Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Visible light driven metal-free intramolecular cyclization: a facile synthesis to 3-substituted 3,4-dihydroisoquinolin-1(*2H*)-one

Shuai Zou, Shu Geng, Lina Chen, Haitao Wang and Feng Huang*

State Key Laboratory of NBC Protection for Civilian, Beijing 102205, P. R. China.

*E-mail: john_hf@163.com

Table of Contents

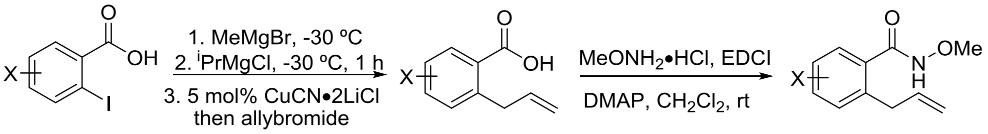
1.General information

All reactions were carried out under nitrogen atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise noted. EosinY Na was purchased from Solarbio (China). DBU was purchased from J& K and transferred under an nitrogen atmosphere. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Analytical thin layer chromatography (TLC) was performed on precoated silica gel HSGF254 plates. Flash column chromatography was performed using Yantai silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm), iodine or $KMnO_4$ solution. HPLC analysis were completed by Waters 2998 Photodiode Array Detector, Waters 1525 Binary HPLC Pump and Waters 2707 Autosampler. NMR spectra were recorded on Bruker AVANCE-300 spectrometer at 300 MHz for ^1H NMR, 75 MHz for ^{13}C NMR in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ^1H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectrometry (HRMS) spectra were obtained on a Agilent 6520Q-TOF instrument.

2. Experimental Section

2.1 Synthesis and Characterization of Substrates

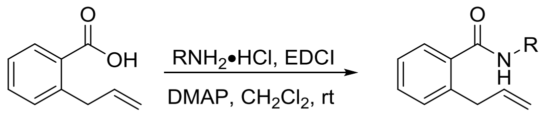
General synthesis of substrates 1a-1f, 1h and 1k[1, 2]:



1.To a stirred solution of 2-iodobenzoic acid (2.48 g, 10 mmol) and THF (30.4 mL) at -30 ^{0}C in an oven-dried flask under argon was added MeMgBr (10 mL, 1 equiv., 1 M in THF) and stirred for 5 minutes. ^{i}PrMgCl (6.0 mL, 1.2 equiv., 2 M in THF) was added slowly and the reaction was stirred at -30 ^{0}C for 1 hour or until the reaction was complete by GC/MS (an aliquot was quenching with water before analysis). The reaction was then cooled to -40 ^{0}C and a solution of CuCN 2LiCl in THF (0.09 mL, 5 mol%, 0.34 M,) was added slowly and stirred for 10 minutes while warming to -30 ^{0}C. Allyl bromide (3 equiv. 2.6 mL) was added at once and the reaction was allowed to warm to ambient temperature overnight. The reaction was diluted with EtOAc, acidified with 1 M HCl to a pH of 3, and extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. The crude mixture was concentrated and purified by column chromatography on silica gel to yield 2-allylbenzoic acid (white solid 94%).

2.To a solution of 2-allylbenzoic acid (1.62 g, 10 mmol) in CH_2Cl_2 (50 mL) was added $MeONH_2$ HCl (1.26 g, 1.5 equiv., 15 mmol), EDCI (3.85 g, 2.0 equiv. 20 mmol) and DMAP (1.25 g, 2 equiv., 20 mmol) successively. The resulting mixture was stirred at room temperature overnight. The reaction was quenched by adding HCl (2 M, 25 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and filtrated. The filtrate was concentrated and purified by column chromatography on silica gel to yield 2-allyl-*N*-methoxybenzamide (white solid 81%).

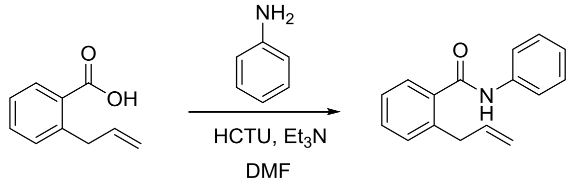
General synthesis of substrates 1g[2]:



R = Me; R = OEt

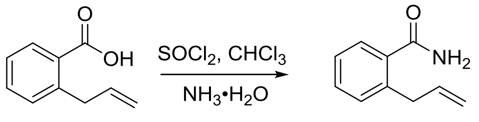
To a solution of 2-allyllbenzoic acid (1.62 g, 10 mmol) in CH_2Cl_2 (50 mL) was added $MeNH_2$.HCl (1.03 g, 1.5 equiv., 15 mmol), EDCI (3.85 g, 2.0 equiv. 20 mmol) and DMAP (1.25 g, 2 equiv. 20 mmol) successively. The resulting mixture was stirred at room temperature overnight. The reaction was quenched by adding HCl (2 M, 25 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and filtrated. The filtrate was concentrated. Purification by column chromatography gave the product.

Synthesis of substrates 2-allyl-*N*-phenylbenzamide[3]:



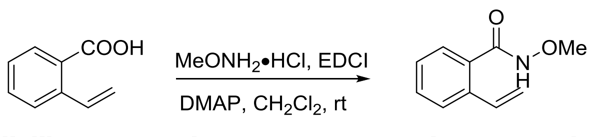
To a solution of 2-allyllbenzoic acid (487 mg, 3.0 mmol), HCTU (1.37 g, 3.3 mmol) in 6 mL DMF was added Et_3N (459 μL, 3.3 mmol). The reaction mixture was stirred at room temperature for 10 minutes. Then aniline (302 μL, 3.3 mmol) was added. The resulting reaction mixture was stirred at room temperature for 4 h, and diluted with CH_2Cl_2 (30 mL) and water (30 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to yield the compound (472 mg, 67%) as a white solid.

Synthesis of substrates 2-allylbenzamide[4]:



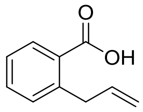
The solution of 2-allylbenzoic acid (324 mg, 2 mmol) and thionyl chloride (286 mg, 2.4 mmol) in $CHCl_3$ was stirred at 70 ℃ for 2 h, then cooled to room temperature. The mixture was added slowly to aqueous ammonia (3 mL). The mixture was extracted with $CHCl_3$ and the combined organic layer was washed with brine. The solvent was removed under reduce pressure to afford pure product as a white solid.

General synthesis of substrates 1i-1j[2]:



To a solution of 2-allyllbenzoic acid (1.48 g, 10 mmol) in CH_2Cl_2 (50 mL) was added $MeONH_2$ ·HCl (1.26 g, 1.5 equiv. 15 mmol), EDCI (3.85 g, 2.0 equiv. 20 mmol) and DMAP (1.25

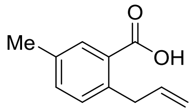
g, 2 equiv. 20 mmol) successively. The resulting mixture was stirred at room temperature overnight. The reaction was quenched by adding HCl (2M, 25 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and filtrated. The filtrate was concentrated. Purification by column chromatography gave the product.



2-allylbenzoic acid[5], white soild.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 12.16 (s, 1H), 8.07 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.51 (td, *J* = 7.7, 1.4 Hz, 1H), 7.39 – 7.29 (m, 2H), 6.06 (ddt, *J* = 15.6, 11.3, 6.5 Hz, 1H), 5.11 – 4.95 (m, 2H), 3.85 (d, *J* = 6.5 Hz, 2H).

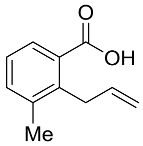
^{13}C NMR (75 MHz, Chloroform-*d*) δ 142.8, 137.3, 131.7, 131.2, 128.2, 126.4, 115.8, 38.6.



2-allyl-5-methylbenzoic acid[5], colorless oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 6.05 (dq, *J* = 15.1, 7.3 Hz, 1H), 5.05 (d, *J* = 12.7 Hz, 2H), 3.80 (d, *J* = 6.3 Hz, 2H), 2.38 (s, 3H).

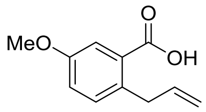
^{13}C NMR (75 MHz, Chloroform-*d*) δ 173.5, 139.8, 137.6, 136.0, 133.9, 132.1, 131.1, 128.1, 115.5, 38.2.



2-allyl-3-methylbenzoic acid[5], white soild.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 5.99 (ddt, *J* = 16.2, 10.6, 5.7 Hz, 1H), 4.97 (dd, *J* = 33.0, 13.6 Hz, 2H), 3.82 (d, *J* = 5.5 Hz, 2H), 2.38 (s, 3H).

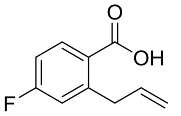
^{13}C NMR (75 MHz, Chloroform-*d*) δ 173.8, 139.8, 138.5, 136.3, 134.9, 129.4, 126.1, 115.1, 34.1, 19.9.



2-allyl-5-methoxybenzoic acid[5], yellow oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.03 (dq, *J* = 15.8, 6.6 Hz, 1H), 5.08 – 4.96 (m, 2H), 3.85 (s, 3H), 3.77 (d, *J* = 6.1 Hz, 2H).

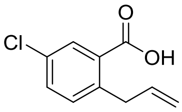
^{13}C NMR (75 MHz, Chloroform-*d*) δ 172.7, 157.8, 137.7, 134.9, 132.3, 128.9, 119.6, 115.8, 115.4, 55.5, 37.8.



2-allyl-4-fluorobenzoic acid[5], white soild.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.01 (ddd, *J* = 9.7, 7.0, 3.9 Hz, 2H), 6.02 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.17 – 5.02 (m, 2H), 3.84 (d, *J* = 6.5 Hz, 2H).

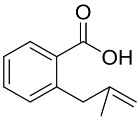
^{13}C NMR (75 MHz, Chloroform-*d*) δ 171.9, 167.2, 163.8, 146.7, 136.3, 134.5, 124.1, 118.0, 117.7, 116.6, 113.6, 113.3, 38.5.



2-allyl-5-chlorobenzoic acid[5], baby blue oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.84 (s, 1H), 8.04 (s, 1H), 7.44 (s, 1H), 7.31 (s, 1H), 6.01 (s, 1H), 5.04 (t, *J* = 11.5 Hz, 2H), 3.82 (s, 2H).

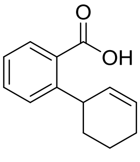
^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.7, 133.1, 116.2.



2-(2-methylallyl)benzoic acid[6], colorless oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 4.81 (s, 1H), 4.48 (s, 1H), 3.80 (s, 2H), 1.77 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 145.4, 142.2, 132.8, 131., 131.5, 128.9, 126.3, 111.6, 41.8, 23.0.



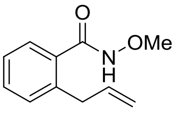
1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-carboxylic acid, white soild. R_f = 0.44 (PE/EA= 5:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 5.94 (d, *J* = 9.9 Hz, 1H), 5.67 (d, *J* = 10.0 Hz, 1H), 4.46 (s, 1H), 2.27 – 2.03 (m, 3H), 1.82 – 1.60 (m, 2H), 1.51 (q, *J* = 9.9 Hz, 1H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 173.3, 148.9, 132.7, 131.2, 130.3, 128.6, 128.2, 125.9, 37.8, 32.3, 25.0, 21.3.

IR(neat):$\nu_{\max}$ 2932, 1691, 1573, 1412, 1315, 1307, 931, 762, 649 cm^{-1}.

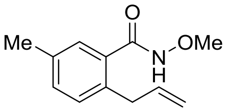
HRMS (ESI) m/z calcd for $C_{13}H_{14}O_2$ [M-H]$^-$: 201.0921, found: 201.0963.



1a: 2-allyl-*N*-methoxybenzamide[2b, 7], white soild.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.46 – 7.33 (m, 2H), 7.27 (d, *J* = 1.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 6.00 (ddt, *J* = 16.6, 10.1, 6.3 Hz, 1H), 5.15 – 4.95 (m, 2H), 3.88 (s, 3H), 3.56 (d, *J* = 6.3 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 138.4, 137.4, 132.6, 130.9, 127.7, 126.4, 116.38, 64.7, 37.3.



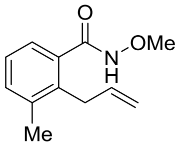
1b: 2-allyl-*N*-methoxy-5-methylbenzamide, white soild. R$_f$ = 0.31 (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 7.20 (s, 2H), 7.14 (d, *J* = 8.1 Hz, 1H), 5.99 (ddt, *J* = 16.5, 11.2, 6.5 Hz, 1H), 5.04 (dd, *J* = 22.5, 13.6 Hz, 2H), 3.87 (s, 3H), 3.52 (d, *J* = 6.1 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 137.7, 136.1, 135.2, 132.5, 131.5, 130.6, 128.3, 116.1, 64.6, 37.0, 20.8.

IR(neat):ν_{max} 3143, 2978, 1645, 1607, 1320, 1049, 948, 944, 830 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{12}H_{15}NO_2$ [M+H]$^+$: 206.1176, found: 206.0818.



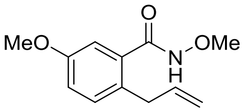
1c: 2-allyl-*N*-methoxy-3-methylbenzamide, white soild. R$_f$ = 0.18 (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.19 – 7.11 (m, 1H), 5.99 (ddt, *J* = 15.8, 10.7, 5.6 Hz, 1H), 5.06 (dq, *J* = 10.2, 1.7 Hz, 1H), 4.86 (dd, *J* = 17.2, 1.7 Hz, 1H), 3.86 (s, 3H), 3.52 (dt, *J* = 5.5, 1.7 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.2, 138.2, 136.5, 135.5, 133.7, 132.6, 126.4, 125.6, 115.7, 64.6, 34.1, 19.6.

IR(neat):ν_{max} 3143, 2974, 2822, 1636, 1446, 1324, 1058, 806, 784, 602 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{12}H_{15}NO_2$ [M-OMe]$^+$: 174.0913, found: 174.0562.



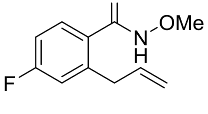
1d: 2-allyl-*N*,5-dimethoxybenzamide, orange soild. R$_f$ = 0.13 (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 30.1 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.93 (s, 2H), 6.01 (dt, *J* = 14.7, 7.2 Hz, 1H), 5.03 (dd, *J* = 28.1, 13.5 Hz, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.48 (d, *J* = 4.3 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.9, 133.6, 131.8, 129.9, 116.6, 116.0, 113.1, 64.7, 55.5, 36.5.

IR(neat):ν_{max} 3143, 2974, 2822, 1636, 1446, 1324, 1058, 806, 784, 602 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{12}H_{15}NO_3$ [M+H]$^+$: 222.1125, found: 222.1251.



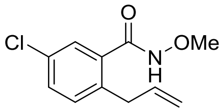
1e: 2-allyl-4-fluoro-*N*-methoxybenzamide, white soild. $R_f = 0.14$ (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.39 (dd, *J* = 8.4, 5.7 Hz, 1H), 6.95 (qd, *J* = 9.1, 8.2, 2.5 Hz, 2H), 5.97 (ddt, *J* = 16.6, 10.1, 6.4 Hz, 1H), 5.17 – 4.99 (m, 2H), 3.87 (s, 3H), 3.56 (d, *J* = 6.4 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 141.9, 141.8, 136.4, 129.7, 128.8, 117.7, 117.4, 117.1, 113.5, 113.2, 64.7, 37.2.

IR(neat):ν_{max} 3426, 2323, 2940, 1653, 1607, 1505, 1248, 1041, 927, 822, 585 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{11}H_{12}FNO_2$ $[M+H]^+$: 210.0925, found: 210.0929.



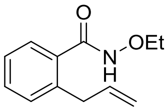
1f: 2-allyl-5-chloro-*N*-methoxybenzamide, white soild. $R_f = 0.44$ (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 7.43 – 7.30 (m, 2H), 7.20 (d, *J* = 7.7 Hz, 1H), 6.04 – 5.86 (m, 1H), 5.05 (dd, *J* = 28.5, 13.6 Hz, 2H), 3.86 (s, 3H), 3.51 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 136.9, 136.7, 134.1, 132.2, 132.0, 130.8, 127.7, 116.8, 64.7, 36.7.

IR(neat):ν_{max} 3231, 2978, 1666, 1505, 1315, 1054, 1037, 893, 767, 662 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{11}H_{12}ClNO_2$ $[M+H]^+$: 226.0629, found: 226.0648.

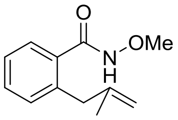


1g: 2-allyl-*N*-ethoxybenzamide, yellow oil. $R_f = 0.38$ (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.23 (dd, *J* = 11.6, 7.9 Hz, 2H), 6.08 – 5.90 (m, 1H), 5.03 (dd, *J* = 20.0, 13.7 Hz, 2H), 4.20 – 3.92 (m, 2H), 3.54 (d, *J* = 5.8 Hz, 2H), 1.31 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 167.7, 138.4, 137.4, 132.9, 130.7, 130.5, 127.7, 126.3, 116.3, 37.3, 13.5.

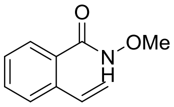
HRMS (ESI) m/z calcd for $C_{12}H_{15}NO_2$ $[M+H]^+$: 206.1176, found: 206.1194.



1h: *N*-methoxy-2-(2-methylallyl)benzamide[7], colorless oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.97 (s, 1H), 7.40 – 7.29 (m, 2H), 7.25 – 7.15 (m, 2H), 4.82 (s, 1H), 4.48 (s, 1H), 3.78 (s, 3H), 3.44 (s, 2H), 1.71 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 137.8, 133.1, 130.5, 128.0, 112.4, 64.4, 41.1, 22.8.

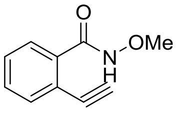


1i: *N*-methoxy-2-vinylbenzamide[8], white soild.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 7.62 – 7.55 (m, 1H), 7.49 – 7.38 (m, 2H), 7.34

– 7.27 (m, 1H), 7.03 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.74 (dd, *J* = 17.4, 0.9 Hz, 1H), 5.39 (dd, *J* = 11.0, 0.9 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 133.9, 130.9, 127.8, 127.7, 126.4, 117.4, 64.7.

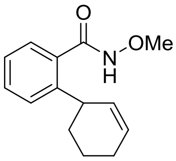


1j: 2-ethynyl-*N*-methoxybenzamide, yellow oil. R$_f$ = 0.23 (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.74 (s, 1H), 7.83 (s, 1H), 7.58 – 7.48 (m, 1H), 7.47 – 7.36 (m, 2H), 3.86 (s, 3H), 3.47 (s, 1H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 164.8, 133.8, 130.9, 129.5, 129.4, 118.8, 83.5, 81.8, 64.5.

HRMS (ESI) m/z calcd for $C_{10}H_9NO_2$ $[M+H]^+$: 176.0706, found: 176.0714.



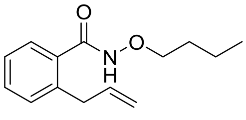
1k: *N*-methoxy-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-carboxamide, colorless oil.
R$_f$ = 0.20 (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 7.35 (td, *J* = 20.7, 17.6, 8.1 Hz, 3H), 7.20 (t, *J* = 6.7 Hz, 1H), 5.90 (d, *J* = 9.8 Hz, 1H), 5.62 (d, *J* = 10.0 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 1H), 2.07 (s, 3H), 1.66 (d, *J* = 26.4 Hz, 2H), 1.57 – 1.40 (m, 1H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 168.1, 145.4, 130.6, 129.8, 128.8, 127.1, 125.9, 64.6, 38.2, 32.6, 24.9, 21.3.

IR(neat):$\nu_{\max}$ 3181, 2936, 1662, 1505, 1438, 1033, 881, 762, 657 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{14}H_{17}NO_2$ $[M+H]^+$: 232.1332, found: 232.1329.



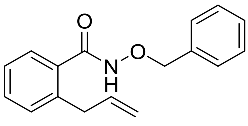
1l: 2-allyl-*N*-butoxybenzamide, colorless oil. R$_f$ = 0.36 (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 1H), 6.00 (ddd, *J* = 16.3, 8.2, 4.1 Hz, 1H), 5.05 (dd, *J* = 22.9, 13.6 Hz, 2H), 4.03 (s, 2H), 3.56 (d, *J* = 5.9 Hz, 2H), 1.79 – 1.63 (m, 2H), 1.53 – 1.34 (m, 2H), 0.95 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 138.3, 137.4, 132.9, 130.8, 127.7, 126.4, 116.3, 37.3, 30.1, 19.1, 13.9.

IR(neat):$\nu_{\max}$ 3185, 2966, 2873, 1653, 1514, 1315, 1159, 1033, 914, 754 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{14}H_{19}NO_2$ $[M+H]^+$: 234.1489, found: 234.1490.



1m: 2-allyl-*N*-(benzyloxy)benzamide, white soild. R$_f$ = 0.33 (PE/EA= 3:1)

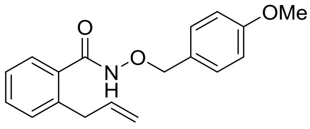
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.44 (s, 2H), 7.42 – 7.28 (m, 5H), 7.23 (d, *J* =

7.8 Hz, 2H), 5.91 (ddt, *J* = 16.7, 11.3, 6.6 Hz, 1H), 5.17 – 4.85 (m, 4H), 3.51 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 138.3, 137.4, 132.7, 130.8, 130.6, 129.3, 128.9, 128.7, 127.8, 116.3, 37.3.

IR(neat):ν_{max} 3181, 2974, 1640, 1501, 1455, 1307, 1159, 1024, 1020, 910, 750, 699, 509 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{17}H_{17}NO_2$ [M+H]$^+$: 268.1332, found: 268.1321.



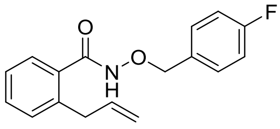
1n: 2-allyl-*N*-((4-methoxybenzyl)oxy)benzamide, white soild. R_f = 0.22 (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.46 – 7.34 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 9.1 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 2H), 6.02 – 5.86 (m, 1H), 5.00 (q, *J* = 17.2, 13.7 Hz, 4H), 3.82 (s, 3H), 3.52 (d, *J* = 5.8 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 160.1, 138.4, 137.4, 132.8, 131.0, 130.8, 130.6, 127.7, 127.3, 126.4, 116.3, 114.0, 55.3, 37.3.

IR(neat):ν_{max} 3185, 2953, 1649, 1615, 1518, 1256, 1176, 1033, 914, 826, 754, 526 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{18}H_{19}NO_3$ [M+Na]$^+$: 320.1257, found: 320.1250.



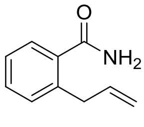
1o: 2-allyl-*N*-((4-fluorobenzyl)oxy)benzamide, white soild. R_f = 0.26 (PE/EA= 3:1)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.40 (dd, *J* = 15.2, 6.9 Hz, 3H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.08 (t, *J* = 8.3 Hz, 2H), 5.94 (ddt, *J* = 15.9, 11.1, 5.9 Hz, 1H), 5.12 – 4.86 (m, 4H), 3.52 (d, *J* = 6.1 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 164.7, 161.4, 132.6, 131.3, 131.2, 130.9, 130.7, 127.7, 126.4, 116.35, 115.8, 115.5, 37.3.

IR(neat):ν_{max} 3189, 2982, 1649, 1598, 1514, 1227, 1159, 1020, 914, 830, 754, 513 cm^{-1}.

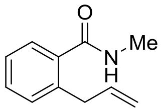
HRMS (ESI) m/z calcd for $C_{17}H_{16}FNO_2$ [M+H]$^+$: 286.1238, found: 286.1240.



1p: 2-allylbenzamide[9], colorless oil.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.56 (td, *J* = 7.6, 1.4 Hz, 1H), 7.40 – 7.31 (m, 2H), 6.06 (ddt, *J* = 17.0, 10.7, 6.5 Hz, 1H), 5.14 – 5.00 (m, 2H), 3.86 (d, *J* = 6.5 Hz, 2H).

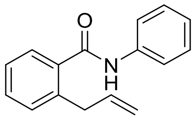
^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.6, 144.0, 136.7, 133.7, 131.5, 131.4, 127.6, 126.5, 116.2, 38.4.



1q: 2-allyl-*N*-methylbenzamide[2], white soild.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 7.31 (m, 2H), 7.26 (s, 1H), 7.22 (d, *J* = 6.7 Hz, 1H), 6.01 (ddd, *J* = 16.5, 8.2, 4.4 Hz, 1H), 5.88 (s, 1H), 5.13 – 4.95 (m, 2H), 3.56 (d, *J* = 6.1 Hz, 2H).

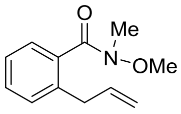
^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.6, 137.7, 137.5, 136.6, 130.4, 130.0, 127.2, 126.3, 115.9, 37.6, 26.6.



1r: 2-allyl-*N*-phenylbenzamide[3], white soild.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 15.4, 7.7 Hz, 4H), 7.46 – 7.27 (m, 5H), 7.20 – 7.12 (m, 1H), 6.09 (ddt, *J* = 16.4, 10.2, 6.1 Hz, 1H), 5.18 – 4.97 (m, 2H), 3.63 (d, *J* = 6.1 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 137.9, 137.4, 136.7, 130.5, 129.1, 127.5, 126.6, 124.5, 119.8, 116.4, 37.6.



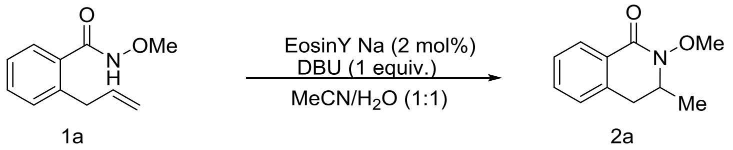
2-allyl-*N*-methoxy-*N*-methylbenzamide[10], white soild.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 1H), 7.27 (s, 1H), 7.21 (d, *J* = 8.9 Hz, 2H), 6.02 – 5.84 (m, 1H), 5.14 – 5.01 (m, 2H), 3.80 – 3.07 (m, 8H).

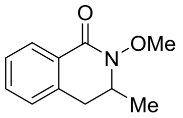
^{13}C NMR (75 MHz, Chloroform-*d*) δ 137.2, 136.6, 135.0, 129.5, 129.4, 126.5, 125.9, 77.4, 61.0, 37.4.

2.2 Synthesis and Characterization of Products

I. Procedure for 3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one



To a Schlenk tube were added **1a** (38.2 mg, 0.2 mmol), EosinY Na (3.14 mg, 0.004 mmol, 2 mol%) and charged with nitrogen for 15 minutes, anhydrous MeCN (1.5 mL) and H_2O (1.5 mL) were added before DBU (0.3 mL, 0.2 mmol) via a syringe. The mixture was then placed around the 10 W Blue LEDs with a distance of 3 centimeters, and was stirred under visible light irradiation until the substrate was consumed (monitored by TLC), filtered, the solvent was removed by rotary evaporation and the resulting residue was purified directly by flash column chromatograph to give the desired product **2a** 86% yield.



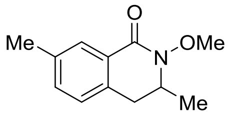
2a: 2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one. White soild.

R_f = 0.20 (PE/EA= 3:1),Yield = 86%.

^{1}H NMR (300 MHz, Chloroform-d) δ 8.12 (dd, J = 7.7, 1.5 Hz, 1H), 7.44 (td, J = 7.4, 1.5 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.19-7.14 (m, 1H), 4.11 (p, J = 6.1 Hz, 1H), 3.90 (d, J = 2.1 Hz, 3H), 3.33 (dd, J = 16.0, 5.5 Hz, 1H), 2.90 (dd, J = 16.1, 5.8 Hz, 1H), 1.32 (dd, J = 6.6, 2.1 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-d) δ 163.8, 136.0, 132.3, 128.3, 128.2, 127.7, 127.1, 77.5, 77.1, 76.7, 63.0, 54.9, 36.3, 17.6.

HRMS (ESI) m/z calcd for $C_{11}H_{14}NO_2$ $[M+H]^+$: 192.1019, found: 192.1025.



2b: 2-methoxy-3,7-dimethyl-3,4-dihydroisoquinolin-1(*2H*)-one. colorless oil.

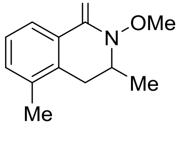
R_f = 0.36 (PE/EA= 3:1), Yield = 72%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.23 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 4.09 (dt, *J* = 11.7, 6.5 Hz, 1H), 3.89 (s, 3H), 3.28 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.85 (dd, *J* = 15.9, 5.5 Hz, 1H), 2.37 (s, 3H), 1.31 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 163.9, 136.8, 133.1, 133.0, 128.5, 128.1, 62.9, 55.0, 36.0, 21.0, 17.6.

IR(neat):ν_{max} 2978, 2970, 1670, 1607, 1467, 1383, 1298, 1016, 741 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{12}H_{16}NO_2$ $[M+H]^+$: 206.1176, found: 206.1373.



2c: 2-methoxy-3,5-dimethyl-3,4-dihydroisoquinolin-1(*2H*)-one. colorless oil.

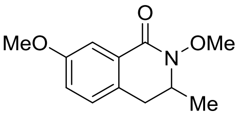
R$_f$ = 0.36 (PE/EA = 3:1), Yield = 73%.

^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.4 Hz, 1H), 7.31 (d, *J* = 6.7 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 4.08 (h, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 3.16 (d, *J* = 5.6 Hz, 1H), 2.86 (dd, *J* = 16.4, 6.2 Hz, 1H), 2.28 (s, 3H), 1.34 (d, *J* = 6.4 Hz, 3H).

^{13}**C NMR** (75 MHz, Chloroform-*d*) δ 164.4, 135.3, 134.5, 133.9, 128.4, 126.7, 126.17, 63.0, 54.3, 33.5, 19.1, 18.1.

IR(neat):ν_{max} 2978, 2974, 2274, 1670, 1615, 1425, 1037, 919, 729 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{12}H_{16}NO_2$ [M+H]$^+$: 206.1176, found: 206.1349.



2d: 2,7-dimethoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one. colorless oil.

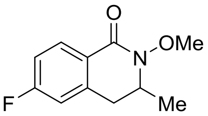
R$_f$ = 0.24 (PE/EA = 3:1), Yield = 63%.

^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 4.06 (p, *J* = 5.6 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.25 (dd, *J* = 15.8, 5.1 Hz, 1H), 2.82 (dd, *J* = 15.9, 5.5 Hz, 1H), 1.31 (d, *J* = 6.2 Hz, 3H).

^{13}**C NMR** (75 MHz, Chloroform-*d*) δ 163.7, 129.3, 128.9, 128.1, 119.9, 111.2, 63.0, 55.6, 55.1, 35.5, 17.6.

IR(neat):ν_{max} 2923, 2852, 1674, 1594, 1383, 1303, 1024, 746 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{12}H_{16}NO_3$ [M+H]$^+$: 222.1125, found: 222.1059.



2e: 6-fluoro-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one. colorless oil.

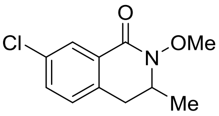
R$_f$ = 0.36 (PE/EA = 3:1), Yield =78%.

^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 8.7, 5.8 Hz, 1H), 7.01 (td, *J* = 8.6, 2.5 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.09 (h, *J* = 6.0 Hz, 1H), 3.89 (s, 3H), 3.31 (dd, *J* = 16.2, 5.4 Hz, 1H), 2.88 (dd, *J* = 16.2, 5.8 Hz, 1H), 1.32 (d, *J* = 6.4 Hz, 3H).

^{13}**C NMR** (75 MHz, Chloroform-*d*) δ 166.8, 163.5, 163.1, 139.0, 138.8, 131.1, 130.9, 124.7, 124.7, 114.6, 114.5, 114.3, 114.3, 63.1, 54.8, 36.3, 17.6.

IR(neat):ν_{max} 2974, 2847, 2248, 1716, 1674, 1615, 1505, 1429, 1277, 1028, 914, 729 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{12}H_{13}FNO_2$ [M+H]$^+$: 210.0925, found: 210.1299.

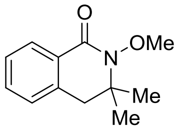


2f: 7-chloro-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one. colorless oil.

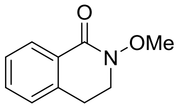
R$_f$ = 0.37 (PE/EA = 3:1), Yield =62%.

^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 4.09 (h, *J* = 6.8, 6.3 Hz, 1H), 3.89 (s, 3H), 3.29 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.86 (dd, *J* = 15.9, 5.2 Hz, 1H), 1.31 (d, *J* = 6.2 Hz, 3H).

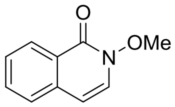
^{13}**C NMR** (75 MHz, Chloroform-*d*) δ 162.4, 133.3, 132.3, 129.2, 128.1, 63.0, 54.8, 35.7, 17.6.
IR(neat):ν_{max} 2978, 2974, 2847, 1678, 1611, 1497, 1260, 1024, 754 cm^{-1}.
HRMS (ESI) m/z calcd for $C_{11}H_{13}ClNO_2$ [M+H]$^+$: 226.0629, found: 226.0804.



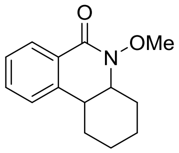
2h: 2-methoxy-3,3-dimethyl-3,4-dihydroisoquinolin-1(*2H*)-one. colorless oil.
R$_f$ = 0.43 (PE/EA = 3:1), Yield =66%.
^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.44 (td, *J* = 7.4, 1.5 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 3.93 (s, 3H), 3.06 (s, 2H), 1.38 (s, 6H).
^{13}**C NMR** (75 MHz, Chloroform-*d*) δ 136.1, 132.4, 128.2, 127.6, 126.9, 64.4, 62.0, 43.3, 24.8.
IR(neat):ν_{max} 2982, 2936, 1683, 1611, 1471, 1463, 1033, 952, 750, 708 cm^{-1}.
HRMS (ESI) m/z calcd for $C_{12}H_{16}NO_2$ [M+H]$^+$: 206.1176, found: 206.1095.



2i: 2-methoxy-3,4-dihydroisoquinolin-1(*2H*)-one, colorless oil.
R$_f$ = 0.27 (PE/EA = 2:1), Yield = 49%.
^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.44 (td, *J* = 7.4, 1.5 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 3.90 (s, 3H), 3.83 (t, *J* = 6.7 Hz, 2H), 3.17 (t, *J* = 6.7 Hz, 2H).
^{13}**C NMR** (75 MHz, Chloroform-*d*) δ 163.8, 137.3, 132.2, 128.7, 128.4, 127.2, 62.1, 47.9, 29.2.
IR(neat):ν_{max} 2978, 2932, 1678, 1611, 1463, 1332, 1083, 902, 746, 695, 686 cm^{-1}.
HRMS (ESI) m/z calcd for $C_{10}H_{12}NO_2$ [M+H]$^+$: 178.0863, found: 178.1065.



2j: 2-methoxyisoquinolin-1(*2H*)-one. colorless oil.
R$_f$ = 0.24 (PE/EA = 3:1), Yield =28%.
^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 14.1, 7.3 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 4.11 (s, 3H).
^{13}**C NMR** (75 MHz, Chloroform-*d*) δ 158.2, 136.2, 132.3, 129.4, 126.9, 126.2, 105.60, 64.4, 29.7.
IR(neat):ν_{max} 2919, 2847, 1678, 1311, 1235, 1020, 935, 927, 746 cm^{-1}.
HRMS (ESI) m/z calcd for $C_{10}H_{10}NO_2$ [M+H]$^+$: 176.0706, found: 176.0877.



2k: 5-methoxy-1,3,4,4a,5,10b-hexahydrophenanthridin-6(*2H*)-one. white soild.

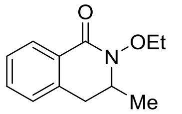
R$_f$ = 0.40 (PE/EA = 3:1), Yield =48%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.23 (s, 1H), 3.99 (d, *J* = 5.8 Hz, 1H), 3.92 (s, 3H), 3.29 (s, 1H), 2.17 (s, 1H), 1.91 – 1.65 (m, 4H), 1.56 – 1.41 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 163.7, 132.5, 128.6, 128.5, 126.9, 125.8, 62.4, 59.3, 40.0, 29.7, 28.2, 26.5, 22.6.

IR(neat):ν_{max} 2919, 2852, 1391, 1020, 872, 674, 475 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{14}H_{18}NO_2$ [M+H]$^+$: 232.1332, found: 232.1928.



2g: 2-ethoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one. colorless oil.

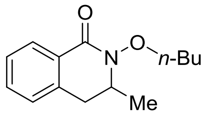
R$_f$ = 0.56 (PE/EA = 3:1), Yield =61%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 4.10 (ddd, *J* = 14.0, 10.1, 6.8 Hz, 3H), 3.34 (dd, *J* = 15.9, 5.2 Hz, 1H), 2.87 (dd, *J* = 16.1, 5.0 Hz, 1H), 1.36 – 1.29 (m, 6H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 163.9, 132.2, 128.5, 128.1, 127.7, 127.0, 76.6, 70.8, 55.4, 36.2, 17.6.

IR(neat):ν_{max} 2982, 2978, 2847, 2252, 1678, 1598, 1573, 1429, 1235, 1024, 914, 733 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{12}H_{16}NO_2$ [M+H]$^+$: 206.1176, found: 206.1434.



2l: 2-butoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one, colorless oil.

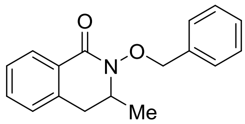
R$_f$ = 0.56 (PE/EA = 3:1), Yield =60%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 4.06 (t, *J* = 6.2 Hz, 3H), 3.35 (dd, *J* = 16.0, 5.1 Hz, 1H), 2.88 (dd, *J* = 16.0, 4.8 Hz, 1H), 1.72 (p, *J* = 6.8 Hz, 2H), 1.47 (q, *J* = 7.3 Hz, 2H), 1.31 (d, *J* = 6.2 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 163.7, 135.9, 132.2, 128.5, 128.1, 127.0, 75.1, 55.3, 36.2, 30.3, 19.3, 17.6, 14.0.

IR(neat):ν_{max} 2962, 2936, 2873, 1678, 1467, 1379, 1298, 1016, 746 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{14}H_{19}NO_2$ [M+H]$^+$: 234.1489, found: 234.1512.



2m: 2-(benzyloxy)-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one, colorless oil.

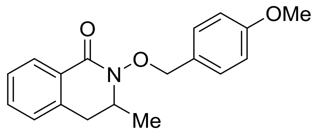
R$_f$ = 0.50 (PE/EA = 3:1), Yield =47%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 3.9 Hz, 2H), 7.48 – 7.30 (m, 5H), 7.15 (d, *J* = 7.5 Hz, 1H), 5.09 (s, 2H), 3.79 (q, *J* = 6.0 Hz, 1H), 3.19 (dd, *J* = 16.1, 5.7 Hz, 1H), 2.74 (dd, *J* = 16.0, 4.9 Hz, 1H), 1.28 – 1.24 (m, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 163.9, 136.0, 135.7, 132.3, 129.8, 128.7, 128.5, 128.1, 127.8, 127.0, 56.0, 35.9, 29.7, 17.4.

IR(neat):$v_{\max}$ 2915, 2847, 1674, 1463, 910, 733, 522 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{17}H_{17}NO_2$ [M+H]$^+$: 268.1332, found: 268.1355.



2n: 2-((4-methoxybenzyl)oxy)-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one, colorless oil.

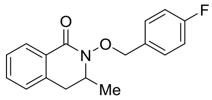
R$_f$ = 0.39 (PE/EA = 3:1), Yield =45%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.39 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.90 (dd, *J* = 8.7, 2.2 Hz, 2H), 5.09 – 4.96 (m, 2H), 3.82 (d, *J* = 2.3 Hz, 3H), 3.75 (q, *J* = 6.1 Hz, 1H), 3.18 (dd, *J* = 16.0, 5.6 Hz, 1H), 2.73 (dd, *J* = 16.0, 4.8 Hz, 1H), 1.25 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 163.7, 159.9, 136.0, 132.3, 131.4, 128.5, 128.1, 127.9, 127.8, 127.0, 113.8, 56.0, 55.3, 35.8, 29.7, 17.4.

IR(neat):$v_{\max}$ 3455, 1661, 1611, 1518, 1252, 910, 733, 644 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{18}H_{19}NO_3$ [M+Na]$^+$: 320.1257, found: 320.1250.



2o: 2-((4-fluorobenzyl)oxy)-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one, colorless oil.

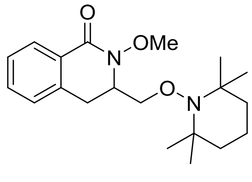
R$_f$ = 0.49 (PE/EA = 3:1), Yield =43%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.18 – 8.08 (m, 1H), 7.57 – 7.41 (m, 3H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.07 (td, *J* = 7.7, 6.8, 1.9 Hz, 2H), 5.12 – 4.97 (m, 2H), 3.80 (p, *J* = 5.9 Hz, 1H), 3.21 (dd, *J* = 16.1, 5.6 Hz, 1H), 2.78 (dd, *J* = 16.1, 5.1 Hz, 1H), 1.25 (dd, *J* = 6.2, 2.1 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 164.0, 136.0, 132.4, 131.7, 131.6, 128.4, 128.1, 127.8, 127.1, 56.03, 35.9, 17.5.

IR(neat):$v_{\max}$ 2919, 2852, 1670, 1607, 1509, 1463. 1374, 1227, 1155, 1016, 830, 737, 535, 530 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{17}H_{16}FNO_2$ [M+H]$^+$: 286.1238, found: 286.1240.



2-methoxy-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-3,4-dihydroisoquinolin-1(*2H*)-one, white soild.

R$_f$ = 0.27 (PE/EA = 3:1).

