Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Self-detachable protecting group function of CO_2 in the electrochemical reduction of aryl azides

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General Information

All glassware was oven dried at 100 ºC for hours and cooled down under vacuum. Anhydrous DMF and MeCN was prepared by distillation from CaH_2. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292C) (made in China), the Mg (1×1×0.05 cm^3), Pt (1×1×0.02 cm^3), Zn (1×1×0.05 cm^3), Al (1×1×0.05 cm^3), were purchased from Xuzhou Xinke Instrument and Meter Co. LTD. The thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Purification of reaction products was carried out by flash chromatography on silica gel (300~400 mesh). ^{1}H NMR spectra were recorded at 500 MHz, ^{13}C NMR spectra were recorded at 125 MHz, and in $CDCl_3$ or DMSO-d_6 (containing 0.03% TMS) solutions with Bruker Advance III spectrometers. ^{1}H NMR spectra were recorded with Me_4Si (δ = 0.00), $CDCl_3$ (δ = 7.26) or DMSO-d_6 (δ = 2.50) as the internal reference and ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.16) or DMSO-d_6 (δ = 39.52) as the internal reference. High-resolution mass spectra were obtained using a Bruker Maxis Impact mass spectrometer with a TOF (for ESI) analyzer.

The substrates **1a-z** are known compounds and are synthesized based on previous reports.[1] The spectroscopic data are in agreement with that previously reported.

1aa were purchased from Energy Chemical Co., Ltd.

CV experiments:

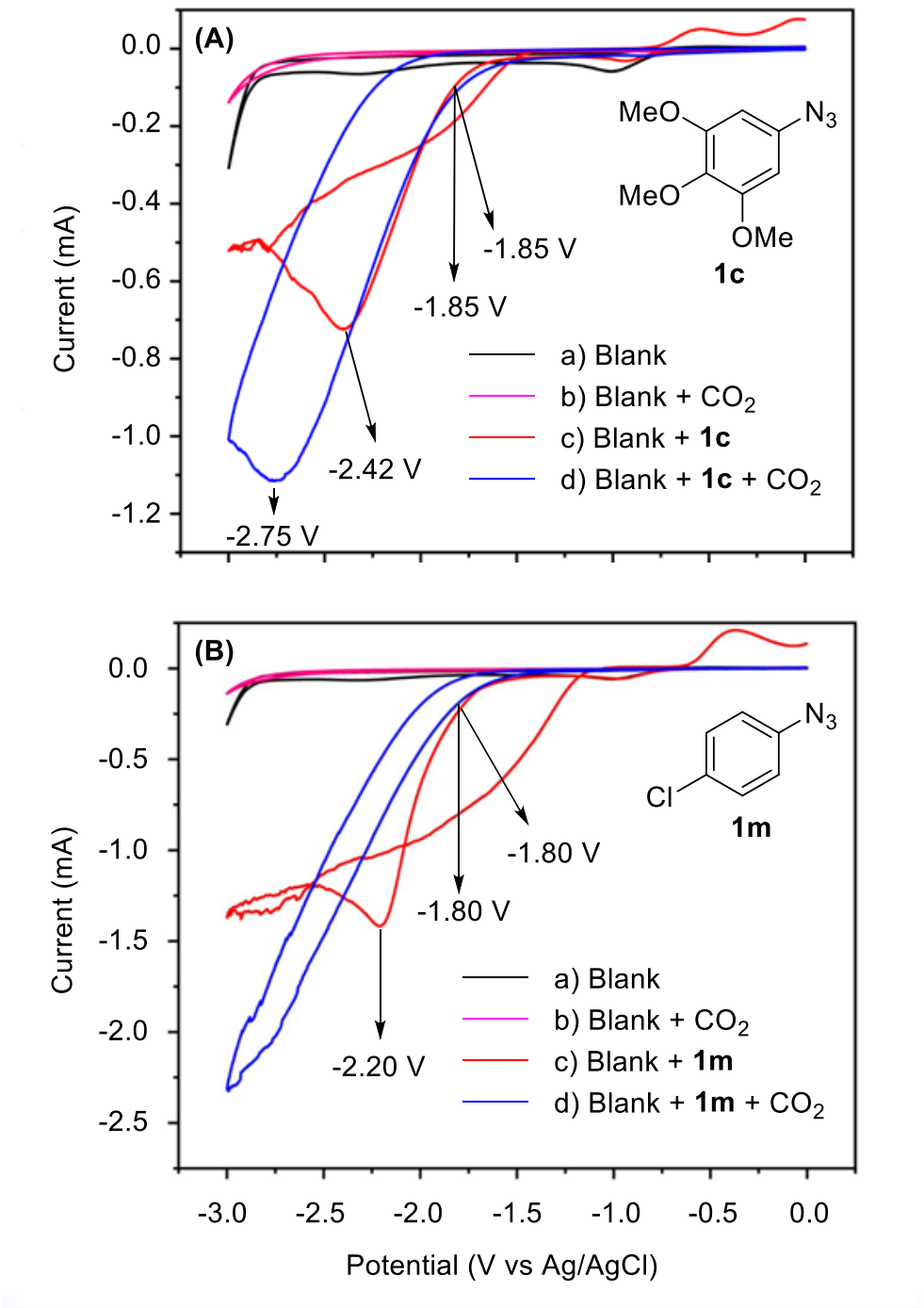
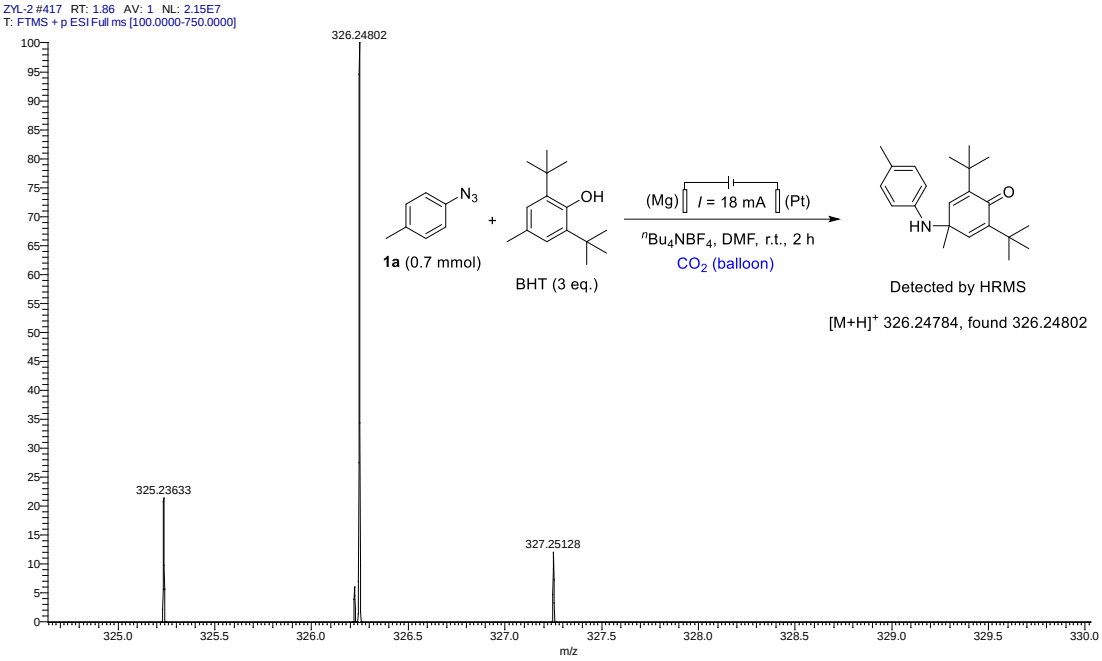
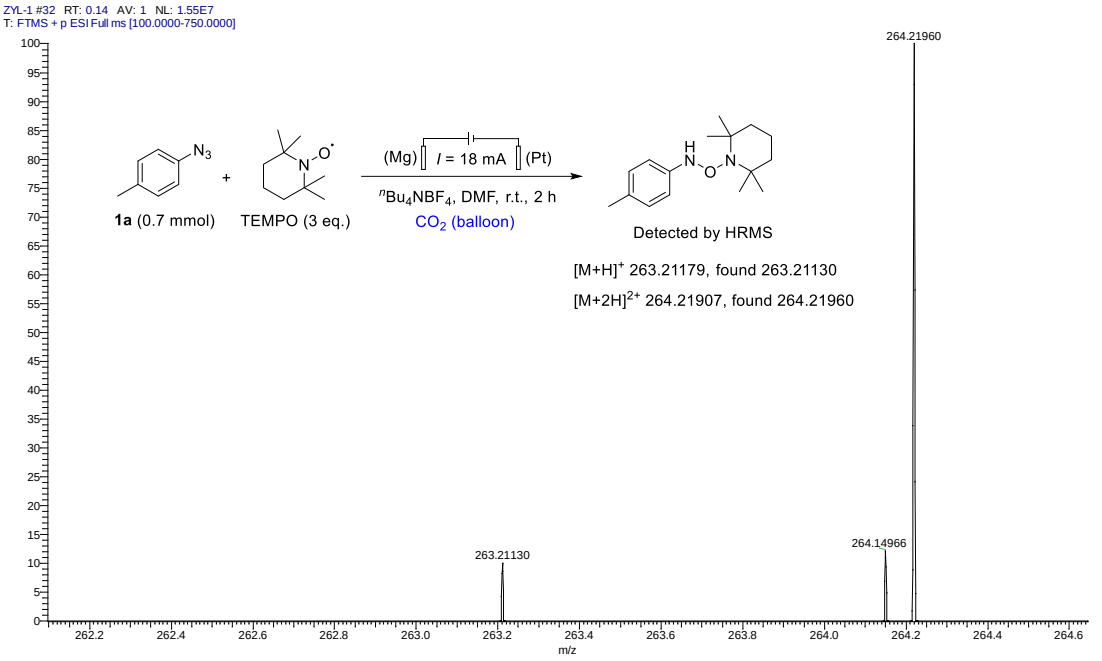


Figure S1. Cyclic voltammograms at grass carbon as work electrode, Pt plate (1×1 cm^2) as counter electrode and Ag/AgCl (KCl) as reference electrode in 0.1 M $^{n}Bu_4NBF_4$, DMF (5 mL), scan rate: 100 mV/s. (a) back-ground, 0.1 $^{n}Bu_4NBF_4$; (b) with CO_2 saturated; (c) **1c** or **1m** (0.7 mmol); (d) **1c** or **1m** (0.7 mmol) + CO_2 saturated.

Radical trapping experiments





X-ray crystal structure of **3b**

The displacement ellipsoids are drawn at the 50% probability level. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the mixed solution of CH_2Cl_2/petroleum ether (1/3, v/v). Supplementary crystallographic data was deposited at the Cambridge Crystallographic Data Centre (CCDC) under the number CCDC 2305738 (**3b**) and can be obtained free of charge from via www.ccdc.cam.ac.uk/data_request.cif.

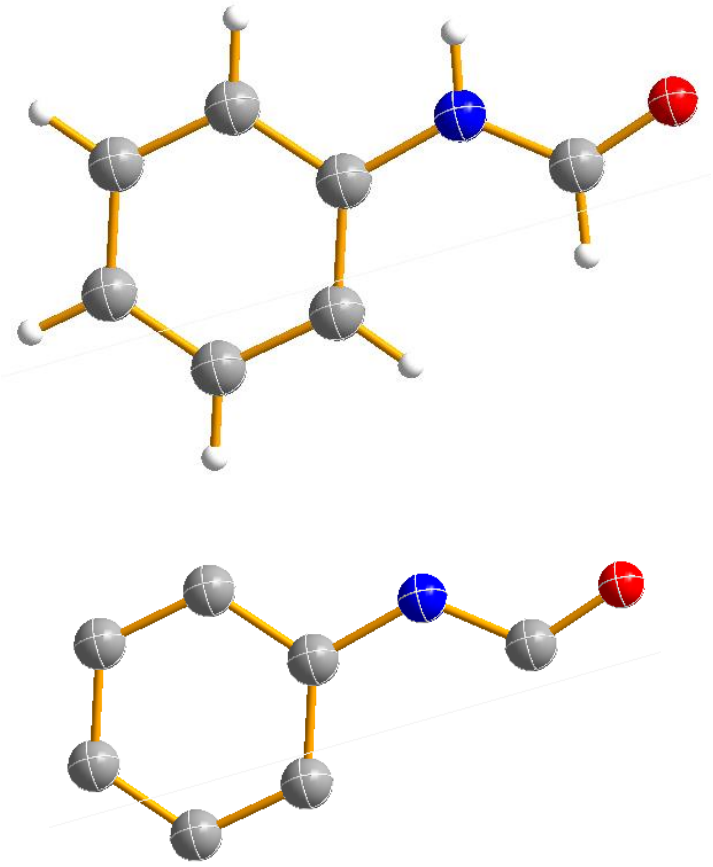
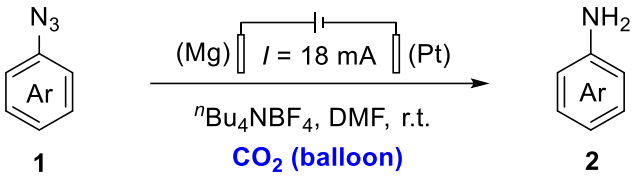


Figure S2. X-ray ORTEP illustration of *N*-phenylformamide (**3b**) (50% probability ellipsoids)

Table S4. Crystal data and structure refinement for **3b**.

Identification code	lmh1229	
Empirical formula	$C_{14}H_{14}N_2O_2$	
Formula weight	242.27	
Temperature	298 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	I 1 2/a 1	
Unit cell dimensions	a = 14.764(3) Å	α= 90 °
	b = 6.1667(13) Å	β= 95.238(16) °
	c = 28.554(4) Å	γ = 90 °
Volume	2588.8(8) $Å^3$	
Z	8	
Density (calculated)	1.243 mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	1024	
Theta range for data collection	2.8400 to 20.9880 °	
Index ranges	-19<=h<=19, -8<=k<=5, -29<=l<=38	
Reflections collected	9347	
Independent reflections	3041 [R(int) = 0.0498]	
Completeness to theta = 25.242 °	84.4 %	
Max. and min. transmission	0.844 and 1.000	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3041 / 0 / 163	
Goodness-of-fit on F^2	0.980	
Final R indices [I>2sigma(I)]	R1 = 0.0540, wR2 = 0.1184	
R indices (all data)	R1 = 0.1394, wR2 = 0.1482	
Largest diff. peak and hole	0.109 and -0.173 $e.Å^{-3}$	

Synthesis and characterization of 2



In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, **1** (0.7 mmol), and $^{n}Bu_4NBF_4$ (164.6 mg, 0.5 mmol) were added. The bottle was equipped with magnesium plate (1×1×0.05 cm^3) anode and platinum plate (1×1×0.02 cm^3) cathode. The vessel was evacuated and refilled with CO_2 five times. Then, DMF (5 mL, pre-deoxygenated by purging with high-purity CO_2 gas up to 5 mins) was added. The mixture was stirred (600 rpm) and electrolyzed at a constant current of 18 mA. After the reaction finished as monitored with TLC, the reaction mixture was diluted with water and extracted with ethyl acetate (15 mL×3). The organic layers were combined, washed with water, dried over Na_2SO_4, and concentrated in vacuum. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 1:1-20:1).

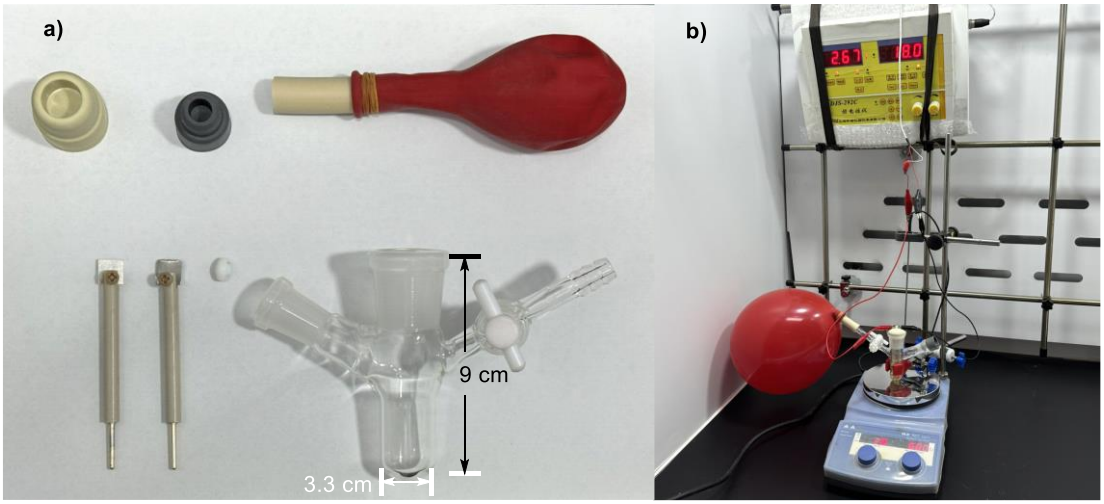
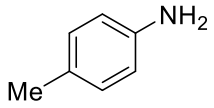


Figure S3. Set-up of Experiments (the photographs come from our lab). a) Experimental equipment. b) Reaction process diagram.



2a

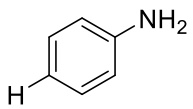
P-toluidine (2a)[2]

Compound **2a** was prepared in 90% yield (68 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 20/1); White solid; mp 41-42 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99 (d, J = 7.9 Hz, 2H), 6.63 (d, J = 8.2 Hz, 2H), 3.47 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 129.9, 127.9, 115.4, 20.6. Analytical data for **2a** was consistent with that previously reported.[2]

Note:

(a) If the sacrificial Mg anode was replaced with sacrificial reagent (e.g., DIPEA, 3 equiv, 2.1 mmol, 366 uL) and Pt anode (1×1×0.02 cm^3), **2a** can also be obtained, but the yield is reduced to 9% (7 mg).

(b) If the mode of CO_2 supply was changed to bubbling, the bubbling rate will affect the ratio of products **2a**/**3a**. Using DMF that is not pre-deoxygenated: when the bubbling rate of CO_2 is relatively fast, no formylation product **3a** is observed; when the rate of CO_2 bubbling is very slow (one bubble per ten seconds; inside diameter of needle: 1 mm), formylation product **3a** is observed (**2a/3a** = 6/1; **2a**, 66%, 50mg; **3a**, 11%, 10 mg).

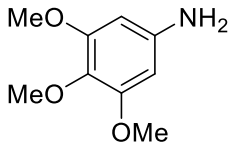


2b

Aniline (**2b**)[2]

Compound **2b** was prepared in 85% yield (55 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 20/1); Colorless oil; ^{1}H NMR (500 MHz,

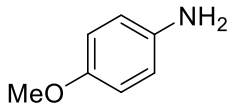
$CDCl_3$): δ 7.19-7.16 (m, 2H), 6.79-6.76 (m, 1H), 6.71-6.69 (m, 2H), 3.46 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.5, 129.4, 118.6, 115.2. Analytical data for **2b** was consistent with that previously reported.[2]



2c

3,4,5-Trimethoxyaniline (2c)[3]

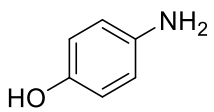
Compound **2c** was prepared in 79% yield (101 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 1/1); Yellow solid; mp 110-111 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 5.93 (s, 2H), 3.80 (s, 6H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.0, 143.0, 130.9, 92.8, 61.1, 56.0. Analytical data for **2c** was consistent with that previously reported.[3]



2d

4-Methoxyaniline (2d)[2]

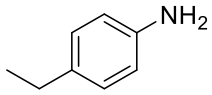
Compound **2d** was prepared in 91% yield (78 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 5/1); Yellow solid; mp 56-57 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 6.76-6.74 (m, 2H), 6.66-6.64 (m, 2H), 3.75 (s, 3H), 3.28 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 140.0, 116.5, 114.9, 55.8. Analytical data for **2d** was consistent with that previously reported.[2]



2e

4-Aminophenol (2e)[4]

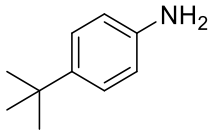
Compound **2e** was prepared in 62% yield (47 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 4/1); White solid; mp 187-188 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.31(s, 1H), 6.48-6.46 (m, 2H), 6.42-6.40 (m, 2H), 4.35 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 148.2, 140.7, 115.6, 115.3. Analytical data for **2e** was consistent with that previously reported.[4]



2f

4-Ethylaniline (2f)[5]

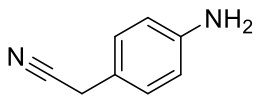
Compound **2f** was prepared in 81% yield (69 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.04-7.03 (m, 2H), 6.66 (d, J = 8.2 Hz, 2H), 3.47 (s, 2H), 2.59 (q, J = 7.5 Hz, 2H), 1.25-1.22 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 134.5, 128.7, 115.4, 28.1, 16.0. Analytical data for **2f** was consistent with that previously reported.[5]



2g

4-(Tert-butyl)aniline (2g)[6]

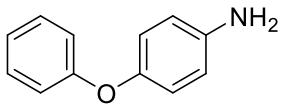
Compound **2g** was prepared in 92% yield (96 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (d, J = 8.3 Hz, 2H), 6.68-6.65(m, 2H), 3.40 (s, br, 2H), 1.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 141.6, 126.2, 115.1, 34.0, 31.7. Analytical data for **2g** was consistent with that previously reported.[6]



2h

2-(4-Aminophenyl)acetonitrile (2h)[7]

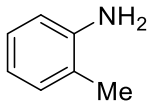
Compound **2h** was prepared in 68% yield (63 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 45-46 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 8.1 Hz, 2H), 3.71 (s, 2H), 3.62 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 148.1, 128.7, 119.9, 117.4, 114.1, 21.5. Analytical data for **2h** was consistent with that previously reported.[7]



2i

4-Phenoxyaniline (2i)[7]

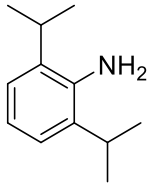
Compound **2i** was prepared in 85% yield (110 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); Brown solid; mp 82-73 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.27 (m, 2H), 7.03-7.00 (m, 1H), 6.95-6.93 (m, 2H), 6.90-6.86 (m, 2H), 6.70-6.67 (m, 2H), 3.58 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 148.7, 142.8, 129.6, 122.2, 121.3, 117.4, 116.4. Analytical data for **2i** was consistent with that previously reported.[7]



2j

O-toluidine (2j)[4]

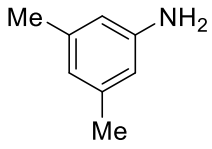
Compound **2j** was prepared in 76% yield (57 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10-7.06 (m, 2H), 6.77-6.74 (m, 1H), 6.71 (d, J = 7.7 Hz, 1H), 3.56 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.6, 130.5, 127.0, 122.4, 118.7, 115.0, 17.4. Analytical data for **2j** was consistent with that previously reported.[4]



2k

2,6-Diisopropylaniline (2k)[8]

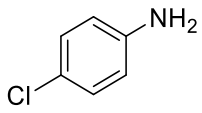
Compound **2k** was prepared in 84% yield (104 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (d, J = 7.7 Hz, 2H), 6.87-6.84 (m, 1H), 3.77 (s, br, 2H), 3.02-2.94 (m, 2H), 1.33 (d, J = 6.9 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.4, 132.5, 122.9, 118.6, 28.1, 22.6. Analytical data for **2k** was consistent with that previously reported.[8]



2l

3,5-Dimethylaniline (2l)[9]

Compound **2l** was prepared in 77% yield (65 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.44 (s, 1H), 6.35 (s, 2H), 3.35 (s, br, 2H), 2.24 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.3, 139.1, 120.7, 113.3, 21.4. Analytical data for **2l** was consistent with that previously reported.[9]

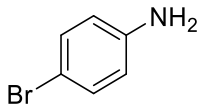


2m

4-Chloroaniline (2m)[7]

Compound **2m** was prepared in 85% yield (76 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 10/1); White solid; mp 67-68 °C; ^{1}H NMR

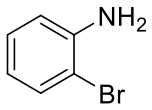
(500 MHz, $CDCl_3$): δ 7.11-7.09 (m, 2H), 6.60 (d, J = 8.7 Hz, 2H), 3.59 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.1, 129.2, 123.2, 116.3. Analytical data for **2m** was consistent with that previously reported.[7]



2n

4-Bromoaniline (2n)[2]

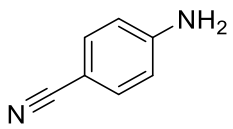
Compound **2n** was prepared in 61% yield (73 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); Yellow solid; mp 56-57 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.25 (s, 2H), 6.58 (s, 2H), 3.65 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.5, 132.1, 116.8, 110.3. Analytical data for **2n** was consistent with that previously reported.[2]



