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Electronic Supplementary Information (ESI)

Tetrathienoanthracene-functionalized Conjugated Microporous Polymers As an Efficient, Metal-Free Visible-Light Solid Organocatalyst for Heterogeneous Photocatalysis

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1. Summary of Schemes , Tables and Figures

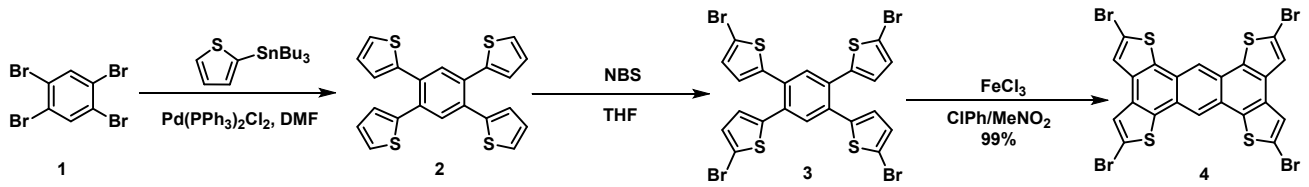
2. General Information

(1) Materials: All reagents were purchased from commercial sources and used as received without further purification. All the substrates were purchased from Energy Chemical (Shanghai, China) and used as received. DMF was dried by calcium hydride and used after distillation. [$Pd(PPh_3)_2Cl_2$] and 1,3,5-tri(4-ethynylphenyl)benzene were prepared and purified according to the literature procedures. All anhydrous reactions were carried out under dry nitrogen by using Schlenk tube techniques. All catalytic reactions were performed in a 10 mL glass tube.

(2) **Methods:** Chemicals and solvents were purchased from commercial suppliers. All equipment was thoroughly oven-dried. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. Flash column chromatography (FCC) was carried out with silica gel (200–300 mesh). ^{1}H and ^{13}C liquid NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer. N_2 adsorption and desorption isotherms were measured at 77 K using a Quantachrome autosorb IQ-2. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDPT) method. Solid-state NMR experiments were performed on a Bruker Avance II WB 400 MHz NMR spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 3 ms (ramp 100) and the recycle delay of 2 s on a 2.5 mm double resonance probe. FT-IR spectra were collected on a Nicolet 6700 instrument. Thermal properties of the synthesized materials were evaluated on a STA PT1600 Linseis thermogravimetric analysis (TGA) instrument in the temperature range of 25 to 1000 °C under nitrogen atmosphere with a heating rate of 10 °C/min. Surface morphologies and microstructures of the synthesized materials were examined with a ZEISS Gemini-500 scanning electron microscope (SEM) and with a JEOL JEM-2010 transmission electron microscope (TEM) operated at 200 kV. The UV-Visible absorption spectra of the TTA and the TTA-CMP were recorded on UV-Vis spectrometer (U-4100) in solid state powder at room temperature. Cyclic voltammetry (CV) experiment was carried out using CHI 760E in a three-electrode electrochemical cell with a scan rate of 0.1 V/s. The experiment was conducted in anhydrous acetonitrile with tertrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The auxiliary electrode was a platinum wire. The reference electrode was based on the calomel electrode. The working electrode was a glassy carbon electrode.

3. Synthetic Procedures

(1) Synthesis of functionalized tetrathienoanthracene (FBB-TTA)[1]

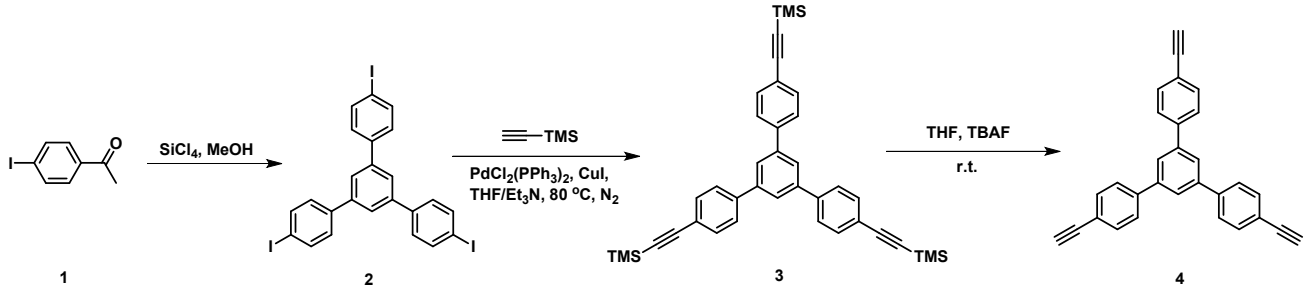


Scheme S1. Synthesis of FBB-TTA

Compounds 2, 3 and 4 were prepared according to previously reported synthetic procedures (see: *Chem. Mater.* **2008**, *20*, 2482-2494), and showed identical spectroscopic properties to those reported therein. 1,2,4,5-tetrabromobenzene (10.0 g, 25.3 mmol), palladium(II) chloride (320 mg, 1.80 mmol), triphenylphosphine (950 mg, 3.62 mmol), and 2-(tributylstannyl)thiophene (41.0 mL, 129 mmol) were stirred at 130 °C in DMF (5 mL) for 16 h. After being cooled to room temperature, the reaction mixture was filtered and the product (10.14 g, 25.5 mmol, 99%) rinsed with hexane. *N*-bromosuccinimide (6.80 g, 38.2 mmol) was added to a solution of **2** (2.53 g, 6.22 mmol) in THF (125 mL) and stirred at room temperature for 16 h. The resulting white precipitate was filtered, rinsed with acetone, and washed in water before drying in air to give the product **3** as a white solid (3.68 g, 82%). Mp: 258–262 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 2H), 6.97 (d, J = 3.8 Hz, 4H), 6.75 (d, J = 3.8 Hz, 4H).. ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.22, 133.14, 132.73, 130.14, 128.01, 113.60.

A solution of iron(III) chloride (1.5 g, 9.24 mmol) in nitromethane (25 mL) was added dropwise to a solution of **3** (1.08 g, 1.50 mmol) in warm chlorobenzene (50 mL), and the reaction mixture was stirred for 30–60 min. The resulting yellow precipitate was filtered, rinsed with DCM, and dried in air. The solid was then stirred in 10% HCl/H_2O for 15 min, filtered, combined with hot methanol (200 mL), filtered, rinsed with methanol, and dried in air to give FBB-TTA **4** as a yellow solid (1.07 g, 1.48 mmol, 100%), which was used without further purification. Mp: >350 °C (dec). UV: λmax = 340 nm (broad). IR: 1546.11 (m), 1482.93 (s), 1457.41 (s), 1429.82 (w), 1406.58 (w), 1392.24 (w), 1377.11 (m), 1304.20 (w), 1297.96 (m), 1262.48 (w), 1185.63 (w), 1128.94 (w), 978.63 (w), 971.77 (w), 960.91 (m), 913.36 (s), 860.06 (s), 816.64 (m), 800.24 (s), 722.01 (w), 697.16 (w), 655.41 (w), 613.36 (m), 559.32 (m), 494.10 (s), 434.07 (s) cm^{-1}. Given the low solubility of this compound, ^{1}H and ^{13}C NMR spectroscopy was not possible.

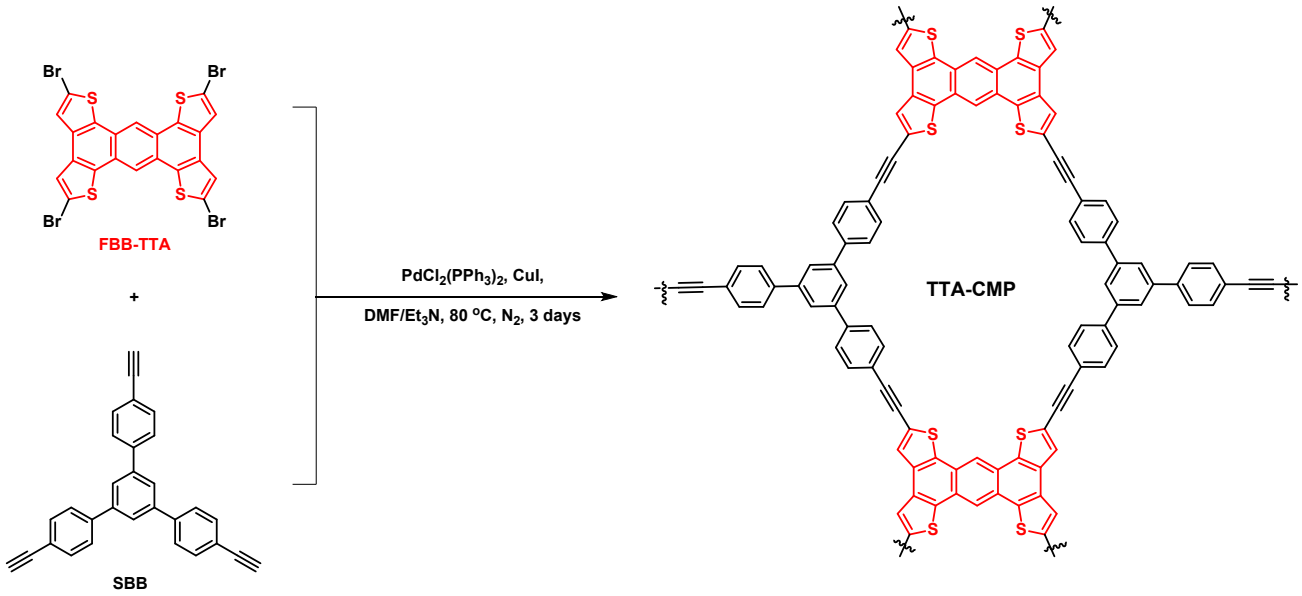
(2) Synthesis of 1,3,5-tri(4-ethynylphenyl)benzene (SBB)[2]



Scheme S2. Synthesis of 1,3,5-tri(4-ethynylphenyl)benzene (SBB)

4-iodooacetophenone (500 mg, 2.03 mmol) was dissolved in ethanol (5 mL) andsilicon tetrachloride (575 mg, 3.39 mmol) was quickly added at 0 °C (a tube is needed to release hydrogen chloride into the fume hood) and the resulting orange solution was stirred at room temperature for 3 d. The mixture was quenched with water (5 mL) and the solution was concentrated to 6 mL. CH_2Cl_2 (5 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on aluminum oxide (hexane/ethyl acetate = 10:1) to give 1,3,5-tris(4-iodophenyl)benzene (396 mg, 85%) as a yellow solid. A mixture of 1,3,5-tris(4-iodophenyl)benzene (350 mg, 512 μmol), ethynyltrimethylsilane (201 mg, 2.05 mmol), $PdCl_2(PPh_3)_2$ (60 mg), and CuI (10 mg) in THF (2.5 mL) and triethylamine (2.5 mL) was heated to 80 °C for 16 h under N_2 atmosphere. The volatile components were removed under reduced pressure and the residue was diluted with CH_2Cl_2 (10 mL). Satd. aq. NH_4Cl solution (10 mL) was added, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to give **3** (211 mg, 70%) as a pale brownish solid. A solution of **3** (200 mg, 336 μmol) and TBAF (1.2 ml, 1.18 mmol, 1 M in THF) in THF (2 mL) was stirred at room temperature for 30 min. The mixture was quenched with satd. aq. NH_4Cl solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 10:1) to give 1,3,5-tri(4-ethynylphenyl)benzene (102 mg, 80%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (s, 3H); 7.67-7.61 (m, 12H); 3.17 (s, 3H). ^{13}CNMR (100 MHz, $CDCl_3$): δ (ppm) 141.6, 141.2, 132.7, 127.2, 125.3, 121.5, 83.4, 78.2.

(3) Synthesis of **TTA-CMP**[3]



Scheme S3. Synthesis of TTA-CMP

1,3,5-tri(4-ethynylphenyl)benzene (210 mg, 0.56 mmol), FBB-TT**A** (300 mg, 0.42 mmol), bis-(triphenylphosphine)palladium(II) dichloride (50 mg), and copper iodide (25 mg) were dissolved in a mixture of dried dimethylformamide (10 mL) and Et_3N (10 mL). The reaction mixture was heated to 80 °C and stirred for 72 h under nitrogen atmosphere. The mixture was then cooled to room temperature, and the precipitated TTA-CMP frameworks was filtered and washed four times (once each) with chloroform, water, methanol, and acetone to remove any unreacted substrates or catalyst residues. Further purification of the TTA-CMP frameworks was carried out by Soxhlet extraction with methanol for 48 h. The product was dried in vacuum for 24 h at 80 °C (368 mg, yield: 98%). Anal. calcd for $(C_{62}H_{30}S_4)_n$: C 82.48; H 3.32; S 14.19. Elemental analysis (%) Found: C 67.88; H 3.57; S 10.95.

4. Characterization of TTA-CMP

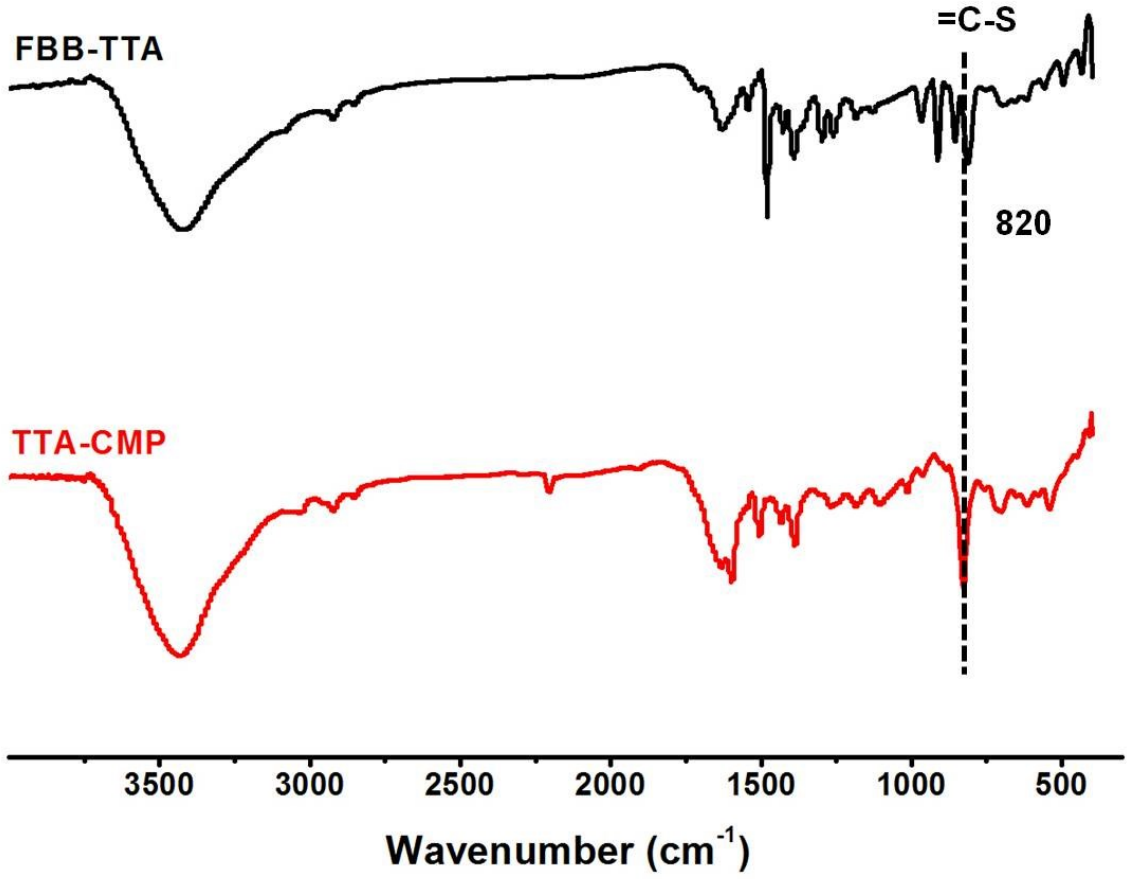


Figure S1. FT-IR spectra of FBB-TTA and TTA-CMP

The FT-IR spectra of TTA-CMP showed peaks at 820 cm^{-1}, which demonstrated the presence of =C-S bonds that come from thiophene units. The signal imply that tetrathienoanthracene monomer was incorporated into the networks of TTA-CMP.

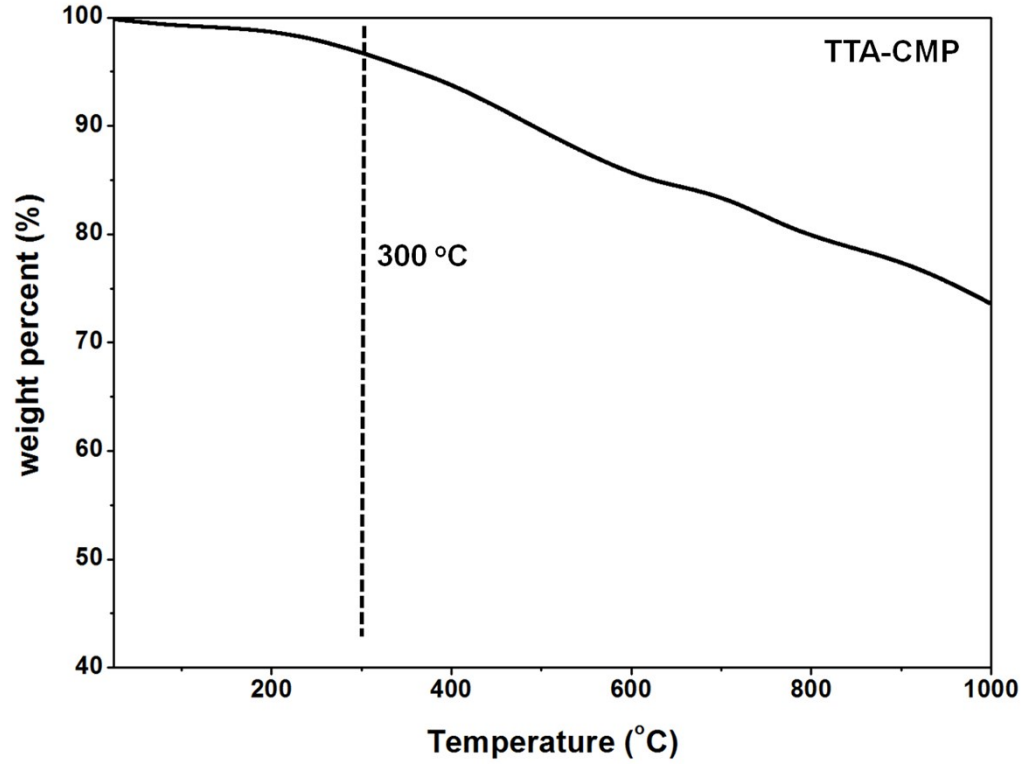


Figure S2. TGA curves of TTA-CMP

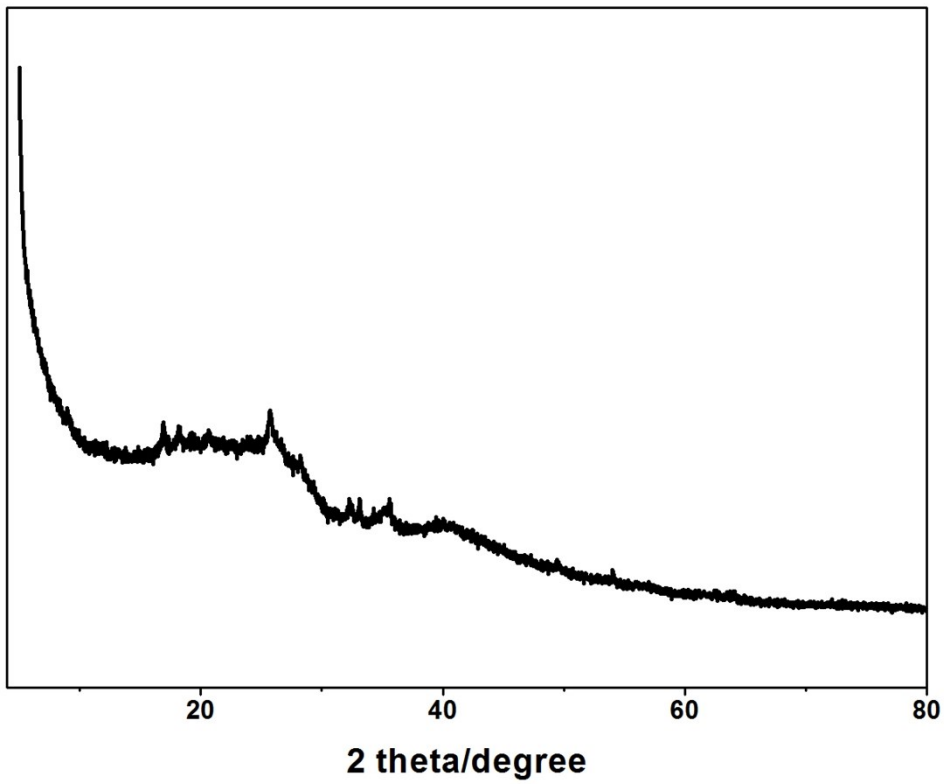


Figure S3. Powder X-ray diffraction pattern of TTA-CMP. No intensive diffraction peaks were observable. This result proved that the TTA-CMP was amorphous material.

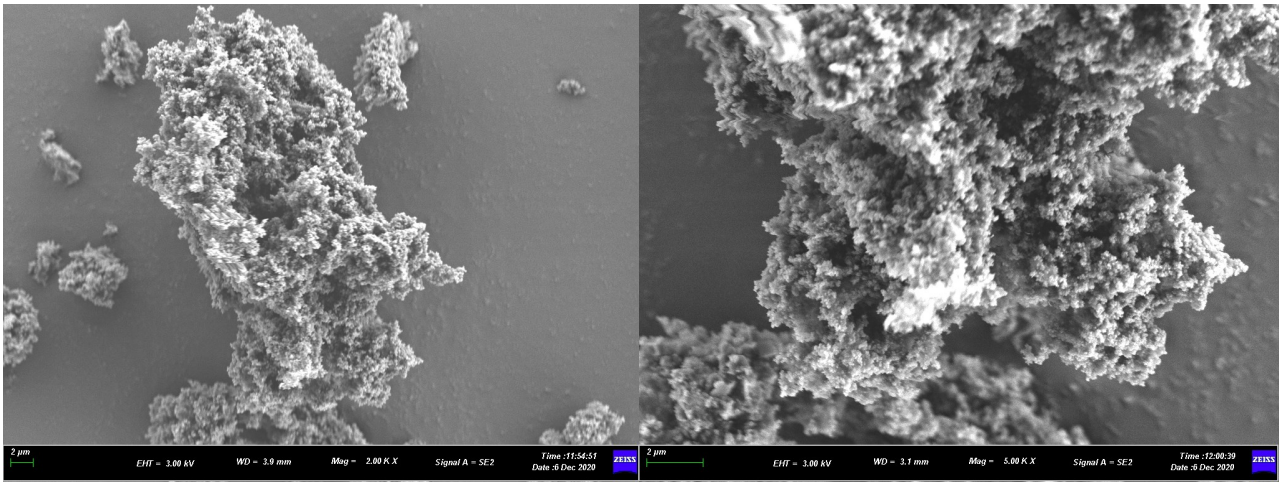


Figure S4. SEM images of TTA-CMP

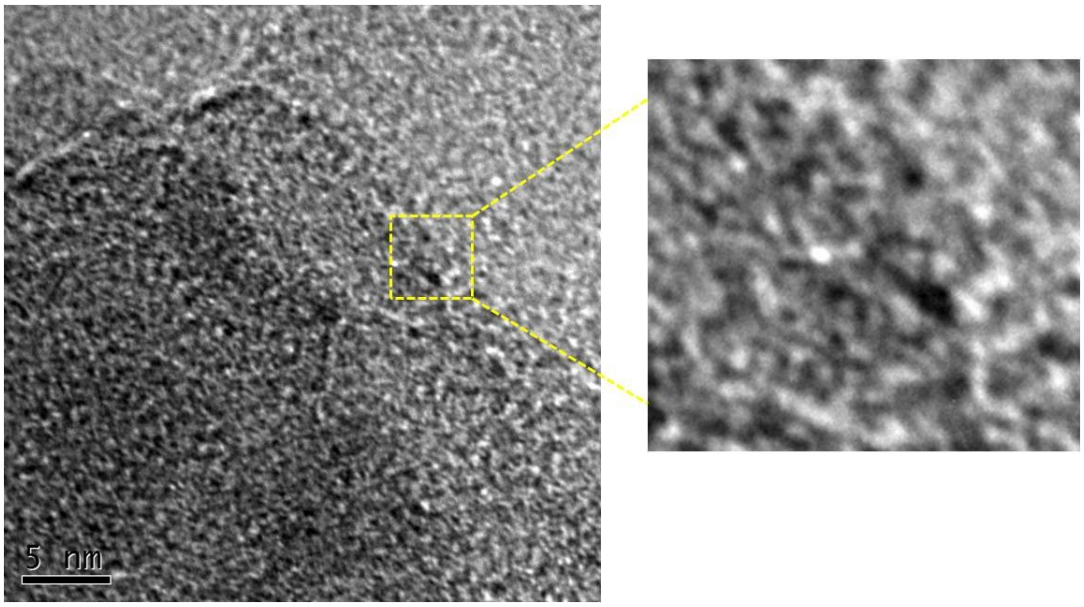


Figure S5. TEM images of TTA-CMP

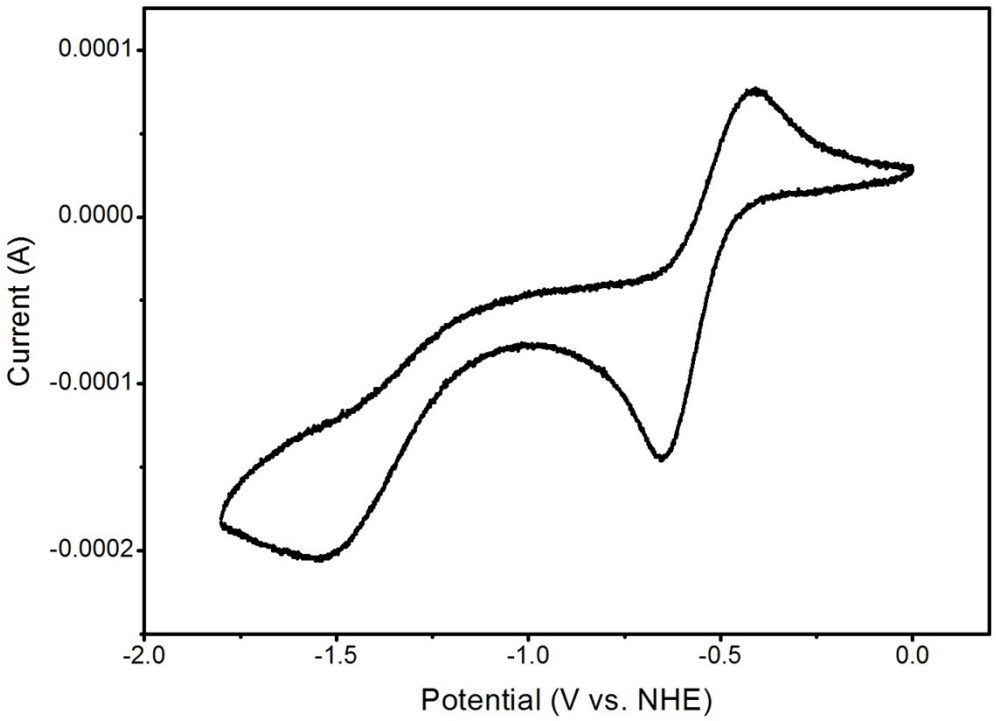
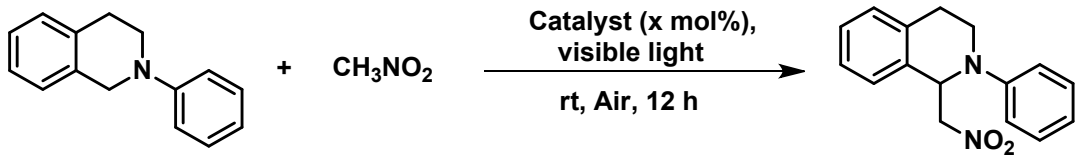


Figure S6. Cyclic voltammetry curves of TTA-CMP. The experiments wereconducted in anhydrous acetonitrile solution of Bu_4NPF_6 (0.1 M) at a scan rate of 0.1 V/s. According to Figure S8, the conduction band positions (*vs.* SCE) for TTA-CMP could be estimated as -1.20 V.

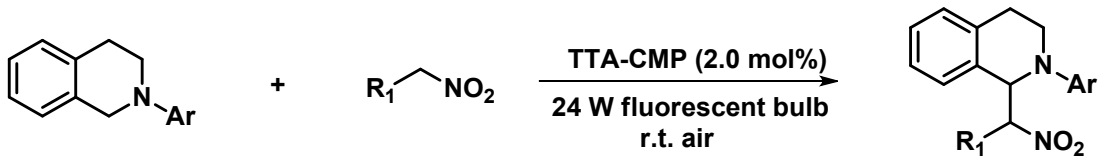
5. Typical Procedure for the Dehydrogenative Coupling Catalysed by TTA-CMP[4]

Table S1. Optimization of the reaction conditions[a]

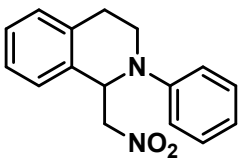


Entry	Catalyst	x	Light source	Yield[b]
1	TTA-CMP	1.0	24 W bulb	56
2	TTA-CMP	2.0	24 W bulb	96
3	TTA-CMP	5.0	24 W bulb	87
4	TTA-CMP	2.0	Natural light	38
5	TTA-CMP	2.0	dark	0
6	------	------	24 W bulb	trace
7[c]	CMP-1	2.0	24 W bulb	trace
8[d]	TTA-CMP	2.0	24 W bulb	29
9[e]	FBB-TTA	2.0	24 W bulb	35

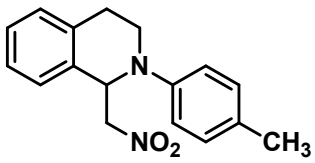
[a]Reaction condition: 2-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol), nitromethane (1.0 mL), and **TTA-CMP**, rt., 24 W household bulb, in air. [b]Isolated yield after silica gel column chromatography. [c]non-photoactive CMP-1[3] as the heterogeneous catalyst. [d] The reaction was carried out under N_2. [e]The homogeneous catalyst (2.0 mol%) was applied as a reference.



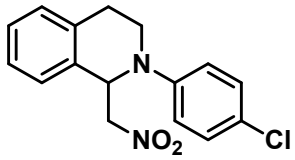
N-Aryltetradroisoquinolines (0.2 mmol), nitroalkane (1.0 mL), and **TTA-CMP** (4.7 mg, 2.0 mol%) were added into a 15-mL glass tube. The tube was sealed with a rubber stopper and the reaction mixture was connected to the air through a needle in the stopper. The tube was subsequently stirred at room temperature under irradiation with visible light using a cool daylight energy-saving bulb (24 W) until all starting material had been consumed. After the reaction was completed (monitored by TLC), the mixture was centrifugated and the solid was washed with EtOAc (3 x 5 mL). The combined organic phase was then concentrated and purified by flash column chromatography with petroleum ether/EtOAc = 10:1 as the eluent to give the pure product.



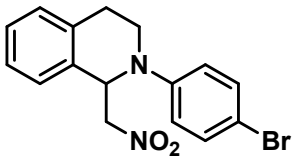
1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **TTA-CMP** (4.7 mg), 2-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (51.5 mg, 96%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 5H), 7.11 (d, *J* = 7.0 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 5.53 (t, *J* = 7.2 Hz, 1H), 4.85 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.54 (dd, *J* = 11.8, 6.6 Hz, 1H), 3.71 – 3.51 (m, 2H), 3.17 – 3.01 (m, 1H), 2.77 (dt, *J* = 16.3, 4.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.45, 135.31, 132.94, 129.54, 129.23, 128.15, 127.03, 126.72, 119.45, 115.13, 78.80, 58.23, 42.08, 26.47.



1-(Nitromethyl)-2-(4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **TTA-CMP** (4.7 mg), 2-(4-methylphenyl) -1,2,3,4-tetrahydroisoquinoline (44.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-(4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline (53.2 mg, 94%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.09 (m, 4H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.92 – 6.84 (m, 2H), 5.55 – 5.42 (m, 1H), 4.84 (dd, *J* = 11.8, 8.1 Hz, 1H), 4.54 (dd, *J* = 11.8, 6.4 Hz, 1H), 3.71 – 3.51 (m, 2H), 3.12 – 2.96 (m, 1H), 2.74 (dt, *J* = 16.4, 4.5 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.39, 135.36, 132.96, 129.99, 129.29, 129.13, 128.01, 126.98, 126.64, 115.92, 78.85, 58.41, 42.33, 26.25, 20.38.

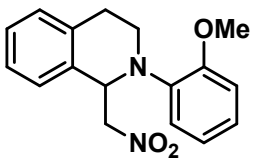


1-(Nitromethyl)-2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **TTA-CMP** (4.7 mg), 2-(4-chlorophenyl) -1,2,3,4-tetrahydroisoquinoline (48.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-(4- chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (58.2 mg, 96%) as a yellow soild. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.09 (m, 5H), 7.06 (d, *J* = 7.1 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 2H), 5.49 – 5.34 (m, 1H), 4.78 (dd, *J* = 12.0, 8.1 Hz, 1H), 4.49 (dd, *J* = 12.0, 6.3 Hz, 1H), 3.58 – 3.49 (m, 2H), 3.04 – 2.91 (m, 1H), 2.71 (dt, *J* = 16.4, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.98, 135.03, 132.41, 129.35, 129.33, 128.30, 126.96, 126.87, 124.61, 116.62, 78.64, 58.31, 42.41, 26.15.



1-(Nitromethyl)-2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **TTA-CMP** (4.7 mg), 2-(4-bromophenyl) -1,2,3,4-tetrahydroisoquinoline (57.6 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (68.6 mg, 98%) as a yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 9.0 Hz, 2H), 7.22 – 7.03 (m, 4H), 6.79 (d, J = 9.0 Hz, 2H), 5.41 (t, J = 7.2 Hz, 1H), 4.79 (dd, J = 12.0, 8.1 Hz, 1H), 4.50 (dd, J = 12.0, 6.4 Hz, 1H), 3.54 (dd, J = 8.4, 4.6 Hz, 2H), 3.08 – 2.91 (m, 1H), 2.73 (dt, J = 16.4, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.32, 134.98, 132.35, 132.27, 129.31, 128.33, 126.96, 126.89, 116.93, 116.48, 111.86, 78.59, 58.23, 42.37, 26.18.

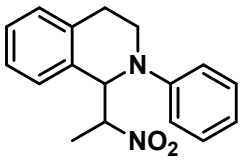
1-(Nitromethyl)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **TTA-CMP** (4.7 mg), 2-(4-fluorophenyl) -1,2,3,4-tetrahydroisoquinoline (44.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-(4- fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (53.7 mg, 94%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.13 (m, 4H), 7.02 – 6.84 (m, 4H), 5.44 (dd, J = 8.5, 6.0 Hz, 1H), 4.86 (dd, J = 12.0, 8.7 Hz, 1H), 4.59 (dd, J = 12.0, 5.9 Hz, 1H), 3.61 (dd, J = 9.2, 4.3 Hz, 2H), 3.13 – 2.95 (m, 1H), 2.74 (dt, J = 16.5, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.36, 156.27 (d, J^F = 33.0 Hz), 145.29, 135.24, 132.55, 129.45, 128.10, 126.86 (d, J^F = 17.0 Hz), 117.94 (d, J^F = 8.0 Hz), 115.87 (d, J^F = 22.0 Hz), 78.87, 58.73, 42.85, 25.79.



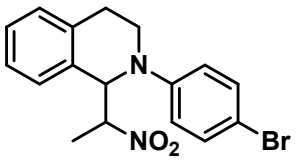
1-(Nitromethyl)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **TTA-CMP** (4.7 mg), 2-(2-methoxyphenyl) -1,2,3,4-tetrahydroisoquinoline (47.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (56.6 mg, 95%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (qt, J = 7.2, 3.6 Hz, 2H), 7.08 (dd, J = 6.0, 2.8 Hz, 2H), 6.95 (td, J = 8.2, 1.7 Hz, 1H), 6.86 – 6.71 (m, 3H), 5.43 (dd, J = 8.2, 5.1 Hz, 1H), 4.75 (dd, J = 12.1, 8.5 Hz, 1H), 4.46 (dd, J = 12.1, 5.0 Hz, 1H), 3.75

(s, 3H), 3.59 – 3.46 (m, 1H), 3.46 – 3.34 (m, 1H), 2.91 (ddd, *J* = 17.1, 11.3, 6.2 Hz, 1H), 2.64 (d, *J* = 16.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.09, 138.83, 135.37, 133.63, 129.57, 127.60, 126.84, 126.46, 124.17, 121.97, 121.04, 112.48, 79.18, 58.21, 55.81, 43.01, 26.86.

