

Electronic Supplementary Information

Visible-light induced C(sp³)-H arylation of glycine derivatives by cerium catalysis

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1. Experiment Information

1.1 General information

Unless otherwise noted, all reagents were purchased from commercial sources and used as received without further purification. *N*-arylglycine derivatives^{1,2} were prepared according to literature procedures. Unless otherwise indicated, all experiments were carried out under air atmosphere. Irradiation of photochemical reactions was carried out using an 18 W blue LED bulb or 5 W LED waveband light source. The silica gel (200–300 meshes) was used for column chromatography and TLC inspections were taken on silica gel GF254 plates. Liquid ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High resolution mass spectra (HRMS) were obtained on a mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QTof).

1.2 General procedure for the visible-light induced oxidative dehydrogenative coupling of glycine esters and electron-rich arenes.

To a solution of *N*-arylglycine derivative **1** (0.2 mmol, 1 eq) in dry CH₃CN (4 mL) was added Ce(OTf)₃ (30 mol%). The mixed solution was irradiated with 18 W blue LEDs under air atmosphere at room temperature, until the glycine derivative reacted completely (monitored by TLC). Then **2** (0.22 mmol, 1.1 eq) was added and stirred at room temperature (without the irradiation of blue LEDs). After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was purified by silica gel column chromatography (with PE/EA = 16/1 to 10/1 as eluent) to afford the products.

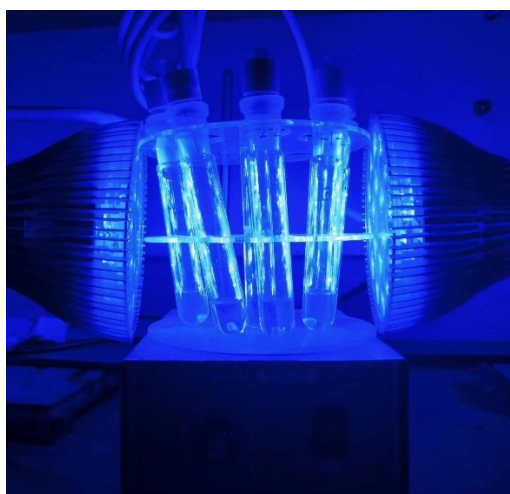
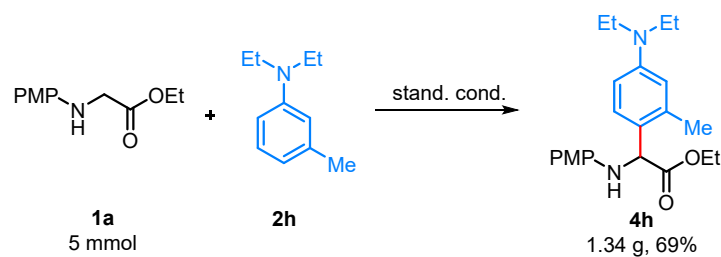


Fig. S1 Picture of photoreaction device.

1.3 Gram-scale synthesis



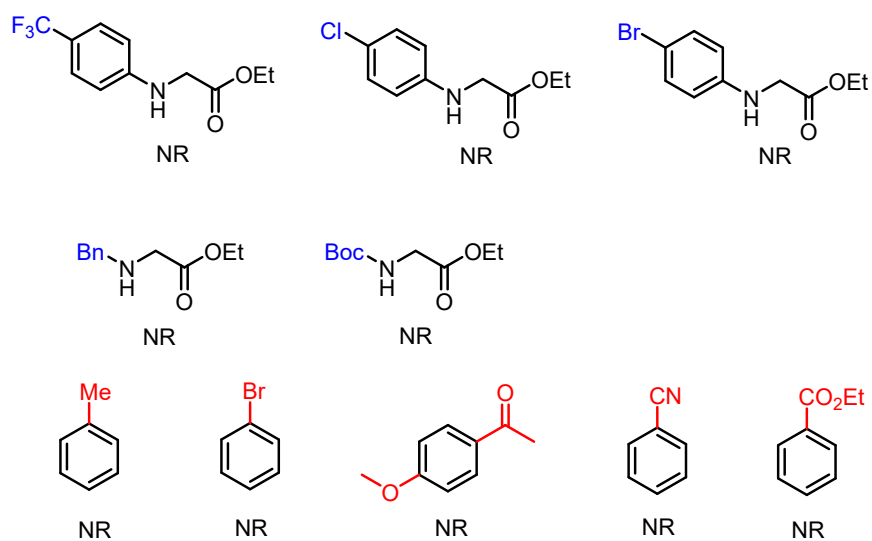
Scheme S1 Gram scale experiment.

