Tandem Catalysis: Rh^{III}-Catalyzed C–H Allylation/Pd^{II}-Catalyzed *N*-Allylation Toward the Synthesis of Vinyl-substituted *N*-Heterocycles

Shang-Shi Zhang, Jia-Qiang Wu, Xuge Liu, Honggen Wang*

School of Pharmaceutical Sciences, Sun Yat-sen University Guangzhou 510006, China

**Email: wanghg3@mail.sysu.edu.cna*

Supporting information

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1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen in flame-dried glassware. If reaction was not carried out at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous CF_3CH_2OH, CH_3CN, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar and TCI and used as received unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (200-300 mesh) by standard technique.

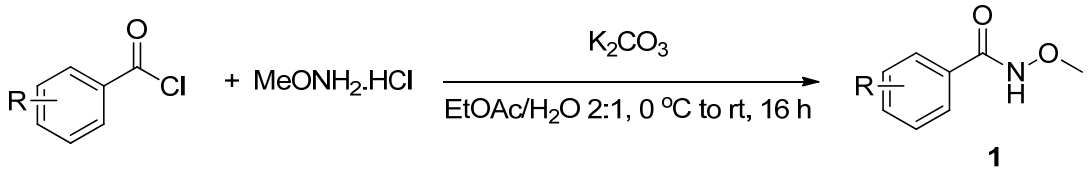
^1H were recorded on a Bruker AV 400in solvents as indicate. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H=7.26ppm, δ_C=77.16ppm;DMSO-d_6: δ_H=2.50ppm, δ_C=39.52ppm; MeOD-d_4: δ_H=3.31ppm, δ_C=49.00ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR spectra were recorded on 101 MHz spectrometers. Chemical shifts were reported in parts per million relative to tetramethylsilane (δ = 0). High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of Substrates 1 and 2

2.1 Synthesis of *N*-methoxybenzamide and *N*-methoxymethacrylamide:

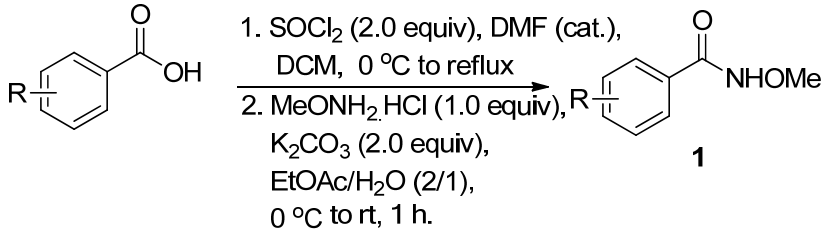
General procedure A:



1

Following a modified procedure by Fagnou et al[1] in a 100 mL round-bottom flask, *O*-methylhydroxylamine (835 mg, 10.0 mmol, 1.0 equiv) and K_2CO_3 (2.76 g, 20.00 mmol, 2.0 equiv) were combined in a 2:1 mixture of EtOAc (50 mL) and H_2O (25 mL). The flask was capped and the mixture was cooled in an ice bath. No special precautions were taken to exclude moisture and air. The acid chloride (10.0 mmol, 1.0 equiv) was added dropwise and the mixture was stirred at room temperature for 16 h. The reaction mixture was then diluted with EtOAc (30 mL) and washed twice with sat. $NaHCO_3$ and brine. The organic layers were dried over Na_2SO_4, filtered and concentrated. The purification was made by flash column chromatography using an appropriate solvent mixture (petroleum ether/ethyl acetate = 2/1) to obtain the pure product.

General procedure B:



1

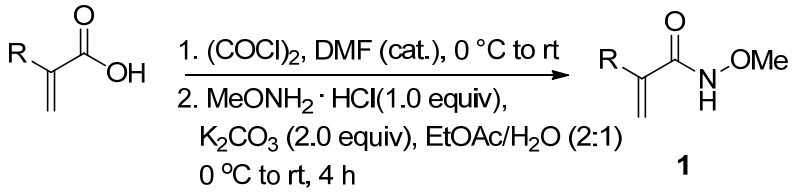
Following a procedure by Fagnou et. al.[1]

1) To a solution of the carboxylic acid (10.0 mmol, 1.0 equiv) in dry CH_2Cl_2 (60 mL) at 0°C under an atmosphere of N_2 was added dropwise of $SOCl_2$ (1.5 mL, 20.0 mmol, 2.0 equiv) followed by a catalytic amount of dry DMF (3 drops). The reaction was

allowed to stir at room temperature until completion (typically 3 h). The solvent was then removed under reduce pressure to afford the corresponding crude acid chloride.

2) Methoxyamine hydrochloride (835.2 mg, 10.0 mmol, 1.0 equiv) was added to the mixture of K_2CO_3 (2.76 g, 6.0 mmol, 2.0 equiv) in a 2:1 mixture of EtOAc (50 mL) and H_2O (25 mL). The resulting solution was cooled to 0°C followed by a dropwise addition of the unpurified acid chloride dissolved in a minimum amount of EtOAc. The flask containing the acid chloride was then rinsed with additional EtOAc. The reaction was allowed to stir for 30 min at rt. Afterwards, the phases were separated and the aqueous phase was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The pure products were purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent.

General Procedure C:



1

Following a modified procedure by Singh et al.[2]

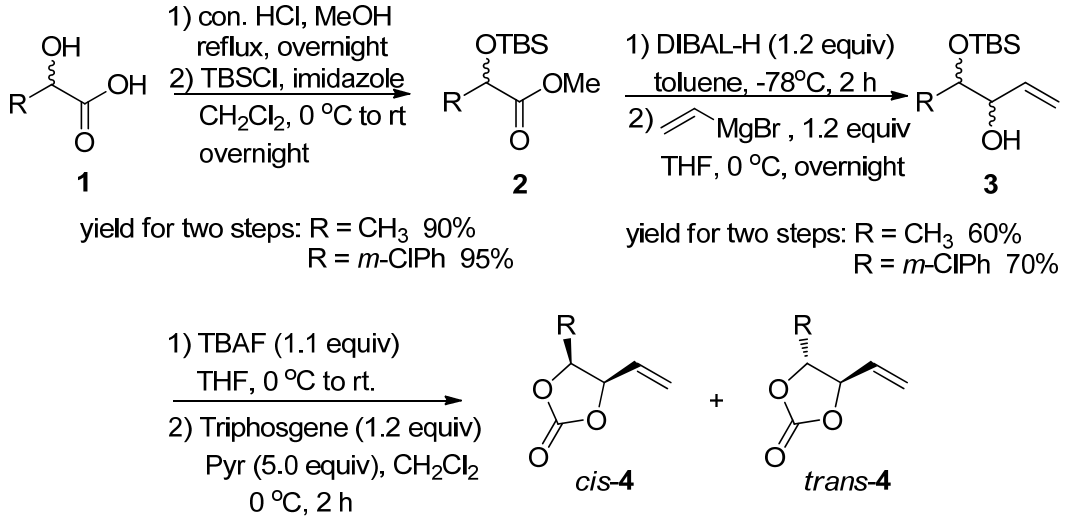
1) To a solution of the carboxylic acid (10.0 mmol, 1.0 equiv) in dry CH_2Cl_2 (60 mL) at 0°C under N_2 was added dropwise of $(COCl)_2$ (0.64 mL, 10 mmol, 1 equiv) followed by a catalytic amount of dry DMF (2 drops). The reaction was allowed to stir at room temperature until completion (typically 3 h). The solvent was then removed under reduce pressure to afford the corresponding crude acid chloride.

2) Methoxyamine hydrochloride (920 mg, 11.0 mmol, 1.1 equiv) was added to a mixture of Et_3N (1.9 mL, 15.0 mmol, 1.5 equiv) in dry CH_2Cl_2 (30 mL). The resulting solution was cooled to 0°C followed by a dropwise addition of the unpurified acid chloride dissolved in a minimum amount of dry CH_2Cl_2. The reaction was allowed to stir overnight at rt. Afterwards, the phases were separated and the aqueous phase was

extracted twice with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The pure products were purified by flash chromatography on silica gel using petroleum ether and ethyl acetate as eluent.

2.2Synthesis of 4-(3-chlorophenyl)-5-vinyl-1,3-dioxolan-2-one 2

General procedure D:



yield for two steps: R = CH_3 90%
R = *m*-ClPh 95%

yield for two steps: R = CH_3 60%
R = *m*-ClPh 70%

To a mixture of 2-hydroxyl acetic acid **1** (10 mmol), in MeOH (10 mL) and toluene (5 mL), was added concentrated HCl (0.5 mL). The resulting mixture was heated to reflux and stirred overnight. After cooling to room temperature, the reaction mixture was neutralized to pH = 7 with saturated $NaHCO_3$. The solvent was evaporated and diluted with ethyl acetate, washed with brine, dried over Na_2SO_4, and evaporated to give the corresponding α-hydro-methyl ester.[3]

The crude α-hydroxy ester and imidazole (2.0 equiv) were dissolved in anhydrous dichloromethane (15 mL). A solution of tert-butyldimethylsilyl chloride (1.5 equiv) in anhydrous dichloromethane was added to the above solution dropwise at 0°C. The reaction mixture solution was warmed to room temperature and stirred overnight. After filtration and extracting with ethyl acetate, the organic layer was dried (Na_2SO_4), evaporated and purified by flash column chromatography.[4]

To a solution of above product in toluene was added DIBAL-H (1.0 M in THF, 1.2 equiv) dropwise at -78°C. The mixture was maintained at the same temperature for 2 h.The reaction was quenched by pouring into a mixture of 100 g of ice and 100 mL of dichloromethane and stirred vigorously for 30 min. After separation of the dichloromethane layer, the aqueous phase was washed with 100 mL of dichloromethane. The dichloromethane layer was combined and washed with brine, water, dried over Na_2SO_4 and concentrated to afford the corresponding aldehyde. The aldehyde was not further purified and was immediately utilized in the next step.[5]

To the above crude aldehyde was added vinylmagnesium bromide(1.9 M in THF, 1.2 equiv) at 0°C in THF. The reaction mixture was stirred at 0°C overnight. The reaction was quenched with sat. $NaHCO_3$ and the organic layer was extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4, concentrated and purified by flash chromatography to afford the corresponding product **3**.[6]

To a solution of **3** was added Tetrabutylammonium fluoride (TBAF, 1.1 equiv) in THF at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with water and extracted with ethyl acetate for three times. The combined organic layers were dried over Na_2SO_4 and evaporated at reduced pressure to give the crude dihydroxyl compound which was utilized in the next step.[6]

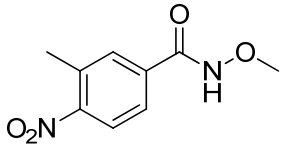
The crude dihydroxyl compound and pyridine (5.0 equiv) were dissolved in anhydrous dichloromethane (20 mL) and the mixture was cooled to 0°C. A solution of triphosgene (1.1 equiv) in dry CH_2Cl_2 (10 mL) was added dropwise. The mixture was allowed to stir for 2 h and quenched cautiously with sat. NH_4Cl (10 mL), extracted with methyl tertiary butyl ether (MTBE) three times. The combined organic layers was washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4. After removal of the solvent under reduced pressure, the resulting mixture was purified by flash chromatography to give the compound *cis*-**4** and *trans*-**4**.[7]

Characterization of substrates

Preparation and Characterization of *N*-methoxybenzamides1and *N*-methoxymethacryl amides.

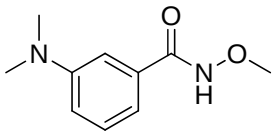
N-methoxybenzamides **1a-1h**, **1p-1u**, **1k, 1n** were prepared following the procedure reported by Fagnou.[1]*N*-methoxymethacryl amides **1v-1y**were prepared following the procedure reported by Singh.[2] All the characteristic data are consistent with the data reported before.[8-11]

***N*-methoxy-3-methyl-4-nitrobenzamide (1i)**



Following general procedure B, The product **1i** was obtained in 90 % yield (2.10 g, 10.0 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.25 . ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.85 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.2, 150.5, 136.1, 132.8, 131.4, 125.8, 124.5, 63.3, 19.2. **ESI-MS**: calculated $C_9H_{11}N_2O_4[M+H]^+$, 211.0713; Found 211.0723.

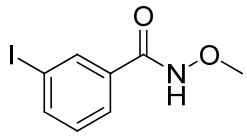
3-(dimethylamino)-*N*-methoxybenzamide (1j)



Following general procedure B, The product **1j** was obtained in 76 % yield (1.47 g, 7.6 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 1H), 7.13 (s, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.81 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.83 (s, 3H), 2.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 150.6,

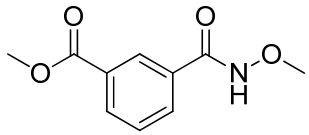
132.6, 129.1, 115.7, 114.2, 111.1, 64.3, 40.4.**ESI-MS**: calculated $C_{10}H_{15}N_2O_2[M+H]^+$, 195.1128; Found 195.1141.

3-iodo-*N*-methoxybenzamide (1l)



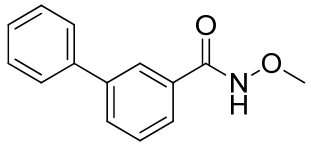
Following general procedure B, The product **1l** was obtained in 72 % yield (1.00 g, 3.6 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 3.87 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 140.9, 136.1, 133.7, 130.3, 126.3, 94.2, 64.6. **ESI-MS**: calculated $C_8H_8INO_2[M-H]^-$, 275.9527; Found 275.9533.

methyl 3-(methoxycarbamoyl)benzoate (1m)



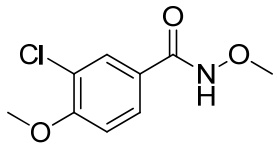
Following general procedure B, The product **1m** was obtained in 88 % yield (0.87 g, 4.2 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 1:1): 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.16 (d, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.4, 132.9, 132.2, 131.9, 130.5, 128.9, 127.8, 64.5, 52.4.**ESI-MS**: calculated $C_{10}H_{12}NO_4[M+H]^+$, 210.0761; Found 210.0772.

***N*-methoxy-[1,1'-biphenyl]-3-carboxamide (1o)**



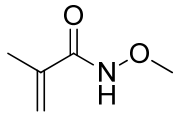
Following general procedure B, The product **1o** was obtained in 88 % yield (0.57 g, 2.5 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (t, *J* = 1.6 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.58 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.50 – 7.40 (m, 3H), 7.36 (m, 1H), 3.88 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 141.8, 139.9, 132.4, 130.6, 129.1, 128.9, 127.8, 127.1, 125.9, 125.8, 64.5. **ESI-MS**: calculated $C_{14}H_{14}NO_2[M+H]^+$, 228.1019; Found 228.1025.

3-chloro-*N*,4-dimethoxybenzamide (1r)



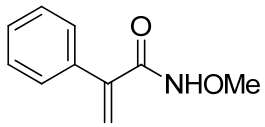
Following general procedure B, The product **1r** was obtained in 86 % yield (0.64 g, 3.0 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 1:1): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.1 Hz, 1H), 7.68 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 3.93 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 157.9, 129.2, 127.3, 124.7, 122.7, 111.5, 64.5, 56.3. **ESI-MS**: calculated $C_9H_{11}ClNO_3[M+H]^+$, 216.0422; Found 216.0436.

***N*-methoxymethacrylamide (1v)**



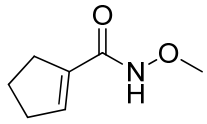
Following general procedure C, **1v** was obtained in 32 % yield (368 mg, 3.2 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). $\mathbf{R_F}$ (Petroleum ether /EtOAc 2:1): 0.21. The characteristics data is consistent with the one reported before.[10]

***N*-methoxy-2-phenylacrylamide (1w)**



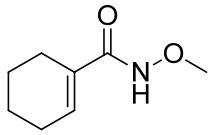
Following general procedure C, **1w** was obtained in 80 % yield (437 mg, 2.4 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.32. The characteristics data is consistent with the one reported before.[11]

***N*-methoxycyclopent-1-enecarboxamide (1x)**



Following general procedure C, **1x** was obtained in 81 % yield (340.7mg, 2.4 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.16. The characteristics data is consistent with the one reported before.[11]

***N*-methoxycyclohex-1-enecarboxamide (1y)**

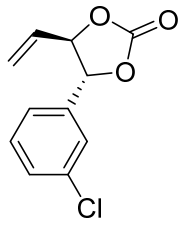


Following general procedure C, **1y** was obtained in 51 % yield (235.9mg, 1.5 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.17. The characteristics data is consistent with the one reported before.[10]

Preparation and Characterization of4-vinyl-1,3-dioxolan-2-one 2

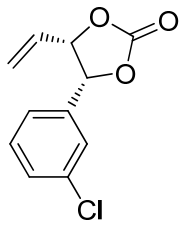
4-vinyl-1,3-dioxolan-2-one **2b, 2d, 2e** were prepared following the procedure reported by Trombini.[12] All the characteristic data are consistent with the data reported before.[12]

***rac*-(4R,5R)-4-(3-chlorophenyl)-5-vinyl-1,3-dioxolan-2-one (*trans*-2c)**



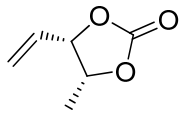
Following general procedure D, The product *trans*-**2c** was obtained in 14 % yield (168 mg, 0.75 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 8:1): 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 3H), 7.24 (d, *J* = 6.8 Hz, 1H), 5.98 (m, 1H), 5.52 (d, *J* = 8.4 Hz, 1H), 5.48 (d, *J* = 15.0 Hz, 1H), 5.25 (d, *J* = 8.0 Hz, 1H), 4.84 (dd, *J* = 7.9, 7.3 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 136.8, 135.2, 130.9, 130.5, 129.8, 125.9, 123.8, 122.5, 84.5, 82.0. **ESI-MS**: calculated $C_{11}H_9ClO_3Na[M+Na]^+$, 247.0132; Found 247.0132.

***rac*-(4R,5S)-4-(3-chlorophenyl)-5-vinyl-1,3-dioxolan-2-one (*cis*-2c)**



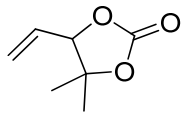
Following general procedure D, The product *cis*-**2c** was obtained in 33 % yield (394 mg, 1.75 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 8:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.23 (d, *J* = 1.9 Hz, 1H), 7.14 – 7.09 (m, 1H), 5.75 (d, *J* = 7.9 Hz, 1H), 5.49 – 5.21 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 135.1, 134.9, 130.1, 129.8, 129.4, 126.3, 124.3, 121.8, 80.9, 79.7.**ESI-MS**: calculated $C_{11}H_9ClO_3Na[M+Na]^+$, 247.0132; Found 247.0137.

***rac*-(4R,5S)-4-methyl-5-vinyl-1,3-dioxolan-2-one (*cis*-2f)**



Following general procedure D, The product *cis*-**2c** was obtained in 20 % yield (153.7 mg, 1.20 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 8:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (m, 1H), 5.52 (d, J = 17.2 Hz, 1H), 5.48 (d, J = 10.5 Hz, 1H), 5.10 (t, J = 7.3 Hz, 1H), 4.95 – 4.85 (m, 1H), 1.34 (d, J = 6.6 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 129.3, 121.5, 80.1, 76.0, 15.5. **ESI-MS**: calculated $C_6H_8O_3Na[M+Na]^+$, 151.0366; Found 151.0371.

4,4-dimethyl-5-vinyl-1,3-dioxolan-2-one (2g)



Following general procedure D, The product **2g** was obtained in 16 % yield (89.2 mg, 0.63 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 8:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.77 (m, 1H), 5.51 (d, J = 17.1 Hz, 1H), 5.45 (d, J = 10.5 Hz, 1H), 4.69 (dt, J = 7.1, 1.1 Hz, 1H), 1.52 (s, 3H), 1.34 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 129.5, 121.4, 85.8, 84.2, 25.8, 22.1.**ESI-MS**: calculated $C_7H_{10}O_3Na[M+Na]^+$, 165.0522; Found 165.0524.

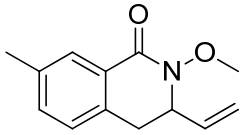
3. General procedure and characterization of products

General procedure E

To a 15 mL-schlenk tube charged with a stirring bar, was added *N*-methoxybenzamide **1** (0.2 mmol, 1.0 equiv), 4-vinyl-1,3-dioxolan-2-one **2a** (0.3 mmol, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.32 mg, 0.01 mmol, 5.0 mol%), $Pd_2(dba)_3$ (9.16 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3(13.0 mg, 0.04 mmol, 20 mol%), CsOAc (38.0 mg, 0.2 mmol, 1.0 equiv) and CH_3CN (1.0 mL). No special precautions were taken to exclude moisture and air. The reaction was allowed to stir at 50 °C until the complete consumption of **1** as monitored by TLC analysis (typically 12 hours). The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **4**.

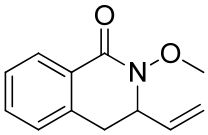
Characterization of products

2-methoxy-7-methyl-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4a)



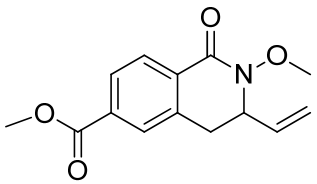
Following the general procedure E (12 h), The product **4a** was obtained in 74 % yield (32.2 mg, 0.147 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 6:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 5.85 (m, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.27 (dt, *J* = 17.1, 1.0 Hz, 1H), 5.18 (dt, *J* = 10.4, 0.9 Hz, 1H), 4.57 – 4.38 (m, 1H), 3.90 (s, 3H), 3.38 (dd, *J* = 15.9, 5.9 Hz, 1H), 3.00 (dd, *J* = 15.9, 4.8 Hz, 1H), 2.37 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 136.9, 134.9, 133.1, 132.4, 128.4, 128.1, 127.4, 117.9, 62.8, 61.6, 34.7, 20.99. **ESI-MS**: calculated $C_{13}H_{16}NO_2[M+H]^+$, 218.1176; Found 218.1183.

2-methoxy-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4b)



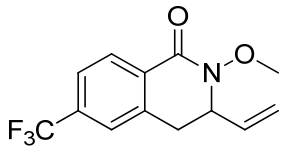
Following the general procedure E (24 h), The product **4b** was obtained in 31 % yield (12.5 mg, 0.061 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 6:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 6:1): 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 5.85 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.27 (d, *J* = 17.1 Hz, 1H), 5.18 (d, *J* = 10.3 Hz, 1H), 4.51 (dd, *J* = 11.4, 5.8 Hz, 1H), 3.90 (s, 3H), 3.42 (dd, *J* = 16.0, 5.9 Hz, 1H), 3.04 (dd, *J* = 16.0, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 135.5, 134.8, 132.3, 128.4, 128.1, 127.5, 127.1, 118.1, 62.9, 61.5, 35.0. **ESI-MS**: calculated $C_{12}H_{14}NO_2[M+H]^+$, 204.1019 ; Found.204.1023.

methyl 2-methoxy-1-oxo-3-vinyl-1,2,3,4-tetrahydroisoquinoline-6-carboxylate (4c)



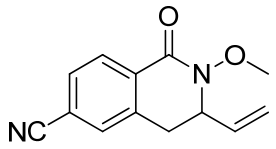
Following the general procedure E (3 h), The product **4c** was obtained in 54 % yield (28.3 mg, 0.108 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.79 (s, 1H), 5.75 (m, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 4.48 (dd, *J* = 6.0, 4.7 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.41 (dd, *J* = 16.1, 6.0 Hz, 1H), 3.04 (dd, *J* = 16.1, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 162.4, 135.5, 134.4, 133.4, 132.1, 128.8, 128.3, 128.2, 118.4, 62.9, 61.2, 52.4, 34.8. **ESI-MS**: calculated $C_{14}H_{16}NO_4[M+H]^+$, 262.1074; Found 262.1075.

2-methoxy-6-(trifluoromethyl)-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4d)



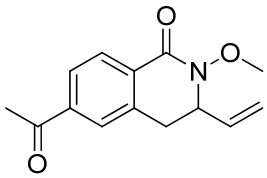
Following the general procedure E (4 h), The product **4d** was obtained in 56 % yield (30.5 mg, 0.112 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.44 (s, 1H), 5.83 (m, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.29 (d, *J* = 17.1 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 4.56 (dd, *J* = 11.0, 5.9 Hz, 1H), 3.92 (s, 3H), 3.49 (dd, *J* = 16.2, 6.0 Hz, 1H), 3.11 (dd, *J* = 16.2, 4.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 136.1, 134.2, 133.9 (q, *J* = 32.6 Hz), 131.5, 128.7, 124.6 (q, *J* = 3.5 Hz), 124.1 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 273.6 Hz), 118.6, 62.9, 61.1, 34.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0.**ESI-MS**: calculated $C_{13}H_{13}F_3NO_2[M+H]^+$, 272.0893; Found 272.0896.

2-methoxy-1-oxo-3-vinyl-1,2,3,4-tetrahydroisoquinoline-6-carbonitrie (4e)



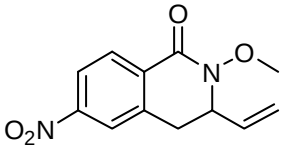
Following the general procedure E (11 h), The product **4e** was obtained in 53 % yield (23.7 mg, 0.106 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 5.74 (m, *J* = 16.9, 10.3, 6.3 Hz, 1H), 5.21 (d, *J* = 17.3 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 4.50 (dt, *J* = 6.0, 4.8 Hz, 1H), 3.84 (s, 3H), 3.41 (dd, *J* = 16.3, 6.0 Hz, 1H), 3.03 (dd, *J* = 16.3, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 136.4, 133.9, 132.2, 131.2, 130.8, 128.8, 118.7, 117.8, 115.7, 63.0, 60.8, 34.5. **ESI-MS**: calculated $C_{13}H_{13}N_2O_2[M+H]^+$, 229.0972; Found 229.0975.

6-acetyl-2-methoxy-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4f)



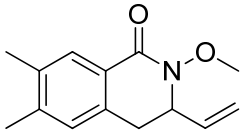
Following the general procedure E (5 h), The product **4f** was obtained in 40 % yield (19.6 mg, 0.080 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.77 (s, 1H), 5.83 (m, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.28 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.56 (dd, *J* = 10.8, 5.8 Hz, 1H), 3.92 (s, 3H), 3.50 (dd, *J* = 15.2, 6.9 Hz, 1H), 3.13 (dd, *J* = 16.1, 4.4 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 162.3, 139.8, 135.8, 134.3, 132.1, 128.5, 127.3, 127.1, 118.4, 62.9, 61.1, 34.9, 26.8.**ESI-MS**: calculated $C_{14}H_{16}NO_3[M+H]^+$, 246.1125; Found 246.1128.

2-methoxy-6-nitro-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4g)



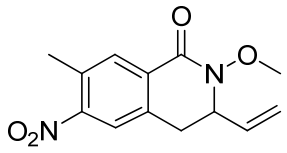
Following the general procedure E (18 h), The product **4g** was obtained in 57 % yield (28.0 mg, 0.114 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.6 Hz, 1H), 8.18 (dd, *J* = 8.5, 2.0 Hz, 1H), 8.08 – 8.04 (s, 1H), 5.82 (m, *J* = 16.8, 10.4, 6.3 Hz, 1H), 5.30 (dd, *J* = 17.1, 0.6 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 4.68 – 4.52 (m, 1H), 3.94 (s, 3H), 3.55 (dd, *J* = 16.3, 6.1 Hz, 1H), 3.18 (dd, *J* = 16.3, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 150.0, 137.0, 133.8, 133.7, 129.6, 122.7, 122.2, 118.8, 63.0, 60.9, 34.7.**ESI-MS**: calculated $C_{12}H_{13}N_2O_4[M+H]^+$, 249.0870; Found 249.0867.

2-methoxy-6,7-dimethyl-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4h)



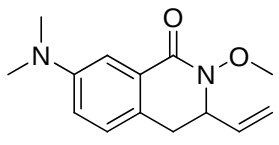
Following the general procedure E (13 h), The product **4h** was obtained in 49 % yield (22.6 mg, 0.098 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 6:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 6.92 (s, 1H), 5.85 (m, 1H), 5.26 (d, *J* = 17.1 Hz, 1H), 5.17 (d, *J* = 10.3 Hz, 1H), 4.47 (dd, *J* = 11.3, 6.0 Hz, 1H), 3.89 (s, 3H), 3.34 (dd, *J* = 15.9, 5.9 Hz, 1H), 2.96 (dd, *J* = 15.9, 4.8 Hz, 1H), 2.27 (d, *J* = 2.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 141.7, 135.6, 135.0, 132.9, 128.9, 128.7, 125.9, 117.8, 62.8, 61.6, 34.6, 19.8, 19.2. **ESI-MS**: calculated$C_{14}H_{18}NO_2[M+H]^+$, 232.1332; Found 232.1329.

2-methoxy-7-methyl-6-nitro-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4i)



Following the general procedure E (13 h), The product **4i** was obtained in 75 % yield (39.2 mg, 0.150 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.68 (s, 1H), 5.81 – 5.68 (m, 1H), 5.21 (d, *J* = 17.1 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 4.50 (d, *J* = 3.7 Hz, 1H), 3.85 (s, 3H), 3.40 (dd, *J* = 16.0, 5.3 Hz, 1H), 3.02 (d, *J* = 16.0 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 151.2, 134.2, 134.0, 132.6, 132.2, 131.9, 123.6, 118.6, 63.0, 61.0, 34.2, 19.7. **ESI-MS**: calculated $C_{13}H_{15}N_2O_4[M+H]^+$, 263.1026; Found 263.1022.

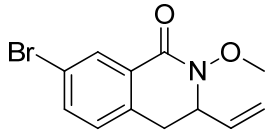
7-(dimethylamino)-2-methoxy-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4j)



Following the general procedure E (5 h), The product **4j** was obtained in 58 % yield (29.0 mg, 0.116 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.4 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.73 (dd, *J* = 8.3, 2.6 Hz, 1H), 5.79 (m, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 5.09 (d, *J* = 10.3 Hz, 1H), 4.38 (dd, *J*

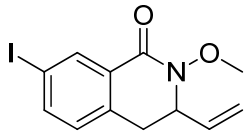
= 11.5, 5.7 Hz, 1H), 3.82 (s, 3H), 3.24 (dd, *J* = 15.7, 5.8 Hz, 1H), 2.90 (s, 6H), 2.85 (dd, *J* = 15.8, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 149.8, 135.3, 128.8, 128.2, 123.0, 117.7, 116.5, 111.3, 62.7, 61.9, 40.6, 34.1. **ESI-MS**: calculated $C_{14}H_{18}N_2O_2[M+H]^+$, 247.1441; Found 247.1436.

7-bromo-2-methoxy-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4k)



Following the general procedure E (5 h), The product **4k** was obtained in 58 % yield (32.9 mg, 0.116 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 2.1 Hz, 1H), 7.56 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 1H), 5.84 (m , 1H), 5.28 (d, *J* = 17.1 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 4.52 (dt, *J* = 11.1, 5.4 Hz, 1H), 3.91 (s, 3H), 3.38 (dd, *J* = 16.1, 5.9 Hz, 1H), 3.02 (dd, *J* = 16.2, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 135.2, 134.4, 134.2, 131.0, 130.2, 129.3, 121.1, 118.4, 62.9, 61.2, 34.5. **ESI-MS**: calculated $C_{12}H_{13}BrNO_2[M+H]^+$, 282.0124; Found 282.0120.

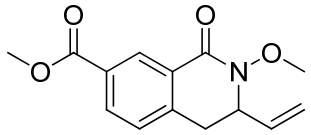
7-iodo-2-methoxy-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4l)



Following the general procedure E (10 h), The product **4l** was obtained in 44 % yield (28.7 mg, 0.088 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 1.8 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.82 (m , 1H), 5.27 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 4.51 (dt, *J* = 6.0, 4.8 Hz, 1H), 3.89 (s, 3H), 3.36 (dd, *J* = 16.2, 6.0 Hz, 1H), 2.99 (dd, *J* = 16.2, 4.6 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 141.1, 136.8, 134.8, 134.4, 130.2, 129.4,

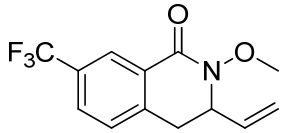
118.4, 92.0, 62.9, 61.1, 34.6. **ESI-MS**: calculated$C_{12}H_{13}INO_2[M+H]^+$, 329.9986; Found 329.9987.

methyl 2-methoxy-1-oxo-3-vinyl-1,2,3,4-tetrahydroisoquinoline-7-carboxylate (4m)



Following the general procedure E (3 h), The product **4m** was obtained in 91 % yield (47.4 mg, 0.182 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 1.7 Hz, 1H), 8.11 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 5.83 (m , 1H), 5.28 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 4.55 (dd, *J* = 11.0, 6.0 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.48 (dd, *J* = 16.4, 6.0 Hz, 1H), 3.11 (dd, *J* = 16.4, 4.6 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 162.6, 140.3, 134.4, 133.2, 129.6, 129.4, 128.8, 127.9, 118.3, 62.9, 61.0, 52.2, 35.1. **ESI-MS**: calculated$C_{14}H_{16}NO_4[M+H]^+$, 262.1074; Found 262.1075.

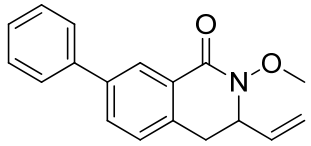
2-methoxy-7-(trifluoromethyl)-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4n)



Following the general procedure E (3 h), The product **4n** was obtained in 73 % yield (40.5 mg, 0.146 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.69 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 5.83 (m, 1H), 5.29 (d, *J* = 17.1 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 4.56 (ddd, *J* = 11.0, 4.8, 1.1 Hz, 1H), 3.92 (s, 3H), 3.49 (dd, *J* = 16.3, 6.0 Hz, 1H), 3.12 (dd, *J* = 16.4, 4.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 139.2, 134.2, 129.9 (q, *J* = 33.1 Hz), 129.2, 128.8 (q, *J* = 3.4 Hz), 128.3, 125.3 (q, *J* = 3.9 Hz), 123.7 (q, *J* = 272.3 Hz), 118.5,

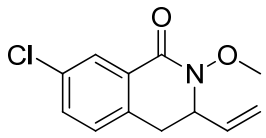
62.9, 61.0, 34.8.^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7. **ESI-MS**: calculated$C_{13}H_{13}F_3NO_2[M+H]^+$, 272.0893; Found 272.0892.

2-methoxy-7-phenyl-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4o)



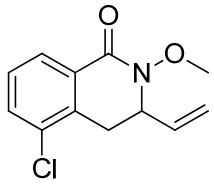
Following the general procedure E (3 h), The product **4o** was obtained in 82 % yield (45.0 mg, 0.164 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.9 Hz, 1H), 7.60 (dd, *J* = 7.8, 2.0 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.39 – 7.33 (m, 2H), 7.31 – 7.25 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 5.81 (m, 1H), 5.23 (d, *J* = 17.1 Hz, 1H), 5.13 (d, *J* = 10.3 Hz, 1H), 4.46 (td, *J* = 6.0, 3.0 Hz, 1H), 3.85 (s, 3H), 3.38 (dd, *J* = 16.1, 5.9 Hz, 1H), 3.00 (dd, *J* = 16.1, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 140.3, 139.8, 134.9, 134.3, 130.8, 128.8, 128.1, 127.6, 127.0, 126.6, 118.2, 62.9, 61.5, 34.8. **ESI-MS**: calculated $C_{18}H_{17}NO_2[M+H]^+$,280.1332; Found 280.1333.

7-chloro-2-methoxy-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4p)



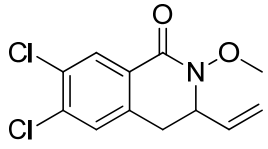
Following the general procedure E (14 h), The product **4p** was obtained in 46 % yield (21.8 mg, 0.092 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.2 Hz, 1H), 7.40 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 5.83 (m, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 4.51 (ddd, *J* = 11.1, 4.8, 1.1 Hz, 1H), 3.90 (s, 3H), 3.39 (dd, *J* = 16.1, 5.9 Hz, 1H), 3.02 (dd, *J* = 16.1, 4.7 Hz, 1H). ^{13}C NMR (101 MH, $CDCl_3$) δ 162.2, 134.4, 133.7, 133.3, 132.3, 130.0, 129.0, 128.0, 118.3, 62.9, 61.2, 34.4.**ESI-MS**: calculated$C_{12}H_{13}ClNO_2[M+H]^+$, 238.0629; Found238.0625.

5-chloro-2-methoxy-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4p')



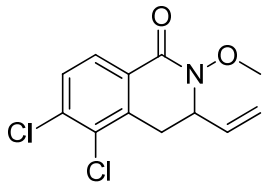
Following the general procedure E (14 h), The product **4p'** was obtained in 10 % yield (4.9 mg, 0.020 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.51 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 5.85 (m, 1H), 5.29 (d, *J* = 17.1 Hz, 1H), 5.21 (d, *J* = 10.3 Hz, 1H), 4.58 – 4.51 (m, 1H), 3.91 (s, 3H), 3.37 (dd, *J* = 16.9, 6.1 Hz, 1H), 3.30 (dd, *J* = 16.9, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 134.5, 133.4, 132.9, 132.9, 130.2, 128.1, 126.8, 118.3, 62.9, 60.6, 32.2. **ESI-MS**: calculated$C_{12}H_{13}ClNO_2[M+H]^+$, 238.0629; Found 238.0622.

6,7-dichloro-2-methoxy-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4q)



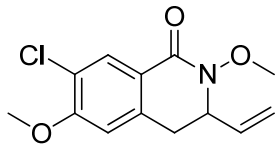
Following the general procedure E (4 h), The product **4q** was obtained in 37 % yield (19.9 mg, 0.074 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 5:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.30 (s, 1H), 5.83 (m, 1H), 5.29 (d, *J* = 17.1 Hz, 1H), 5.24 (d, *J* = 10.3 Hz, 1H), 4.53 (dt, *J* = 6.0, 4.8 Hz, 1H), 3.92 (s, 3H), 3.40 (dd, *J* = 16.2, 6.0 Hz, 1H), 3.02 (dd, *J* = 16.2, 4.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 136.6, 135.0, 134.1, 131.9, 130.0, 129.5, 128.3, 118.6, 63.0, 61.1, 34.2. **ESI-MS**: calculated $C_{12}H_{12}Cl_2NO_2[M+H]^+$, 272.0240; Found 272.0233.

5,6-dichloro-2-methoxy-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4q')



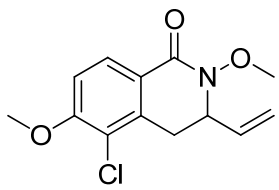
Following the general procedure E (4 h), The product **4q'** was obtained in 8 % yield (4.5 mg, 0.016 mmol) as a white soild after column chromatography (eluent = Petroleum ether/EtOAc 5:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 5.84 (m, 1H), 5.29 (d, *J* = 17.1 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 4.54 (dt, *J* = 6.1, 5.0 Hz, 1H), 3.90 (s, 3H), 3.41 (dd, *J* = 17.0, 6.0 Hz, 1H), 3.34 (dd, *J* = 17.0, 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 137.4, 135.5, 134.3, 131.2, 129.0, 128.4, 127.2, 118.5, 63.0, 60.5, 33.2. **ESI-MS**: calculated $C_{12}H_{12}Cl_2NO_2[M+H]^+$, 272.0240; Found 272.0243.

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



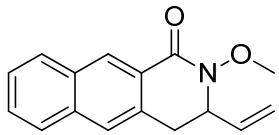
Following the general procedure E (6 h), The product **4r** was obtained in 49 % yield (26.2 mg, 0.098 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 6.66 (s, 1H), 5.84 (m, 1H), 5.28 (d, *J* = 17.1 Hz, 1H), 5.21 (d, *J* = 10.3 Hz, 1H), 4.52 – 4.45 (m, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.39 (dd, *J* = 16.1, 5.9 Hz, 1H), 3.00 (dd, *J* = 16.1, 4.9 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 158.0, 136.0, 134.6, 130.1, 121.8, 121.8, 118.3, 110.4, 62.9, 61.4, 56.3, 35.1. **ESI-MS**: calculated$C_{13}H_{15}ClNO_3[M+H]^+$, 268.0735; Found 268.0732.

5-chloro-2,6-dimethoxy-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one (4r')



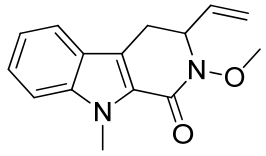
Following the general procedure E (6 h), The product **4r'** was obtained in 23 % yield (12.1 mg, 0.046 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.7 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 5.85 (m, 1H), 5.28 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.51 (dd, *J* = 11.3, 5.9 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 3.36 (dd, *J* = 16.9, 5.9 Hz, 1H), 3.30 (dd, *J* = 16.9, 5.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 158.2, 135.4, 134.7, 128.1, 122.1, 120.7, 118.2, 110.0, 62.9, 60.7, 56.3, 32.6.**ESI-MS**: calculated $C_{13}H_{15}ClNO_3[M+H]^+$, 268.0735; Found 268.0732.

2-methoxy-3-vinyl-3,4-dihydrobenzo[g]isoquinolin-1(2*H*)-one (4s)



Following the general procedure E (12 h), The product **4s** was obtained in 38 % yield (19.0 mg, 0.076 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.51 (s, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 5.84 – 5.70 (m, 1H), 5.21 (d, *J* = 17.0 Hz, 1H), 5.08 (d, *J* = 10.3 Hz, 1H), 4.50 (d, *J* = 4.8 Hz, 1H), 3.88 (s, 3H), 3.51 (dd, *J* = 15.6, 5.4 Hz, 1H), 3.12 (d, *J* = 15.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 135.1, 134.9, 132.0, 131.3, 129.4, 129.3, 128.2, 127.0, 126.5, 126.2, 126.1, 118.0, 62.8, 61.4, 35.3.**ESI-MS**: calculated$C_{16}H_{16}NO_2[M+H]^+$,254.1176; Found 254.1166.

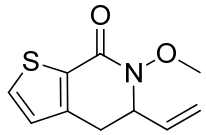
2-methoxy-9-methyl-3-vinyl-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-b]indol-1-one (4t)



Following the general procedure E (18 h), The product **4t** was obtained in 50 % yield (24.3 mg, 0.100 mmol) as a colorless oil after column chromatography (eluent =

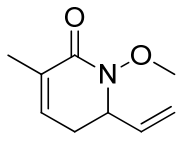
Petroleum ether/EtOAc 8:1 v/v). **R_F** (Petroleum ether/EtOAc 8:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.23 (m, 2H), 7.07 (m, 1H), 5.93 (m, 1H), 5.25 (d, *J* = 17.1 Hz, 1H), 5.14 (d, *J* = 10.3 Hz, 1H), 4.47 (q, *J* = 6.2 Hz, 1H), 4.04 (s, 3H), 3.82 (s, 3H), 3.28 (dd, *J* = 16.1, 6.2 Hz, 1H), 3.05 (dd, *J* = 16.1, 5.9 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 139.7, 135.5, 125.0, 124.8, 124.1, 120.2, 118.0, 116.8, 110.3, 100.0, 64.1, 63.4, 31.3, 27.2.**ESI-MS**: calculated$C_{15}H_{17}N_2O_2[M+H]^+$, 257.1285; Found 257.1277.

6-methoxy-5-vinyl-5,6-dihydrothieno[2,3-c]pyridin-7(4*H*)-one (4u)



Following the general procedure E (6 h), The product **4u** was obtained in 56 % yield (23.4 mg, 0.112 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 4.9 Hz, 1H), 6.88 (d, *J* = 4.9 Hz, 1H), 5.92 (m, 1H), 5.30 (d, *J* = 17.1 Hz, 1H), 5.23 (d, *J* = 10.3 Hz, 1H), 4.51 (dt, *J* = 12.1, 6.0 Hz, 1H), 3.87 (s, 3H), 3.26 (dd, *J* = 16.4, 6.1 Hz, 1H), 3.02 (dd, *J* = 16.4, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 141.7, 134.8, 132.4, 130.6, 126.8, 118.3, 63.4, 63.3, 31.5.**ESI-MS**: calculated$C_{10}H_{12}NO_2S[M+H]^+$, 210.0583; Found 210.0594.

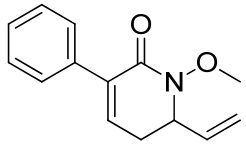
1-methoxy-3-methyl-6-vinyl-5,6-dihydropyridin-2(1*H*)-one (6a)



Following the general procedure E (23 h), The product **6a** was obtained in 49 % yield (17.8 mg, 0.098 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 5:1 v/v). **R_F** (Petroleum ether/EtOAc 4:1): 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (td, *J* = 4.6, 1.6 Hz, 1H), 5.89 (m, 1H), 5.24 (d, *J* = 15.9 Hz, 1H), 5.21 (d, *J* = 9.1 Hz, 1H), 4.29 (q, *J* = 6.6 Hz, 1H), 3.79 (s, 3H), 2.73 – 2.61 (m, 1H), 2.48 – 2.34 (m, 1H), 1.88 (dd, *J* = 3.6, 1.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

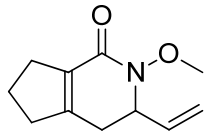
166.6, 135.4, 132.5, 131.0, 117.8, 62.8, 62.1, 31.3, 16.5.**ESI-MS**: calculated$C_9H_{14}NO_2Na[M+Na]^+$, 190.0839; Found 190.0850.

1-methoxy-3-phenyl-6-vinyl-5,6-dihydropyridin-2(1*H*)-one (6b)



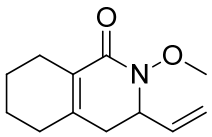
Following the general procedure E (24 h), The product **6b** was obtained in 46 % yield (17.5 mg, 0.092 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 6:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.36 – 7.27 (m, 3H), 6.52 (t, 1H), 5.96 (m, 1H), 5.32 (d, *J* = 17.1 Hz, 1H), 5.26 (d, *J* = 10.3 Hz, 1H), 4.42 (q, *J* = 6.5 Hz, 1H), 3.84 (s, 3H), 2.89 (ddd, *J* = 18.1, 6.6, 3.9 Hz, 1H), 2.62 (ddd, *J* = 18.1, 5.9, 5.0 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 135.8, 135.6, 135.1, 135.1, 128.8, 127.9, 127.8, 118.0, 63.0, 61.7, 31.6.**ESI-MS**: calculated$C_{14}H_{16}NO_2[M+H]^+$, 230.1176; Found 230.1173.

