Supporting Information

Vanadium-doped Molybdenum Carbides as Promising Catalyst for C-N/C-C coupling reactions

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I. Materials and methods

All the reactions reacted in the air. All the obtained products were characterized ^{1}H NMR spectra and ^{13}C NMR spectra. NMR spectra were obtained on Varian 400 MHz spectrometers; TLC was performed using commercially prepared 200-300 mesh silica gel plates; All the reagents were purchased from commercial sources (Energy Chemical, TCI, J&K Chemic, Meryer Chemic), and used without further purification. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4000–400 cm^{-1} region. TG analysis was carried out using a STA409 instrument in dry air at a heating rate of 25 ^{o}C/min from 25 to 900 ^{o}C. SEM was performed on a HITACHI S-4800 field-emission scanning electron microscope. TEM was obtained using a JEOL JEM-2100 microscope operated at 200 kV. XRD patterns were collected on a Bruker D8 Advance powder diffractometer, using a Ni-filtered Cu/Kα radiation source at 40 kV and 20 mA, from 3° to 80° with a scan rate of 4°/min. The specific surface areas were evaluated using the Brunauer–Emmett–Teller (BET) method and the pore distribution was calculated by the BJH method from adsorption branches of isotherms.

II. Catalysts and Compounds Characterization

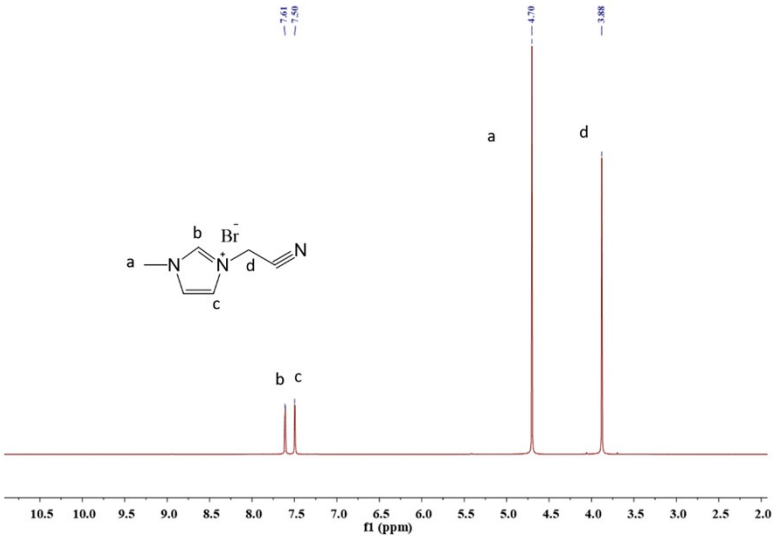


Figure S1. ^{1}H NMR spectrum of [CMim]Br.

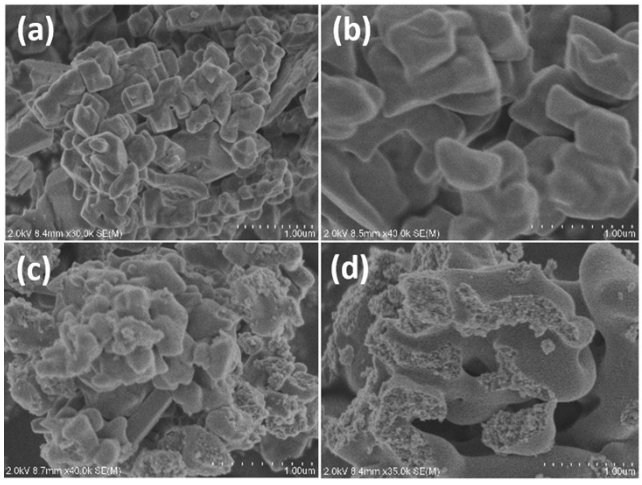


Figure S2. SEM images of (a) PMoV-CMim, (b) V-Mo_2C@NC_{450}, (c) V-Mo_2C@NC_{600}, and (d) V-Mo_2C@NC_{800}.

