Electronic Supplementary Information (ESI)

Organic sponge photocatalysis

Xingrong Li, Yaoyao Li, Yuxing Huang, Teng Zhang, Yizhen Liu, Bo Yang, Chuanxin He, Xuechang Zhou and Junmin Zhang*

College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, 518060, P. R. China
E-mail: zhangjm@szu.edu.cn

Index of Contents

I. General Information

All commercially available materials were purchased from Alfa Aesar or Aladdin without further purification. Proton and carbon NMR spectra were recorded on Varian 400 spectrometer using $CDCl_3$ as a solvent. Chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.0 ppm), or with the solvent reference relative to TMS employed as an internal standard ($CDCl_3$, δ 7.26 ppm). The following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad and all combinations thereof can be explained by their integral parts. High resolution mass spectral analysis (HRMS) was performed on AB SEIX TOF/TOF™ 5800 System. SEM images were measured and analyzed on a scanning electron microscope (Hitachi S-3400N). All of the photocatalytic reactions were conducted using a green light-emitting diode (LED belt, 12 W) as the visible-light source.

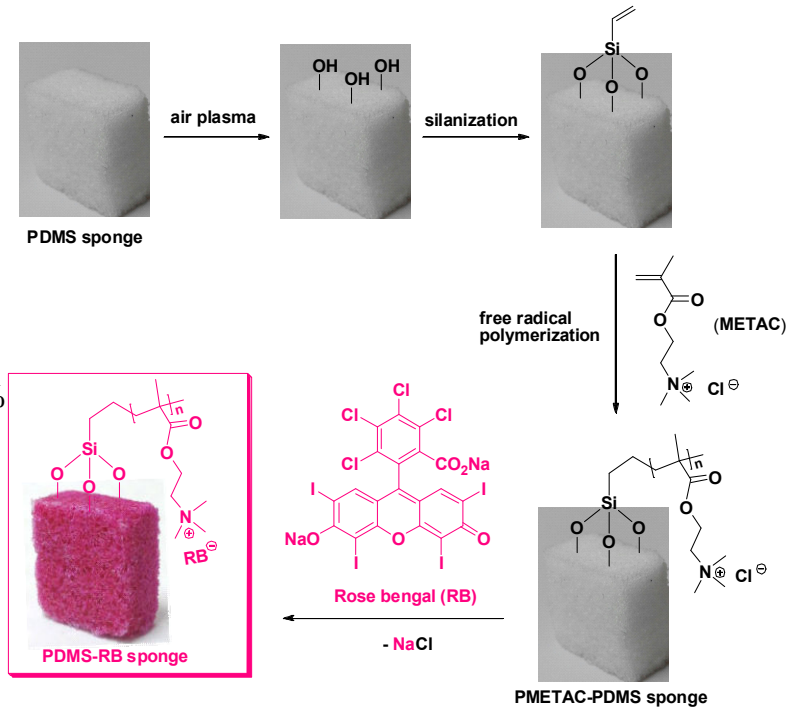
II. Preparation of PDMS-RB sponge photocatalyst

II-1. Fabrication of poly(dimethlysiloxane) (PDMS) sponge[S1]

Sugar cubes were used as template for preparing the PDMS sponges. Subsequently, PDMS prepolymer and curing agent at a weight ratio of 10:1 (Sylgard 184, Dow Corning Corporation, Midland, MI, USA) were used to immerse the cube sugars, followed by degassing in a vacuum for 2 h. The mixture infiltrated into the sugar cubes. After curing at 60 °C atmospheric conditions for 3 h, PDMS on the surface of the sugar template was excised out to expose the sugar. The sugar was then dissolved in water and washed away at 60 °C under stirring. Finally, PDMS sponges were obtained after drying at 60 °C atmospheric conditions for 10 h.

II-2. Preparation of PDMS-RB sponge photocatalyst

After air plasma treatment for 7 min to drive the surface of PDMS sponges hydrophilic, PDMS sponges were immersed in a 2% (v/v) VTMS ethanol solution (pH = 4) for 1 h to allow the reaction of silane molecules with hydroxyl groups on the surface of PDMS sponges. The VTMS-modified PDMS sponges were then immersed in a 10% (v/v) METAC aqueous solution under stirring for 3 h at 80 °C to carry out the free-radical polymerization on the surface of sponges using potassium persulfate (KPS) as initiator. As a result, PMETAC-PDMS sponges were obtained. Then, PMETAC-PDMS sponges were immersed in 50 mg/mL RB H_2O/EtOH solution (V_{H2O}:V_{EtOH}=1:1) and stirred for overnight. The sponges were washed with water to remove the unreacted RB until the water was colorless, then they were transferred to the vacuum dry oven at 50℃ for 12h to get the final product PDMS-RB sponge catalyst.

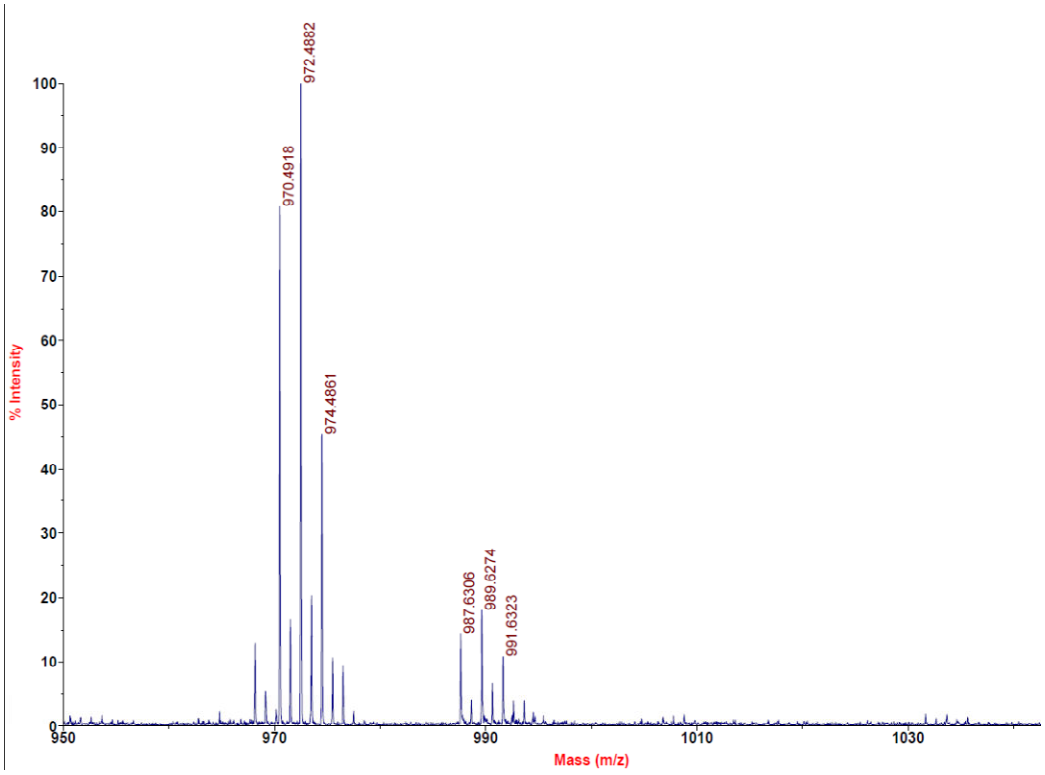


II-3. Quantification of RB loading in PDMS-RB sponge photocatalyst

To 0.2 g PDMS-RB sponge, 1mL trifluoroacetic acid (TFA) was added to degrade the sponge and a pink precipitate was formed. The mixture was then centrifuged to separate the supernatant and the precipitate. The supernatant was proved to be RB free by UV-Vis spectroscopy. On the other hand, the proton NMR of the precipitate was identical to the acid form of RB in $CDCl_3$. Therefore the RB loading in PDMS-RB sponge can be quantified by ^{1}H NMR spectroscopy. The loading of RB in PDMS-RB sponge used in this study was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard and the results show that the RB loading on PDMS-RB sponge is 0.01 mmol/g.

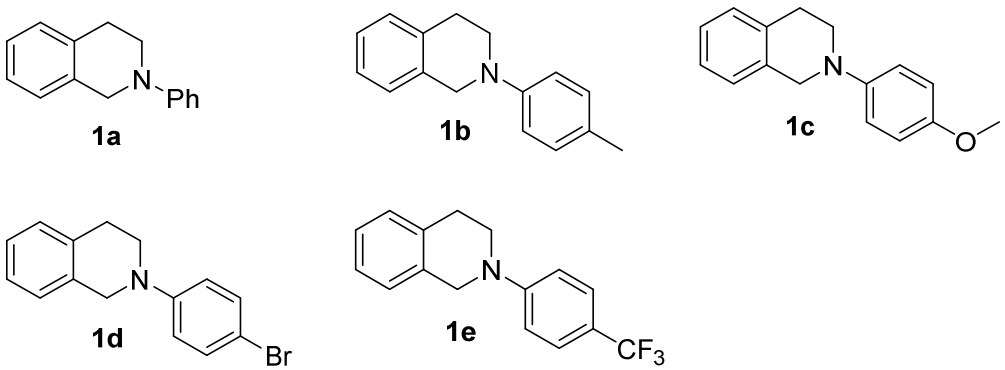
II-4. Identification of RB fragment in PDMS-RB sponge photocatalyst

The PDMS-RB sponge was degraded by trifluoroacetic acid (TFA) and a pink precipitate was formed. The mixture was then centrifuged to collect the precipitate. The precipitate was then dissolved in methanol and mixed with CHCA MALDI matrix. After that, the mixture was subjected to high resolution mass spectral analysis with MALDI-TOF/TOF under negative and reflector mode. **HRMS** *m/z*: calcd for $C_{20}H_3Cl_4I_4O_5^-$ $[M-H]^-$: 972.4889, Found 972.4882.



Ⅲ. Synthesis of the substrates and the sponge photocatalytic CDC reactions

III-1. Synthesis of the substrates



The substrates **1a-e** were synthesized according to literature procedures[S2,S3,S4]. A typical procedure is described as following for the synthesis of **1a**:

To a Schlenk tube, copper (I) iodide (1.0 mmol, 200 mg) and potassium phosphate (20.0 mmol, 4.25 g) were added. The tube was then evacuated and back filled with nitrogen for three times. After that, 2-propanol (10.0 mL), ethylene glycol (20.0 mmol, 1.1 mL), 1,2,3,4-tetrahydroisoquinoline (15 mmol, 2.0 mL) and 4-iodotoluene (10.0 mmol, 1.2 mL) were added successively via syringe at room temperature. The reaction mixture was heated at 85 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were added, and the aqueous layer was extracted by diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed via rotary evaporation, and the remaining residue was purified via column chromatography on silica gel (hexane/ethyl acetate=20:1) to give the desired product.

III-2. CDC reaction of N-phenyl-tetrahydroisoquinoline derivatives and nitroalkanes

To a 10 mL test tube equipped with a magnetic stirring bar was charged with N-phenyl-tetrahydroisoquinoline **1a** (0.1 mmol, 21 mg), nitromethane (1.0 mmol, 54 μL), 2 mol% PDMS-RB and 2 mL EtOH. After sealed with rubber cap, the reaction mixture was stirred at room temperature with the irradiation of a 12 W green LED belt for 24 h. PDMS-RB sponge was then grabbed out of the reaction mixture and washed with 5 mL EtOH for three times. The EtOH solution was combined with reaction solution and transferred to a 50 mL round bottom flask for evaporation to dry the solvent. The remaining residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate=3:1) to give the desired product.

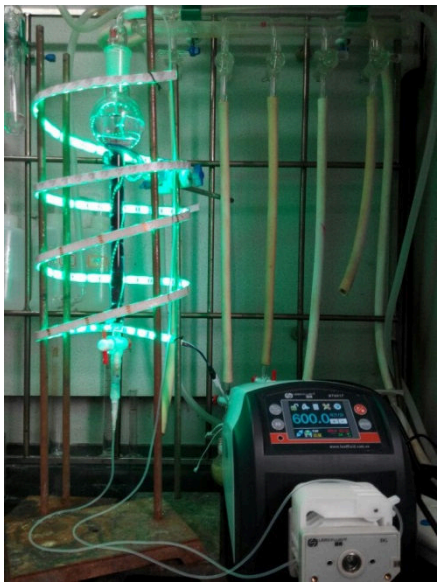
III-3. CDC reaction of N-phenyl-tetrahydroisoquinoline derivatives and acetone

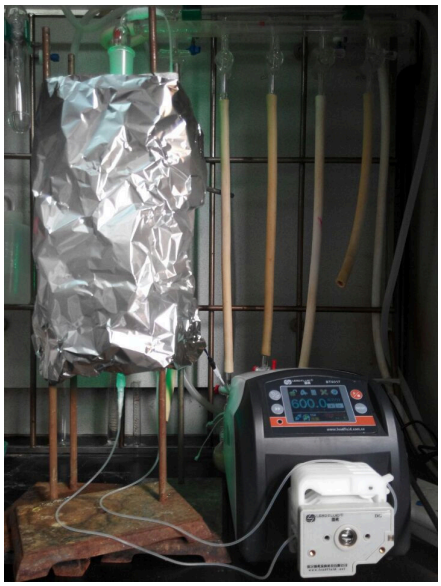
To a 10 mL test tube equipped with a magnetic stir bar was charged with N-phenyl-tetrahydroisoquinoline derivatives (0.1 mmol), 30 mol% pyrrolidine/TFA, acetone (2 mL), PDMS-RB 0.2 g (2 mol %). After sealed with rubber cap, the reaction mixture was stirred at room temperature with the irradiation of a green LED belt for 24 h. The reaction solution was transferred to a 50 mL round bottom flask, after that the PDMS-RB sponge was washed with ethyl acetate 3*5 mL. After combining the solutions, the solvent was removed via rotary evaporation, and the remaining residue was purified by column chromatography.

III-4. CDC reaction of N-phenyl-tetrahydroisoquinoline derivatives and ethyl diazoacetate

To a 10 mL test tube equipped with a magnetic stirring bar was charged with N-phenyl-tetrahydroisoquinoline derivatives (0.1 mmol) and 2 mol% PDMS-RB, ethyl diazoacetate (1.0 mmol) and 1 mL of CH_2Cl_2. After sealed with rubber cap, the reaction mixture was stirred at room temperature under 1 atm of O_2 with the irradiation of a 12 W green LED belt for 24 h. The reaction solution was transferred to a 50 mL round bottom flask, after that the PDMS-RB sponge was washed with ethyl acetate 3*5 mL. After combining the solutions, the solvent was removed via rotary evaporation, and the remaining residue was purified by column chromatography.

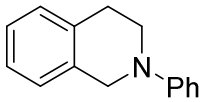
Ⅳ. Gram scale reaction between N-phenyl tetrahydroisoquinoline and nitromethane





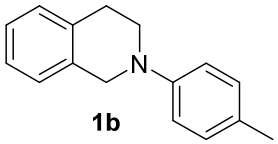
A continuous flow reactor was built up by connecting a peristaltic pump with a glass column filled with PDMS-RB sponge catalyst (6.7 g，1.4 mol%). A green LED belt was wrapped around the column for irradiation. The reaction mixture of N-phenyl tetrahydroisoquinoline (1.0 g, 4.78mmol), nitromethane (2.6 mL, 47.8mmol) and ethanol (40 mL) as solvent was added into the column before the system was tightly sealed (note: the up outlet of silicone tube connecting with peristaltic pump was immersed into the reaction solution). The pump was then started and the reaction was left for running. After 48 h the reaction was stopped the product was isolated by silica gel chromatograph and the yield was 88% (1.136 g).

Ⅴ. ^{1}H and ^{13}C NMR data of substrates and products[S4]



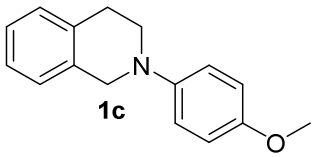
1a

2-phenyl-1,2,3,4-tetrahydroisoquinoline (1a): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.16 – 7.11 (m, 4H), 6.97 – 6.95(d, *J* = 8.0 Hz, 2H), 6.83 – 6.79 (t, *J* = 7.3 Hz, 1H), 4.38 (s, 2H), 3.54 – 3.51 (t, *J* = 5.8 Hz, 2H), 2.96 – 2.93 (t, *J* = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.50, 134.81, 134.41, 129.14, 128.45, 126.48, 126.26, 125.96, 118.60, 115.09, 50.67, 46.46, 29.07.



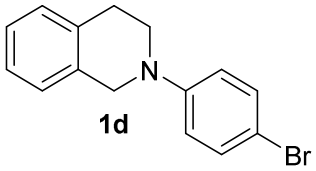
1b

2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (1b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 6H), 7.15 – 7.13 (d, *J* = 8.5 Hz, 2H), 4.56 (s, 1H), 3.71 – 3.68 (t, *J* = 5.8 Hz, 2H), 3.19 – 3.16 (t, *J* = 5.7 Hz, 2H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.47, 134.55, 134.39, 129.55, 128.40, 128.05, 126.36, 126.06, 125.75, 115.65, 51.25, 47.05, 28.95, 20.28.



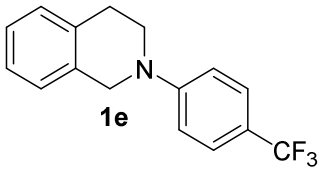
1c

2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (1c): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.09 (m, 4H), 6.96 – 6.94 (d, 2H), 6.86 – 6.83 (d, 2H), 4.26 (s, 2H), 3.74 (s, 3H), 3.42 – 3.39 (t, *J* = 5.8 Hz, 2H), 2.96 – 2.94 (t, *J* = 5.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.40, 145.26, 134.52, 134.44, 128.58, 126.41, 126.15, 125.80, 117.91, 114.48, 55.50, 52.56, 48.33, 29.03.



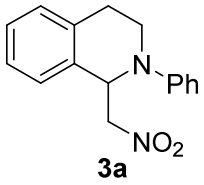
1d

2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (1d): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.28 (d, *J* = 8.7 Hz, 2H), 7.13 – 7.09 (m, 4H), 6.75 – 6.73 (d, *J* = 8.7 Hz, 2H), 4.28 (s, 2H), 3.44 – 3.41 (t, *J* = 5.6 Hz, 2H), 2.90 – 2.84 (t, *J* = 5.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.22, 134.54, 133.86, 131.73, 128.33, 126.37, 126.35, 126.01, 116.27, 110.22, 50.19, 46.08, 28.81.



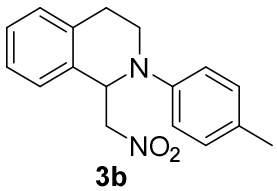
1e

2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (1e): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.16 (d, *J* = 7.5 Hz, 4H), 6.91 – 6.89 (d, *J* = 8.2 Hz, 2H), 4.44 (s, 2H), 3.60 – 3.57 (t, *J* = 5.4 Hz, 2H), 2.97 – 2.95 (t, *J* = 5.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.11, 134.88, 133.78, 128.30, 126.67, 126.47, 126.43, 126.31, 123.63, 118.99 (q, $J_{F\text{-}C}$ = 32.7 Hz), 112.90, 49.37, 45.17, 28.93.



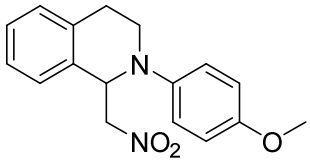
3a

1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.11 (m, 5H), 6.98 – 6.96 (d, *J* = 8.0 Hz, 2H), 6.86 – 6.82(t, *J* = 7.3 Hz, 1H), 5.56 – 5.52(t, *J* = 7.1 Hz, 1H), 4.88 – 4.83 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.57 – 4.52 (dd, *J* = 11.8, 6.6 Hz, 1H), 3.68 – 3.57 (m, 2H), 3.11 – 3.03 (m, 1H), 2.81 – 2.75 (dt, *J* = 16.2, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.40, 135.24, 132.90, 129.47, 129.15, 128.08, 126.96, 126.66, 119.40, 115.09, 78.75, 58.16, 42.05, 26.44.