To a solution of **1a** (1.05 g, 5.0 mmol, 1 eq) in dry CH₃CN (100 mL) was added Ce(OTf)₃ (0.88 g, 30 mol%). The mixed solution was irradiated with 18 W blue LEDs under air atmosphere at room temperature, until the **1a** reacted completely (monitored by TLC). Then **2h** (1.02 g, 7.5 mmol, 1.5 eq) were added and stirred at room temperature (without the irradiation of blue LEDs). After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was purified by silica gel column chromatography (with PE/EA = 16/1 as eluent) to afford the product **4h** (1.34 g, 69 % yield) as a yellow oil.



Fig. S2 Picture of set-up for the gram scale reaction.

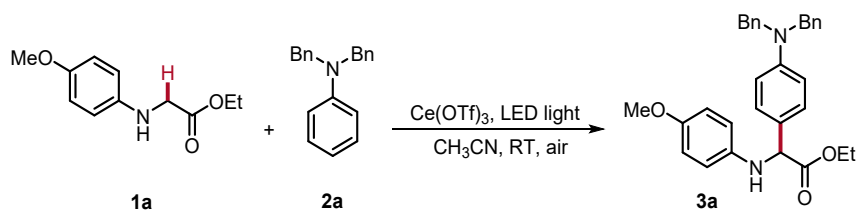
1.4 Substrate limitation



Scheme S2 Unsuccessful glycine derivatives and arenes (NR means no reaction).

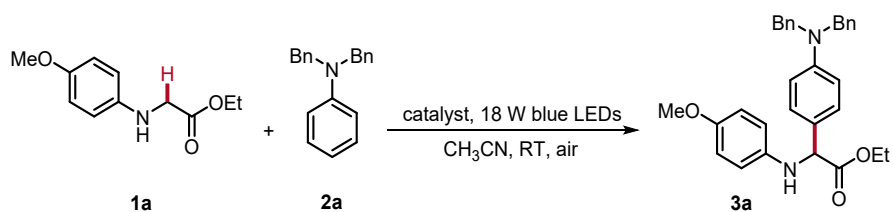
2. Optimization of Reaction Conditions

Table S1. Screening of light sources ^a



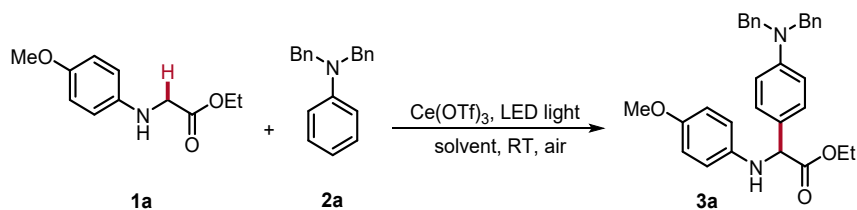
Entry	Light Source	Yield (%) ^b
1	365-375 nm	67
2	380-385 nm	85
3	390-400 nm	82
4	Blue LED	95
5	White LED	82
6	Green LED	65
7	dark	trace

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.11 mmol), $\text{Ce}(\text{OTf})_3$ (30 mol%), CH_3CN (2.0 mL), LED light irradiation under air at room temperature. ^bYields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

Table S2. Screening of catalysts ^a

Entry	Catalyst	Yield (%) ^b
1	CuSO ₄ ·5H ₂ O	NR
2	FeSO ₄ ·7H ₂ O	NR
3	CuI	NR
4	AgOTf	NR
5	CeCl ₃	65
6	—	NR
7 ^c	Ce(OTf) ₃	71
8 ^d	Ce(OTf) ₃	68

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.11 mmol), catalyst (30 mol%), CH₃CN (2 mL), blue LED light irradiation under air at room temperature. ^b Yields were determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. ^c 15 mol% Ce(OTf)₃ was used. ^d 40 mol% Ce(OTf)₃ was used.

