Supplementary Information (SI) for New Journal of Chemistry.

Red-Light-Induced High Efficiency Oxidation and Functionalization of Tetrahydroisoquinoline Derivatives Using Chlorophyll as Photocatalyst

Rong Zeng,[‡a,b] Peng Yan,[‡b,c] Bo Xu,[‡b,c] Zhi-Liang Jing,[b] He Liu,[b] Wen-Jing Lai,[‡b,c] Hao-Tian Xie,[c] Sheng-Li Niu,[*a b] Shi-Ming Yang,[*a] and Qin Ouyang[*b]

[a] Xinqiao Hospital, the Second Affiliated Hospital of Army Medical University (Third Military Medical University), Chongqing 400037, China
[b] Department of Medicinal Chemistry, Third Military Medical University, Shapingba, Chongqing 400038 China.
[c] College of Chemistry and Environmental Engineering, Sichuan University of Science and Engineering, Zigong, 643000, China.
[‡] These authors contributed equally.

***Correspondence:**
Qin Ouyang
ouyangq@tmmu.edu.cn
Shi-Ming Yang
Yangshiming@tmmu.edu.cn
Sheng-Li Niu
niushengl@163.com

Supporting information

1. General methods

^{1}H NMR or ^{13}C NMR spectra were recorded on Agilent 600 or 150 MHz NMR spectrometer, respectively (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, td = triple doublet, dt = double triplet, m = multiplet, and coupling constants (J) are reported in Hertz (Hz). ESI-HRMS was recorded on a Waters SYNAPT G2. Column chromatography was performed on silica gel (300-400 mesh) eluting with ethyl acetate and petroleum ether or dichloromethane (CH_2Cl_2)/methanol (MeOH). TLC was performed on glass-backed silica plates. UV light, I_2, cerium molybdate, phosphomolybdic acid and $KMnO_4$ were used to visualize products or the starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether (60–90 °C) was redistilled. Unless otherwise noted, all reactions were carried out under ambient atmosphere.

2. General procedure for extraction of chlorophyll

Fresh spinach leaves were simply removed from the excess water, then chopped into the wall breaker along with a small amount of calcium carbonate. Added an appropriate amount of ethanol, and then turned on the wall breaker for juice extraction. Added petroleum ether to extract the spinach juice and filtered to remove the residues. The crude extract was then quickly passed through the column with 100-200 mesh silica gel to collect the dark green band, which was subsequently concentrated to obtain crude chlorophyll as photocatalyst.

3. General procedure for preparation of tetrahydroisoquinolines

Procedure **1**: $Pd_2(dba)_3$ (0.02 mmol, 20.6 mg), BINAP (0.05 mmol, 28.6 mg) and NaO-t-Bu (1.1 mmol, 100.5 mg) were added into a 25 mL well dried bottom flasks with two necks then evacuated and back filled three times with Argon. After that, 3.0 mL of toluene was injected to bottom. The reaction was refluxing at 110 ℃ for 15 min and then added 1,2,3,4-tetrahydroisoquinoline (2.2 mmol, 0.6 mL) or 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (2.2 mmol, 849 mg), and an aryl bromide (1.1 mmol,2 equiv) after cool to room temperature. The mixture was stirred at 110 ℃ overnight. When the reaction completed, it was quenched with water and extracted with ethyl acetate. Then purification the crude by column chromatography using petroleum / ethyl acetate to afford pure product of **1a-c**.[1]

Procedure **2**: To a stirred solution of 1,2,3,4-tetrahydroisoquinoline (0.625 mL, 5 mmol) or 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (0.625 mL, 5 mmol) in dry DMF (10 mL) was added NaH (60 % w/w in oil, 400 mg, 10 mmol) followed by 1-bromoalkanes (5.5 mmol). The resulting solution was stirred at 50 °C. After complete consumption of the starting material 1,2,3,4-tetrahydroisoquinoline, as indicated by TLC, water (60 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 60 mL). The combined organic layer was washed with water (3 × 20 mL) followed by drying Na2SO4 and concentrated in vacuo. Purification by flash column chromatography (petroleum ether : ethyl acetate = 60:1) afforded the desired products **1i**, **1f**, **1e**, **1r**, **1p**, **1o**, **1x**.[2]

Procedure **3**: 1,2,3,4-tetrahydroisoquinoline (1.0 mmol, 1.0 equiv) or 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (1.0 mmol, 1.0 equiv) and K_2CO_3 (10 mmol, 10 equiv) were added into a 25 mL well dried bottom flasks. After that, injection 8.0 mL of acetonitrile to bottom. Then add 6-iodo-1-hexyne (1.2 mmol, 1.2 equiv) to bottom. The mixture was stirred at 25 °C overnight. When the reaction completed, it was quenched with water and extracted with ethyl acetate. Then purification the crude by column chromatography using petroleum / ethyl acetate to afford pure product of **1d**, **1j**, **1k**, **1l**, **1m**, **1n**, **1q**, **1s**, **1t**, **1u**, **1v**, **1y**.[2]

Procedure **4**: The solution of allyl bromide (726 mg, 6 mmol) in diethyl ether (3 mL) was added slowly to a stirred solution of 1,2,3,4-tetrahydroisoquinoline (400 mg, 3 mmol) in diethyl ether (2 mL) at 5 °C. After addition was complete, the reaction mixture was allowed to stir at room temperature for overnight. The resulting mixture was diluted with diethyl ether (20 mL), and the white precipitate was removed by filtration. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purification by flash column chromatography (petroleum ether : ethyl acetate = 20:1) afforded the desired products **1g**.[2]

Procedure **5**: Add copper (I) iodide (1.0 mmol) and potassium phosphate (20.0 mmol) to a Schlenk tube.Evacuate the tube and back fill with nitrogen. Add 2-Propanol (10.0 mL), ethylene glycol (1.11 mL, 20.0 mmol), 1, 2, 3, 4-tetrahydroisoquinoline (15 mmol) and Iodobenzene (1.11 mL, 10.0 mmol) successively via a micro-syringe at room temperature. Heat the reaction mixture at 85-90 °C and keep for 24 h. Allow to cool to room temperature. Add diethyl ether (20 mL) and water (20 mL). Extract the aqueous layer by diethyl ether (2×20 mL). Wash the combine organic phases with brine and dry over magnesium sulfate.Remove the solvent via rotary evaporation. Purification by flash column chromatography (petroleum ether : ethyl acetate = 20:1) afforded the desired products **1z**.[3]

4. General procedure for red light induced oxidation/ α-nucleophilic substitution of tetrahydroisoquinolines

General procedure (**GP 1**): Tetrahydroisoquinoline (0.1 mmol, 1.0 equiv.), chlorophyll (0.002 mmol, 2.0 mol%) and DMAP (0.1 mmol, 1.0 equiv.) were dissolved with acetonitrile (1.0 mL) in a transparent reaction tube. Then, the reaction mixture was stirred and irradiated by 30 W red LEDs at room temperature under air atmosphere for 12 h (**Figure S1**). After completion, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the products **2a-y**.

General procedure (**GP 2**): Tetrahydroisoquinoline (0.1 mmol, 1.0 equiv.), chlorophyll (0.002 mmol, 2.0 mol%) and nucleophile (0.5 mmol, 5.0 equiv.) were dissolved with DMF (1.0 mL) in a transparent reaction tube. Then, the reaction mixture was stirred and irradiated by 15 W red LEDs at room temperature under air atmosphere for 12 h (**Figure S1**). When the reaction completed, it was quenched with water and extracted with ethyl acetate. Then purification the crude by column chromatography using petroleum/ethyl acetate to afford pure products **4a-p**.

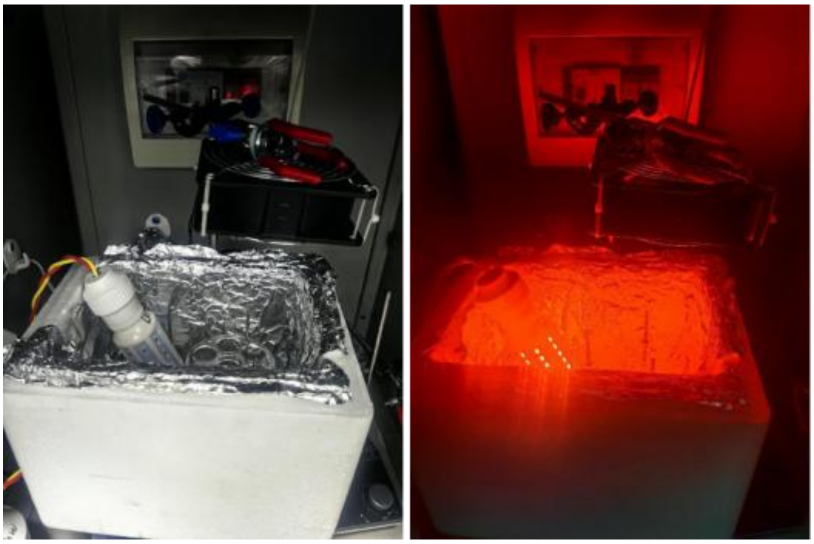


Figure S1 Reaction setup (30 W or 15 W red LEDs)

5. Light "on/off" experiments.

According to **GP 1**: 2-phenyl-1,2,3,4-tetrahydroisoquinoline (156.8 mg, 0.75 mmol, 1.0 equiv), chlorophyll (13.2 mg, 0.015 mmol, 2 mol%), DMAP (91.5 mg, 0.75 mmol, 1.0 equiv), and 1,1,2,2-tetrachloroethane (125.3 mg, 0.75 mmol, 1equiv) were placed in a 25 mL round bottom flask. Finally, CD_3CN (7.5 mL) was added as solvent. Then, the flask was irradiated by 15 W red LEDs at room temperature and turn on or off the lamp at an interval of 1 h. The ^1H NMR yields were measured at a specific time interval with 0.5 mL reaction mixtures.

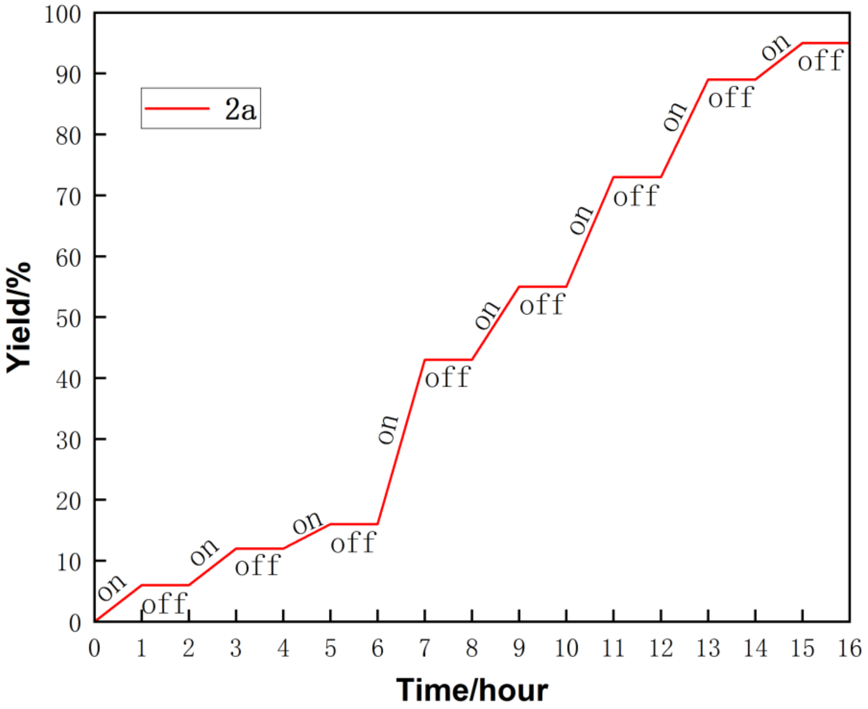


Figure S2 Light on-off experiments.

6. Kinetic curve determination

According to **GP 1**: 2-phenyl-1,2,3,4-tetrahydroisoquinoline (156.8 mg, 0.75 mmol, 1.0 equiv), chlorophyll (13.2 mg, 0.015 mmol, 2 mol%), DMAP (91.5 mg, 0.75 mmol, 1.0 equiv), and 1,1,2,2-tetrachloroethane (125.3 mg, 0.75 mmol, 1.0 equiv) were placed in a 25 mL round bottom flask. CD_3CN (7.5 mL) was added as solvent. The reaction mixture was divided into 12 parts (0.5 mL for each) in transparent tubes. All the tubes were irradiated by 15 W red LEDs at room temperature. Then, the ^1H NMR yields of products **2a** and substrate **1a** were measured by sampling at 0 h, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, 9 h, 10 h, 11 h and 12 h.

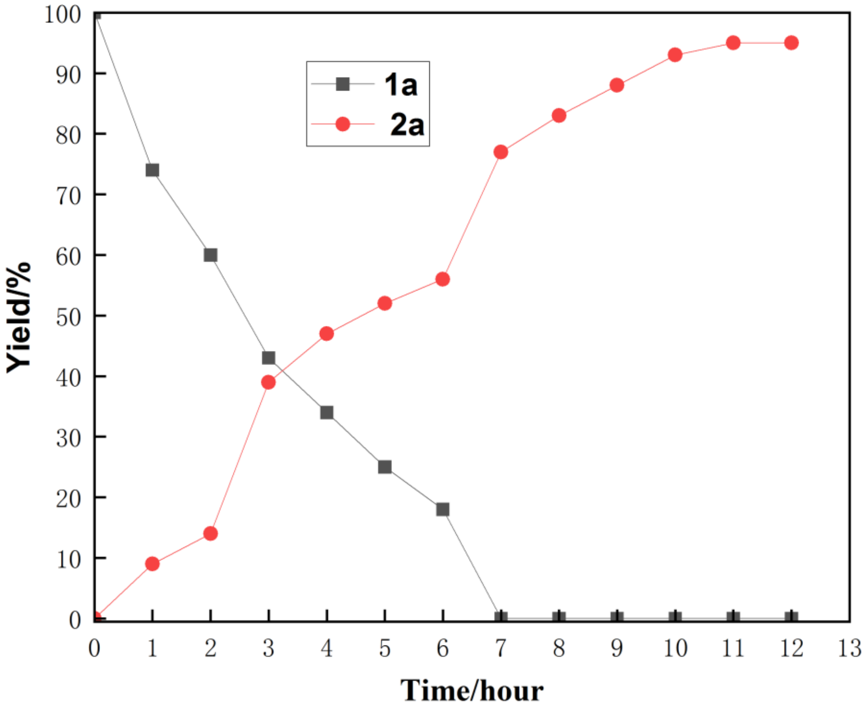
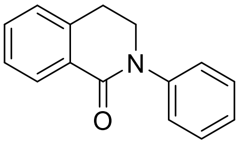


Figure S3 Kinetic experiments.

7. Cell viability assay

Compound **4i** was dissolved with DMSO into a 50 mM solution before being diluted to corresponding concentrations with the culture medium. The OGD modeling cells or control cells were treated with indicated concentrations of compound **4i** for 22 h, and cell viability was then measured by Cell Counting Kit-8 (CCK-8, Beyotime, Chongqing, China) assay. CCK-8 (100 μL/mL) was added to each well and incubated away from light at 37 °C for 3 h. Then, absorbance was recorded by the SpectraMax i3 multimode detector (Paradigm, Molecular Devices, USA) at 450 nm. An equivalent volume of solvent was added for the vehicle group.

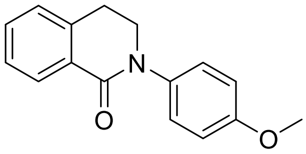
8. Characterizations of products.



2a

2-phenyl-3,4-dihydroisoquinolin-1(2*H*)-one (2a)

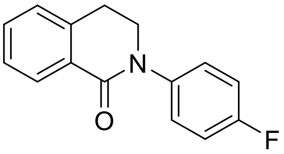
According to **GP 1** with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2a** as white solid (21.8 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 6.9 Hz, 1H), 7.43 – 7.35 (m, 5H), 7.24 (t, *J* = 8.4 Hz, 2H), 3.99 (t, *J* = 6.4 Hz, 2H), 3.14 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.20, 143.10, 138.29, 132.02, 129.70, 128.91, 128.75, 127.19, 126.93, 126.25, 125.31, 49.41,28.62. This characterization data are in accordance with the reported literature.[4]



2b

2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2*H*)-one

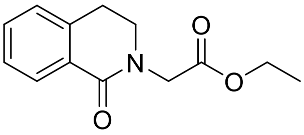
According to **GP 1** with 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (23.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2b** as white solid (22.5 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.46 (t, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 1H), 6.97 – 6.91 (m, 2H), 3.97 – 3.93 (m, 2H), 3.82 (s, 3H), 3.13 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.37, 157.80, 138.26, 136.09, 131.89, 129.76, 128.68, 127.14, 126.90, 126.65, 114.23, 55.46, 49.69, 28.63. This characterization data are in accordance with the reported literature.[4]



2c

2-(4-fluorophenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (2c)

According to **GP 1** with 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (22.7 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2c** as white solid (17.5 mg, 73%). ^{1}H NMR (600 MHz, CDCl3) δ 8.14 (d, *J* = 7.0 Hz, 1H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 8.7 Hz, 2H), 4.01 – 3.92 (m, 2H), 3.15 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.36, 160.69 (d, *J* = 277.5 Hz), 139.03 (d, *J* = 3.3 Hz), 138.22, 132.15, 129.47, 128.73, 127.27,127.11 (d, *J* = 41.4 Hz),127.08 (d, *J* = 8.4 Hz), 115.73 (d, *J* = 22.5 Hz), 49.56, 28.58. This characterization data are in accordance with the reported literature.[4]

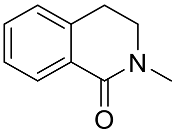


2d

ethyl 2-(1-oxo-3,4-dihydroisoquinolin-2(1*H*)-yl)acetate (2d)

According to **GP 1** with ethyl 2-(3,4-dihydroisoquinolin-2(1H)-yl)acetate (21.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002mmol, 2 mol%), and DMAP (12.2

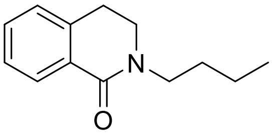
mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2d** as yellow oil (16.8 mg, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.43 (t, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 4.34 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.70 – 3.64 (m, 2H), 3.07 (t, *J* = 6.6 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.21, 164.89, 138.37, 131.84, 128.86, 128.44, 126.98, 126.89, 61.17, 49.13, 47.35, 28.05, 14.13. This characterization data are in accordance with the reported literature.[2]



2e

2-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (2e)

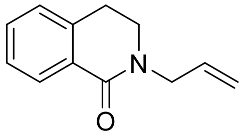
According to **GP 1** with 2-methyl-1,2,3,4-tetrahydroisoquinoline (14.7 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2e** as yellow oil (13.0 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 3.55 (t, *J* = 6.7 Hz, 2H), 3.14 (s, 3H), 2.99 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.80, 137.94, 131.50, 129.33, 128.08, 126.97, 126.85, 48.11, 35.16, 27.88. This characterization data are in accordance with the reported literature.[5]



2f

2-butyl-3,4-dihydroisoquinolin-1(2*H*)-one (2f)

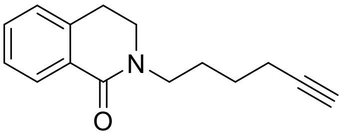
According to **GP 1** with 2-butyl-1,2,3,4-tetrahydroisoquinoline (18.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2f** as yellow oil (12.6 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 3.56 (dt, *J* = 10.5, 7.1 Hz, 4H), 2.98 (t, *J* = 6.6 Hz, 2H), 1.61 (p, *J* = 7.5 Hz, 2H), 1.38 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.24, 137.93, 131.40, 129.71, 128.20, 126.99, 126.75, 47.22, 46.04, 29.85, 28.20, 20.20, 13.91. This characterization data are in accordance with the reported literature.[2]



2g

2-allyl-3,4-dihydroisoquinolin-1(2*H*)-one (2g)

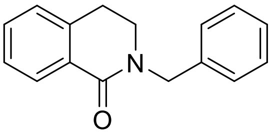
According to **GP 1** with 2-allyl-1,2,3,4-tetrahydroisoquinoline (17.3 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2g** as yellow oil (11.4 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.3 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 5.86 (ddt, *J* = 17.3, 10.2, 5.9 Hz, 1H), 5.28 – 5.19 (m, 2H), 4.21 (d, *J* = 8.9 Hz, 2H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.98 (t, *J* = 6.6 Hz, 2H).^{13}C NMR (150 MHz, $CDCl_3$) δ 164.26, 138.06, 133.13, 131.62, 129.41, 128.32, 127.02, 126.88, 117.45, 49.58, 45.30, 28.07. This characterization data are in accordance with the reported literature.[2]



2h

2-(hex-5-yn-1-yl)-3,4-dihydroisoquinolin-1(2*H*)-one (2h)

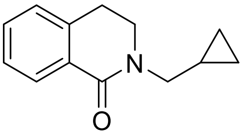
According to **GP 1** with 2-(hex-5-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline (21.3 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2h** as yellow oil (15.4 mg, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 3.59 (t, *J* = 7.2 Hz, 2H), 3.56 (t, *J* = 6.6 Hz, 2H), 2.99 (t, *J* = 6.6 Hz, 2H), 2.26 (t, *J* = 8.1 Hz, 2H), 1.95 (s, 1H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.59 (p, *J* = 7.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.34, 137.90, 131.47, 129.58, 128.22, 127.00, 126.76, 84.08, 68.57, 46.70, 45.97, 28.18, 26.70, 25.68, 18.13. HRMS-EI (m/z): $[M+H]^+$ calcd for, 228.1383; found, 228.1385.



2i

3-benzyl-3,4-dihydroisoquinolin-1(2*H*)-one (2i)

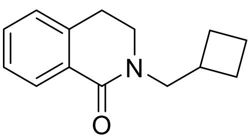
According to **GP 1** with ethyl 2-benzyl-1,2,3,4-tetrahydroisoquinoline (22.3 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2i** as yellow oil (14.7 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 6.8 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.38 – 7.30 (m, 5H), 7.30 – 7.27 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 4.80 (s, 2H), 3.49 (t, *J* = 6.7 Hz, 2H), 2.94 (t, *J* = 6.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.58, 138.04, 137.43, 131.68, 129.37, 128.63, 128.44, 128.04, 127.43, 127.06, 126.88, 50.44, 45.34, 28.08. This characterization data are in accordance with the reported literature.[2]



2j

2-(cyclopropylmethyl)-3,4-dihydroisoquinolin-1(2*H*)-one (2j)

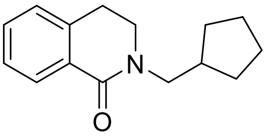
According to **GP 1** with 2-(cyclopropylmethyl)-1,2,3,4-tetrahydroisoquinoline (18.7 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2j** as yellow oil (13.1 mg, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.3 Hz, 1H), 7.40 (t, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.16 (s, 1H), 3.64 (t, *J* = 6.7 Hz, 2H), 3.47 (s, 2H), 3.00 (t, *J* = 6.6 Hz, 2H), 1.09 – 1.01 (m, 1H), 0.56 – 0.49 (m, 2H), 0.30 (dt, *J* = 6.0, 4.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.29, 138.00, 131.45, 129.65, 128.25, 126.97, 126.79, 51.43, 46.07, 28.15, 9.61, 3.45. This characterization data are in accordance with the reported literature.[6]



2k

2-(cyclobutylmethyl)-3,4-dihydroisoquinolin-1(2*H*)-one (2k)

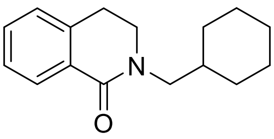
According to **GP 1** with 2-(cyclobutylmethyl)-1,2,3,4-tetrahydroisoquinoline (20.1 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2k** as yellow oil (12.9 mg, 60%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 3.61 (d, *J* = 7.4 Hz, 2H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.95 (t, *J* = 6.5 Hz, 2H), 2.68 (dt, *J* = 15.5, 7.7 Hz, 1H), 2.05 (s, 2H), 1.90 (dt, *J* = 16.2, 7.9 Hz, 2H), 1.81 (p, *J* = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 164.32, 137.94, 131.35, 129.73, 128.26, 126.95, 126.69, 52.40, 46.49, 34.49, 28.21, 26.51, 18.52. HRMS-EI (m/z): [M+H]$^+$ calcd for, 216.1383; found, 216.1386.



2l

2-(cyclopentylmethyl)-3,4-dihydroisoquinolin-1(2*H*)-one (2l)

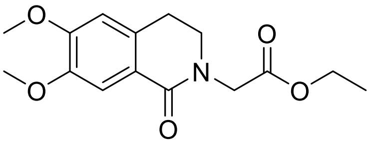
According to **GP 1** with 2-(cyclopentylmethyl)-1,2,3,4-tetrahydroisoquinoline (21.5 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2l** as yellow oil (14.2 mg, 62%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 3.57 (t, *J* = 6.5 Hz, 2H), 3.52 (d, *J* = 7.7 Hz, 2H), 2.98 (t, *J* = 6.6 Hz, 2H), 2.28 (p, *J* = 7.7 Hz, 1H), 1.73 (dd, *J* = 12.0, 7.1 Hz, 2H), 1.68 (s, 2H), 1.59 – 1.51 (m, 2H), 1.30 (dt, *J* = 12.1, 7.0 Hz, 2H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 164.38, 137.92, 131.33, 129.84, 128.27, 126.95, 126.67, 51.94, 46.42, 38.76, 30.46, 28.25, 25.02. HRMS-EI (m/z): [M+H]$^+$ calcd for, 230.1539; found, 230.1541.



2m

2-(cyclohexylmethyl)-3,4-dihydroisoquinolin-1(2*H*)-one (2m)

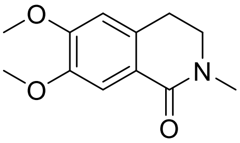
According to **GP 1** with 2-(cyclohexylmethyl)-1,2,3,4-tetrahydroisoquinoline (22.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 15/1) to afford the desired product **2m** as colourless oil (8.7 mg, 36%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 3.53 (t, *J* = 6.6 Hz, 2H), 3.39 (d, *J* = 7.0 Hz, 2H), 2.97 (t, *J* = 6.5 Hz, 2H), 1.72 (d, *J* = 9.8 Hz, 5H), 1.31 – 1.12 (m, 4H), 1.02 (dd, *J* = 22.7, 12.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.48, 137.92, 131.35, 129.73, 128.23, 126.95, 126.68, 53.91, 46.99, 36.67, 30.92, 28.19, 26.42, 25.87. HRMS-EI (m/z): $[M+H]^+$ calcd for, 244.1696; found, 244.1696.



2n

ethyl 2-(6,7-dimethoxy-1-oxo-3,4-dihydroisoquinolin-2(1*H*)-yl)acetate (2n)

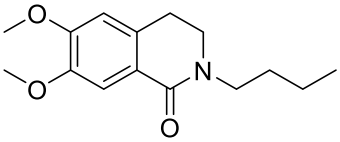
According to **GP 1** with ethyl 2-(6,7-dimethoxy-3,4-dihydroisoquinolin-2(1H)-yl)acetate (27.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 5/1) to afford the desired product **2n** as yellow oil (18.2 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 6.64 (s, 1H), 4.31 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.91 (d, *J* = 3.2 Hz, 6H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.99 (t, *J* = 6.6 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.38, 165.03, 152.08, 148.02, 132.14, 121.39, 110.76, 109.35, 61.16, 56.05, 56.00, 49.22, 47.64, 27.67, 14.15. HRMS-EI (m/z): $[M+H]^+$ calcd for, 294.1336; found, 294.1336.



2o

6,7-dimethoxy-2-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (2o)

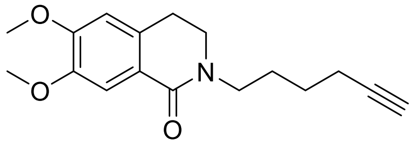
According to **GP 1** with 6,7-dimethoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (20.7 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2q** as yellow oil (15.0 mg, 68%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.59 (s, 1H), 6.62 (s, 1H), 3.91 (d, *J* = 6.0 Hz, 6H), 3.54 (t, *J* = 6.7 Hz, 2H), 3.13 (s, 3H), 2.93 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 164.88, 151.59, 147.87, 131.50, 121.94, 110.38, 109.18, 56.07, 55.99, 48.37, 35.16, 27.50. This characterization data are in accordance with the reported literature.[7]



2p

4-butyl-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2*H*)-one (2p)

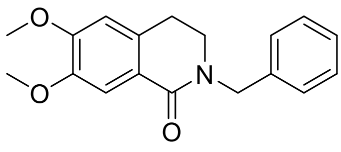
According to **GP 1** with 2-butyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (24.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2p** as yellow oil (23.4 mg, 89%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.58 (s, 1H), 6.61 (s, 1H), 3.90 (d, *J* = 4.7 Hz, 6H), 3.52 (dt, *J* = 10.5, 7.0 Hz, 4H), 2.89 (t, *J* = 6.7 Hz, 2H), 1.63 – 1.55 (m, 2H), 1.40 – 1.32 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 164.28, 151.51, 147.86, 131.45, 122.26, 110.47, 109.12, 56.03, 55.99, 47.14, 46.26, 29.90, 27.78, 20.17, 13.90. HRMS-EI (m/z): [M+H]$^+$ calcd for, 264.1594; found, 264.1590.



2q

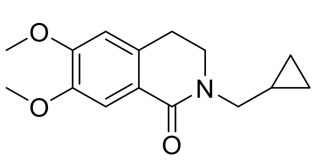
2-(hex-5-yn-1-yl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2*H*)-one (2q)

According to **GP 1** with 2-(hex-5-yn-1-yl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (27.3 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2q** as yellow oil (18.4 mg, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (s, 1H), 6.61 (s, 1H), 3.90 (d, *J* = 4.3 Hz, 6H), 3.56 (t, *J* = 7.2 Hz, 2H), 3.52 (t, *J* = 6.7 Hz, 2H), 2.90 (t, *J* = 6.7 Hz, 2H), 2.24 (td, *J* = 7.0, 2.6 Hz, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.74 (p, *J* = 7.3 Hz, 2H), 1.58 (p, *J* = 7.1 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.37, 151.65, 147.95, 131.47, 122.15, 110.55, 109.20, 84.10, 68.56, 56.03, 55.99, 46.62, 46.19, 27.78, 26.75, 25.67, 18.13. HRMS-EI (m/z): $[M+H]^+$ calcd for, 288.1594; found, 288.1591.


2r

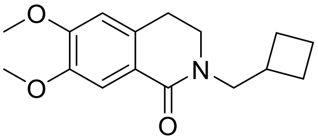
5-benzyl-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2*H*)-one (2r)

According to **GP 1** with 2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (28.3 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2r** as yellow oil (15.7 mg, 53%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.33 (d, *J* = 4.4 Hz, 4H), 7.30 – 7.26 (m, 1H), 6.61 (s, 1H), 4.77 (s, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 3.47 (t, *J* = 6.7 Hz, 2H), 2.87 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.69, 151.82, 147.96, 137.57, 131.68, 128.62, 128.02, 127.40, 121.84, 110.69 (d, *J* = 7.3 Hz), 109.23 (d, *J* = 7.1 Hz), 56.10 (d, *J* = 8.4 Hz), 56.03 (d, *J* = 8.9 Hz), 50.47, 45.63, 27.69. This characterization data are in accordance with the reported literature.[8]


2s

2-(cyclopropylmethyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2*H*)-one (2s)

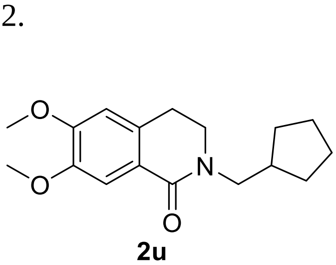
According to **GP 1** with 2-(cyclopropylmethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (24.7 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2s** as yellow oil (17.2 mg, 66%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.59 (s, 1H), 6.62 (s, 1H), 3.91 (d, *J* = 4.5 Hz, 6H), 3.62 (t, *J* = 6.7 Hz, 2H), 3.44 (d, *J* = 7.0 Hz, 2H), 2.92 (t, *J* = 6.7 Hz, 2H), 1.09 – 1.01 (m, 1H), 0.55 – 0.48 (m, 2H), 0.31 – 0.26 (m, 2H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 164.32, 151.55, 147.85, 131.55, 122.20, 110.52, 109.14, 56.04, 56.00, 51.43, 46.33, 27.76, 9.63, 3.44. HRMS-EI (m/z): [M+H]$^+$ calcd for, 262.1438; found, 262.1435.



2t

2-(cyclobutylmethyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2*H*)-one (2t)

According to **GP 1** with 2-(cyclobutylmethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (26.7 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2t** as yellow oil (17.9 mg, 65%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.59 (s, 1H), 6.61 (s, 1H), 3.90 (d, *J* = 7.3 Hz, 6H), 3.58 (d, *J* = 7.4 Hz, 2H), 3.50 (t, *J* = 6.7 Hz, 2H), 2.87 (t, *J* = 6.7 Hz, 2H), 2.66 (p, *J* = 7.7 Hz, 1H), 2.04 (dtt, *J* = 11.7, 5.3, 2.8 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.84 – 1.77 (m, 2H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 164.36, 151.57, 147.92, 131.48, 122.30, 110.63, 109.17, 56.03, 55.99, 52.35, 46.72, 34.55, 27.81, 26.51, 18.53. HRMS-EI (m/z): [M+H]$^+$ calcd for, 276.1594; found, 276.1592.

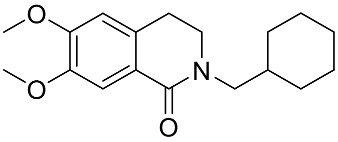


2u

2-(cyclopentylmethyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(2*H*)-one (2u)

According to **GP 1** with 2-(cyclopentylmethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (27.5 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002

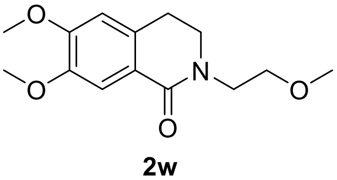
mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2u** as yellow oil (18.2 mg, 63%)^{1}H NMR (600 MHz, CDCl$_3$) δ 7.59 (s, 1H), 6.62 (s, 1H), 3.91 (d, *J* = 4.6 Hz, 6H), 3.54 (t, *J* = 6.7 Hz, 2H), 3.48 (d, *J* = 7.7 Hz, 2H), 2.89 (t, *J* = 6.7 Hz, 2H), 2.26 (p, *J* = 7.6 Hz, 1H), 1.76 – 1.71 (m, 2H), 1.69 – 1.63 (m, 2H), 1.57 – 1.50 (m, 2H), 1.34 – 1.25 (m, 2H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 164.41, 151.56, 147.93, 131.45, 122.36, 110.64, 109.16, 56.02, 55.99, 51.84, 46.62, 38.79, 30.43, 27.84, 25.02. HRMS-EI (m/z): [M+H]$^+$ calcd for, 290.1751; found, 290.1746.



