Supporting Information

Synthesis of *N*-alkoxy amines and hydroxylamines via the iridium-catalyzed transfer hydrogenation of oximes

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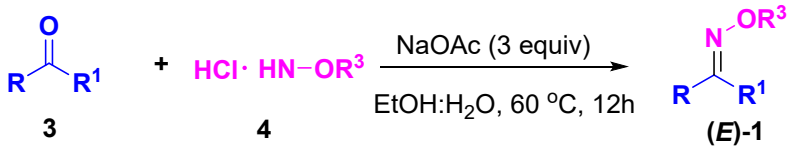
List of Contents

A. Experimental section

General Methods: ^{1}H and ^{13}C NMR spectra were recorded by using a Bruker ADVANCE-400 spectrometer (400 MHz for ^{1}H; 100 MHz for ^{13}C), using $CDCl_3$ as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Chemical shifts (δ) are reported in ppm and quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (7.26 ppm for ^{1}H) or TMS (0 ppm for ^{1}H) and $CDCl_3$ (77.0 ppm for ^{13}C). Data are reported as follows: Chemical shift (number of protons, multiplicity, coupling constants). Coupling constants were quoted to the nearest 0.1 Hz and multiplicity reported according to the following convention: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. GC-MS was obtained using electron ionization. TLC was performed by using commercially prepared 100-400 mesh silica gel plates, and visualization was affected at 254 nm.

B. General procedure for the preparation of oximes (*E*-1)[1]



To a 250.0 mL dried tube was added the mixture of ketone **3** (10.0 mmol), alkoxyamine hydrochloride **4** (10.0 equiv), NaOAc (3.0 equiv), in EtOH (16.0 mL) and H_2O (4.0 mL) successively. The mixture was stirred at room temperature for 12 h under 60 °C. After the reaction was completed, the mixture diluted with H_2O (45.0 mL), and extracted with EtOAc (45.0 mL∗3). The organic extract was washed with brine and dried over anhydrous $MgSO_4$. After removal of the EtOAc in vacuum, the crude product was purified by column chromatography on silica gel with hexanes or petroleum ether/ethyl acetate (100:1 to 200:1) to give oximes **1**.

C. Analytical Data of 1

(*E*)-1-phenylethan-1-one O-benzyl oxime (1a):[2]

Yield: 1.96 g (87%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 6.5, 3.1 Hz, 2H), 7.41 (d, J = 7.1 Hz, 2H), 7.37-7.25 (m, 6H), 5.24 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 138.2, 136.7, 129.1, 128.5, 128.2, 127.8, 126.2, 76.3, 13.0.

(*E*)-1-(p-tolyl)ethan-1-one *O*-benzyl oxime (1b):[3]

Yield: 2.03 g (85%), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 2H), 7.45-7.26 (m, 5H), 7.15 (d, J = 8.0 Hz, 2H), 5.23 (s, 2H), 2.35 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 139.1, 138.2, 133.8, 129.1, 128.4, 128.2, 127.7, 126.0, 76.1, 21.3, 12.9. HRMS-ESI (m/z): calcd for $C_{16}H_{18}NO$, [M+H]: 240.1388, found 240.1392.

(*E*)-1-(4-(tert-butyl)phenyl)ethan-1-one *O*-benzyl oxime (1c):

Yield: 2.39 g (85%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.7 Hz, 2H), 7.33 (ddd, J = 33.6, 18.5, 7.1 Hz, 7H), 5.22 (s, 2H), 2.23 (s, 3H), 1.33-1.25 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 152.3, 138.4, 134.0, 128.5, 128.3, 127.9, 126.0, 125.5, 76.3, 34.8, 31.4, 13.0. HRMS-ESI (m/z): calcd for $C_{19}H_{24}NO$, [M+H]: 282.1858, found 282.1866.

(*E*)-1-(3-methoxyphenyl)ethan-1-one *O*-benzyl oxime (1d):[4]

Yield: 2.04 g (80%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.4 Hz, 2H), 7.57-7.34 (m, 6H), 7.05 (d, J = 7.2 Hz, 1H), 5.44 (s, 2H), 3.92 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 154.9, 138.3, 138.2, 129.5, 128.6, 128.4, 128.0, 118.9, 115.0, 111.6, 76.4, 55.3, 13.1.

(*E*)-1-(4-isopropylphenyl)ethan-1-one *O*-benzyl oxime (1e):

Yield: 2.09 g (78%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 7.5 Hz, 2H), 7.29 (dt, J = 25.2, 7.1 Hz, 3H), 7.18 (d, J = 8.2 Hz, 2H), 5.22 (s, 2H), 2.97-2.80 (m, 1H), 2.23 (s, 3H), 1.22 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 150.1, 138.4, 134.4, 128.5, 128.2, 127.8, 126.6, 126.2, 76.2, 34.1, 24.0, 13.0. HRMS-ESI (m/z): calcd for $C_{18}H_{22}NO$, [M+H]: 268.1701, found 268.1698.

(*E*)-1-(4-chlorophenyl)ethan-1-one *O*-benzyl oxime (1f):[5]

Yield: 1.45 g (56%), light yellow solid, mp: 54-55℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 2H), 7.34 (ddd, J = 18.9, 12.8, 4.3 Hz, 7H), 5.22 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 138.0, 135.1, 128.6, 128.5, 128.2, 127.9, 127.4, 76.4, 12.7.

(*E*)-1-(4-bromophenyl)ethan-1-one *O*-benzyl oxime (1g) :[4]

Yield: 1.64 g (54%), light yellow solid, mp: 57-58℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.15 (m, 9H), 5.22 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 138.0, 135.5, 131.6, 128.5, 128.3, 127.9, 127.7, 123.4, 76.4, 12.7.

(*E*)-1-(3-(trifluoromethyl)phenyl)ethan-1-one *O*-benzyl oxime (1h):

Yield: 1.91 g (65%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.47-7.20 (m, 6H), 5.24 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 137.9, 137.5, 130.9 (q, J = 32 Hz), 129.3, 128.9, 128.3, 128.0, 125.6 (q, J = 3 Hz), 122.9 (q, J = 4 Hz), 120.1, 76.6, 12.6. HRMS-ESI (m/z): calcd for $C_{16}H_{15}F_3NO$, [M+H]: 294.1106, found 294.1109.

(*E*)-1-(2-fluorophenyl)ethan-1-one *O*-benzyl oxime (1i):[6]

Yield: 1.41 g (58%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.25 (m, 7H), 7.15-7.01 (m, 2H), 5.24 (s, 2H), 2.28 (d, J = 2.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, J = 244 Hz), 153.7,

137.9, 130.6 (d, J = 8 Hz), 129.7 (d, J = 4 Hz), 128.4, 128.1, 127.8, 125.4 (d, J = 13 Hz), 124.1 (d, J = 3 Hz), 116.1 (d, J = 22 Hz), 76.3, 15.8 (d, J = 5 Hz).

(*E*)-1-(3,5-dimethylphenyl)ethan-1-one *O*-benzyl oxime (1j):

Yield: 2.10 g (83%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.5 Hz, 2H), 7.35 – 7.20 (m, 5H), 6.94 (s, 1H), 5.23 (s, 2H), 2.28 (s, 6H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 138.3, 138.0, 136.7, 130.9, 128.5, 128.2, 127.9, 124.1, 76.3, 21.5, 13.3. HRMS-ESI (m/z): calcd for $C_{17}H_{20}NO$, [M+H]: 254.1545, found 254.1545.

(*E*)-1-(4-fluoro-3-methoxyphenyl)ethan-1-one *O*-benzyl oxime (1k):

Yield: 1.80 g (66%), light yellow solid, mp: 55-57°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.23 (m, 7H), 6.89 (t, J = 8.6 Hz, 1H), 5.21 (s, 2H), 3.86 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5 (d, J = 3 Hz), 152.2 (d, J = 246 Hz), 148.5 (d, J = 11 Hz), 138.1, 129.7 (d, J = 7 Hz), 128.4, 128.2, 127.8, 122.1 (d, J = 3 Hz), 113.7 (d, J = 20 Hz), 112.8 (d, J = 2 Hz), 76.3, 56.2, 12.6. HRMS-ESI (m/z): calcd for $C_{16}H_{17}FNO_2$, [M+H]: 274.1243, found 274.1243.

(*E*)-1-(naphthalen-2-yl)ethan-1-one *O*-benzyl oxime (1l):

Yield: 2.20 g (80%), light yellow solid, mp: 97-98°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.92 (d, J = 8.7 Hz, 1H), 7.81 (ddd, J = 16.6, 9.4, 5.9 Hz, 3H), 7.50-7.26 (m, 7H), 5.29 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 138.1, 134.0, 133.7, 133.2, 128.5, 128.5, 128.3, 128.0, 127.9, 127.7, 126.6, 126.3, 125.8, 123.6, 76.4, 12.7. HRMS-ESI (m/z): calcd for $C_{19}H_{18}NO$, [M+H]: 276.1388, found 276.1391.

(*E*)-1-(6-methylpyridin-2-yl)ethan-1-one *O*-benzyl oxime (1m):

Yield: 1.27 g (53%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.45-7.27 (m, 5H), 7.07 (d, J = 7.5 Hz, 1H), 5.26 (s, 2H), 2.55 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 156.6, 153.8, 138.1, 136.3, 128.4, 128.1, 127.8, 123.0, 117.7, 76.4, 24.6, 11.6. HRMS-ESI (m/z): calcd for $C_{15}H_{17}N_2O$, [M+H]: 243.1341, found 243.1342.

(*E*)-1-(thiophen-2-yl)ethan-1-one *O*-benzyl oxime (1n):

Yield: 1.06 g (46%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.14 (m, 7H), 7.00 (t, J = 4.2 Hz, 1H), 5.20 (s, 2H), 2.25 (d, J = 9.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 140.5, 137.8, 128.4, 128.3, 127.9, 127.0, 126.8, 126.2, 76.4, 13.1. HRMS-ESI (m/z): calcd for $C_{13}H_{14}NOS$, [M+H]: 232.0791, found 232.0806.

(*E*)-2,3-dihydro-1H-inden-1-one *O*-benzyl oxime (1o):

Yield: 1.80 g (76%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 7.4 Hz, 2H), 7.29 (t, J = 7.3 Hz, 2H), 7.26-7.12 (m, 4H), 5.20 (s, 2H), 2.85 (d, J = 7.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 148.4, 138.5, 136.4, 130.4, 128.5, 128.3, 127.9, 127.1, 125.7, 121.8, 76.4, 28.7, 26.8. HRMS-ESI (m/z): calcd for $C_{16}H_{16}NO$, [M+H]: 238.1232, found 238.1238.

(*E*)-7-fluoro-2,3-dihydro-1H-inden-1-one *O*-benzyl oxime (1p):

Yield: 1.94 g (76%), light yellow solid, mp: 70-72°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.19 (m, 6H), 7.04 (d, J = 7.5 Hz, 1H), 6.91 (t, J = 9.0 Hz, 1H), 5.26 (s, 2H), 3.10-2.97 (m, 2H), 2.94 (dd, J = 8.3, 4.4

Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, J = 5 Hz), 158.4 (d, J = 236 Hz), 151.3 (d, J = 3 Hz), 138.0, 131.4 (d, J = 7 Hz), 128.4, 128.3, 127.9, 123.6 (d, J = 13 Hz), 121.3 (d, J = 4 Hz), 114.2 (d, J = 19 Hz), 76.6, 28.9, 27.0. HRMS-ESI (m/z): calcd for $C_{16}H_{15}FNO$, [M+H]: 256.1138, found 256.1147.

(*E*)-5-fluoro-2,3-dihydro-1H-inden-1-one *O*-benzyl oxime (1q)：

Yield: 1.99 g (78%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 8.0, 5.6 Hz, 1H), 7.34 (ddd, J = 23.5, 16.9, 7.2 Hz, 5H), 6.94 (dd, J = 14.7, 8.4 Hz, 2H), 5.20 (s, 2H), 2.95 (dt, J = 7.8, 6.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (d, J = 248 Hz), 161.8, 150.6 (d, J = 9 Hz), 138.2, 132.2 (d, J = 3 Hz), 128.4, 128.1, 127.8, 123.0 (d, J = 8 Hz), 114.8 (d, J = 3 Hz), 112.3 (d, J = 229 Hz), 76.2, 28.6, 27.0. HRMS-ESI (m/z): calcd for $C_{16}H_{15}FNO$, [M+H]: 256.1138, found 256.1148.

***(E)* -6-methyl-2,3-dihydro-1H-inden-1-one O-benzyl oxime (1r)：**

Yield: 2.04 g (81%), light yellow solid, mp: 68-70℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.45-7.24 (m, 5H), 7.16 (dd, J = 17.9, 7.7 Hz, 2H), 5.22 (s, 2H), 2.94 (dd, J = 10.7, 6.3 Hz, 4H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 145.5, 138.3, 136.7, 136.2, 131.4, 128.3, 128.0, 127.7, 125.2, 121.8, 76.1, 28.2, 27.0, 21.1. HRMS-ESI (m/z): calcd for $C_{17}H_{18}NO$, [M+H]: 252.1388, found 252.1395.

(*E*)-3,4-dihydronaphthalen-1(2H)-one *O*-benzyl oxime (1s)：

Yield: 2.14 g (85%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.5 Hz, 1H), 7.38 (d, J = 7.2 Hz, 2H), 7.34-7.21 (m, 3H), 7.20-7.09 (m, 2H), 7.04 (d, J = 7.4 Hz, 1H), 5.21 (s, 2H), 2.69 (dt, J = 12.1, 6.4 Hz, 4H), 1.85-1.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 139.7, 138.4, 130.9, 129.1, 128.7, 128.5, 128.3, 127.9, 126.5, 124.5, 76.4, 29.9, 24.8, 21.6. HRMS-ESI (m/z): calcd for $C_{17}H_{18}NO$, [M+H]: 252.1388, found 252.1394.

(*E*)-3,4-dihydronaphthalen-1(2H)-one *O*-methyl oxime (1t)：

Yield: 1.40 g (80%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.6 Hz, 1H), 7.25-7.13 (m, 2H), 7.09 (d, J = 7.4 Hz, 1H), 3.97 (s, 3H), 2.71 (dd, J = 8.4, 5.0 Hz, 4H), 1.81 (dt, J = 12.7, 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 139.5, 130.8, 129.0, 128.6, 126.4, 124.3, 62.0, 29.8, 24.3, 21.5. HRMS-ESI (m/z): calcd for $C_{11}H_{14}NO$, [M+H]: 176.1075, found 176.1083.

(*E*)-7-methoxy-3,4-dihydronaphthalen-1(2H)-one O-benzyl oxime (1v)：

Yield: 2.02 g (72%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 2.2 Hz, 1H), 7.31 (ddd, J = 25.3, 20.8, 7.3 Hz, 5H), 6.97 (d, J = 8.4 Hz, 1H), 6.79 (dd, J = 8.4, 2.6 Hz, 1H), 5.22 (s, 2H), 3.74 (s, 3H), 2.72 (t, J = 6.6 Hz, 2H), 2.65-2.52 (m, 2H), 1.80-1.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 154.4, 138.45, 132.36, 131.6, 129.7, 128.5, 128.3, 127.9, 116.6, 107.9, 76.4, 55.42, 29.07, 24.57, 21.83.

(*E*)-6-chloro-3,4-dihydronaphthalen-1(2H)-one *O*-benzyl oxime (1w)：

Yield: 1.89 g (66%), colorless oil；^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 1H), 7.34 (ddd, J = 23.8, 16.7, 7.1 Hz, 5H), 7.17-6.98 (m, 2H), 5.21 (s, 2H), 2.71 (dt, J = 12.0, 6.3 Hz, 4H), 1.80 (dd, J = 12.6, 6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 141.2, 138.1, 134.7, 129.3, 128.4, 128.4, 128.2, 127.8, 126.7, 125.9, 76.4, 29.6, 24.4, 21.2. HRMS-ESI (m/z): calcd for $C_{17}H_{17}ClNO$, [M+H]: 286.0999, found 286.1004.

***(E)*-1-phenylbutan-1-one O-benzyl oxime (1x):**

Yield: 0.88 g (35%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.49 (m, 2H), 7.36-7.14 (m, 8H), 5.13 (d, J = 5.0 Hz, 2H), 2.71-2.61 (m, 2H), 1.47 (dt, J = 12.7, 7.4 Hz, 2H), 0.84 (td, J = 7.3, 4.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 138.4, 136.0, 129.1, 128.5, 128.5, 128.2, 127.8, 126.5, 76.2, 28.8, 20.1, 14.4.

Phenyl(p-tolyl)methanone *O*-methyl oxime (1y):[22]

Yield: 1.78 g (79%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 7.8, 1.6 Hz, 1H), 7.40-7.11 (m, 7H), 7.07 (d, J = 8.1 Hz, 1H), 3.93 (d, J = 7.3 Hz, 3H), 2.31 (d, J = 19.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 156.9, 139.5, 138.9, 136.8, 133.8, 133.7, 130.5, 129.5, 129.4, 129.4, 129.2, 129.0, 128.9, 128.4, 128.3, 128.1, 128.0, 62.5, 62.5, 21.7, 21.5.

(*E*)-1-phenylethan-1-one oxime (1ba):[7]

Yield: 0.97 g (72%), light yellow solid, mp: 50-51°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.62 (dd, J = 6.6, 3.0 Hz, 2H), 7.38 (dd, J = 4.9, 1.7 Hz, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 136.5, 129.3, 128.6, 126.1, 12.4.

(*E*)-1-(4-fluorophenyl)ethan-1-one oxime (1bb):[14]

Yield: 1.33 g (87%), white solid, mp: 68-73°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.70-7.51 (m, 2H), 7.04 (t, J = 8.7 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5 (d, J = 247 Hz), 155.34, 132.6 (d, J = 3 Hz), 128.0 (d, J = 8 Hz), 115.6 (d, J = 22 Hz), 12.5.

(*E*)-1-(4-chlorophenyl)ethan-1-one oxime (1bc):[15]

Yield: 1.44 g (85%), white solid, mp: 97-100°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.53 (d, J = 5.7 Hz, 2H), 7.32 (d, J = 5.1 Hz, 2H), 2.26 (d, J = 2.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 135.4, 134.8, 128.8, 127.4, 12.5.

(*E*)-1-(p-tolyl)ethan-1-one oxime (1bd):[16]

Yield: 1.18 g (79%), white solid, mp: 78-88°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.50 (dd, J = 7.3, 5.4 Hz, 2H), 7.16 (dd, J = 7.2, 5.1 Hz, 2H), 2.43 – 2.18 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 139.4, 133.7, 129.3, 126.1, 21.3, 12.5.

(*E*)-1-(4-(tert-butyl)phenyl)ethan-1-one oxime (1be):[17]

Yield: 1.55 g (81%), white solid, mp: 100-101°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 2.30 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 152.5, 133.8, 125.9, 125.6, 34.8, 31.3, 12.5.

(*E*)-1-(naphthalen-2-yl)ethan-1-one oxime (1bf):[18]

Yield: 1.20 g (65%), white solid, mp: 143-146°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.03 (s, 1H), 7.93-7.77 (m, 4H), 7.56-7.44 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 133.8, 133.7, 133.1, 128.5, 128.2, 127.7, 126.7, 126.4, 126.0, 123.3, 12.2.

(*E*)-1-(furan-2-yl)ethan-1-one oxime (1bg):[21]

Yield: 1.04 g (83%), white solid, mp: 102-104°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.46 (d, J = 1.5 Hz, 1H), 6.63 (d, J = 3.4 Hz, 1H), 6.43 (dd, J = 3.3, 1.8 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.4, 143.7, 111.3, 110.1, 11.2.

(*E*)-benzaldehyde *O*-benzyl oxime (1bh):[11]

Yield: 1.77 g (84%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.57 (dd, J = 6.2, 2.7 Hz, 2H), 7.42 (d, J = 7.2 Hz, 2H), 7.39-7.26 (m, 6H), 5.21 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 137.5, 132.3, 129.9, 128.7, 128.5, 128.4, 128.0, 127.1, 76.4.

(*E*)-4-fluorobenzaldehyde *O*-benzyl oxime (1bi):[12]

Yield: 1.74 g (76%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.55 (dd, J = 7.6, 5.7 Hz, 2H), 7.45-7.30 (m, 5H), 7.04 (t, J = 8.3 Hz, 2H), 5.19 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 (d, J = 248 Hz), 147.9, 137.5, 129.0, 128.9, 128.5, 128.4, 128.0, 115.8 (d, J = 21 Hz), 76.5.

(*E*)-4-methylbenzaldehyde *O*-benzyl oxime (1bj):

Yield: 1.69 g (75%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.40 (dd, J = 15.6, 7.7 Hz, 4H), 7.34-7.20 (m, 3H), 7.07 (d, J = 7.8 Hz, 2H), 5.17 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 140.1, 137.9, 129.7, 129.6, 128.6, 128.6, 128.1, 127.3, 76.5, 21.6. HRMS-ESI (m/z): calcd for $C_{15}H_{16}NO$, [M+H]: 226.1232, found 226.1239.

(*E*)-2-naphthaldehyde *O*-benzyl oxime (1bk):[12]

Yield: 2.04 g (78%), Light yellow solid, mp: 57-58°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.81 (dt, J = 12.6, 8.5 Hz, 5H), 7.52-7.27 (m, 7H), 5.24 (d, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 137.6, 134.16, 133.2, 130.0, 128.6, 128.5, 128.5, 128.4, 128.1, 127.9, 126.9, 126.6, 123.1, 76.6.

(*E*)-furan-2-carbaldehyde *O*-benzyl oxime (1bl):[13]

Yield: 1.37 g (68%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.35 (ddd, J = 22.0, 17.1, 9.8 Hz, 6H), 6.55 (d, J = 3.3 Hz, 1H), 6.40 (d, J = 1.8 Hz, 1H), 5.20 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 144.3, 139.4, 137.2, 128.5, 128.5, 128.1, 112.9, 111.7, 76.8.

propan-2-one *O*-benzyl oxime (1aa):[8]

Yield: 0.77 g (47%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.12 (m, 5H), 5.07 (s, 2H), 1.88 (d, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 138.4, 128.3, 127.9, 127.6, 75.3, 21.9, 15.8.

(*E*)-3,3-dimethylbutan-2-one *O*-benzyl oxime (1ab):

Yield: 0.82 g (40%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.18 (m, 5H), 5.07 (s, 2H), 1.82 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 138.6, 128.2, 128.1, 127.5, 75.4, 37.1, 27.7, 10.7. HRMS-ESI (m/z): calcd for $C_{13}H_{20}NO$, [M+H]: 206.1545, found 206.1551.

pentan-3-one O-benzyl oxime (1ac):

Yield: 1.62 g (85%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 5H), 5.06 (s, 2H), 2.33 (q, J = 7.6 Hz, 2H), 2.18 (q, J = 7.5 Hz, 2H), 1.06 (dt, J = 10.6, 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 138.5, 128.3, 128.0, 127.6, 75.3, 27.2, 21.5, 11.2, 10.5.

1-(4-fluorophenyl)ethan-1-one oxime (1ad):

Yield: 1.49 g (78%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 5H), 5.06 (d, J = 10.4 Hz, 2H), 2.37-2.10 (m, 1H), 1.84 (d, J = 6.1 Hz, 3H), 1.50 (dt, J = 14.7, 7.4 Hz, 2H), 0.91 (dt, J = 12.0, 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 158.3, 138.5, 138.4, 128.3, 127.9, 127.8, 127.6, 127.6, 75.3, 75.2, 37.8, 31.4, 20.0, 19.9, 19.1, 14.2, 14.1, 13.7.

Cyclohexanone *O*-benzyl oxime (1af):[2]

Yield: 1.63 g (80%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dt, J = 17.0, 6.5 Hz, 5H), 5.06 (s, 2H), 2.50 (t, J = 5.5 Hz, 2H), 2.30-2.06 (m, 2H), 1.71-1.44 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 138.4, 128.3, 127.9, 127.6, 75.2, 32.3, 27.1, 25.9, 25.8, 25.5.

5-methoxy-3,4-dihydronaphthalen-2(1H)-one *O*-benzyl oxime (1ag):

Yield: 2.19 g (78%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.22 (m, 5H), 7.13 (t, J = 7.9 Hz, 1H), 6.82-6.61 (m, 2H), 5.11 (d, J = 17.6 Hz, 2H), 3.81 (s, 4H), 3.49 (s, 1H), 2.86 (dd, J = 12.6, 6.2 Hz, 2H), 2.68 (t, J = 6.7 Hz, 1H), 2.51 (t, J = 6.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 158.4, 156.7, 156.2, 138.3, 138.1, 136.5, 134.8, 128.4, 128.4, 128.0, 127.9, 127.8, 127.7, 127.0, 127.0, 126.4, 125.7, 121.0, 120.2, 108.4, 107.6, 75.6, 75.5, 55.5, 55.4, 35.0, 29.3, 28.5, 24.3, 21.9, 19.9. HRMS-ESI (m/z): calcd for $C_{18}H_{20}NO_2$, [M+H]: 282.1494, found 282.1494.

Cyclohexanone *O*-methyl oxime (1ah):[10]

Yield: 0.99 g (78%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 2.44 (t, J = 6.1 Hz, 2H), 2.25-2.14 (m, 2H), 1.73-1.53 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 60.9, 32.2, 27.0, 25.8, 25.7, 25.1.

4-phenylbutan-2-one *O*-benzyl oxime (1ai):

Yield: 2.03 g (80%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (ddd, J = 25.4, 14.7, 7.4 Hz, 7H), 7.18-7.09 (m, 3H), 5.07 (d, J = 8.1 Hz, 2H), 2.78 (dd, J = 15.9, 8.0 Hz, 2H), 2.44 (dd, J = 16.0, 8.0 Hz, 2H), 1.84 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 157.3, 141.4, 141.4, 138.7, 138.6, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.1, 128.1, 127.8, 127.8, 126.3, 126.2, 75.6, 75.5, 37.9, 37.9, 32.9, 32.9, 14.8, 14.8. HRMS-ESI (m/z): calcd for $C_{17}H_{20}NO$, [M+H]: 254.1545, found 254.1558.

Cyclobutanone *O*-benzyl oxime (1aj):[9]

Yield: 1.44 g (82%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.20 (m, 5H), 5.03 (s, 2H), 2.89 (dt, J = 14.9, 7.6 Hz, 4H), 2.08-1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 138.3, 128.4, 128.1, 127.8, 75.6, 31.7, 31.3, 14.6.

cyclohexanone oxime (1ak):[21]

Yield: 0.86 g (76%), white solid, mp: 83-88^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 2.61-2.44 (m, 2H), 2.27-2.15 (m, 2H), 1.76-1.51 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 32.2, 26.9, 25.8, 25.6, 24.5.

5-methoxy-3,4-dihydronaphthalen-2(1H)-one oxime (1al):[19]

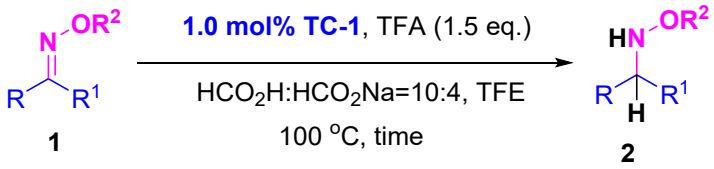
Yield: 1.38 g (72%), brown solid, mp: 135-141^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.15 (t,

J = 7.9 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.72 (d, J = 8.1 Hz, 1H), 3.83 (d, J = 4.3 Hz, 5H), 2.88 (t, J = 6.6 Hz, 2H), 2.54 (t, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159. 8, 159.0, 156.6, 156.2, 136.2, 134.6, 127.0, 127.0, 126.3, 125.7, 121.1, 120.2, 108.4, 107.7, 55.5, 55.4, 34.9, 28.6, 28.5, 23.5, 21.7, 19.8.

(*E*)-4-phenylbutan-2-one oxime (1am):[20]

Yield: 1.09 g (67%), white solid, mp: 83-86°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.35-7.27 (m, 2H), 7.21 (dd, J = 7.2, 5.1 Hz, 3H), 2.84 (dd, J = 9.5, 6.7 Hz, 2H), 2.61-2.41 (m, 2H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 141.2, 128.6, 128.4, 126.2, 37.8, 32.9, 14.0.

D. General procedure for the preparation of *N*-alkoxy amines (2):



To a 25.0 mL dried tube was added the mixture of oximes **1** (0.25 mmol), TC-1 (1.0 mol %), CF_3COOH (1.5 equiv), HCOOH (1.25 equiv), HCOONa (0.5 eqquiv) in trifluoroethanol (2.0 mL) successively. The mixture was stirred at 100°C for 14 h under an N_2 atmosphere. After the reaction was completed, the mixture was cooled to room temperature and diluted with H_2O (15.0 mL), neutralized with $NaHCO_3$ (aq.), and extracted with EtOAc (10.0 mL × 3). The organic extract was washed with H_2O (10.0 mL × 3) and dried over anhydrous $MgSO_4$. After removal of the EtOAc in vacuum, the crude product was purified by column chromatography on silica gel with hexanes or petroleum ether/ethyl acetate (50:1~100:1) to give the desired products **2**. The enantioselectivity of **2a** was determined by chiral AD-H coloumn, hexane/*i*-PrOH=99:1, 0.5 mL/min.

E. Analytical Data of 2

***O*-benzyl-*N*-(1-phenylethyl)hydroxylamine (2a)**:[23]

Yield: 51.7 mg (91%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (ddd, J = 16.2, 14.0, 7.3 Hz, 10H), 5.56 (s, 1H), 4.61 (q, J = 11.4 Hz, 2H), 4.15 (q, J = 6.6 Hz, 1H), 1.35 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 137.9, 128.6, 128.5, 128.4, 127.9, 127.5, 127.3, 76.9, 60.7, 20.0.

***O*-benzyl-*N*-(1-(p-tolyl)ethyl)hydroxylamine (2b)**:

Yield: 56.1 mg (93%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.16 (m, 7H), 7.13 (d, J = 7.5 Hz, 2H), 5.57 (s, 1H), 4.62 (q, J = 11.5 Hz, 2H), 4.12 (q, J = 6.5 Hz, 1H), 2.32 (s, 3H), 1.34 (d, J = 6.4

Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 138.0, 137.1, 129.2, 128.6, 128.4, 127.8, 127.2, 76.8, 60.4, 21.2, 20.0. HRMS-ESI (m/z): calcd for $C_{16}H_{20}NO$, [M+H]: 242.1545, found 242.1536.

***O*-benzyl-*N*-(1-(4-(tert-butyl)phenyl)ethyl)hydroxylamine (2c):**

Yield: 63.0 mg (89%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.20 (m, 9H), 5.59 (s, 1H), 4.64 (dd, J = 27.2, 11.4 Hz, 2H), 4.14 (q, J = 6.5 Hz, 1H), 1.37 (d, J = 6.6 Hz, 3H), 1.30 (d, J = 11.3 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 139.7, 138.0, 128.6, 128.4, 127.8, 127.0, 125.4, 76.8, 60.3, 34.6, 31.5, 19.9. HRMS-ESI (m/z): calcd for $C_{19}H_{26}NO$, [M+H]: 284.2014, found 284.2027.

***O*-benzyl-*N*-(1-(3-methoxyphenyl)ethyl)hydroxylamine (2d):**

Yield: 52.7 mg (82%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.16 (m, 6H), 6.93 (d, J = 12.5 Hz, 2H), 6.80 (d, J = 8.1 Hz, 1H), 5.61 (s, 1H), 4.63 (q, J = 11.5 Hz, 2H), 4.13 (q, J = 6.5 Hz, 1H), 3.78 (s, 3H), 1.33 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 144.7, 137.9, 129.4, 128.5, 128.4, 127.8, 119.6, 112.9, 112.8, 76.8, 60.7, 55.2, 20.0. HRMS-ESI (m/z): calcd for $C_{16}H_{20}NO$, [M+H]: 258.1494, found 258.1492.

***O*benzyl-*N*-(1-(4-isopropylphenyl)ethyl)hydroxylamine (2e):**

Yield: 61.2 mg (91%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.20 (m, 7H), 7.18 (d, J = 8.1 Hz, 2H), 5.58 (s, 1H), 4.63 (dd, J = 26.5, 11.4 Hz, 2H), 4.13 (q, J = 6.6 Hz, 1H), 2.88 (dt, J = 13.8, 6.9 Hz, 1H), 1.36 (d, J = 6.6 Hz, 3H), 1.24 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 140.1, 138.0, 128.6, 128.4, 127.8, 127.3, 126.5, 76.9, 60.4, 33.9, 24.2, 20.0. HRMS-ESI (m/z): calcd for $C_{18}H_{24}NO$, [M+H]: 270.1858, found 270.1851.

***O*-benzyl-*N*-(1-(4-chlorophenyl)ethyl)hydroxylamine (2f):**

Yield: 34.4 mg (57%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.14 (m, 9H), 5.57 (s, 1H), 4.58 (q, J = 11.5 Hz, 2H), 4.13 (q, J = 6.7 Hz, 1H), 1.30 (d, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 137.7, 133.0, 128.6, 128.5, 128.5, 128.4, 127.9, 76.8, 60.0, 19.9. HRMS-ESI (m/z): calcd for $C_{15}H_{16}ClNO$, [M+H]: 262.0999, found 262.0998.

***O*-benzyl-*N*-(1-(4-bromophenyl)ethyl)hydroxylamine (2g):**

Yield: 41.9 mg (55%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.37 – 7.10 (m, 7H), 5.56 (s, 1H), 4.58 (q, J = 11.5 Hz, 2H), 4.11 (q, J = 6.7 Hz, 1H), 1.30 (d, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 137.7, 131.5, 129.0, 128.5, 128.4, 127.9, 121.1, 76.8, 60.0, 19.9. HRMS-ESI (m/z): calcd for $C_{15}H_{17}BrNO$, [M+H]: 306.0494, found 306.0493.

***O*-benzyl-*N*-(1-(3-(trifluoromethyl)phenyl)ethyl)hydroxylamine (2h):**

Yield: 34.0 mg (46%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.54 (t, J = 7.0 Hz, 2H), 7.44 (t, J = 7.6 Hz, 1H), 7.34-7.20 (m, 5H), 5.62 (s, 1H), 4.58 (q, J = 11.4 Hz, 2H), 4.22 (q, J = 6.5 Hz, 1H), 1.34 (d, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 137.5, 130.6, 128.8, 128.5, 128.4, 127.9, 124.2, (q, J = 270 Hz), 124.2 (q, J = 4 Hz), 124.0 (q, J = 4 Hz), 76.7, 60.2, 19.9. HRMS-ESI (m/z): calcd for $C_{16}H_{17}F_3NO$, [M+H]: 296.1262, found 296.1268.

***O*-benzyl-*N*-(1-(2-fluorophenyl)ethyl)hydroxylamine (2i):**

Yield: 33.1 mg (54%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, J = 7.4 Hz, 1H), 7.36-7.16 (m, 6H), 7.11 (t, J = 7.5 Hz, 1H), 7.05-6.98 (m, 1H), 5.68 (s, 1H), 4.72-4.59 (m, 2H), 4.52 (q, J = 6.6 Hz, 1H), 1.36 (d, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 246 Hz), 137.8, 129.9 (d, J = 13 Hz), 128.6 (d, J = 8 Hz), 128.4 (d, J = 8 Hz), 128.2, 128.2, 127.8, 124.1 (d, J = 4 Hz), 115.5 (d, J = 22 Hz), 76.6, 53.8 (d, J = 2 Hz), 18.7. HRMS-ESI (m/z): calcd for $C_{15}H_{17}FNO$, [M+H]: 246.1294, found 246.1301.

***O*-benzyl-*N*-(1-(3,5-dimethylphenyl)ethyl)hydroxylamine (2j)：**

Yield: 59.3 mg (93%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 9.9 Hz, 5H), 6.95 (s, 2H), 6.89 (s, 1H), 5.58 (s, 1H), 4.64 (dd, J = 25.8, 11.5 Hz, 2H), 4.09 (q, J = 6.5 Hz, 1H), 2.30 (s, 6H), 1.34 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 138.0, 137.9, 129.2, 128.6, 128.4, 127.8, 125.1, 76.8, 60.7, 21.4, 20.0. HRMS-ESI (m/z): calcd for $C_{17}H_{22}NO$, [M+H]: 256.1701, found 26.1691.

***O*-benzyl-*N*-(1-(4-fluoro-3-methoxyphenyl)ethyl)hydroxylamine (2k)：**

Yield: 44.0 mg (64%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dt, J = 18.7, 6.9 Hz, 5H), 7.07 (dd, J = 26.4, 10.4 Hz, 2H), 6.90 (t, J = 8.4 Hz, 1H), 5.55 (s, 1H), 4.60 (q, J = 11.5 Hz, 2H), 4.15-4.04 (m, 1H), 3.87 (s, 3H), 1.30 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2 (d, J = 244 Hz), 146.8 (d, J = 10 Hz), 137.8, 136.2 (d, J = 6 Hz), 128.5, 128.4, 127.8, 122.9 (d, J = 3 Hz), 114.9 (d, J = 19 Hz), 113.2, 76.8, 59.7, 56.3, 19.9. HRMS-ESI (m/z): calcd for $C_{16}H_{19}FN_2O$, [M+H]: 276.1400, found 286.1396.

***O*-benzyl-*N*-(1-(naphthalen-2-yl)ethyl)hydroxylamine (2l)：**

Yield: 65.1 mg (94%), light yellow solid, mp: 101-102℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 9.2, 4.9 Hz, 4H), 7.55-7.38 (m, 3H), 7.35-7.13 (m, 5H), 5.68 (s, 1H), 4.61 (dt, J = 15.8, 9.3 Hz, 2H), 4.38-4.25 (m, 1H), 1.54-1.34 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 138.0, 133.5, 133.1, 128.6, 128.4, 128.2, 128.0, 127.9, 127.8, 126.2, 126.1, 125.8, 125.5, 76.9, 60.8, 20.1. HRMS-ESI (m/z): calcd for $C_{19}H_{20}NO$, [M+H]: 278.1454, found 278.1551.

***O*-benzyl-*N*-(1-(6-methylpyridin-2-yl)ethyl)hydroxylamine (2m)：**

Yield: 36.2 mg (61%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, J = 7.6 Hz, 1H), 7.35-7.23 (m, 5H), 7.09 (d, J = 7.6 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.21 (s, 1H), 4.67 (dd, J = 11.4, 3.9 Hz, 2H), 4.21 (q, J = 6.7 Hz, 1H), 2.53 (s, 3H), 1.33 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 158.0, 138.1, 136.7, 128.3, 128.3, 127.7, 121.8, 118.4, 76.3, 61.4, 24.5, 18.7. HRMS-ESI (m/z): calcd for $C_{15}H_{19}N_2O$, [M+H]: 243.1497, found 243.1504.

***O*-benzyl-*N*-(1-(thiophen-2-yl)ethyl)hydroxylamine (2n)：**

Yield: 28.0 mg (48%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.24 (m, 5H), 7.21 (d, J = 5.0 Hz, 1H), 7.05-6.86 (m, 2H), 5.57 (s, 1H), 4.78-4.62 (m, 2H), 4.43 (q, J = 6.6 Hz, 1H), 1.46 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 137.7, 128.6, 128.4, 127.9, 126.5, 124.5, 124.4, 76.8, 56.4, 20.6. HRMS-ESI (m/z): calcd for $C_{13}H_{16}NOS$, [M+H]: 243.0953, found 243.0942.

***O*-benzyl-*N*-(2,3-dihydro-1H-inden-1-yl)hydroxylamine (2o)：**

Yield: 50.2 mg (84%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.2 Hz, 1H), 7.36-7.26 (m, 5H), 7.20 (dd, J = 16.4, 5.7 Hz, 3H), 5.59 (s, 1H), 4.71 (s, 2H), 4.64-4.57 (m, 1H), 3.01 (dd, J =

15.6, 7.6 Hz, 1H), 2.89-2.76 (m, 1H), 2.29 (dd, *J* = 13.9, 7.0 Hz, 1H), 2.08-1.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.3, 138.0, 128.5, 128.4, 128.1, 127.8, 126.4, 125.2, 124.9, 76.6, 65.9, 30.5, 30.5. HRMS-ESI (m/z): calcd for $C_{16}H_{18}NO$, [M+H]: 240.1388, found 240.1382.

***O*-benzyl-*N*-(7-fluoro-2,3-dihydro-1H-inden-1-yl)hydroxylamine (2p)：**

Yield: 47.6 mg (74%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 5H), 7.18 (td, *J* = 7.9, 5.5 Hz, 1H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.83 (t, *J* = 8.8 Hz, 1H), 5.88 (s, 1H), 4.80 (dd, *J* = 6.7, 3.7 Hz, 1H), 4.70 (s, 2H), 3.09 (dt, *J* = 16.2, 8.1 Hz, 1H), 2.83 (ddd, *J* = 16.2, 8.2, 4.6 Hz, 1H), 2.29-2.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (d, *J* = 246 Hz), 148.8(d, *J* = 5 Hz), 137.8, 130.1 (d, *J* = 7 Hz), 128.5, 128.4, 127.9, 127.7 (d, *J* = 16 Hz), 120.7 (d, *J* = 3 Hz), 113.1 (d, *J* = 21 Hz), 76.8, 63.6, 31.1 (d, *J* = 1 Hz), 30.4. HRMS-ESI (m/z): calcd for $C_{16}H_{17}FNO$, [M+H]: 258.1294, found 258.1303.

***O*-benzyl-*N*-(5-fluoro-2,3-dihydro-1H-inden-1-yl)hydroxylamine (2q)：**

Yield: 51.4 mg (80%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.25 (m, 6H), 7.00-6.78 (m, 2H), 5.55 (s, 1H), 4.69 (s, 2H), 4.54 (dd, *J* = 7.1, 4.5 Hz, 1H), 3.08-2.94 (m, 1H), 2.88-2.74 (m, 1H), 2.31 (ddt, *J* = 13.7, 8.7, 7.0 Hz, 1H), 2.04 (ddd, *J* = 13.4, 9.1, 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1(d, *J* = 243 Hz), 146.9 (d, *J* = 8 Hz), 138.0 (d, *J* = 2 Hz), 137.8, 128.5, 128.4, 127.9, 126.2 (d, *J* = 9 Hz), 113.3 (d, *J* = 22 Hz), 111.7 (d, *J* = 22 Hz), 76.6, 65.0, 30.6 (d, *J* = 11 Hz). HRMS-ESI (m/z): calcd for $C_{16}H_{17}FNO$, [M+H]: 258.1294, found 258.1290.

***O*-benzyl-*N*-(6-methyl-2,3-dihydro-1H-inden-1-yl)hydroxylamine (2r)：**

Yield: 55.7 mg (88%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.20 (m, 5H), 7.19 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 5.53 (s, 1H), 4.69 (s, 2H), 4.57-4.49 (m, 1H), 3.01-2.85 (m, 1H), 2.81-2.66 (m, 1H), 2.32-2.15 (m, 4H), 2.03-1.94 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 141.6, 138.2, 136.0, 129.0, 128.6, 128.5, 127.9, 125.8, 124.7, 76.7, 66.0, 30.9, 30.2, 21.4. HRMS-ESI (m/z): calcd for $C_{17}H_{20}NO$, [M+H]: 254.1545, found 254.1552.

***O*-benzyl-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2s)：**

Yield: 55.7 mg (88%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.22 (m, 6H), 7.18-7.04 (m, 3H), 5.50 (s, 1H), 4.83-4.64 (m, 2H), 4.13 (t, *J* = 3.9 Hz, 1H), 2.85-2.62 (m, 2H), 2.17 (ddt, *J* = 13.1, 6.3, 3.3 Hz, 1H), 2.05-1.90 (m, 1H), 1.84-1.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.1, 134.7, 129.8, 129.3, 128.6, 128.4, 127.9, 127.4, 125.8, 76.8, 58.1, 29.5, 26.4, 18.3. HRMS-ESI (m/z): calcd for $C_{17}H_{20}NO$, [M+H]: 258.1545, found 254.1557.

***O*-methyl-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylaminee (2t)：**

Yield: 34.6 mg (78%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 1H), 7.22-6.97 (m, 3H), 5.51 (s, 1H), 4.11 (d, *J* = 3.1 Hz, 1H), 3.57 (d, *J* = 3.0 Hz, 3H), 2.87-2.64 (m, 2H), 2.19-2.08 (m, 1H), 2.07-1.92 (m, 1H), 1.85-1.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 134.7, 129.6, 129.3, 127.4, 125.8, 62.4, 57.9, 29.5, 26.3, 18.3. HRMS-ESI (m/z): calcd for $C_{11}H_{16}NO$, [M+H]: 178.1232, found 178.1238.

O-benzyl-N-(7-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2v)：

Yield: 65.1 mg (92%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (ddd, *J* = 22.1, 9.8, 4.8 Hz, 5H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 2.6 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.7 Hz, 1H), 5.50 (s, 1H), 4.73 (q, *J*

= 11.6 Hz, 2H), 4.08 (t, *J* = 4.2 Hz, 1H), 3.73 (s, 3H), 2.78-2.53 (m, 2H), 2.11 (dtd, *J* = 9.4, 6.2, 3.2 Hz, 1H), 1.99-1.87 (m, 1H), 1.83-1.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 138.1, 135.8, 130.6, 130.1, 128. 7, 128.1, 127.9, 114.2, 114.0, 76.8, 58.4, 55.3, 28.7, 26.6, 18.7. HRMS-ESI (m/z): calcd for $C_{18}H_{22}NO_2$, [M+H]: 284.1651, found 284.1648.

***O*-benzyl-*N*-(6-chloro-1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2w)：**

Yield: 45.2 mg (63%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.24 (m, 5H), 7.24-7.18 (m, 1H), 7.08 (dd, *J* = 10.8, 2.5 Hz, 2H), 5.44 (s, 1H), 4.86-4.56 (m, 2H), 4.07 (t, *J* = 4.1 Hz, 1H), 2.83-2.57 (m, 2H), 2.13 (ddd, *J* = 13.6, 6.3, 3.2 Hz, 1H), 1.99-1.85 (m, 1H), 1.81-1.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 137.9, 133.4, 132.9, 131.2, 128.9, 128.6, 128.4, 127.9, 126.0, 76.8, 57.5, 29.4, 26.3, 18.1. HRMS-ESI (m/z): calcd for $C_{17}H_{19}ClNO$, [M+H]: 288.1155, found 288.1144.

***O*-benzyl-*N*-(1-phenylbutyl)hydroxylamine (2x):**

Yield: 40.8 mg (64%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.17 (m, 10H), 5.65 (s, 1H), 4.56 (ddd, *J* = 28.3, 11.4, 3.4 Hz, 2H), 4.02-3.93 (m, 1H), 1.73 (td, *J* = 9.6, 5.0 Hz, 1H), 1.63-1.52 (m, 1H), 1.28-1.15 (m, 2H), 0.85 (td, *J* = 7.3, 3.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 138.0, 128.6, 128.439, 128.4, 127.9, 127.8, 127.4, 76.8, 65.8, 36.0, 19.5, 14.2.

***O*-methyl-N-(phenyl(p-tolyl)methyl)hydroxylamine (2y):**

Yield: 14.8 mg (26%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.9 Hz, 2H), 7.26 (dtd, *J* = 14.5, 7.6, 1.1 Hz, 5H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.84 (s, 1H), 5.18 (s, 1H), 3.50 (d, *J* = 1.2 Hz, 3H), 2.30 (s, 3H). ^{13}C NMR (100 Hz, $CDCl_3$) δ 141.4, 138.1, 137.2, 129.3, 128.5, 127.7, 127.6, 127.4, 69.1, 62.4, 21.2. HRMS-ESI (m/z): calcd for $C_{15}H_{18}NO$, [M+H]: 228.1388, found 228.1398.

***N*-(1-phenylethyl)hydroxylamine (2ba)：**

Yield: 24.0 mg (70%), light yellow solid, mp: 63-65℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.13 (m, 5H), 5.81 (s, 2H), 4.08 (q, *J* = 6.6 Hz, 1H), 1.37 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 128.6, 127.7, 127.3, 76.8, 61.8, 19.3. HRMS-ESI (m/z): calcd for $C_8H_{12}NO$, [M+H]: 138.0919, found 138.0910.

***N*-(1-(4-fluorophenyl)ethyl)hydroxylamine (2bb)**[24]

Yield: 34.9 mg (90%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.20 (m, 2H), 7.08-6.89 (m, 2H), 5.72 (s, 2H), 4.07 (q, *J* = 6.7 Hz, 1H), 1.35 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 244 Hz), 138.0 (d, *J* = 3 Hz), 128.8 (d, *J* = 8 Hz), 115.4 (d, *J* = 21 Hz), 61.1, 19.4.

***N*-(1-(4-chlorophenyl)ethyl)hydroxylamine (2bc)**[25]

Yield: 35.9 mg (84%), white solid, mp: 68-73^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 22.2, 8.4 Hz, 4H), 5.34 (s, 2H), 4.07 (dd, *J* = 13.3, 6.6 Hz, 1H), 1.34 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 133.3, 128.7, 128.6, 61.1, 19.3.

***N*-(1-(p-tolyl)ethyl)hydroxylamine (2bd)**[24]

Yield: 33.6 mg (89%), white solid, mp: 66-72°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 5.85 (s, 2H), 4.04 (q, J = 6.6 Hz, 1H), 2.32 (s, 3H), 1.36 (d, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.4, 129.3, 127.2, 61.5, 21.2, 19.3.

***N*-(1-(4-(tert-butyl)phenyl)ethyl)hydroxylamine (2be)**

Yield: 38.1 mg (79%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 5.04 (s, 2H), 4.07 (q, J = 6.6 Hz, 1H), 1.38 (d, J = 6.7 Hz, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 138.9, 126.94, 125.5, 61.4, 34.5, 31.4, 19.1. HRMS-ESI (m/z): calcd for $C_{12}H_{20}NO$, [M+H]: 194.1545, found 194.1541.

***N*-(1-(naphthalen-2-yl)ethyl)hydroxylamine (2bf)**[26]

Yield: 40.7 mg (87%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.73 (m, 4H), 7.62-7.35 (m, 3H), 5.14 (s, 2H), 4.24 (dd, J = 13.2, 6.6 Hz, 1H), 1.43 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 133.4, 133.0, 128.3, 127.9, 127.7, 126.2, 126.1, 125.9, 125.1, 61.9, 19.4.

***N*-(1-(furan-2-yl)ethyl)hydroxylamine (2bg)**[29]

Yield: 8.3 mg (26%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.31 (m, 1H), 6.41-6.29 (m, 1H), 6.28-6.17 (m, 1H), 5.30 (s, 2H), 4.17 (q, J = 6.8 Hz, 1H), 1.43 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 141.9, 110.2, 106.8, 55.2, 16.2.

***N*,*O*-dibenzylhydroxylamine (2bh)：**

Yield: 16.0 mg (30%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.18 (m, 10H), 5.72 (s, 1H), 4.66 (s, 2H), 4.05 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.6, 129.0, 128.5, 128.4, 128.4, 127.8, 127.5, 76.3, 56.6. HRMS-ESI (m/z): calcd for $C_{14}H_{16}NO$, [M+H]: 214.1232, found 214.1242.

***O*-benzyl-*N*-(4-fluorobenzyl)hydroxylamine (2bi)：**

Yield: 11.6 mg (20%), yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dt, J = 12.1, 4.2 Hz, 7H), 7.00 (t, J = 8.5 Hz, 2H), 5.68 (s, 1H), 4.62 (s, 2H), 4.00 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 244 Hz), 137.8, 133.5 (d, J = 3 Hz), 130.6 (d, J = 8 Hz), 128.5, 128.4, 127.9, 115.2 (d, J = 21 Hz), 76.4, 55.7. HRMS-ESI (m/z): calcd for $C_{14}H_{15}FNO$, [M+H]: 232.1138, found 238.1141.

***O*-benzyl-*N*-(4-methylbenzyl)hydroxylamine (2bj)：**

Yield: 14.2 mg (25%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.26 (m, 5H), 7.26-7.20 (m, 2H), 7.14 (d, J = 7.7 Hz, 2H), 5.68 (s, 1H), 4.66 (s, 2H), 4.01 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.1, 134.5, 129.1, 128.9, 128.5, 128.4, 127.8, 76.3, 56.3, 21.2. HRMS-ESI (m/z): calcd for $C_{15}H_{18}NO$, [M+H]: 228.1388, found 228.1388.

***O*-benzyl-*N*-(naphthalen-2-ylmethyl)hydroxylamine (2bk)：**

Yield: 20.4 mg (31%), light yellow solid, mp: 61-63℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.70 (m, 4H), 7.47 (dd, J = 11.3, 6.7 Hz, 3H), 7.38-7.24 (m, 5H), 5.82 (s, 1H), 4.66 (s, 2H), 4.21 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 135.2, 133.4, 132.9, 128.5, 128.4, 128.1, 127.8, 127.8, 127.7, 127.1, 126.1, 125.8, 76.4, 56.7. HRMS-ESI (m/z): calcd for $C_{18}H_{18}NO$, [M+H]: 264.1388, found 264.1391.

***O*-benzyl-*N*-(furan-2-ylmethyl)hydroxylamine (2bl)：**

Yield: 12.2 mg (22%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.10 (m, 6H), 6.48-6.13 (m, 2H), 5.41 (d, J = 234.9 Hz, 1H), 4.67 (s, 2H), 4.05 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 142.1, 137.8, 128.4, 128.4, 127.9, 110.4, 108.3, 76.3, 49.0. HRMS-ESI (m/z): calcd for $C_{12}H_{14}NO_2$, [M+H]: 204.1025, found 204.1011.

***O*-benzyl-*N*-isopropylhydroxylamine (2aa):**

Yield: 21.5 mg (52%), colorless oil ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.26 (m, 5H), 5.93-4.93 (m, 1H), 4.72 (s, 2H), 3.20 (dt, J = 12.6, 6.3 Hz, 1H), 1.07 (d, J = 6.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 128.4, 128.4, 127.8, 76.8, 51.7, 20.2. HRMS-ESI (m/z): calcd for $C_{10}H_{16}NO$, [M+H]: 166.1232, found 166.1243.

***O*-benzyl-*N*-(3,3-dimethylbutan-2-yl)hydroxylamine (2ab):**

Yield: 7.8 mg (15%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.24 (m, 5H), 5.42 (s, 1H), 4.67 (s, 2H), 2.87-2.70 (m, 1H), 1.09 (d, J = 6.4 Hz, 3H), 0.89 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 128.5, 128.3, 127.7, 76.3, 64.3, 33.2, 26.8, 13.9. HRMS-ESI (m/z): calcd for $C_{13}H_{22}NO$, [M+H]: 208.1701, found 208.1709.

***O*-benzyl-*N*-(pentan-3-yl)hydroxylamine (2ac):**

Yield: 35.7 mg (74%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 5H), 5.96-5.03 (m, 1H), 4.69 (s, 2H), 2.77-2.68 (m, 1H), 1.52-1.42 (m, 4H), 0.89 (t, J = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 128.4, 128.4, 127.8, 76.6, 63.2, 24.0, 10.2.

***O*-benzyl-*N*-(pentan-2-yl)hydroxylamine (2ad):**

Yield: 41.5 mg (86%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.21 (m, 5H), 5.30 (s, 1H), 4.70 (s, 2H), 3.03 (dt, J = 12.3, 6.2 Hz, 1H), 1.52-1.44 (m, 1H), 1.39-1.19 (m, 4H), 1.06 (d, J = 6.4 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 128.4, 127.8, 76.8, 56.0, 36.3, 19.2, 18.3, 14.3.

***O*-benzyl-*N*-cyclohexylhydroxylamine (2af):**

Yield: 48.8 mg (95%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.18 (m, 5H), 5.06 (d, J = 112.2 Hz, 1H), 4.70 (s, 2H), 2.88 (t, J = 10.3 Hz, 1H), 1.88 (d, J = 11.5 Hz, 2H), 1.74 (d, J = 12.4 Hz, 2H), 1.62 (d, J = 12.0 Hz, 1H), 1.30-1.05 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 128.4, 128.4, 127.8, 76.8, 59.5, 30.7, 26.2, 24.7. HRMS-ESI (m/z): calcd for $C_{13}H_{20}NO$, [M+H]: 206.1545, found 206.1553.

***O*-benzyl-*N*-(5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2ag):**

Yield: 48.2 mg (68%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.26 (m, 5H), 7.09 (t, J = 7.9 Hz, 1H), 6.68 (dd, J = 17.1, 7.9 Hz, 2H), 5.56 (s, 1H), 4.76 (s, 2H), 3.81 (s, 3H), 3.40-3.30 (m, 1H), 3.03-2.84 (m, 2H), 2.70-2.53 (m, 2H), 1.61 (dtd, J = 12.8, 10.4, 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 137.9, 136.1, 128.4, 128.4, 127.9, 126.3, 125.1, 121.6, 107.1, 76.7, 55.9, 55.3, 33.7, 26.5, 21.7. HRMS-ESI (m/z): calcd for $C_{18}H_{22}NO_2$, [M+H]: 284.1651, found 284.1648.

***N*-cyclohexyl-*O*-methylhydroxylamine (2ah):**

Yield: 29.4 mg (91%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (s, 1H), 3.54 (s, 3H), 2.83 (dd, J = 8.7, 5.4 Hz, 1H), 1.95-1.67 (m, 4H), 1.36-1.00 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.7, 62.6, 59.3, 30.6, 26.1, 24.6. HRMS-ESI (m/z): calcd for $C_7H_{16}NO$, [M+H]: 130.1232, found 130.1233.

***O*-benzyl-*N*-(4-phenylbutan-2-yl)hydroxylamine (2ai):**

Yield: 60.0 mg (94%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.19 (m, 7H), 7.15 (d, J = 6.9 Hz, 3H), 5.34 (s, 1H), 4.69 (s, 2H), 3.05 (dd, J = 12.5, 6.2 Hz, 1H), 2.62 (dt, J = 14.0, 7.0 Hz, 2H), 1.91 -1.76 (m, 1H), 1.67-1.52 (m, 1H), 1.10 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 138.1, 128.5, 127.9, 125.9, 76.8, 55.8, 35.9, 32.4, 18.3. HRMS-ESI (m/z): calcd for $C_{17}H_{22}NO$, [M+H]: 256.1701, found 256.1714.

***O*-benzyl-*N*-cyclobutylhydroxylamine (2aj):**

Yield: 38.1 mg (86%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.12 (m, 5H), 5.42 (s, 1H), 4.72 (s, 2H), 3.75-3.60 (m, 1H), 2.21-2.07 (m, 2H), 1.94-1.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 128.4, 128.3, 127.8, 76.4, 55.8, 27.8, 15.3. HRMS-ESI (m/z): calcd for $C_{11}H_{16}NO$, [M+H]: 178.1232, found 178.1237.

***N*-cyclohexylhydroxylamine (2ak)**[28]

Yield: 12.9 mg (45%), white solid, mp: 115-118^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 2H), 2.82 (tt, J = 10.5, 3.5 Hz, 1H), 1.91 (d, J = 11.5 Hz, 2H), 1.83-1.70 (m, 2H), 1.38-1.02 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.5, 30.3, 26.1, 24.6.

***N*-(5-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)hydroxylamine (2al)**

Yield: 40.6 mg (84%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, J = 7.9 Hz, 1H), 6.68 (dd, J = 19.5, 7.9 Hz, 2H), 5.74 (s, 2H), 3.80 (s, 3H), 3.40-3.17 (m, 1H), 3.06-2.82 (m, 2H), 2.73-2.51 (m, 2H), 2.20-2.07 (m, 1H), 1.60 (dtd, J = 12.6, 10.3, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 135.8, 126.4, 124.9, 121.6, 107.2, 57.0, 55.3, 33.2, 26.1, 21.6. HRMS-ESI (m/z): calcd for $C_{11}H_{20}N_2O$, [M+H]: 194.1181, found 194.1185.

***N*-(4-phenylbutan-2-yl)hydroxylamine (2am)**[27]

Yield: 35.5 mg (86%), white solid, mp: 58-63^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 10.8, 4.2 Hz, 2H), 7.15-7.02 (m, 3H), 6.00 (s, 2H), 3.00-2.85 (m, 1H), 2.65-2.46 (m, 2H), 1.89-1.75 (m, 1H), 1.50 (dddd, J = 17.4, 13.4, 7.7, 1.5 Hz, 1H), 1.04 (dd, J = 6.4, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 128.4, 128.3, 125.9, 56.8, 35.4, 32.3, 17.7.

Furmecyclox (BASF)[30]

Yield: 213 mg (93%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 1H), 4.23 (dd, J = 15.9, 7.6 Hz, 1H), 3.64 (s, 3H), 2.45 (s, 3H), 2.24 (s, 3H), 1.83 (s, 4H), 1.73-1.63 (m, 3H), 1.39-1.28 (m, 2H), 1.15 (ddd, J = 11.8, 10.8, 4.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 155.8, 149.4, 115.2, 106.2, 64.7, 58.2, 30.2, 25.7, 25.4, 13.7, 13.2.