1-(Nitromethyl)-2-(3-methylphenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **TTA-CMP** (4.7 mg), 2-(3-methylphenyl) -1,2,3,4-tetrahydroisoquinoline (44.8 mg, 0.2 mmol), and nitromethane (1.0 mL) afforded 1-(nitromethyl)-2-(3-methylphenyl)-1,2,3,4-tetrahydroisoquinoline (50.8 mg, 90%) as a yellow solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.12 (m, 5H), 6.86 – 6.79 (m, 2H), 6.71 (d, *J* = 7.4 Hz, 1H), 5.56 (t, *J* = 7.2 Hz, 1H), 4.90 (dd, *J* = 11.8, 7.7 Hz, 1H), 4.58 (dd, *J* = 11.8, 6.7 Hz, 1H), 3.76 – 3.54 (m, 2H), 3.20 – 3.00 (m, 1H), 2.82 (dt, *J* = 16.3, 5.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.24, 139.36, 135.23, 132.87, 129.38, 129.20, 128.14, 126.97, 126.73, 120.68, 116.10, 112.38, 78.75, 58.34, 42.48, 26.51, 21.91.

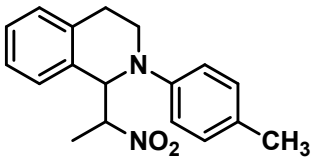


1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **TTA-CMP** (4.7 mg), 2-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol), and nitroethane (1.0 mL) afforded 1-(1-nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (54.1 mg, 96%) as a orange oil. Major diastereoisomer δ 7.31–7.10 (m, 6 H), 7.03 (t, *J* = 8.0 Hz, 2 H), 6.85 (t, *J* = 7.3 Hz, 1 H), 5.27 (d, *J* = 8.0 Hz, 1 H), 5.08 (dq, *J* = 13.5, 6.7 Hz, 1 H), 3.86 (ddd, *J* = 13.4, 8.0, 5.7 Hz, 1 H), 3.64–3.51 (m, 2 H), 3.07 (dt, *J* = 14.1, 7.0 Hz, 1 H), 2.98–2.92 (m, 1 H), 1.56 (d, *J* = 6.6 Hz, 3 H). Minor diastereomer (representative signals): δ 7.31–7.10 (m, 6 H), 7.03 (t, *J* = 8.0 Hz, 2 H), 6.85 (t, *J* = 7.3 Hz, 1 H), 4.93 (dq, *J* = 13.7, 6.9 Hz, 1 H), 1.72 (d, *J* = 6.8 Hz, 3 H).



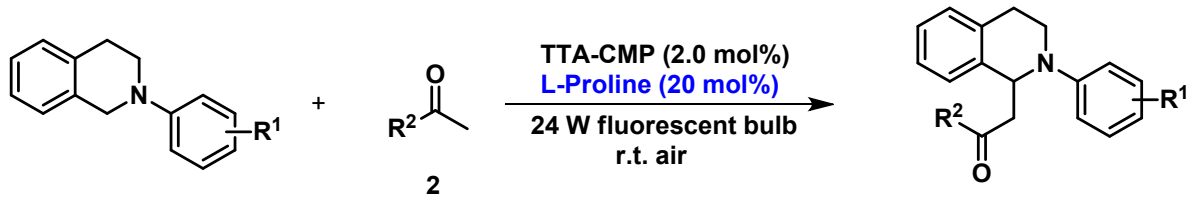
1-(1-Nitroethyl)-2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **TTA-CMP** (4.7 mg), 2-(4-bromophenyl) -1,2,3,4-tetrahydroisoquinoline (57.6 mg, 0.2 mmol), and nitroethane (1.0 mL) afforded 1-(1-nitroethyl)-2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (66.4 mg, 92%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) Major diastereoisomer δ 7.32–7.03 (m, 6 H), , 6.77 (dd, *J* =

9.2, 3.0 Hz, 2 H), 5.07 (d, *J* = 8.7 Hz, 1 H), 4.95–4.85 (m, 1 H), 3.49–3.42 (m, 2 H), 3.02–2.90 (m, 1 H), 2.83 (ddd, *J* = 21.6, 13.8, 6.1 Hz, 1 H), 1.47 (d, *J* = 6.6 Hz, 3 H). Minor diastereomer (representative signals): δ 5.12 (d, *J* = 8.8 Hz, 1 H), 4.79 (dq, *J* = 13.7, 6.8 Hz, 1 H), 3.89 (t, *J* = 6.5 Hz, 1 H), 3.78–3.67 (m, 1 H), 1.59 (d, *J* = 6.8 Hz, 3 H).

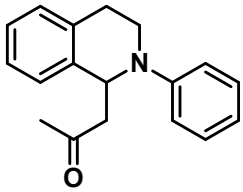


1-(1-Nitroethyl)-2-(4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline: Following the general procedure, **TTA-CMP** (4.7 mg), 2-(4-methylphenyl) -1,2,3,4-tetrahydroisoquinoline (44.8 mg, 0.2 mmol), and nitroethane (1.0 mL) afforded 1-(1-nitroethyl)-2-(4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline (54.9 mg, 93%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) Major diastereoisomer δ 7.27–7.13 (m, 4 H), 7.11–6.99 (m, 2 H), 6.92 (dd, *J* = 19.6, 9.3 Hz, 2 H), 5.19 (t, *J* = 9.1 Hz, 1 H), 5.06 (dq, *J* = 13.4, 6.7 Hz, 1 H), 3.69–3.45 (m, 2 H), 3.12–2.98 (m, 1 H), 2.98–2.81 (m, 1 H), 2.25 (s, 3 H), 1.55 (d, *J* = 6.6 Hz, 3 H). Minor diastereomer (representative signals): δ 4.97–4.80 (m, 1 H), 3.83 (ddd, *J* = 13.5, 8.2, 5.6 Hz, 2 H), 2.27 (s, 3 H), 1.71 (dd, *J* = 6.6, 2.4 Hz, 3 H).

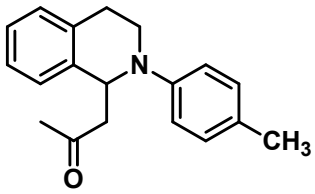
6. Typical Procedure for the Dehydrogenative-Mannich reaction Catalysed by TTA-CMP[5]



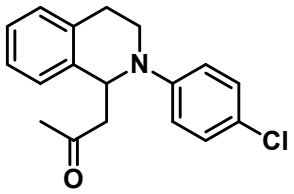
N-Aryltetradroisoquinolines (0.1 mmol), **TTA-CMP** (2.4 mg, 2.0 mol%), L-proline (2.3 mg, 20 mol%) and 1.0 mL the appropriate ketone were added into a 15-mL glass tube. The tube was sealed with a rubber stopper and the reaction mixture was connected to the air through a needle in the stopper. The tube was subsequently stirred at room temperature under irradiation with 24 W fluorescent bulb until the starting material had been consumed. After the reaction was completed (monitored by TLC), the mixture was centrifugated and the solid was washed with EtOAc (3 x 5 mL). The combined organic phase was then concentrated and purified by flash column chromatography with petroleum ether/EtOAc as the eluent to give the corresponding products.



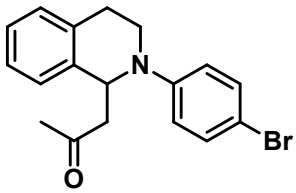
1-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one: Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 10/1 as eluent). White solid, 24.9 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 7.16 – 7.14 (m, 4H), 6.93 (d, J = 8.3 Hz, 2H), 6.77 (t, J = 6.8 Hz, 1H), 5.40 (t, J = 6.1 Hz, 1H), 3.73 – 3.61 (m, 1H), 3.59 – 3.46 (m, 1H), 3.15 – 2.93 (m, 2H), 2.92 – 2.71 (m, 2H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.26, 148.86, 138.27, 134.43, 129.34, 128.66, 126.86, 126.79, 126.27, 118.25, 114.76, 54.78, 50.21, 42.05, 31.09, 27.20.



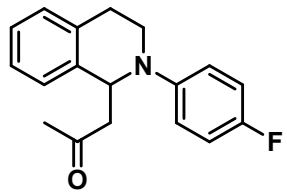
1-(2-p-tolyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one: Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 10/1 as eluent). Colourless oil, 22.9 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.12 (m, 4H), 7.05 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 5.34 (t, J = 6.3 Hz, 1H), 3.70 – 3.56 (m, 1H), 3.57 – 3.42 (m, 1H), 3.13 – 2.96 (m, 2H), 2.78 (ddd, J = 15.9, 10.2, 5.6 Hz, 2H), 2.25 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.38, 146.89, 138.29, 134.40, 129.82, 128.78, 126.84, 126.69, 126.18, 115.67 , 55.16, 50.08, 42.19, 31.00, 26.98, 20.31.



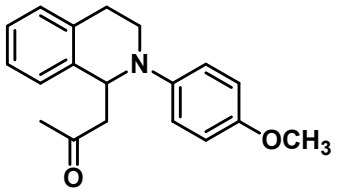
1-(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one: Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 10/1 as eluent). Colourless oil, 24.8 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 9.9, 6.5 Hz, 6H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.34 (t, *J* = 6.3 Hz, 1H), 3.67 – 3.56 (m, 1H), 3.57 – 3.45 (m, 1H), 3.11 – 2.97 (m, 2H), 2.82 (dd, *J* = 16.5, 6.6 Hz, 2H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.02, 147.45, 137.93, 134.19, 129.13, 128.70, 126.95, 126.81, 126.40, 123.00, 115.82, 54.76, 50.15, 42.20, 31.11, 27.00.



1-(2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one: Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 10/1 as eluent). Pale yellow oil, 28.2 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 9.1 Hz, 2H), 7.22 – 7.08 (m, 4H), 6.80 (d, *J* = 9.0 Hz, 2H), 5.32 (dd, *J* = 15.8, 9.5 Hz, 1H), 3.58 (dq, *J* = 10.8, 5.4 Hz, 1H), 3.54 – 3.44 (m, 1H), 3.12 – 2.95 (m, 2H), 2.89 – 2.78 (m, 2H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.97, 147.78, 137.87, 134.16, 132.00, 128.65, 126.95, 126.78, 126.39, 116.09, 110.05, 54.60, 50.10, 42.10, 31.10, 27.01.

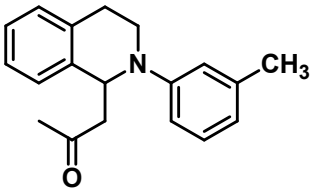


1-(2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one: Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 10/1 as eluent). Colourless oil, 27.1 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.08 (m, 4H), 6.91 (ddd, *J* = 13.9, 9.2, 3.6 Hz, 4H), 5.28 (t, *J* = 6.3 Hz, 1H), 3.65 – 3.53 (m, 1H), 3.54 – 3.42 (m, 1H), 3.01 (dt, *J* = 15.4, 6.3 Hz, 2H), 2.87 – 2.68 (m, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.16, 156.11 (d, J^F = 236.0 Hz), 145.75, 138.02, 134.20, 128.86, 126.55 (d, J^F = 48.0 Hz), 117.11 (d, J^F = 7.0 Hz), 115.66 (d, J^F = 22.0 Hz), 55.55, 50.10, 42.65, 31.00, 26.72.

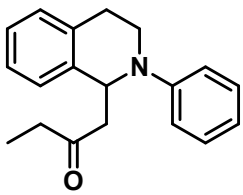


1-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one: Purified by flash column chromatography (silica gel, petroleum

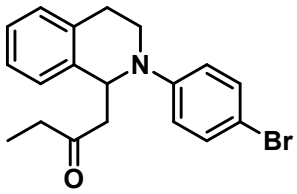
ether/EtOAc = 10/1 as eluent). Colourless oil, 25.9 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.04 (m, 4H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.24 (t, *J* = 6.3 Hz, 1H), 3.74 (s, 3H), 3.61 – 3.51 (m, 1H), 3.51 – 3.39 (m, 1H), 3.00 (ddd, *J* = 15.9, 11.0, 4.9 Hz, 2H), 2.74 (ddd, *J* = 13.2, 11.6, 5.0 Hz, 2H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.37, 153.26, 143.66, 138.24, 134.29, 128.91, 126.78, 126.60, 126.15, 118.37, 114.60, 55.94, 55.57, 49.94, 42.84, 30.85, 26.71.



1-(2-m-tolyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one: Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 10/1 as eluent). Colourless oil, 23.7 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.09 (m, 5H), 6.74 (d, *J* = 7.8 Hz, 2H), 6.61 (d, *J* = 7.4 Hz, 1H), 5.39 (t, *J* = 6.3 Hz, 1H), 3.71 – 3.58 (m, 1H), 3.58 – 3.44 (m, 1H), 3.12 – 2.97 (m, 2H), 2.81 (dd, *J* = 16.1, 6.2 Hz, 2H), 2.31 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.31, 148.95, 139.02, 138.33, 134.46, 129.17, 128.66, 126.87, 126.75, 126.23, 119.23, 115.62, 111.98, 54.83, 50.20, 42.04, 31.09, 27.23, 21.89.

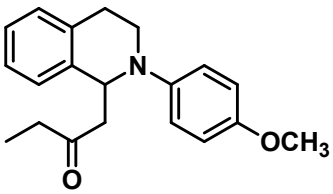


1-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one: Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 10/1 as eluent). White solid, 22.3 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 2H), 7.16 (d, *J* = 12.3 Hz, 4H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 5.42 (t, *J* = 6.3 Hz, 1H), 3.69 – 3.60 (m, 1H), 3.59 – 3.45 (m, 1H), 3.05 (ddd, *J* = 15.9, 10.9, 5.7 Hz, 2H), 2.81 (ddd, *J* = 23.1, 12.8, 5.9 Hz, 2H), 2.45 – 2.16 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.93, 148.83, 138.35, 134.42, 129.31, 128.61, 126.84, 126.75, 126.21, 118.09, 114.56, 55.06, 48.93, 41.91, 37.24, 27.25, 7.48.



1-(2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one: Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 10/1 as eluent). Pale yellow oil, 28.6 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 9.0 Hz, 2H), 7.21 – 7.06 (m, 4H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.35 (t, *J* = 6.3 Hz, 1H), 3.54 (tdd, *J* = 12.8, 10.5, 5.1 Hz, 2H), 3.15 – 2.94

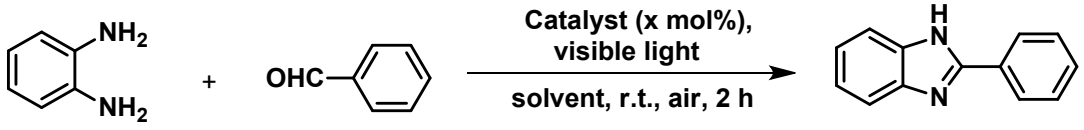
(m, 2H), 2.92 – 2.72 (m, 2H), 2.51 – 2.19 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.69, 147.77, 137.95, 134.18, 131.99, 128.63, 126.93, 126.78, 126.36, 115.95, 109.93, 54.93, 48.84, 41.99, 37.29, 27.06, 7.47.



1-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one: Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 10/1 as eluent). Pale yellow oil, 26.4 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.05 (m, 4H), 6.91 (d, J = 9.1 Hz, 2H), 6.81 (d, J = 9.1 Hz, 2H), 5.27 (t, J = 6.3 Hz, 1H), 3.74 (s, 3H), 3.60 – 3.50 (m, 1H), 3.50 – 3.41 (m, 1H), 3.09 – 2.92 (m, 2H), 2.73 (ddd, J = 15.8, 10.7, 5.2 Hz, 2H), 2.41 – 2.19 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.01, 153.11, 143.64, 138.38, 134.28, 128.87, 126.81, 126.57, 126.11, 118.07, 114.62, 56.15, 55.60, 48.68, 42.63, 37.03, 26.83, 7.51.

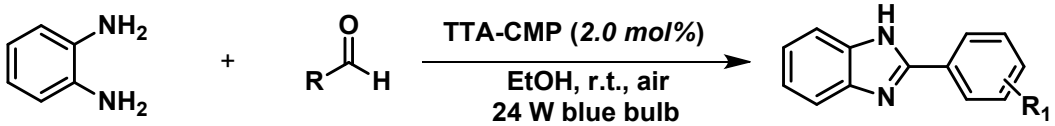
7. Typical Procedure for Photocatalytic Synthesis of 2-substituted Benzimidazoles[6]

Table S2. Optimization of the reaction conditions[a]

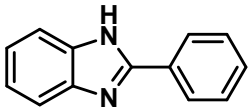


Entry	Catalyst	x	Solvent	Light source	Yield[b]
1	**TTA-CMP**	1.0	EtOH	24 W bule bulb	68
2	**TTA-CMP**	2.0	EtOH	24 W bule bulb	98
3	**TTA-CMP**	3.0	EtOH	24 W bule bulb	95
4	**TTA-CMP**	2.0	THF	24 W bule bulb	Trace
5	**TTA-CMP**	2.0	DMF	24 W bule bulb	Trace
6	**TTA-CMP**	2.0	Acetone	24 W bule bulb	Trace
7	**TTA-CMP**	2.0	Toluene	24 W bule bulb	70
8	**TTA-CMP**	2.0	CH_3CN	24 W bule bulb	25
9	**TTA-CMP**	2.0	H_2O	24 W bule bulb	35
10	**TTA-CMP**	2.0	MeOH	24 W bule bulb	93
11	**TTA-CMP**	2.0	EtOH/H_2O	24 W bule bulb	62
12	**TTA-CMP**	2.0	EtOH	24 W fluorescent bulb	92
13	**TTA-CMP**	2.0	EtOH	Natural light	38
14[c]	**TTA-CMP**	2.0	EtOH	dark	Trace
15[d]	**None**	----	EtOH	24 W bule bulb	28
16[e]	**CMP-1**	2.0	EtOH	24 W bule bulb	Trace
17[f]	**FBB-TTA**	2.0	EtOH	24 W bule bulb	72
18[g]	**TTA-CMP**	2.0	EtOH	24 W bule bulb	Trace

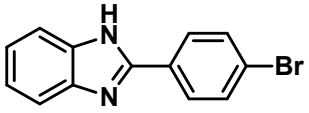
[a] Reaction condition (unless otherwise noted): 1,2-phenylenediamine (0.25 mmol), benzaldehyde (0.25 mmol), solvent (3.0 mL), irradiation with 24 W bule bulb, room temperature, 2 h, in air. [b] The isolated yield after silica gel column chromatography. [c] Reaction carried out in absence of visible-light (dark). [d] Reaction carried out without any catalyst. [e] non-photoactive CMP-1[3] as the heterogeneous catalyst. [f] The homogeneous catalyst (2.0 mol%) was applied as a reference. [g] The reaction was carried out under N_2 (without O_2).



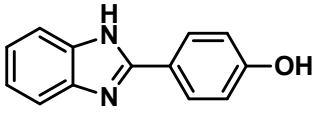
To a stirred solution of TTA-CMP catalyst (5.8 mg, 2.0 mol%) in ethanol (3.0 mL) in 10 mL glass tube, aldehyde (0.25 mmol, 1 equiv) and *o*-Phenylenediamine (0.25 mmol, 1 equiv) were added and the mixture was stirred at room temperature under irradiation with visible light using a cool blue bulb (24 W) until all starting substrates had been consumed. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was centrifugated and the solid catalyst was washed with EtOH (4 x 5.0 mL). The combined organic phase was evaporated at reduced pressure and the residue was purified by flash column chromatography using silica gel with petroleum ether/ethanol or petroleum ether/ethanol mixture as eluent to give the desired product as white solid.



2-phenyl-1H-benzo[d]imidazole: Prepared according to the general procedure with *o*-Phenylenediamine and benzaldehyde. The product was collected as white solid in 98% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.91 (s, 1H), 8.19 (d, J = 7.1 Hz, 2H), 7.78 – 7.34 (m, 5H), 7.21 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.69, 144.30, 135.48, 130.65, 130.30, 129.72, 129.42, 126.90, 122.99, 122.13, 119.35, 111.79.

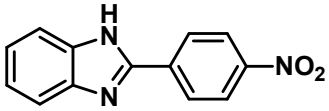


2-(4-bromophenyl)-1H-benzo[d]imidazole: Prepared according to the general procedure with *o*-Phenylenediamine and 4-bromobenzaldehyde. The product was collected as white solid in 98% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.00 (s, 1H), 8.12 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.71 – 7.49 (m, 2H), 7.22 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.69, 144.22, 135.49, 132.46, 129.88, 128.83, 123.72, 123.27, 122.32, 119.44, 111.91.

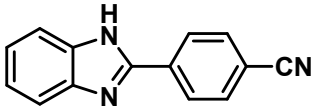


4-(1H-benzo[d]imidazol-2-yl)phenol: Prepared according to the general procedure with *o*-Phenylenediamine and 4-hydroxybenzaldehyde. The product was collected as white solid in 90% yield after silica gel chromatography (petroleum ether/ethanol = 6:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.63 (s, 1H), 9.95 (s, 1H), 8.01 (d, J = 8.6 Hz, 2H), 7.53 (s, 2H), 7.15 (dd, J = 5.9, 3.1 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz,

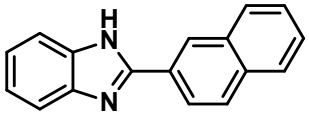
DMSO-d_6) δ 191.42, 163.83, 159.58, 152.24, 132.64, 128.61, 122.05, 121.63, 116.32, 116.14, 111.35.



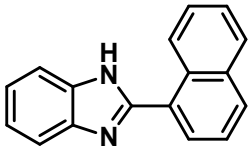
2-(4-nitrophenyl)-1H-benzo[d]imidazole: Prepared according to the general procedure with *o*-Phenylenediamine and 4-nitrobenzaldehyde. The product was collected as white solid in 83% yield after silica gel chromatography (petroleum ether/ethanol = 6:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.30 (s, 1H), 8.43 (s, 4H), 7.67 (d, J = 50.6 Hz, 2H), 7.28 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.69, 149.48, 148.28, 144.32, 136.52, 135.72, 127.86, 124.77, 124.06, 122.78, 121.50, 119.93, 112.28.



4-(1H-benzo[d]imidazol-2-yl)benzonitrile: Prepared according to the general procedure with *o*-Phenylenediamine and 4-formylbenzonitrile. The product was collected as white solid in 88% yield after silica gel chromatography (petroleum ether/ethanol = 6:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.18 (s, 1H), 8.34 (d, J = 8.3 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H), 7.65 (dd, J = 55.7, 7.3 Hz, 2H), 7.45 – 7.05 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.84, 144.23, 135.59, 134.75, 133.45, 127.45, 123.89, 122.68, 119.84, 119.10, 112.36, 112.19.

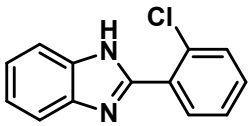


2-(naphthalen-2-yl)-1H-benzo[d]imidazole: Prepared according to the general procedure with *o*-Phenylenediamine and 2-naphthaldehyde. The product was collected as white solid in 94% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.08 (s, 1H), 8.75 (s, 1H), 8.40 – 8.18 (m, 1H), 8.04 (ddd, J = 23.1, 11.3, 6.2 Hz, 3H), 7.83 – 7.50 (m, 4H), 7.23 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.72, 144.41, 135.63, 133.94, 133.29, 129.02, 128.92, 128.27, 128.10, 127.58, 127.39, 126.29, 124.42, 123.14, 122.23, 119.38, 111.84.

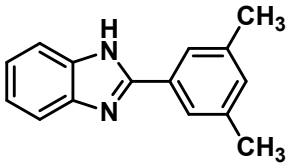


2-(naphthalen-1-yl)-1H-benzo[d]imidazole: Prepared according to the general procedure with *o*-Phenylenediamine and 1-naphthaldehyde. The product was collected as white solid in 98% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.95 (s, 1H),

9.12 (d, J = 8.2 Hz, 1H), 8.24 – 7.91 (m, 3H), 7.90 – 7.51 (m, 5H), 7.26 (d, J = 4.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.84, 144.38, 134.93, 134.10, 130.98, 130.62, 128.86, 128.34, 128.00, 127.54, 126.82, 125.75, 125.38, 123.11, 122.08, 119.56, 111.83.



2-(2-chlorophenyl)-1H-benzo[d]imidazole: Prepared according to the general procedure with *o*-Phenylenediamine and 2-chlorobenzaldehyde. The product was collected as white solid in 87% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.72 (s, 1H), 7.91 (dd, J = 7.2, 2.1 Hz, 1H), 7.76 – 7.43 (m, 5H), 7.24 (d, J = 3.9 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.56, 144.09, 135.16, 132.56, 132.11, 131.67, 130.82, 130.46, 127.91, 123.20, 122.15, 119.56, 112.17.



2-(3,5-dimethylphenyl)-1H-benzo[d]imidazole: Prepared according to the general procedure with *o*-Phenylenediamine and 3,5-dimethylbenzaldehyde. The product was collected as white solid in 91% yield after silica gel chromatography (petroleum ether/ethanol = 10:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.82 (s, 1H), 7.81 (s, 2H), 7.70 – 7.45 (m, 2H), 7.18 (dd, J = 23.8, 19.5 Hz, 3H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.90, 144.28, 138.46, 138.18, 135.43, 131.70, 130.51, 127.46, 124.70, 122.79, 122.06, 119.21, 111.71, 21.43.

8. Scale-up Experiment for the Photocatalytic Synthesis of 2-substituted

Benzimidazoles

o-Phenylenediamine (6.0 mmol, 648.0 mg, 1.0 equiv), benzaldehyde (6.0 mmol, 636.7 mg, 1.0 equiv) , TTA-CMP (139 mg, 2.0 mol%) and EtOH (80 mL) were added into a reaction round-bottom flask. The reaction mixture was opened to air and stirred at room temperature under 24 W blue bulb. After the reaction was completed (ca. 6 hours, monitored by TLC), the heterogeneous catalyst could be isolated through filtration and thoroughly washed by EtOH (10 mL × 3) and acetone (10 mL × 3). Collected the light brown mother liquid and removed the organic solvent under reduced pressure. The resulted crude product was further washed with a small amount of cold petroleum ether /EtOH (v/v, 10/1), and then dried under vacuum for 12 h at 80 °C to give pure **8a** as off-white solid (1.11 g, 95% yield).

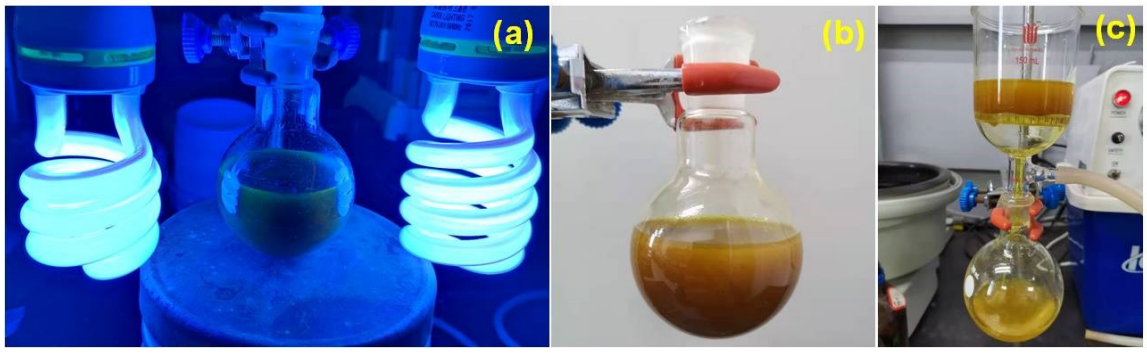


Figure S7. Scale-up experiment of **3a** with TTA-CMP as photocatalyst. (a) Photocatalytic reaction equipment; (b) The completed reaction system that contain product **8a** and TTA-CMP catalyst; (c) Separation of **8a** and recovery of TTA-CMP through filtration.

9. The geometries of the reactants and product

The geometries of reactants and product were fully optimized with the Gaussian 09 package [7] at B3LYP/6-31G(d) level in combination with frequency calculations. Then, using Monte-Carlo method embedded in Gaussian 09, the Volume=Tight keyword was employed to carry out single-point calculations at the same basis set level to obtain molecular volumes based on 0.001 e/bohr^3 density envelope, with the IOp (6/45=2000) keyword to define the number of points per bohr^3 as 2000. In the structural optimizations and volume calculations, the solvent effect was evaluated with the polarizable continuum model (PCM) to simulate the ethanol environments. Our theoretical results predicted the molecular volumes of 1,2-phenylenediamine, benzaldehyde and 2-phenyl-benzimidazole to be 144.89, 138.94 and 239.43 Å^3, respectively. Considering the optimized structures, molecular volumes and electron dispersions, the three dimensional sizes of1,2-phenylenediamine, benzaldehyde and 2-phenyl-benzimidazole were estimated to be 7.8 Å × 7.4 Å × 2.5 Å, 8.5 Å × 6.7 Å × 2.4 Å, and 13.3 Å × 7.4 Å × 2.4 Å, as depicted in Figure S2.

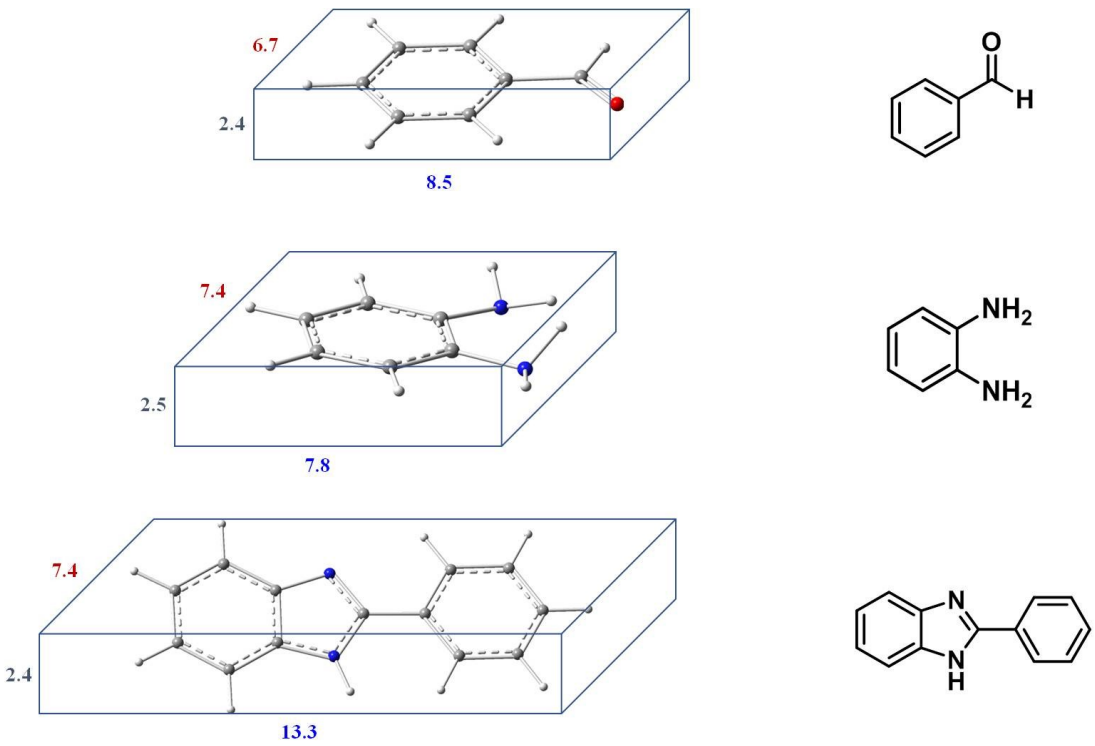
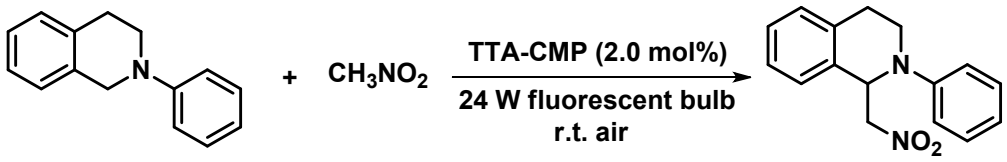


Figure S8. The geometries of the reactants and products

10. Recyclability Tests of TTA-CMP

The recycling experiments were performed by recovering the **TTA-CMP** catalyst using the centrifugation method. The recovered **TTA-CMP** catalyst was washed with EtOAc or EtOH to remove the residual product and simply dried before resuse. We chose the dehydrogenative coupling reaction of 2-phenyl-1,2,3,4-tetrahydroisoquinoline and nitromethane, the dehydrogenative-Mannich reaction of 2-phenyl-1,2,3,4-tetrahydroisoquinoline and acetone, the photocatalytic synthesis of 2-phenyl-1H-benzo[d]imidazole with *o*-Phenylenediamine and benzaldehyde to investigate the recyclability of **TTA-CMP** catalyst, and the results are summarized in **Table S3, Table S4, Table S5.**

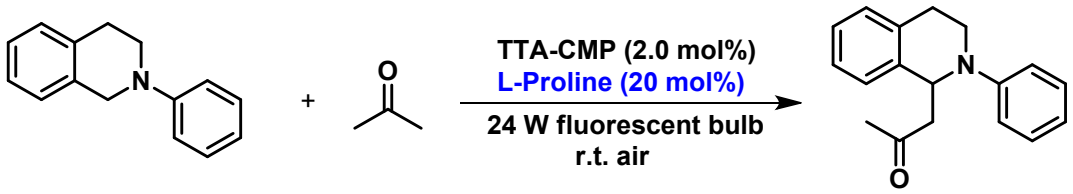
Table S3. Recycling of **TTA-CMP** catalyst for the dehydrogenative coupling reaction. [a]



Cycle	Time (h)	Yield (%) [b]	Cycle	Time (h)	Yield (%) [b]
1	5	96	7	8	94
2	5	95	8	12	94
3	6	95	9	12	94
4	6	95	10	12	92
5	8	95			
6	8	94			

[a] General condition: 2-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol), nitromethane (1.0 mL), and **TTA-CMP** (4.7 mg, 2.0 mol%), r.t., 24 W household bulb, in air. [b] Isolated yield after silica gel column chromatography.

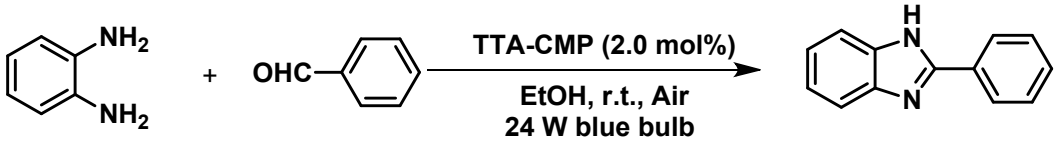
Table S4. Recycling of **TTA-CMP** catalyst for the dehydrogenative-Mannich reaction. [a]



Cycle	Time (h)	Yield (%) [b]	Cycle	Time (h)	Yield (%) [b]
1	5	94	7	8	90
2	5	94	8	12	90
3	5	92	9	12	90
4	8	92	10	12	89
5	8	92			
6	8	92			

[a] General condition: 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol), acetone (1.0 mL), and **TTA-CMP** (2.4 mg, 2.0 mol%), L-proline (2.3 mg, 20 mol%) r.t., 24 W household bulb, in air. [b] Isolated yield after silica gel column chromatography.

Table S5. Recycling of **TTA-CMP** catalyst for the the photocatalytic synthesis of 2-phenyl-1H-benzo[d]imidazole. [a]



Cycle	Time (h)	Yield (%) [b]	Cycle	Time (h)	Yield (%) [b]
1	2	98	7	7	96
2	2	98	8	7	97
3	3	98	9	8	95
4	3	98	10	8	93
5	5	96	11	12	93
6	5	96	12	12	92

[a] General condition: *o*-Phenylenediamine (27.0 mg, 0.25 mmol), benzaldehyde (26.5 mg, 0.25 mmol), and **TTA-CMP** (5.8 mg, 2.0 mol%), r.t., 24 W bule bulb, EtOH (3.0 mL), in air . [b] Isolated yield after silica gel column chromatography.

