Supporting information for:

The Merger of CF_3SO_2Na and Palladium Catalysis to Enable Decarboxylative Cross-Coupling for the Synthesis of Aromatic Ketones under Room Temperature

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Supporting Information

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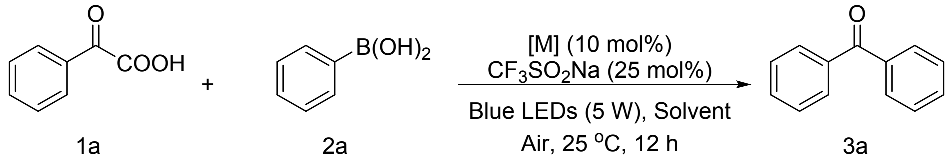
1. General information

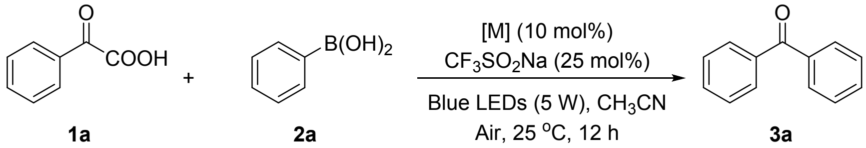
Unless otherwise indicated, all reactions and manipulations were performed under air. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020SL). All starting materials and solvents were purchased from Adamas-beta, Alfa Aesar, Chempur, Merck as well as Sigma Aldrich,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

2. Optimization of the reaction conditions



A mixture of phenylglyoxylic acid (**1a**), phenylboronic acid (**2a**), sodium trifluoromethanesulfonate, transition-metal-catalyst and solvent was added into a quartz tube which was placed in a photochemical reactor. The reaction mixture was stirred at the designed temperature under air. After concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel and eluted with EtOAc/petroleum ether (1/100~10/1) to afford the desired product.

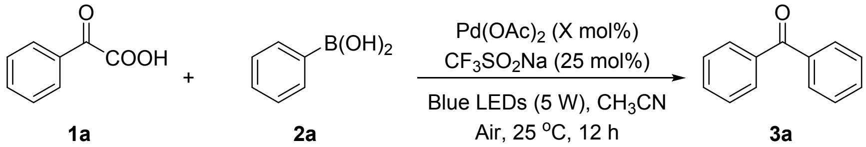
Table 1. Screening of catalysts[a]



Entry	M(10mol%)	Yeild (%)
1	-	0
2	Cu $(OAc)_2$	30
3	$PdCl_2$	35
4	$Pd(acac)_2$	47
5	Pd $(MeCN)_4BF_4$	54
6	Pd $(OAc)_2$	76

[a] **1a** (0. 5 mmol), **2a** (0.25 mmol), [M] (10 mol%), CF_3SO_2Na (25 mol%), CH_3CN (1.0 mL) under air at room temperature (25 ℃), blue LEDs (380-385 nm, 5 W) for 12 h, isolated yield.

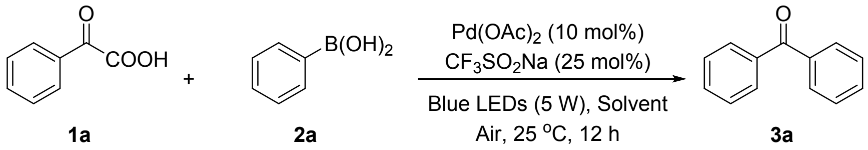
Table 2. screening of the catalyst loading[a]



Entry	Pd $(OAc)_2$(X mol%)	Yield (%)
1	1	40
2	5	65
3	10	76
4	20	80

[a] **1a** (0. 5 mmol), **2a** (0.25 mmol), $Pd(OAc)_2$, CF_3SO_2Na (25 mol%), CH_3CN (1.0 mL) under air at room temperature (25 ℃), blue LEDs (380-385 nm, 5 W) for 12 h, isolated yield.

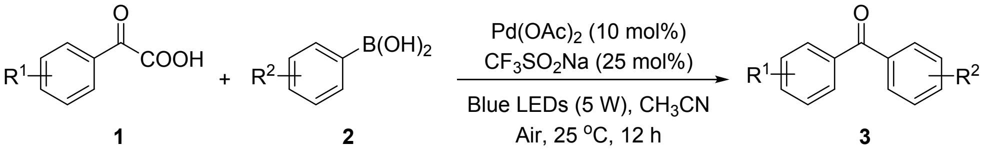
Table 3. Screening of solvents[a]



Entry	Solvent	Yield (%)
1	MeCN	76
2	DMF	45
3	Toluene	50
4	DMSO	40
5	THF	30

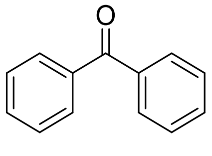
[a] **1a** (0. 5 mmol), **2a** (0.25 mmol), Pd (OAc)$_2$ (10 mol%), CF_3SO_2Na (25 mol%), solvent (1.0 mL) under air at room temperature (25 ℃), blue LEDs (380-385 nm, 5 W) for 12 h, isolated yield.

3. General procedure for decarboxylation coupling reaction



A mixture of **1** (0.4 mmol), **2** (0.2 mmol), Pd (OAc)$_2$ (10 mol%, 4.5 mg), CF_3SO_2Na (25 mol%, 7.8 mg) and CH_3CN (1.0 mL) was added into a quartz tube which was placed in a photochemical reactor (Blue LED, 380-385 nm, 5 W). The reaction mixture was stirred at 25 °C under air for 12 h. After concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel and eluted with EtOAc/petroleum ether (1/100~10/1) to afford the desired product.

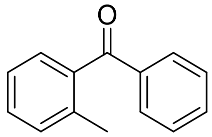
4. Experimental characterization data for products



Benzophenone (3a). The product **3a** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as a white solid.

Known compound, mp 47-48 °C, spectroscopic data matched those previously reported.[1]

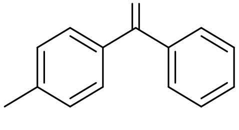
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 - 7.81 (m, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.60, 137.67, 132.36, 130.00, 128.26.



2-Methylbenzophenone (3b). The product **3b** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as colorless liquid.

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

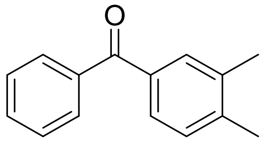
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.45 - 7.39 (m, 2H), 7.37 (t, J = 7.8 Hz, 1H), 7.31 (d, J = 7.3 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.44, 138.71, 137.82, 136.70, 133.10, 131.02, 130.16, 128.48, 125.22, 19.95.



4-Methylbenzophenone (3c). The product **3c** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as a white solid.

Known compound, mp 59-62 °C, spectroscopic data matched those previously reported.[3]

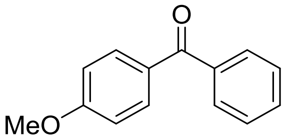
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.81 (m, 2H), 7.77 (d, J = 8.1 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.43, 143.18, 137.97, 134.90, 132.10, 130.26, 129.88, 128.94, 128.17, 21.60.



3,4-Dimethylbenzophenone (3d). The product **3d** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as a white solid.

Known compound, mp 46-49 °C, spectroscopic data matched those previously reported.[4]

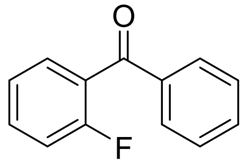
1H NMR (400 MHz, CDCl3) δ 7.83 (dd, J = 8.1, 0.9 Hz, 2H), 7.66 (s, 1H), 7.64 - 7.56 (m, 2H), 7.51 (t, J = 7.6 Hz, 2H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.62, 141.90, 138.13, 136.71, 135.35, 132.03, 131.17, 129.90, 129.43, 128.08, 19.95, 19.71.



4-Methoxybenzophenone (3e). The product **3e** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/10, v/v) as a yellow solid.

Known compound, mp 59-61 °C, spectroscopic data matched those previously reported.[1]

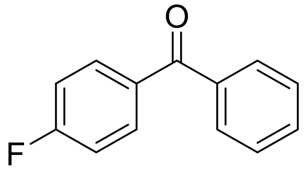
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 7.6 Hz, 2H), 7.80 (d, J = 7.0 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.45, 163.24, 138.34, 132.50, 131.82, 130.22, 129.67, 128.15, 113.56, 55.45.



2-Fluorobenzophenone (3f). The product **3f** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as colorless oil.

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

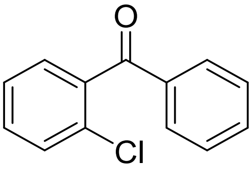
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 6.7 Hz, 2H), 7.50 (dd, J = 28.9, 7.2 Hz, 5H), 7.29 - 7.18 (m, 1H), 7.14 (d, J = 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.26, 160.06 (d, J = 252 Hz), 158.80, 137.41, 133.39, 133.05, 130.66, 129.74, 128.47, 127.06, 124.29, 116.32, 116.11.



4-Fluoroacetophenone (3g). The product **3g** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as yellow oil.

Known compound, spectroscopic data matched those previously reported.[6]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 - 7.87 (m, 2H), 7.82 (d, J = 7.4 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 8.6 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 195.12, 165.38 (d, J = 254 Hz), 137.56, 133.86, 132.84 ,132.18, 129.81, 128.31, 115.51, 115.29.

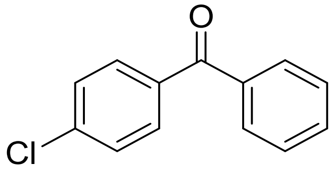


2-Chlorobenzophenone (3h). The product **3h** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as a white solid.

Known compound, mp 51-54 °C, spectroscopic data matched those previously reported.[7]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89-7.85 (m, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.54 - 7.47 (m, 4H), 7.42 (d, J = 2.7 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$)

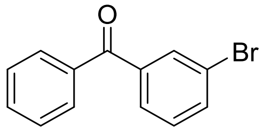
δ 195.18, 138.68, 136.55, 133.63, 131.33, 131.08, 130.04, 129.11, 128.59, 126.65.



4-Chlorobenzophenone (3i). The product **3i** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as a yellow solid.

Known compound, mp 75-78 °C, spectroscopic data matched those previously reported. [1]

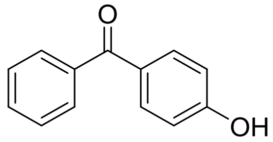
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (t, *J* = 7.5 Hz, 4H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (m, 4H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 195.35, 138.86, 137.31, 135.94, 132.56, 131.39, 129.78, 128.60, 128.36.



3-Bromobenzophenone (3j). The product **3j** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as a white solid.

Known compound, mp 74-77 °C, spectroscopic data matched those previously reported. [1]

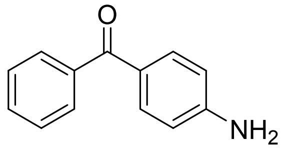
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (s, 1H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.76 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.41 (t, J = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.08, 139.53, 136.96, 135.25, 132.80, 129.94, 128.50, 122.59.



4-Hydroxybenzophenone (3k). The product **3k** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/10, v/v) as a white solid.

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

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, J = 8.1 Hz, 4H), 7.62 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.34 (s, 1H), 6.99 (d, J = 8.2 Hz, 2H);^{13}C NMR (101 MHz, $CDCl_3$) δ 196.84, 160.79, 138.06, 133.11, 132.19, 129.84, 129.60, 128.27, 115.40.

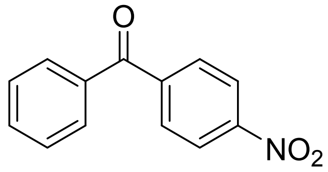


4-Aminobenzophenone (3l). The product **3l** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15-1/3, v/v) as a yellow solid.

Known compound, mp 121-123 °C, spectroscopic data matched those previously reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 - 7.73 (m, 4H), 7.57 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.4 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 4.23 (s, 2H); ^{13}C NMR

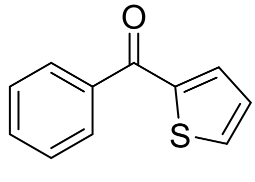
(101 MHz, $CDCl_3$) δ 195.29, 151.02, 138.93, 132.91, 131.37, 129.49, 128.06, 127.40, 113.62.



4-Nitrobenzophenone (3m). The product **3m** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/10-1/1, v/v) as a yellow solid.

Known compound, mp 135-137 °C, spectroscopic data matched those previously reported.[1]

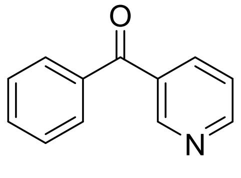
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 7.9 Hz, 2H), 7.99 (d, J = 7.9 Hz, 2H), 7.86 (d, J = 7.1 Hz, 2H), 7.70 (d, J = 6.8 Hz, 1H), 7.58 (t, J = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.72, 149.86, 142.90, 136.32, 133.42, 130.65, 130.06, 128.66, 123.51.



2-benzoylthiophene (3n). The product **3n** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/10, v/v) as yellow oil.

Known compound, spectroscopic data matched those previously reported.[1]

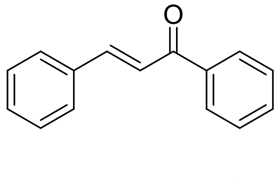
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.74 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.68 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.61 (dd, *J* = 7.4, 3.6 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.19 (dd, *J* = 4.9, 3.8 Hz, 1H);^{13}C NMR (101 MHz, CDCl$_3$) δ 188.14, 143.63, 138.18, 134.89, 134.18, 132.26, 129.14, 128.41, 127.98.



3-benzoyl pyridine (3o). The product **3d** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15-1/10, v/v) as yellow oil.