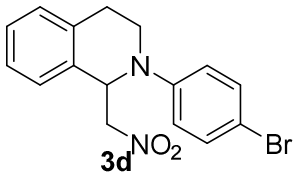
3b

1-(nitromethyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (3b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.05 (m, 6H), 6.88 – 6.86 (d, *J* = 8.5 Hz, 2H), 5.50 – 5.46 (t, *J* = 7.2 Hz, 1H), 4.85 – 4.80 (dd, *J* = 11.8, 8.1 Hz, 1H), 4.55 – 4.51 (dd, *J* = 11.8, 6.3 Hz, 1H), 3.65 – 3.52 (m, 2H), 3.08 – 3.00(m, 1H), 2.76 – 2.69 (dt, *J* = 16.4, 4.4 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.33, 135.29, 132.89, 129.91, 129.22, 129.04, 127.93, 126.91, 126.55, 115.86, 78.76, 58.33, 42.25, 26.17, 20.30.



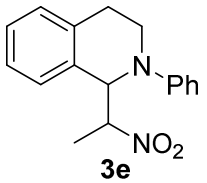
3c

2-(4-methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 4H), 6.92 – 6.90 (d, *J* = 9.0 Hz, 2H), 6.82 – 6.79 (d, *J* = 9.0 Hz, 2H), 5.40 – 5.36 (m, 1H), 4.84 – 4.79 (dd, *J* = 11.9, 8.6 Hz, 1H), 4.57 – 4.52 (dd, *J* = 11.9, 5.8 Hz, 1H), 3.74 (s, 3H), 3.04 – 2.96 (m, 1H), 2.70 – 2.66 (dd, *J* = 12.8, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.94, 143.02, 135.38, 132.85, 129.40, 127.84, 126.86, 126.56, 118.81, 114.67, 78.90, 58.87, 55.5, 43.09, 25.76.



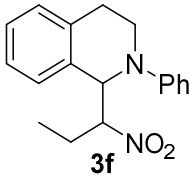
3d

2-(4-bromophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (3d): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.11 (m, 6H), 6.84 – 6.82 (d, *J* = 8.9 Hz, 2H), 5.49 – 5.46 (t, *J* = 7.2 Hz, 1H), 4.85 – 4.80 (dd, *J* = 11.9, 8.1 Hz, 1H), 4.57 – 4.53 (dd, *J* = 11.9, 6.4 Hz, 1H), 3.63 – 3.54 (m, 2H), 3.09 – 3.01 (m, 1H), 2.80 – 2.74(dt, *J* = 16.3, 4.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.45, 134.98, 132.40, 132.17, 129.23, 128.22, 126.92, 126.77, 116.73, 111.50, 78.56, 58.05, 42.04, 26.15.



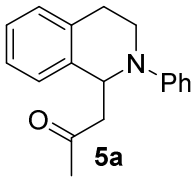
3e

1-(1-nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3e): Yellow oil. Isolated diastereomeric ratio = 2.2:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.08 (m, mixture of isomers), 6.99 – 6.97 (m, mixture of isomers), 6.83 – 6.78 (m, mixture of isomers), 5.26 – 5.21 (m, mixture of isomers), 5.06 – 4.99 (m, 1H, major isomer), 4.91 – 4.84 (m, 1H, minor isomer), 3.85 – 3.78 (m, 1H, minor isomer), 3.60 – 3.50 (m, 1H, major isomer), 3.07 – 2.99 (m, mixture of isomers), 2.92 – 2.82 (m, mixture of isomers), 1.69 – 1.67 (d, *J* = 6.8 Hz, 3H, minor isomer), 1.52 – 1.51 (d, *J* = 6.6 Hz, 3H, major isomer). ^{13}C NMR (100 MHz, $CDCl_3$); major isomer: δ 148.84, 135.56, 131.99, 126.06, 119.27, 115.39, 85.39, 62.69, 42.64, 26.35, 16.33; minor isomer: δ 149.12, 134.74, 133.77, 129.04, 127.19, 126.52, 118.75, 114.47, 88.89, 61.12, 43.50, 26.69, 17.35.



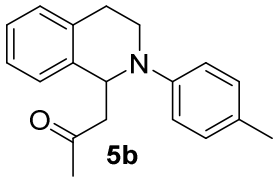
3f

1-(1-nitropropyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3f): Yellow oil. Isolated diastereomeric ratio = 1.6:1;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.12 (m, mixture of isomer), 6.99 – 6.92 (m, mixture of isomer), 6.82 – 6.76 (m, mixture of isomer), 5.23 (d, *J* = 9.2 Hz, 1H, minor isomer), 5.12 (d, *J* = 9.5 Hz, 1H, major isomer), 4.88 – 4.82 (m, 1H, major isomer), 4.70 – 4.64 (m, 1H, minor isomer), 3.87 – 3.80(m, 1H mixture of isomer), 3.68 – 3.47 (m, 3 H, mixture of isomer), 3.09 – 3.01 (m, 3 H, mixture of isomer), 2.92 – 2.82 (m, 1 H, mixture of isomer), 2.22 – 2.03 (m, 3H, mixture of isomers), 1.84 – 1.78 (m, 1 H mixture of isomer), 0.95 – 0.88 (m, 3 H, mixture of isomers). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.99, 135.50 (134.66), 133.87 (132.50), 129.56 (128.98), 128.59 (128.15), 127.16 (126.56), 125.85 (119.34), 118.52 (115.78), 115.08 (114.08), 96.10 (93.01), 62.14 (60.66), 43.48 (42.27), 29.66, 26.77 (25.68), 24.95 (24.58), 10.64.



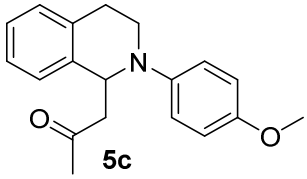
5a

1-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (5a): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.13 (m, 6H), 6.93 – 6.91 (d, *J* = 8.0 Hz, 2H), 6.78 – 6.74 (t, *J* = 7.1 Hz, 1H), 5.41 – 5.37 (t, *J* = 6.1 Hz, 1H), 3.66 – 3.48(m, 2H), 3.06 – 3.00 (m, 2H), 2.83 – 2.77 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.17, 148.80, 138.21, 134.36, 129.27, 128.60, 126.78, 126.73, 126.20, 118.19, 114.70, 54.72, 50.13, 41.98, 31.01, 27.14.



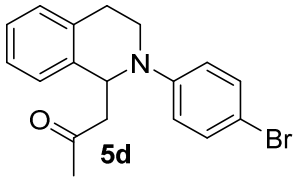
5b

1-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (5b): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.11 (m, 4H), 7.05 – 7.03 (d, 2H), 6.86 – 6.84 (d, 2H), 5.35 – 5.31 (t, *J* = 6.4 Hz, 1H), 3.64 – 3.59 (m, 1H), 3.51 – 3.44 (m, 1H), 3.06 – 2.98 (m, 2H), 2.81 – 2.73 (m, 2H), 2.24 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.33, 146.86, 138.24, 134.35, 129.78, 128.74, 127.92, 126.79, 126.64, 126.14, 115.64, 55.13, 50.03, 42.15, 30.94, 26.94, 20.28.



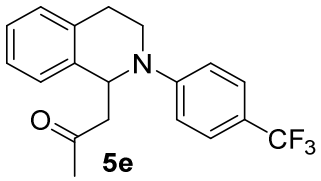
5c

1-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (5c): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.11 (d, 4H), 6.91 – 6.89 (d, 2H), 6.81 – 6.79 (d, 2H), 5.25 – 5.22 (t, J = 6.2 Hz, 1H), 3.73 (s, 3H), 3.56 – 3.41 (m, 2H), 3.02 – 2.96 (m, 2H), 2.78 – 2.70 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.31, 153.25, 143.64, 138.22, 134.26, 128.88, 126.74, 126.57, 126.12, 118.35, 114.59, 55.92, 55.55, 49.92, 42.84, 30.80, 26.70.



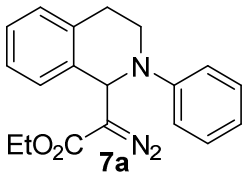
5d

1-(2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (5d): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (d, 2H), 7.17 – 7.12 (m, 4H), 6.80 – 6.78 (d, 2H), 5.35 – 5.32 (t, J = 6.3 Hz, 1H), 3.61 – 3.46 (m, J = 12.9, 10.5, 5.0 Hz, 2H), 3.06 – 2.98 (m, 21H), 2.84 – 2.78 (m, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.95, 147.75, 137.82, 134.13, 131.95, 128.62, 126.92, 126.73, 126.35, 116.05, 110.00, 54.57, 50.06, 42.07, 31.06, 26.98.



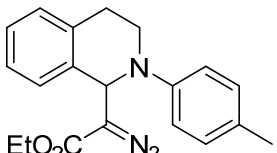
5e

1-(2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (5e): White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.45 (d, 2H), 7.18 – 7.15 (m, 4H), 6.94 – 6.92 (d, 2H), 5.47 – 5.44 (dd, J = 7.3, 5.2 Hz, 1H), 3.66 – 3.55 (m, 2H), 3.09 – 3.01 (m, 2H), 2.93 – 2.84 (m, 2H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.72, 150.61, 137.74, 134.16, 128.47, 127.15, 126.79, 126.62, 126.58, 126.52, 118.81 (q, $J_{F\text{-}C}$ = 32.6 Hz), 112.47, 65.53, 54.09, 50.12, 42.13, 31.12, 27.35, 19.14, 13.67.



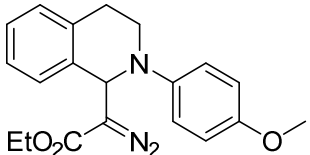
7a

ethyl 2-diazo-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (7a): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (t, 3H), 7.23 – 7.20 (m, 2H), 7.16 – 7.14 (m, 1H), 7.07 – 7.05 (d, J = 8.3 Hz, 2H), 6.88 – 6.84 (t, J = 7.2 Hz, 1H), 5.79 (s, 1H), 4.23 – 4.18 (m, J = 6.9, 5.8 Hz, 2H), 3.60 – 3.57 (t, J = 5.9 Hz, 2H), 3.06 – 2.85 (m, 2H), 1.25 – 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.34, 148.87, 135.17, 134.50, 129.16, 128.60, 127.47, 127.44, 126.60, 119.57, 116.17, 60.92, 56.29, 43.70, 27.91, 14.37.



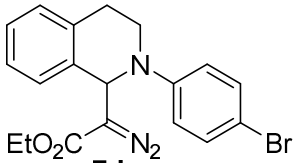
7b

ethyl 2-diazo-2-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (7b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.27 (m, 1H), 7.20 – 7.17 (m, 2H), 7.15 – 7.12 (m, 1H), 7.09 – 7.07 (d, J = 8.3 Hz, 2H), 6.99 – 6.97 (d, J = 8.5 Hz, 2H), 5.72 (s, 1H), 4.21 – 4.15 (dd, J = 14.2, 7.1 Hz, 2H), 3.55 – 3.52 (m, 2H), 3.02 – 2.84 (m, 2H), 2.26 – 2.22 (d, 3H), 1.28 – 1.19 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.37, 146.83, 135.17, 134.54, 129.63, 129.34, 128.58, 127.44, 127.30, 126.50, 117.07, 60.82, 56.59, 44.42, 28.06, 20.38, 14.33.



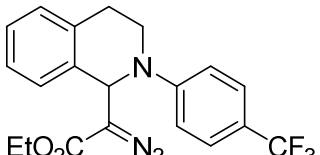
7c

ethyl 2-diazo-2-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (7c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 1H), 7.21 – 7.19 (m, 2H), 7.15 – 7.13 (m, 1H), 7.07 – 7.05 (d, 2H), 6.86 – 6.84 (d, J = 9.0 Hz, 2H), 5.62 (s, 1H), 4.17 – 4.12 (dd, J = 14.0, 7.0 Hz, 2H), 3.76 (s, 3H), 3.50 – 3.39 (m, 2H), 3.01 – 2.88 (m, 2H), 1.20 – 1.17 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.41, 154.51, 143.52, 135.16, 134.47, 128.68, 127.42, 127.23, 126.45, 120.39, 114.36, 60.77, 57.69, 55.45, 45.93, 28.43, 14.32.



7d

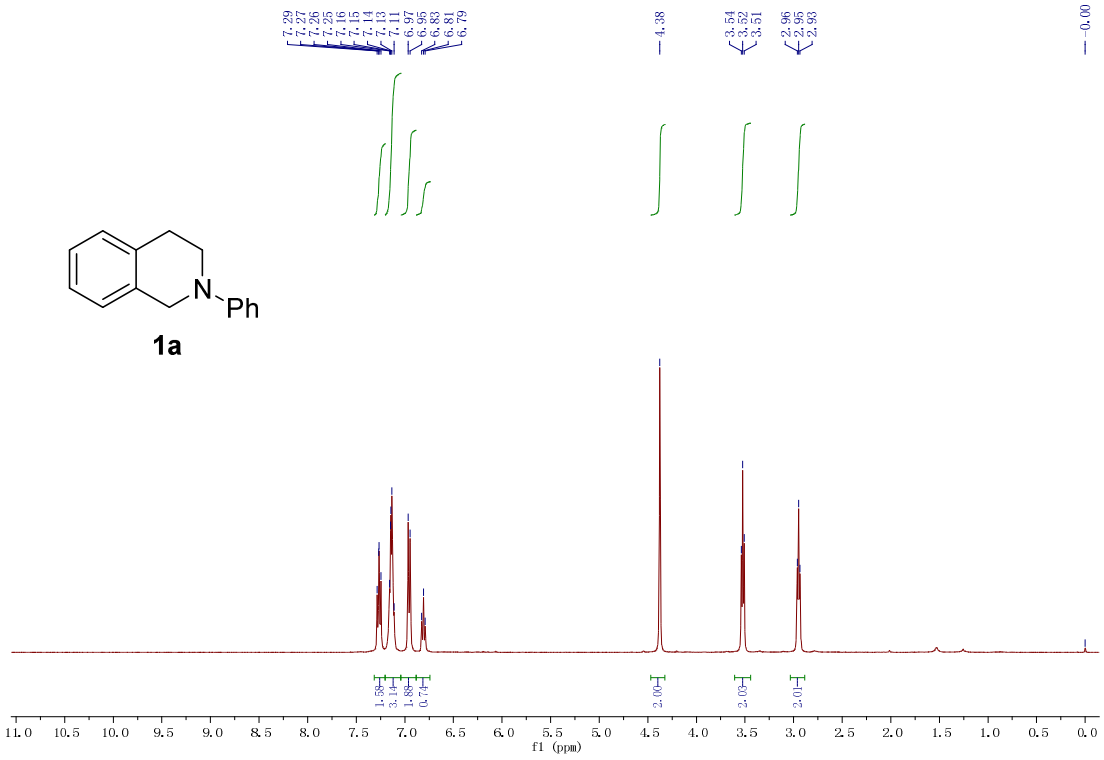
ethyl 2-(2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-2-diazoacetate (7d): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.33 (d, 2H), 7.28 – 7.26 (m, 1H), 7.23 – 7.19 (m, 2H), 7.16 – 7.14 (m, 1H), 6.94 – 6.92 (d, J = 9.0 Hz, 2H), 5.74 (s, 1H), 4.24 – 4.19 (q, J = 7.1 Hz, 2H), 3.60 – 3.53 (m, 2H), 3.04 – 2.97 (m, J = 13.5, 6.6 Hz, 1H), 2.89 – 2.82 (m, J = 16.1, 5.1 Hz, 1H), 1.26 – 1.22 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.17, 147.77, 134.86, 133.95, 131.87, 128.65, 127.58, 127.40, 126.70, 117.62, 111.61, 61.02, 56.13, 43.49, 27.61, 14.34.