2v

2-(cyclohexylmethyl)-6,7-dimethoxy-3,4-dihydroisoquinolin-1(*2H*)-one (2v)

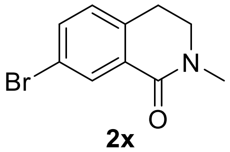
According to **GP 1** with 2-(cyclohexylmethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (28.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2v** as yellow oil (20.3 mg, 67%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.59 (s, 1H), 6.62 (s, 1H), 3.91 (d, *J* = 4.1 Hz, 6H), 3.52 (t, *J* = 6.7 Hz, 2H), 3.37 (d, *J* = 6.9 Hz, 2H), 2.90 (t, *J* = 6.6 Hz, 2H), 1.72 (d, *J* = 9.1 Hz, 5H), 1.65 (d, *J* = 9.7 Hz, 1H), 1.24 – 1.13 (m, 3H), 1.02 (q, *J* = 11.7, 11.2 Hz, 2H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 164.50, 151.62, 147.98, 131.46, 122.37, 110.71, 109.21, 56.00, 55.98, 53.83, 47.19, 36.77, 30.94, 27.80, 26.43, 25.88. HRMS-EI (m/z): [M+H]$^+$ calcd for, 304.1907; found, 304.1906.



2w

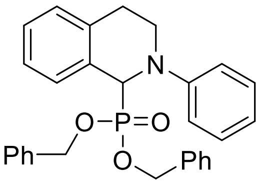
6,7-dimethoxy-2-(2-methoxyethyl)-3,4-dihydroisoquinolin-1(2*H*)-one (2w)

According to **GP 1** with 6,7-dimethoxy-2-(2-methoxyethyl)-1,2,3,4-tetrahydroisoquinoline (25.1 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2w** as yellow oil (17.2 mg, 72%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.57 (s, 1H), 6.61 (s, 1H), 3.90 (d, *J* = 4.4 Hz, 6H), 3.71 (t, *J* = 5.4 Hz, 2H), 3.62 (dt, *J* = 11.0, 6.0 Hz, 4H), 3.34 (s, 3H), 2.89 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 164.53, 151.63, 147.84, 131.89, 122.03, 110.39, 109.18, 71.40, 58.87, 56.03, 55.99, 47.99, 47.57, 27.83. HRMS-EI (m/z): [M+H]$^+$ calcd for, 266.1387; found, 266.1389.


2x

7-bromo-2-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (2x)

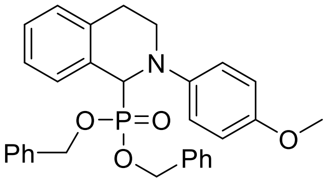
According to **GP 1** with 7-bromo-2-methyl-1,2,3,4-tetrahydroisoquinoline (22.5 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and DMAP (12.2 mg, 0.1 mmol, 1.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **2x** as yellow oil (21.9 mg, 92%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.18 (s, 1H), 7.49 (d, *J* = 10.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 3.54 (t, *J* = 6.7 Hz, 2H), 3.13 (s, 3H), 2.94 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 163.42, 136.67, 134.33, 131.04, 131.00, 128.63, 120.82, 47.88, 35.25, 27.36. This characterization data are in accordance with the reported literature.[9]


4a

dibenzyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (4a)

According to **GP 2** with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002mmol, 2 mol%), and dibenzyl phosphate (110 µL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4a** as yellow oil (42.2 mg, 90%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.33 (s, 1H), 7.31 – 7.27 (m, 2H), 7.27 – 7.18 (m, 7H), 7.13 (dd, *J* = 17.1, 8.2 Hz, 3H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 5.29 (d, *J* = 19.5 Hz, 1H), 5.01 (dd, *J* = 11.6, 7.2 Hz, 1H), 4.94 (dd, *J* = 11.7, 7.0 Hz, 1H), 4.90 – 4.84 (m, 1H), 4.80 – 4.73 (m, 1H), 4.04 – 3.96

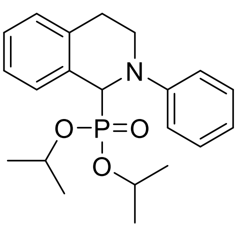
(m, 1H), 3.65 – 3.58 (m, 1H), 3.05 (d, *J* = 17.7 Hz, 1H), 2.98 (d, *J* = 15.9 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 149.18 (d, *J* = 5.7 Hz), 136.45 (d, *J* = 5.6 Hz), 136.27 (d, *J* = 6.0 Hz), 136.15 (d, *J* = 5.9 Hz), 130.28, 129.16, 128.77 (d, *J* = 2.7 Hz), 128.39, 128.31, 128.23, 128.17, 128.14, 127.98 (d, *J* = 6.0 Hz), 127.54 (d, *J* = 3.5 Hz), 125.96 (d, *J* = 2.9 Hz), 118.66, 114.93, 68.73 (d, *J* = 7.4 Hz), 67.85 (d, *J* = 7.7 Hz), 58.99 (d, *J* = 157.8 Hz), 43.57, 26.79. This characterization data are in accordance with the reported literature.[10]



4b

dibenzyl (2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (4b)

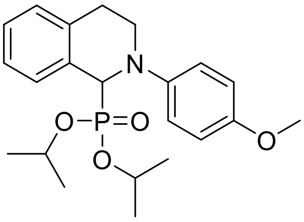
According to **GP 2** with 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (23.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and dibenzyl phosphate (110 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4b** as yellow oil (36.4 mg, 73%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.36 – 7.17 (m, 10H), 7.13 (d, *J* = 7.2 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 5.12 (d, *J* = 21.1 Hz, 1H), 5.02 (dd, *J* = 11.6, 7.0 Hz, 1H), 4.94 (dd, *J* = 11.7, 7.1 Hz, 1H), 4.90 – 4.85 (m, 1H), 4.82 (dd, *J* = 11.5, 7.7 Hz, 1H), 4.03 (t, *J* = 13.3 Hz, 1H), 3.73 (s, 3H), 3.56 – 3.48 (m, 1H), 2.91 (m, 2H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 153.27, 143.98 (d, *J* = 7.9 Hz), 136.43 (dd, *J* = 5.9, 3.6 Hz), 136.28 (d, *J* = 5.9 Hz), 130.23, 128.94 (d, *J* = 4.6 Hz), 128.35 (d, *J* = 10.5 Hz), 128.21, 128.18, 128.09, 127.98, 127.88, 127.36 (d, *J* = 3.4 Hz), 125.87 (d, *J* = 2.7 Hz), 117.74, 114.58, 68.64 (d, *J* = 7.3 Hz), 67.66 (d, *J* = 7.8 Hz), 59.74 (d, *J* = 156.9 Hz), 55.62, 44.73, 26.22. This characterization data are in accordance with the reported literature.[10]



4c

diisopropyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (4c)

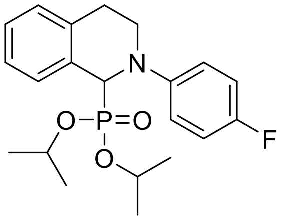
According to **GP 2** with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and Diisopropyl phosphate (83 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4c** as yellow oil (23.1 mg, 62%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40 (d, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.0 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 5.14 (d, *J* = 21.2 Hz, 1H), 4.62 (dt, *J* = 11.6, 6.0 Hz, 2H), 4.09 – 4.01 (m, 1H), 3.65 (d, *J* = 12.8 Hz, 1H), 3.00 (d, *J* = 15.9 Hz, 2H), 1.29 (dd, *J* = 11.4, 6.2 Hz, 6H), 1.16 (d, *J* = 6.2 Hz, 3H), 0.95 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 149.53 (d, *J* = 6.6 Hz), 136.39 (d, *J* = 5.6 Hz), 130.91, 128.95, 128.66 (d, *J* = 2.6 Hz), 128.40 (d, *J* = 4.5 Hz), 127.22 (d, *J* = 3.4 Hz), 125.58 (d, *J* = 2.7 Hz), 118.25, 115.03, 72.18 (d, *J* = 7.7 Hz), 70.83 (d, *J* = 8.2 Hz), 58.77 (d, *J* = 160.9 Hz), 43.48, 26.57, 24.54 (d, *J* = 2.8 Hz), 24.09 (d, *J* = 3.3 Hz), 23.70 (d, *J* = 5.6 Hz), 23.27 (d, *J* = 5.5 Hz). This characterization data are in accordance with the reported literature.[10]



4d

diisopropyl (2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (4d)

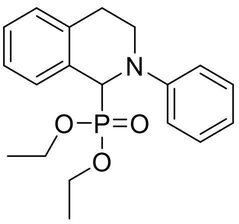
According to **GP 2** with 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (23.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and Diisopropyl phosphate (83 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4d** as yellow oil (30.6 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 6.6 Hz, 1H), 7.17 (t, *J* = 4.7 Hz, 2H), 7.10 (d, *J* = 6.2 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.1 Hz, 2H), 4.95 (d, *J* = 22.9 Hz, 1H), 4.69 – 4.59 (m, 2H), 4.07 (t, *J* = 13.8 Hz, 1H), 3.74 (s, 3H), 3.58 – 3.52 (m, 1H), 2.86 (t, *J* = 17.9 Hz, 2H), 1.30 (dd, *J* = 10.4, 6.2 Hz, 6H), 1.18 (d, *J* = 6.2 Hz, 3H), 1.00 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.99, 144.32 (d, *J* = 9.4 Hz), 136.37 (d, *J* = 5.7 Hz), 130.80, 128.82 (d, *J* = 2.4 Hz), 128.48 (d, *J* = 4.4 Hz), 127.05 (d, *J* = 3.5 Hz), 125.52 (d, *J* = 2.9 Hz), 117.76, 114.40, 72.10 (d, *J* = 7.7 Hz), 70.68 (d, *J* = 8.2 Hz), 59.39 (d, *J* = 160.7 Hz), 55.60, 44.73, 25.84, 24.56 (d, *J* = 2.8 Hz), 24.09 (d, *J* = 3.3 Hz), 23.73 (d, *J* = 5.7 Hz), 23.37 (d, *J* = 5.6 Hz). This characterization data are in accordance with the reported literature.[10]



4e

diisopropyl (2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (4e)

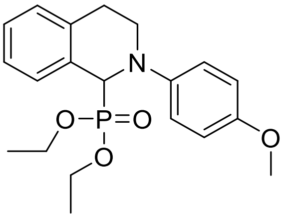
According to **GP 2** with 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (22.7 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and diisopropyl phosphate (166 µL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4e** as yellow oil (25 mg, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 1H), 7.16 (dd, *J* = 14.9, 7.0 Hz, 2H), 7.12 (d, *J* = 7.1 Hz, 1H), 6.94 – 6.82 (m, 4H), 4.99 (d, *J* = 21.4 Hz, 1H), 4.60 (dt, *J* = 16.8, 6.3 Hz, 2H), 4.07 – 3.96 (m, 1H), 3.59 – 3.49 (m, 1H), 2.95 (ddd, *J* = 25.7, 16.1, 6.4 Hz, 2H), 1.27 (t, *J* = 6.7 Hz, 6H), 1.14 (d, *J* = 6.2 Hz, 3H), 0.95 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.34 (d, *J* = 237.5 Hz), 146.27 (dd, *J* = 2.1, 1.9 Hz), 136.24 (d, *J* = 5.5 Hz), 130.60, 128.73 (d, *J* = 2.5 Hz), 128.42 (d, *J* = 4.5 Hz), 127.30 (d, *J* = 3.5 Hz), 125.67 (d, *J* = 2.8 Hz), 116.77 (d, *J* = 7.5 Hz), 115.32 (d, *J* = 22.1 Hz), 72.21 (d, *J* = 7.8 Hz), 70.89 (d, *J* = 8.2 Hz), 59.29 (d, *J* = 160.7 Hz), 44.31, 26.31, 24.52 (d, *J* = 2.8 Hz), 24.09 (d, *J* = 3.3 Hz), 23.70 (d, *J* = 5.6 Hz), 23.32 (d, *J* = 5.6 Hz). This characterization data are in accordance with the reported literature.[11]



4f

diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (4f)

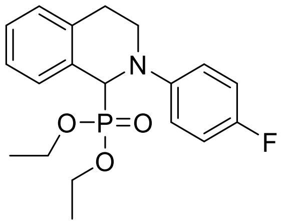
According to **GP 2** with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and diethyl phosphate (62 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4f** as yellow oil (24.2 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.21 – 7.12 (m, 3H), 7.00 – 6.93 (m, 2H), 6.78 (d, *J* = 1.0 Hz, 1H), 5.18 (d, *J* = 20.0 Hz, 1H), 4.12 – 4.06 (m, 1H), 4.06 – 3.99 (m, 2H), 3.96 (q, *J* = 1.4 Hz, 1H), 3.92 – 3.85 (m, 1H), 3.62 (dt, *J* = 11.9, 5.5 Hz, 1H), 3.10 – 3.03 (m, 1H), 3.02 – 2.95 (m, 1H), 1.26 – 1.21 (m, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.38 (d, *J* = 4.5 Hz), 136.43 (d, *J* = 4.5 Hz), 130.64, 129.12, 128.73 (d, *J* = 3.0 Hz), 128.11 (d, *J* = 4.5 Hz), 127.41 (d, *J* = 4.5 Hz), 125.85 (d, *J* = 3.0 Hz), 118.44, 114.76, 63.30 (d, *J* = 7.5 Hz), 62.31 (d, *J* = 7.5 Hz), 58.79 (d, *J* = 159.0 Hz), 43.46, 26.74, 16.44 (d, *J* = 6.0 Hz), 16.36 (d, *J* = 6.0 Hz). This characterization data are in accordance with the reported literature.[10]



4g

diethyl (2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (4g)

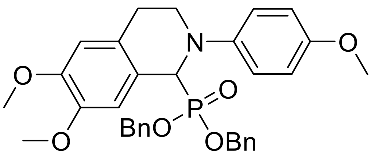
According to **GP 2** with 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (23.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and diethyl phosphate (62 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4g** as yellow oil (22.9 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.7 Hz, 1H), 7.21 – 7.06 (m, 3H), 6.91 (d, *J* = 9.1 Hz, 2H), 6.80 (d, *J* = 9.1 Hz, 2H), 5.01 (d, *J* = 21.5 Hz, 1H), 4.12 – 4.06 (m, 1H), 4.06 – 3.98 (m, 2H), 3.98 – 3.90 (m, 2H), 3.74 (s, 3H), 3.56 – 3.50 (m, 1H), 2.92 (q, *J* = 4.6 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.08, 144.15 (d, *J* = 8.2 Hz), 136.40 (d, *J* = 5.8 Hz), 130.49, 128.90 (d, *J* = 2.5 Hz), 128.15 (d, *J* = 4.4 Hz), 127.26 (d, *J* = 3.5 Hz), 125.80 (d, *J* = 2.9 Hz), 117.56, 114.48, 63.35 (d, *J* = 7.2 Hz), 62.22 (d, *J* = 7.6 Hz), 59.43 (d, *J* = 158.8 Hz), 55.62, 44.64, 26.10, 16.48 (d, *J* = 5.6 Hz), 16.38 (d, *J* = 5.9 Hz). This characterization data are in accordance with the reported literature.[10]



4h

diethyl (2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (4h)

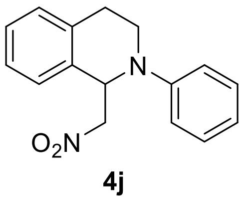
According to **GP 2** with 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (22.7 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and diethyl phosphate (62 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4h** as yellow oil (18.1 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.13 (m, 3H), 6.98 – 6.87 (m, 4H), 5.03 (s, 1H), 4.10 – 3.86 (m, 5H), 3.56 – 3.49 (m, 1H), 2.98 (d, *J* = 34.8 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.14 (d, *J* = 14.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.42 (d, *J* = 237.7 Hz), 146.13 (dd, *J* = 6.6, 2.0 Hz), 136.28 (d, *J* = 5.5 Hz), 130.36, 128.79 (d, *J* = 2.7 Hz), 128.13 (d, *J* = 4.6 Hz), 127.47 (d, *J* = 3.5 Hz), 125.92 (d, *J* = 2.8 Hz), 116.54 (d, *J* = 7.4 Hz), 115.47 (d, *J* = 22.1 Hz), 63.28 (d, *J* = 7.3 Hz), 62.33 (d, *J* = 7.7 Hz), 59.31 (d, *J* = 159.0 Hz), 44.27, 26.52, 16.43 (d, *J* = 5.5 Hz), 16.35 (d, *J* = 5.9 Hz). This characterization data are in accordance with the reported literature.[12]



4i

dibenzyl (6,7-dimethoxy-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (4i)

According to **GP 2** with 6,7-dimethoxy-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (30 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and dibenzyl phosphate (110 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3/1) to afford the desired product **4i** as white solid (30.5 mg, 55%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.35 (s, 2H), 7.31 – 7.26 (m, 6H), 7.19 (d, *J* = 3.4 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 6.81 – 6.74 (m, 3H), 6.58 (s, 1H), 5.11 – 5.06 (m, 1H), 5.00 (d, *J* = 21.5 Hz, 1H), 4.92 (dt, *J* = 11.7, 7.5 Hz, 3H), 4.11 – 4.02 (m, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 3.56 (d, *J* = 13.0 Hz, 1H), 3.52 (s, 3H), 2.90 – 2.78 (m, 1H), 2.69 (dd, *J* = 15.8, 3.4 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 153.44, 148.28 (d, *J* = 3.5 Hz), 147.09 (d, *J* = 2.8 Hz), 144.13 (d, *J* = 9.9 Hz), 136.38 (dd, *J* = 53.7, 6.3 Hz), 128.65 (d, *J* = 2.8 Hz), 128.47, 128.34 (d, *J* = 2.8 Hz), 128.11 (d, *J* = 2.2 Hz), 127.94 (d, *J* = 11.6 Hz), 121.48, 118.34, 114.52, 111.27 (d, *J* = 100.6 Hz), 68.86 (d, *J* = 7.2 Hz), 67.29 (d, *J* = 7.7 Hz), 59.29 (d, *J* = 158.6 Hz), 55.79, 55.60 (d, *J* = 4.1 Hz), 44.97, 29.66, 25.21. HRMS-EI (m/z): $[M+H]^+$ calcd for, 560.2197; found, 560.2183.

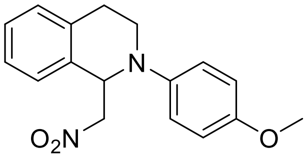


4j

1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4j)

According to **GP 2** with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and nitromethane (27 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4j** as yellow oil (21.4 mg, 80%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.31 – 7.23 (m, 3H), 7.23 –

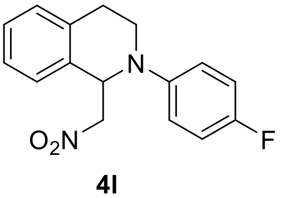
7.15 (m, 2H), 7.14 (d, *J* = 1.4 Hz, 1H), 7.00 – 6.95 (m, 2H), 6.85 (d, *J* = 1.1 Hz, 1H), 5.55 (t, *J* = 7.2 Hz, 1H), 4.87 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.56 (dd, *J* = 11.9, 6.6 Hz, 1H), 3.73 – 3.55 (m, 2H), 3.21 – 3.04 (m, 1H), 2.79 (dt, *J* = 16.3, 5.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.40, 135.26, 132.90, 129.49, 129.18, 128.11, 126.98, 126.69, 119.41, 115.09, 78.77, 58.19, 42.07, 26.45. This characterization data are in accordance with the reported literature.[13]



4k

2-(4-methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (4k)

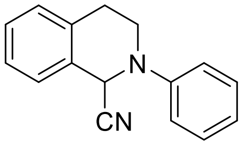
According to **GP 2** with 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (23.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and nitromethane (27 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4d** as yellow oil (20.3 mg, 68%). ^{1}H NMR (600 MHz,$CDCl_3$) δ 7.23 (dd, *J* = 16.7, 7.5 Hz, 2H), 7.15 (dd, *J* = 14.3, 7.7 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.1 Hz, 2H), 5.39 (dd, *J* = 8.7, 5.8 Hz, 1H), 4.82 (dd, *J* = 12.0, 8.7 Hz, 1H), 4.56 (dd, *J* = 12.0, 5.8 Hz, 1H), 3.75 (s, 3H), 3.61 – 3.52 (m, 2H), 3.04 – 2.98 (m, 1H), 2.69 (dt, *J* = 16.4, 4.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.96, 143.04, 135.43, 132.86, 129.46, 127.89, 126.91, 126.61, 118.85, 114.68, 78.95, 58.90 (d, *J* = 5.5 Hz), 55.57 (d, *J* = 8.7 Hz), 43.12, 25.77. This characterization data are in accordance with the reported literature.[13]



4l

2-(4-fluorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (4l)

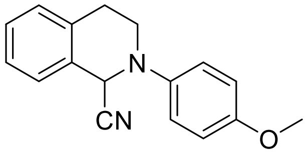
According to **GP 2** with 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (22.7 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and nitromethane (27 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4l** as yellow oil (12.6 mg, 44%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.25 (d, *J* = 1.7 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.90 (d, *J* = 4.5 Hz, 2H), 5.42 (dd, *J* = 8.7, 5.9 Hz, 1H), 4.84 (dd, *J* = 12.0, 8.7 Hz, 1H), 4.57 (dd, *J* = 12.0, 5.9 Hz, 1H), 3.62 – 3.55 (m, 2H), 3.02 (t, *J* = 16.1 Hz, 1H), 2.72 (dt, *J* = 16.5, 4.2 Hz, 1H). ^{13}C NMR (150 MHz,CDCl$_3$) δ 157.15 (d, *J* = 237.9 Hz), 145.28 (d, *J* = 237.9 Hz), 135.23, 132.53, 129.44, 128.08, 126.93, 126.75, 117.91 (d, *J* = 7.6 Hz), 115.84 (d, *J* = 22.2 Hz), 78.84 (dd, *J* = 14.9, 9.2 Hz), 58.70 (d, *J* = 7.7 Hz), 42.82, 25.75 (d, *J* = 2.8 Hz). This characterization data are in accordance with the reported literature.[13]



4m

1-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4m)

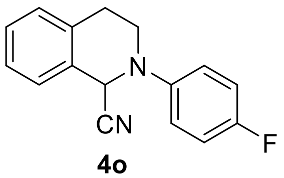
According to **GP 2** with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and trimethylsilyl cyanide (62 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4m** as yellow oil (20.6 mg, 88%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.40 – 7.34 (m, 2H), 7.30 (ddt, *J* = 12.6, 7.7, 4.0 Hz, 3H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.07 (m, 2H), 7.02 (d, *J* = 1.1 Hz, 1H), 5.52 (s, 1H), 3.87 – 3.67 (m, 1H), 3.50 (d, *J* = 1.6 Hz, 1H), 3.17 (t, *J* = 5.8 Hz, 1H), 2.98 (dt, *J* = 16.3, 3.5 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 148.37, 134.61, 129.57, 129.36, 128.76, 127.06, 126.85, 121.90, 117.75, 117.60, 53.23, 44.18, 28.54. This characterization data are in accordance with the reported literature.[14]



4n

2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4n)

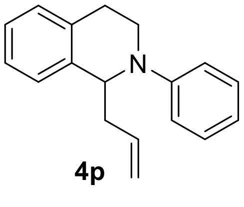
According to **GP 2** with 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (23.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and trimethylsilyl cyanide (62 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4n** as yellow oil (23.8 mg, 90%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.33 – 7.28 (m, 1H), 7.27 – 7.25 (m, 2H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.94 – 6.86 (m, 2H), 5.36 (s, 1H), 3.80 (s, 3H), 3.61 – 3.52 (m, 1H), 3.44 (td, *J* = 11.7, 3.9 Hz, 1H), 3.16 (s, 1H), 2.93 (d, *J* = 18.6 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 155.69, 142.58, 134.34, 129.67, 129.47, 128.66, 127.07, 126.70, 121.02, 117.59, 114.78, 55.57 (dd, *J* = 12.2, 7.6 Hz), 44.89, 28.70, 1.02. This characterization data are in accordance with the reported literature.[14]



4o

2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4o)

According to **GP 2** with 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (22.7 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and trimethylsilyl cyanide (62 μL, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **4o** as yellow oil (17.9 mg, 71%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.32 (dt, *J* = 7.5, 4.3 Hz, 1H), 7.27 (d, *J* = 4.2 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.10 – 7.04 (m, 4H), 5.40 (s, 1H), 3.63 (dd, *J* = 11.6, 5.6 Hz, 1H), 3.45 (ddd, *J* = 12.1, 11.0, 4.0 Hz, 1H), 3.16 (ddd, *J* = 17.0, 11.1, 6.1 Hz, 1H), 2.95 (d, *J* = 16.9 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 159.61 (d, *J* = 240.7 Hz), 145.06 (d, *J* = 2.5 Hz), 134.25, 129.44, 129.34, 128.80, 126.93 (d, *J* = 30.2 Hz), 120.47 (d, *J* = 8.0 Hz), 117.39, 116.18 (d, *J* = 22.5 Hz), 54.76, 44.76, 28.58. This characterization data are in accordance with the reported literature.[15]



4p

1-allyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (4p)

According to **GP 2** with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol, 1.0 equiv), chlorophyll (2.0 mg, 0.002 mmol, 2 mol%), and Potassium allyltrifluoroborate (74 mg, 0.5 mmol, 5.0 equiv). The crude reaction was quenched with water and extracted with ethyl acetate. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether) to afford the desired product **4p** as colourless oil (15 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (dt, *J* = 7.5, 4.3 Hz, 1H), 7.27 (d, *J* = 4.2 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.10 – 7.04 (m, 4H), 5.40 (s, 1H), 3.63 (dd, *J* = 11.6, 5.6 Hz, 1H), 3.45 (ddd, *J* = 12.1, 11.0, 4.0 Hz, 1H), 3.16 (ddd, *J* = 17.0, 11.1, 6.1 Hz, 1H), 2.95 (d, *J* = 16.9 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.47, 138.17, 135.67, 134.97, 129.24, 128.51, 127.35, 126.54, 125.72, 117.25, 116.97, 113.94, 59.35, 41.93, 40.93, 27.43. This characterization data are in accordance with the reported literature.[16]

9. Referencres

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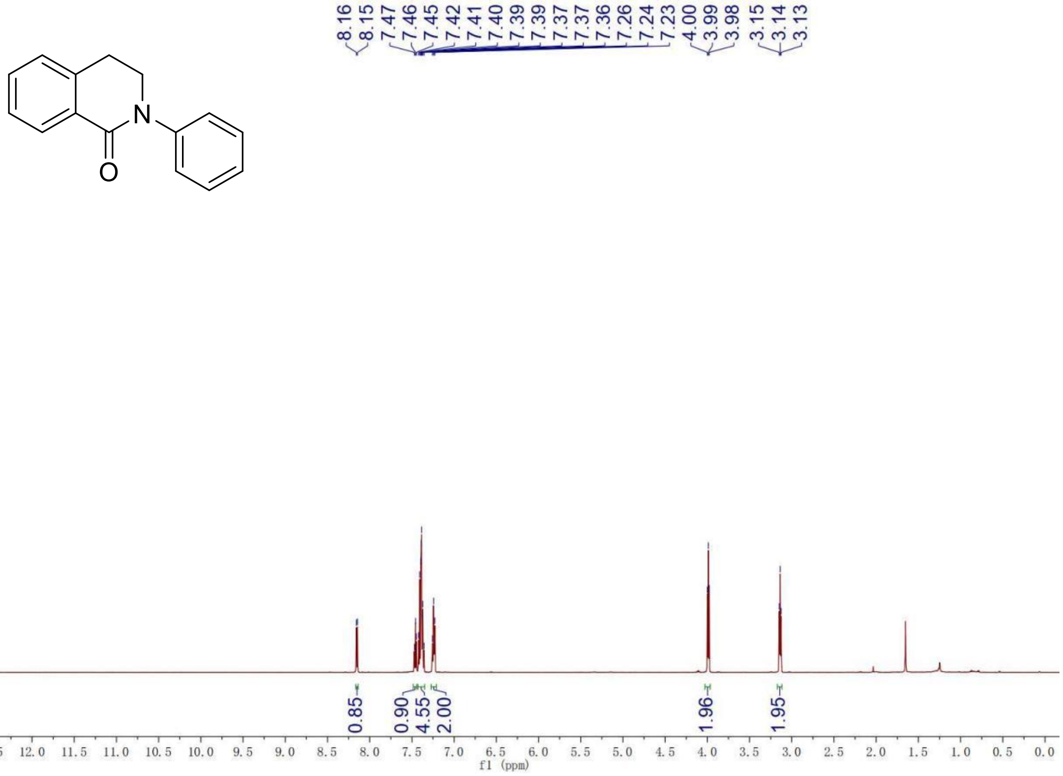
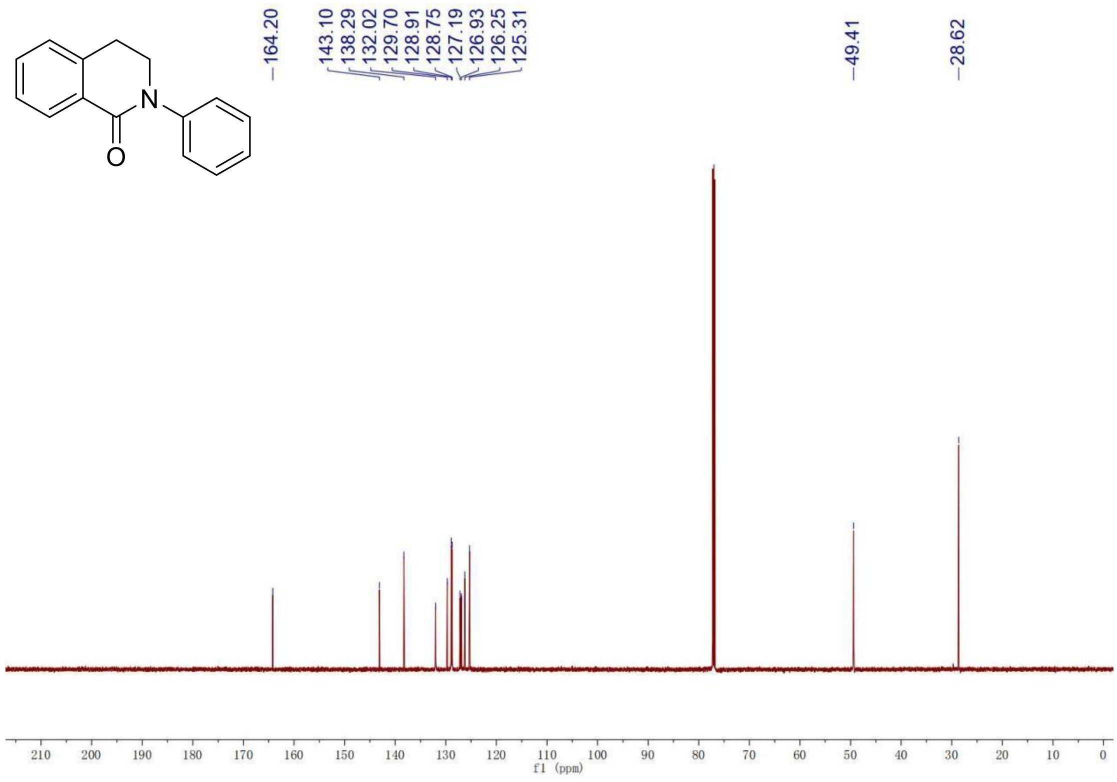
10.^{1}H and ^{13}C spectra

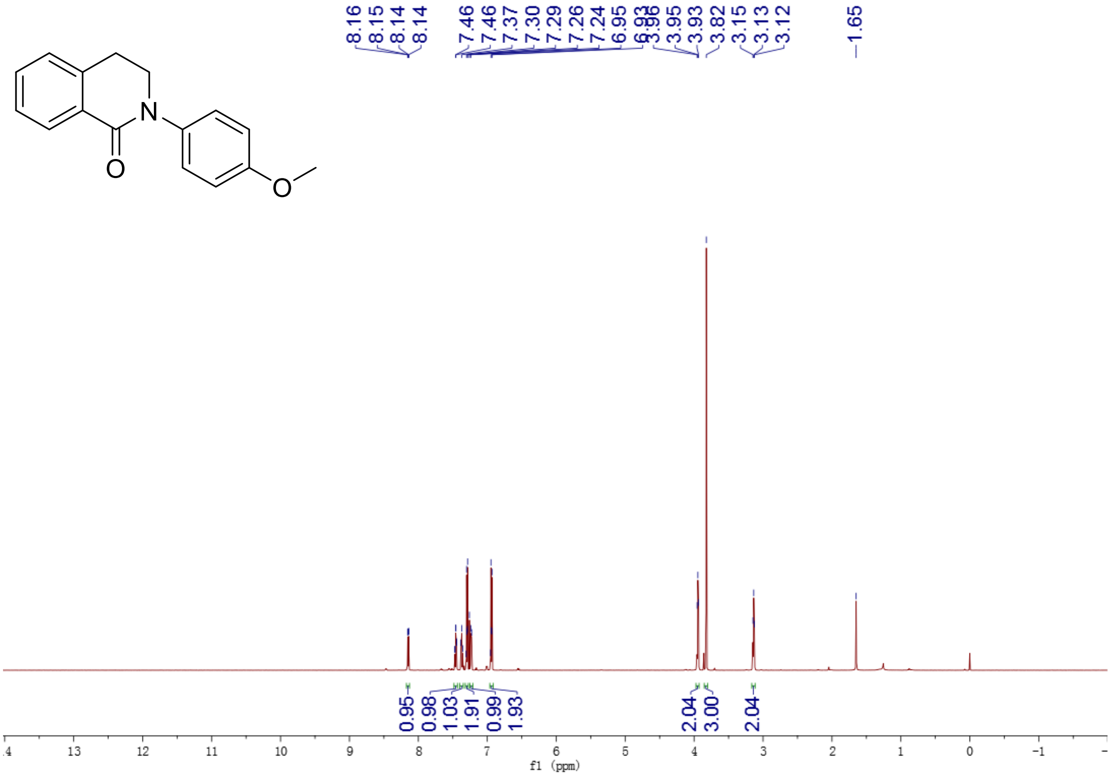
^{1}H NMR spectrum of compound **2a**



^{13}C NMR spectrum of compound **2a**


164.20
143.10
138.29
132.02
129.70
128.91
128.75
127.19
126.93
126.25
125.31
49.41
28.62
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR spectrum of compound **2b**



