Supporting information

CuX_2-Mediated Oxybromination/Aminochlorination of Unsaturated Amides: Synthesis of Iminolactones and Lactams

Zhi-Qiang Zhang,[†] and Feng Liu*[,†]

[†]Jiangsu Key Laboratory of Translational Research and Therapy for Neuro-Psycho-Diseases and Department of Medicinal Chemistry, College of Pharmaceutical Sciences, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu 215123, People's Republic of China

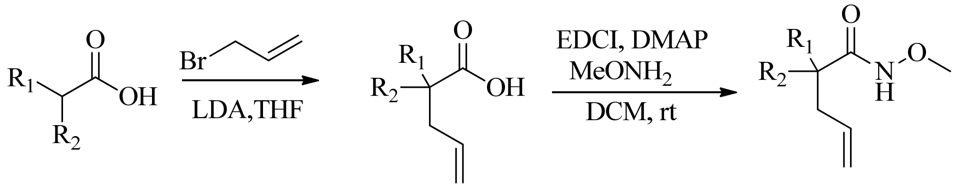
E-mail: fliu2@suda.edu.cn

Table of Contents

1. General experimental details

Infrared (FT-IR) spectra were recorded on a Varian 1000 FT-IR, ν_{max} in cm^{-1}. ^{1}H-NMR spectra were recorded on a VARIAN NMR ststem (300 MHz) or BRUKER AVANCE Ⅲ HD (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26, DMSO-d_6: δ 2.50). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C-NMR spectra were recorded on a VARIAN NMR ststem (300 MHz), Agelent DD2 NMR ststem (600 MHz) or BRUKER AVANCE Ⅲ HD (400 MHz) pectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16, DMSO-d_6 δ 39.52). Mass spectra were measured with an Agelent Technologies 6120 Quadrupole LC/MS. High resolution mass spectrometry (HRMS) were measured with a GCT Premier^{TM}. Melting points were measured using SGW, X-4B and values are uncorrected. Microwave reaction was run with the CEM DISCOVER-SP W/ACTIVENT.

2.General procedure for the synthesis of γ, δ-unsaturated amides 1a-1h, 1s, 1t, 10



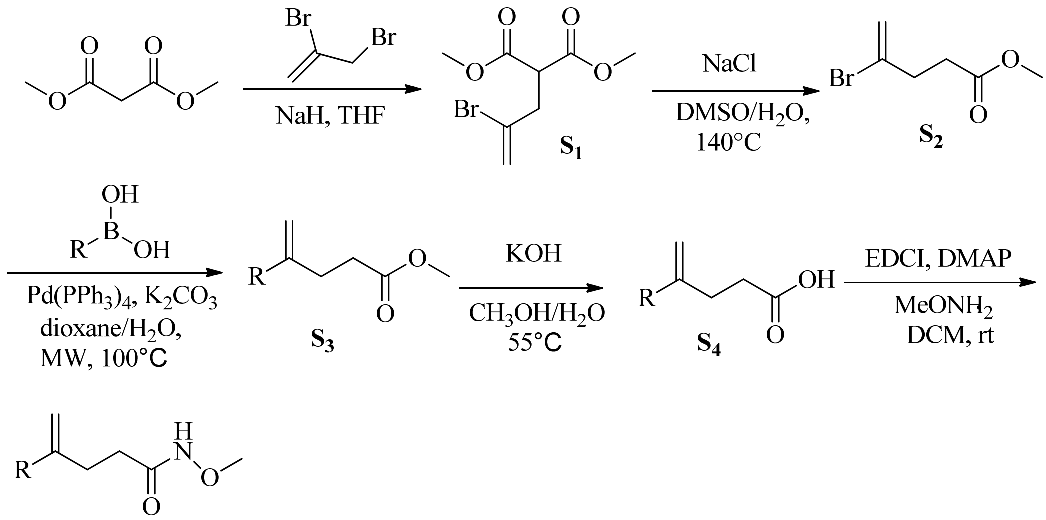
Step 1: Synthesis of unsaturated acids [1] A solution of diphenylacetic acid (10.0 mmol, 1.0 equiv) in anhydrous THF (8 mL) was added to freshly prepared LDA (22 mmol, 2.2 equiv) at 0 ℃. The reaction mixture was then heated at 45 ℃ for 30 min. The red reaction mixture was cooled to room temperature, and then allylbromide (1.75 mL, 20.0 mmol, 2.0 equiv) was added dropwise. The color dissipated and the reaction mixture was heated at 45 ℃ for 4 h. Then the reaction mixture was cooled to room temperature and 50 mL of Et_2O and 75 mL of H_2O were added. The layers were separated and the aqueous layer was acidified with 2 M HCl and extracted with Et_2O (3 x 50 mL). The organic layer was dried with Na_2SO_4, filtered, and the solvent was removed. Purification of the residue by flash chromatography on silica gel (40% EtOAc/1% AcOH/Hexanes) afforded unsaturated acids as a white solid.

Step 2: Synthesis of γ, δ-unsaturated amides [2] To a solution of unsaturated acids (5.0 mmol, 1.0 equiv) in CH_2Cl_2 (8 mL) was added Et_3N (1.1 mL , 8.0 mmol, 1.6 equiv) and the reaction mixture stirred for 5 min. EDCI (1.72 g, 9.0 mmol, 1.8 equiv) and $MeONH_2$•HCl (668 mg, 8.0 mmol, 1.6 equiv) were then added in one portion . After 10 h , aqueous HCl (1 M, 20 mL) was added and the aqueous phase extracted with EtOAc (4 x 15 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue purified by flash chromatography on silica gel (EtOAc) to provide γ, δ-unsaturated amides

[1] Barczak, N. T.; Jarvo, E. R. *Chem.-Eur. J.* **2011**, *17*, 12912-12916.

[2] Wardrop, D. J.; Bowen, E. G.; Forslund, R. E.; Sussman, A. D.; Weerasekera, S. L. *J. Am. Chem.Soc.* **2010** , *132*, 1188-1189.

3. General procedure for the synthesis of γ, δ-unsaturated amides 1i-1k



Step 1: Synthesis of S_1 [3] To a suspension of sodium hydride (500 mg, 12.5 mmol) in anhydrous THF was added a solution of dimethyl malonate (1.17 mL, 10 mmol) in anhydrous THF (5 mL) at -10 ℃ under argon. The reaction mixture was heated at 50 ℃ for 1 hour and then cooled to -10 ℃ again, followed by adding a solution of 2,3-dibromopropene (1.22 mL, 10 mmol) in anhydrous THF (5 mL). The reaction mixture was stirred for 1 h, and quenched with aq. HCl (4 M, 8.8 mL) and extracted with ether (3 x 15 mL). The organic fractions were collected, dried over $MgSO_4$, and the solvent was removed in vacuo. The crude oil was purified via silica gel chromatography (hexane/EA 50:1) to obtain the titled product as a colorless oil (1.63 g, 65% yield).

Step 2: Synthesis of S_2 [4] A mixture of dimethyl-2-(2-bromo-prop-2-enyl)-malonate (1.49 g, 6.0 mmol, 1 eq.), sodium chloride (0.772 g, 13.2 mmol, 2.2 eq.), water (0.65 mL, 36 mmol, 6 eq.) in DMSO (10 mL) was stirred at 140 ℃ for 6 h. The resulting purple to black solution was diluted with water (20 mL) and extracted with ether (3 x 20 mL). The combined organic phases were washed with brine (20 mL) and the solvent was removed under reduced pressure. The black residue was purified by column chromatography (hexane/EA 50:1) to yield S_2 (485 mg, 2.52 mmol) as colorless liquid.

Step 3: Synthesis of S_3 [5] A mixture of methyl 4-bromopent-4-enoate (193 mg, 1.0 mmol, 1.0 eq.), aryl boronic acid (1.2 mmol, 1.2 eq), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol, 0.05 eq), and Na_2CO_3 (233 mg, 2.2 mmol, 2.2 eq) in dioxane/H_2O (7:1, v/v) (8 mL) was stirred at 100 ℃ under MW for 1 h. The solvent was removed under reduced pressure and the residue was diluted with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (hexane/EtOAc 50:1) to give the corresponding ester **S_3**

Step 4: S_4 was synthesized by following the procedure for **S_6.**

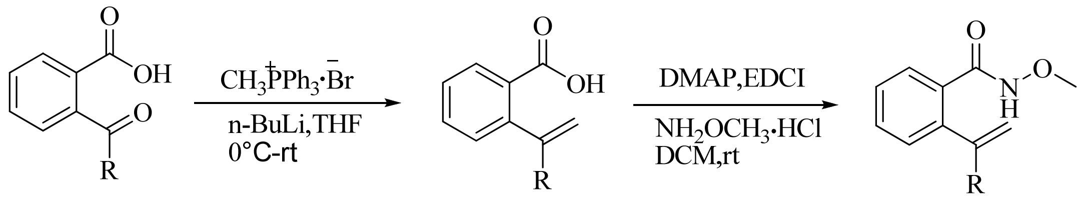
Step 5: The procedure used for preparation of the amides from acids was followed for synthesis of **1a**.

[3] Organ, M. G.; Cooper, J. T.; Rogers, L. R.; Soleymanzadeh, F.; Paul, T. *J. Org. Chem.* **2000**, *65*, 7959-7970.

[4] Fischer, D. F.; Sarpong, R. *J. Am. Chem.Soc.* 2010, *132*, 5926-5927

[5] Zhou, L.; Chen, J.; Tan, C. K.; Yeung,Y. *J. Am. Chem.Soc.* **2011,** *133*, 9164-9167.

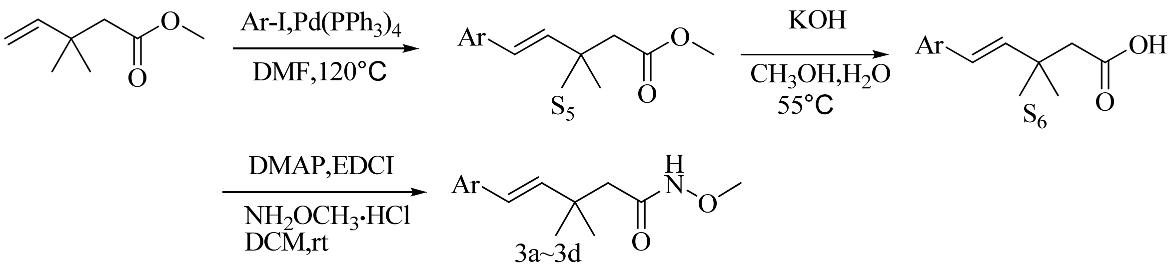
4. General procedure for the synthesis of unsaturated amides 1l-1q



Step 1: Synthesis of unsaturated acids [6] To a suspension of methyl triphenylphosphonium bromide (2.15g , 6mmol, 1.2 equiv.) in THF (10 mL) was added n-BuLi (4 mL, 2.5 M in hexanes, 2 equiv.) at 0 ℃ and the resulting yellow suspension was stirred for 45 min. To this suspension, a solution of ketone (5 mmol, 1.0 equiv.) in THF (5 mL) was added dropwise and the resulting mixture was warmed gradually to rt and stirred at rt. for 16 h . The reaction mixture was concentrated under reduced pressure and filtered. The filtrate was concentrated under reduced pressure to yield a yellow oil. Purification by column chromatography over silica gel using petroleum ether as eluent afforded unsaturated acids as a white solid.

Step 2: The procedure used for preparation of the amides from acids was followed for synthesis of **1a**.

5. General procedure for the synthesis of γ, δ-unsaturated amides 3a-3d



Step 1: Synthesis of S_5 [7] General Procedure for the Heck Reaction: A mixture of aryl halide (2 mmol), alkene (4 mmol), Et_3N (404 mg, 4 mmol), and $Pd(PPh_3)_4$ (6 mg, 0.2 mol %) in 5 mL of DMF was stirred at 120 ℃ for the appropriate time. The reaction was monitored by TLC and after completion of the reaction, the mixture was extracted with ethyl acetate three times. The combined organic extracts were dried using anhydrous Na_2SO_4 and evaporated under reduced pressure, and the mixture was then purified by column chromatography over silica gel to afford product with high purity.

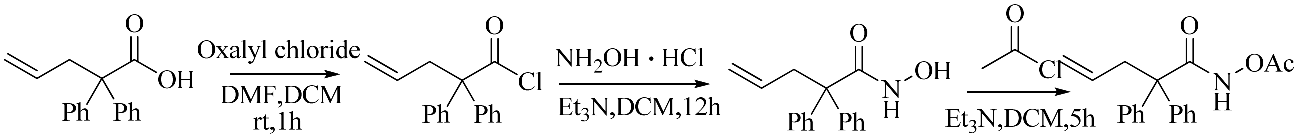
Step 2: Synthesis of S_6 To a solution of ester (1.7 mmol) in water (8.5 mL) and methanol (3 mL) was added 1 N NaOH (3.4 mL, 2 eq.). The reaction mixture was stirred at ambient temperature for 6 h. To the reaction mixture was added 50 mL of brine and the pH was adjusted to 3 with 1N HCl to provide a white precipitate which was filtered and dried to provide the title compound as a white solid.

Step 3: The procedure used for preparation of the amides from acids was followed for synthesis of **1a**.

[6] Xu, Y.; Lu, J.; Loh, T. *J. Am. Chem.Soc.* **2009**, *131*, 1372-1373.

[7] Zhang, Z.; Wang, Z. *J. Org. Chem.* **2006**, 71, 7485-7487.

6. General procedure for the synthesis of 1r

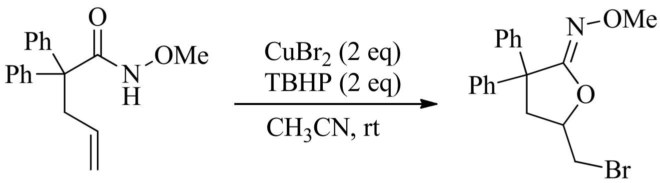


Step 1: Synthesis of acyl chloride To a solution of unsaturated acids (500 mg, 2 mmol) in dichloromethane (10 mL) was added oxalyl chloride (1.02 g, 8 mmol), followed by adding 2 drops of DMF. The mixture was stirred at room temperature for 1 h, then excess oxalyl chloride and dichloromethane were removed *in vacuo* to provide crude acyl chloride.

Step 2: Synthesis of hydroxamic acid To a solution of the acyl chloride (499 mg, 2 mmol) in DCM (10 mL) hydroxylamine hydrochloride (278 mg, 4 mmol) and sodium bicarbonate (326 mg, 4 mmol) were added. After stirring for 12 h at room temperature, the reaction mixture was quenched by addition of saturated ammonium chloride solution (10 mL). The layers were separated. The water layer was extracted with ethyl acetate (4 x 10 mL). The solvent of the combined organic layers, was removed *in vacuo*. Precipitation of the crude product out of ethyl acetate by adding petroleum ether yielded the hydroxamate (309 mg, 58% yield) as a white solid.

Step 3: Synthesis of 1r To a solution of hydroxamic acid (309 mg, 1.16 mmol) in dry DCM (10 mL) was added acetyl chloride (89 mg, 1.16 mmol) and the mixture was stirred for 5 min at 0 ℃. Et_3N (233 mg, 2.36 mmol) was added and the mixture was stirred for 5 h. Then the solvent was removed under reduced pressure, The residue was purified by column chromatography (hexane/EA 10:1) to furnish **1r** (268 mg, 75% yield) as colorless oil.

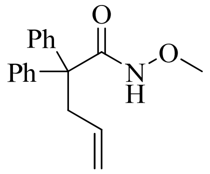
7. Typical procedure for CuX_2-mediated halocyclization of unsaturated amides.



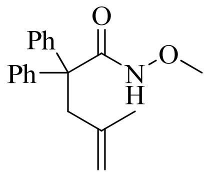
1a **2a**

To a mixture of **1a** (28 mg, 0.10 mmol) and $CuBr_2$ (44.6 mg, 0.20 mmol) in acetonitrile (1 mL) was added TBHP (18.0 mg, 0.20 mmol) at rt. The reaction mixture was stirred for 0.5 h at rt. After the removal of solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford **2a** (34 mg, 95% yield) as white solid.

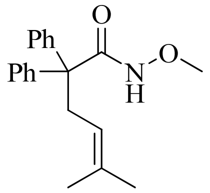
8. Characterization of substrates and products



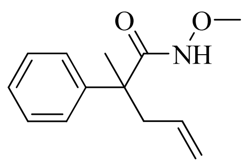
1a: white solid; m.p. 111-113 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.40 – 7.22 (m, 10H), 5.88 – 5.66 (m, 1H), 5.15 – 4.91 (m, 2H), 3.72 (s, 3H), 3.23 (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 142.2, 134.7, 129.0, 128.6, 127.4, 118.5, 64.4, 43.5; HRMS [CI] calc. for $C_{18}H_{20}NO_2$ $[M+H]^+$ 282.1494, found 282.1490; IR (neat, cm^{-1}) 3274, 3059, 1650, 1489.



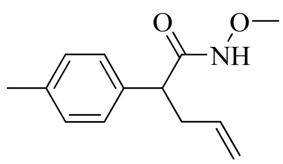
1b: white solid; m.p. 119-121 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.44 – 7.18 (m, 10H), 4.77 (s, 1H), 4.54 (s, 1H), 3.67 (s, 3H), 3.21 (s, 2H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 142.4, 142.3, 129.1, 128.3, 127.2, 115.9, 64.0, 59.7, 46.1, 24.9 ; HRMS[CI] calc. for $C_{19}H_{22}NO_2$ $[M+H]^+$ 296.1651, found 296.1638; IR (neat, cm^{-1}) 3306, 3002, 1648, 1491.



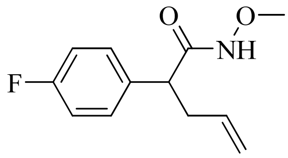
1c: white solid; m.p. 129-131 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.42 – 7.06 (m, 10H), 5.12 (t, J = 6.1 Hz, 1H), 3.68 (s, 3H), 3.13 (d, J = 6.7 Hz, 2H), 1.59 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 142.3, 134.8, 128.9, 128.2, 127.0, 119.9, 63.9, 59.4, 37.24, 25.9, 17.8; HRMS [CI] calc. for $C_{20}H_{24}NO_2$ $[M+H]^+$ 310.1807, found 310.1805; IR (neat, cm^{-1}) 3245, 3057, 1656, 1599 1493, 1443.



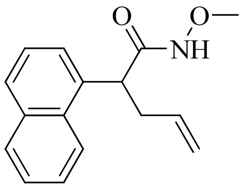
1d: white solid; m.p. 77-78 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.49 – 7.13 (m, 5H), 5.67 – 5.34 (m, 1H), 5.17 – 4.93 (m, 2H), 3.65 (s, 3H), 2.85 – 2.68 (m, 2H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 142.4, 133.6, 128.9, 127.4, 126.8, 118.8, 64.2, 48.8, 43.5, 23.5; HRMS [CI] calc. for $C_{13}H_{18}NO_2$ $[M+H]^+$ 220.1338, found 220.1335; IR (neat, cm^{-1}) 3228, 2972, 1651,1599.



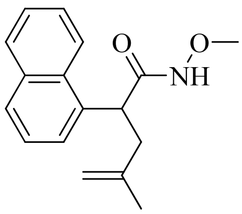
1e: white solid; m.p. 64-66 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.21 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 5.80 – 5.60 (m, 1H), 5.15 – 4.93 (m, 2H), 3.65 (s, 3H), 3.35 (m, 1H), 2.95 – 2.77 (m, 2H), 2.60 – 2.41 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 137.1, 135.7, 135.5, 129.5, 127.9, 117.1, 64.3, 49.3, 37.3, 21.1; HRMS [CI] calc. for $C_{13}H_{18}NO_2$ $[M+H]^+$ 220.1338, found 220.1341; IR (neat, cm^{-1}) 3136, 3068, 1648, 1525.



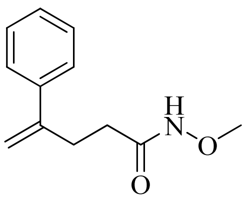
1f: white solid; m.p. 131-133 ℃; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.32 (s, 1H), 7.35 (dd, J = 8.1, 5.8 Hz, 2H), 7.12 (t, J = 8.8 Hz, 2H), 5.78 – 5.55 (m, 1H), 5.05 (d, J = 17.2 Hz, 1H), 4.97 (d, J = 10.2 Hz, 1H), 3.53 (s, 3H), 3.33 (t, 1H), 2.75 – 2.58 (m, 1H), 2.45 – 2.28 (m, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.8, 161.3 (d, J = 242.8 Hz), 135.7 (d, J = 2.6 Hz), 135.5, 129.5 (d, J = 8.0 Hz), 117.0, 115.1 (d, J = 21.2 Hz). 63.2, 47.1, 36.8; HRMS [CI] calc. For $C_{12}H_{15}FNO_2$ $[M+H]^+$ 224.1087 found 224.1086; IR (neat, cm^{-1}) 3134, 3075, 1670, 1533.



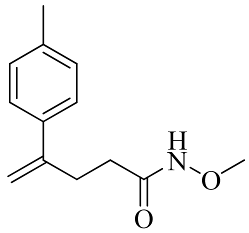
1g: white solid; m.p. 133-135 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.50 (s, 1H), 7.03 – 6.94 (m, 3H), 6.92 (s, 1H), 6.65 – 6.54 (m, 3H), 4.91 – 4.72 (m, 1H), 4.27 – 4.03 (m, 2H), 2.65 (s, 3H), 2.61 (dd, J = 8.7, 6.8 Hz, 1H), 1.97 – 1.86 (m, 1H), 1.69 – 1.57 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 137.2, 135.7, 132.9, 132.1, 127.8, 127.7, 127.5, 126.2, 126.1, 126.1, 125.8, 116.9, 63.2, 48.1, 36.6; HRMS [CI] calc. for $C_{16}H_{18}NO_2$ $[M+H]^+$ 256.1338, found 256.1338; IR (neat, cm^{-1}) 3132, 3070, 1671, 1648,1598.



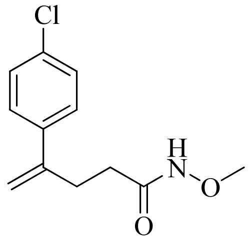
1h: white solid; m.p. 105-107 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.96 – 7.61 (m, 4H), 7.58 – 7.43 (m, 3H), 4.76 (s, 1H), 4.74 (s, 1H), 3.73 (s, 3H), 3.50 (m, 1H), 3.04 (dd, J = 14.2, 7.8 Hz, 1H), 2.60 (dd, J = 13.4, 6.7 Hz, 1H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 142.5, 136.7, 133.5, 132.7, 128.4, 127.9, 127.7, 126.9, 126.1, 126.0, 125.9, 112.7, 64.1, 48.0, 40.8, 22.7; HRMS [CI] calc. for $[M+H]^+$ $C_{17}H_{20}NO_2$ 270.1494, found 270.1493, IR (neat, cm^{-1}) 3148, 3073, 1644, 1599.



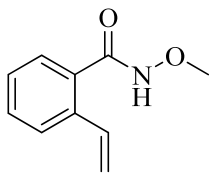
1i: yellow solid; m.p. 52-54 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.38 (d, J = 6.9 Hz, 2H), 7.35 – 7.20 (m, 3H), 5.29 (s, 1H), 5.09 (s, 1H), 3.67 (s, 3H), 2.83 (t, J = 7.7 Hz, 2H), 2.24 (t, J = 7.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 146.7, 140.3, 128.4, 127.6, 126.1, 113.1, 64.1, 31.9, 30.7; HRMS [CI] calc. for $C_{12}H_{16}NO_2$ $[M+H]^+$ 206.1181, found 206.1176; IR (neat, cm^{-1}) 3147, 2974, 1661, 1641, 1536.



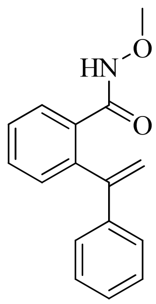
1j: white solid; m.p. 70-72 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 5.28 (d, *J* = 3.3 Hz, 1H), 5.05 (s, 1H), 3.69 (s, 3H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.33 (s, 3H), 2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 146.6, 137.7, 137.5, 129.3, 126.1, 112.7, 64.4, 32.2, 31.0, 21.3; HRMS [CI] calc. for $C_{13}H_{18}NO_2$ $[M+H]^+$ 220.1338, found 220.1340 ; IR (neat, cm^{-1}) 3183, 3082, 1645,1560.



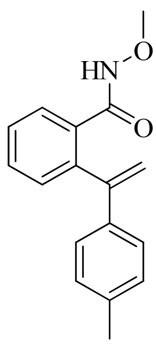
1k: white solid; m.p. 78-80 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.35 – 7.25 (m, 4H),, 5.28 (s, 1H), 5.09 (s, 1H), 3.68 (s, 3H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.32 – 2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 145.6, 138.8, 133.5, 128.6, 127.5, 113.8, 64.2, 31.8, 30.6; HRMS [CI] calc. for $C_{12}H_{15}ClNO_2$ $[M+H]^+$ 240.0791, found 240.0799; IR (neat, cm^{-1}) 3213, 3094, 1652, 1626.



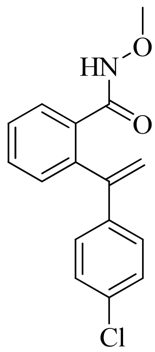
1l: white solid; m.p. 75-77 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.1 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.79 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.57 (d, *J* = 17.4 Hz, 1H), 5.17 (d, *J* = 11.0 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 136.2, 133.6, 131.5, 130.4, 127.6, 127.3, 125.7, 116.5, 63.9; HRMS [CI] calc. for $C_{10}H_{12}NO_2$ $[M+H]^+$ 178.0868, found 178.0860; IR (neat, cm^{-1}) 3128, 3065, 1632, 1593, 1567.



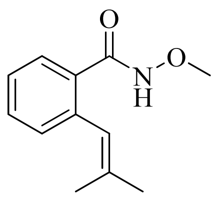
1m:white solid; m.p. 103-105 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.43 – 7.37 (m, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.25 (m, 5H), 5.80 (s, 1H), 5.38 (s, 1H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, overlapping peaks) δ 166.6, 148.6, 140.1, 139.8, 132.6, 131.0, 129.0, 128.6, 128.3, 128.2, 127.0, 116.3, 63.80 ; HRMS [CI] calc. for $C_{16}H_{16}NO_2$ $[M+H]^+$ 254.1181, found 254.1174; IR (neat, cm^{-1}) 3134, 3067, 1649, 1592.



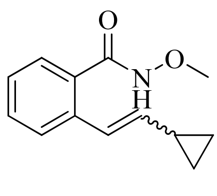
1n: white solid; m.p. 106-108 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.3 Hz, 1H), 7.42 (td, *J* = 7.5, 1.3 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 5.80 (s, 1H), 5.34 (s, 1H), 3.45 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 148.5, 140.1, 138.4, 136.9, 132.6, 131.1, 130.9, 129.4, 129.2, 128.3, 126.9, 115.5, 63.9, 21.3 ; HRMS [CI] calc. for $C_{17}H_{18}NO_2$ $[M+H]^+$ 268.1338 found 268.1338; IR (neat, cm^{-1}) 3176, 3055, 1650, 1592.



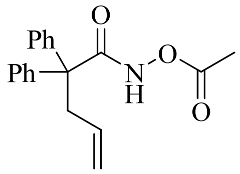
1o: white solid; m.p. 92-94 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.50 (td, *J* = 7.5, 1.2 Hz, 1H), 7.41 (td, *J* = 7.5, 1.2 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 5.76 (s, 1H), 5.39 (s, 1H), 3.45 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 166.6, 147.7, 139.8, 138.5, 134.2, 132.6, 131.1, 131.0, 128.8, 128.7, 128.4, 128.3, 116.6, 63.9; HRMS [CI] calc. for $C_{16}H_{15}ClNO_2$ $[M+H]^+$ 288.0762, found 288.0787; IR (neat, cm^{-1}) 3142, 2961, 1706, 1654.



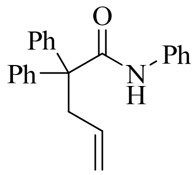
1p: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 10.9, 4.2 Hz, 1H), 7.20 – 7.11 (m, 2H), 6.32 (s, 1H), 3.73 (s, 3H), 1.85 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, overlapping peaks) δ 167.2, 137.9, 136.5, 132.0, 130.2,128.3, 126.3, 122.8, 64.2, 26.1, 19.3; HRMS [CI] calc. for $C_{12}H_{16}NO_2$ $[M+H]^+$ 206.1181 found 206.1178; IR (neat, cm^{-1}) 3177, 2969, 1648, 1595, 1568.



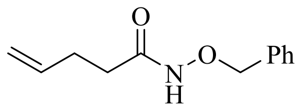
1q: yellow oil; *E*, *Z* isomers (1 : 1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.91 (s, 0.5 H) & 8.83 (s, 0.5 H), 7.58 (d, *J* = 7.6 Hz, 0.5H), 7.49 – 7.22 (m, 3H), 7.13 (t, *J* = 7.4 Hz, 0.5H), 6.71 (d, *J* = 15.7 Hz, 0.5H) & 6.46 (d, *J* = 11.4 Hz, 0.5H), 5.65 (dd, J = 15.7, 9.1 Hz, 0.5H) & 5.14 (t, J = 10.8 Hz, 0.5H), 3.82 (s, 1.5H) & 3.80 (s, 1.5H), 1.68 – 1.47 (m, 1H), 0.88 – 0.70 (m, 2H), 0.56 – 0.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 139.4 & 138.5, 136.4 & 135.7, 131.8 & 130.7, 130.5 & 130.0, 128.7 & 127.8, 126.9 & 126.3, 125.8, 124.6 & 123.9, 64.5, 14.8 & 11.0, 8.0, 7.5; HRMS [CI] calc. for $C_{13}H_{16}NO_2$ $[M+H]^+$ 218.1181, found 218.1176; IR (neat, cm^{-1}) 3182, 3000, 1641, 1593, 1525.



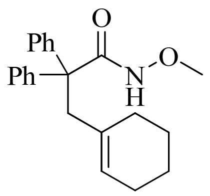
1r: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.60 – 7.40 (m, 10H), 6.04 – 5.86 (m, 1H), 5.30 – 5.07 (m, 2H), 3.43 (d, J = 6.8 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 168.8, 141.8, 134.6, 129.0, 128.6, 127.5, 118.5, 59.6, 43.4, 18.3; HRMS [CI] calc. for $C_{19}H_{20}NO_3$ $[M+H]^+$ 310.1443, found 310.1436 ; IR (neat, cm^{-1}) 3032, 1793, 1698.



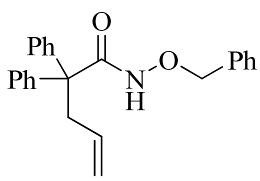
1s: white solid; m.p. 94-96 ℃;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 10H), 7.34 – 7.23 (m, 5H), 7.08 (t, J = 7.4 Hz, 1H), 5.89 – 5.74 (m, 1H), 5.11 – 4.95 (m, 2H), 3.33 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 142.6, 137.8, 135.2, 129.1, 129.0, 128.6, 127.4, 124.5, 119.8, 118.2, 61.6, 43.5; HRMS [CI] calc. for $C_{23}H_{22}NO$ $[M+H]^+$ 328.1701, found: 328.1690 ; IR (neat, cm^{-1}) 3368, 3287, 1667, 1596.



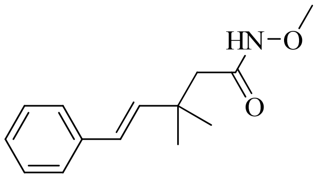
1t: white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.40 – 7.29 (m, 5H), 5.88 – 5.58 (m, 1H), 5.11 – 4.90 (m, 2H), 4.87 (s, 2H), 2.38 – 2.25 (m, 2H), 2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 136.7, 135.5, 129.3, 128.8, 128.7, 116.0, 78.2, 32.6, 29.3.



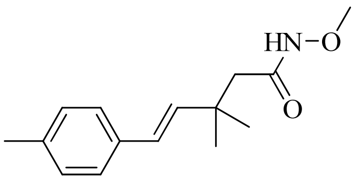
1u: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.34 (d, J = 7.3 Hz, 4H), 7.32 – 7.21 (m, 6H), 5.19 (s, 1H), 3.61 (s, 3H), 3.09 (s, 2H), 1.81 (m, 2H), 1.53 (m, 2H), 1.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 142.4, 133.9, 129.1, 127.9, 127.1, 126.9, 63.7, 60.0, 46.4, 30.3, 25.5, 23.0, 21.9 ; HRMS [CI] calc. for $C_{22}H_{26}NO_2$ $[M+H]^+$ 336.1964, found: 336.1952; IR (neat, cm^{-1}) 3242, 3055, 1653, 1598.



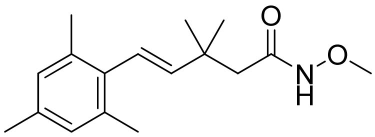
1v: White solid; m.p. 80-81 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.40 – 7.17 (m, 15H), 5.88 – 5.60 (m, 1H), 5.08 – 4.90 (m, 2H), 4.87 (s, 2H), 3.21 (d, J = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 142.1, 135.1, 134.7, 129.5, 128.9, 128.8, 128.7, 128.5, 127.3, 118.4, 78.2, 59.3, 43.4 ; HRMS [CI] calc. for $C_{24}H_{24}NO_2$ $[M+H]^+$ 358.1807, found: 358.1822 ; IR (neat, cm^{-1}) 3263, 3064, 1666, 1492.



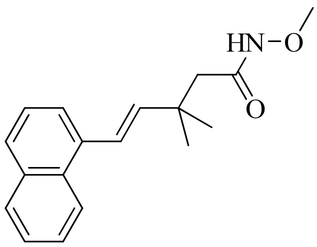
3a: Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.35 (d, J = 7.3 Hz, 2H), 7.28 (t, J = 7.3 Hz, 2H), 7.19 (t, J = 7.1 Hz, 1H), 6.35 (d, J = 16.1 Hz, 1H), 6.27 (d, J = 16.4 Hz, 1H), 3.66 (s, 3H), 2.16 (s, 2H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 138.7, 137.4, 128.6, 127.3, 126.8, 126.3, 64.3, 46.0, 36.1, 27.5; HRMS [CI] calc. for $C_{14}H_{20}NO_2$ $[M+H]^+$ 234.1494, found 234.1494; IR (neat, cm^{-1}) 3157, 2961, 1651, 1599.



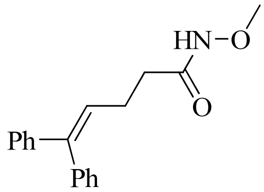
3b: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.25 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.7 Hz, 2H), 6.33 (d, J = 16.0 Hz, 1H), 6.23 (d, J = 16.2 Hz, 1H), 3.66 (s, 3H), 2.32 (s, 3H), 2.18 (s, 2H), 1.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 137.7, 136.9, 134.7, 129.3, 126.6, 126.1, 64.2, 46.0, 36.1, 27.5, 21.2; HRMS [CI] calc. for $C_{15}H_{22}NO_2$ $[M+H]^+$ 248.1651, found 248.1656,; IR (neat, cm^{-1}) 3172, 2961, 1649, 1513.



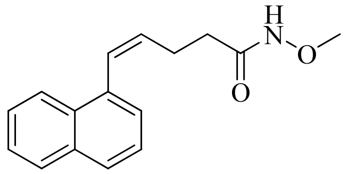
3c: yellow solid; m.p. 79-80 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.52 (s, 1H), 6.85 (s, 2H), 6.27 (d, J = 16.5 Hz, 1H), 5.72 (d, J = 16.5 Hz, 1H), 3.71 (s, 3H), 2.27 (s, 3H), 2.25 (s, 6H), 2.20 (s, 2H), 1.28 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, overlapping peaks) δ 169.1, 143.5, 135.7, 134.3, 128.4, 124.0, 64.1, 45.5, 36.4, 27.4, 20.9, 20.8; HRMS [CI] calc. for $C_{17}H_{26}NO_2$ $[M+H]^+$ 276.1964, found 276.1961; IR (neat, cm^{-1}) 3240, 2985, 1679, 1653.



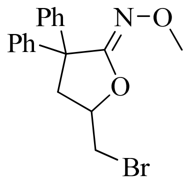
3d: yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.08 (d, J = 7.2 Hz, 1H), 7.89 – 7.77 (m, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 7.0 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.39 (t, J = 7.7 Hz, 1H), 7.08 (d, J = 15.9 Hz, 1H), 6.28 (d, J = 15.9 Hz, 1H), 3.64 (s, 3H), 2.22 (s, 2H), 1.32 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, overlapping peaks) δ 168.9, 142.2, 135.4, 133.6, 131.3, 128.5, 127.6, 125.9, 125.8, 125.7, 123.9, 123.8, 64.2, 45.8, 36.6, 27.5; HRMS [CI] calc. For $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1651, found 284.1650; IR (neat, cm^{-1}) 3169, 3044, 1649, 1509.



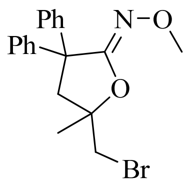
3e: yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.40 – 7.13 (m, 10H), 6.07 (t, J = 7.1 Hz, 1H), 3.67 (s, 3H), 2.55 – 2.43 (m, 2H), 2.26 (t, J = 6.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, overlapping peaks) δ 170.2, 142.8, 142.3, 139.6, 129.7, 128.2, 128.0, 127.2, 127.0, 127.0, 63.8, 32.9, 25.7; HRMS [CI] calc. for $C_{18}H_{20}NO_2$ $[M+H]^+$ 282.1494, found: 282.1491; IR (neat, cm^{-1}) 3176, 3055, 1652, 1598.



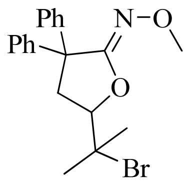
3f: yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.94 (s, 1H), 7.88 – 7.81 (m, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.59 – 7.39 (m, 3H), 7.37 – 7.29 (m, 1H), 6.92 (d, J = 11.2 Hz, 1H), 5.97 – 5.79 (m, 1H), 3.60 (s, 3H), 2.55 – 2.42 (m, 2H), 2.20 – 2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 134.1, 133.6, 131.9, 131.8, 128.5, 128.4, 127.5, 126.4, 125.9, 125.9, 125.4, 124.9, 64.1, 33.0, 24.5. HRMS [CI] calc. for $C_{16}H_{18}NO_2$ $[M+H]^+$ 256.1338, found 256.1345; IR (neat, cm^{-1}) 3169, 3057, 1651, 1438.



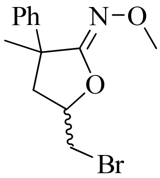
2a: white solid; m.p. 122-123 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.20 (m, 10H), 4.54 – 4.44 (m, 1H), 3.86 (s, 3H), 3.65 (dd, J = 10.5, 4.4 Hz, 1H), 3.49 (dd, J = 10.5, 7.4 Hz, 1H), 3.07 (dd, J = 12.8, 4.9 Hz, 1H), 2.81 (dd, J = 12.8, 9.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, overlapping peaks) δ 159.6, 142.3, 141.7, 128.8, 128.2, 127.7, 127.6, 127.2, 78.5, 62.8, 57.6, 44.3, 32.5; HRMS [CI] calc. for $C_{18}H_{19}BrNO_2$ $[M+H]^+$ 360.0599, found 360.0584; IR (neat, cm^{-1}) 1664, 1496, 634.



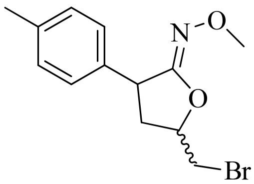
2b: white solid; m.p. 134-136 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 7.5 Hz, 2H), 7.40 – 7.21 (m, 8H), 3.86 (s, 3H), 3.47 – 3.32 (m, 2H), 3.24 (d, J = 10.4 Hz, 1H), 2.85 (d, J = 13.7 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, overlapping peaks) δ 160.0, 143.6, 142.7, 128.5, 128.5, 128.0, 127.4, 127.2, 85.8, 62.9, 58.1, 48.4, 39.0, 25.6; HRMS [CI] calc. for $C_{19}H_{21}BrNO_2$ $[M+H]^+$ 374.0756, found 374.0748; IR (neat, cm^{-1}) 1655, 1593, 631.



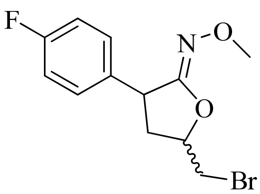
2c: white solid; m.p. 145-147 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.23 (m, 6H), 4.16 (dd, *J* = 10.7, 4.9 Hz, 1H), 3.87 (s, 3H), 3.06 (dd, *J* = 12.8, 4.9 Hz, 1H), 3.00 – 2.90 (m, 1H), 1.89 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 142.8, 141.7, 128.8, 128.4, 128.1, 127.9, 127.6, 127.1, 85.9, 64.4, 62.8, 57.7, 42.8, 31.3, 29.3; HRMS [CI] calc. for $C_{20}H_{23}BrNO_2$ $[M+H]^+$ 388.0912, found 388.0913; IR (neat, cm^{-1}) 1655, 1624, 612.



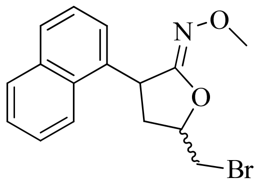
2d: two isomers (58 : 42), one isomer (major): white solid; m.p. 104-106 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 1H), 7.31 – 7.23 (m, 1H), 4.42 – 4.25 (m, 1H), 3.90 (s, 3H), 3.63 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.47 (dd, *J* = 10.4, 7.3 Hz, 1H), 2.75 (dd, *J* = 12.6, 4.6 Hz, 1H), 2.24 – 1.98 (m, 1H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 143.3, 128.9, 127.4, 125.9, 78.7, 62.7, 49.5, 45.3, 32.6, 26.8; HRMS [CI] calc. for $C_{13}H_{17}BrNO_2$ $[M+H]^+$ 298.0443, found 298.0440; IR (neat, cm^{-1}) 1672, 1516, 623. The other isomer (minor): white solid; m.p. 105-106 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 4.82 – 4.69 (m, 1H), 3.84 (s, 3H), 3.48 (dd, *J* = 10.3, 4.6 Hz, 1H), 3.16 (dd, *J* = 10.1, 8.5 Hz, 1H), 2.61 (dd, *J* = 13.1, 6.5 Hz, 1H), 2.48 (dd, *J* = 13.1, 6.9 Hz, 1H), 1.65 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 144.0, 128.7, 127.2, 126.2, 79.5, 62.7, 48.2, 44.4, 32.5, 27.7; HRM [CI] calc. for $C_{13}H_{17}BrNO_2$ $[M+H]^+$ 298.0443, found 298.0442; IR (neat, cm^{-1}) 1665, 1496, 650



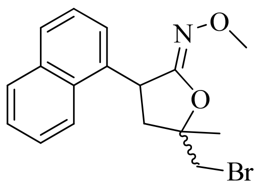
2e: two isomers (54 : 46), one isomer (major): white solid; m.p. 128-130 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.09 (m, 4H), 4.84 – 4.75 (m, 1H), 4.15 (dd, *J* = 8.7, 5.2 Hz, 1H), 3.80 (s, 3H), 3.63 (dd, *J* = 10.6, 4.2 Hz, 1H), 3.51 (dd, *J* = 10.5, 7.4 Hz, 1H), 2.55 – 2.46 (m, 1H), 2.42 – 2.35 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 137.2, 136.4, 129.7, 127.3, 80.4, 62.6, 44.2, 37.9, 33.0, 21.2; HRMS [CI] calc. for $C_{13}H_{17}BrNO_2$ $[M+H]^+$ 298.0443, found 298.0438; IR (neat, cm^{-1}) 1668, 1514, 638. The other isomer (minor): white solid; m.p. 128-130 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.74 – 4.63 (m, 1H), 4.09 (dd, *J* = 11.4, 8.4 Hz, 1H), 3.77 (s, 3H), 3.69 (dd, *J* = 10.6, 4.2 Hz, 1H), 3.53 (dd, *J* = 10.5, 7.2 Hz, 1H), 2.76 (ddd, *J* = 13.8, 8.4, 5.6 Hz, 1H), 2.34 (s, 3H), 2.19 – 2.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 137.3, 135.2, 129.6, 128.0, 80.1, 62.6, 45.4, 39.3, 32.9, 21.2; HRMS [CI] calc. For $C_{13}H_{17}BrNO_2$ $[M+H]^+$ 298.0443, found: 298.0433; IR (neat, cm^{-1}) 1672, 1516, 623.



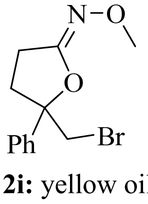
2f: two isomers (55 : 45), one isomer (major): white solid; m.p. 134-136 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 4.83 – 4.75 (m, 1H), 4.20 (dd, *J* = 8.8, 5.7 Hz, 1H), 3.82 (s, 3H), 3.65 (dd, *J* = 10.6, 4.1 Hz, 1H), 3.54 (dd, *J* = 10.6, 7.4 Hz, 1H), 2.63 – 2.46 (m, 1H), 2.44 – 2.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 160.9, 158.9, δ 135.1 (d, *J* = 3.3 Hz), 129.2 (d, *J* = 8.1 Hz), 115.9 (d, *J* = 21.6 Hz). 80.4, 62.7, 43.9, 37.8, 32.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.1 (1F, m); HRMS [CI] calc. for $C_{12}H_{14}BrFNO_2$ $[M+H]^+$ 302.0192, found 302.0195; IR (neat, cm^{-1}) 1665, 1604, 1509, 628. The other isomer (minor): white solid; m.p. 134-135 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.03 (t, J = 8.7 Hz, 2H), 4.74 – 4.63 (m, 1H), 4.11 (dd, J = 11.6, 8.4 Hz, 1H), 3.76 (s, 3H), 3.68 (dd, J = 10.6, 4.1 Hz, 1H), 3.54 (dd, J = 10.6, 7.0 Hz, 1H), 2.82 – 2.71 (m, 1H), 2.15 – 2.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 161.0, 158.7, δ 133.9 (d, J = 3.3 Hz), 129.8 (d, J = 8.1 Hz), 115.9 (d, J = 21.6 Hz). 80.0, 62.7, 45.1, 39.3, 32.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.9 (1F, m); HRMS [CI] calc. for $C_{12}H_{14}BrFNO_2$ $[M+H]^+$ 302.0192, found 302.0185; IR (neat, cm^{-1}) 1666, 1604, 1509, 625.



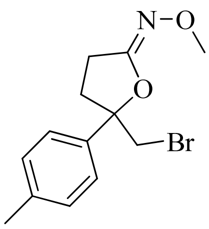
2g: two isomers (62 : 38), one isomer (major): white solid; m.p. 164-166 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 3H), 7.72 (s, 1H), 7.54 – 7.43 (m, 2H), 7.37 (d, J = 8.5 Hz, 1H), 4.93 – 4.82 (m, 1H), 4.36 (dd, J = 8.5, 5.4 Hz, 1H), 3.82 (s, 3H), 3.67 (dd, J = 10.6, 4.2 Hz, 1H), 3.60 – 3.49 (m, 1H), 2.66 – 2.56 (m, 1H), 2.56 – 2.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 136.8, 133.5, 132.7, 129.0, 128.0, 127.7, 126.5, 126.2, 126.2, 125.5, 80.5, 62.7, 44.8, 37.8, 33.0; HRMS [CI] calc. for $C_{16}H_{17}BrNO_2$ $[M+H]^+$ 334.0443, found 334.0435; IR (neat, cm^{-1}) 1668, 1600, 647. The other isomer (minor): white solid; m.p. 163-165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.75 (m, 4H), 7.50 – 7.41 (m, 3H), 4.80 – 4.68 (m, 1H), 4.30 (dd, J = 11.3, 8.5 Hz, 1H), 3.77 (s, 3H), 3.71 (dd, J = 10.6, 4.2 Hz, 1H), 3.58 (dd, J = 10.6, 7.1 Hz, 1H), 2.90 – 2.75 (m, 1H), 2.24 (dd, J = 22.5, 11.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 135.6, 133.4, 132.8, 128.9, 127.9, 127.8, 127.3, 126.4, 126.2, 125.8, 80.3, 62.7, 45.9, 39.0, 32.9; HRMS [CI] calc. for $C_{16}H_{17}BrNO_2$ $[M+H]^+$ 334.0443, found 334.0445; IR (neat, cm^{-1}) 1668, 1601, 621.



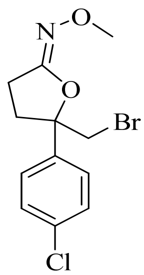
2h: two isomers (61 : 39), one isomer (major): white solid; m.p. 156-158 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.75 (m, 4H), 7.52 – 7.43 (m, 2H), 7.40 (dd, J = 8.5, 1.6 Hz, 1H), 4.46 (t, J = 9.7 Hz, 1H), 3.78 (s, 3H), 3.70 – 3.49 (m, 2H), 2.97 (dd, J = 13.4, 9.4 Hz, 1H), 2.17 (dd, J = 13.3, 10.0 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 136.6, 133.5, 132.8, 128.9, 127.9, 127.8, 127.1, 126.4, 126.2, 125.7, 87.1, 62.7, 45.9, 43.2, 38.2, 26.0; HRMS [CI] calc. for $C_{17}H_{19}BrNO_2$ $[M+H]^+$ 348.0599, found 348.0595; IR (neat, cm^{-1}) 1668, 1461, 616. Theother isomer (minor): white solid; m.p. 157-159 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 – 7.76 (m, 4H), 7.53 – 7.41 (m, 3H), 4.40 (t, J = 9.8 Hz, 1H), 3.77 (s, 3H), 3.65 (d, J = 10.7 Hz, 1H), 3.59 (d, J = 10.6 Hz, 1H), 2.52 (d, J = 9.8 Hz, 2H), 1.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 135.8, 133.4, 132.8, 128.9, 127.9, 127.8, 127.2, 126.4, 126.1, 125.9, 86.3, 62.7, 45.4, 43.4, 39.4, 24.4; HRMS [CI] calc. for $C_{17}H_{19}BrNO_2$ $[M+H]^+$ 348.0422, found 348.0452 ; IR (neat, cm^{-1}) 1670, 1508, 620.



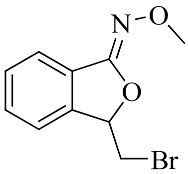
2i: yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 5H), 3.84 (s, 3H), 3.79 (d, J = 11.3 Hz, 1H), 3.71 (d, J = 11.3 Hz, 1H), 2.87 – 2.62 (m, 2H), 2.62 – 2.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 140.4, 128.8, 128.6, 125.2, 90.4, 62.5, 39.9, 33.3, 26.4; HRMS [CI] calc. for $C_{12}H_{15}BrNO_2$ $[M+H]^+$ 284.0286, found 284.0294 ; IR (neat, cm^{-1}) 1673, 610.



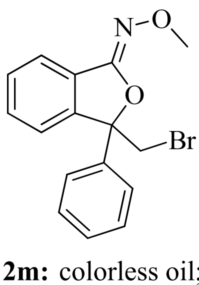
2j: yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 3.77 (s, 3H), 3.71 (d, J = 11.3 Hz, 1H), 3.62 (d, J = 11.3 Hz, 1H), 2.77 – 2.66 (m, 1H), 2.65 – 2.54 (m, 1H), 2.54 – 2.42 (m, 1H), 2.40 – 2.31 (m, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 138.5, 137.3, 129.5, 125.1, 90.4, 62.4, 39.9, 33.3, 26.4, 21.2; HRMS[CI] calc. for $C_{13}H_{17}BrNO_2$ $[M+H]^+$ 298.0443 , found 298.0433 ; IR (neat, cm^{-1}) 1673, 1648, 645.



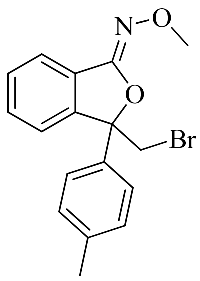
2k: yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 4H), 3.82 (s, 3H), 3.73 (d, J = 11.2 Hz, 1H), 3.65 (d, J = 11.3 Hz, 1H), 2.83 – 2.73 (m, 1H), 2.71 – 2.61 (m, 1H), 2.58 – 2.48 (m, 1H), 2.46 – 2.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 138.9, 134.6, 129.0, 126.8, 89.9, 62.5, 39.4, 33.4, 26.3; HRMS [CI] calc. for $C_{12}H_{14}BrClNO_2$ $[M+H]^+$ 317.9896, found 317.9895; IR (neat, cm^{-1})1674, 1597, 627.



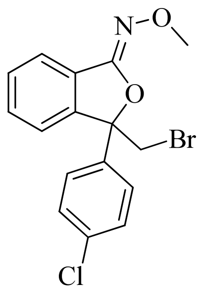
2l: yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.1 Hz, 1H), 7.53 – 7.42 (m, 3H), 5.79 (t, J = 4.8 Hz, 1H), 3.95 (s, 3H), 3.82 – 3.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 141.8, 131.1, 129.8, 129.0, 122.2, 121.9, 83.6, 63.0, 33.0; HRMS [CI] calc. for $C_{10}H_{11}BrNO_2$ $[M+H]^+$ 255.9973, found 255.9964; IR (neat, cm^{-1}) 1660, 619.



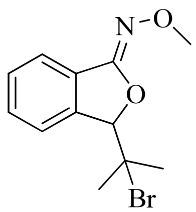
2m: colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.5 Hz, 1H), 7.57 – 7.43 (m, 5H), 7.41 – 7.30 (m, 3H), 4.16 (d, J = 11.3 Hz, 1H), 4.12 (d, J = 11.3 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 144.4, 138.5, 131.0, 129.7, 129.2, 129.0, 129.0, 125.6, 122.4, 121.9, 91.89, 63.04, 38.37; HRMS [CI] calc. for $C_{16}H_{15}BrNO_2$ $[M+H]^+$ 332.0286, found 332.0280; IR (neat, cm^{-1}) 1657, 1494, 616.



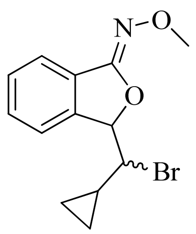
2n: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.4 Hz, 1H), 7.54 – 7.42 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.15 (d, *J* = 11.3 Hz, 1H), 4.10 (d, *J* = 11.3 Hz, 1H), 3.99 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 144.6, 139.0, 135.5, 131.0, 129.65, 129.62, 129.3, 125.6, 122.5, 121.9, 92.0, 63.0, 38.4, 21.2; HRMS [CI] calc. for $C_{17}H_{17}BrNO_2$ $[M+H]^+$ 348.0422 , found 348.0441; IR (neat, cm^{-1}) 1659, 1510, 621.



2o: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 1H), 7.52 – 7.41 (m, 5H), 7.34 (d, *J* = 8.7 Hz, 2H), 4.09 (d, *J* = 11.3 Hz, 1H), 4.05 (d, *J* = 11.4 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 154.1, 144.0, 137.1, 135.1, 131.1, 129.9, 129.1, 127.1, 122.4, 122.0, 121.7, 91.3, 63.1, 37.9; HRMS [CI] calc. for $C_{16}H_{14}BrClNO_2$ $[M+H]^+$ 367.9876, found 367.9883 , IR (neat, cm^{-1}) 1660, 1490, 648.

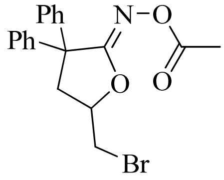


2p: white solid; m.p. 98-100℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.28 (m, 3H), 5.08 (s, 1H), 3.96 (s, 3H), 1.71 (s, 3H), 1.41 (s, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ 148.3, 134.8, 130.5, 129.2, 128.2, 125.3, 124.1, 78.8, 63.0, 54.6, 28.0, 25.8; HRMS [CI] calc. for $C_{12}H_{15}BrNO_2$ $[M+H]^+$ 284.0286, found 284.0280; IR (neat, cm^{-1}) 1661, 1619, 632.

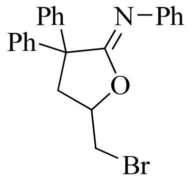


2q: inseparable two isomers (65 : 35), white solid; m.p. 97-99 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.86 (m, 1H), 7.46 – 7.20 (m, 3H), 5.31 (d, *J* = 1.6 Hz, 0.35H) & 5.22 (s, 0.65H), 3.93 (dd, *J* = 9.6, 1.8 Hz, 0.35H) & 3.23 (dd, *J* = 8.9, 1.4 Hz, 0.65H), 1.67 – 1.54 (m, 0.35H) & 0.96 – 0.51 (m, 3.65H), 0.43 – 0.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149. 4& 147.7, 136.0 & 133.2, 130.5 & 130.3, 129.5 & 129.4, 128.5 & 127.3, 125.7 & 125.4, 124.7 & 124.4, 86.3 & 83.1, 62.94 & 62.88, 49.4 & 46.0, 14.7 & 14.0, 4.6 & 4.5, 3.5 & 1.9; HRMS[CI] calc. for

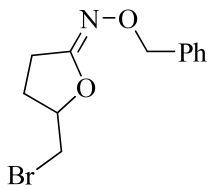
$C_{13}H_{15}BrNO_2$ $[M+H]^+$ 296.0286 , found 296.0281; IR (neat, cm^{-1}) 1662, 1597, 606.



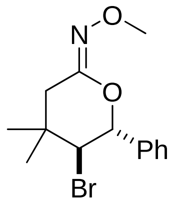
2r: white solid; m.p. 139-141 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.25 (m, 5H), 7.25 – 7.20 (m, 1H), 4.55 (td, *J* = 10.6, 4.8 Hz, 1H), 3.61 (dd, *J* = 10.8, 4.6 Hz, 1H), 3.52 (dd, *J* = 10.8, 6.6 Hz, 1H), 3.12 (dd, *J* = 13.0, 4.8 Hz, 1H), 2.86 (dd, *J* = 12.9, 10.1 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 167.4, 141.4, 140.4, 129.0, 128.5, 128.2, 128.0, 127.7, 127.4, 79.7, 58.8, 44.1, 32.1, 19.6; HRMS [CI] calc. for $C_{19}H_{19}BrNO_3$ $[M+H]^+$ 388.0548, found 388.0557; IR (neat, cm^{-1}) 1749, 1658, 1597, 634.



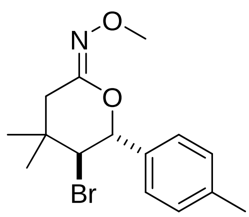
2s: white solid; m.p. 112-114 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.40 – 7.32 (m, 5H), 7.31 – 7.25 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 4.55 – 4.44 (m, 1H), 3.64 – 3.50 (m, 2H), 3.12 (dd, *J* = 12.9, 4.9 Hz, 1H), 2.92 (dd, *J* = 12.5, 10.4 Hz, 1H);^{13}C NMR (100MHz, $CDCl_3$) δ 163.0, 146.7, 143.3, 141.7, 128.8, 128.7, 128.5, 128.3, 127.9, 127.6, 127.1, 123.9, 122.8, 76.7, 58.4, 43.4, 33.6; HRMS [CI] calc. for $C_{23}H_{21}BrNO$ $[M+H]^+$ 406.0807, found 406.0811 ; IR (neat, cm^{-1}) 1710, 1593, 618.



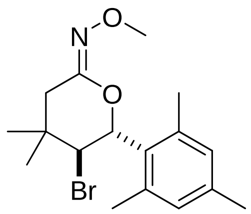
2t: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.25 (m, 1H), 4.99 (s, 2H), 4.77 – 4.69 (m, 1H), 3.61 (dd, *J* = 10.5, 3.6 Hz, 1H), 3.46 (dd, *J* = 10.1, 7.8 Hz, 1H), 2.78 – 2.57 (m, 2H), 2.42 – 2.23 (m, 1H), 2.15 – 1.94 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 138.1, 128.4, 128.3, 127.8, 82.1, 76.3, 33.2, 27.7, 26.3; HRMS [CI] calc. for $C_{12}H_{15}BrNO_2$ $[M+H]^+$ 284.0286, found 284.0272; IR (neat, cm^{-1}) 1634, 637.



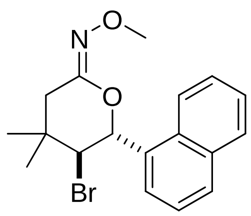
4a: yellow solid; m.p. 88-90 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.31 (m, 5H), 5.12 (d, *J* = 10.8 Hz, 1H), 4.06 (d, *J* = 10.8 Hz, 1H), 3.76 (s, 3H), 2.55 (d, *J* = 15.0 Hz, 1H), 2.43 (d, *J* = 15.1 Hz, 1H), 1.24 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 137.8, 129.2, 128.5, 128.0, 82.3, 63.7, 62.2, 39.8, 35.6, 30.0, 20.6; HRMS [CI] calc. for $C_{14}H_{19}BrNO_2$ $[M+H]^+$ 312.0599, found 312.0599; IR (neat, cm^{-1}) 1642,1458, 616.



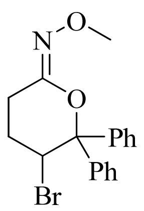
4b: white solid; m.p. 115-118 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 7.7 Hz, 2H), 5.10 (d, *J* = 10.8 Hz, 1H), 4.07 (d, *J* = 10.8 Hz, 1H), 3.76 (s, 3H), 2.55 (d, *J* = 15.1 Hz, 1H), 2.42 (d, *J* = 15.1 Hz, 1H), 2.36 (s, 3H), 1.24 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 139.1, 134.9, 129.2, 127.9, 82.2, 63.9, 62.2, 39.9, 35.6, 30.1, 21.4, 20.5; HRMS [CI] calc. for $C_{15}H_{21}BrNO_2$ $[M+H]^+$ 326.0756, found 326.0742; IR (neat, cm^{-1}) 1642, 1464, 648.



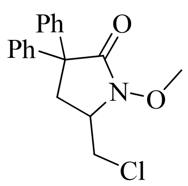
4c: yellow solid; m.p. 118-120 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 5.64 (d, *J* = 11.4 Hz, 1H), 4.58 (d, *J* = 11.4 Hz, 1H), 3.75 (s, 3H), 2.56 (d, *J* = 15.3 Hz, 1H), 2.44 (d, *J* = 15.3 Hz, 1H), 2.42 (s, 6H), 2.24 (s, 3H), 1.26 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 138.3, 131.7, 130.1, 129.4, 77.7, 62.1, 61.1, 39.8, 35.8, 30.1, 21.0, 20.5. HRMS[CI] calc. for $C_{17}H_{25}BrNO_2$ $[M+H]^+$ 354.1069, found 354.1068; IR (neat, cm^{-1}) 1638, 1611, 645.



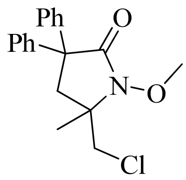
4d: white solid; m.p. 162-164 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.59 – 7.45 (m, 3H), 5.91 (d, *J* = 10.9 Hz, 1H), 4.50 (d, *J* = 10.9 Hz, 1H), 3.89 – 3.67 (s, 3H), 2.66 (d, *J* = 15.2 Hz, 1H), 2.58 (d, *J* = 15.2 Hz, 1H), 1.37 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 134.1, 133.3, 131.5, 130.0, 129.1, 126.7, 126.4, 125.8, 125.2, 123.6, 79.1, 63.1, 62.1, 40.0, 36.0, 30.1, 20.8; HRMS [CI] calc. for $C_{18}H_{21}BrNO_2$ $[M+H]^+$ 362.0756, found: 362.0751; IR (neat, cm^{-1}) 1684, 1638, 625.



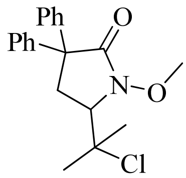
4e: yellow solid; m.p. 132-134 ℃; ^{1}H NMR (300 MHz,$CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 4H), 7.38 – 7.28 (m, 4H), 7.27 – 7.19 (m, 2H), 5.51 – 5.40 (m, 1H), 3.93 (s, 3H), 3.02 – 2.79 (m, 1H), 2.38 – 2.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 143.8, 142.0, 129.3, 128.3, 128.0, 127.4, 125.1, 124.7, 86.6, 62.2, 53.9, 27.3, 20.6; HRMS [CI] calc. for $C_{18}H_{19}BrNO_2$ $[M+H]^+$ 360.0599, found 360.0592; IR (neat, cm^{-1}) 1639, 1594, 619.



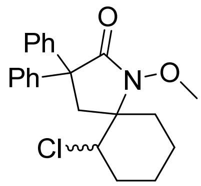
5a: white solid; m.p. 92-94 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 8H), 7.15 – 7.08 (m, 2H), 3.88 – 3.80 (m, 1H), 3.78 (s, 3H), 3.62 (d, *J* = 3.8 Hz, 2H), 2.76 (dd, *J* = 13.1, 6.1 Hz, 1H), 2.55 (dd, *J* = 13.1, 8.7 Hz, 1H); ^{13}C NMR (150 MHz, $cdcl_3$) δ 172.7, 143.3, 141.4, 128.8, 128.6, 127.83, 127.76, 127.5, 127.2, 63.5, 56.0, 54.5, 43.9, 36.2; HRMS[CI] calc. for $C_{18}H_{19}ClNO_2$ $[M+H]^+$ 316.1104, found 316.1106; IR (neat, cm^{-1}) 1657, 1494, 616.



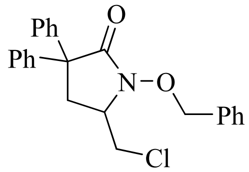
5b: white solid; m.p. 100-102 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 4H), 7.38 – 7.30 (m, 4H), 7.29 – 7.22 (m, 2H), 4.02 (s, 3H), 3.56 (s, 2H), 3.21 (d, *J* = 13.7 Hz, 1H), 2.64 (d, *J* = 13.7 Hz, 1H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 143.5, 143.3, 128.6, 128.5, 127.8, 127.7, 127.1, 127.0, 64.5, 61.8, 53.7, 49.0, 42.0, 22.6; HRMS[CI] calc. for $C_{19}H_{21}ClNO_2$ $[M+H]^+$ 330.1261, found 330.1271; IR (neat, cm^{-1}) 1687, 1496, 646.



