Supplementary Information (SI) for Organic Chemistry Frontiers.

Supplementary Information

Photoredox Catalyzed Visible Light-Induced Reduction of Nitroarenes into Anilines

Weiqiang Sun,[a] Hao Guo,*[a] Aishun Ding,*[a]

[a] Department of Chemistry, Fudan University, 2005 Songhu Road, Shanghai 200438, PR China, E-mail: Hao_Guo@fudan.edu.cn, dingaishun@fudan.edu.cn

Contents

Experimental Section

General information

All the photo reactions were carried out using purple LED strip (λ = 415 nm, height: 10 cm, diameter: 15 cm, 30 W, manufacturer: Xuzhou Ai Jia Electronic Technology Co. LTD, model: DT 415) at a distance of 3-5 cm at rt (maintained with three cooling fans) unless stated otherwise. ^{1}H (400 MHz) NMR spectra of samples in $CDCl_3$ or DMSO-d_6 or methanol-d_4 were recorded on an AVANCE III 400 spectrometer. Anhydrous *n*-hexane, ethyl ether, and EtOH were commercially available. Anhydrous DCM, DCE, MeCN, and toluene were distilled with CaH_2. Anhydrous THF was distilled with Na using benzophenone as a monitor. **1a**, **1b**, **1c**, **1d**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r**, **1s**, **1t**, **1u**, **1v**, **1w**, **1x**, **1y**, **1z**, **1aa**, **1ab**, and **1ac** were commercially available and used as purchased without further purification. **1e**[1] was synthesized according to literature procedures.

Figure S1. Spectral distribution of irradiance density for the purple LED strip

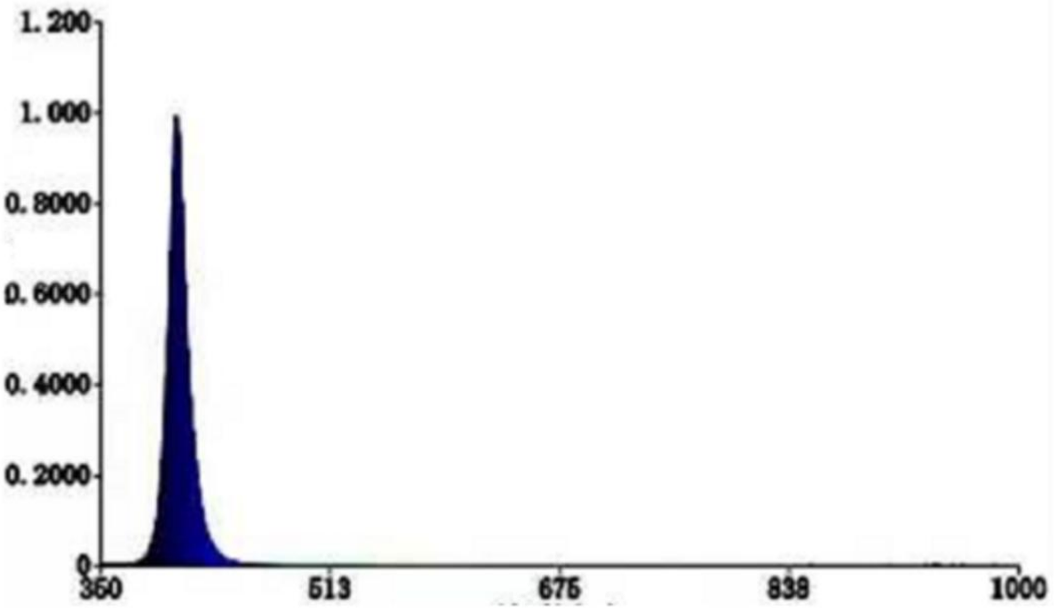
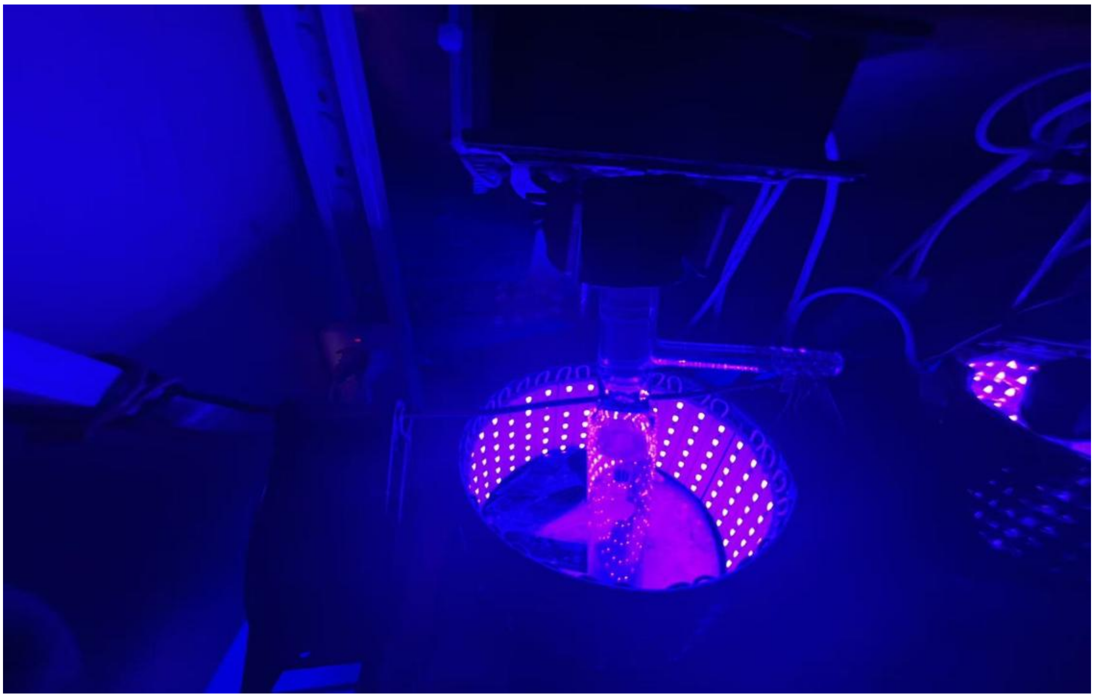
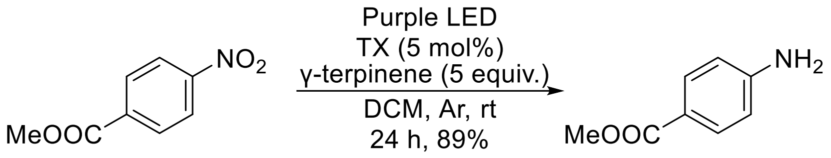


Figure S2. General setup for the photoreaction



Typical Procedure for the photoreaction

Synthesis of 4-(methoxycarbonyl)aniline (2a)

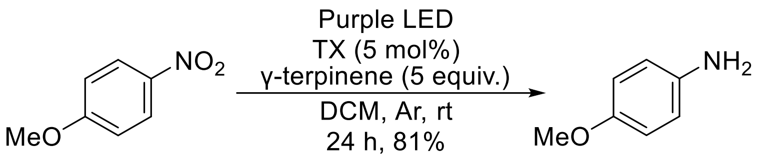


1a **2a**

To a flame dried 25 mL of Pyrex sealed tube were added TX (2.1 mg, 0.01 mmol), **1a** (36.3 mg, 0.2 mmol), anhydrous DCM (20 mL), and γ-terpinene (160 μL, 1.0 mmol). The reaction mixture was irradiated by purple LED strip (λ = 415 nm, height: 10 cm, diameter: 15 cm, 30 W) at a distance of 3-5 cm under argon atmosphere at rt (maintained with three cooling fans). The reaction was completed after 24 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 50:1). The solvent was removed, and the residue was purified by flash chromatography on silica gel (eluent: DCM) to afford **2a**[2] as a solid (27.1 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.4 Hz, 2 H), 6.64 (d, J = 8.4 Hz, 2 H), 4.03 (brs, 2 H), 3.85 (s, 3 H).

The following compounds were synthesized according to Typical Procedure.

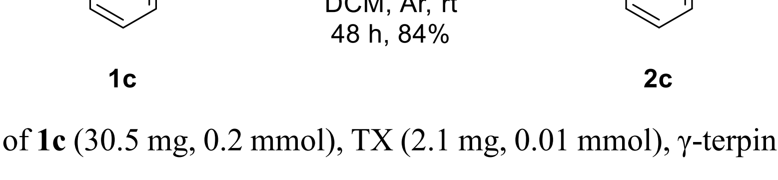
1) 4-Methoxyaniline (2b)`



1b **2b**

The reaction of **1b** (30.7 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2b**[2] as a white solid (20.1 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, J = 8.8 Hz, 2 H), 6.64 (d, J = 8.8 Hz, 2 H), 3.74 (s, 3 H), 3.41 (brs, 2 H).

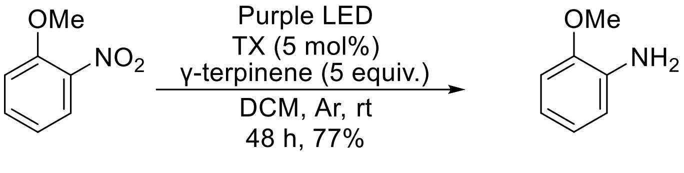
2) 3-Methoxyaniline (2c)`



1c **2c**

The reaction of **1c** (30.5 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2c**[3] as a liquid (20.7 mg, 84%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.06 (dd, J = 8.0, 8.0 Hz, 1 H), 6.35-6.22 (m, 3 H), 3.76 (s, 3 H), 3.65 (brs, 2 H).

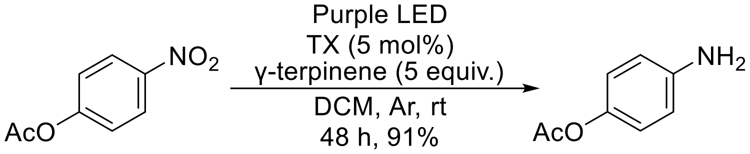
3) 2-Methoxyaniline (2d)`



1d **2d**

The reaction of **1d** (30.3 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2d**[3] as a liquid (18.9 mg, 77%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.82-6.69 (m, 4 H), 3.84 (s, 3 H), 3.46 (brs, 2 H).

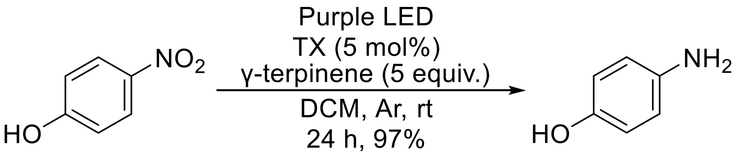
4) 4-Acetoxyaniline (2e)



1e **2e**

The reaction of **1e** (36.4 mg, 0.2 mmol), TX (2.0 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2e**[4] as a white solid (27.5 mg, 91%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.85 (d, J = 8.8 Hz, 2 H), 6.64 (d, J = 8.8 Hz, 2 H), 3.62 (brs, 2 H), 2.25 (s, 3 H).

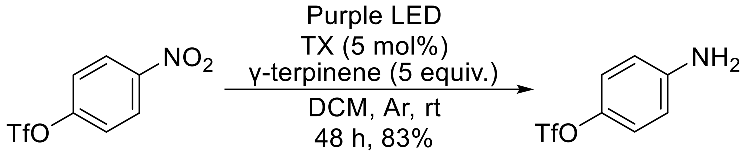
5) 4-Hydroxyaniline (2f)



1f **2f**

The reaction of **1f** (28.0 mg, 0.2 mmol), TX (2.2 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2f**[5] as a solid (21.3 mg, 97%). ^{1}H NMR (400 MHz, CD$_3$OD) δ 6.67-6.56 (m, 4 H).

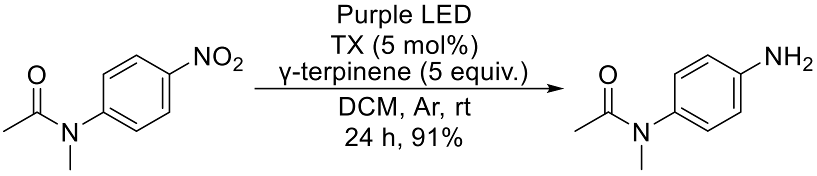
6) 4-(((Trifluoromethyl)sulfonyl)oxy)aniline (2g)



1g **2g**

The reaction of **1g** (54.2 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2g**[6] as a white solid (40.0 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 8.8 Hz, 2 H), 6.65 (d, J = 8.8 Hz, 2 H), 3.80 (brs, 2 H).

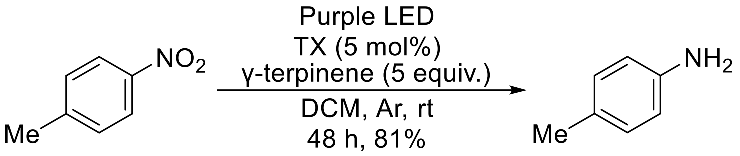
7) 4-(*N*-methylacetamido)aniline (2h)



1h **2h**

The reaction of **1h** (38.9 mg, 0.2 mmol), TX (2.2 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2h**[7] as a solid (29.9 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, J = 8.4 Hz, 2 H), 6.68 (d, J = 8.4 Hz, 2 H), 3.87 (brs, 2 H), 3.20 (s, 3 H), 1.85 (s, 3 H).

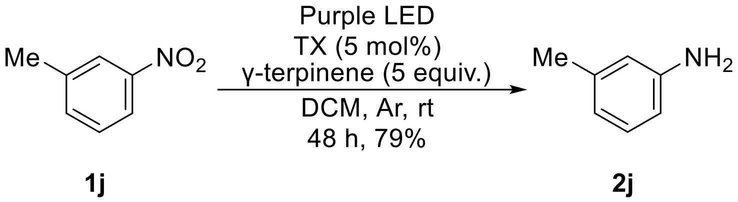
8) *p*-Toluidine (2i)



1i **2i**

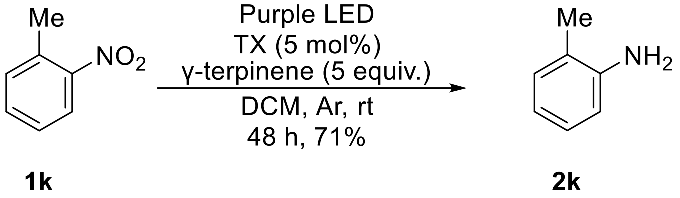
The reaction of **1i** (27.5 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2i**[8] as a solid (17.4 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, J = 8.8 Hz, 2 H), 6.61 (d, J = 8.8 Hz, 2 H), 3.29 (brs, 2 H), 2.23 (s, 3 H).

9) *m*-Toluidine (2j)



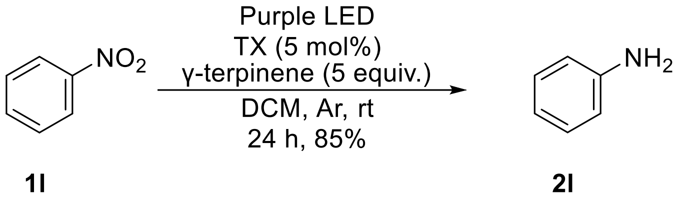
The reaction of **1j** (24 μL, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2j**[3] as a liquid (16.9 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (dd, J = 7.6, 7.2 Hz, 1 H), 6.58 (d, J = 7.2 Hz, 1 H), 6.53-6.46 (m, 2 H), 3.36 (brs, 2 H), 2.26 (s, 3 H).

10) *o*-Toluidine (2k)



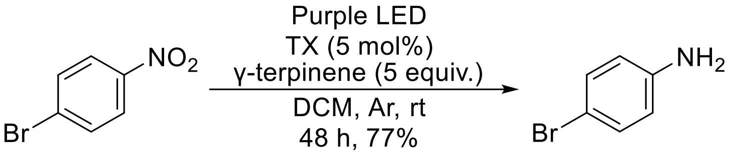
The reaction of **1k** (24 μL, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2k**[3] as a liquid (15.2 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07-7.00 (m, 2 H), 6.74-6.64 (m, 2 H), 3.53 (brs, 2 H), 2.16 (s, 3 H).

11) Aniline (2l)



The reaction of **1l** (24.5 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2l**[2] as a liquid (15.8 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 2 H), 7.03-6.97 (m, 3 H), 6.20 (brs, 2 H).