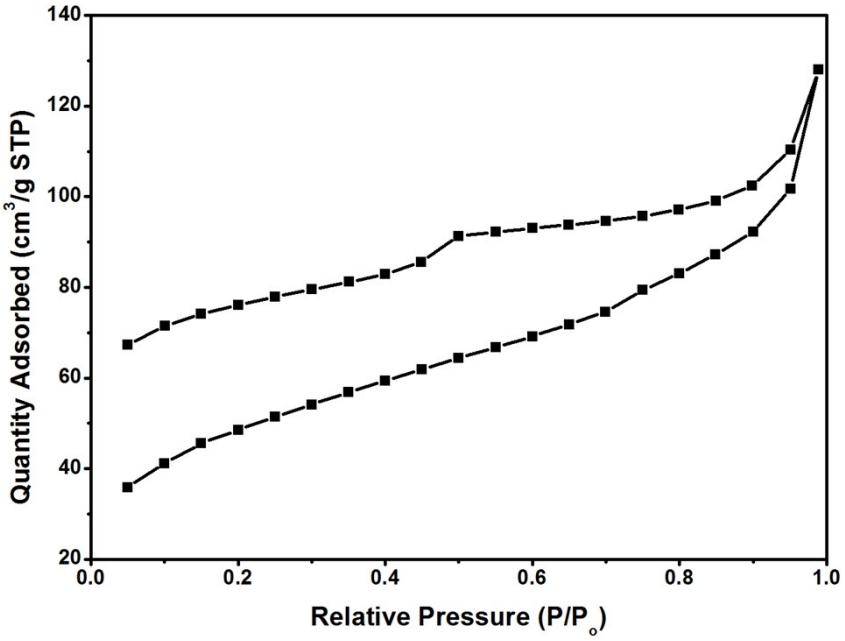


Figure S9. N_2 adsorption-desorption isotherms of the recycled TTA-CMP after the 10th run. The BET surface area of TTA-CMP decreased to 159 m^2g^{-1} after the 10th recycled used. We believe that the substrates or the products have blocked the partial micropores of TTA-CMP lead to the decrease in BET surface area.

As shown in Table S5, the TTA-CMP could even remain a good catalytic activity after 12^{th} run, though the reaction rate tended to be slow with the increase of recycling time. In combination with the nitrogen desorption tests (Figure S9) of the recycled catalyst, a clear finding here was that the BET surface areas of porous organic polymers were crucial for excellent catalytic effects.

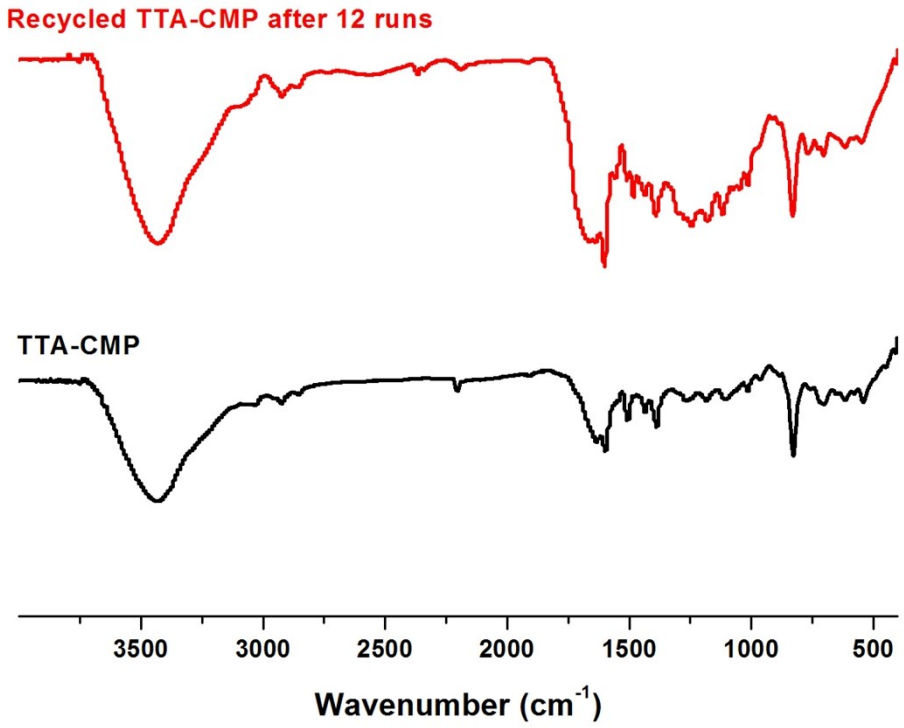


Figure S10. FT-IR spectra of fresh and recycled TTA-CMP.

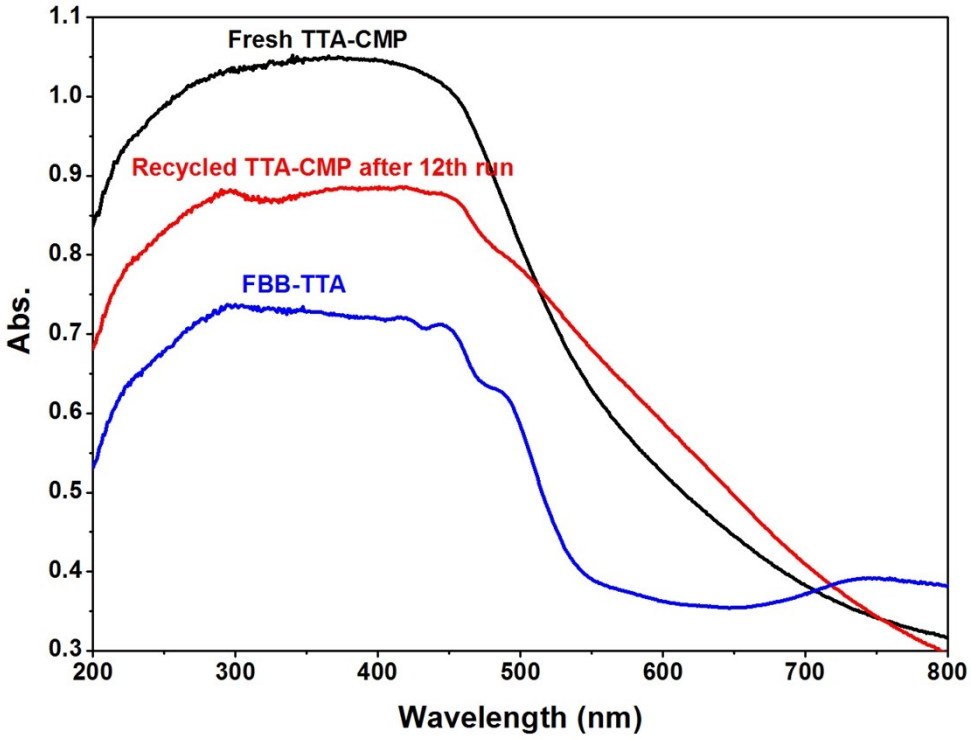


Figure S11. UV/vis adsorption spectra of recycled TTA-CMP after 12 times run (red).

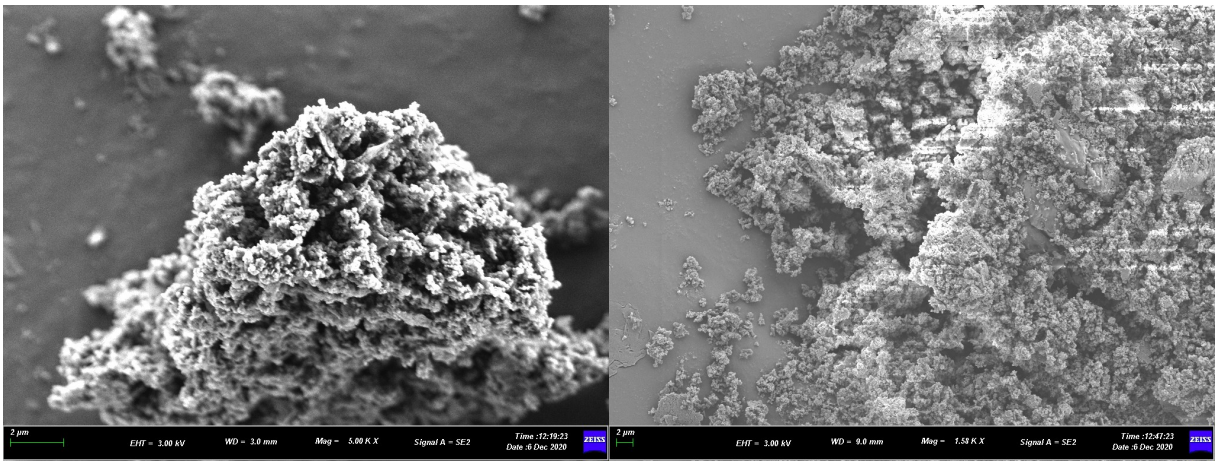


Figure S12. TEM images of TTA-CMP after the 12th run of catalysis. The unchanged SEM images indicated that TTA-CMP is stable after photocatalytic cycles.

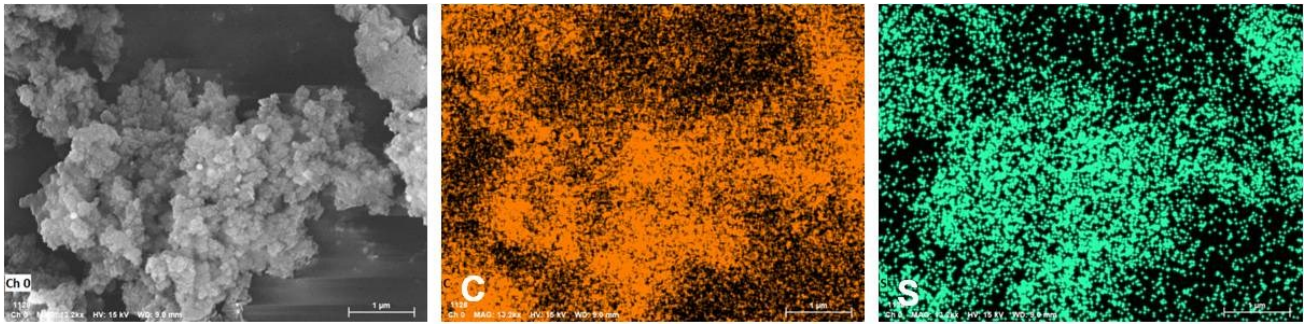


Figure S13. EDX elemental mapping of TTA-CMP after the 12th run of catalysis. The EDX elemental mapping showed that the elements C and S were also well-dispersed in the TTA-CMP frameworks after the 12th of catalysis, which indicated that TTA-CMP is stable after photocatalytic cycles.

11. Study for the Reaction Mechanism

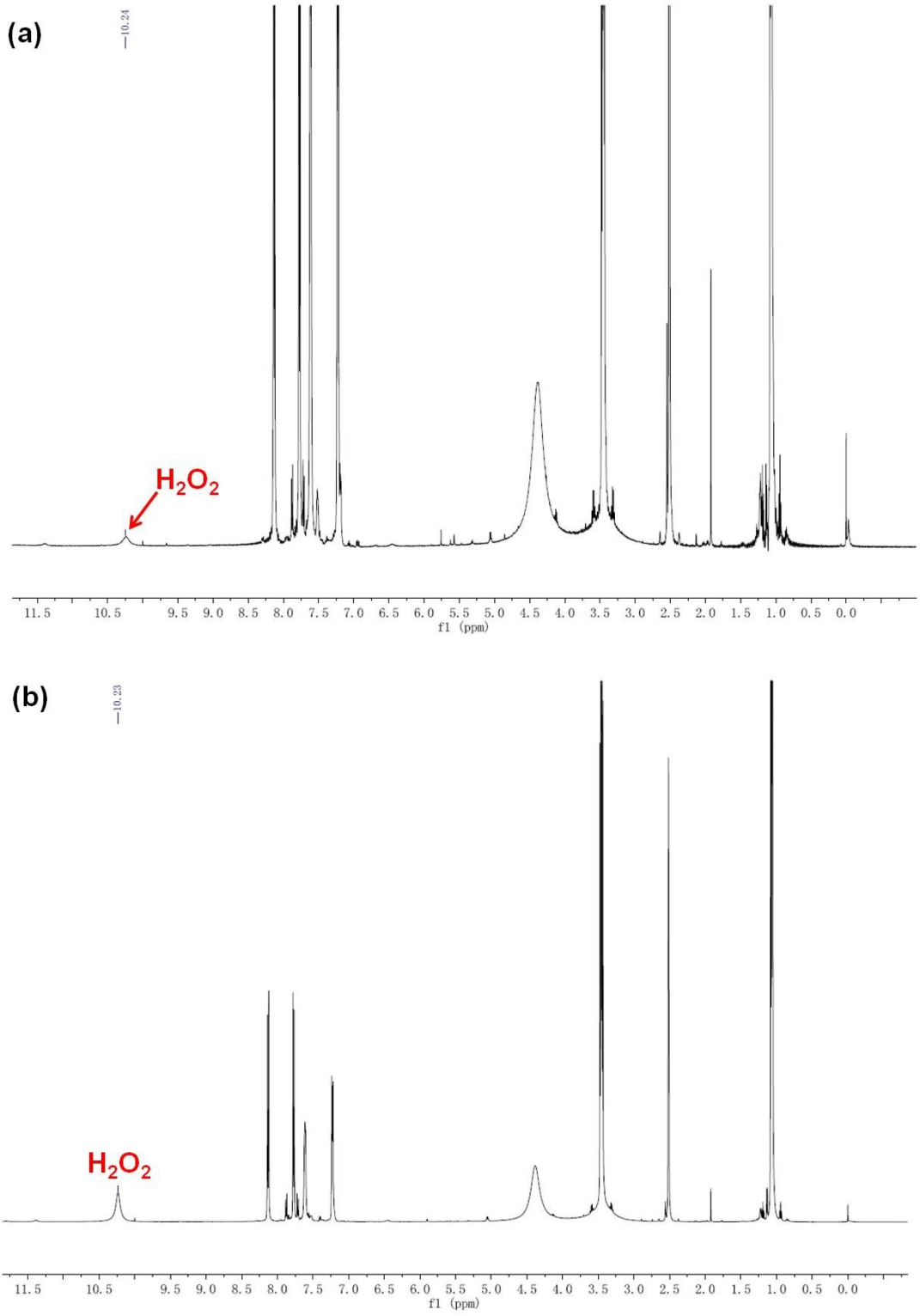


Figure S14. Detection of H_2O_2 via ^1H NMR (*DMSO-d_6*) spectra: (a) photocatalytic system (6+7b); (b) 30% H_2O_2 solution and photocatalytic system (6+7b)

12. References

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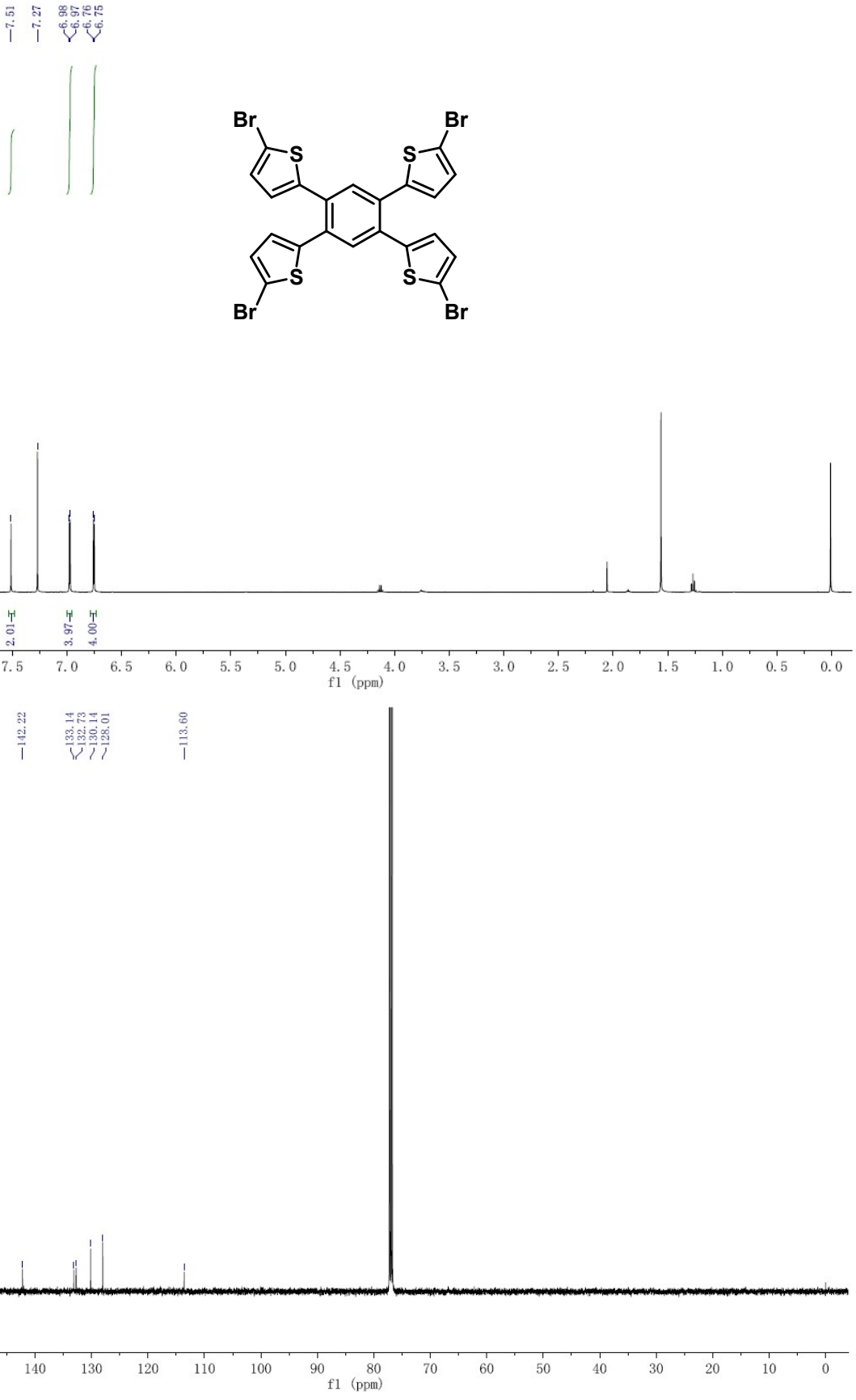
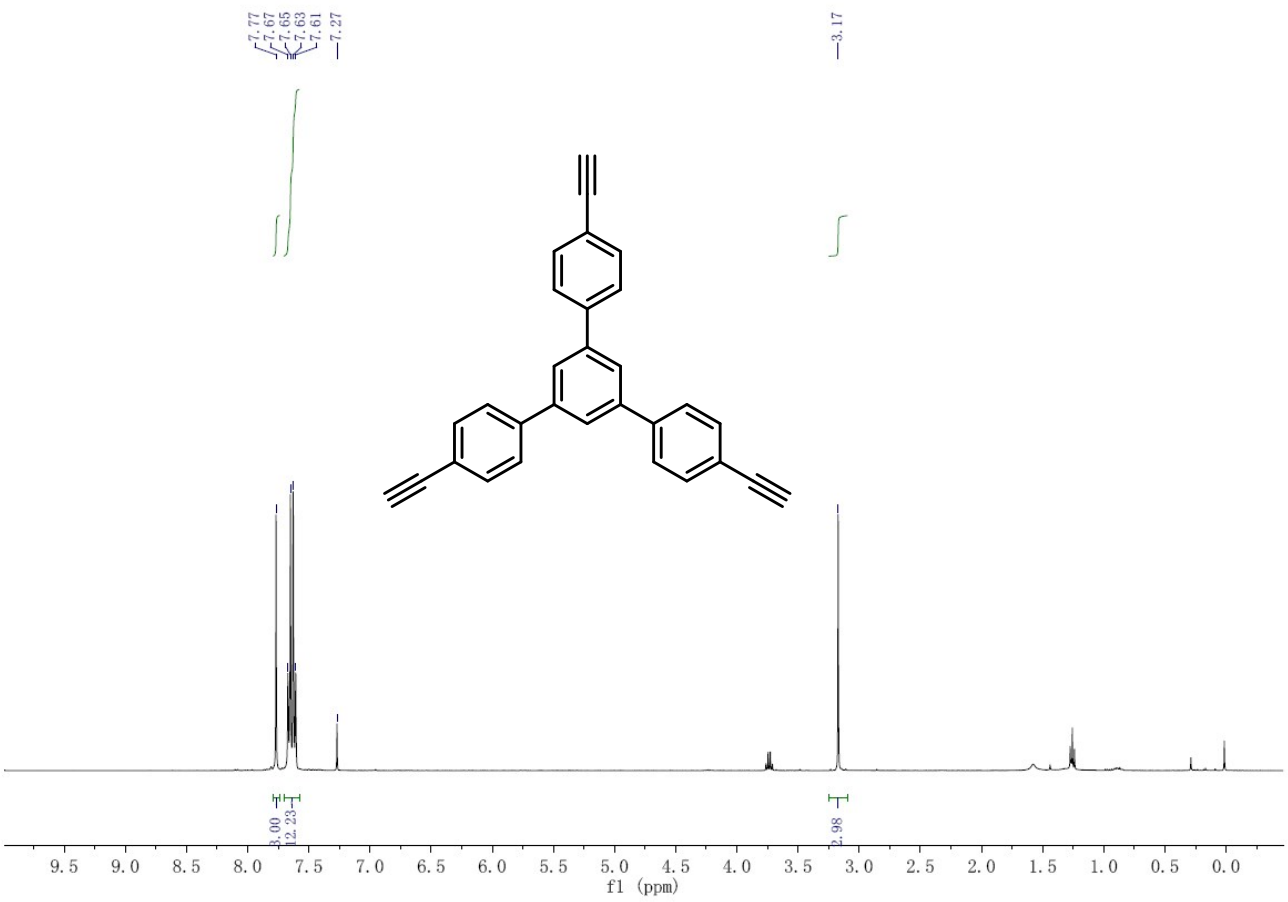
7. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox. Gaussian 09, Revision C.01, Gaussian Inc., Wallingford CT, **2010**.

13. ^{1}H NMR and ^{13}C NMR spectra for the products

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12.23
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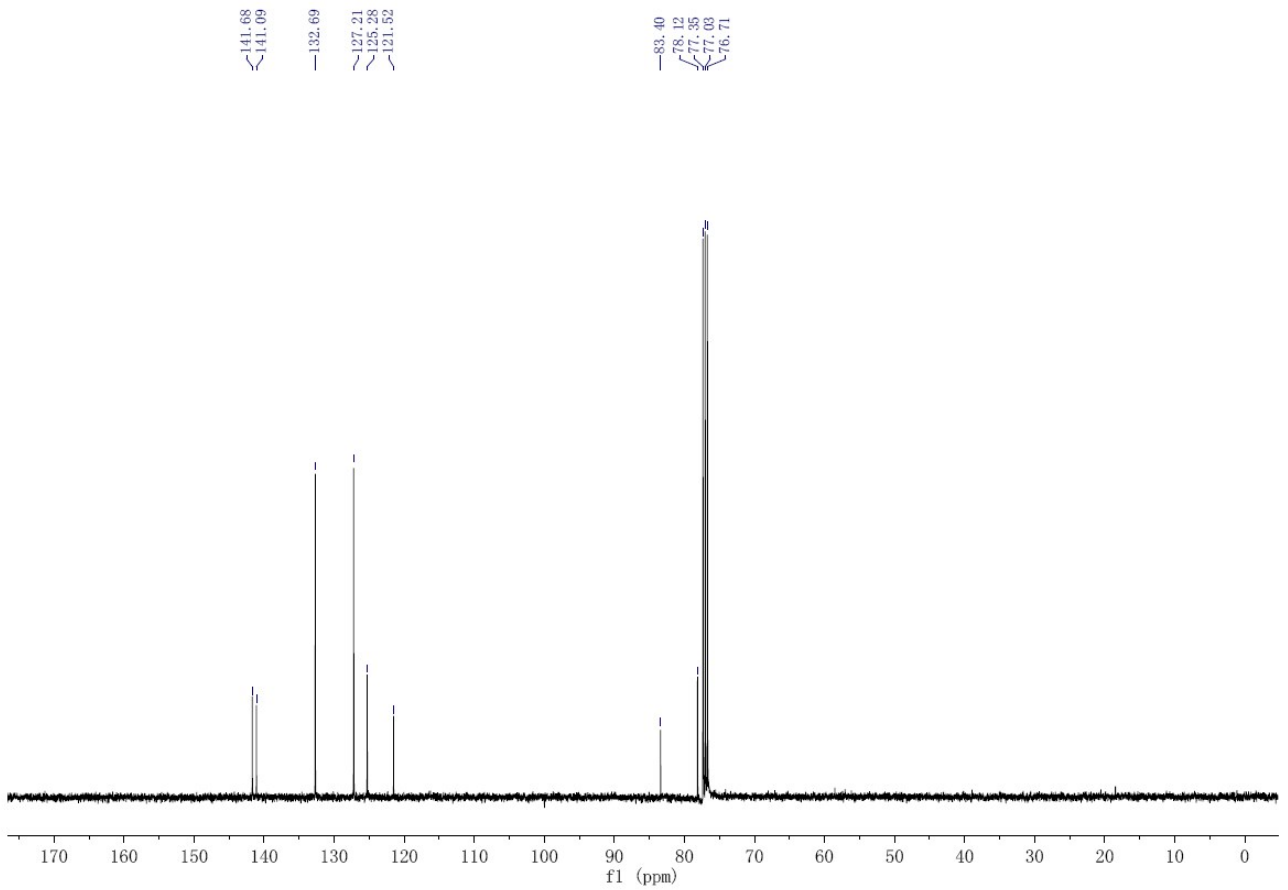
f1 (ppm)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77.03
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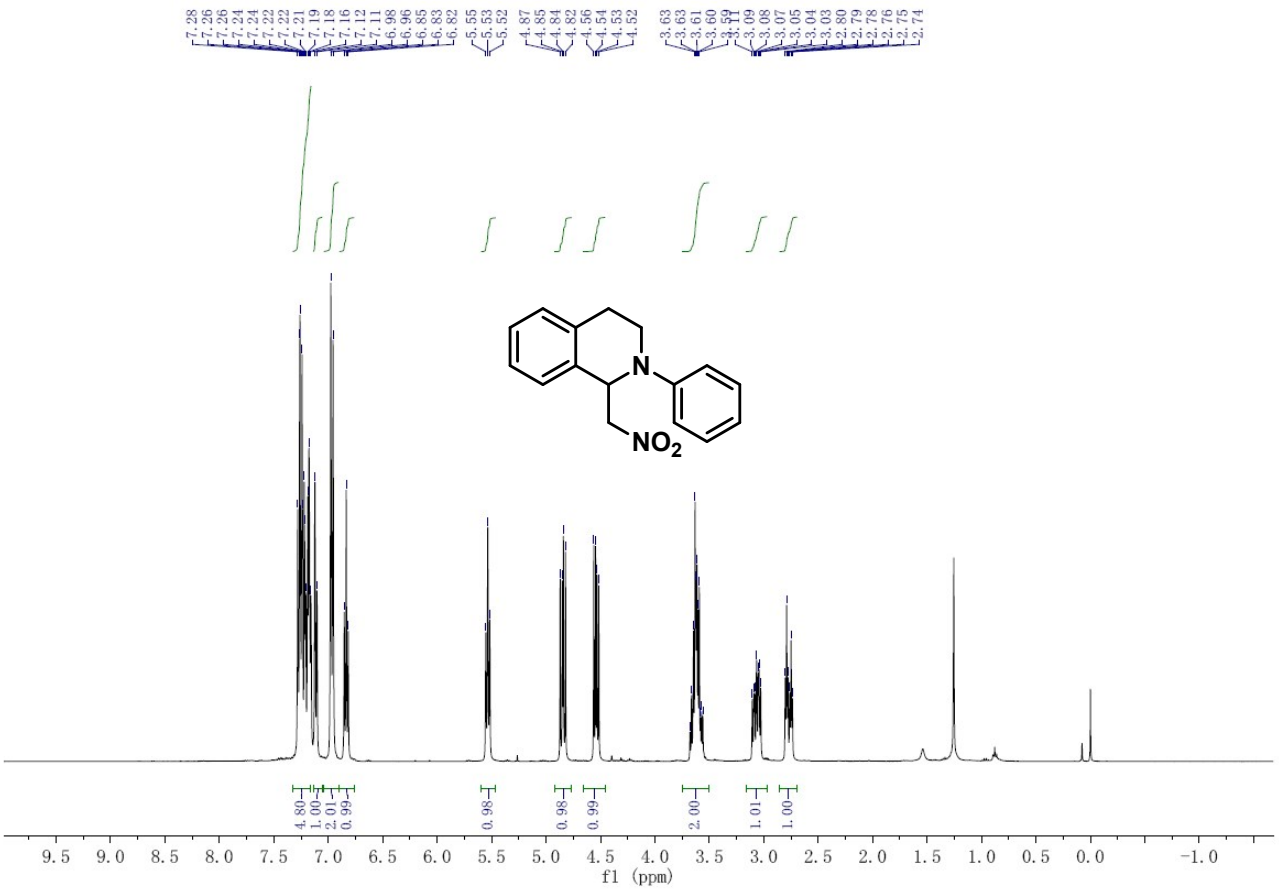
f1 (ppm)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7.11
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6.85
6.83
6.82
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5.53
5.52
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4.85
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4.82
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4.54
4.53
4.52
3.63
3.63
3.61
3.60
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3.09
3.08
3.07
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3.04
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2.79
2.78
2.76
2.75
2.74
N
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0.98
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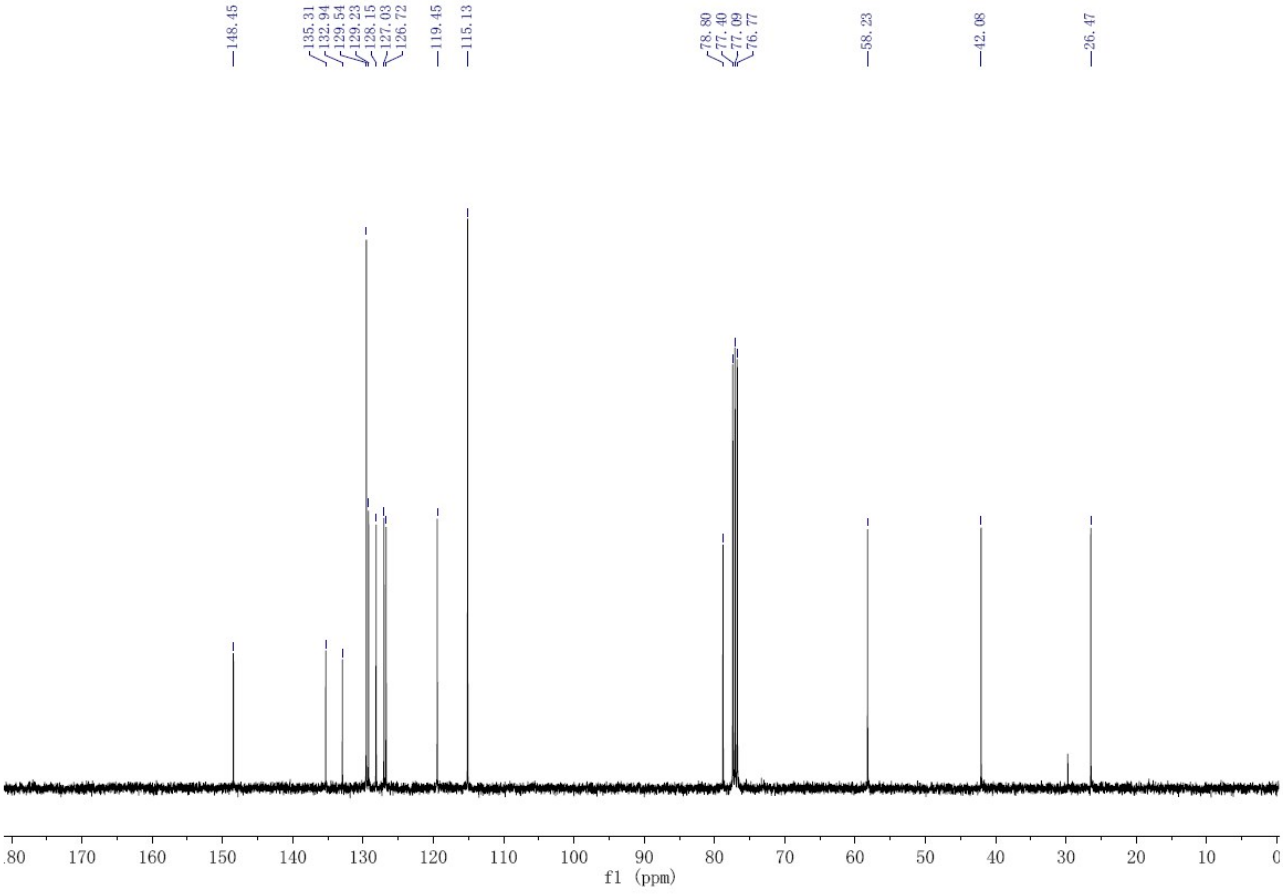
1.00
f1 (ppm)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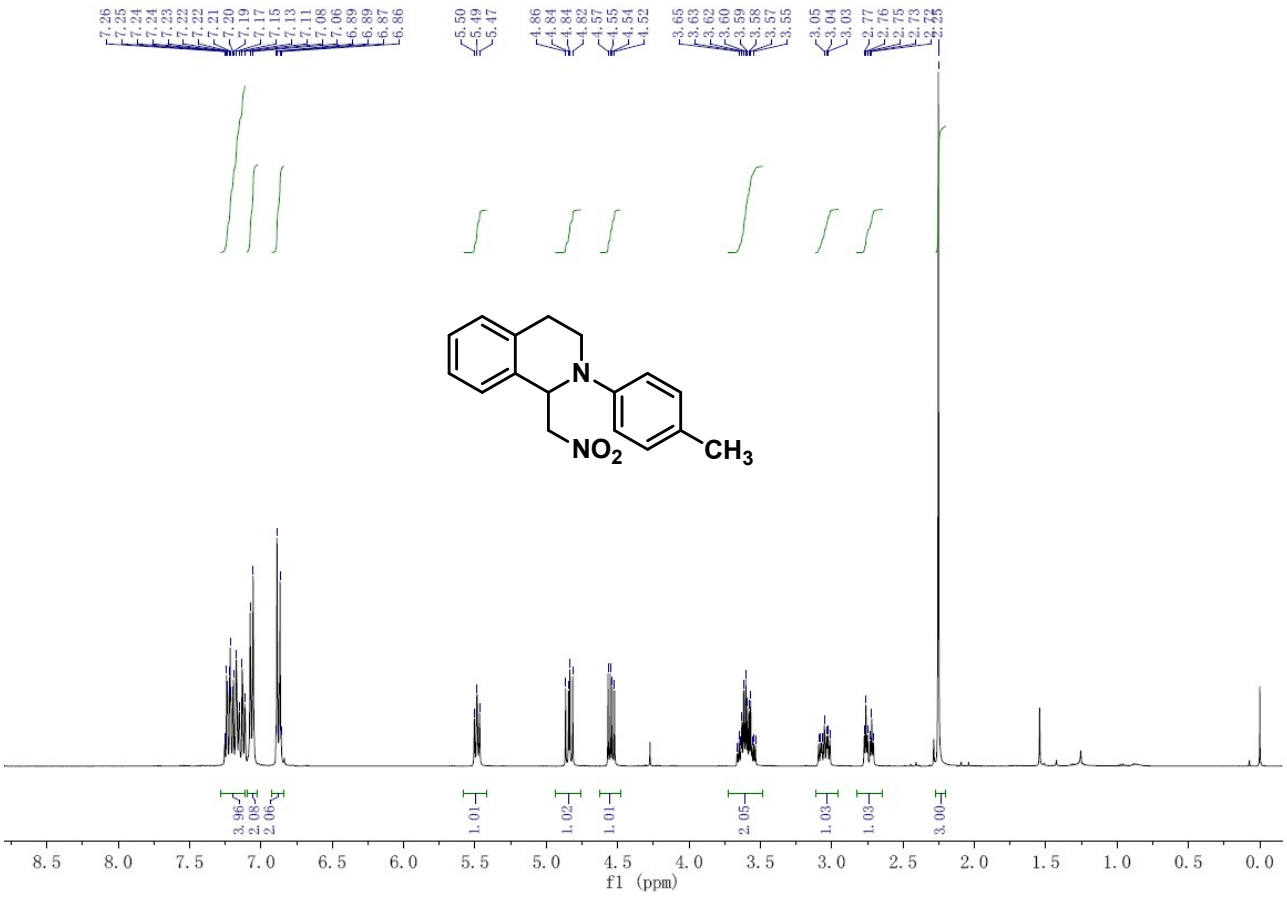
26.47
f1 (ppm)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6.87
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5.49
5.47
4.86
4.84
4.84
4.82
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4.55
4.54
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3.63
3.62
3.60
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3.04
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CH3
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1.02
1.01
2.05
1.03
1.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
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2.5
2.0
1.5
1.0
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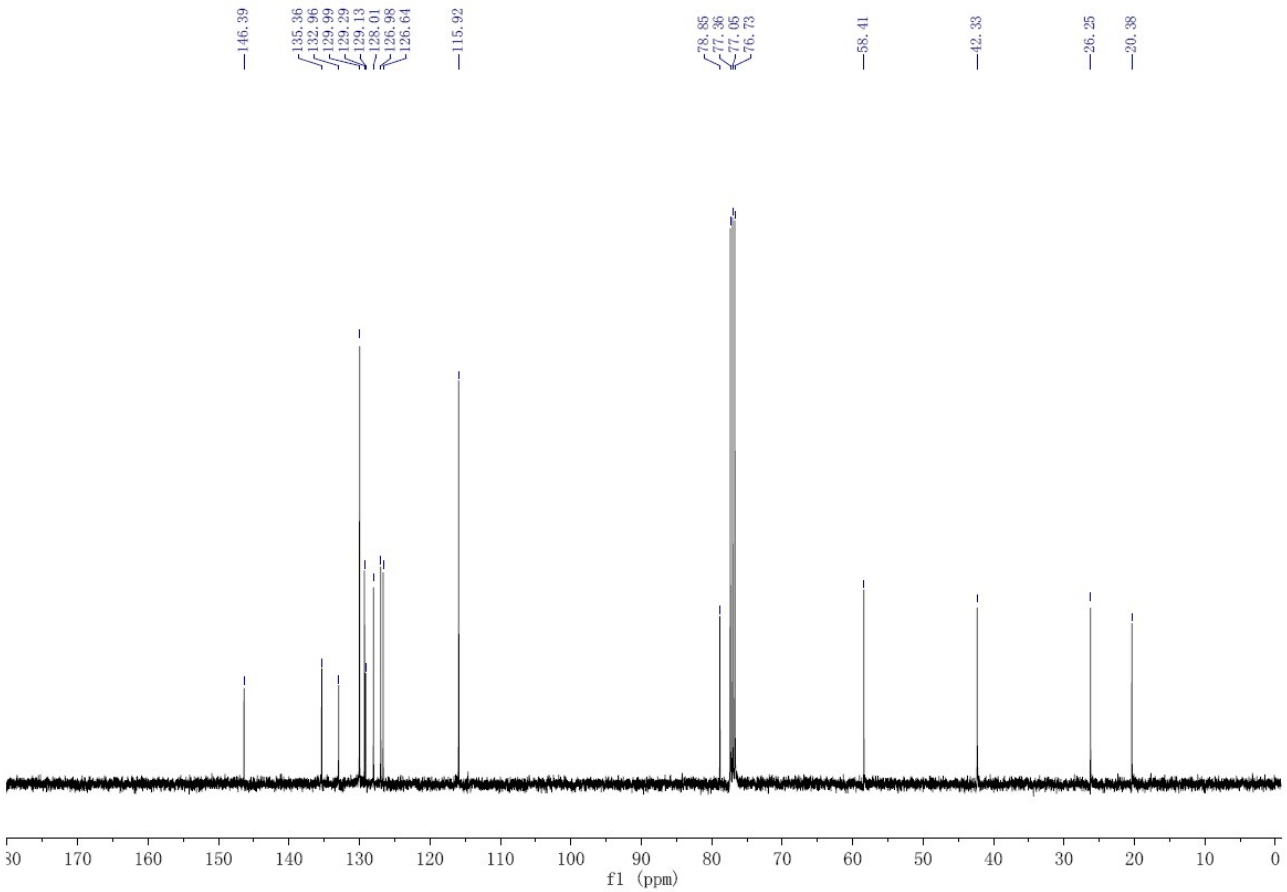
0.0
f1 (ppm)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76.73
58.41
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26.25
20.38
30
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130
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50
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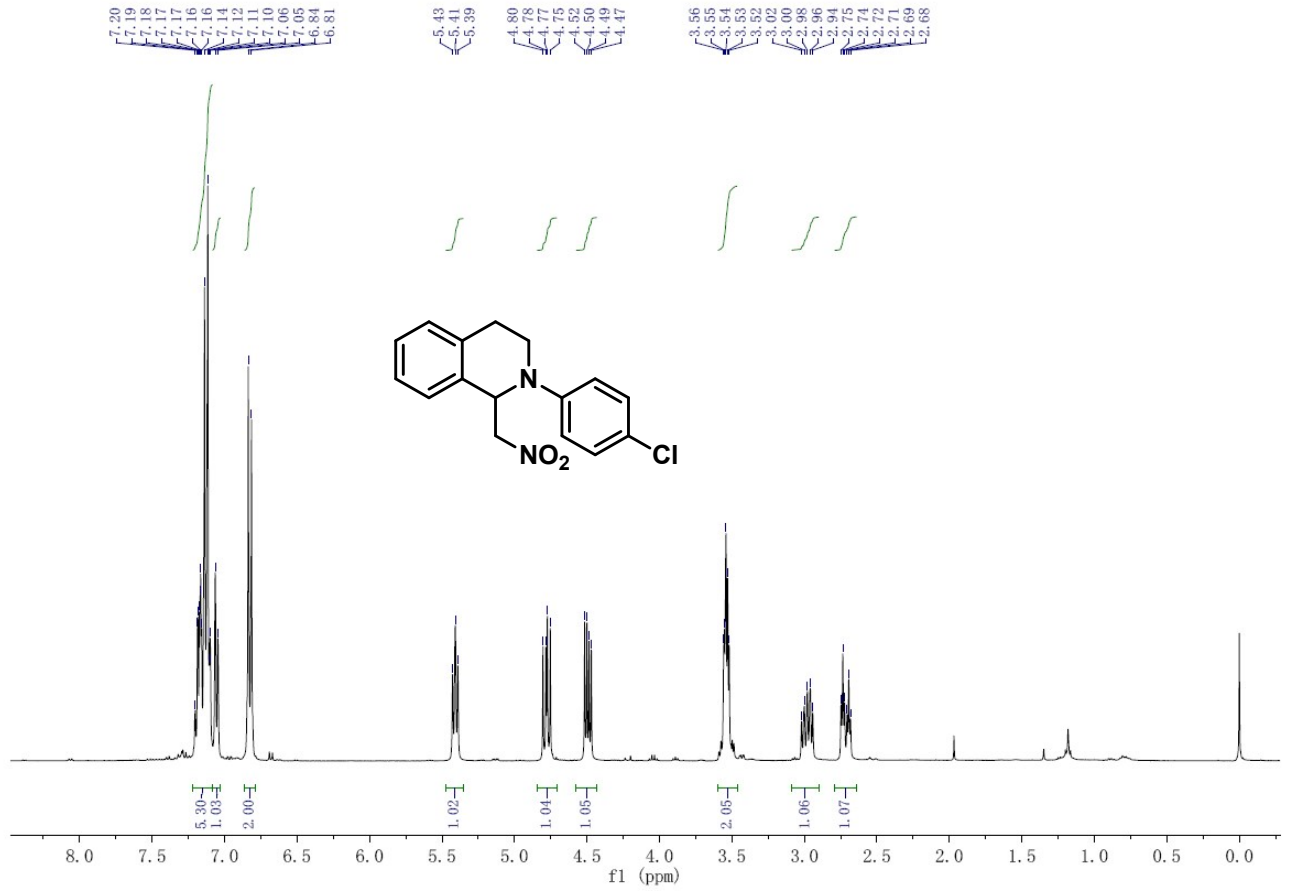
f1 (ppm)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5.39
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4.77
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2.68
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Cl
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1.05
2.05
1.06
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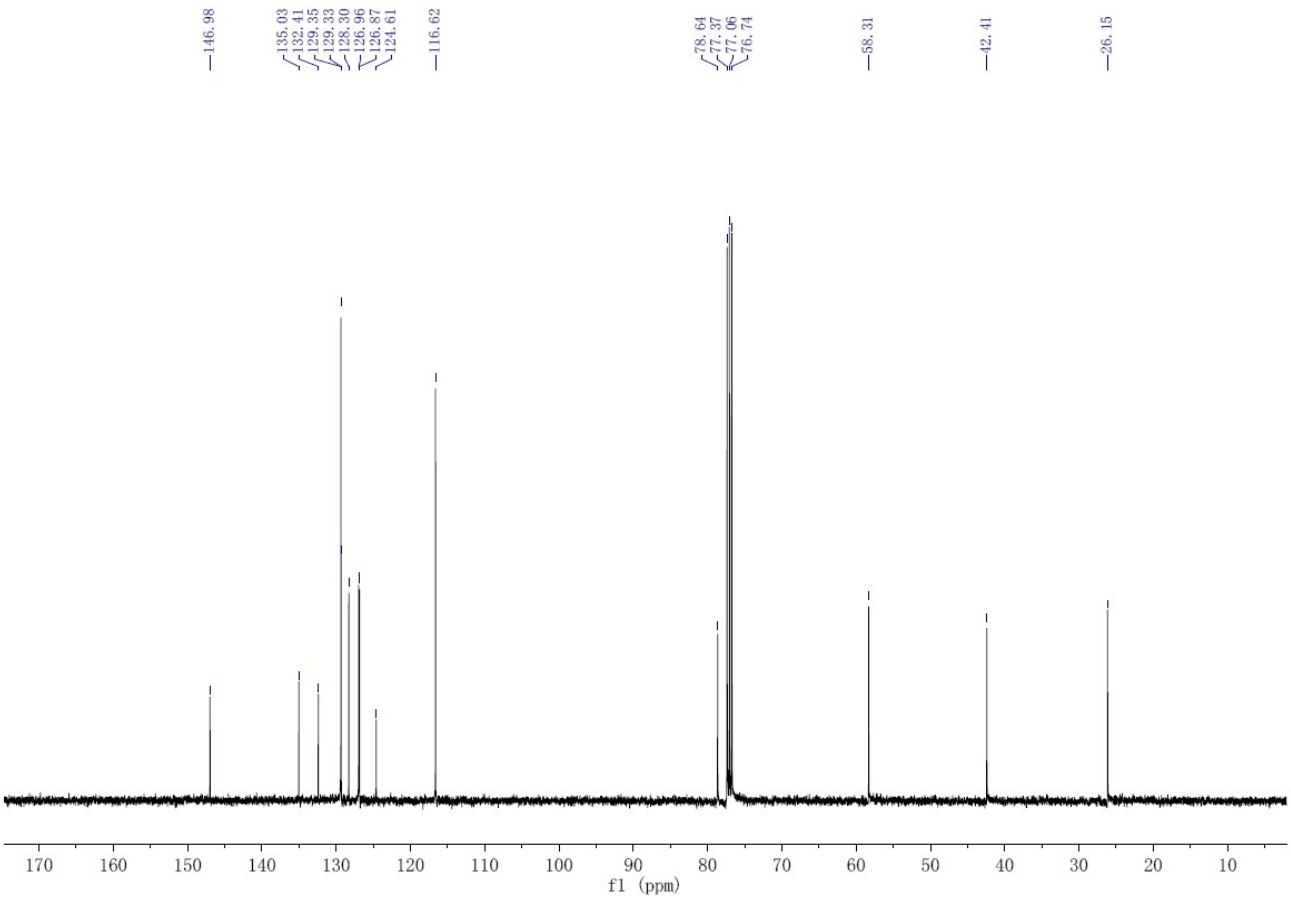
0.0
f1 (ppm)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42.41
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100
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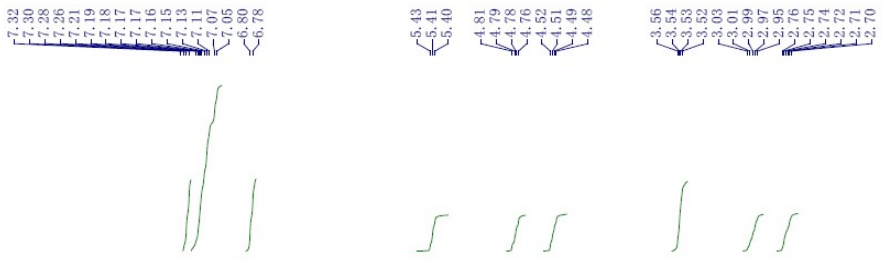
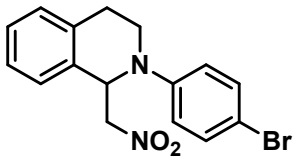
f1 (ppm)

