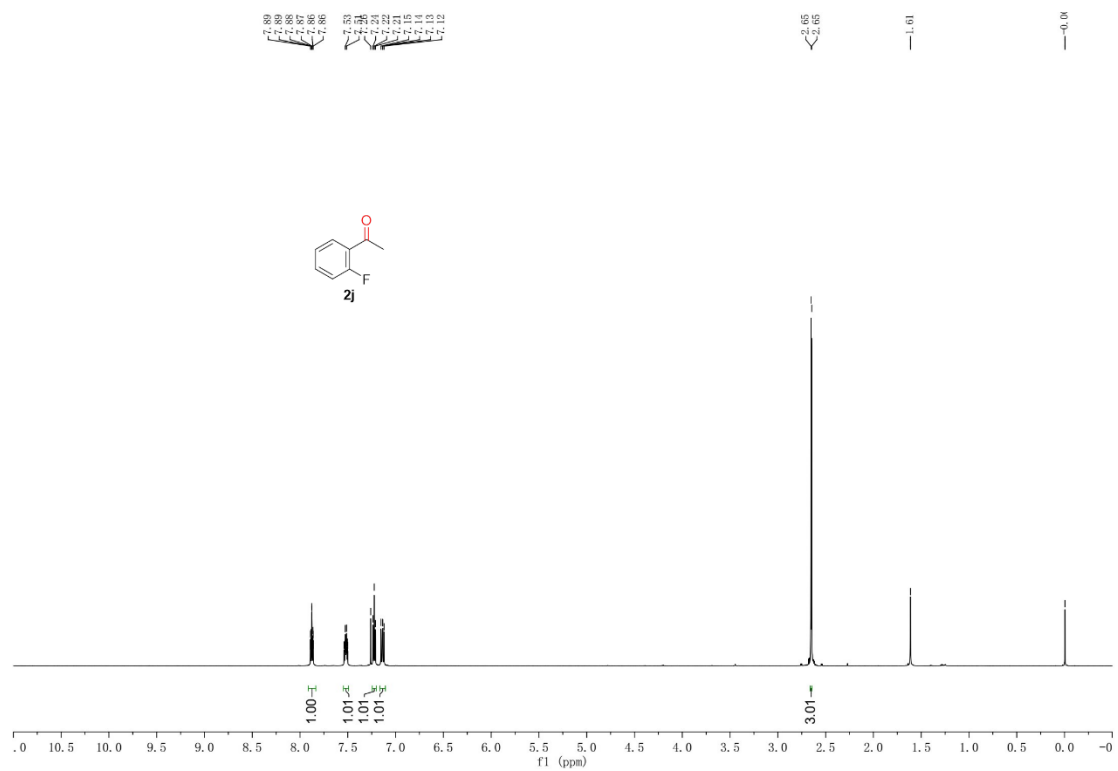


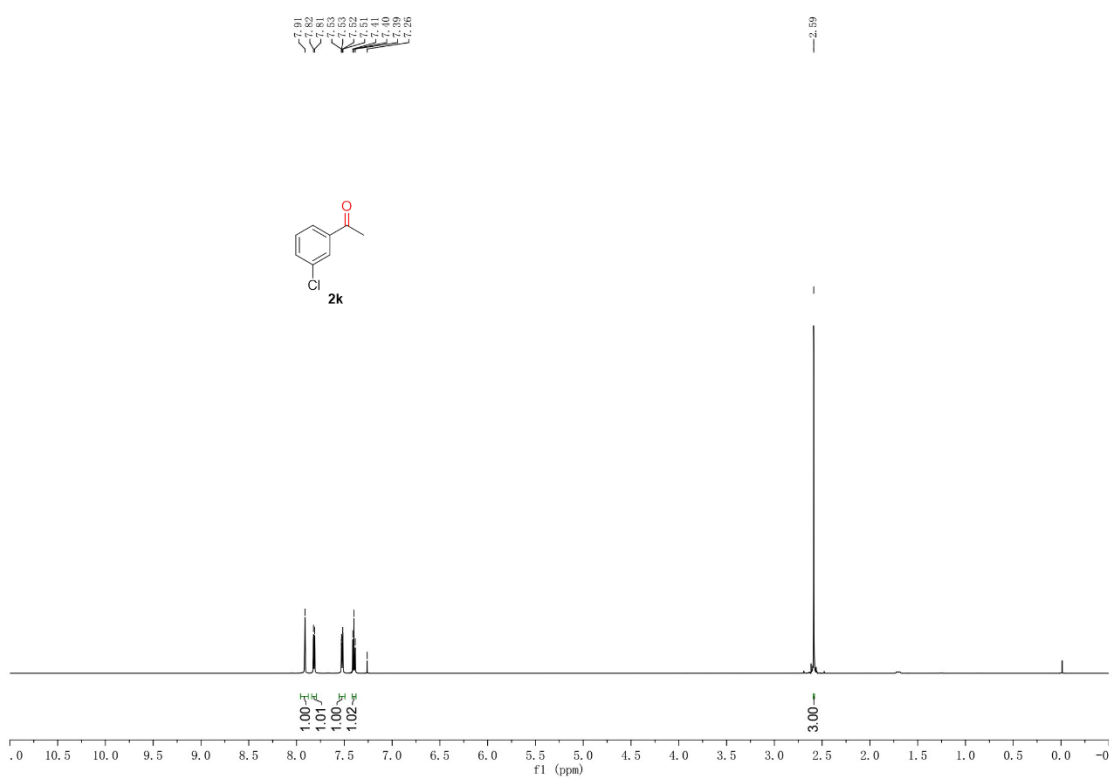
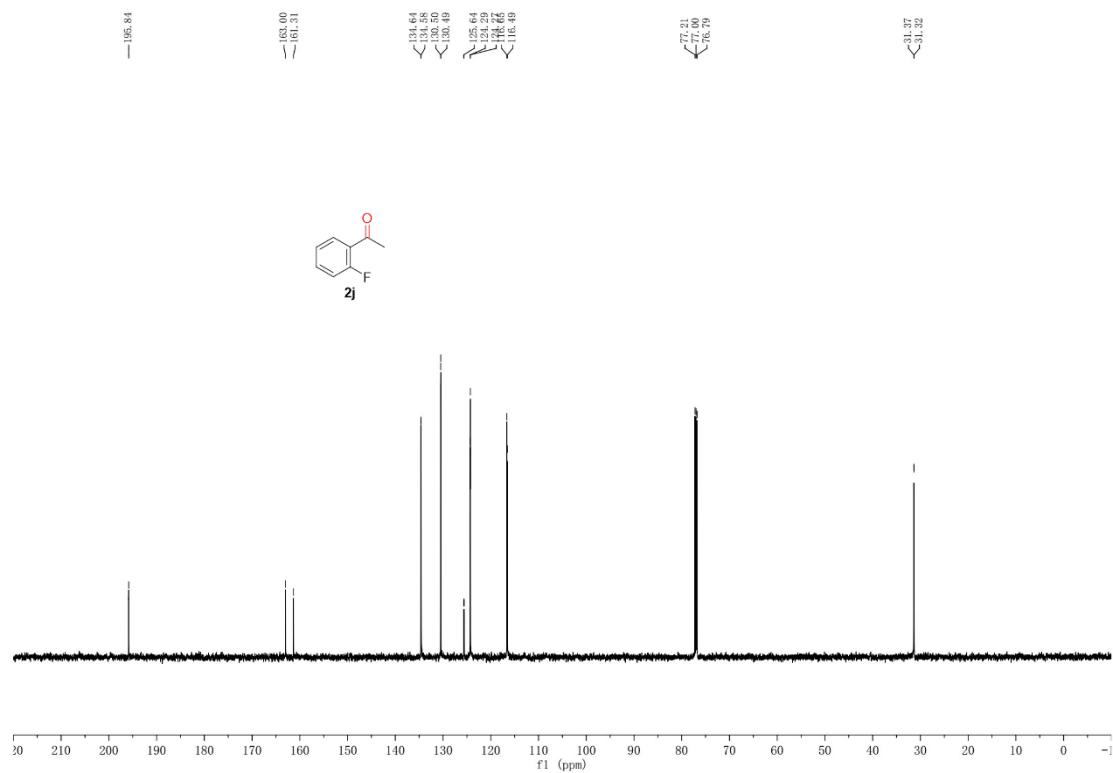


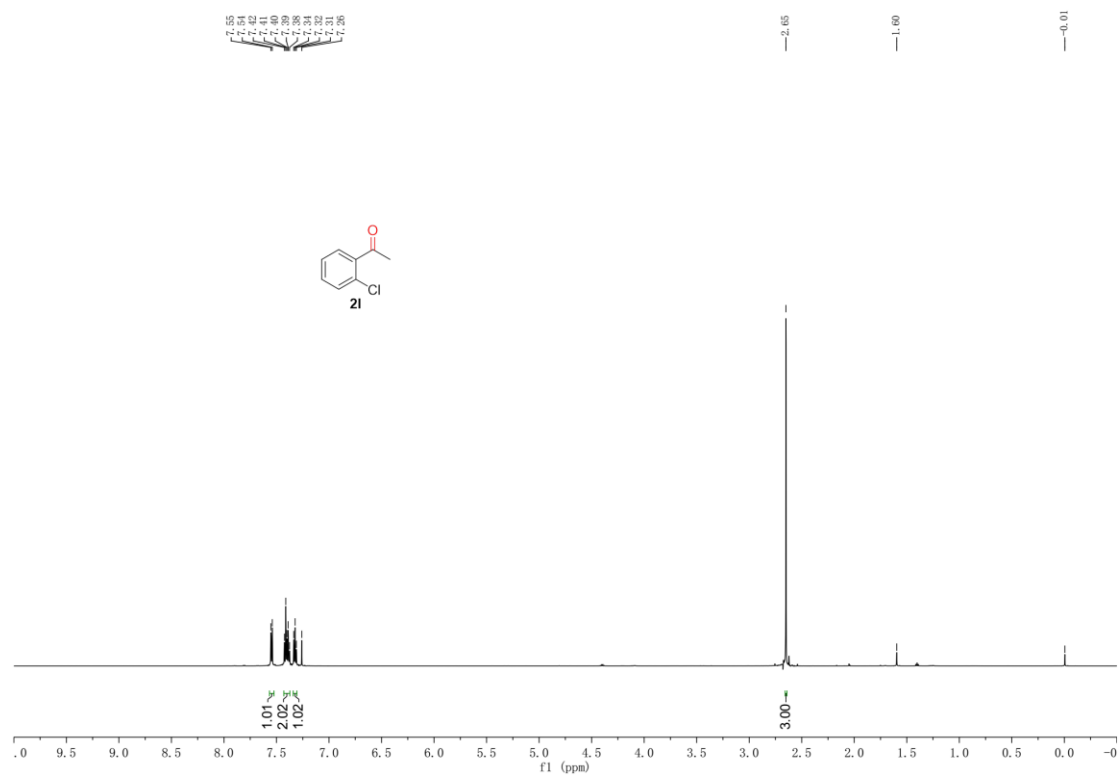
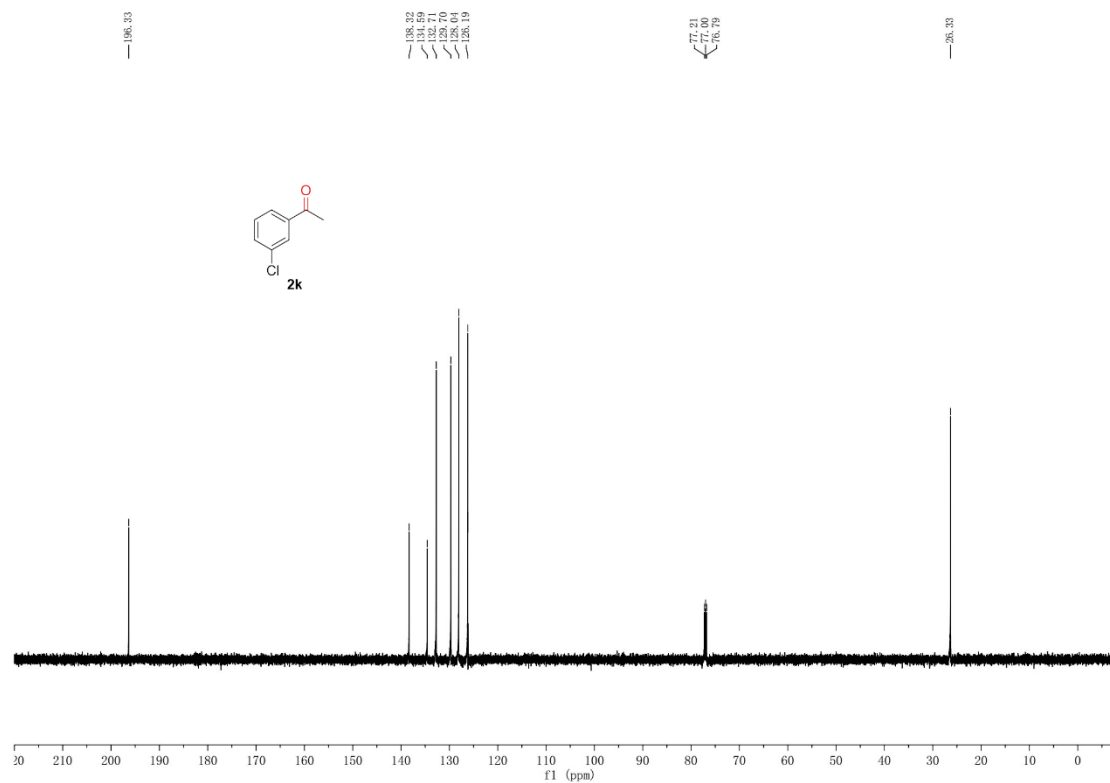