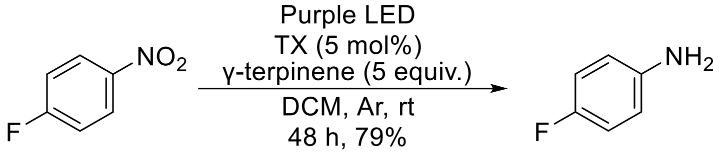
12) 4-Bromoaniline (2m)



1m **2m**

The reaction of **1m** (40.5 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2m**[2] as a liquid (26.5 mg, 77%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.22 (d, J = 8.8 Hz, 2 H), 6.54 (d, J = 8.8 Hz, 2 H), 3.65 (brs, 2 H).

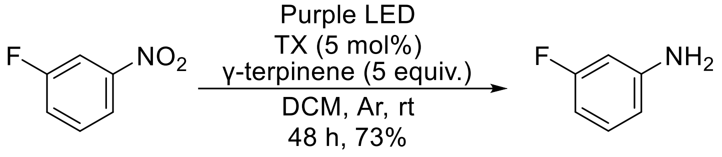
13) 4-Fluoroaniline (2n)



1n **2n**

The reaction of **1n** (28.3 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2n**[2] as a liquid (17.6 mg, 79%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.85 (dd, J = 8.8, 8.4 Hz, 2 H), 6.61 (dd, J = 8.8, 4.4 Hz, 2 H), 3.52 (brs, 2 H).

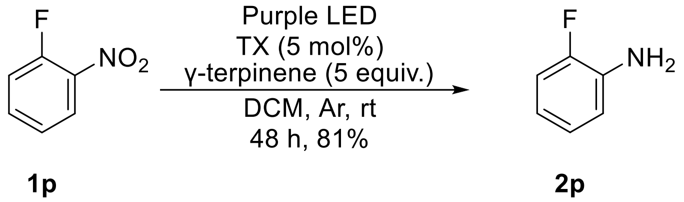
14) 3-Fluoroaniline (2o)



1o **2o**

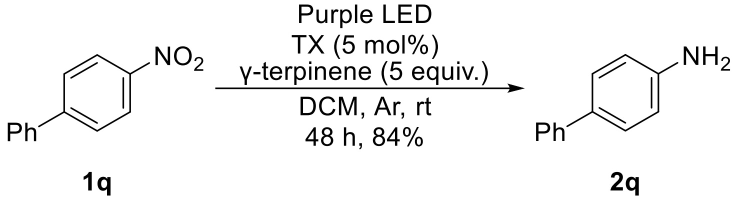
The reaction of **1o** (28.3 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2o**[3] as a liquid (16.2 mg, 73%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13-7.03 (m, 1 H), 6.47-6.34 (m, 3 H), 3.71 (brs, 2 H).

15) 2-Fluoroaniline (2p)



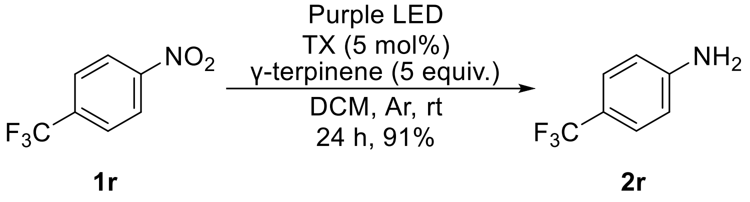
The reaction of **1p** (28.4 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2p**[3] as a liquid (18.0 mg, 81%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.02-6.89 (m, 2 H), 6.82-6.73 (m, 1 H), 6.72-6.64 (m, 1 H), 3.57 (brs, 2 H).

16) 4-Phenylaniline (2q)



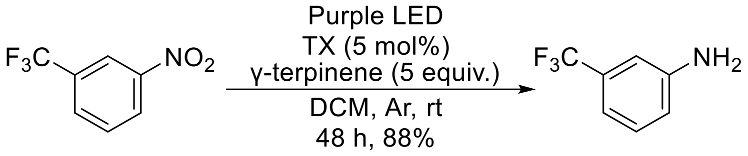
The reaction of **1q** (40.1 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2q**[2] as a white solid (28.4 mg, 84%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (d, J = 6.8 Hz, 2 H), 7.44-7.35 (m, 4 H), 7.26 (t, J = 7.2 Hz, 1 H), 6.75 (d, J = 8.4 Hz, 2 H), 3.71 (brs, 2 H).

17) 4-(Trifluoromethyl)aniline (2r)



The reaction of **1r** (38.4 mg, 0.2 mmol), TX (2.2 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2r**[2] as a white solid (29.2 mg, 91%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, J = 8.0 Hz, 2 H), 6.69 (d, J = 8.0 Hz, 2 H), 3.93 (brs, 2 H).

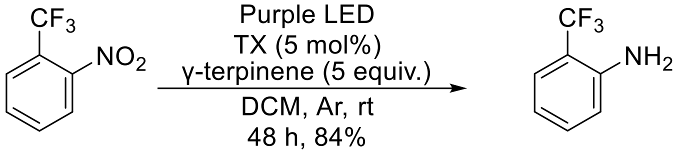
18) 3-(Trifluoromethyl)aniline (2s)



1s **2s**

The reaction of **1s** (38.3 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2s**[3] as a liquid (28,4 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, J = 8.0, 7.6 Hz, 1 H), 6.99 (d, J = 7.6 Hz, 1 H), 6.89 (s, 1 H), 6.82 (d, J = 8.0 Hz, 1 H), 3.77 (brs, 2 H)..

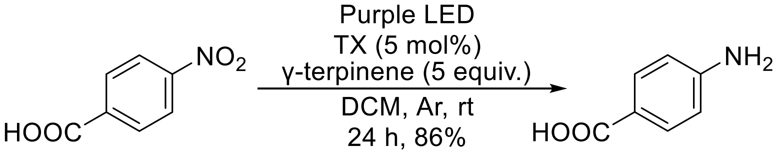
19) 2-(Trifluoromethyl)aniline (2t)



1t **2t**

The reaction of **1t** (38.2 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2t**[9] as a a liquid (27.1 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 6.0 Hz, 1 H), 7.28 (d, J = 8.8 Hz, 1 H), 6.80-6.72 (m, 2 H), 3.82 (brs, 2 H).

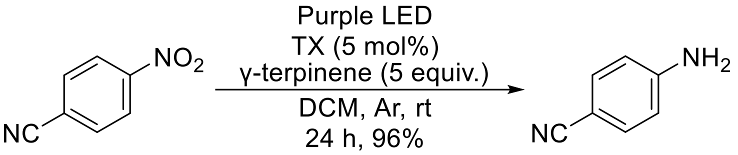
20) 4-Carboxyaniline (2u)



1u **2u**

The reaction of **1u** (33.2 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2u**[10] as a solid (23.6 mg, 86%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 (d, J = 8.8 Hz, 2 H), 6.57 (d, J = 8.4 Hz, 2 H), 5.86 (brs, 2 H), 3.57 (brs, 1 H).

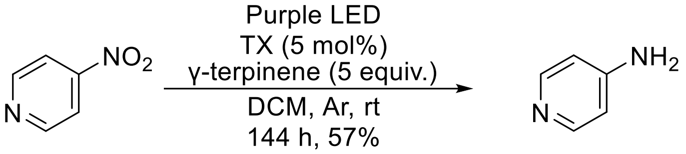
21) 4-Cyanoaniline (2v)



1v **2v**

The reaction of **1v** (29.7 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2v**[2] as a solid (22.6 mg, 96%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, *J* = 8.4 Hz, 2 H), 6.65 (d, *J* = 8.4 Hz, 2 H).

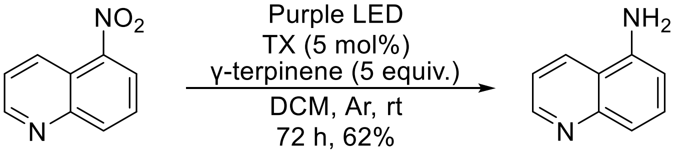
22) Pyridine-4-amine (2w)



1w **2w**

The reaction of **1w** (25.0 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2w**[11] as a solid (10.7 mg, 57%). ^{1}H NMR (400 MHz, CD$_3$OD) δ 7.94 (d, *J* = 6.4 Hz, 2 H), 6.54 (d, *J* = 6.4 Hz, 2 H).

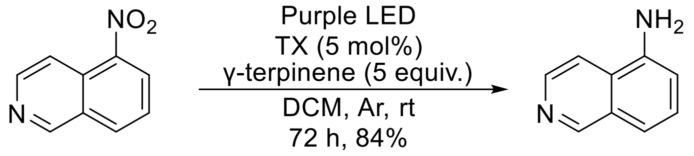
23) Quinolin-5-amine (2x)



1x **2x**

The reaction of **1x** (34.9 mg, 0.2 mmol), TX (2.0 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2x**[10] as a solid (17.9 mg, 62%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.78 (dd, *J* = 4.0, 1.6 Hz, 1 H), 8.54 (d, *J* = 8.4 Hz, 1 H), 7.43 (dd, *J* = 8.0, 8.0 Hz, 1 H), 7.35 (dd, *J* = 8.4, 4.0 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 1 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 5.99 (brs, 2 H).

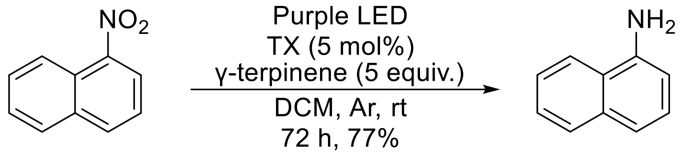
24) Isoquinolin-5-amine (2y)



1y **2y**

The reaction of **1y** (34.9 mg, 0.2 mmol), TX (2.2 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2y**[10] as a solid (25.1 mg, 84%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (s, 1 H), 8.38 (d, J = 6.0 Hz, 1 H), 7.97 (d, J = 6.0 Hz, 1 H), 7.36 (dd, J = 8.0, 7.6 Hz, 1 H), 7.23 (d, J = 8.0 Hz, 1 H), 6.90 (d, J = 7.6 Hz, 1 H), 5.99 (brs, 2 H).

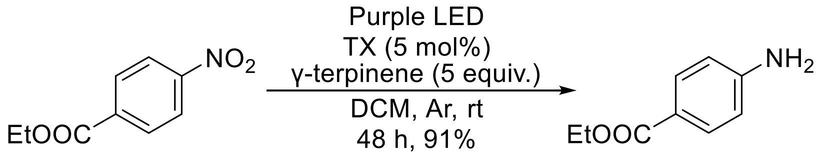
25) Naphthalen-1-amine (2z)



1z **2z**

The reaction of **1z** (34.7 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2z**[5] as a solid (22.1 mg, 77%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84-7.76 (m, 2 H), 7.49-7.40 (m, 2 H), 7.34-7.22 (m, 2 H), 6.77 (dd, J = 6.8, 1.6 Hz, 1 H), 4.12 (brs, 2 H).

26) Benzocaina (2aa)

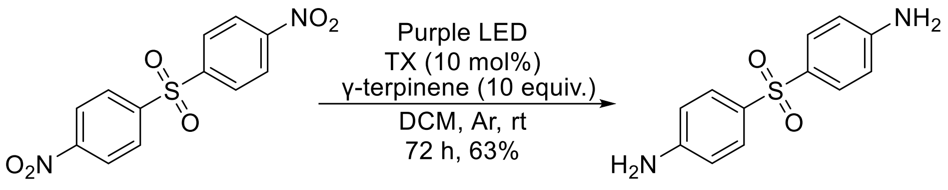


Benzocaina

1aa **2aa**

The reaction of **1aa** (39.2 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2aa**[2] as a white solid (30.1 mg, 91%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, J = 8.4 Hz, 2 H), 6.62 (d, J = 8.4 Hz, 2 H), 4.31 (q, J = 7.2 Hz, 2 H), 4.09 (brs, 2 H), 1.35 (t, J = 7.2 Hz, 3 H).

27) Dapsone Tablet (2ab)

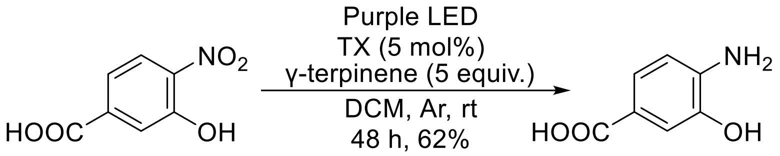


Dapsone Tablet

1ab **2ab**

The reaction of **1ab** (61.8 mg, 0.2 mmol), TX (4.2 mg, 0.02 mmol), γ-terpinene (320 μL, 2.0 mmol), and anhydrous DCM (20 mL) afforded **2ab**[12] as a white solid (31.2 mg, 63%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 (d, J = 8.8 Hz, 4 H), 6.65 (d, J = 8.8 Hz, 4 H), 5.99 (brs, 4 H).

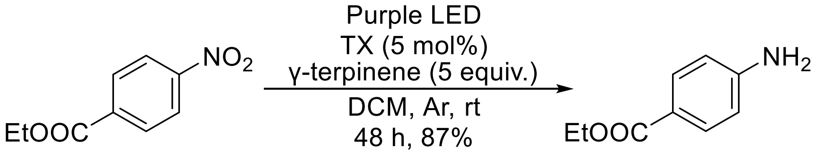
28) 4-Carboxy-3-hydroxyaniline (2ac)



1ac **2ac**

The reaction of **1ac** (36.4 mg, 0.2 mmol), TX (2.1 mg, 0.01 mmol), γ-terpinene (160 μL, 1.0 mmol), and anhydrous DCM (20 mL) afforded **2ac**[13] as a solid (19.0 mg, 62%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (brs, 1 H), 9.35 (brs, 1 H), 7.25-7.19 (m, 2 H), 6.57 (d, J = 8.0 Hz, 1 H), 5.27 (brs, 2 H).

Gram-scale reaction of 1aa



1aa **2aa**

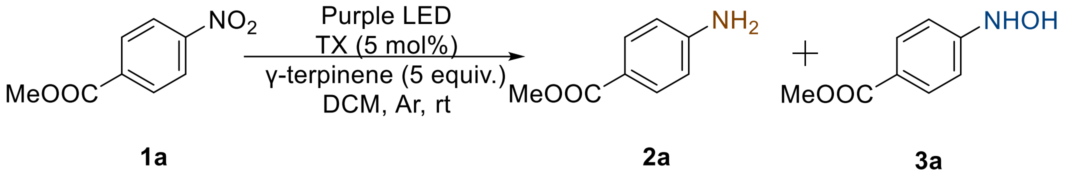
To a flame dried 500 mL of Pyrex sealed flask were added TX (64.1 mg, 0.3 mmol), **1aa** (1.173 g, 6 mmol), anhydrous DCM (500 mL), and γ-terpinene (4.8 mL, 30 mmol). The reaction mixture was irradiated by purple LED strip (λ = 415 nm, height: 10 cm, diameter: 15 cm, 30 W) at a distance of 3-5 cm under argon atmosphere at rt (maintained with three cooling fans). The reaction was completed after 48 h as monitored by TLC (eluent: petroleum ether/DCM = 1:1). The solvent was removed, and the residue was purified by flash chromatography on silica gel (eluent: DCM) to afford **2aa**[2] as a solid (0.862 g, 87%).