2-methoxy-3-vinyl-2,3,4,5,6,7-hexahydro-1*H*-cyclopenta[c]pyridin-1-one (6c)



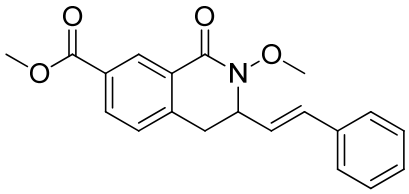
Following the general procedure E (48 h), The product **6c** was obtained in 42 % yield (16.2 mg, 0.084 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (m, 1H), 5.24 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 4.33 (dd, *J* = 13.4, 6.6 Hz, 1H), 3.78 (s, 3H), 2.74 – 2.56 (m, 3H), 2.52 – 2.38 (m, 3H), 1.96 (dt, *J* = 11.5, 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 151.2, 135.8, 131.9, 117.5, 63.0, 62.5, 36.4, 32.3, 30.0, 22.4.**ESI-MS**: calculated$C_{11}H_{16}NO_2[M+H]^+$,194.1176; Found 194.1175.

2-methoxy-3-vinyl-3,4,5,6,7,8-hexahydroisoquinolin-1(2*H*)-one (6d)



Following the general procedure E (24 h), The product **6d** was obtained in 72 % yield (28.8 mg, 0.144 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 6:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 6:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (m, 1H), 5.23 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.23 (dd, *J* = 13.3, 7.0 Hz, 1H), 3.78 (s, 3H), 2.63 – 2.53 (m, 1H), 2.38 – 2.20 (m, 3H), 2.07 (s, 2H), 1.68 – 1.53 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 144.0, 135.7, 126.1, 117.6, 62.9, 61.4, 36.7, 30.2, 22.8, 21.9, 21.8. **ESI-MS**: calculated$C_{12}H_{18}NO_2[M+H]^+$, 208.1332; Found 208.1334.

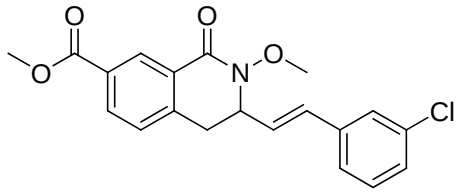
(*E*)-methyl-2-methoxy-1-oxo-3-styryl-1,2,3,4-tetrahydroisoquinoline-7-carboxylate (4v)



Following the general procedure E (23 h), with *trans*-**2b** yield: (38.0 mg, 0.112 mmol, 56%), with *cis*-**2b** yield: (21.2 mg, 0.060 mmol, 30%), The product **4v** was obtained as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 2:1): 0.46. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 1.7 Hz, 1H), 8.12 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.32 – 7.27 (m, 4H), 7.26 – 7.19 (m, 2H), 6.61 (d, *J* = 15.4 Hz, 1H), 6.15 (dd, *J* = 15.8, 7.2 Hz, 1H), 4.70 (m, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.56 (dd, *J* = 16.3, 6.0 Hz, 1H), 3.19 (dd, *J* = 16.4, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 162.5, 140.4, 135.7, 133.5, 133.2, 129.6, 129.5, 128.8, 128.5, 128.1, 128.0, 126.6, 125.4, 63.0, 61.0, 52.2, 35.6. **ESI-MS**: calculated$C_{20}H_{20}NO_4[M+H]^+$, 338.1387; Found 338.1375.

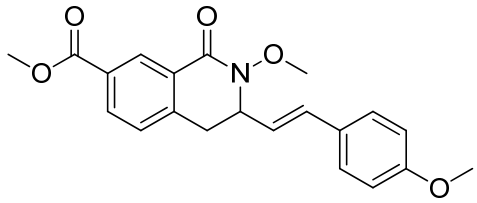
(*E*)-methyl-3-(3-chlorostyryl)-2-methoxy-1-oxo-1,2,3,4-tetrahydroisoquinoline-

7-carboxylate (4w)



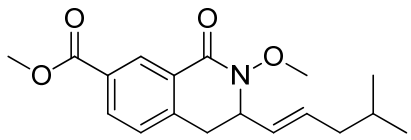
Following the general procedure E (22 h), with *trans*-**2c** yield: (48.9 mg, 0.130 mmol, 65%), with *cis*-**2c** yield: (24.9 mg, 0.066 mmol, 33%), The product **4w** was obtained as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 3:1 v/v). **R_F** (Petroleum ether/EtOAc 2:1): 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 1.7 Hz, 1H), 8.13 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.12 (m, 3H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.16 (dd, *J* = 15.8, 7.0 Hz, 1H), 4.70 (dt, *J* = 6.0, 4.8 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.58 (dd, *J* = 16.4, 5.9 Hz, 1H), 3.19 (dd, *J* = 16.5, 4.4 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 162.5, 140.1, 137.6, 134.5, 133.3, 132.2, 129.8, 129.6, 128.7, 128.6, 128.1, 128.0, 127.0, 126.4, 124.8, 63.0, 60.7, 52.2, 35.4. **ESI-MS**: calculated$C_{20}H_{19}ClNO_4[M+H]^+$, 372.0997; Found 372.0978.

(*E*)-methyl-2-methoxy-3-(4-methoxystyryl)-1-oxo-1,2,3,4-tetrahydroisoquinoline-7-carboxylate (4x)



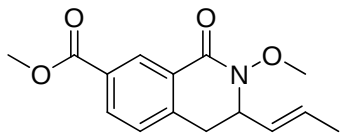
Following the general procedure E (27 h), with *trans*-**2d** yield: (47.6 mg, 0.128 mmol, 64%), with *cis*-**2d** yield: (14.8 mg, 0.040 mmol, 20%), The product **4x** was obtained as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). **R_F** (Petroleum ether/EtOAc 2:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.12 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.26 (s, 1H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.00 (dd, *J* = 15.8, 7.3 Hz, 1H), 4.68 (dd, *J* = 11.8, 5.7 Hz, 1H), 3.93 (s, 6H), 3.78 (s, 3H), 3.55 (dd, *J* = 16.4, 5.9 Hz, 1H), 3.18 (dd, *J* = 16.4, 4.6 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 162.5, 159.6, 140.5, 133.2, 133.0, 129.6, 129.5, 128.8, 128.5, 128.0, 127.8, 123.1, 113.9, 63.0, 61.1, 55.2, 52.2, 35.7.**ESI-MS**: calculated$C_{21}H_{22}NO_5[M+H]^+$,368.1492; Found 368.1477.

(*E*)-methyl-2-methoxy-3-(4-methylpent-1-en-1-yl)-1-oxo-1,2,3,4-tetrahydroisoquinoline-7-carboxylate (4y)



Following the general procedure E (72 h), with *trans*-**2e** yield: (12.4 mg, 0.038 mmol, 19%), with *cis*-**2e** yield: (31.4 mg, 0.098 mmol, 49%), The product **4y** was obtained as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 5:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 1.7 Hz, 1H), 8.11 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 5.67 (dt, *J* = 14.6, 7.2 Hz, 1H), 5.42 (dd, *J* = 15.3, 7.0 Hz, 1H), 4.50 (dd, *J* = 11.8, 5.7 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.44 (dd, *J* = 16.3, 5.8 Hz, 1H), 3.08 (dd, *J* = 16.3, 4.9 Hz, 1H), 1.86 (t, *J* = 7.0 Hz, 2H), 1.55 (m,1H), 0.78 (dd, *J* = 11.3, 6.7 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 162.5, 140.7, 133.9, 133.1, 129.5, 129.4, 128.9, 127.9, 127.1, 62.8, 60.7, 52.2, 41.3, 35.7, 28.0, 22.1, 21.9. **ESI-MS**: calculated$C_{18}H_{24}NO_4[M+H]^+$, 318.1700; Found 318.1705.

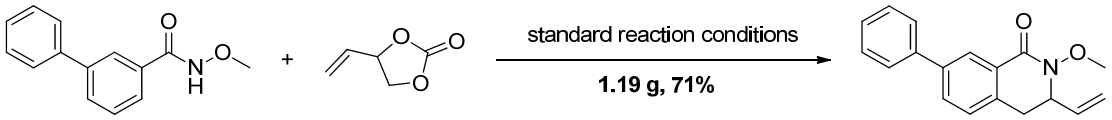
(*E*)-methyl-2-methoxy-1-oxo-3-(prop-1-en-1-yl)-1,2,3,4-tetrahydroisoquinoline-7-carboxylate (4z)



Following the general procedure E (37 h), with *cis*-**2f** yield: (26.5 mg, 0.096 mmol, 48%), The product **4z** was obtained as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). $\mathbf{R_F}$ (Petroleum ether/EtOAc 4:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 1.7 Hz, 1H), 8.11 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 1H), 5.73 (m, 1H), 5.49 – 5.41 (m, 1H), 4.47 (dd, *J* = 11.8, 5.8 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.45 (dd, *J* = 16.4, 5.8 Hz, 1H), 3.06 (dd, *J* = 16.4, 4.6 Hz, 1H), 1.65 (dd, *J* = 6.5, 1.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 162.5, 140.6,

133.1, 129.9, 129.5, 129.4, 128.8, 127.9, 127.3, 62.8, 60.7, 52.2, 35.6, 17.6. **ESI-MS**: calculated$C_{15}H_{18}NO_4[M+H]^+$, 276.1230; Found 276.1225.

4. Gram-scale reaction

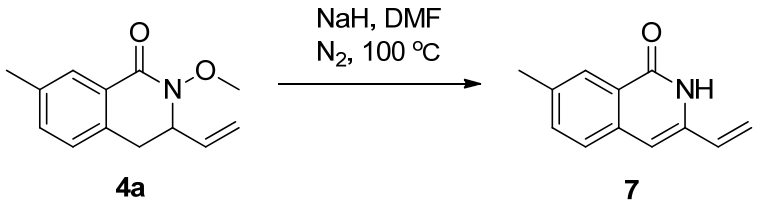


1o 2a 4o

Without any particular precautions to exclude air and moisture, to a round flask (50 mL in volume) equipped with a stirring bar, was added *N*-methoxy-[1,1'-biphenyl]-3-carboxamidesubstrate **1o** (1.36 g, 6.0 mmol, 1.0 equiv), $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (124.8 mg, 0.15 mmol, 2.5 mol%), $Pd_2(dba)_3$(137.4 mg, 0.15 mmol, 2.5 mol%), Cs_2CO_3(391 mg, 1.2 mmol, 20 mol%), CsOAc (1.15 g, 6 mmol, 1.0 equiv), subsequently, CH_3CN (30 mL) was then added followed by 4-vinyl-1,3-dioxolan-2-one **2a** (0.9 mL, 9.0 mmol, 1.5 equiv). The reaction was allowed to stir at 50 ^oC for 9 h. The reaction mixture was then diluted with EtOAc (100 mL) and washed with water. The aqueous phase was extracted with EtOAc again. Afterwards, the organic layer was combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with Petroleum ether:EtOAc (4:1) to afford the pure product **4o** (1.19 g, 71%).

5. Derivatization of the product

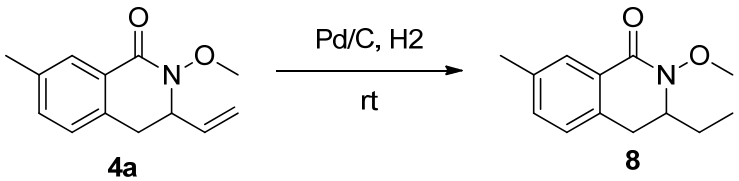
5.1 Synthesis of 7-methyl-3-vinylisoquinolin-1(2*H*)-one(7)



4a **7**

To a solution of 60% NaH (16 mg, 0.4 mmol, 2 equiv) in dry DMF (2 mL) was added 2-methoxy-7-methyl-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one **4a** (44 mg, 0.2 mmol, 1.0 equiv) at 100 ºC (oil bath) under nitrogen atmosphere. The reaction was stirred until the complete consumption of **4a** as monitored by TLC analysis (4 h). After cooling the reaction mixture to room temperature, it was diluted with EtOAc (20 mL) and washed with water. The aqueous phase was extracted with EtOAc again. The organic layer was combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica (Petroleum ether:EtOAc = 4:1, **Rf**: 0.34) to afford the pure product **7** (33.8 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.47 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 6.51 (dd, *J* = 17.8, 11.3 Hz, 1H), 6.45 (s, 1H), 5.95 (d, *J* = 17.8 Hz, 1H), 5.47 (d, *J* = 11.3 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 137.1, 135.6, 135.5, 134.3, 130.4, 127.2, 126.4, 125.7, 115.1, 107.2, 21.4. **ESI-MS**: calculated$C_{12}H_{12}NO[M+H]^+$, 186.0913; Found 186.0924.

5.2 Synthesis of 3-ethyl-2-methoxy-7-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (8)

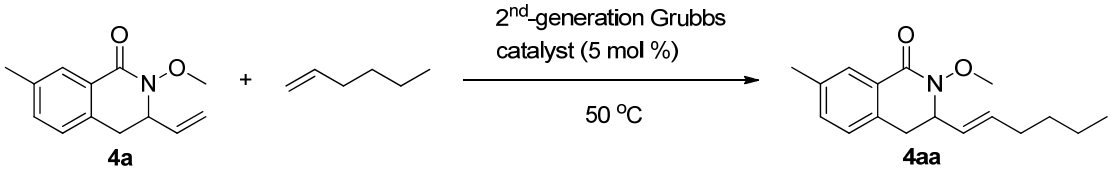


4a **8**

To a solution of 2-methoxy-7-methyl-3-vinyl-3,4-dihydroisoquinolin-1(2*H*)-one **4a** (44 mg, 0.2 mmol, 1.0 equiv) in dry MeOH (10 mL) was added Pd/C (4.3 mg, 10 mol%) at room temperature. The reaction was stirred at hydrogen atmosphere using balloon until the complete consumption of **4a** as monitored by TLC analysis (22 h). The reaction

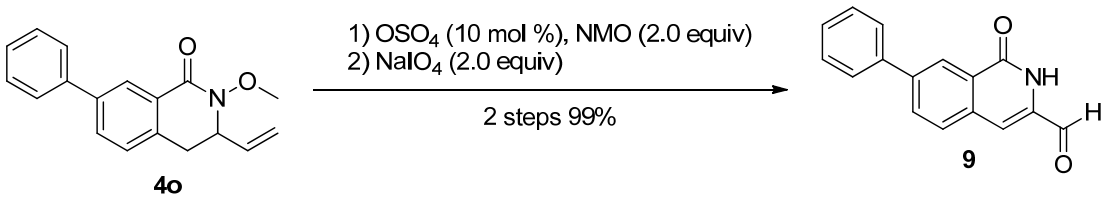
mixture was then diluted with EtOAc (20 mL) and washed with water. The aqueous phase was extracted with EtOAc again. The organic layer was combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica (Petroleum ether:EtOAc = 6:1, **Rf**: 0.21) to afford the pure product **8** (39.5 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.24 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 3.89 (s, 3H), 3.87 – 3.80 (m, 1H), 3.30 (dd, *J* = 16.0, 5.8 Hz, 1H), 2.94 (dd, *J* = 16.0, 4.1 Hz, 1H), 2.37 (s, 3H), 1.91 (m, 1H), 1.57 – 1.44 (m, 1H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 136.7, 133.0, 132.7, 128.3, 128.2, 127.6, 62.5, 60.3, 32.3, 23.9, 20.9, 10.4. **ESI-MS**: calculated$C_{13}H_{18}NO_2[M+H]^+$, 220.1332; Found 220.1332.

5.3Synthesisof(*E*)-3-(hex-1-en-1-yl)-2-methoxy-7-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (4aa)



Compound **4a**(44 mg, 0.2 mmol, 1.0 equiv) and 1-hexene (125 uL, 1.0 mmol, 5.0 equiv) were dissolved in dry DCM (2.0 mL) at room temperature. 2nd-generation Grubbs catalyst (5 mol%) was added to the solution and then the reaction mixture was heated to 50^{o}C under nitrogen atmosphere for 7 h, After cooling the reaction mixture to room temperature, it was then diluted with EtOAc (20 mL) and washed with water. The aqueous phase was extracted with EtOAc again. The organic layer was combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica (Petroleum ether:EtOAc = 6:1, **Rf**: 0.29) to afford the pure product **4aa** (46.7 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.24 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 5.75 – 5.63 (m, 1H), 5.45 (m, 1H), 4.42 (dd, *J* = 12.5, 5.5 Hz, 1H), 3.88 (s, 3H), 3.34 (dd, *J* = 15.9, 5.7 Hz, 1H), 2.95 (dd, *J* = 15.9, 5.1 Hz, 1H), 2.37 (s, 3H), 1.97 (dt, *J* = 7.6, 3.9 Hz, 2H), 1.33 – 1.16 (m, 4H), 0.83 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 136.8, 134.8, 133.0, 132.8, 128.3, 128.2, 127.4, 126.5, 62.7, 61.3, 35.3, 31.7, 30.9, 21.9, 20.9, 13.8.**ESI-MS**: calculated$C_{17}H_{24}NO_2[M+H]^+$, 274.1802; Found 274.1797.

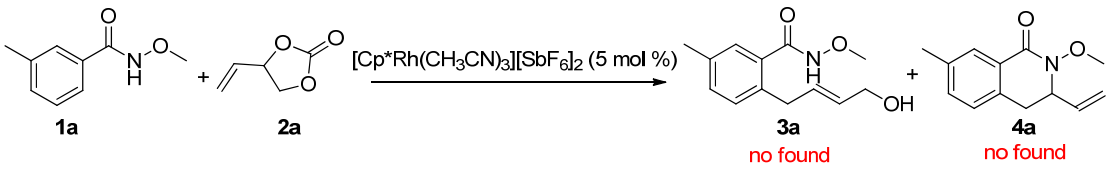
5.4 Synthesis of 1-oxo-7-phenyl-1,2-dihydroisoquinoline-3-carbaldehyde (9)



To a solution of **4o** (56 mg, 0.2 mmol, 1.0 equiv) in CH_3CN (0.7 mL) and H_2O (0.3 mL) were added OsO_4 (5.08 mg, 10 mol%) and NMO (47 mg, 0.4 mmol, 2.0 equiv). The reaction was stirred at room temperature overnight. The reaction mixture was quenched with a saturated aqueous $Na_2S_2O_3$ solution, and the aqueous phase was extracted with EtOAc. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo to give the corresponding diol as a white oil. The crude diol was dissolved in THF (2.0 mL) and H_2O (1.0 mL). To the reaction mixture was added $NaIO_4$ (85 mg, 0.4 mmol, 2.0 equiv). The mixture was stirred for 40 minute at room temperature and then diluted with a saturated aqueous $Na_2S_2O_3$ solution. The aqueous phase was extracted with EtOAc. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Flash chromatography (Petroleum ether:EtOAc = 2:1, **Rf**: 0.21) afforded **9** (49.4 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.73 (d, *J* = 1.9 Hz, 1H), 8.03 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.74 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.43 (ddd, *J* = 7.4, 3.7, 1.2 Hz, 1H), 7.20 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.9, 161.2, 143.4, 139.1, 134.8, 134.2, 132.0, 129.8, 129.1, 129.1, 128.5, 127.3, 126.3, 118.0.**ESI-MS**: calculated$C_{16}H_{12}NO_2[M+H]^+$, 250.0863; Found 250.0848.

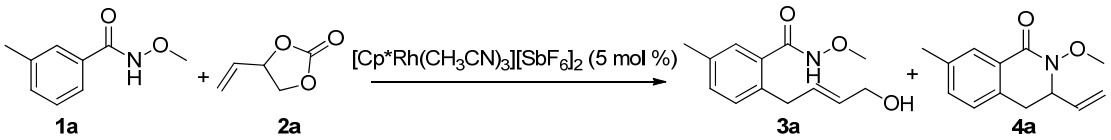
6. Mechanistic experiments

6.1 Stepwise reaction under the catalysis of rhodium



To a 15 mL-schlenk tube charged with a stirring bar, was added *N*-methoxy-3-methylbenzamide **1a** (33 mg, 0.2 mmol, 1.0 equiv), 4-vinyl-1,3-dioxolan-2-one **2a** (30 uL, 0.3 mmol, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.32 mg, 0.01 mmol, 5 mol%) and CH_3CN (1.0 mL). The reaction was allowed to stir at 50°C with standard 12 hours. No formation of **3a** or **4a** was found.

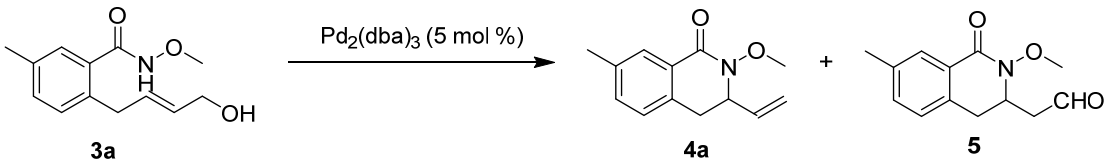
6.2 Stepwise reaction under the catalysis of rhodium in the presence of bases



To a 15 mL-schlenk tube charged with a stirring bar, was added *N*-methoxy-3-methylbenzamide **1a** (33.0 mg, 0.2 mmol, 1.0 equiv), 4-vinyl-1,3-dioxolan-2-one **2a** (0.3 mmol, 1.5 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.32 mg, 0.01 mmol, 5 mol%), Cs_2CO_3(13.0 mg, 0.04 mmol, 20 mol%), CsOAc (38.0 mg, 0.2 mmol, 1.0 equiv), and CH_3CN (1.0 mL). The reaction was allowed to stir at 50°C for12 hours. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the product **3a** (Petroleum ether/EtOAc 1:3, 9.4 mg, 0.040 mmol, 20%**)** and trace amount of product **4a** (1.2 mg, 0.006 mmol, 3%**)**. **3a:** $\mathbf{R_F}$ (Petroleum ether/EtOAc 1:3): 0.28. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.20 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 5.72 – 5.62 (m, 1H), 5.54 (m, 1H), 3.87 (t, *J* = 4.4 Hz, 2H), 3.69 (s, 3H), 3.39 (d, *J* =

6.5 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.7, 135.6, 134.9, 133.4, 131.5, 130.4, 129.7, 128.3, 127.9, 63.0, 61.2, 34.6, 20.3. **ESI-MS**: calculated$C_{13}H_{17}NO_3Na[M+Na]^+$, 258.1101; Found 258.1091.

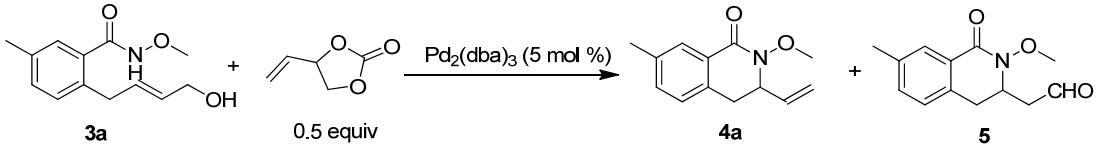
6.3 Stepwise *N*-allylation reaction under the catalysis of $Pd_2(dba)_3$



3a **4a** **5**

To a 15 mL-schlenk tube charged with a stirring bar, was added(*E*)-2-(4-hydroxybut-2-en-1-yl)-*N*-methoxy-5-methylbenzamide **3a** (47 mg, 0.2 mmol, 1.0 equiv), $Pd_2(dba)_3$ (9.16 mg, 0.01 mmol, 5 mol%), Cs_2CO_3 (13.0 mg, 0.04 mmol, 20 mol%), CsOAc (38.0 mg, 0.2 mmol, 1.0 equiv) and CH_3CN (1.0 mL). The reaction was allowed to stir at 50 ^oC with standard 12 hours. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with appropriate solvent to afford **4a** (3.9 mg, 0.018 mmol, 9%) and **5 (**Petroleum ether/EtOAc 2:1, 22.7 mg**,** 0.096 mmol, 48%). **5: R_F** (Petroleum ether/EtOAc 2:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 7.94 (s, 1H), 7.28 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 4.53 (m, 1H), 3.88 (s, 3H), 3.39 (dd, *J* = 16.2, 5.5 Hz, 1H), 3.03 – 2.93 (m, 2H), 2.64 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 164.2, 137.3, 133.5, 132.2, 128.6, 127.8, 127.7, 62.8, 54.2, 45.1, 33.6, 20.9. ESI-MS: calculated$C_{13}H_{16}NO_3[M+H]^+$, 234.1125; Found 234.1119.

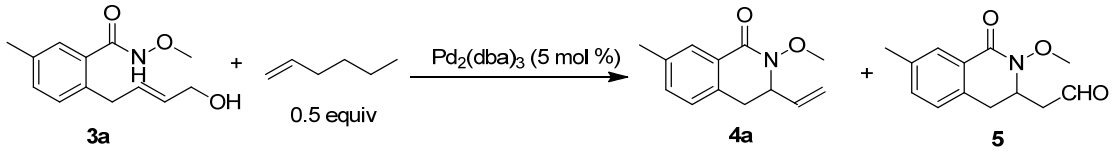
6.4 Stepwise *N*-allylation reaction under the catalysis of $Pd_2(dba)_3$ in the presence of excess amount of 2a



3a 0.5 equiv **4a** **5**

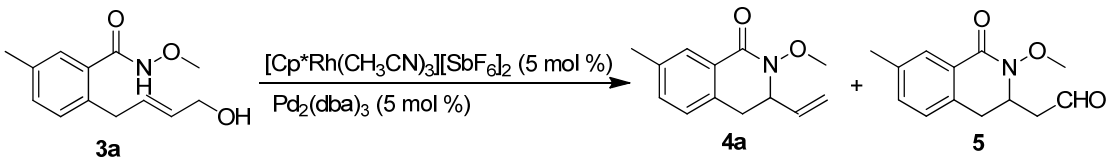
To a 15 mL-schlenk tube charged with a stirring bar, was added (*E*)-2-(4-hydroxybut-2-en-1-yl)-*N*-methoxy-5-methylbenzamide **3a** (47 mg, 0.2 mmol, 1.0 equiv), 4-vinyl-1,3-dioxolan-2-one **2a** (0.1 mmol, 0.5 equiv), $Pd_2(dba)_3$ (9.16 mg, 0.01 mmol, 5 mol%),Cs_2CO_3(13.0 mg, 0.04 mmol, 20 mol%), CsOAc (38.0 mg, 0.2 mmol, 1.0 equiv) and CH_3CN (1.0 mL). The reaction was allowed to stir at 50ºC for 12 hours. After the reaction was cooled to room temperature, 1-iodo-4-methoxybenzene (23.4 mg, 0.1 mmol, 0.5 equiv, internal standard) added to reaction mixture. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The yields of **4a**(88%) and **5**(8%) were determined by ^{1}H NMR.

6.5 Stepwise *N*-allylation reaction under the catalysis of $Pd_2(dba)_3$ in the presence of 0.5 equiv ofhex-1-ene



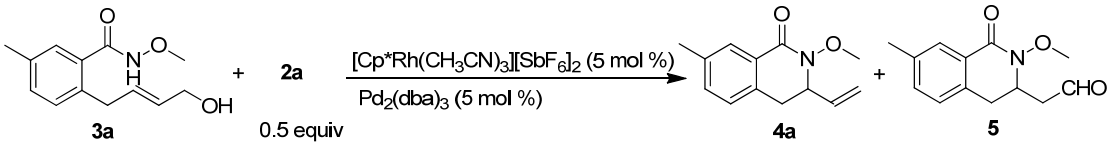
To a 15 mL-schlenk tube charged with a stirring bar, was added (*E*)-2-(4-hydroxybut-2-en-1-yl)-*N*-methoxy-5-methylbenzamide **3a** (47 mg, 0.2 mmol, 1.0 equiv), hex-1-ene (0.1 mmol, 0.5 equiv), $Pd_2(dba)_3$ (9.16 mg, 0.01 mmol, 5 mol%),Cs_2CO_3(13.0 mg, 0.04 mmol, 20 mol%), CsOAc (38.0 mg, 0.2 mmol, 1.0 equiv), CH_3CN (1.0 mL) were added into the reaction vessel. The reaction was allowed to stir at 50ºC with standard 12 hours. After cooling the reaction mixture to room temperature, 1-iodo-4-methoxybenzene (23.4 mg, 0.1 mmol, 0.5 equiv) was choosed as internalstandardsubstanceadded to reaction mixture. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The yield of **4a** and **5** was determined by ^{1}H NMR, it was showed that produce **4a** (42%) and **5** (34%).

6.6 Stepwise *N*-allylation reaction under the standard reaction conditions



To a 15 mL-schlenk tube charged with a stirring bar, was added (*E*)-2-(4-hydroxybut-2-en-1-yl)-*N*-methoxy-5-methylbenzamide **3a** (47 mg, 0.2 mmol, 1.0 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.32 mg, 0.01 mmol, 5 mol%), $Pd_2(dba)_3$ (9.16 mg, 0.01 mmol, 5 mol%),Cs_2CO_3(13.0 mg, 0.04 mmol, 20 mol%), CsOAc (38.0 mg, 0.2 mmol, 1.0 equiv)and CH_3CN (1.0 mL). The reaction was allowed to stir at 50ºC for 12 hours. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford**5 (**9.9 mg**,** 0.042 mmol, 21%**)** and **4a** (7.2 mg, 0.034 mmol, 17%).

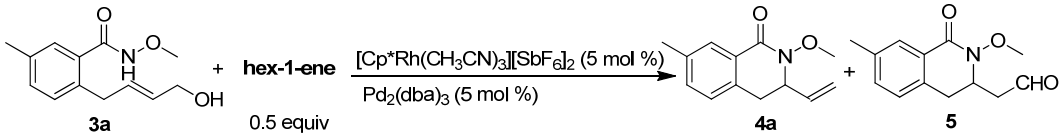
6.7 Stepwise *N*-allylation reaction under the standard reaction conditionsin the presence of 0.5 equiv of 2a



To a 15 mL-schlenk tube charged with a stirring bar, were added (*E*)-2-(4-hydroxybut-2-en-1-yl)-*N*-methoxy-5-methylbenzamide **3a** (47 mg, 0.2 mmol, 1.0 equiv), 4-vinyl-1,3-dioxolan-2-one **2a** (0.1 mmol, 0.5 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.32 mg, 0.01 mmol, 5 mol%), $Pd_2(dba)_3$ (9.16 mg, 0.01 mmol, 5 mol%),Cs_2CO_3(13.0 mg, 0.04 mmol, 20 mol%), CsOAc (38.0 mg, 0.2 mmol, 1.0 equiv) and CH_3CN (1.0 mL). The reaction was allowed to stir at 50ºC for 12 hours. After cooling the reaction mixture to room temperature, 1-iodo-4-methoxybenzene (23.4 mg, 0.1 mmol, 0.5 equiv, internal standard) was added to reaction mixture. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The

aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The yields of **4a** (40%) and **5** (14%) were determined by ^1H NMR

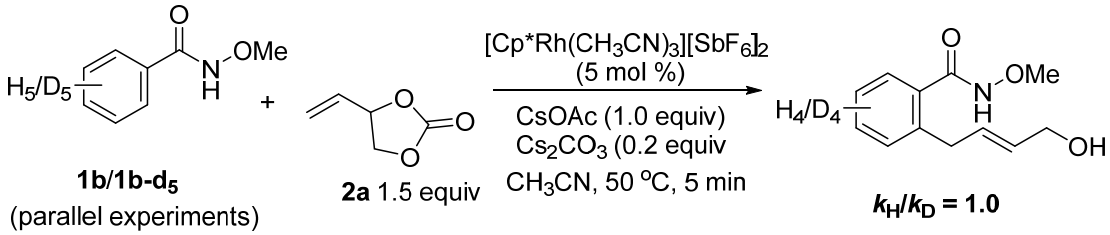
6.8 Stepwise *N*-allylation reaction under the standard reaction conditionsin the presence of 0.5 equivhex-1-ene



To a 15 mL-schlenk tube charged with a stirring bar, was added (*E*)-2-(4-hydroxybut-2-en-1-yl)-*N*-methoxy-5-methylbenzamide **3a** (47 mg, 0.2 mmol, 1.0 equiv), hex-1-ene (0.1 mmol, 0.5 equiv), $[Cp^*Rh(CH_3CN)_3][SbF_6]_2$ (8.32 mg, 0.01 mmol, 5 mol%), $Pd_2(dba)_3$ (9.16 mg, 0.01 mmol, 5 mol%),Cs_2CO_3(13.0 mg, 0.04 mmol, 20 mol%), CsOAc (38.0 mg, 0.2 mmol, 1.0 equiv) and CH_3CN (1.0 mL). The reaction was allowed to stir at 50°C for 12 hours. After cooling the reaction mixture to room temperature, 1-iodo-4-methoxybenzene (23.4 mg, 0.1 mmol, 0.5 equiv, internal standard) was added to reaction mixture. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The yield of **4a**(36%) and **5**(26%) were determined by ^1H NMR.

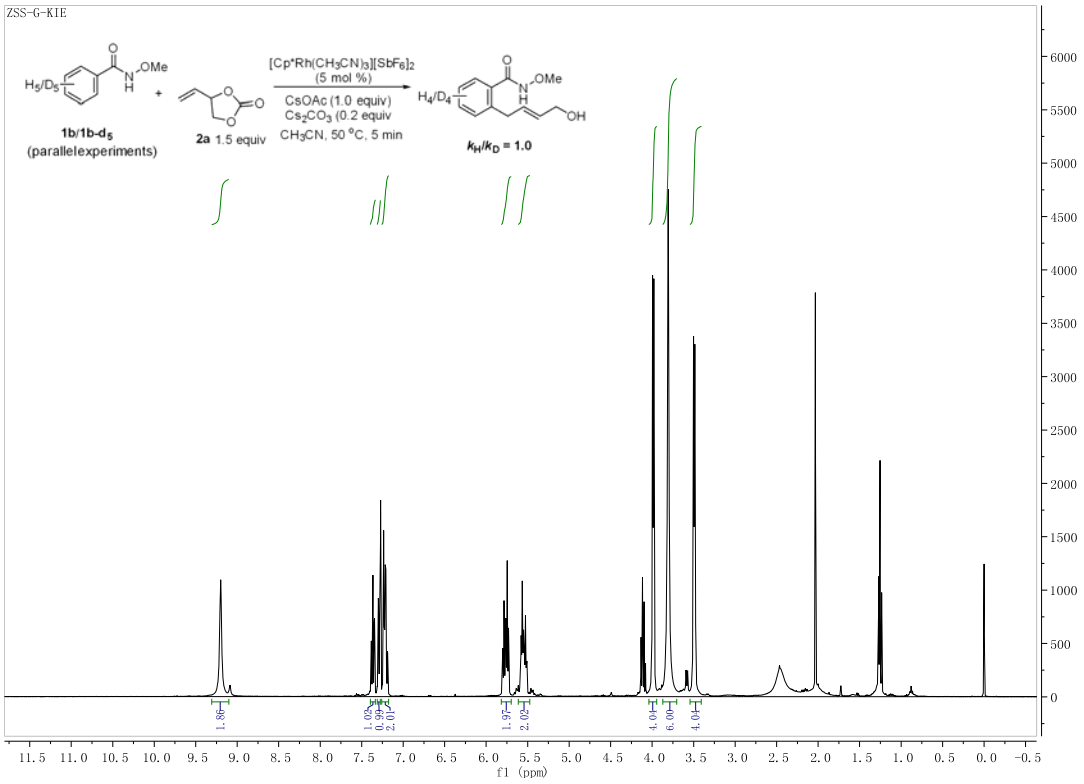
6.8 Kinetic isotope effect

A kinetic isotope effect experiment was conducted to explore the mechanism of the rhodium(III) cycle.

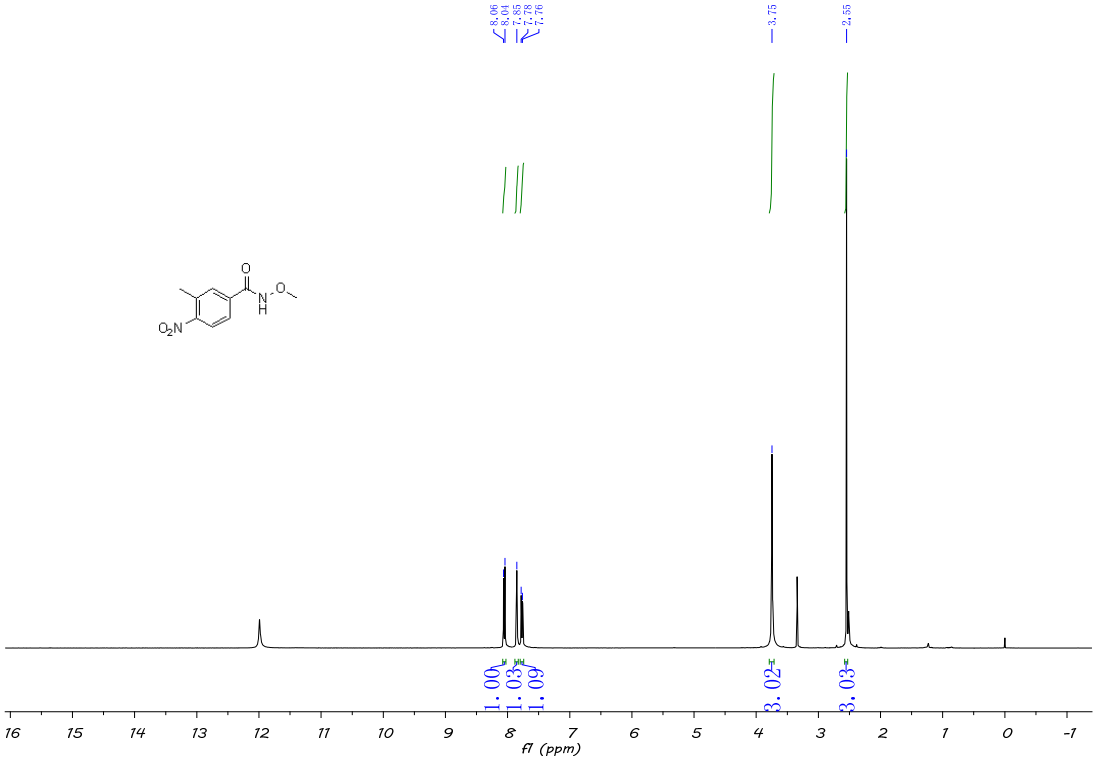


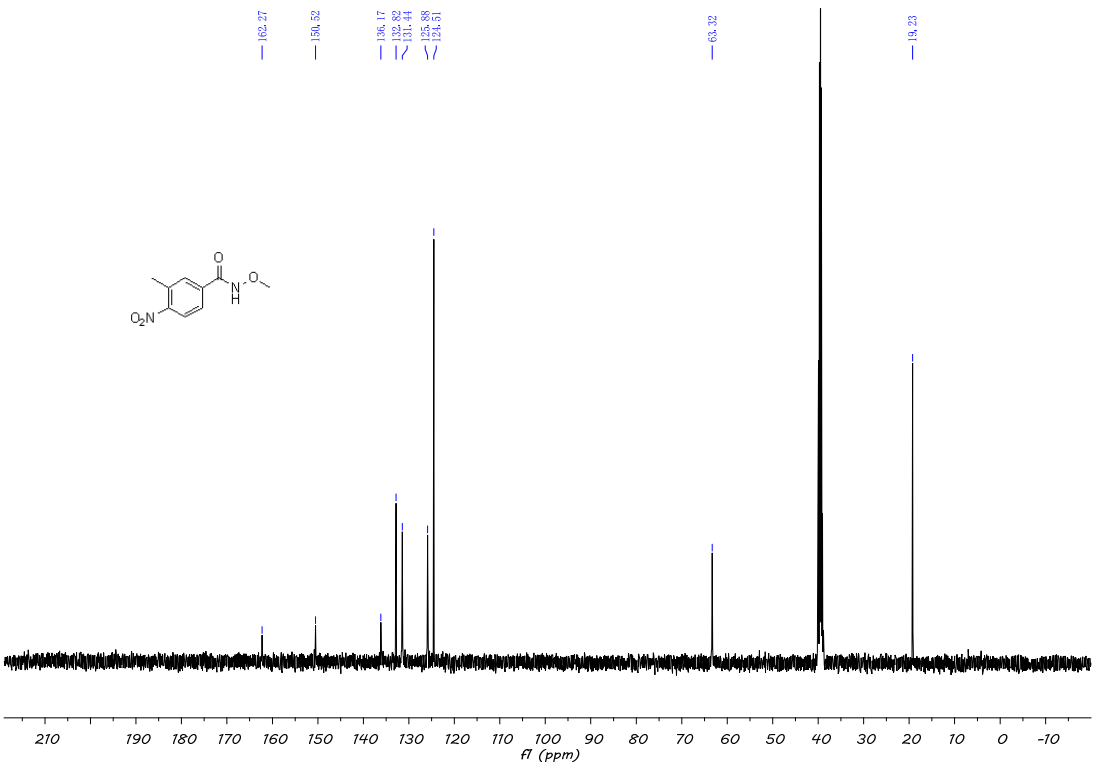
To a schlenk tube (25 mL in volume) equipped with a stirring bar, were added $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (16.6 mg, 0.02 mmol, 5 mol%), Cs_2CO_3 (26.0 mg, 0.08

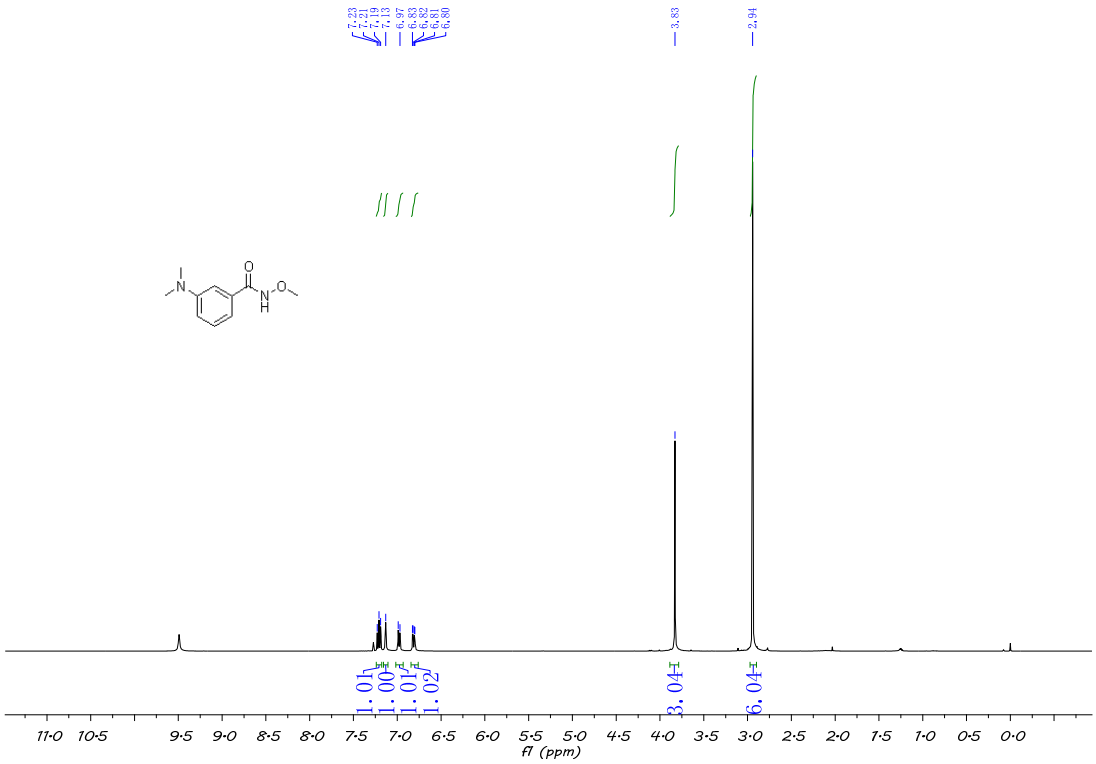
mmol, 0.2 equiv), CsOAc (77.0 mg, 0.4 mmol, 1.0 equiv), **1b** (60 mg, 0.4 mmol, 1.0 equiv), **2a** (58.0 mg, 0.6 mmol, 1.5 equiv) and CH_3CN (2 mL) under air. In another schlenk tube, identical conditions were used except that **1b-d_5** (62 mg, 0.4 mmol, 1.0 equiv) was used instead of **1b**. The two reactions were allowed to stir at 50 ºC for 5 min. Afterwards, the two reaction mixtures were diluted with EtOAc (10 mL) and water (10 mL), and then combined. The organic phase was separated and the aqueous phase was extracted with EtOAc again. The organic layer was combined, washed with brine and dried over Na_2SO_4. The corresponding product (30.3 mg) was obtained by flash column chromatography (eluent: PE/EA = 1:3) in combined 17% yield. The KIE value was determined by ^1H NMR.