Table S3. Screening of solvents ^a

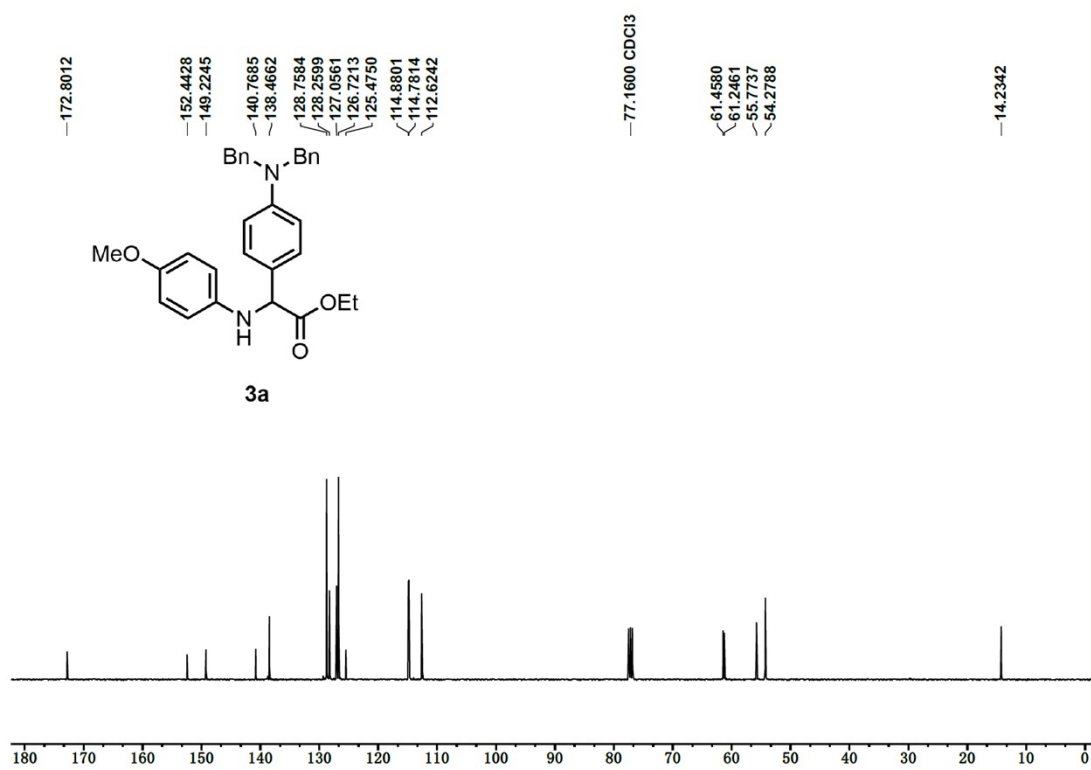
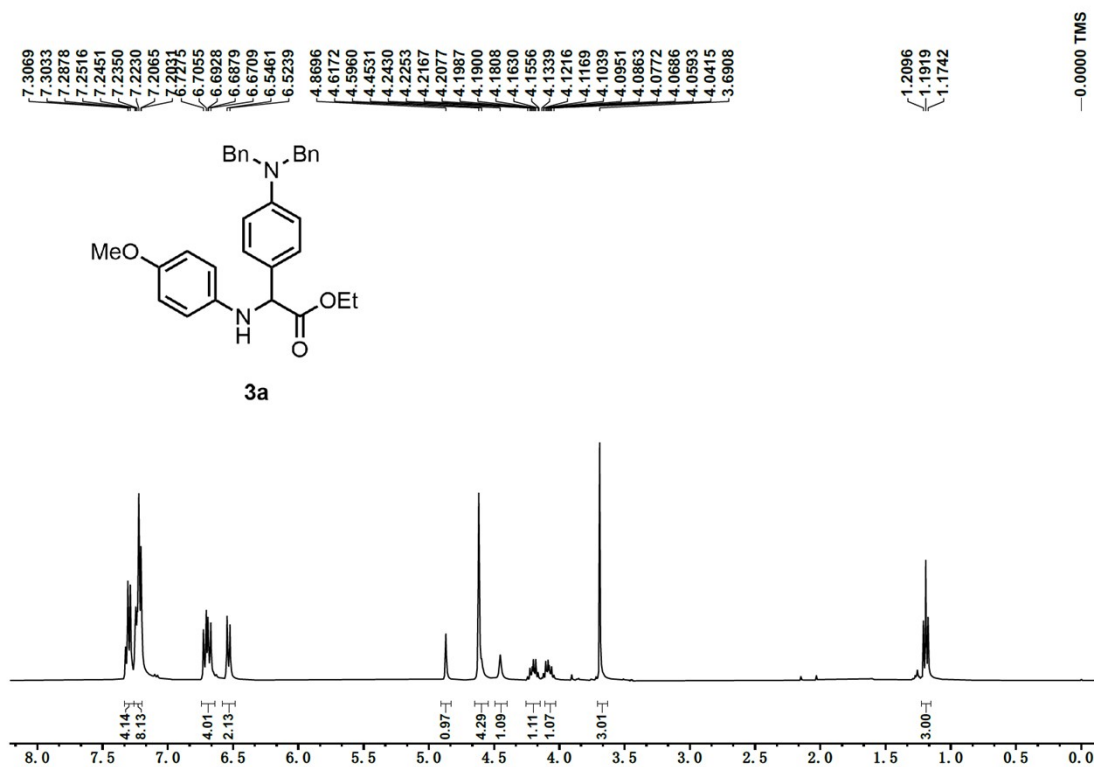
Entry	Solvent	Yield (%) ^b
1	CH ₃ OH	trace
2	THF	trace
3	DMF	trace
4	DMSO	trace
5	CHCl ₃	66
6	DCM	58
7	DCE	67
8	1,4-Dioxane	trace
9	Toluene	trace
10	Et ₂ O	trace
11	EtOAc	trace
12 ^c	CH ₃ CN	75
13 ^d	CH ₃ CN	86