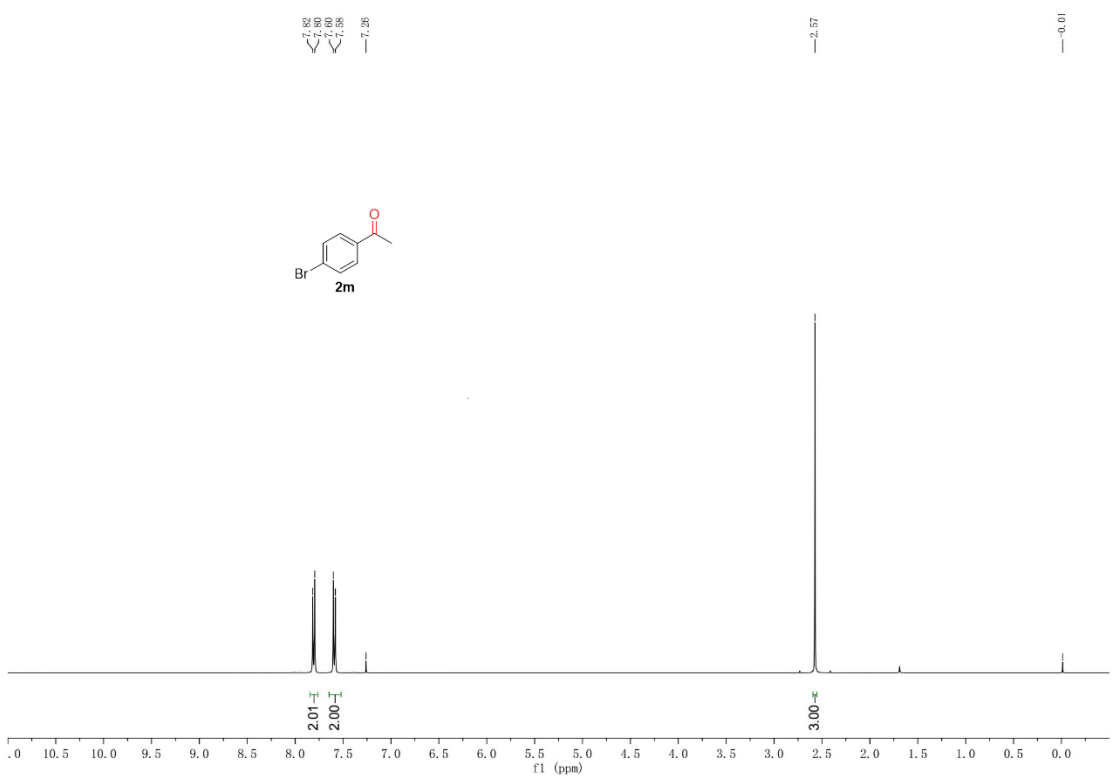
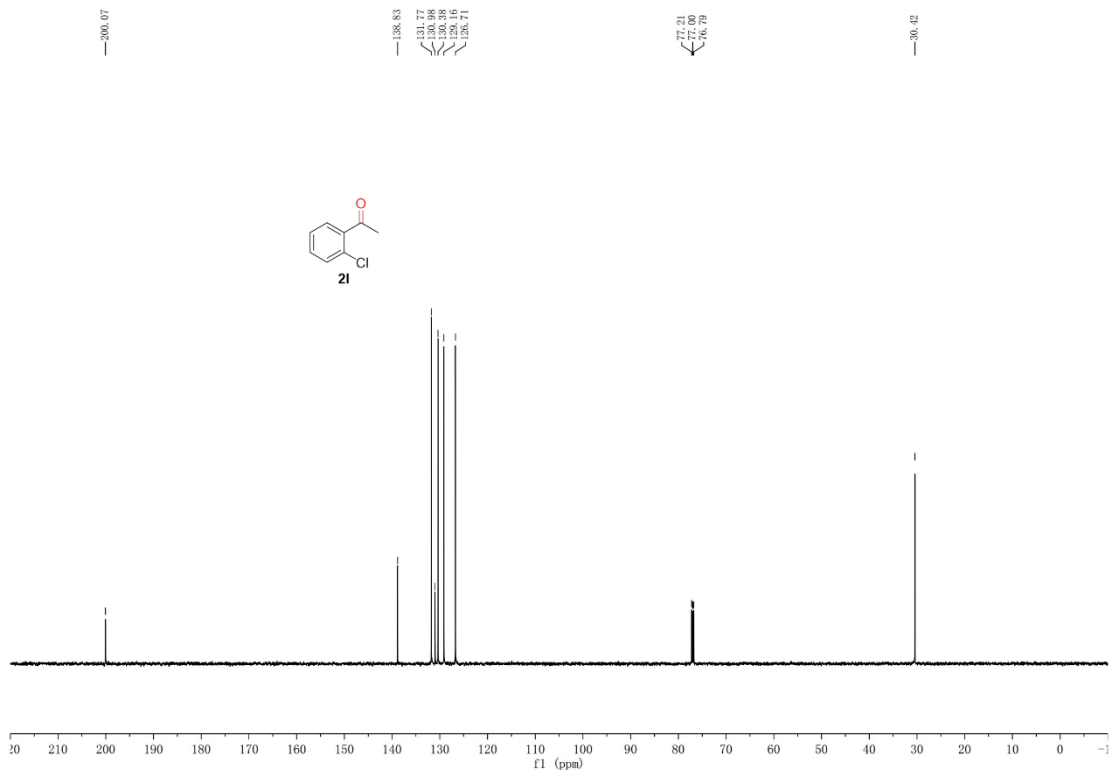


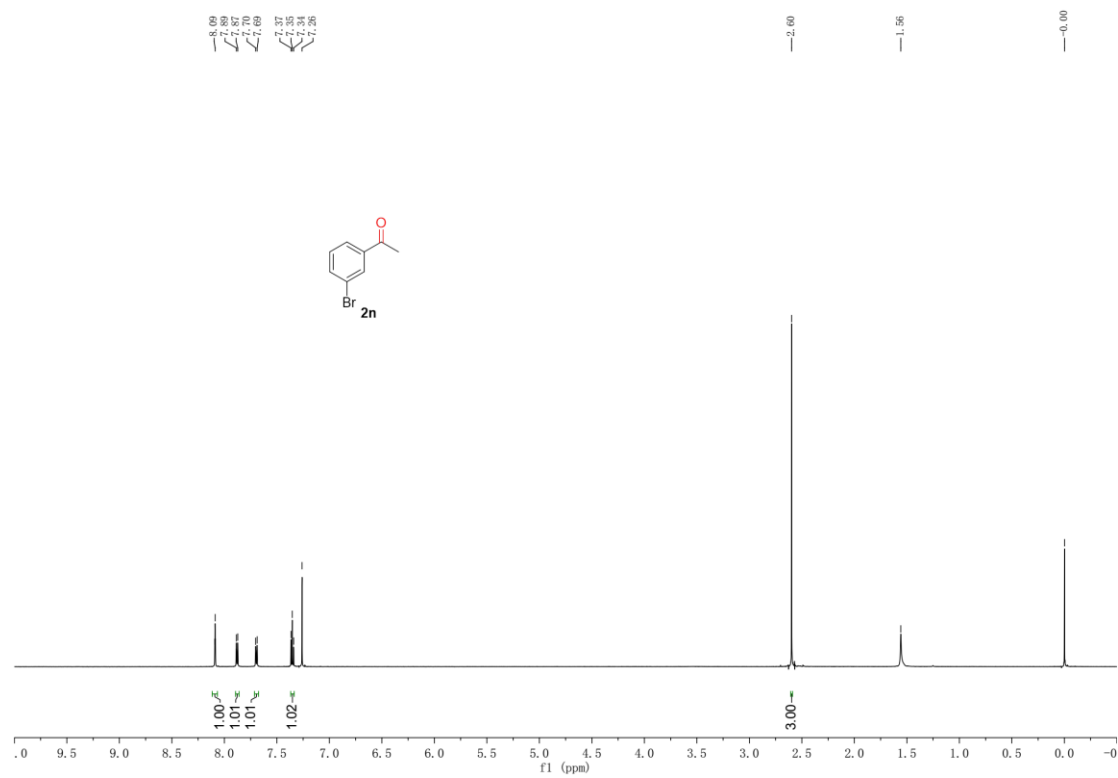
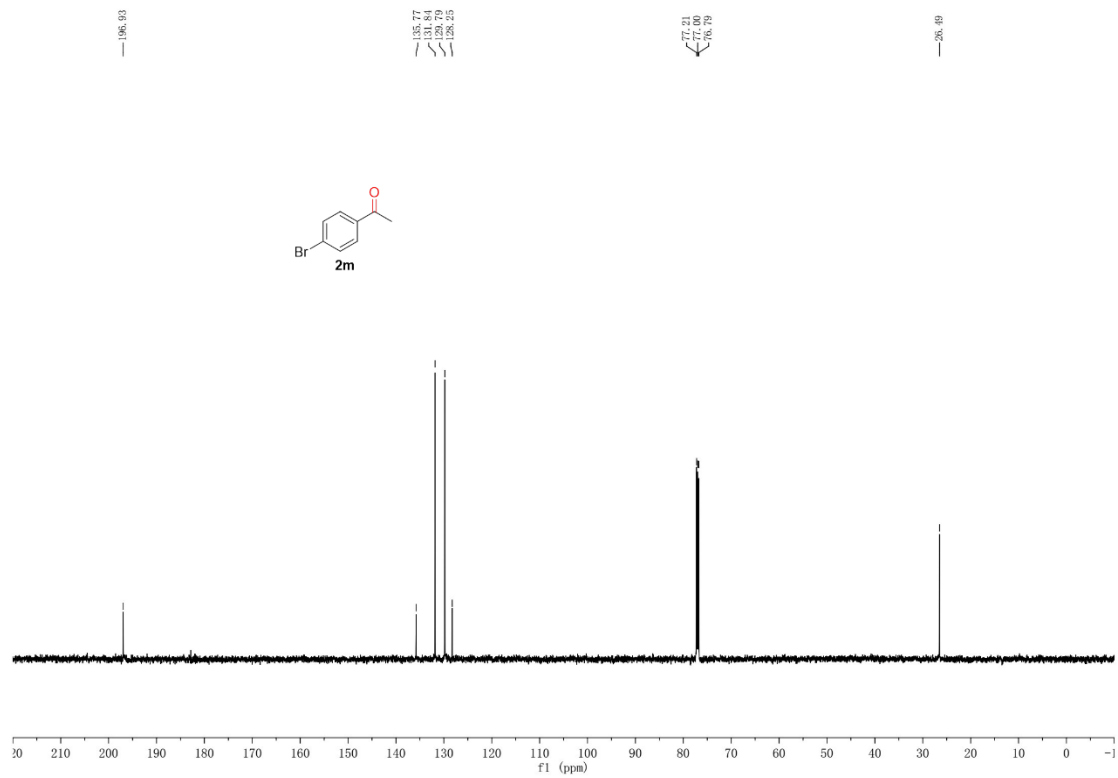


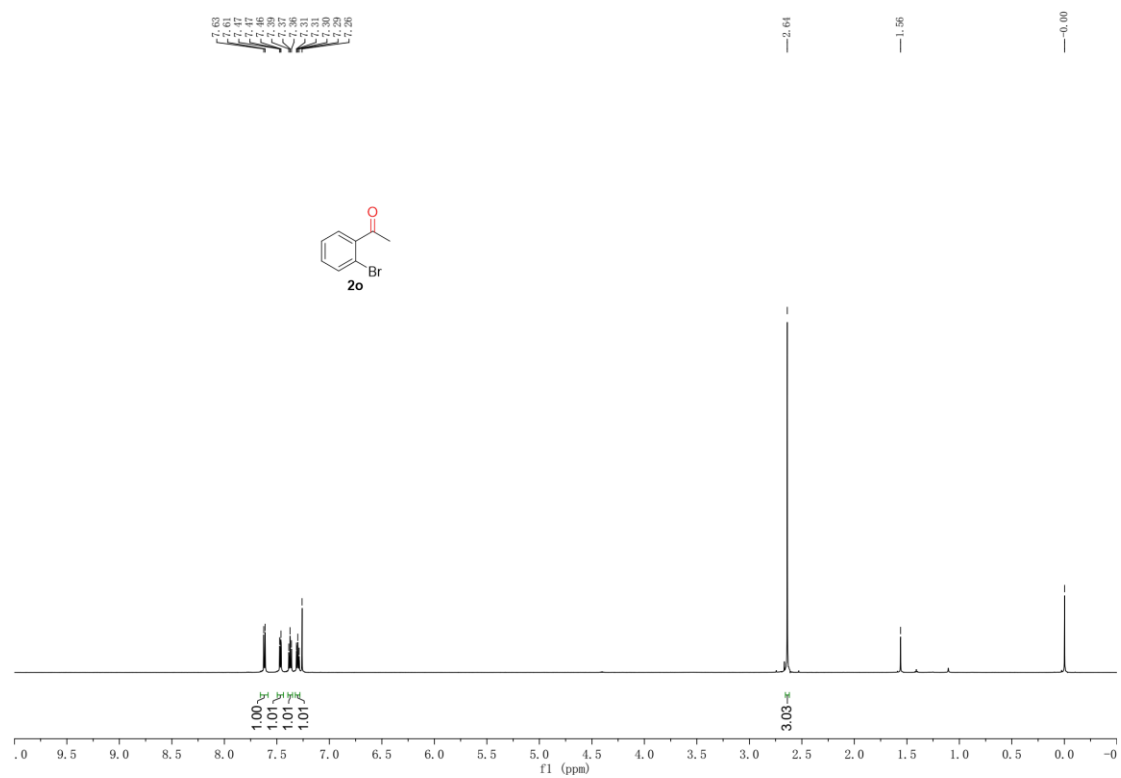
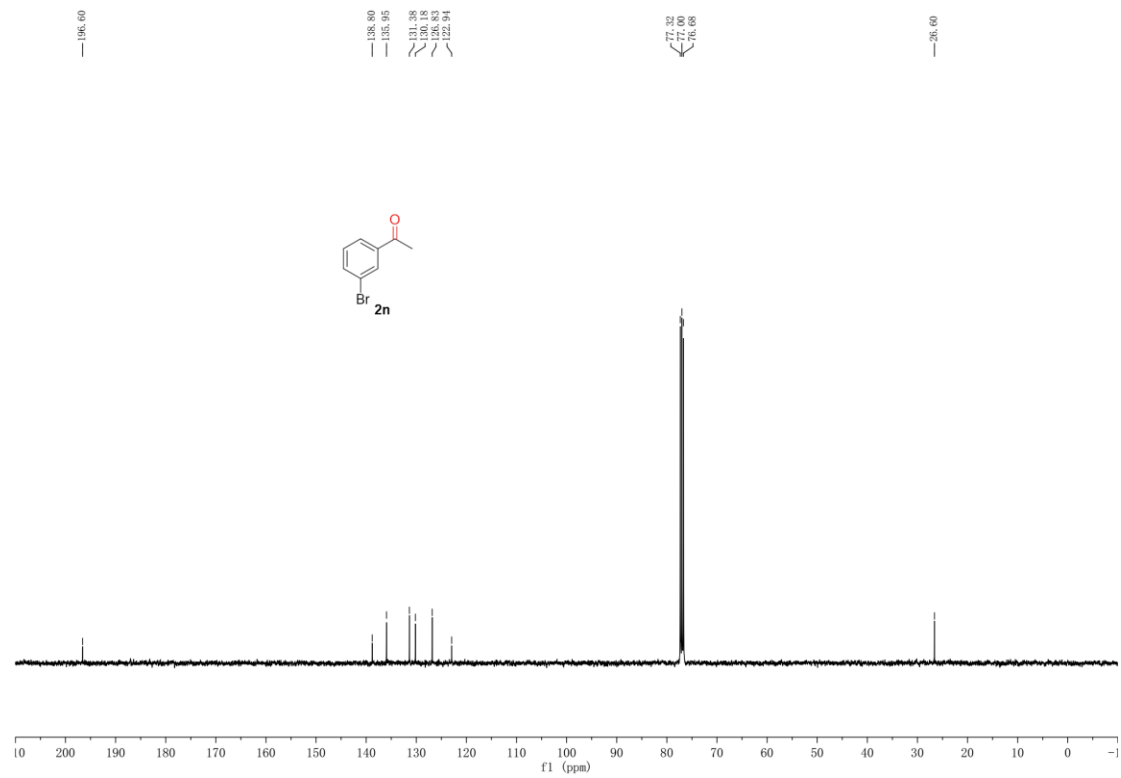