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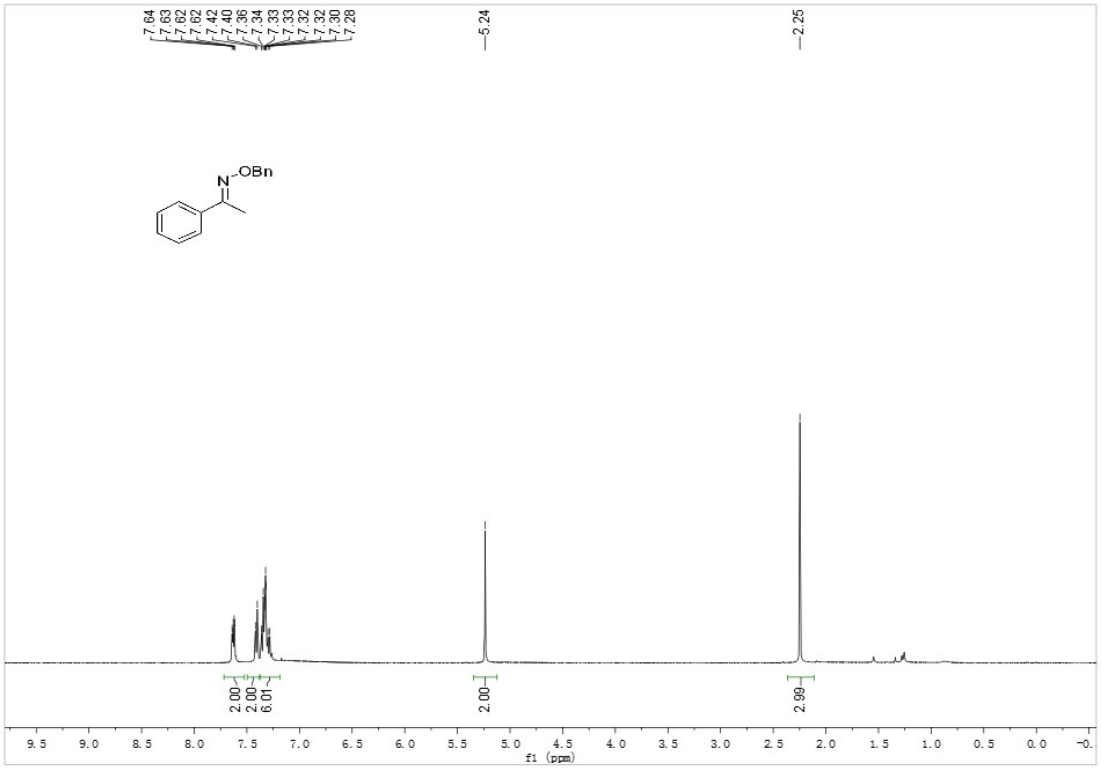
F. NMR Spectra

^{1}H NMR spectra of (*E*)-1-phenylethan-1-one *O*-benzyl oxime (1a)



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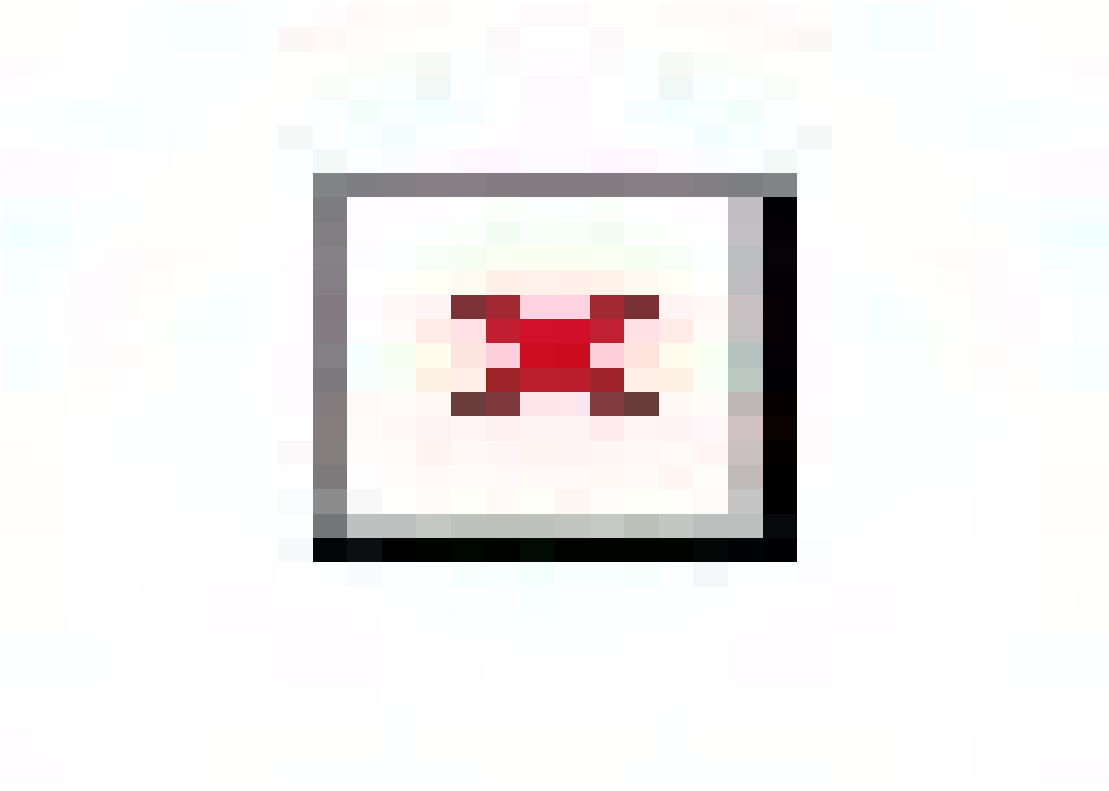
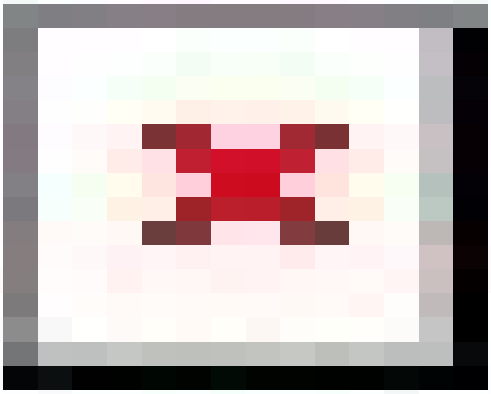


^{1}H NMR spectra of (*E*)-1-(*p*-tolyl)ethan-1-one *O*-benzyl oxime (1b)



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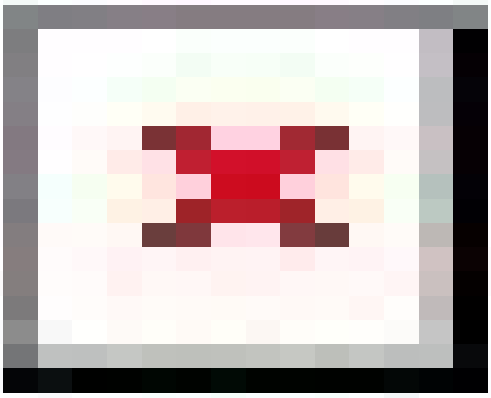

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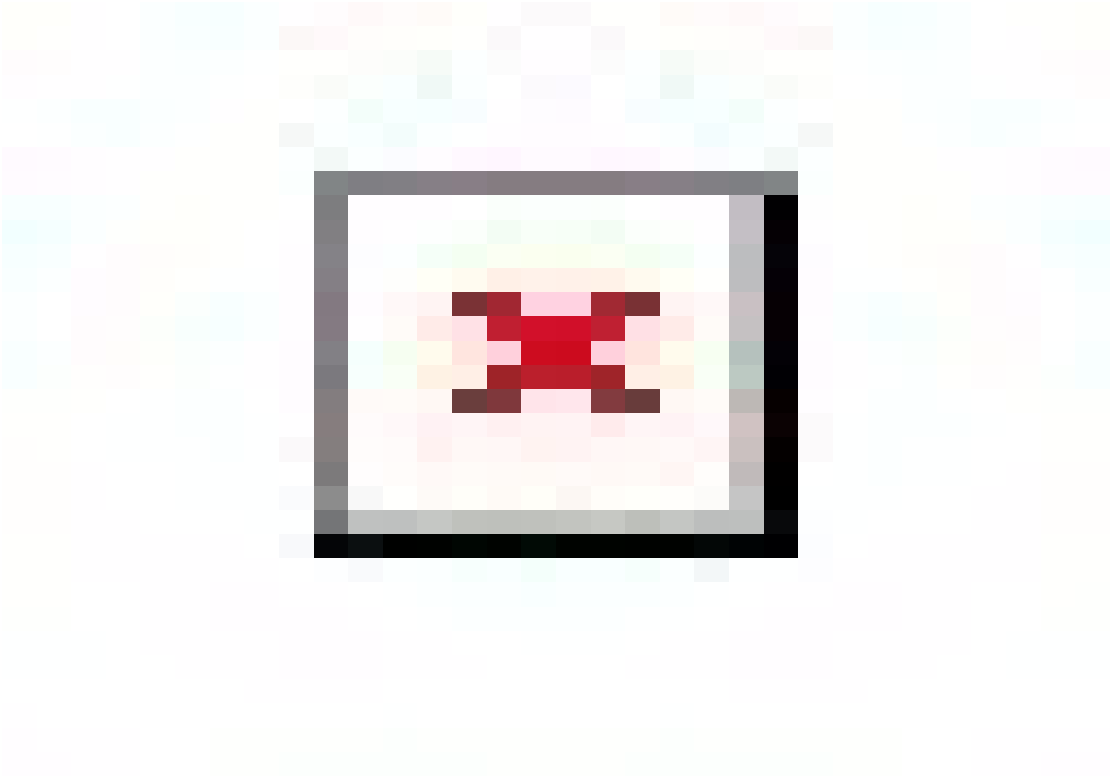

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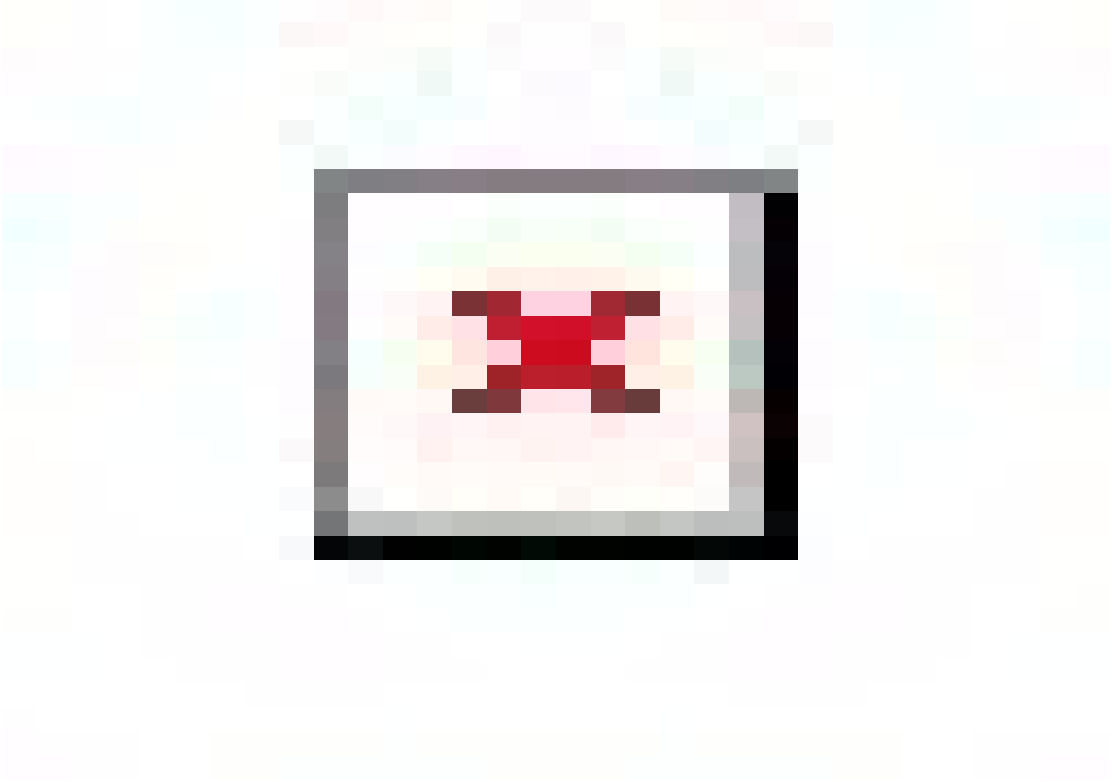

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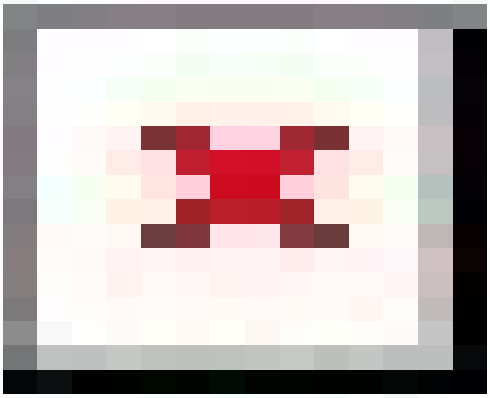

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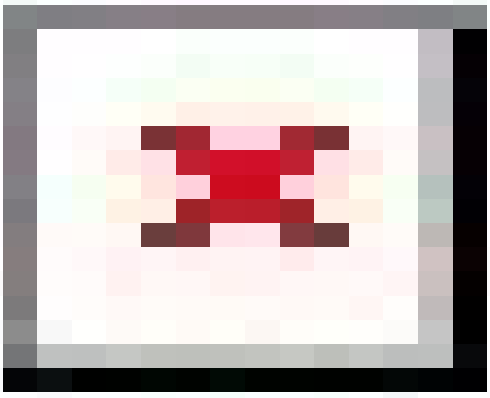

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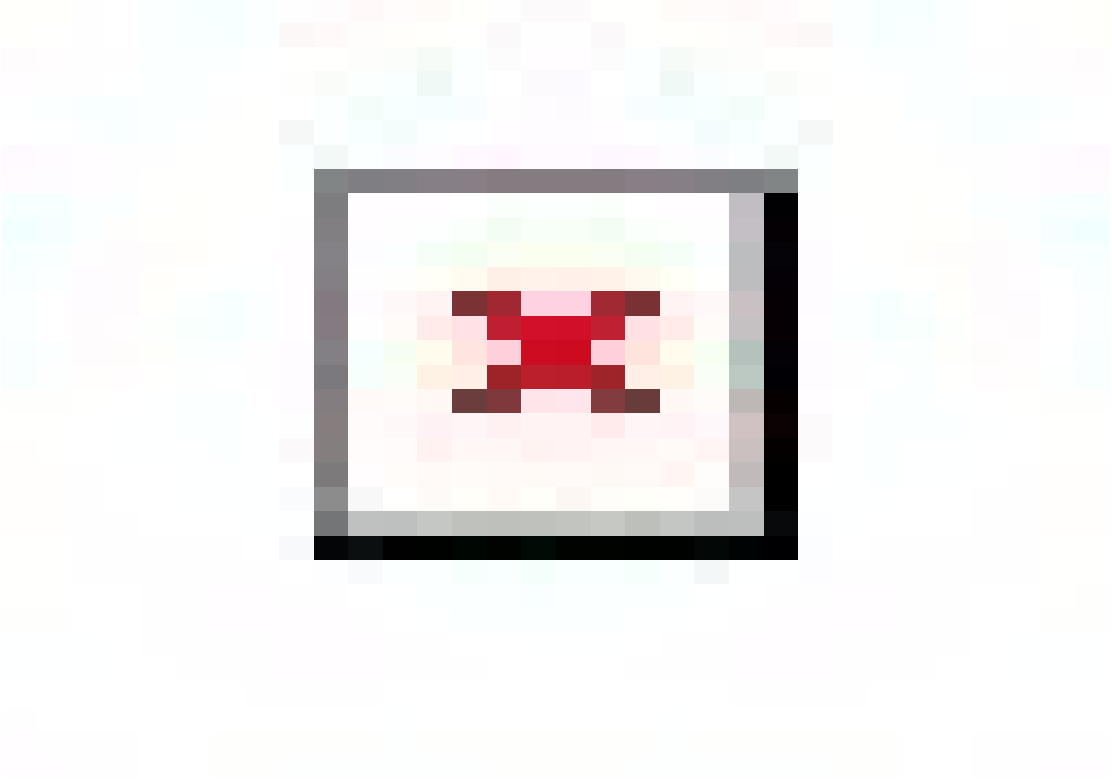

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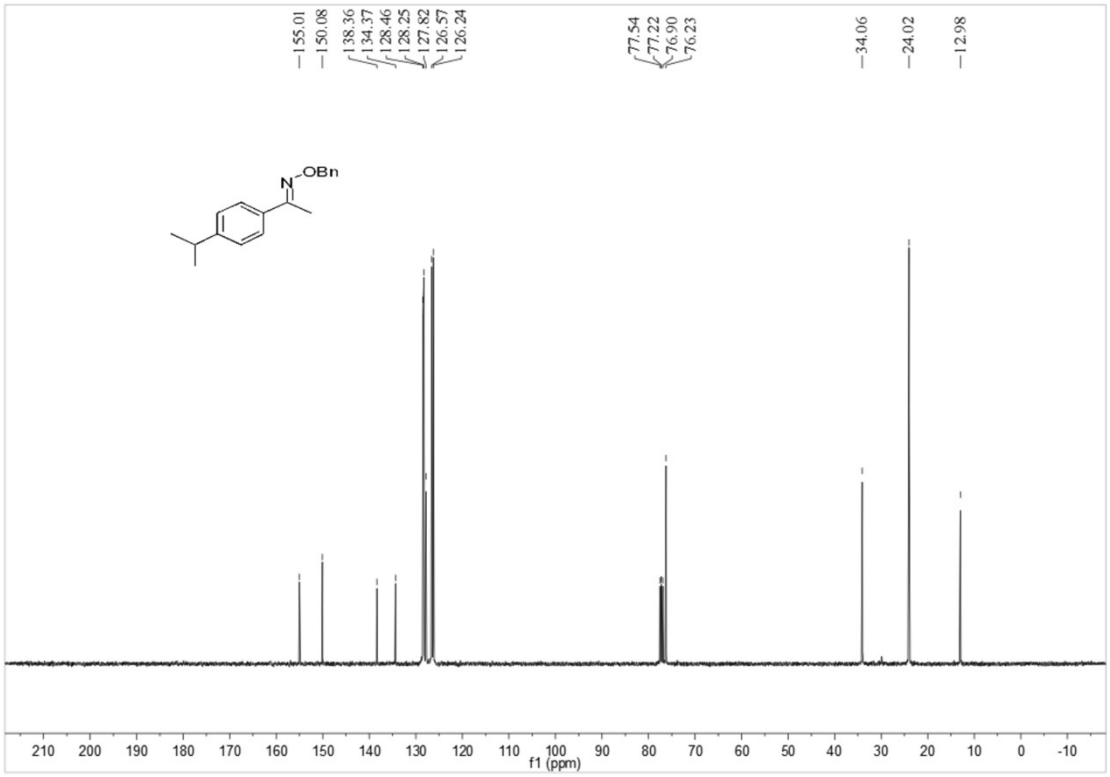
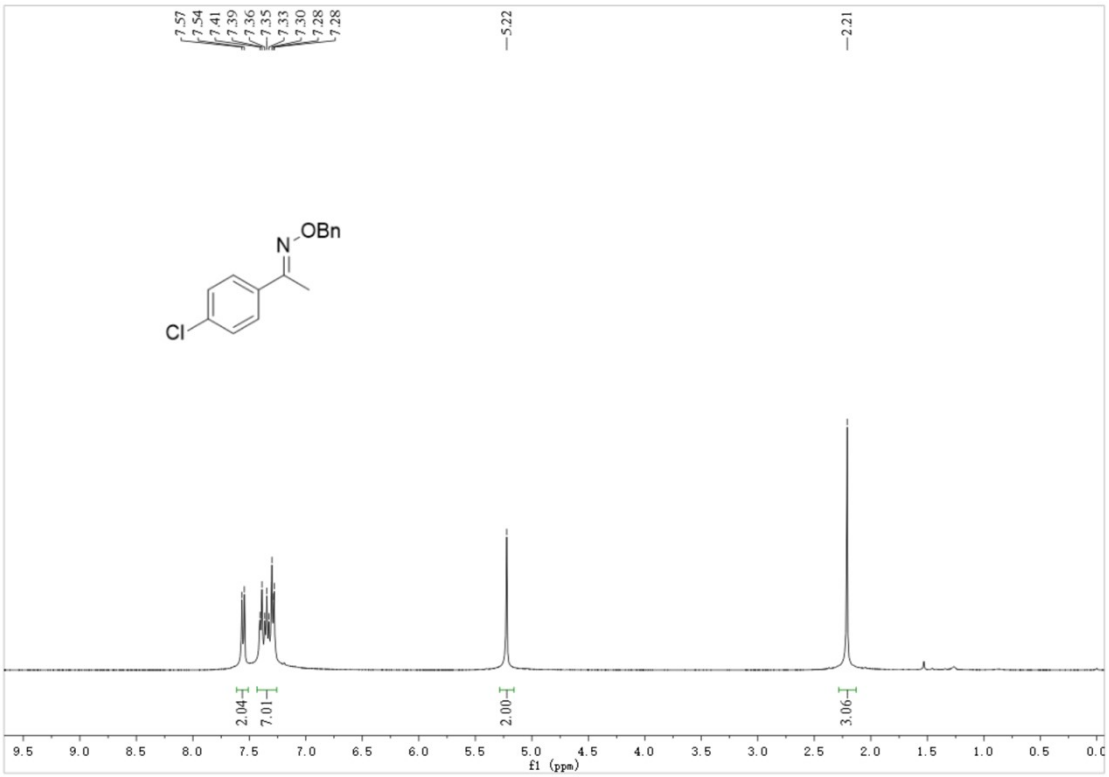


^{1}H NMR spectra of (*E*)-1-(4-chlorophenyl)ethan-1-one *O*-benzyl oxime (1f)



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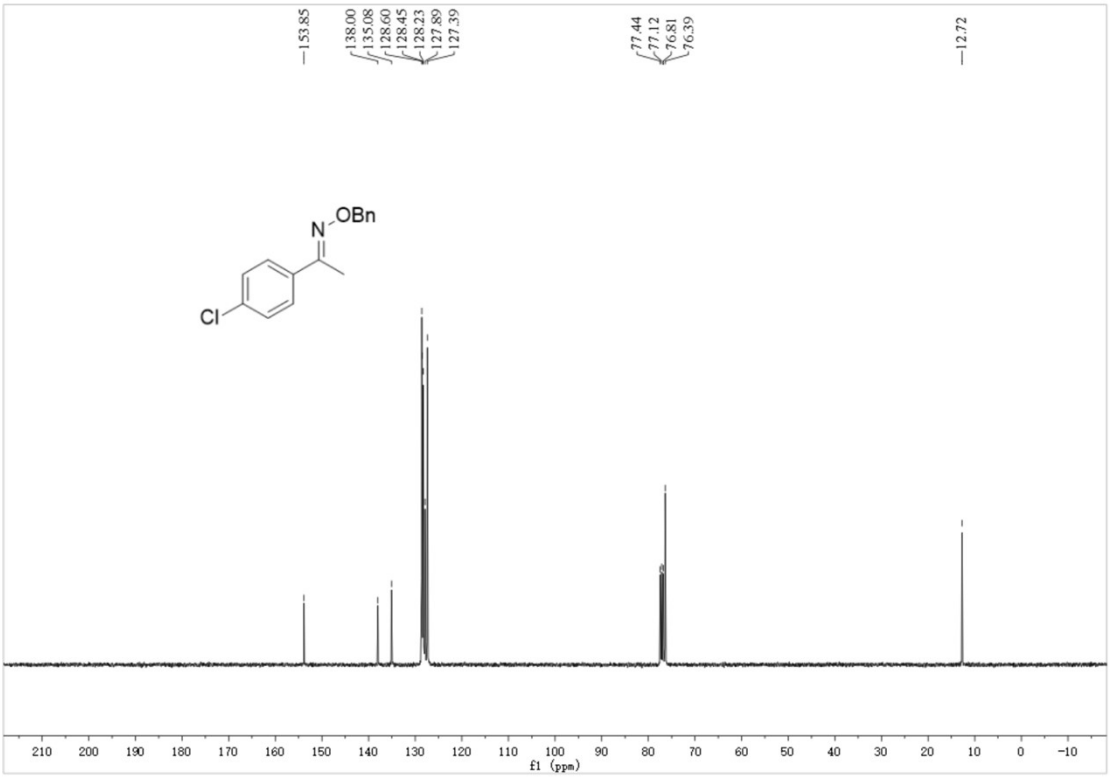

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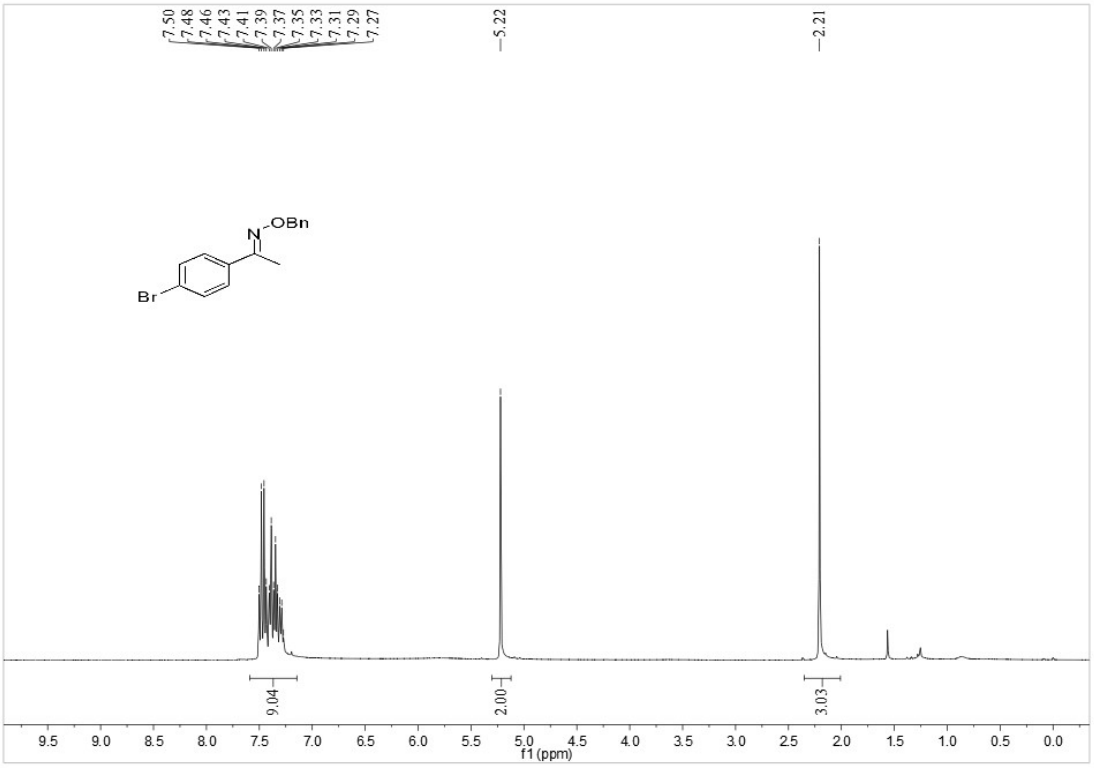

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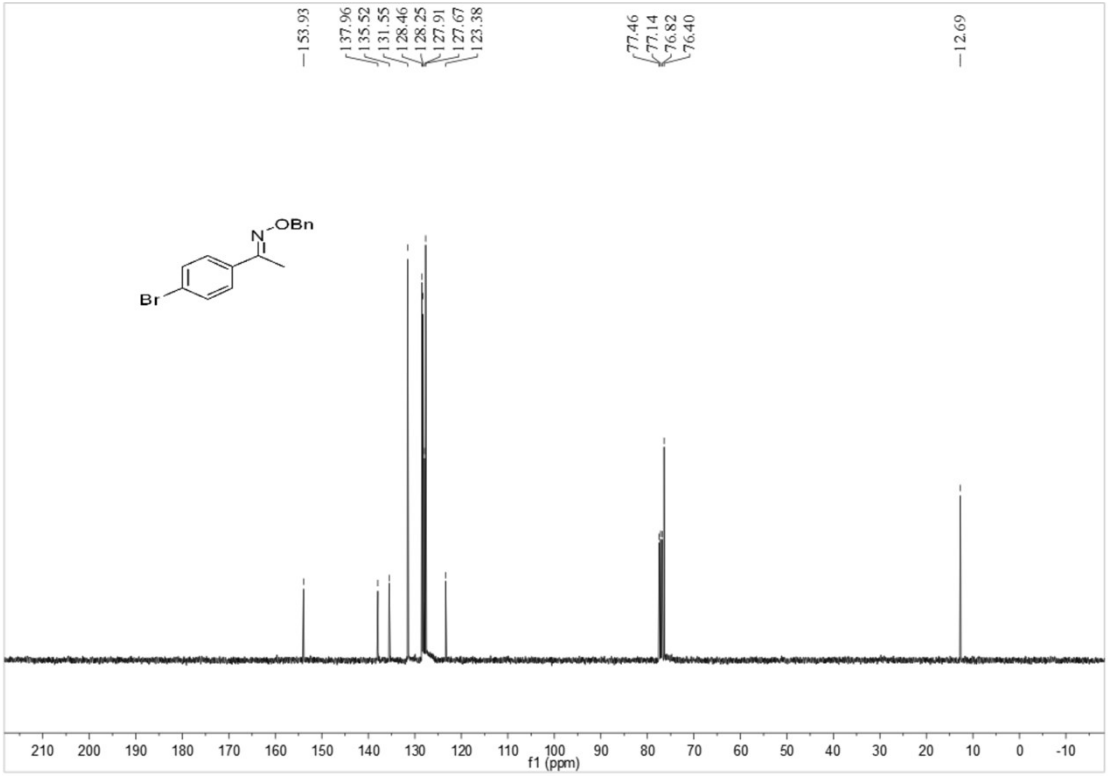
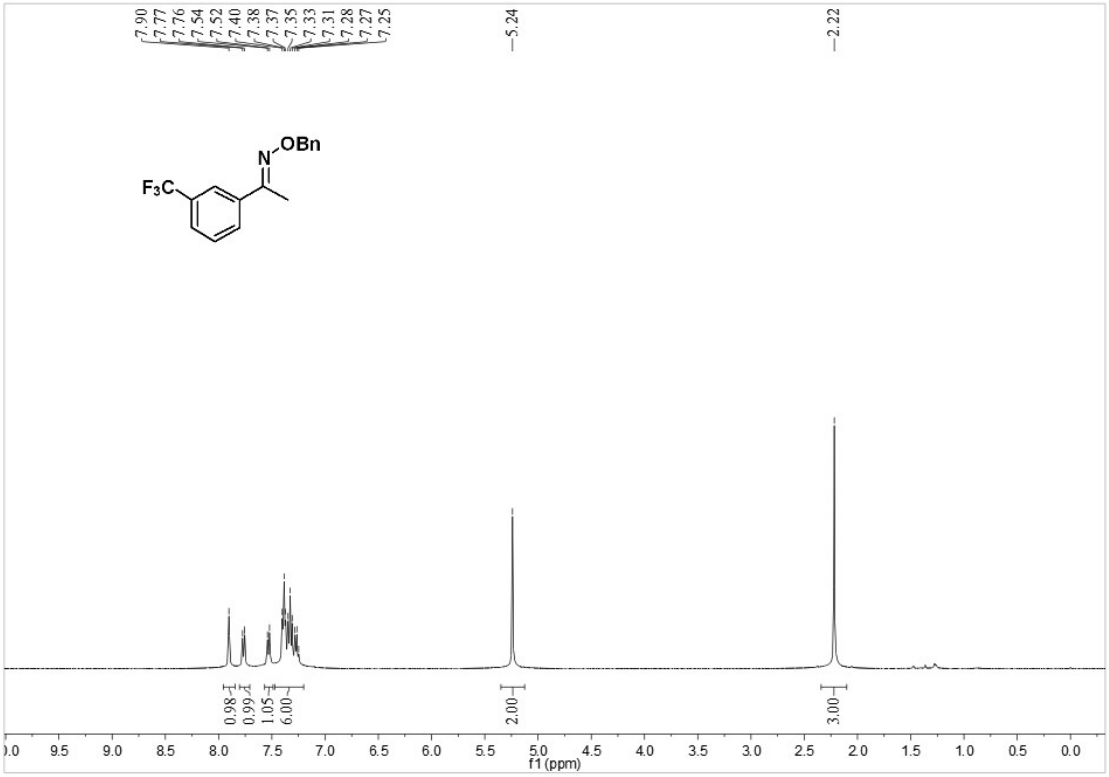


^{1}H NMR spectra of (*E*)-1-(3-(trifluoromethyl)phenyl)ethan-1-one *O*-benzyl oxime (1h)



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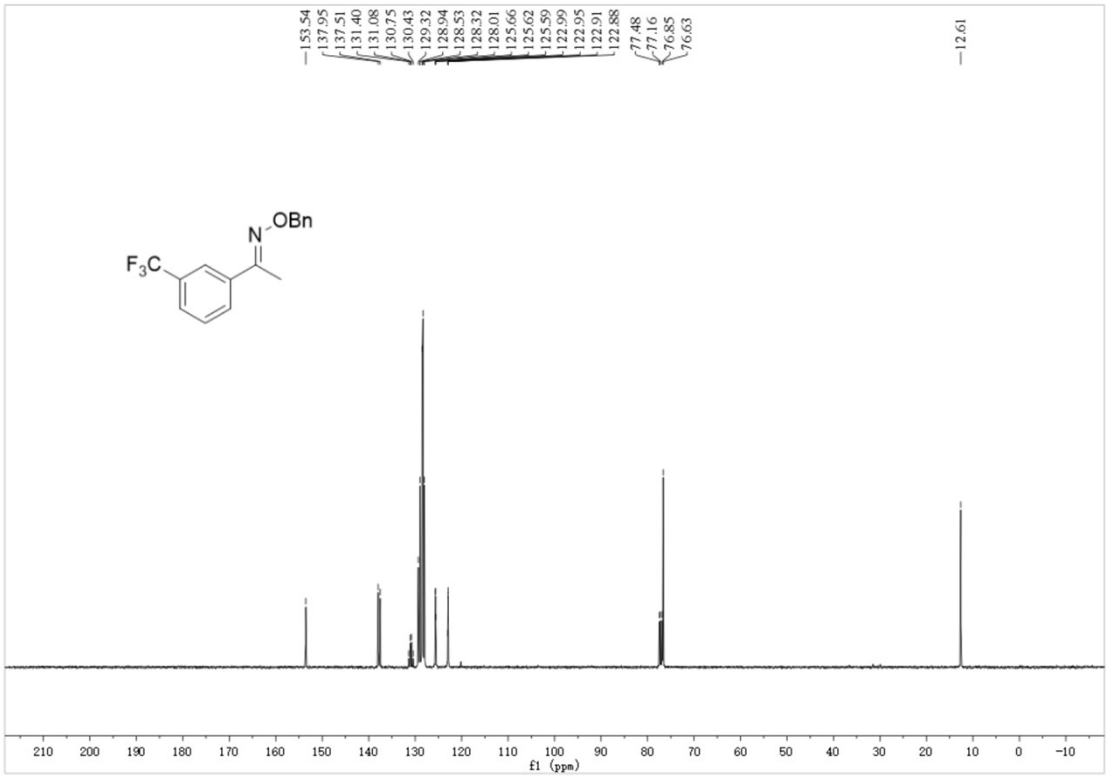
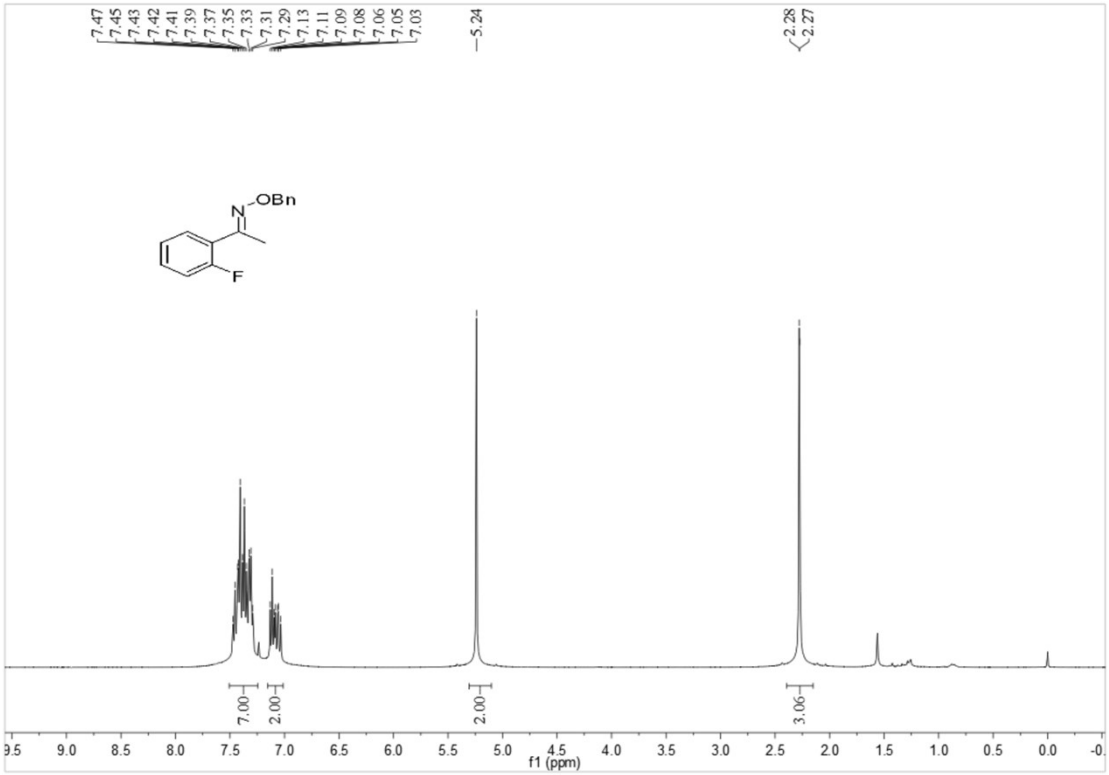


^{1}H NMR spectra of (*E*)-1-(2-fluorophenyl)ethan-1-one *O*-benzyl oxime (1i)



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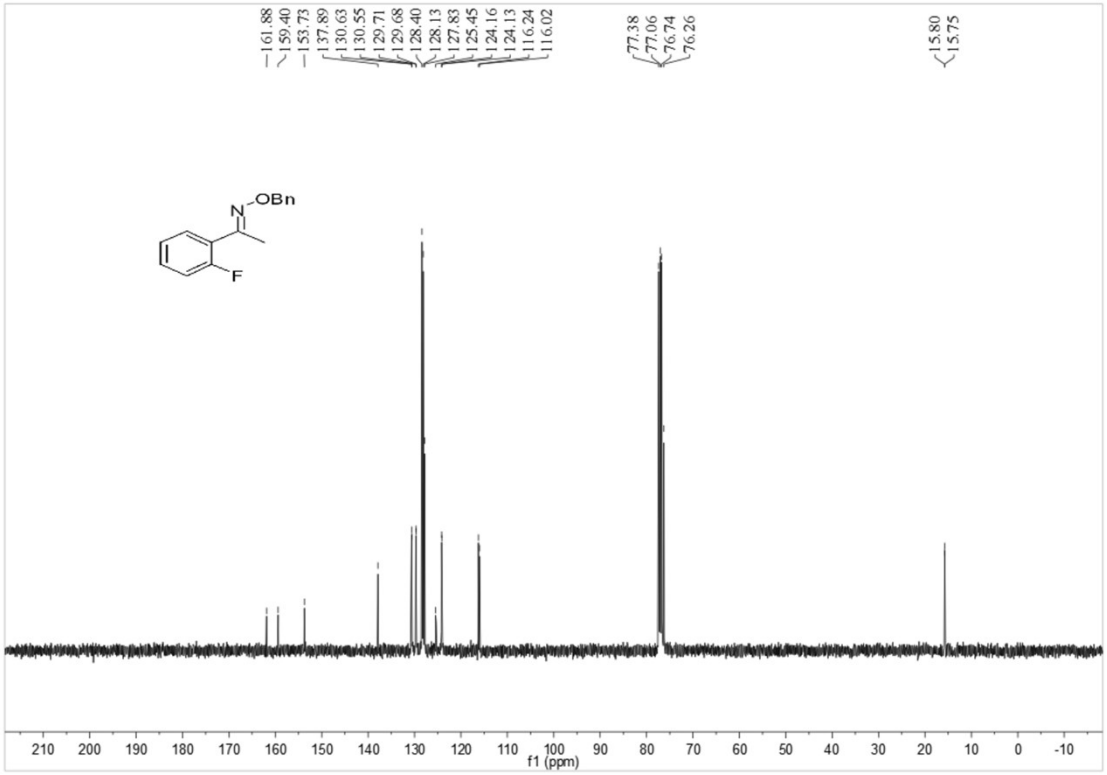
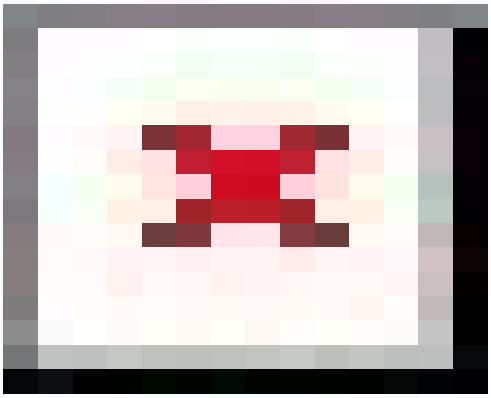


^{1}H NMR spectra of (*E*)-1-(3,5-dimethylphenyl)ethan-1-one *O*-benzyl oxime (1j)



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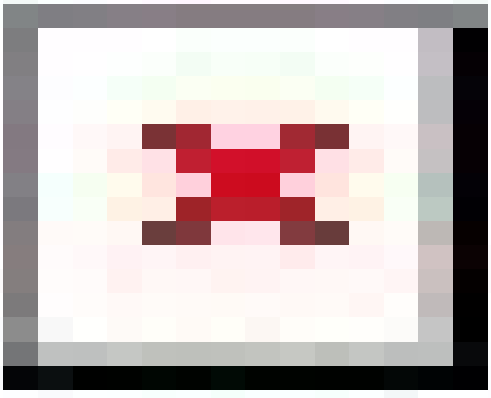
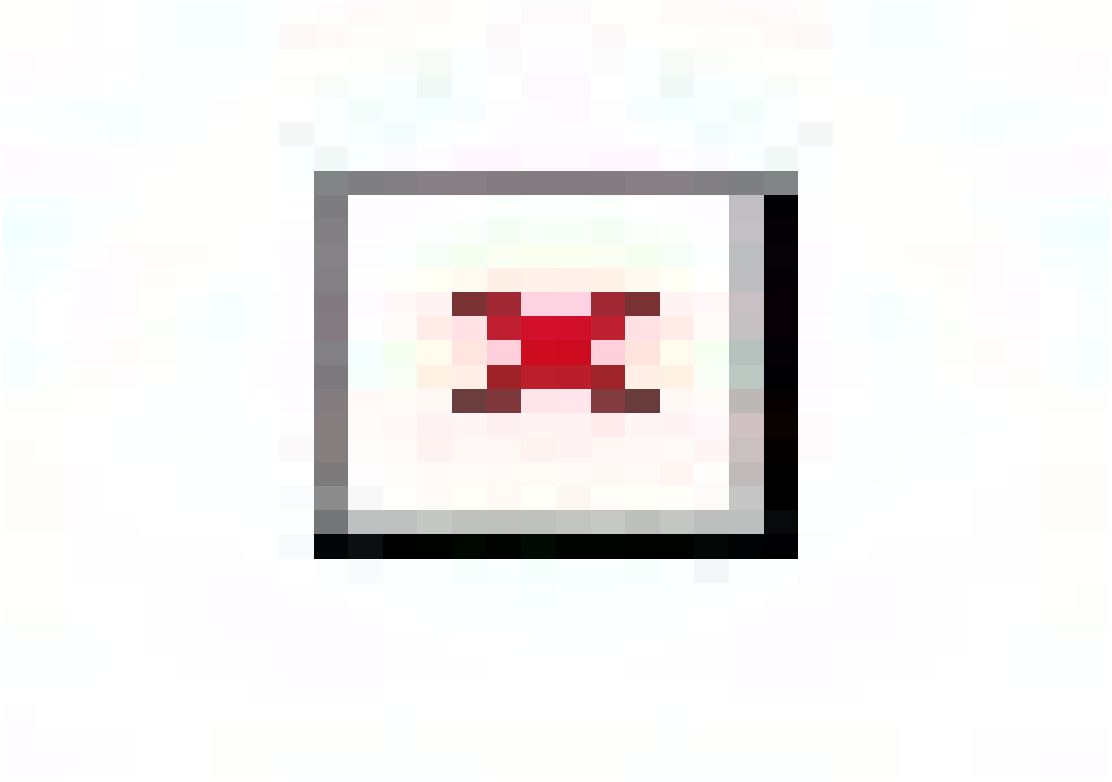


^{1}H NMR spectra of (*E*)-1-(4-fluoro-3-methoxyphenyl)ethan-1-one *O*-benzyl oxime (1k)



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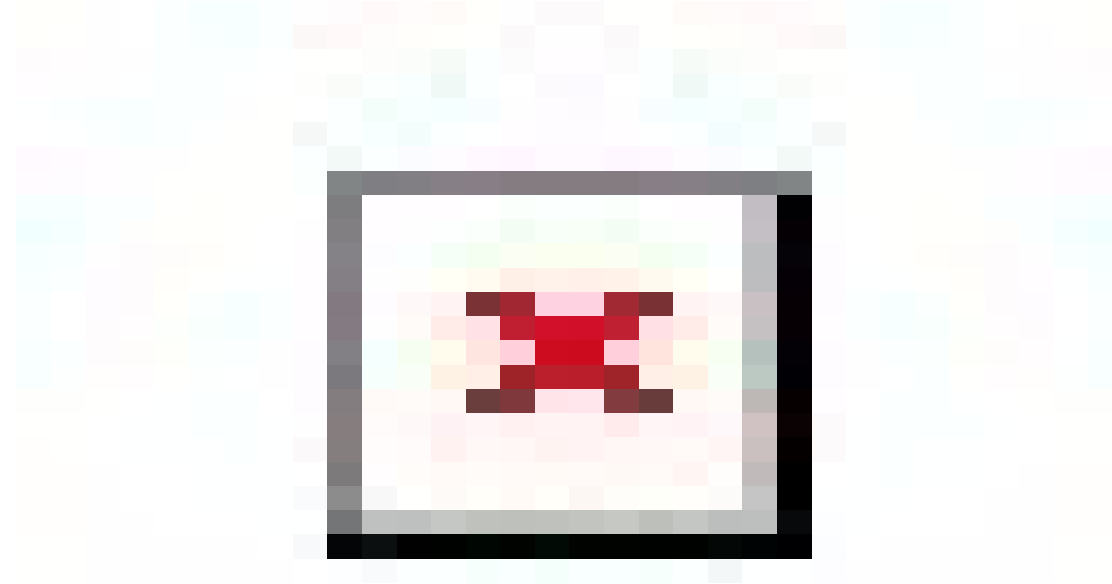

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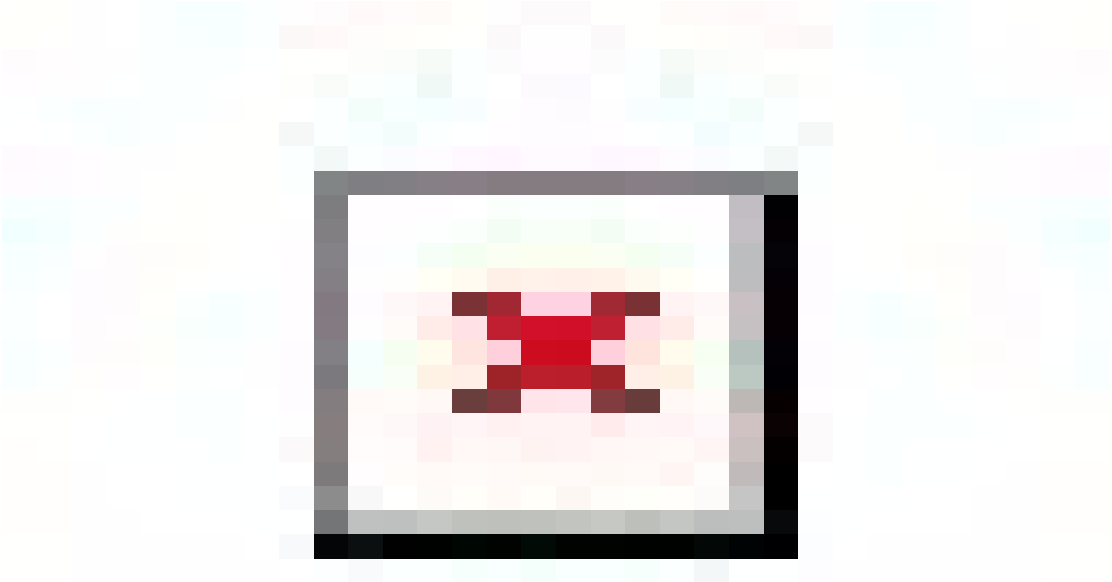

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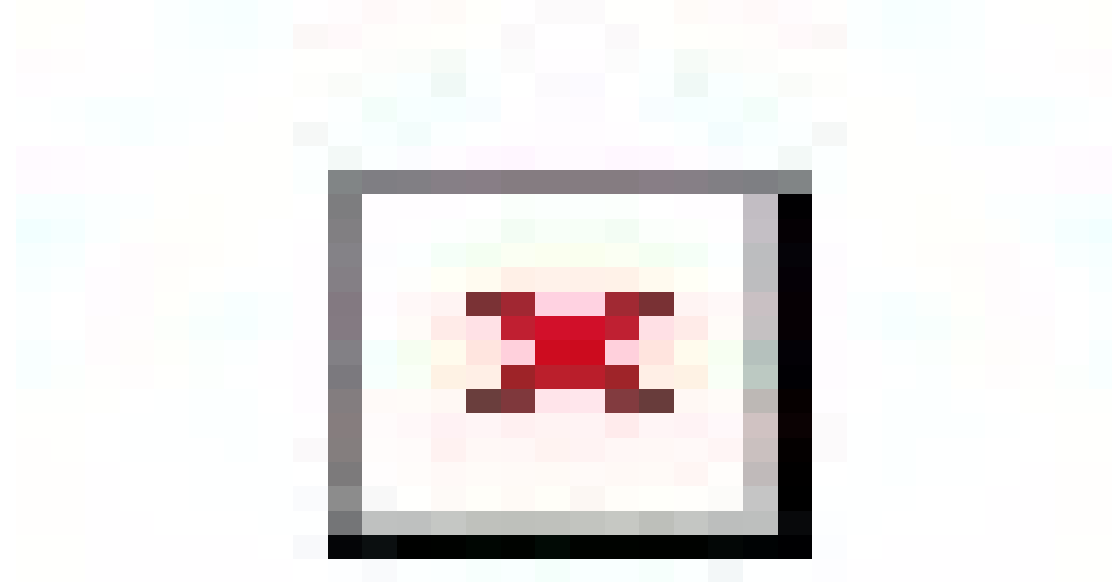

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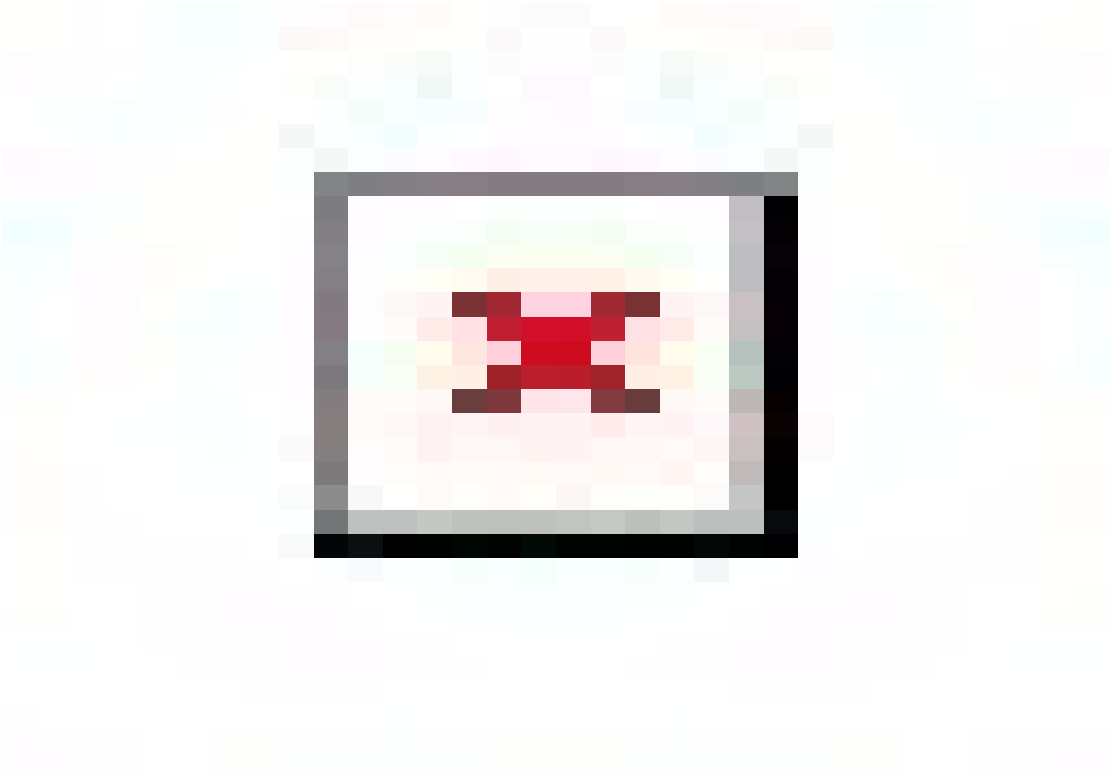

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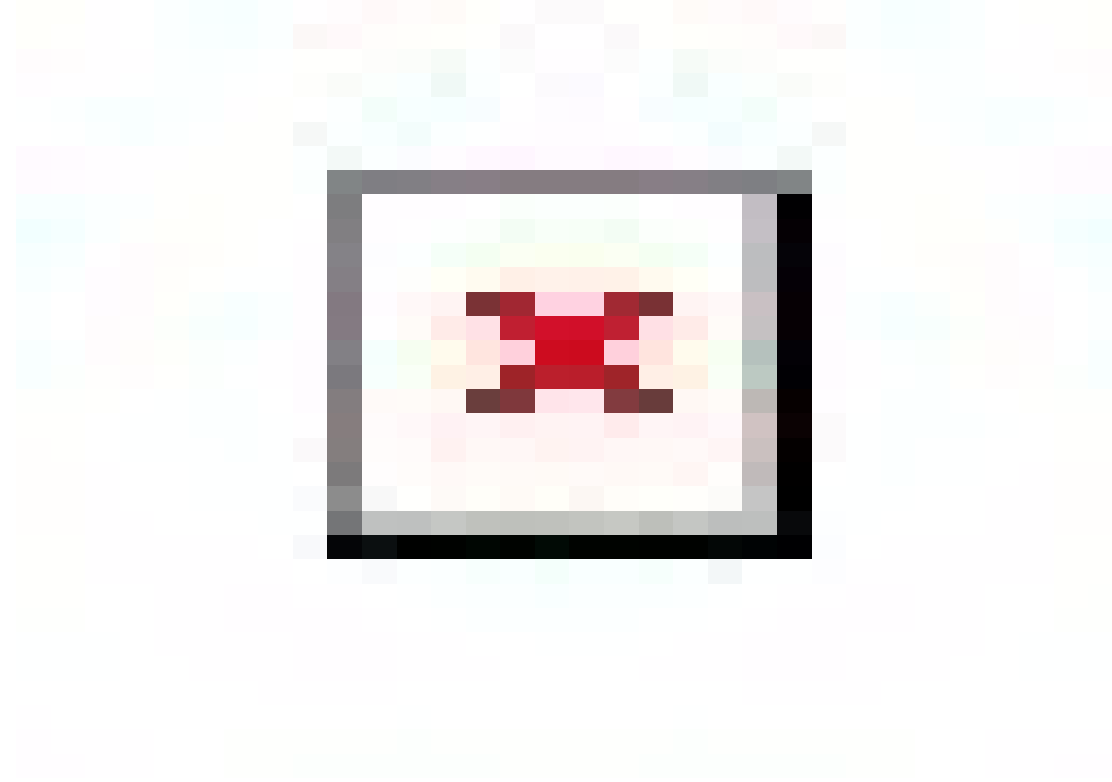
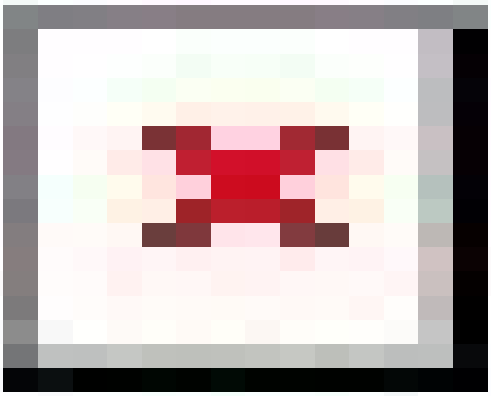


^{1}H NMR spectra of (*E*)-1-(thiophen-2-yl)ethan-1-one *O*-benzyl oxime (1n)



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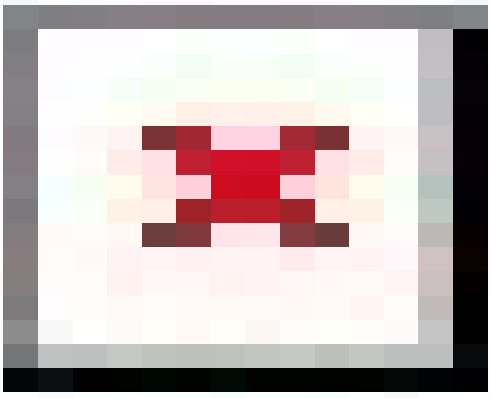

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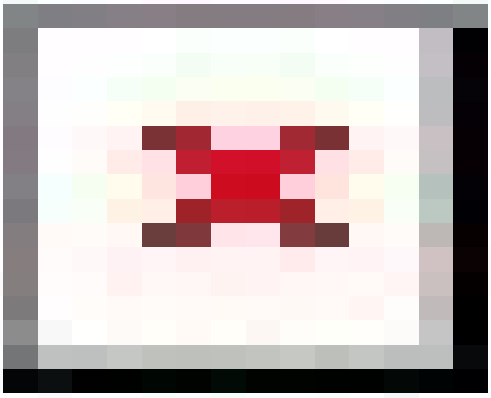
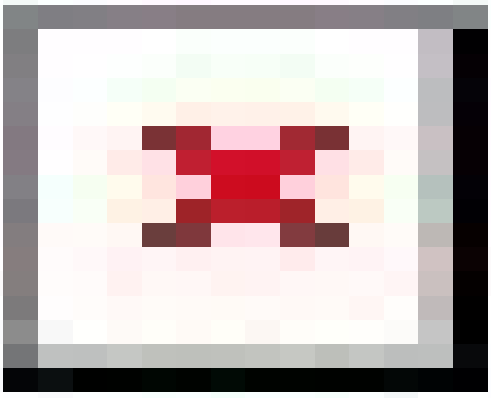
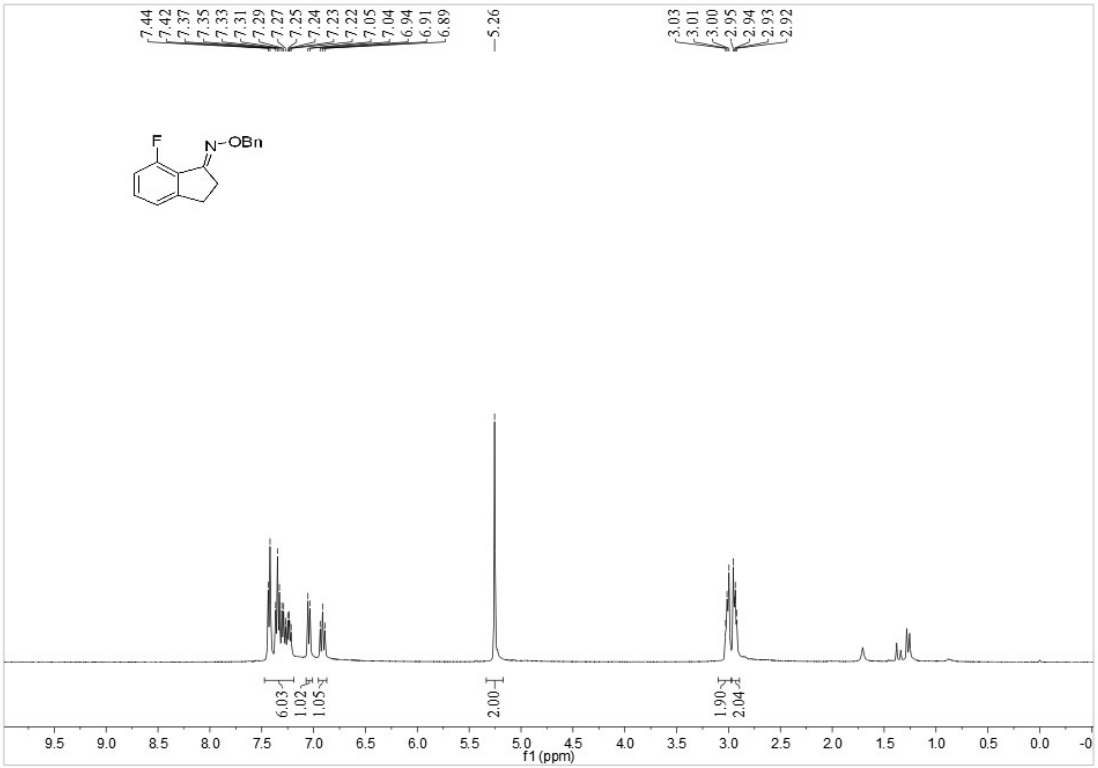