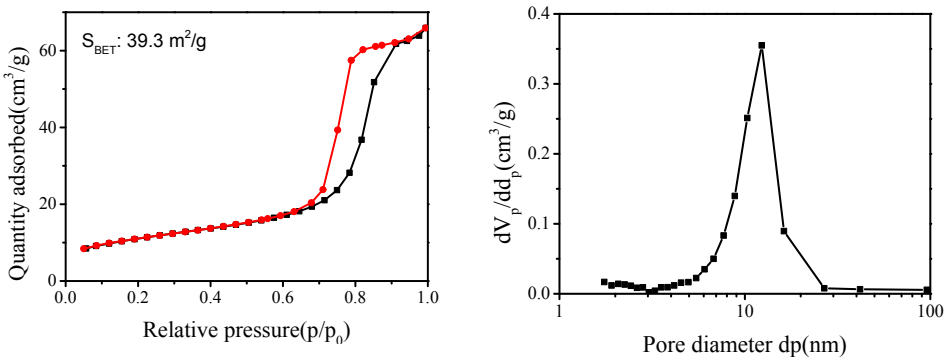


Figure S3. (A) N_2 sorption analysis and (B) the corresponding pore size distribution of $Mo_2C@NC_{800}$.

Table S1. Porous features of different samples.

Entry	Sample	BET (m^2/g)	Pore size (nm)	Pore volume (m^3)
1	PMoV-CMim	2.9	—	0.004
2	V-$Mo_2C@NC_{450}$	2.5	—	0.004
3	V-$Mo_2C@NC_{600}$	27.1	3.2	0.022
4	V-$Mo_2C@NC_{800}$	43.3	6.8	0.074

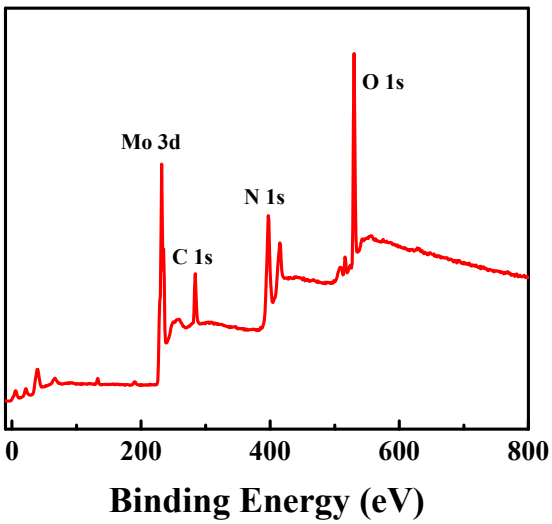


Figure S4. XPS survey spectrum of V-Mo_2C@NC_{800}.

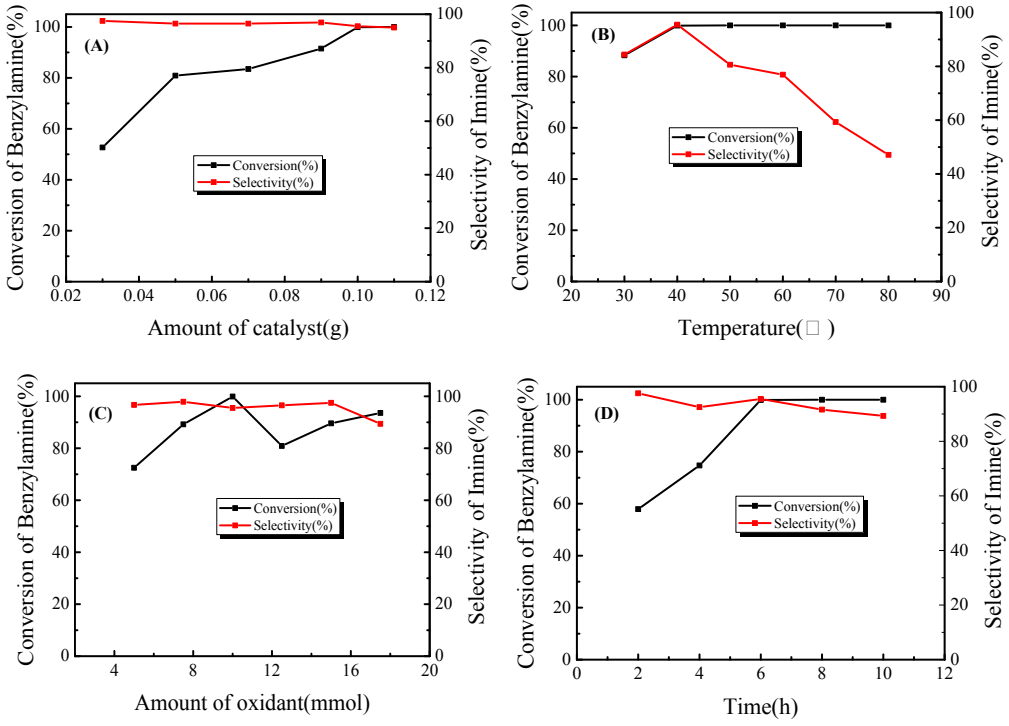


Figure S5. Effect of (A) Amount of catalyst, (B) Temperature, (C) Amount of oxidant and (D) Time on the conversion and selectivity of the oxidative coupling of benzylamine over V-Mo_2C@NC_{800}.

