Supporting Information

Highly Efficient and Selective Photocatalytic Hydrogenation of Functionalized Nitrobenzenes

Xiu-Jie Yang,[†] Bin Chen,*[,‡] Li-Qiang Zheng,*[,†] Li-Zhu Wu,*[,‡] and Chen-Ho Tung[†‡]

† Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, China

‡ Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, The Chinese Academy of Science, Beijing 100190, China

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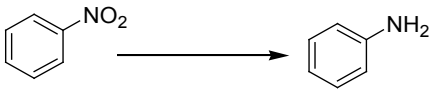
Detailed experimental

Procedure for the photocatalytic reduction of nitrobenzene: Appropriate amount ethanol (3 mL) was used to dissolve nitrobenzenes (0.2 mmol) as their solubility in water was poor (sonication or heating for a few minutes was employed to make nitrobenzenes to solubilize in ethanol if necessary). Then water (2 mL), triethanolamine (TEOA) and EY (1 mol %) were added in sequence to make a homogeneous solution. The pH value of the solution was adjusted to 8.50 using concentrated HCl solution. Before irradiation, the samples were deaerated by bubbling argon for 30 min. For the photoirradiation, a 3 W LED (λ = 525 nm, green) light source was used. Aliquots of 20 μL of photocatalytic solutions were syringed out at different time periods and diluted by a fractor of 150 in EtOH/H_2O (3:2). UV-Vis spectra were obtained to monitor the reaction process. After irradiation, the mixture was extracted with $CHCl_3$ (3 × 20 mL). The combined organic phase was washed with 5% $NaHCO_3$ aqueous solution (3 × 20 mL) and saturated NaCl solution (3 × 20 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give the final products for further identification. The photocatalytic products were then characterized by using ^{1}H NMR, EI-MS, and GC spectrometers.

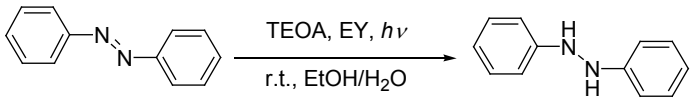
Table S1. Photocatalytic reaction of nitrobenzene.[a]



Entry	TEOA[b]	pH	t / h[c]	Conversion[d][%]
1[e]	20	8.5	0	0
2	0	8.5	8	0
3[f]	20	8.5	8	0
4	20	8.5	8	100
5	20	4	8	0
6	20	7	8	14
7	20	10	8	99
8	20	12	8	94
9	6	8.5	8	19
10	6	8.5	16	61
11	6	8.5	24	99
12	3	8.5	24	35
13	3	8.5	40	92

[a] Nitrobenzene: 0.2 mmol; EtOH/H_2O (3:2): 5 mL; room temperature; EY: 1 mol %; LED (green light, 525 nm). [b] Equivalent of TEOA. [c] Irradiation time. [d] Determined by ^{1}H NMR ($CDCl_3$). [e] Stirred for 8 h in dark. [f] Without EY.

Table S2. Photocatalytic reduction of azobenzene.[a]



Entry	TEOA / equiv.	t / h[b]	Yield[c][%]
1	6	24	2
2	6	120	80
3	20	8	48

[a] Azobenzene amount: 0.2 mmol; EY: 1 mol %; $EtOH/H_2O$ (3:2): 5 mL; LED (green light, 525 nm); room temperature; pH = 8.50. [b] Irradiation time. [c] Determined by ^1H NMR ($CDCl_3$).

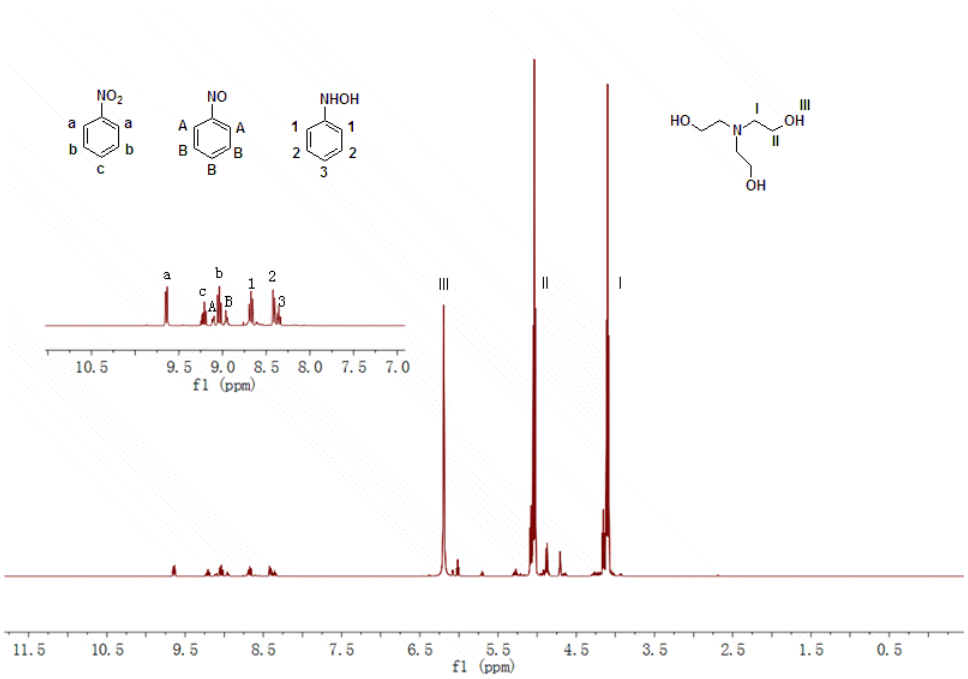


Figure S1. ^1H NMR spectroscopy of nitrobenzene (0.032 mmol), EY (1 mol%), TEOA (6 equiv.) in 0.8 mL CD_3OD/D_2O (3:2) taken at the initial time of irradiation (green LED, 525 nm).

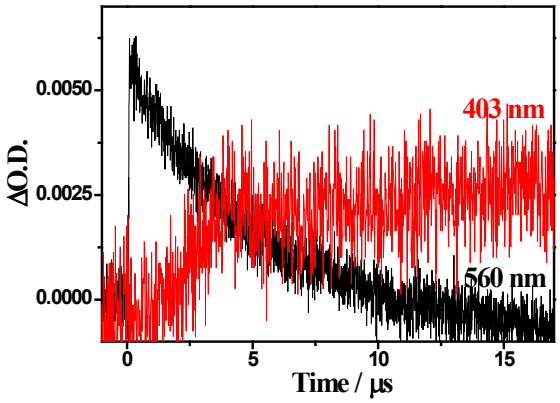


Figure S2. Decay and rise-time profiles at 560 nm and 403 nm respectively for the solution of EY (1×10^{-5} M) and TEOA (2.4×10^{-3} M) in EtOH/H_2O (3:2) upon excitation with pulse 532 nm light.