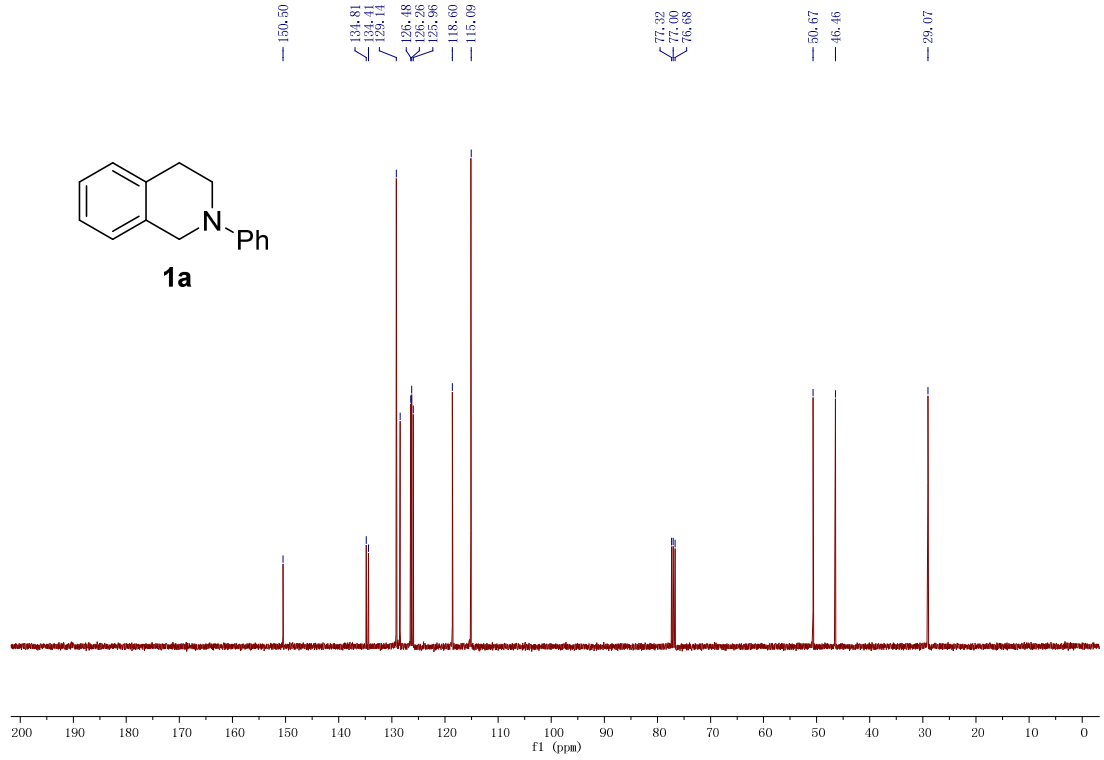


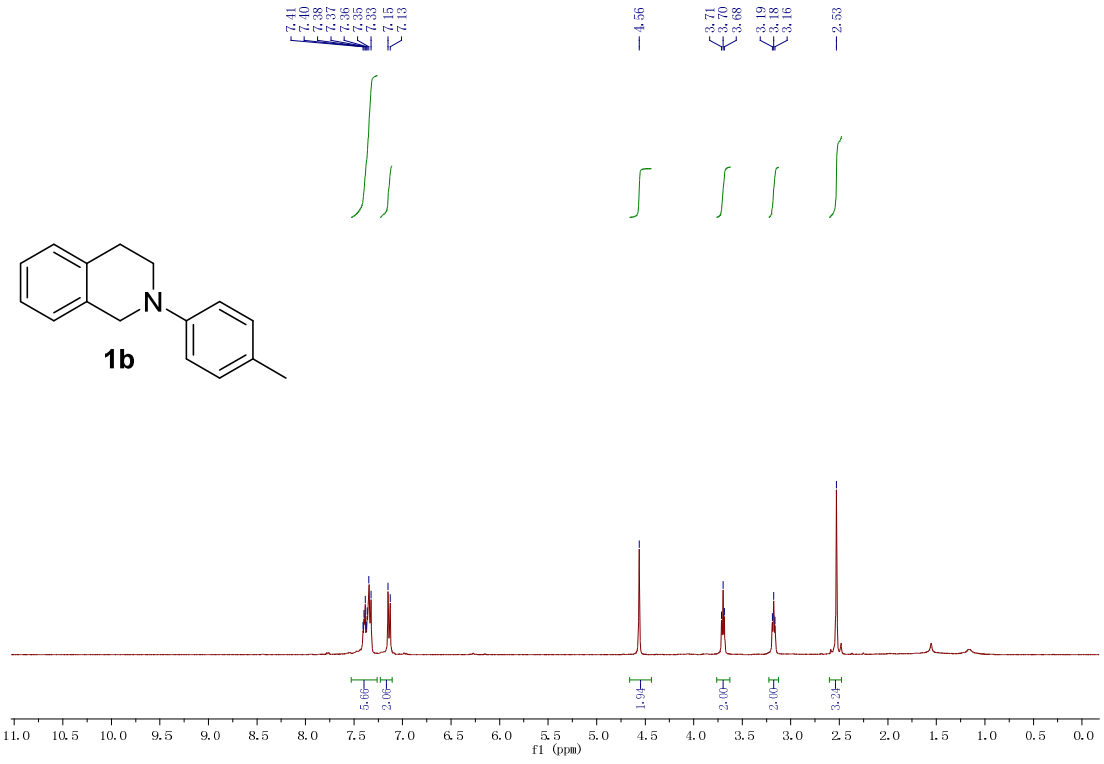
7e

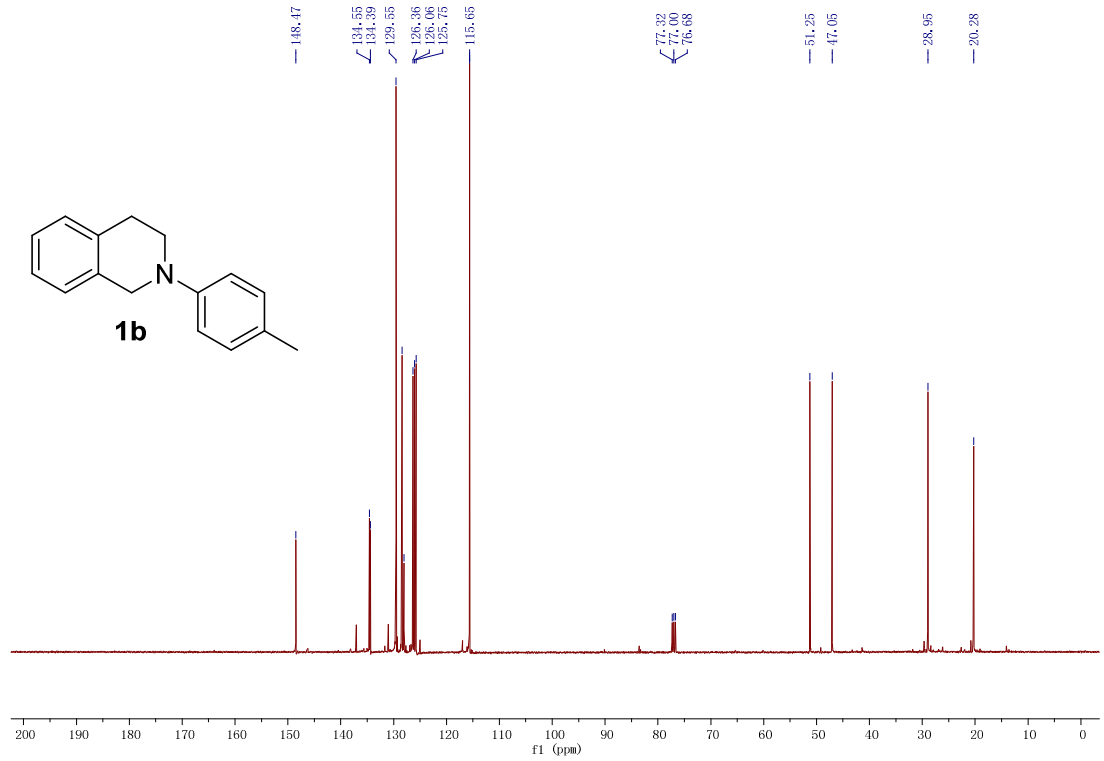
ethyl 2-diazo-2-(2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetate (7e): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (d, 2H), 7.31 – 7.29 (m, 1H), 7.23 – 7.21 (m, 2H), 7.18 – 7.16 (m, 1H), 7.10 – 7.07 (d, J = 8.6 Hz, 2H), 5.87 (s, 1H), 4.29 – 4.23 (q, J = 7.1 Hz, 2H), 3.72 – 3.59 (m, 2H), 3.09 – 3.02 (m, 1H), 2.91 – 2.84 (m, 1H), 1.29 – 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.14, 150.69, 134.82, 133.86, 128.71, 127.83, 127.44, 126.90, 126.54, 126.51, 123.42, 120.14 (q, $J_{F\text{-}C}$ = 32.5 Hz), 113.91, 61.18, 55.57, 42.75, 27.44, 14.37.

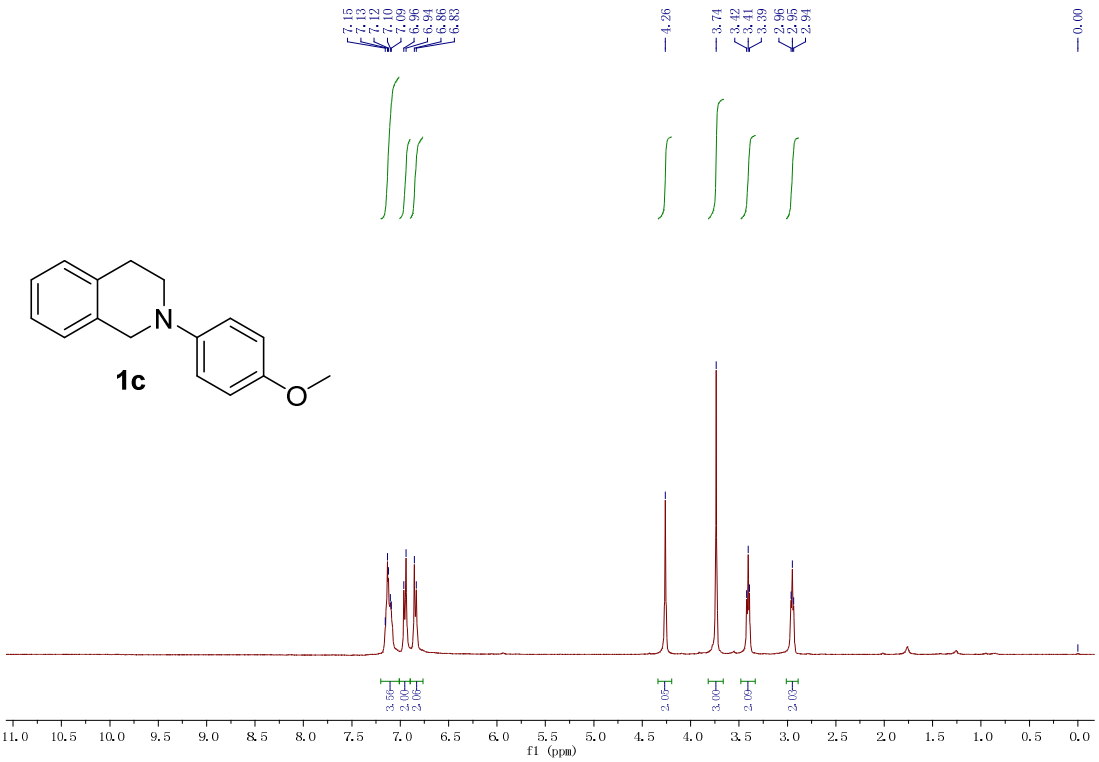
Ⅵ. ^{1}H NMR and ^{13}C NMR spectra

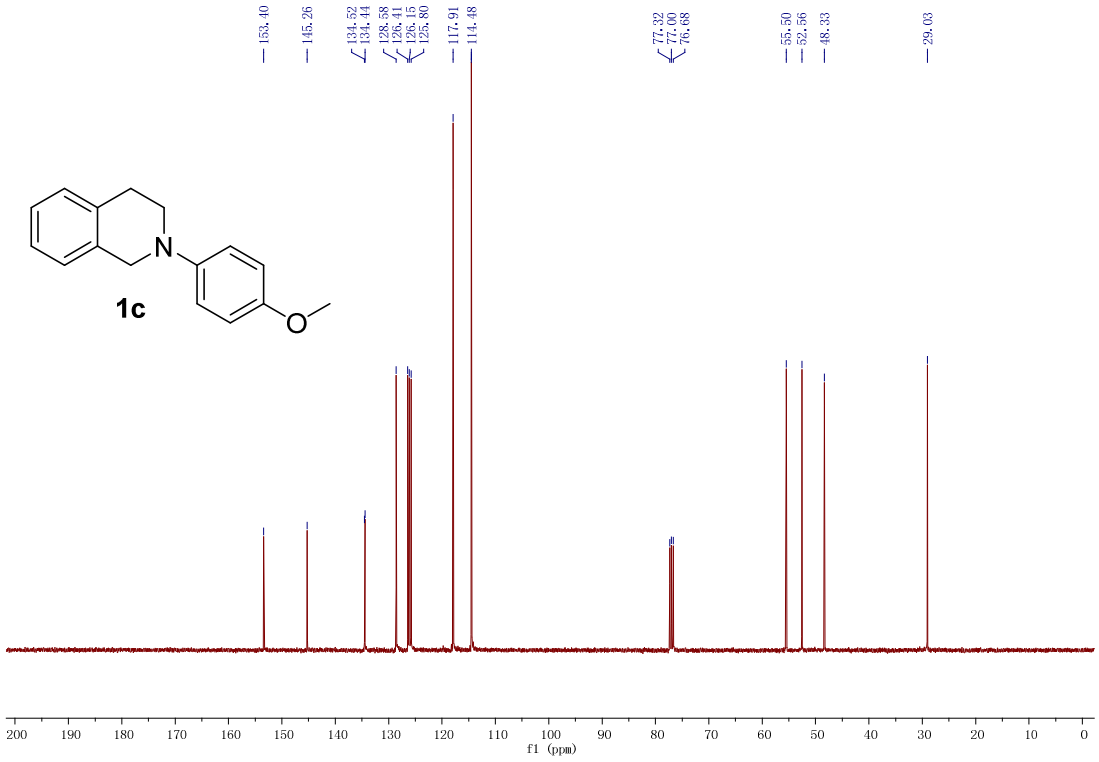


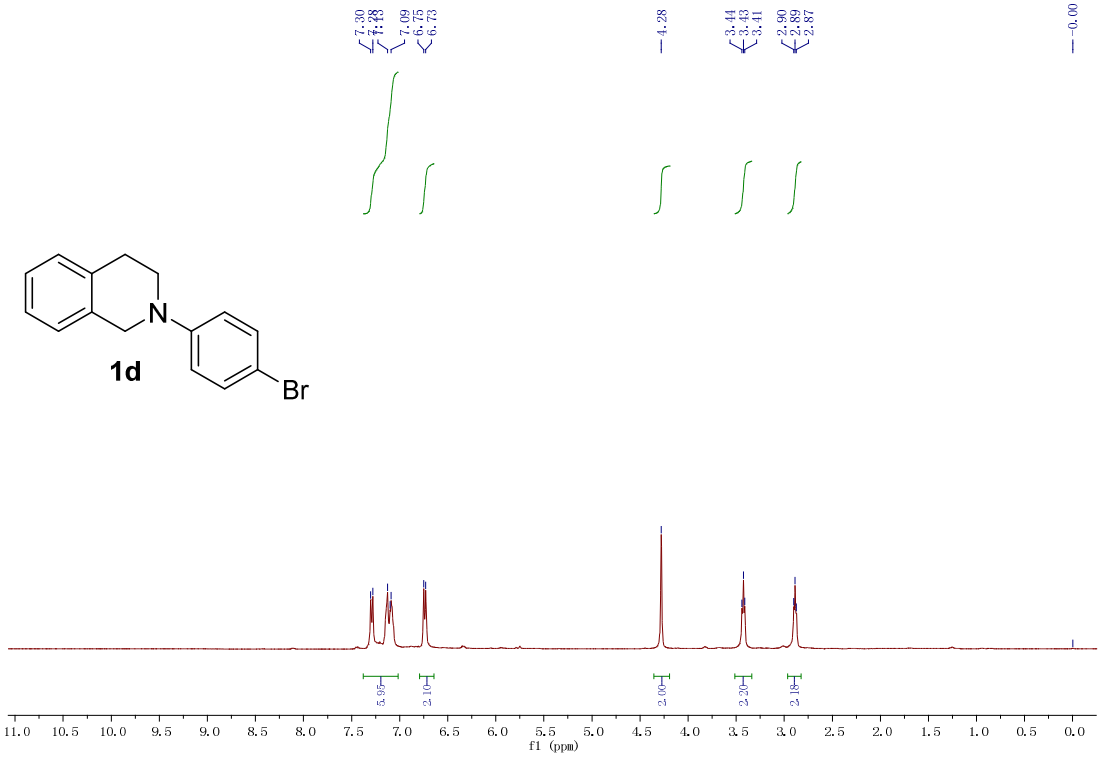


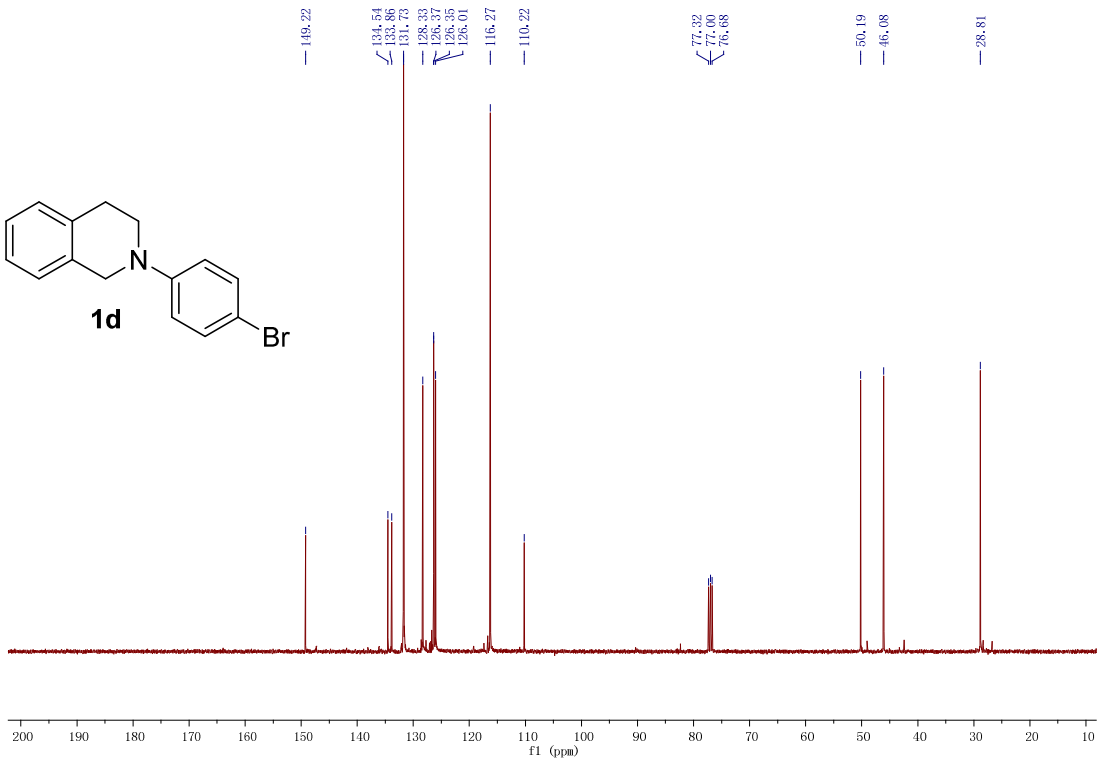

7.41
7.40
7.38
7.37
7.36
7.35
7.33
7.15
7.13
4.56
3.71
3.70
3.68
3.19
3.18
3.16
2.53
1b
5.66
2.06
1.94
2.00
2.00
3.24
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

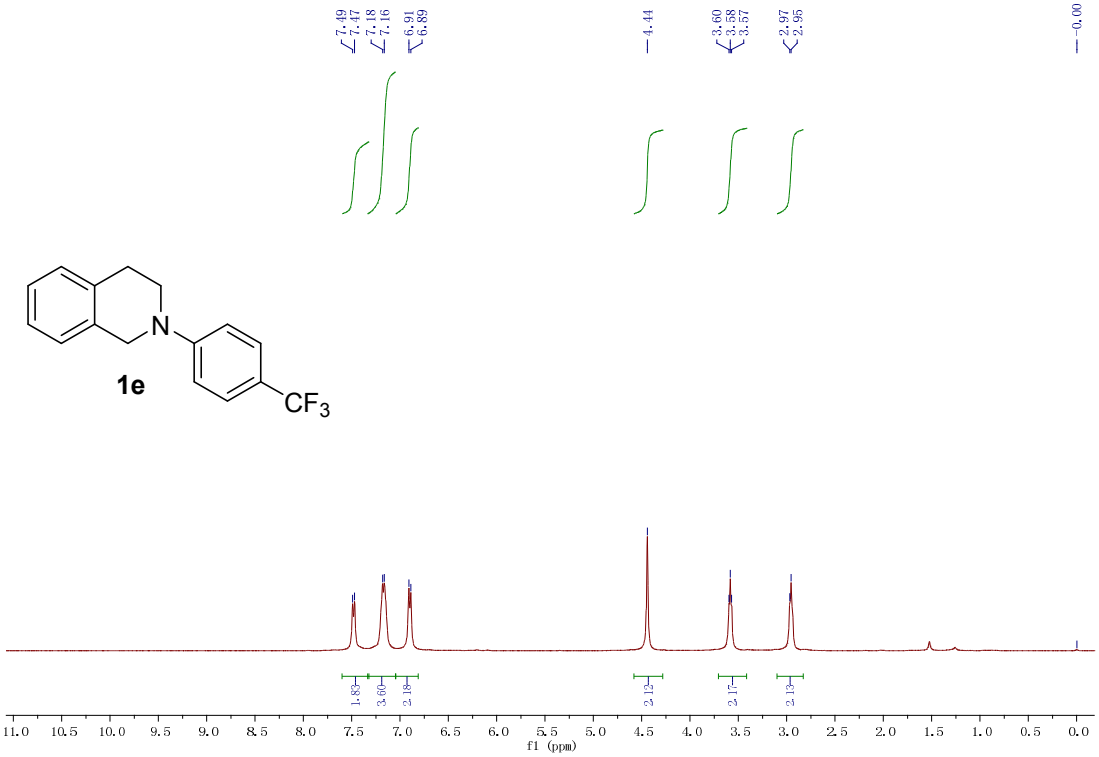

148.47
134.55
134.39
129.55
126.36
126.06
125.75
115.65
77.32
77.00
76.68
51.25
47.05
28.95
20.28
1b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

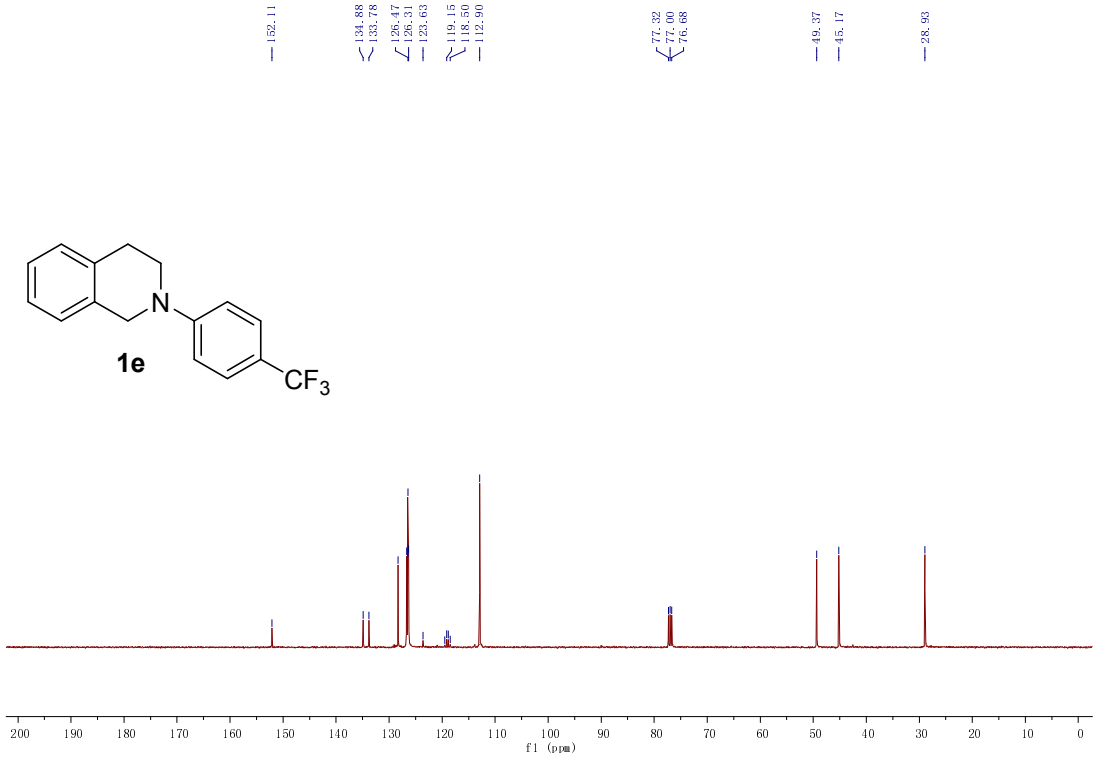

7.15
7.13
7.12
7.10
7.09
6.96
6.94
6.85
6.83
4.26
3.74
3.42
3.41
3.39
2.96
2.95
2.94
0.00
1c
3.56
2.00
2.06
2.05
3.00
2.09
2.03
f1 (ppm)