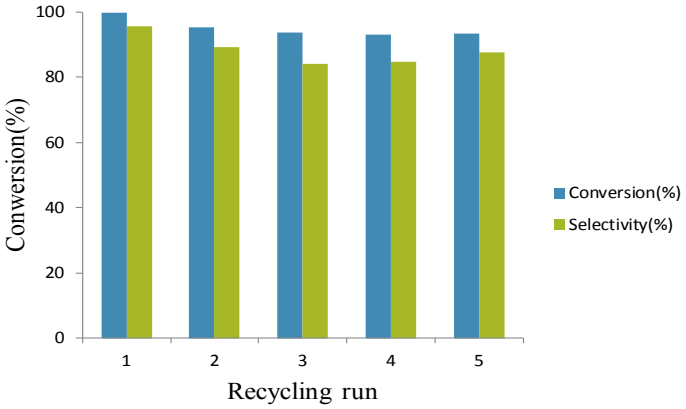
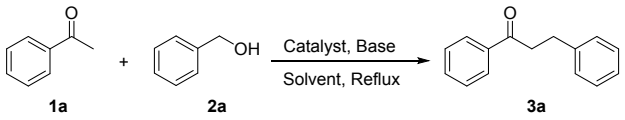


Figure S6. Catalytic reusability of V-Mo_2C@NC_{800} for coupling of benzylamine.

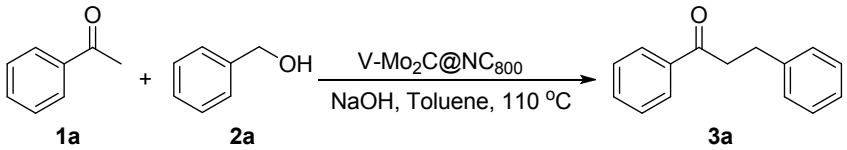
Table S2. Screening of reaction conditions [a]



1a **2a** **3a**

Entry	Base	Solvent	Yield [%][b]
1	NaOH	Toluene	85
2	Na_2CO_3	Toluene	65
3	Cs_2CO_3	Toluene	69
4	KO*t*Bu	Toluene	72
5	NaOH	DCM	< 5
6	NaOH	THF	34
7	NaOH	H_2O	< 5
8	NaOH	Xylene	76

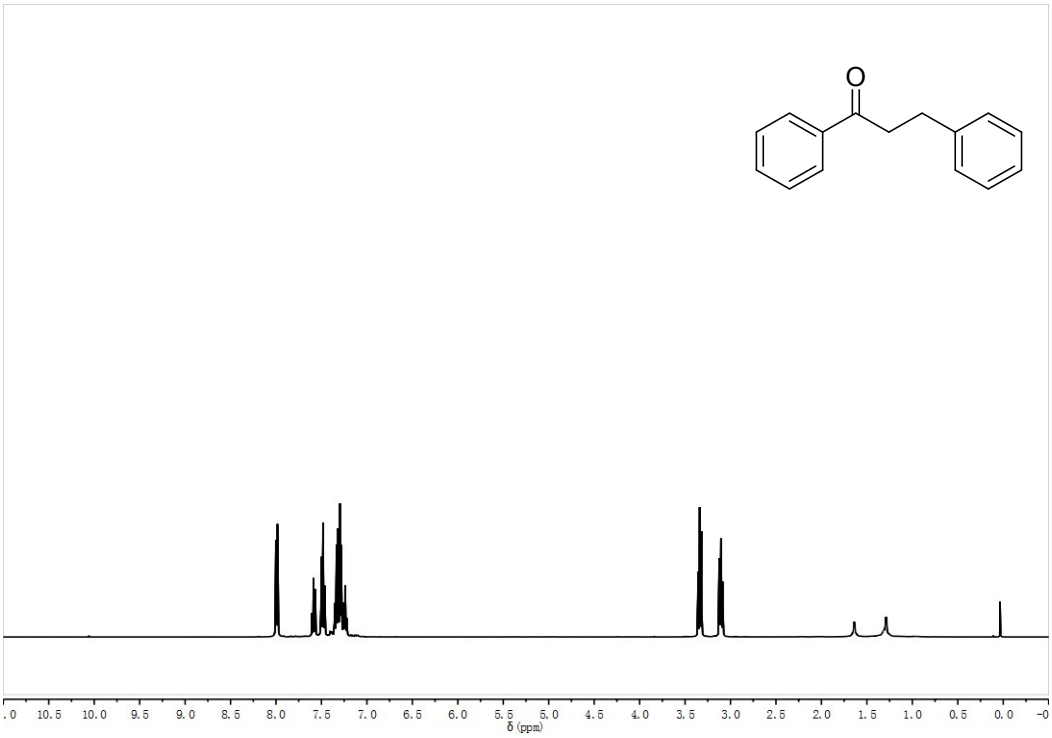
[a]Reagents and conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), V-Mo_2C@NC_{800} (0.01 g), base (1.0 mmol), solvent (3 mL), 110 °C or reflux, 15 h, under air. [b] Isolated yields based on **1a**.