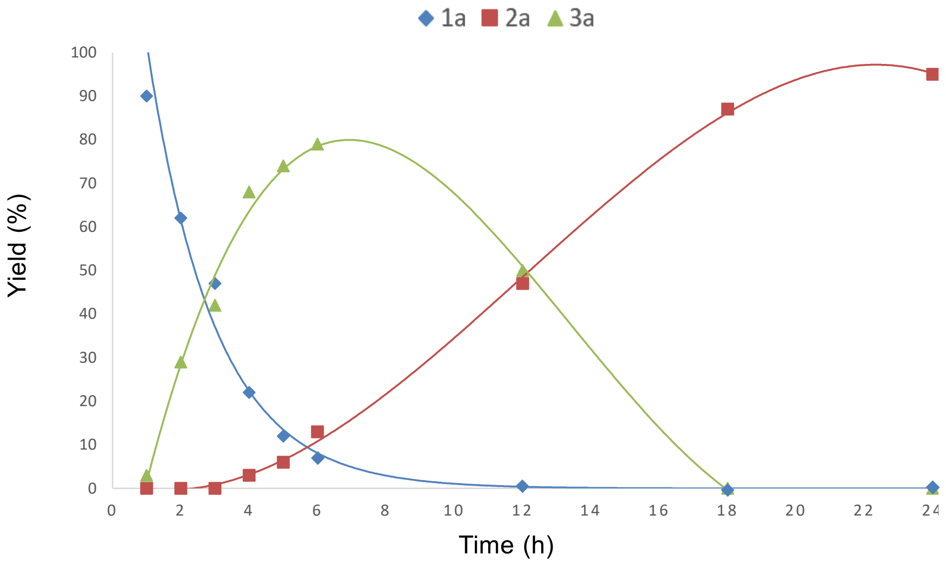
Mechanism studies

Time-course study

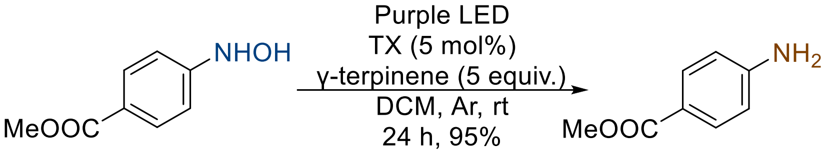
A solution of **1a** (18.1 mg, 0.1 mmol), TX (1.1 mg, 0.005 mmol), and γ-terpinene (80 μL, 0.5 mmol) in anhydrous DCM (10 mL) was irradiated by purple LED strip (λ = 415 nm, height: 10 cm, diameter: 15 cm, 30 W) at a distance of 3-5 cm at rt (maintained with three cooling fans) under argon atmosphere. The conversion of **1a** was determined by ^{1}H NMR analysis (400 MHz) of the crude reaction mixture using 1,3,5-trimethoxybenzene (0.01 mmol) as the internal standard (Figure S3).

Figure S3. Time-course study





3a as the reactant:



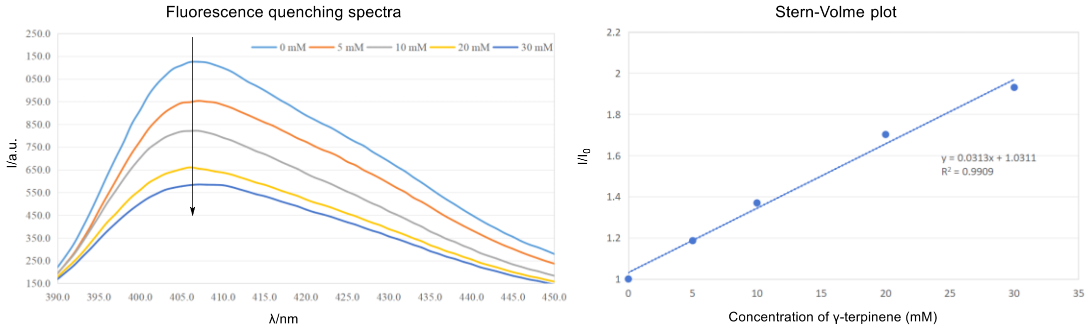
3a **2a**

To a flame dried 10 mL of Pyrex sealed tube were added TX (1.1 mg, 0.005 mmol), **3a** (16.7 mg, 0.1 mmol), anhydrous DCM (10 mL), and γ-terpinene (80 μL, 0.5 mmol). The reaction mixture was irradiated by purple LED strip (λ = 415 nm, height: 10 cm, diameter: 15 cm, 30 W) at a distance of 3-5 cm under argon atmosphere at rt (maintained with three cooling fans). The reaction was completed after 24 h, and the yield of **2a** was determined by ^{1}H NMR analysis (400 MHz) of the crude reaction mixture using 1,3,5-trimethoxybenzene (0.01 mmol) as the internal standard.

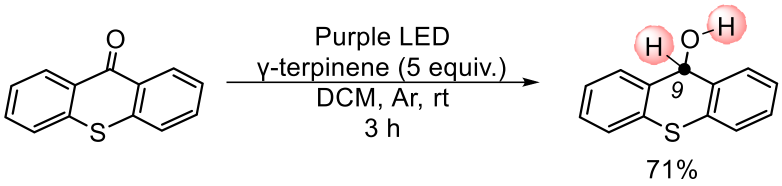
Fluorescence quenching studies and Stern-Volmer analysis

Fluorescence emission quenching experiments were measured on a Hitachi F-7000 fluorescence spectrometer with a 4 mL quartz cuvette with a cap. TX was irradiated at 370 nm and the emission spectrums was recorded from 380 nm to 450 nm. In a typical experiment, the emission spectrum of a 1.0 × 10^{-4} M solution of TX in DCM was collected. Then, different amounts of γ-terpinene were added to a solution of TX (10^{-4} M) in DCM (Figure S4).

Figure S4. Fluorescence quenching spectra and Stern-Volmer plot

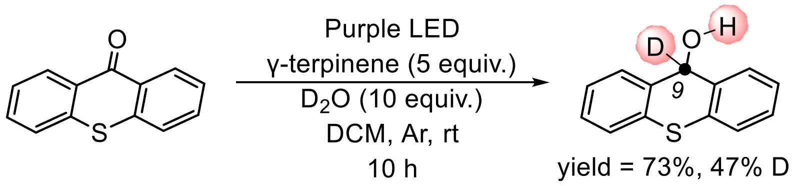


Studies of key intermediate:



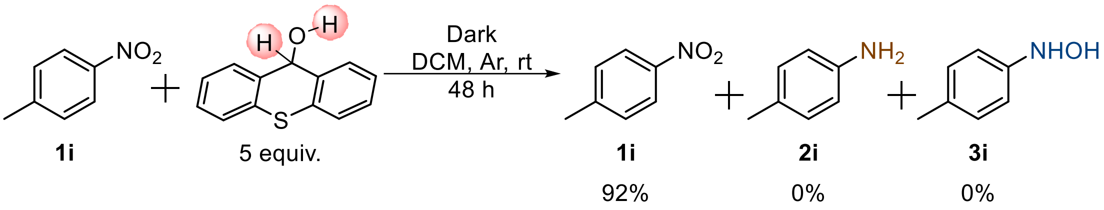
To a flame dried 25 mL of Pyrex sealed tube were added TX (212.9 mg, 1 mmol), anhydrous DCM (20 mL), and γ-terpinene (800 μL, 5 mmol). The reaction mixture was irradiated by purple LED strip (λ = 415 nm, height: 10 cm, diameter: 15 cm, 30 W) at a distance of 3-5 cm under argon atmosphere at rt (maintained with three cooling fans). The reaction was completed after 3 h. The mixture was concentrated in vacuo. The residue was dissolved in MeOH (50mL), and then washed with *n*-hexane (20 mL x 3). The MeOH layer was concentrated under reduced pressure to afford the crude 9*H*-thioxanthen-9-ol[14] as a solid (154.8 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.2 Hz, 2 H), 7.41 (d, J = 7.2 Hz, 2 H), 7.27-7.16 (m, 4 H), 5.40 (s, 1 H).

Deuterium labeling experiment



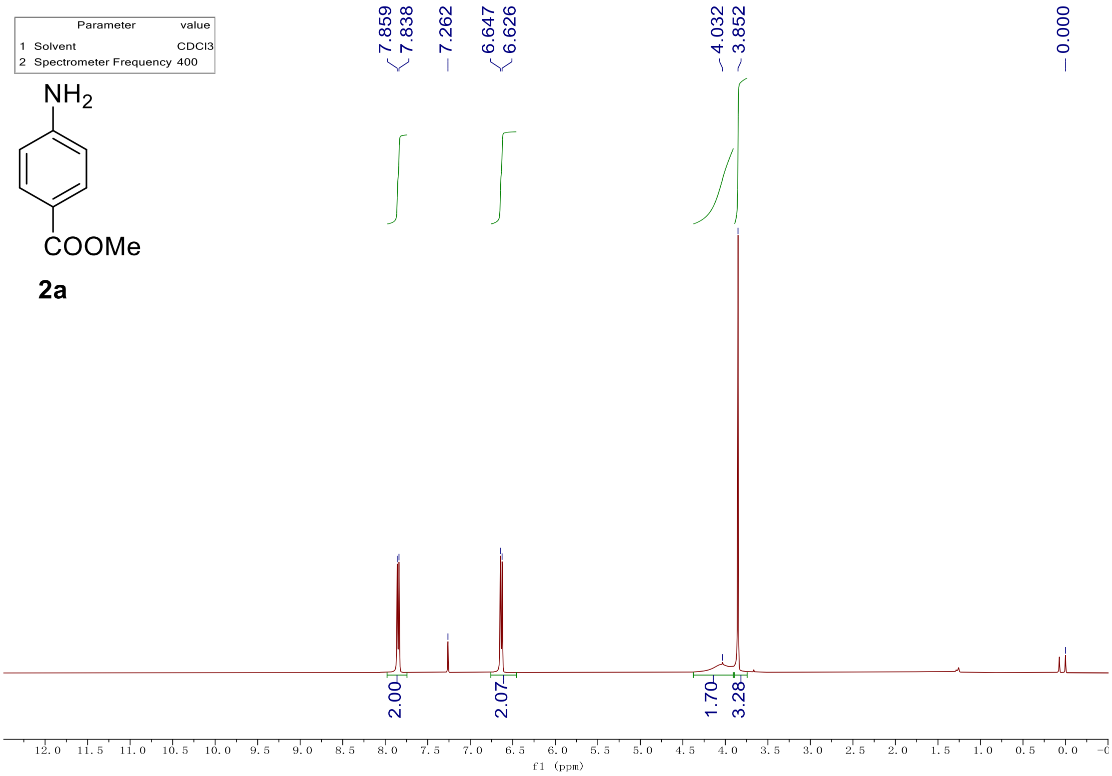
To a flame dried 25 mL of Pyrex sealed tube were added TX (212.7 mg, 1 mmol), anhydrous DCM (20 mL), D_2O (180 μL, 10 mmol), and γ-terpinene (800 μL, 5 mmol). The reaction mixture was irradiated by purple LED strip (λ = 415 nm, height: 10 cm, diameter: 15 cm, 30 W) at a distance of 3-5 cm under argon atmosphere at rt (maintained with three cooling fans). The reaction was completed after 10 h. The mixture was concentrated in vacuo. The residue was dissolved in MeOH (50 mL), and then washed with *n*-hexane (20 mL x 3). The MeOH layer was concentrated under reduced pressure to afford the crude 9*H*-thioxanthen-9-ol[14] as a solid (156.2 mg, 73%) with 47% deuterium incorporation on the 9-site of 9*H*-Thioxanthen-9-ol (Deuterium ratio was determined by ^{1}H NMR analysis). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 2 H), 7.47 (d, *J* = 7.6 Hz, 2 H), 7.334-7.20 (m, 4 H), 5.52 (s, 0.53 H).

9*H*-thioxanthen-9-ol as reductant

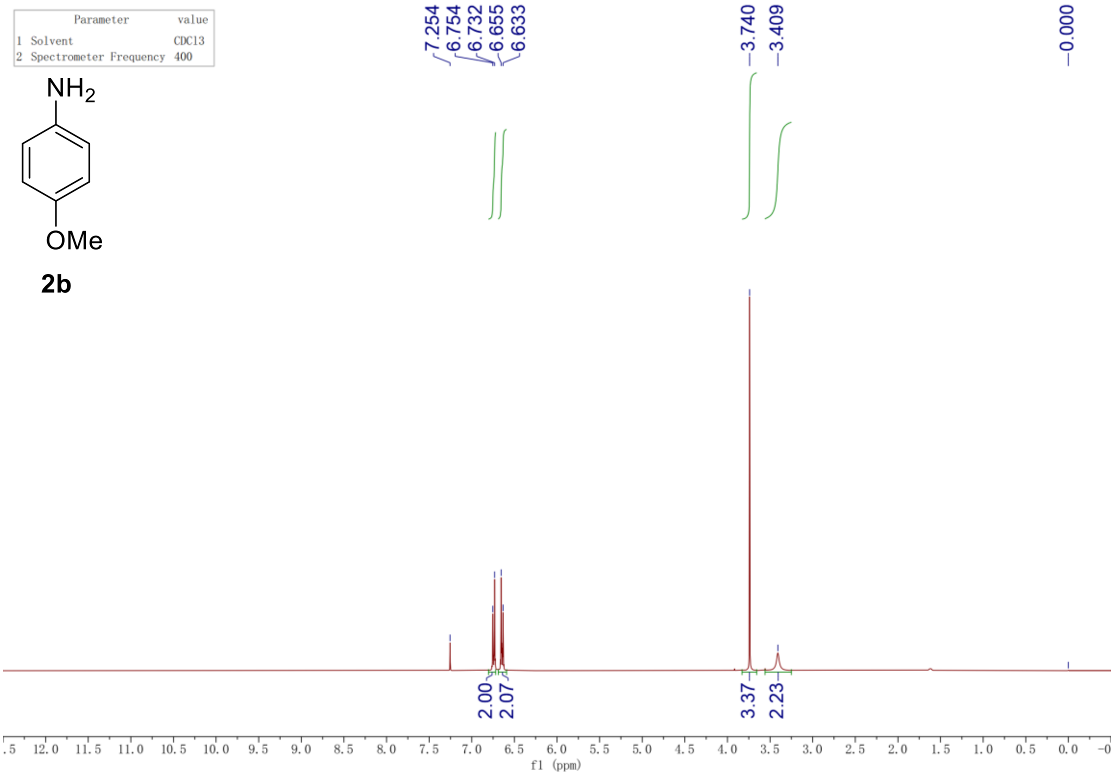


To a flame dried 10 mL of Pyrex sealed tube were added **1i** (13.7 mg, 0.1 mmol), 9*H*-thioxanthen-9-ol (107.3 mg, 0.5 mmol), and anhydrous DCM (10 mL), The reaction mixture was stirred under argon atmosphere at rt. The reaction was completed after 48 h. The yield of **2i** and **3i** and recovery of **1i** was determined by ^{1}H NMR analysis (400 MHz) of the crude reaction mixture using 1,3,5-trimethoxybenzene (0.01 mmol) as the internal standard.