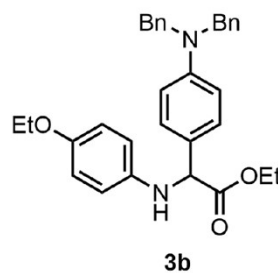
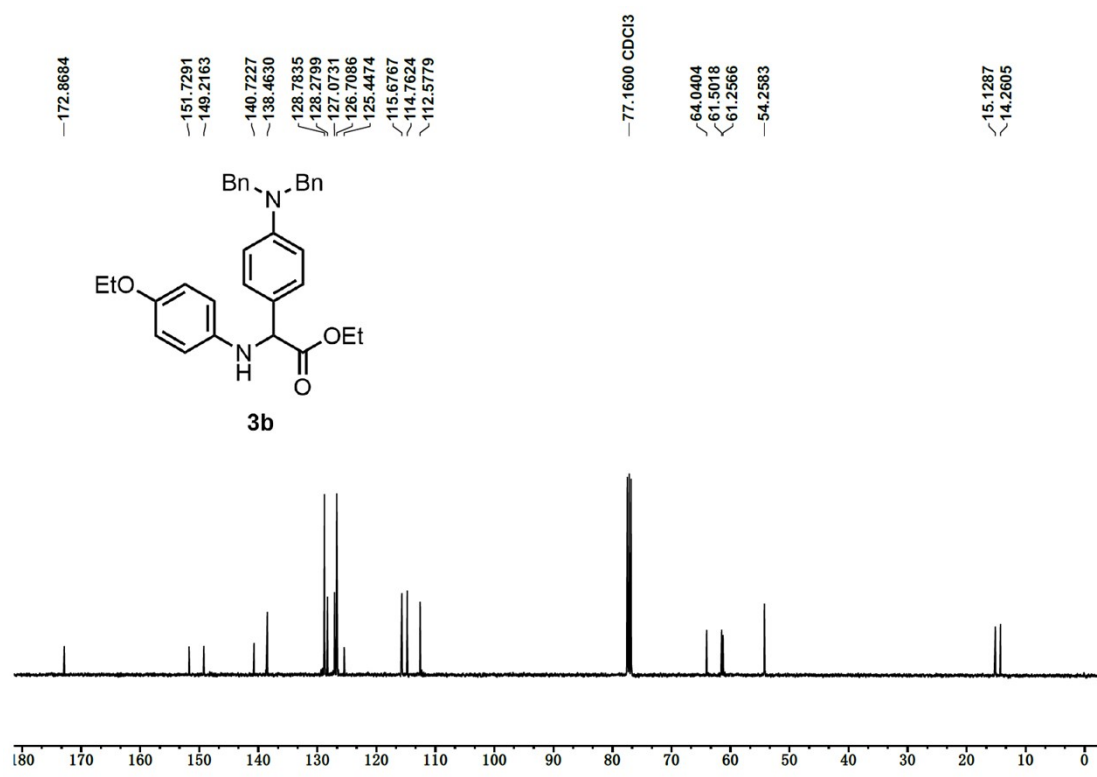
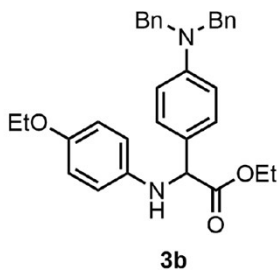
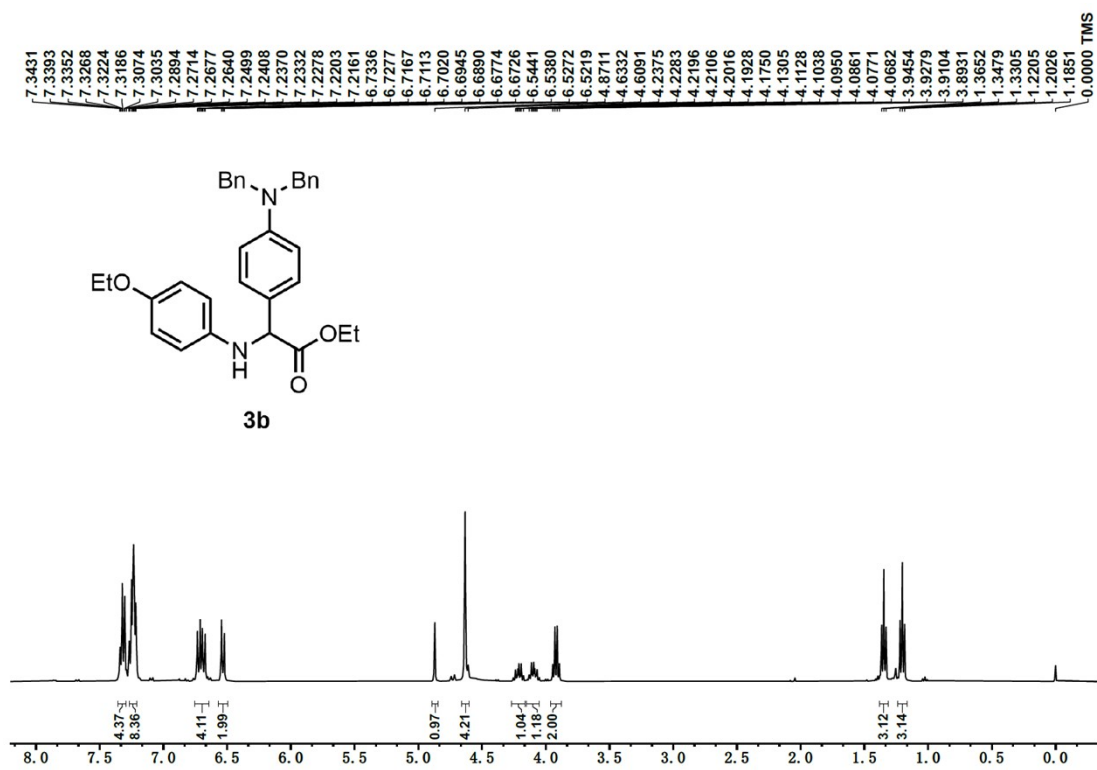
^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.11 mmol), Ce(OTf)₃ (30 mol%), solvent (2.0 mL), blue LED light irradiation under air at room temperature. ^b Yields were determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. ^c 1.0 mL CH₃CN was used. ^d 0.5 mL CH₃CN was used.

