Supporting Information

Base-mediated tandem sulfonylation and oximation of alkenes in water

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Contents:

General Remarks

All substrates were purchased commercially without further purification. The yields were determined based on indoles.^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 FT spectrometer at 400 MHz and100 MHz, respectively, with tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass).

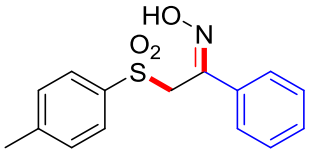
General Procedures for the Synthesis of Arylsulfonyl Hydrazides

Arylsulfonyl hydrazides **2b**-**2s** were prepared according to the literature procedure.[1] To a solution of an arylsulfonyl chloride (3.0 mmol) in tetrahyrdofuran (15 mL), was added hydrazine monohydrate (375 mg, 7.5 mmol) dropwise under nitrogen at 0 ℃. After vigorous stirring for 30 min at 0 ℃, the reaction mixture was added ethyl acetate (60 mL), and washed with saturated brine (3 × 10 mL). The organic layer was dried over sodium sulfate, filtered, concentrated and added to hexane (12 mL) over 5 min. The mixture was filtered, and the collected solid was dried in vacuum.

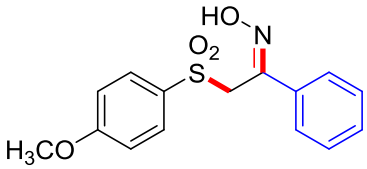
Typical Procedure for the Synthesis of α-Sulfonylethanone Oximes

A mixture of sulfonyl hydrazides (0.25 mmol), styrene (0.75 mmol), TBN (0.50 mmol) and imidazole (0.25 mmol) in 1.5 mL NMP/water (v:v = 1:1) was put into a Schlenk tube at 100 ℃ under magnetic stirring for 6 h under air. After the reaction was complete, the mixture was extracted with EtOAc (3 ×5 mL) and then the combined organic extracts were washed with brine (10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (dichlormethane/ethyl acetate = 25 : 1) to give compound **3aa**.

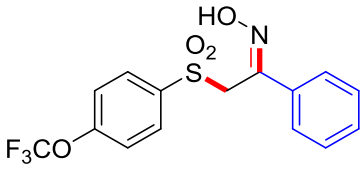
Characterization Data of Products



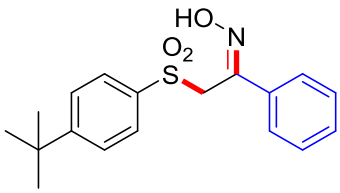
1-phenyl-2-tosylethanone oxime (3aa). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 82.1% yield; mp=201-202 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.78 (s, 1H), 7.65 – 7.61 (m, 4H), 7.36– 7.32 (m, 5H), 4.91 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.13, 144.83, 137.32, 135.02, 129.94, 129.41, 128.67, 128.34, 126.85, 51.89, 21.56; IR (film, v/cm^{-1}): 3062, 2924,2359,1593,1316,1185; HRMS[M+H]$^{+}$ calcd for $C_{15}H_{16}NO_3S$: 290.0851, found 290.0857. This compound was known.[2]



2-((4-methoxyphenyl)sulfonyl)-1-phenylethanone oxime (3ab). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a light yellow solid: 83% yield; mp= 153-154 ℃;^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (s, 1H), 7.67 – 7.62 (m, 4H), 7.39 – 7.32 (m, 3H), 7.08 – 7.04 (m, 2H), 4.89 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.76, 146.26, 135.04, 131.67, 130.62, 129.40, 128.66, 126.85, 114.65, 56.22, 52.05; IR (film, v/cm^{-1}):3356, 2995, 2360, 1909, 1593, 1316; HRMS[M+H]$^{+}$ calcd for $C_{15}H_{16}NO_4S$: 306.0800, found 306.0808.

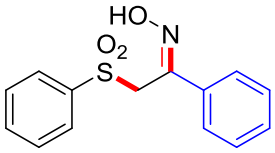


1-phenyl-2-((4-(trifluoromethoxy)phenyl)sulfonyl)ethan-1-one oxime (3ac). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 64 % yield; mp= 137-139 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.86 (s, 1H), 7.86 (d, J=7.2Hz, 2H), 7.61(d, J=7.2Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.37 – 7.31 (m, 3H), 5.01 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.37, 145.89, 138.76, 134.79, 131.23, 129.47, 128.67, 126.83,124.12, 121.52, 118.98, 51.74; IR (film, v/cm^{-1}): 3062, 2999, 2922, 2360, 1587, 1330, 1172; HRMS [M+H]$^{+}$ calcd for $C_{15}H_{13}F_3NO_4S$: 360.0517, found 360.0514.

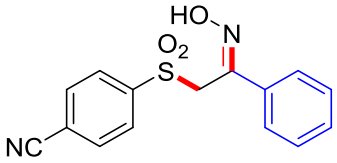


2-((4-(tert-butyl)phenyl)sulfonyl)-1-phenylethan-1-one oxime (3ad). This title compound was prepared

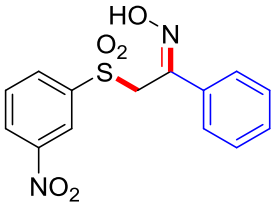
according to the general working procedure and purified by column chromatography to give the product as a white solid: 66 % yield; mp= 174-175 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.86 (s, 1H), 7.66 – 7.64 (m, 2H), 7.58 (dd, 7.6, 1.6Hz, 2H),7.55-7.53(m, 2H),7.35-7.27(m,3H), 4.92 (s, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.37, 146.12, 137.38, 134.96, 129.34, 128.61, 128.16, 126.78, 126.35, 51.82, 35.39, 31.21. IR (film, v/cm^{-1}): 3064, 2965, 2359, 1592, 1311, 1155; HRMS[M+H]$^{+}$ calcd for $C_{18}H_{21}NO_3S$: 332.1320, found 332.1322.



1-phenyl-2-(phenylsulfonyl)ethan-1-one oxime (3ae). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 64 % yield; mp= 137-138 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.81 (s, 1H), 7.77– 7.75 (d, J = 7.6 Hz ,2H), 7.72-7.64 (m, 3H), 7.56 (t, J = 7.6 Hz, 2H), 7.36 – 7.32 (m, 3H), 4.96 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.02, 140.14, 134.98, 134.35, 129.52, 129.48, 128.69, 128.29, 126.84, 51.80; IR (film, v/cm^{-1}): 3067,2924,2360,1581,1307,1151; HRMS[M+H]$^{+}$ calcd for $C_{14}H_{13}NO_3S$: 276.0694, found 276.0700. This compound was known.[3]

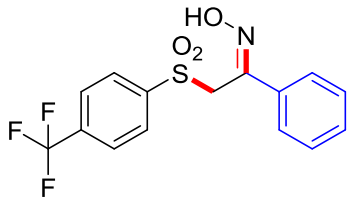


4-((2-(hydroxyimino)-2-phenylethyl)sulfonyl)benzonitrile (3af). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 55 % yield; mp= 160-161 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.81 (s, 1H), 8.07 – 8.05 (m, 2H), 7.94 – 7.92 (m, 2H), 7.68 – 7.63 (m, 2H), 7.41 – 7.34 (m, 3H), 5.05 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.68, 143.85, 134.74, 133.57, 129.60, 129.34, 128.77, 126.87, 118.08, 116.71, 51.63; IR (film, v/cm^{-1}): 3094,2360,2235,1596,1321,1160; HRMS[M+H]$^{+}$ calcd for $C_{15}H_{13}N_2O_3S$: 301.0647, found 301.0654.

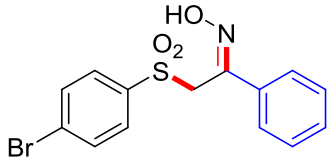


2-((3-nitrophenyl)sulfonyl)-1-phenylethan-1-one oxime (3ag). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 39 % yield; mp= 168-169 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.87 (s, 1H), 8.54-8.51 (m, 1H), 8.38 (s, 1H),8.20-8.18 (m, 1H), 7.87 (t, J = 8.0 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.37 – 7.30 (m, 3H), 5.11 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.89, 145.88, 141.36, 134.65, 134.58, 131.65, 129.61, 128.97, 128.77, 126.87, 123.55, 51.73; IR (film, v/cm^{-1}): 3237, 3092, 2994, 2944, 2360, 1529, 1328, 1169; HRMS[M+H]$^{+}$ calcd for $C_{14}H_{13}N_2O_5S$:

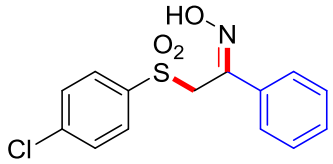
321.0545, found 321.0553.



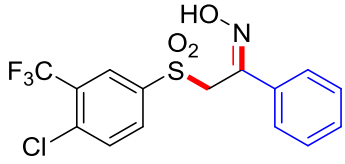
1-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethan-1-one oxime (3ai). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 59 % yield; mp= 146-147 ℃;^{1}H NMR (400 MHz, DMSO-d_6) δ 11.85 (s, 1H), 7.98 – 7.93 (m, 4H), 7.65-7.63 (m, *J* = 7.4, 2H), 7.39 – 7.32 (m, 3H), 5.05 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.75, 143.71, 134.76, 133.91 (q, J_{CF} = 32Hz), 129.58, 129.53, 128.72, 126.86, 126.65 (q, J_{CF} = 3.7 Hz), 123.85 (q, J_{CF} = 272Hz), 51.64. IR (film, v/cm^{-1}): 3388, 2989, 2936, 2359, 1573, 1318, 1124; HRMS[M+H]$^{+}$ calcd for $C_{15}H_{13}F_3NO_3S$: 344.0568, found 344.0574.



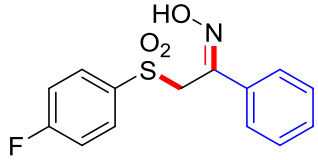
2-((4-bromophenyl)sulfonyl)-1-phenylethan-1-one oxime (3aj). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 72 % yield; mp= 157-158 ℃;^{1}H NMR (400 MHz, DMSO-d_6) δ 11.80 (s, 1H), 7.79 – 7.77 (m, 2H), 7.67–7.65 (m, 4H), 7.37-7.35 (m, 3H), 4.97 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.90, 139.20, 134.85, 132.57, 130.44, 129.49, 128.71, 128.61, 126.86, 51.80. IR (film, v/cm^{-1}): 3079, 2925, 2359, 1570, 1313, 1153; HRMS[M+H]$^{+}$ calcd for $C_{14}H_{13}BrNO_3S$: 353.9800, found 353.9797.



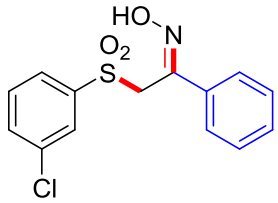
2-((4-chlorophenyl)sulfonyl)-1-phenylethan-1-one oxime (3ak). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 76 % yield; mp= 135-136 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.81 (s, 1H), 7.75 – 7.73 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.63 (m, 4H), 7.40 – 7.33 (m, 3H), 4.98 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.92, 139.48, 138.75, 134.85, 130.43, 129.63, 129.51, 128.72, 126.87, 51.80. IR (film, v/cm^{-1}): 3082, 2924, 2359, 1582, 1314, 1194; HRMS[M+Na]$^{+}$ calcd for $C_{14}H_{12}ClNNaO_3S$: 332.0124, found 332.0127. This compound was known.[2]



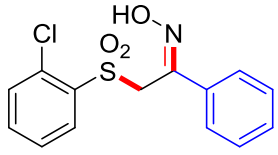
2-((4-chloro-3-(trifluoromethyl)phenyl)sulfonyl)-1-phenylethan-1-one oxime (3al). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 55% yield; mp= 162-163 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.93 (s, 1H), 8.03 (dd, J = 8.4, 1.6 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.59 (d, J = 7.2 Hz, 2H), 7.38-7.30 (m, 3H), 5.12 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.84, 139.18, 137.25, 134.56, 134.15, 133.22, 129.60, 128.73, 128.00 (q, J_{CF} = 22Hz), 127.57 (q, J_{CF} = 127Hz), 126.84, 122.42 (q, J_{CF} = 271Hz), 51.66; IR (film, v/cm^{-1}): 3469,3071,2359,2235,1599,1302,1132; HRMS[M+H]$^{+}$ calcd for $C_{15}H_{12}ClF_3NO_3S$: 378.0179, found 378.0187.



2-((4-fluorophenyl)sulfonyl)-1-phenylethan-1-one oxime (3am). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 85% yield; mp= 120-121 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.80 (s, 1H), 7.82 – 7.78 (m, 2H), 7.65 – 7.63 (m, 2H), 7.42 – 7.33 (m, 5H), 4.97 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.85, 164.34, 146.01, 136.29 (d, J_{CF} = 2.81Hz), 134.88, 131.68 (d, J_{CF} = 10.0Hz), 129.50, 128.71, 126.85, 116.68 (d, J_{CF} = 228.8Hz), 51.86. IR (film, v/cm^{-1}): 3388, 2360, 1896, 1587, 1295, 1153; HRMS[M+H]$^{+}$ calcd for $C_{14}H_{13}FNO_3S$: 294.0600, found 294.0599.

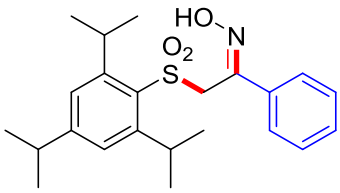


2-((3-chlorophenyl)sulfonyl)-1-phenylethan-1-one oxime (3an). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 55 % yield; mp= 112-113 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.89 (s, 1H), 7.79-7.76 (ddd, J_1 = 8.0, J_2 = 2.0, J_3 = 0.8Hz, 1H), 7.72-7.70 (m, 2H), 7.65 – 7.57 (m, 3H), 7.39 – 7.32 (m, 3H), 5.03 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.88, 141.80, 134.79, 134.34, 134.07, 131.55, 129.58, 128.71, 128.08, 127.10, 126.84, 51.71; IR (film, v/cm^{-1}): 3074, 2917, 2360, 1579, 1321, 1156; HRMS[M+Na]$^{+}$ calcd for $C_{14}H_{12}ClNNaO_3S$: 332.0124, found 332.0124.

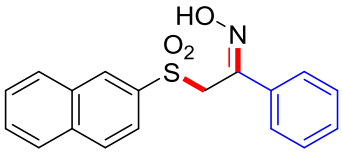


2-((2-chlorophenyl)sulfonyl)-1-phenylethan-1-one oxime (3ao). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a light yellow solid: 21% yield; mp= 103-104 ℃; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.13 (s, 1H), 7.87 (d, J = 8.4Hz, 1H), 7.53 – 7.51 (m, 2H), 7.44 – 7.41 (m, 2H), 7.36 – 7.27 (m, 4H), 5.01 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.59, 137.45, 134.88, 133.63, 133.06, 131.79, 131.66, 129.95, 128.61, 127.17, 126.65, 50.92; IR (film, v/cm^{-1}):

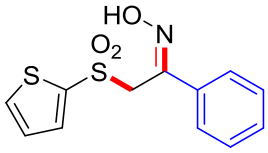
3368, 3065, 2983, 2937, 2360, 1577, 1318, 1165; HRMS[M+H]$^+$ calcd for $C_{14}H_{12}ClNNaO_3S$: 332.0124, found 332.0127.



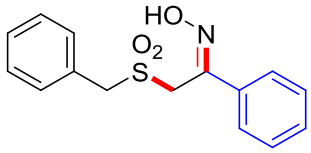
1-phenyl-2-((2,4,6-triisopropylphenyl)sulfonyl)ethan-1-one oxime (3ap). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a light yellow solid: 37 % yield; mp= 164-165 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.88 (s, 1H), 7.78-7.74 (m, 2H), 7.43-7.39 (m, 3H), 7.23 (s, 2H), 4.99 (s, 2H), 3.98-3.88 (m, 2H), 2.97-2.87 (m, 1H), 1.21-1.20 (d, *J* = 6.8 Hz, 6H),1.18-1.16 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.60, 151.28, 145.80, 135.38, 135.29, 129.53, 128.69, 126.67, 124.13, 53.21, 33.83, 29.82, 25.19, 23.85; IR (film, v/cm^{-1}): 3285,2957,2868,2360,1600,1292,1123; HRMS[M+H]$^+$ calcd for $C_{23}H_{32}NO_3S$: 402.2103, found 402.2096.



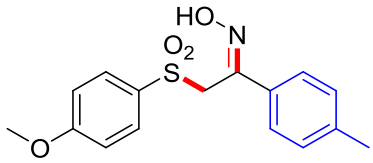
2-(naphthalen-2-ylsulfonyl)-1-phenylethan-1-one oxime (3ar). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 73 % yield; mp= 174-175 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.74 (s, 1H), 8.42 (d, *J* = 1.2 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 8 Hz, 1H), 7.80(dd, *J* = 8.6,1.8Hz, 1H), 7.76 – 7.72 (m, 1H), 7.69-7.66 (m, 3H), 7.36-7.31 (m, 3H), 5.04 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.06, 137.24, 135.31, 135.01, 131.96, 130.00, 129.99, 129.80, 129.52, 129.43, 128.64, 128.31, 128.04, 126.87, 123.38, 51.88; IR (film, v/cm^{-1}): 3057,2918,2360,1589,1315,1192; HRMS[M+H]$^+$ calcd for $C_{18}H_{15}NO_3S$: 326.0851, found 326.0859. This compound was known.[2]



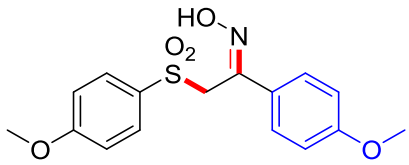
1-phenyl-2-(thiophen-2-ylsulfonyl)ethan-1-one oxime (3as). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a light yellow solid: 41 % yield; mp= 100-101 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.90 (s, 1H), 8.05 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.61 (dd, *J* = 3.6, 1.2 Hz, 1H),7.37-7.35(m, 3H), 7.17 (dd, *J* = 4.8, 4.0 Hz, 1H), 5.04 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.96, 140.60, 136.14, 135.18, 134.95, 129.50, 128.70, 128.57, 126.80, 52.94. IR (film, v/cm^{-1}): 3260, 3117, 2919, 2360, 1598, 1313, 1130; HRMS[M+H]$^+$ calcd for $C_{12}H_{12}NO_3S_2$: 282.0259, found 282.0262.