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

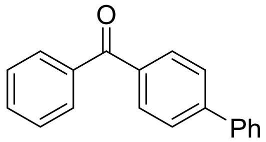
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.74 (d, *J* = 4.7 Hz, 1H), 8.13 - 8.09 (m, 2H), 8.06 (d, *J* = 7.8 Hz, 1H), 7.90 (td, *J* = 7.7, 1.7 Hz, 1H), 7.60 (dd, *J* = 10.6, 4.2 Hz, 1H), 7.51 (t, *J* = 6.2 Hz, 2H), 7.48 (dd, *J* = 6.1, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 193.77, 155.13, 148.52, 137.00, 136.31, 132.86, 130.96, 128.12, 126.11, 124.54.



(E)-chalcone (3r). The product **3r** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as a yellow solid.

Known compound, mp 55-59 °C, spectroscopic data matched those previously reported [12].

^{1}HNMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.86 Hz, 2H), 7.81 (d, *J* = 11.72 Hz, 1H), 7.65-7.63 (m, 2H), 7.58 (t, *J* = 7.35 Hz, 1H), 7.54-7.49 (m, 3H), 7.42-7.41 (m, 3H); ^{13}CNMR (151 MHz, $CDCl_3$) δ 190.5, 144.8, 138.2, 134.9, 132.8, 130.5, 128.9, 128.6, 128.5, 128.4, 122.1.



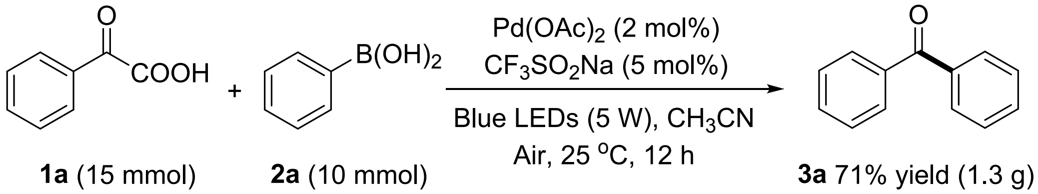
4-Benzoylbiphenyl (3s). The product **3s** was obtained via the *general procedure* and isolated by flash column chromatography (sila gel, ethyl acetate / petroleum ether = 1/15, v/v) as a white solid.

Known compound, mp 101-103 °C, spectroscopic data matched those previously reported.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.95 - 7.89 (m, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 7.3 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.57 (dd, *J* = 15.2, 7.8 Hz, 4H), 7.48 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.27, 145.23, 139.99, 137.82, 136.29, 132.35, 130.72, 129.99, 128.98, 128.25, 127.30, 126.97.

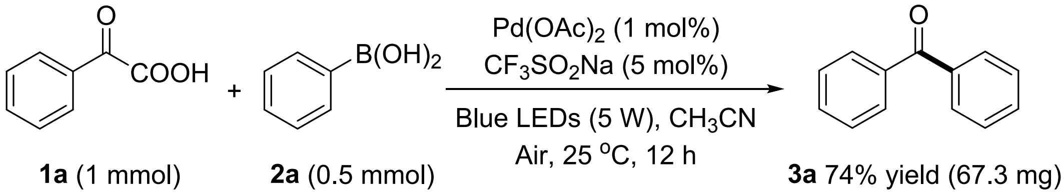
5. The reaction practicability emanations

5.1 Gram-scale reaction



A mixture of **1a** (15 mmol, 2.25 g), **2a** (10 mmol, 1.22 g), Pd $(OAc)_2$ (2 mol%, 44.9 mg), CF_3SO_2Na (5 mol%, 78 mg) and CH_3CN (10 mL) was added into a quartz tube which was placed in a photochemical reactor (Blue LED, 380-385 nm, 5 W). The reaction mixture was stirred at 25 °C under air for 12 h. After concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel and eluted with EtOAc/petroleum ether (1/15) to afford the benzophenone in 71% yield (1.3 g).

5.2 Reaction at low catalyst loading

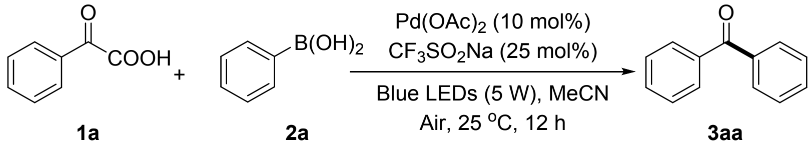


A mixture of **1a** (1.0 mmol, 150 mg), **2a** (0.5 mmol, 61 mg), Pd $(OAc)_2$ (1 mol%, 1.1 mg), CF_3SO_2Na (5 mol%, 3.9 mg) and CH_3CN (1 mL) was added into a quartz tube which was placed in a photochemical reactor (Blue LED, 380-385 nm, 5 W). The reaction mixture was stirred at 25 °C under air for 12 h. After concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel and eluted with EtOAc/petroleum ether (1/15) to afford the benzophenone in 74% yield (67.3 mg).

6. Mechanistic studies

6.1 Control experiments

To explore the reaction mechanism for our decarboxylative cross-coupling process, some control experiments were first carried out.



Entry	Variation from "standard conditions"	Yield (%)
1	No light irradiation	< 5
2	No $Pd(OAc)_2$	< 5
3	No CF_3SO_2Na	< 5
4	N_2 atmosphere	< 5
5	CFL (10 W) instead of blue LED	8

Reaction condition: [a] **1a** (0. 4 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol%), CF_3SO_2Na (25 mol%), CH_3CN (1.0 mL) under air at room temperature (25 ℃), Blue LEDs (380-385 nm, 5 W) for 12 h, isolated yield.

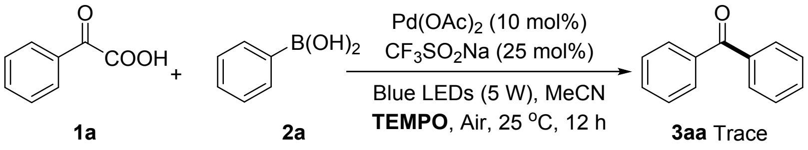
The results demonstrated that the importance of blue light irradiation, Pd catalyst, CF_3SO_2Na and air (O_2) and none of them can be excluded. The absence of any one lead to the obviously inhibition of this process.

6.2 Radical scavenger effect studies

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

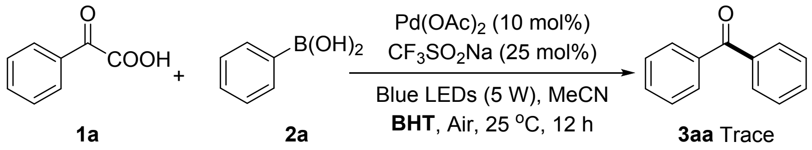
a) Reaction in the presence of TEMPO

A mixture of **1a** (0.4 mmol, 60.0 mg), **2a** (0.2 mmol, 24.4 mg), Pd $(OAc)_2$ (10 mol%, 4.5 mg), CF_3SO_2Na (25 mol%, 7.8 mg), TEMPO (0.2 mmol, 31.2 mg) and CH_3CN (1.0 mL) was added into a quartz tube which was placed in a photochemical reactor (Blue LED, 380-385 nm, 5 W). The reaction mixture was stirred at 25 ^{o}C under air. After 12 h, only trace amount of product was observed.



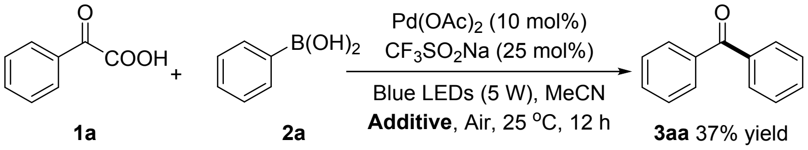
b) Reaction in the presence of BHT

A mixture of **1a** (0.4 mmol, 60.0 mg), **2a** (0.2 mmol, 24.4 mg), Pd $(OAc)_2$ (10 mol%, 4.5 mg), CF_3SO_2Na (25 mol%, 7.8 mg), BHT (0.2 mmol, 44.0 mg) and CH_3CN (1.0 mL) was added into a quartz tube which was placed in a photochemical reactor (Blue LED, 380-385 nm, 5 W). The reaction mixture was stirred at 25 ^{o}C under air. After 12 h, only trace amount of product was observed.



6.3 Quenching experiments

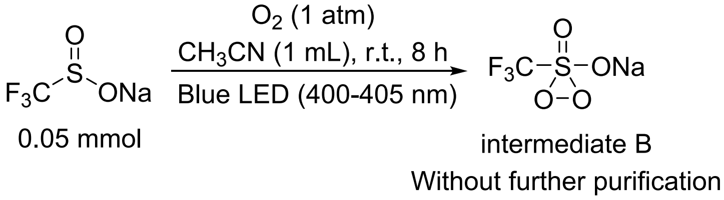
Finally, singlet oxygen quenchers, sodium azide and DABCO was added to the standard reaction respectively, and the yield decreased obviously, which demonstrated the singlet oxygen species was involved in the reaction.



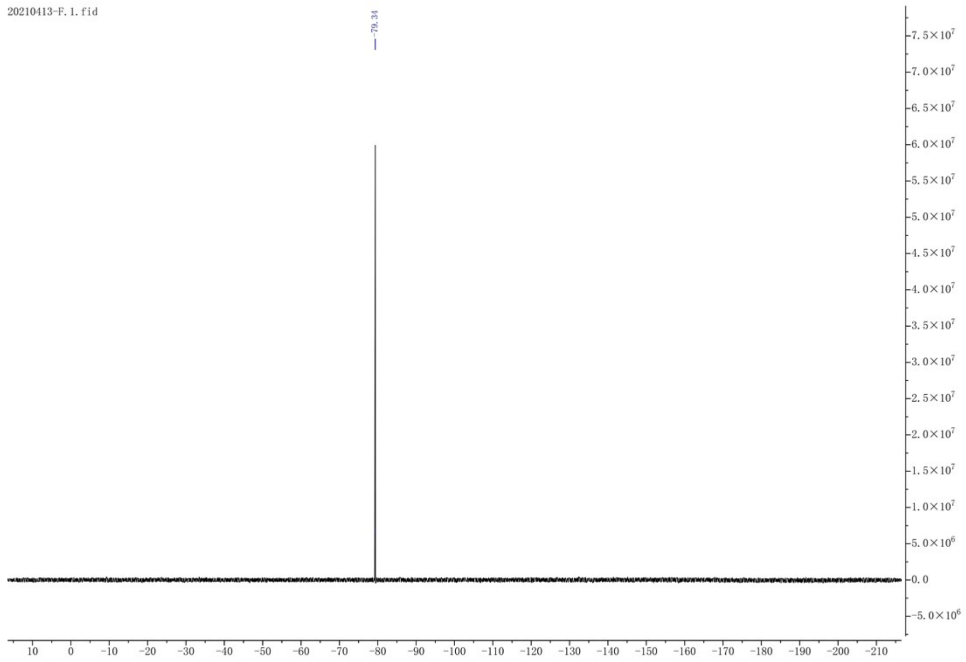
Additive	**Yield**	**Conclusions**
DABCO (2.0 equiv)	29%	Singlet oxygen
Sodium azide (2.0 equiv)	37%	Singlet oxygen

6.4 The reaction intermidiate experiments

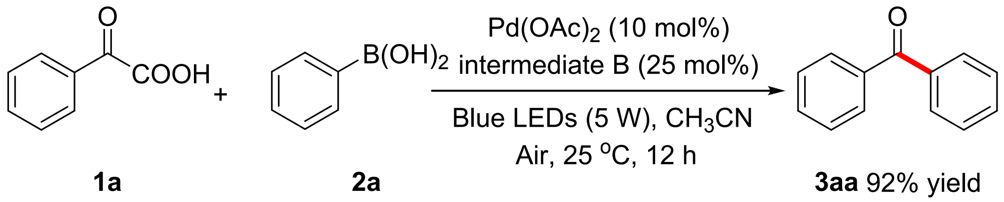
The preparation of intermediate **B**



CF_3SO_2Na (0.05 mmol) and CH_3CN (1.0 mL) were added to an oven-dried reaction tube. Under the illumination of 5 W blue LED (380-385 nm), the reaction mixture was stirring for 8 h under O_2 atmosphere. After the reaction completed, the resulting solution was detected by liquid ^{19}F NMR spectrometer. The result demonstrated that the CF_3SO_2Na had completely converted into intermediate **B**.



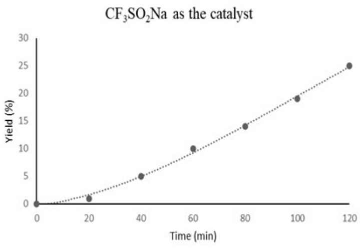
The coupling reaction with intermediate **B** *as the catalyst*

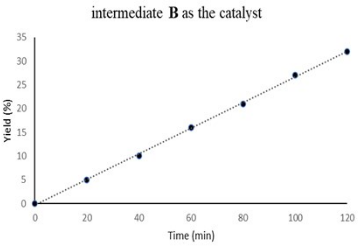


Phenylglyoxylic acid (**1a**, 0.4 mmol), phenylboronic acid (**2a**, 0.2 mmol) and $Pd(OAc)_2$ (10 ml%) were added to the resulting solution generated above. Under the illumination of 5 W blue LED (380-385 nm), the reaction mixture was stirring for additional 12 h under air. Finally, the benzophenone was obtained as the product in 92% yield. This result revealed that the intermediate **B** should be one active catalytic species in this process.