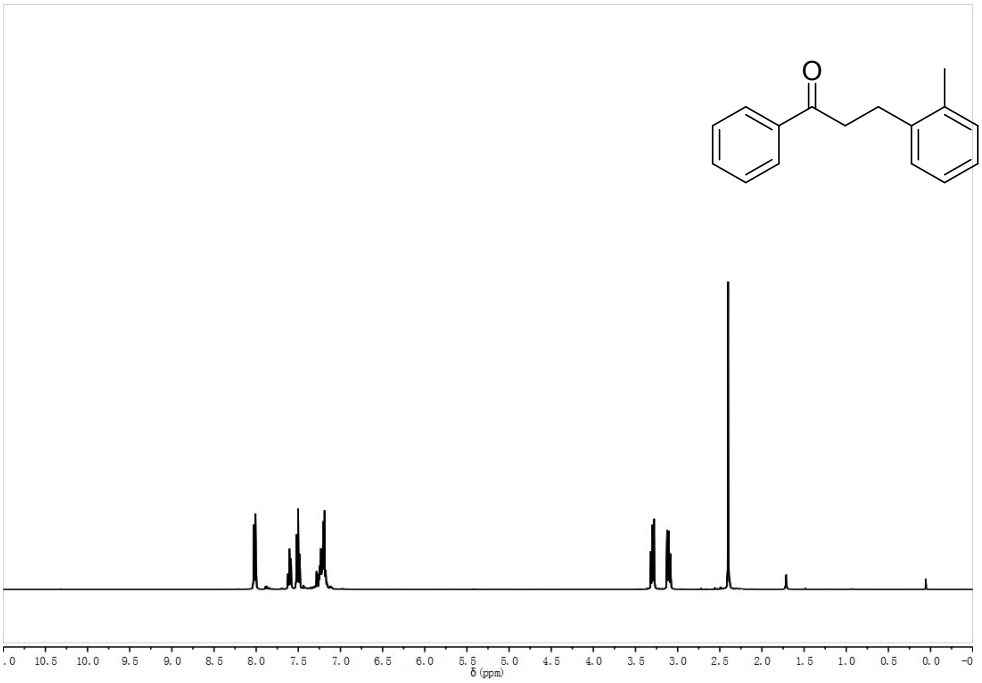
Recycled times	**0**	**1**	**2**	**3**	**4**	**5**
Yields	85%	82%	81%	80%	78%	78%

Scheme 1. Recycled experiments.