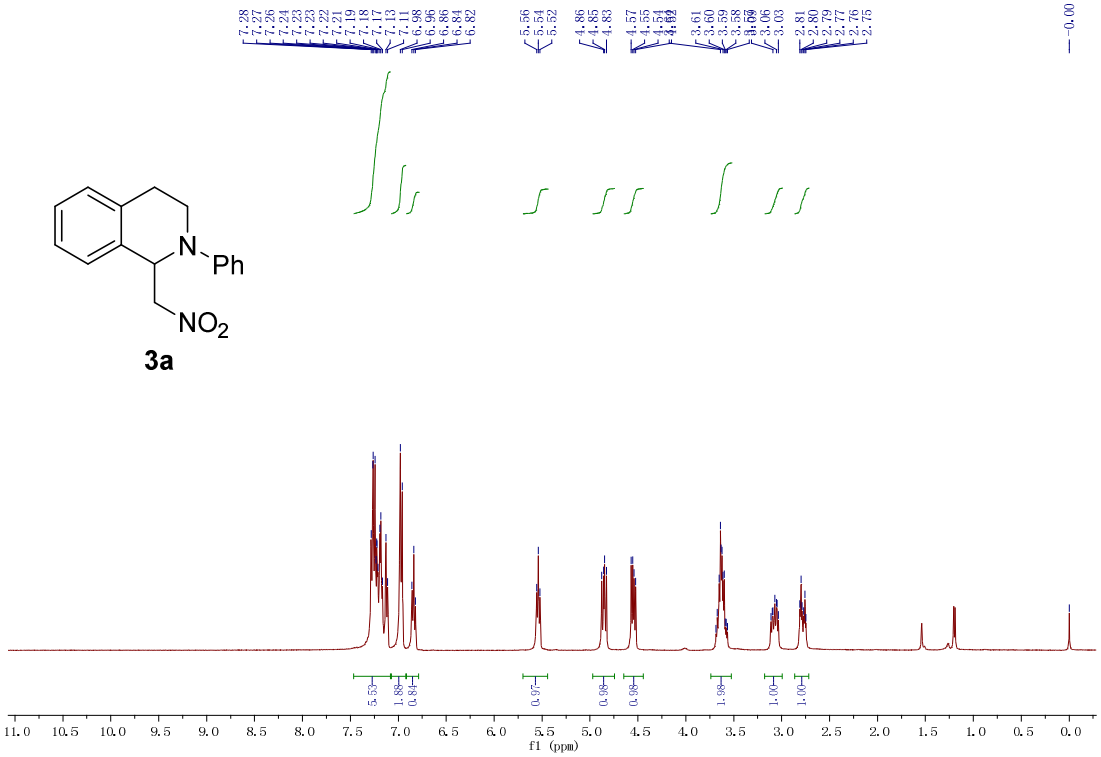

153.40
145.26
134.52
134.44
128.58
126.41
126.15
125.80
117.91
114.48
77.32
77.00
76.68
55.50
52.56
48.33
29.03
1c
f1 (ppm)

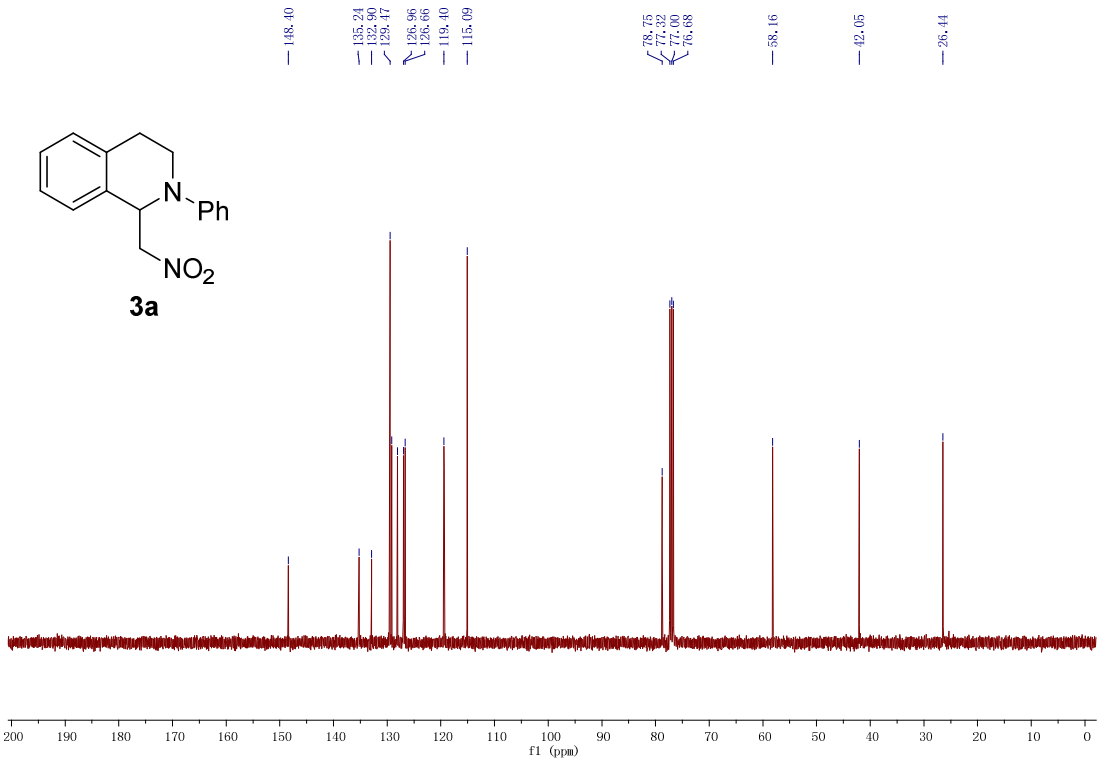

7.30
7.28
7.23
7.09
6.75
6.73
4.28
3.44
3.43
3.41
2.90
2.89
2.87
0.00
1d
Br
5.89
2.10
2.00
2.20
2.18
f1 (ppm)

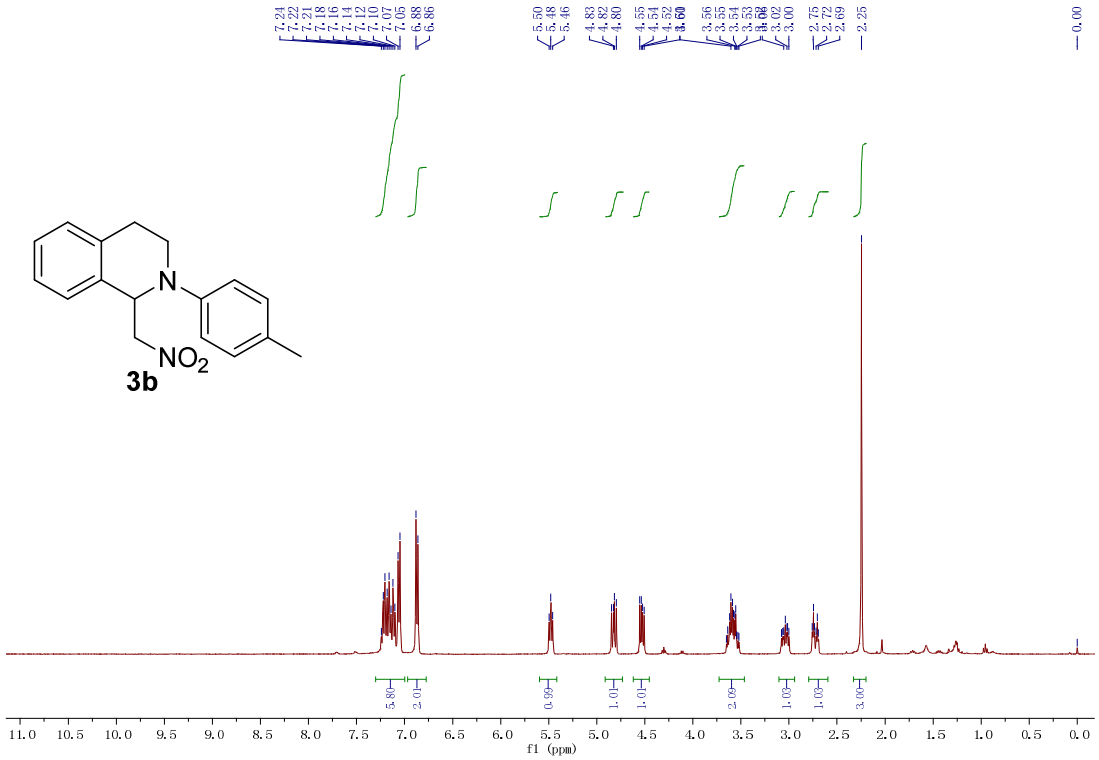

149.22
134.54
133.86
131.73
128.33
126.37
126.35
126.01
116.27
110.22
77.32
77.00
76.68
50.19
46.08
28.81
1d
Br
f1 (ppm)

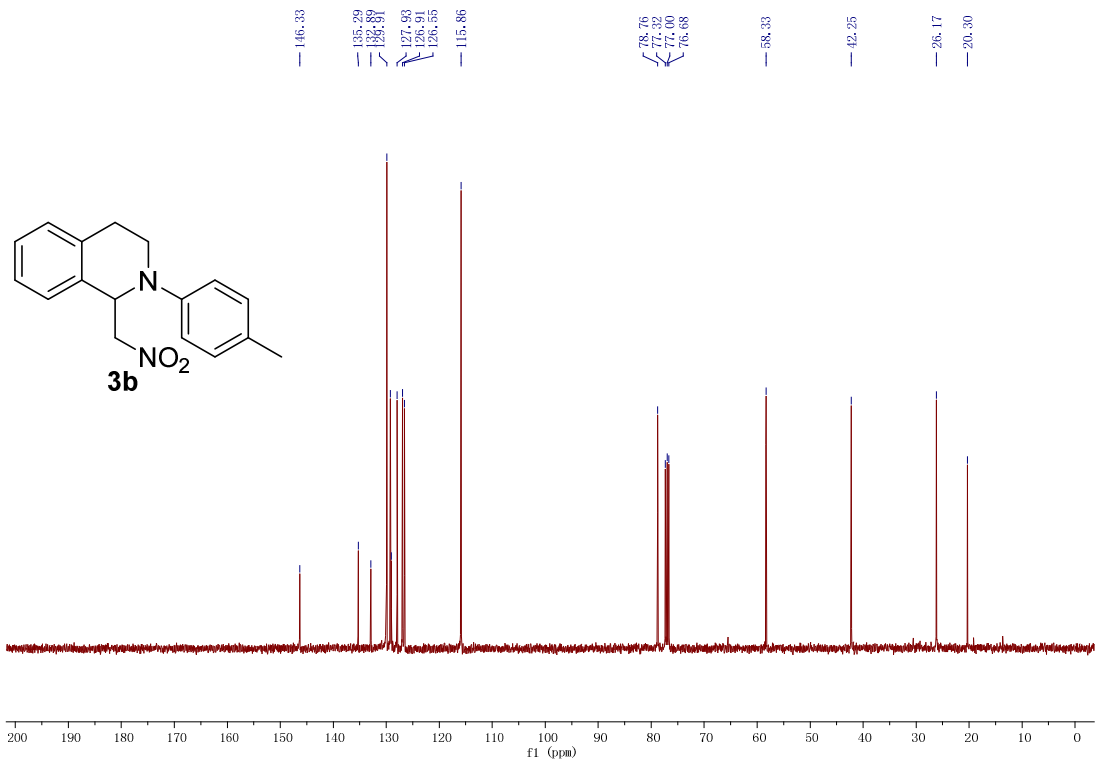

7.49
7.47
7.18
7.16
6.91
6.89
4.44
3.60
3.58
3.57
2.97
2.95
0.00
1e
CF3
1.83
3.60
2.18
2.12
2.17
2.13
f1 (ppm)

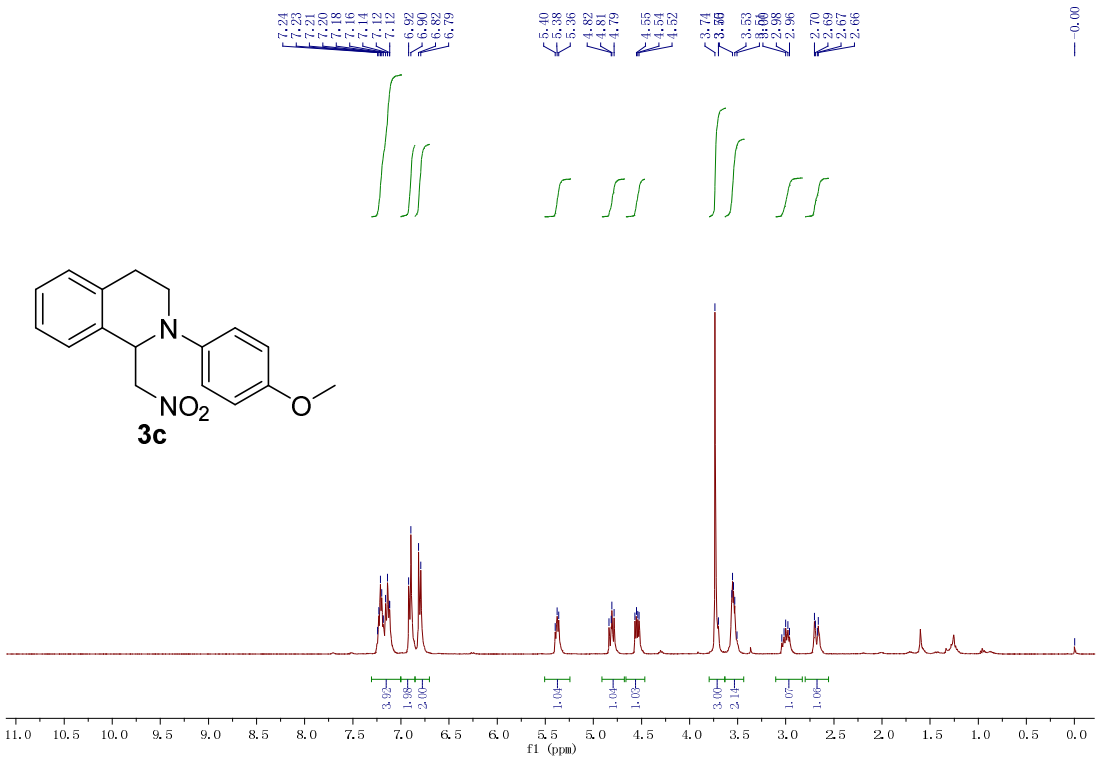

162.11
134.88
133.78
126.47
126.31
123.63
119.15
118.50
112.90
77.32
77.00
76.68
49.37
45.17
28.93
1e
CF3
f1 (ppm)

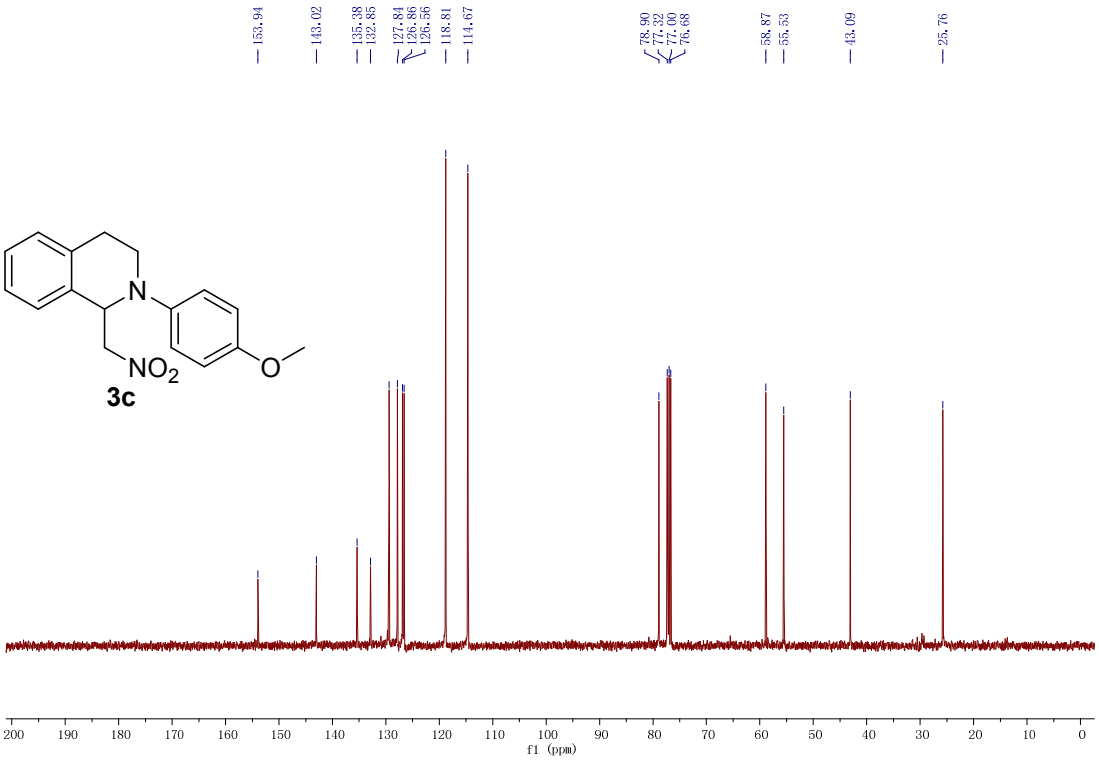

7.28
7.27
7.26
7.24
7.23
7.22
7.21
7.19
7.18
7.17
7.13
7.11
6.98
6.96
6.86
6.84
6.82
5.56
5.54
5.52
4.86
4.85
4.83
4.57
4.55
4.54
3.61
3.60
3.59
3.58
3.06
3.03
2.81
2.80
2.79
2.77
2.76
2.75
0.00
N
Ph
NO2
3a
5.53
1.88
0.84
0.97
0.98
0.98
1.98
1.00
1.00
f1 (ppm)