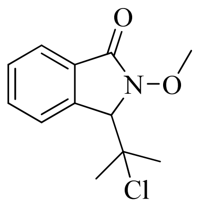
5c: white solid; m.p. 135-137 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.21 (m, 10H), 3.87 (dd, *J* = 9.3, 6.3 Hz, 1H), 3.81 (s, 3H), 2.99 (dd, *J* = 13.3, 6.2 Hz, 1H), 2.50 (dd, *J* = 13.2, 9.5 Hz, 1H), 1.69 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 143.9, 140.9, 128.8, 128.6, 128.0, 127.8, 127.6, 127.1, 69.5, 63.1, 61.0, 53.9, 36.5, 30.7, 28.7; HRMS[CI] calc. for $C_{20}H_{23}ClNO_2$ $[M+H]^+$ 344.1417, found 344.1391; IR (neat, cm^{-1}) 1650, 1594, 620.



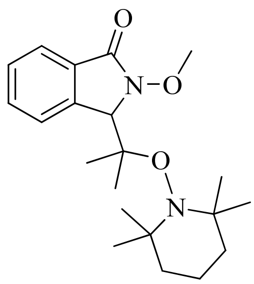
6: two isomer (46 : 54); one isomer (minor): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.16 (m, 8H), 4.05 (s, 3H), 3.93 (dd, *J* = 9.3, 4.1 Hz, 1H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.74 (d, *J* = 13.5 Hz, 1H), 2.27 – 2.01 (m, 3H), 1.91 – 1.73 (m, 2H), 1.50 – 1.29 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, overlapping peaks) δ 172.0, 144.7, 142.8, 128.6, 128.6, 128.2, 127.7, 127.2, 127.0, 65.1, 64.2, 63.3, 53.4, 45.2, 33.2, 22.1; HRMS[CI] calc. for $C_{22}H_{25}ClNO_2$ $[M+H]^+$ 370.1574 , found 370.1585 ; IR (neat, cm^{-1}) 1702, 1445, 696. The other isomer (major): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.17 (m, 6H), 4.29 (dd, *J* = 12.5, 3.8 Hz, 1H), 4.06 (s, 3H), 2.97 (d, *J* = 13.7 Hz, 1H), 2.89 (d, *J* = 13.7 Hz, 1H), 2.23 (d, *J* = 13.7 Hz, 1H), 1.82 – 1.71 (m, 2H), 1.71 – 1.60 (m, 2H), 1.55 (d, *J* = 13.7 Hz, 1H), 1.42 – 1.29 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 145.0, 143.0, 128.7, 128.3, 128.09, 128.08, 127.2, 126.8, 65.7, 64.2, 63.1, 53.8, 36.5, 33.6, 33.5, 25.7, 22.2; HRMS[CI] calc. for $C_{22}H_{25}ClNO_2$ $[M+H]^+$ 370.1574 , found 370.1577; IR (neat, cm^{-1}) 1702, 1446, 697.



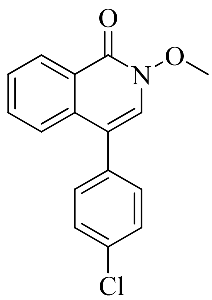
7: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.23 (m, 15H), 5.18 (d, *J* = 10.4 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 3.78 – 3.62 (m, 2H), 3.58 (dd, *J* = 11.3, 6.1 Hz, 1H), 2.90 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.59 (dd, *J* = 13.1, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 143.7, 141.3, 134.9, 130.0, 129.2, 128.8, 128.8, 128.6, 127.9, 127.9, 127.5, 127.1, 77.6, 56.6, 54.3, 44.0, 36.4; HRMS[CI] calc. for $C_{24}H_{22}ClNO_2$ $[M+H]^+$ 392.1417, found 392.1434 ; IR (neat, cm^{-1})1708, 1580, 648.



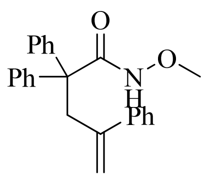
8a: yellow solid; m.p. 91-93℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 4.92 (s, 1H), 3.92 (s, 3H), 1.89 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 140.1, 132.3, 130.5, 129.3, 125.6, 123.9, 70.2, 67.1, 62.3, 32.3, 26.4; HRMS [CI] calc. for $C_{12}H_{15}ClNO_2$ $[M+H]^+$ 240.0791, found 240.0789 ; IR (neat, cm^{-1}) 1693, 1467, 627.



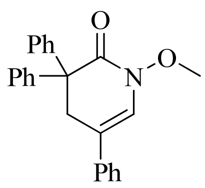
8b: yellow solid; m.p.124-126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 4.97 (s, 1H), 3.93 (s, 3H), 1.61 – 1.51 (m, 7H), 1.42 – 1.24 (m, 8H), 1.21 (s, 3H), 1.16 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 142.0, 132.1, 130.5, 128.4, 125.5, 123.5, 82.1, 66.5, 62.2, 59.9, 59.6, 41.2, 41.1, 35.5, 34.8, 24.1, 23.5, 22.3, 21.4, 17.3; HRMS [CI] calc. for $C_{21}H_{33}N_2O_3$ $[M+H]^+$ 361.2491, found 361.2498 ; IR (neat, cm^{-1}) 1659, 1510.



9: yellow solid; m.p.96-97 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.9 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.31 (s, 1H), 4.15 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 135.5, 134.5, 133.7, 132.9, 131.4, 129.2, 128.4, 127.9, 127.7, 126.8, 125.0, 119.6, 65.0; HRMS [CI] calc. for $C_{16}H_{14}ClNO_2$ $[M+H]^+$ 286.0635, found 286.0634 ; IR (neat, cm^{-1}) 3068, 1655, 1598.

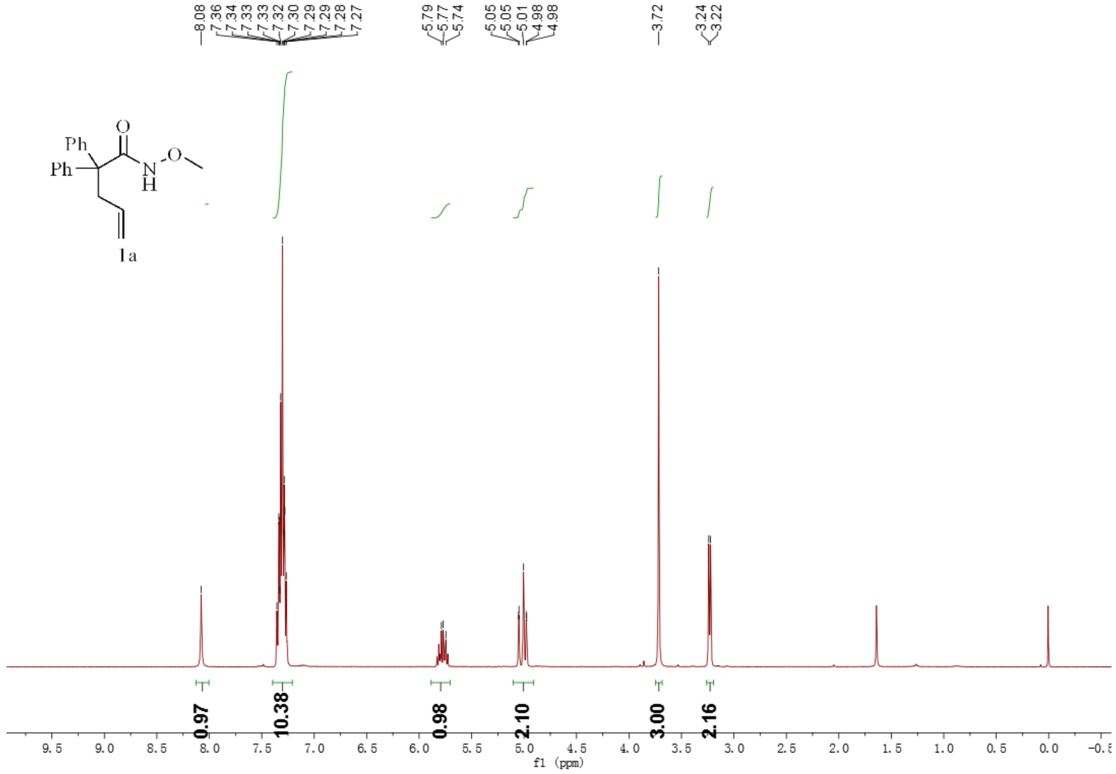


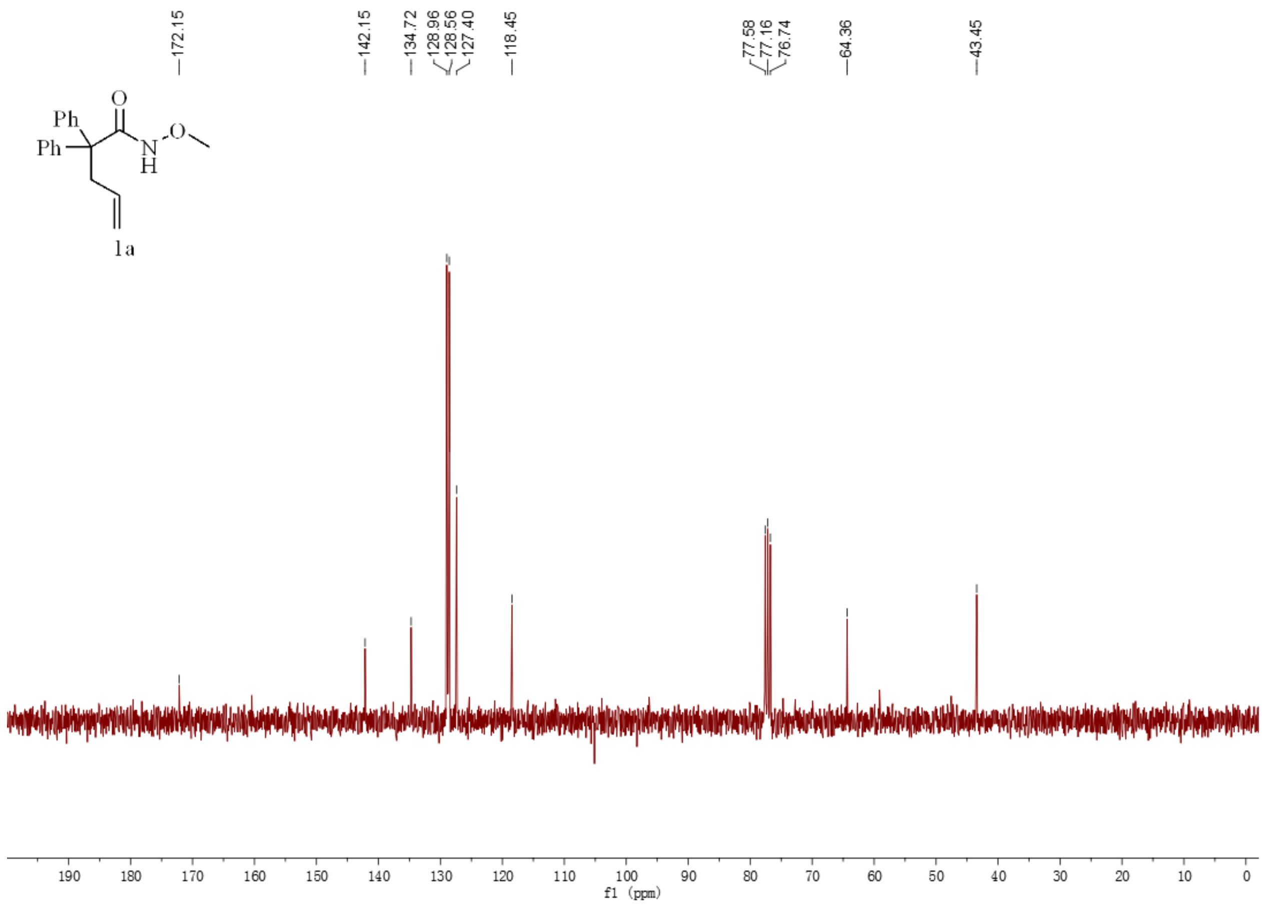
10:colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.32 (d, *J* = 7.1 Hz, 4H), 7.27 – 7.15 (m, 6H), 7.14 – 7.07 (m, 5H), 5.24 (s, 1H), 4.97 (s, 1H), 3.68 (s, 2H), 3.58 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.7, 144.9, 143.1, 141.9, 129.3, 128.2, 127.9, 127.2, 126.9, 126.5, 118.4, 64.0, 60.2, 43.1; HRMS [CI] calc. for $C_{24}H_{24}NO_2$ $[M+H]^+$ 358.1807, found 358.1822 ; IR (neat, cm^{-1}) 3240, 3055, 1654, 1574 1492.

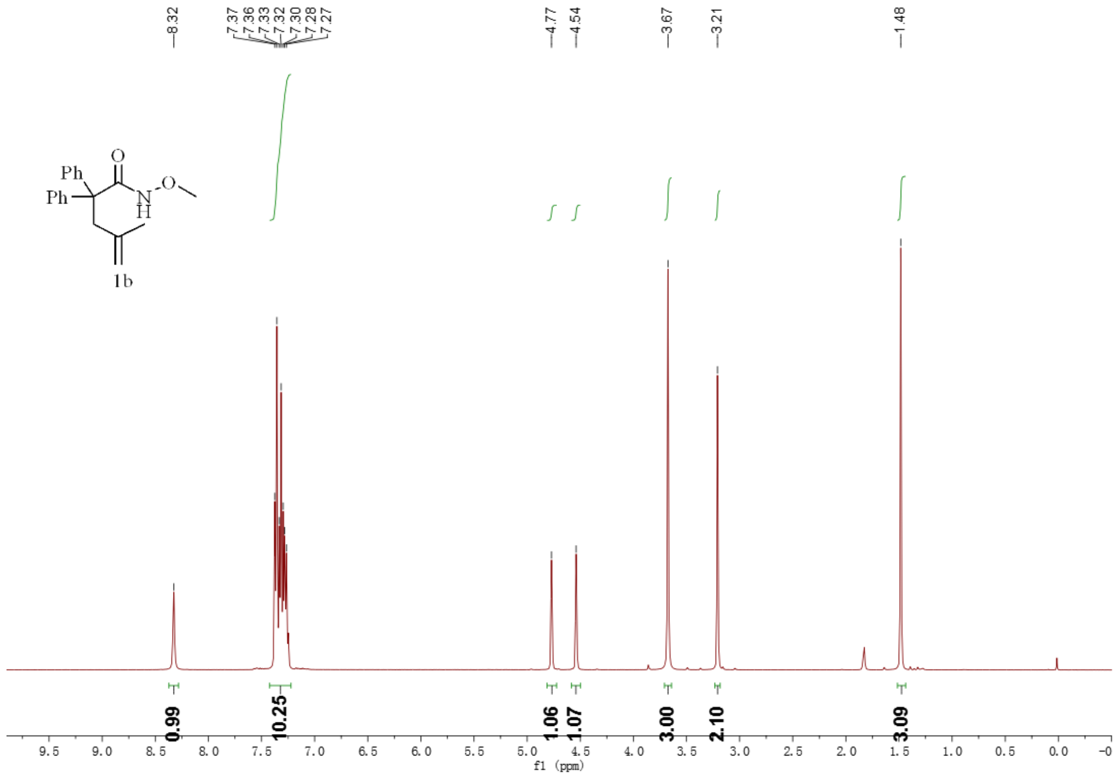


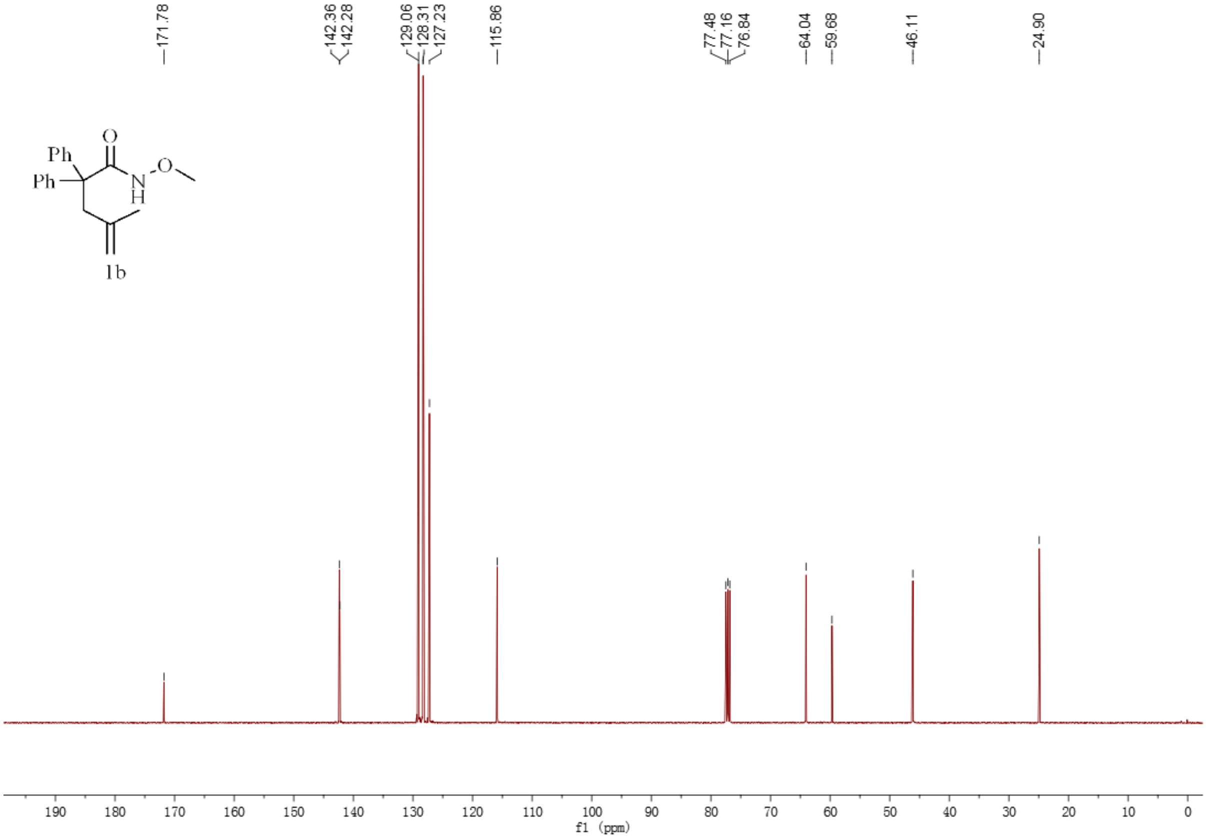
11: yellow solid; m.p.173-175 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 11H), 7.17 (d, *J* = 6.8 Hz, 4H), 6.56 (s, 1H), 3.86 (s, 3H), 3.34 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 141.3, 137.1, 129.0, 128.6, 128.4, 127.5, 127.3, 124.6, 124.2, 118.1, 63.3, 56.7, 38.4; HRMS[CI] calc. for $C_{24}H_{22}NO_2$ $[M+H]^+$ 356.1651, found 356.1645; IR (neat, cm^{-1}) 3065, 1684, 1549.

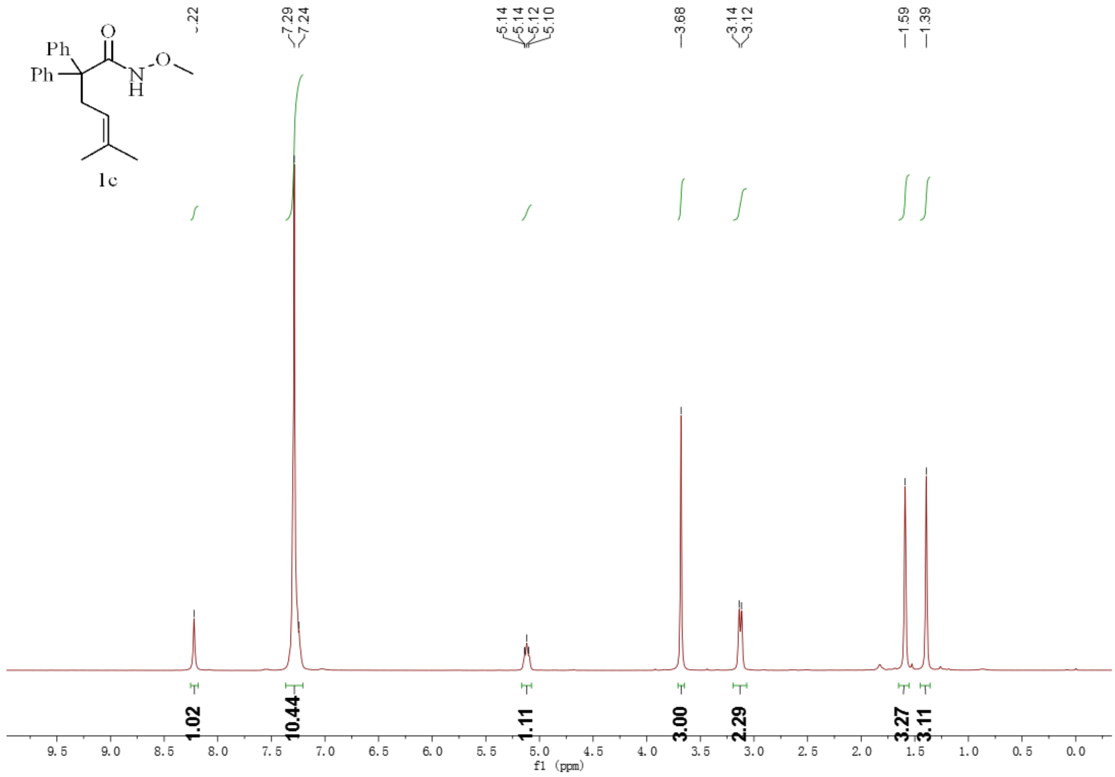
9. ^{1}H and ^{13}C NMR spectrs

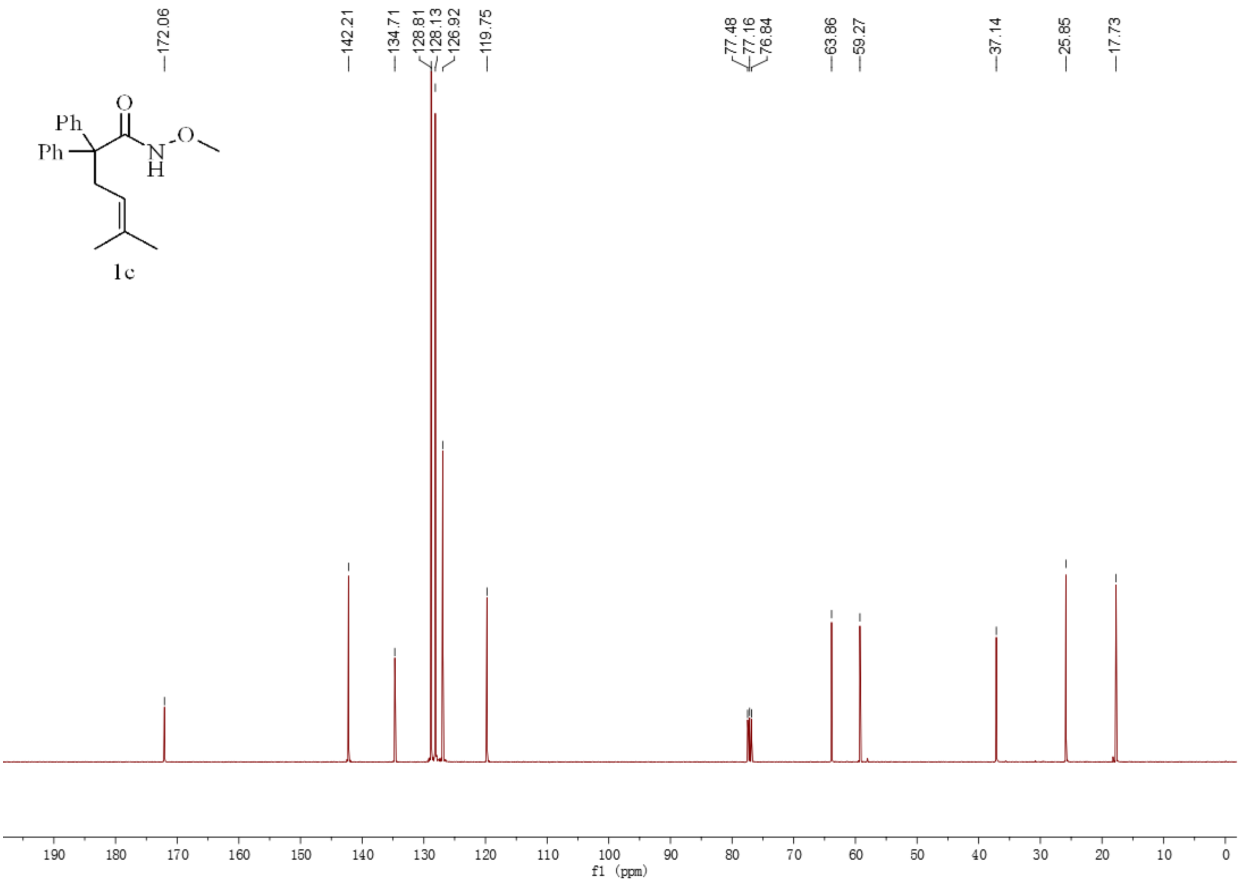


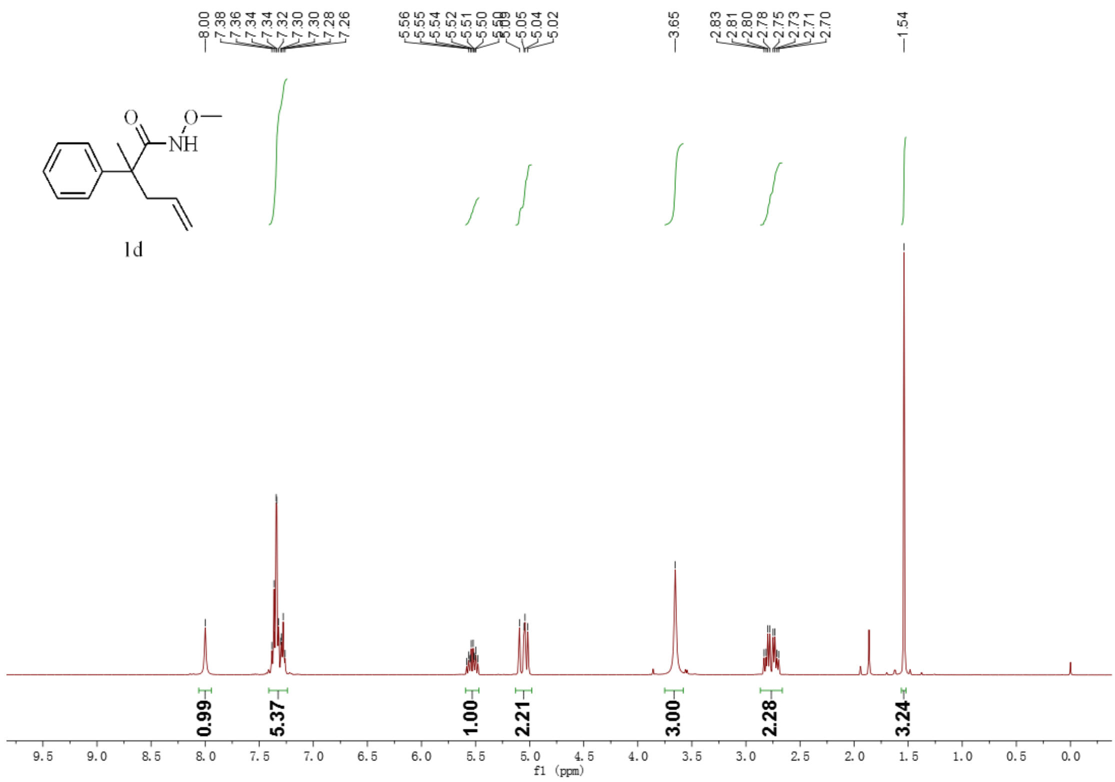


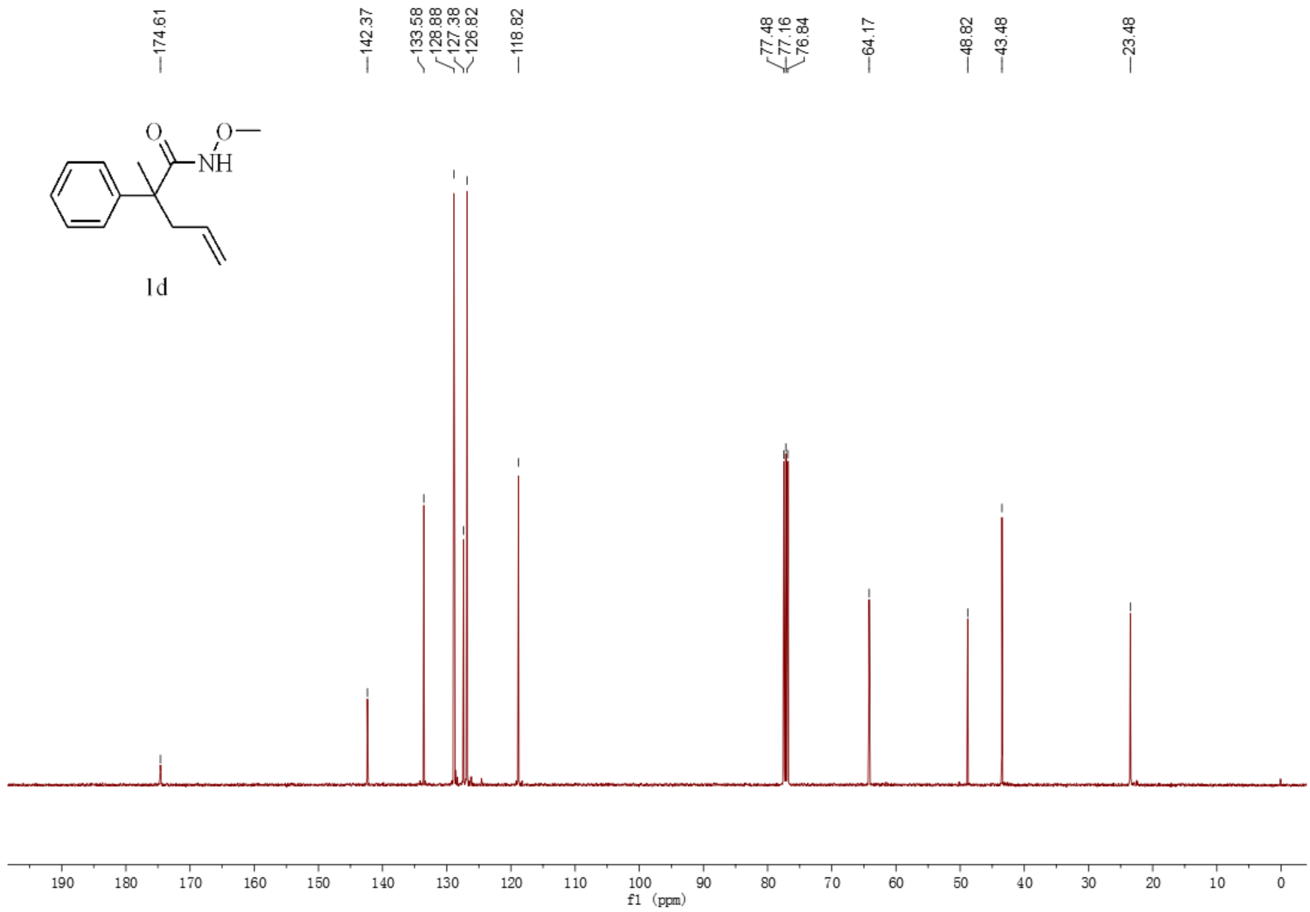

8.32
7.37
7.36
7.33
7.32
7.30
7.28
7.27
4.77
4.54
3.67
3.21
1.48
Ph
Ph
O
N
H
O
1b
0.99
10.25
1.06
1.07
3.00
2.10
3.09
f1 (ppm)

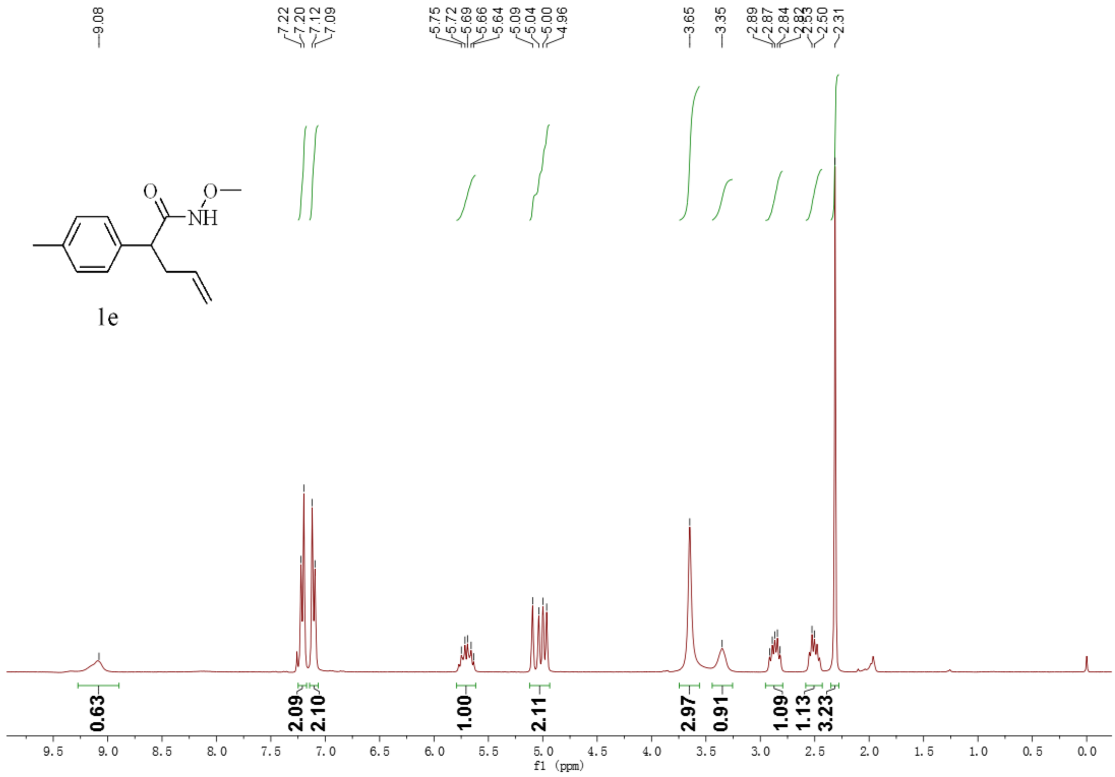

171.78
142.36
142.28
129.06
128.31
127.23
115.86
77.48
77.16
76.84
64.04
59.68
46.11
24.90
Ph
Ph
O
N
H
O
1b
f1 (ppm)

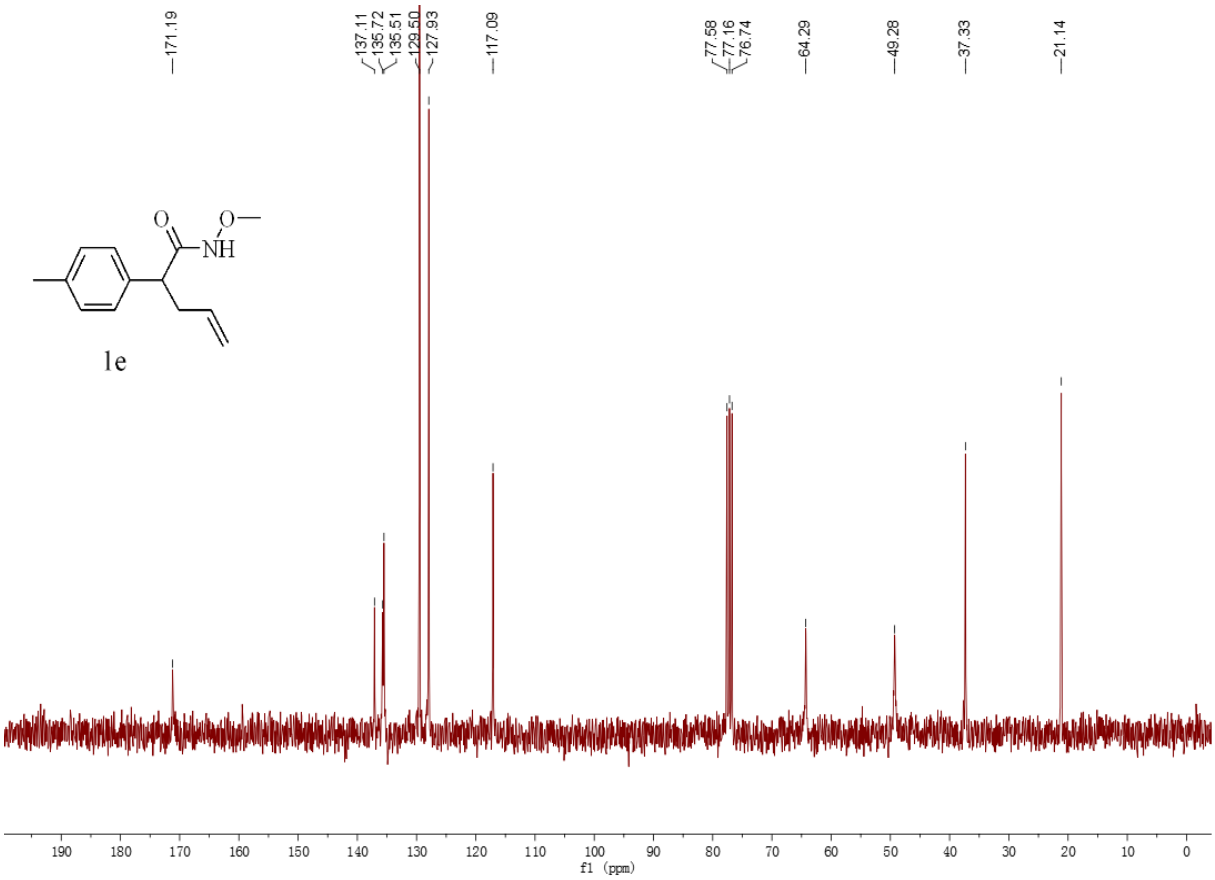

Ph
Ph
O
N
H
O
1c
.22
7.29
7.24
5.14
5.14
5.12
5.10
3.68
3.14
3.12
1.59
1.39
1.02
10.44
1.11
3.00
2.29
3.27
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

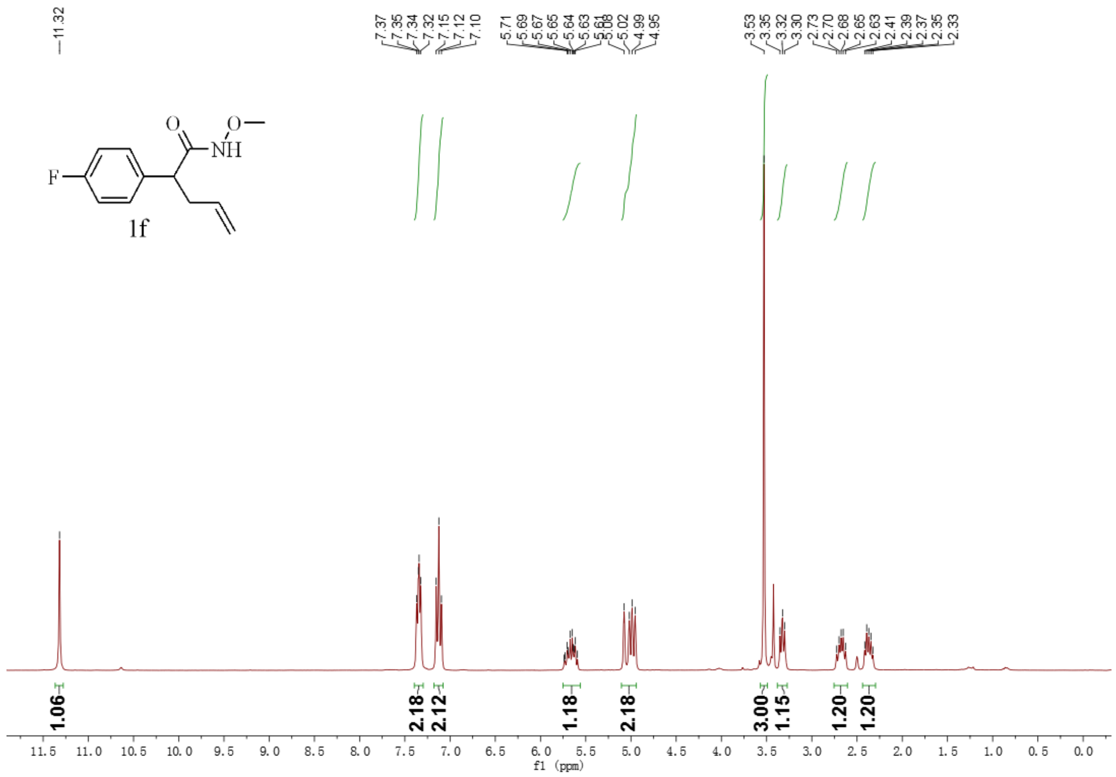

Ph
Ph
O
N
H
O
1c
172.06
142.21
134.71
128.81
128.13
126.92
119.75
77.48
77.16
76.84
63.86
59.27
37.14
25.85
17.73
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

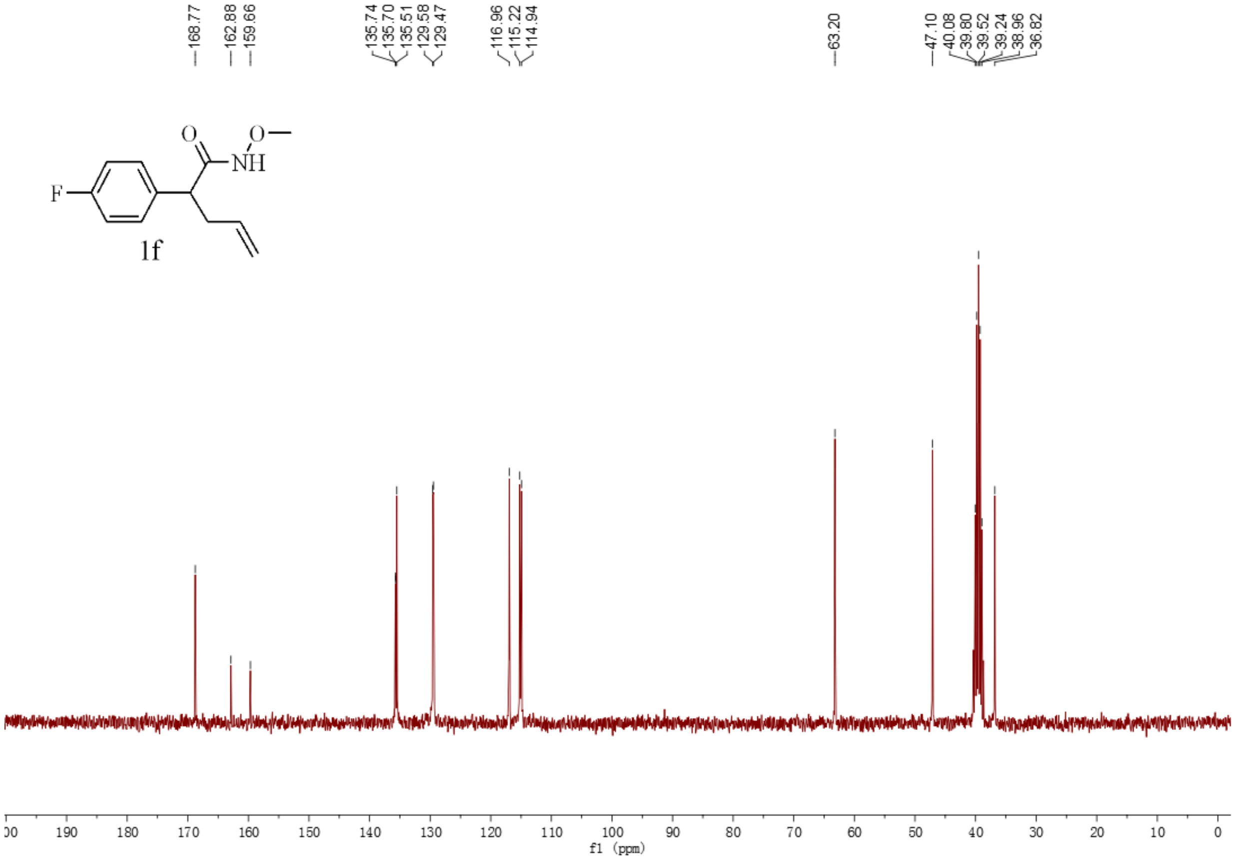


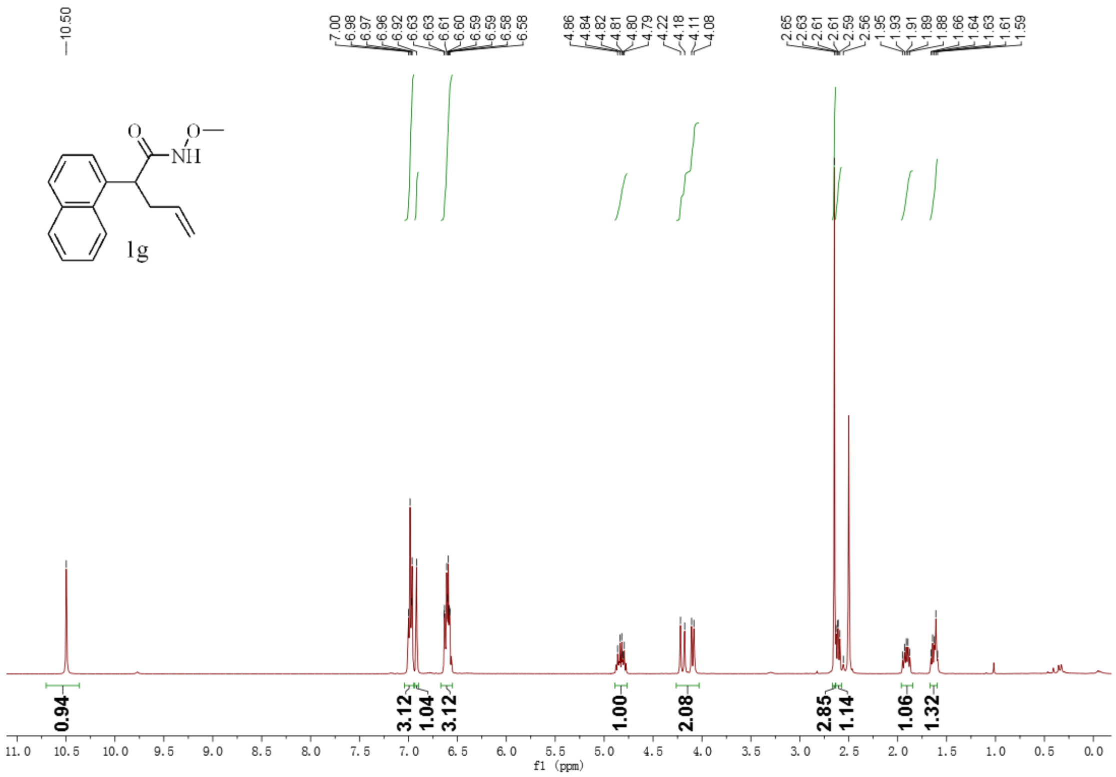


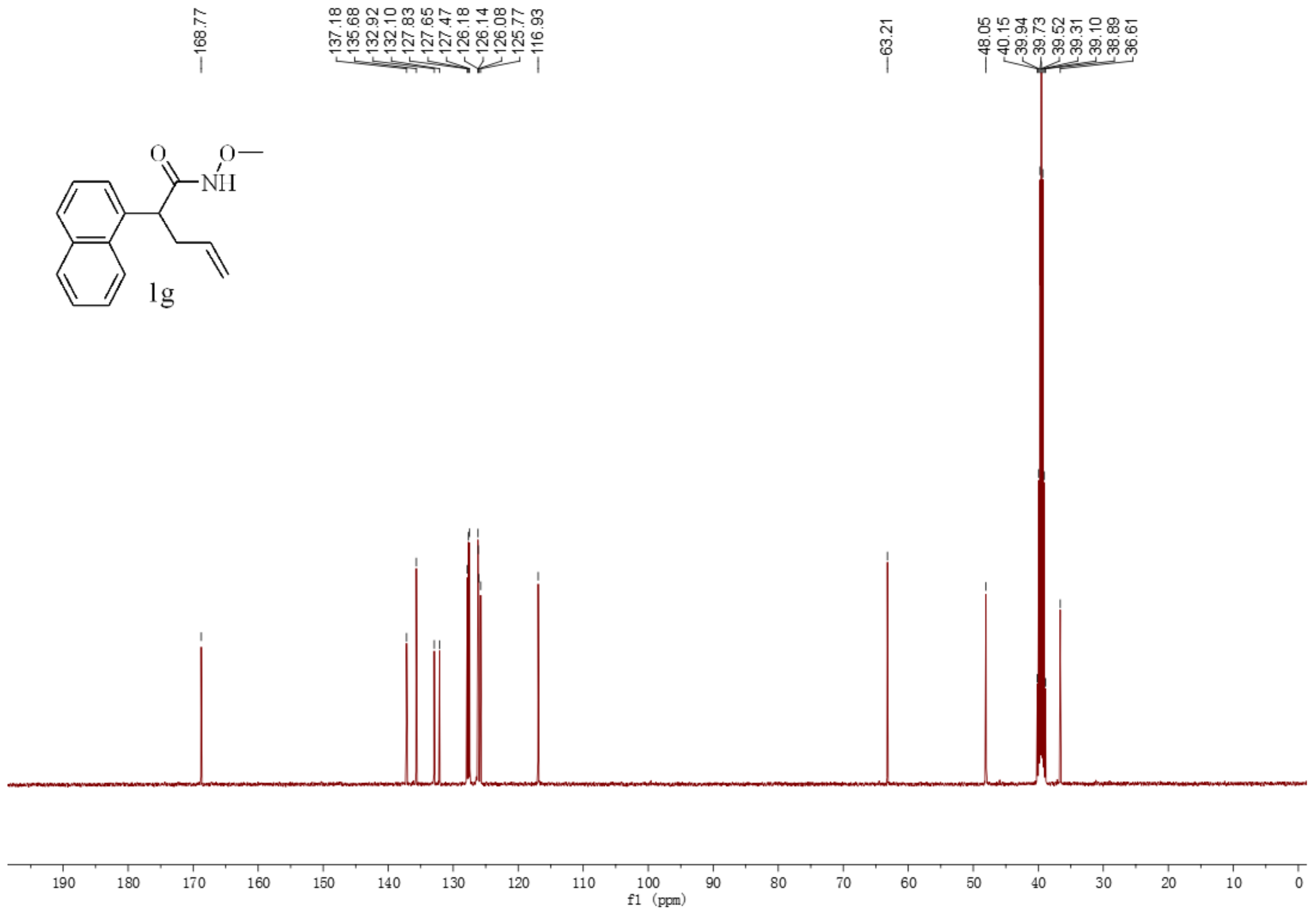

9.08
7.22 7.20 7.12 7.09
5.75 5.72 5.69 5.66 5.64 5.09 5.04 5.00 4.96
3.65
3.35
2.89 2.87 2.84 2.82 2.53 2.50 2.31
O
NH
O
1e
0.63
2.09
2.10
1.00
2.11
2.97
0.91
1.09
1.13
3.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

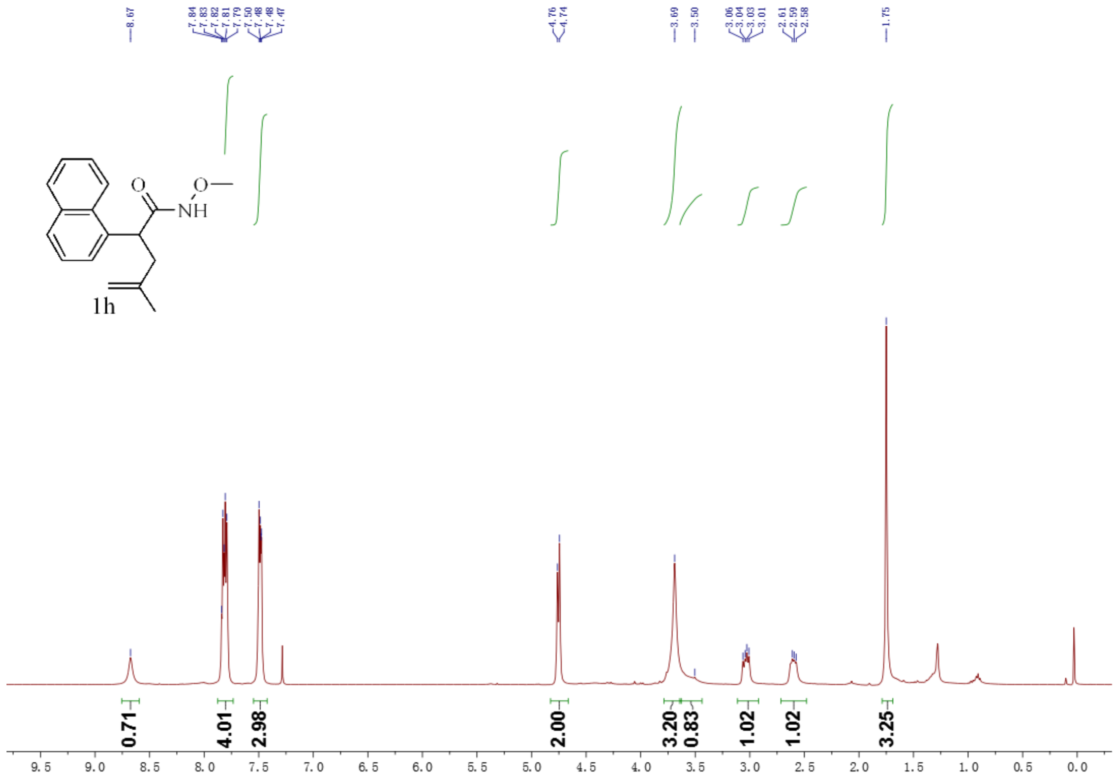

171.19
137.11 135.72 135.51 129.50 127.93
117.09
77.58 77.16 76.74
64.29
49.28
37.33
21.14
O
NH
O
1e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

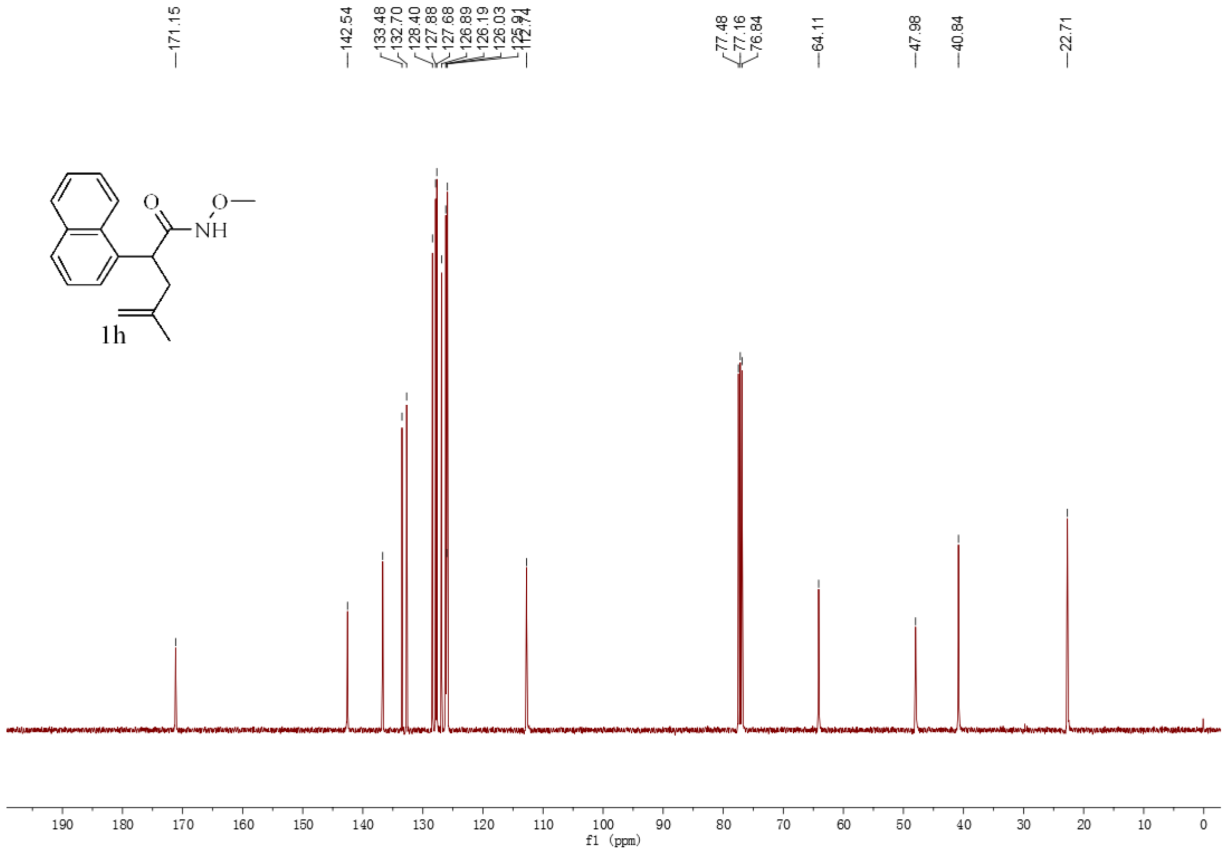


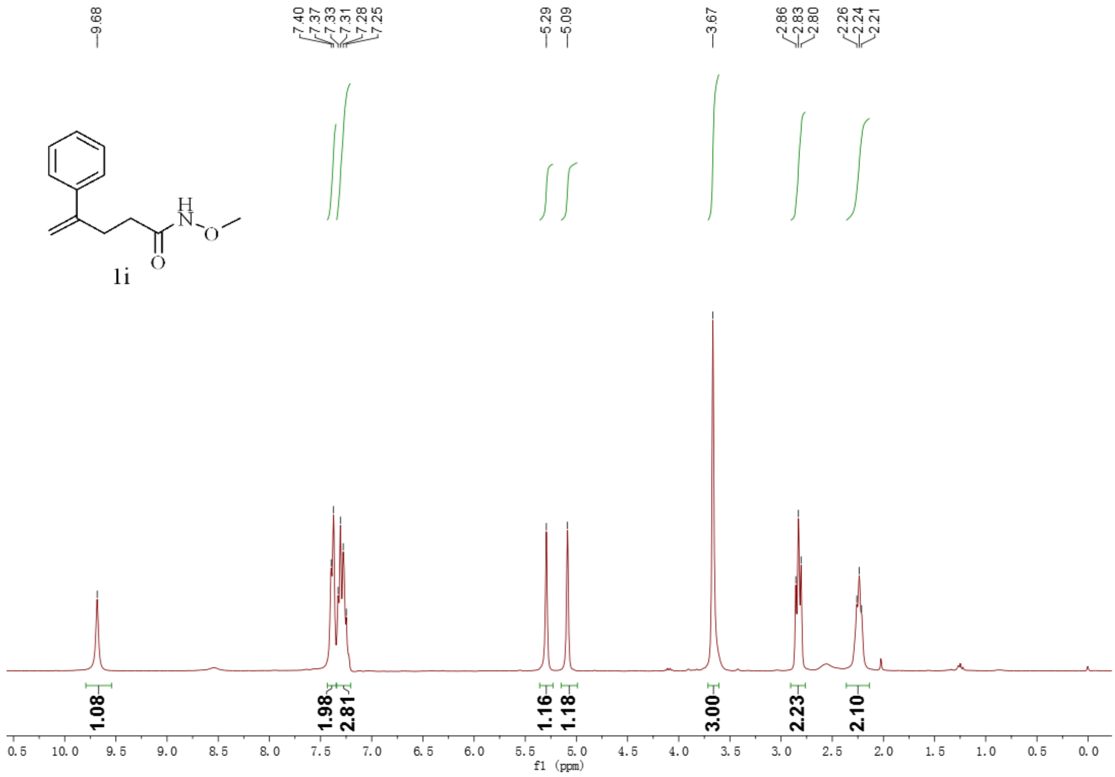


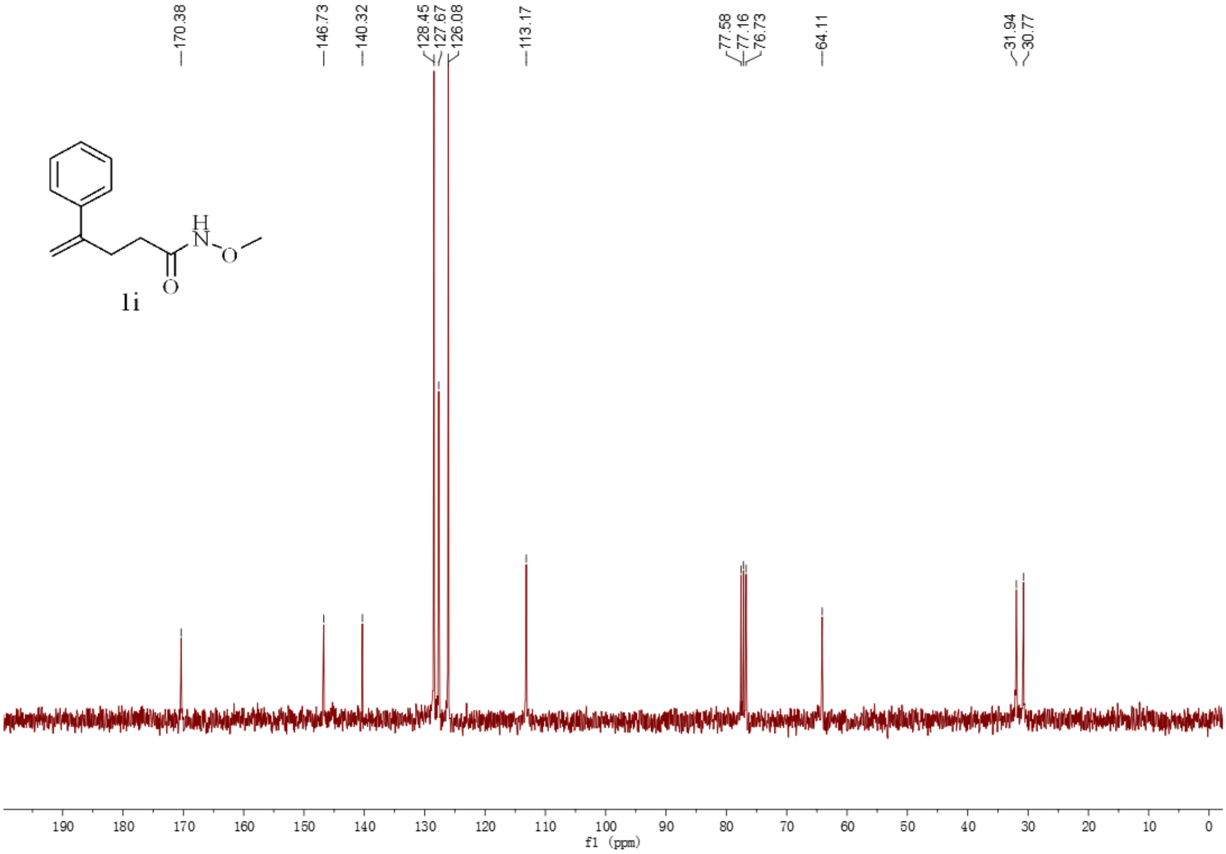

1g

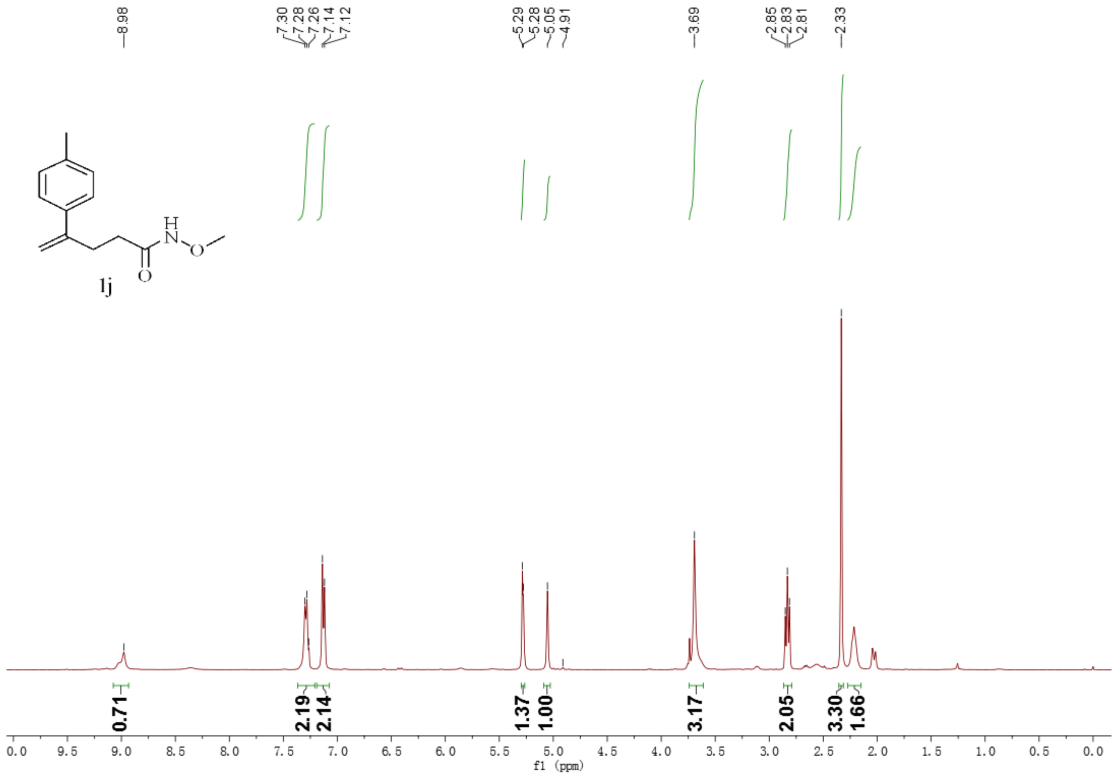

1g

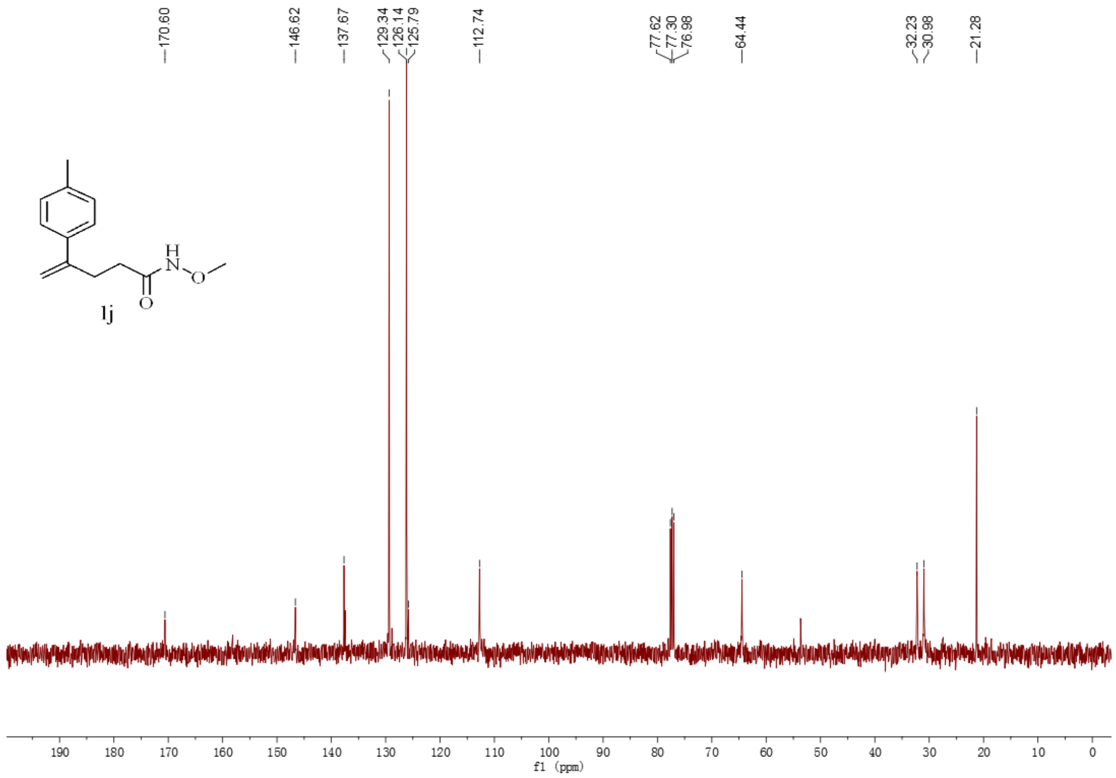

8.67
7.84
7.83
7.82
7.81
7.79
7.50
7.48
7.48
7.47
4.76
4.74
3.69
3.50
3.06
3.04
3.03
3.01
2.61
2.59
2.58
1.75
O
O
NH
1h
0.71
4.01
2.98
2.00
3.20
0.83
1.02
1.02
3.25