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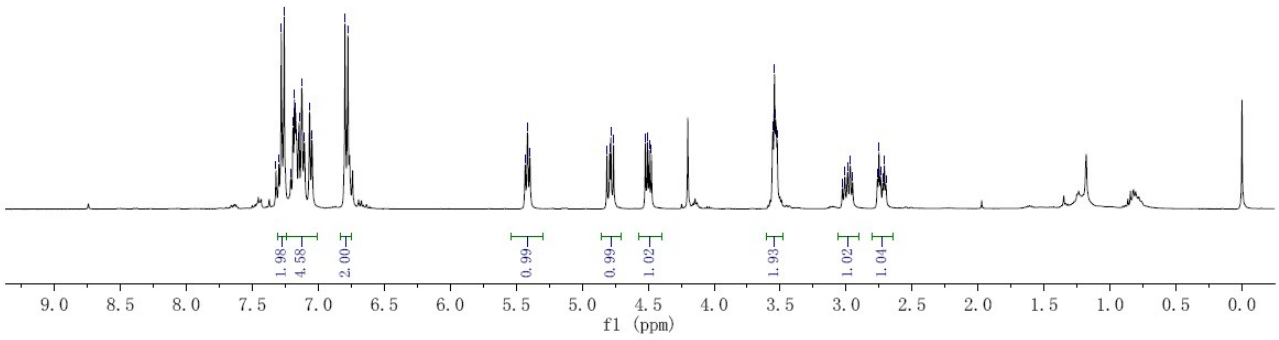
Br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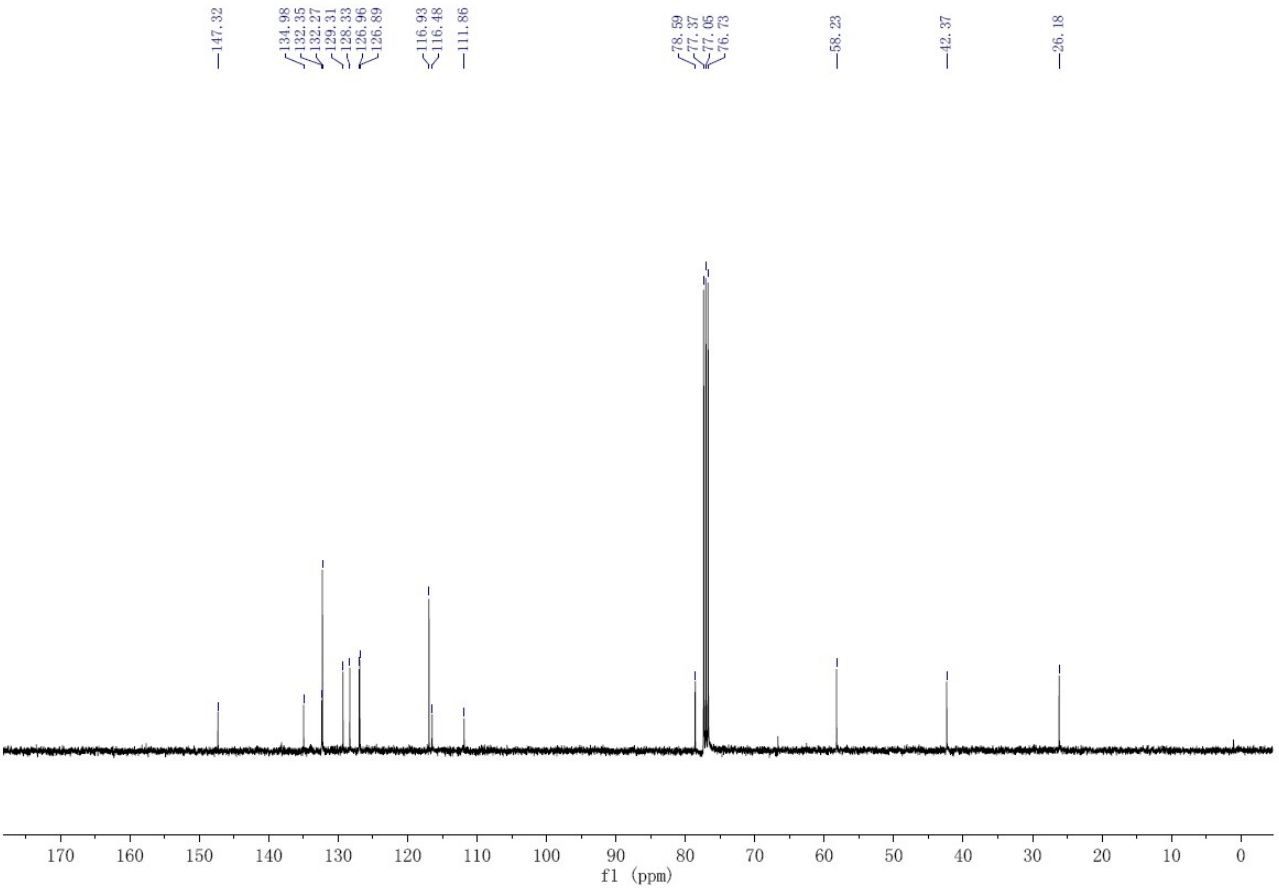
1.02
1.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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42.37
26.18
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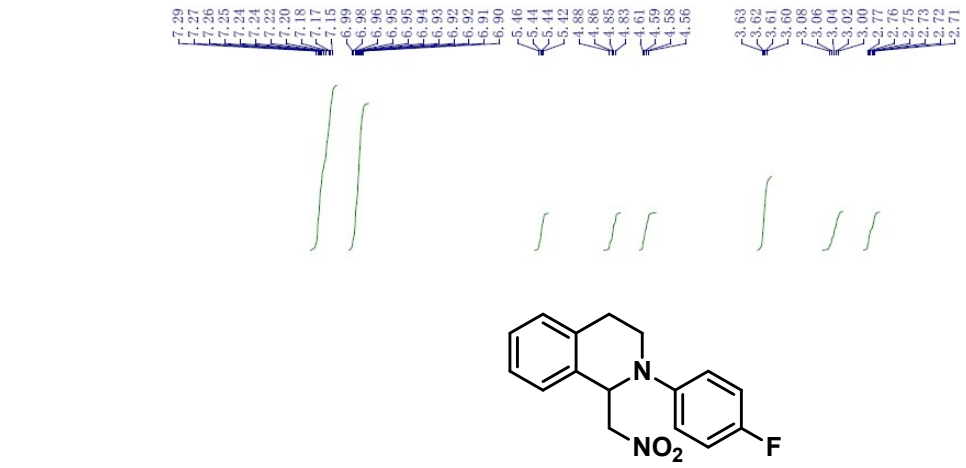
f1 (ppm)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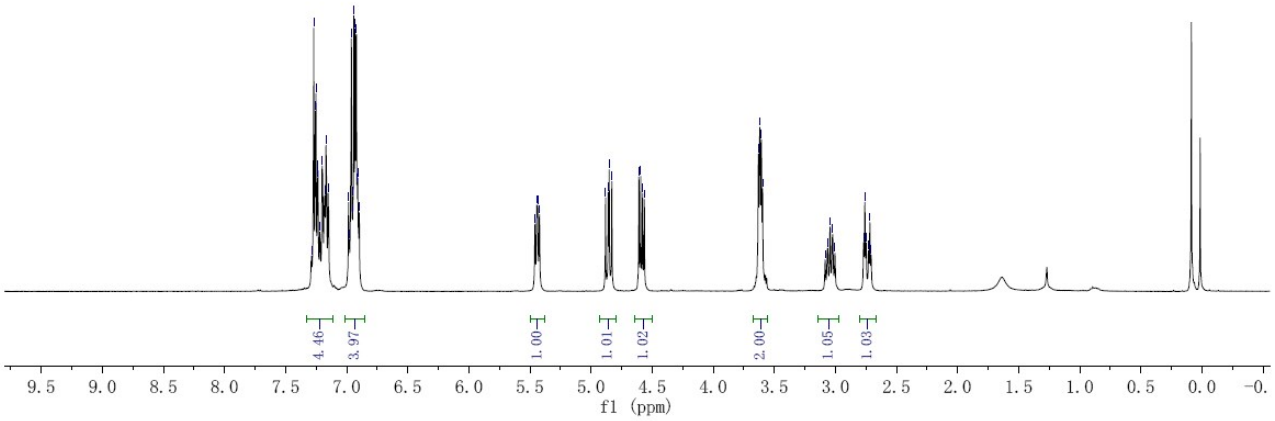
F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1.03
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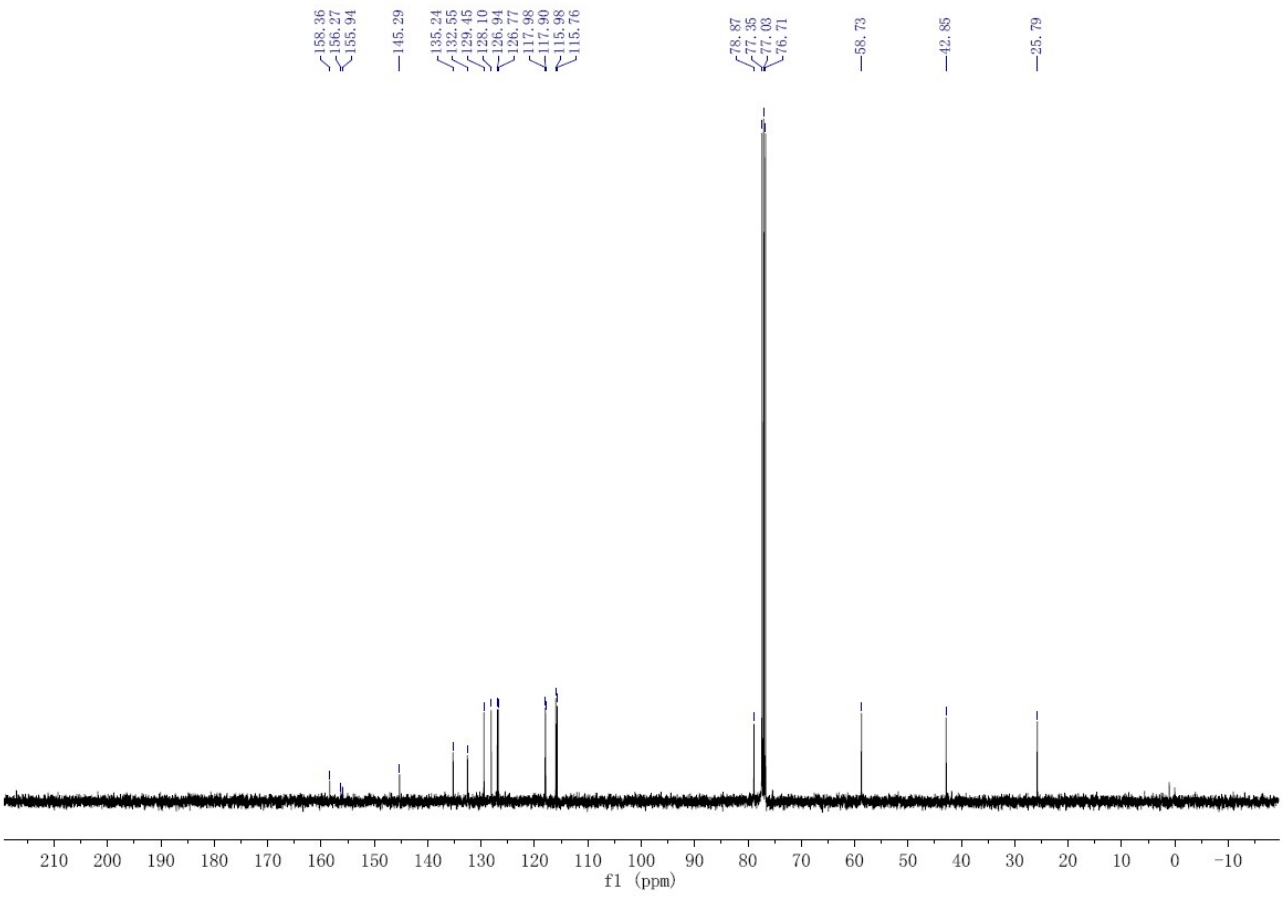
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115.98
115.76
78.87
77.35
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58.73
42.85
25.79
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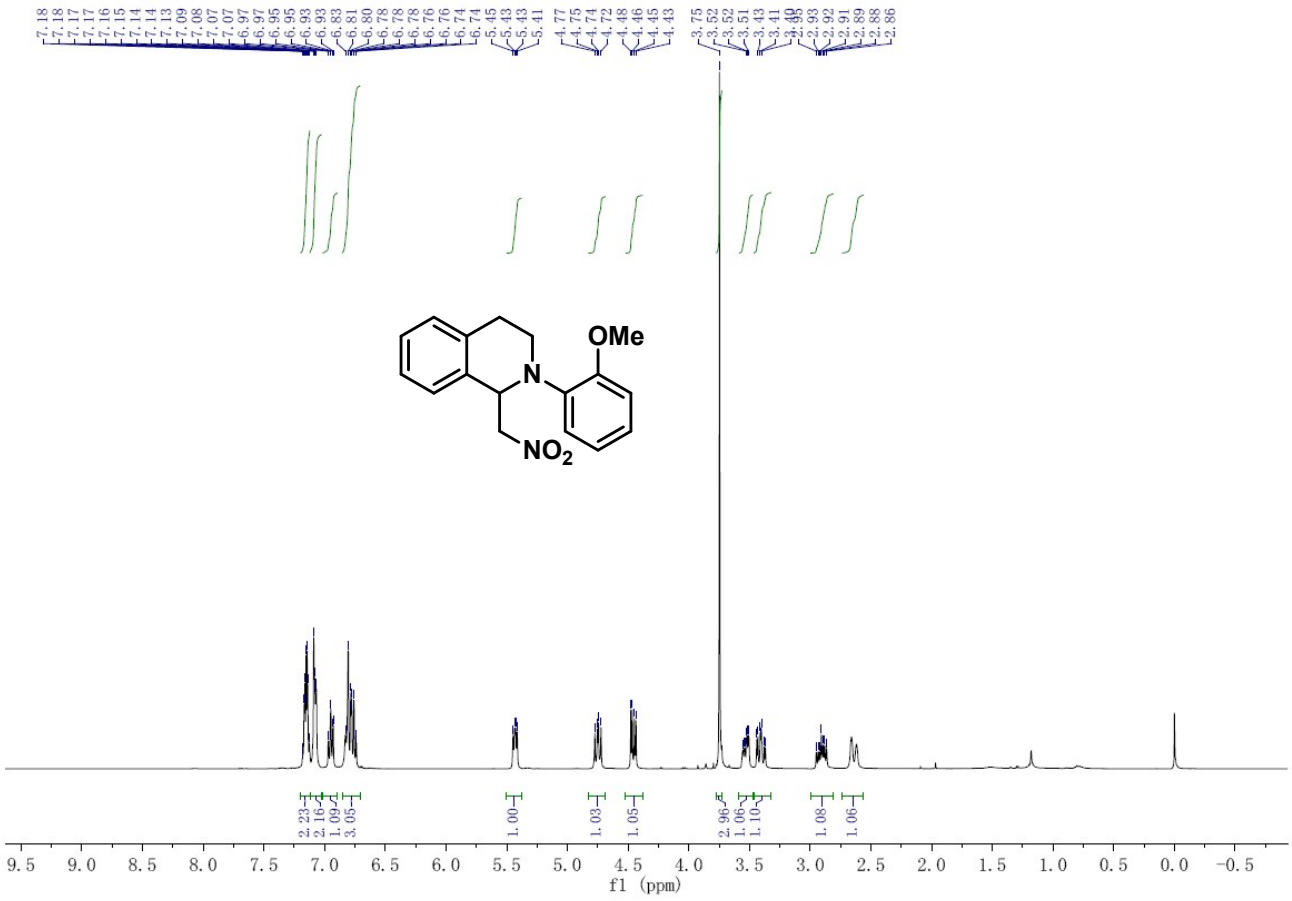
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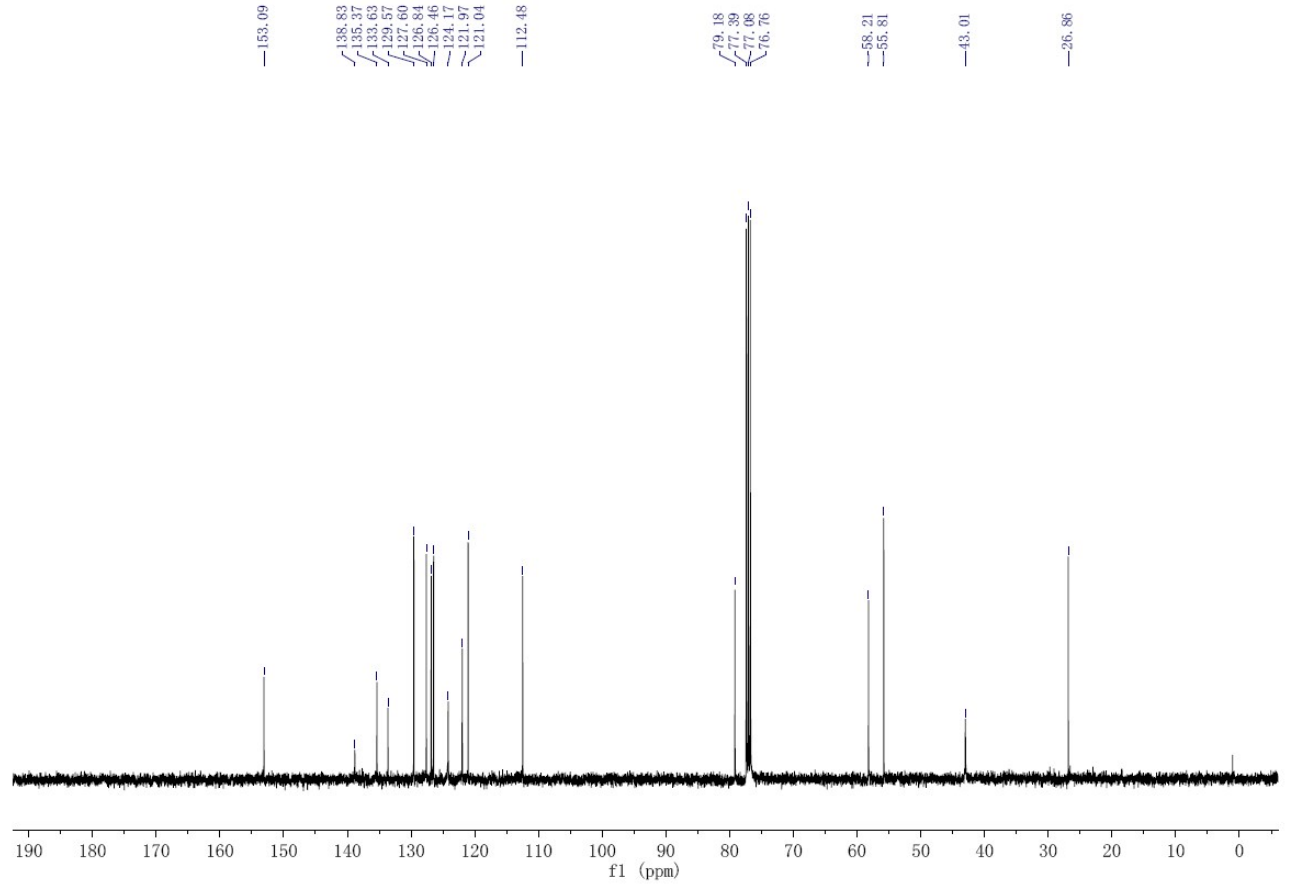
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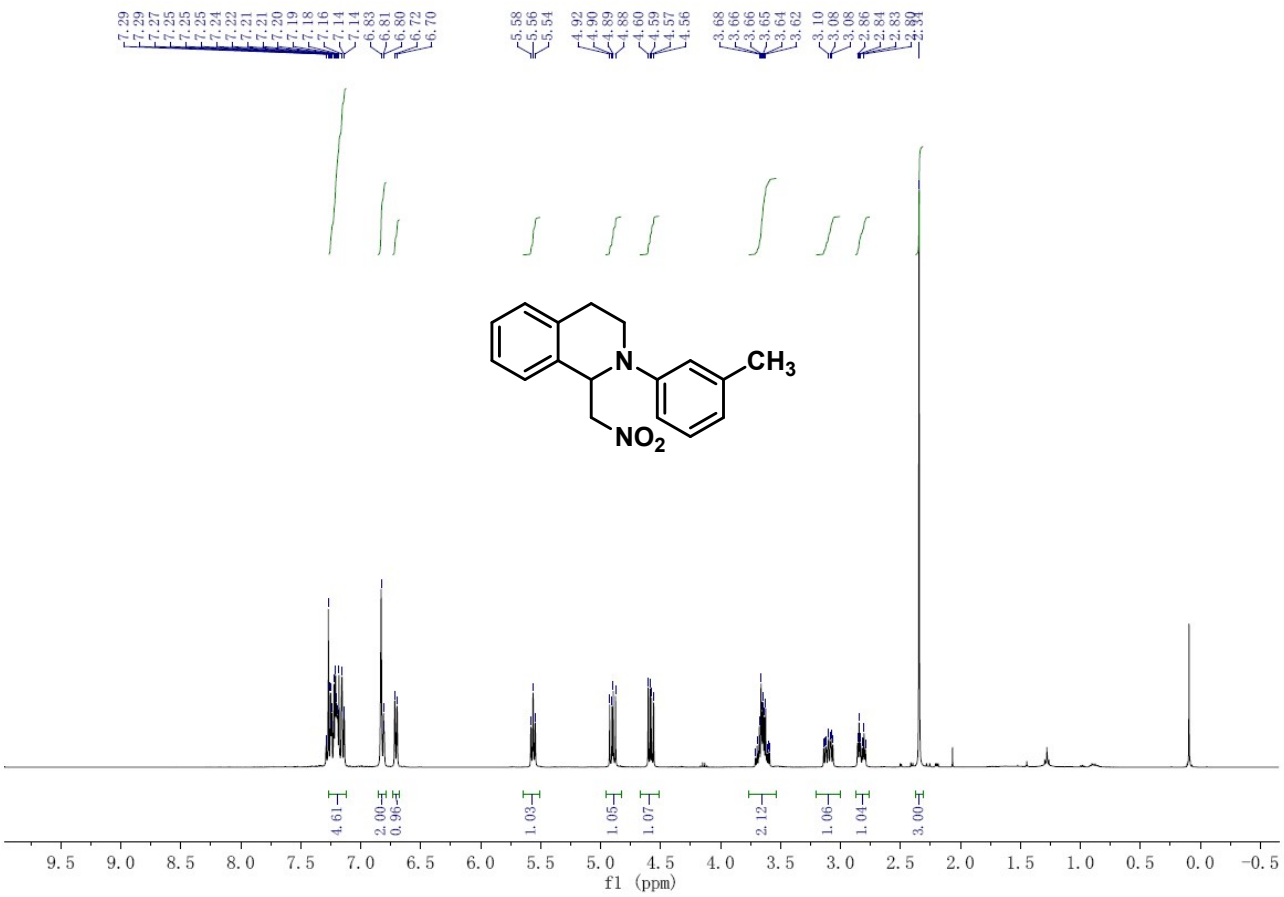
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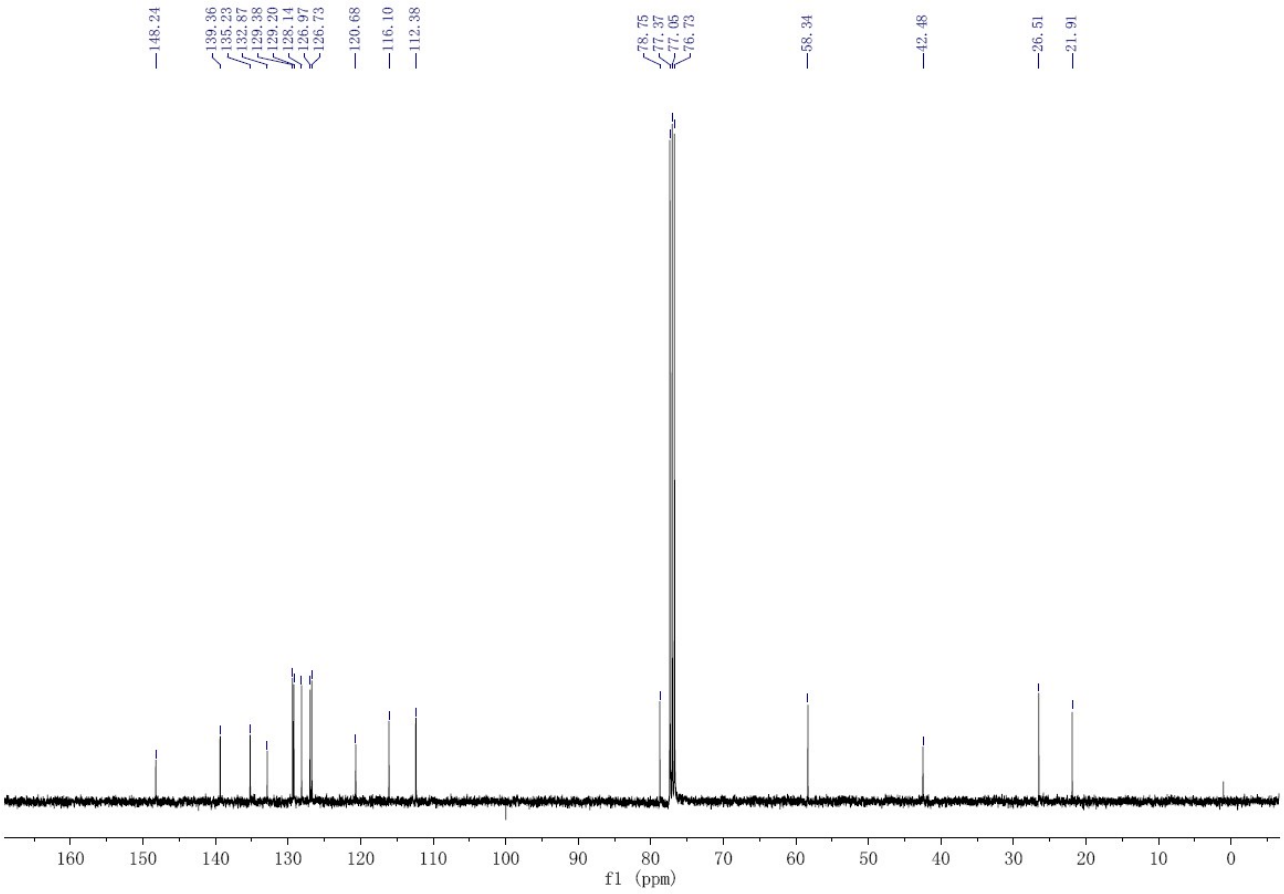
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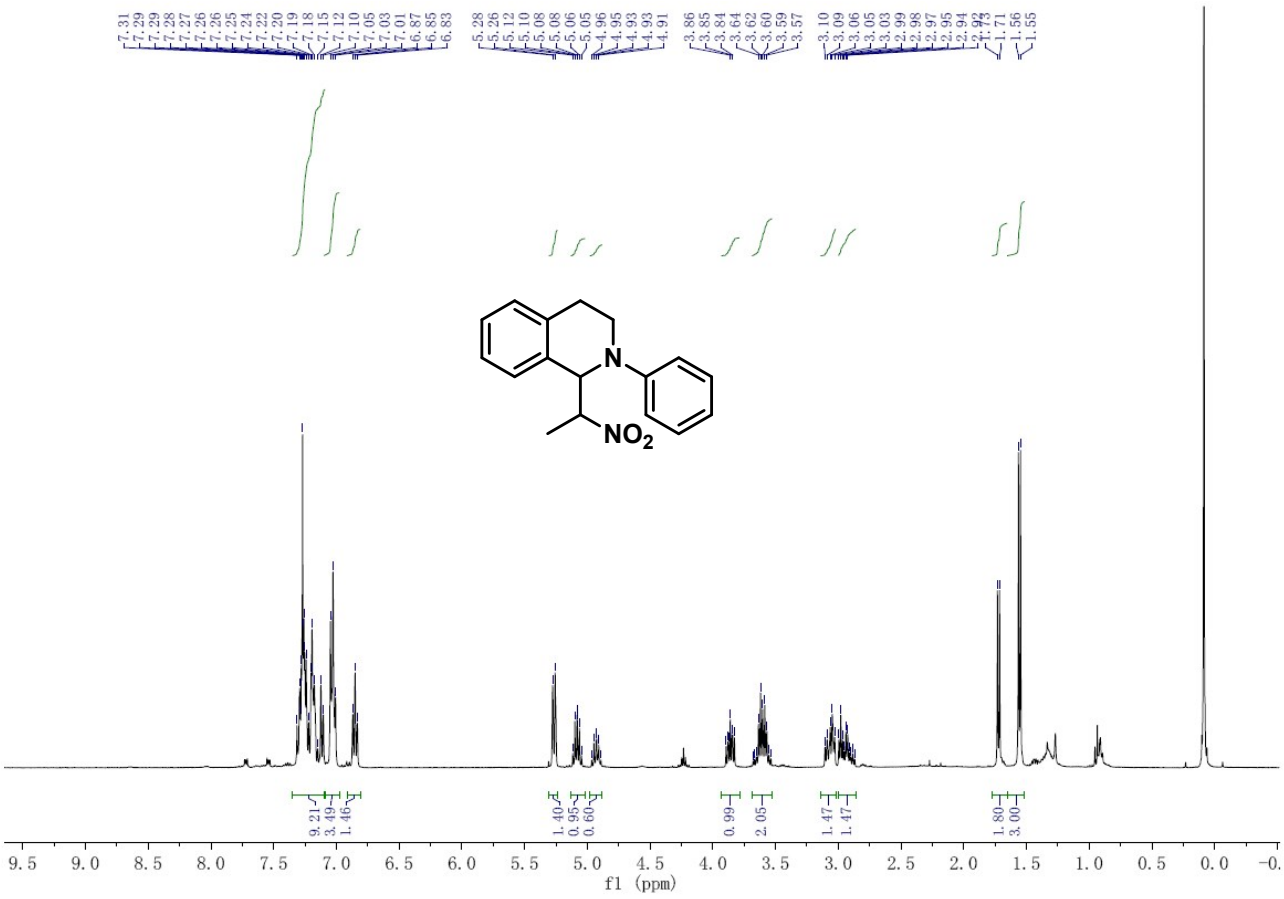
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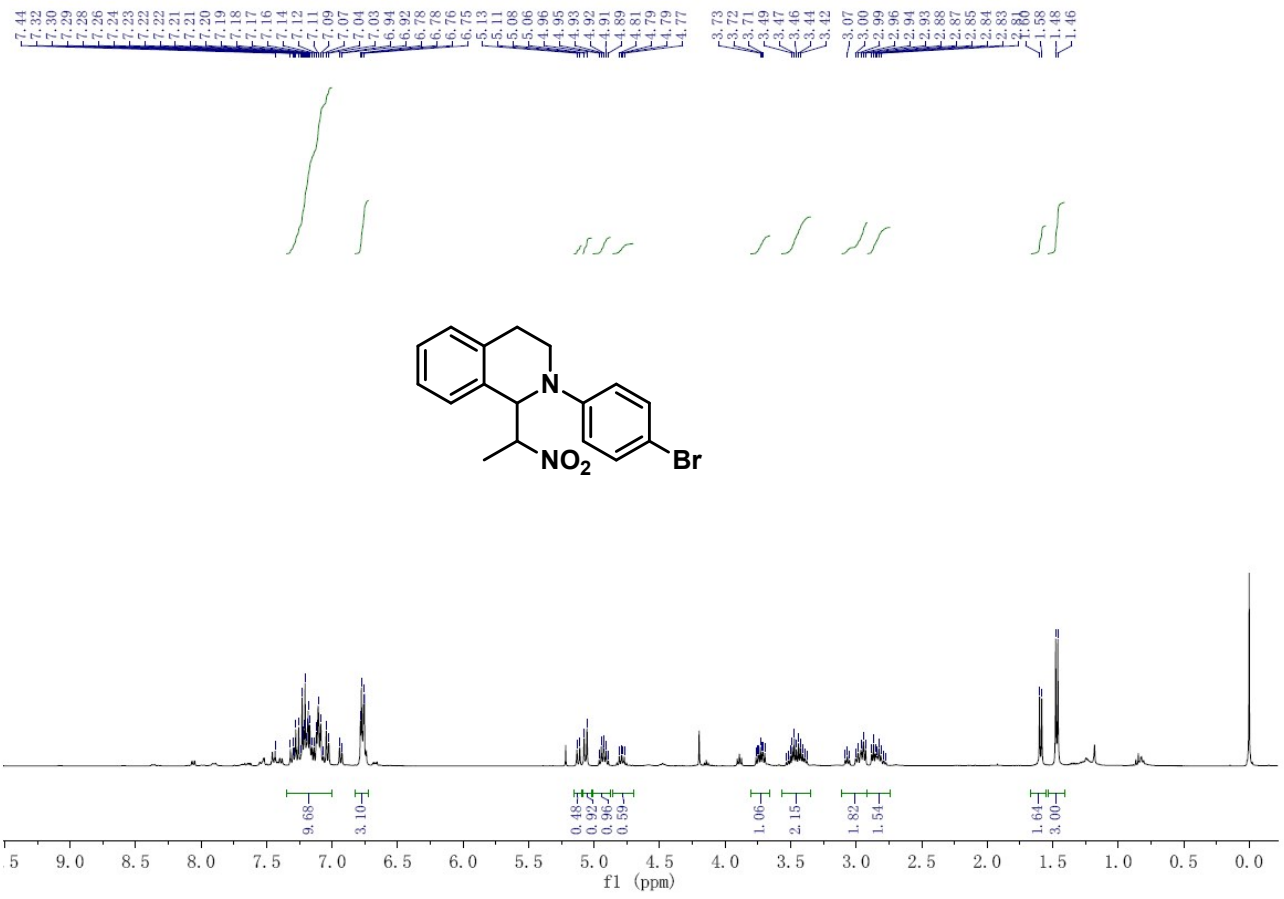
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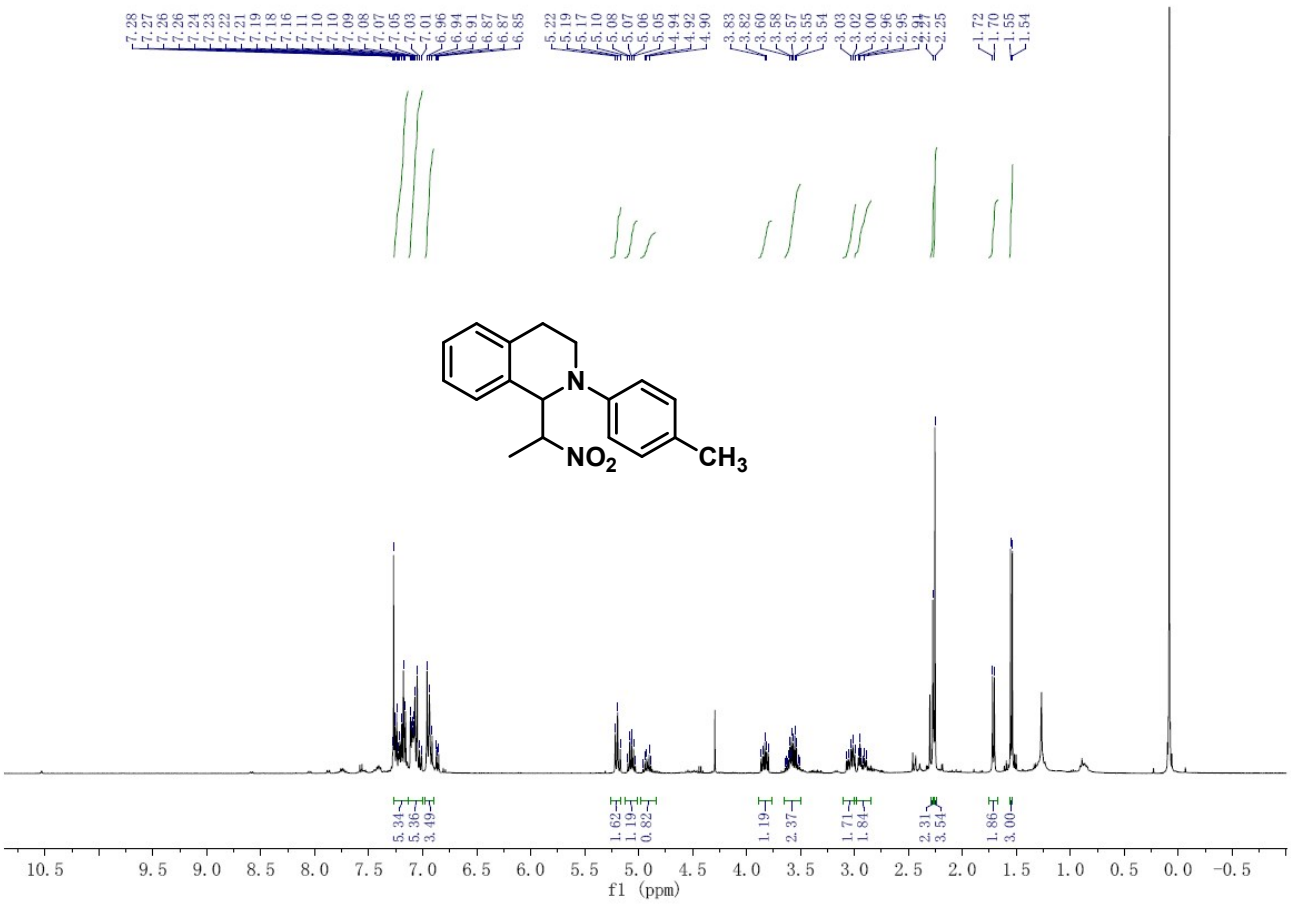
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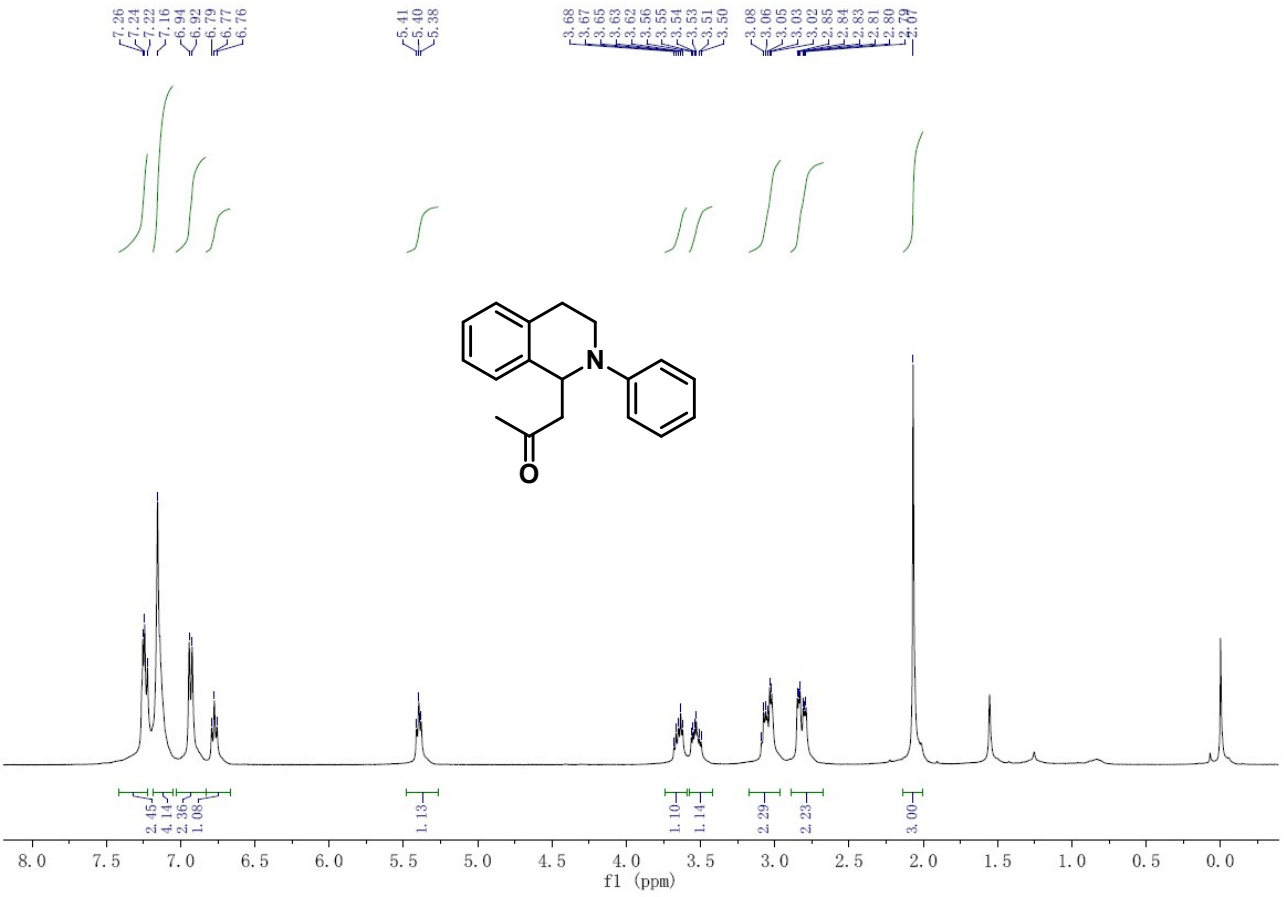
5.22 5.19 5.17 5.10 5.08 5.07 5.06 5.05 4.94 4.92 4.90
3.83 3.82 3.60 3.58 3.57 3.55 3.54 3.03 3.02 3.00 2.96 2.95 2.27 2.25
1.72 1.70 1.55 1.54
N
NO2
CH3
5.34 5.36 3.49 1.62 1.19 0.82 1.19 2.37 1.71 1.84 2.31 3.54 1.86 3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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3.53
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3.06
3.05
3.03
3.02
2.85
2.84
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2.80
2.79
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1.13
1.10
1.14
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2.23
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6.5
6.0
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3.5
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1.0
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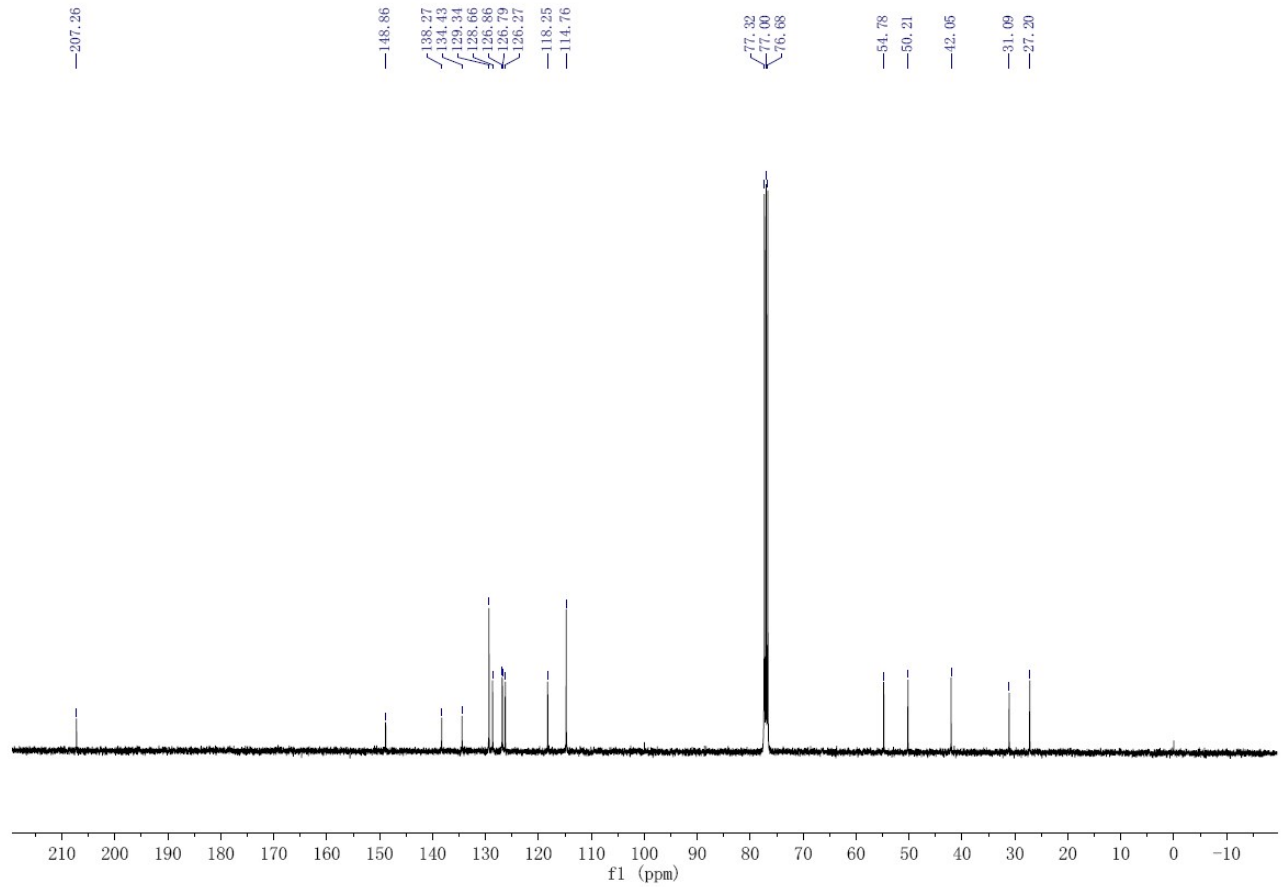
f1 (ppm)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77.00
76.68
54.78
50.21
42.05
31.09
27.20
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200
190
180
170
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100
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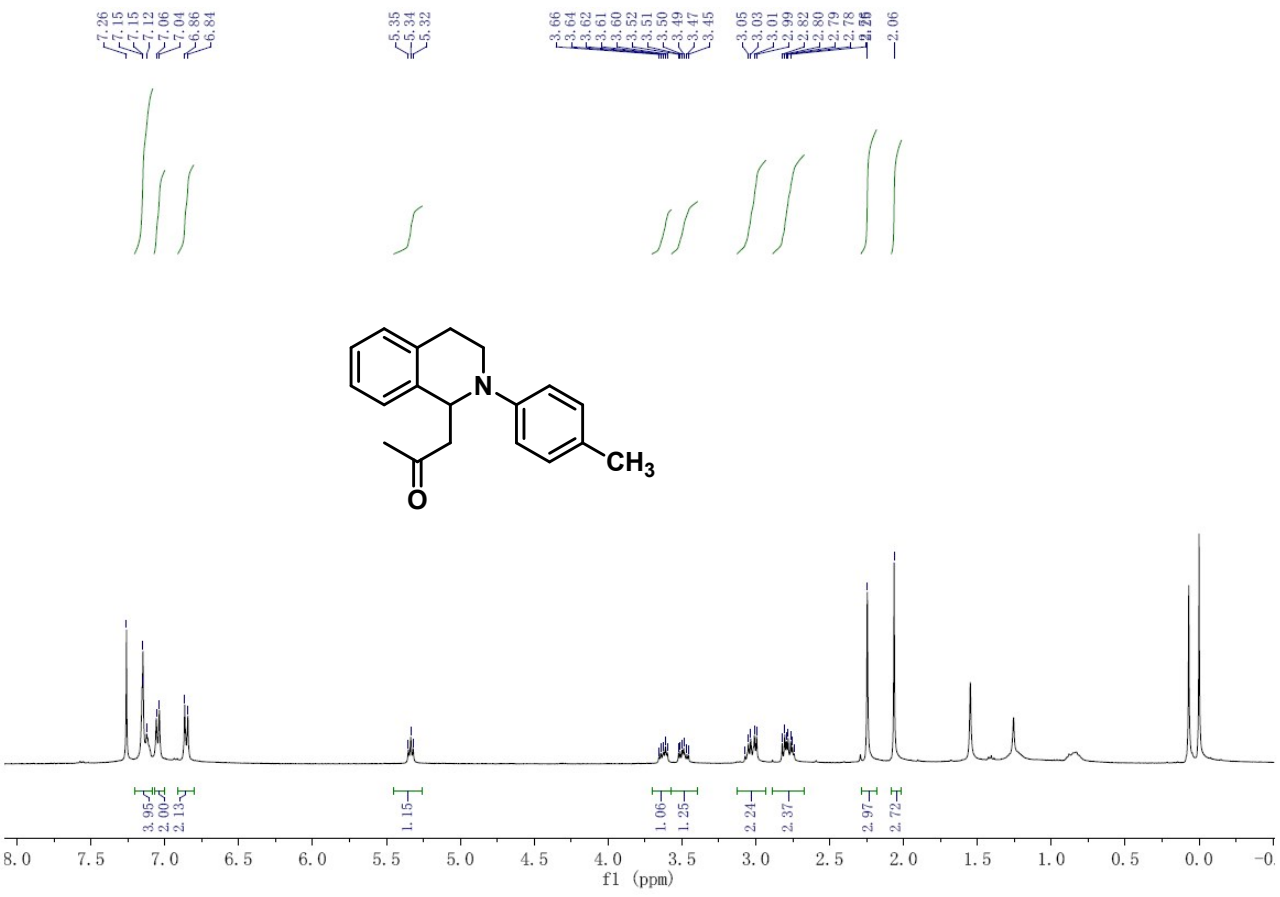
-10
f1 (ppm)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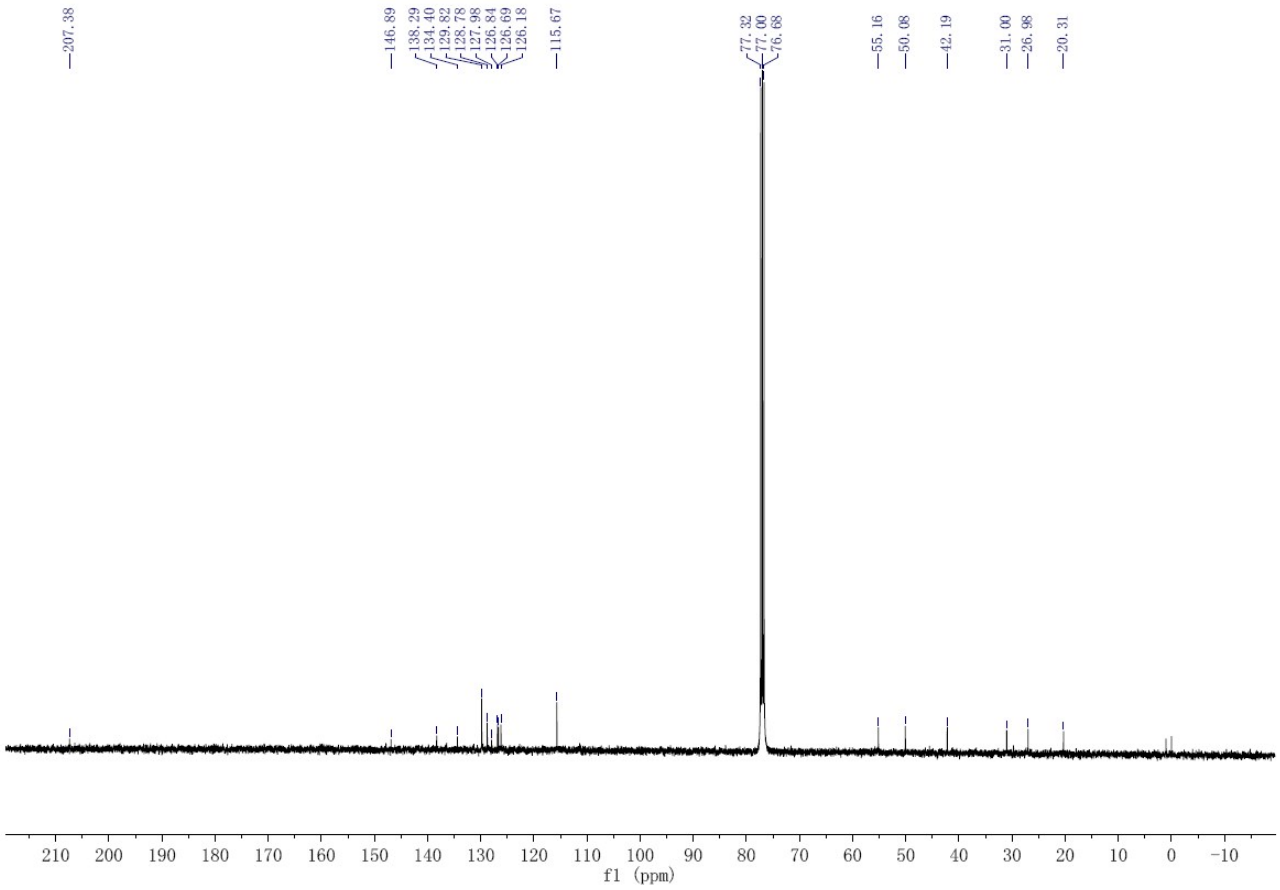
2.72
f1 (ppm)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31.00
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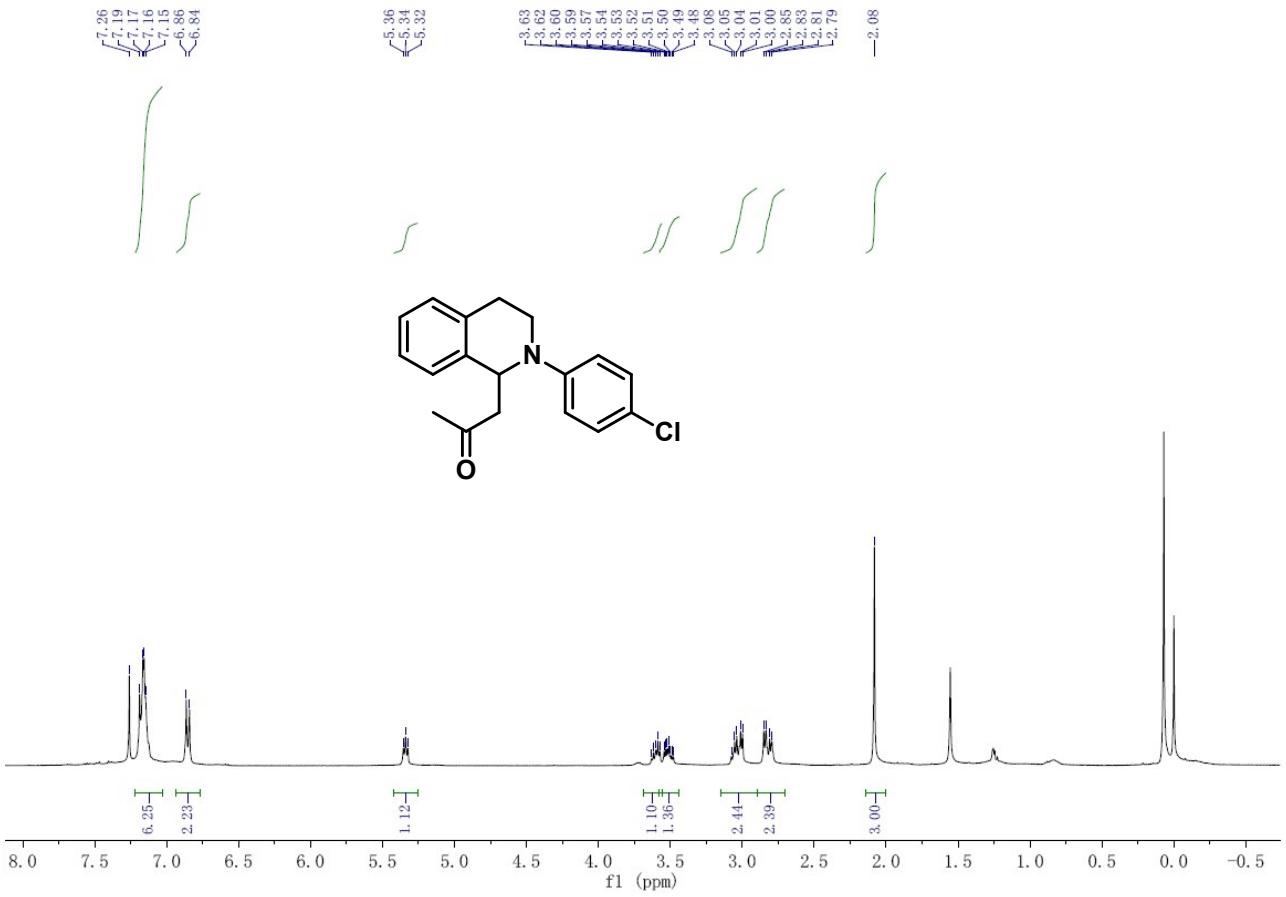
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7.19
7.17
7.16
7.15
6.86
6.84
5.36
5.34
5.32
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3.59
3.57
3.54
3.53
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3.50
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3.04
3.01
3.00
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2.81
2.79
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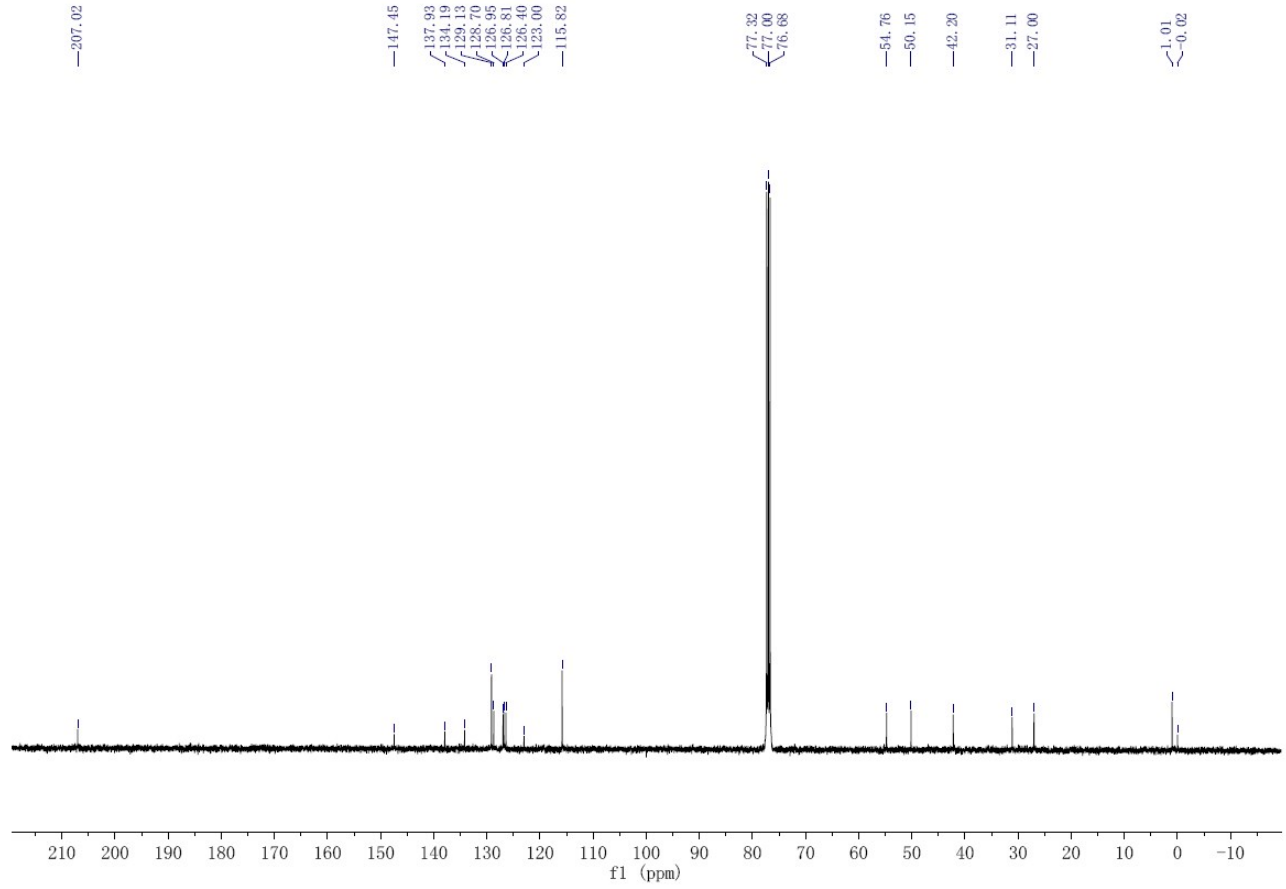
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27.00
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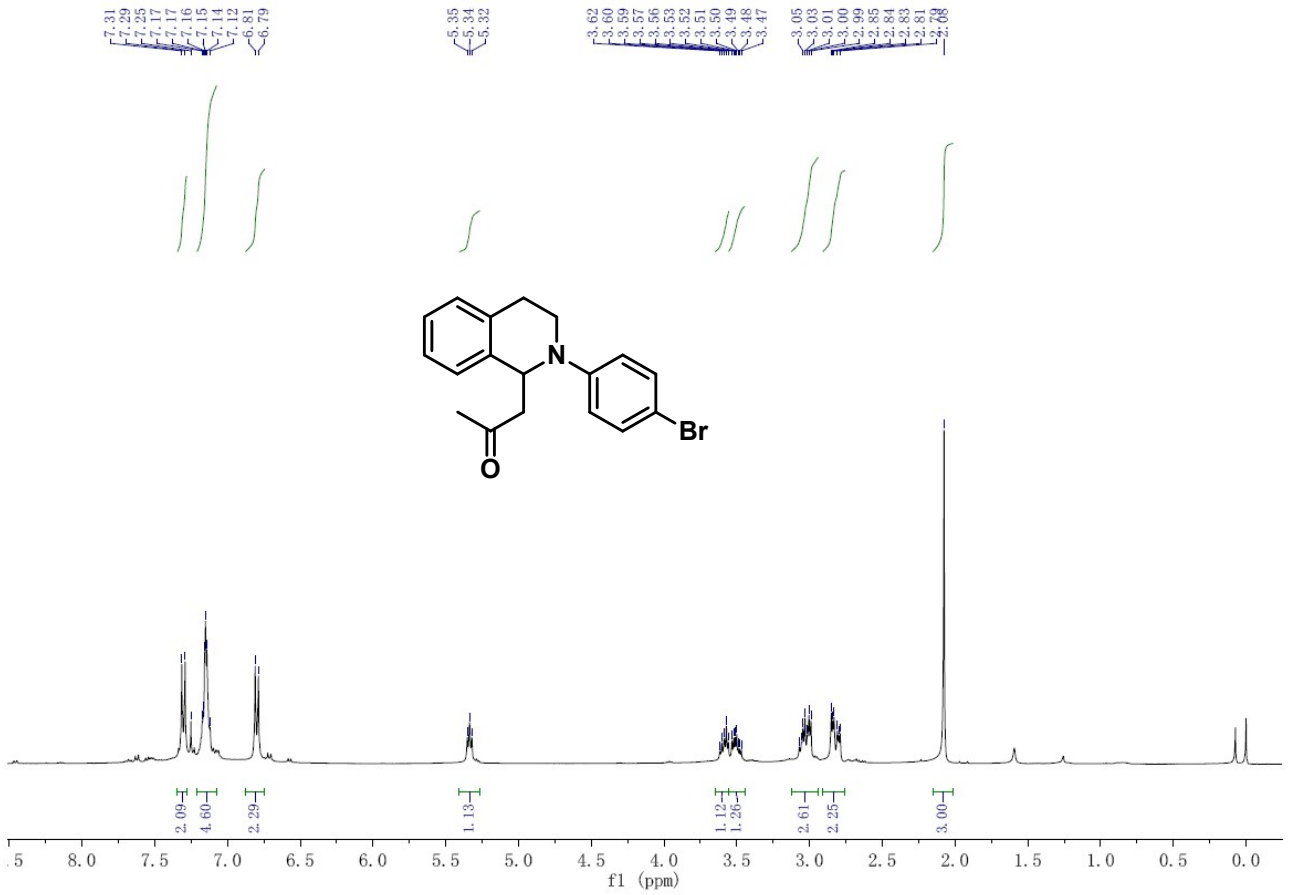
0.02
f1 (ppm)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3.60
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3.57
3.56
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3.50
3.49
3.48
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3.05
3.03
3.01
3.00
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2.85
2.84
2.83
2.81
2.08
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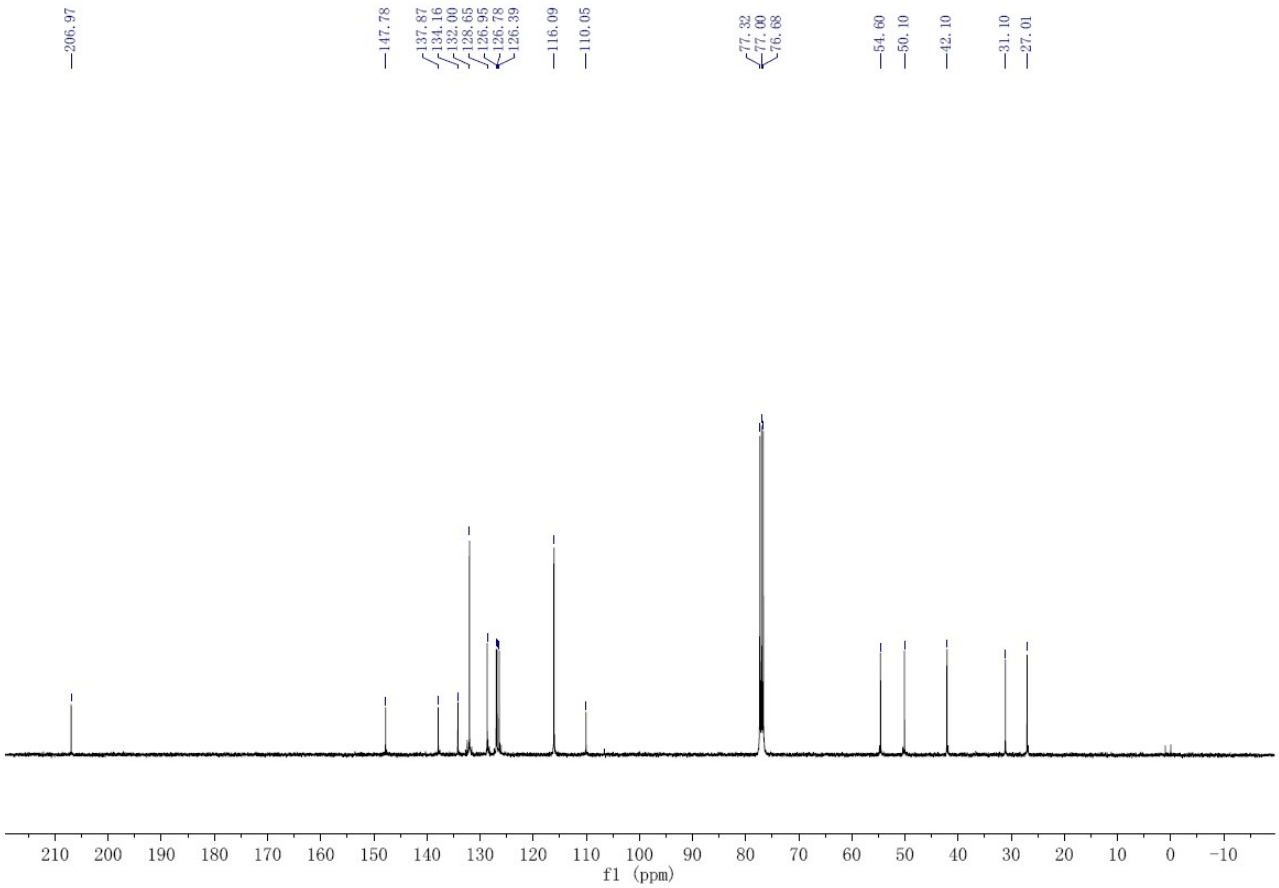
f1 (ppm)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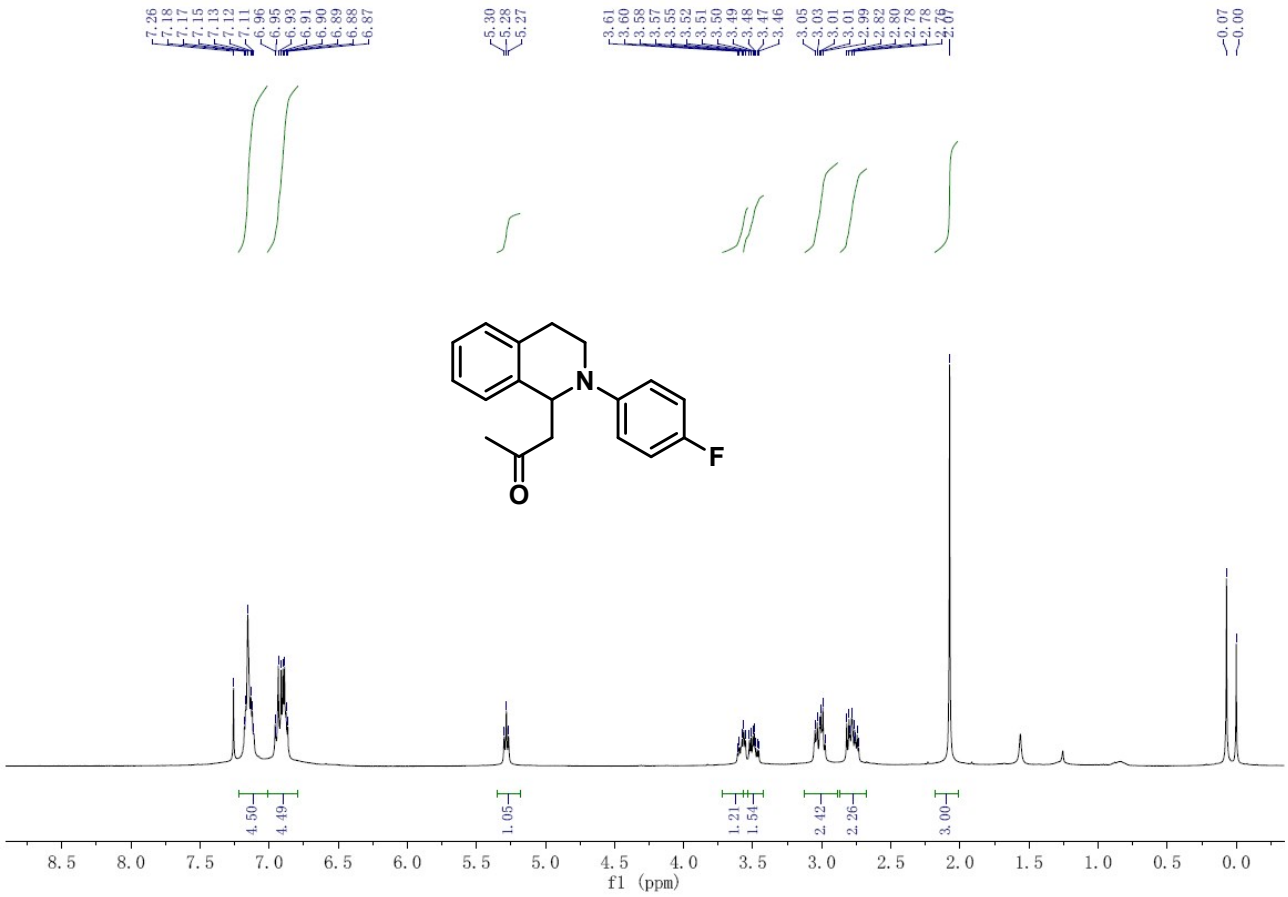
31.10
27.01
f1 (ppm)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6.87
5.30
5.28
5.27
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3.60
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3.57
3.55
3.52
3.51
3.50
3.49
3.48
3.47
3.46
3.05
3.03
3.01
3.01
2.99
2.82
2.80
2.78
2.78
2.76
2.07
0.07
0.00
N
F
O
4.50
4.49
1.05
1.21
1.54
2.42
2.26
3.00
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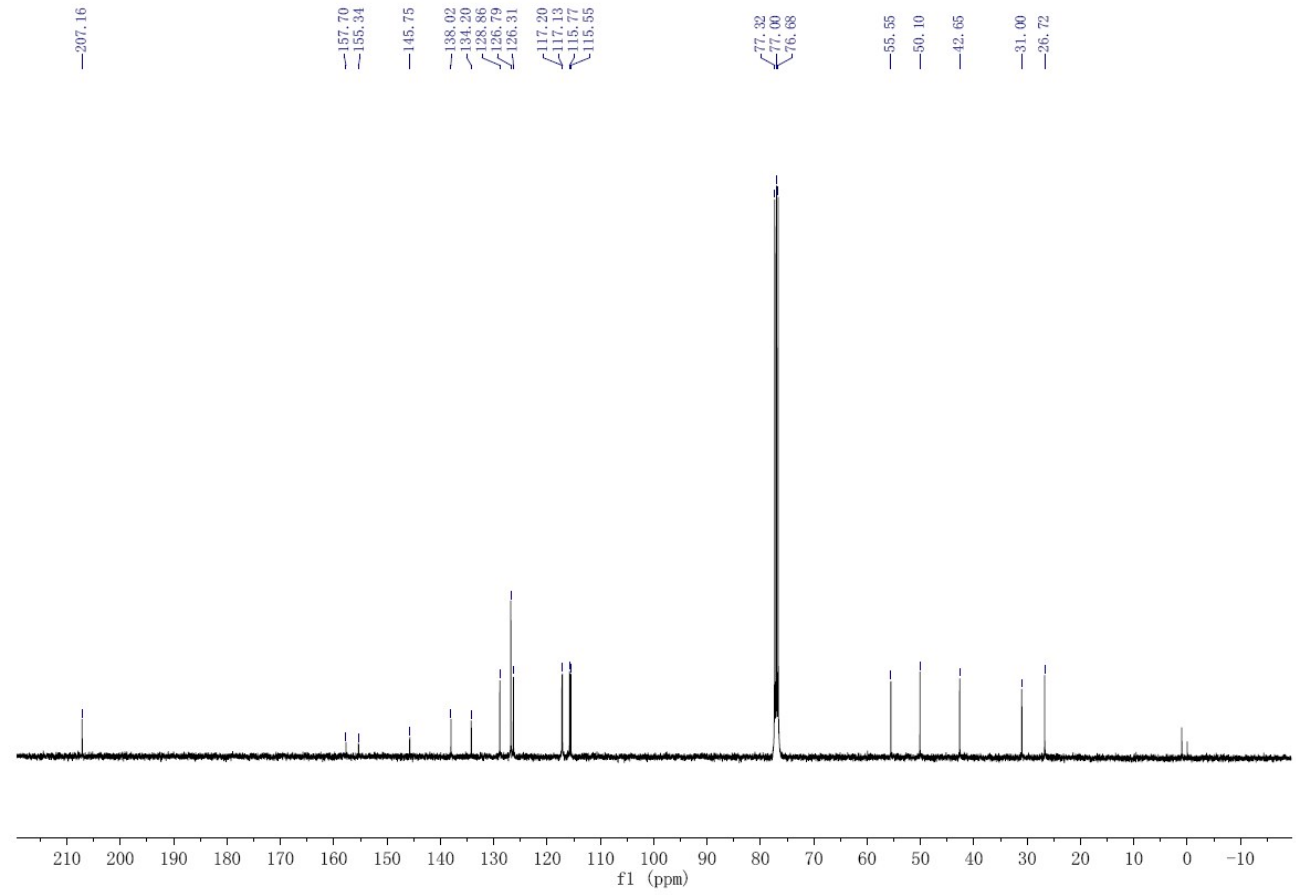
f1 (ppm)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77.32
77.00
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31.00
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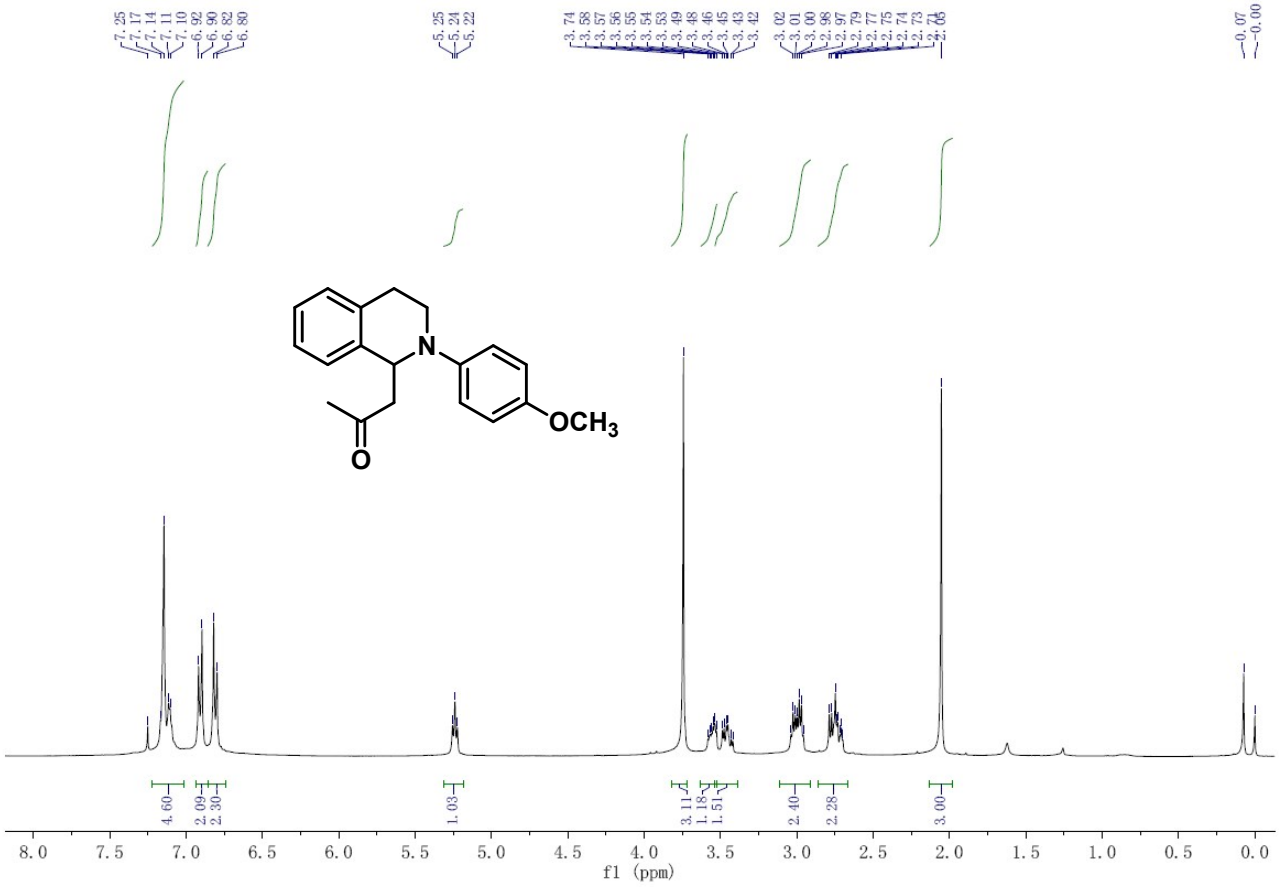
f1 (ppm)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3.58
3.57
3.56
3.55
3.54
3.53
3.49
3.48
3.46
3.45
3.43
3.42
3.02
3.01
3.00
2.98
2.97
2.79
2.77
2.75
2.74
2.73
2.65
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OCH3
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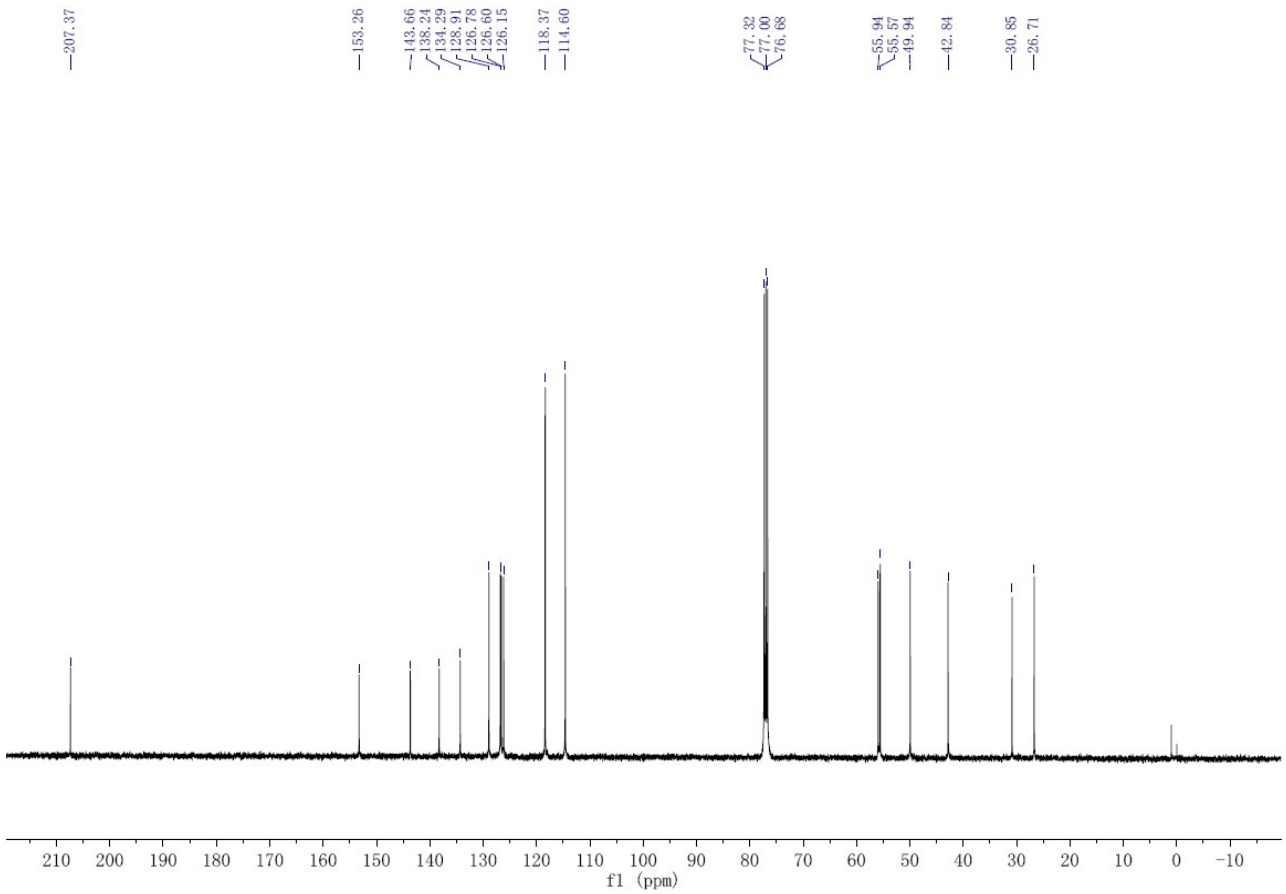
3.00
f1 (ppm)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126.15
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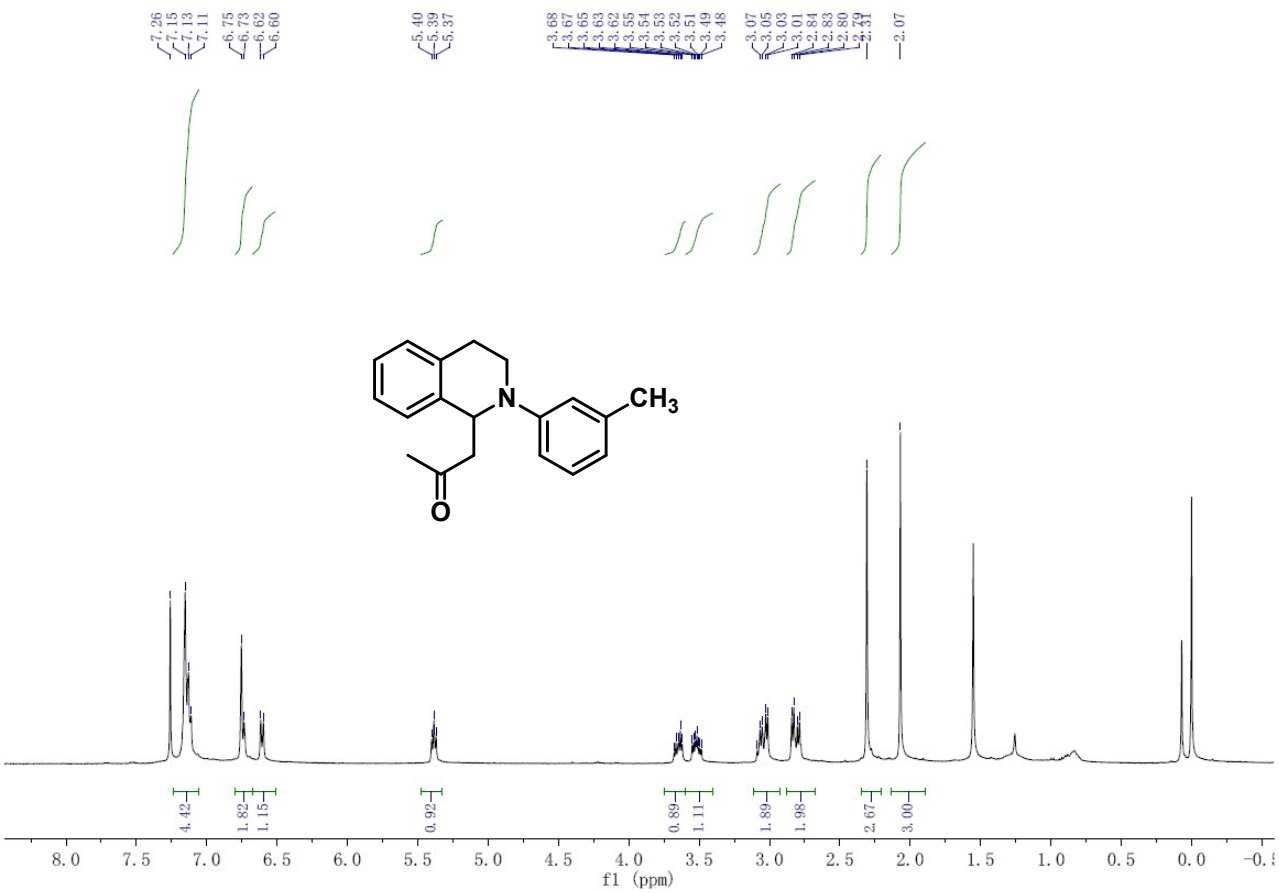
49.94
42.84
30.85
26.71
f1 (ppm)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3.62
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3.07
3.05
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3.01
2.84
2.83
2.80
2.79
2.51
2.07
N
CH3
O
4.42
1.82
1.15
0.92
0.89
1.11
1.89
1.98
2.67
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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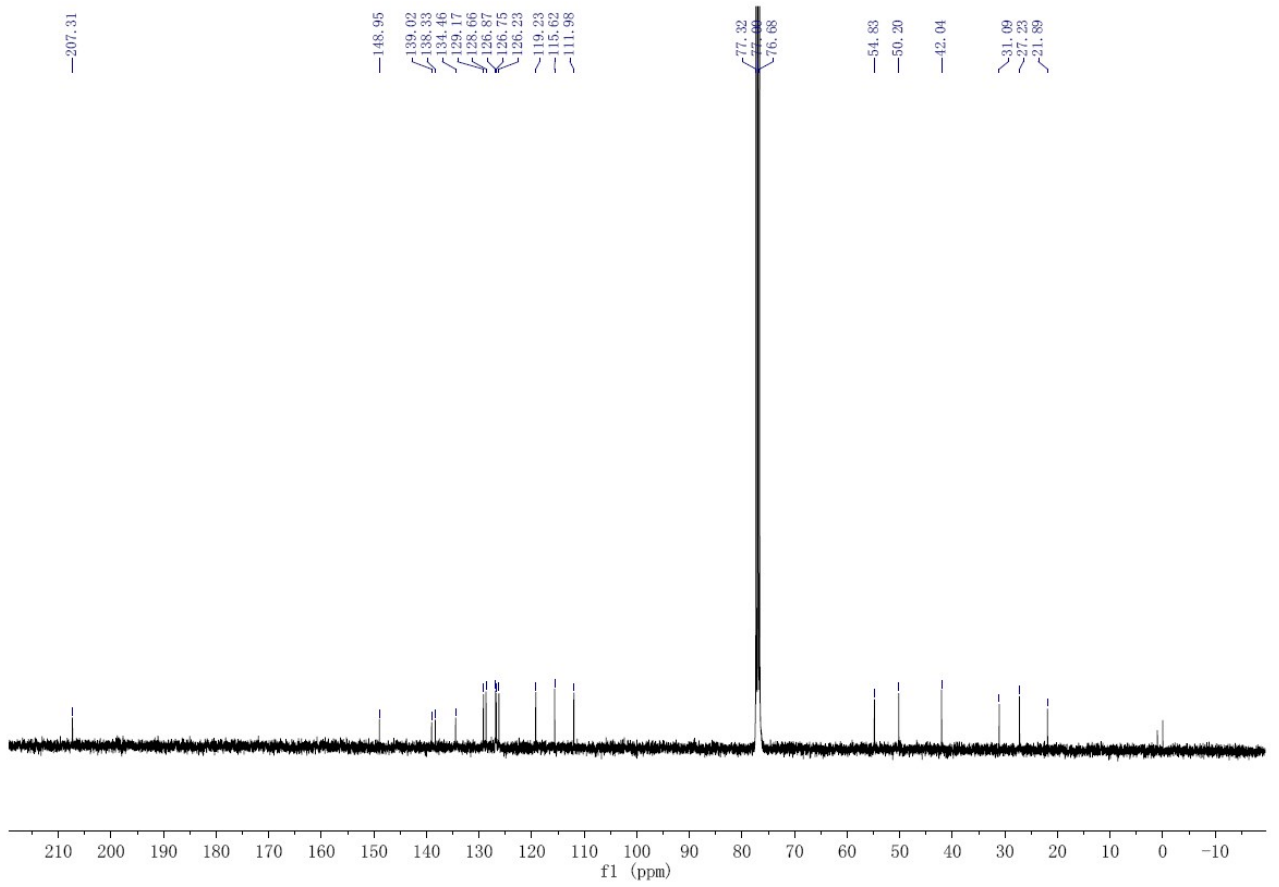
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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77.00
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42.04
31.09
27.23
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180
170
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140
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120
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100
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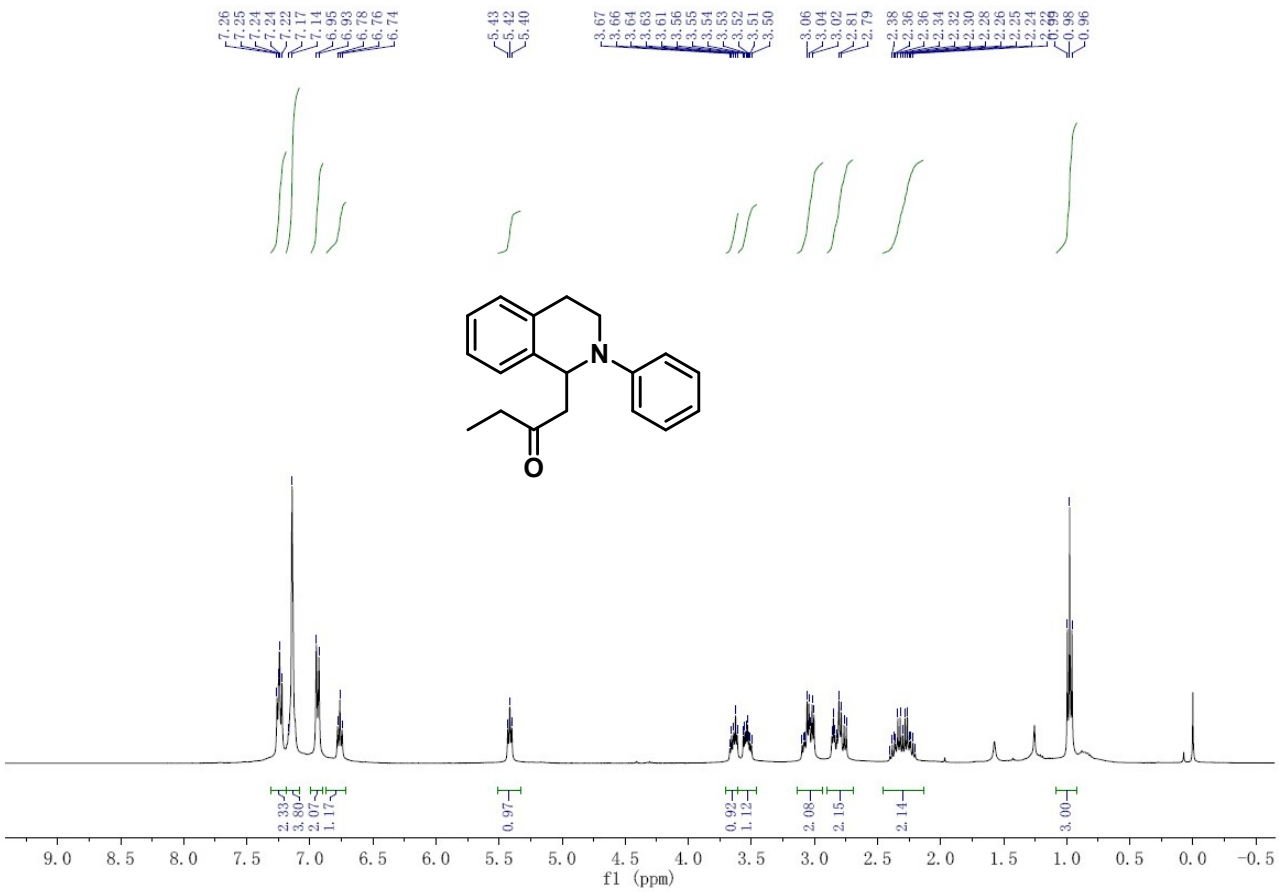
-10
f1 (ppm)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6.78
6.76
6.74
5.43
5.42
5.40
3.67
3.66
3.64
3.63
3.61
3.56
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3.54
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2.25
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O
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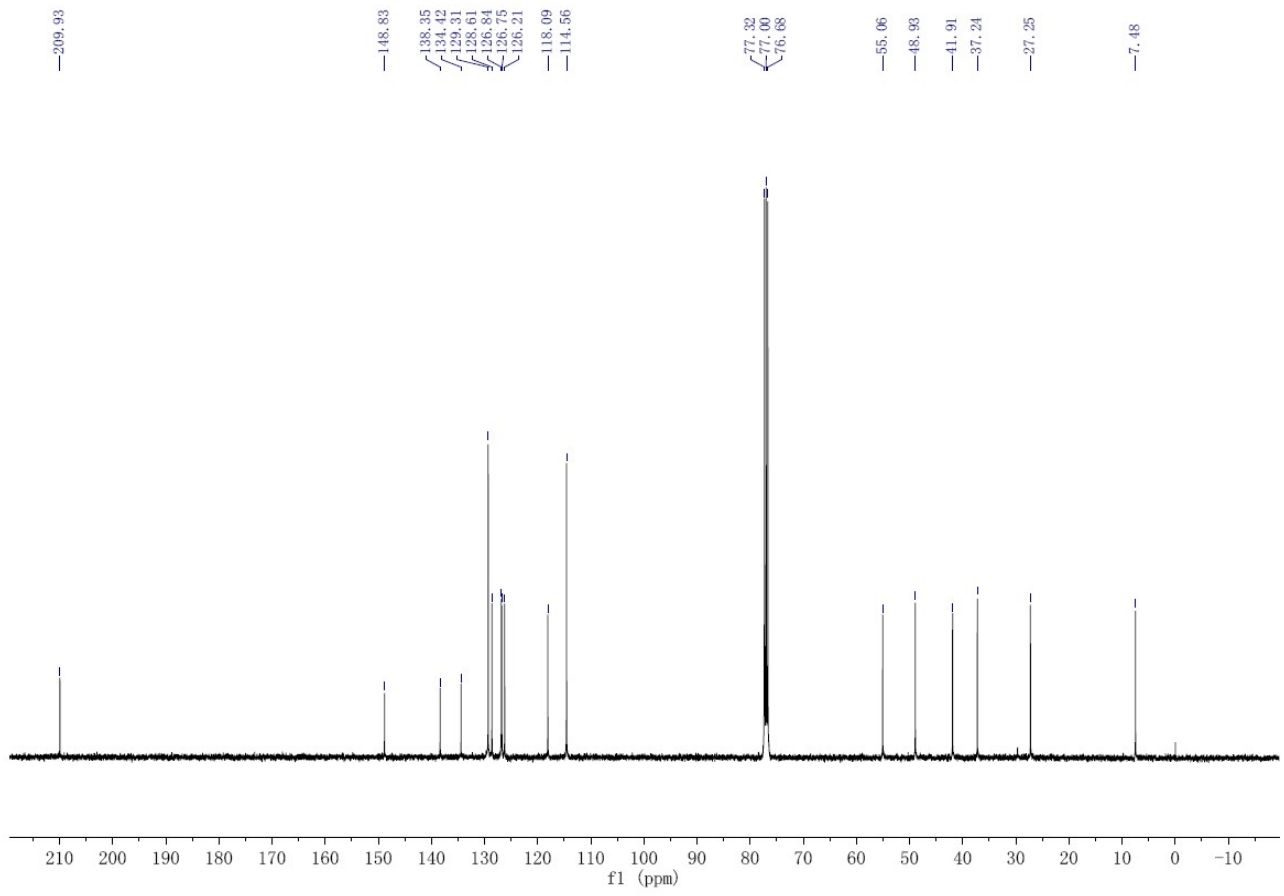
3.80
2.07
1.17
0.97
0.92
1.12
2.08
2.15
2.14
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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126.75
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118.09
114.56
77.32
77.00
76.68
55.06
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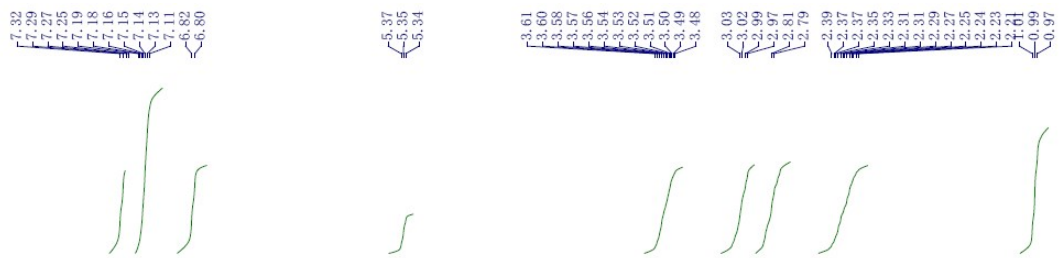
37.24
27.25
7.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.80
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5.34
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3.56
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3.53
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3.51
3.50
3.49
3.48
3.03
3.02
2.99
2.97
2.81
2.79
2.39
2.37
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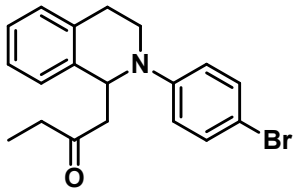
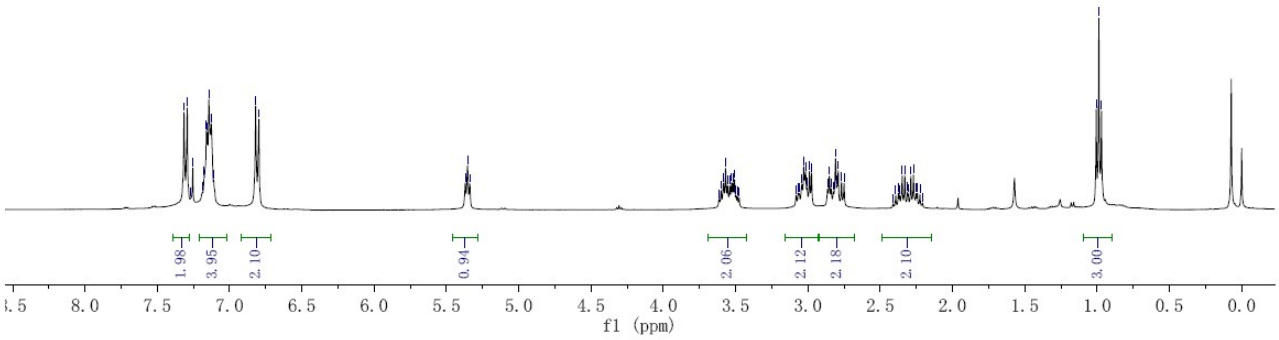