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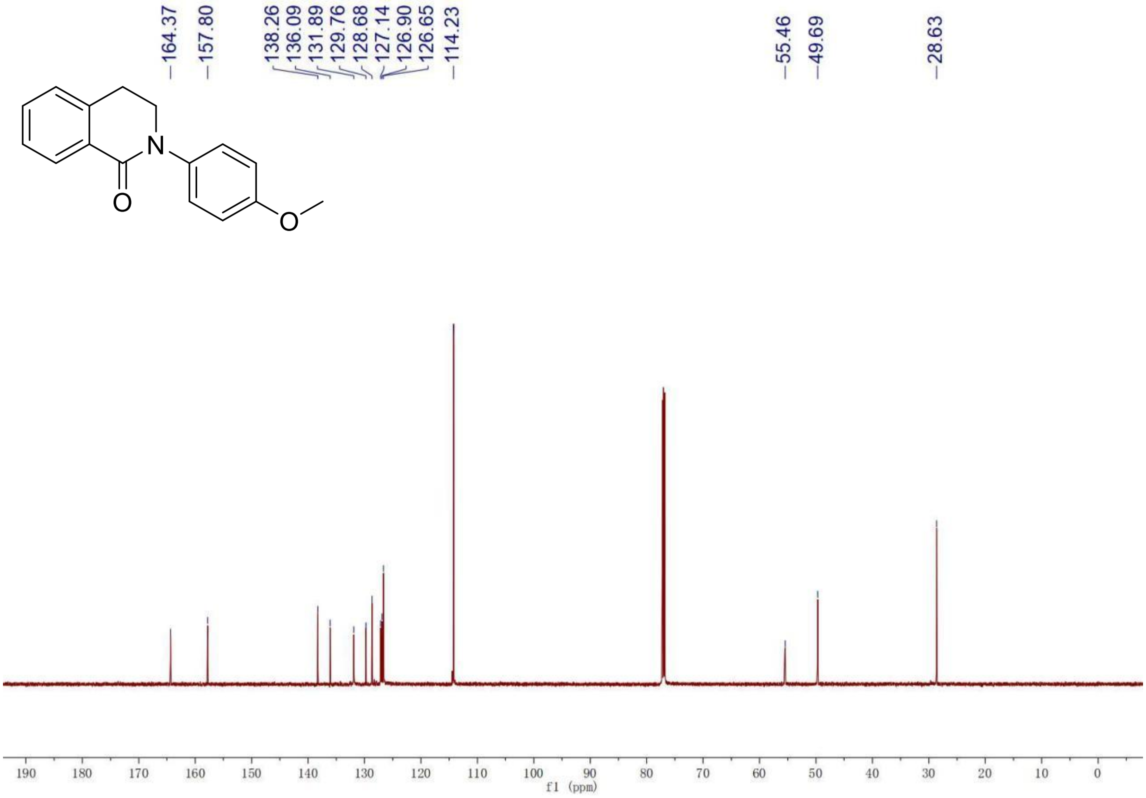
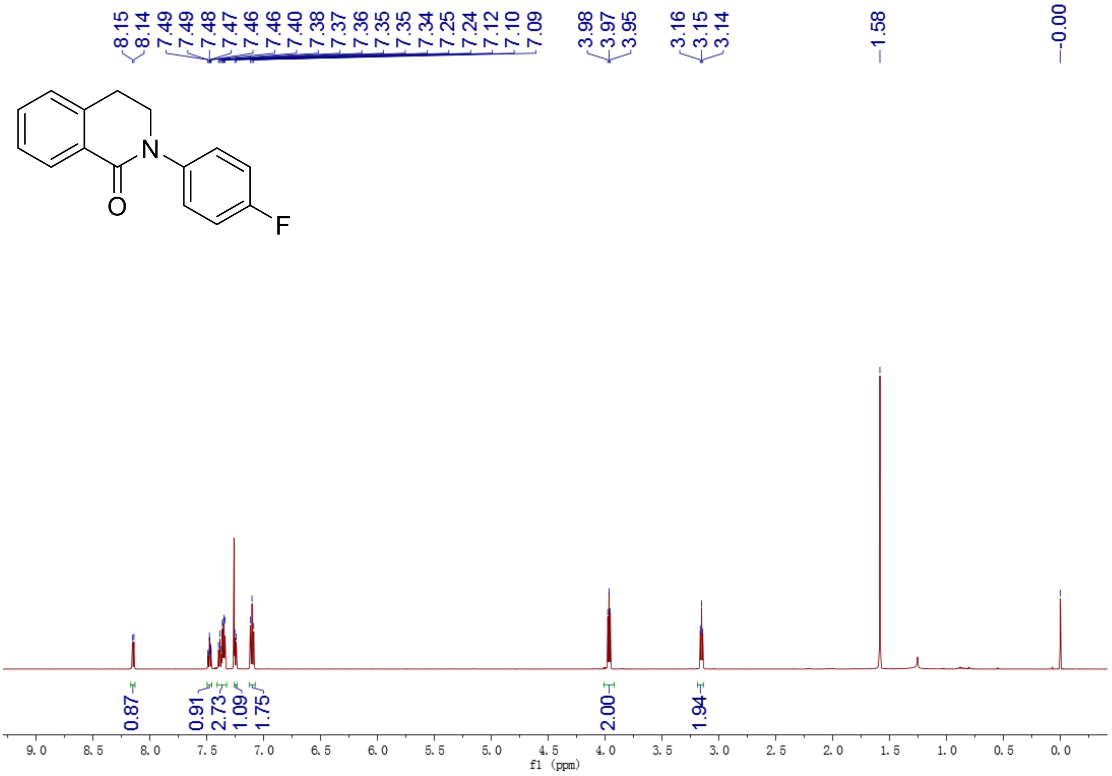
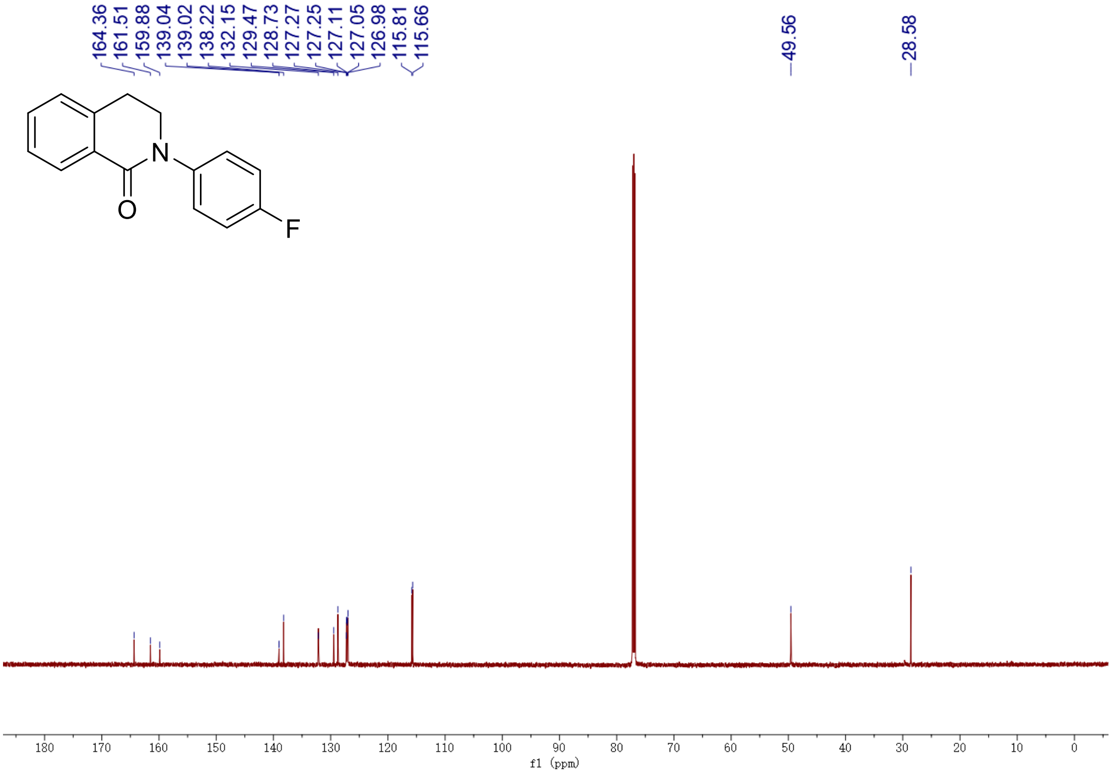


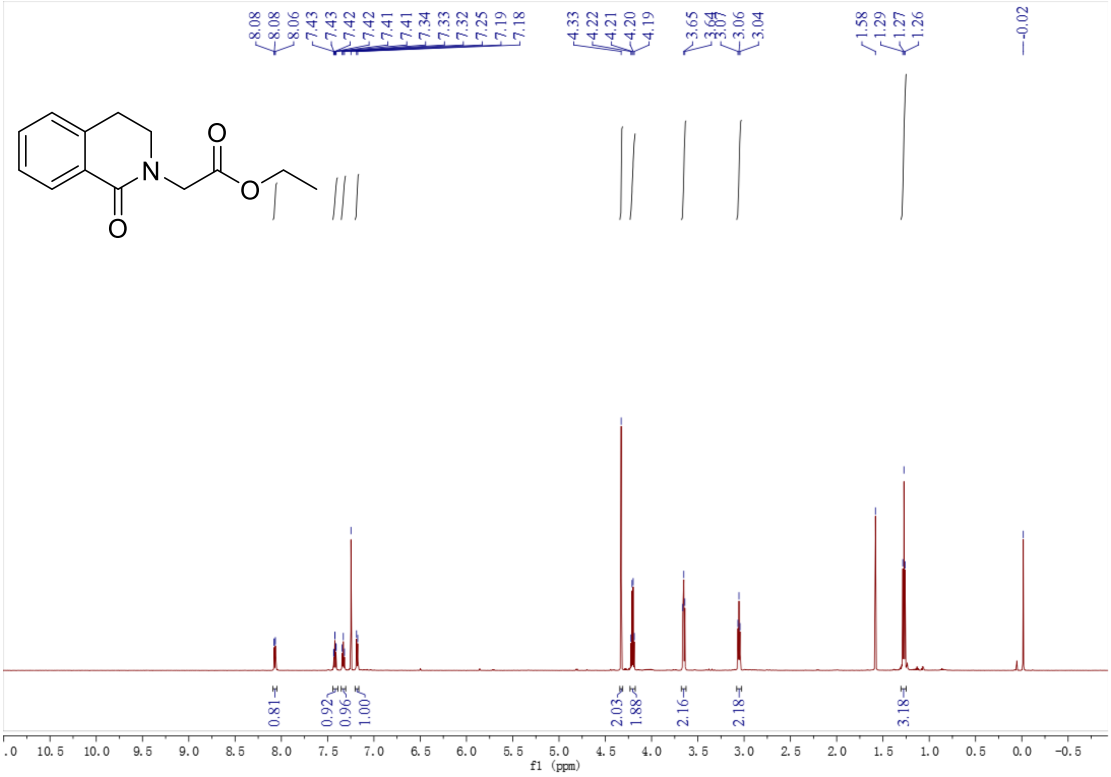
=^{1}H NMR spectrum of compound **2c**



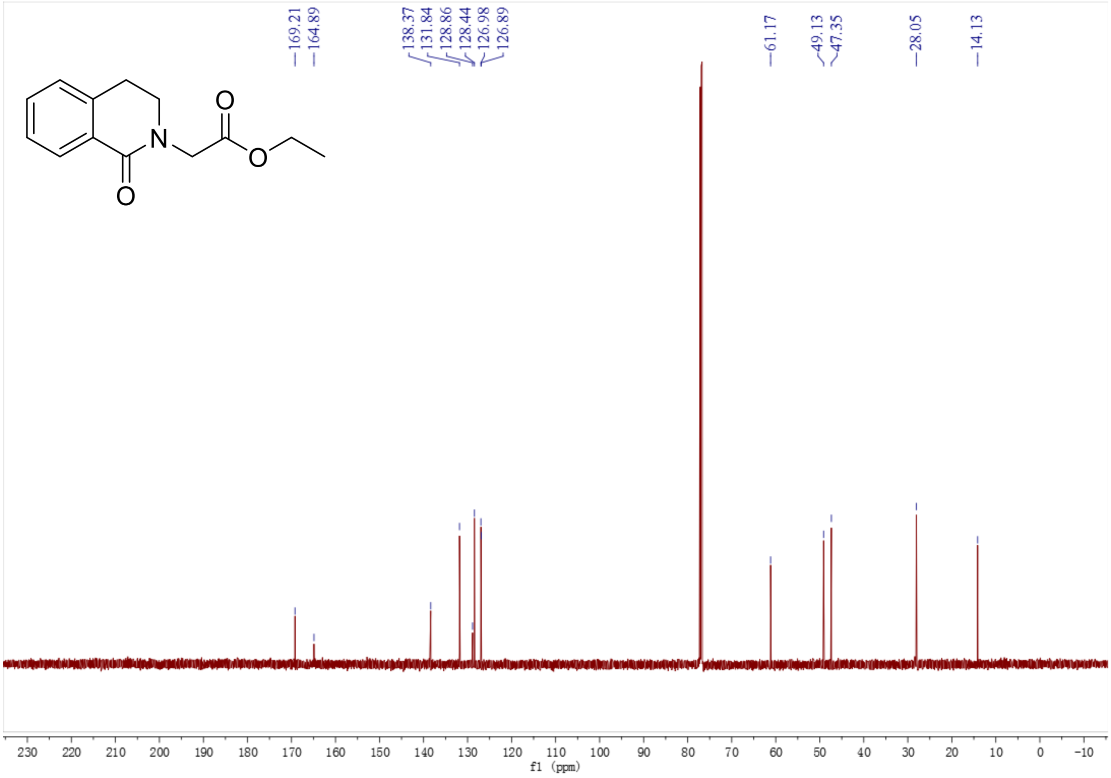
^{13}C NMR spectrum of compound **2c**



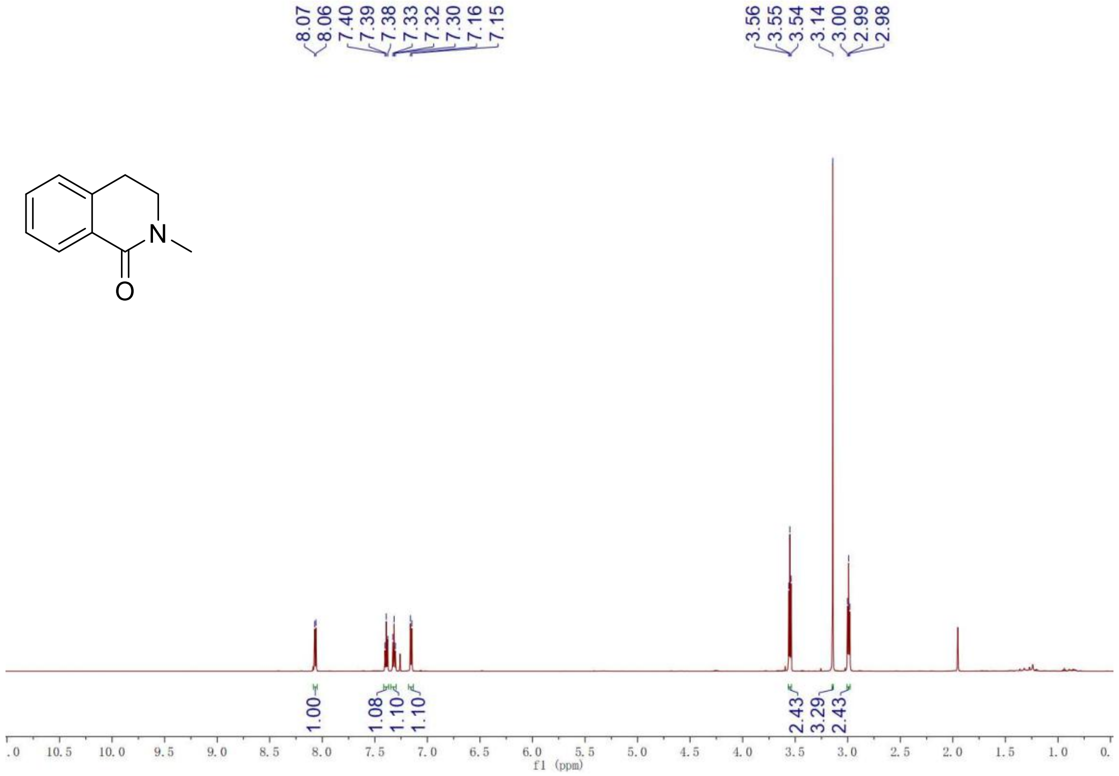
^{1}H NMR spectrum of compound **2d**



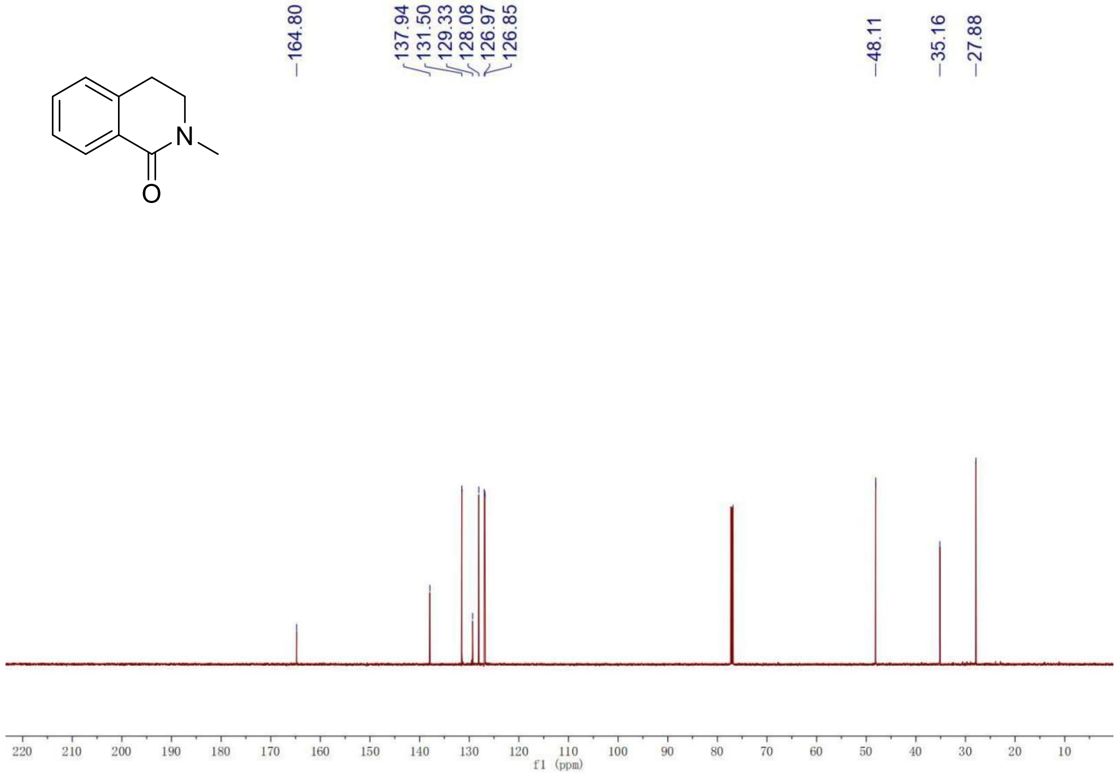
^{13}C NMR spectrum of compound **2d**



^{1}H NMR spectrum of compound **2e**



^{13}C NMR spectrum of compound **2e**



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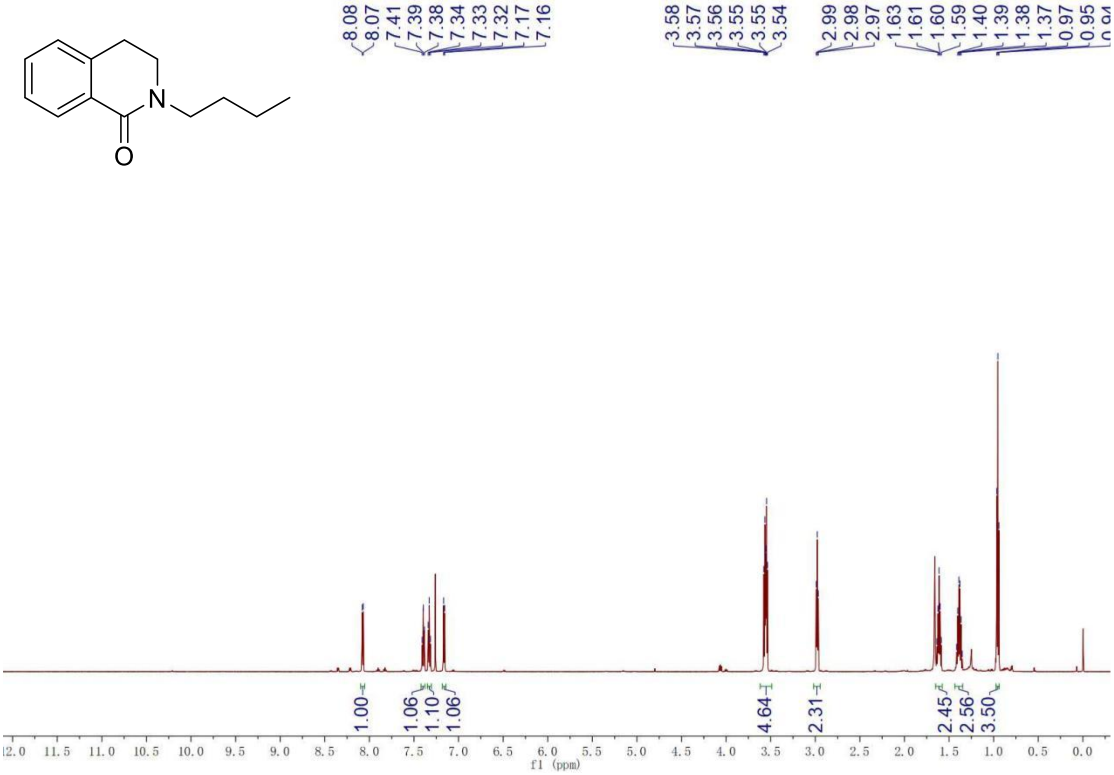
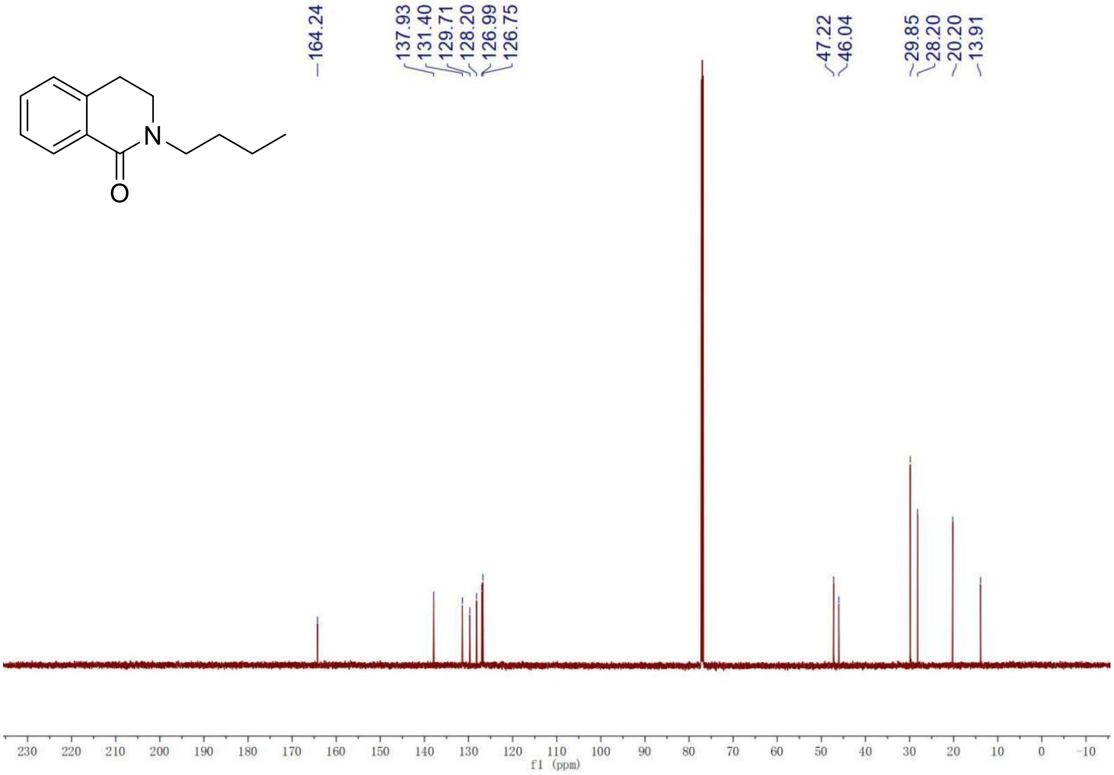


^{13}C NMR spectrum of compound **2f**



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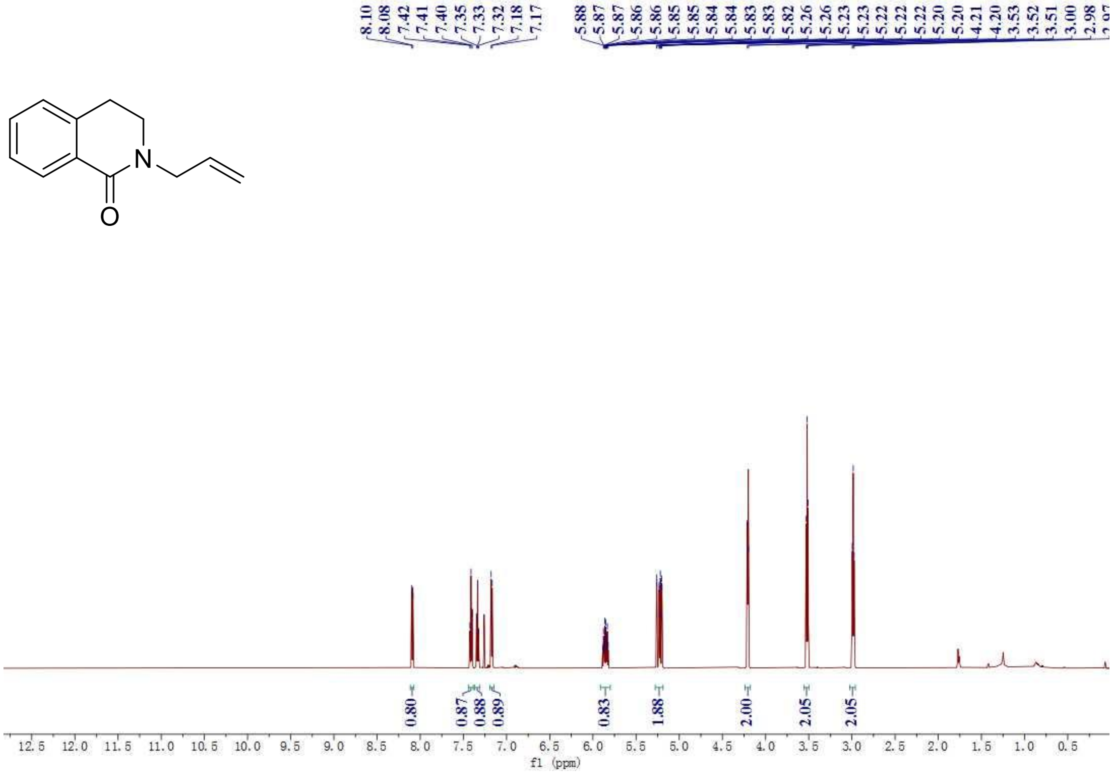
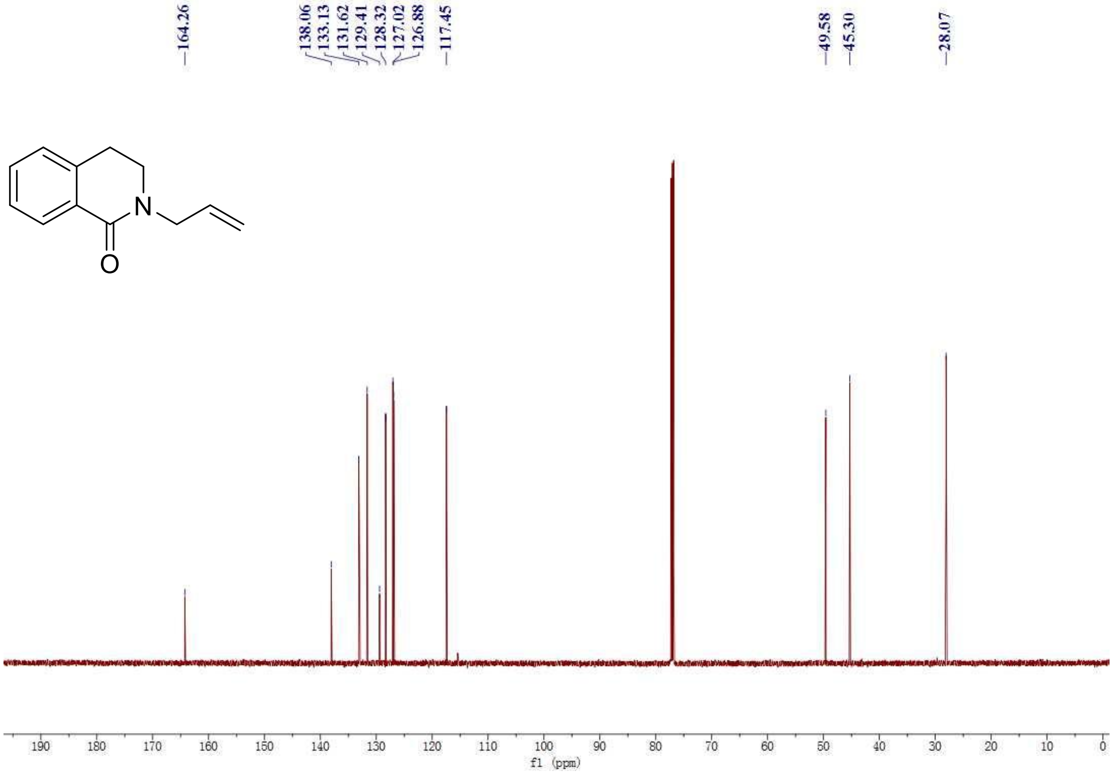
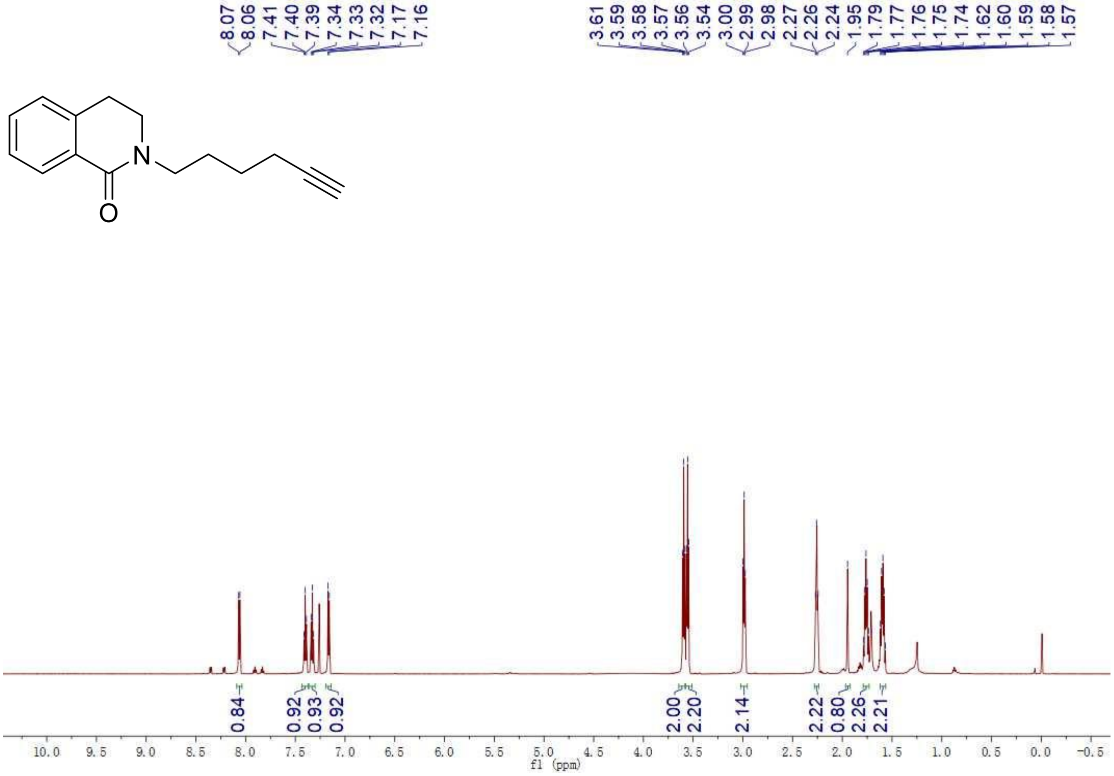


^{13}C NMR spectrum of compound **2g**



^{1}H NMR spectrum of compound **2h**



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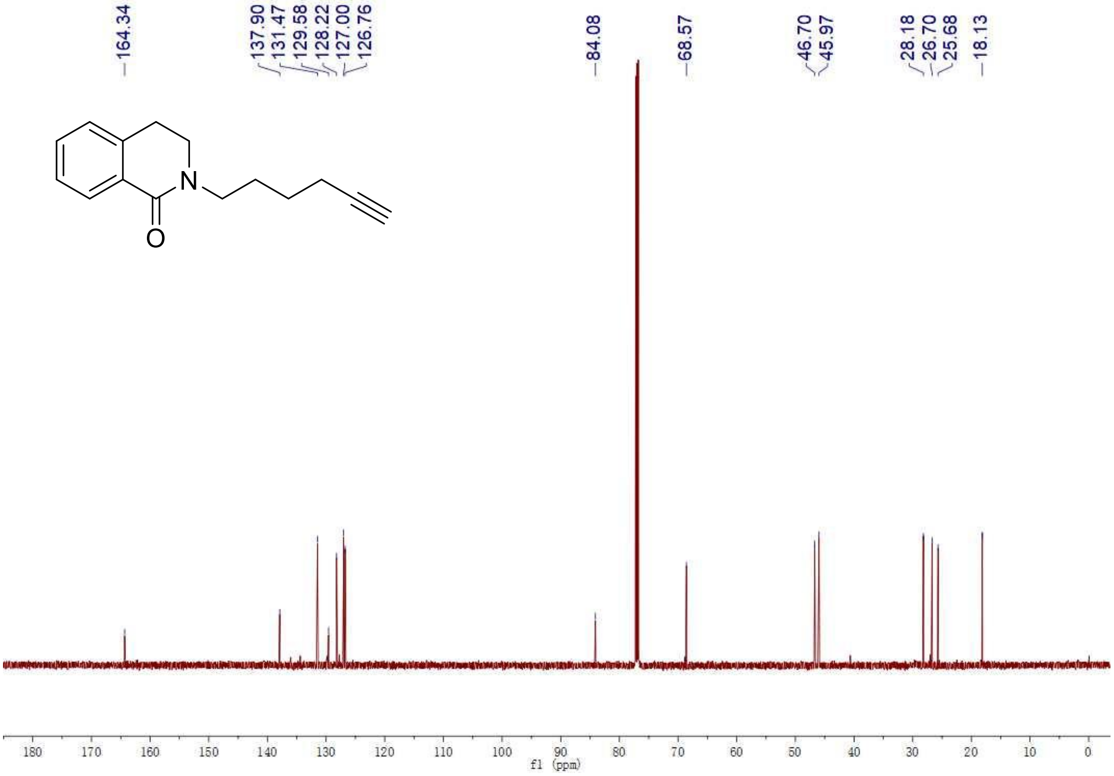