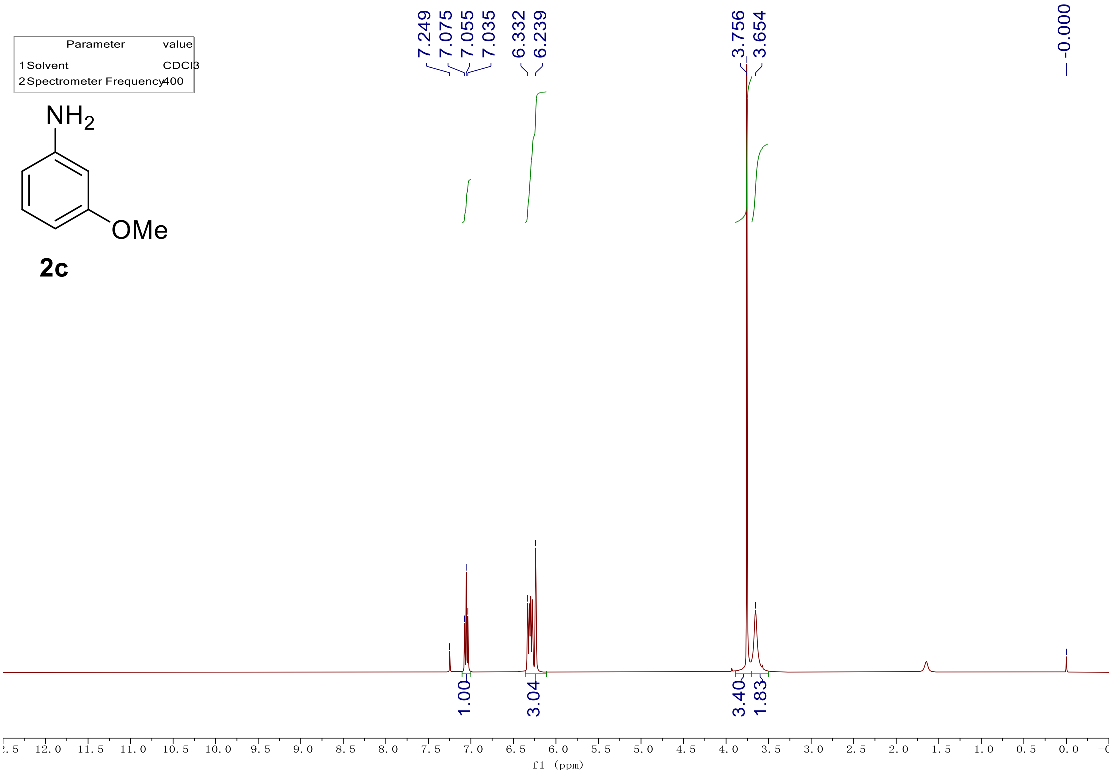
NMR spectra



2a

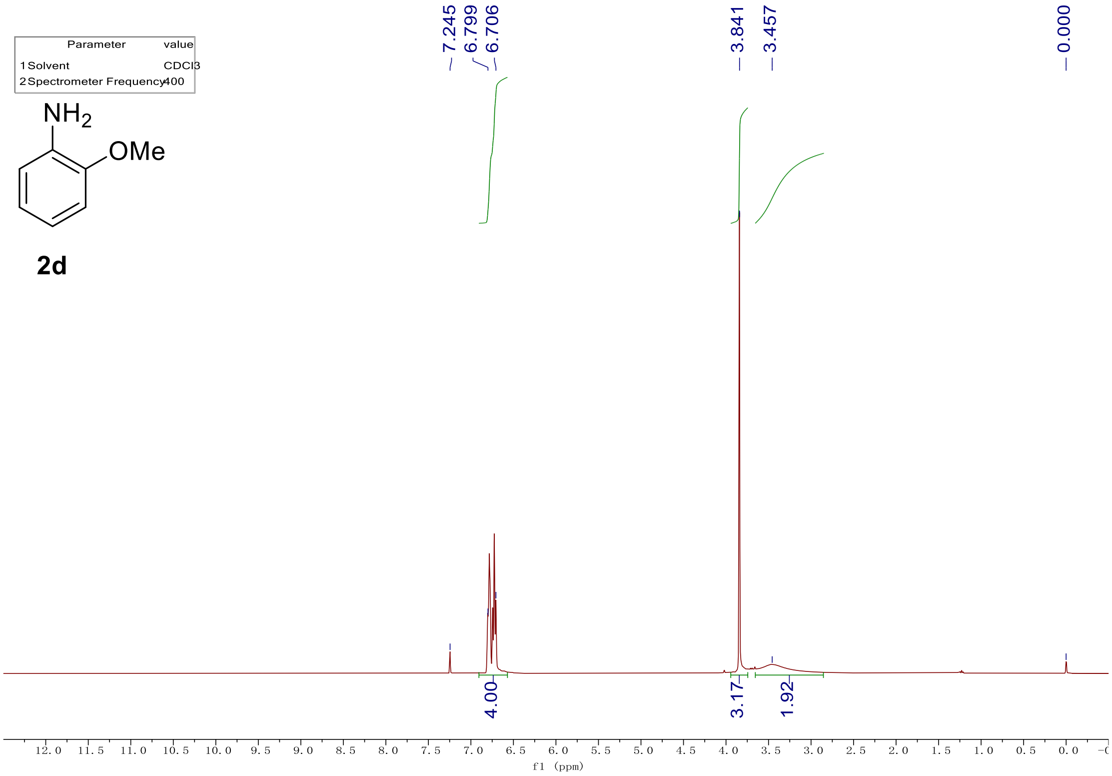


2b



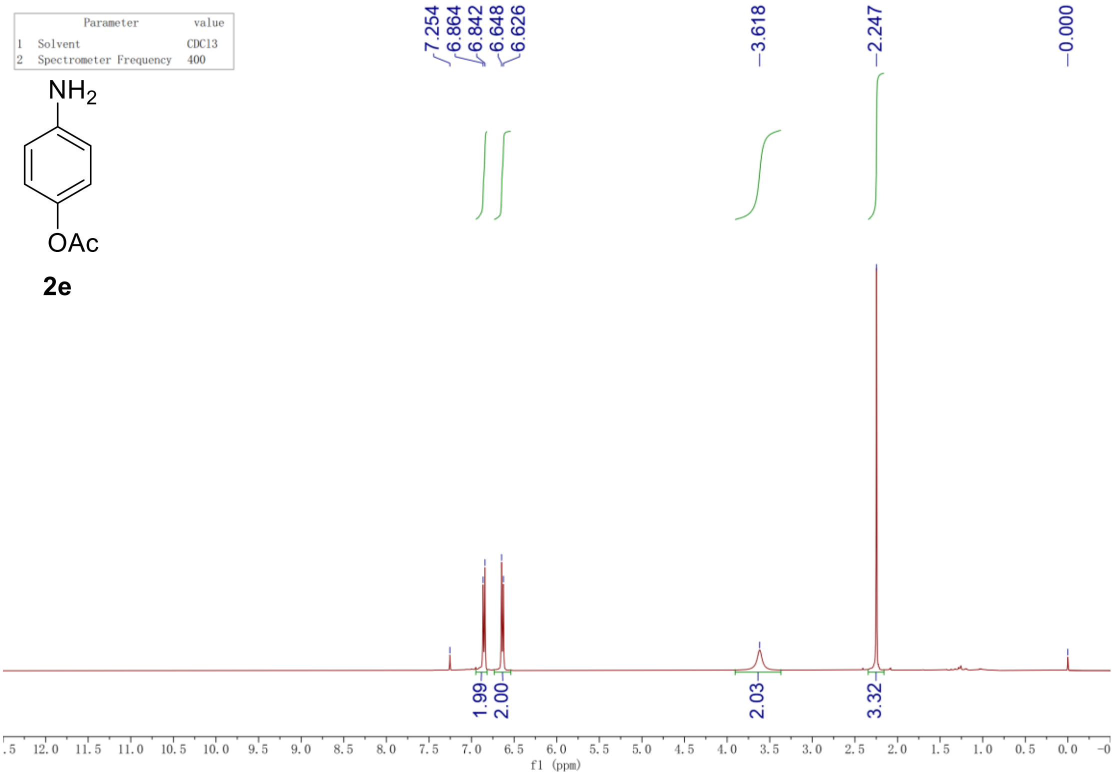
	Parameter	value
1	Solvent	CDCl3
2	Spectrometer Frequency	400

2c

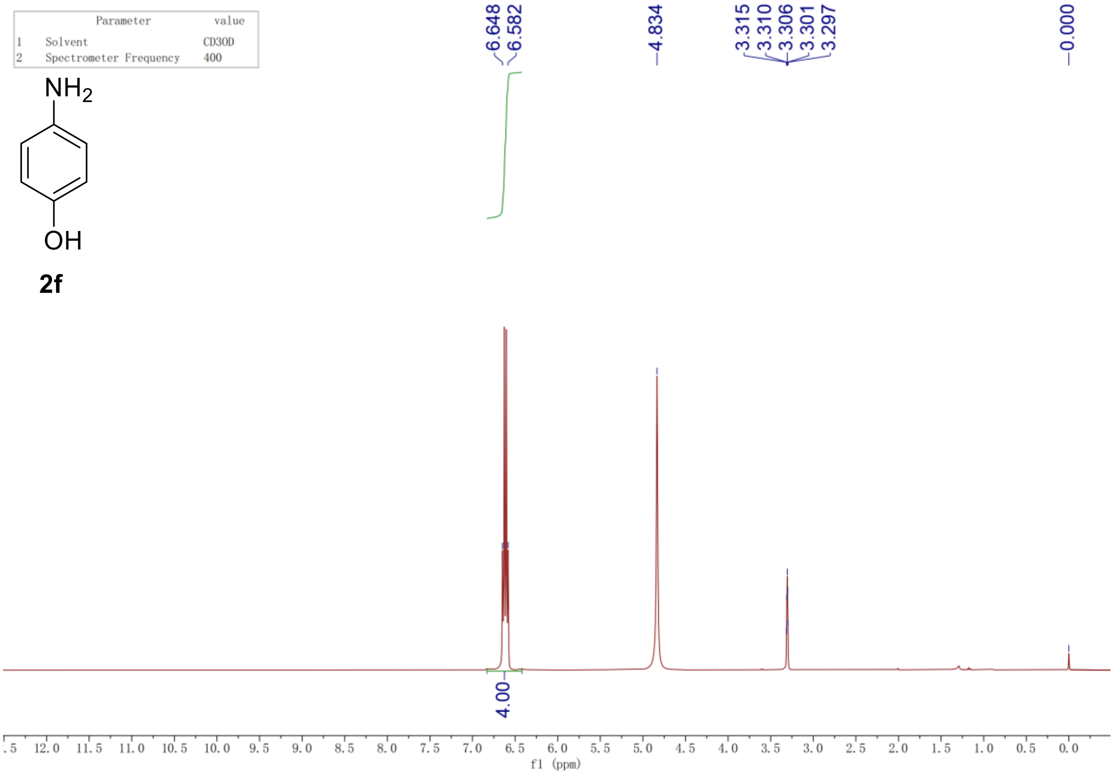


	Parameter	value
1	Solvent	CDCl3
2	Spectrometer Frequency	400

2d


Parameter value
1 Solvent CDCl3
2 Spectrometer Frequency 400
NH2
OAc
7.254
6.864
6.842
6.648
6.626
3.618
2.247
0.000
1.99
2.00
2.03
3.32
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

2e


Parameter value
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2 Spectrometer Frequency 400
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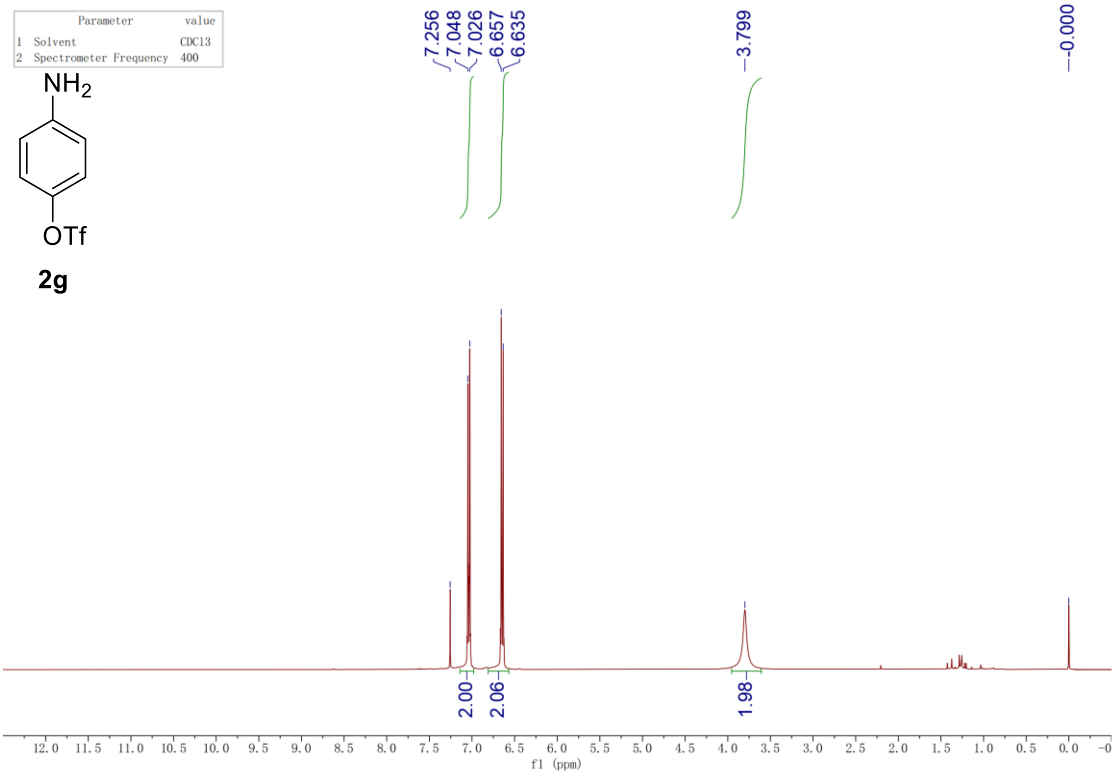
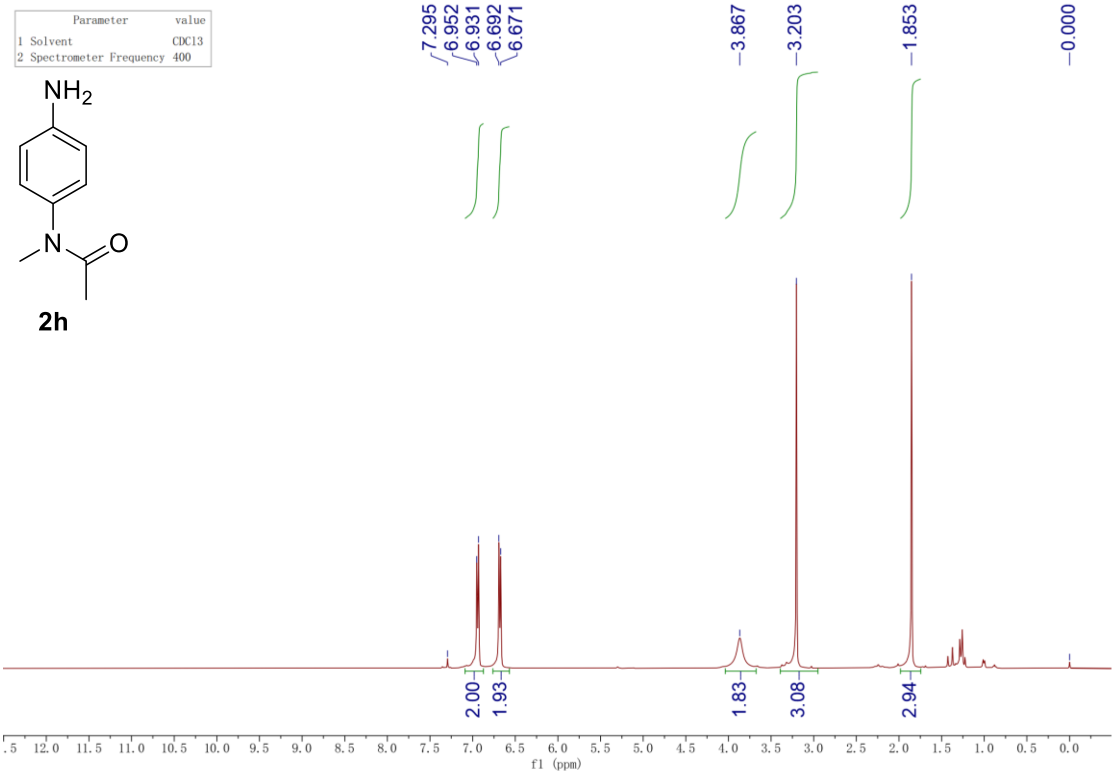
6.582
4.834
3.315
3.310
3.306
3.301
3.297
0.000
4.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

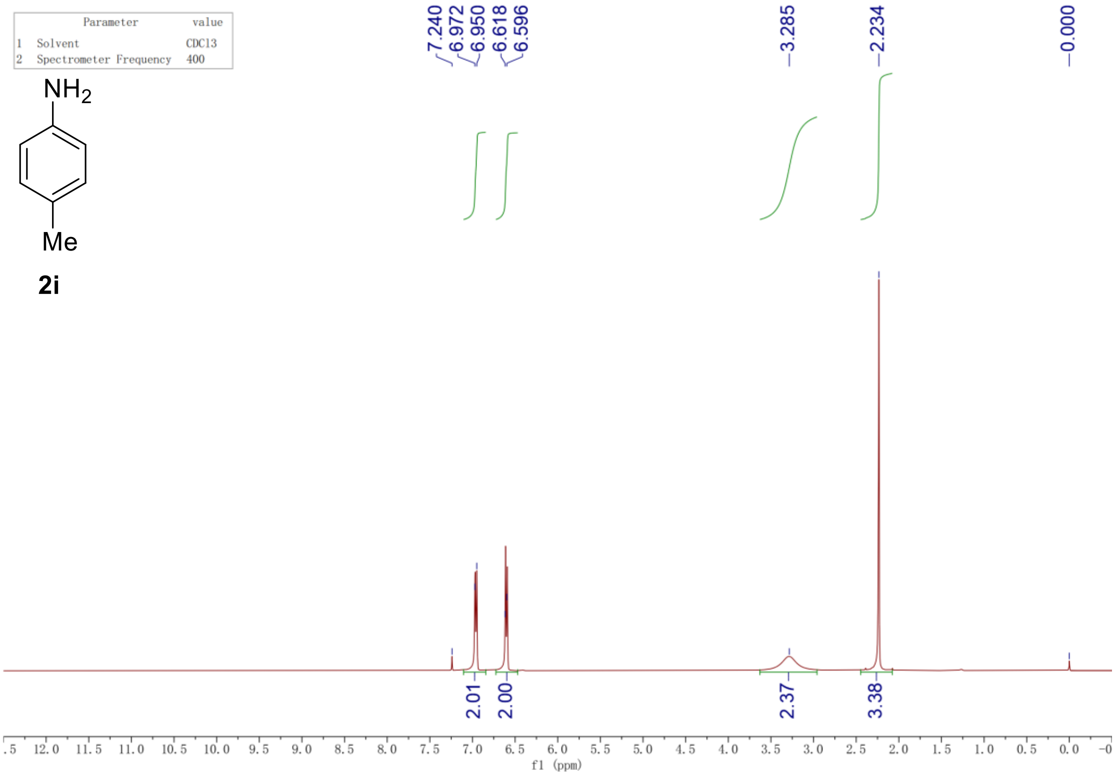
2f


2g

Parameter value
1 Solvent CDCl3
2 Spectrometer Frequency 400
NH2
OTf
7.256
7.048
7.026
6.657
6.635
3.799
-0.000
2.00
2.06
1.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