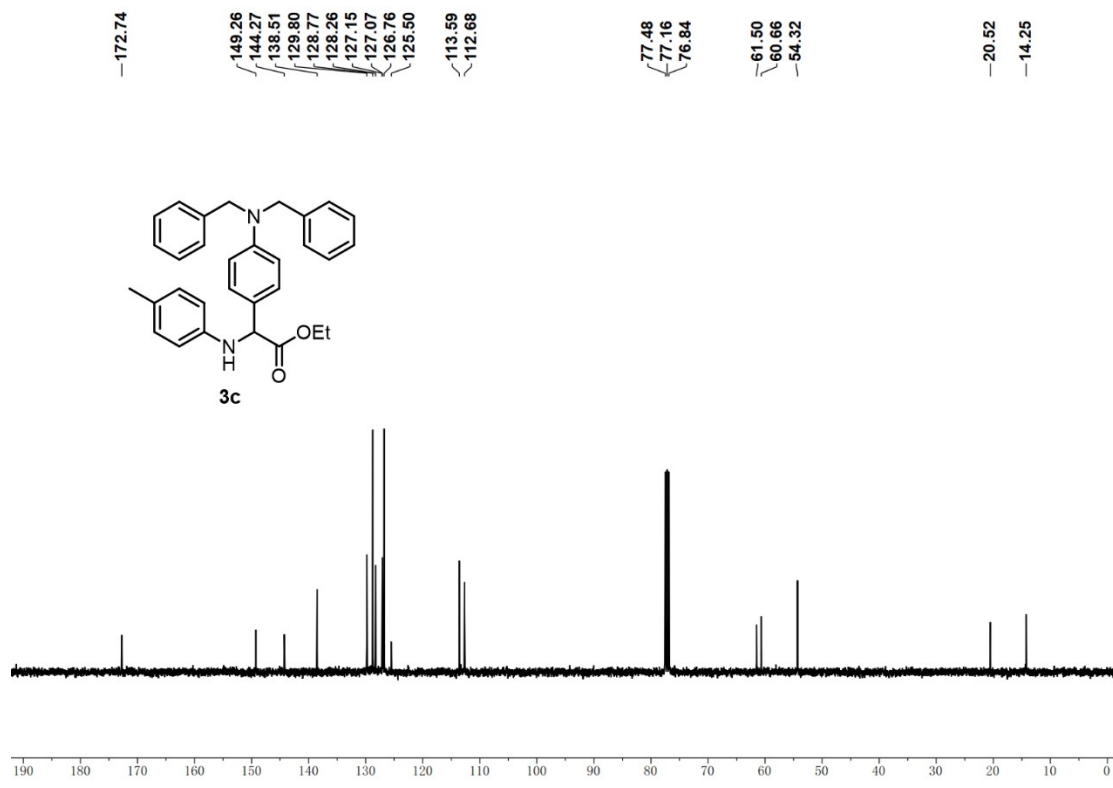
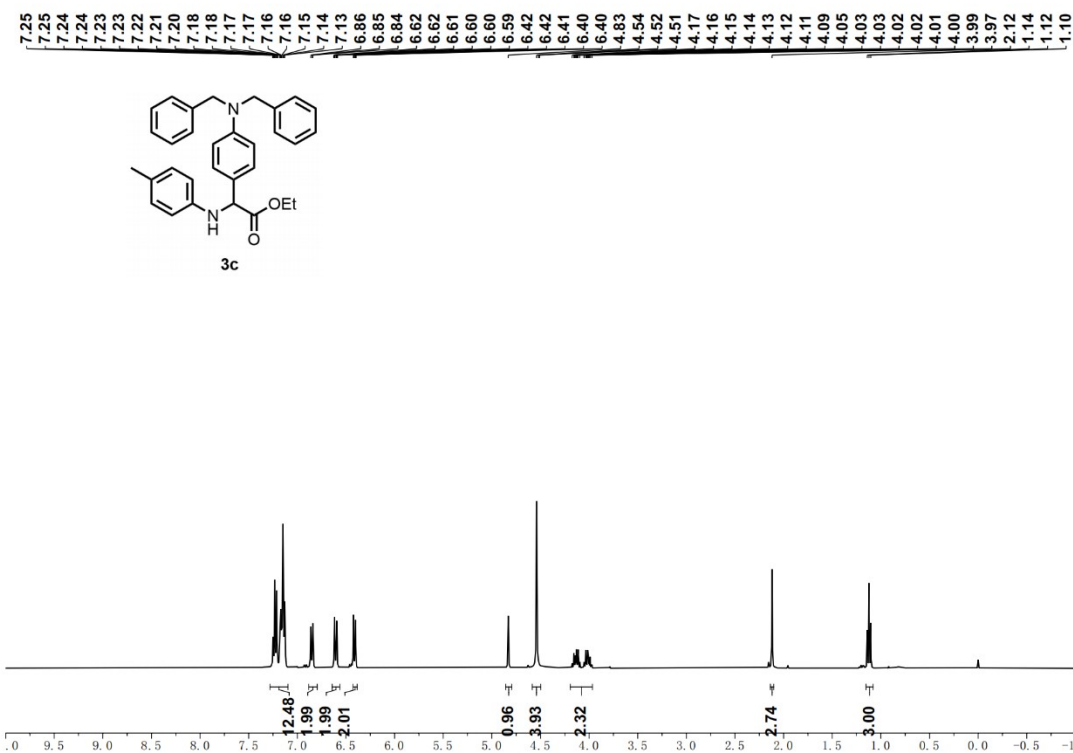
3. References