7. Characteristic spectra



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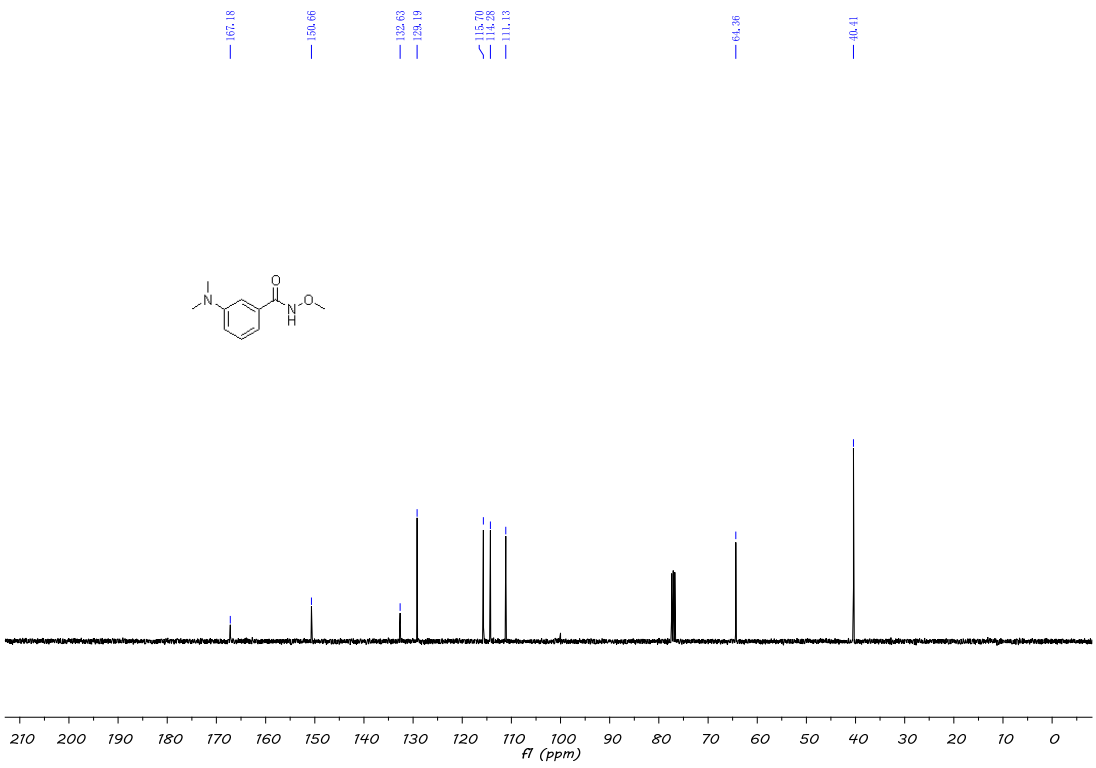
7.11
7.09
7.13
6.97
6.83
6.82
6.81
6.80
3.83
2.94
1.01
1.00
1.01
1.02
3.04
6.04
f1 (ppm)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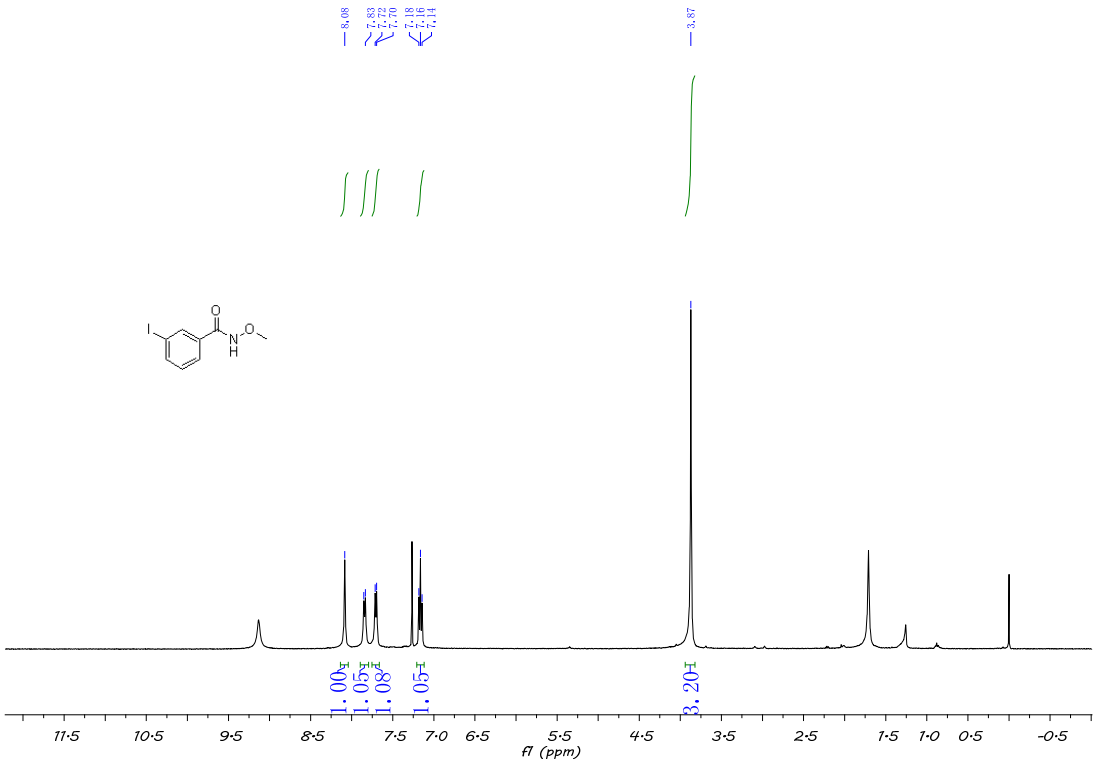
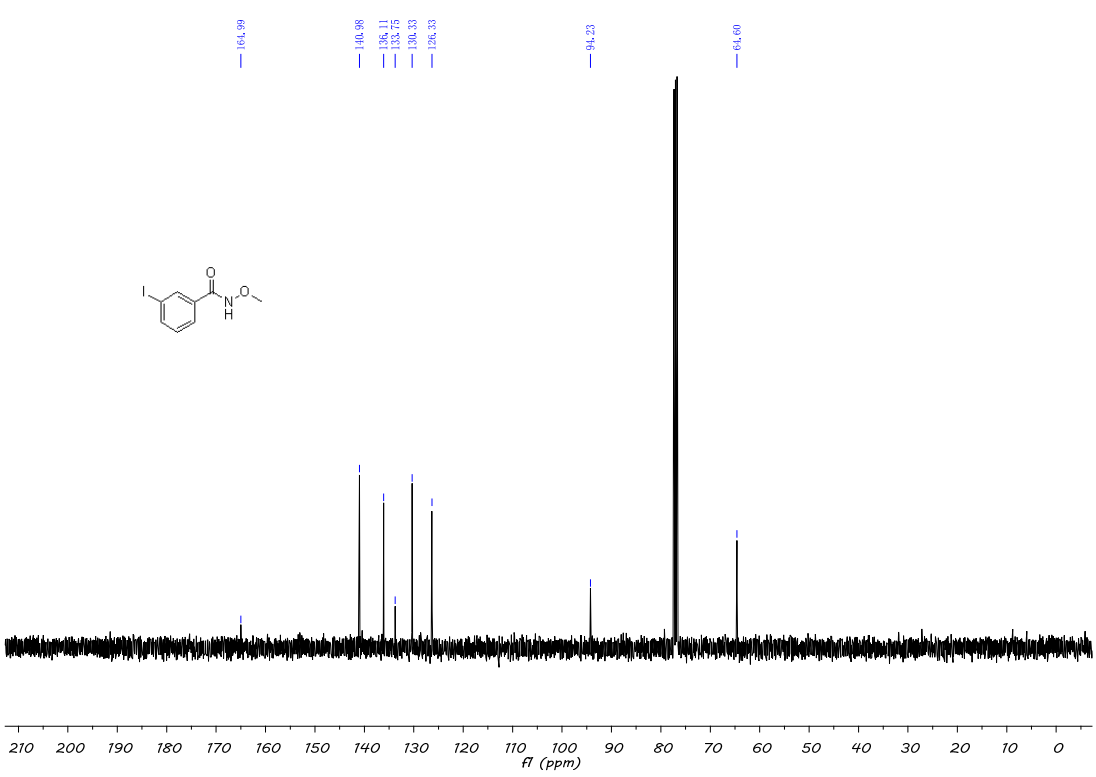
150.66
132.63
129.19
115.70
114.28
111.13
64.36
40.41
f1 (ppm)


8.08
7.83
7.72
7.70
7.18
7.16
7.14
3.87
1.00
1.05
1.08
1.05
3.20
f1 (ppm)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136.11
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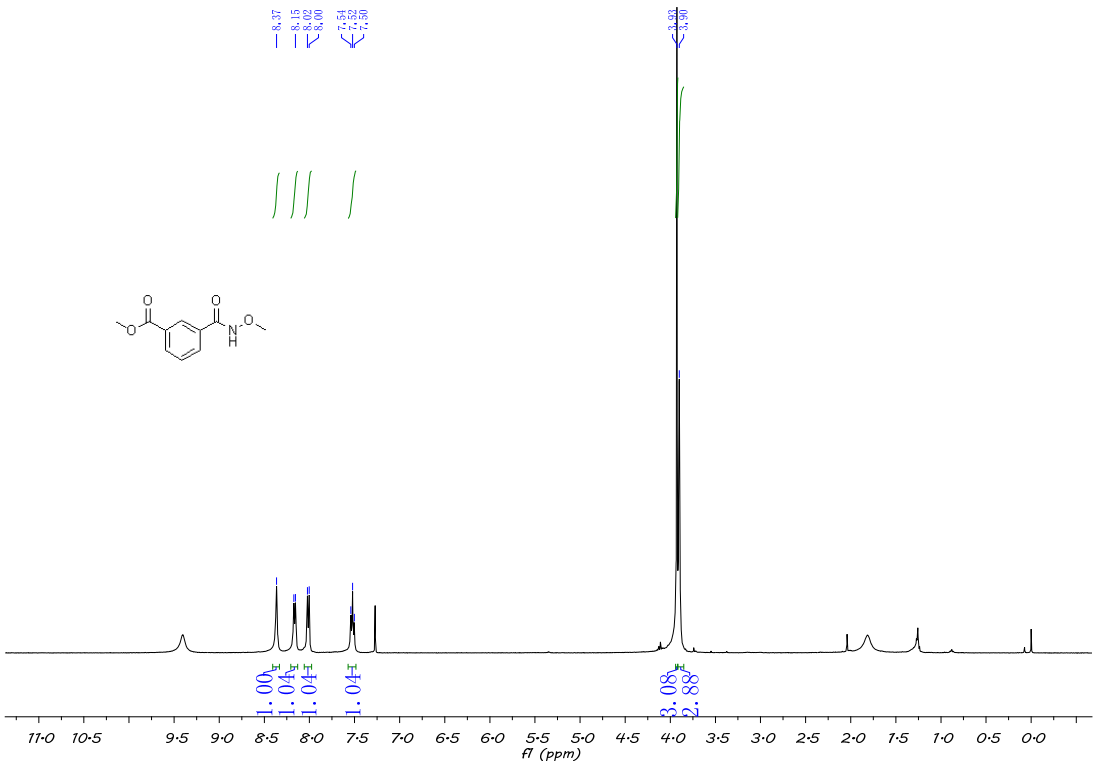
130.33
126.33
94.23
64.60
f1 (ppm)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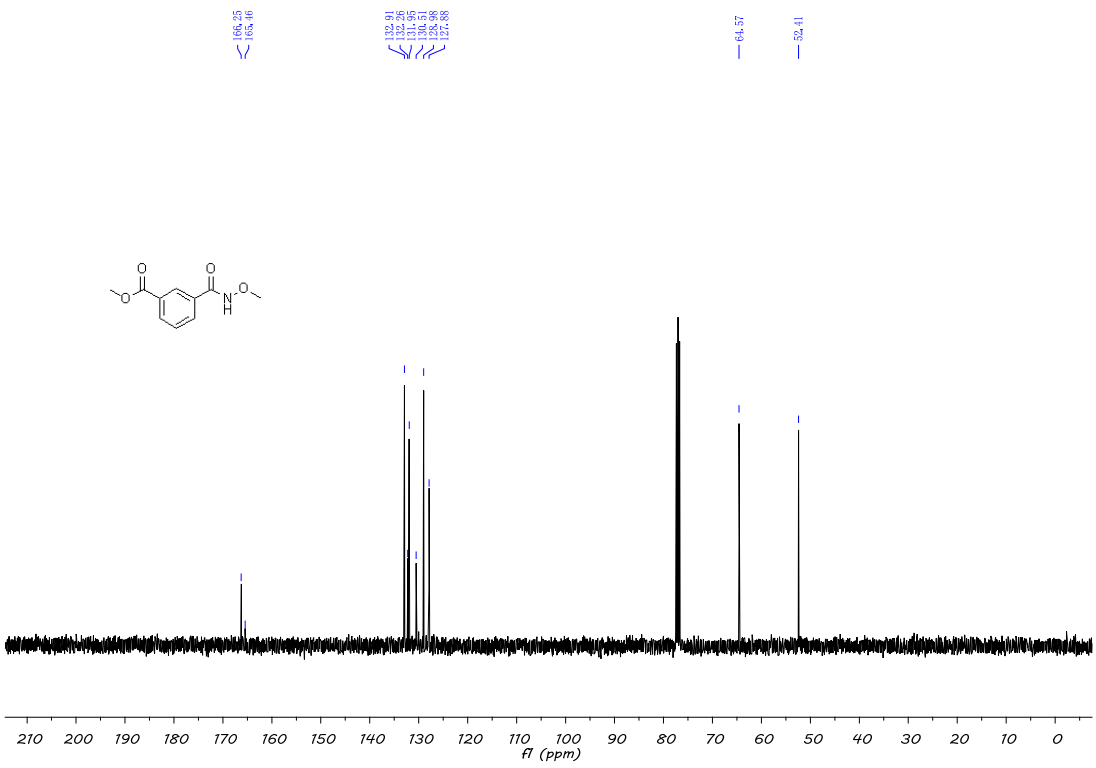
8.15
8.02
8.00
7.54
7.52
7.50
3.93
3.90
1.00
1.04
1.04
1.04
3.08
2.88
f1 (ppm)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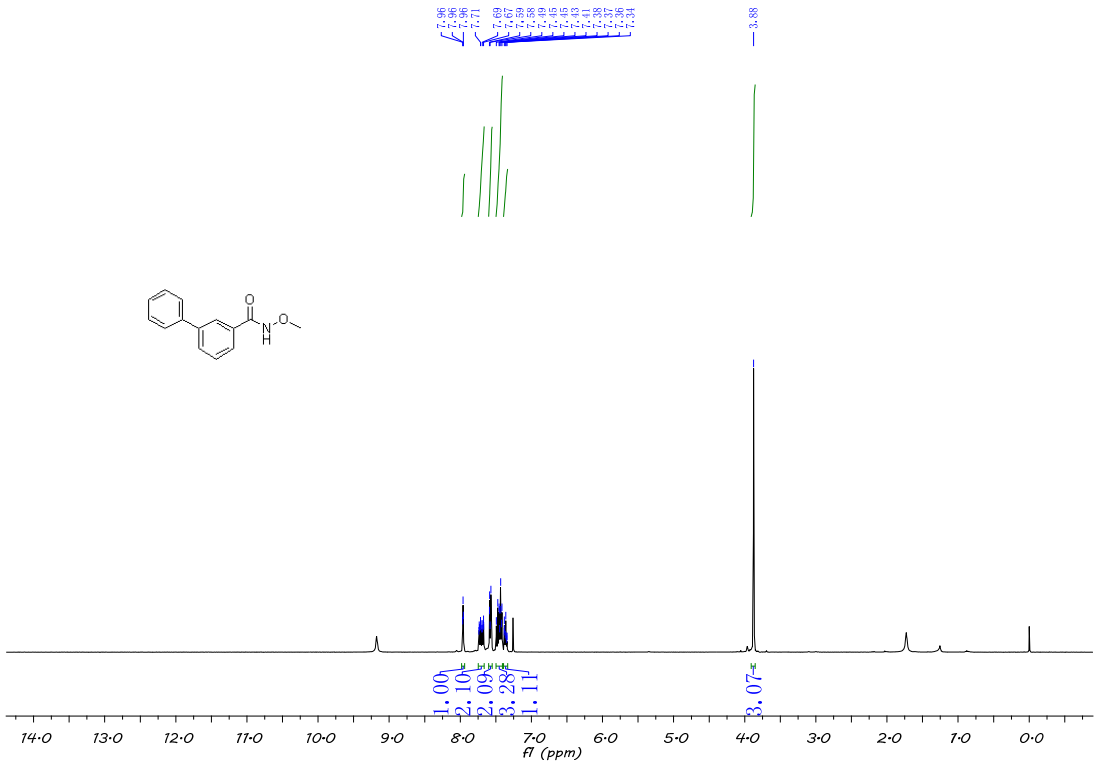
165.46
132.91
132.26
131.95
130.51
129.88
125.88
64.57
52.41
f1 (ppm)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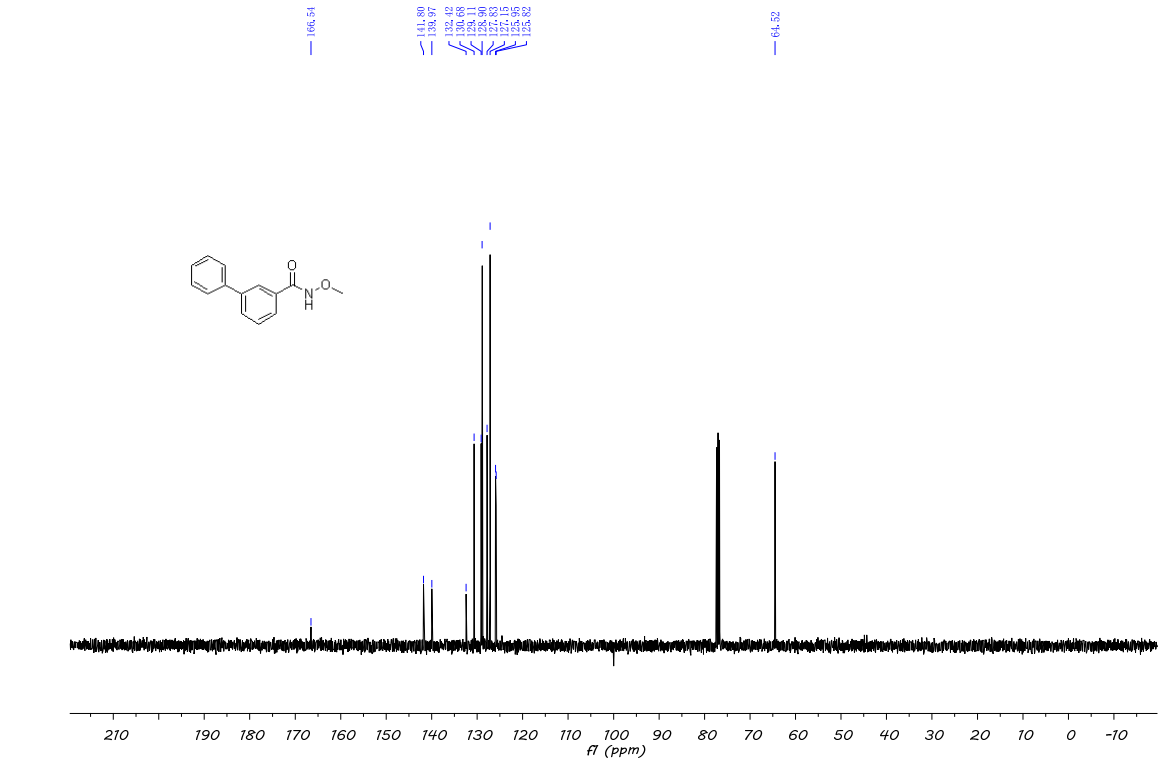
7.96
7.96
7.71
7.69
7.67
7.59
7.58
7.49
7.47
7.45
7.43
7.41
7.38
7.37
7.36
7.34
3.88
1.00
2.10
2.09
3.28
1.11
3.07
14·0
13·0
12·0
11·0
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0·0
f1 (ppm)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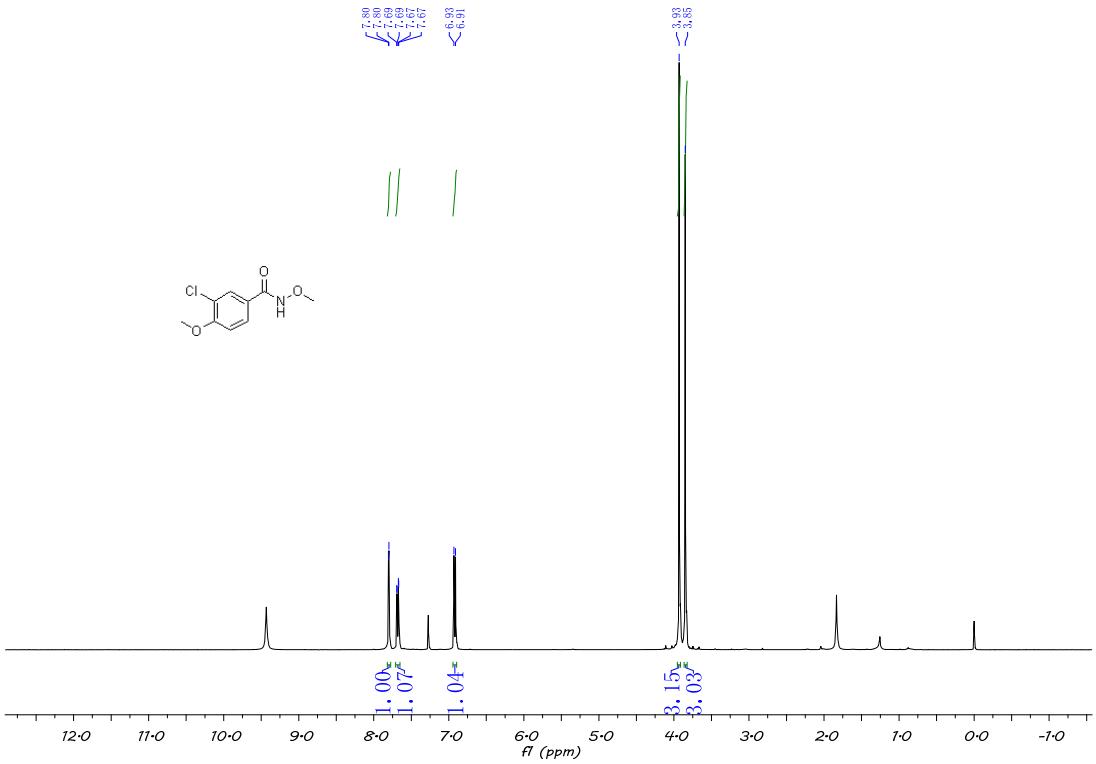
141.80
139.97
132.42
130.68
128.11
128.90
127.83
127.15
125.95
125.82
64.52
210
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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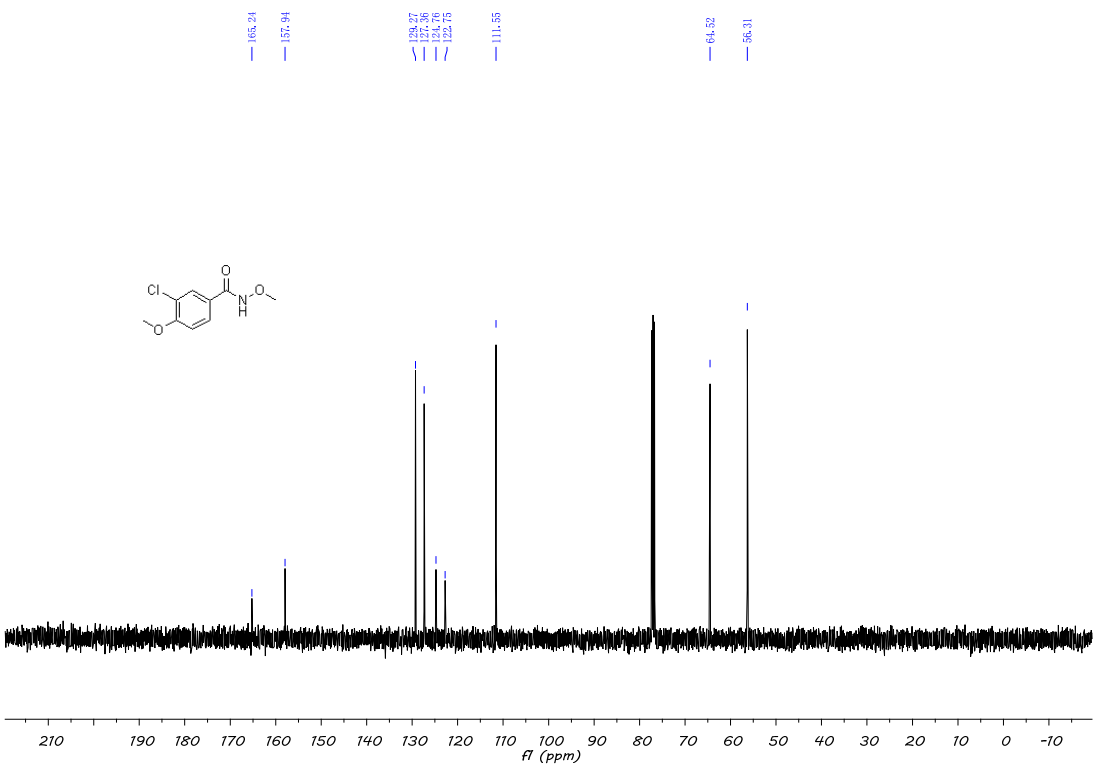
7.80
7.69
7.69
7.67
7.67
6.93
6.91
3.93
3.85
1.00
1.07
1.04
3.15
3.03
f1 (ppm)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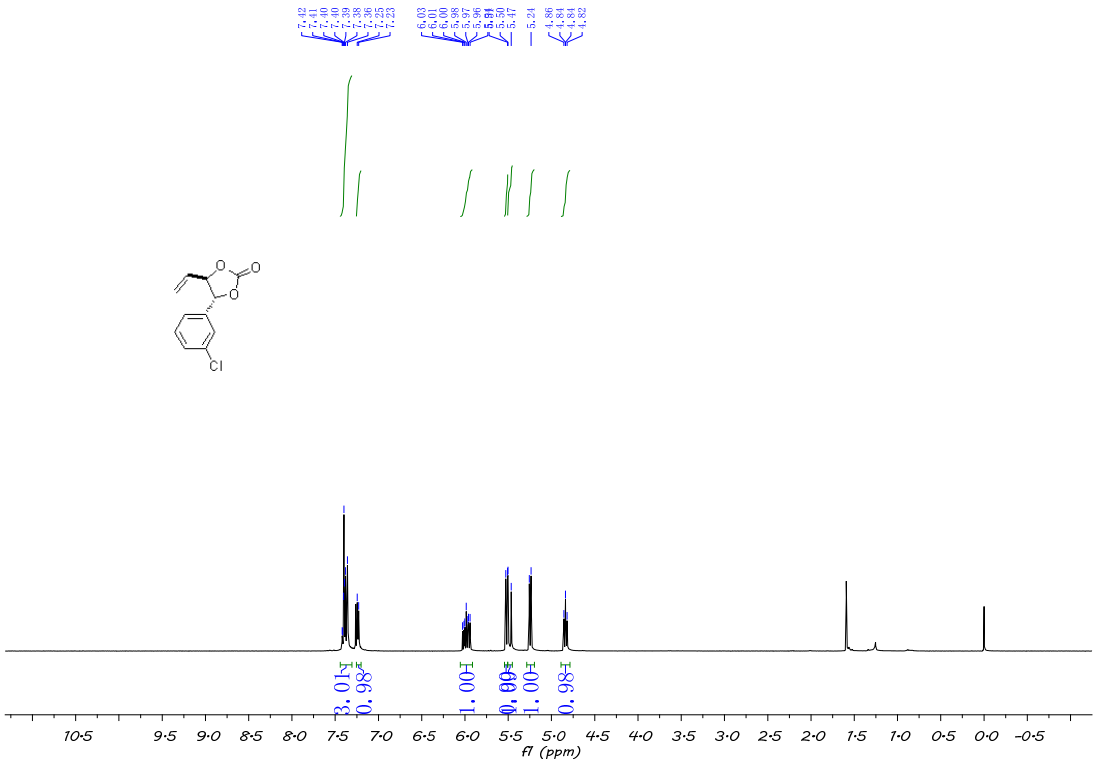
124.76
122.75
111.55
64.52
56.31
f1 (ppm)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7.40
7.39
7.38
7.36
7.25
7.23
6.03
6.01
6.00
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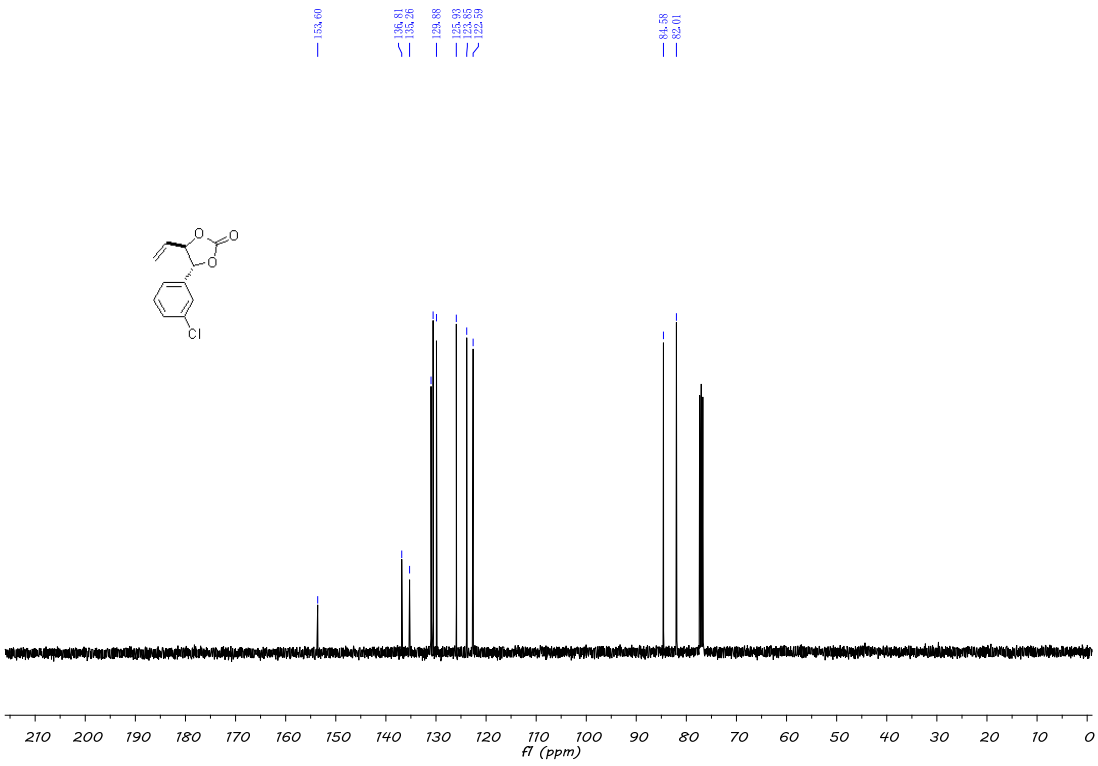
5.97
5.96
5.94
5.93
5.47
5.24
4.86
4.84
4.84
4.82
Cl
3.01
0.98
1.00
0.98
f1 (ppm)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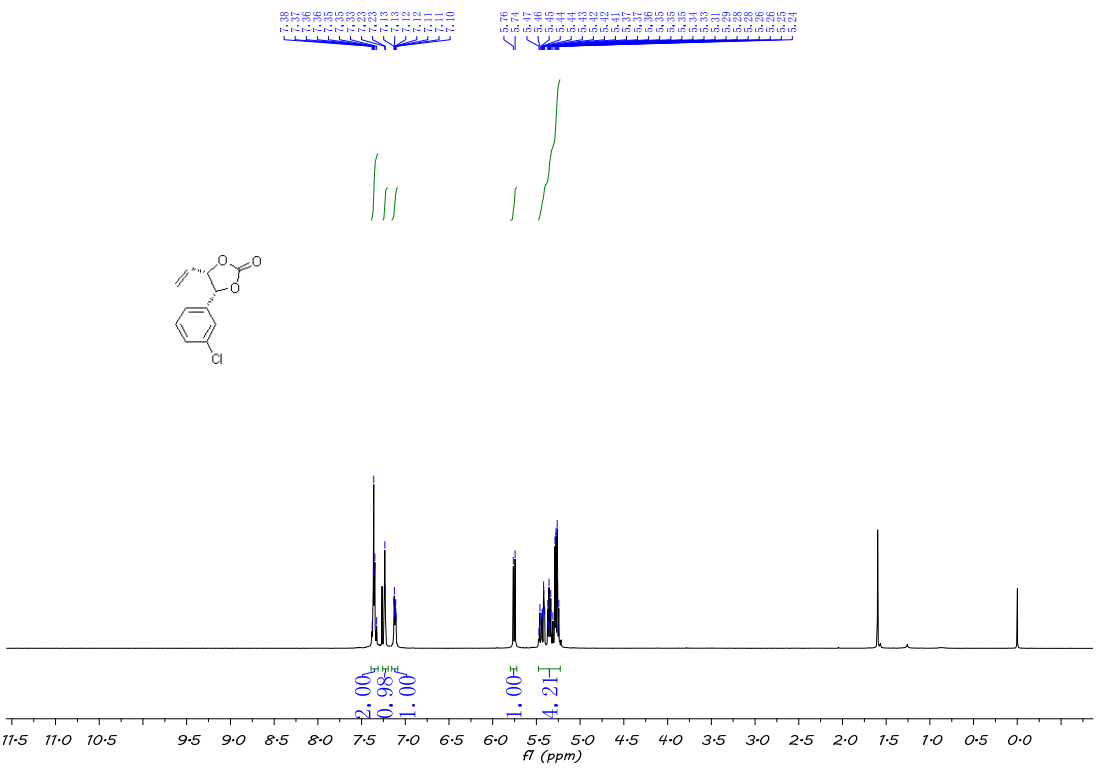
136.81
135.26
129.88
125.93
125.85
122.59
84.58
82.01
Cl
f1 (ppm)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7.35
7.35
7.33
7.33
7.23
7.13
7.13
7.12
7.12
7.11
7.11
7.10
5.76
5.74
5.47
5.46
5.45
5.44
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5.43
5.42
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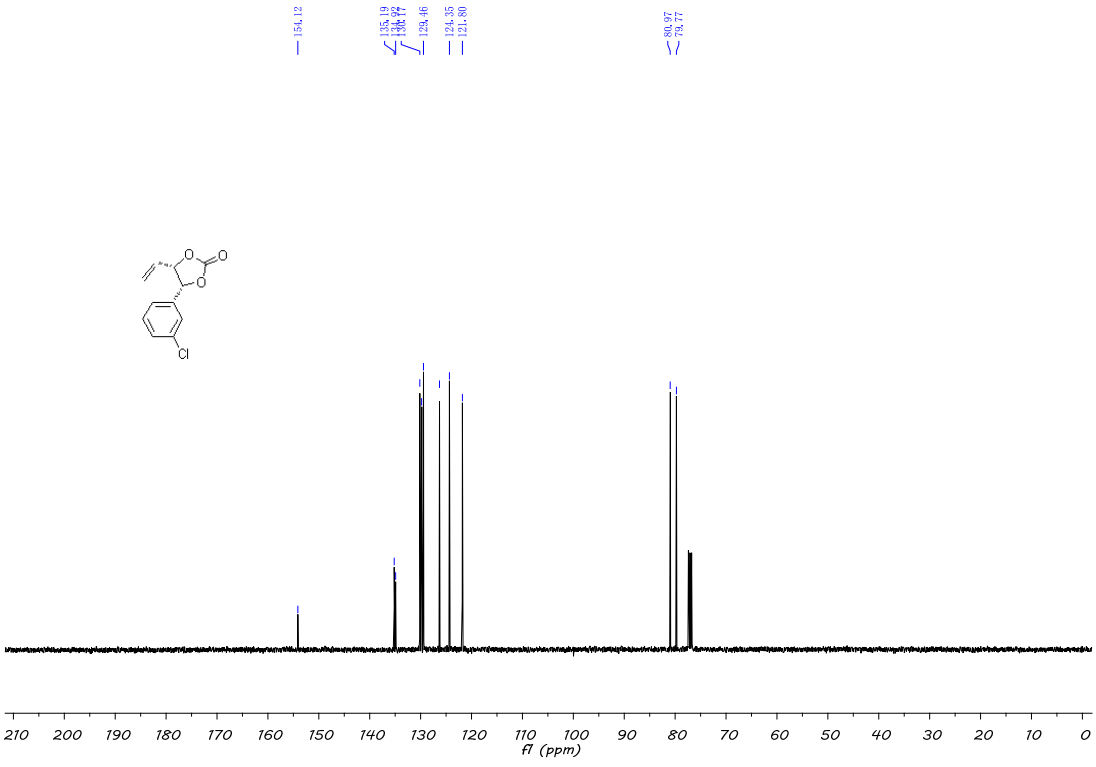
5.36
5.35
5.35
5.34
5.33
5.31
5.29
5.28
5.26
5.25
5.24
O
O
O
Cl
2.00
0.98
1.00
1.00
4.21
11·5 11·0 10·5 9·5 9·0 8·5 8·0 7·5 7·0 6·5 6·0 5·5 5·0 4·5 4·0 3·5 3·0 2·5 2·0 1·5 1·0 0·5 0·0
f1 (ppm)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135.19
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130.17
129.46
124.35
121.80
80.97
79.77
O
O
O
Cl
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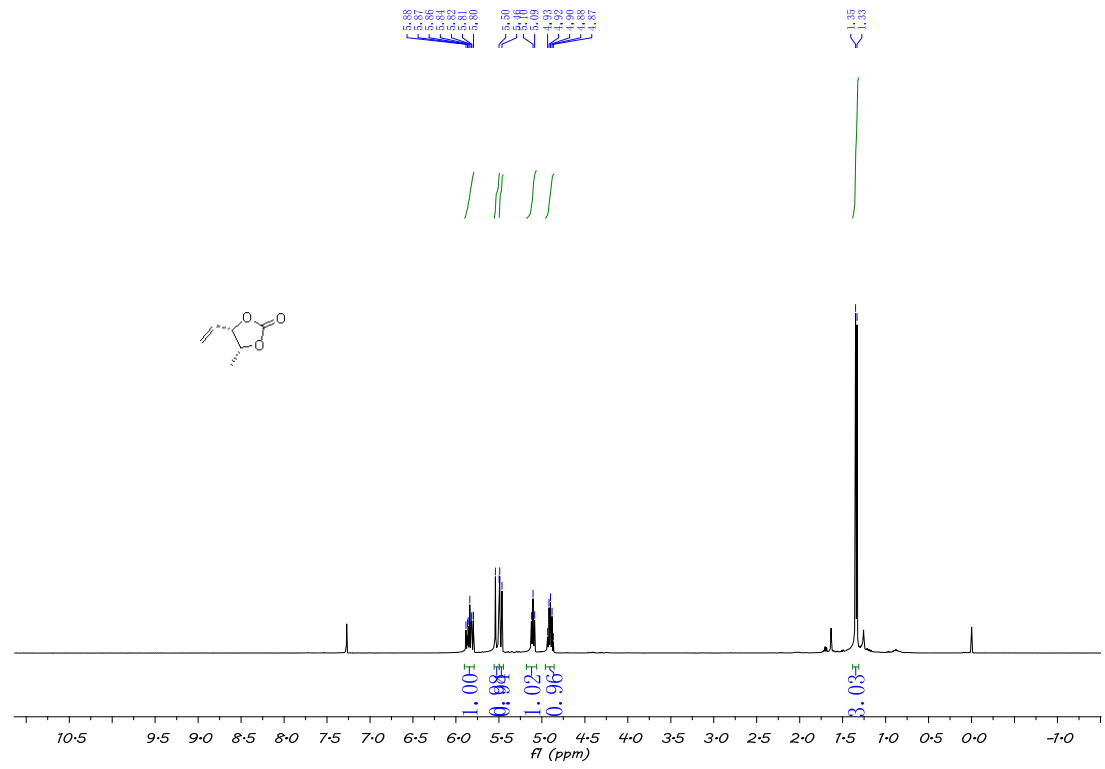
f1 (ppm)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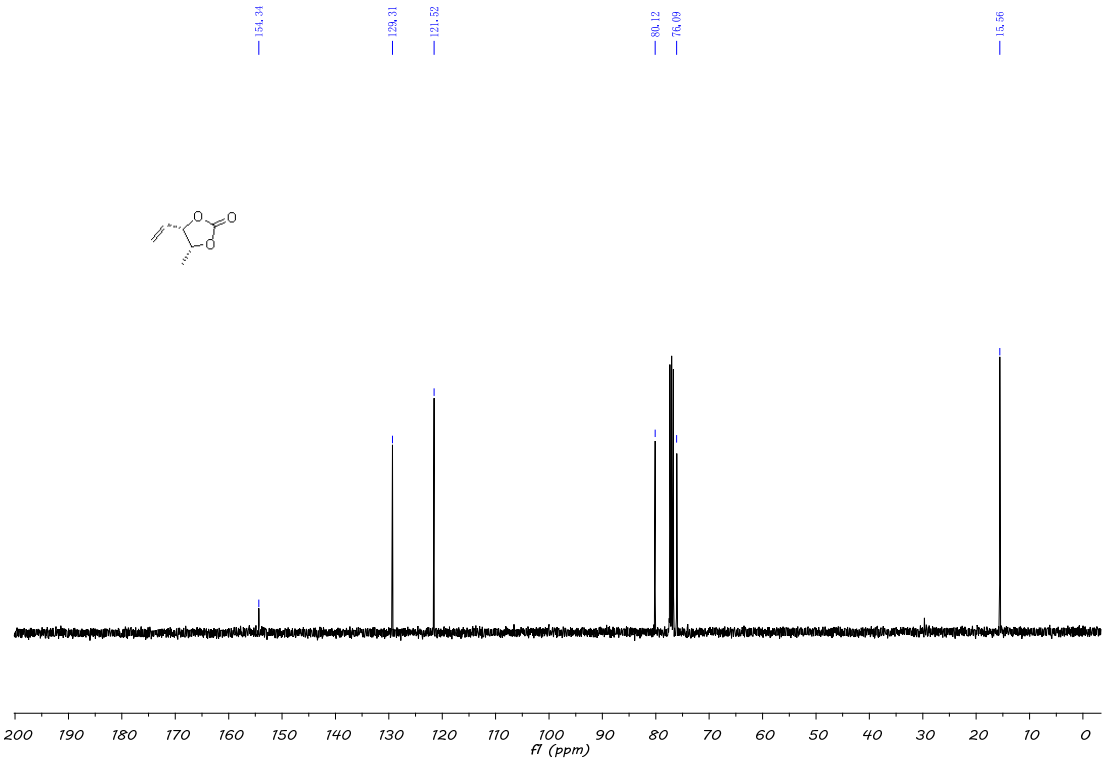
5.84
5.82
5.81
5.80
5.50
5.46
5.10
5.09
4.93
4.92
4.90
4.88
4.87
1.35
1.33
1.00
0.98
1.02
0.96
3.03
f1 (ppm)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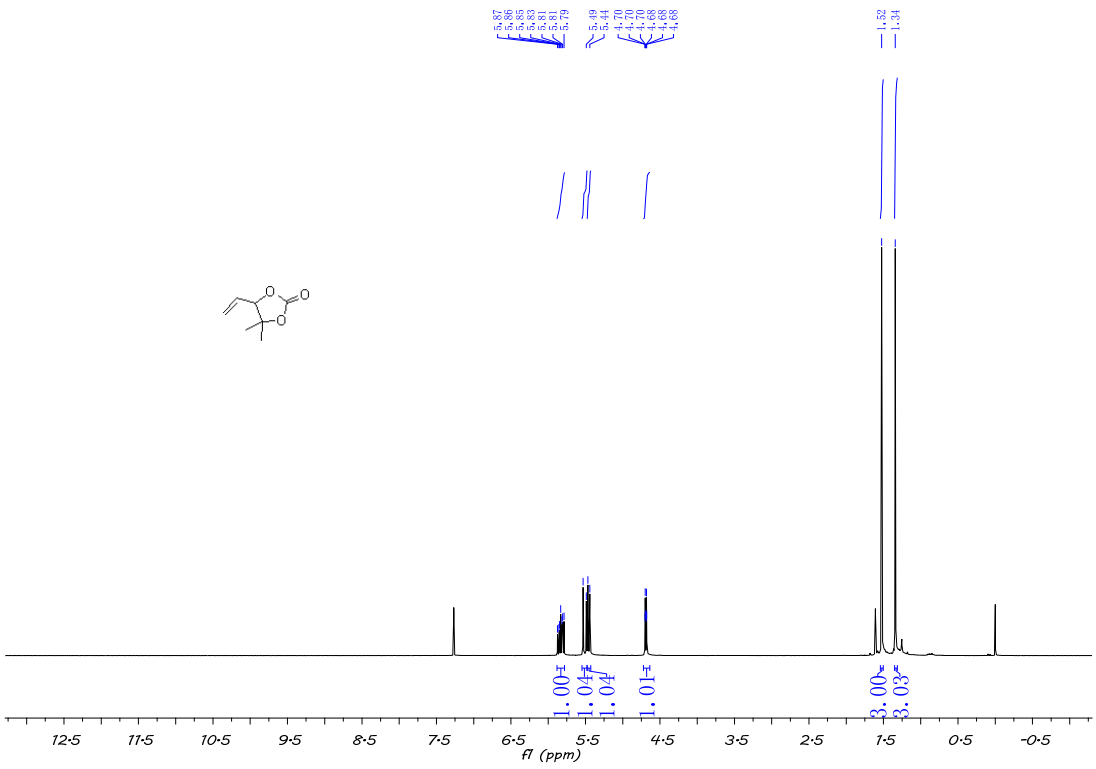
15.56
f1 (ppm)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5.81
5.79
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5.44
4.70
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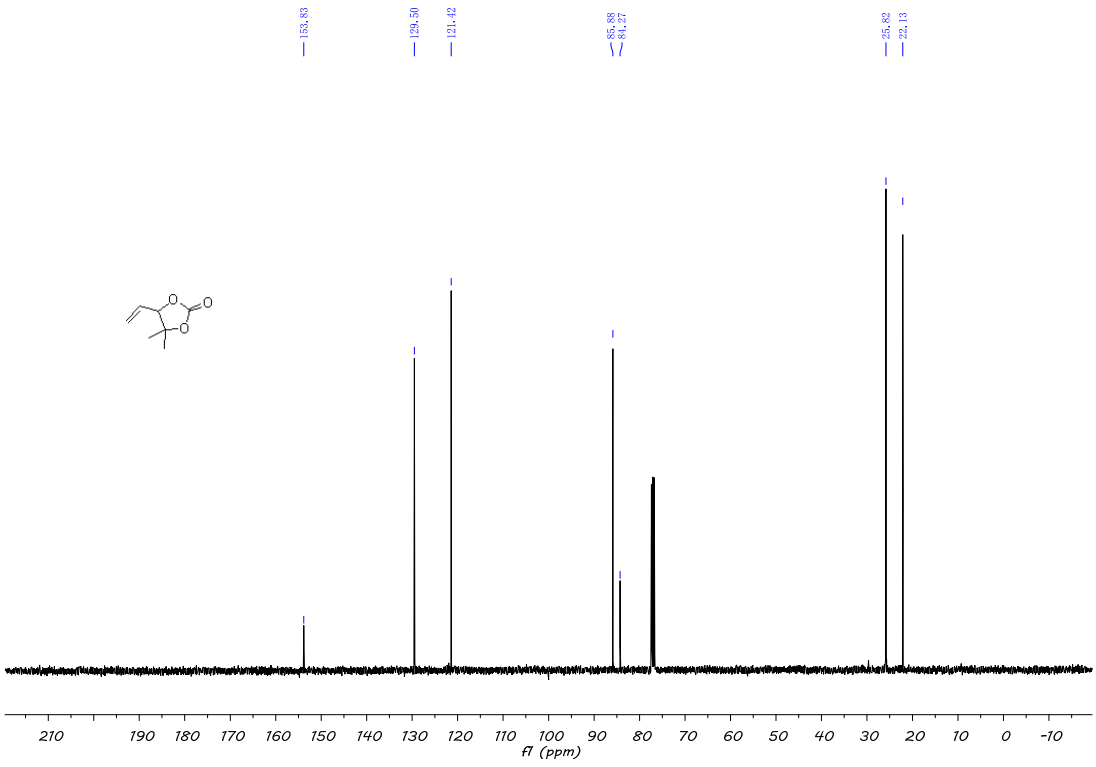
4.68
1.52
1.34
1.00
1.04
1.04
1.01
3.00
3.03
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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121.42
85.88
84.27
25.82
22.13
210
190
180
170
160
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110
100
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80
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30
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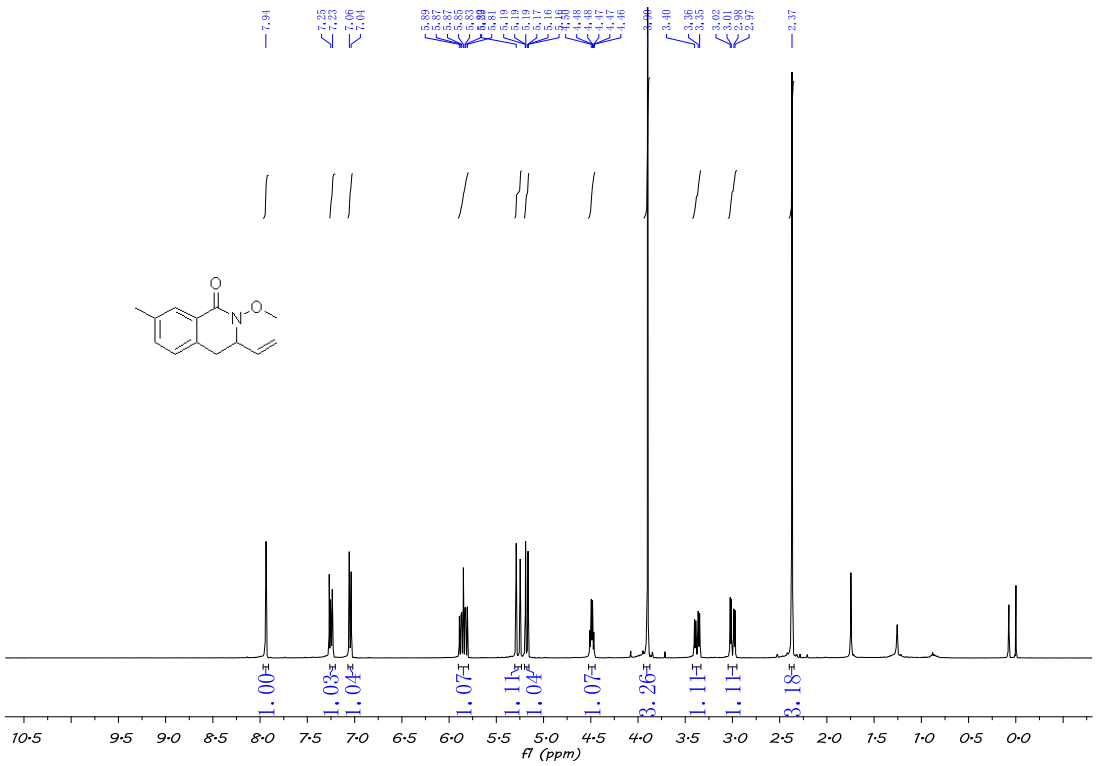
0
-10
f1 (ppm)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7.23
7.06
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5.87
5.85
5.83
5.81
5.19
5.19
5.19
5.17
5.16
4.48
4.48
4.47
4.47
4.46
3.40
3.36
3.35
3.02
3.01
2.98
2.97
2.37
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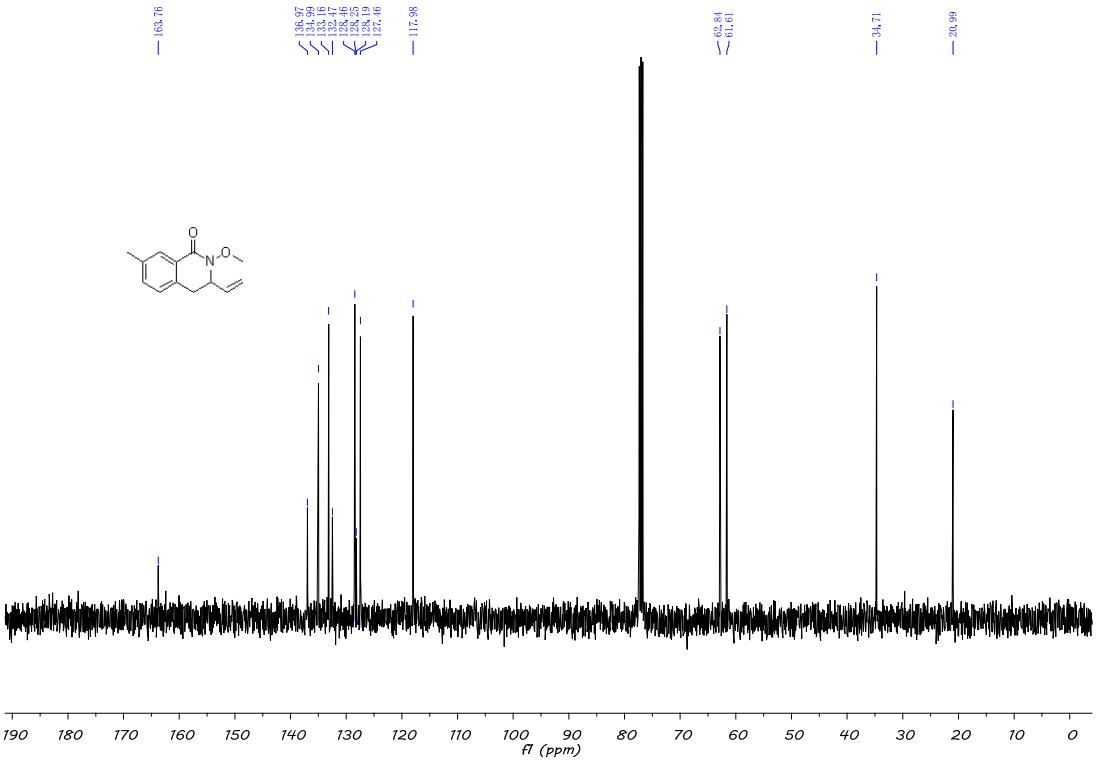
1.07
1.11
1.04
1.07
3.26
1.11
1.11
3.18
fl (ppm)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134.99
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132.47
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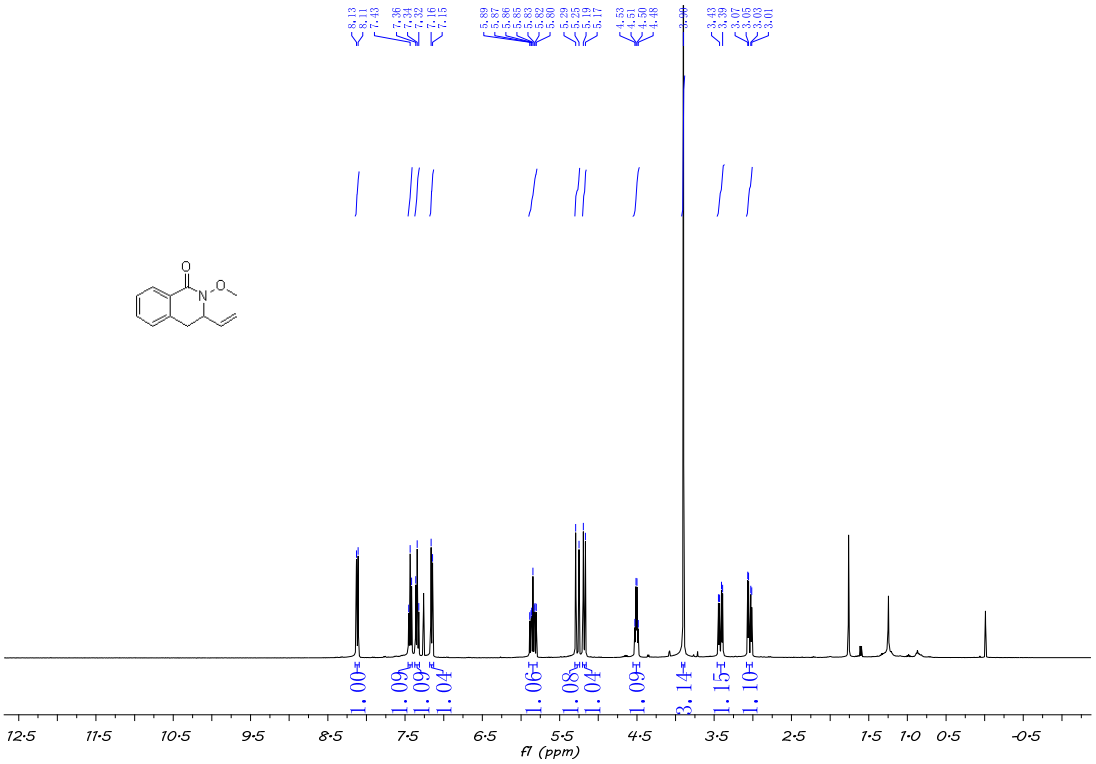
128.25
128.19
127.46
117.98
62.84
61.61
34.71
20.99
fl (ppm)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8.11
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7.36
7.34
7.32
7.16
7.15
5.89
5.87
5.86
5.85
5.83
5.82
5.80
5.39
5.25
5.19
5.17
4.53
4.51
4.50
4.48
3.43
3.39
3.07
3.05
3.03
3.01
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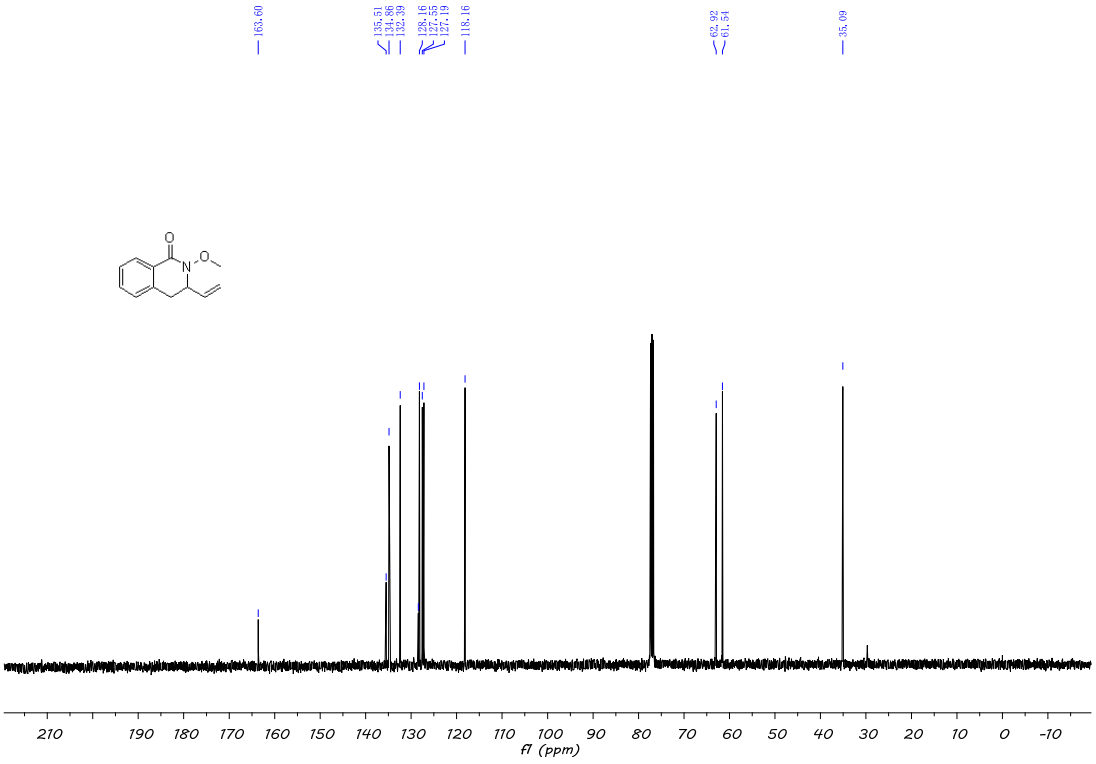
1.09
3.14
1.15
1.10
f1 (ppm)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135.51
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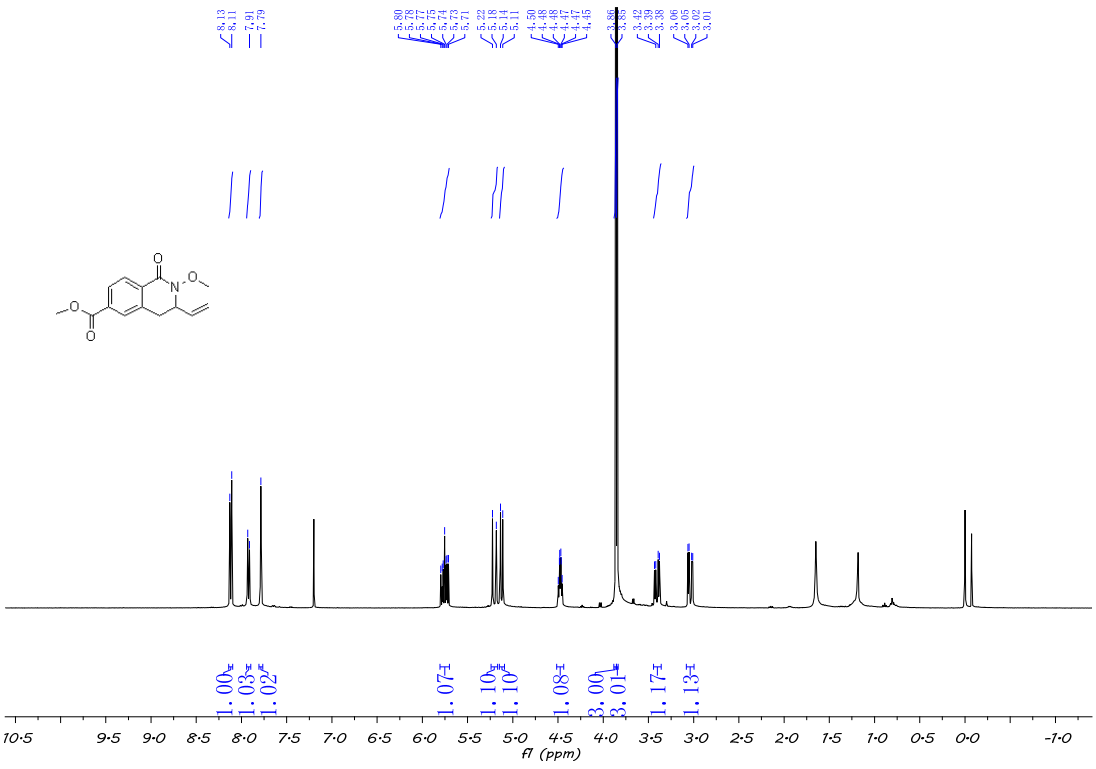
127.55
127.19
118.16
62.92
61.54
35.09
f1 (ppm)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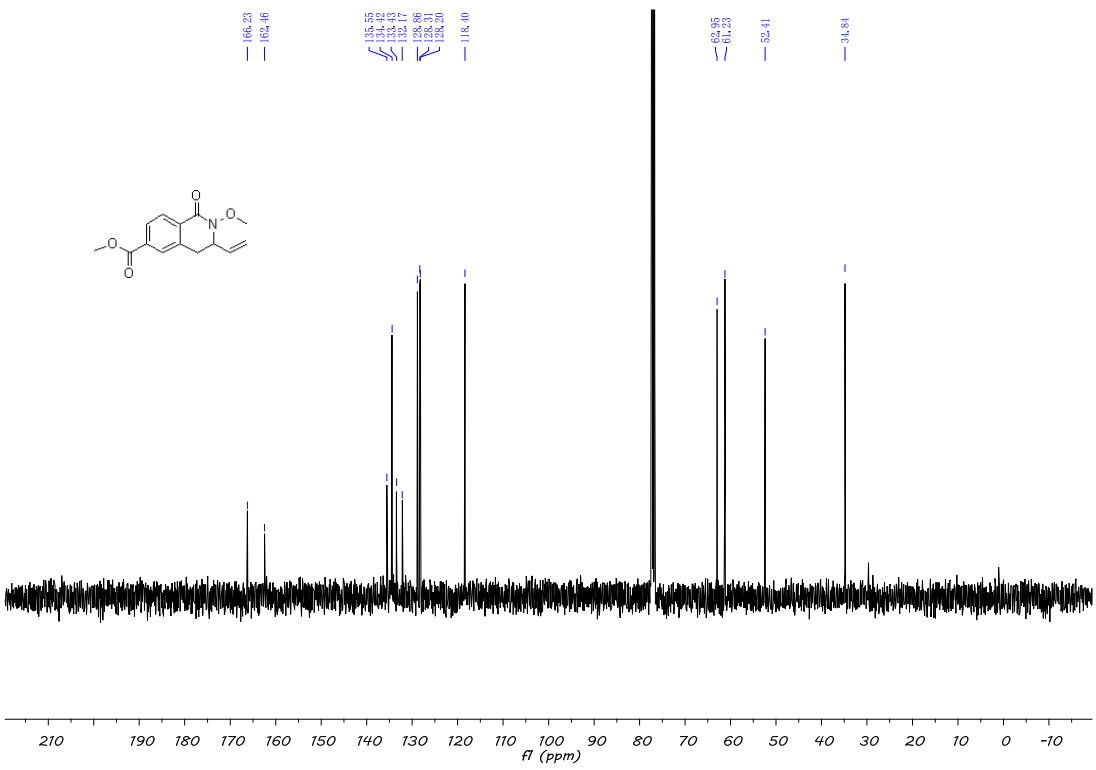
7.91
7.79
5.80
5.78
5.77
5.75
5.74
5.73
5.71
5.22
5.18
5.14
5.11
4.50
4.48
4.47
4.47
4.45
3.86
3.42
3.39
3.38
3.06
3.05
3.02
3.01
1.00
1.03
1.02
1.07
1.10
1.10
1.08
3.00
3.01
1.17
1.13
f1 (ppm)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162.46
135.55
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133.42
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128.86
128.31
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118.40
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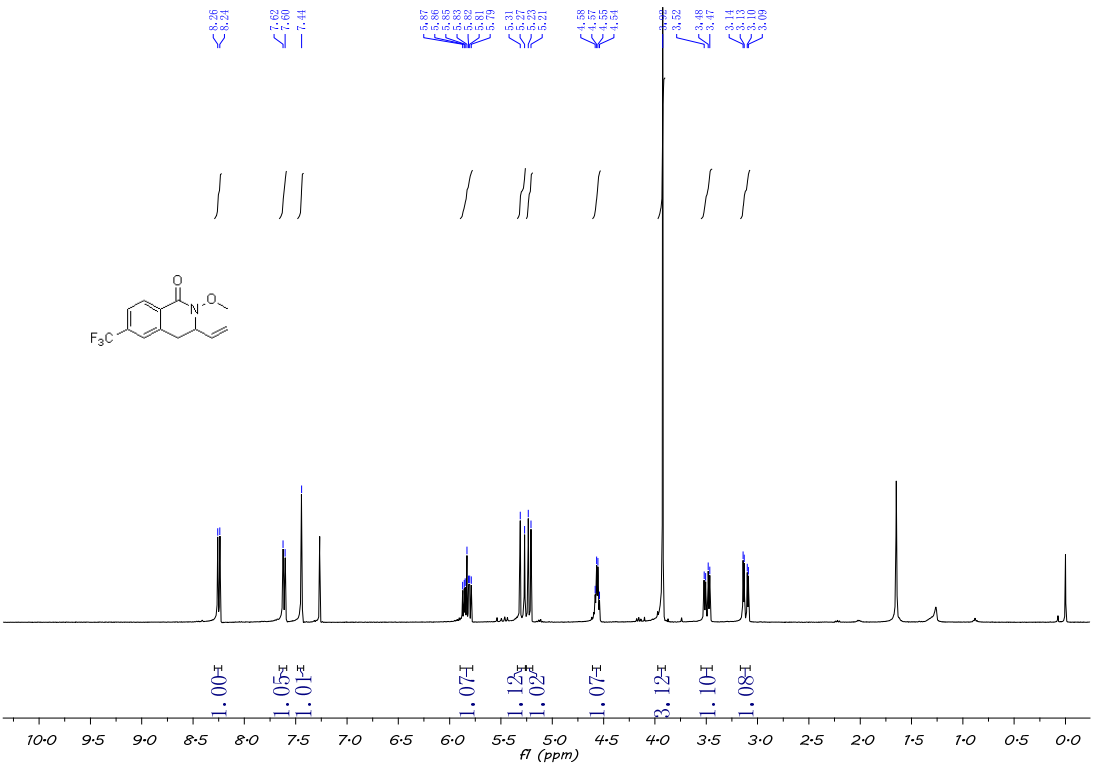
61.23
52.41
34.84
f1 (ppm)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8.24
7.62
7.60
7.44
5.87
5.86
5.85
5.83
5.82
5.81
5.79
5.31
5.27
5.23
5.21
4.58
4.57
4.55
4.54
3.52
3.48
3.47
3.14
3.13
3.10
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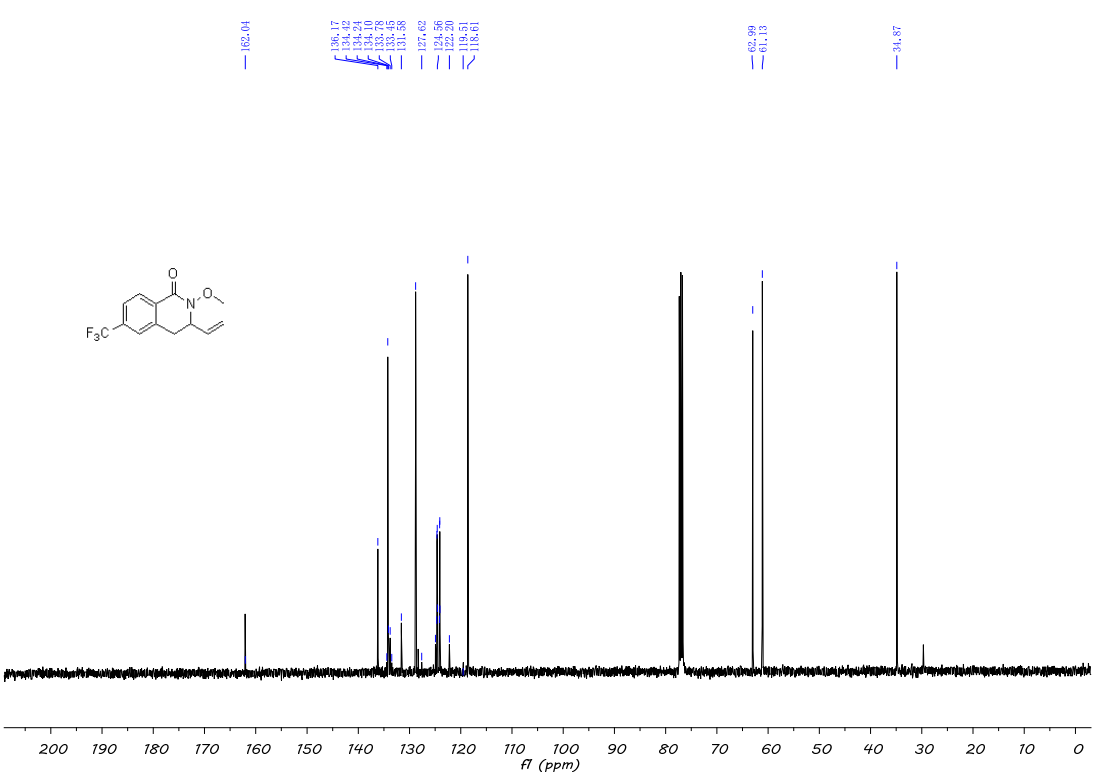
1.07
3.12
1.10
1.08
f1 (ppm)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136.17
134.42
134.24
134.10
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133.45
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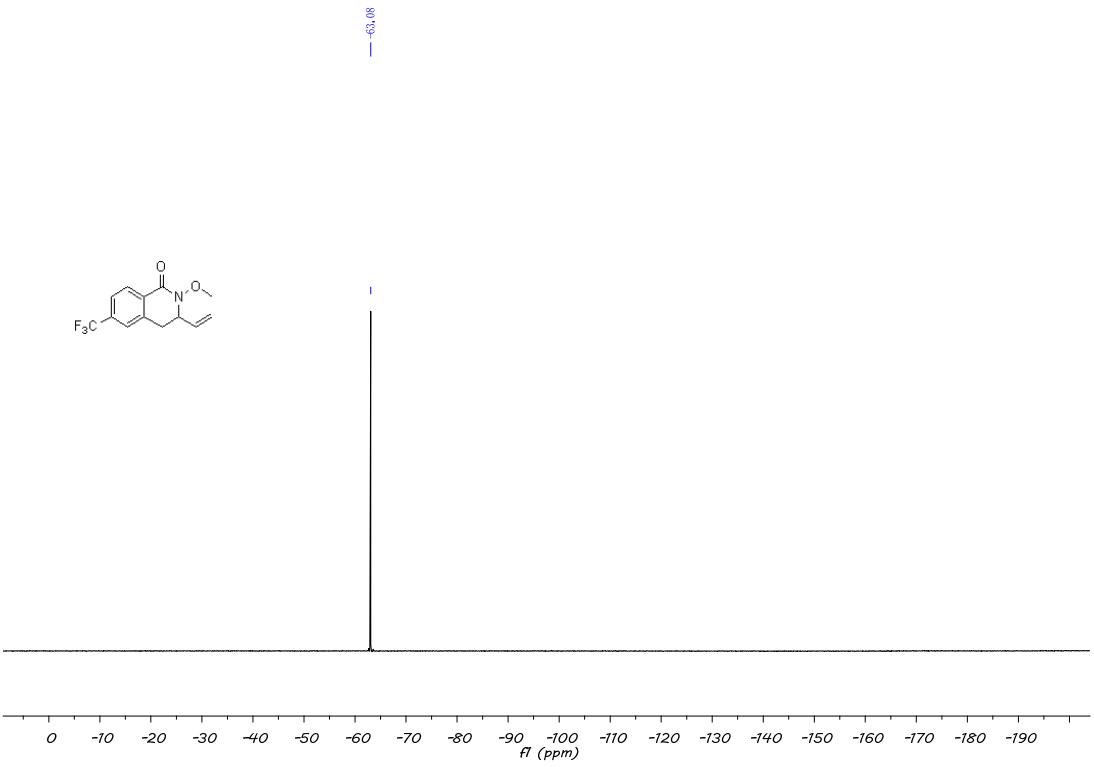
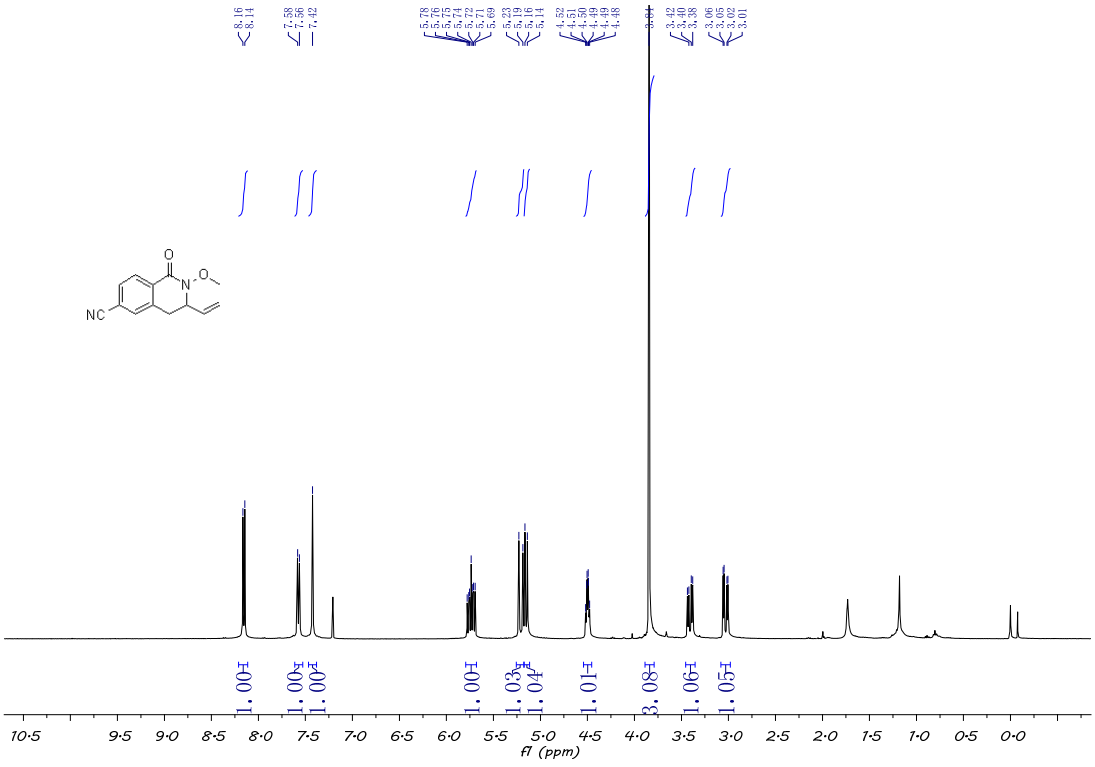
127.62
124.56
122.20
119.51
118.61
62.99
61.13
34.87
f1 (ppm)