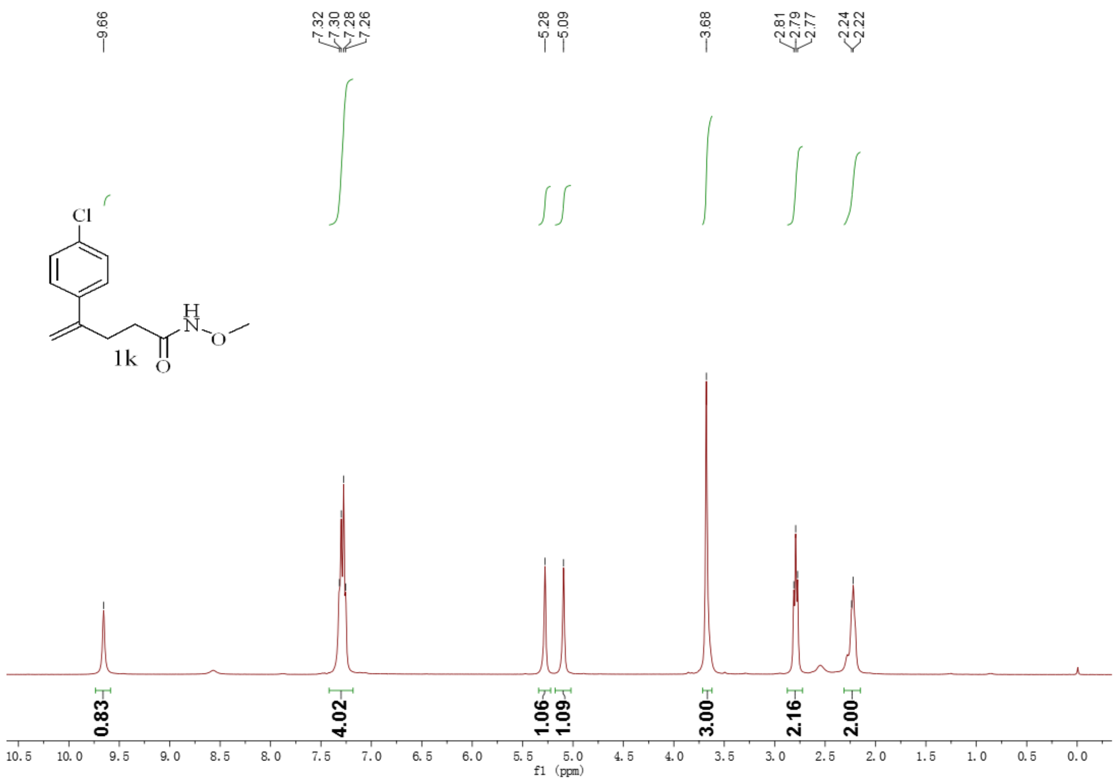

171.15
142.54
133.48
132.70
128.40
127.88
127.68
126.89
126.19
126.03
125.91
112.74
77.48
77.16
76.84
64.11
47.98
40.84
22.71
O
O
NH
1h
f1 (ppm)

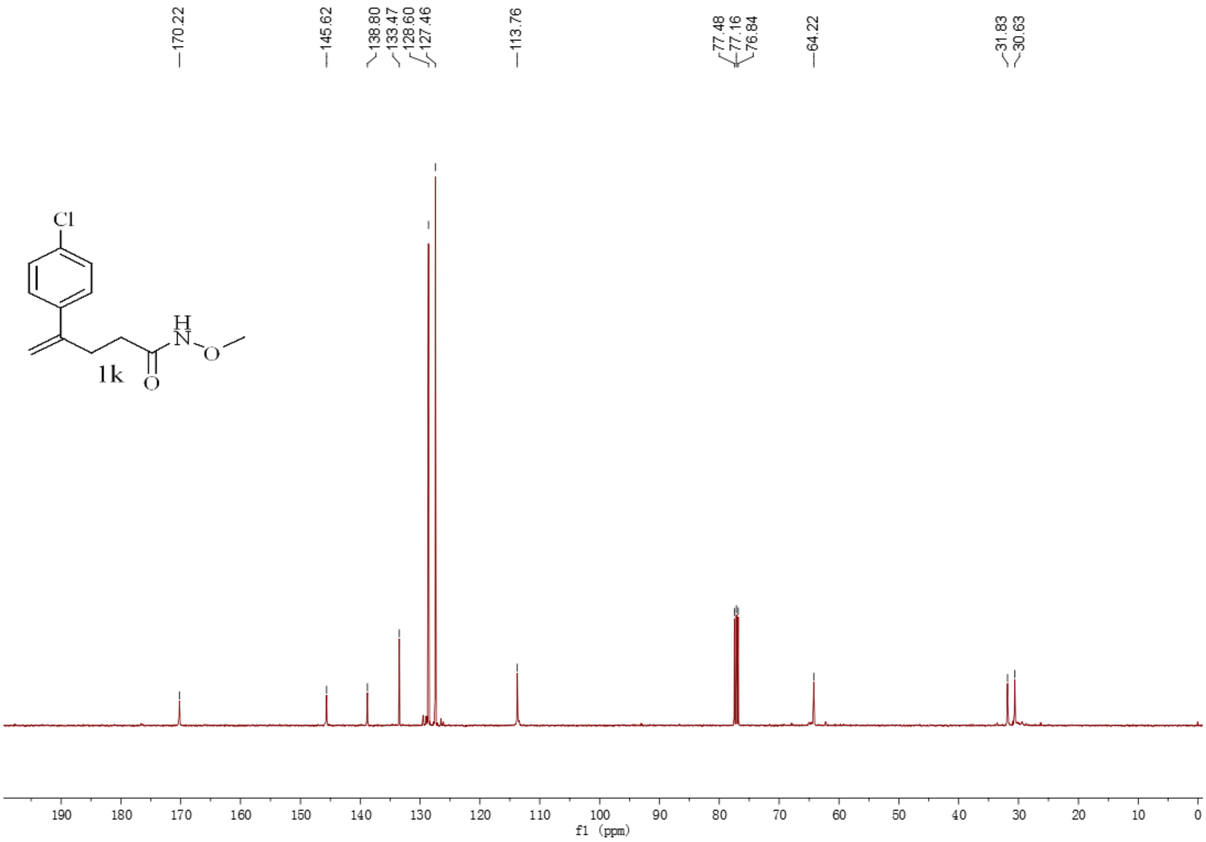

1i
9.68
7.40
7.37
7.33
7.31
7.28
7.25
5.29
5.09
3.67
2.86
2.83
2.80
2.26
2.24
2.21
1.08
1.98
2.81
1.16
1.18
3.00
2.23
2.10
f1 (ppm)

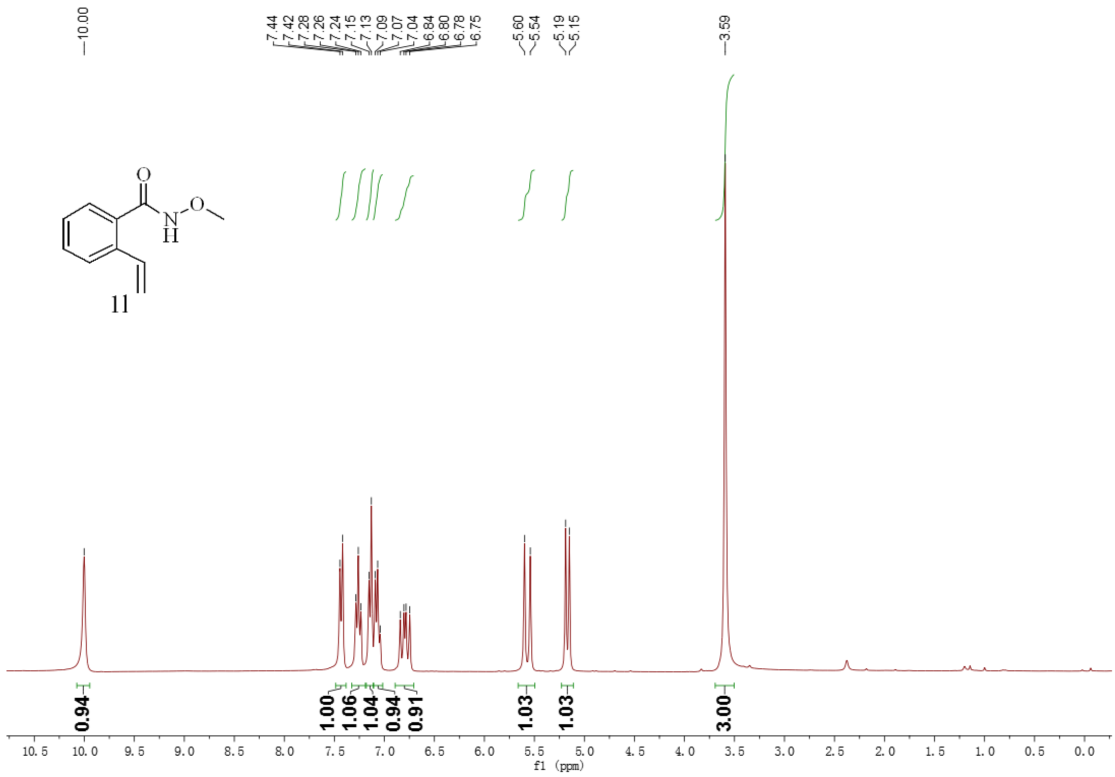

1i
170.38
146.73
140.32
128.45
127.67
126.08
113.17
77.58
77.16
76.73
64.11
31.94
30.77
f1 (ppm)


8.98
7.30
7.28
7.26
7.14
7.12
5.29
5.28
5.05
4.91
3.69
2.85
2.83
2.81
2.33
1j
0.71
2.19
2.14
1.37
1.00
3.17
2.05
3.30
1.66
f1 (ppm)

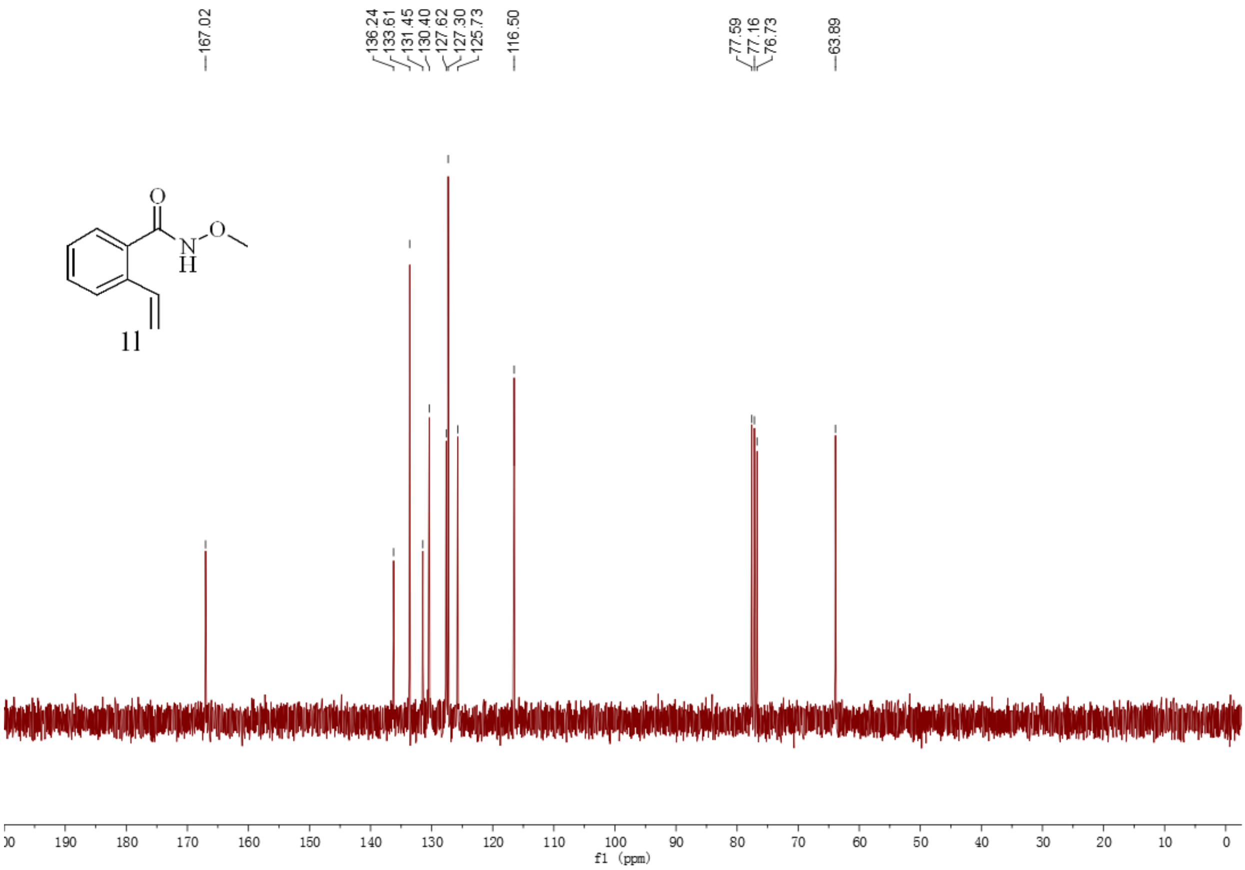

170.60
146.62
137.67
129.34
126.14
125.79
112.74
77.62
77.30
76.98
64.44
32.23
30.98
21.28
1j
f1 (ppm)


9.66
7.32
7.30
7.28
7.26
5.28
5.09
3.68
2.81
2.79
2.77
2.24
2.22
Cl
H
N
O
1k
0.83
4.02
1.06
1.09
3.00
2.16
2.00
f1 (ppm)

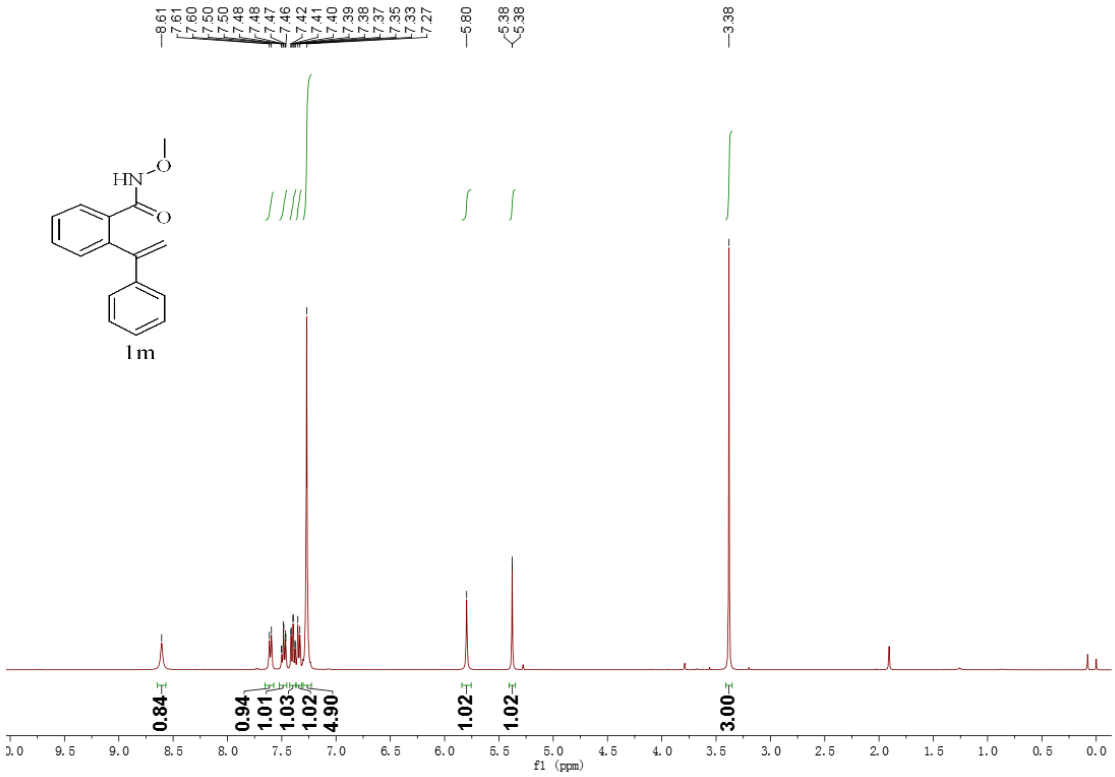

170.22
145.62
138.80
133.47
128.60
127.46
113.76
77.48
77.16
76.84
64.22
31.83
30.63
Cl
H
N
O
1k
f1 (ppm)

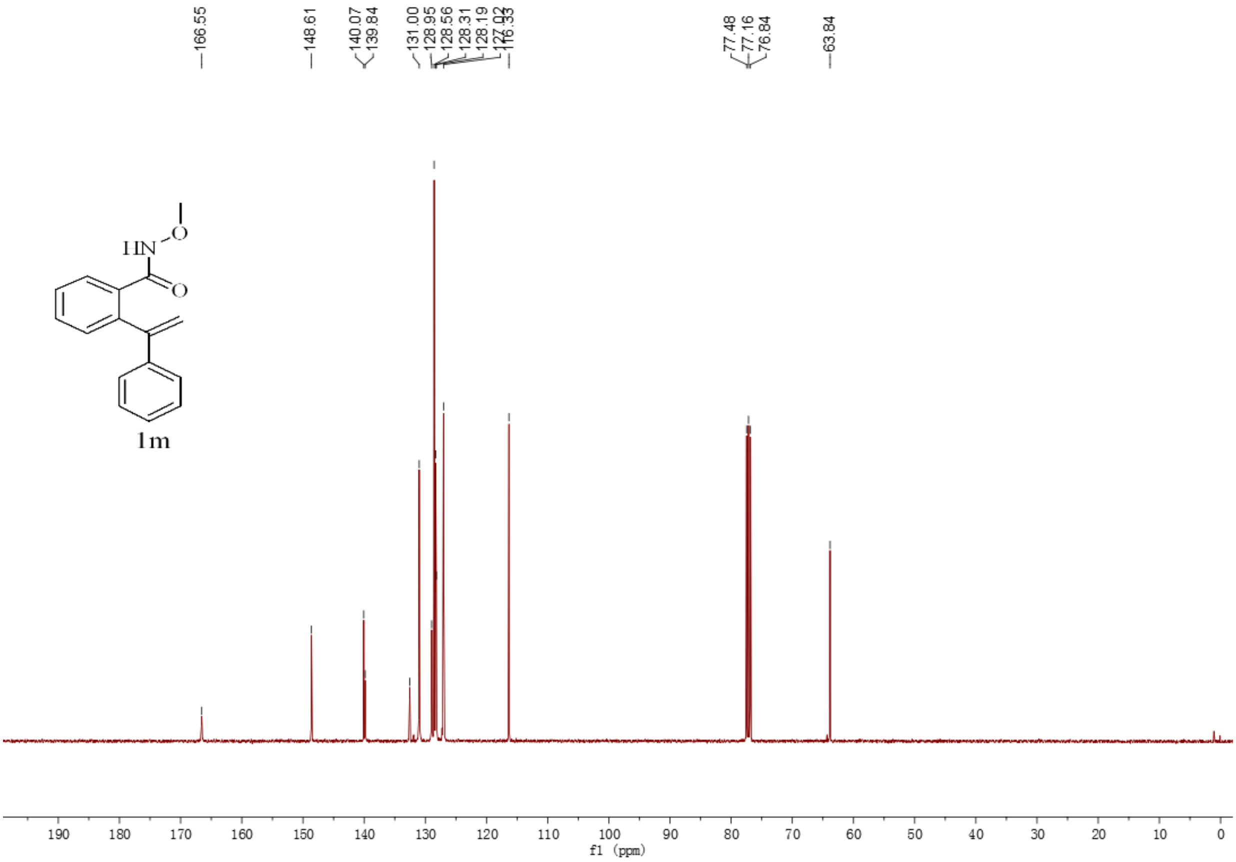


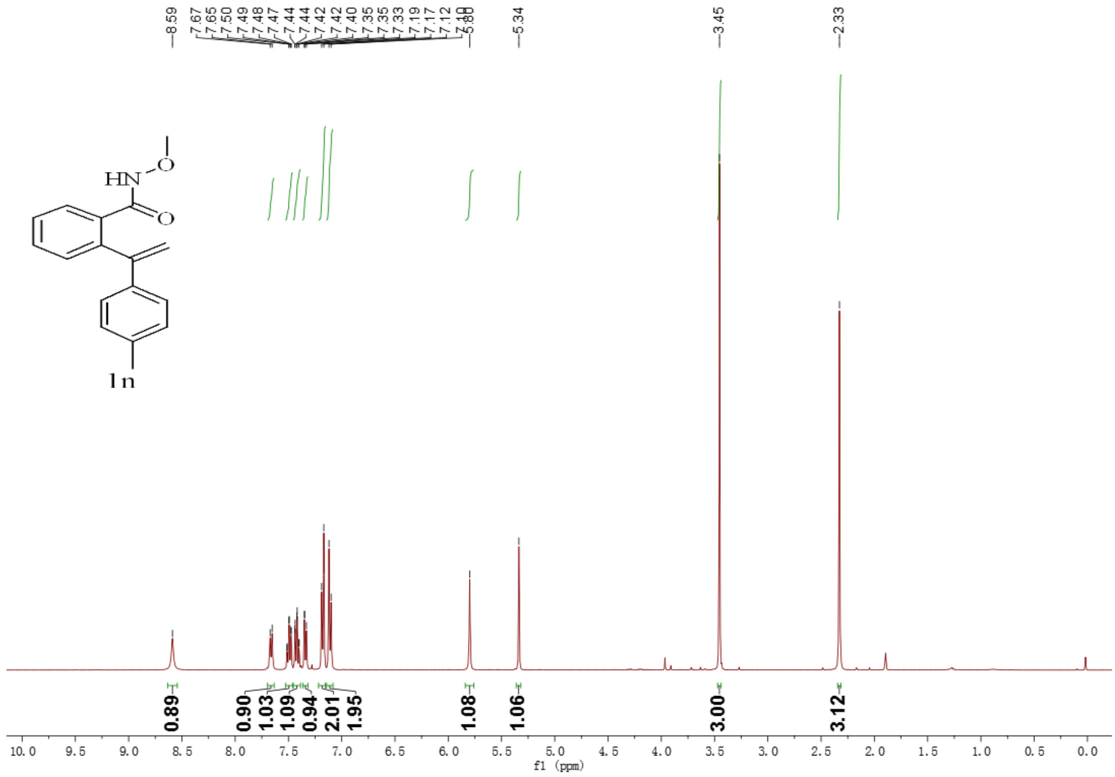
10.00
7.44
7.42
7.28
7.26
7.24
7.15
7.13
7.09
7.07
7.04
6.84
6.80
6.78
6.75
5.60
5.54
5.19
5.15
3.59
11
0.94
1.00
1.06
1.04
0.94
0.91
1.03
1.03
3.00
f1 (ppm)

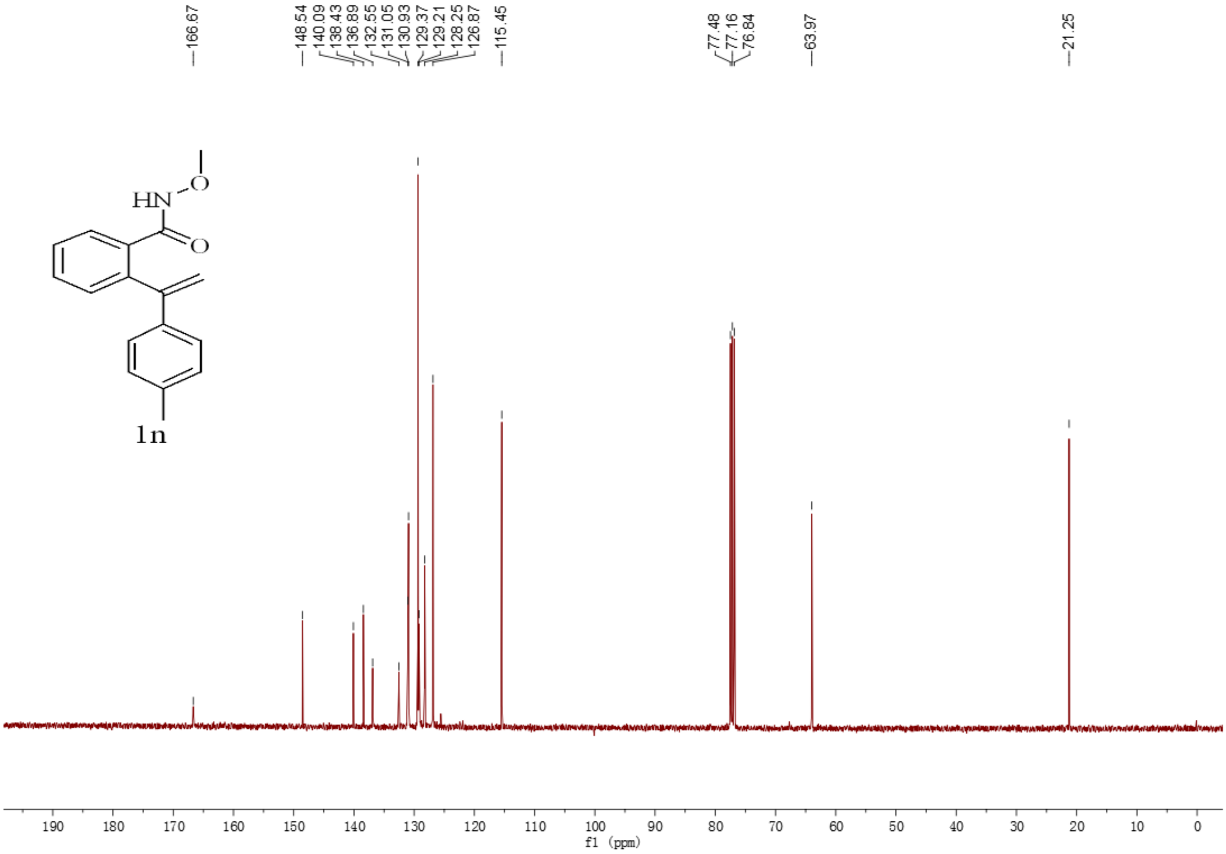


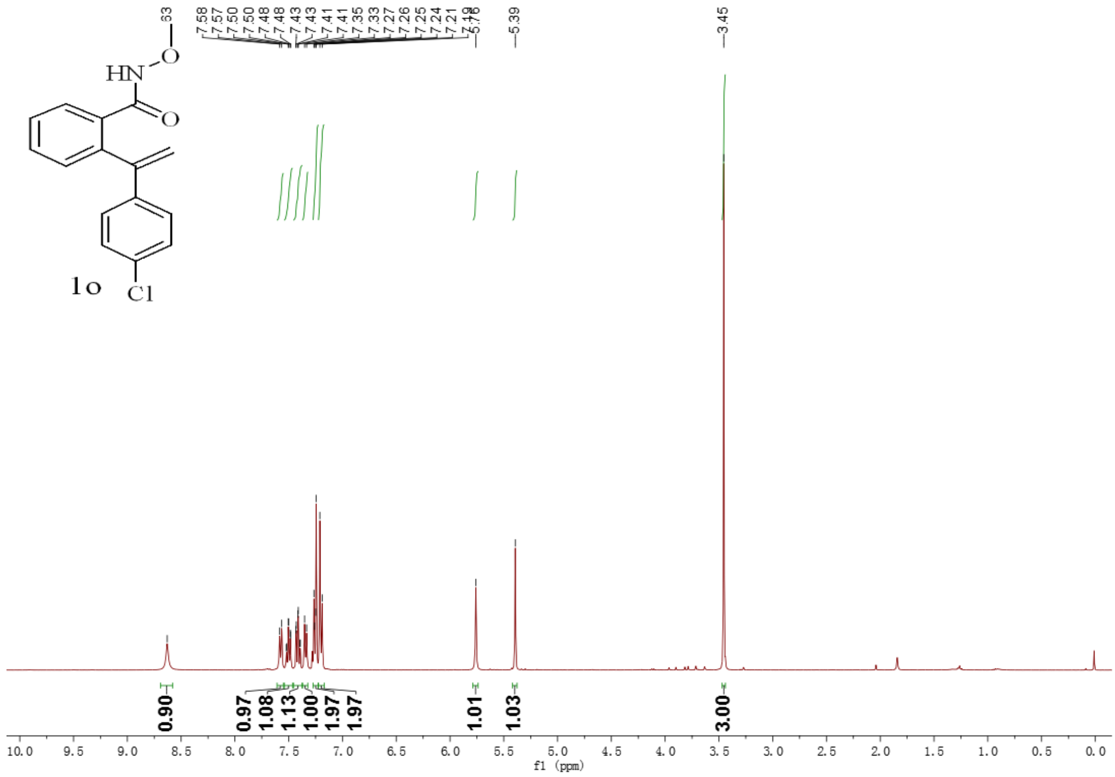
167.02
136.24
133.61
131.45
130.40
127.62
127.30
125.73
116.50
77.59
77.16
76.73
63.89
11
f1 (ppm)

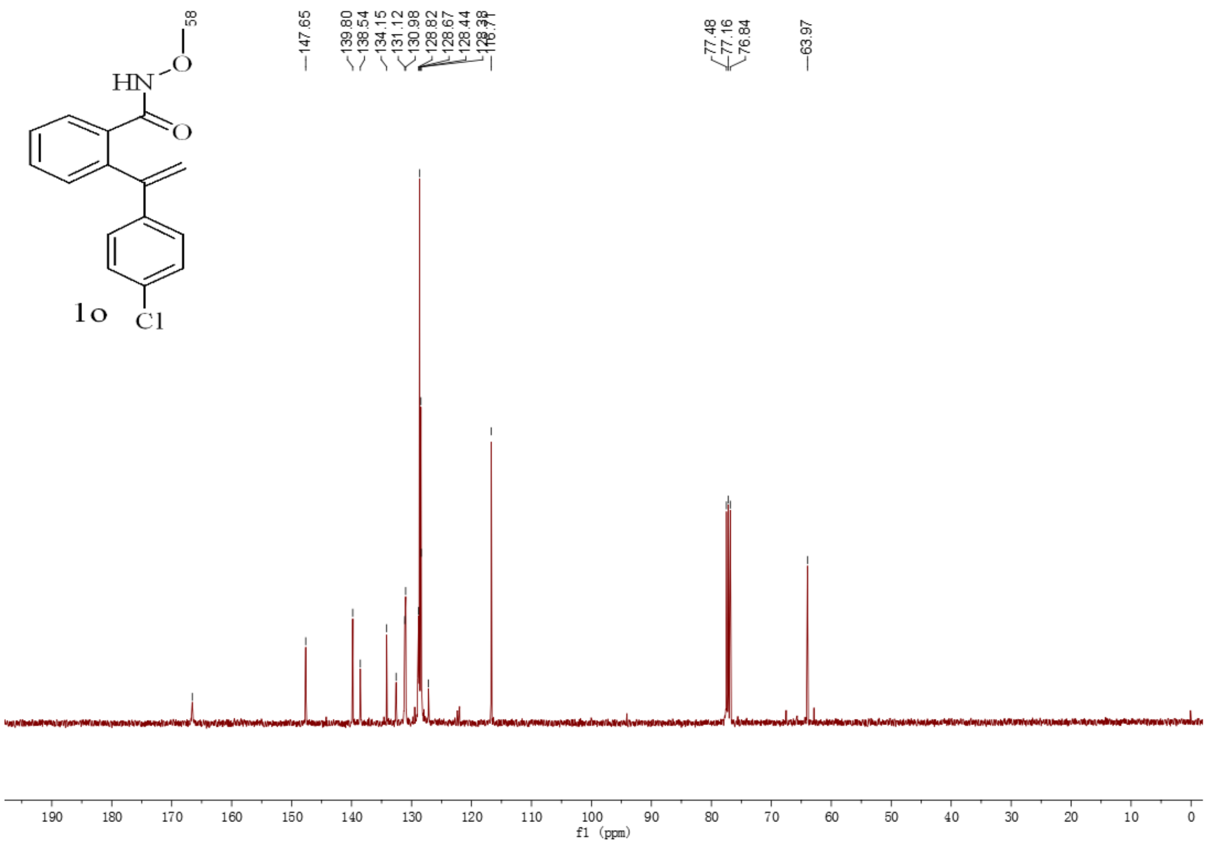


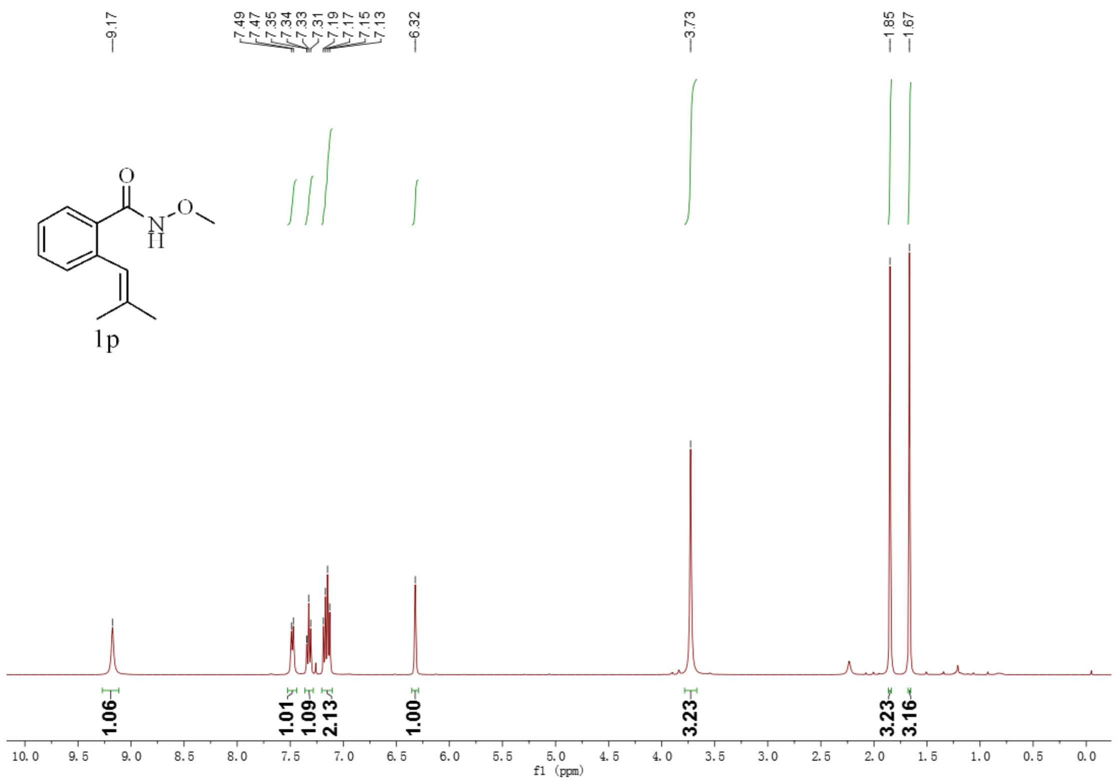


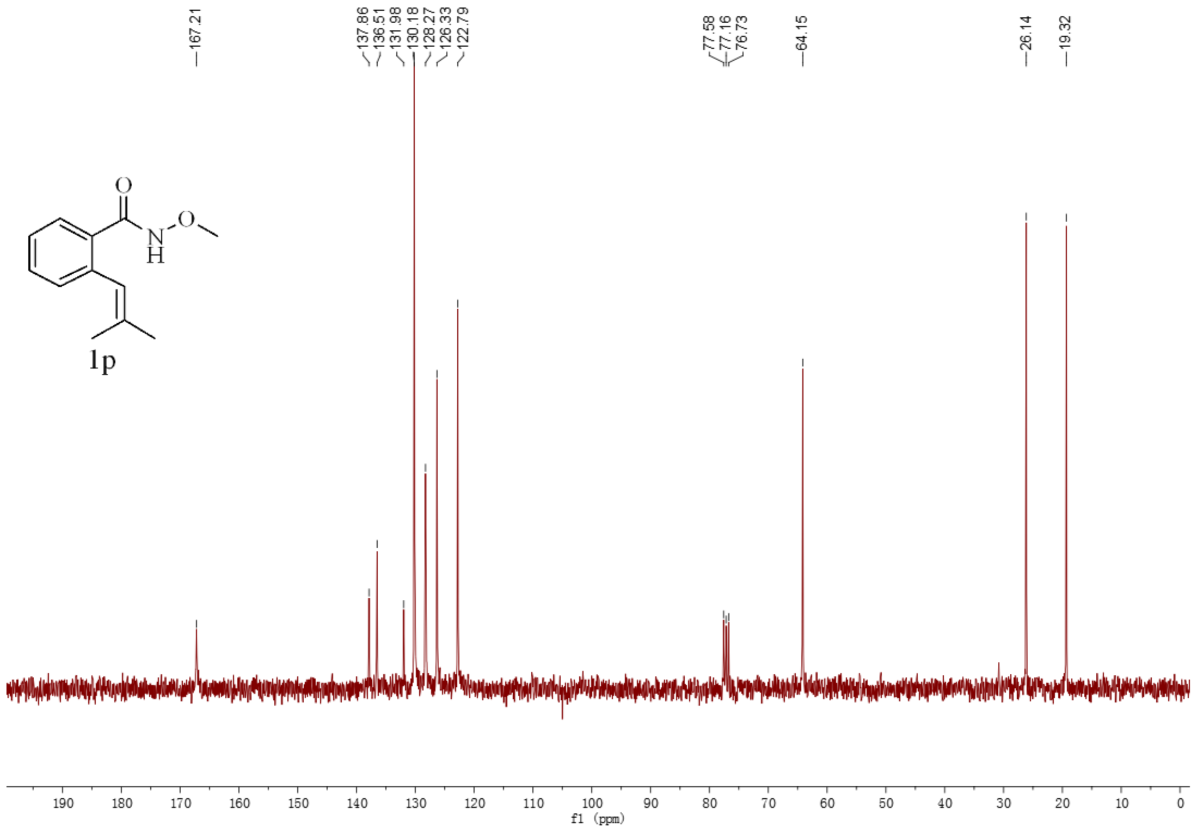

1n
f1 (ppm)

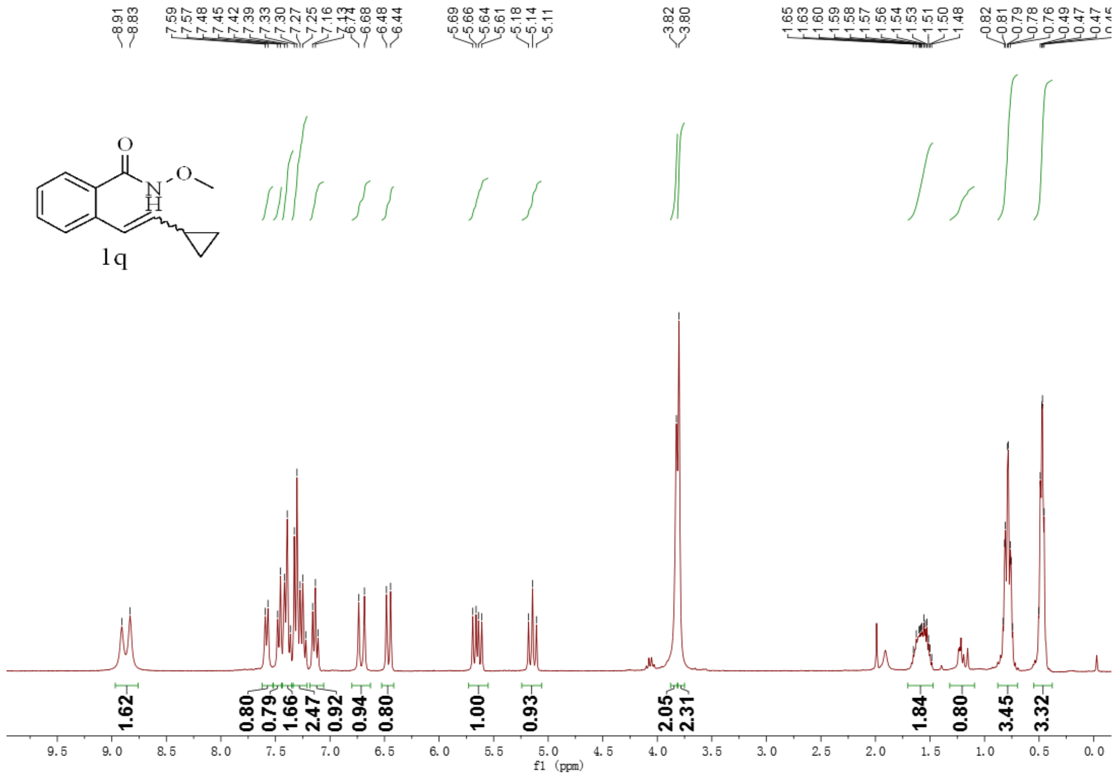

1n
f1 (ppm)

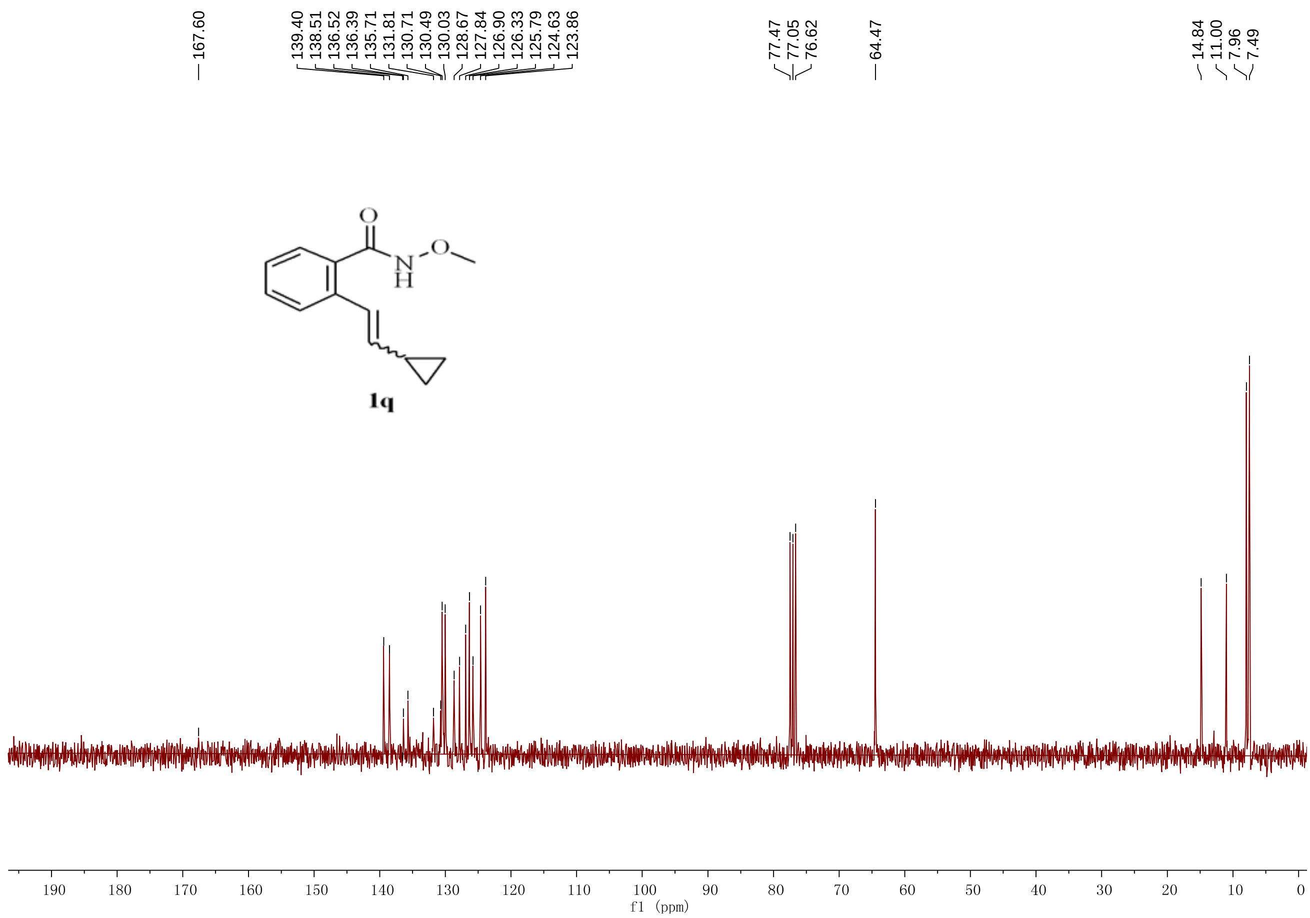


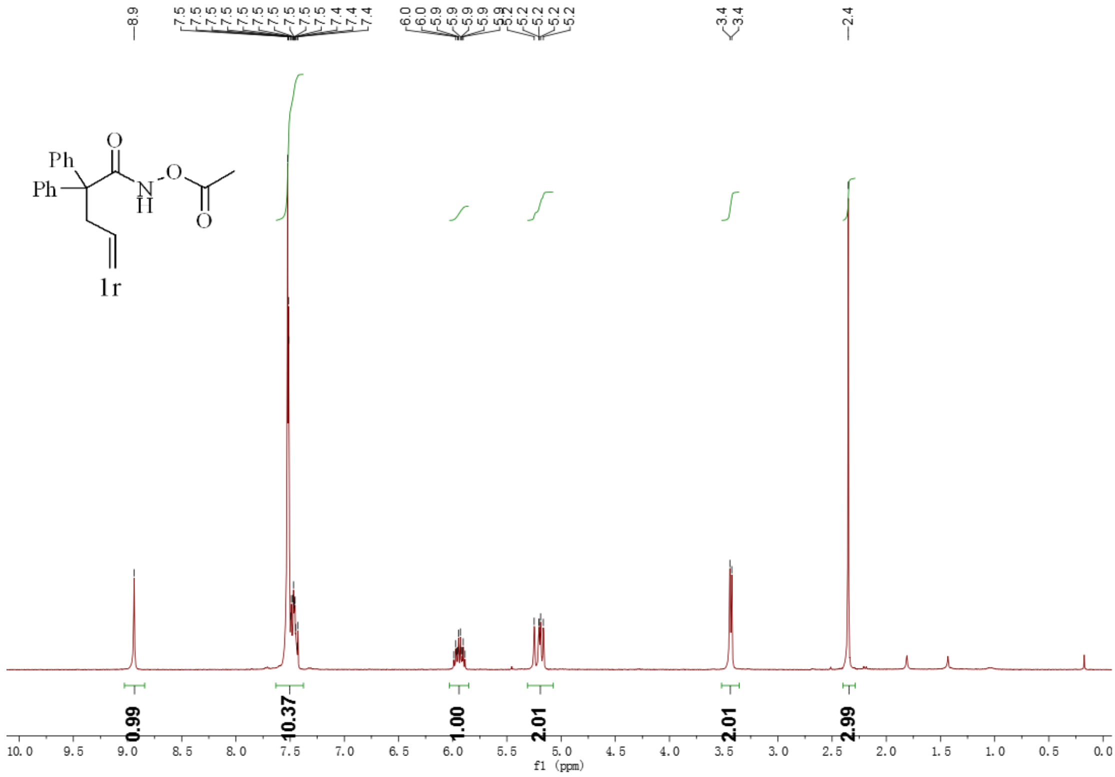


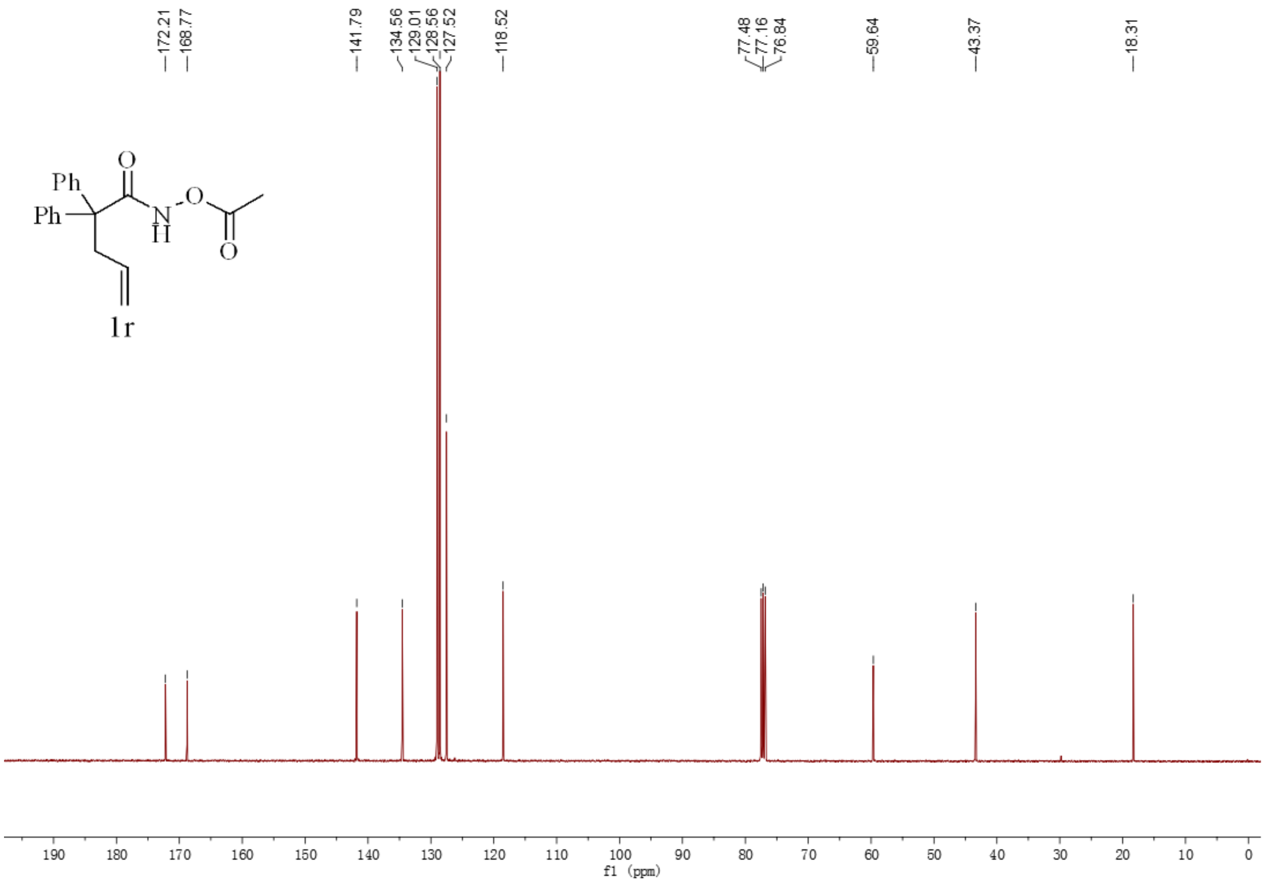


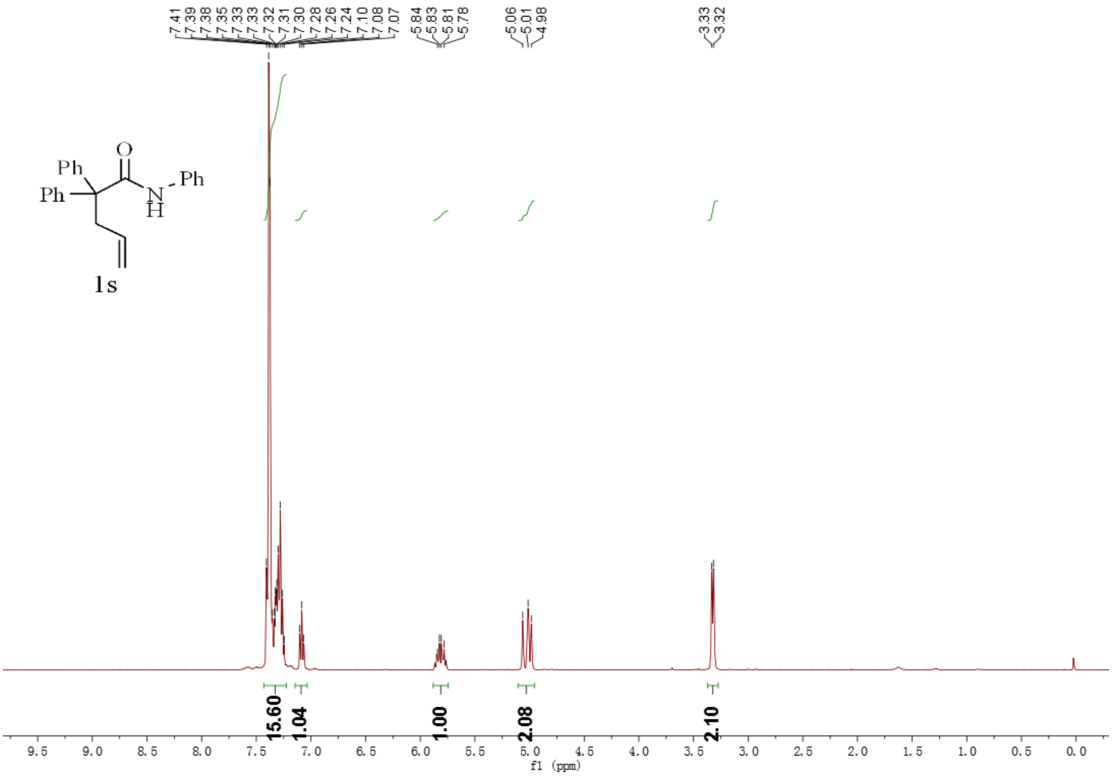


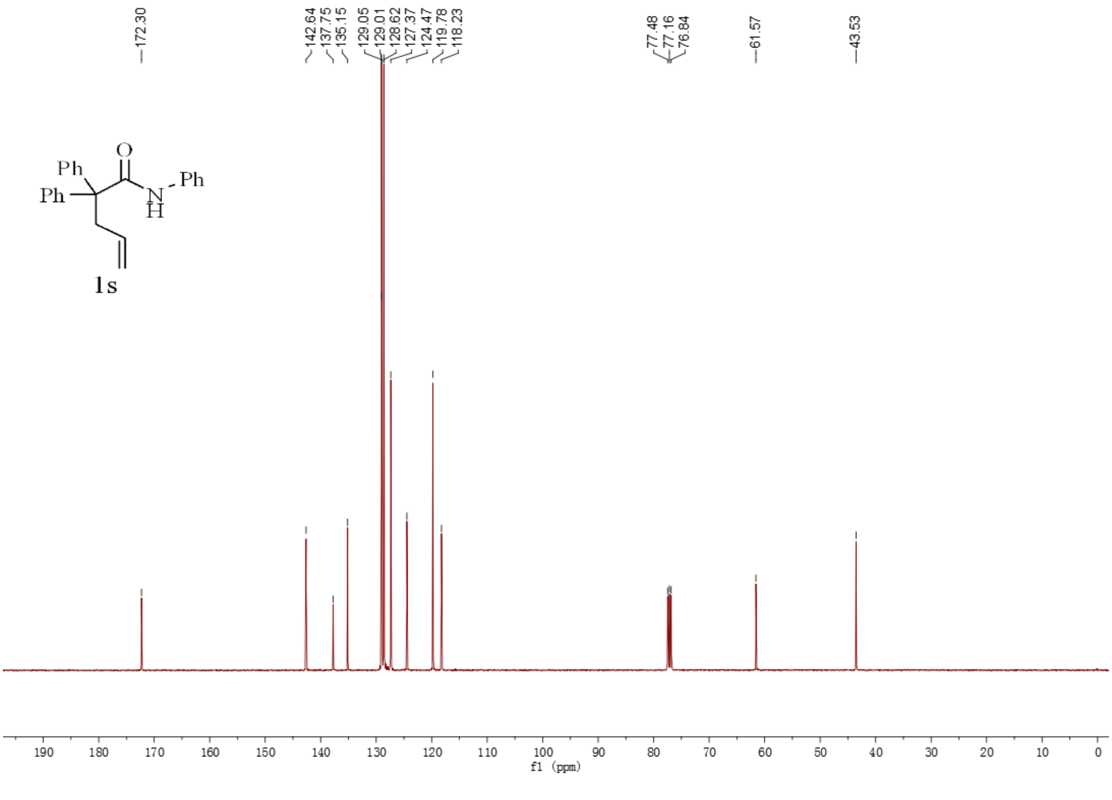

8.91
8.83
7.59
7.57
7.48
7.45
7.42
7.39
7.33
7.30
7.27
7.25
7.16
7.13
6.68
6.48
6.44
5.69
5.66
5.64
5.61
5.18
5.14
5.11
3.82
3.80
1.65
1.63
1.60
1.59
1.58
1.57
1.56
1.54
1.53
1.51
1.50
1.48
0.82
0.81
0.79
0.78
0.76
0.49
0.47
O
N
O
H
1q
1.62
0.80
0.79
1.66
2.47
0.92
0.94
0.80
1.00
0.93
2.05
2.31
1.84
0.80
3.45
3.32
f1 (ppm)

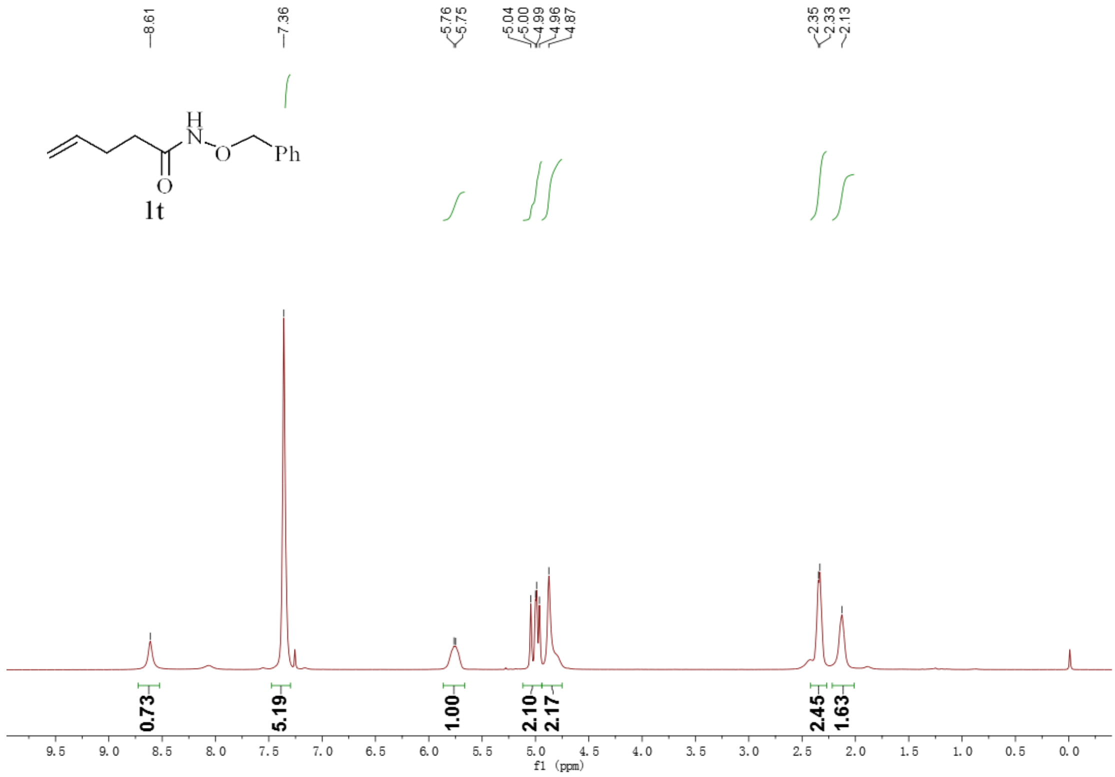

167.60
139.40
138.51
136.52
136.39
135.71
131.81
130.71
130.49
130.03
128.67
127.84
126.90
126.33
125.79
124.63
123.86
77.47
77.05
76.62
64.47
14.84
11.00
7.96
7.49
O
N
O
H
1q
f1 (ppm)


8.9
7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.5 7.4 7.4 7.4
6.0 6.0 5.9 5.9 5.9 5.9 5.9 5.2 5.2 5.2 5.2 5.2
3.4 3.4
2.4
Ph
Ph
O
N
H
O
O
1r
0.99
10.37
1.00
2.01
2.01
2.99
f1 (ppm)

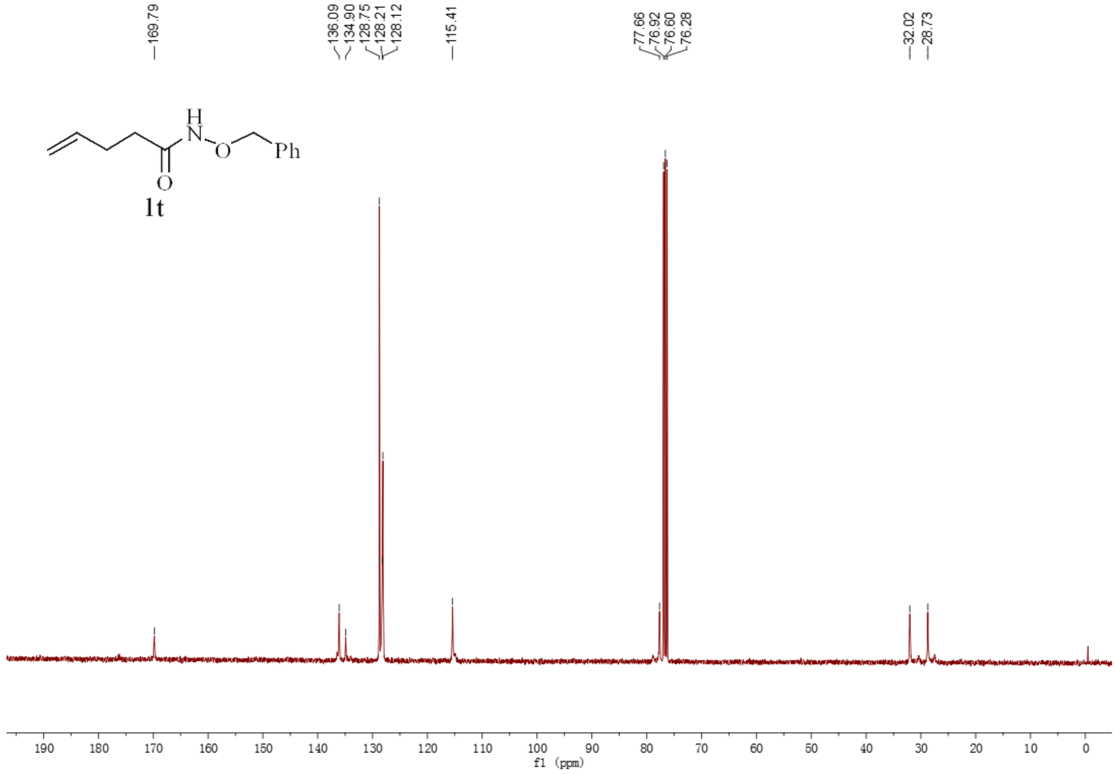

172.21
168.77
141.79
134.56
129.01
128.56
127.52
118.52
77.48
77.16
76.84
59.64
43.37
18.31
Ph
Ph
O
N
H
O
O
1r
f1 (ppm)