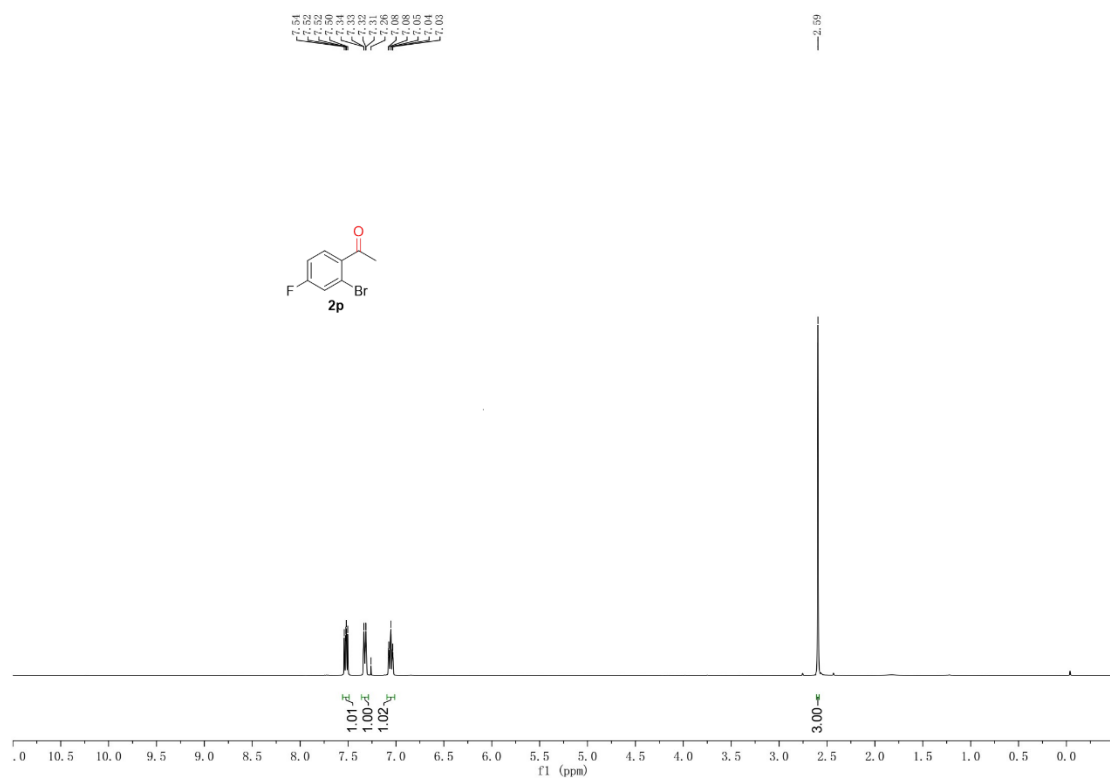
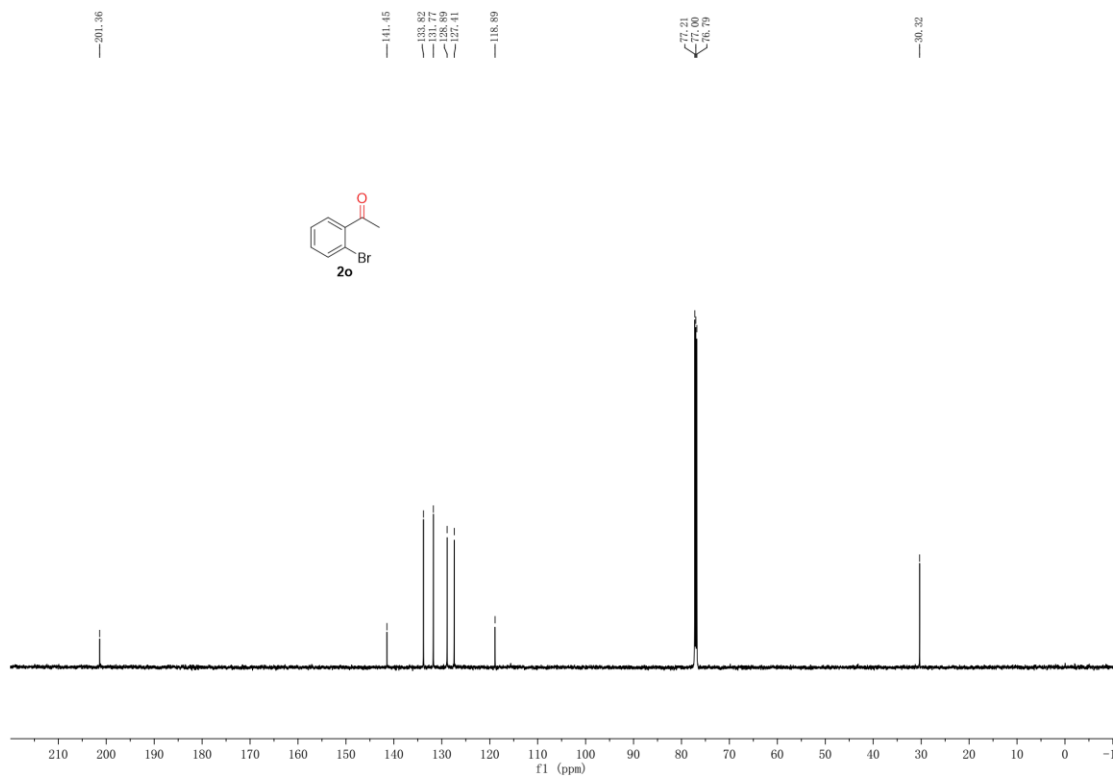


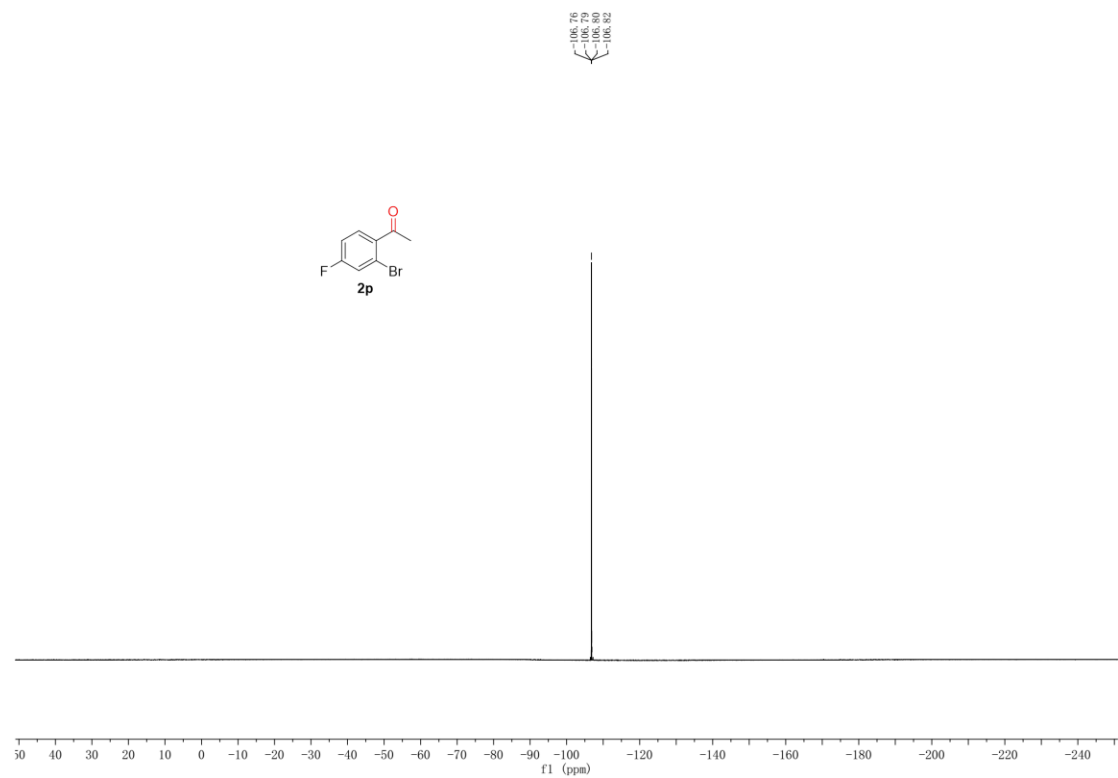
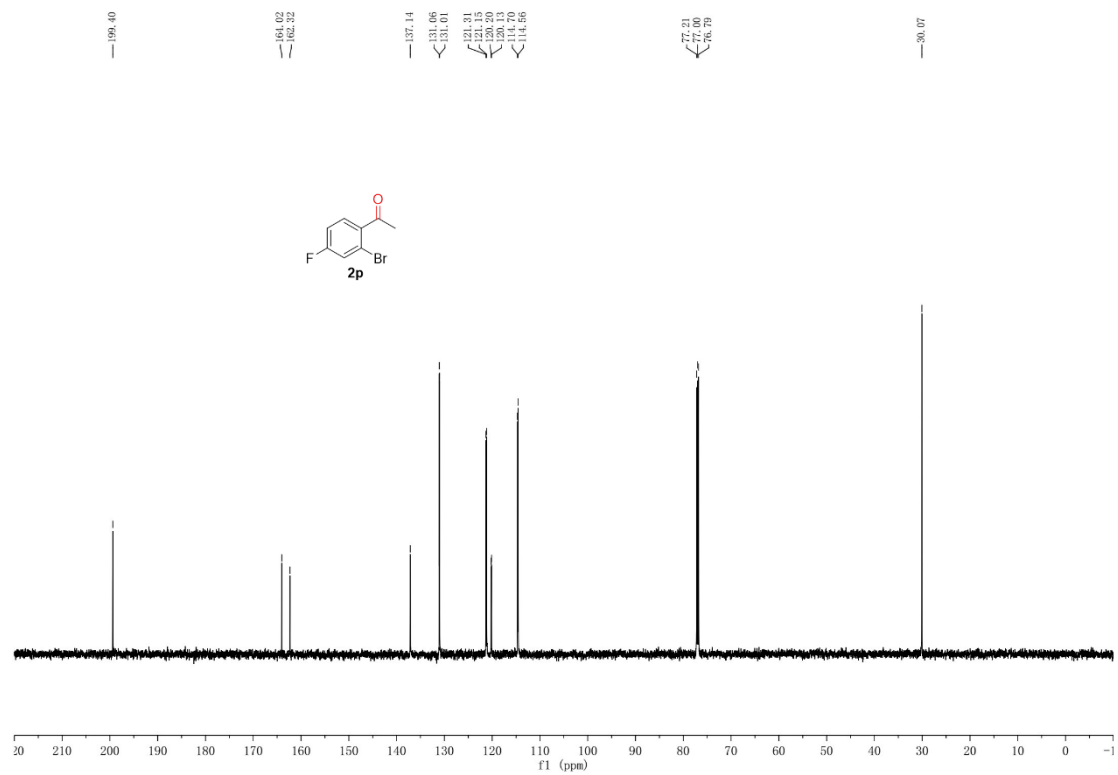