-63.08
F3C
O
N
O
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)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8.14
7.58
7.56
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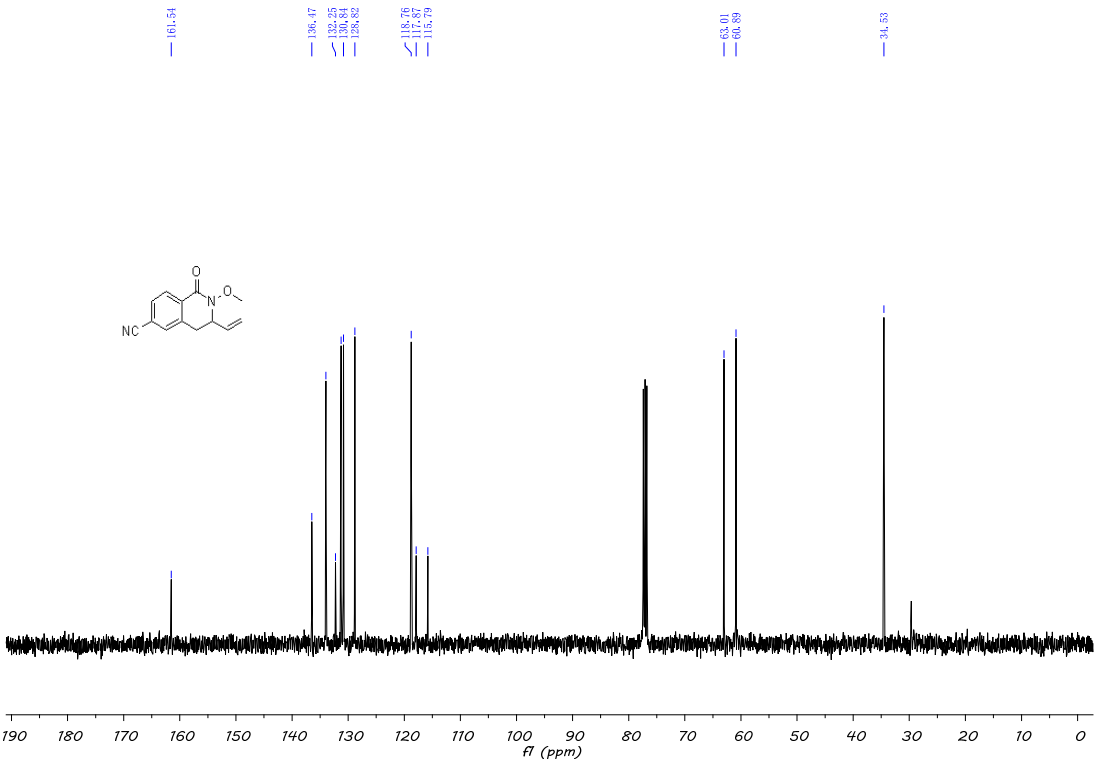
5.78
5.76
5.75
5.74
5.72
5.71
5.69
5.23
5.19
5.16
5.14
4.52
4.51
4.50
4.49
4.49
4.48
3.42
3.40
3.38
3.06
3.05
3.02
3.01
O
N
O
NC
1.00
1.00
1.00
1.00
1.03
1.04
1.01
3.08
1.06
1.05
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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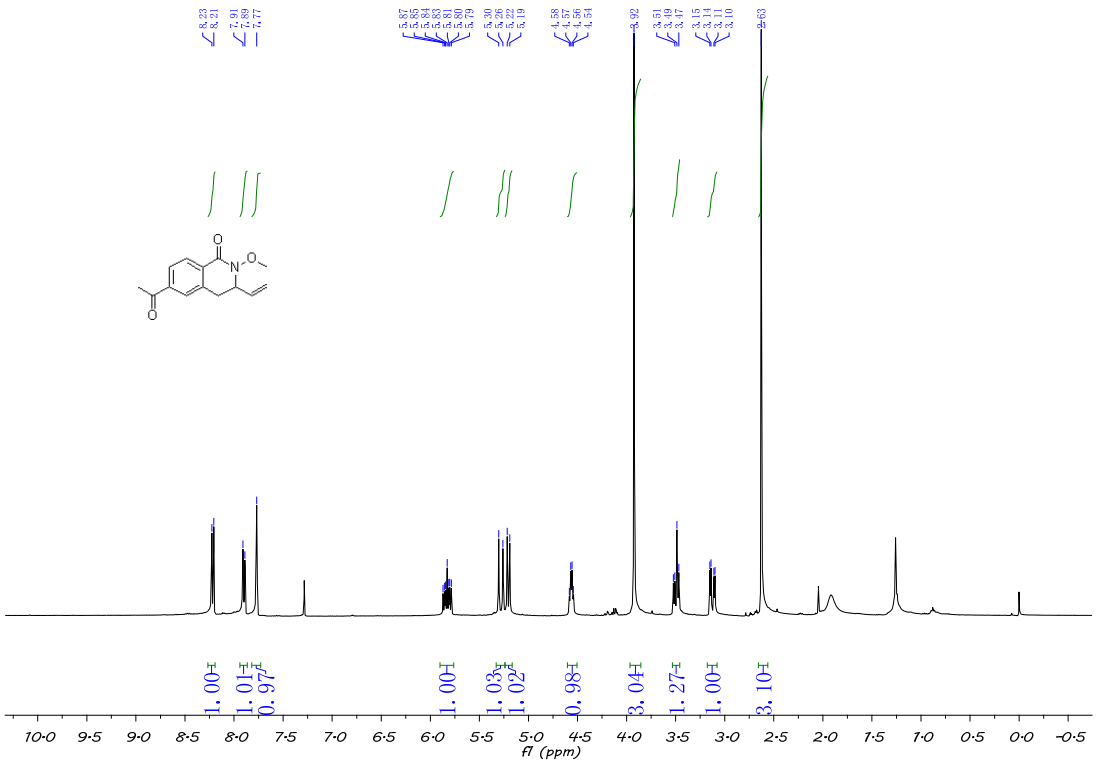
128.82
118.76
117.87
115.79
63.01
60.89
34.53
NC
O
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.23
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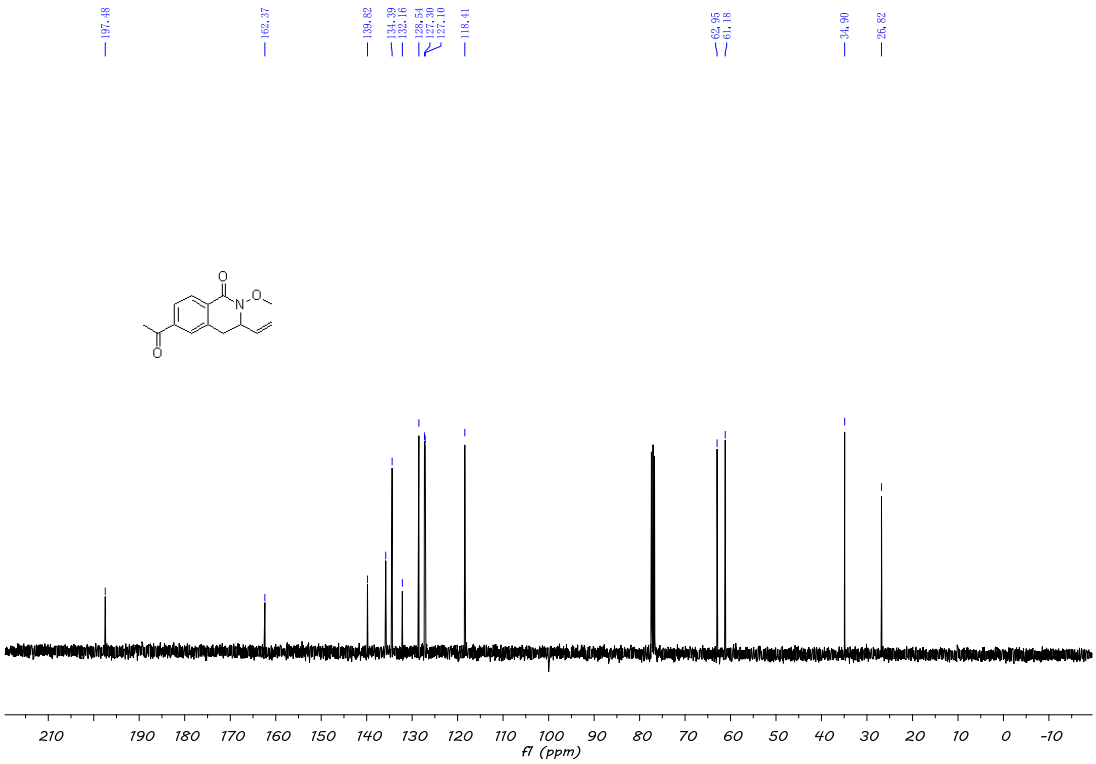
7.89
7.77
5.87
5.85
5.84
5.83
5.81
5.80
5.79
5.30
5.26
5.22
5.19
4.58
4.57
4.56
4.54
3.92
3.51
3.49
3.47
3.15
3.14
3.11
3.10
2.63
O
N
O
O
1.00
1.01
0.97
1.00
1.03
1.02
0.98
3.04
1.27
1.00
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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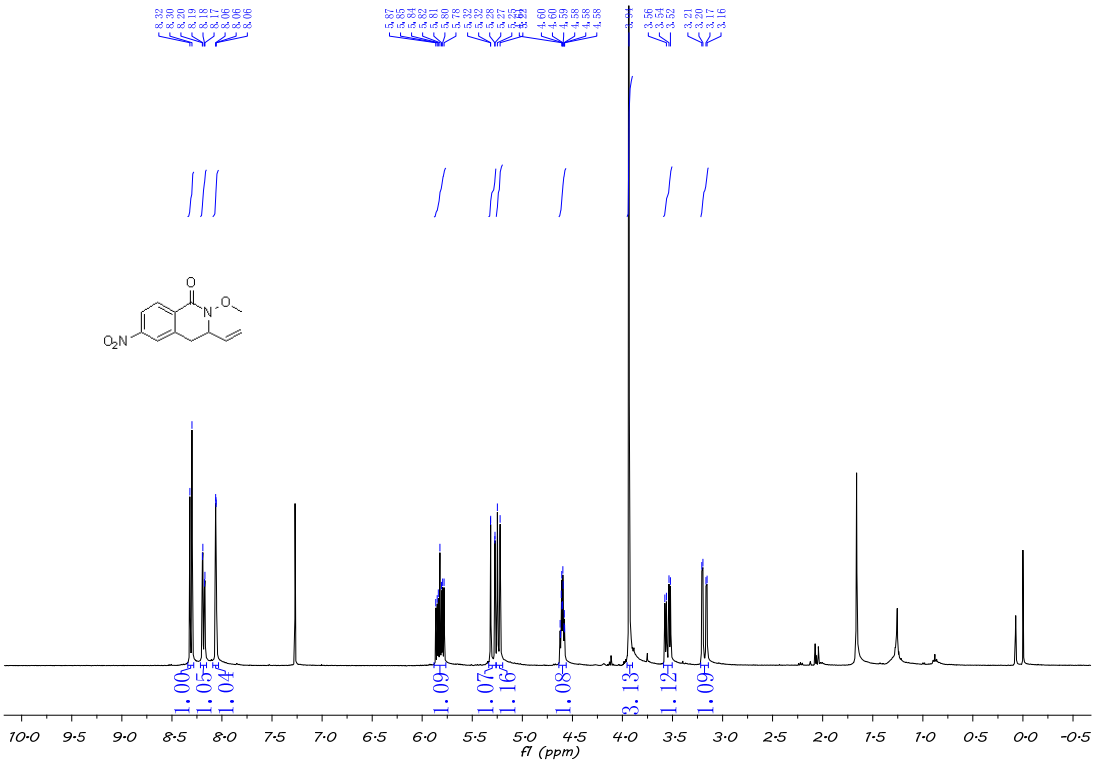
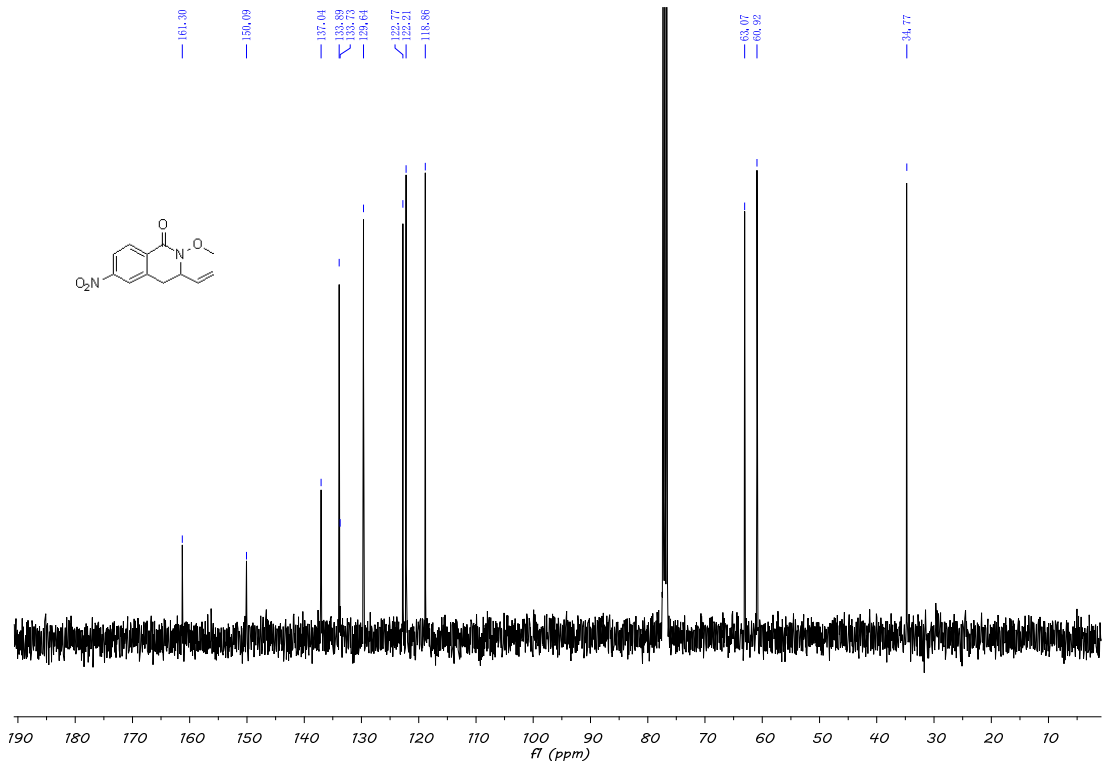
134.39
132.16
128.54
122.90
127.10
118.41
62.95
61.18
34.90
26.82
f1 (ppm)


1.00
1.05
1.04
1.09
1.07
1.16
1.08
3.13
1.12
1.09
f1 (ppm)