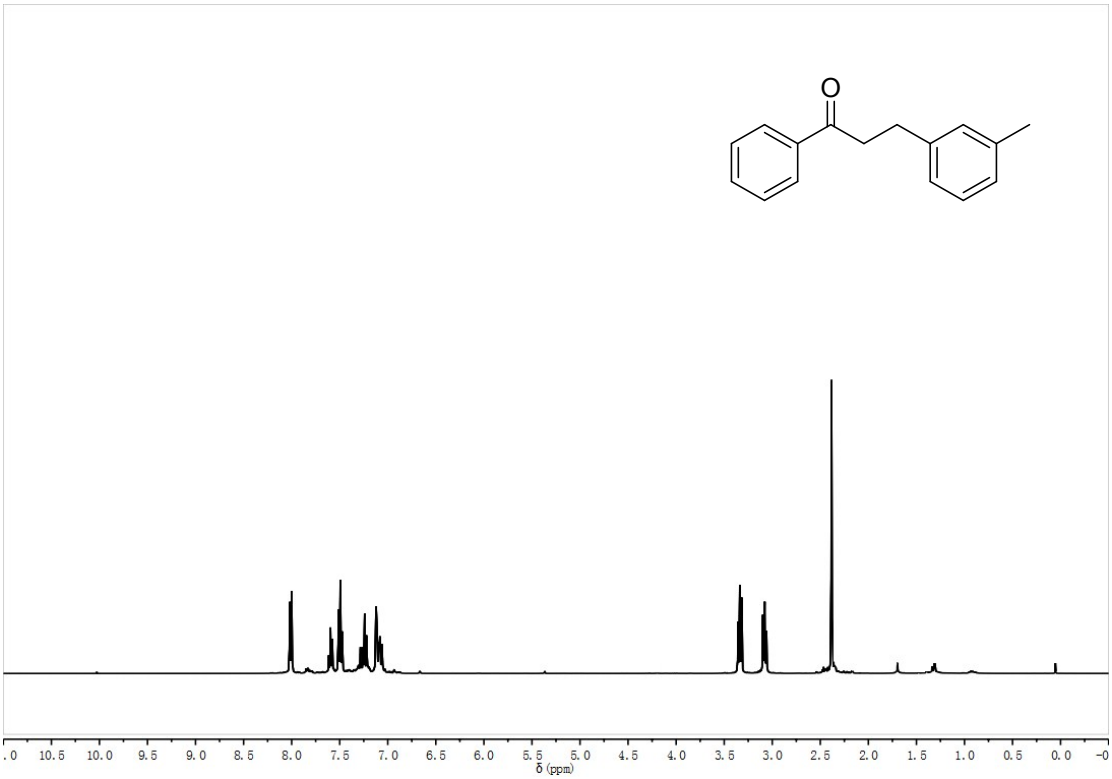
III. ^{1}H NMR and ^{13}C NMR Spectra



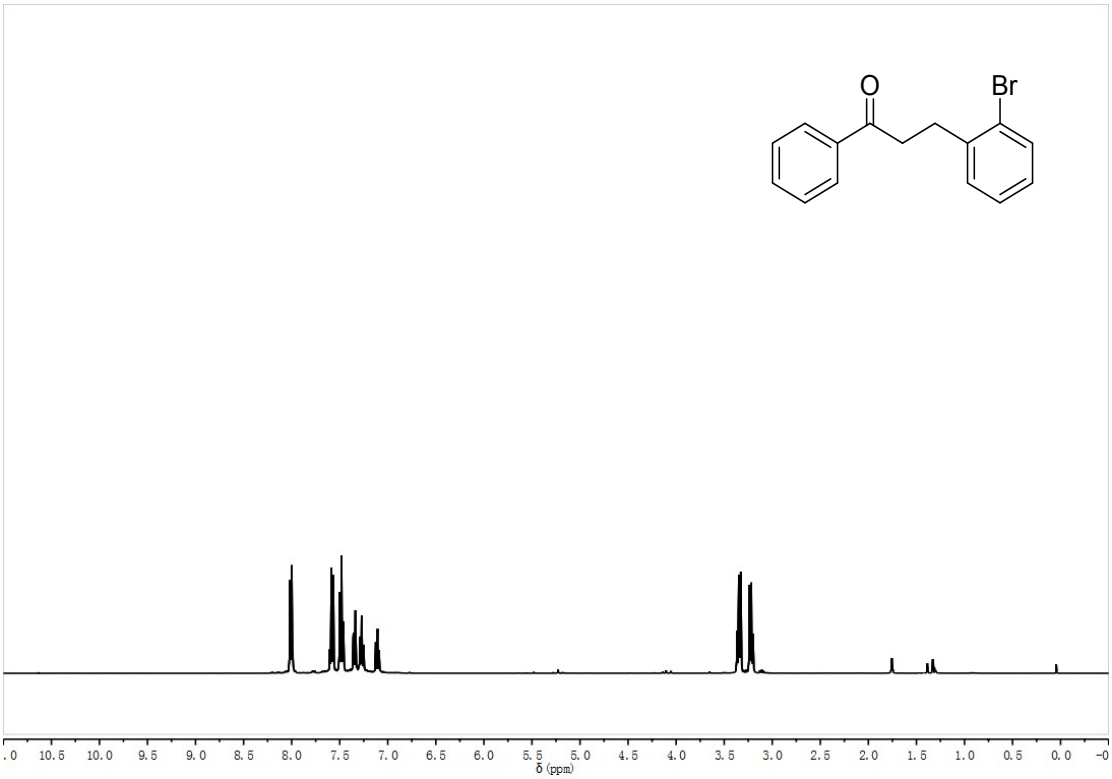
^{1}H NMR for **3a**