2o

2-Bromoaniline (2o)[7]

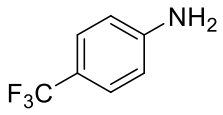
Compound **2o** was prepared in 63% yield (76 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 15/1); White solid; mp 32-33 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, J = 8.0 Hz, 1H), 7.12-7.09 (m, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.64-6.61 (m, 1H), 4.08 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 132.7, 128.4, 119.5. 115.9, 109.4. Analytical data for **2o** was consistent with that previously reported.[7]



2p

4-Aminobenzonitrile (2p)[10]

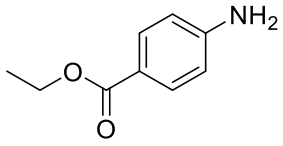
Compound **2p** was prepared in 81% yield (67 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 5/1); Yellow solid; mp 83-84 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41-7.37 (m, 2H), 6.65-6.62 (m, 2H), 4.23 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8, 133.9, 120.4, 114.5, 99.8. Analytical data for **2p** was consistent with that previously reported.[10]



2q

4-(Trifluoromethyl)aniline (2q)[11]

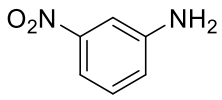
Compound **2q** was prepared in 88% yield (99 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 7/1); Colourless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 3.93 (s, br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 126.8 (q, J^3 = 3.8 Hz), 125.0 (q, J^1 = 268.8 Hz), 120.3 (q, J^2 = 31.6 Hz), 114.3; ^{19}F NMR (470 MHz, $CDCl_3$): δ -61.2. Analytical data for **2q** was consistent with that previously reported.[11]



2r

Ethyl 4-aminobenzoate (2r)[4]

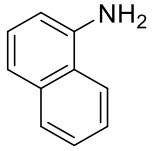
Compound **2r** was prepared in 77% yield (89 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 5/1); White solid; mp 89-90 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 6.6 Hz, 2H), 6.63 (d, J = 6.6 Hz, 2H). 4.32-4.30 (m, 2H), 4.07 (s, 2H), 1.36 (t, J = 3.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.8, 150.9, 131.6, 120.1, 113.9, 60.4, 14.5. Analytical data for **2r** was consistent with that previously reported.[4]



2s

3-Nitroaniline (2s)[12]

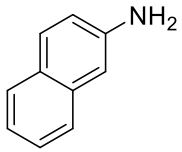
Compound **2s** was prepared in 83% yield (80 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 4/1); Yellow solid; mp 111-112 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58-6.96 (m, 4H), 4.03 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.3, 147.6, 130.0, 120.7, 113.2, 109.1. Analytical data for **2s** was consistent with that previously reported.[12]



2t

Naphthalen-1-amine (2t)[2]

Compound **2t** was prepared in 82% yield (82 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 5/1); Yellow solid; mp 47-48 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84-7.80 (m, 2H), 7.49-7.45 (m, 2H), 7.34-7.28 (m, 2H), 6.79 (d, J = 7.0 Hz, 1H), 3.83 (s, br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.2, 134.5, 128.7, 126.4, 126.0, 125.0, 123.8, 120.9, 119.1, 109.8. Analytical data for **2t** was consistent with that previously reported.[2]

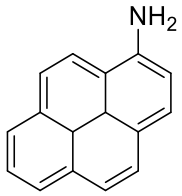


2u

Naphthalen-2-amine (2u)[9]

Compound **2u** was prepared in 81% yield (81 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 5/1); White solid; mp 111-112 ºC; ^{1}H NMR

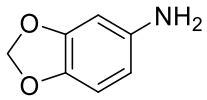
(500 MHz, $CDCl_3$): δ 7.75-7.70 (m, 2H), 7.64 (d, J = 8.3 Hz, 1H), 7.43-7.40 (m, 1H), 7.30-7.27 (m, 1H), 7.03 (d, J = 1.9 Hz, 1H), 6.99 (dd, J = 8.6, 2.3 Hz, 1H), 3.85 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 135.0, 129.3, 128.1, 127.8, 126.5, 125.9, 122.6, 118.4, 108.7. Analytical data for **2u** was consistent with that previously reported.[9]



2v

Pyren-1-amine (2v)[19]

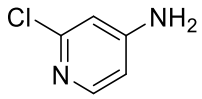
Compound **2v** was prepared in 67% yield (103 mg) and according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 10/1); Green solid; mp 115-116 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 8.07-8.04 (m, 2H), 8.00-7.91 (m, 5H), 7.82 (d, J = 8.9 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 4.49 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.0, 132.3, 131.7, 127.7, 126.1, 126.1, 126.1, 125.6, 124.4, 124.2, 123.8, 123.6, 120.2, 116.9, 114.0. Analytical data for 2w was consistent with that previously reported.[19]



2w

Benzo[d][1,3]dioxol-5-amine (2w)[13]

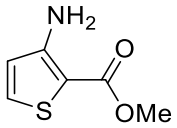
Compound **2w** was prepared in 87% yield (84 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 5/1); Black solid; mp 39-40 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 6.62 (d, J = 8.2 Hz, 1H), 6.28 (d, J = 1.5 Hz, 1H), 6.13 (dd, J = 8.2, 1.4 Hz, 1H), 5.85 (d, J = 0.7 Hz, 2H), 3.16 (s, br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.3, 141.5, 140.5, 108.7, 107.0, 100.8, 98.2. Analytical data for **2w** was consistent with that previously reported.[13]



2x

2-Chloropyridin-4-amine (2x)[7]

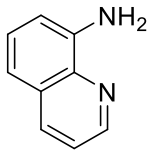
Compound **2x** was prepared in 79% yield (71 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 2/1); White solid; mp 90-91 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.76 (d, J = 5.7 Hz, 1H), 6.47 (d, J = 2.0 Hz, 1H), 6.44 (dd, J = 5.7, 2.1 Hz, 1H), 6.36 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 156.8, 150.8, 149.1, 108.5, 106.8. Analytical data for **2x** was consistent with that previously reported.[7]



2y

Methyl 3-aminothiophene-2-carboxylate (2y)[14]

Compound **2y** was prepared in 34% yield (37 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 10/1); White solid; mp 62-63 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, J = 5.2 Hz, 1H), 6.53 (d, J = 5.3 Hz, 1H), 5.47 (s, 2H), 3,82(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.1, 154.1, 131.7, 119.9, 101.3, 51.4. Analytical data for **2y** was consistent with that previously reported.[14]

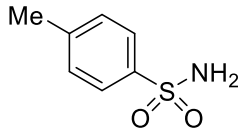


2z

Quinolin-8-amine (2z)[8]

Compound **2z** was prepared in 67% yield (68 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 5/1); Yellow solid; mp 60-61 °C; ^{11}H NMR (500 MHz, $CDCl_3$): δ 8.76 (dd, J = 4.2, 1.7 Hz, 1H), 8.06 (dd, J = 8.3, 1.6 Hz, 1H),

7.37-7.32 (m, 2H), 7.15 (dd, J = 8.1, 0.9 Hz, 1H), 6.93 (dd, J = 7.5, 1.1 Hz, 1H), 4.98 (s, br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.5, 144.1, 138.6, 136.1, 129.0, 127.5, 121.4, 116.2, 110.2. Analytical data for **2z** was consistent with that previously reported.[8]

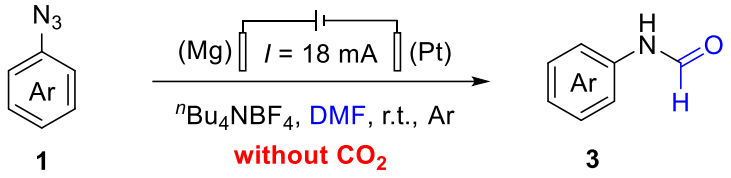


2aa

4-Methylbenzenesulfonamide (2aa)[12]

Compound **2aa** was prepared in 55% yield (66 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); White solid; mp 134-135 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.71 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.28 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 141.9, 141.5, 129.3, 125.7, 20.9. Analytical data for **2aa** was consistent with that previously reported.[12]

Synthesis and characterization of 3



In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 1 (0.7 mmol), DMF (5 mL), $^{n}Bu_4NBF_4$ (164.6 mg, 0.5 mmol) were added. The vessel was evacuated and refilled with Ar five times. The bottle was equipped with platinum plate ($1\times1\times0.05$ cm^3) anode and platinum plate ($1\times1\times0.02$ cm^3) cathode, under an argon atmosphere. The mixture was stirred (600 rpm) and electrolyzed at a constant current of 18 mA. After the reaction finished as monitored with TLC, the reaction mixture was diluted with water and extracted with ethyl acetate (15 mL ×3). The organic layers were combined, washed with water, dried over Na_2SO_4, and concentrated in vacuum. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 1:1-3:1).

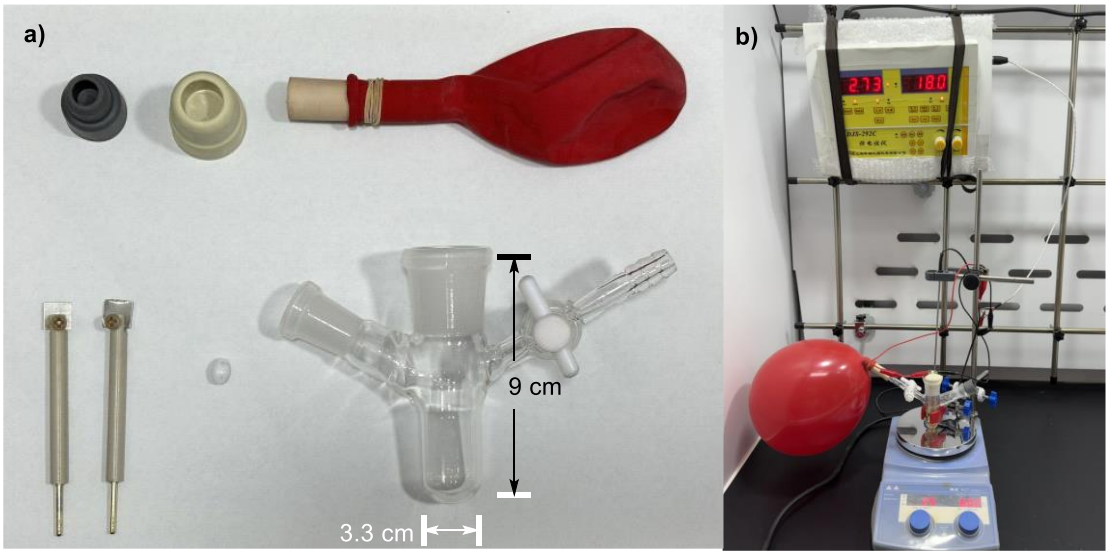
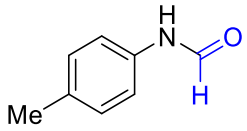


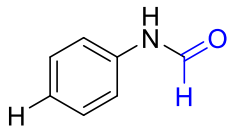
Figure S4. Set-up of Experiments (the photographs come from our lab). a) Experimental equipment. b) Reaction process diagram.



3a

N-p-tolylformamide (3a)[15]

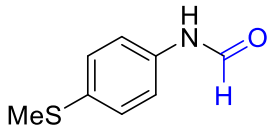
Compound **3a** was prepared in 67% yield (63 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); Brown solid; mp 51-52 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.62 (d, *J* = 11.5 Hz, 0.52H), 8.34 (d, *J* = 1.5 Hz, 0.46H), 8.04 (s, 0.41H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.34 (s, 0.46H), 7.16-7.12 (m, 2H), 6.98 (d, *J* = 8.3 Hz, 1H), 2.33 (s, 1.59H), 2.32 (s, 1.40H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0, 159.2, 135.3, 134.6, 134.5, 134.2, 130.3, 129.7, 120.2, 119.3, 21.0, 20.9. Analytical data for **3a** was consistent with that previously reported.[15]



3b

N-phenylformamide (3b)[15]

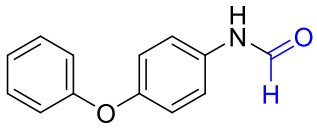
Compound **3b** was prepared in 56% yield (47 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); Brown solid; mp 46-47 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (d, *J* = 11.3 Hz, 0.57H), 8.57 (s, 0.47H), 8.36 (s, 0.47H), 7.70 (s, 0.41H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.37-7.31 (m, 2H), 7.20-7.09 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.9, 159.3, 137.1, 136.9, 129.8, 129.2, 125.4, 124.9, 120.1, 118.9. Analytical data for **3b** was consistent with that previously reported.[15]



3c

N-(4-(methylthio)phenyl)formamide (3c)[16]

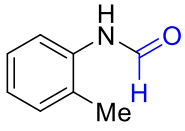
Compound **3c** was prepared in 47% yield (55 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); Yellow solid; mp 69-70 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56 (d, J = 11.4 Hz, 0.51H), 8.36 (d, J = 8.8 Hz, 0.45H), 8.27 (d, J = 1.5 Hz, 0.62H), 7.55 (s, 0.56H), 7.40 (d, J = 8.8 Hz, 0.45H), 7.19-7.14 (m, 2H), 6.96 (d, J = 8.6 Hz, 1H), 2.49 (s, 1.39H), 2.48 (s, 1.58H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.8, 159.2, 135.4, 134.5, 134.4, 134.2, 128.5, 127.9, 120.7, 119.7, 16.6, 16.6. Analytical data for **3c** was consistent with that previously reported.[16]



3d

N-(4-phenoxyphenyl)formamide (3d)[16]

Compound **3d** was prepared in 55% yield (82 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); Brown solid; mp 52-53 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.59 (d, J = 11.5 Hz, 0.45H), 8.35 (d, J = 1.6 Hz, 0.54H), 8.17 (d, J = 8.5 Hz, 0.41H), 7.52-7.49 (m, 1H), 7.47 (s, br, 0.45H), 7.36-7.31 (m, 2H), 7.13-7.06 (m, 2H), 7.02-6.98 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0, 159.1, 157.5, 157.2, 155.1, 154.1, 132.4, 132.0, 130.0, 129.9, 123.6, 123.4, 121.9, 121.3, 120.2, 119.7, 118.8, 118.7. Analytical data for **3d** was consistent with that previously reported.[16]

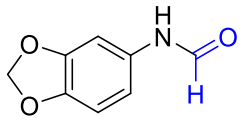


3e

N-o-tolylformamide (3e)[17]

Compound **3e** was prepared in 48% yield (45 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); Brown solid; mp 56-57 °C ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (d, J = 11.3 Hz, 0.62H), 8.35 (s, 0.38H), 8.07 (s, 0.59H), 7.79 (d,

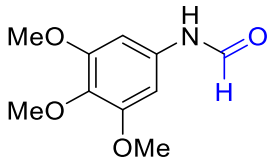
J = 7.9 Hz, 0.38H), 7.23-7.00 (m, 4H), 2.23 (s, 1.86H), 2.20 (s, 1.14H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6, 159.4, 135.2, 134.7, 131.3, 130.7, 129.9, 128.8, 127.2, 126.9, 126.2, 125.6, 123.2, 120.9, 17.8, 17.8. Analytical data for **3e** was consistent with that previously reported.[17]



3f

N-(benzo[d][1,3]dioxol-5-yl)formamide (3f)[15]

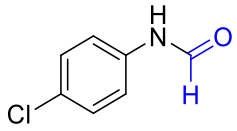
Compound **3f** was prepared in 57% yield (66 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); Yellow solid; mp 80-81 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (d, J = 11.4 Hz, 0.44H), 8.29 (d, J = 1.6 Hz, 0.47H), 8.21 (s, 0.42H), 7.52 (s, 0.46H), 7.22 (d, J = 2.1 Hz, 0.46H), 6.84 (dd, J = 8.3, 2.1 Hz, 0.51H), 6.77-6.72 (m, 1H), 6.62 (d, J = 2.2 Hz, 0.43H), 6.54 (dd, J = 8.2, 2.2 Hz, 0.48H), 5.97 (s, 0.87H), 5.94 (s, 1.04H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.2, 159.1, 148.7, 148.0, 145.8, 144.8, 131.1, 130.9, 113.3, 108.8, 108.2, 103.0, 102.2, 101.8, 101.5. Analytical data for **3f** was consistent with that previously reported.[15]



3g

N-(3,4,5-trimethoxyphenyl)formamide (3g)[18]

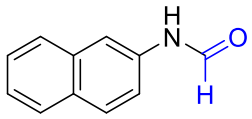
Compound **3g** was prepared in 60% yield (89 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 1/1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (d, J = 11.4 Hz, 0.41H), 8.32 (d, J = 1.5 Hz, 0.59H), 8.10 (d, J = 10.6 Hz, 0.39H), 7.55 (s, 0.62H), 6.84 (s, 1H), 6.30 (s, 1H), 3.84-3.80 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.8, 159.2, 154.1, 153.4, 135.9, 135.0, 133.3, 132.8, 97.8, 97.4, 61.1, 61.1, 56.3, 56.2. Analytical data for **3g** was consistent with that previously reported.[18]



3h

N-(4-chlorophenyl)formamide (3h)[16]

Compound **3h** was prepared in 63% yield (69 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); Yellow solid; mp 103-104 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65 (d, J = 11.3 Hz, 0.45H), 8.49 (s, 0.33H), 8.36 (s, 0.56H), 7.60 (s, 0.41H), 7.49 (d, J = 8.8 Hz, 1H), 7.33-7.28 (m, 2H), 7.04 (d, J = 8.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7, 159.2, 135.6, 135.4, 130.9, 130.0, 129.2, 121.4, 120.2. Analytical data for **3h** was consistent with that previously reported.[16]

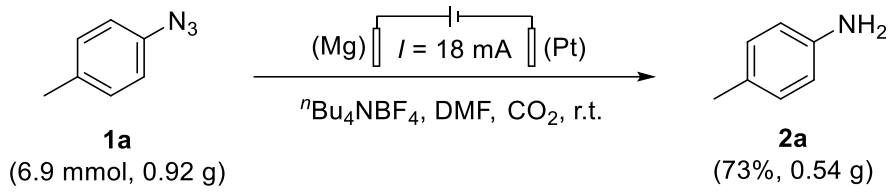


3i

N-(naphthalen-2-yl)formamide (3i)[18]

Compound **3i** was prepared in 45% yield (54 mg) according to the general procedure. R_f = 0.2 (petroleum ether/ethyl acetate = 3/1); Yellow solid; mp 134-135 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.85 (d, J = 11.3 Hz, 0.48H), 8.50 (s, br, 0.42H), 8.45 (s, 0.53H), 8.23 (s, 0.5H), 7.85-7.77 (m, 3H), 7.63 (s, 0.54H), 7.52-7.40 (m, 3H), 7.25-7.24 (m, 0.48H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.4, 134.3, 133.9, 133.9, 131.2, 131.0, 130.1, 129.1, 127.9, 127.8, 127.7, 127.4, 127.3, 126.8, 125.6, 125.4, 119.7, 118.9, 117.2, 115.3. Analytical data for **3i** was consistent with that previously reported.[18]

Scale-up Reaction:



1a
(6.9 mmol, 0.92 g)

2a
(73%, 0.54 g)

In an oven-dried undivided three-necked bottle (50 mL) equipped with a stir bar, **1a** (0.92 g, 6.9 mmol), DMF (30 mL) and $^{n}Bu_4NBF_4$ (0.99 g, 3.0 mmol) were added. The bottle was equipped with magnesium plate (1×1×0.05 cm^3) anode and platinum plate (1×1×0.02 cm^3) cathode, and continuously bubbling of CO_2 into the solution (direct connection to the CO_2 gas cylinder). Then, the mixture was stirred (600 rpm) and electrolyzed at a constant current of 18 mA under room temperature for about 12 h. After the reaction finished as monitored with TLC, the reaction mixture was diluted with water and extracted with ethyl acetate (50 mL×3). The organic layers were combined, washed with water, dried over Na_2SO_4, and concentrated in vacuum. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 20:1) to afford the **2a** (0.54 g, 73%).

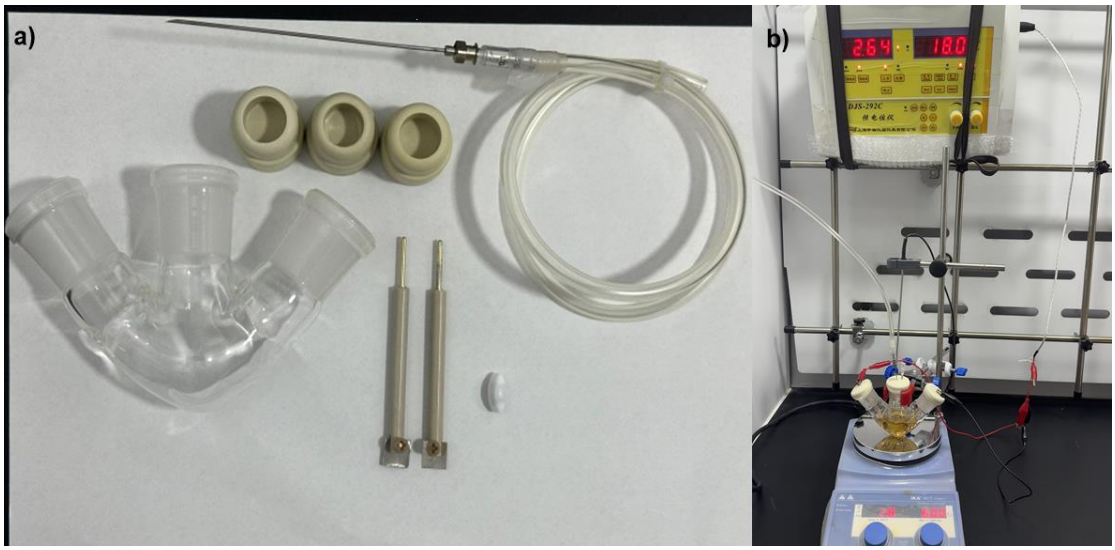
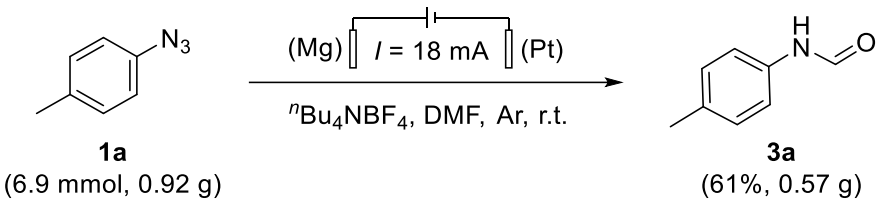


Figure S5. Set-up of Experiments (the photographs come from our lab). a) Experimental equipment. b) Reaction process diagram.



1a
(6.9 mmol, 0.92 g)

3a
(61%, 0.57 g)

In an oven-dried undivided three-necked bottle (50 mL) equipped with a stir bar, **1a** (0.92 g, 6.9 mmol), DMF (30 mL) and $^{n}Bu_4NBF_4$ (0.99 mg, 3.0 mmol) were added. The vessel was evacuated and refilled with argon five times. The bottle was equipped with magnesium plate (1×1×0.05 cm^3) anode and platinum plate (1×1×0.02 cm^3) cathode, under an argon atmosphere. The mixture was stirred (600 rpm) and electrolyzed at a constant current of 18 mA under room temperature for about 7 h. After the reaction finished as monitored with TLC, the reaction mixture was diluted with water and extracted with ethyl acetate (50 mL×3). The organic layers were combined, washed with water, dried over Na_2SO_4, and concentrated in vacuum. The pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 3:1) to afford the **3a** (0.57 g, 61%).

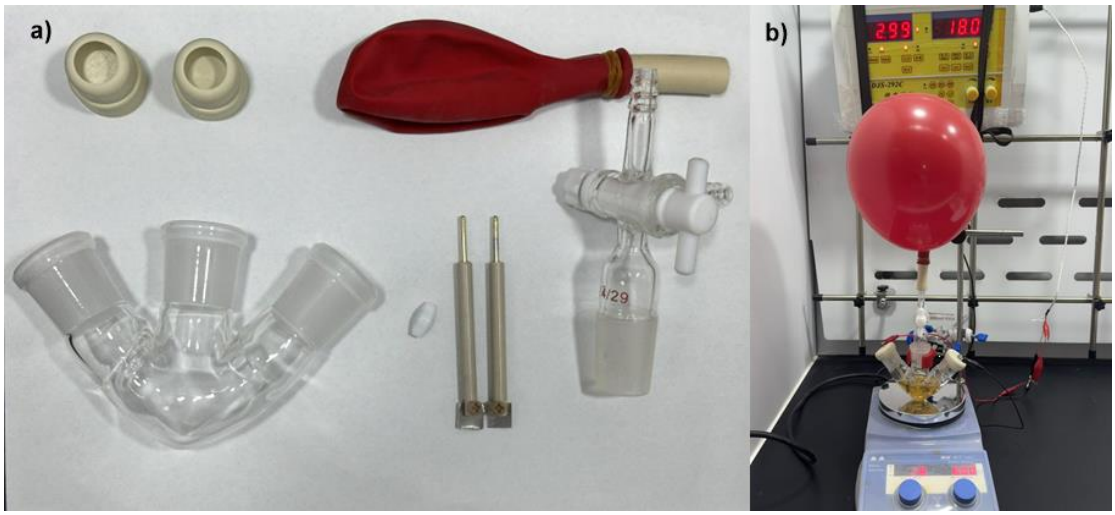


Figure S6. Set-up of Experiments (the photographs come from our lab). a) Experimental equipment. b) Reaction process diagram.