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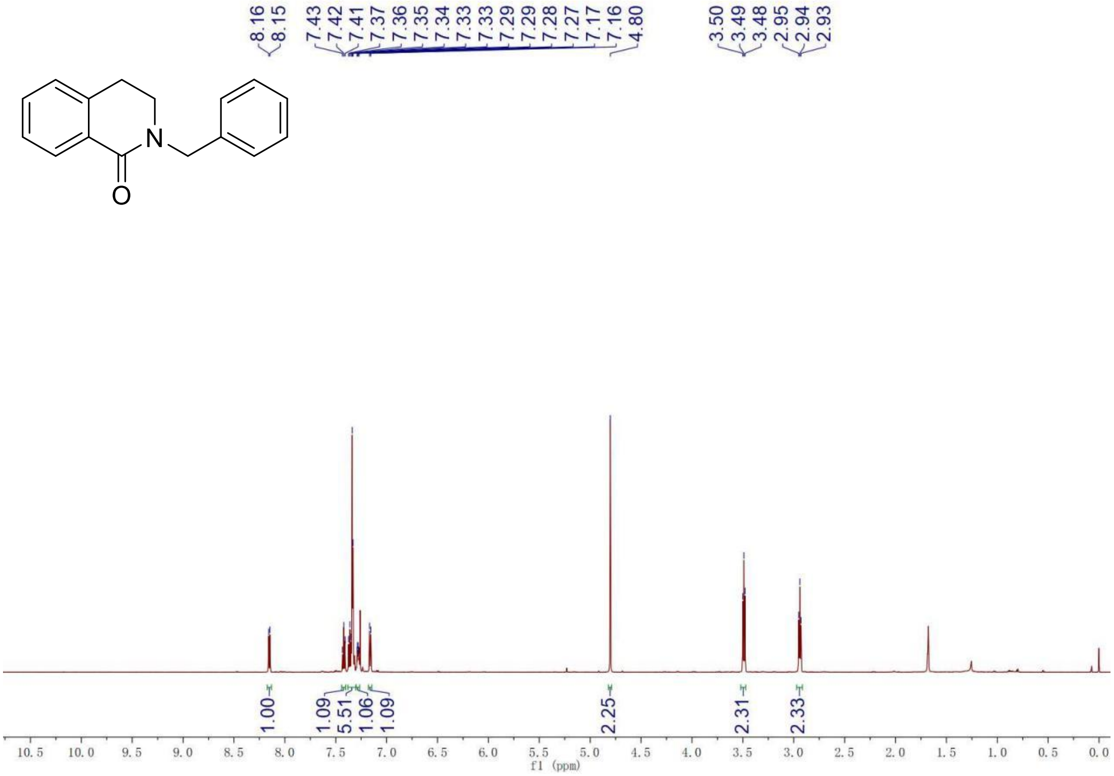
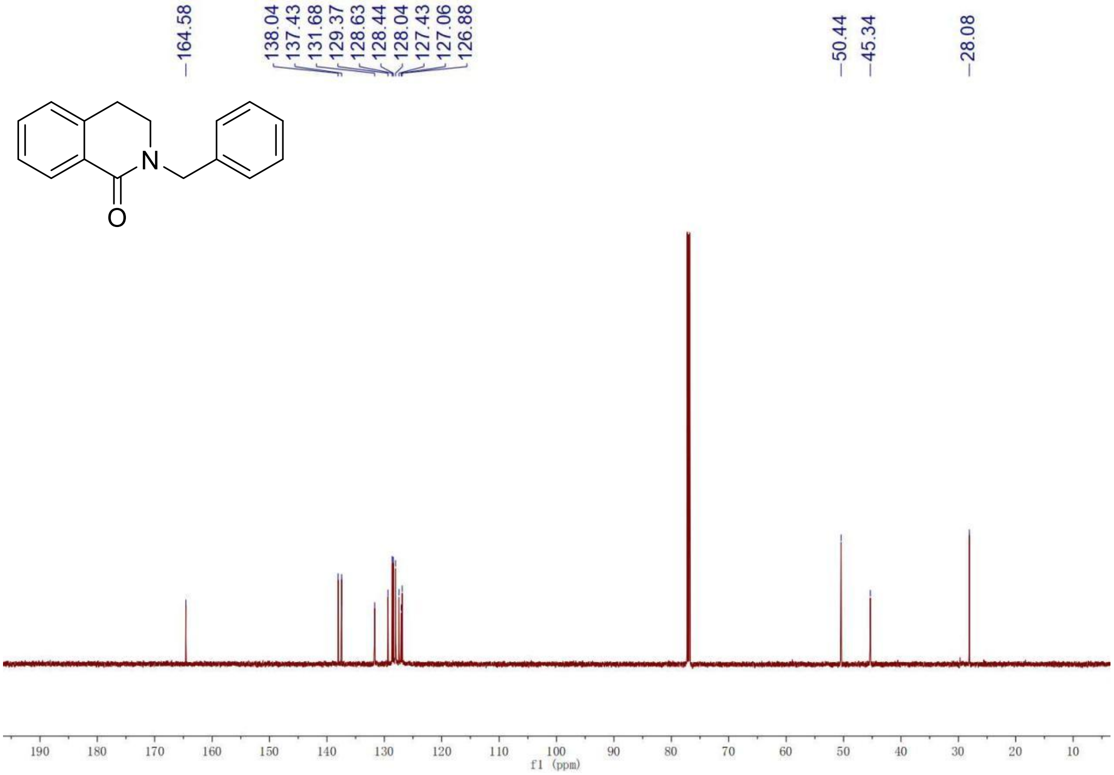
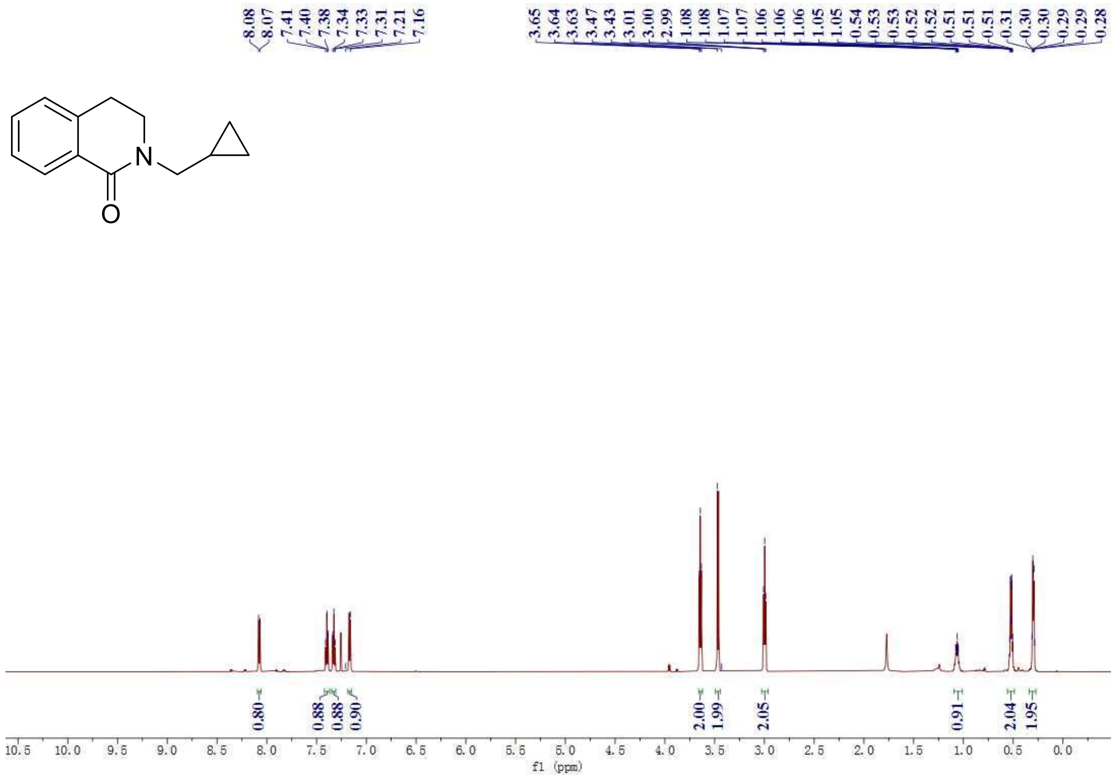


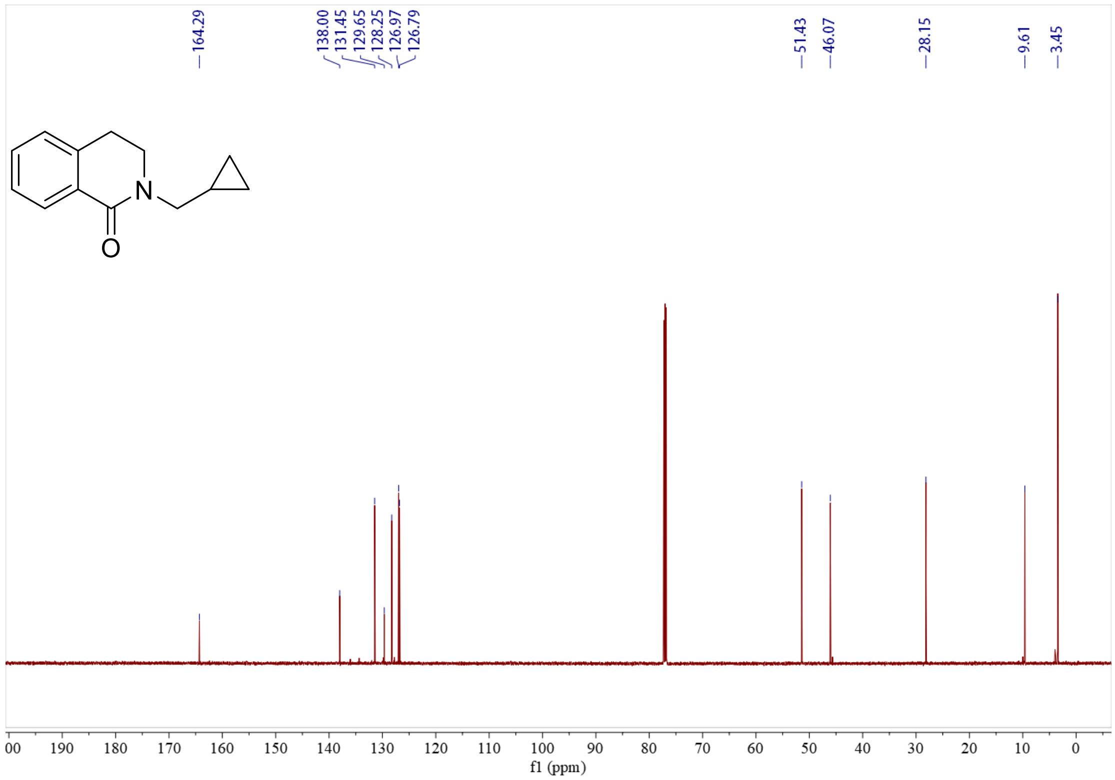
^{13}C NMR spectrum of compound **2i**



^{1}H NMR spectrum of compound **2j**



^{13}C NMR spectrum of compound **2j**



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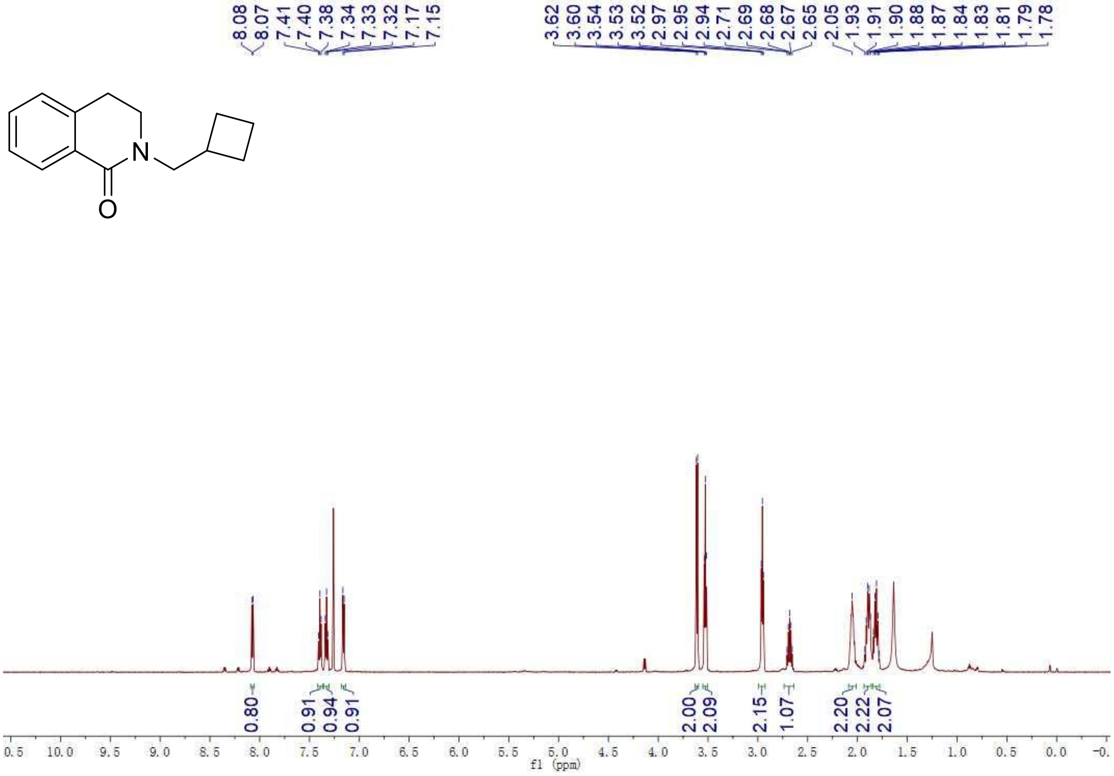
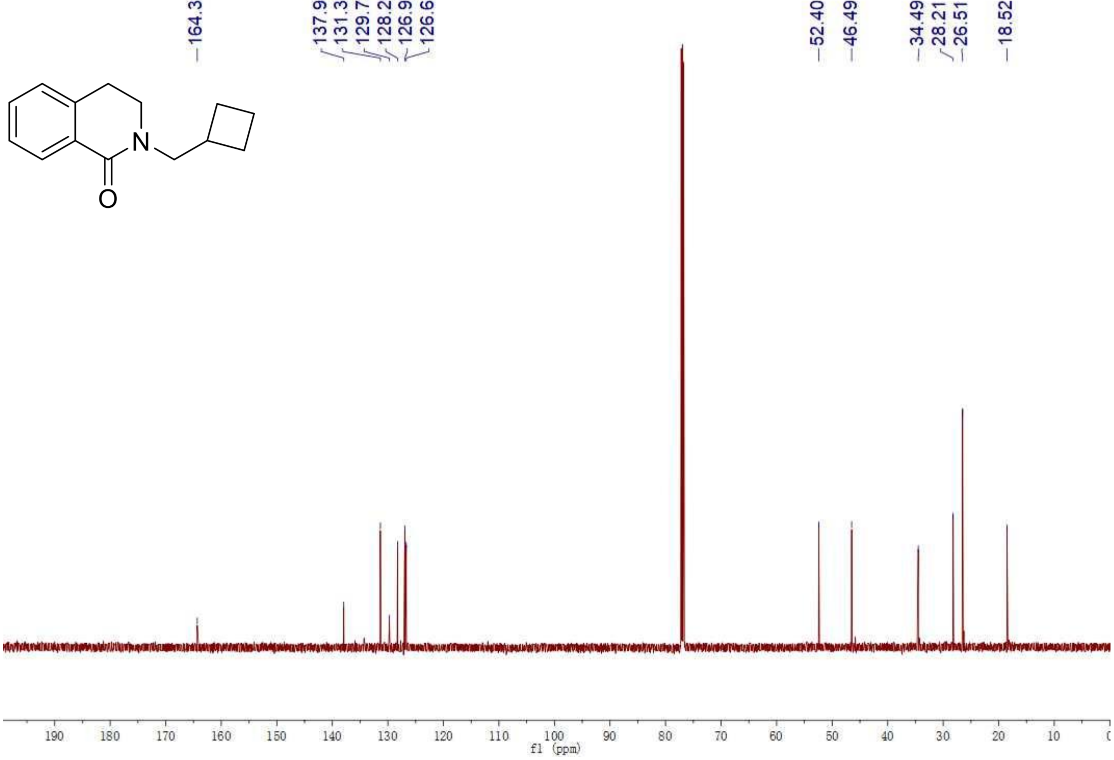
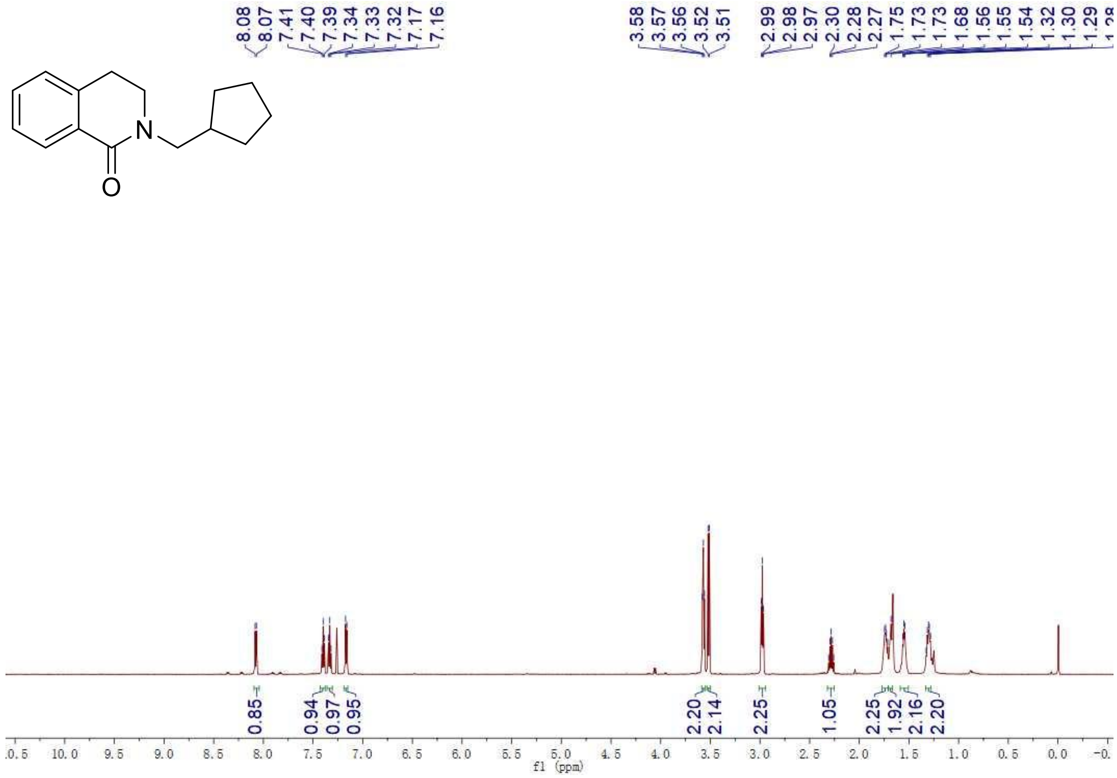