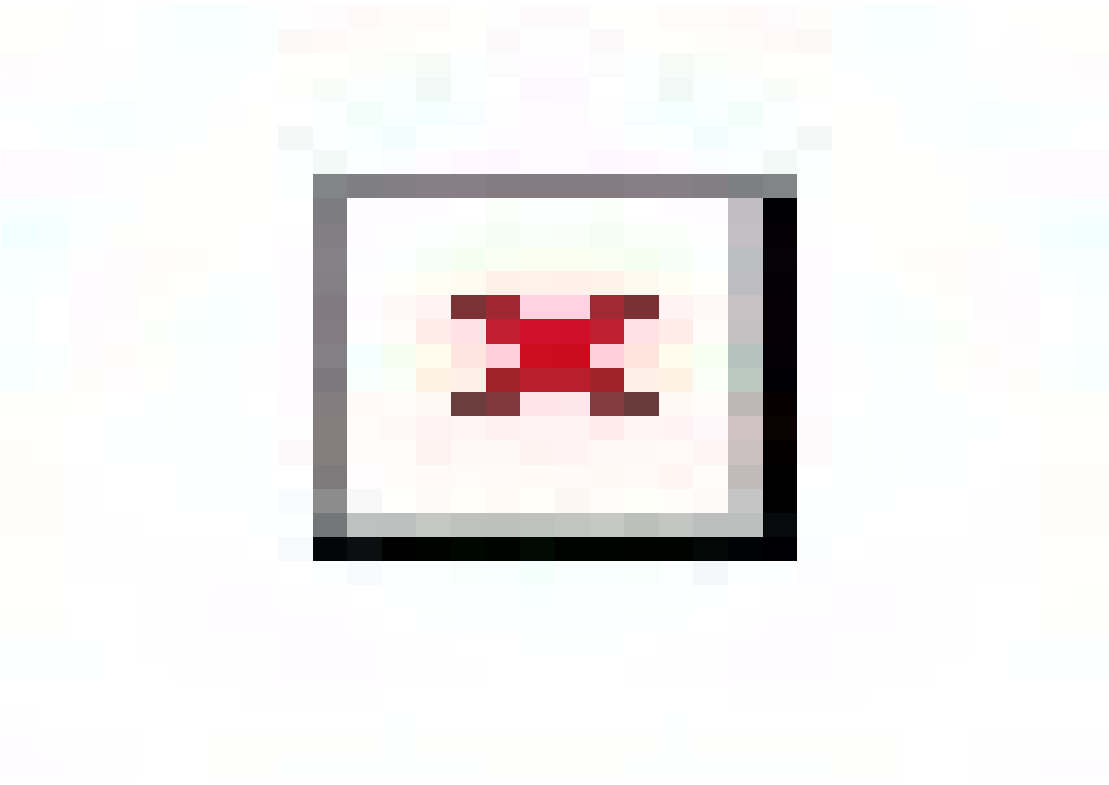
^{13}C NMR spectra of (*E*)-2,3-dihydro-1H-inden-1-one *O*-benzyl oxime (1o)



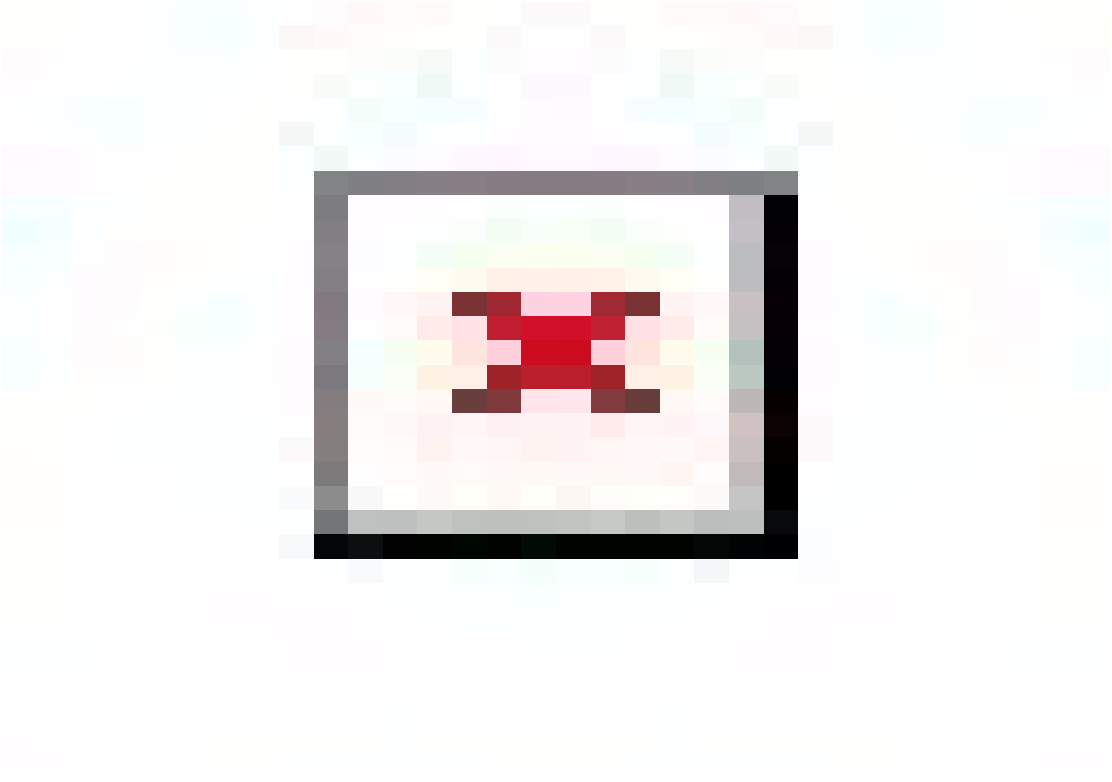
^{1}H NMR spectra of (*E*)-7-fluoro-2,3-dihydro-1H-inden-1-one *O*-benzyl oxime (1p)



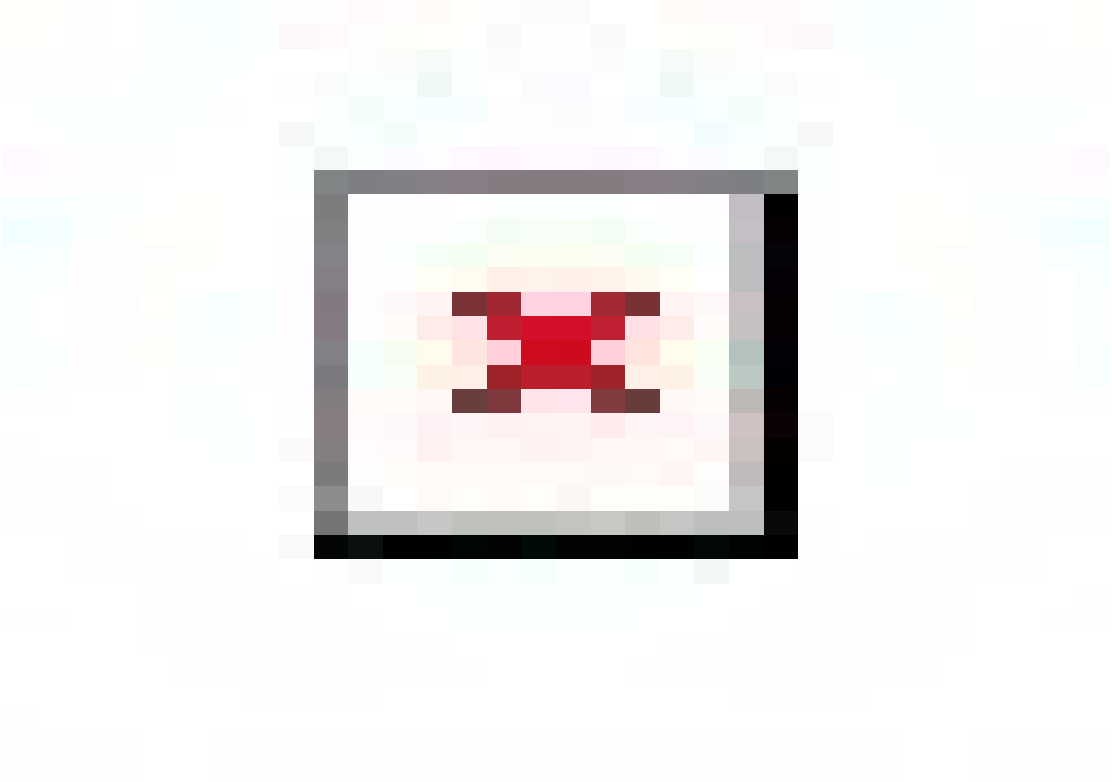
^{13}C NMR spectra of (*E*)-7-fluoro-2,3-dihydro-1H-inden-1-one *O*-benzyl oxime (1p)



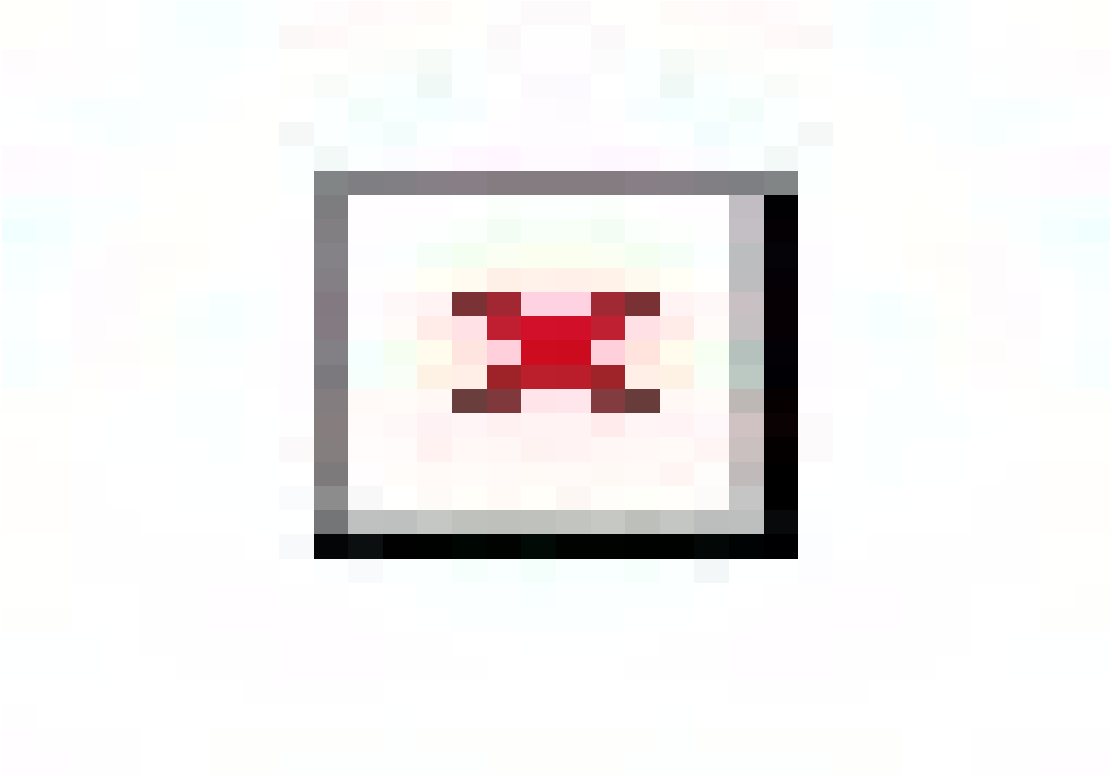
^{1}H NMR spectra of (*E*)-5-fluoro-2,3-dihydro-1H-inden-1-one *O*-benzyl oxime (1q)



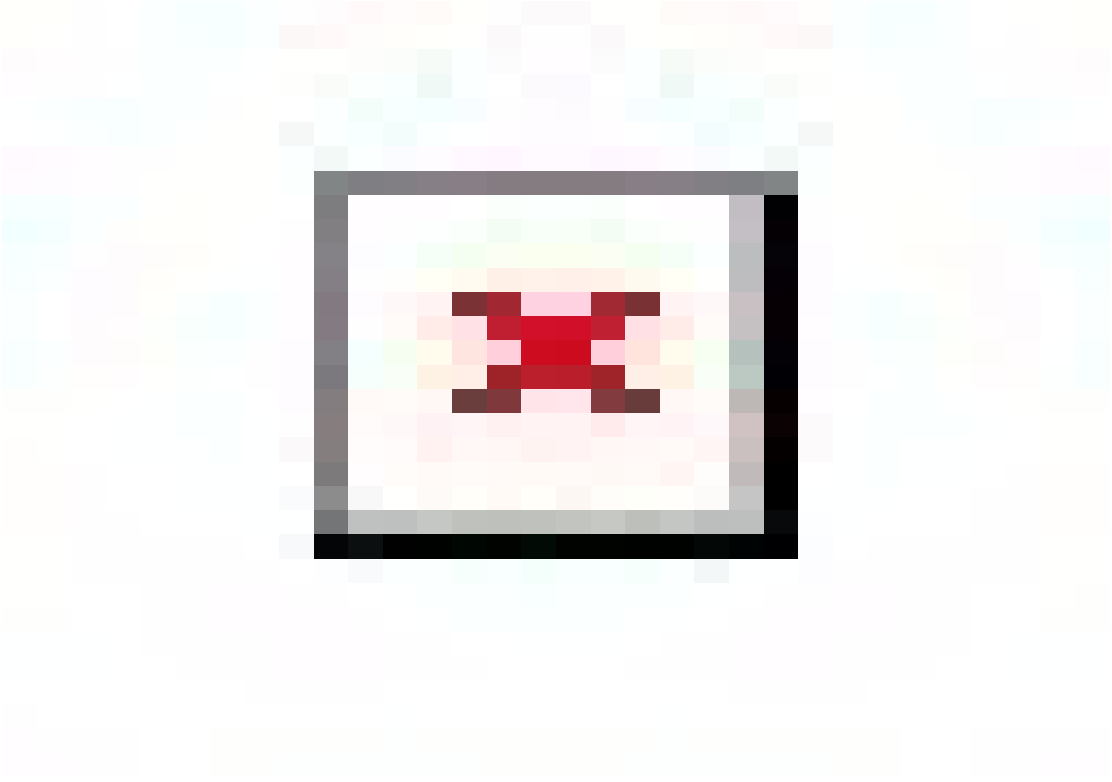
^{13}C NMR spectra of (*E*)-5-fluoro-2,3-dihydro-1H-inden-1-one *O*-benzyl oxime (1q)



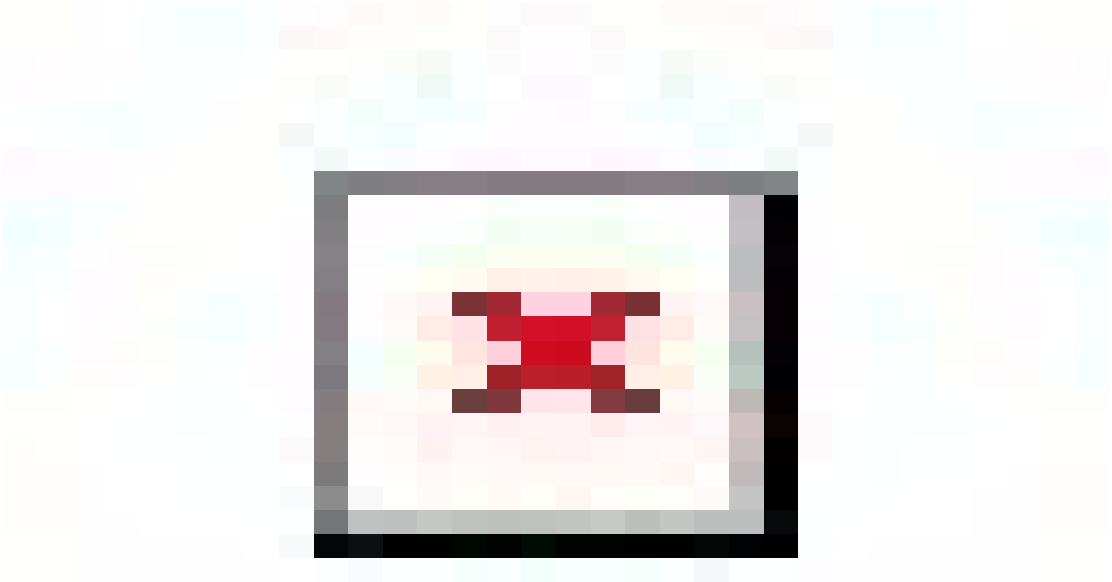
^{1}H NMR spectra of (*E*)-6-methyl-2,3-dihydro-1H-inden-1-one *O*-benzyl oxime (1r)



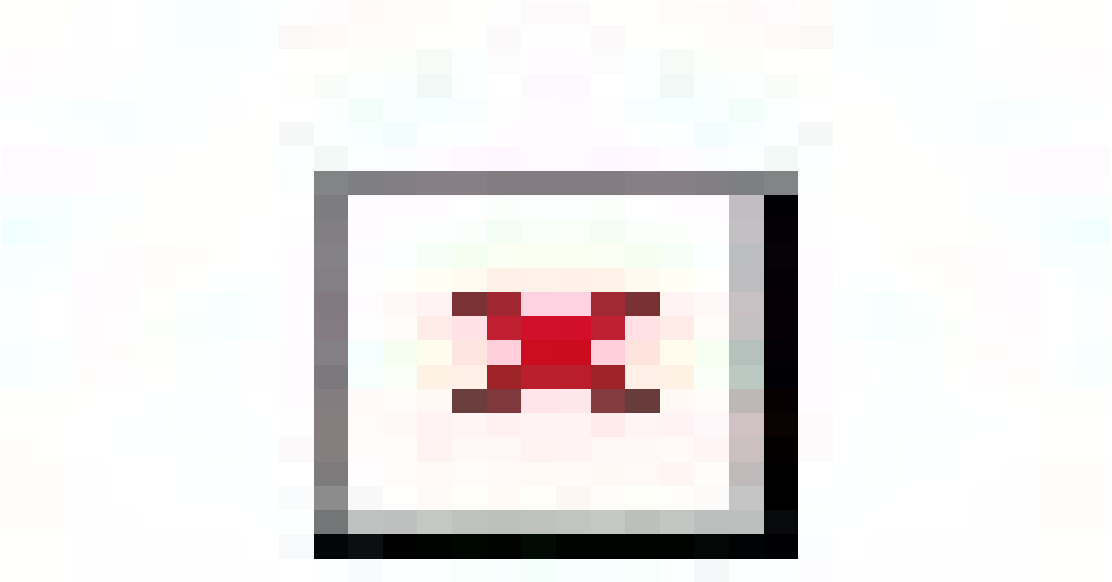
^{13}C NMR spectra of (*E*)-6-methyl-2,3-dihydro-1H-inden-1-one *O*-benzyl oxime (1r)



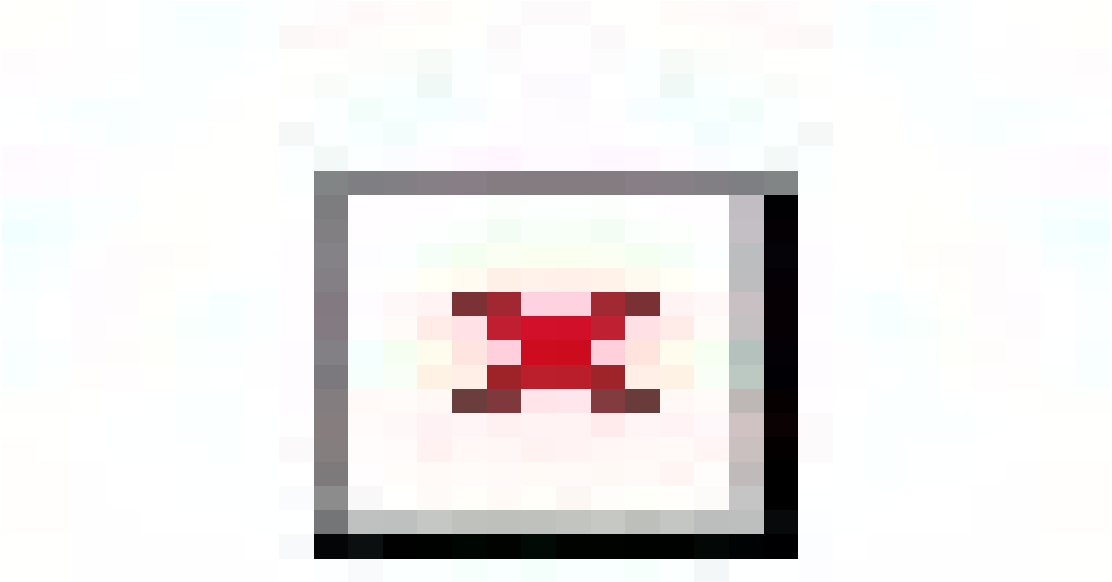
^{1}H NMR spectra of (*E*)-3,4-dihydronaphthalen-1(2H)-one *O*-benzyl oxime (1s)



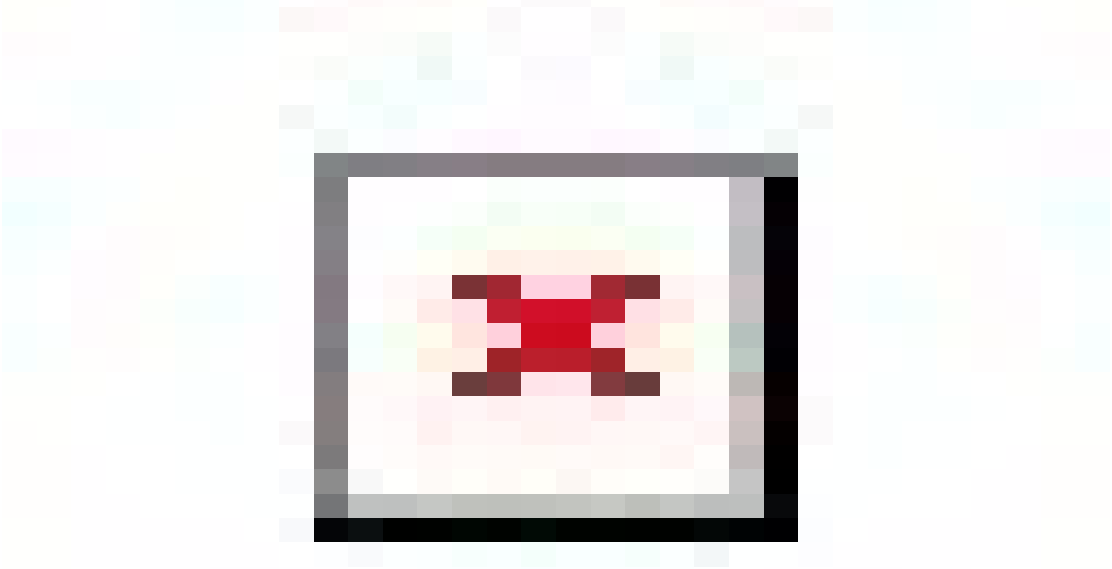
^{13}C NMR spectra of (*E*)-3,4-dihydronaphthalen-1(2H)-one *O*-benzyl oxime (1s)



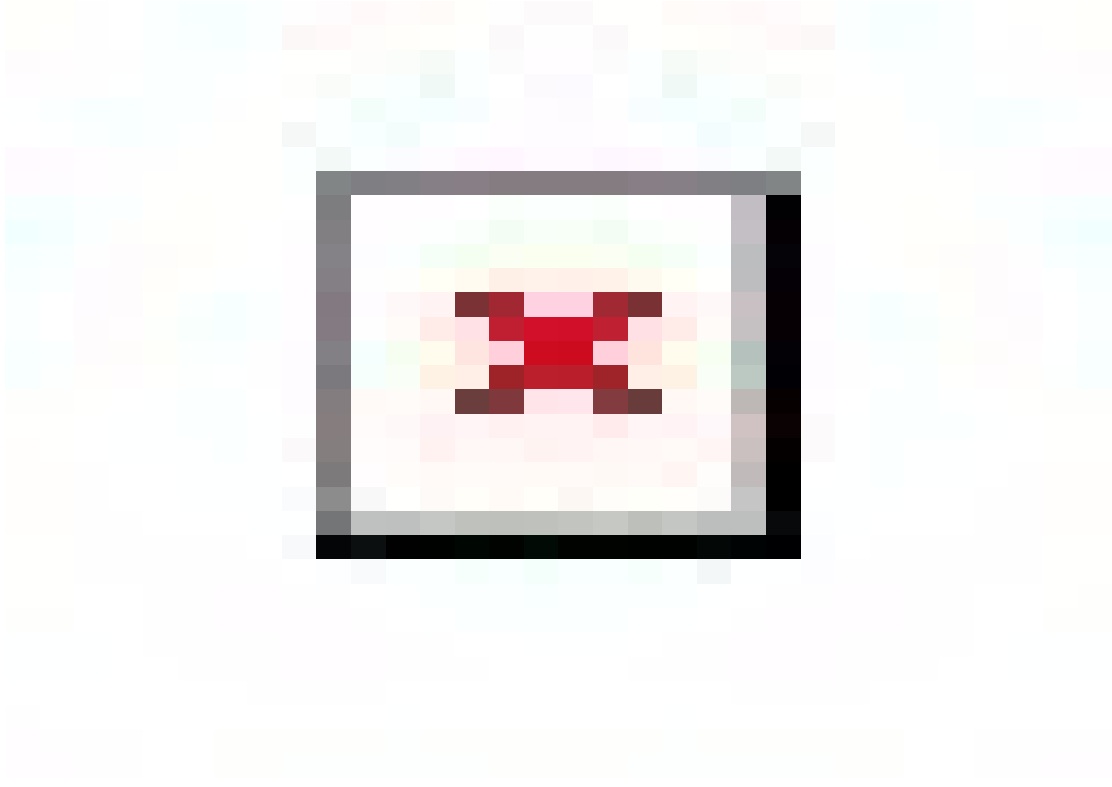
^{1}H NMR spectra of (*E*)-3,4-dihydronaphthalen-1(2H)-one *O*-methyl oxime (1t)



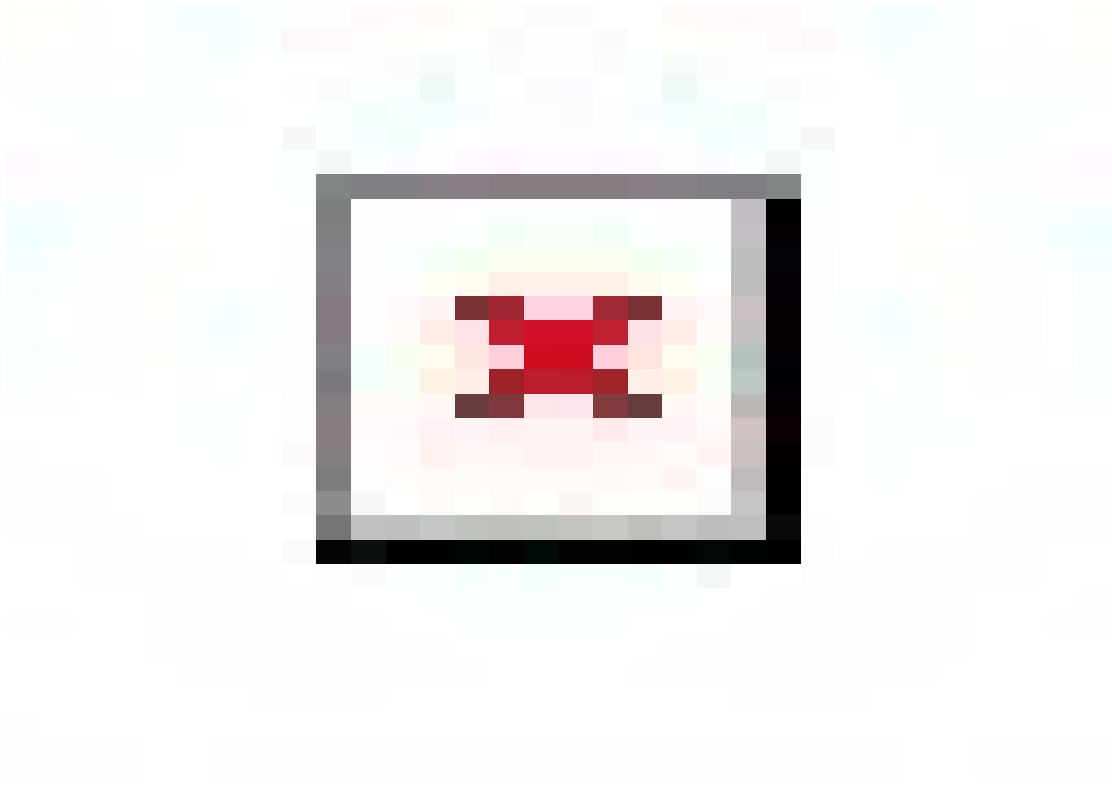
^{13}C NMR spectra of (*E*)-3,4-dihydronaphthalen-1(2H)-one *O*-methyl oxime (1t)



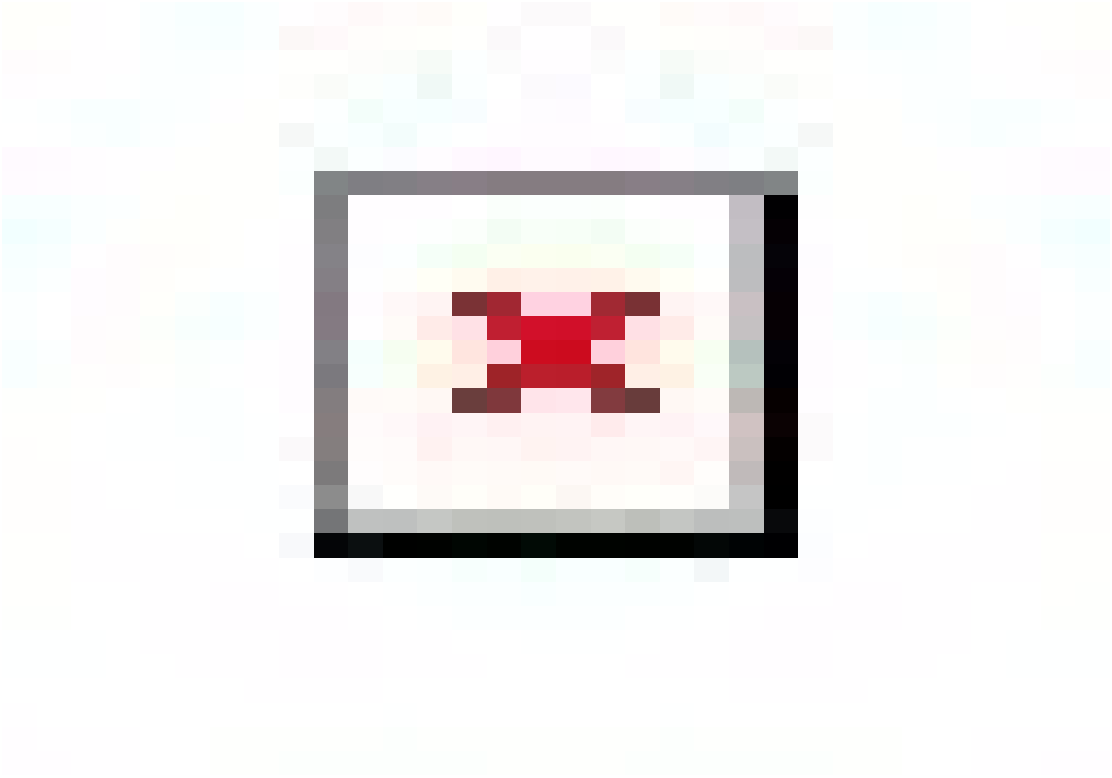
^{1}H NMR spectra of (E)-7-methoxy-3,4-dihydronaphthalen-1(2H)-one O-benzyl oxime (1v):



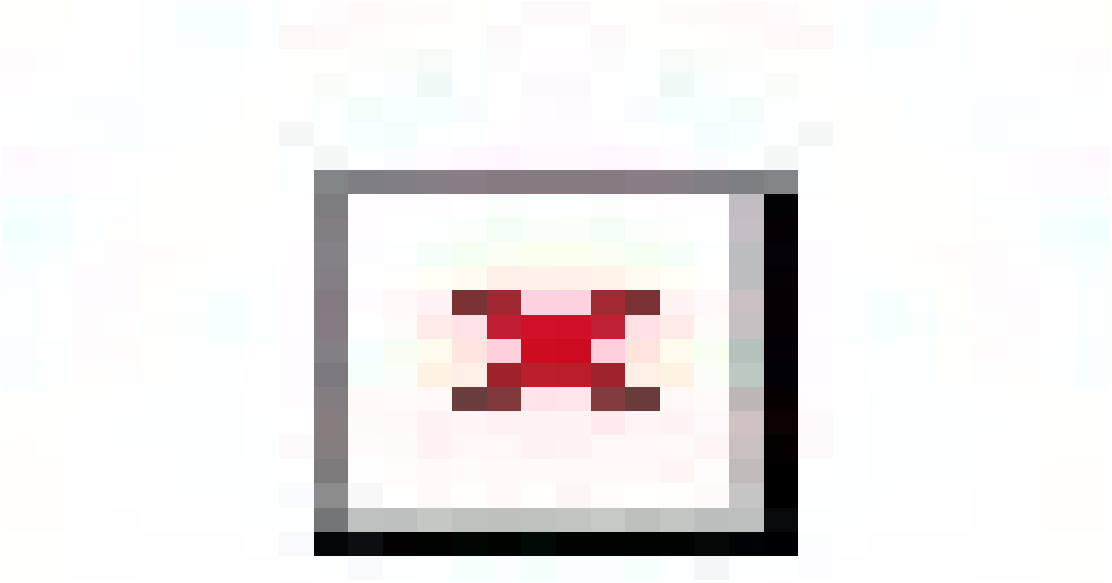
^{13}C NMR spectra of (E)-7-methoxy-3,4-dihydronaphthalen-1(2H)-one O-benzyl oxime (1v):



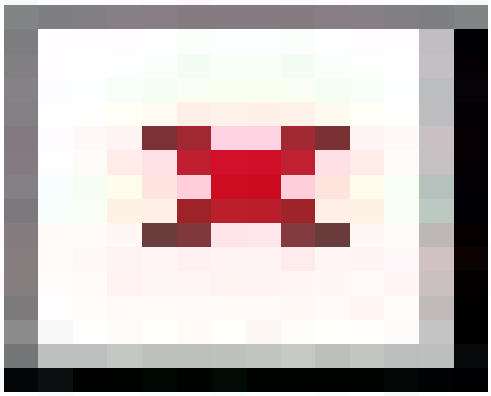
^{1}H NMR spectra of (*E*)-6-chloro-3,4-dihydronaphthalen-1(2H)-one *O*-benzyl oxime (1w)



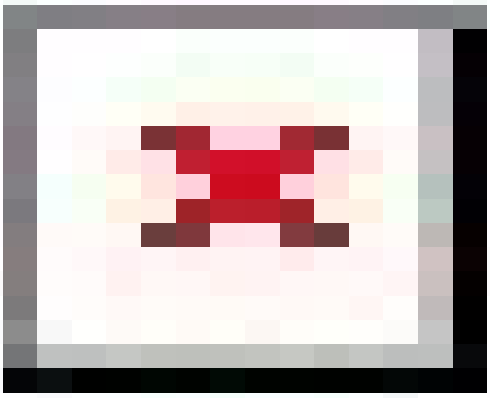
^{13}C NMR spectra of (*E*)-6-chloro-3,4-dihydronaphthalen-1(2H)-one *O*-benzyl oxime (1w)



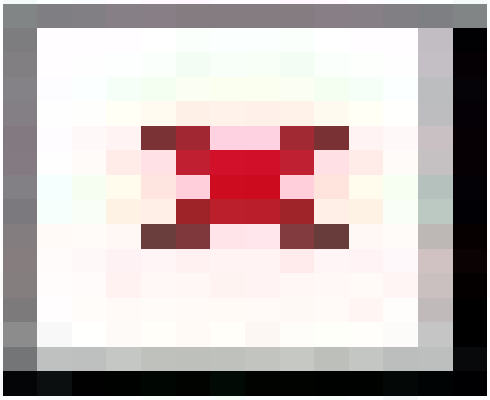
^{1}H NMR spectra of (*E*)-1-phenylbutan-1-one O-benzyl oxime (1x)



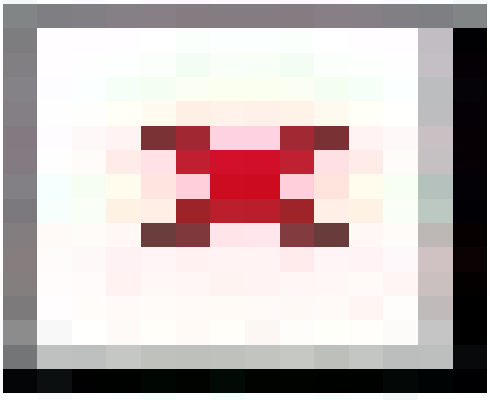
^{13}C NMR spectra of (*E*)-1-phenylbutan-1-one O-benzyl oxime (1x)



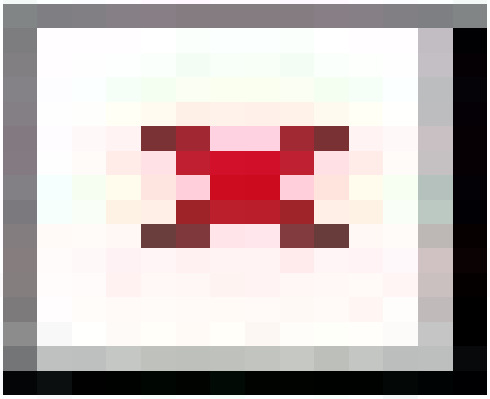
^{1}H NMR spectra of Phenyl(p-tolyl)methanone *O*-methyl oxime (1y)



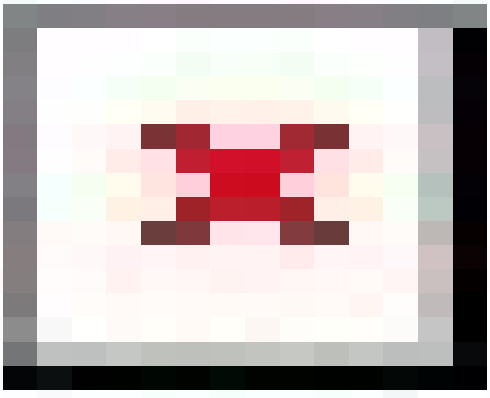
^{13}C NMR spectra of Phenyl(p-tolyl)methanone O-methyl oxime (1y)



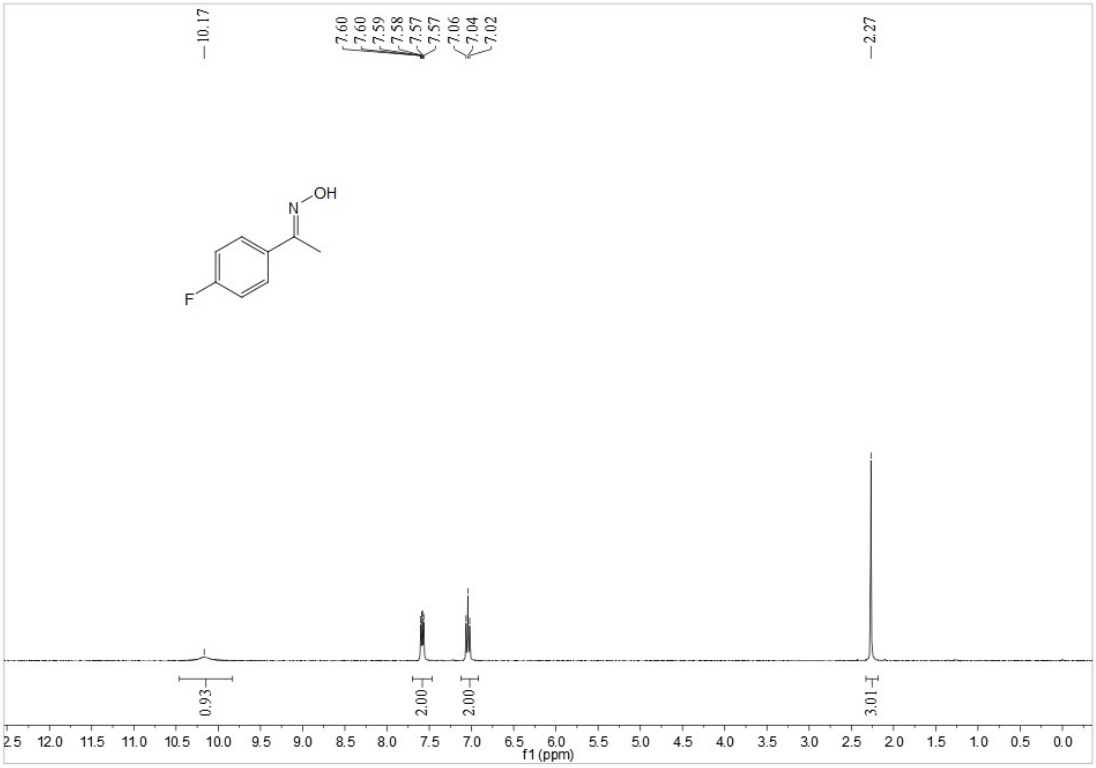
^{1}H NMR spectra of (*E*)-1-phenylethan-1-one oxime (1ba)



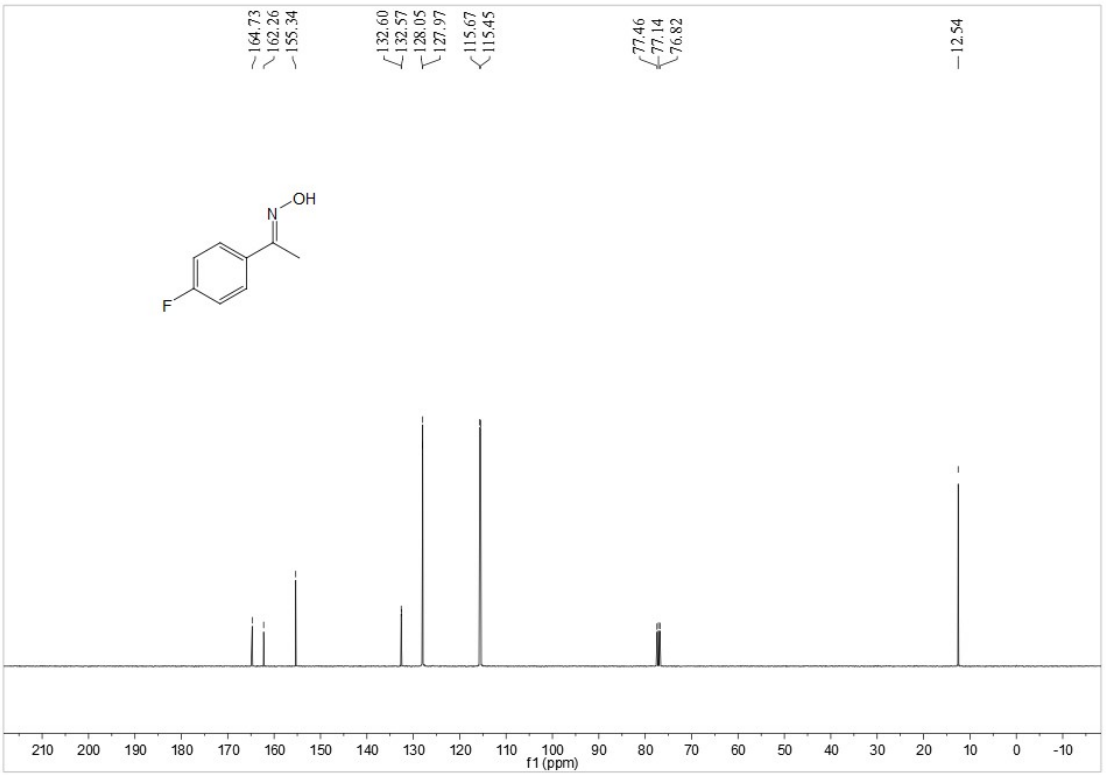
^{13}C NMR spectra of (*E*)-1-phenylethan-1-one oximee (1ba)



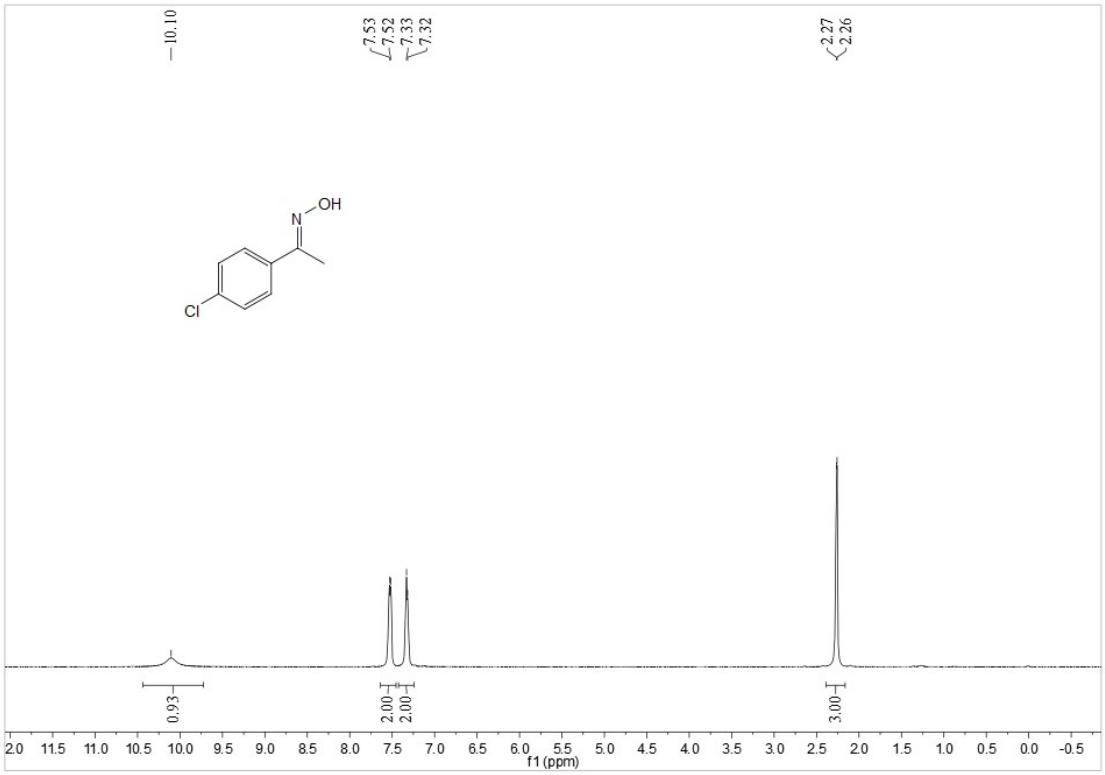
^{1}H NMR spectra of (*E*)-1-(4-fluorophenyl)ethan-1-one oxime (1bb)



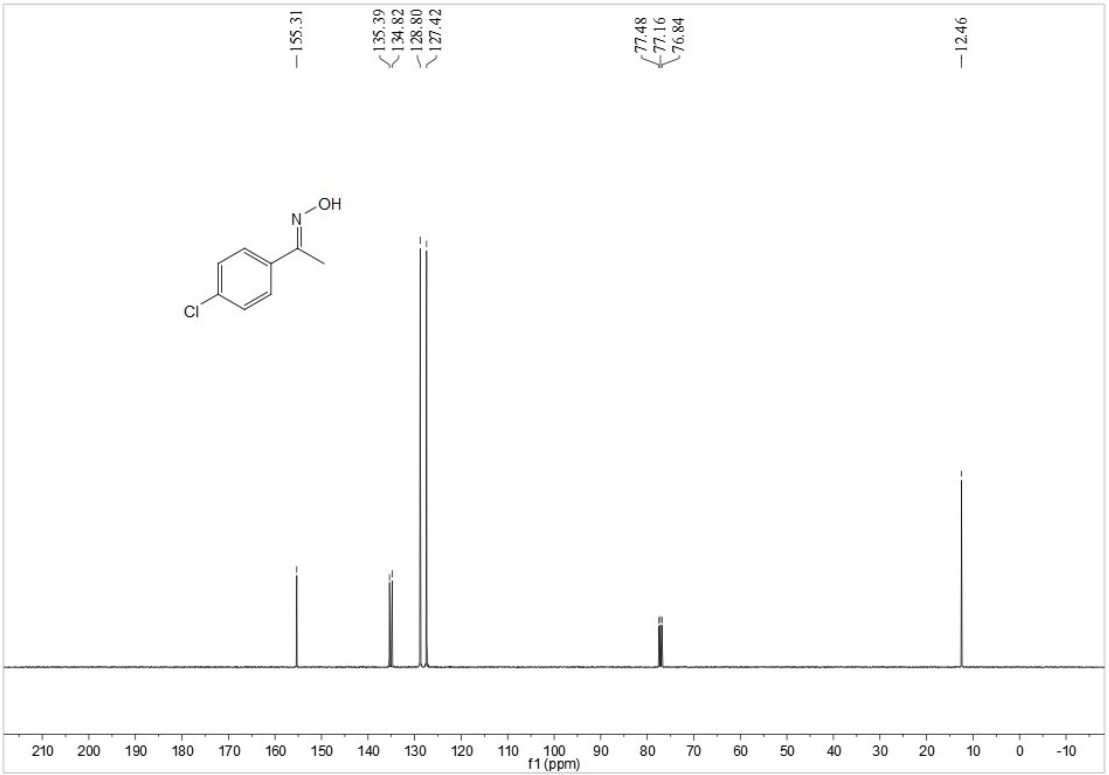
^{13}C NMR spectra of (*E*)-1-(4-fluorophenyl)ethan-1-one oxime (1bb)



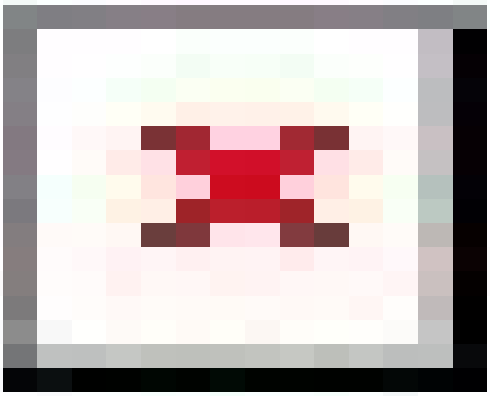
^{1}H NMR spectra of (*E*)-1-(4-chlorophenyl)ethan-1-one oxime (1bc)



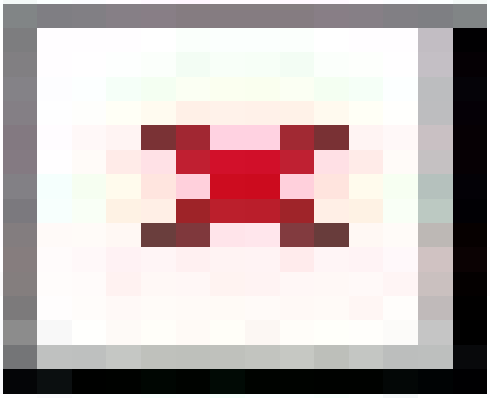
^{13}C NMR spectra of (*E*)-1-(4-chlorophenyl)ethan-1-one oxime (1bc)



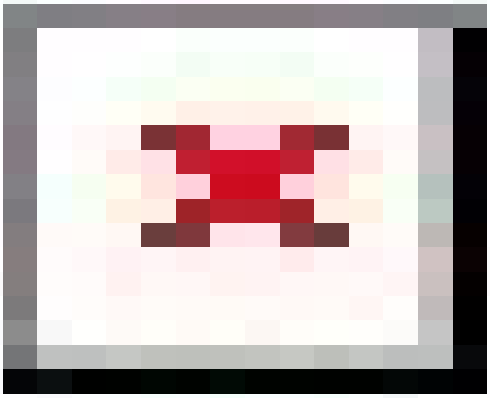
^{1}H NMR spectra of (*E*)-1-(p-tolyl)ethan-1-one oxime (1bd)



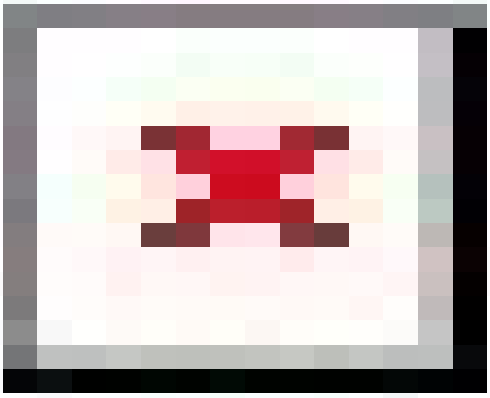
^{13}C NMR spectra of (*E*)-1-(p-tolyl)ethan-1-one oxime (1bd)



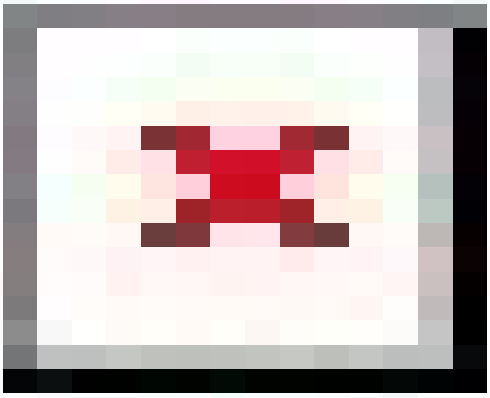
^{1}H NMR spectra of (*E*)-1-(4-(tert-butyl)phenyl)ethan-1-one oxime (1be)



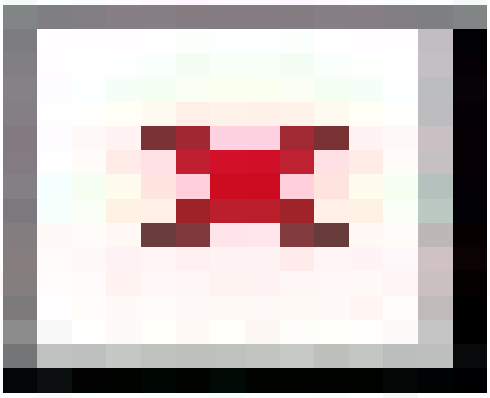
^{13}C NMR spectra of (*E*)-1-(4-(tert-butyl)phenyl)ethan-1-one oxime (1be)



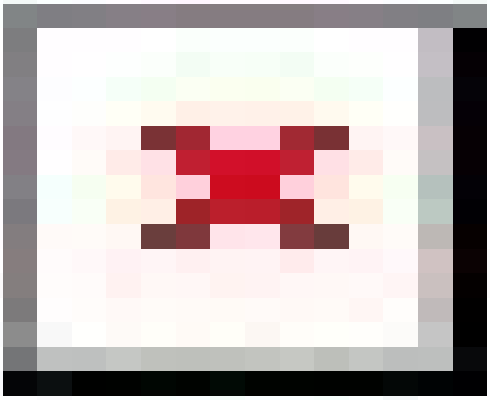
^{1}H NMR spectra of (*E*)-1-(naphthalen-2-yl)ethan-1-one oxime (1bf)



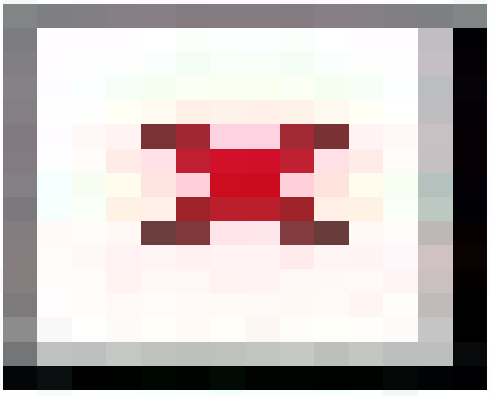
^{13}C NMR spectra of (*E*)-1-(naphthalen-2-yl)ethan-1-one oxime (1bf)



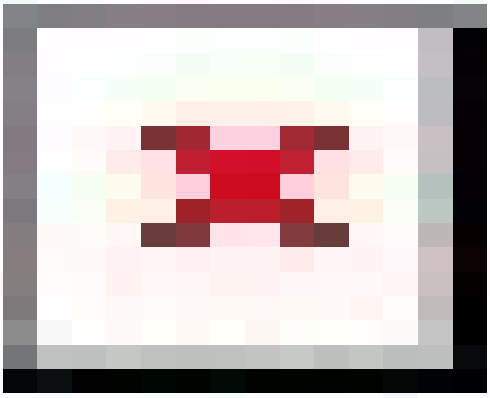
^{1}H NMR spectra of (E)-1-(furan-2-yl)ethan-1-one oxime (1bg)



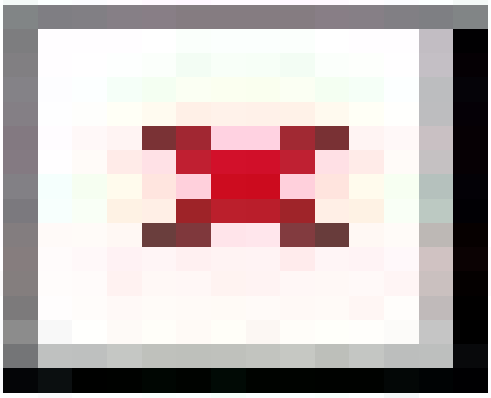
^{13}C NMR spectra of (E)-1-(furan-2-yl)ethan-1-one oxime (1bg)



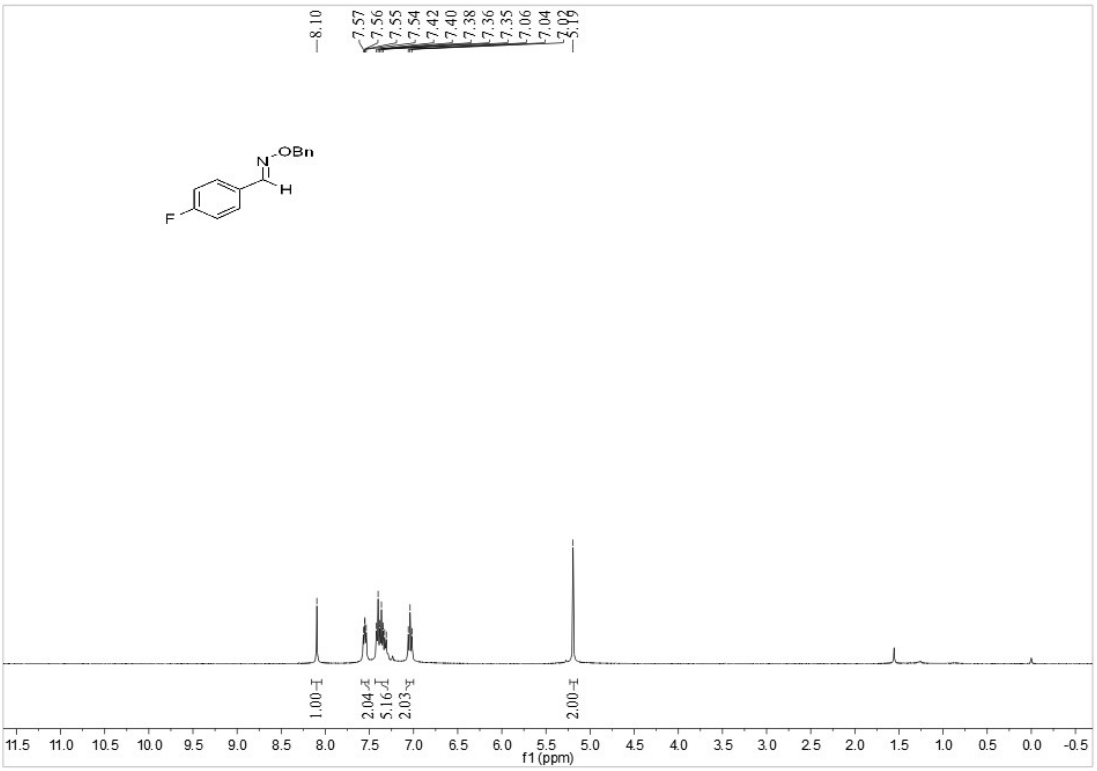
^{1}H NMR spectra of (*E*)-benzaldehyde *O*-benzyl oxime (1bh)



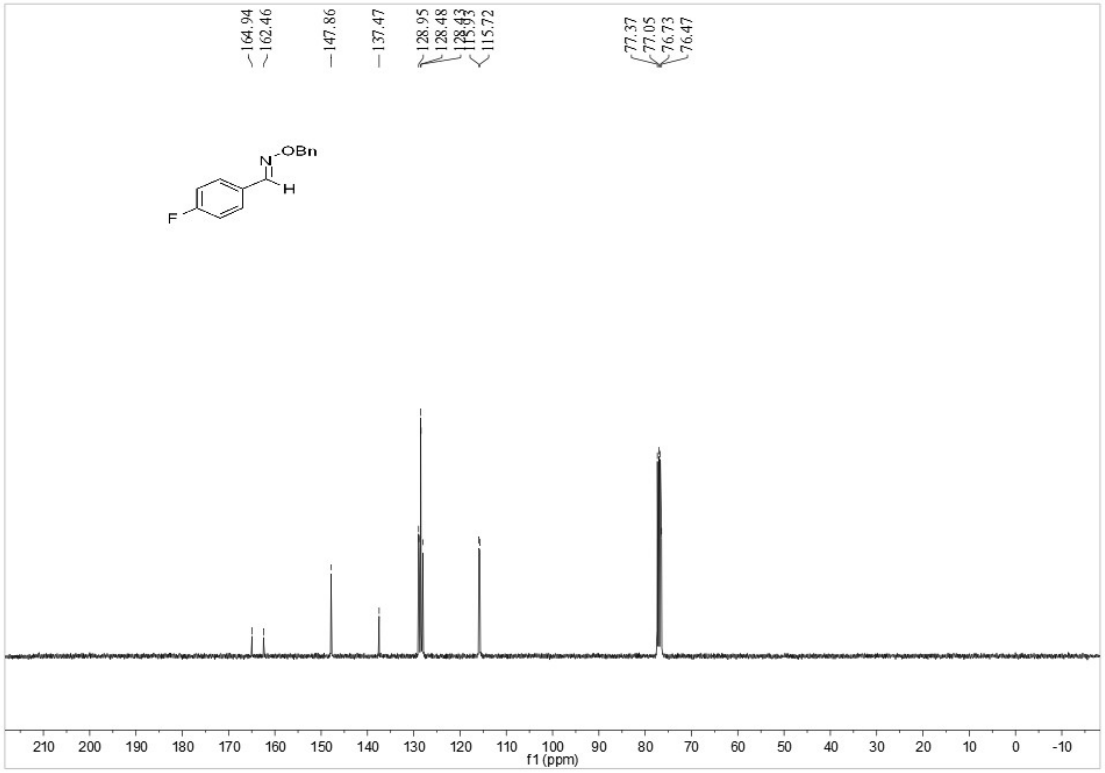
^{13}C NMR spectra of (*E*)-benzaldehyde *O*-benzyl oxime (1bh)