1. J. Xie and Z.-Z. Huang, *Angew. Chem., Int. Ed.*, 2010, **49**, 10181-10185.
2. R. Martín-Rapún, S. Sayalero and M. A. Pericàs, *Green Chem.*, 2013, **15**, 3295-3301.

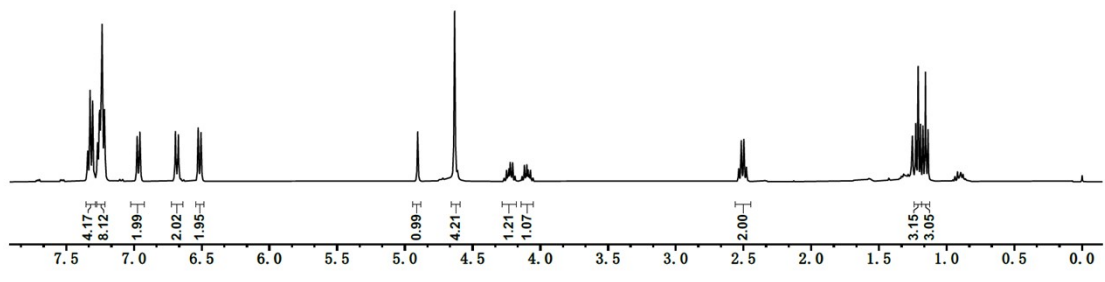
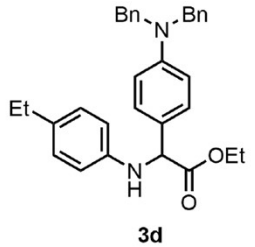
4. Copies of ^1H and ^{13}C NMR Spectra







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