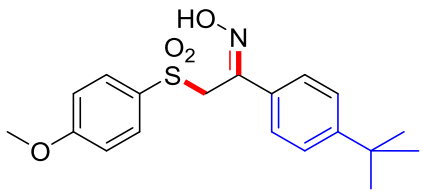
2-(benzylsulfonyl)-1-phenylethan-1-one oxime (3at). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a light yellow oil: 20 % yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.24 (s, 1H), 7.74 – 7.71 (m, 2H), 7.40 (s, 8H), 4.77 (s, 2H), 4.54 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.39, 135.41, 131.75, 129.58, 128.99, 128.93, 128.78, 128.47, 126.81, 60.67, 48.82. IR (film, v/cm^{-1}): 3278, 3060, 2900, 2360, 1578, 1303, 1209; HRMS[M+H]$^{+}$ calcd for $C_{15}H_{16}NO_3S$: 290.0851, found 290.0858.



2-((4-methoxyphenyl)sulfonyl)-1-(p-tolyl)ethan-1-one oxime (4aa). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 75 % yield; mp= 168-169 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.63 (s, 1H), 7.65 – 7.63 (m, 2H), 7.53 (d, J=8.0Hz,2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.07 – 7.05 (m, 2H), 4.86 (s, 2H), 3.83 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.75, 146.14, 138.93, 132.28, 131.67, 130.62, 129.25, 126.79, 114.61, 56.20, 52.04, 21.26; IR (film, v/cm^{-1}): 3219,3002,2907,1592,1300,1153; HRMS[M+H]$^{+}$ calcd for $C_{16}H_{18}NO_4S$: 320.0957, found 320.0957. This compound was known.[2]

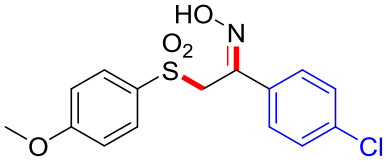


1-(4-methoxyphenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-one oxime (4ab). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 67 % yield; mp= 130-131 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (s, 1H), 7.60 (dd, *J* = 25.2, 8.4 Hz, 4H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.85 (s, 2H), 3.83 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.72, 160.35, 145.78, 131.67, 130.62, 128.26, 127.46, 114.61, 114.08, 56.19, 55.64, 52.02; IR (film, v/cm^{-1}): 3228,1593,1321,1156; HRMS[M+H]$^{+}$ calcd for $C_{16}H_{18}NO_5S$: 336.0906, found 336.0905.

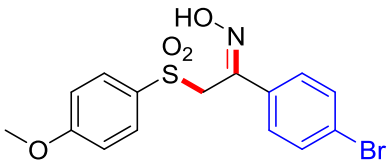


1-(4-(tert-butyl)phenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-one oxime (4ac). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 83% yield; mp= 193-194 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.67 (s, 1H), 7.64 – 7.61 (m,

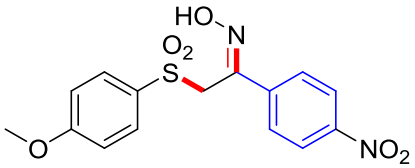
2H), 7.55 – 7.53 (m, 2H), 7.34 – 7.32 (m, 2H), 7.05 – 7.01 (m, 2H), 4.87 (s, 2H), 3.82 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.69, 151.89, 146.08, 132.19, 131.69, 130.63, 126.56, 125.40, 114.58, 56.17, 52.01, 34.80, 31.43; IR (film, v/cm^{-1}): 3064,2954,1595,1298,1134; HRMS[M+H]$^+$ calcd for $C_{19}H_{23}NO_4S$: 362.1426, found 362.1425.



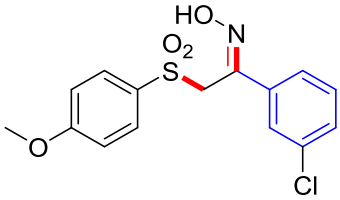
1-(4-chlorophenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-one oxime (4ad). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 67 % yield; mp= 168-170 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.90 (s, 1H), 7.65 (dd, 8.8,2.8Hz, 4H), 7.41 (d, 8.8Hz,2H), 7.06 (d, 8.8Hz, 2H), 4.91 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.83, 145.46, 134.15, 133.92, 131.43, 130.67, 128.69, 128.63, 114.68, 56.21, 51.85; IR (film, v/cm^{-1}): 3212, 2940, 2360, 1593, 1300, 1143; HRMS[M+H]$^+$ calcd for $C_{15}H_{15}ClNO_4S$: 340.0410, found 340.0414.



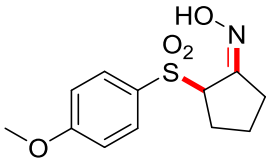
1-(4-bromophenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-one oxime (4ae). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 44 % yield; mp= 170-171 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.90 (s, 1H), 7.65 – 7.62 (m, 2H), 7.59 – 7.53 (m, 4H), 7.07 – 7.04 (m, 2H), 4.89 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.83, 145.57, 134.29, 131.61, 131.41, 130.67, 128.91, 122.87, 114.68, 56.23, 51.80; IR (film, v/cm^{-1}): 3279, 2994, 2929, 1593, 1320, 1152; HRMS[M+H]$^+$ calcd for $C_{15}H_{15}BrNO_4S$: 383.9905, found 383.9905.



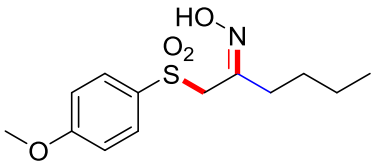
2-((4-methoxyphenyl)sulfonyl)-1-(4-nitrophenyl)ethan-1-one oxime (4af). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a light yellow solid: 41 % yield; mp= 167-168 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.33 (s, 1H), 8.21 – 8.19 (m, 2H), 7.92 – 7.90 (m, 2H), 7.67-7.63 (m, 2H), 7.08 – 7.04 (m, 2H), 5.76 (s, 1H), 4.99 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.92, 147.86, 145.27, 141.31, 131.24, 130.73, 128.05, 123.81, 114.76, 56.23, 51.74. IR (film, v/cm^{-1}): 3230, 3093, 2994, 2944, 1530, 1327, 1116; HRMS[M+H]$^+$ calcd for $C_{15}H_{15}N_2O_6S$: 351.0651, found 351.0648.



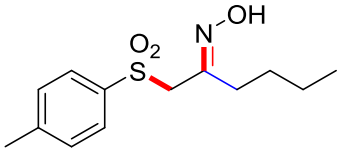
1-(3-chlorophenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-one oxime (4ag). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 49 % yield; mp= 113-114 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.99 (s, 1H), 7.66 – 7.60 (m, 4H), 7.43 – 7.36 (m, 2H), 7.08 – 7.04 (m, 2H), 4.92 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.82, 145.36, 137.08, 133.56, 131.38, 130.64, 130.52, 129.19, 126.63, 125.44, 114.69, 56.21, 51.79; IR (film, v/cm^{-1}): 3409, 3005, 2954, 2845, 1899, 1592, 1292, 1133; HRMS[M+H]$^{+}$ calcd for $C_{15}H_{15}ClNO_4S$: 340.0410, found 340.0413.



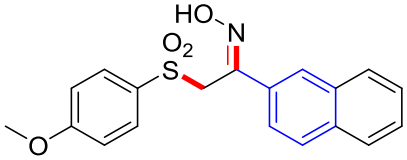
2-tosylcyclopentan-1-one oxime (4ak). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a colorless crystal: 30 % yield; mp= 163-164 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.13 (s, 1H), 7.77 – 7.74 (m, 2H), 7.16 – 7.14 (m, 2H), 4.34 (dd, J = 8.0, 2.4 Hz, 1H), 3.86 (s, 3H), 2.46 – 2.37 (m, 1H), 2.33 – 2.18 (m, 2H), 2.11-1.99(m, 1H), 1.86 – 1.64 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.70, 157.63, 131.34, 130.03, 114.82, 66.37, 56.23, 27.34, 27.20, 22.12; IR (film, v/cm^{-1}): 3328,2919,2848,1920,1594,1290,1181; HRMS[M+H]$^{+}$ calcd for $C_{12}H_{15}NO_4S$: 270.0800, found 270.0803.



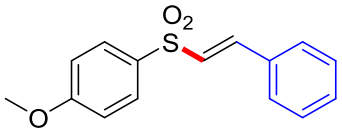
(Z)-1-tosylhexan-2-one oxime (4al). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 25 % yield; mp= 134-135 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.09 (s, 1H), 7.77– 7.75 (m, 2H), 7.16 – 7.14 (m, 2H), 4.13 (s, 2H), 3.85 (s, 3H), 2.34 – 2.30 (m, 2H), 1.45-1.37 (m, 2H), 1.28-1.18 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.75, 150.25, 130.73, 114.92, 60.08, 56.25, 27.36, 26.99, 22.78, 14.11; IR(film, v/cm^{-1}): 3227, 3118, 2963, 2931, 2871, 1594, 1320, 1130; HRMS[M+Na]$^{+}$ calcd for $C_{13}H_{19}NNaO_4S$: 308.0932, found 308.0935.



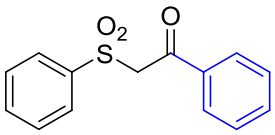
(E)-1-tosylhexan-2-one oxime (4al'). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 15 % yield; mp= 125-126 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.83 (s, 1H), 7.78 – 7.76 (m, 2H), 7.14 – 7.12 (m, 2H), 4.34 (s, 2H), 3.85 (s, 3H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.44 (m, 2H), 1.25 (m, 2H), 0.85 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.78, 147.12, 131.63, 130.54, 114.81, 56.23, 53.18, 33.19, 27.90, 22.17, 14.13; IR (film, v/cm^{-1}): 3226, 2964, 2932, 2872, 1596, 1319, 1132; HRMS[M+H]$^{+}$ calcd for $C_{13}H_{20}NO_4S$: 286.1113, found 286.1116.



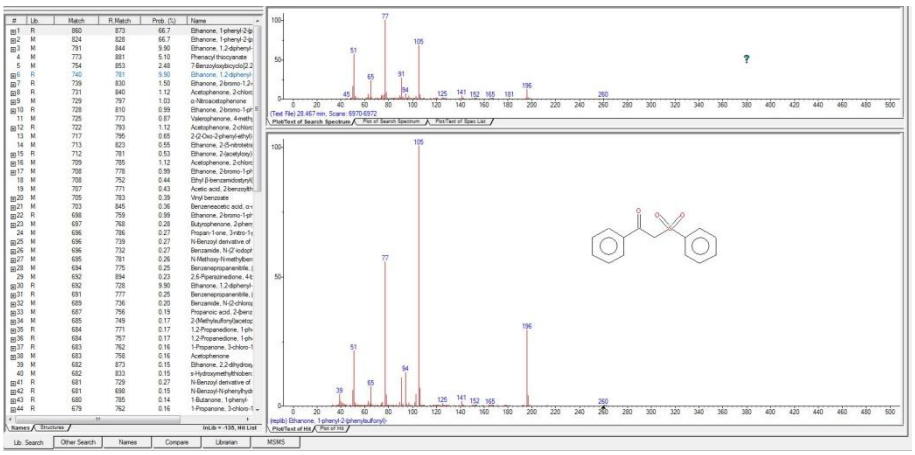
2-((4-methoxyphenyl)sulfonyl)-1-(naphthalen-2-yl)ethan-1-one oxime (4am). This title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 42 % yield; mp= 123-124 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.90 (s, 1H), 8.08 (s, 1H), 7.90 – 7.84 (m, 4H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.55 (s, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 5.03 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.71, 146.25, 133.43, 132.98, 132.31, 131.60, 130.68, 128.82, 128.16, 127.91, 127.17, 127.06, 126.88, 123.85, 114.61, 56.09, 51.88; IR (film, v/cm^{-1}): 3250,2940,2359,1596,1317,1182;HRMS[M+H]$^{+}$ calcd for $C_{19}H_{18}NO_4S$: 356.0957, found 356.0956.

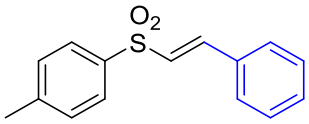


(E)-1-methoxy-4-(styrylsulfonyl)benzene (5a). ^{1}H NMR (400 MHz, DMSO) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.65 – 7.54 (m, 2H), 7.48 – 7.39 (m, 3H), 7.18 (d, *J* = 8.3 Hz, 2H), 3.86 (s, 3H).



1-phenyl-2-(phenylsulfonyl)ethan-1-one (5b).





(E)-1-methyl-4-(styrylsulfonyl)benzene (5c).

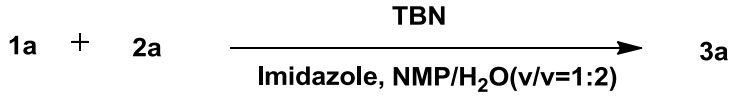
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 15.4 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.43 – 7.37 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H).

4-methoxybenzenesulfonamide (5d).

^{1}H NMR (400 MHz, DMSO) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.22 (s, 2H), 7.10 – 7.07 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 162.09 (s), 136.64 (s), 128.13 (s), 114.47 (s), 56.05 (s).

Mechanistic Studies

1. Radial Trapping Experiments



TEMPO	Trace
BHT	Trace

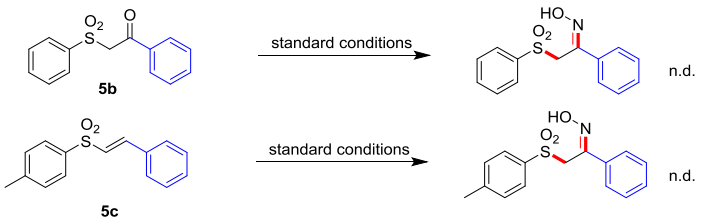
2. Intermediate Experiments

a. General procedures for the synthesis of 1-phenyl-2-(phenylsulfonyl)ethanone **5b**

1-phenyl-2-(phenylsulfonyl)ethanone **5b** was prepared according to the literature procedure.[4] At ambient temperature, 1 mmol of ketones in the presence of (121 mg, 1.2 mmol) Et_3N was stirred for 30 min in 5 mL of MeOH, then the mixture was treated with 1.2 mmol of benzene sulfinic acid sodium, (254 mg, 1 mmol) of molecular iodine and stirred in dark (aluminium foil wrapped around vessel) at room temperature. After completion of the reaction (monitored by TLC) solvent was removed in vacuum, diluted with ethyl acetate (15 mL) and washed sequentially with sat. sodium thiosulfate soln, water then brine. The organic layer was dried over Na_2SO_4. Removal of the solvent in vacuum and purification of the residue by silica gel chromatography with n-hexane-acetone as eluent gave the desired products **5b**.

b. General procedures for the synthesis of (E)-1-methyl-4-(styrylsulfonyl)benzene **5c**

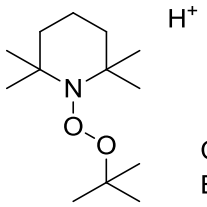
(E)-1-methyl-4-(styrylsulfonyl)benzene **5c** was prepared according to the literature procedure.[5] A 15mL Schlenk tube equipped with a magnetic stirring bar was charged with I_2 (1.5 equiv., 380 mg), alkenes (1.0 mmol), substituted various Sodium methylbenzene sulfonate (1.5 mmol) and H_2O (2 mL). The mixture was then stirred at room temperature for 2 h under air atmosphere, and then a saturated aqueous $Na_2S_2O_3$ solution (2 mL) was added. Following that, the solution was extracted with ethyl acetate (15–20 mL). Finally, the combined organic phases were concentrated and the remaining residue was purified by column chromatography on silica gel to provide the desired product **5c**.



5b

5c

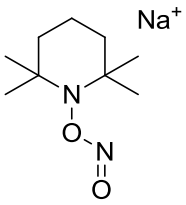
3. High Resolution Quality Spectrum Data



H^+

9

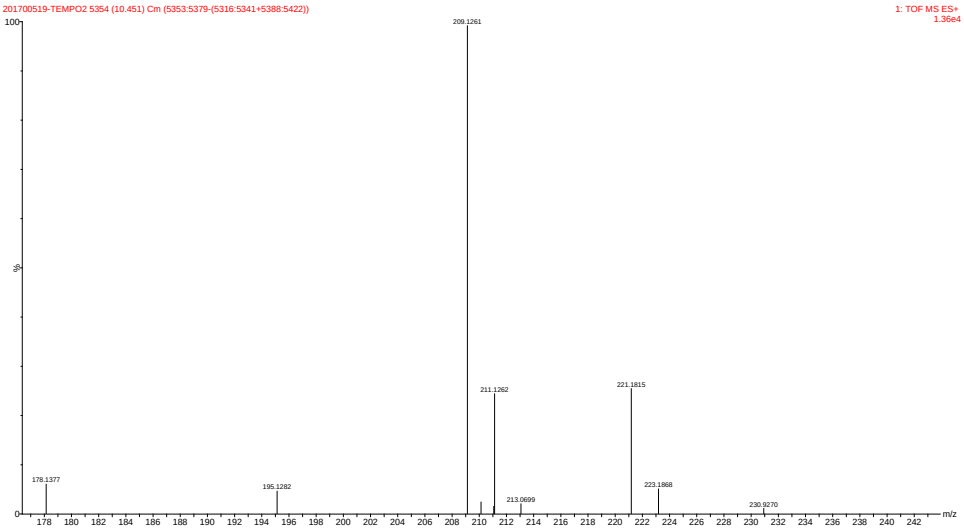
Chemical Formula: $C_{13}H_{28}NO_2$
Exact Mass: 230.2115

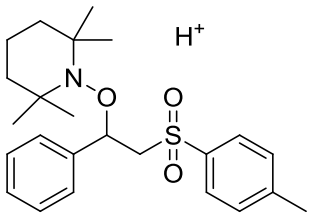


Na^+

10

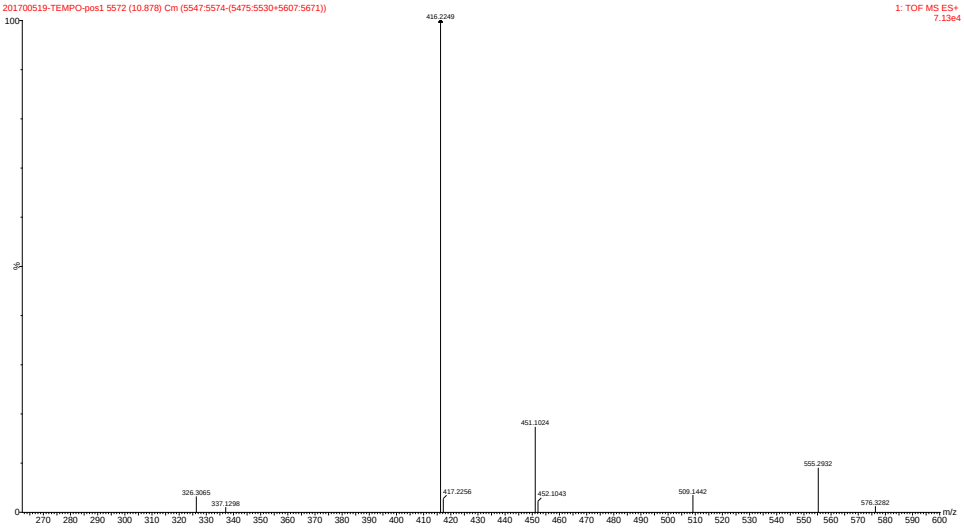
Chemical Formula: $C_9H_{18}N_2NaO_2$
Exact Mass: 209.1260





11

Chemical Formula: $C_{24}H_{34}NO_3S$
Exact Mass: 416.2259



General Procedure for Ultra Performance Liquid Chromatography (UPLC)

1. UPLC Analysis Methods

HPLC grade methanol was procured from Merck (Darmstadt, Germany). Water for UPLC analysis was purified by a Milli Q water purification system (Millipore Corporation, MA, USA). PTFE membrane filter (0.22 μm) was purchased from Waters Co. (Milford, MA). The sample was weighed in electronic balance (BP211D, Sartorius, Germany). The UPLC system (Agilent technologies co., USA) was equipped with a dual pump, an autosampler including a column oven controller, which was connected in ultraviolet detector (UV) quantitative analyzing and UV spectra acquisition. The chromatographic separation was performed on a EclipsePlusC_{18} column (1.8 μm, ø 2.1 mm × 100 mm, agilent, USA). The mobile phase was methanol (A) and water (B). A gradient program was as follows: 0-3 min, 30% A; 5-8 min, 45 % A; 9-12 min, 90 % A. The beginning gradient was held for 5 min. The flow rate was 0.4 mL/min. The injection

volume was 1 μL and the column temperature was maintained at 25 °C. The detection wavelength was set at 250 nm.