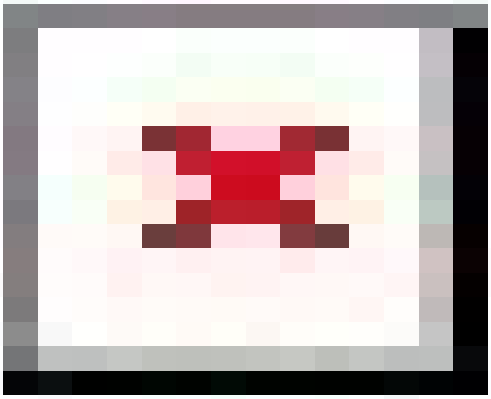
^{1}H NMR spectra of (*E*)-4-fluorobenzaldehyde *O*-benzyl oxime (1bi)



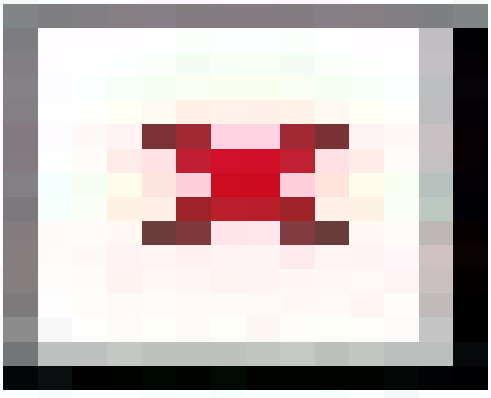
^{13}C NMR spectra of (*E*)-4-fluorobenzaldehyde *O*-benzyl oxime (1bi)



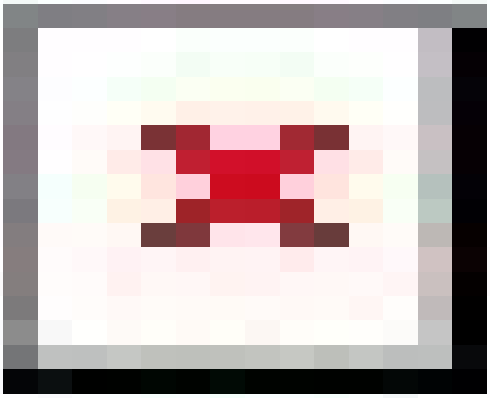
^{1}H NMR spectra of (*E*)-4-methylbenzaldehyde *O*-benzyl oxime (1bj)



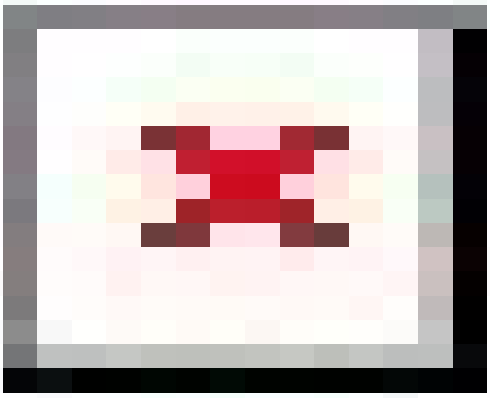
^{13}C NMR spectra of (*E*)-4-methylbenzaldehyde *O*-benzyl oxime (1bj)



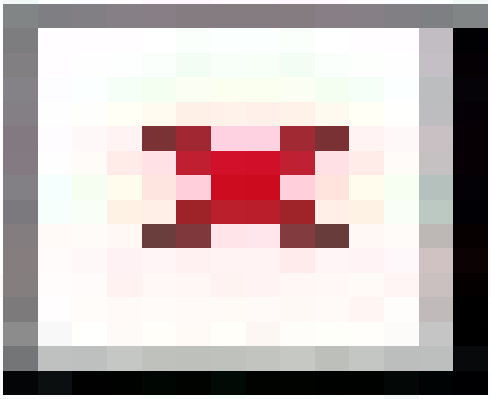
^{1}H NMR spectra of (*E*)-2-naphthaldehyde *O*-benzyl oxime (1bk)



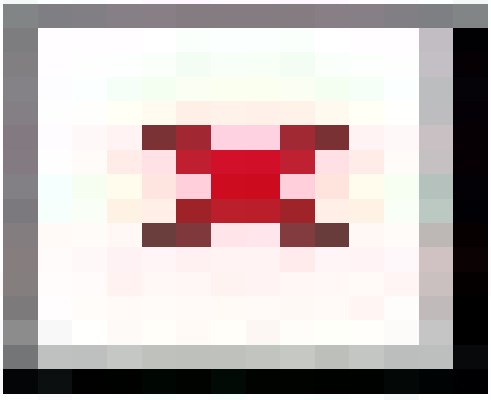
^{13}C NMR spectra of (*E*)-2-naphthaldehyde *O*-benzyl oxime (1bk)



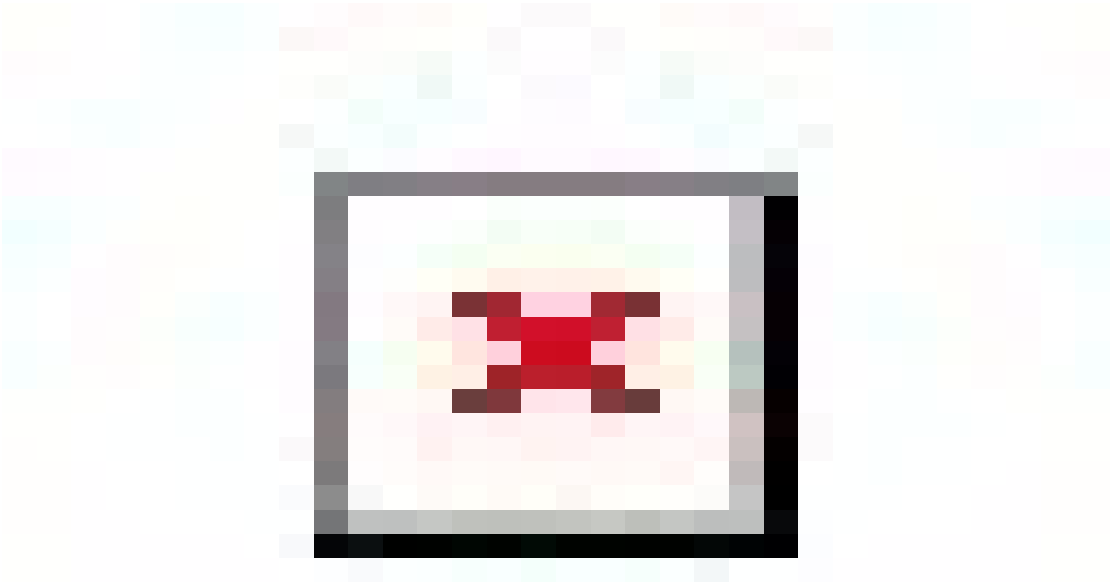
^{1}H NMR spectra of (*E*)-furan-2-carbaldehyde *O*-benzyl oxime (1bl)



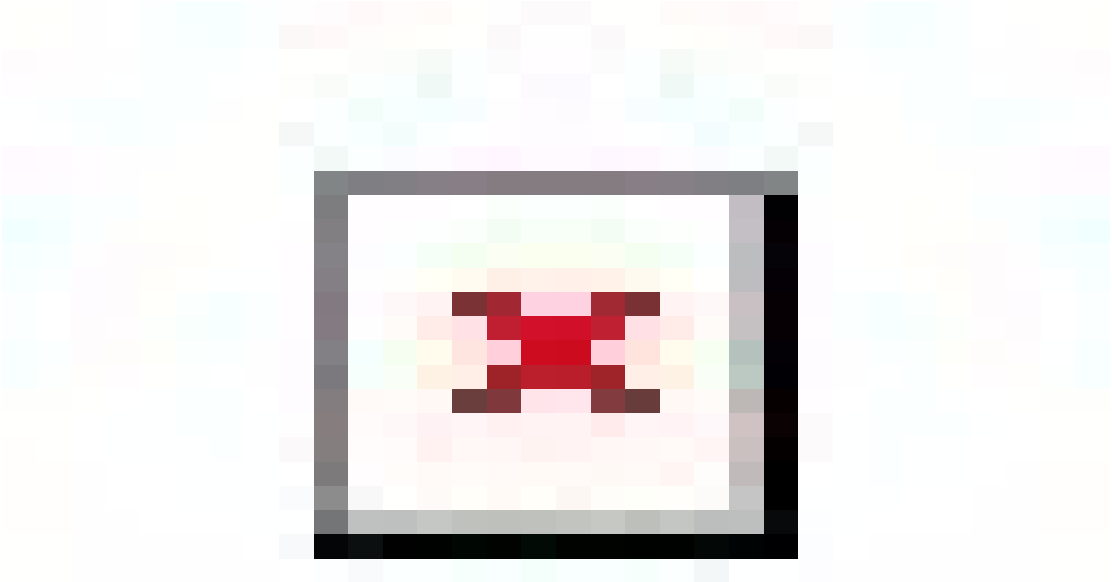
^{13}C NMR spectra of (*E*)-furan-2-carbaldehyde *O*-benzyl oxime (1bl)



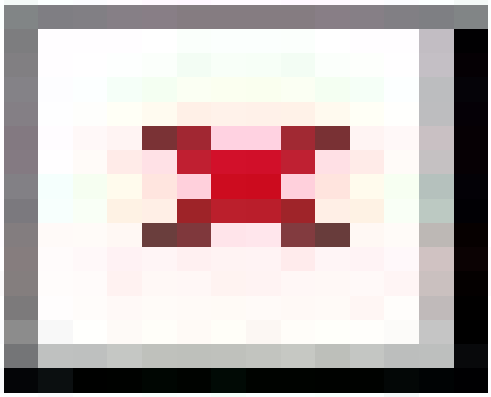
^{1}H NMR spectra of propan-2-one O-benzyl oxime (1aa)



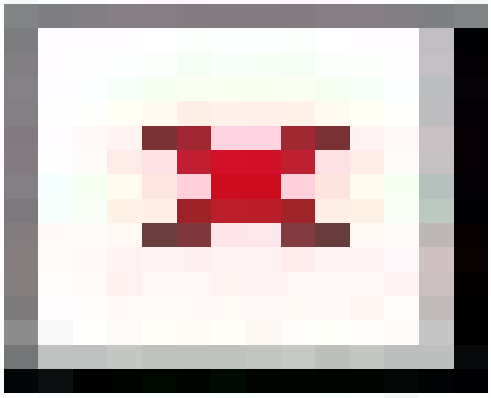
^{13}C NMR spectra of propan-2-one O-benzyl oxime (1aa)



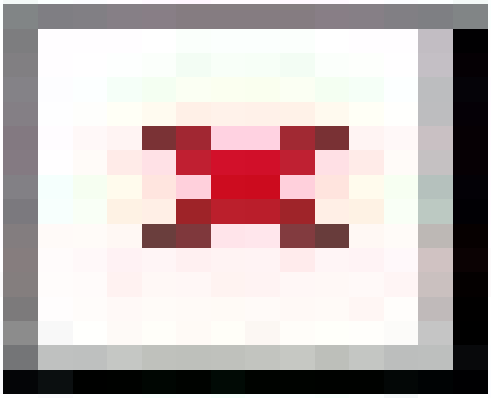
^{1}H NMR spectra of (*E*)-3,3-dimethylbutan-2-one *O*-benzyl oxime (1ab)



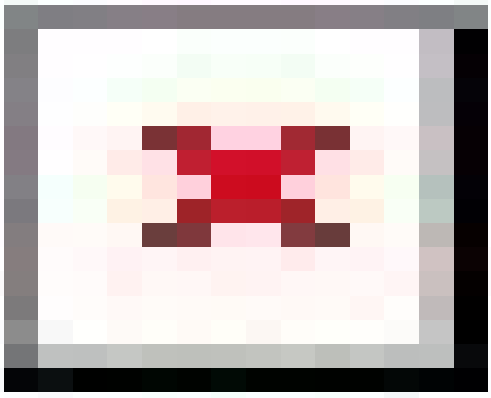
^{13}C NMR spectra of (*E*)-3,3-dimethylbutan-2-one *O*-benzyl oxime (1ab)



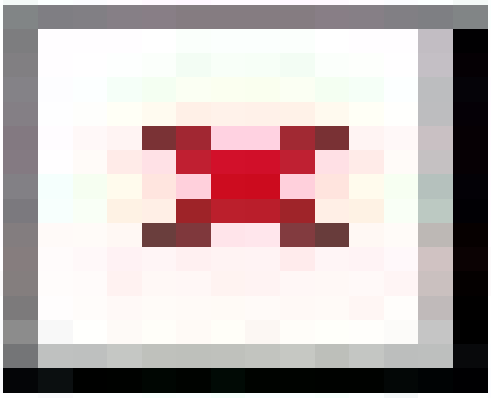
^{1}H NMR spectra of pentan-3-one O-benzyl oxime (1ac)



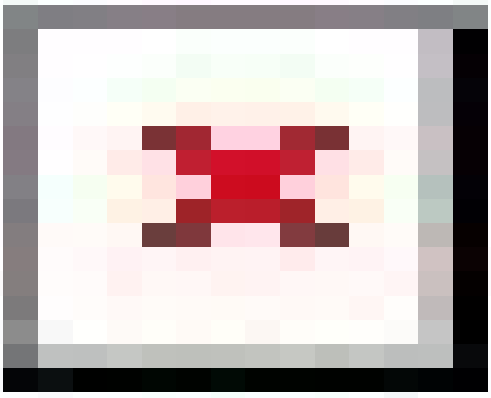
^{13}C NMR spectra of pentan-3-one O-benzyl oxime (1ac)



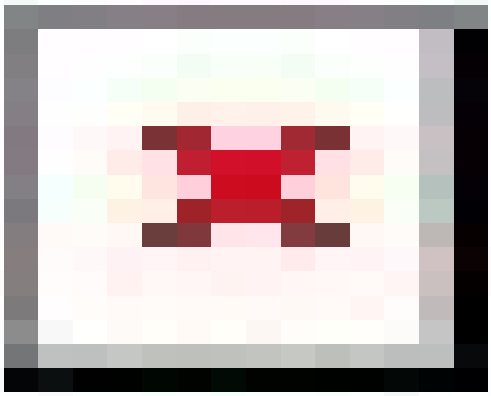
^{1}H NMR spectra of pentan-2-one O-benzyl oxime (1ad)



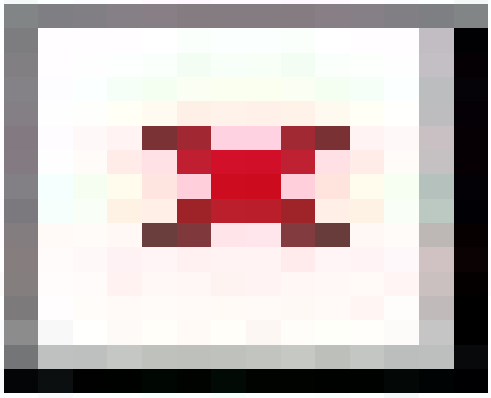
^{13}C NMR spectra of pentan-2-one O-benzyl oxime (1ad)



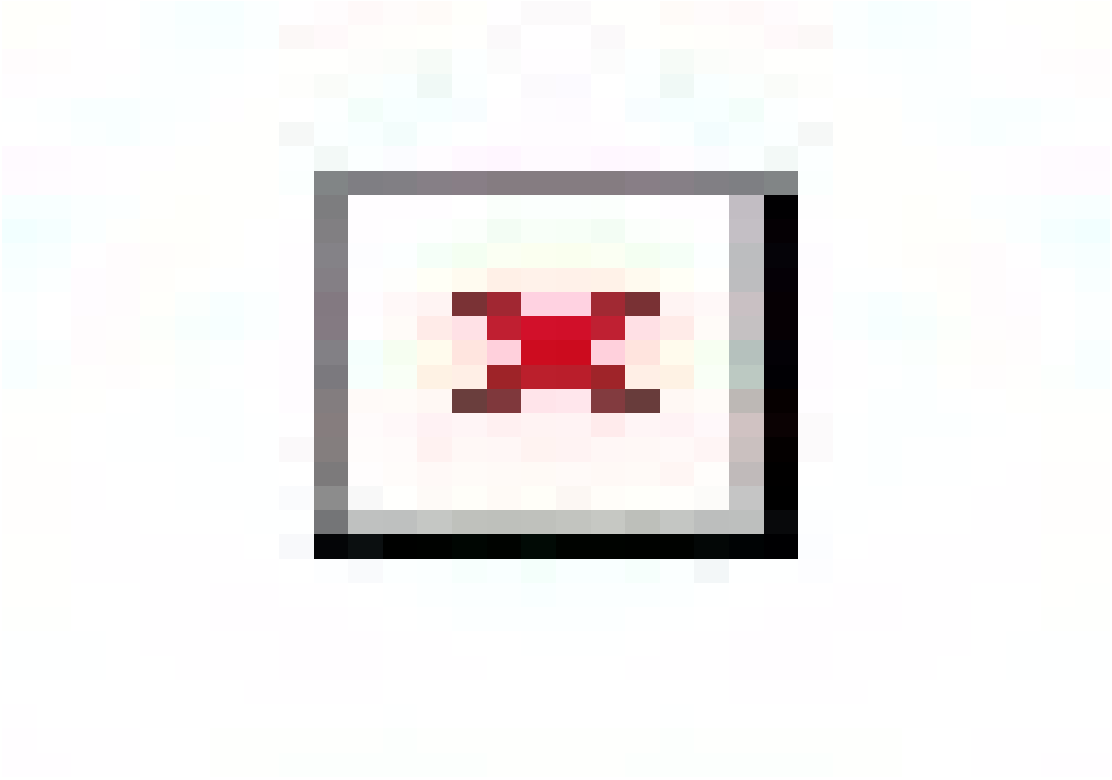
^{1}H NMR spectra of cyclohexanone *O*-benzyl oxime (1af)



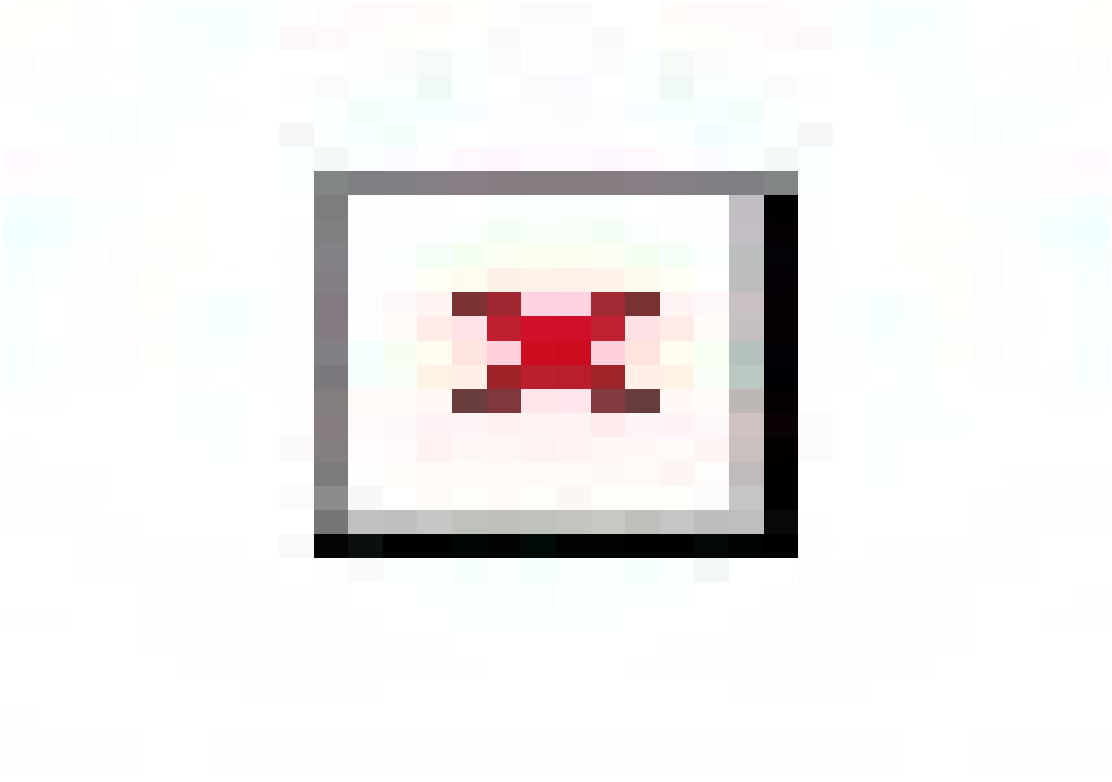
^{13}C NMR spectra of cyclohexanone *O*-benzyl oxime (1af)



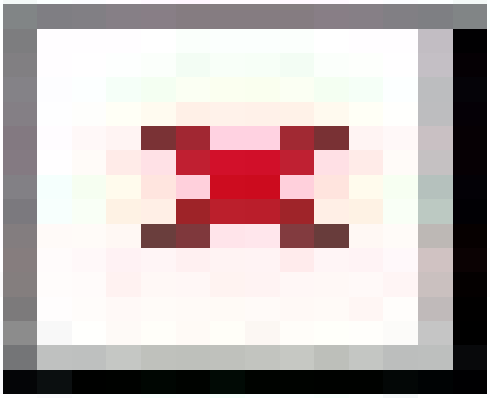
^{1}H NMR spectra of 5-methoxy-3,4-dihydronaphthalen-2(1H)-one *O*-benzyl oxime (1ag)



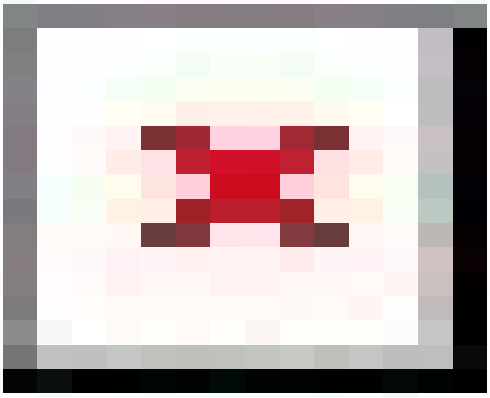
^{13}C NMR spectra of 5-methoxy-3,4-dihydronaphthalen-2(1H)-one *O*-benzyl oxime (1ag)



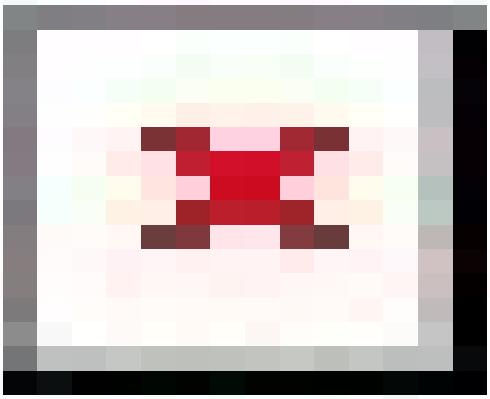
^{1}H NMR spectra of cyclohexanone *O*-methyl oxime (1ah)



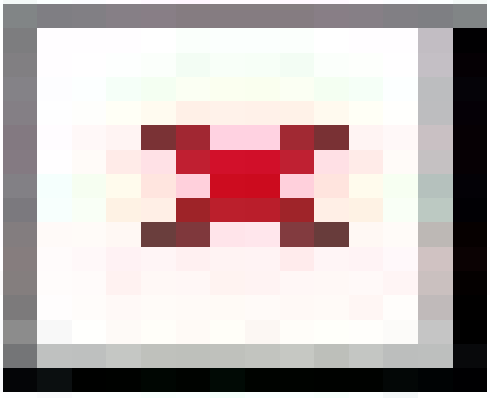
^{13}C NMR spectra of cyclohexanone *O*-methyl oxime (1ah)



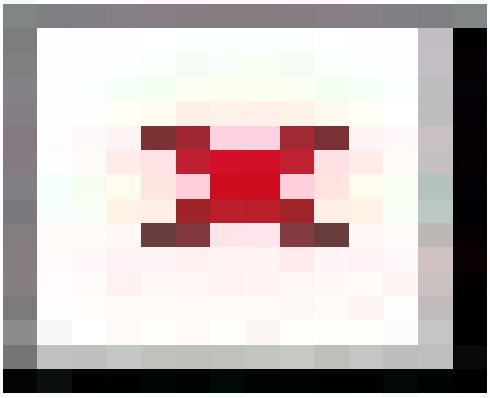
^{1}H NMR spectra of (*E*)-4-phenylbutan-2-one *O*-benzyl oxime (1ai)



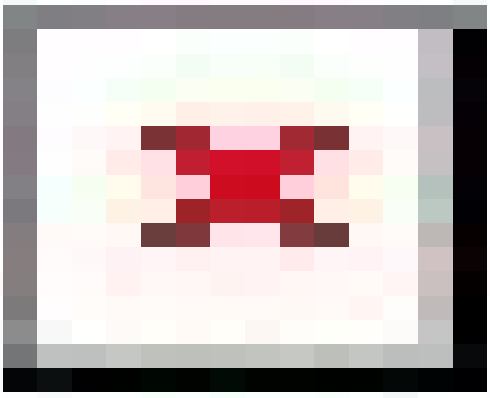
^{13}C NMR spectra of (E)-4-phenylbutan-2-one O-benzyl oxime (1ai)



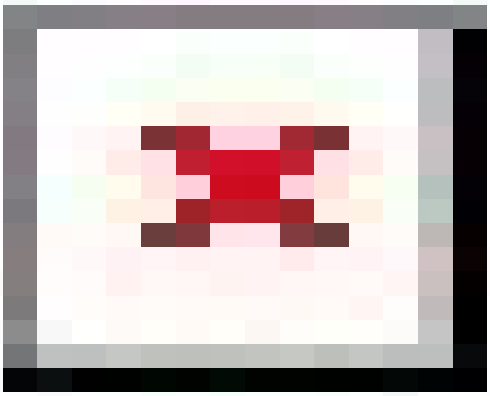
^{1}H NMR spectra of cyclobutanone *O*-benzyl oxime (1aj)



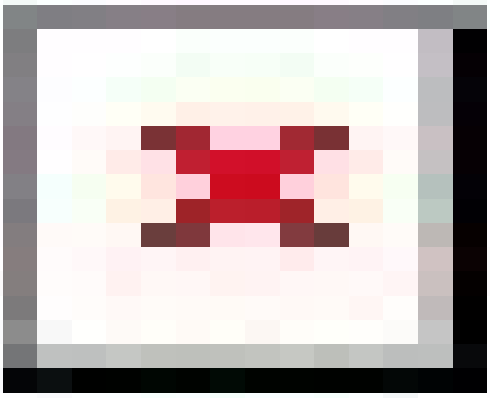
^{13}C NMR spectra of cyclobutanone *O*-benzyl oxime (1aj)



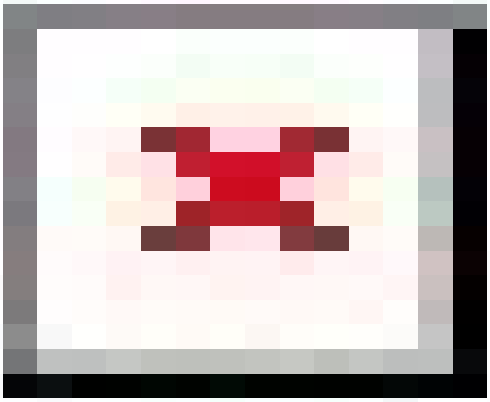
^{1}H NMR spectra of cyclohexanone oxime (1ak)



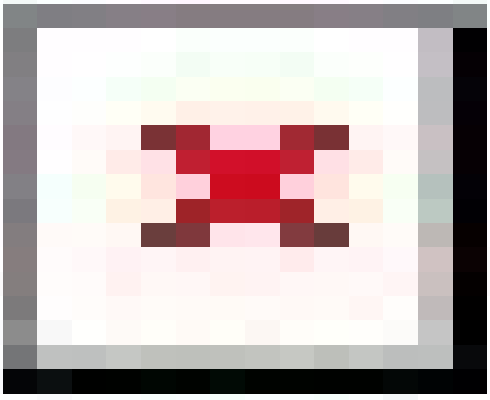
^{13}C NMR spectra of cyclohexanone oxime (1ak)



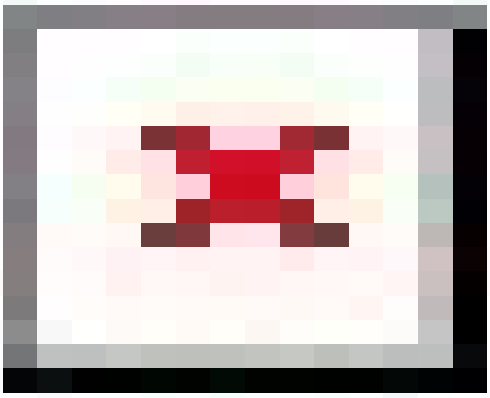
^{1}H NMR spectra of (*E*)-5-methoxy-3,4-dihydronaphthalen-2(1H)-one oxime (1al)



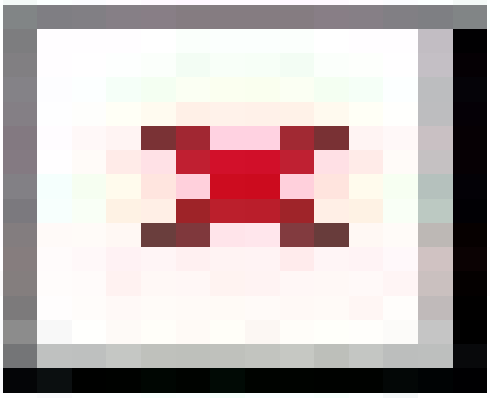
^{13}C NMR spectra of (*E*)-5-methoxy-3,4-dihydronaphthalen-2(1H)-one oxime (1al)



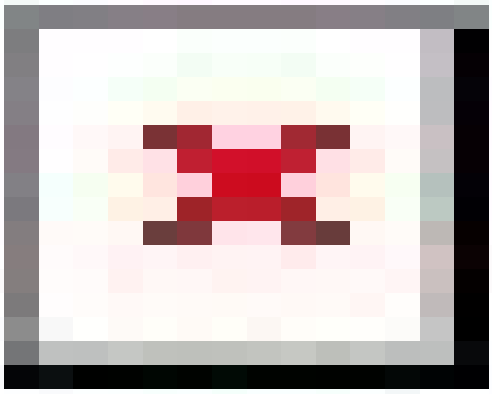
^{1}H NMR spectra of (*E*)-4-phenylbutan-2-one oxime (1am)



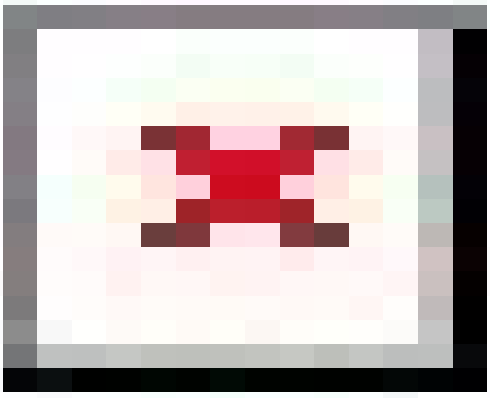
^{13}C NMR spectra of (*E*)-4-phenylbutan-2-one oxime (1am)



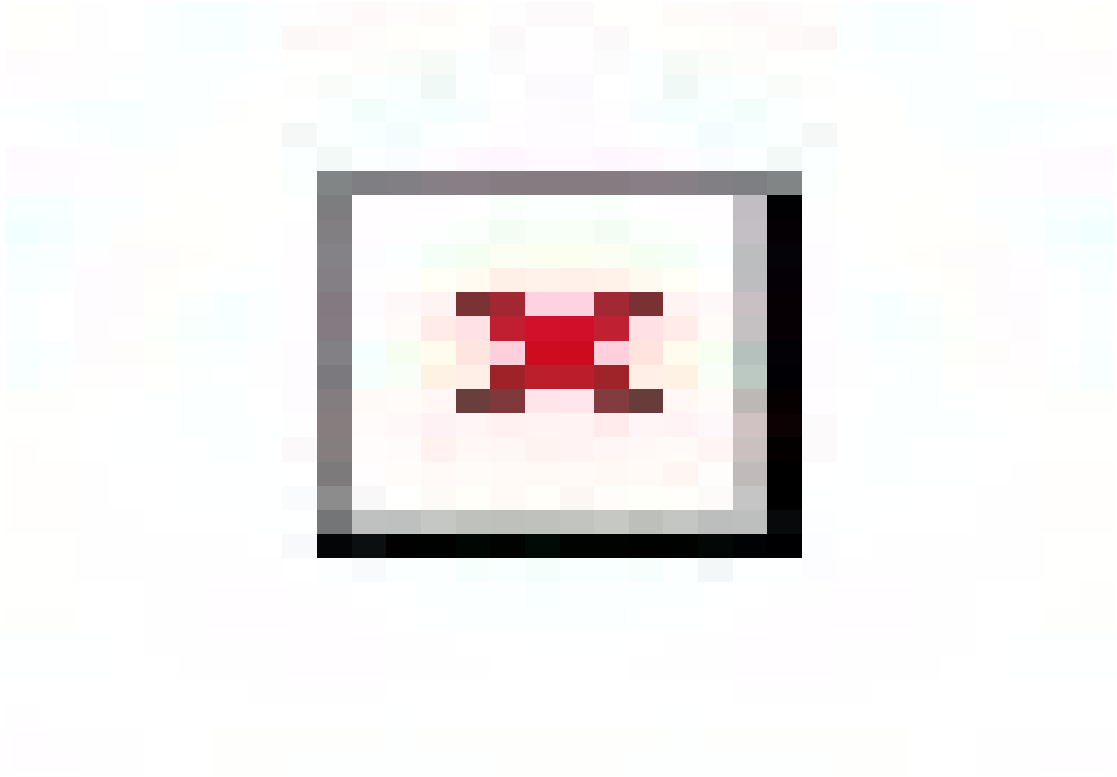
^{1}H NMR spectra of *O*-benzyl-*N*-(1-phenylethyl)hydroxylamine (2a)



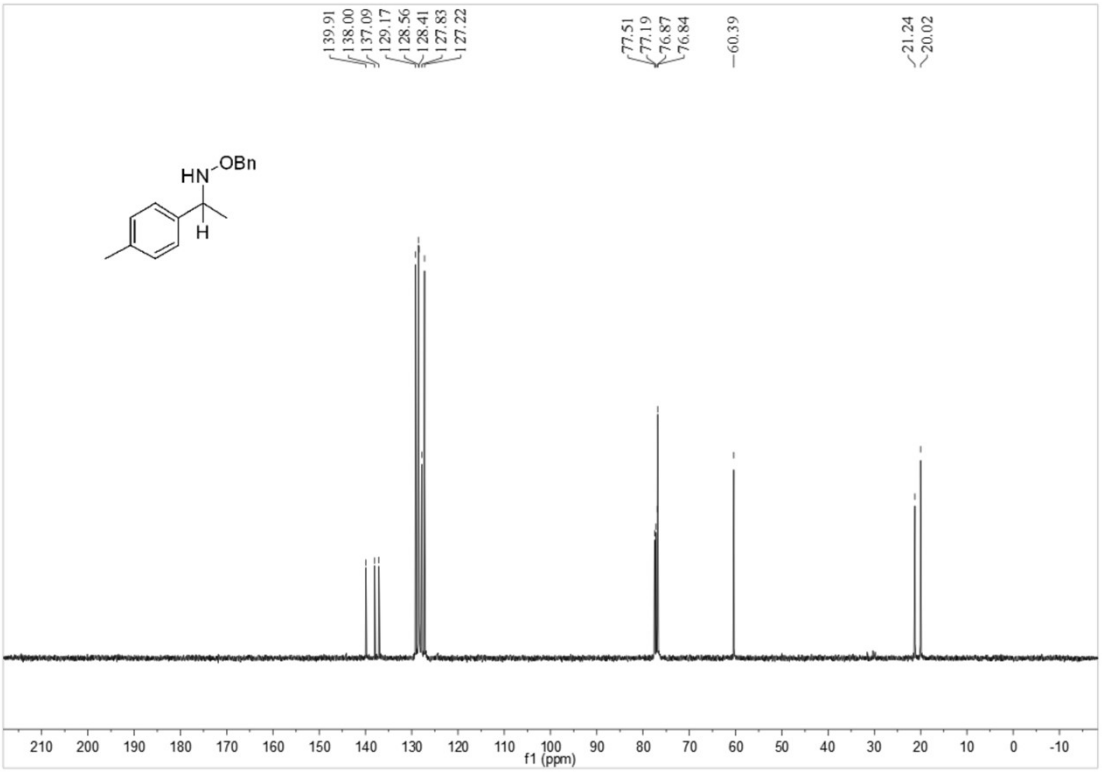
^{13}C NMR spectra of *O*-benzyl-*N*-(1-phenylethyl)hydroxylamine (2a)



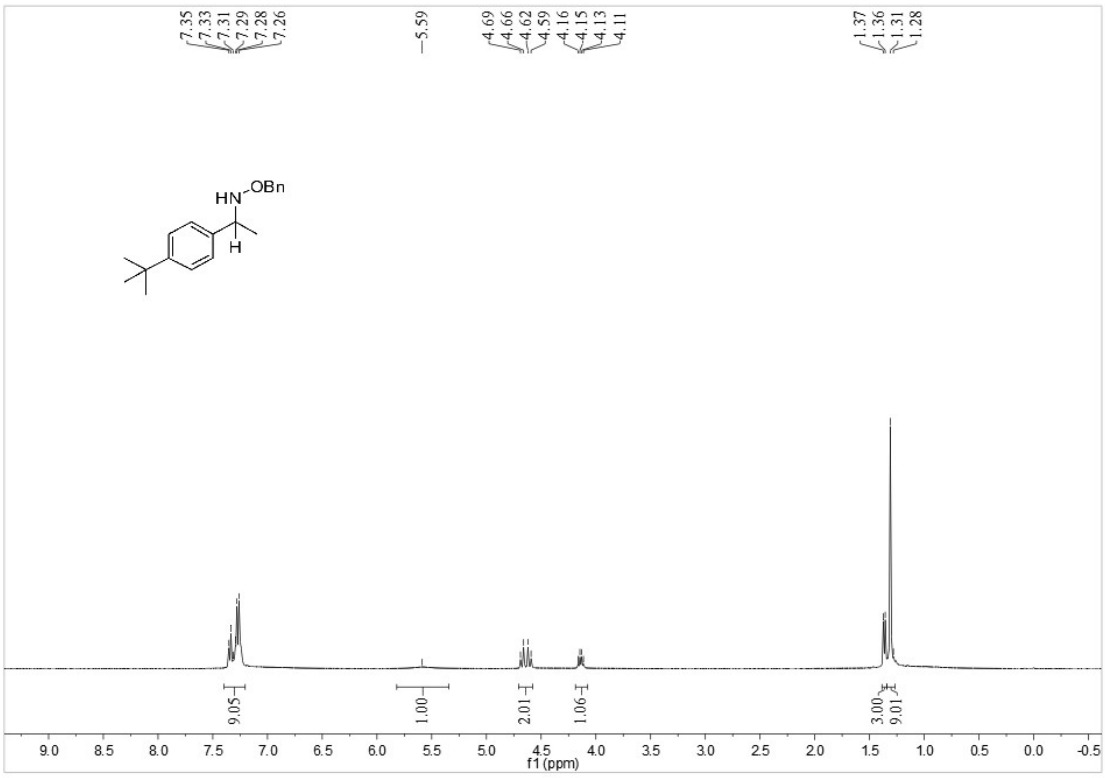
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(p-tolyl)ethyl)hydroxylamine (2b)



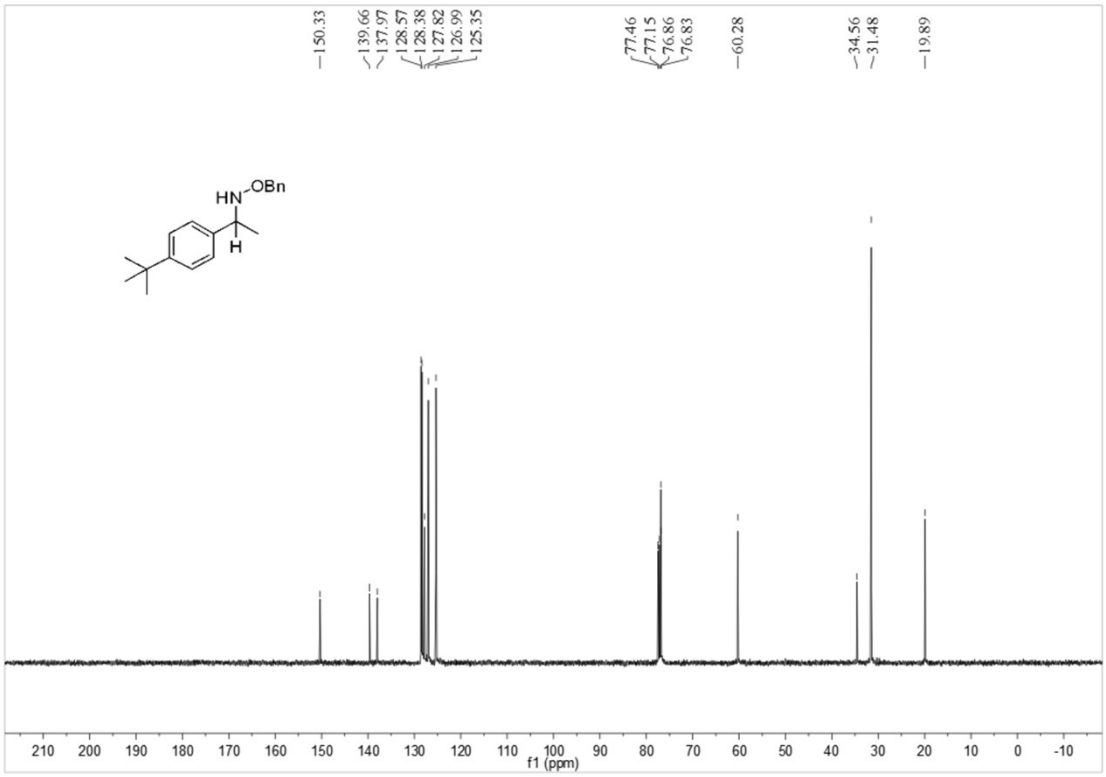
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(p-tolyl)ethyl)hydroxylamine (2b)



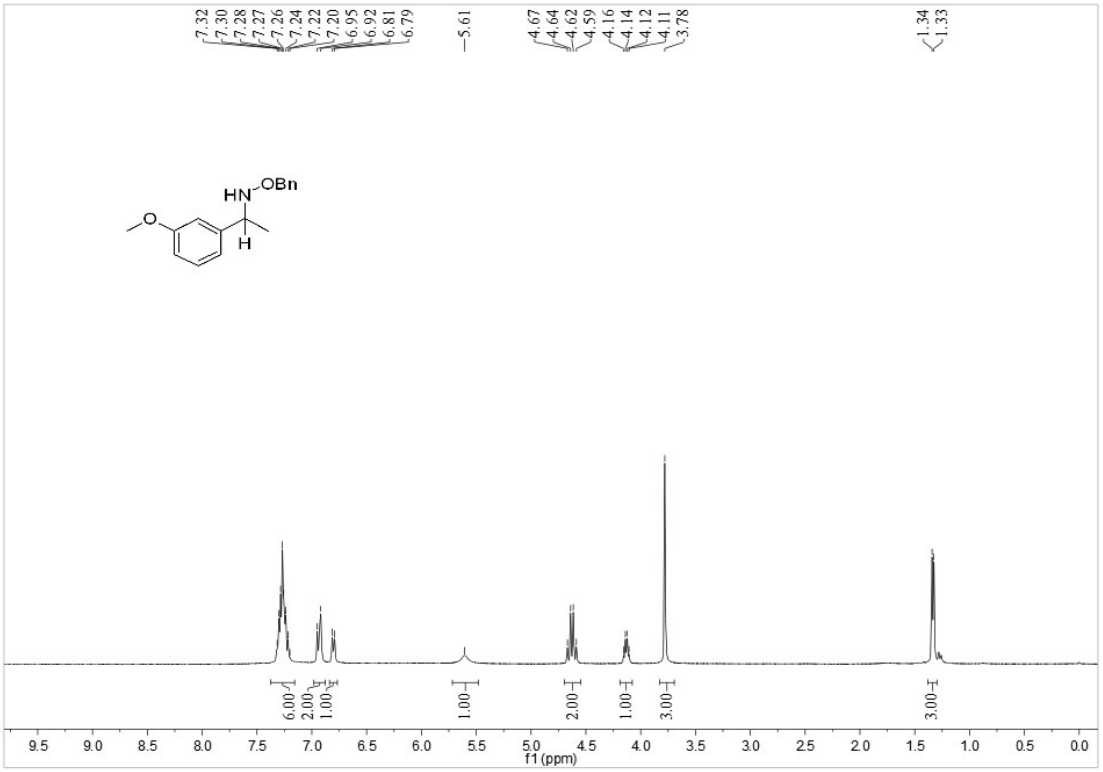
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(4-(tert-butyl)phenyl)ethyl)hydroxylamine (2c)



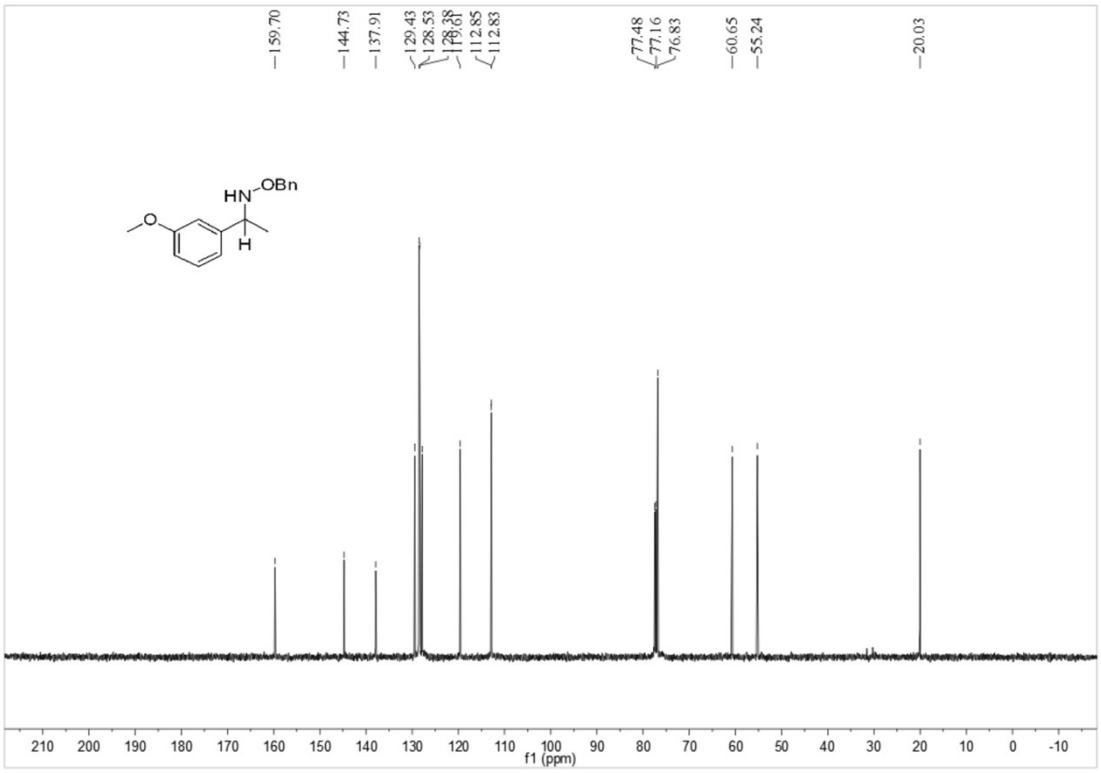
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(4-(tert-butyl)phenyl)ethyl)hydroxylamine (2c)



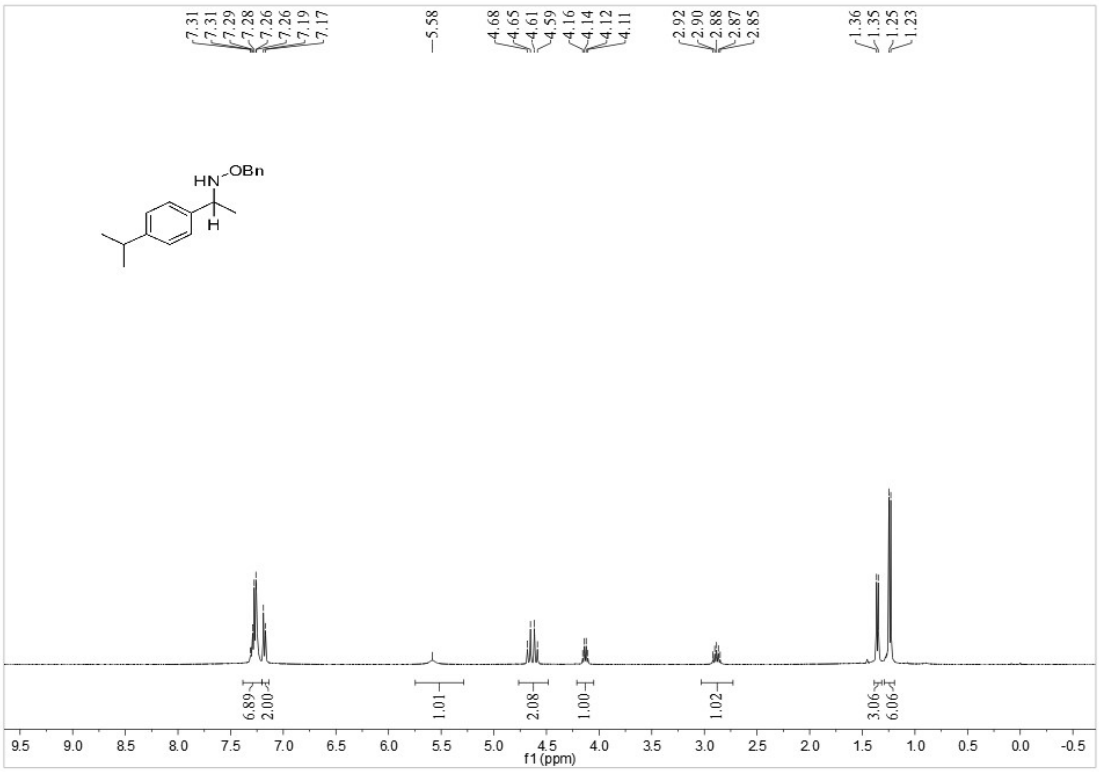
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(3-methoxyphenyl)ethyl)hydroxylamine (2d)



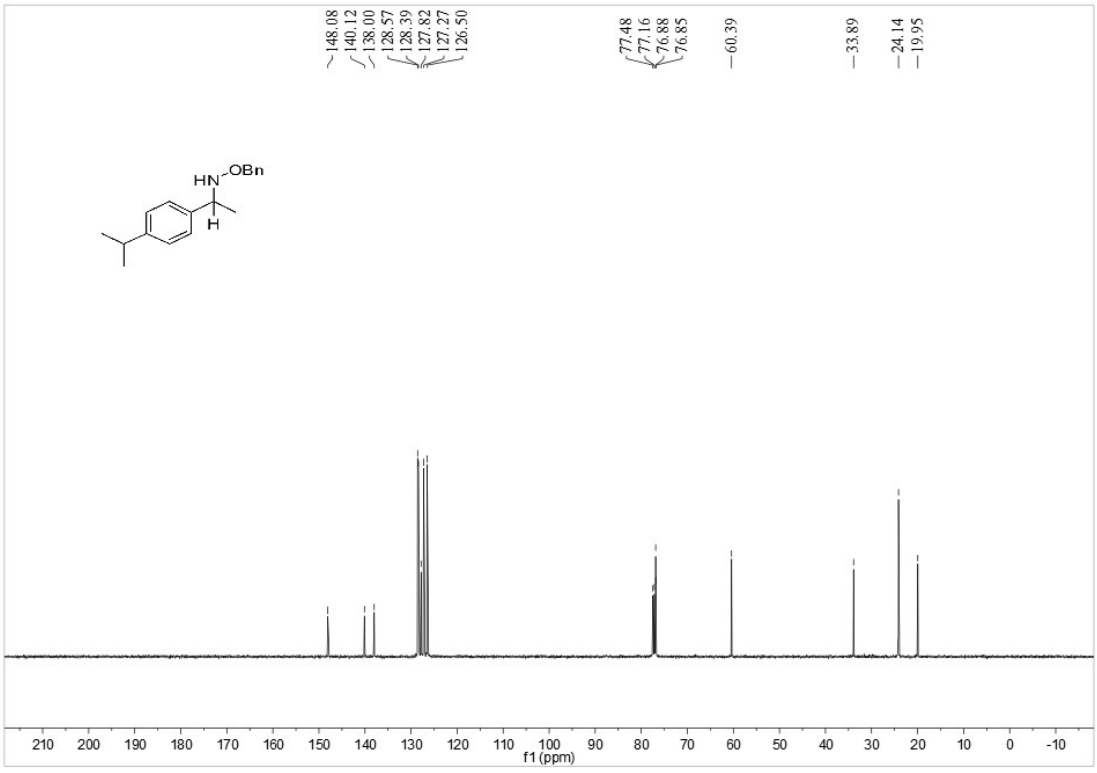
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(3-methoxyphenyl)ethyl)hydroxylamine (2d)



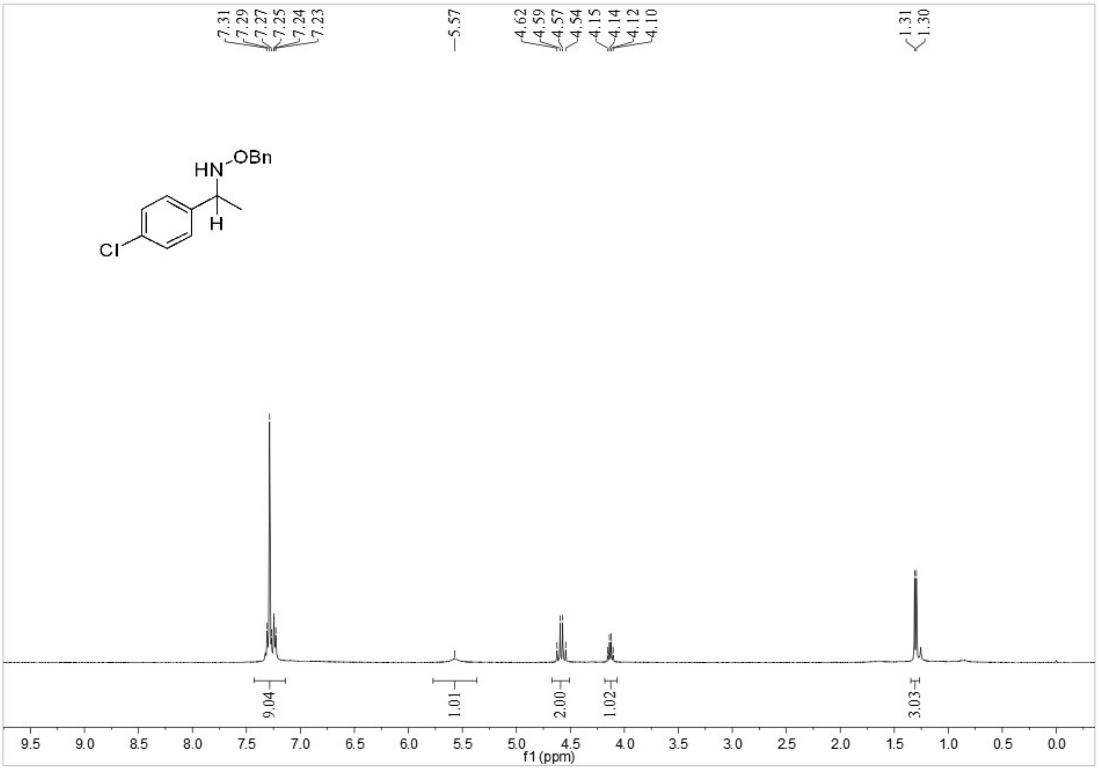
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(4-isopropylphenyl)ethyl)hydroxylamine (2e)



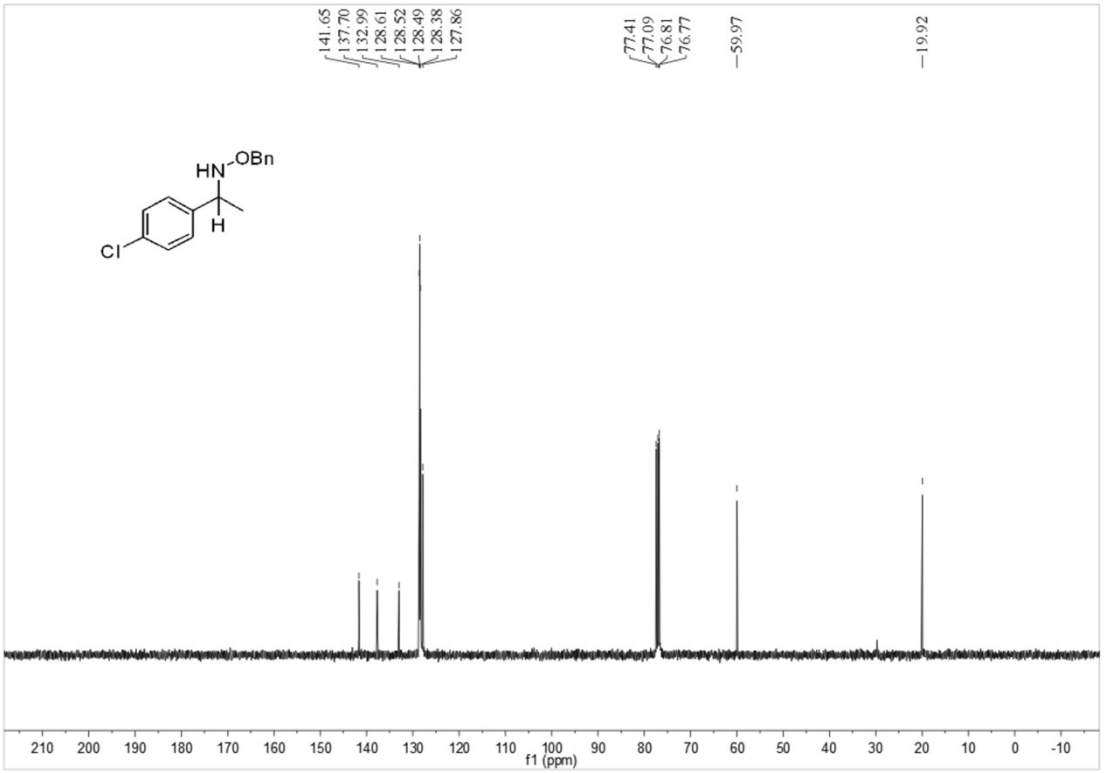
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(4-isopropylphenyl)ethyl)hydroxylamine (2e)



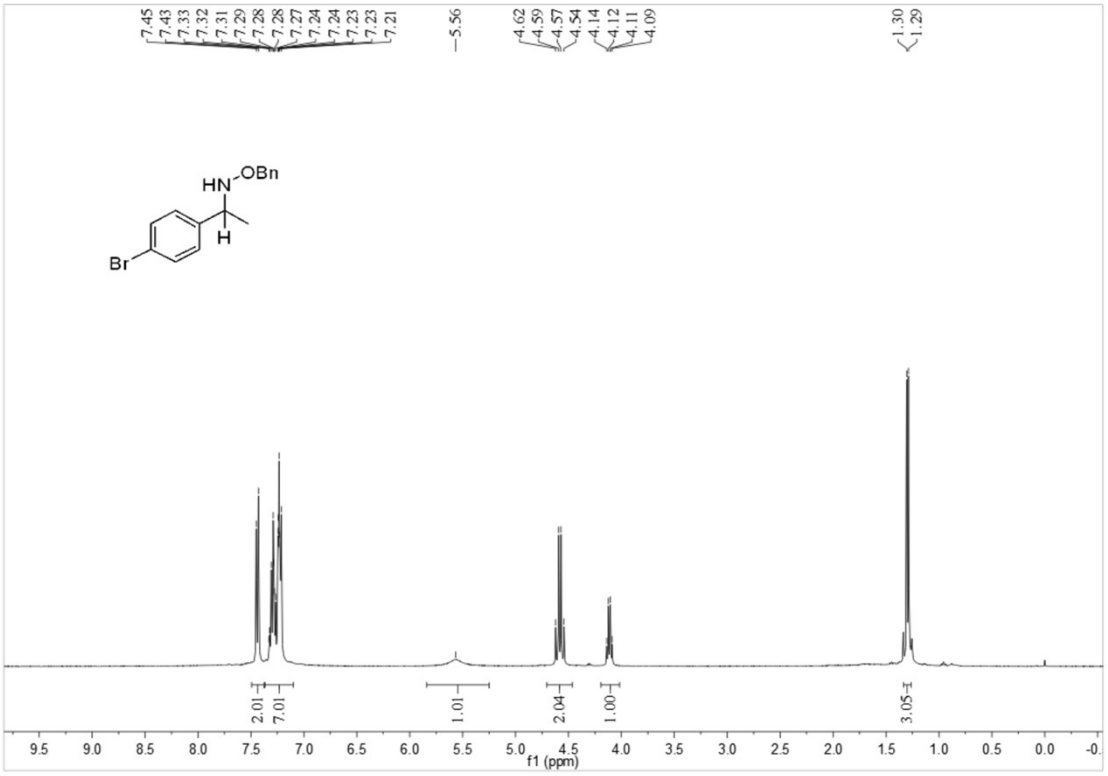
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(4-chlorophenyl)ethyl)hydroxylamine (2f)