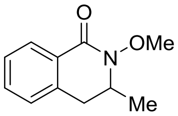
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.40 (td, *J* = 7.4, 1.4 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 4.07 (ddd, *J* = 6.5, 4.7, 2.6 Hz, 1H), 4.01 (dd, *J* = 8.9, 5.8 Hz, 1H), 3.90 (s, 3H), 3.86 (dd, *J* = 8.8, 2.5 Hz, 1H), 3.50 (dd, *J* = 16.3, 6.5 Hz, 1H), 3.14 (dd, *J* = 16.3, 2.4 Hz, 1H), 1.48 – 1.22 (m, 6H), 1.03 (d, *J* = 19.3 Hz, 6H), 0.87 (s, 3H), 0.64 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 163.4, 136.3, 131.9, 128.9, 127.7, 127.0, 126.7, 75.1, 62.6, 59.9, 57.5, 39.6, 32.8, 32.8, 32.6, 20.0, 19.7, 16.9.

IR(neat):ν_{max} 2923, 2847, 1383, 1020, 876, 674, 475, 471 cm^{-1}.

HRMS (ESI) m/z calcd for $C_{20}H_{31}N_2O_3$ $[M+H]^+$: 347.2329, found: 347.2160.

The purified product of D_2O experiment:



2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one. White soild. R_f = 0.20 (PE/EA= 3:1)

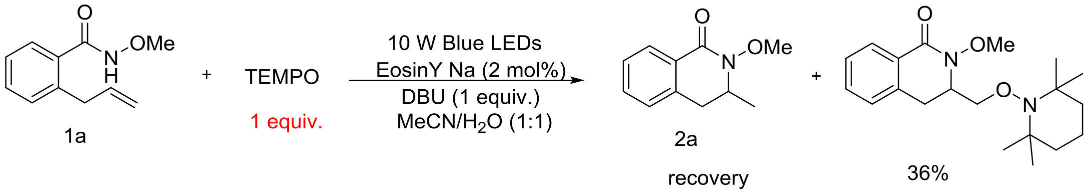
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.44 (td, *J* = 7.4, 1.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 4.10 (h, *J* = 6.2 Hz, 1H), 3.90 (d, *J* = 2.1 Hz, 3H), 3.33 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.90 (dd, *J* = 16.0, 5.8 Hz, 1H), 1.32 (d, *J* = 6.4 Hz, 3H).

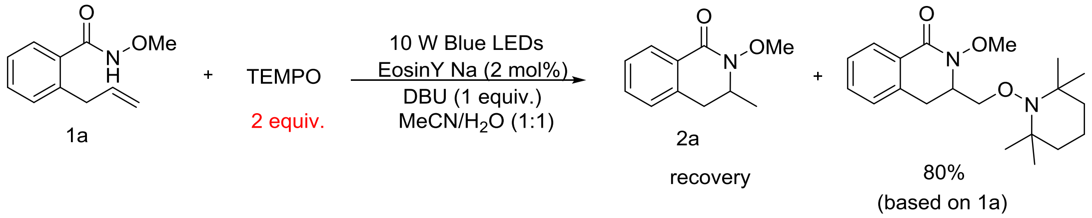
^{13}C NMR (75 MHz, Chloroform-*d*) δ 163.8, 136.0, 132.3, 128.3, 128.2, 127.7, 127.0, 63.0, 54.9, 36.3, 17.7.

HRMS (ESI) m/z calcd for $C_{11}H_{14}NO_2$ $[M+H]^+$: 192.1019, found: 192.1020.

2.3. Mechanism Investigation.

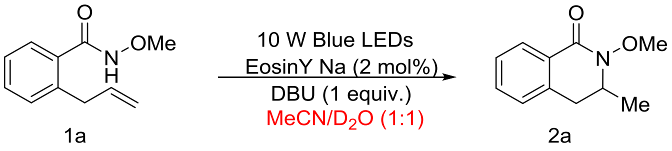
(1) Radical trapping experiment





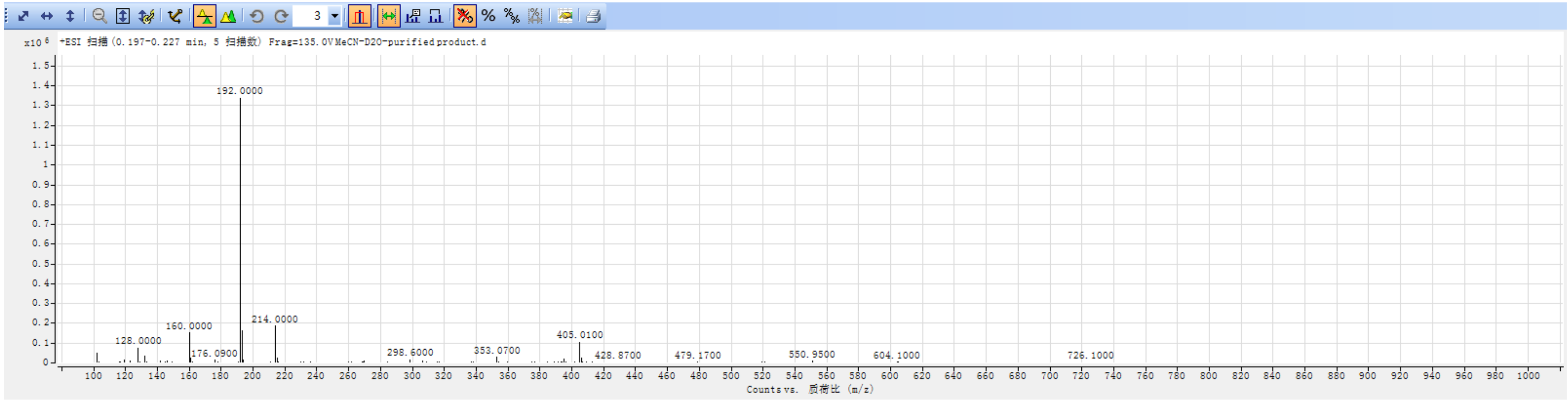
To a Schlenk tube were added **1a** (38.2 mg, 0.2 mmol), EosinY Na (3.14 mg, 0.004 mmol, 2 mol%), TEMPO (31.3 mg, 0.2 mmol, 1 equiv.) and charged with nitrogen for 15 minutes, anhydrous MeCN (1.5 mL) and H_2O (1.5 mL) were added before DBU (0.03 mL, 0.2 mmol) via a syringe. The mixture was then placed around the 10 W Blue LEDs with a distance of 3 centimeters, and was stirred under visible light irradiation until the substrate was consumed (monitored by TLC), filtered, the solvent was removed by rotary evaporation and the resulting residue was purified directly by flash column chromatograph to give the 2-methoxy-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-3,4-dihydroisoquinolin-1(*2H*)-one product as a white soild (25 mg, 36% yield); $R_f = 0.27$(Pet:EtOA = 3:1).

(2) D_2O experiment



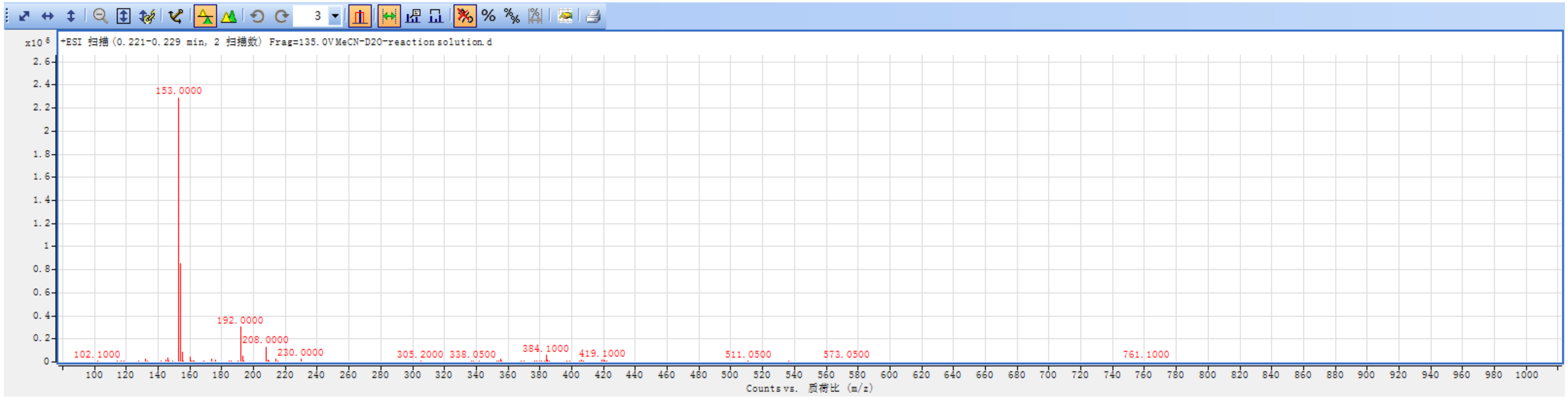
To a Schlenk tube were added **1a** (38.2 mg, 0.2 mmol), EosinY Na (3.14 mg, 0.004 mmol, 2 mol%) and charged with argon for 15 minutes, anhydrous MeCN (1.5 mL) and D_2O (1.5 mL) were added before DBU (0.03 mL, 0.2 mmol) via a syringe. The mixture was then placed around the 10 W Blue LEDs with a distance of 3 centimeters, and was stirred under visible light irradiation until the substrate was consumed (monitored by TLC), filtered, the solvent was removed by rotary evaporation and the resulting residue was purified directly by flash column chromatograph to give the desired product **2a** 78%. M(product): 191.0946

We provided an exact mass spectra of the purified product (Figure 1) and the reaction solution (Figure 2). of the D_2O experiment. We carefully examined the mass spectrum of the mixture and don’t found molecular weight of the various complexes such as the substrate and DBU+H.



+ESI 扫描 (0. 197-0. 227 min, 5 扫描数) Frag=135. 0V MeCN-D2O-purified product. d

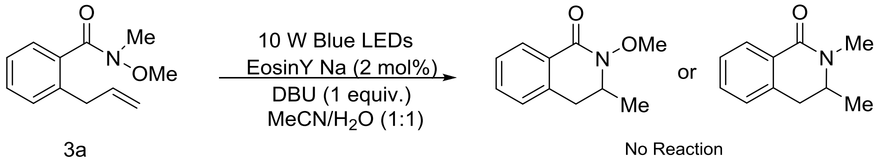
Figure 1. The mass spectra of the purified product



+ESI 扫描 (0. 221-0. 229 min, 2 扫描数) Frag=135. 0V MeCN-D2O-reaction solution. d

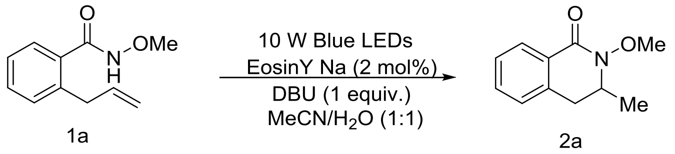
Figure 2. The mass spectra of the reaction solution

(3) Proton-free experiment on nitrogen



To a Schlenk tube were added **3a** (41 mg, 0.2 mmol), EosinY Na (3.14 mg, 0.004 mmol, 2 mol%) and charged with nitrogen for 15 minutes, anhydrous MeCN (1.5 mL) and H_2O (1.5 mL) were added before DBU (0.03 mL, 0.2 mmol) via a syringe. The mixture was then placed around the 10 W Blue LEDs with a distance of 3 centimeters, and was stirred under visible light irradiation (monitored by TLC), filtered, the solvent was removed by rotary evaporation and the resulting residue was purified directly by flash column chromatograph, the raw materials **3a** were almost completely recovered.

2.4. Gram-scale Reaction



To a Schlenk tube were added **1a** (0.573 g, 3 mmol), EosinY Na (47.1 mg, 0.06 mmol, 2 mol%) and charged with nitrogen for 15 minutes, anhydrous MeCN (10 mL) and H_2O (10 mL) were added before DBU (0.45 mL, 3 mmol) via a syringe. The mixture was then placed around the two 10 W Blue LEDs with a distance of 3 centimeters, and was stirred under visible light irradiation until the substrate was consumed (monitored by TLC), filtered, the solvent was removed by rotary evaporation and the resulting residue was purified directly by flash column chromatograph to give the desired product **2a** 70%.

2.5 UV-Vis Spectral Analysis

(a) The emission spectra of the 10 W Blue LEDs

We measured the emission spectra of the 10 W Blue LEDs used in our experiments by AULTT-P series fiber optic spectrometer (Figure 3.). As we can see from Figure 3, the Blue LED used in the experiment has a maximum emission wavelength of 554 nm and is located in the blue region (435-480nm).

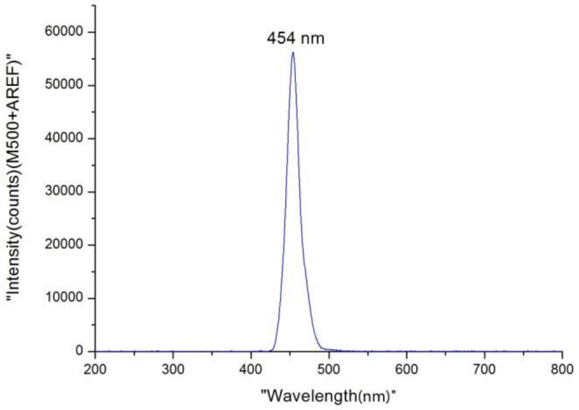


Figure 3. The emission spectra of 10 W Blue LEDs

(b) In order to understand the light absorption characteristics of this reaction system, the UV-Vis spectrum of the photocatalyst EsionY Na in MeCN/H_2O (1:1)、 the UV-Vis spectrum of the reaction solution、the UV-Vis spectrum of substrate (1a) in MeCN/H_2O (1:1) and the UV-Vis spectrum of DBU in MeCN/H_2O (1:1) were measured by an UV-Vis spectrophotometer.

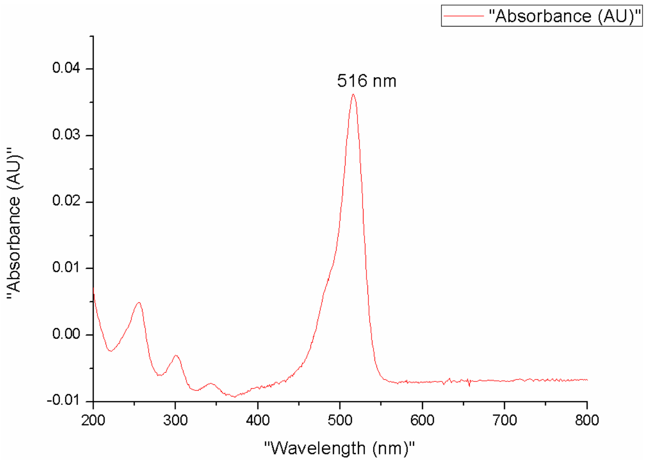


Figure 4. UV-Vis spectrum of EosinY Na in MeCN/H_2O (1:1)

As shown in the figure, the UV-visible absorption spectrum of EosinY Na, which is easily soluble in MeCN/H_2O (1:1). Its characteristic absorption wavelength is between 400-550 nm and the maximum absorption wavelength is 516 nm, located in the green area (492-560 nm).

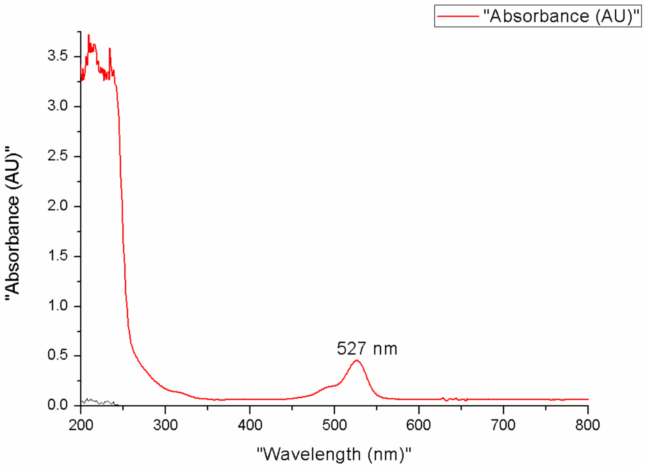


Figure 5. UV-Vis spectrum of the reaction solution

As shown in the figure, the characteristic absorption wavelength of the reaction solution is between 450-550 nm and the maximum absorption wavelength is 527 nm, located in the green area as well.

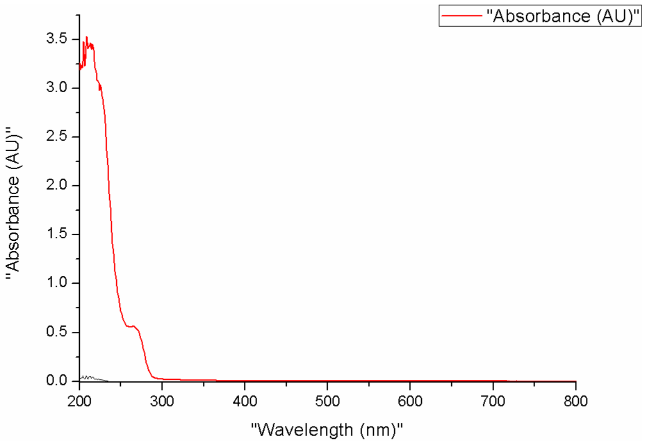


Figure 6. UV-Vis spectrum of substrate (1a) in MeCN/H_2O (1:1)

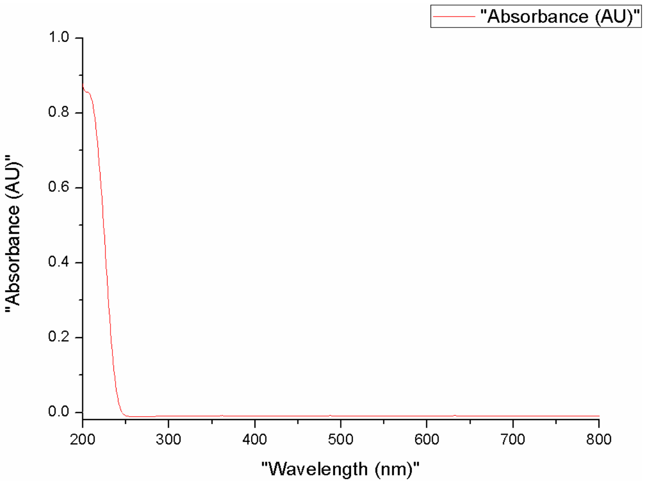


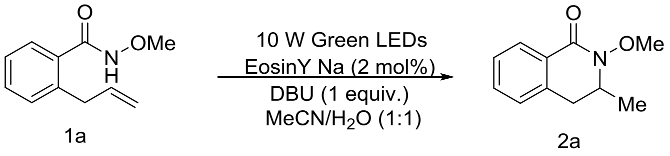
Figure 7. UV-Vis spectrum UV-Vis spectrum of DBU in MeCN/H2O(1:1)

Using 2-allyl-*N*-methoxybenzamide **1a** as a benchmark substrate. As shown in Figures 4-7 above, we examined the UV-visible absorption spectra of EosinY Na, reaction solution, substrate (1a) and DBU in the same solvent MeCN/H_2O (1:1). The maximum absorption wavelength of EosinY Na in MeCN/H_2O (1:1) is 516 nm (Figure 4). the maximum absorption wavelength of the reaction solution is 527 nm, substrate (1a) and DBU only absorb in the near-ultraviolet region in MeCN/H_2O (1:1) (Figure 6 and 7). This indicates that only EosinY Na absorbs visible light in the our system to induce the reaction.

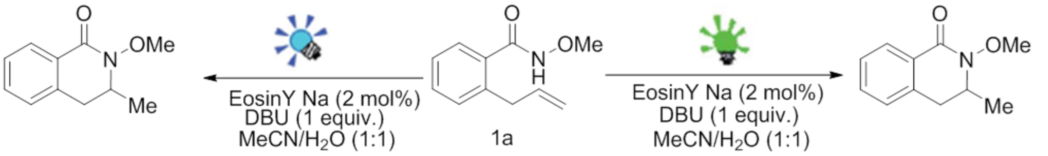
2.6 Comparison Experiment between Blue and Green Light Source

The characteristic absorption of the reaction system mainly occurs in the blue and green light range of the visible light region. Therefore, the effects of light sources provided by blue and green light on the reaction system are compared.

(1) Green Light Experiment



To a Schlenk tube were added **1a** (38.2 mg, 0.2 mmol), EosinY Na(3.14 mg, 0.004 mmol, 2 mol%) and charged with argon for 15 minutes, anhydrous MeCN (1.5 mL) and H_2O (1.5 mL) were added before DBU (0.03 mL, 0.2 mmol) via a syringe. The mixture was then placed around the 10 W Green LEDs with a distance of 3 centimeters, and was stirred under visible light irradiation until the substrate was consumed (monitored by TLC), filtered, the solvent was removed by rotary evaporation and the resulting residue was purified directly by flash column chromatograph to give the desired product **2a** (70% in 45 h vs 86% in 11 h).



86% (11 h) 70% (45 h)

(2) Comparison Experiment between Blue and Green Light Source by HPLC

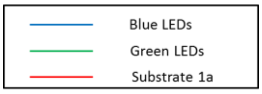
In order to more intuitively show the effect of blue and green light sources on the reaction, using HPLC time-lapse monitoring reaction.

HPLC spectrum

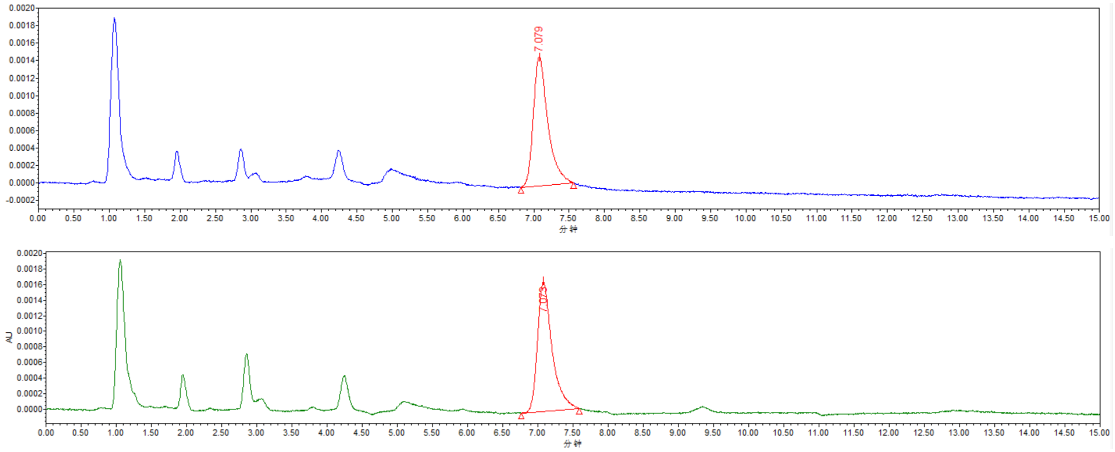
To two Schlenk tubes were added **1a** (38.2 mg, 0.2 mmol), EosinY Na (3.14 mg, 0.004 mmol, 2 mol%) and charged with argon for 15 minutes, anhydrous MeCN (1.5 mL) and H_2O (1.5 mL) were added before DBU (0.03 mL, 0.2 mmol) via a syringe separately. The mixture was then placed separately around the 10 W Blue LEDs and 10 W Green LEDs with a distance of 3 centimeters, and was stirred under visible light irradiation until the substrate was consumed (monitored by HPLC, 30% MeCN in H_2O as the eluent). Taking the reaction solution every two hours and observing the chromatogram change (As shown below).

Compared the liquid crystal spectra, it can be intuitively seen that the reaction rate of blue light as a light source is significantly higher than that of a green light source. At 11 hours, the reaction material for blue light irradiation is almost completely consumed, while the reaction for green light irradiation takes 45 hours.

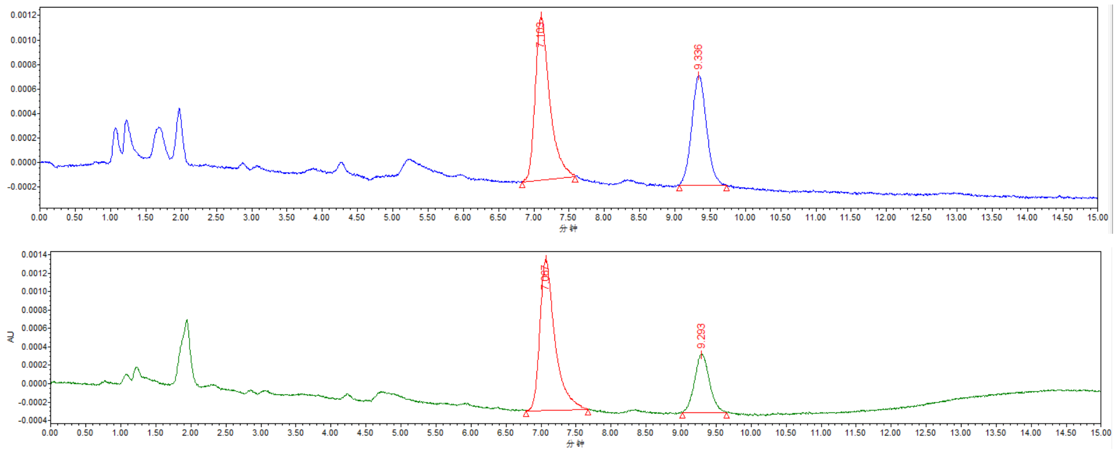
In summary, blue light is the most suitable light source in the reaction system we have reported.



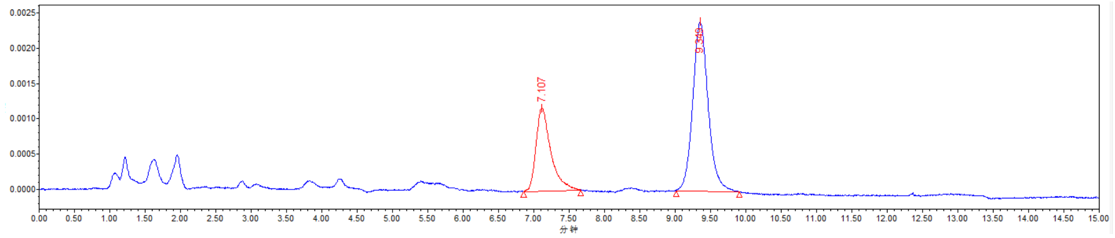
0 h:

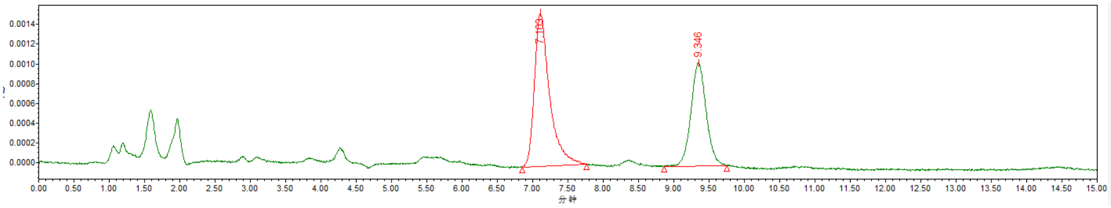


2 h:



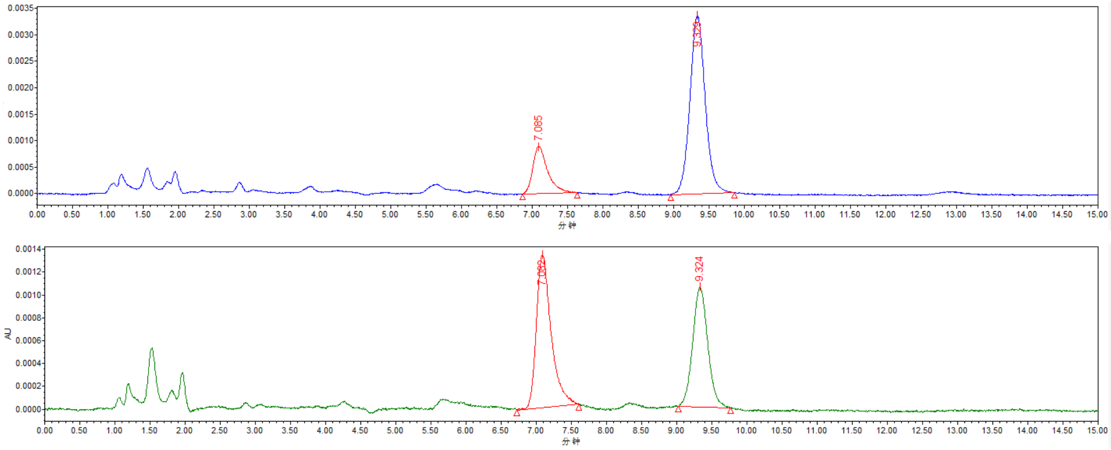
4 h:





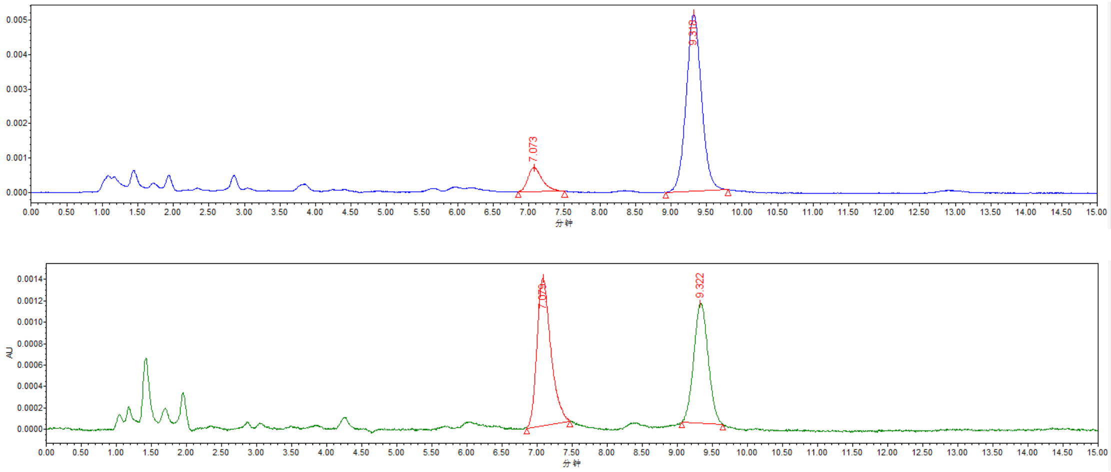
7.103
9.346
0.0014
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
0.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00 4.50 5.00 5.50 6.00 6.50 7.00 7.50 8.00 8.50 9.00 9.50 10.00 10.50 11.00 11.50 12.00 12.50 13.00 13.50 14.00 14.50 15.00
分钟

6 h:



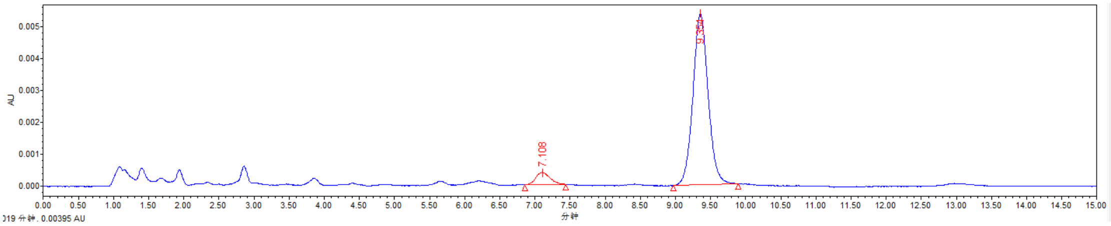
7.085
9.324
AU
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
0.0014
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
0.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00 4.50 5.00 5.50 6.00 6.50 7.00 7.50 8.00 8.50 9.00 9.50 10.00 10.50 11.00 11.50 12.00 12.50 13.00 13.50 14.00 14.50 15.00
分钟

8 h:

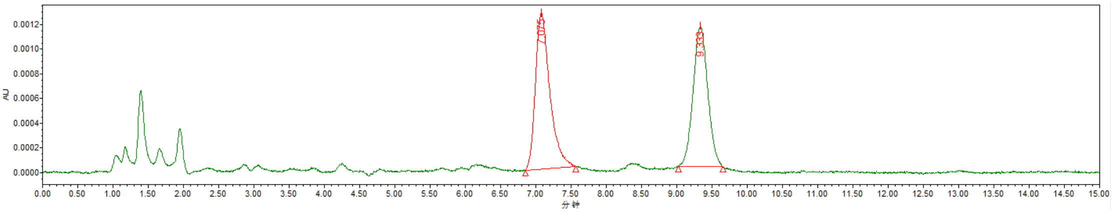


7.073
9.322
AU
0.005
0.004
0.003
0.002
0.001
0.000
0.0014
0.0012
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
0.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00 4.50 5.00 5.50 6.00 6.50 7.00 7.50 8.00 8.50 9.00 9.50 10.00 10.50 11.00 11.50 12.00 12.50 13.00 13.50 14.00 14.50 15.00
分钟

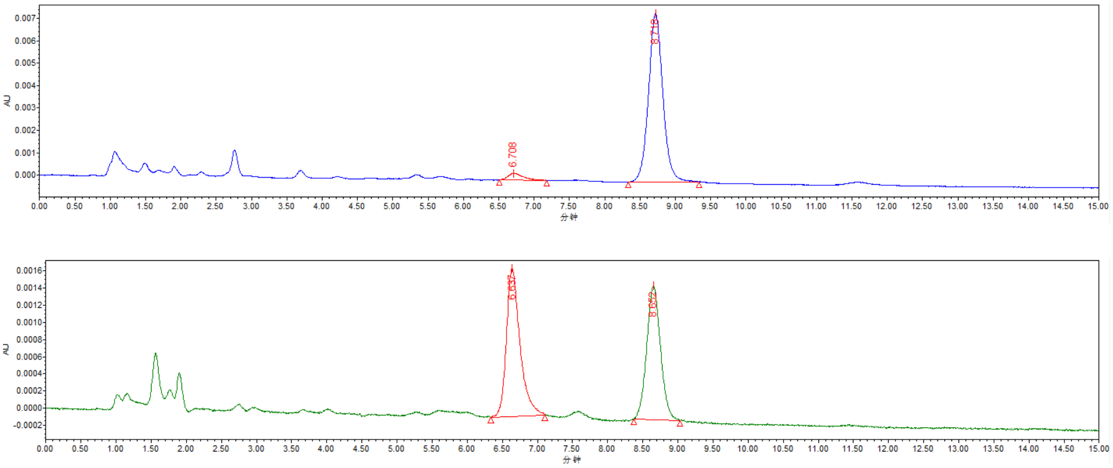
10 h:



7.108
AU
0.005
0.004
0.003
0.002
0.001
0.000
0.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00 4.50 5.00 5.50 6.00 6.50 7.00 7.50 8.00 8.50 9.00 9.50 10.00 10.50 11.00 11.50 12.00 12.50 13.00 13.50 14.00 14.50 15.00
分钟
019 分钟, 0.00395 AU



11 h:



45 h:

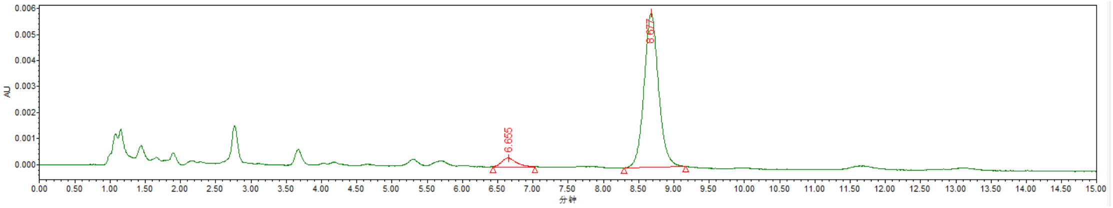


Figure 8. Comparison between Blue and Green Light Source by HPLC

3. References

1 F. Kopp, S. Wunderlich and P. Knochel, *Chem. Commun.* 2007, **20**, 2075-2077.

2 (a) K. Shen and Q. Wang, *Chem. Sci.* 2015, **6**, 4279-4283; (b) K. Shen and Q. Wang, *Org. Chem. Front.* 2016, **3**, 222-226; (c) D. J. Wardrop, E. G. Bowen, R. E. Forslund, A. D. Sussman and S. L. Weerasekera, *J. Am. Chem. Soc.* 2010, **132**, 1188-1189.

3 Z.-Y. Chen, L.-Y. Wu, H.-S. Fang, T. Zhang, Z.-F. Mao, Y. Zou, X.-J. Zhang and M. Yan, *Adv. Synth. Catal.* 2017, **359**, 3894-3899.

4 (a) D. E. Korte, L. S. Hegedus and R. K. Wirth, *J. Org. Chem.* 1977, **42**, 1329-1336; (b) L. E. Fisher, J. M. Muchowski, and R. D. Clark, *J. Org. Chem.* 1992, **57**, 2700-2705; (c) C. F. Bender, and R. A. Widenhoefer, *Chem. Commun.* 2008, **24**, 2741-2743.

5 K. C. Miles, C. C. Le and J. P. Stambuli, *Chemistry*, 2014, **20**, 11336-11339.

6 B. N. Hemric, K. Shen, and Q. Wang, *J. Am. Chem. Soc.* 2016, **138**, 5813-5816.

7 K. Shen, Q. Wang, *J Am Chem Soc* **2017**, *139*, 13110-13116.

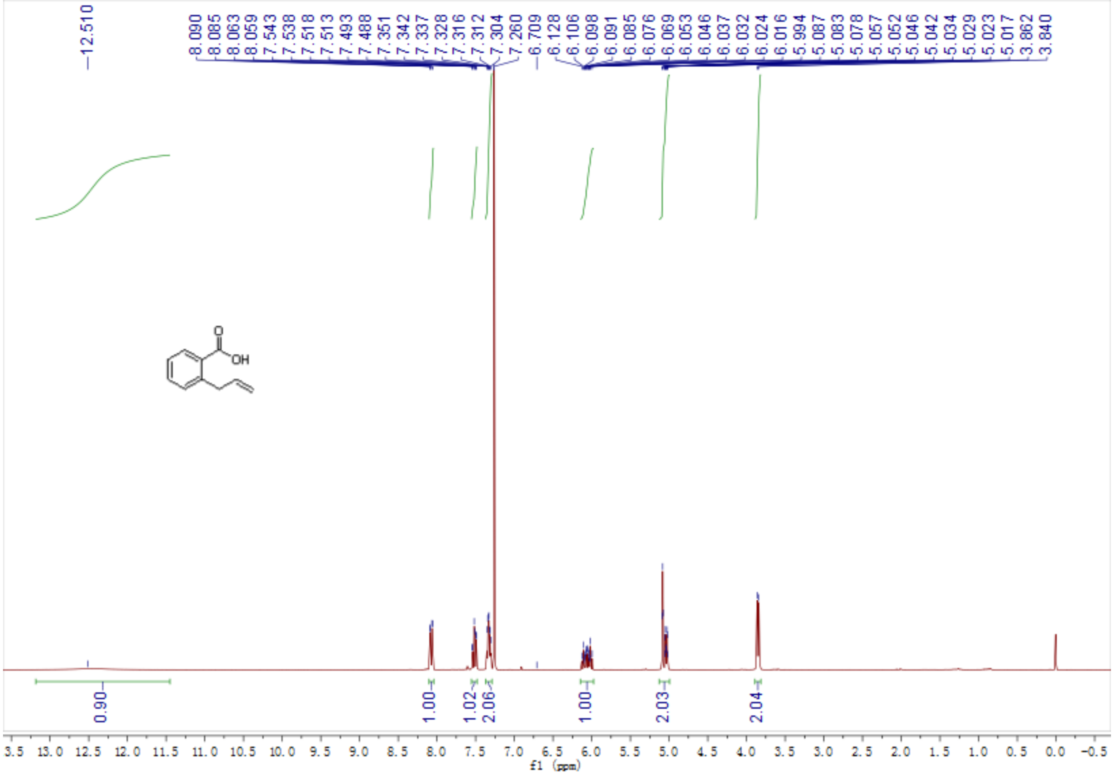
8 (a) T. Takesue, M. Fujita, T. Sugimura and H. Akutsu, *Org. Lett.* 2014, **16**, 4634-4637; (b) Z. Q. Zhang and F. Liu, *Org. Biomol. Chem.* 2015, **13**, 6690-6693.

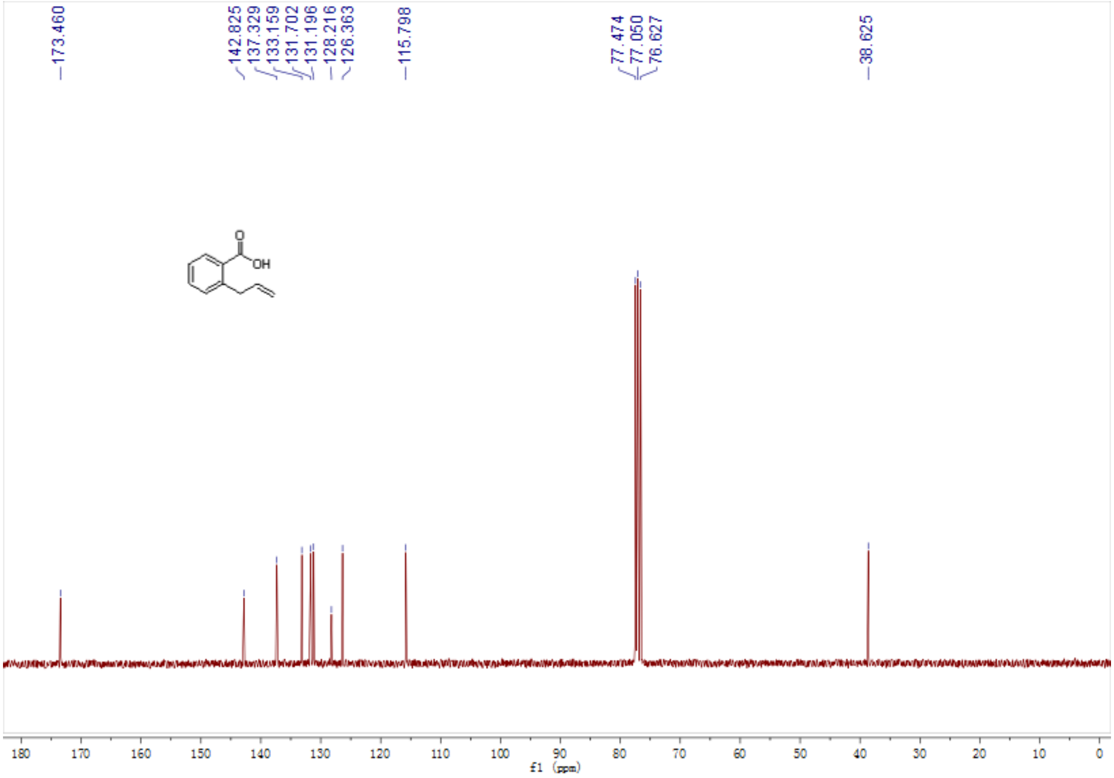
9 N. Okamoto, K. Takeda and R. Yanada, *J. Org. Chem.* 2010, **75**, 7615-7625.