N
Br
O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7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
1.0
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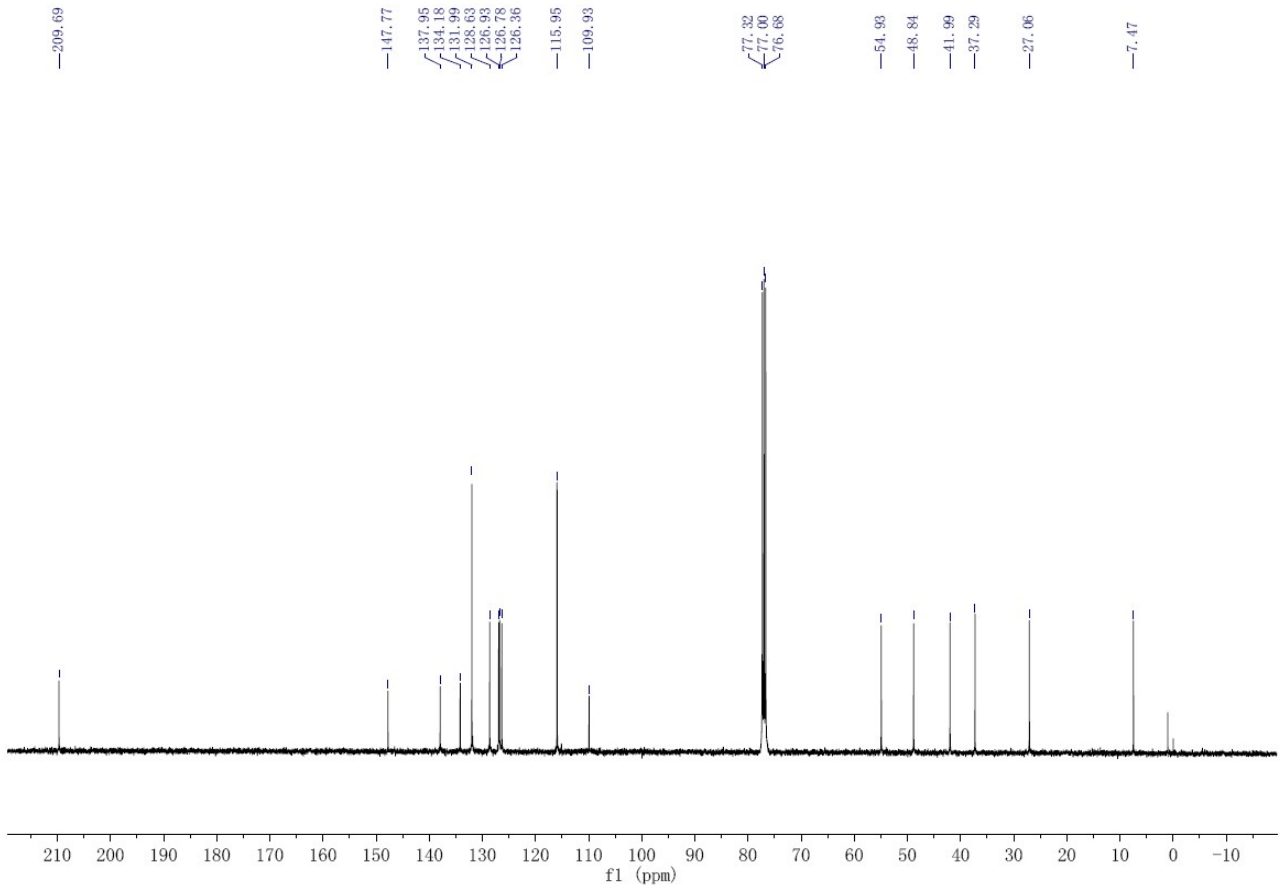
0.0
f1 (ppm)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27.06
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200
190
180
170
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120
110
100
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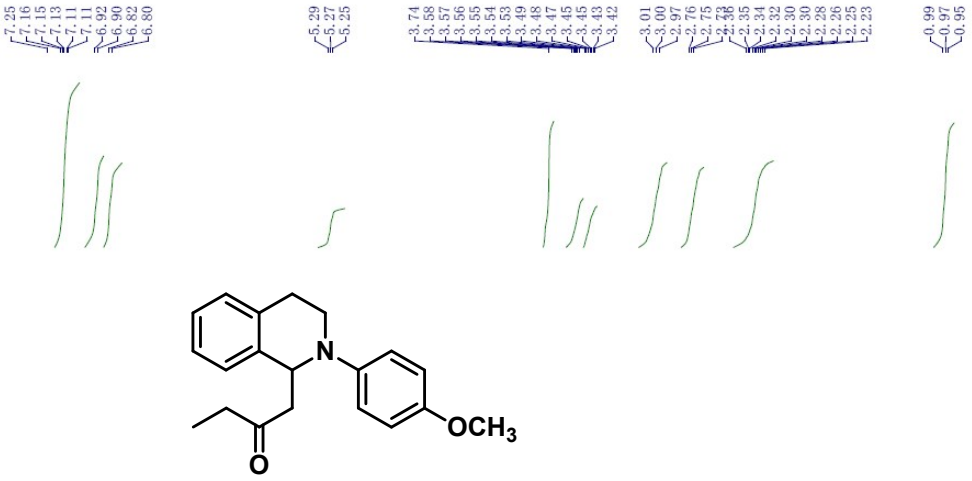
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.80
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5.27
5.25
3.74
3.58
3.57
3.56
3.55
3.54
3.53
3.49
3.48
3.47
3.45
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3.43
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3.00
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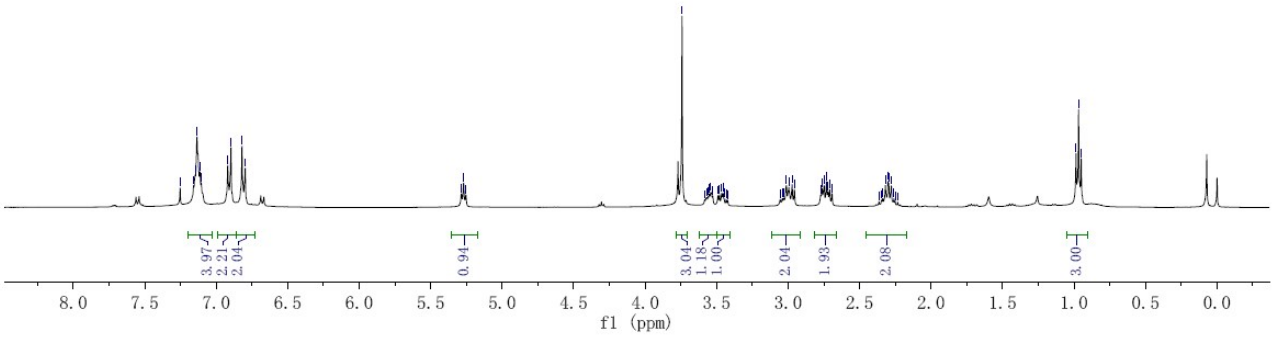
OCH3
O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2.04
1.93
2.08
3.00
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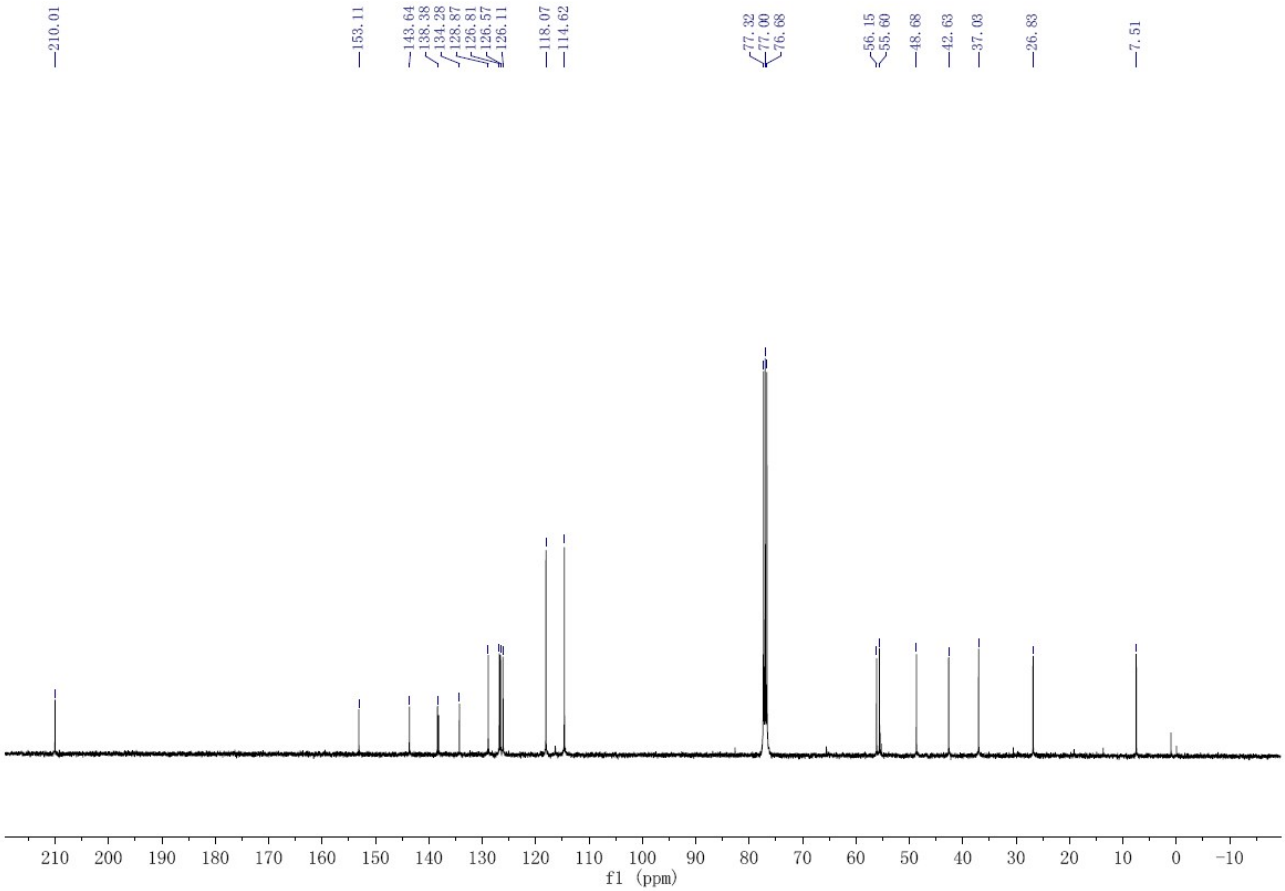
f1 (ppm)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126.11
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76.68
56.15
55.60
48.68
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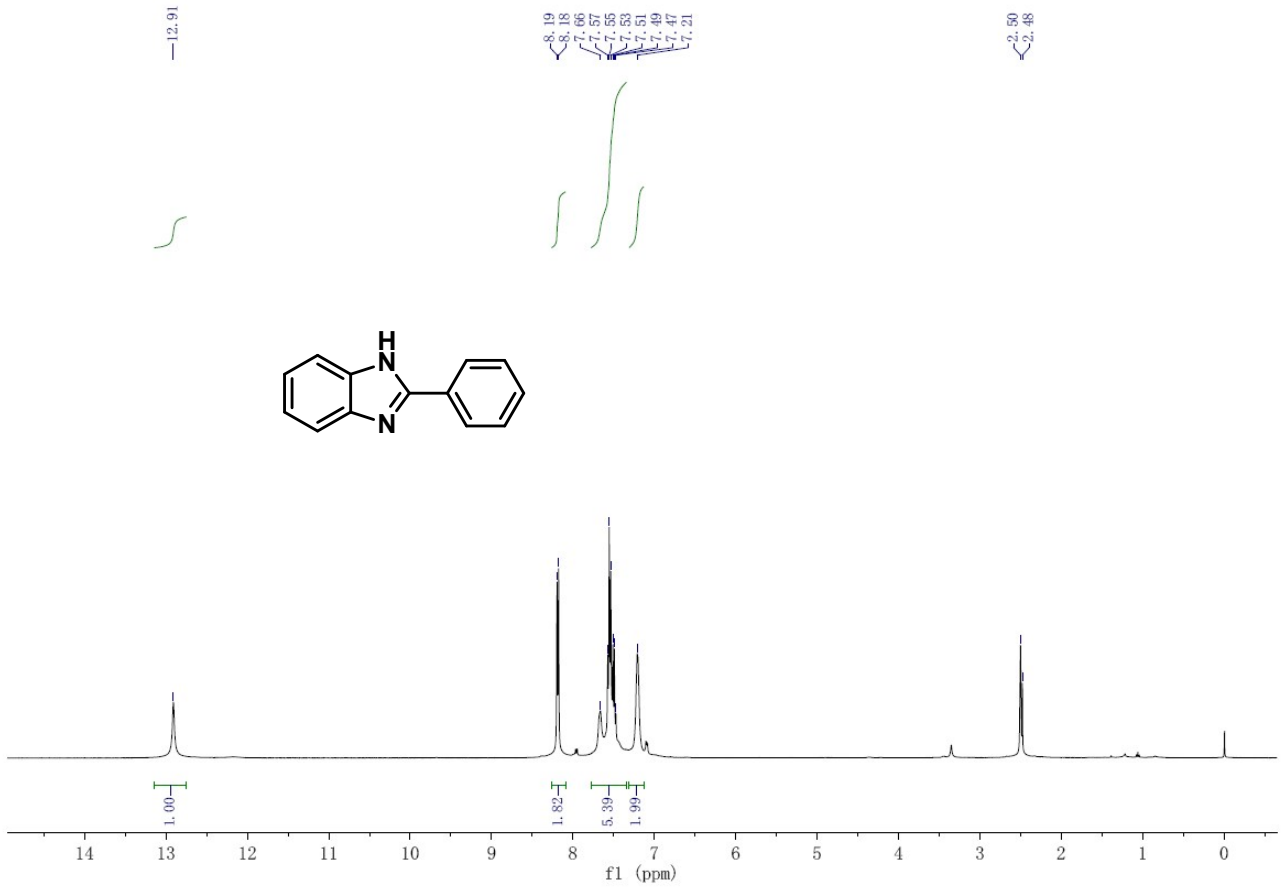
37.03
26.83
7.51
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.51
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7.47
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2.50
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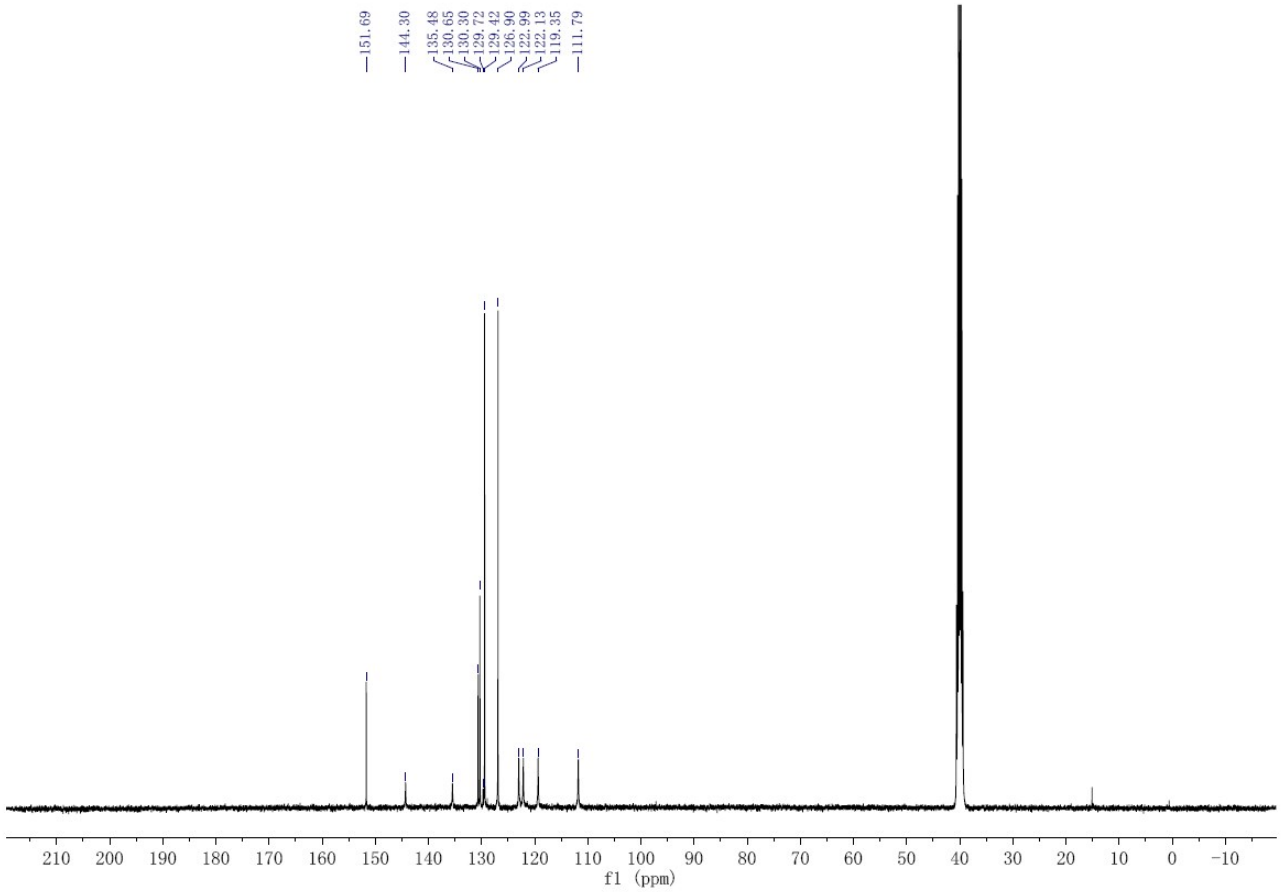
1.00
1.82
5.39
1.99
f1 (ppm)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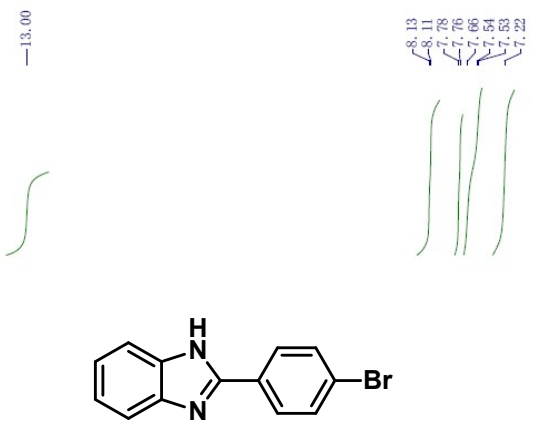
122.99
122.13
119.35
111.79
f1 (ppm)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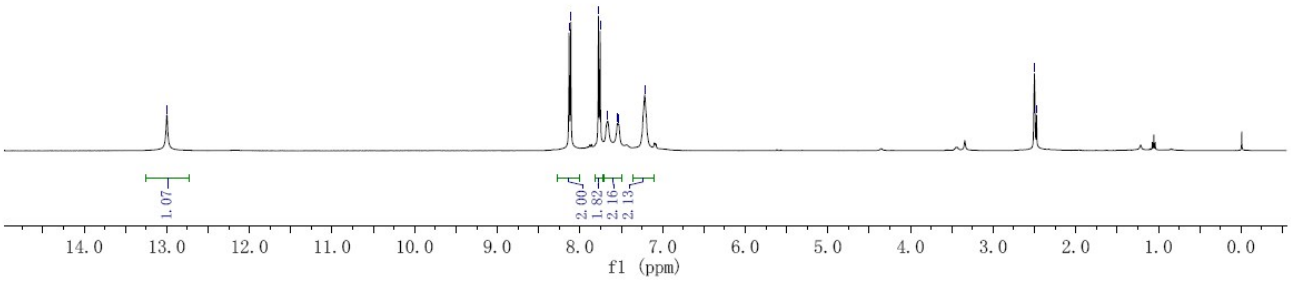
7.76
7.66
7.54
7.53
7.22
2.50
2.47
H
N
N
Br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2.00
1.82
2.16
2.13
14.0
13.0
12.0
11.0
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9.0
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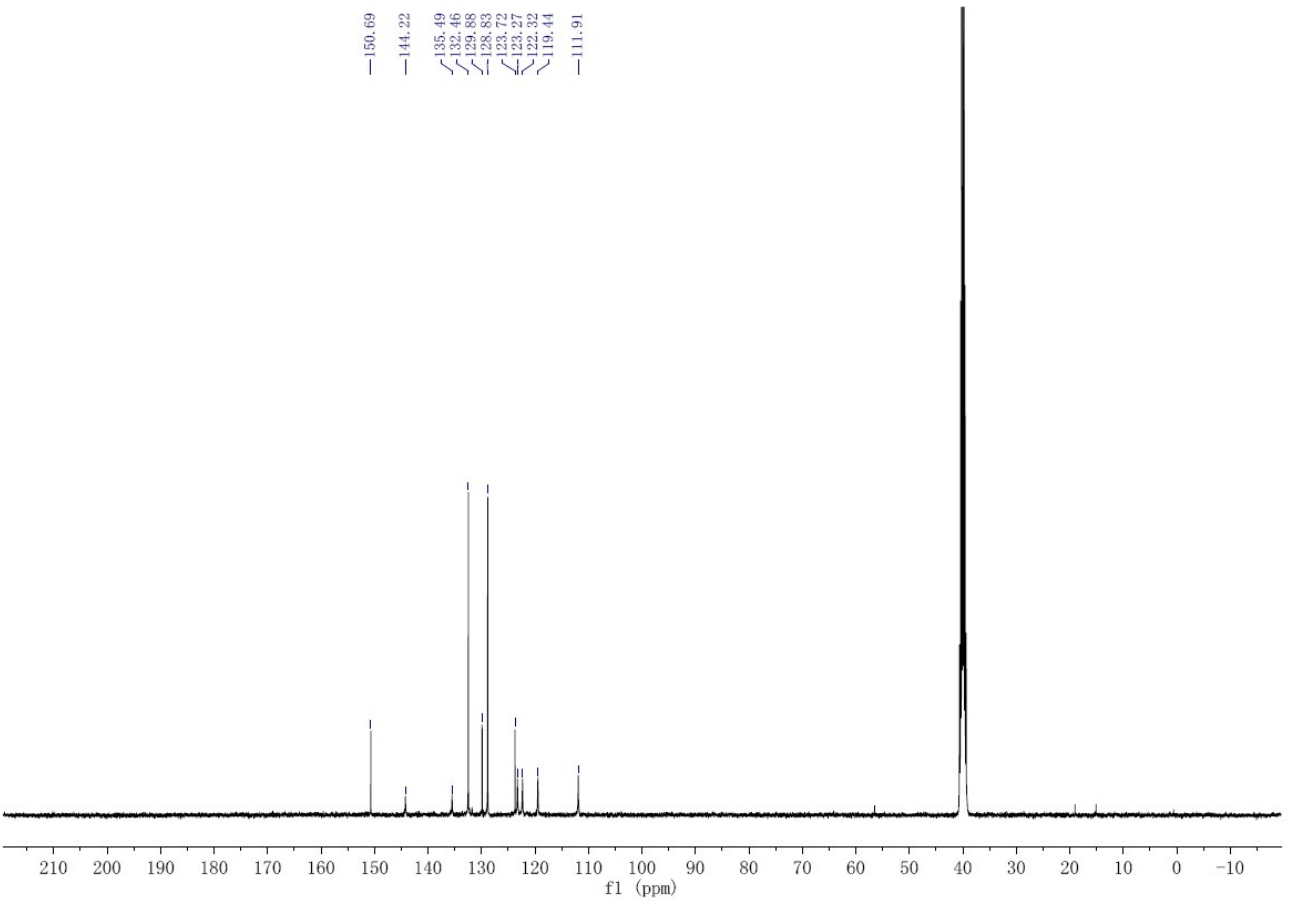
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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200
190
180
170
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100
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80
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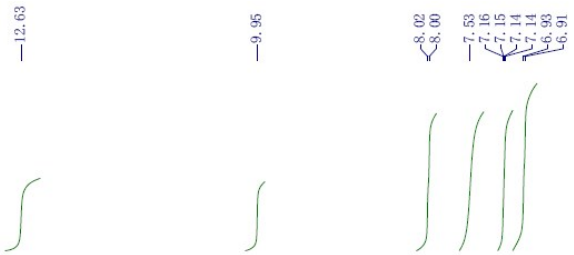
40
30
20
10
0
-10
f1 (ppm)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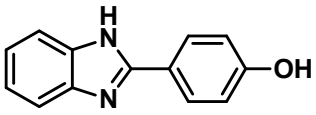
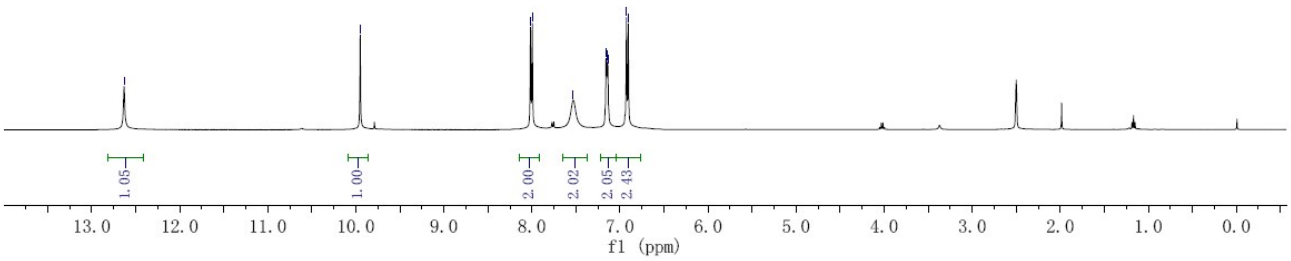
7.14
6.93
6.91