2. Preparation of Standard Solutions and Calibration Curves

The reference standard was dissolved in methanol to final concentration of 1.009 mg mL^{-1} for product **3aa**. Calibration standard working solutions were prepared by diluting the above standard solutions in appropriate proportions with methanol, to gain the desired concentrations. Each calibration curve was constructed by running samples at six different concentrations in triplicate. The calibration curve was obtained by plotting the peak area of the compound at each level prepared versus the concentration of the sample. All standard solutions were stored in the refrigerator at 4 ℃ and were filtered through a 0.22 μm syringe filter before use.

3. Preparation of Samples

After the end of model reaction of different optimization conditions, the reaction solution including product 3aa was diluted to the same volume. The obtained sample solutions was then diluted to desired concentrations with methanol and passed through a 0.22 μm Millipore membrane filte prior to analysis.

Reference

[1] F. Yang, X. Ma and S. Tian, *Chem. - Eur. J.*, 2012, **18**, 1582.

[2] F. Chen, N. Zhou, J. Zhan, B. Han and W. Yu, *Org. Chem. Front.*, 2017, **4**, 135.

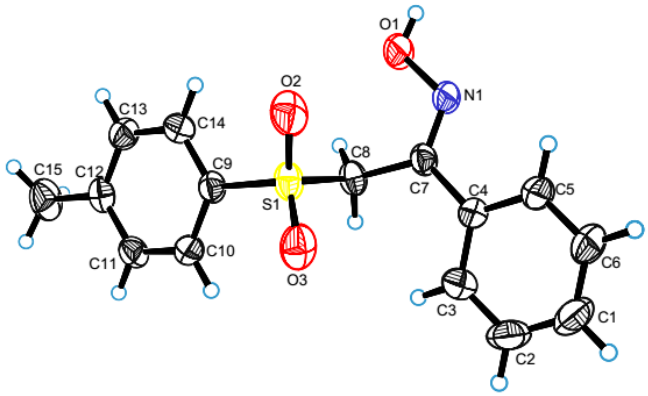
[3] J. Yang, Y. Liu, R. Song, Z. Peng and J. Li, *Adv. Synth. Catal.*, 2016, **358**, 2286.

[4] V. S. Rawat, P. L. M. Reddy and B. Sreedhar, *RSC Adv.*, 2014, **4**, 5165.

[5] N. Zhang, D. Yang, W. Wei, L. Yuan, Y. Cao and H. Wang, *RSC Adv.*, 2015, **5**, 37013.

Crystal Structure

The Product **3aa** crystals were grown in dichloromethane and petroleum ether mixed solvent. The structures are given below. The corresponding .cif file has been uploaded separately as supporting information.



CCDC-1577443

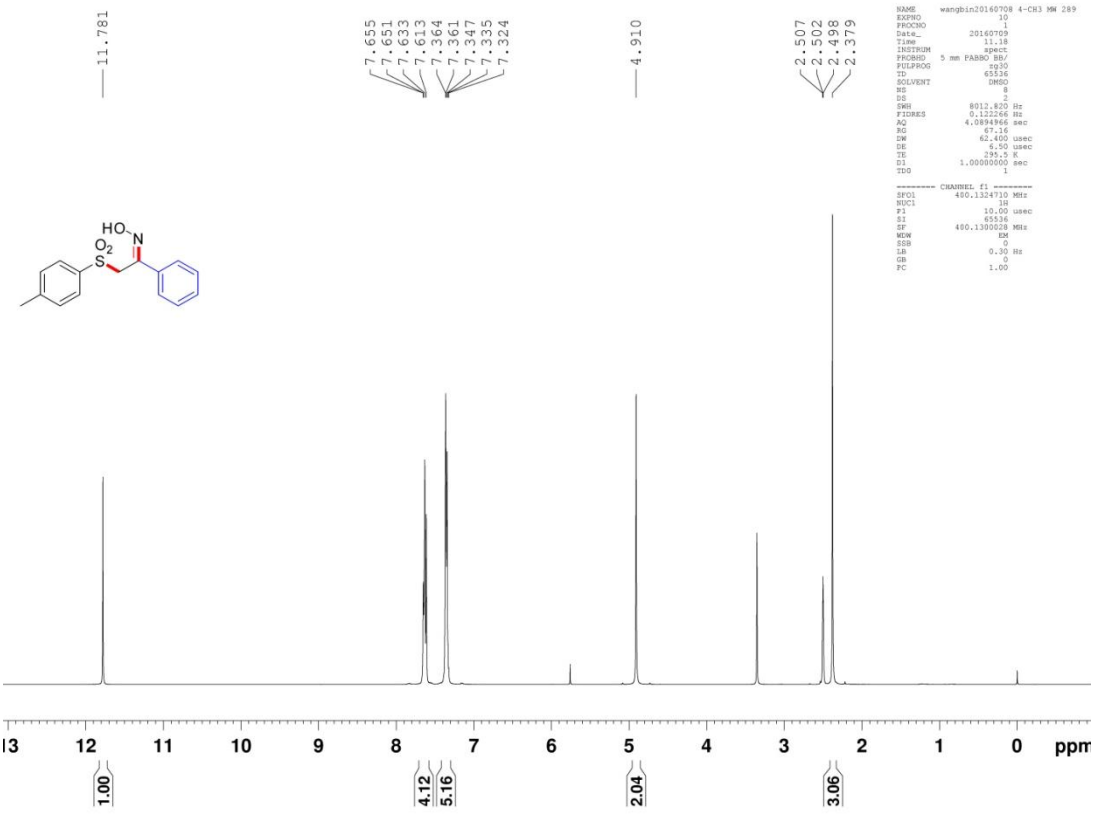
Empirical formula	$C_{15}H_{15}NO_3S$
Formula weight	289.34
Temperature/K	292(2)
Crystal system	monoclinic

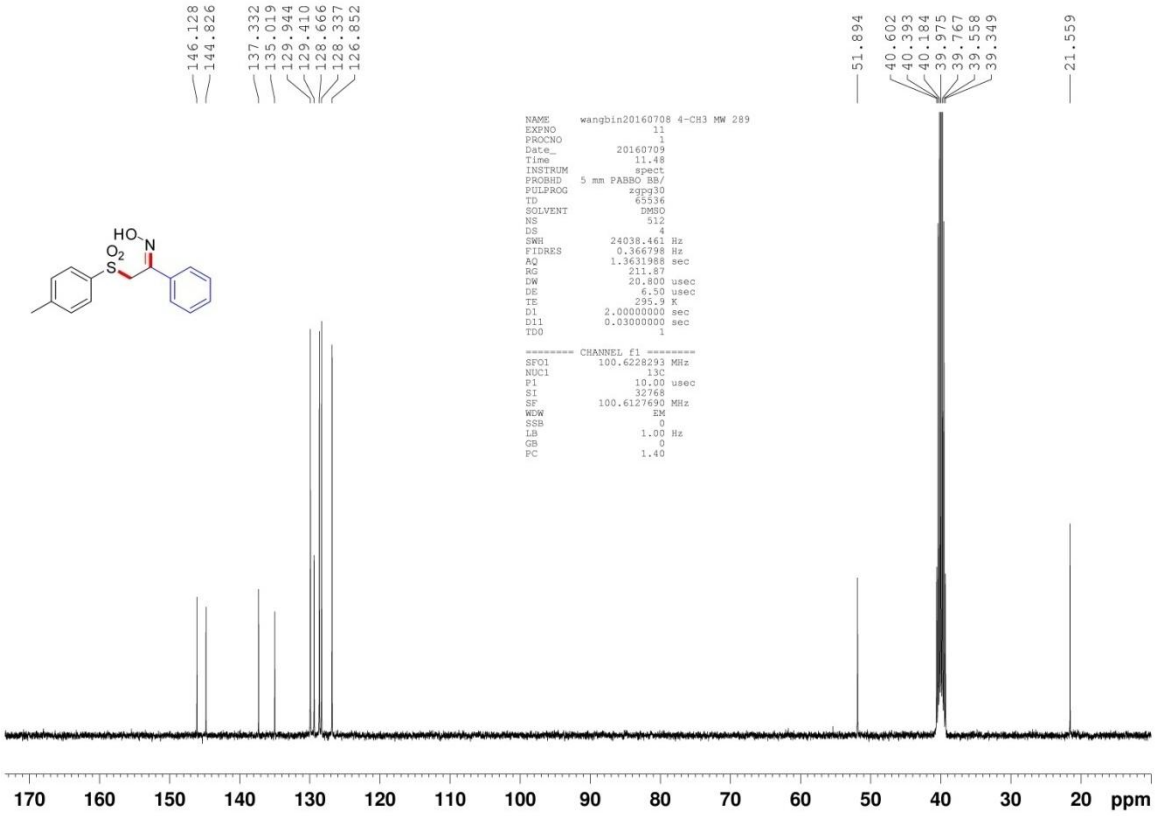
Space group	$P2_1/c$
a/Å	15.2479(4)
b/Å	5.55410(10)
c/Å	16.8079(3)
α/°	90
β/°	95.501(2)
γ/°	90
Volume/$Å^3$	1416.88(5)
Z	4
$\rho_{calc}g/cm^3$	1.356

Reflections collected/ independent: 4536/2663 [R (int) = 0.0133]; Goodness-of-fit on F^2: 1.048; Final R indexes [I>=2σ (I)]: R_1=0.0375, wR_2= 0.1044; Final R indexes [all data]: R_1= 0.0407, wR_2= 0.1077.

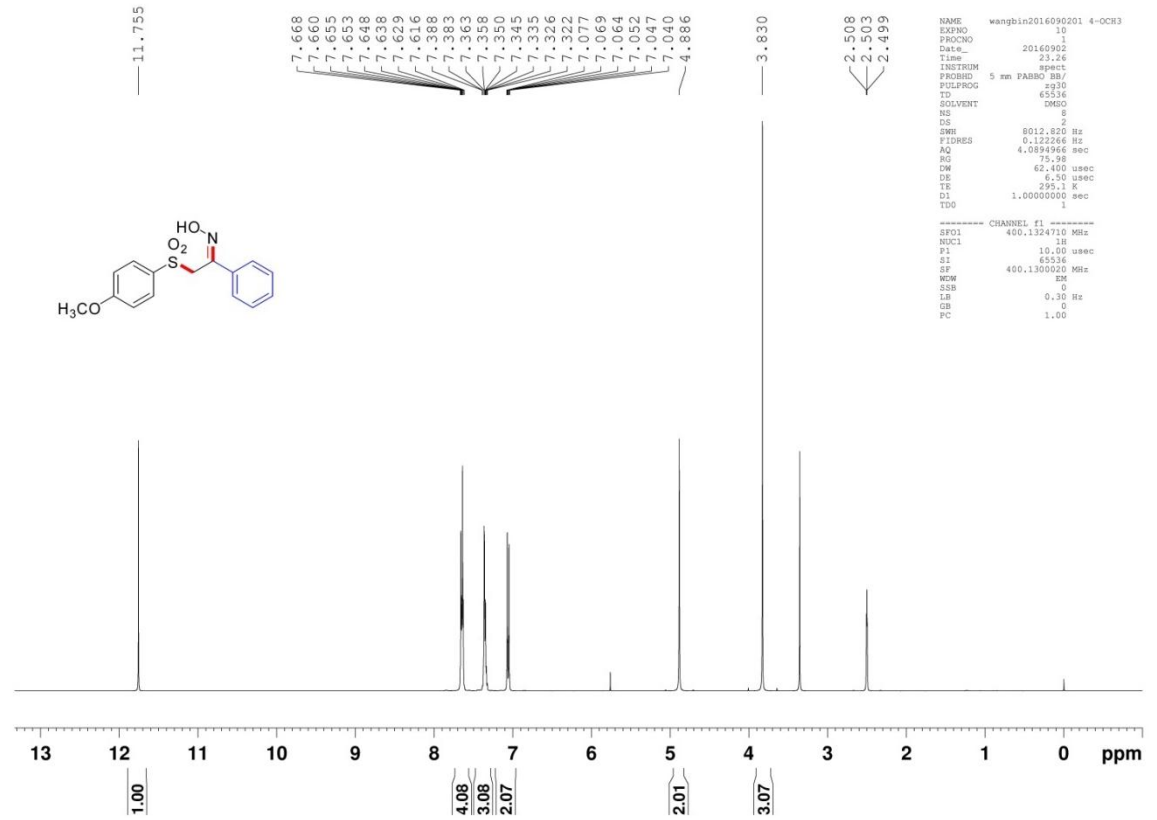
^{1}H NMR and ^{13}C NMR Spectra of products

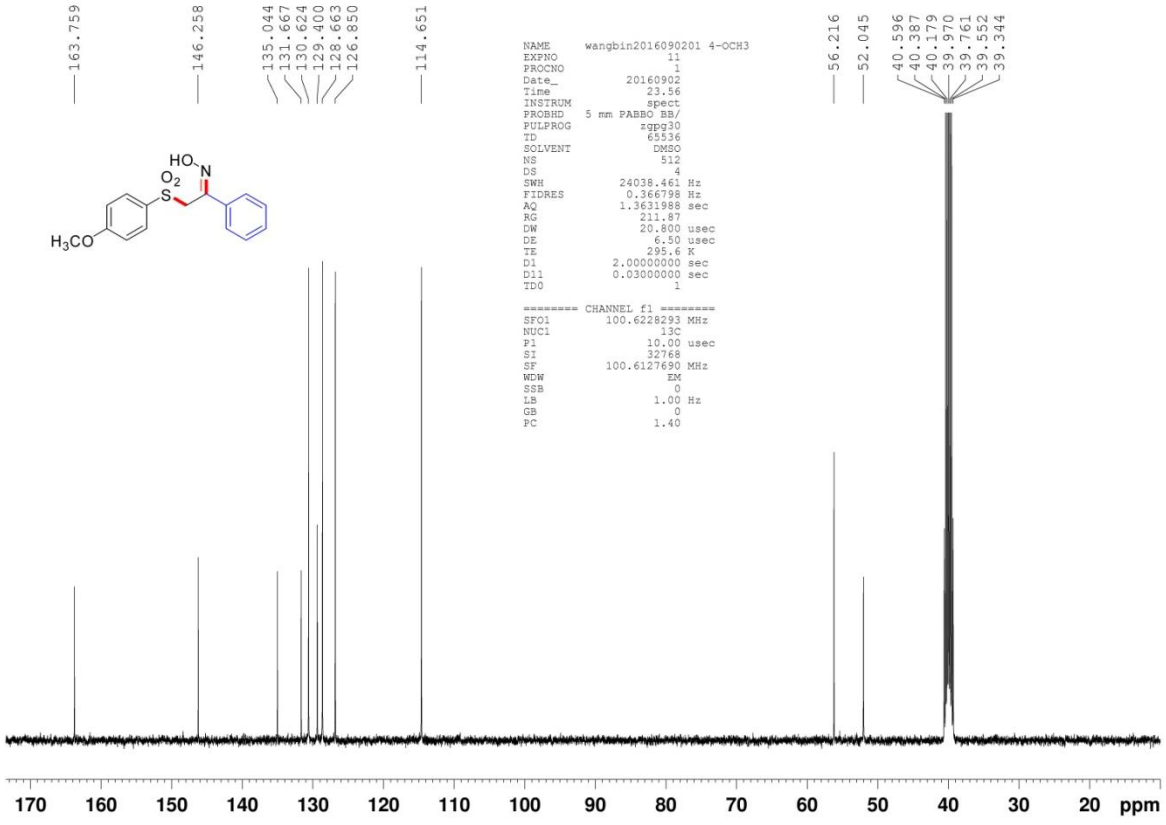
1-phenyl-2-tosylethanone oxime (**3aa**).