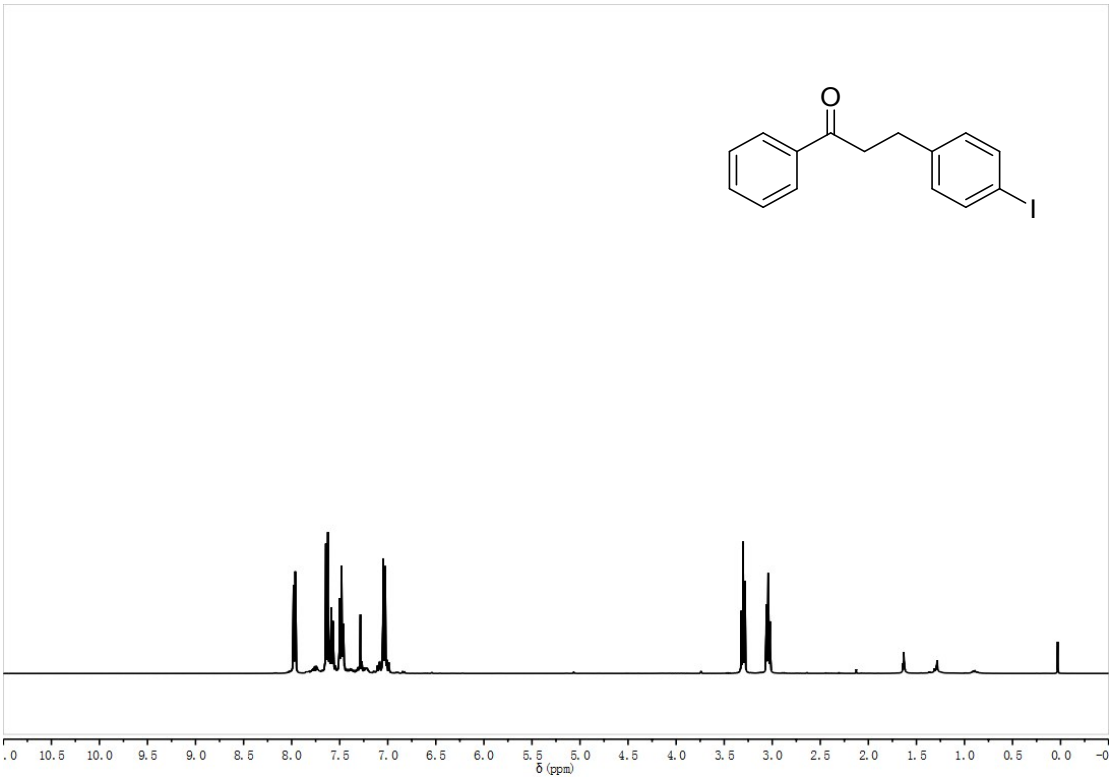
^{1}H NMR for **3b**



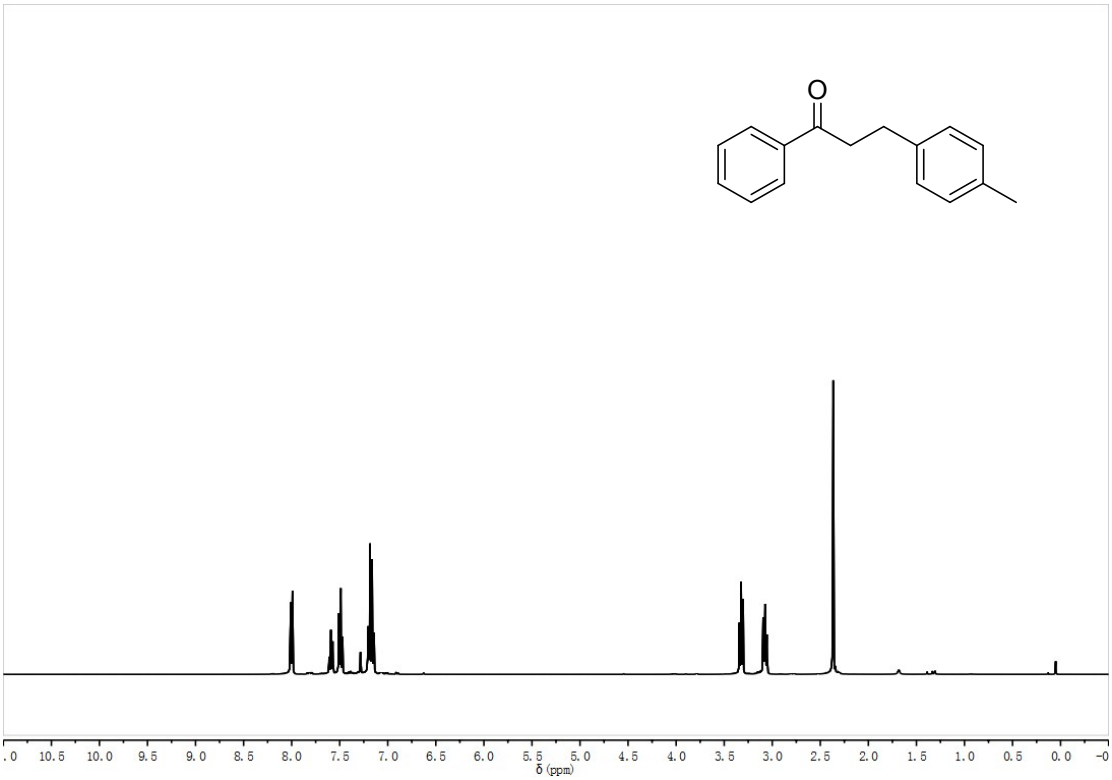
^{1}H NMR for **3c**



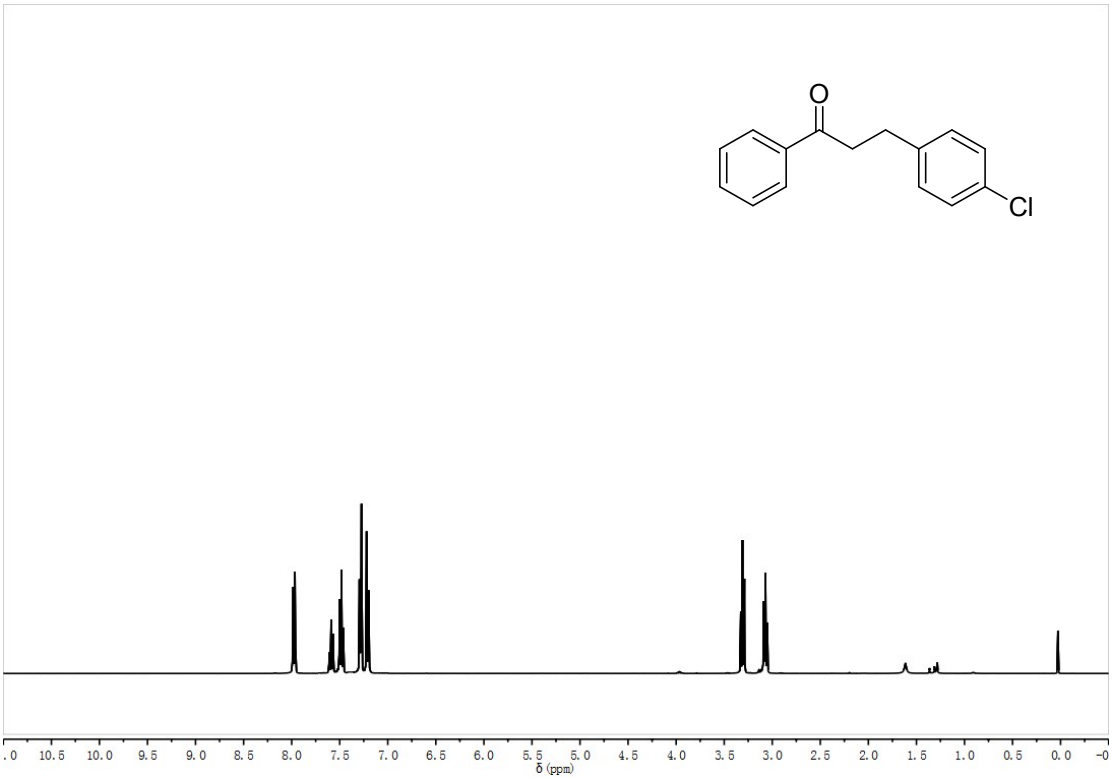