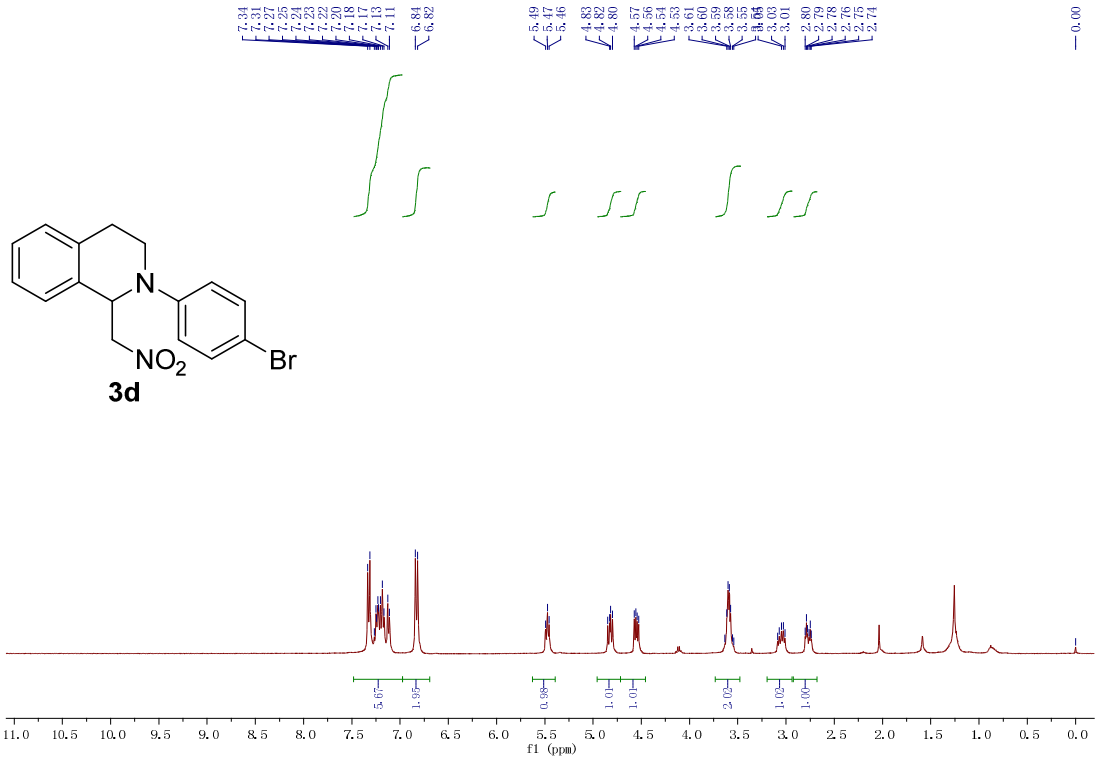

148.40
135.24
132.90
129.47
126.96
126.66
119.40
115.09
78.75
77.32
77.00
76.68
58.16
42.05
26.44
N
Ph
NO2
3a
f1 (ppm)

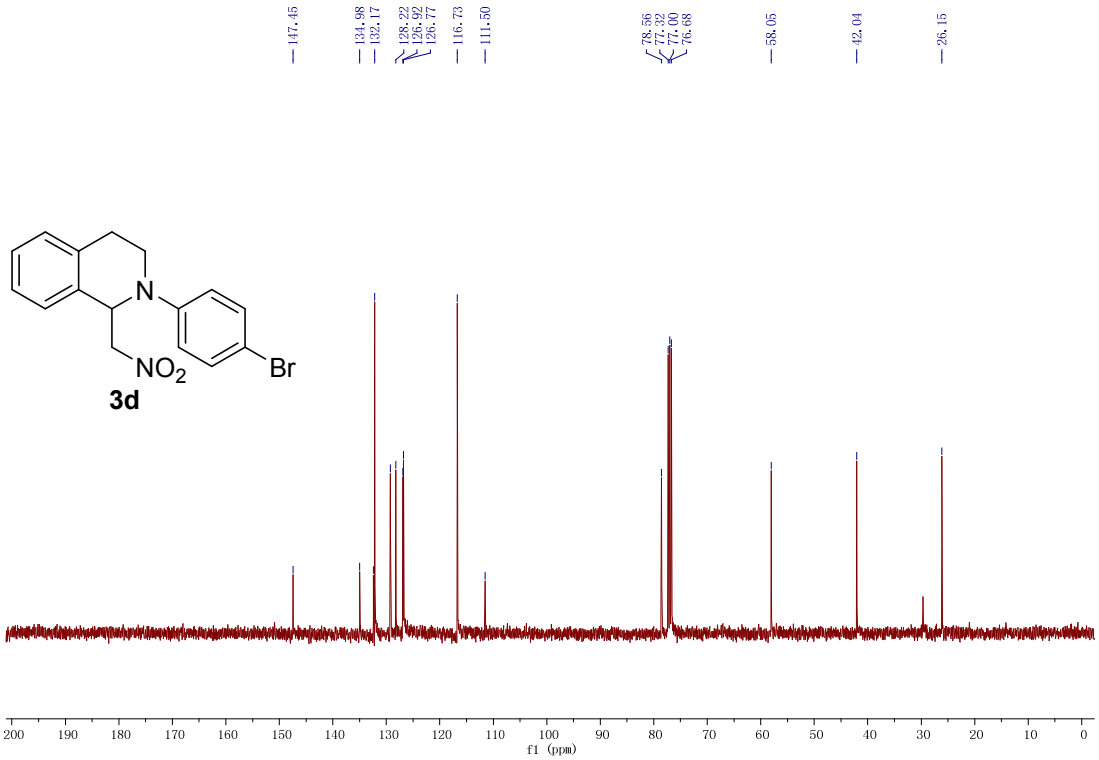

7.24
7.22
7.21
7.18
7.16
7.14
7.12
7.10
7.07
7.05
6.88
6.86
5.50
5.48
5.46
4.83
4.82
4.80
4.55
4.54
4.52
3.56
3.55
3.54
3.53
3.02
3.00
2.75
2.72
2.69
2.25
0.00
N
NO2
3b
5.80
2.01
0.99
1.01
1.01
2.09
1.03
1.03
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

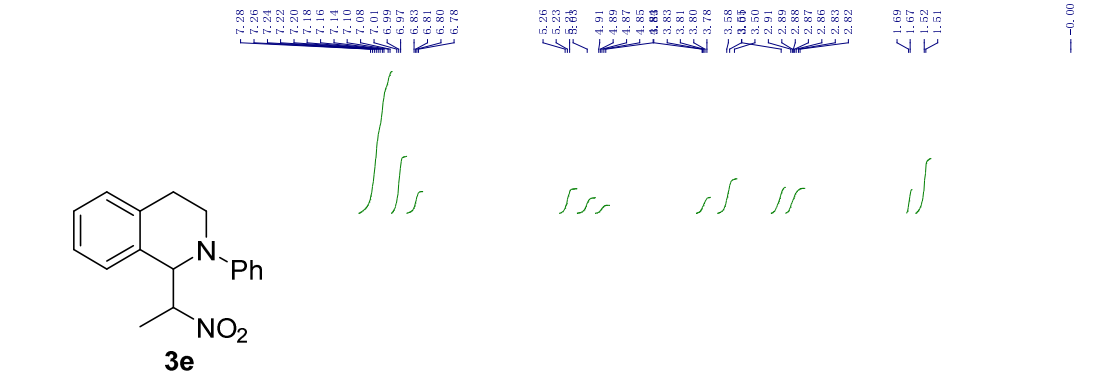

146.33
135.29
132.89
129.91
127.93
126.91
126.55
115.86
78.76
77.32
77.00
76.68
58.33
42.25
26.17
20.30
N
NO2
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

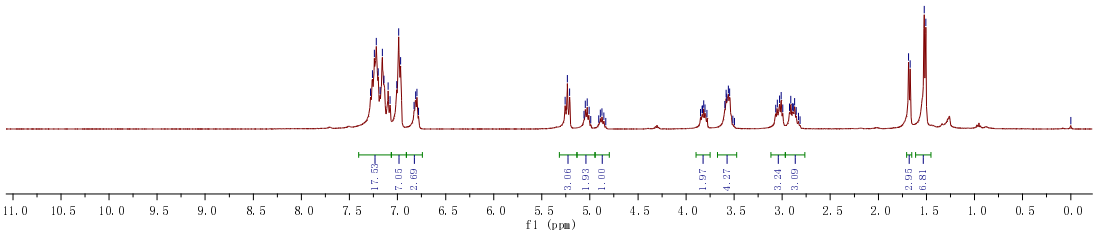

7.24
7.23
7.21
7.20
7.18
7.16
7.14
7.12
7.12
6.92
6.90
6.82
6.79
5.40
5.38
5.36
4.82
4.81
4.79
4.55
4.54
4.52
3.74
3.53
2.98
2.96
2.70
2.69
2.67
2.66
0.00
N
NO2
O
3c
3.92
1.98
2.00
1.04
1.04
1.03
3.00
2.14
1.07
1.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

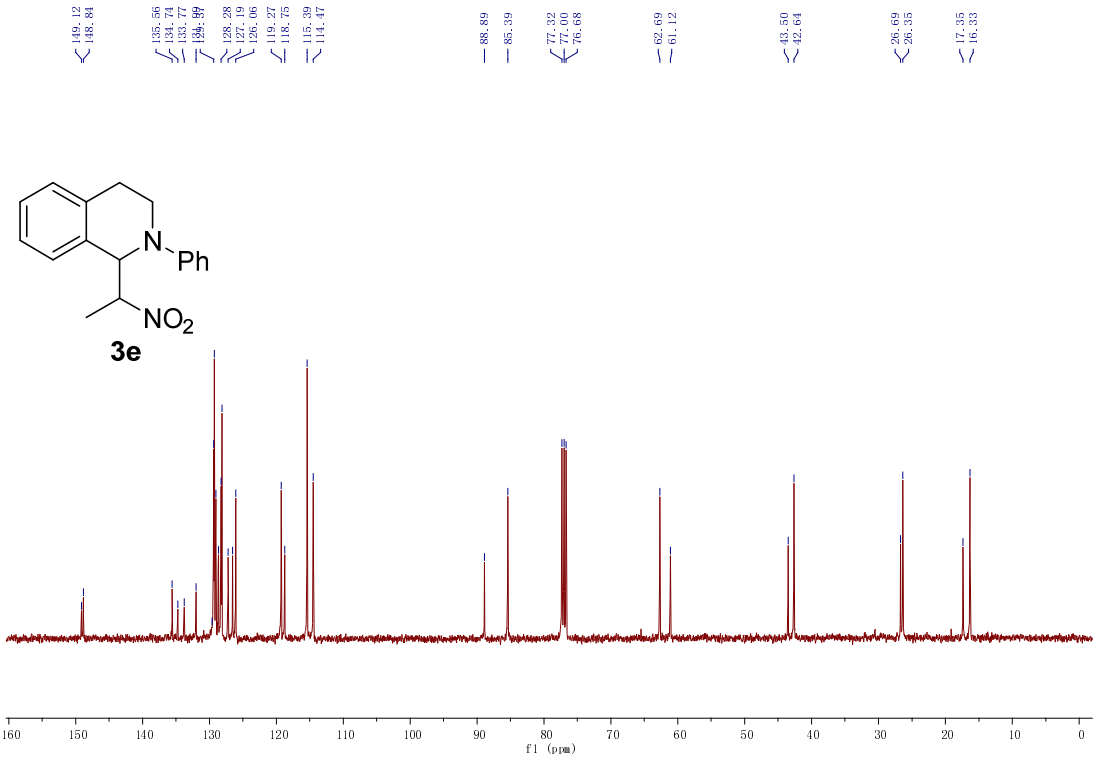

153.94
143.02
135.38
132.85
127.84
126.86
126.56
118.81
114.67
78.90
77.32
77.00
76.68
58.87
55.53
43.09
25.76
N
NO2
O
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

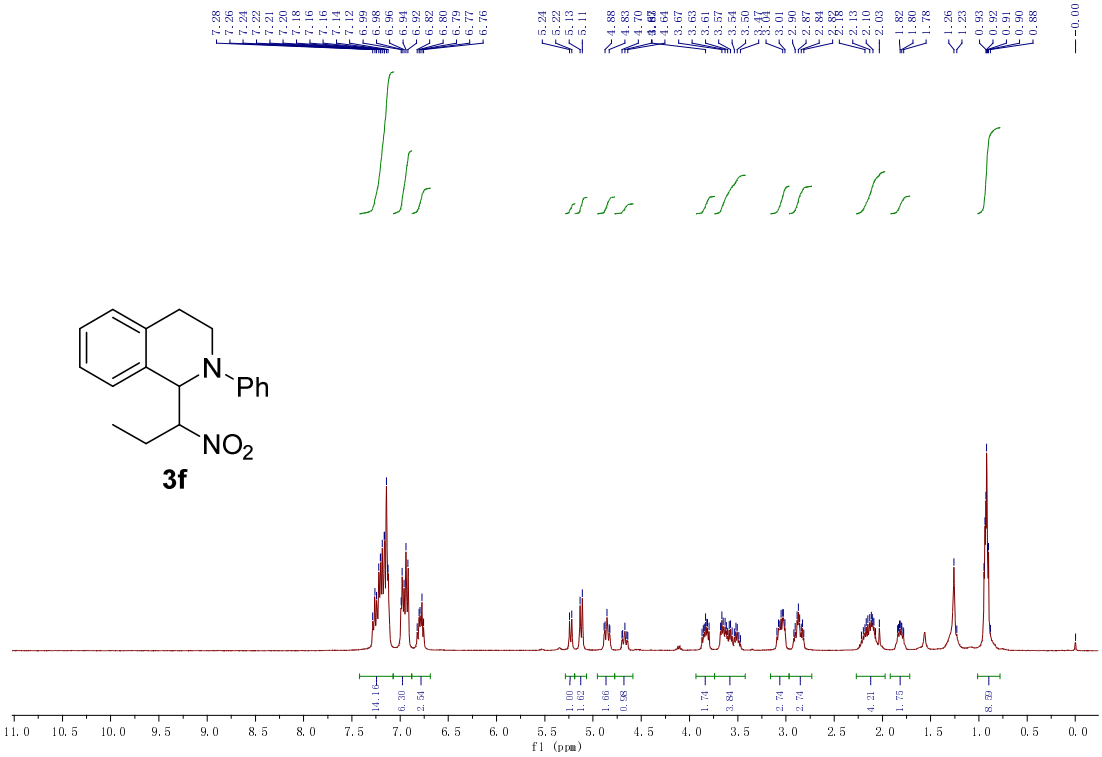

N
NO2
Br
3d
f1 (ppm)

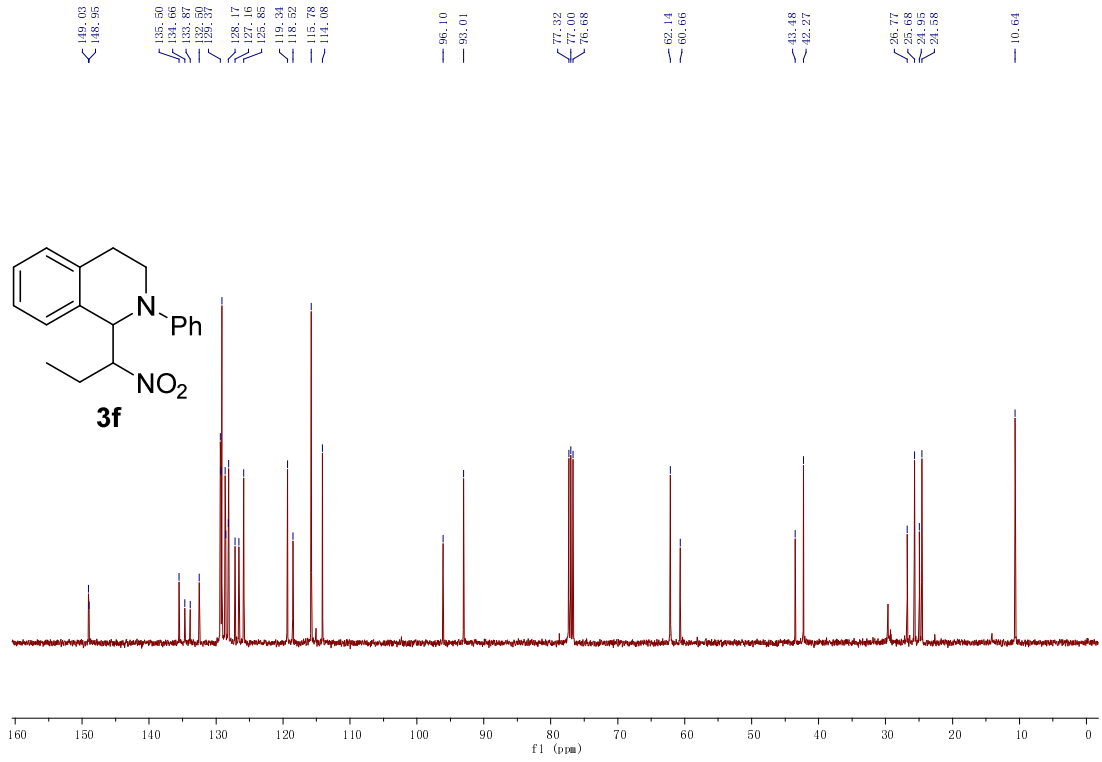

N
NO2
Br
3d
f1 (ppm)

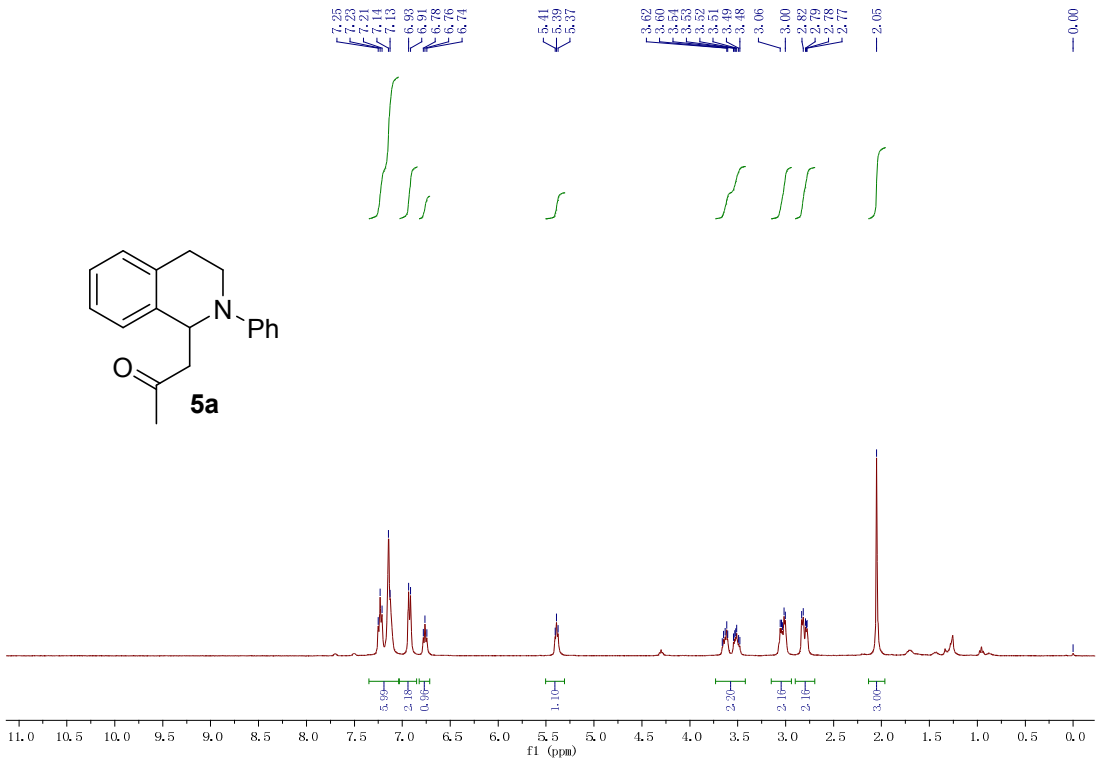

7.28
7.26
7.24
7.22
7.20
7.18
7.16
7.14
7.10
7.08
7.01
6.99
6.97
6.83
6.81
6.80
6.78
5.26
5.23
4.91
4.89
4.87
4.85
3.83
3.81
3.80
3.78
3.58
3.50
2.91
2.89
2.88
2.87
2.86
2.83
2.82
1.69
1.67
1.52
1.51
0.00
N
Ph
NO2
3e