References:

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NMR spectra of compounds 2

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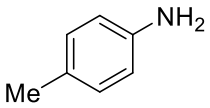

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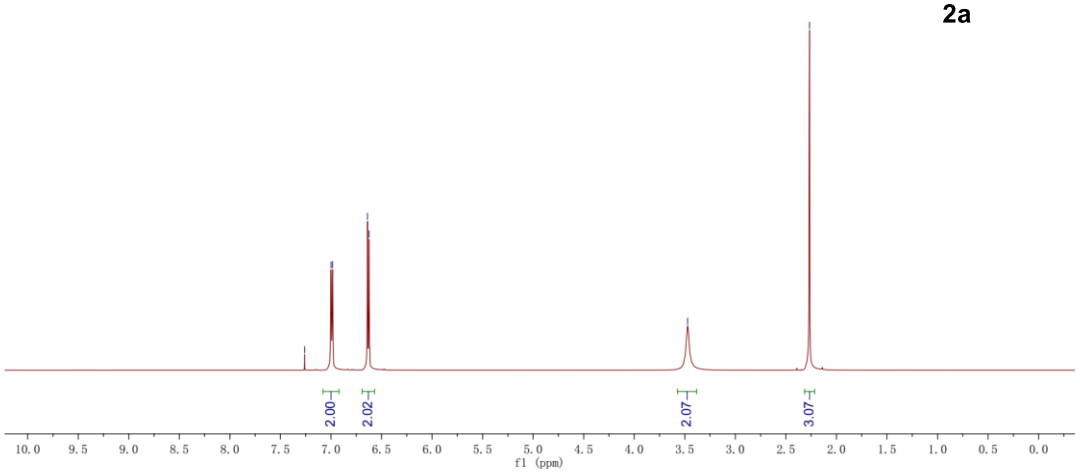

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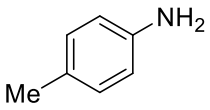

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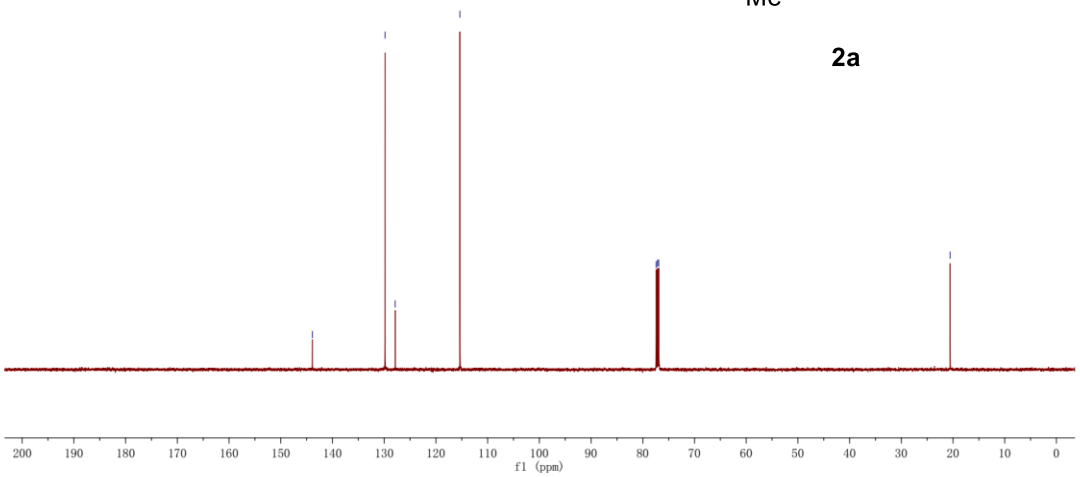

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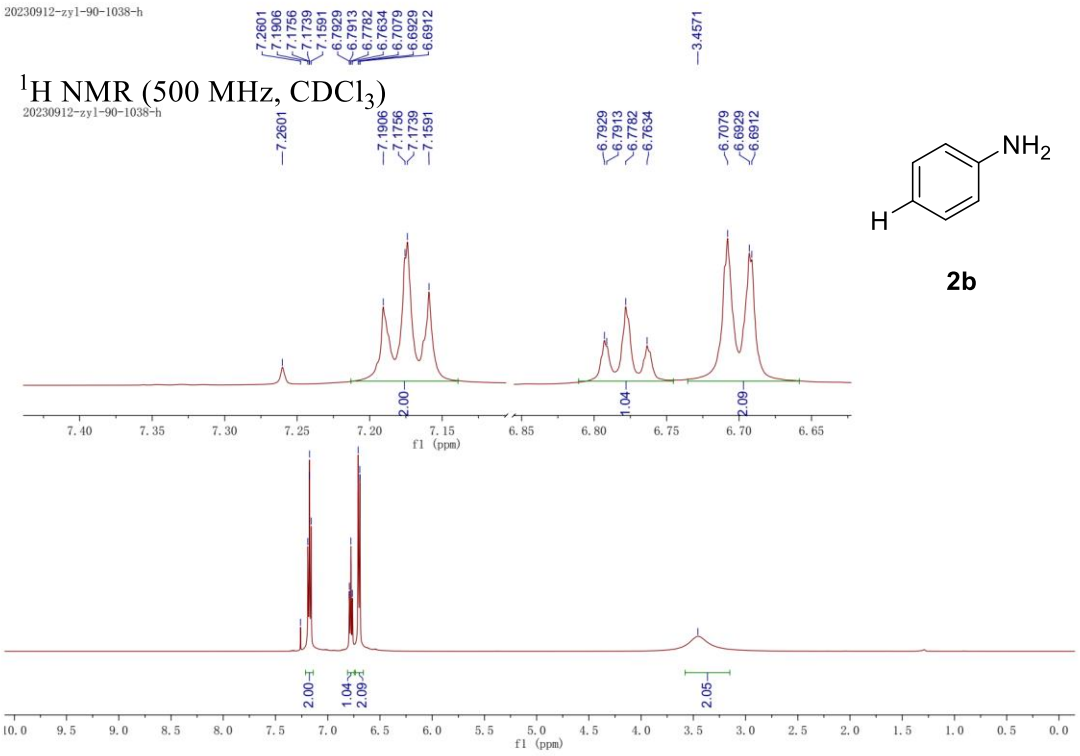

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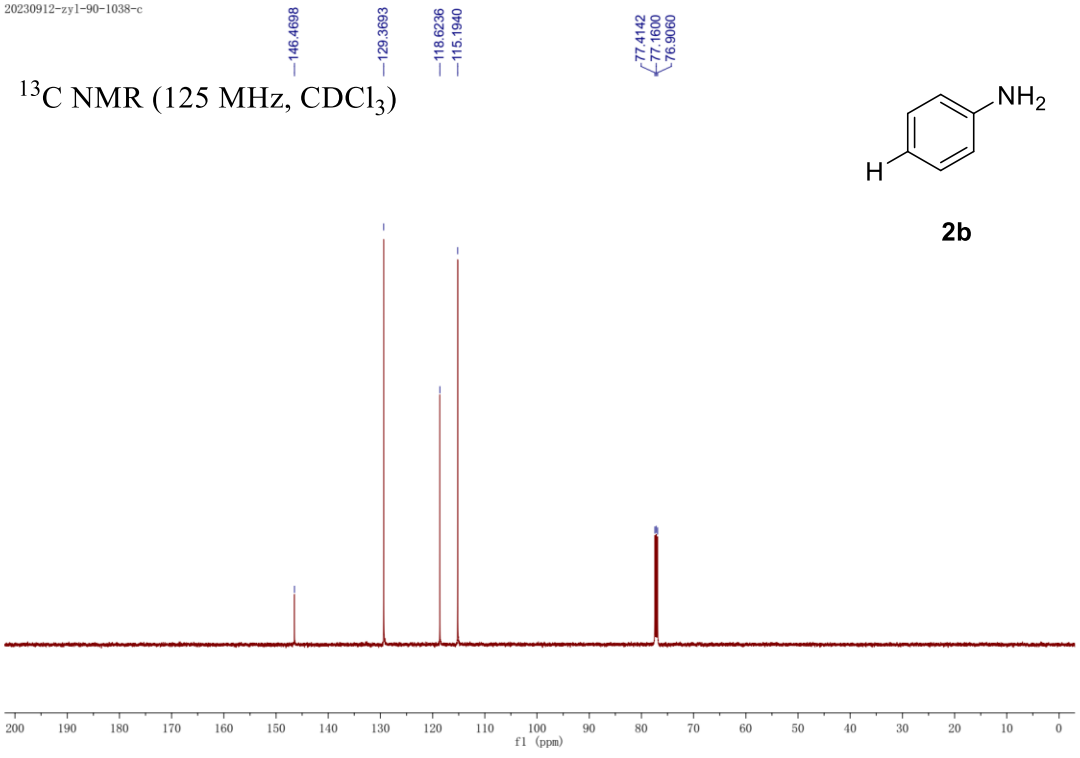

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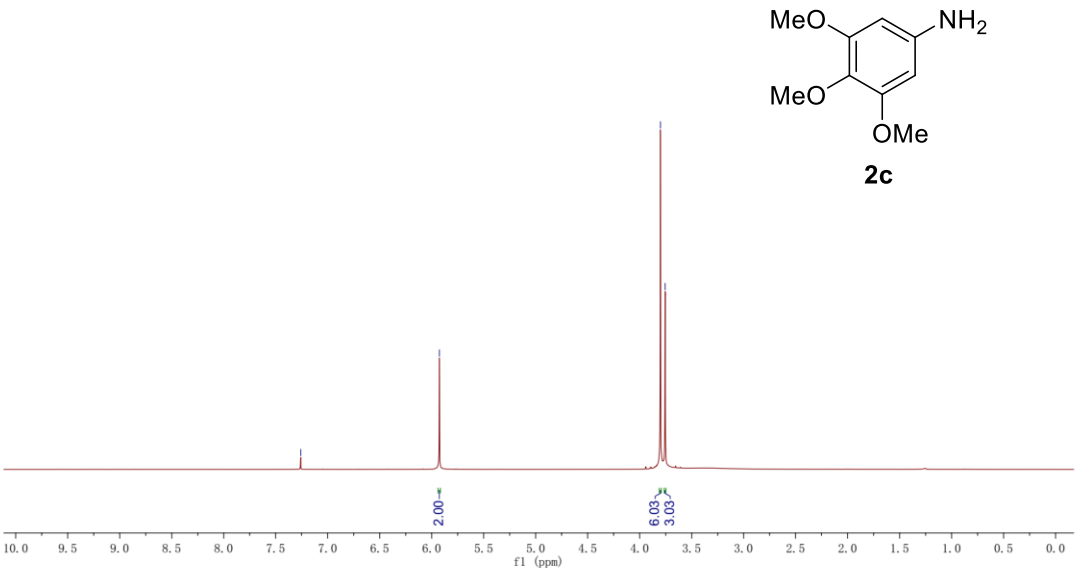

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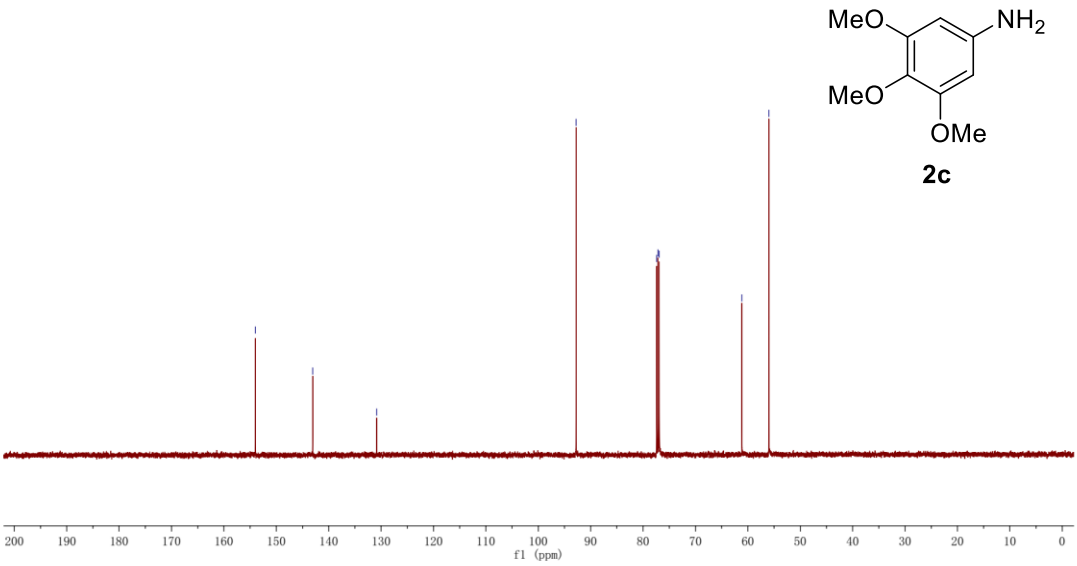

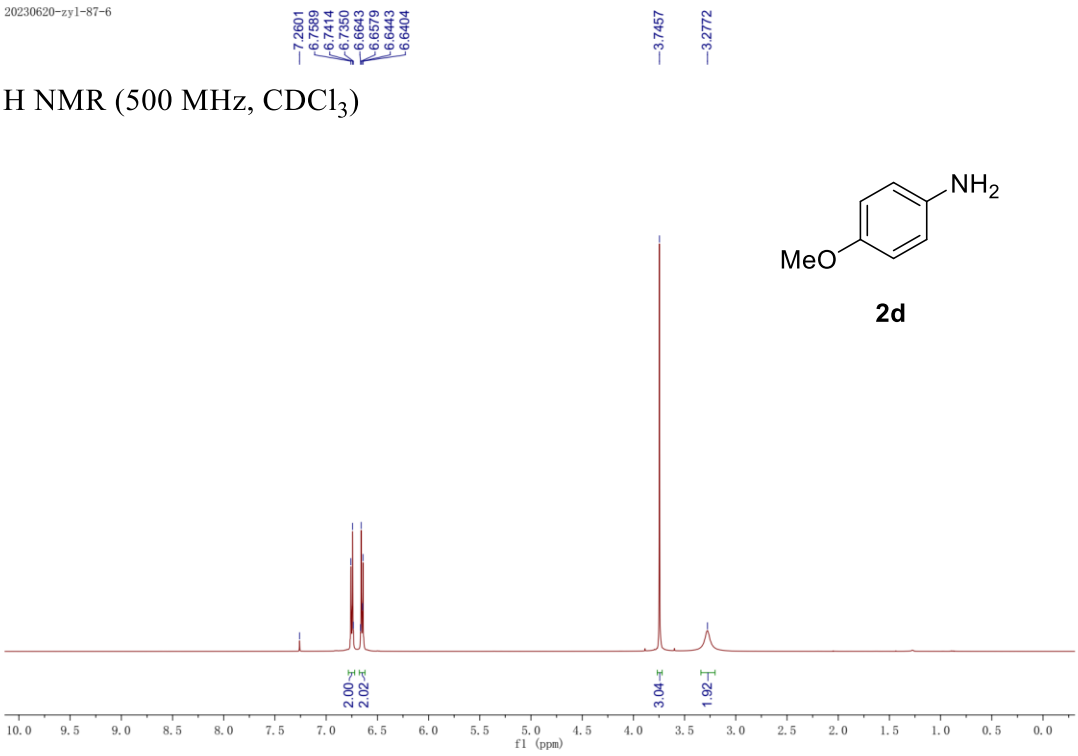

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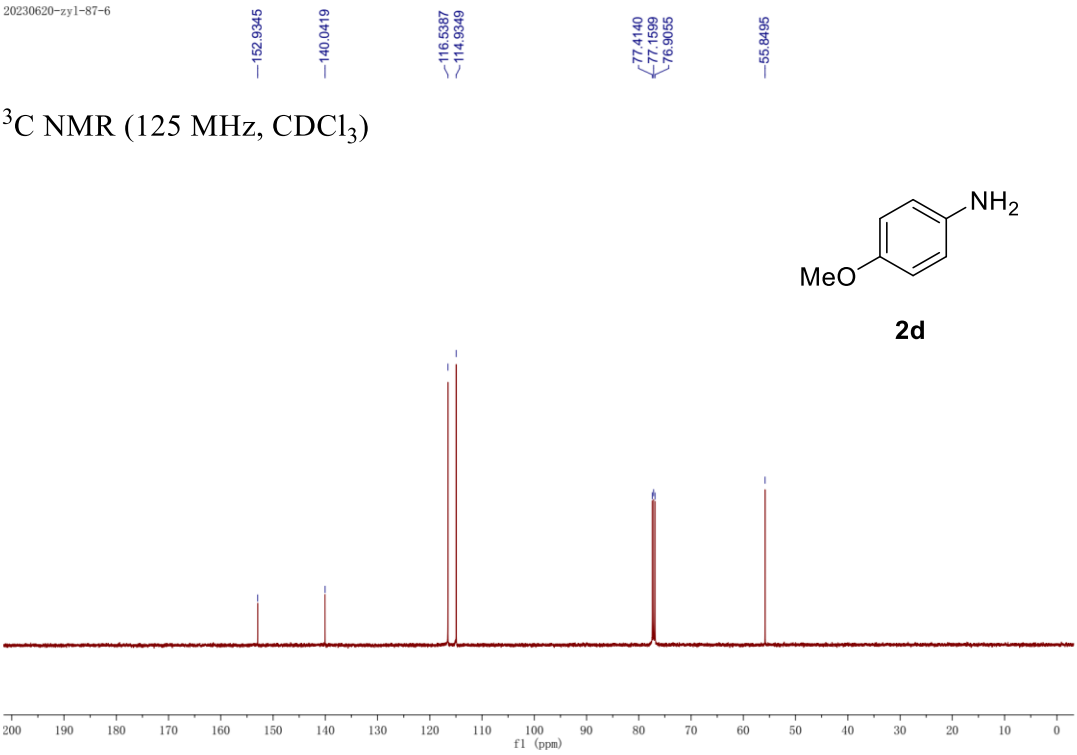

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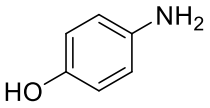

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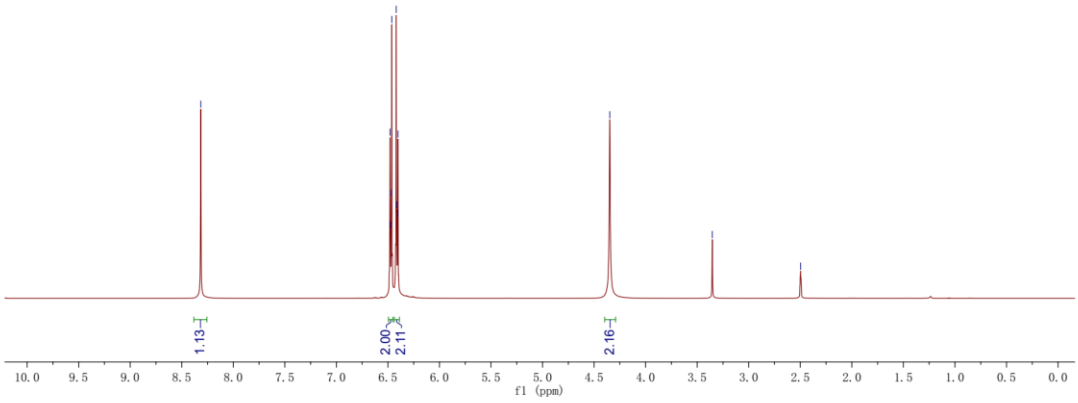

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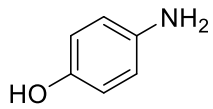

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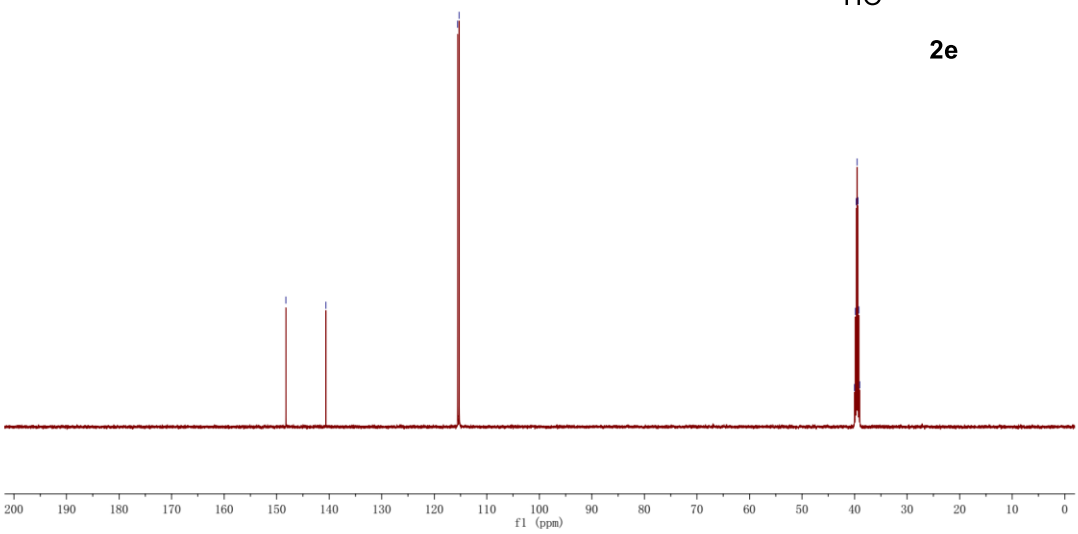

20230616-zyl-87-9

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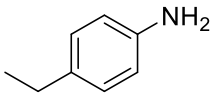
7.0439
7.0426
7.0283
6.6717
6.6554
3.4674
2.6108
2.5959
2.5808
2.5657
1.2527
1.2513
1.2488
1.2375
1.2361
1.2338
1.2223
1.2209
1.2185

^{1}H NMR (500 MHz, $CDCl_3$)



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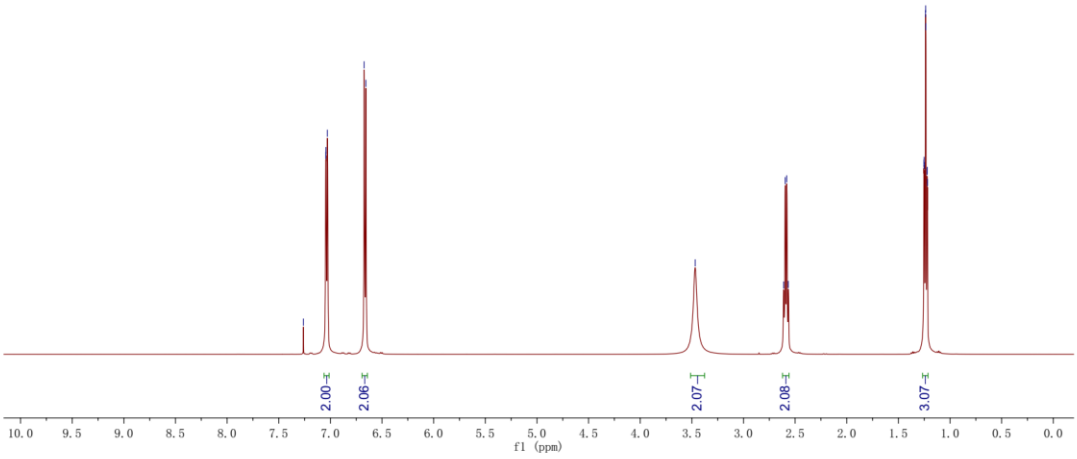

20230616-zyl-87-9

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134.5083
128.6587
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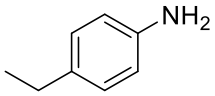
77.4139
77.1598
76.9052
28.0588
16.0287

^{13}C NMR (125 MHz, $CDCl_3$)