161.30
150.09
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133.73
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122.77
122.21
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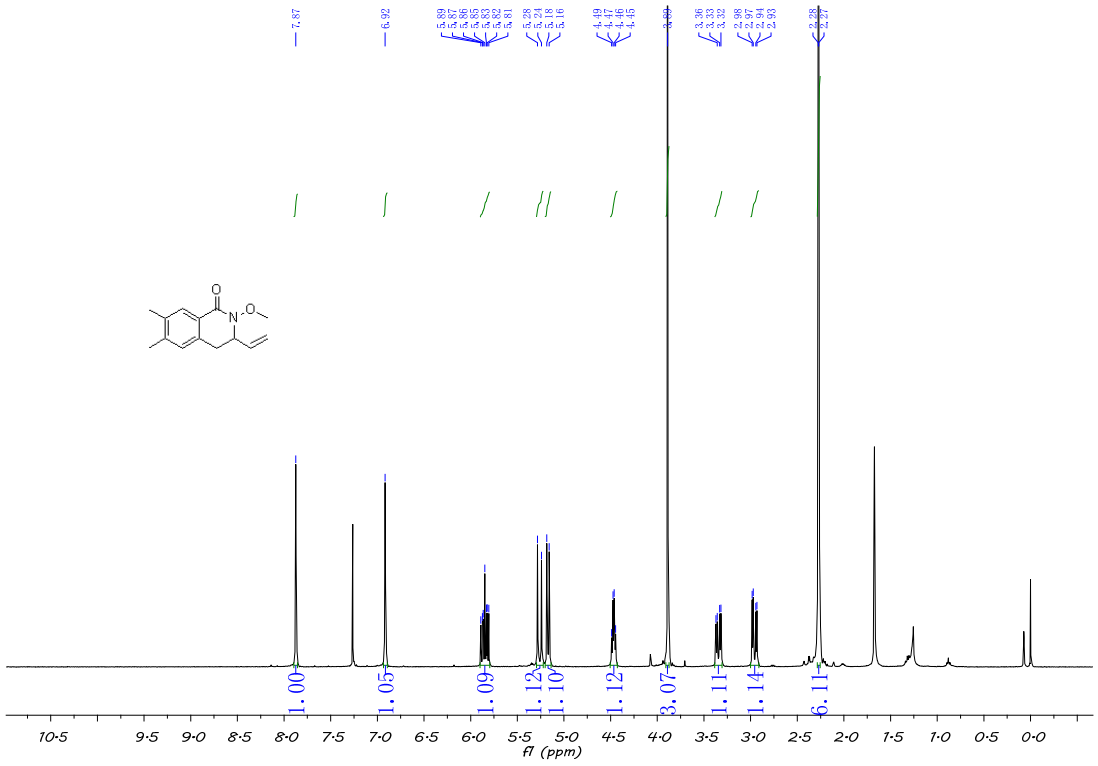
63.07
60.92
34.77
O
N
O
O2N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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5.85
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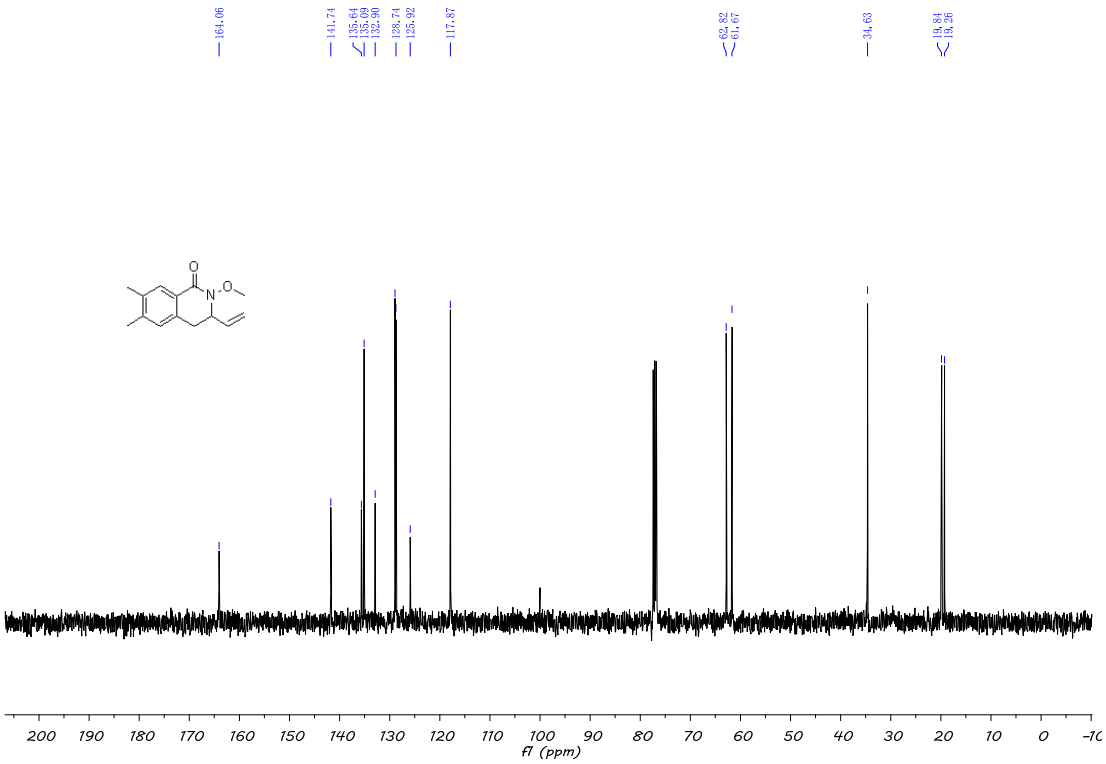
5.82
5.81
5.28
5.24
5.18
5.16
4.49
4.47
4.46
4.45
3.89
3.36
3.33
3.32
2.98
2.97
2.94
2.93
2.28
2.27
O
N
O
1.00
1.05
1.09
1.12
1.10
1.12
3.07
1.11
1.14
6.11
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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141.74
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135.09
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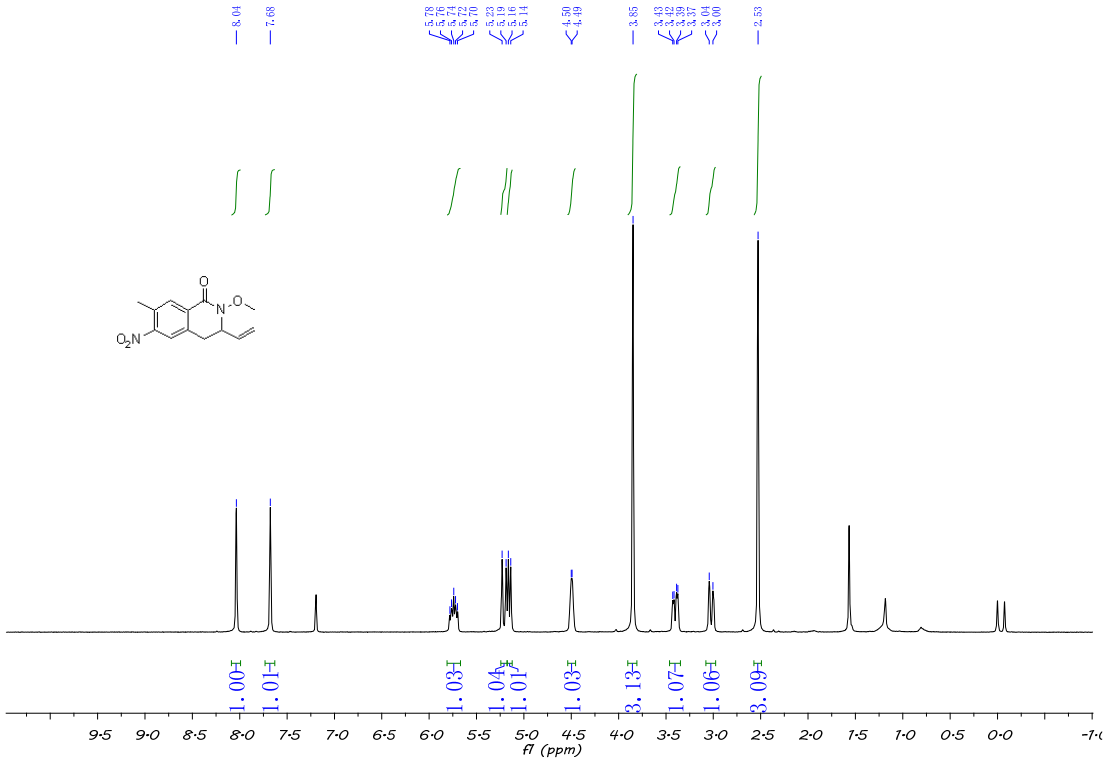
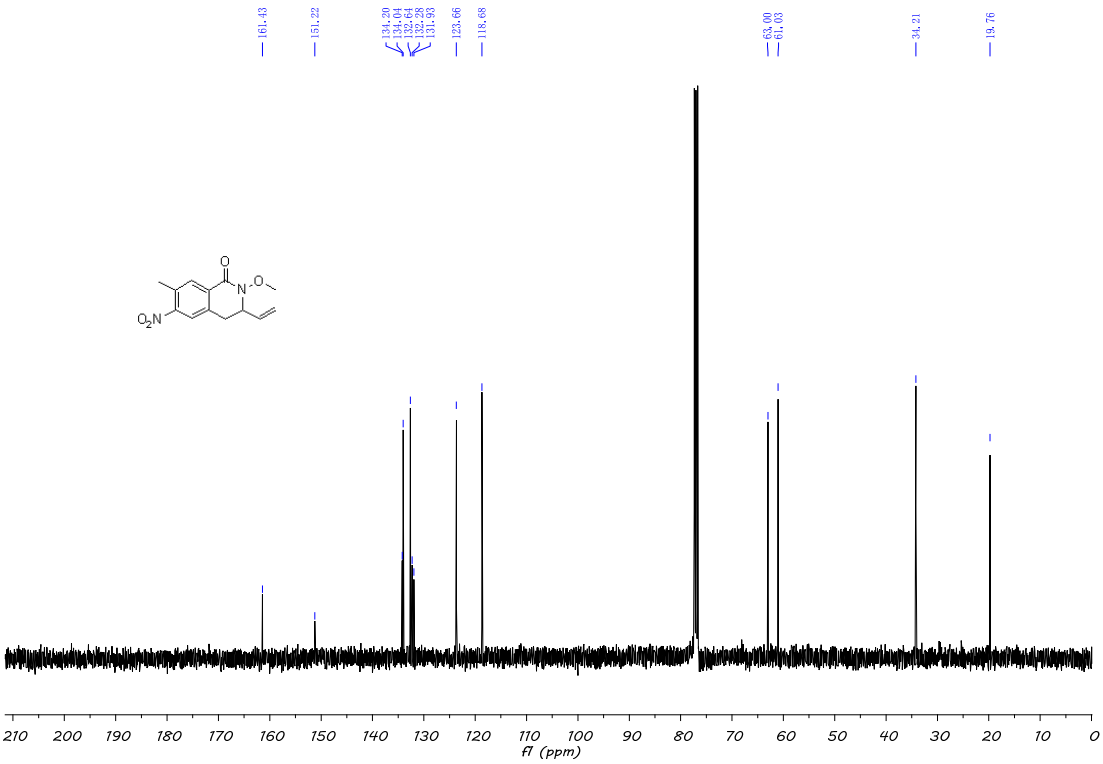
125.92
117.87
62.82
61.67
34.63
19.84
14.26
f1 (ppm)