7.41
7.39
7.38
7.35
7.33
7.33
7.32
7.31
7.30
7.28
7.26
7.24
7.10
7.08
7.07
5.84
5.83
5.81
5.78
5.06
5.01
4.98
3.33
3.32
15.60
1.04
1.00
2.08
2.10
f1 (ppm)

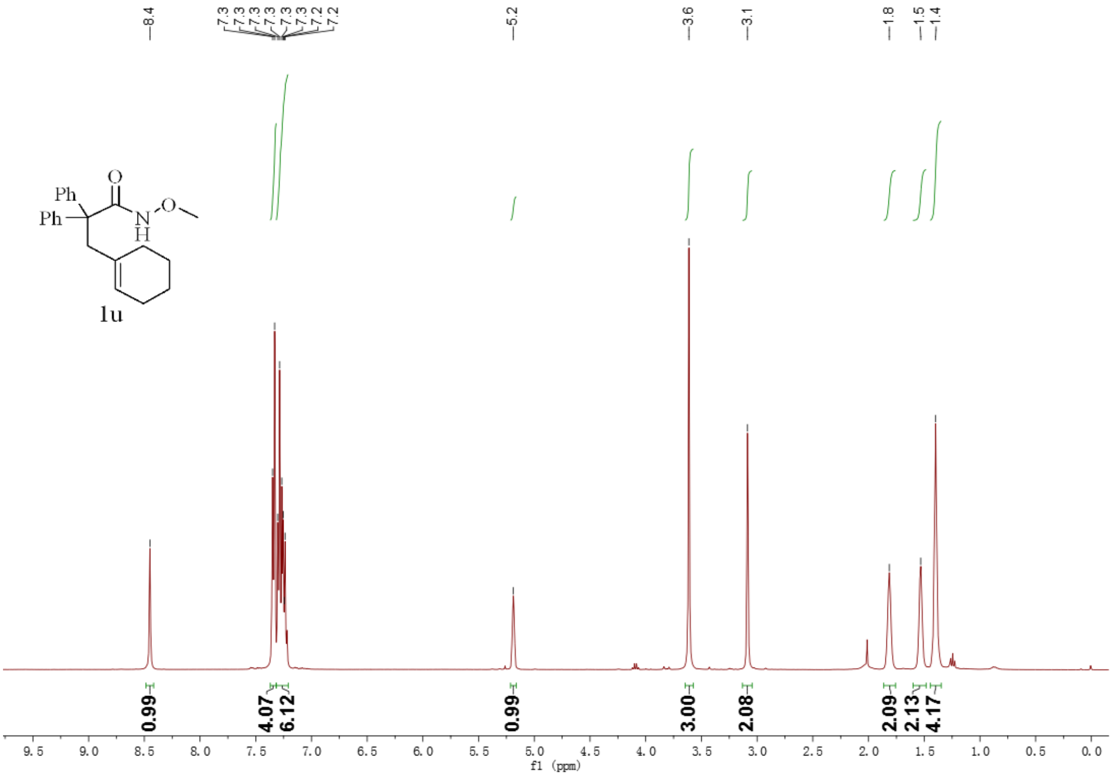

172.30
142.64
137.75
135.15
129.05
129.01
128.62
127.37
124.47
119.78
118.23
77.48
77.16
76.84
61.57
43.53
f1 (ppm)



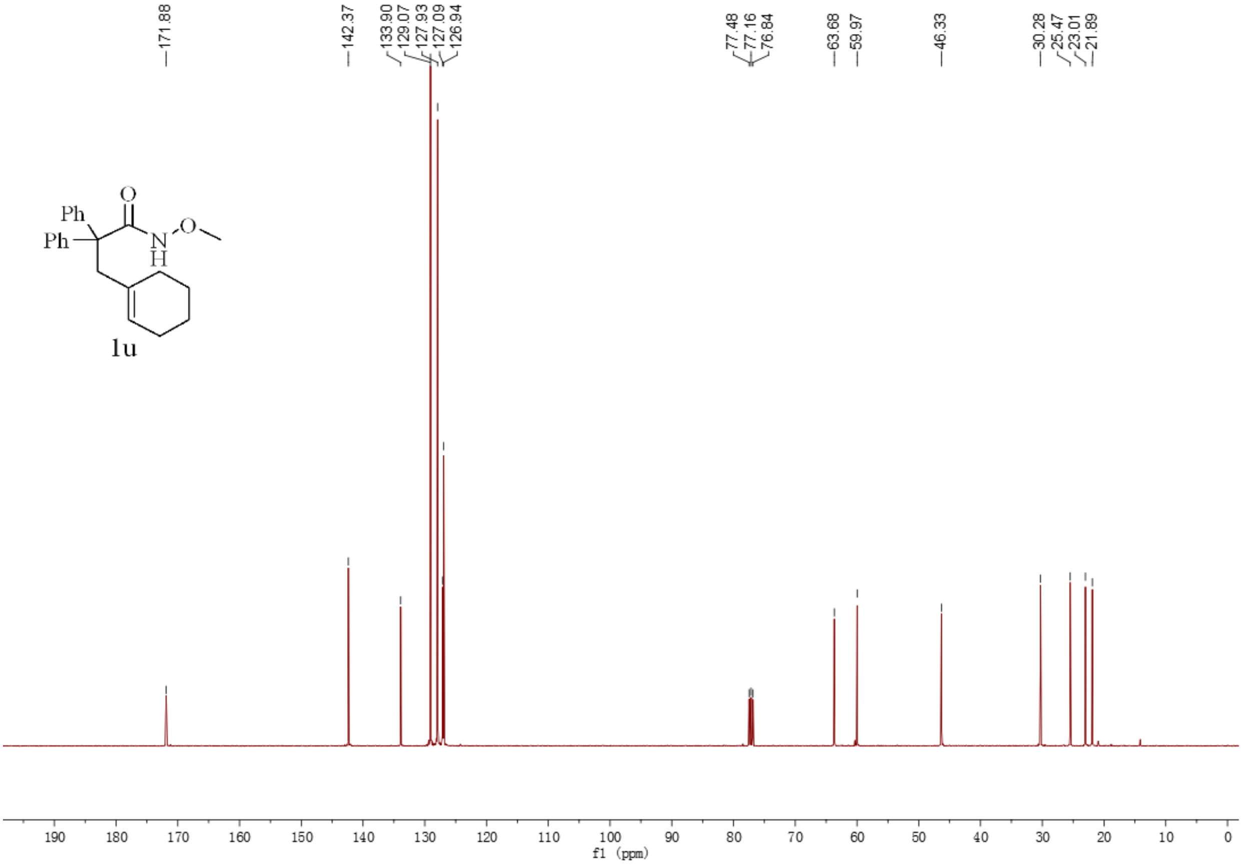
1t



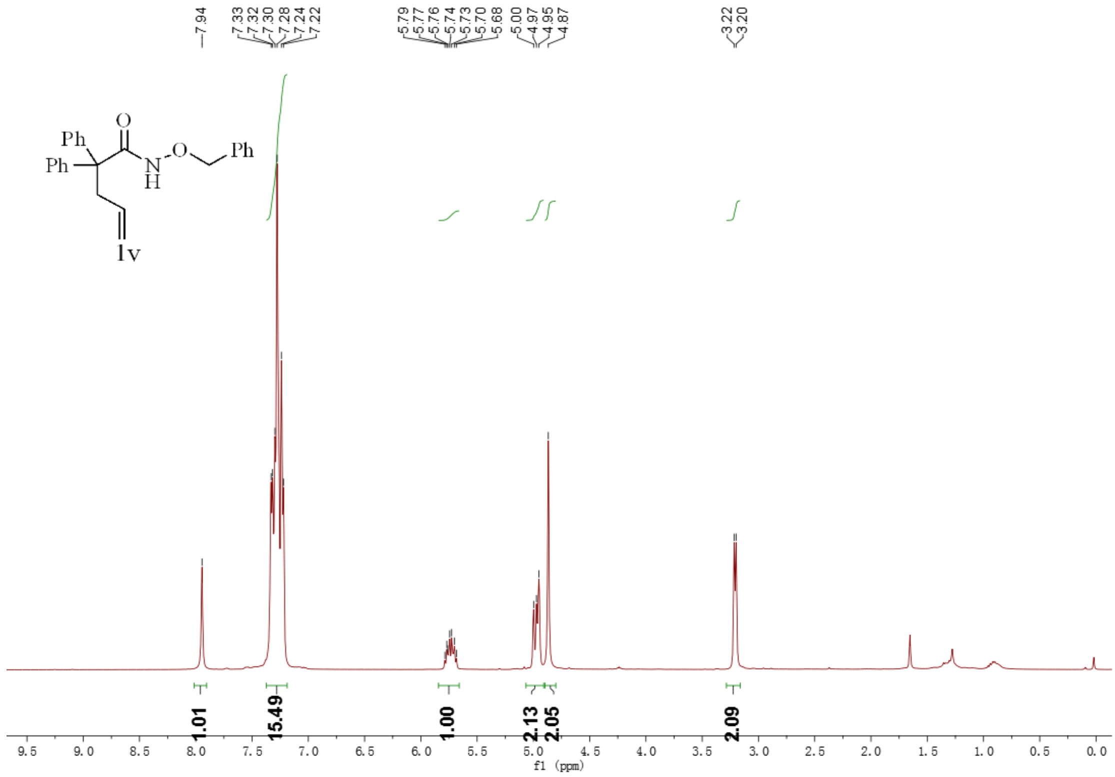
1t

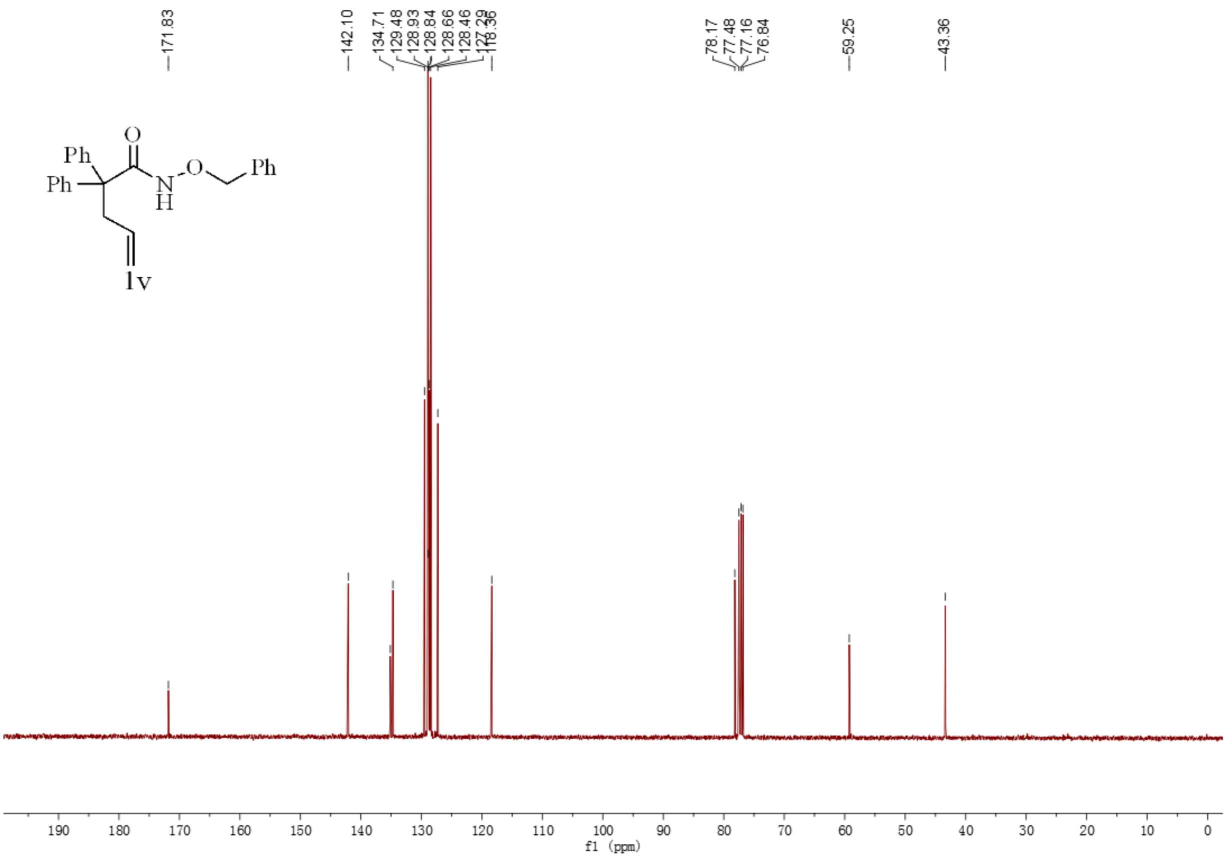


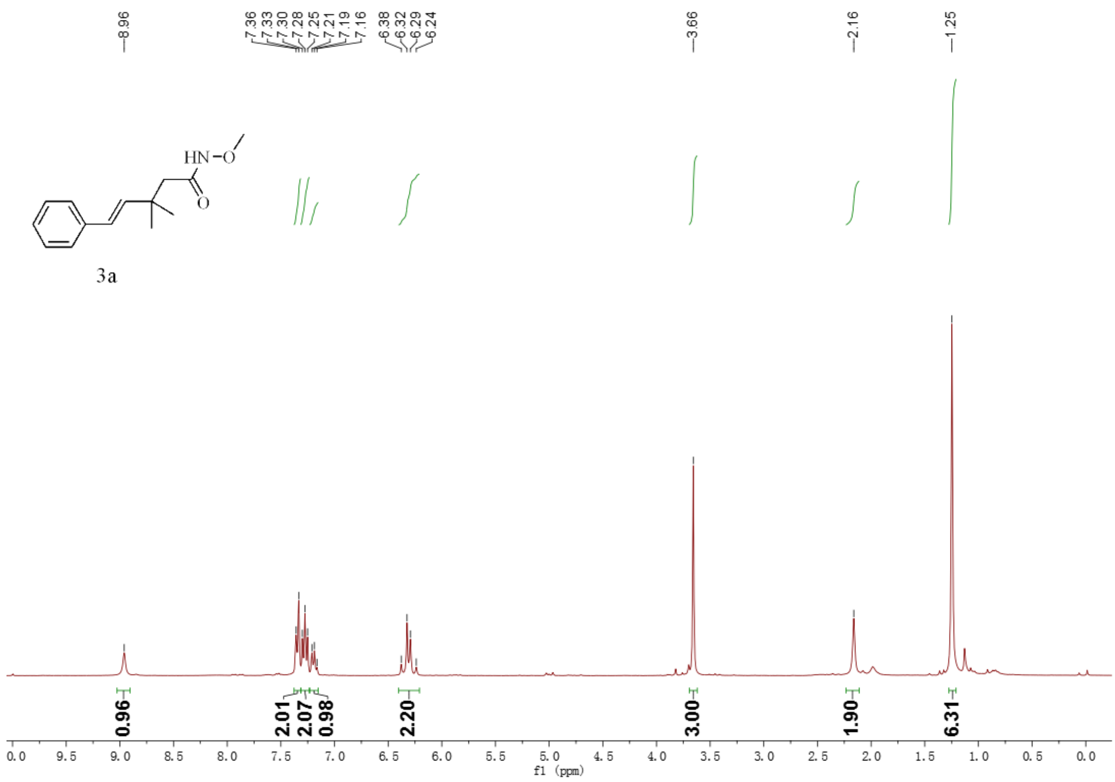
8.4
7.3
7.3
7.3
7.3
7.3
7.3
7.2
7.2
5.2
3.6
3.1
1.8
1.5
1.4
Ph
Ph
O
N
H
O
1u
0.99
4.07
6.12
0.99
3.00
2.08
2.09
2.13
4.17
f1 (ppm)



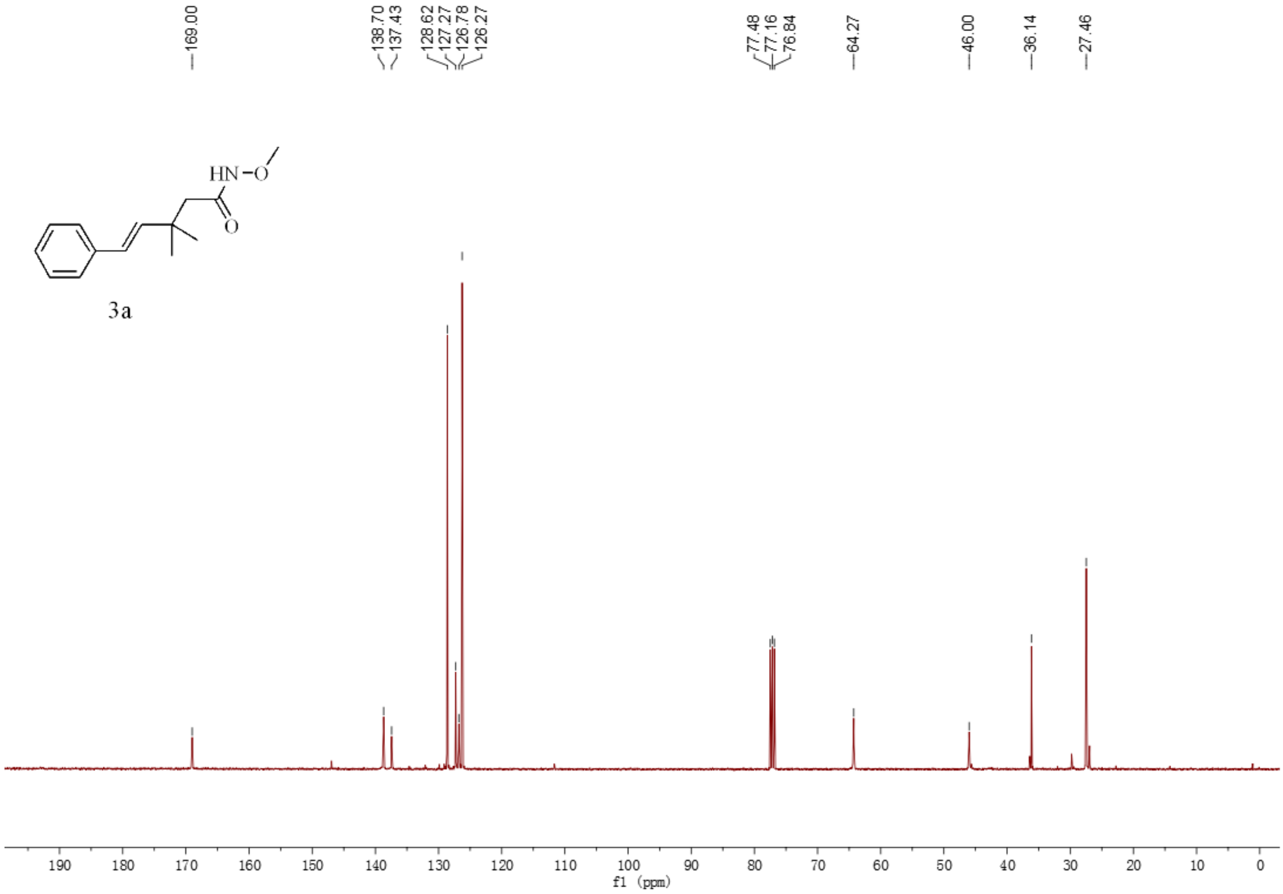
171.88
142.37
133.90
129.07
127.93
127.09
126.94
77.48
77.16
76.84
63.68
59.97
46.33
30.28
25.47
23.01
21.89
Ph
Ph
O
N
H
O
1u
f1 (ppm)


7.94
7.33
7.32
7.30
7.28
7.24
7.22
5.79
5.77
5.76
5.74
5.73
5.70
5.68
5.00
4.97
4.95
4.87
3.22
3.20
Ph
Ph
O
N
H
O
Ph
1v
1.01
15.49
1.00
2.13
2.05
2.09
f1 (ppm)

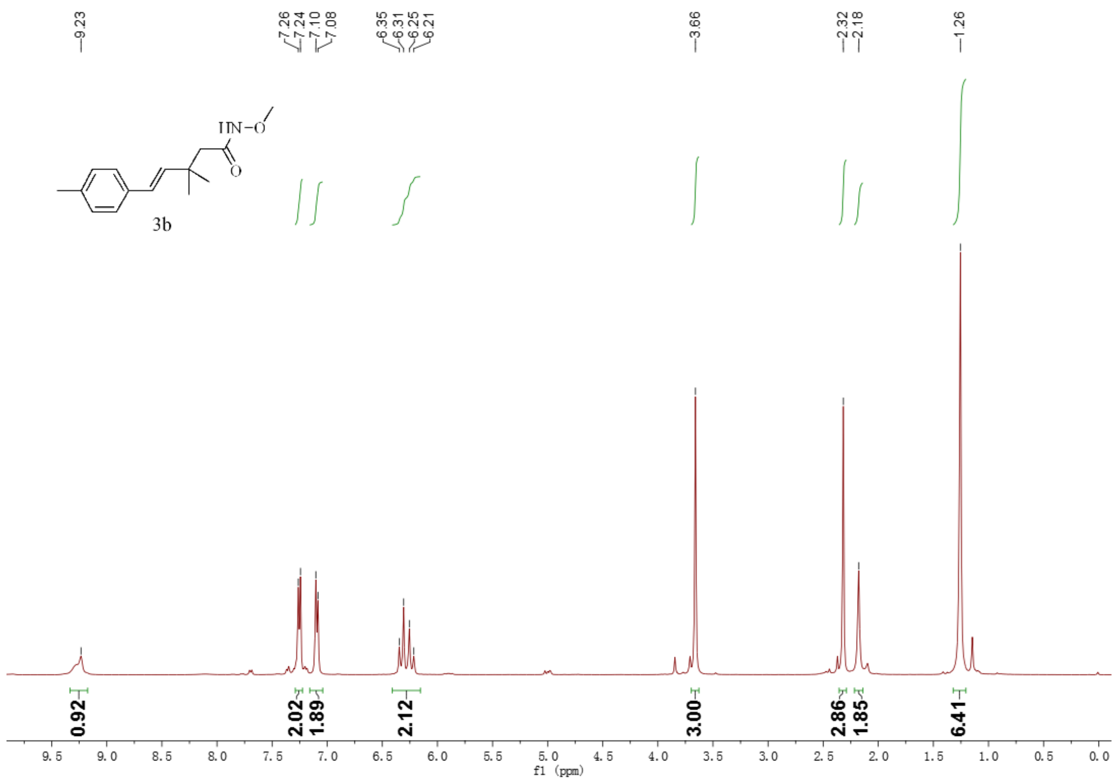

171.83
142.10
134.71
129.48
128.93
128.84
128.66
128.46
127.29
118.36
78.17
77.48
77.16
76.84
59.25
43.36
Ph
Ph
O
N
H
O
Ph
1v
f1 (ppm)

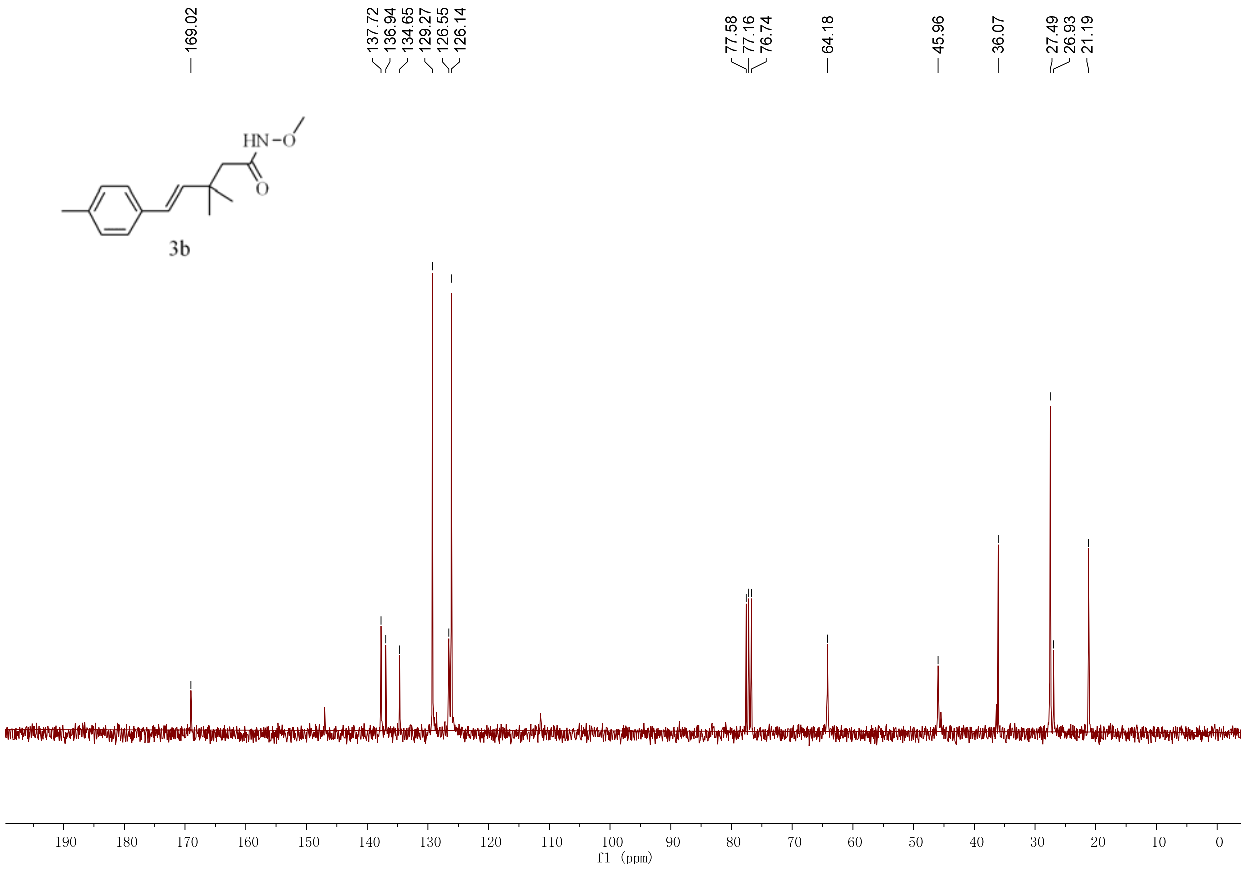


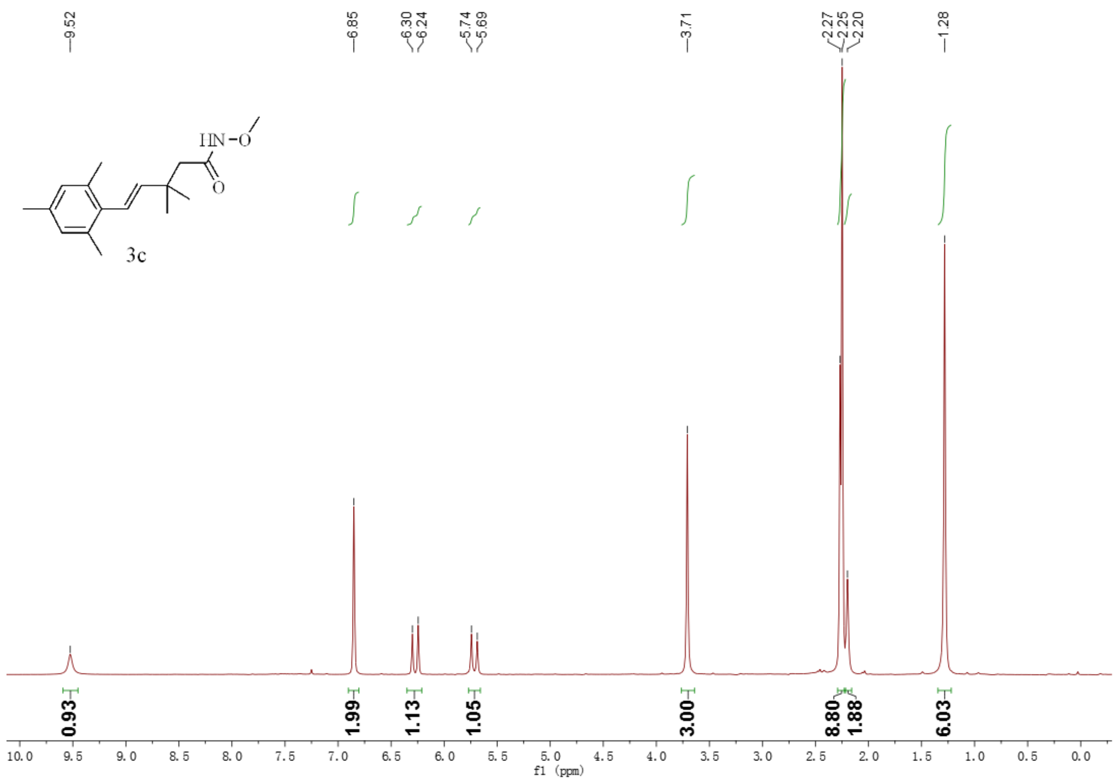
3a

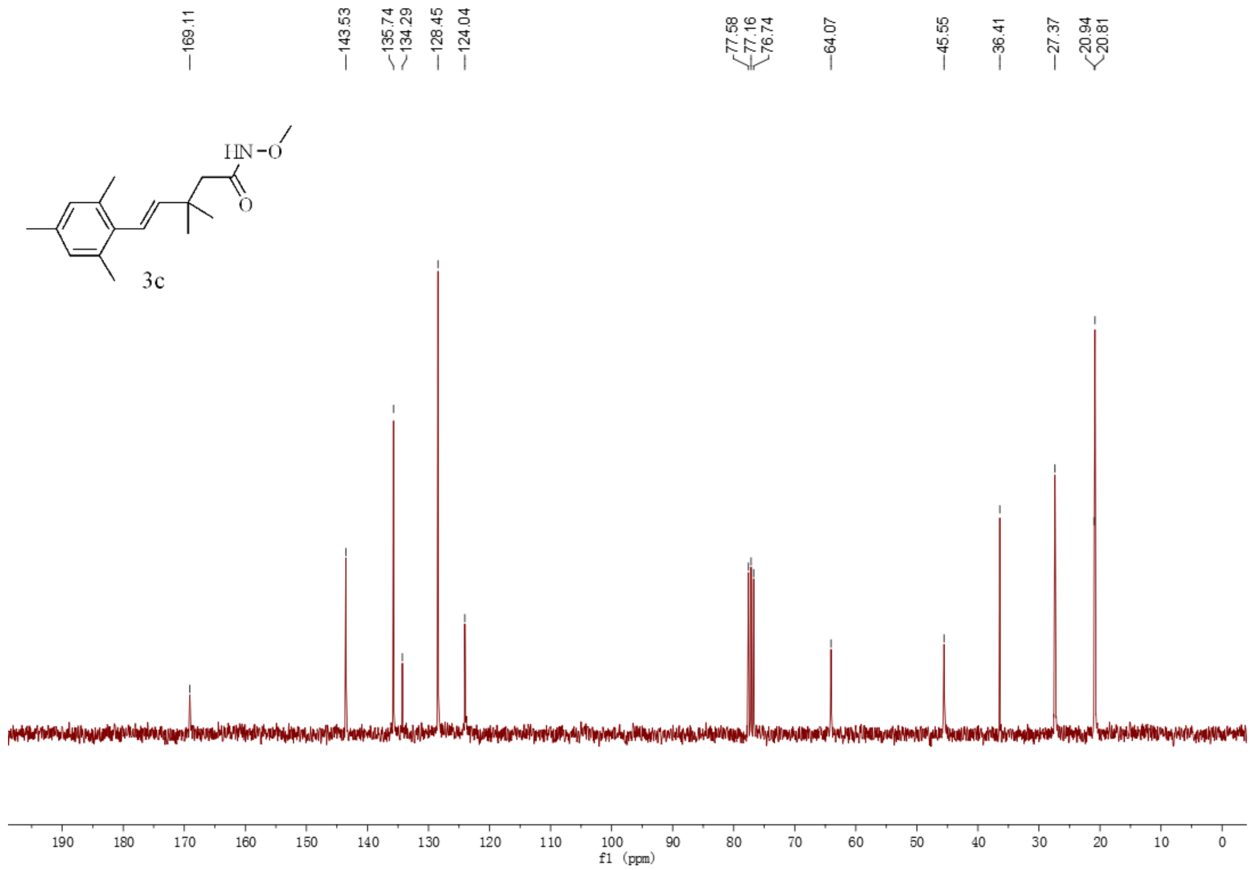


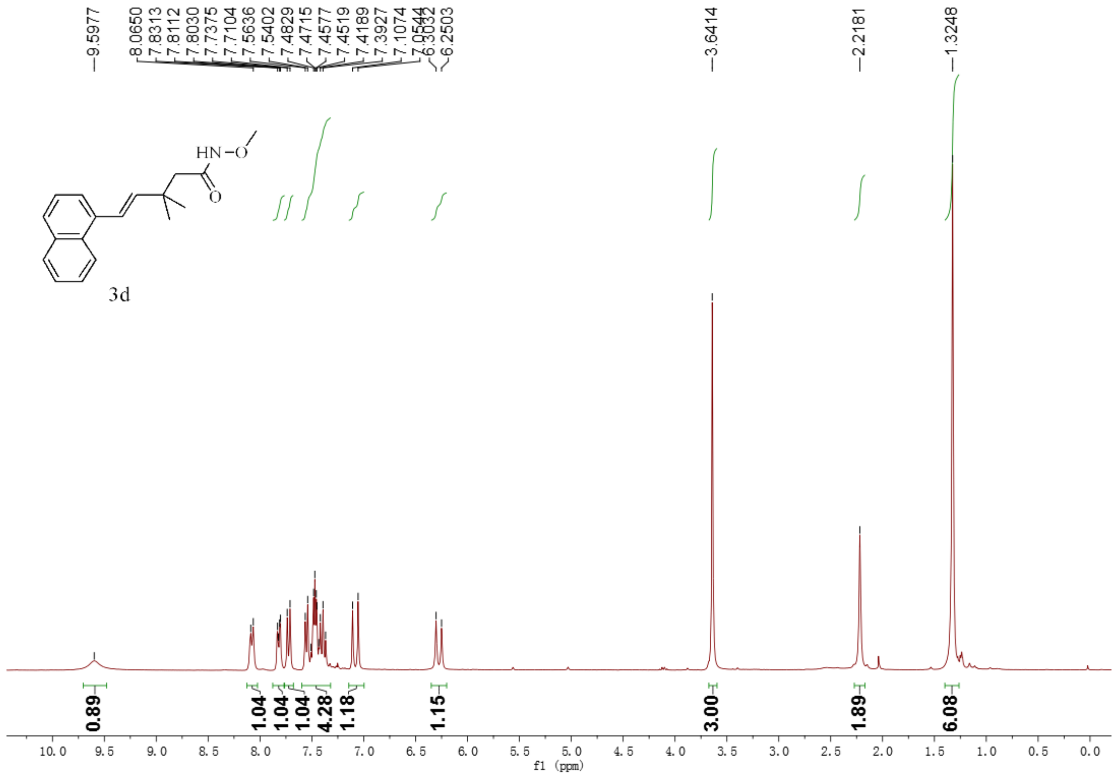
3a

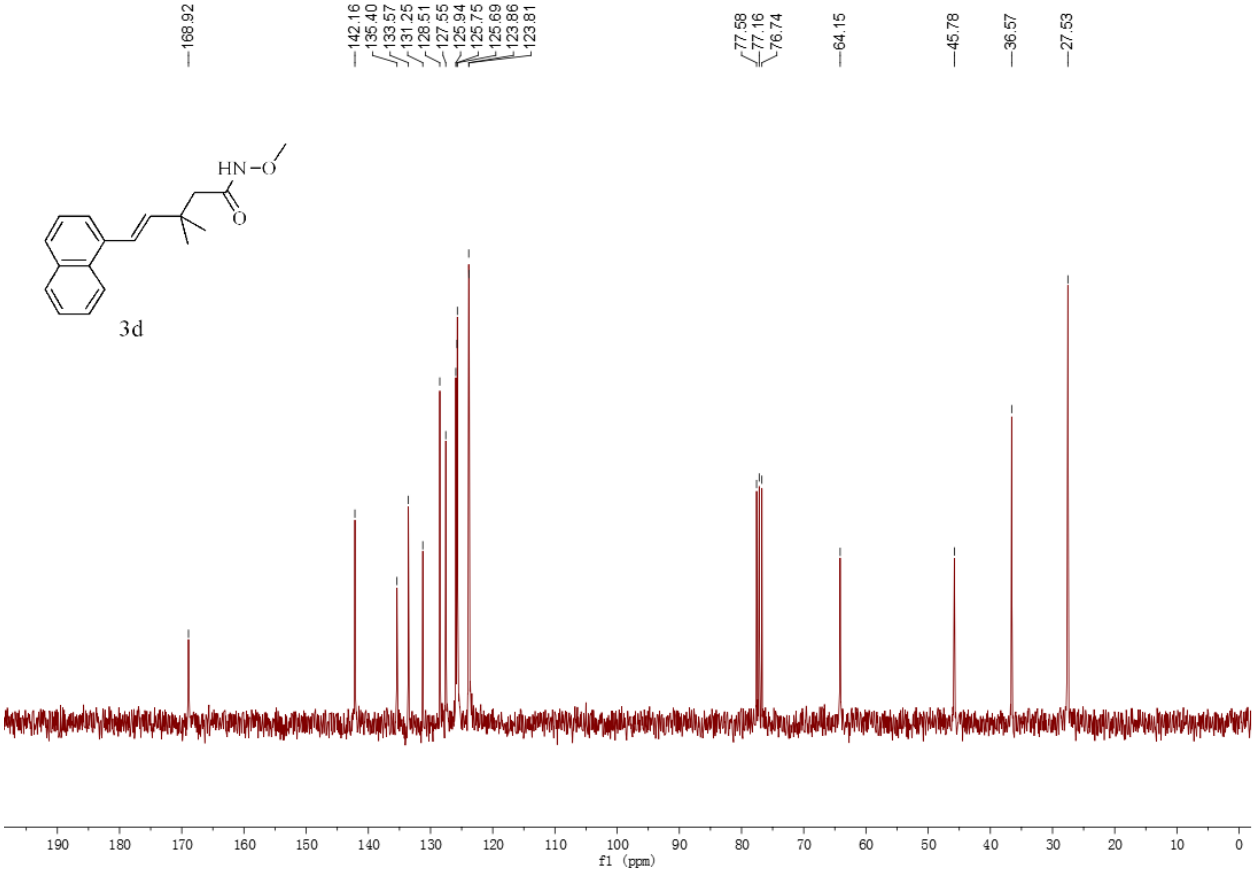


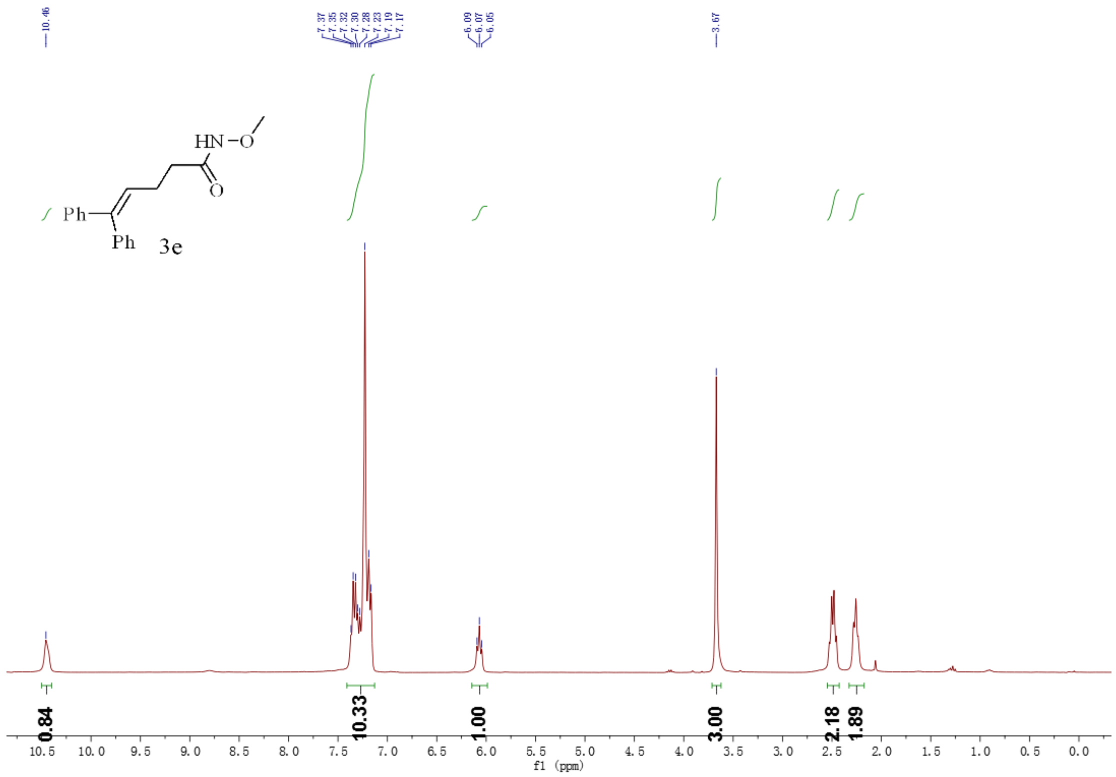


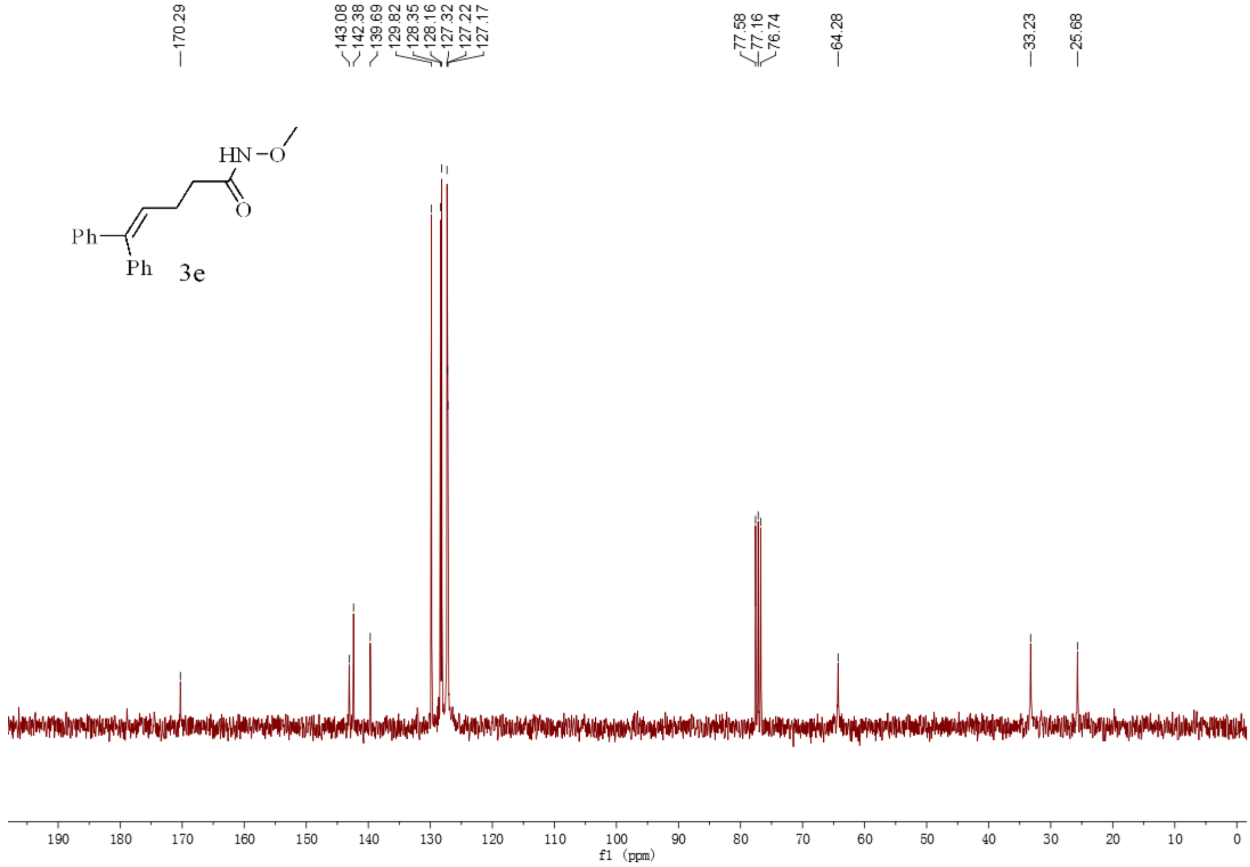


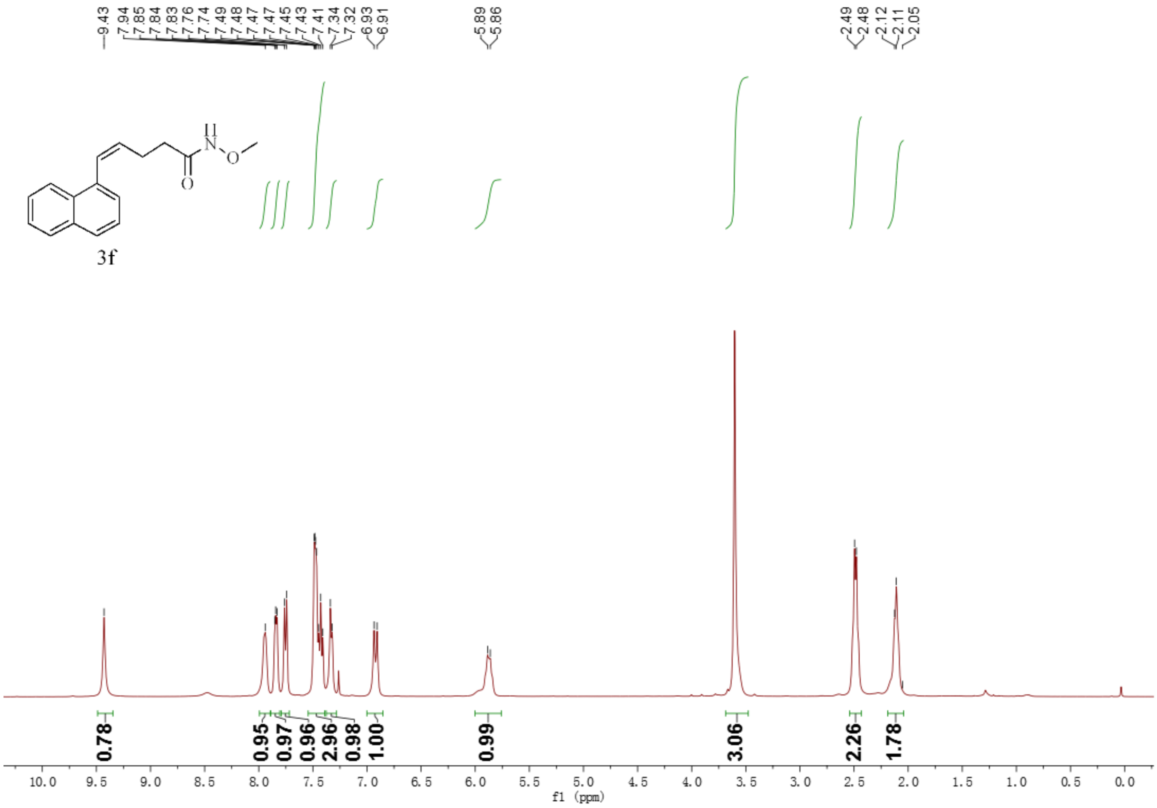



9.5977
8.0650
7.8313
7.8112
7.8030
7.7375
7.7104
7.5636
7.5402
7.4829
7.4715
7.4577
7.4519
7.4189
7.3927
7.1074
7.0544
6.3032
6.2503
3.6414
2.2181
1.3248
HN–O
O
3d
0.89
1.04
1.04
1.04
4.28
1.18
1.15
3.00
1.89
6.08
f1 (ppm)

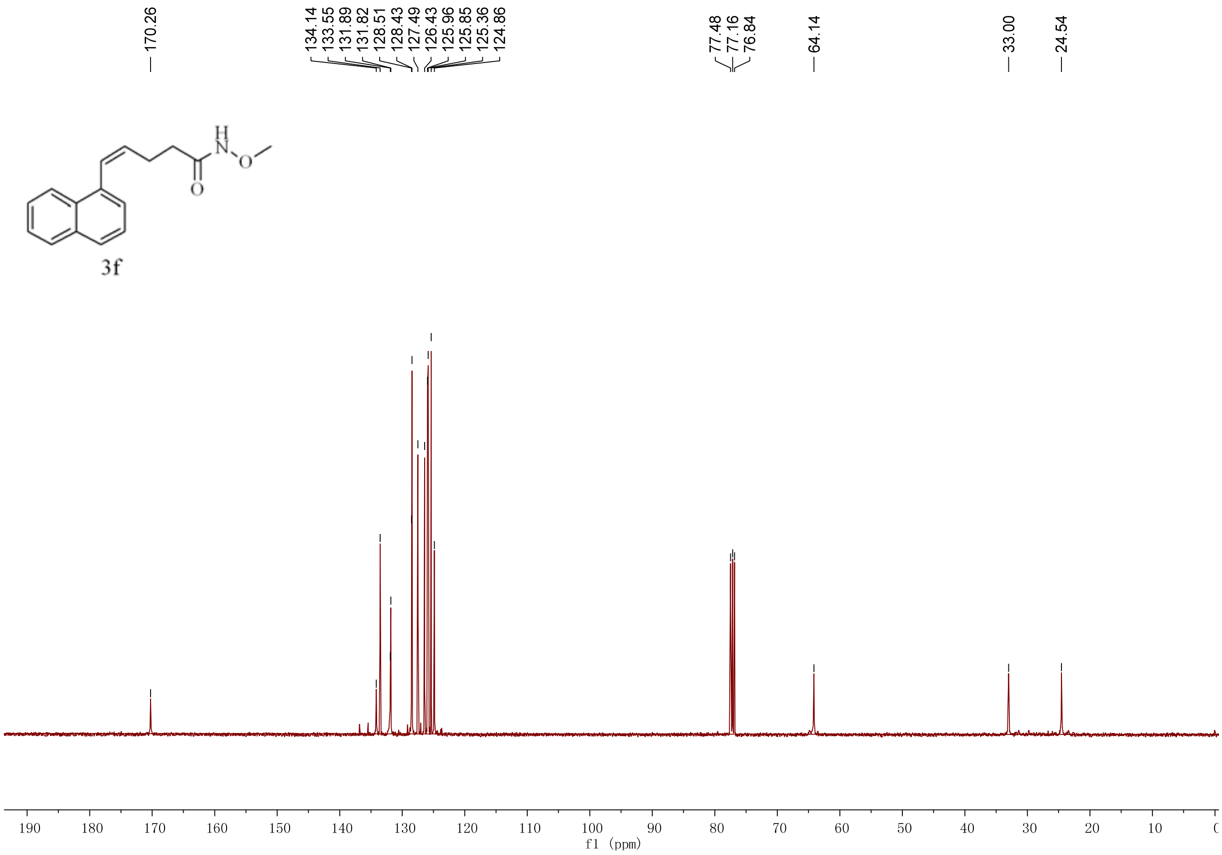

168.92
142.16
135.40
133.57
131.25
128.51
127.55
125.94
125.75
125.69
123.86
123.81
77.58
77.16
76.74
64.15
45.78
36.57
27.53
HN–O
O
3d
f1 (ppm)


10.46
7.37
7.35
7.32
7.30
7.28
7.23
7.19
7.17
6.09
6.07
6.05
3.67
HN
O
O
Ph
Ph
3e
0.84
10.33
1.00
3.00
2.18
1.89
f1 (ppm)

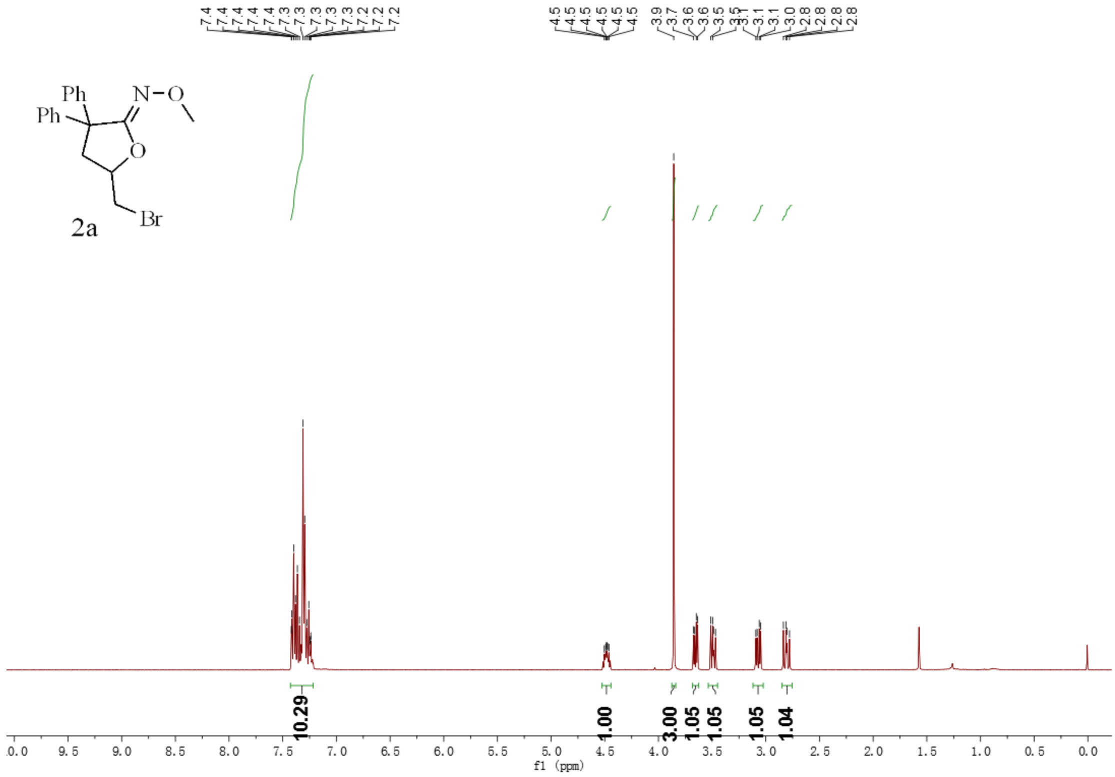

170.29
143.08
142.38
139.69
129.82
128.35
128.16
127.32
127.22
127.17
77.58
77.16
76.74
64.28
33.23
25.68
HN
O
O
Ph
Ph
3e
f1 (ppm)



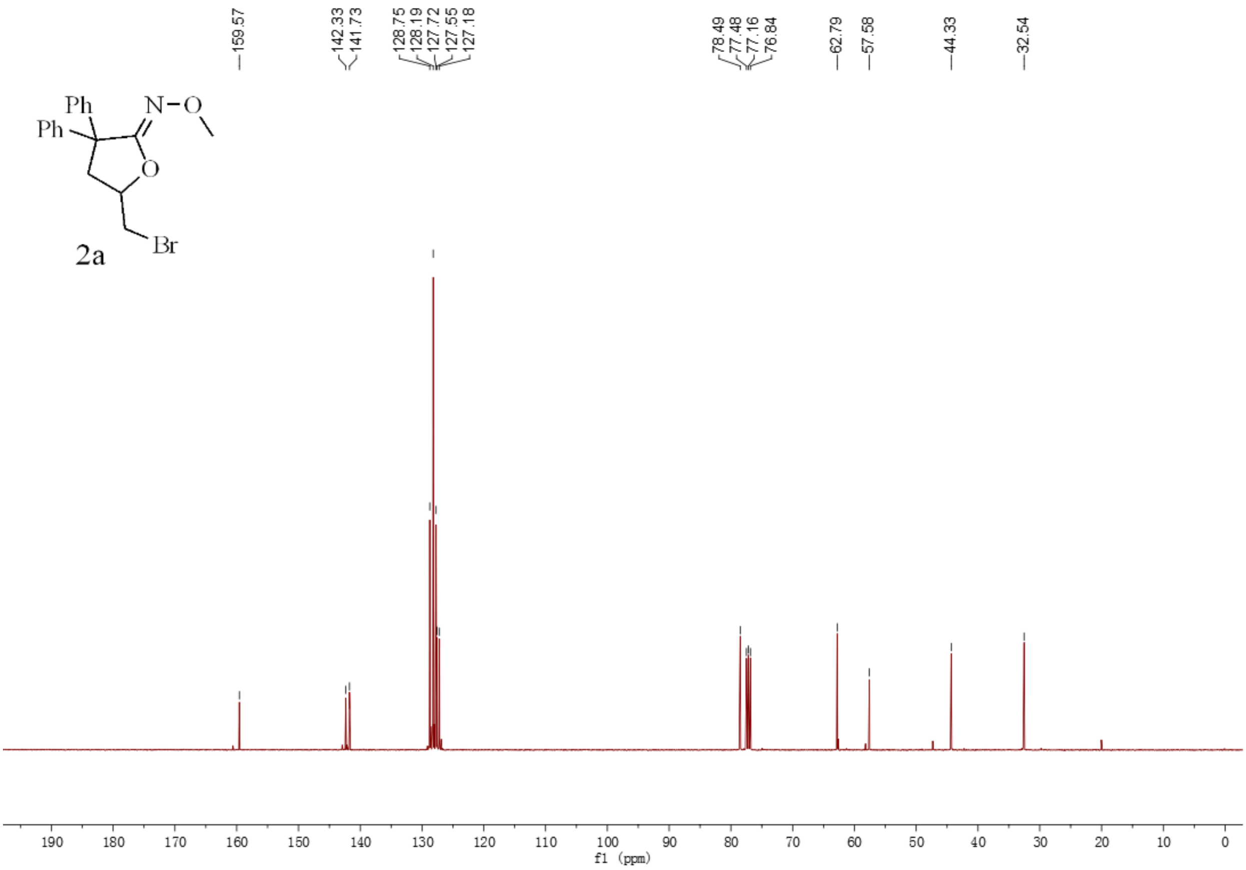
3f



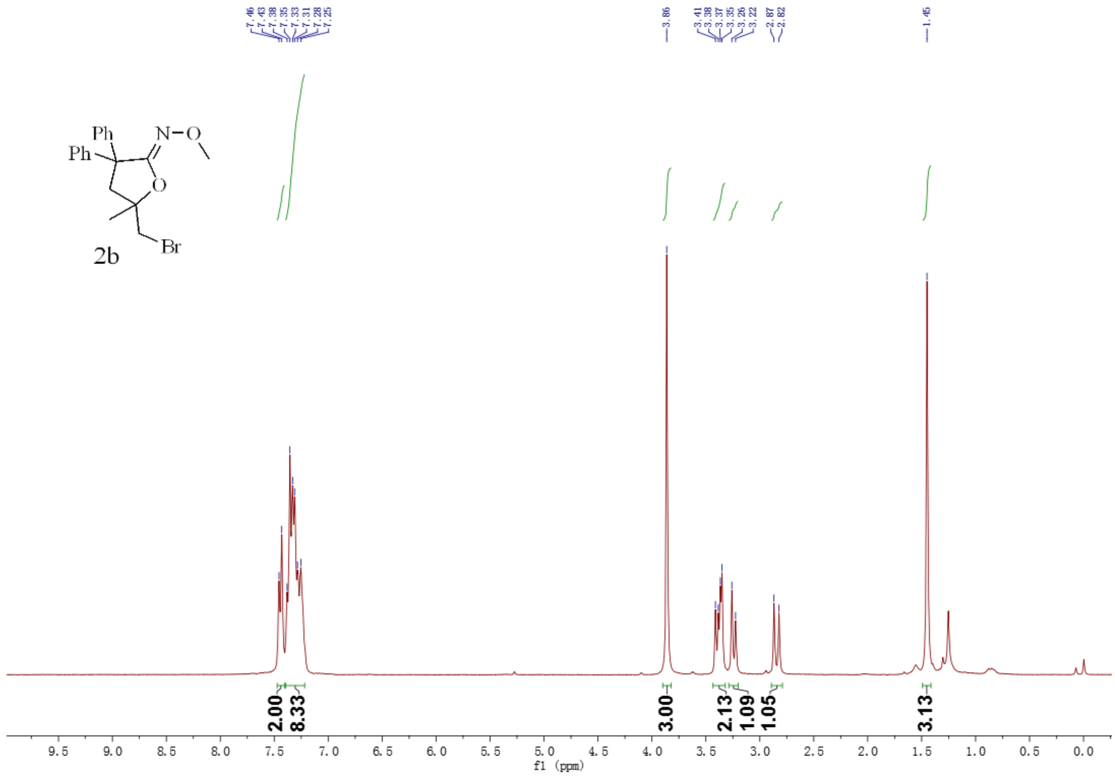
3f


10.29
1.00
3.00
1.05
1.05
1.05
1.04
f1 (ppm)

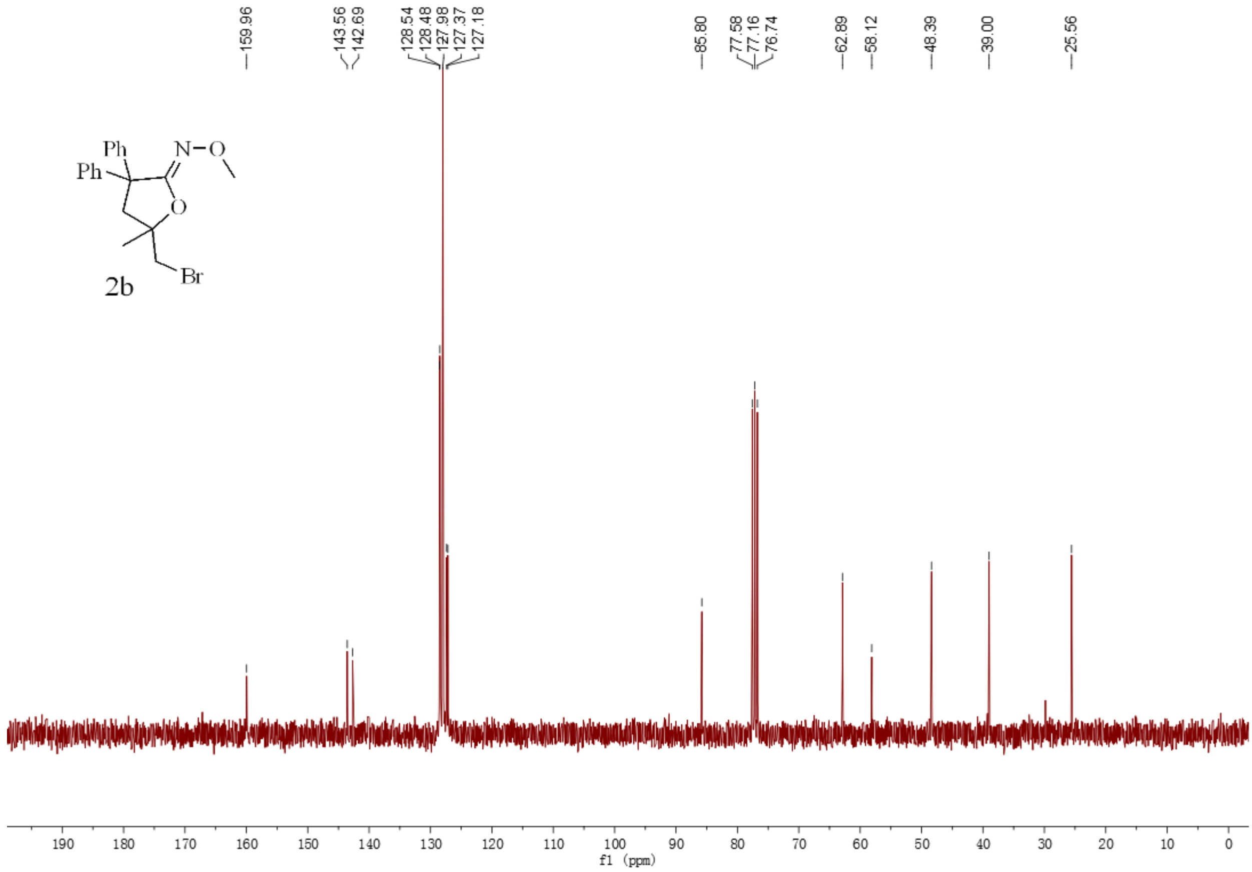
2a


159.57
142.33
141.73
128.75
128.19
127.72
127.55
127.18
78.49
77.48
77.16
76.84
62.79
57.58
44.33
32.54
f1 (ppm)