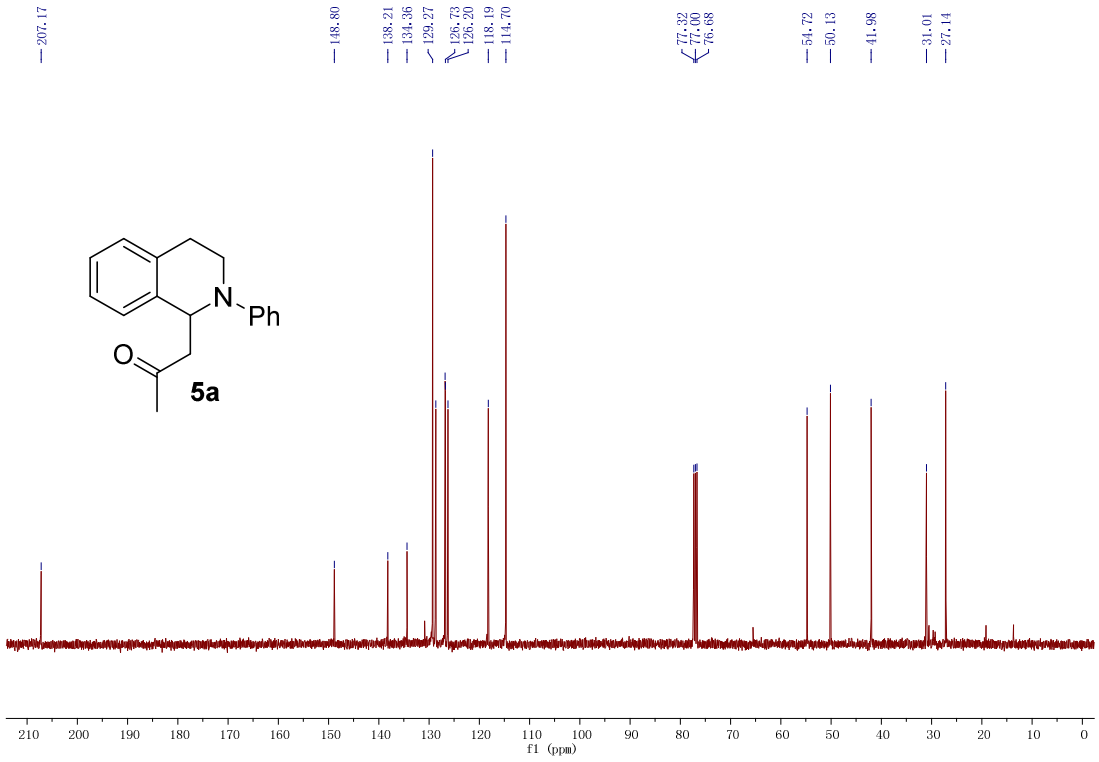

17.53
7.05
2.69
3.66
1.93
1.00
1.97
4.27
3.24
3.09
2.95
6.81
f1 (ppm)

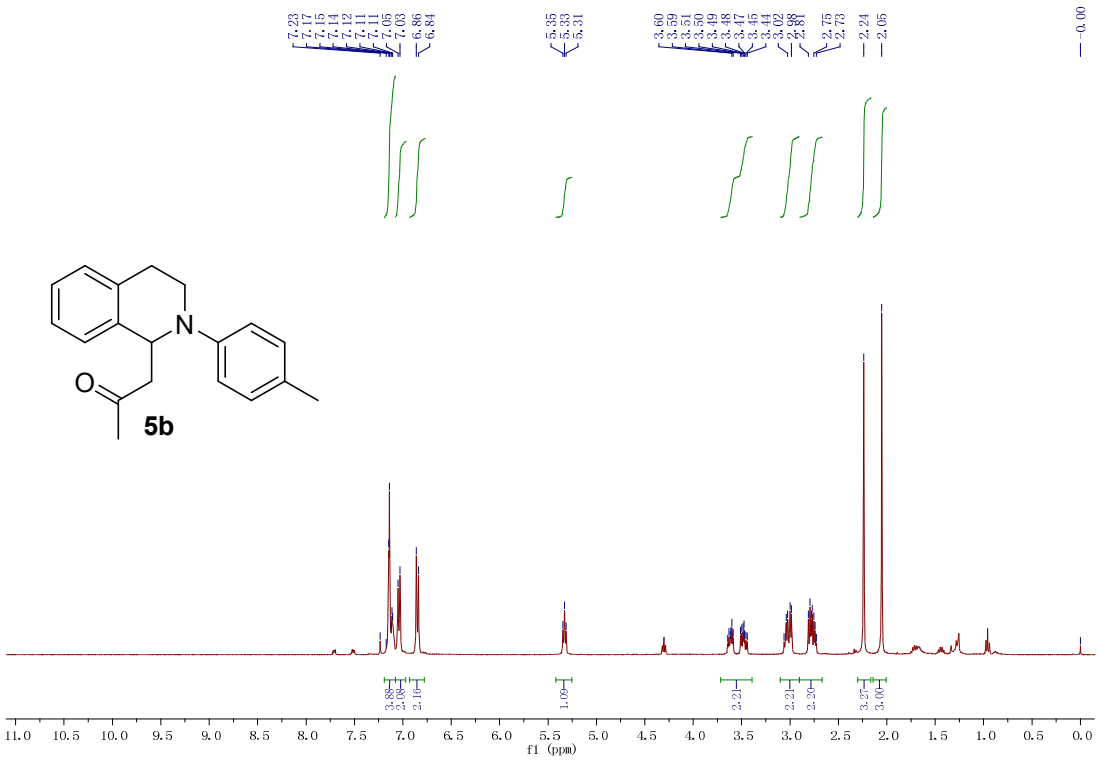

149.12
148.84
135.56
134.74
133.77
128.28
127.19
126.06
119.27
118.75
115.39
114.47
88.89
85.39
77.32
77.00
76.68
62.69
61.12
43.50
42.64
26.69
26.35
17.35
16.33
N
Ph
NO2
3e
f1 (ppm)

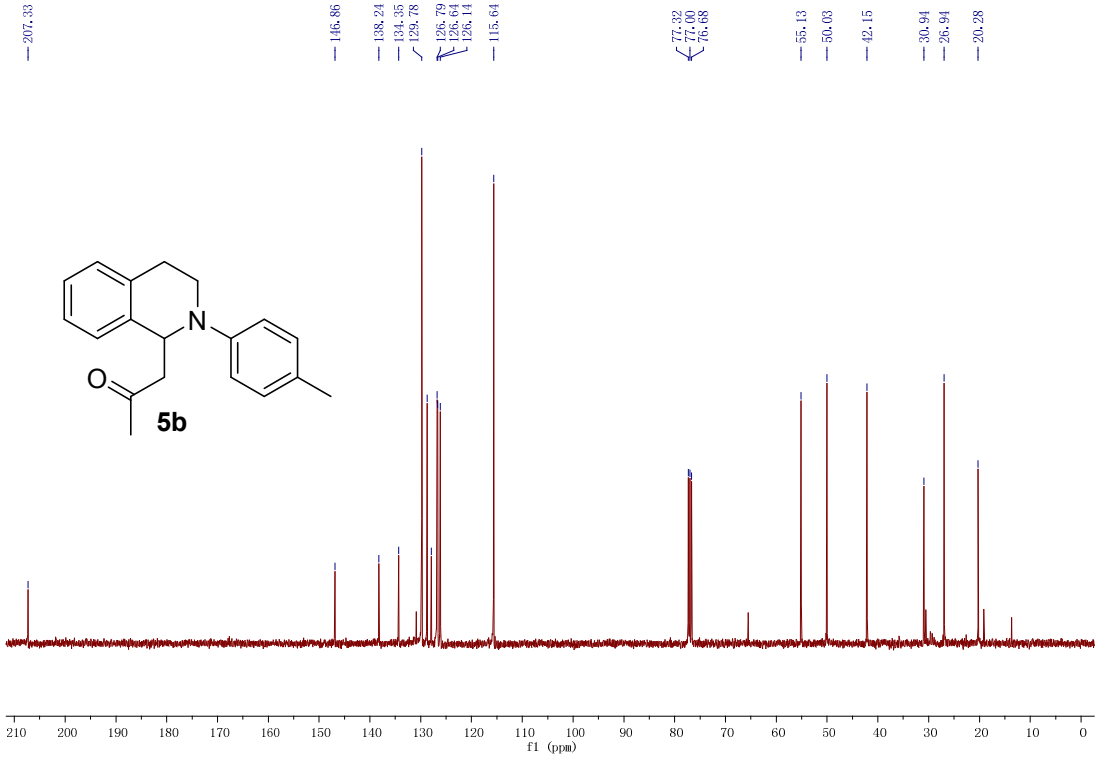

7.28
7.26
7.24
7.22
7.21
7.20
7.18
7.16
7.16
7.14
7.12
6.99
6.98
6.96
6.94
6.92
6.82
6.80
6.79
6.77
6.76
5.24
5.22
5.13
5.11
4.88
4.83
4.70
4.64
3.67
3.63
3.61
3.57
3.54
3.50
3.01
2.90
2.87
2.84
2.13
2.10
2.03
1.82
1.80
1.78
1.26
1.23
0.93
0.92
0.91
0.90
0.88
-0.00
N
Ph
NO2
3f
14.16
6.30
2.54
1.00
1.02
1.66
0.88
1.74
3.84
2.74
2.74
4.21
1.75
8.79
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)

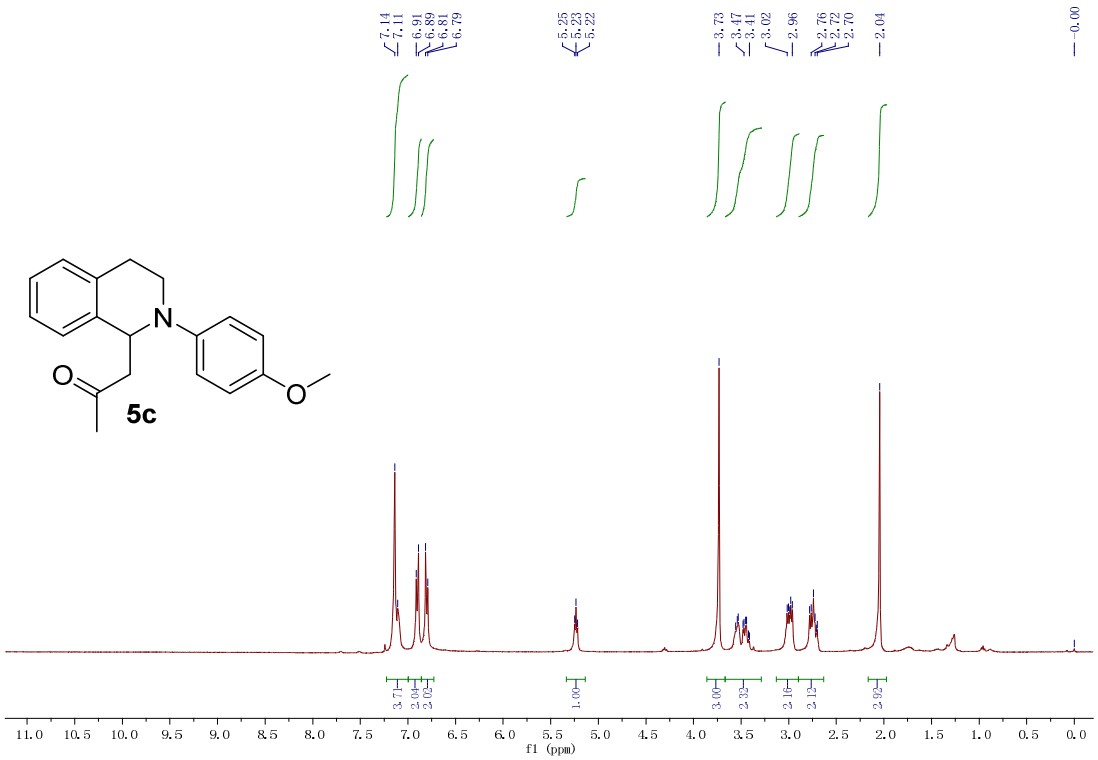

149.03
148.95
135.50
134.66
133.87
132.50
129.37
128.17
127.16
125.85
119.34
118.52
115.78
114.08
96.10
93.01
77.32
77.00
76.68
62.14
60.66
43.48
42.27
26.77
25.68
24.95
24.58
10.64
N
Ph
NO2
3f
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

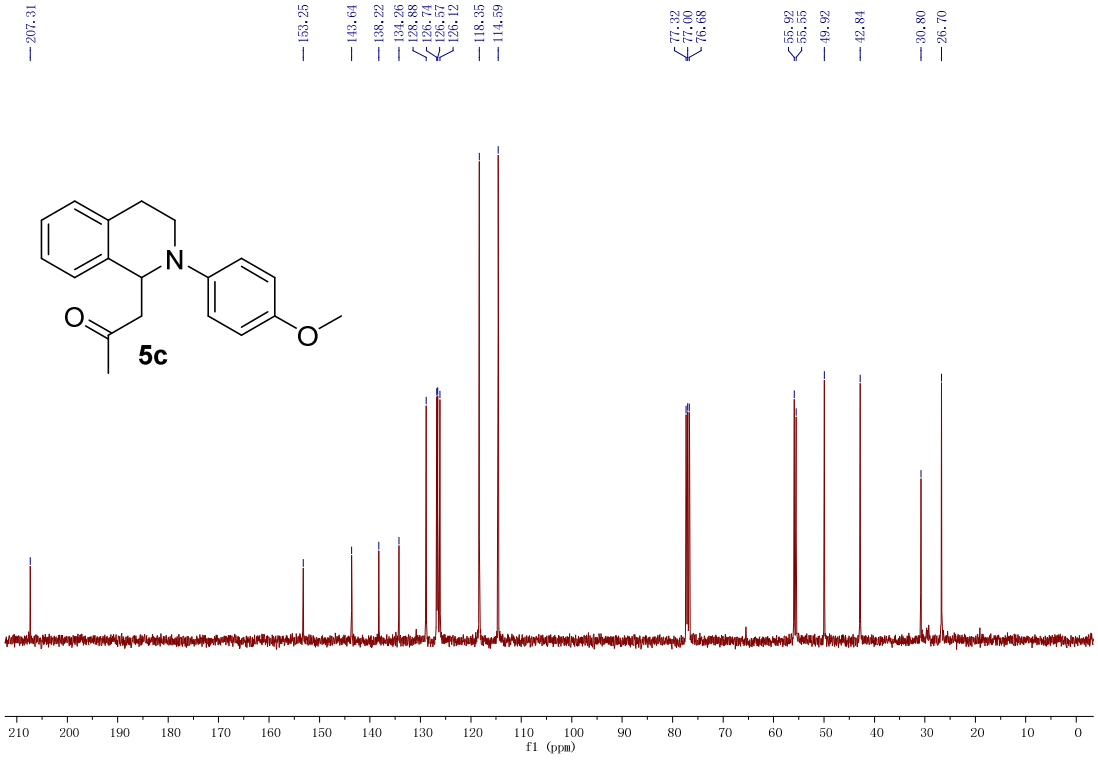

7.25
7.23
7.21
7.14
7.13
6.93
6.91
6.78
6.76
6.74
5.41
5.39
5.37
3.62
3.60
3.54
3.53
3.52
3.51
3.49
3.48
3.06
3.00
2.82
2.79
2.78
2.77
2.05
0.00
N
Ph
O
5a
5.99
2.18
0.96
1.10
2.20
2.16
2.16
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

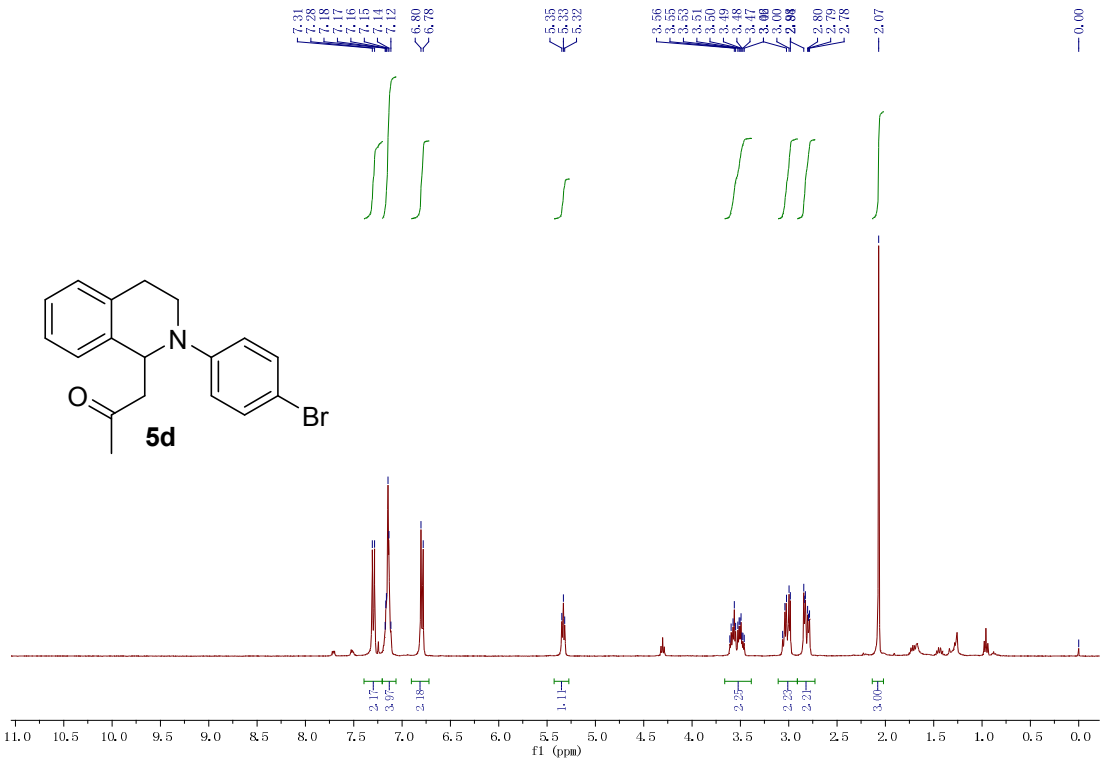

207.17
148.80
138.21
134.36
129.27
126.73
126.20
118.19
114.70
77.32
77.00
76.68
54.72
50.13
41.98
31.01
27.14
N
Ph
O
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

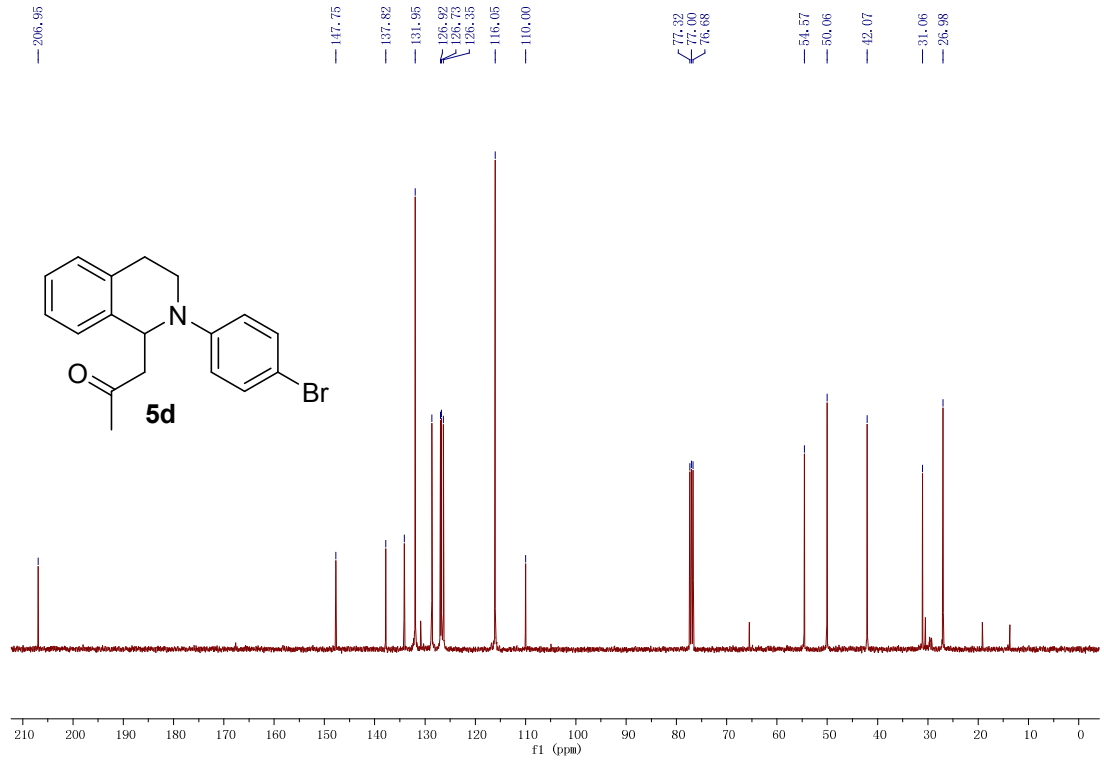

7.23
7.17
7.15
7.14
7.12
7.11
7.11
7.05
7.03
6.86
6.84
5.35
5.33
5.31
3.60
3.59
3.51
3.50
3.49
3.48
3.47
3.45
3.44
3.02
2.98
2.88
2.75
2.73
2.24
2.05
0.00
N
O
5b
3.88
2.08
2.16
1.09
2.21
2.21
2.20
3.27
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