Kinetic experiments

Two model reactions were carried out in parallel, with CF_3SO_2Na and the intermediate B as the catalyst separately. At the first 2 h, the yield was determined every 20 minutes by GC analysis.





when CF_3SO_2Na was used as the catalyst, an obvious induction period was observed. However, the induction period almost completely disappeared if intermediate **B** was instead of CF_3SO_2Na. This demonstrated the three-membered ring intermediate would initiate this oxidation process.

7. References

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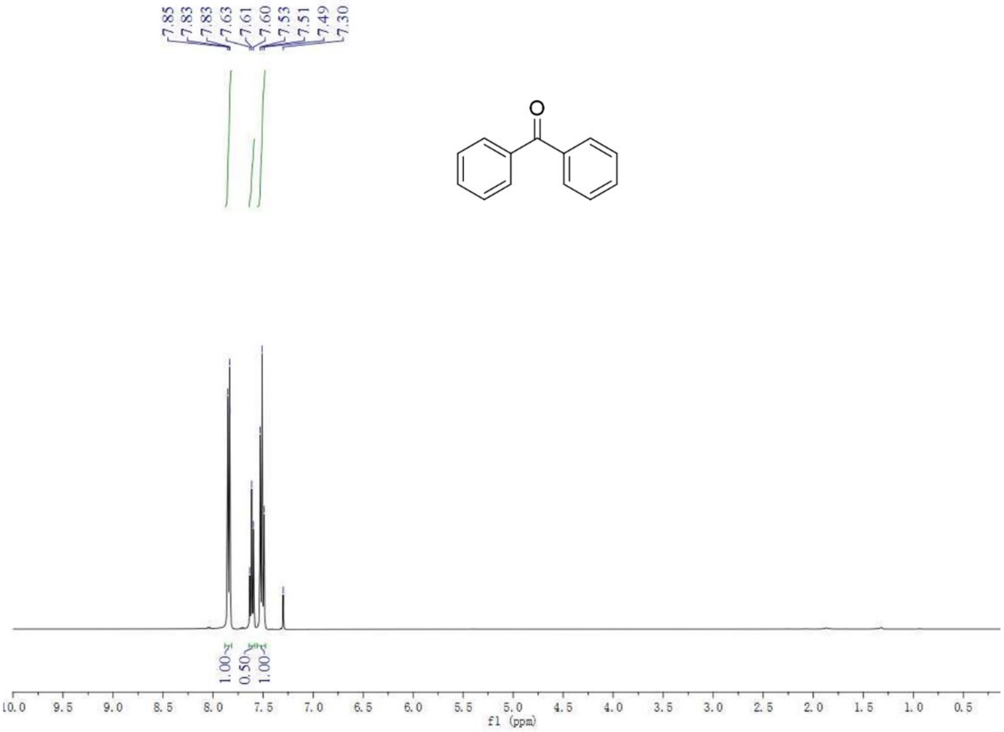
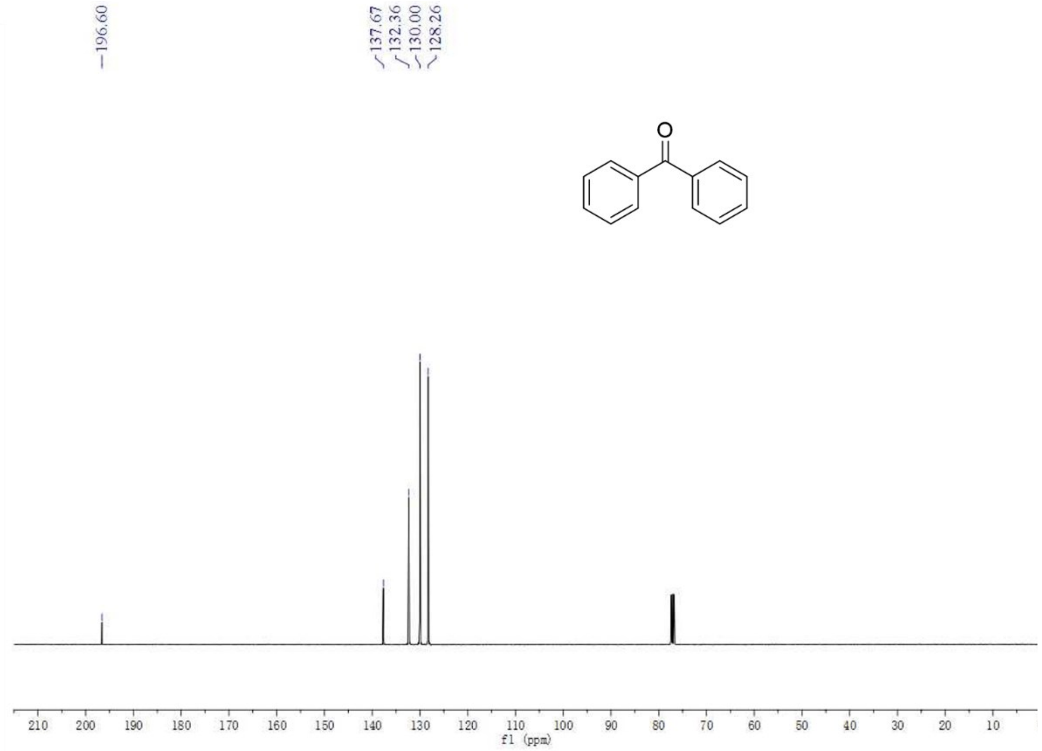
8. NMR spectra

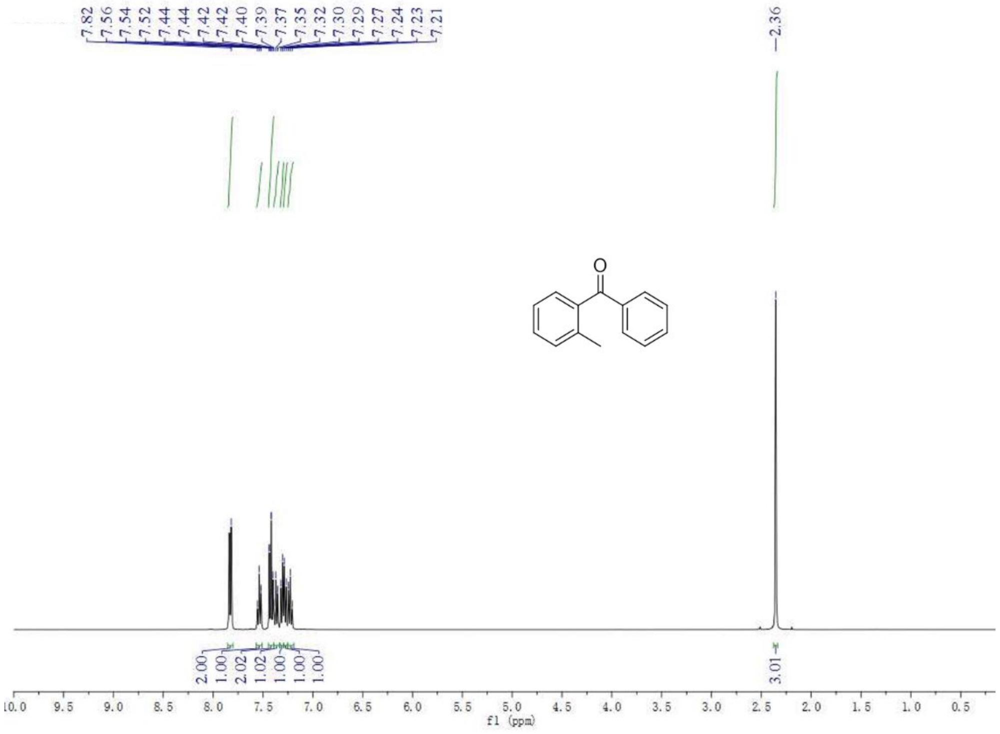
^{1}H NMR spectrum of **3a** in $CDCl_3$ at 400 MHz



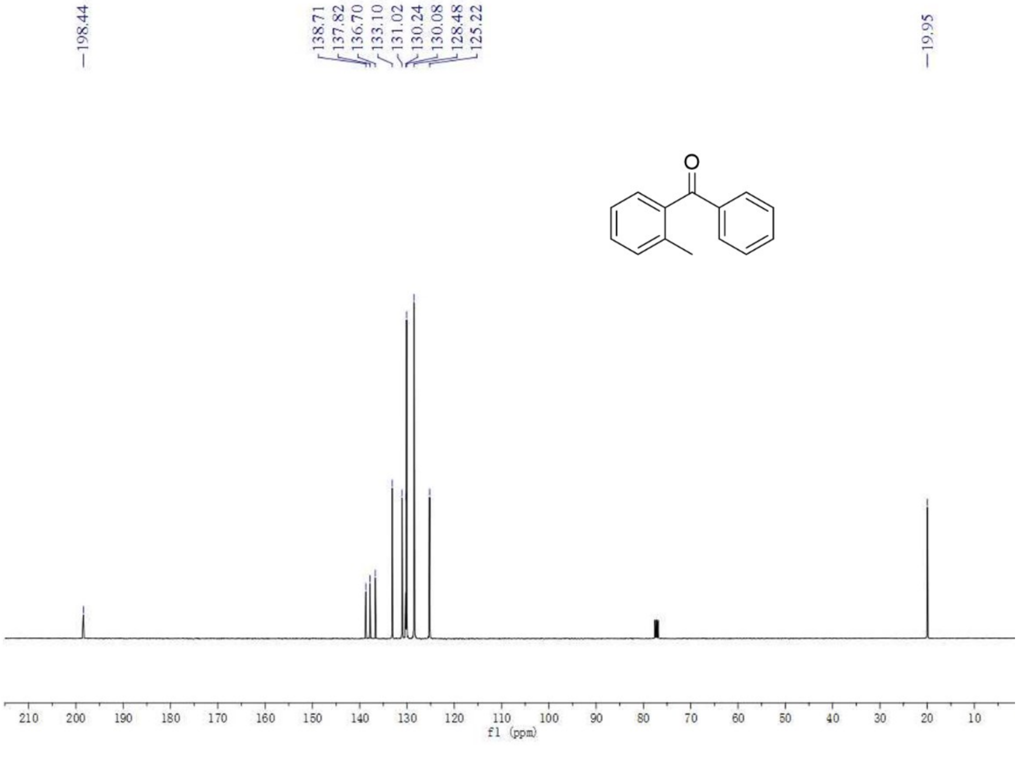
^{13}C NMR spectrum of **3a** in $CDCl_3$ at 101 MHz



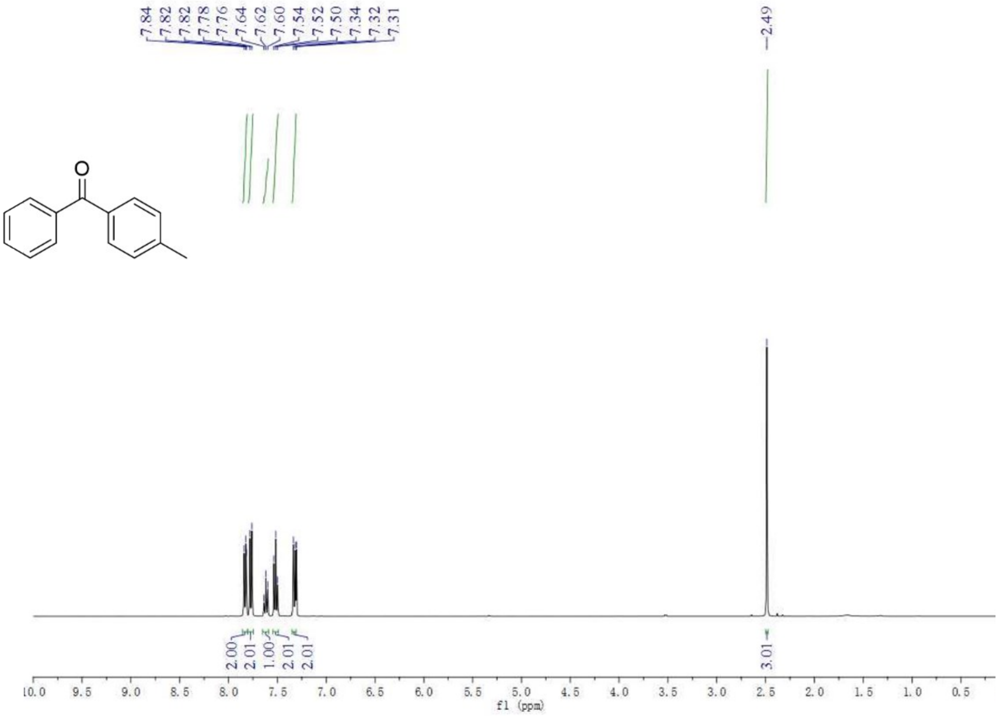
^{1}H NMR spectrum of **3b** in $CDCl_3$ at 400 MHz