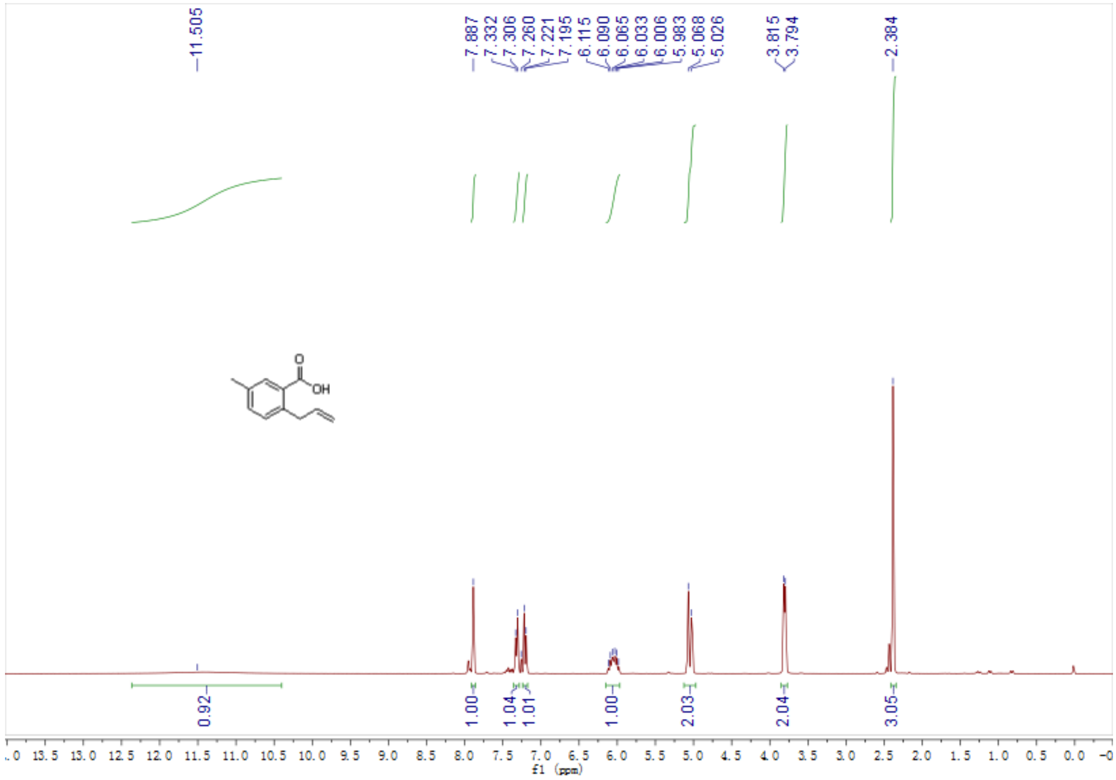
10 J. Einhorn, C. Einhorn and J.-L. Luche, Synthetic Commun., 1990, **20**, 1105-1112.

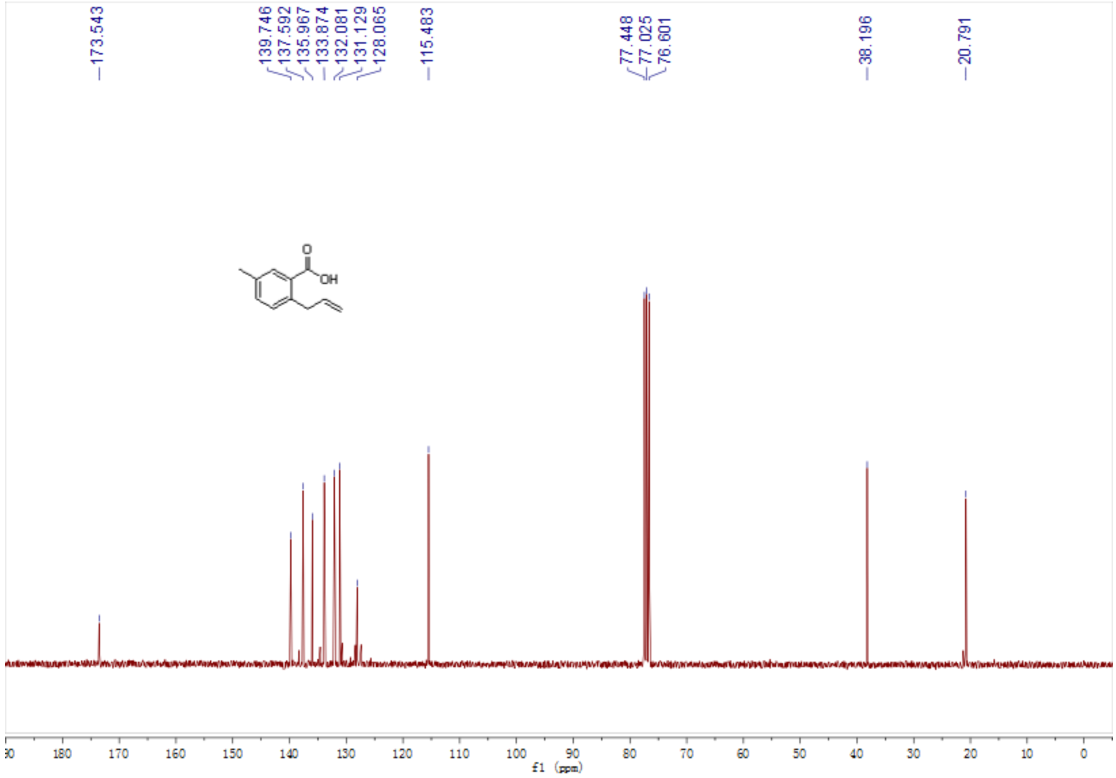
4. NMR Spectra

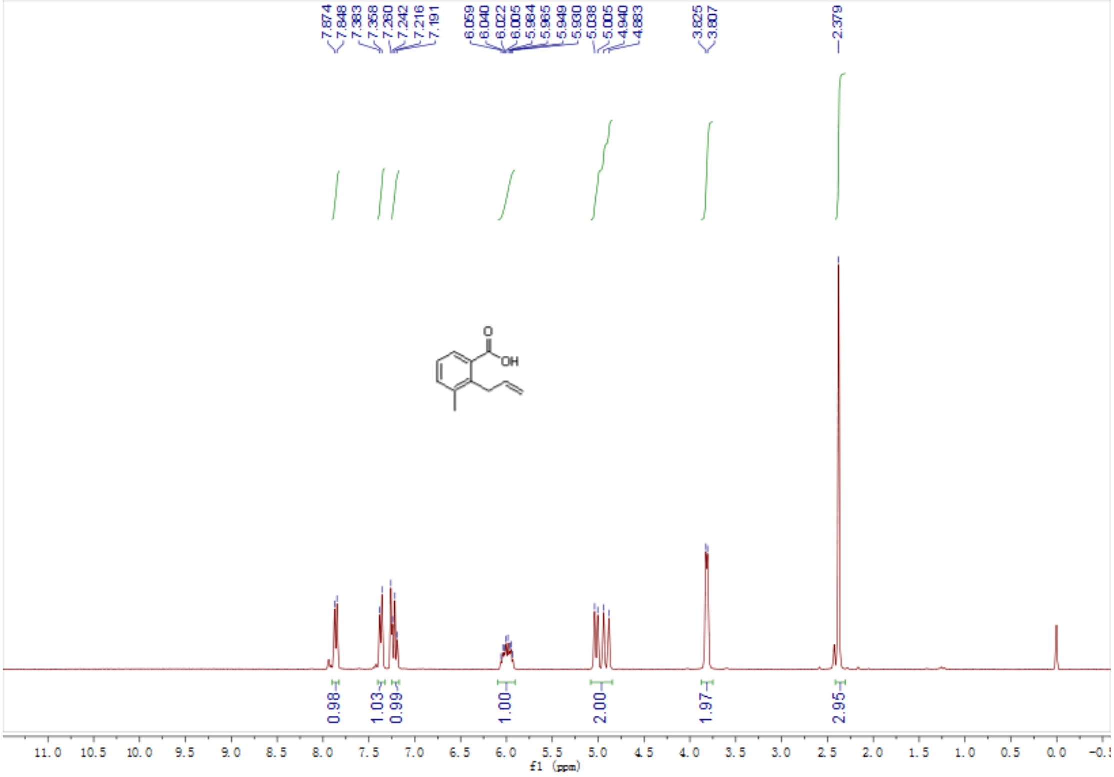
^{1}H NMR, ^{13}C NMR spectra of Substrates:

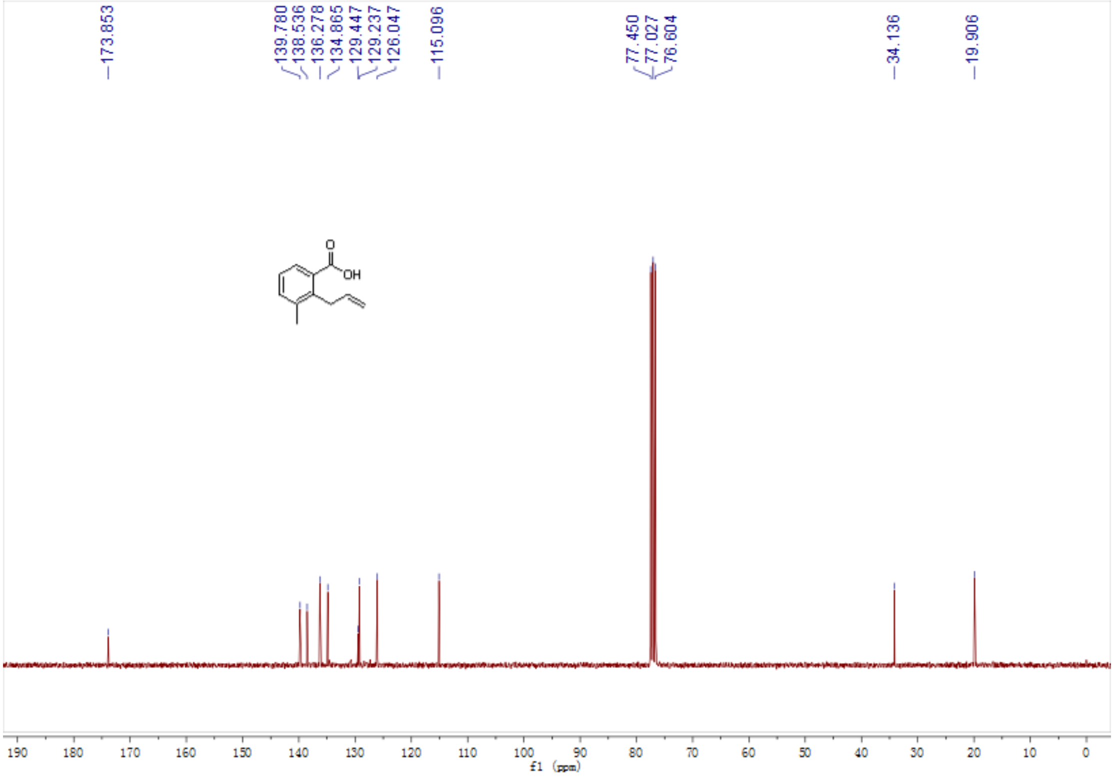


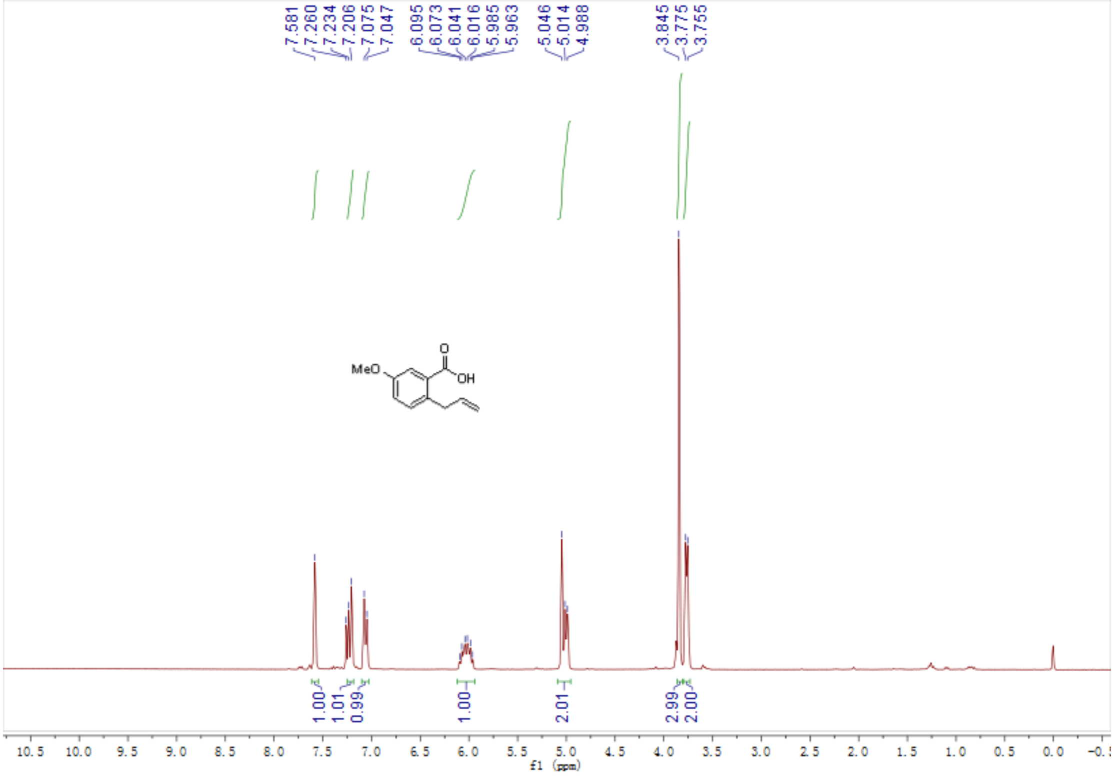


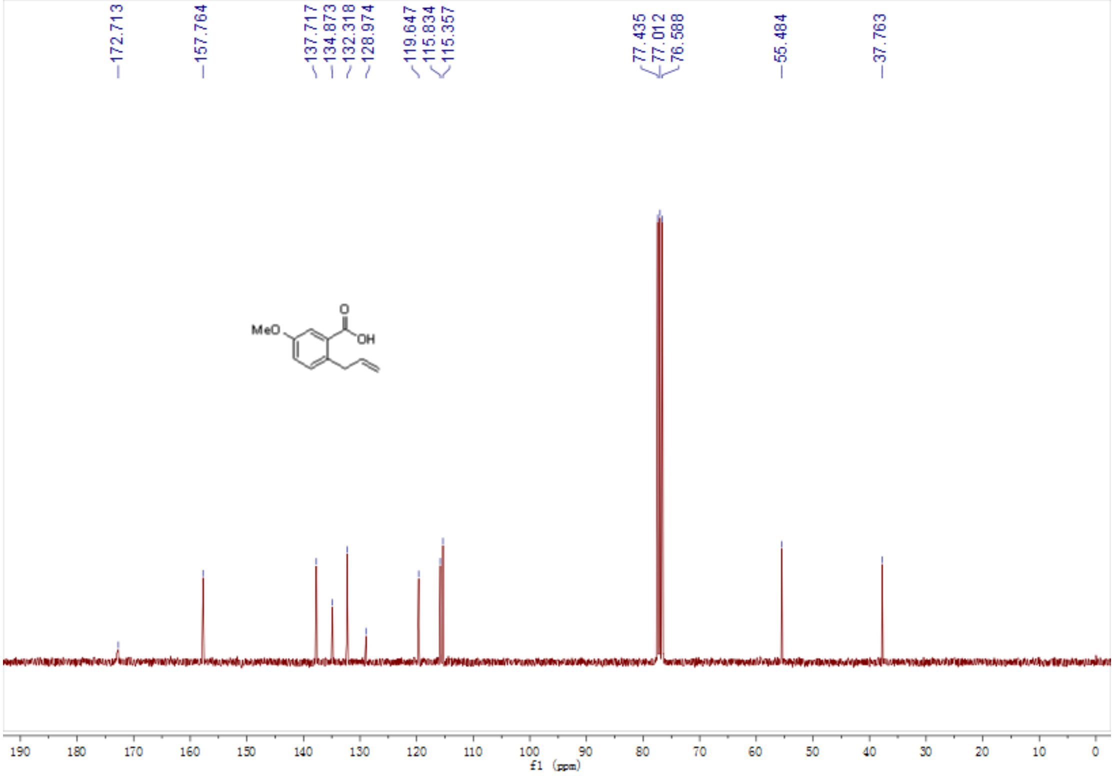

11.505
7.887
7.332
7.306
7.260
7.221
7.195
6.115
6.090
6.065
6.033
6.006
5.983
5.068
5.026
3.815
3.794
2.384
O
OH
0.92
1.00
1.04
1.01
1.00
2.03
2.04
3.05
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

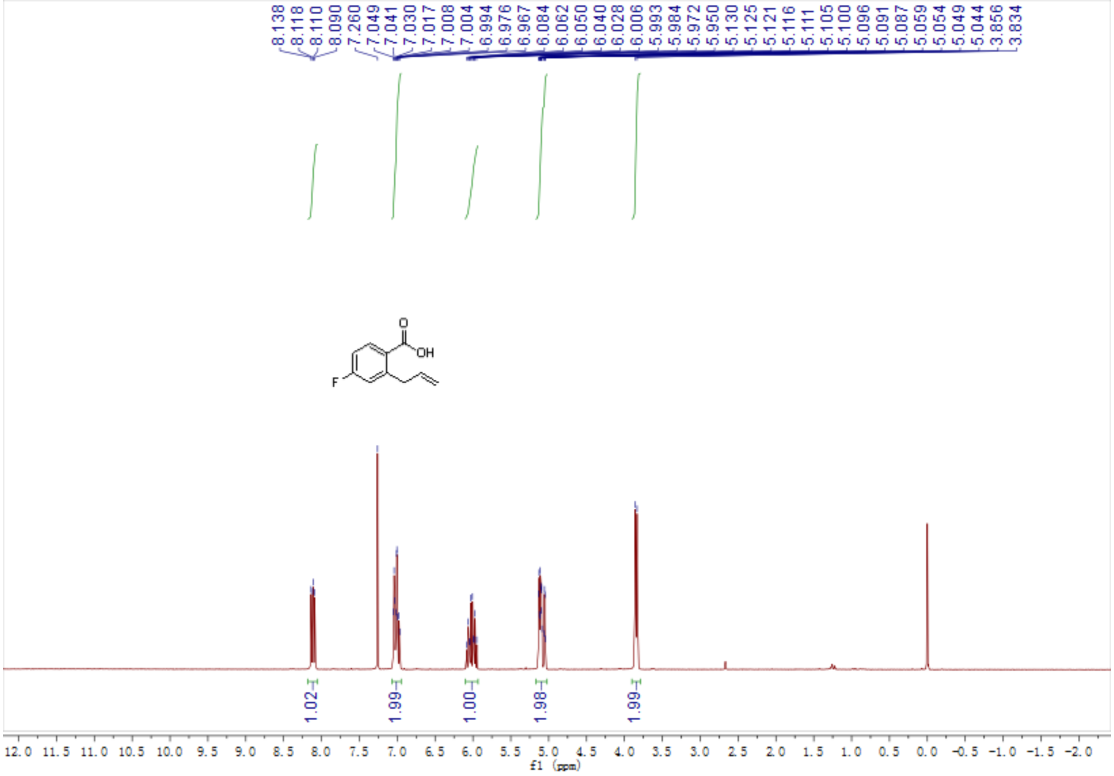

173.543
139.746
137.592
135.967
133.874
132.081
131.129
128.065
115.483
77.448
77.025
76.601
38.196
20.791
O
OH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

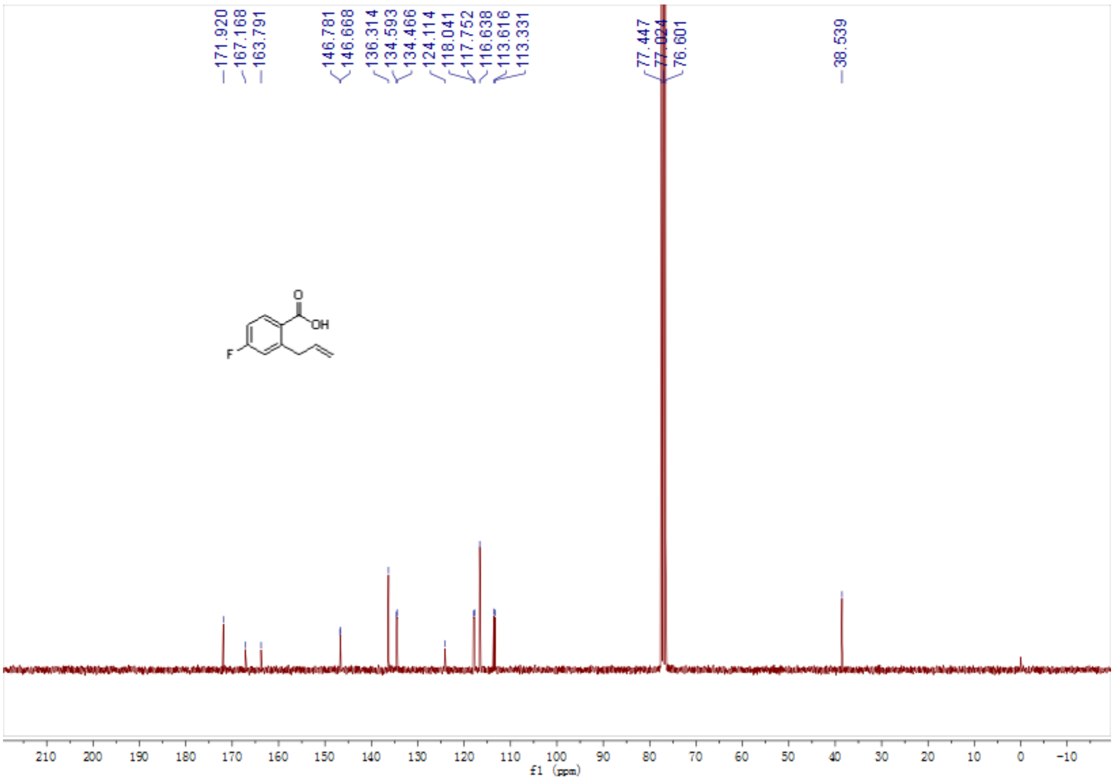

7.874
7.848
7.383
7.358
7.260
7.242
7.216
7.191
6.059
6.040
6.022
6.005
5.984
5.965
5.949
5.930
5.038
5.005
4.940
4.883
3.825
3.807
2.379
O
OH
0.98
1.03
0.99
1.00
2.00
1.97
2.95
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

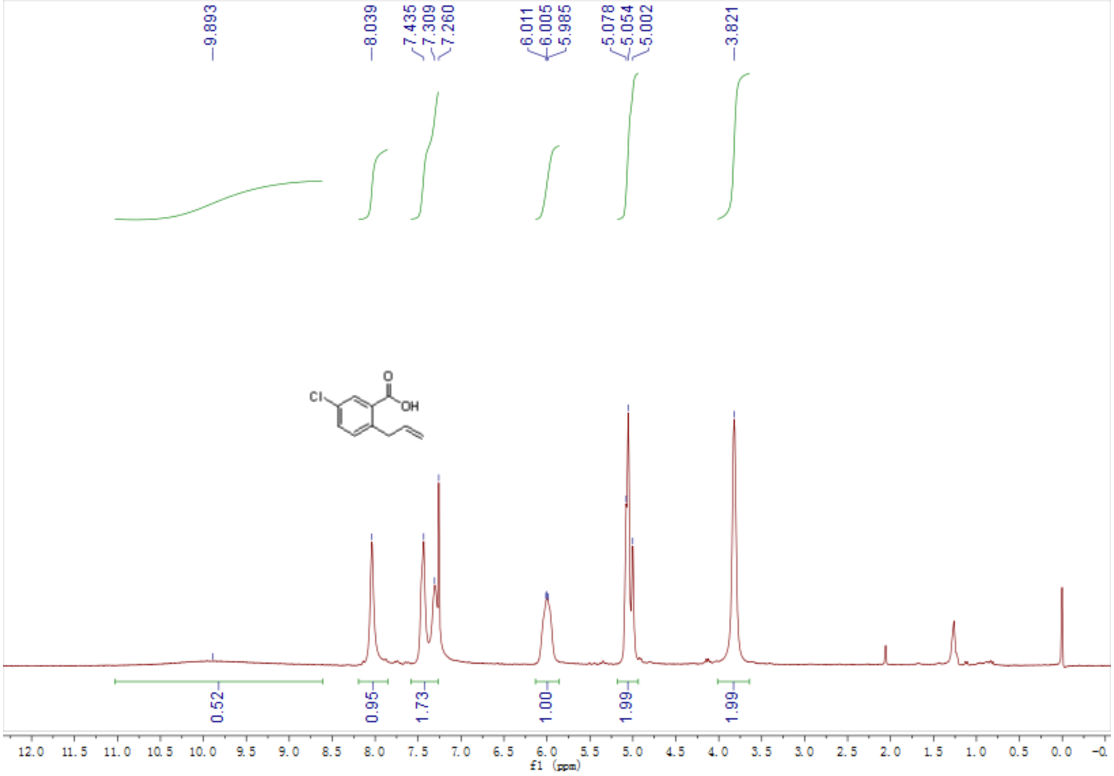

173.853
139.780
138.536
136.278
134.865
129.447
129.237
126.047
115.096
77.450
77.027
76.604
34.136
19.906
O
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

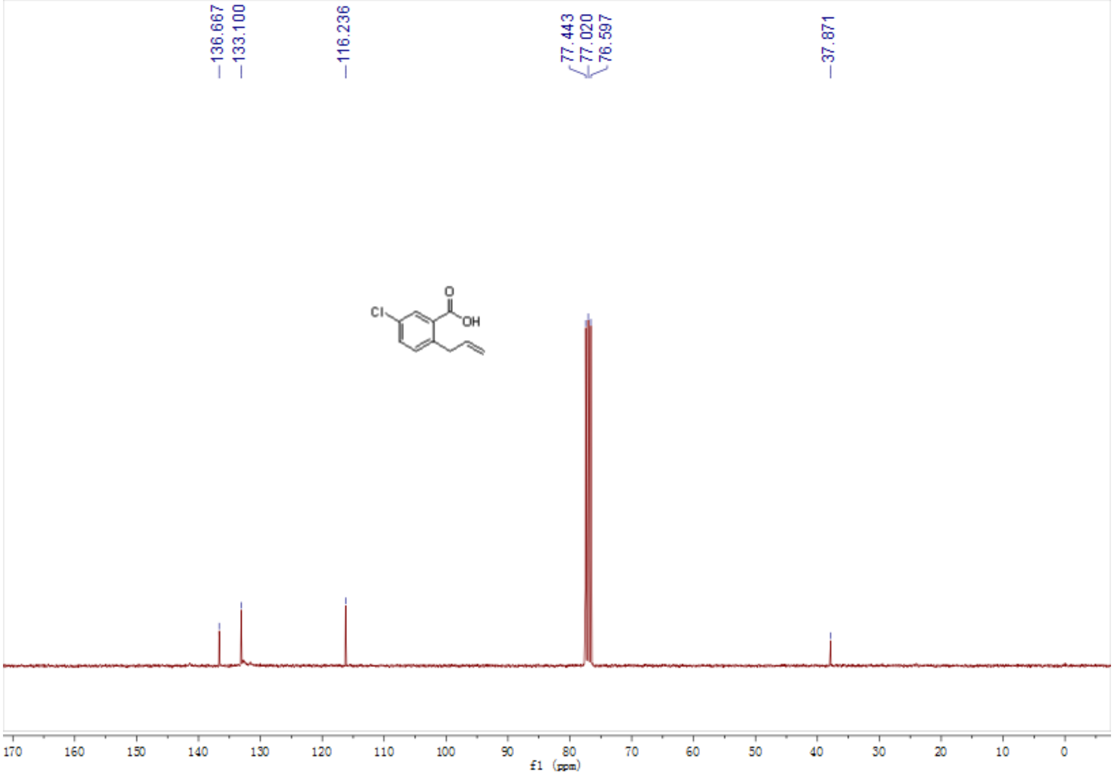

7.581
7.260
7.234
7.206
7.075
7.047
6.095
6.073
6.041
6.016
5.985
5.963
5.046
5.014
4.988
3.845
3.775
3.755
MeO
O
OH
1.00
1.01
0.99
1.00
2.01
2.99
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

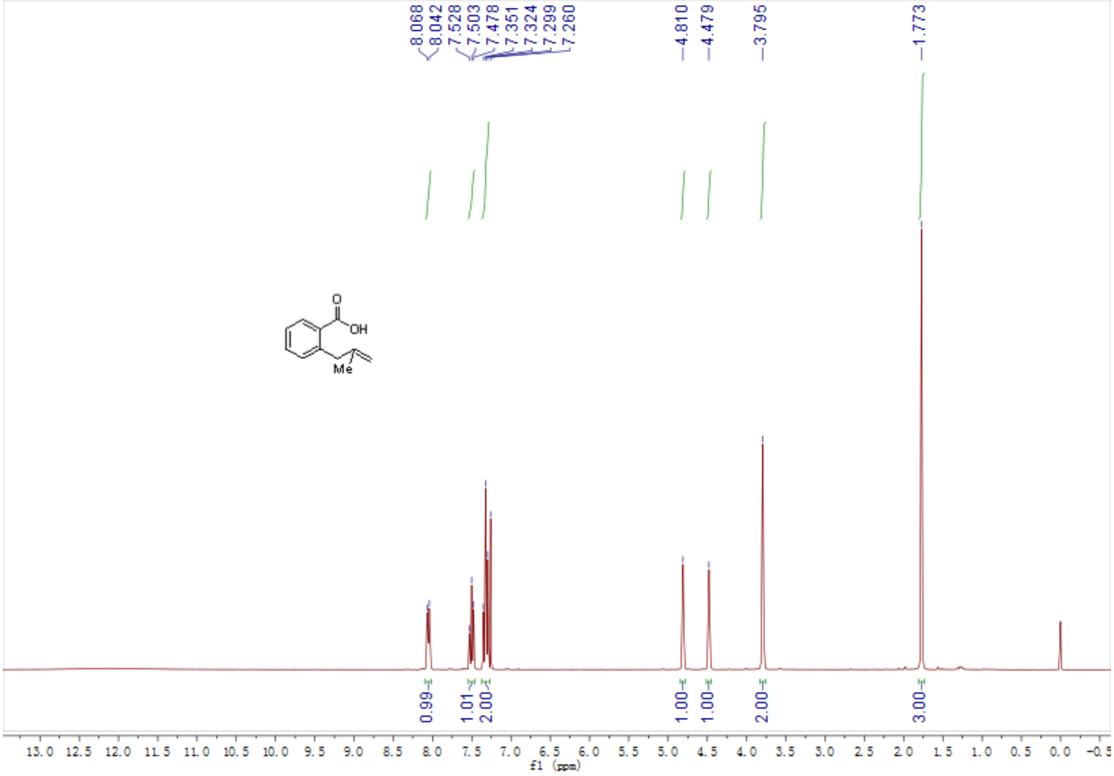

172.713
157.764
137.717
134.873
132.318
128.974
119.647
115.834
115.357
77.435
77.012
76.588
55.484
37.763
MeO
O
OH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

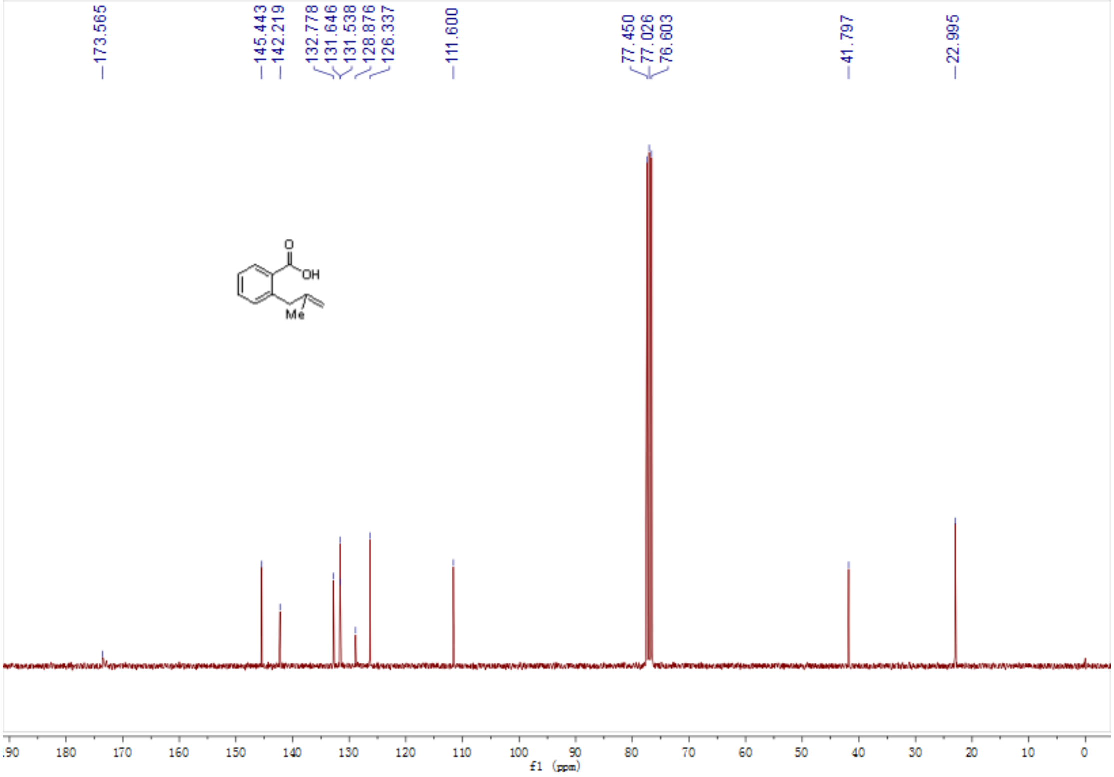

8.138
8.118
8.110
8.090
7.260
7.049
7.041
7.030
7.017
7.008
7.004
6.994
6.976
6.967
6.084
6.062
6.050
6.040
6.028
6.006
5.993
5.984
5.972
5.950
5.130
5.125
5.121
5.116
5.111
5.105
5.100
5.096
5.091
5.087
5.059
5.054
5.049
5.044
3.856
3.834
O
OH
F
1.02
1.99
1.00
1.98
1.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

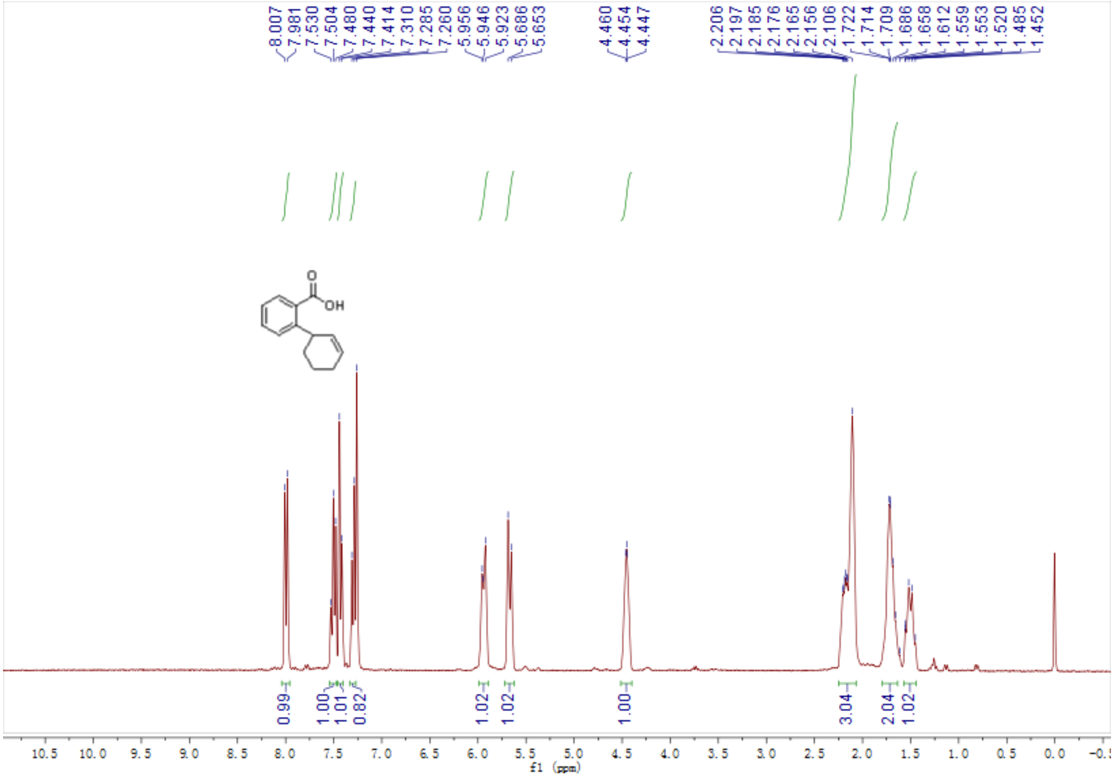

171.920
167.168
163.791
146.781
146.668
136.314
134.593
134.466
124.114
118.041
117.752
116.638
113.616
113.331
77.447
77.024
76.601
38.539
O
OH
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

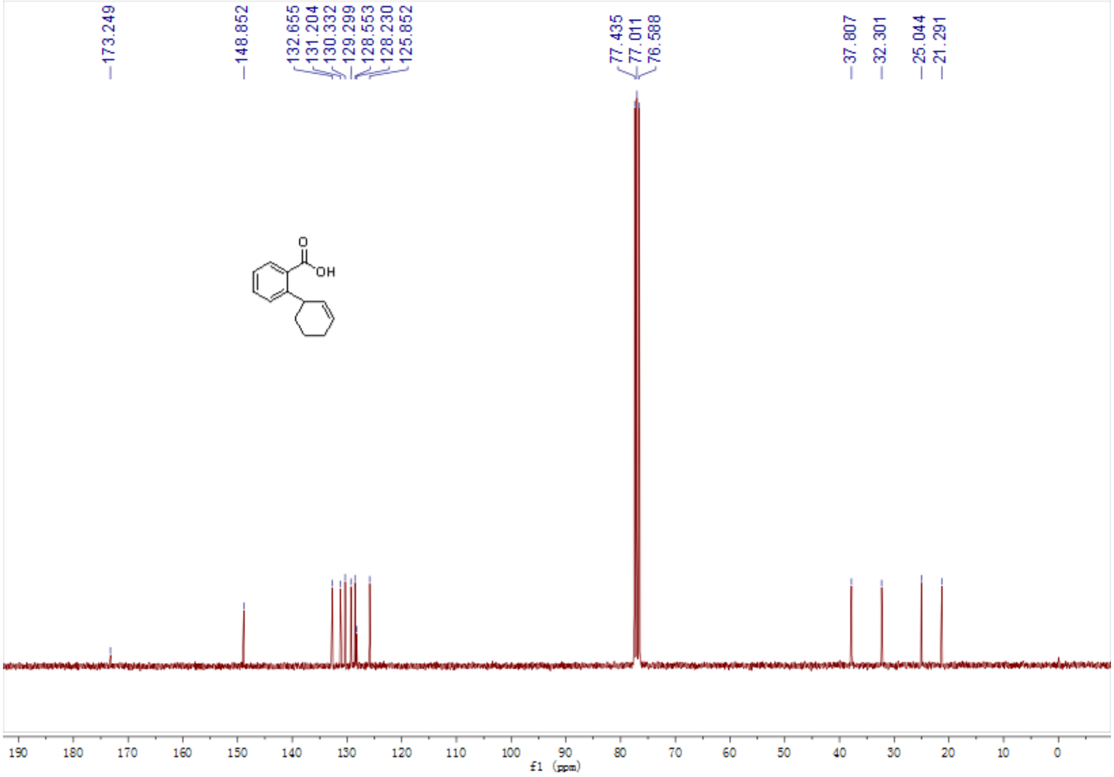

9.893
8.039
7.435
7.309
7.260
6.011
6.005
5.985
5.078
5.054
5.002
3.821
Cl
O
OH
0.52
0.95
1.73
1.00
1.99
1.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