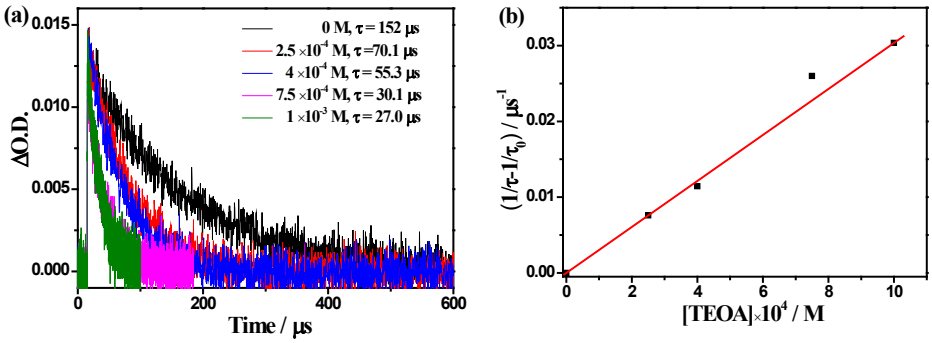
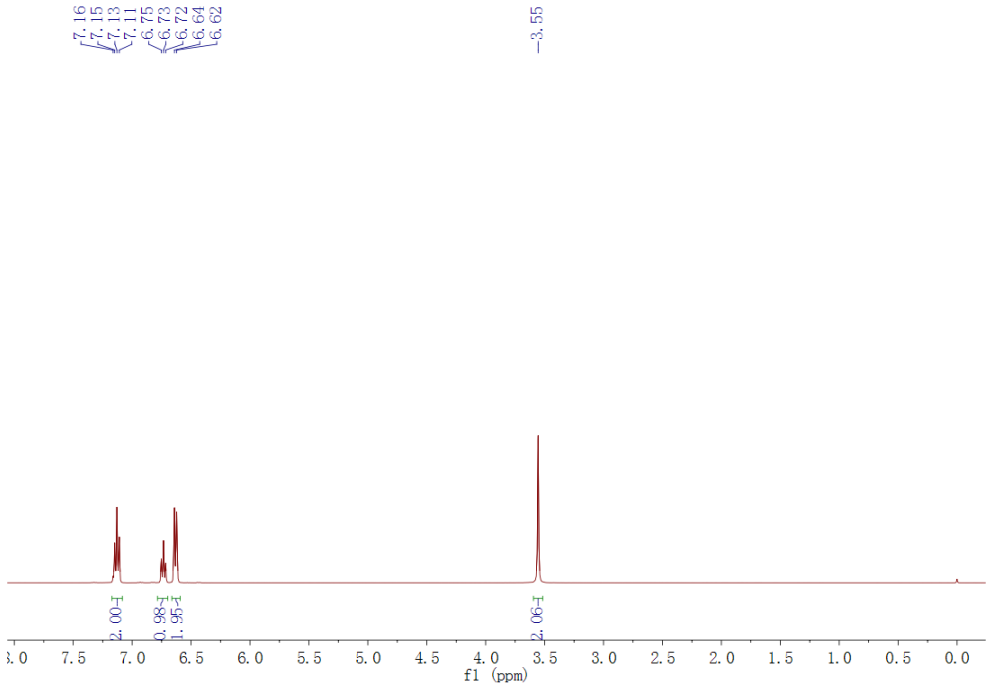


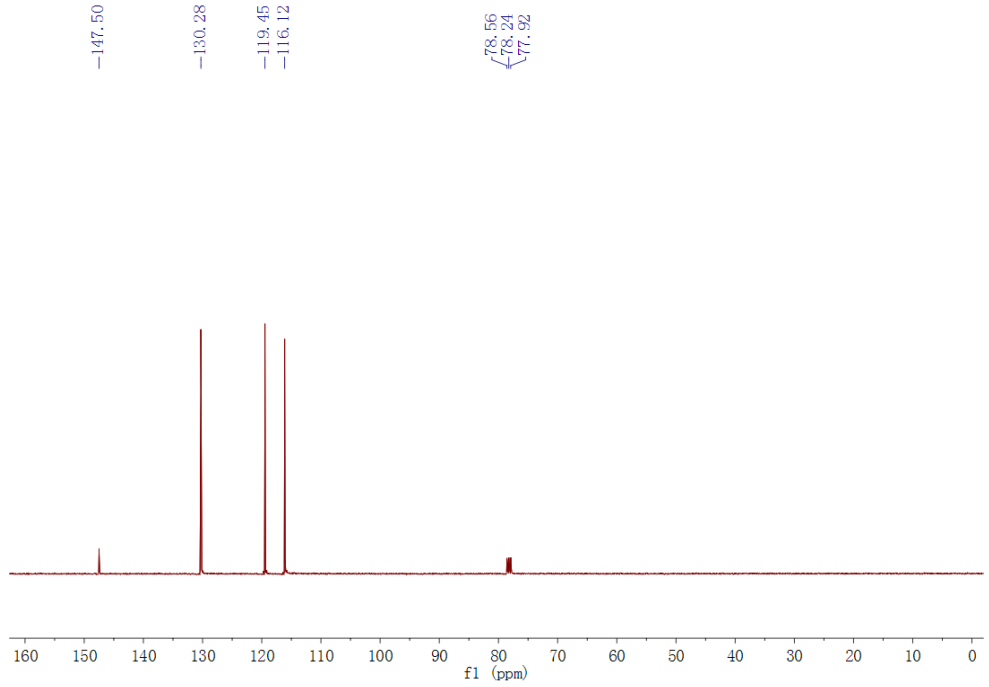
Figure S3. (a) Kinetic traces at 560 nm obtained on laser photolysis of EY (1×10^{-5} M) and TEOA at different concentrations ranging from 0 M to 1×10^{-3} M in deaerated EtOH/H_2O (3:2); (b) Stern-Volmer plots.

(a) aniline

^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.14 (dd, *J* = 14.4, 6.9 Hz, 2H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 2H), 3.55 (s, 2H).

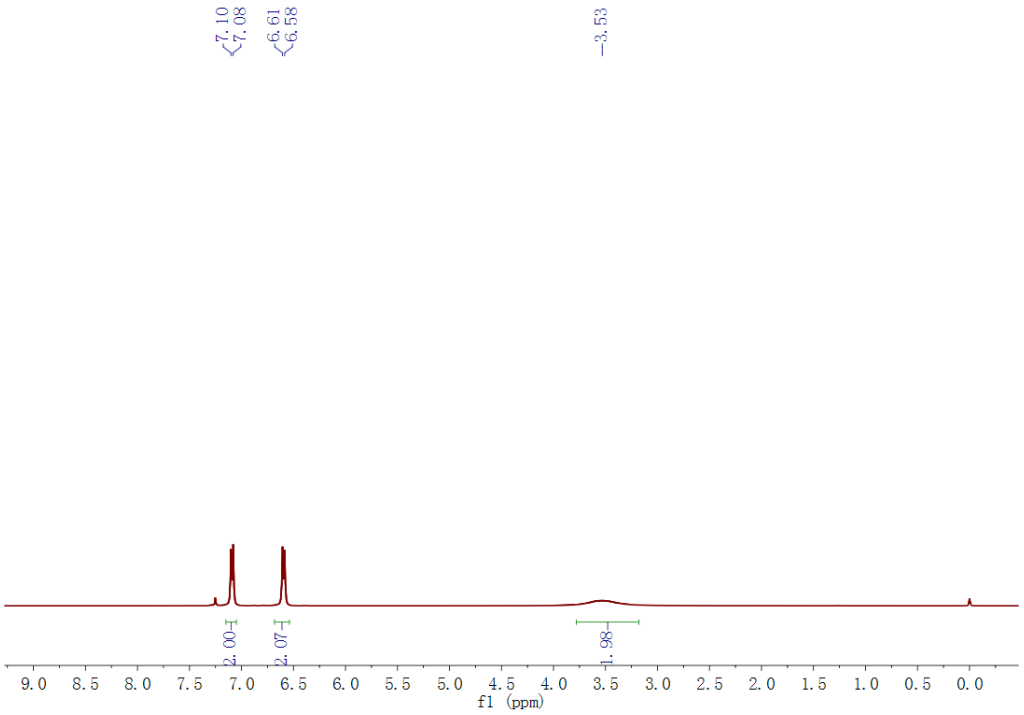


^{13}C NMR ($CDCl_3$, 100MHz): δ = 147.5, 130.3, 119.5, 116.1.