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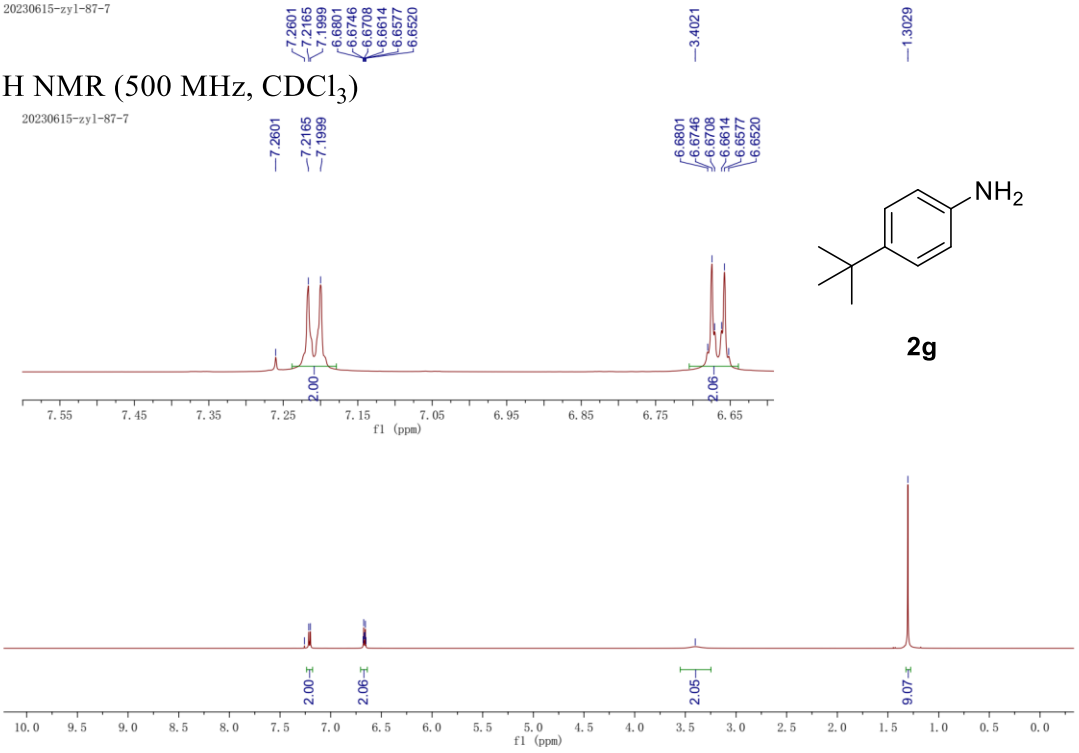
^{1}H NMR (500 MHz, $CDCl_3$)



2g

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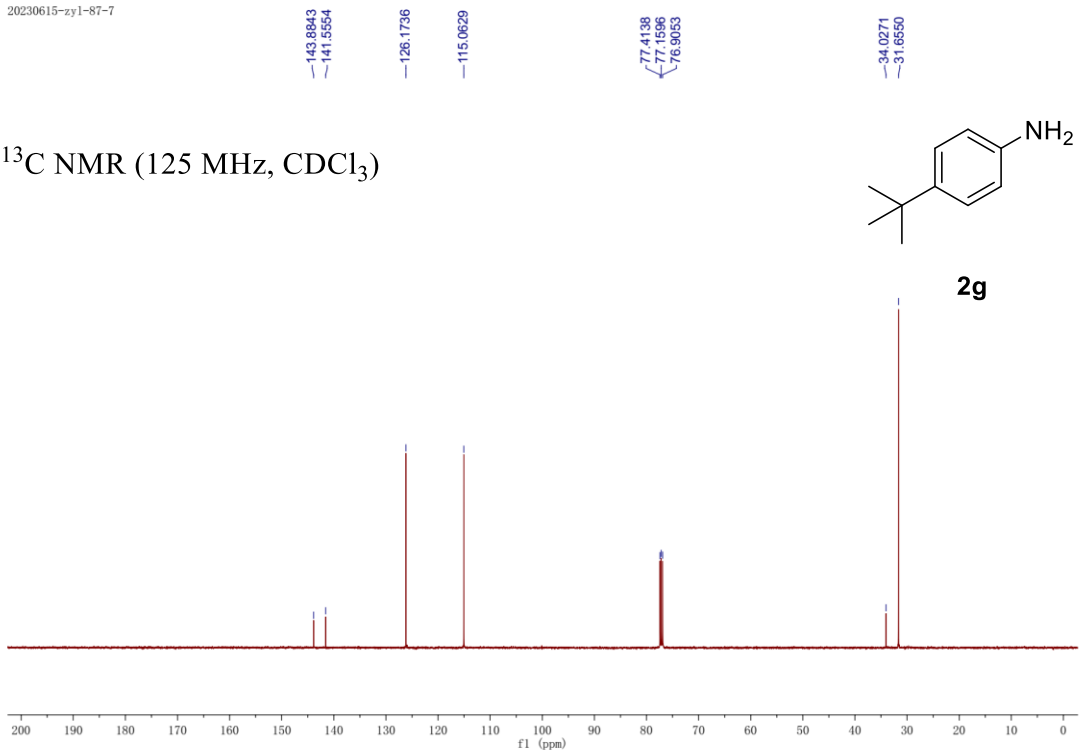

2g

20230907-zyl-90-181

7.2597
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3.7114
3.6207

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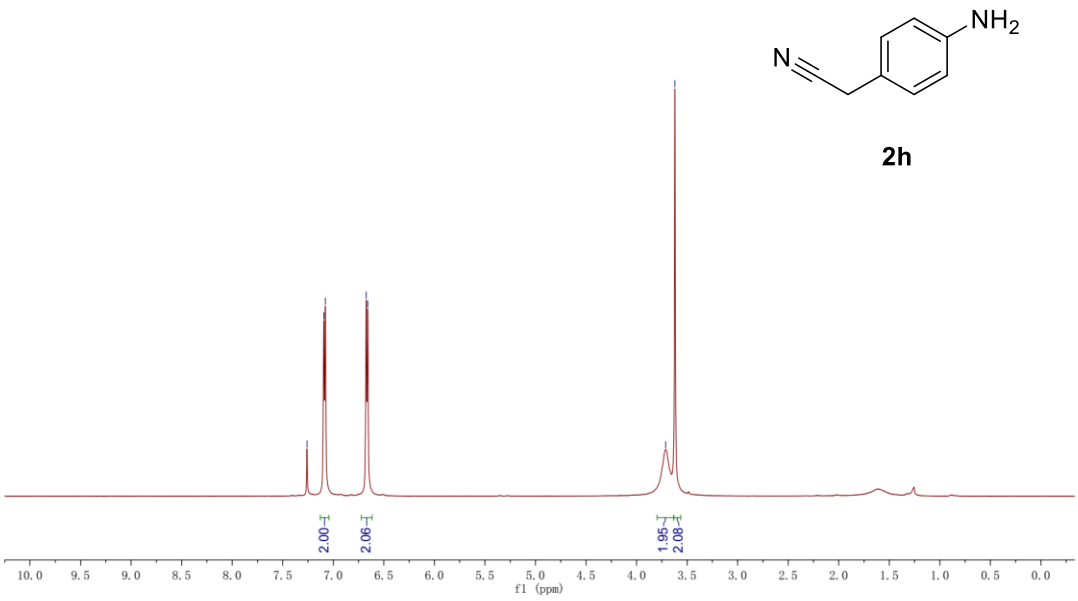

2h

20230911-zyl-c-90-181

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119.8917
117.3929
114.1287
40.0197
39.8532
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39.5195
39.3526
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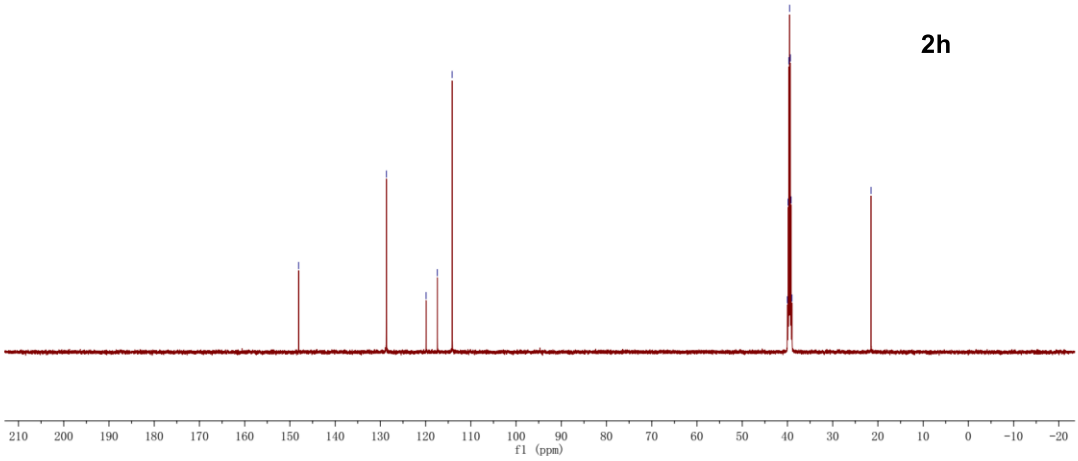
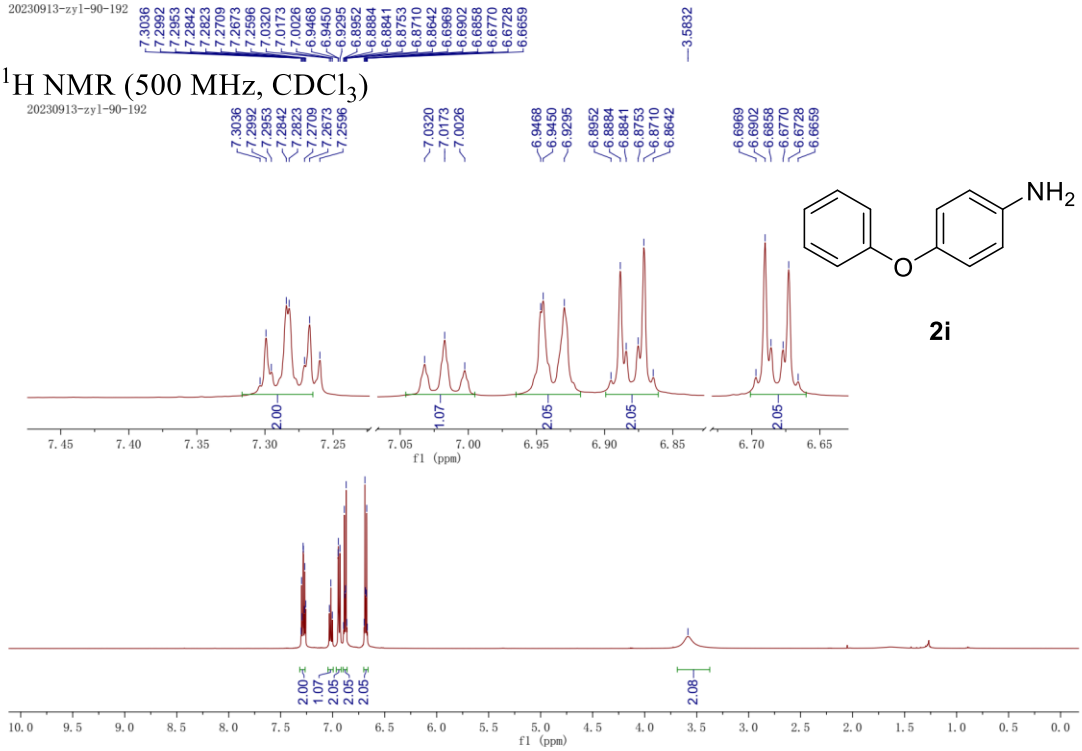
^{13}C NMR (500 Mhz, DMSO-d_6)

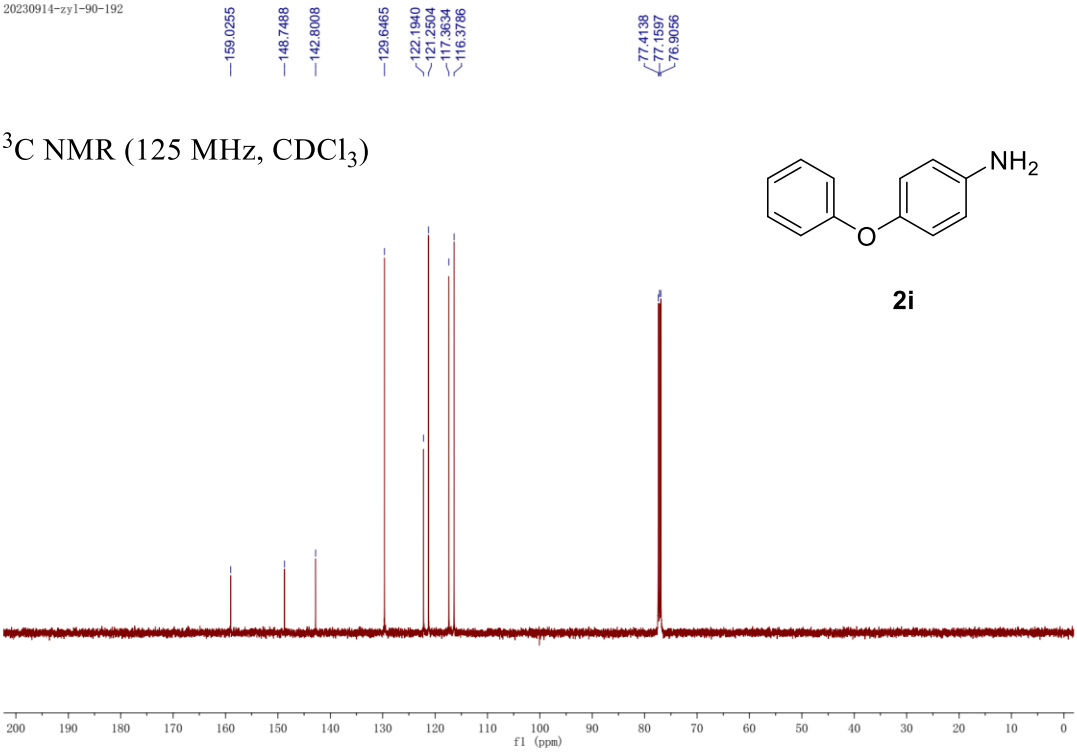


2h

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



20230615-zyl-87-14

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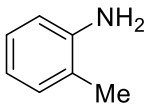

2j

20230615-zyl-87-14

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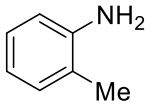
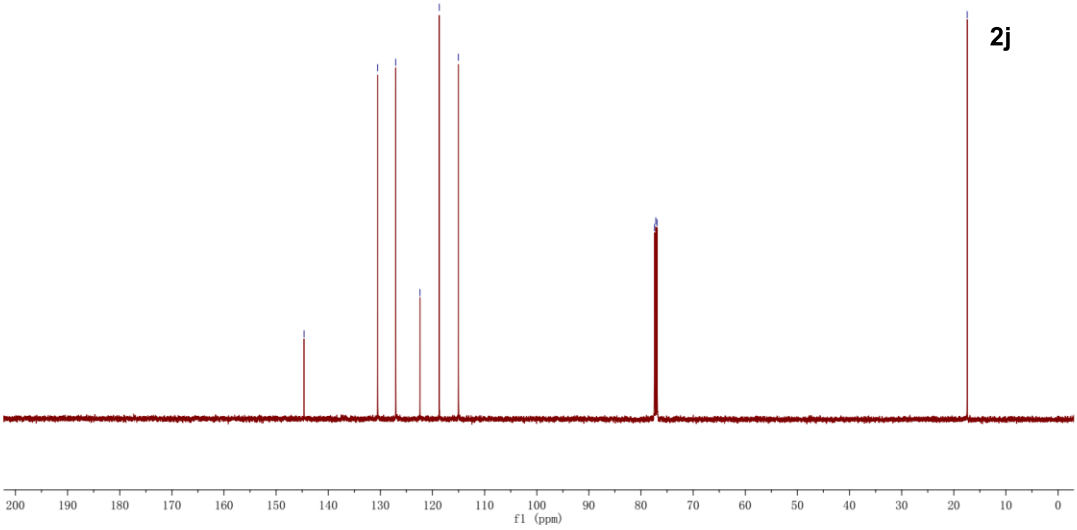
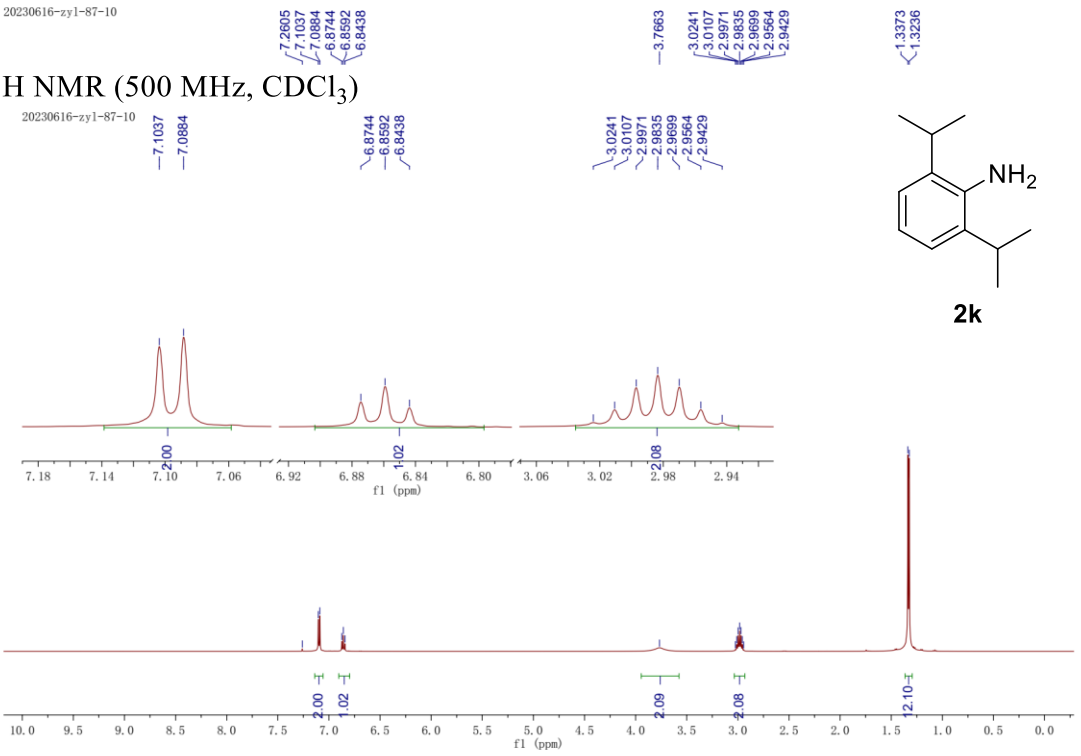


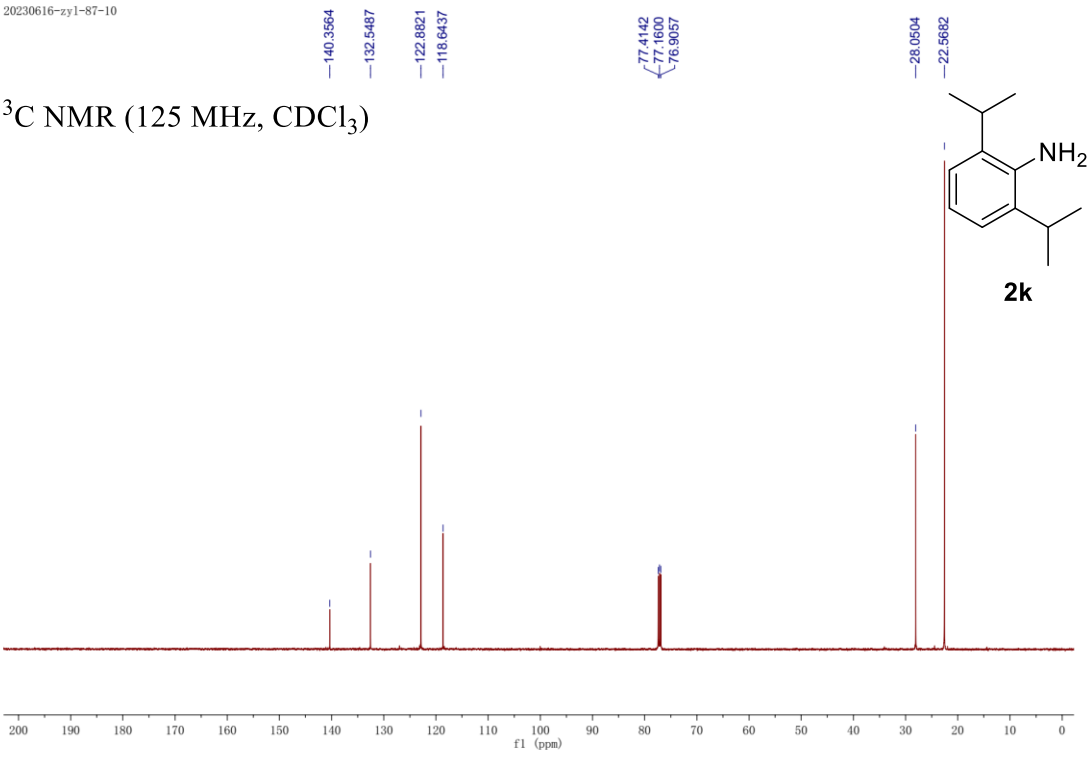
2j



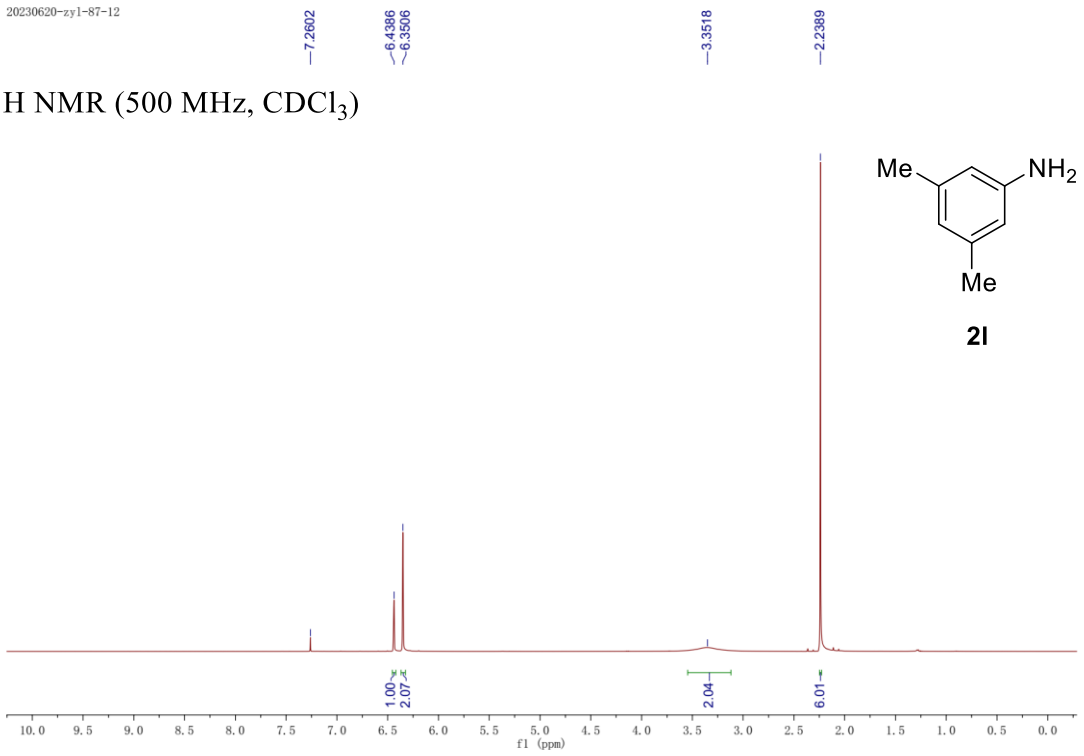
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