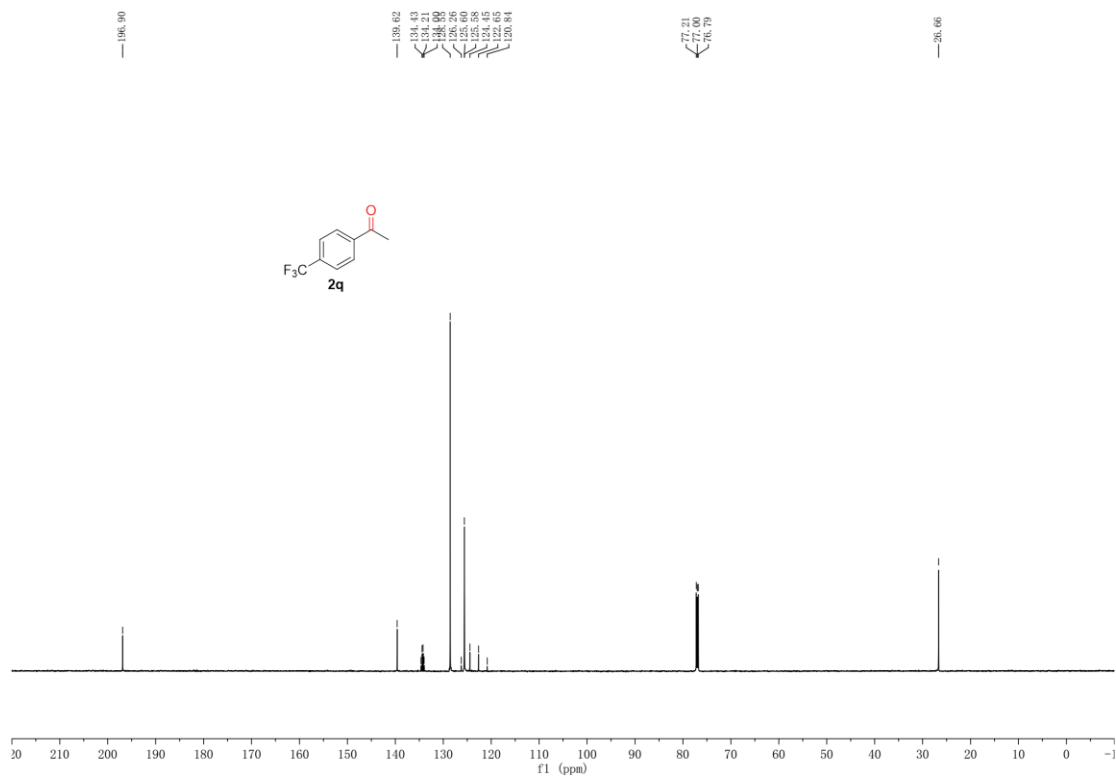
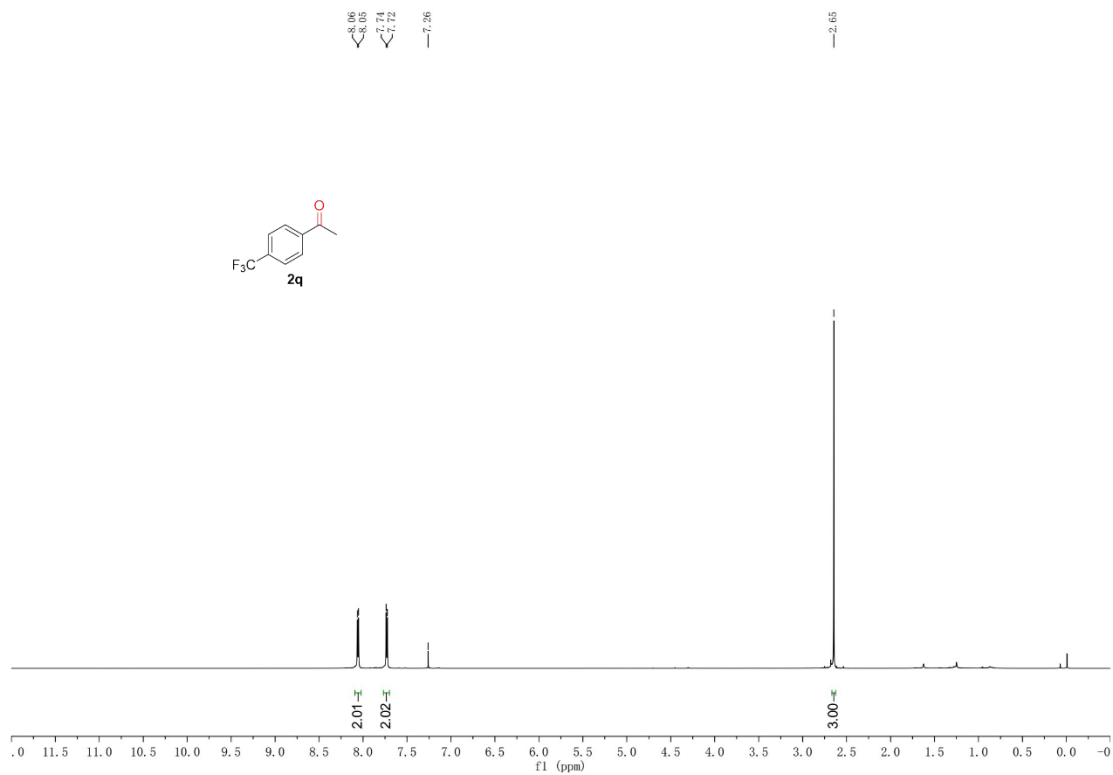


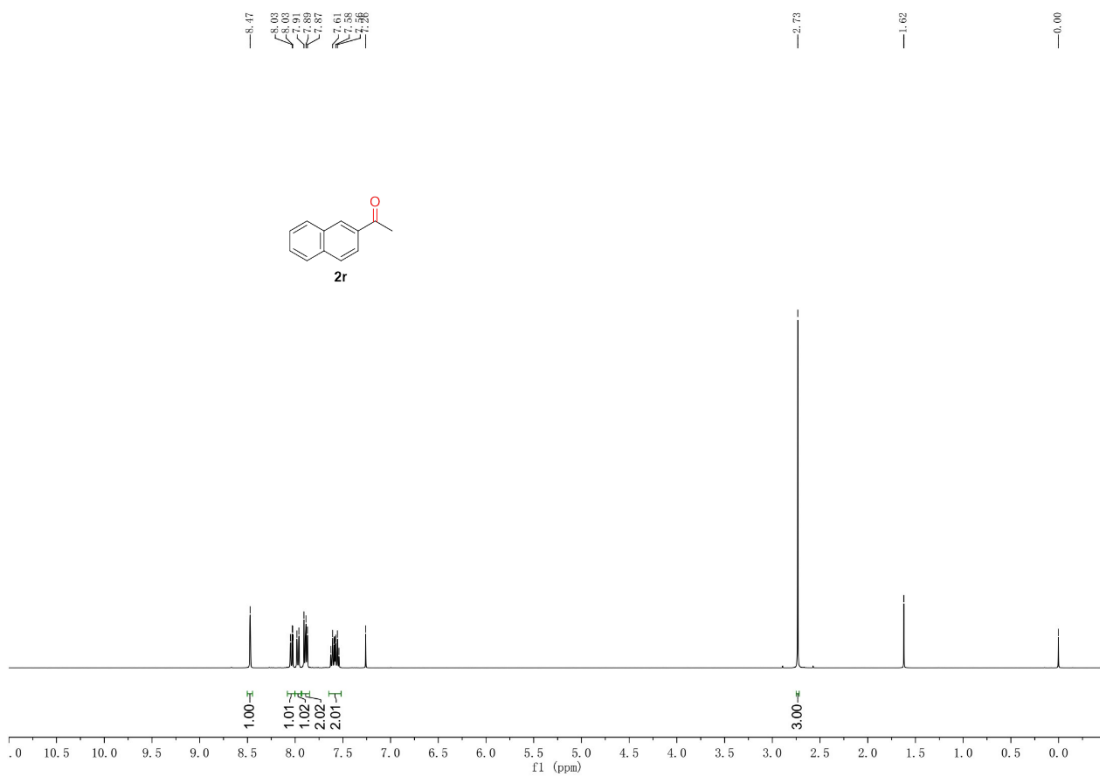
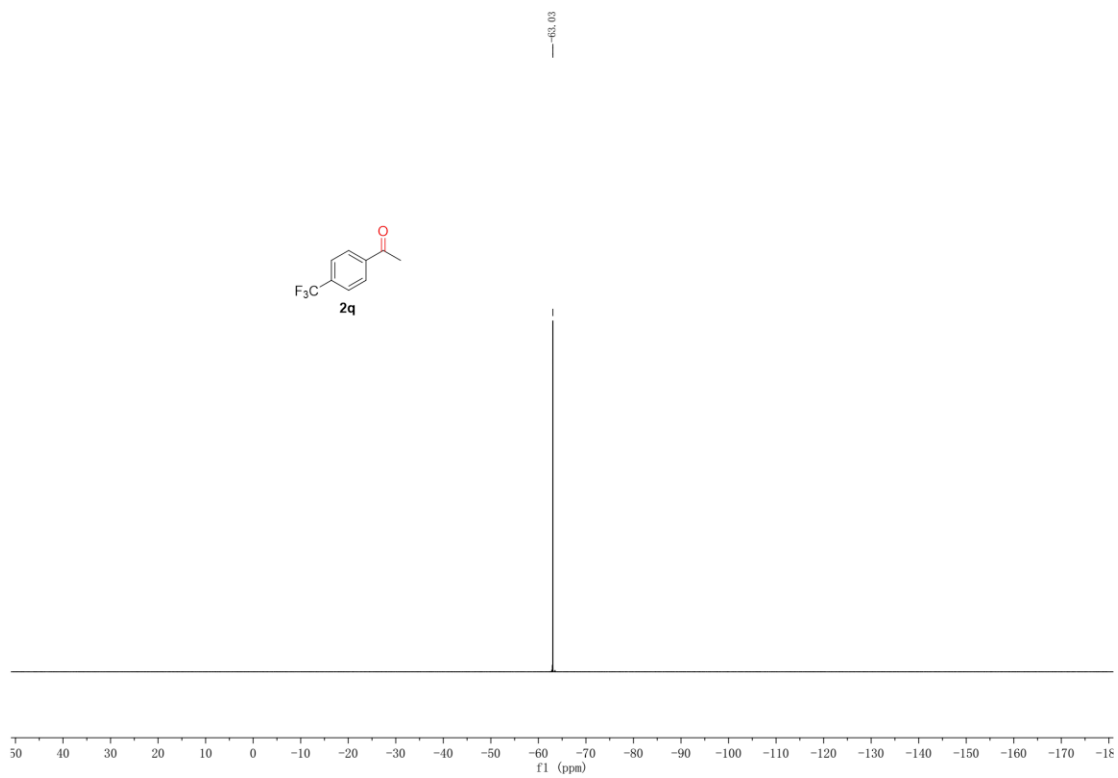


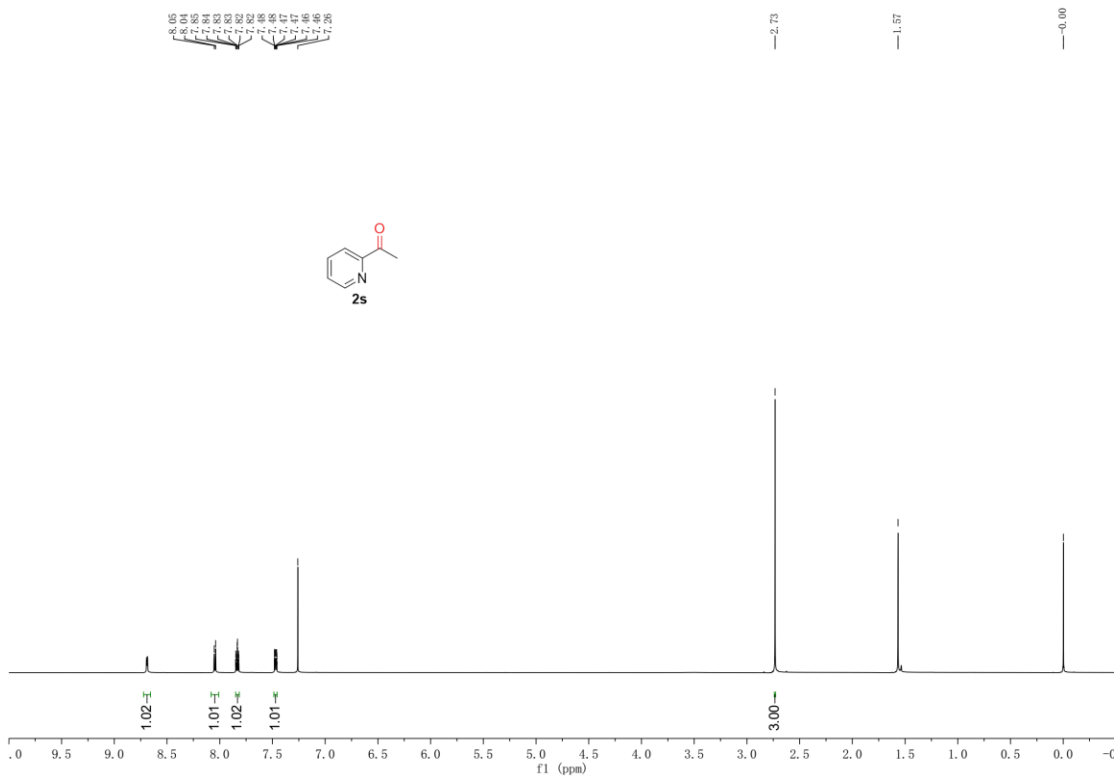
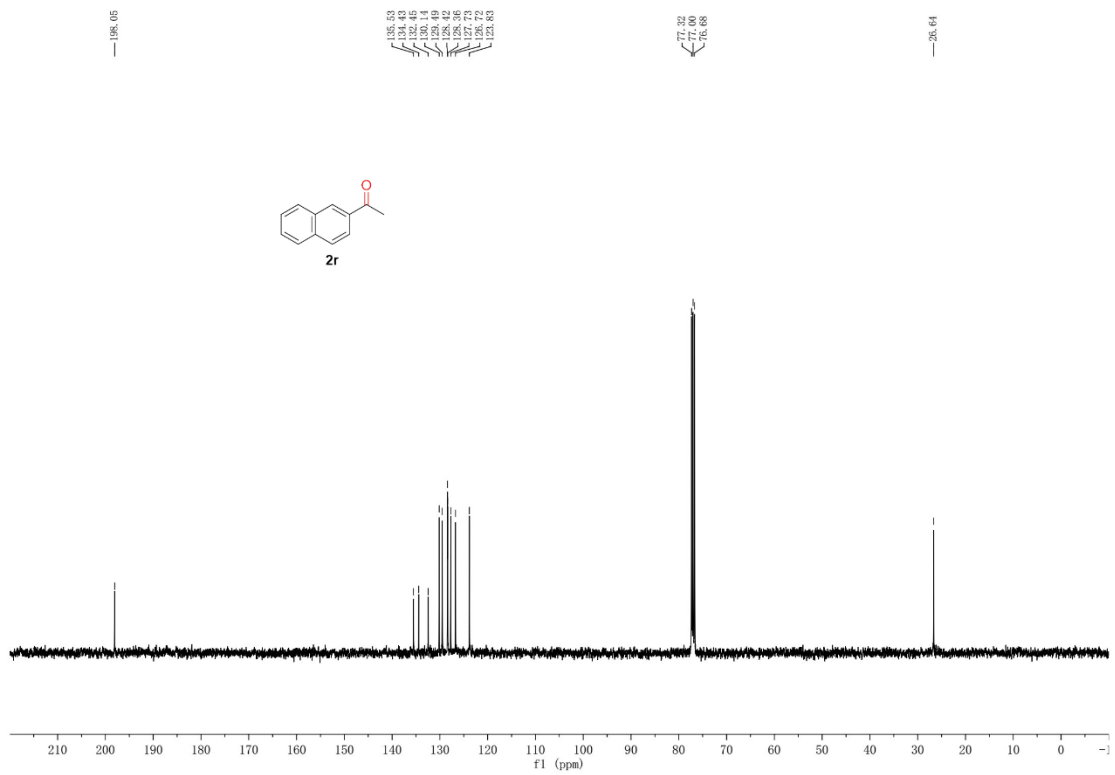