H
N
N
OH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1.00
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2.05
2.43
13.0
12.0
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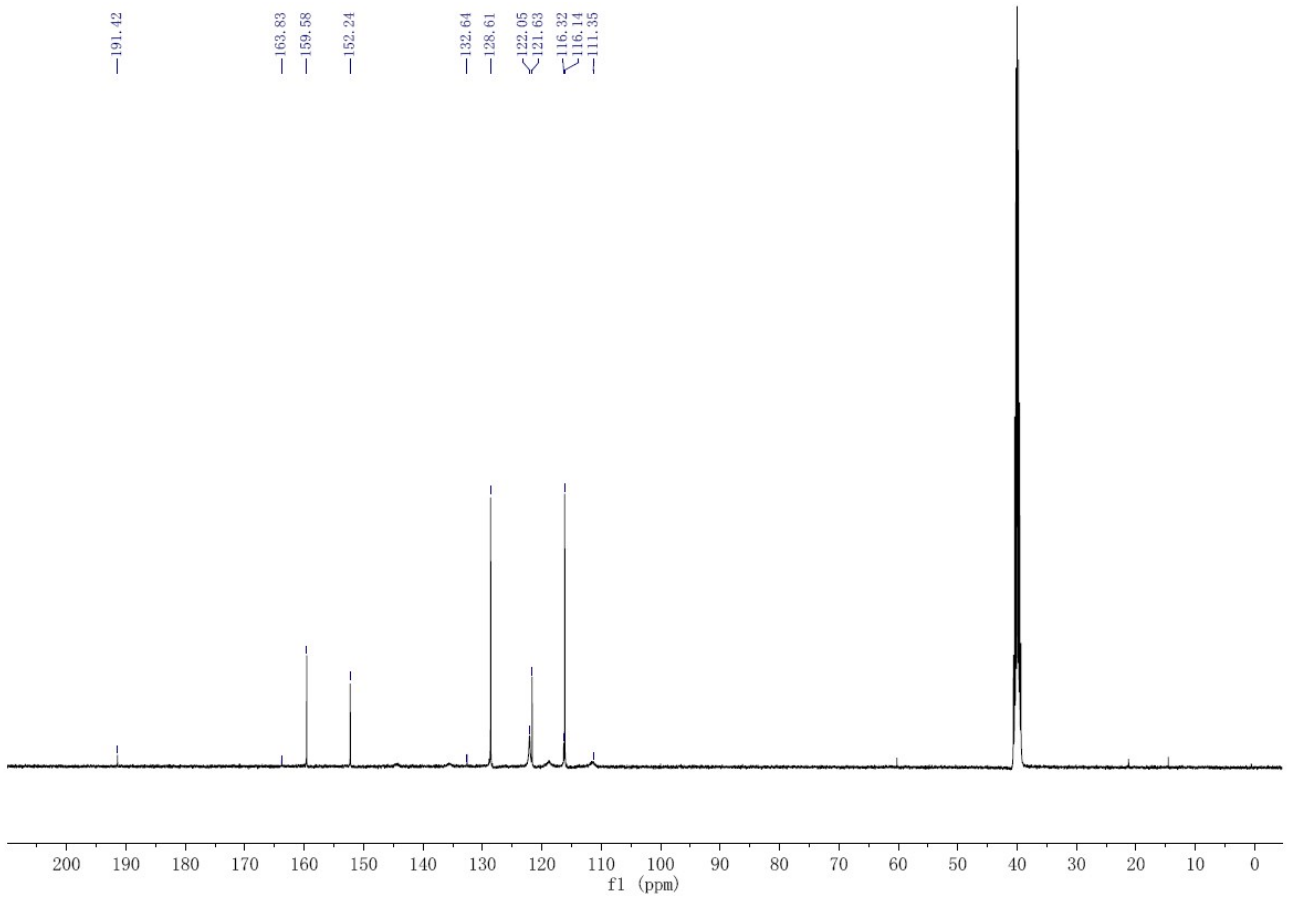
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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121.63
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116.14
111.35
200
190
180
170
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120
110
100
90
80
70
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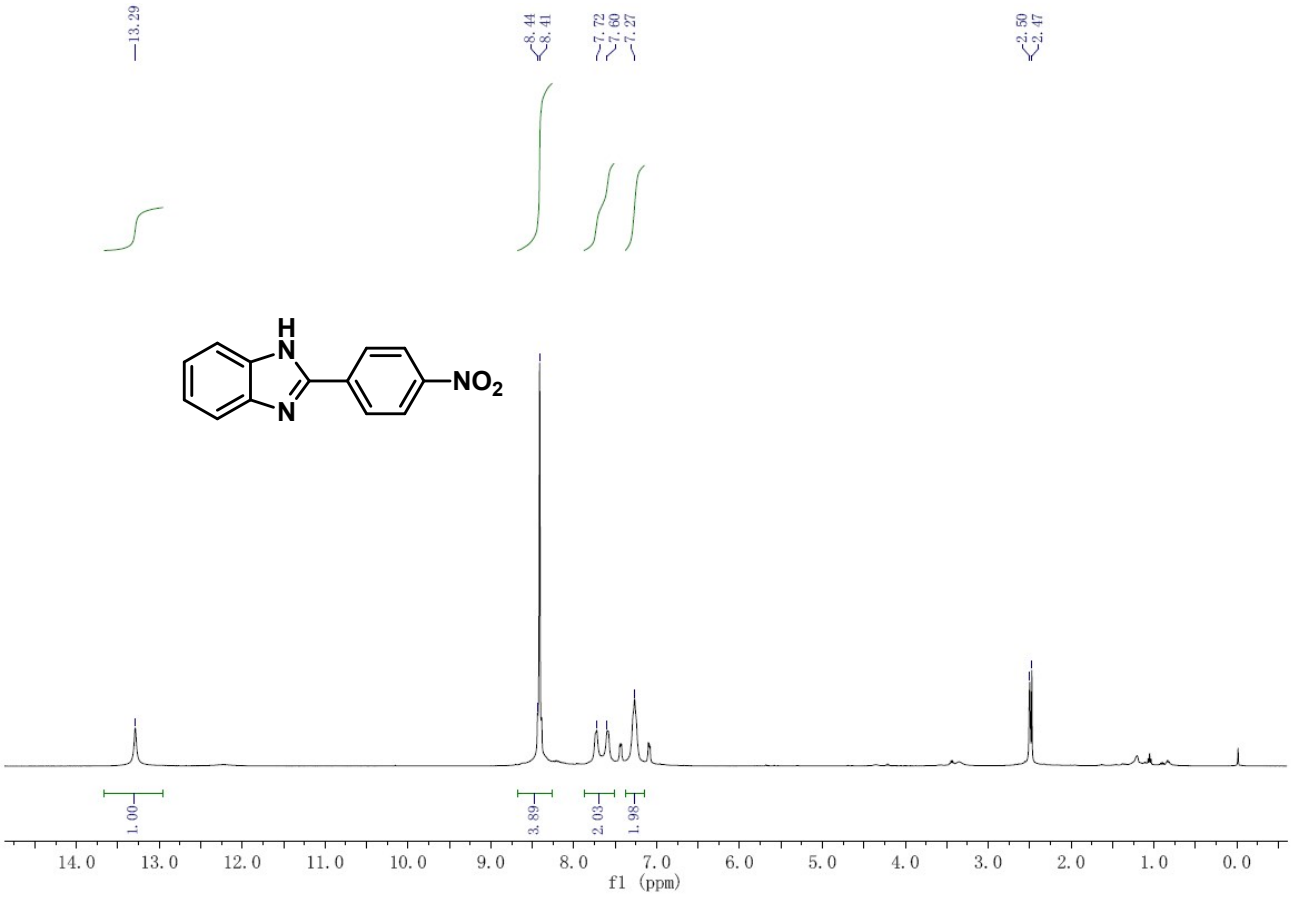
50
40
30
20
10
0
f1 (ppm)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2.50
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N
N
NO2
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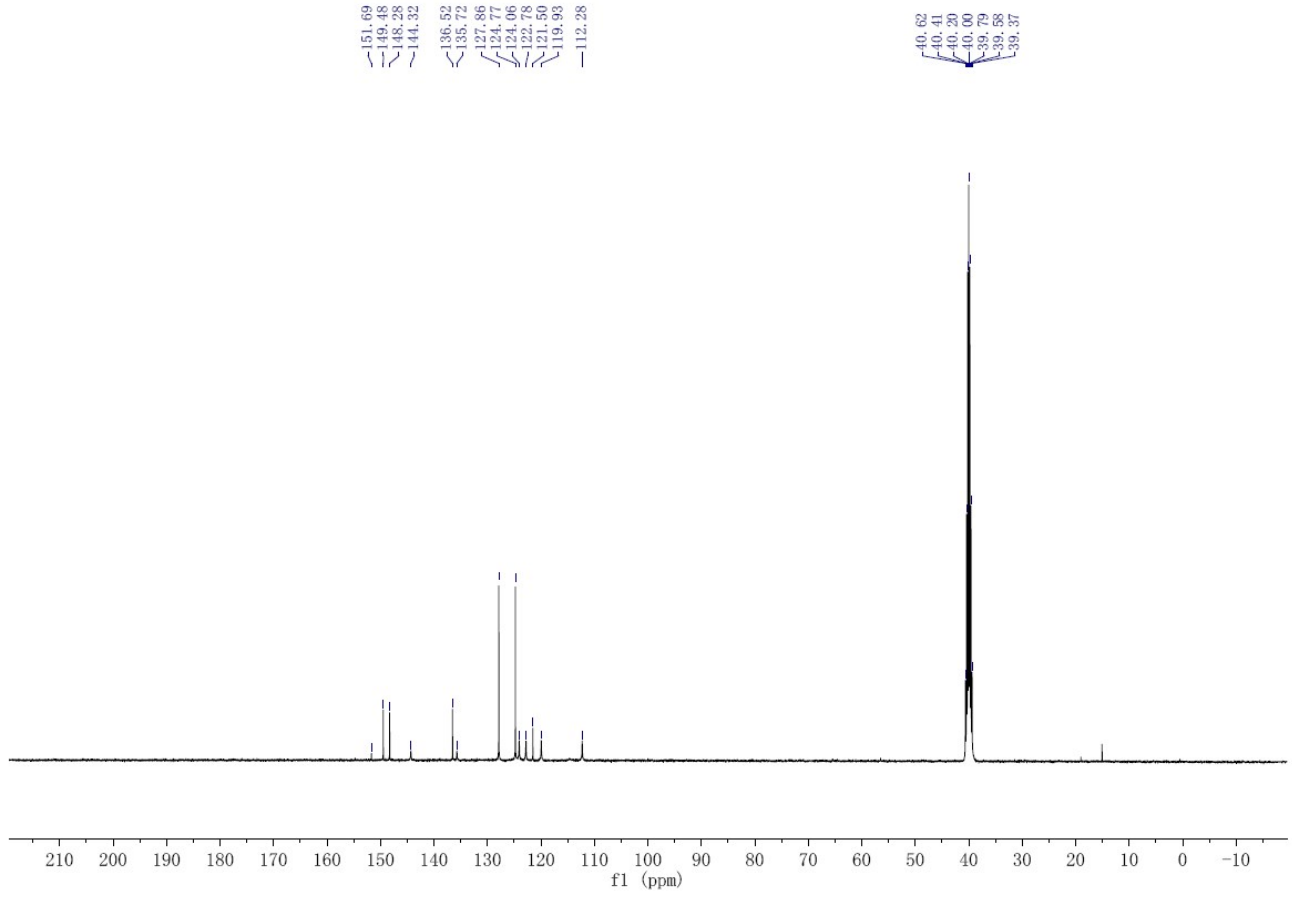
3.89
2.03
1.98
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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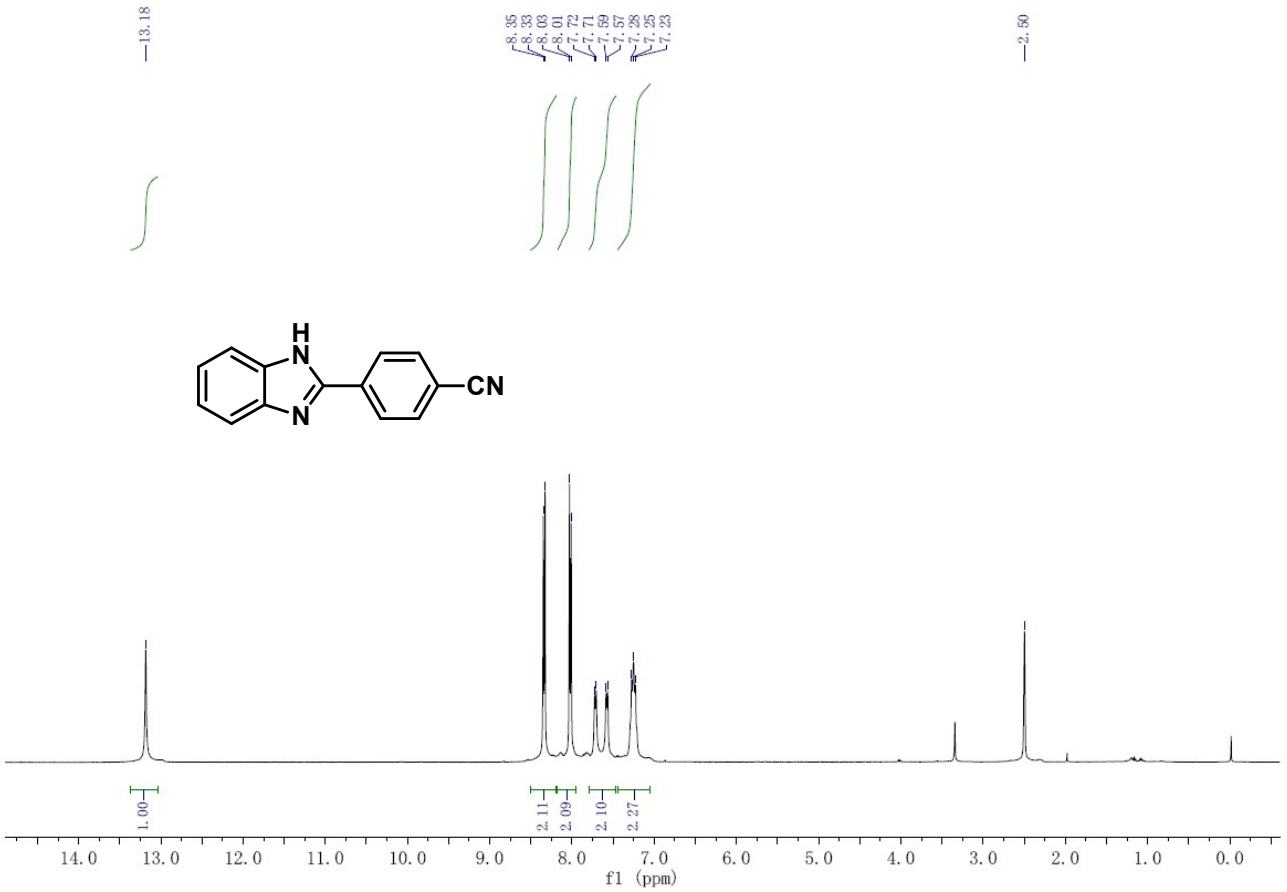
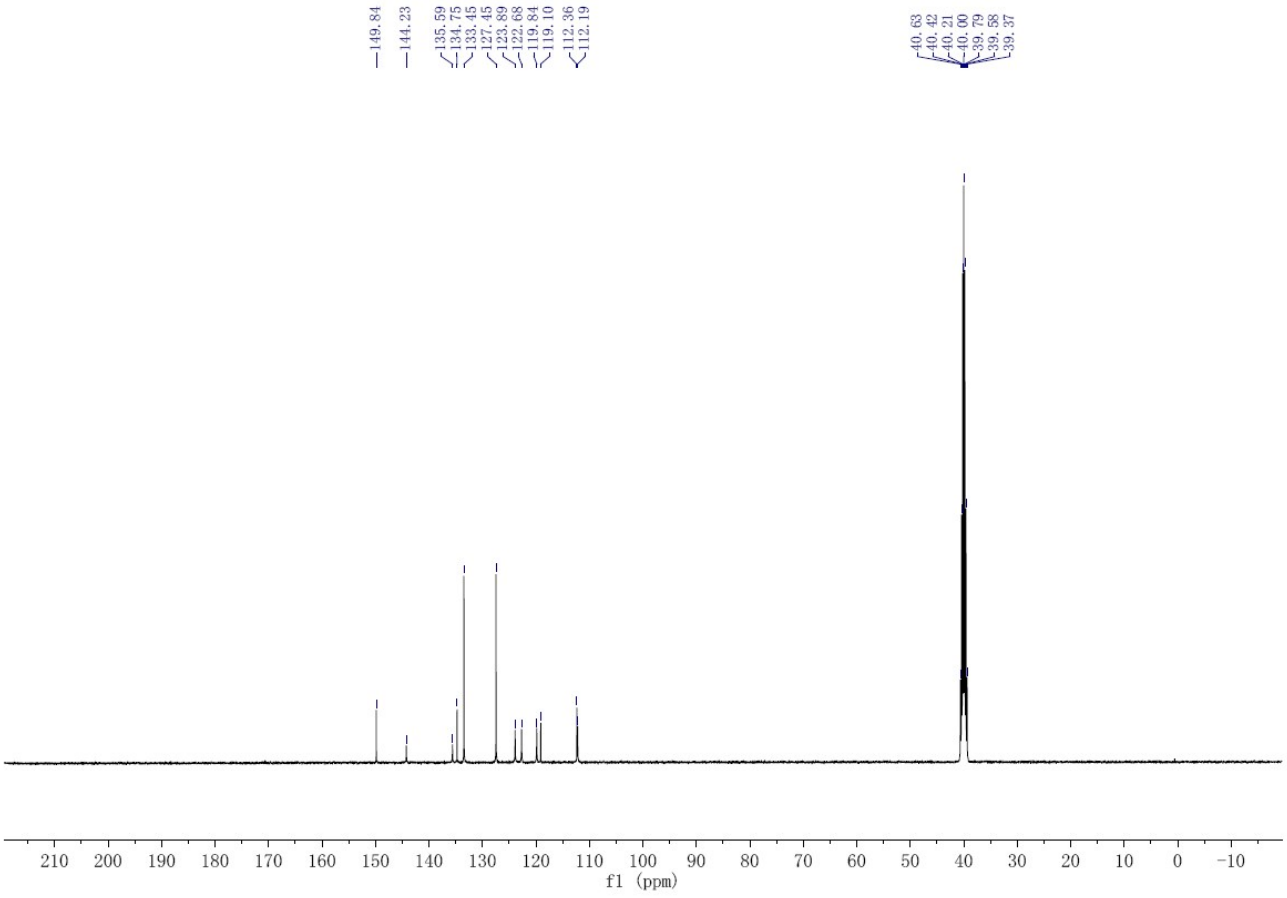
149.48
148.28
144.32
136.52
135.72
127.86
124.77
124.06
122.78
121.60
119.93
112.28
40.62
40.41
40.20
40.00
39.79
39.58
39.37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