2h

Parameter value
1 Solvent CDCl3
2 Spectrometer Frequency 400
NH2
N
O
7.295
6.952
6.931
6.692
6.671
3.867
3.203
1.853
-0.000
2.00
1.93
1.83
3.08
2.94
.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2i

Parameter value
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2 Spectrometer Frequency 400
NH2
Me
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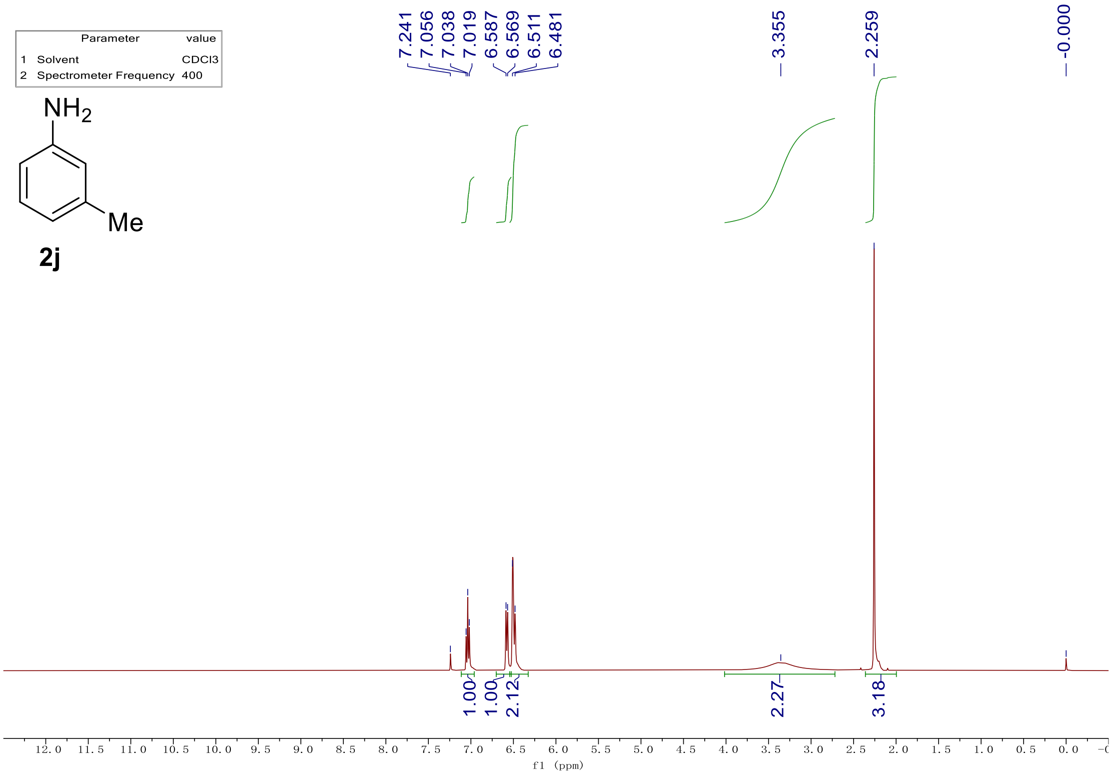
6.972
6.950
6.618
6.596
3.285
2.234
-0.000
2.01
2.00
2.37
3.38
.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


2j

Parameter value
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2 Spectrometer Frequency 400
NH2
Me
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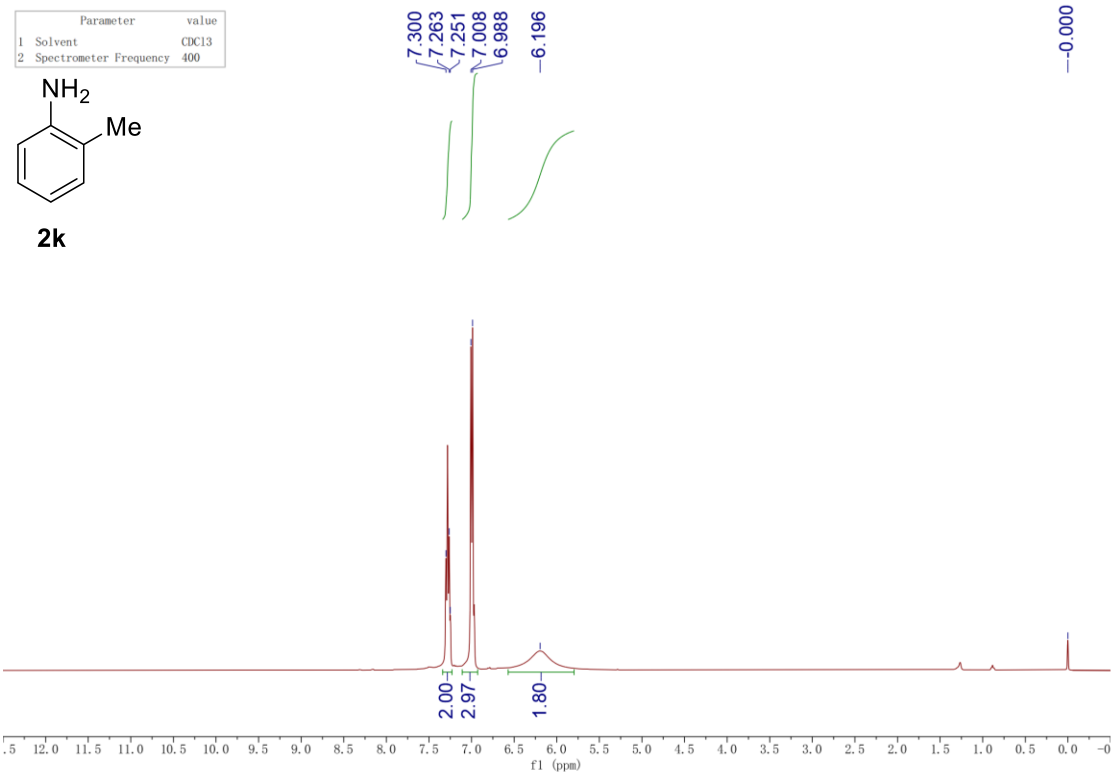
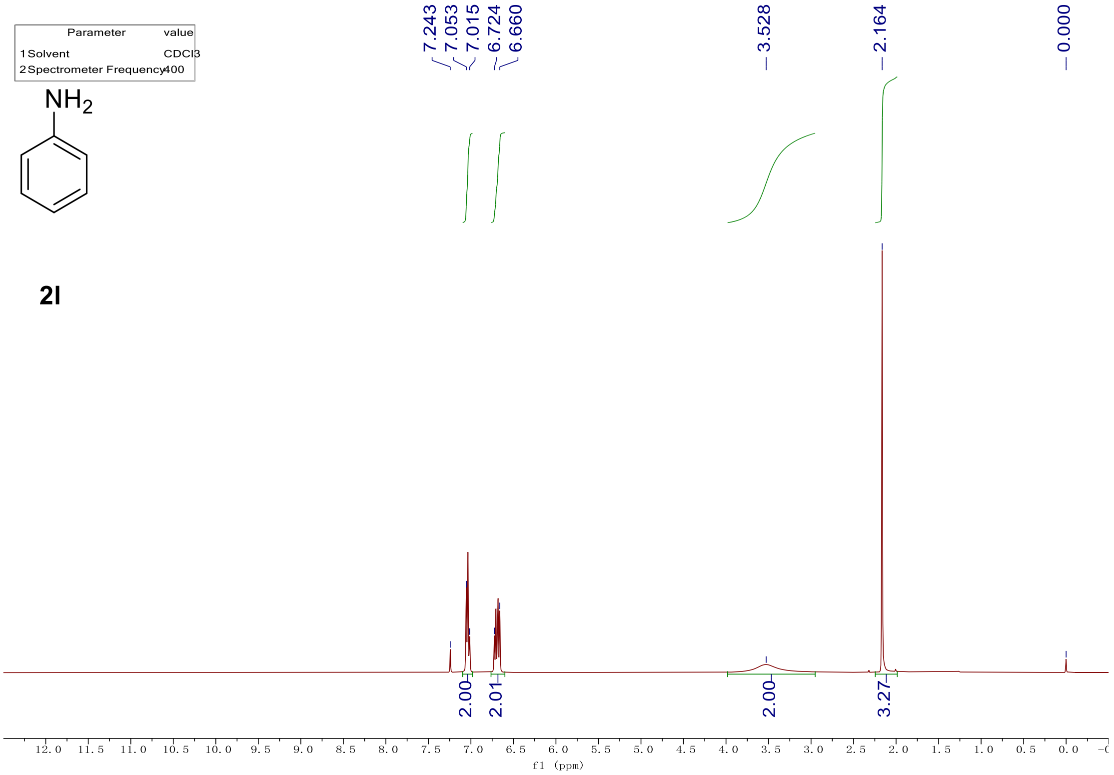
7.056
7.038
7.019
6.587
6.569
6.511
6.481
3.355
2.259
-0.000
1.00
1.00
2.12
2.27
3.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

Parameter	value
1 Solvent	CDCl3
2 Spectrometer Frequency	400

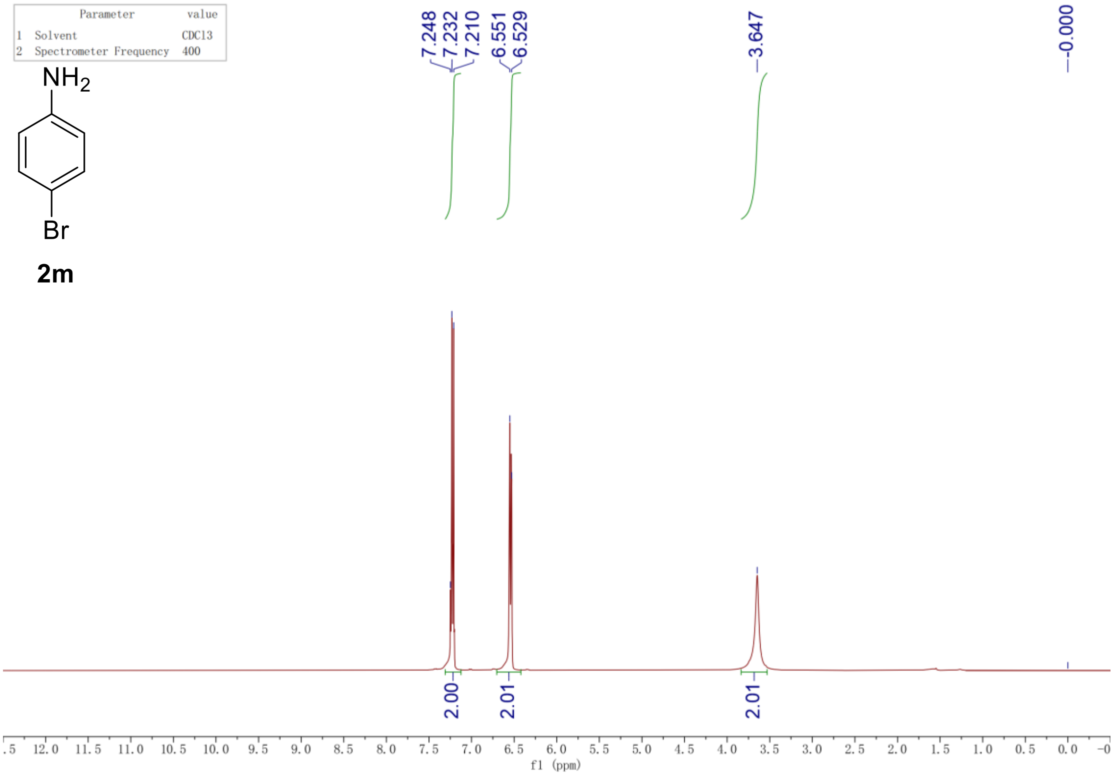


2k

Parameter	value
1 Solvent	CDCl3
2 Spectrometer Frequency	400



2l



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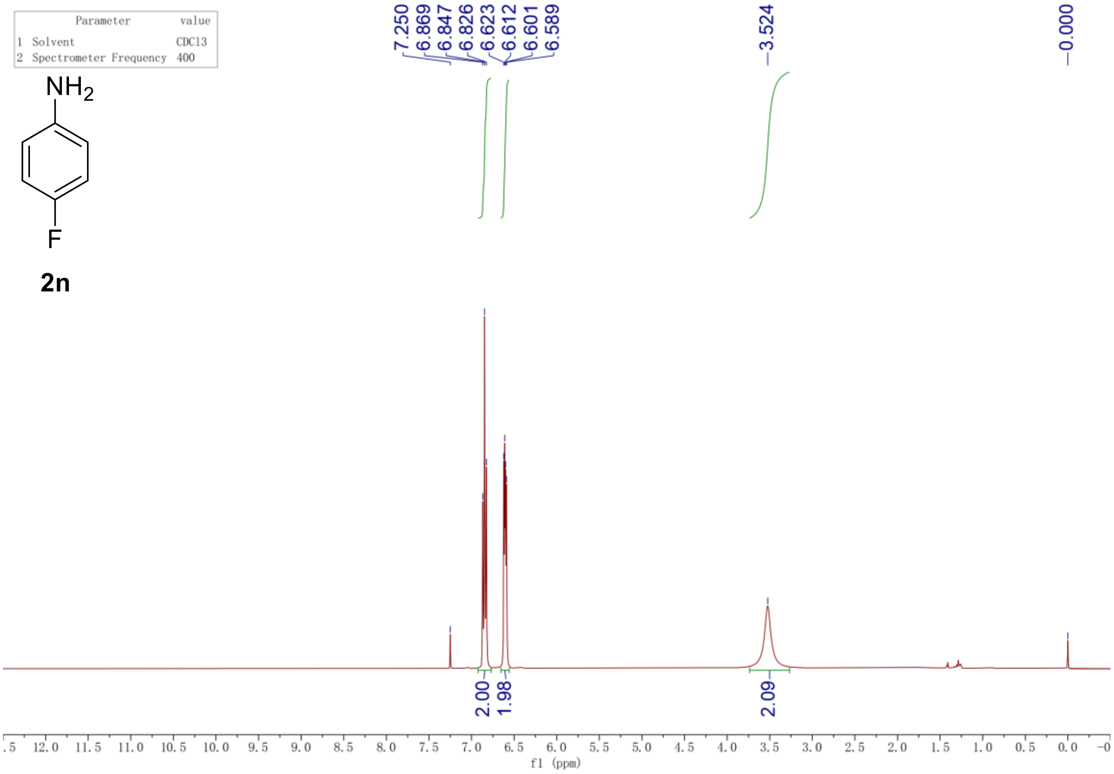
2	Spectrometer Frequency	400