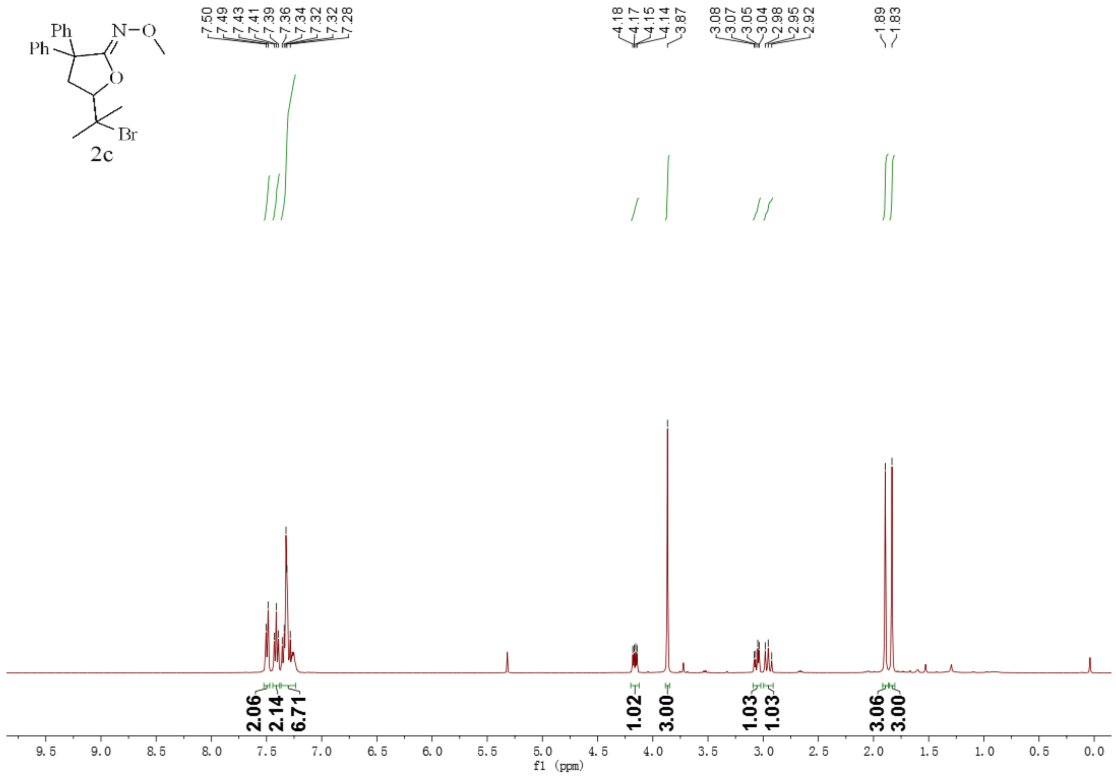
2a

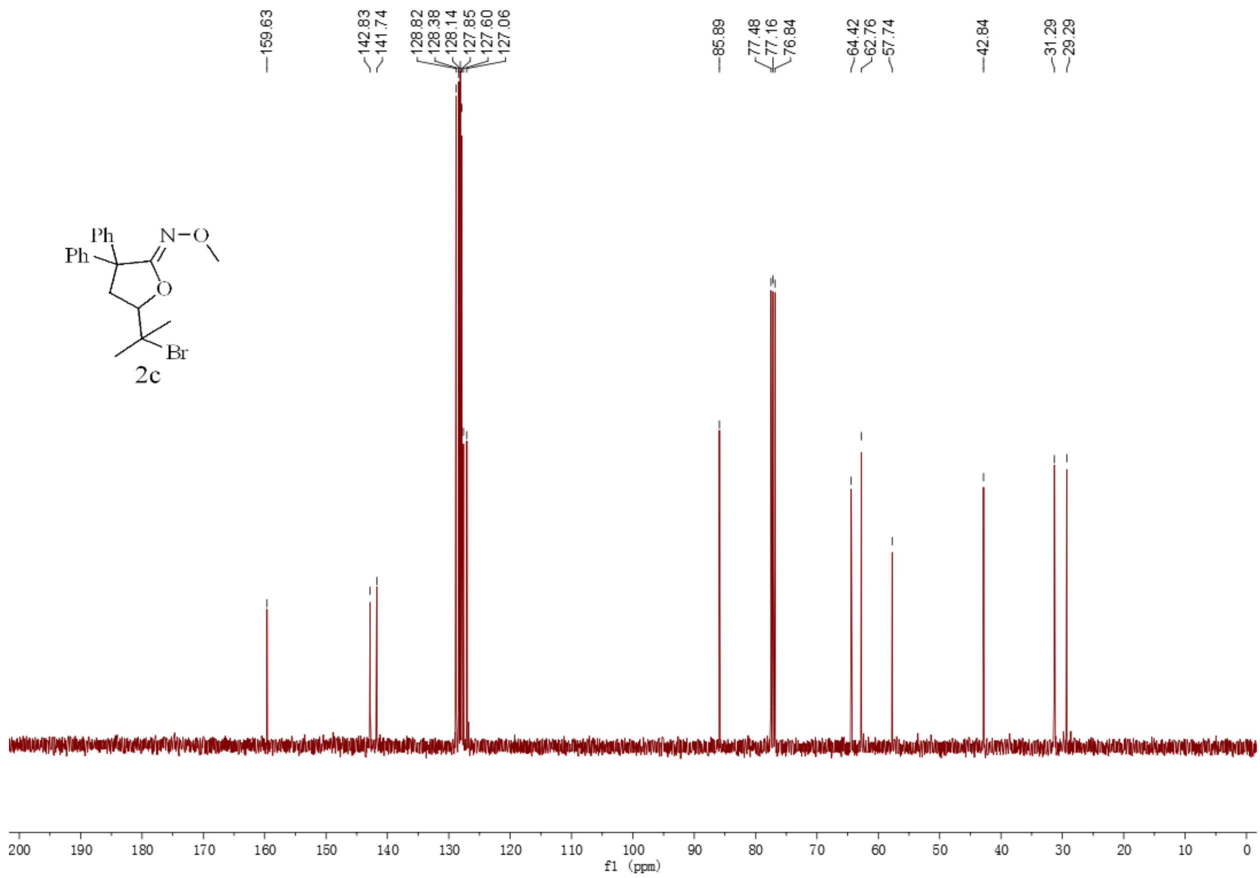


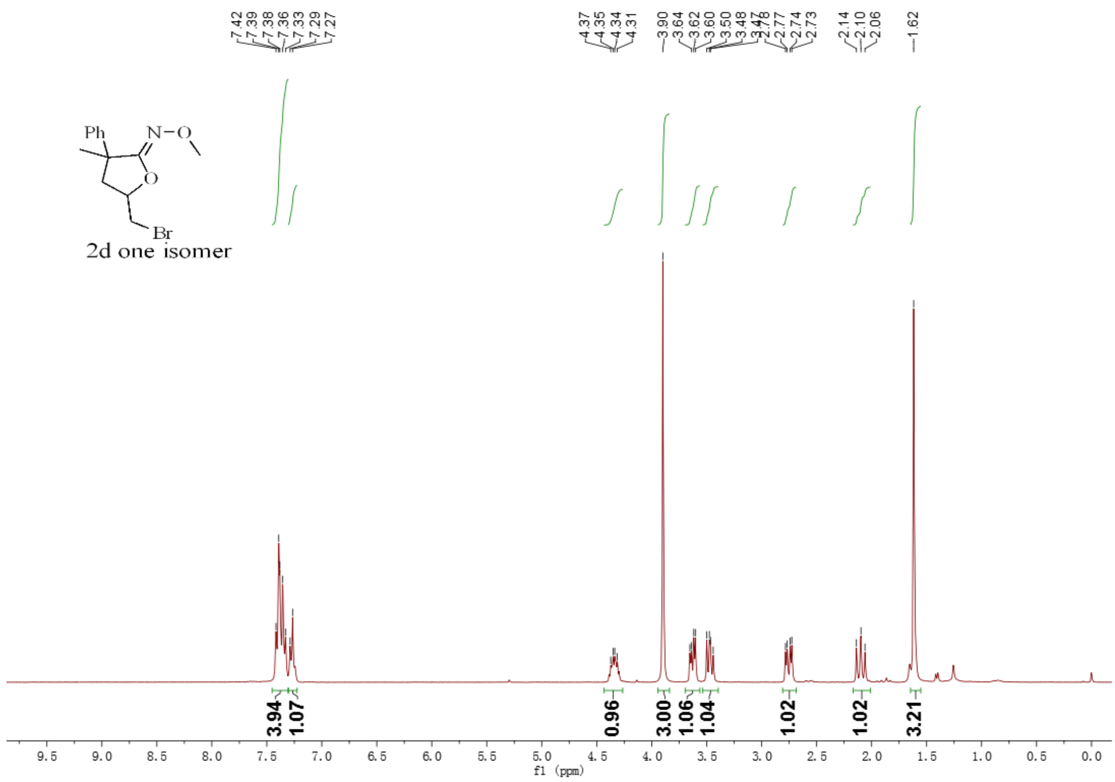
7.46
7.43
7.38
7.35
7.33
7.31
7.28
7.25
3.86
3.41
3.38
3.37
3.35
3.26
3.22
2.87
2.82
1.45
Ph
Ph
N−O
O
Br
2b
2.00
8.33
3.00
2.13
1.09
1.05
3.13
f1 (ppm)

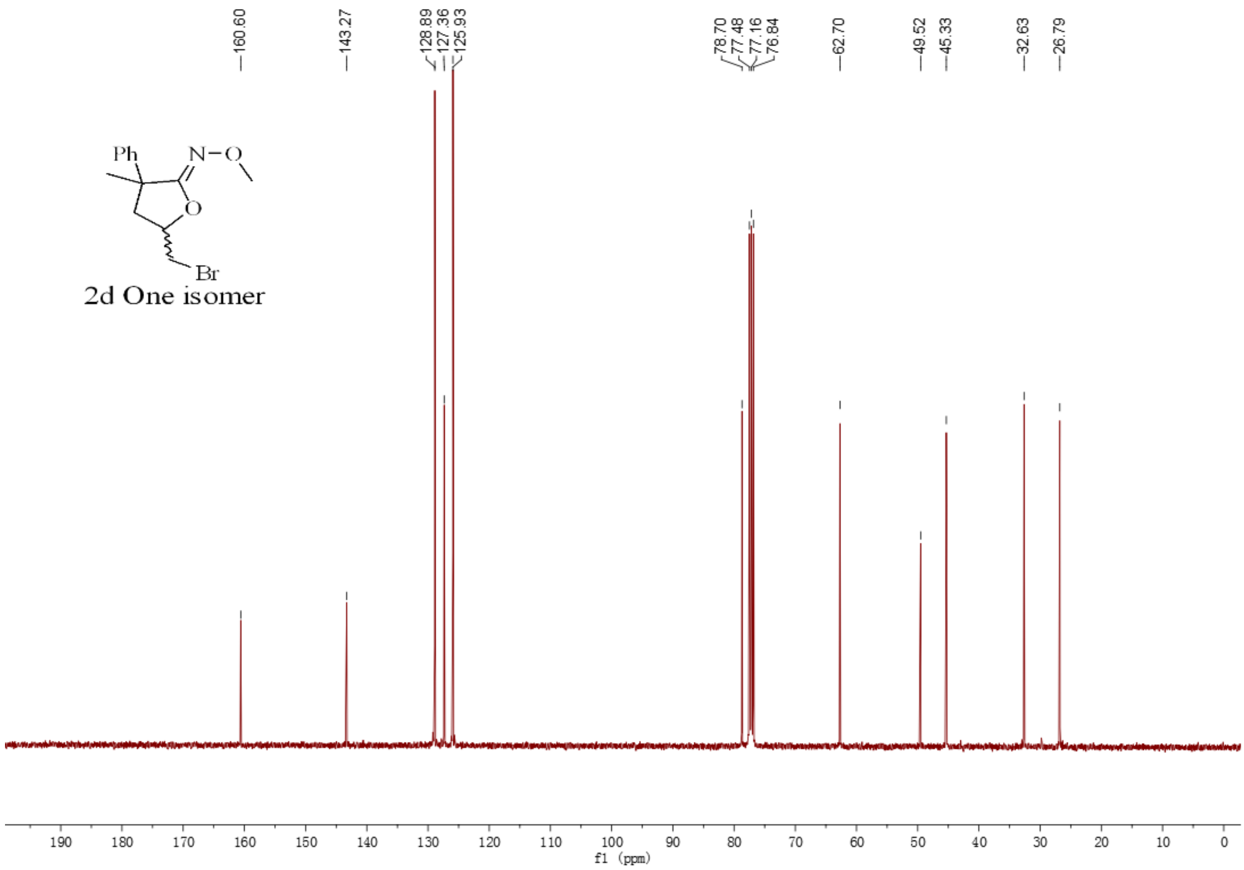


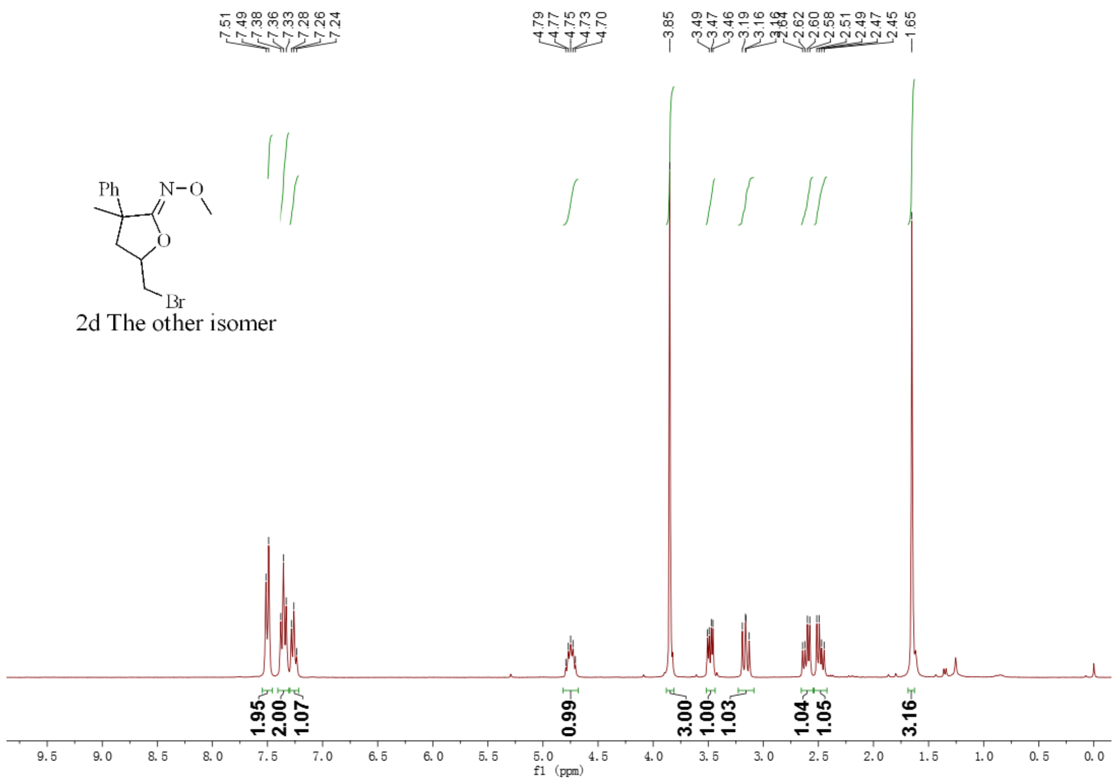
159.96
143.56
142.69
128.54
128.48
127.98
127.37
127.18
85.80
77.58
77.16
76.74
62.89
58.12
48.39
39.00
25.56
Ph
Ph
N−O
O
Br
2b
f1 (ppm)

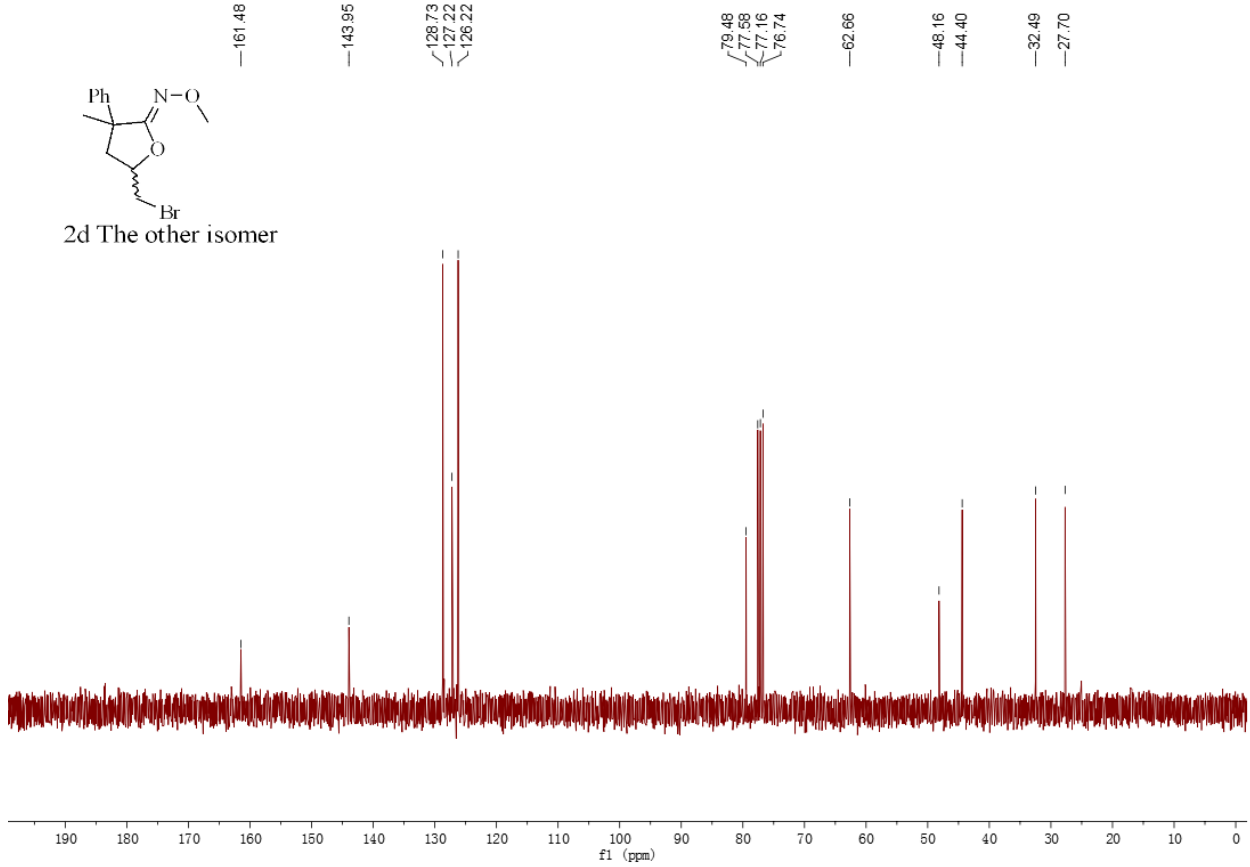


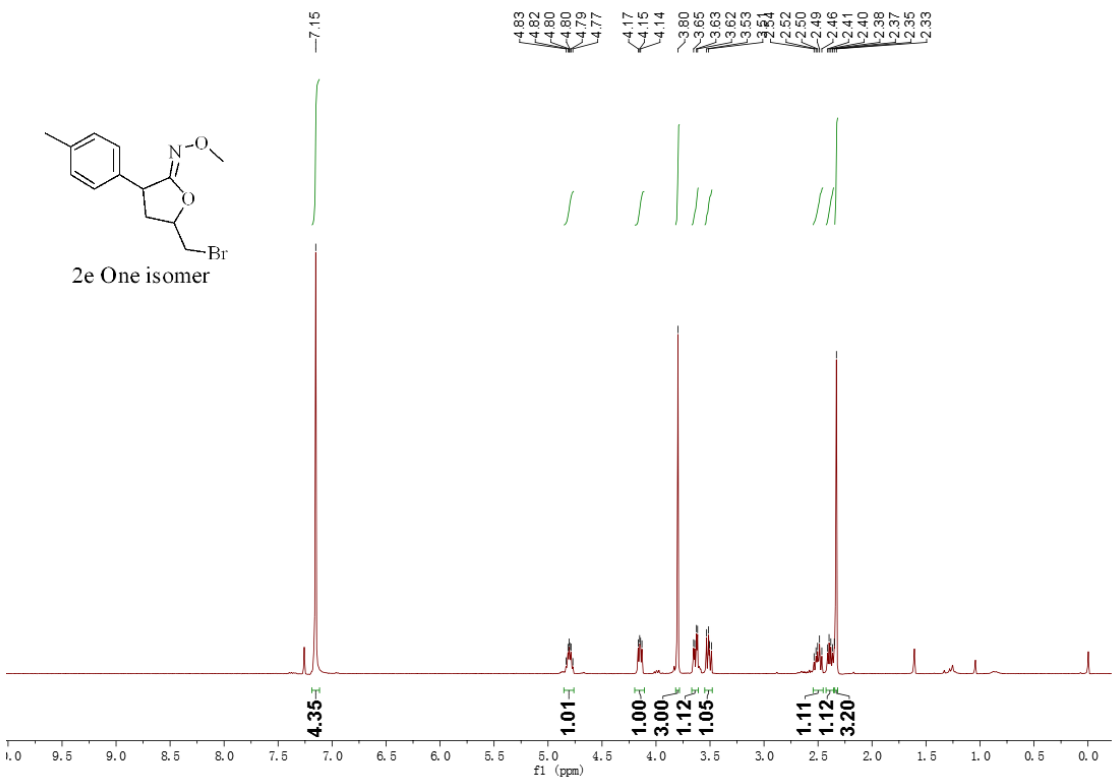


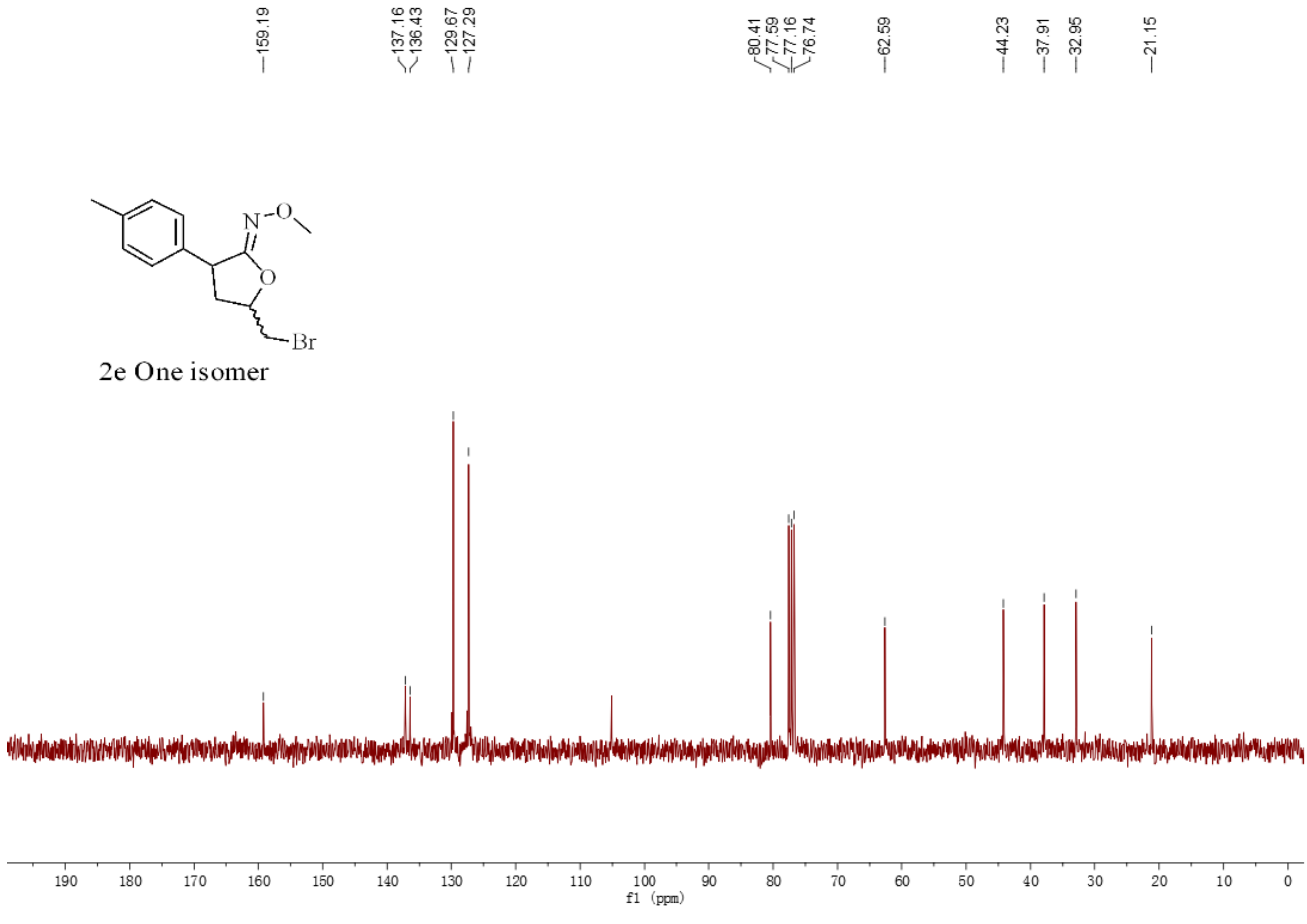

2d one isomer

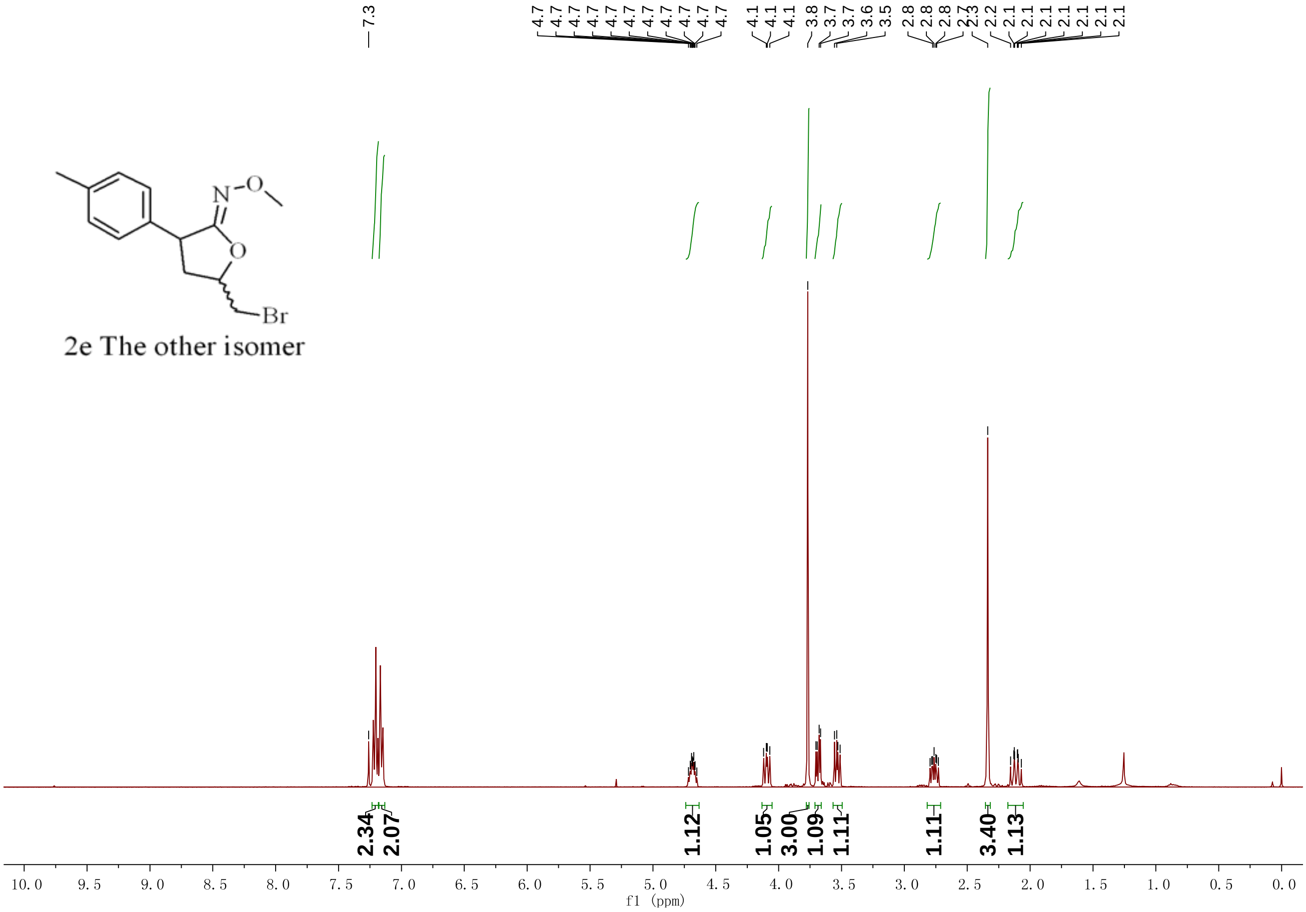

2d One isomer

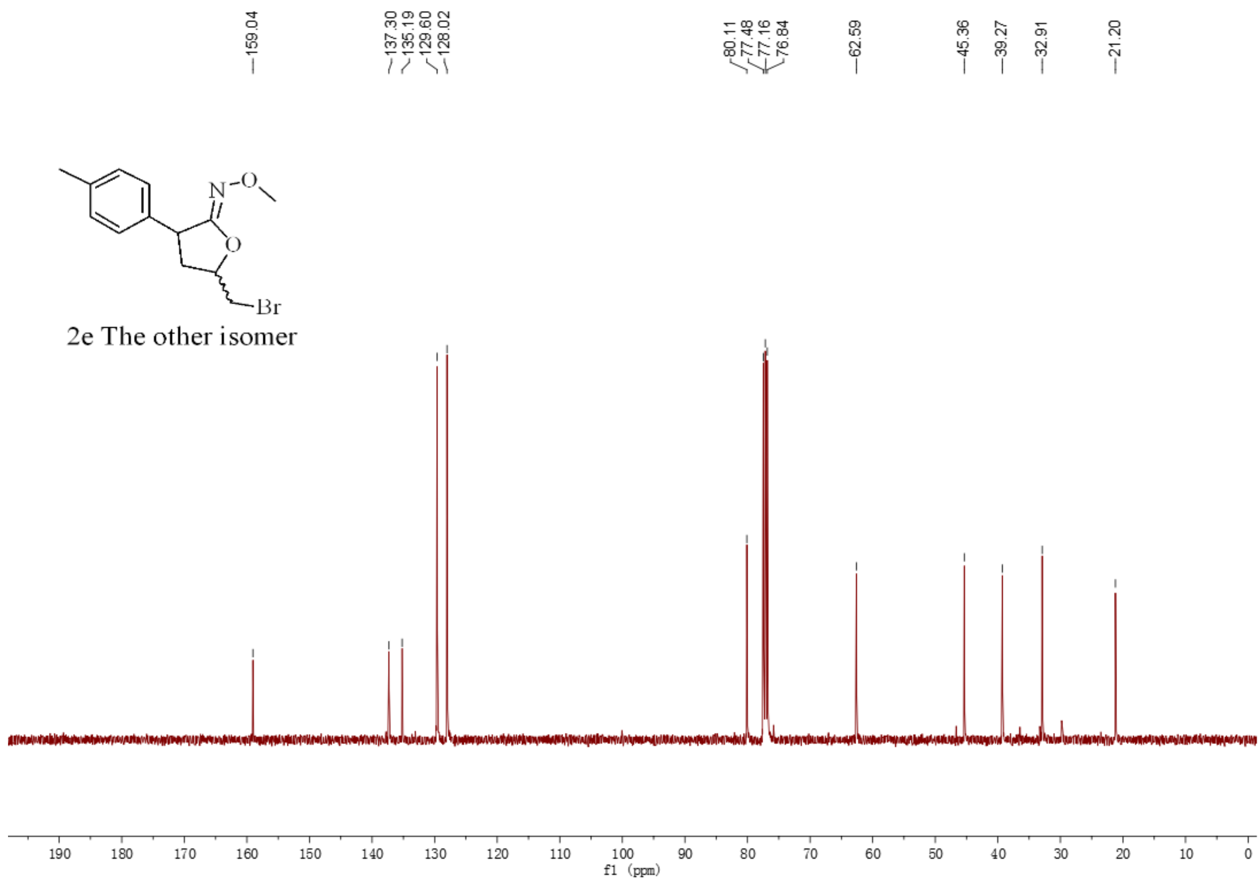

2d The other isomer

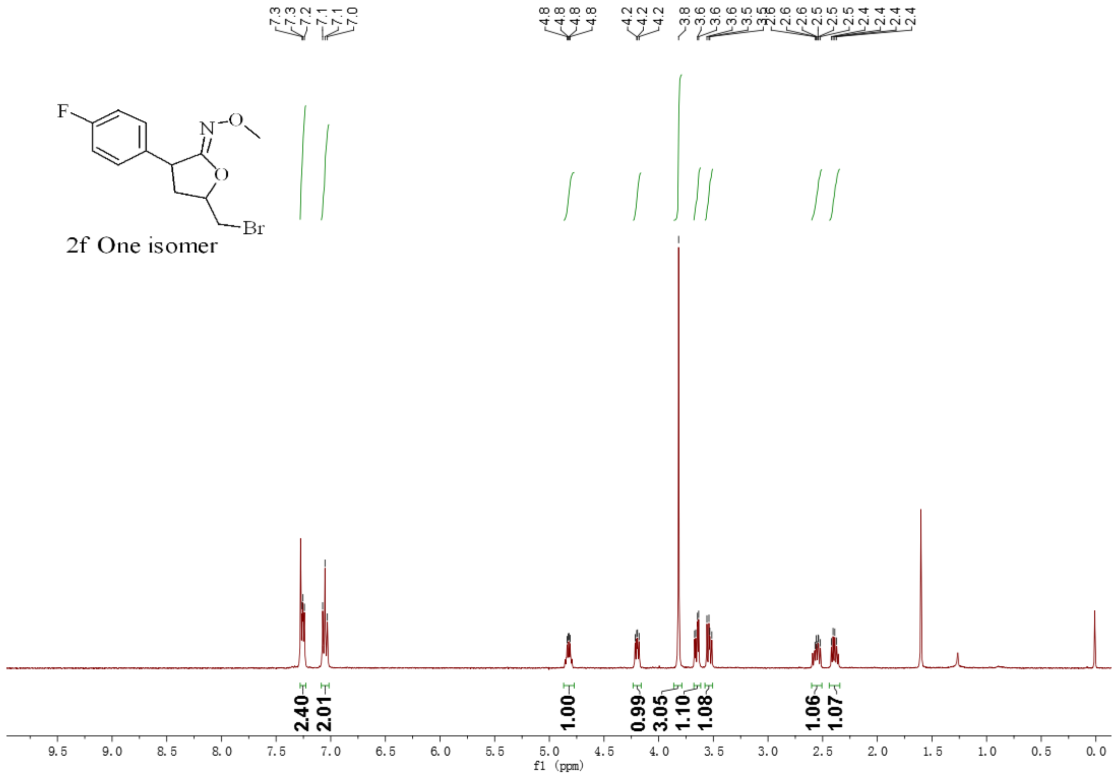

2d The other isomer

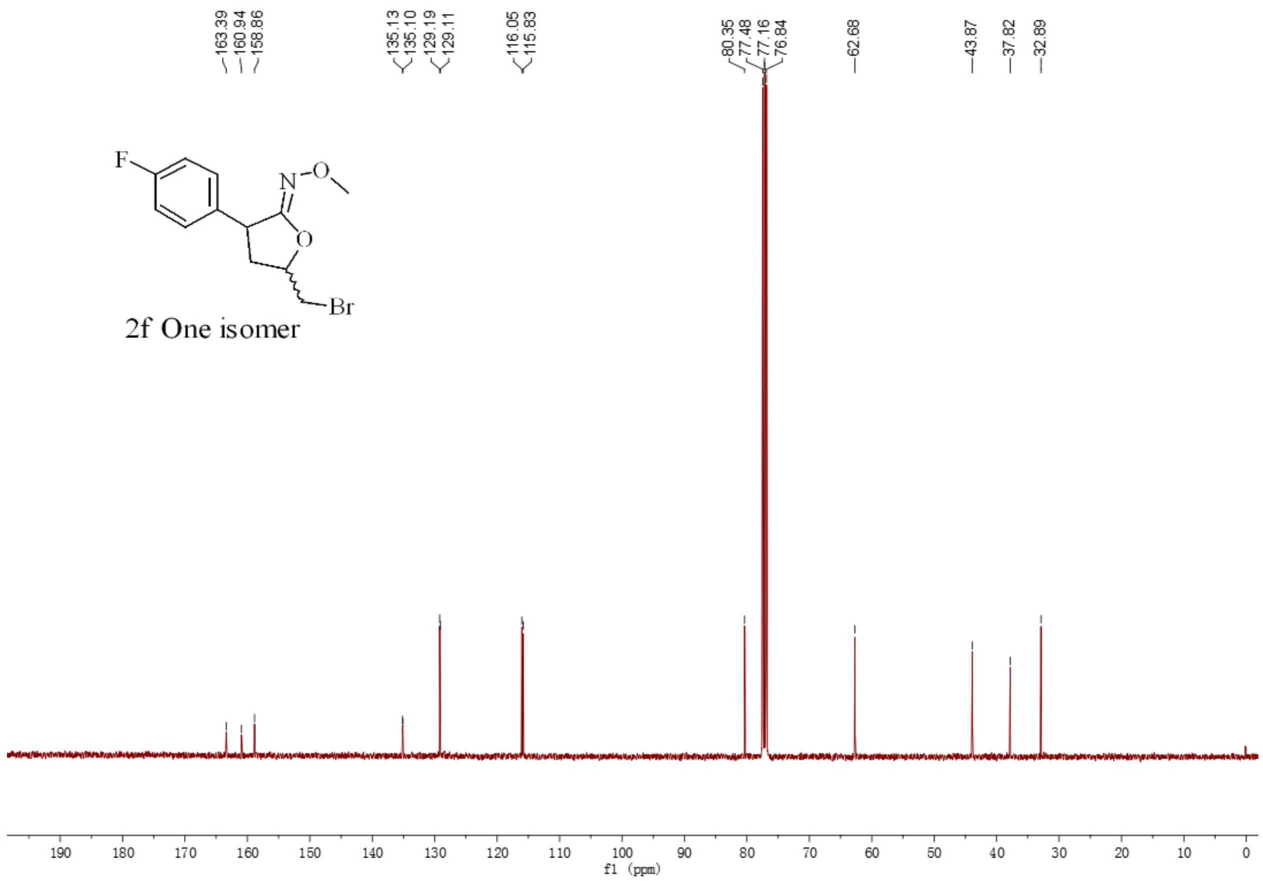

2e One isomer
7.15
4.83 4.82 4.80 4.79 4.77
4.17 4.15 4.14
3.80 3.65 3.63 3.62 3.53 3.51 3.54
2.52 2.50 2.49 2.46 2.41 2.40 2.38 2.37 2.35 2.33
4.35
1.01
1.00
3.00
1.12
1.05
1.11
1.12
3.20
f1 (ppm)

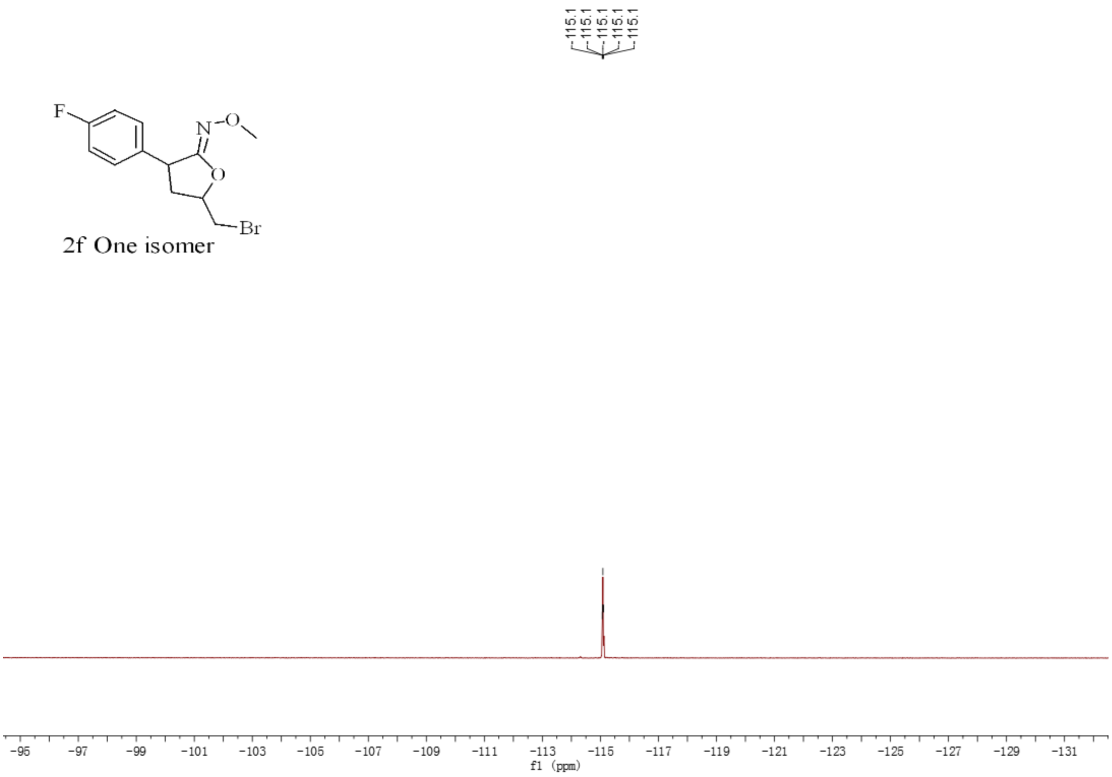

159.19
137.16 136.43
129.67 127.29
80.41 77.59 77.16 76.74
62.59
44.23
37.91
32.95
21.15
2e One isomer
f1 (ppm)


2e The other isomer
f1 (ppm)

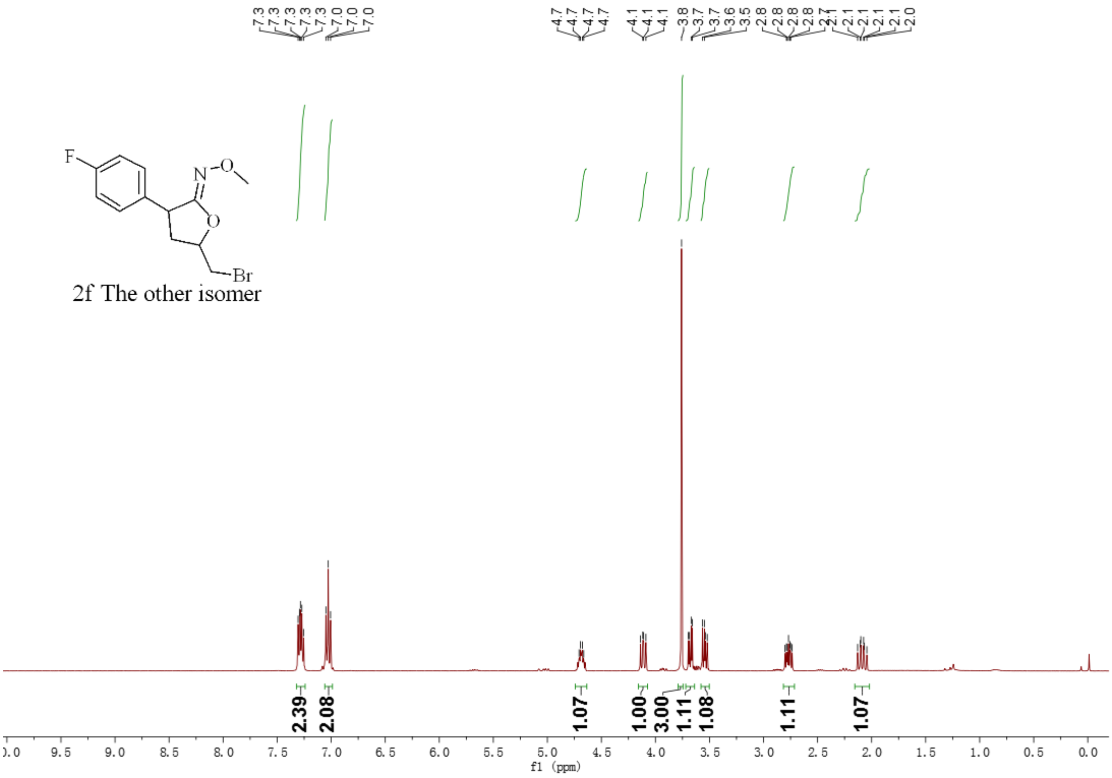

2e The other isomer
159.04
137.30
135.19
129.60
128.02
80.11
77.48
77.16
76.84
62.59
45.36
39.27
32.91
21.20
f1 (ppm)


2f One isomer
2.40
2.01
1.00
0.99
3.05
1.10
1.08
1.06
1.07
f1 (ppm)

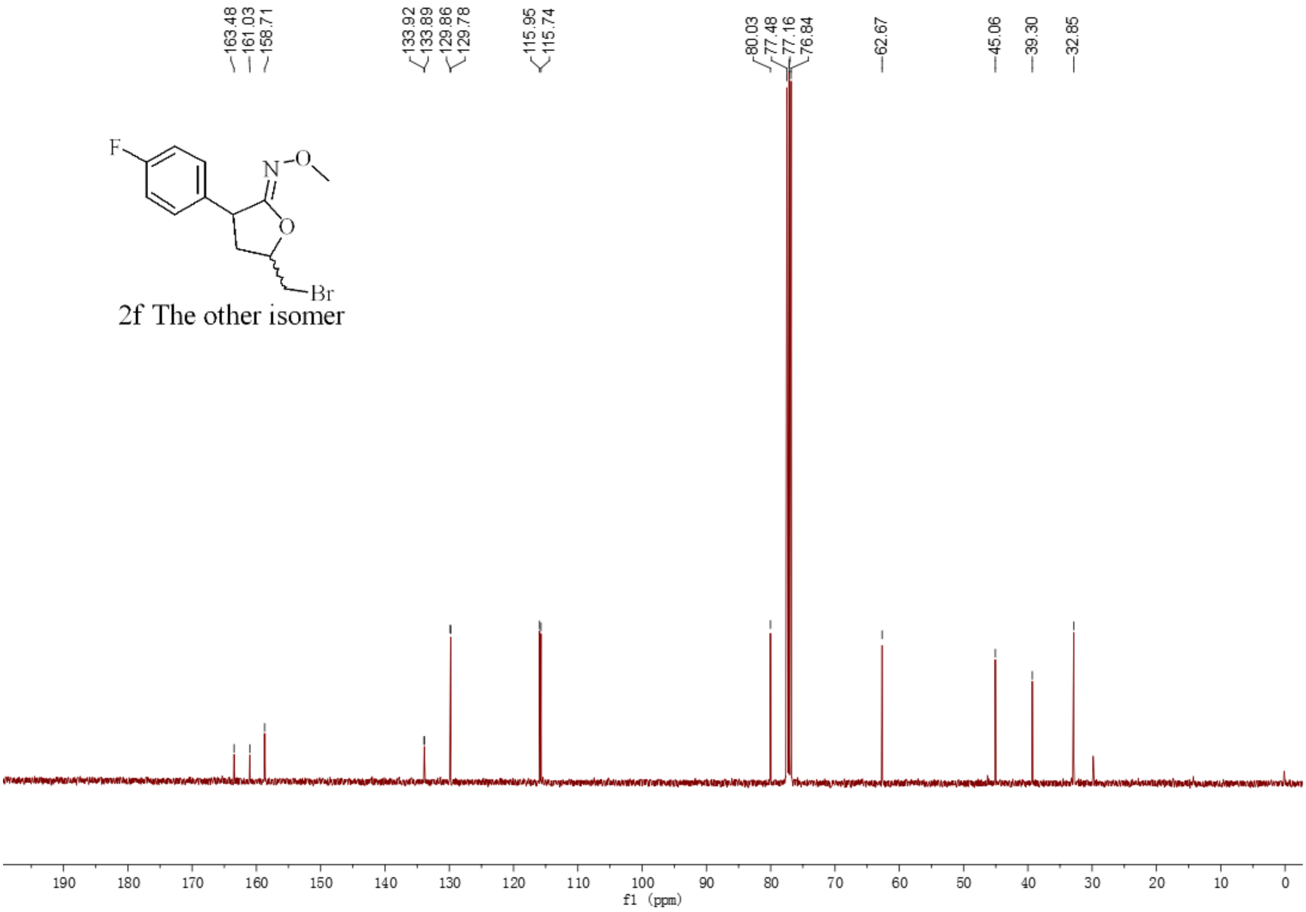

163.39
160.94
158.86
135.13
135.10
129.19
129.11
116.05
115.83
80.35
77.48
77.16
76.84
62.68
43.87
37.82
32.89
2f One isomer
f1 (ppm)

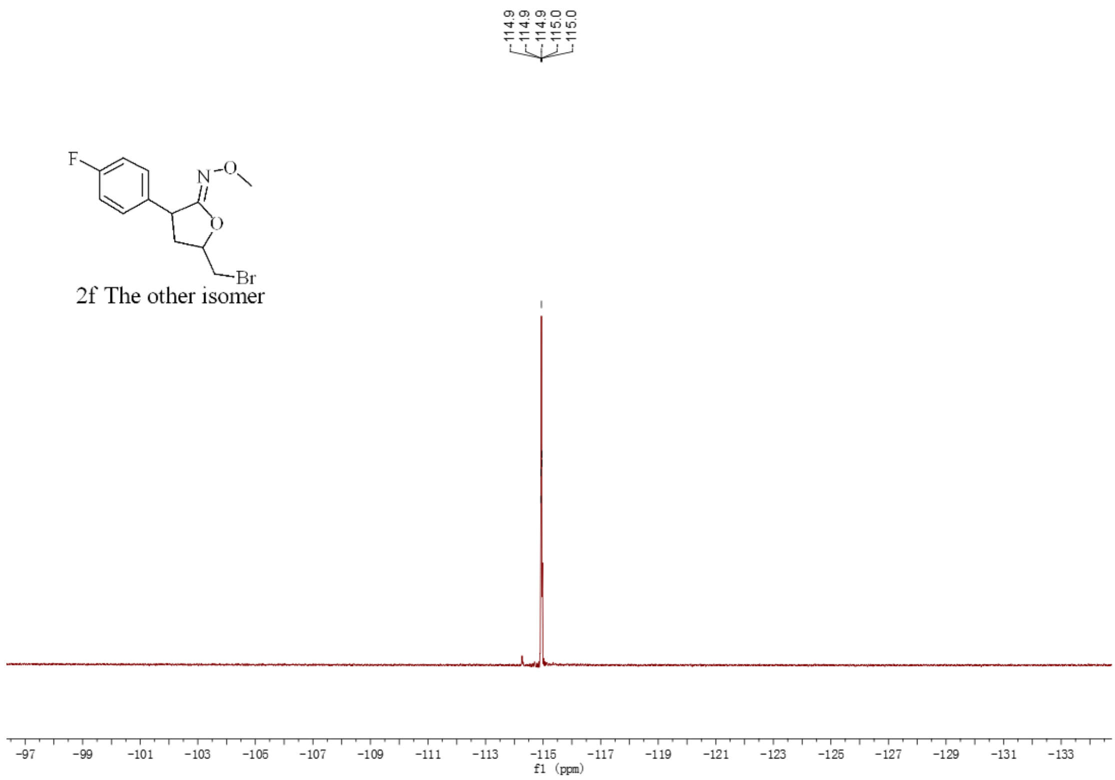


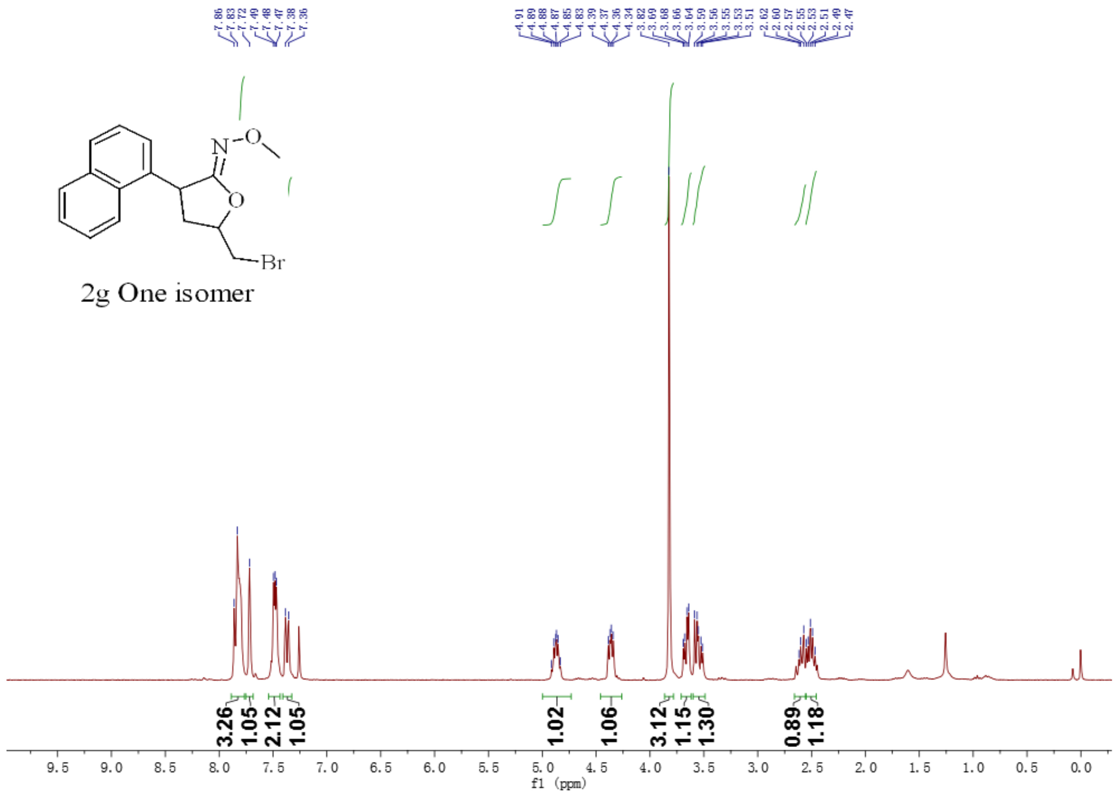
2f One isomer

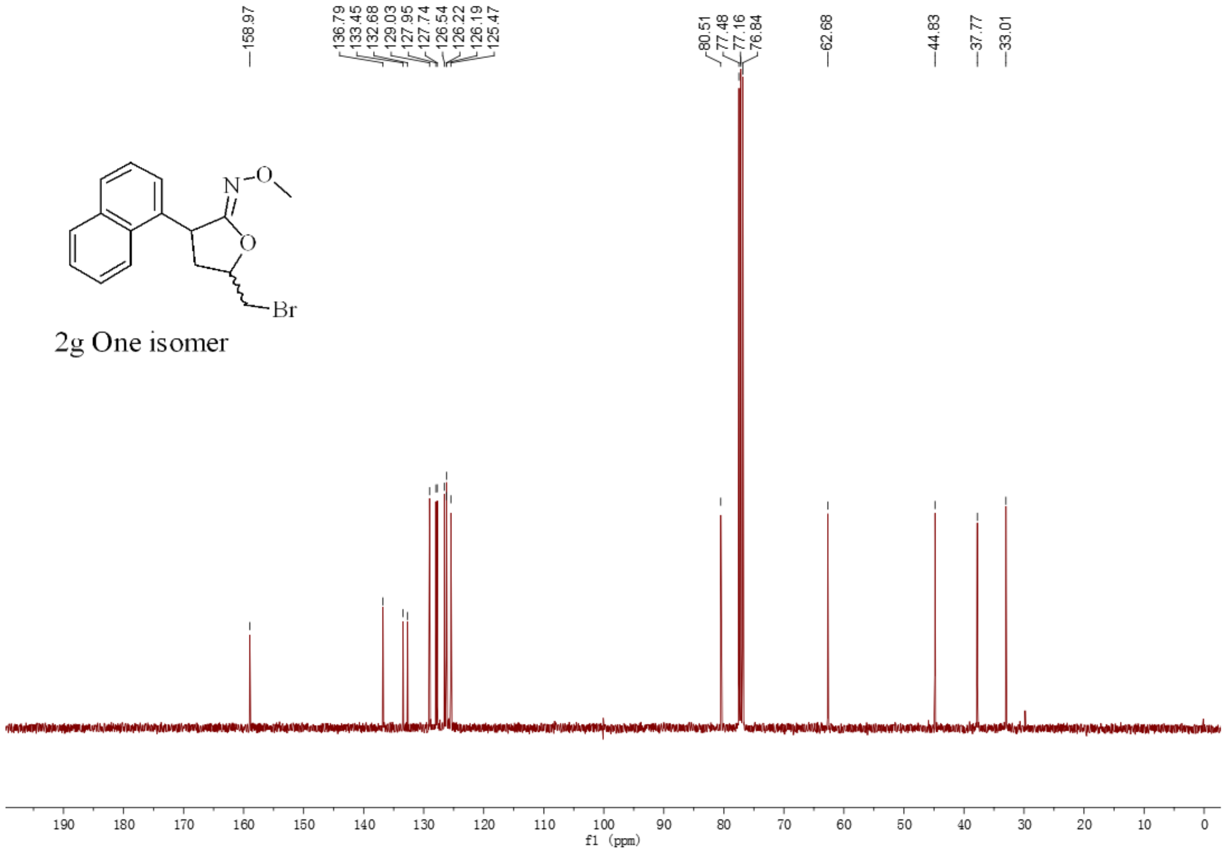


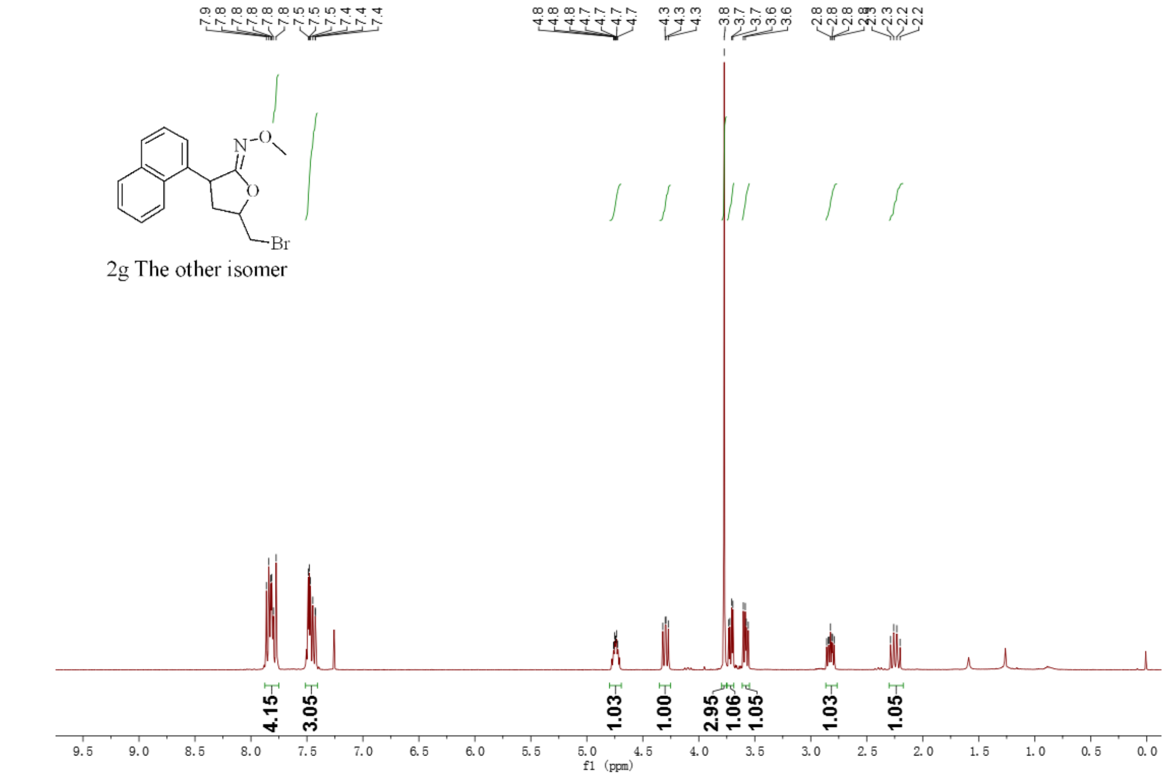
2f The other isomer


163.48
161.03
158.71
133.92
133.89
129.86
129.78
115.95
115.74
80.03
77.48
77.16
76.84
62.67
45.06
39.30
32.85
F
N
O
O
Br
2f The other isomer
f1 (ppm)

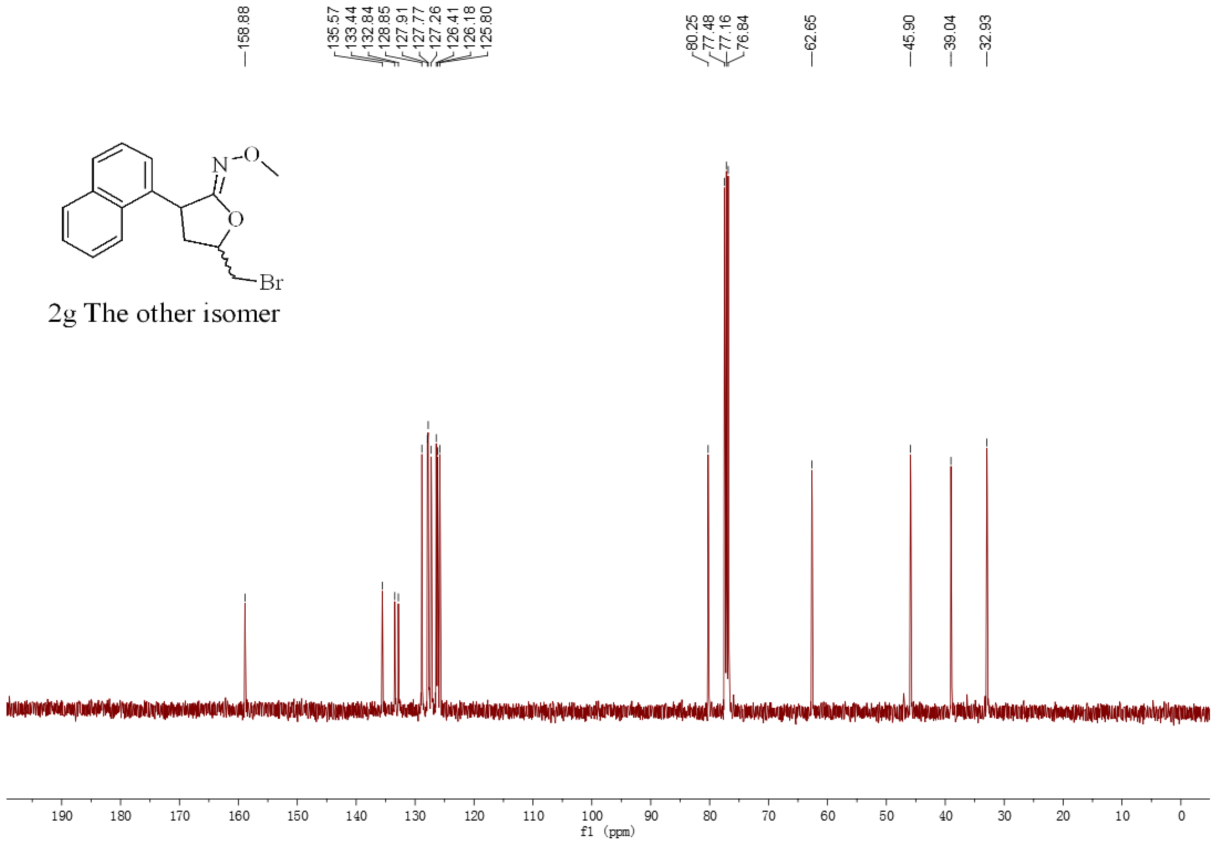

-114.9
-114.9
-114.9
-115.0
-115.0
F
N
O
O
Br
2f The other isomer
f1 (ppm)


7.86
7.83
7.72
7.49
7.48
7.47
7.38
7.36
4.91
4.89
4.88
4.87
4.85
4.83
4.39
4.37
4.36
4.34
3.82
3.69
3.68
3.66
3.64
3.59
3.56
3.55
3.53
3.51
2.62
2.60
2.57
2.55
2.53
2.51
2.49
2.47
N
O
O
Br
2g One isomer
3.26
1.05
2.12
1.05
1.02
1.06
3.12
1.15
1.30
0.89
1.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