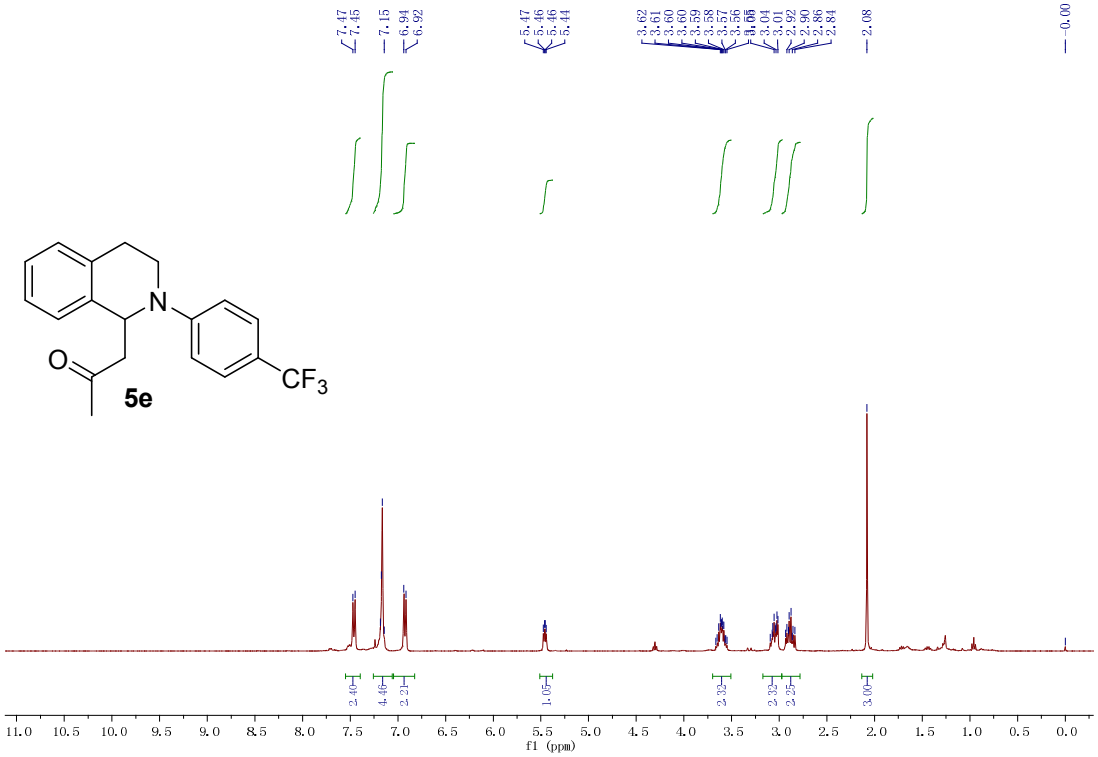

207.33
146.86
138.24
134.35
129.78
126.79
126.64
126.14
115.64
77.32
77.00
76.68
55.13
50.03
42.15
30.94
26.94
20.28
N
O
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

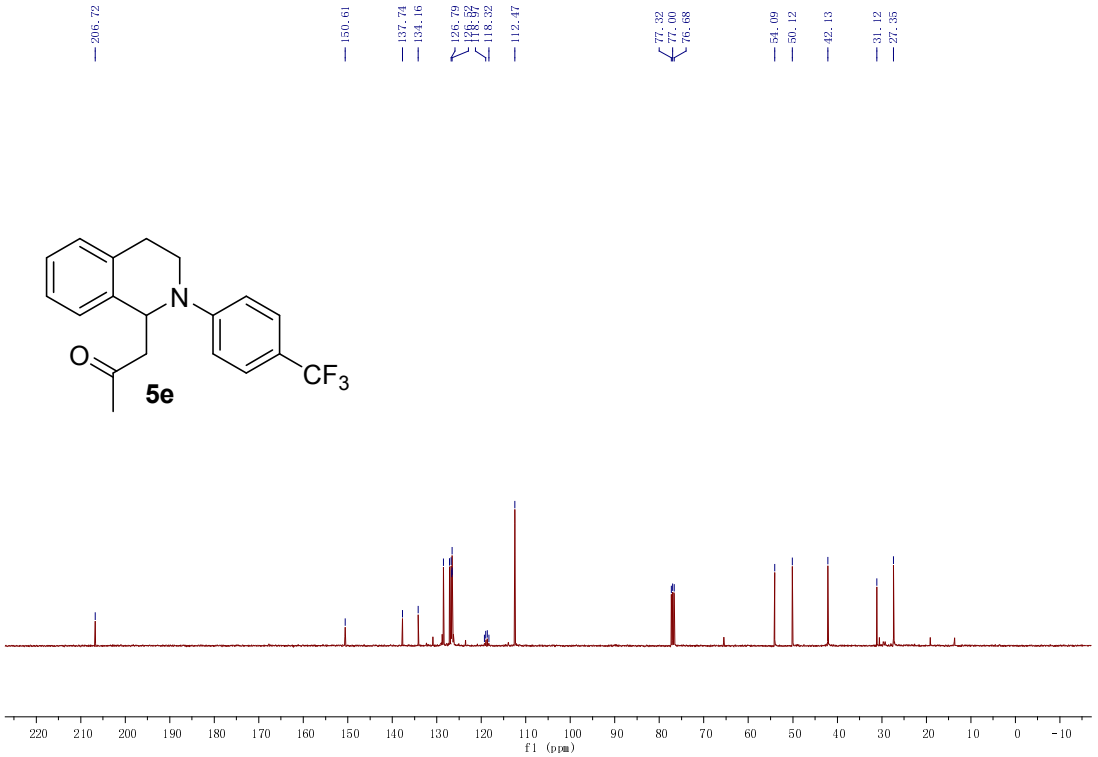

7.14
7.11
6.91
6.89
6.81
6.79
5.25
5.23
5.22
3.73
3.47
3.41
3.02
2.96
2.76
2.72
2.70
2.04
0.00
5c
3.74
2.04
2.02
1.00
3.00
2.32
2.16
2.12
2.92
f1 (ppm)

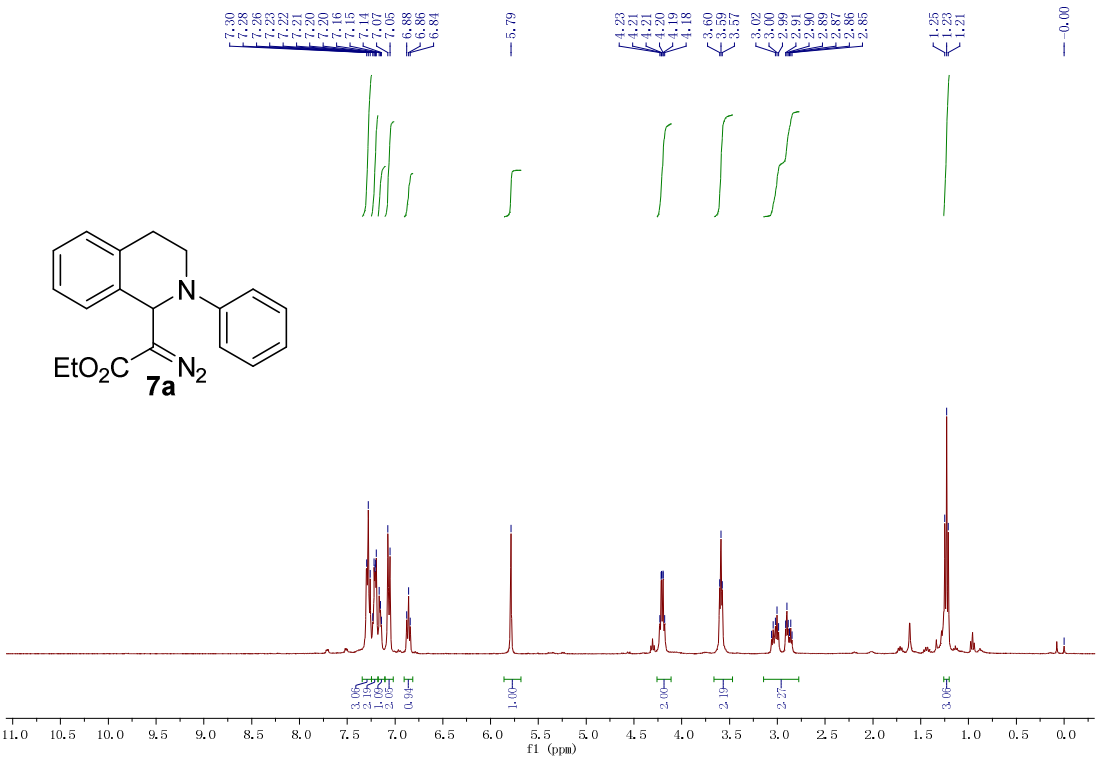

207.31
153.25
143.64
138.22
134.26
128.88
128.74
126.57
126.12
118.35
114.59
77.32
77.00
76.68
55.92
55.55
49.92
42.84
30.80
26.70
5c
f1 (ppm)

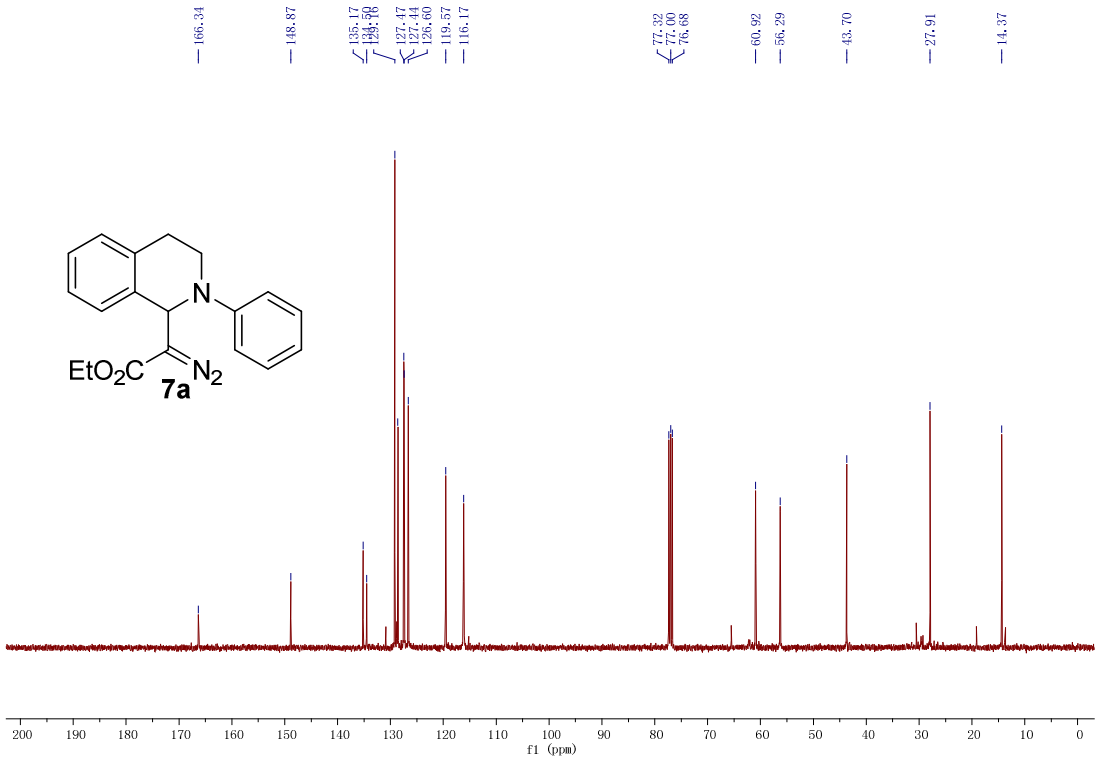

7.31
7.28
7.18
7.17
7.16
7.15
7.14
7.12
6.80
6.78
5.35
5.33
5.32
3.56
3.55
3.53
3.51
3.50
3.49
3.48
3.47
2.80
2.79
2.78
2.07
0.00
N
O
Br
5d
2.17
3.97
2.18
1.11
2.25
2.23
2.21
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

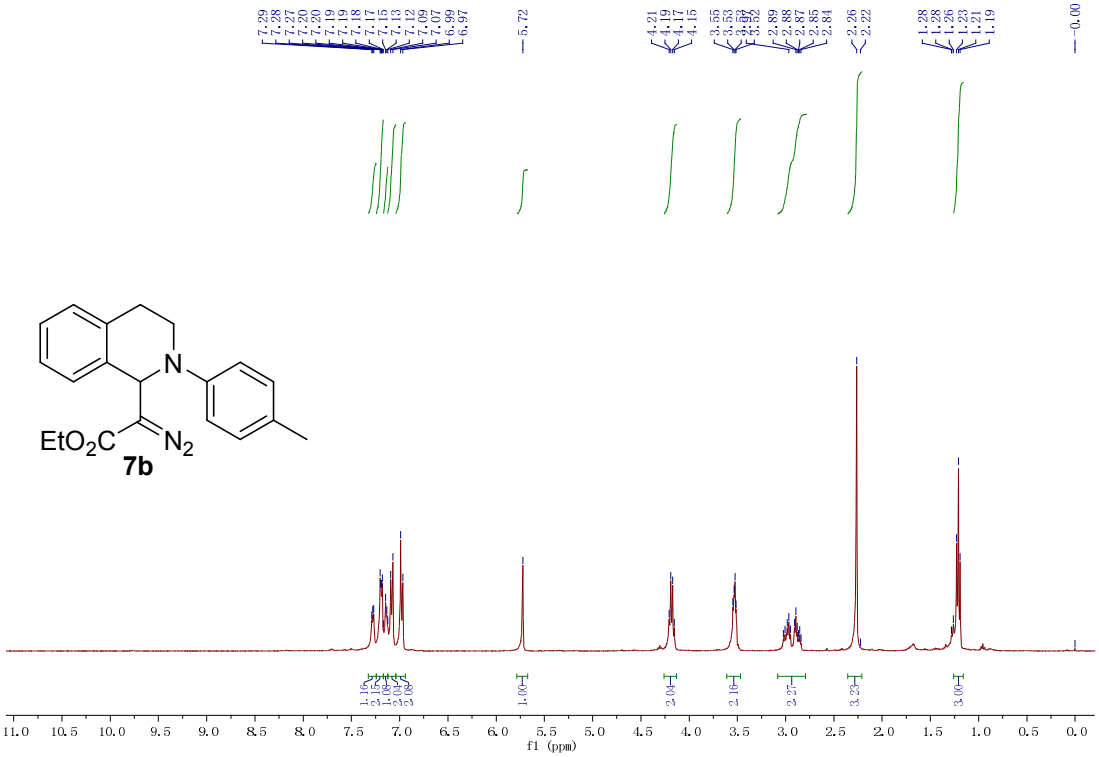

206.95
147.75
137.82
131.95
126.92
126.73
126.35
116.05
110.00
77.32
77.00
76.68
54.57
50.06
42.07
31.06
26.98
N
O
Br
5d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

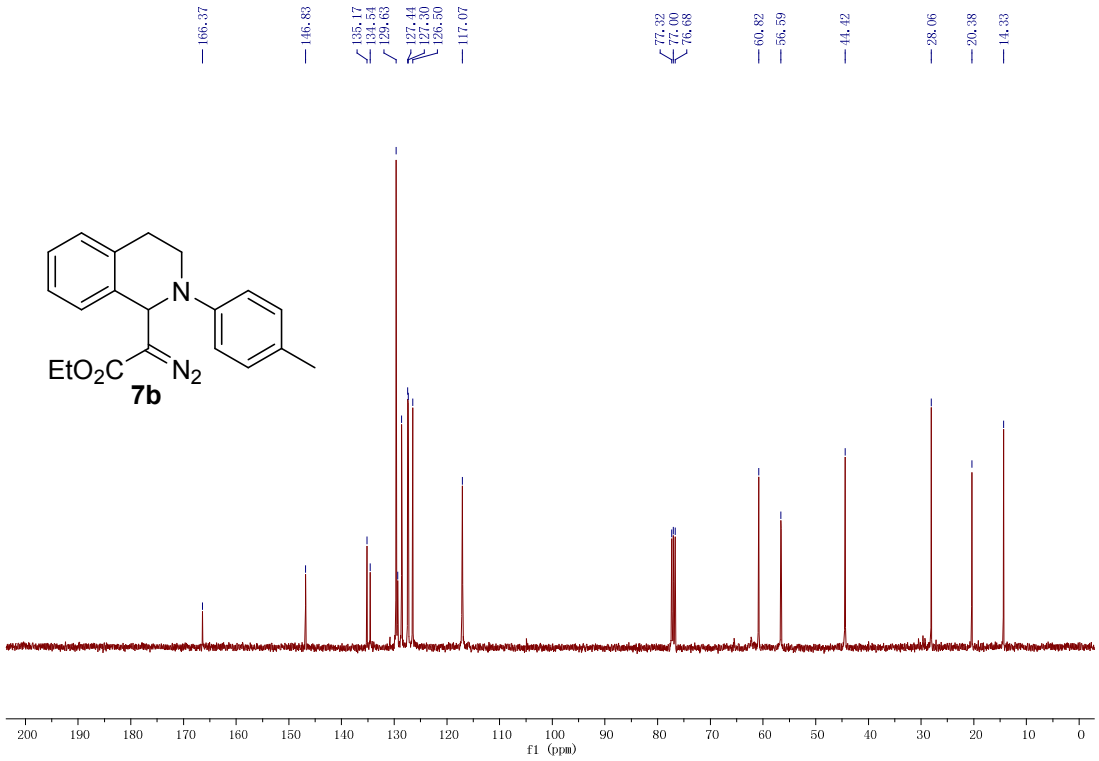

7.47
7.45
7.15
6.94
6.92
5.47
5.46
5.44
3.62
3.61
3.60
3.59
3.58
3.57
3.56
3.04
3.01
2.92
2.90
2.88
2.84
2.08
0.00
N
O
CF3
5e
2.40
4.46
2.21
1.05
2.33
2.32
2.25
3.00
f1 (ppm)