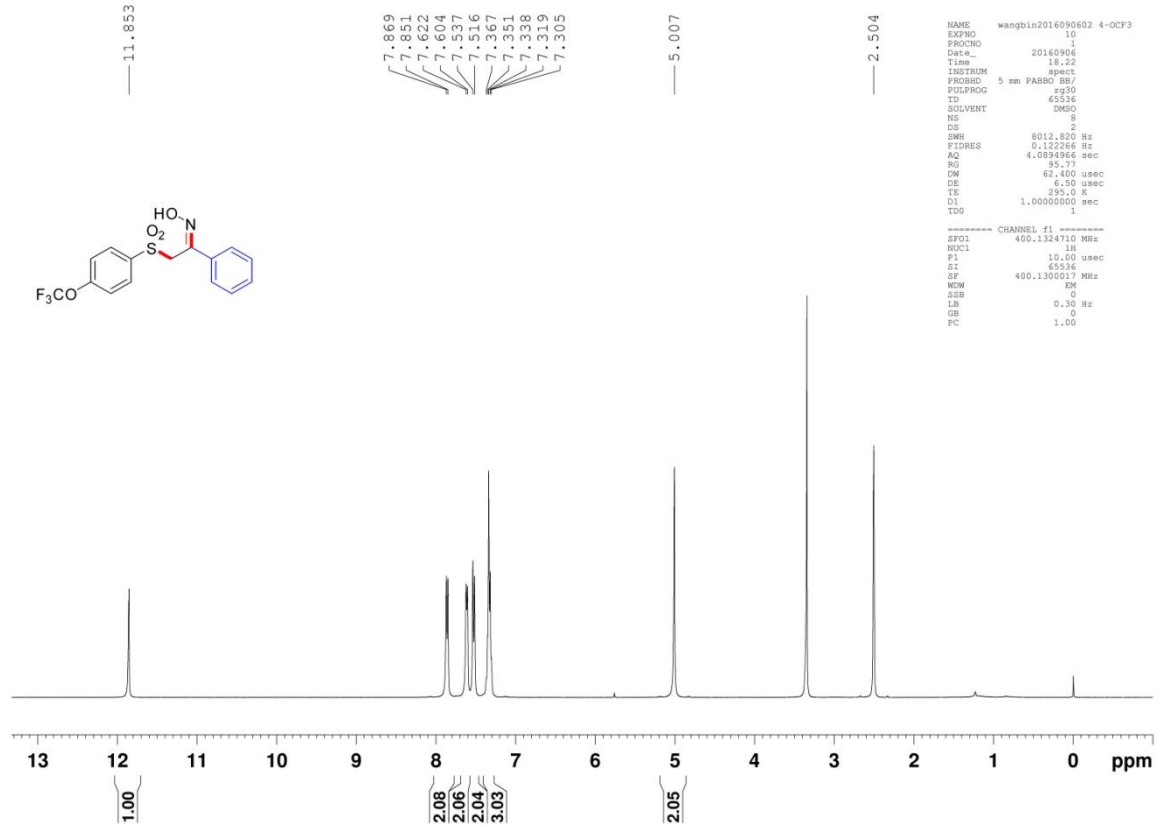


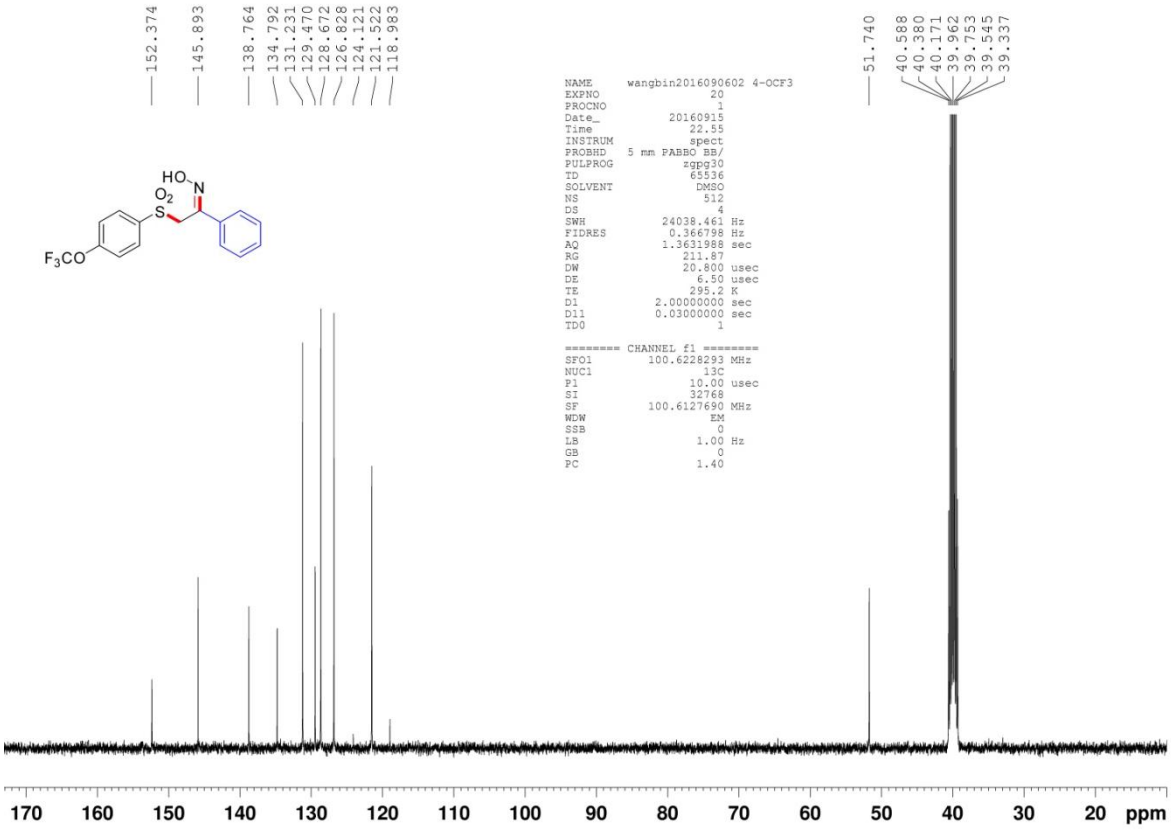
2-((4-methoxyphenyl)sulfonyl)-1-phenylethanone oxime (**3ab**).



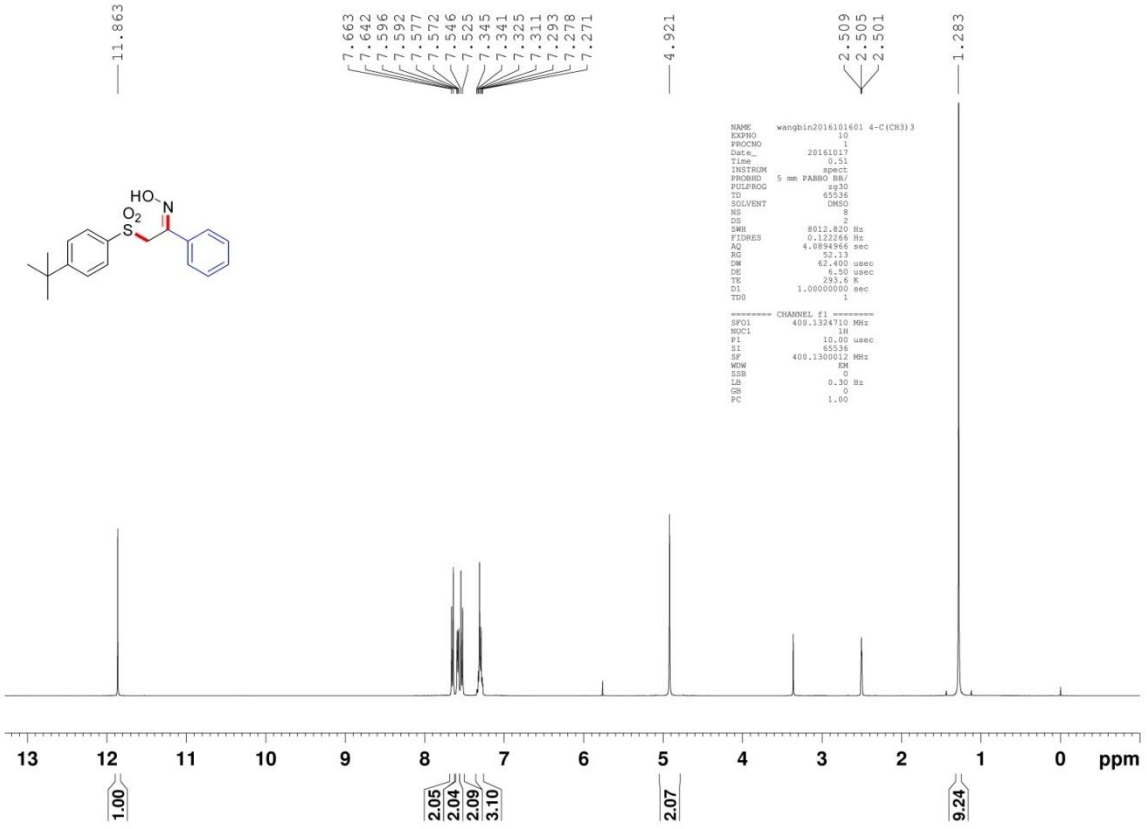


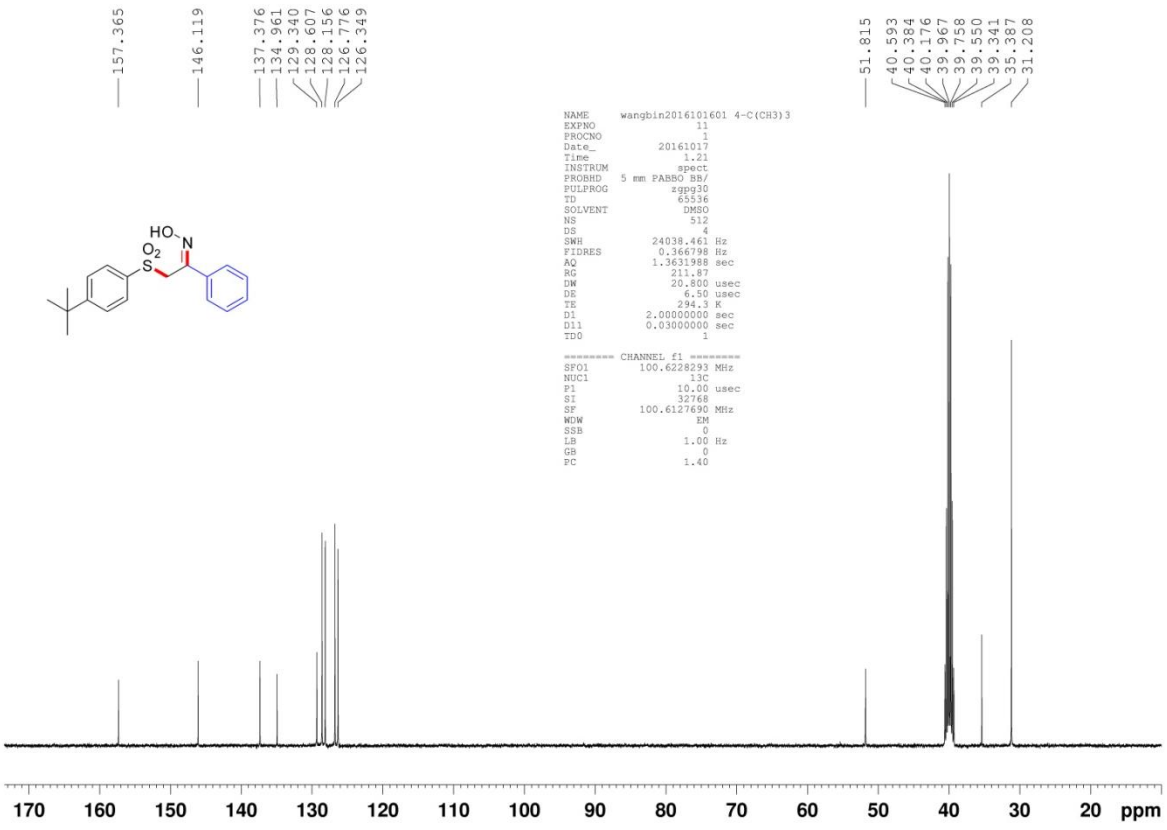
1-phenyl-2-((4-(trifluoromethoxy)phenyl)sulfonyl)ethan-1-one oxime (**3ac**).



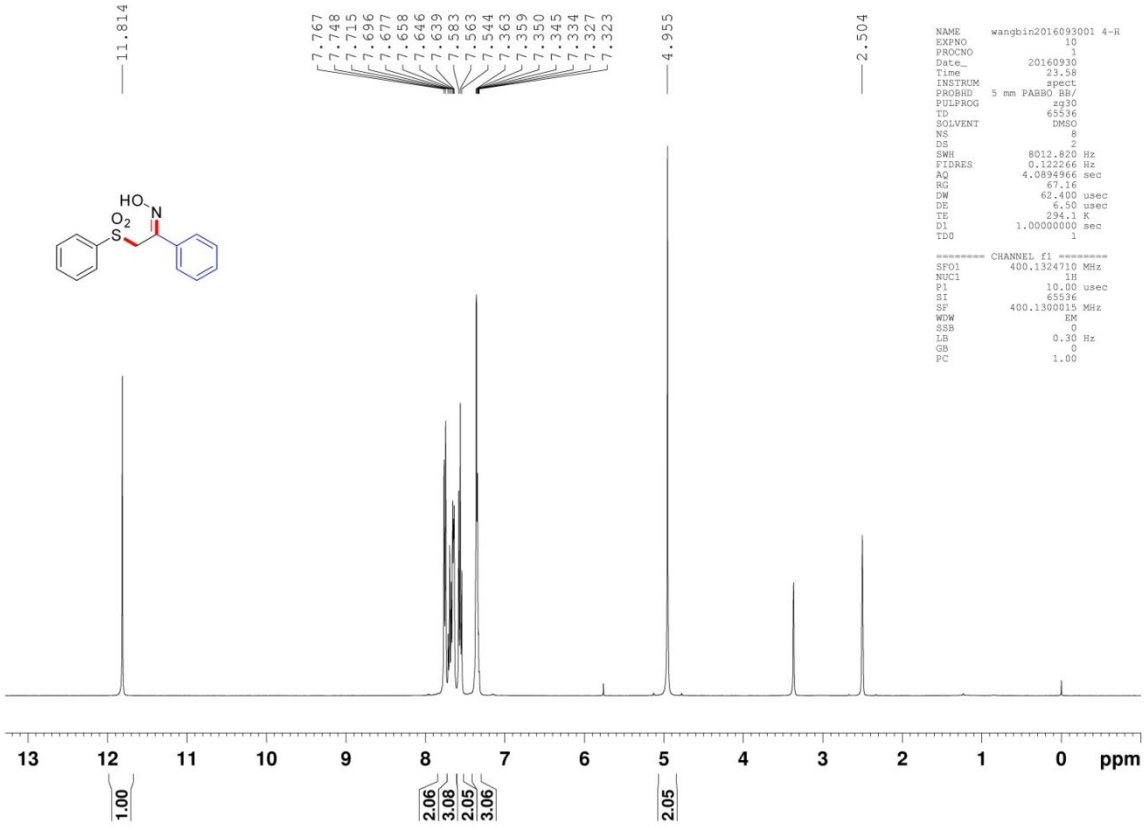


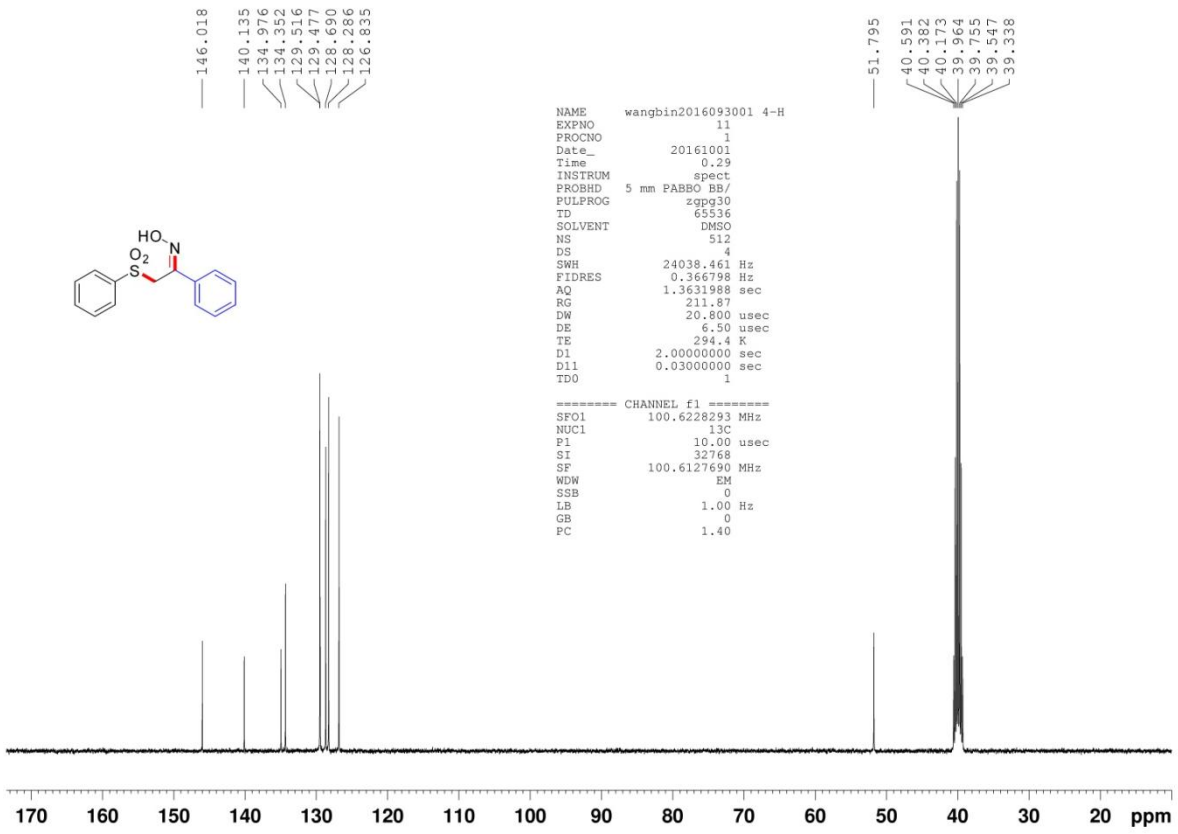
2-((4-(tert-butyl)phenyl)sulfonyl)-1-phenylethan-1-one oxime (**3ad**).