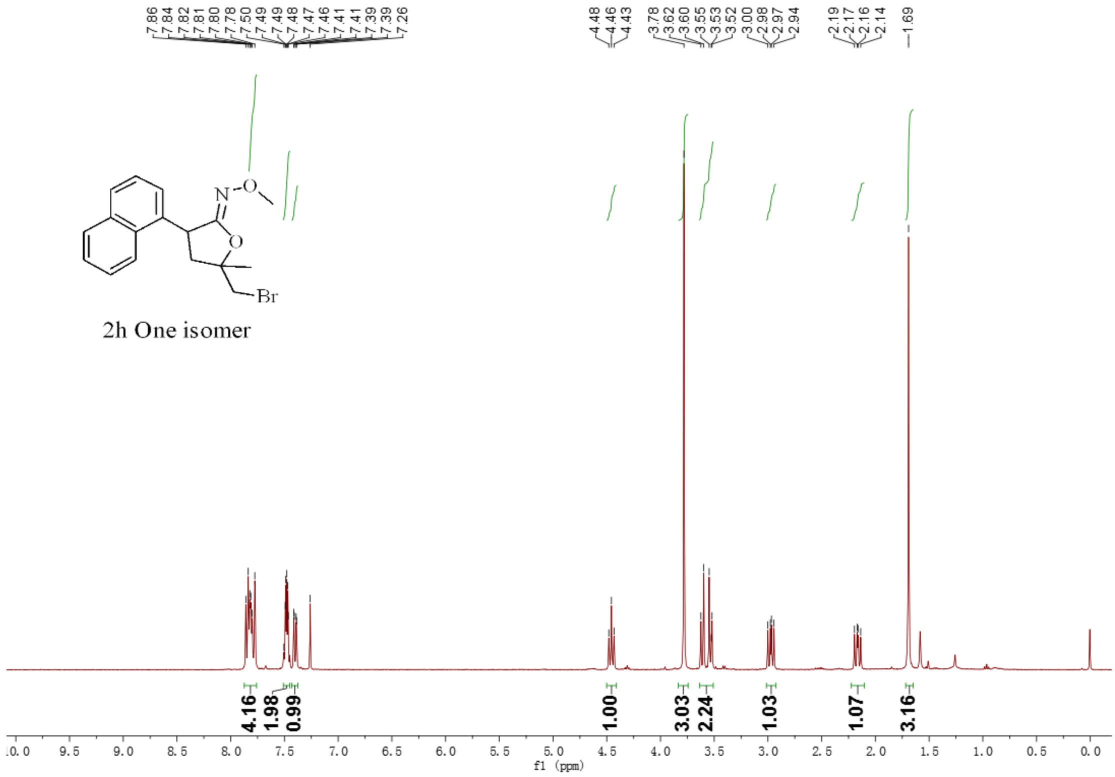

158.97
136.79
133.45
132.68
129.03
127.95
127.74
126.54
126.22
126.19
125.47
80.51
77.48
77.16
76.84
62.68
44.83
37.77
33.01
N
O
O
Br
2g One isomer
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

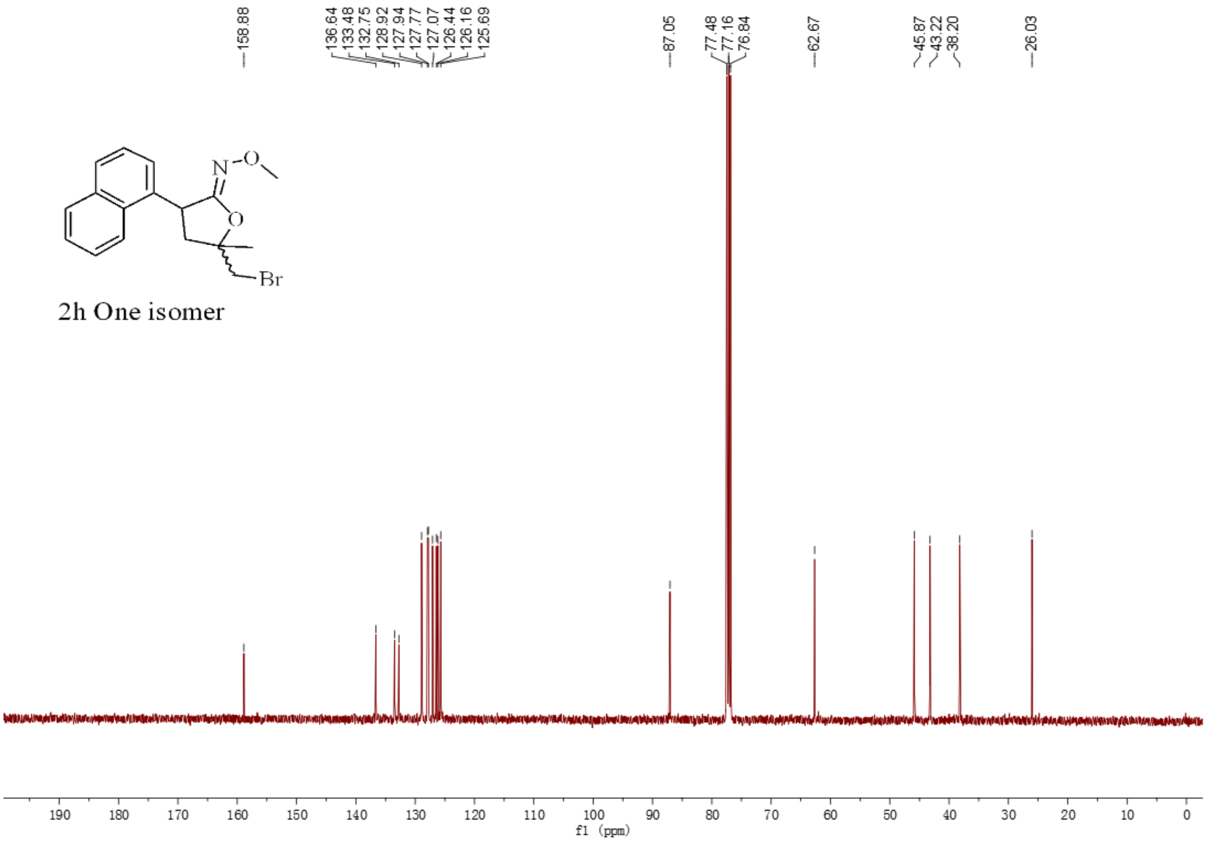


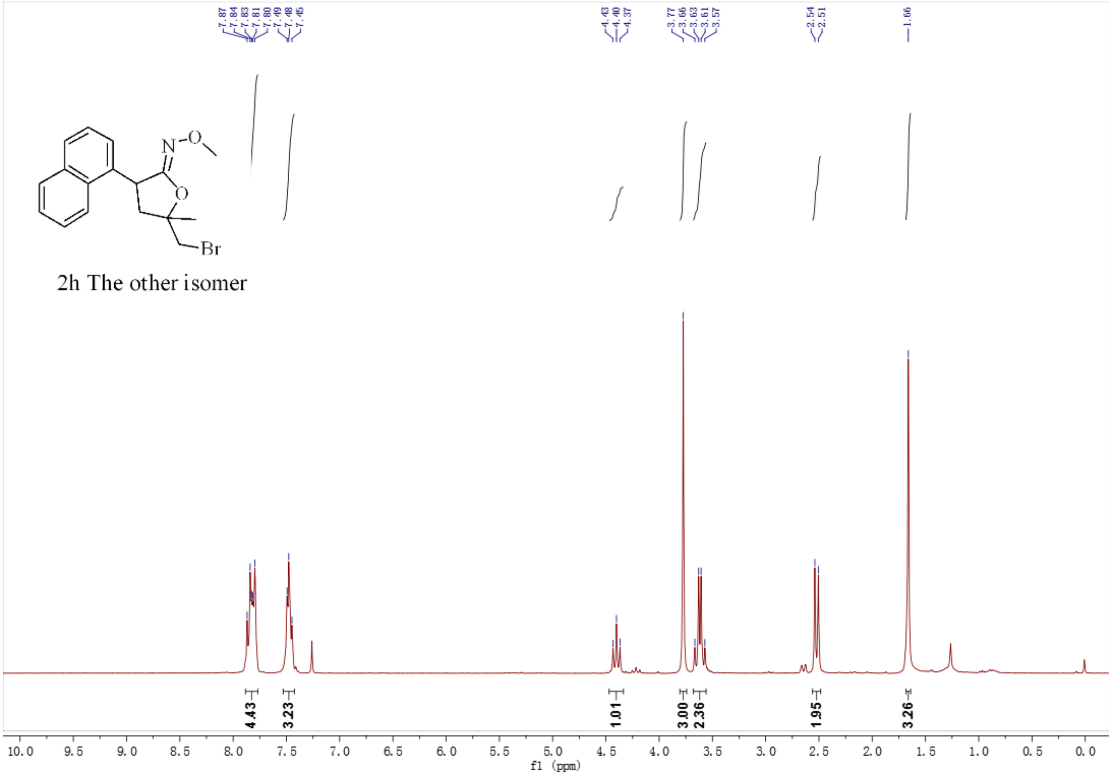
2g The other isomer

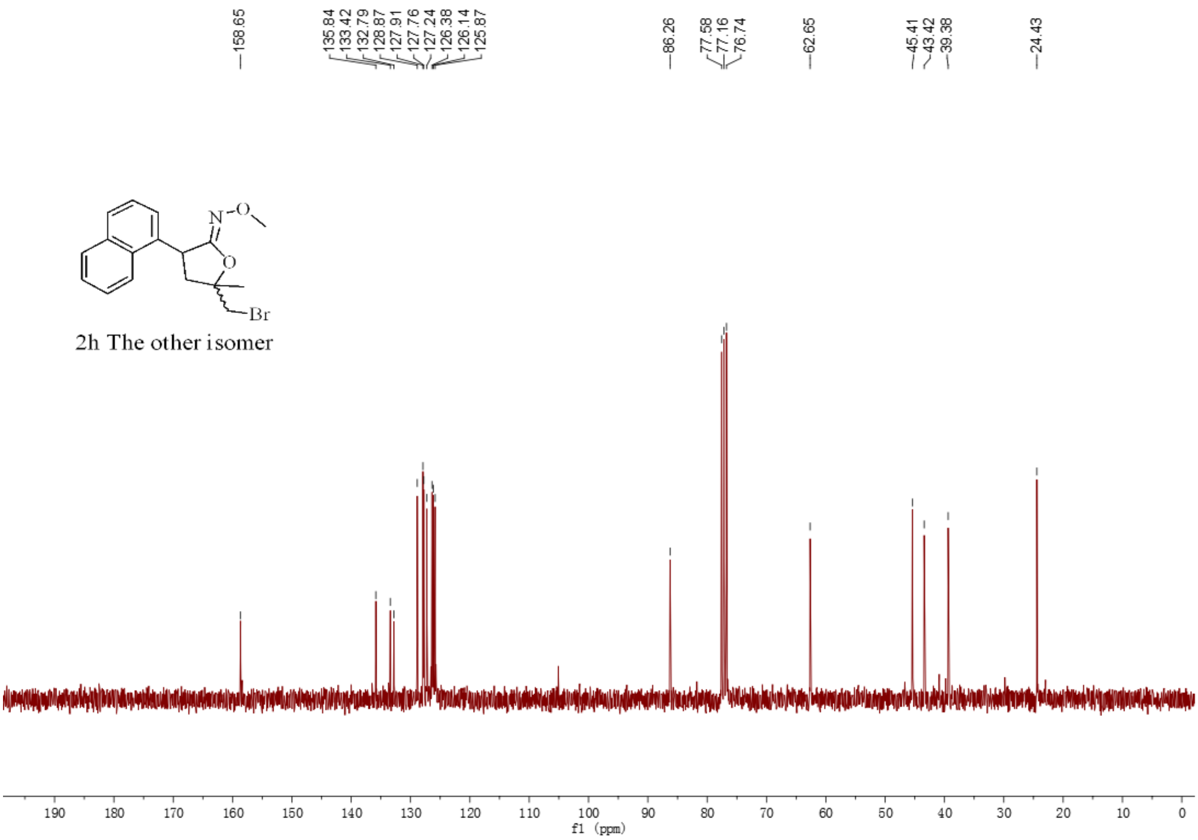


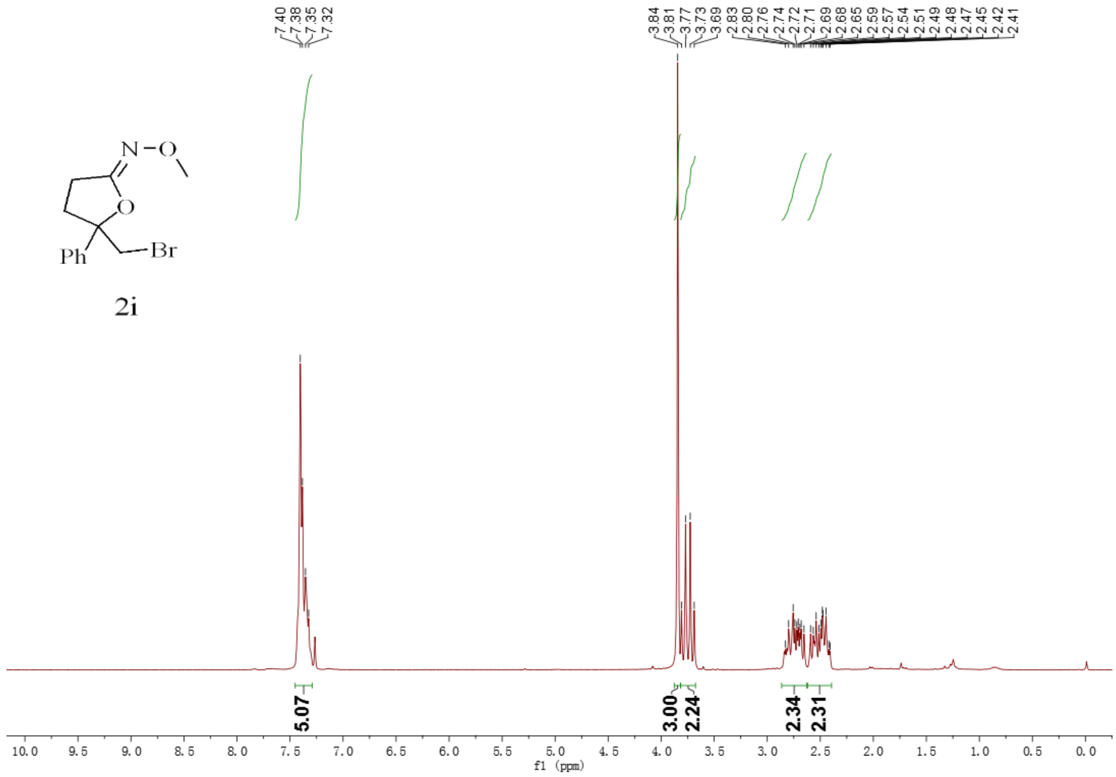
2g The other isomer


2h One isomer

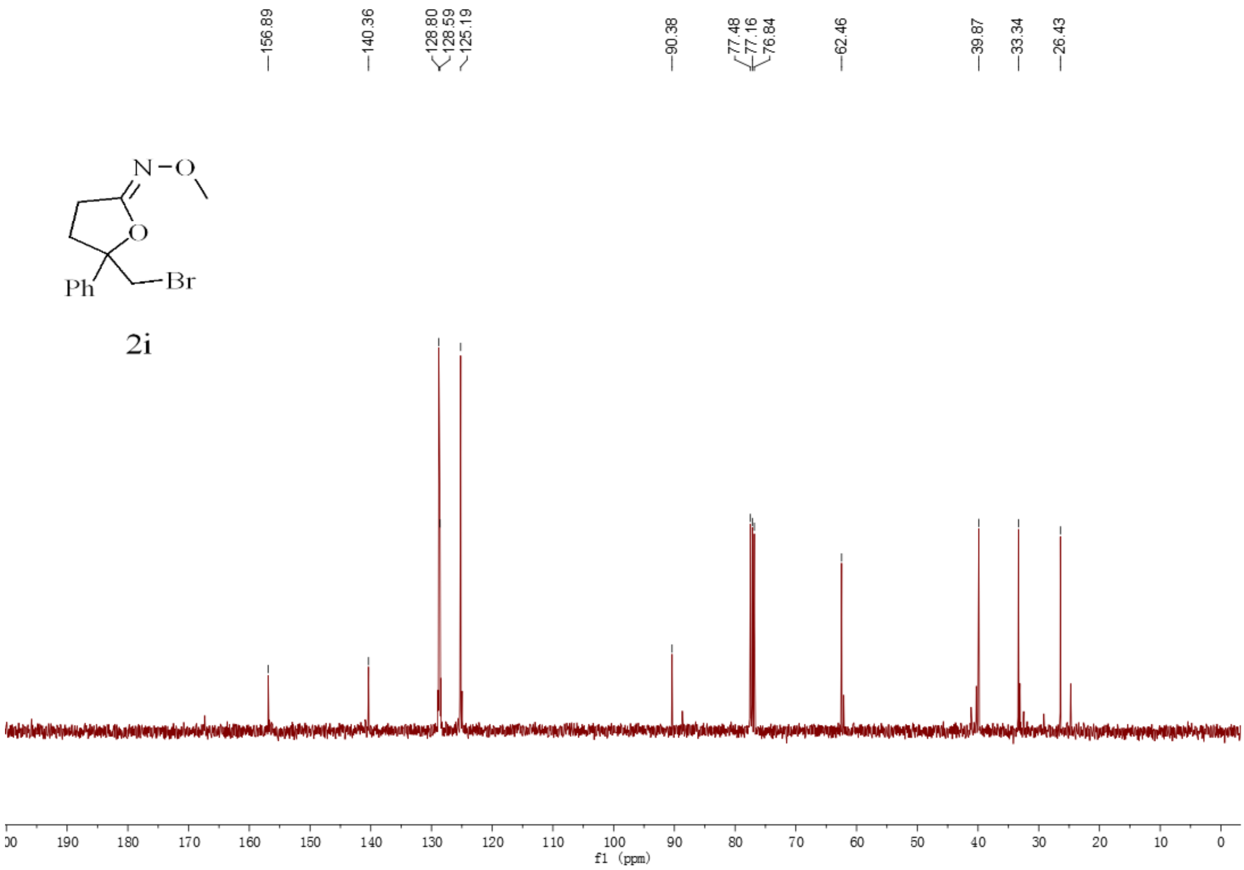

2h One isomer


7.87 7.84 7.83 7.81 7.80 7.49 7.48 7.45
4.43 4.40 4.37
3.77 3.66 3.63 3.61 3.57
2.54 2.51
1.66
N
O
O
Br
2h The other isomer
4.43
3.23
1.01
3.00
2.36
1.95
3.26
f1 (ppm)

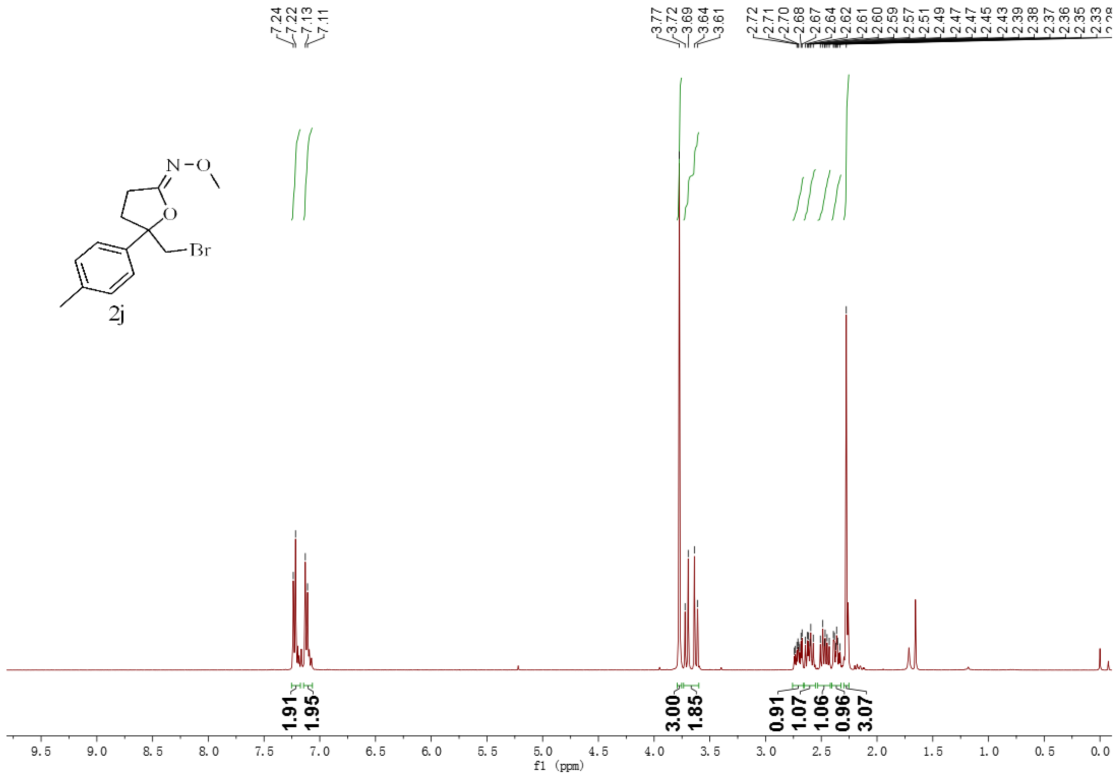

158.65
135.84 133.42 132.79 128.87 127.91 127.76 127.24 126.38 126.14 125.87
86.26
77.58 77.16 76.74
62.65
45.41 43.42 39.38
24.43
N
O
O
Br
2h The other isomer
f1 (ppm)

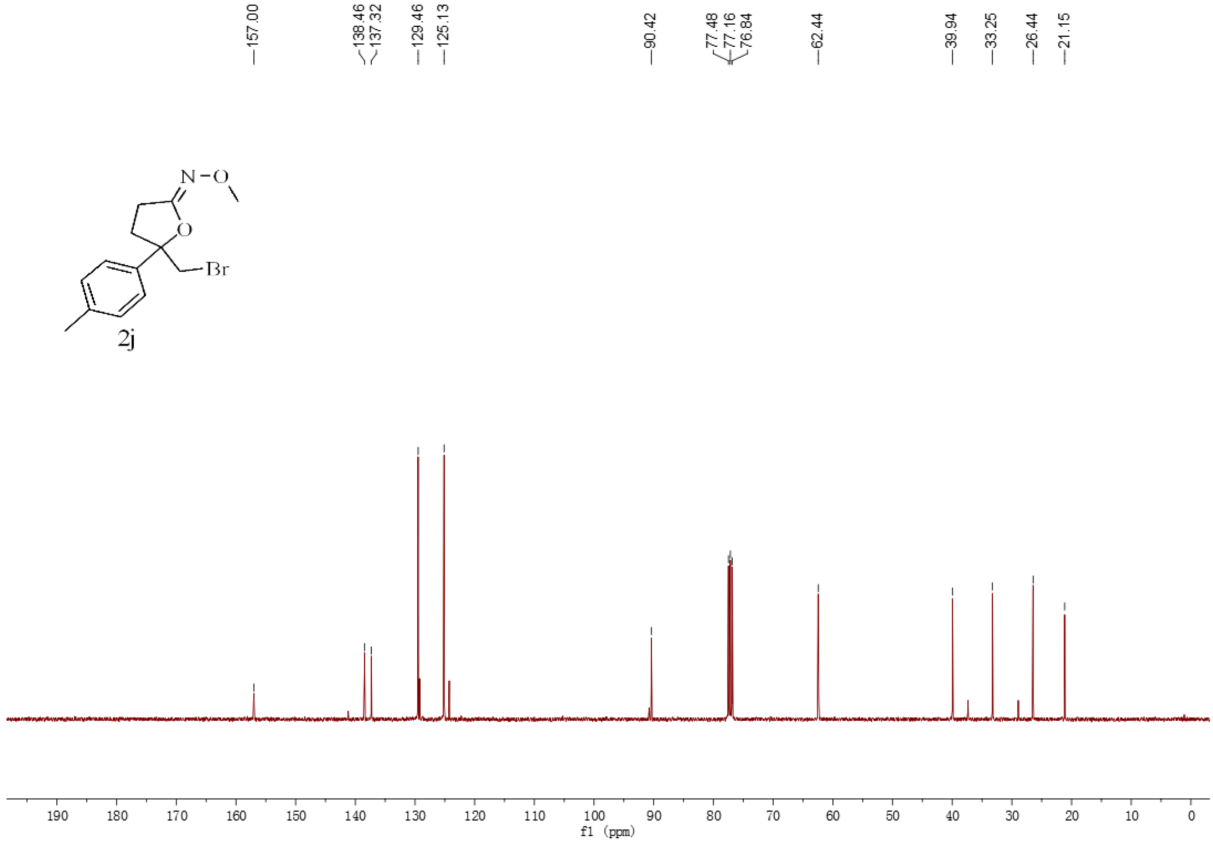


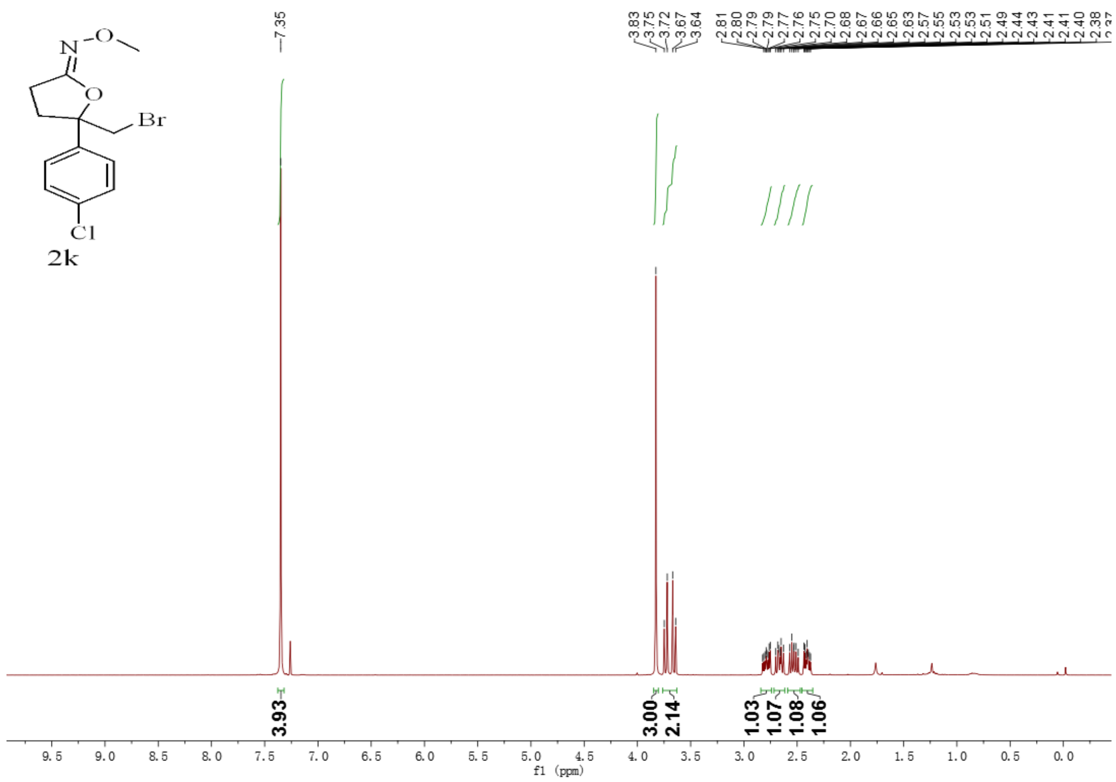
7.40
7.38
7.35
7.32
3.84
3.81
3.77
3.73
3.69
2.83
2.80
2.76
2.74
2.72
2.71
2.69
2.68
2.65
2.59
2.57
2.54
2.51
2.49
2.48
2.47
2.45
2.42
2.41
N–O
O
Ph
Br
2i
5.07
3.00
2.24
2.34
2.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

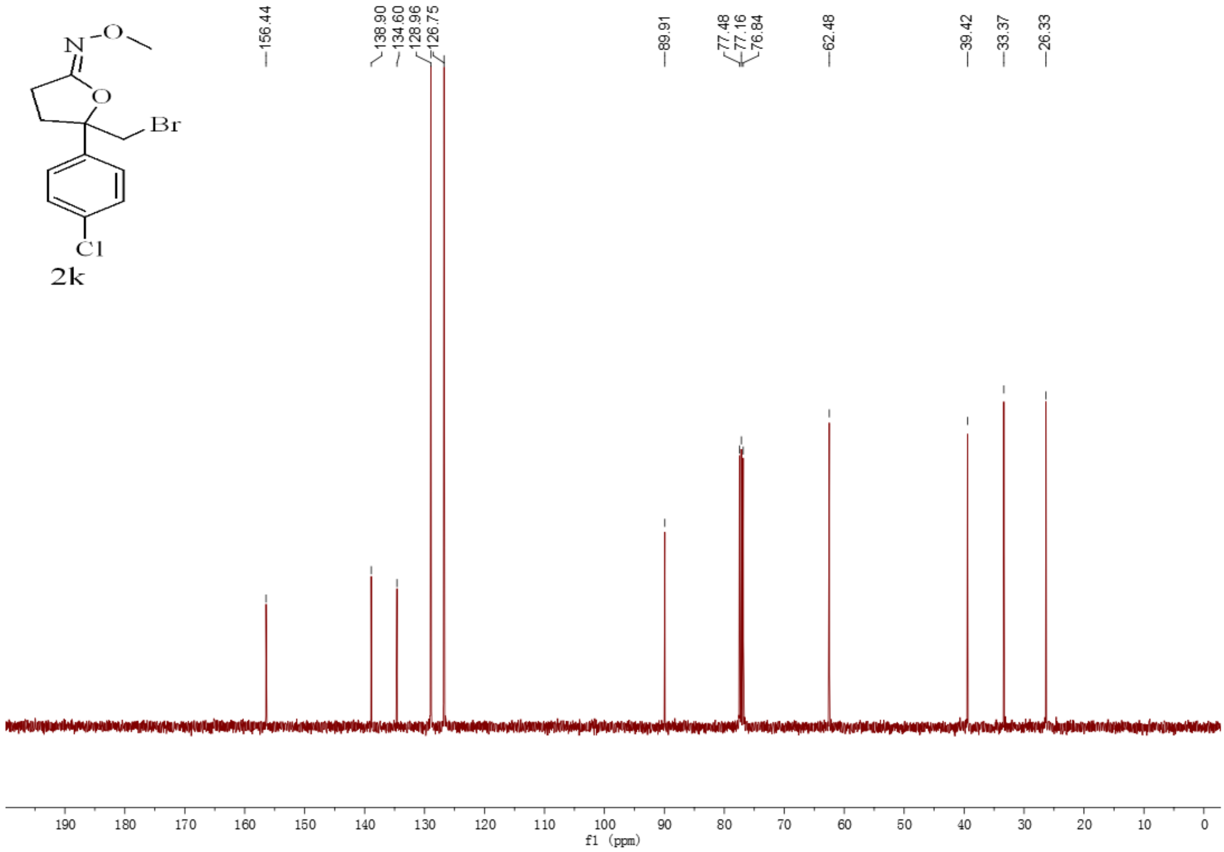


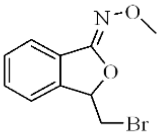
156.89
140.36
128.80
128.59
125.19
90.38
77.48
77.16
76.84
62.46
39.87
33.34
26.43
N–O
O
Ph
Br
2i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


2j
f1 (ppm)

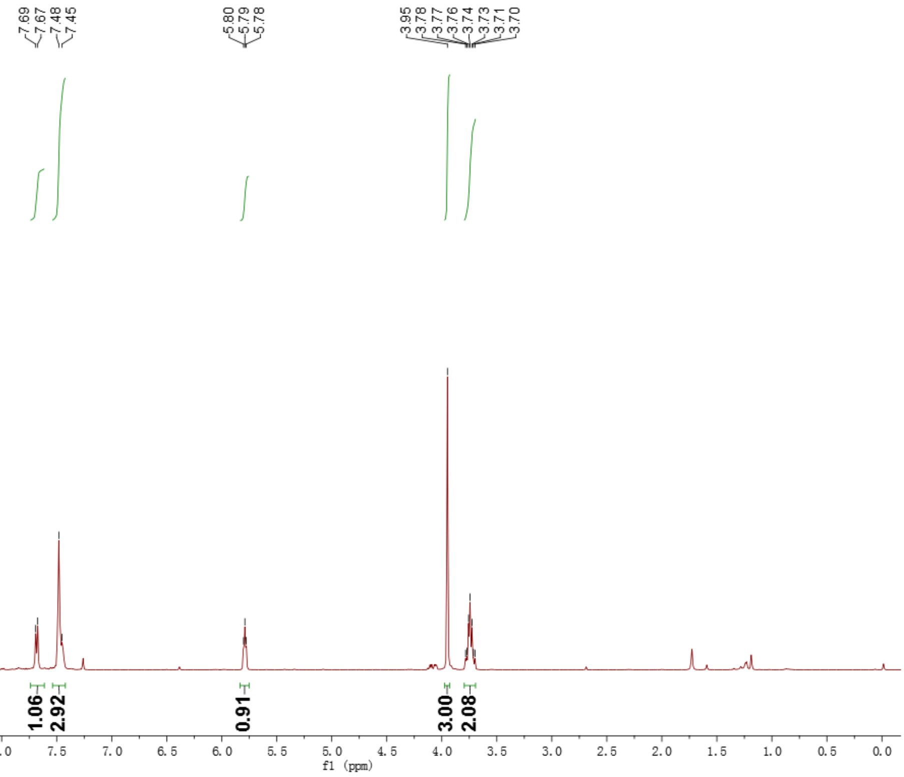

2j
f1 (ppm)


2k
7.35
3.83
3.75
3.72
3.67
3.64
3.93
3.00
2.14
1.03
1.07
1.08
1.06
f1 (ppm)

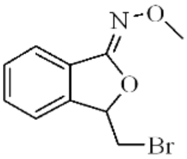

2k
156.44
138.90
134.60
128.96
126.75
89.91
77.48
77.16
76.84
62.48
39.42
33.37
26.33
f1 (ppm)



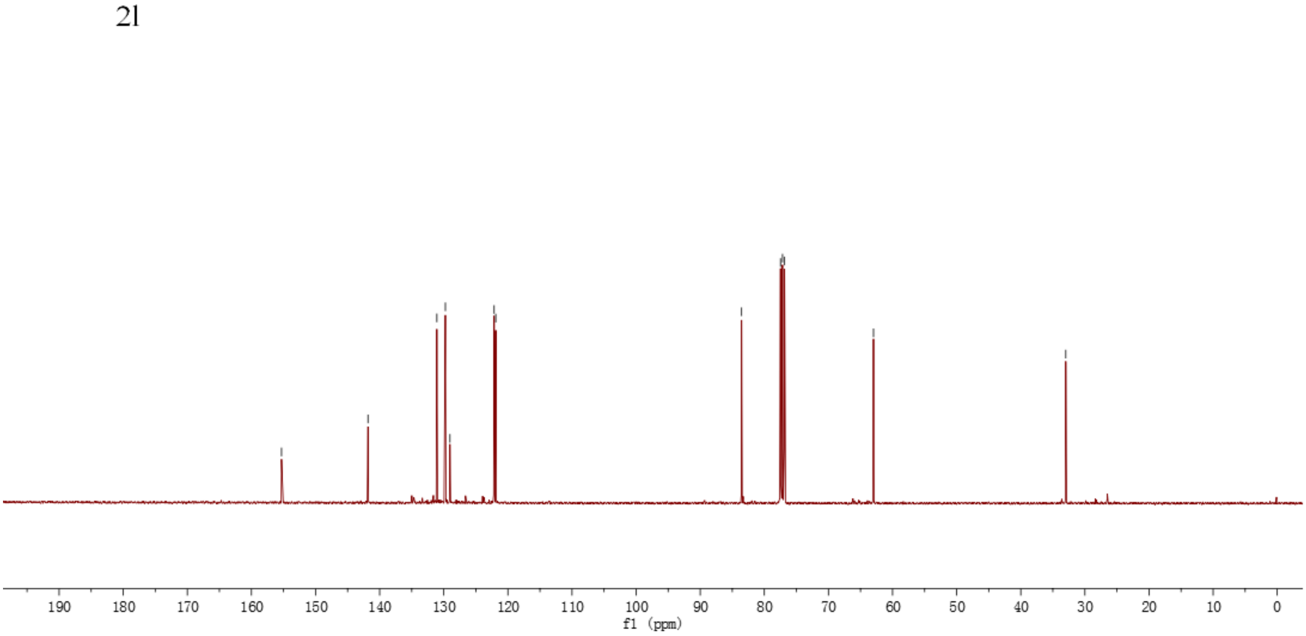
2l



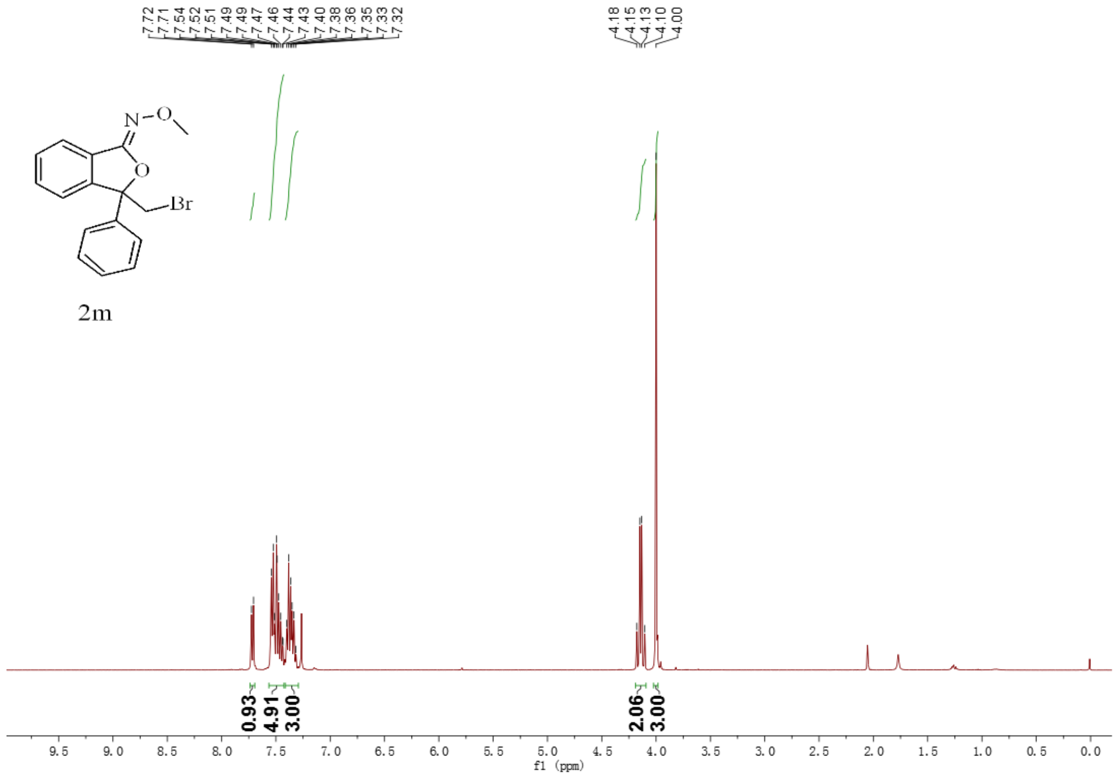
7.69
7.67
7.48
7.45
5.80
5.79
5.78
3.95
3.78
3.77
3.76
3.74
3.73
3.71
3.70
1.06
2.92
0.91
3.00
2.08
f1 (ppm)



2l

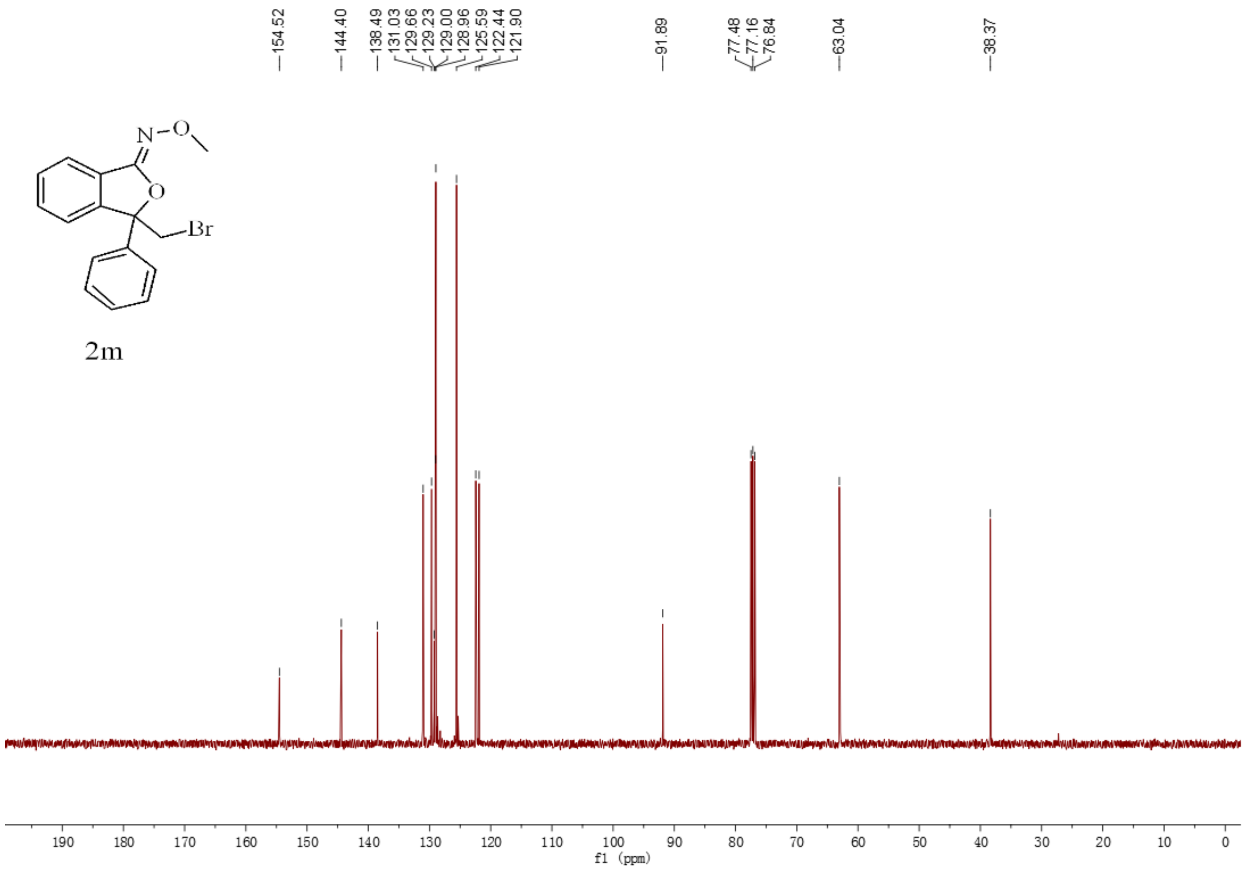


155.31
141.82
131.08
129.75
129.04
122.15
121.89
83.55
77.48
77.16
76.84
62.97
32.98
f1 (ppm)



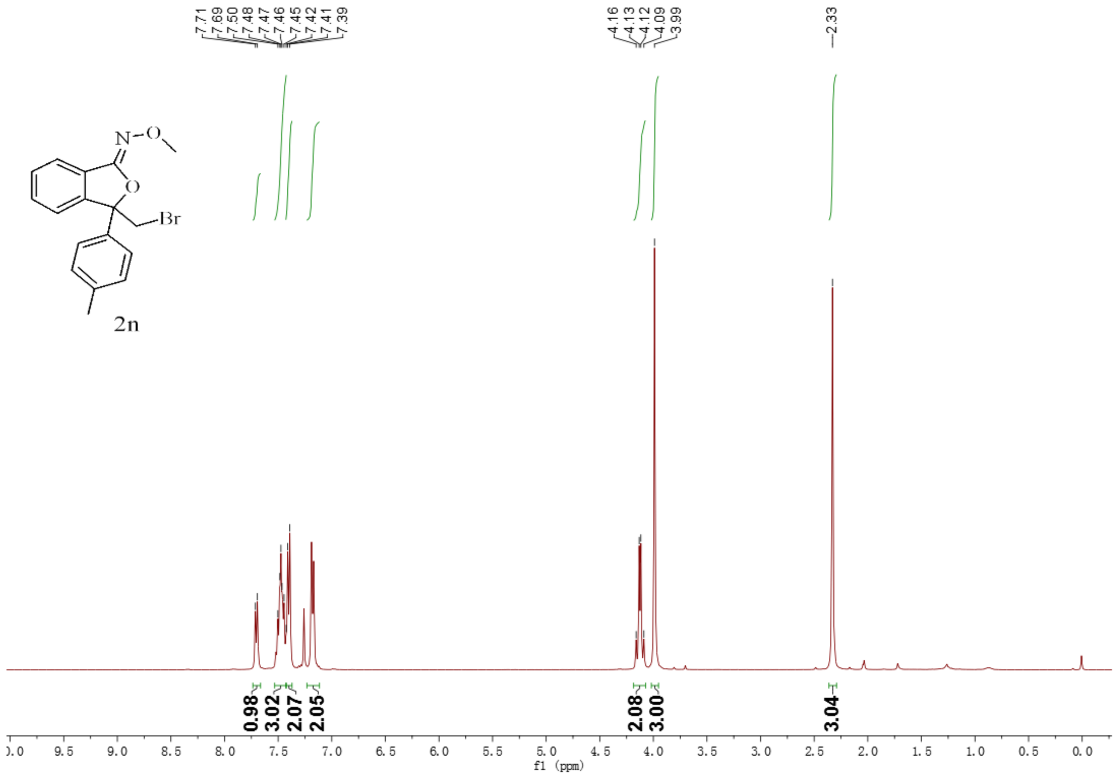
7.72
7.71
7.54
7.52
7.51
7.49
7.49
7.47
7.46
7.44
7.43
7.40
7.38
7.36
7.35
7.33
7.32
4.18
4.15
4.13
4.10
4.00
0.93
4.91
3.00
2.06
3.00
f1 (ppm)

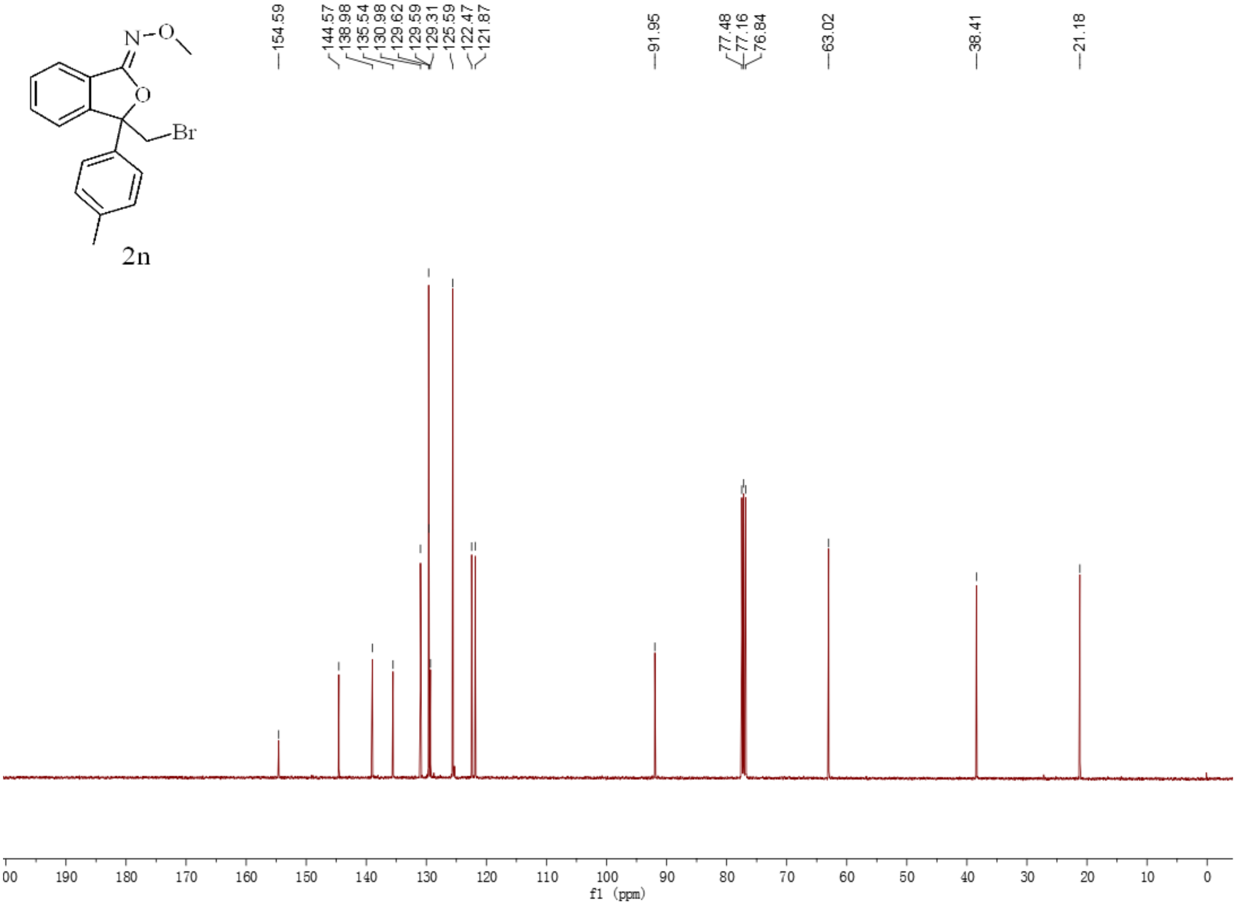
2m

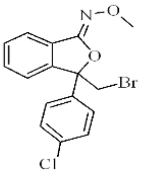


154.52
144.40
138.49
131.03
129.66
129.23
129.00
128.96
125.59
122.44
121.90
91.89
77.48
77.16
76.84
63.04
38.37
f1 (ppm)

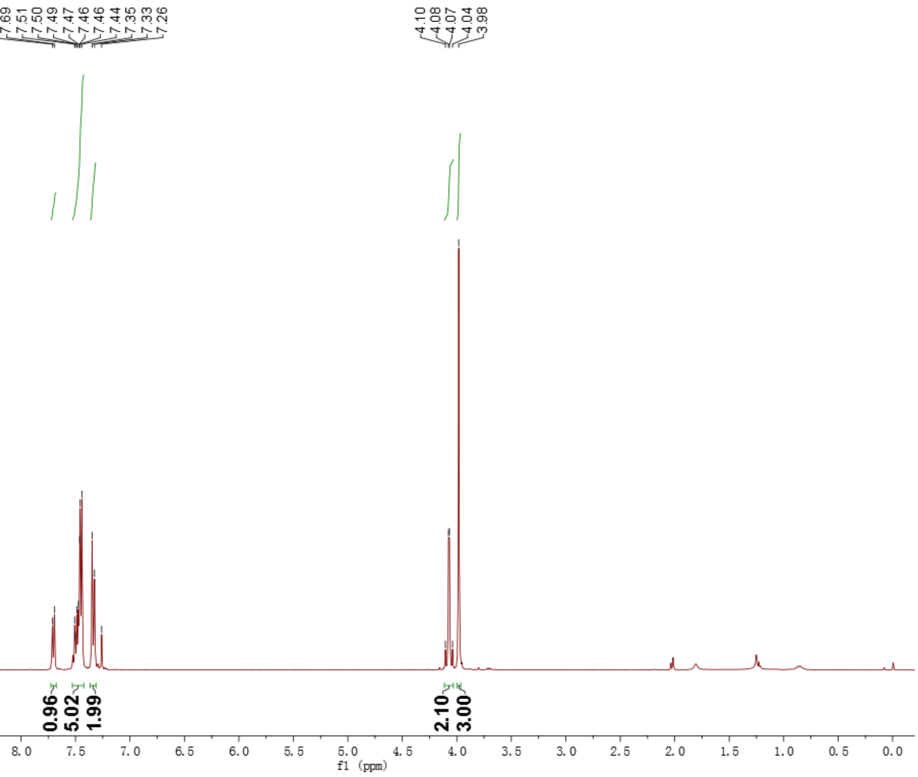
2m

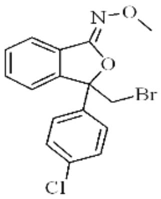

7.71
7.69
7.50
7.48
7.47
7.46
7.45
7.42
7.41
7.39
4.16
4.13
4.12
4.09
3.99
2.33
2n
0.98
3.02
2.07
2.05
2.08
3.00
3.04
f1 (ppm)


154.59
144.57
138.98
135.54
130.98
129.62
129.59
129.31
125.59
122.47
121.87
91.95
77.48
77.16
76.84
63.02
38.41
21.18
2n
f1 (ppm)

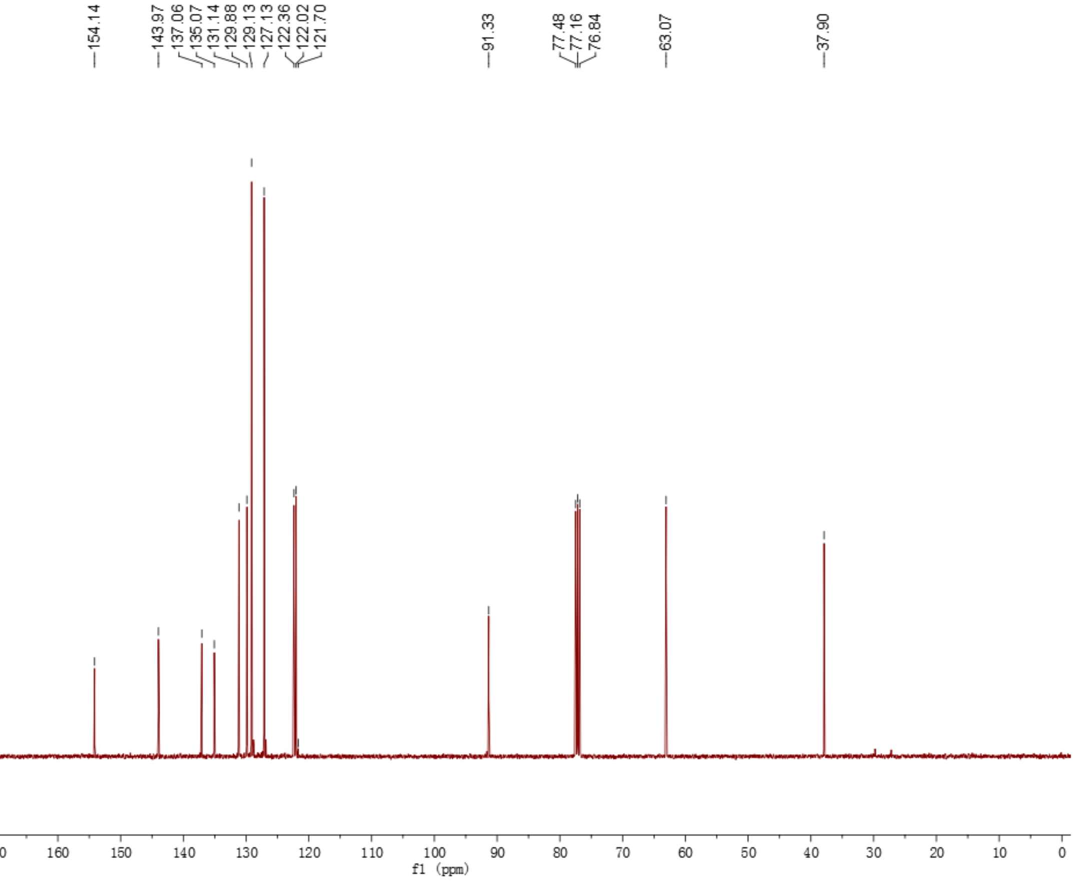

N–O
O
Br
Cl

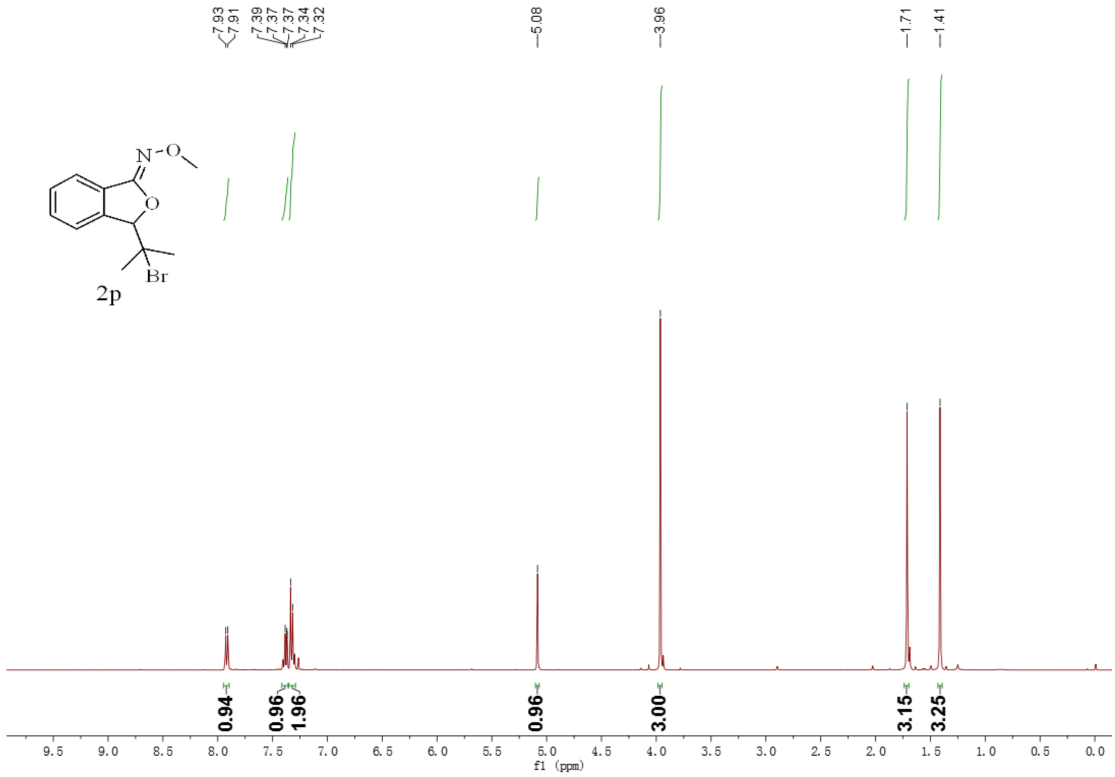
2o

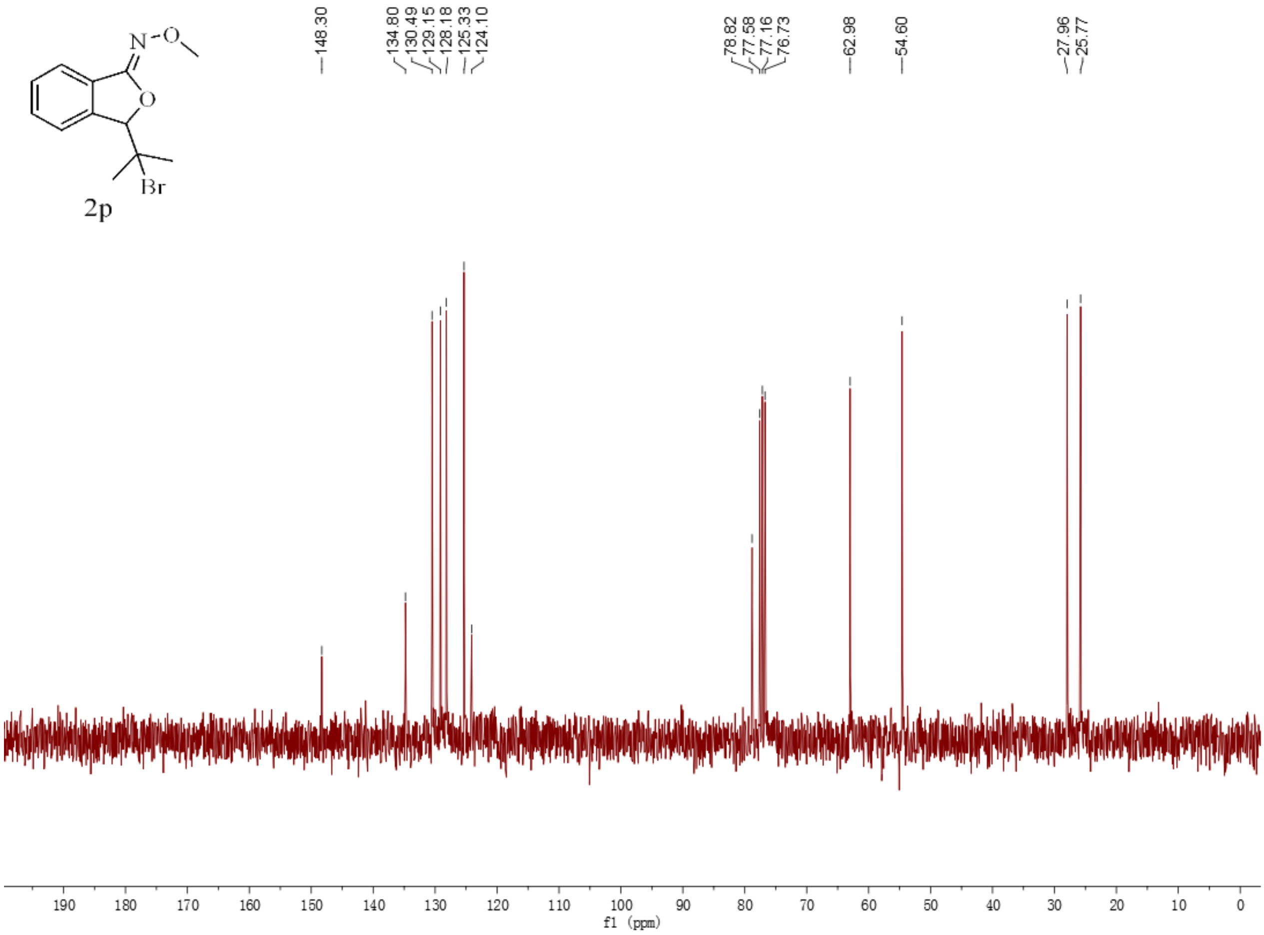

7.71 7.69 7.51 7.50 7.49 7.47 7.46 7.46 7.44 7.35 7.33 7.26
4.10 4.08 4.07 4.04 3.98
0.96 5.02 1.99
2.10 3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

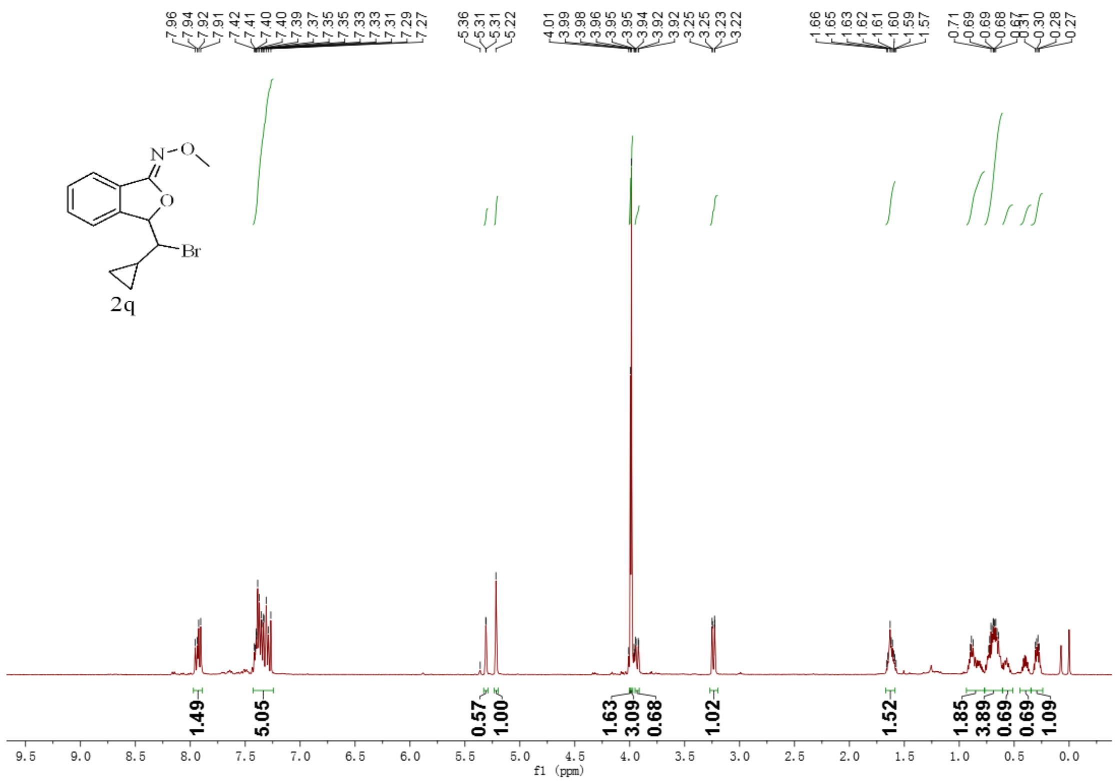

N–O
O
Br
Cl

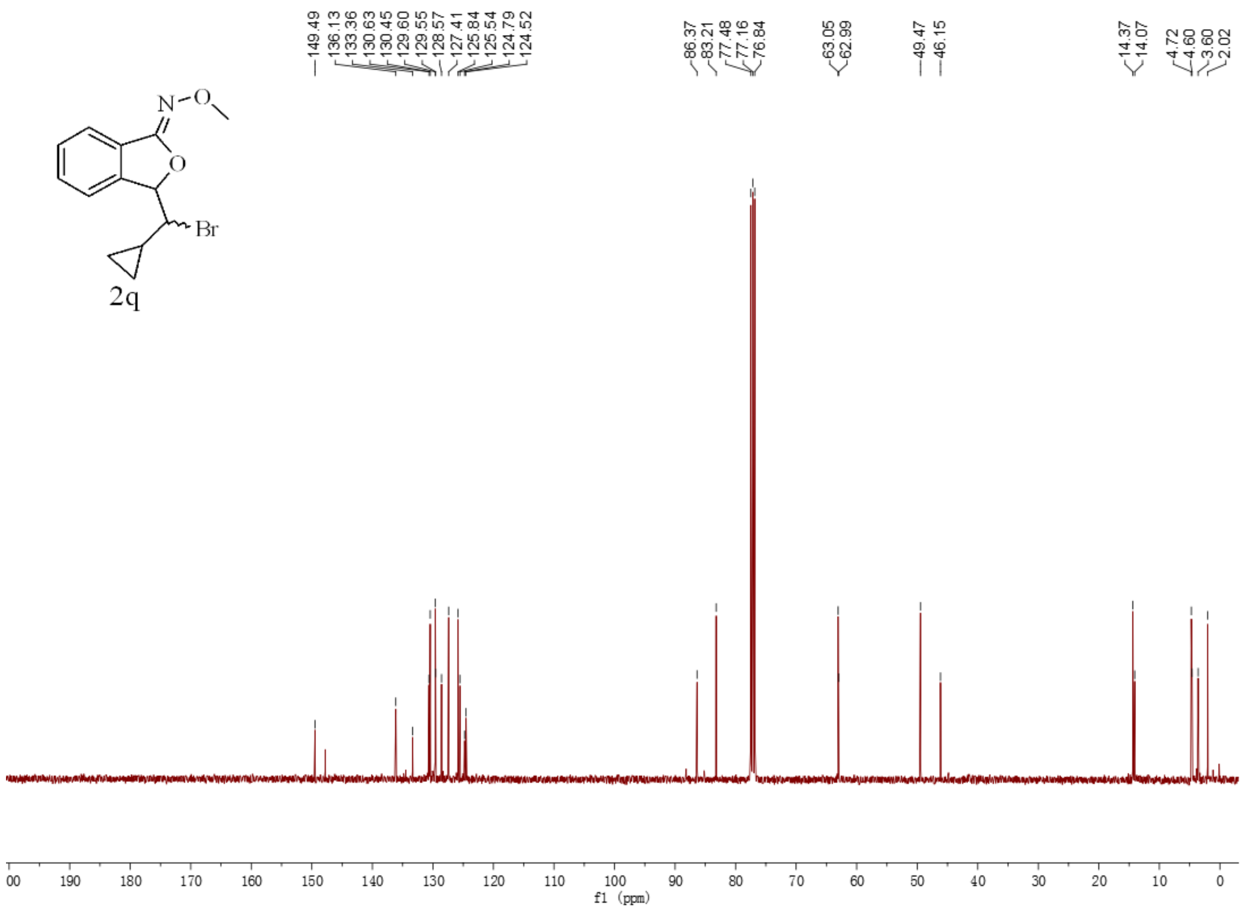
2o

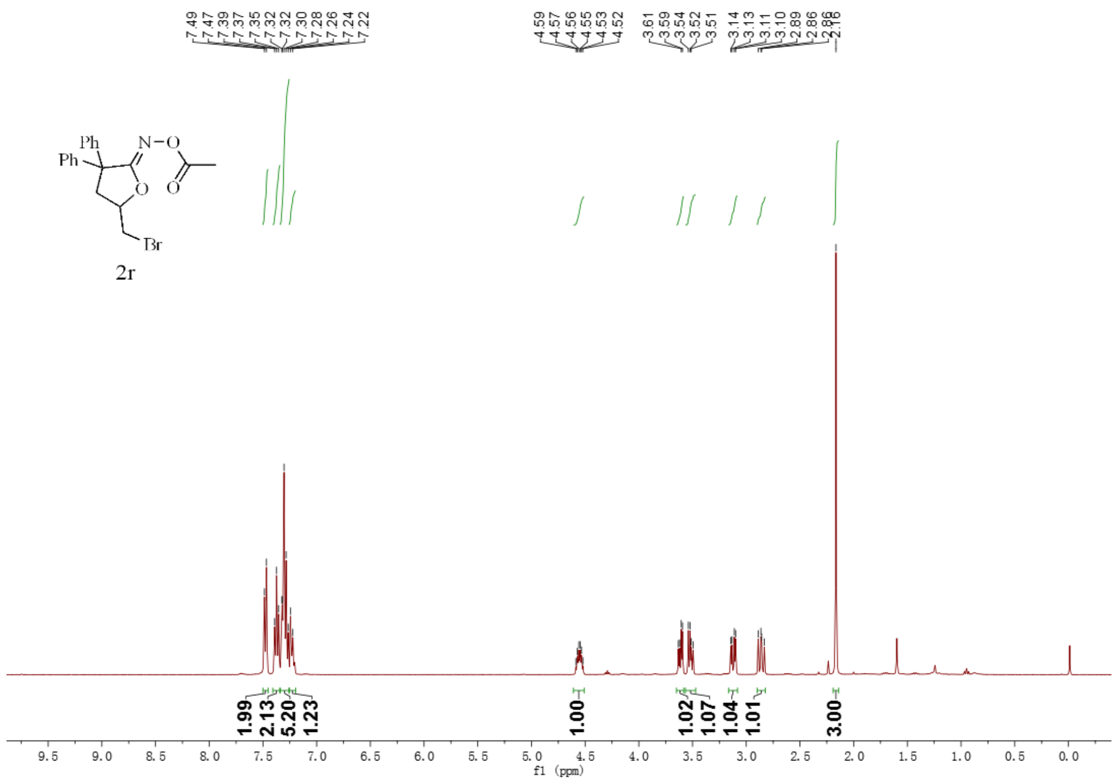

154.14
143.97 137.06 135.07 131.14 129.88 129.13 127.13 122.36 122.02 121.70
91.33
77.48 77.16 76.84
63.07
37.90
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

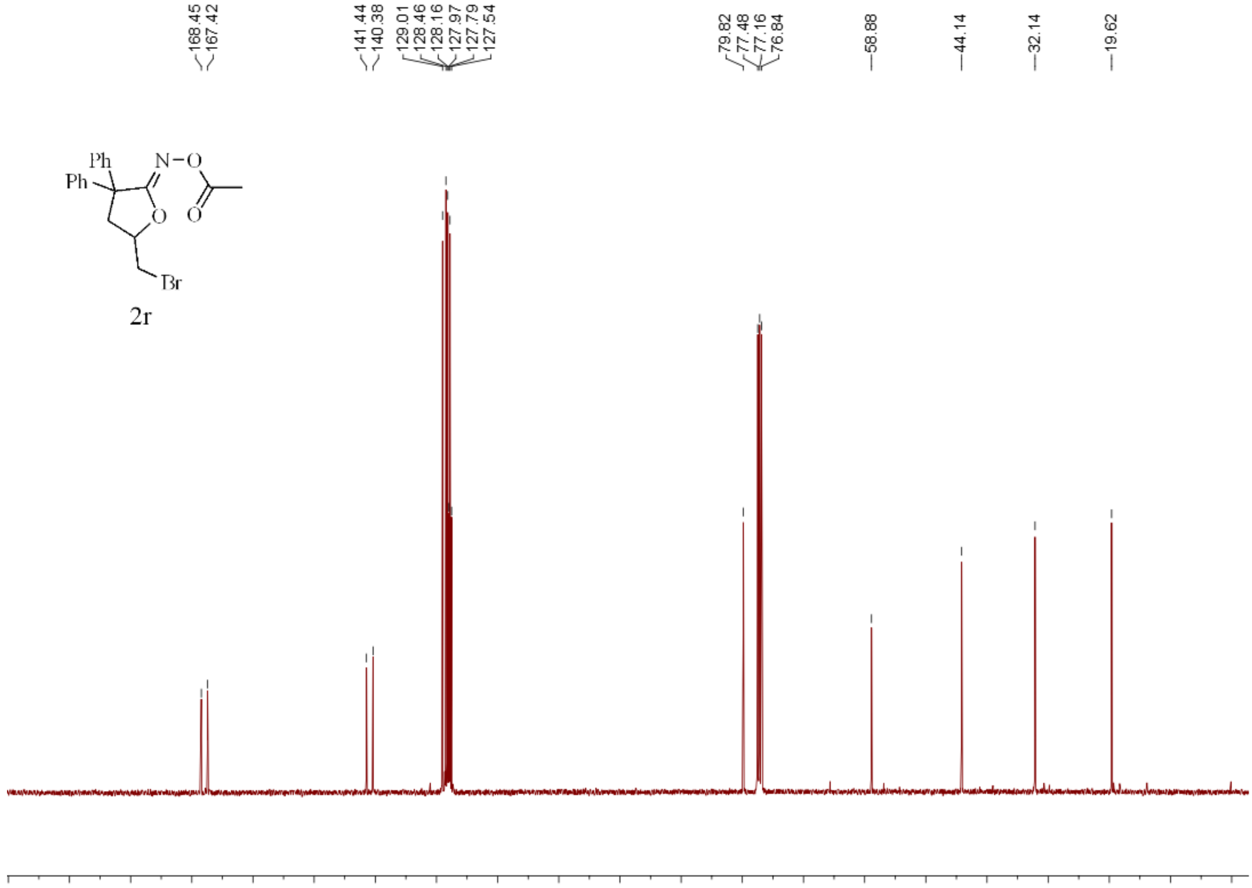

7.93
7.91
7.39
7.37
7.37
7.34
7.32
5.08
3.96
1.71
1.41
N
O
O
Br
2p
0.94
0.96
1.96
0.96
3.00
3.15
3.25
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

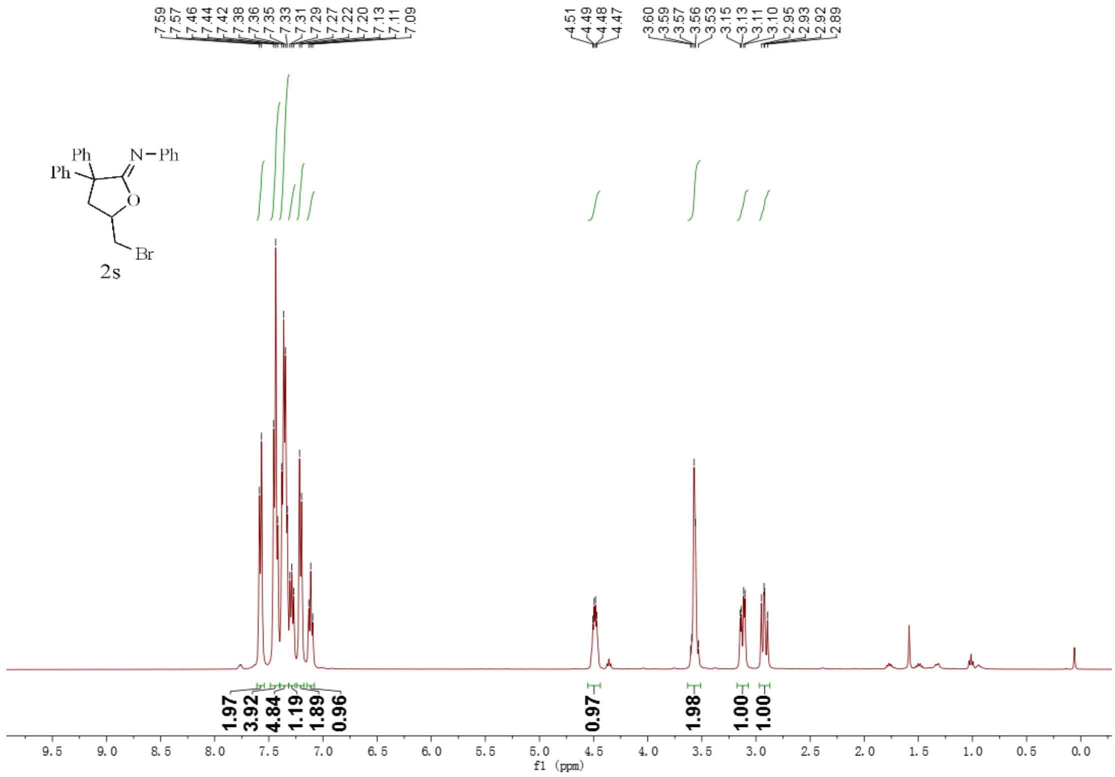

148.30
134.80
130.49
129.15
128.18
125.33
124.10
78.82
77.58
77.16
76.73
62.98
54.60
27.96
25.77
N
O
O
Br
2p
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

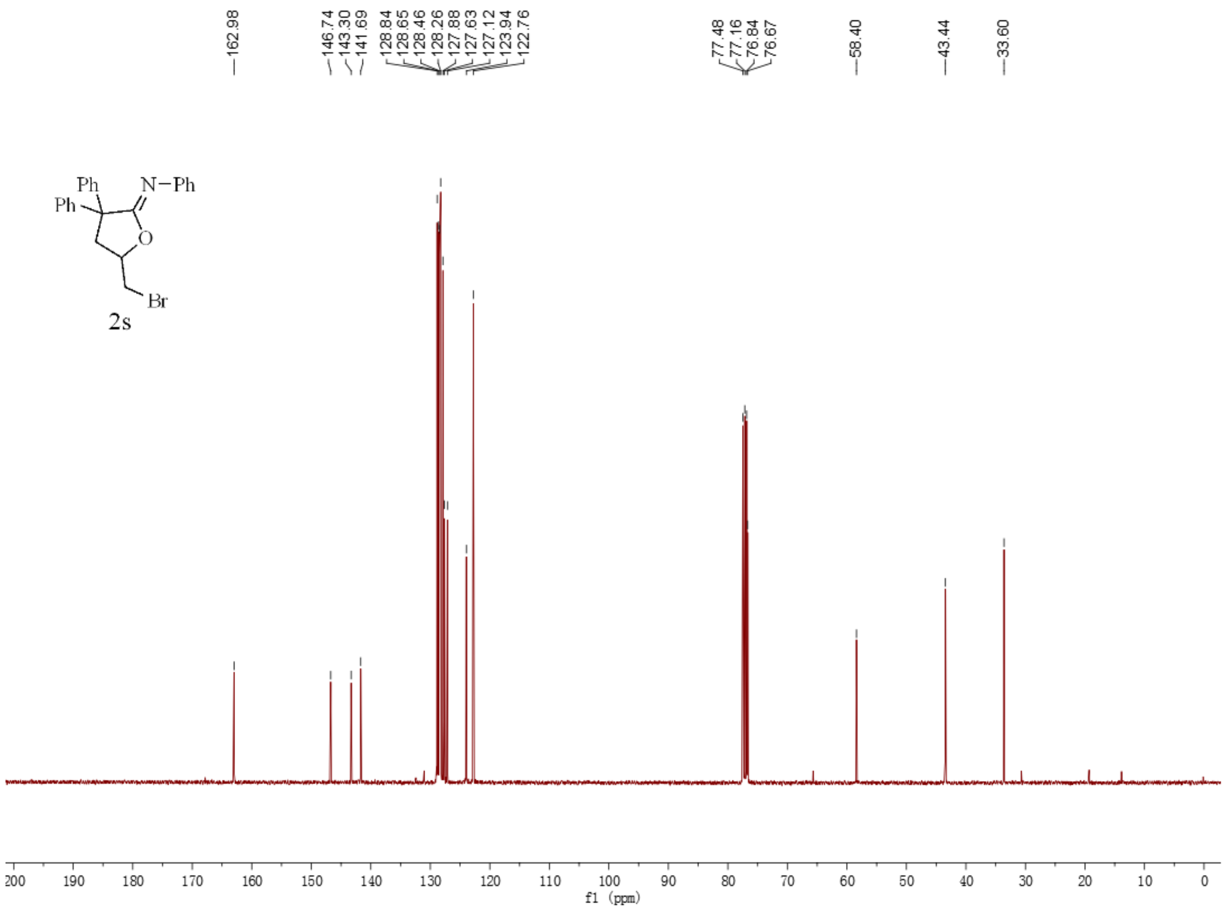

2q

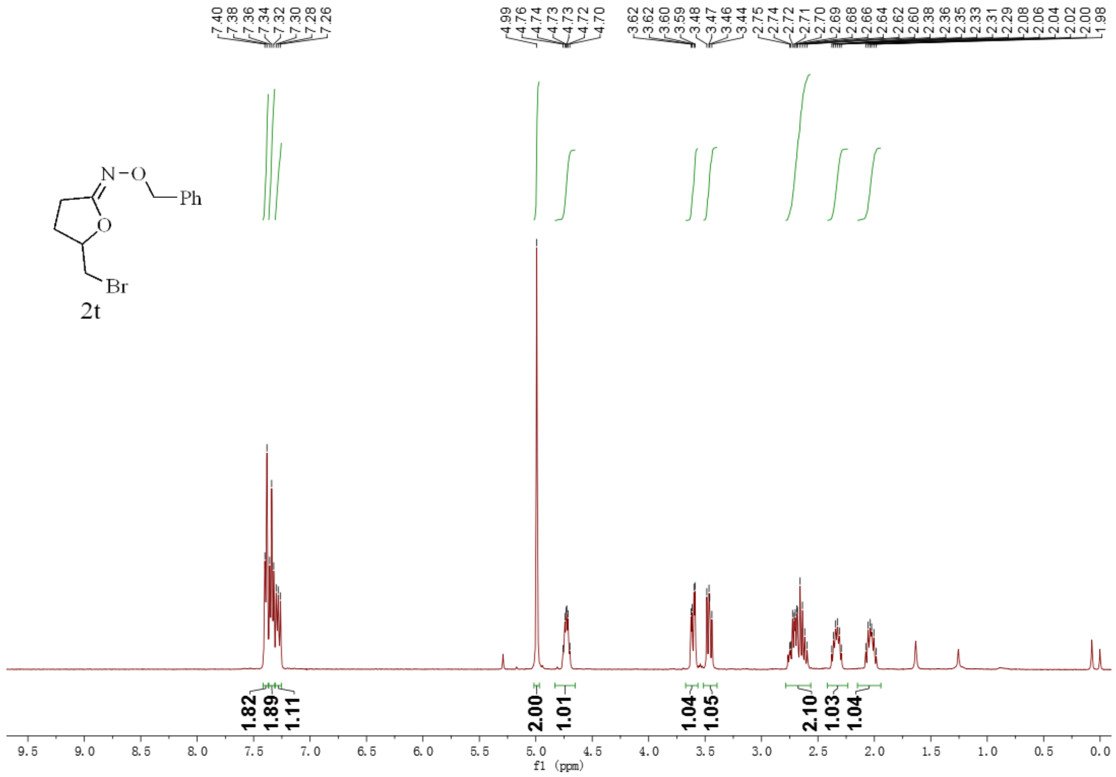

2q



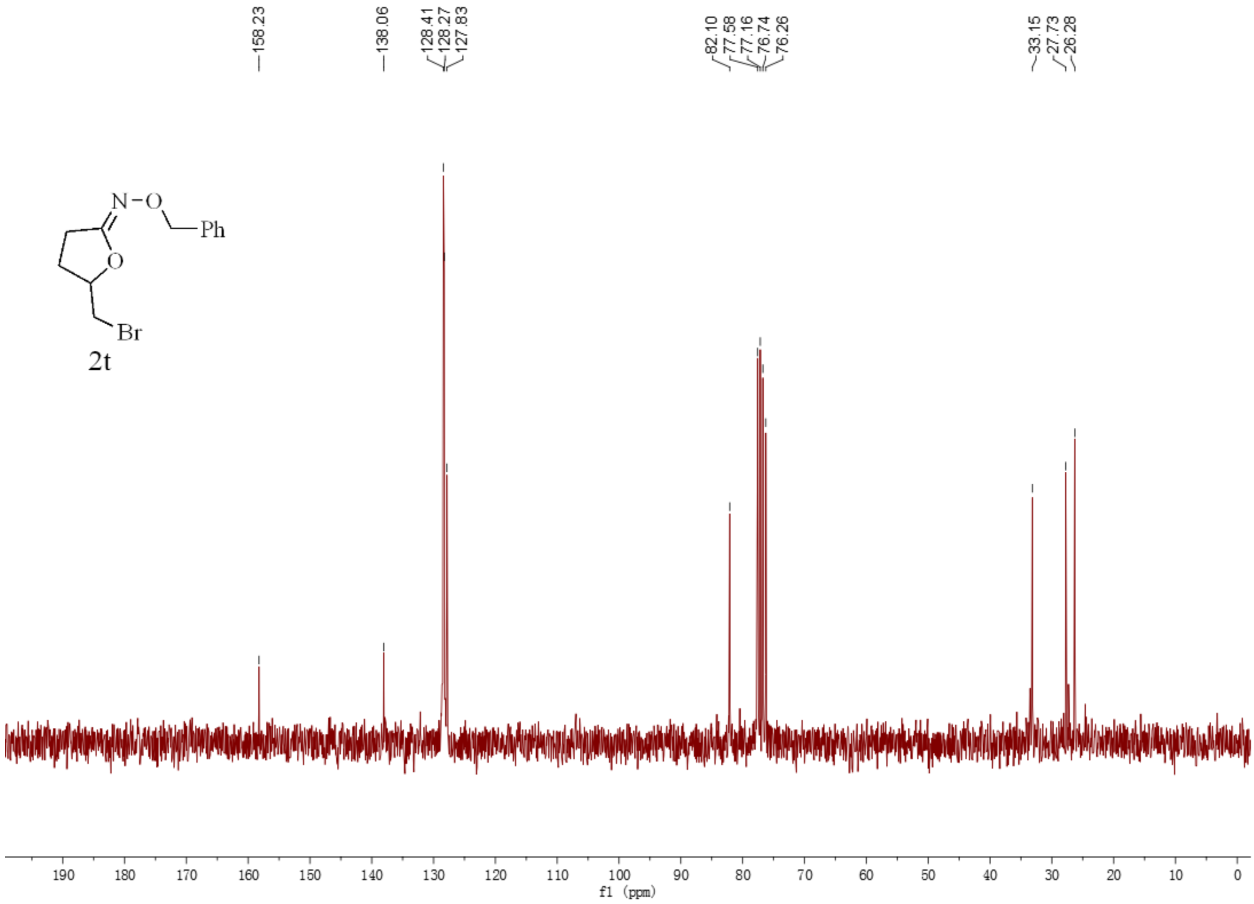



7.59 7.57 7.46 7.44 7.42 7.38 7.36 7.35 7.33 7.31 7.29 7.27 7.22 7.20 7.13 7.11 7.09
4.51 4.49 4.48 4.47
3.60 3.59 3.57 3.56 3.53 3.15 3.13 3.11 3.10 2.95 2.93 2.92 2.89
Ph
N−Ph
Ph
O
Br
2s
1.97 3.92 4.84 1.19 1.89 0.96
0.97
1.98
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

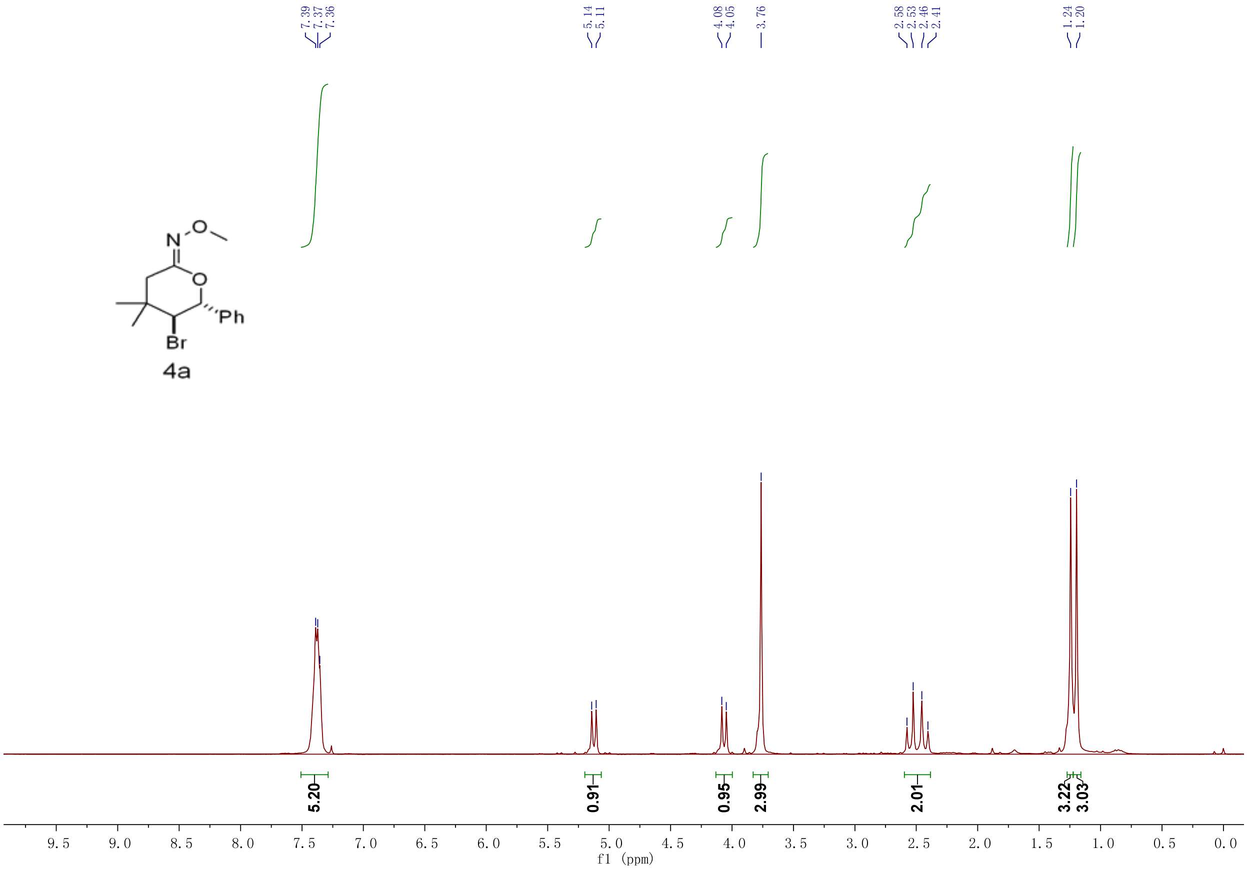

162.98
146.74 143.30 141.69
128.84 128.65 128.46 128.26 127.88 127.63 127.12 123.94 122.76
77.48 77.16 76.84 76.67
58.40
43.44
33.60
Ph
N−Ph
Ph
O
Br
2s
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

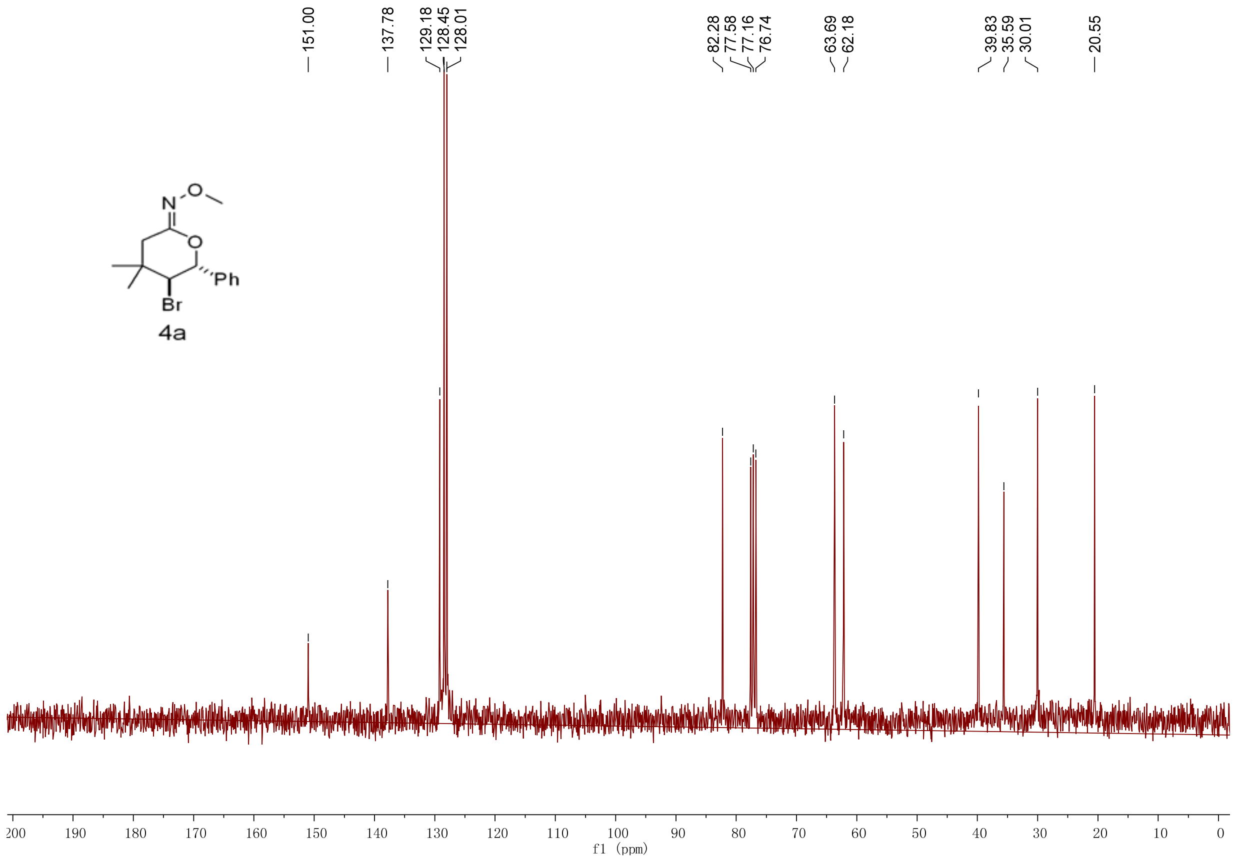


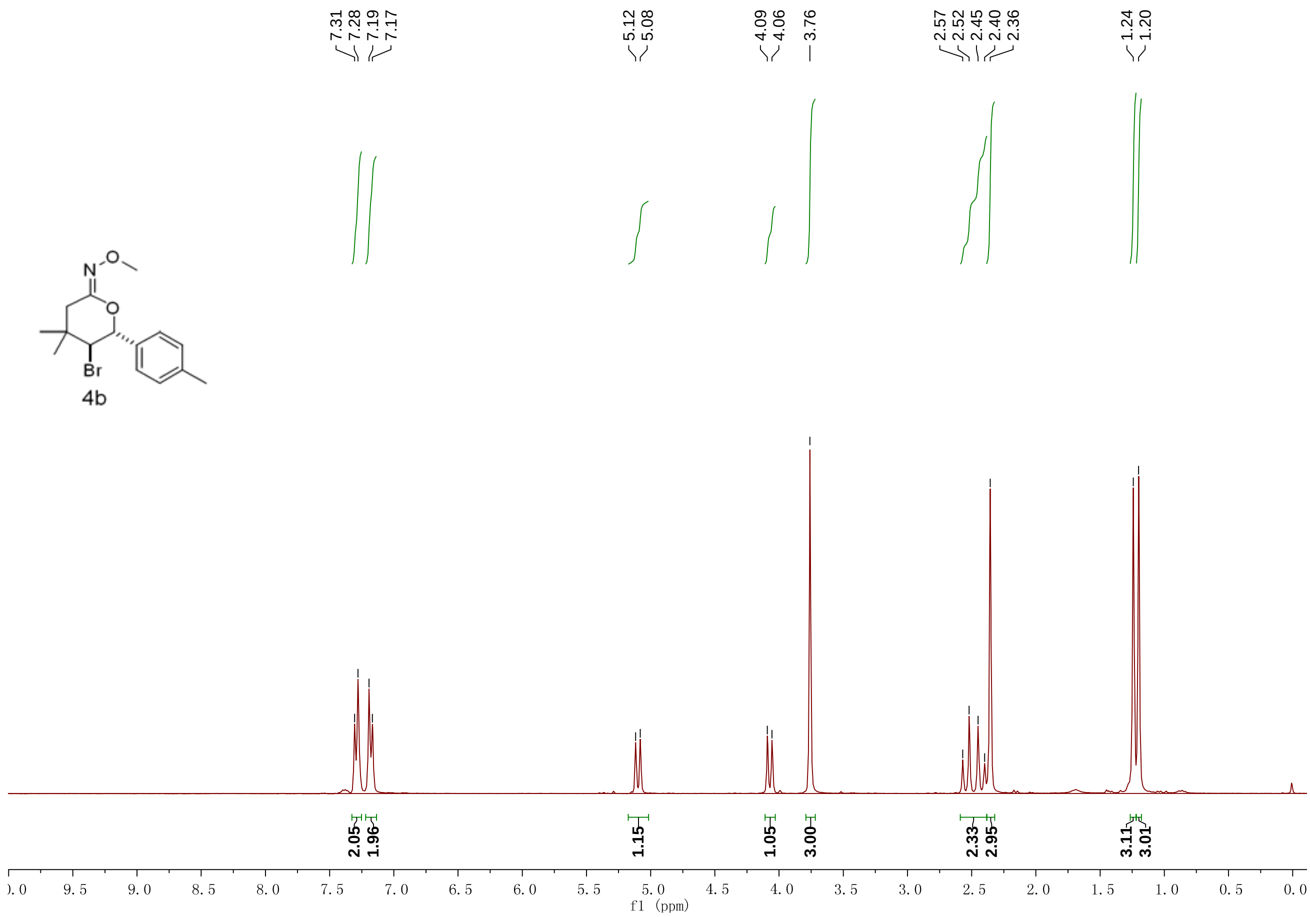
7.40
7.38
7.36
7.34
7.32
7.30
7.28
7.26
4.99
4.76
4.74
4.73
4.73
4.72
4.70
3.62
3.62
3.60
3.59
3.48
3.47
3.46
3.44
2.75
2.74
2.72
2.71
2.70
2.69
2.68
2.66
2.64
2.62
2.60
2.38
2.36
2.35
2.33
2.31
2.29
2.08
2.06
2.04
2.02
2.00
1.98
N–O
Ph
O
Br
2t
1.82
1.89
1.11
2.00
1.01
1.04
1.05
2.10
1.03
1.04
f1 (ppm)

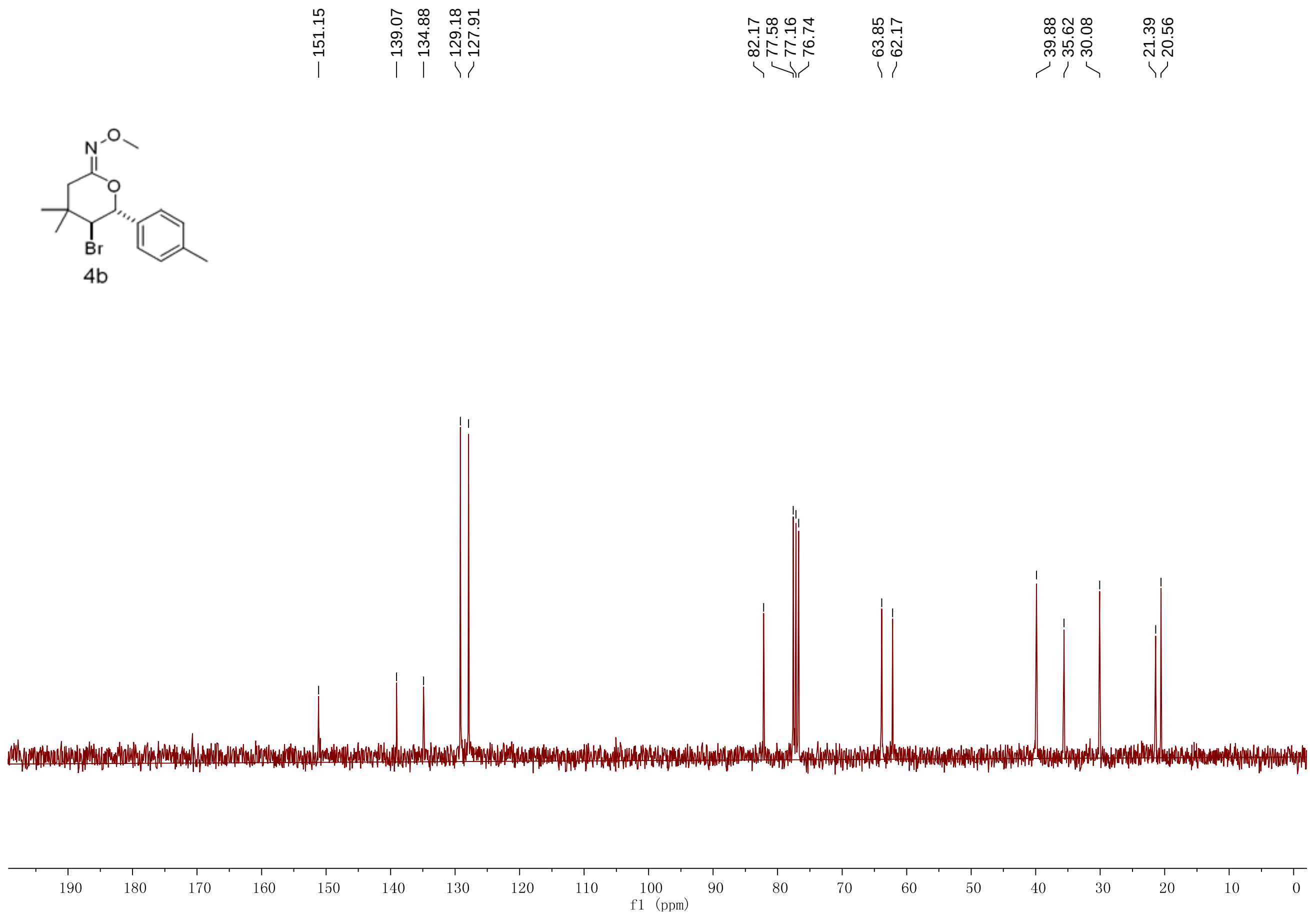


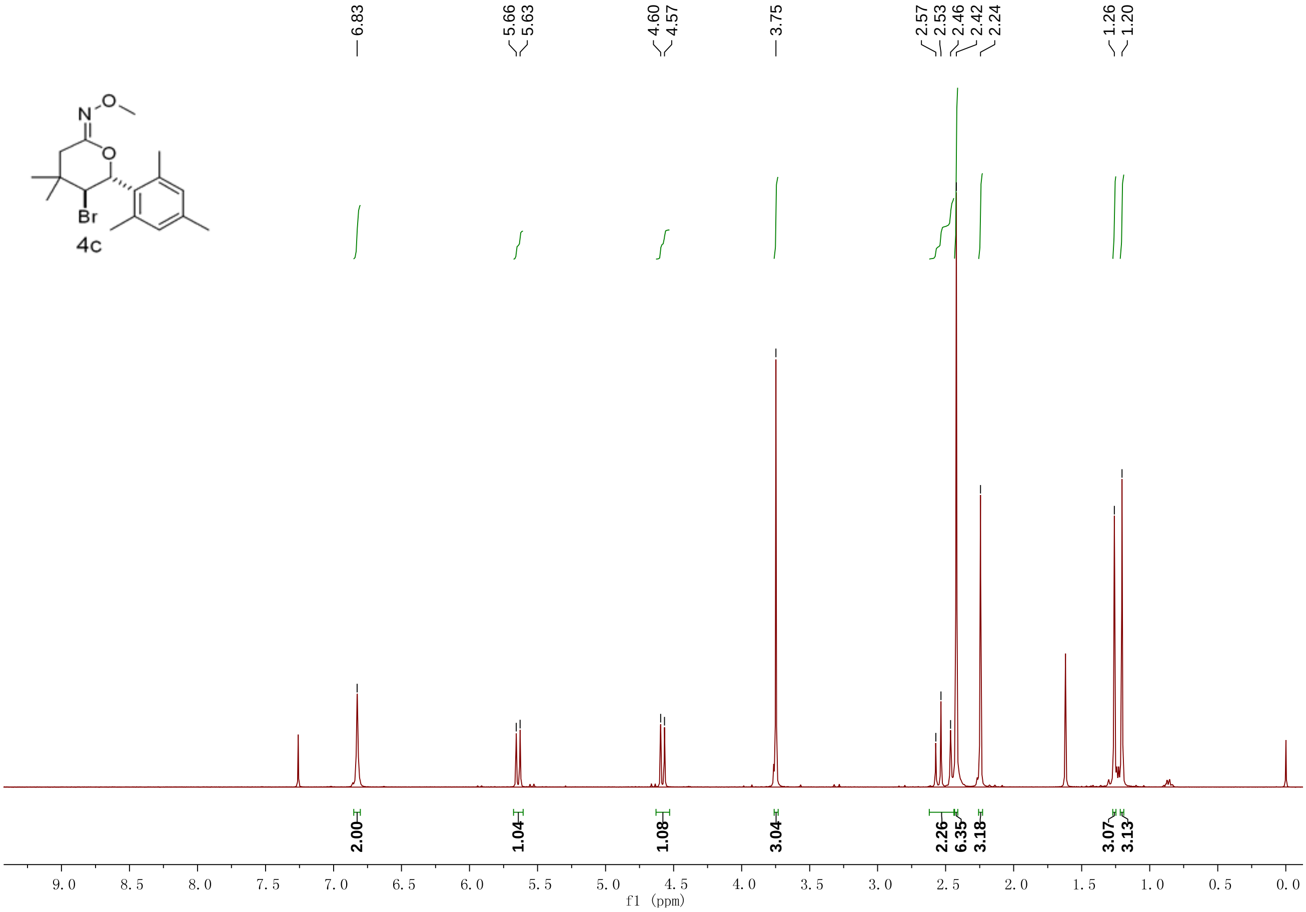
158.23
138.06
128.41
128.27
127.83
82.10
77.58
77.16
76.74
76.26
33.15
27.73
26.28
N–O
Ph
O
Br
2t
f1 (ppm)

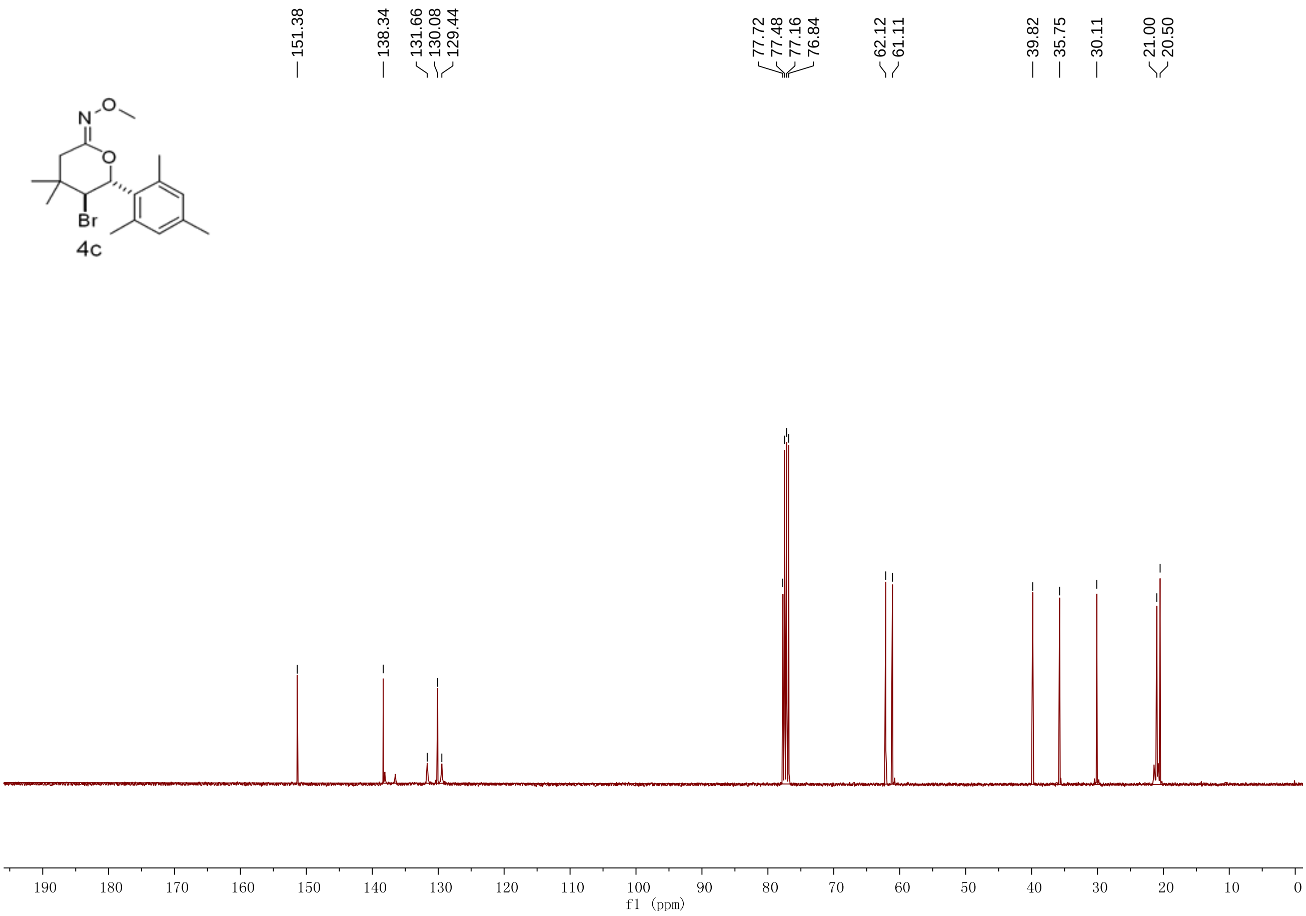

7.39
7.37
7.36
5.14
5.11
4.08
4.05
3.76
2.58
2.53
2.46
2.41
1.24
1.20
N
O
O
Ph
Br
4a
5.20
0.91
0.95
2.99
2.01
3.22
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

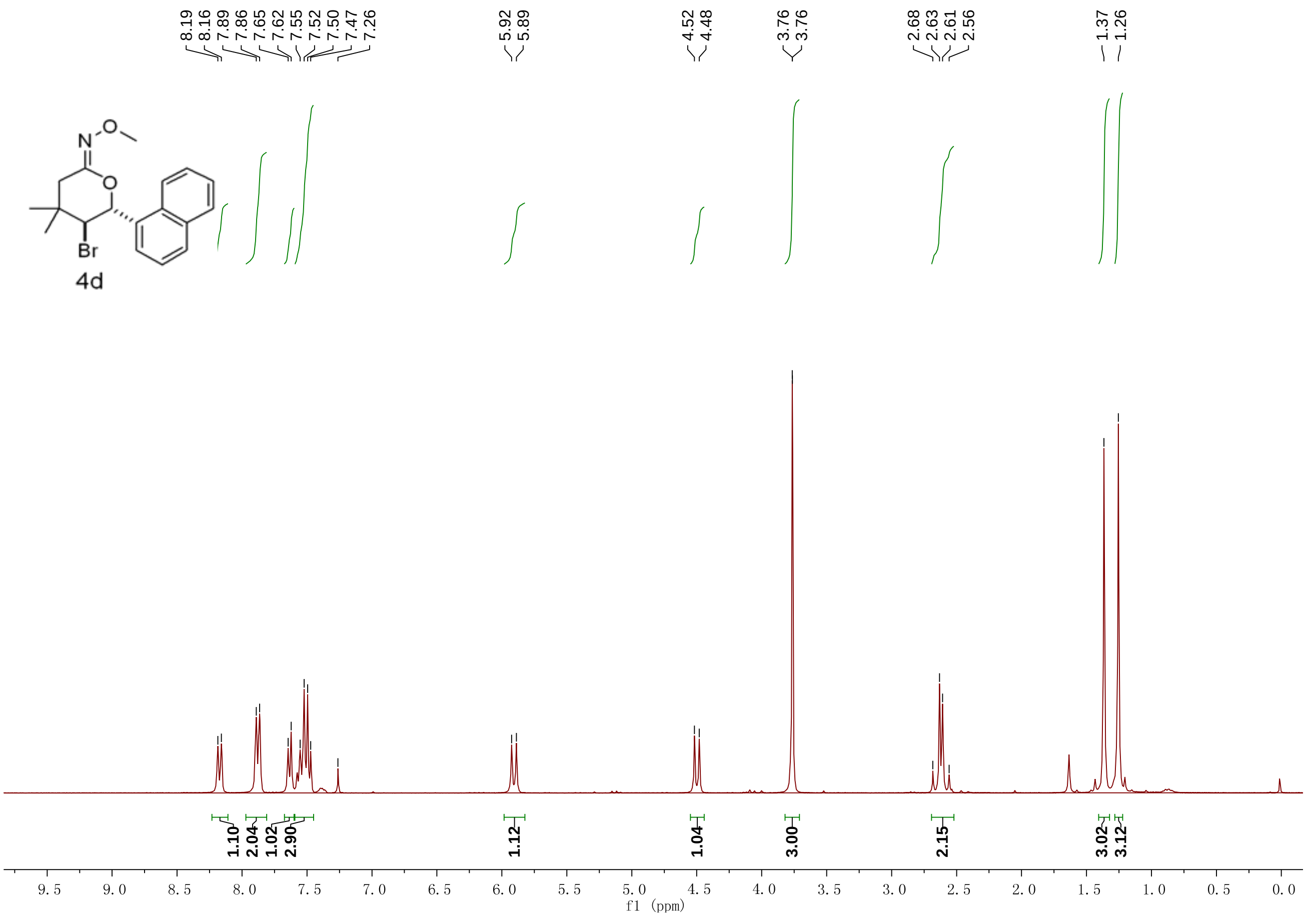

151.00
137.78
129.18
128.45
128.01
82.28
77.58
77.16
76.74
63.69
62.18
39.83
35.59
30.01
20.55
N
O
O
Ph
Br
4a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

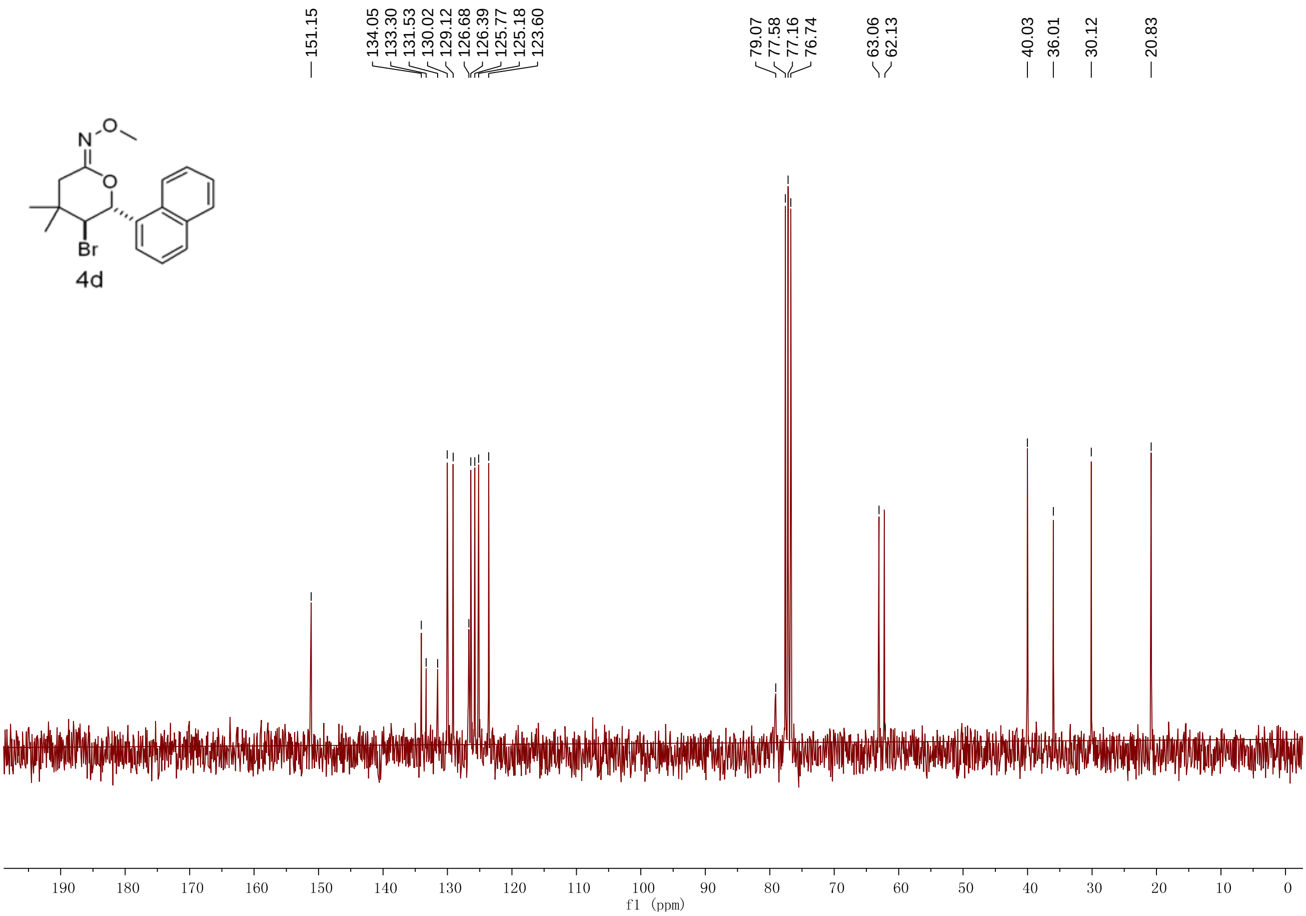

7.31
7.28
7.19
7.17
5.12
5.08
4.09
4.06
3.76
2.57
2.52
2.45
2.40
2.36
1.24
1.20
4b
Br
N
O
2.05
1.96
1.15
1.05
3.00
2.33
2.95
3.11
3.01
f1 (ppm)

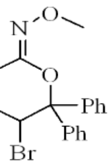

151.15
139.07
134.88
129.18
127.91
82.17
77.58
77.16
76.74
63.85
62.17
39.88
35.62
30.08
21.39
20.56
4b
Br
N
O
f1 (ppm)


6.83
5.66
5.63
4.60
4.57
3.75
2.57
2.53
2.46
2.42
2.24
1.26
1.20
N
O
Br
4c
2.00
1.04
1.08
3.04
2.26
6.35
3.18
3.07
3.13
f1 (ppm)

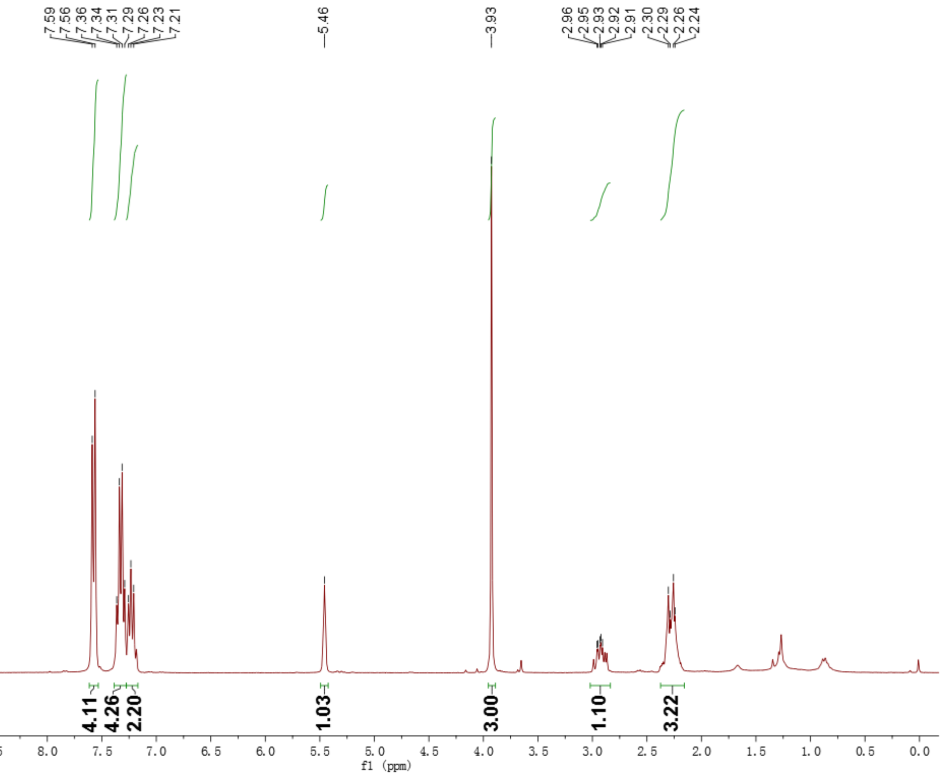

151.38
138.34
131.66
130.08
129.44
77.72
77.48
77.16
76.84
62.12
61.11
39.82
35.75
30.11
21.00
20.50
N
O
Br
4c
f1 (ppm)

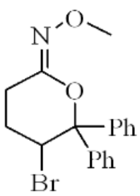

8.19
8.16
7.89
7.86
7.65
7.62
7.55
7.52
7.50
7.47
7.26
5.92
5.89
4.52
4.48
3.76
3.76
2.68
2.63
2.61
2.56
1.37
1.26
N
O
O
Br
4d
1.10
2.04
1.02
2.90
1.12
1.04
3.00
2.15
3.02
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


151.15
134.05
133.30
131.53
130.02
129.12
126.68
126.39
125.77
125.18
123.60
79.07
77.58
77.16
76.74
63.06
62.13
40.03
36.01
30.12
20.83
N
O
O
Br
4d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

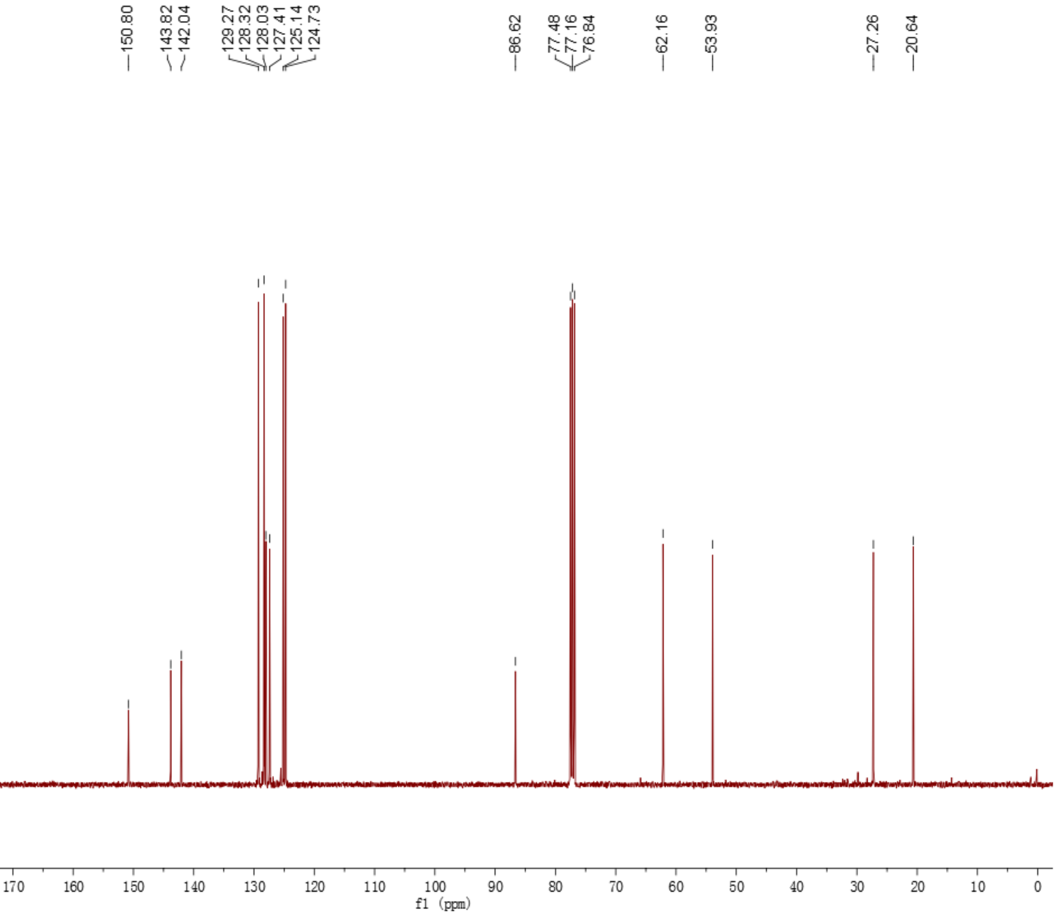


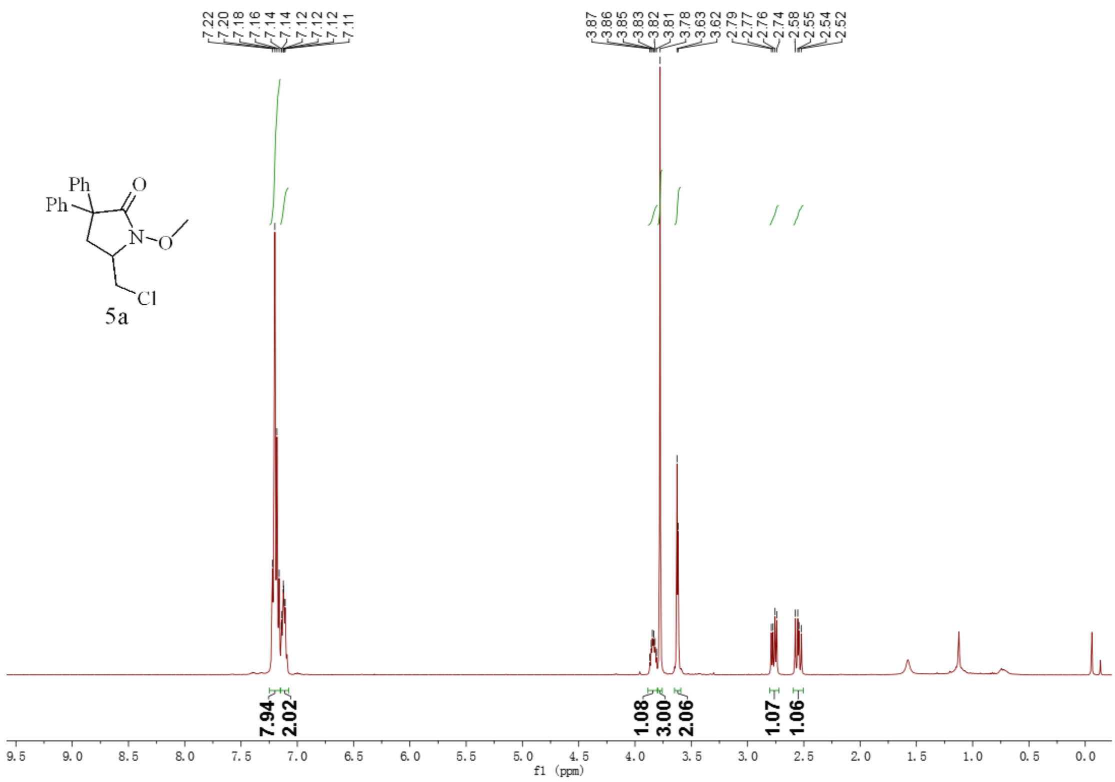
4e

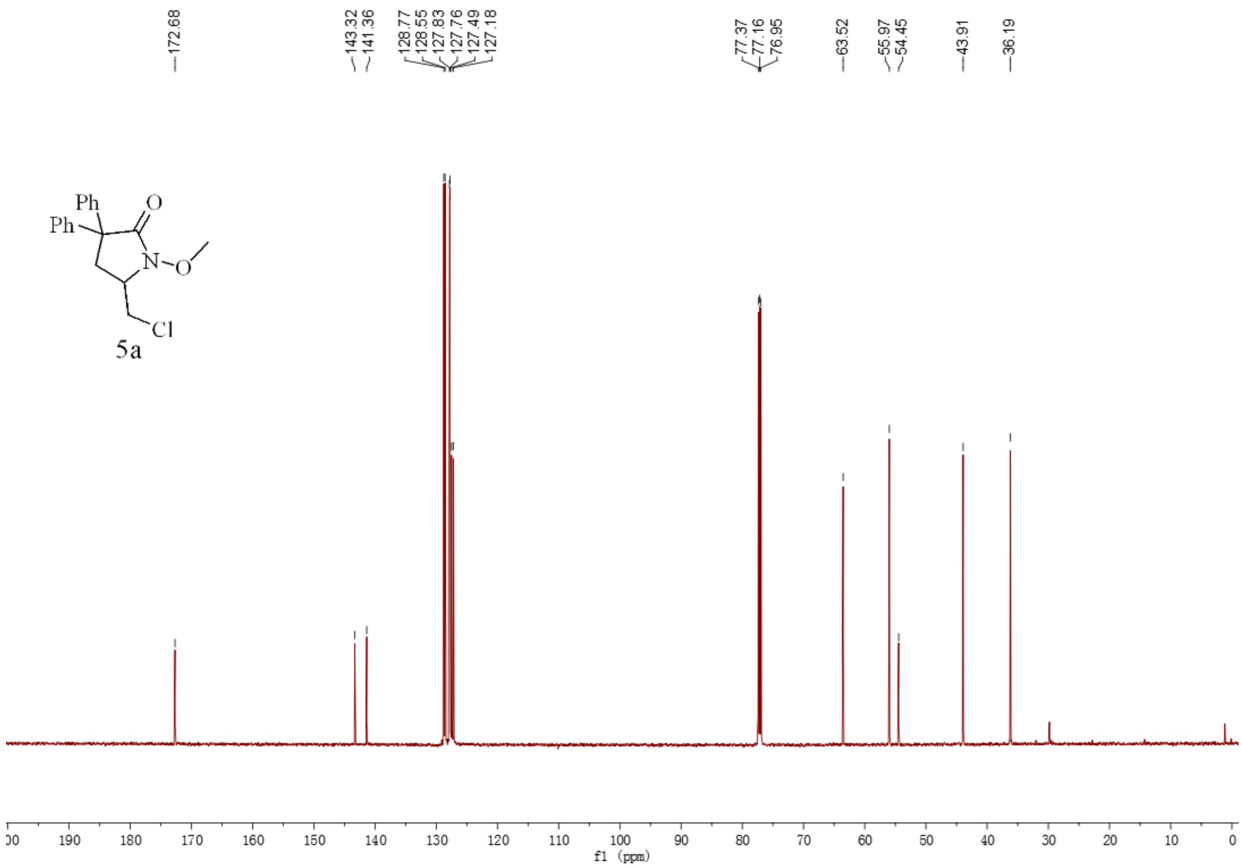

7.59
7.56
7.36
7.34
7.31
7.29
7.26
7.23
7.21
5.46
3.93
2.96
2.95
2.93
2.92
2.91
2.30
2.29
2.26
2.24
4.11
4.26
2.20
1.03
3.00
1.10
3.22
f1 (ppm)

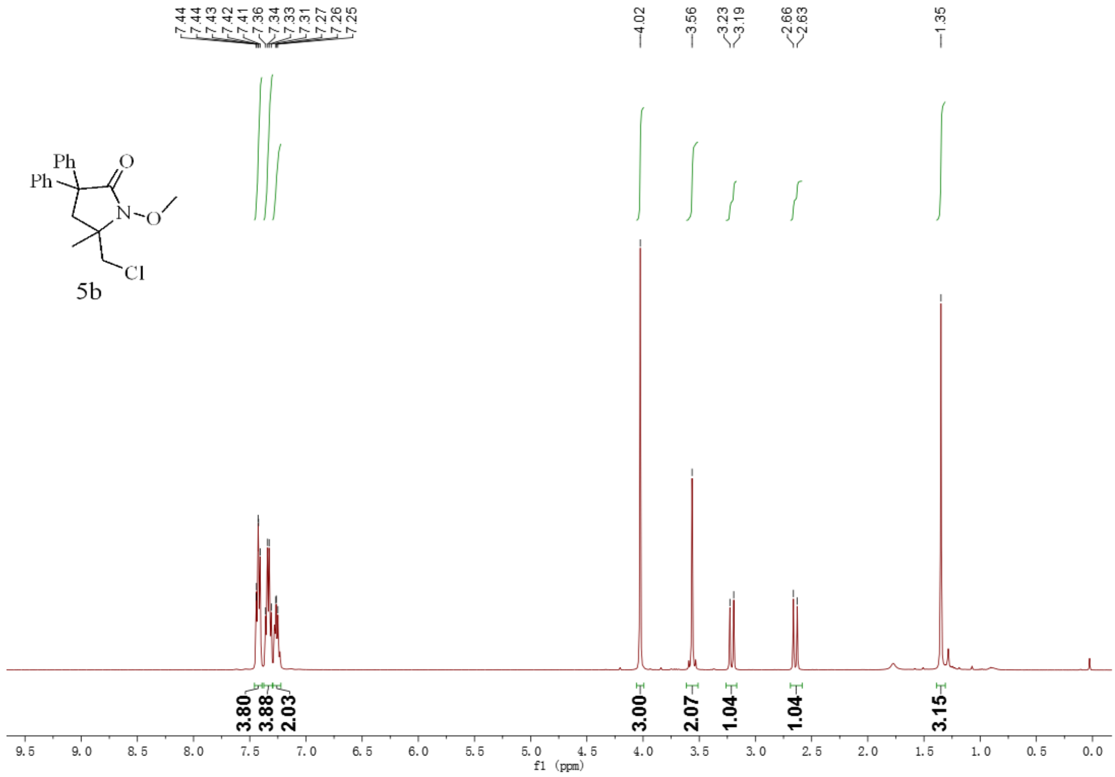


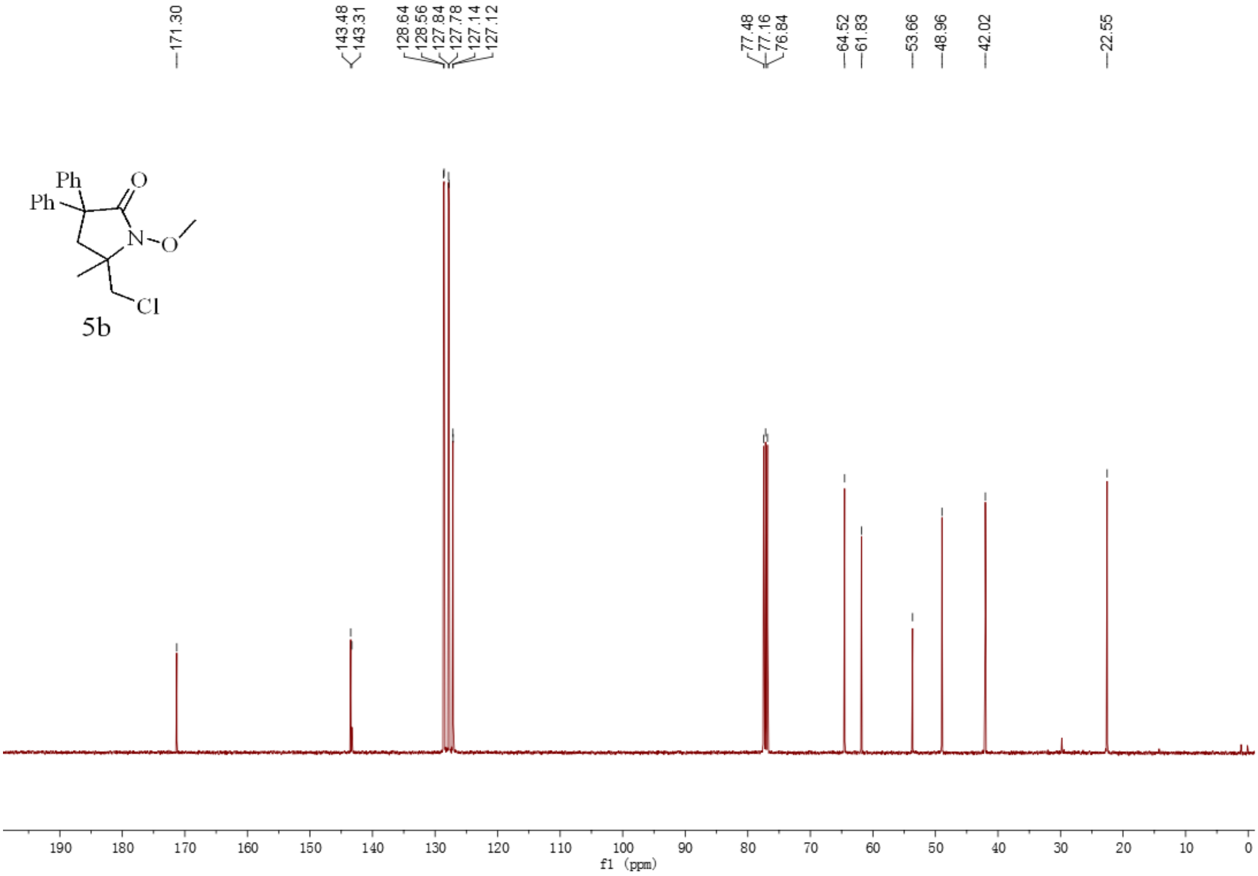
4e

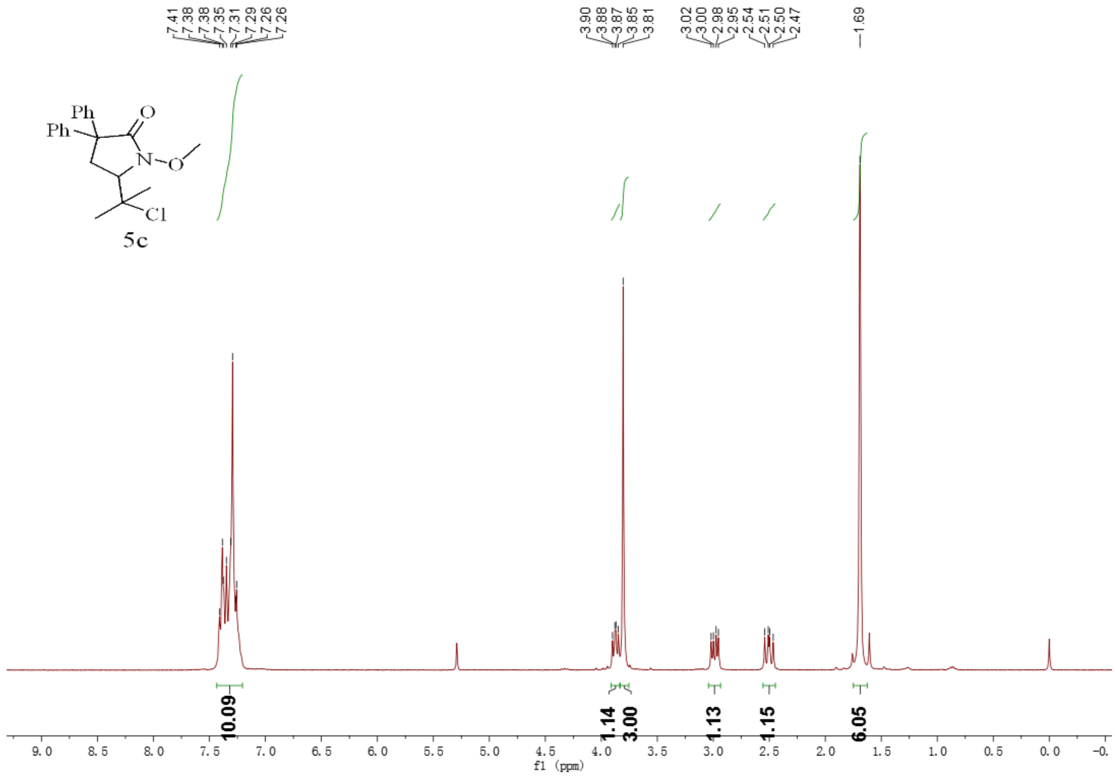

150.80
143.82
142.04
129.27
128.32
128.03
127.41
125.14
124.73
86.62
77.48
77.16
76.84
62.16
53.93
27.26
20.64
f1 (ppm)

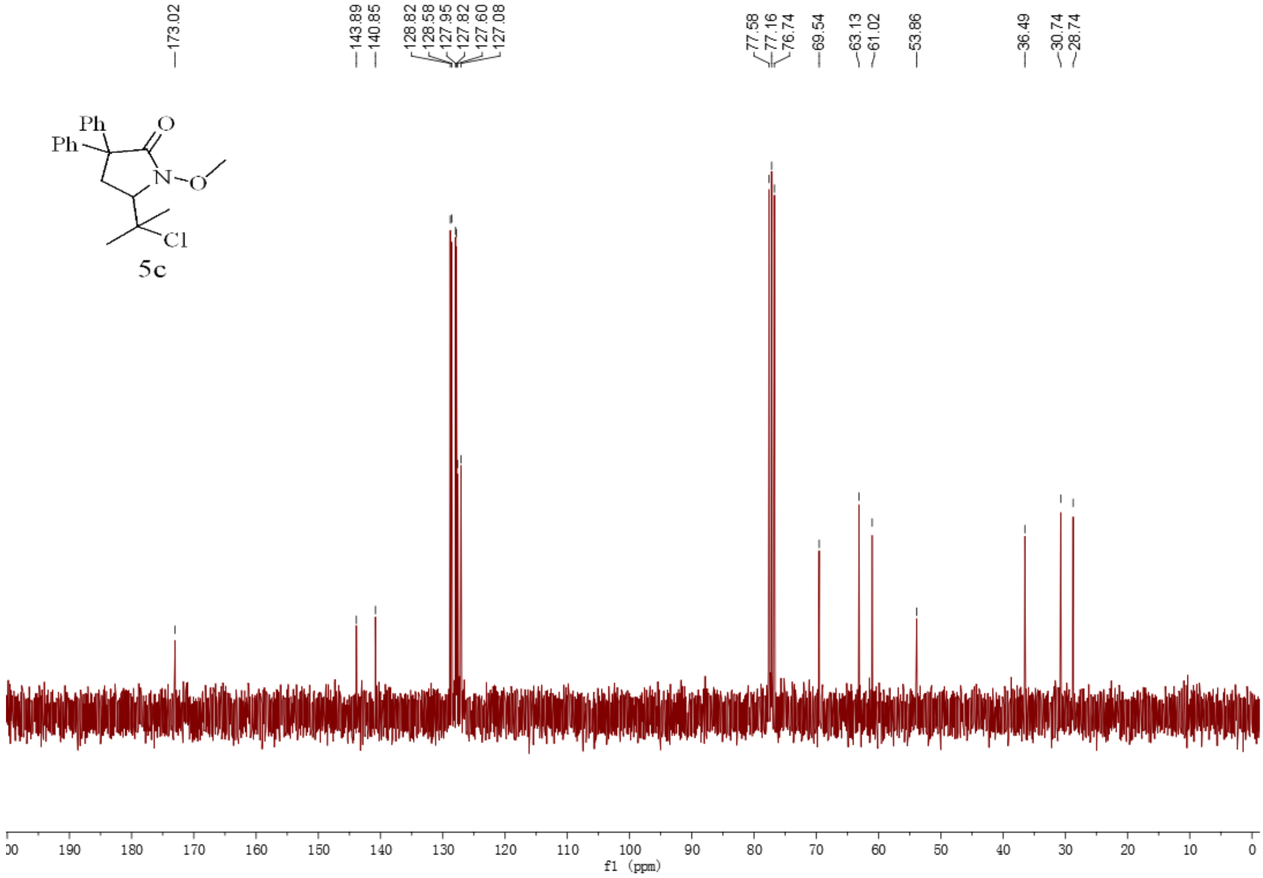

7.22
7.20
7.18
7.16
7.14
7.14
7.12
7.12
7.12
7.11
3.87
3.86
3.85
3.83
3.82
3.81
3.78
3.63
3.62
2.79
2.77
2.76
2.74
2.58
2.55
2.54
2.52
Ph
Ph
O
N
O
Cl
5a
7.94
2.02
1.08
3.00
2.06
1.07
1.06
f1 (ppm)

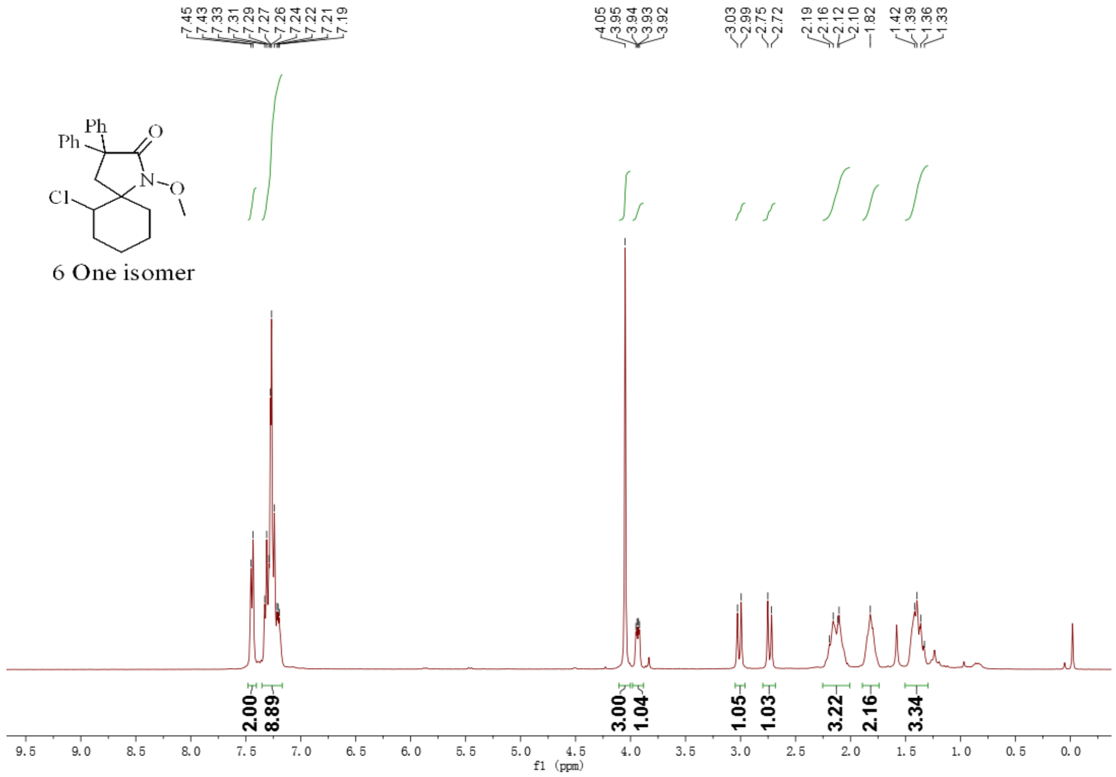

172.68
143.32
141.36
128.77
128.55
127.83
127.76
127.49
127.18
77.37
77.16
76.95
63.52
55.97
54.45
43.91
36.19
Ph
Ph
O
N
O
Cl
5a
f1 (ppm)

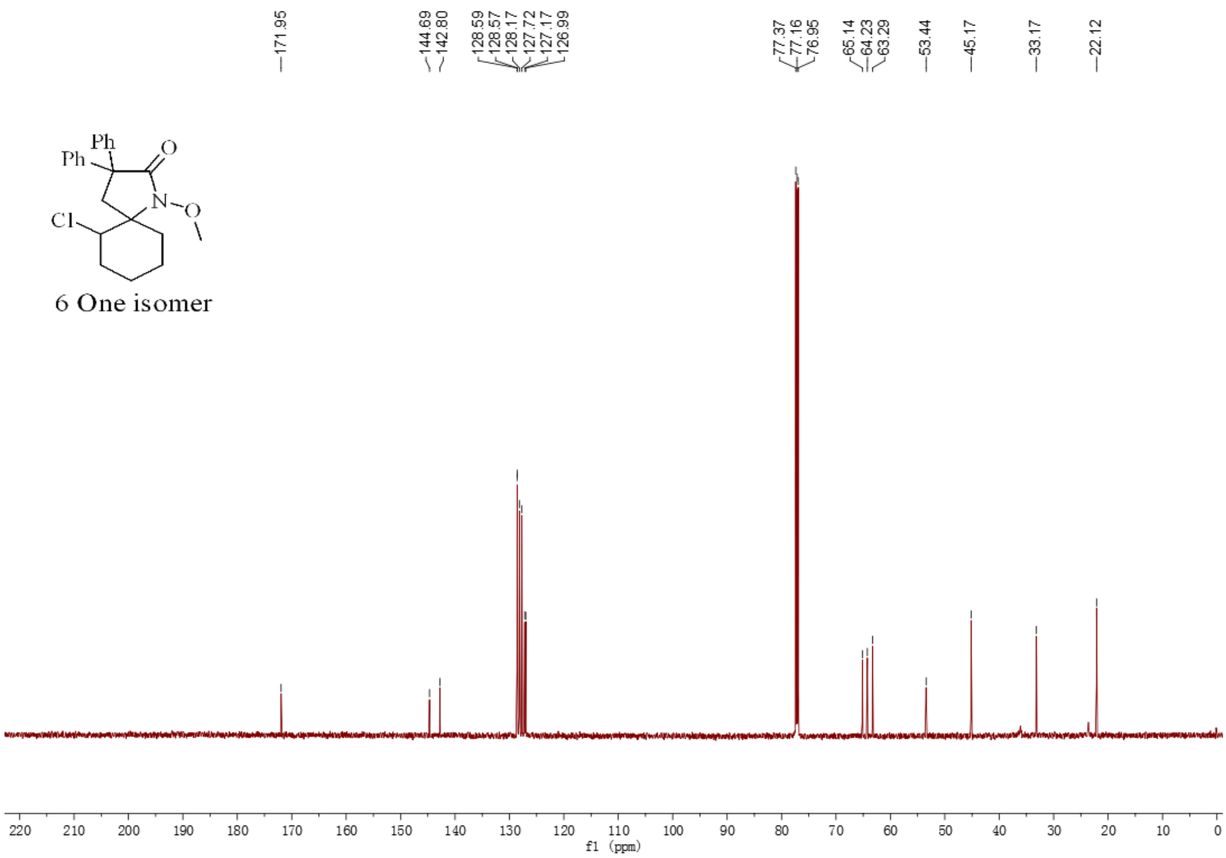

7.44
7.44
7.43
7.42
7.41
7.36
7.34
7.33
7.31
7.27
7.26
7.25
4.02
3.56
3.23
3.19
2.66
2.63
1.35
Ph
Ph
O
N
O
Cl
5b
3.80
3.88
2.03
3.00
2.07
1.04
1.04
3.15
f1 (ppm)

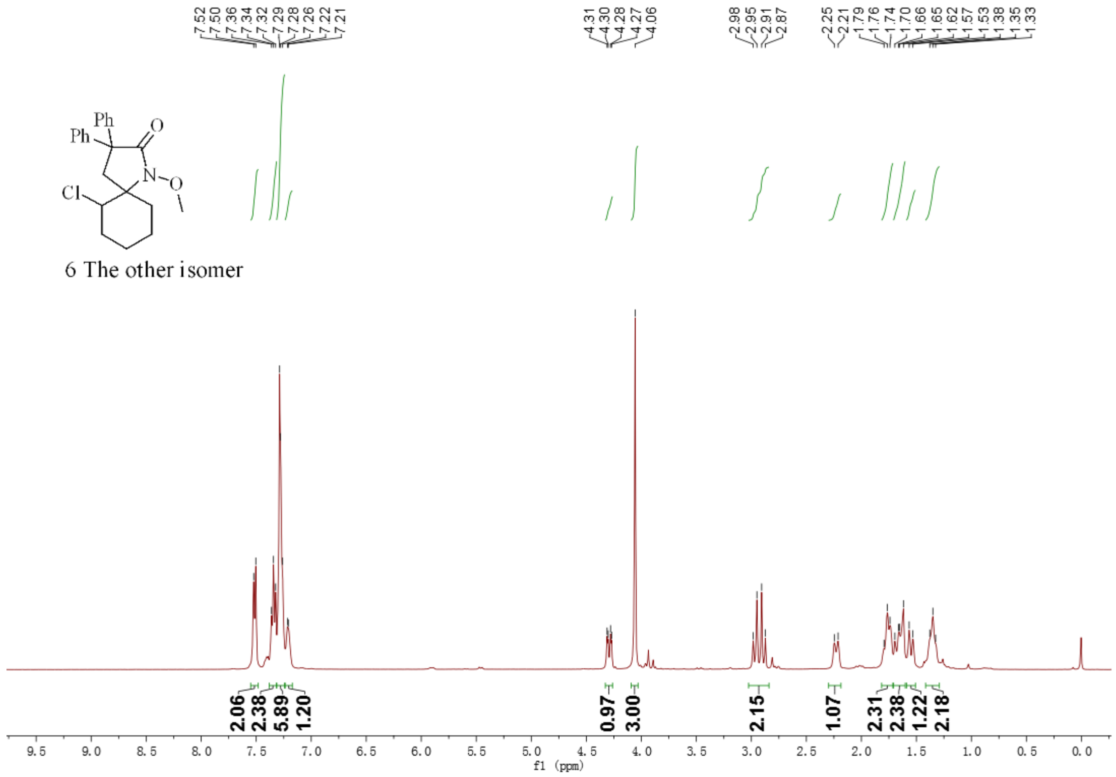

171.30
143.48
143.31
128.64
128.56
127.84
127.78
127.14
127.12
77.48
77.16
76.84
64.52
61.83
53.66
48.96
42.02
22.55
Ph
Ph
O
N
O
Cl
5b
f1 (ppm)

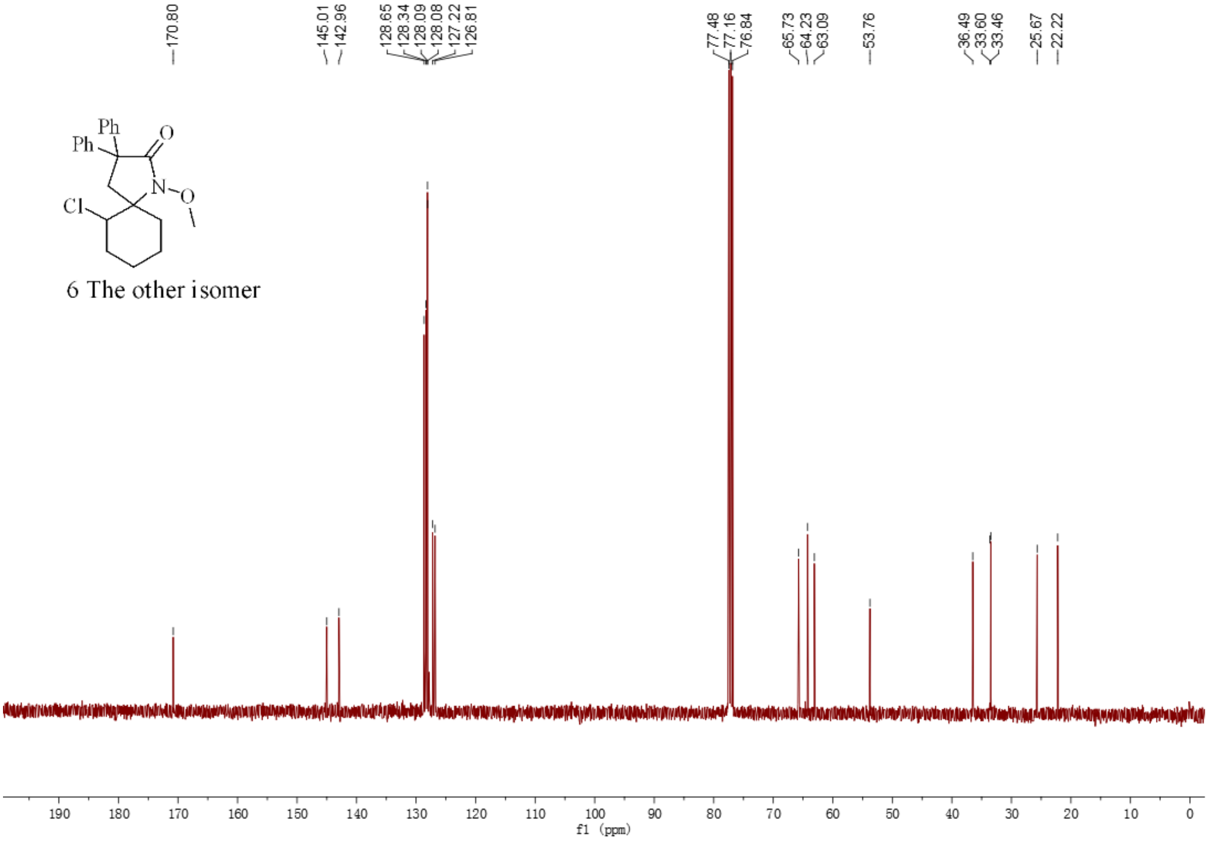


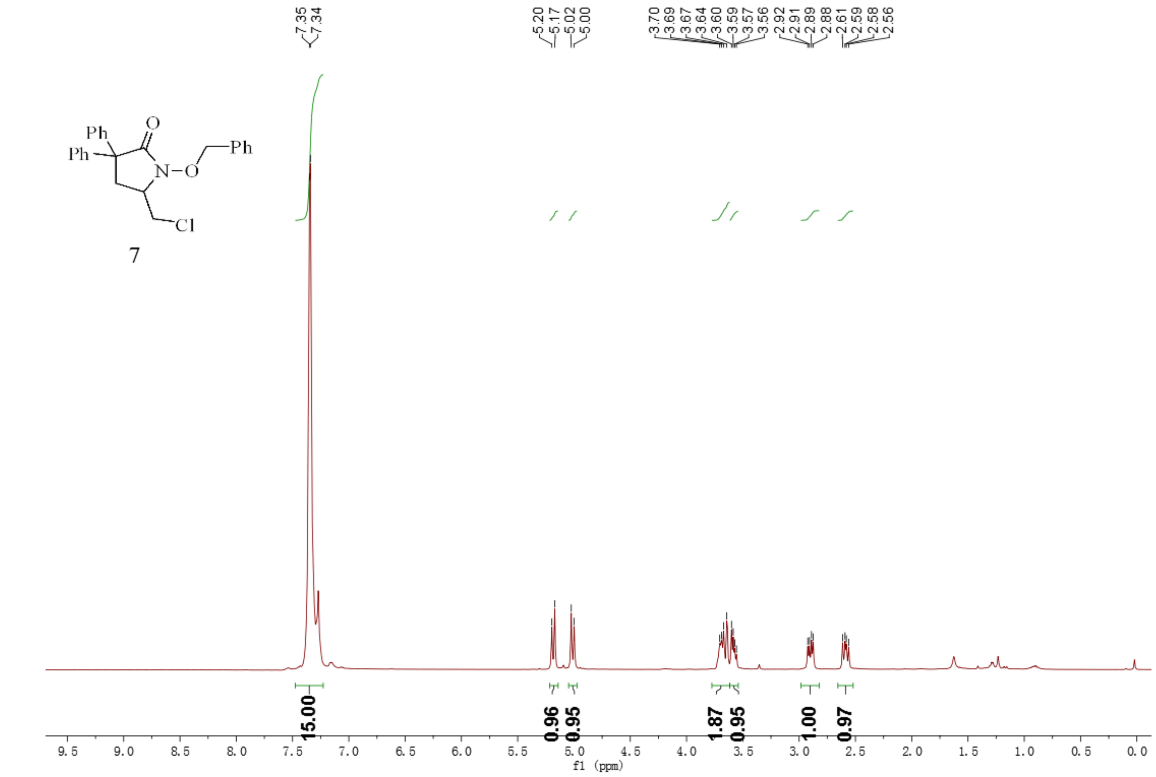


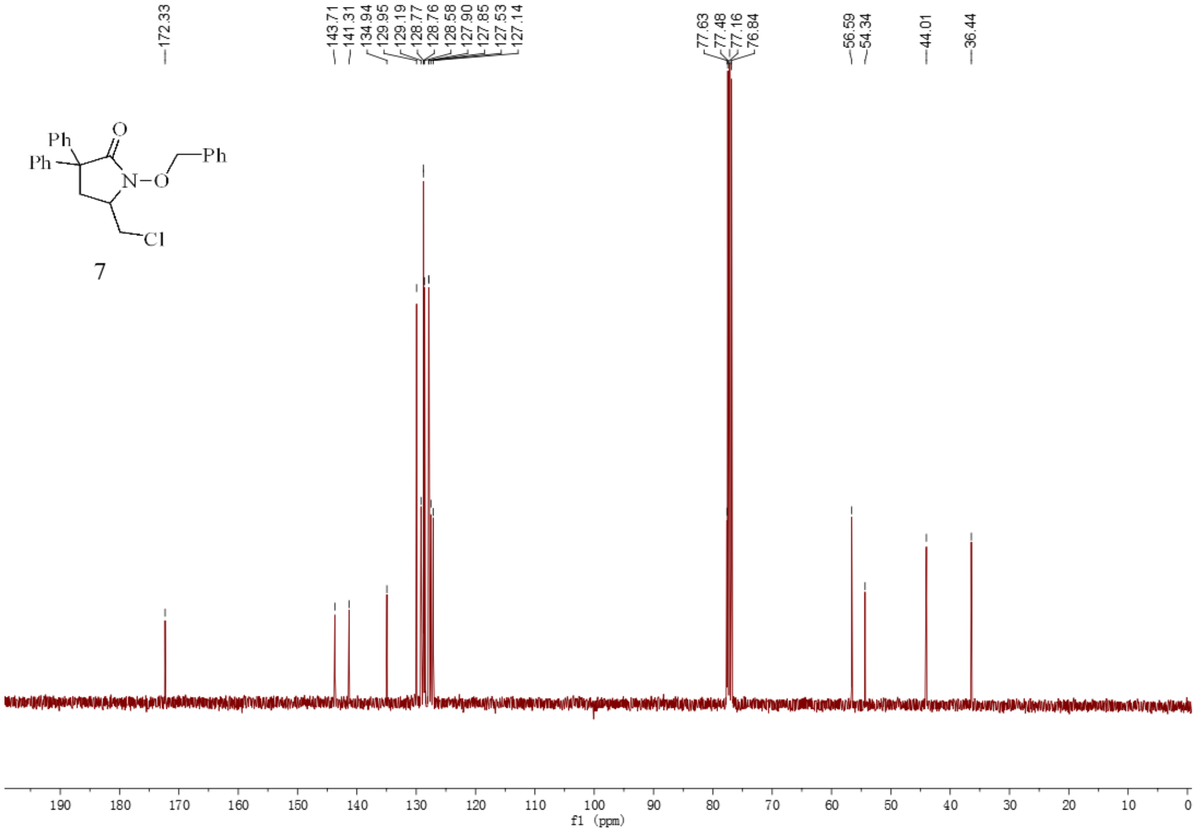

7.45
7.43
7.33
7.31
7.29
7.27
7.26
7.24
7.22
7.21
7.19
4.05
3.95
3.94
3.93
3.92
3.03
2.99
2.75
2.72
2.19
2.16
2.12
2.10
1.82
1.42
1.39
1.36
1.33
Ph
Ph
O
N
O
Cl
6 One isomer
2.00
8.89
3.00
1.04
1.05
1.03
3.22
2.16
3.34
f1 (ppm)

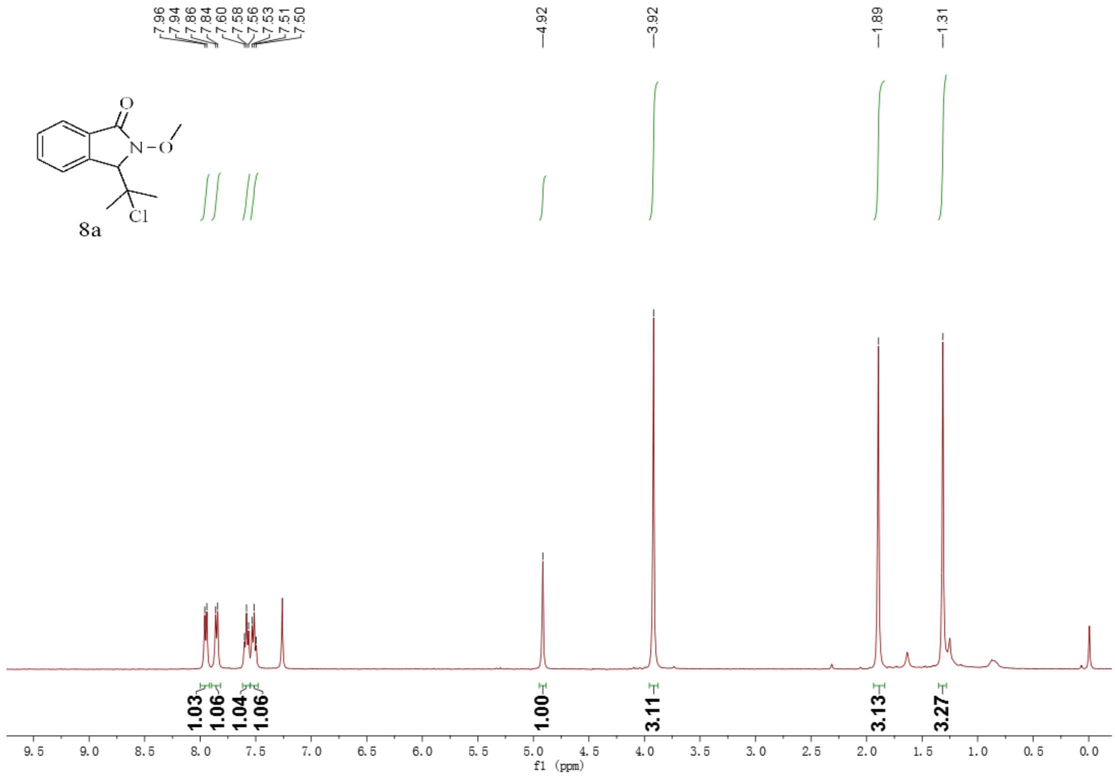

171.95
144.69
142.80
128.59
128.57
128.17
127.72
127.17
126.99
77.37
77.16
76.95
65.14
64.23
63.29
53.44
45.17
33.17
22.12
Ph
Ph
O
N
O
Cl
6 One isomer
f1 (ppm)


7.52
7.50
7.36
7.34
7.32
7.29
7.28
7.26
7.22
7.21
4.31
4.30
4.28
4.27
4.06
2.98
2.95
2.91
2.87
2.25
2.21
1.79
1.76
1.74
1.70
1.66
1.65
1.62
1.57
1.53
1.38
1.35
1.33
Ph
Ph
O
N
O
Cl
6 The other isomer
2.06
2.38
5.89
1.20
0.97
3.00
2.15
1.07
2.31
2.38
1.22
2.18
f1 (ppm)

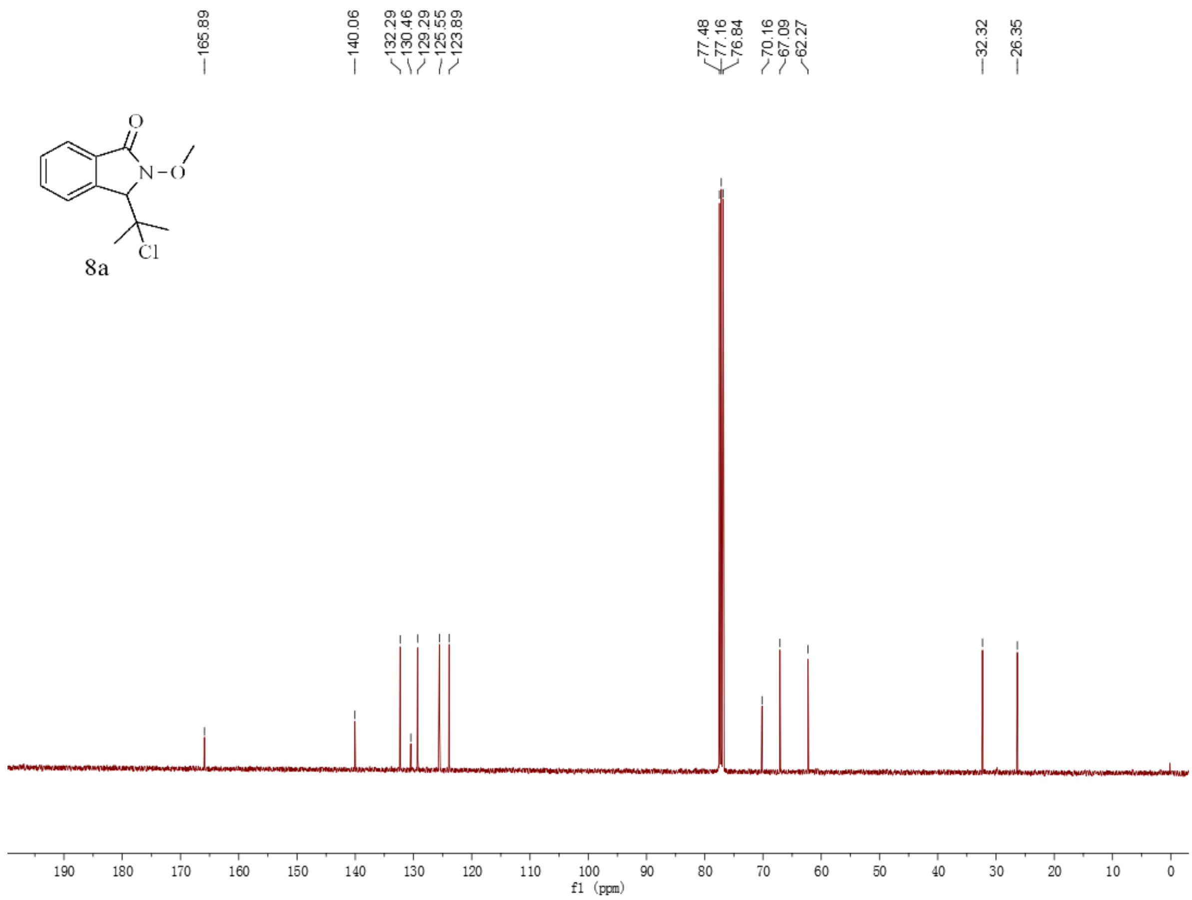

170.80
145.01
142.96
128.65
128.34
128.09
128.08
127.22
126.81
77.48
77.16
76.84
65.73
64.23
63.09
53.76
36.49
33.60
33.46
25.67
22.22
Ph
Ph
O
N
O
Cl
6 The other isomer
f1 (ppm)


7.35
7.34
5.20
5.17
5.02
5.00
3.70
3.69
3.67
3.64
3.60
3.59
3.57
3.56
2.92
2.91
2.89
2.88
2.61
2.59
2.58
2.56
Ph
Ph
O
N
O
Ph
Cl
7
15.00
0.96
0.95
1.87
0.95
1.00
0.97
f1 (ppm)

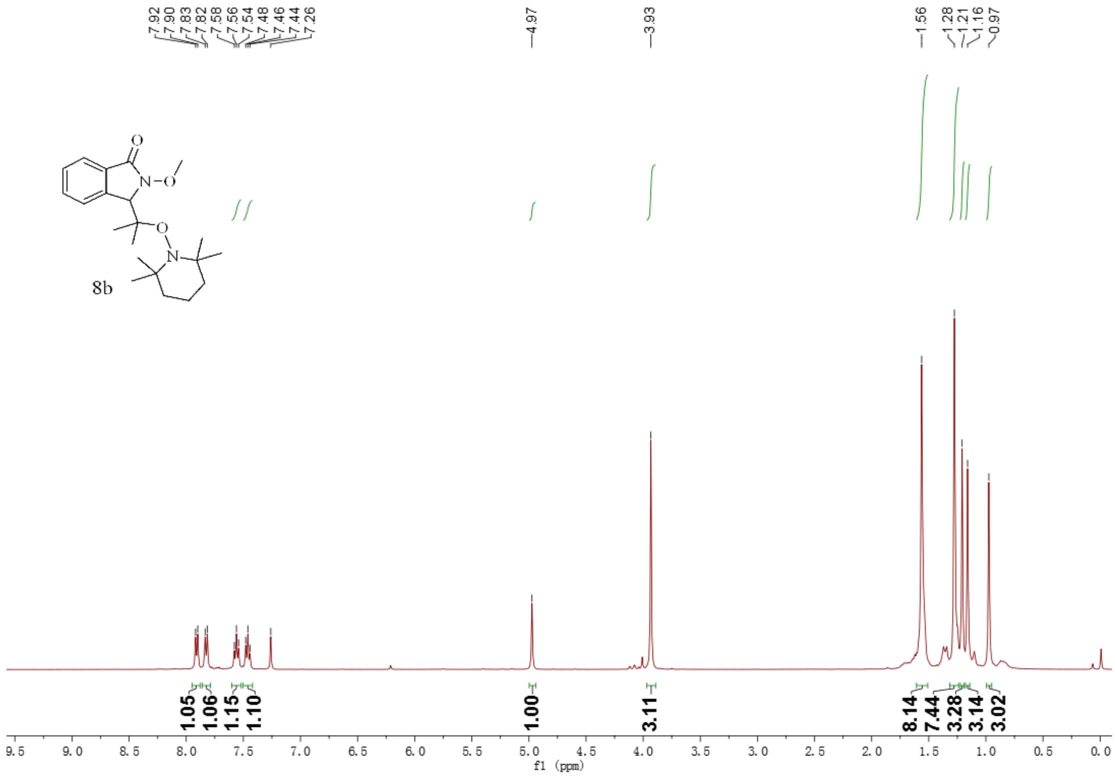

172.33
143.71
141.31
134.94
129.95
129.19
128.77
128.76
128.58
127.90
127.85
127.53
127.14
77.63
77.48
77.16
76.84
56.59
54.34
44.01
36.44
Ph
Ph
O
N
O
Ph
Cl
7
f1 (ppm)

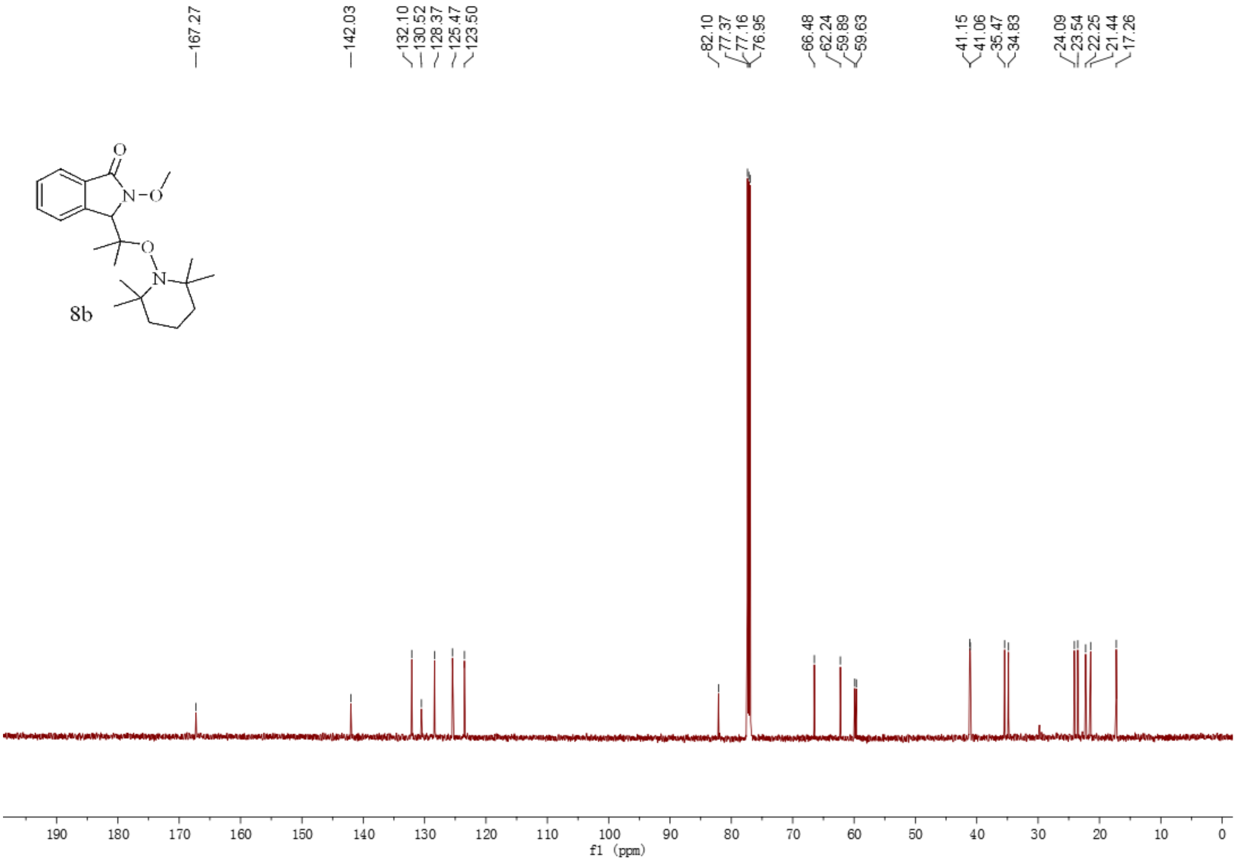


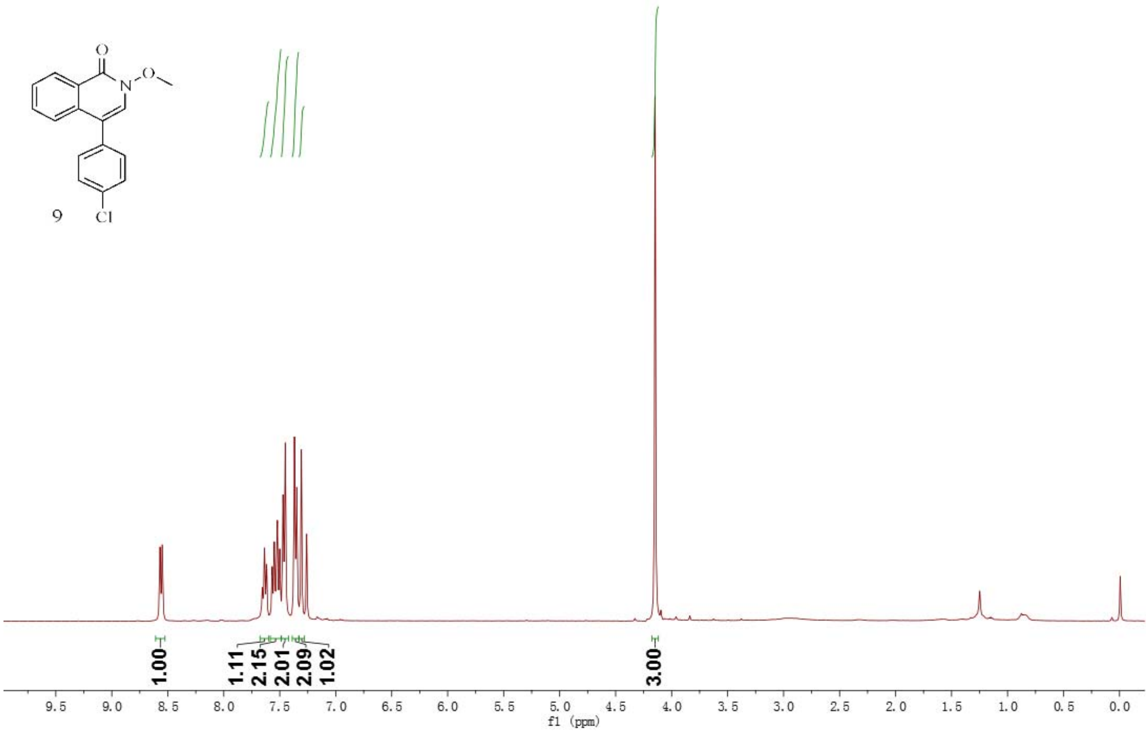
7.96 7.94 7.86 7.84 7.60 7.58 7.56 7.53 7.51 7.50
4.92
3.92
1.89
1.31
8a
Cl
1.03 1.06 1.04 1.06
1.00
3.11
3.13
3.27
f1 (ppm)

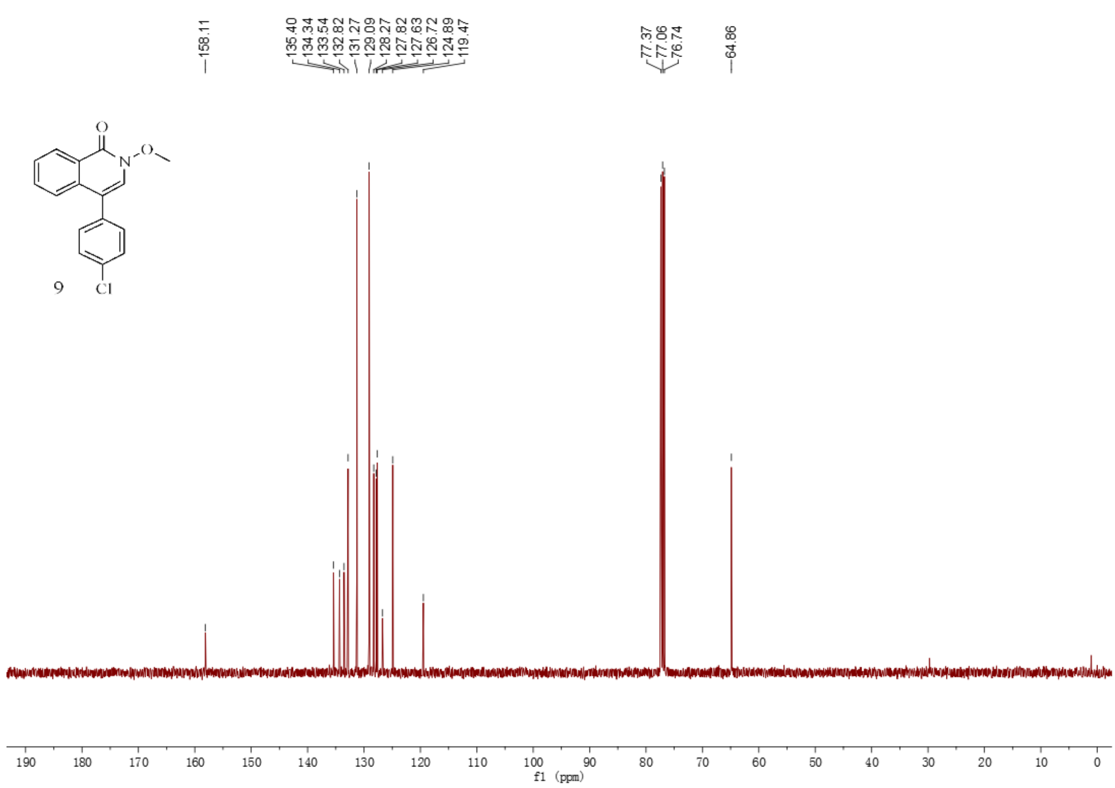


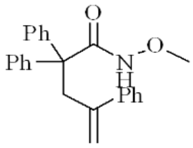
165.89
140.06
132.29 130.46 129.29 125.55 123.89
77.48 77.16 76.84
70.16 67.09 62.27
32.32
26.35
8a
Cl
f1 (ppm)


7.92
7.90
7.83
7.82
7.58
7.56
7.54
7.48
7.46
7.44
7.26
4.97
3.93
1.56
1.28
1.21
1.16
0.97
8b
1.05
1.06
1.15
1.10
1.00
3.11
8.14
7.44
3.28
3.14
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

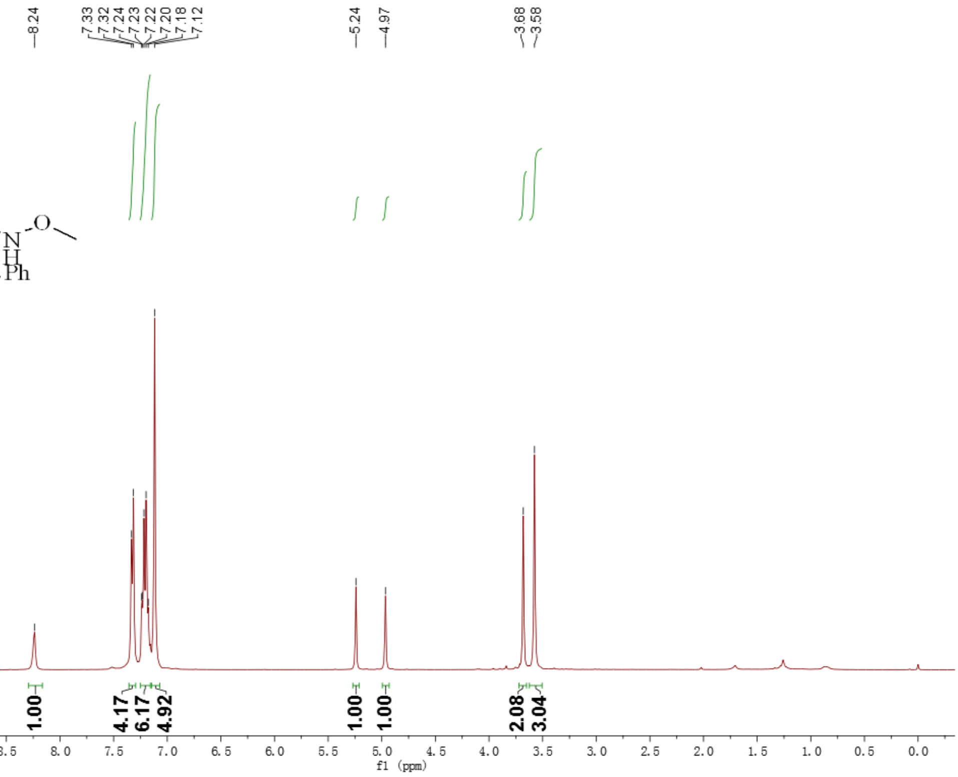

167.27
142.03
132.10
130.52
128.37
125.47
123.50
82.10
77.37
77.16
76.95
66.48
62.24
59.89
59.63
41.15
41.06
35.47
34.83
24.09
23.54
22.25
21.44
17.26
8b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9
1.00
1.11
2.15
2.01
2.09
1.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

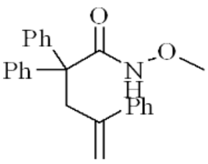

158.11
135.40
134.34
133.54
132.82
131.27
129.09
128.27
127.82
127.63
126.72
124.89
119.47
77.37
77.06
76.74
64.86
9
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



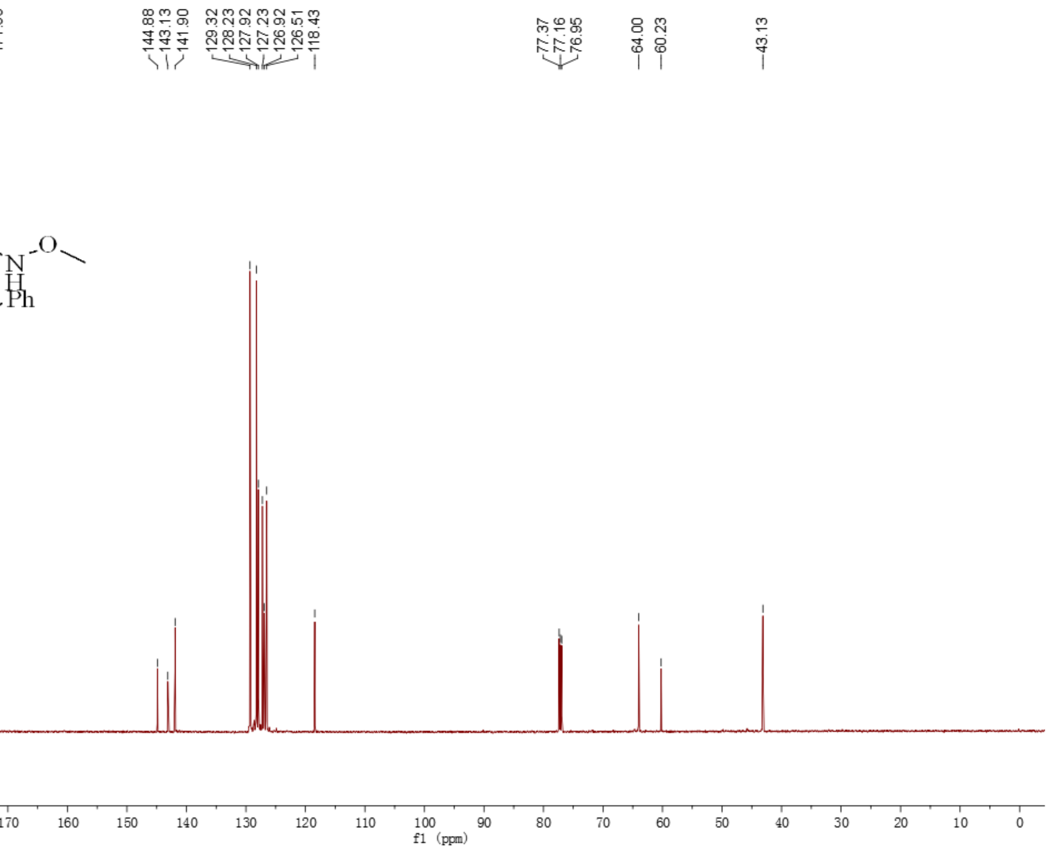
10



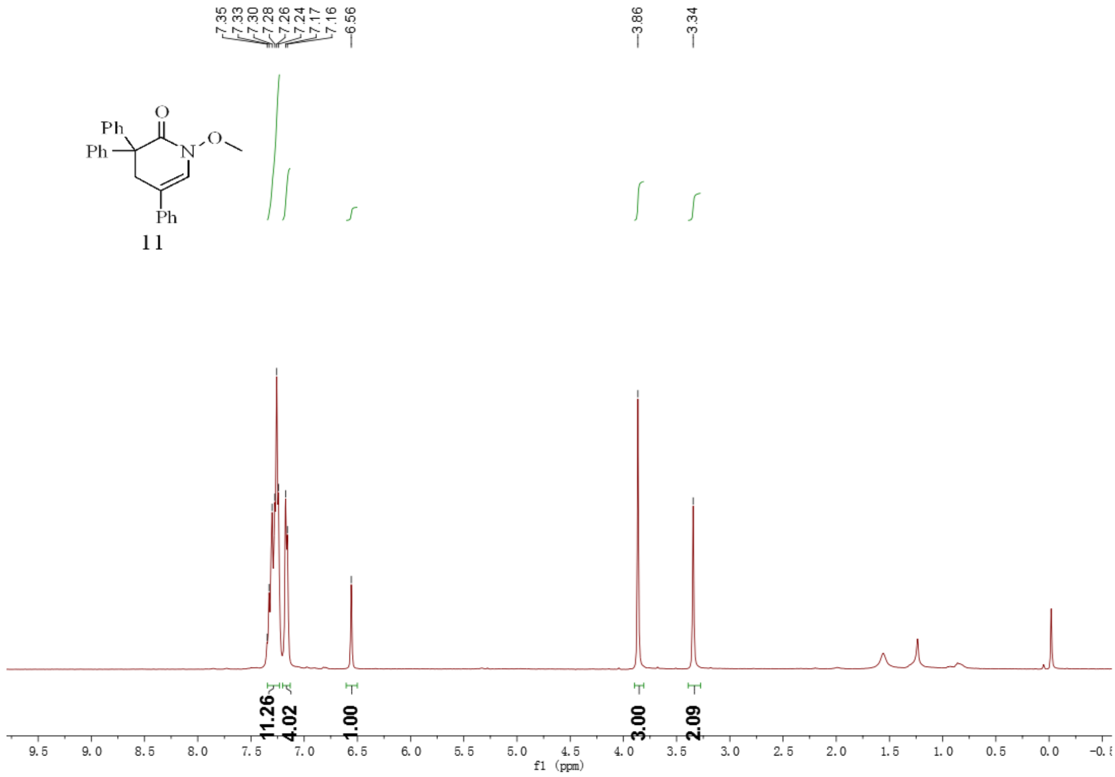
8.24
7.33
7.32
7.24
7.23
7.22
7.20
7.18
7.12
5.24
4.97
3.68
3.58
1.00
4.17
6.17
4.92
1.00
1.00
2.08
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

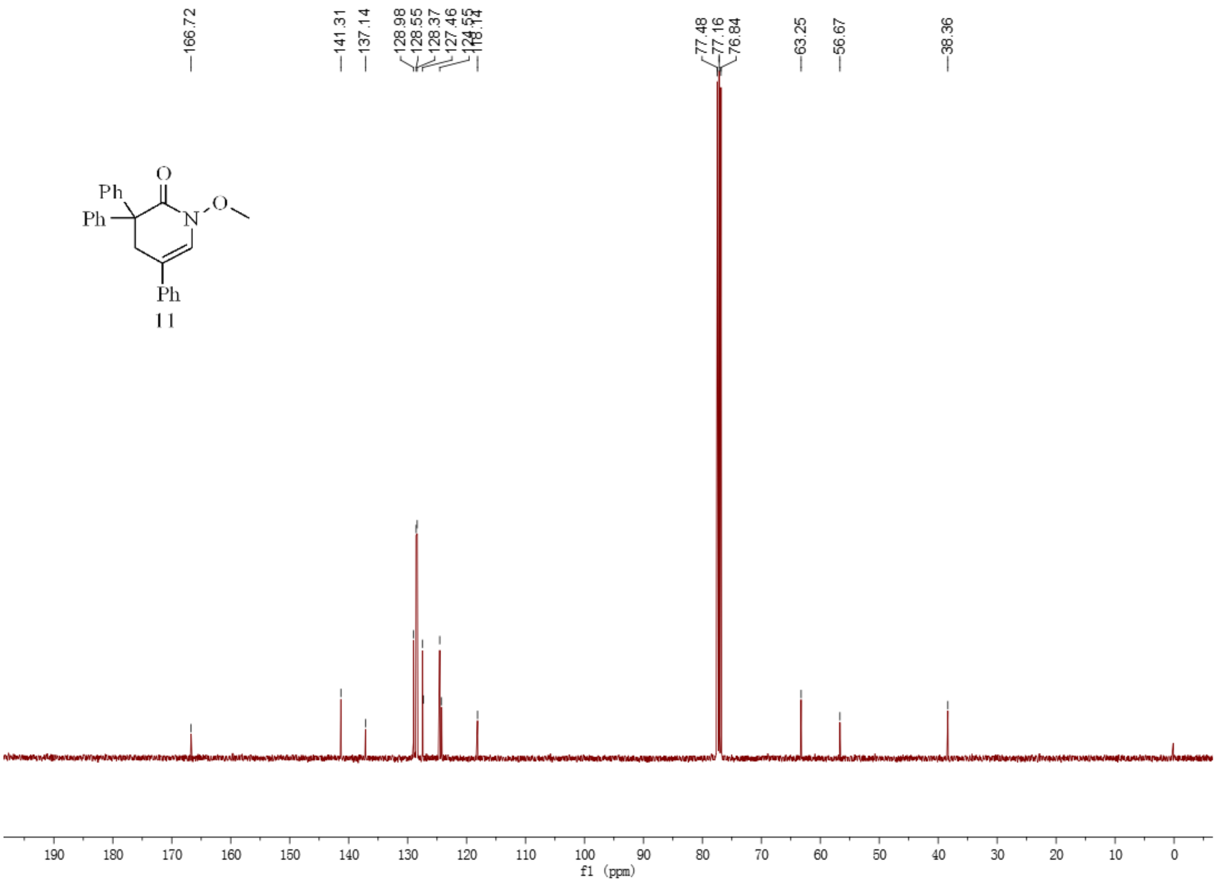


10



171.66
144.88
143.13
141.90
129.32
128.23
127.92
127.23
126.92
126.51
118.43
77.37
77.16
76.95
64.00
60.23
43.13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.35
7.33
7.30
7.28
7.26
7.24
7.17
7.16
6.56
3.86
3.34
Ph
Ph
O
N
O
Ph
11
11.26
4.02
1.00
3.00
2.09
f1 (ppm)


166.72
141.31
137.14
128.98
128.55
128.37
127.46
124.55
118.14
77.48
77.16
76.84
63.25
56.67
38.36
Ph
Ph
O
N
O
Ph
11
f1 (ppm)