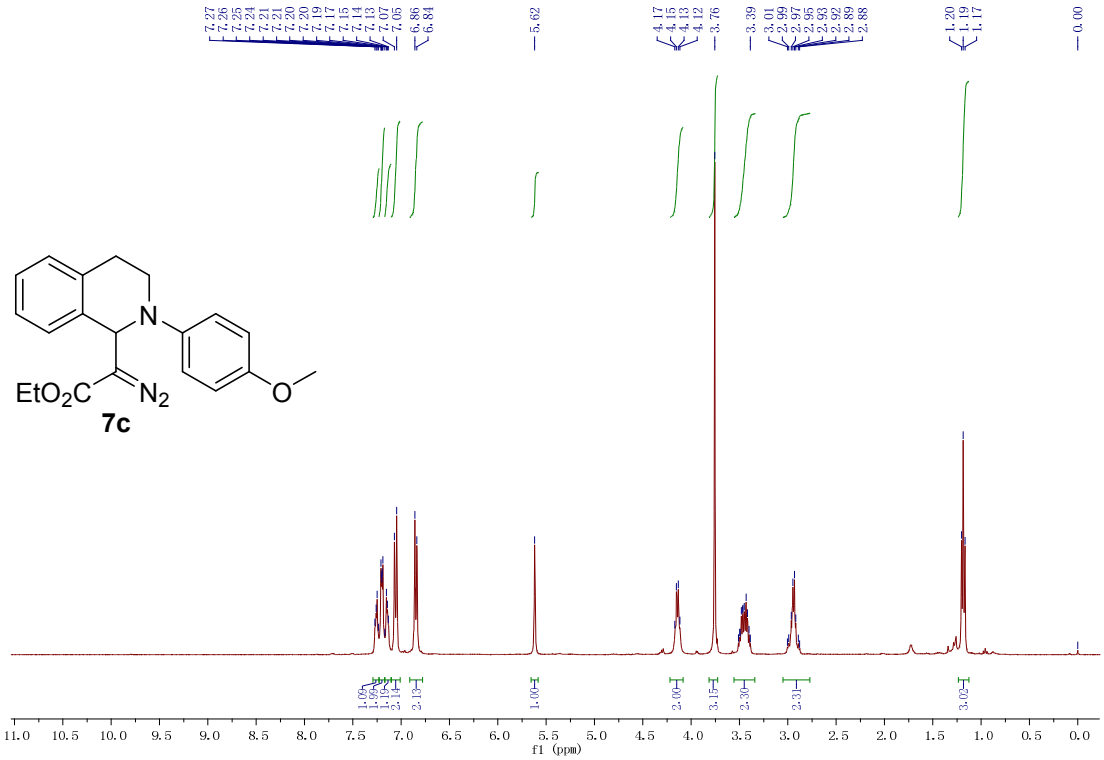

206.72
150.61
137.74
134.16
126.79
126.62
125.97
118.32
112.47
77.32
77.00
76.68
54.09
50.12
42.13
31.12
27.35
N
O
CF3
5e
f1 (ppm)

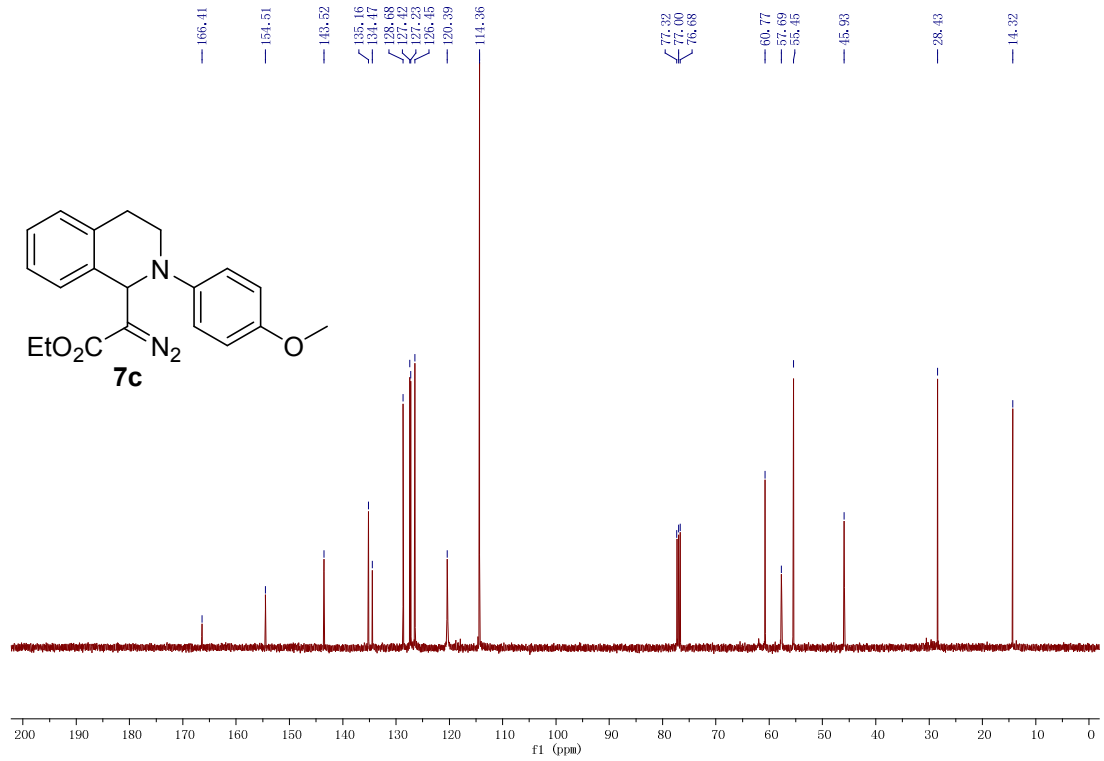

7.30
7.28
7.26
7.23
7.22
7.21
7.20
7.20
7.16
7.15
7.14
7.07
7.05
6.88
6.86
6.84
5.79
4.23
4.21
4.21
4.20
4.19
4.18
3.60
3.59
3.57
3.02
3.00
2.99
2.91
2.90
2.89
2.87
2.86
2.85
1.25
1.23
1.21
0.00
N
EtO2C
N2
7a
3.06
2.19
1.09
2.05
0.94
1.00
2.00
2.19
2.27
3.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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)

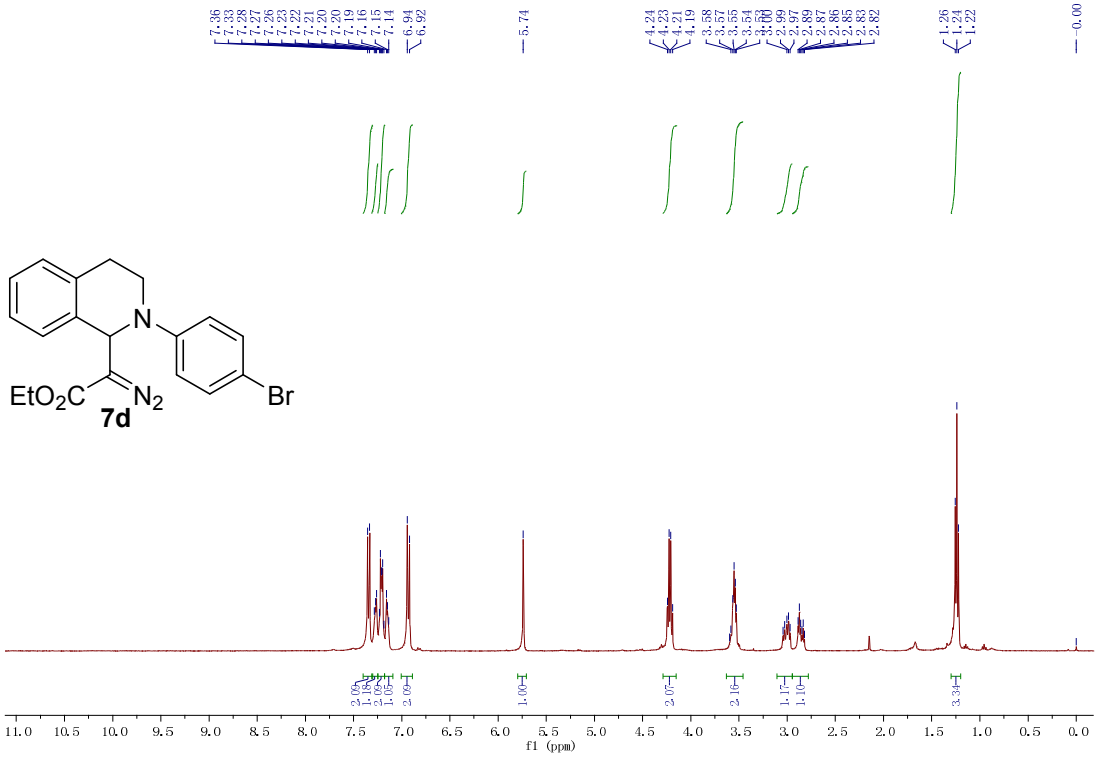

166.34
148.87
135.17
134.50
129.16
127.47
127.44
126.60
119.57
116.17
77.32
77.00
76.68
60.92
56.29
43.70
27.91
14.37
N
EtO2C
N2
7a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

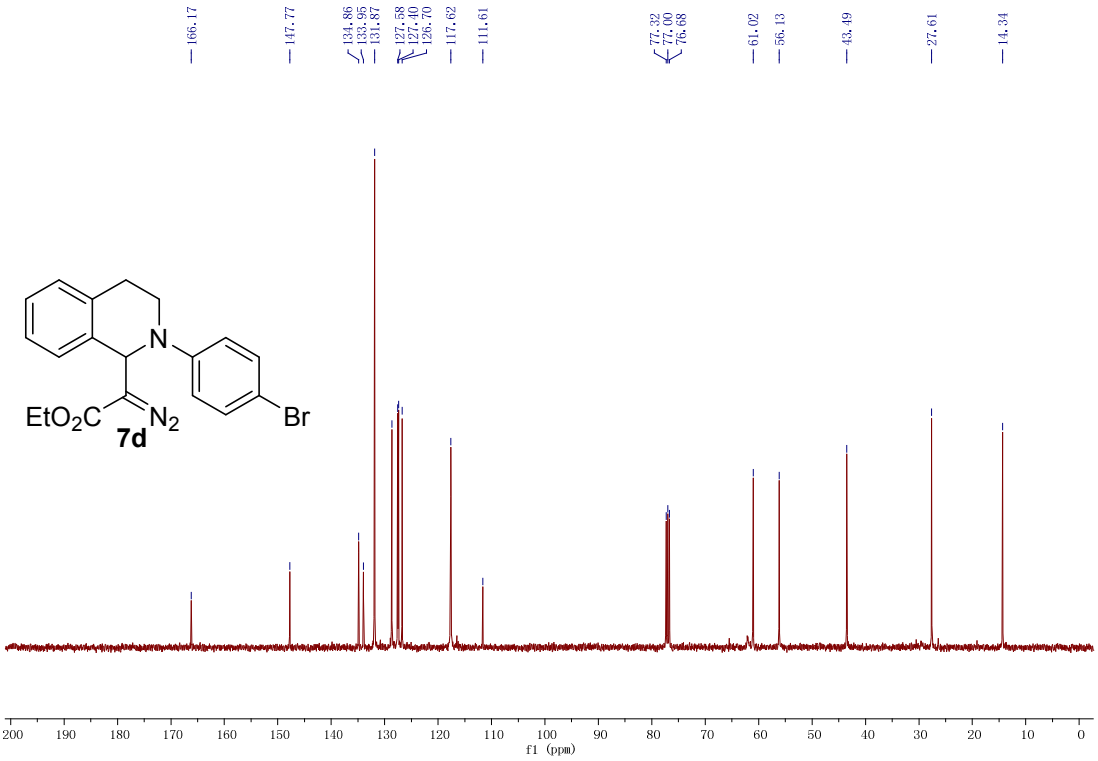

7.29
7.28
7.27
7.20
7.19
7.18
7.17
7.15
7.13
7.12
7.09
7.07
6.99
6.97
5.72
4.21
4.19
4.17
4.15
3.55
3.53
3.52
2.89
2.88
2.87
2.85
2.84
2.26
2.22
1.28
1.26
1.23
1.21
1.19
0.00
N
EtO2C
N2
7b
1.16
3.15
1.08
1.04
2.08
1.00
2.04
2.16
2.27
3.23
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

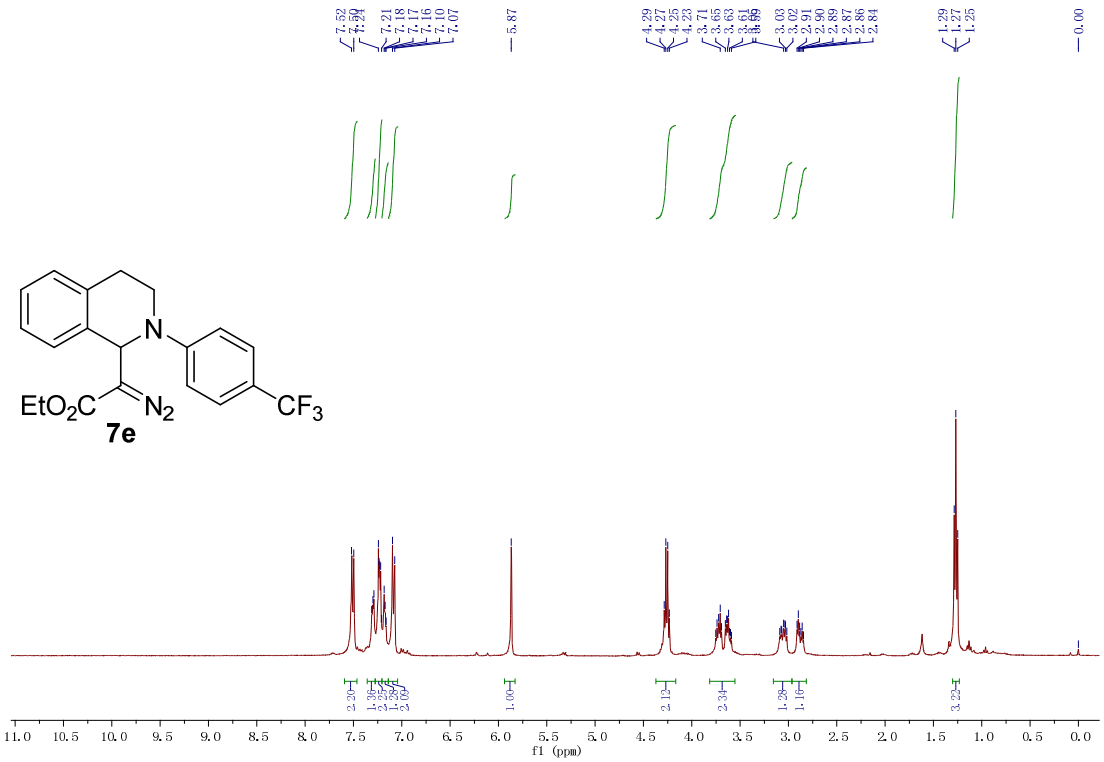

166.37
146.83
135.17
134.54
129.63
127.44
127.30
126.50
117.07
77.32
77.00
76.68
60.82
56.59
44.42
28.06
20.38
14.33
N
EtO2C
N2
7b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

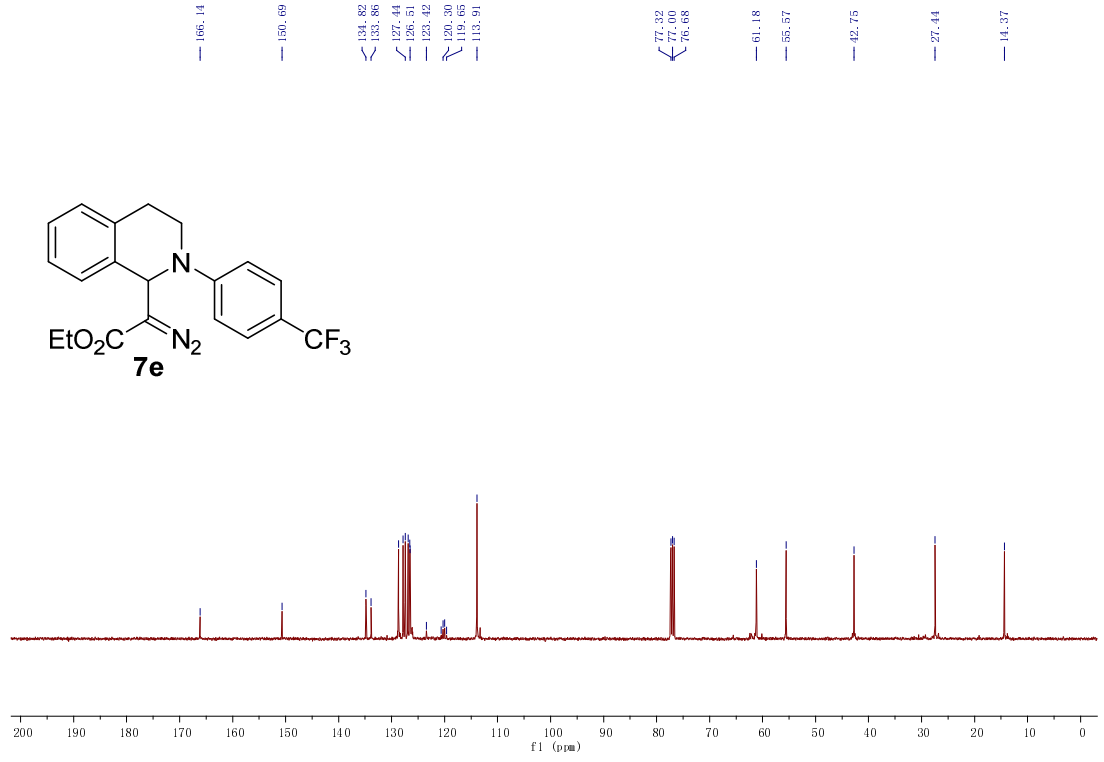

7.27
7.26
7.25
7.24
7.21
7.21
7.20
7.20
7.19
7.17
7.15
7.14
7.13
7.07
7.05
6.86
6.84
5.62
4.17
4.15
4.13
4.12
3.76
3.39
3.01
2.99
2.97
2.95
2.93
2.92
2.89
2.88
1.20
1.19
1.17
0.00
1.09
1.99
1.19
3.14
2.13
1.00
2.00
3.15
2.30
2.31
3.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
EtO2C
N2
N
O
7c


166.41
154.51
143.52
135.16
134.47
128.68
127.42
127.23
126.45
120.39
114.36
77.32
77.00
76.68
60.77
57.69
55.45
45.93
28.43
14.32
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
EtO2C
N2
N
O
7c


7.36
7.33
7.28
7.27
7.26
7.23
7.22
7.21
7.20
7.19
7.16
7.15
7.14
6.94
6.92
5.74
4.24
4.23
4.21
4.19
3.58
3.57
3.55
3.54
3.53
3.00
2.99
2.97
2.89
2.87
2.86
2.85
2.83
2.82
1.26
1.24
1.22
0.00
N
EtO2C
N2
Br
7d
2.05
1.08
2.09
1.05
2.09
1.00
3.07
2.16
1.17
1.10
3.34
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)


166.17
147.77
134.86
133.95
131.87
127.58
127.40
126.70
117.62
111.61
77.32
77.00
76.68
61.02
56.13
43.49
27.61
14.34
N
EtO2C
N2
Br
7d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.52
7.51
7.24
7.21
7.18
7.17
7.16
7.10
7.07
5.87
4.29
4.27
4.25
4.23
3.71
3.65
3.63
3.61
3.03
3.02
2.91
2.90
2.89
2.87
2.86
2.84
1.29
1.27
1.25
0.00
N
EtO2C
N2
CF3
7e
2.20
1.36
3.25
1.28
2.09
1.00
2.12
2.34
1.28
1.16
3.22
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)


166.14
150.69
134.82
133.86
127.44
126.51
123.42
120.30
119.65
113.91
77.32
77.00
76.68
61.18
55.57
42.75
27.44
14.37
N
EtO2C
N2
CF3
7e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Ⅶ. **References (cited in SI)**

S1. S.-J. Choi, T.-H. Kwon, H. Im, D.-I. Moon, D. J. Baek, M.-L. Seol, J. P. Duarte, Y.-K. Choi, *ACS Appl. Mater. Interfaces* **2011**, *3*, 4552-4556.

S2. Z. Li, C.-J. Li, *J. Am. Chem. Soc.* **2005**, *127*, 6968-6969.

S3. a) X.-Z. Shu, X.-F. Xia, Y.-F. Yang, K.-G. Ji, X.-Y. Liu, Y.-M. Liang, *J. Org. Chem.* **2009**, *74*, 7464-7469; b) A. Sud, D. Sureshkumar, M. Klussmann, *Chem. Commun.* **2009**, 3169-3171.

S4. All of the substrates and products are known compounds, see: a) Y. H. Pan, C. W. Kee, L. Chen, C. H. Tan, *Green Chem.* **2011**, *13*, 2682-2685; b) A. Tanoue, W. J. Yoo, S. Kobayashi, *Org Lett.* **2014**, *16*, 2346-2349; c) T. B. Xiao, L. Y. Li, G. L. Lin, Z. W. Mao, L. Zhou, *Org Lett.* **2014**, *16*, 4232-4235; d) H. E. Ho, Y. Ishikawa, N. Asao, Y. Yamamoto, T. Jin, *Chem Commun.* **2015**, *51*, 12764-12767.