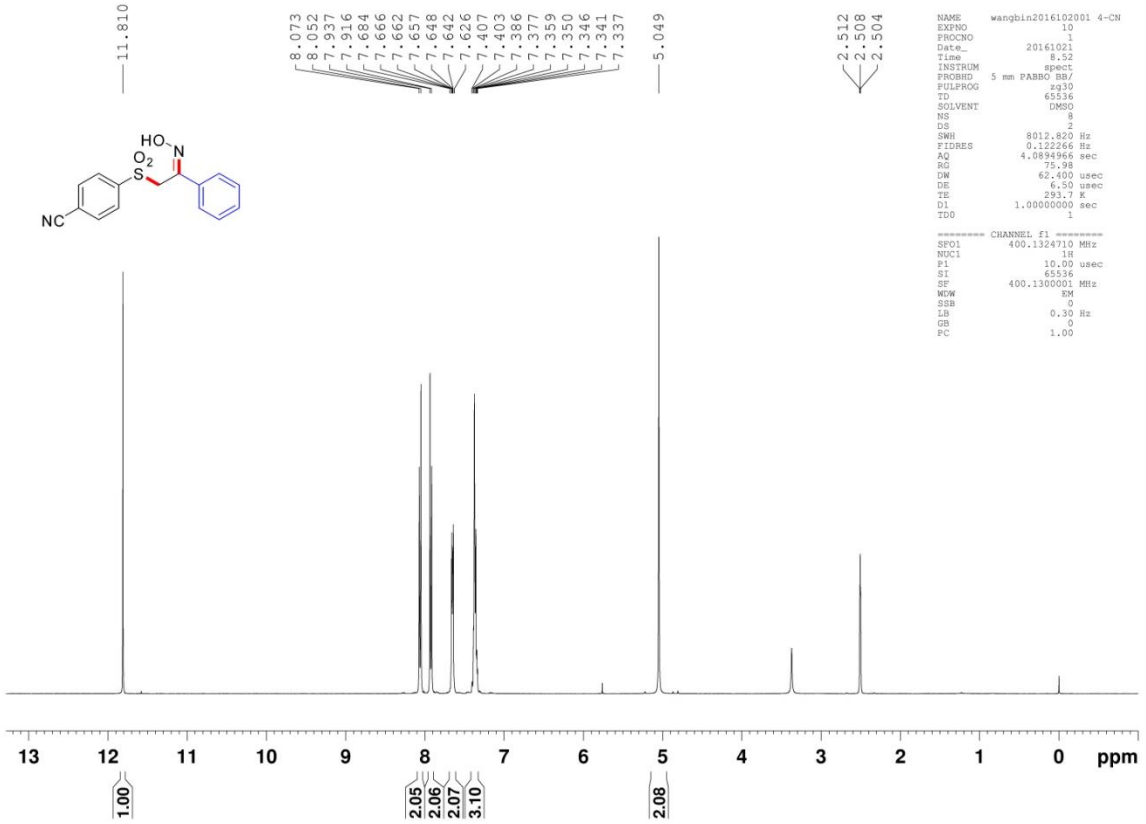


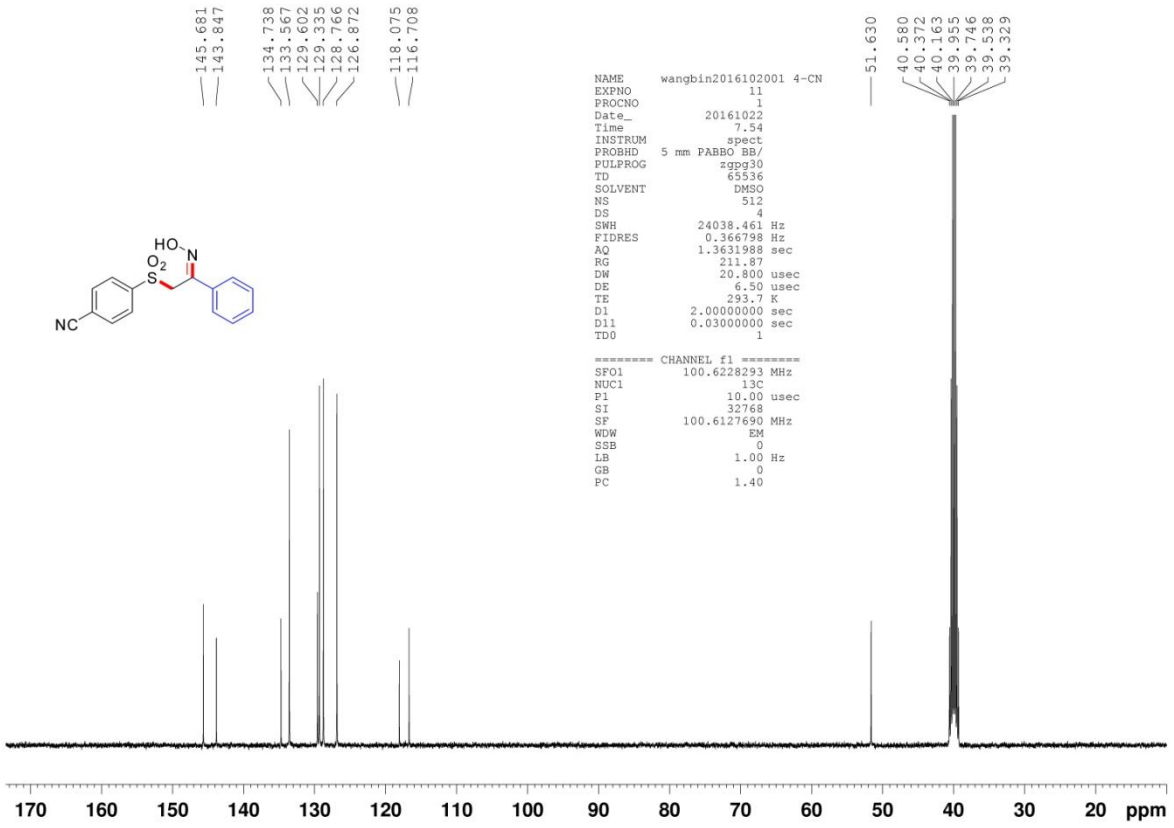
1-phenyl-2-(phenylsulfonyl)ethan-1-one oxime (**3ae**).



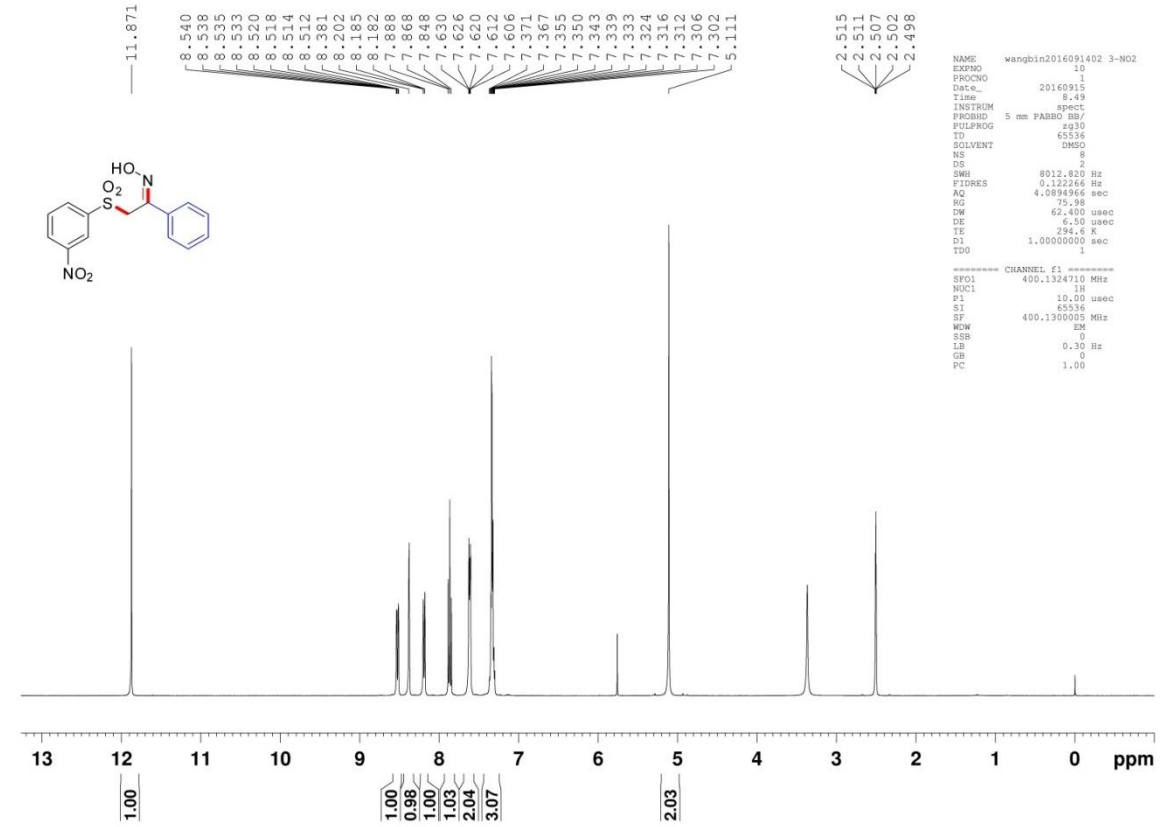


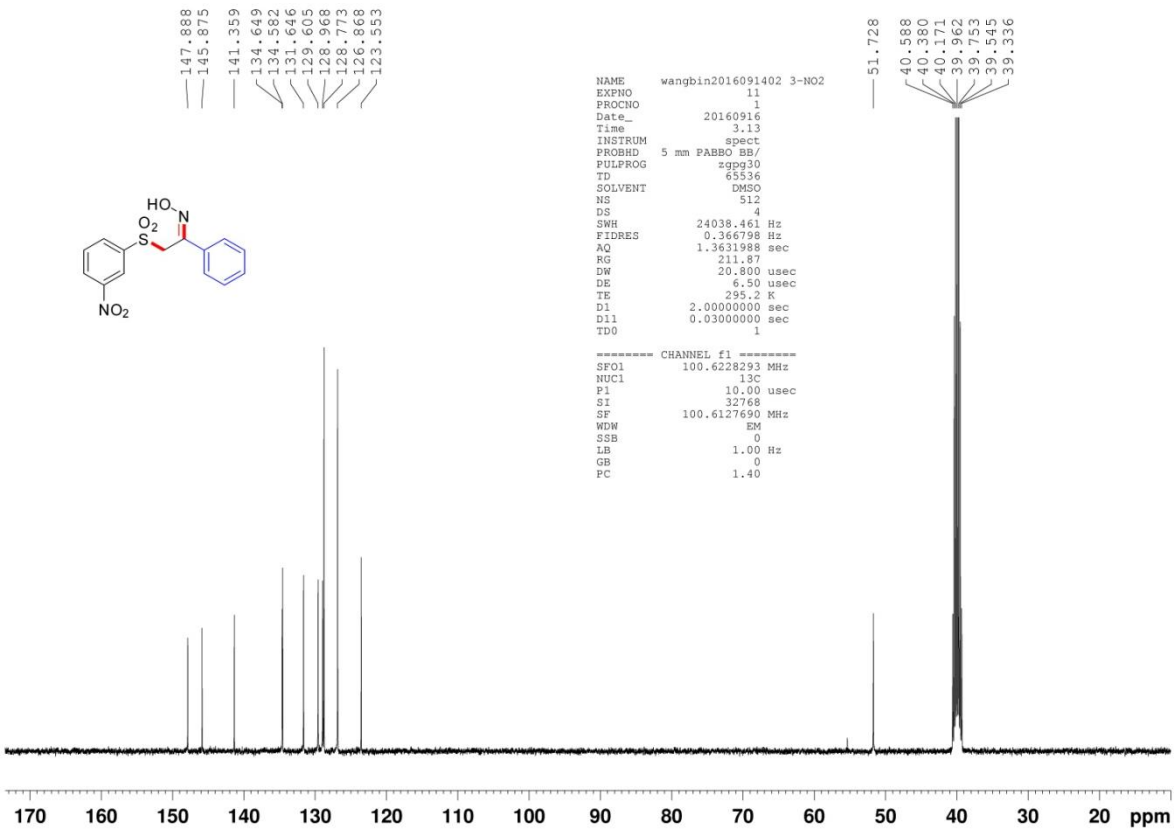
4-((2-(hydroxyimino)-2-phenylethyl)sulfonyl)benzonitrile (**3af**).



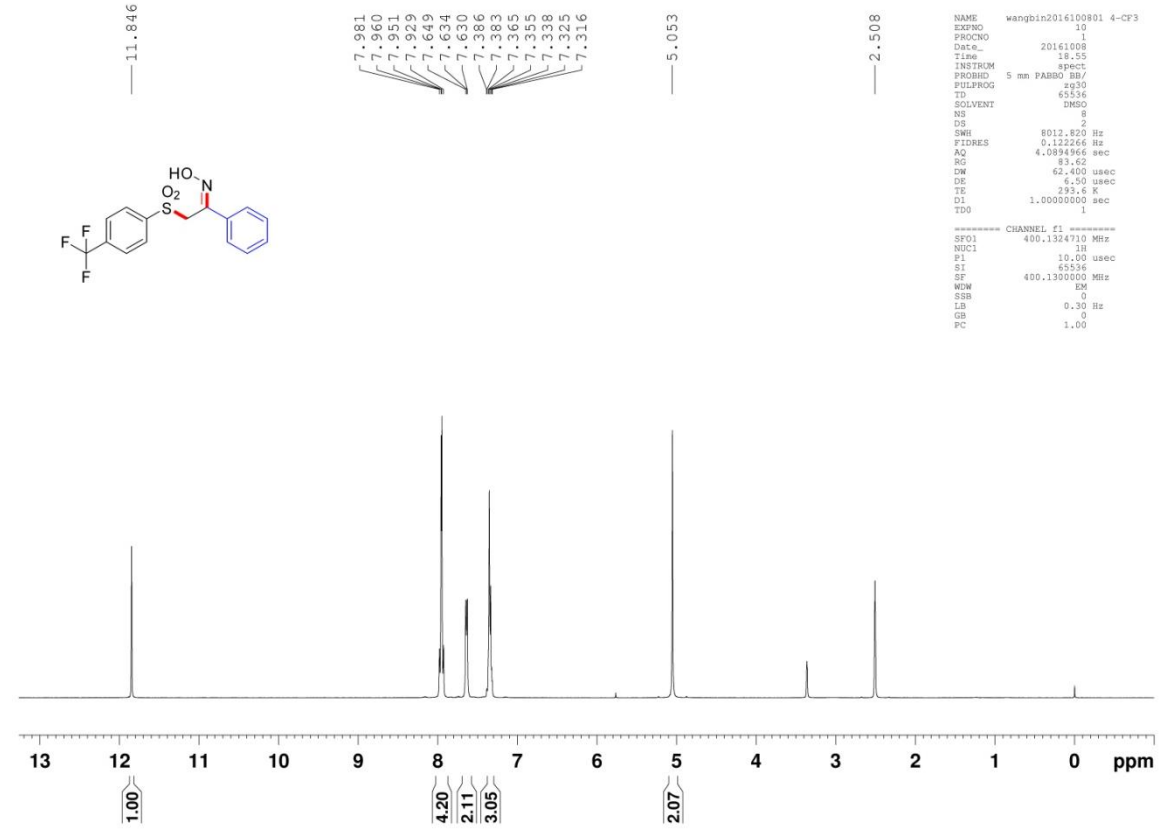


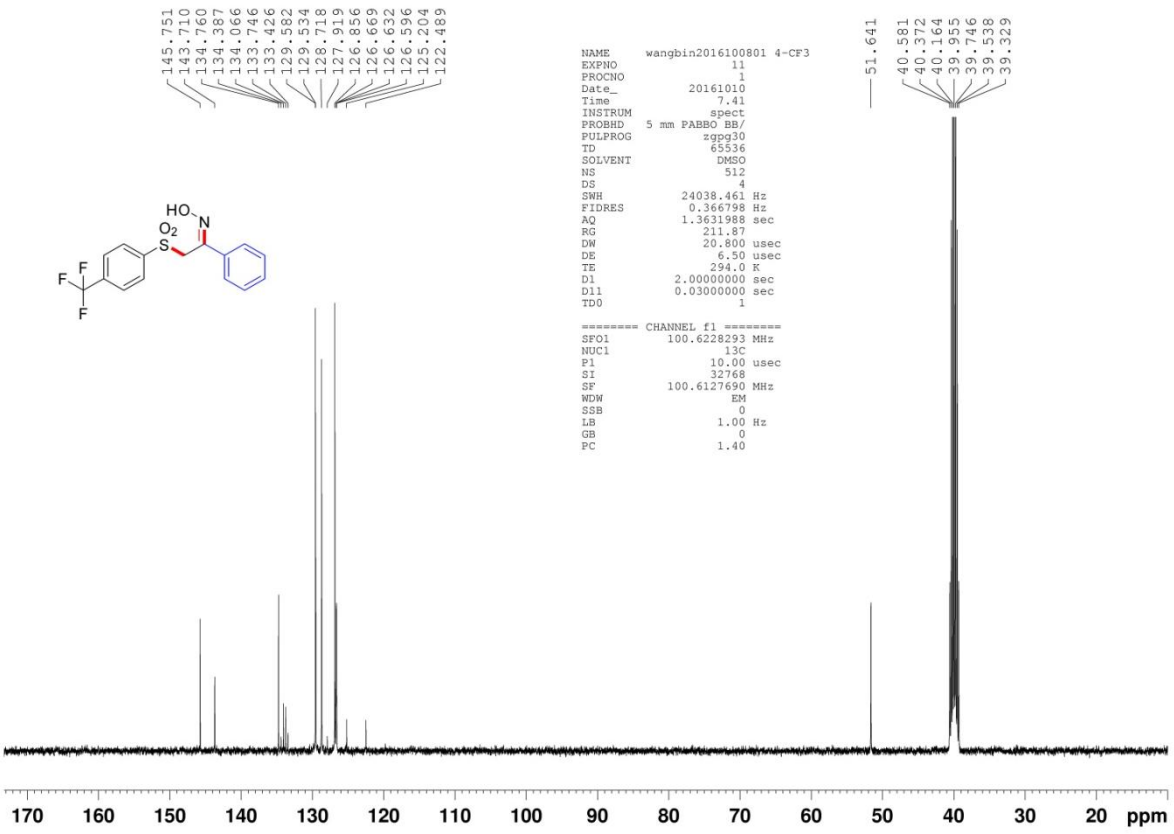
2-((3-nitrophenyl)sulfonyl)-1-phenylethan-1-one oxime (**3ag**).