8.04
7.68
5.78
5.76
5.74
5.72
5.70
5.23
5.19
5.16
5.14
4.50
4.49
3.85
3.43
3.42
3.39
3.37
3.04
3.00
2.53
1.00
1.01
1.03
1.04
1.01
1.03
3.13
1.07
1.06
3.09
f1 (ppm)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151.22
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132.28
131.93
123.66
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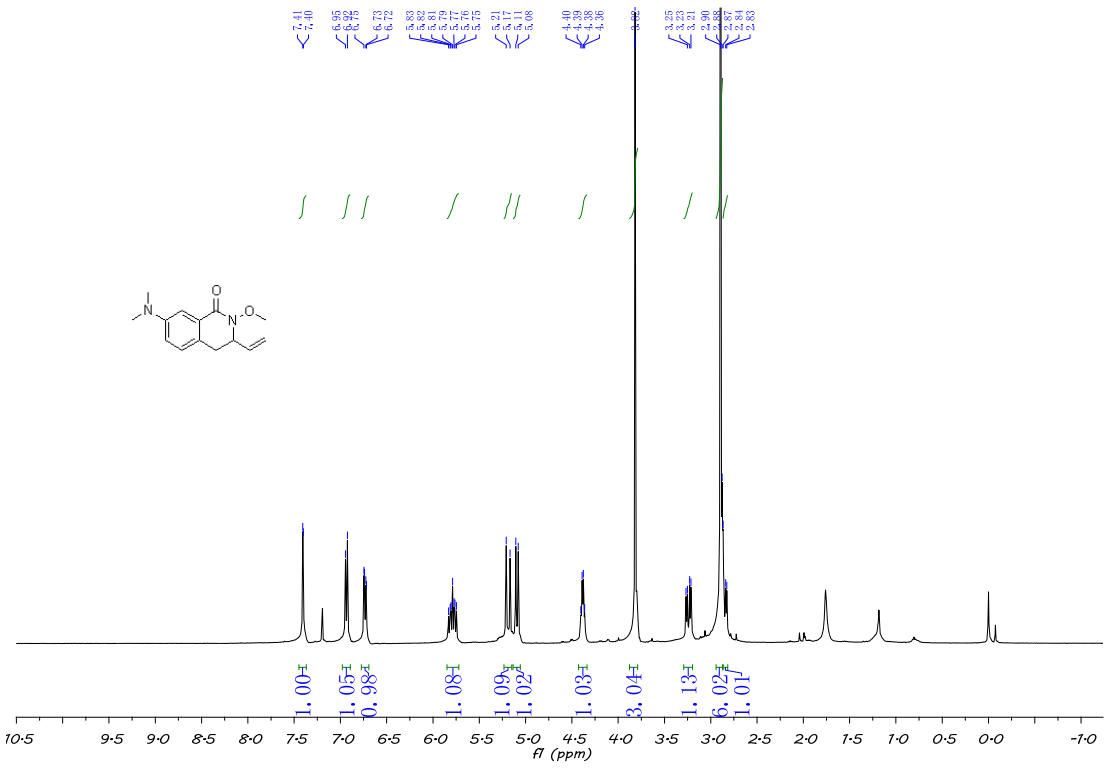
63.00
61.03
34.21
19.76
f1 (ppm)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6.42
6.73
6.72
5.83
5.82
5.81
5.79
5.77
5.76
5.75
5.21
5.17
5.11
5.08
4.40
4.39
4.38
4.36
3.25
3.23
3.21
2.90
2.88
2.87
2.84
2.83
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1.05
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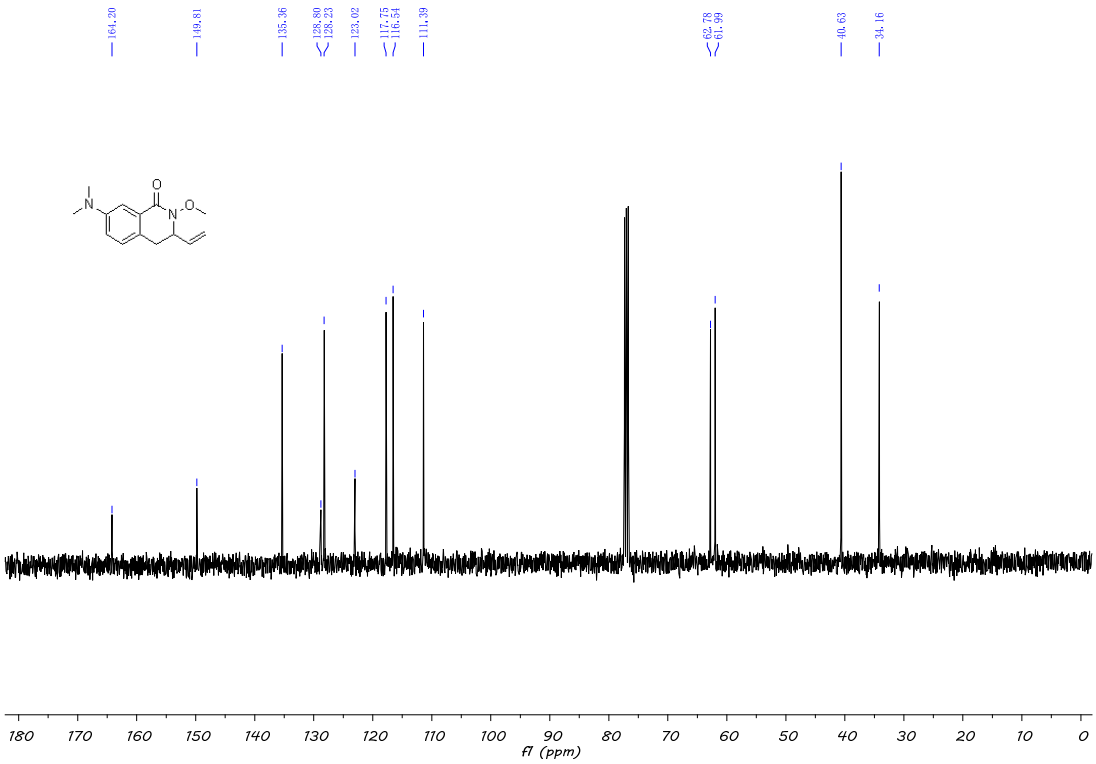
1.08
1.09
1.02
1.03
3.04
1.13
6.02
1.01
f1 (ppm)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149.81
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123.02
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116.54
111.39
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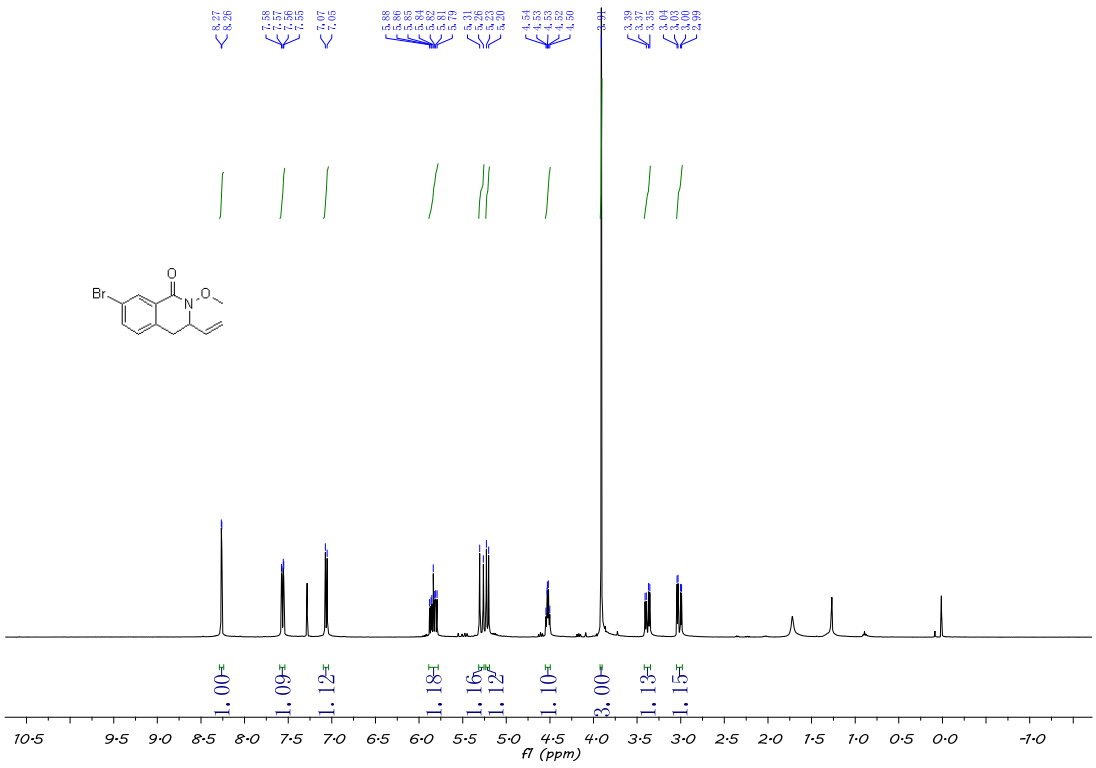
61.99
40.63
34.16
f1 (ppm)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7.55
7.07
7.05
5.88
5.86
5.85
5.84
5.82
5.81
5.79
5.31
5.26
5.23
5.20
4.54
4.53
4.52
4.50
3.39
3.37
3.35
3.04
3.03
3.00
2.99
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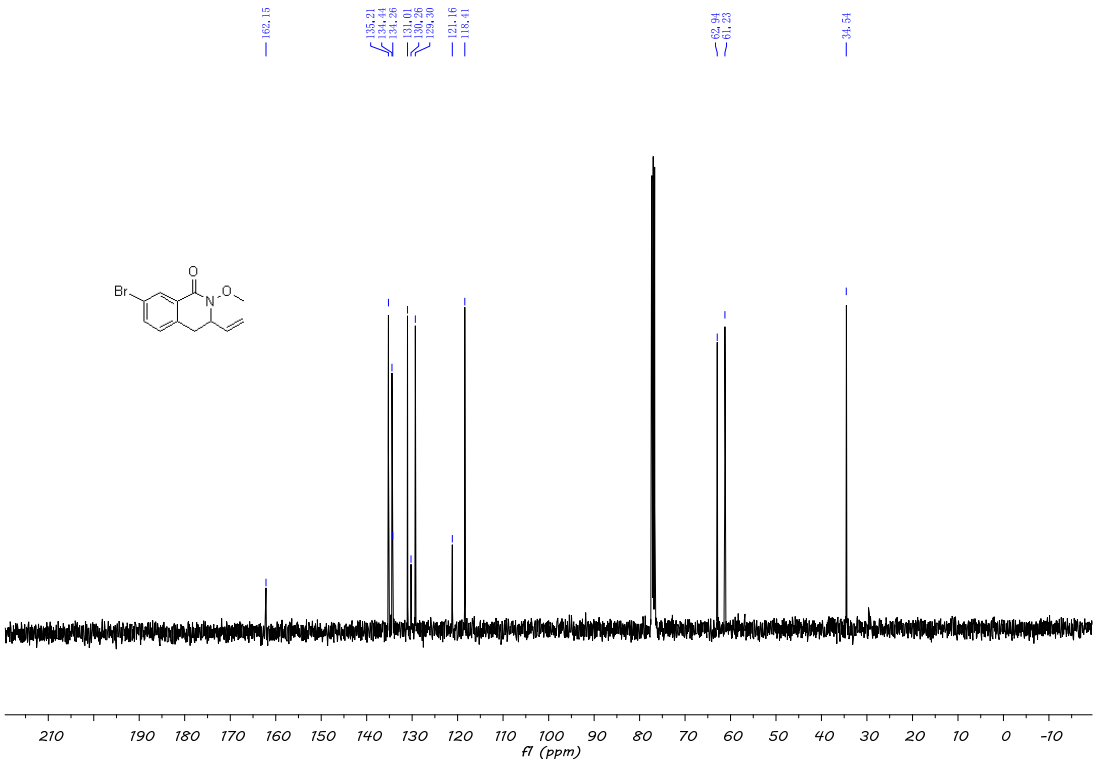
1.00
1.09
1.12
1.18
1.16
1.12
1.10
3.00
1.13
1.15
f1 (ppm)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130.95
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61.23
34.54
Br
O
N
O
210
190
180
170
160
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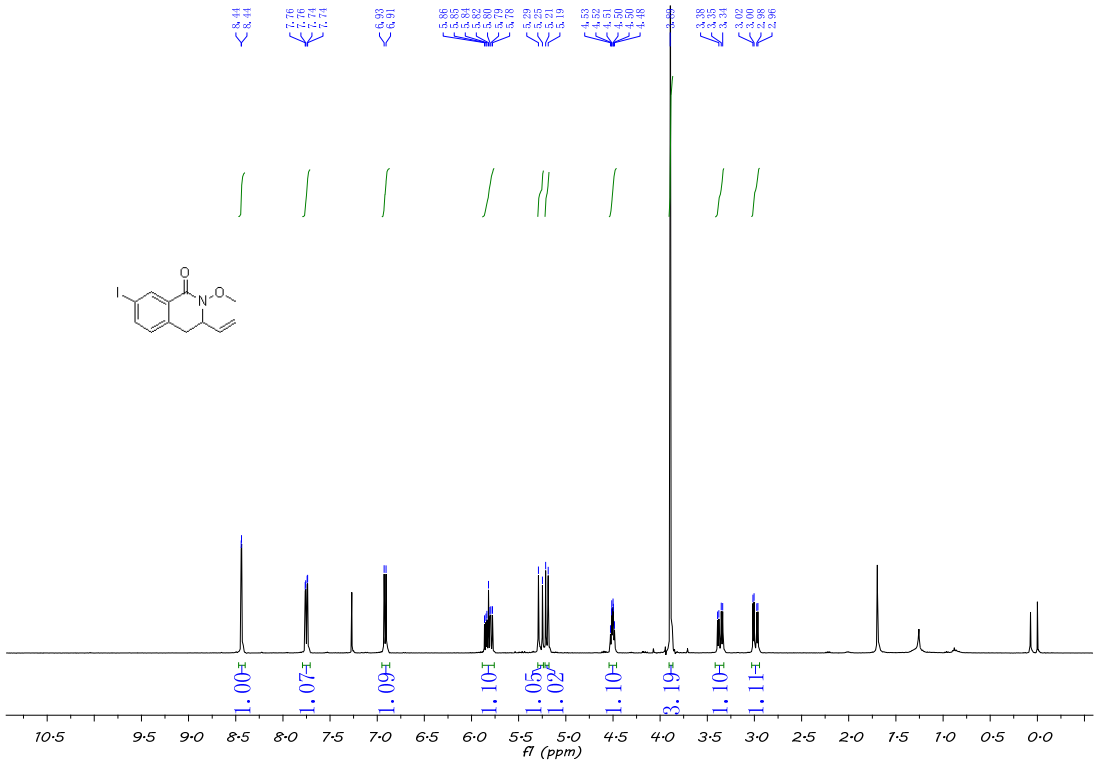
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.74
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5.84
5.82
5.80
5.79
5.78
5.29
5.25
5.21
5.19
4.53
4.52
4.51
4.50
4.50
4.48
3.69
3.38
3.35
3.34
3.02
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2.98
2.96
I
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1.00
1.07
1.09
1.10
1.05
1.02
1.10
3.19
1.10
1.11
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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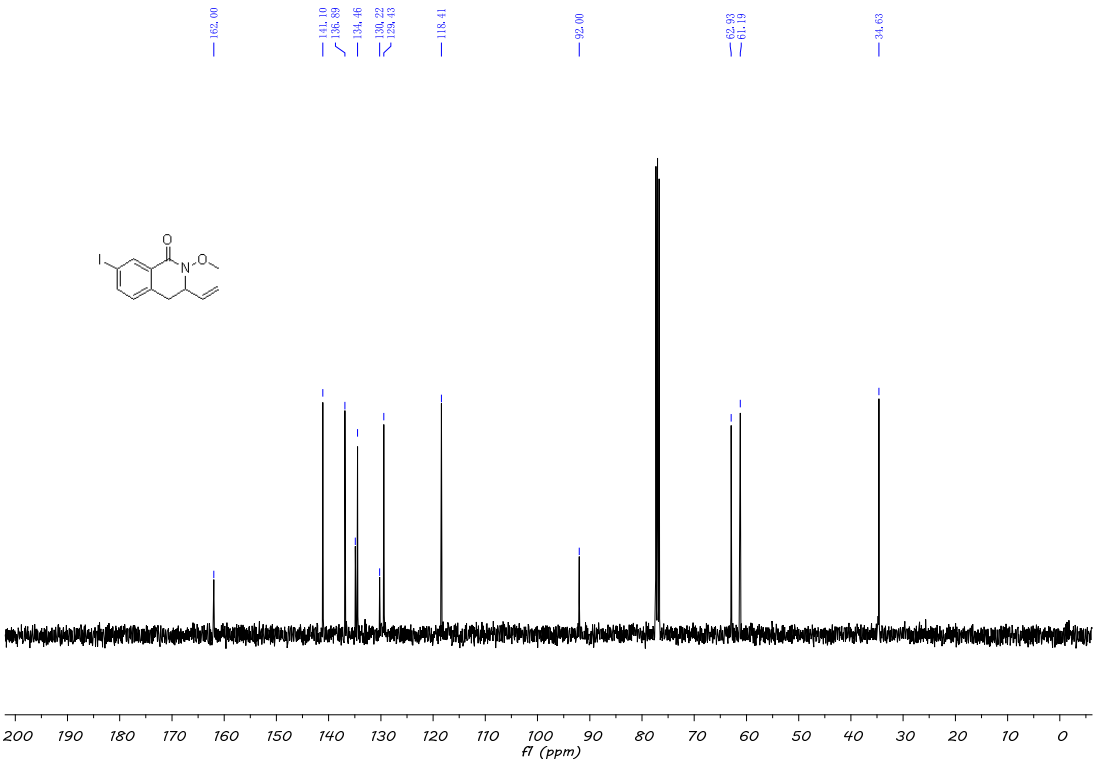
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.46
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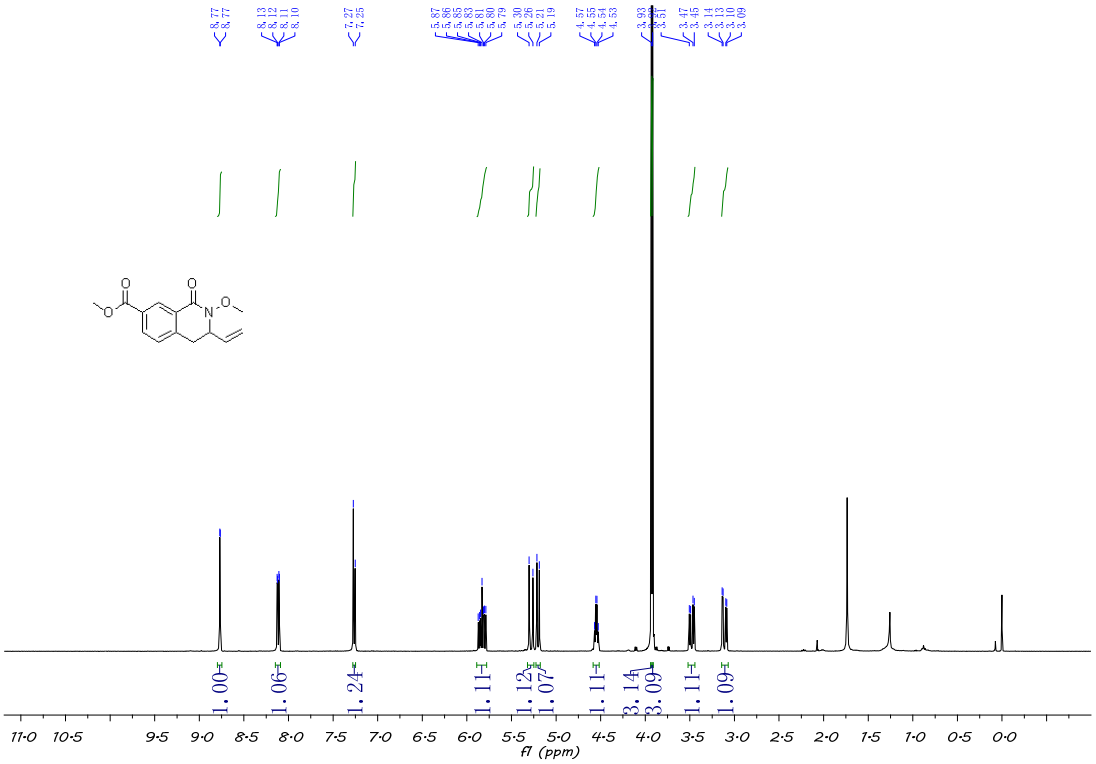
128.43
118.41
92.00
62.93
61.19
34.63
f1 (ppm)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8.10
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7.25
5.87
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5.81
5.80
5.79
5.30
5.26
5.21
5.19
4.57
4.55
4.54
4.53
3.93
3.91
3.47
3.46
3.14
3.13
3.10
3.09
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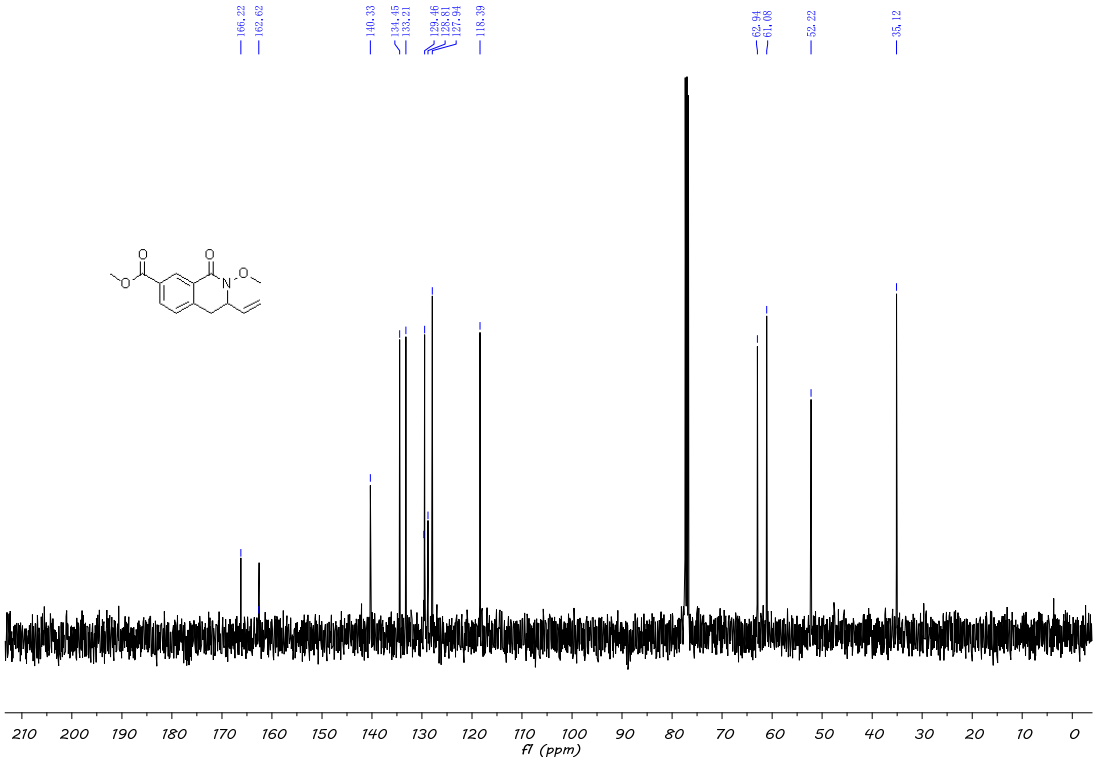
3.14
3.09
1.11
1.09
f1 (ppm)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133.21
129.46
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127.94
118.39
62.94
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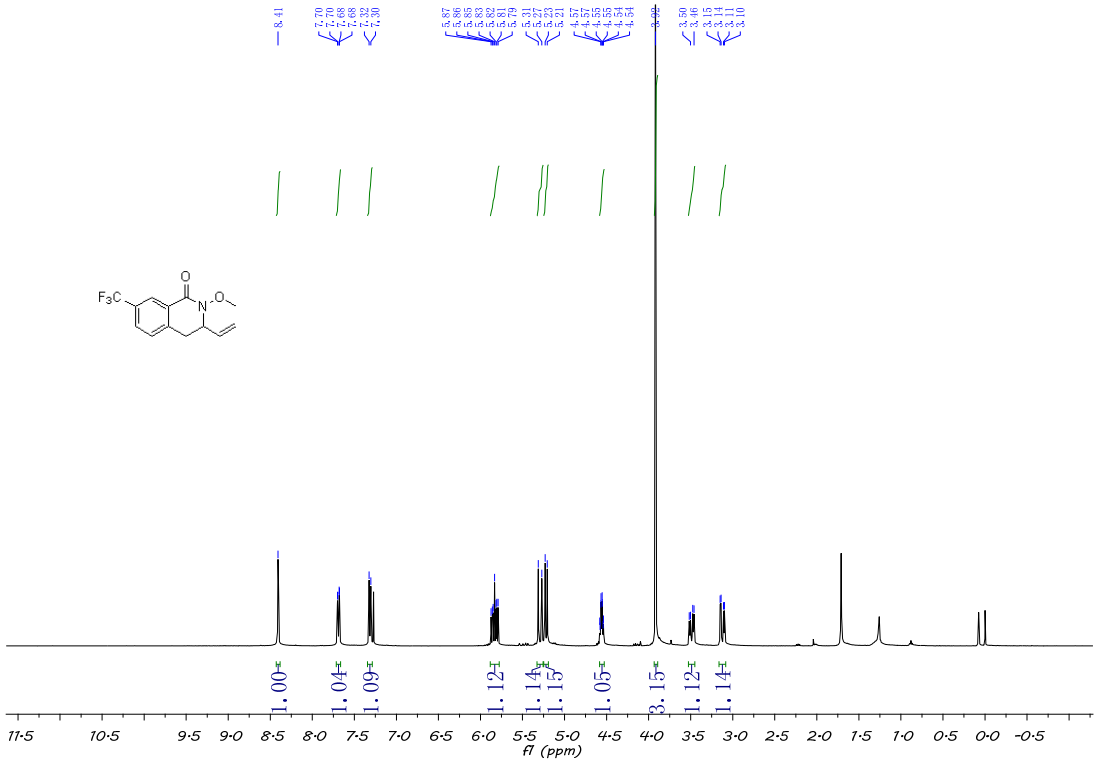
52.22
35.12
O
O
O
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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5.82
5.81
5.79
5.27
5.27
5.23
5.21
4.57
4.57
4.55
4.55
4.54
4.54
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3.50
3.46
3.15
3.14
3.11
3.10
F3C
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O
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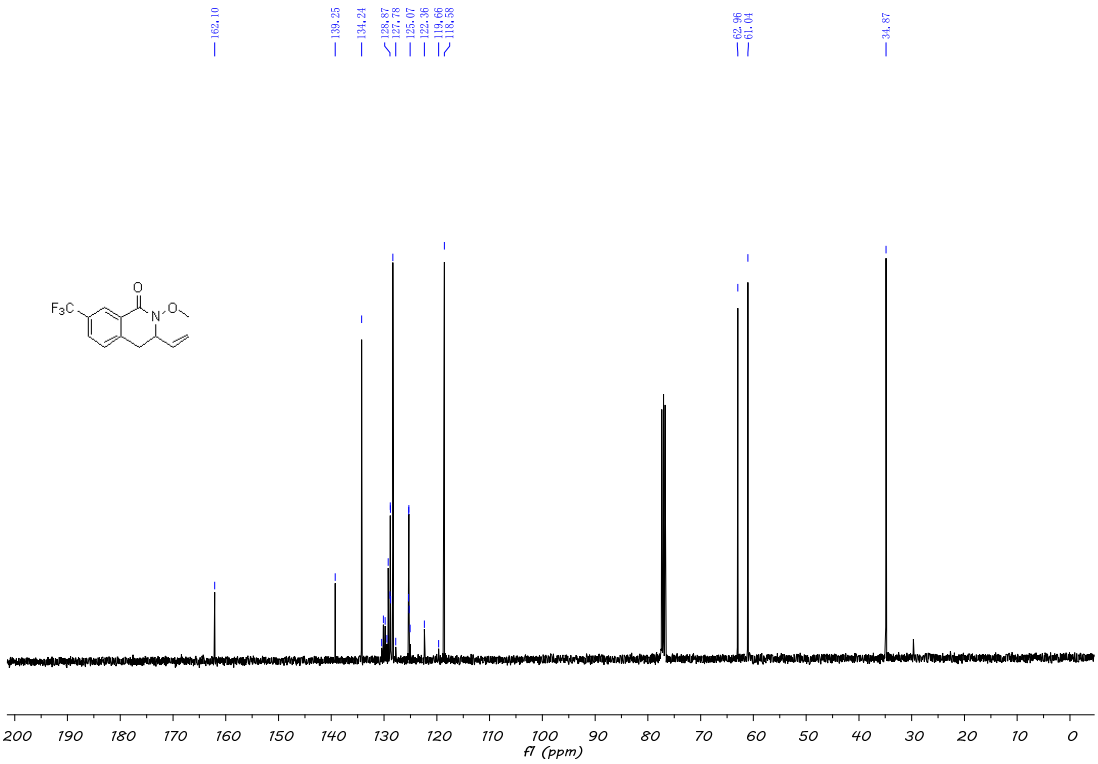
1.05
3.15
1.12
1.14
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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122.36
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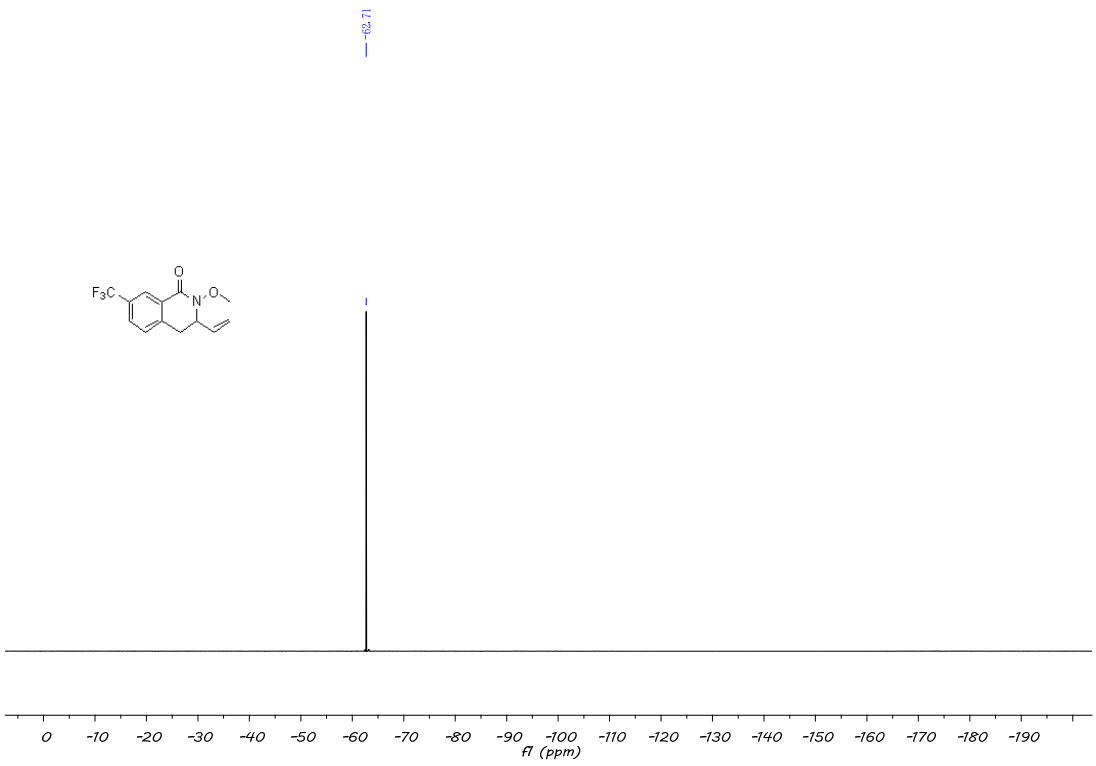
34.87
F3C
O
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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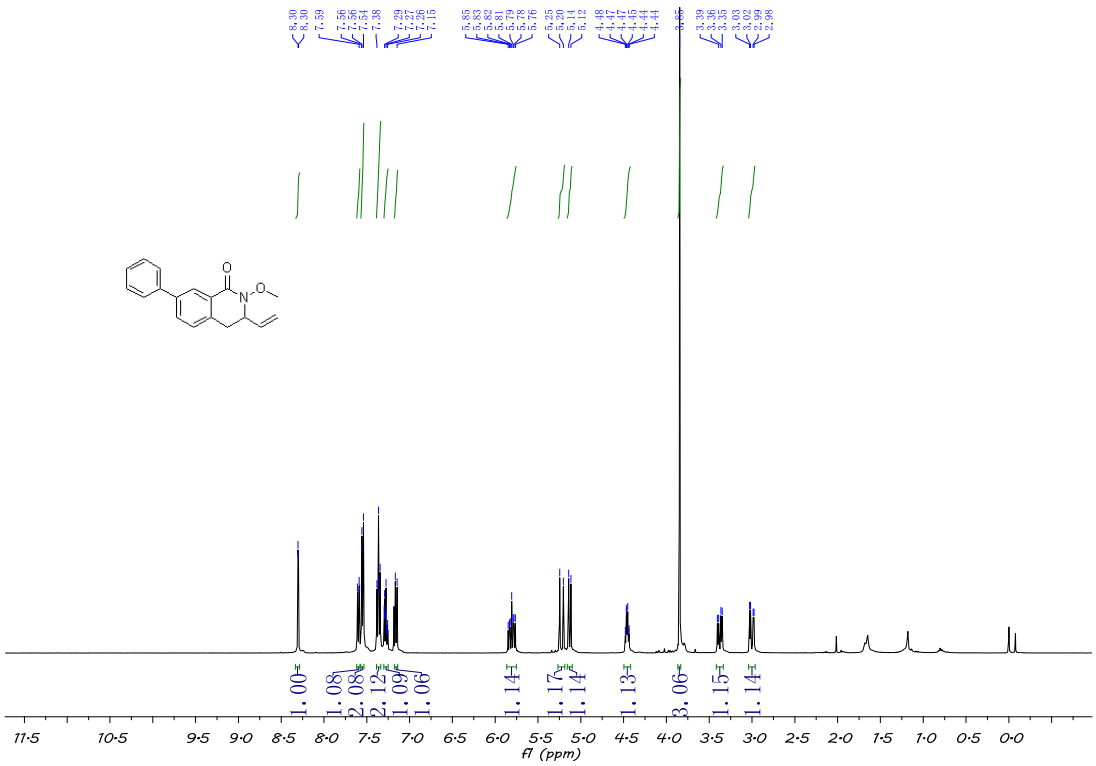
f1 (ppm)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5.76
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5.20
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4.47
4.47
4.46
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4.44
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3.35
3.03
3.02
2.99
2.98
1.00
1.08
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1.17
1.14
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3.06
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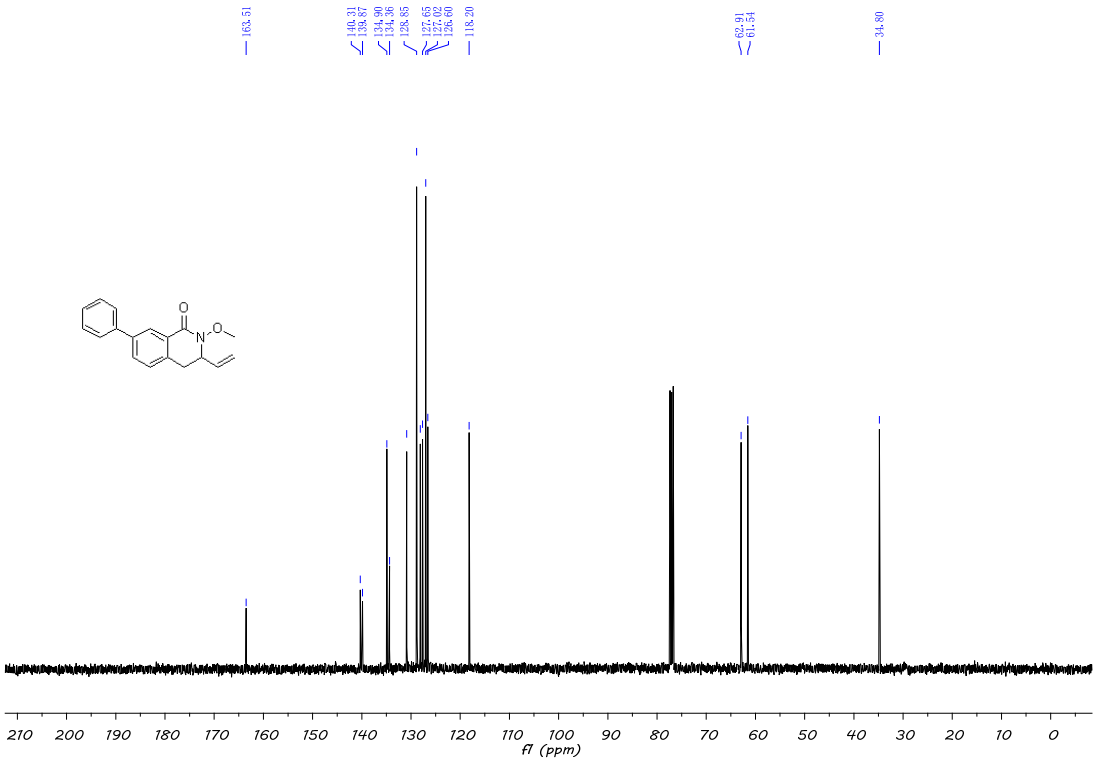
1.14
f1 (ppm)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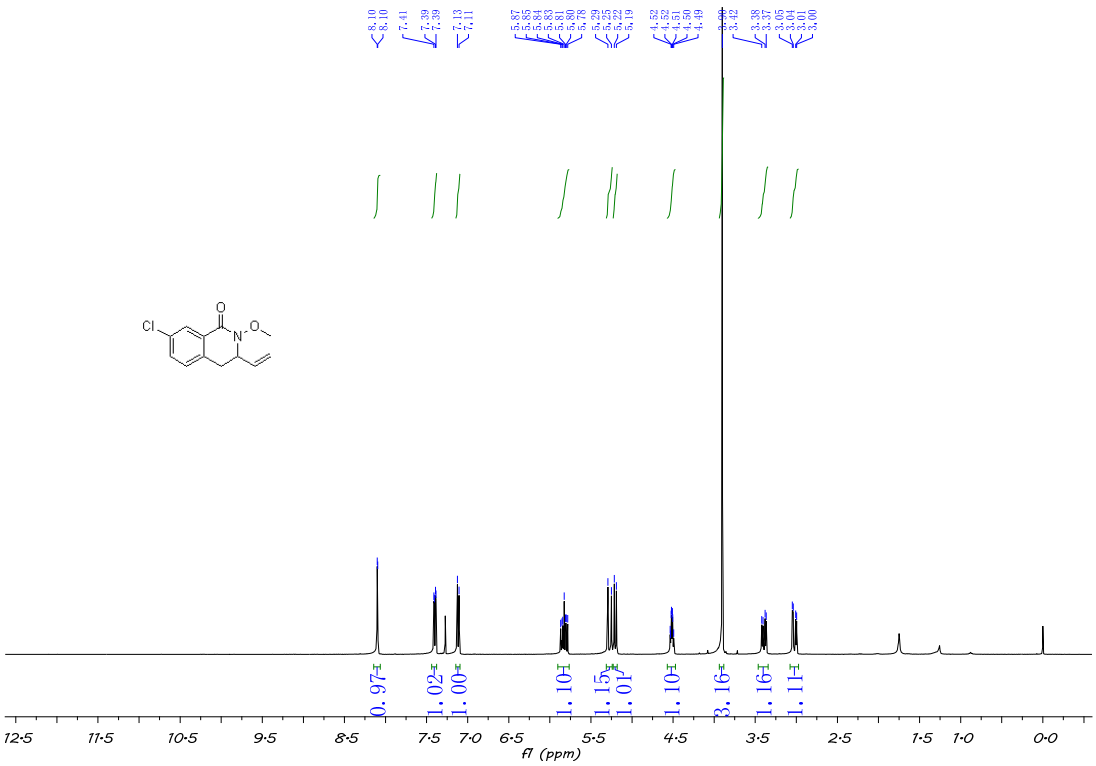
f1 (ppm)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4.50
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3.37
3.37
3.05
3.04
3.01
3.00
0.97
1.02
1.00
1.10
1.15
1.01
1.10
3.16
1.16
1.11
Cl
O
N
O
12.5
11.5
10.5
9.5
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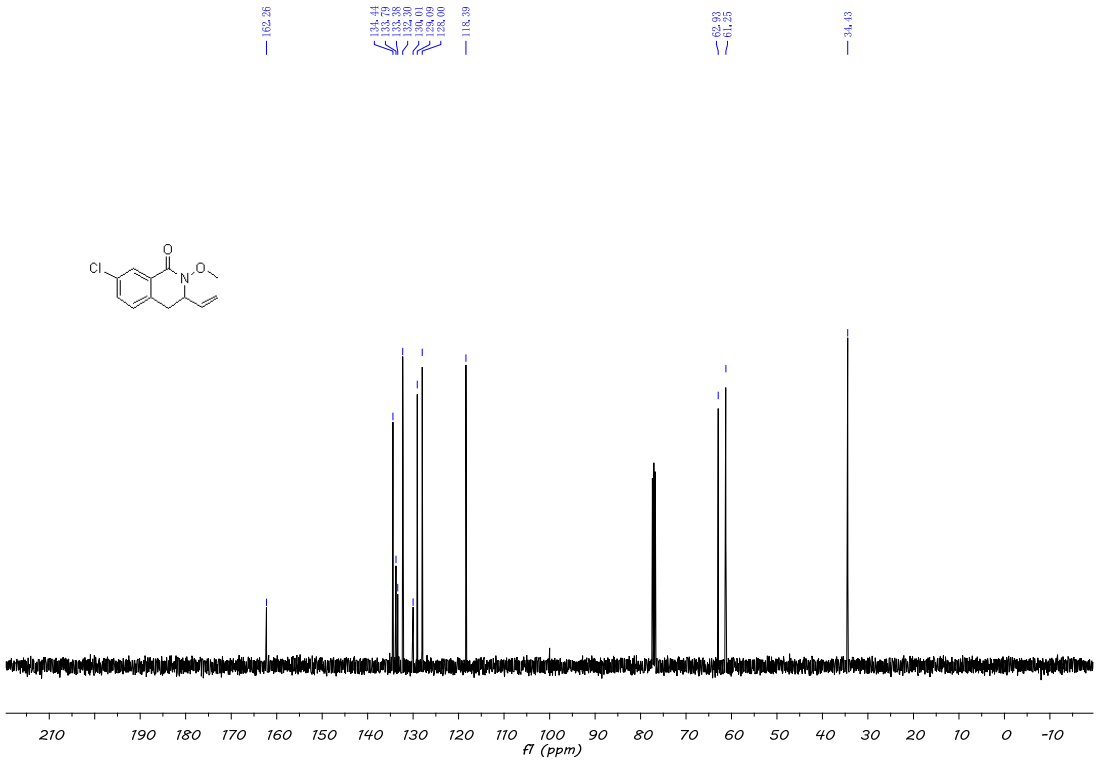
0.0
f1 (ppm)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O
N
O
210
190
180
170
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120
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100
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80
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30
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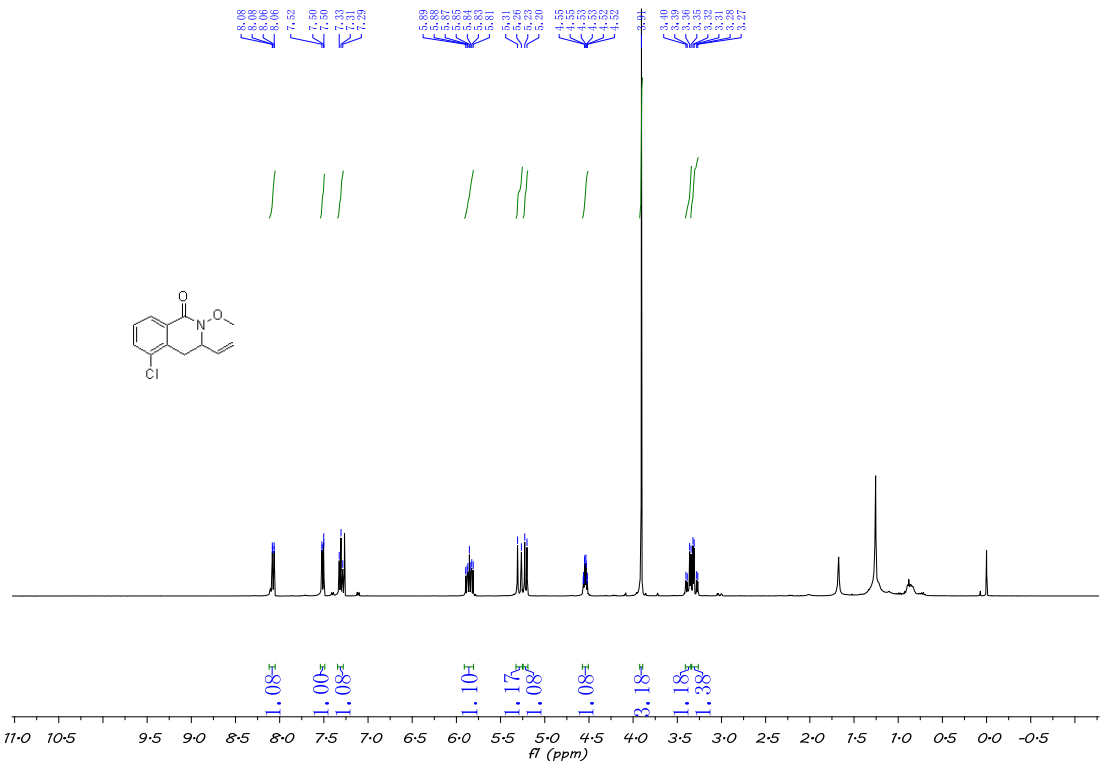
-10
f1 (ppm)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4.55
4.53
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4.52
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3.40
3.39
3.35
3.35
3.32
3.31
3.28
3.27
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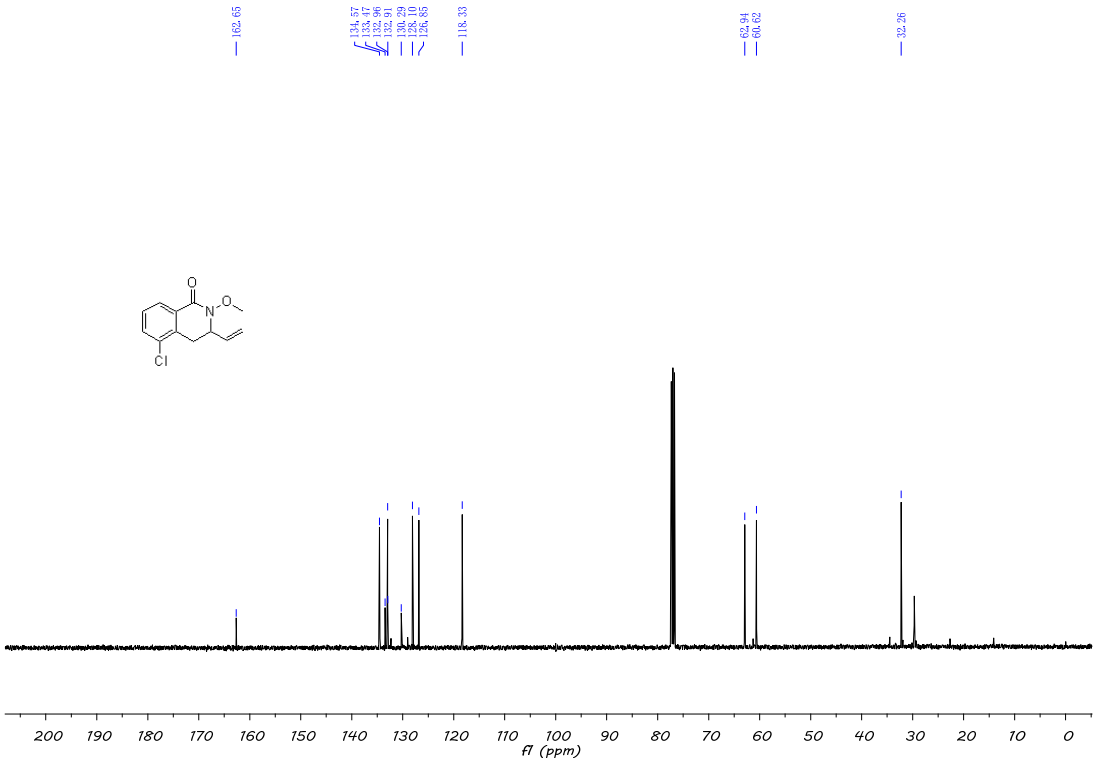
1.18
1.38
f1 (ppm)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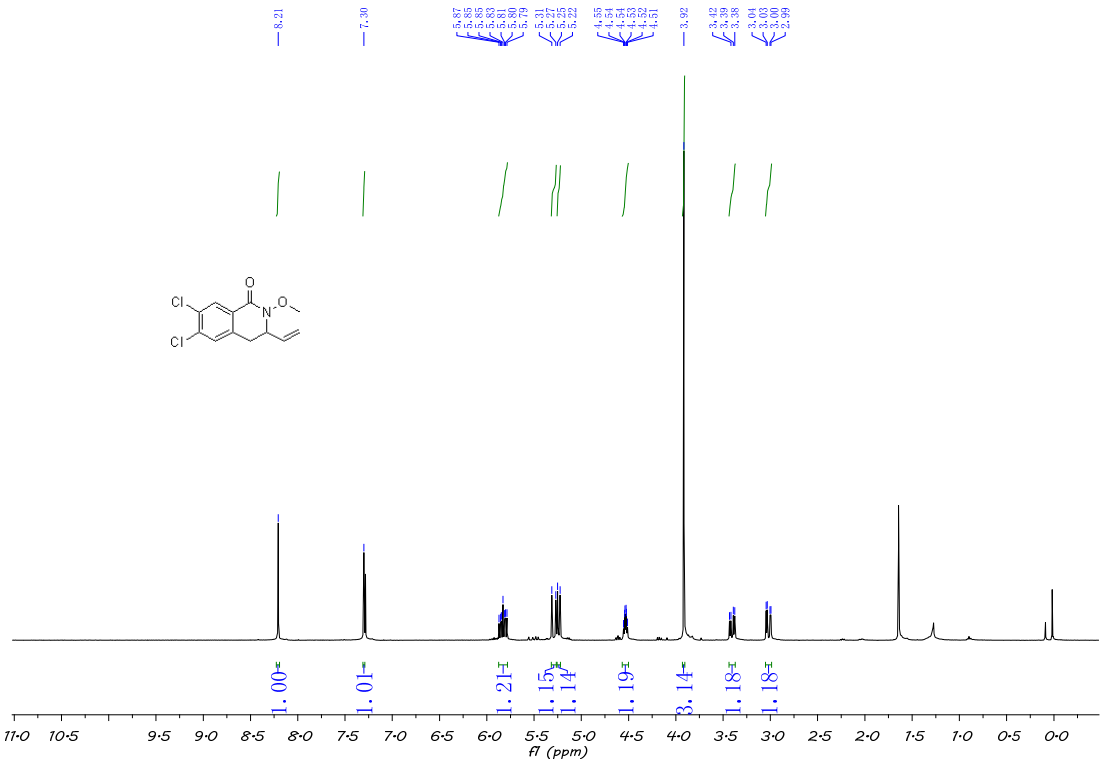
32.26
Cl
f1 (ppm)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4.54
4.54
4.53
4.52
4.51
3.92
3.42
3.39
3.38
3.04
3.03
3.00
2.99
Cl
Cl
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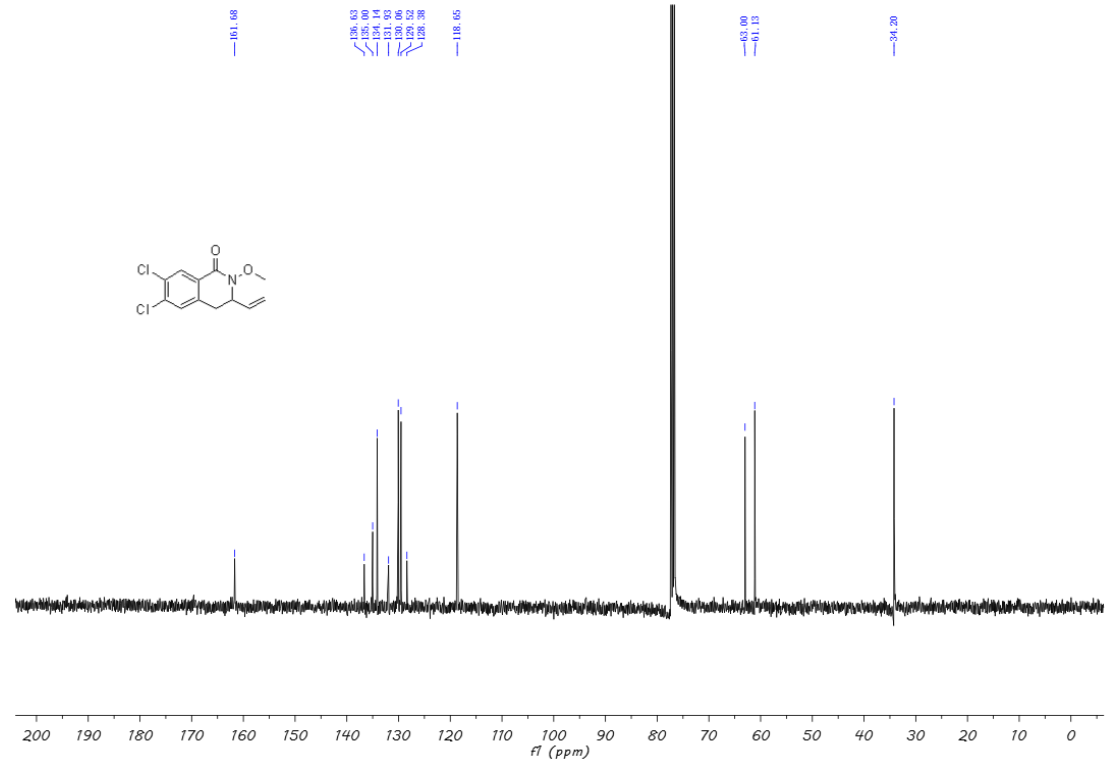
1.18
f1 (ppm)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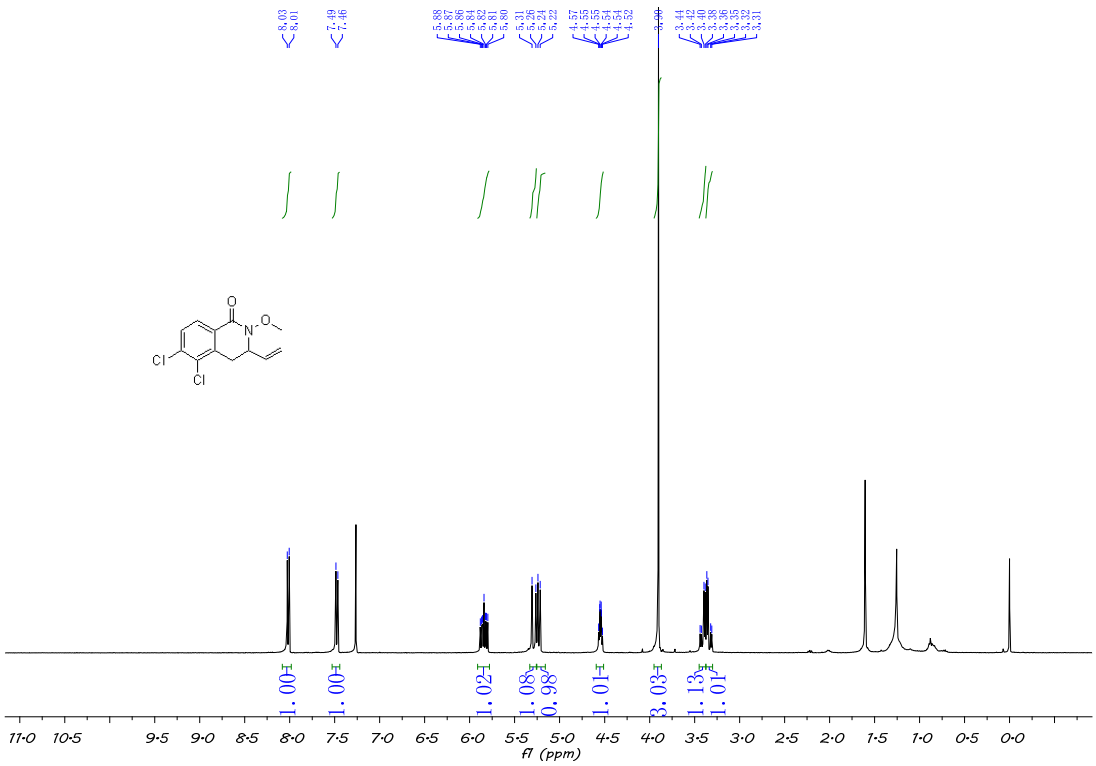
Cl
Cl
O
N
O
f1 (ppm)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5.24
5.22
4.57
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4.54
4.54
4.52
3.44
3.42
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3.35
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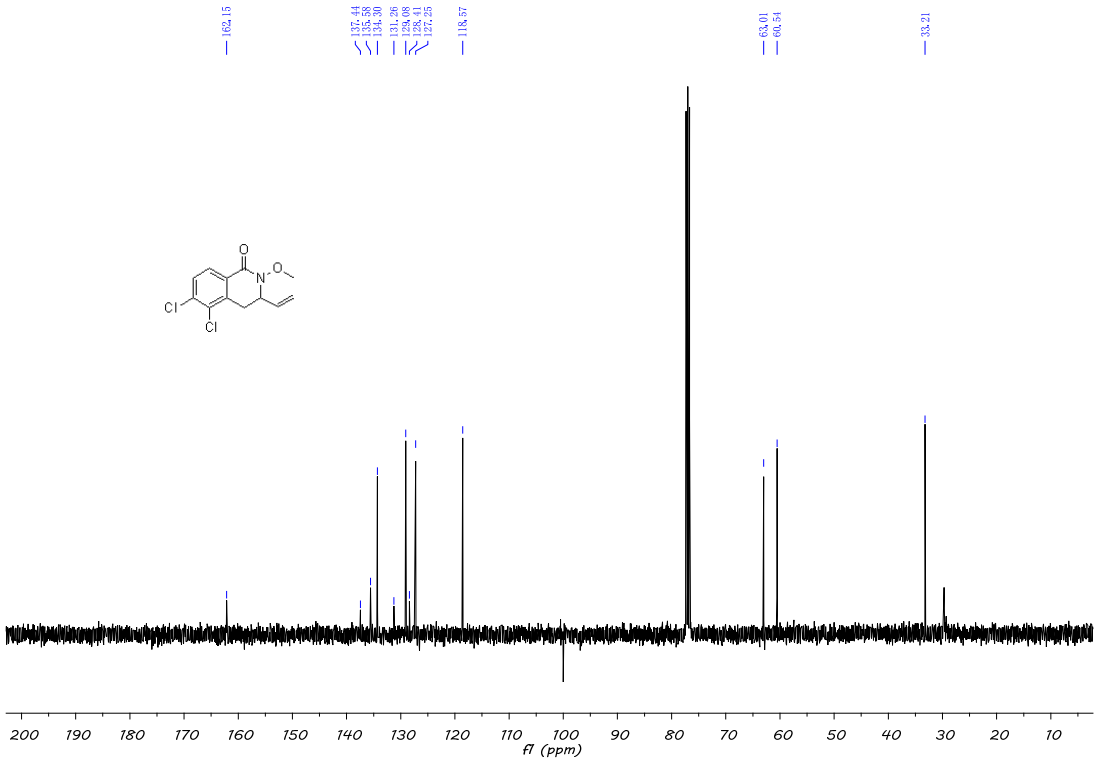
1.08
0.98
1.01
3.03
1.13
1.01
f1 (ppm)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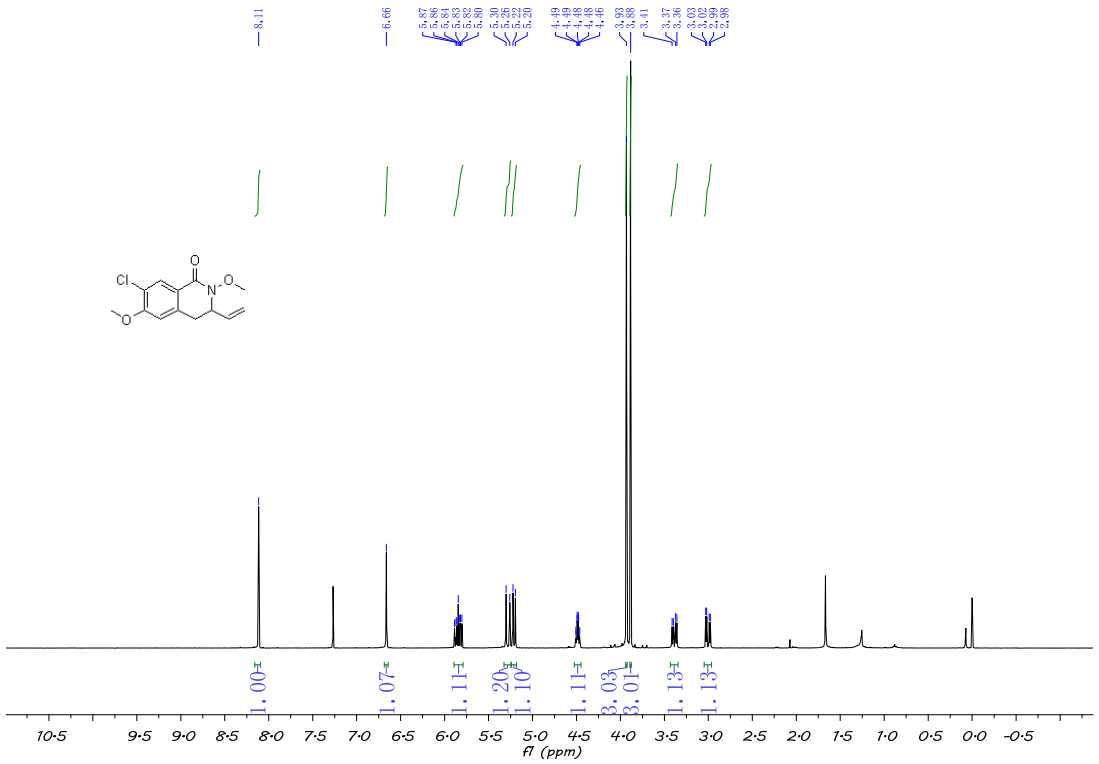
60.54
33.21
f1 (ppm)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3.41
3.37
3.36
3.03
3.02
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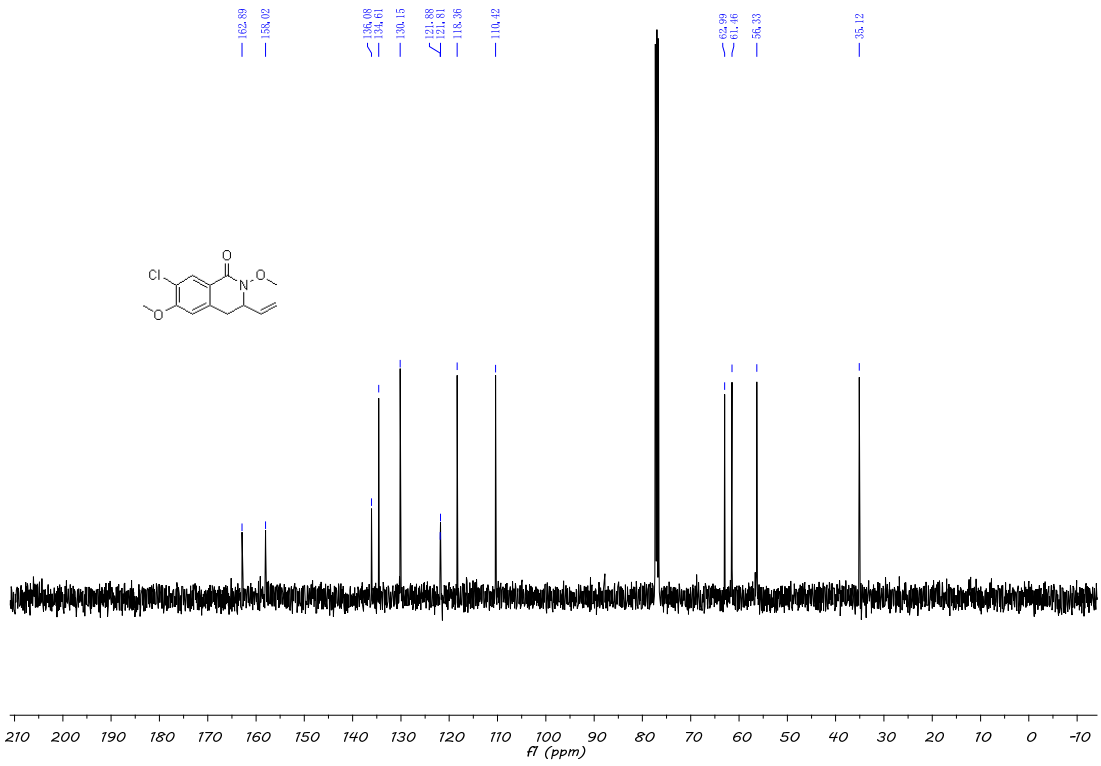
1.10
1.11
3.03
3.01
1.13
1.13
f1 (ppm)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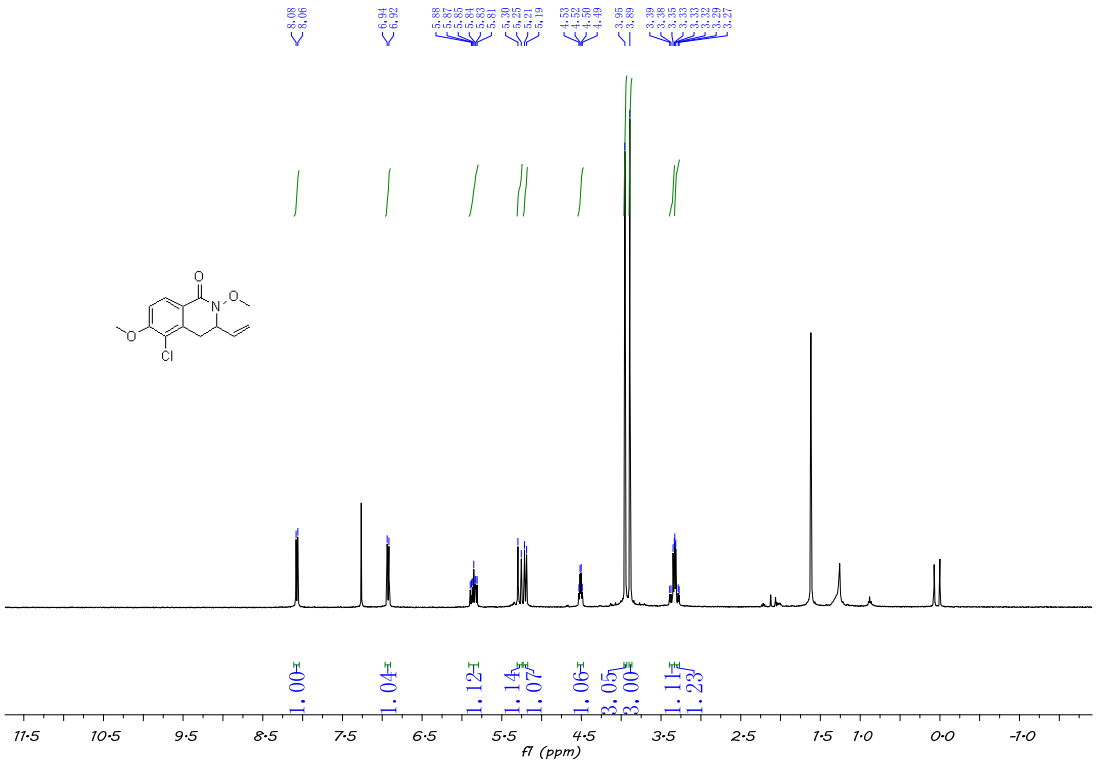
35.12
f1 (ppm)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3.33
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3.29
3.27
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1.04
1.12
1.14
1.07
1.06
3.05
3.00
1.11
1.23
11.5
10.5
9.5
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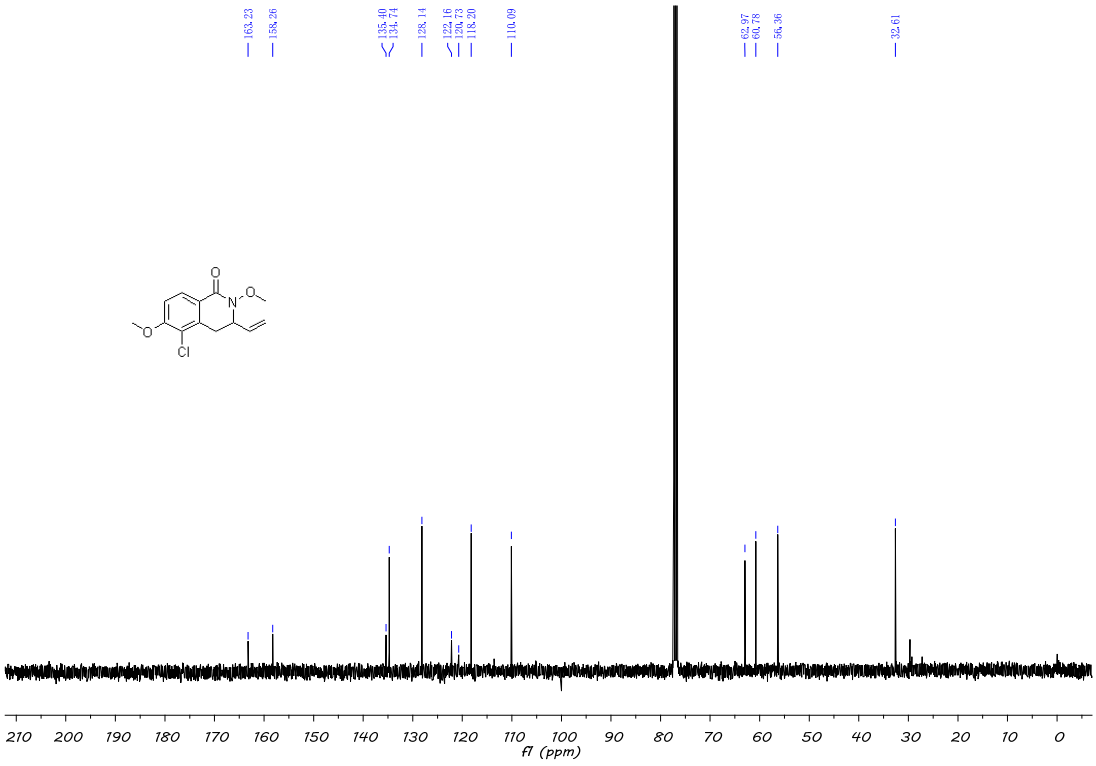
-1.0
f1 (ppm)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32.61
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200
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180