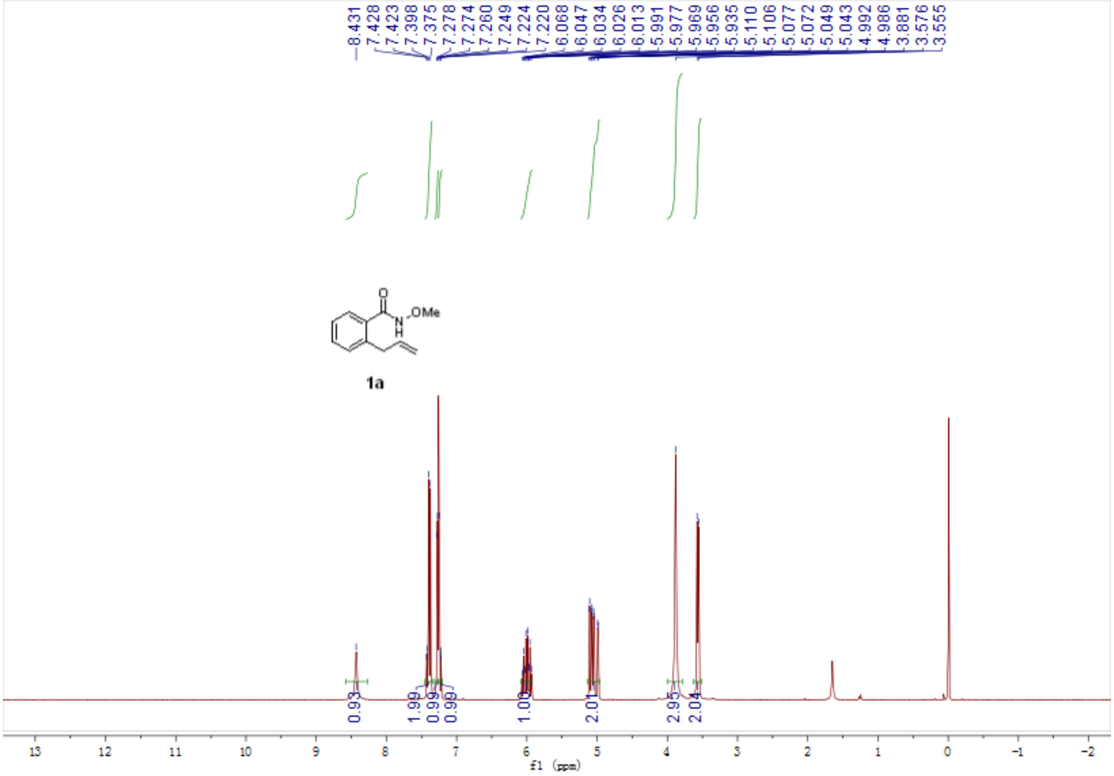

136.667
133.100
116.236
77.443
77.020
76.597
37.871
Cl
O
OH
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

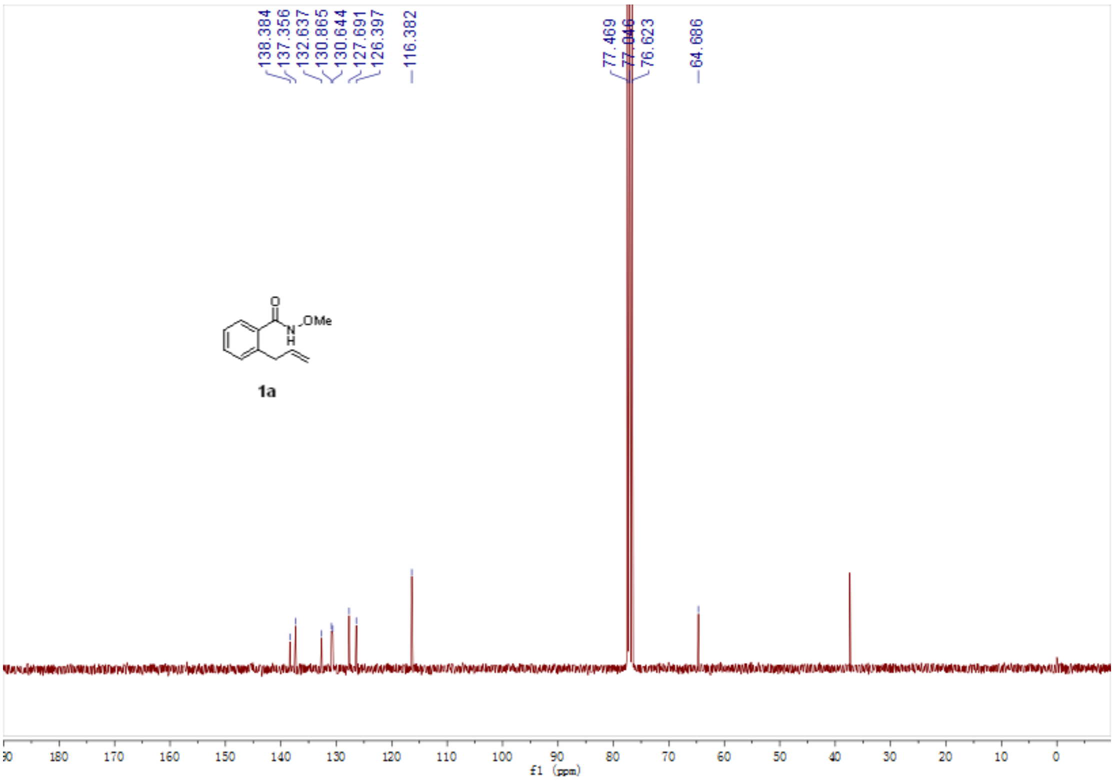

8.068
8.042
7.528
7.503
7.478
7.351
7.324
7.299
7.260
4.810
4.479
3.795
1.773
O
OH
Me
0.99
1.01
2.00
1.00
1.00
2.00
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

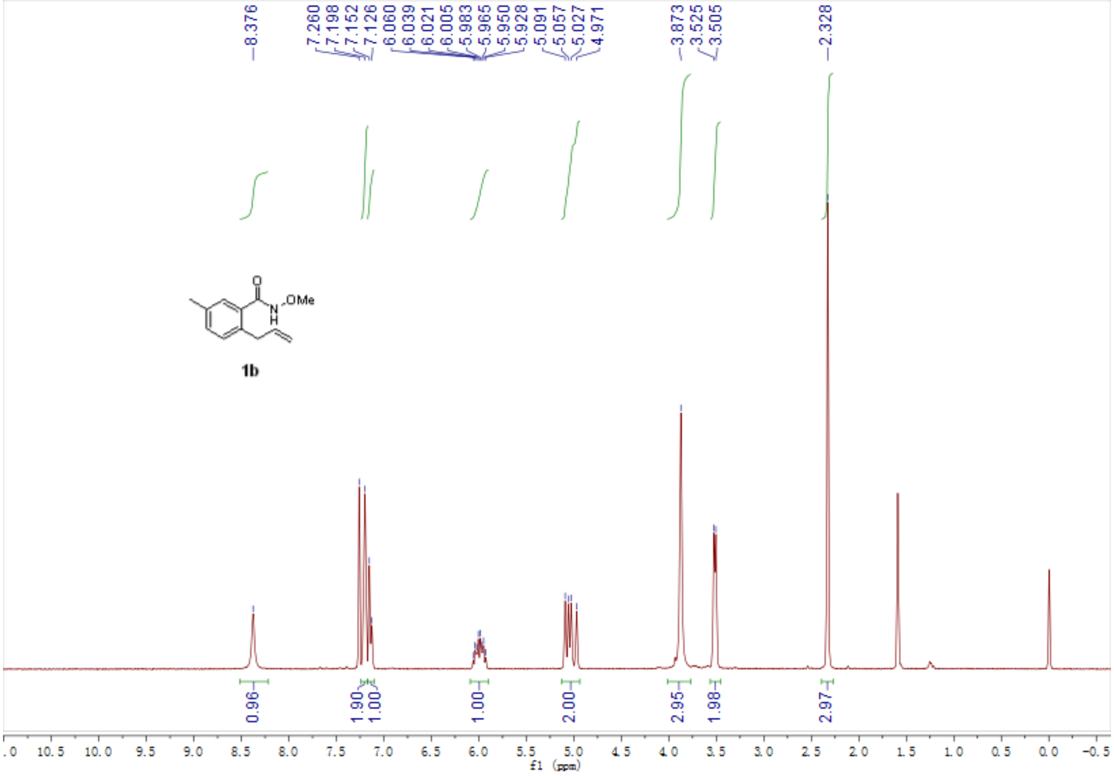

173.565
145.443
142.219
132.778
131.646
131.538
128.876
126.337
111.600
77.450
77.026
76.603
41.797
22.995
O
OH
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

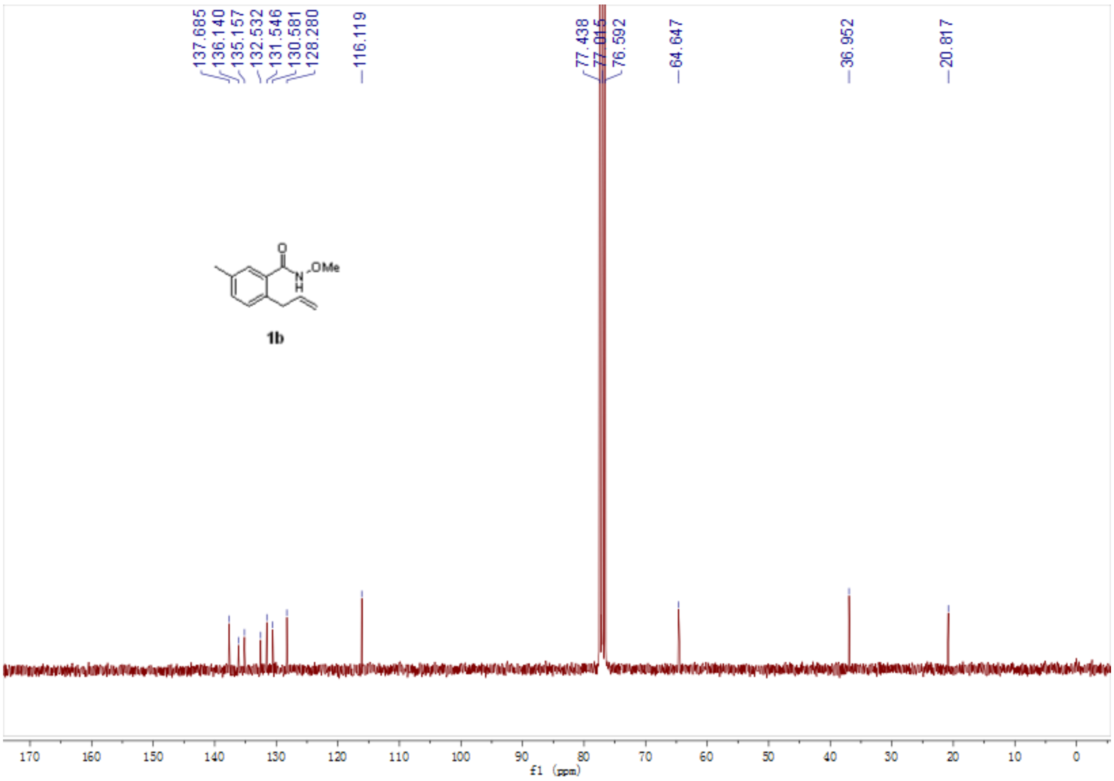

8.007
7.981
7.530
7.504
7.480
7.440
7.414
7.310
7.285
7.260
5.956
5.946
5.923
5.686
5.653
4.460
4.454
4.447
2.206
2.197
2.185
2.176
2.165
2.156
2.106
1.722
1.714
1.709
1.686
1.658
1.612
1.559
1.553
1.520
1.485
1.452
O
OH
0.99
1.00
1.01
0.82
1.02
1.02
1.00
3.04
2.04
1.02
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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)

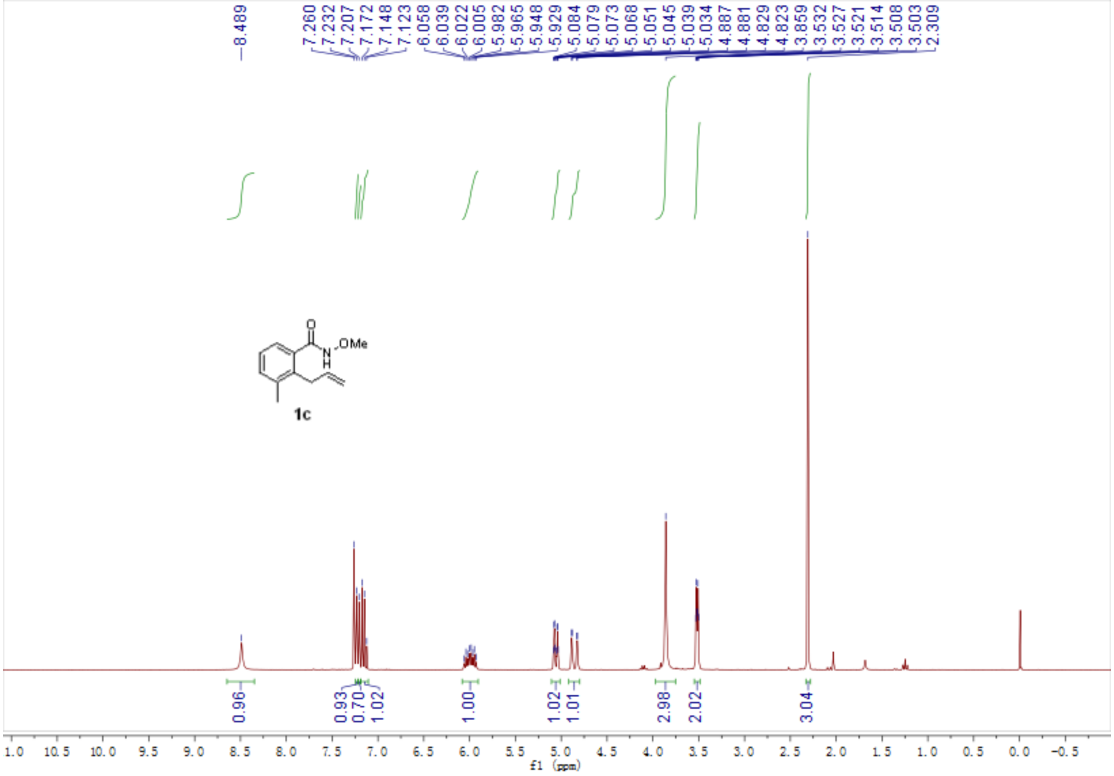

173.249
148.852
132.655
131.204
130.332
129.299
128.553
128.230
125.852
77.435
77.011
76.588
37.807
32.301
25.044
21.291
O
OH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

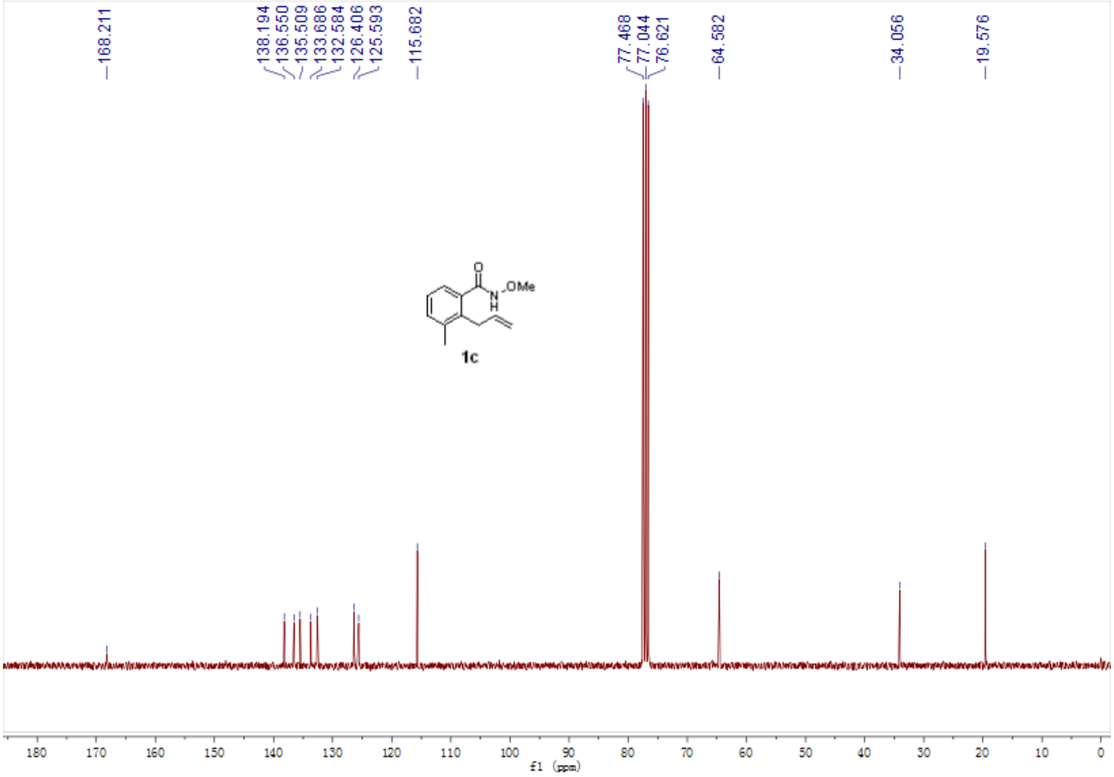

8.431
7.428
7.423
7.398
7.375
7.278
7.274
7.260
7.249
7.224
7.220
6.068
6.047
6.034
6.026
6.013
5.991
5.977
5.969
5.956
5.935
5.110
5.106
5.077
5.072
5.049
5.043
4.992
4.986
3.881
3.576
3.555
OMe
N
H
O
1a
0.93
1.99
0.99
0.99
1.00
2.01
2.95
2.04
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)

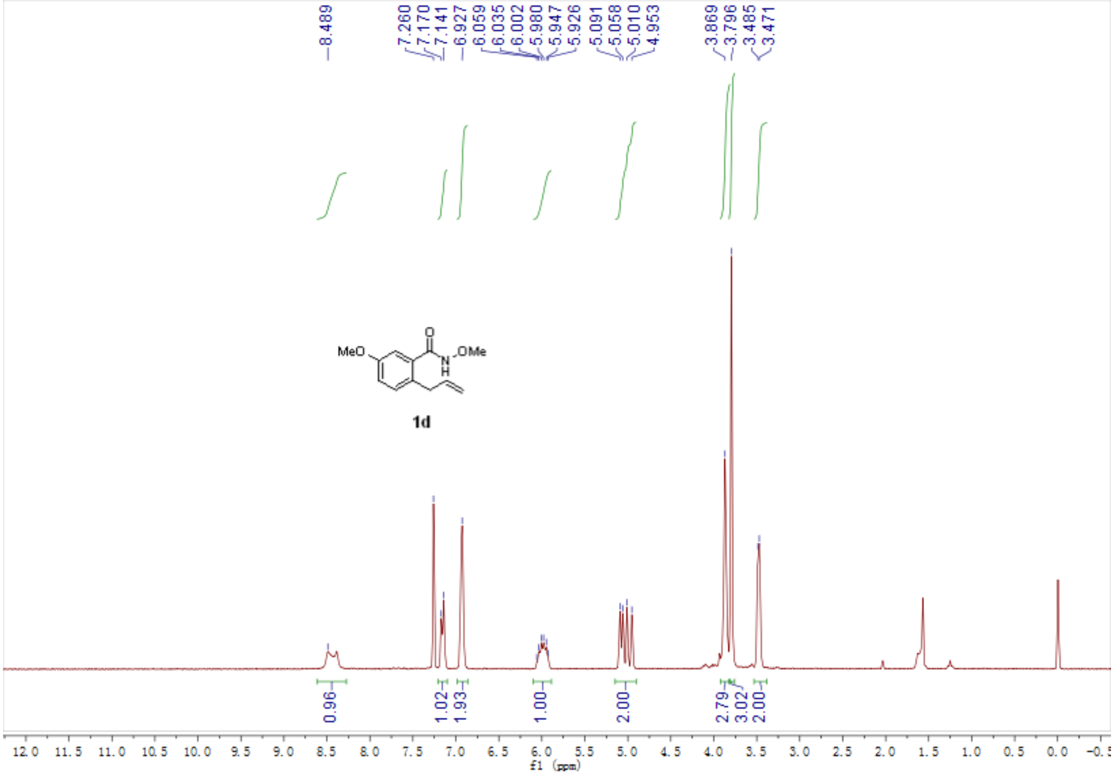

138.384
137.356
132.637
130.865
130.644
127.691
126.397
116.382
77.469
77.046
76.623
64.686
OMe
N
H
O
1a
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

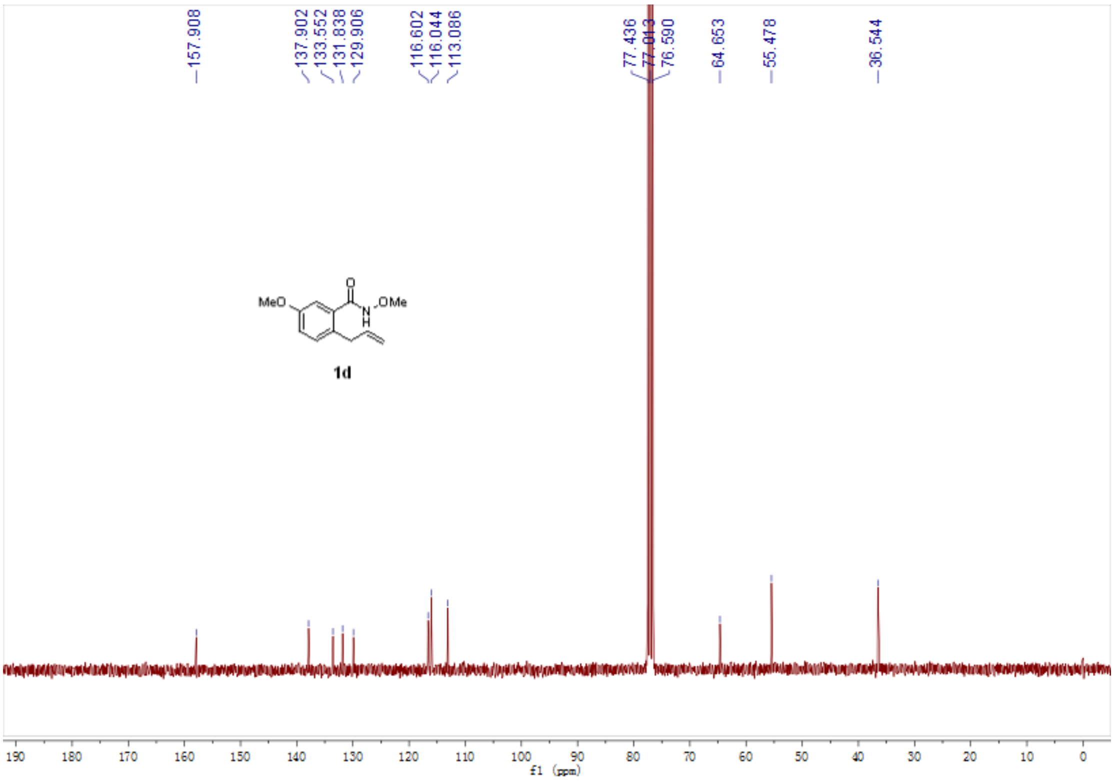

8.376
7.260
7.198
7.152
7.126
6.060
6.039
6.021
6.005
5.983
5.965
5.950
5.928
5.091
5.057
5.027
4.971
3.873
3.525
3.505
2.328
O
N
H
OMe
1b
0.96
1.90
1.00
1.00
2.00
2.95
1.98
2.97
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

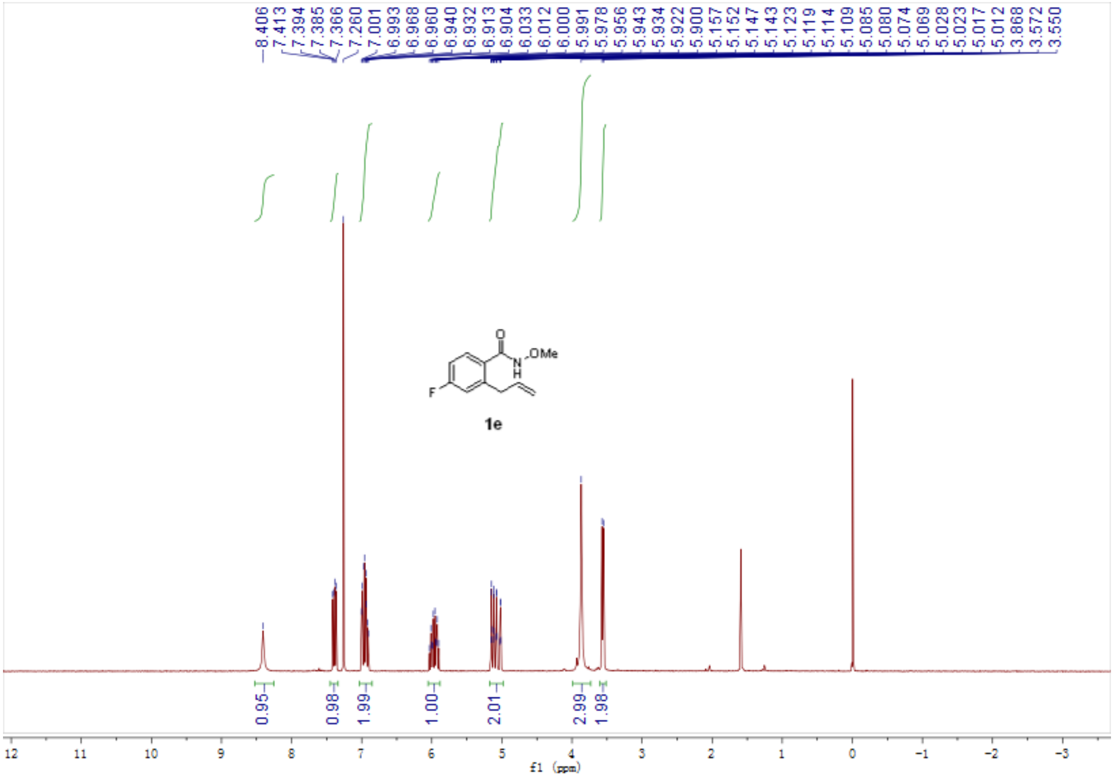

137.685
136.140
135.157
132.532
131.546
130.581
128.280
116.119
77.438
77.015
76.592
64.647
36.952
20.817
O
N
H
OMe
1b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

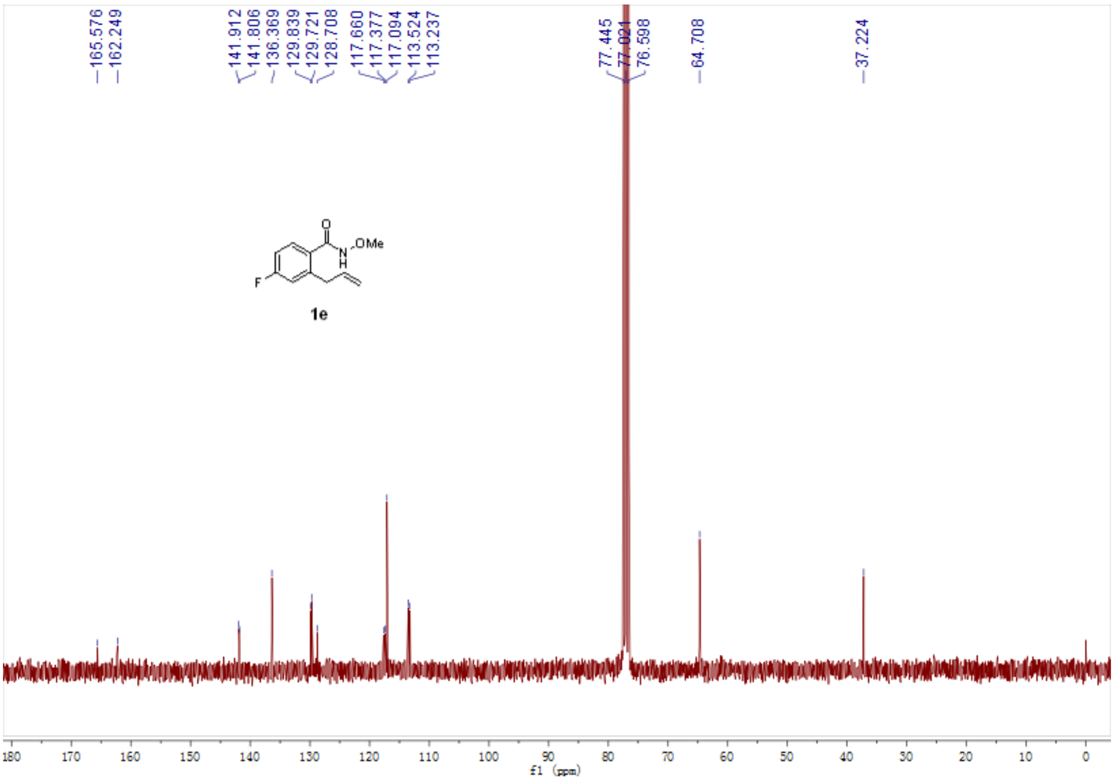

8.489
7.260
7.232
7.207
7.172
7.148
7.123
6.058
6.039
6.022
6.005
5.982
5.965
5.948
5.929
5.084
5.079
5.073
5.068
5.051
5.045
5.039
5.034
4.887
4.881
4.829
4.823
3.859
3.532
3.527
3.521
3.514
3.508
3.503
2.309
O
N
H
OMe
1c
0.96
0.93
0.70
1.02
1.00
1.02
1.01
2.98
2.02
3.04
f1 (ppm)

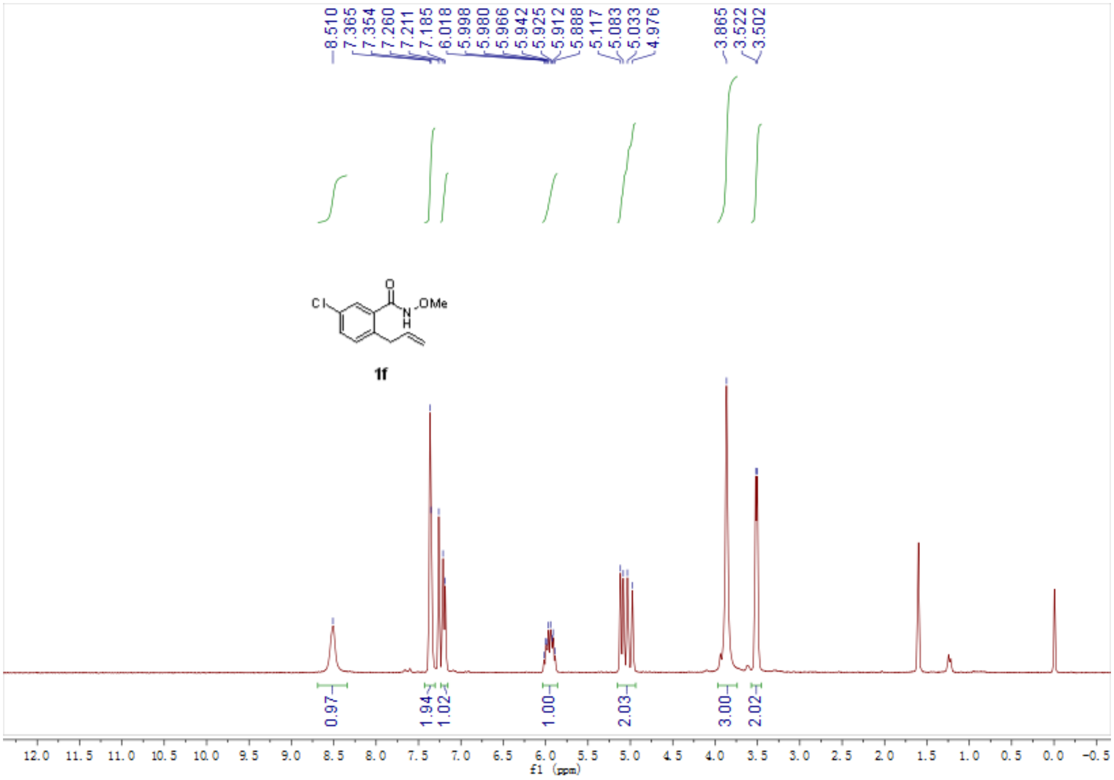

168.211
138.194
136.550
135.509
133.686
132.584
126.406
125.593
115.682
77.468
77.044
76.621
64.582
34.056
19.576
O
N
H
OMe
1c
f1 (ppm)

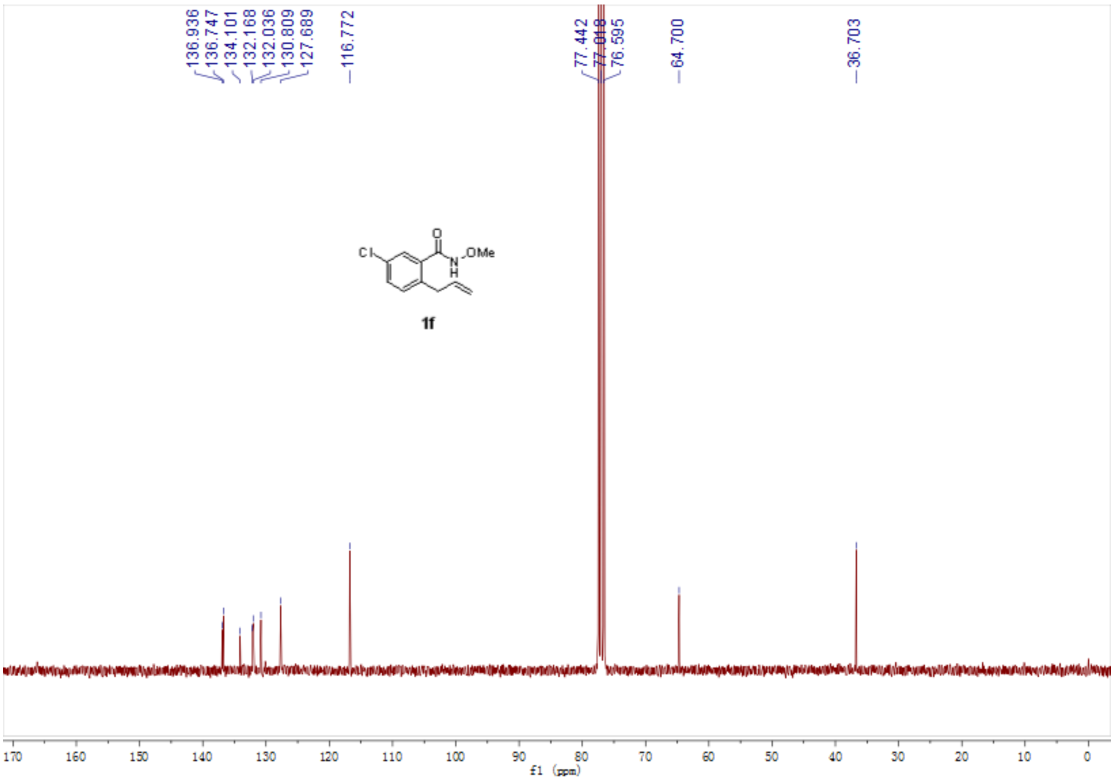

8.489
7.260
7.170
7.141
6.927
6.059
6.035
6.002
5.980
5.947
5.926
5.091
5.058
5.010
4.953
3.869
3.796
3.485
3.471
MeO
O
N
H
OMe
1d
0.96
1.02
1.93
1.00
2.00
2.79
3.02
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

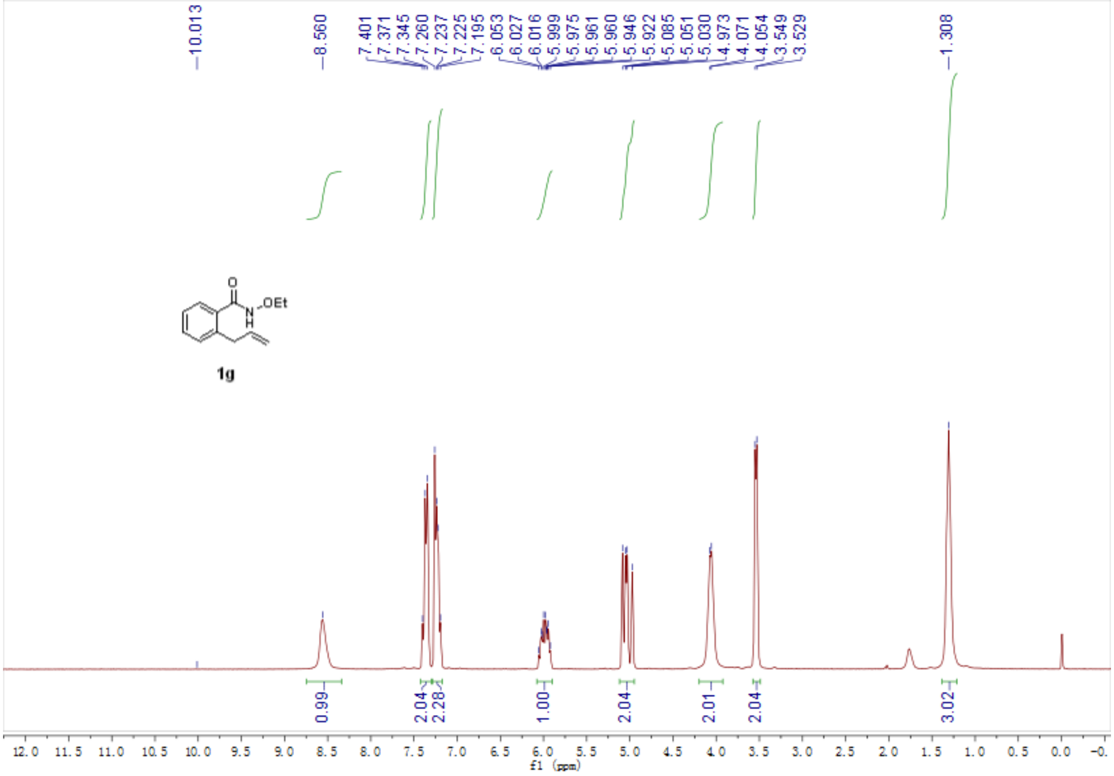

157.908
137.902
133.552
131.838
129.906
116.602
116.044
113.086
77.436
77.013
76.590
64.653
55.478
36.544
MeO
O
N
H
OMe
1d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

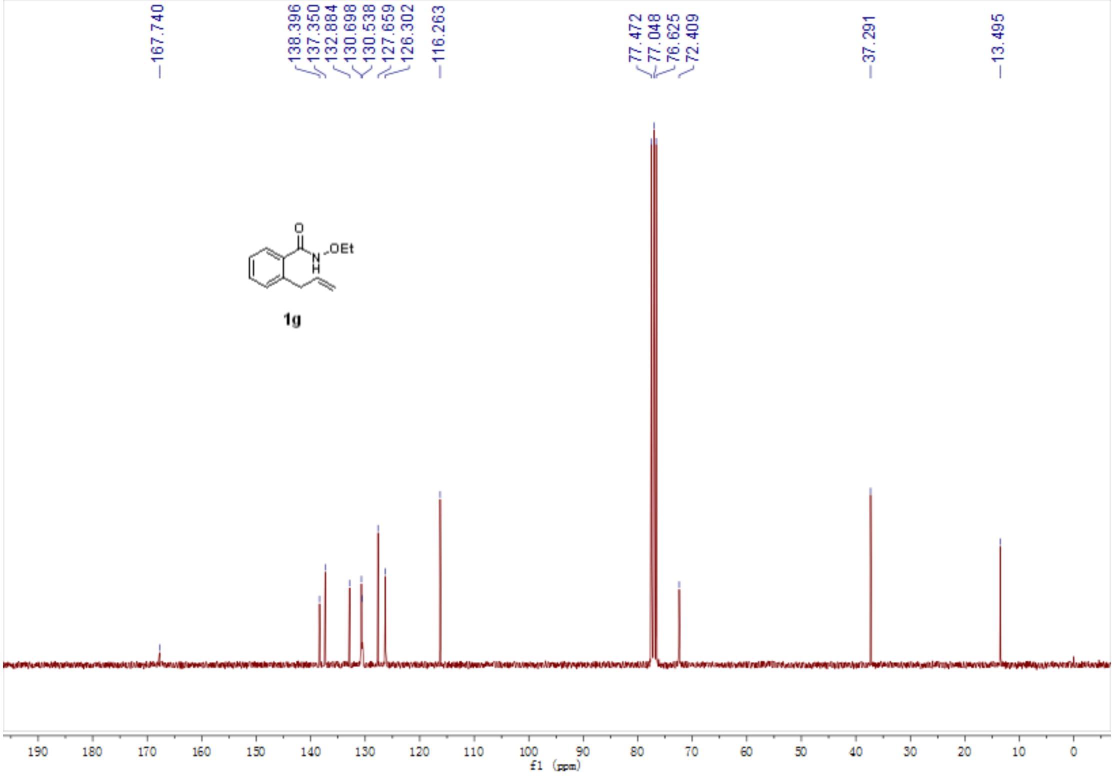

8.406
7.413
7.394
7.385
7.366
7.260
7.001
6.993
6.968
6.960
6.940
6.932
6.913
6.904
6.033
6.012
6.000
5.991
5.978
5.956
5.943
5.934
5.922
5.900
5.157
5.152
5.147
5.143
5.123
5.119
5.114
5.109
5.085
5.080
5.074
5.069
5.028
5.023
5.017
5.012
3.868
3.572
3.550
O
N
H
OMe
F
1e
0.95
0.98
1.99
1.00
2.01
2.99
1.98
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