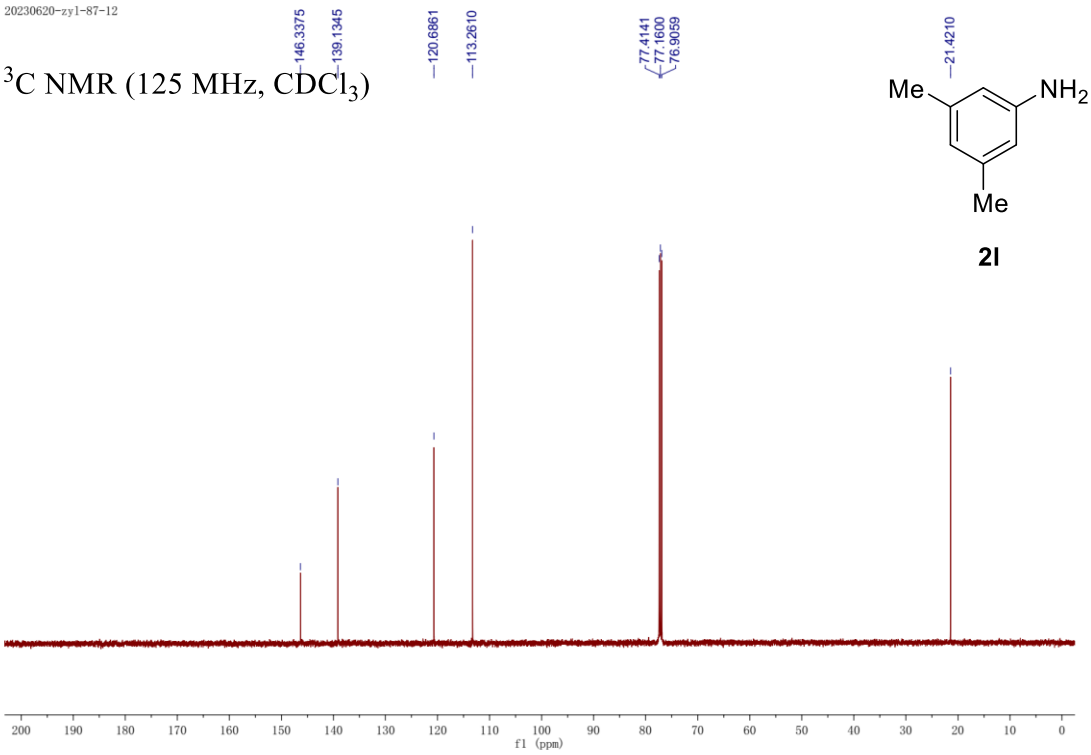


^{1}H NMR (500 MHz, $CDCl_3$)



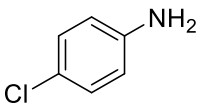
2l

^{13}C NMR (125 MHz, $CDCl_3$)

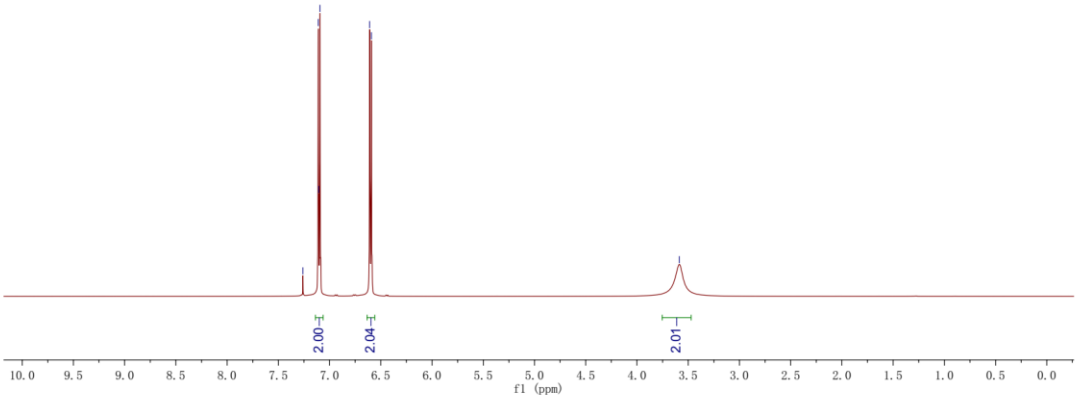


2l

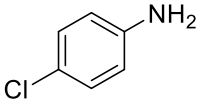
^{1}H NMR (500 MHz, $CDCl_3$)



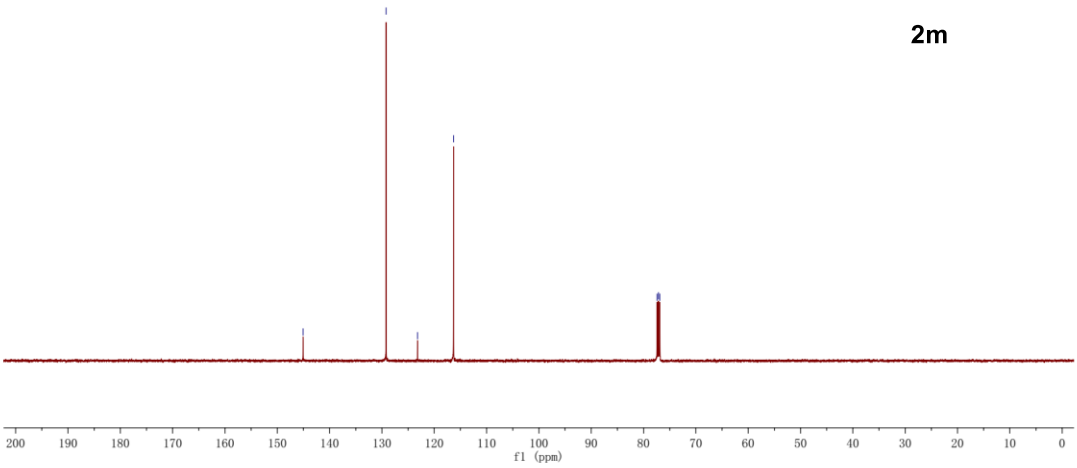
2m



^{13}C NMR (125 MHz, $CDCl_3$)



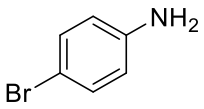
2m



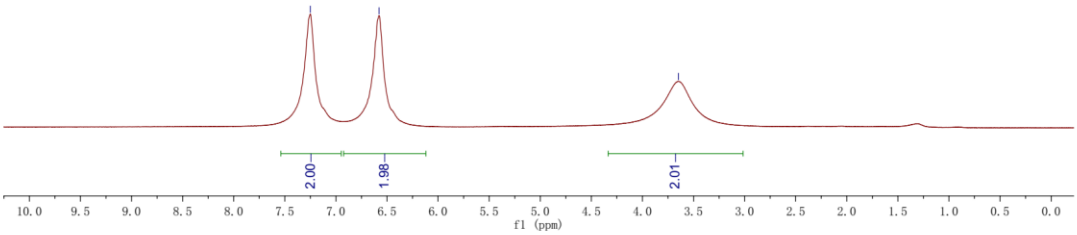
20230620-zyl-87-8

7.2508
6.5775
3.6485

^{1}H NMR (500 MHz, $CDCl_3$)



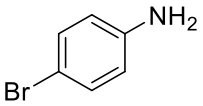
2n



20230620-zyl-87-8

145.5403
132.1309
116.8338
110.3231
77.4141
77.1600
76.9057

^{13}C NMR (125 MHz, $CDCl_3$)



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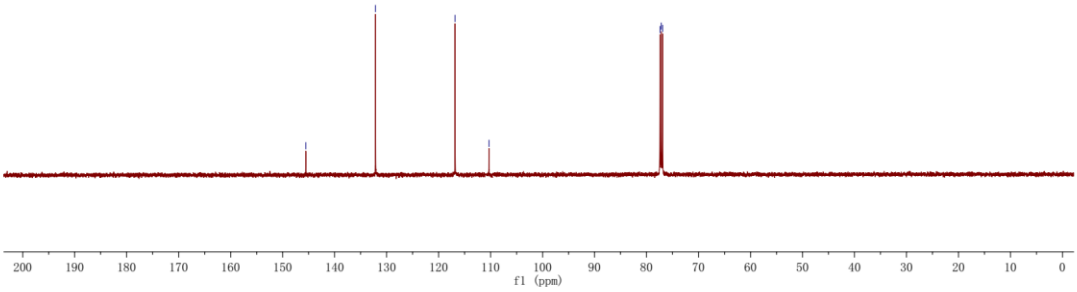
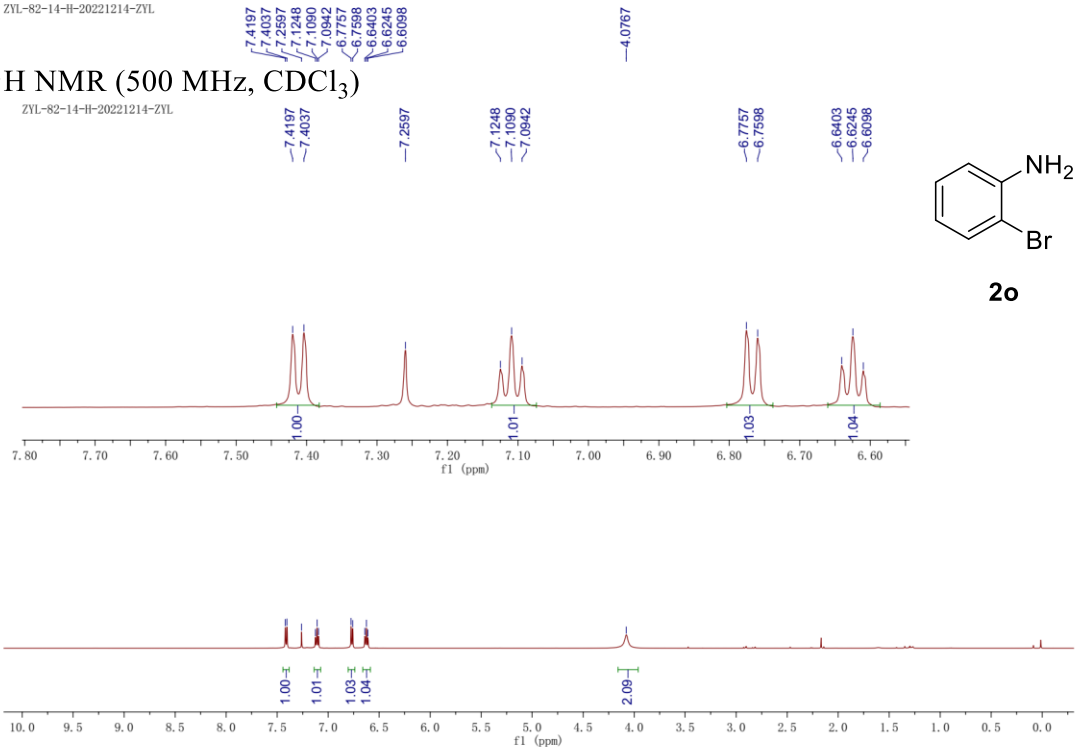
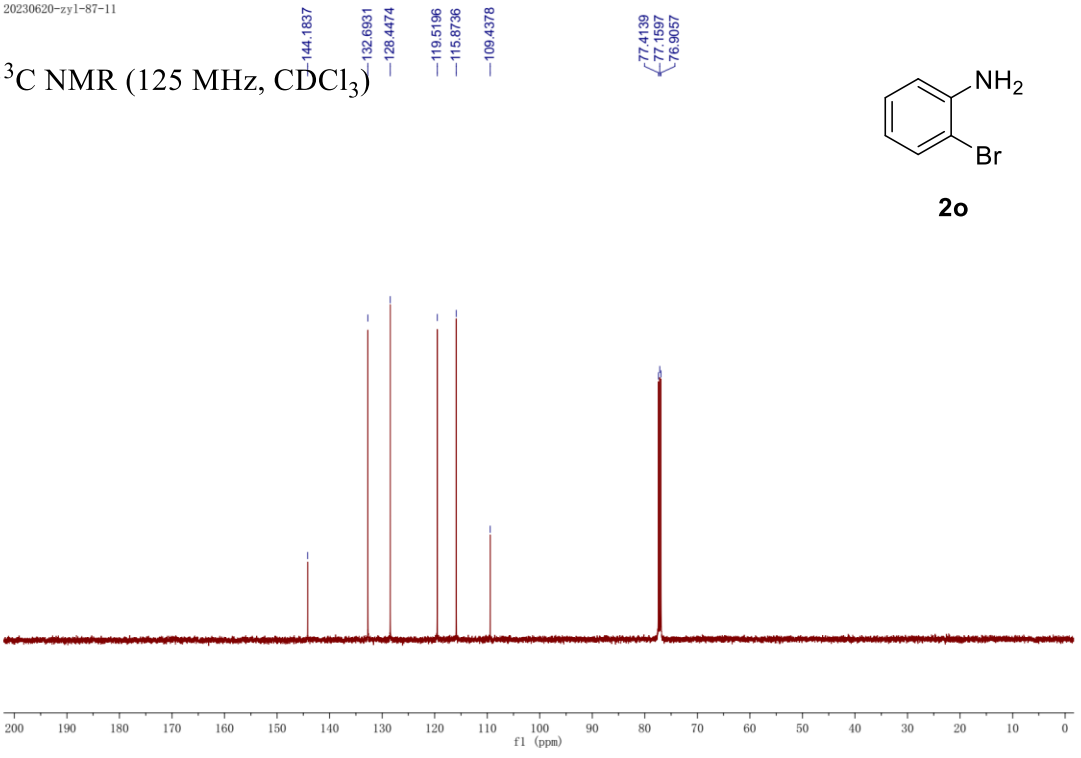


^{1}H NMR (500 MHz, $CDCl_3$)



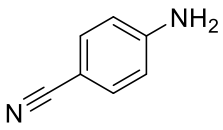
2o

^{13}C NMR (125 MHz, $CDCl_3$)

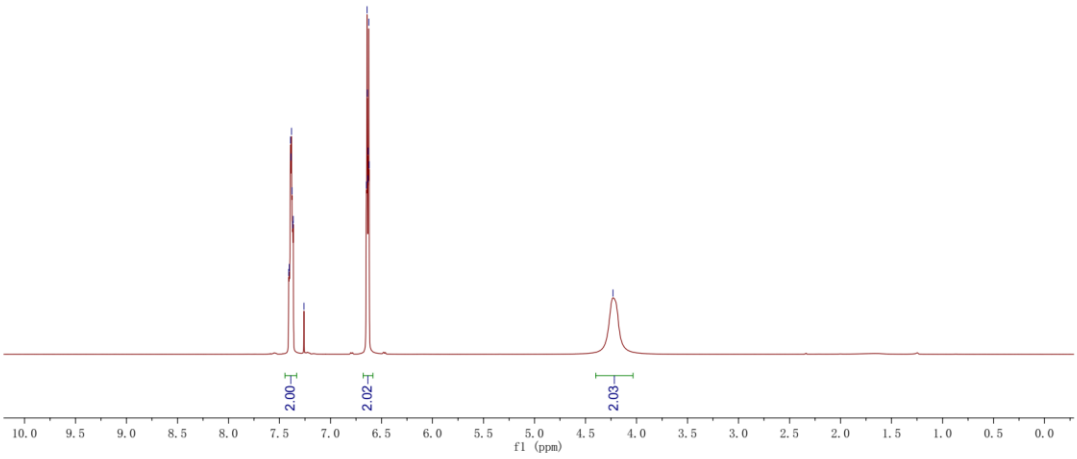


2o

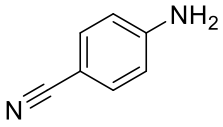
^{1}H NMR (500 MHz, $CDCl_3$)



2p



^{13}C NMR (125 MHz, $CDCl_3$)



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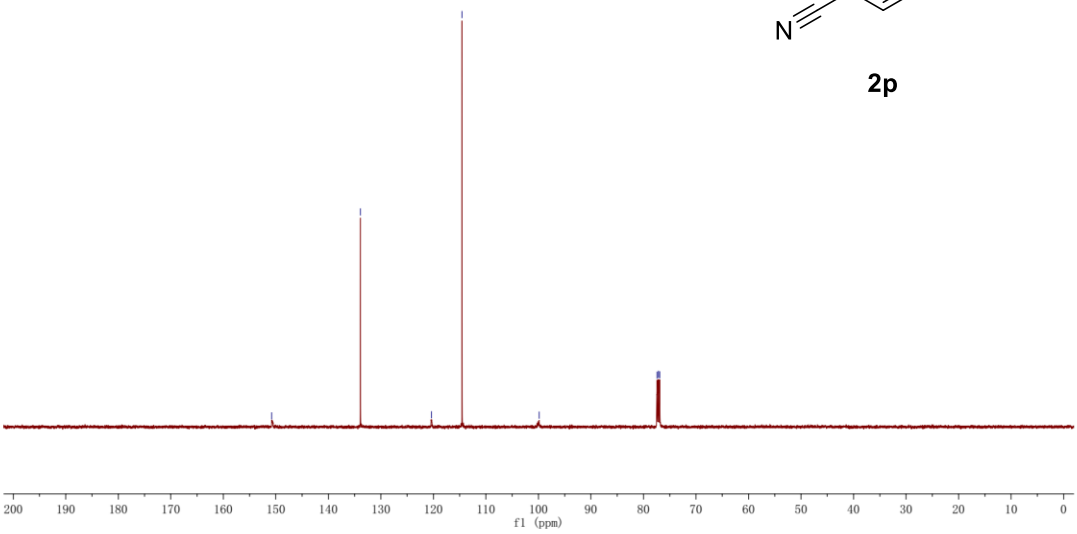
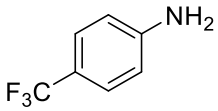


20230911-zyl-90-106

7.3998
7.3830
7.2596
6.6949
6.6781
3.9293

^{1}H NMR (500 MHz, $CDCl_3$)

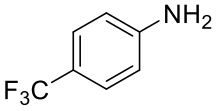


2q

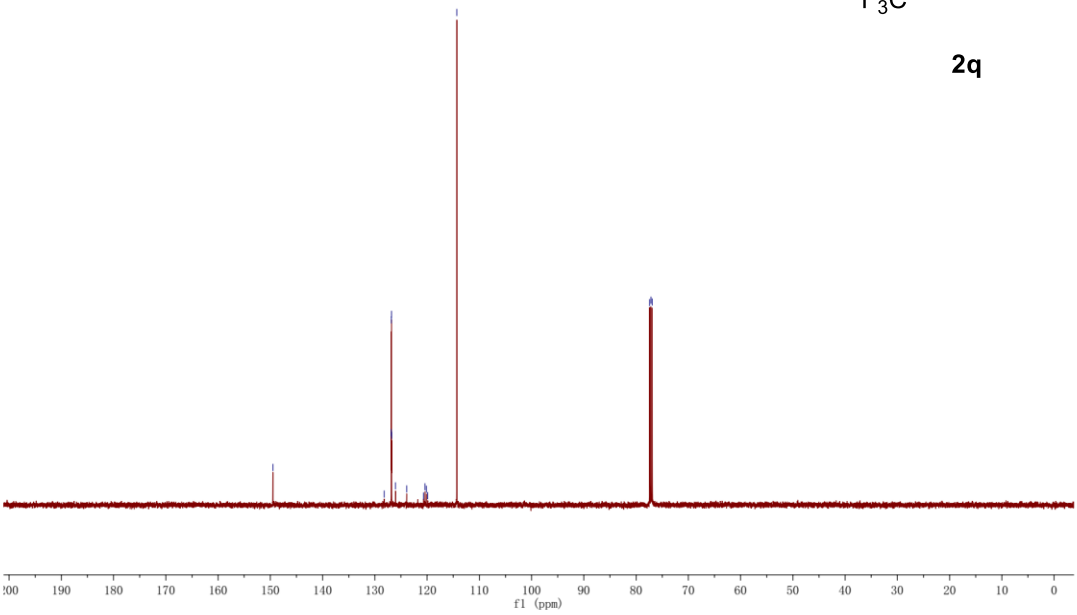
20230911-zyl-c-90-106

149.5140
128.2046
126.8682
126.8381
126.8076
126.7779
126.0432
123.8927
120.6747
120.3990
120.1494
119.8990
114.3060
77.4139
77.1598
76.9058

^{13}C NMR (125 MHz, $CDCl_3$)



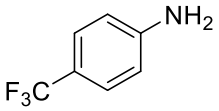
2q



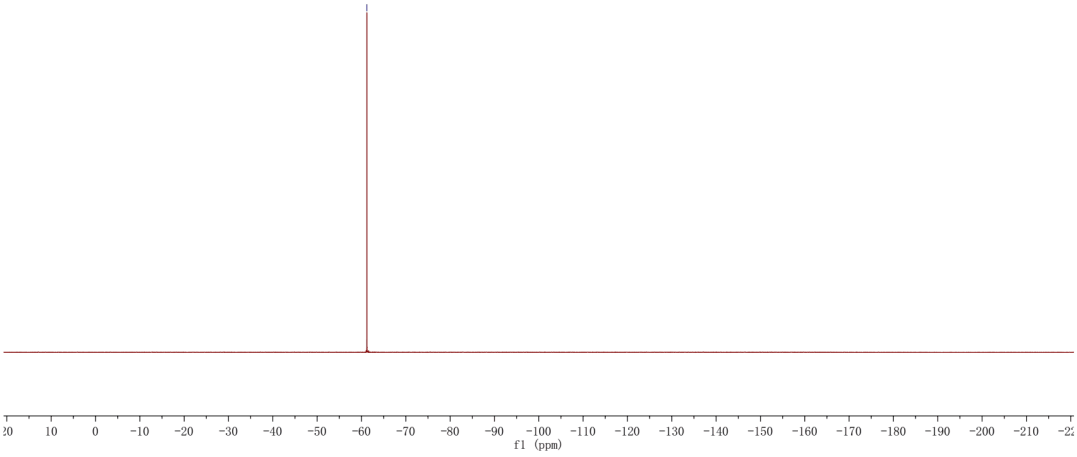
20231204-zyl-97-49

-61.2213

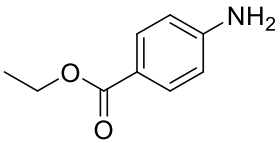
^{19}F NMR (470 MHz, $CDCl_3$)



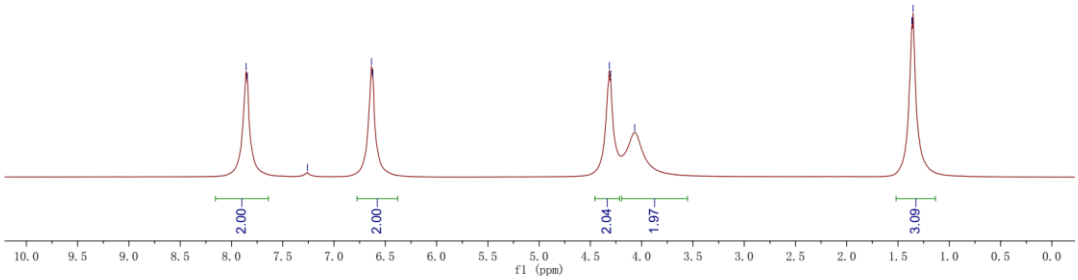
2q



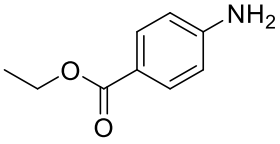
^{1}H NMR (500 MHz, $CDCl_3$)



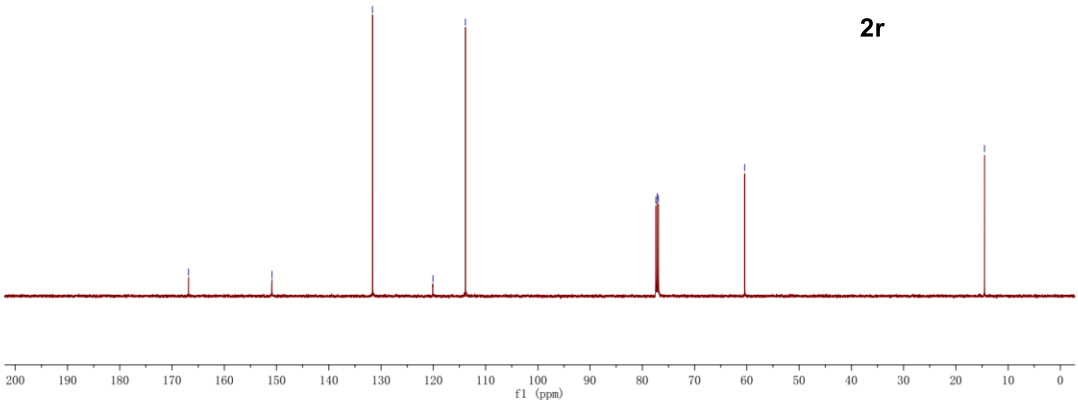
2r



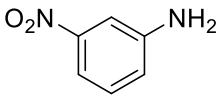
^{13}C NMR (125 MHz, $CDCl_3$)