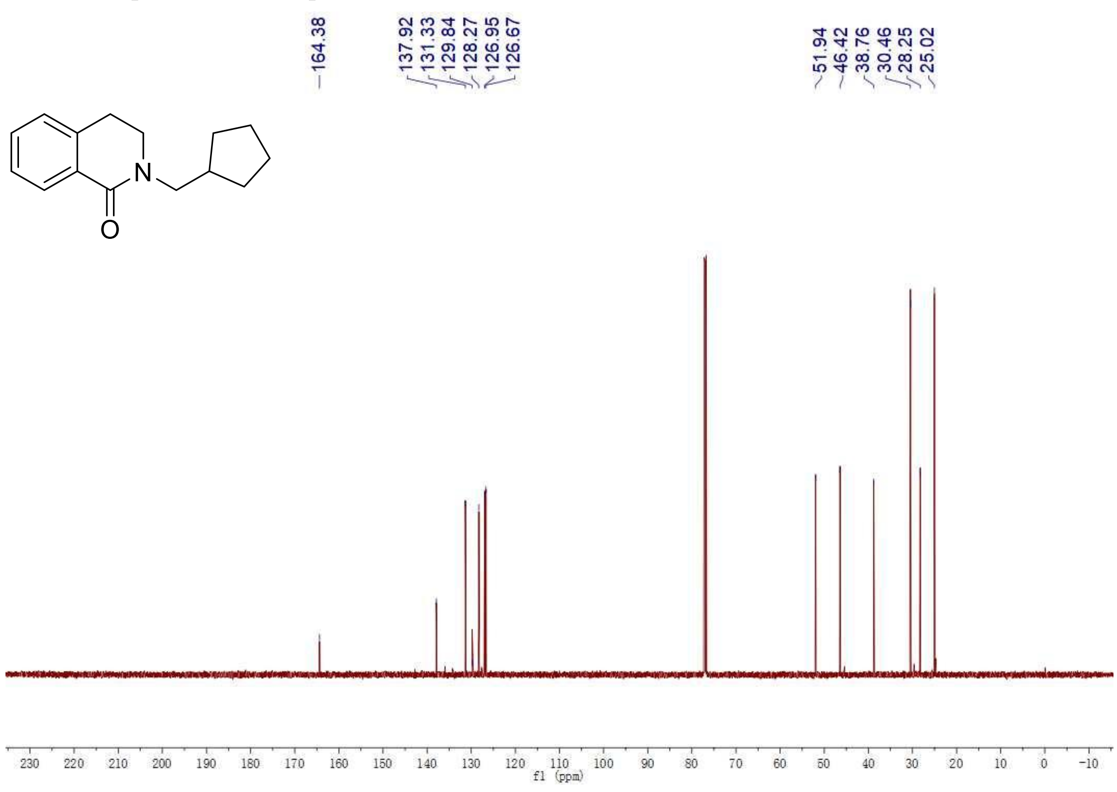
^{13}C NMR spectrum of compound **2k**



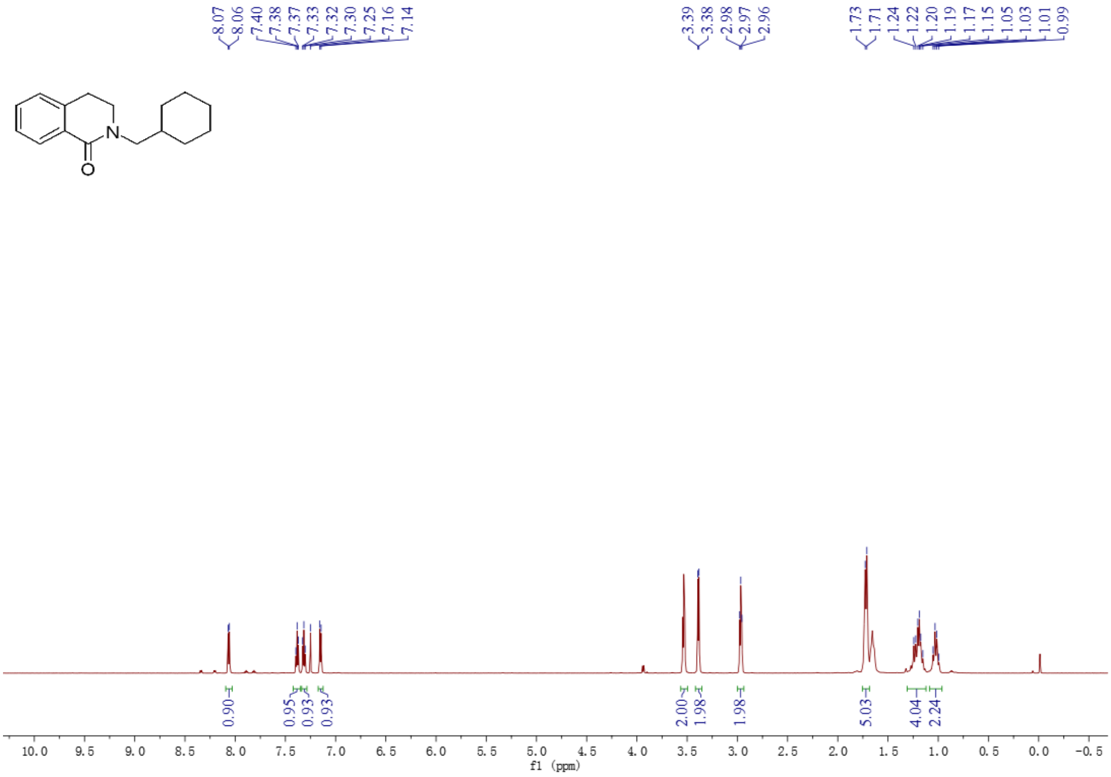
^{1}H NMR spectrum of compound **2l**



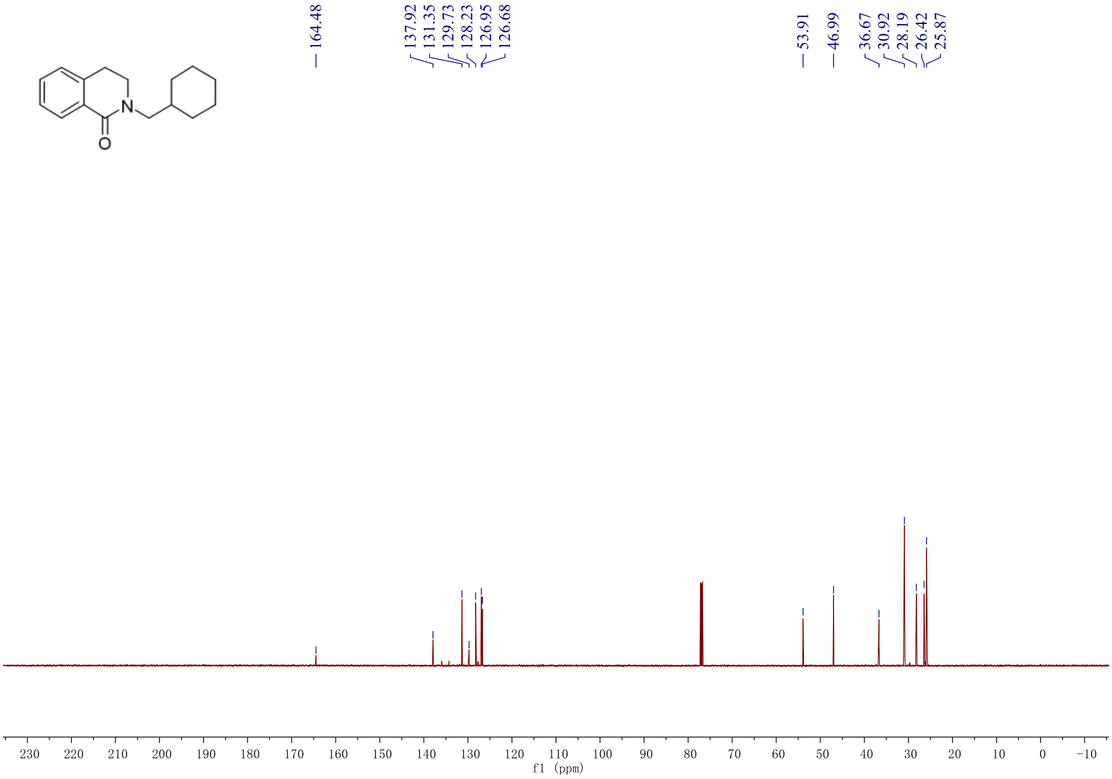
^{13}C NMR spectrum of compound **2l**



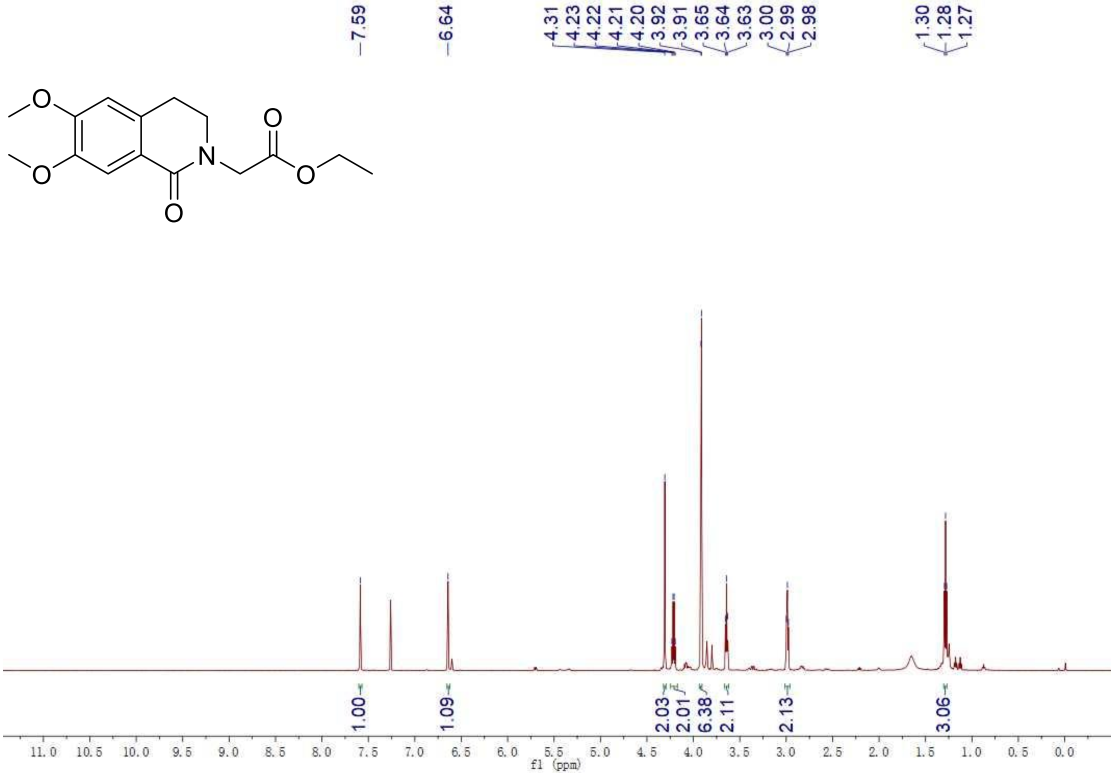
^{1}H NMR spectrum of compound **2m**



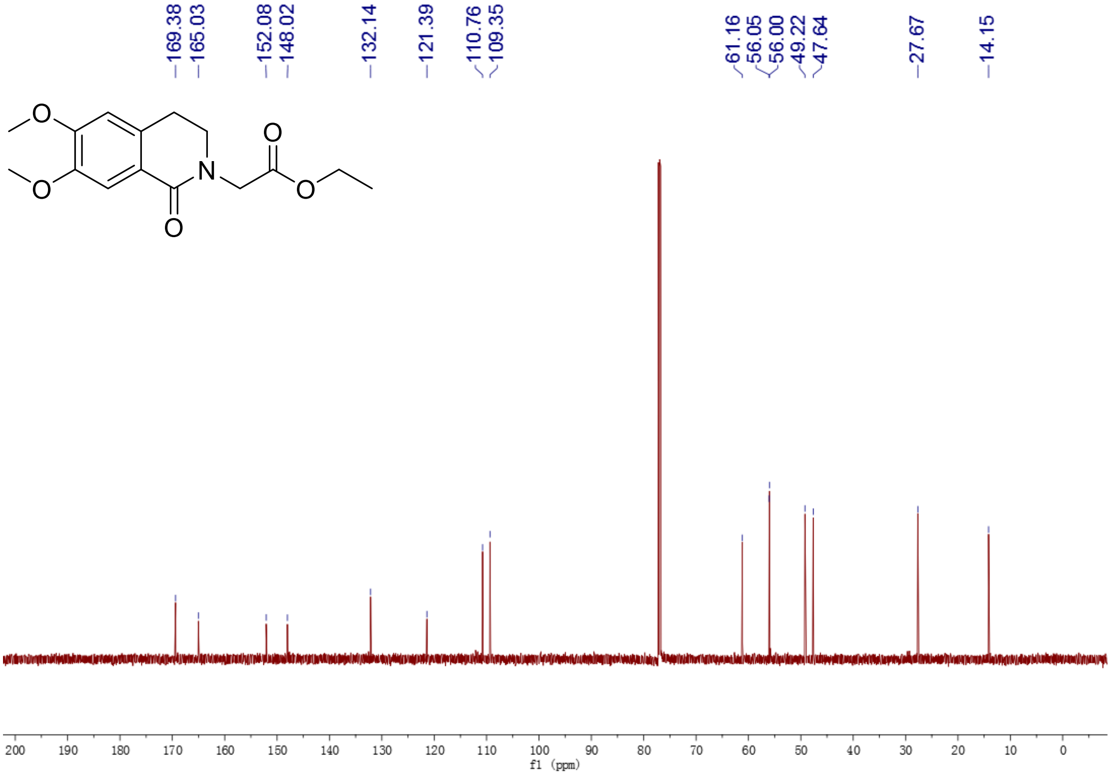
^{13}C NMR spectrum of compound **2m**



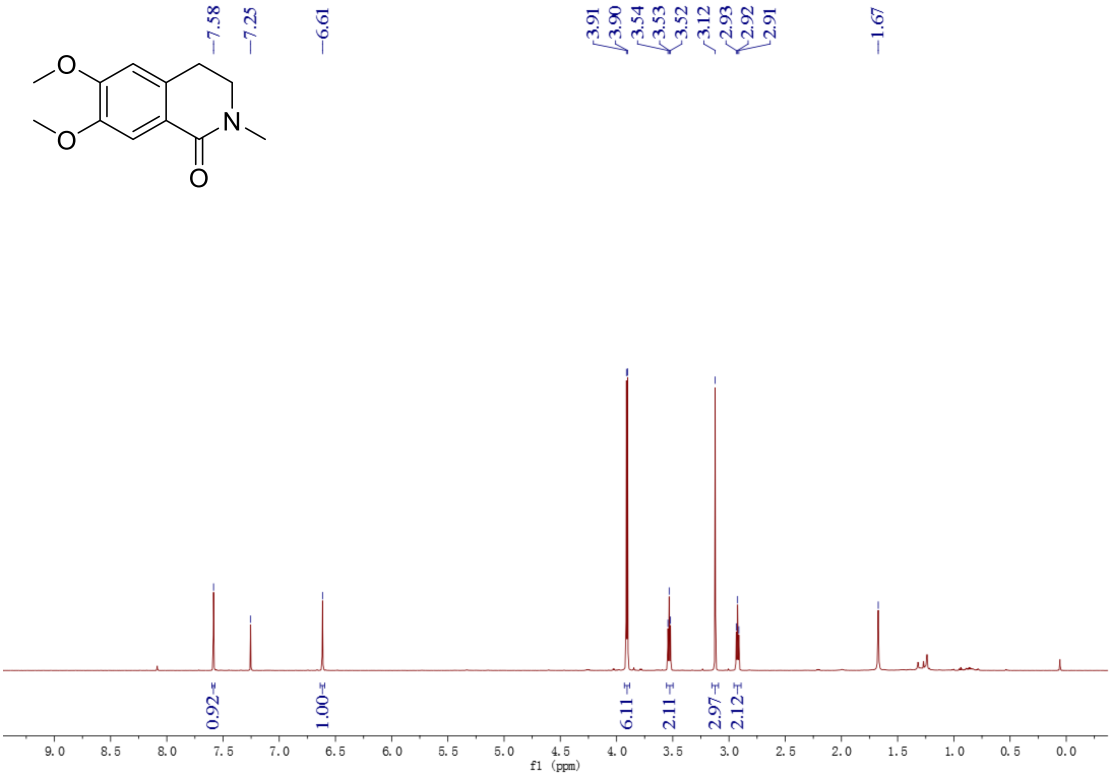
^{1}H NMR spectrum of compound **2n**



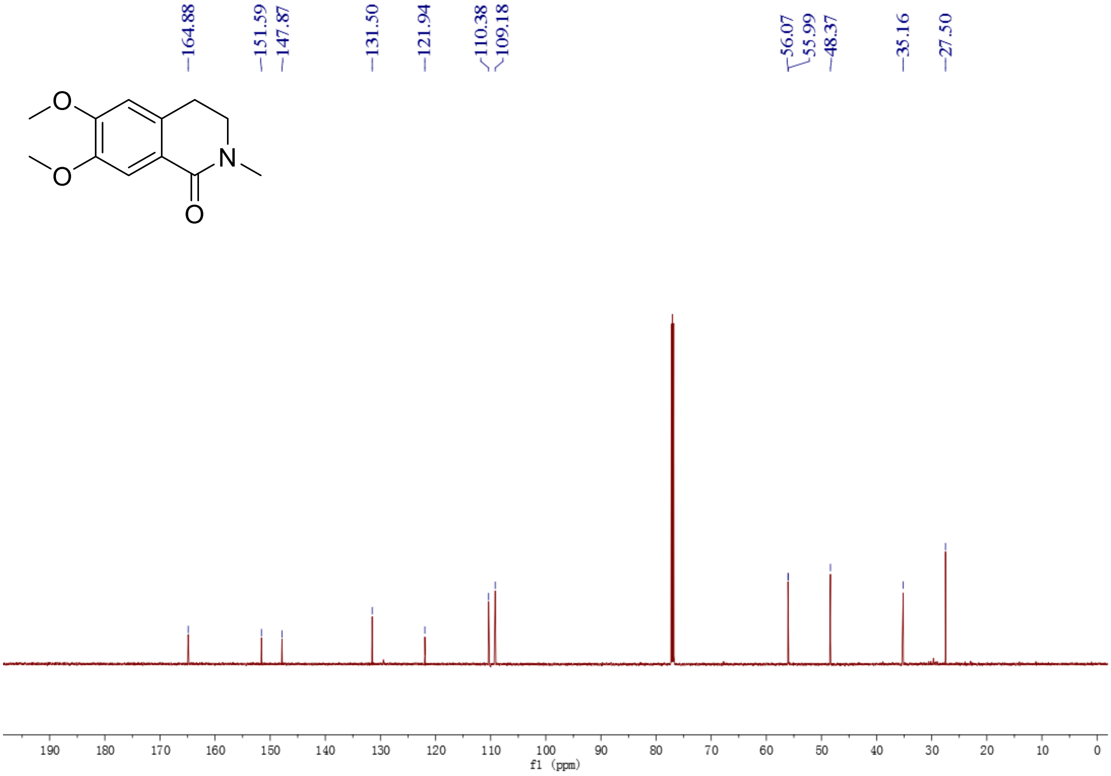
^{13}C NMR spectrum of compound **2n**



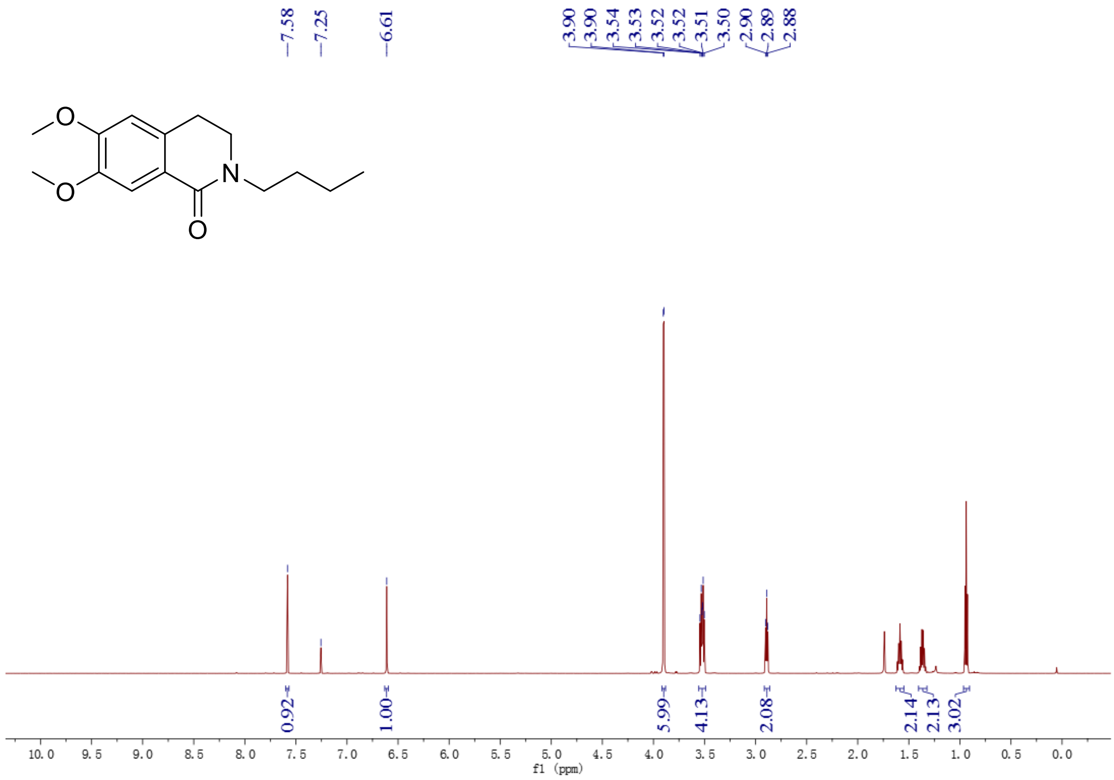
^{1}H NMR spectrum of compound **2o**



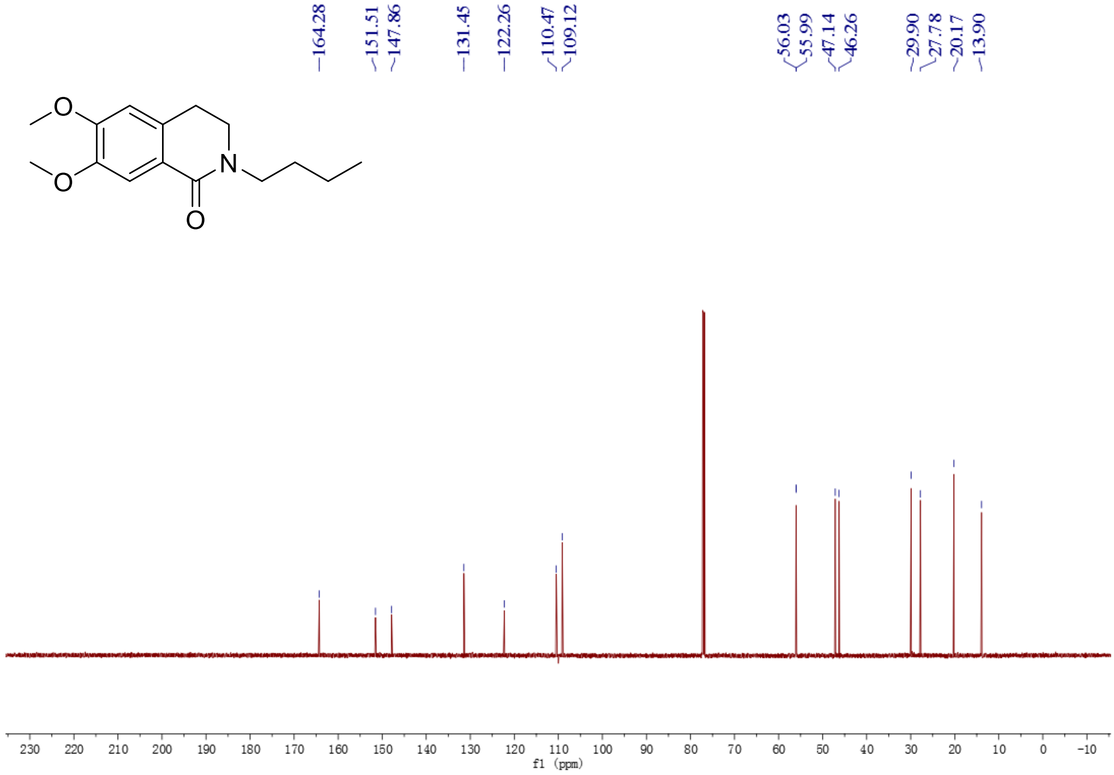
^{13}C NMR spectrum of compound **2o**



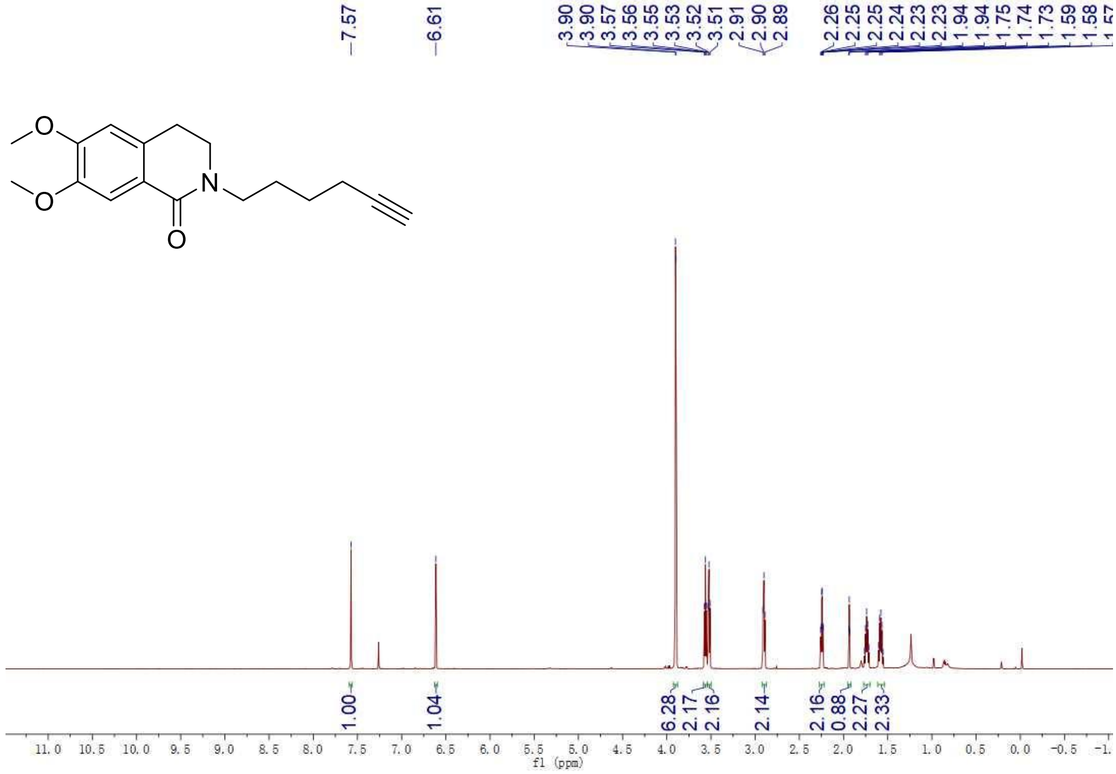
^{1}H NMR spectrum of compound **2p**



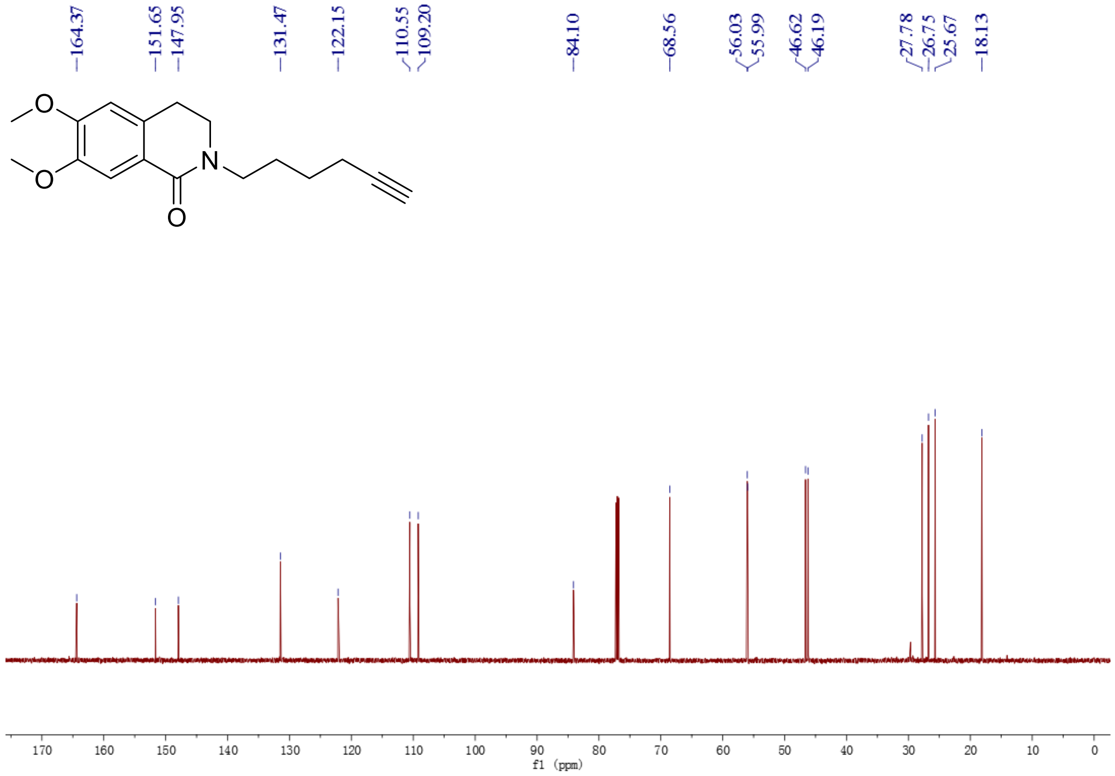
^{13}C NMR spectrum of compound **2p**



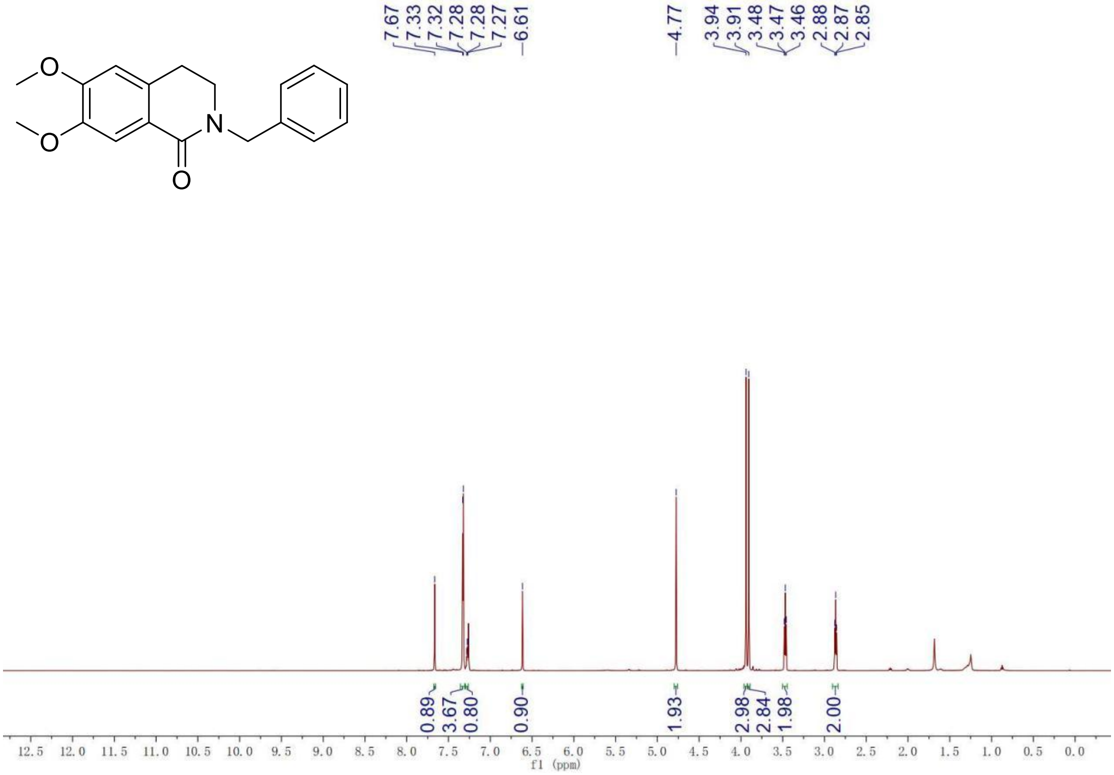
^{1}H NMR spectrum of compound **2q**



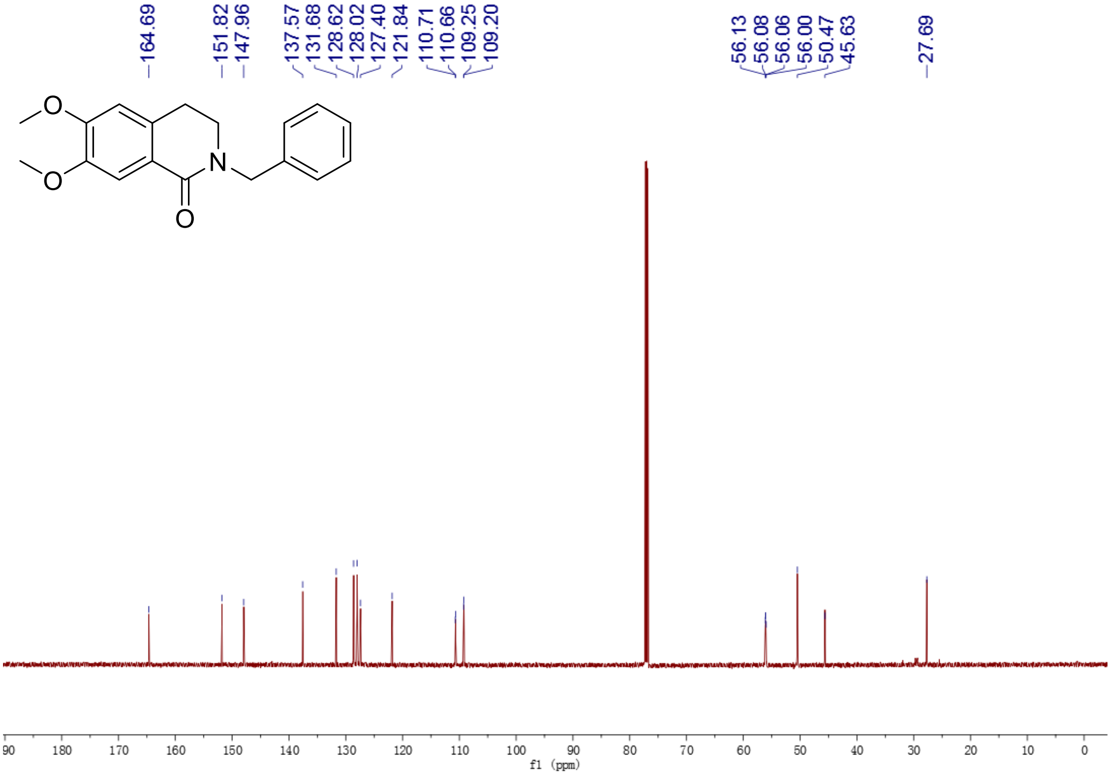
^{13}C NMR spectrum of compound **2q**



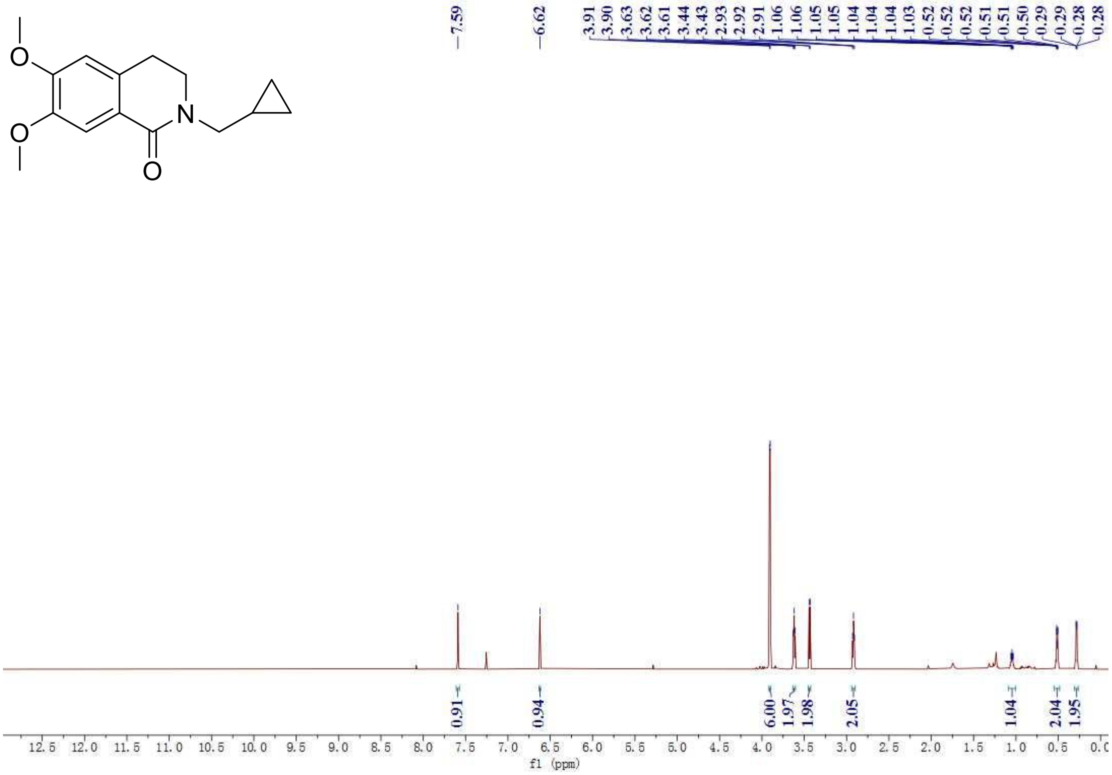
^{1}H NMR spectrum of compound **2r**



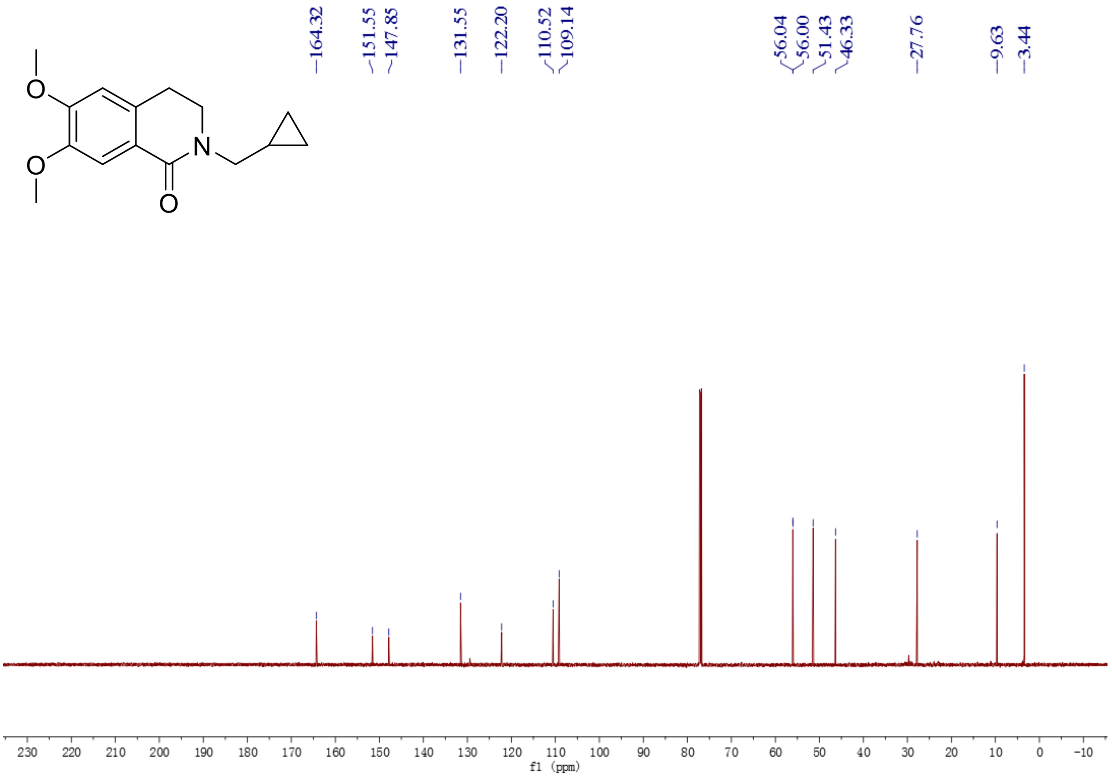