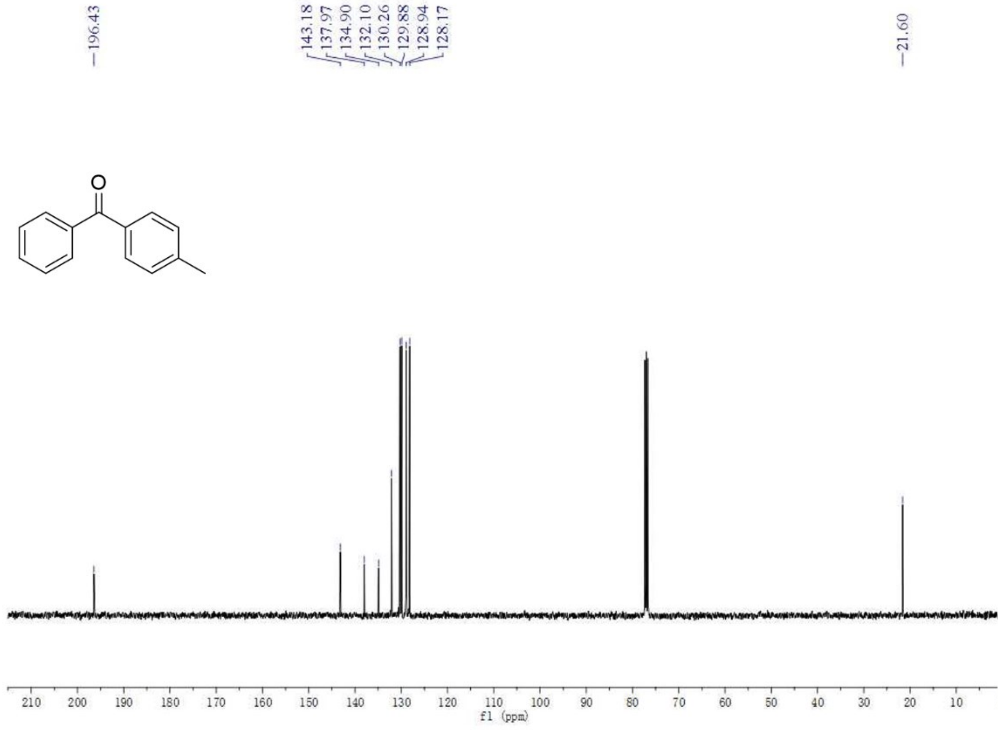
^{13}C NMR spectrum of **3b** in $CDCl_3$ at 101 MHz



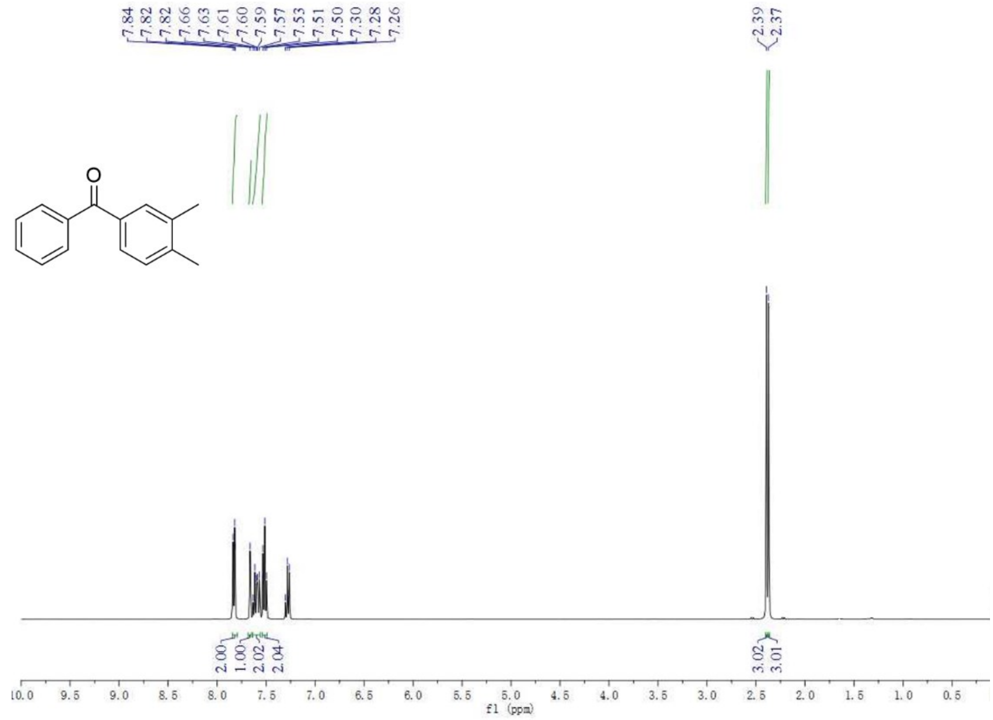
^{1}H NMR spectrum of **3c** in $CDCl_3$ at 400 MHz



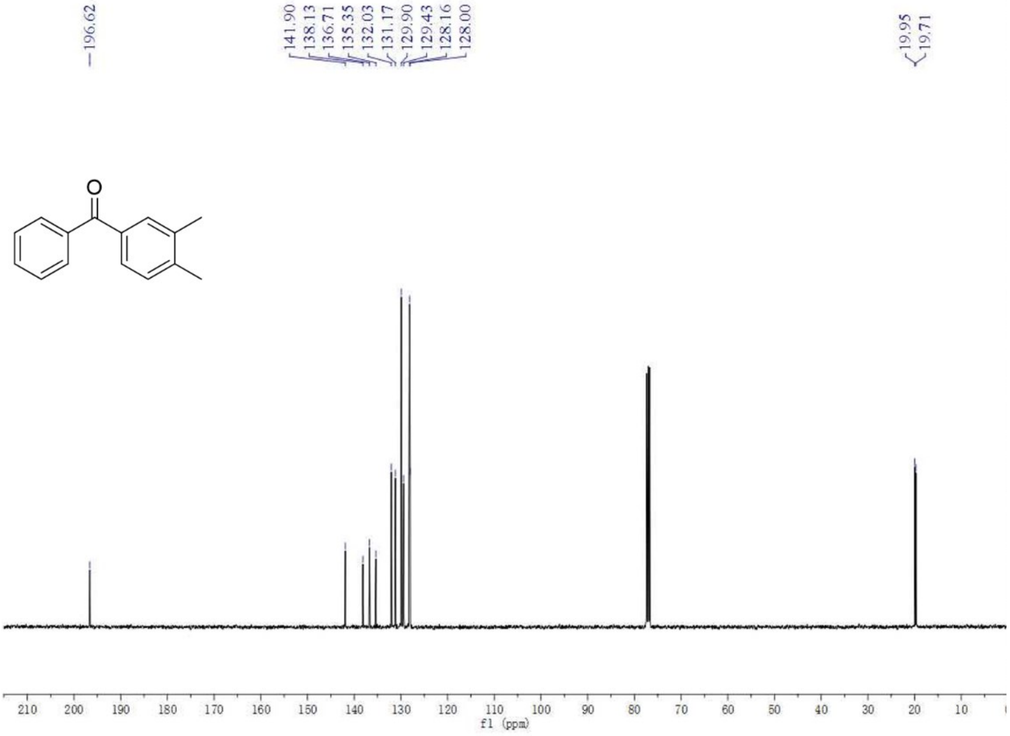
^{13}C NMR spectrum of **3c** in $CDCl_3$ at 101 MHz



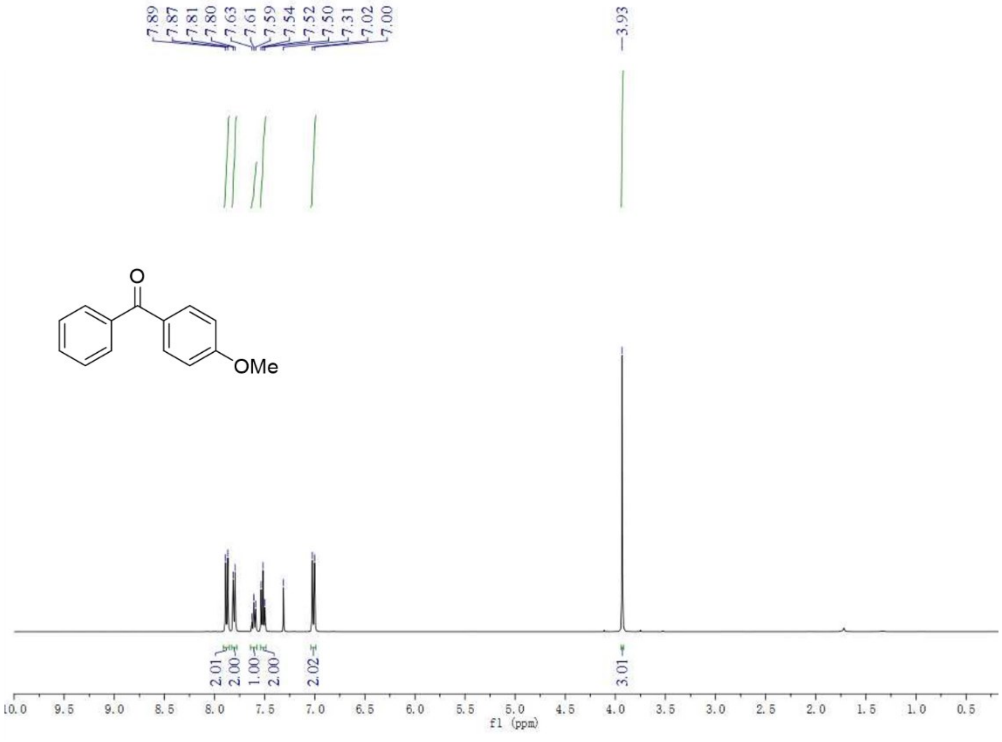
^{1}H NMR spectrum of **3d** in $CDCl_3$ at 400 MHz



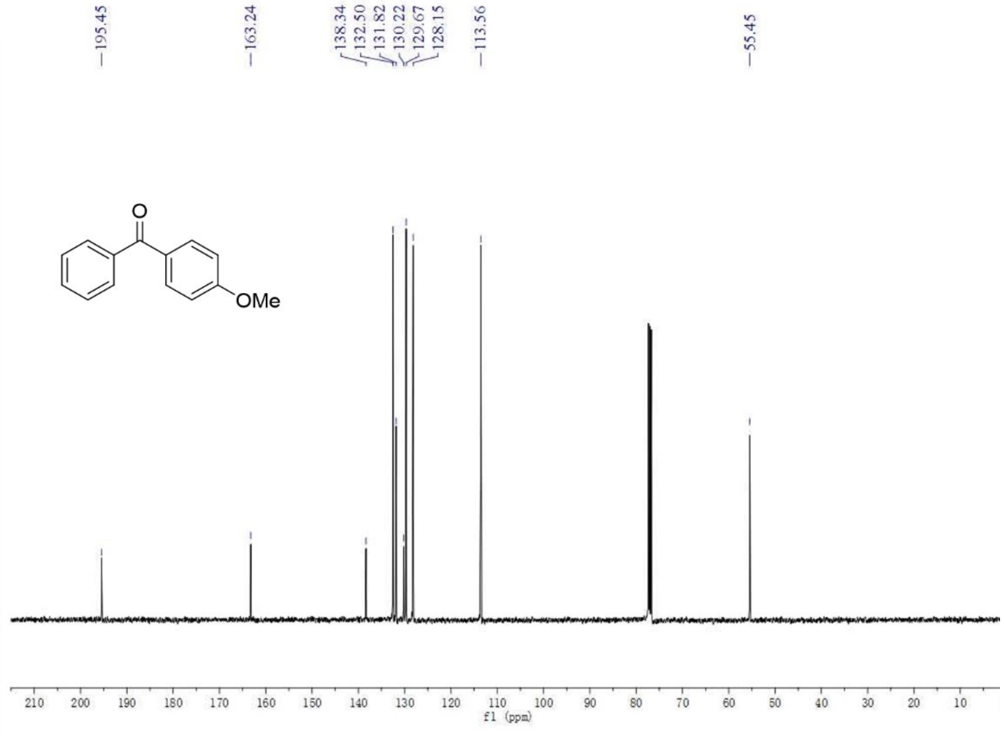
^{13}C NMR spectrum of **3d** in $CDCl_3$ at 101 MHz



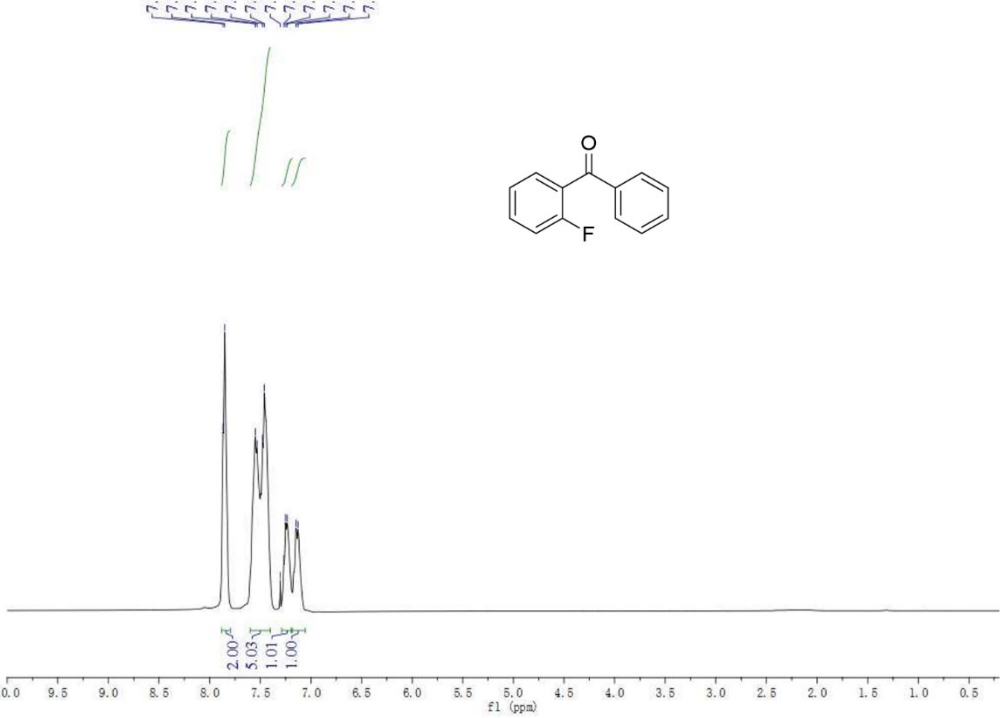
^{1}H NMR spectrum of **3e** in $CDCl_3$ at 400 MHz