2m



	Parameter	value
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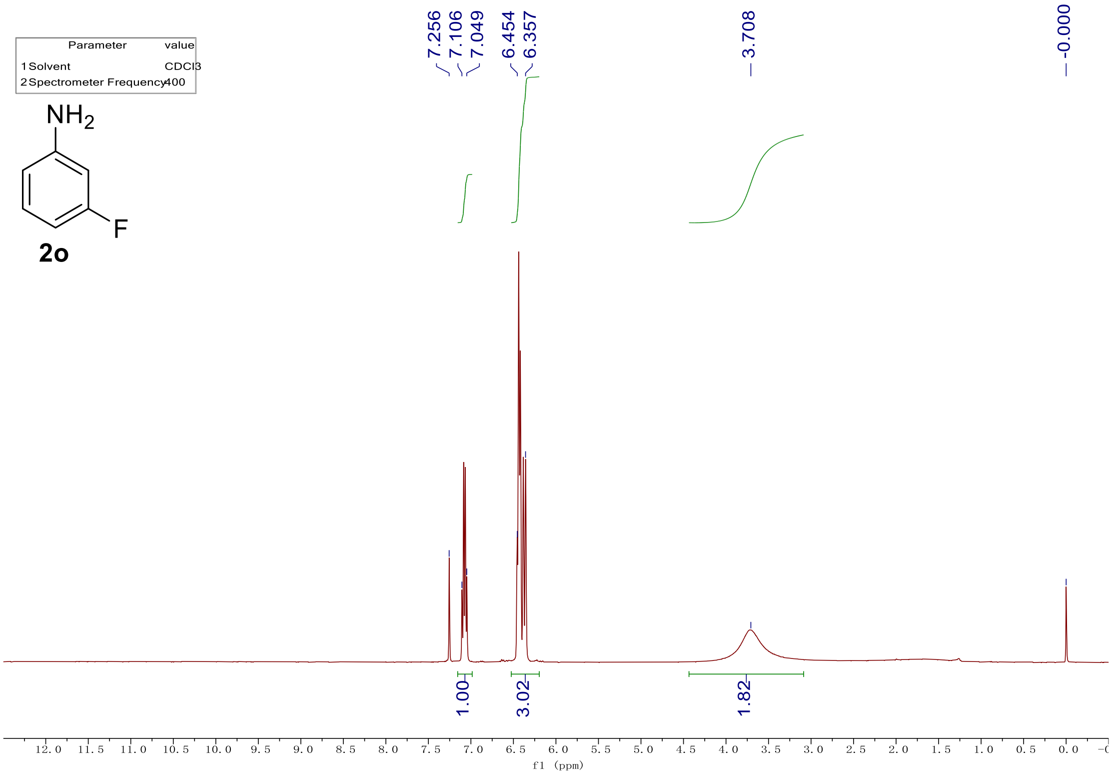
2	Spectrometer Frequency	400

2n



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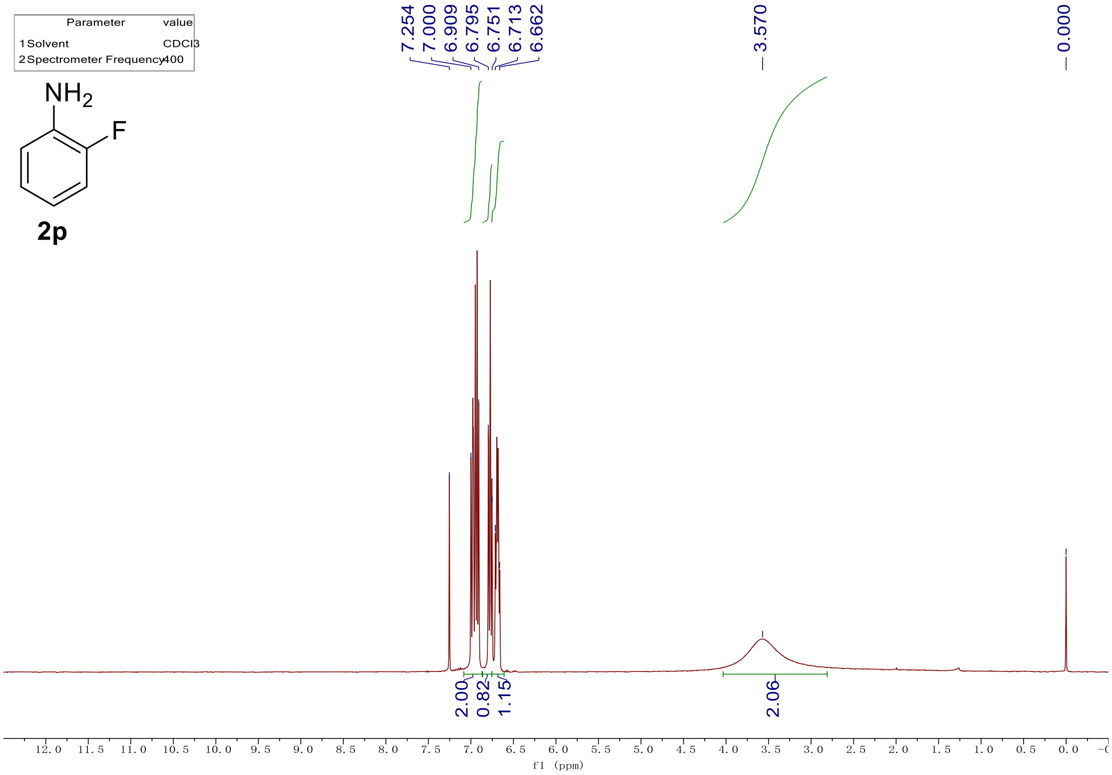
2	Spectrometer Frequency	400

2o



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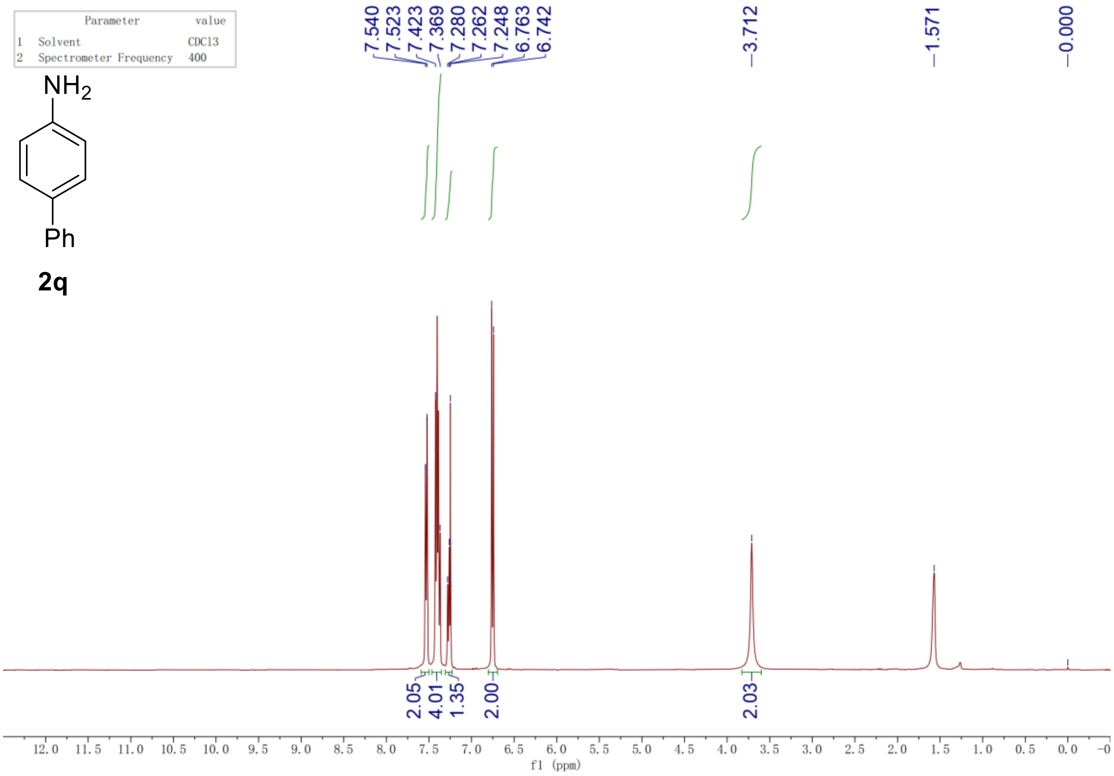
2	Spectrometer Frequency	400

2p



Parameter value
1 Solvent CDCl3
2 Spectrometer Frequency 400
NH2
Ph
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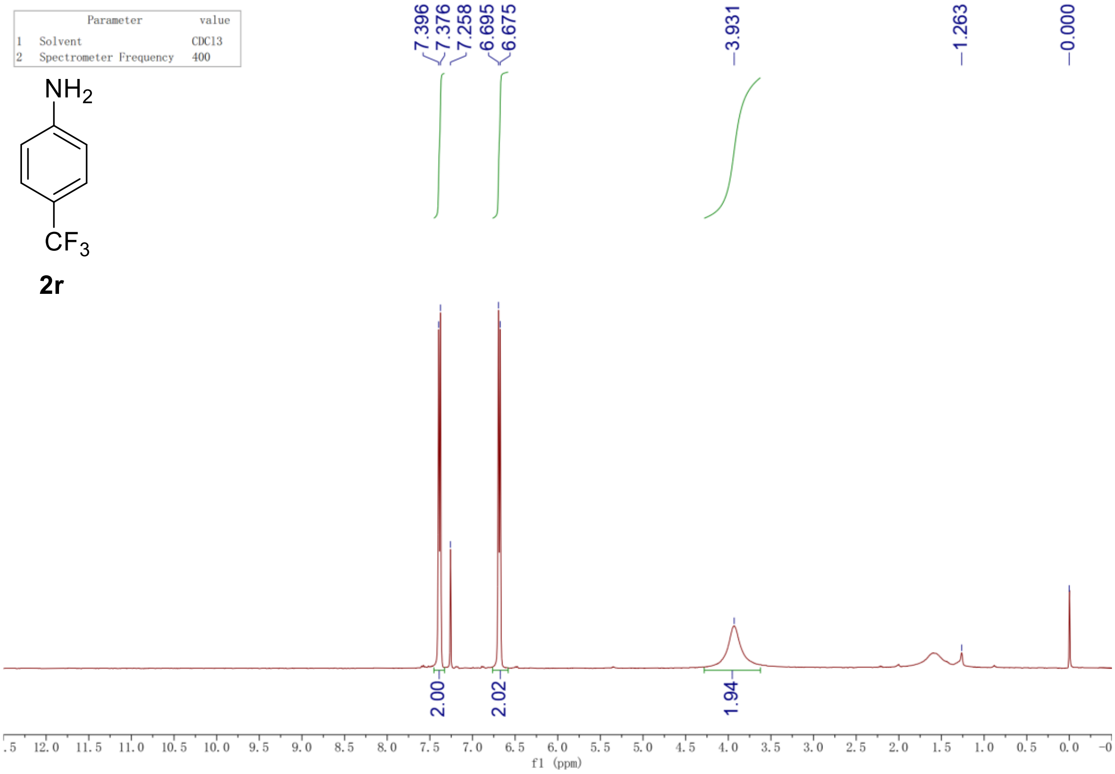
7.423
7.369
7.280
7.262
7.248
6.763
6.742
3.712
1.571
0.000
2.05
4.01
1.35
2.00
2.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

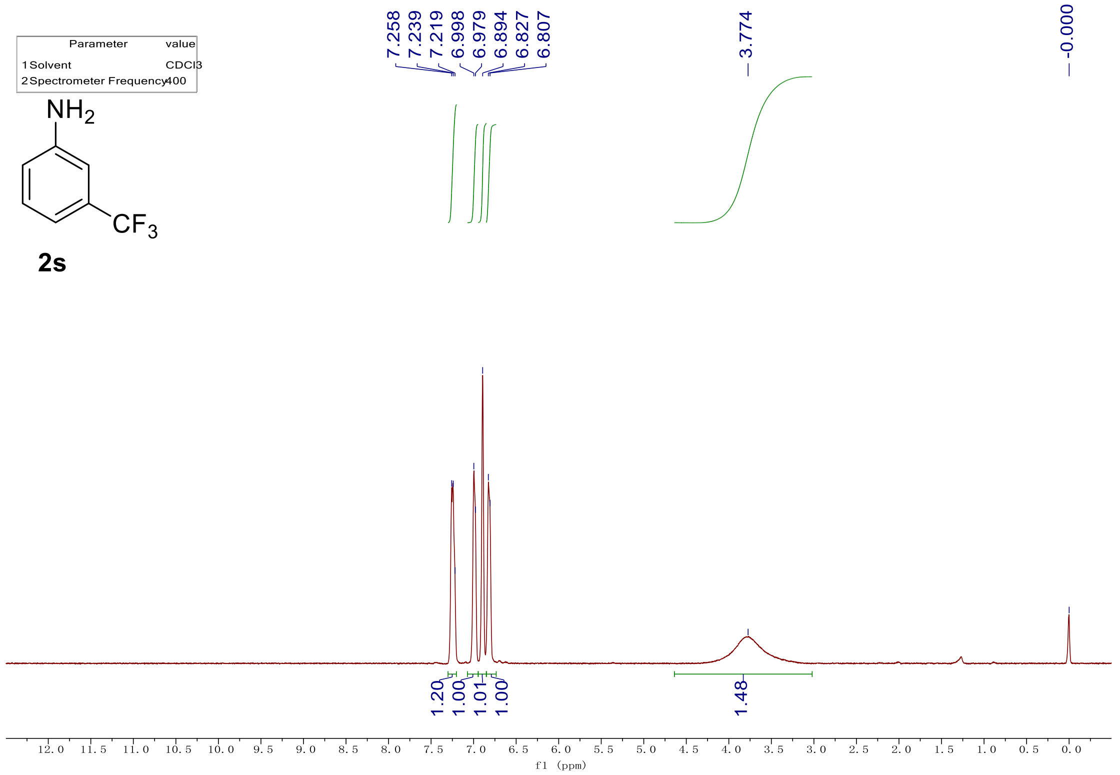
2q



Parameter value
1 Solvent CDCl3
2 Spectrometer Frequency 400
NH2
CF3
7.396
7.376
7.258
6.695
6.675
3.931
1.263
0.000
2.00
2.02
1.94
.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