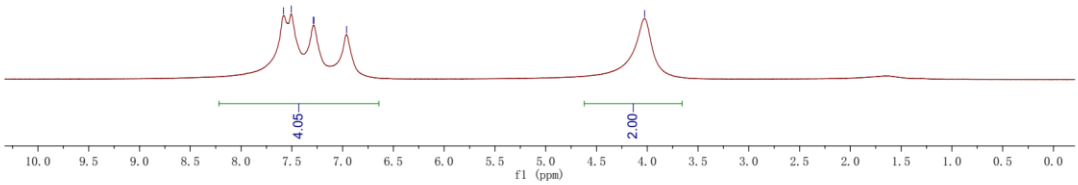
2r



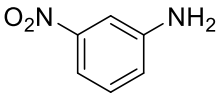
^{1}H NMR (500 MHz, $CDCl_3$)



2s

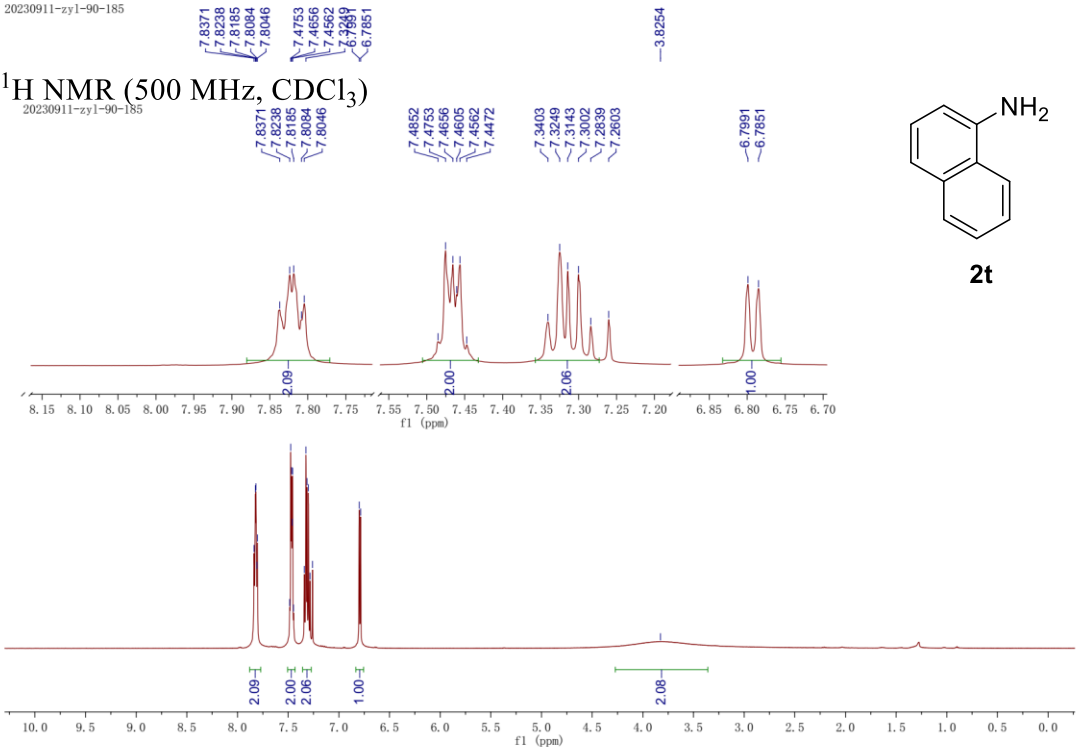


^{13}C NMR (125 MHz, $CDCl_3$)



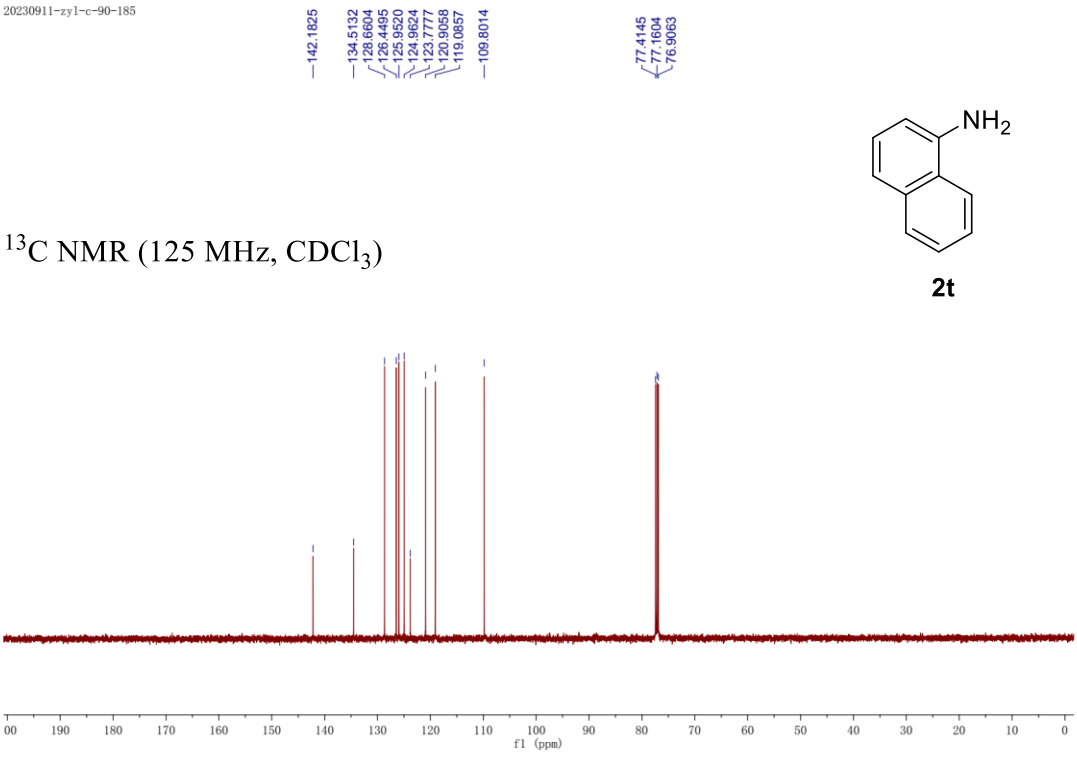
2s

^{1}H NMR (500 MHz, $CDCl_3$)



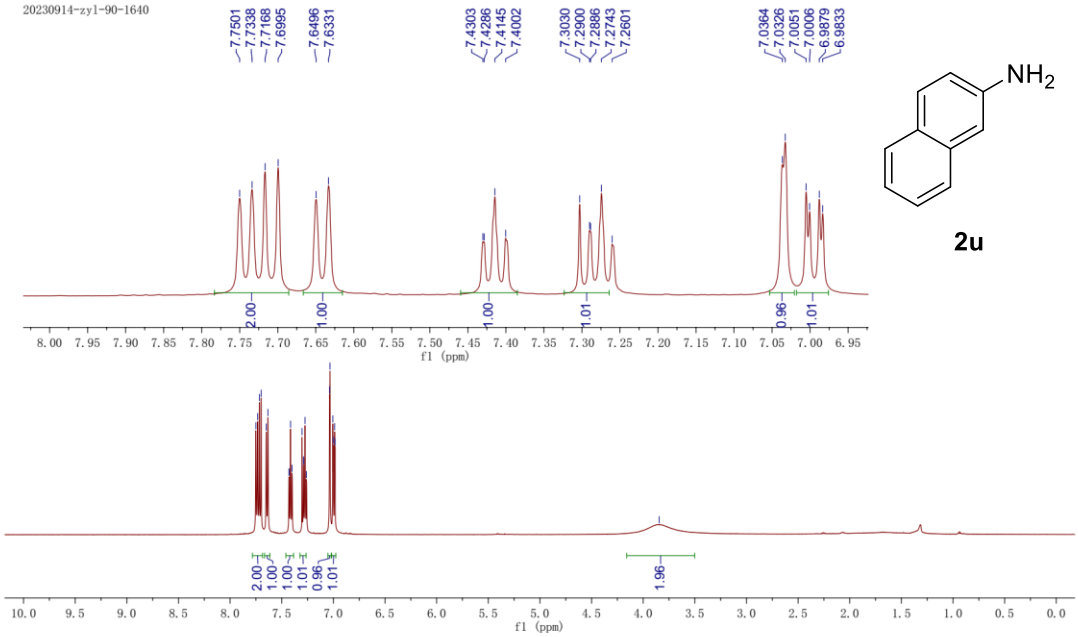
2t

^{13}C NMR (125 MHz, $CDCl_3$)

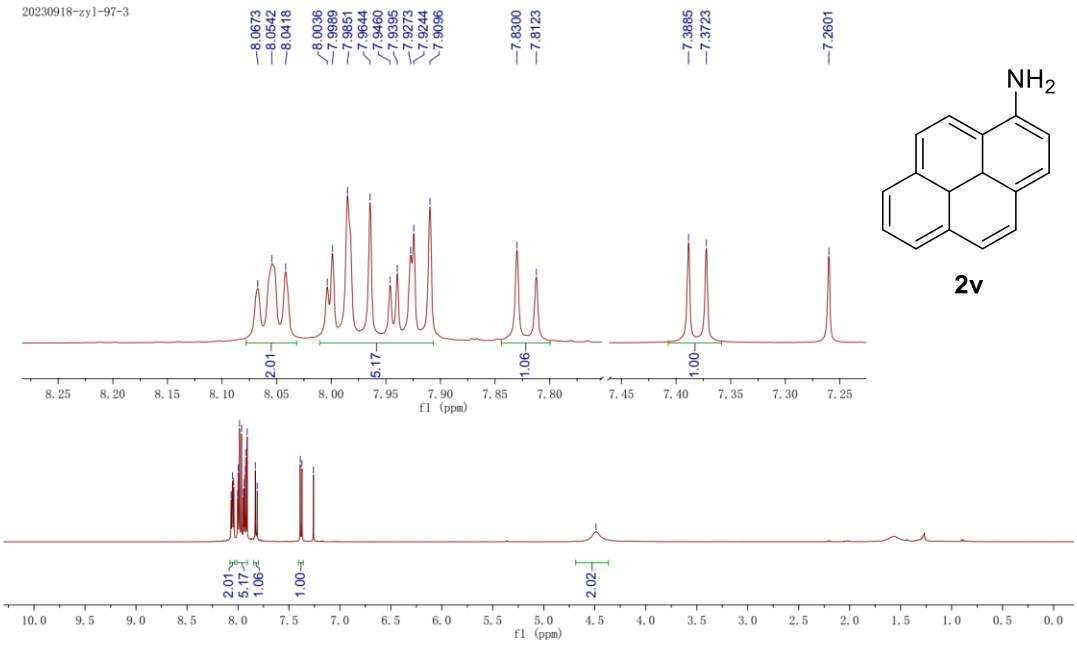


2t

^{1}H NMR (500 MHz, $CDCl_3$)

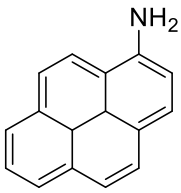


^{1}H NMR (500 MHz, $CDCl_3$)

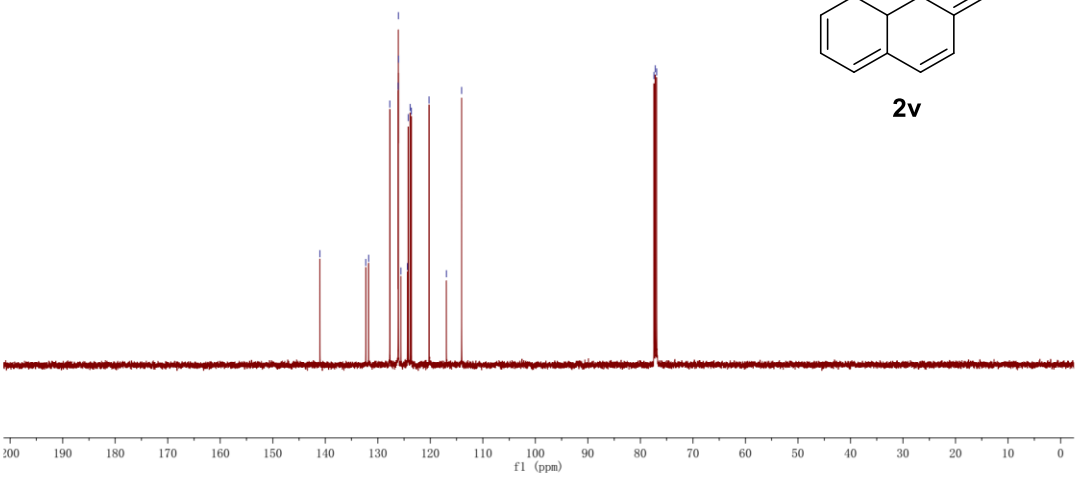


2v

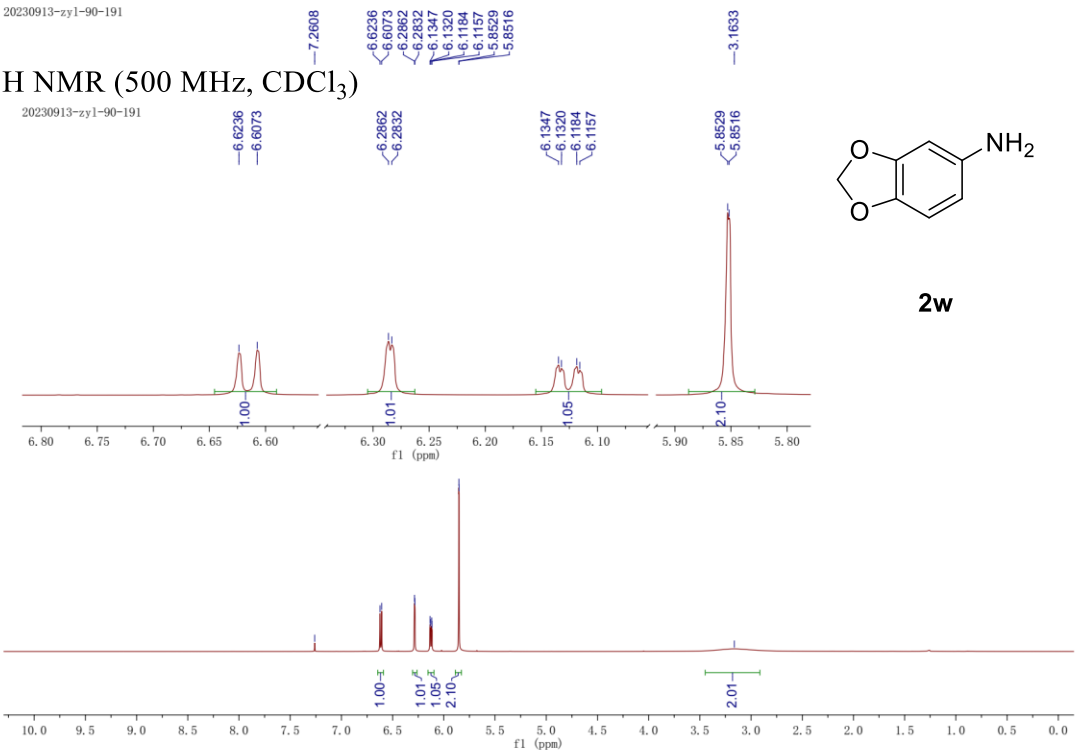
^{13}C NMR (125 MHz, $CDCl_3$)



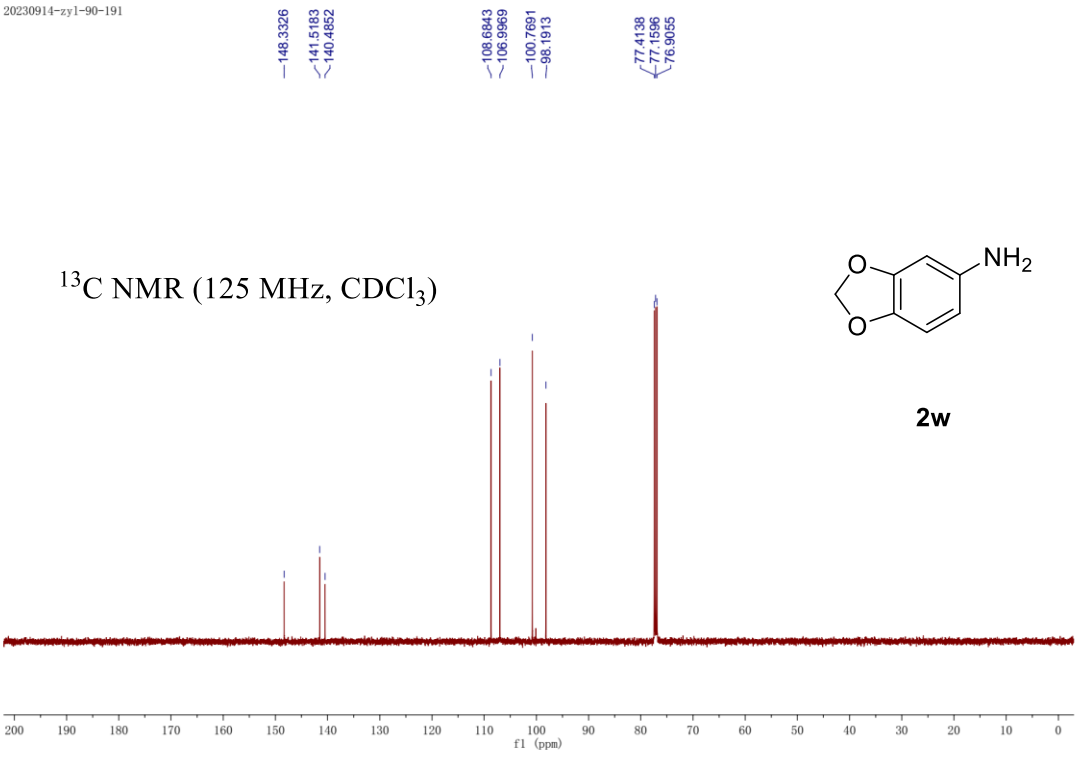
2v



^{1}H NMR (500 MHz, $CDCl_3$)

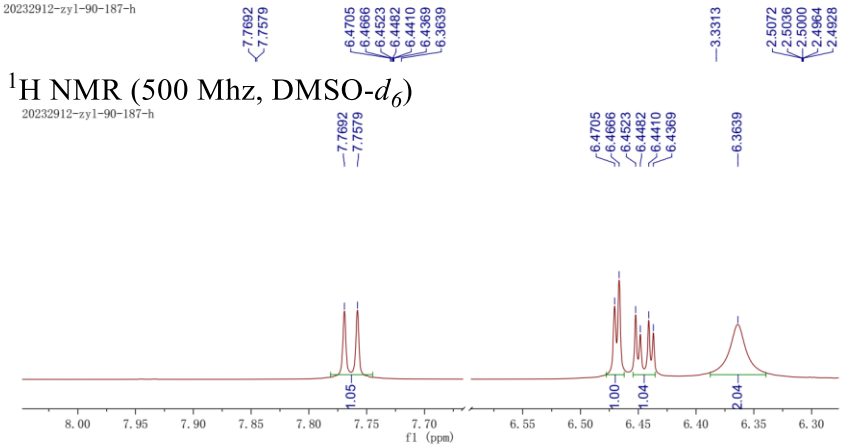


2w

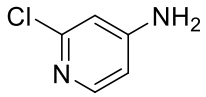


^{13}C NMR (125 MHz, $CDCl_3$)

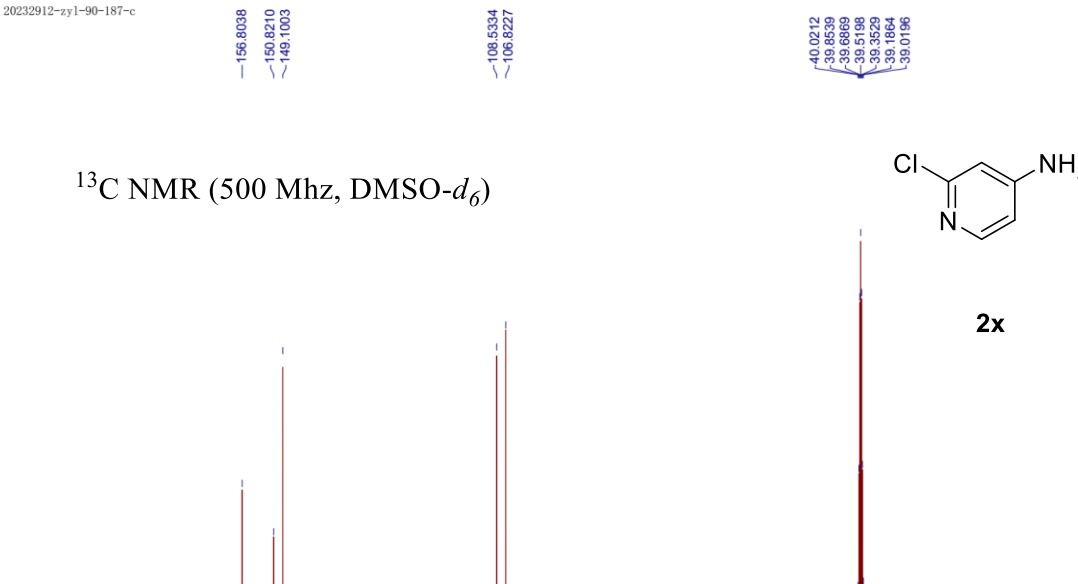
2w



^{1}H NMR (500 Mhz, DMSO-d_6)



2x



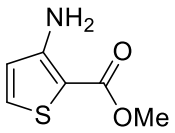
^{13}C NMR (500 Mhz, DMSO-d_6)

2x

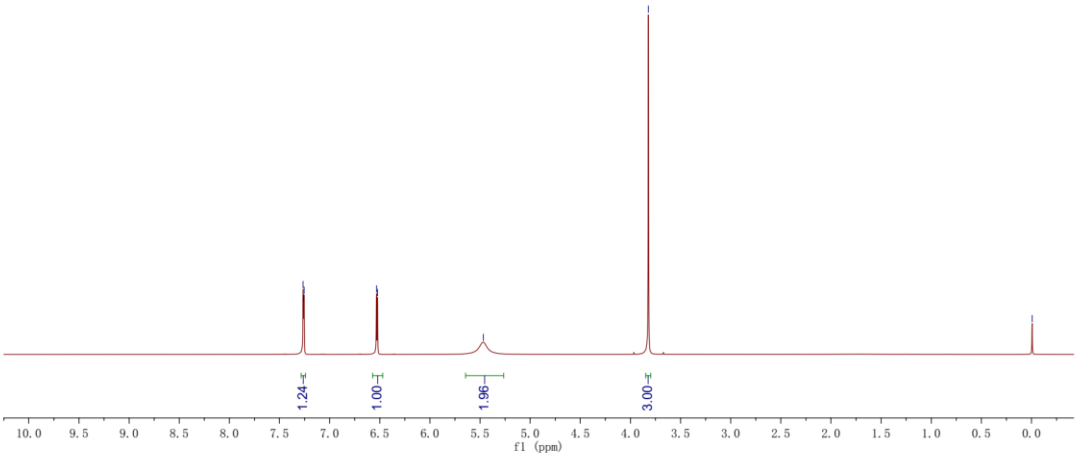
20230425-zy1-90-47

7.2649
7.2602
7.2546
6.5328
6.5222
5.4684
3.8203
0.0070

^{1}H NMR (500 MHz, $CDCl_3$)



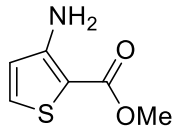
2y



20230425-zy1-90-47

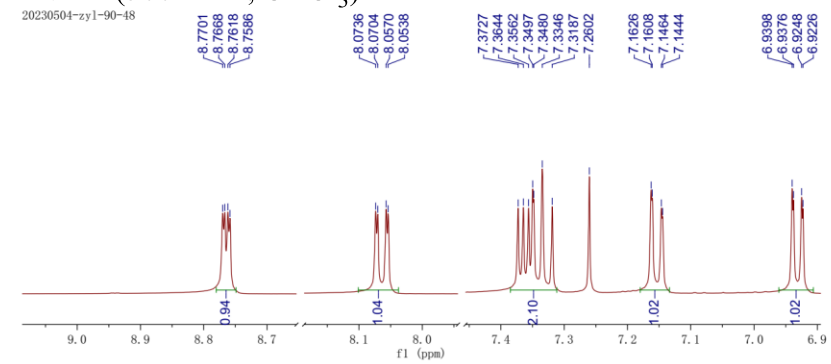
165.1276
154.1166
131.6615
119.9202
101.2924
77.4143
77.1601
76.9060
51.3707