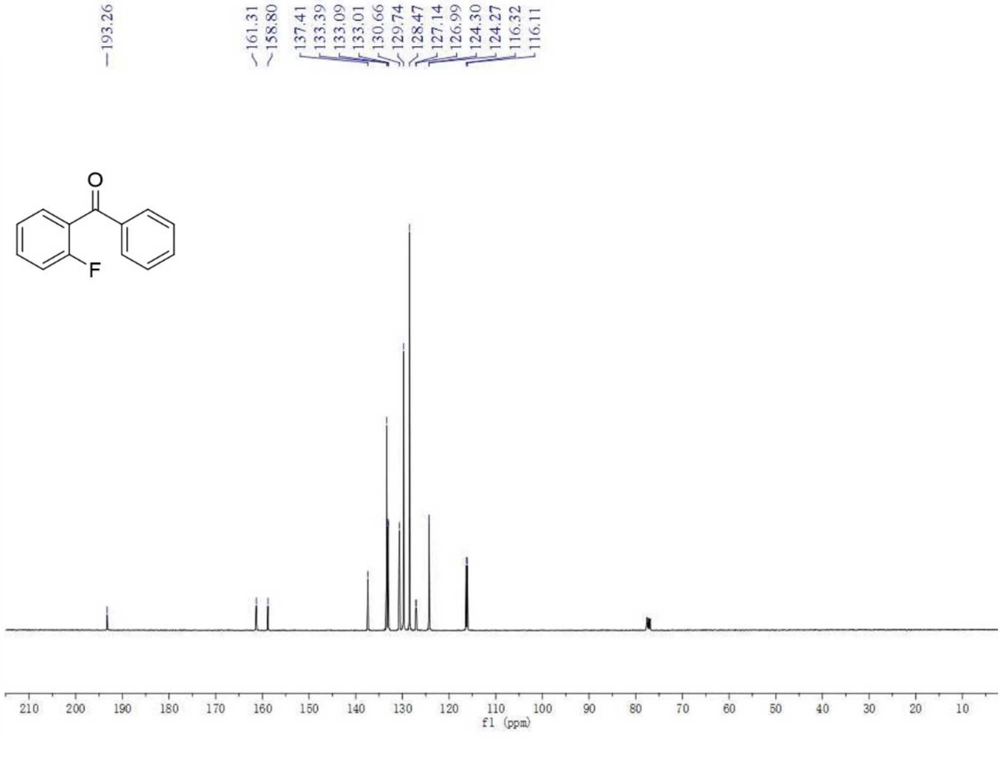
^{13}C NMR spectrum of **3e** in $CDCl_3$ at 101 MHz



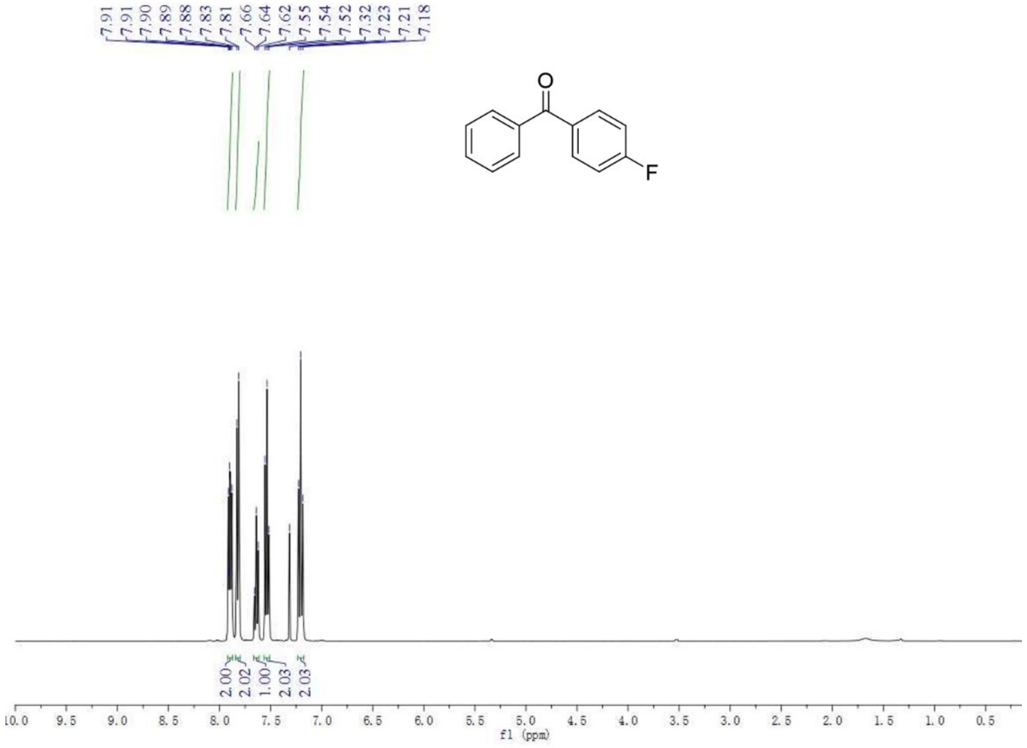
^{1}H NMR spectrum of **3f** in $CDCl_3$ at 400 MHz



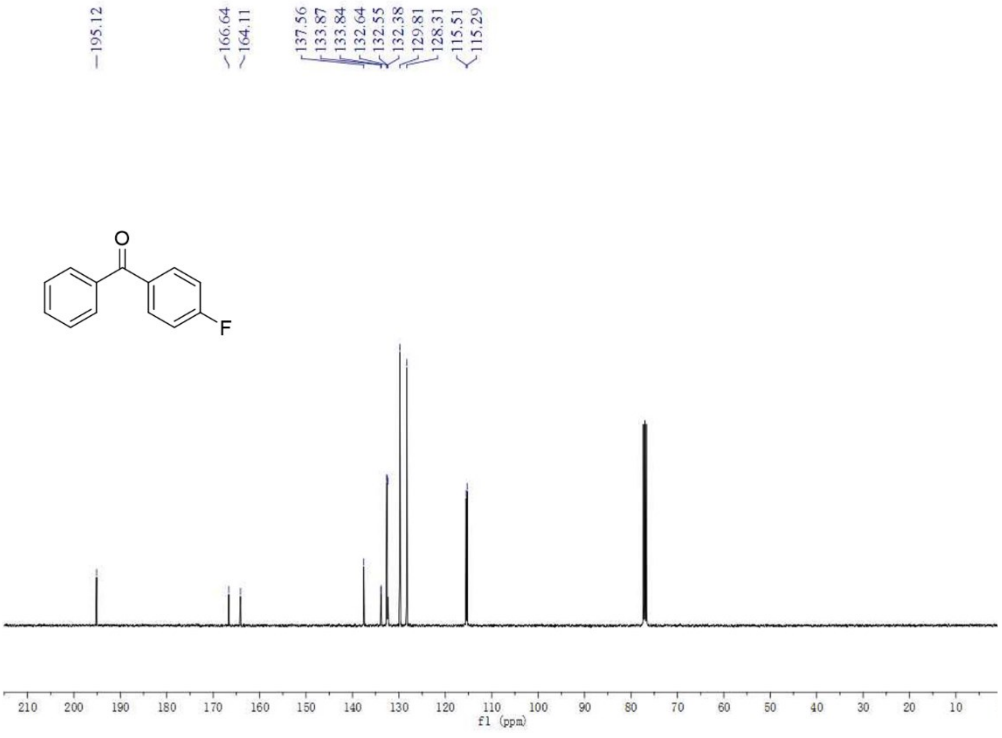
^{13}C NMR spectrum of **3f** in $CDCl_3$ at 101 MHz



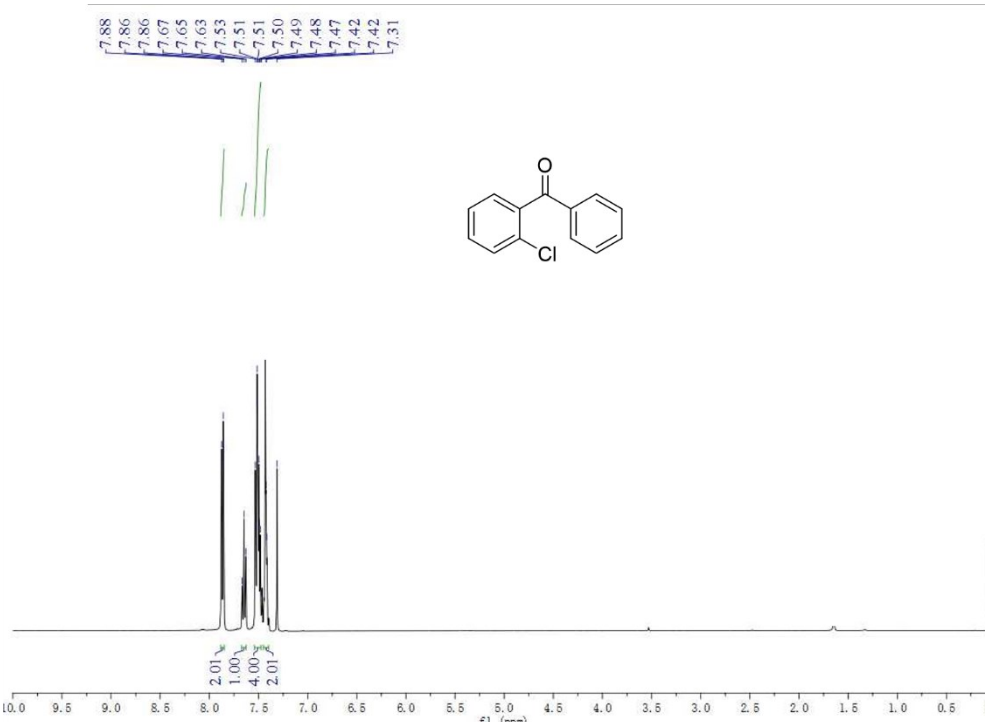
^{1}H NMR spectrum of **3g** in $CDCl_3$ at 400 MHz



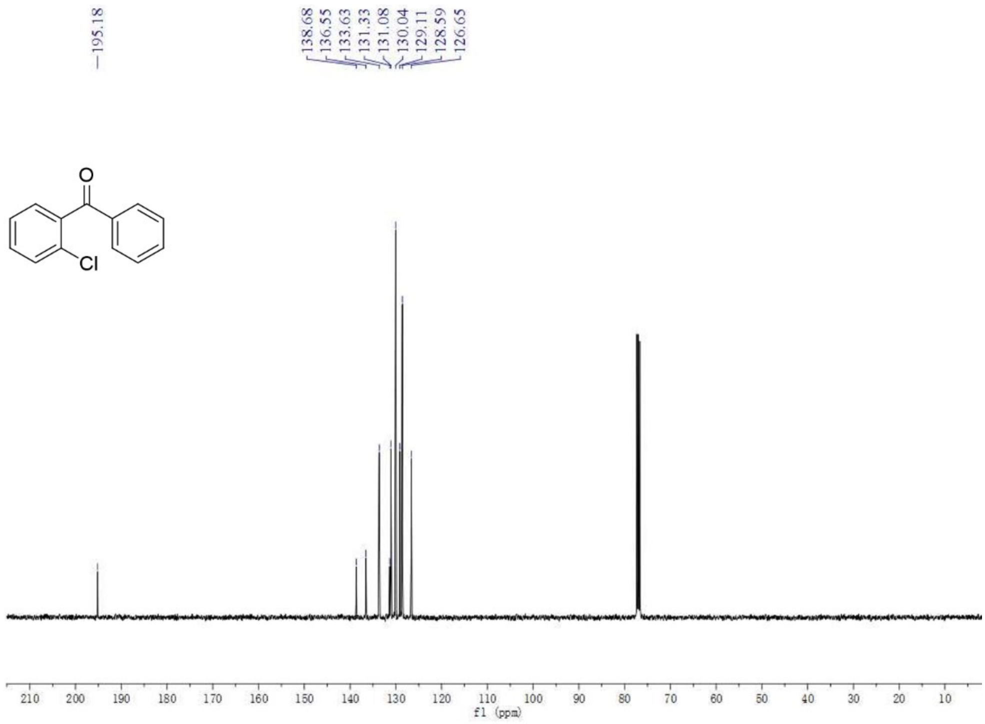
^{13}C NMR spectrum of **3g** in $CDCl_3$ at 101 MHz