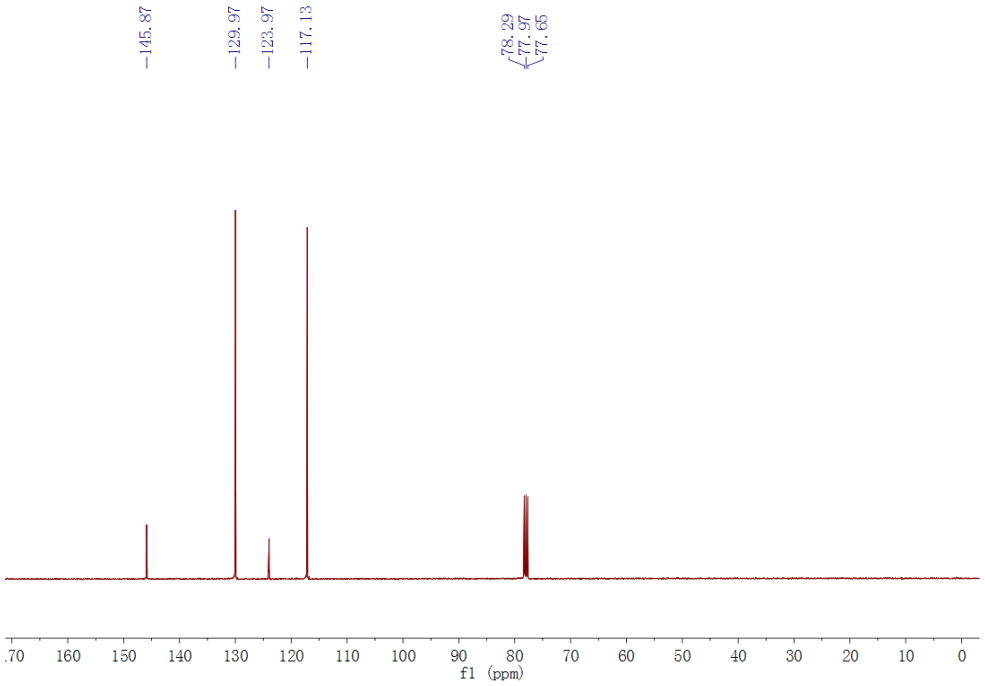


(b) 4-chloroaniline

^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.09 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 3.53 (s, 2H).

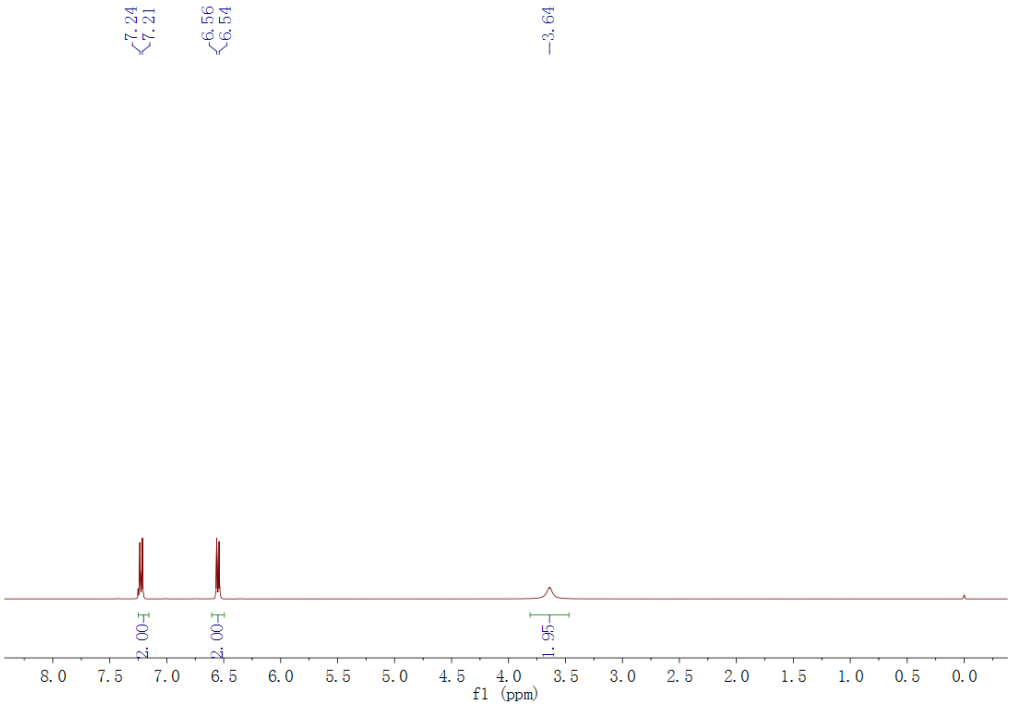


^{13}C NMR ($CDCl_3$, 100MHz): δ = 145.9, 129.9, 123.9, 117.1.

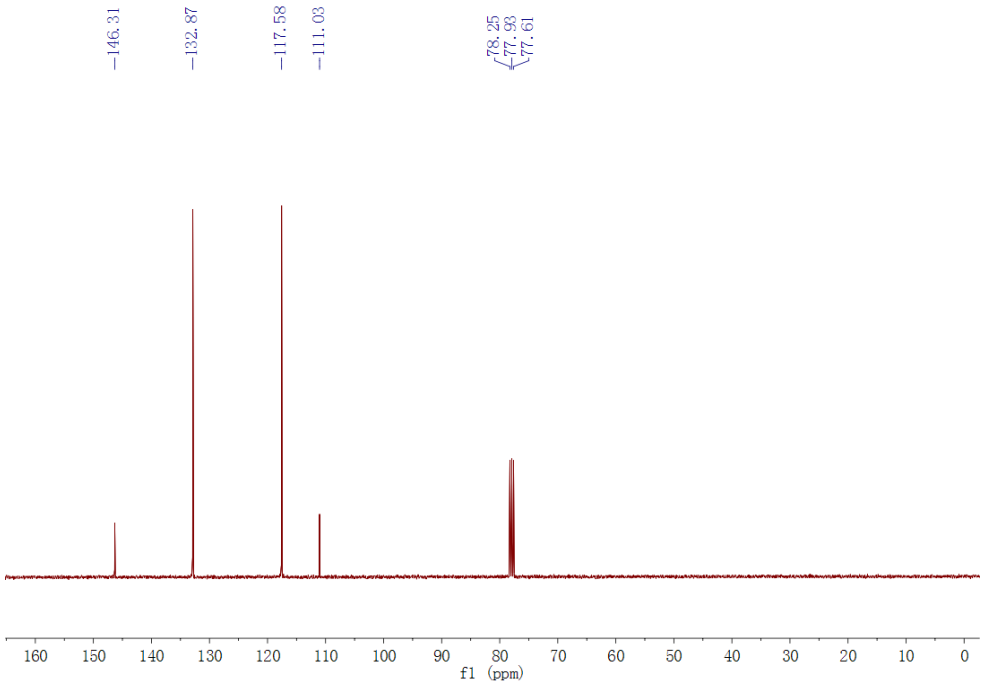


(c) 4-bromoaniline

^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.22 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 3.64 (s, 2H).