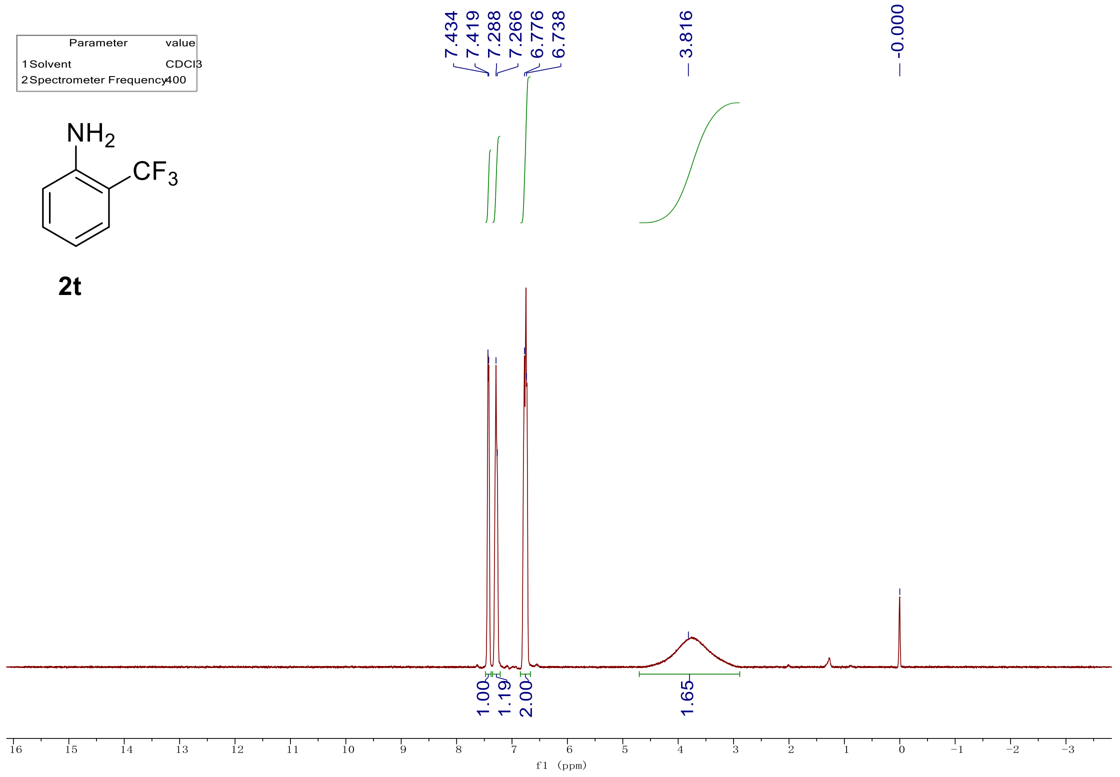
2r

	Parameter	value
1	Solvent	CDCl3
2	Spectrometer Frequency	400

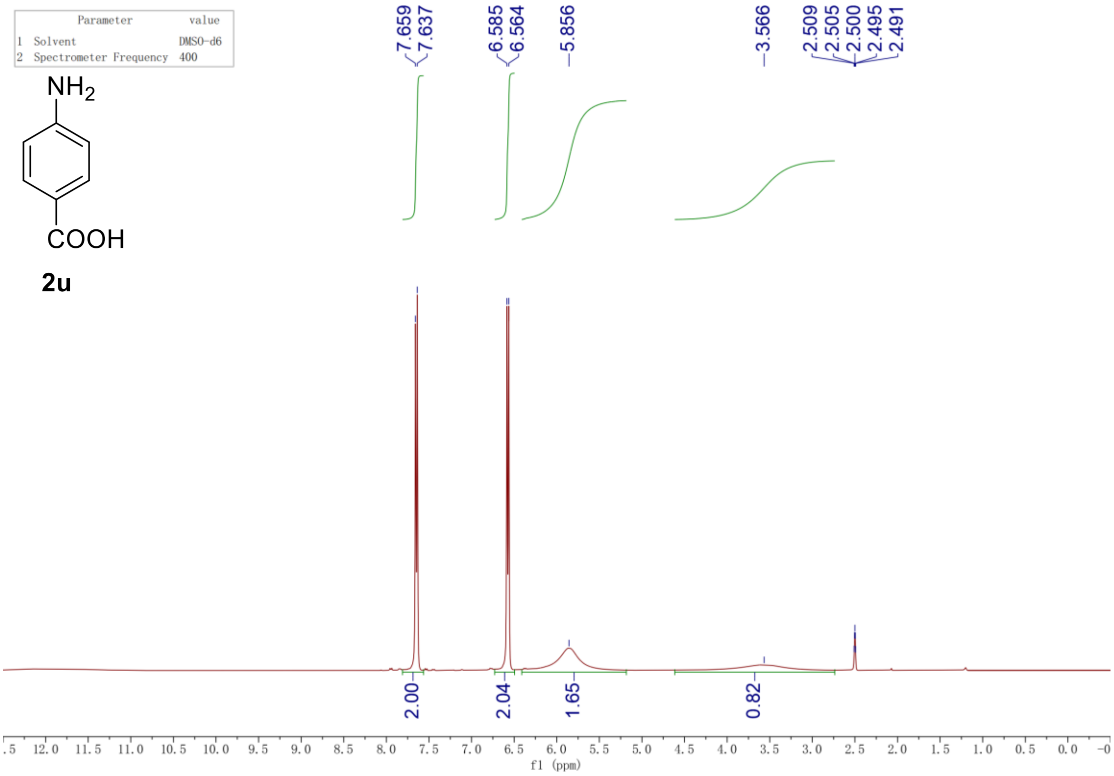


2s

	Parameter	value
1	Solvent	CDCl3
2	Spectrometer Frequency	400

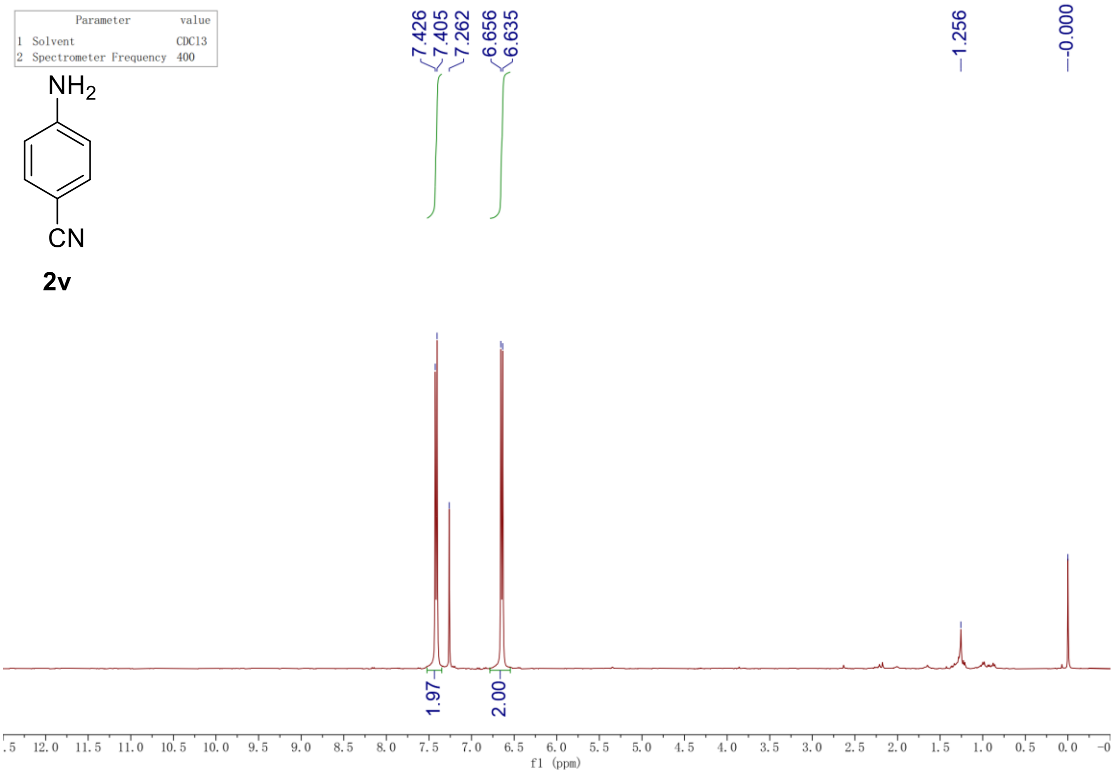


2t



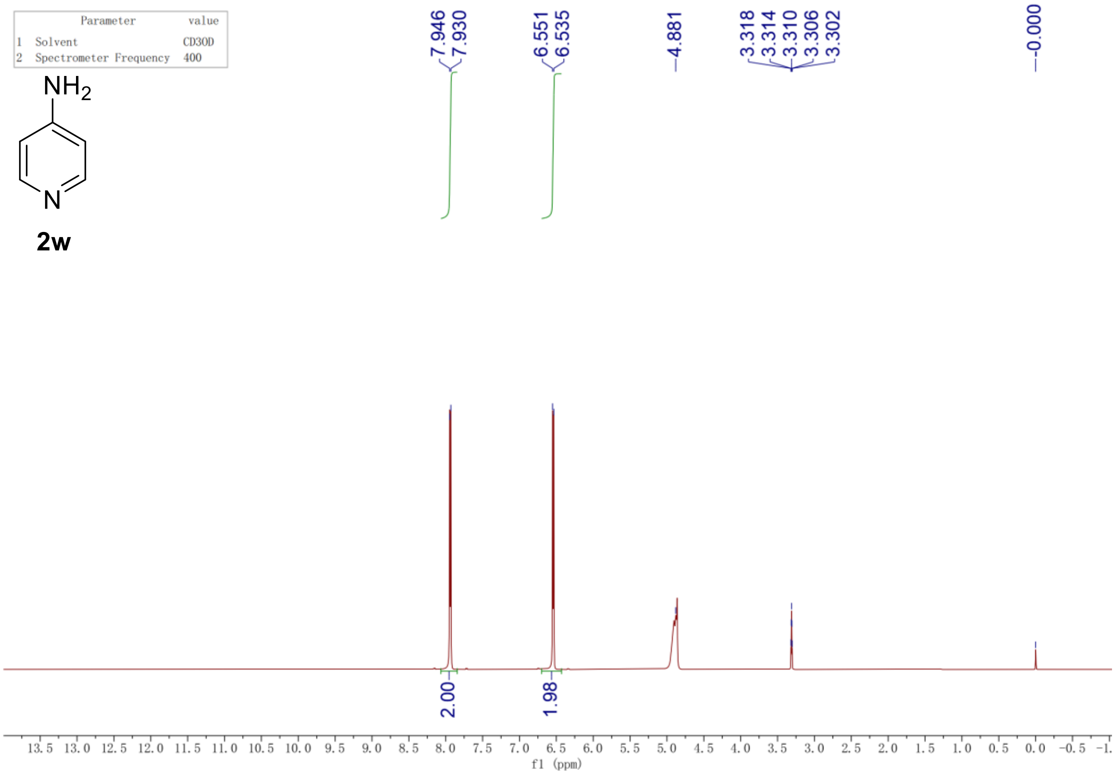
Parameter	value
1 Solvent	DMSO-d6
2 Spectrometer Frequency	400

2u



Parameter	value
1 Solvent	CDCl3
2 Spectrometer Frequency	400

2v


Parameter value
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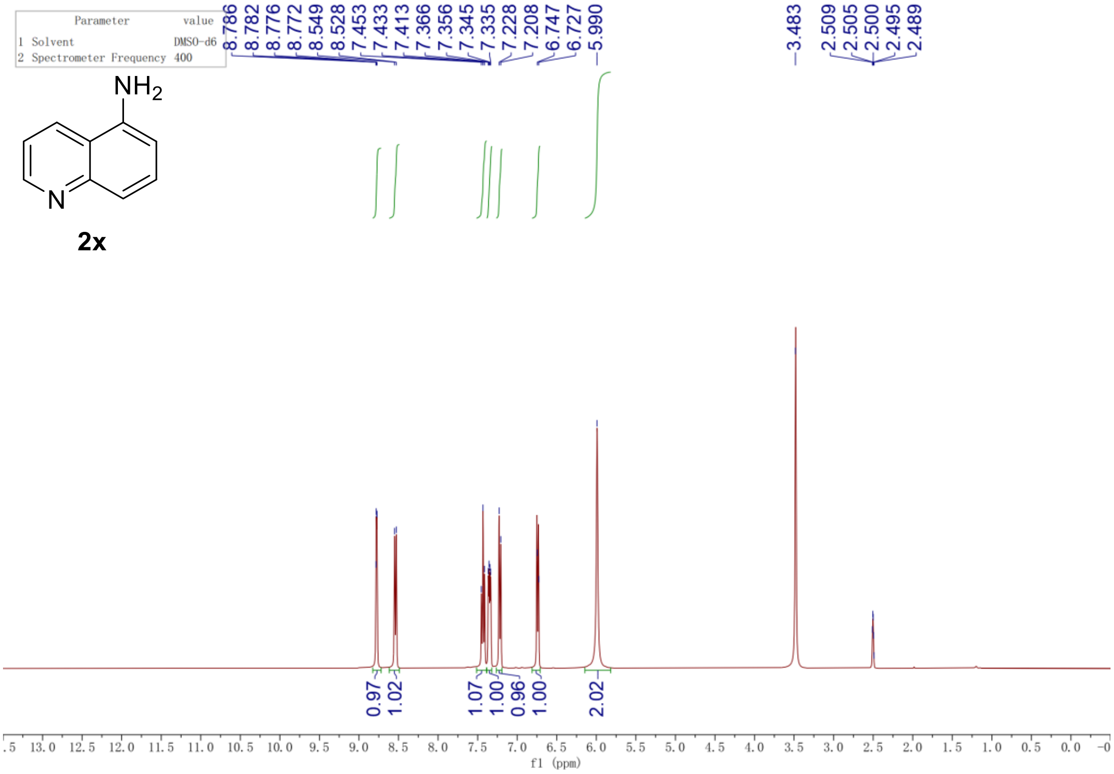
2 Spectrometer Frequency 400
NH2
N
7.946
7.930
6.551
6.535
4.881
3.318
3.314
3.310
3.306
3.302
-0.000
2.00
1.98
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

2w


Parameter value
1 Solvent DMSO-d6
2 Spectrometer Frequency 400
NH2
N
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8.772
8.549
8.528
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7.433
7.413
7.366
7.356
7.345
7.335
7.228
7.208
6.747
6.727
5.990
3.483
2.509
2.505
2.500
2.495
2.489
0.97
1.02
1.07
1.00
0.96
1.00
2.02
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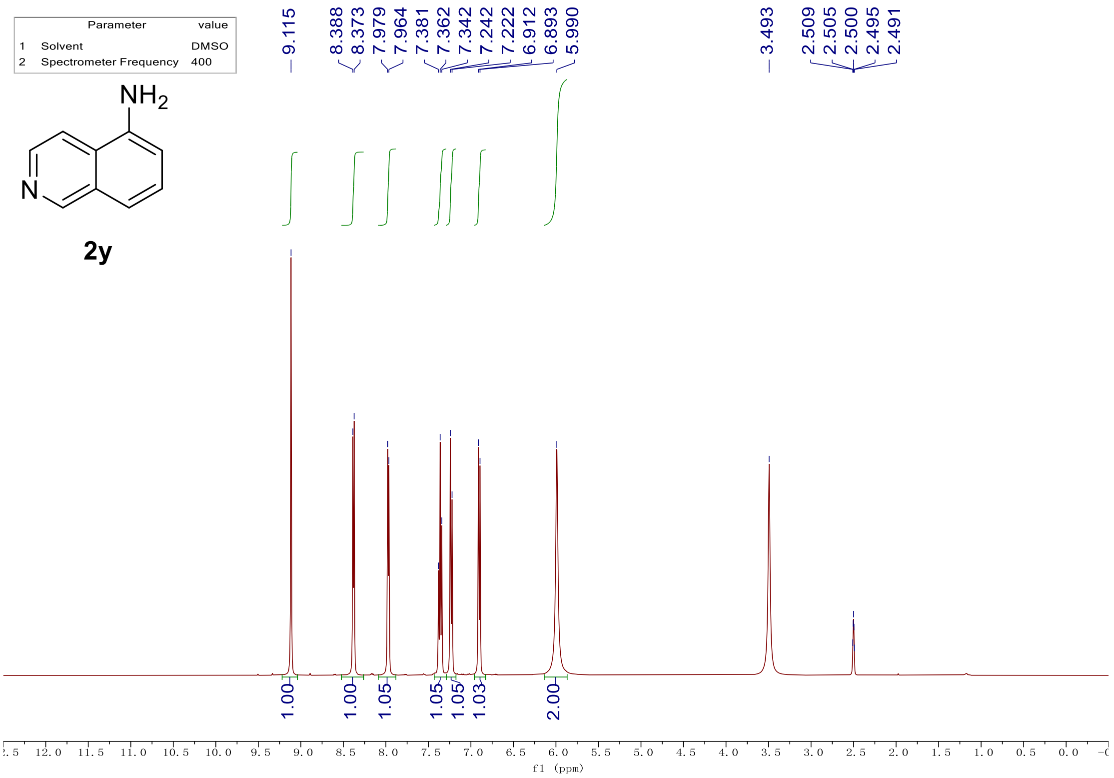
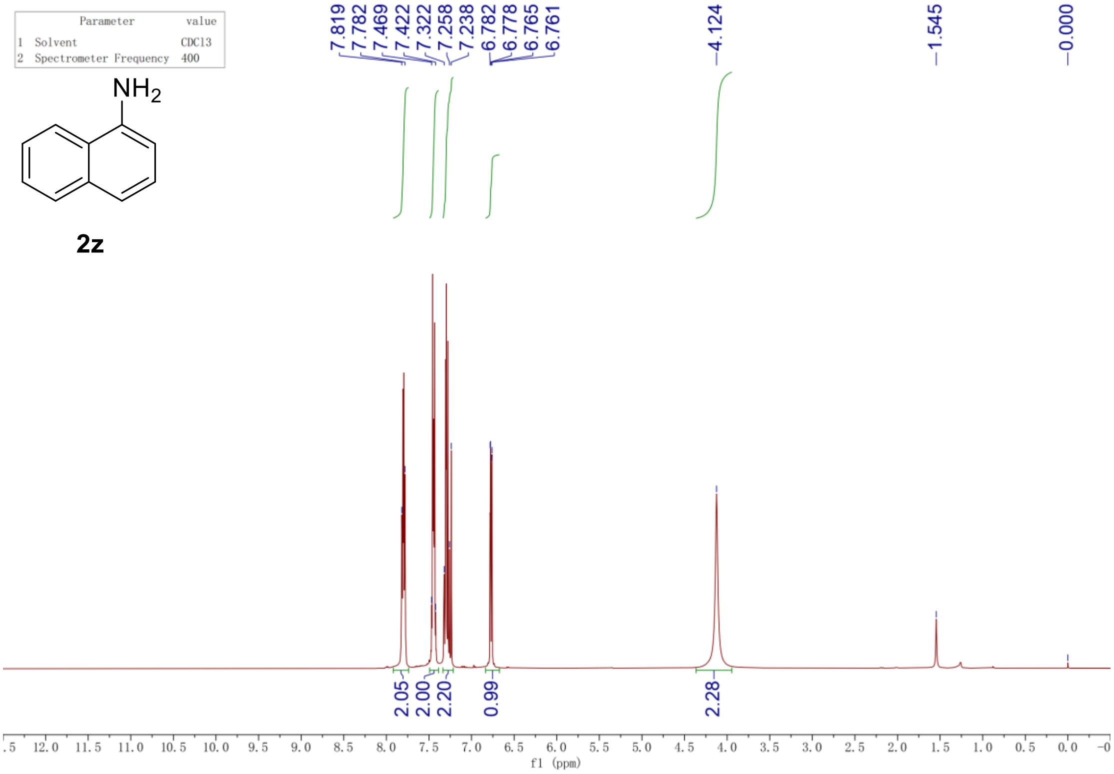
f1 (ppm)