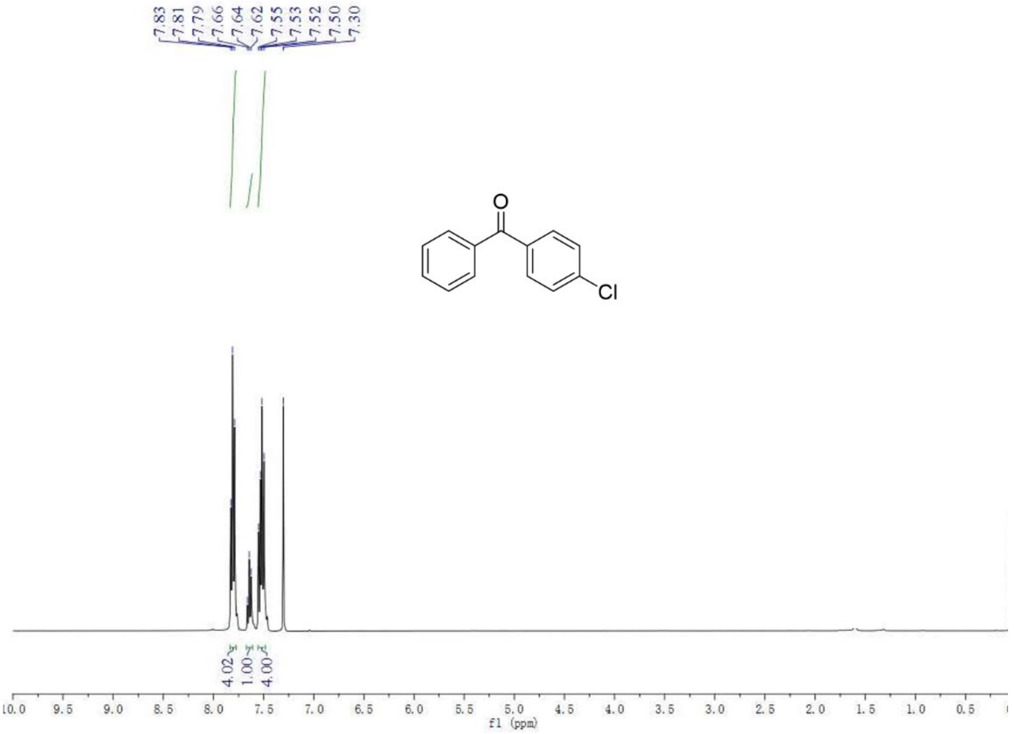
^{1}H NMR spectrum of **3h** in $CDCl_3$ at 400 MHz



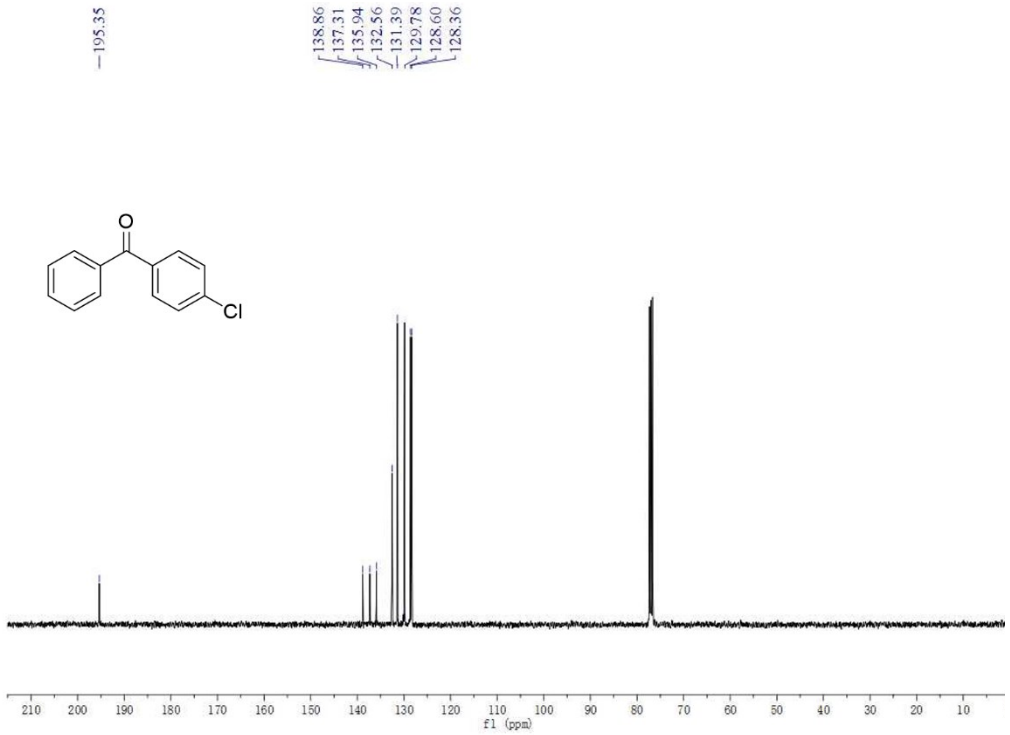
^{13}C NMR spectrum of **3h**in $CDCl_3$ at 101 MHz



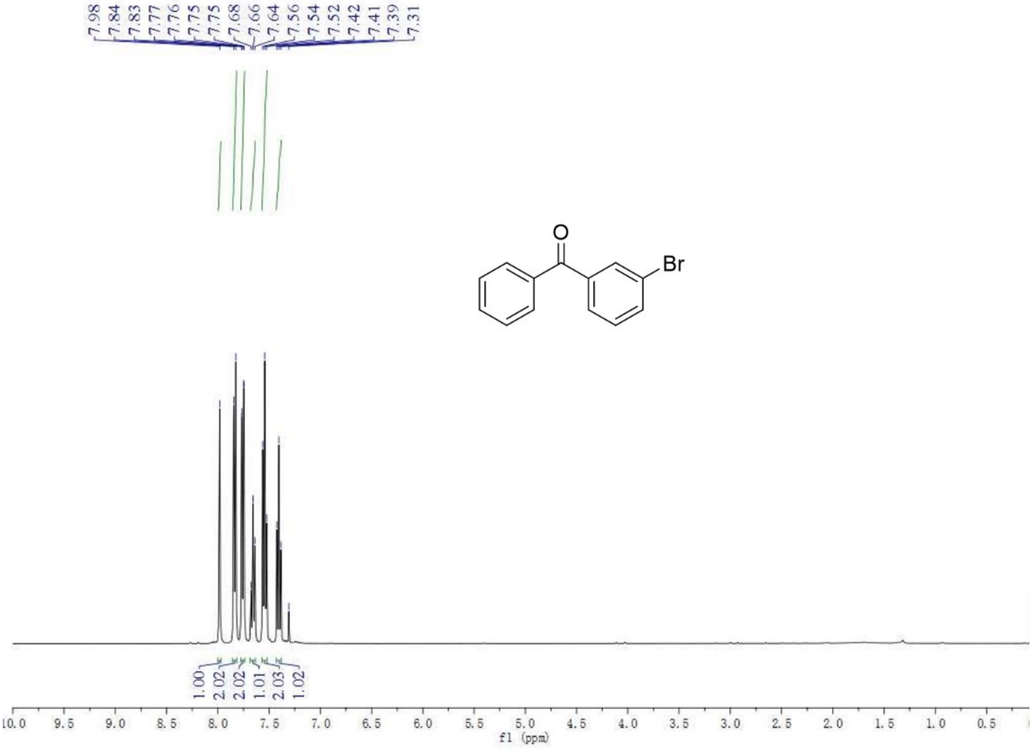
^{1}H NMR spectrum of **3i** in $CDCl_3$ at 400 MHz



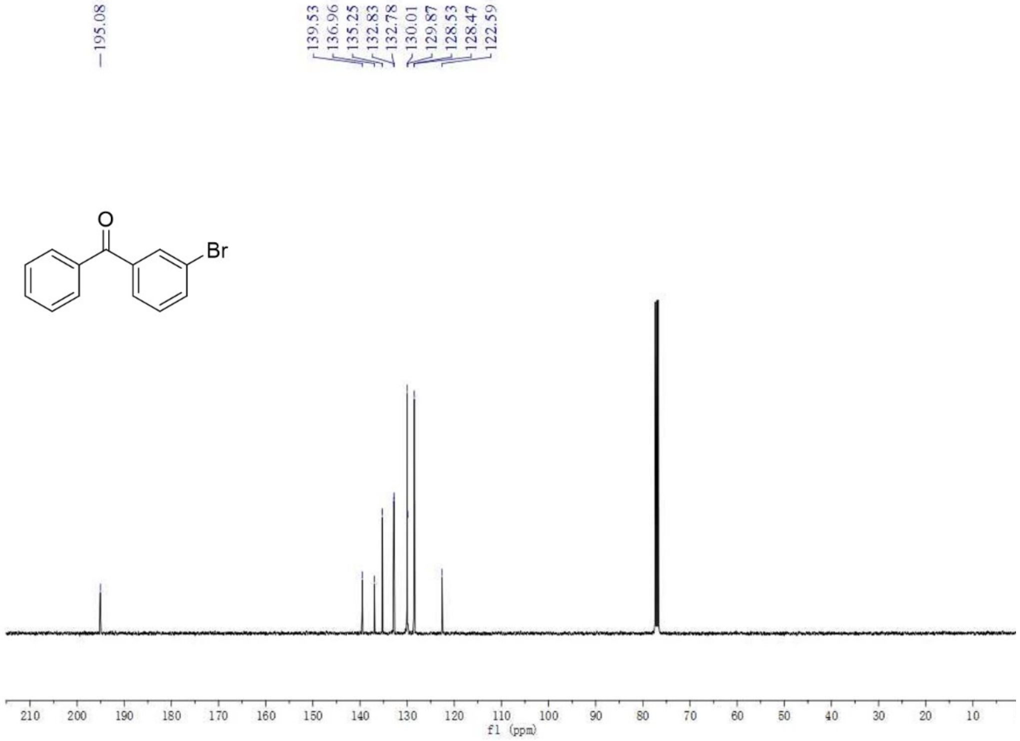
^{13}C NMR spectrum of **3i** in $CDCl_3$ at 101 MHz



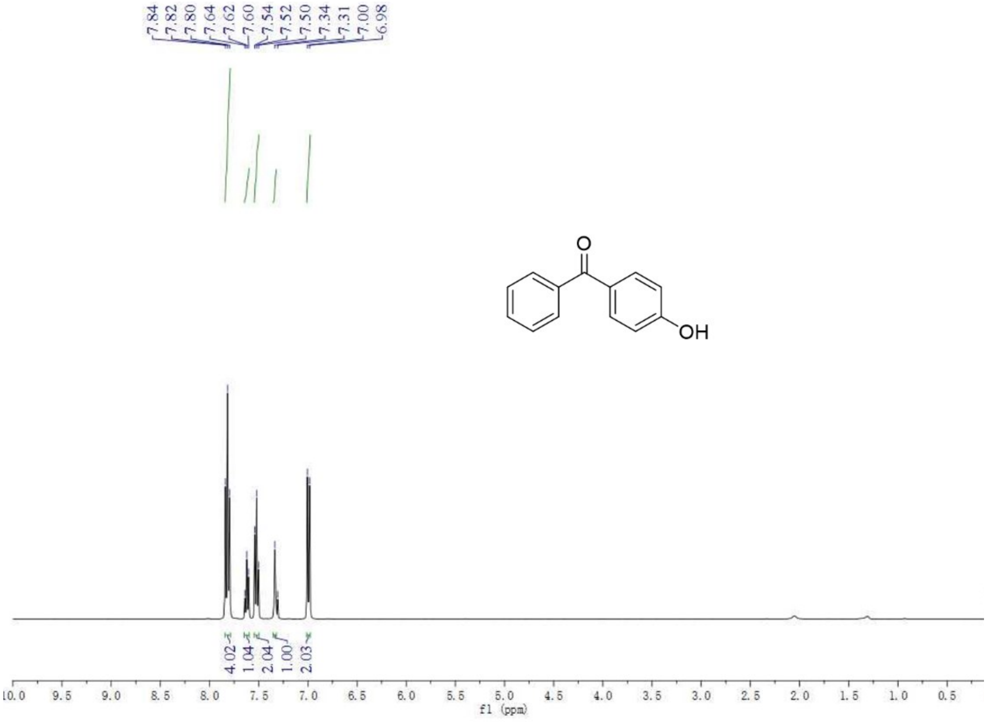
^{1}H NMR spectrum of **3j** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **3j** in $CDCl_3$ at 101 MHz