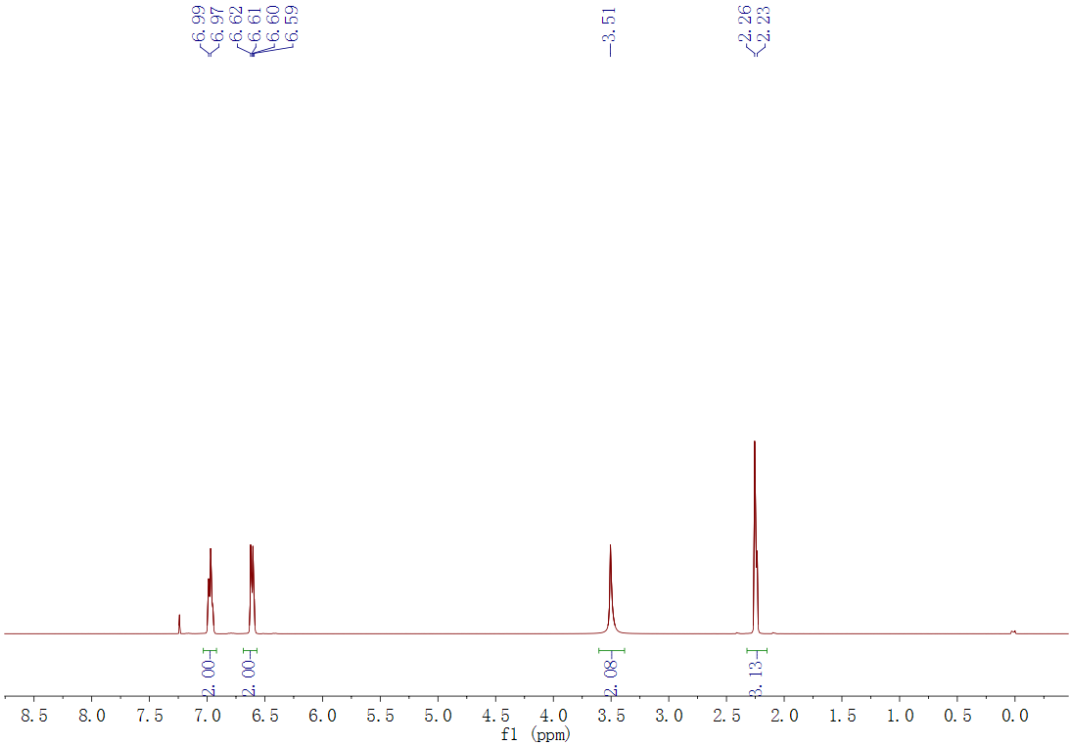


^{13}C NMR ($CDCl_3$, 100MHz): δ = 146.3, 132.9, 117.6, 111.0.

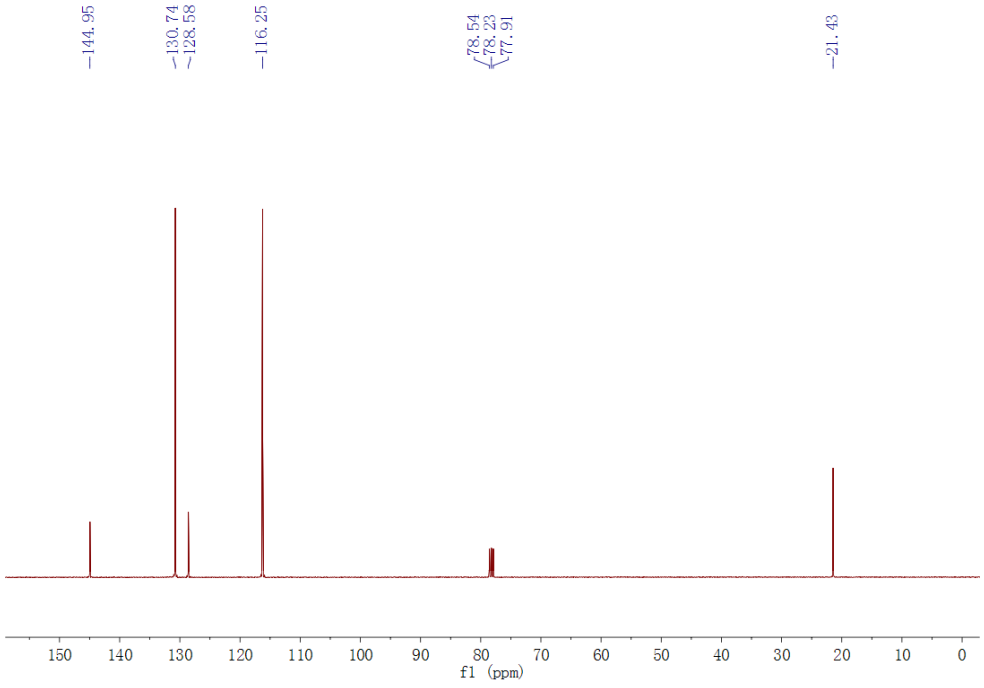


(d) 4-methylaniline

^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.98 (d, *J* = 7.2 Hz, 2H), 6.61 (dd, *J* = 8.1, 4.5 Hz, 2H), 3.51 (s, 2H), 2.25 (d, *J* = 8.7 Hz, 3H).

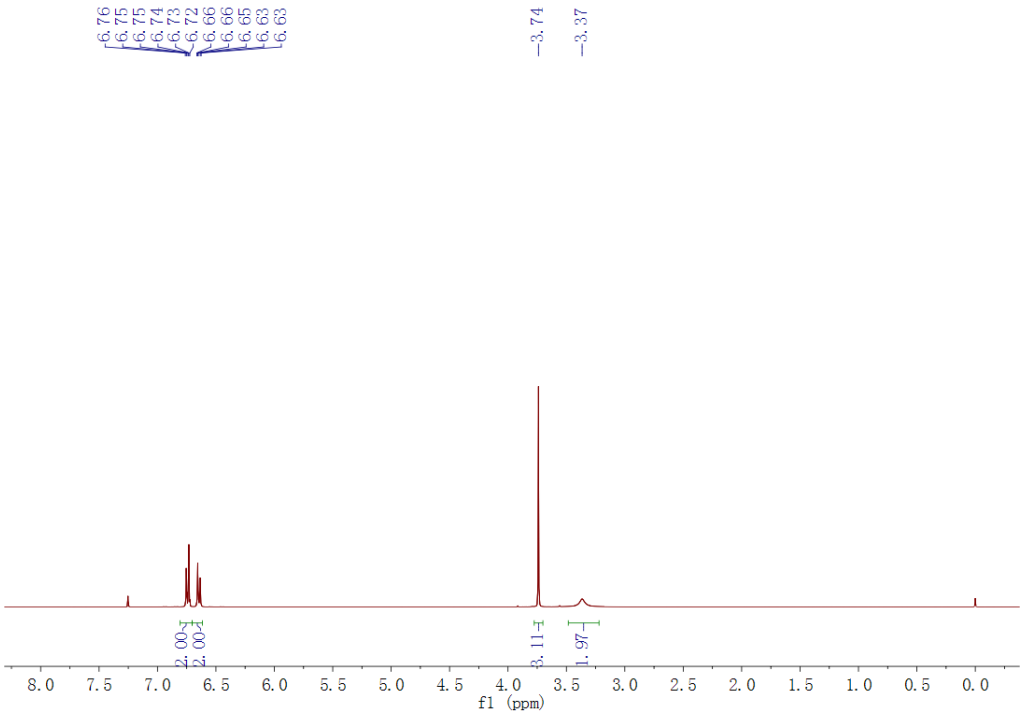


^{13}C NMR ($CDCl_3$, 100MHz): δ = 144.9, 130.7, 128.6, 116.3, 21.4.