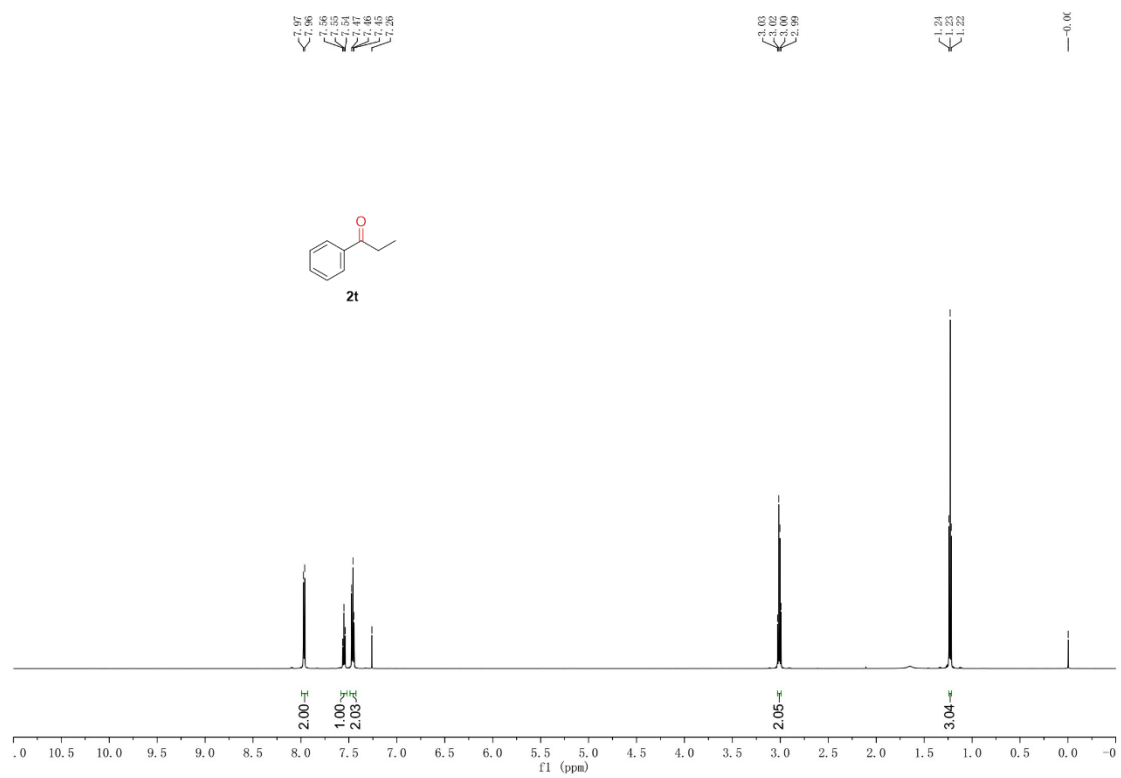
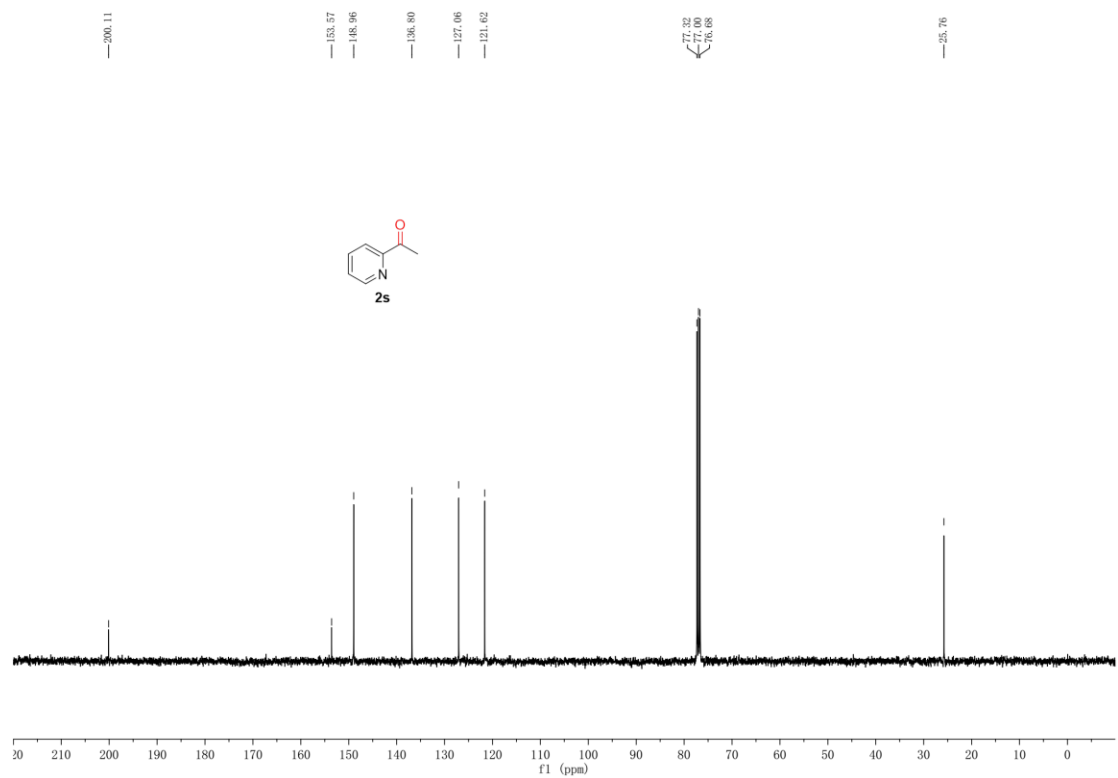


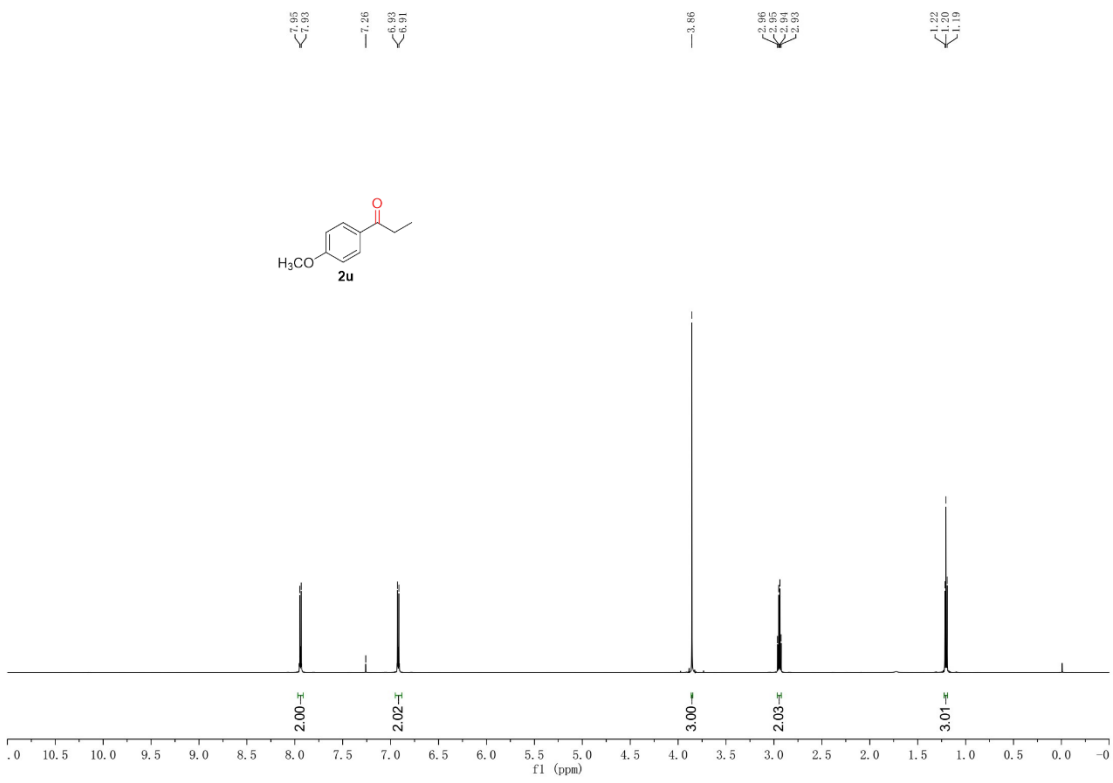
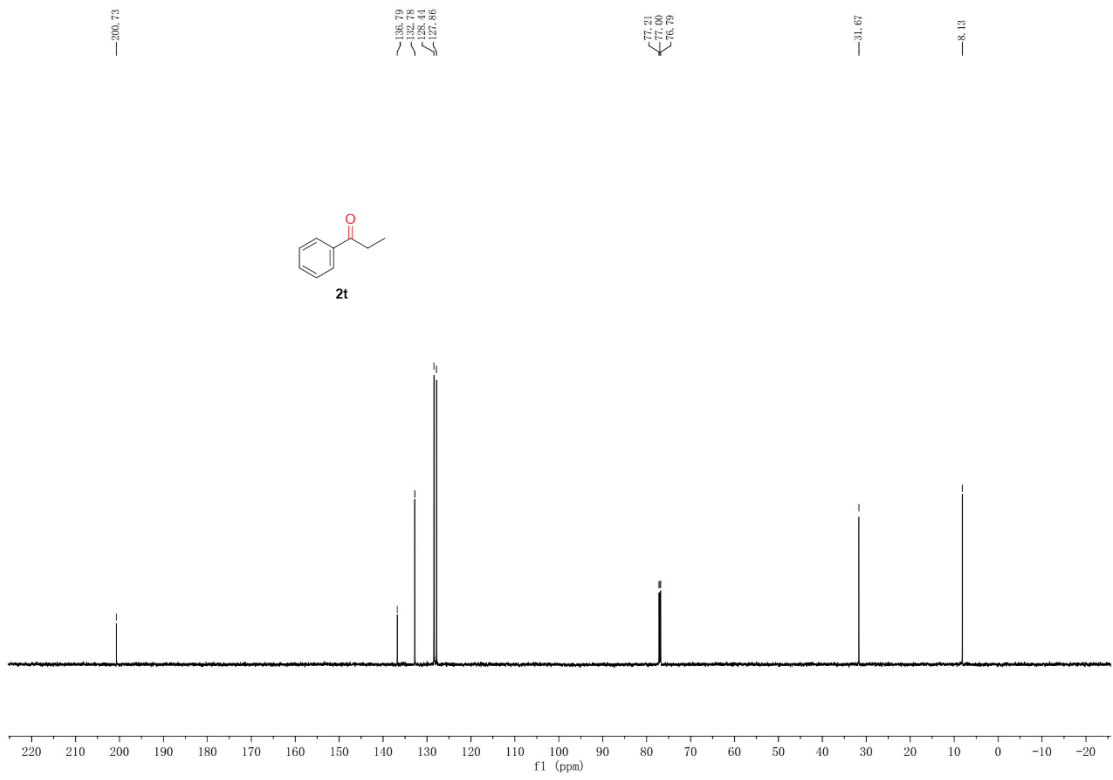


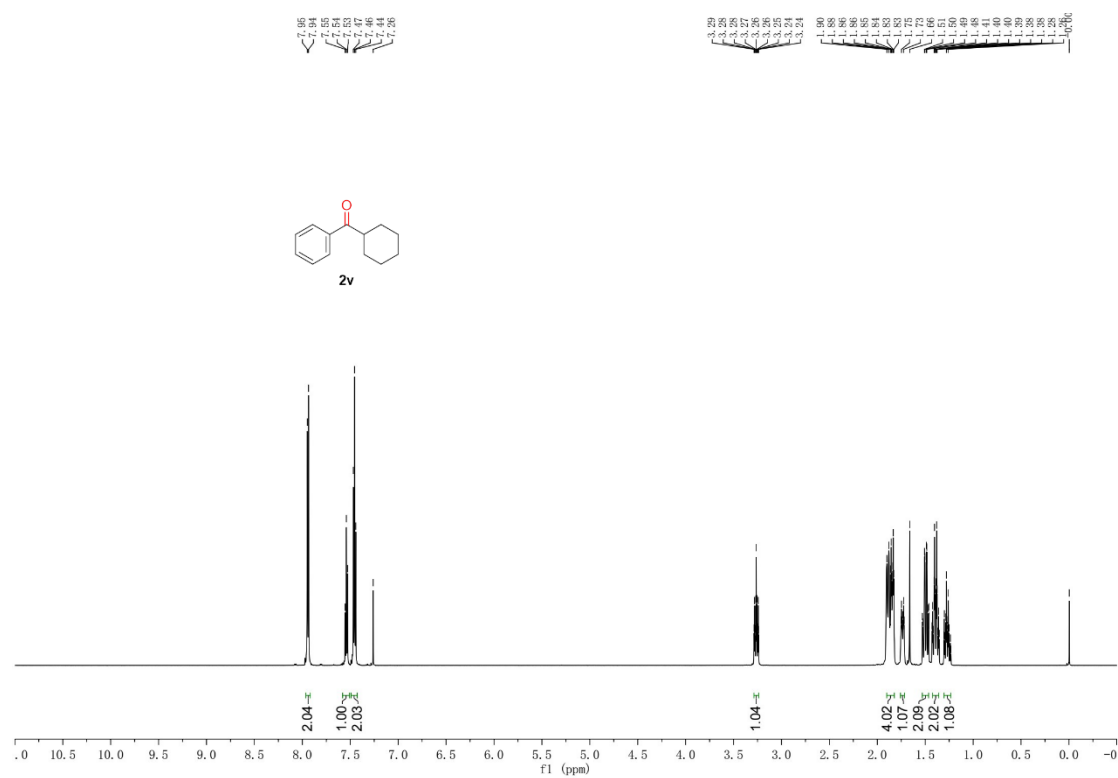
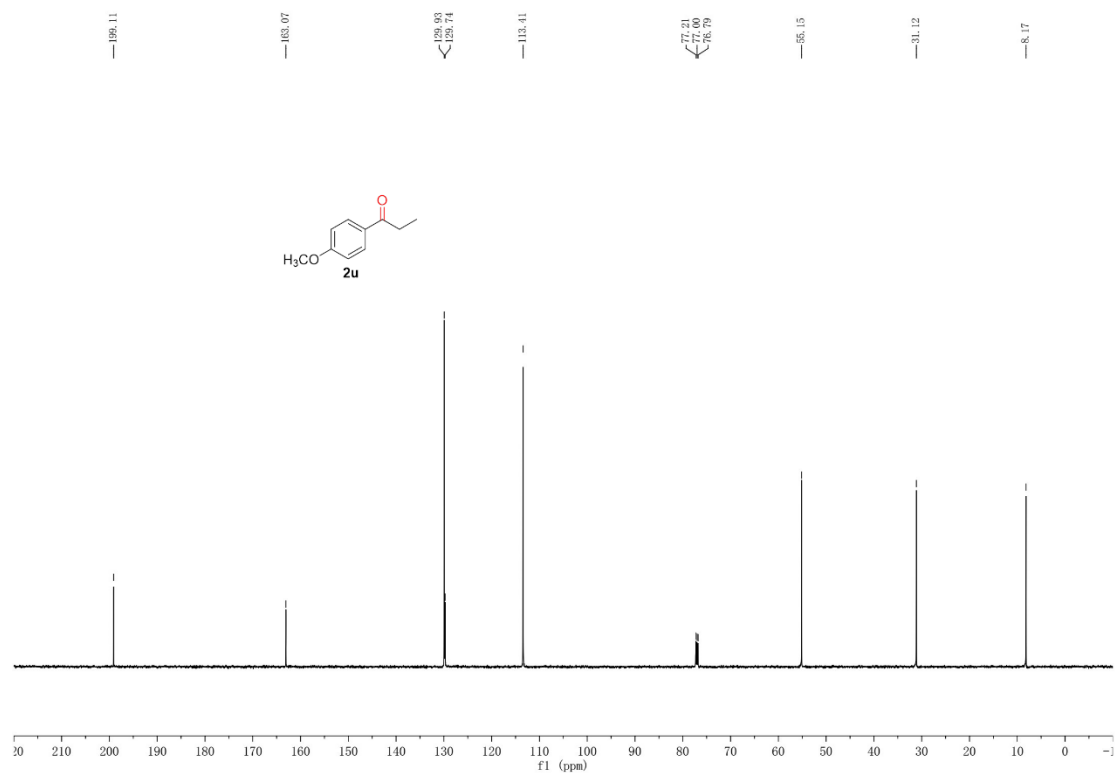