13.18
8.35
8.33
8.03
8.01
7.72
7.71
7.59
7.57
7.28
7.25
7.23
2.50
H
N
N
CN
1.00
2.11
2.09
2.10
2.27
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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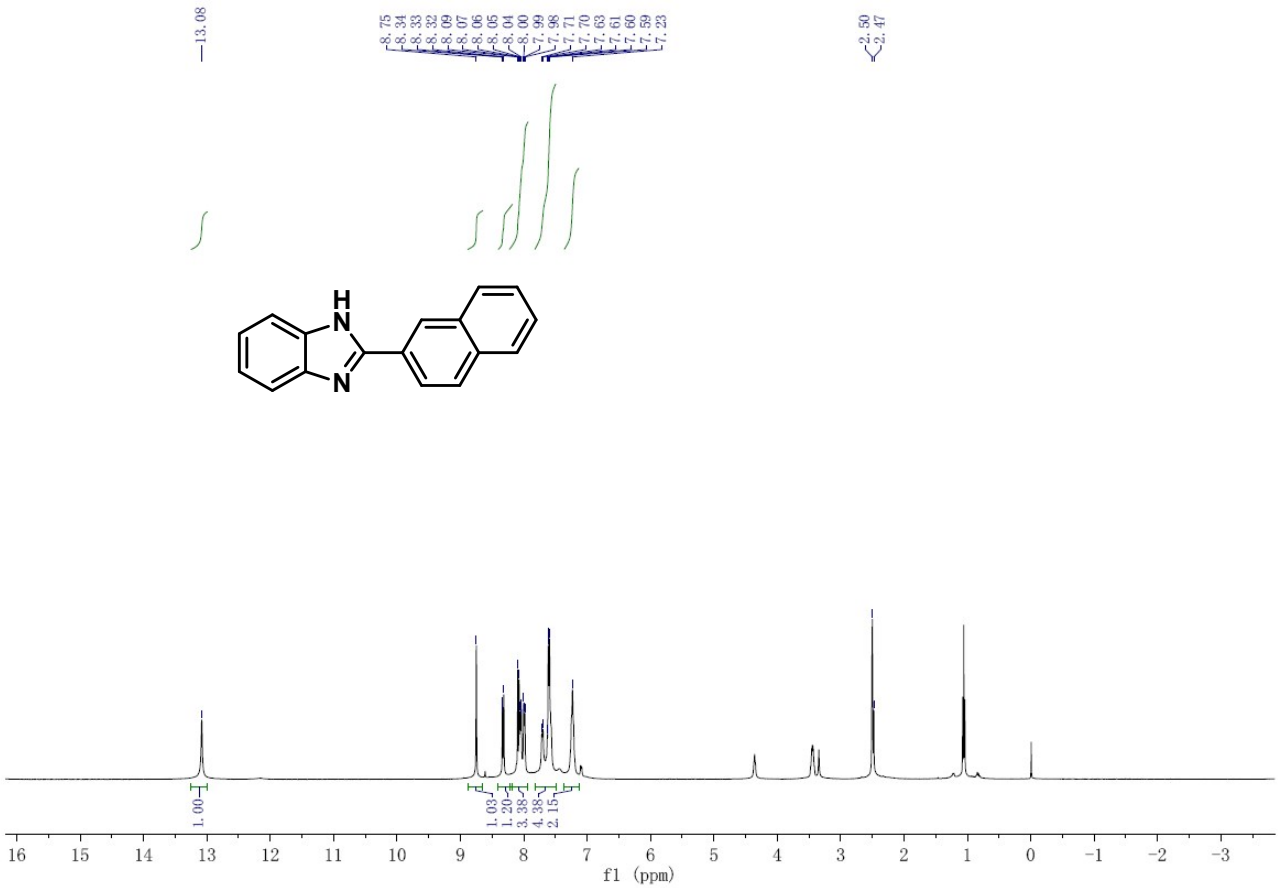
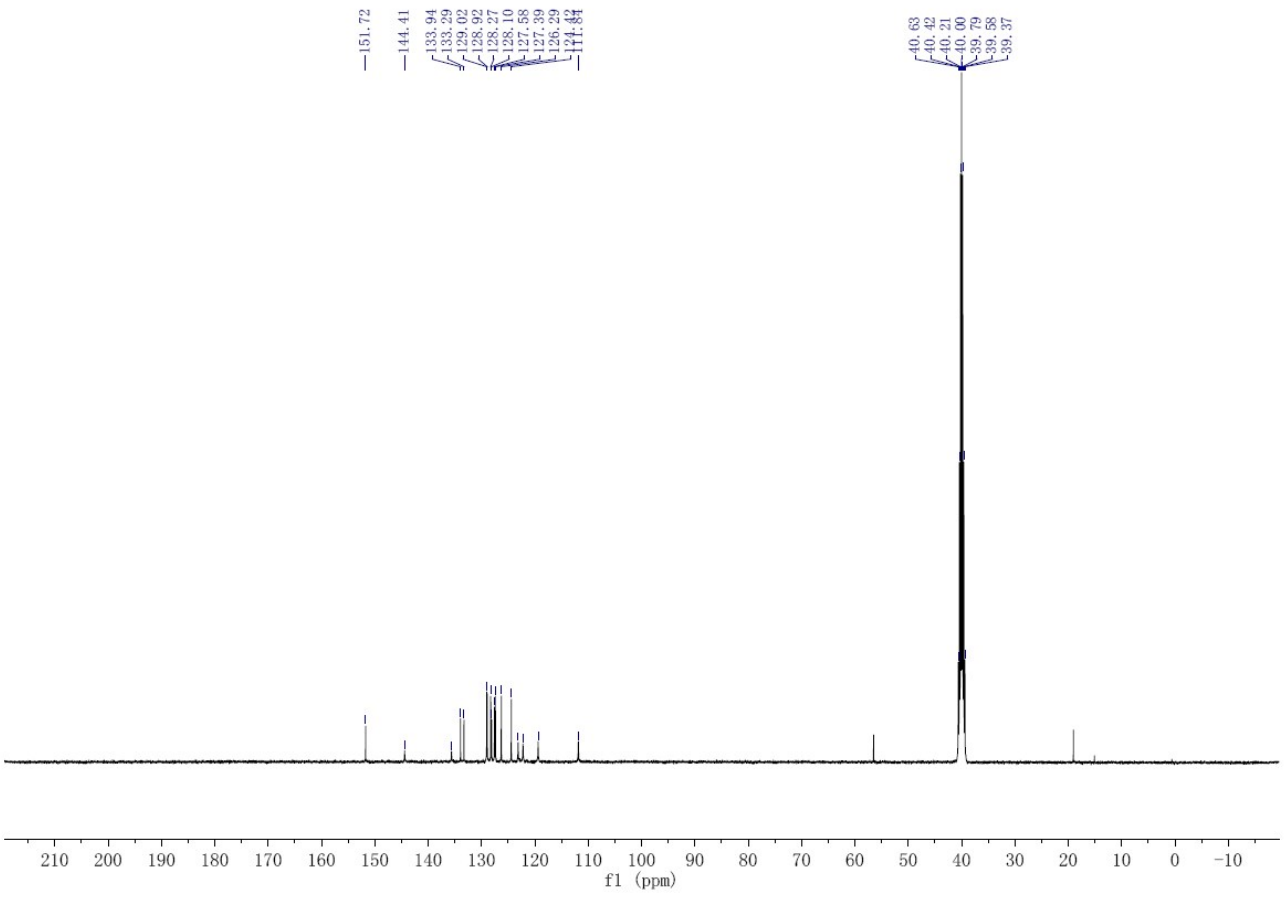
144.23
135.59
134.75
133.45
127.45
123.89
122.68
119.84
119.10
112.36
112.19
40.63
40.42
40.21
40.00
39.79
39.58
39.37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