^{1}H NMR spectrum of **3k** in $CDCl_3$ at 400 MHz



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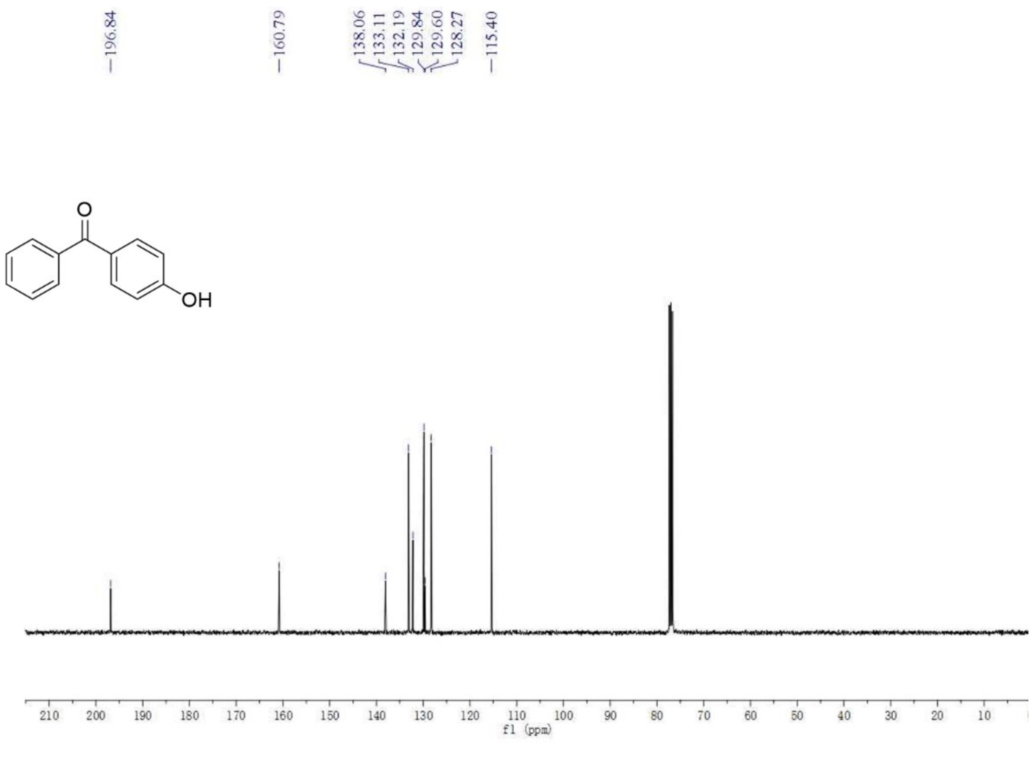
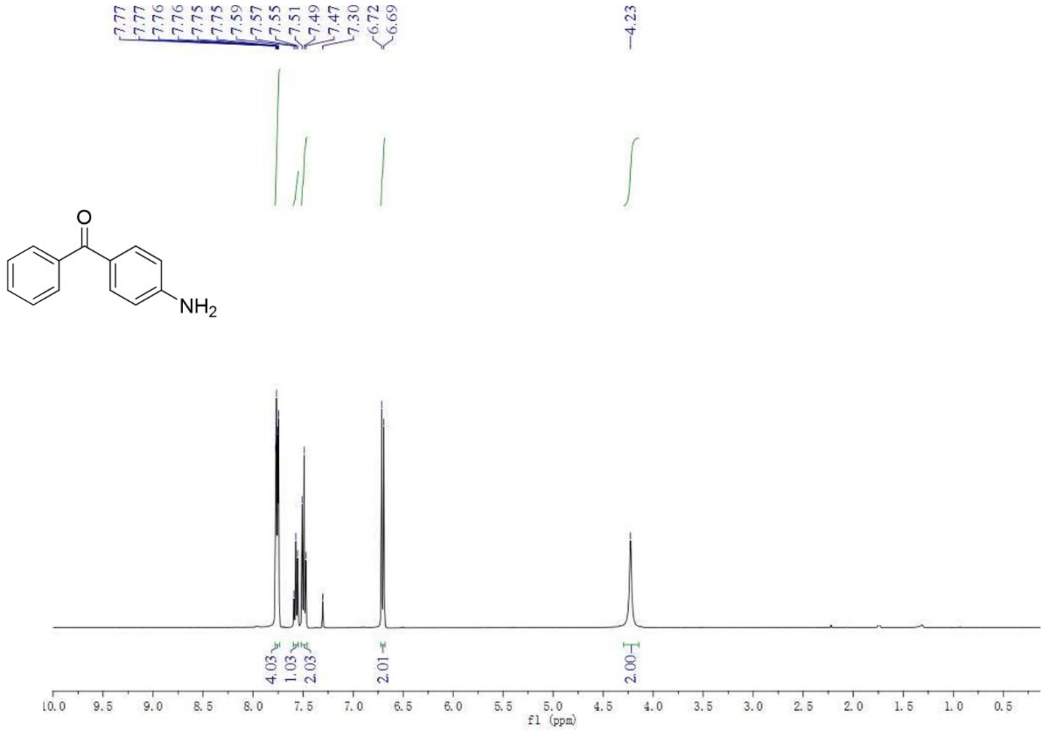


^{1}H NMR spectrum of **3l** in $CDCl_3$ at 400 MHz



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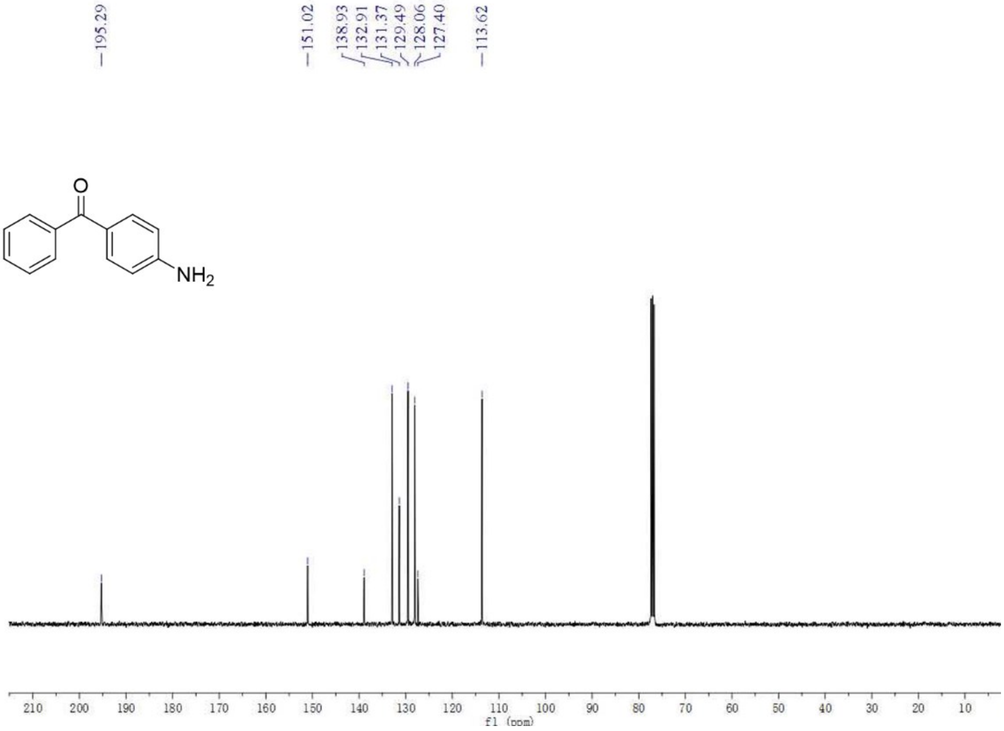
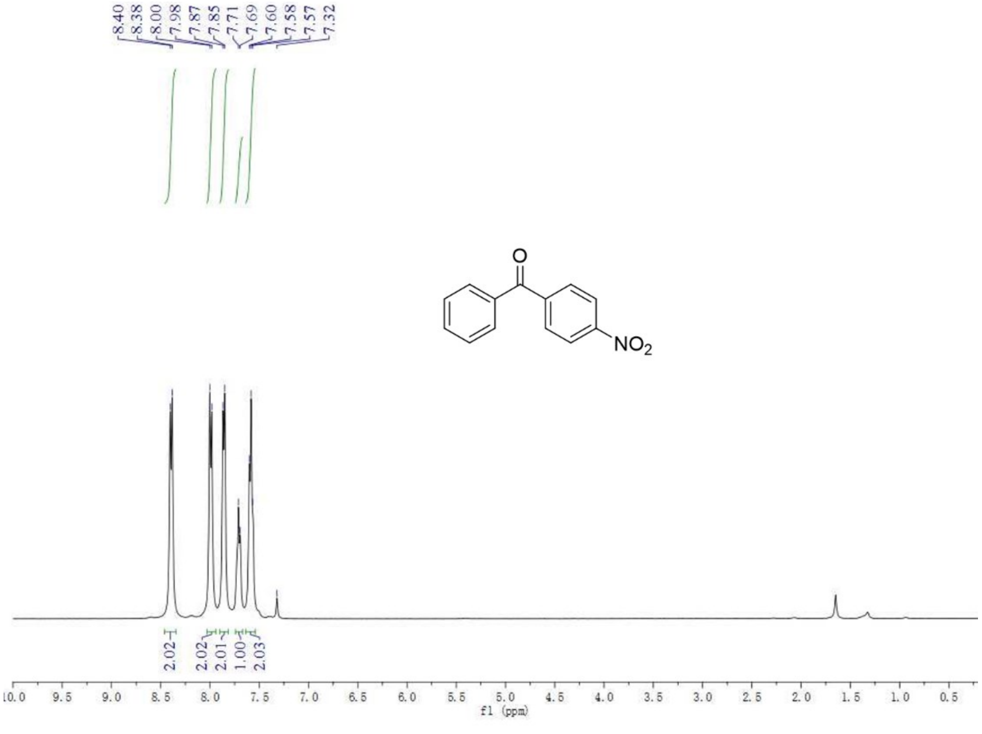
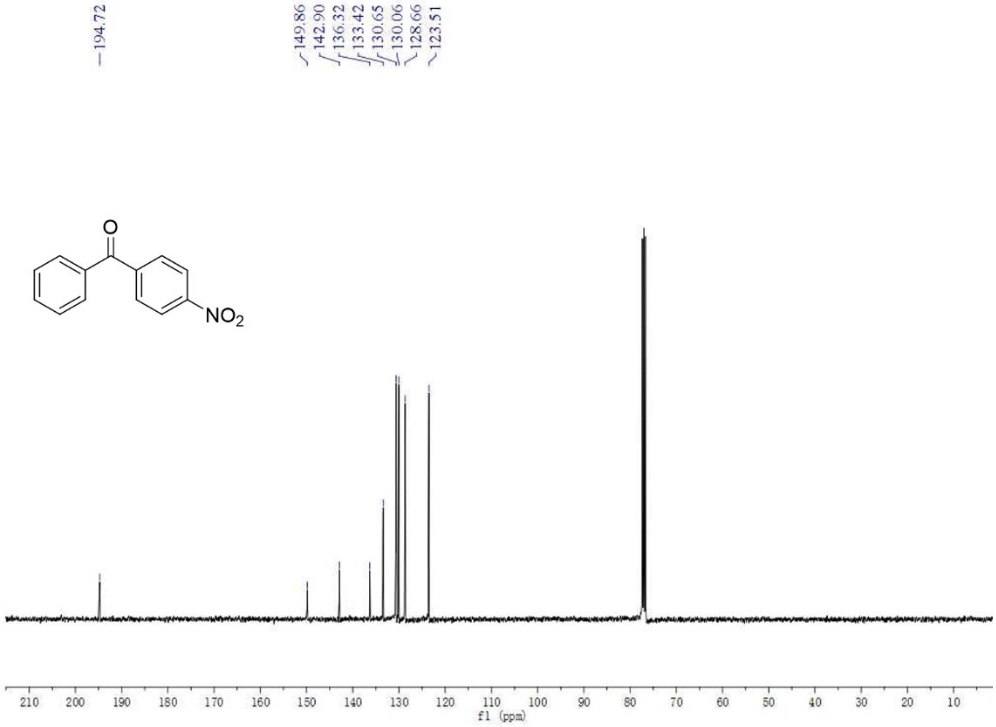


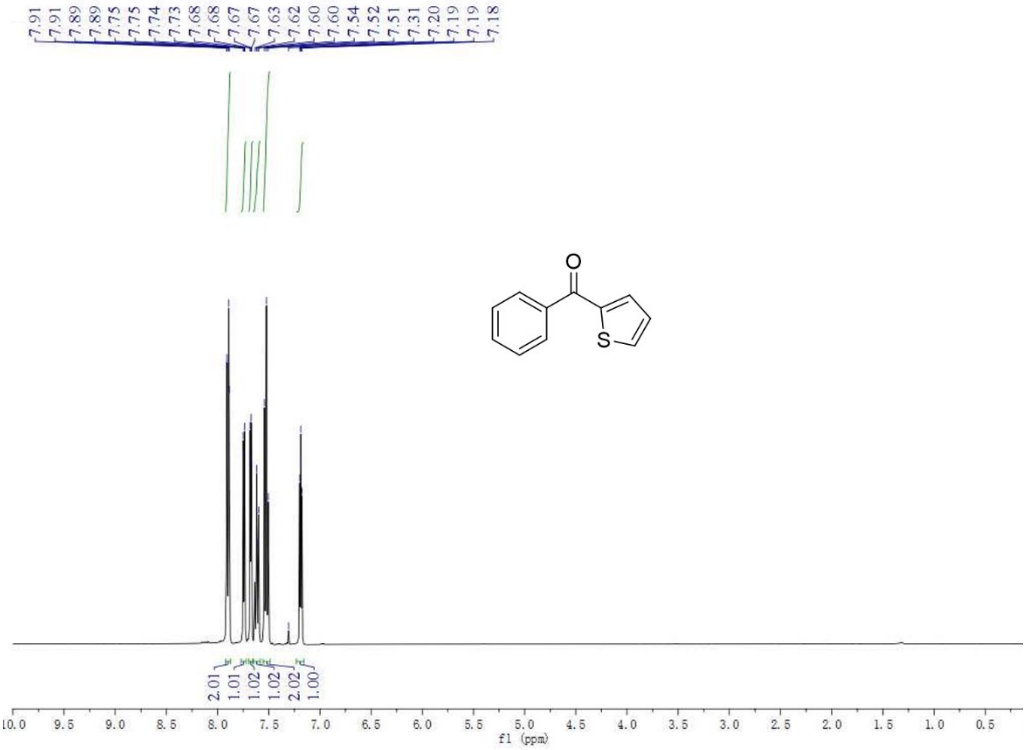
^{1}H NMR spectrum of **3m** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **3m** in $CDCl_3$ at 101 MHz