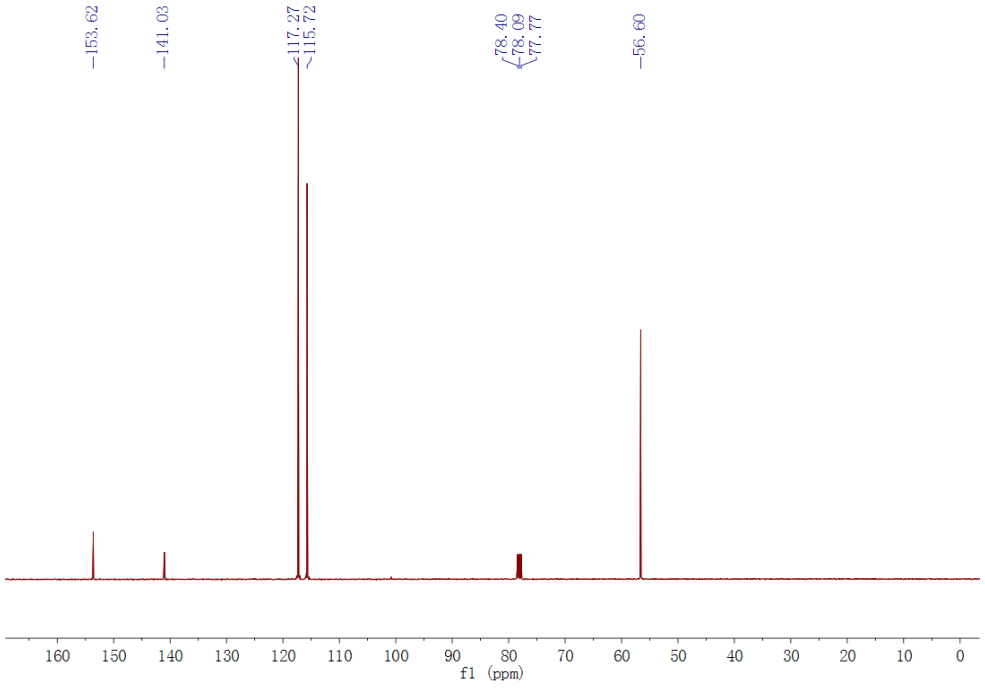


(e) 4-methoxyaniline

^{1}H NMR ($CDCl_3$, 400MHz): δ = 6.79 – 6.70 (m, 2H), 6.69 – 6.58 (m, 2H), 3.74 (s, 3H), 3.37 (s, 2H).

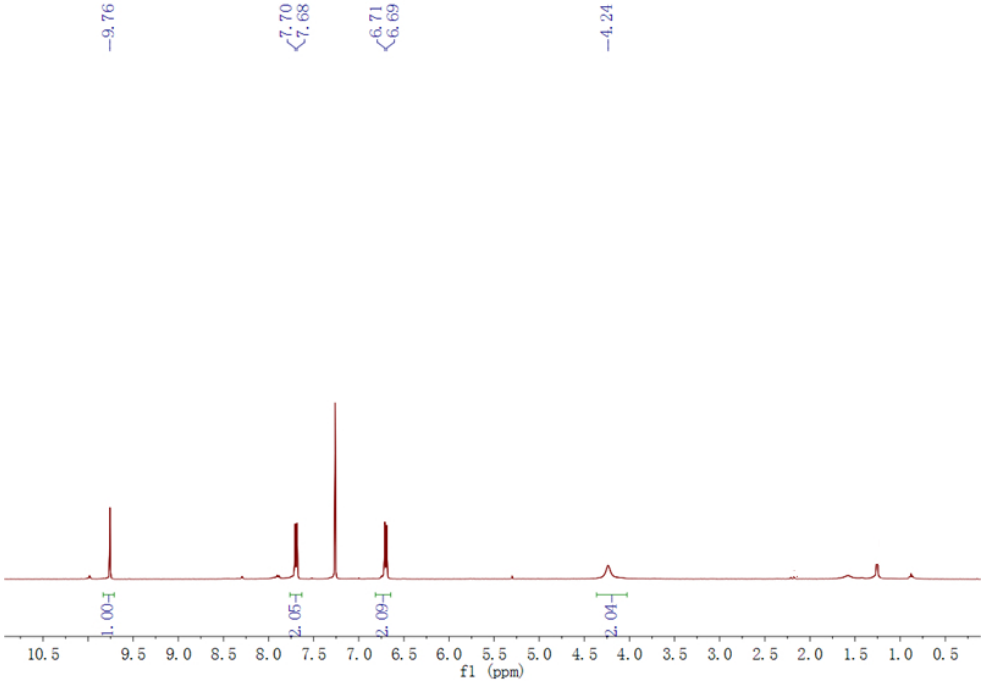


^{13}C NMR ($CDCl_3$, 100MHz): δ = 153.6, 141.0, 117.3, 115.7, 56.6.

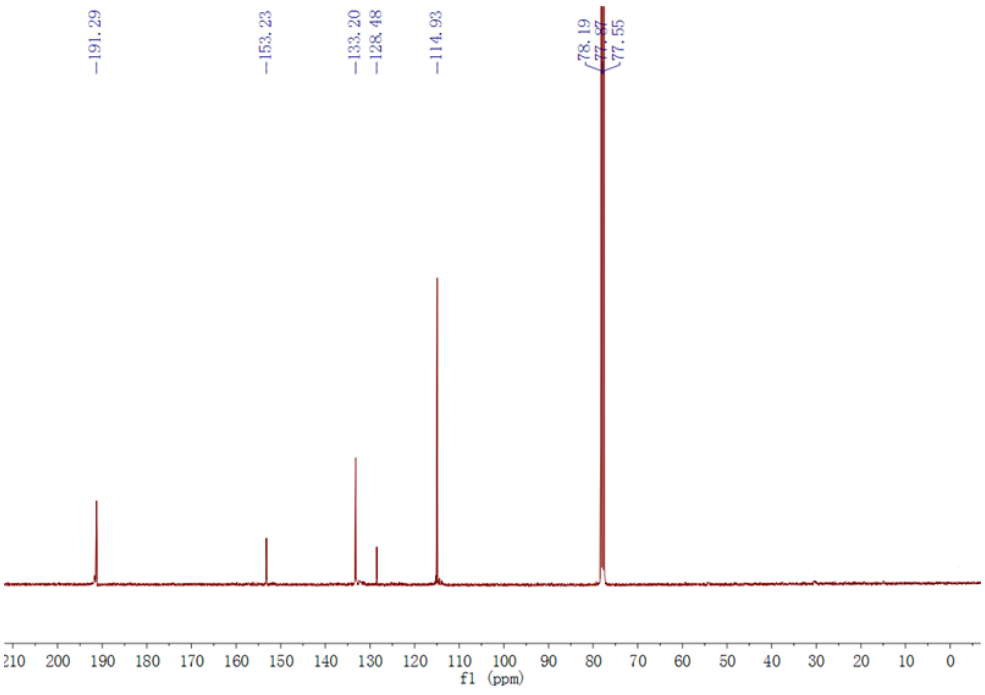


(f) 4-aminobenzaldehyde

^{1}H NMR ($CDCl_3$, 400MHz): δ = 9.76 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 4.24 (s, 2H).

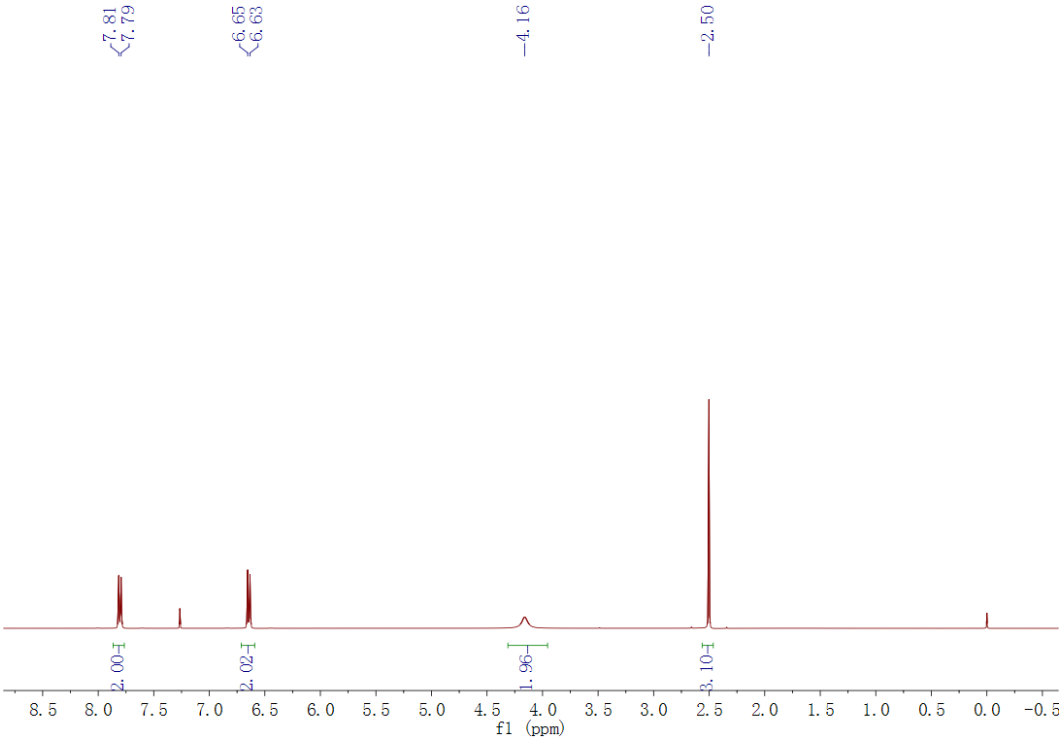


^{13}C NMR ($CDCl_3$, 100MHz): δ = 191.3, 153.2, 133.2, 128.5, 114.9.