2x



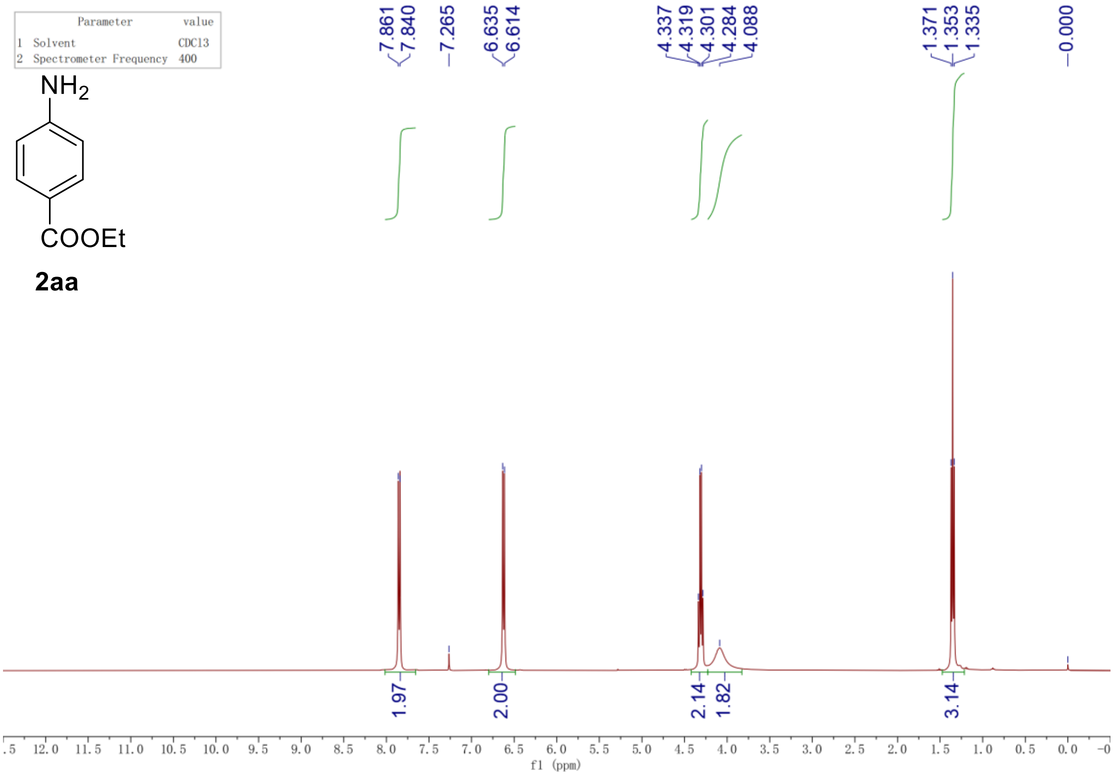
	Parameter	value
1	Solvent	DMSO
2	Spectrometer Frequency	400

2y



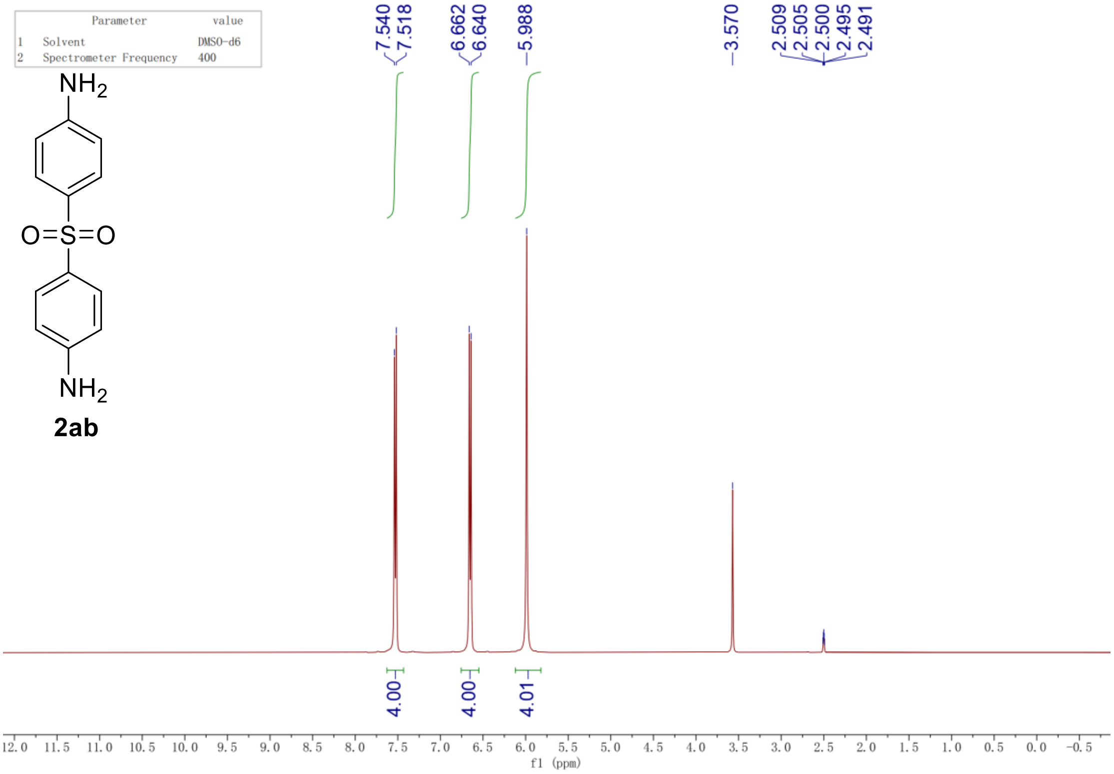
	Parameter	value
1	Solvent	CDCl3
2	Spectrometer Frequency	400

2z



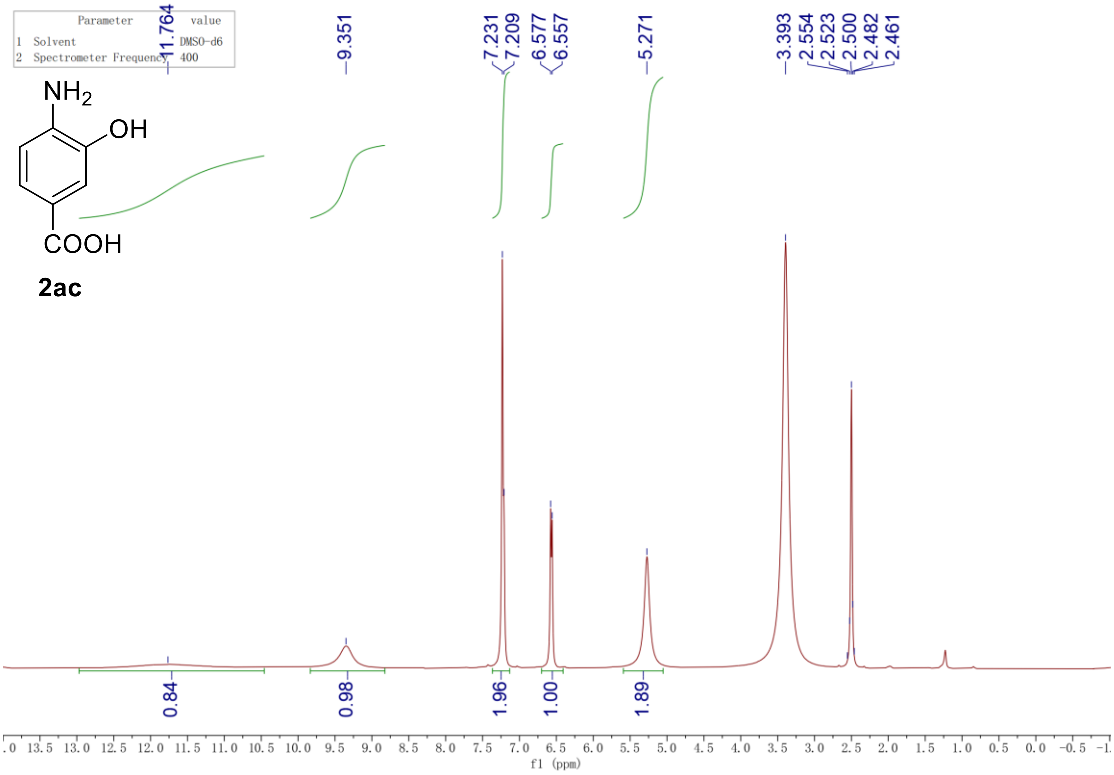
	Parameter	value
1	Solvent	CDCl3
2	Spectrometer Frequency	400

2aa

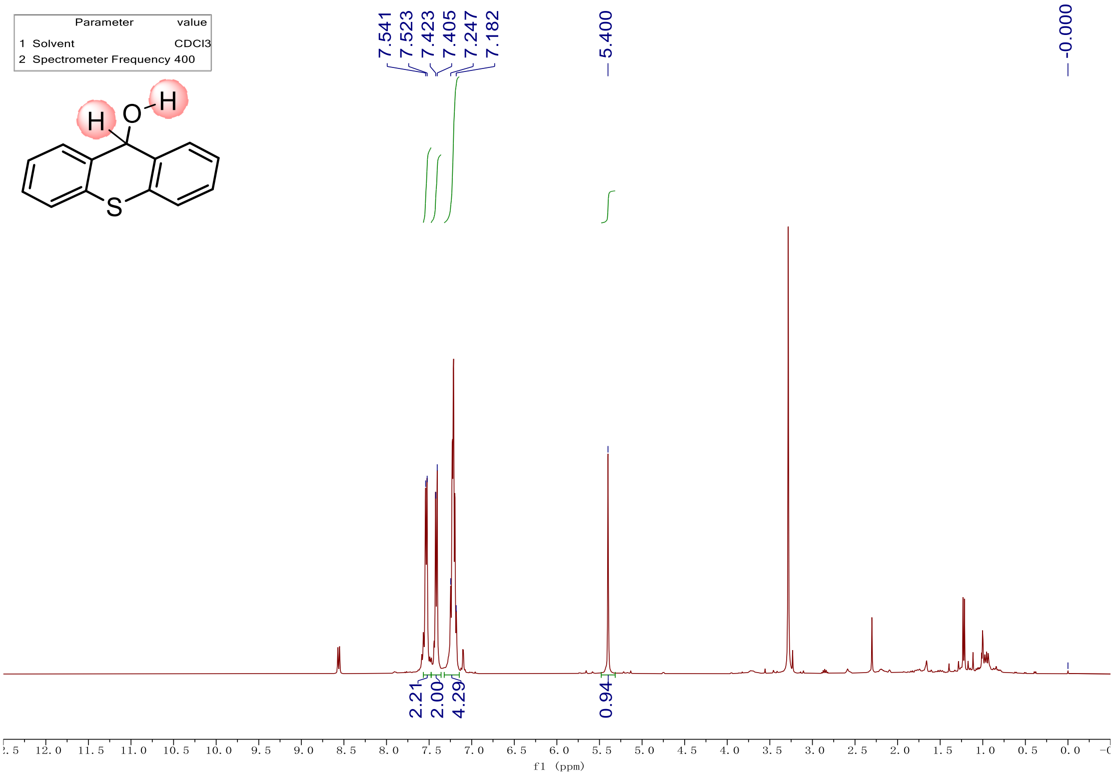


	Parameter	value
1	Solvent	DMSO-d6
2	Spectrometer Frequency	400

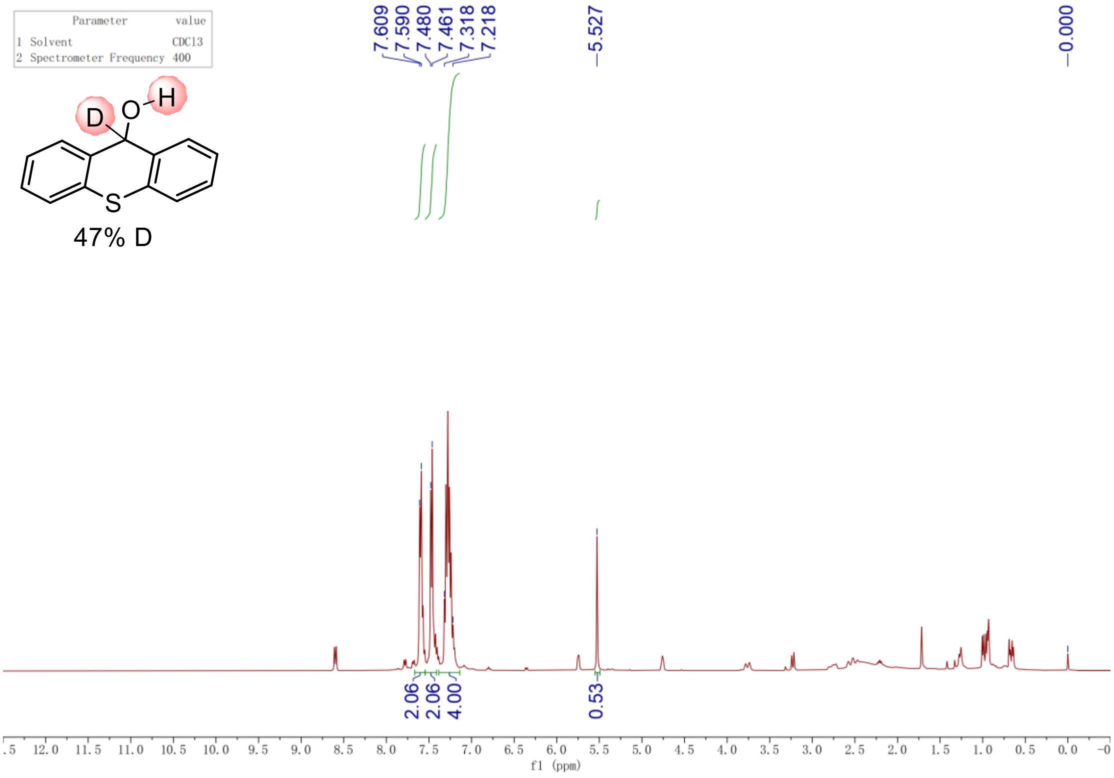
2ab


Parameter value
1 Solvent DMSO-d6
2 Spectrometer Frequency 400
11.764
9.351
7.231
7.209
6.577
6.557
5.271
3.393
2.554
2.523
2.500
2.482
2.461
NH2
OH
COOH
0.84
0.98
1.96
1.00
1.89
f1 (ppm)

2ac


Parameter value
1 Solvent CDCl3
2 Spectrometer Frequency 400
7.541
7.523
7.423
7.405
7.247
7.182
5.400
-0.000
H
O
H
S
2.21
2.00
4.29
0.94
f1 (ppm)

Parameter	value
1 Solvent	CDCl3
2 Spectrometer Frequency	400



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