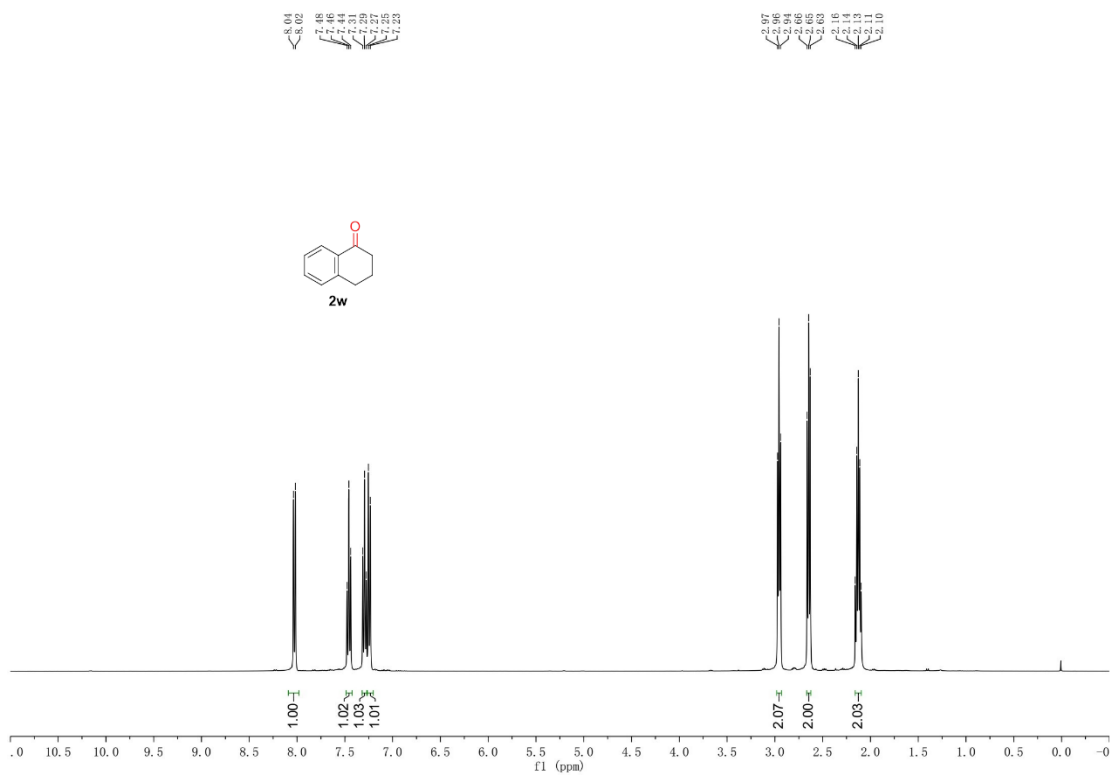
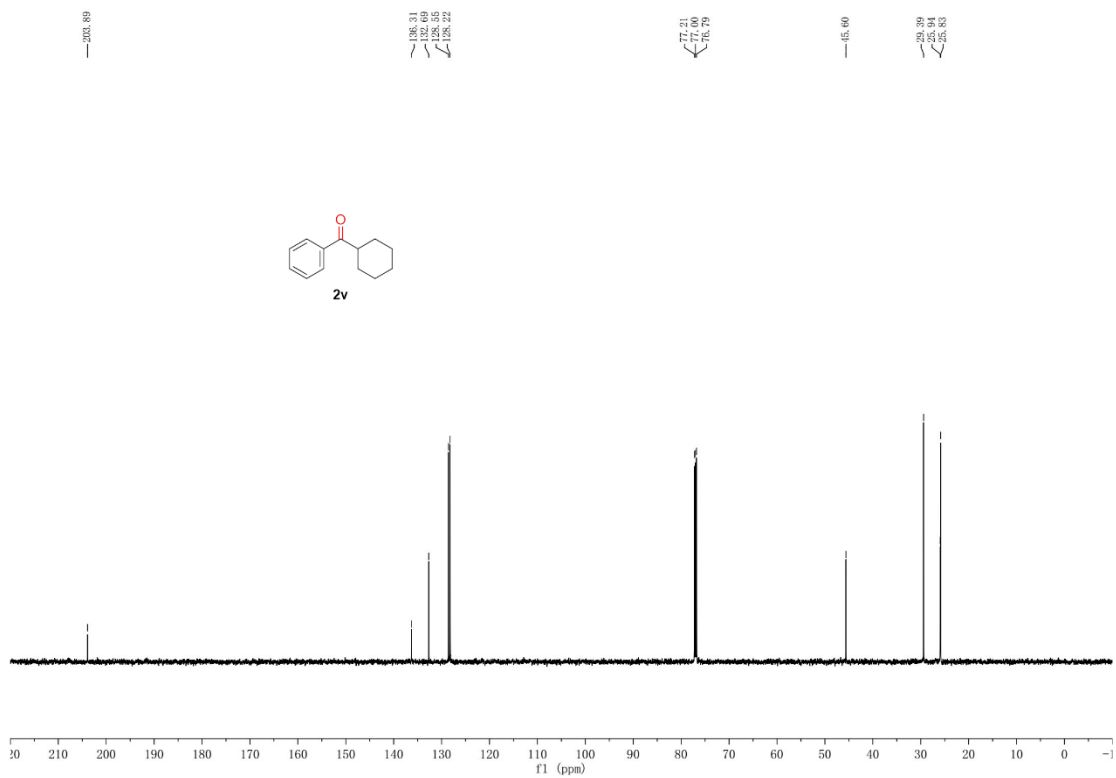


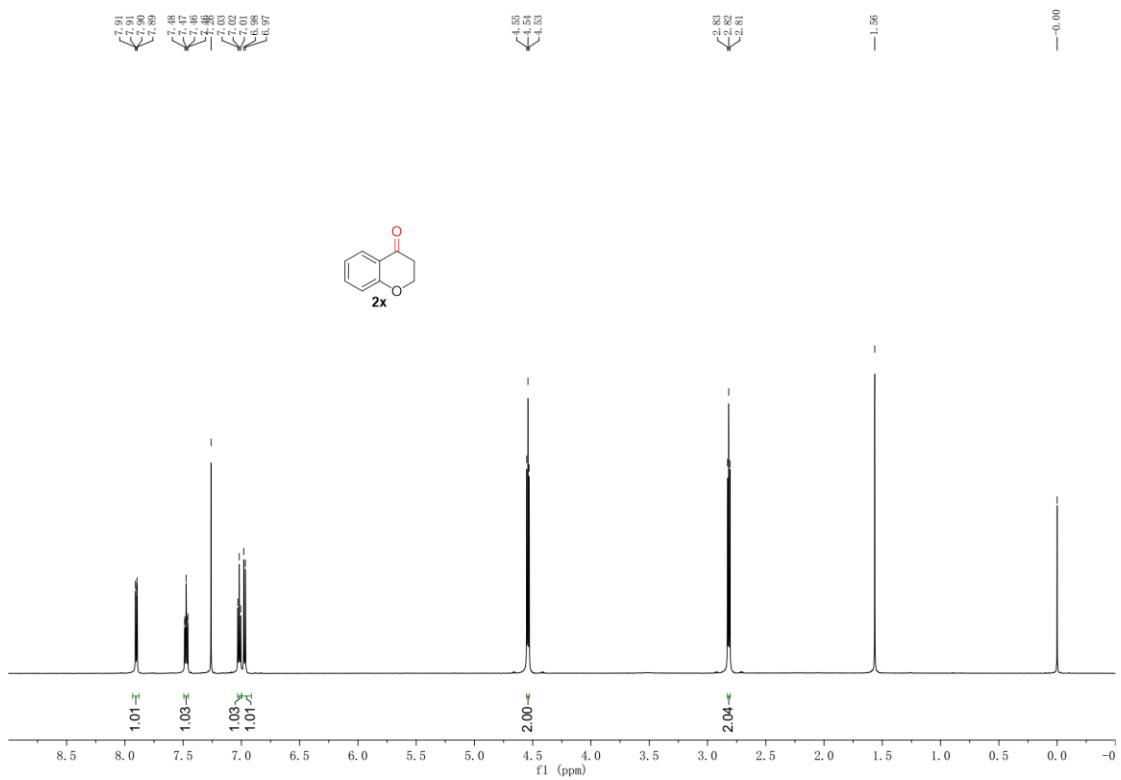
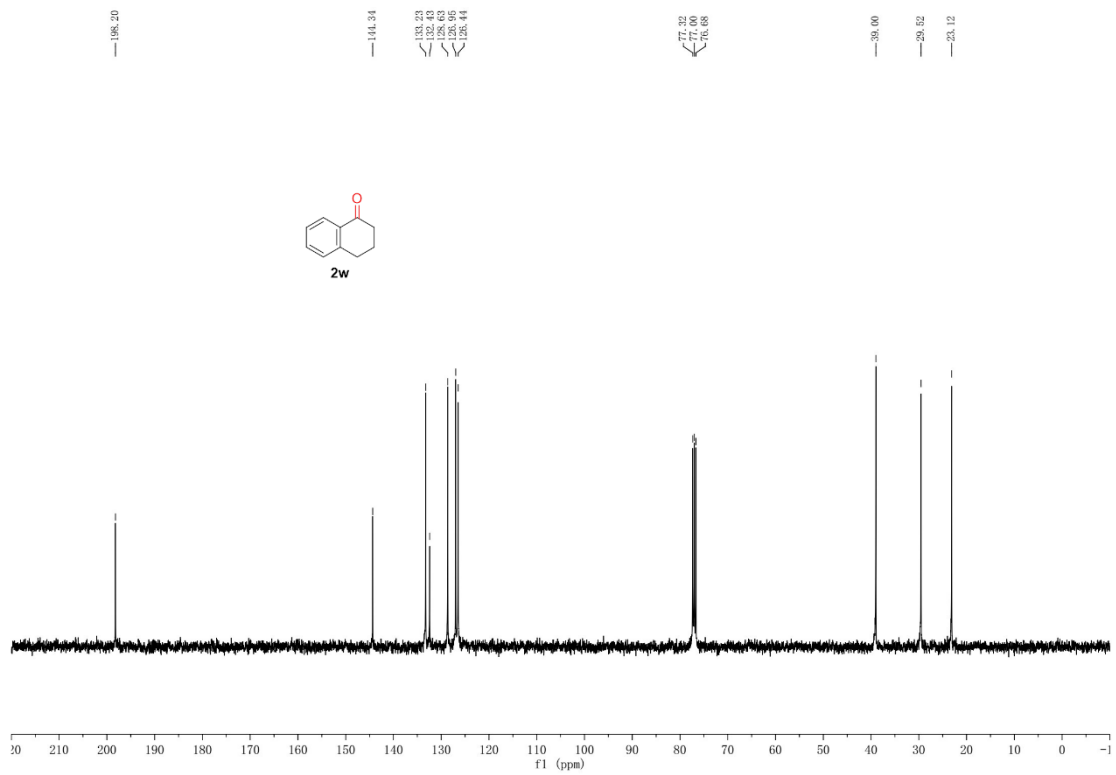