^{13}C NMR spectrum of compound **2r**



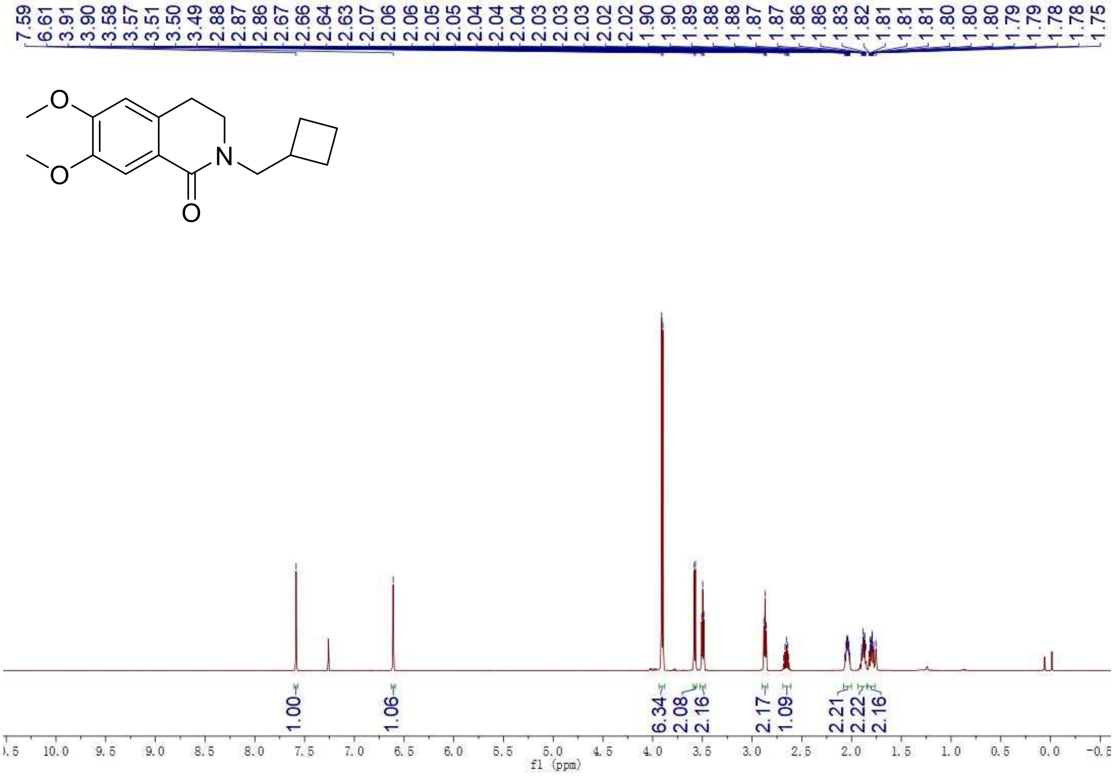
^{1}H NMR spectrum of compound **2s**



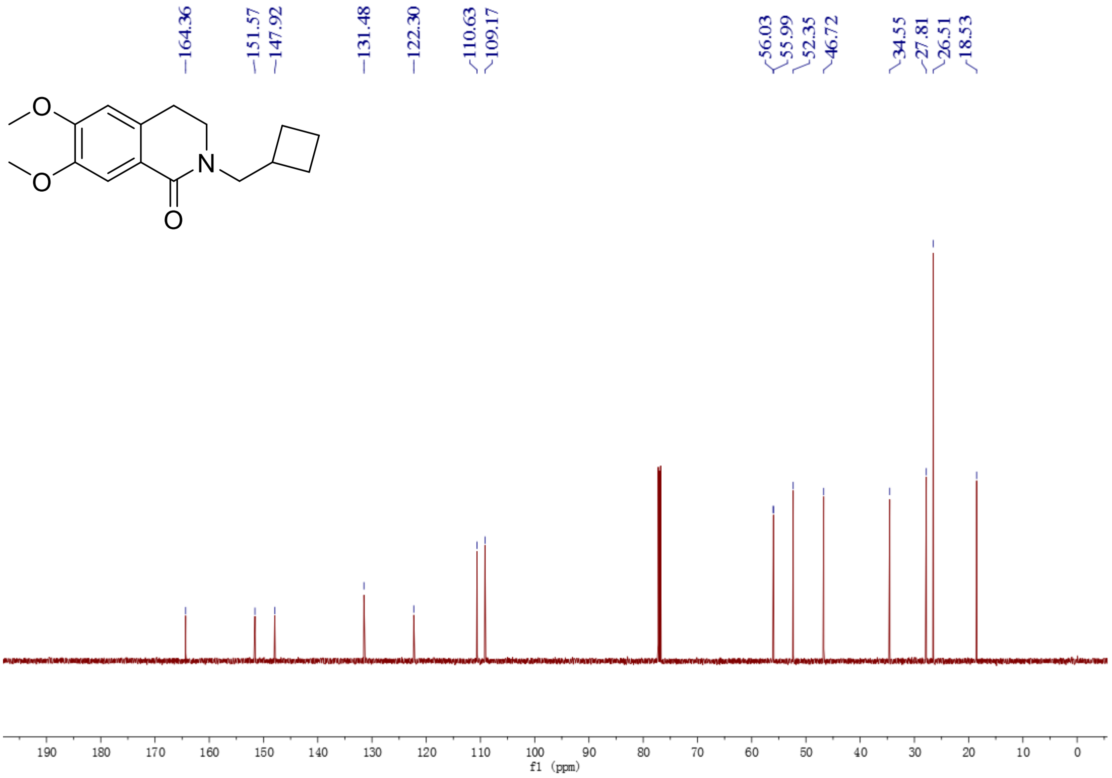
^{13}C NMR spectrum of compound **2s**



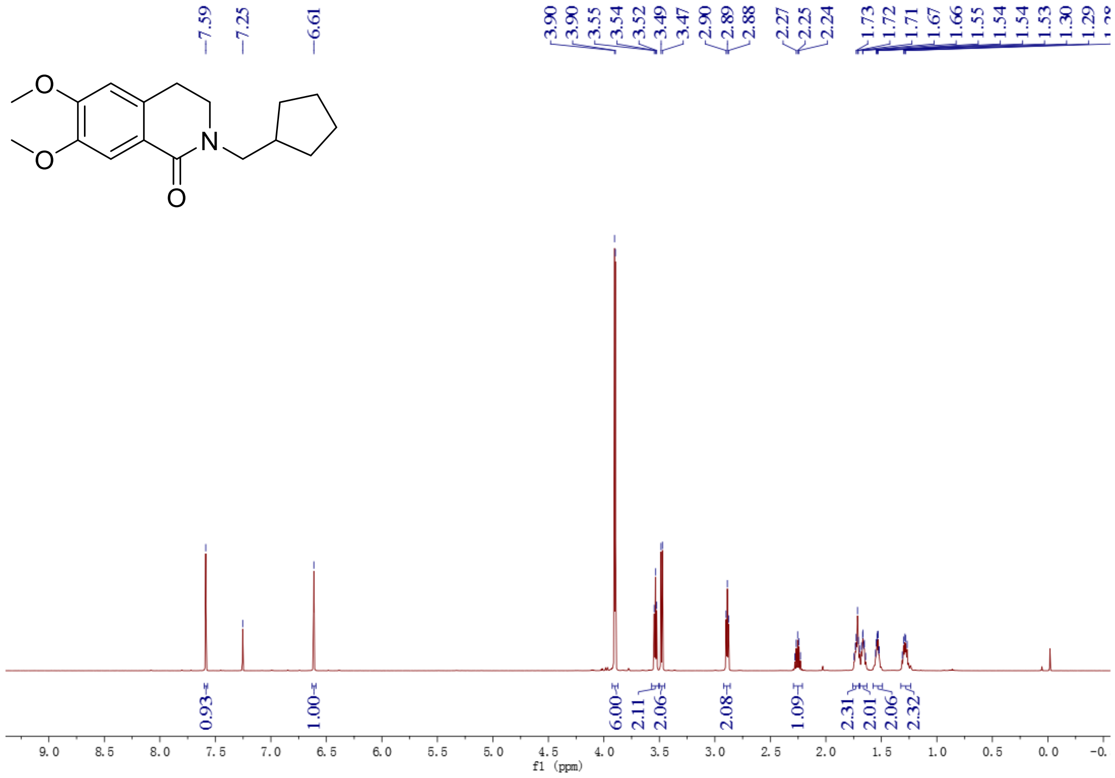
^{1}H NMR spectrum of compound **2t**



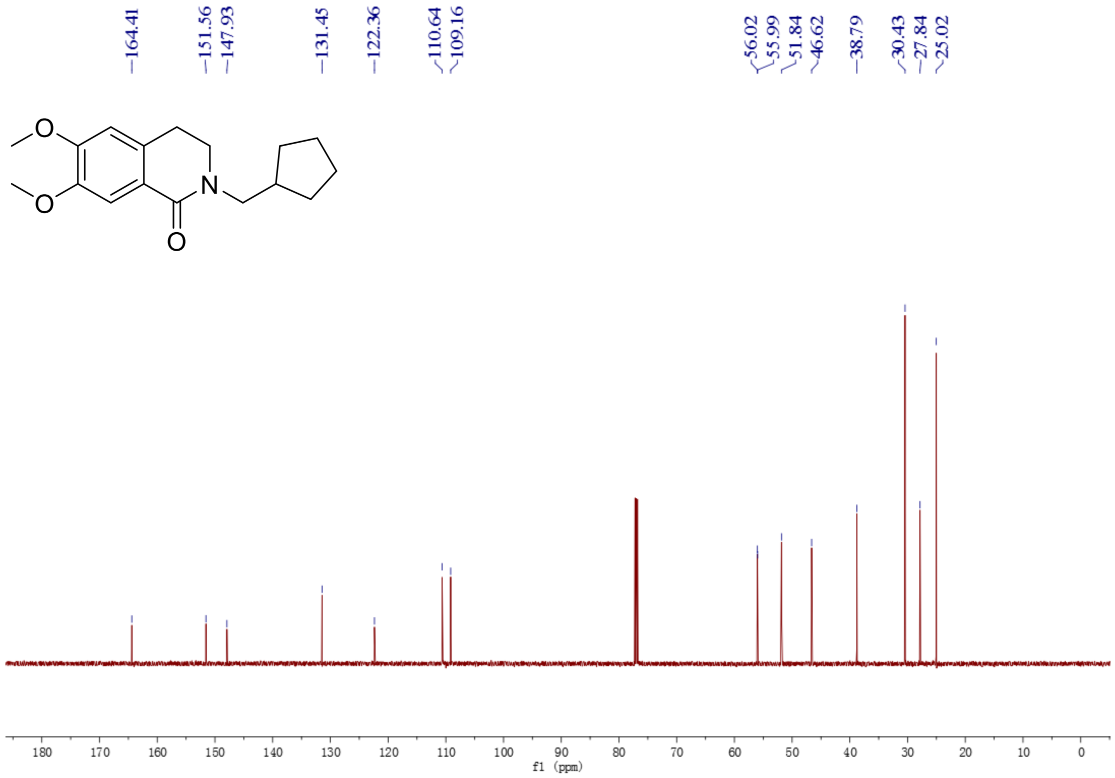
^{13}C NMR spectrum of compound **2t**



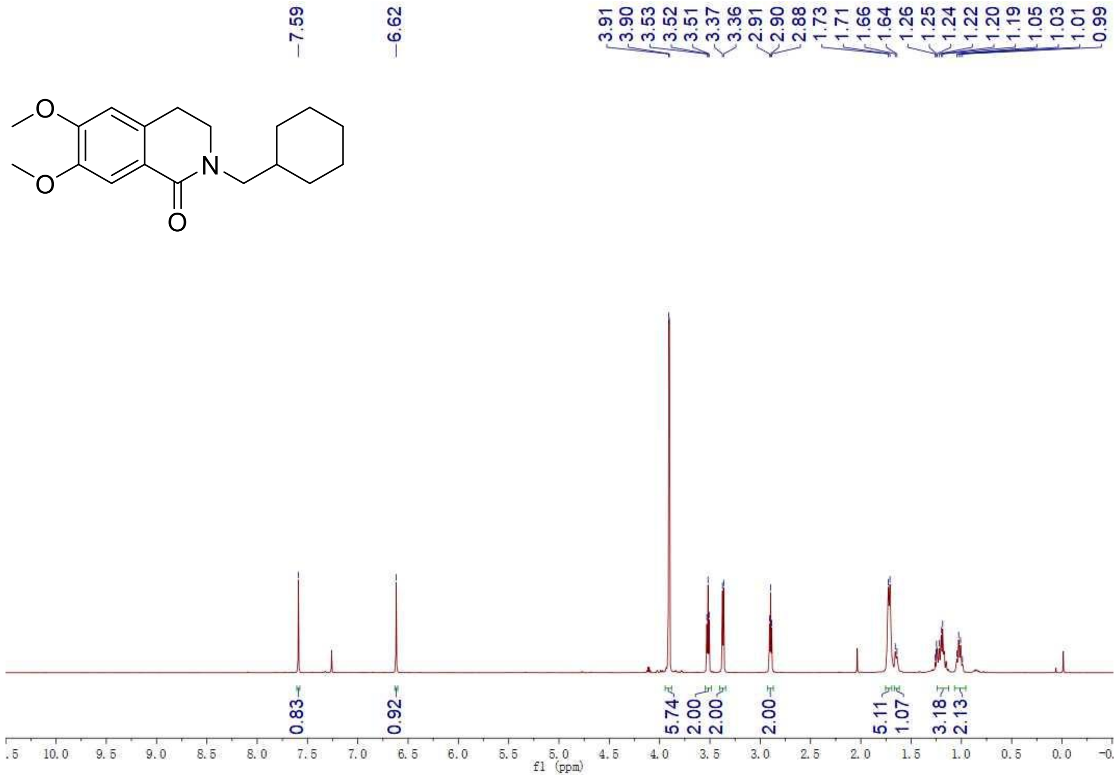
^{1}H NMR spectrum of compound **2u**



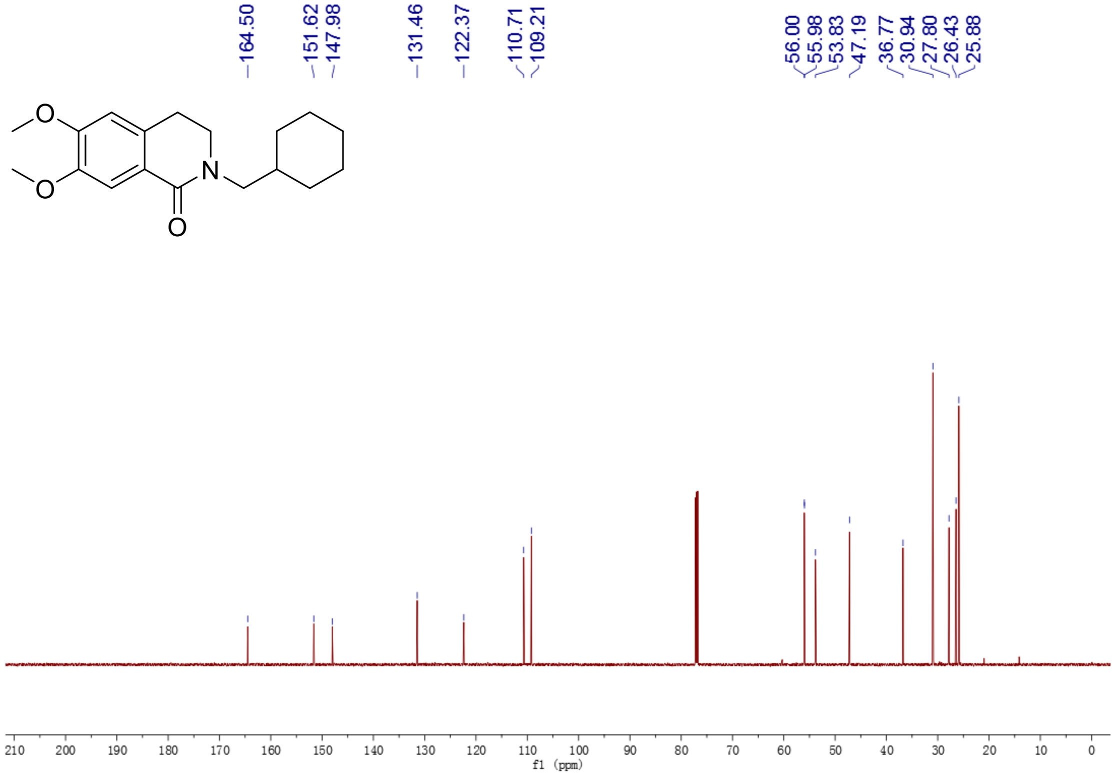
^{13}C NMR spectrum of compound **2u**



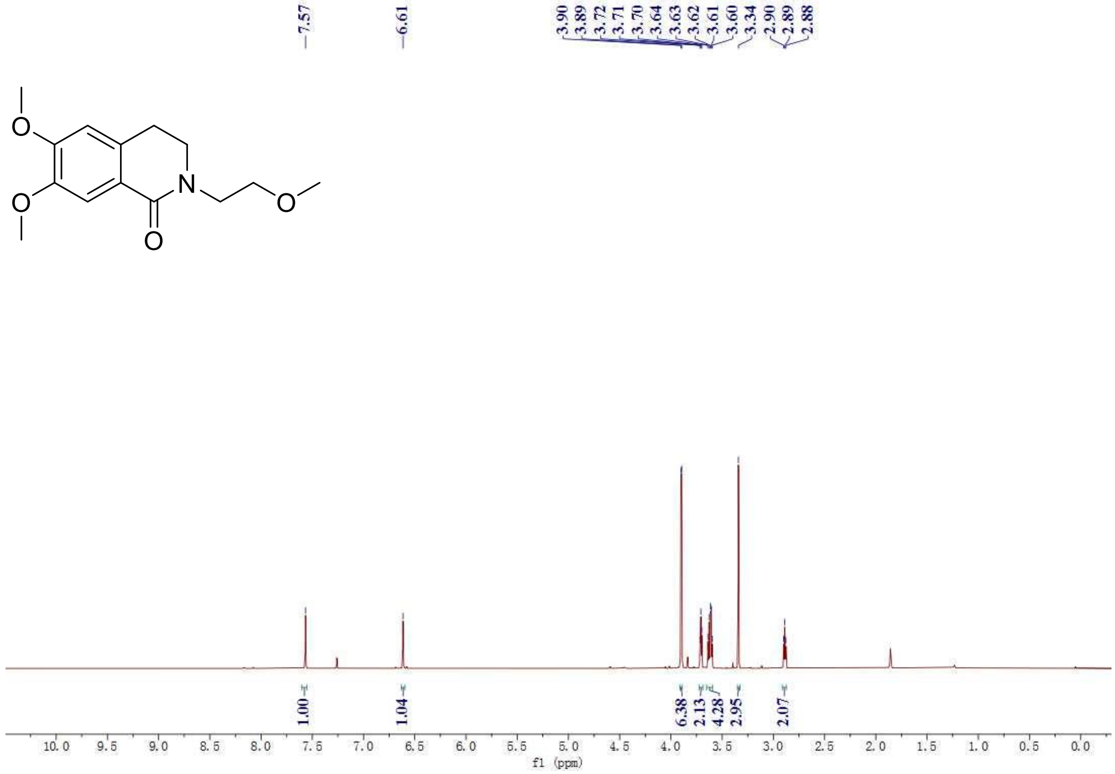
^{1}H NMR spectrum of compound **2v**



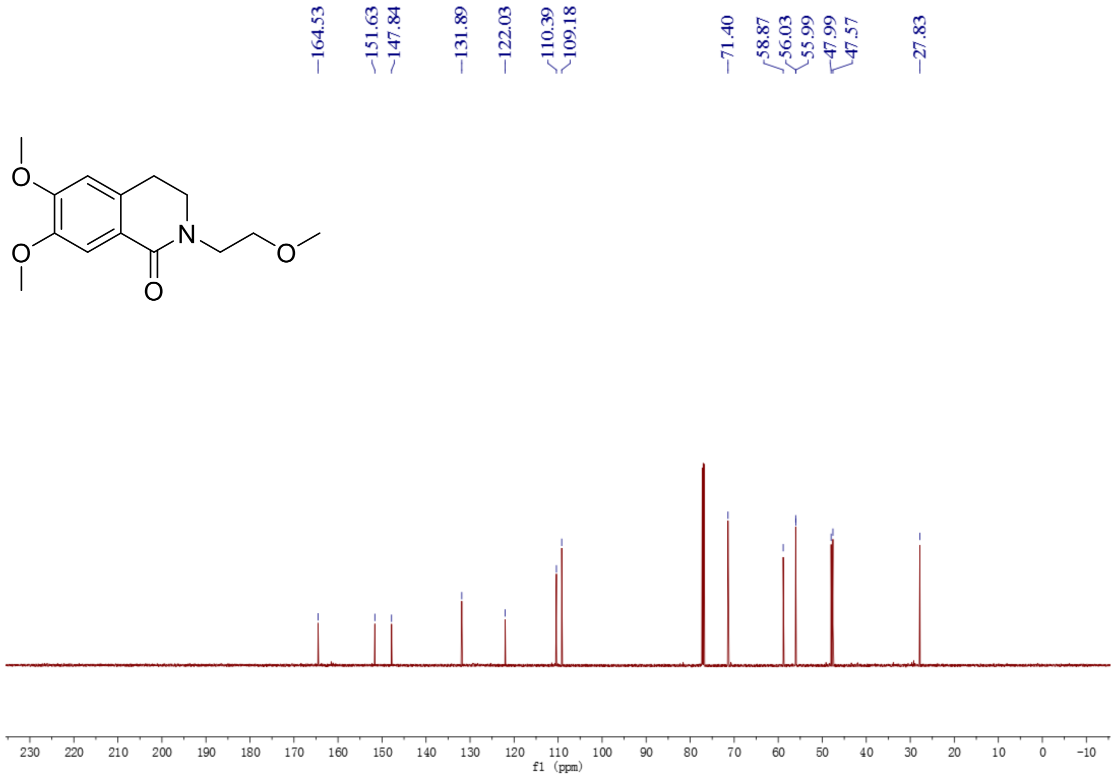
^{13}C NMR spectrum of compound **2v**



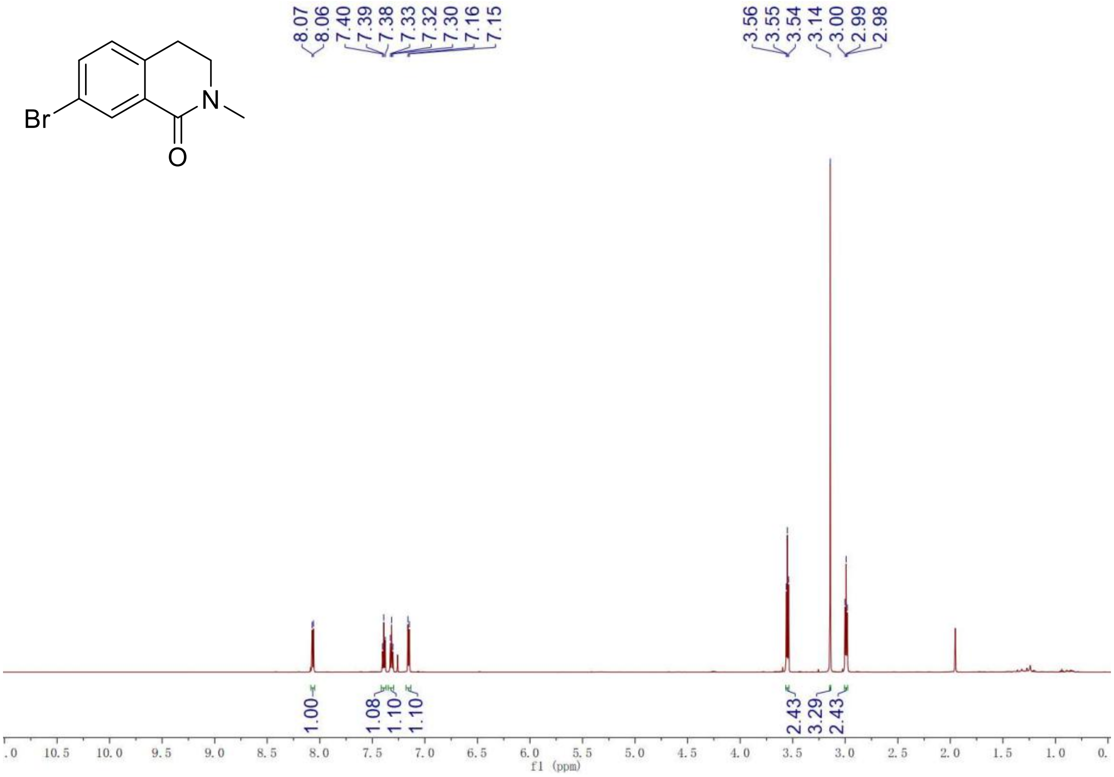
^{1}H NMR spectrum of compound **2w**



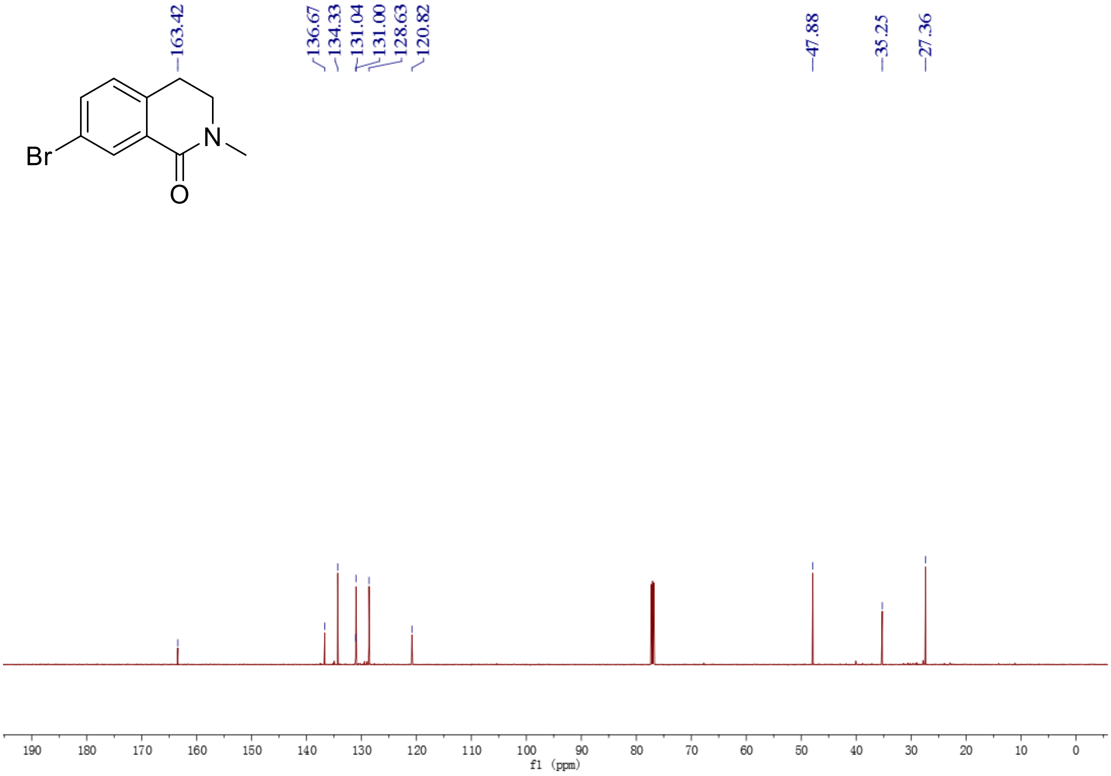
^{13}C NMR spectrum of compound **2w**



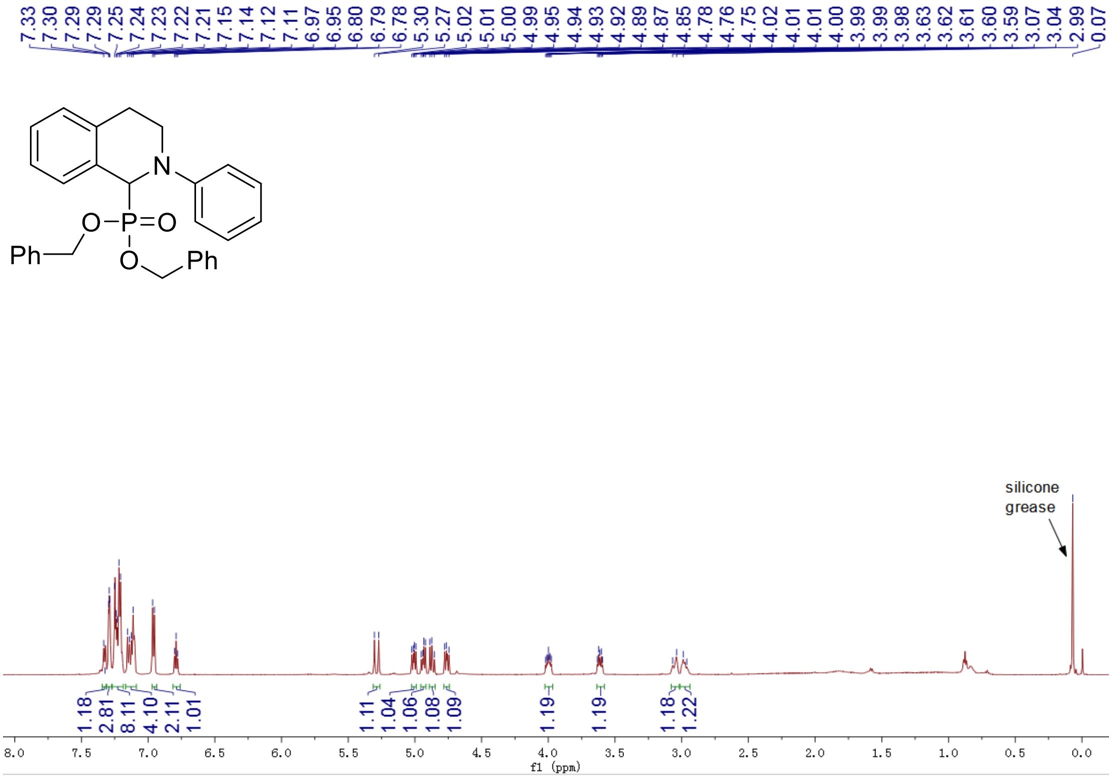
^{1}H NMR spectrum of compound **2x**



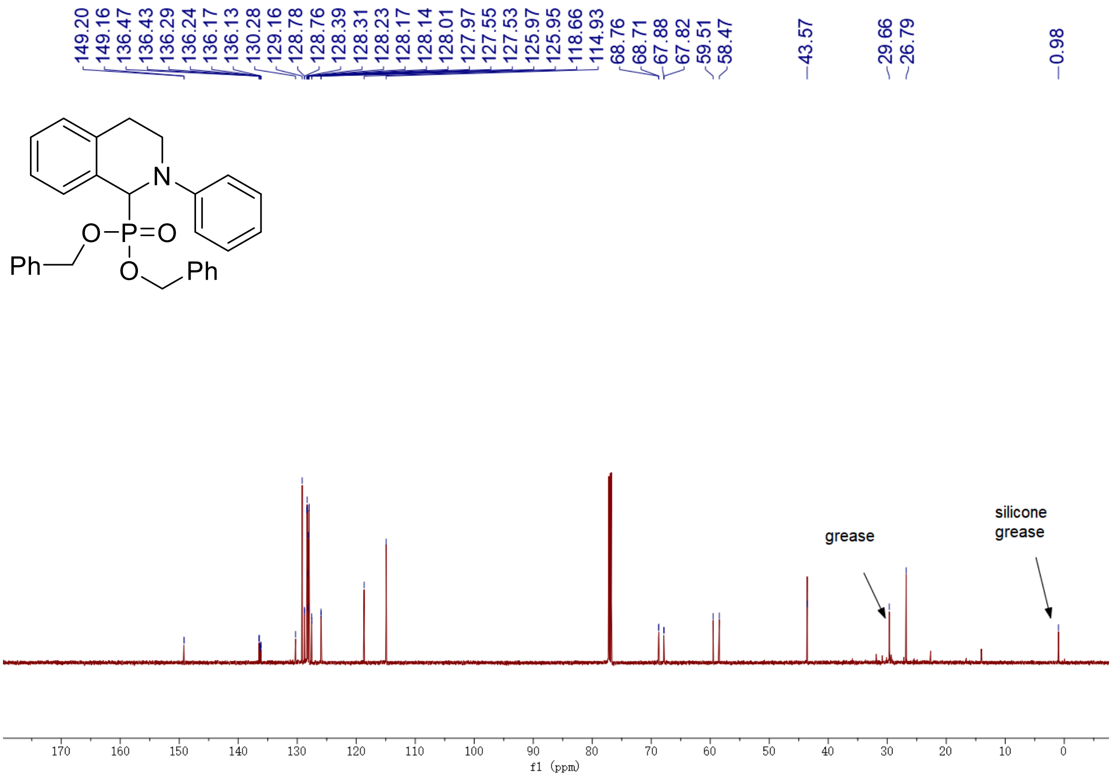
^{13}C NMR spectrum of compound **2x**



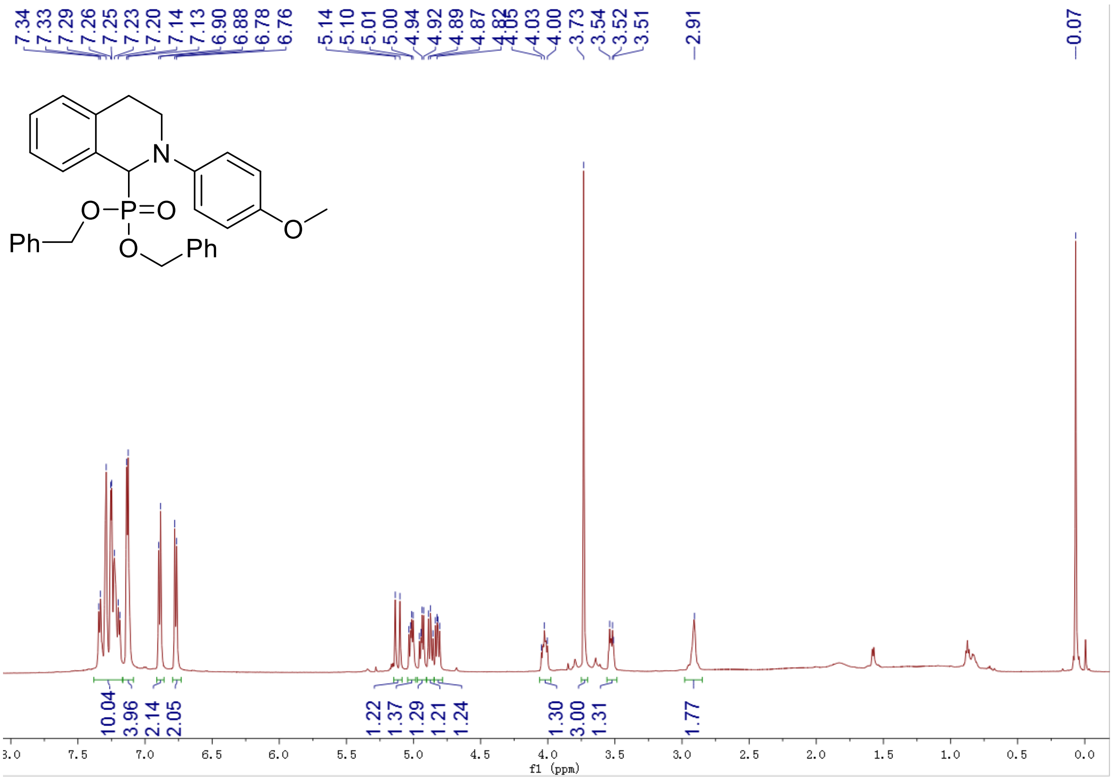
^{1}H NMR spectrum of compound **4a**



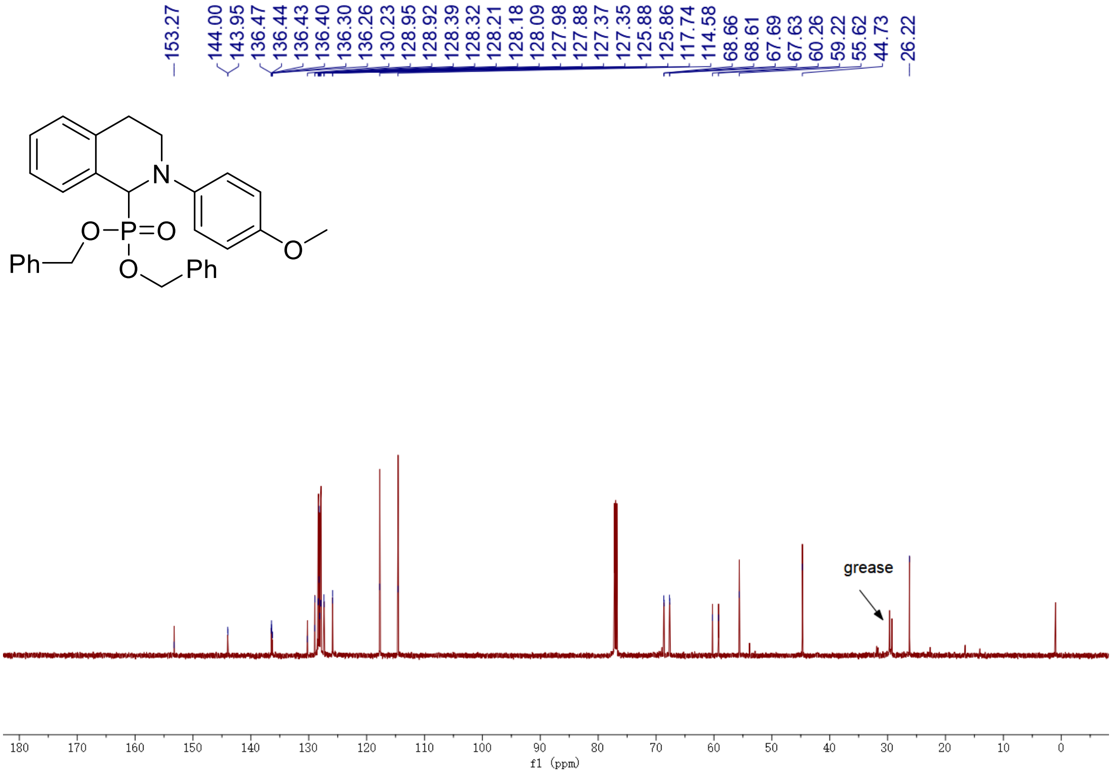