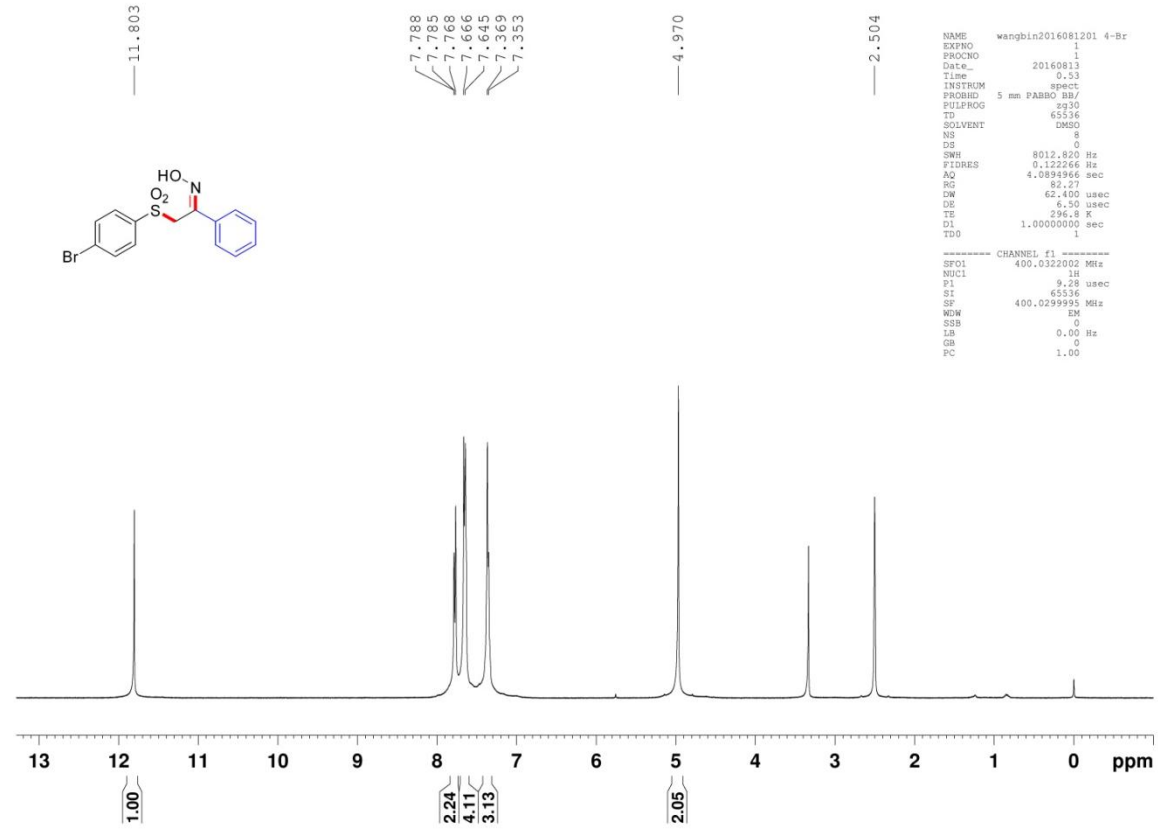


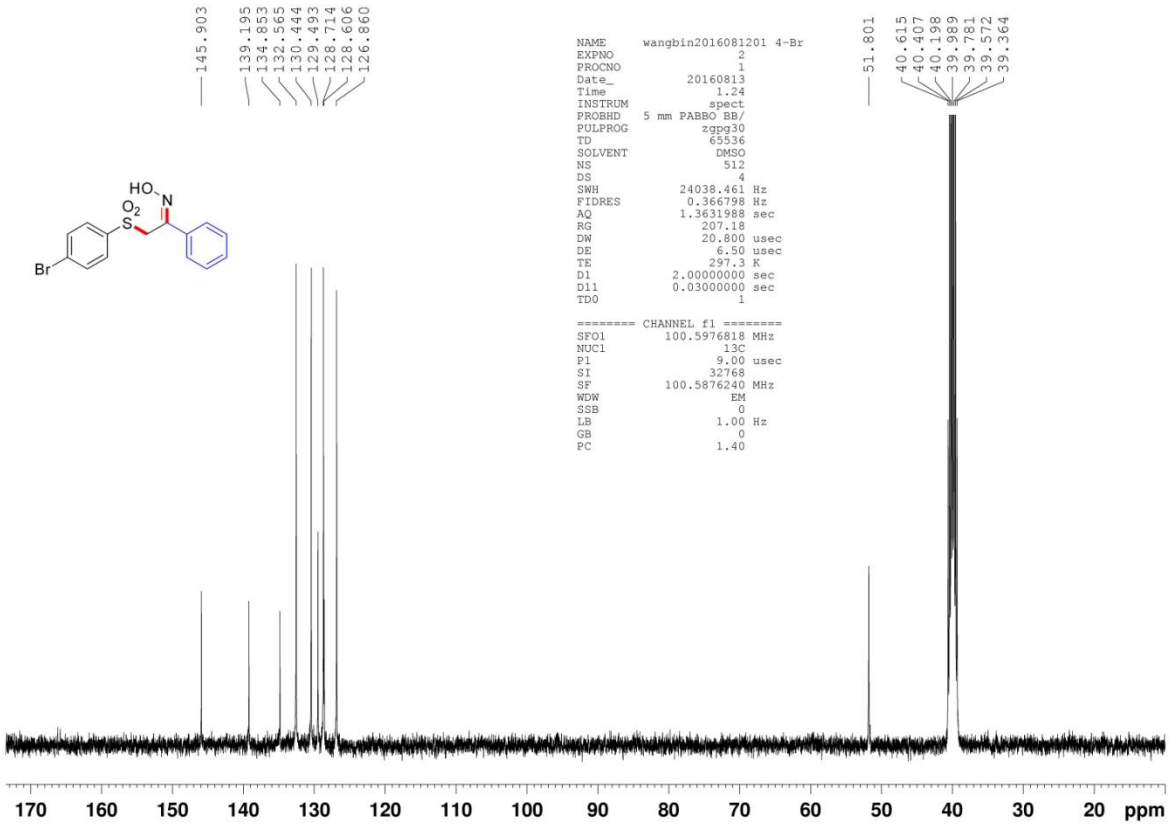
1-phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethan-1-one oxime (**3ai**).



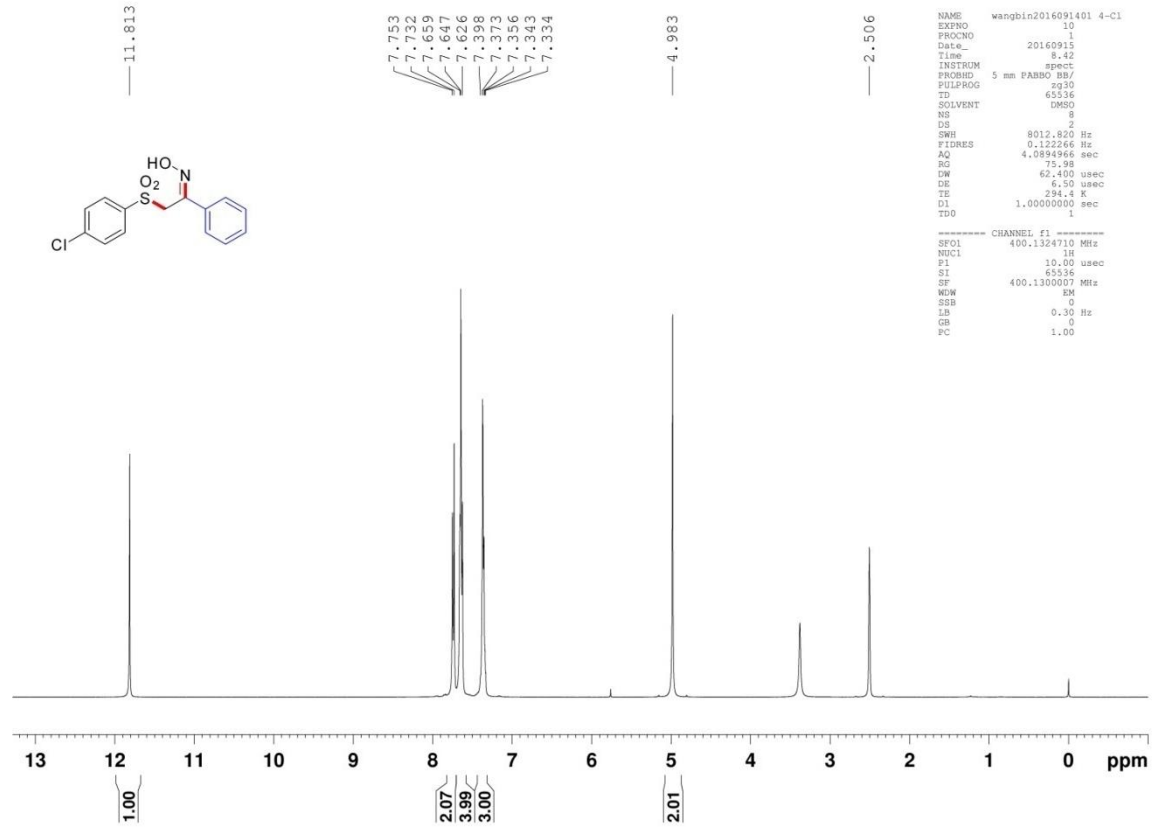


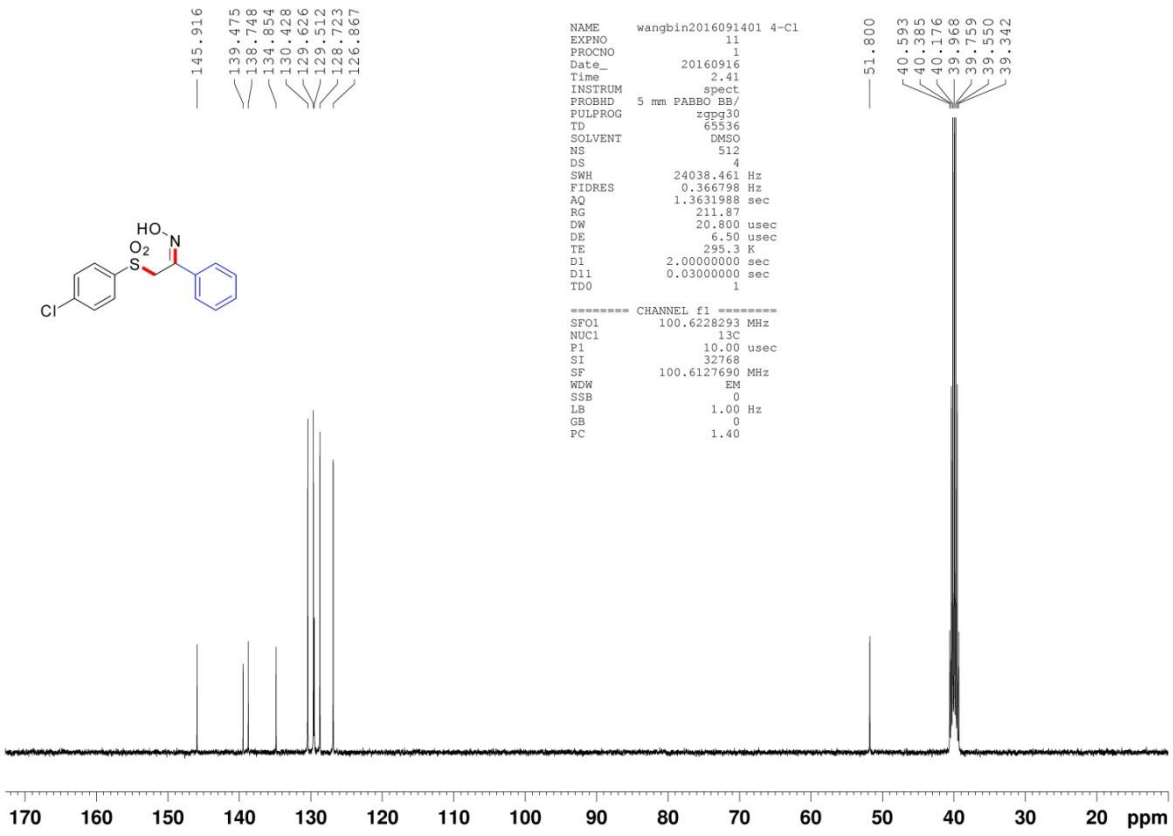
2-((4-bromophenyl)sulfonyl)-1-phenylethan-1-one oxime (**3aj**).



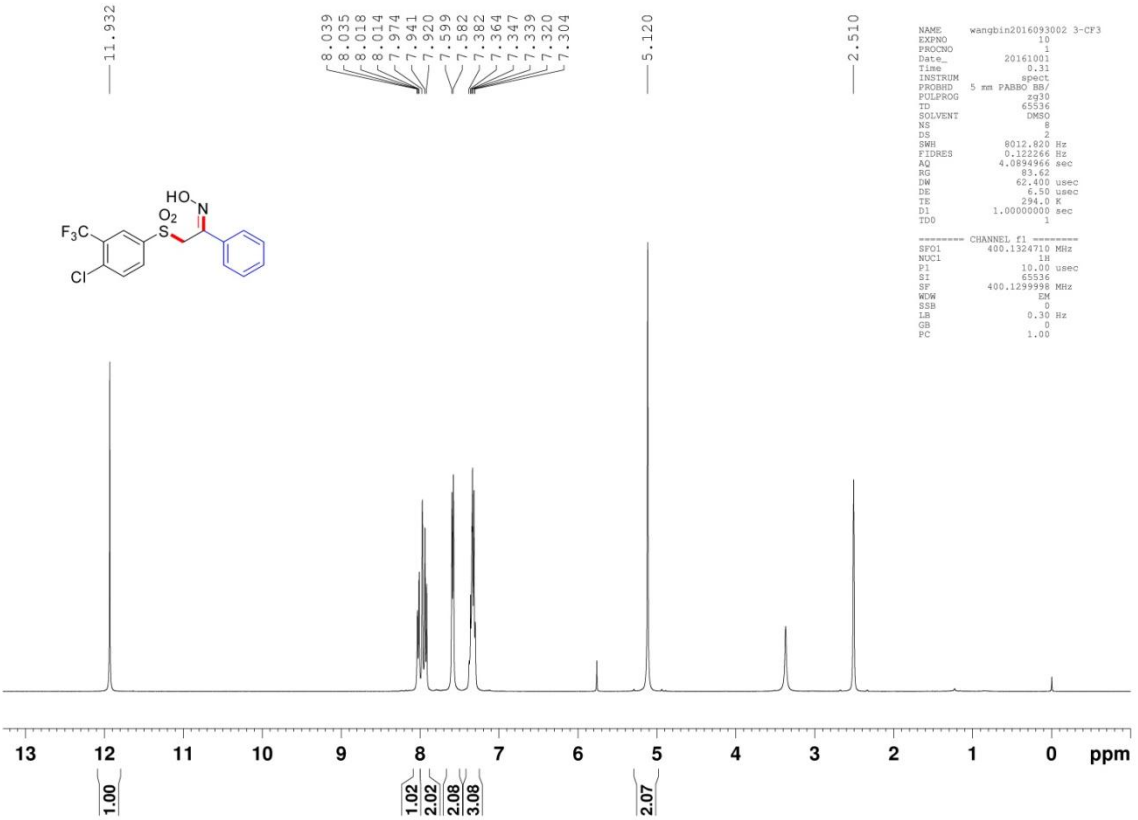


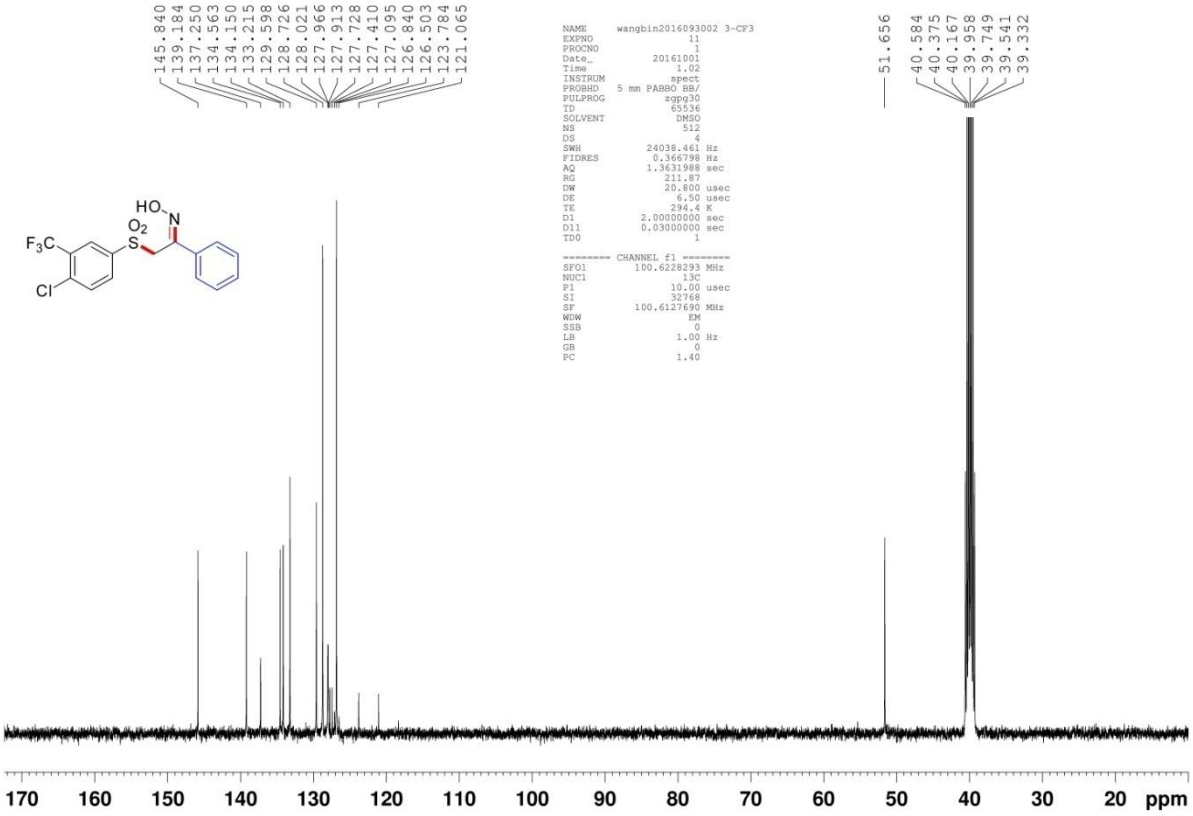
2-((4-chlorophenyl)sulfonyl)-1-phenylethan-1-one oxime (**3ak**).