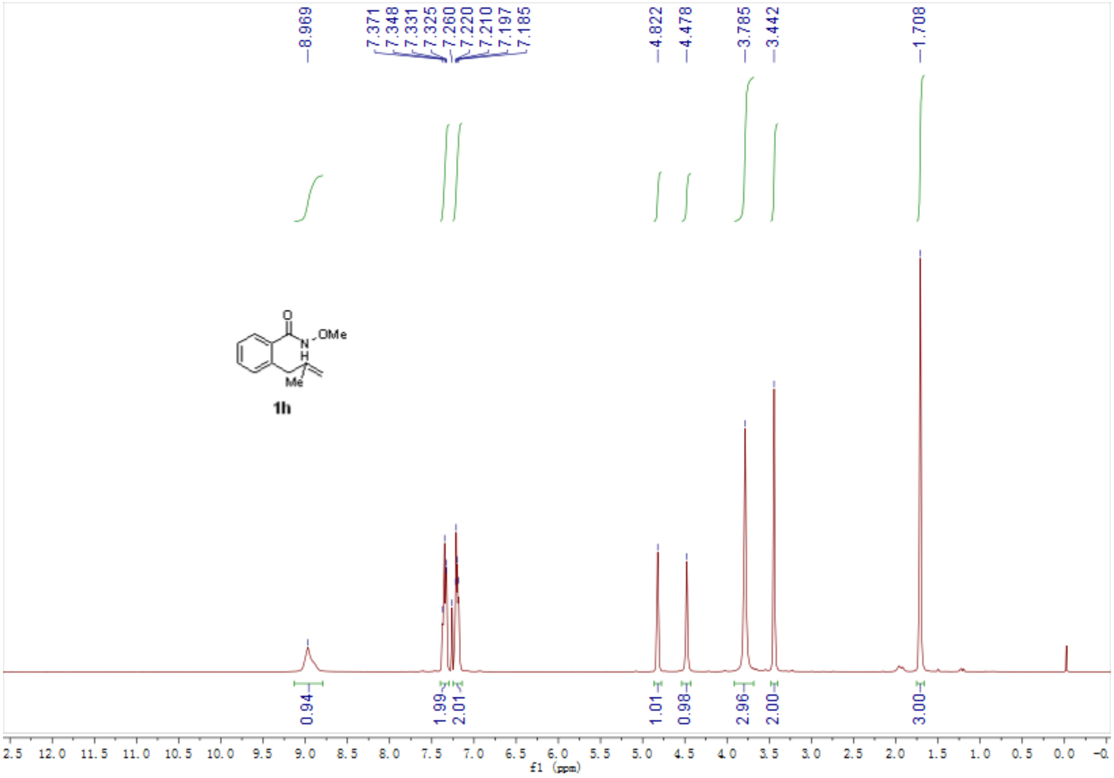

165.576
162.249
141.912
141.806
136.369
129.839
129.721
128.708
117.660
117.377
117.094
113.524
113.237
77.445
77.021
76.598
64.708
37.224
O
N
H
OMe
F
1e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

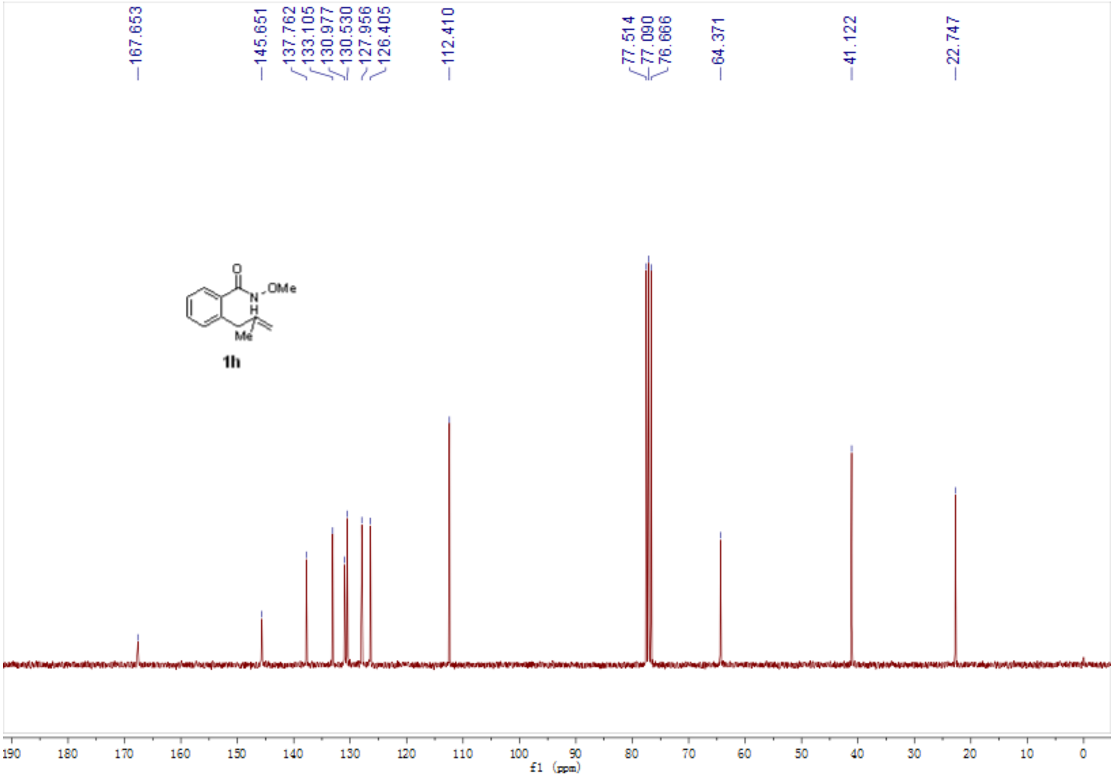

8.510
7.365
7.354
7.260
7.211
7.185
6.018
5.998
5.980
5.966
5.942
5.925
5.912
5.888
5.117
5.083
5.033
4.976
3.865
3.522
3.502
Cl
O
N
H
OMe
1f
0.97
1.94
1.02
1.00
2.03
3.00
2.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

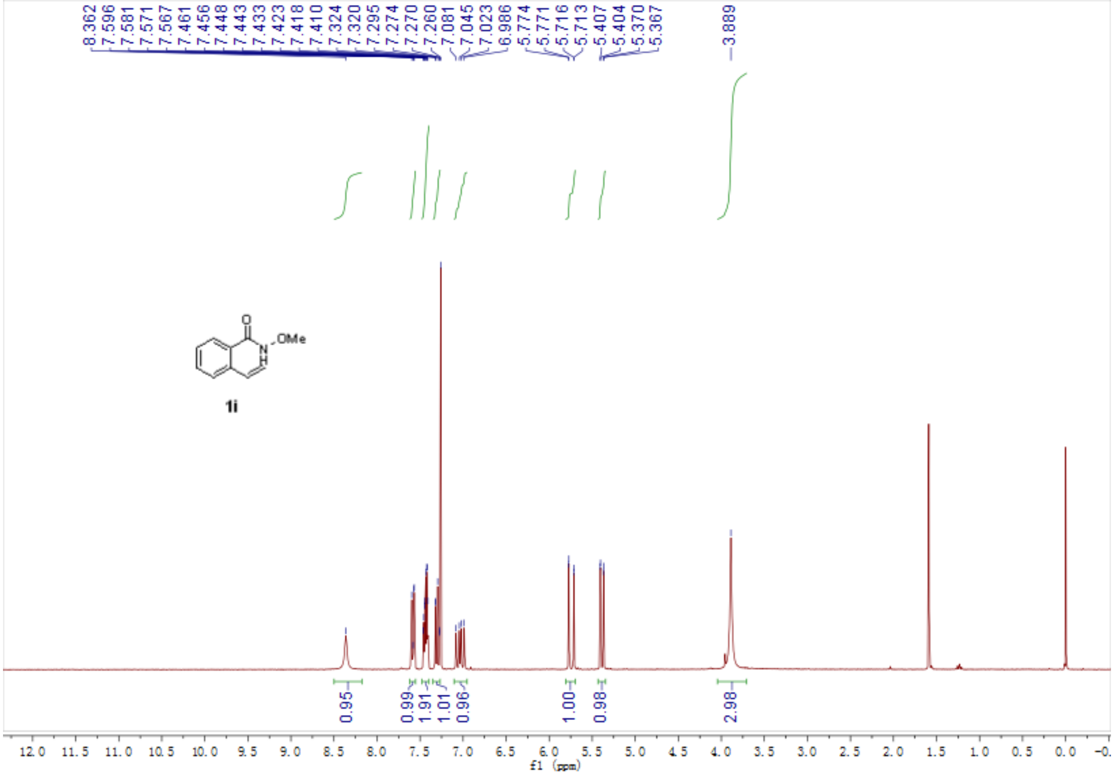

136.936
136.747
134.101
132.168
132.036
130.809
127.689
116.772
77.442
77.018
76.595
64.700
36.703
Cl
O
N
H
OMe
1f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

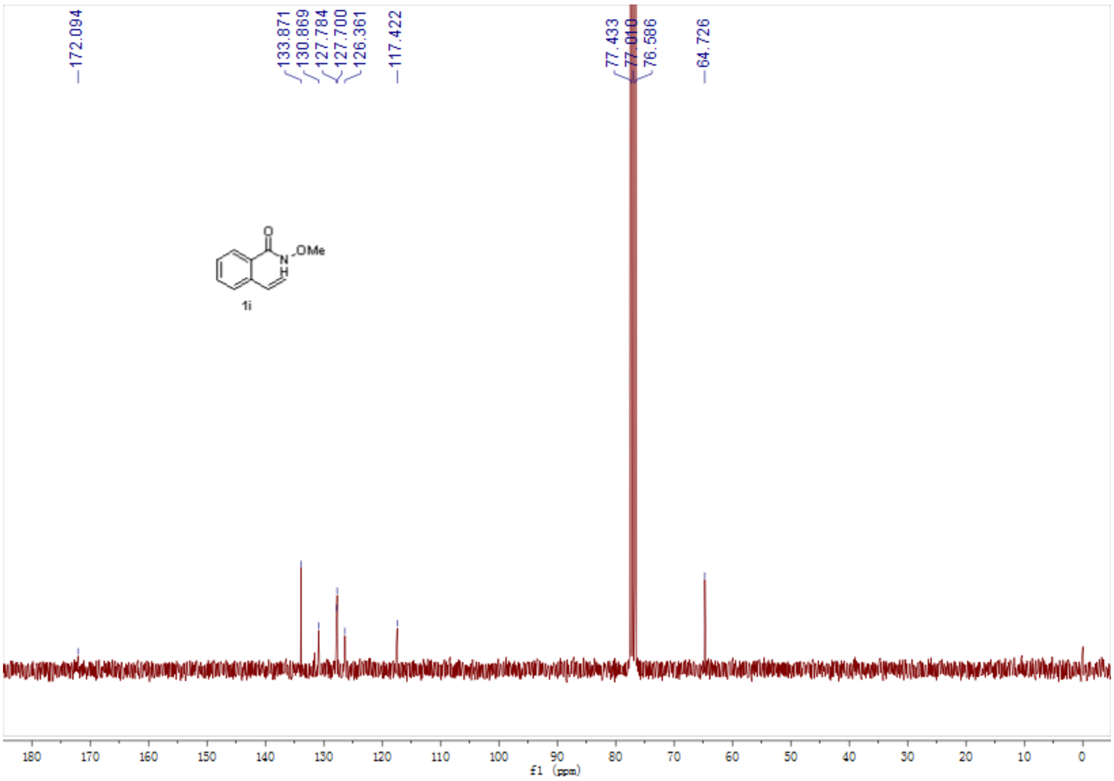

10.013
8.560
7.401
7.371
7.345
7.260
7.237
7.225
7.195
6.053
6.027
6.016
5.999
5.975
5.961
5.960
5.946
5.922
5.085
5.051
5.030
4.973
4.071
4.054
3.549
3.529
1.308
O
N
H
OEt
1g
0.99
2.04
2.28
1.00
2.04
2.01
2.04
3.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

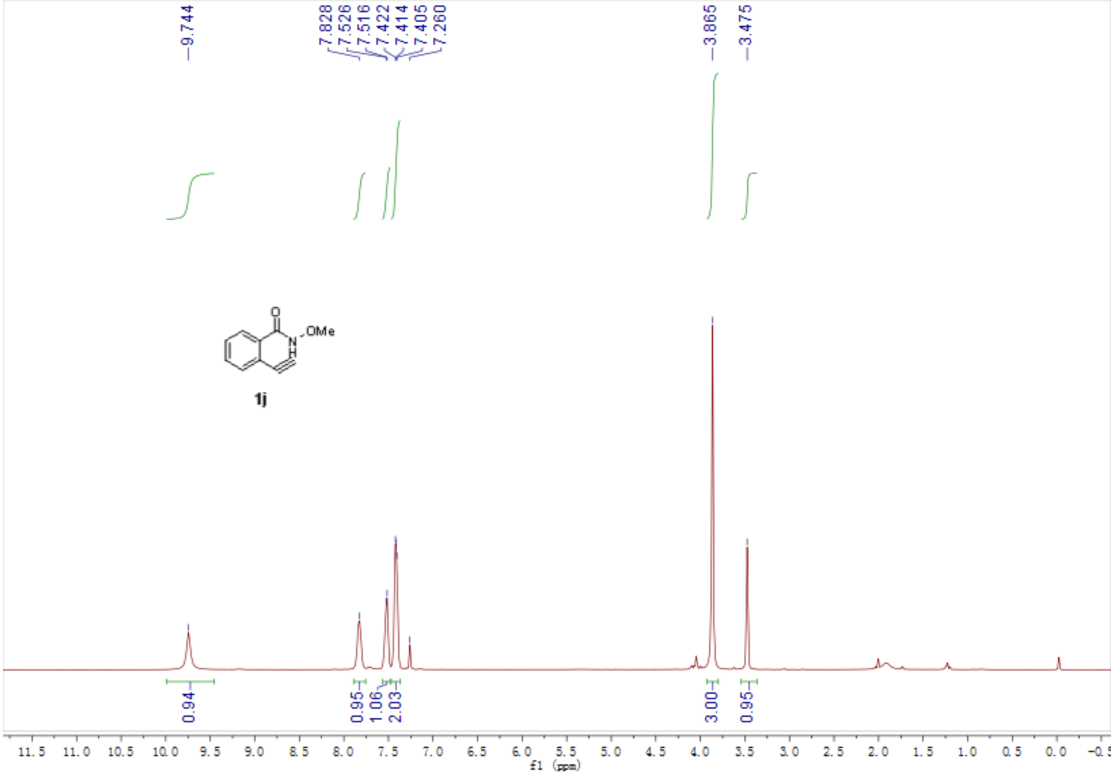

167.740
138.396
137.350
132.884
130.698
130.538
127.659
126.302
116.263
77.472
77.048
76.625
72.409
37.291
13.495
O
N
H
OEt
1g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

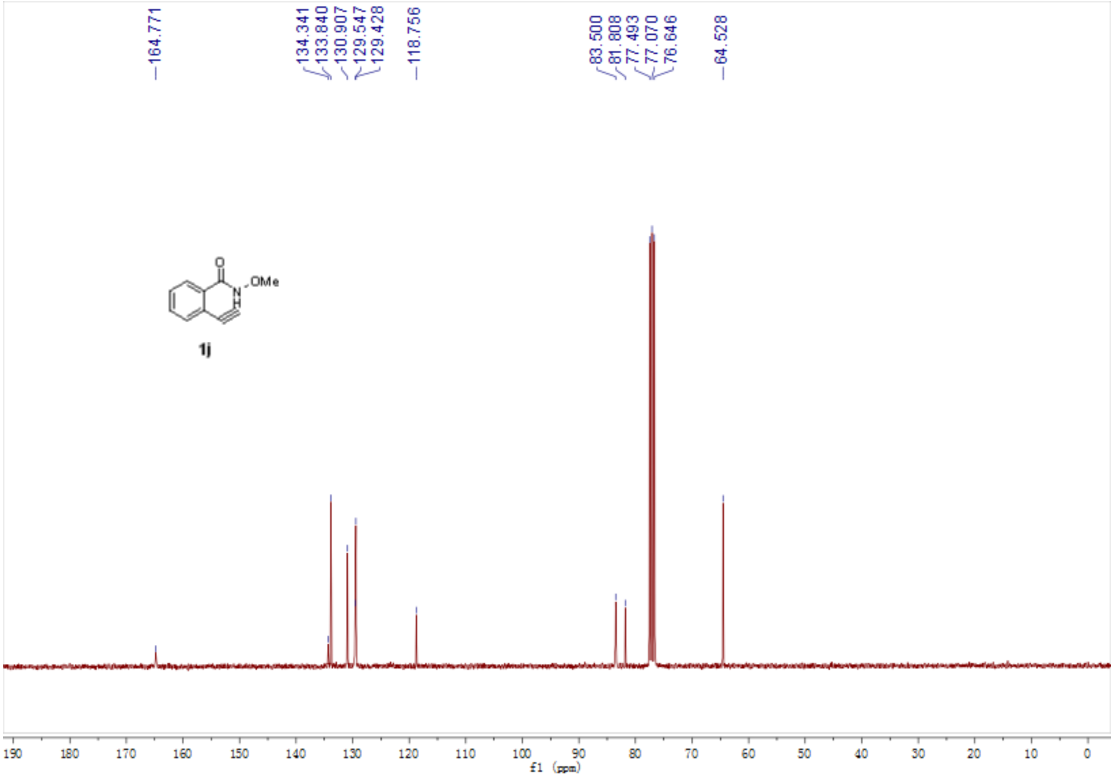

8.969
7.371
7.348
7.331
7.325
7.260
7.220
7.210
7.197
7.185
4.822
4.478
3.785
3.442
1.708
O
N
H
OMe
Me
1h
0.94
1.99
2.01
1.01
0.98
2.96
2.00
3.00
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

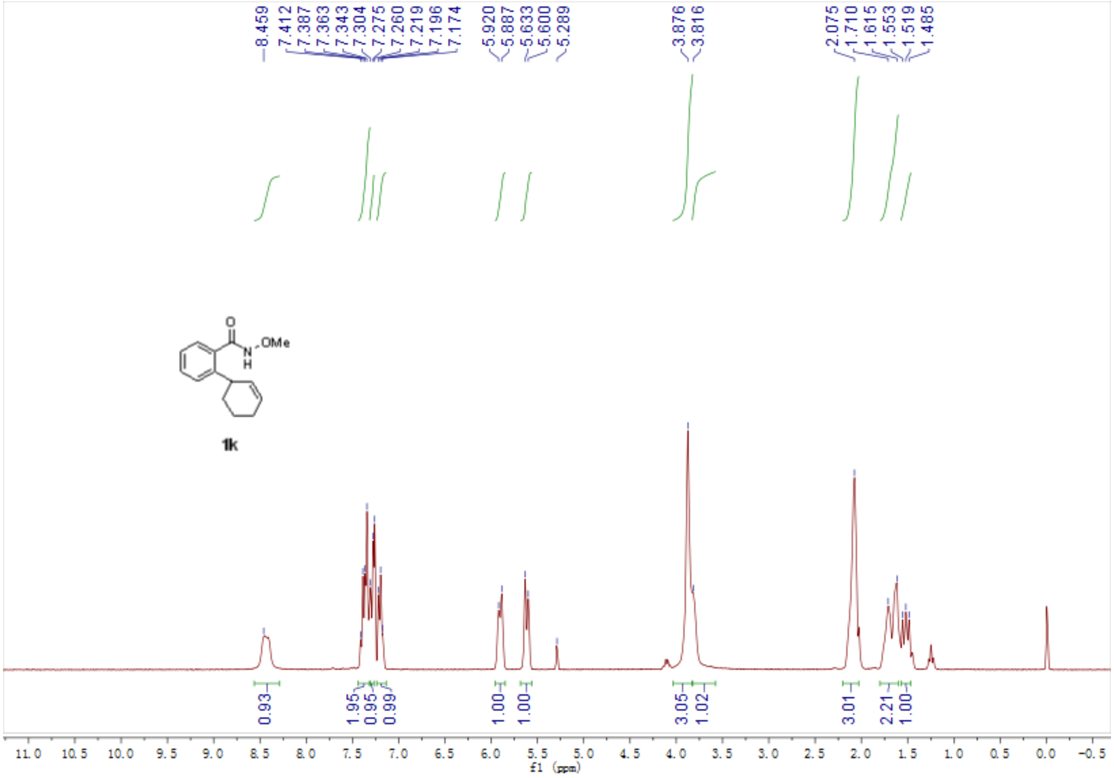

167.653
145.651
137.762
133.105
130.977
130.530
127.956
126.405
112.410
77.514
77.090
76.666
64.371
41.122
22.747
O
N
H
OMe
Me
1h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

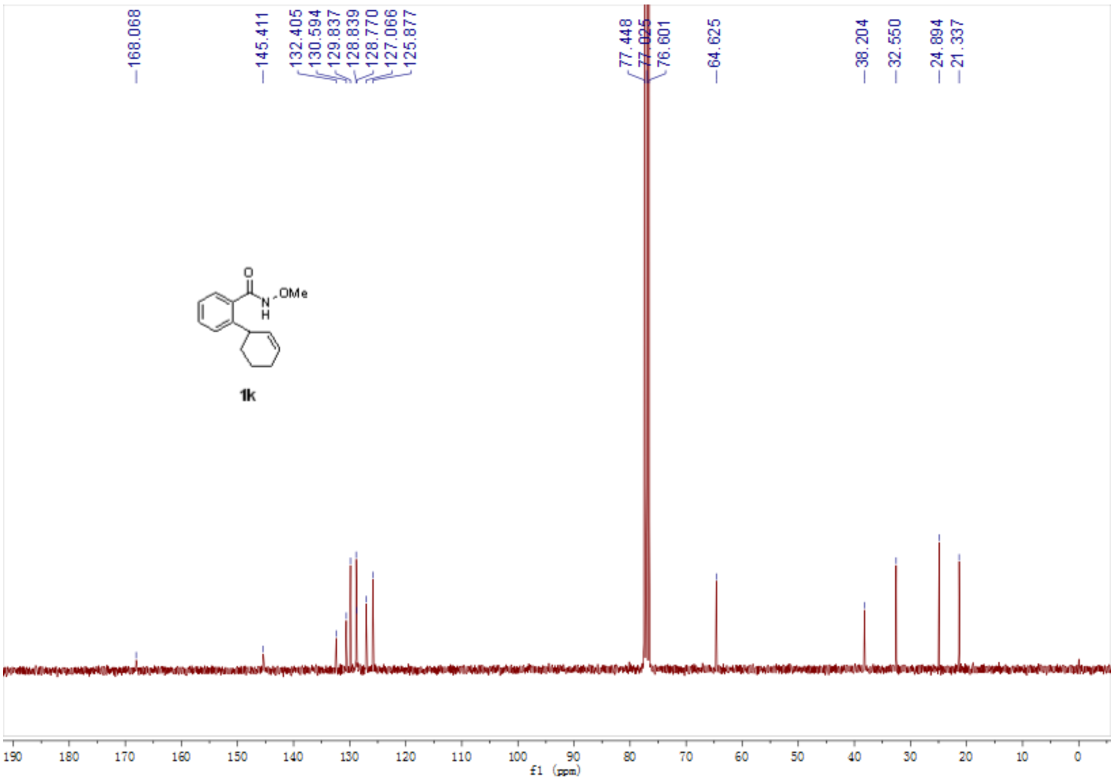

8.362
7.596
7.581
7.571
7.567
7.461
7.456
7.448
7.443
7.433
7.423
7.418
7.410
7.324
7.320
7.295
7.274
7.270
7.260
7.081
7.045
7.023
6.986
5.774
5.771
5.716
5.713
5.407
5.404
5.370
5.367
3.889
OMe
N
H
O
1i
0.95
0.99
1.91
1.01
0.96
1.00
0.98
2.98
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

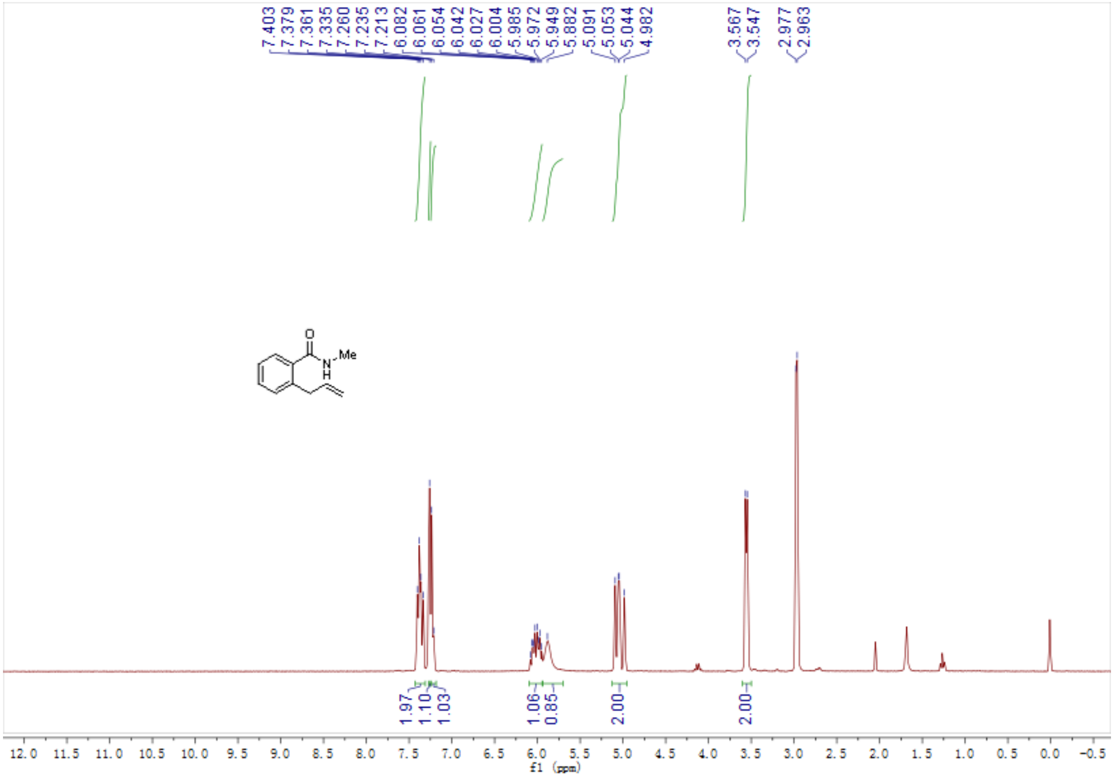

172.094
133.871
130.869
127.784
127.700
126.361
117.422
77.433
77.010
76.586
64.726
OMe
N
H
O
1i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

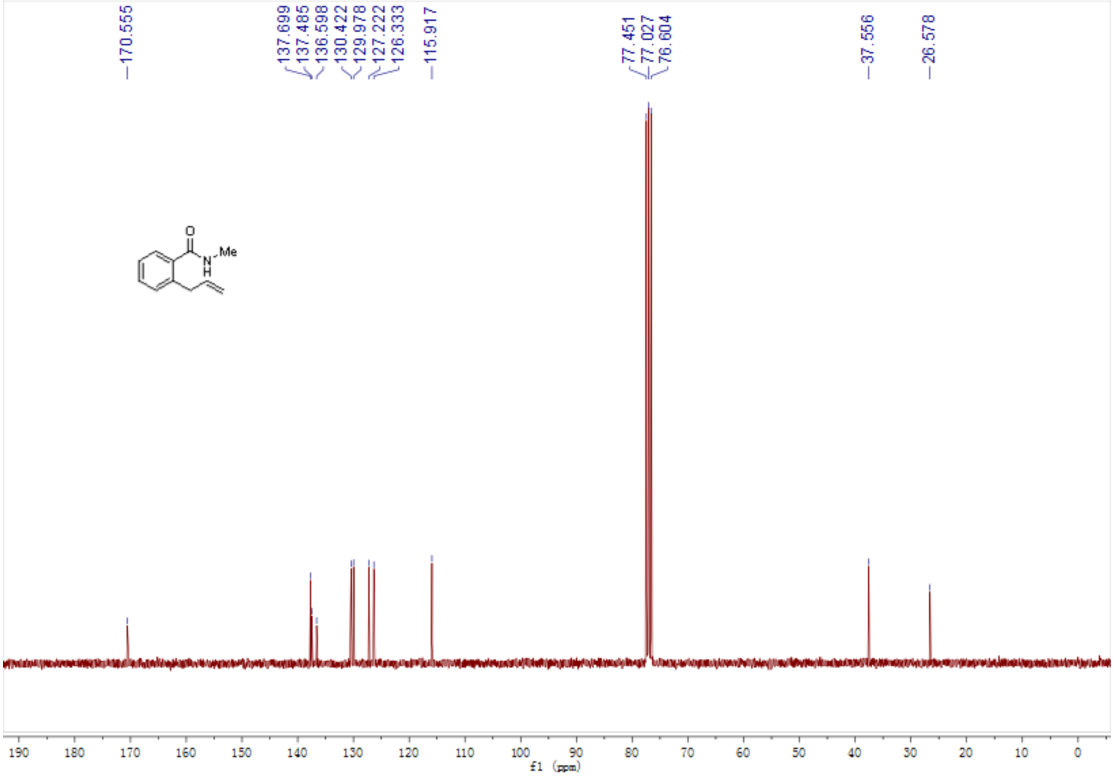

9.744
7.828
7.526
7.516
7.422
7.414
7.405
7.260
3.865
3.475
OMe
N
H
O
1j
0.94
0.95
1.06
2.03
3.00
0.95
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

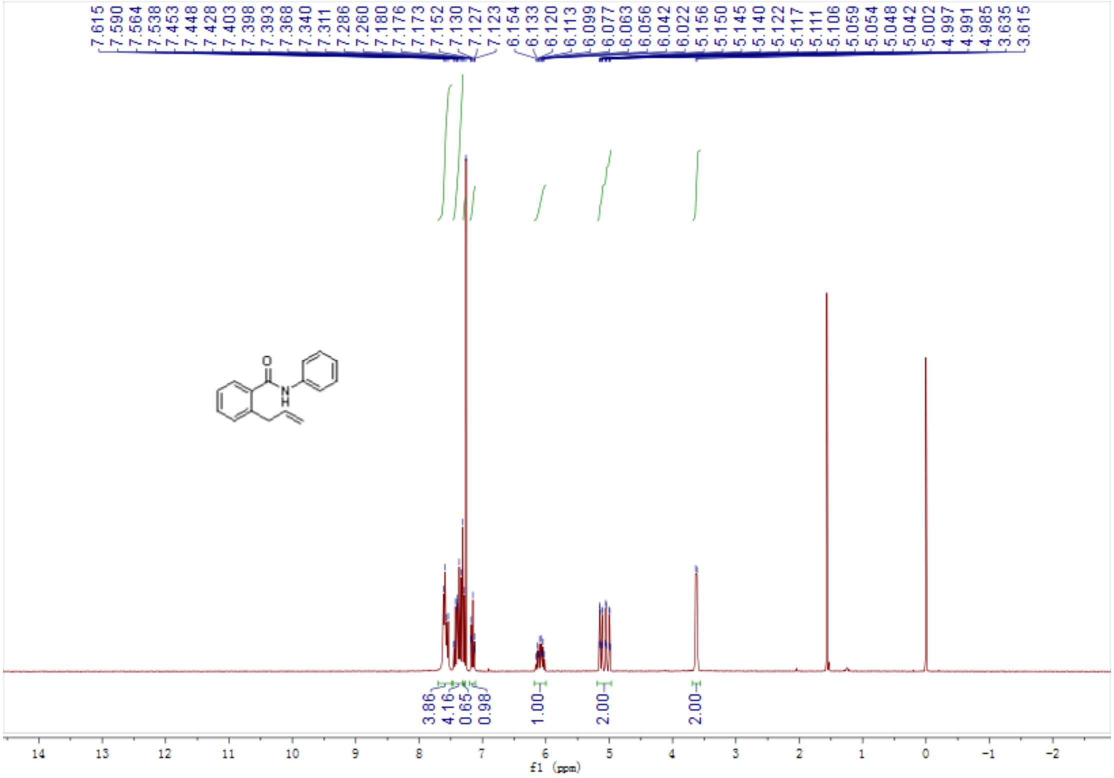

164.771
134.341
133.840
130.907
129.547
129.428
118.756
83.500
81.808
77.493
77.070
76.646
64.528
OMe
N
H
O
1j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

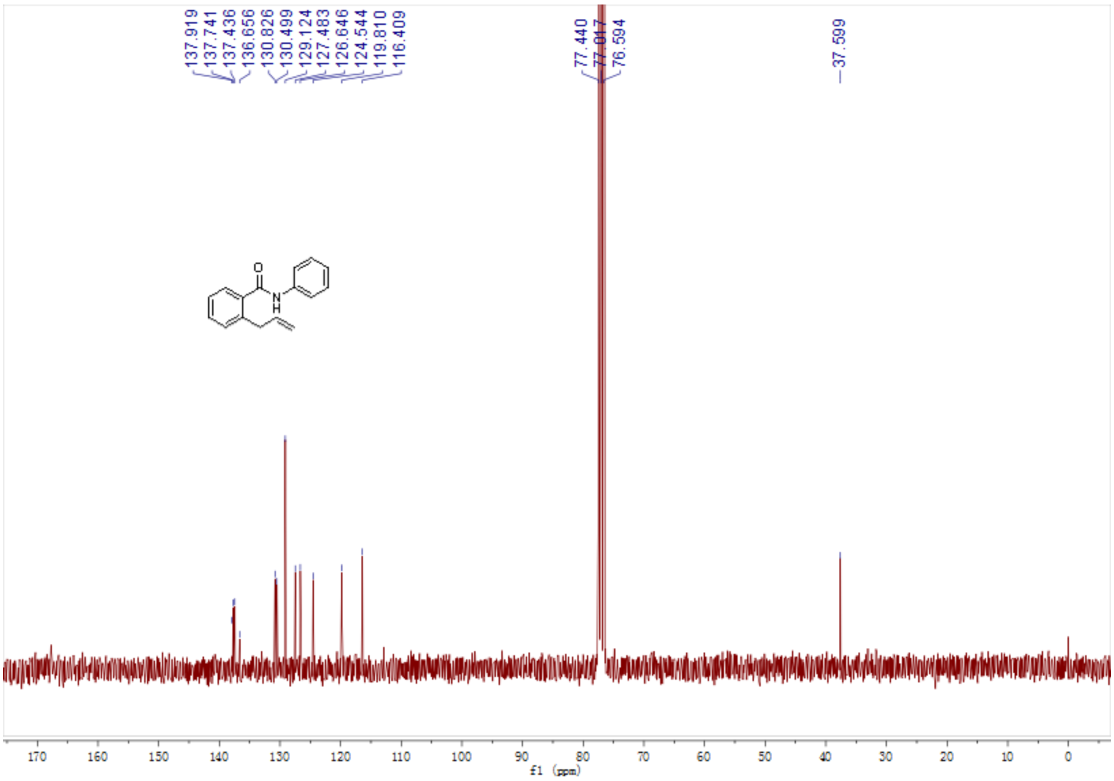

8.459
7.412
7.387
7.363
7.343
7.304
7.275
7.260
7.219
7.196
7.174
5.920
5.887
5.633
5.600
5.289
3.876
3.816
2.075
1.710
1.615
1.553
1.519
1.485
O
N
OMe
H
1k
0.93
1.95
0.95
0.99
1.00
1.00
3.05
1.02
3.01
2.21
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

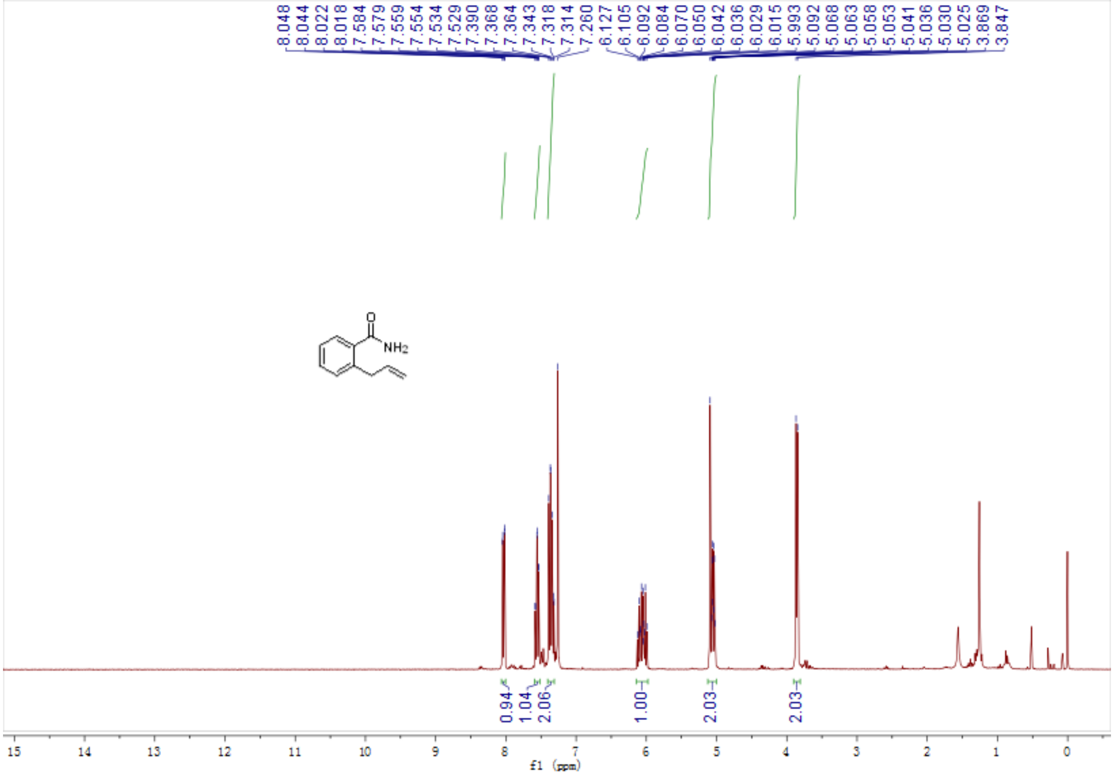

168.068
145.411
132.405
130.594
129.837
128.839
128.770
127.066
125.877
77.448
77.025
76.601
64.625
38.204
32.550
24.894
21.337
O
N
OMe
H
1k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

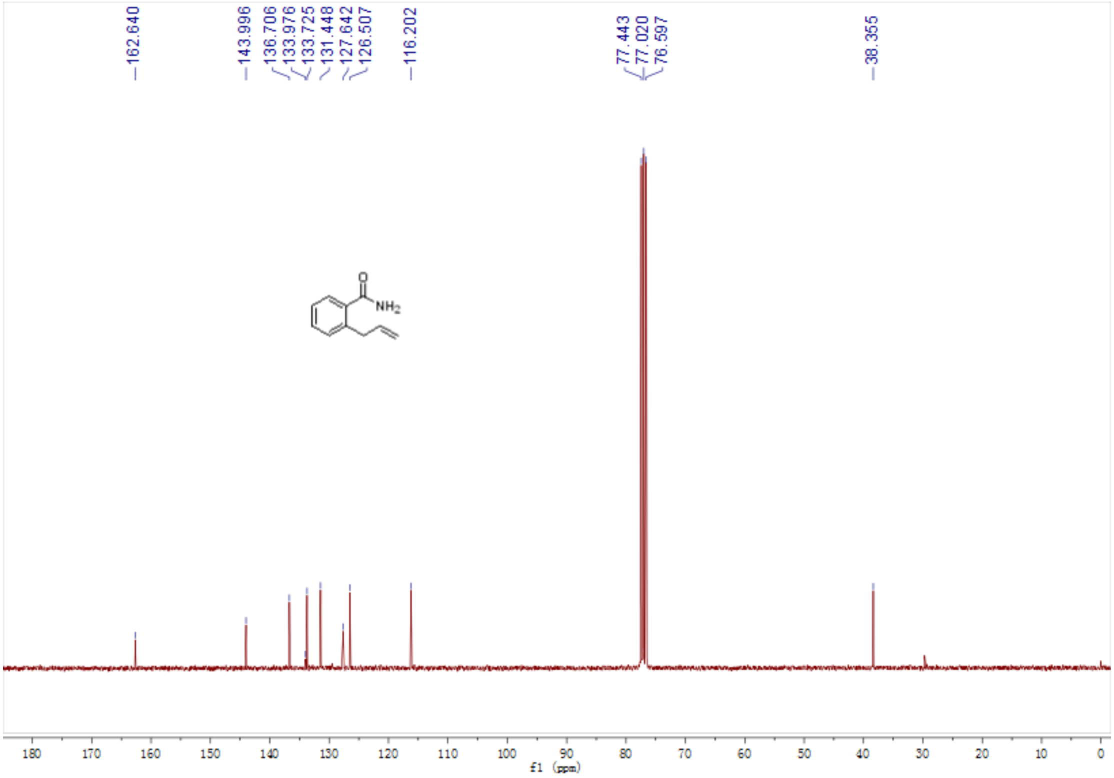

7.403
7.379
7.361
7.335
7.260
7.235
7.213
6.082
6.061
6.054
6.042
6.027
6.004
5.985
5.972
5.949
5.882
5.091
5.053
5.044
4.982
3.567
3.547
2.977
2.963
O
N
H
Me
1.97
1.10
1.03
1.06
0.85
2.00
2.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