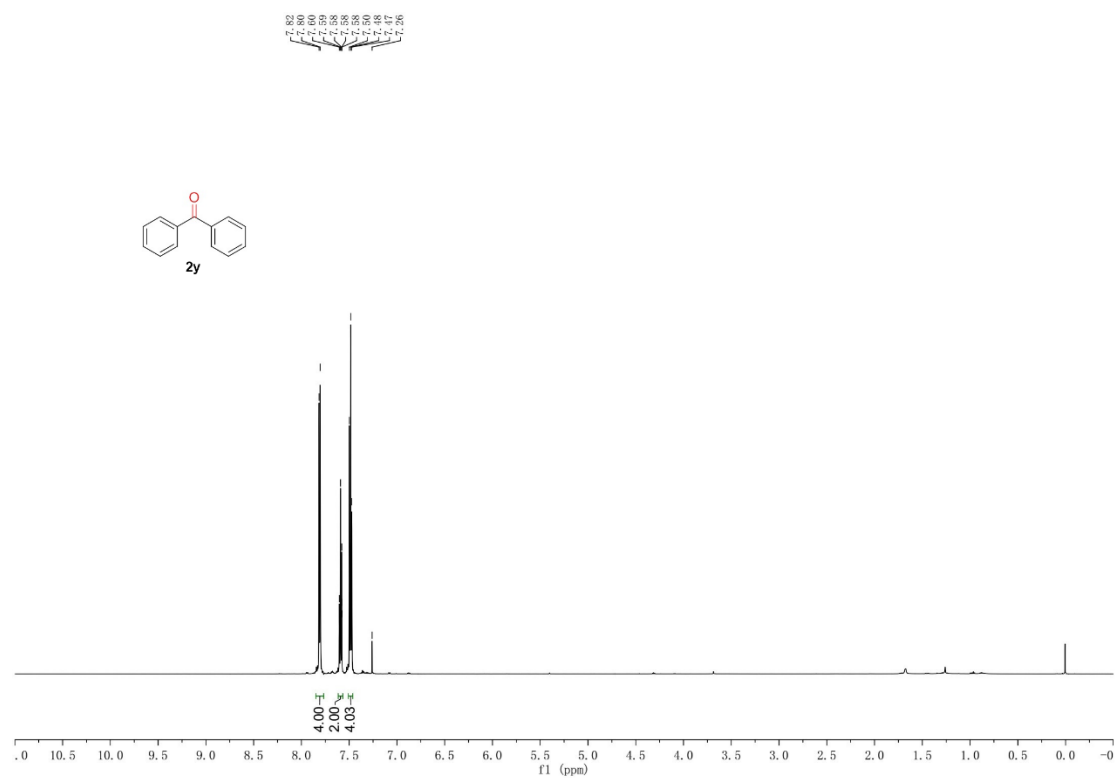
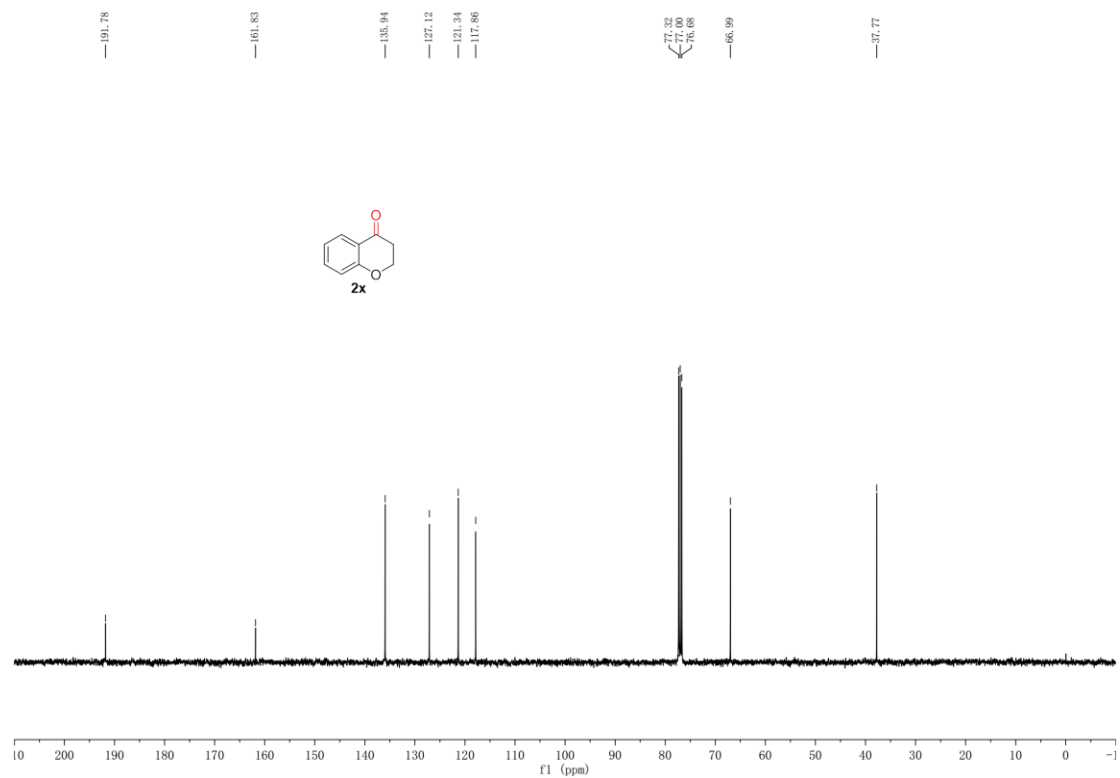


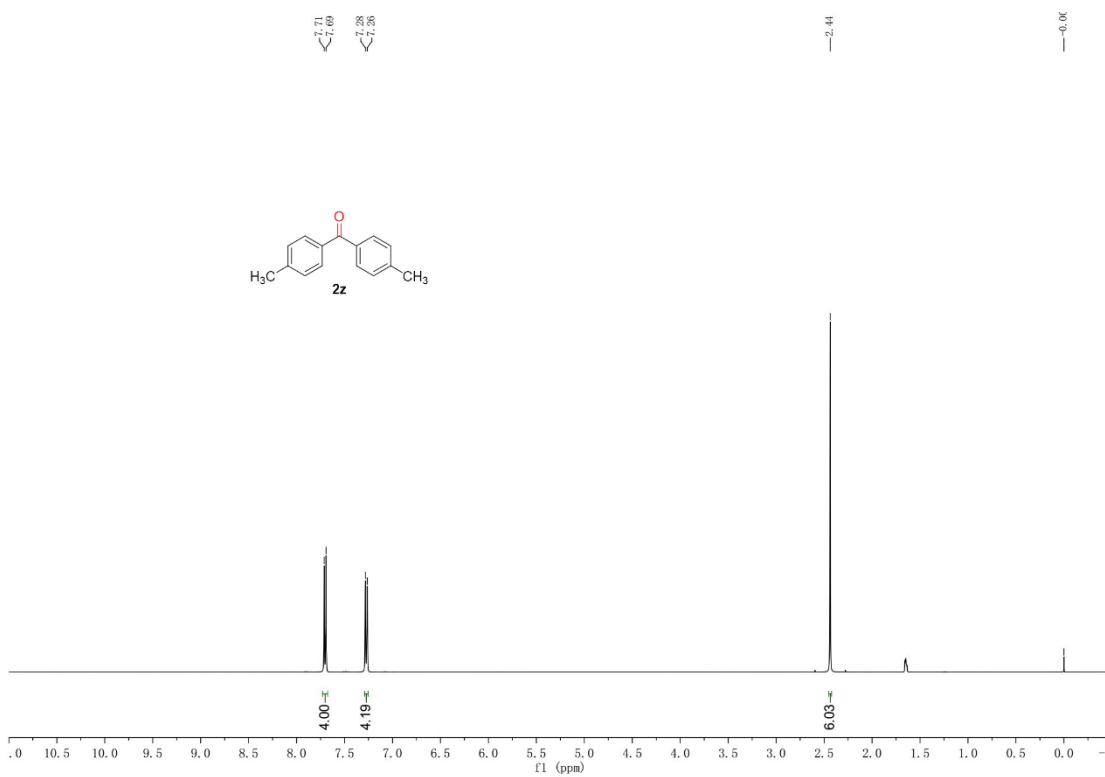
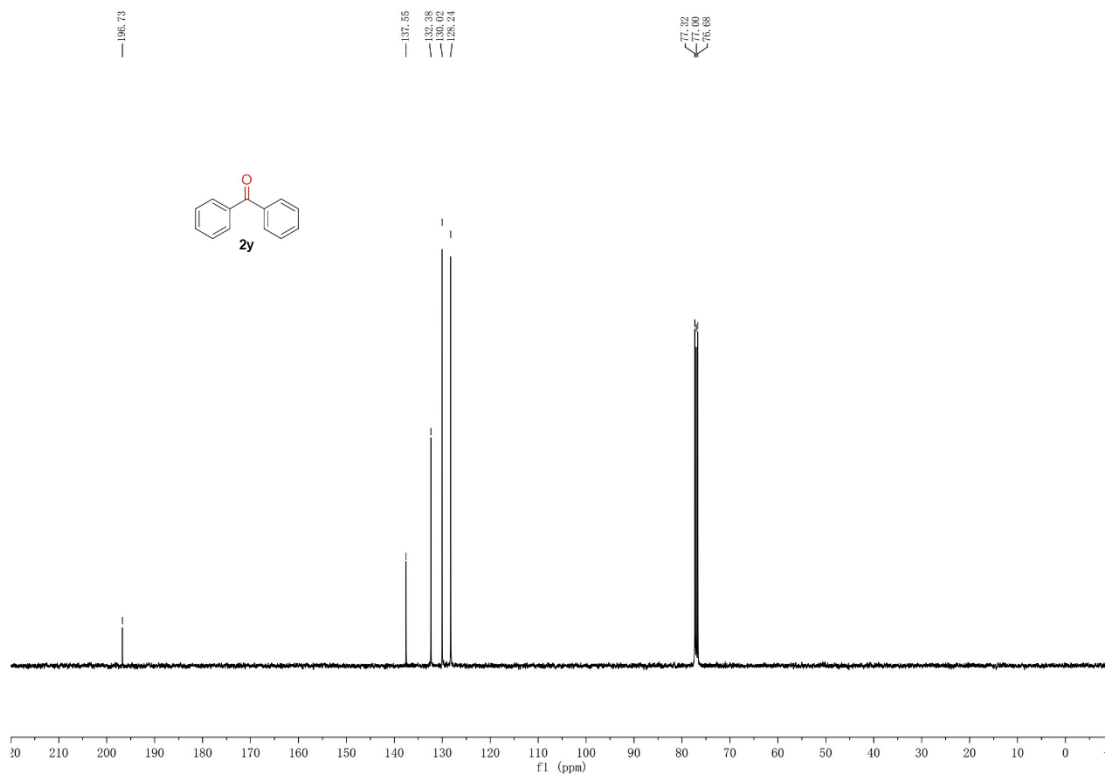


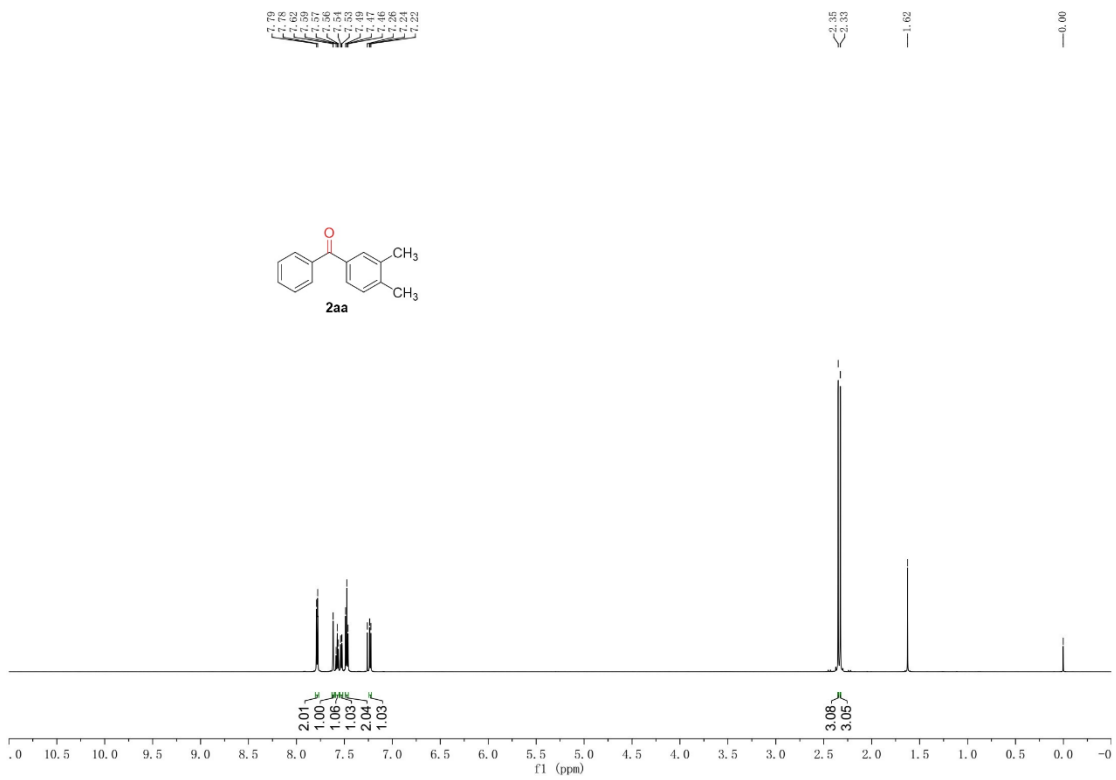
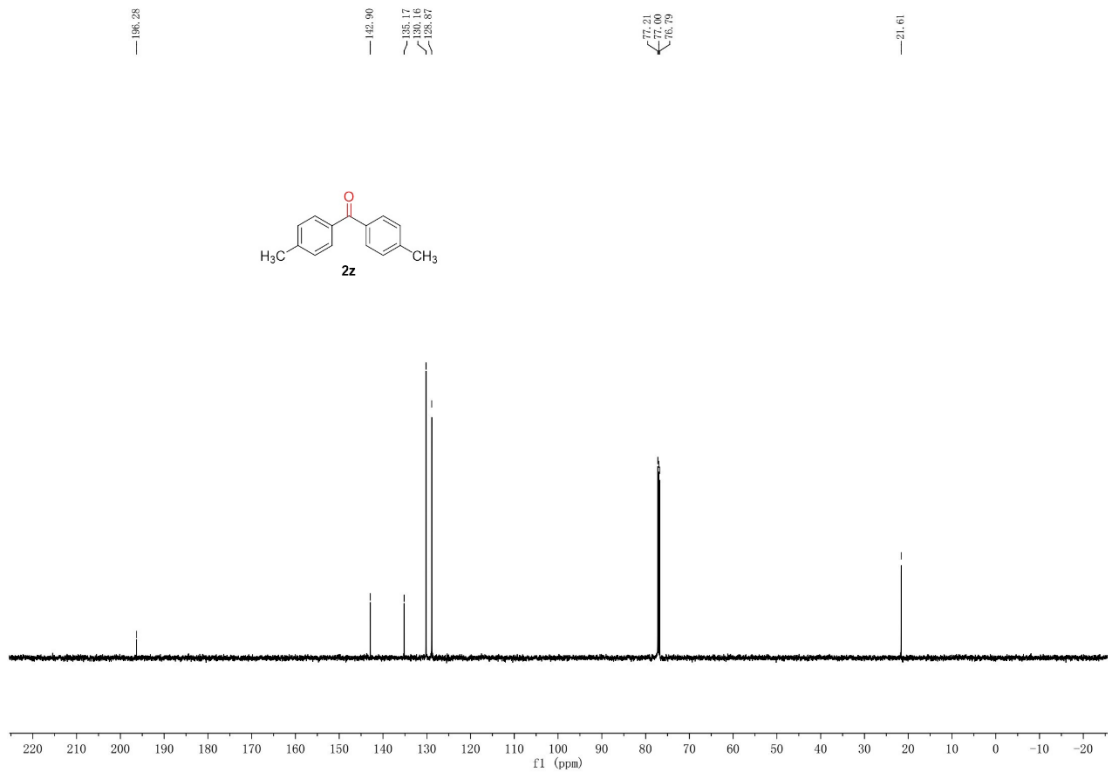