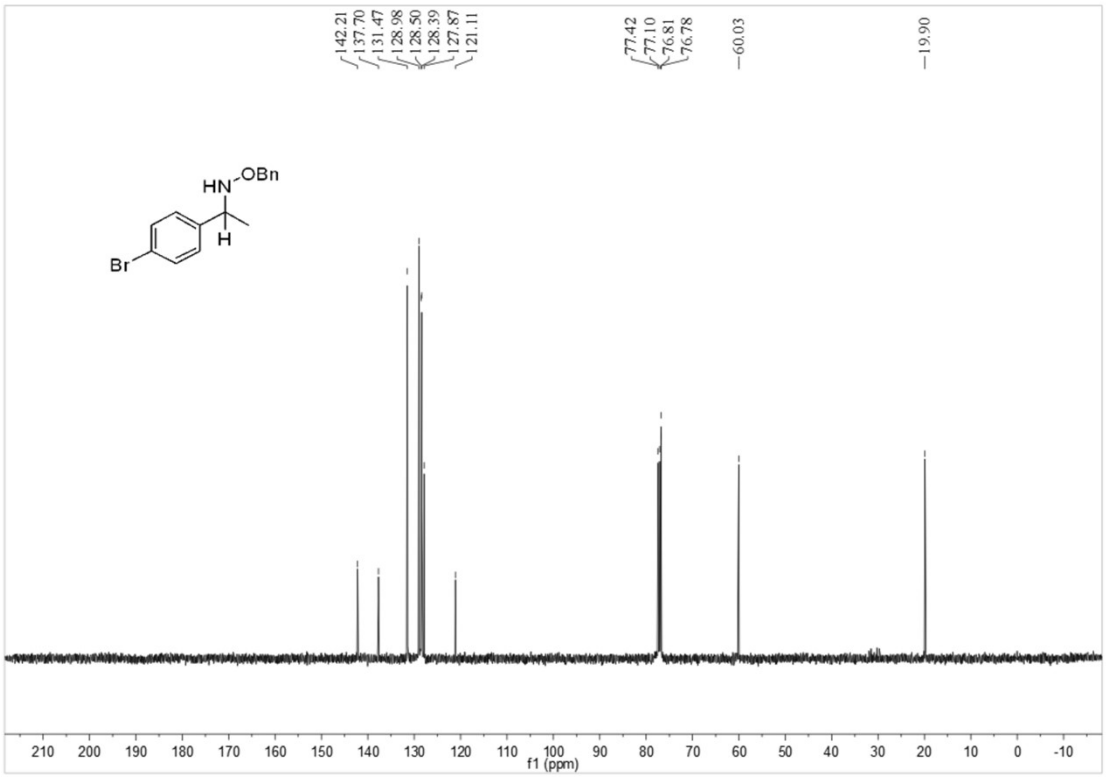
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(4-chlorophenyl)ethyl)hydroxylamine (2f)



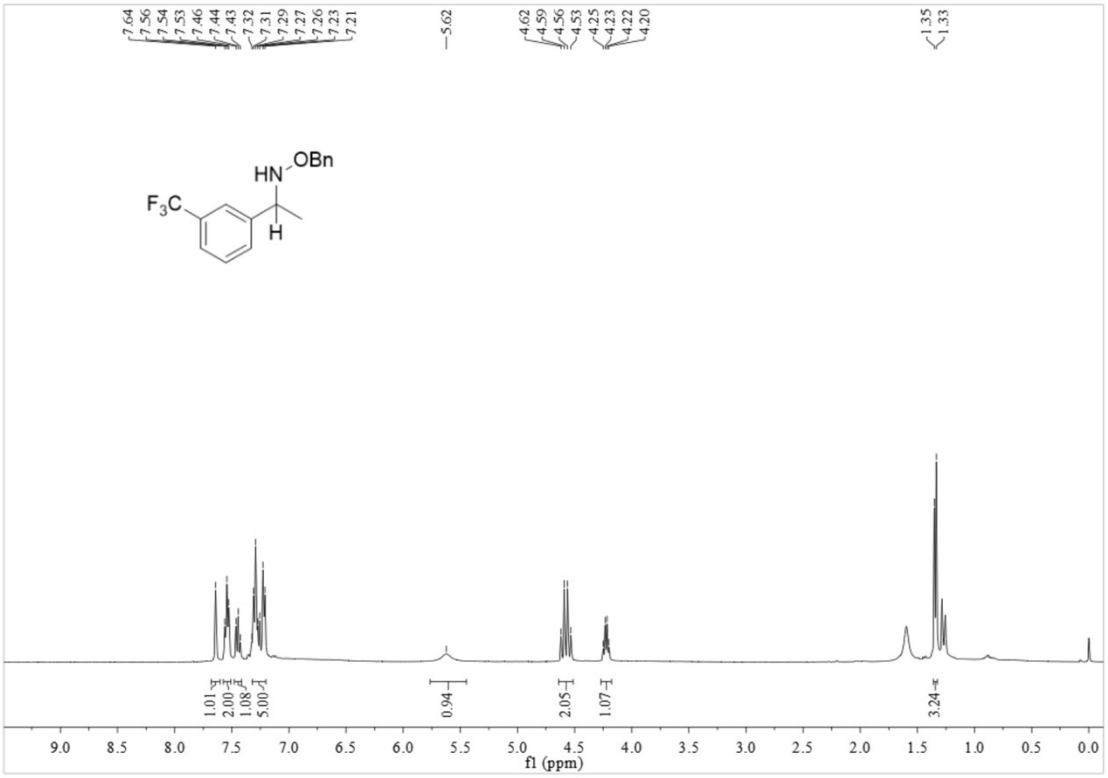
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(4-bromophenyl)ethyl)hydroxylamine (2g)



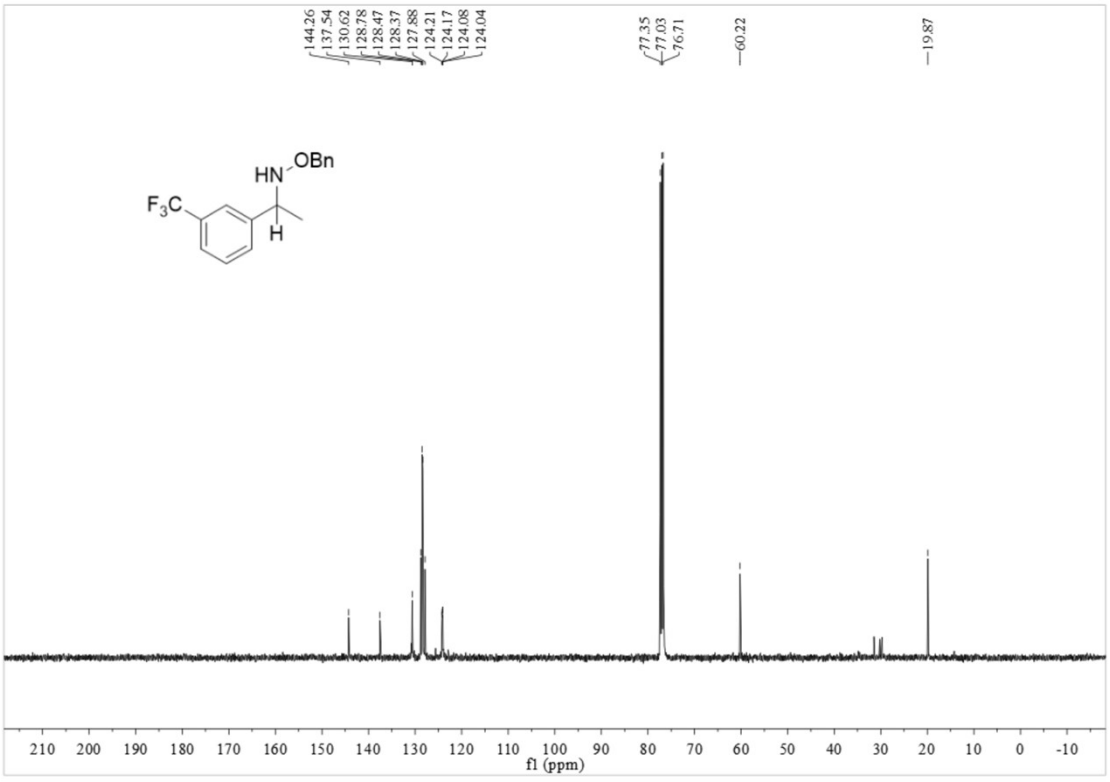
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(4-bromophenyl)ethyl)hydroxylamine (2g)



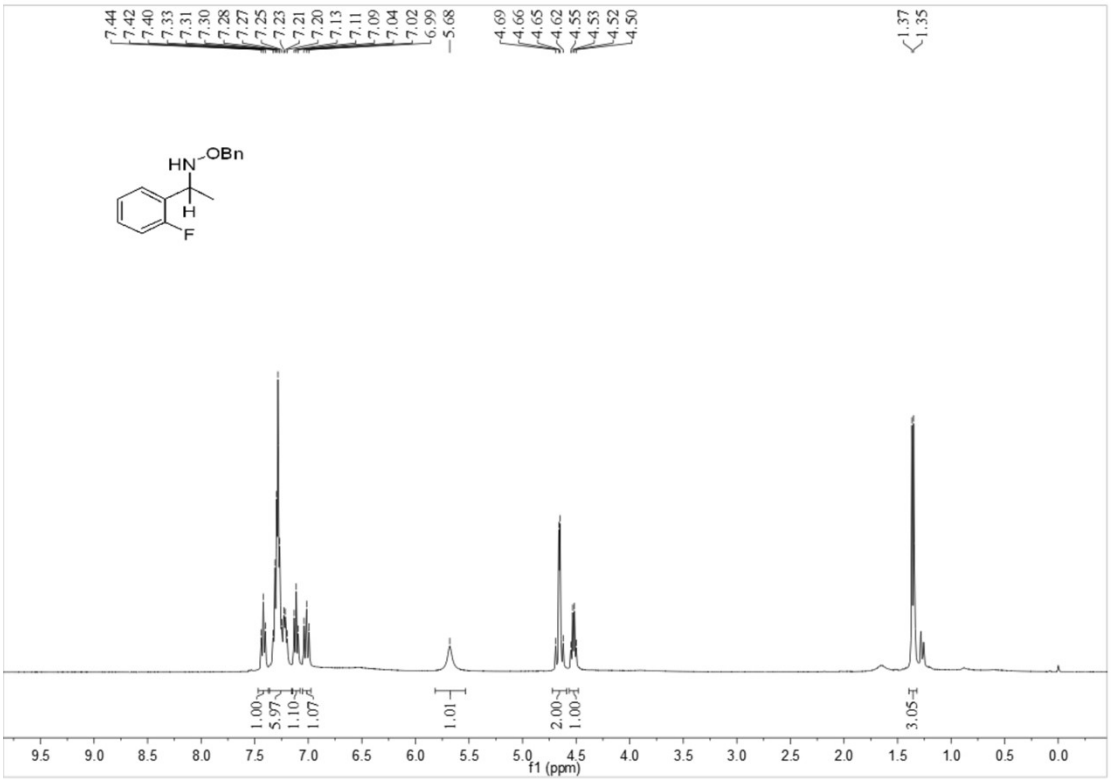
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(3-(trifluoromethyl)phenyl)ethyl)hydroxylamine (2h)



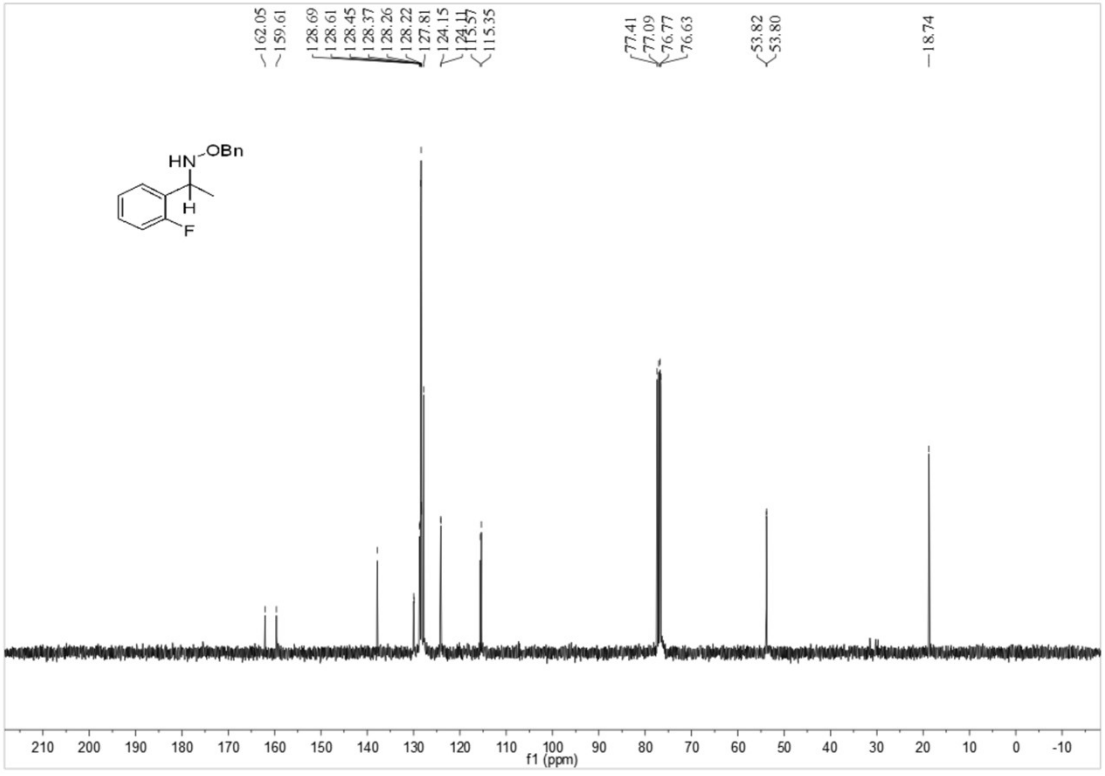
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(3-(trifluoromethyl)phenyl)ethyl)hydroxylamine (2h)



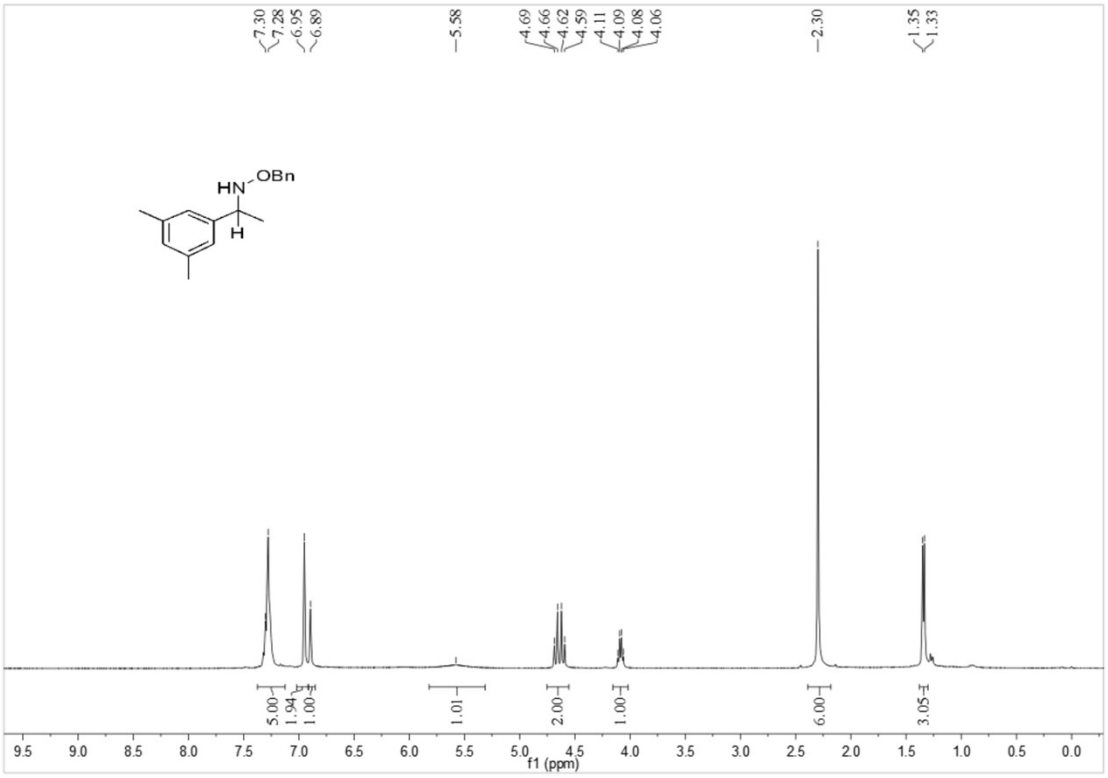
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(2-fluorophenyl)ethyl)hydroxylamine (2i)



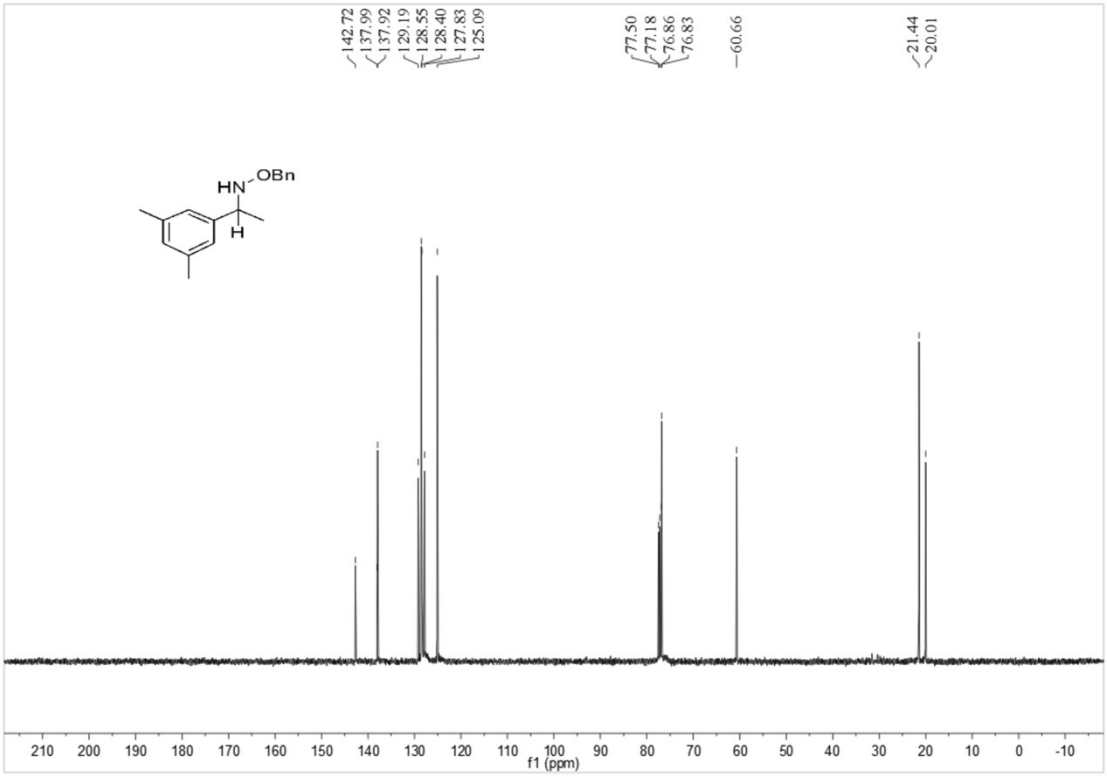
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(2-fluorophenyl)ethyl)hydroxylamine (2i)



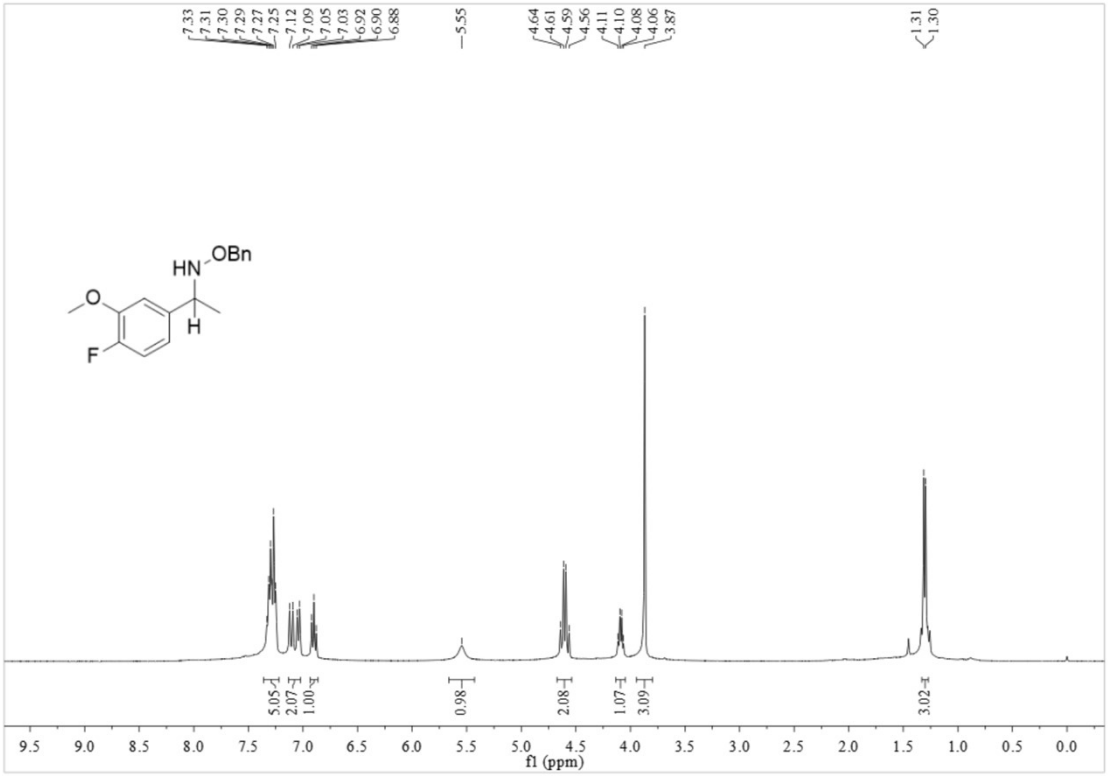
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(3,5-dimethylphenyl)ethyl)hydroxylamine (2j)



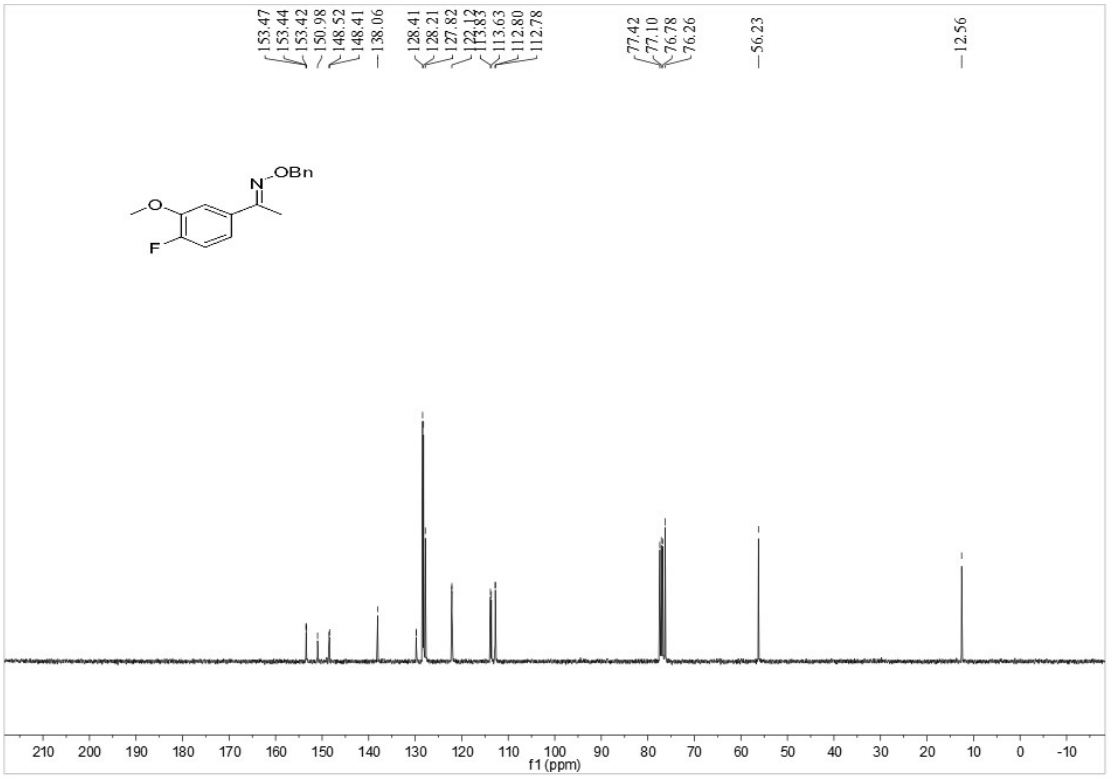
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(3,5-dimethylphenyl)ethyl)hydroxylamine (2j)



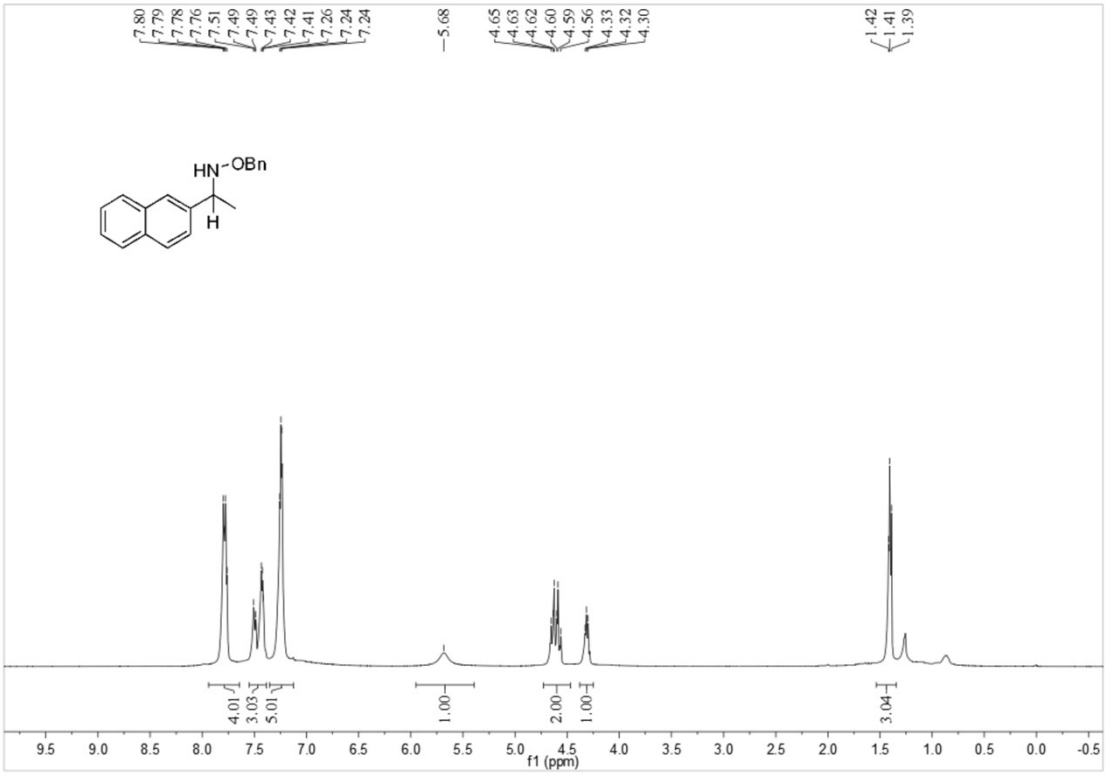
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(4-fluoro-3-methoxyphenyl)ethyl)hydroxylamine (2k)



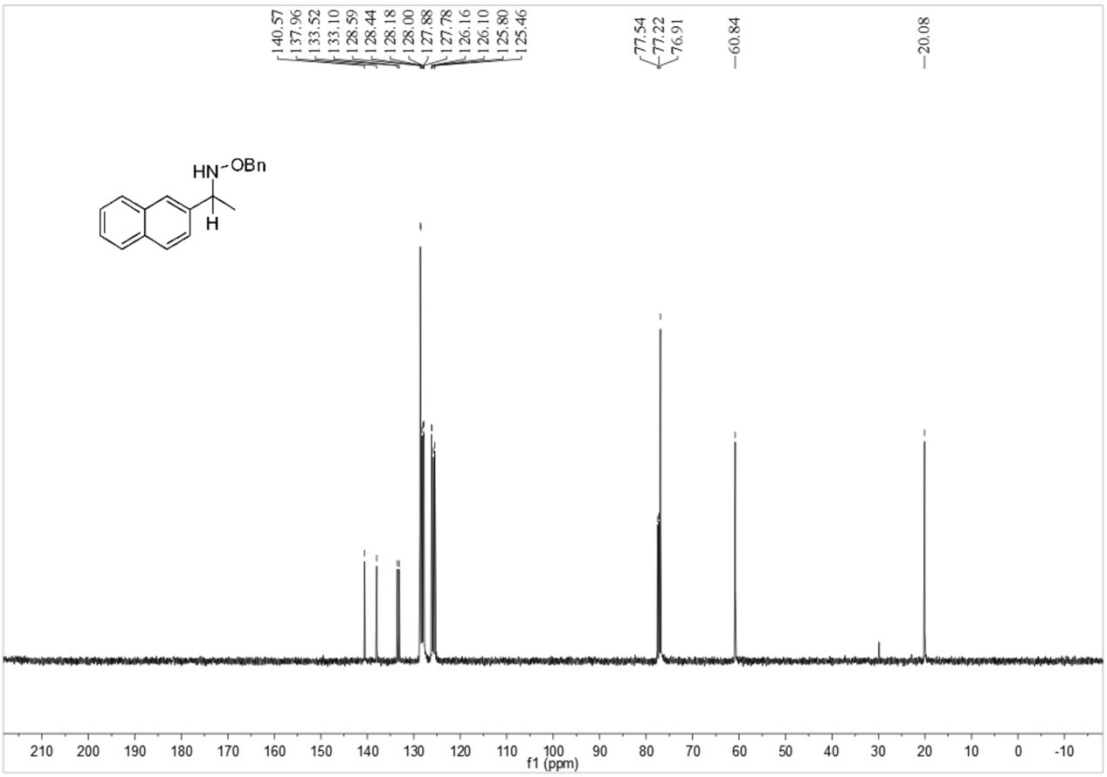
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(4-fluoro-3-methoxyphenyl)ethyl)hydroxylamine (2k)



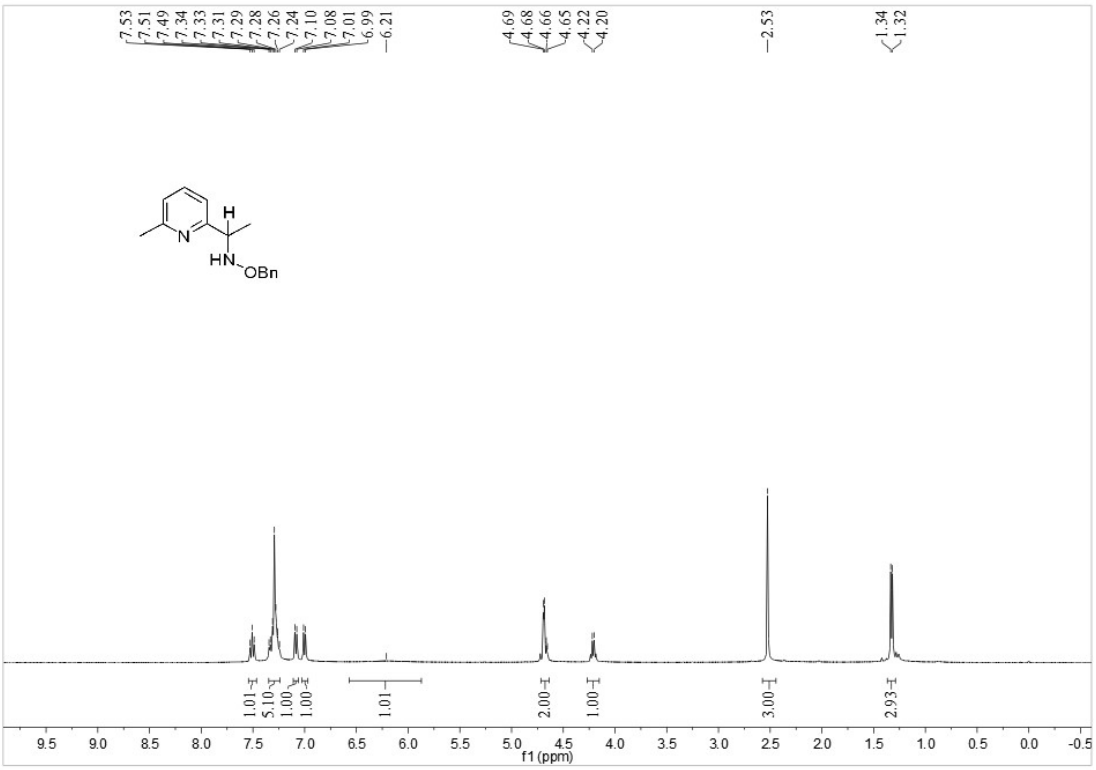
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(naphthalen-2-yl)ethyl)hydroxylamine (2l)



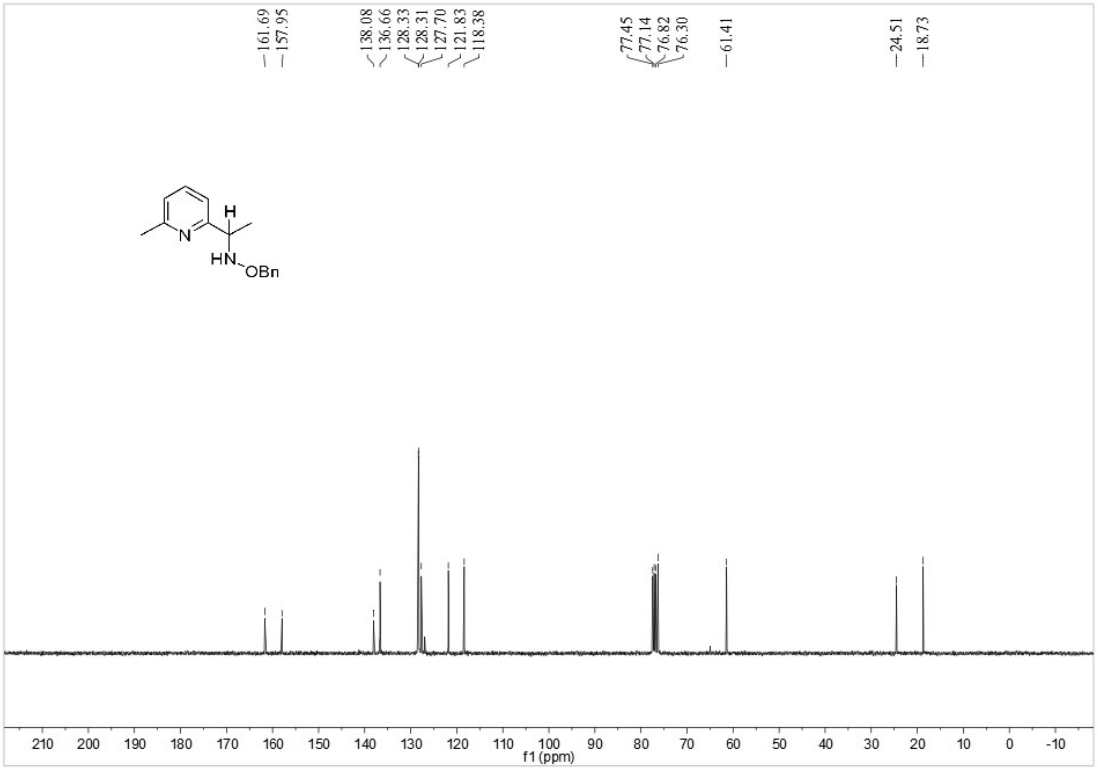
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(naphthalen-2-yl)ethyl)hydroxylamine (2l)



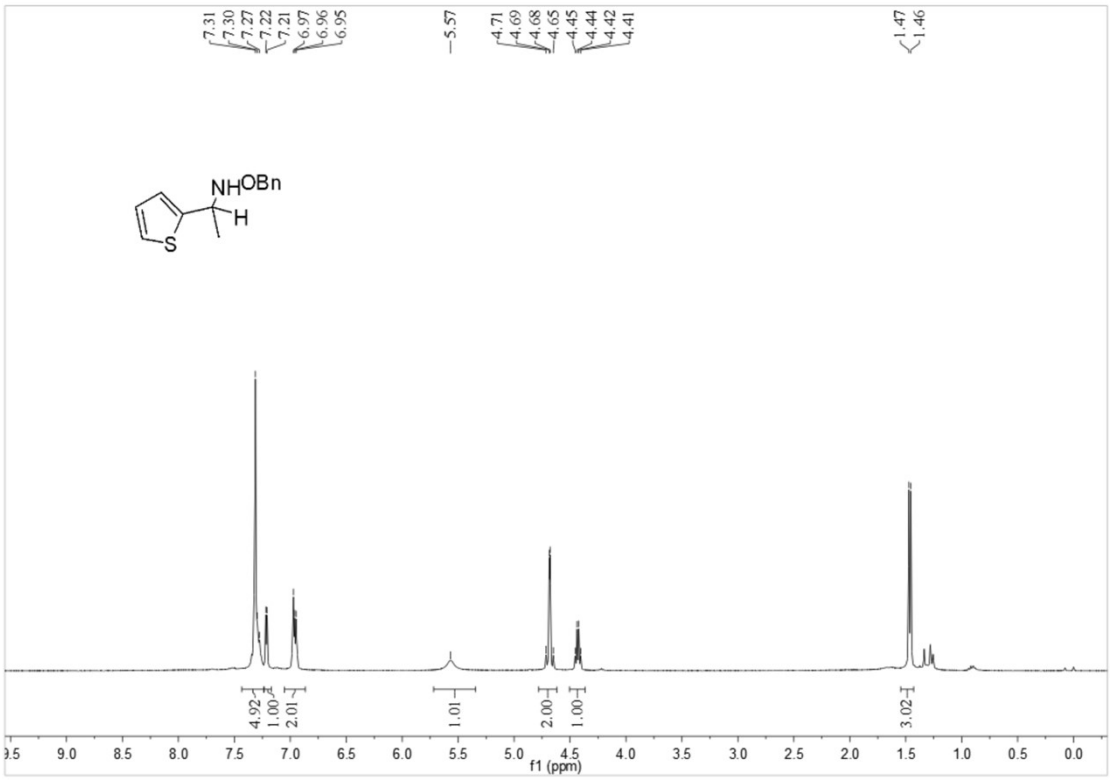
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(6-methylpyridin-2-yl)ethyl)hydroxylamine (2m)



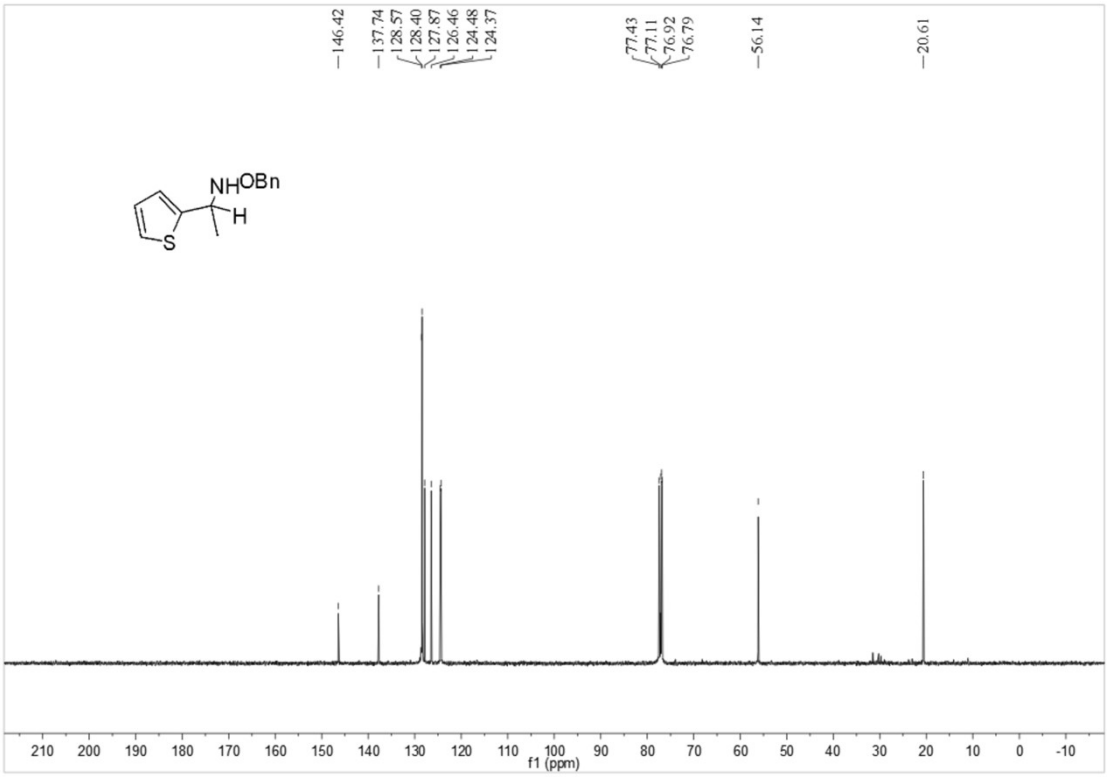
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(6-methylpyridin-2-yl)ethyl)hydroxylamine (2m)



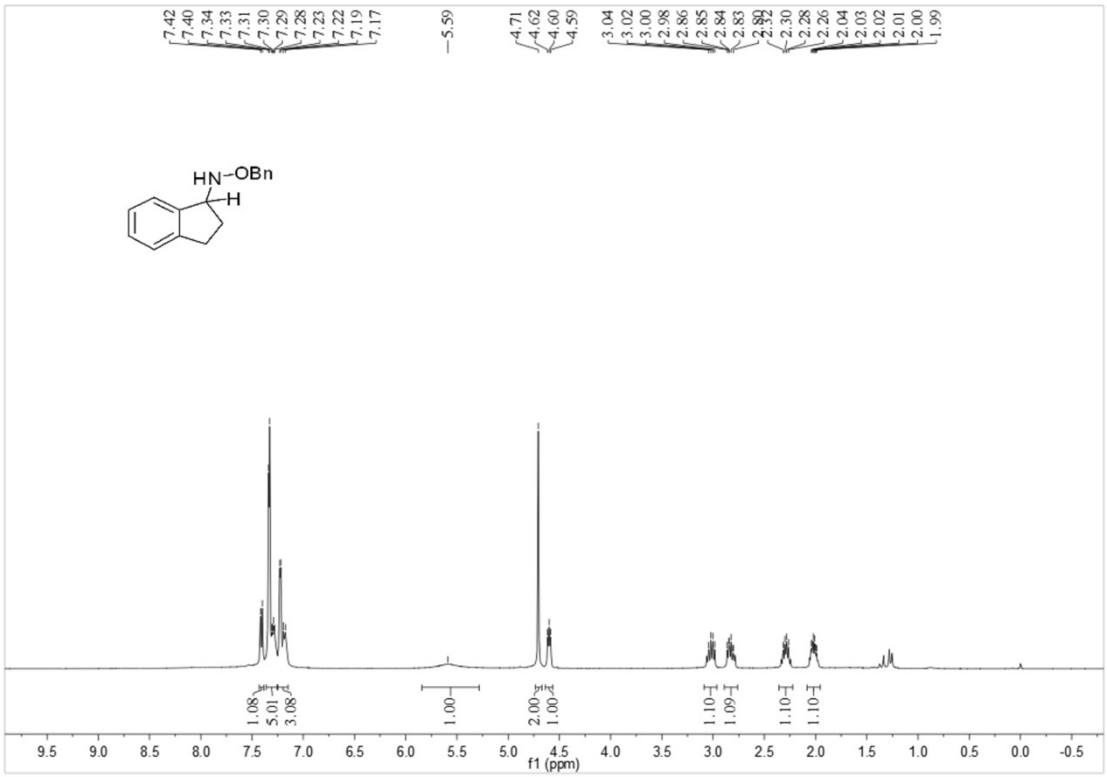
^{1}H NMR spectra of *O*-benzyl-*N*-(1-(thiophen-2-yl)ethyl)hydroxylamine (2n)



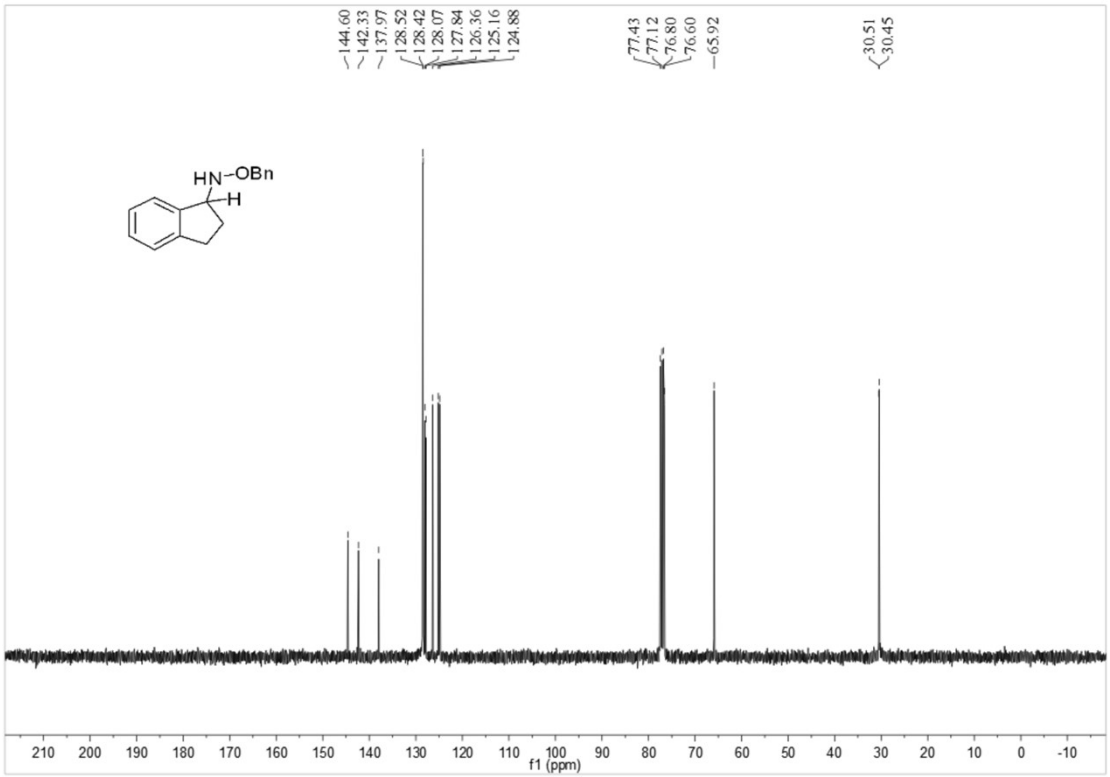
^{13}C NMR spectra of *O*-benzyl-*N*-(1-(thiophen-2-yl)ethyl)hydroxylamine (2n)



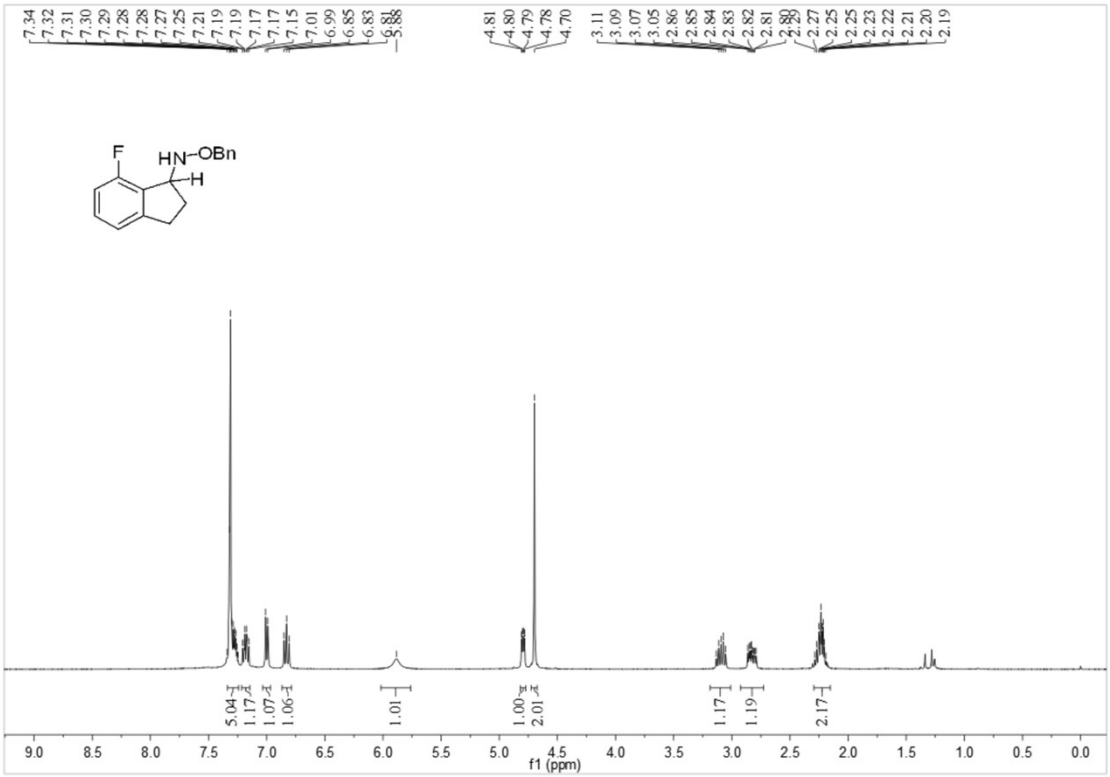
^{1}H NMR spectra of *O*-benzyl-*N*-(2,3-dihydro-1H-inden-1-yl)hydroxylamine (2o)



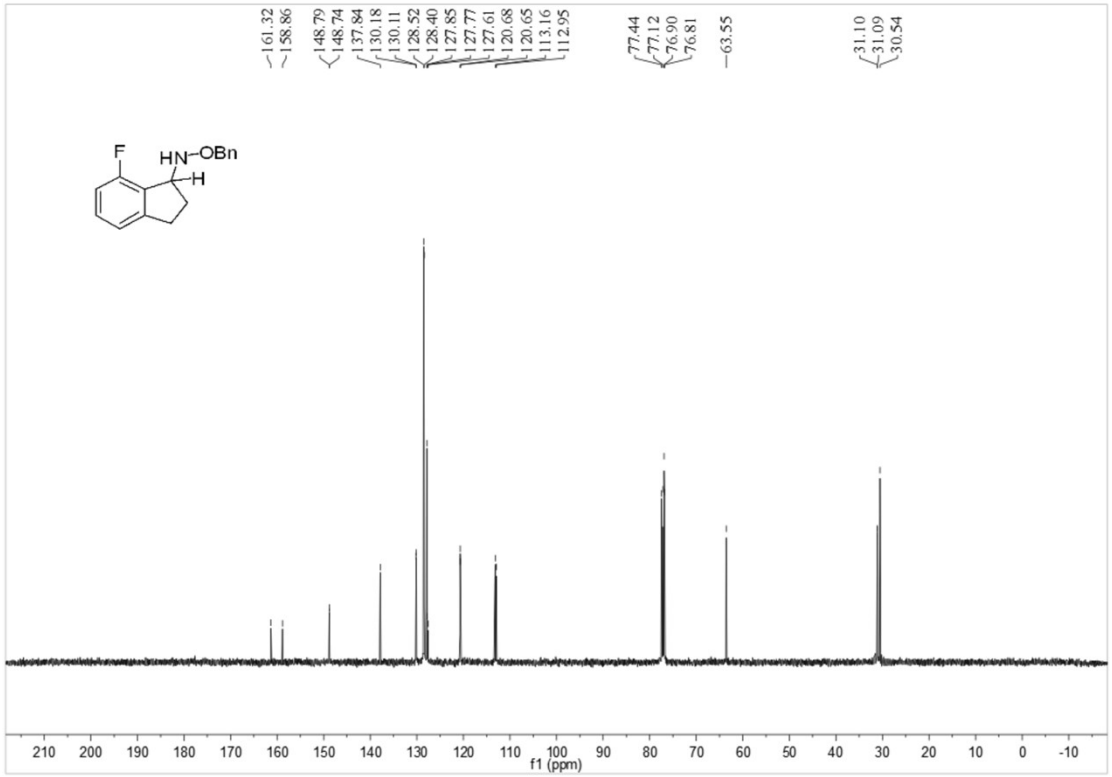
^{13}C NMR spectra of *O*-benzyl-*N*-(2,3-dihydro-1H-inden-1-yl)hydroxylamine (2o)



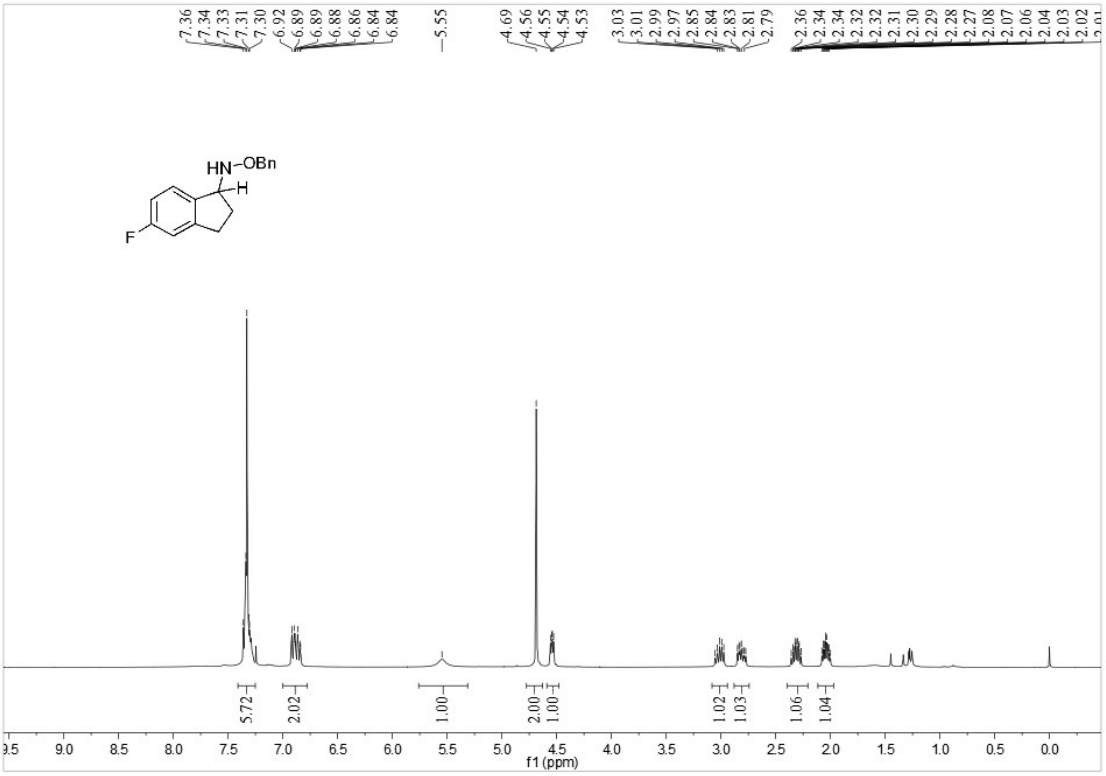
^{1}H NMR spectra of *O*-benzyl-*N*-(7-fluoro-2,3-dihydro-1H-inden-1-yl)hydroxylamine (2p)



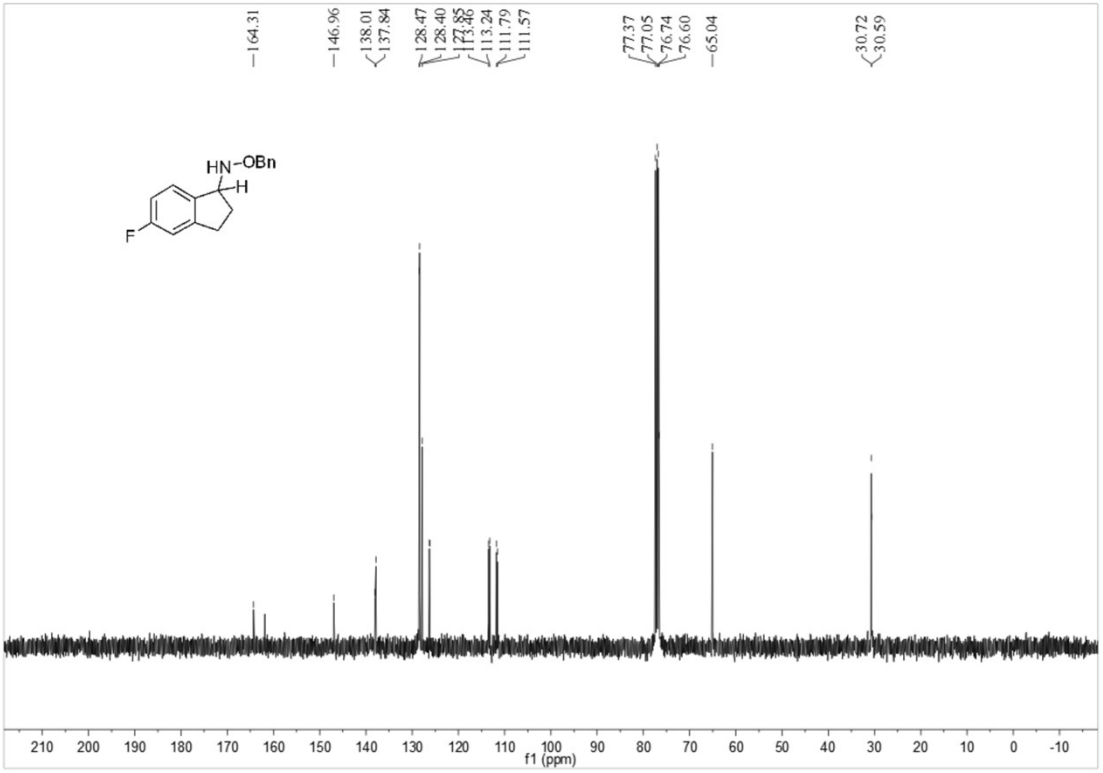
^{13}C NMR spectra of *O*-benzyl-*N*-(7-fluoro-2,3-dihydro-1H-inden-1-yl)hydroxylamine (2p)



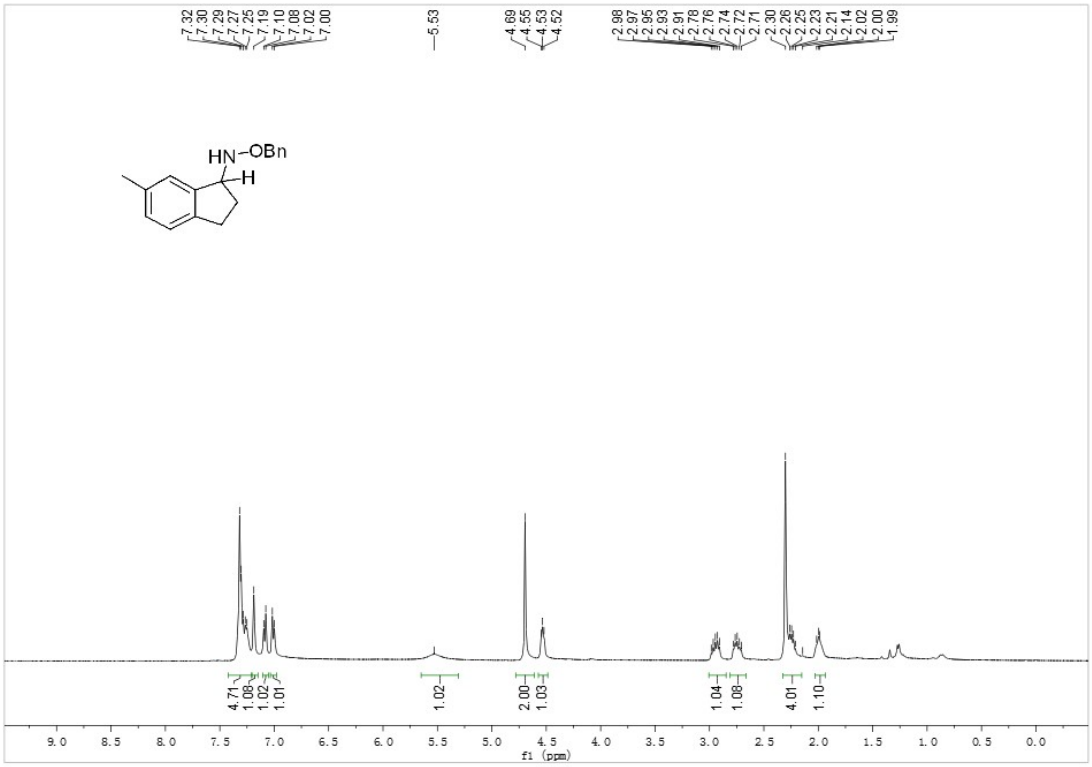
^{1}H NMR spectra of *O*-benzyl-*N*-(5-fluoro-2,3-dihydro-1H-inden-1-yl)hydroxylamine (2q)