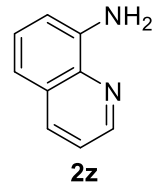
^{13}C NMR (125 MHz, $CDCl_3$)



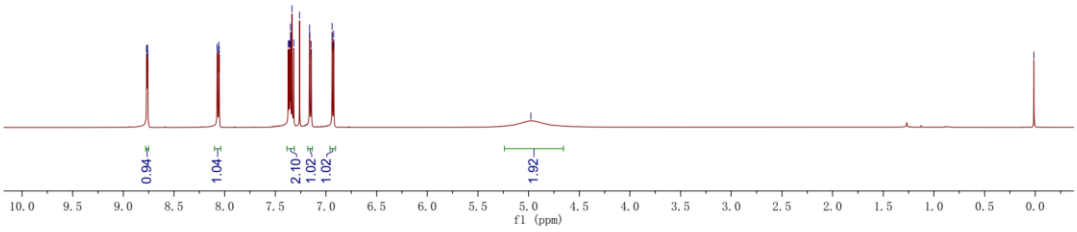
2y

^{1}H NMR (500 MHz, $CDCl_3$)

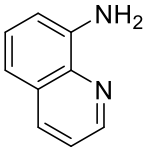




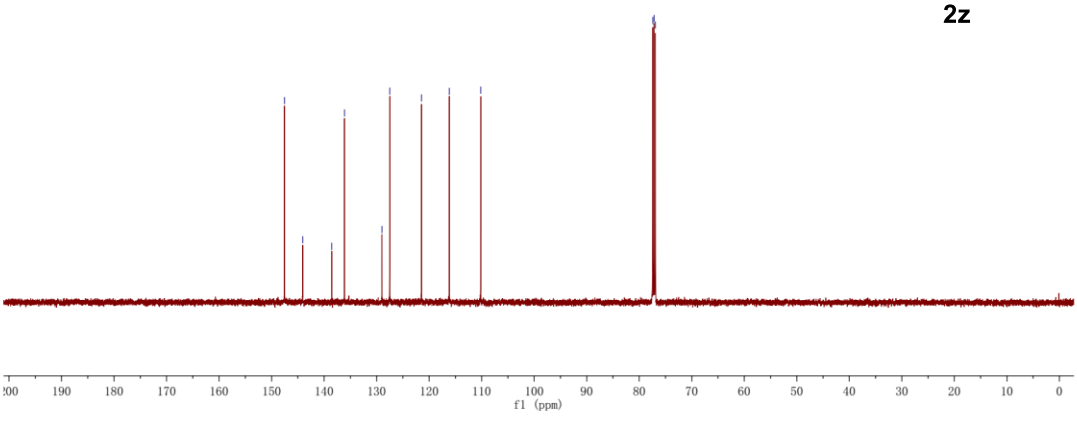
2z

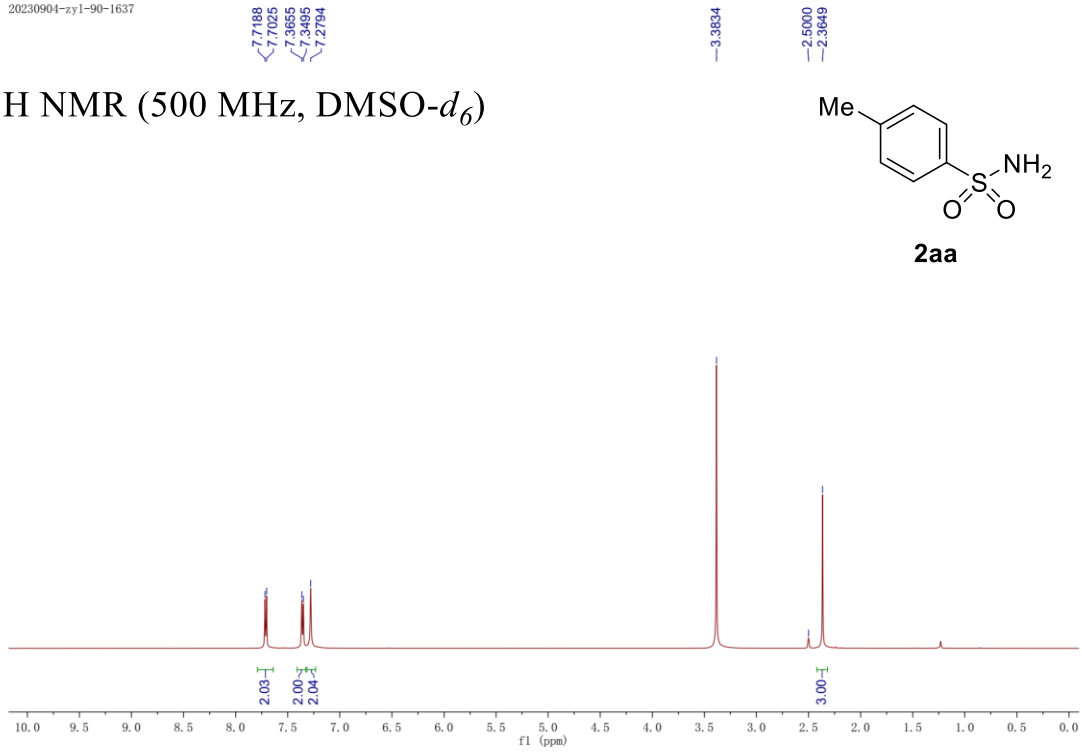


^{13}C NMR (125 MHz, $CDCl_3$)



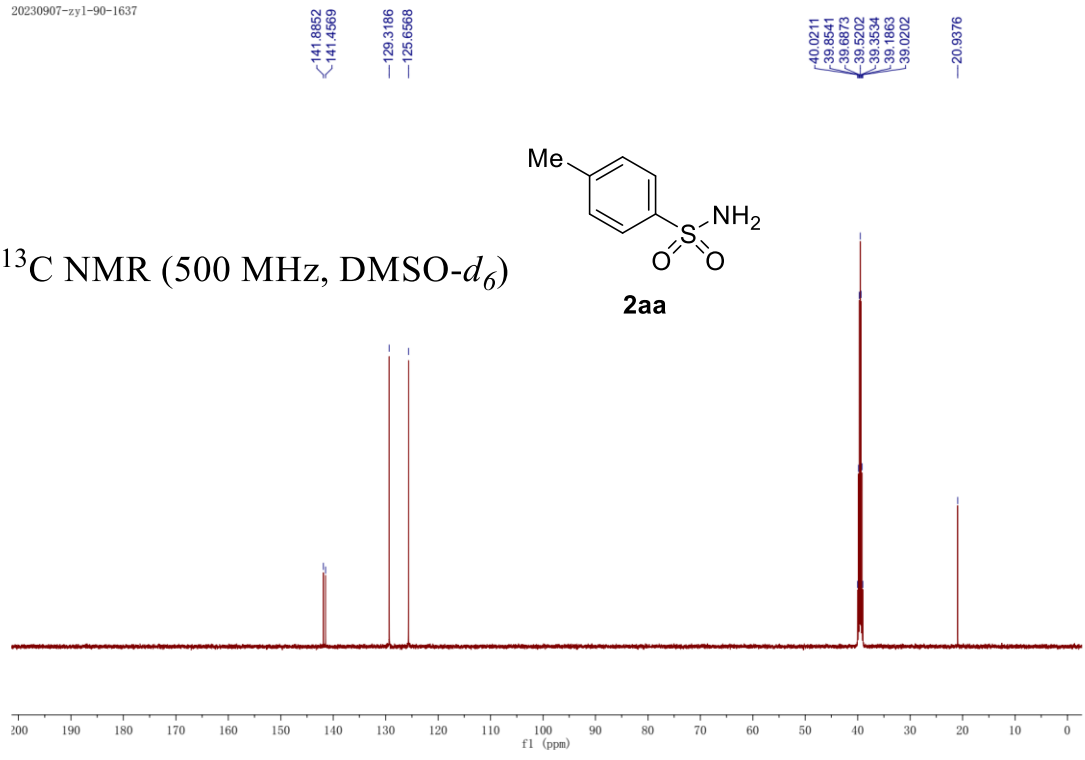
2z





^{1}H NMR (500 MHz, DMSO-d_6)

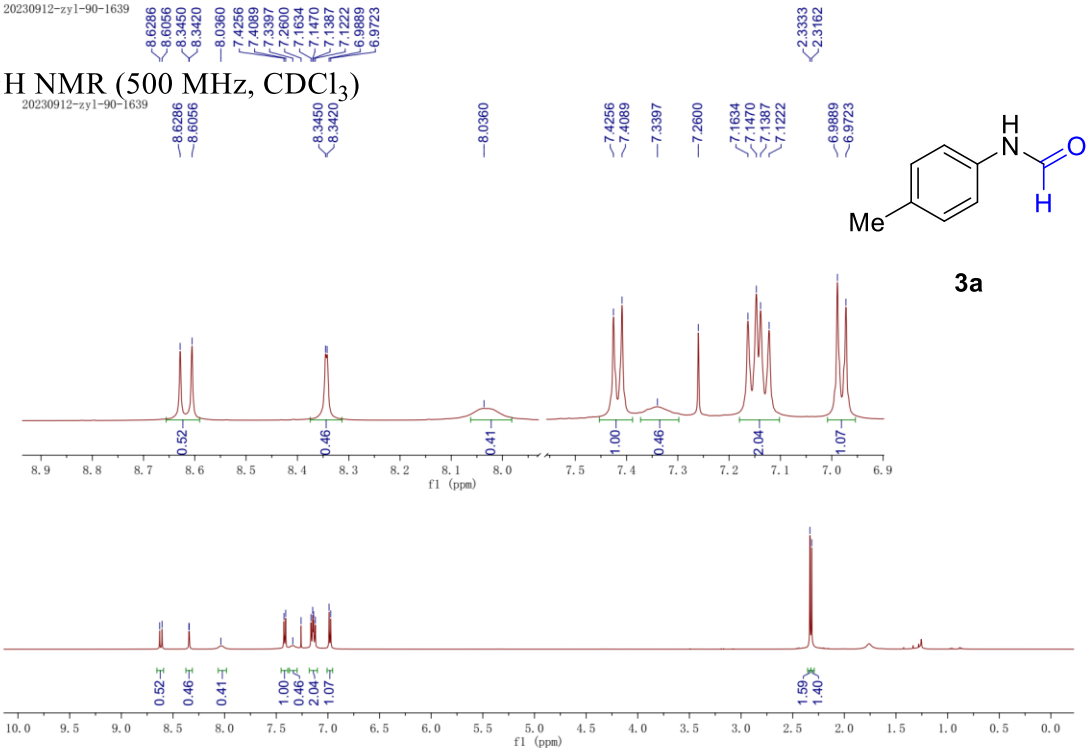
2aa



^{13}C NMR (500 MHz, DMSO-d_6)

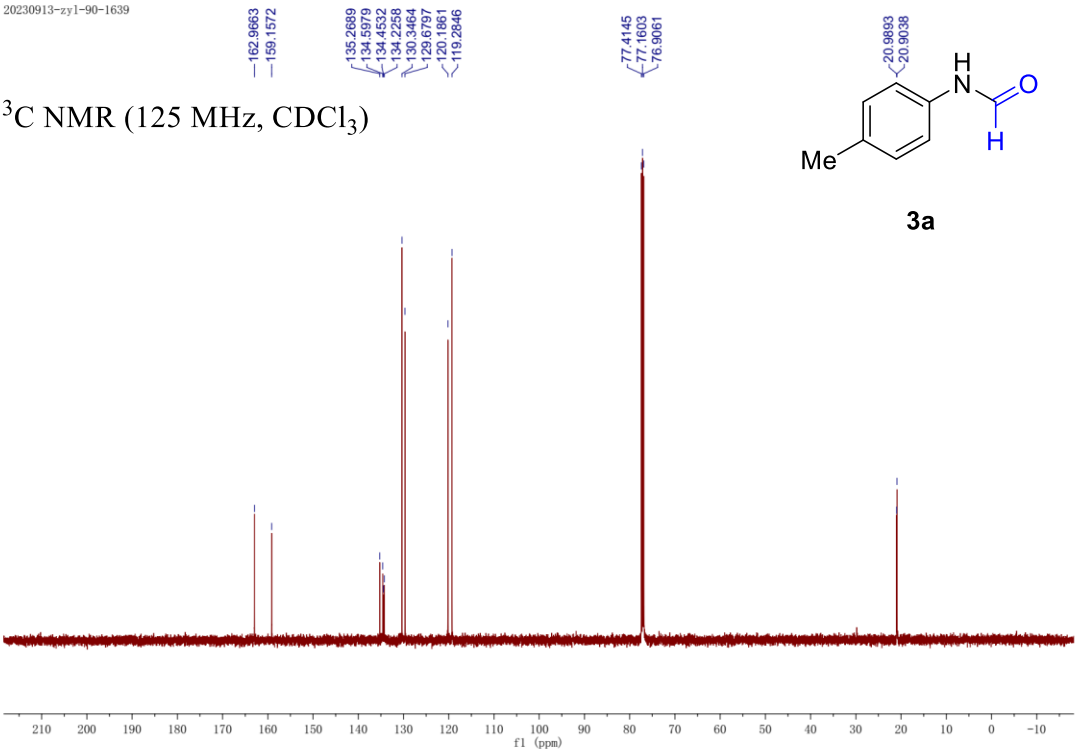
2aa

^{1}H NMR (500 MHz, $CDCl_3$)



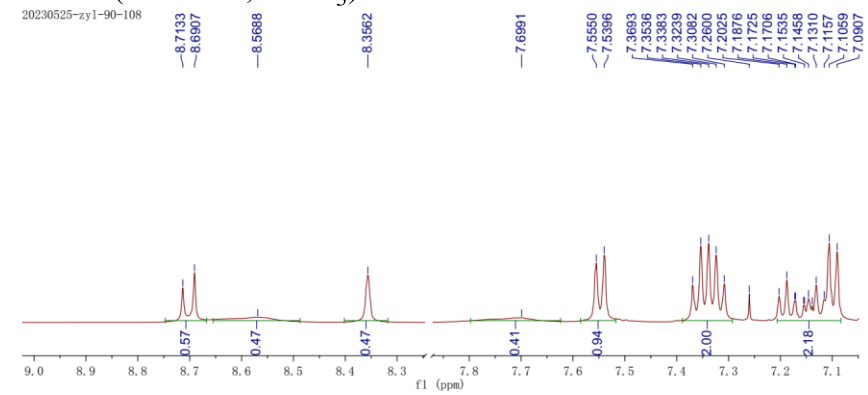
3a

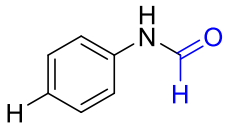
^{13}C NMR (125 MHz, $CDCl_3$)



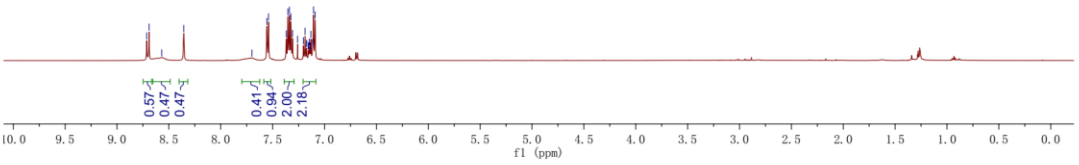
3a

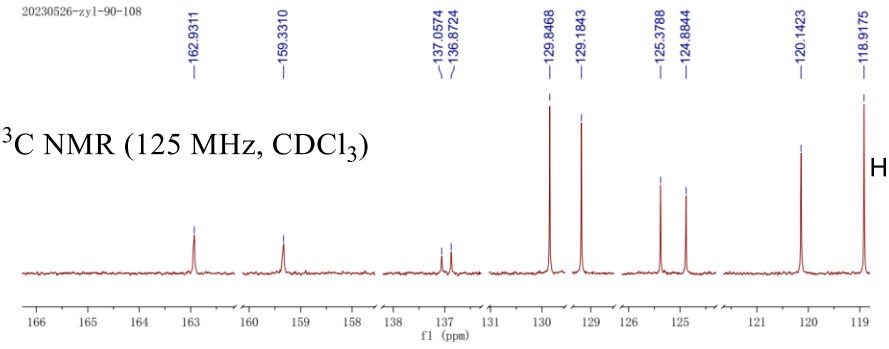
^{1}H NMR (500 MHz, $CDCl_3$)



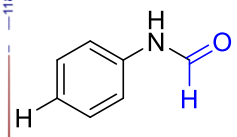


3b

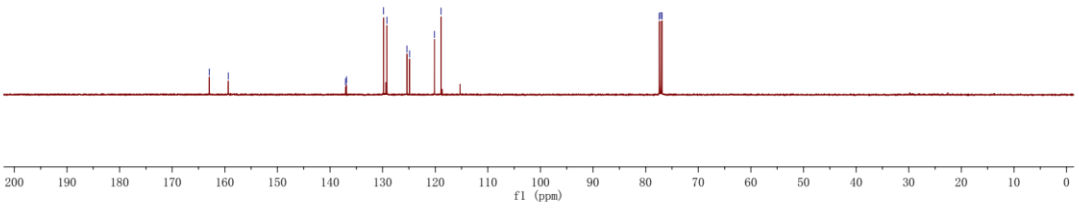


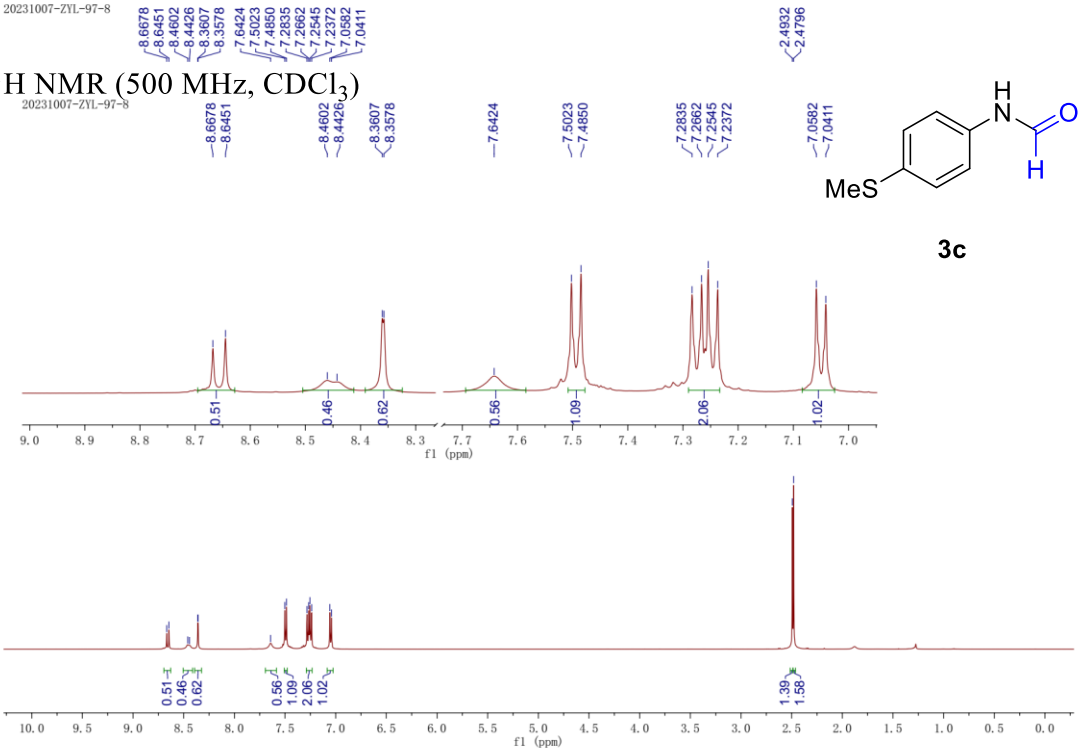


^{13}C NMR (125 MHz, $CDCl_3$)

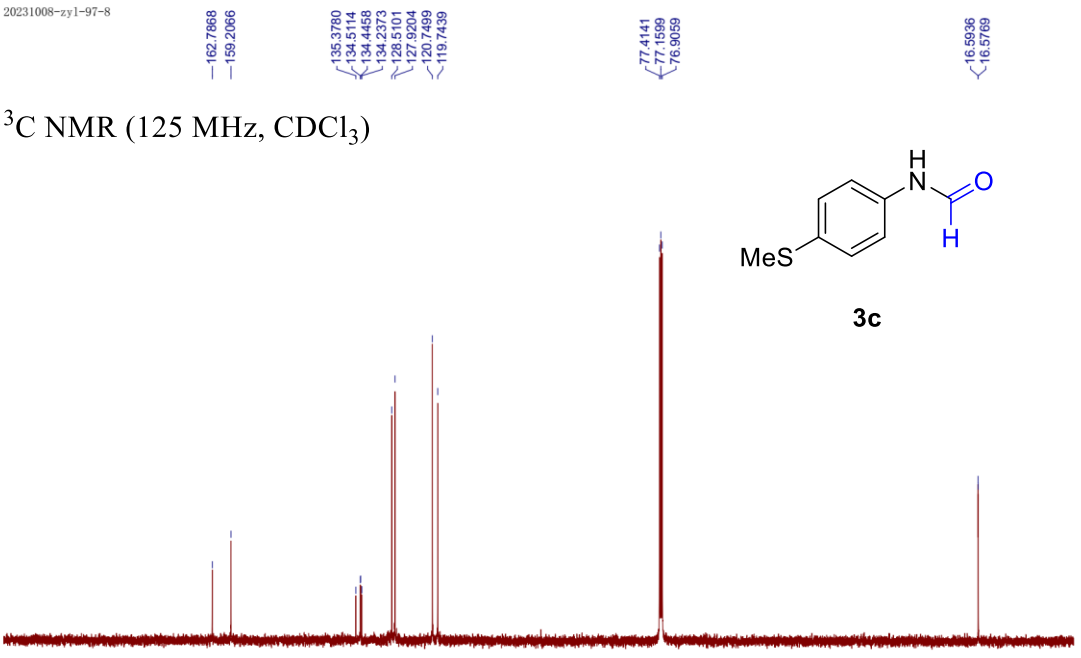


3b



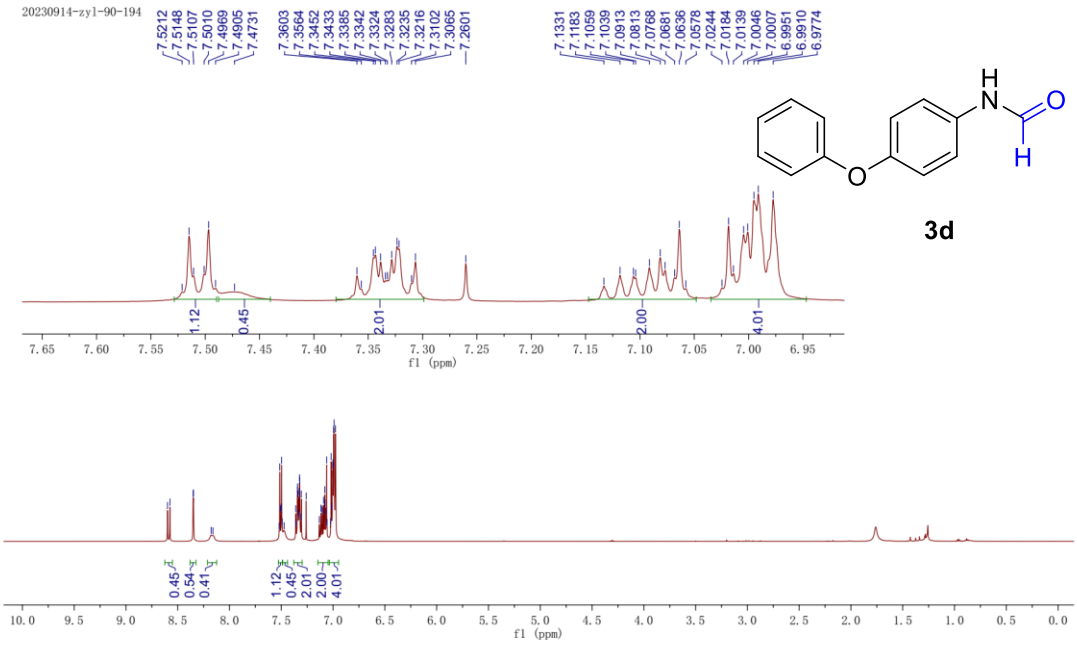


^{1}H NMR (500 MHz, $CDCl_3$)

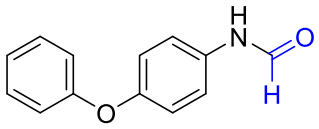


^{13}C NMR (125 MHz, $CDCl_3$)