^{1}H NMR spectrum of **3n** in $CDCl_3$ at 400 MHz



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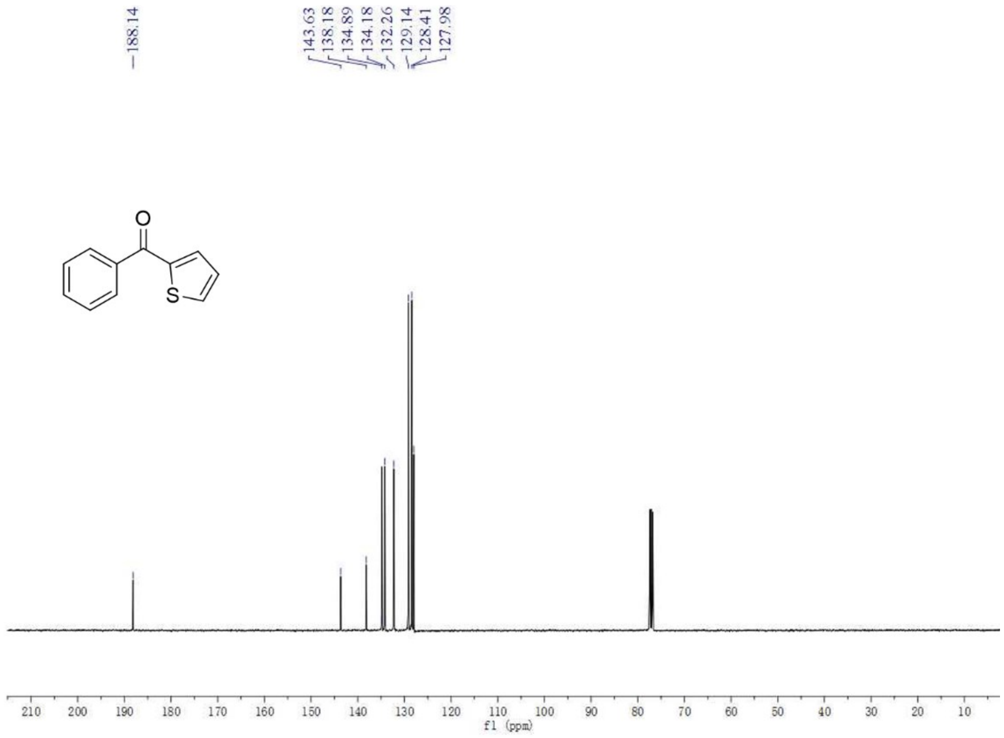
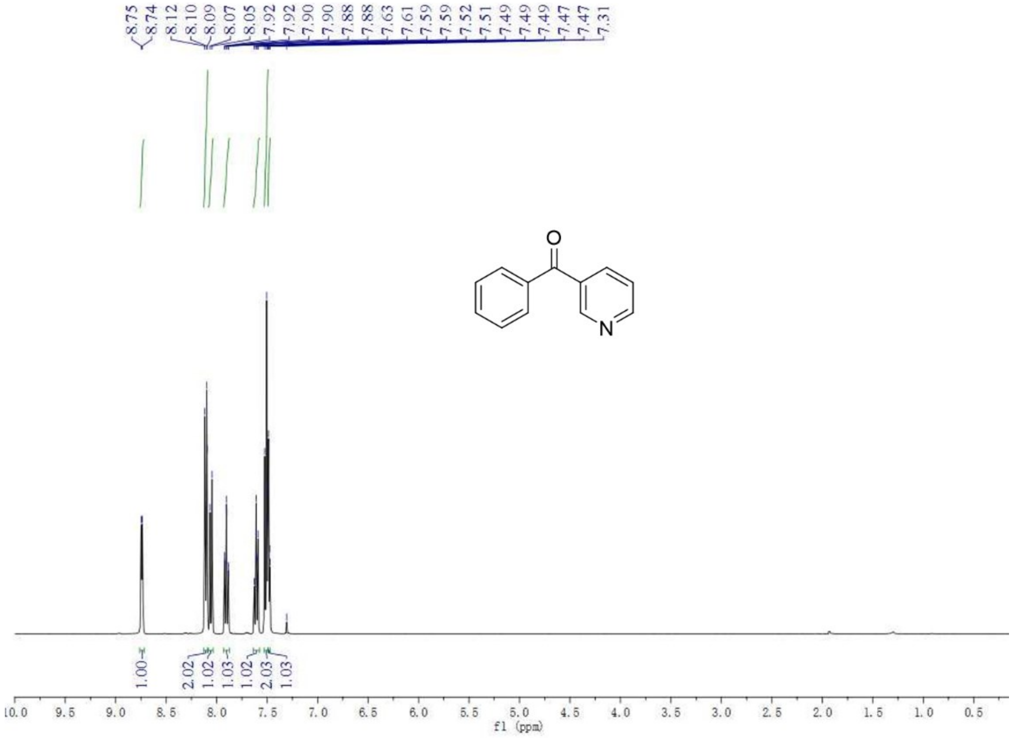


^{1}H NMR spectrum of **3o** in $CDCl_3$ at 400 MHz



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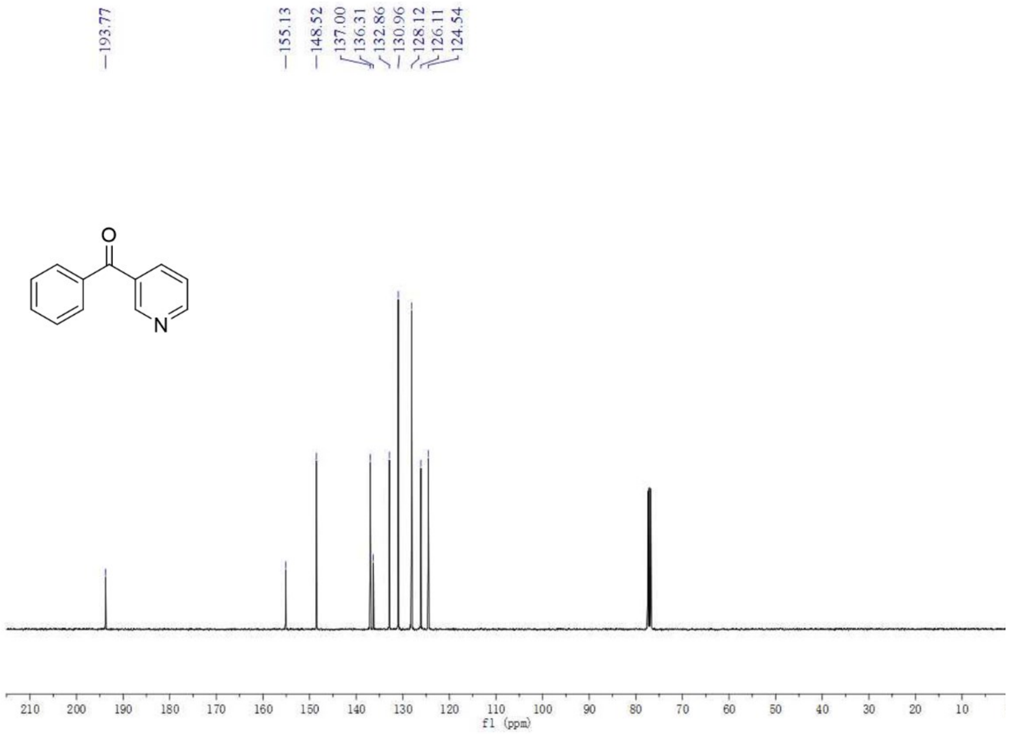

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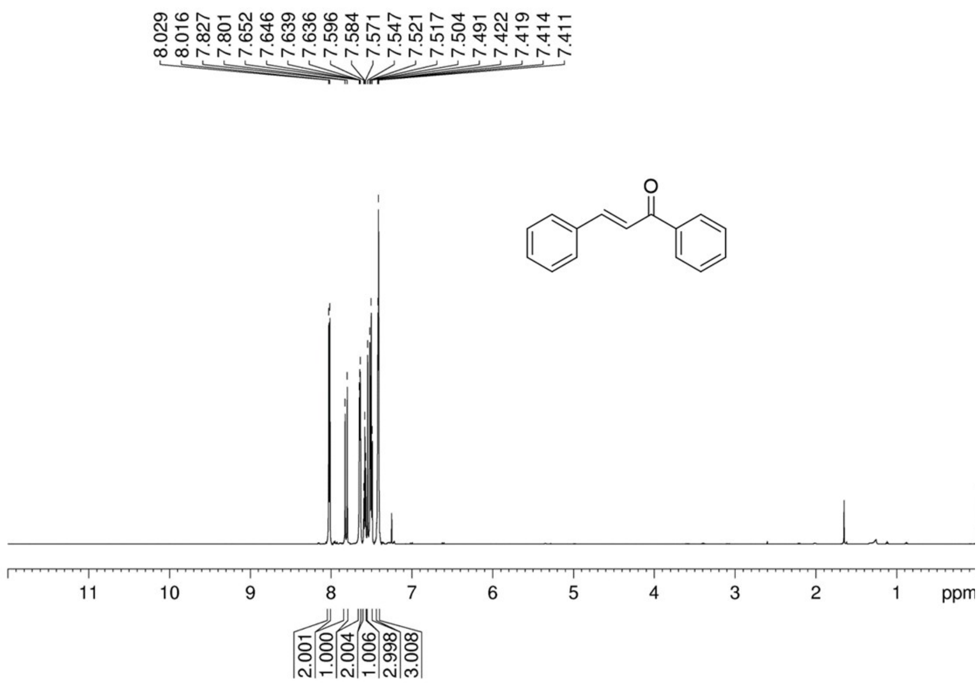
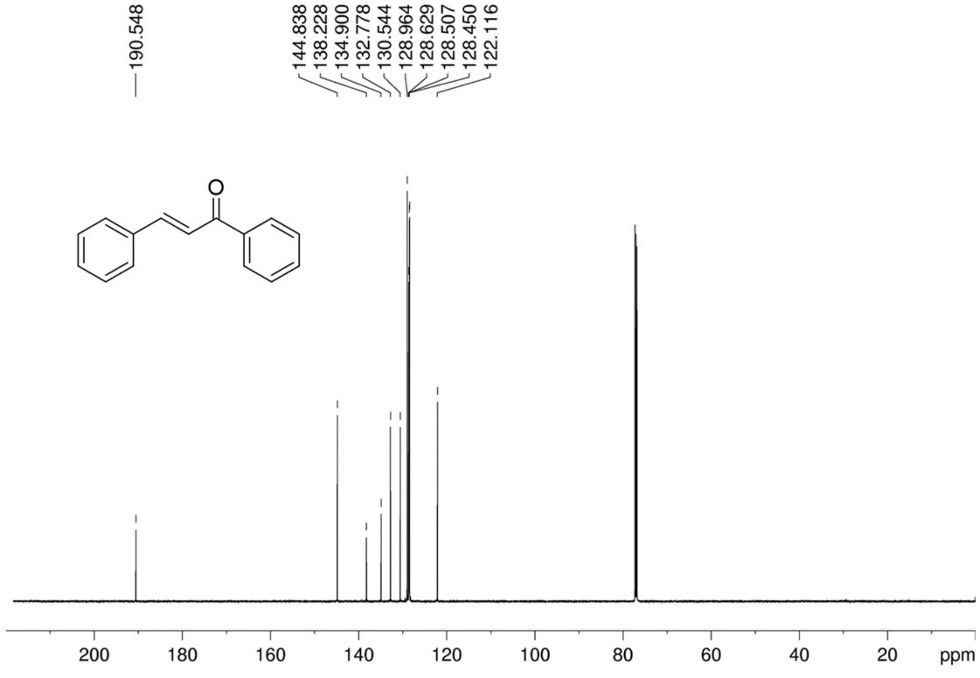
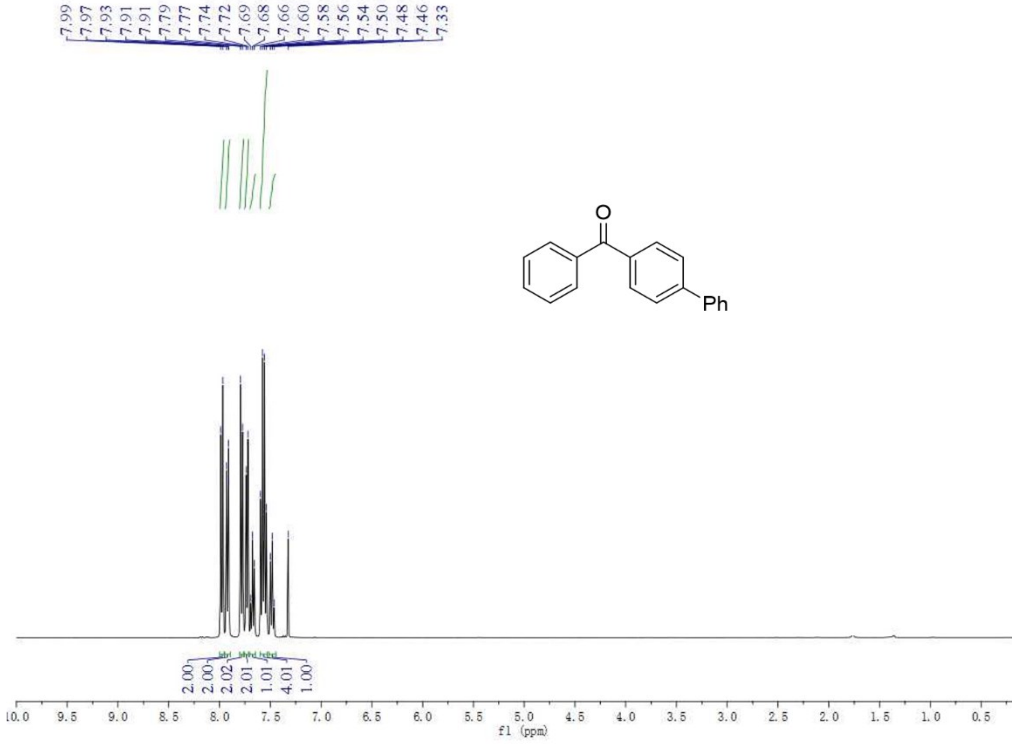


^{13}C NMR spectrum of **3r** in $CDCl_3$ at 151 MHz



^{1}H NMR spectrum of **3s** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **3s** in $CDCl_3$ at 101 MHz