^{1}H NMR for **3d**



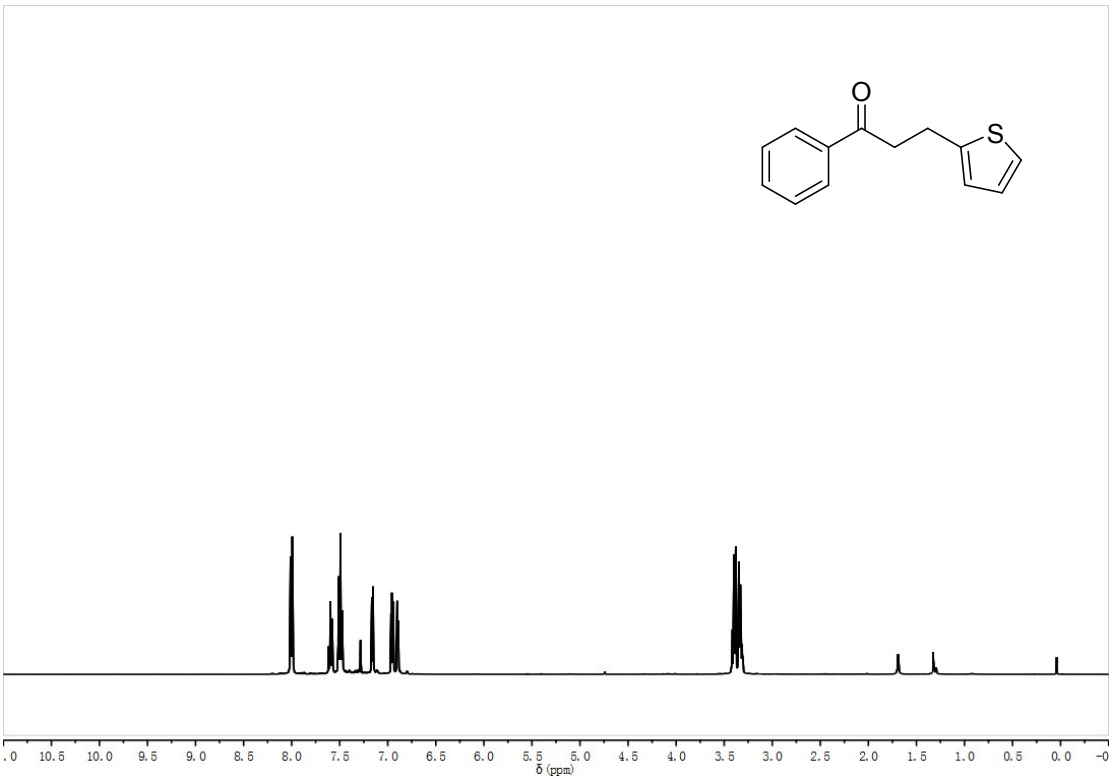
^{1}H NMR for **3e**



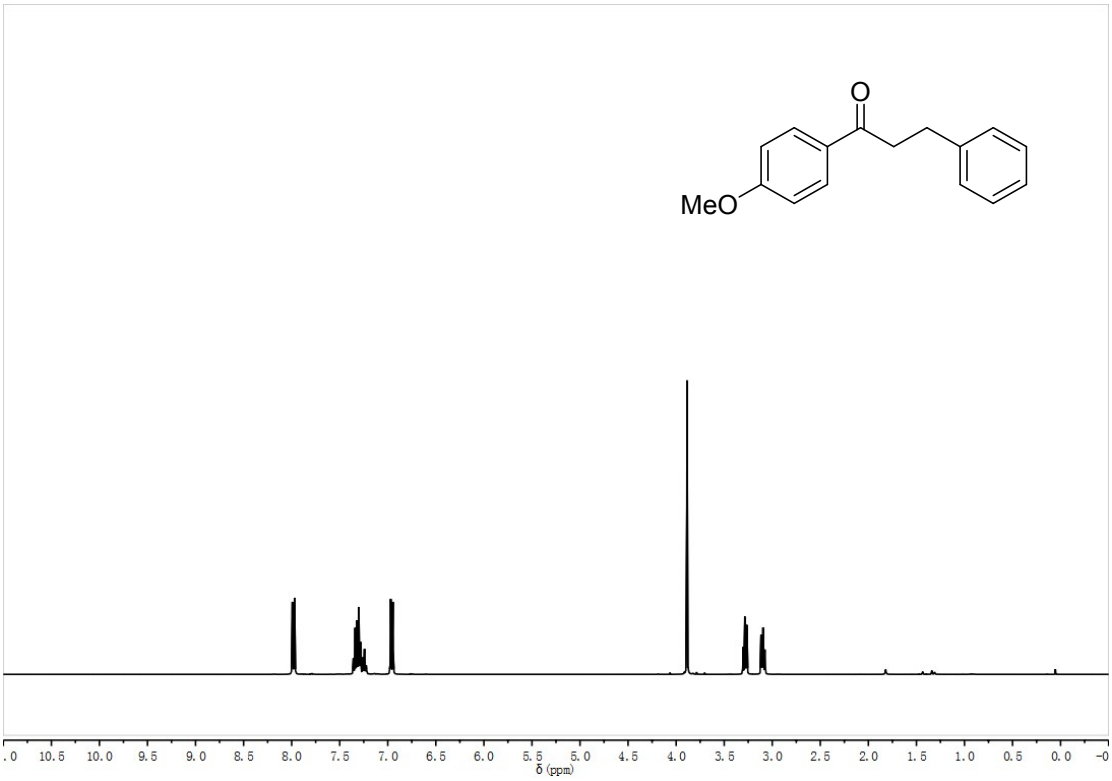
^{1}H NMR for **3f**



^{1}H NMR for **3g**



^{1}H NMR for **3h**


O
MeO
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
δ (ppm)

^{1}H NMR for **3i**