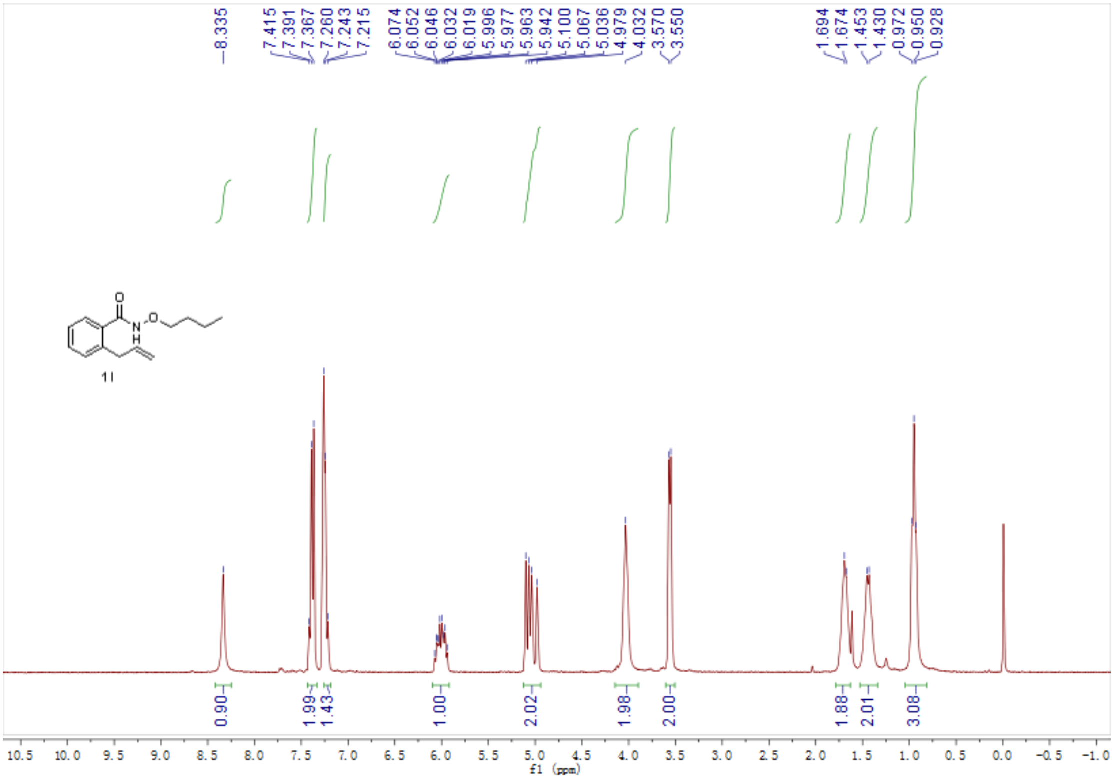

170.555
137.699
137.485
136.598
130.422
129.978
127.222
126.333
115.917
77.451
77.027
76.604
37.556
26.578
O
N
H
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

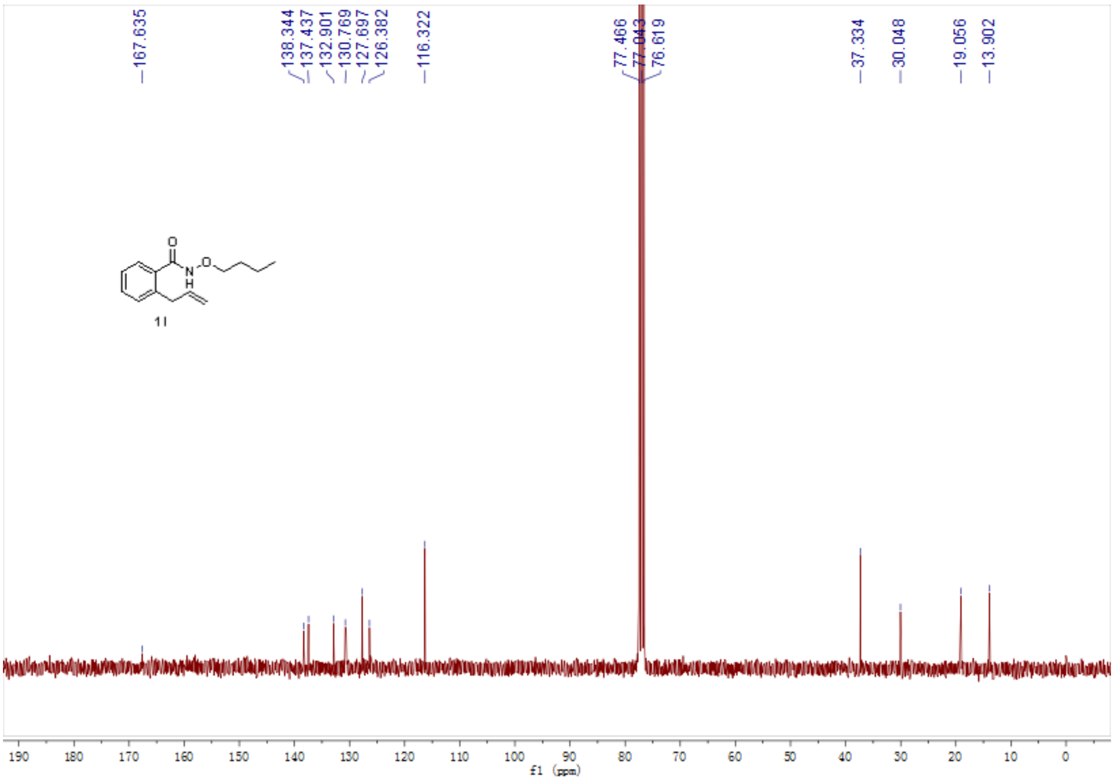

7.615
7.590
7.564
7.538
7.453
7.448
7.428
7.403
7.398
7.393
7.368
7.340
7.311
7.286
7.260
7.180
7.176
7.173
7.152
7.130
7.127
7.123
6.154
6.133
6.120
6.113
6.099
6.077
6.063
6.056
6.042
6.022
5.156
5.150
5.145
5.140
5.122
5.117
5.111
5.106
5.059
5.054
5.048
5.042
5.002
4.997
4.991
4.985
3.635
3.615
O
N
H
3.86
4.16
0.65
0.98
1.00
2.00
2.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)

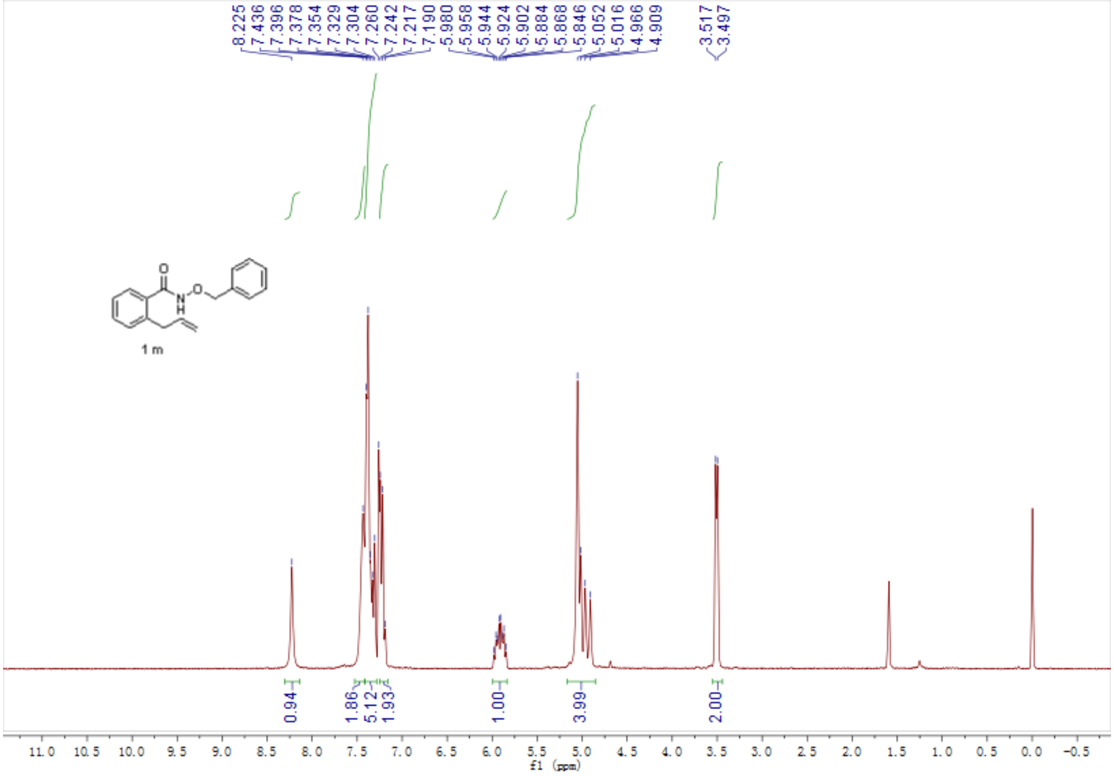

137.919
137.741
137.436
136.656
130.826
130.499
129.124
127.483
126.646
124.544
119.810
116.409
77.440
77.017
76.594
37.599
O
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

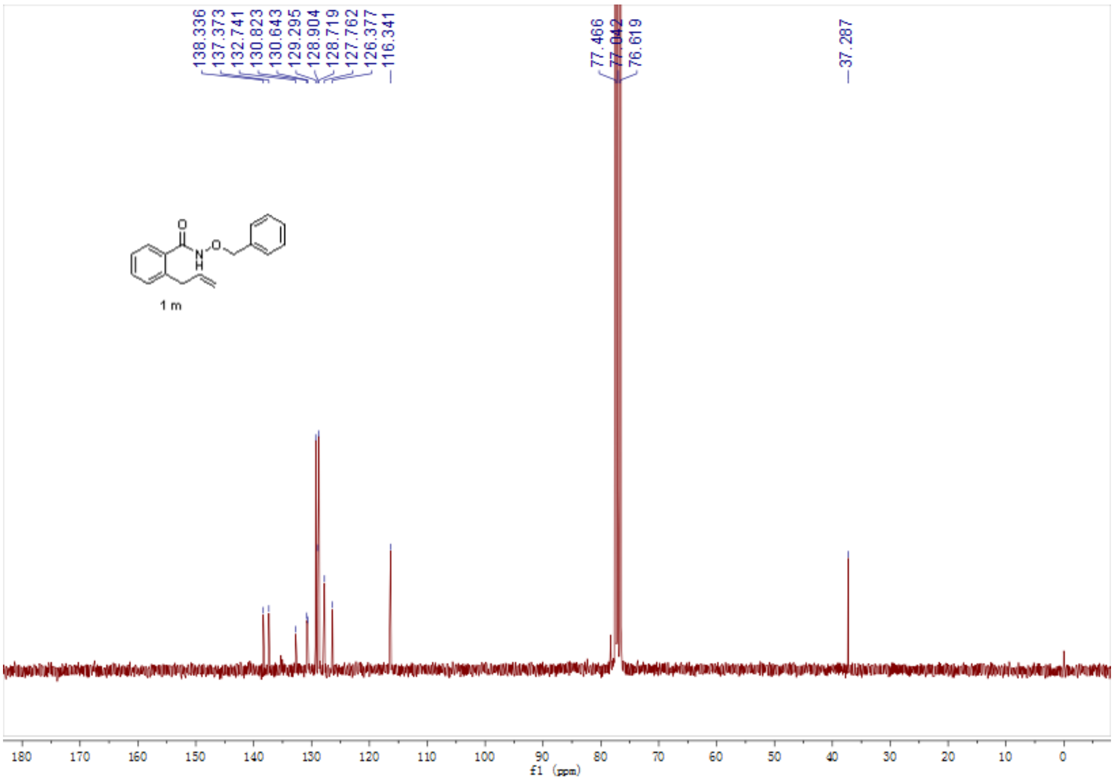

8.048
8.044
8.022
8.018
7.584
7.579
7.559
7.554
7.534
7.529
7.390
7.368
7.364
7.343
7.318
7.314
7.260
6.127
6.105
6.092
6.084
6.070
6.050
6.042
6.036
6.029
6.015
5.993
5.092
5.068
5.063
5.058
5.053
5.041
5.036
5.030
5.025
3.869
3.847
O
NH2
0.94
1.04
2.06
1.00
2.03
2.03
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

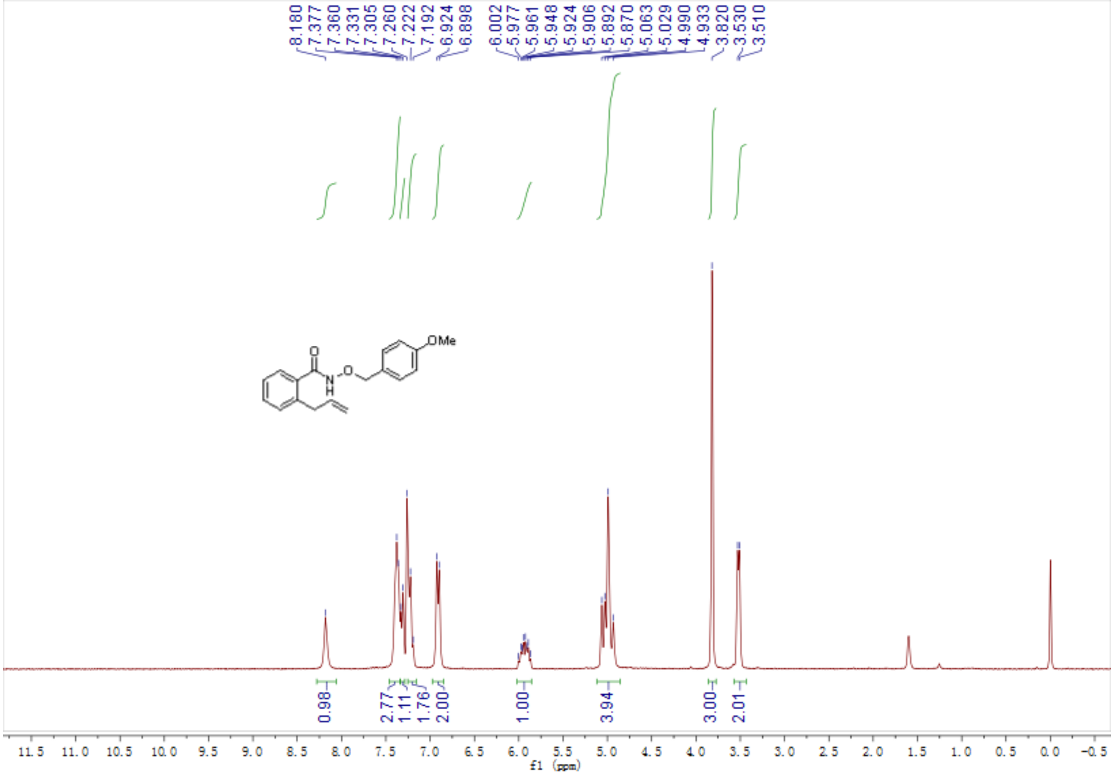

162.640
143.996
136.706
133.976
133.725
131.448
127.642
126.507
116.202
77.443
77.020
76.597
38.355
O
NH2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

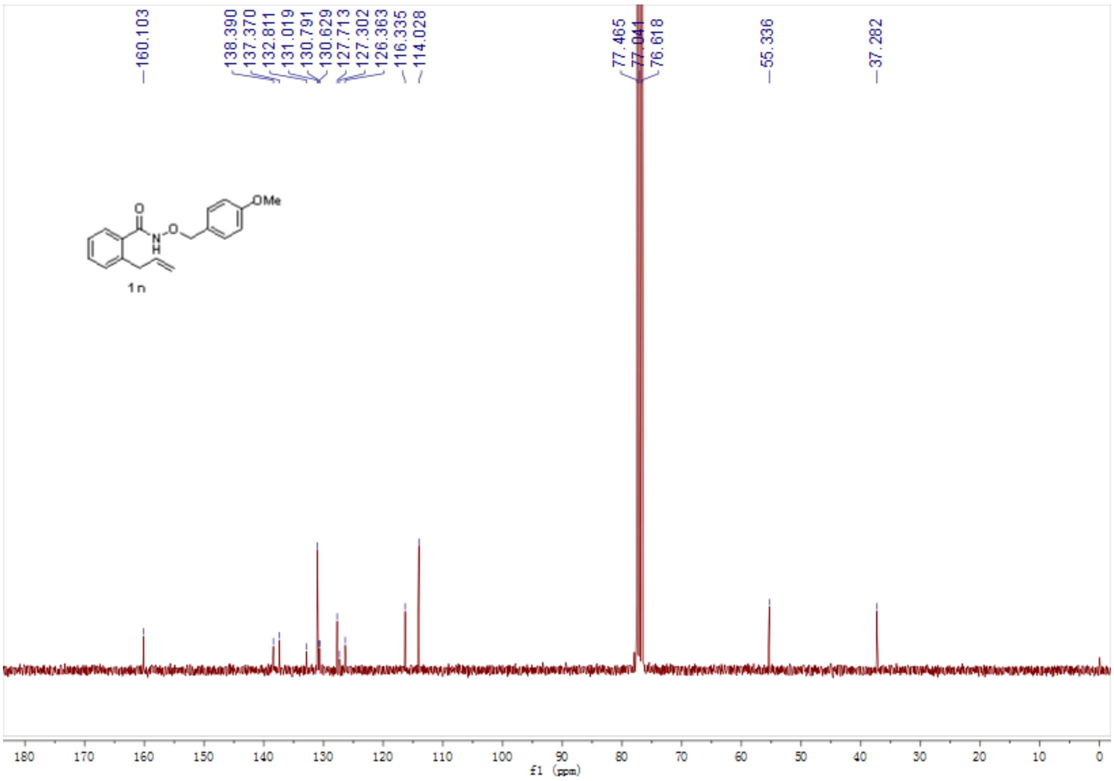

8.335
7.415
7.391
7.367
7.260
7.243
7.215
6.074
6.052
6.046
6.032
6.019
5.996
5.977
5.963
5.942
5.100
5.067
5.036
4.979
4.032
3.570
3.550
1.694
1.674
1.453
1.430
0.972
0.950
0.928
O
N
H
O
1l
0.90
1.99
1.43
1.00
2.02
1.98
2.00
1.88
2.01
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

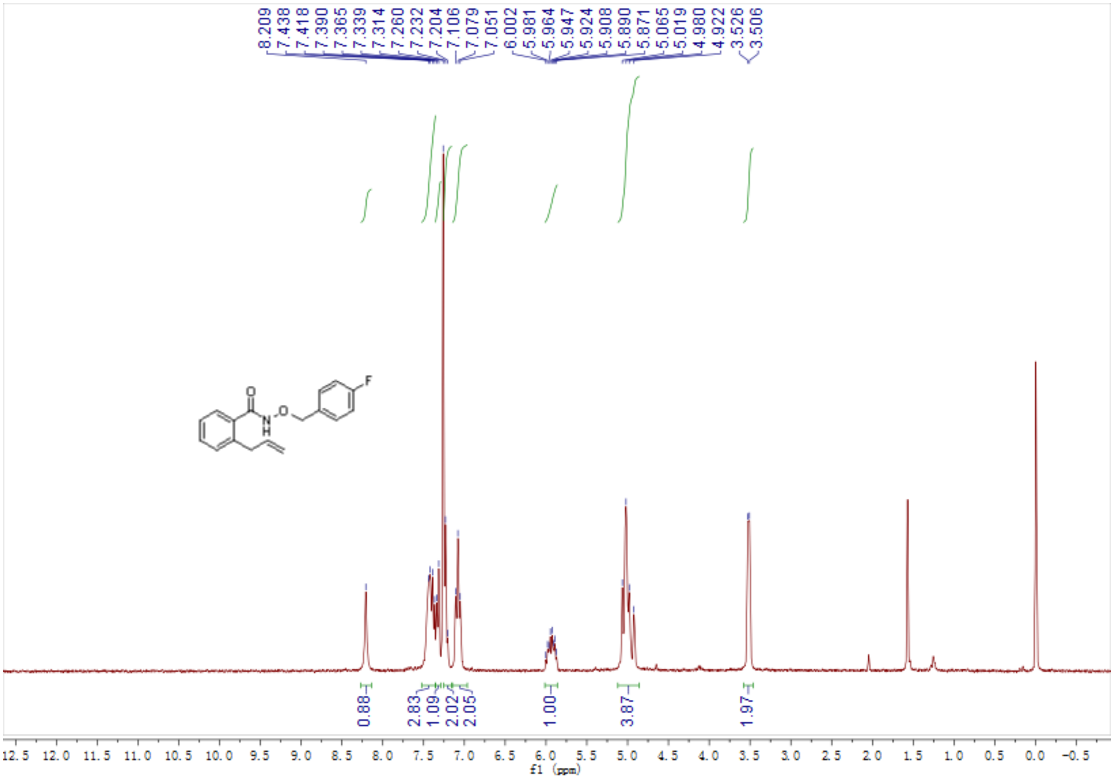

167.635
138.344
137.437
132.901
130.769
127.697
126.382
116.322
77.466
77.043
76.619
37.334
30.048
19.056
13.902
O
N
H
O
1l
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

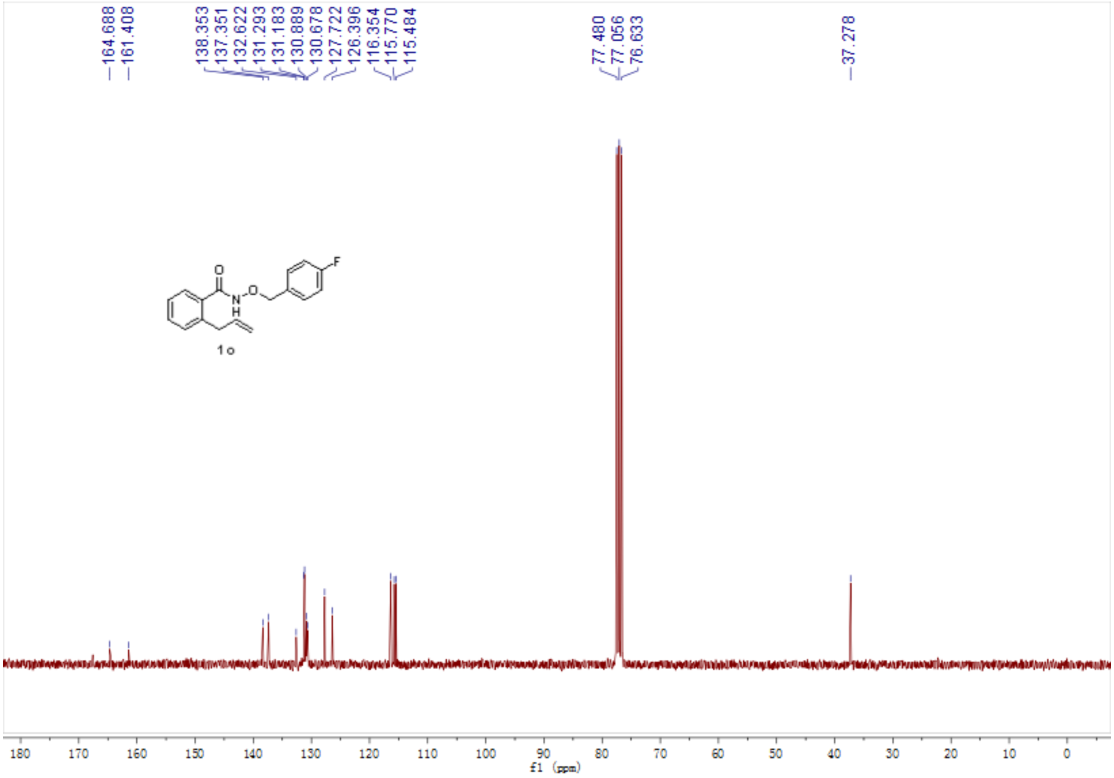

8.225
7.436
7.396
7.378
7.354
7.329
7.304
7.260
7.242
7.217
7.190
5.980
5.958
5.944
5.924
5.902
5.884
5.868
5.846
5.052
5.016
4.966
4.909
3.517
3.497
O
N
H
O
1 m
0.94
1.86
5.12
1.93
1.00
3.99
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

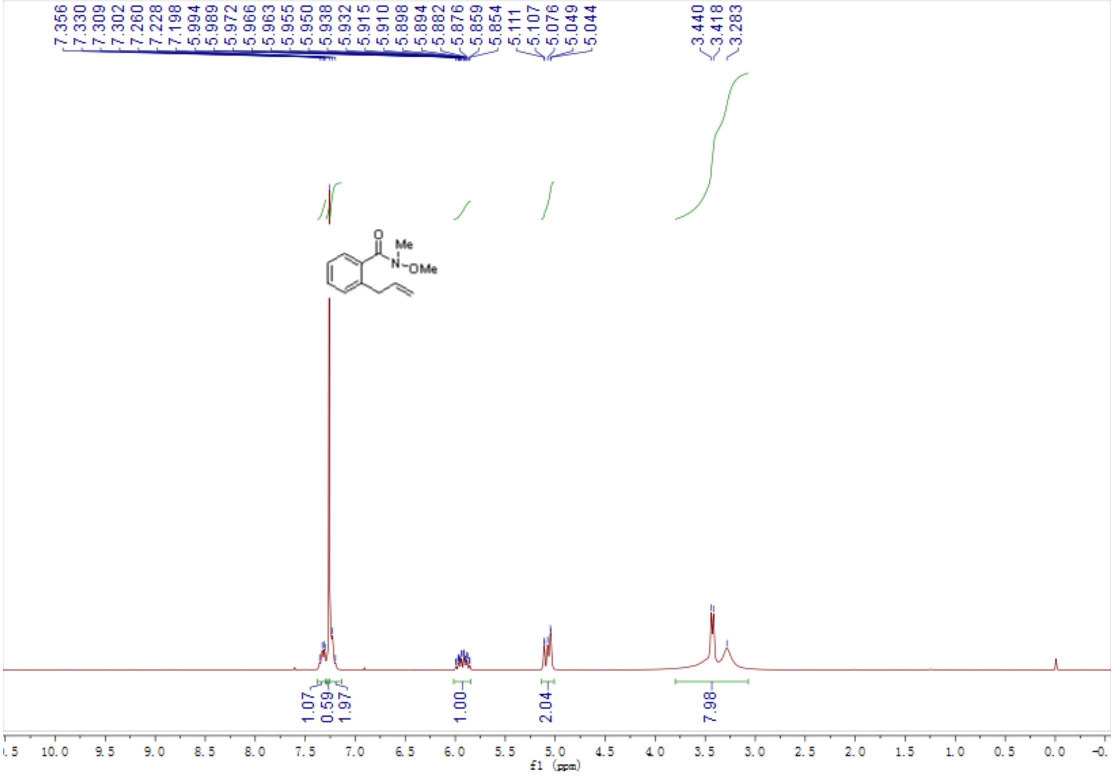

138.336
137.373
132.741
130.823
130.643
129.295
128.904
128.719
127.762
126.377
116.341
77.466
77.042
76.619
37.287
O
N
H
O
1 m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

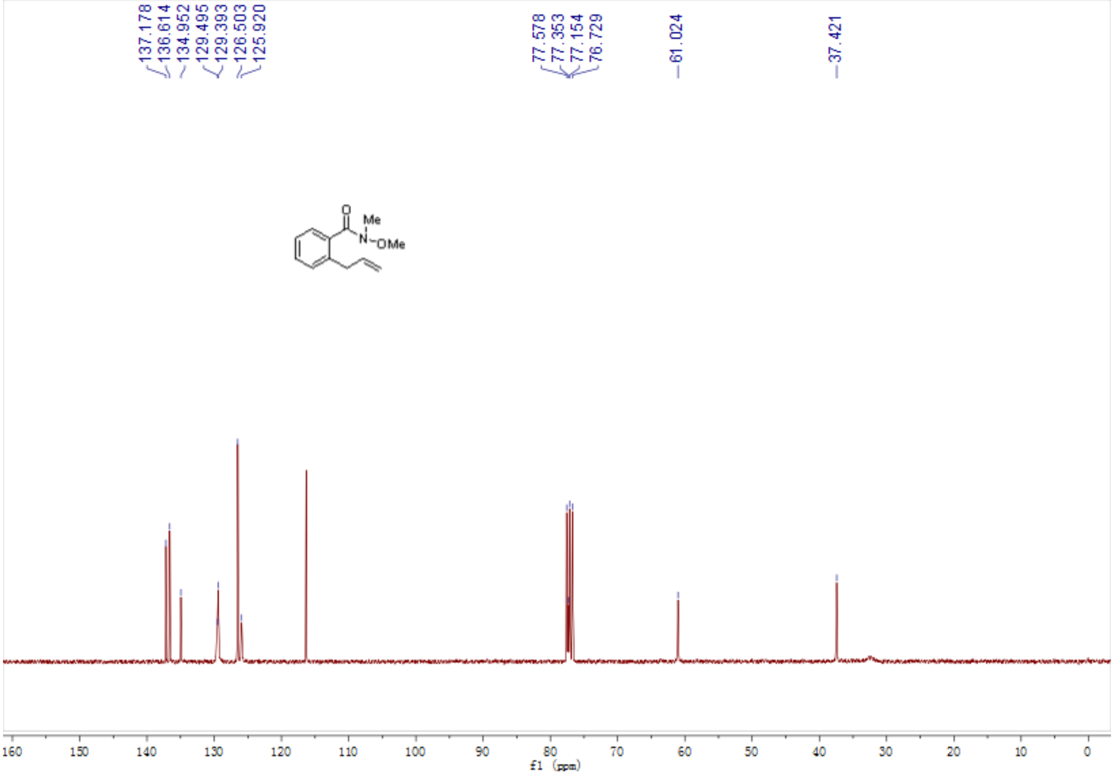

8.180
7.377
7.360
7.331
7.305
7.260
7.222
7.192
6.924
6.898
6.002
5.977
5.961
5.948
5.924
5.906
5.892
5.870
5.063
5.029
4.990
4.933
3.820
3.530
3.510
O
N
H
O
OMe
0.98
2.77
1.11
1.76
2.00
1.00
3.94
3.00
2.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


160.103
138.390
137.370
132.811
131.019
130.791
130.629
127.713
127.302
126.363
116.335
114.028
77.465
77.041
76.618
55.336
37.282
O
N
H
O
OMe
1n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

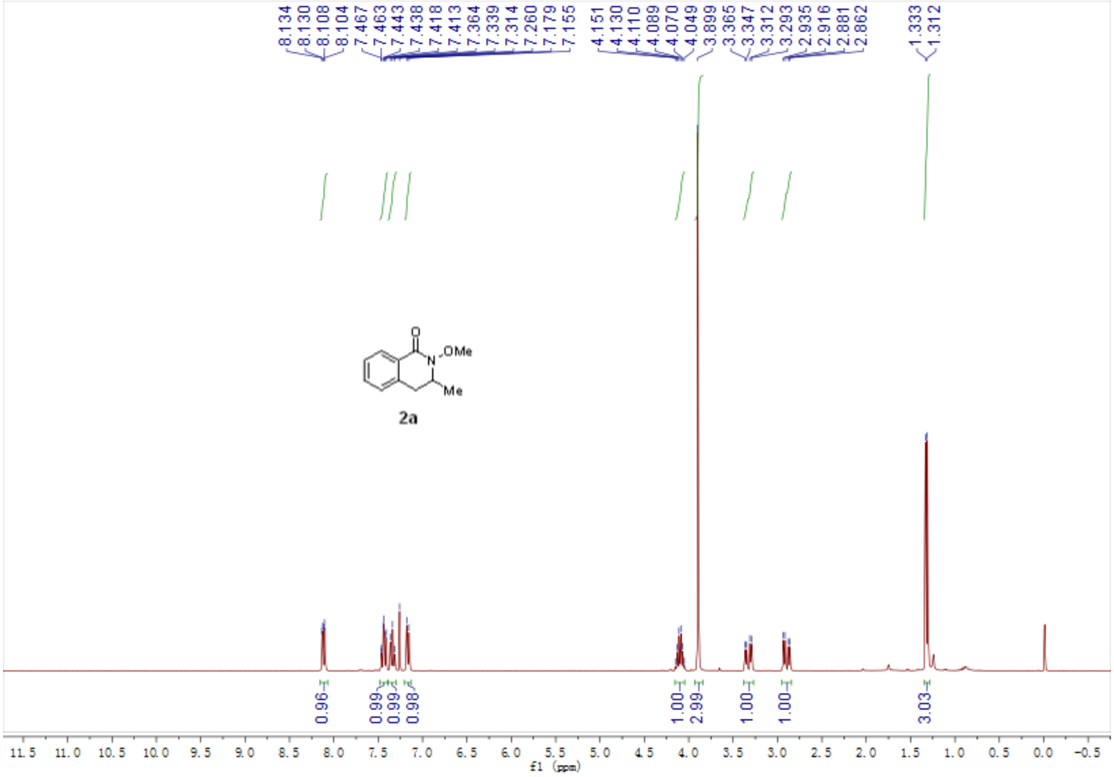

8.209
7.438
7.418
7.390
7.365
7.339
7.314
7.260
7.232
7.204
7.106
7.079
7.051
6.002
5.981
5.964
5.947
5.924
5.908
5.890
5.871
5.065
5.019
4.980
4.922
3.526
3.506
O
N
H
O
F
0.88
2.83
1.09
2.02
2.05
1.00
3.87
1.97
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

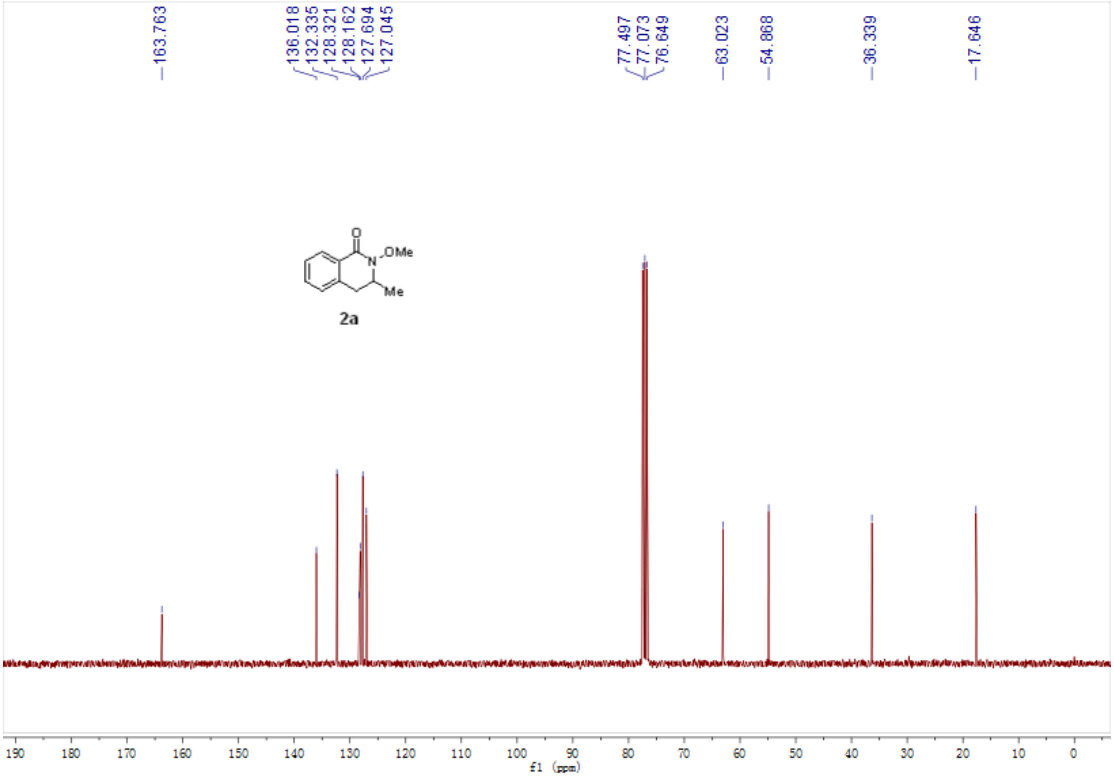

164.688
161.408
138.353
137.351
132.622
131.293
131.183
130.889
130.678
127.722
126.396
116.354
115.770
115.484
77.480
77.056
76.633
37.278
O
N
H
O
F
1o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

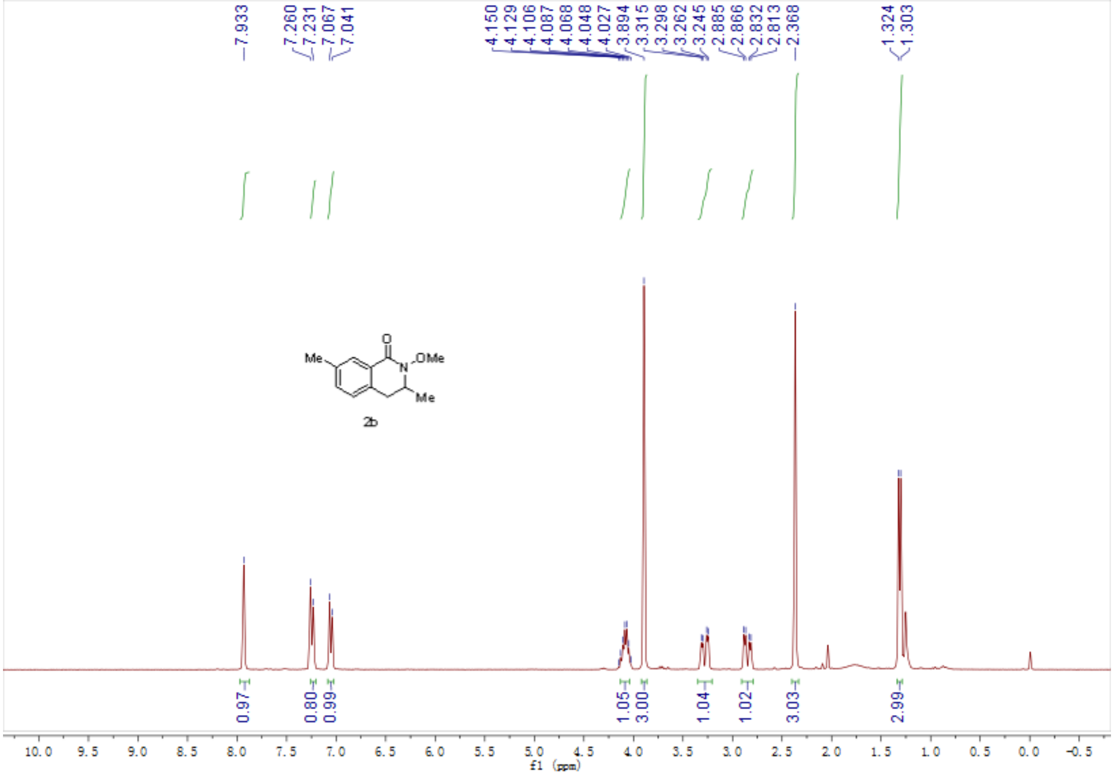

7.356
7.330
7.309
7.302
7.260
7.228
7.198
5.994
5.989
5.972
5.966
5.963
5.955
5.950
5.938
5.932
5.915
5.910
5.898
5.894
5.882
5.876
5.859
5.854
5.111
5.107
5.076
5.049
5.044
3.440
3.418
3.283
O
Me
N
OMe
1.07
0.59
1.97
1.00
2.04
7.98
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

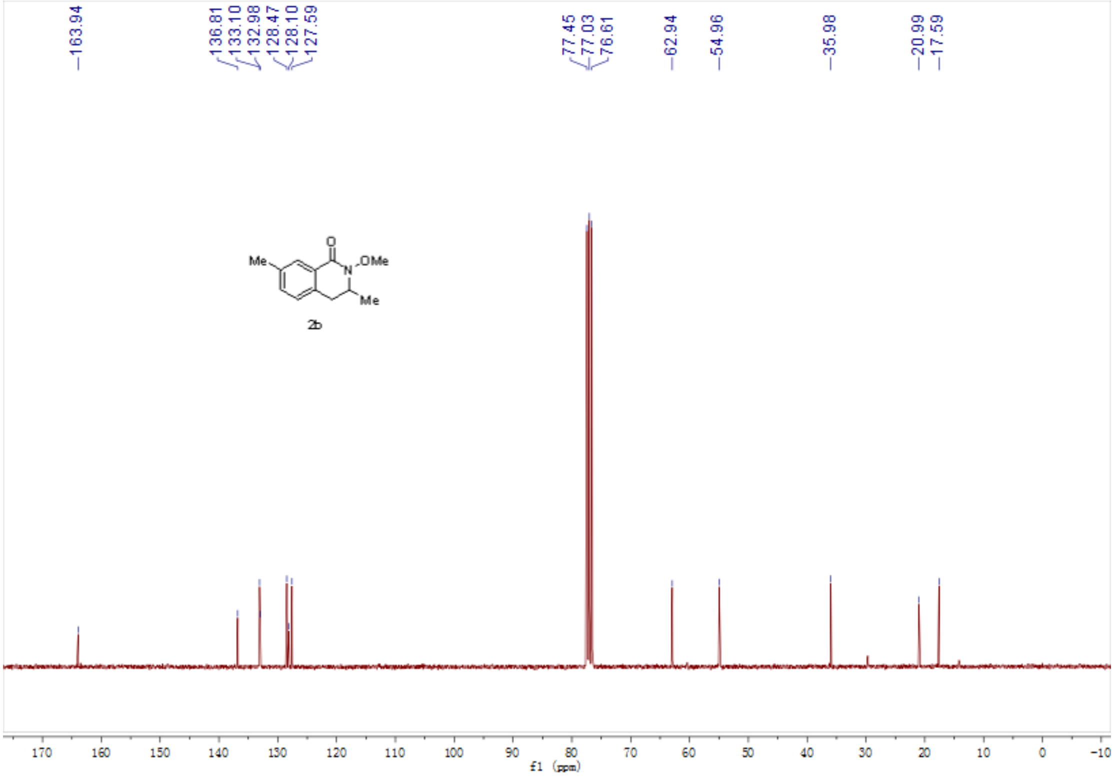

137.178
136.614
134.952
129.495
129.393
126.503
125.920
77.578
77.353
77.154
76.729
61.024
37.421
O
Me
N
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