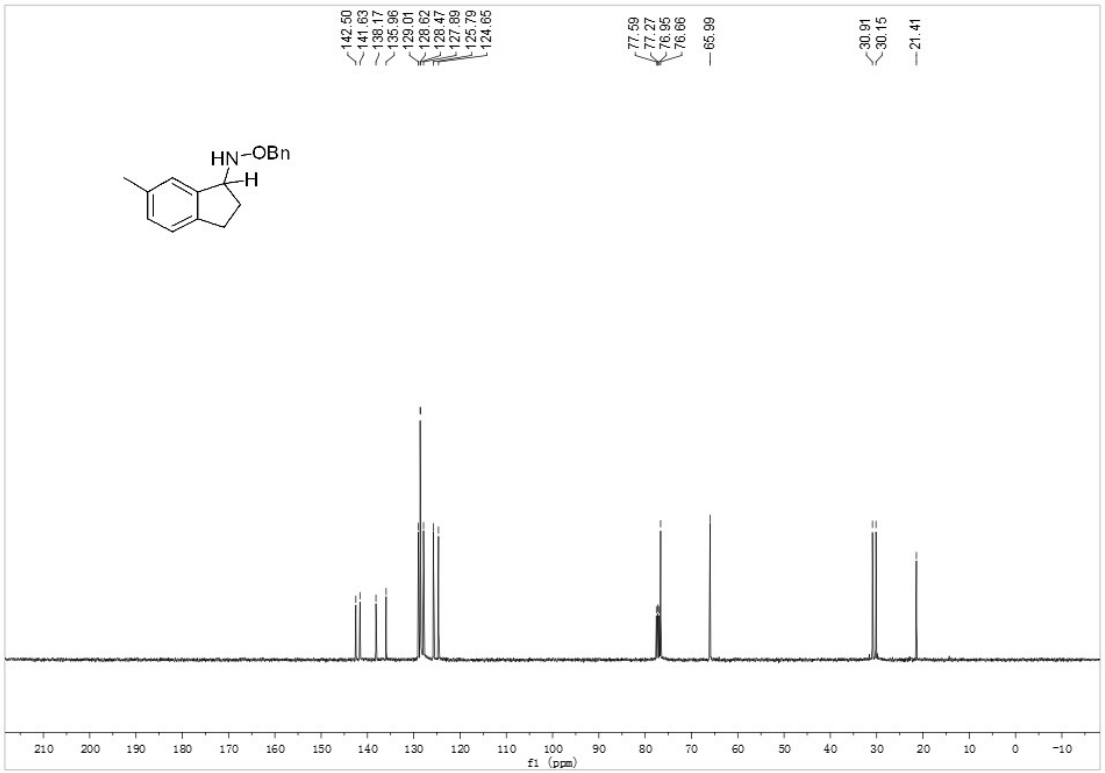
^{13}C NMR spectra of *O*-benzyl-*N*-(5-fluoro-2,3-dihydro-1H-inden-1-yl)hydroxylamine (2q)



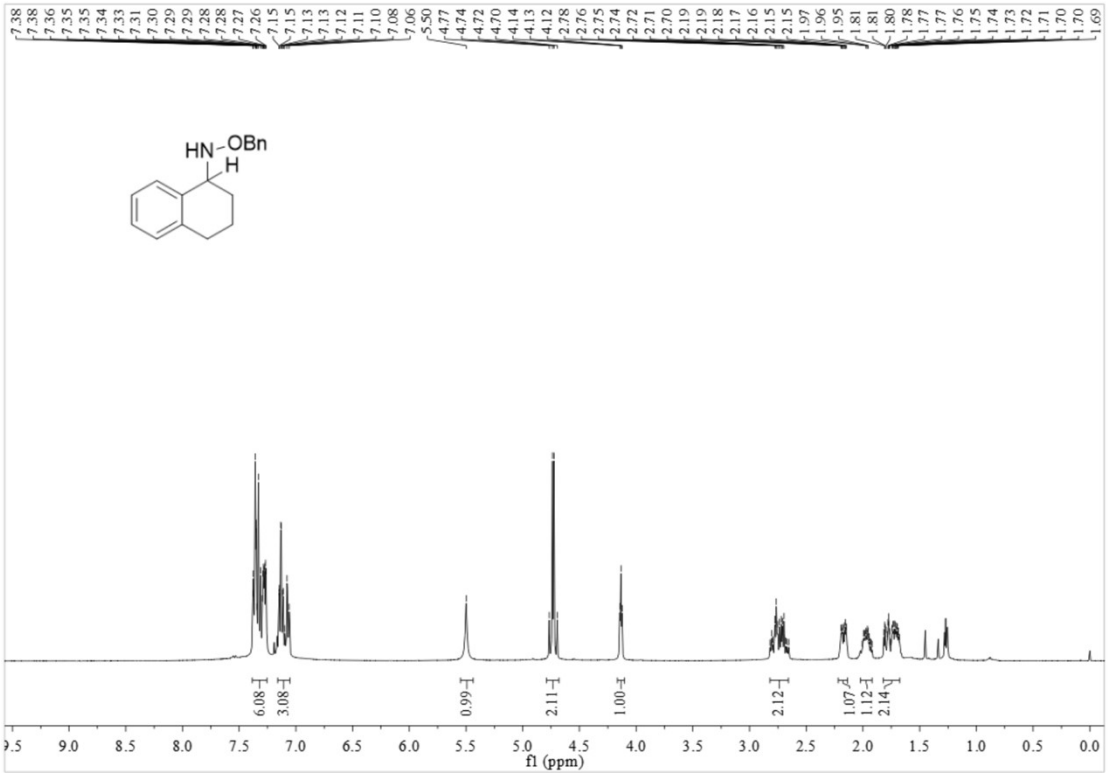
^{1}H NMR spectra of *O*-benzyl-*N*-(6-methyl-2,3-dihydro-1H-inden-1-yl)hydroxylamine (2r)



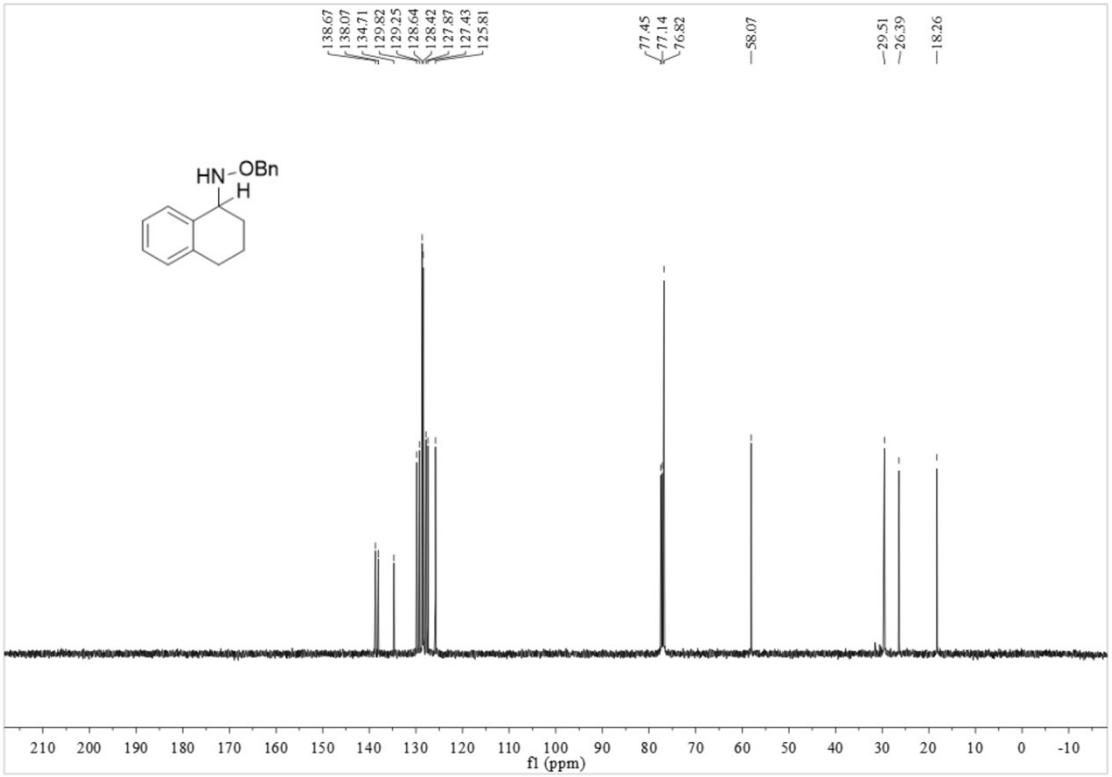
^{13}C NMR spectra of *O*-benzyl-*N*-(6-methyl-2,3-dihydro-1H-inden-1-yl)hydroxylamine (2r)



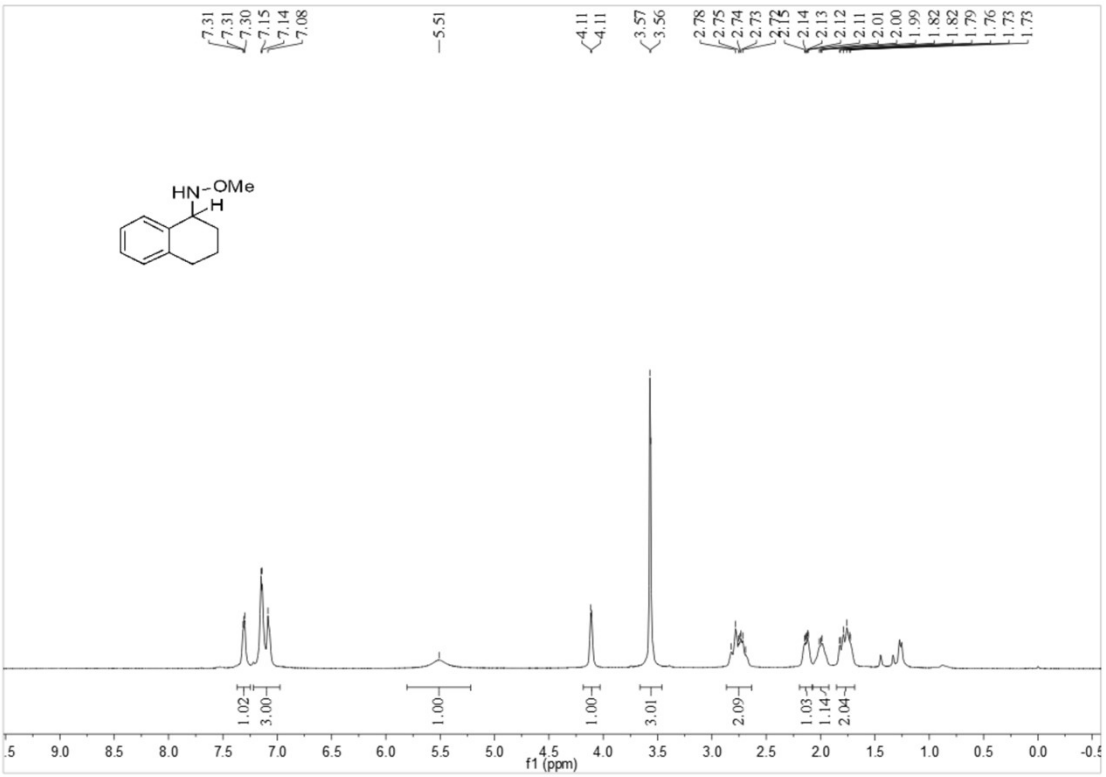
^{1}H NMR spectra of *O*-benzyl-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2s)



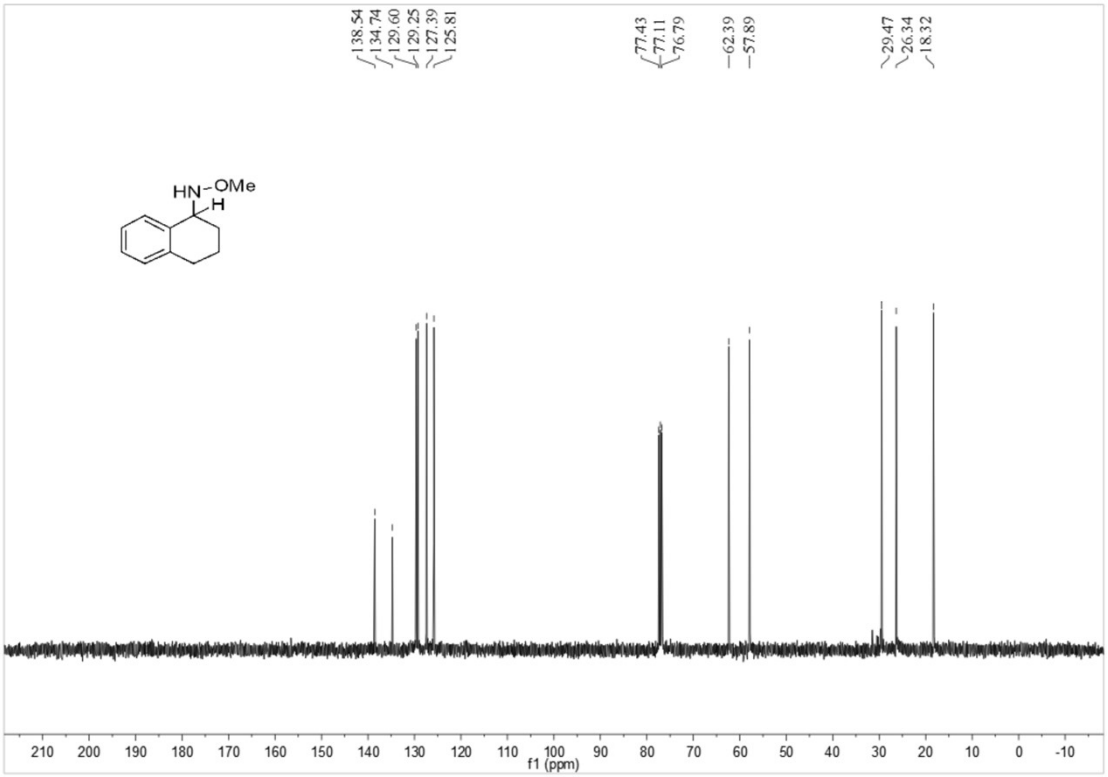
^{13}C NMR spectra of *O*-benzyl-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2s)



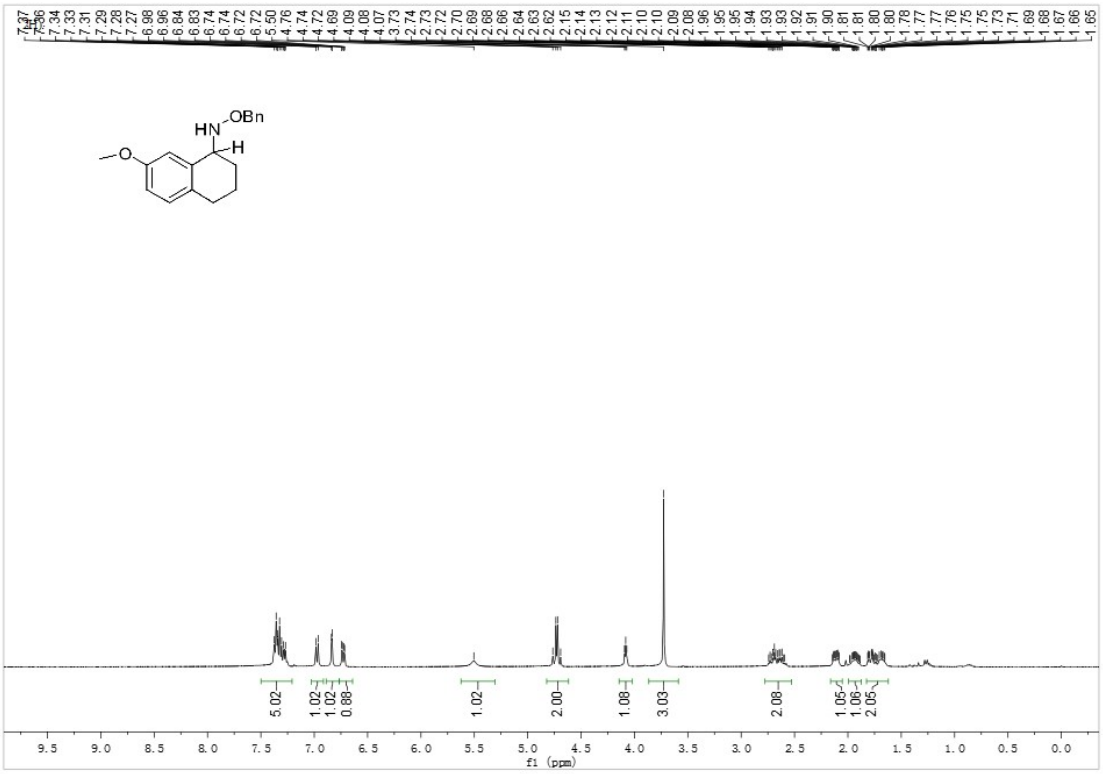
^{1}H NMR spectra of *O*-methyl-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylaminee (2t)



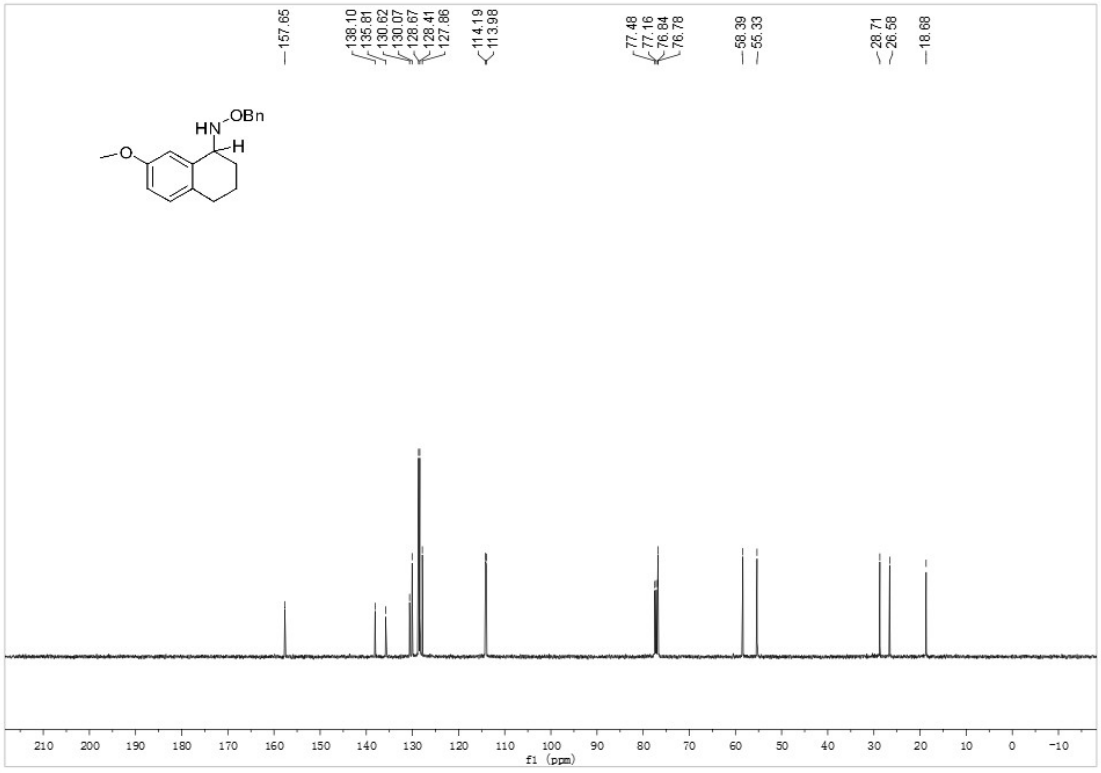
^{13}C NMR spectra of *O*-methyl-*N*-(1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2t)



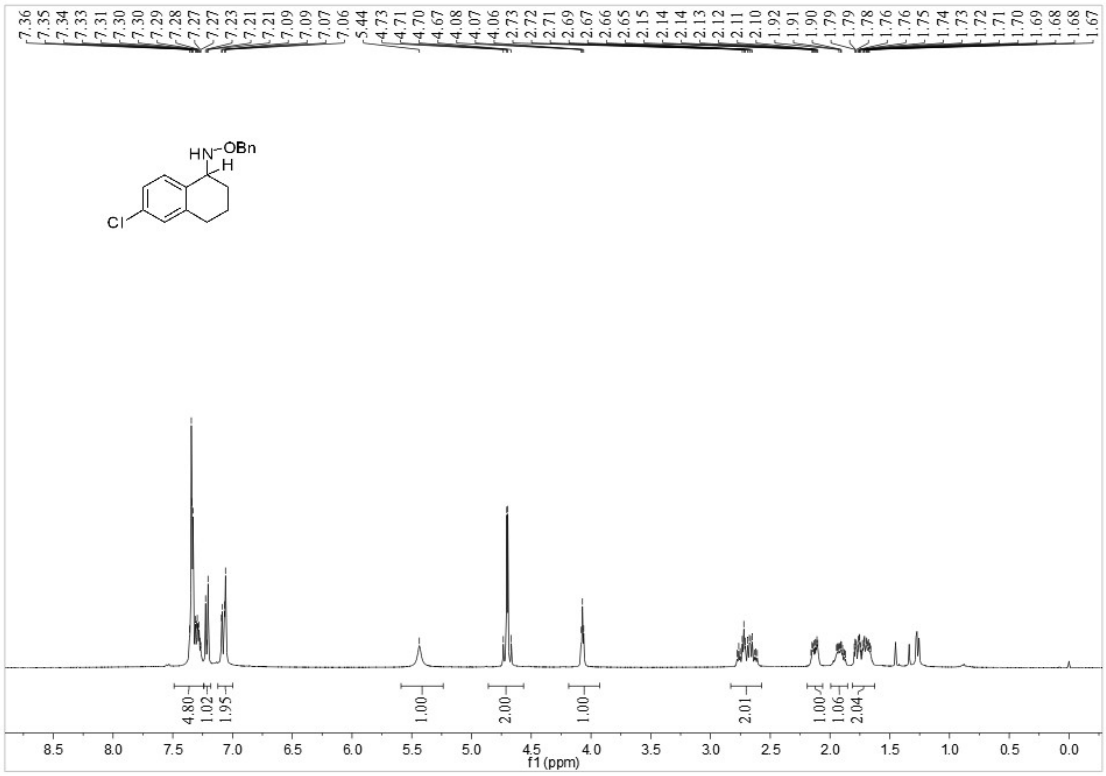
^{1}H NMR spectra of *O*-benzyl-*N*-(7-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2v):



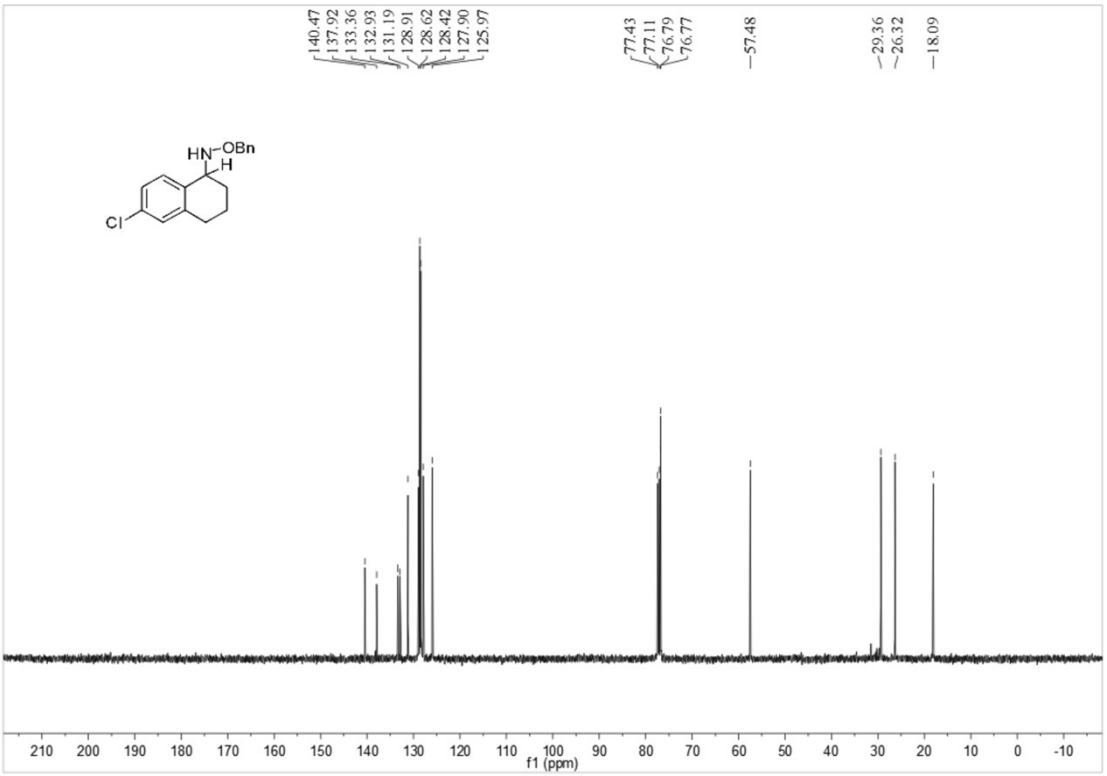
^{13}C NMR spectra of *O*-benzyl-*N*-(7-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2v):



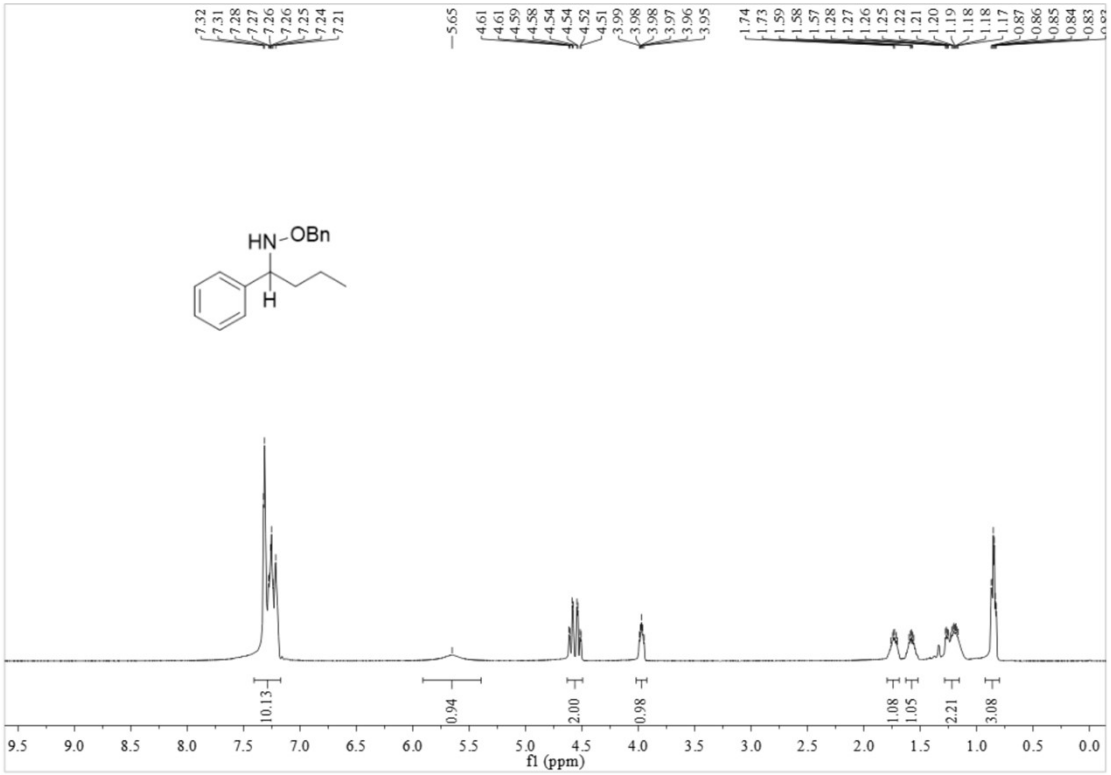
^{1}H NMR spectra of *O*-benzyl-*N*-(6-chloro-1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2w)



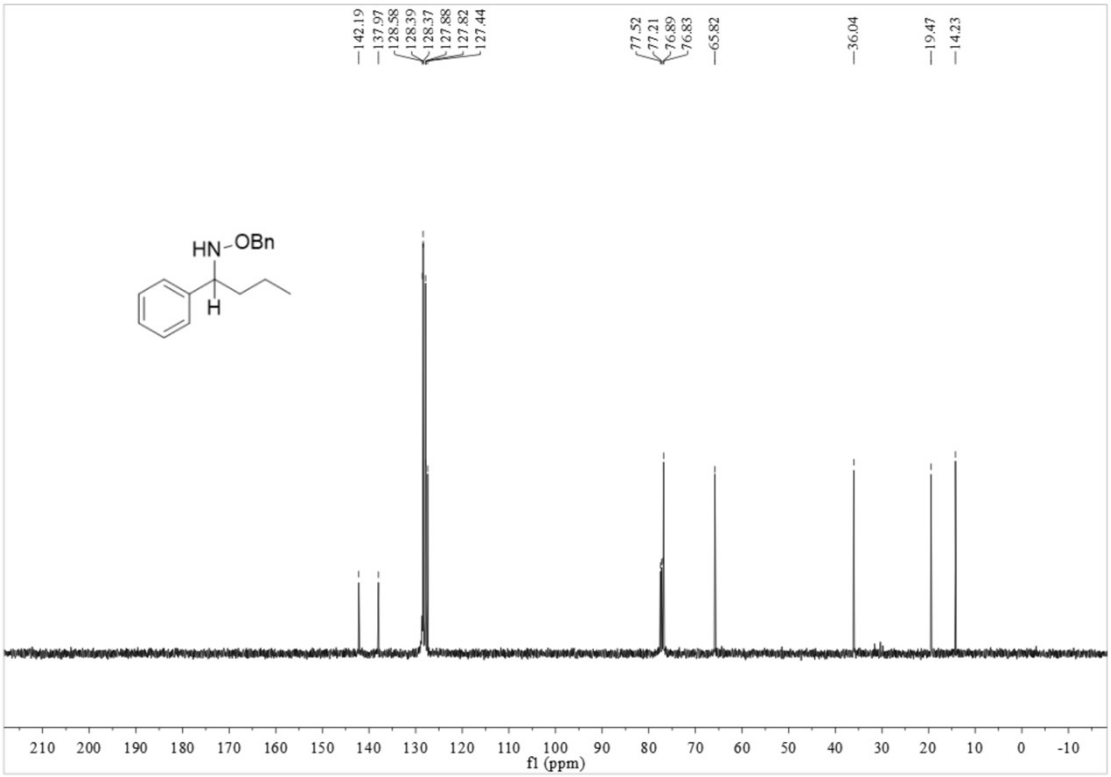
^{13}C NMR spectra of *O*-benzyl-*N*-(6-chloro-1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2w)



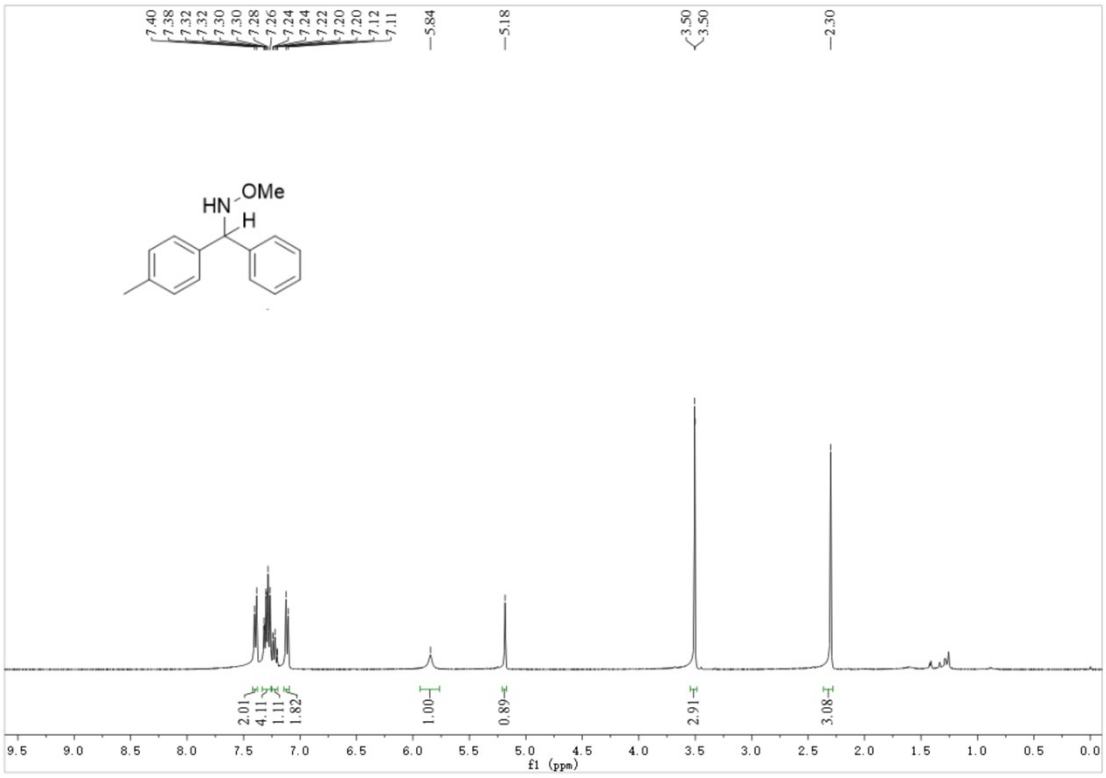
^{1}H NMR spectra of *O*-benzyl-*N*-(1-phenylbutyl)hydroxylamine (2x):



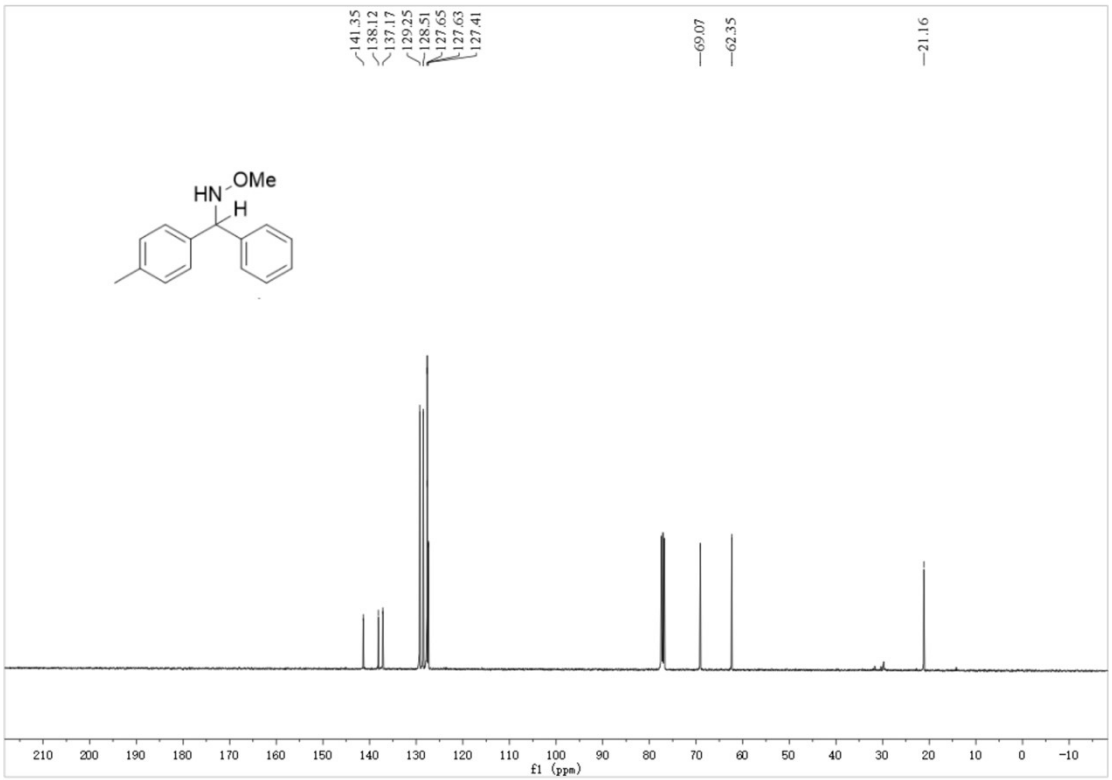
^{13}C NMR spectra of *O*-benzyl-*N*-(1-phenylbutyl)hydroxylamine (2x):



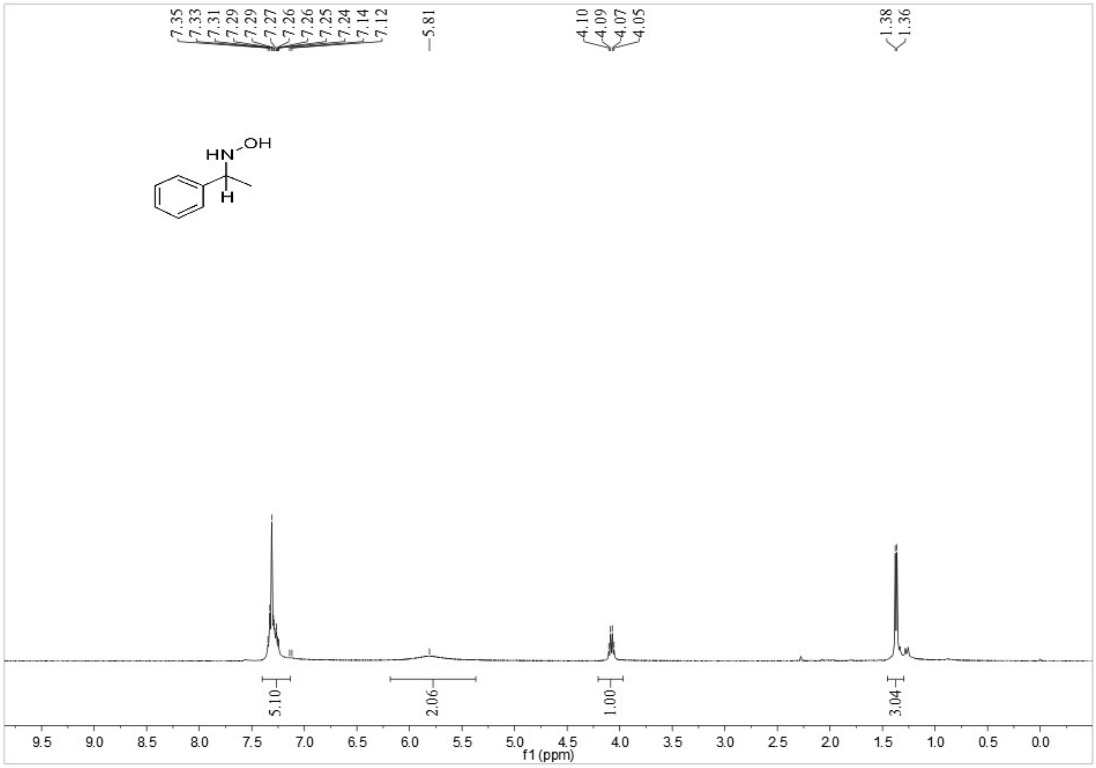
^{1}H NMR spectra of *O*-methyl-N-(phenyl(p-tolyl)methyl)hydroxylamine (2y)



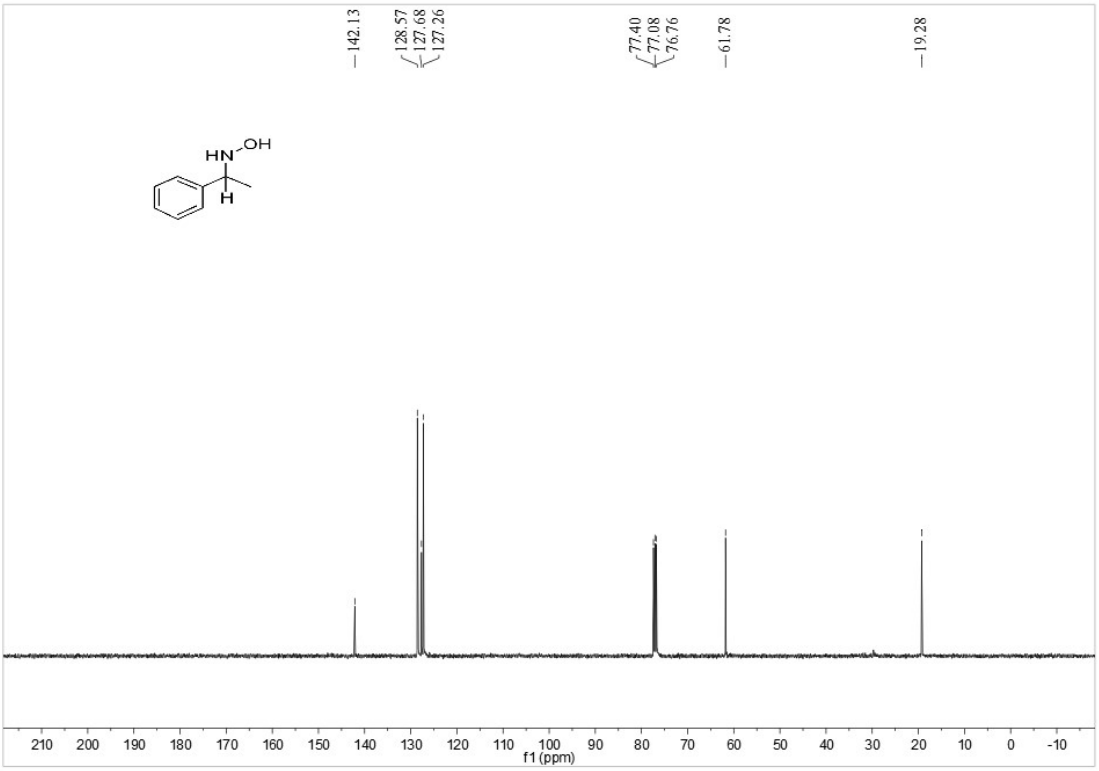
^{13}C NMR spectra of *O*-methyl-N-(phenyl(p-tolyl)methyl)hydroxylamine (2y)



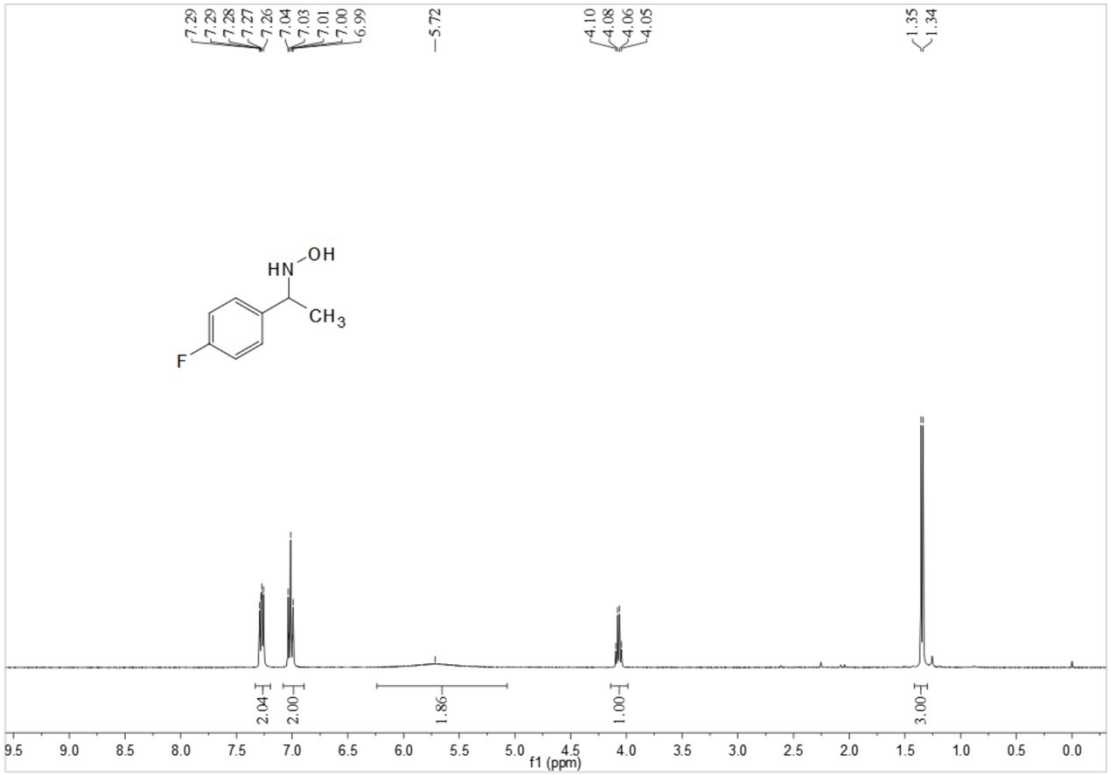
^{1}H NMR spectra of *N*-(1-phenylethyl)hydroxylamine (2ba)



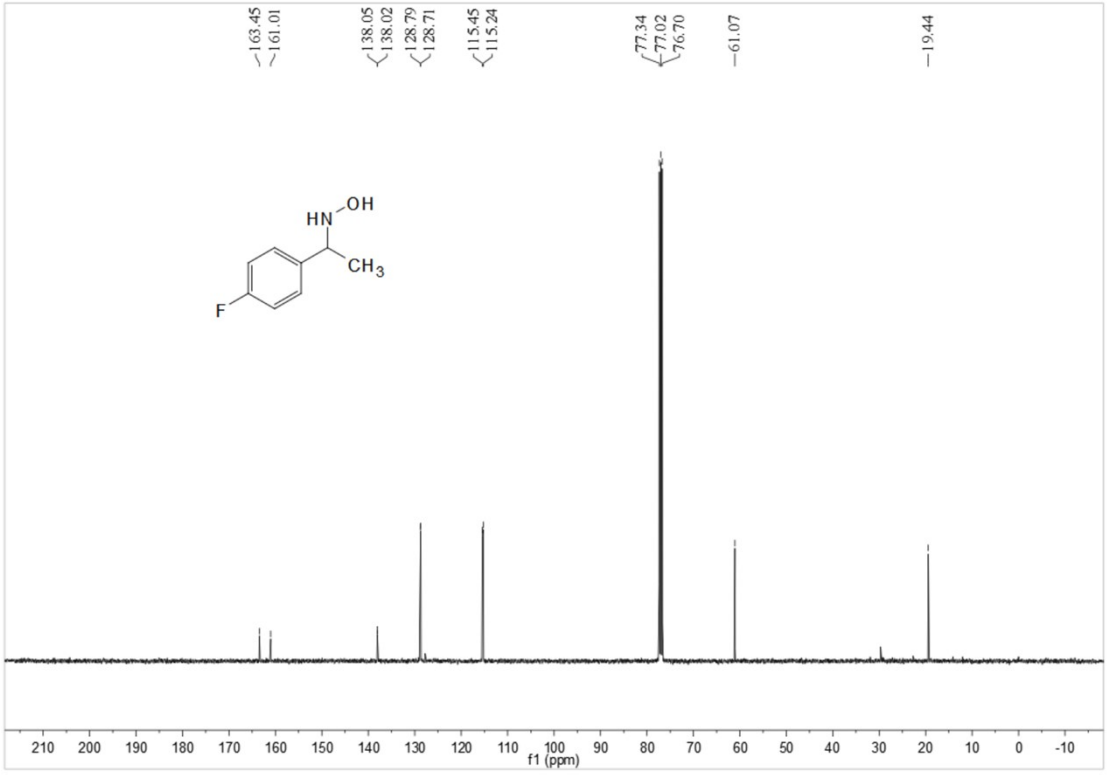
^{13}C NMR spectra of *N*-(1-phenylethyl)hydroxylamine (2ba)



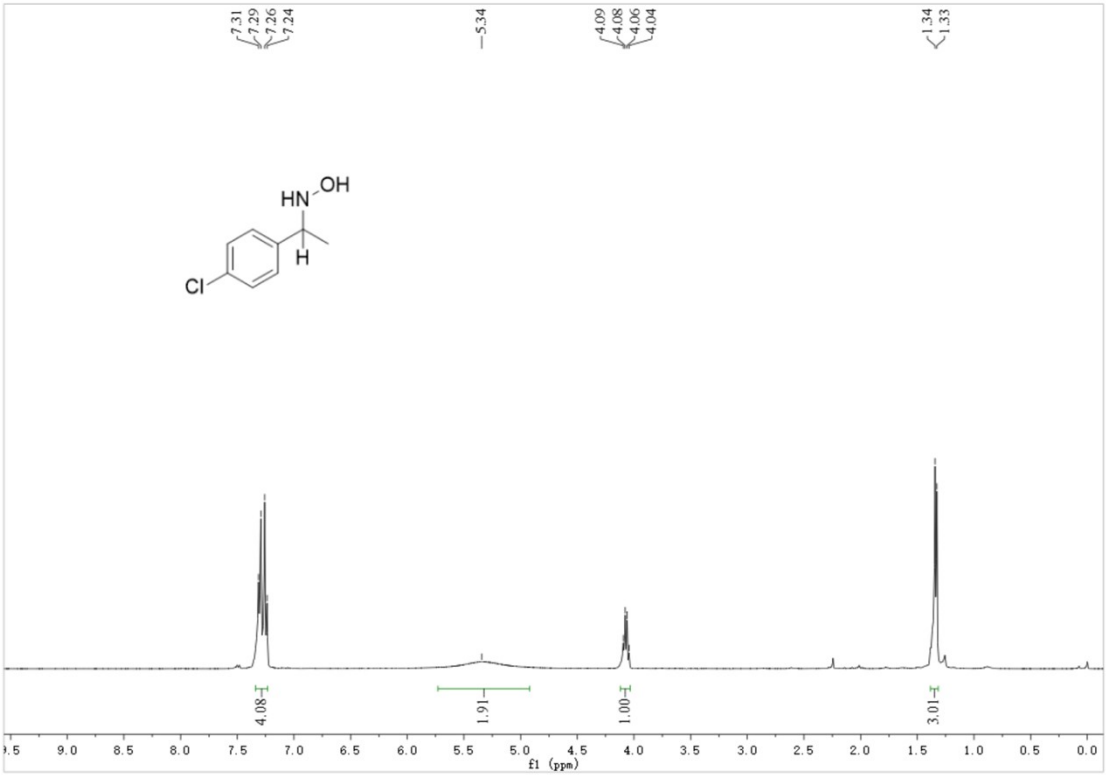
^{1}H NMR spectra of *N*-(1-(4-fluorophenyl)ethyl)hydroxylamine (2bb)



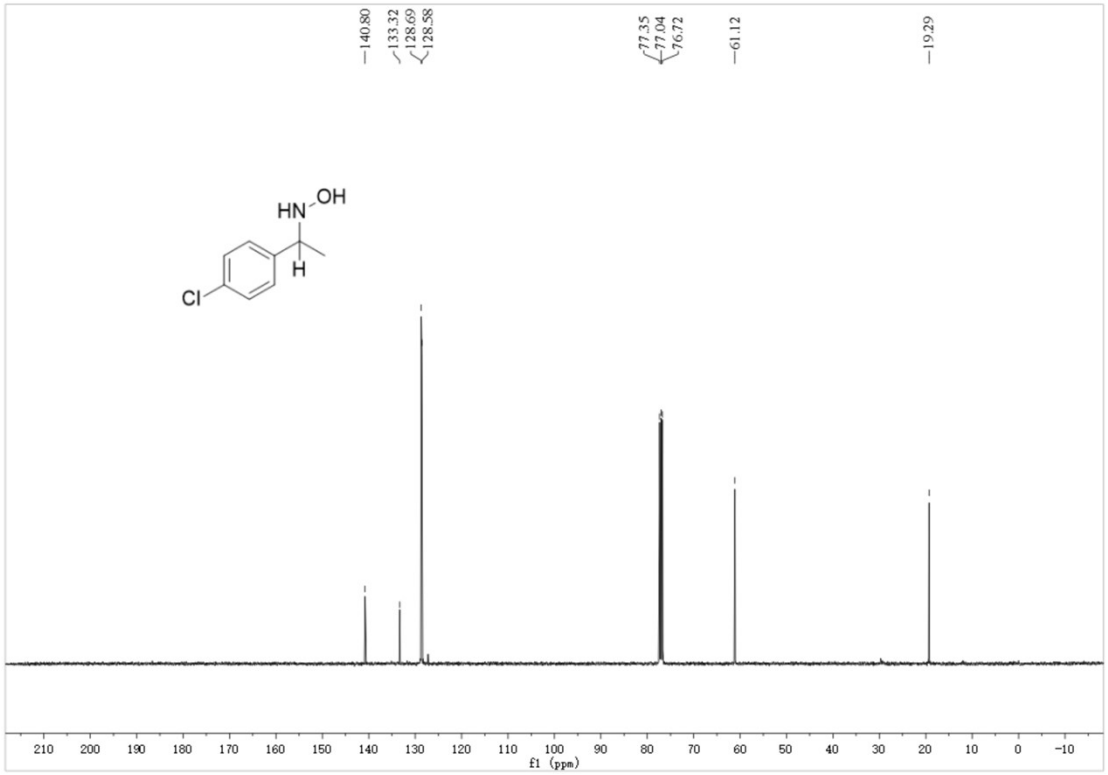
^{13}C NMR spectra of *N*-(1-(4-fluorophenyl)ethyl)hydroxylamine (2bb)



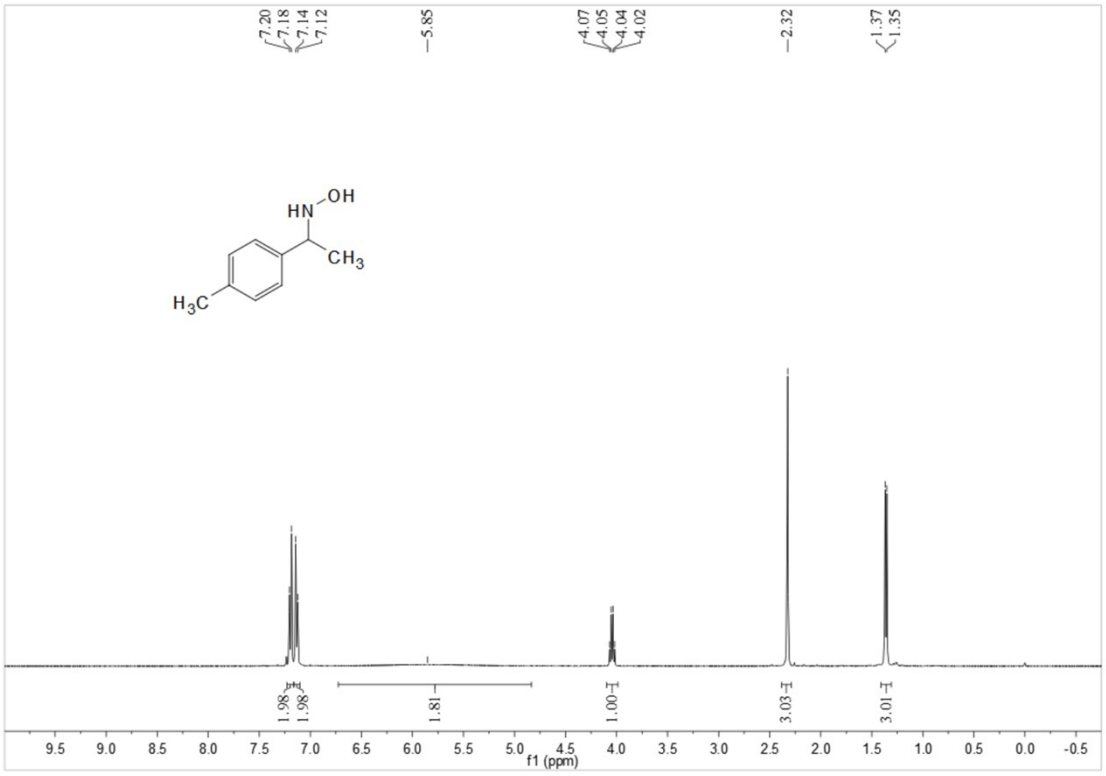
^{1}H NMR spectra of *N*-(1-(4-chlorophenyl)ethyl)hydroxylamine (2bc)



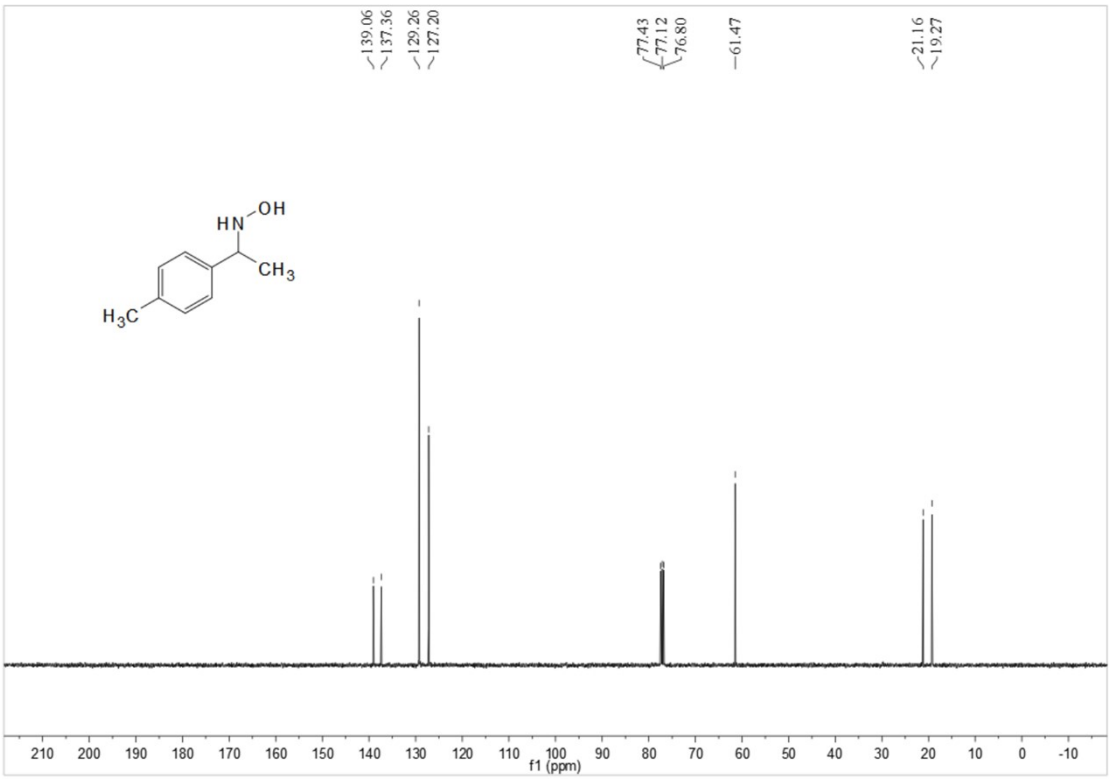
^{13}C NMR spectra of *N*-(1-(4-chlorophenyl)ethyl)hydroxylamine (2bc)



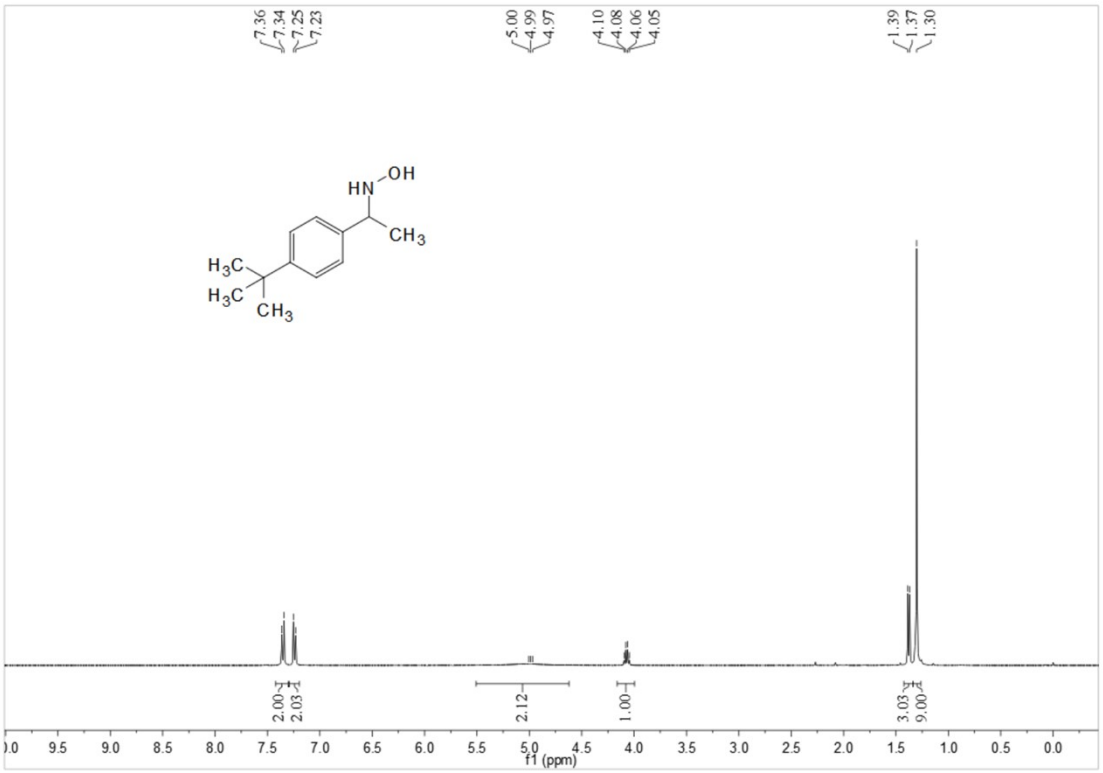
^{1}H NMR spectra of *N*-(1-(p-tolyl)ethyl)hydroxylamine (2bd)