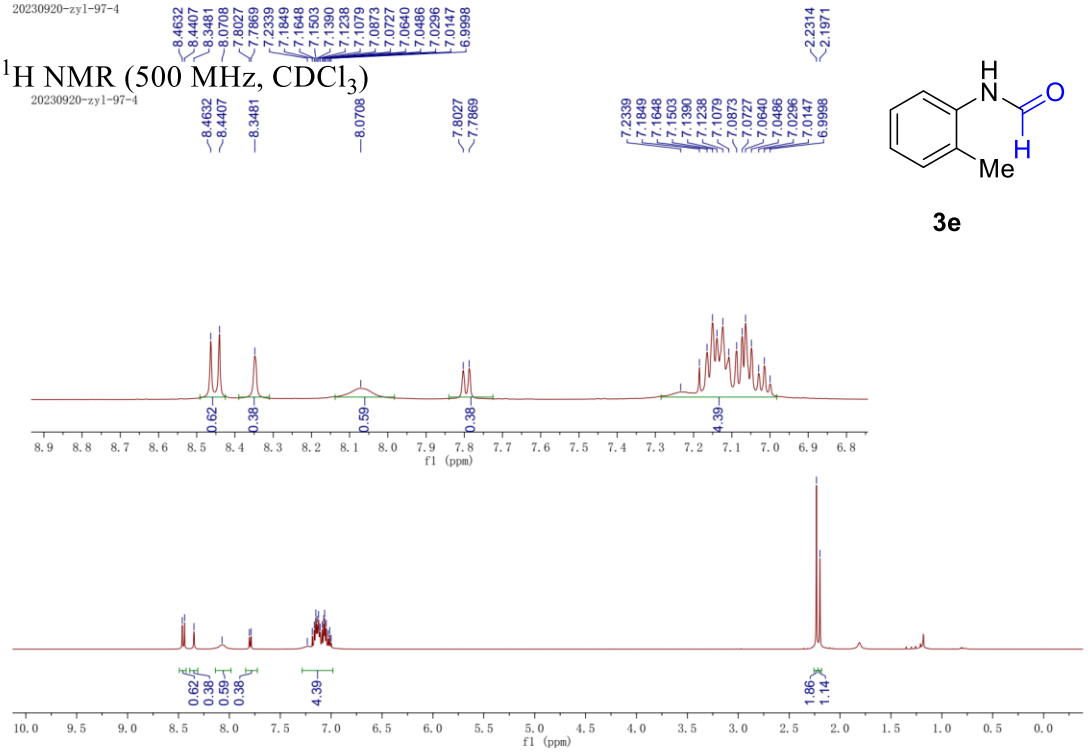
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

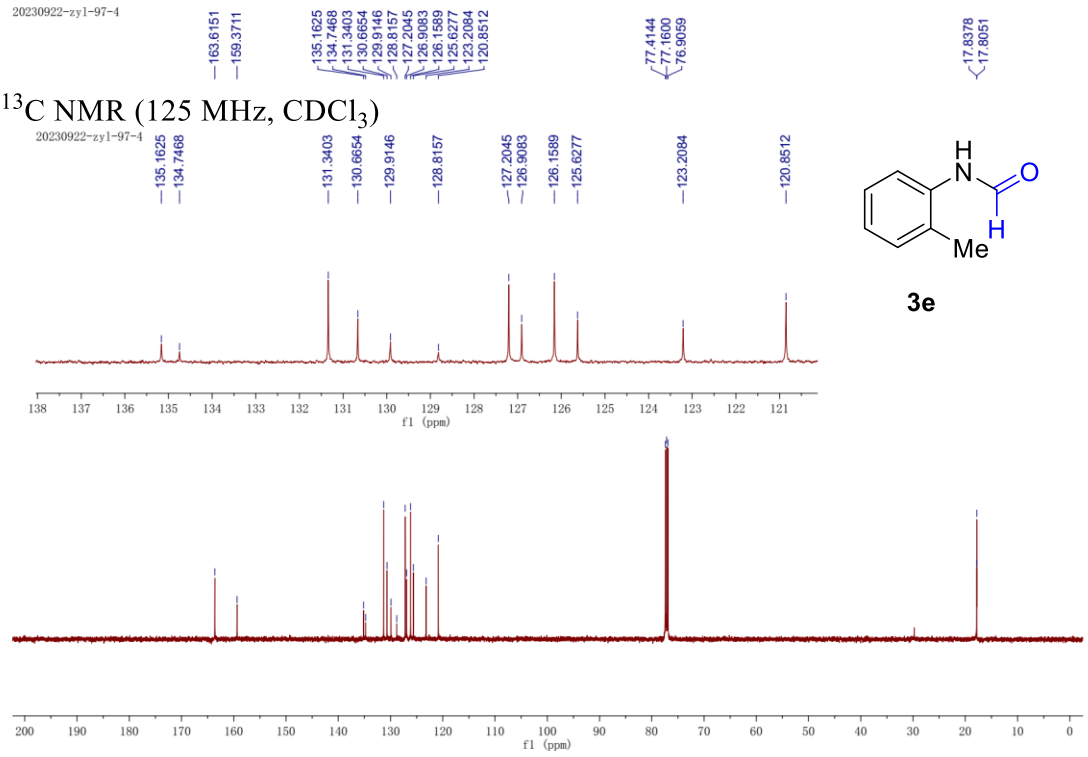


^{1}H NMR (500 MHz, $CDCl_3$)



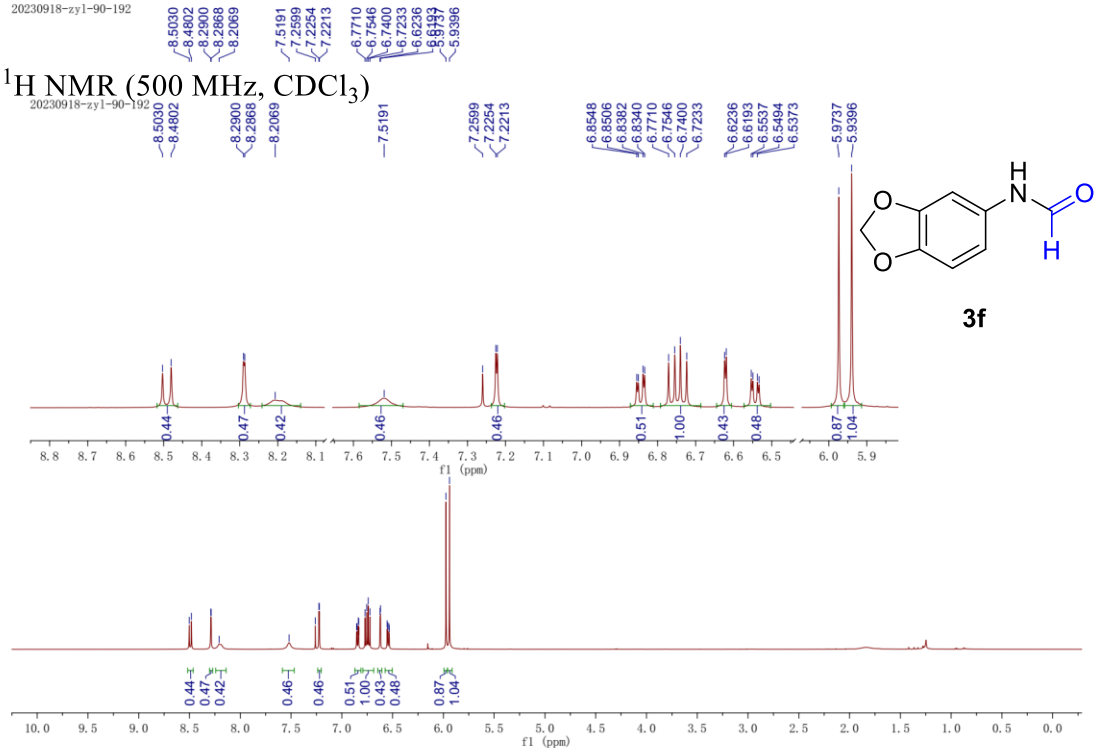
3e

^{13}C NMR (125 MHz, $CDCl_3$)

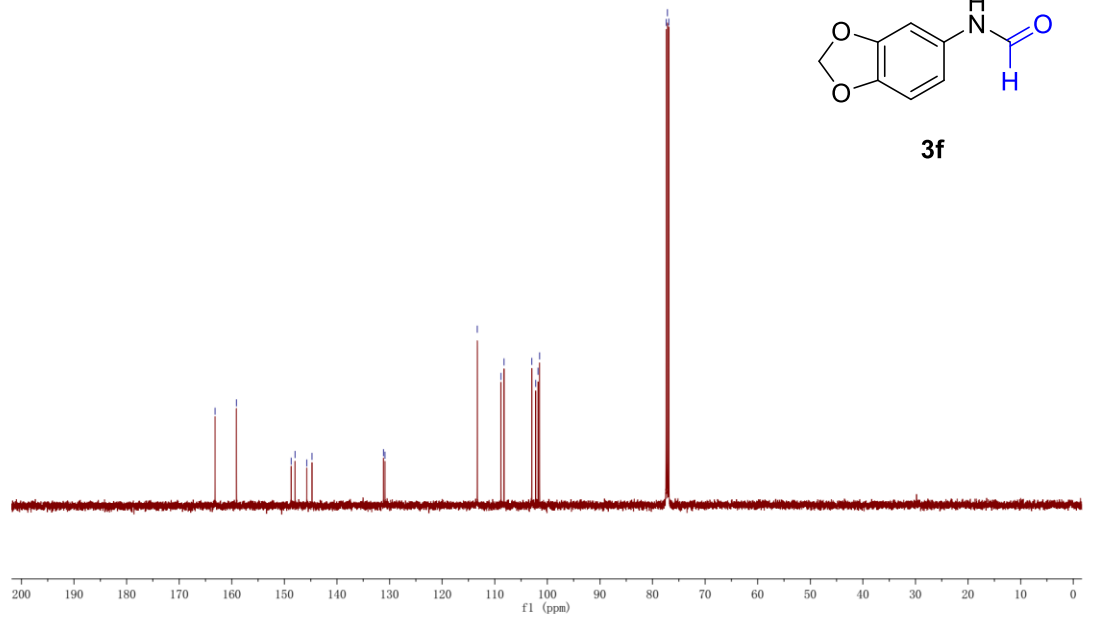


3e

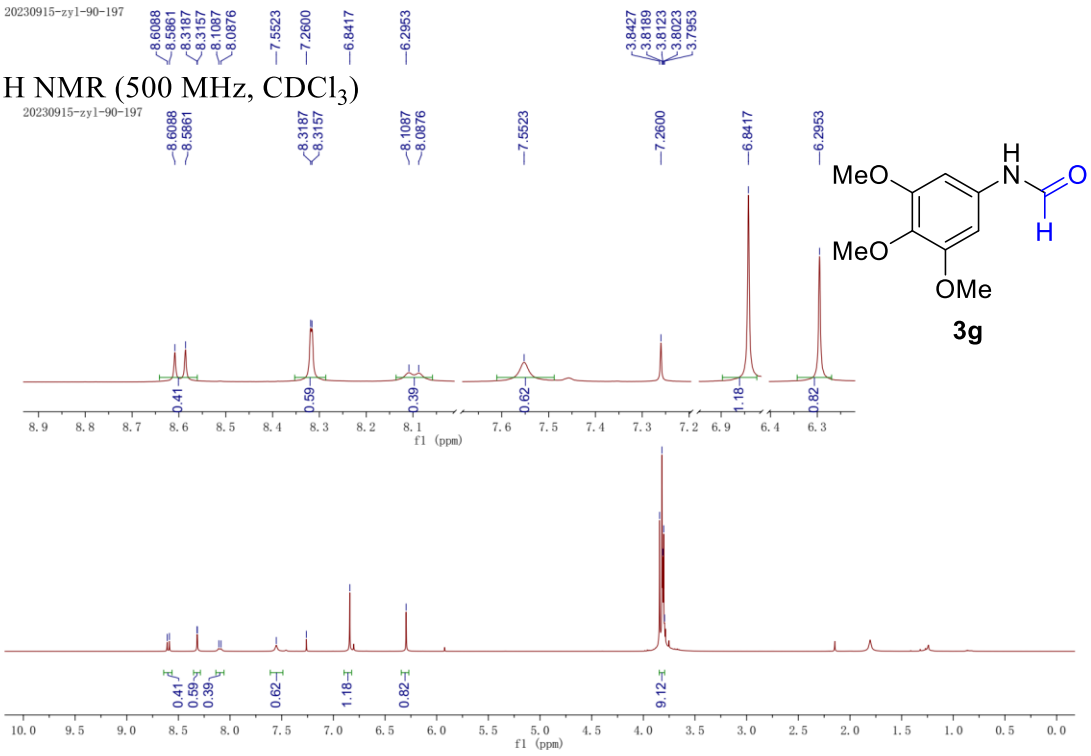
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

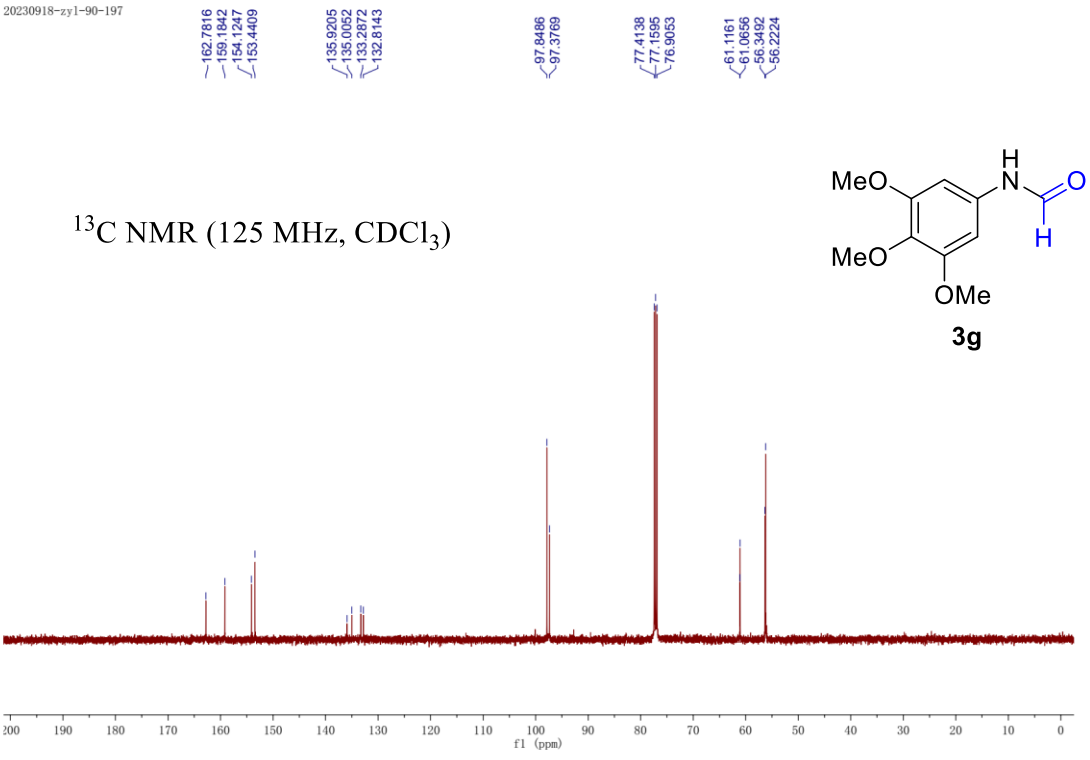


^{1}H NMR (500 MHz, $CDCl_3$)



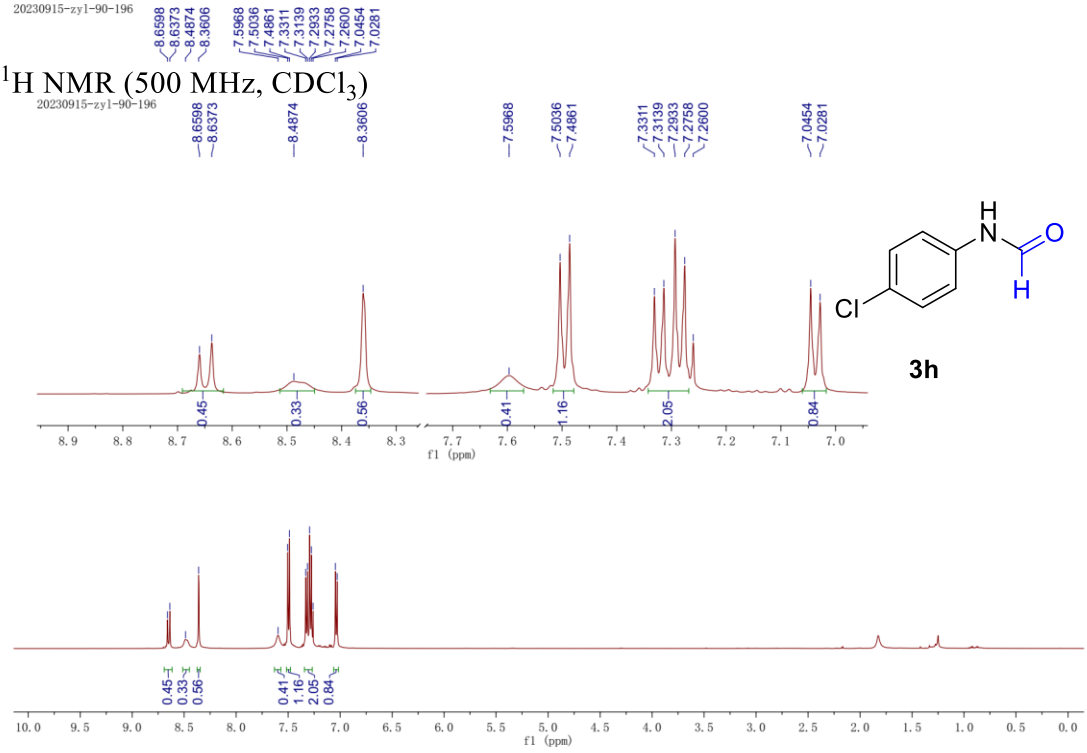
3g

^{13}C NMR (125 MHz, $CDCl_3$)



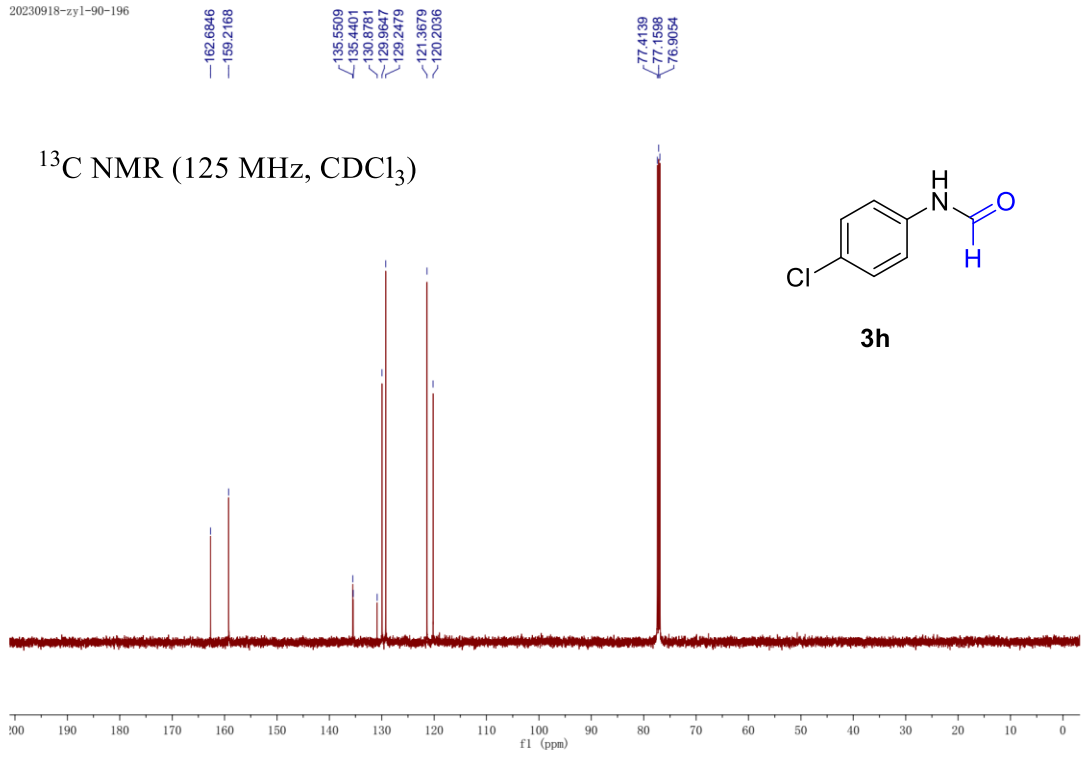
3g

^{1}H NMR (500 MHz, $CDCl_3$)



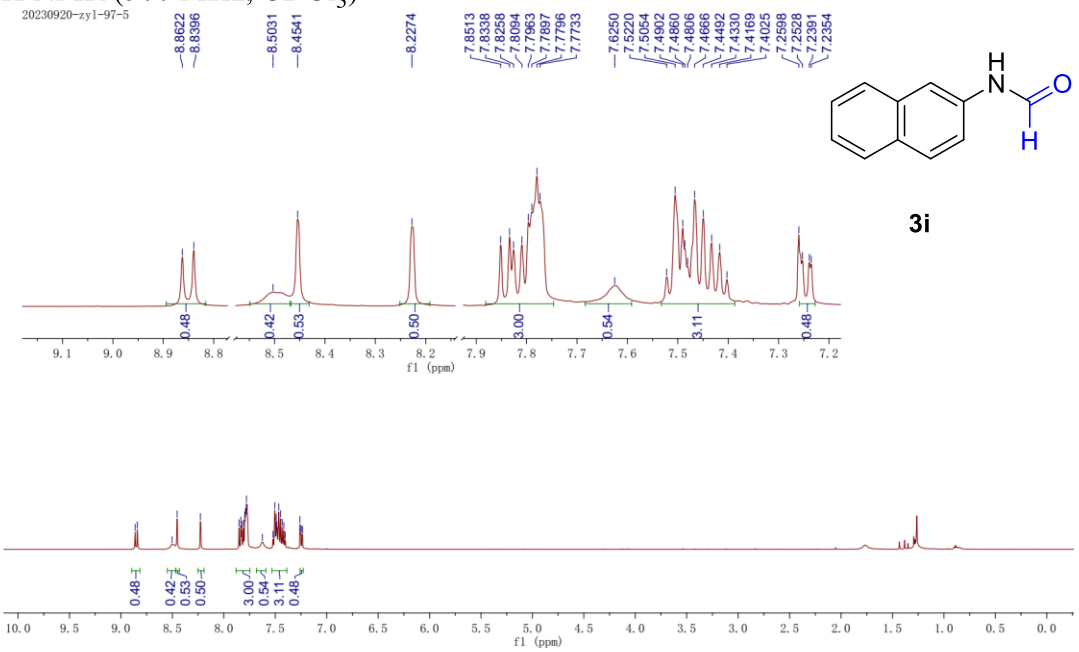
3h

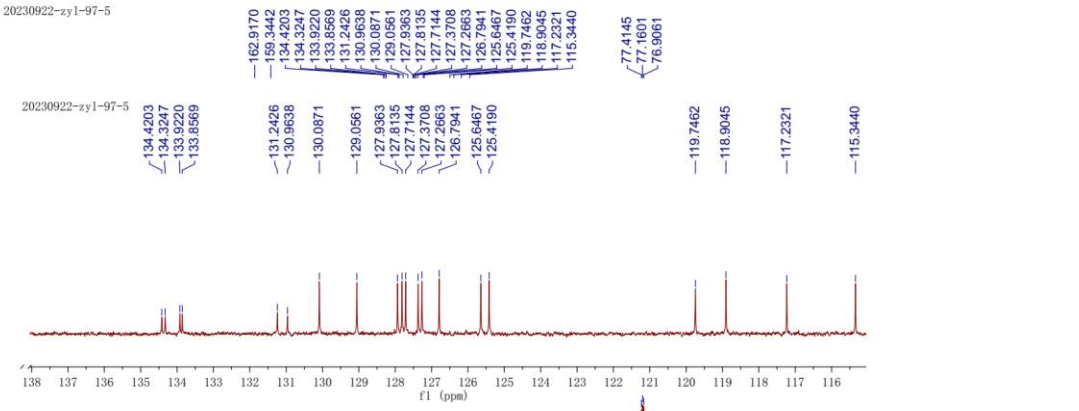
^{13}C NMR (125 MHz, $CDCl_3$)



3h

^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)