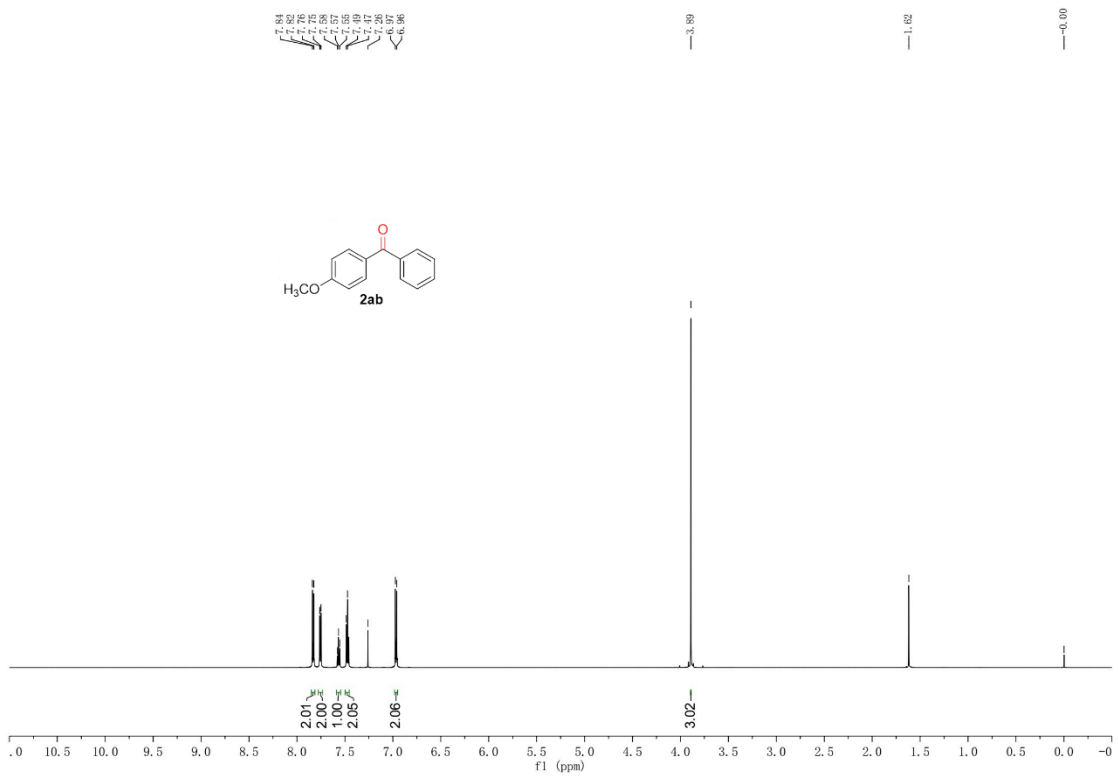
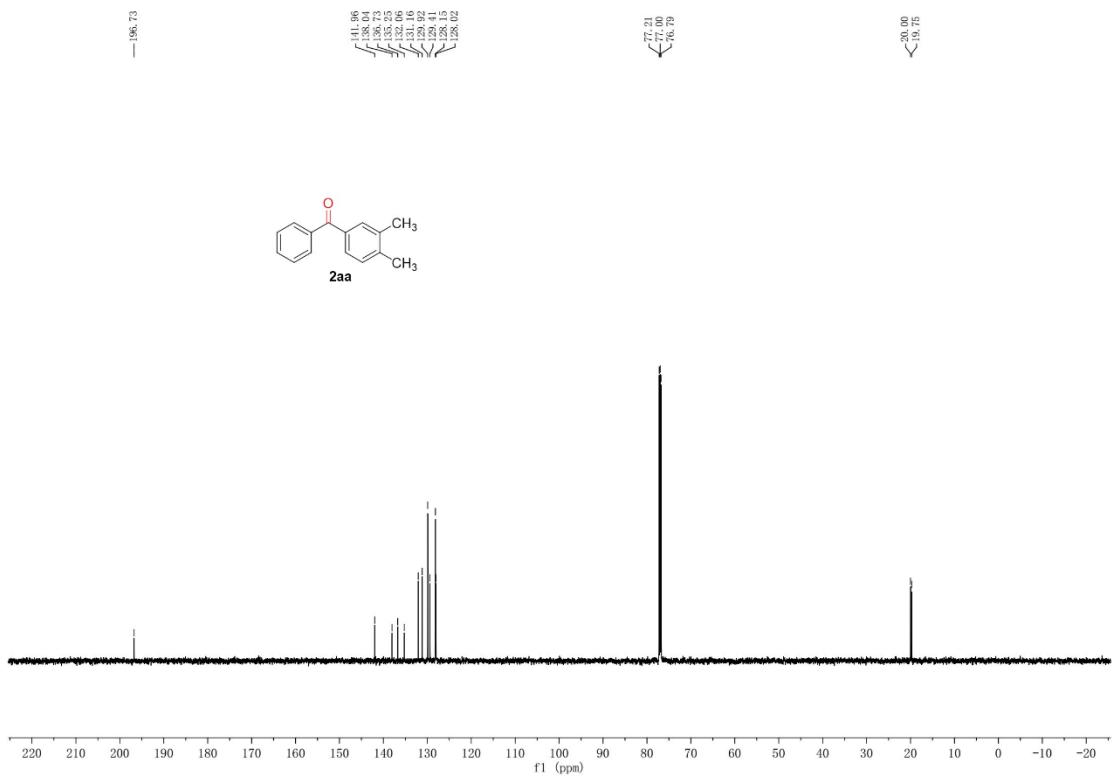


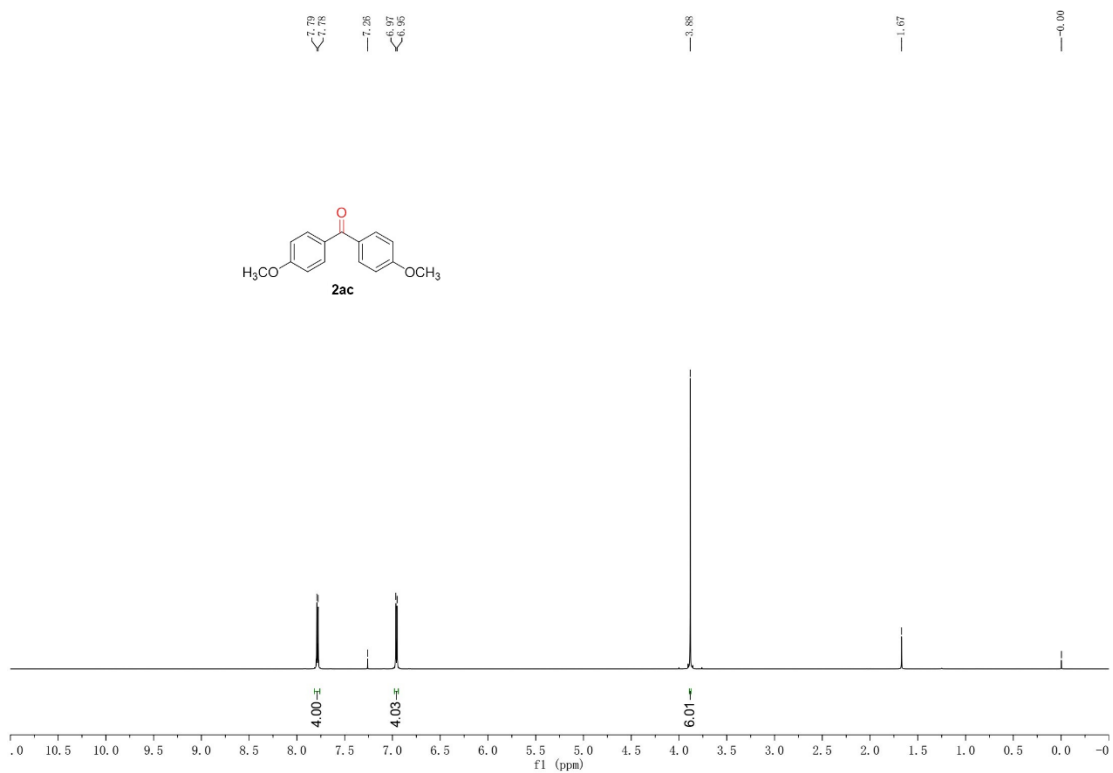
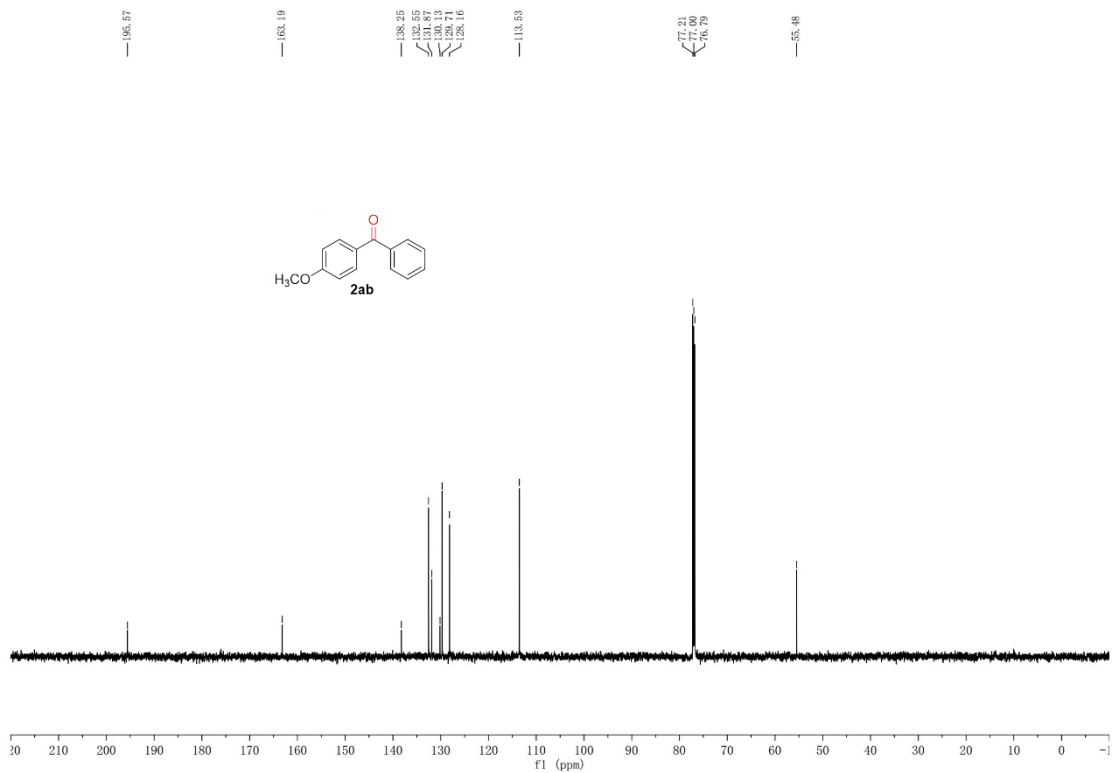


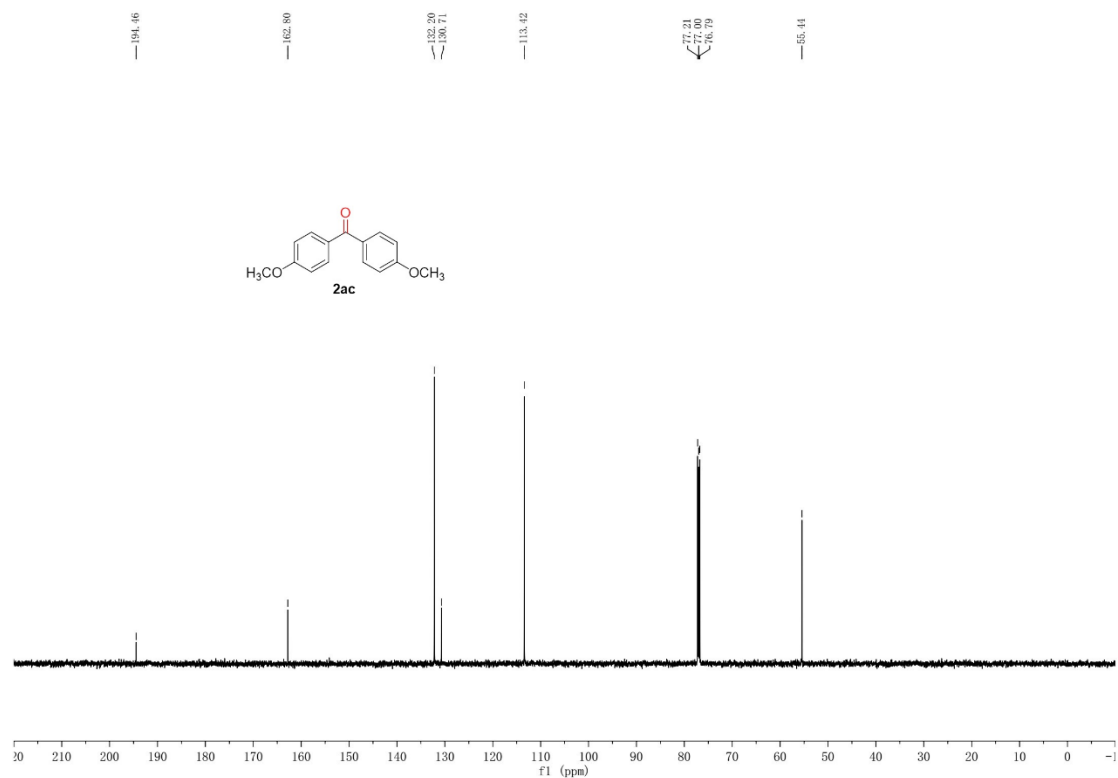












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