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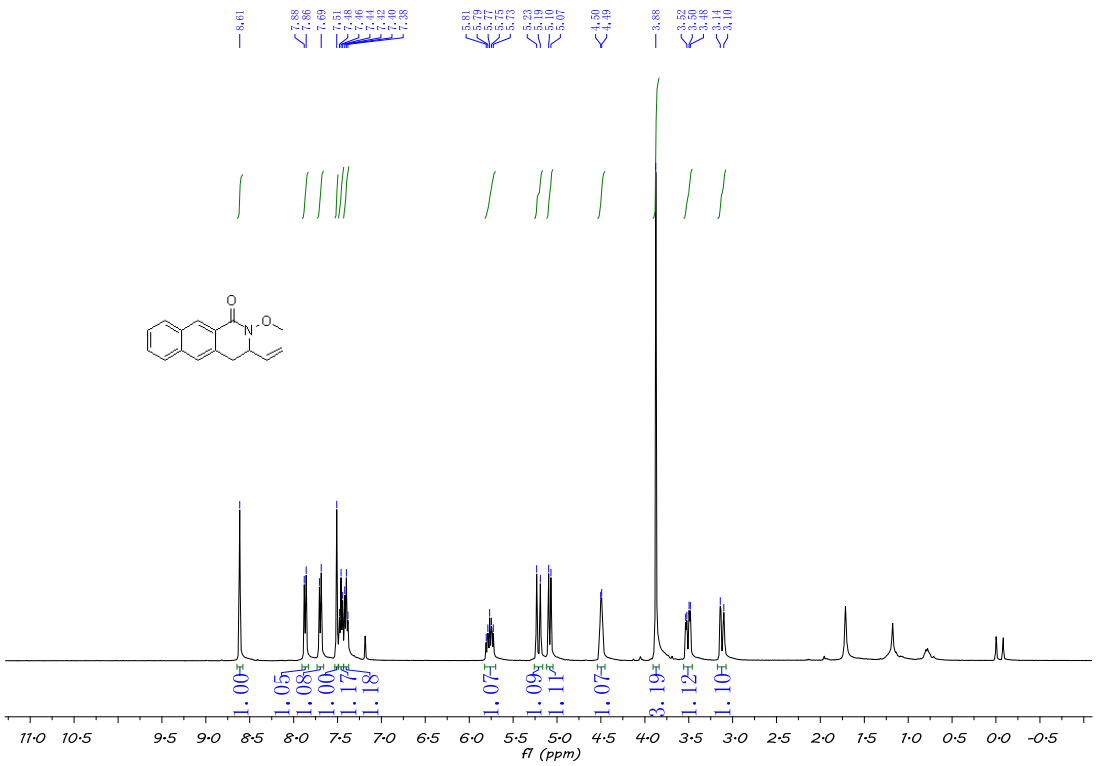
f1 (ppm)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1.05
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1.07
3.19
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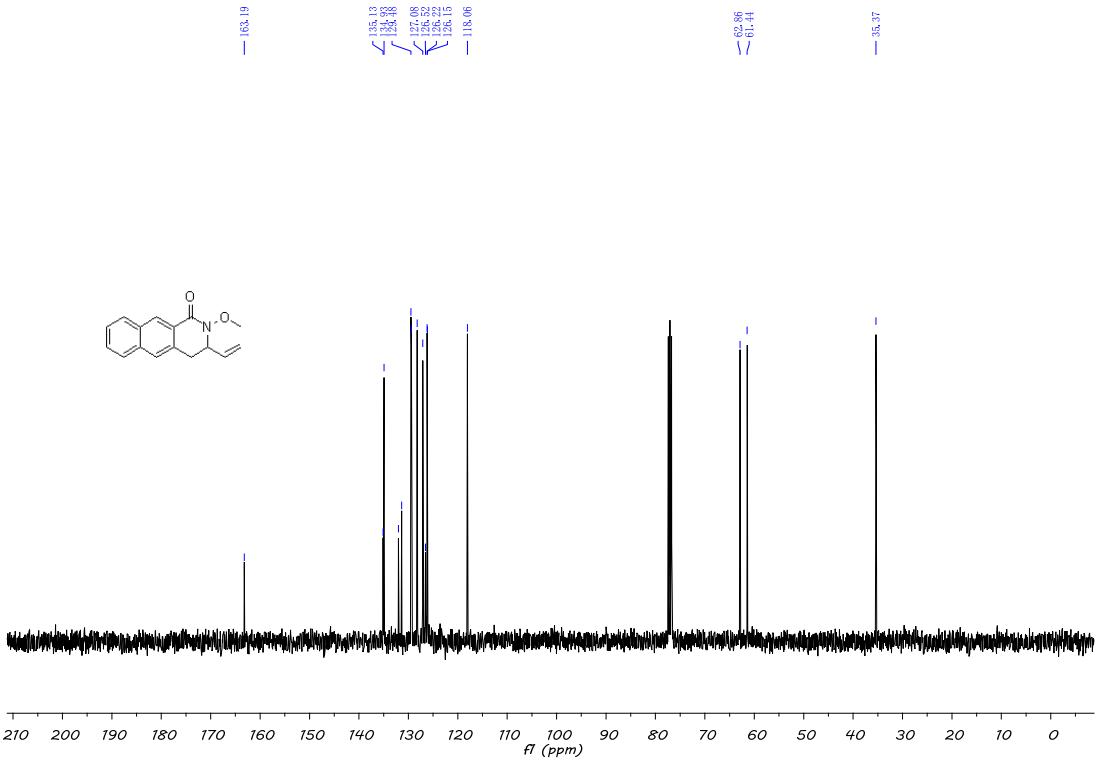
1.10
f1 (ppm)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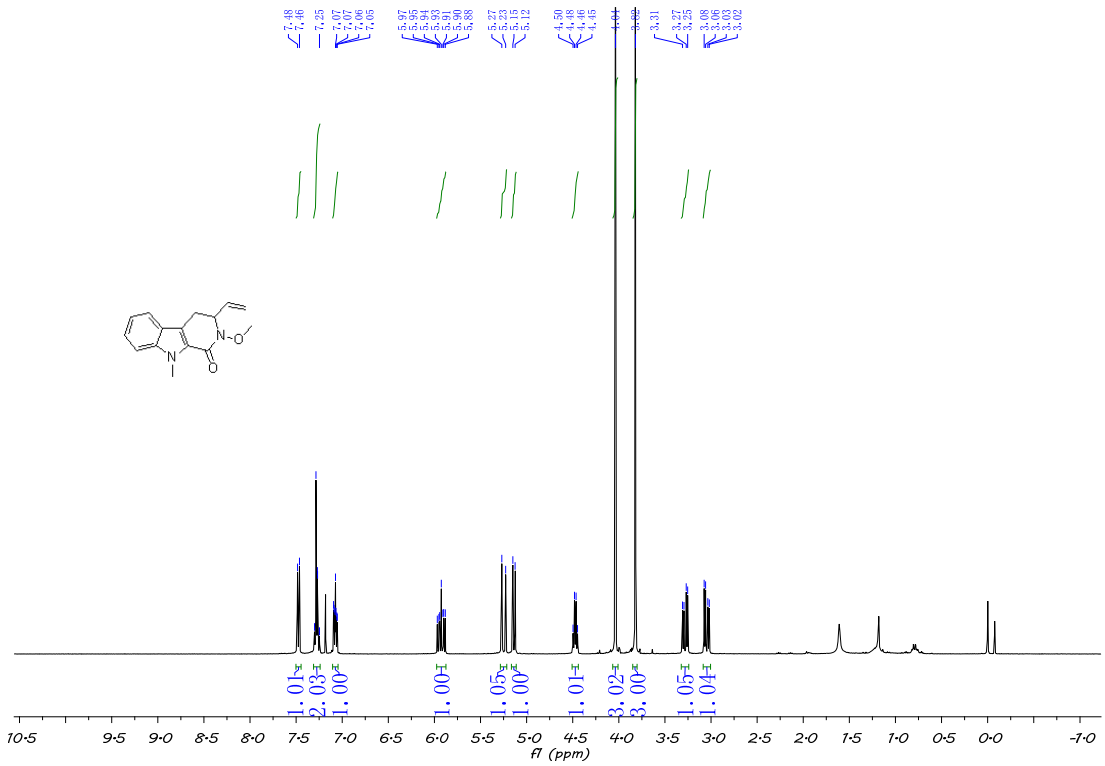
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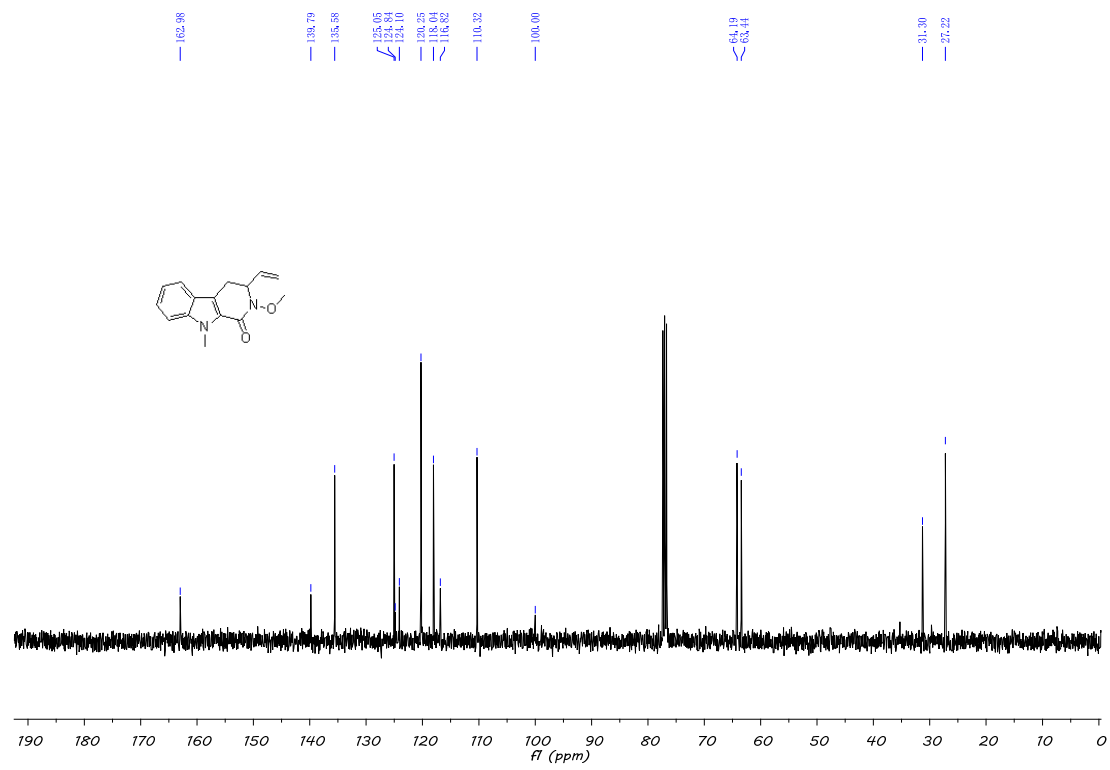
f1 (ppm)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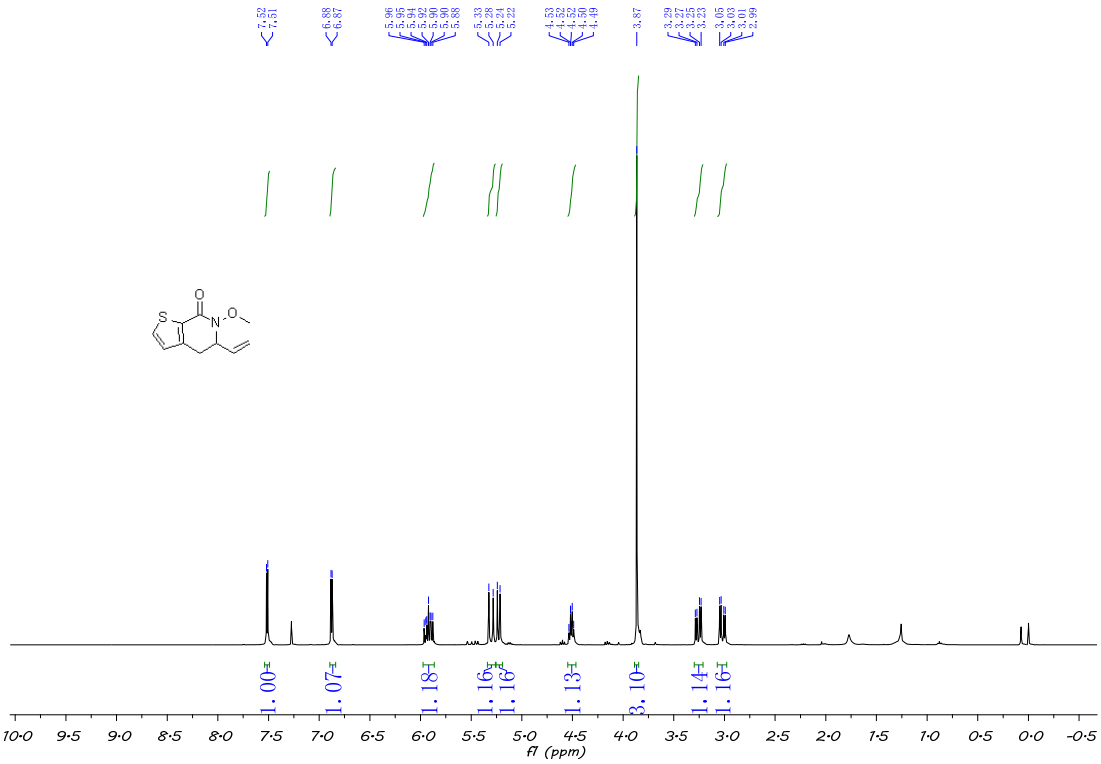
27.22
f1 (ppm)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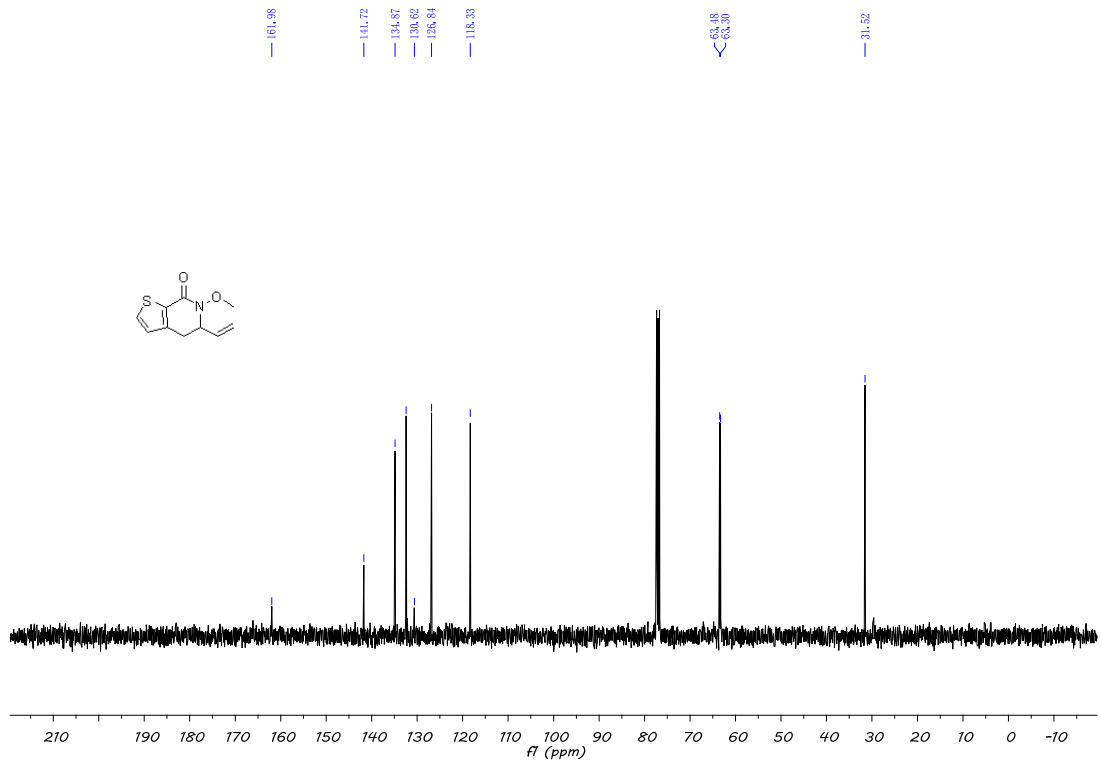
f1 (ppm)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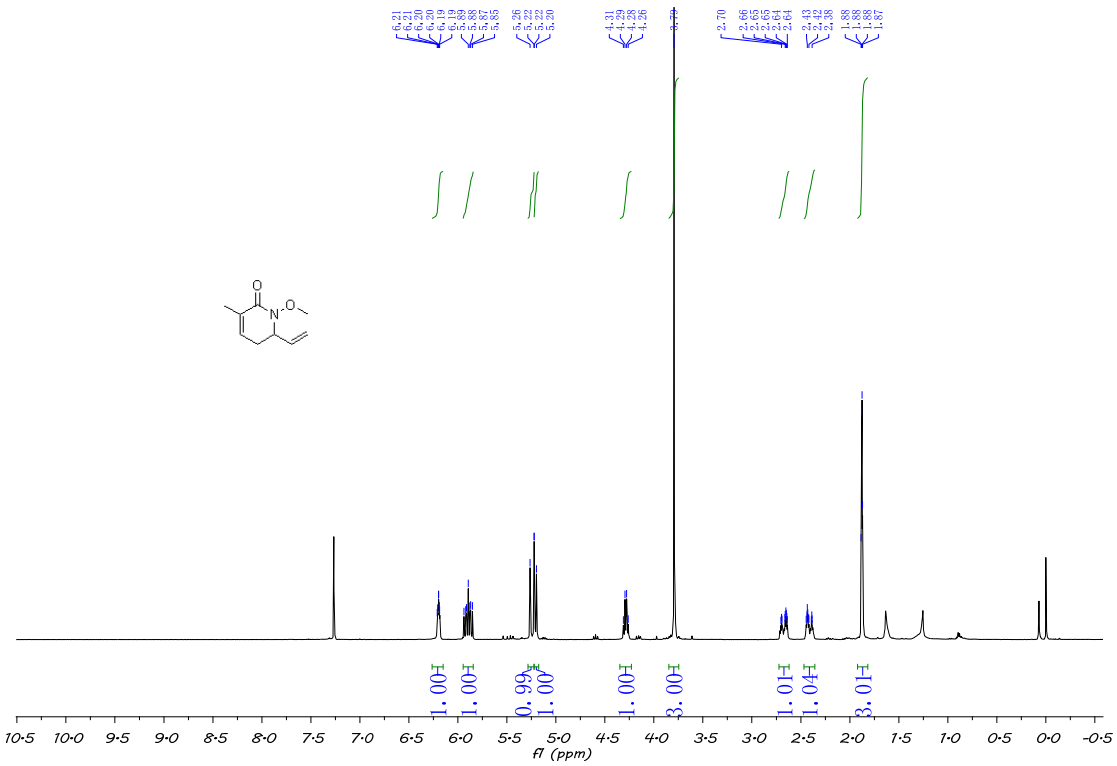
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2.42
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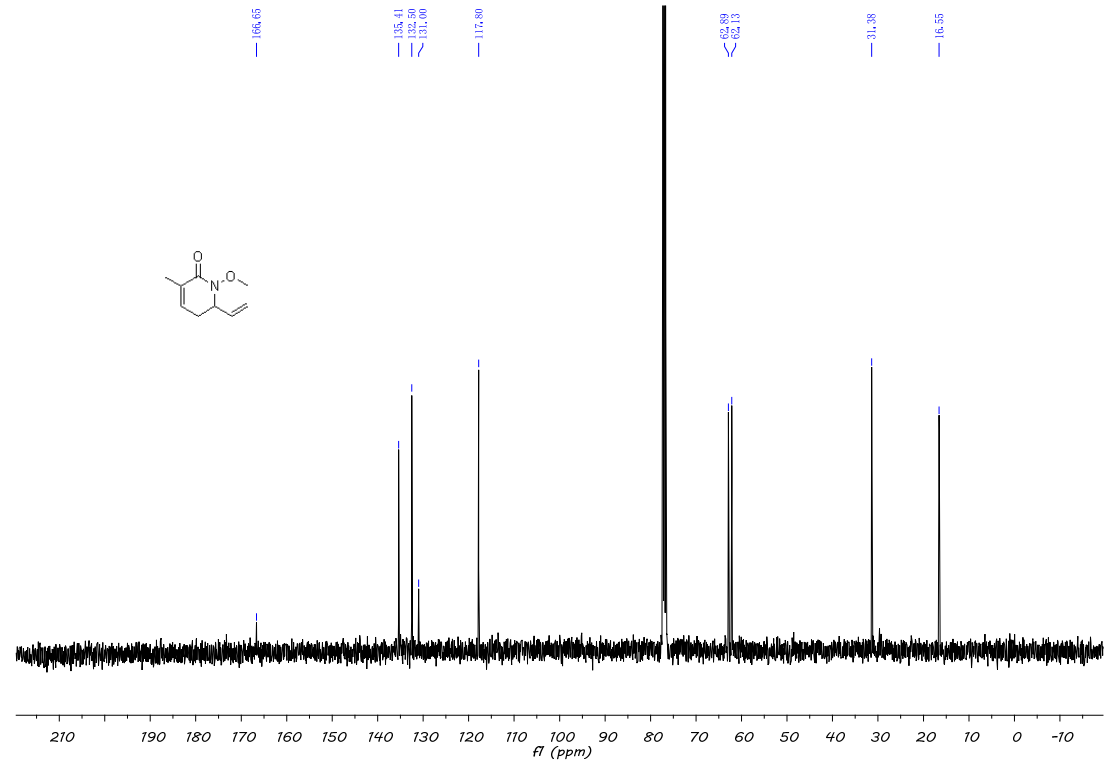
1.88
1.88
1.87
1.00
1.00
0.99
1.00
1.00
3.00
1.01
1.04
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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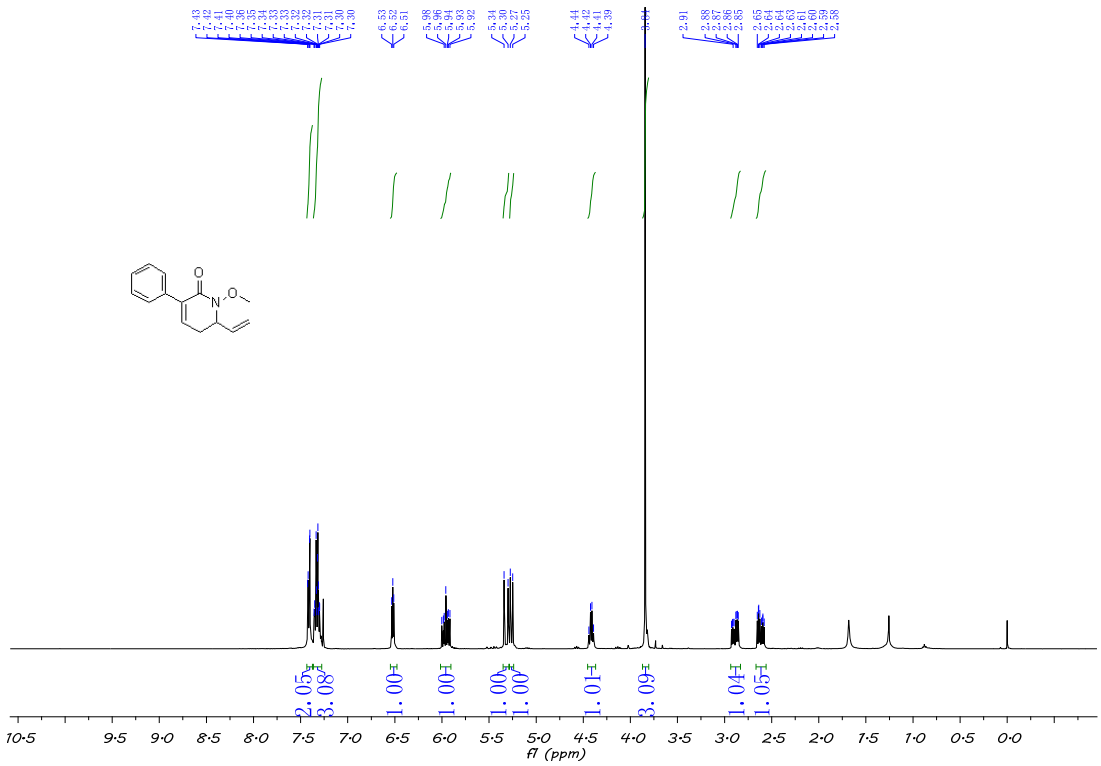
f1 (ppm)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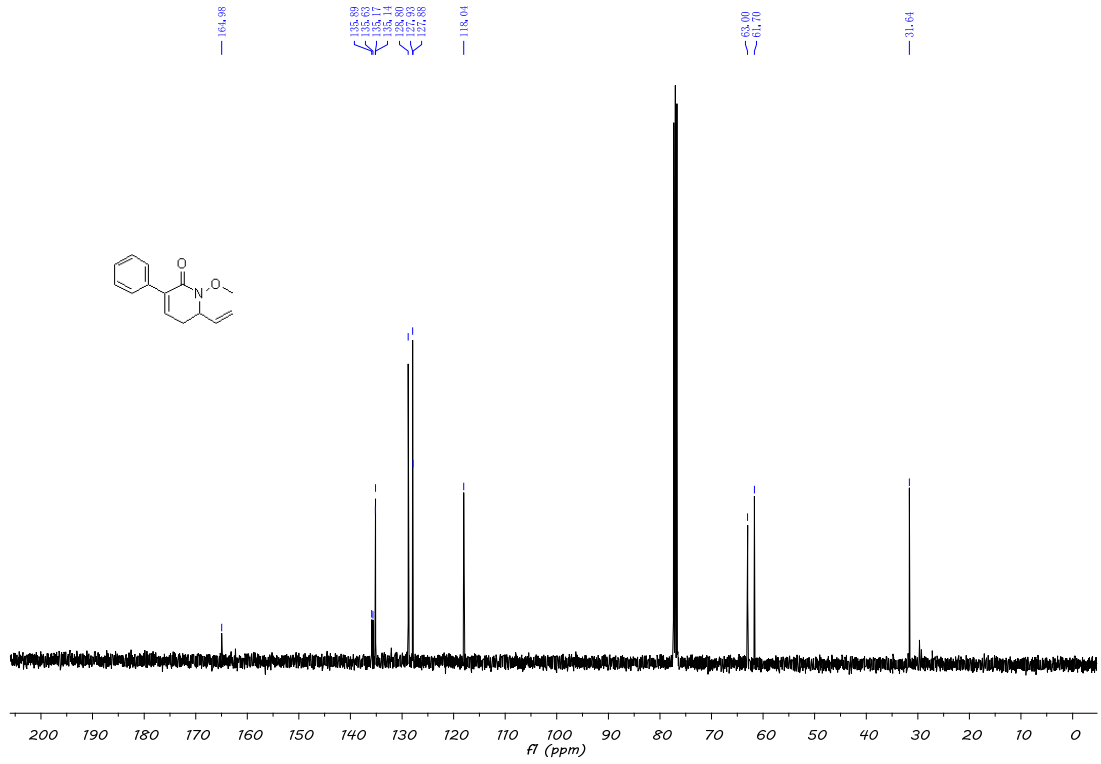
1.05
f1 (ppm)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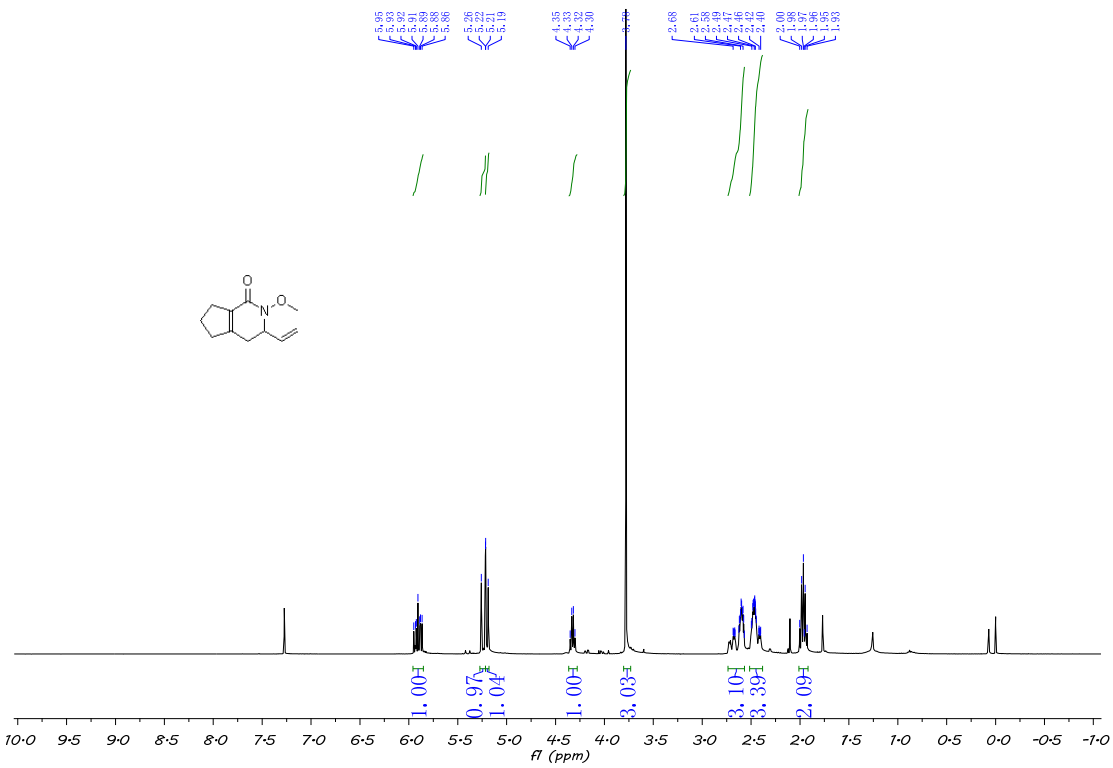
f1 (ppm)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1.00
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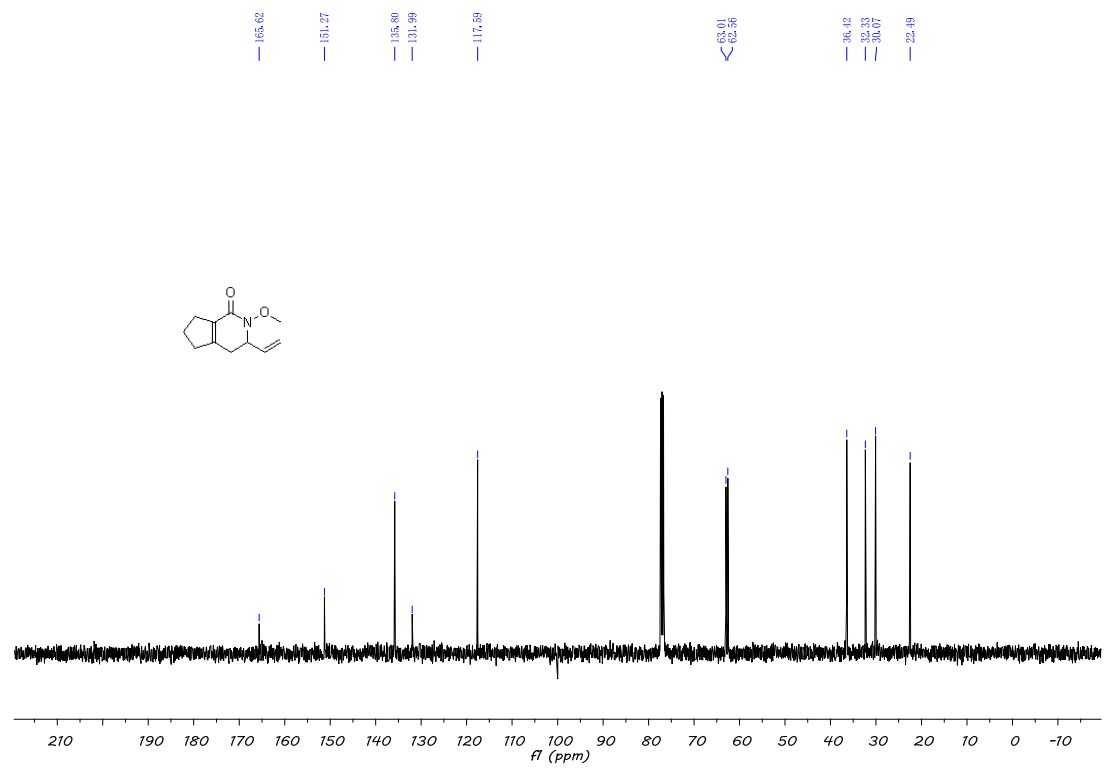
f1 (ppm)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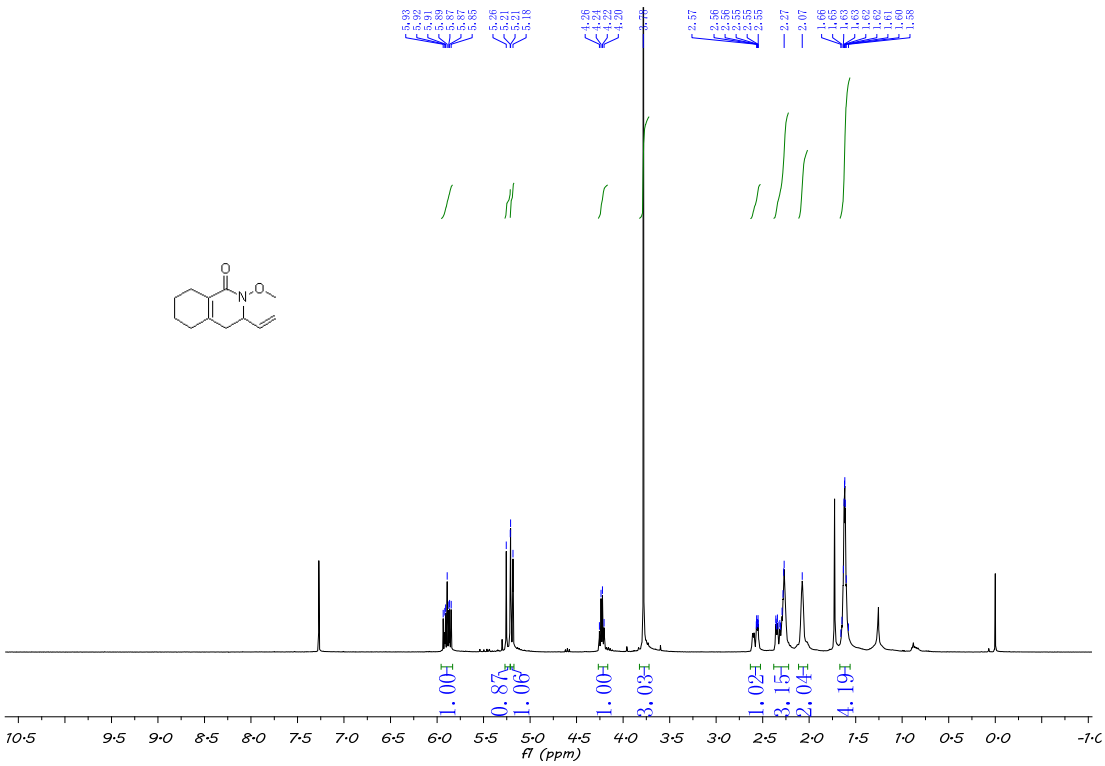
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4.20
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2.56
2.56
2.55
2.55
2.55
2.27
2.07
1.66
1.65
1.63
1.63
1.62
1.61
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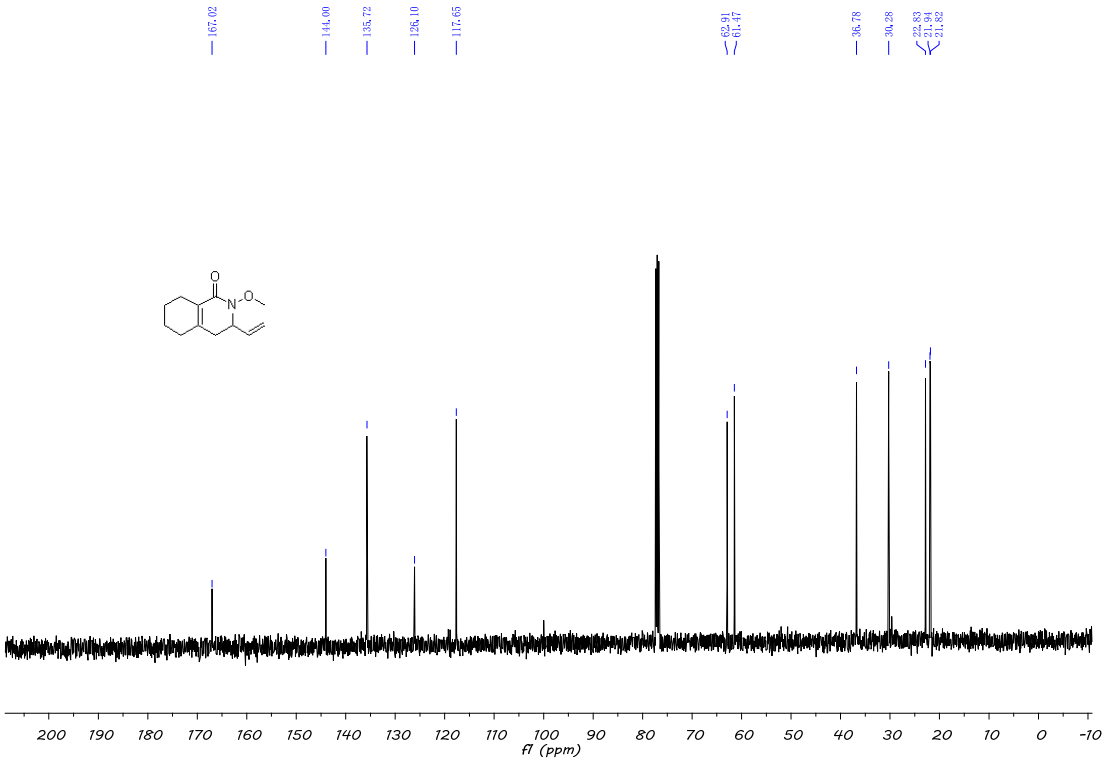
f1 (ppm)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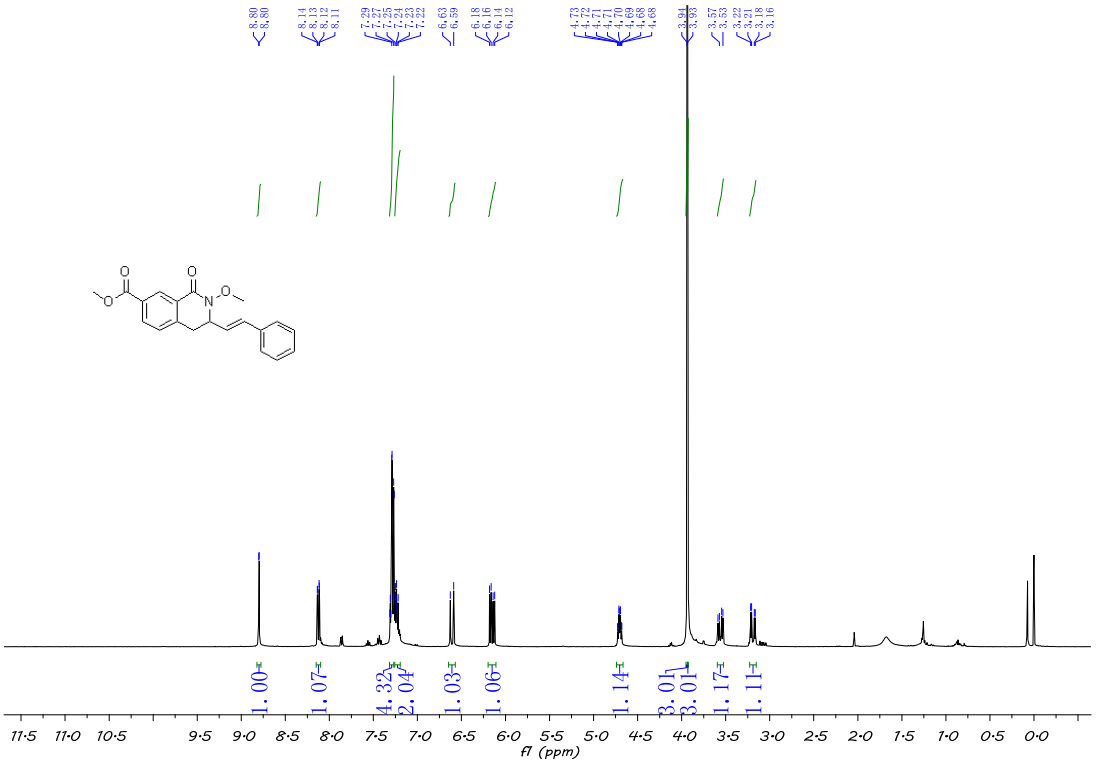
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6.18
6.16
6.14
6.12
4.73
4.72
4.71
4.71
4.70
4.69
4.68
4.68
3.94
3.93
3.57
3.53
3.22
3.21
3.18
3.16
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1.14
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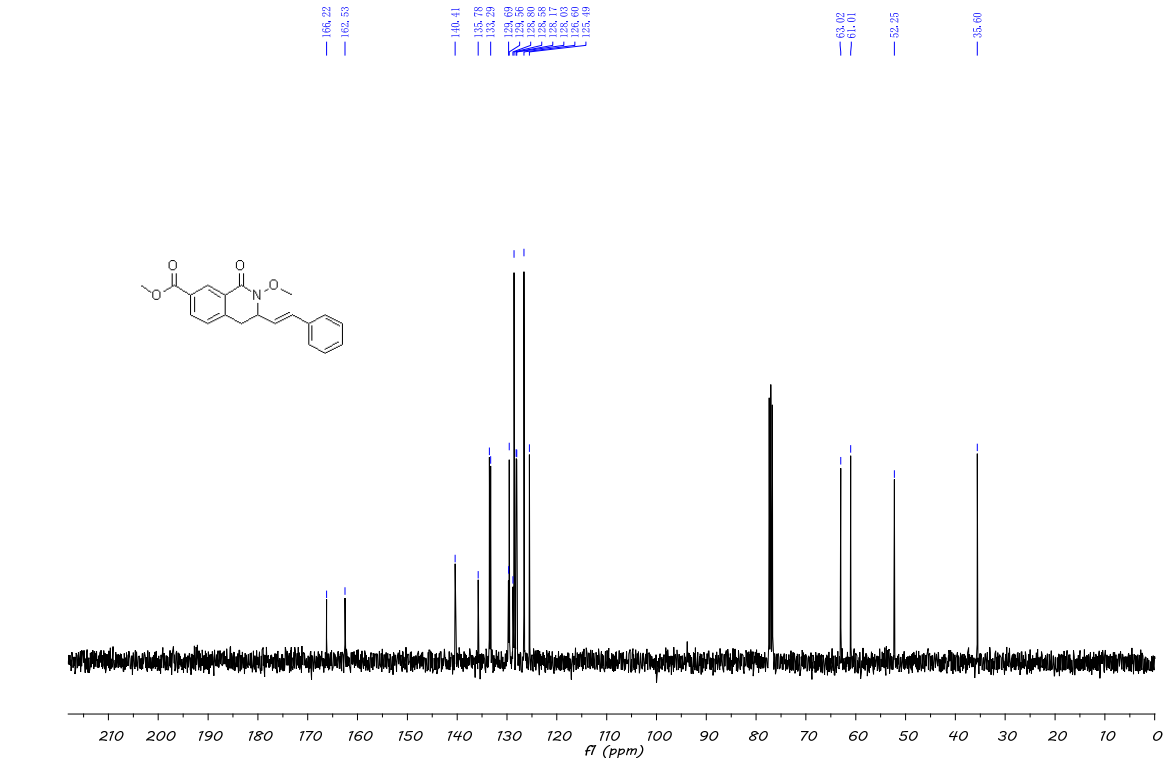
f1 (ppm)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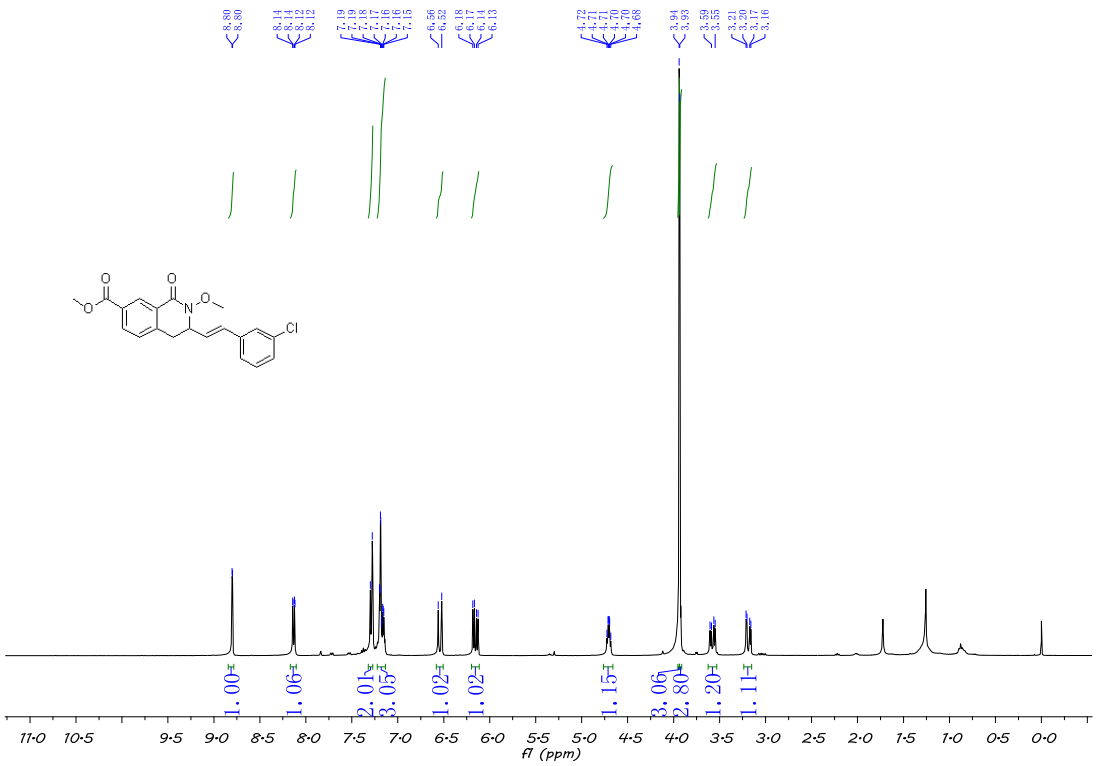
61.01
52.25
35.60
f1 (ppm)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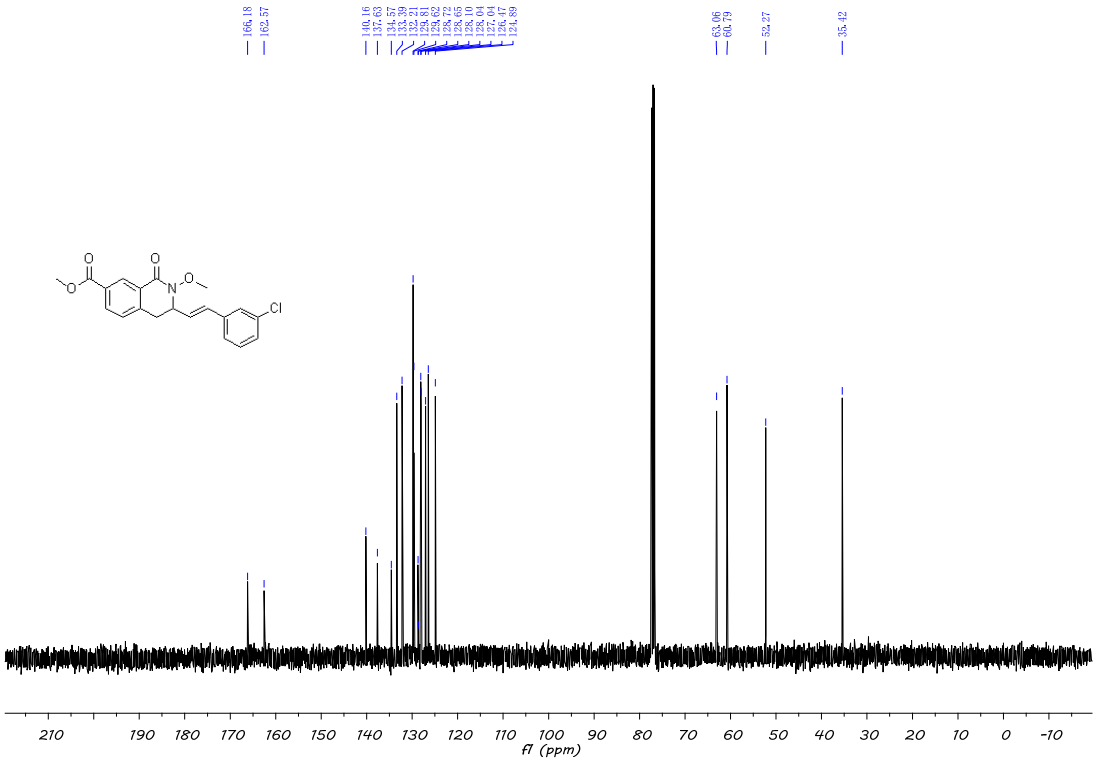
7.15
6.56
6.52
6.18
6.17
6.14
6.13
4.72
4.71
4.71
4.70
4.68
3.94
3.93
3.59
3.55
3.21
3.20
3.17
3.16
O
O
O
N
O
Cl
1.00
1.06
2.01
3.05
1.02
1.02
1.15
3.06
2.80
1.20
1.11
11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.72
128.45
128.10
126.04
125.04
124.47
124.89
63.06
60.79
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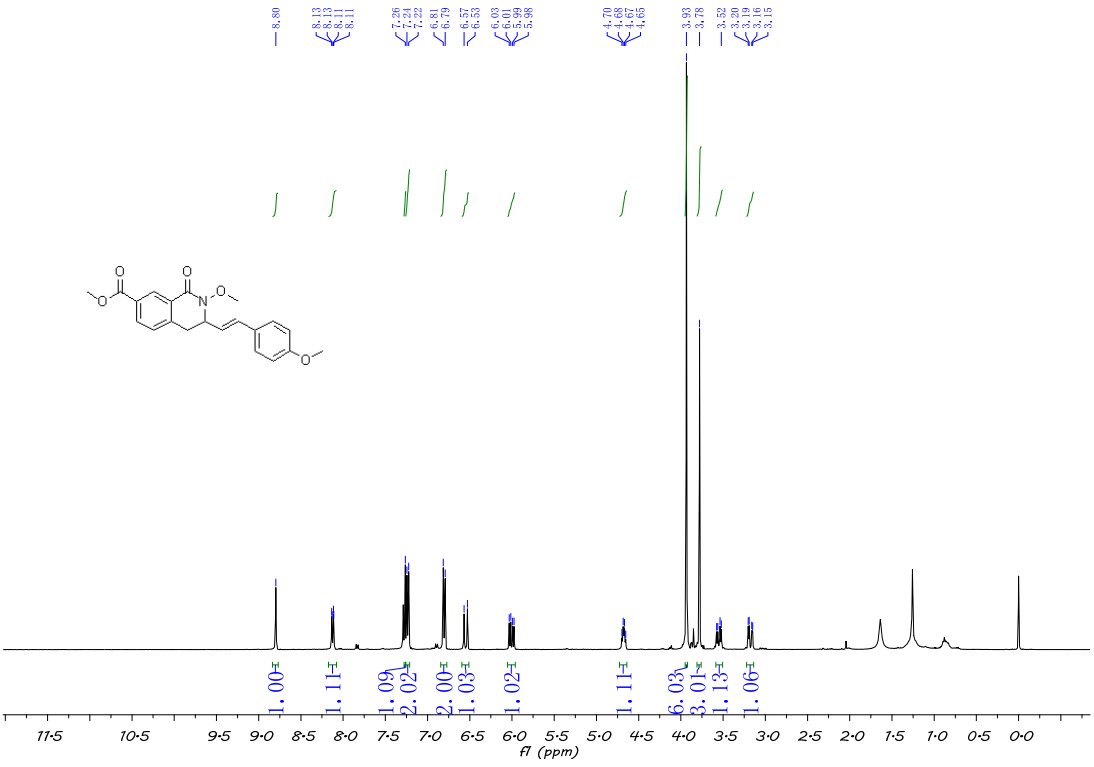
35.42
O
O
O
N
O
Cl
210 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.22
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6.79
6.57
6.53
6.03
6.01
5.99
5.98
4.70
4.68
4.67
4.65
3.93
3.78
3.52
3.20
3.19
3.16
3.15
1.00
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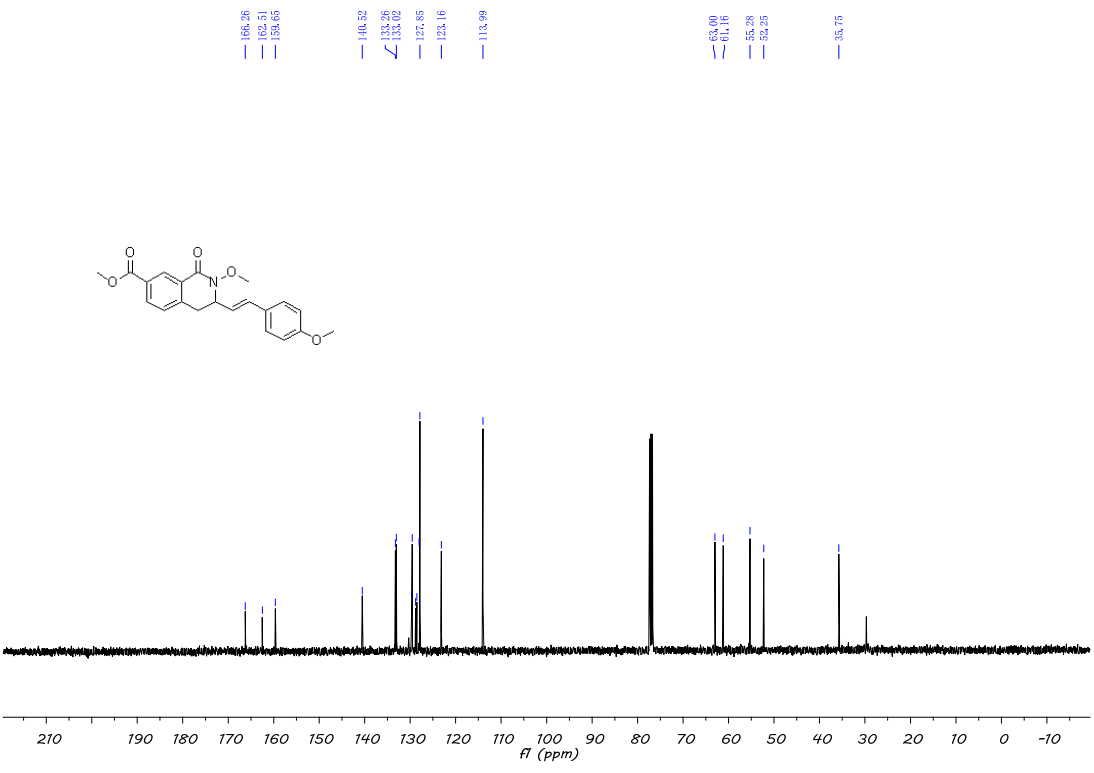
2.02
2.00
1.03
1.02
1.11
6.03
3.01
1.13
1.06
f1 (ppm)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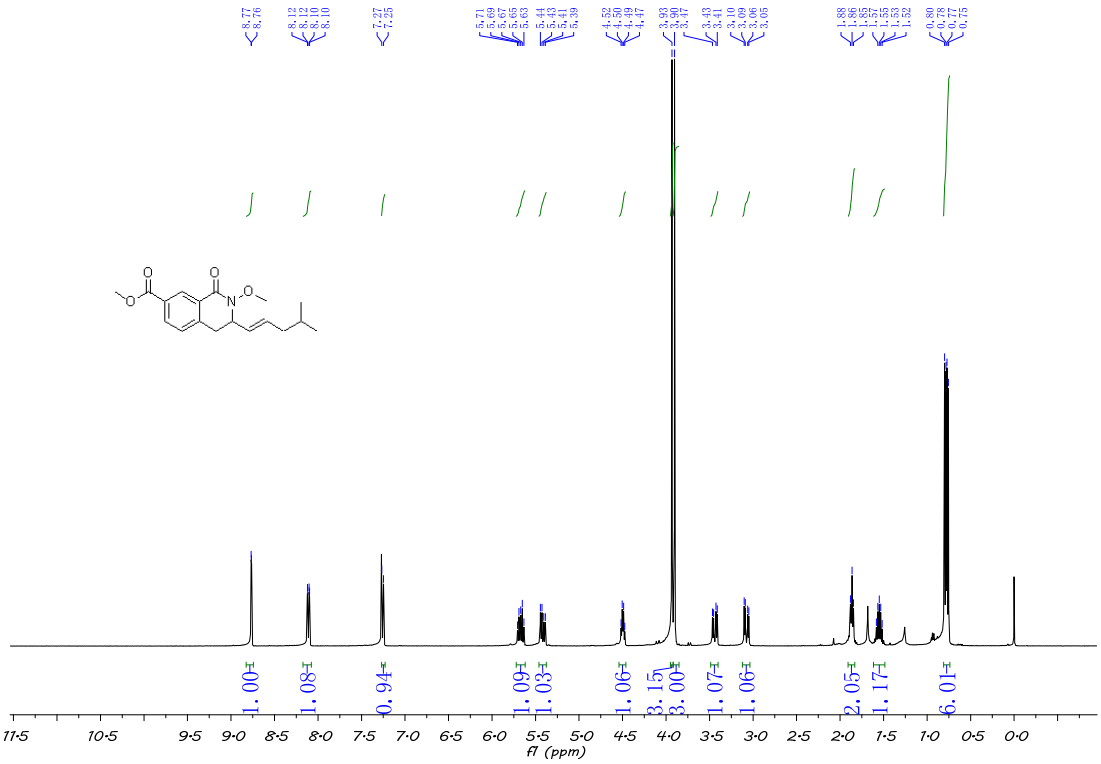
63.00
61.16
55.28
52.25
35.75
f1 (ppm)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8.10
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5.69
5.67
5.65
5.63
5.44
5.43
5.41
5.39
4.52
4.50
4.49
4.47
3.93
3.90
3.47
3.43
3.41
3.10
3.09
3.06
3.05
1.88
1.86
1.85
1.57
1.55
1.53
1.52
0.80
0.78
0.77
0.75
1.00
1.08
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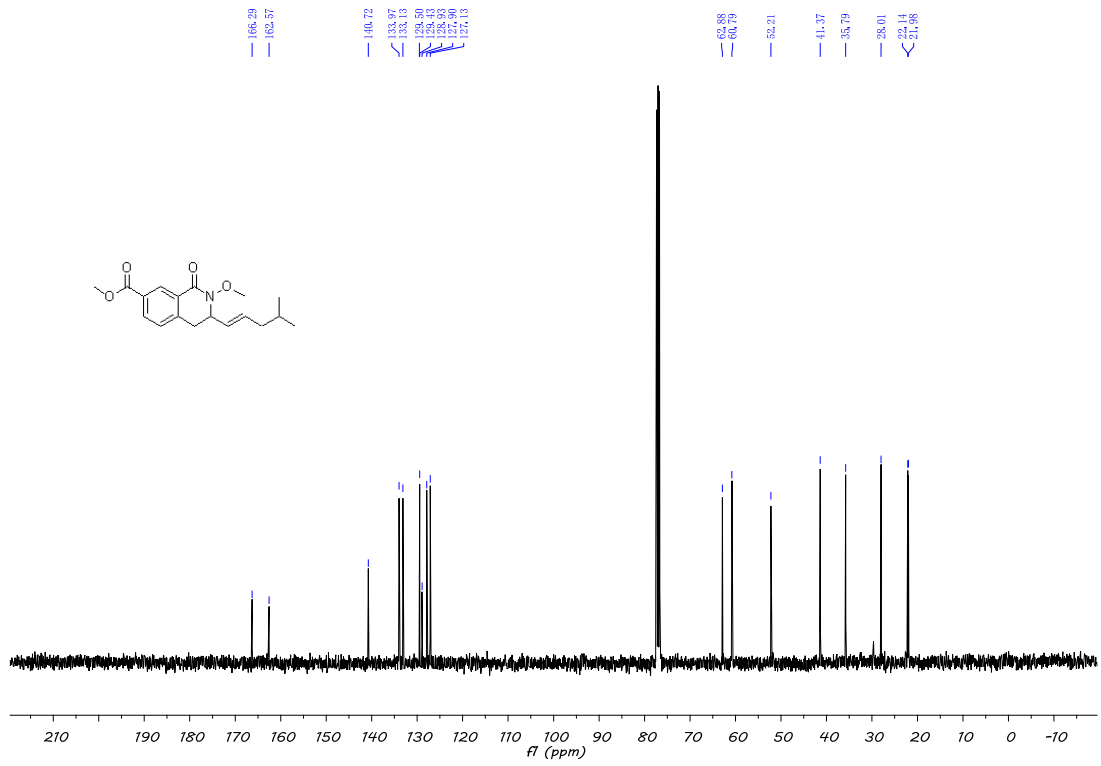
1.09
1.03
1.06
3.15
3.00
1.07
1.06
2.05
1.17
6.01
f1 (ppm)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127.80
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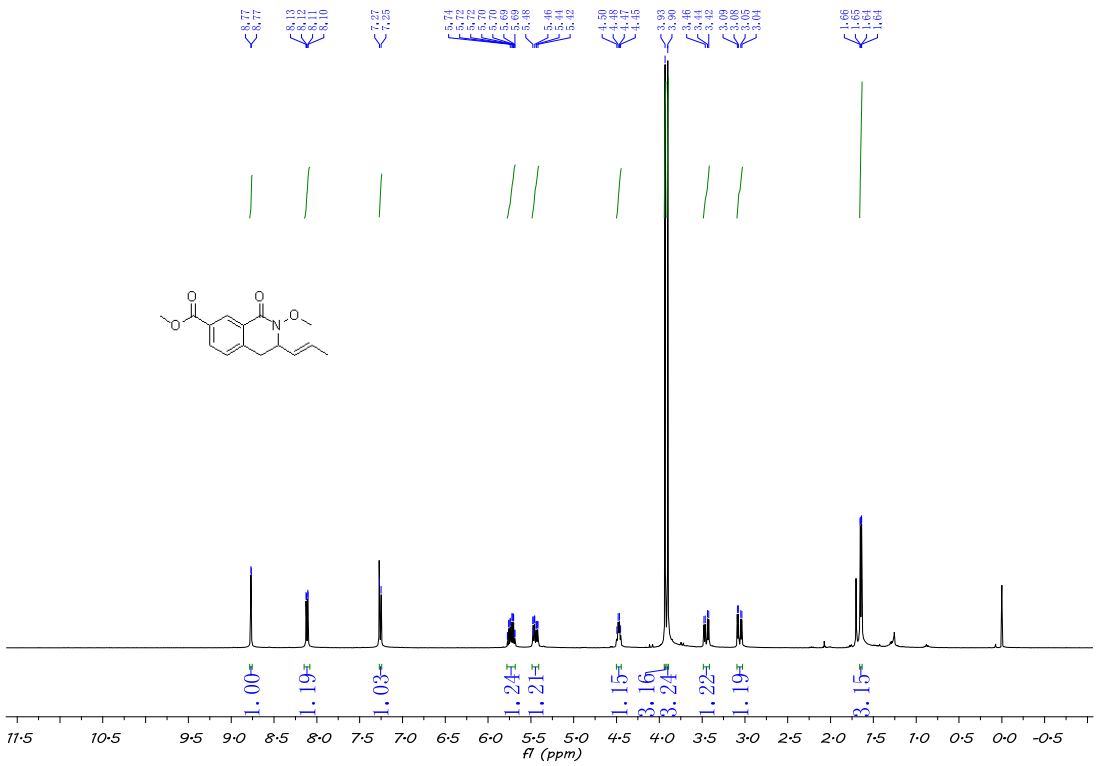
62.79
52.21
41.37
35.79
28.01
22.14
21.98
f1 (ppm)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5.69
5.68
5.46
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5.42
4.50
4.48
4.47
4.45
3.93
3.90
3.46
3.44
3.42
3.09
3.08
3.05
3.04
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1.65
1.64
1.64
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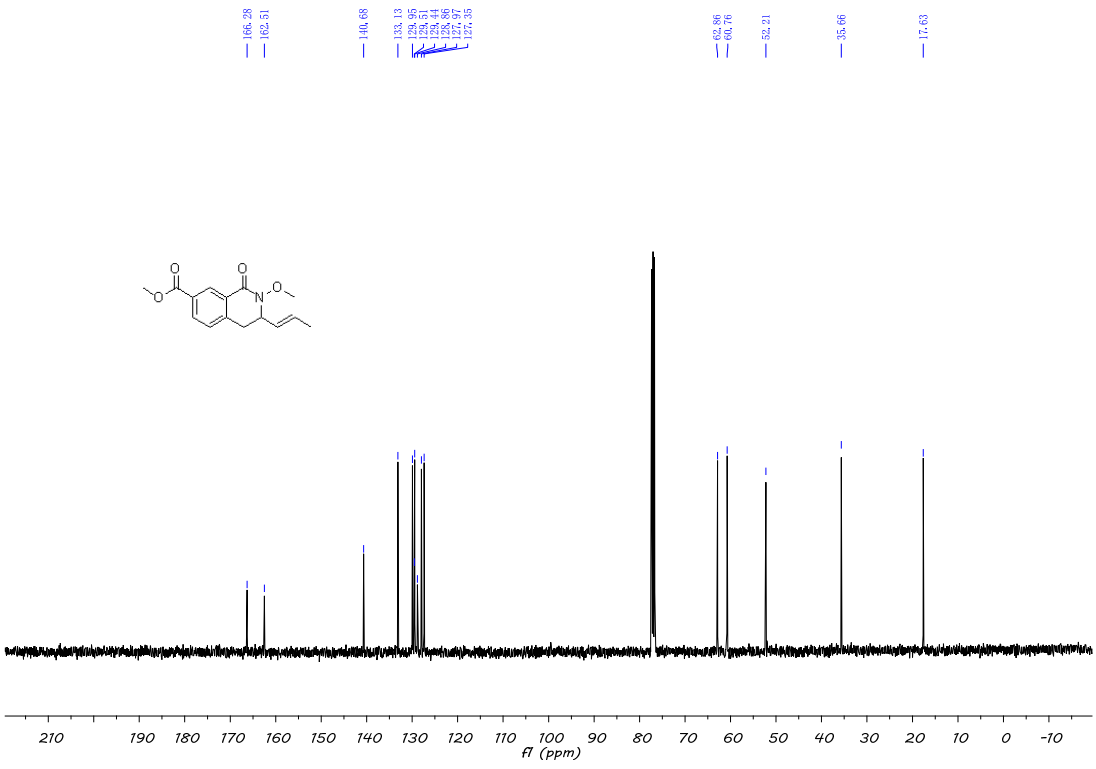
1.24
1.21
1.15
3.16
3.24
1.22
1.19
3.15
f1 (ppm)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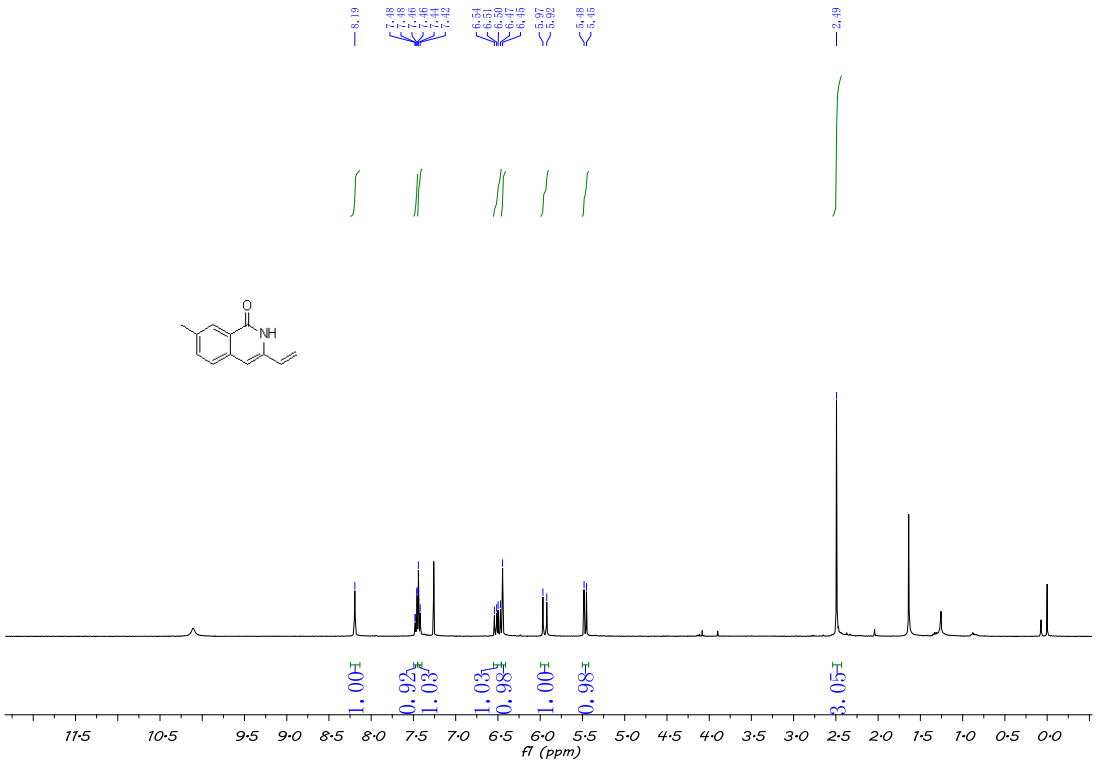
17.63
f1 (ppm)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6.50
6.47
6.45
5.97
5.92
5.48
5.45
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NH
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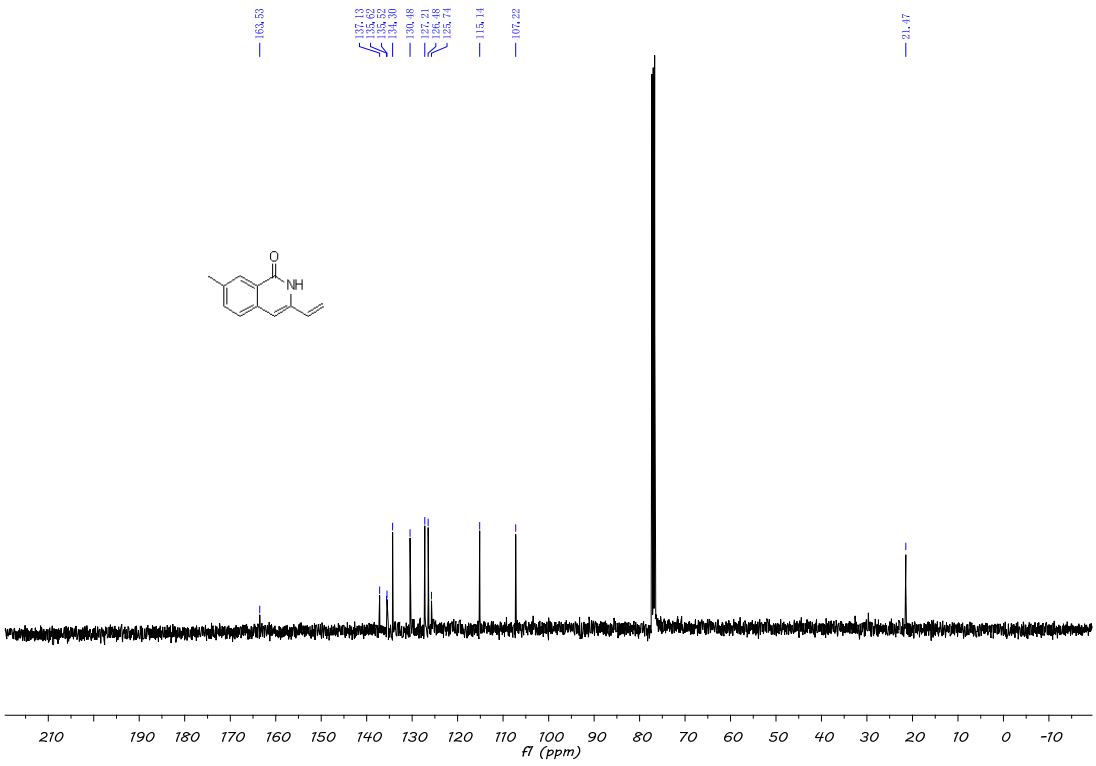
0.92
1.03
1.03
0.98
1.00
0.98
3.05
f1 (ppm)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107.22
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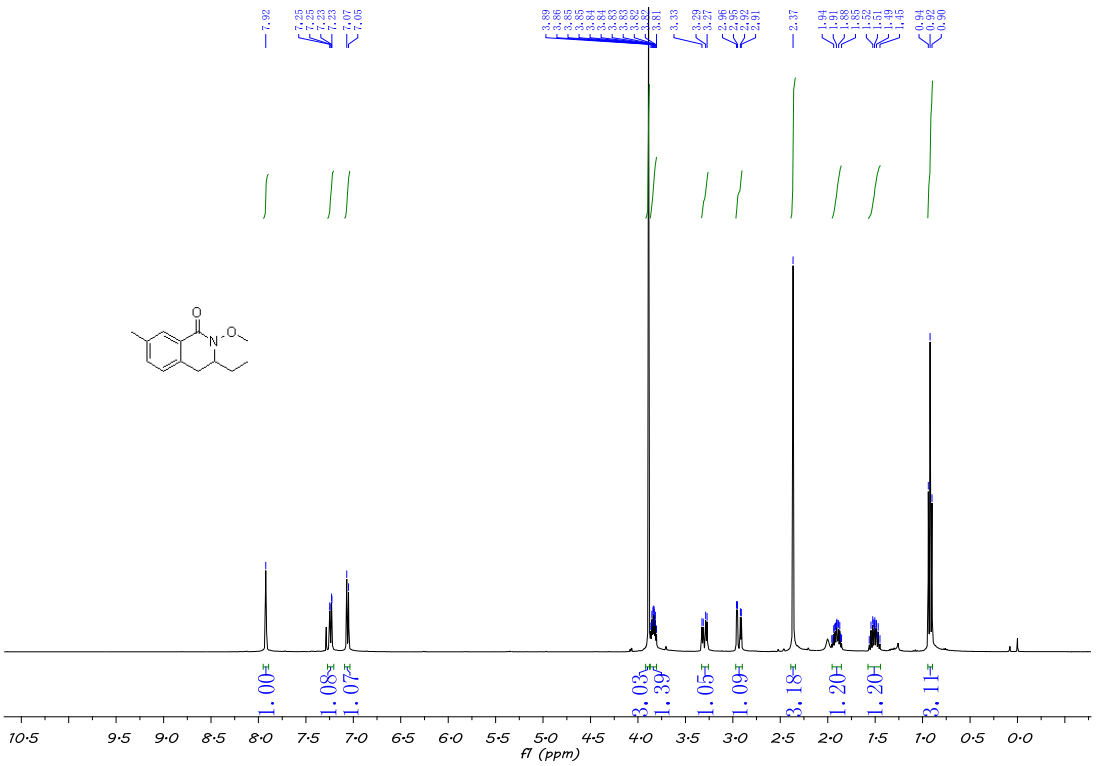
O
NH
f1 (ppm)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3.89
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3.85
3.85
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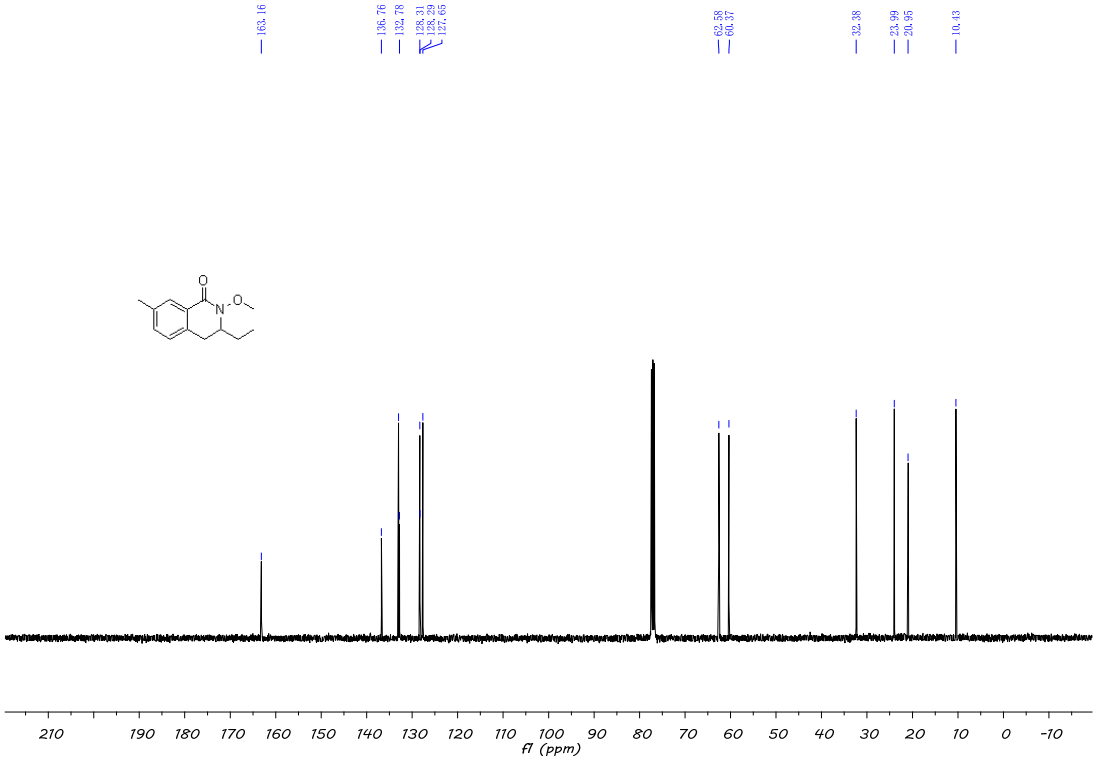
3.84
3.83
3.83
3.82
3.82
3.81
3.33
3.29
3.27
2.96
2.95
2.92
2.91
2.37
1.94
1.91
1.88
1.85
1.52
1.51
1.49
1.46
0.94
0.92
0.90
1.00
1.08
1.07
3.03
1.39
1.05
1.09
3.18
1.20
1.20
3.11
f1 (ppm)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127.65
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60.37
32.38
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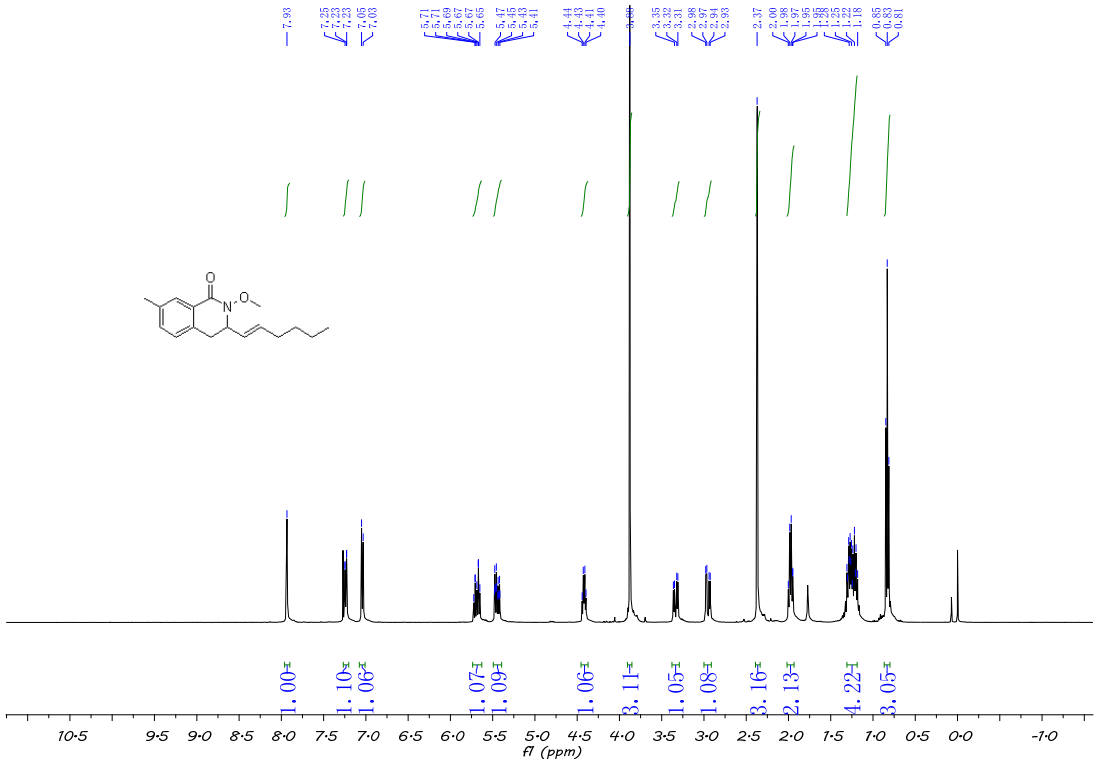
20.95
10.43
f1 (ppm)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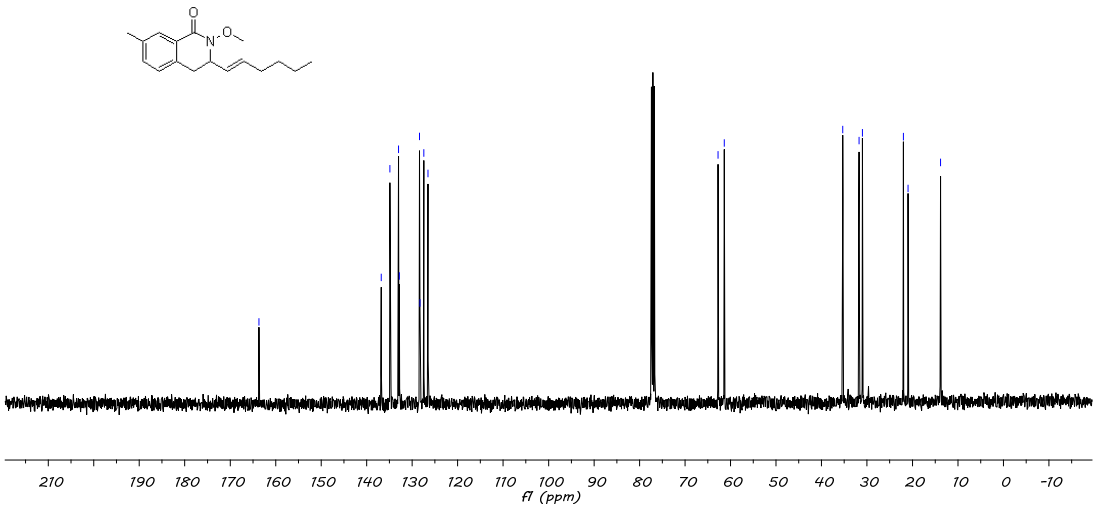
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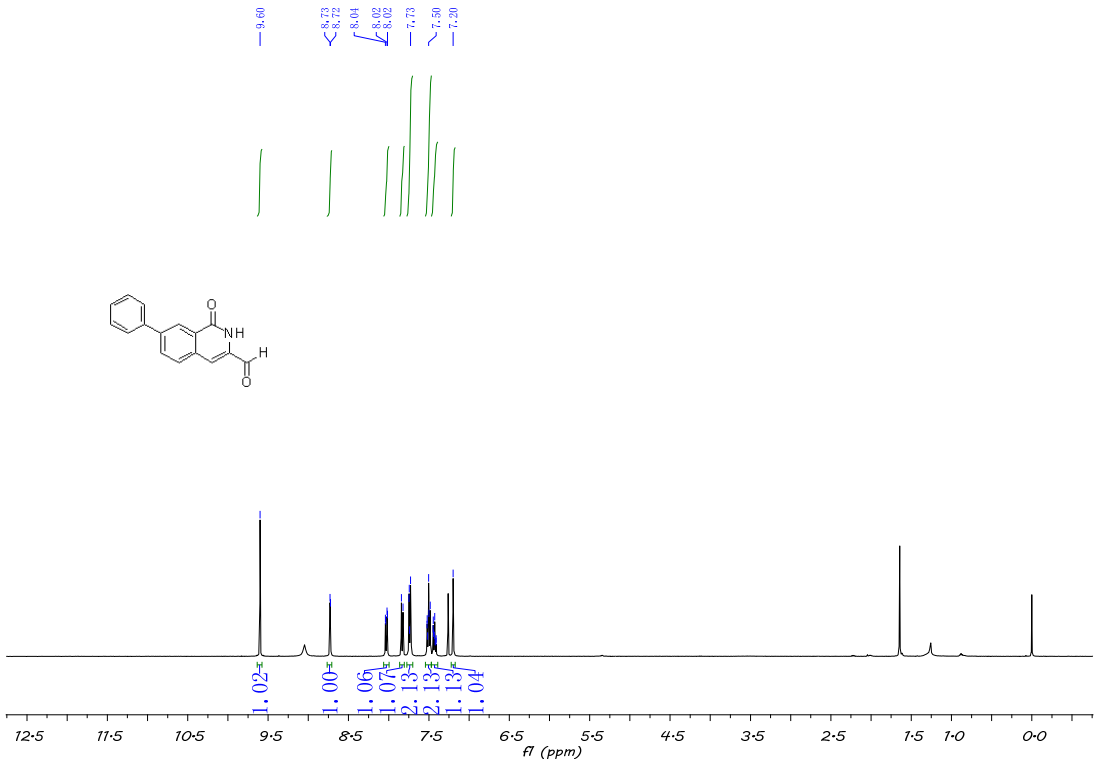
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8.02
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7.50
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1.02
1.00
1.06
1.07
2.13
2.13
1.13
1.04
12.5
11.5
10.5
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8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
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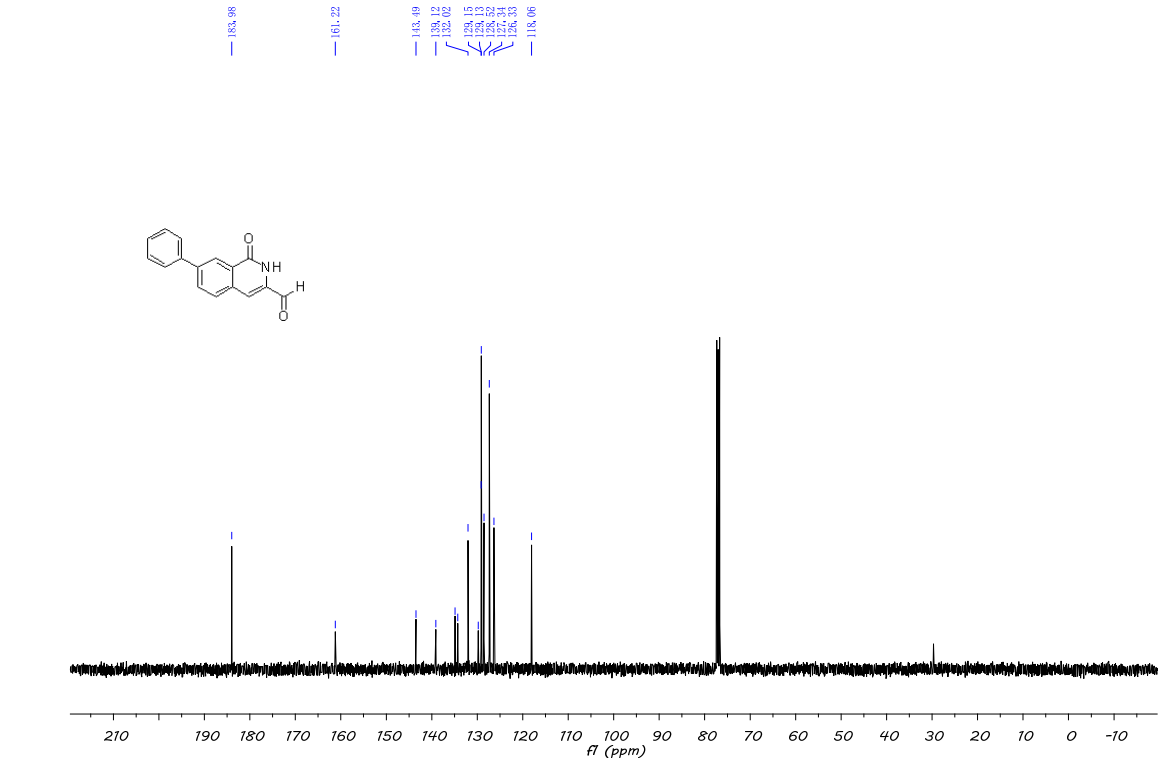
0.0
f1 (ppm)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128.32
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126.33
118.06
210
190
180
170
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140
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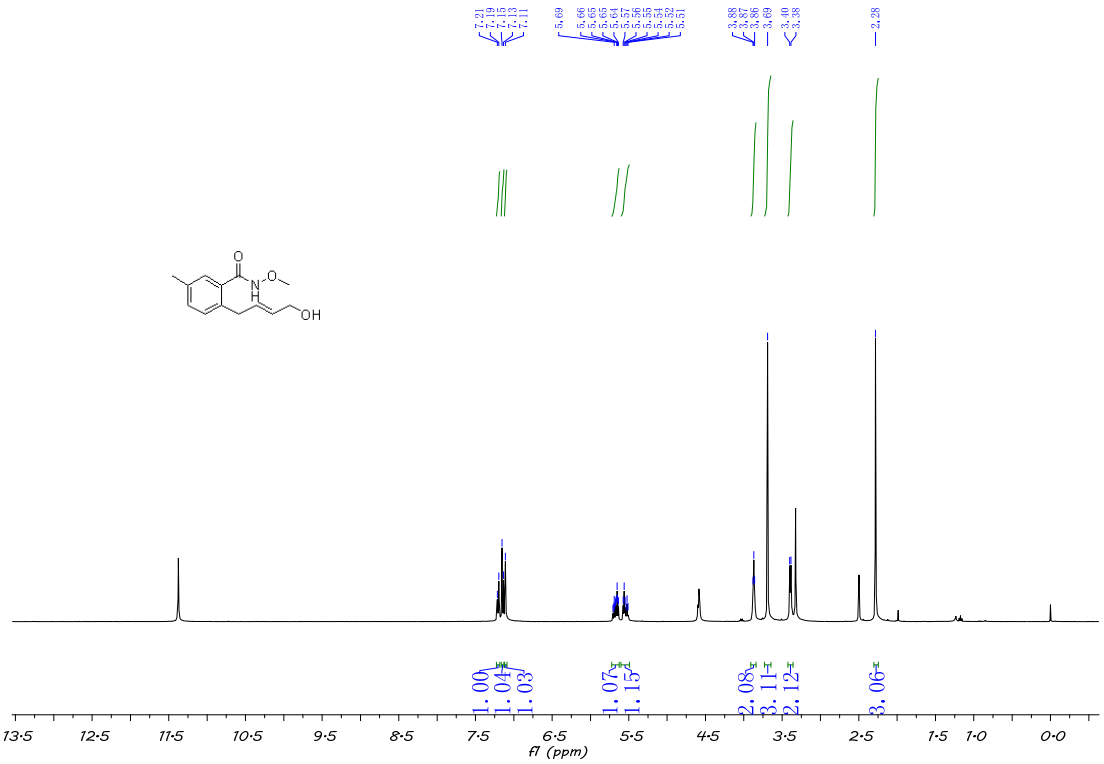
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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5.65
5.64
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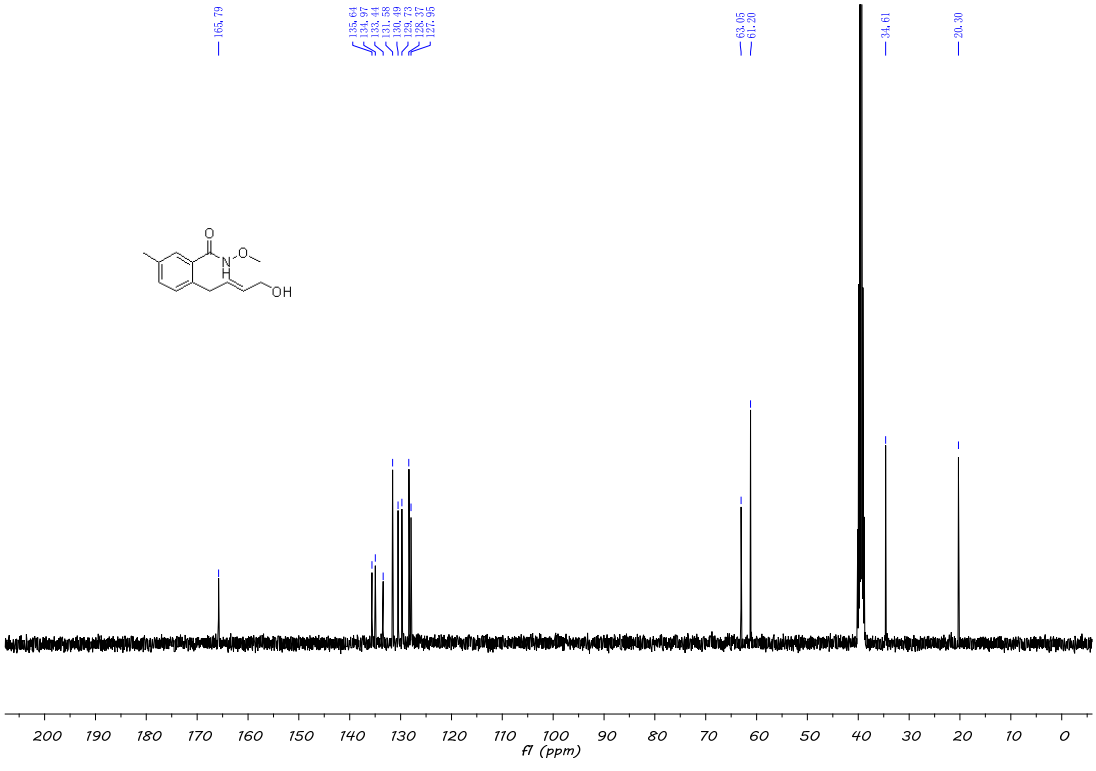
5.56
5.55
5.54
5.52
5.51
3.88
3.87
3.86
3.69
3.40
3.38
2.28
O
N
O
OH
1.00
1.04
1.03
1.07
1.15
2.08
3.11
2.12
3.06
13·5
12·5
11·5
10·5
9·5
8·5
7·5
6·5
5·5
4·5
3·5
2·5
1·5
1·0
0·0
f1 (ppm)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135.64
133.97
133.44
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130.49
129.73
128.57
125.96
63.05
61.20
34.61
20.30
O
N
O
OH
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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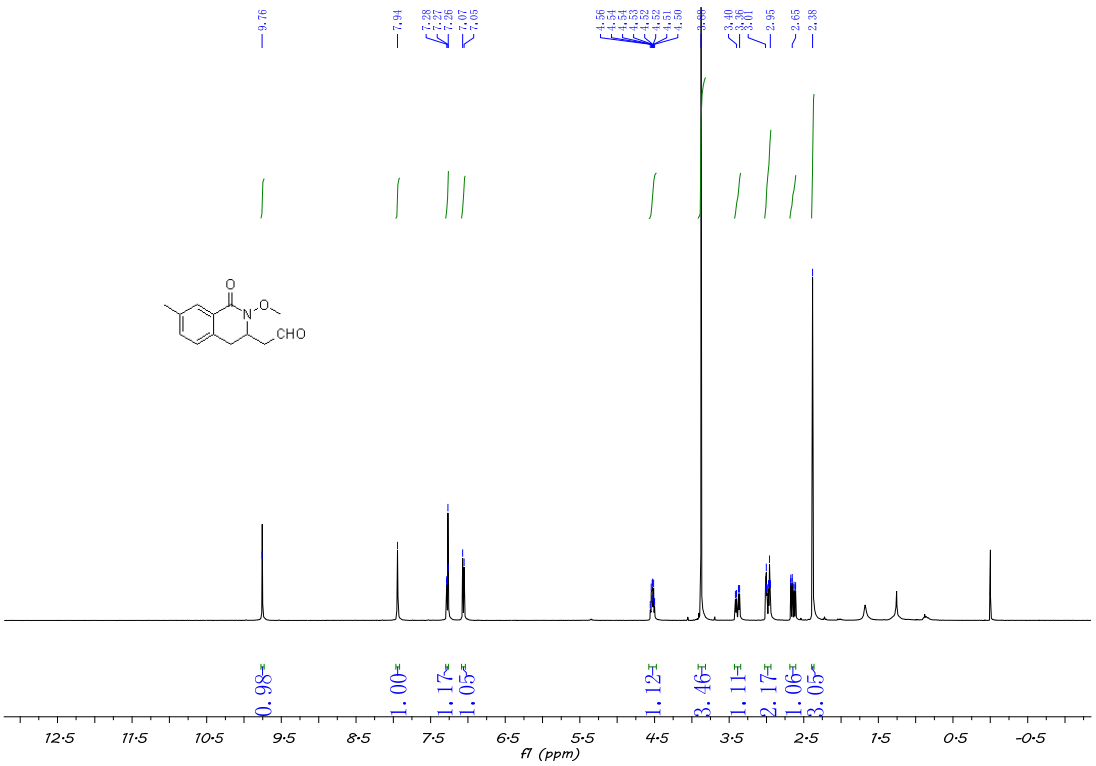
50
40
30
20
10
0
f1 (ppm)