^{13}C NMR spectrum of compound **4a**



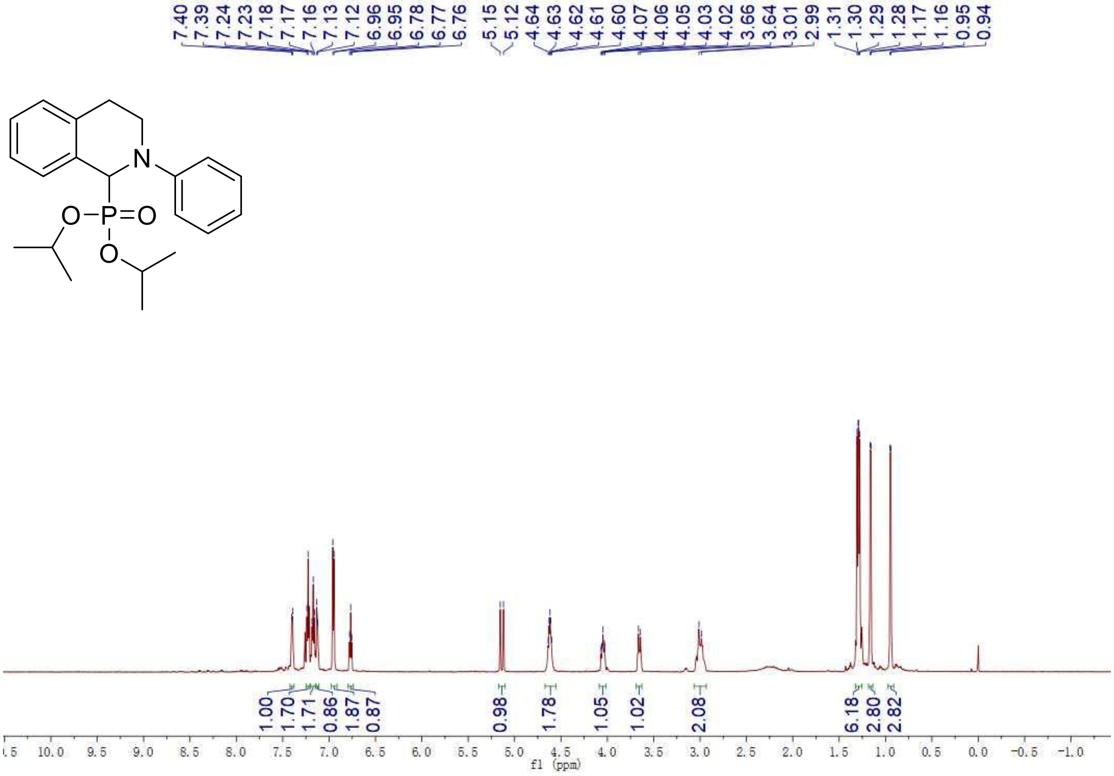
^{1}H NMR spectrum of compound **4b**



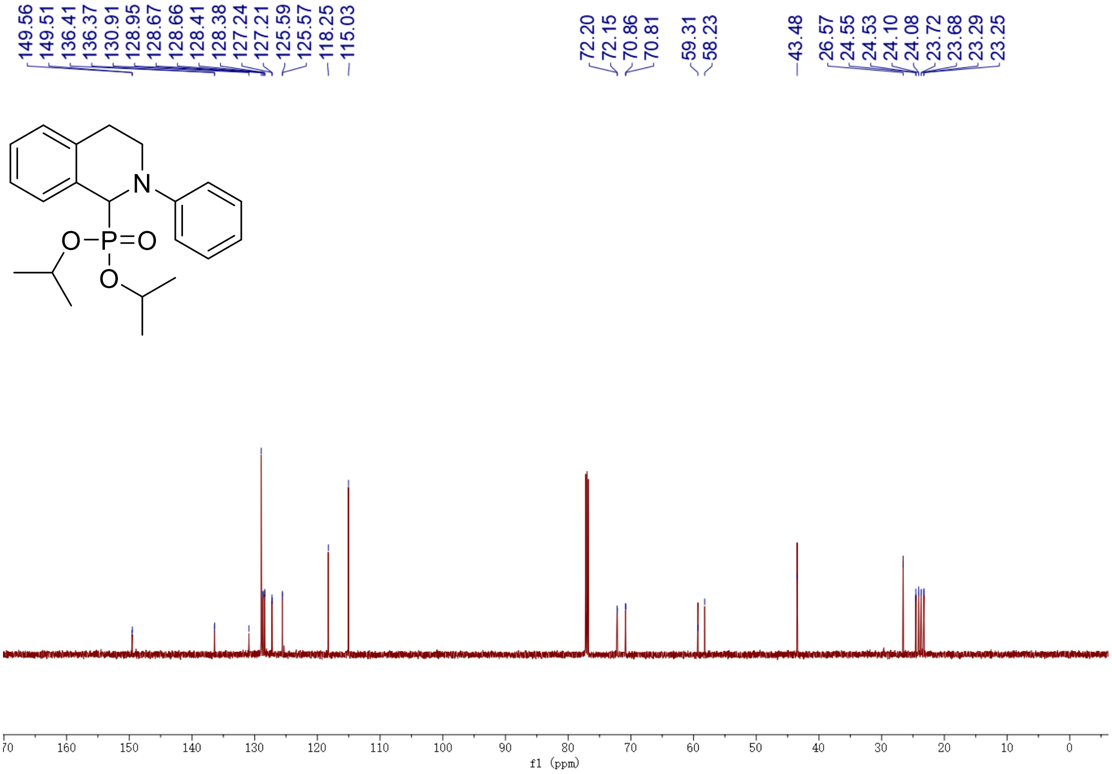
^{13}C NMR spectrum of compound **4b**



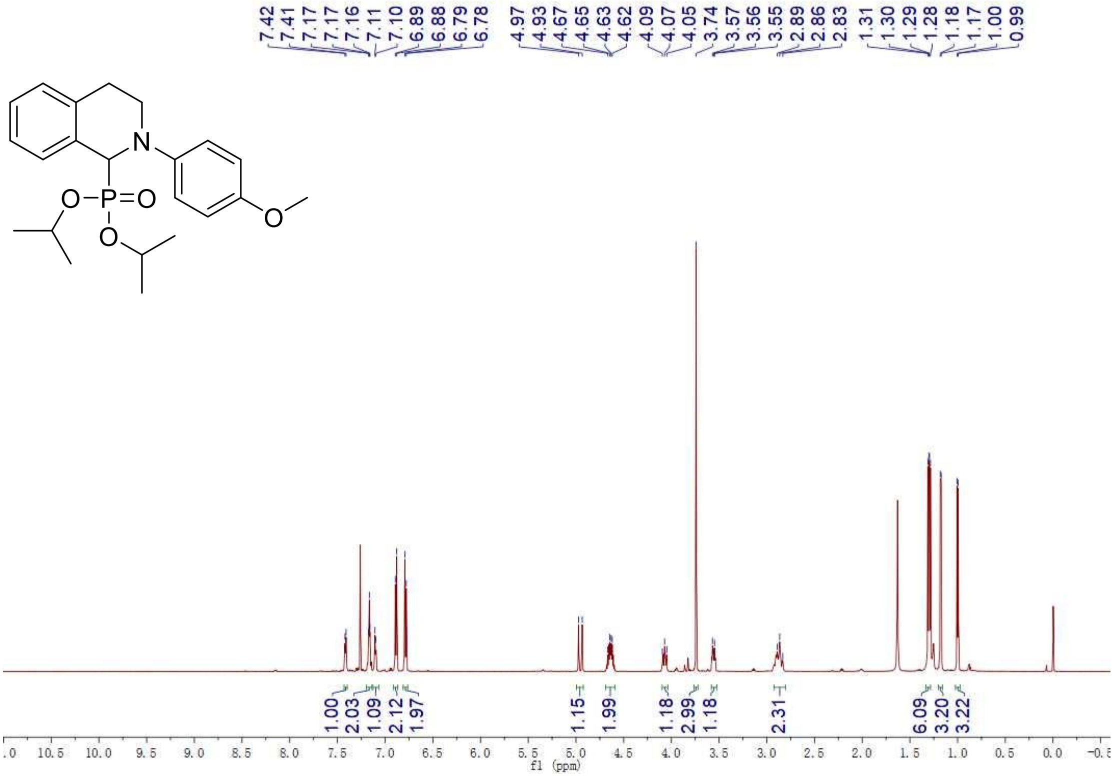
^{1}H NMR spectrum of compound **4c**



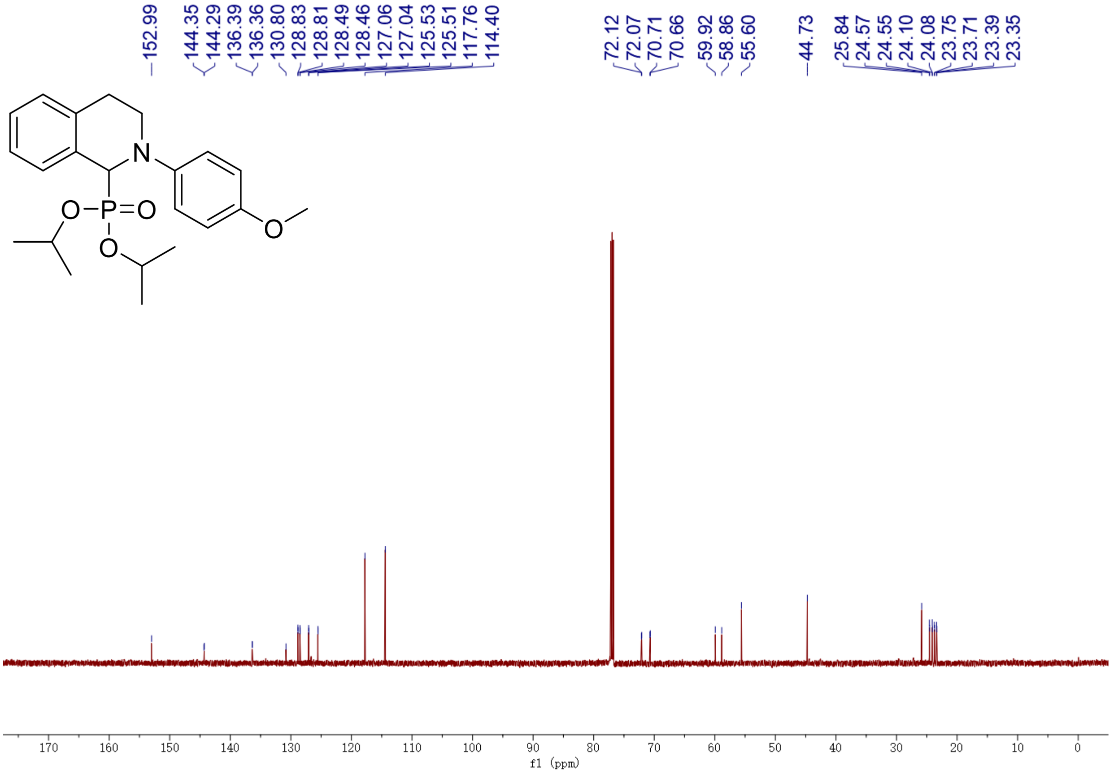
^{13}C NMR spectrum of compound **4c**



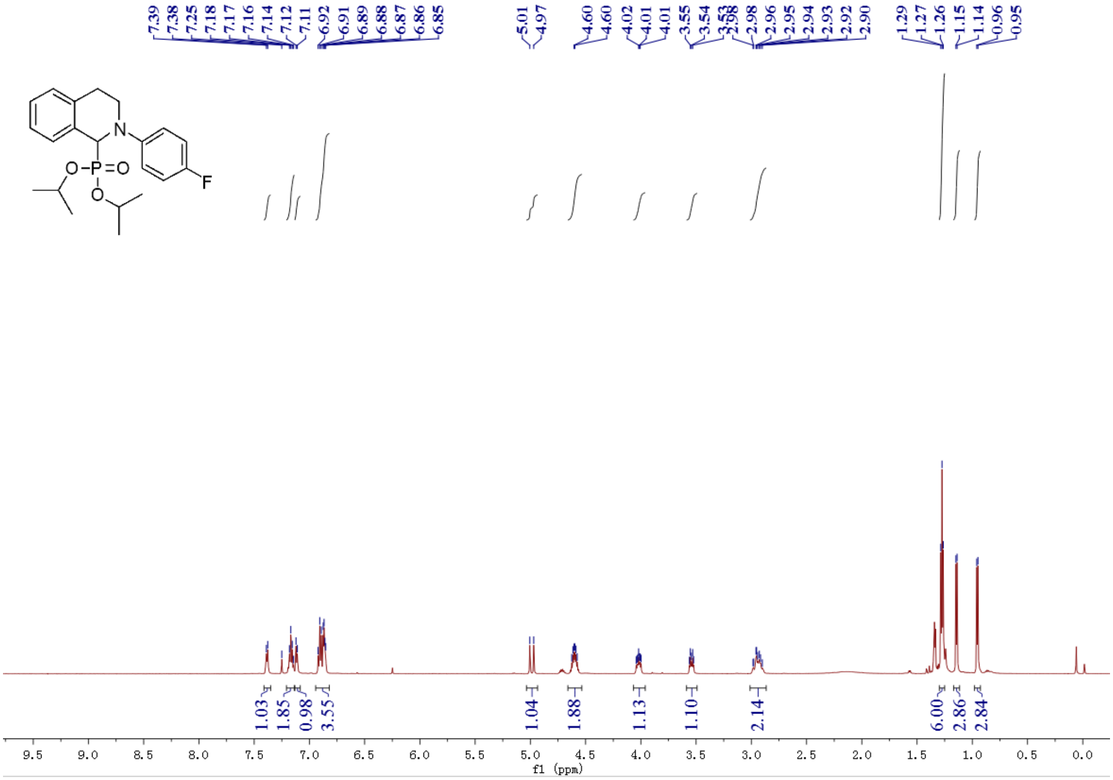
^{1}H NMR spectrum of compound **4d**



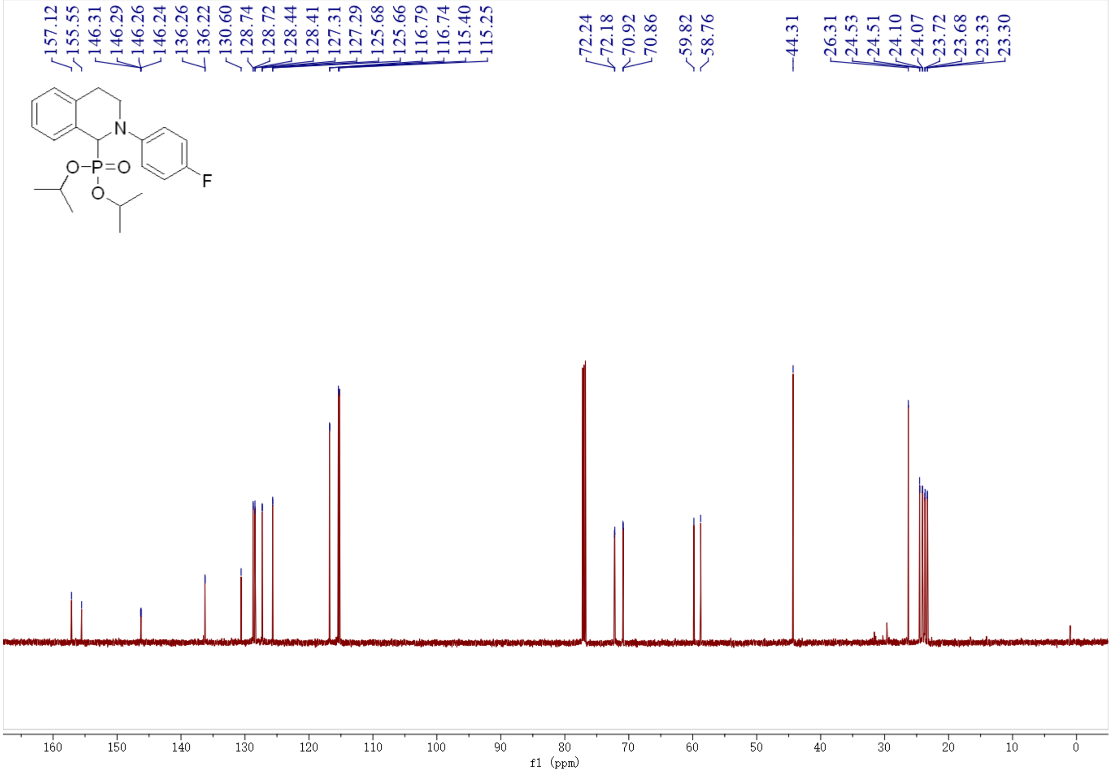
^{13}C NMR spectrum of compound **4d**



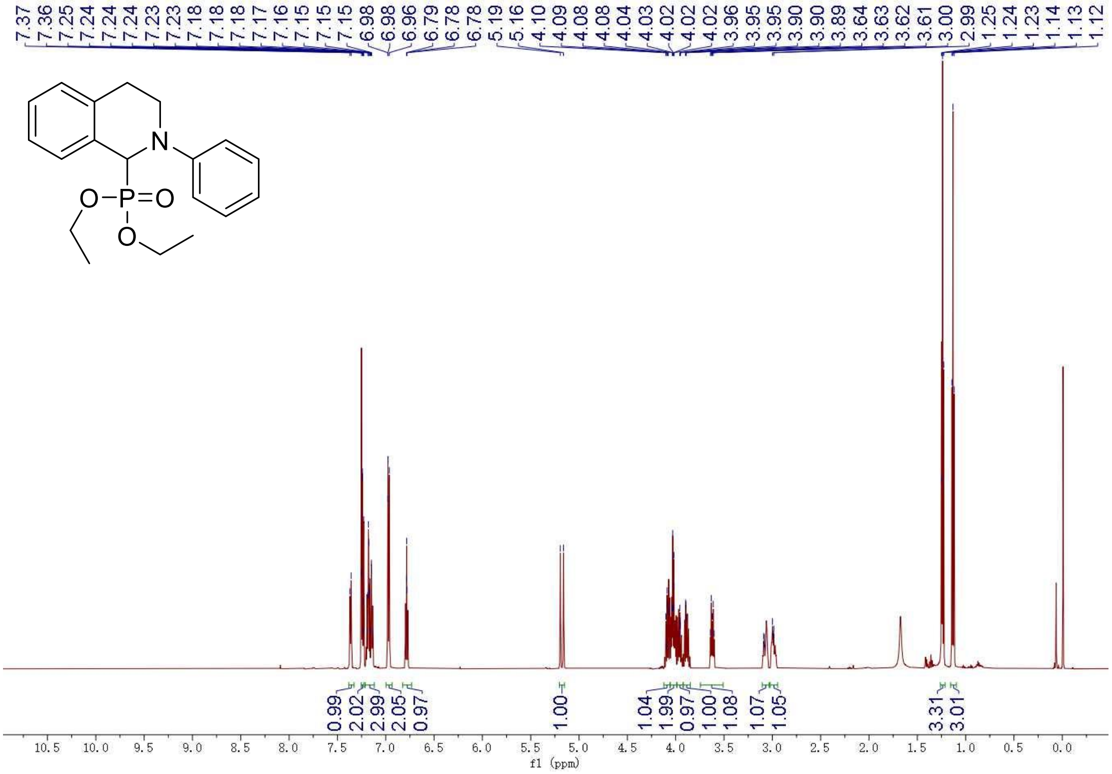
^{1}H NMR spectrum of compound **4e**



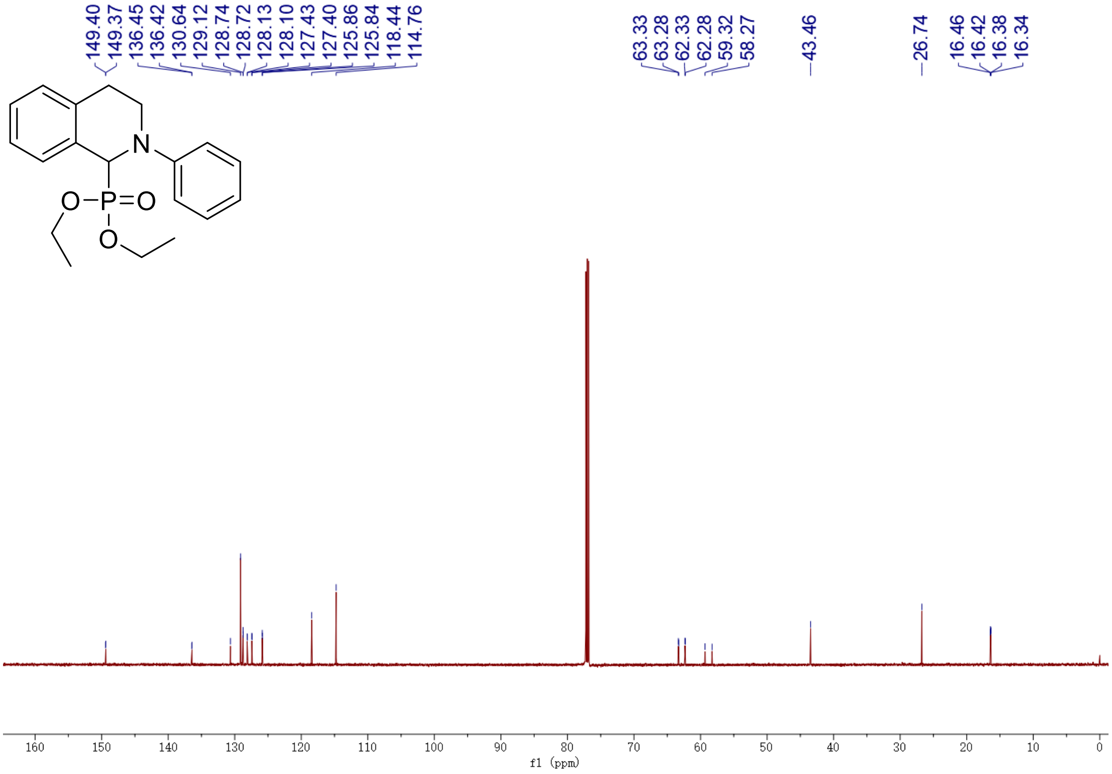
^{13}C NMR spectrum of compound **4e**



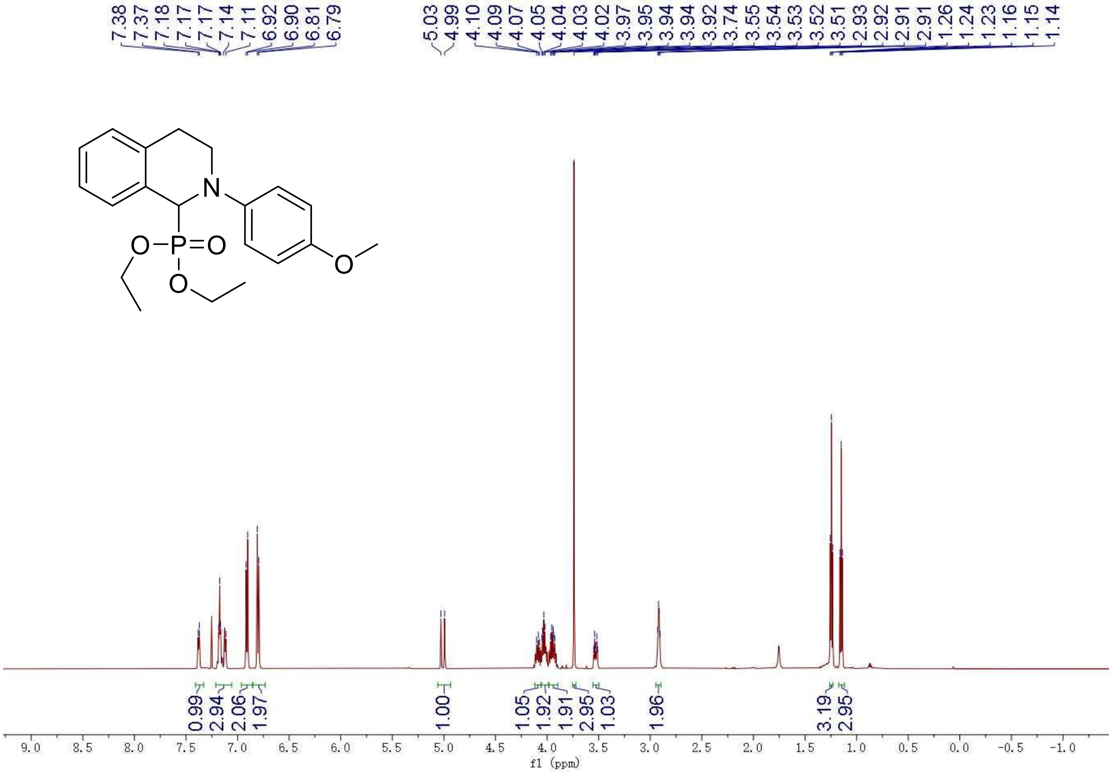
^{1}H NMR spectrum of compound **4f**



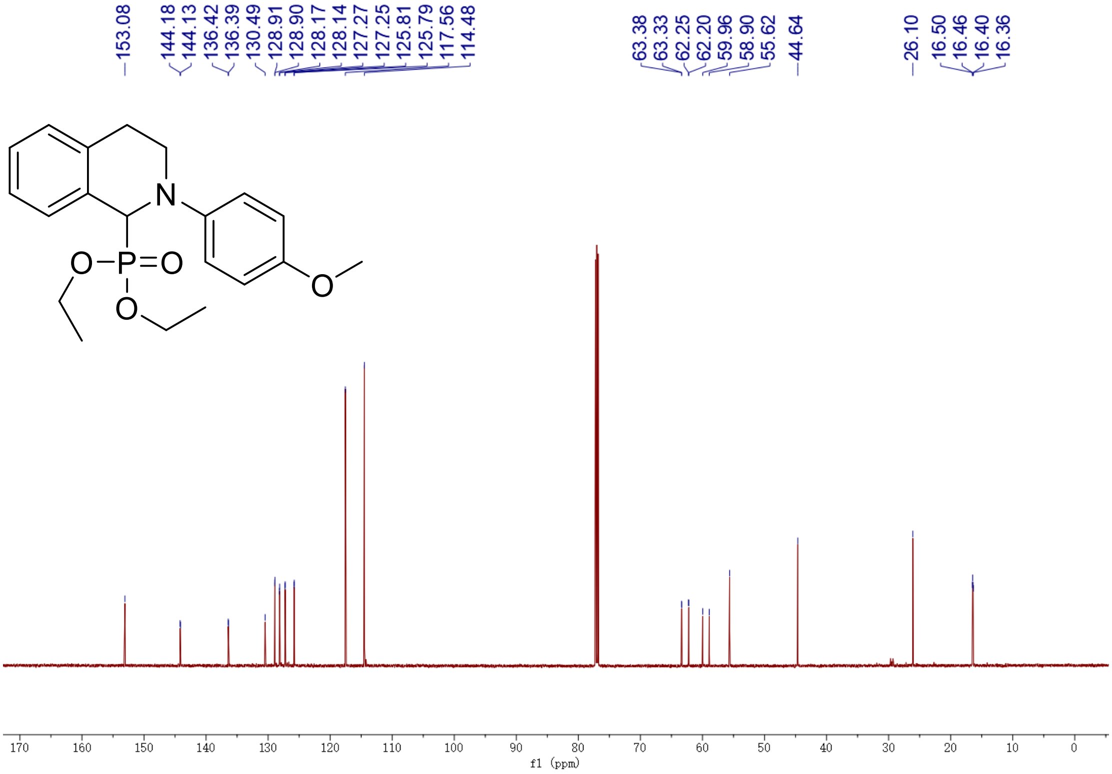
^{13}C NMR spectrum of compound **4f**



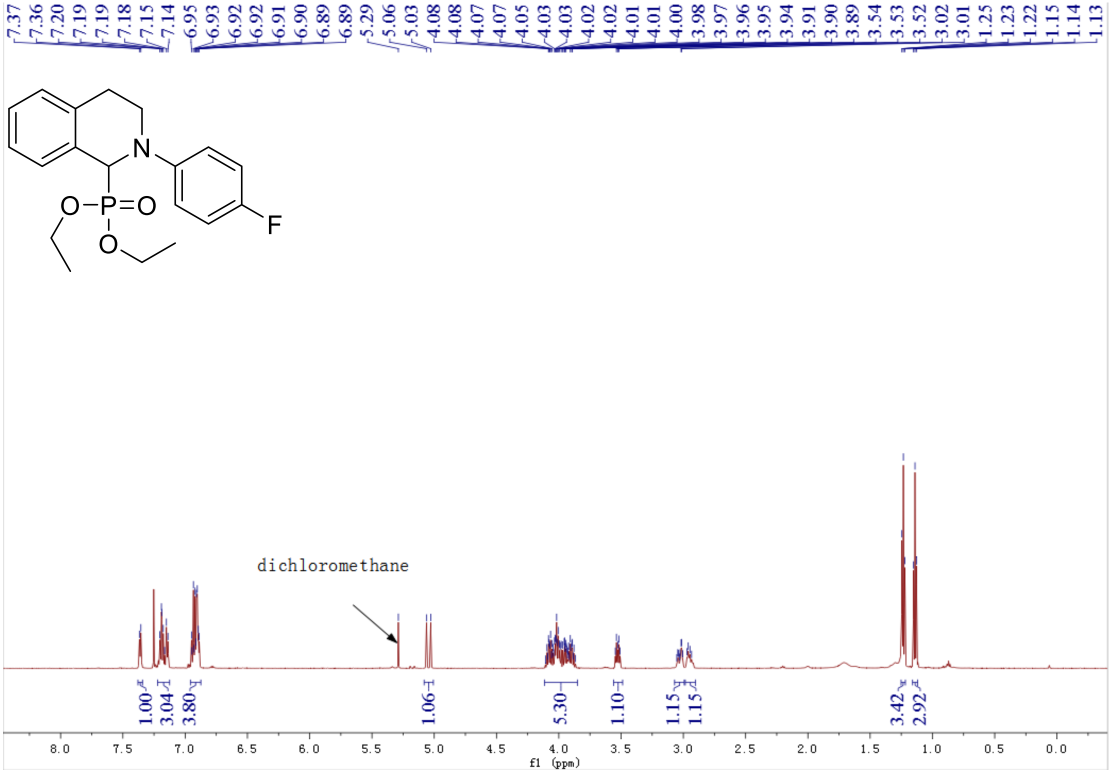
^{1}H NMR spectrum of compound **4g**



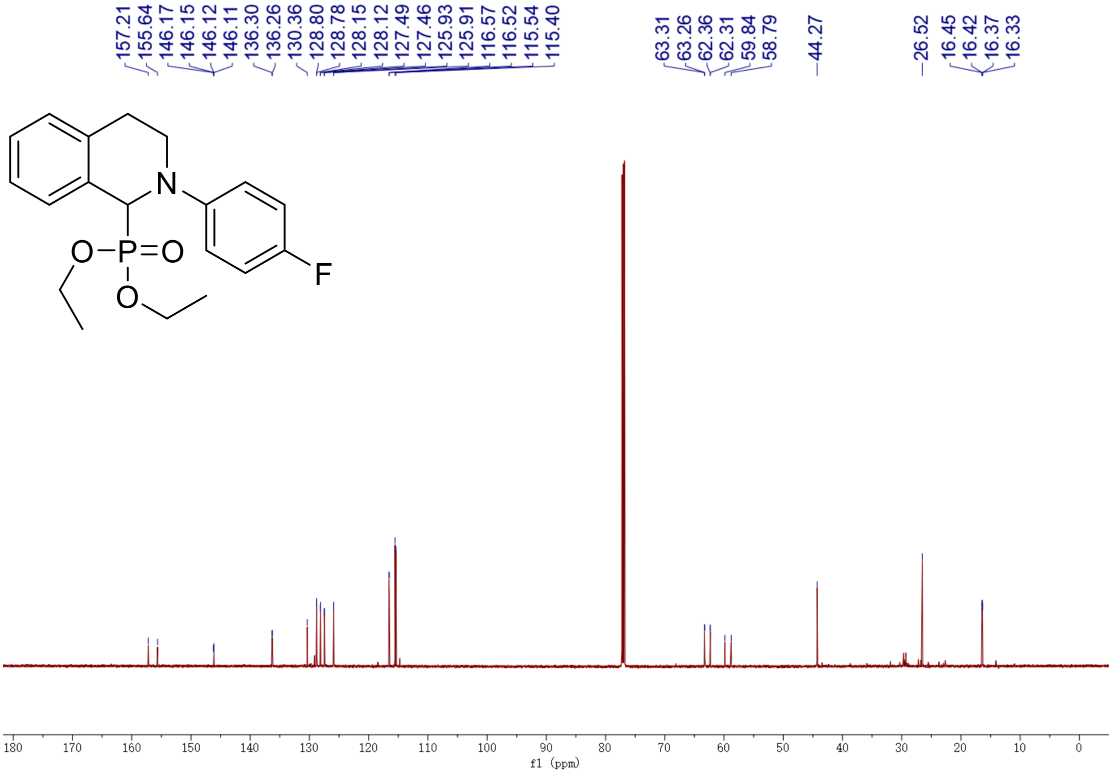
^{13}C NMR spectrum of compound **4g**



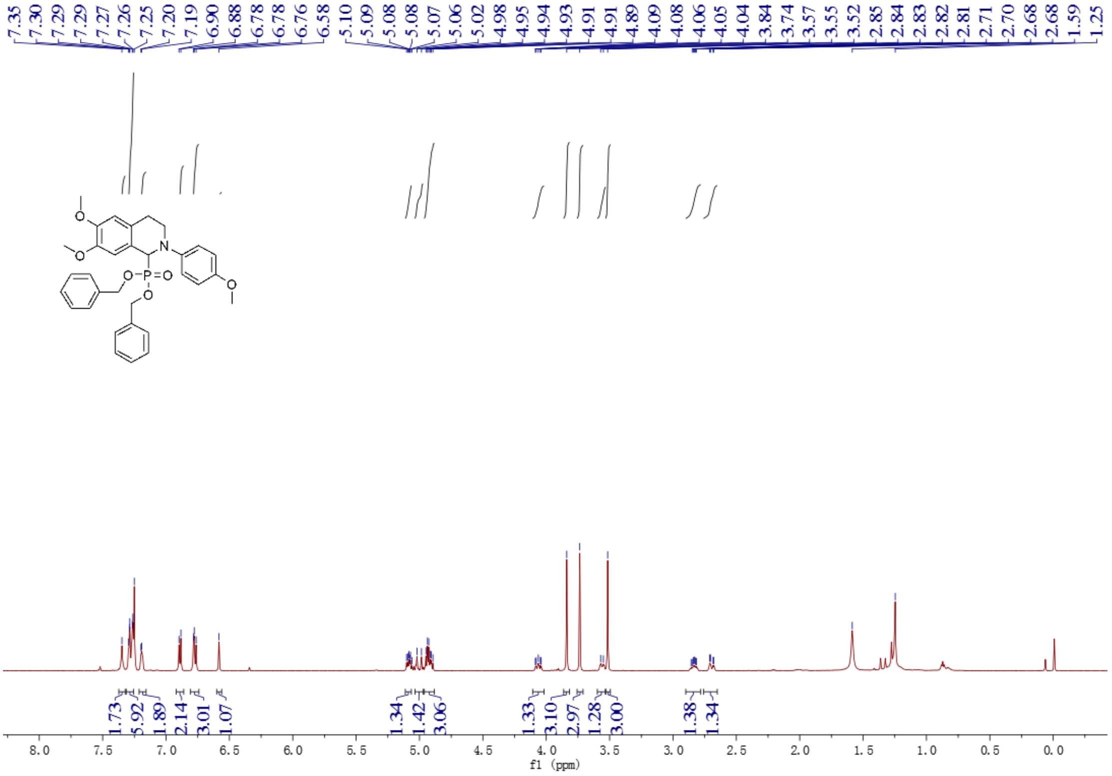
^{1}H NMR spectrum of compound **4h**



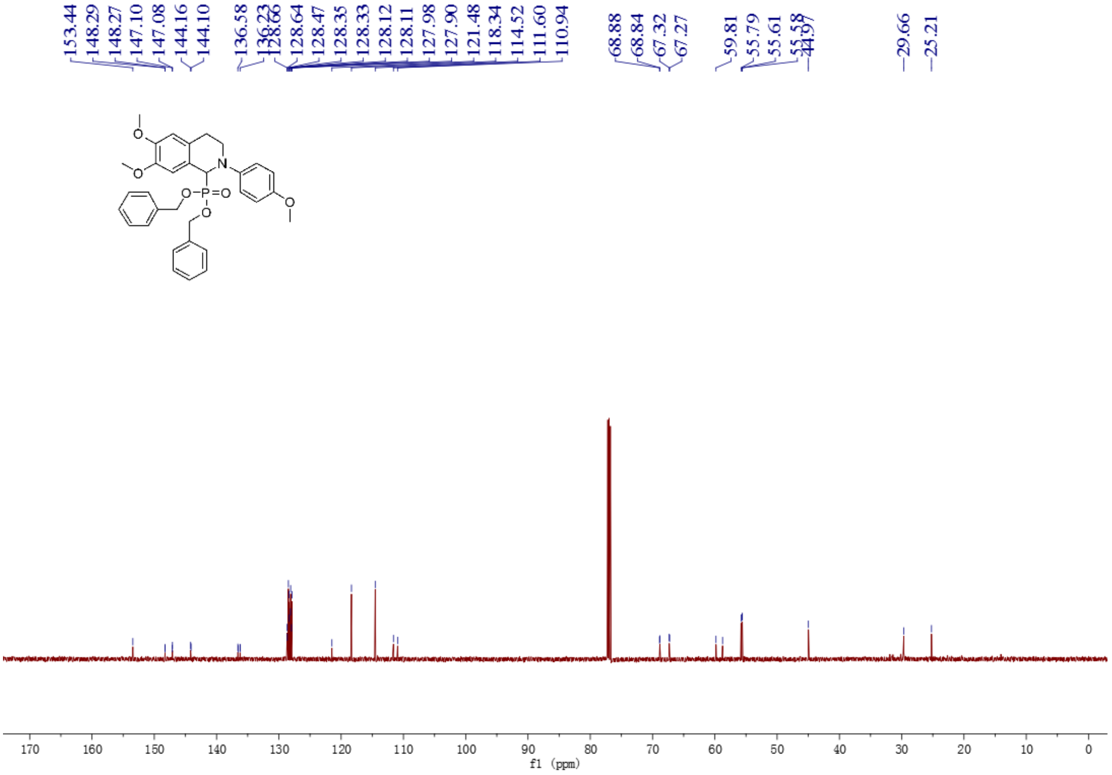
^{13}C NMR spectrum of compound **4h**



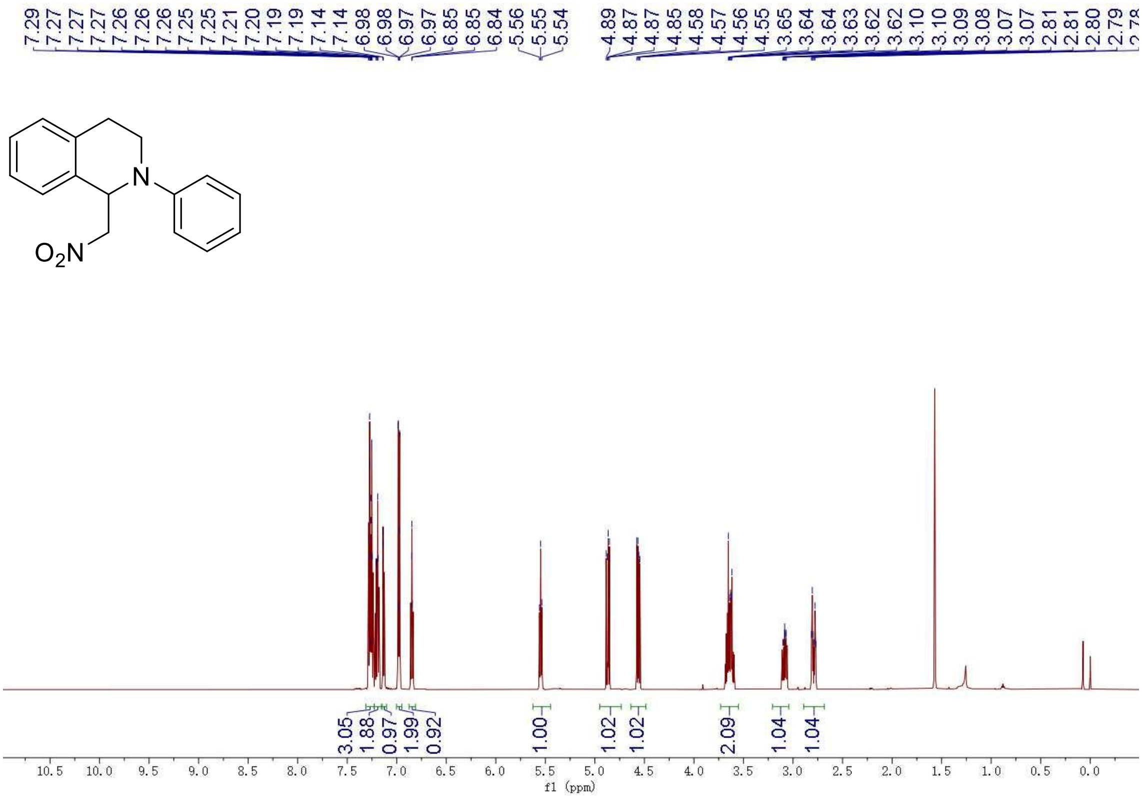
^{1}H NMR spectrum of compound **4i**



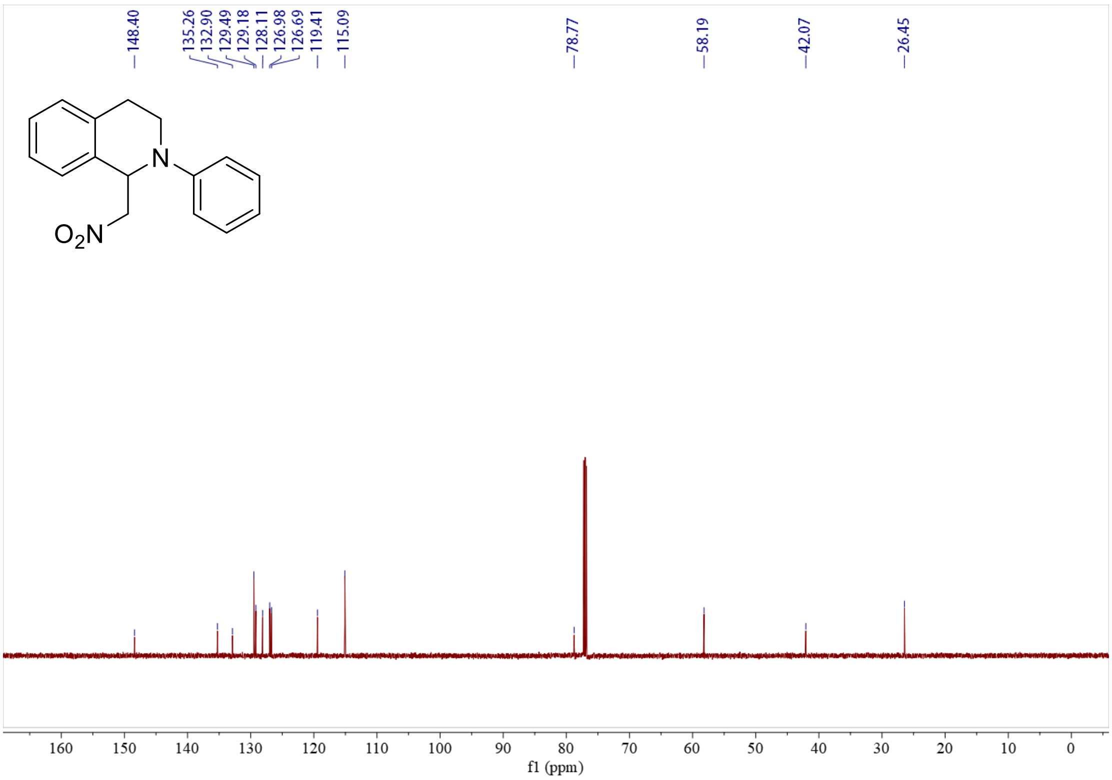
^{13}C NMR spectrum of compound **4i**



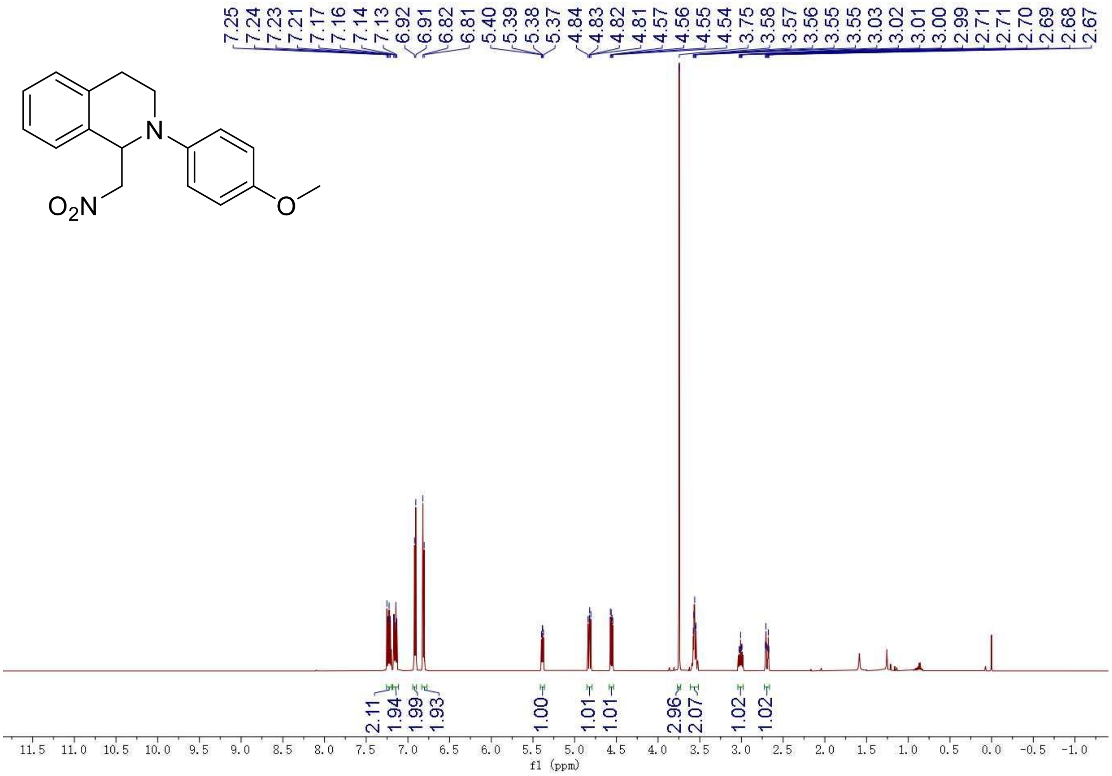
^{1}H NMR spectrum of compound **4j**



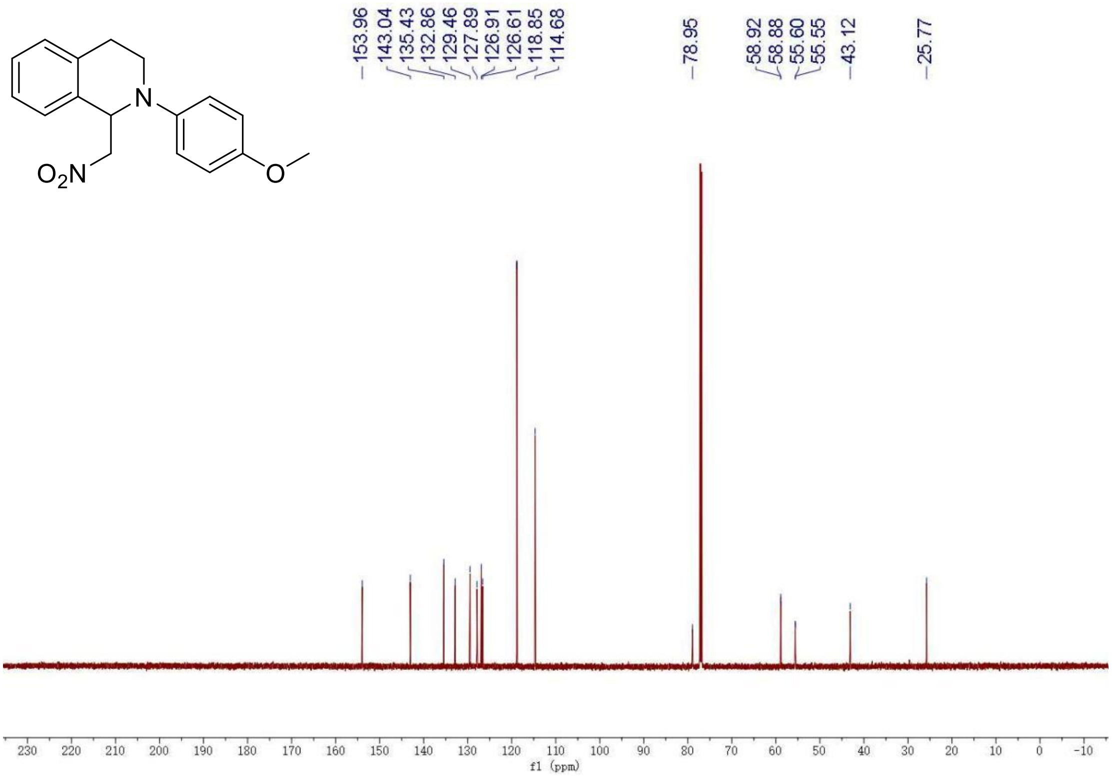
^{13}C NMR spectrum of compound **4j**



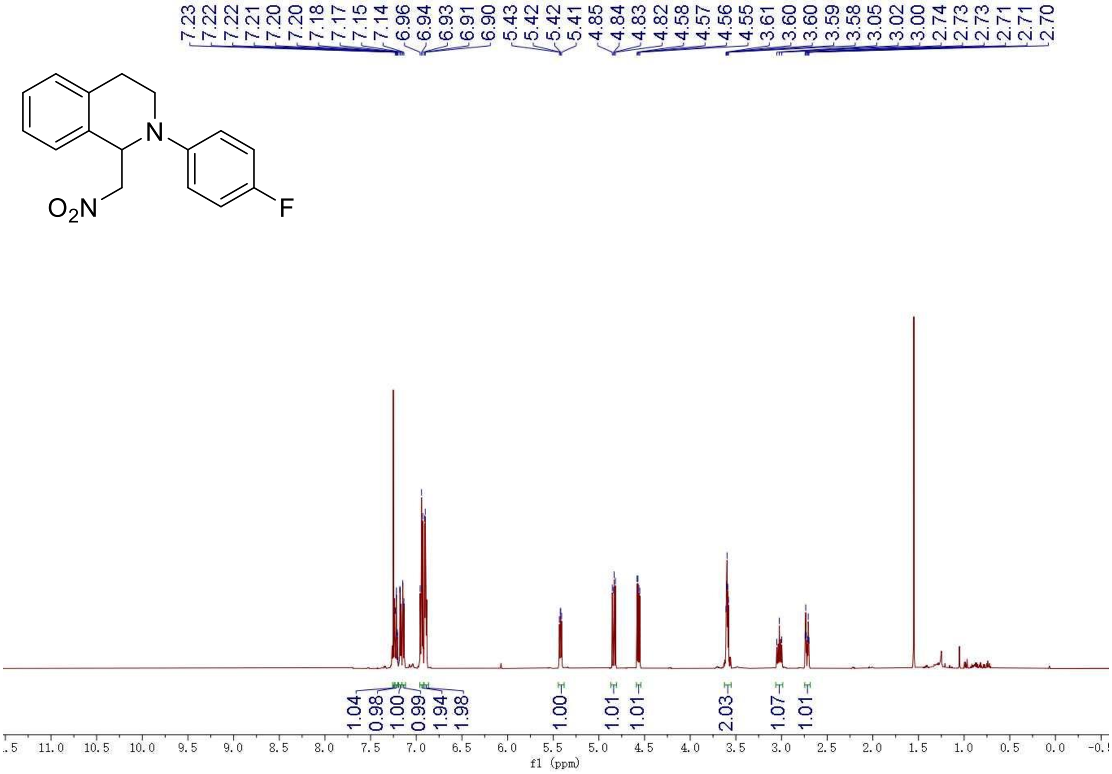
^{1}H NMR spectrum of compound **4k**



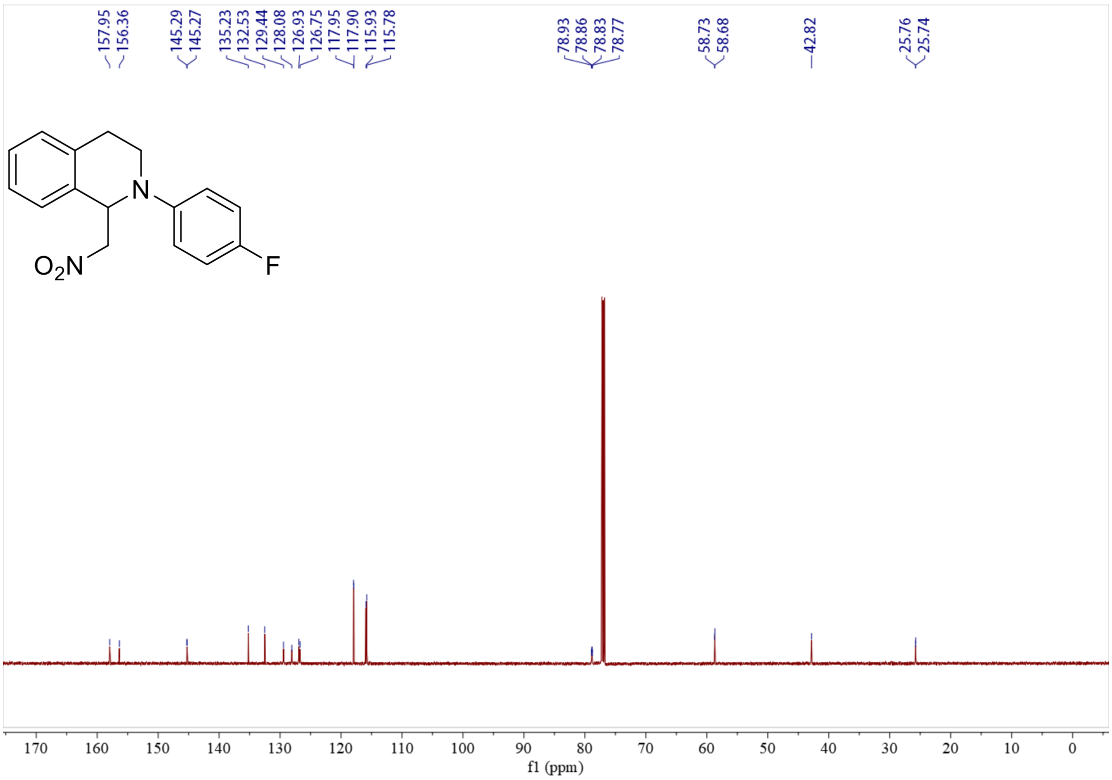
^{13}C NMR spectrum of compound **4k**



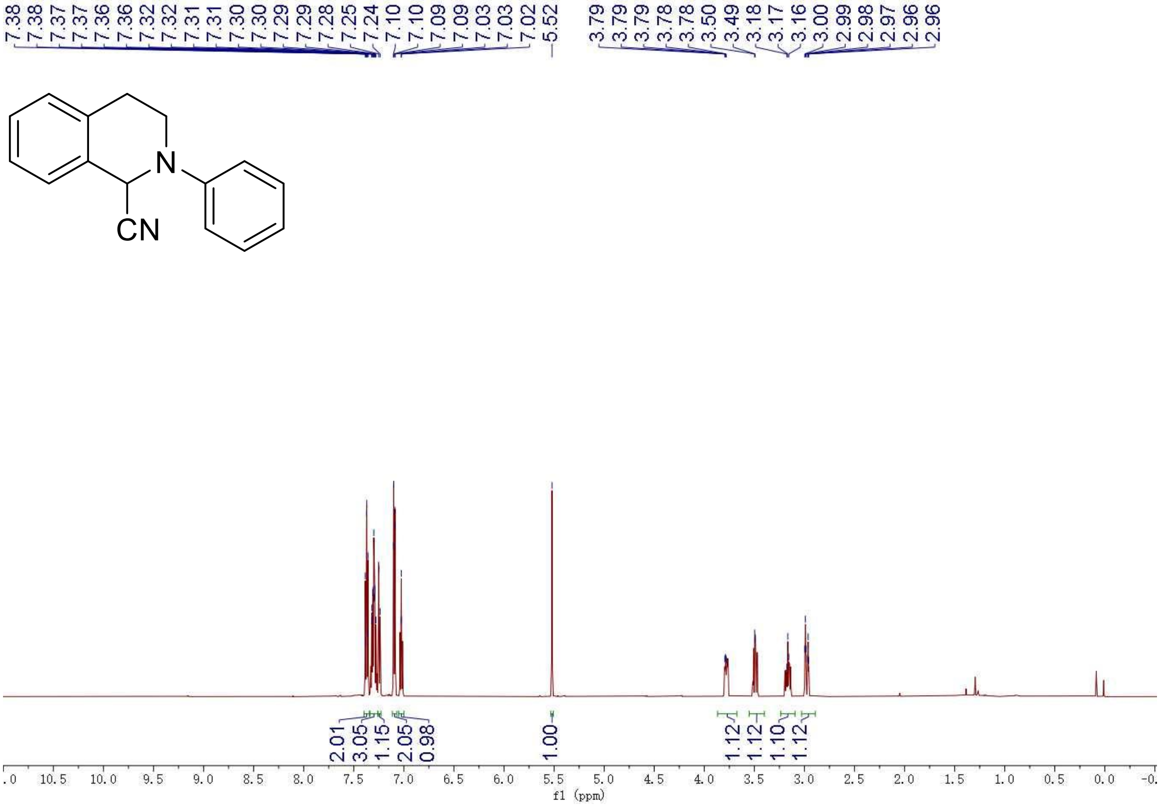
^{1}H NMR spectrum of compound **4l**



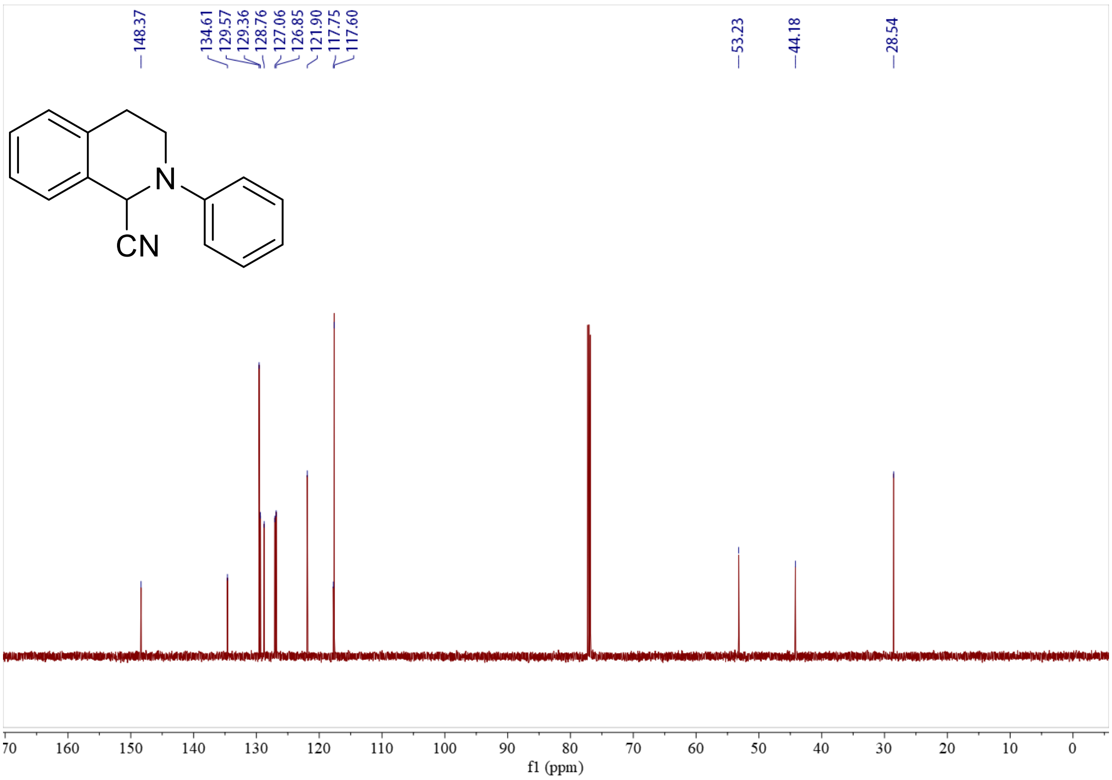
^{13}C NMR spectrum of compound **4l**



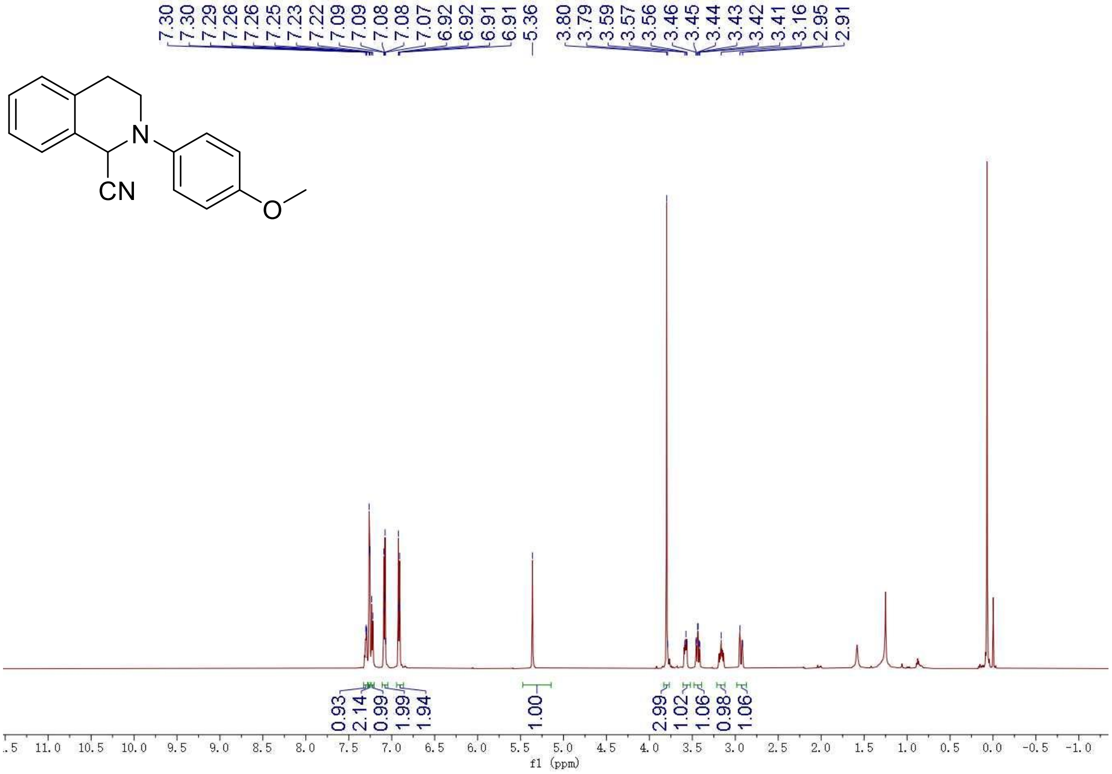
^{1}H NMR spectrum of compound **4m**



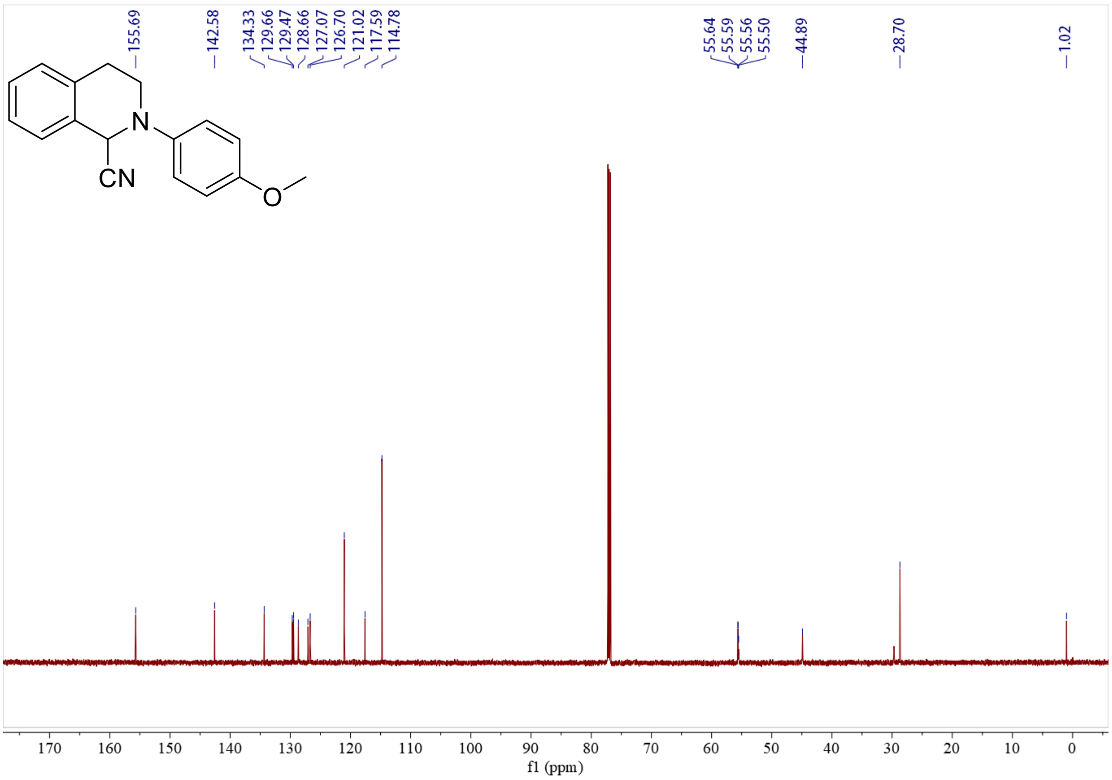
^{13}C NMR spectrum of compound **4m**



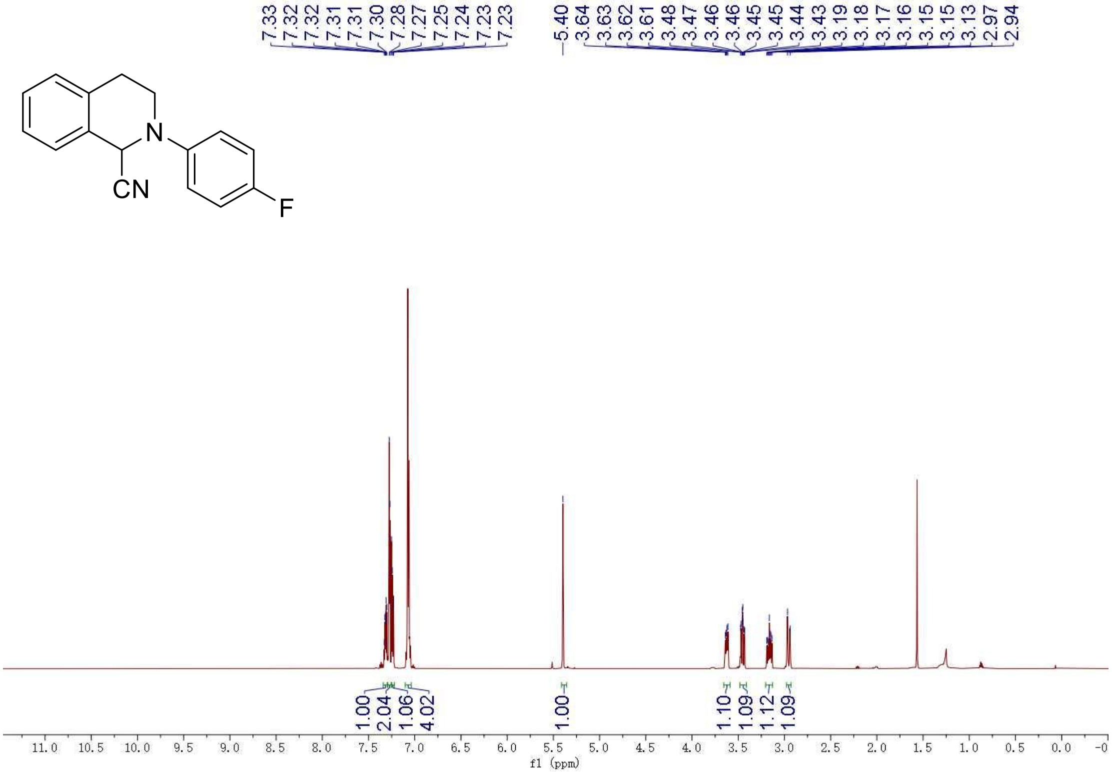
^{1}H NMR spectrum of compound **4n**



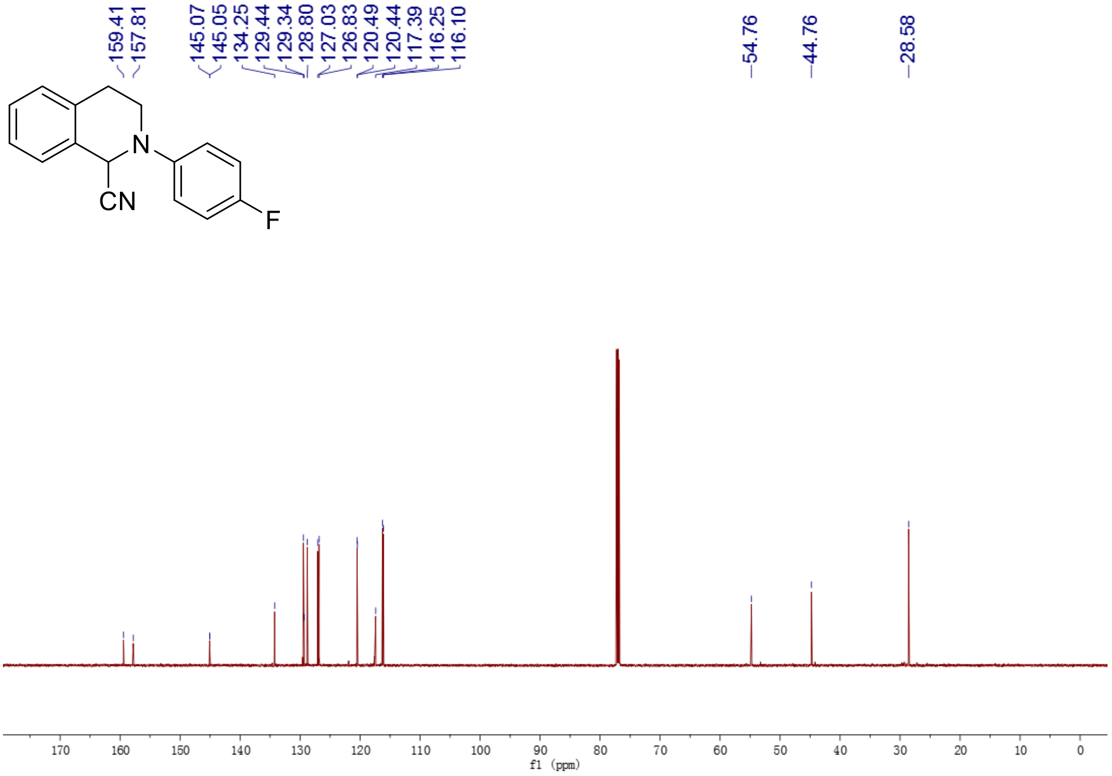
^{13}C NMR spectrum of compound **4n**



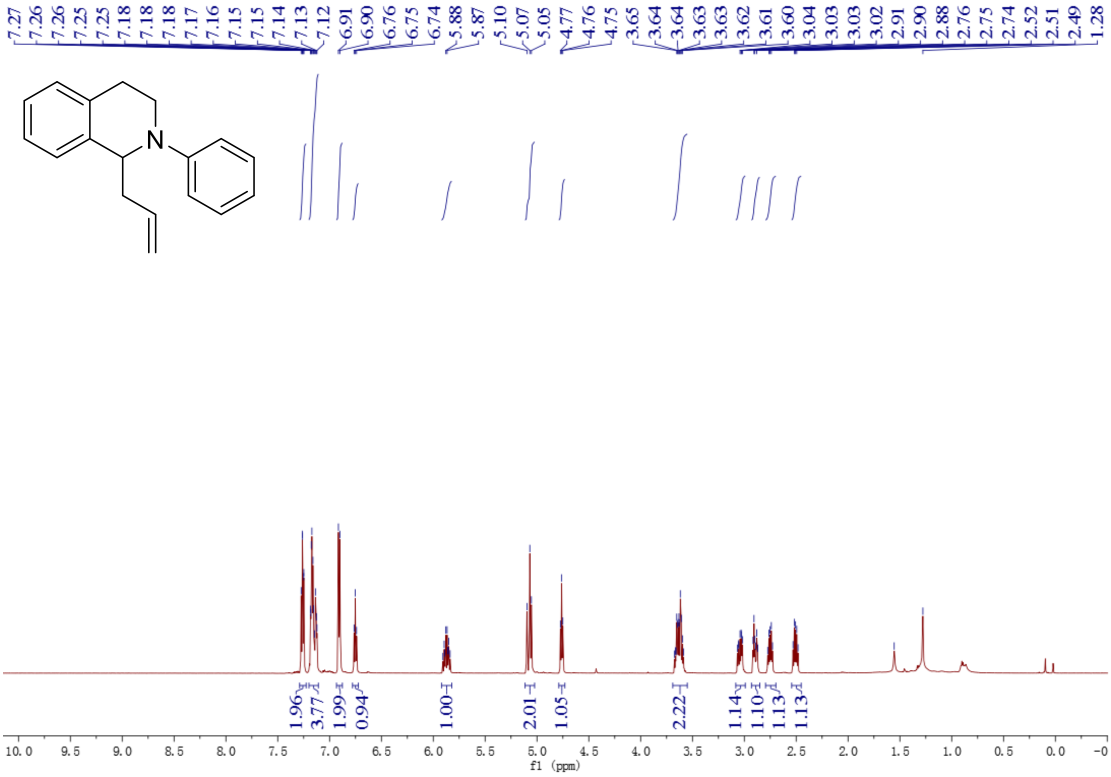
^{1}H NMR spectrum of compound **4o**



^{13}C NMR spectrum of compound **4o**



^{1}H NMR spectrum of compound **4p**



^{13}C NMR spectrum of compound **4p**