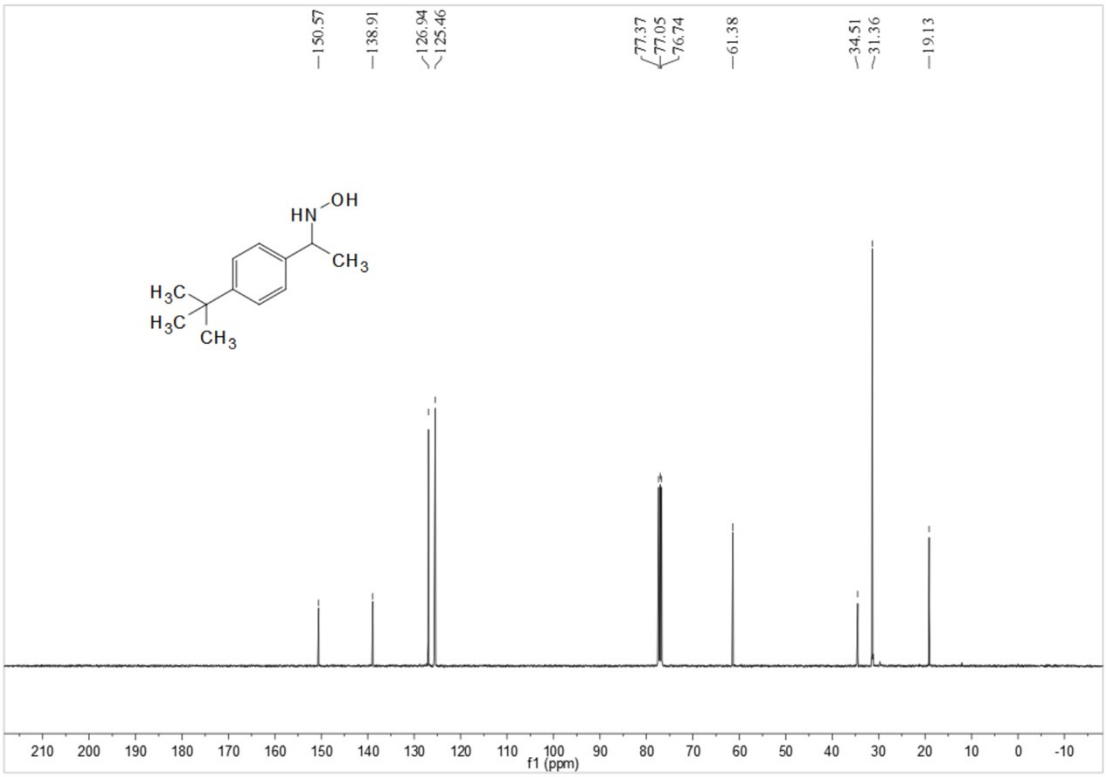
^{13}C NMR spectra of *N*-(1-(p-tolyl)ethyl)hydroxylamine (2bd)



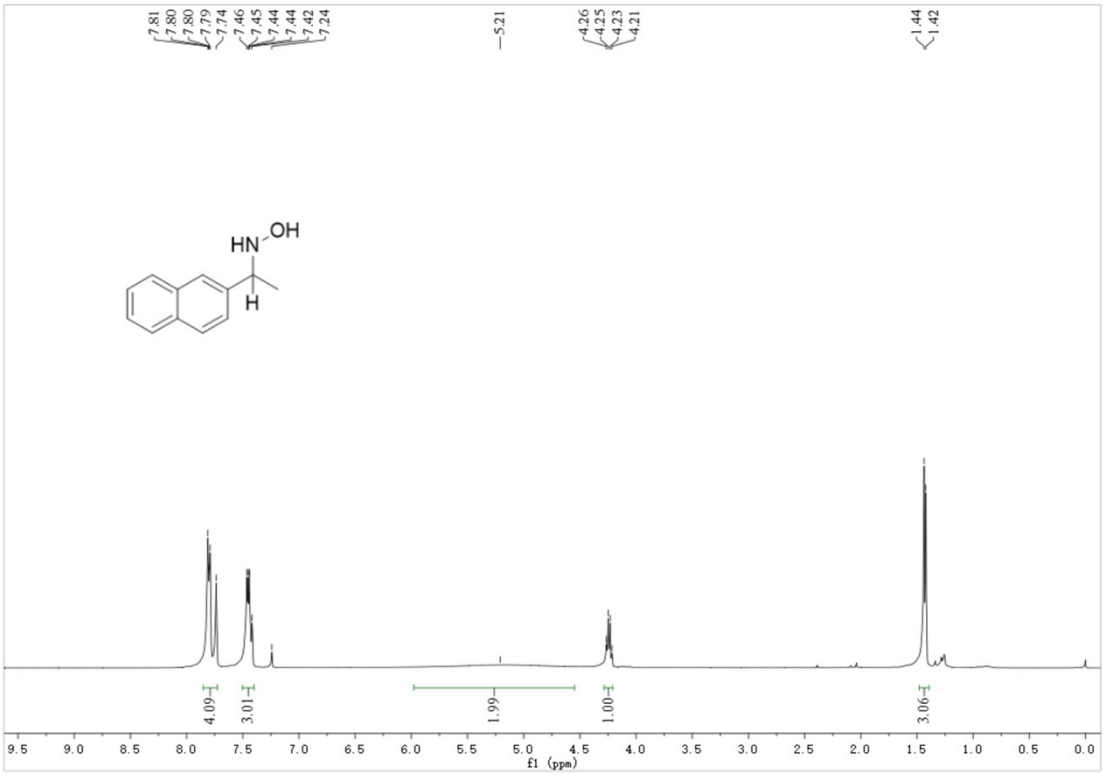
^{1}H NMR spectra of *N*-(1-(4-(tert-butyl)phenyl)ethyl)hydroxylamine (2be)



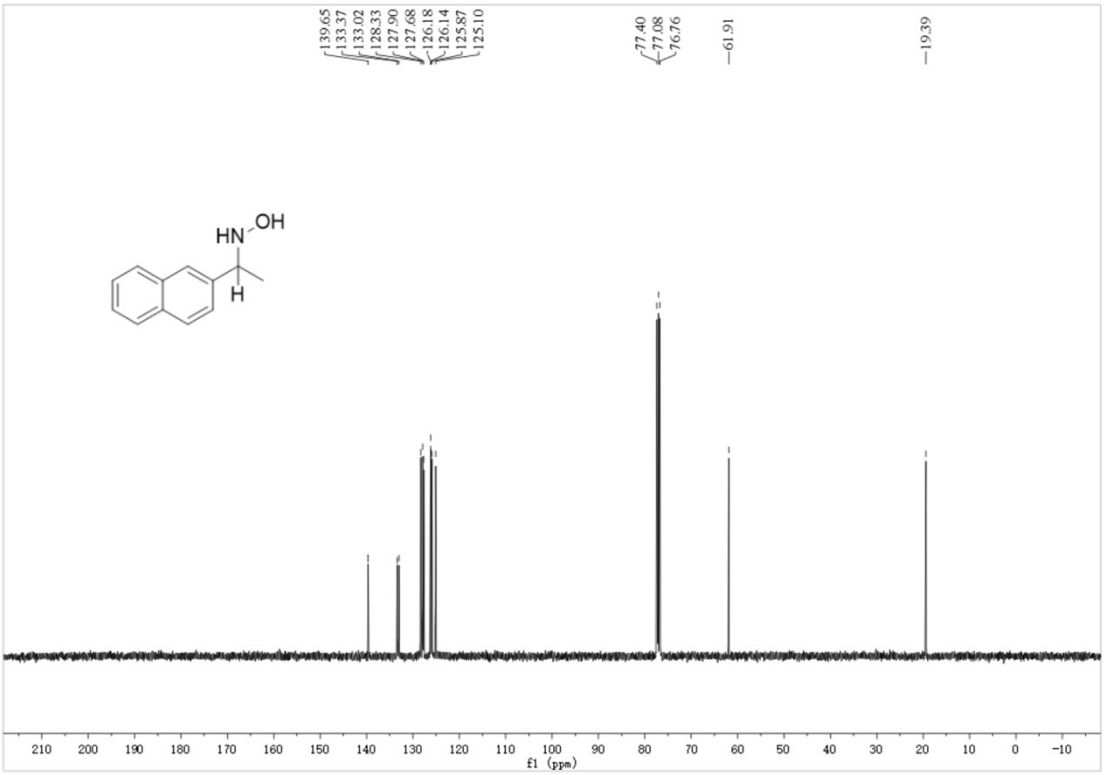
^{13}C NMR spectra of *N*-(1-(4-(tert-butyl)phenyl)ethyl)hydroxylamine (2be)



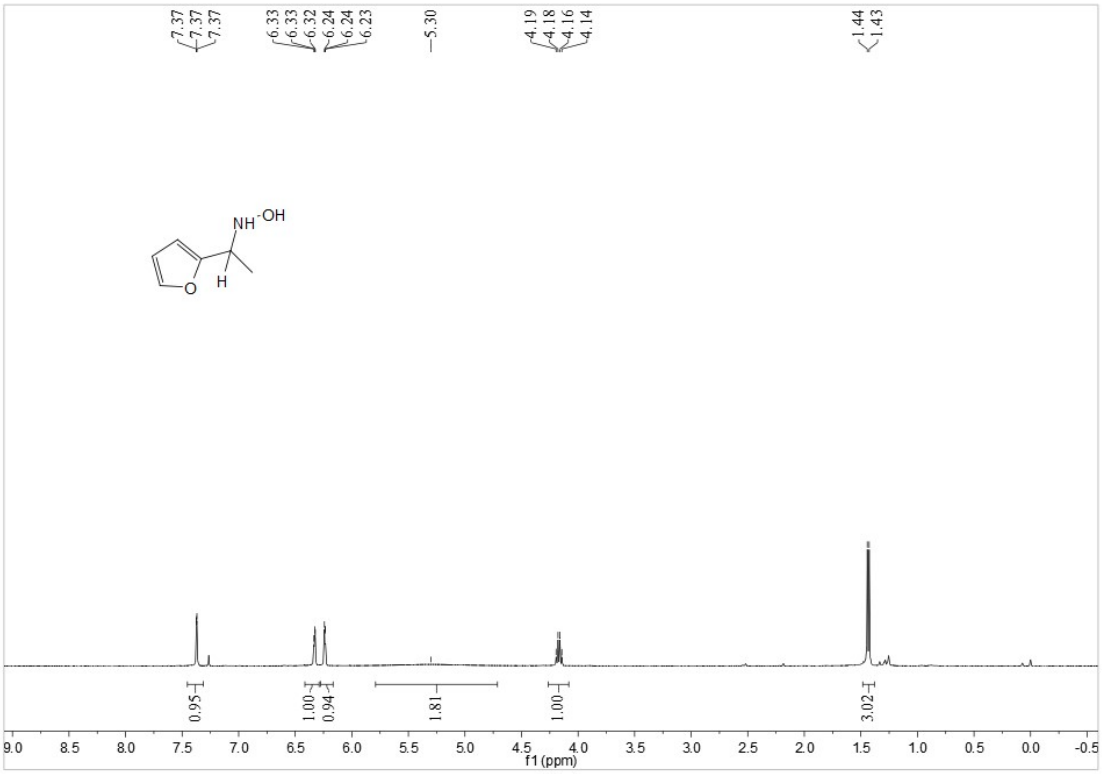
^{1}H NMR spectra of *N*-(1-(naphthalen-2-yl)ethyl)hydroxylamine (2bf)



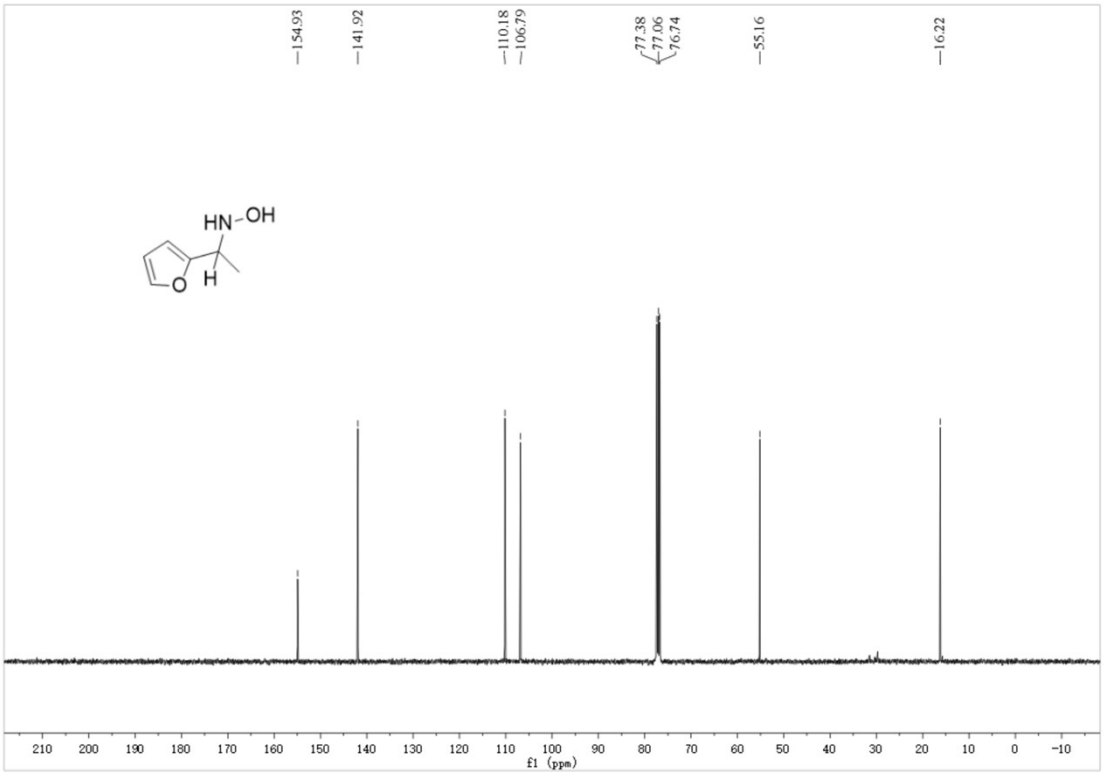
^{13}C NMR spectra of *N*-(1-(naphthalen-2-yl)ethyl)hydroxylamine (2bf)



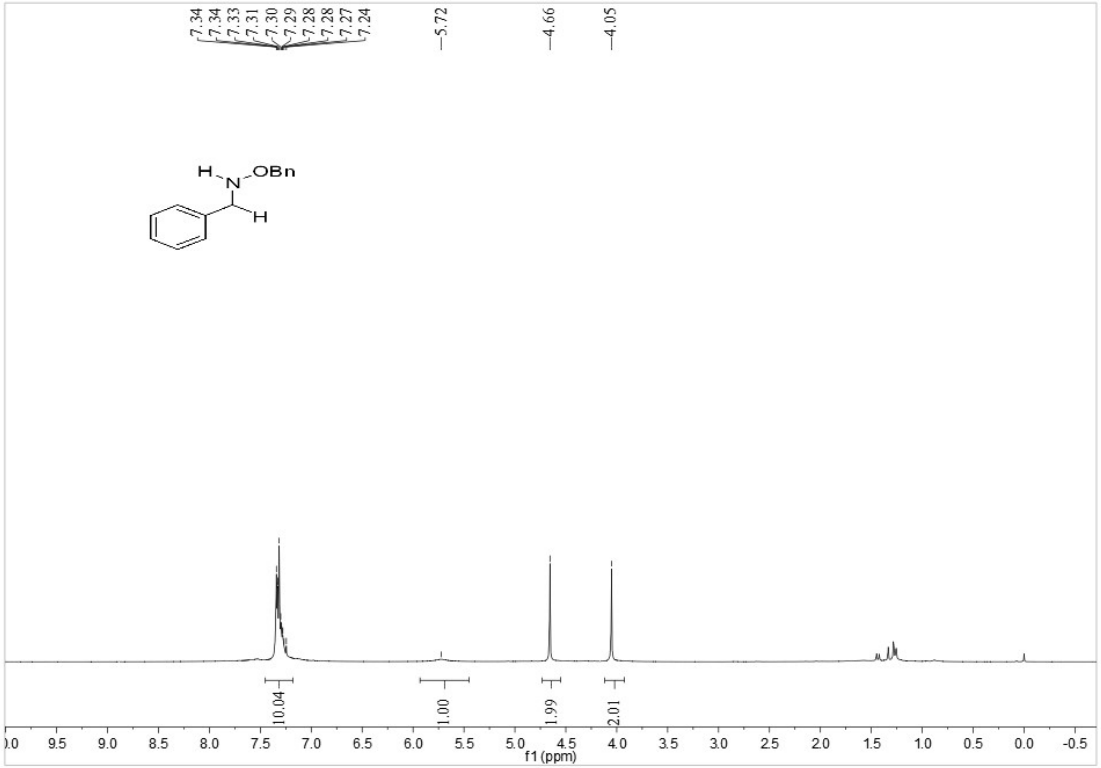
^{1}H NMR spectra of *N*-(1-(furan-2-yl)ethyl)hydroxylamine (2bg)



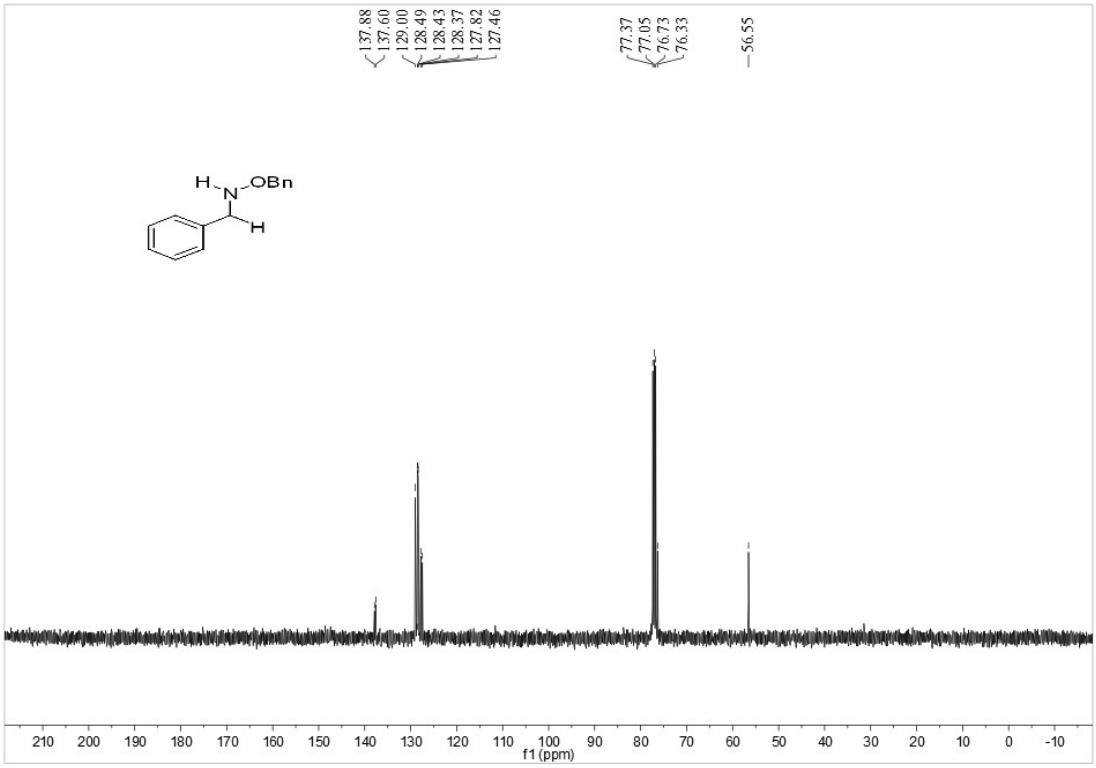
^{13}C NMR spectra of *N*-(1-(furan-2-yl)ethyl)hydroxylamine (2bg)



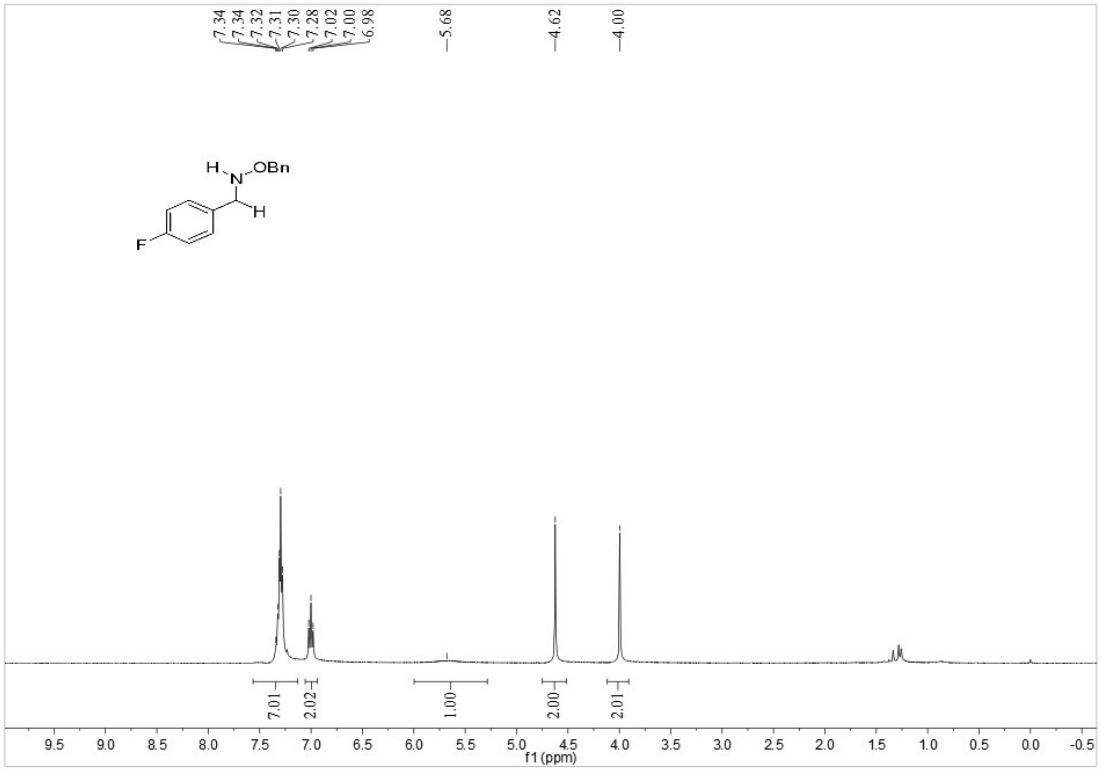
^{1}H NMR spectra of *N*,*O*-dibenzylhydroxylamine (2bh)



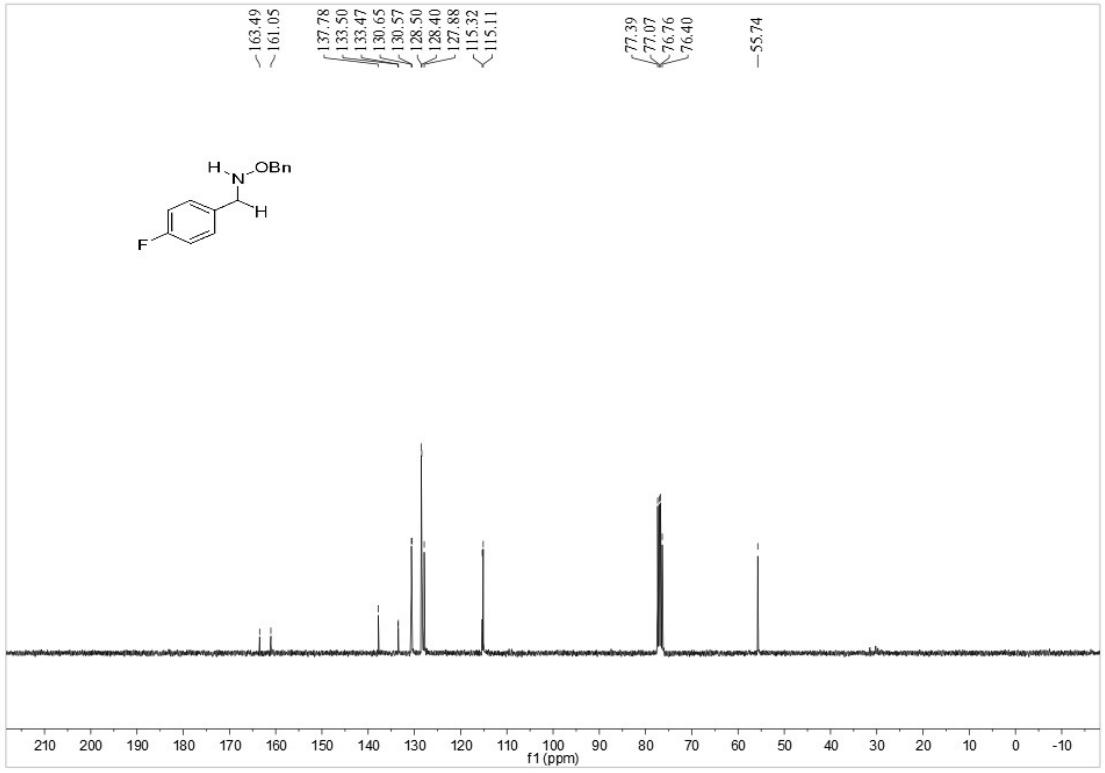
^{13}C NMR spectra of *N*,*O*-dibenzylhydroxylamine (2bh)



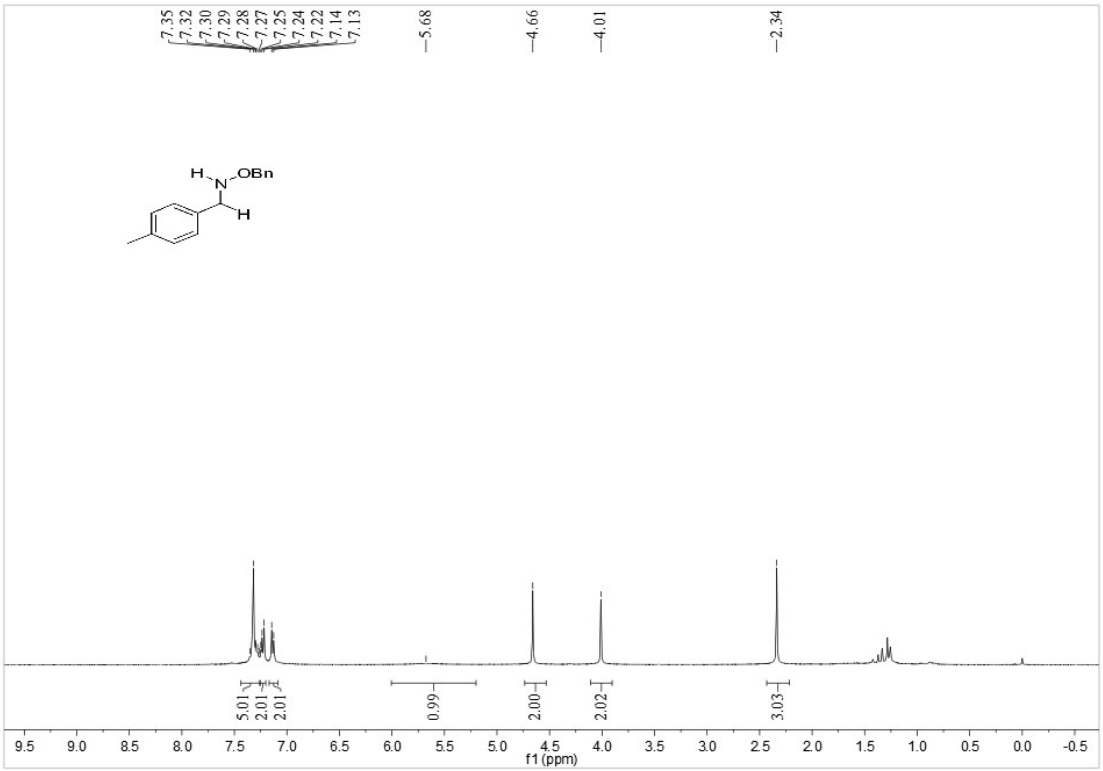
^{1}H NMR spectra of *O*-benzyl-*N*-(4-fluorobenzyl)hydroxylamine (2bi)



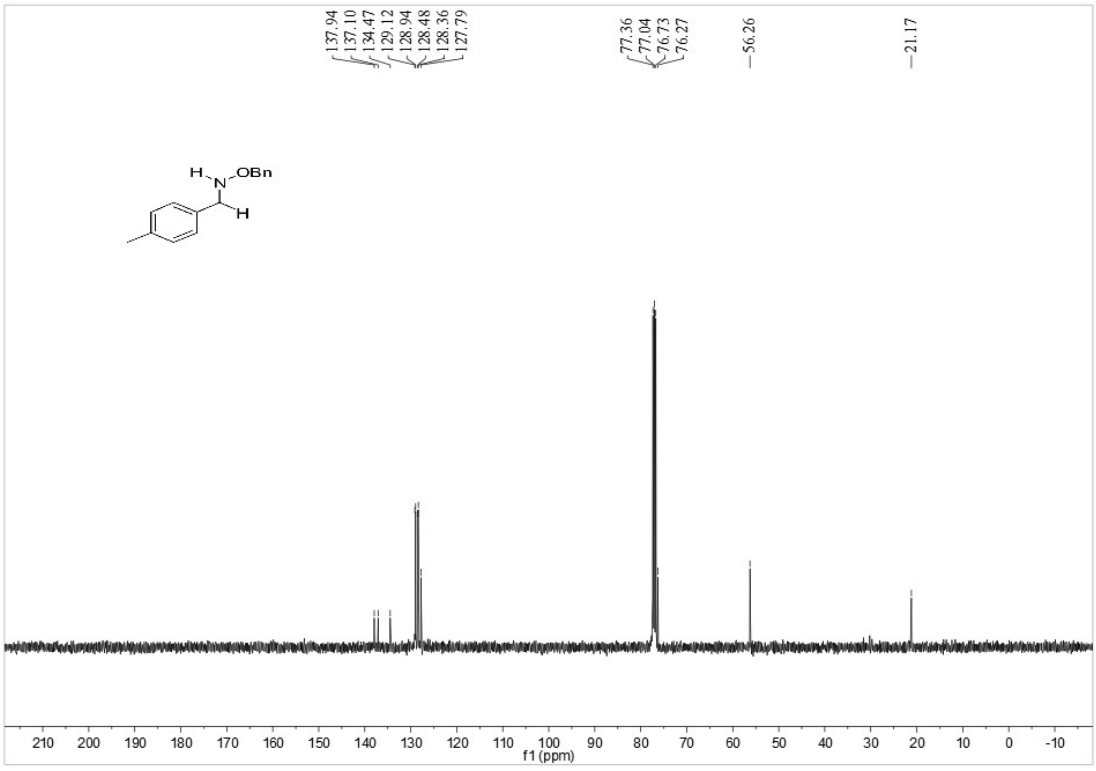
^{13}C NMR spectra of *O*-benzyl-*N*-(4-fluorobenzyl)hydroxylamine (2bi)



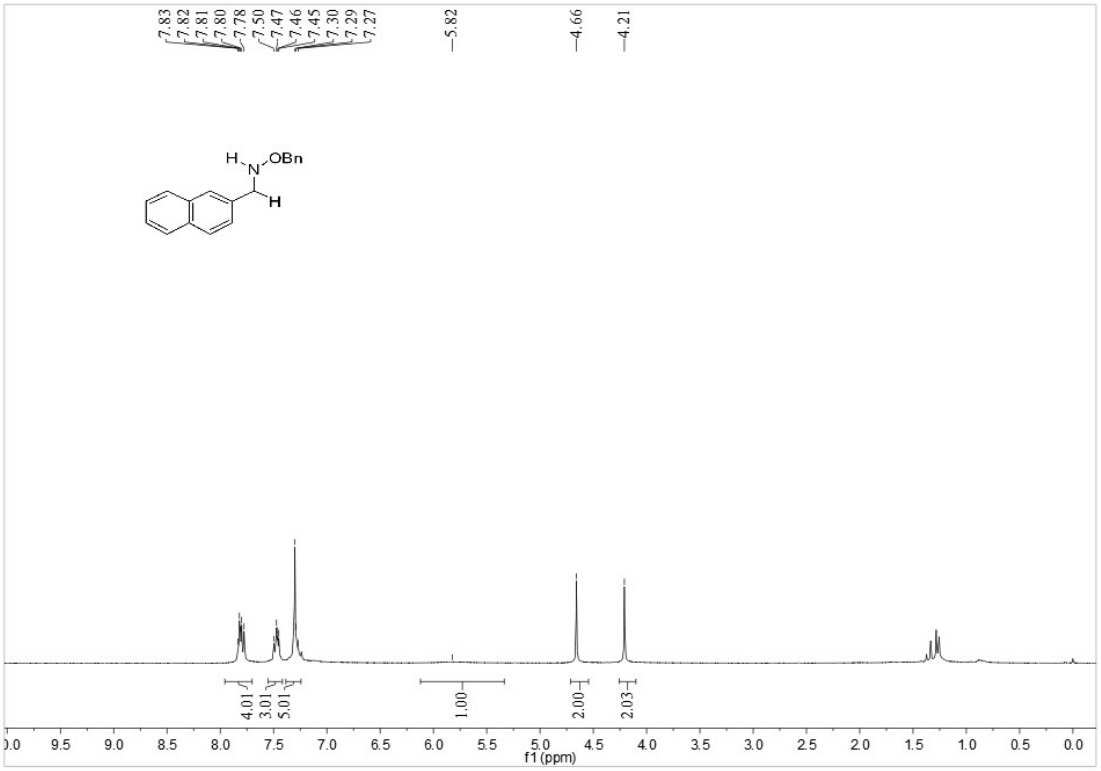
^{1}H NMR spectra of *O*-benzyl-*N*-(4-methylbenzyl)hydroxylamine (2bj)



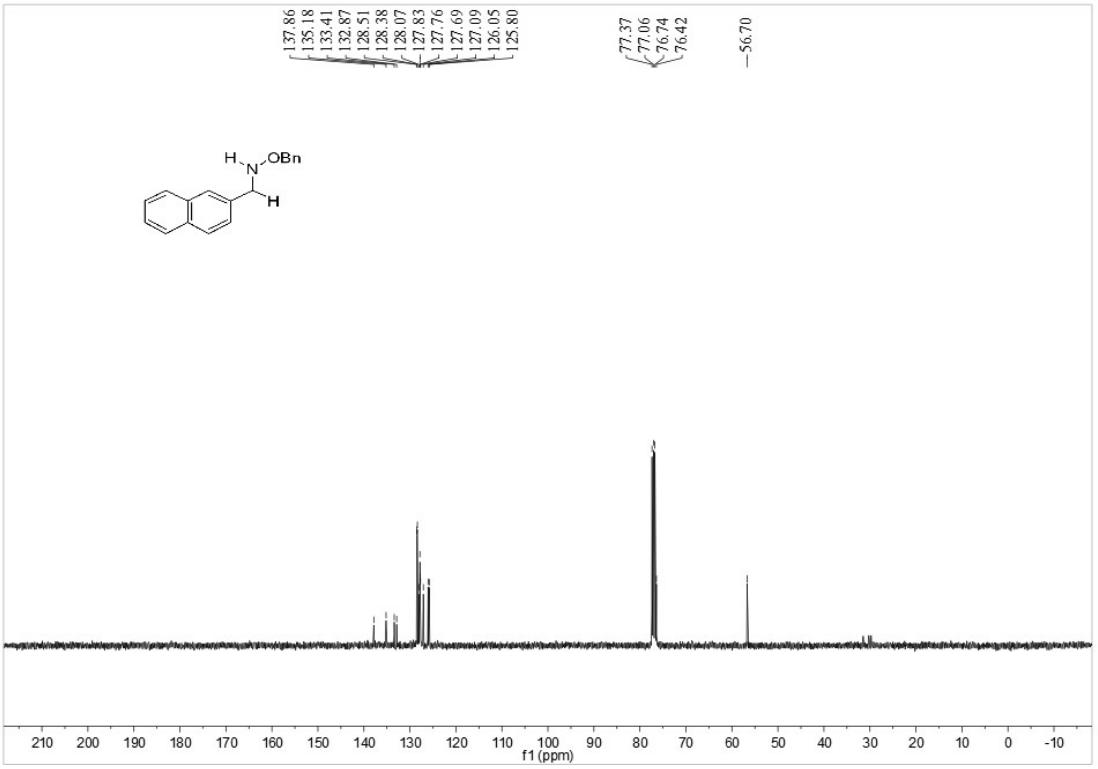
^{13}C NMR spectra of *O*-benzyl-*N*-(4-methylbenzyl)hydroxylamine (2bj)



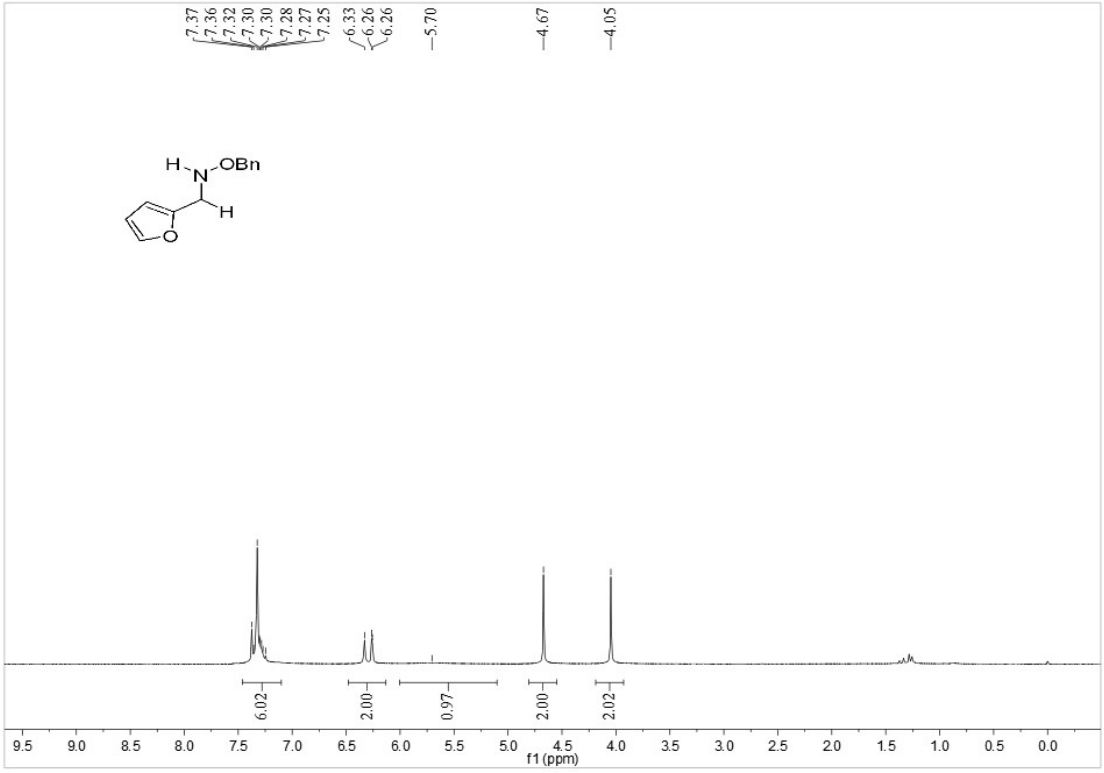
^{1}H NMR spectra of *O*-benzyl-*N*-(naphthalen-2-ylmethyl)hydroxylamine (2bk)



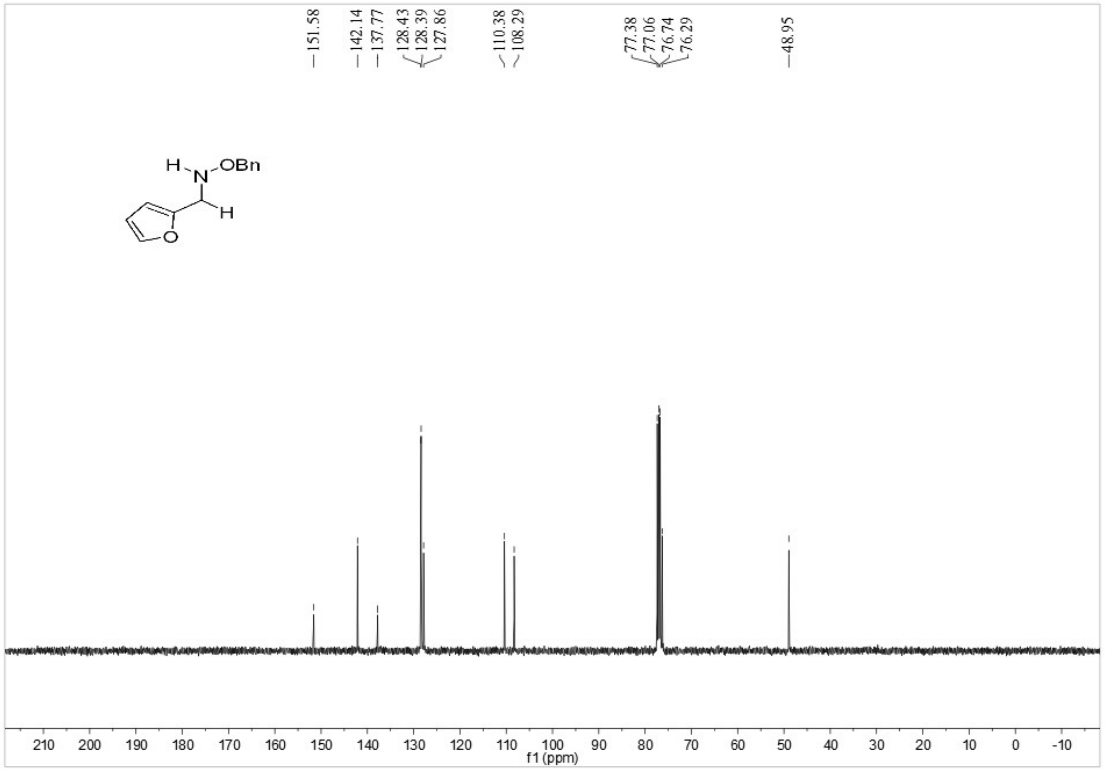
^{13}C NMR spectra of *O*-benzyl-*N*-(naphthalen-2-ylmethyl)hydroxylamine (2bk)



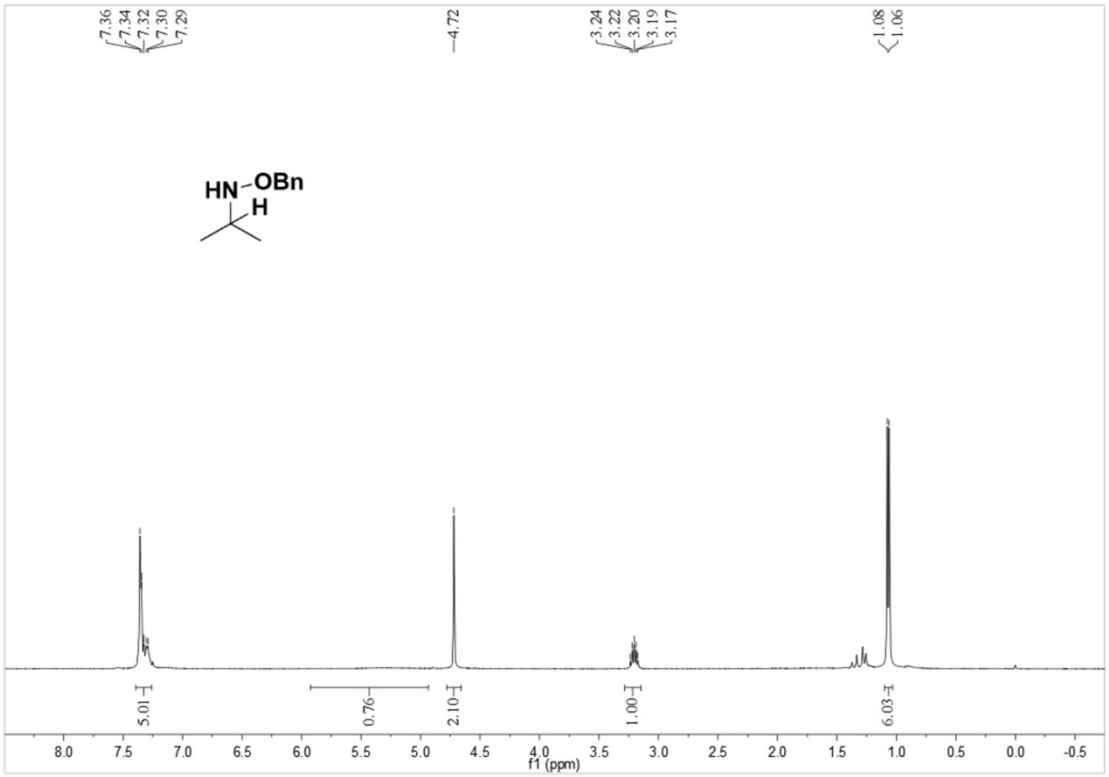
^{1}H NMR spectra of *O*-benzyl-*N*-(furan-2-ylmethyl)hydroxylamine (2bl)



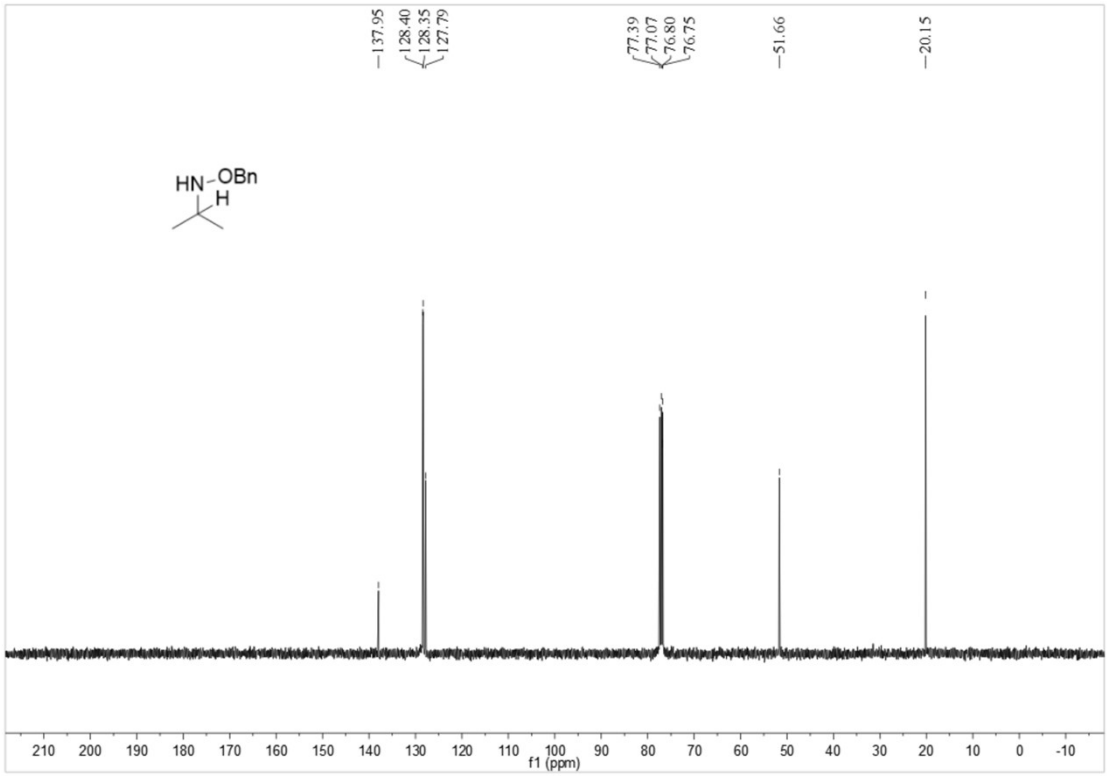
^{13}C NMR spectra of *O*-benzyl-*N*-(furan-2-ylmethyl)hydroxylamine (2bl)



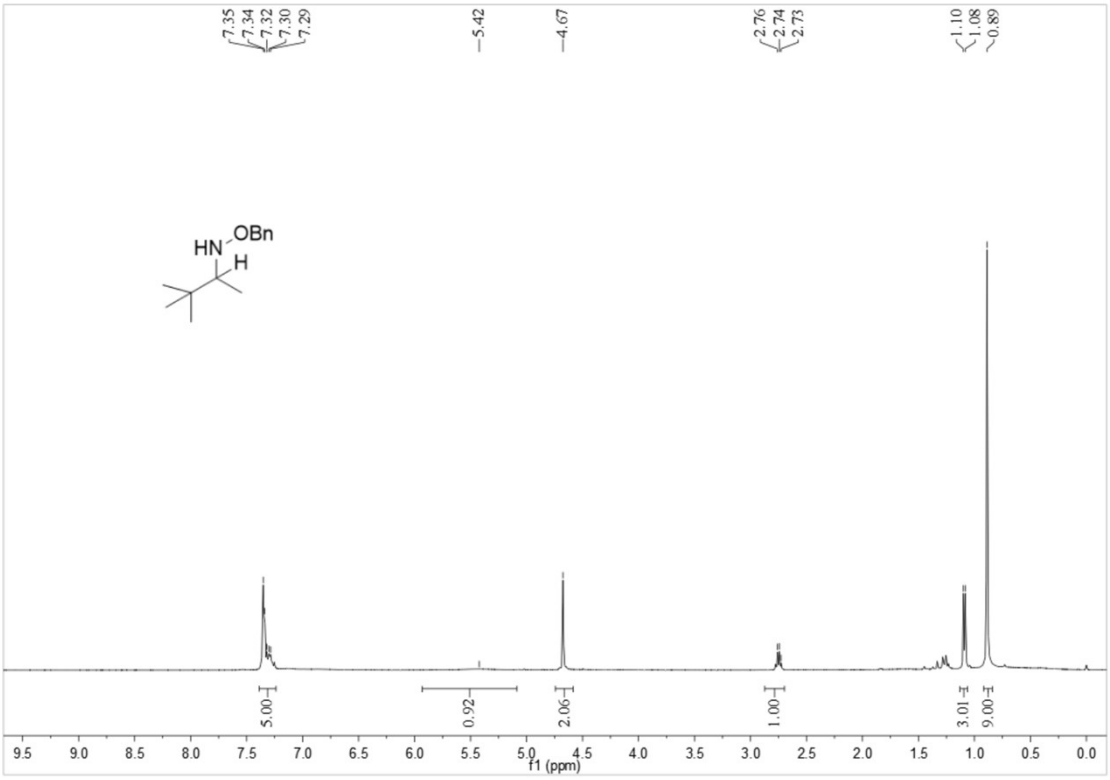
^{1}H NMR spectra of *O*-benzyl-*N*-isopropylhydroxylamine (2aa)



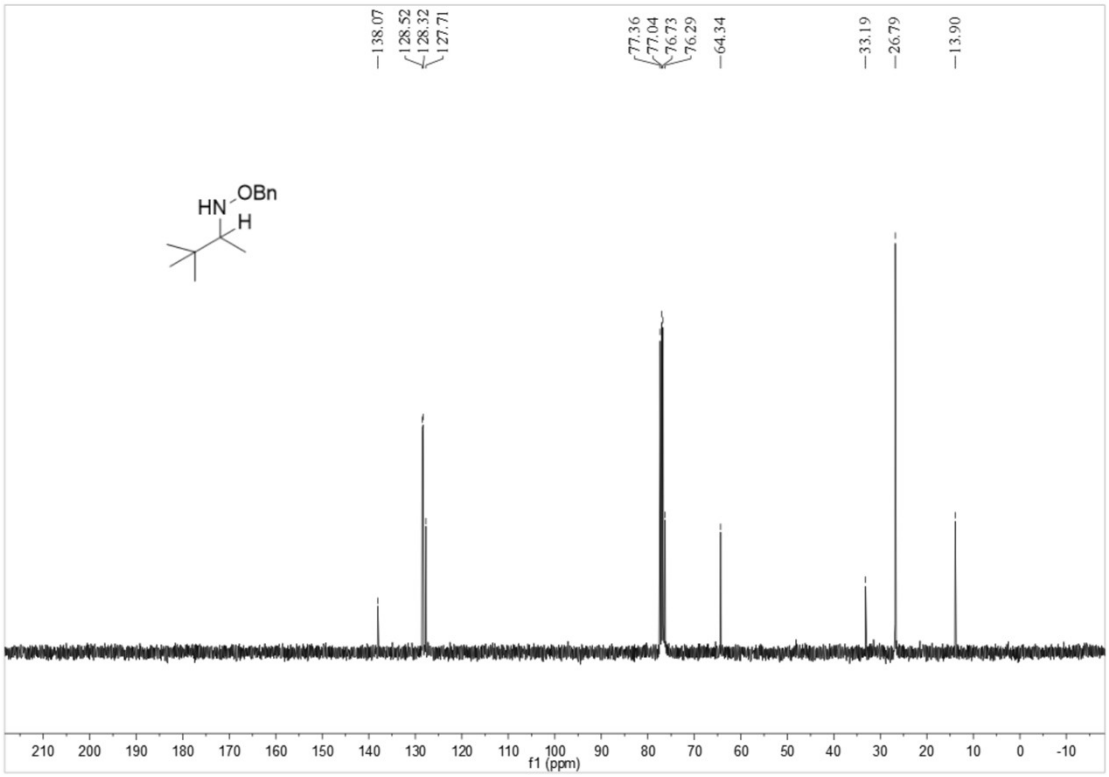
^{13}C NMR spectra of *O*-benzyl-*N*-isopropylhydroxylamine (2aa)



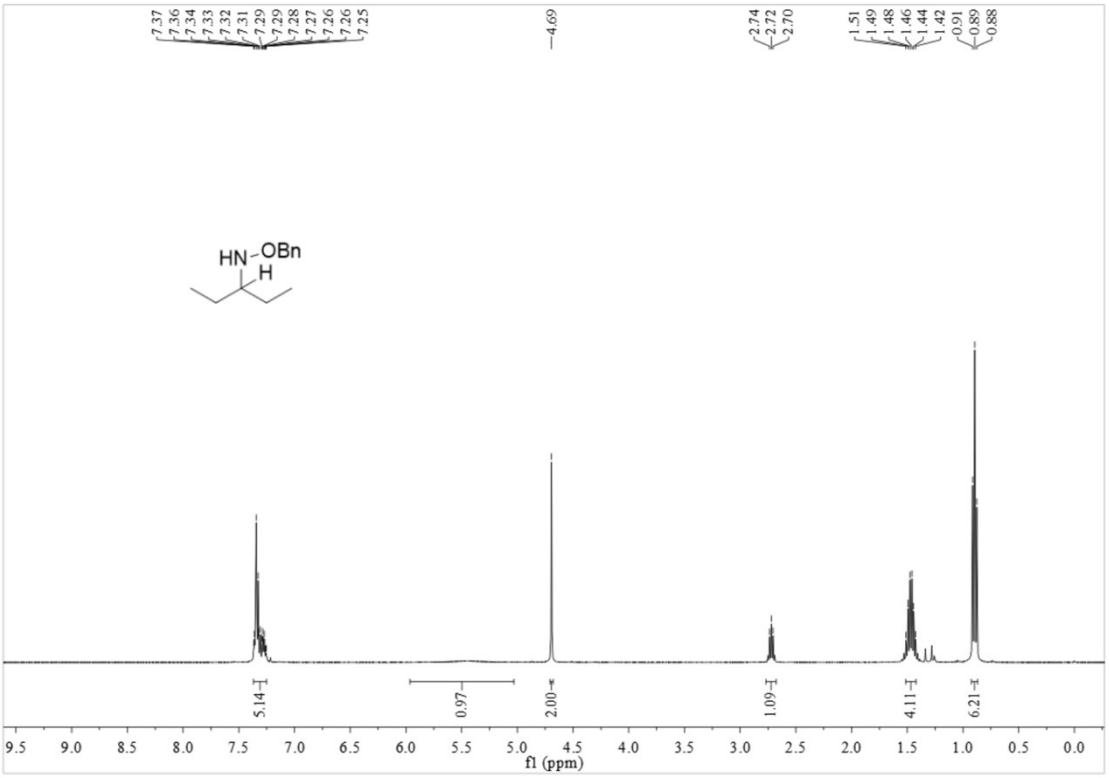
^{1}H NMR spectra of *O*-benzyl-*N*-(3,3-dimethylbutan-2-yl)hydroxylamine (2ab)



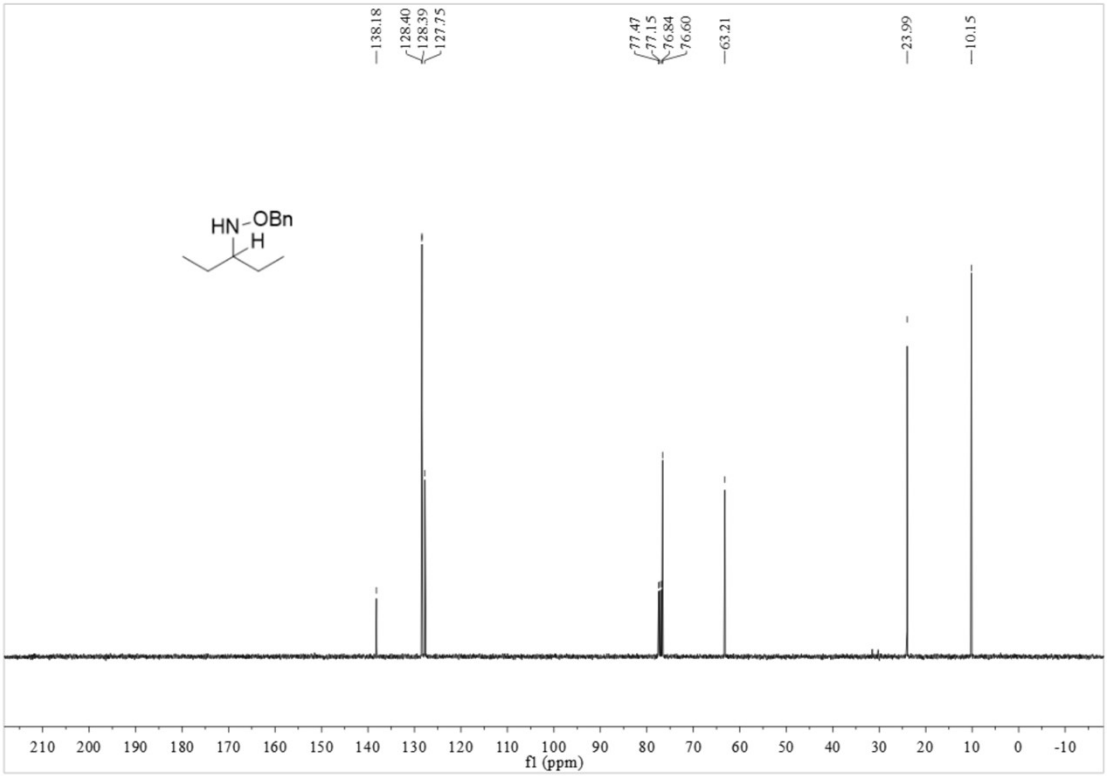
^{13}C NMR spectra of *O*-benzyl-*N*-(3,3-dimethylbutan-2-yl)hydroxylamine (2ab)



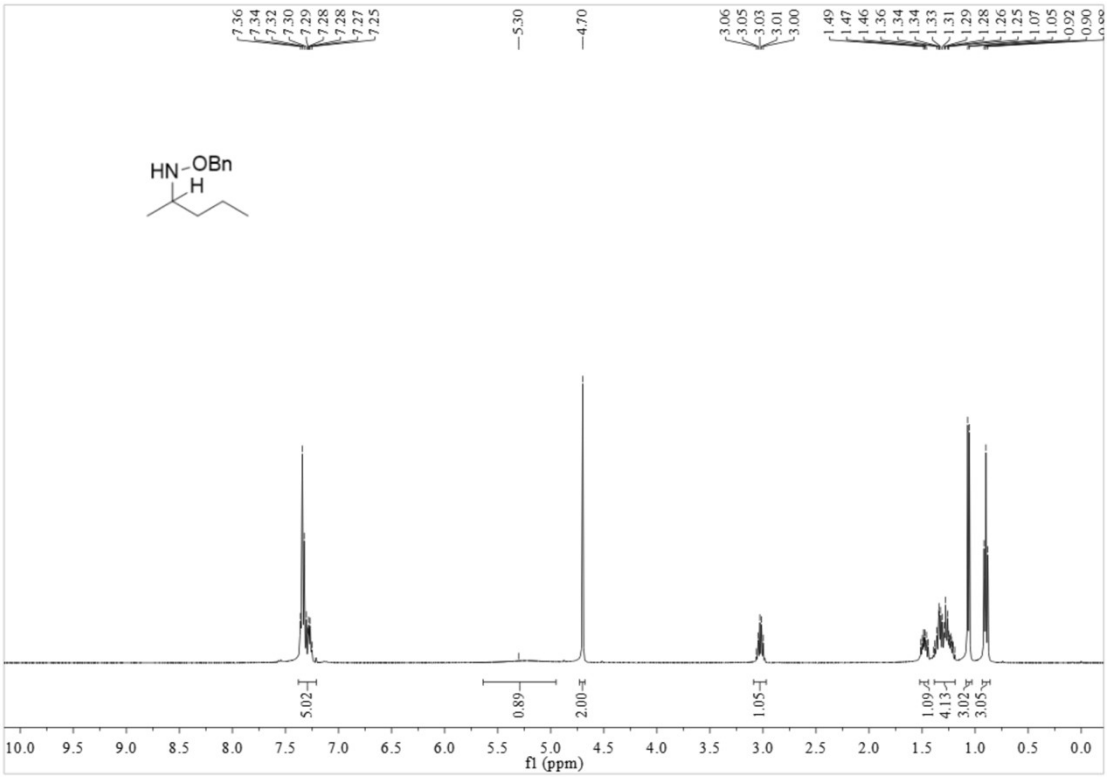
^{1}H NMR spectra of *O*-benzyl-*N*-(pentan-3-yl)hydroxylamine (2ac):