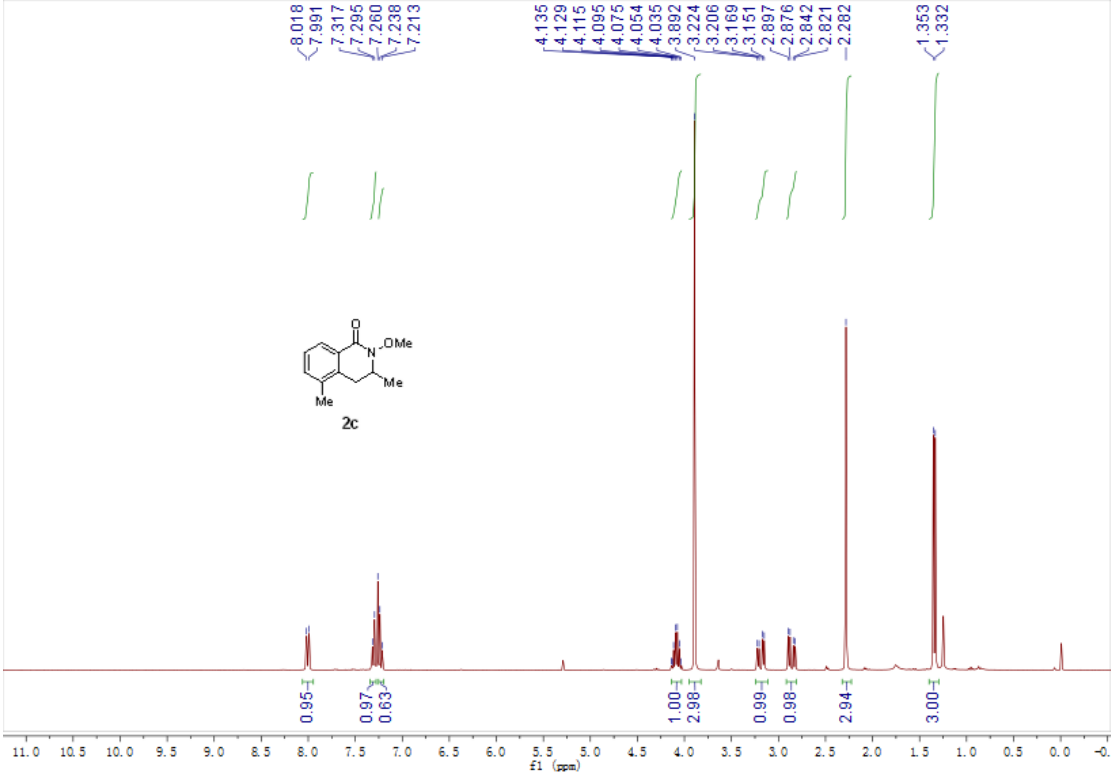
^{1}H NMR, ^{13}C NMR spectra of Products:

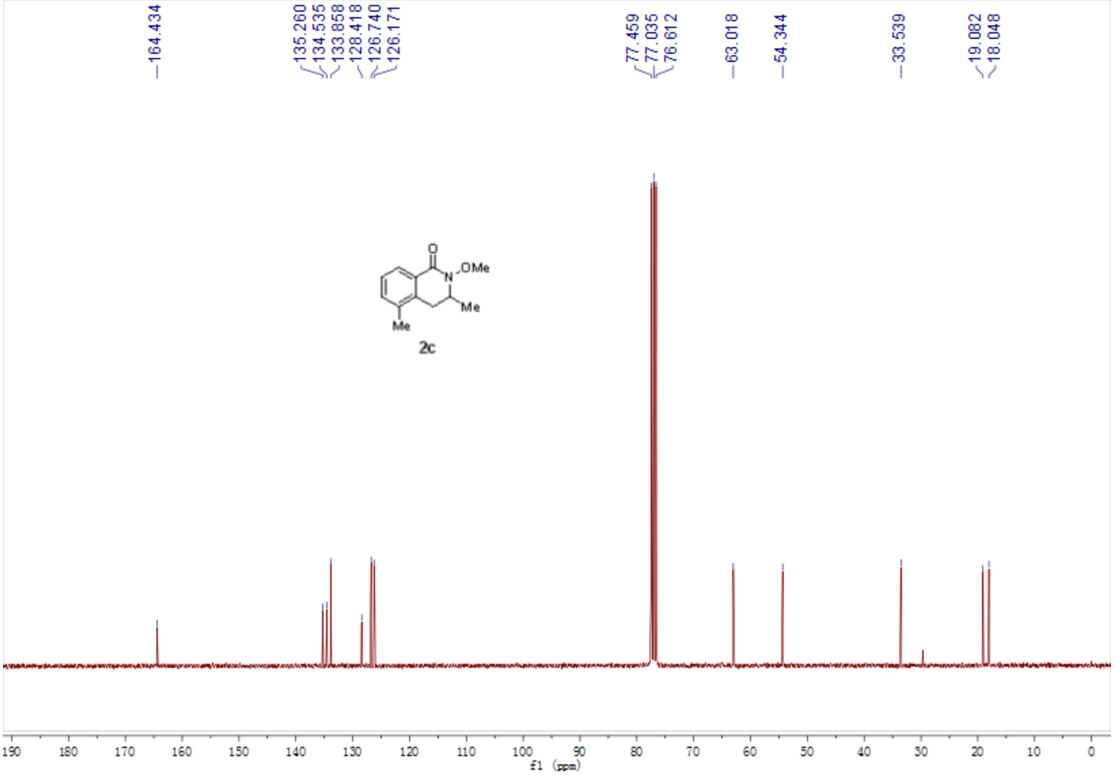


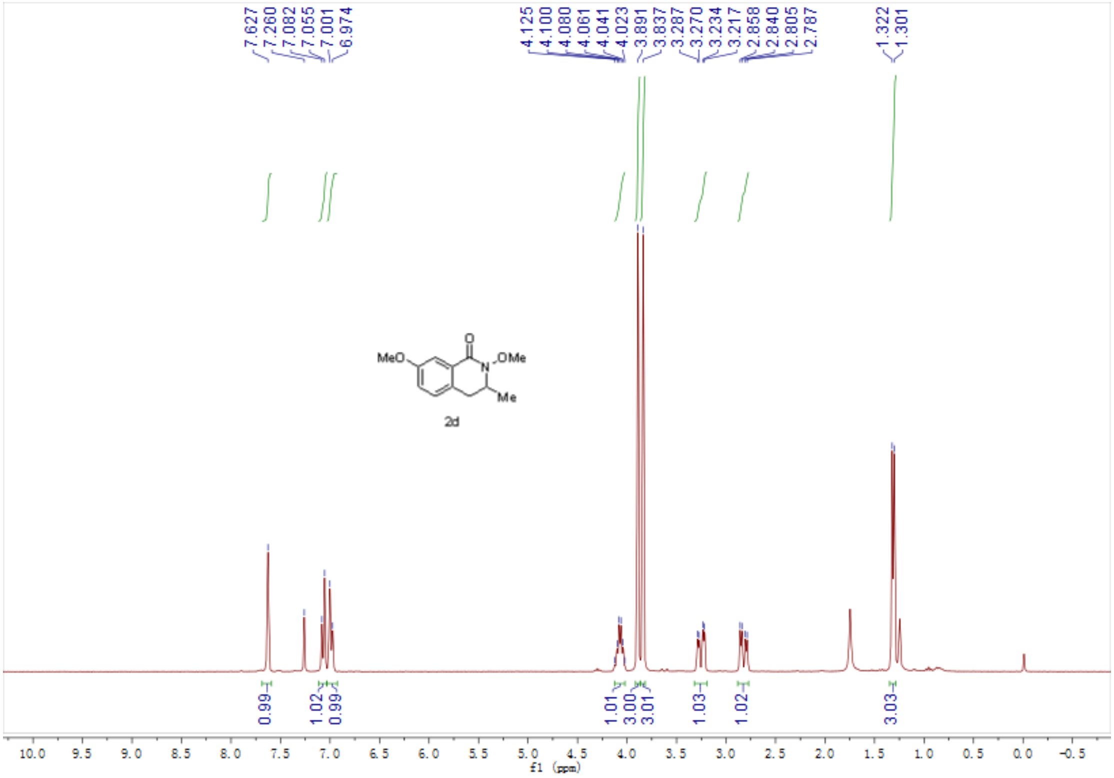


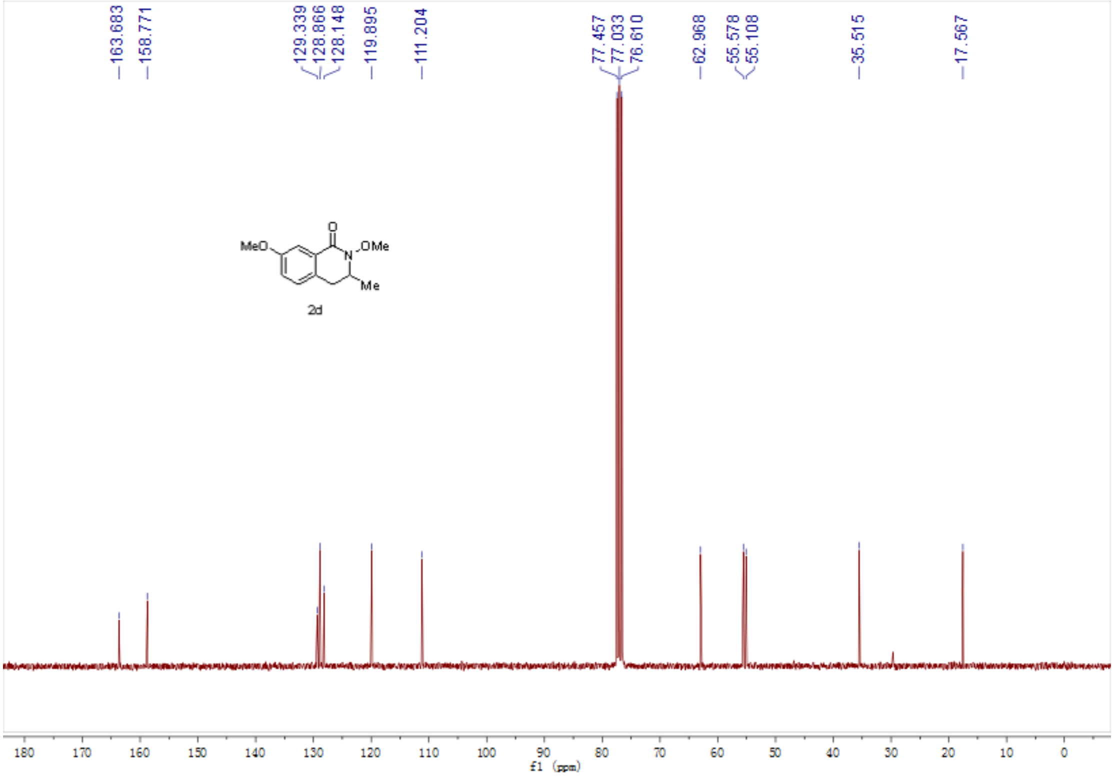

7.933
7.260
7.231
7.067
7.041
4.150
4.129
4.106
4.087
4.068
4.048
4.027
3.894
3.315
3.298
3.262
3.245
2.885
2.866
2.832
2.813
2.368
1.324
1.303
Me
O
N
OMe
Me
2b
0.97
0.80
0.99
1.05
3.00
1.04
1.02
3.03
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

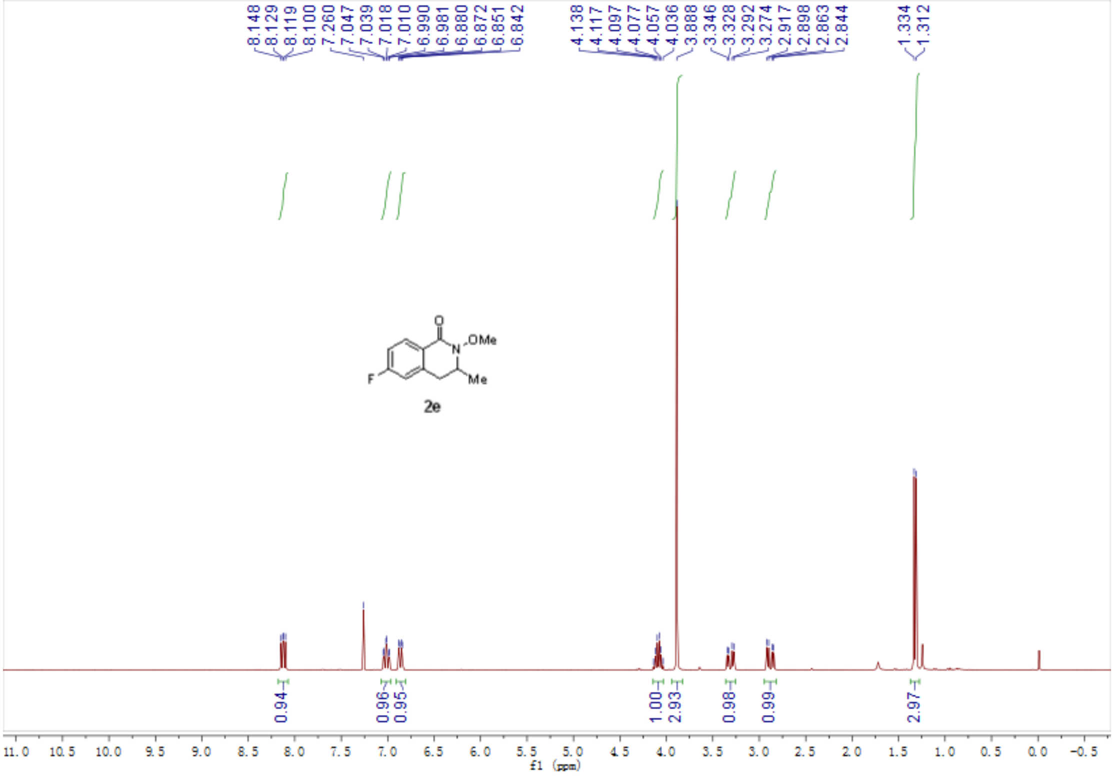

163.94
136.81
133.10
132.98
128.47
128.10
127.59
77.45
77.03
76.61
62.94
54.96
35.98
20.99
17.59
Me
O
N
OMe
Me
2b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

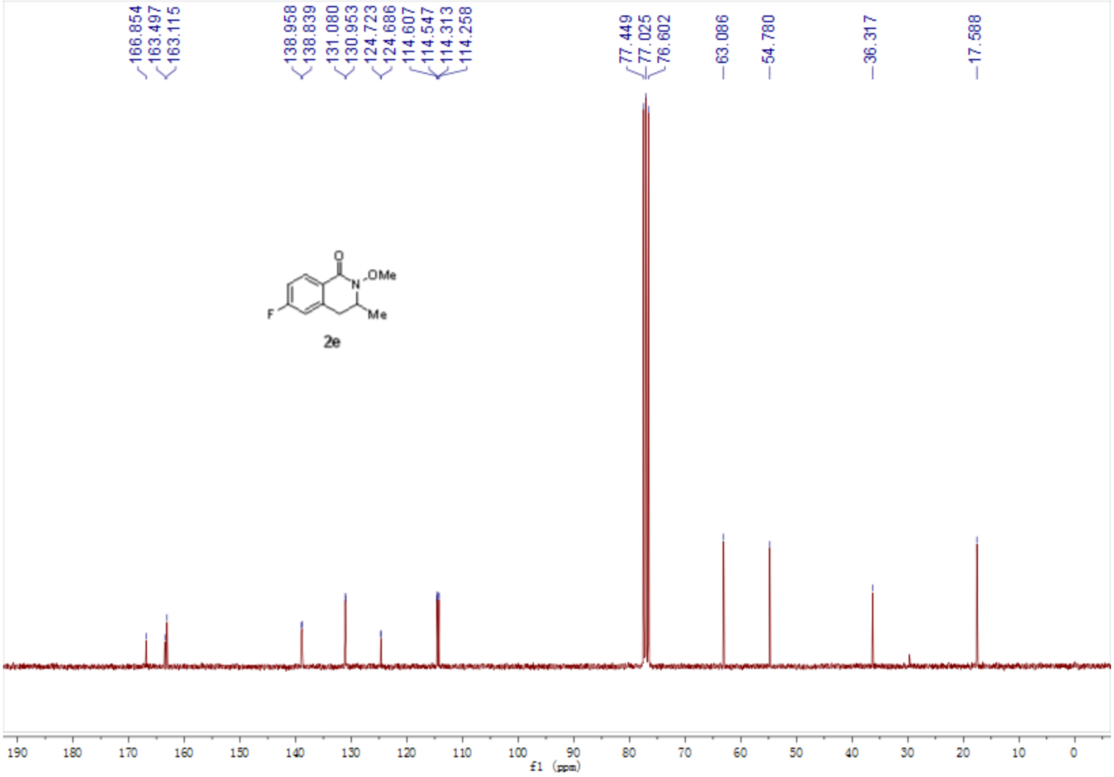

8.018
7.991
7.317
7.295
7.260
7.238
7.213
4.135
4.129
4.115
4.095
4.075
4.054
4.035
3.892
3.224
3.206
3.169
3.151
2.897
2.876
2.842
2.821
2.282
1.353
1.332
O
N
OMe
Me
Me
2c
0.95
0.97
0.63
1.00
2.98
0.99
0.98
2.94
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

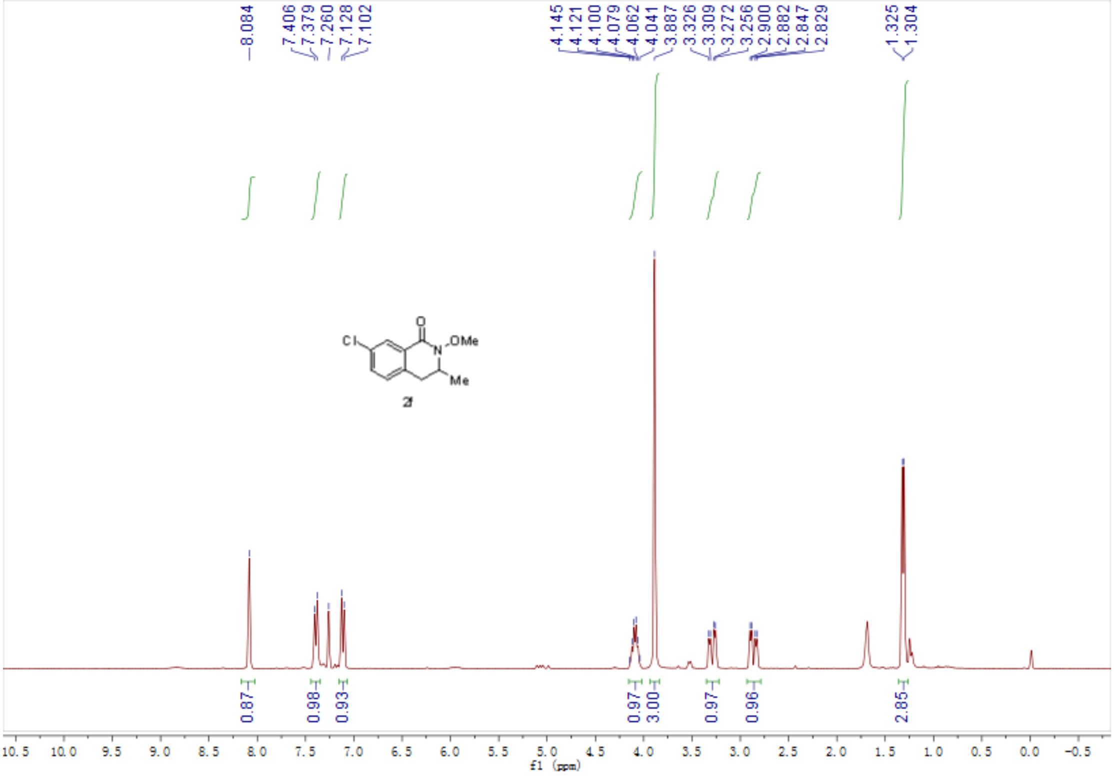

164.434
135.260
134.535
133.858
128.418
126.740
126.171
77.459
77.035
76.612
63.018
54.344
33.539
19.082
18.048
O
N
OMe
Me
Me
2c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

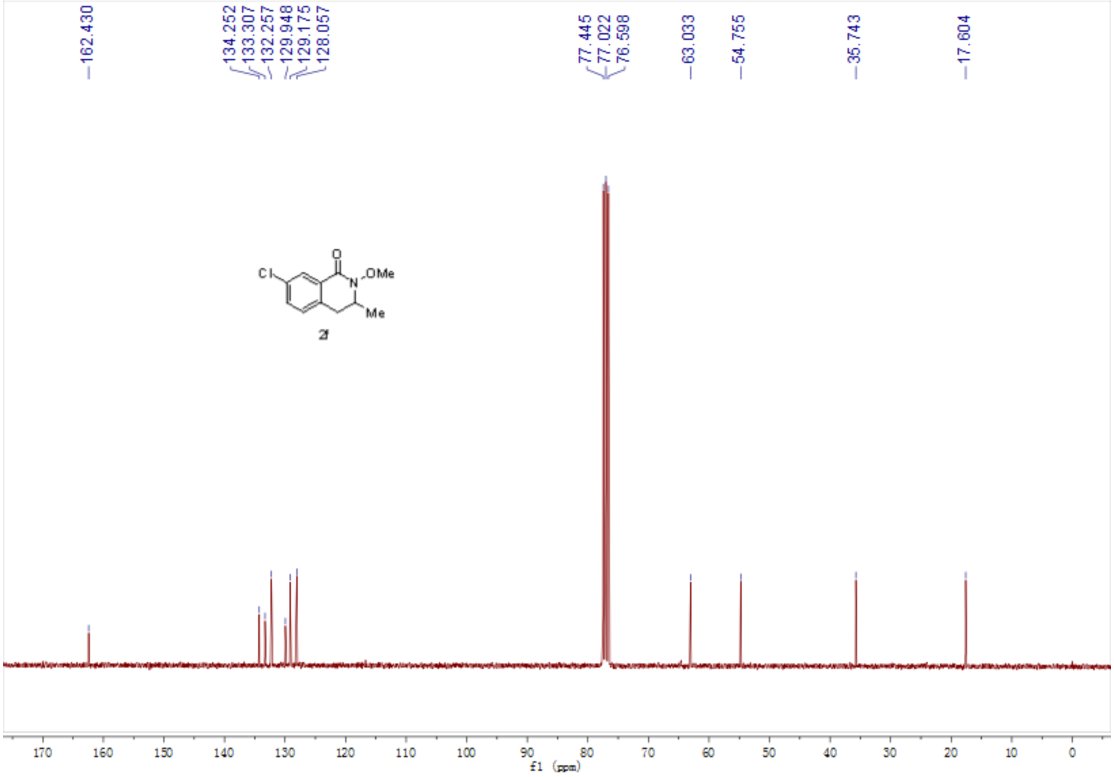

7.627
7.260
7.082
7.055
7.001
6.974
4.125
4.100
4.080
4.061
4.041
4.023
3.891
3.837
3.287
3.270
3.234
3.217
2.858
2.840
2.805
2.787
1.322
1.301
MeO
O
N
OMe
Me
2d
0.99
1.02
0.99
1.01
3.00
3.01
1.03
1.02
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

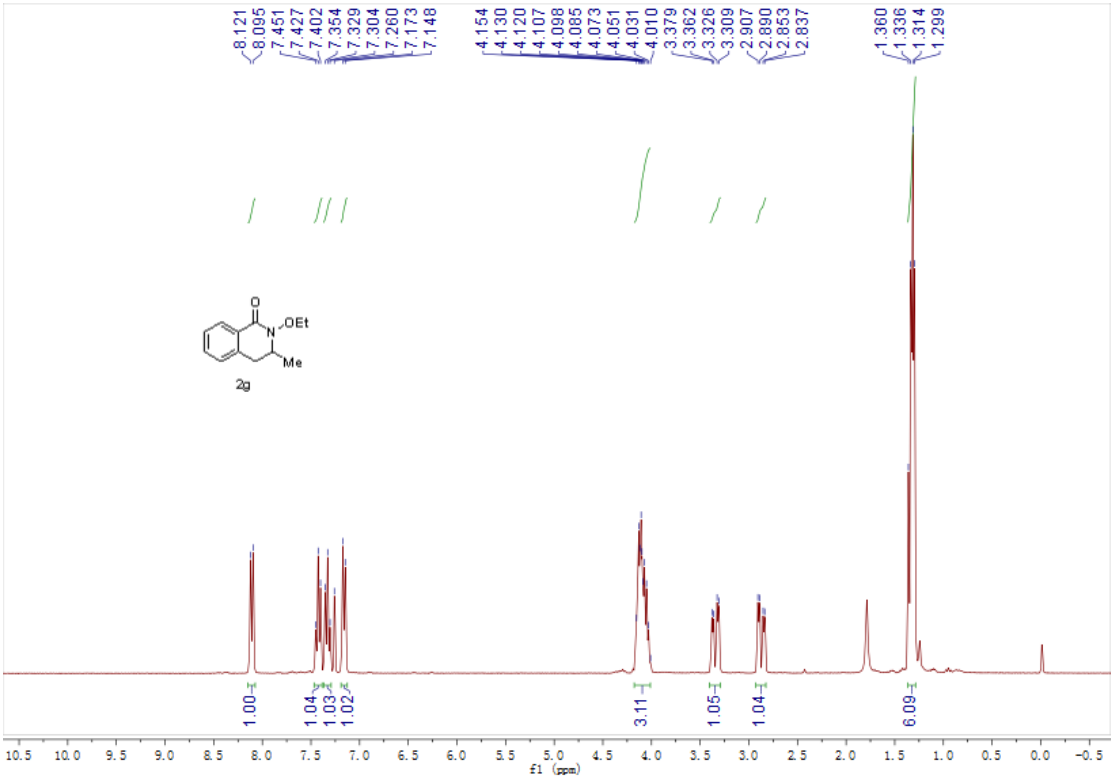

163.683
158.771
129.339
128.866
128.148
119.895
111.204
77.457
77.033
76.610
62.968
55.578
55.108
35.515
17.567
MeO
O
N
OMe
Me
2d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

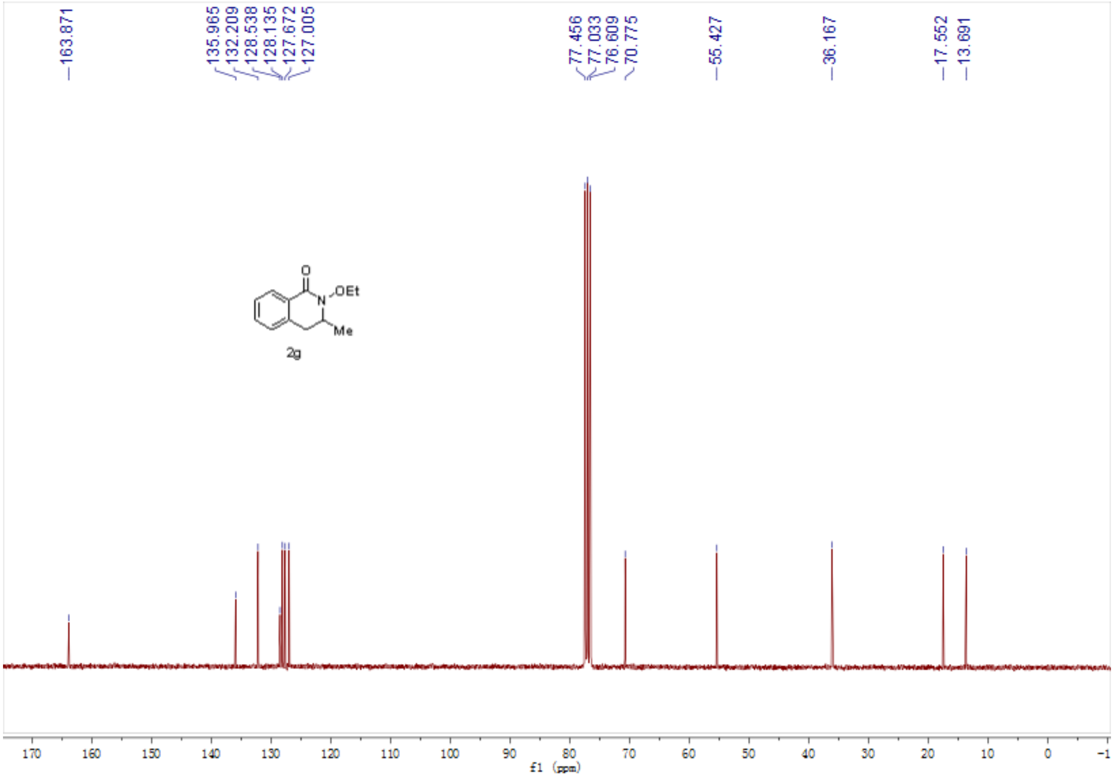

8.148
8.129
8.119
8.100
7.260
7.047
7.039
7.018
7.010
6.990
6.981
6.880
6.872
6.851
6.842
4.138
4.117
4.097
4.077
4.057
4.036
3.888
3.346
3.328
3.292
3.274
2.917
2.898
2.863
2.844
1.334
1.312
O
N
OMe
F
Me
2e
0.94
0.96
0.95
1.00
2.93
0.98
0.99
2.97
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

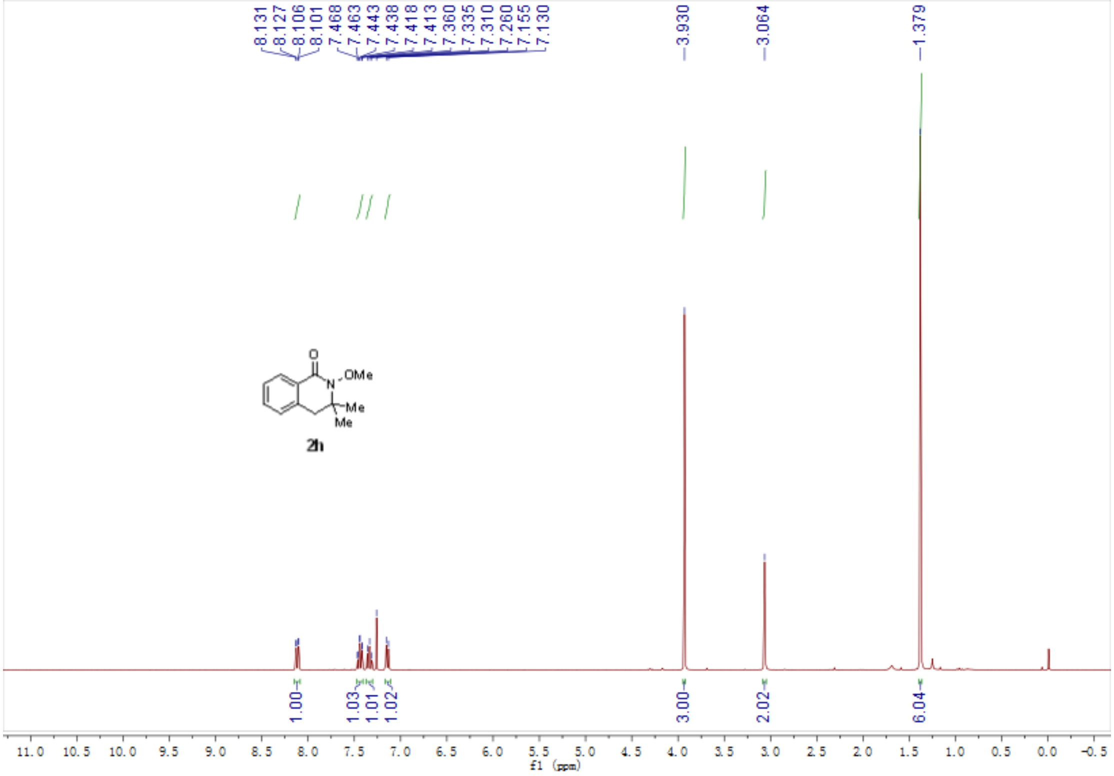

166.854
163.497
163.115
138.958
138.839
131.080
130.953
124.723
124.686
114.607
114.547
114.313
114.258
77.449
77.025
76.602
63.086
54.780
36.317
17.588
O
N
OMe
F
Me
2e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

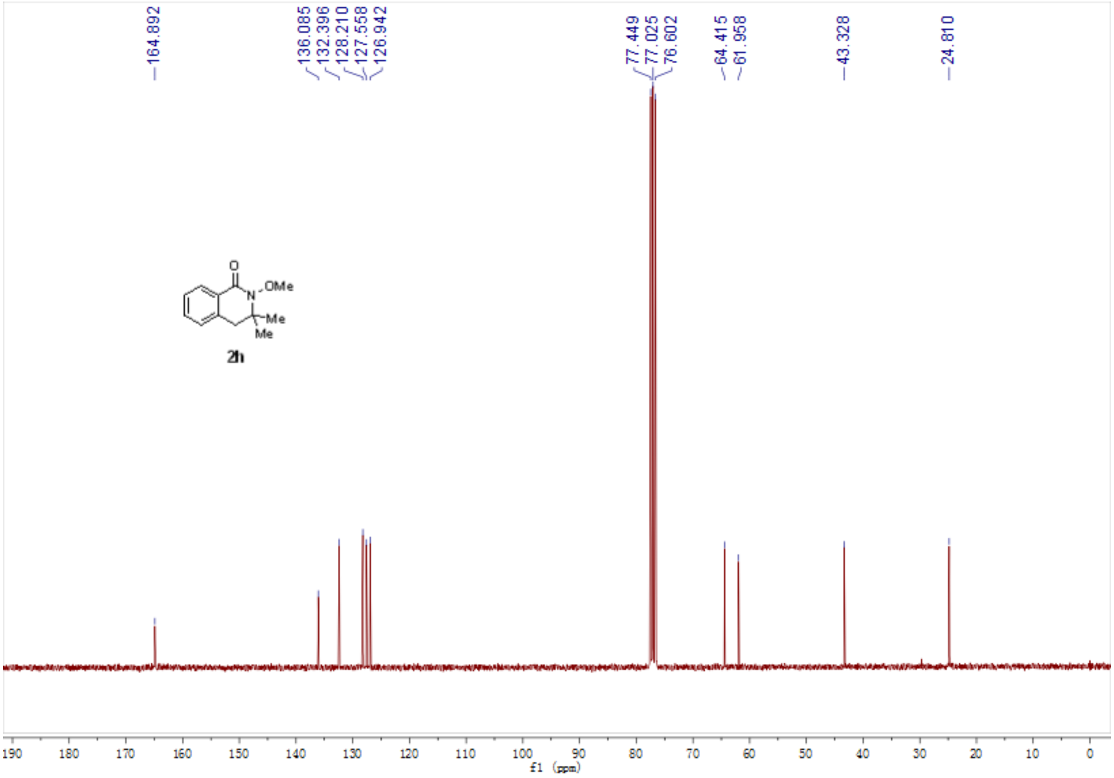

8.084
7.406
7.379
7.260
7.128
7.102
4.145
4.121
4.100
4.079
4.062
4.041
3.887
3.326
3.309
3.272
3.256
2.900
2.882
2.847
2.829
1.325
1.304
Cl
O
N
OMe
Me
2f
0.87
0.98
0.93
0.97
3.00
0.97
0.96
2.85
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

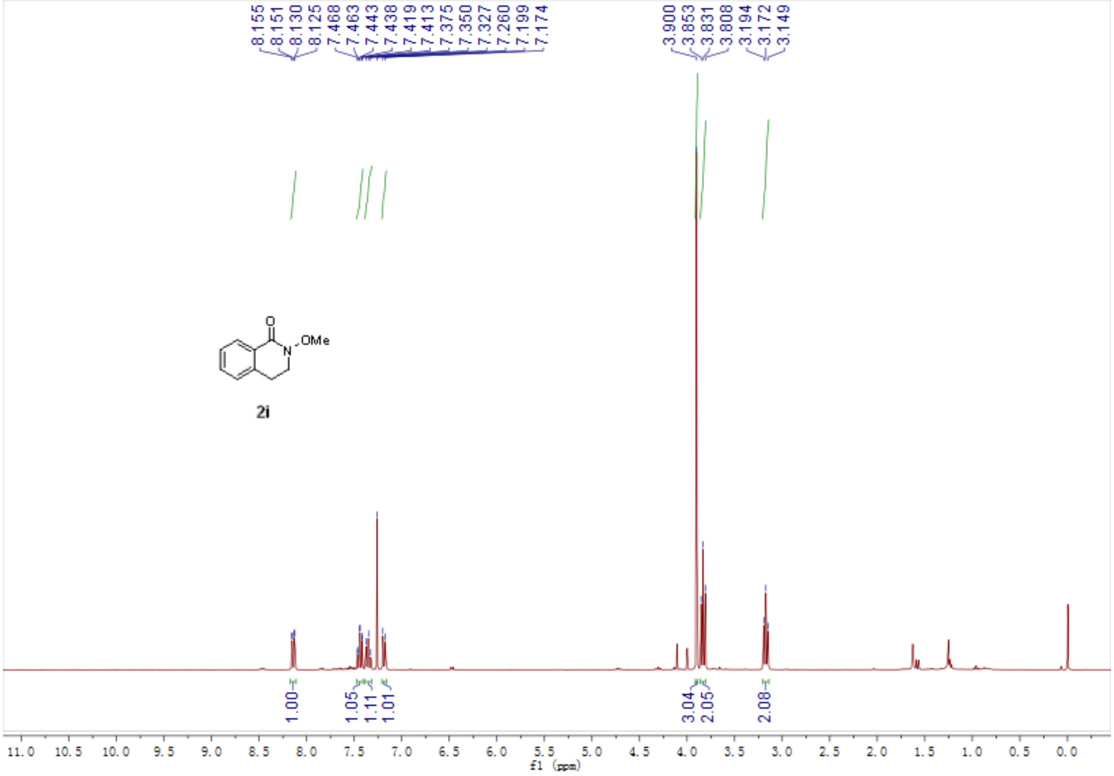

162.430
134.252
133.307
132.257
129.948
129.175
128.057
77.445
77.022
76.598
63.033
54.755
35.743
17.604
Cl
O
N
OMe
Me
2f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

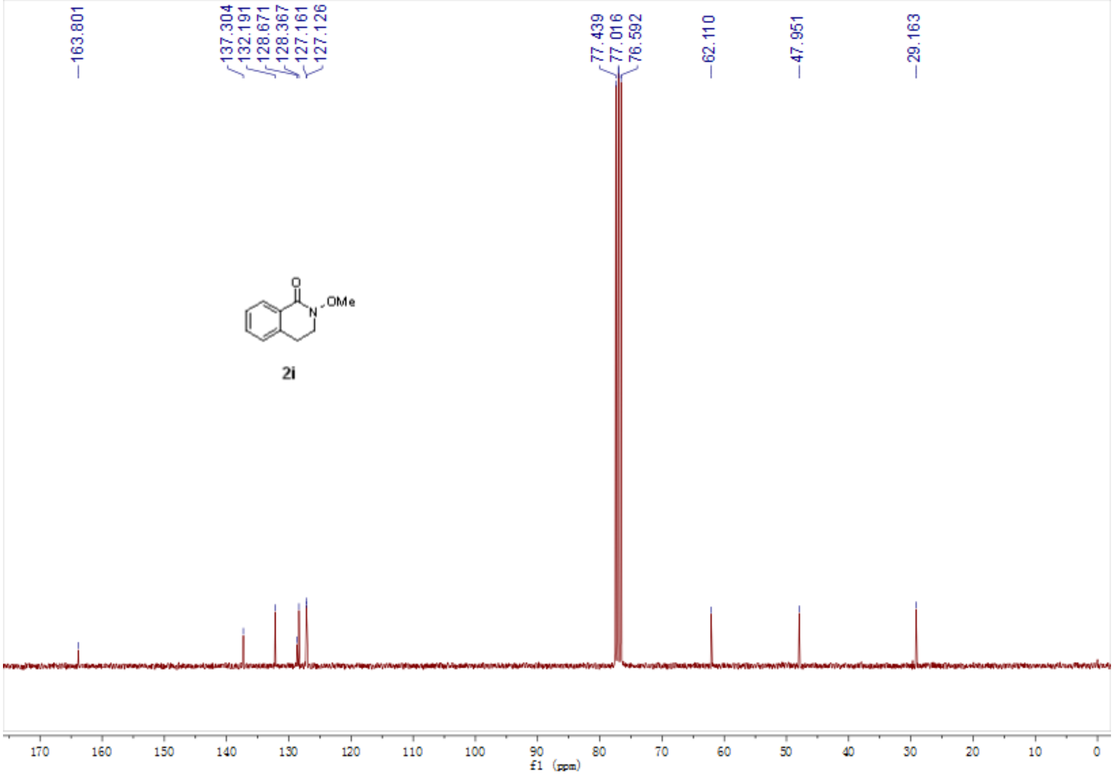

8.121
8.095
7.451
7.427
7.402
7.354
7.329
7.304
7.260
7.173
7.148
4.154
4.130
4.120
4.107
4.098
4.085
4.073
4.051
4.031
4.010
3.379
3.362
3.326
3.309
2.907
2.890
2.853
2.837
1.360
1.336
1.314
1.299
O
N
OEt
Me
2g
1.00
1.04
1.03
1.02
3.11
1.05
1.04
6.09
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