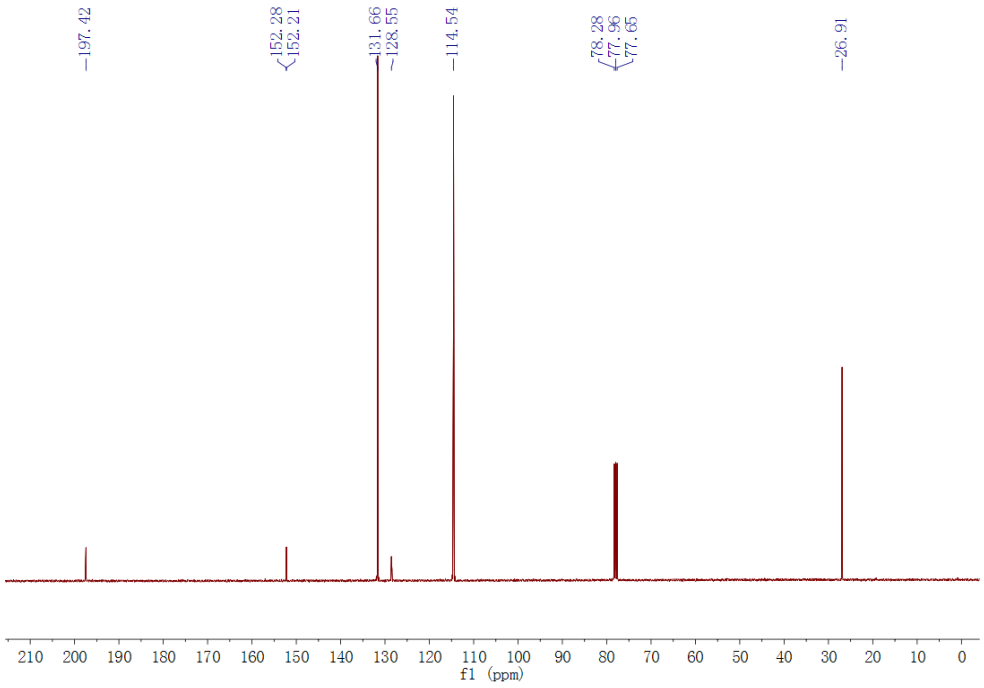


(g) 4-aminoacetophenone

^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.80 (d, *J* = 8.4 Hz, 2H), 6.64 (d, *J* = 8.5 Hz, 2H), 4.16 (s, 2H), 2.50 (s, 3H).

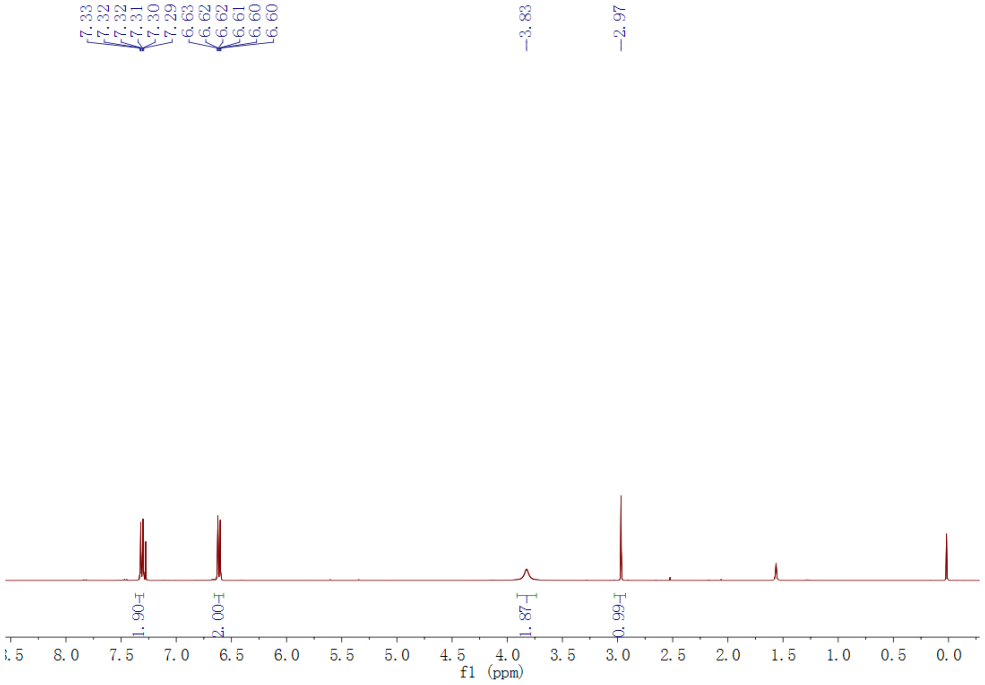


^{13}C NMR ($CDCl_3$, 100MHz): δ =197.4, 152.3, 152.2, 131.6, 128.6, 114.5, 26.9.

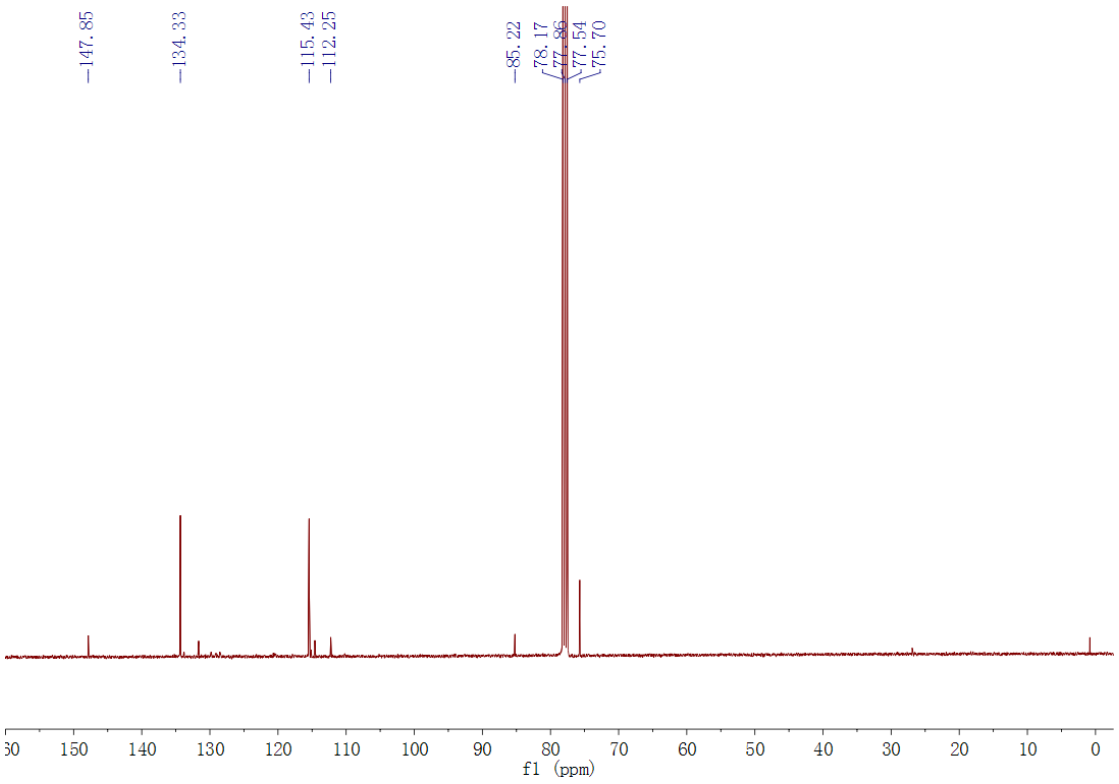


(h) 4-ethnylaniline

^{1}H NMR ($CDCl_3$, 400MHz): δ =7.35 – 7.29 (m, 2H), 6.65 – 6.56 (m, 2H), 3.83 (s, 2H), 2.97 (s, 1H).