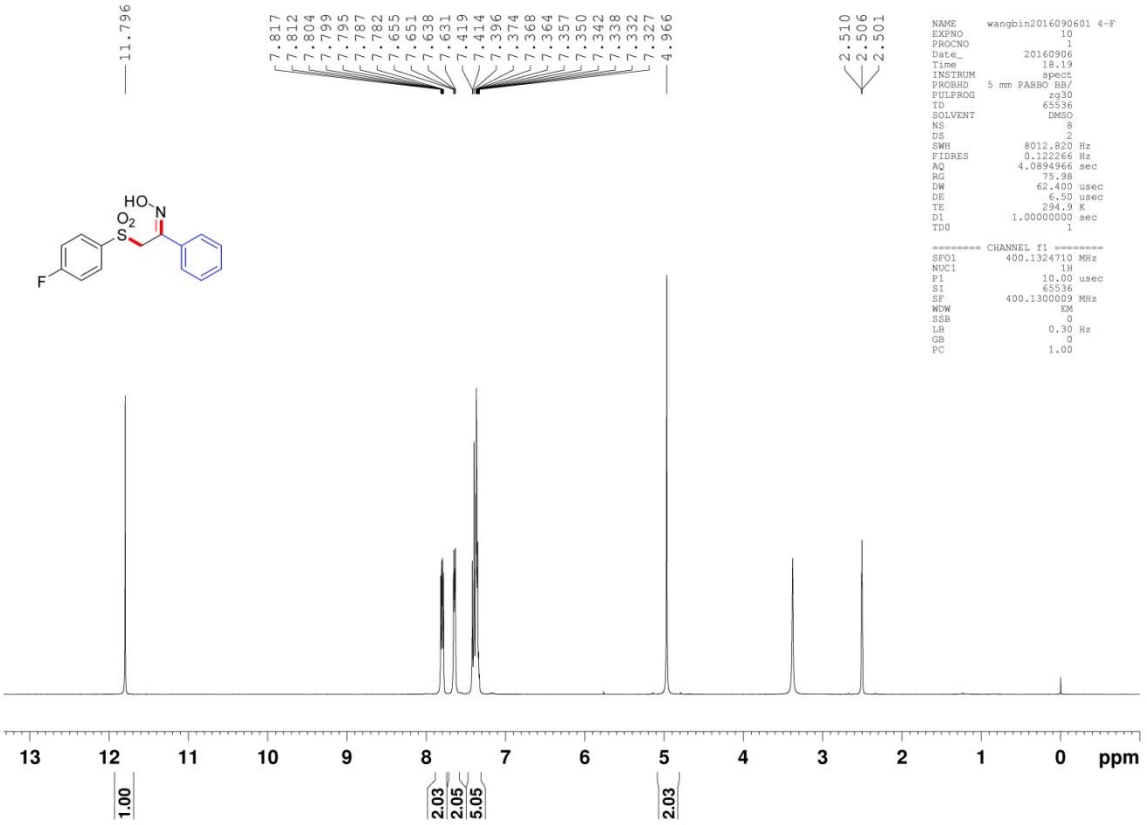


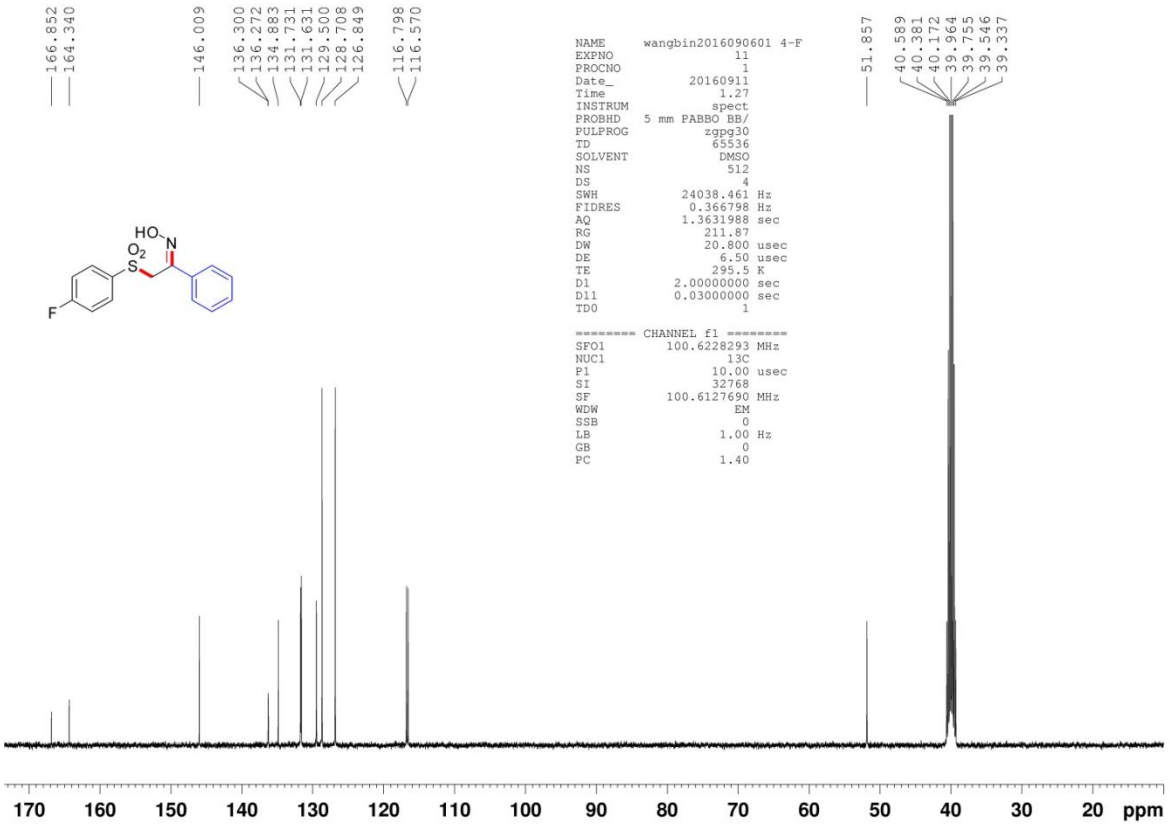
2-((4-chloro-3-(trifluoromethyl)phenyl)sulfonyl)-1-phenylethan-1-one oxime (**3al**).





2-((4-fluorophenyl)sulfonyl)-1-phenylethan-1-one oxime (**3am**).





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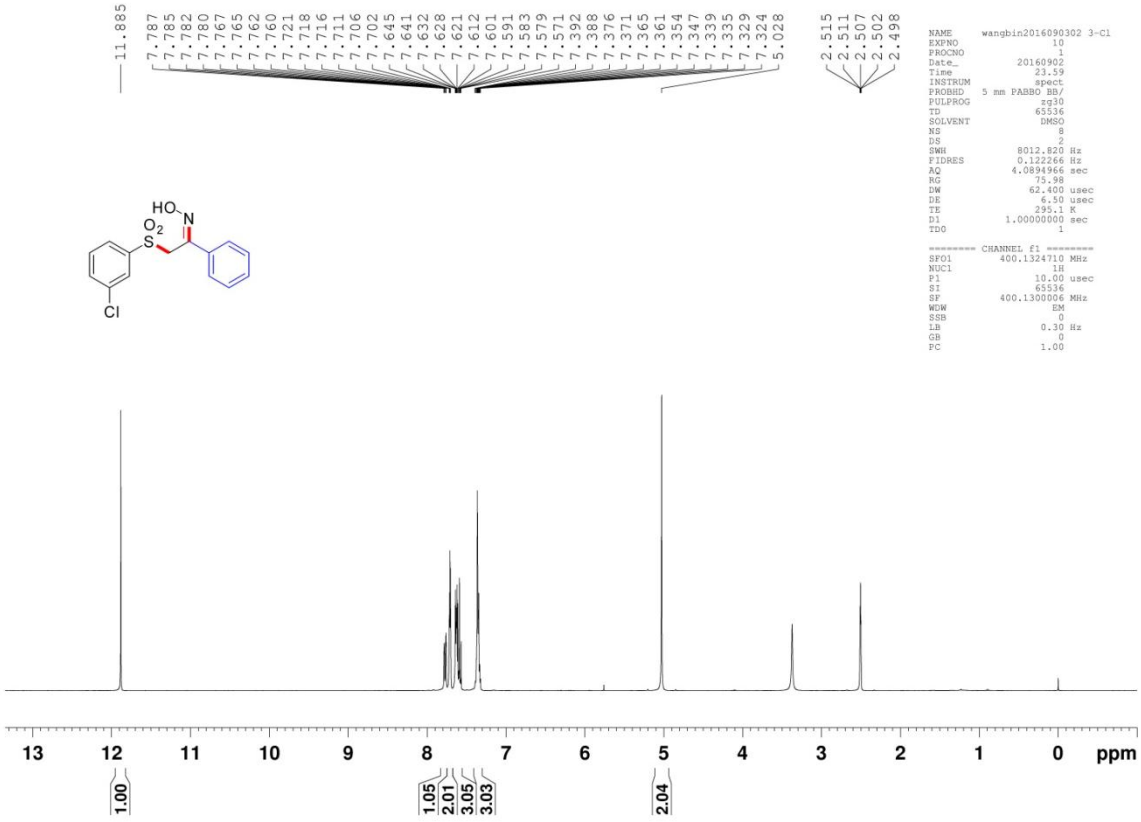
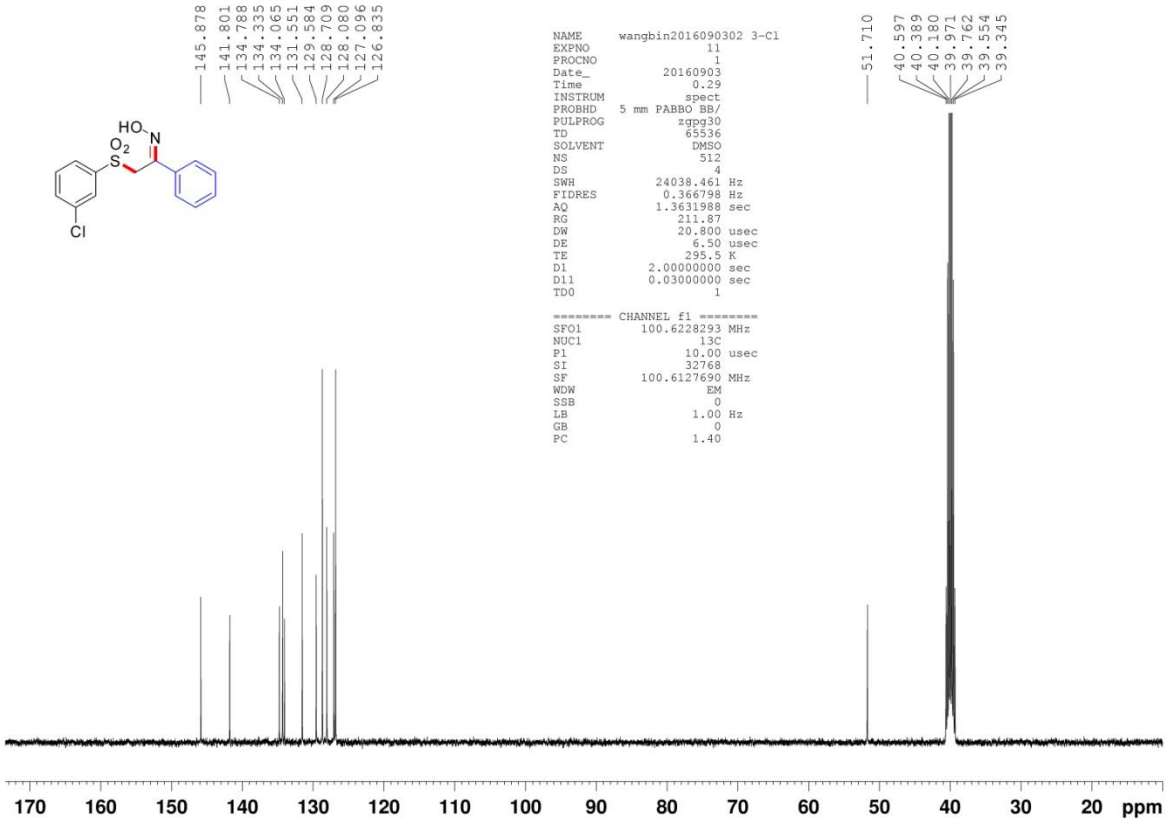
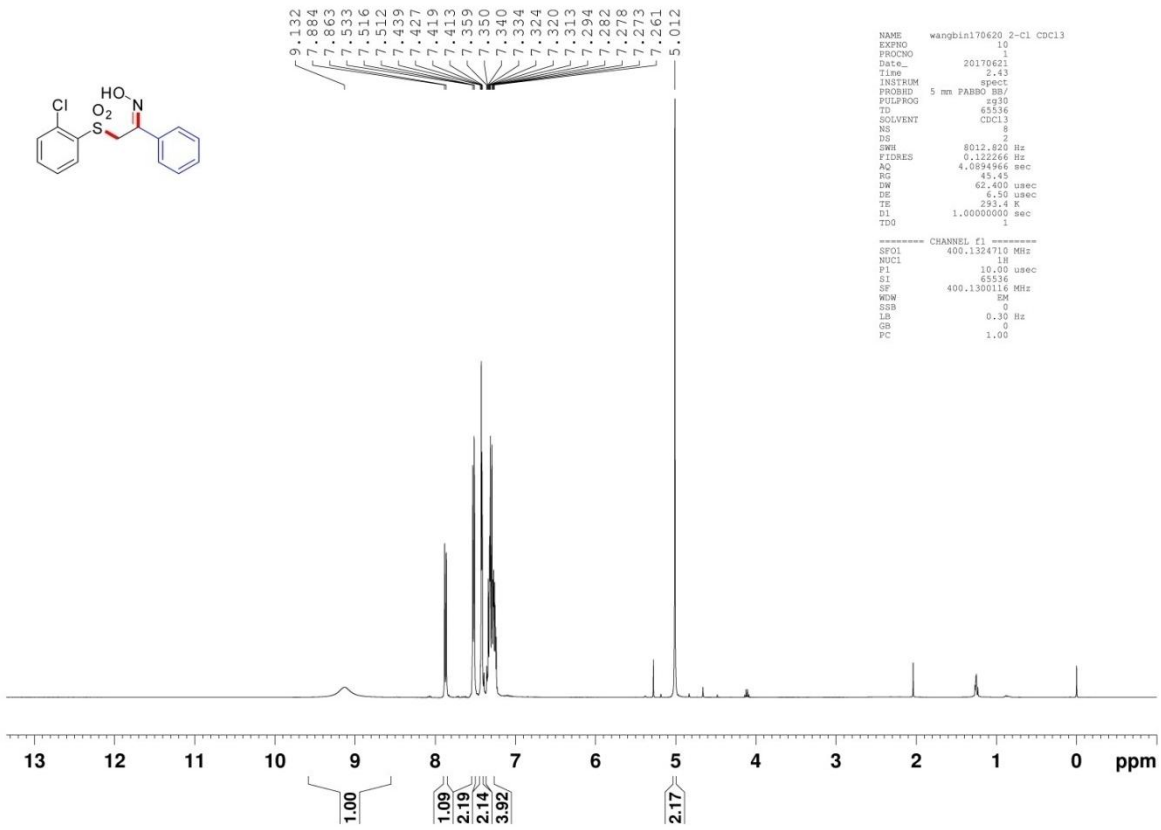
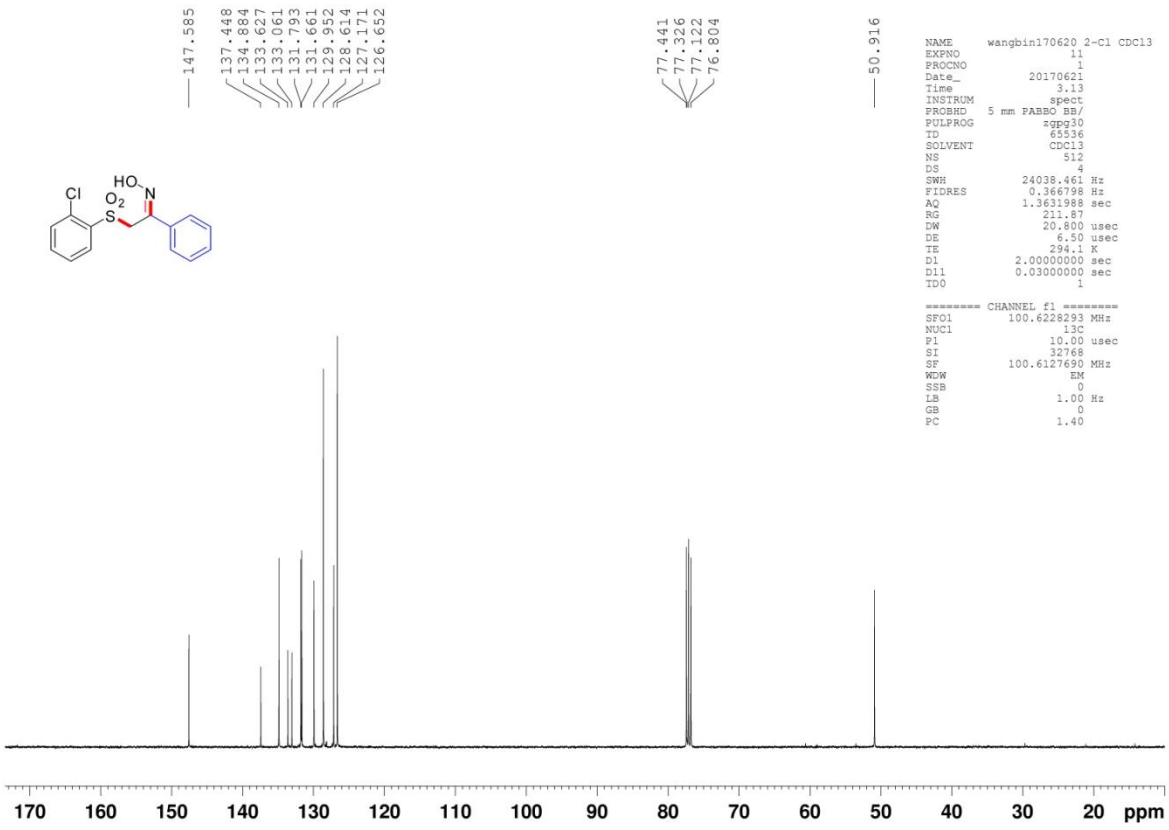