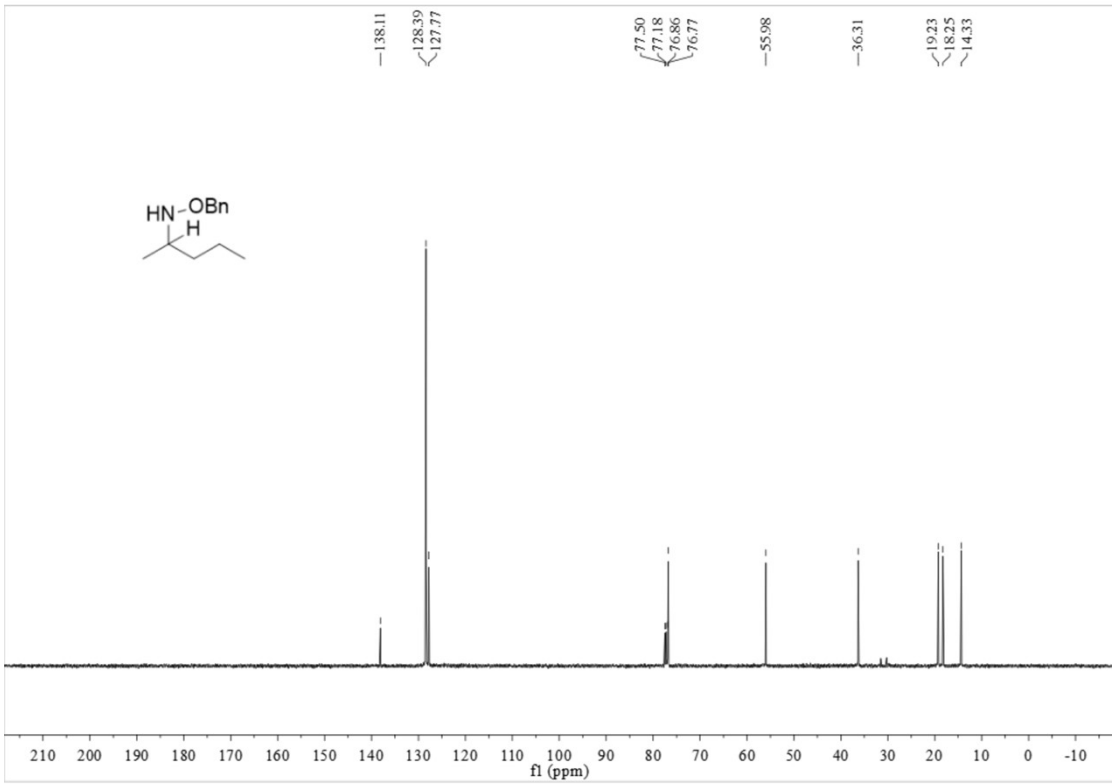
^{13}C NMR spectra of *O*-benzyl-*N*-(pentan-3-yl)hydroxylamine (2ac):



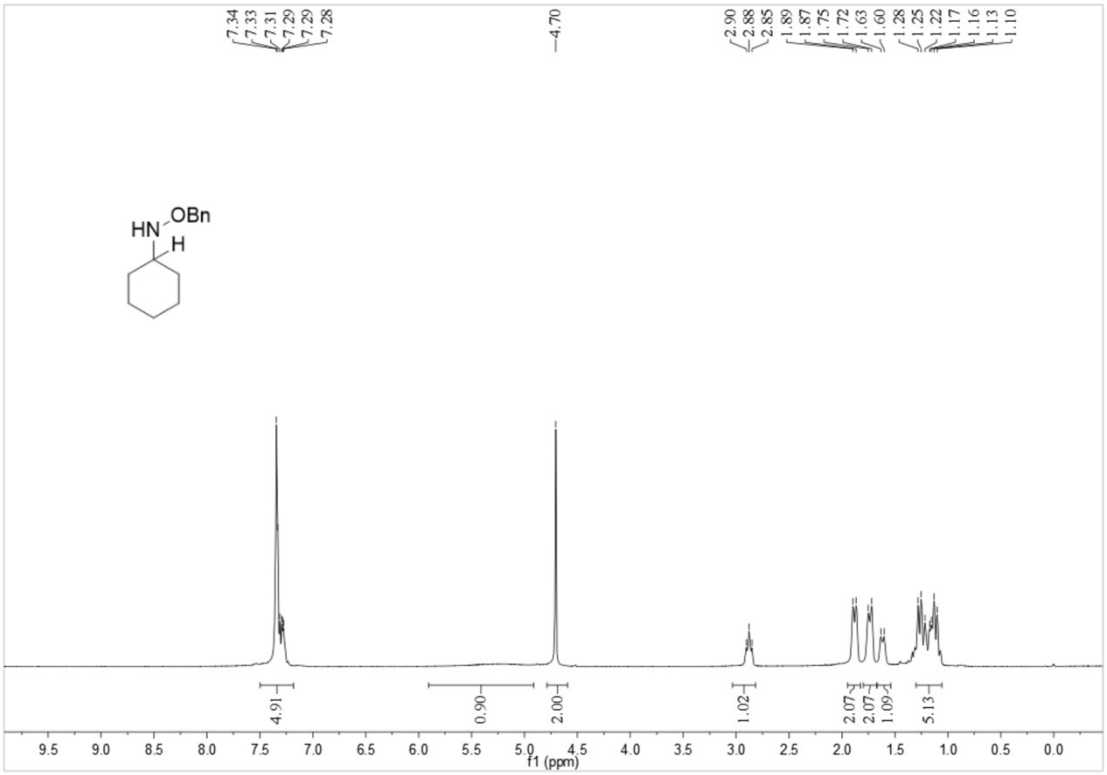
^{1}H NMR spectra of *O*-benzyl-*N*-(pentan-2-yl)hydroxylamine (2ad):



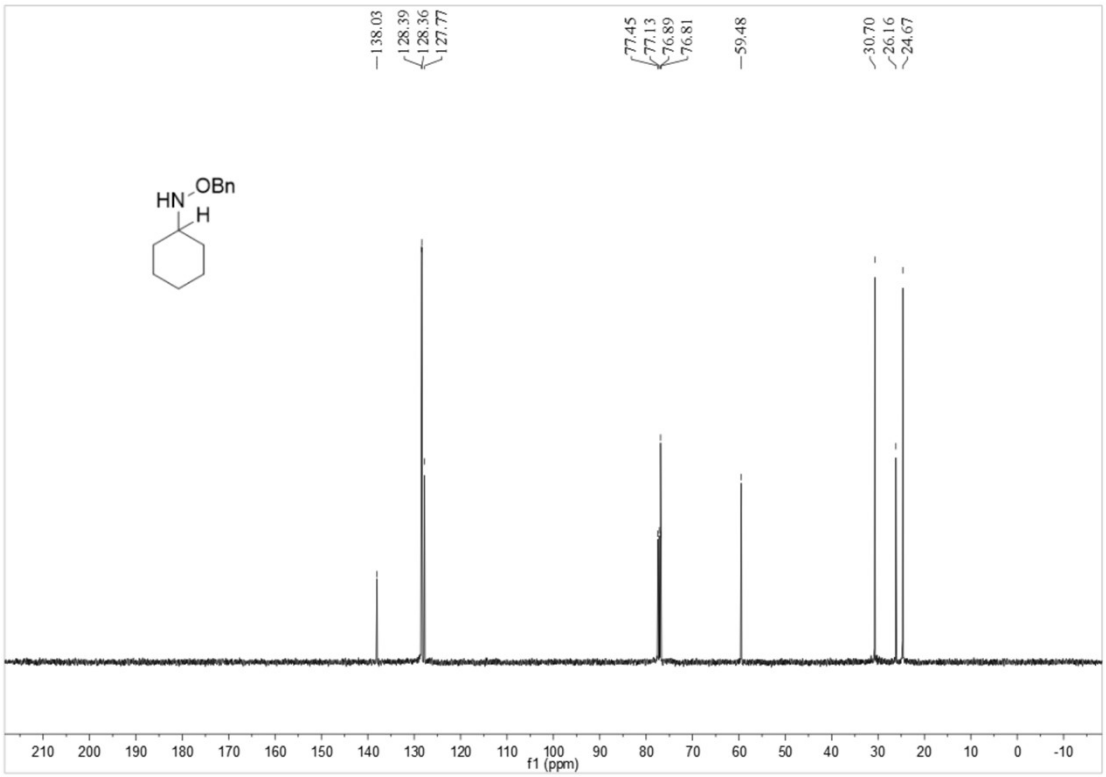
^{13}C NMR spectra of *O*-benzyl-*N*-(pentan-2-yl)hydroxylamine (2ad):



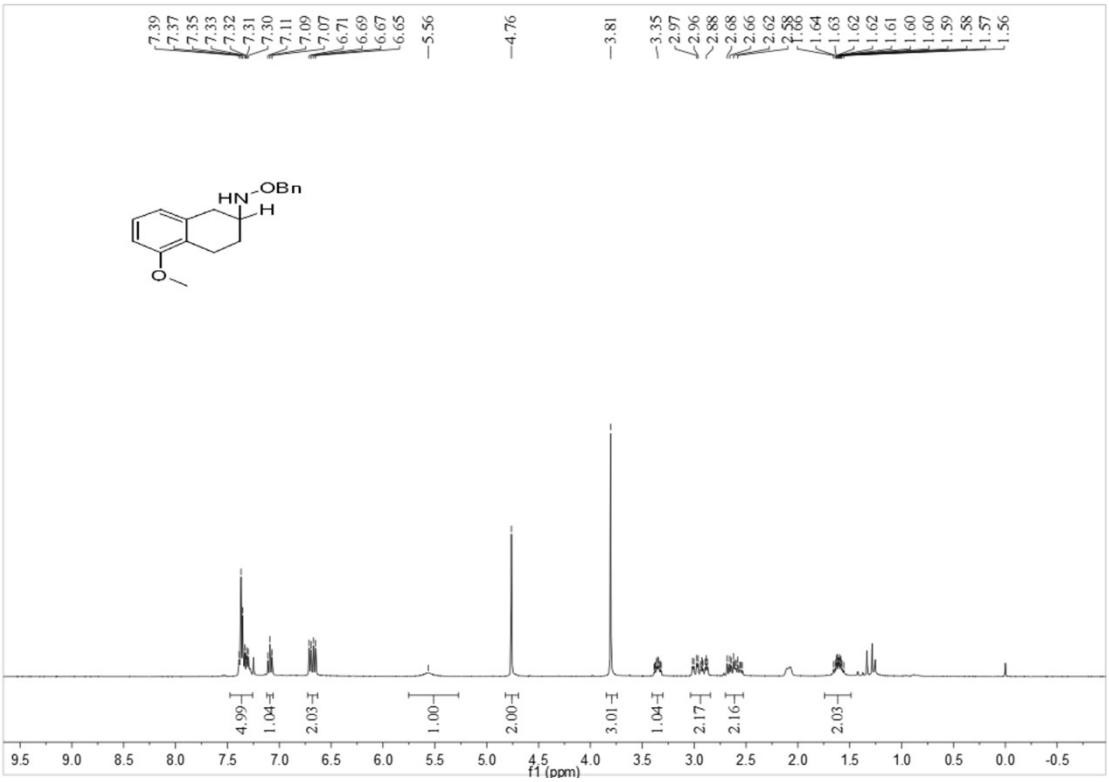
^{1}H NMR spectra of *O*-benzyl-*N*-cyclohexylhydroxylamine (2af)



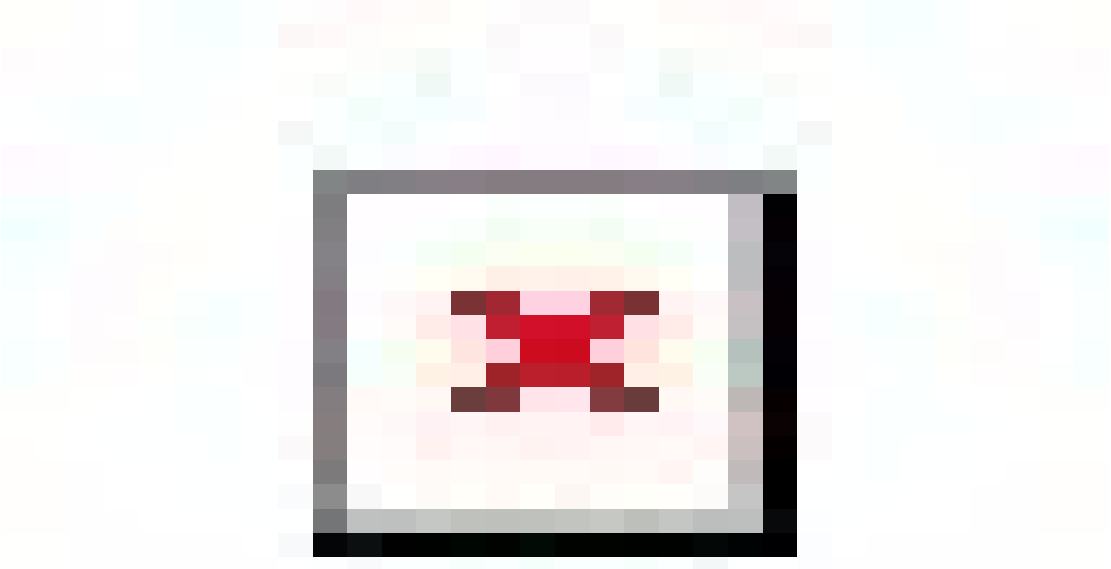
^{13}C NMR spectra of *O*-benzyl-*N*-cyclohexylhydroxylamine (2af)



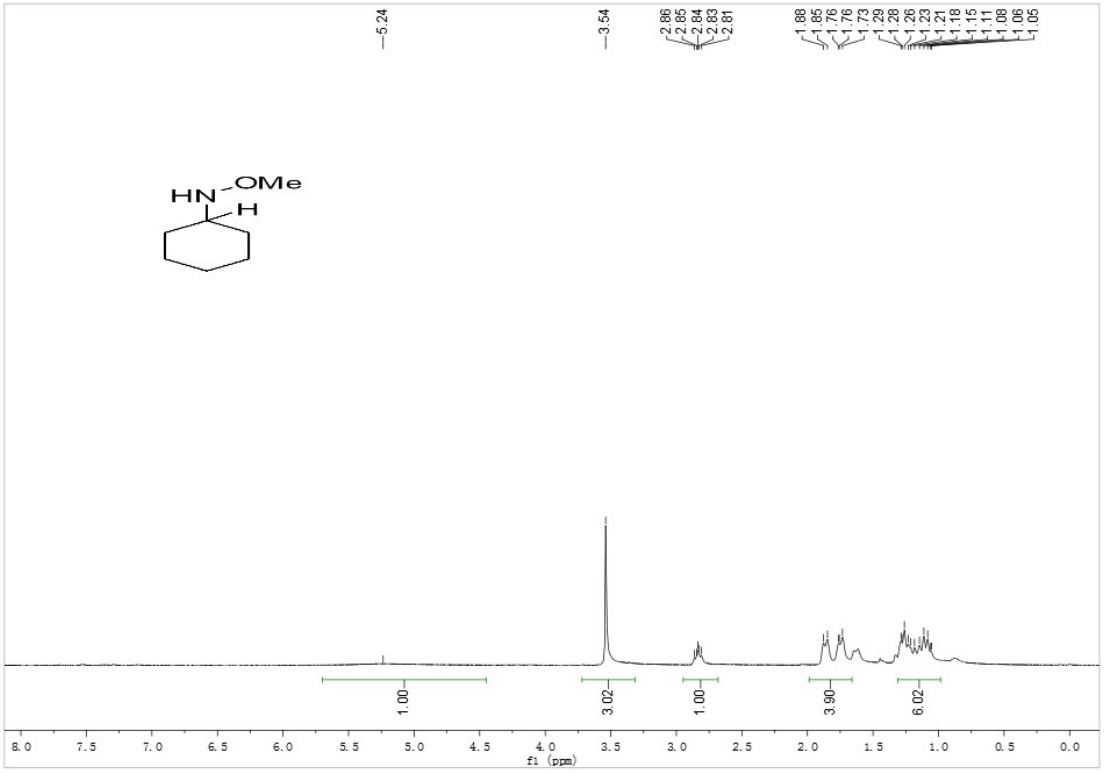
^{1}H NMR spectra of *O*-benzyl-*N*-(5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2ag)



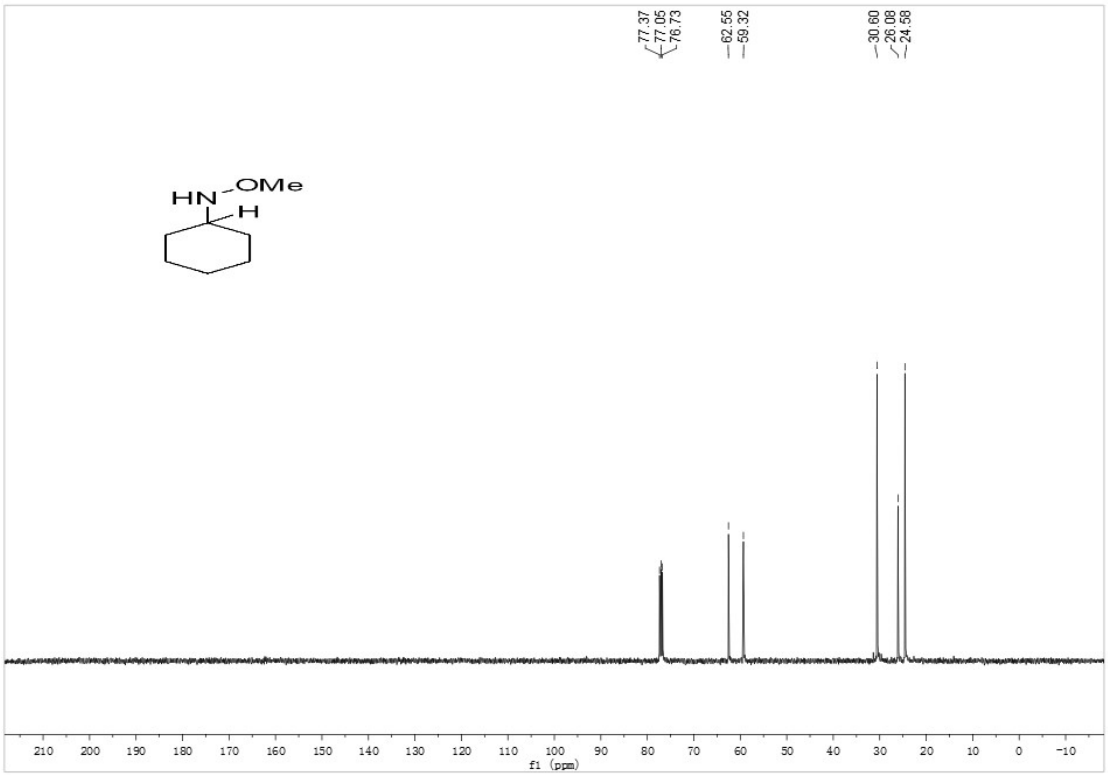
^{13}C NMR spectra of *O*-benzyl-*N*-(5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)hydroxylamine (2ag)



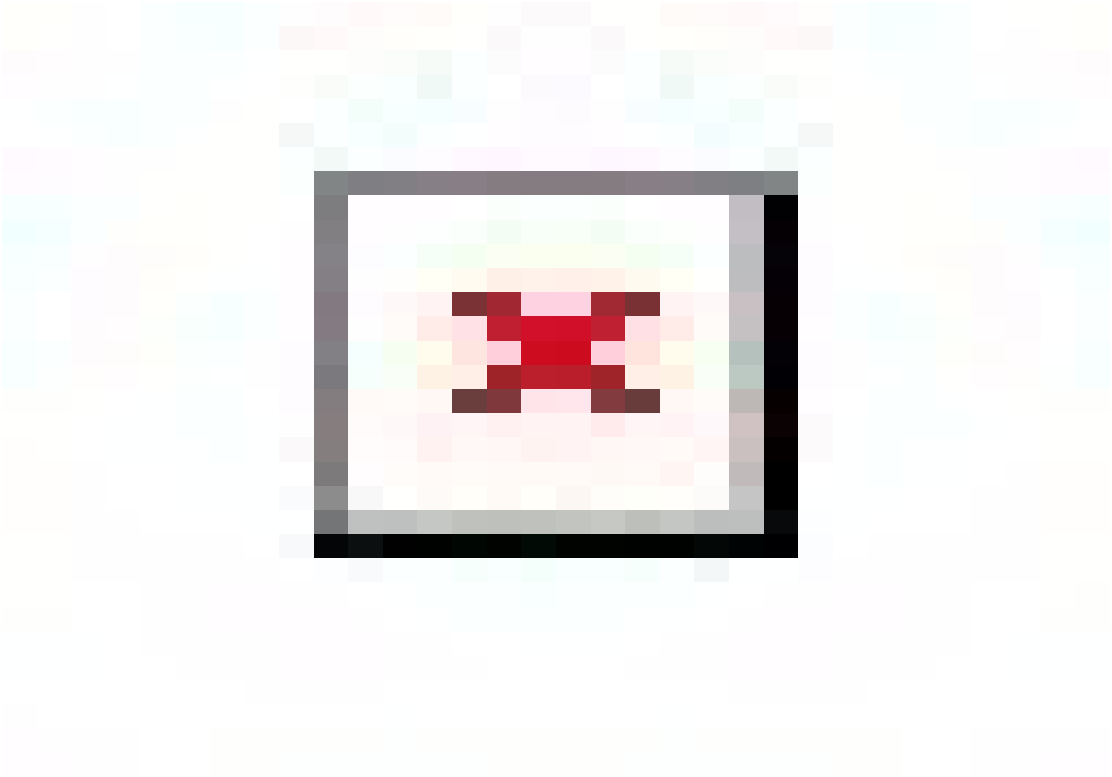
^{1}H NMR spectra of *N*-cyclohexyl-*O*-methylhydroxylamine (2ah)



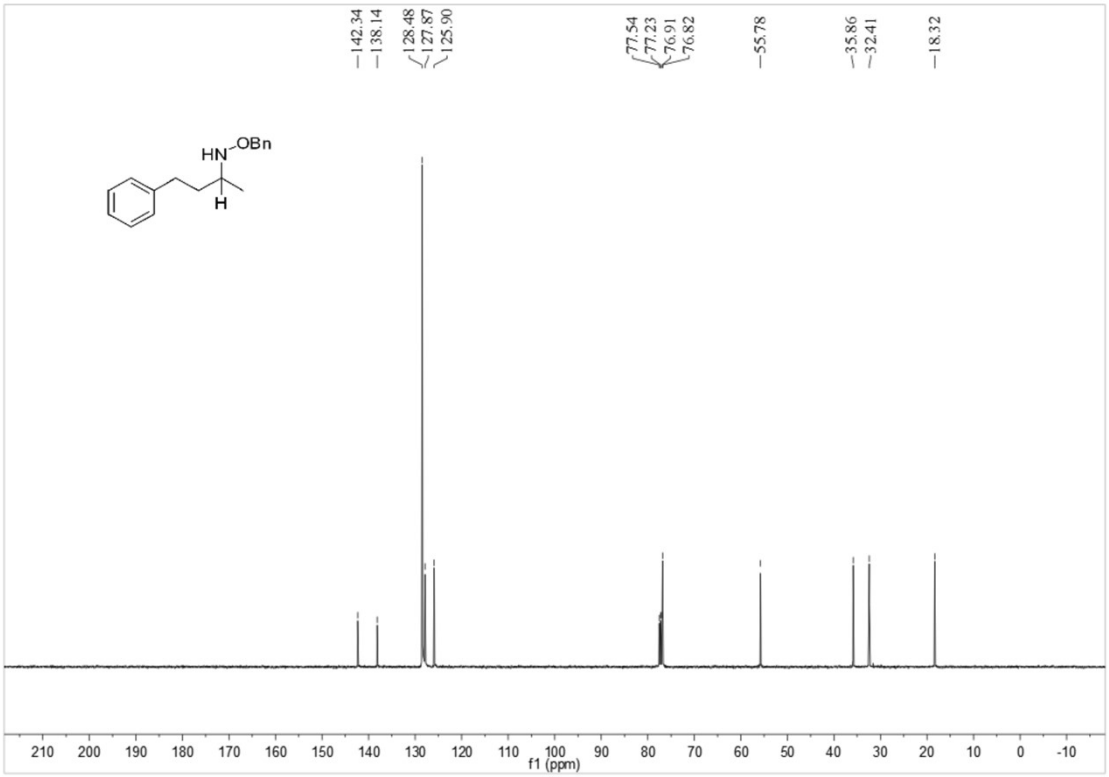
^{13}C NMR spectra of *N*-cyclohexyl-*O*-methylhydroxylamine (2ah)



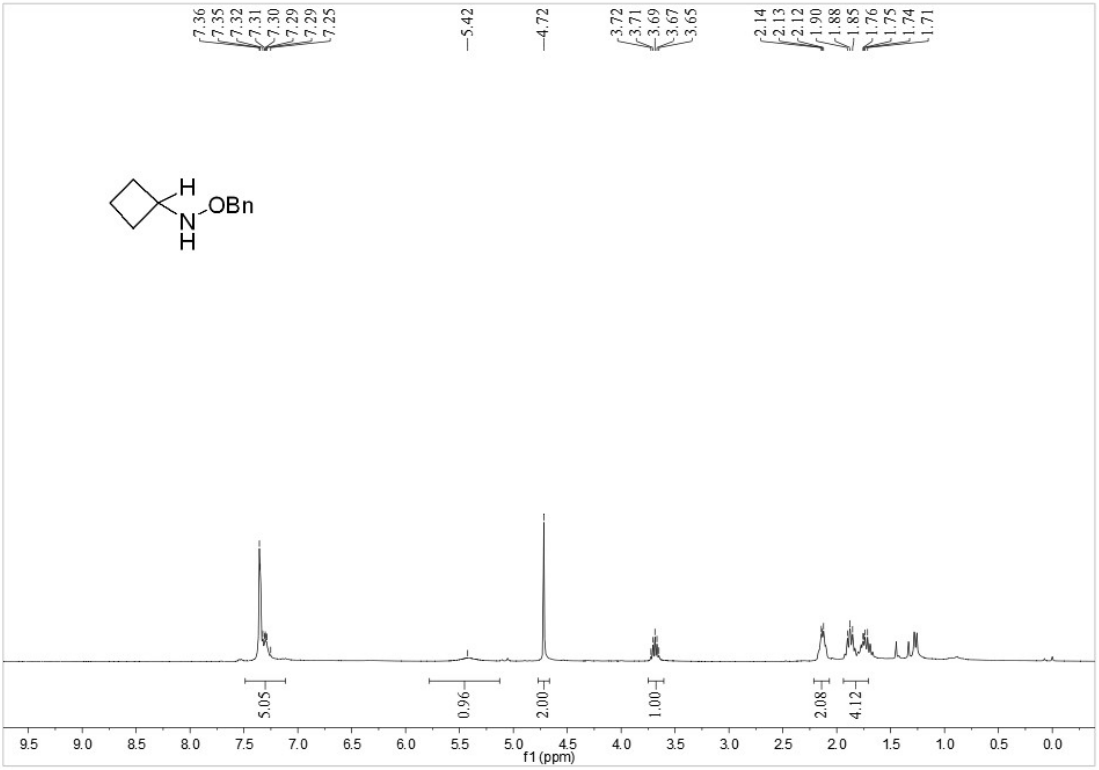
^{1}H NMR spectra of *O*-benzyl-*N*-(4-phenylbutan-2-yl)hydroxylamine (2ai)



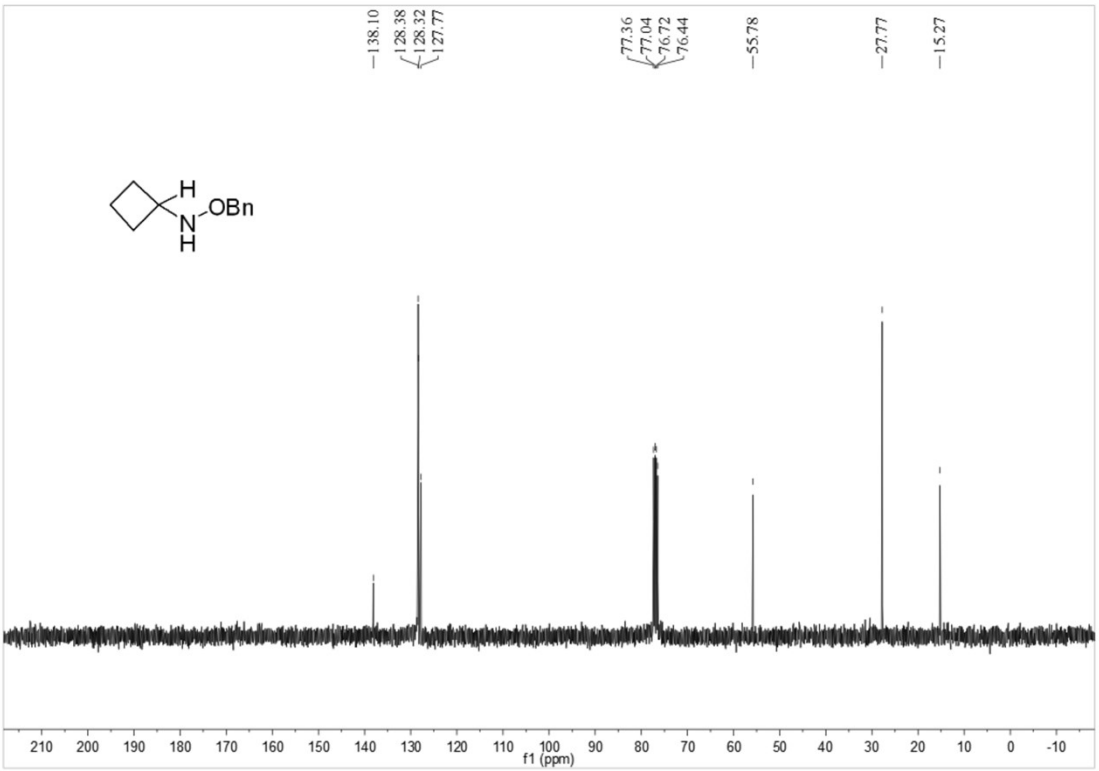
^{13}C NMR spectra of *O*-benzyl-*N*-(4-phenylbutan-2-yl)hydroxylamine (2ai)



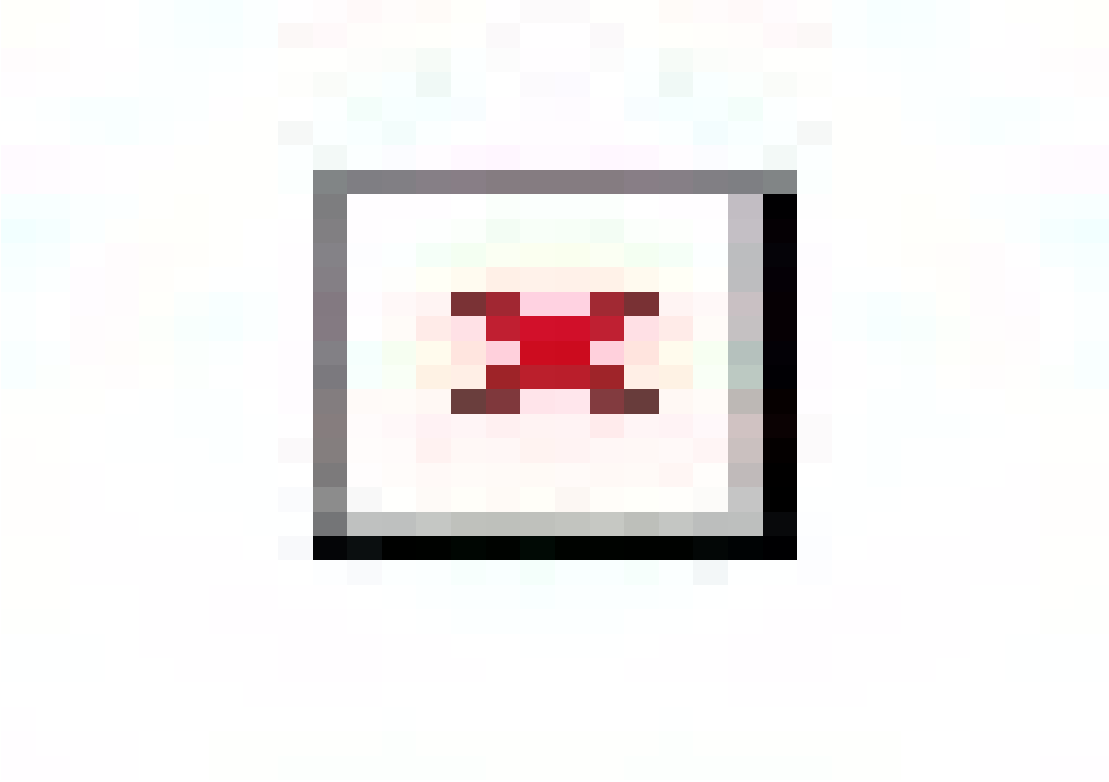
^{1}H NMR spectra of *O*-benzyl-*N*-cyclobutylhydroxylamine (2aj)



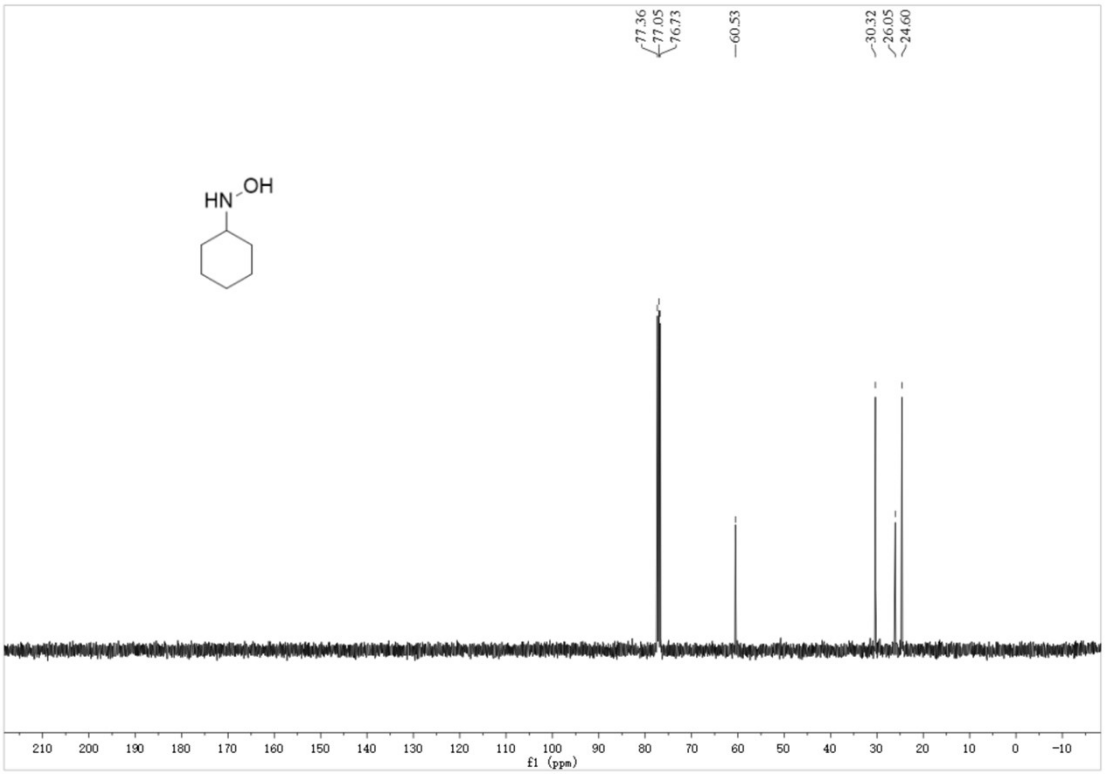
^{13}C NMR spectra of *O*-benzyl-*N*-cyclobutylhydroxylamine (2aj)



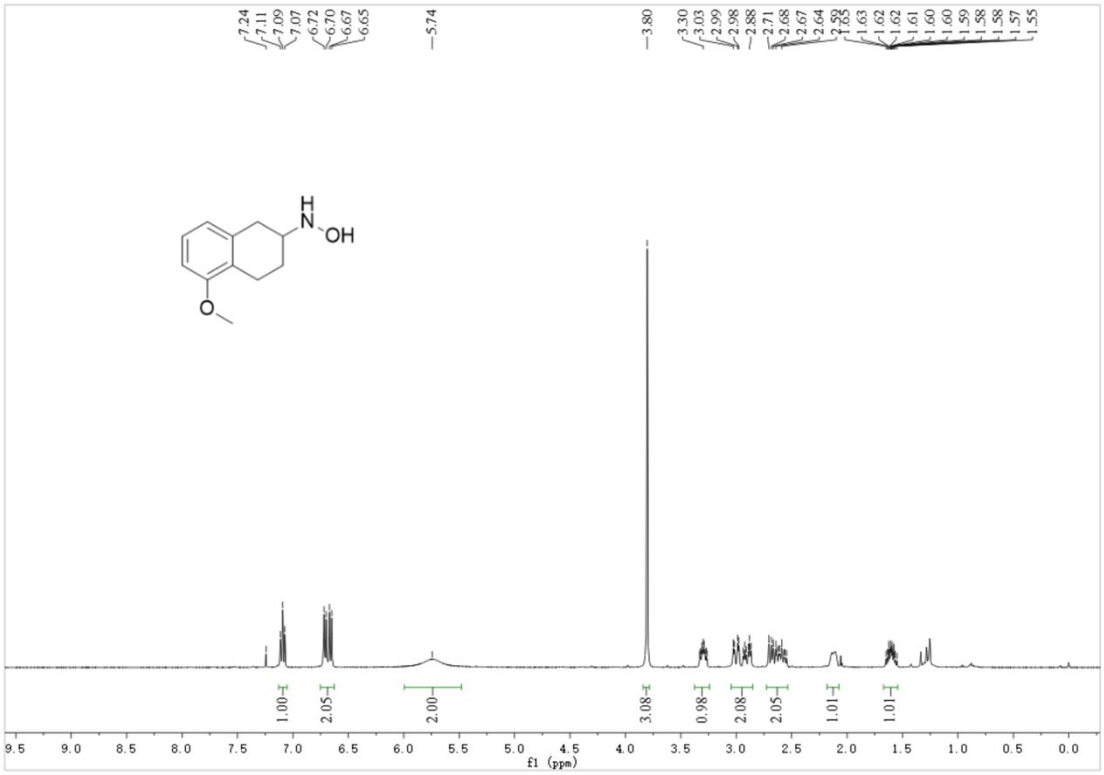
^{1}H NMR spectra of *N*-cyclohexylhydroxylamine (2ak)



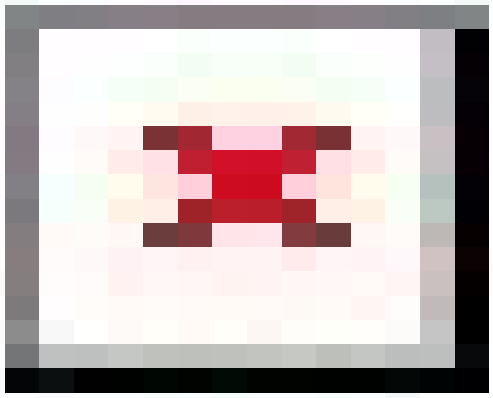
^{13}C NMR spectra of *N*-cyclohexylhydroxylamine (2ak)



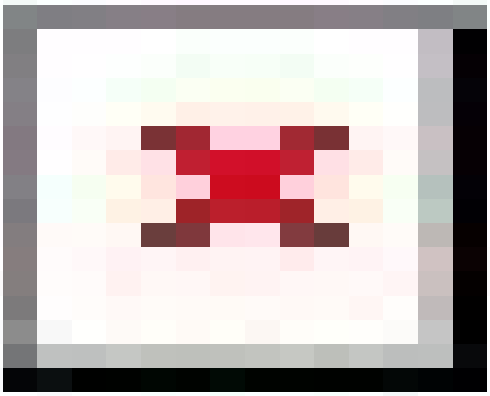
^{1}H NMR spectra of *N*-(5-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)hydroxylamine (2al)



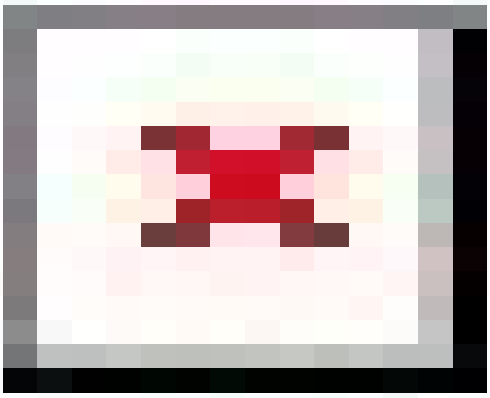
^{13}C NMR spectra of *N*-(5-methoxy-1,2,3,4-tetrahydronaphthalen-2-yl)hydroxylamine (2al)



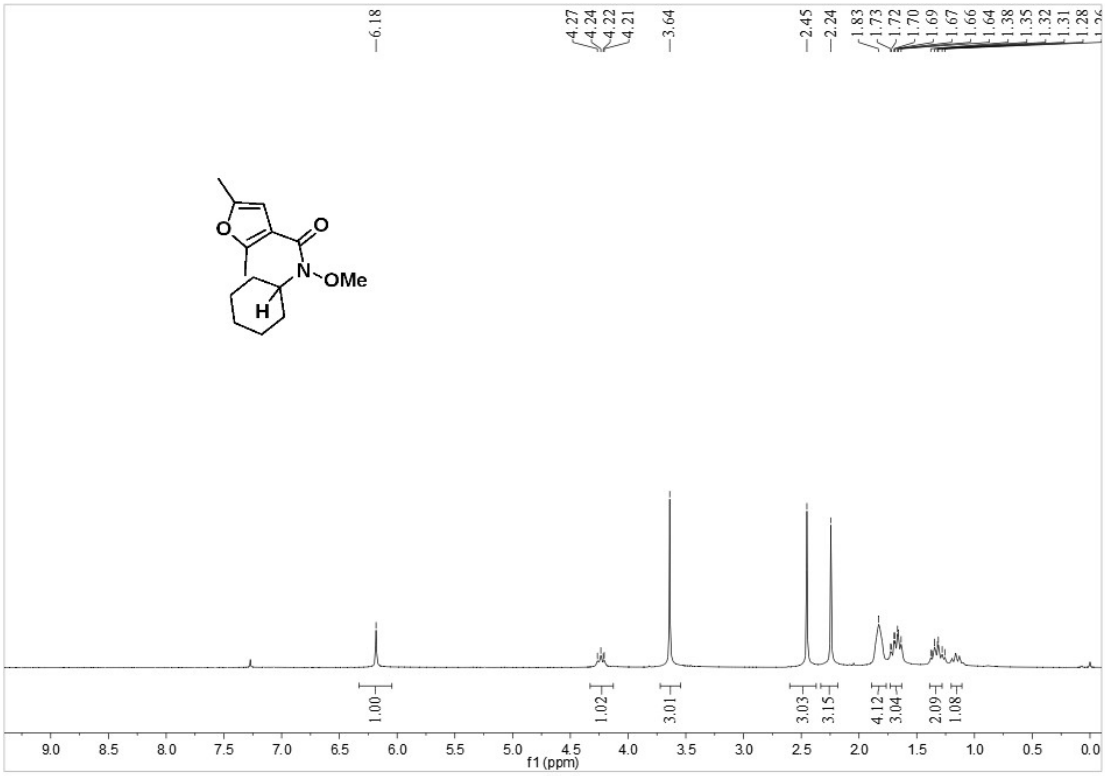
^{1}H NMR spectra of *N*-(4-phenylbutan-2-yl)hydroxylamine (2am)



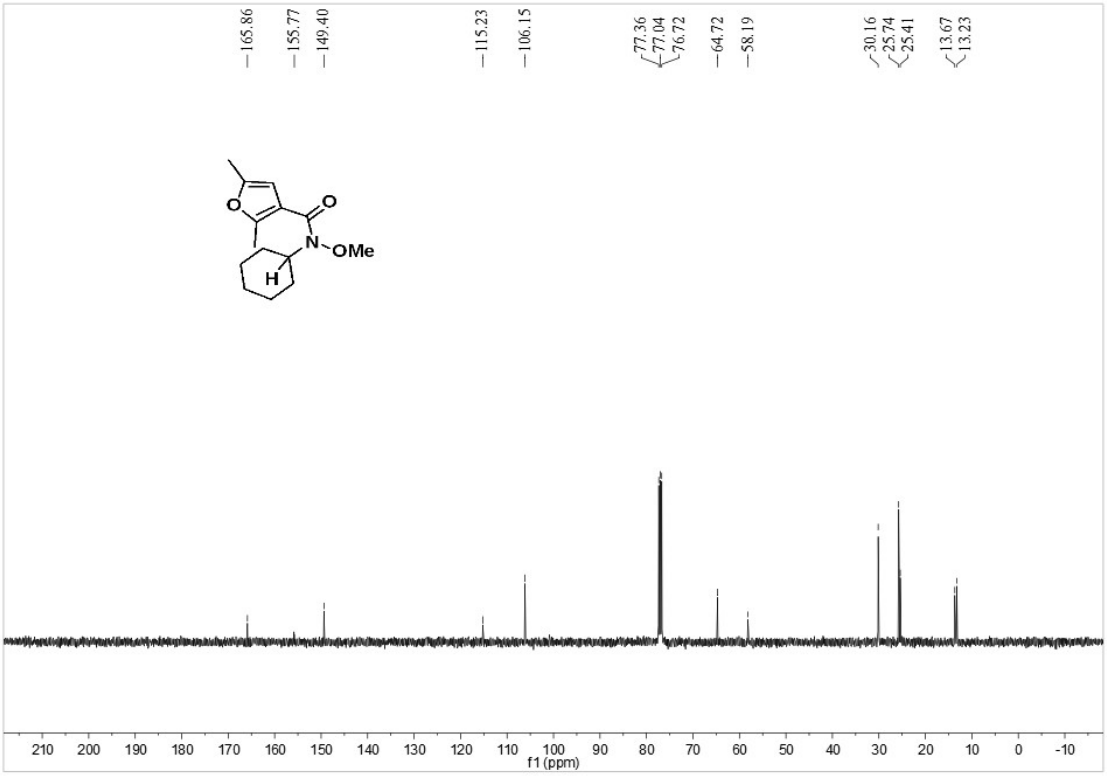
^{13}C NMR spectra of *N*-(4-phenylbutan-2-yl)hydroxylamine (2am)



^{1}H NMR spectra of furmecyclox (BASF)

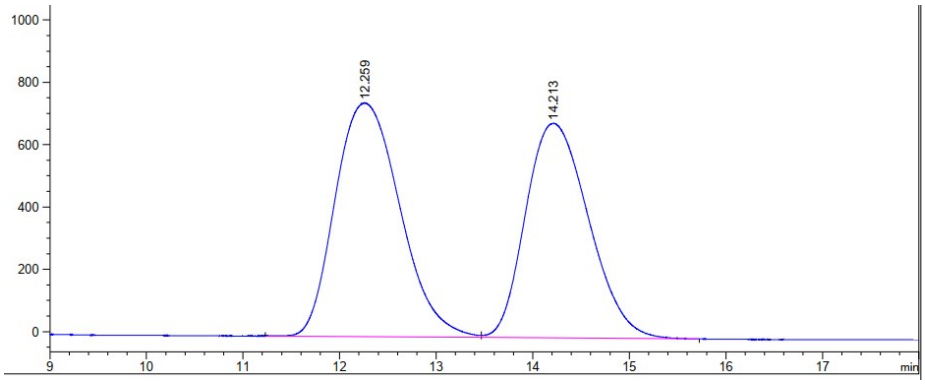


^{13}C NMR spectra of furmecyclox (BASF)



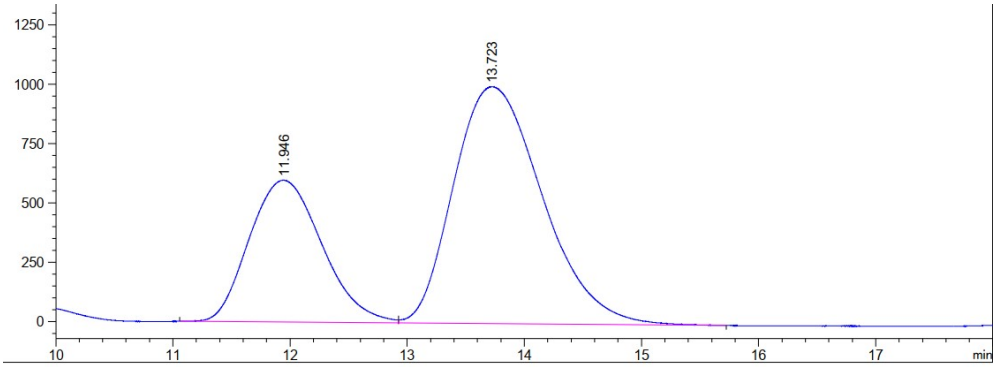
G. HPLC Spectra

Racmate product of *O*-benzyl-*N*-(1-phenylethyl)hydroxylamine (2a)



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.259	VV R	0.5459	3.49924e4	749.92896	52.8096
2	14.213	VV R	0.5330	3.12690e4	688.95001	47.1904
总量：				6.62614e4	1438.87897	

Chiral product of *O*-benzyl-*N*-(1-phenylethyl)hydroxylamine (2a)



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.946	VV R	0.5066	2.57990e4	598.22626	32.8785
2	13.723	VV R	0.6188	5.26688e4	998.59039	67.1215
总量：				7.84678e4	1596.81665	

H. Crystal X-ray diffraction data of TC-5 and 2l

Metrical parameters for the structures of **TC-5** are available free of charge from the Cambridge Crystallographic Data Centre under accession numbers CCDC-2122235.

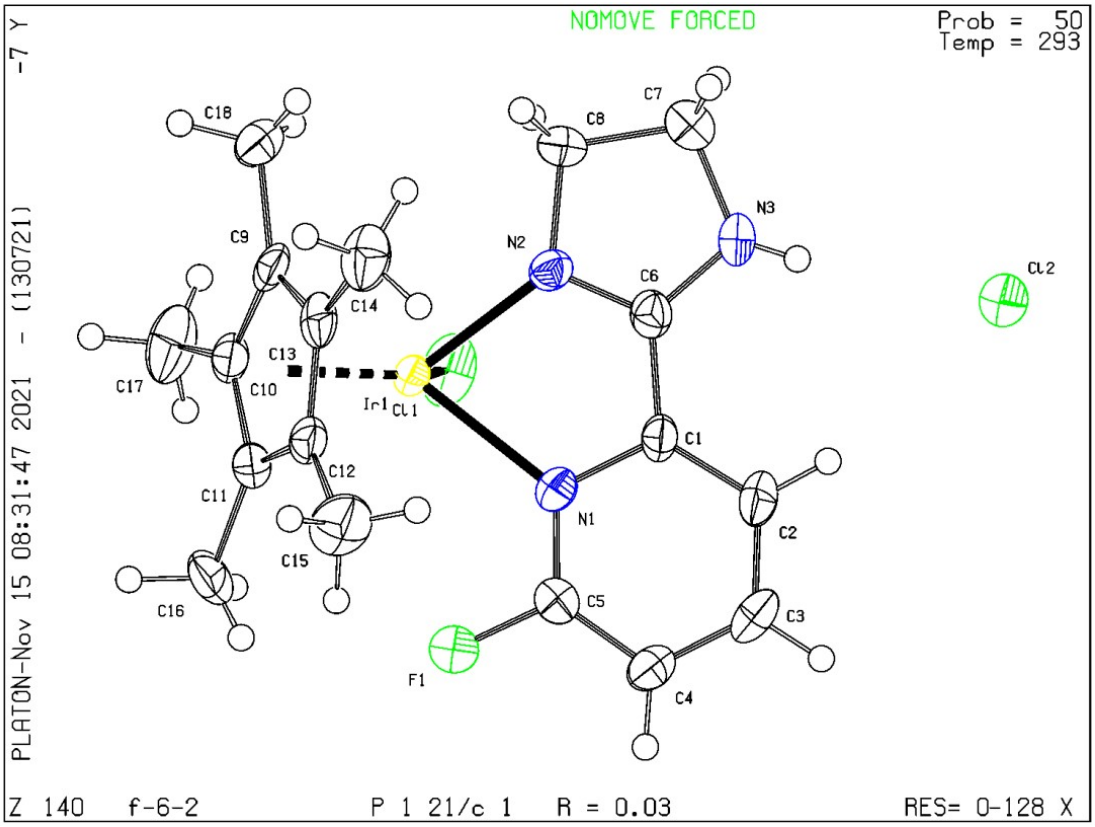


Figure S1. X-ray crystal structure of compound **TC-5**

Table S1. Crystal data and structure refinements for **TC-5**.

Identification code	**TC-5**
Empirical formula	$C_{18}H_{23}Cl_2FIrN_3$
Formula weight	563.49
Temperature/K	292.98(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.8663(5)
b/Å	8.1427(3)
c/Å	16.8048(6)
α/°	90
β/°	93.871(4)
γ/°	90
Volume/Å^3	2029.61(12)
Z	4
ρ_{calc}g/cm^3	1.844
μ/mm^{-1}	6.856
F(000)	1088.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.858 to 49.996
Index ranges	-17 ≤ h ≤ 16, -7 ≤ k ≤ 9, -19 ≤ l ≤ 15
Reflections collected	8631
Independent reflections	3573 [R_{int} = 0.0361, R_{sigma} = 0.0478]
Data/restraints/parameters	3573/0/235
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0641
Final R indexes [all data]	R_1 = 0.0356, wR_2 = 0.0673
Largest diff. peak/hole / e Å^{-3}	0.77/-1.57

Metrical parameters for the structures of **2l** are available free of charge from the Cambridge Crystallographic Data Centre under accession numbers CCDC- 2123580.

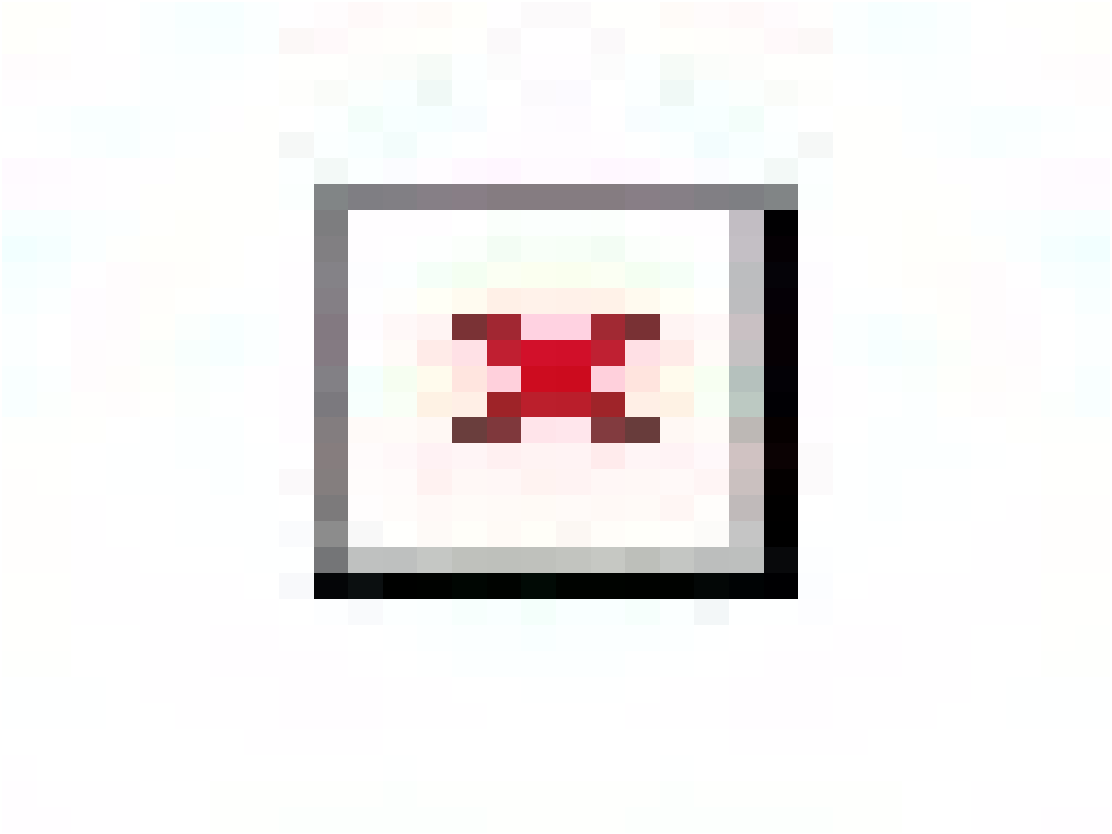


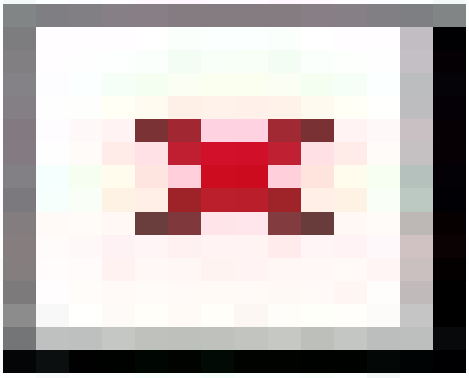
Figure S2. X-ray crystal structure of compound **2l**

Table S2. Crystal data and structure refinements for **2l**.

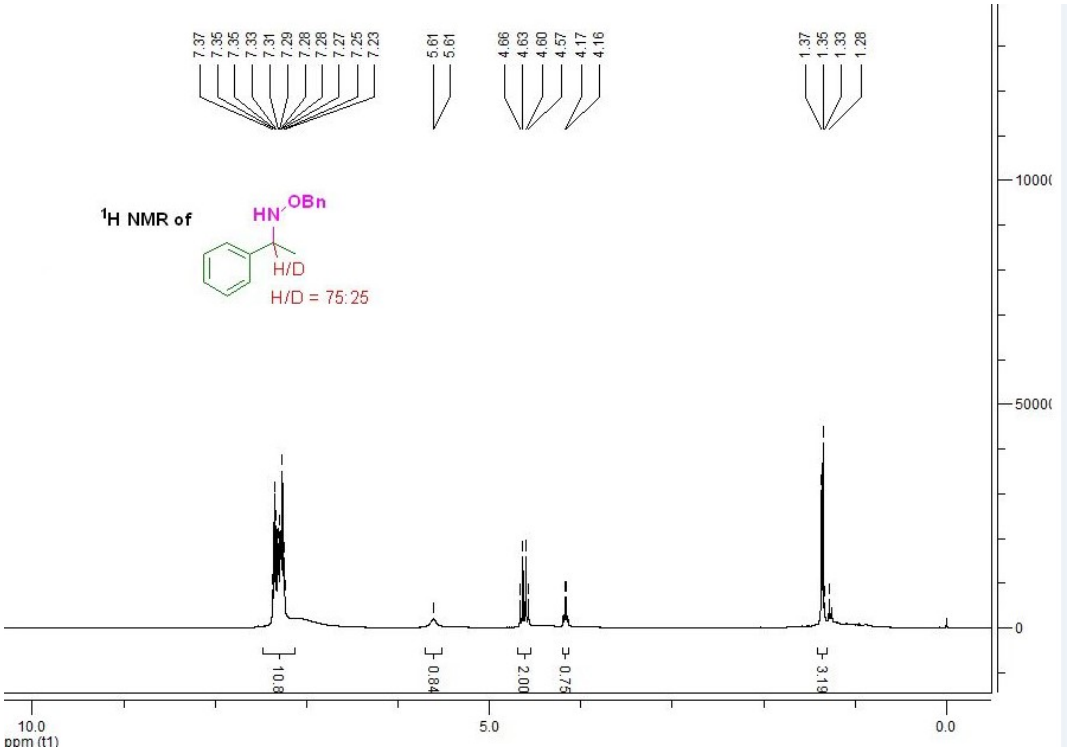
Identification code	**2l**
Empirical formula	$C_{19}H_{19}NO$
Formula weight	277.35
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.7379(3)
b/Å	8.2844(5)
c/Å	31.6487(19)
α/°	90
β/°	91.477(6)
γ/°	90
Volume/Å^3	1503.92(15)
Z	4
ρ_{calc}g/cm^3	1.225
μ/mm^{-1}	0.584
F(000)	592.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.586 to 147.504
Index ranges	$-6 \le h \le 6$, $-10 \le k \le 9$, $-39 \le l \le 36$
Reflections collected	5434
Independent reflections	2933 [R_{int} = 0.0397, R_{sigma} = 0.0498]
Data/restraints/parameters	2933/0/195
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0642, wR_2 = 0.1686
Final R indexes [all data]	R_1 = 0.0784, wR_2 = 0.1769
Largest diff. peak/hole / e Å^{-3}	0.20/-0.29

I. The Deuterated experiment.

Scheme 7a. CF_3CO_2D was employed as additive under standard conditions.



Scheme 7b. DCO_2D was employed as additive under standard conditions.



J. The H^- chemical shift of Ir-H.

The H^- chemical shift of Ir-H determined by ^1H NMR spectra.