13.08
8.75
8.34
8.33
8.32
8.09
8.07
8.06
8.05
8.04
8.00
7.99
7.98
7.71
7.70
7.63
7.61
7.60
7.59
7.23
2.50
2.47
H
N
N
1.00
1.03
1.20
3.38
4.38
2.15
f1 (ppm)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144.41
133.94
133.29
129.02
128.92
128.27
128.10
127.58
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126.29
124.42
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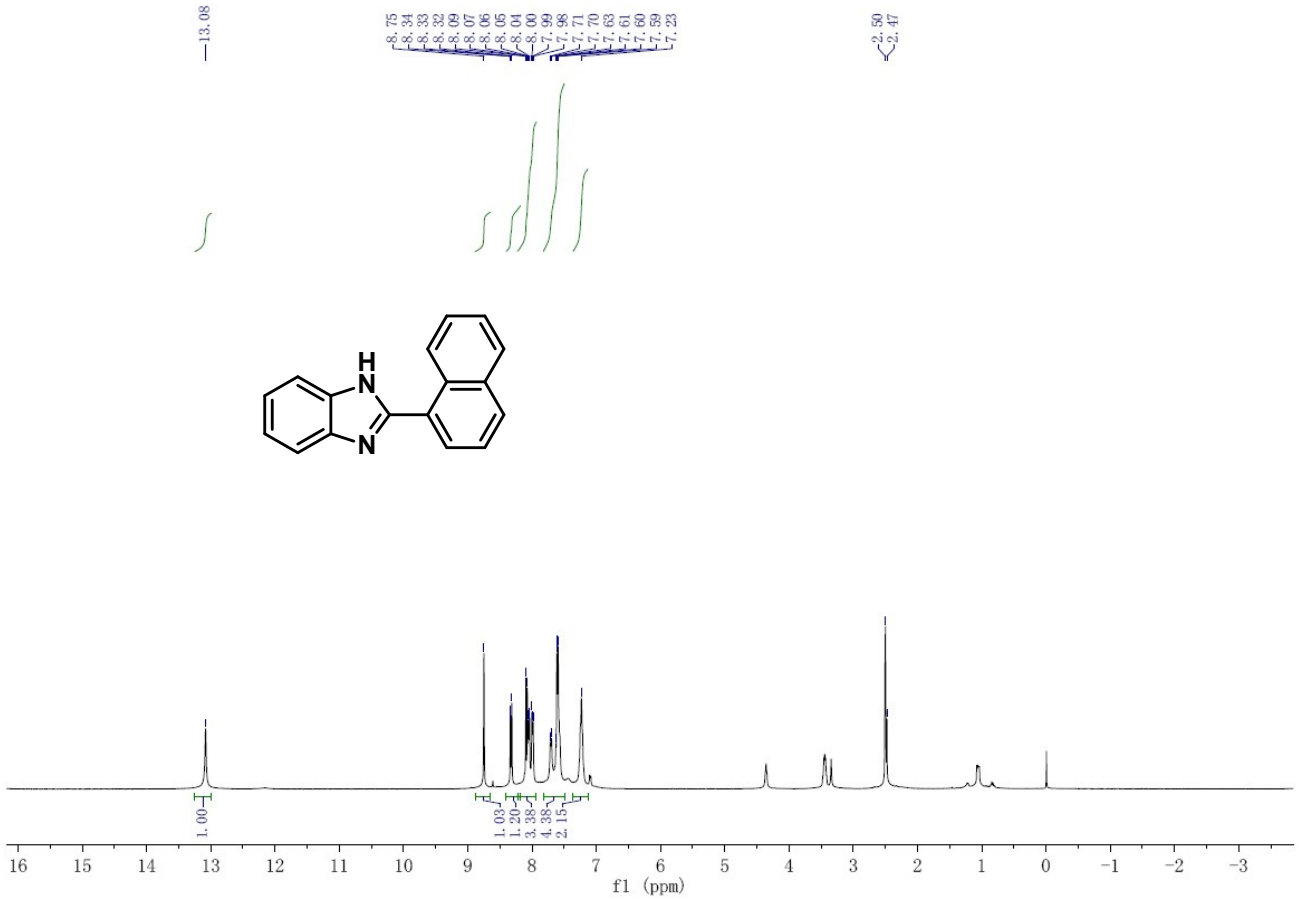
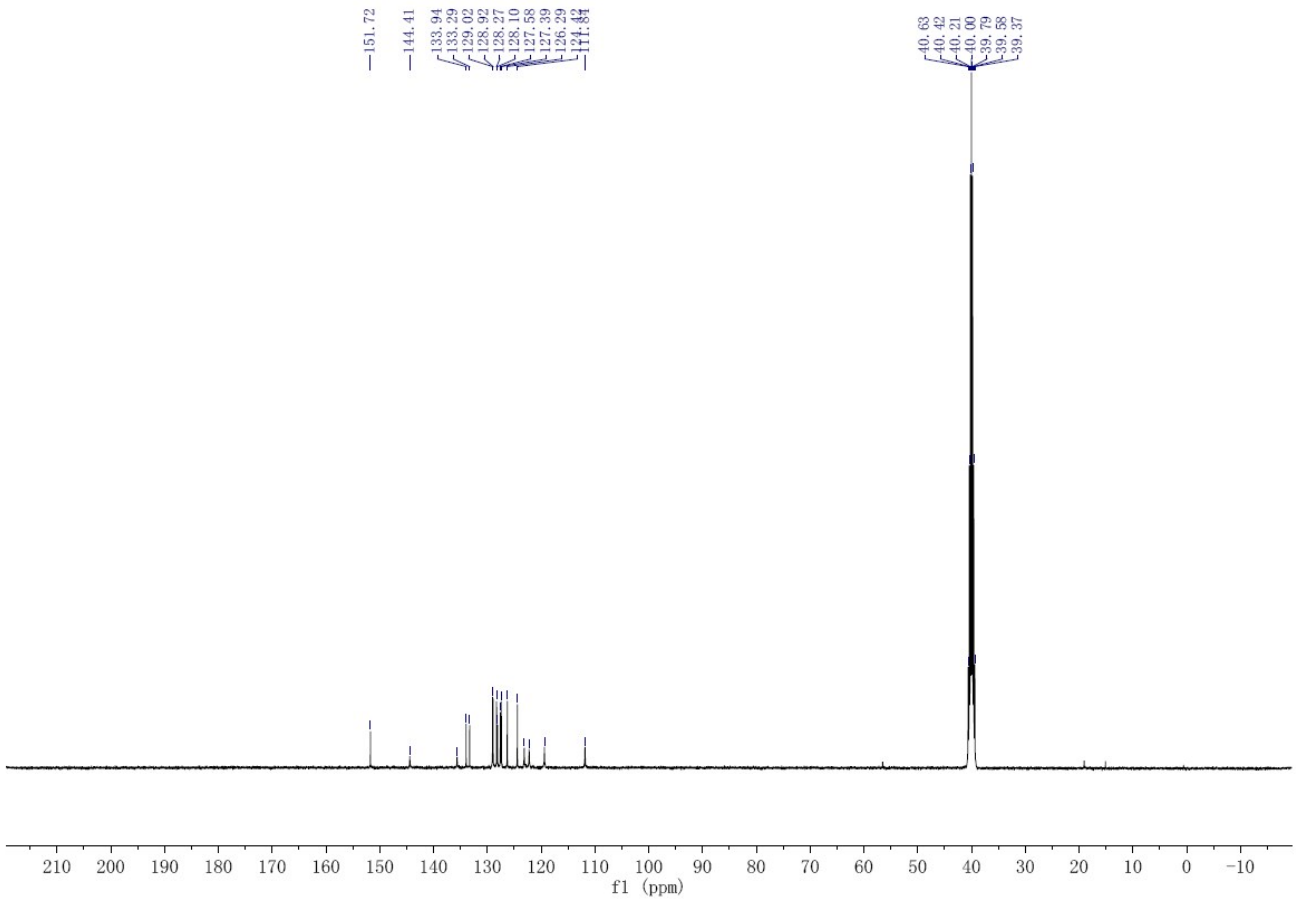
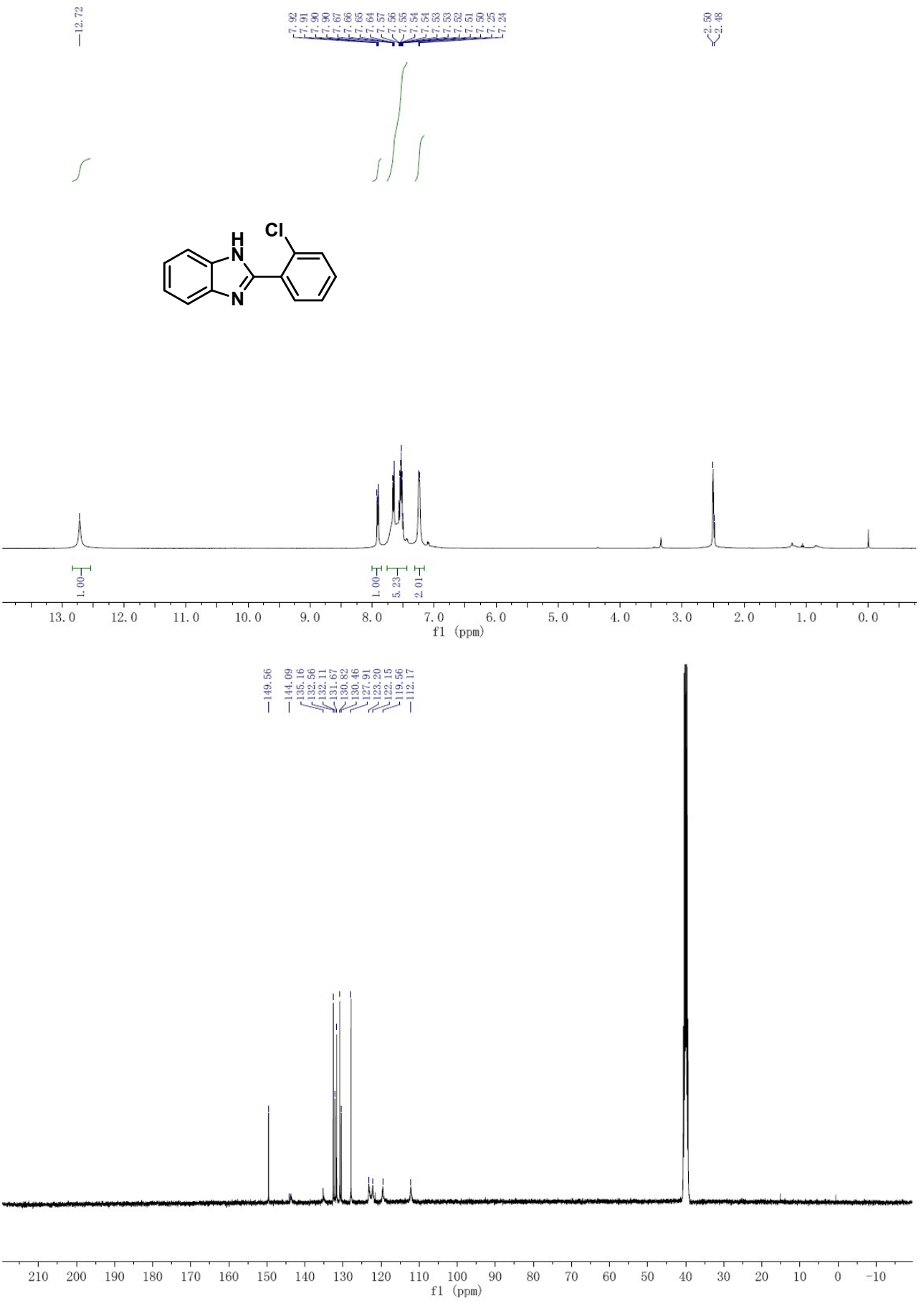
40.00
39.79
39.58
39.37
f1 (ppm)


13.08
8.75
8.34
8.33
8.32
8.09
8.07
8.06
8.05
8.04
8.00
7.99
7.98
7.71
7.70
7.63
7.61
7.60
7.59
7.23
2.50
2.47
H
N
N
1.00
1.03
1.20
3.38
4.38
2.15
f1 (ppm)


151.72
144.41
133.94
133.29
129.02
128.92
128.27
128.10
127.58
127.39
126.29
124.42
111.84
40.63
40.42
40.21
40.00
39.79
39.58
39.37
f1 (ppm)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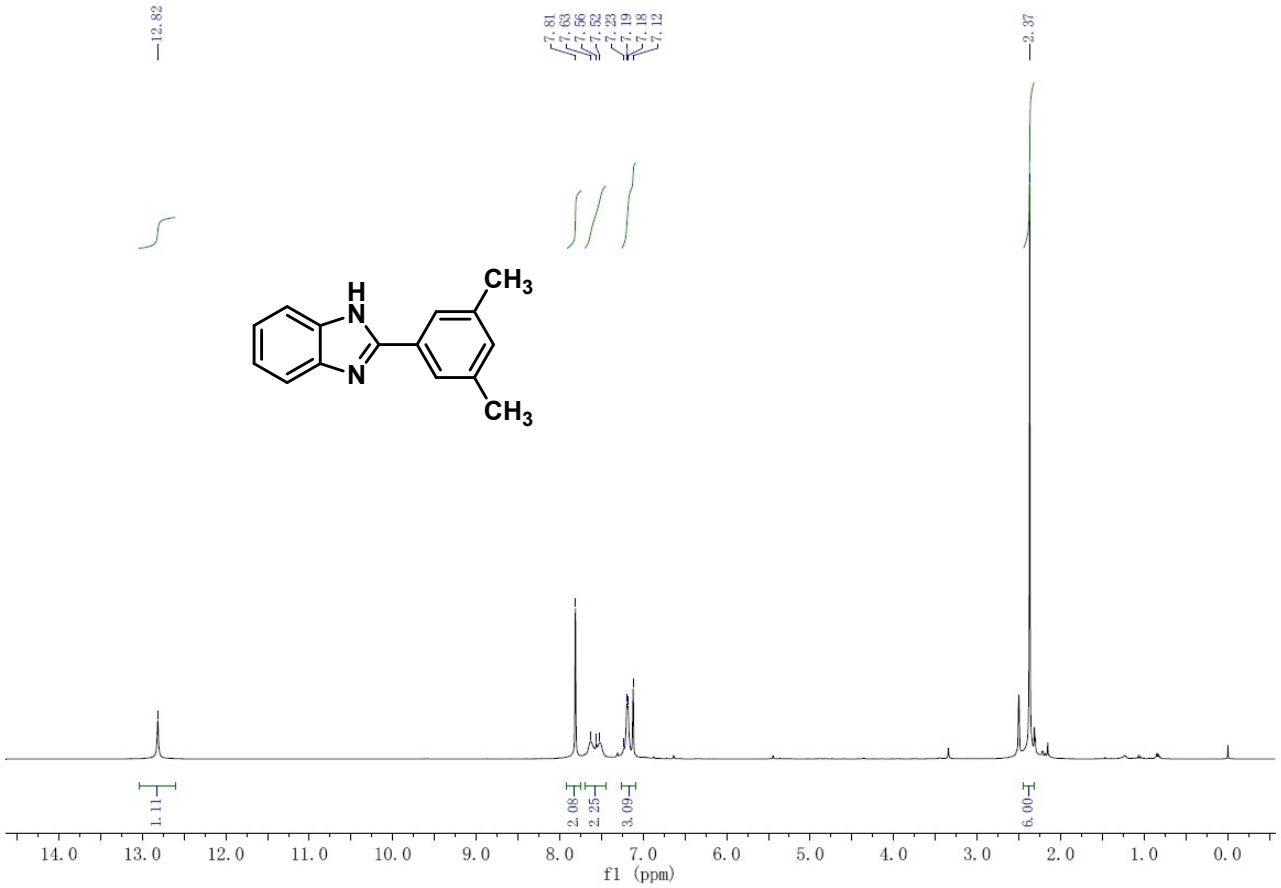
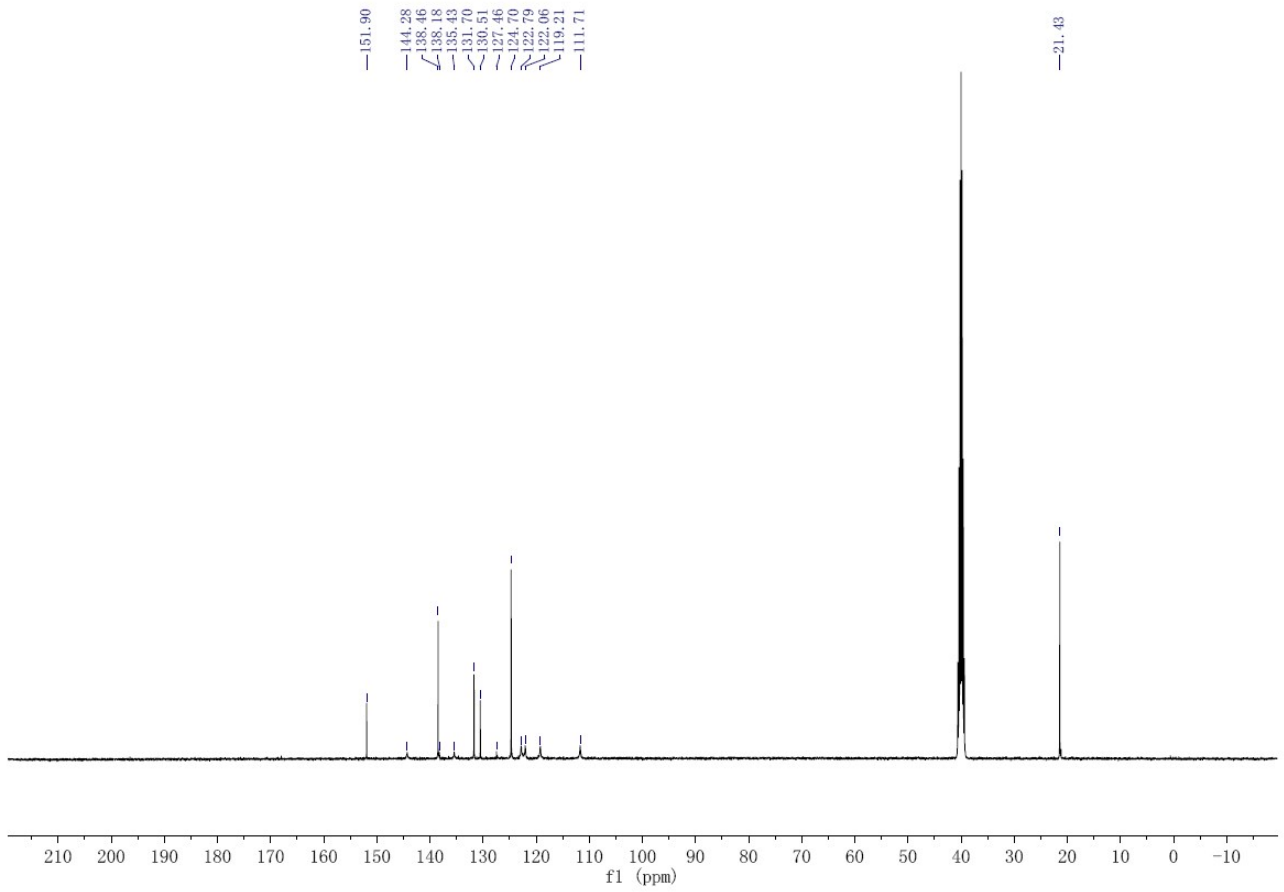
7.91
7.90
7.90
7.67
7.66
7.65
7.64
7.57
7.56
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.50
7.25
7.24
2.50
2.48
Cl
H
N
N
1.00
1.00
5.23
2.01
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
149.56
144.09
135.16
132.56
132.11
131.67
130.82
130.46
127.91
123.20
122.15
119.56
112.17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


12.82
7.81
7.63
7.56
7.52
7.23
7.19
7.18
7.12
2.37
H
N
N
CH3
CH3
1.11
2.08
2.25
3.09
6.00
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


151.90
144.28
138.46
138.18
135.43
131.70
130.51
127.46
124.70
122.79
122.06
119.21
111.71
21.43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)