9.76
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4.54
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4.52
4.52
4.51
4.50
3.40
3.36
3.01
2.95
2.65
2.38
O
N
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CHO
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1.17
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1.12
3.46
1.11
2.17
1.06
3.05
12.5
11.5
10.5
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3.5
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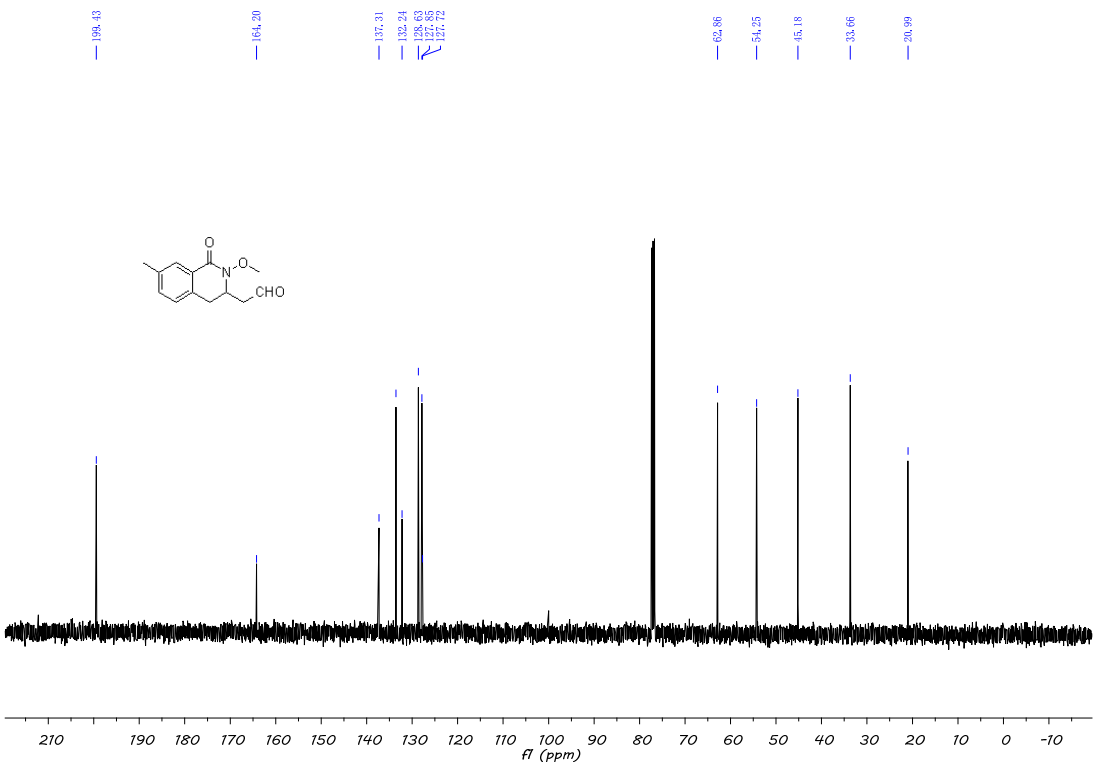
1.5
0.5
-0.5
f1 (ppm)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20.99
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210
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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