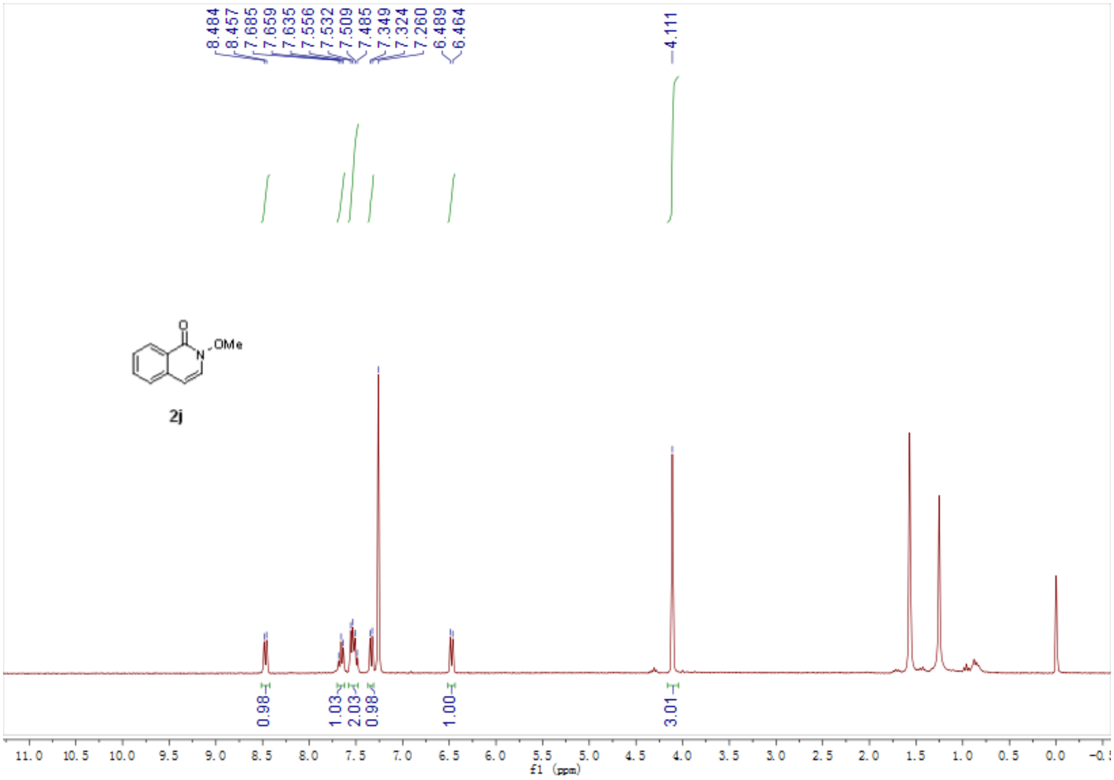

163.871
135.965
132.209
128.538
128.135
127.672
127.005
77.456
77.033
76.609
70.775
55.427
36.167
17.552
13.691
O
N
OEt
Me
2g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

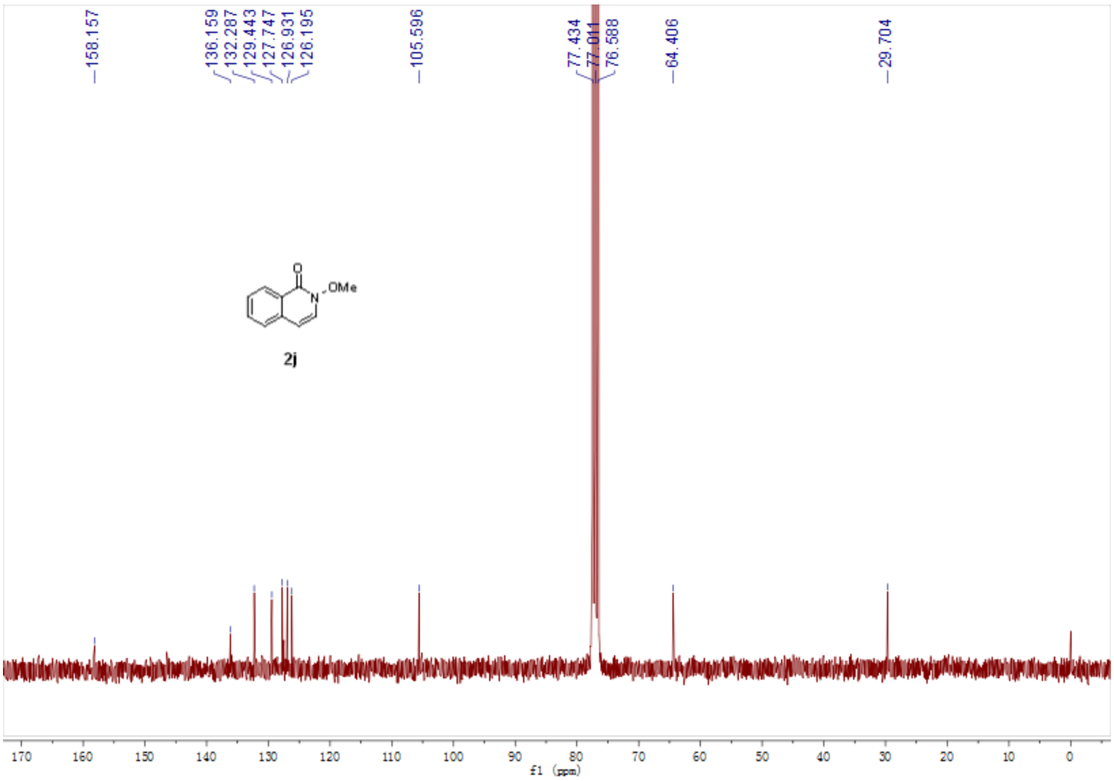

8.131
8.127
8.106
8.101
7.468
7.463
7.443
7.438
7.418
7.413
7.360
7.335
7.310
7.260
7.155
7.130
3.930
3.064
1.379
O
N
OMe
Me
Me
2h
1.00
1.03
1.01
1.02
3.00
2.02
6.04
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

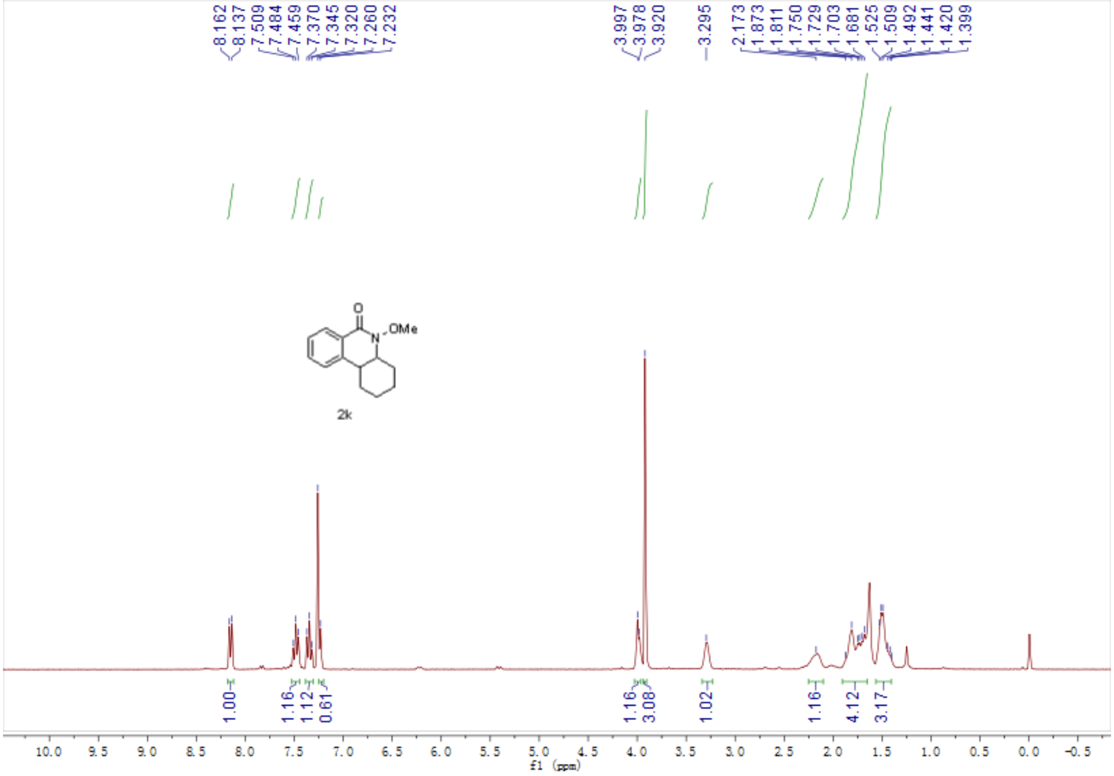

164.892
136.085
132.396
128.210
127.558
126.942
77.449
77.025
76.602
64.415
61.958
43.328
24.810
O
N
OMe
Me
Me
2h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

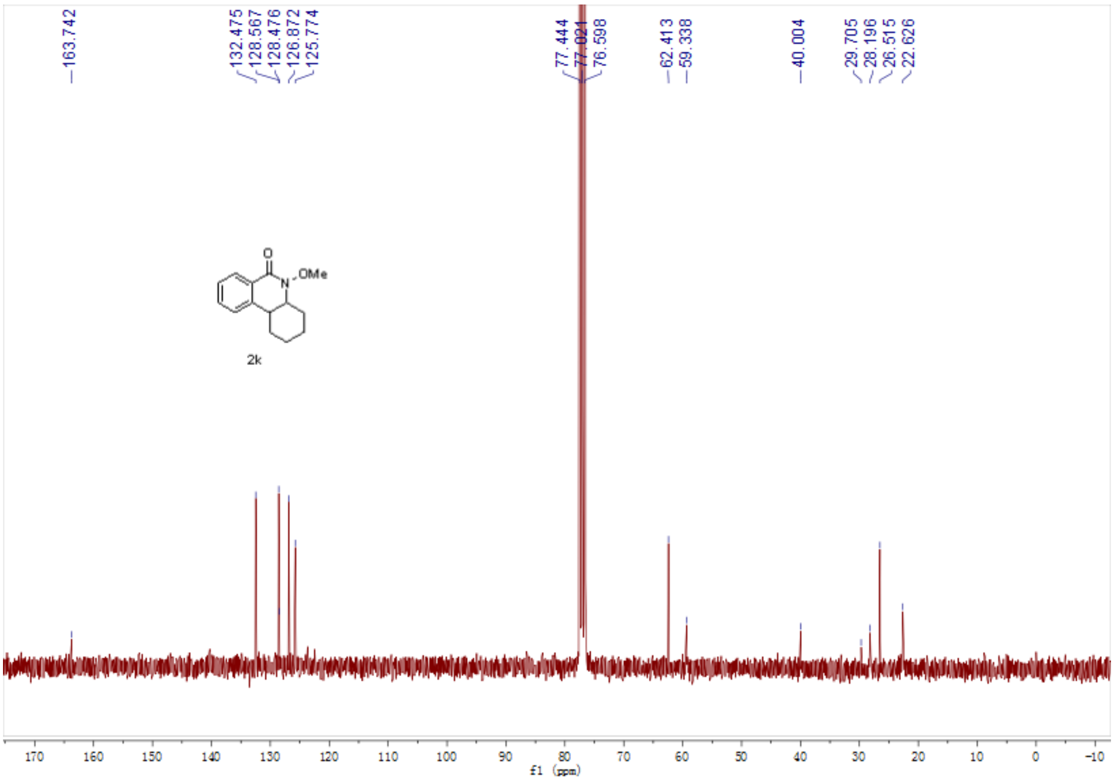

8.155
8.151
8.130
8.125
7.468
7.463
7.443
7.438
7.419
7.413
7.375
7.350
7.327
7.260
7.199
7.174
3.900
3.853
3.831
3.808
3.194
3.172
3.149
O
N
OMe
2i
1.00
1.05
1.11
1.01
3.04
2.05
2.08
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

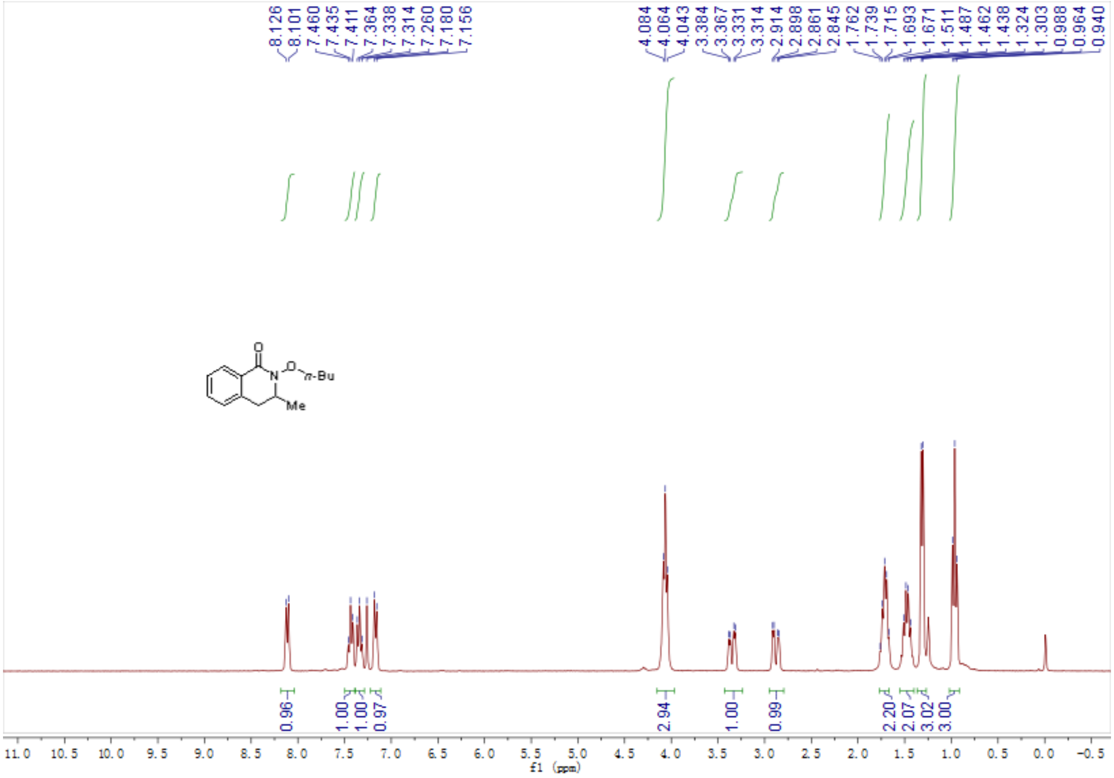

163.801
137.304
132.191
128.671
128.367
127.161
127.126
77.439
77.016
76.592
62.110
47.951
29.163
O
N
OMe
2i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

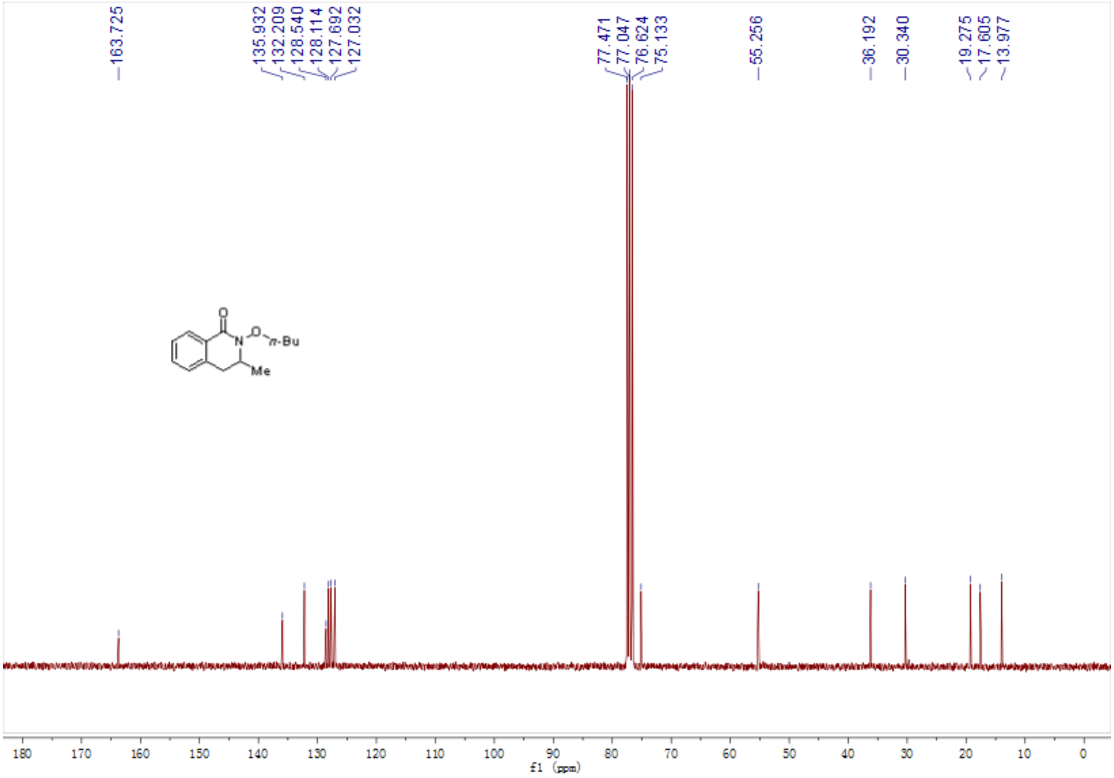

8.484
8.457
7.685
7.659
7.635
7.556
7.532
7.509
7.485
7.349
7.324
7.260
6.489
6.464
4.111
OMe
N
O
2j
0.98
1.03
2.03
0.98
1.00
3.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

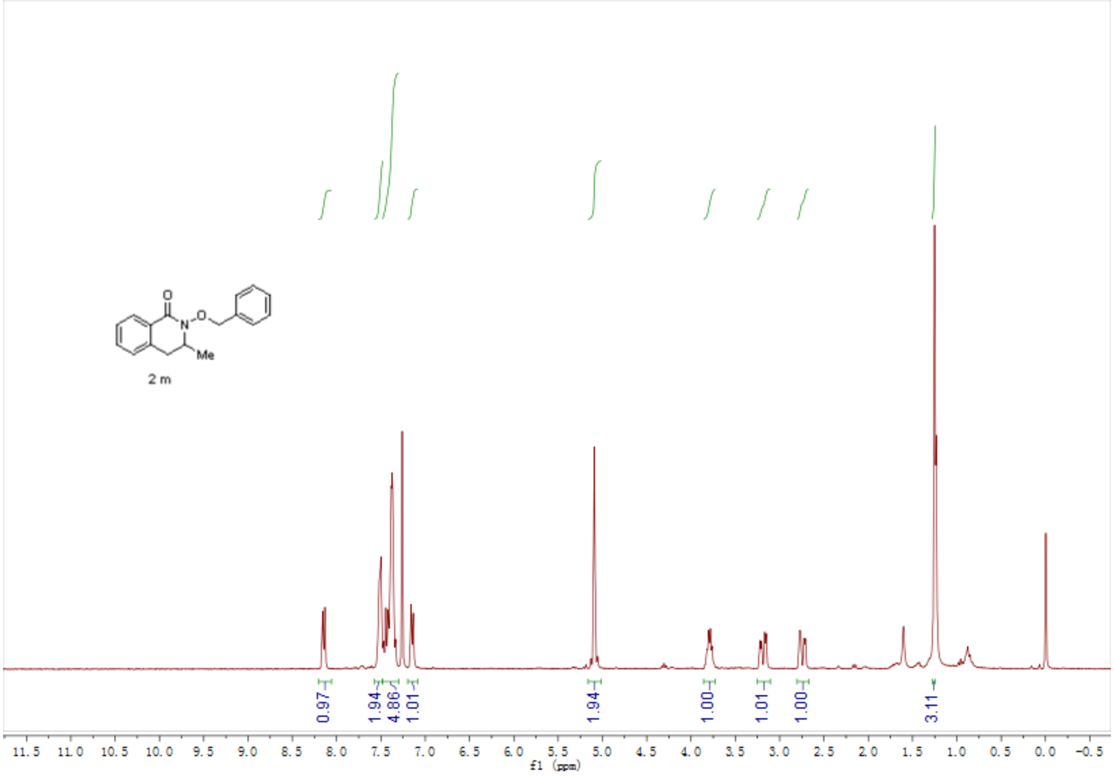

158.157
136.159
132.287
129.443
127.747
126.931
126.195
105.596
77.434
77.011
76.588
64.406
29.704
OMe
N
O
2j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

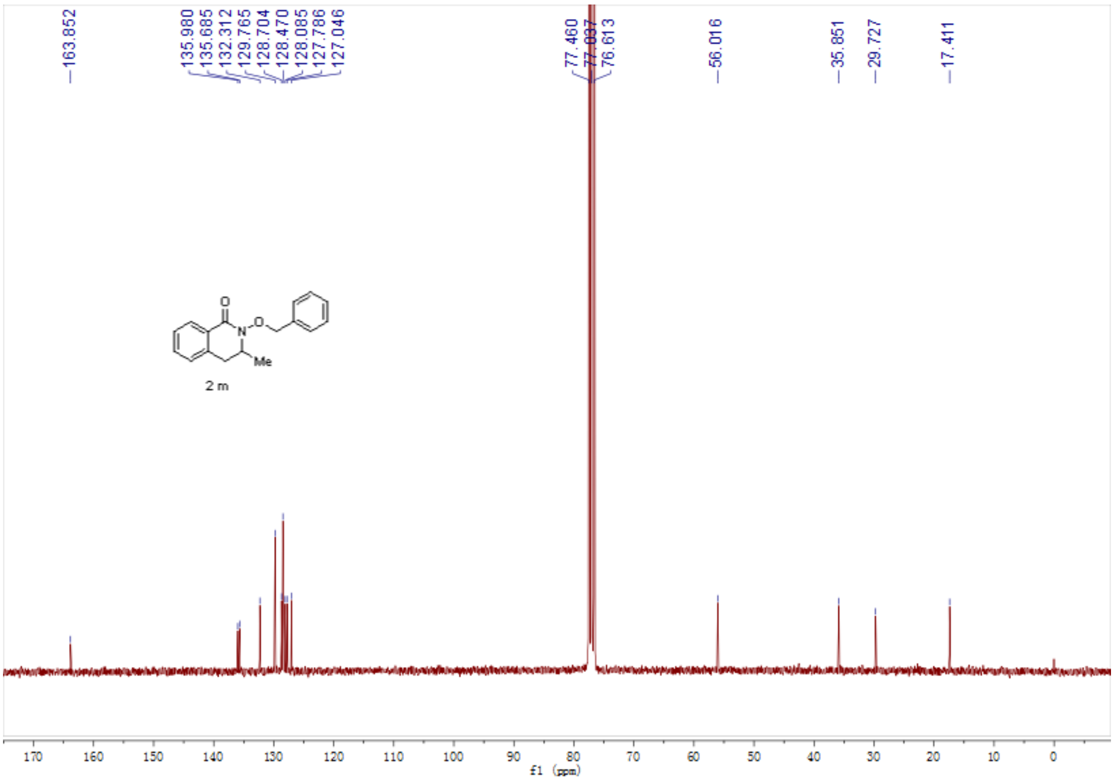

8.162
8.137
7.509
7.484
7.459
7.370
7.345
7.320
7.260
7.232
3.997
3.978
3.920
3.295
2.173
1.873
1.811
1.750
1.729
1.703
1.681
1.525
1.509
1.492
1.441
1.420
1.399
O
N
OMe
2k
1.00
1.16
1.12
0.61
1.16
3.08
1.02
1.16
4.12
3.17
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

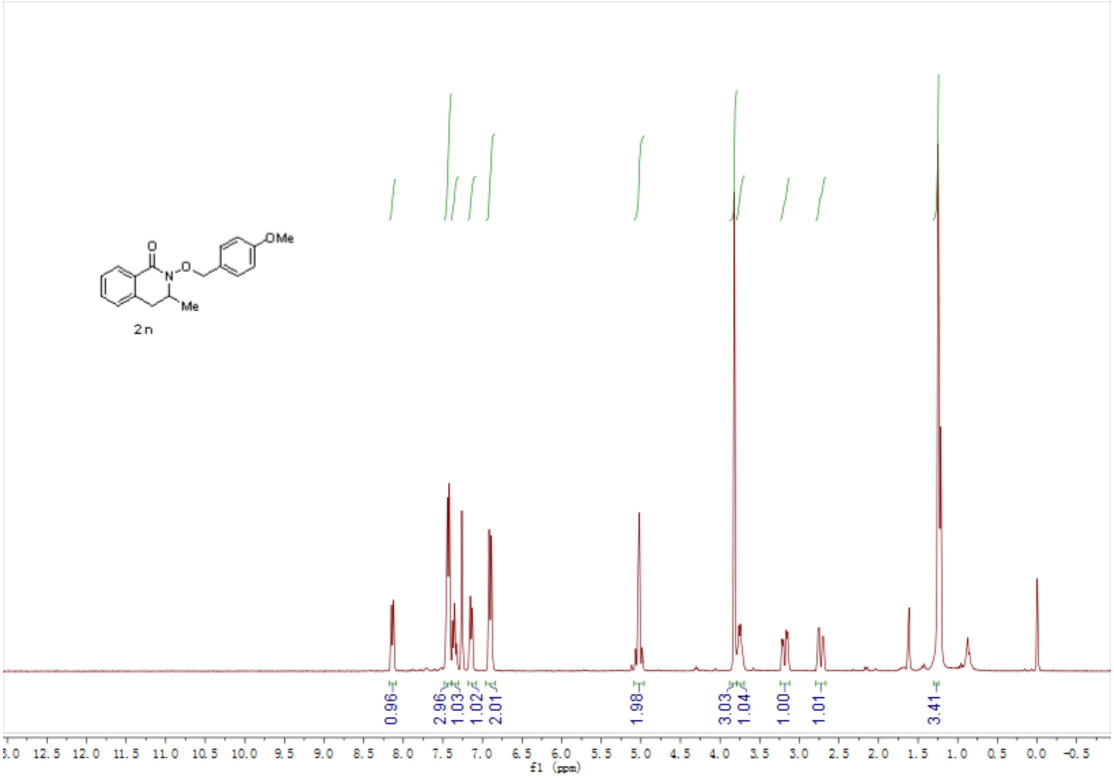

163.742
132.475
128.567
128.476
126.872
125.774
77.444
77.021
76.598
62.413
59.338
40.004
29.705
28.196
26.515
22.626
O
N
OMe
2k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

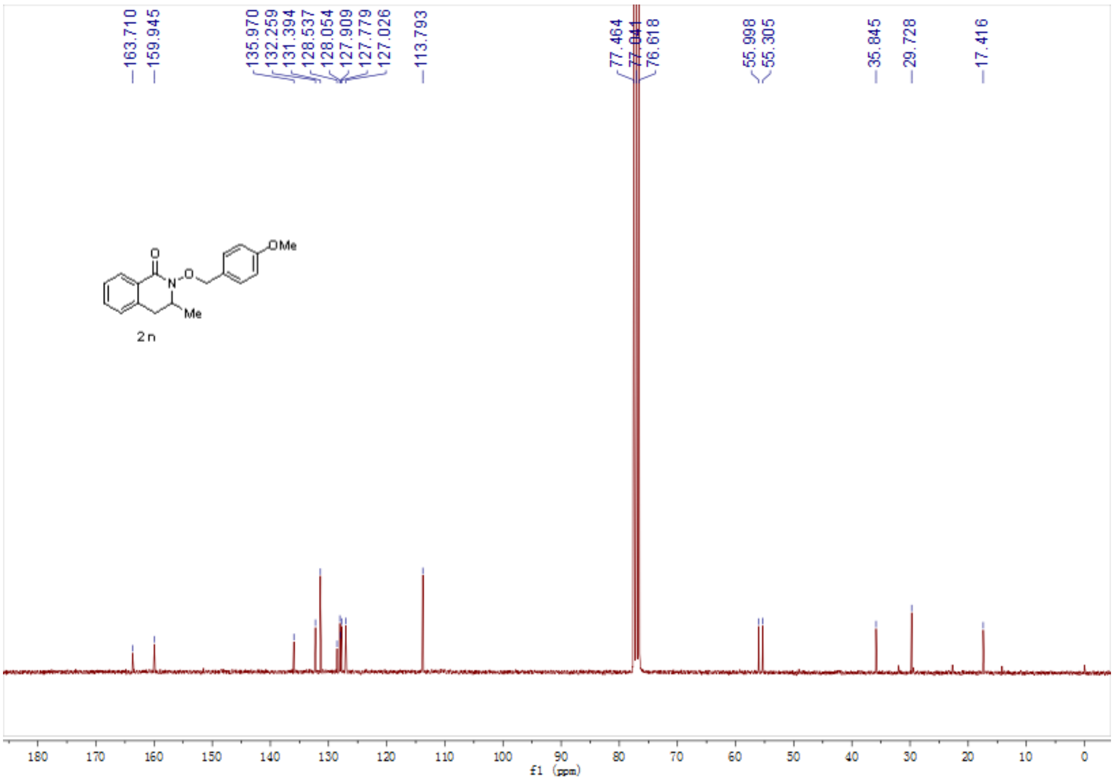

8.126
8.101
7.460
7.435
7.411
7.364
7.338
7.314
7.260
7.180
7.156
4.084
4.064
4.043
3.384
3.367
3.331
3.314
2.914
2.898
2.861
2.845
1.762
1.739
1.715
1.693
1.671
1.511
1.487
1.462
1.438
1.324
1.303
0.988
0.964
0.940
O
N
O
n-Bu
Me
0.96
1.00
1.00
0.97
2.94
1.00
0.99
2.20
2.07
3.02
3.00
11.0 10.5 10.0 9.5 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 -0.5
f1 (ppm)

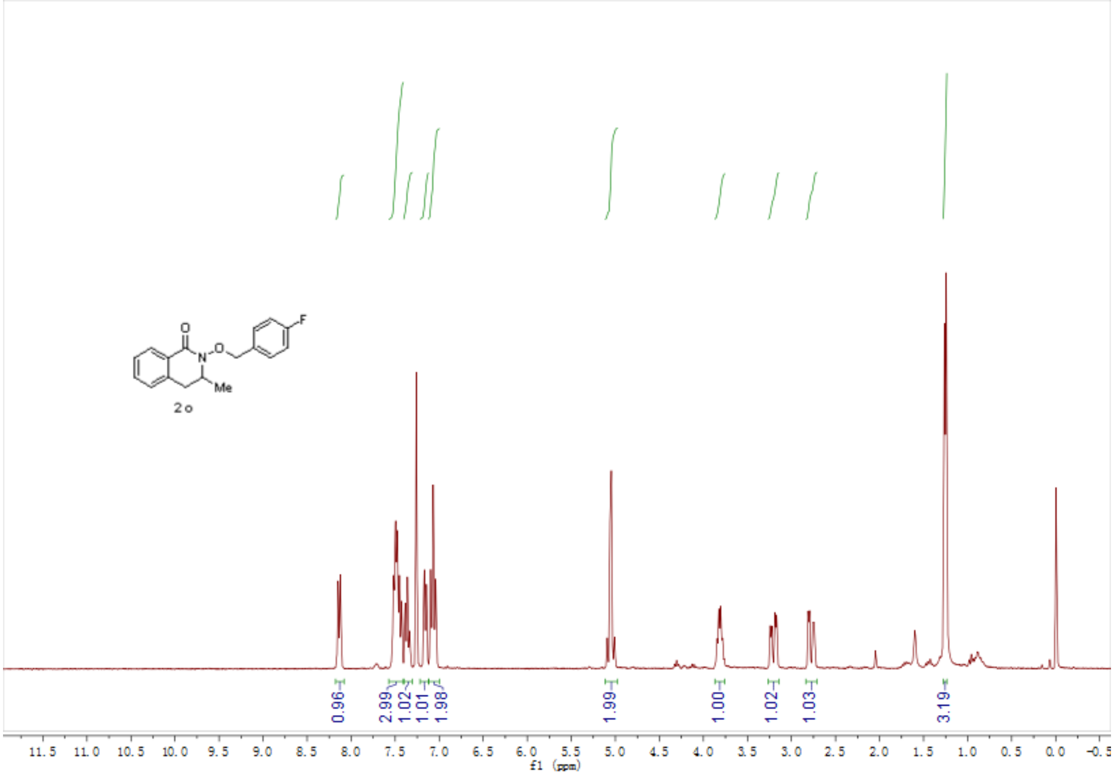

163.725
135.932
132.209
128.540
128.114
127.692
127.032
77.471
77.047
76.624
75.133
55.256
36.192
30.340
19.275
17.605
13.977
O
N
O
n-Bu
Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

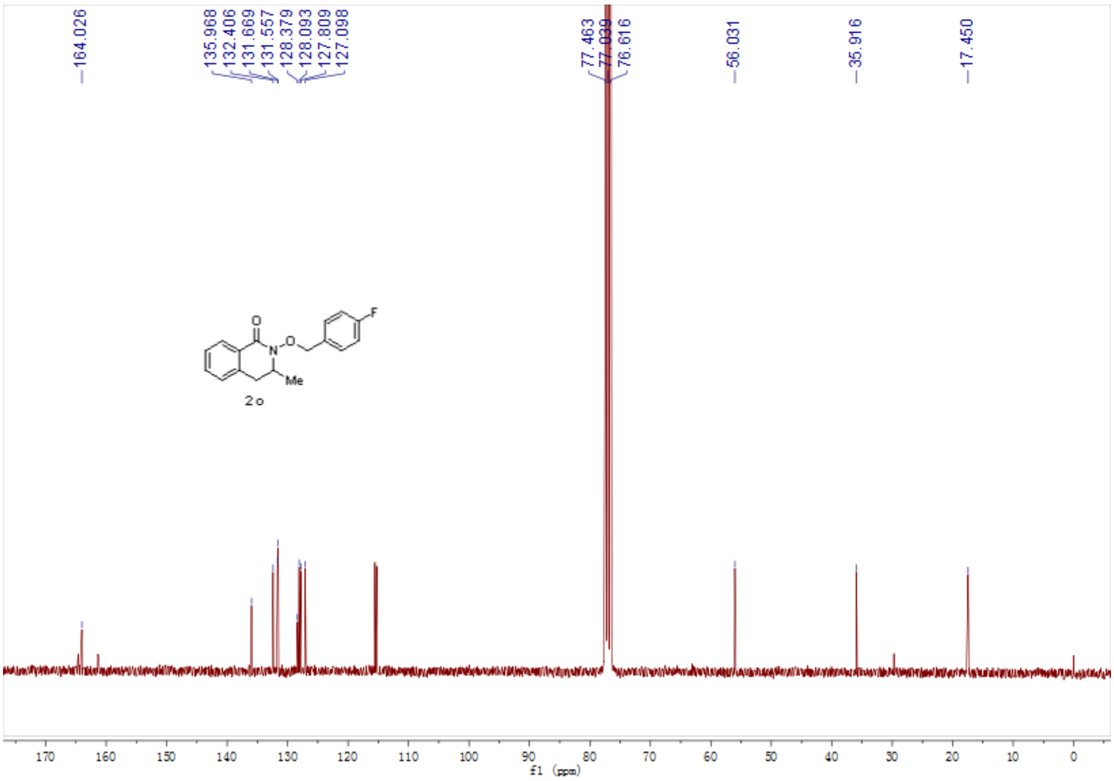

2 m
O
N
O
Me
0.97
1.94
4.86
1.01
1.94
1.00
1.01
1.00
3.11
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

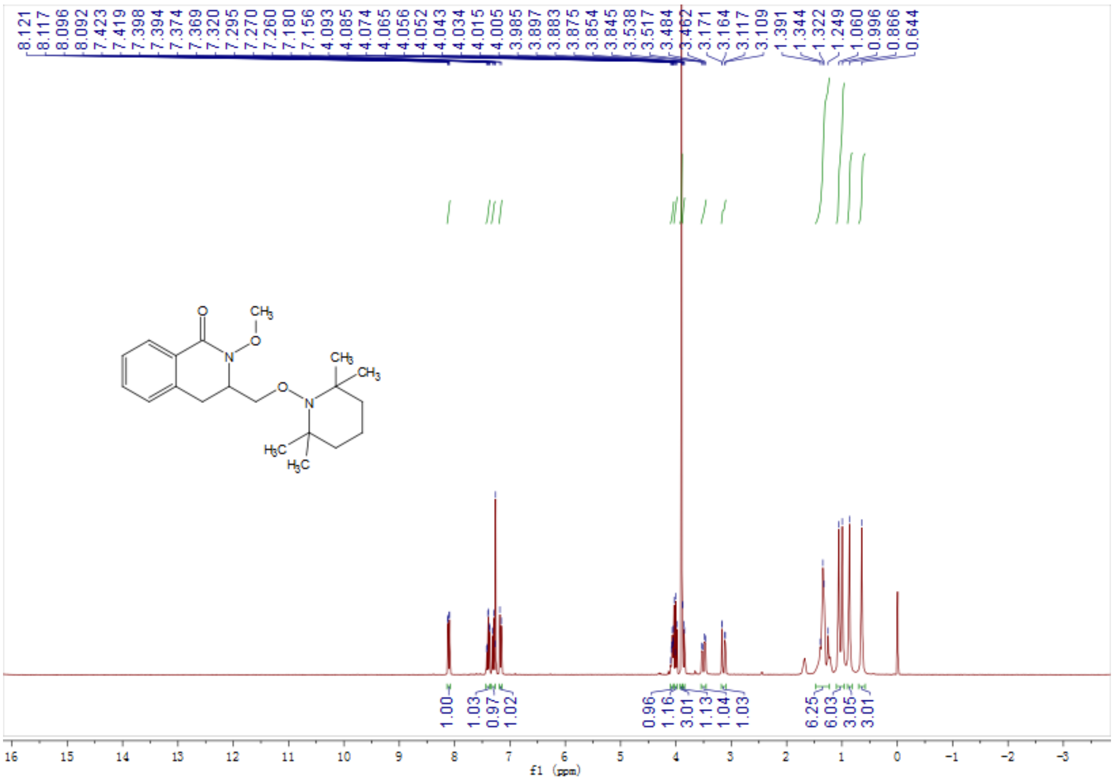

163.852
135.980
135.685
132.312
129.765
128.704
128.470
128.085
127.786
127.046
77.460
77.037
76.613
56.016
35.851
29.727
17.411
2 m
O
N
O
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

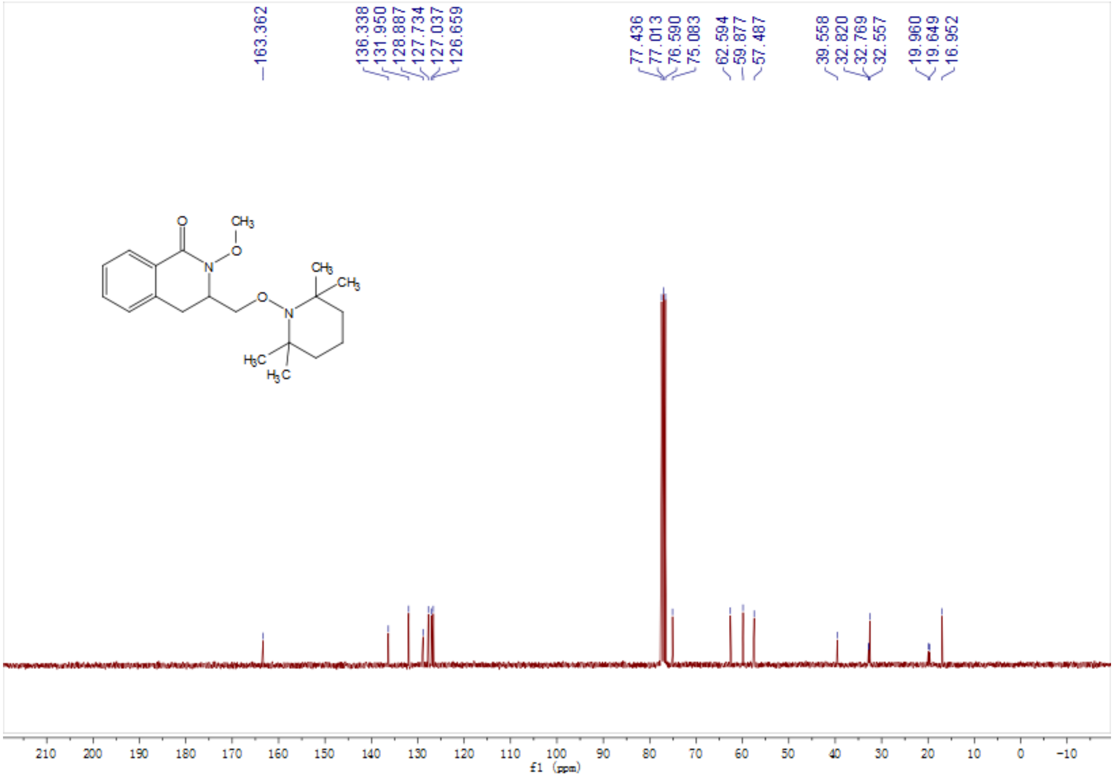

O
N
O
OMe
Me
2n
0.96
2.96
1.03
1.02
2.01
1.98
3.03
1.04
1.00
1.01
3.41
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


163.710
159.945
135.970
132.259
131.394
128.537
128.054
127.909
127.779
127.026
113.793
77.464
77.041
76.618
55.998
55.305
35.845
29.728
17.416
O
N
O
OMe
Me
2n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
O
F
Me
2o
0.96
2.99
1.02
1.01
1.98
1.99
1.00
1.02
1.03
3.19
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


164.026
135.968
132.406
131.669
131.557
128.379
128.093
127.809
127.098
77.463
77.039
76.616
56.031
35.916
17.450
O
N
O
F
Me
2o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.121
8.117
8.096
8.092
7.423
7.419
7.398
7.394
7.374
7.369
7.320
7.295
7.270
7.260
7.180
7.156
4.093
4.085
4.074
4.065
4.056
4.052
4.043
4.034
4.015
4.005
3.985
3.897
3.883
3.875
3.854
3.845
3.538
3.517
3.484
3.462
3.171
3.164
3.117
3.109
1.391
1.344
1.322
1.249
1.060
0.996
0.866
0.644
O
CH3
O
N
CH3
CH3
O
N
H3C
H3C
1.00
1.03
0.97
1.02
0.96
1.16
3.01
1.13
1.04
1.03
6.25
6.03
3.05
3.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


163.362
136.338
131.950
128.887
127.734
127.037
126.659
77.436
77.013
76.590
75.083
62.594
59.877
57.487
39.558
32.820
32.769
32.557
19.960
19.649
16.952
O
CH3
O
N
CH3
CH3
O
N
H3C
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H NMR, ^{13}C NMR spectra of the purified Product in D_2O Experiment: