Pd(Ⅱ)-Catalyzed *β*-C-H Arylation of *O*-Methyl Ketoximes with Iodoarens

（supporting information）

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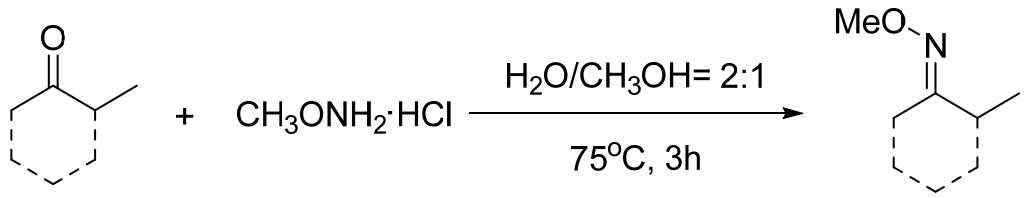
1. General Information.

All new compounds were fully characterized. NMR-spectra were recorded on Bruker ARX-400 MHz. Mass spectra were conducted at Micromass Q-Tof instrument (ESI) and Agilent Technologies 5973N (EI). IR spectra were recorded on a FT-IR spectrometer. All reactions were carried out in inert atmosphere. All of the solvents were dried over molecular sieves. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. General Procedure for Synthesis of *O*-Methyl Ketoximes

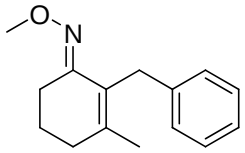


Starting materials are synthesized according to literature.[1], [2] To a dry round-bottomed flask, methoxyammonium chloride (13.5mmol, 2.7 equiv); sodium acetate (22.0mmol, 4.4 equiv), solvent (6mL, H_2O/CH_3OH = 2/1), kotone (5.0mmol, 1.0 equiv) was added in order. The mixture was allowed to heat to 75℃ and refluxed for 3 hours. After cooled to room temperature, the reaction was quenched with 10ml H2O and extracted with ether (3 x 15ml). The combined organic layer was dried by Na2SO4 and evaporated to give an orange liquid. Further purification was carried out by flash chromatography (PE:EA = 200:1).

3. Experimental Procedures and Characterization of Products

General Procedure: After evacuated and recharged with Ar for 3 times, a dry schlenk tube was charged $Pd(OAc)_2$ (0.01 mmol, 2.2 mg), 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (0.02 mmol, 7.0 mg), AgTFA (0.4 mmol, 88.6 mg), *O*-methyl ketoximes（0.2 mmol）and iodoarenes (0.4 mmol). Then 1mL $PhCF_3$ was dropped in under Ar atmosphere. The tube was sealed and the mixture was allowed to stir at 80 ^oC for 10 h. The mixture was then cooled to room temperature. The mixture was quenched with ethyl acetate (5 mL) and filtrated to remove solid phase. The solvent was moved by rotate evaporation, followed by purification on silica gel (petroleum ether/ethyl acetate 200/1 to 100/1) to provide the corresponding ketoximes.

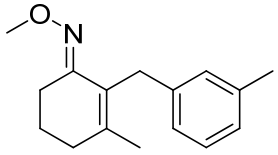
(*E*)-2-Benzyl-3-methylcyclohex-2-enone *O*-methyl oxime (3aa)



3aa

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), 2**a** (81.2mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 33.5 mg (73%) of **3aa** as a yellow liquid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 5H), 3.83 (s, 3H), 3.77 (s, 2H), 2.56 – 2.48 (m, 2H), 2.16 (t, J = 6.2 Hz, 2H), 1.83 (s, 3H), 1.76 – 1.64 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 141.6, 141.4, 128.4, 128.0, 128.0, 125.39, 61.6, 32.1, 31.6, 22.9, 21.1, 21.0; HRMS (ESI, m/z) calcd for $C_{15}H_{20}NO^+$ [$M+H^+$]: 230.1539, found: 230.1539; IR:1682 cm^{-1}, 1603 cm^{-1}.

(*E*)-3-Methyl-2-(3-methylbenzyl)cyclohex-2-enone *O*-methyl oxime (3ab)

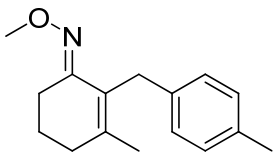


3ab

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), 2**b** (87.2mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10

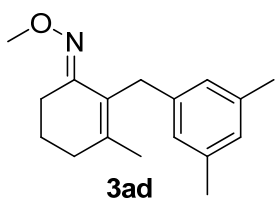
mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 34.5 mg (71%) of **3ab** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (m 1H), 7.05 – 6.92 (m, 3H), 3.83 (s, 3H), 3.73 (s, 2H), 2.52 (t, *J* = 6.7 Hz, 2H), 2.30 (s, 3H), 2.16 (t, *J* = 6.0 Hz, 2H), 1.83 (s, 3H), 1.75 – 1.63 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 141.5, 141.3, 137.4, 129.3, 128.0, 127.9, 126.1, 125.4, 61.6, 32.1, 31.5, 22.9, 21.6, 21.1, 21.0; HRMS (ESI, m/z) calcd for $C_{16}H_{22}NO^+$[M+H$^+$]: 244.1696, found: 244.1697; IR: 1682 cm^{-1}, 1606 cm^{-1}.

(*E*)-3-Methyl-2-(4-methylbenzyl)cyclohex-2-enone-*O*-methyl oxime (3ac)


3ac

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2c** (87.2mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 33.1 mg (68%) of **3ac** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (m, 4H), 3.83 (s, 3H), 3.72 (s, 2H), 2.57 – 2.47 (t, *J* = 6.0 Hz, 2H), 2.29 (s, 3H), 2.15 (t, *J* = 6.1 Hz, 2H), 1.83 (s, 3H), 1.73 – 1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 141.2, 138.5, 134.7, 128.7, 128.3,128.2, 61.6, 32.1, 31.2, 22.9, 21.1, 21.0, 21.0; HRMS (ESI, m/z) calcd for $C_{16}H_{22}NO^+$[M+H$^+$]: 244.1696, found: 244.1697; IR:1684 cm^{-1}, 1630 cm^{-1}.

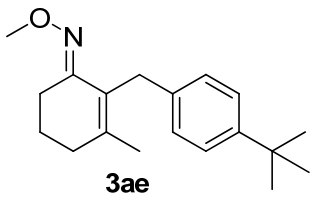
(*E*)-2-(3,5-Dimethylbenzyl)-3-methylcyclohex-2-enone-*O*-methyl oxime（3ad）


3ad

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2d** (92.8mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 38.3 mg (73%) of **3aa** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 6.77 (s, 1H), 3.84 (s, 3H), 3.70 (s, 2H), 2.52 (t, *J* = 6.0 Hz, 2H), 2.26 (s, 6H), 2.16 (t, *J* = 5.8 Hz, 2H), 1.83 (s, 3H), 1.73 – 1.65 (m, 2H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 155.7, 141.4, 141.3, 137.3, 128.0, 127.0, 126.3, 61.6, 32.1, 31.4, 22.9, 21.4, 21.2, 21.0; HRMS (ESI, m/z) calcd for $C_{17}H_{24}NO^+$[M+H^+]: 258.1852, found: 258.1853; IR: 1682 cm^{-1},1603 cm^{-1}.

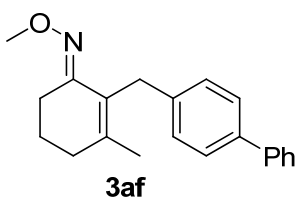
(*E*)-2-(4-*Tert*-butylbenzyl)-3-methylcyclohex-2-enone-*O*-methyl oxime (3ae)



3ae

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2e** (104.0mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 40.2 mg (71%) of **3ae** as a yellow liquid:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 6.4 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 3.84 (s, 3H), 3.74 (s, 2H), 2.52 (t, *J* = 6.7 Hz, 2H), 2.15 (t, *J* = 6.0 Hz, 2H), 1.84 (s, 3H), 1.74 – 1.63 (m, 2H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 147.9, 141.2, 138.5, 128.2, 128.1, 124.9, 61.6, 34.3, 32.1, 31.5, 31.1, 22.9, 21.2, 21.0. HRMS (ESI, m/z) calcd for $C_{19}H_{27}NO^+$ [M+H^+]:258.1852, found: 258.1853; IR: 1682 cm^{-1}, 1603 cm^{-1}.

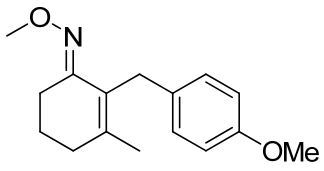
(*E*)-2-(Biphenyl-4-ylmethyl)-3-methylcyclohex-2-enone-*O*-methyl oxime (3af)



3af

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2f** (112.0mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 38.5 mg (63%) of **3af** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.50 – 7.37 (m, 4H), 7.30 (t, *J* = 8.6 Hz,3H), 3.85 (s, 3H), 3.81 (s, 2H), 2.54 (t, *J* = 6.7 Hz, 2H), 2.18 (t, *J* = 6.0 Hz, 2H), 1.87 (s, 3H), 1.77 – 1.67 (m, 2H), 1.57 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 141.5, 141.3, 140.8, 138.3, 128.8, 128.7, 127.9, 127.0, 126.9, 126.8, 61. 7, 32.1, 31.3, 22.9, 21.2, 21.0. HRMS (ESI, m/z) calcd for $C_{21}H_{24}NO^+$ [M+H^+]: 306.1855, found: 306.1855; IR: 1684cm^{-1}, 1617 cm^{-1}.

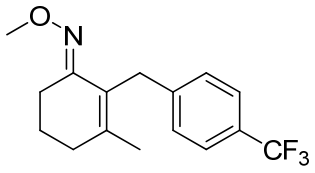
(*E*)-2-(4-methoxybenzyl)-3-methylcyclohex-2-enone-*O*-methyl oxime (3ag)



3ag

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2g** (93.6mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-Binaphthyl-2,2'-diylhydrogen phosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 31.9 mg (62%) of **3ag** as a yellow liquid:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.84 – 6.72 (m, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.70 (s, 2H), 2.62 – 2.42 (m, 2H), 2.15 (t, *J* = 6.0 Hz, 2H), 1.84 (s, 3H), 1.74 – 1.63 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 155.6, 141.1, 133.7, 129.3, 128.3, 113.4, 61.6, 55.2, 32.1, 30.7, 22.9, 21.1, 22.0; HRMS (ESI, m/z) calcd for $C_{16}H_{22}NO_2^+$[M+H$^+$]: 260.1645, found: 260.1646 IR: 1683 cm^{-1},1605 cm^{-1}

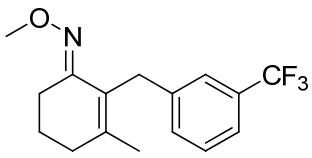
(*E*)-3-Methyl-2-(4-(trifluoromethyl)benzyl)cyclohex-2-enone-*O*-methyl oxime (3ah)



3ah

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2h** (108.8mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 30.3 mg (51%) of **3ah** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.37 (m, 2H), 7.25-7.21 (m, 2H), 3.74 (s, 5H), 2.45 (t, *J* = 8.0 Hz, 2H), 2.10 (t, *J* = 6.1 Hz, 2H), 1.76 (s, 3H), 1.67 – 1.59 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 145.8, 141.9, 128.6, 127.63 (q, *J* = 32.3 Hz), 127.3, 124.5 (q, *J* = 273.0 Hz), 124.90 (q, *J* = 3.9 Hz), 61.6, 32.0, 31.6, 22.8, 21.0, 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.18 (s); HRMS (ESI, m/z) calcd for $C_{16}H_{17}NOF_3^-$[M-H$^-$]: 296.1268, found: 296.1267; IR: 1683 cm^{-1}, 1618 cm^{-1}.

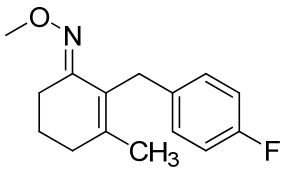
(*E*)-3-Methyl-2-(3-(trifluoromethyl)benzyl)cyclohex-2-enone-*O*-methyl oxime (3ai)



3ai

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2i** (108.8mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 32.1 mg (54%) of **3ai** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.41 – 7.28 (m, 3H), 3.82 (s, 3H), 3.80 (s, 2H), 2.52 (t, *J* = 5.9 Hz, 2H), 2.18 (t, *J* = 5.9 Hz, 2H), 1.87 (s, 3H), 1.74 – 1.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 142.6, 141.8, 131.7, 130.2 (q, *J* = 32.3 Hz), 128.32, 127.3, 125.5 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 273.0 Hz), 122.21 (q, *J* = 4.0Hz), 61.6, 32.1, 31.7, 22.8, 21.1, 20.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.49 (s); HRMS (ESI, m/z) calcd for $C_{16}H_{17}NOF^-$[M-H$^-$]: 296.1268, found: 296.1267; IR: 1683 cm^{-1}, 1620 cm^{-1}.

(*E*)-2-(4-Fluorobenzyl)-3-methylcyclohex-2-enone-O-methyl oxime (3aj)

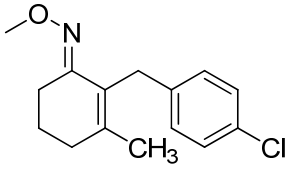


3aj

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2j** (88.8mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 26.1 mg (53%) of **3aj** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (m, 2H), 6.98 – 6.81 (m, 2H), 3.83 (s, 3H), 3.72 (s, 2H), 2.51 (t, *J* = 6.0 Hz, 2H), 2.16 (t, *J* = 6.0 Hz, 2H), 1.83 (s, 3H), 1.73 – 1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, *J* = 243.4Hz), 155.5, 141.4, 137.2 (d, *J* = 2.0Hz), 129.7 (d, *J* = 8.1Hz), 128.0, 114.6 (d, *J* = 21.2Hz), 61.6, 32.1, 30.9, 22.9, 20.0, 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.63 (s); HRMS (ESI, m/z) calcd for $C_{15}H_{19}NOF^+$ [M+H$^+$]: 248.1445, found: 248.1445; IR: 1682 cm^{-1}, 1609cm^{-1}.

(*E*)-2-(4-Chlorobenzyl)-3-methylcyclohex-2-enone-*O*-methyl oxime (3ak)

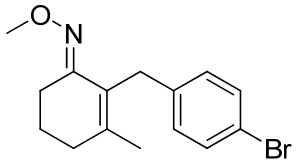
According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2k** (95.2mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and



3ak

1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 31.6 mg (60%) of **3ak** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (m, 4H), 3.82 (s, 3H), 3.72 (s, 2H), 2.51 (t, *J* = 6.7 Hz, 2H), 2.16 (t, *J* = 6.0 Hz, 2H), 1.83 (s, 3H), 1.69 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 141.6, 140.1, 130.9, 129.7, 128.1, 127.6, 61.6, 32.1, 31.1, 22.9, 21.0, 20.9; HRMS (ESI, m/z) calcd for $C_{15}H_{19}ClNO^+[M+H^+]$: 264.1150, found: 246.1149; IR: 1682 cm^{-1}, 1605cm^{-1}.

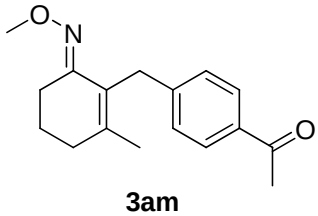
(*E*)-2-(3-Bromobenzyl)-3-methylcyclohex-2-enone-*O*-methyl oxime (3al)



3al

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2l** (112.8mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 35.6 mg (56%) of **3al** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.26 (t, *J* = 3.8 Hz, 1H), 7.10 (dt, *J* = 15.2, 7.7 Hz, 2H), 3.83 (s, 3H), 3.73 (s, 2H), 2.60 – 2.43 (m, 2H), 2.17 (t, *J* = 6.0 Hz, 2H), 1.84 (s, 3H), 1.75 – 1.64 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 144.0, 141.8, 131.5, 129.5, 128.4, 127.3, 127.1, 122.1, 61.7, 32.1, 31.4 , 22.8, 21.1, 20.9; HRMS (ESI, m/z) calcd for $C_{15}H_{19}BrNO^+[M+H^+]$: 308.0645, found: 308.0644; IR: 1680 cm^{-1}, 1603cm^{-1}.

(*E*)-1-(4-((6-(Methoxyimino)-2-methylcyclohex-1-enyl)methyl)phenyl)ethanone (3am)

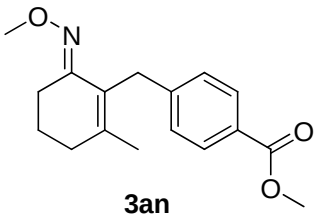


3am

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2m** (98.4mg, 0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 33.6 mg (62%) of **3am** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.91 – 7.77 (m, 2H), 7.29 (m, 2H), 3.81 (s, 5H), 2.56 (s, 3H), 2.55 (t, *J* = 6.0 Hz, 2H), 2.18 (t, *J* = 6.0 Hz, 2H), 1.83 (s, 3H), 1.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 155.4, 147.7, 141.9, 134.7, 128.5, 128.3, 127.2, 61.6, 32.1, 32.0, 26.5, 22.8, 21.1, 20.9; HRMS (ESI, m/z) calcd for $C_{17}H_{22}NO_2^+$[M+H$^+$]: 272.1645, found: 272.1644; IR: 1682cm^{-1}, 1606cm^{-1}.

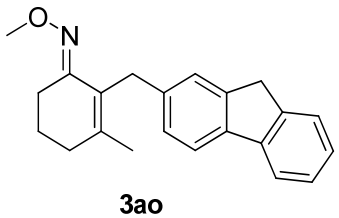
(*E*)-Methyl-4-((6-(methoxyimino)-2-methylcyclohex-1-enyl)methyl)benzoate (3an)



3an

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2n** (104.8mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 29.3 mg (51%) of **3an** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.27 (m, 2H), 3.89 (s, 3H), 3.81 (s, 5H), 2.52 (t, *J* = 8.0 Hz ,2H), 2.18 (t, *J* = 6.0 Hz, 2H), 1.83 (s, 3H), 1.77 – 1.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 155.4, 147.4, 141.9, 129.4, 128.4, 127.3,127.3, 61.6, 51.9, 32.1, 31.9, 22.8, 21.1, 22.9; HRMS (ESI, m/z) calcd for $NaC_{17}H_{21}NO_3^+$[M+Na$^+$]: 310.1414, found: 310.1414; IR: 1720cm^{-1}, 1602cm^{-1}.

(*E*)-2-((9H-Fluoren-2-yl)methyl)-3-methylcyclohex-2-enone-*O*-methyl oxime (3ao)

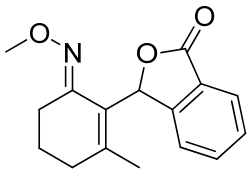


3ao

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2o** (116.8mg, 0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 37.4 mg (59%) of **3ao** as a pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (m, 1H), 7.64 (m, 1H), 7.50 (m, 1H), 7.34 (m, 2H), 7.24 (m 2H), 3.85 (s, 3H), 3.84 (s, 4H), 2.55 (t, *J* = 6.7 Hz, 2H), 2.18 (t,

J = 6.0 Hz, 2H), 1.86 (s, 3H), 1.77 – 1.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 143.2, 143.2, 141.9, 141.5, 140.5, 139.1, 128.1, 127.1, 126.6, 126.1, 125.0, 124.9, 119.5, 119.4, 61.7, 36.9, 32.1, 31.8, 23.0, 21.2, 21.0; HRMS (ESI, m/z) calcd for $C_{22}H_{24}NO^+$ [M+H$^+$]: 318.1853, found: 318.1853; IR: 1682cm^{-1}, 1611cm^{-1}.

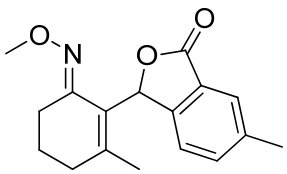
(*E*)-3-(6-(Methoxyimino)-2-methylcyclohex-1-enyl)isobenzofuran-1(3*H*)-one (3ap)



3ap

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2p** (99.2 mg, 0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 33.6mg (62%) of **3ap** as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.6 Hz, 1H), 7.60 (td, *J* = 7.5, 1.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.33 (m, 1H), 6.73 (s, 1H), 3.59 (s, 3H), 2.68 – 2.33 (m, 2H), 2.23 (dd, *J* = 9.8, 5.6 Hz, 2H), 1.85 (s, 3H), 1.79 – 1.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 153.2, 150.6, 147.0, 133.7, 128.3, 127.3, 124.8, 123.9, 121.5, 77.6, 61.6, 33.4, 22.7, 20.6, 20.3; HRMS (ESI, m/z) calcd for $C_{16}H_{18}NO_3^+$[M+H$^+$]: 272.1281, found: 272.1281; IR: 1767cm^{-1}, 1684cm^{-1}, 1605cm^{-1}.

(*E*)-3-(6-(Methoxyimino)-2-methylcyclohex-1-enyl)-6-methylisobenzofuran-1(3H)-one (3aq)

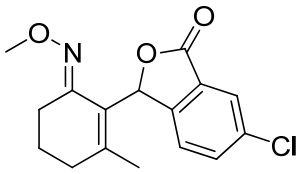


3aq

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2q** (104.8 mg, 0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 35.9mg (63%) of **3aq** as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.41 (d, *J* = 7.8Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H),

6.71 (s, 1H), 3.63 (s, 3H), 2.59-2.37 (m, 2H), 2.45（s, 3H）, 2.21 (dd, *J* = 11.1, 5.4 Hz, 2H), 1.81 (s, 3H), 1.75 – 1.66 (m, 2H). ^{13}C NMR(101 MHz, $CDCl_3$) δ171.7, 153.4, 147.9, 146.7, 138.5, 134.8, 127.4, 124.9, 124.1, 121.3, 77.5, 61.7, 33.4, 22.7, 21.2, 20.6, 20.4; HRMS (ESI, m/z) calcd for $C_{17}H_{20}NO_3^+$[M+H$^+$]: 286.1438, found: 286.1438; IR: 1609cm^{-1}, 1684cm^{-1}.

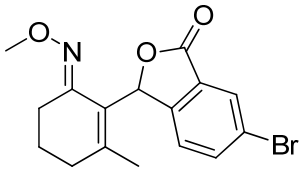
(*E*)-6-Chloro-3-(6-(methoxyimino)-2-methylcyclohex-1-enyl)isobenzofuran-1(3H)-one (3ar)



3ar

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2r** (112.8mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 35.4 mg (58%) of **3ar** as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.8 Hz, 1H), 7.56 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.27 (s, 1H), 6.66 (s, 1H), 3.58 (s, 3H), 2.64 – 2.33 (m, 2H), 2.24 (t, *J* = 5.4 Hz, 1H), 1.90 (s, 3H), 1.78 – 1.63 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 152.9, 148.7, 147.5, 134.5, 133.8, 129.3, 124.7, 123.4, 122.8, 77.5, 61.6 , 33.3, 22.7, 20.7, 20.3; HRMS (ESI, m/z) calcd for $C_{16}H_{17}ClNO_3^+$[M+H$^+$]: 306.0891, found: 306.0893; IR: 1682cm^{-1}, 1611cm^{-1}, 1667cm^{-1}.

(*E*)-6-Bromo-3-(6-(methoxyimino)-2-methylcyclohex-1-enyl)isobenzofuran-1(3H)-one (3as)

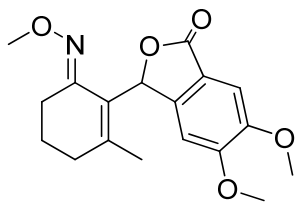


3as

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2s** (130.4mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 34.9 mg (59%) of **3as** as a colorless solid:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 1.7 Hz, 1H), 7.70 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 6.64

(s, 1H), 3.58 (s, 3H), 2.56 – 2.37 (m, 2H), 2.23 (t, *J* = 5.4 Hz, 2H), 1.89 (s, 3H), 1.77 – 1.65 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 152.9, 149.2, 147.5, 136.6, 129.6, 127.8, 123.4, 123.1, 122.1, 77.5, 61.7, 33.3, 22.7, 20.7, 20.3; HRMS (ESI, m/z) calcd for $C_{16}H_{17}BrNO_3$[M+H$^+$]:350.0386, found: 350.0386; IR: 1768cm^{-1}, 1681cm^{-1}, 1662cm^{-1}.

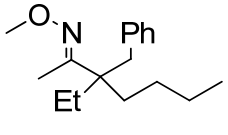
(E)-5,6-dimethoxy-3-(6-(methoxyimino)-2-methylcyclohex-1-enyl)isobenzofuran-1(3H)-one (3at)



3at

According to the general procedure, the reaction of **1a** (30.6 mg, 0.20 mmol), **2t** (123.2 mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 35.7mg (54%) of **3at** as a brown solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 6.76 (s, 1H), 6.71 (s, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.72 (s, 3H), 2.65-2.56 (m, 1H), 2.52-5.40 (m,1H), 2.25-2.18 (m, 2H), 1.75 (s, 3H), 1.30-1.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 154.7, 154.1, 150.0, 147.0, 145.1, 123.9, 118.9, 105.6, 103.3, 76.9, 61.8, 56.4, 56.3, 33.5, 22.8, 20.5, 20.4; HRMS (ESI, m/z) calcd for $C_{16}H_{18}NO_3^+$[M+H$^+$]: 332.1492, found: 332.1491; IR: 1745cm^{-1}, 1684cm^{-1}, 1604cm^{-1}.

(*E*)-3-Benzyl-3-ethylheptan-2-one-*O*-methyl oxime (3ba)

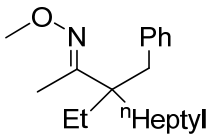


3ba

According to the general procedure, the reaction of **1b** (39.8 mg, 0.20 mmol), **2a** (81.6mg, 0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 40.2 mg (77%) of **3ba** as a pale yellow liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.15 (m, 3H), 7.10 – 7.05 (m, 2H), 3.81 (s, 3H), 2.81 (s, 2H), 1.78 (s, 3H), 1.45 – 1.24 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 160.5, 138.9, 130.3, 127.8, 125.9, 61.3, 47.7, 38.2, 33.8, 26.5, 26.2, 23.2, 14.2, 11.1, 8.4; HRMS (ESI, m/z) calcd for $C_{17}H_{28}NO^+$ [M+H$^+$]: 262.2165, found: 262.2162; IR: 1683cm^{-1}, 1620cm^{-1}.

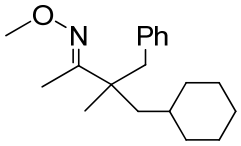
(*E*)-3-Benzyl-3-ethyldecan-2-one *O*-methyl oxime (3ca)



3ca

According to the general procedure, the reaction of **1c** (45.4 mg, 0.20 mmol), **2a** (81.6 mg, 0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 43.0 mg (71%) of **3ca** as a pale yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 3H), 7.09 – 7.04 (m, 2H), 3.81 (s, 3H), 2.81 (s, 2H), 1.78 (s, 3H), 1.48 – 1.19 (m, 14H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 138.9, 130.3, 127.8, 125.9, 61.3, 47.7, 38.2, 34.1, 31.9, 30.14, 29.7, 29.3, 26.5, 23.9, 22.7, 14.1, 11.1, 8.4; HRMS (ESI, m/z) calcd for $C_{20}H_{34}NO^+$ [M+H$^+$]:304.2635, found: 304.2633; IR: 1682cm^{-1}, 1620cm^{-1}.

(*E*)-3-Benzyl-4-cyclohexyl-3-methylbutan-2-one-*O*-methyl oxime (3da)

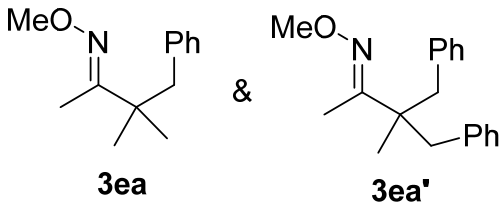


3da

According to the general procedure, the reaction of **1d** (45.0 mg, 0.20 mmol), **2a** (81.6 mg, 0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 37.3 mg (71%) of **3da** as a yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.13 (m, 3H), 7.12 – 7.00 (m, 2H), 3.80 (s, 3H), 2.87(d, *J* = 1.6Hz, 1H), 2.83(d, *J* = 1.2Hz, 1H), 1.79 (s, 3H), 1.69 – 1.56 (m, 6H), 1.50 – 1.20 (m, 8H), 0.87-0.84 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 138.8, 130.4, 127.8, 125.9, 61.3, 47.6, 42.7, 38.7, 34.7, 34.5, 33.9, 26.7, 26.5, 26.4, 25.9, 12.3, 8.4; HRMS (ESI, m/z) calcd for $C_{19}H_{30}NO^+$[M+H$^+$]:288.2322, found:288.2323; IR: 1682cm^{-1}, 1620cm^{-1}.

(*E*)-3,3-Dimethyl-4-phenylbutan-2-one-*O*-methyl oxime (3ea) and

(*E*)-3-Benzyl-3-methyl-4-phenylbutan-2-one-*O*-methyl oxime (3ea')

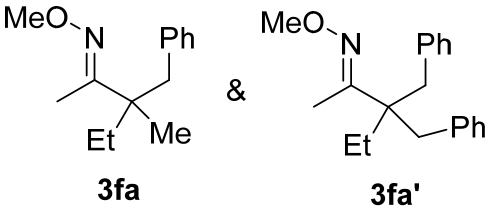


3ea **3ea'**

According to the general procedure, the reaction of **1e** (25.8 mg, 0.20 mmol), **2a** (81.6 mg, 0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar generated a mixture of **3ea** & **3ea'**. Determined by crude ^1H NMR, the ratio is 2.5 to 1. The total isolated yield is 73% and the monoarylated product **3ea** can be separable by column chromatography on silica. **3ea**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.15 (m, 3H), 7.12 – 7.01 (m, 2H), 3.80 (s, 3H), 2.75 (s, 2H), 1.86 (s, 3H), 1.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 138.4, 130.4, 127.7, 126.0, 77.3, 77.0, 76.7, 61.1, 46.1 , 41.0 , 25.1, 11.1; HRMS (ESI, m/z) calcd for $C_{13}H_{20}NO^+[M+H^+]$: 206.1539, found:206.1539; IR: 1684cm^{-1}. **3ea'**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.19 (m, 6H), 7.10-7.05 (m, 4H), 3.77 (s, 3H), 3.04 (d, *J* = 13.4 Hz, 2H), 2.68 (d, *J* = 13.4 Hz, 2H), 1.82 (s, 3H), 0.97 (s, 3H). HRMS (ESI, m/z) calcd for $C_{19}H_{24}NO^+[M+H^+]$: 282.1852, found:282.1853.

(*E*)-3-Benzyl-3-methylpentan-2-one-*O*-methyl oxime (3fa) and

(*E*)-3,3-Dibenzylpentan-2-one-*O*-methyl oxime（3fa'）

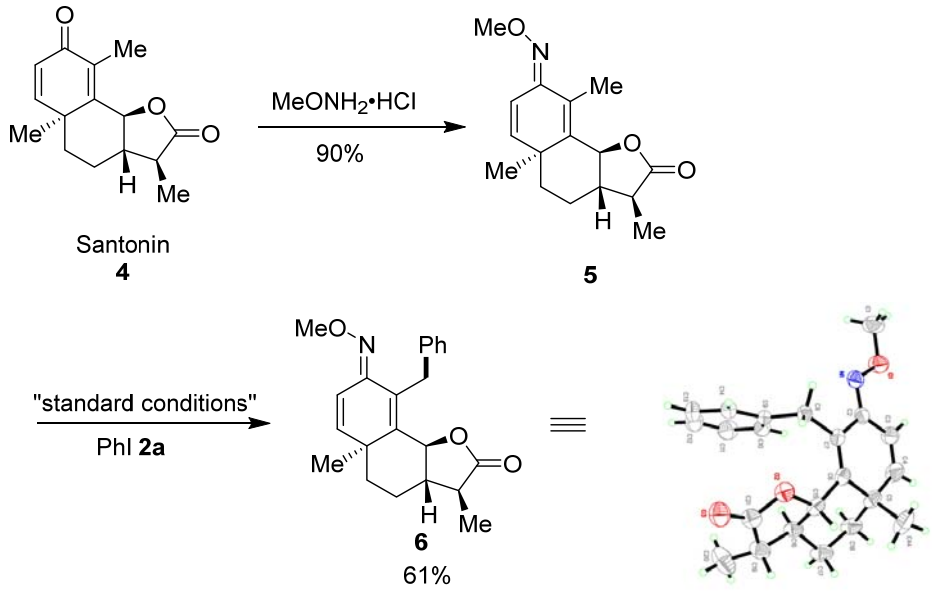


3fa **3fa'**

According to the general procedure, the reaction of **1f** (28.6 mg, 0.20 mmol), **2a** (81.6mg, 0.40mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar generated a mixture of **3fa** & **3fa'**. Determined by crude ^1H NMR, the ratio is 6.3 to 1. The total isolated yield is 77% and the monoarylated product **3fa** can be separable by column chromatography on silica. **3fa**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 3H), 7.10 – 7.05 (m, 2H), 3.79 (s, 3H), 2.82 (d, *J* = 1.6Hz, 1H), 2.67 (d, 1.81,*J* =1.6Hz, 1H), 1.81 (s, 3H), 1.70-1.58 (m, 1H), 1.40-1.29 (m, 1H), 0.98 (s,

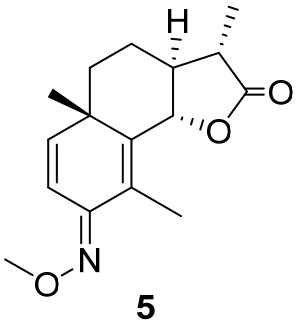
3H), 0.80 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 138.4, 130.5, 127.7, 126.0, 61.2, 44.8, 44.6, 30.9, 21.1, 11.1, 8.7; HRMS (ESI, m/z) calcd for $C_{19}H_{24}NO^+$[M+H$^+$]:220.1696, found: 220.1696; IR: 1683cm^{-1}. **3fa'**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.15 (m, 6H), 7.12-7.05 (m, 4H), 3.83 (s, 3H), 2.92 (d, J = 1.2 Hz, 2H), 2.84 (d, J = 1.5 Hz, 2H), 1.74 (s, 3H), 1.28-1.34 (m, 2H), 0.87 (t, J = 6.0 Hz 3H). HRMS (ESI, m/z) calcd for $C_{20}H_{26}NO^+$ [M+H$^+$]:296.2009, found: 296.2010**.**

4. Late-stage C-H Arylation of Santonin



(3*S*,3a*S*,5a*S*,9b*S*,*E*)-8-(Methoxyimino)-3,5a,9-trimethyl-3a,4,5,5a,8,9b-hexahydro naphtho[1,2-b]furan-2(3*H*)-one (5)[1]

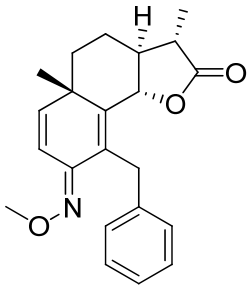
A stirred solution of (-)-Santonin (493 mg, 2.0 mmol) and hydorxylamine hydrochloride (200 mg 2.4 mmol) in pyridine (3 mL) was heated at 115 ^{o}C for overnight. Pyridine was removed under reduced pressure. The residue was diluted with diethyl ether (5 mL) and then washed with water (5 mL). The organic phase was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/PE = 1/5) to give ketoxime 5 (496 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, J = 10.1 Hz, 1H), 5.98 (d, J = 10.1 Hz,



5

1H), 4.78 (dd, *J* = 11.1, 1.3 Hz, 1H), 3.93 (s, 3H), 2.40-2.30 (m, 1H), 2.15 (s, 3H), 2.01-1.95 (m, 1H), 1.82-1.60 (m, 3H), 1.54-1.44 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 149.9, 145.2, 138.4, 122.8, 112.9, 82.3, 77.4, 77.1, 76.7, 62.0, 53.4, 41.1, 40.7, 38.3, 25.8, 23.8, 12.5, 12.0.

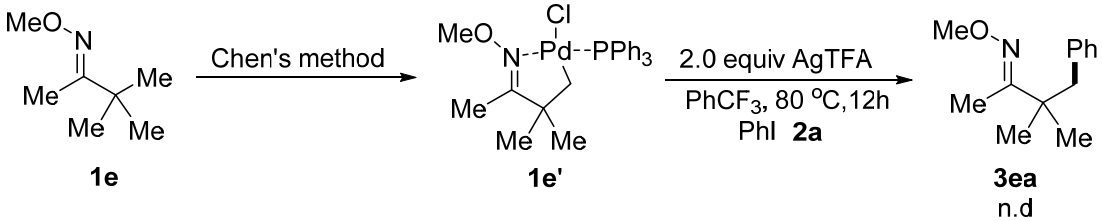
(3*S*,3a*S*,5a*S*,9b*S*,*E*)-9-Benzyl-8-(methoxyimino)-3,5a-dimethyl-3*a*,4,5,5*a*,8,9*b*-hexahydronaphtho[1,2-*b*]furan-2(3*H*)-one (6)



6

According to the general procedure, the reaction of **5** (55.3 mg, 0.20 mmol), **2a** (81.6 mg, 0.40 mmol), $Pd(OAc)_2$ (2.2 mg, 5 mol %), AgTFA (88.6 mg, 0.4 mmol) and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate (7.0 mg, 10 mol %) in $PhCF_3$ (1.0 mL) at 80 ºC under Ar after column chromatography on silica afforded 42.9 mg (61%) of **6** as a colorless solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 4H), 7.09 (m, 1H), 6.82 (d, *J* = 10.1 Hz, 1H), 5.98 (d, *J* = 10.2 Hz, 1H), 4.77 (d, *J* = 10.5 Hz, 0H), 4.29 (d, *J* =12 Hz,1H), 4.06 (d, *J* =16 Hz,1H) , 3.89 (s, 3H), 2.29-2.19 (m, 1H), 2.01 – 1.89 (m, 1H), 1.79 – 1.52 (m, 4H), 1.28 (s, 3H), 1.09 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 148.8, 144.9, 142.3, 139.6, 128.6, 127.8, 126.0, 125.1, 113.1, 82.0, 62.1, 53.0, 41.0, 40.9, 38.8, 30.1, 25.8, 24.0, 12.6; HRMS (ESI, m/z) calcd for $C_{22}H_{26}NO_3^+$ [M+H$^+$]: 352.1907, found:352.1909; IR: 1680cm^{-1}, 1767cm^{-1}, 1604cm^{-1}.

5. Mechanistic Investigation

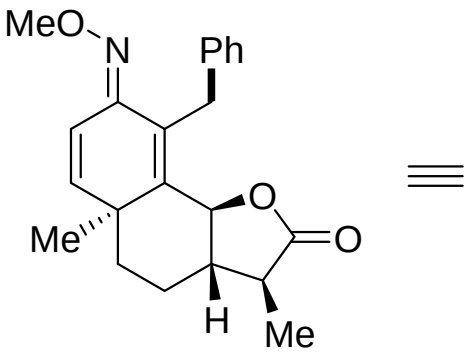


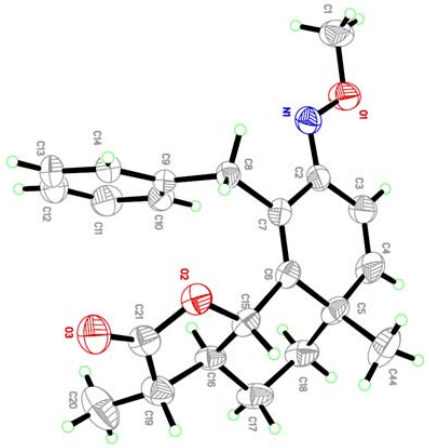
Palladium Complex 1e'[2-3]

A schlenk tube was charged with $Pd(OAc)_2$ (157 mg, 0.7 mmol) and a solution of (*E*)-3,3-dimethylbutan-2-one O-methyl oxime (64.5 mg, 0.5 mmol) in dichloroethane

(1.5 mL) and HFIP (0.5 mL). The tube was sealed and stirred at 85°C for 4h. After this time the reaction mixture was cooled to room temperature and treated with triphenylphosphine (466 mg, 0.7 mmol). The tube was sealed 80 °C for another 2 hours. After this time the reaction mixture was cooled to room temperature and filtered through a thin pad of Celite, eluting with ethyl acetate (30 mL) and DCM (10 mL) and the filtrate was concentrated under reduced pressure. The residue was then re-dissolved in CH2Cl2 (20 mL), washed with brine (2 x 20 mL) and dried over Mg2SO4 and concentrated under vacuum. The crude reaction mixture was purified by flash column chromatography (silica gel, gradient elution: 0% acetone in DCM to 2.5% acetone in DCM) to provide the complex as a pale yellow solid **1e'** (180 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 6H), 7.41– 7.37 (m, 9H), 4.16 (s, 3H), 1.95 (s, 3H), 1.51 (d, *J* = 3.8 Hz, 2H), 1.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.3, 135.0, 134.7, 134.5, 131.8, 131.3, 130.5, 130.2, 128.2, 128.1, 62.7, 48.7, 45.9, 29.0, 12.6.

6. Crystallographic Data





C(1)-O(1)	1.429(5)	C(2)-C(7)	1.476(4)
C(1)-H(1A)	0.9600	C(3)-C(4)	1.322(5)
C(1)-H(1B)	0.9600	C(3)-H(3)	0.9300
C(1)-H(1C)	0.9600	C(4)-C(5)	1.508(5)
C(2)-N(1)	1.294(4)	C(4)-H(4)	0.9300
C(2)-C(3)	1.442(4)	C(5)-C(18)	1.538(5)

C(5)-C(6)	1.536(4)	C(22)-O(4)	1.432(4)
C(5)-C(44)	1.560(5)	C(22)-H(22A)	0.9600
C(6)-C(7)	1.342(4)	C(22)-H(22B)	0.9600
C(6)-C(15)	1.511(4)	C(22)-H(22C)	0.9600
C(7)-C(8)	1.513(4)	C(23)-N(2)	1.288(4)
C(8)-C(9)	1.520(4)	C(23)-C(24)	1.447(5)
C(8)-H(8A)	0.9700	C(23)-C(28)	1.475(4)
C(8)-H(8B)	0.9700	C(24)-C(25)	1.326(5)
C(9)-C(14)	1.381(4)	C(24)-H(24)	0.9300
C(9)-C(10)	1.382(4)	C(25)-C(26)	1.482(5)
C(10)-C(11)	1.396(5)	C(25)-H(25)	0.9300
C(10)-H(10)	0.9300	C(26)-C(27)	1.526(4)
C(11)-C(12)	1.368(6)	C(26)-C(36)	1.550(5)
C(11)-H(11)	0.9300	C(26)-C(43)	1.554(5)
C(12)-C(13)	1.374(6)	C(27)-C(28)	1.352(4)
C(12)-H(12)	0.9300	C(27)-C(39)	1.503(4)
C(13)-C(14)	1.386(5)	C(28)-C(29)	1.517(4)
C(13)-H(13)	0.9300	C(29)-C(30)	1.509(4)
C(14)-H(14)	0.9300	C(29)-H(29A)	0.9700
C(15)-O(2)	1.445(3)	C(29)-H(29B)	0.9700
C(15)-C(16)	1.503(4)	C(30)-C(31)	1.363(5)
C(15)-H(15)	0.9800	C(30)-C(35)	1.375(4)
C(16)-C(19)	1.528(5)	C(31)-C(32)	1.377(6)
C(16)-C(17)	1.525(5)	C(31)-H(31)	0.9300
C(16)-H(16)	0.9800	C(32)-C(33)	1.360(7)
C(17)-C(18)	1.526(5)	C(32)-H(32)	0.9300
C(17)-H(17A)	0.9700	C(33)-C(34)	1.341(7)
C(17)-H(17B)	0.9700	C(33)-H(33)	0.9300
C(18)-H(18A)	0.9700	C(34)-C(35)	1.394(5)
C(18)-H(18B)	0.9700	C(34)-H(34)	0.9300
C(19)-C(20)	1.490(6)	C(35)-H(35)	0.9300
C(19)-C(21)	1.510(5)	C(36)-C(37)	1.528(5)
C(19)-H(19)	0.9800	C(36)-H(36A)	0.9700
C(20)-H(20A)	0.9600	C(36)-H(36B)	0.9700
C(20)-H(20B)	0.9600	C(37)-C(38)	1.504(5)
C(20)-H(20C)	0.9600	C(37)-H(37A)	0.9700
C(21)-O(3)	1.194(4)	C(37)-H(37B)	0.9700
C(21)-O(2)	1.351(4)	C(38)-C(39)	1.512(5)

C(38)-C(40)	1.520(4)	C(18)-C(5)-C(6)	110.2(3)
C(38)-H(38)	0.9800	C(4)-C(5)-C(44)	107.1(3)
C(39)-O(5)	1.446(4)	C(18)-C(5)-C(44)	110.9(3)
C(39)-H(39)	0.9800	C(6)-C(5)-C(44)	110.6(3)
C(40)-C(41)	1.502(5)	C(7)-C(6)-C(15)	126.8(2)
C(40)-C(42)	1.526(6)	C(7)-C(6)-C(5)	125.0(3)
C(40)-H(40)	0.9800	C(15)-C(6)-C(5)	107.7(3)
C(41)-O(6)	1.198(4)	C(6)-C(7)-C(2)	119.0(3)
C(41)-O(5)	1.366(4)	C(6)-C(7)-C(8)	124.1(3)
C(42)-H(42A)	0.9600	C(2)-C(7)-C(8)	116.8(3)
C(42)-H(42B)	0.9600	C(7)-C(8)-C(9)	114.9(2)
C(42)-H(42C)	0.9600	C(7)-C(8)-H(8A)	108.6
C(43)-H(43A)	0.9600	C(9)-C(8)-H(8A)	108.6
C(43)-H(43B)	0.9600	C(7)-C(8)-H(8B)	108.6
C(43)-H(43C)	0.9600	C(9)-C(8)-H(8B)	108.6
C(44)-H(44A)	0.9600	H(8A)-C(8)-H(8B)	107.5
C(44)-H(44B)	0.9600	C(14)-C(9)-C(10)	118.2(3)
C(44)-H(44C)	0.9600	C(14)-C(9)-C(8)	119.8(3)
N(1)-O(1)	1.415(3)	C(10)-C(9)-C(8)	122.0(3)
N(2)-O(4)	1.419(3)	C(9)-C(10)-C(11)	120.9(3)
		C(9)-C(10)-H(10)	119.5
O(1)-C(1)-H(1A)	109.5	C(11)-C(10)-H(10)	119.5
O(1)-C(1)-H(1B)	109.5	C(12)-C(11)-C(10)	119.5(4)
H(1A)-C(1)-H(1B)	109.5	C(12)-C(11)-H(11)	120.3
O(1)-C(1)-H(1C)	109.5	C(10)-C(11)-H(11)	120.3
H(1A)-C(1)-H(1C)	109.5	C(11)-C(12)-C(13)	120.6(4)
H(1B)-C(1)-H(1C)	109.5	C(11)-C(12)-H(12)	119.7
N(1)-C(2)-C(3)	124.1(3)	C(13)-C(12)-H(12)	119.7
N(1)-C(2)-C(7)	116.6(3)	C(12)-C(13)-C(14)	119.6(4)
C(3)-C(2)-C(7)	119.3(3)	C(12)-C(13)-H(13)	120.2
C(4)-C(3)-C(2)	120.8(3)	C(14)-C(13)-H(13)	120.2
C(4)-C(3)-H(3)	119.6	C(9)-C(14)-C(13)	121.2(3)
C(2)-C(3)-H(3)	119.6	C(9)-C(14)-H(14)	119.4
C(3)-C(4)-C(5)	125.7(3)	C(13)-C(14)-H(14)	119.4
C(3)-C(4)-H(4)	117.2	O(2)-C(15)-C(16)	105.2(2)
C(5)-C(4)-H(4)	117.2	O(2)-C(15)-C(6)	118.2(2)
C(4)-C(5)-C(18)	107.9(3)	C(16)-C(15)-C(6)	110.0(2)
C(4)-C(5)-C(6)	110.2(3)	O(2)-C(15)-H(15)	107.6

C(16)-C(15)-H(15)	107.6	O(4)-C(22)-H(22C)	109.5
C(6)-C(15)-H(15)	107.6	H(22A)-C(22)-H(22C)	109.5
C(15)-C(16)-C(19)	100.9(2)	H(22B)-C(22)-H(22C)	109.5
C(15)-C(16)-C(17)	109.8(3)	N(2)-C(23)-C(24)	125.3(3)
C(19)-C(16)-C(17)	120.5(3)	N(2)-C(23)-C(28)	116.4(3)
C(15)-C(16)-H(16)	108.3	C(24)-C(23)-C(28)	118.3(3)
C(19)-C(16)-H(16)	108.3	C(25)-C(24)-C(23)	121.4(3)
C(17)-C(16)-H(16)	108.3	C(25)-C(24)-H(24)	119.3
C(18)-C(17)-C(16)	108.2(3)	C(23)-C(24)-H(24)	119.3
C(18)-C(17)-H(17A)	110.0	C(24)-C(25)-C(26)	125.0(3)
C(16)-C(17)-H(17A)	110.0	C(24)-C(25)-H(25)	117.5
C(18)-C(17)-H(17B)	110.0	C(26)-C(25)-H(25)	117.5
C(16)-C(17)-H(17B)	110.0	C(25)-C(26)-C(27)	111.7(3)
H(17A)-C(17)-H(17B)	108.4	C(25)-C(26)-C(36)	107.1(3)
C(17)-C(18)-C(5)	115.6(3)	C(27)-C(26)-C(36)	109.7(3)
C(17)-C(18)-H(18A)	108.4	C(25)-C(26)-C(43)	107.0(3)
C(5)-C(18)-H(18A)	108.4	C(27)-C(26)-C(43)	111.3(3)
C(17)-C(18)-H(18B)	108.4	C(36)-C(26)-C(43)	109.9(3)
C(5)-C(18)-H(18B)	108.4	C(28)-C(27)-C(39)	127.2(3)
H(18A)-C(18)-H(18B)	107.4	C(28)-C(27)-C(26)	124.0(3)
C(20)-C(19)-C(21)	112.9(4)	C(39)-C(27)-C(26)	108.2(3)
C(20)-C(19)-C(16)	118.0(3)	C(27)-C(28)-C(23)	119.5(3)
C(21)-C(19)-C(16)	101.2(3)	C(27)-C(28)-C(29)	123.9(3)
C(20)-C(19)-H(19)	108.1	C(23)-C(28)-C(29)	116.6(3)
C(21)-C(19)-H(19)	108.1	C(30)-C(29)-C(28)	114.4(2)
C(16)-C(19)-H(19)	108.1	C(30)-C(29)-H(29A)	108.7
C(19)-C(20)-H(20A)	109.5	C(28)-C(29)-H(29A)	108.7
C(19)-C(20)-H(20B)	109.5	C(30)-C(29)-H(29B)	108.7
H(20A)-C(20)-H(20B)	109.5	C(28)-C(29)-H(29B)	108.7
C(19)-C(20)-H(20C)	109.5	H(29A)-C(29)-H(29B)	107.6
H(20A)-C(20)-H(20C)	109.5	C(31)-C(30)-C(35)	118.0(3)
H(20B)-C(20)-H(20C)	109.5	C(31)-C(30)-C(29)	120.3(3)
O(3)-C(21)-O(2)	121.3(3)	C(35)-C(30)-C(29)	121.7(3)
O(3)-C(21)-C(19)	128.0(3)	C(30)-C(31)-C(32)	121.3(4)
O(2)-C(21)-C(19)	110.8(3)	C(30)-C(31)-H(31)	119.4
O(4)-C(22)-H(22A)	109.5	C(32)-C(31)-H(31)	119.4
O(4)-C(22)-H(22B)	109.5	C(33)-C(32)-C(31)	120.2(4)
H(22A)-C(22)-H(22B)	109.5	C(33)-C(32)-H(32)	119.9

C(31)-C(32)-H(32)	119.9	C(41)-C(40)-C(38)	101.4(3)
C(34)-C(33)-C(32)	119.8(4)	C(41)-C(40)-C(42)	112.6(3)
C(34)-C(33)-H(33)	120.1	C(38)-C(40)-C(42)	116.5(3)
C(32)-C(33)-H(33)	120.1	C(41)-C(40)-H(40)	108.6
C(33)-C(34)-C(35)	120.5(4)	C(38)-C(40)-H(40)	108.6
C(33)-C(34)-H(34)	119.7	C(42)-C(40)-H(40)	108.6
C(35)-C(34)-H(34)	119.7	O(6)-C(41)-O(5)	119.6(3)
C(30)-C(35)-C(34)	120.3(4)	O(6)-C(41)-C(40)	129.6(4)
C(30)-C(35)-H(35)	119.9	O(5)-C(41)-C(40)	110.8(3)
C(34)-C(35)-H(35)	119.9	C(40)-C(42)-H(42A)	109.5
C(37)-C(36)-C(26)	114.9(3)	C(40)-C(42)-H(42B)	109.5
C(37)-C(36)-H(36A)	108.5	H(42A)-C(42)-H(42B)	109.5
C(26)-C(36)-H(36A)	108.5	C(40)-C(42)-H(42C)	109.5
C(37)-C(36)-H(36B)	108.5	H(42A)-C(42)-H(42C)	109.5
C(26)-C(36)-H(36B)	108.5	H(42B)-C(42)-H(42C)	109.5
H(36A)-C(36)-H(36B)	107.5	C(26)-C(43)-H(43A)	109.5
C(38)-C(37)-C(36)	108.2(3)	C(26)-C(43)-H(43B)	109.5
C(38)-C(37)-H(37A)	110.1	H(43A)-C(43)-H(43B)	109.5
C(36)-C(37)-H(37A)	110.1	C(26)-C(43)-H(43C)	109.5
C(38)-C(37)-H(37B)	110.1	H(43A)-C(43)-H(43C)	109.5
C(36)-C(37)-H(37B)	110.1	H(43B)-C(43)-H(43C)	109.5
H(37A)-C(37)-H(37B)	108.4	C(5)-C(44)-H(44A)	109.5
C(37)-C(38)-C(39)	110.3(3)	C(5)-C(44)-H(44B)	109.5
C(37)-C(38)-C(40)	120.5(3)	H(44A)-C(44)-H(44B)	109.5
C(39)-C(38)-C(40)	101.6(2)	C(5)-C(44)-H(44C)	109.5
C(37)-C(38)-H(38)	108.0	H(44A)-C(44)-H(44C)	109.5
C(39)-C(38)-H(38)	108.0	H(44B)-C(44)-H(44C)	109.5
C(40)-C(38)-H(38)	108.0	C(2)-N(1)-O(1)	111.4(2)
O(5)-C(39)-C(27)	119.0(3)	C(23)-N(2)-O(4)	110.7(2)
O(5)-C(39)-C(38)	104.8(3)	N(1)-O(1)-C(1)	108.7(3)
C(27)-C(39)-C(38)	109.3(2)	C(21)-O(2)-C(15)	108.1(2)
O(5)-C(39)-H(39)	107.8	N(2)-O(4)-C(22)	108.2(3)
C(27)-C(39)-H(39)	107.8	C(41)-O(5)-C(39)	108.1(3)
C(38)-C(39)-H(39)	107.8		

7. References

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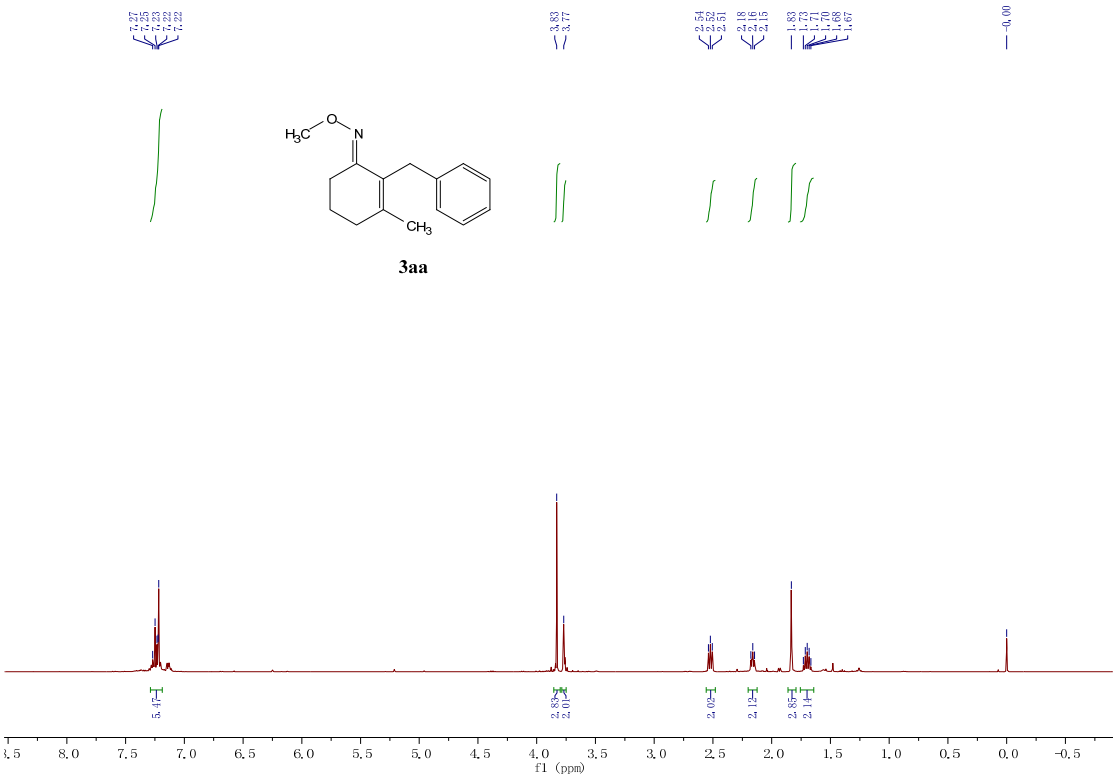
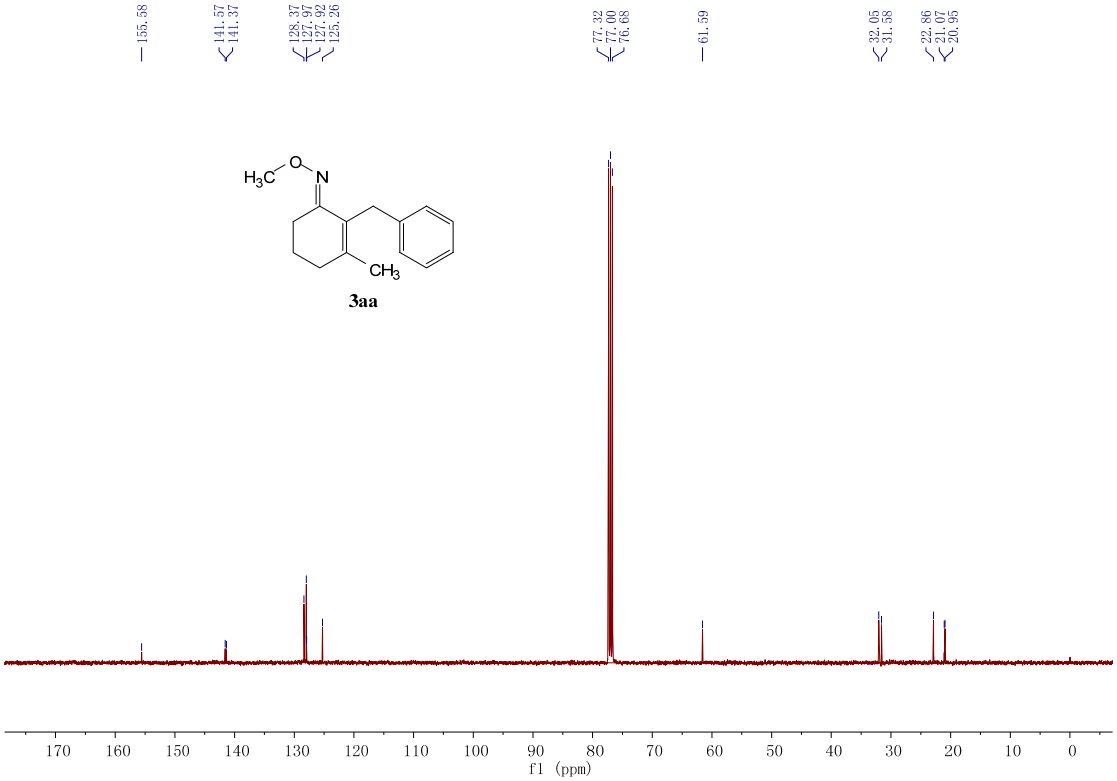
[2] J. Peng, C. Chen and C.-J. Xi, *Chem. Sci.*, 2015, doi: 10.1039/c5sc03903g.

[3] A. McNally, B. Haffemayer, B. S. L. Collins and M. Gaunt, *Nature.,* 2014, **510**, 129.

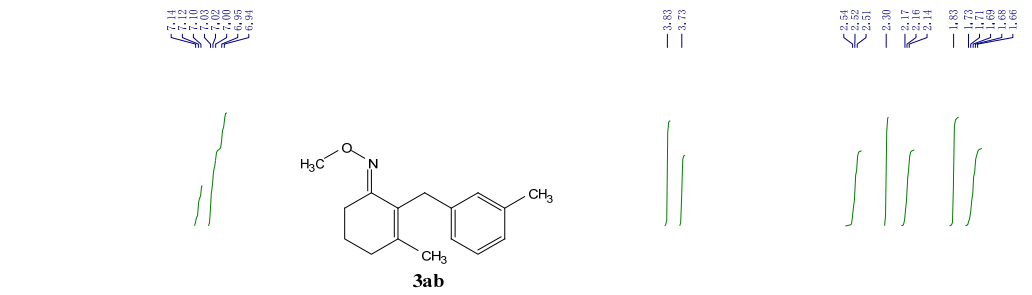
8. ^{1}H, ^{13}C, and ^{19}F NMR Spectra of Substrates and Products



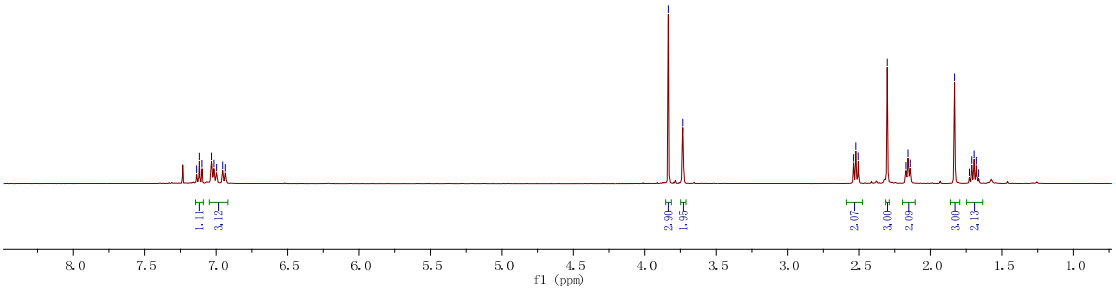
3aa



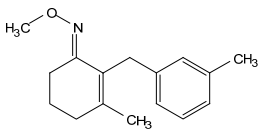
3aa


7.14
7.12
7.10
7.03
7.02
7.00
6.95
6.94
3.83
3.73
2.54
2.52
2.51
2.30
2.17
2.16
2.14
1.83
1.73
1.71
1.69
1.68
1.66
H3C
O
N
CH3
CH3

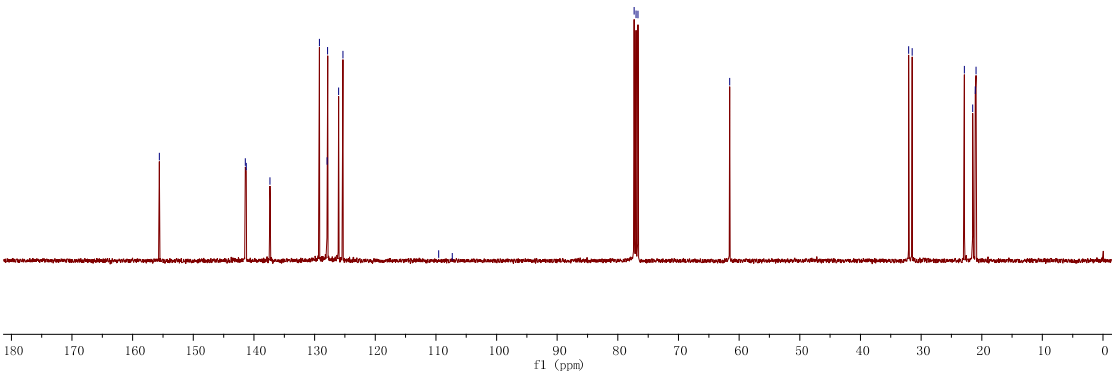
3ab

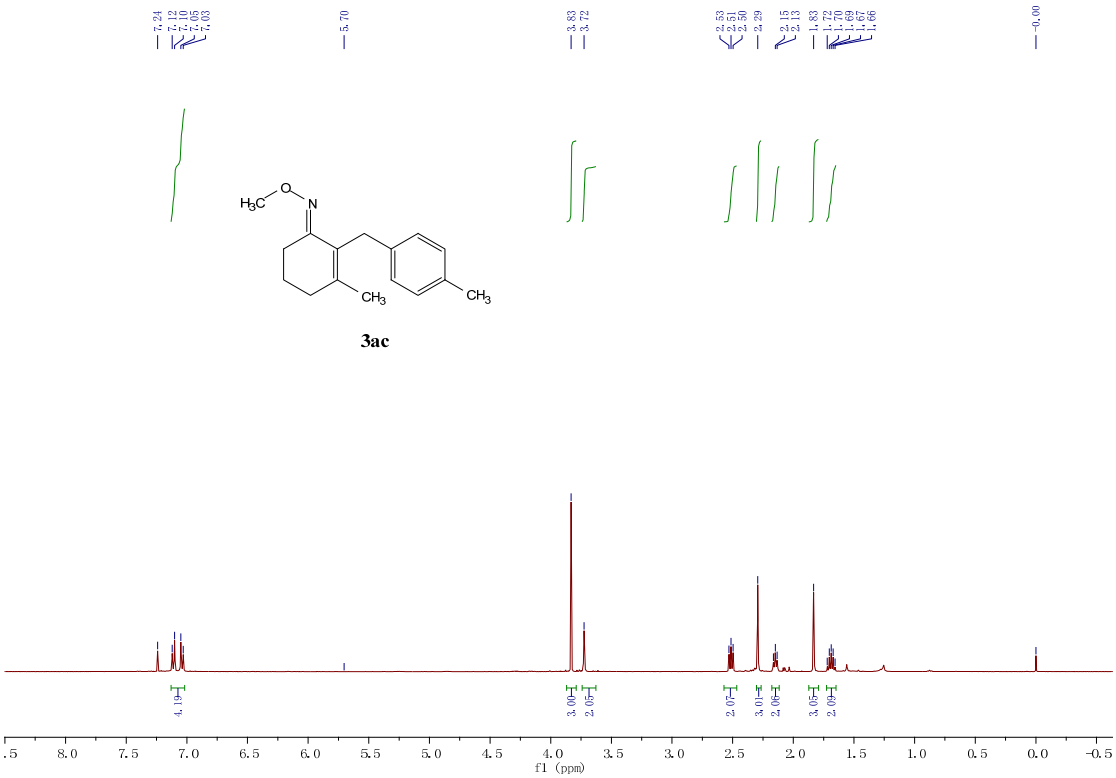

1.11
3.12
2.90
1.95
2.07
3.00
2.09
3.00
2.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


155.60
141.44
141.26
137.36
129.21
127.94
127.85
126.04
125.34
109.54
107.31
77.32
77.00
76.68
61.55
32.04
31.47
22.86
21.48
21.07
20.94

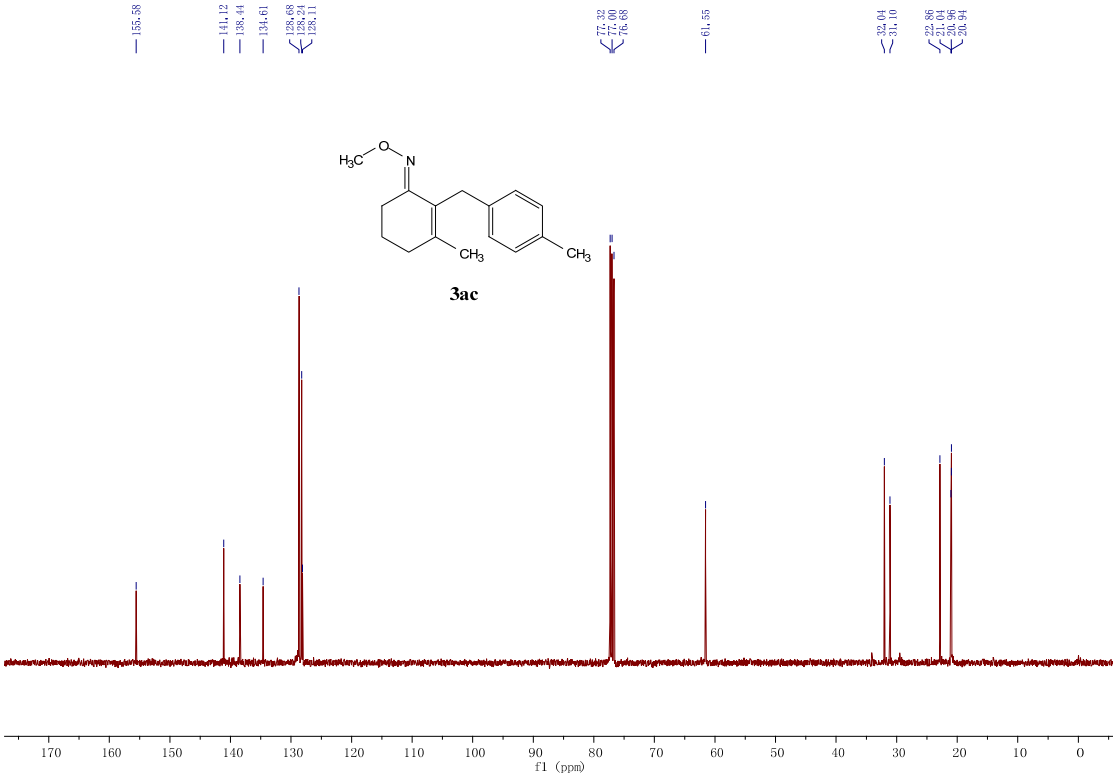

H3C
O
N
CH3
CH3

3ab

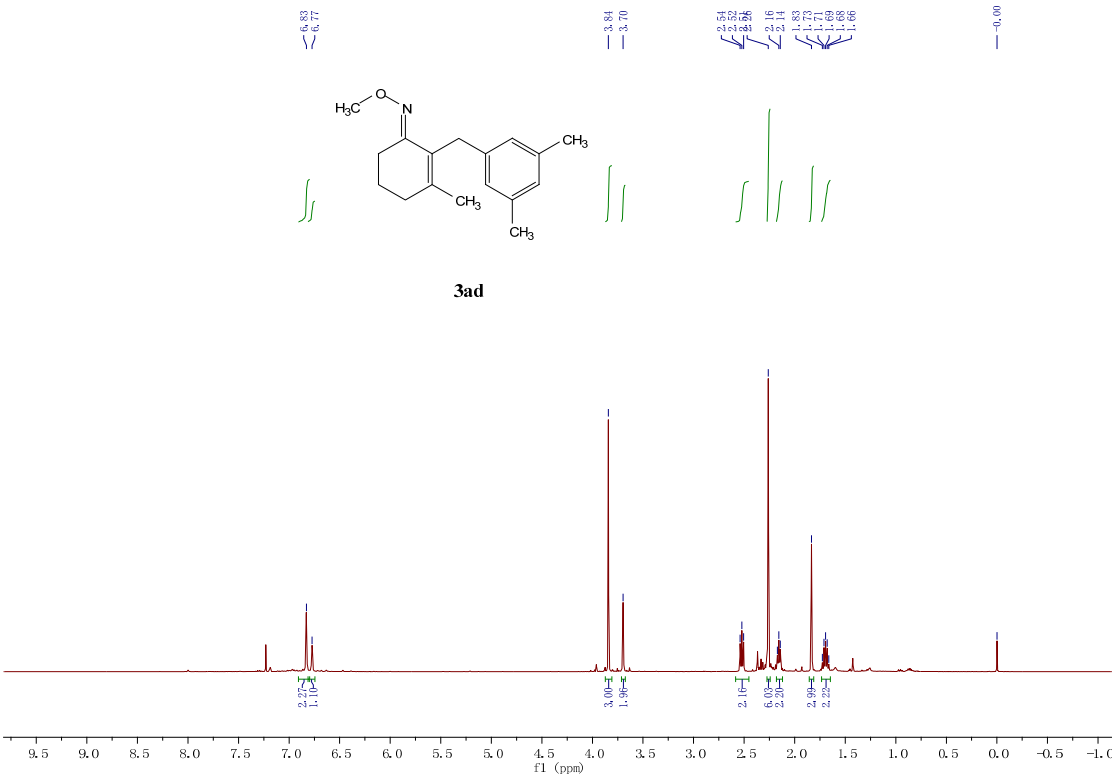

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.24
7.12
7.10
7.05
7.03
5.70
3.83
3.72
2.53
2.51
2.38
2.29
2.15
2.13
1.83
1.72
1.70
1.69
1.67
1.66
0.00
4.19
3.00
2.05
2.07
3.01
2.06
3.05
2.09
f1 (ppm)

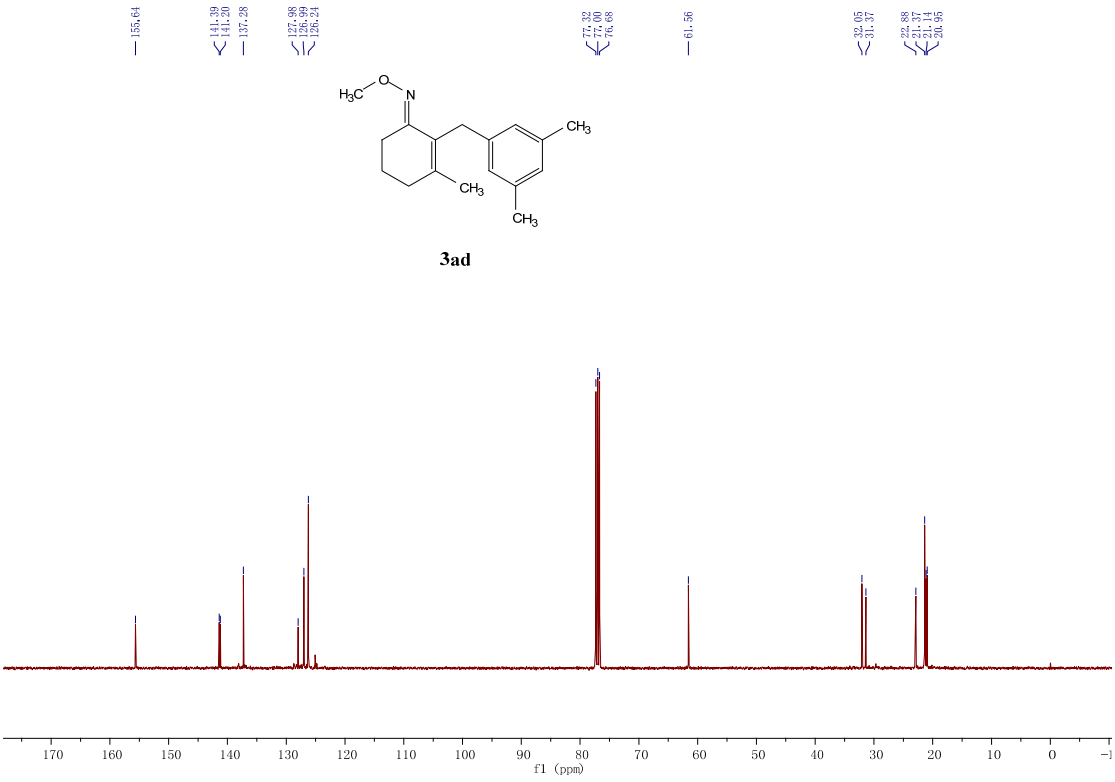
3ac


155.58
141.12
138.44
134.61
128.68
128.24
128.11
77.32
77.00
76.68
61.55
32.04
31.10
22.86
21.04
20.96
20.94
f1 (ppm)

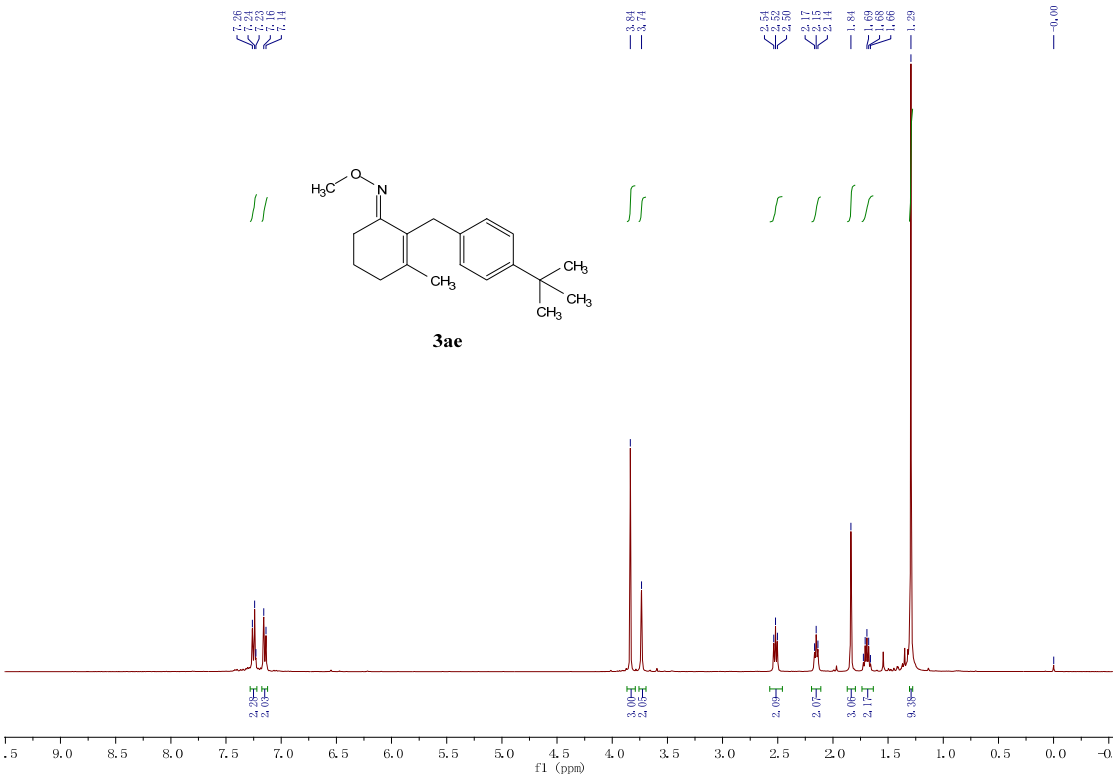
3ac


6.83
6.77
3.84
3.70
2.54
2.52
2.16
2.14
1.83
1.73
1.71
1.69
1.68
1.66
0.00
H3C
O
N
CH3
CH3
CH3
2.27
1.10
3.00
1.96
2.16
6.03
2.20
2.99
2.22
f1 (ppm)

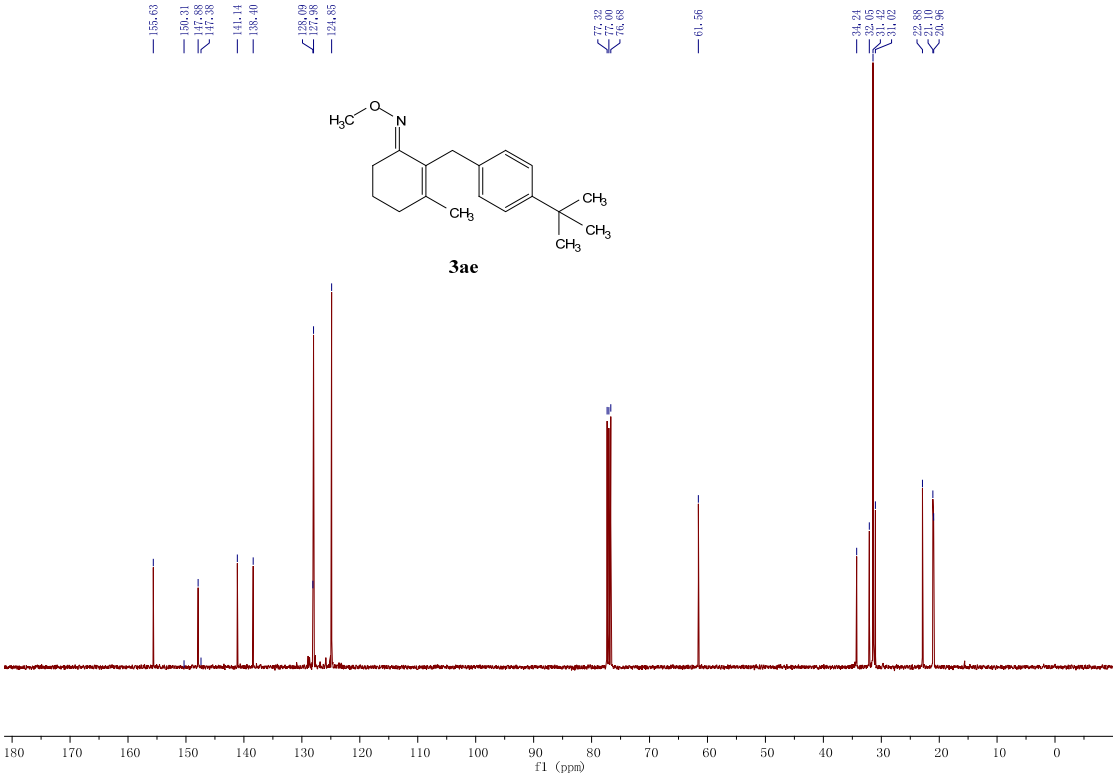
3ad


155.64
141.39
141.20
137.28
127.98
126.99
126.24
77.32
77.00
76.68
61.56
32.05
31.37
22.88
21.37
21.14
20.95
H3C
O
N
CH3
CH3
CH3
f1 (ppm)

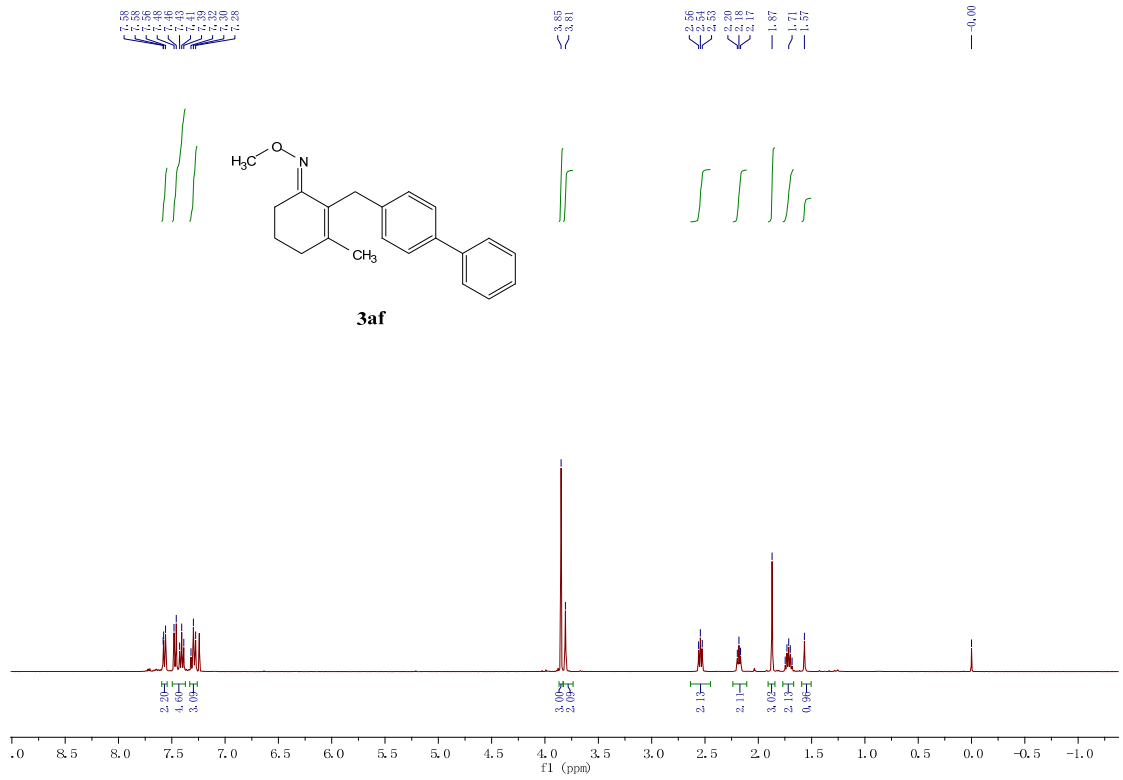
3ad


7.26
7.24
7.23
7.16
7.14
3.84
3.74
2.54
2.52
2.50
2.17
2.15
2.14
1.84
1.69
1.68
1.66
1.29
0.00
H3C
O
N
CH3
CH3
CH3
CH3
2.28
2.03
3.00
2.05
2.09
2.07
3.06
2.17
9.38
f1 (ppm)

3ae


155.63
150.31
147.88
141.38
141.14
138.40
128.09
127.98
124.85
77.32
77.00
76.68
61.56
34.24
32.45
31.42
31.02
22.88
21.10
20.96
H3C
O
N
CH3
CH3
CH3
CH3
f1 (ppm)

3ae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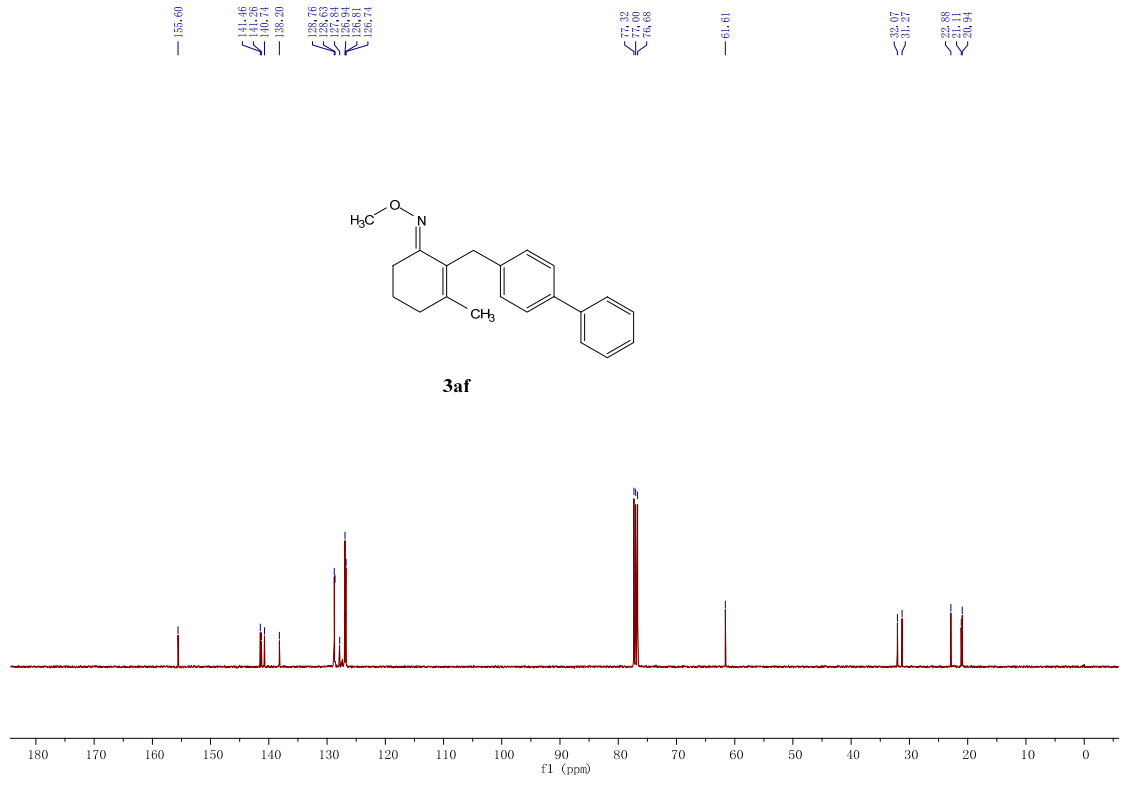
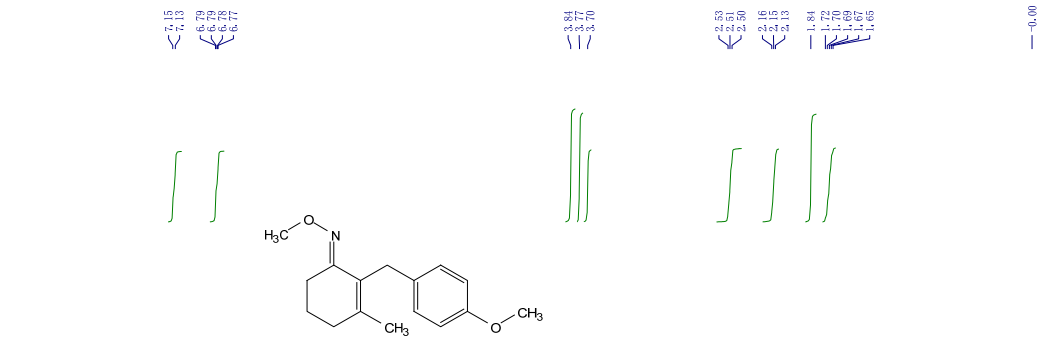
7.58
7.56
7.48
7.46
7.43
7.41
7.39
7.32
7.30
7.28
3.85
3.81
2.56
2.54
2.53
2.20
2.18
2.17
1.87
1.71
1.57
0.00
H3C
O
N
CH3
2.20
4.60
3.00
3.00
2.00
2.13
2.11
3.02
2.19
0.96
f1 (ppm)

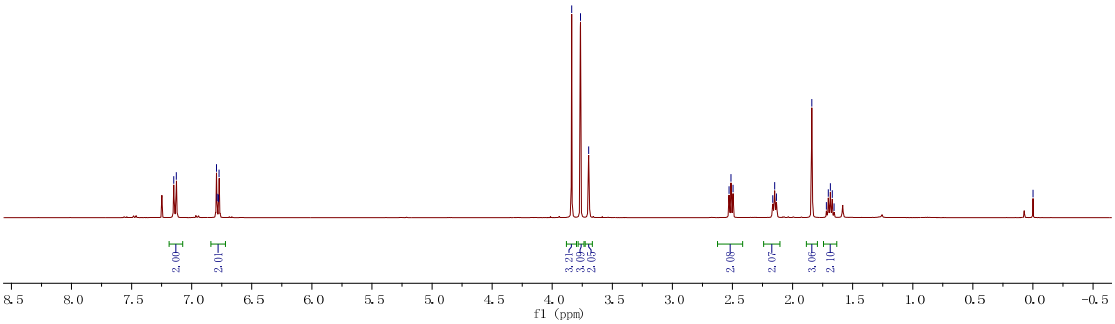
3af

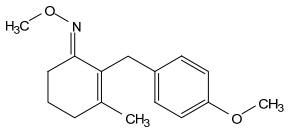

155.60
141.46
141.26
140.74
138.20
128.76
128.63
127.84
126.81
126.74
77.32
77.00
76.68
61.61
32.07
31.27
22.88
21.11
20.94
H3C
O
N
CH3
f1 (ppm)

3af

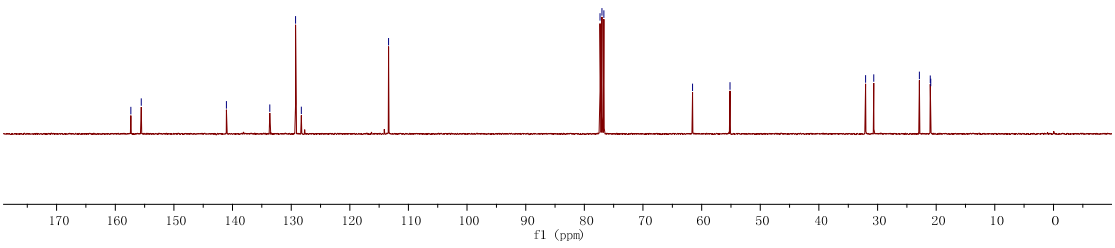


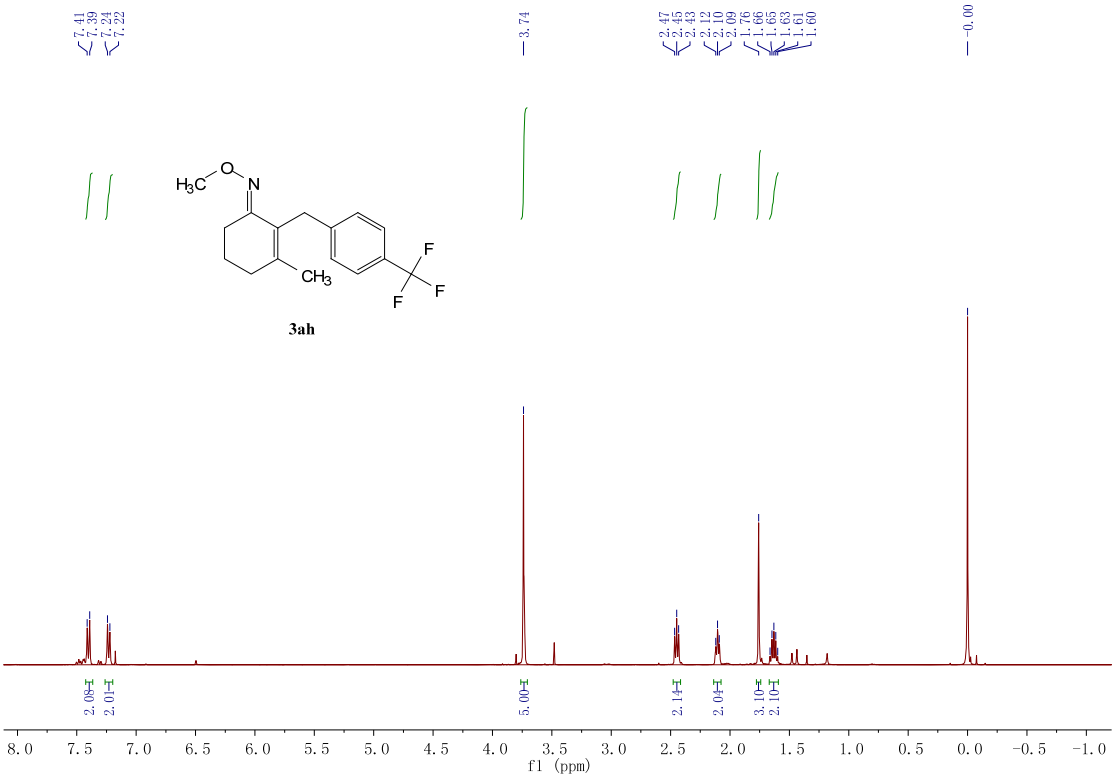
3ag



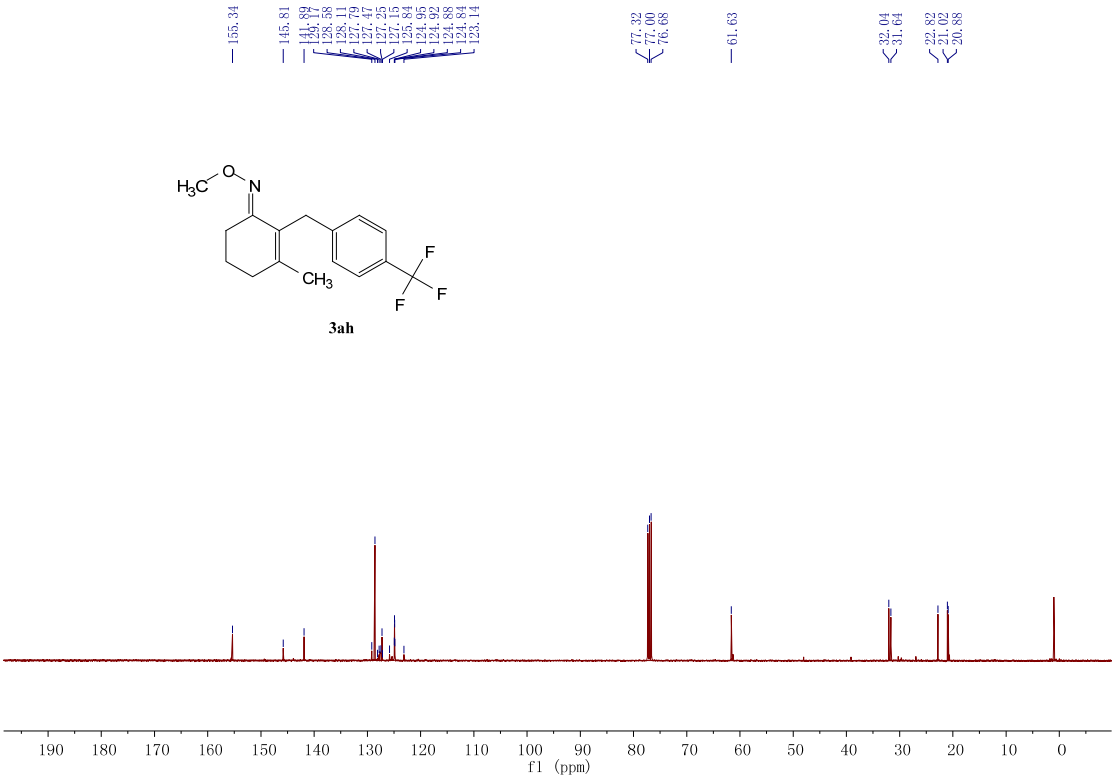


3ag

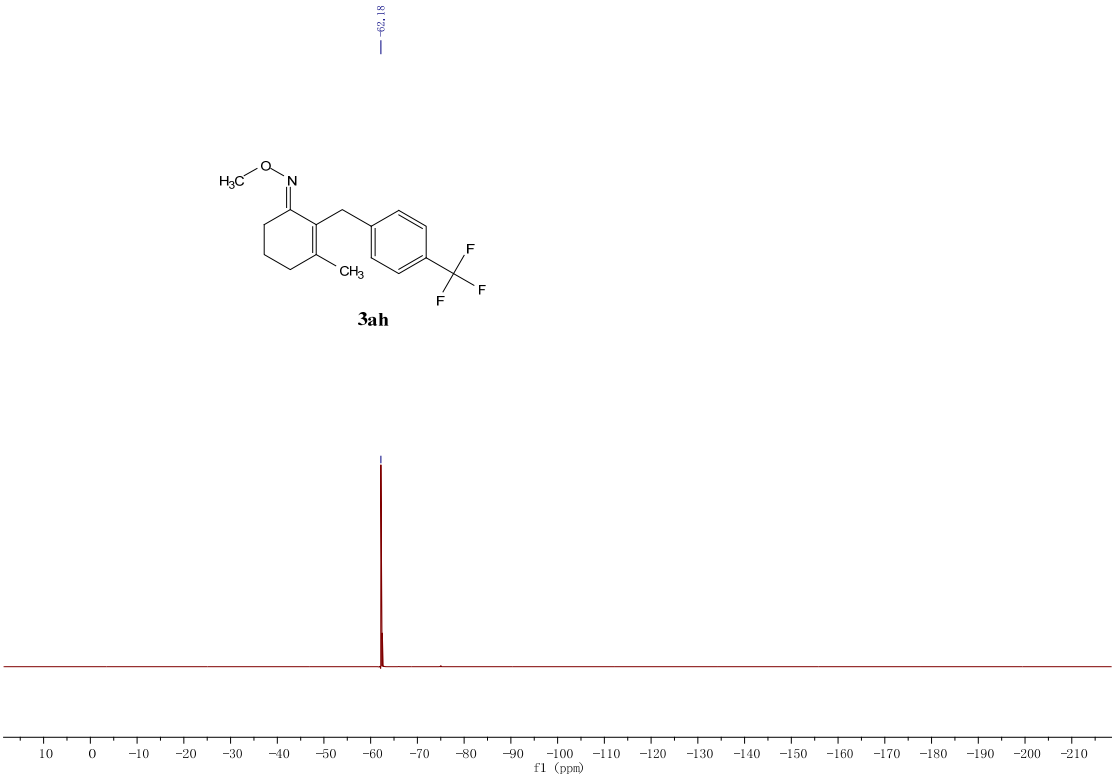



7.41
7.39
7.24
7.22
3.74
2.47
2.45
2.43
2.12
2.10
2.09
1.76
1.66
1.65
1.63
1.61
1.60
-0.00
H3C
O
N
CH3
F
F
F
2.08
2.01
5.00
2.14
2.04
3.10
2.10
f1 (ppm)

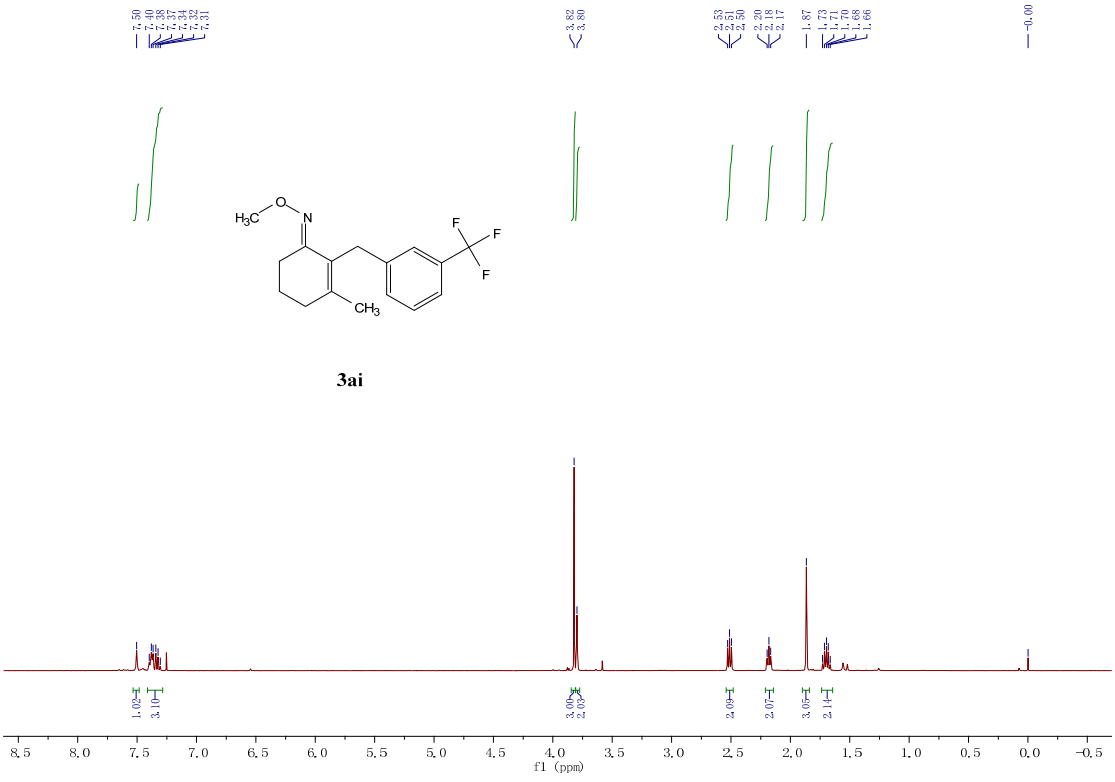
3ah


155.34
145.81
141.89
129.17
128.58
128.11
127.79
127.47
127.25
127.15
125.84
124.95
124.92
124.88
124.84
123.14
77.32
77.00
76.68
61.63
32.04
31.64
22.82
21.02
20.88
H3C
O
N
CH3
F
F
F
f1 (ppm)

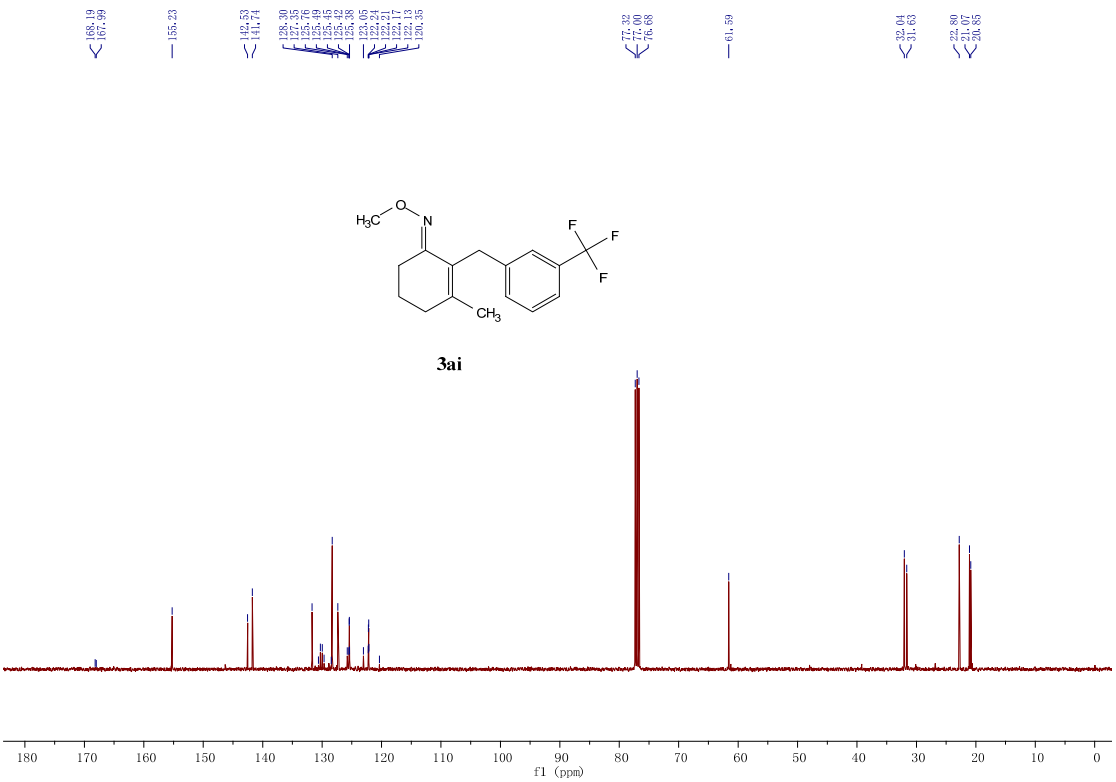
3ah


-62.18
H3C
O
N
CH3
F
F
F
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

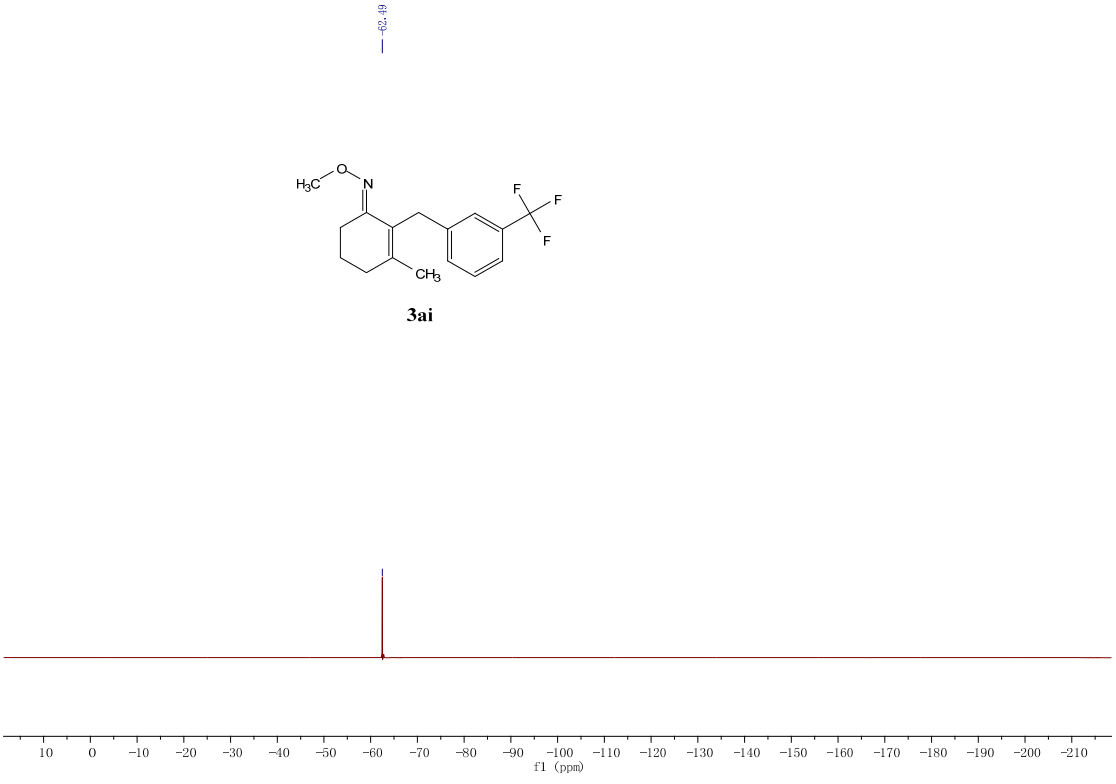
3ah


7.50
7.40
7.38
7.37
7.34
7.32
7.31
3.82
3.80
2.53
2.51
2.50
2.30
2.18
2.17
1.87
1.73
1.71
1.70
1.68
1.66
-0.00
H3C
O
N
CH3
F
F
F
1.02
3.10
3.00
2.03
2.09
2.07
3.05
2.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

3ai


168.19
167.99
155.23
142.53
141.74
128.30
127.35
125.76
125.49
125.45
125.42
125.38
123.05
122.24
122.21
122.17
122.13
120.35
77.32
77.00
76.68
61.59
32.04
31.63
22.80
21.07
20.85
H3C
O
N
F
F
F
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ai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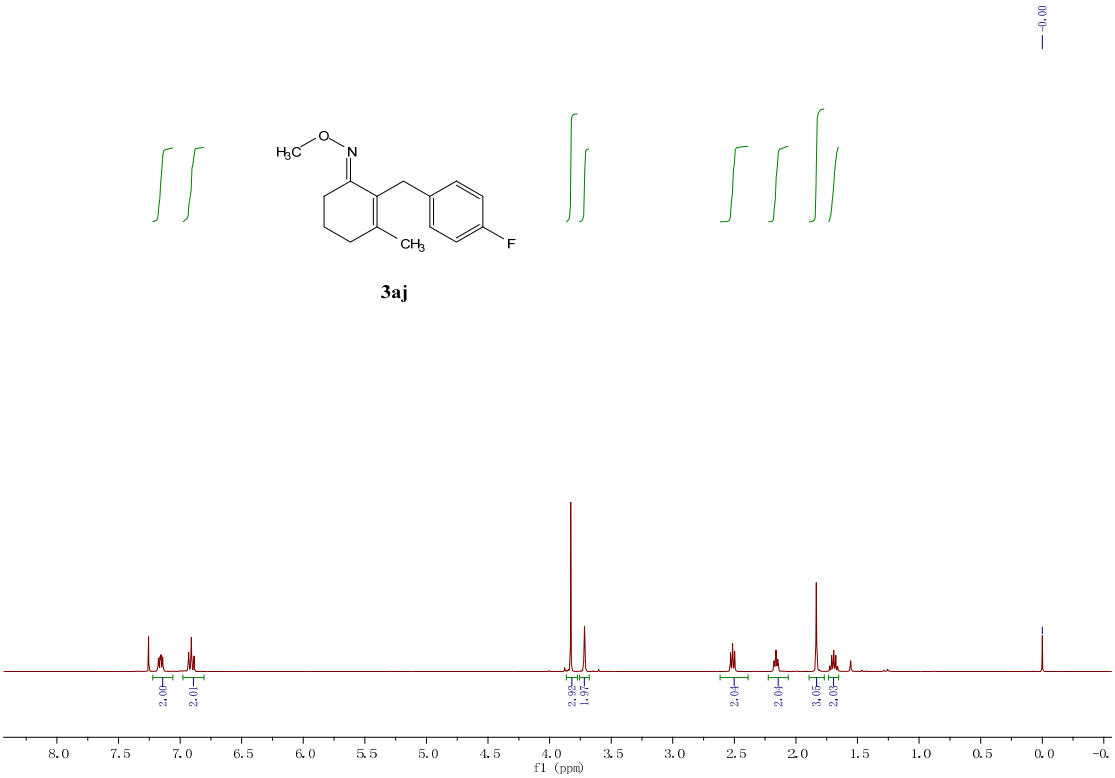
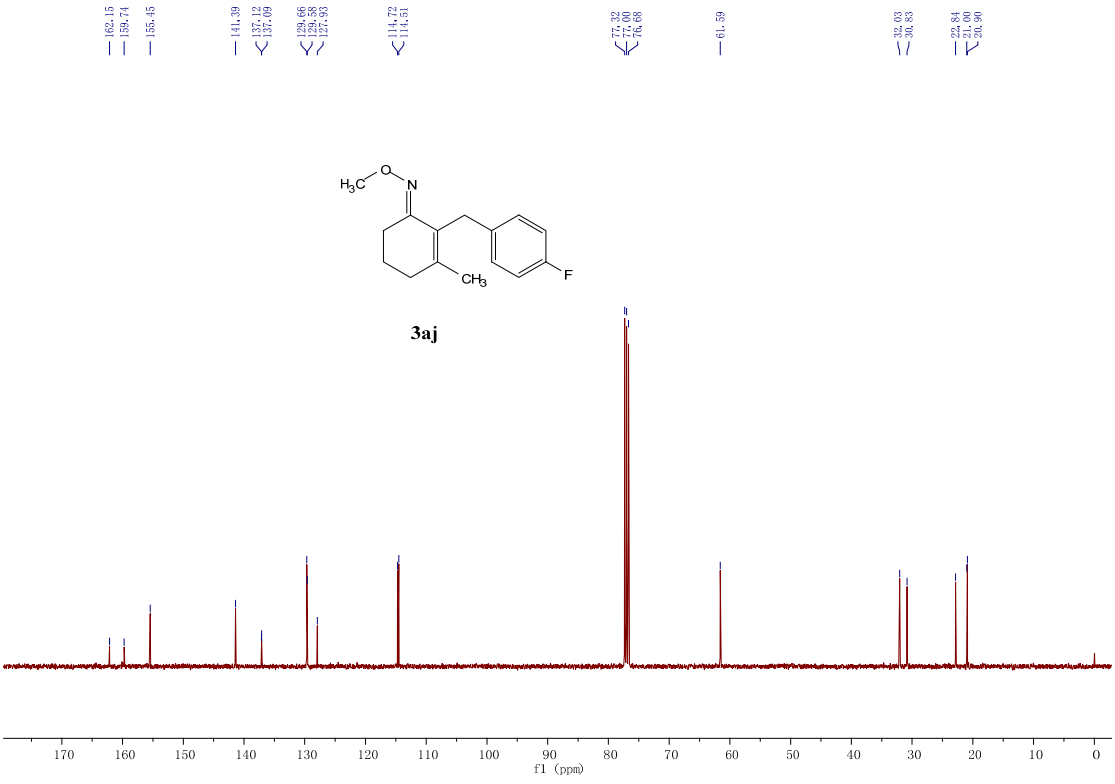
H3C
O
N
F
F
F
CH3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

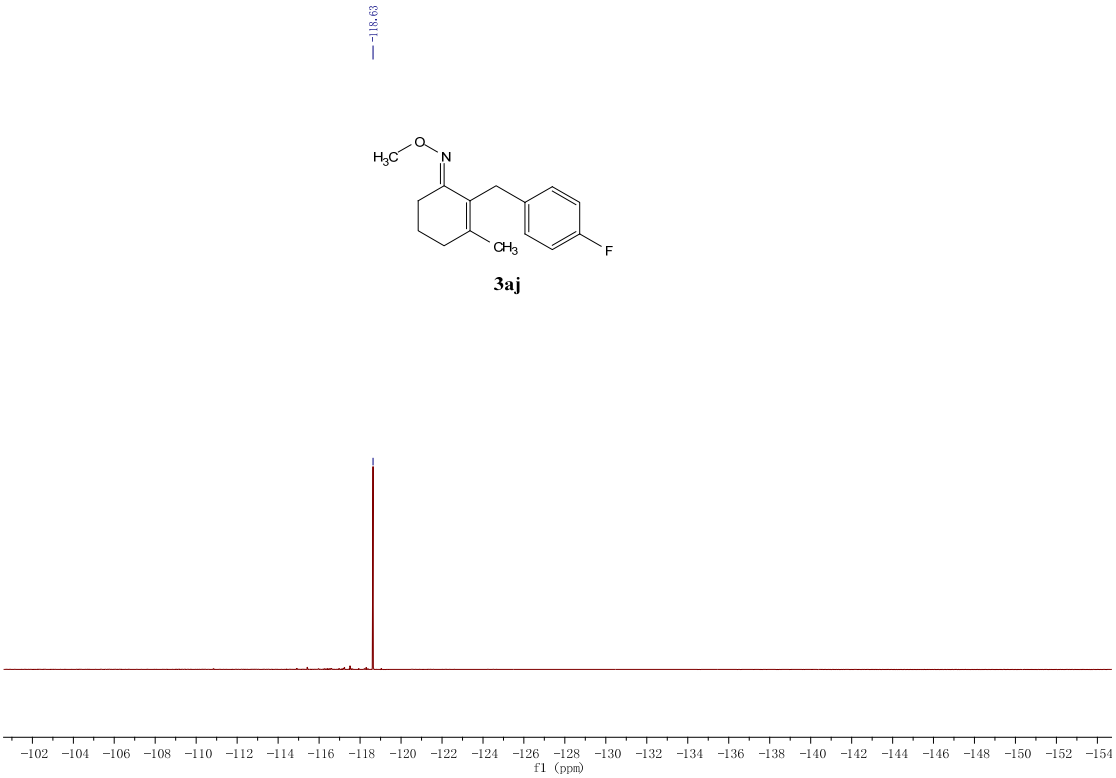
3ai


-0.00
H3C
O
N
CH3
F
2.00
2.01
2.92
1.97
2.04
2.04
3.05
2.03
f1 (ppm)

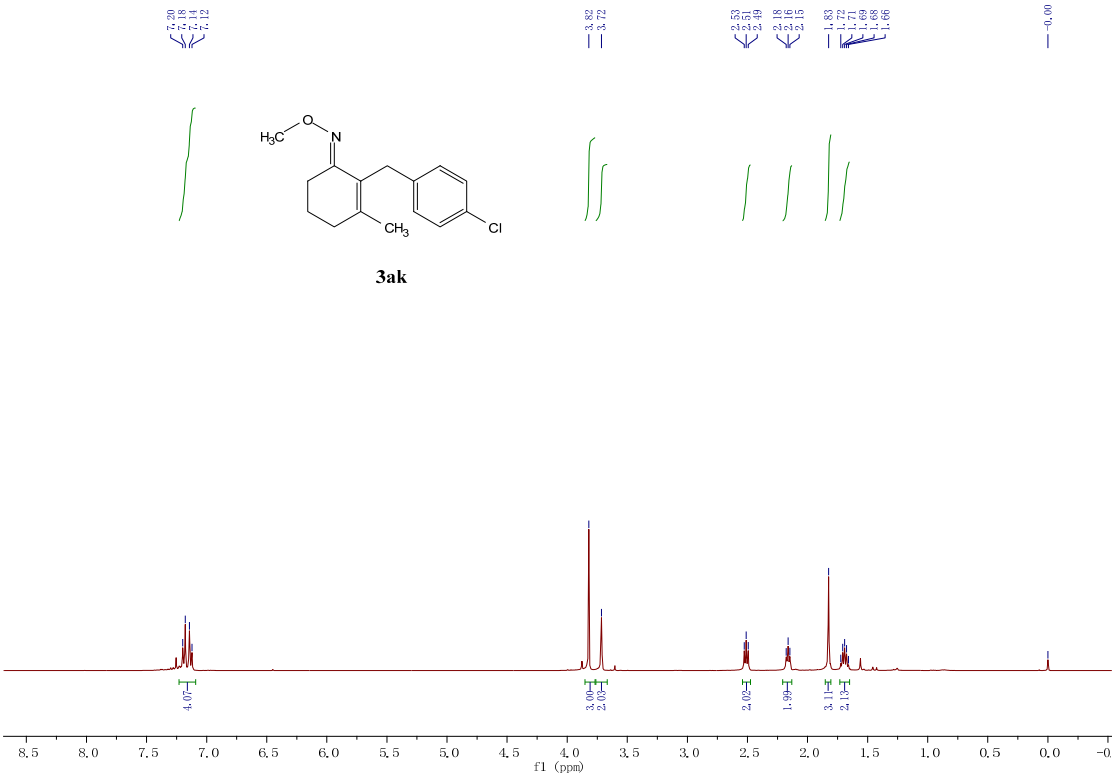
3aj


162.15
159.74
155.45
141.39
137.12
137.09
129.66
129.58
127.93
114.72
114.51
77.32
77.00
76.68
61.59
32.03
30.83
22.84
21.00
20.90
H3C
O
N
CH3
F
f1 (ppm)

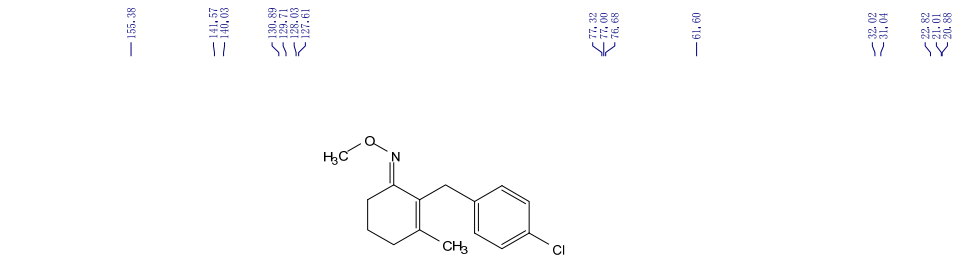
3aj


-118.63
H3C
O
N
CH3
F
-102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154
f1 (ppm)

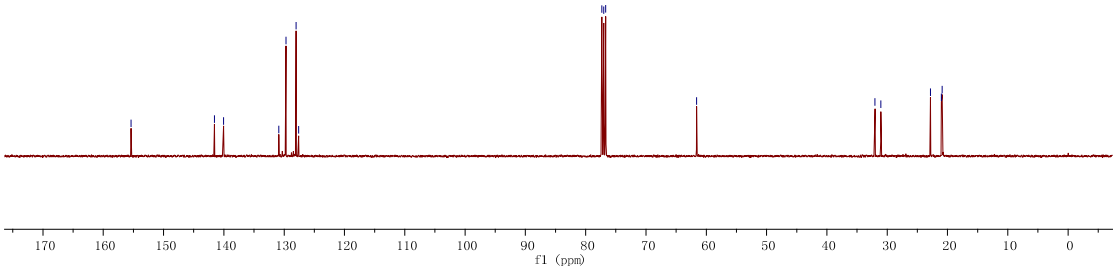
3aj

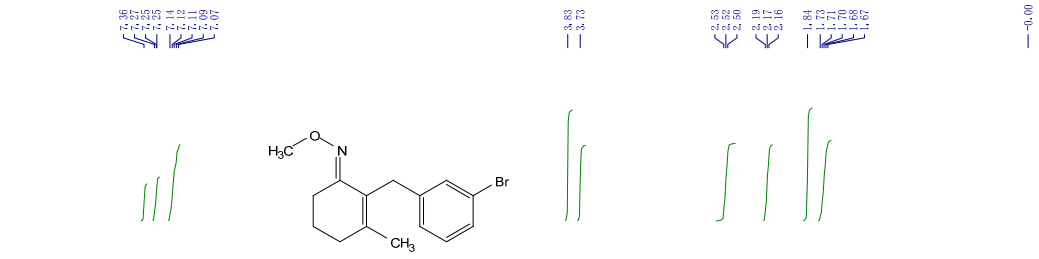

7.20
7.18
7.14
7.12
3.82
3.72
2.53
2.51
2.49
2.18
2.16
2.15
1.83
1.72
1.71
1.69
1.68
1.66
0.00
H3C
O
N
CH3
Cl
4.07
3.00
2.00
2.02
1.99
3.11
2.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ak

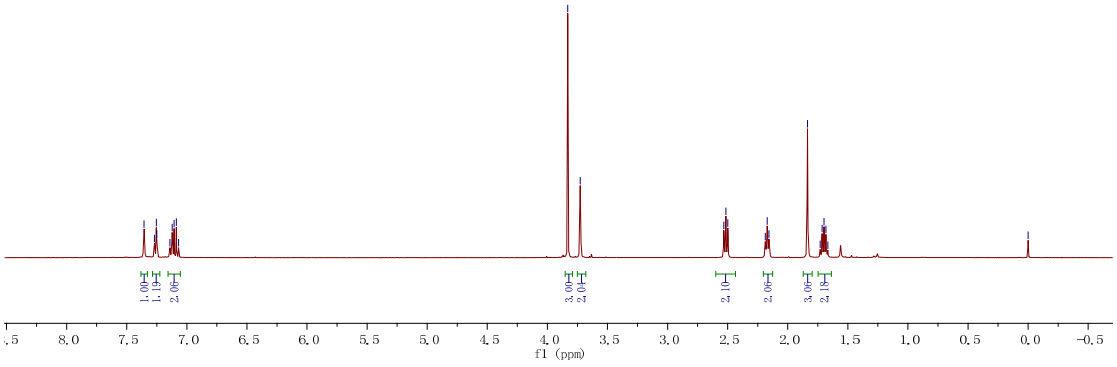

155.38
141.57
140.03
130.89
129.71
128.63
127.61
77.32
77.00
76.68
61.60
32.02
31.04
22.82
21.01
20.88
H3C
O
N
CH3
Cl

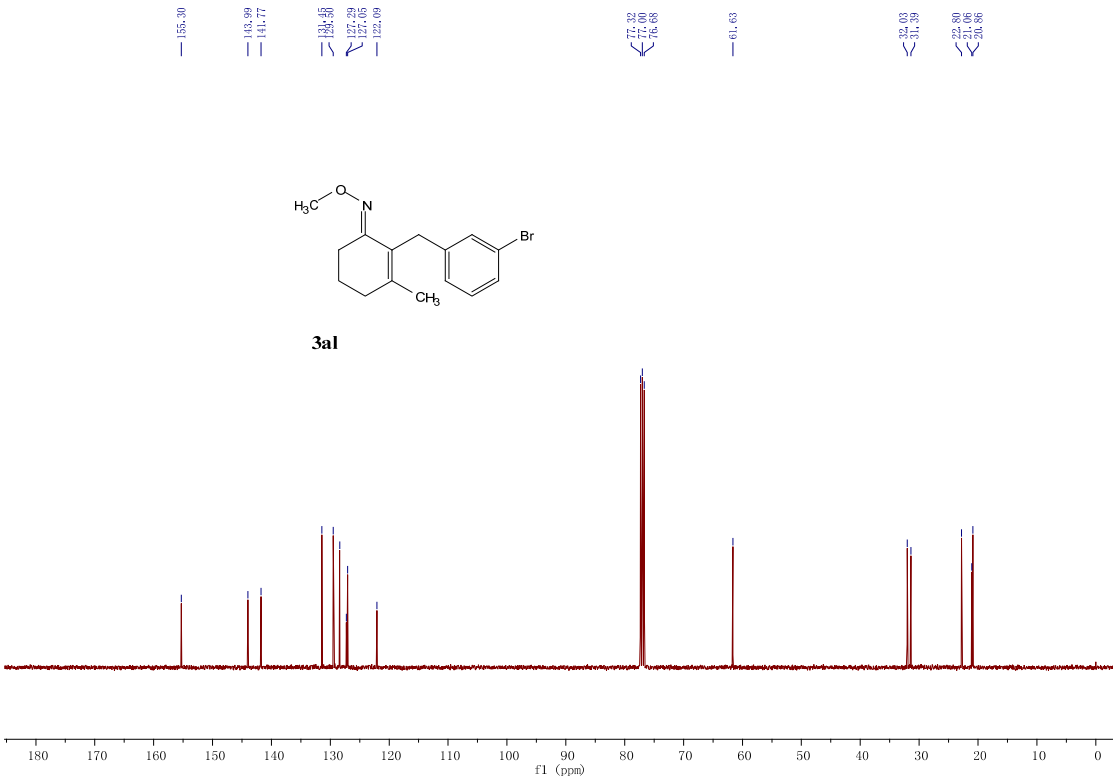
3ak


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

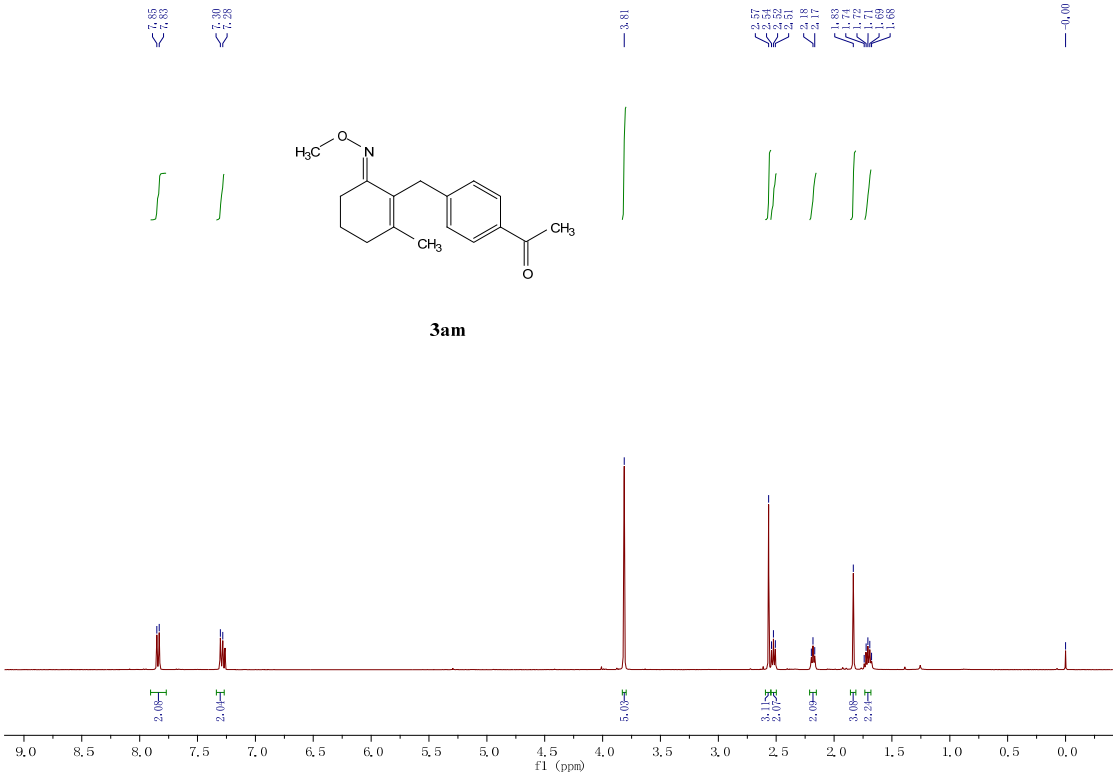

7.36
7.27
7.25
7.25
7.14
7.12
7.11
7.09
7.07
3.83
3.73
2.53
2.52
2.50
2.19
2.17
2.16
1.84
1.73
1.71
1.70
1.68
1.67
0.00
H3C
O
N
Br
CH3

3al

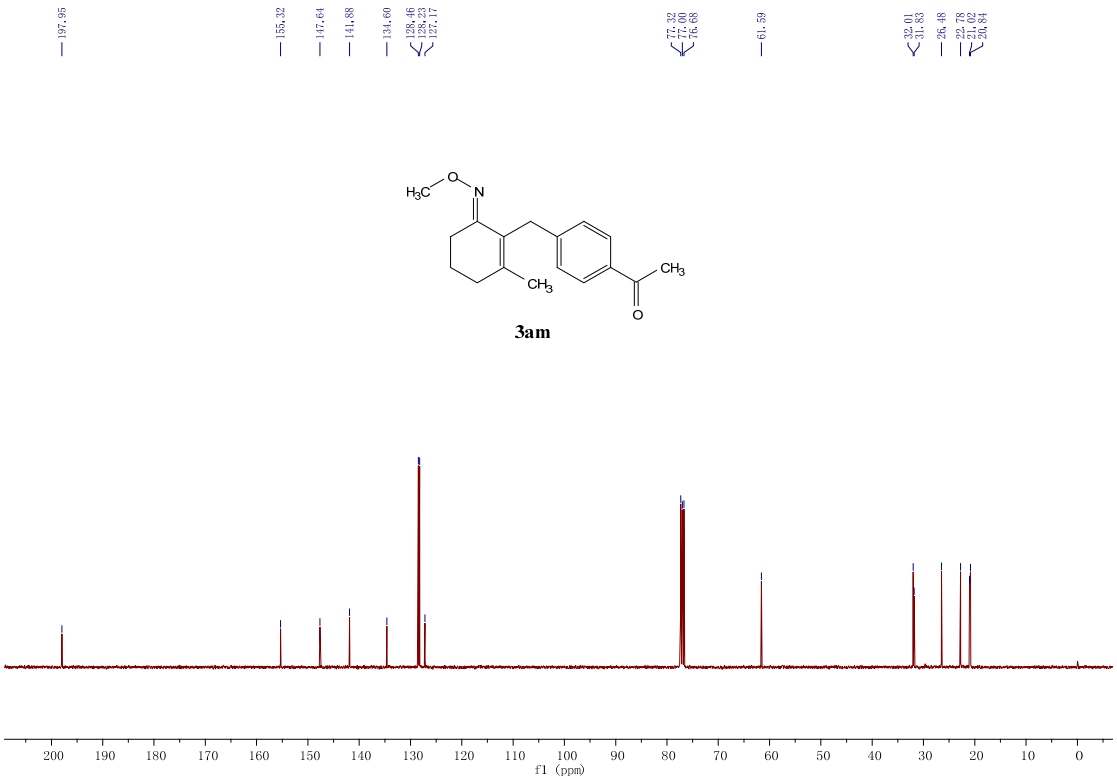

1.00
1.19
2.06
3.00
2.04
2.10
2.06
3.06
2.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


155.30
143.99
141.77
131.45
128.50
127.29
127.05
122.09
77.32
77.00
76.68
61.63
32.03
31.39
22.80
21.06
20.86
O
N
H3C
Br
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

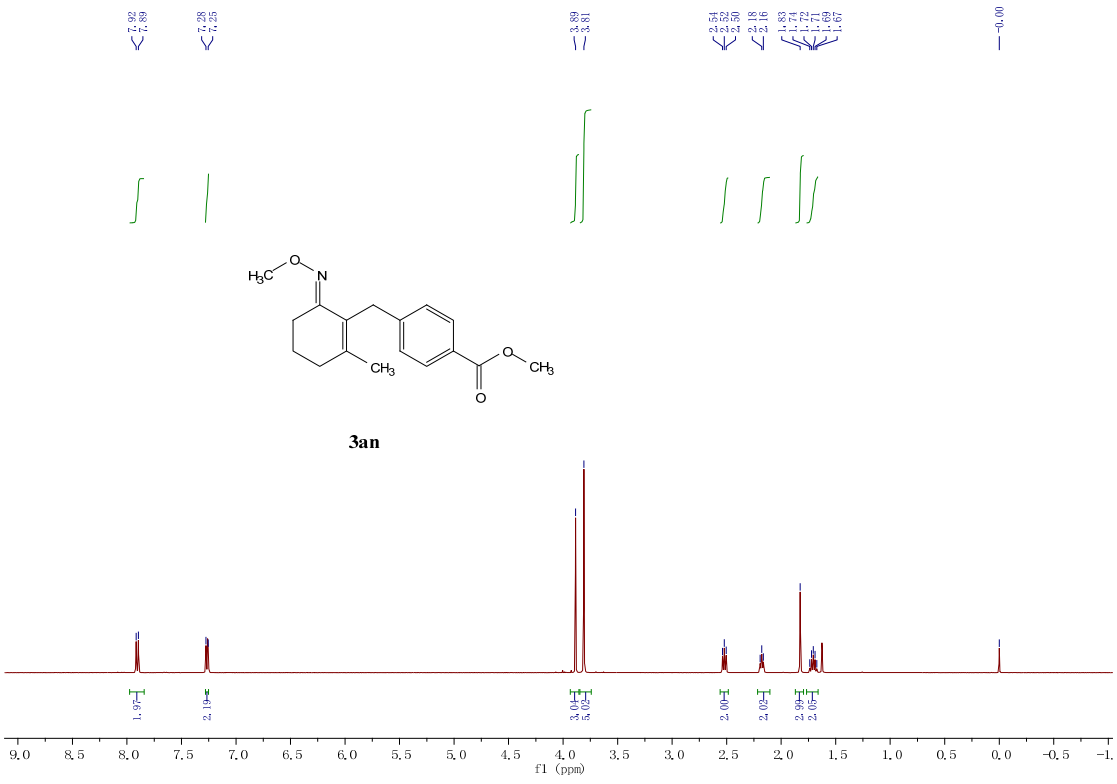
3al


7.85
7.83
7.30
7.28
3.81
2.57
2.54
2.52
2.51
2.18
2.17
1.83
1.74
1.72
1.71
1.69
1.68
0.00
O
N
H3C
CH3
CH3
O
2.08
2.04
5.03
3.11
2.07
2.09
3.09
2.24
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)

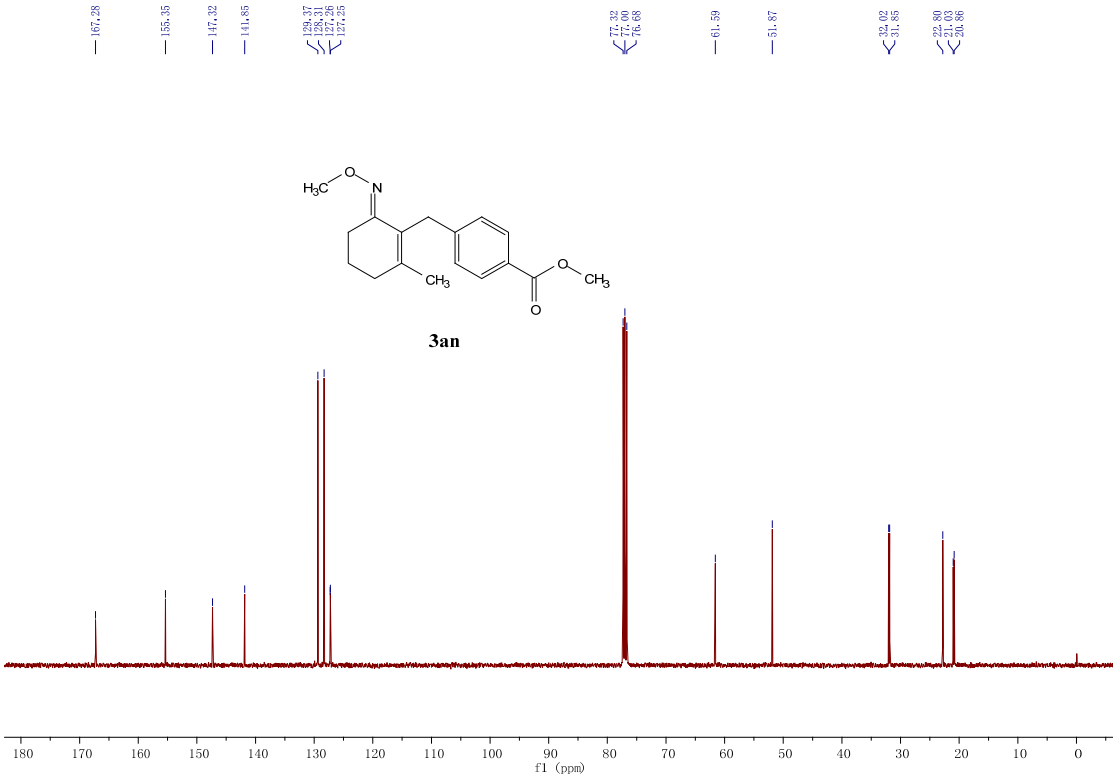
3am


197.95
155.32
147.64
141.88
134.60
128.46
126.23
121.17
77.32
77.00
76.68
61.59
32.01
31.83
26.48
22.78
21.02
20.84
H3C
O
N
CH3
CH3
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

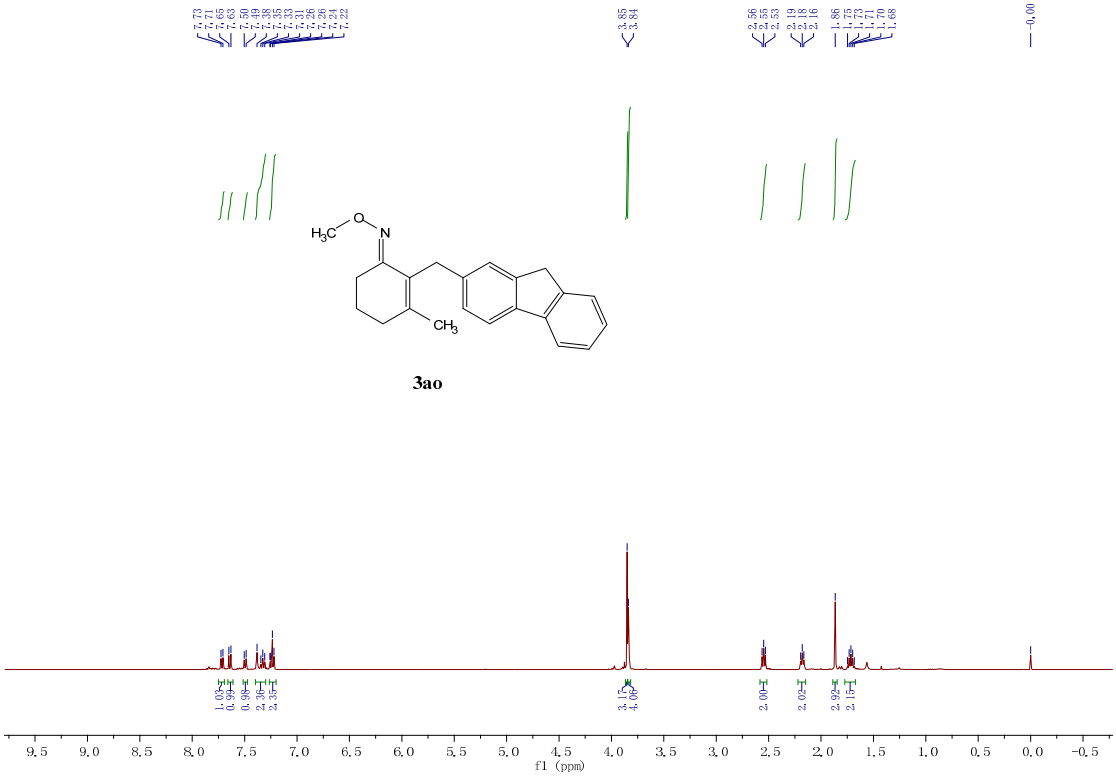
3am


7.92
7.89
7.28
7.25
3.89
3.81
2.54
2.52
2.50
2.18
2.16
1.83
1.74
1.72
1.71
1.69
1.67
0.00
H3C
O
N
CH3
O
CH3
O
1.97
2.19
3.04
5.02
2.00
2.02
2.99
2.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

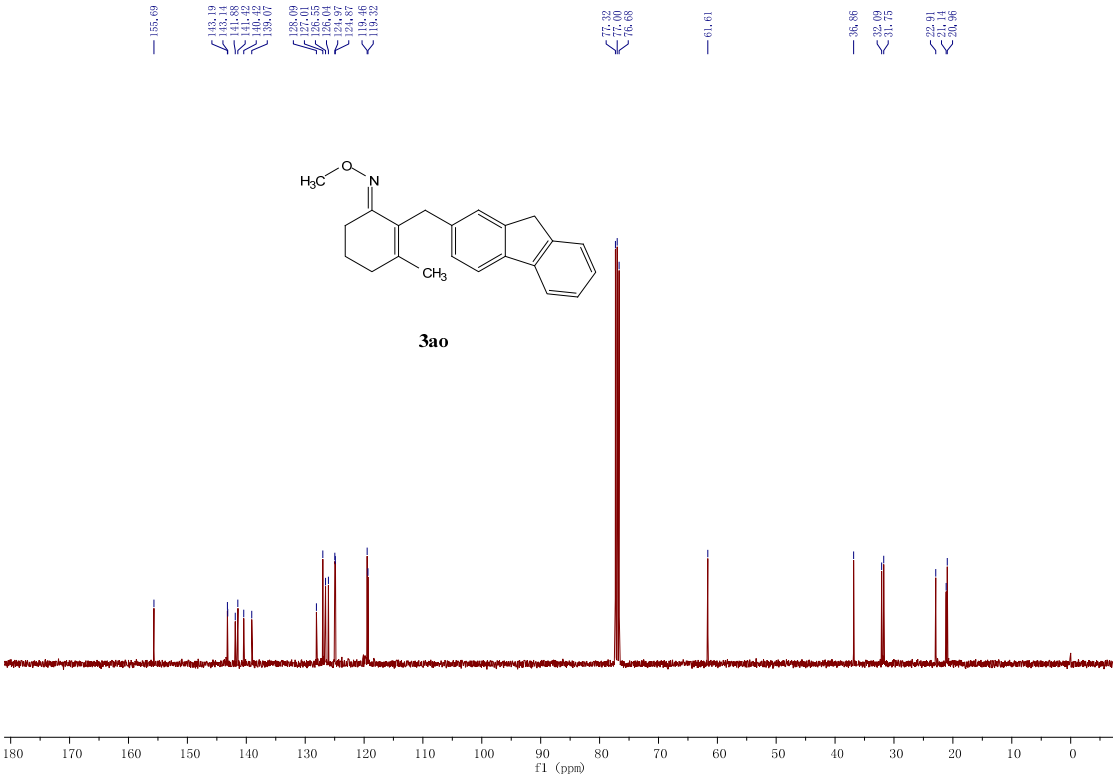
3an


167.28
155.35
147.32
141.85
129.37
128.31
127.26
127.25
77.32
77.00
76.68
61.59
51.87
32.02
31.85
22.80
21.03
20.86
O
N
H3C
CH3
O
CH3
O
f1 (ppm)

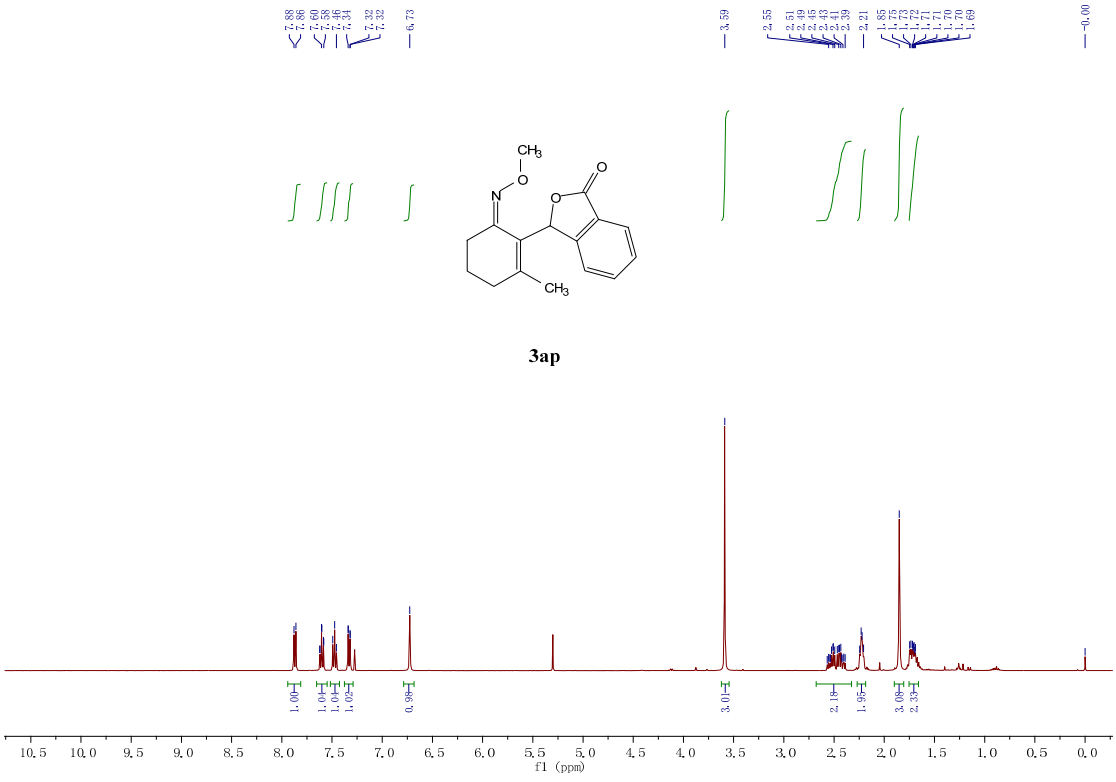
3an


7.73
7.71
7.65
7.63
7.50
7.49
7.38
7.35
7.33
7.31
7.26
7.24
7.22
3.85
3.84
2.56
2.53
2.19
2.18
2.16
1.86
1.75
1.73
1.71
1.70
1.68
-0.00
O
N
H3C
CH3
1.00
0.99
0.98
2.36
2.35
3.17
4.00
2.00
2.02
2.92
2.15
f1 (ppm)

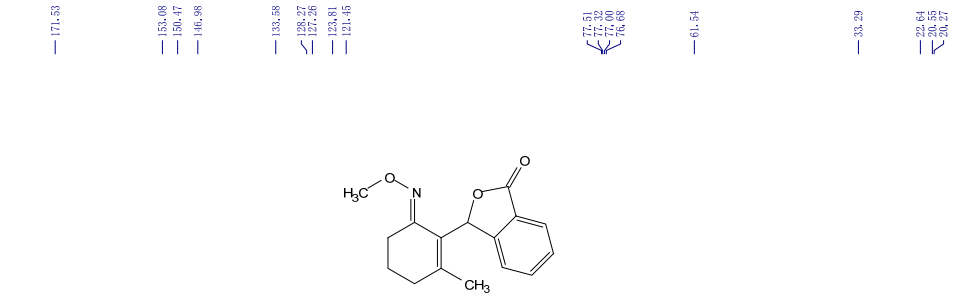
3ao


155.69
143.19
143.14
141.88
141.42
140.42
139.67
128.09
127.01
126.55
126.04
125.67
124.87
119.46
119.32
77.32
77.00
76.68
61.61
36.86
32.09
31.75
23.91
21.14
20.98
H3C
O
N
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

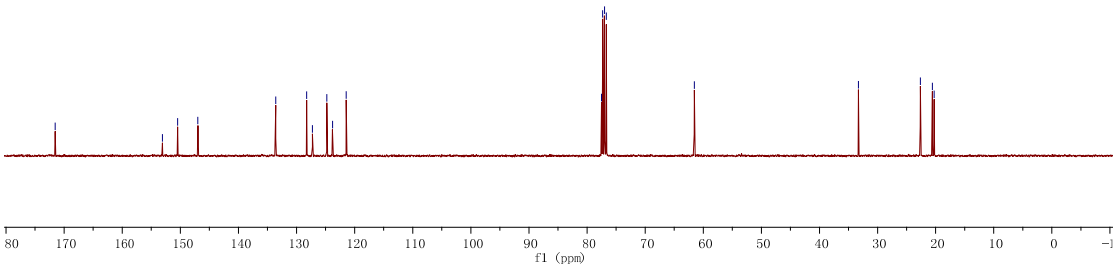
3ao

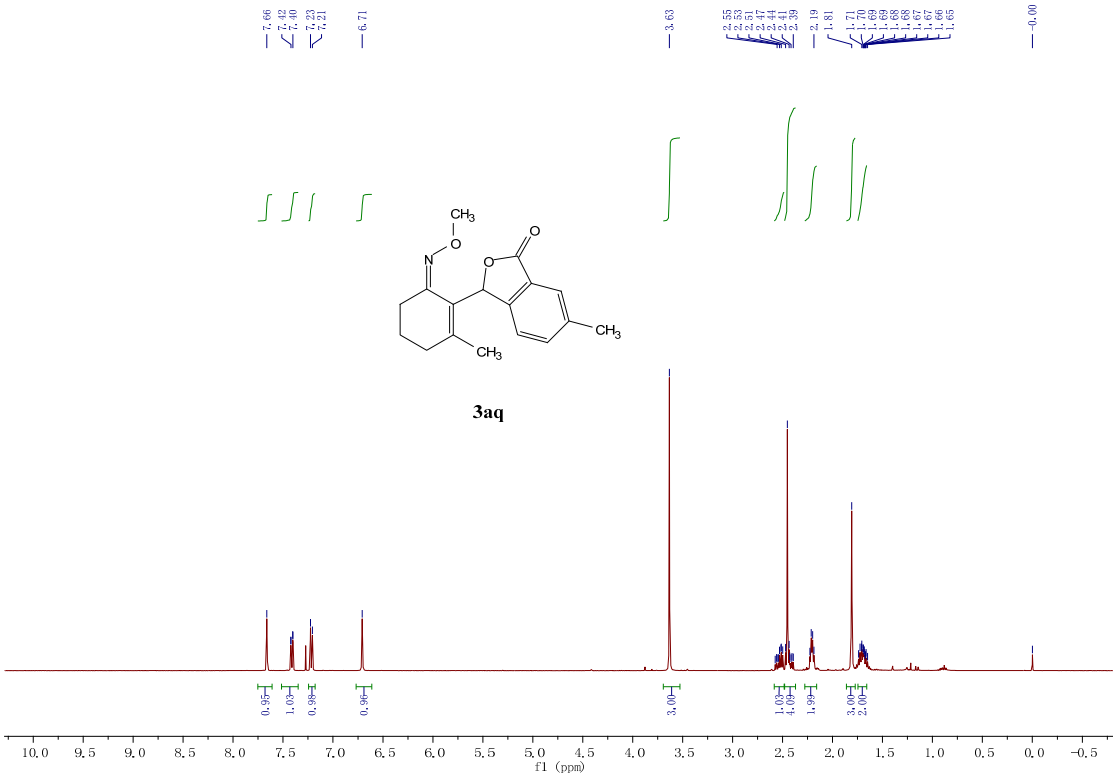

7.88
7.86
7.60
7.58
7.46
7.34
7.32
7.32
6.73
3.59
2.55
2.51
2.49
2.45
2.43
2.41
2.39
2.21
1.85
1.75
1.73
1.72
1.71
1.71
1.70
1.70
1.69
0.00
CH3
O
N
O
O
CH3
1.00
1.04
1.04
1.02
0.98
3.01
2.18
1.95
3.00
2.39
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3ap

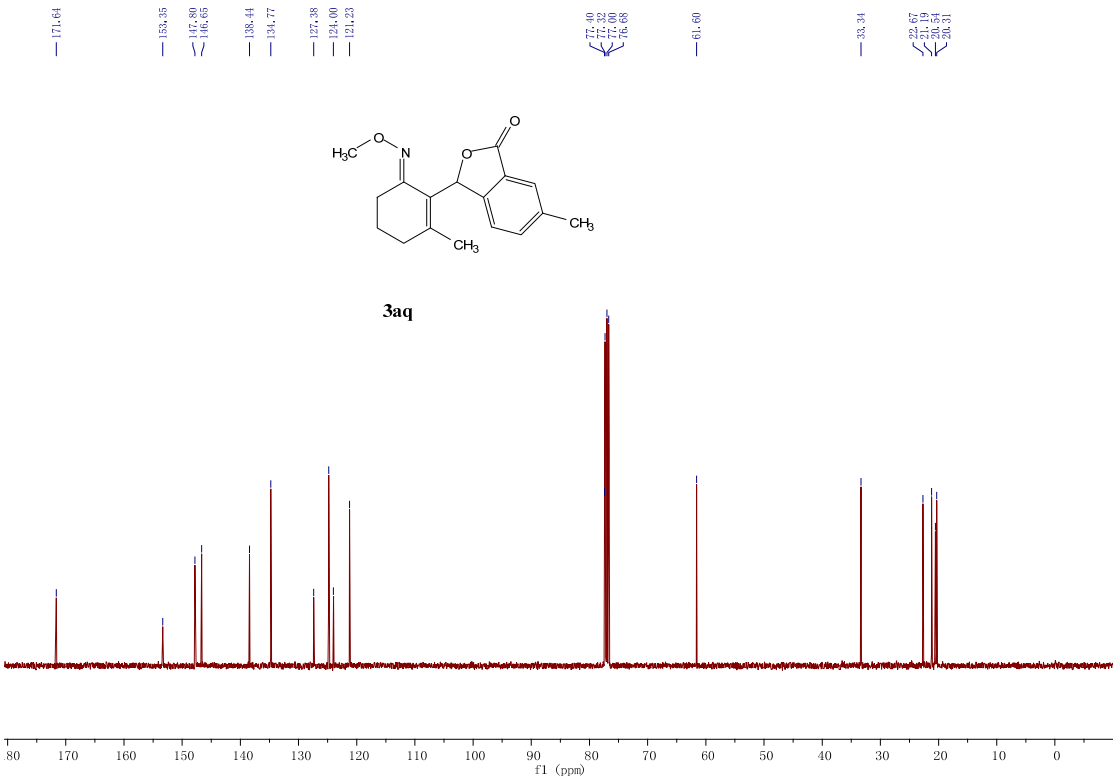


3ap

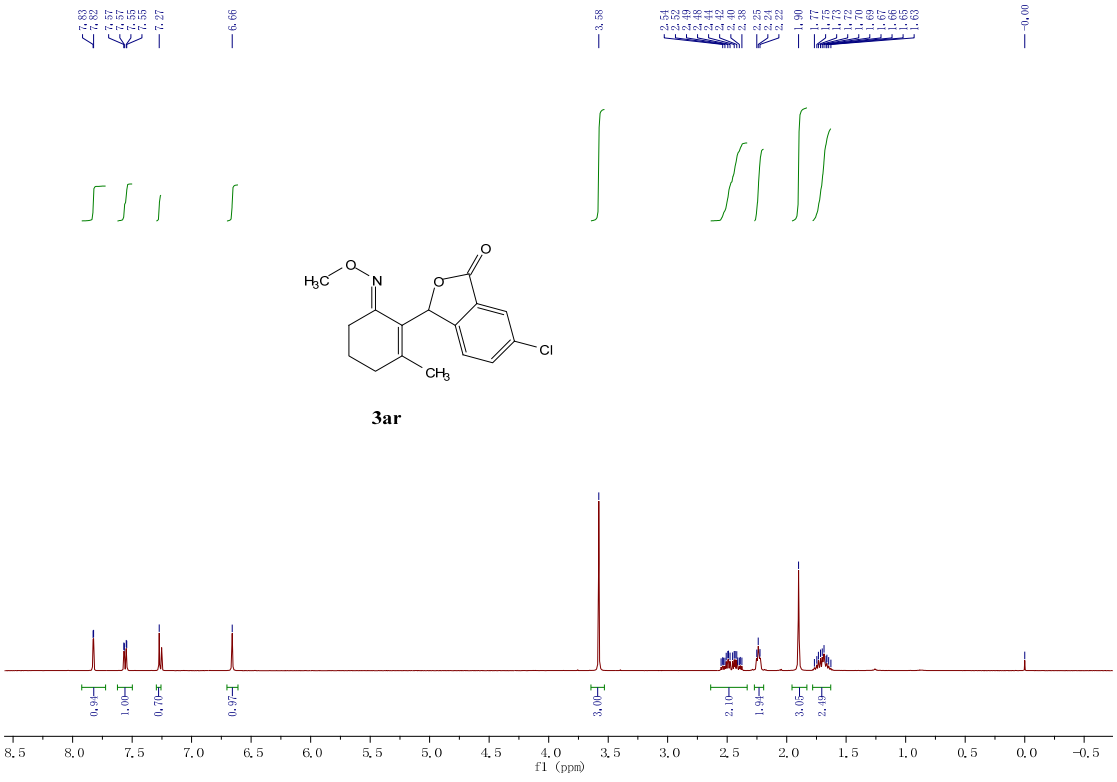




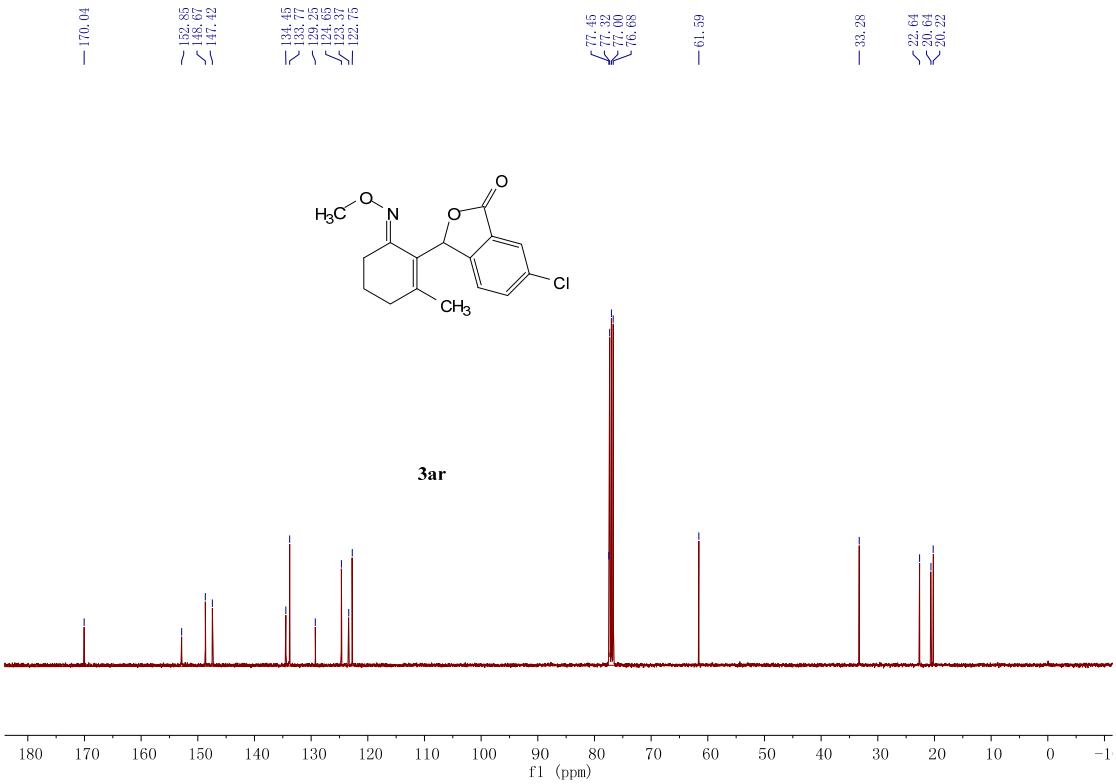
3aq


171.64
153.35
147.80
146.65
138.44
134.77
127.38
124.00
121.23
77.40
77.32
77.00
76.68
61.60
33.34
22.67
21.19
20.54
20.31
H3C
O
N
O
O
CH3
CH3
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

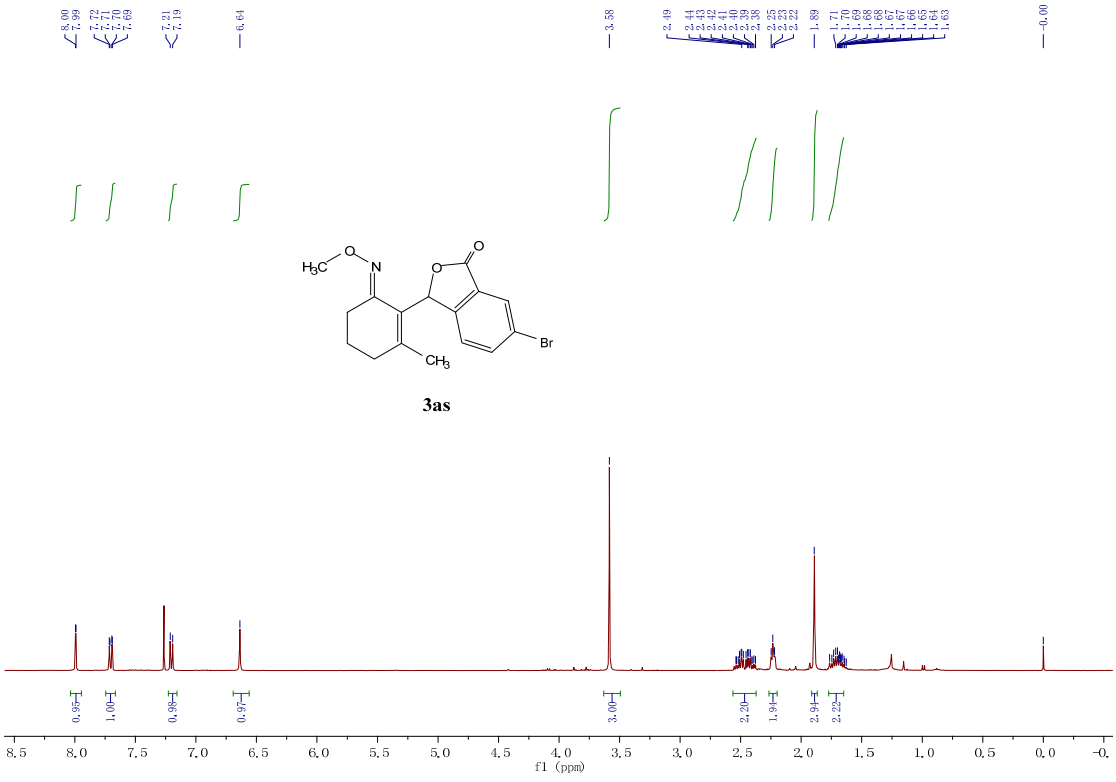
3aq


7.83
7.82
7.57
7.57
7.55
7.55
7.27
6.66
3.58
2.54
2.52
2.49
2.48
2.44
2.42
2.40
2.38
2.25
2.24
2.22
1.90
1.77
1.75
1.73
1.72
1.70
1.69
1.67
1.66
1.65
1.63
0.00
H3C
O
N
O
O
Cl
CH3
0.94
1.00
0.70
0.97
3.00
2.10
1.94
3.05
2.49
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

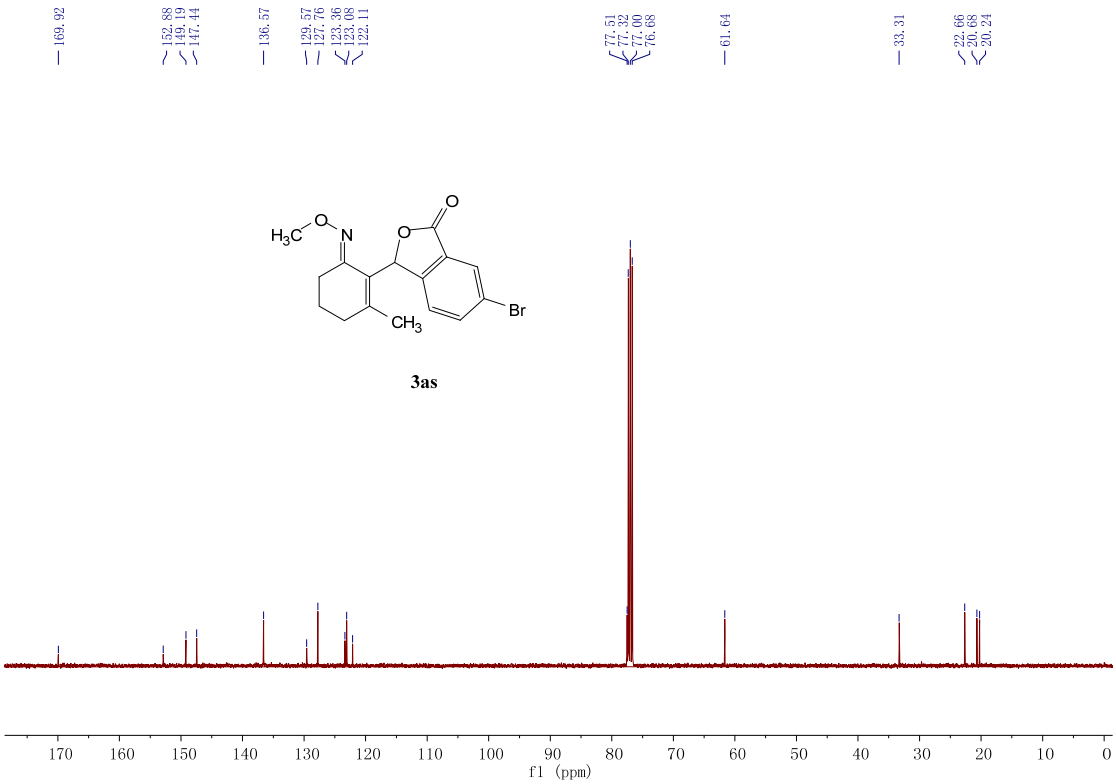
3ar


170.04
152.85
148.67
147.42
134.45
133.77
129.25
124.65
123.37
122.75
77.45
77.32
77.00
76.68
61.59
33.28
22.64
20.64
20.22
O
H3C
O
N
O
Cl
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

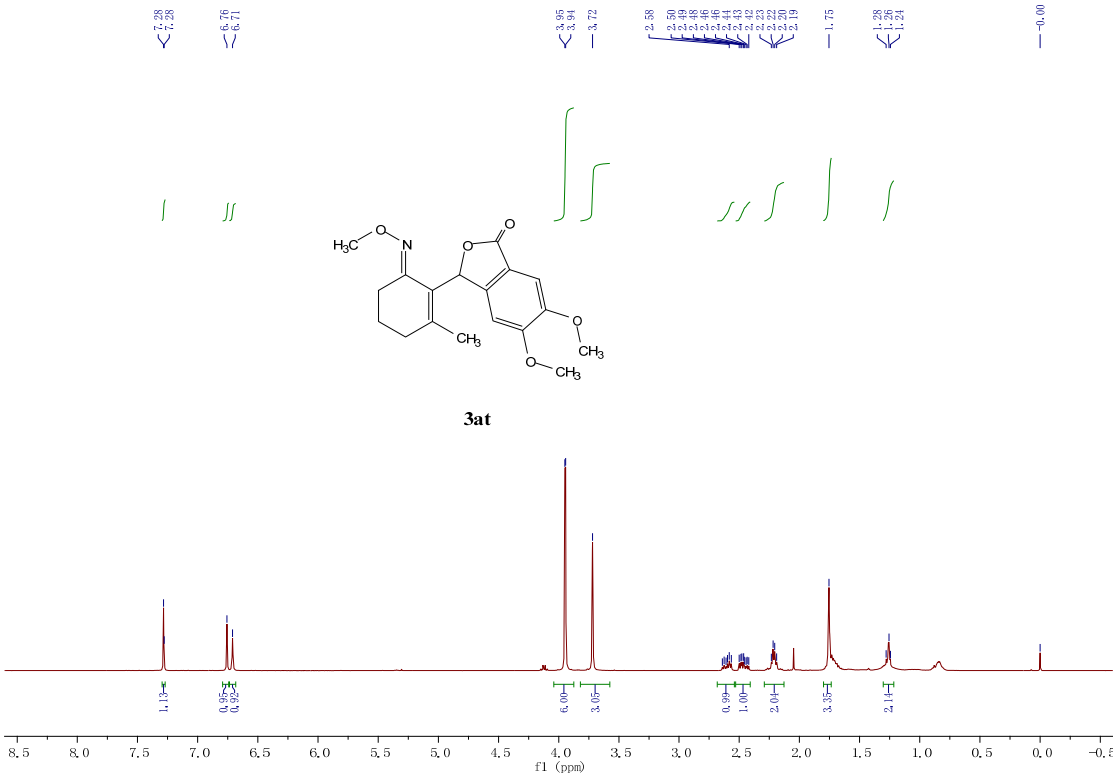
3ar


8.00
7.99
7.72
7.71
7.70
7.69
7.21
7.19
6.64
3.58
2.49
2.44
2.43
2.42
2.41
2.40
2.39
2.38
2.25
2.23
2.22
1.89
1.71
1.70
1.69
1.68
1.68
1.67
1.67
1.66
1.65
1.64
1.63
0.00
H3C
O
N
O
O
Br
CH3
0.95
1.00
0.98
0.97
3.00
2.20
1.94
2.94
2.22
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)

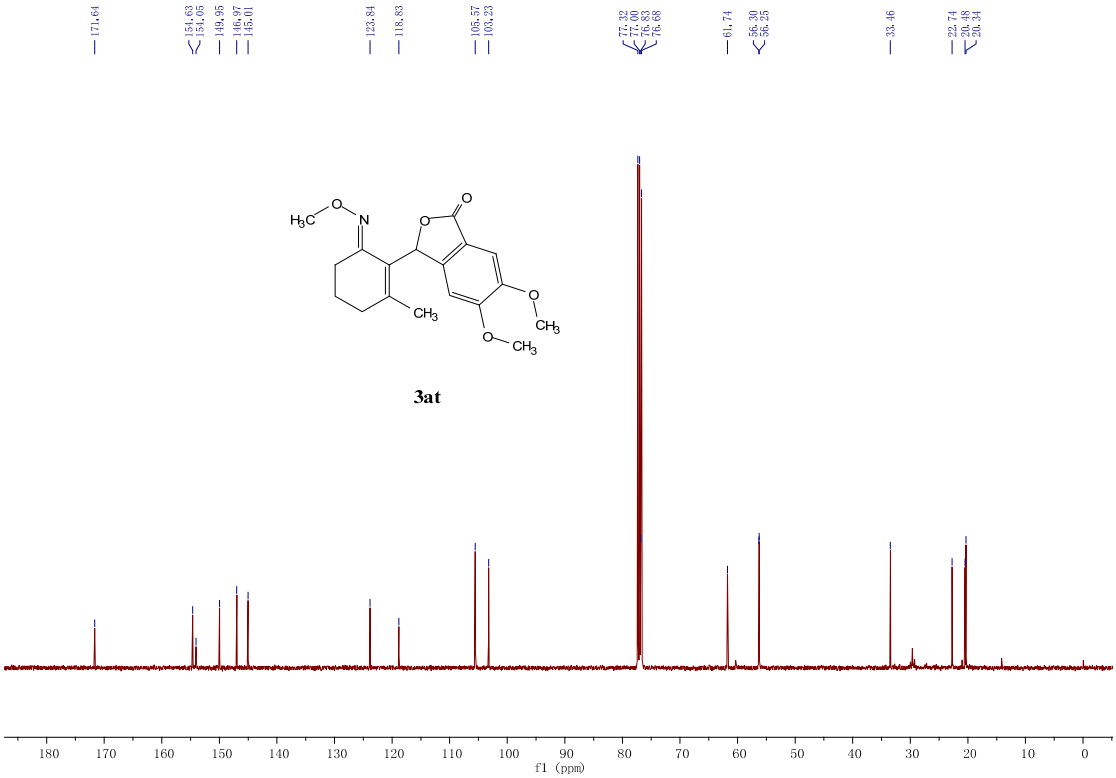
3as


169.92
152.88
149.19
147.44
136.57
129.57
127.76
123.36
123.08
122.11
77.51
77.32
77.00
76.68
61.64
33.31
22.66
20.68
20.24
O
H3C
O
N
O
Br
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

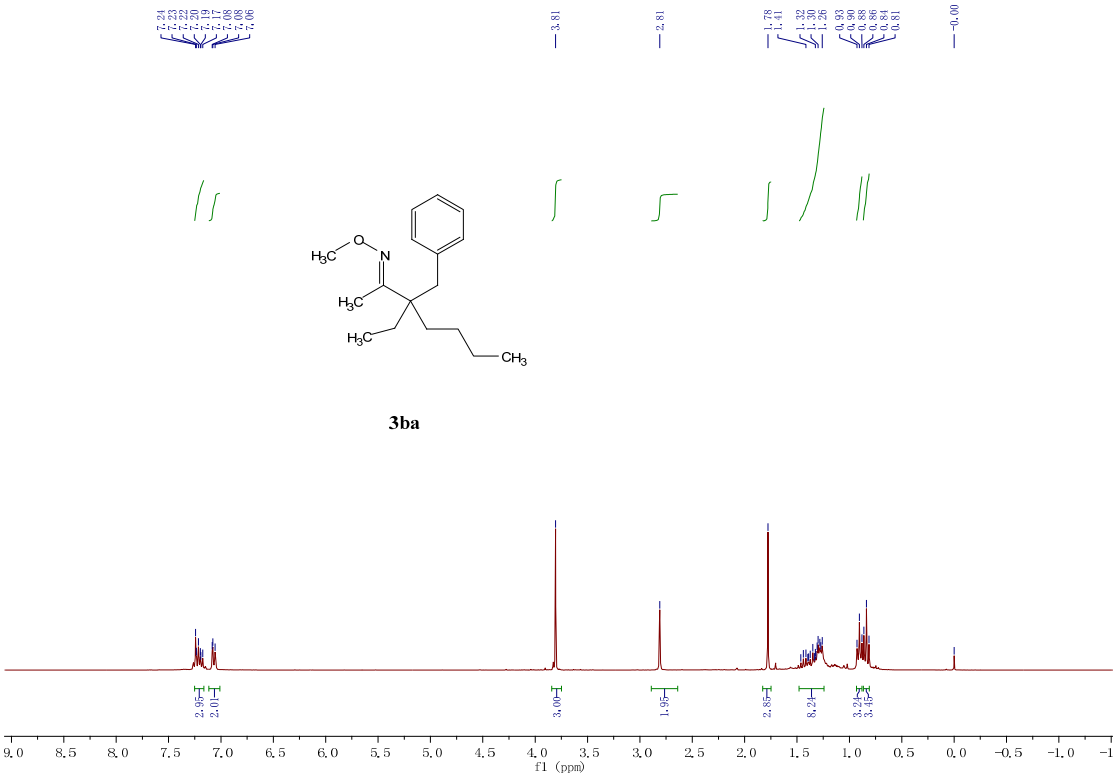
3as


7.28
7.26
6.76
6.71
3.95
3.94
3.72
2.58
2.50
2.49
2.48
2.46
2.44
2.43
2.42
2.23
2.22
2.20
2.19
1.75
1.28
1.26
1.24
0.00
H3C
O
N
O
O
CH3
O
CH3
O
CH3
1.13
0.95
0.92
6.00
3.05
0.99
1.00
2.04
3.35
2.14
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)

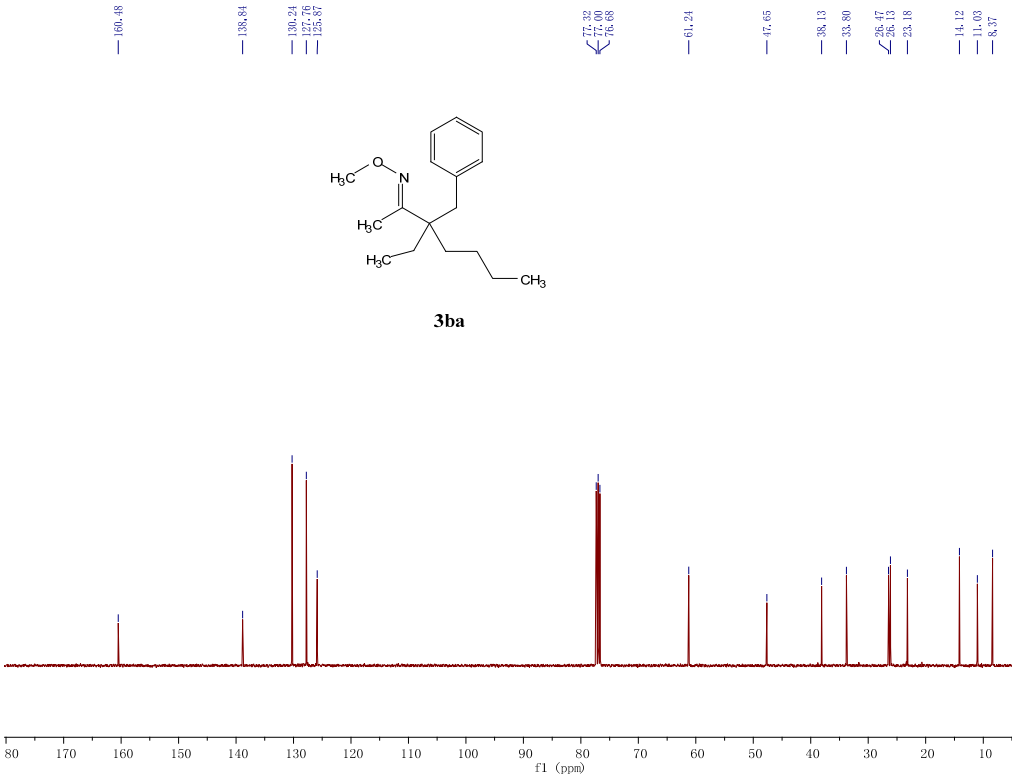
3at


171.64
154.63
154.05
149.95
146.97
145.01
123.84
118.83
105.57
103.23
77.32
77.00
76.83
76.68
61.74
56.30
56.25
33.46
22.74
20.48
20.34
O
N
O
O
CH3
O
CH3
O
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

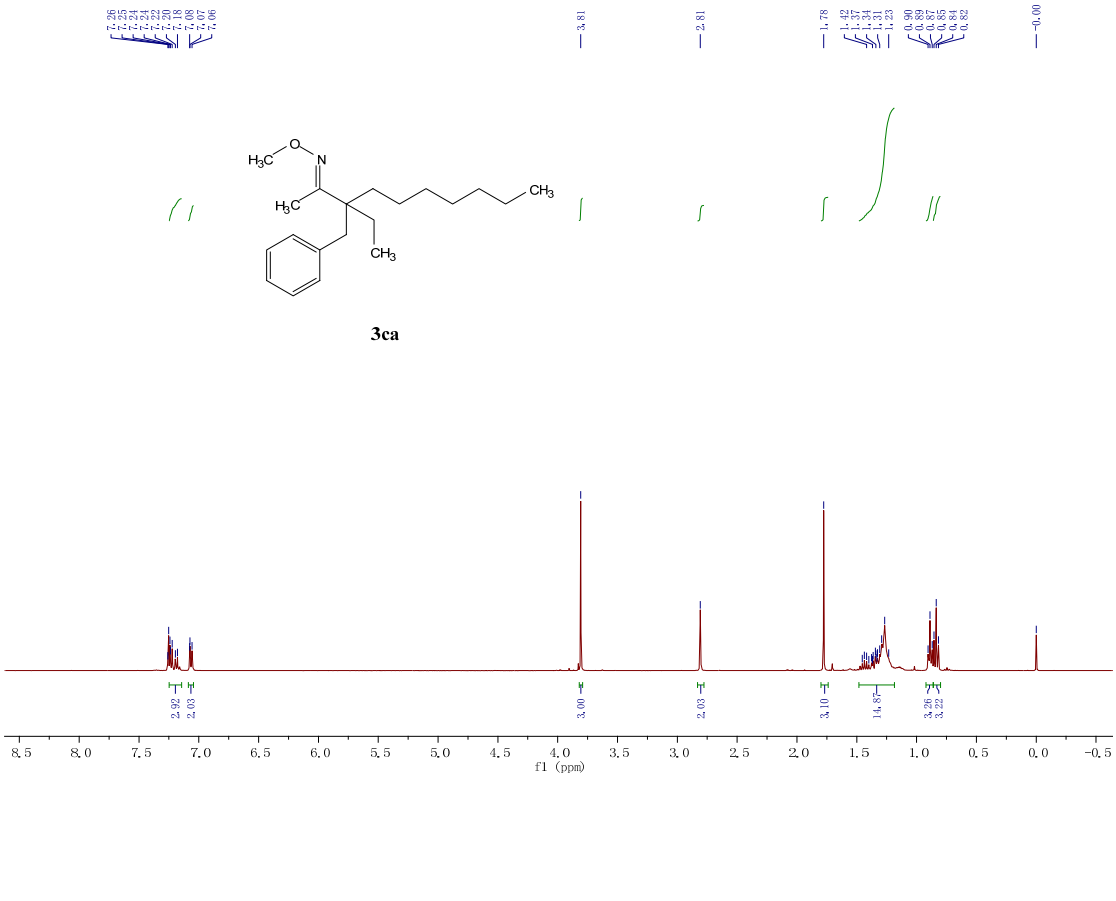
3at


7.24
7.23
7.22
7.20
7.19
7.17
7.08
7.06
3.81
2.81
1.78
1.41
1.32
1.30
1.26
0.93
0.90
0.88
0.86
0.84
0.81
0.00
O
N
H3C
H3C
H3C
CH3
2.95
2.01
3.00
1.95
2.85
8.24
3.24
3.48
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
f1 (ppm)

3ba

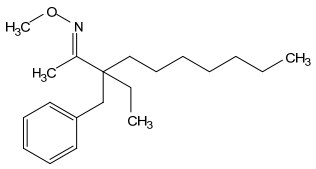

160.48
138.84
130.24
127.76
125.87
77.32
77.00
76.68
61.24
47.65
38.13
33.80
26.47
26.13
23.18
14.12
11.03
8.37
O
N
H3C
H3C
H3C
CH3
f1 (ppm)

3ba

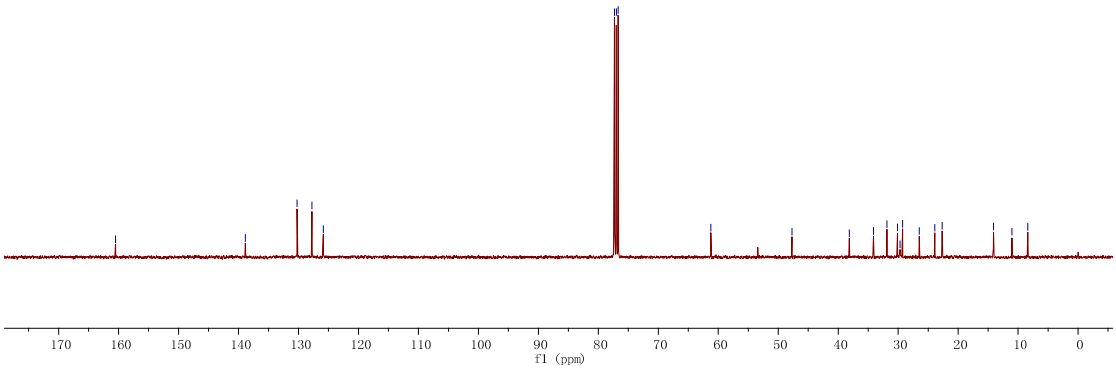

7.26
7.25
7.24
7.23
7.22
7.20
7.18
7.08
7.07
7.06
3.81
2.81
1.78
1.42
1.37
1.34
1.31
1.23
0.90
0.89
0.87
0.85
0.84
0.82
0.00
O
N
H3C
H3C
CH3
CH3
2.92
2.03
3.00
2.03
3.10
14.87
3.26
3.22
f1 (ppm)

3ca

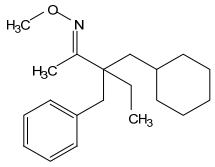

160.51
138.85
130.24
127.76
125.87
77.32
77.00
76.68
61.25
47.69
38.15
34.11
30.11
29.26
26.49
23.90
22.66
14.11
11.04
8.38


H3C
O
N
H3C
CH3
CH3

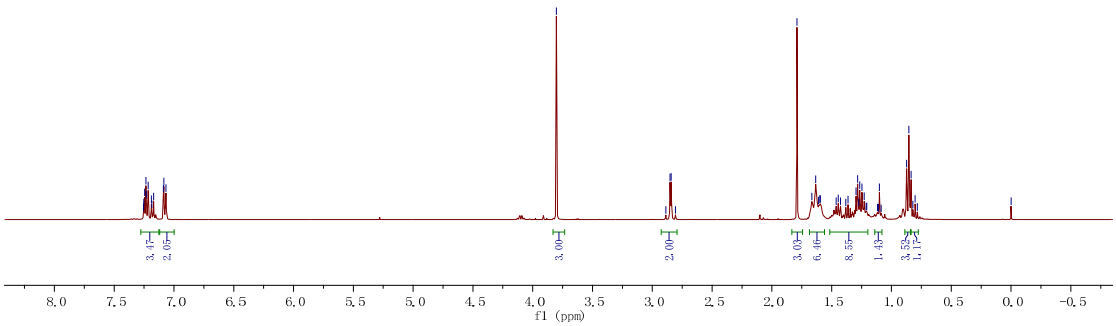
3ca

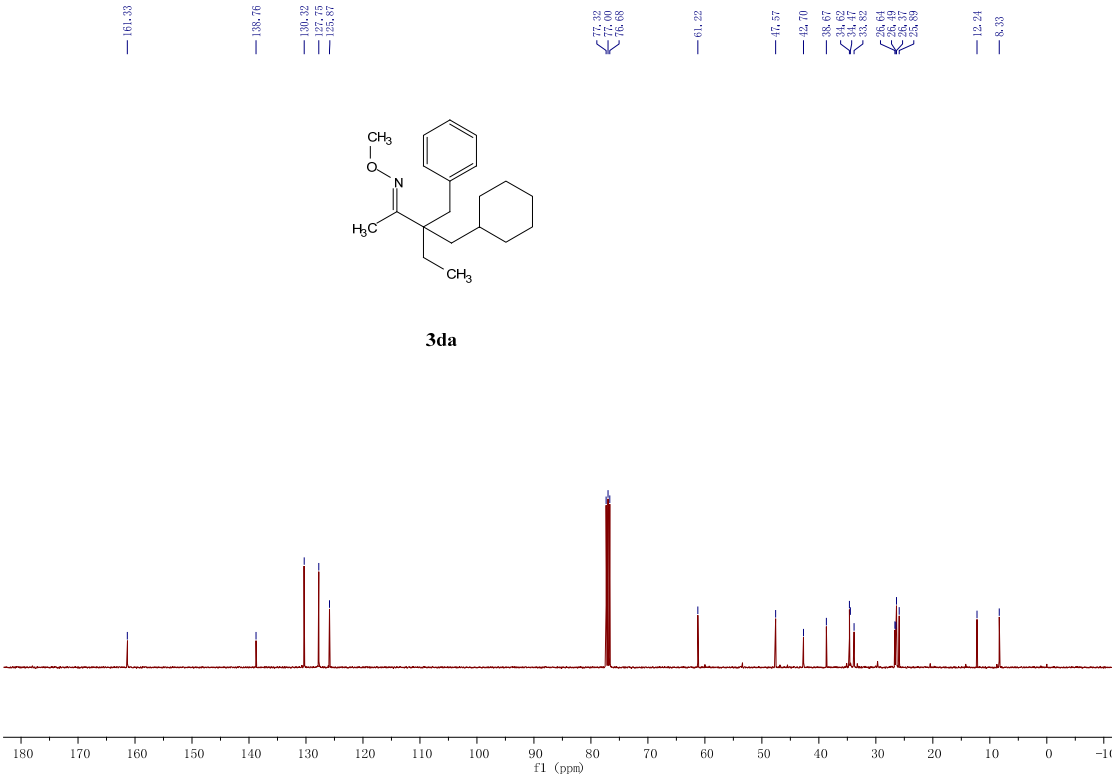

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.25
7.25
7.24
7.23
7.23
7.22
7.19
7.17
7.09
7.08
7.07
3.80
2.89
2.85
2.84
2.81
1.79
1.60
1.44
1.27
1.23
1.12
1.05
0.87
0.85
0.84
0.82
0.80
0.78
-0.00

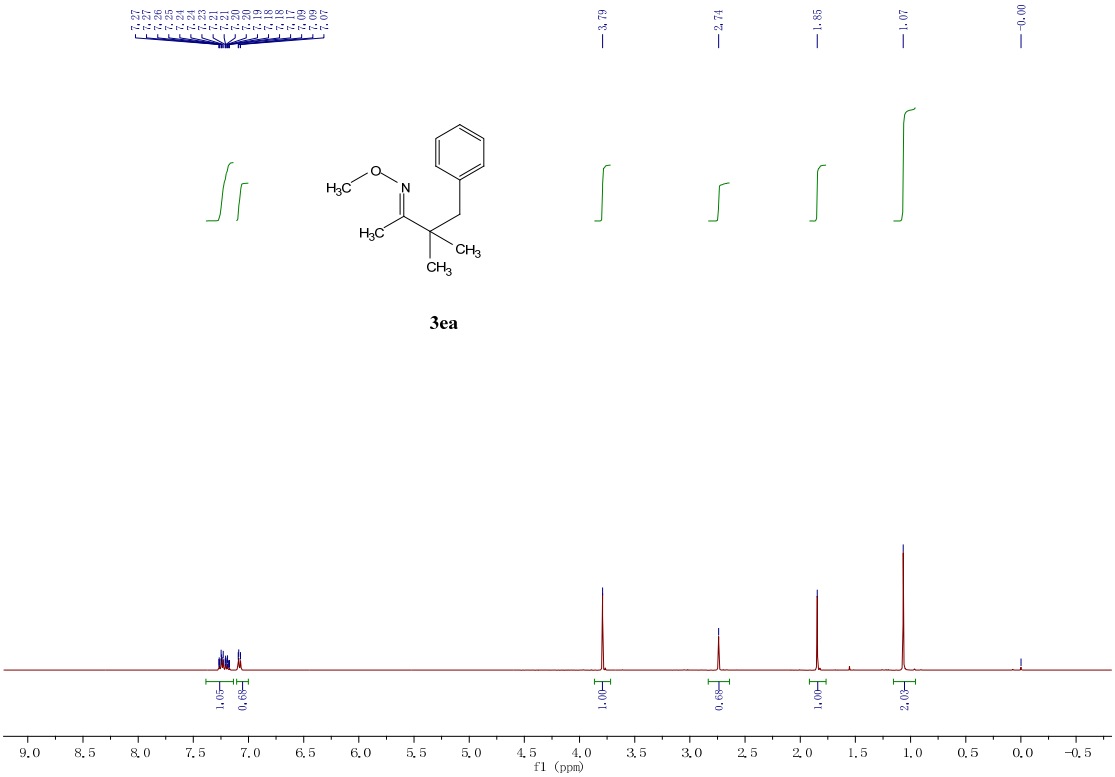

H3C
O
N
H3C
CH3

3da

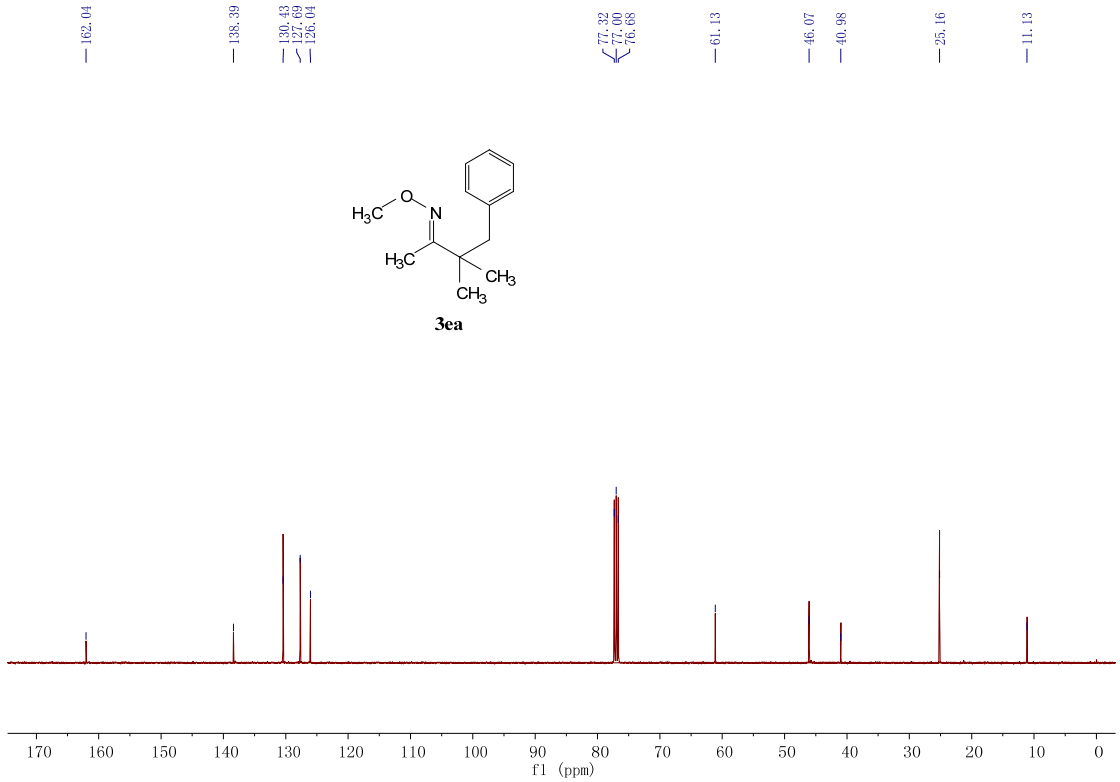

3.47
2.05
3.00
2.00
3.03
6.40
8.55
1.40
3.52
1.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

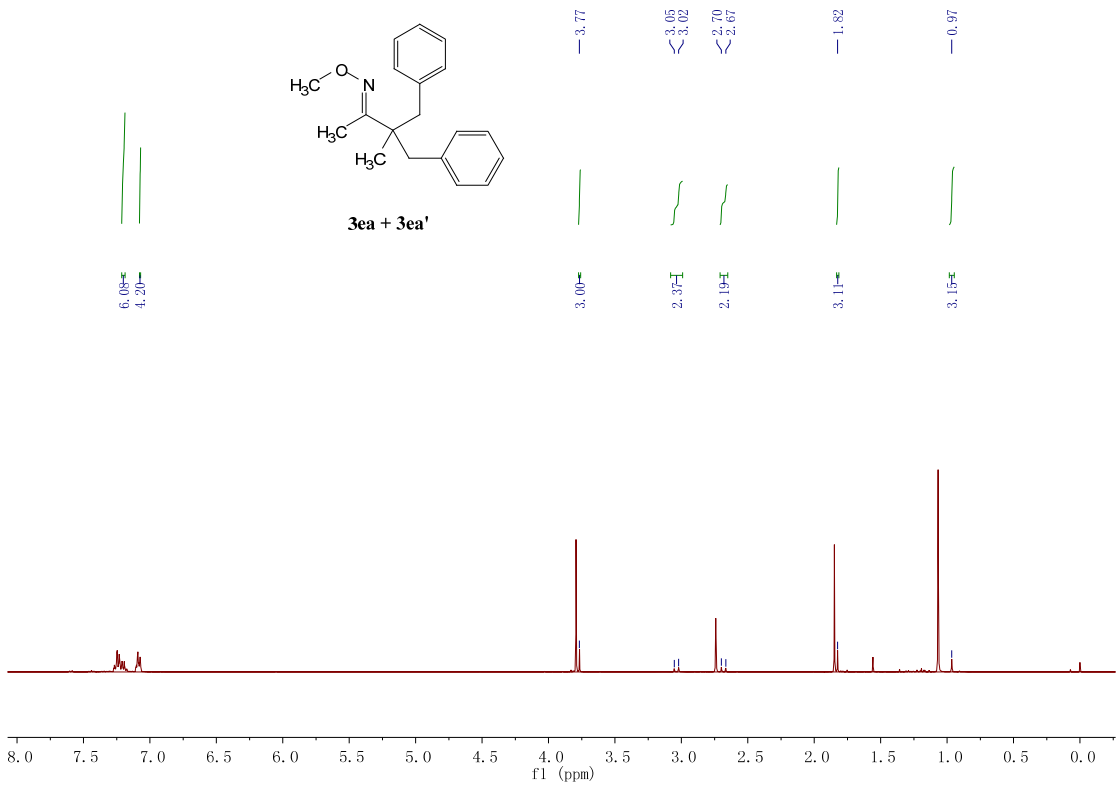

161.33
138.76
130.32
127.75
125.87
77.32
77.00
76.68
61.22
47.57
42.70
38.67
34.62
34.47
33.82
26.64
26.49
26.37
25.89
12.24
8.33
CH3
O
N
H3C
CH3
f1 (ppm)

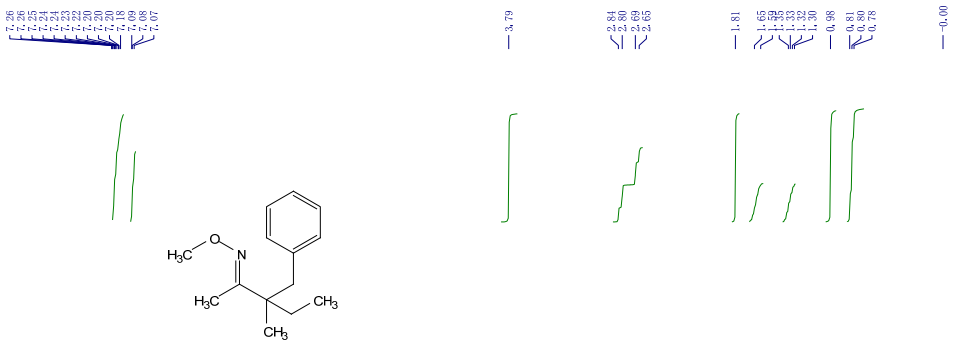
3da


7.27
7.27
7.26
7.25
7.24
7.24
7.23
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.09
7.09
7.07
3.79
2.74
1.85
1.07
0.00
H3C
O
N
H3C
CH3
CH3
1.05
0.68
1.00
0.68
1.00
2.03
f1 (ppm)

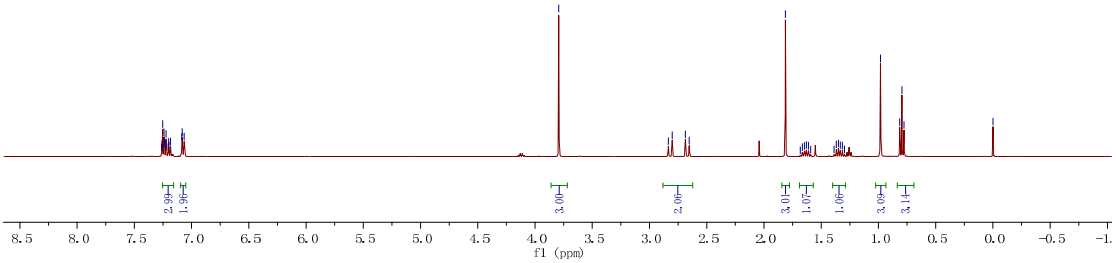
3ea

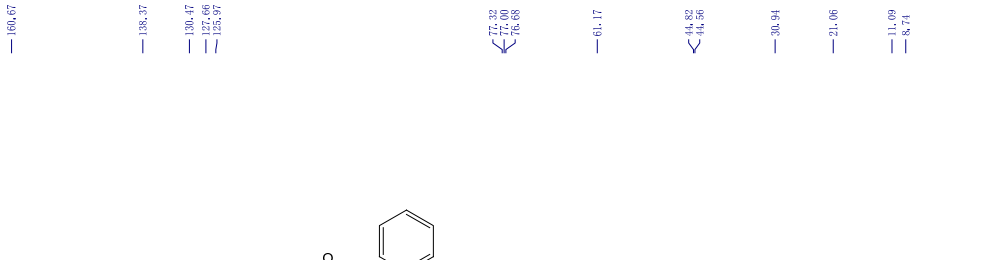

162.04
138.39
130.43
127.69
126.04
77.32
77.00
76.68
61.13
46.07
40.98
25.16
11.13
H3C
O
N
H3C
CH3
CH3
3ea
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

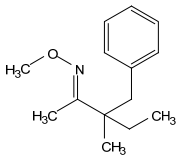

3.77
3.05
3.02
2.70
2.67
1.82
0.97
H3C
O
N
H3C
H3C
3ea + 3ea'
6.08
4.20
3.00
2.37
2.19
3.11
3.15
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



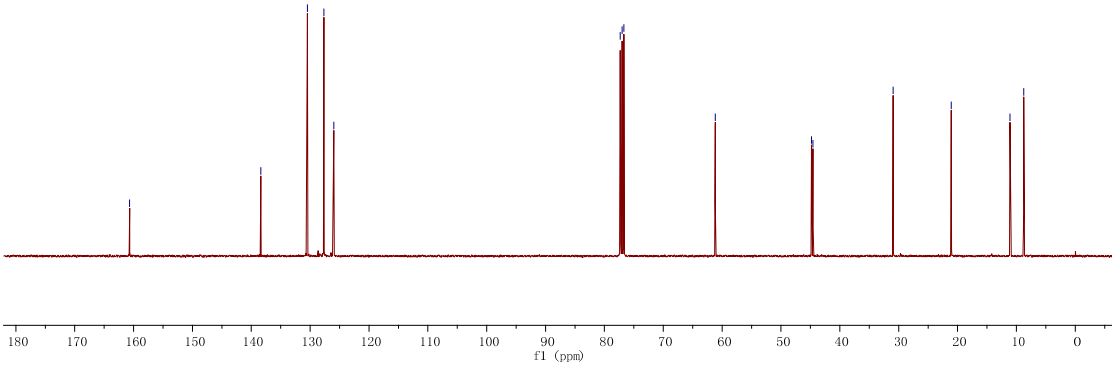
3fa

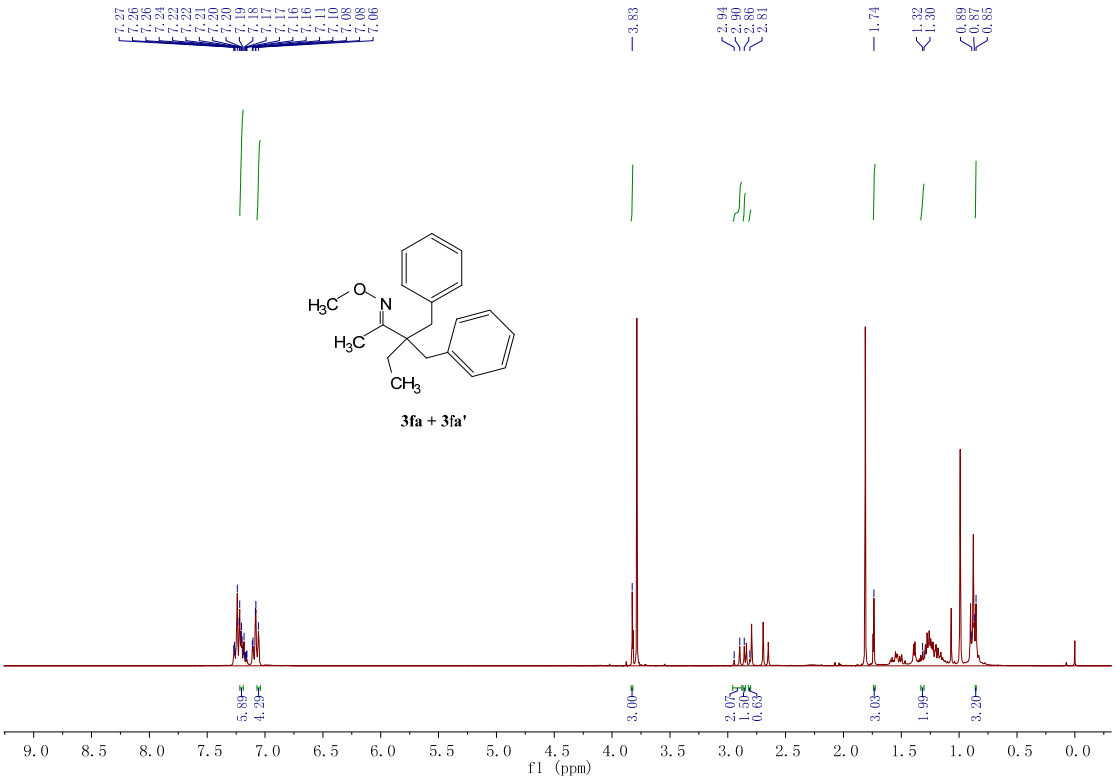


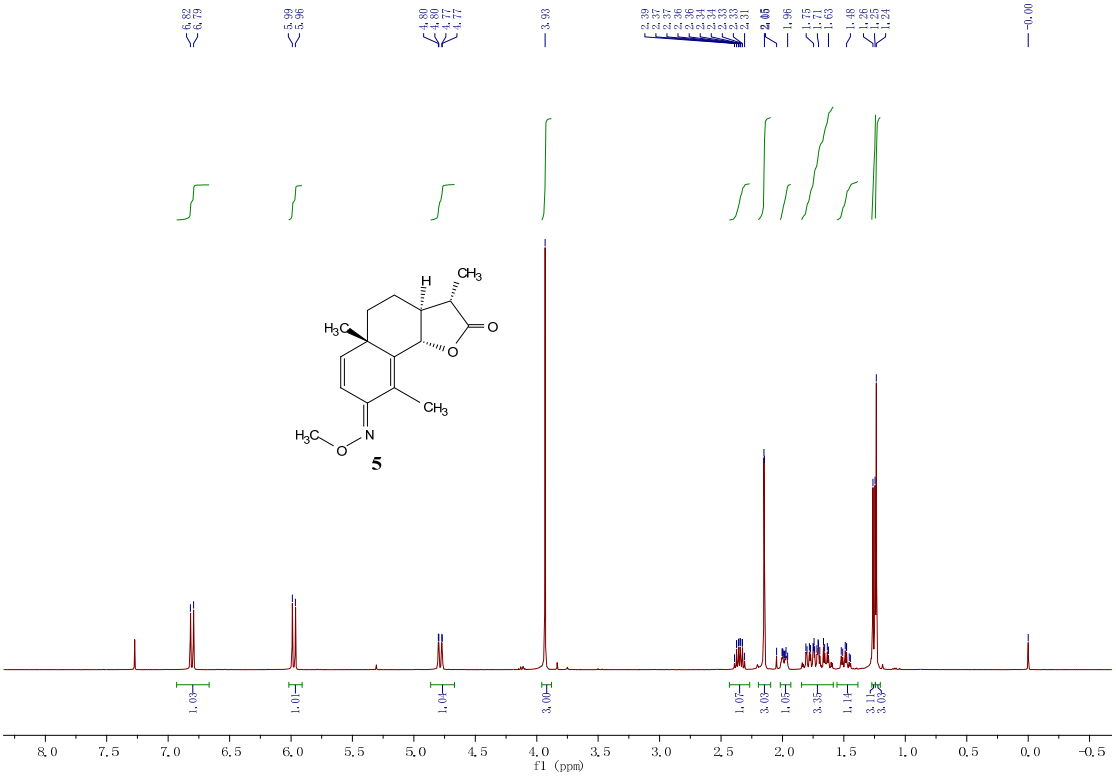


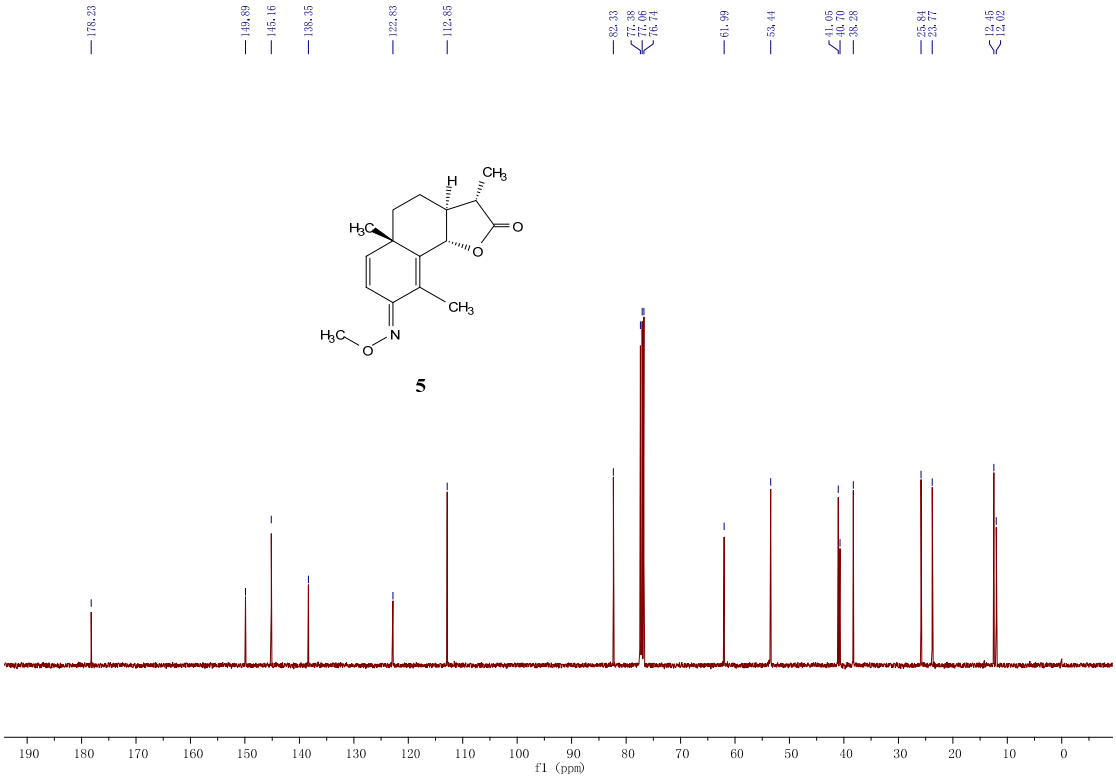


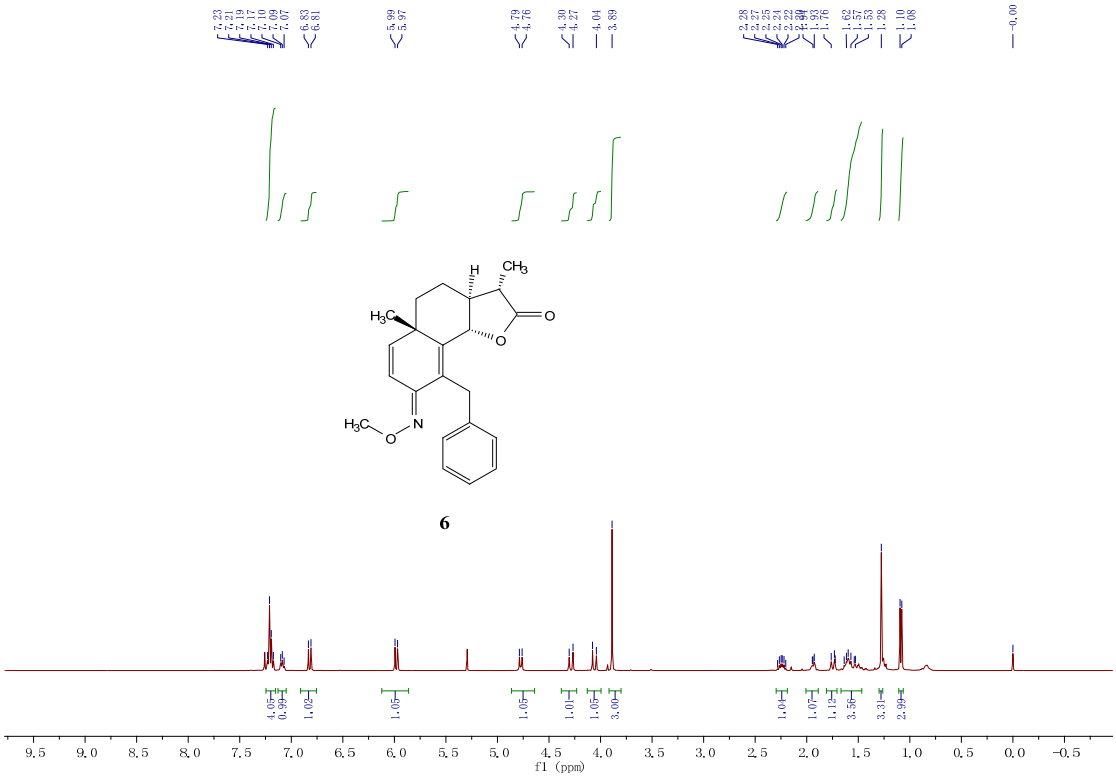
3fa'

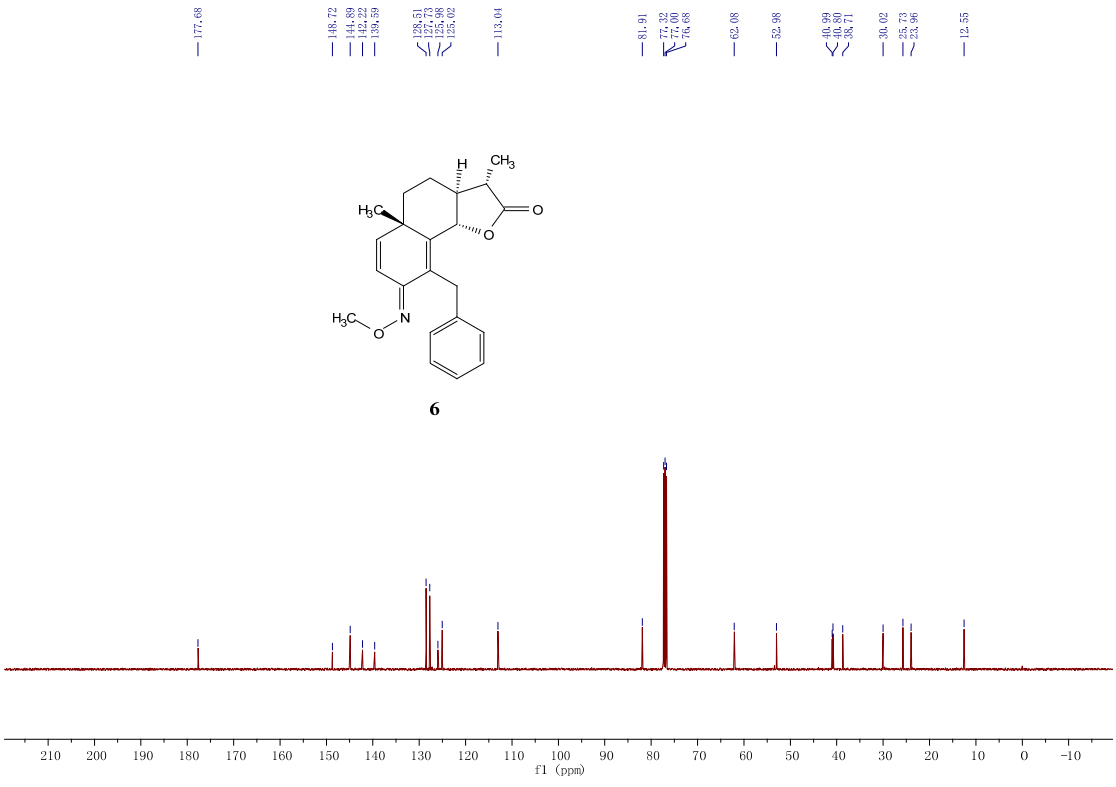



7.27
7.26
7.26
7.24
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.17
7.16
7.16
7.11
7.10
7.08
7.08
7.06
3.83
2.94
2.90
2.86
2.81
1.74
1.32
1.30
0.89
0.87
0.85
H3C
O
N
H3C
CH3
3fa + 3fa'
5.89
4.29
3.00
2.07
1.50
0.63
3.03
1.99
3.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


6.82
6.79
5.99
5.96
4.80
4.80
4.77
4.77
3.93
2.39
2.37
2.36
2.36
2.34
2.33
2.33
2.31
1.96
1.75
1.71
1.63
1.48
1.26
1.25
1.24
-0.00
H
CH3
H3C
O
O
CH3
H3C
O
N
5
1.09
1.01
1.04
3.00
1.07
3.03
1.05
3.35
1.14
3.13
3.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


178.23
149.89
146.16
138.35
122.83
112.85
82.33
77.38
77.06
76.74
61.99
53.44
41.05
40.70
38.28
25.84
23.77
12.45
12.02
H
CH3
H3C
O
O
CH3
H3C
O
N
5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.23
7.21
7.19
7.17
7.10
7.09
7.07
6.83
6.81
5.99
5.97
4.79
4.76
4.30
4.27
4.04
3.89
2.38
2.27
2.25
2.24
2.22
1.76
1.62
1.57
1.53
1.28
1.10
1.08
0.00
H
CH3
H3C
O
O
H3C
O
N
6
4.05
0.99
1.02
1.05
1.05
1.01
1.05
3.00
1.04
1.07
1.12
3.56
3.31
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


177.68
148.72
144.89
142.22
139.59
128.51
127.73
125.98
125.02
113.04
81.91
77.32
77.00
76.68
62.08
52.98
40.99
40.80
38.71
30.02
25.73
23.96
12.55
H
CH3
H3C
O
O
H3C
O
N
6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Characterization of organic palladium complex 1e'