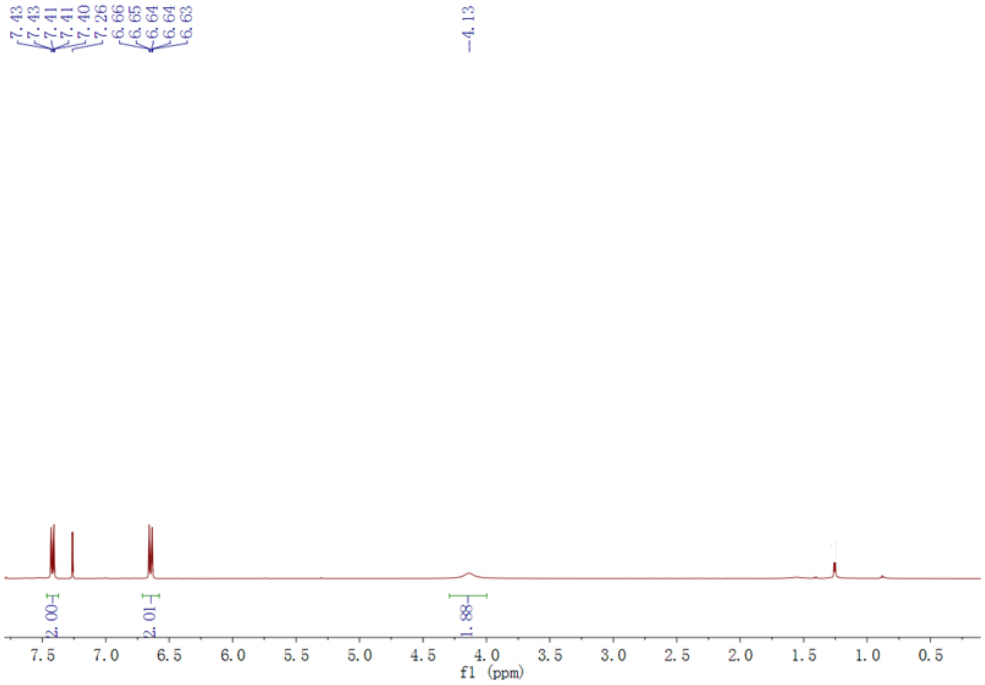


^{13}C NMR ($CDCl_3$, 100MHz): δ = 147.9, 134.3, 115.4, 112.3, 85.2, 75.7.

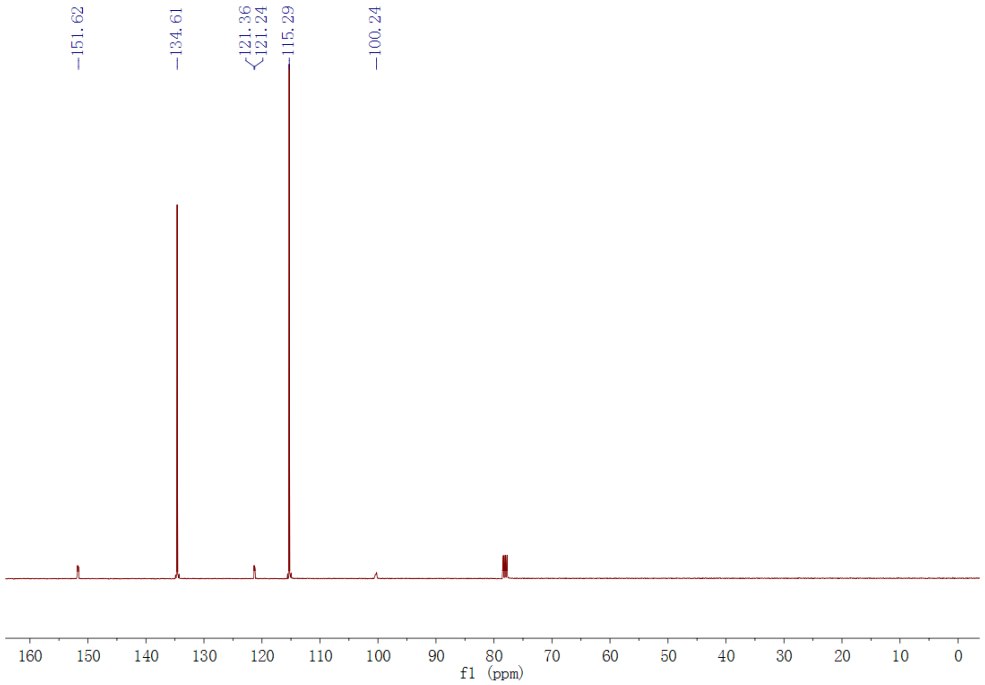


(i) 4-aminobenzonitrile

^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.46 – 7.37 (m, 2H), 6.70 – 6.61 (m, 2H), 4.13 (s, 2H).

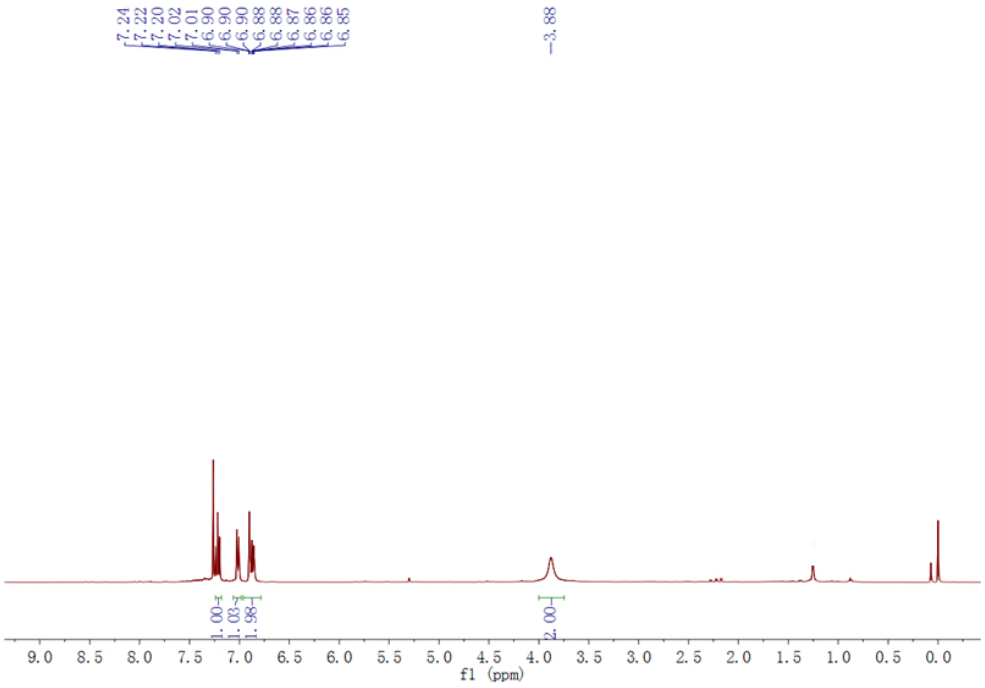


^{13}C NMR ($CDCl_3$, 100MHz): δ = 151.6, 134.6, 121.4, 121.2, 115.3, 100.2.

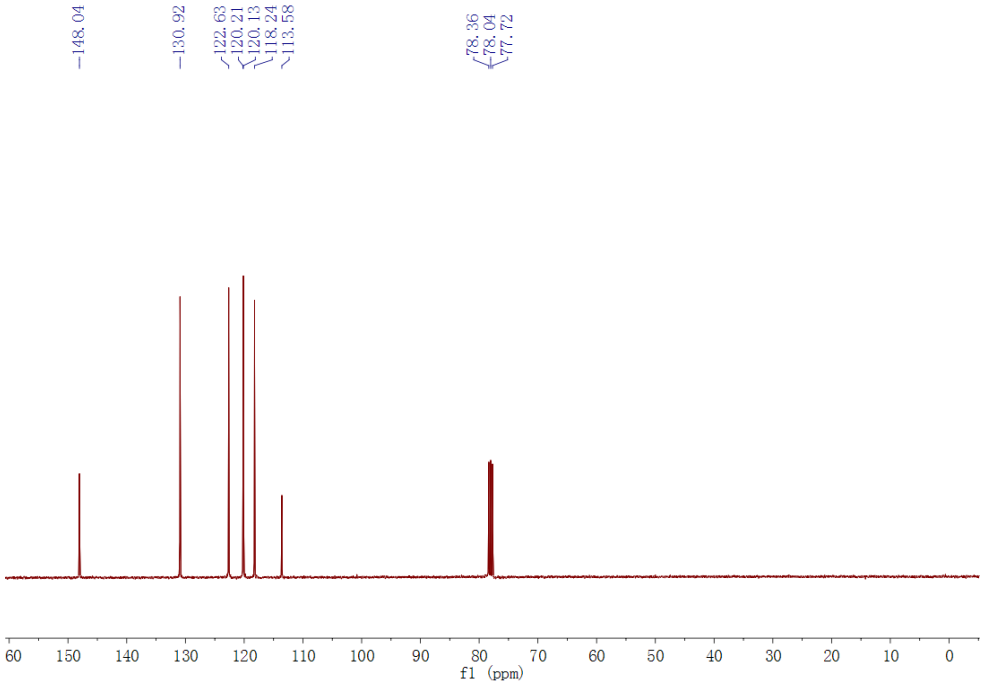


(j) 3-aminobenzonitrile

^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.22 (t, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.93 – 6.82 (m, 2H), 3.88 (s, 2H).

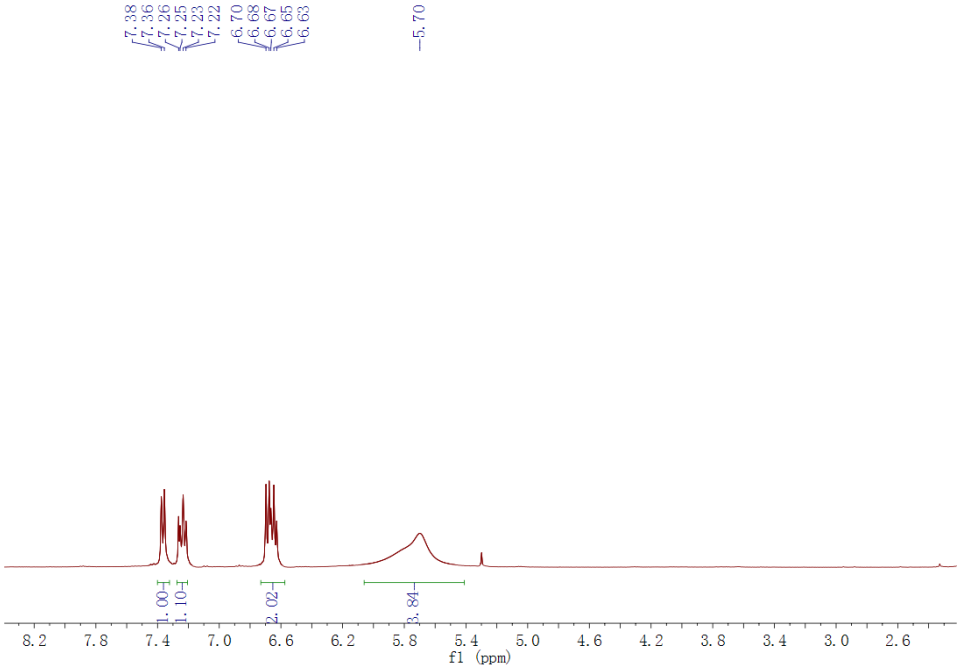


^{13}C NMR ($CDCl_3$, 100MHz): δ = 148.0, 130.9, 122.6, 120.2, 120.1, 118.2, 113.6.



(k) 2-aminobenzamide

^{1}H NMR ($CDCl_3$, 400MHz): δ = 7.37 (d, *J* = 7.9 Hz, 1H), 7.24 (dd, *J* = 13.7, 5.5 Hz, 1H), 6.72 – 6.61 (m, 2H), 5.70 (s, 4H).



^{13}C NMR ($CDCl_3$, 100MHz): δ = 172.5, 150.3, 133.9, 128.9, 118.3, 117.3, 114.9.

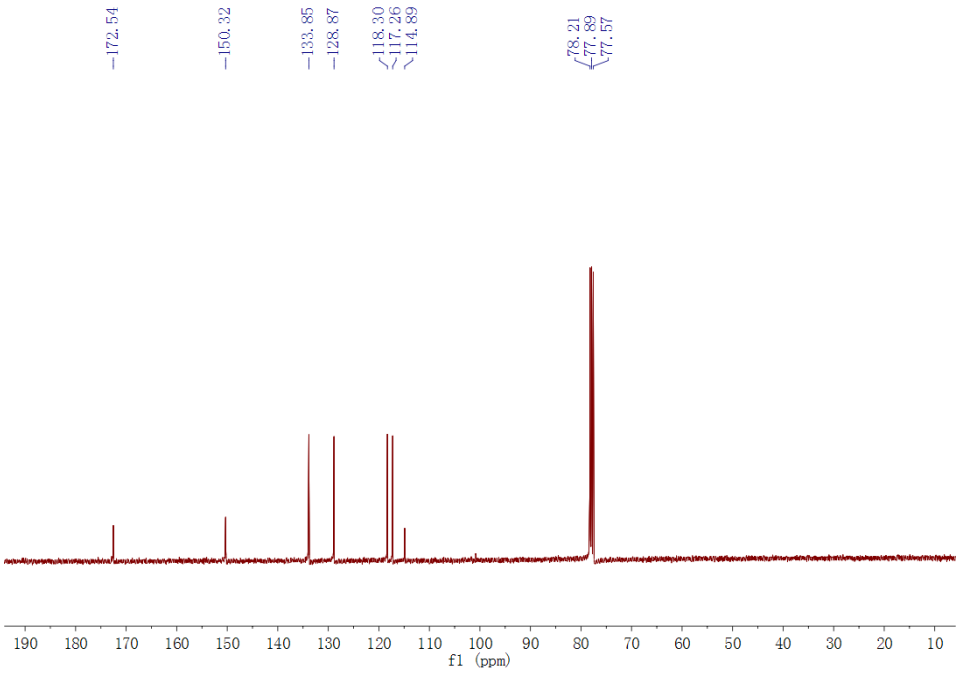


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of the photocatalytic products: (a) aniline; (b) 4-chloroaniline; (c) 4-bromoaniline; (d) 4-methylaniline; (e) 4-methoxyaniline; (f) 4-aminobenzaldehyde; (g) 4-aminoacetophenone; (h) 4-ethnylaniline; (i) 4-aminobenzonitrile; (j) 3-aminobenzonitrile; (k) 2-aminobenzamide.