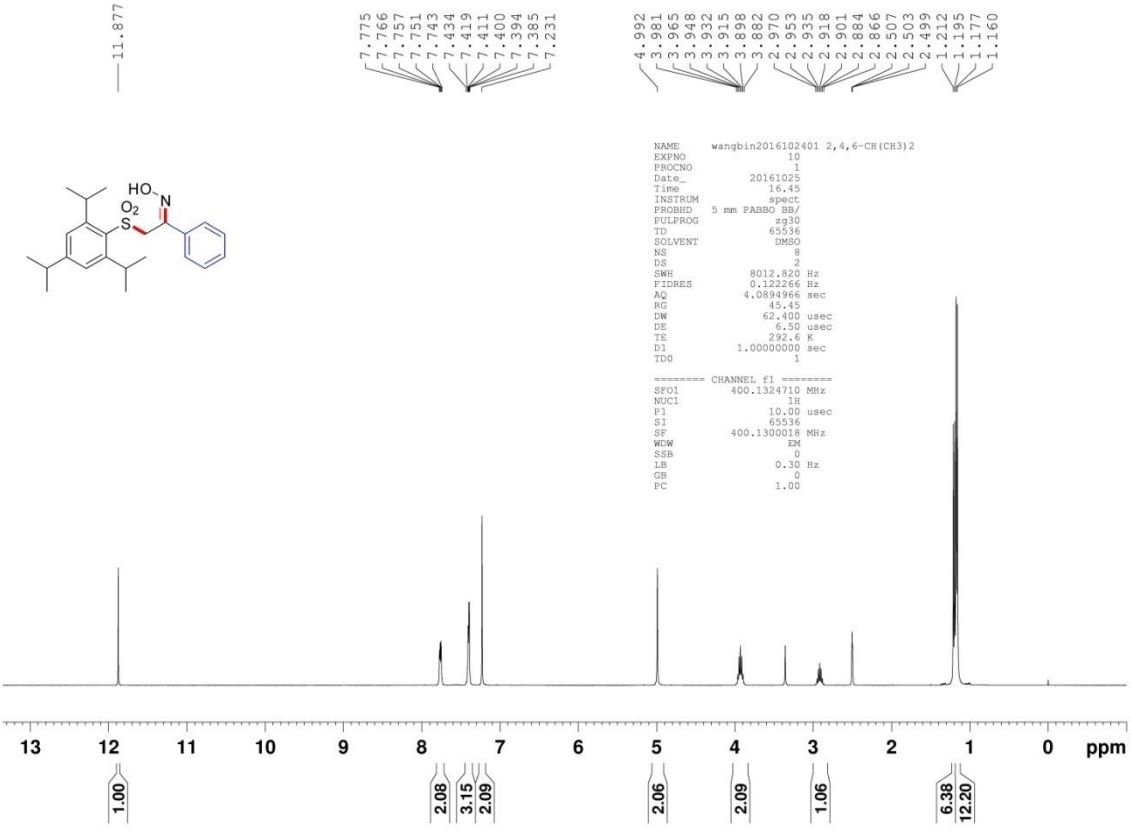


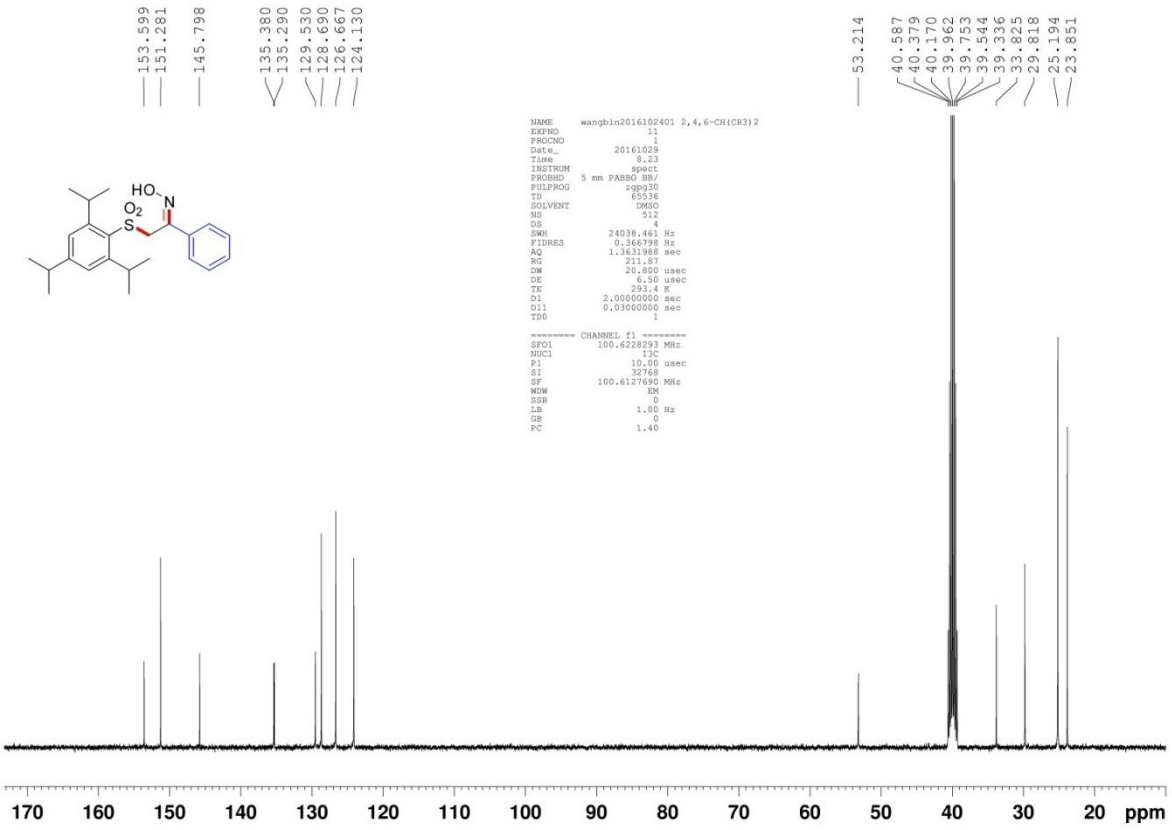
2-((2-chlorophenyl)sulfonyl)-1-phenylethan-1-one oxime (**3ao**).



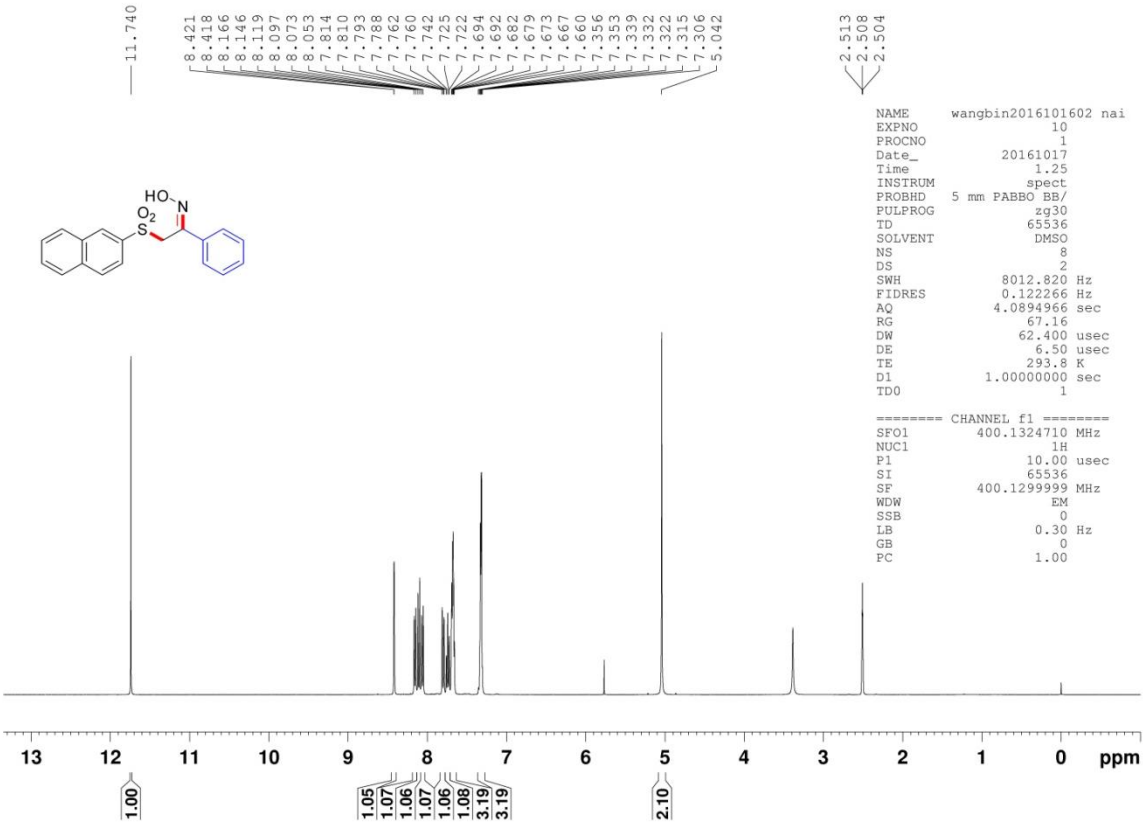


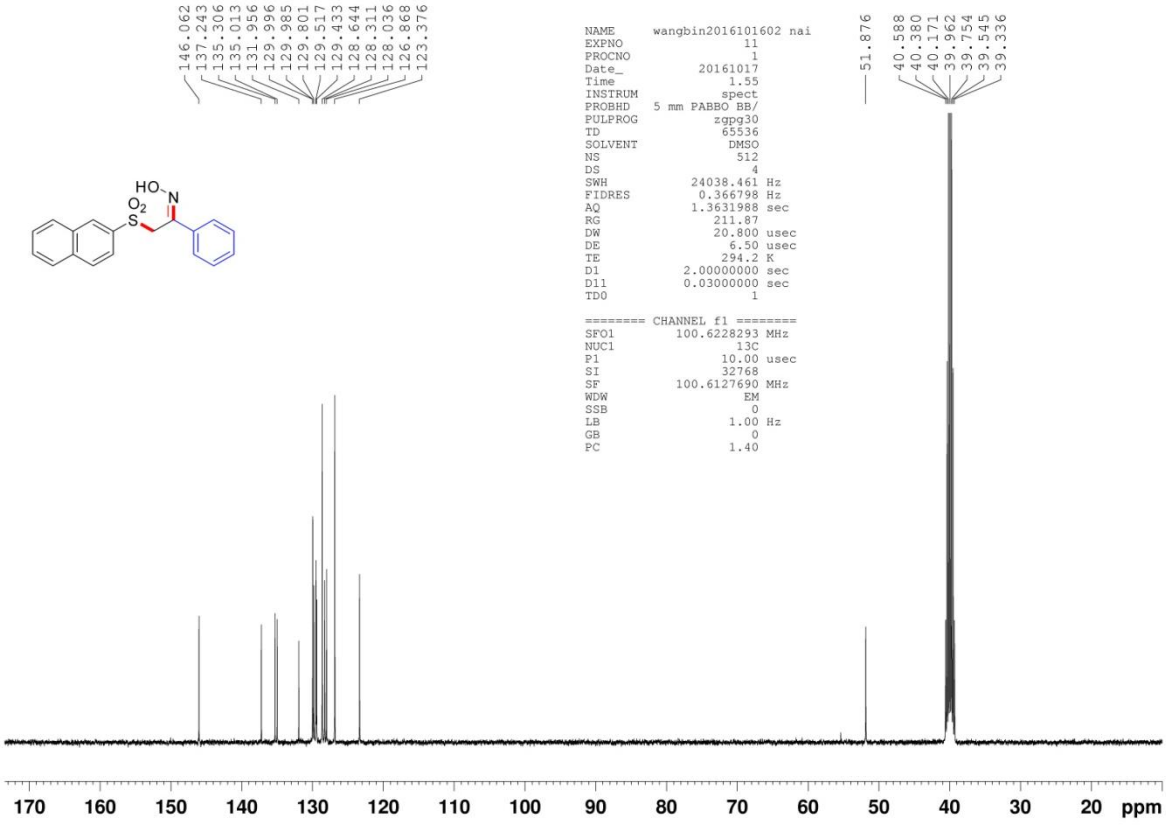
phenyl-2-((2,4,6-triisopropylphenyl)sulfonyl)ethan-1-one oxime (**3ap**).



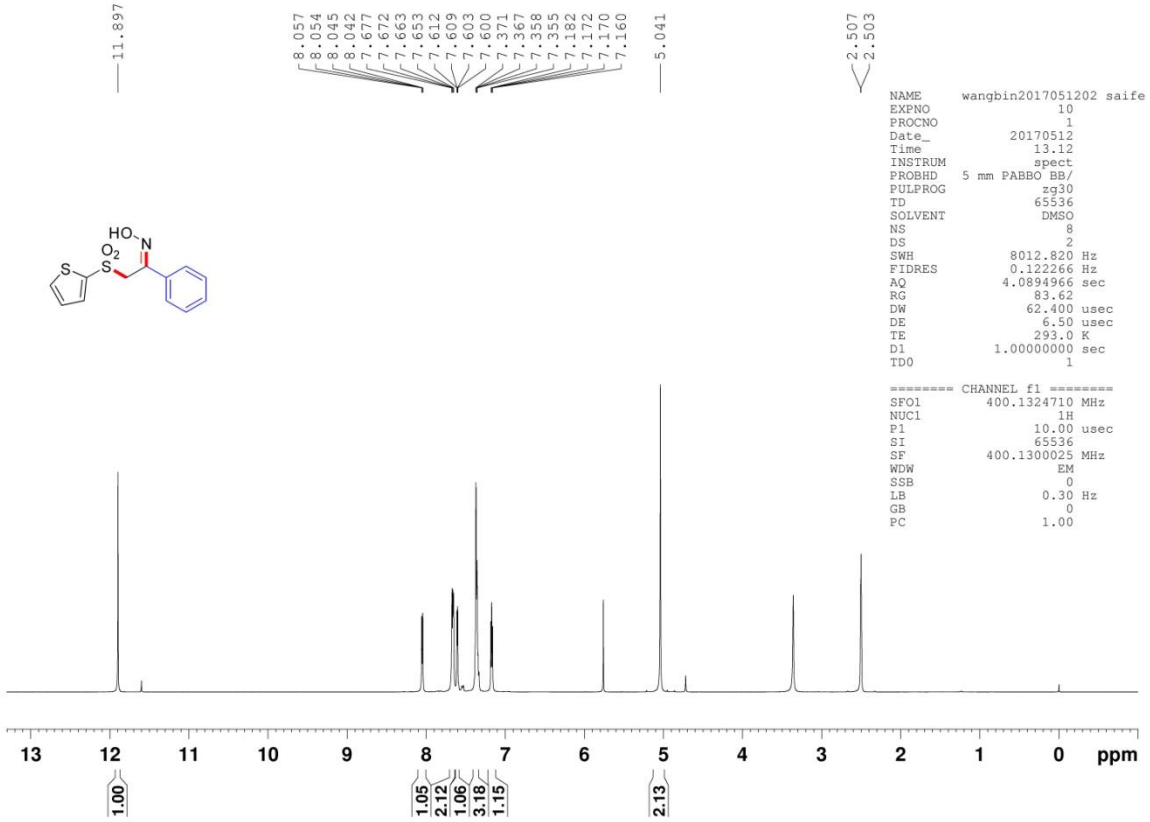


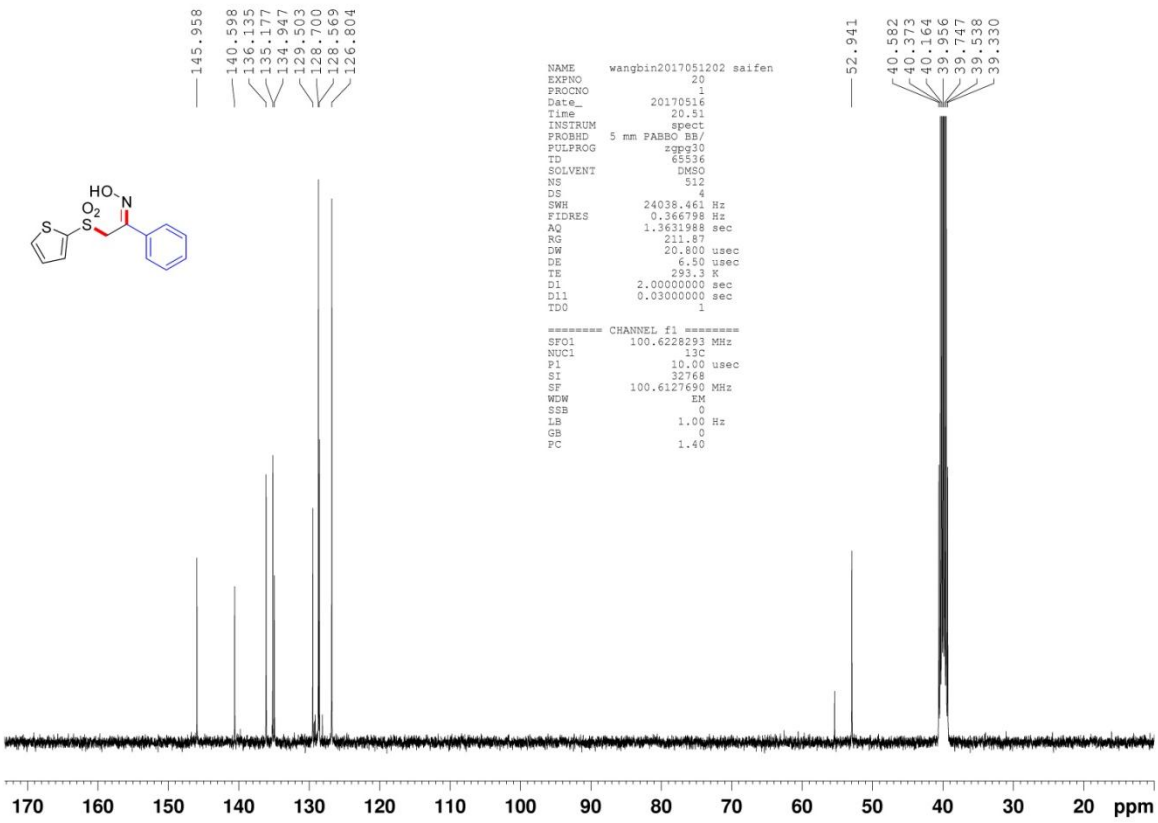
2-(naphthalen-2-ylsulfonyl)-1-phenylethan-1-one oxime (**3ar**).



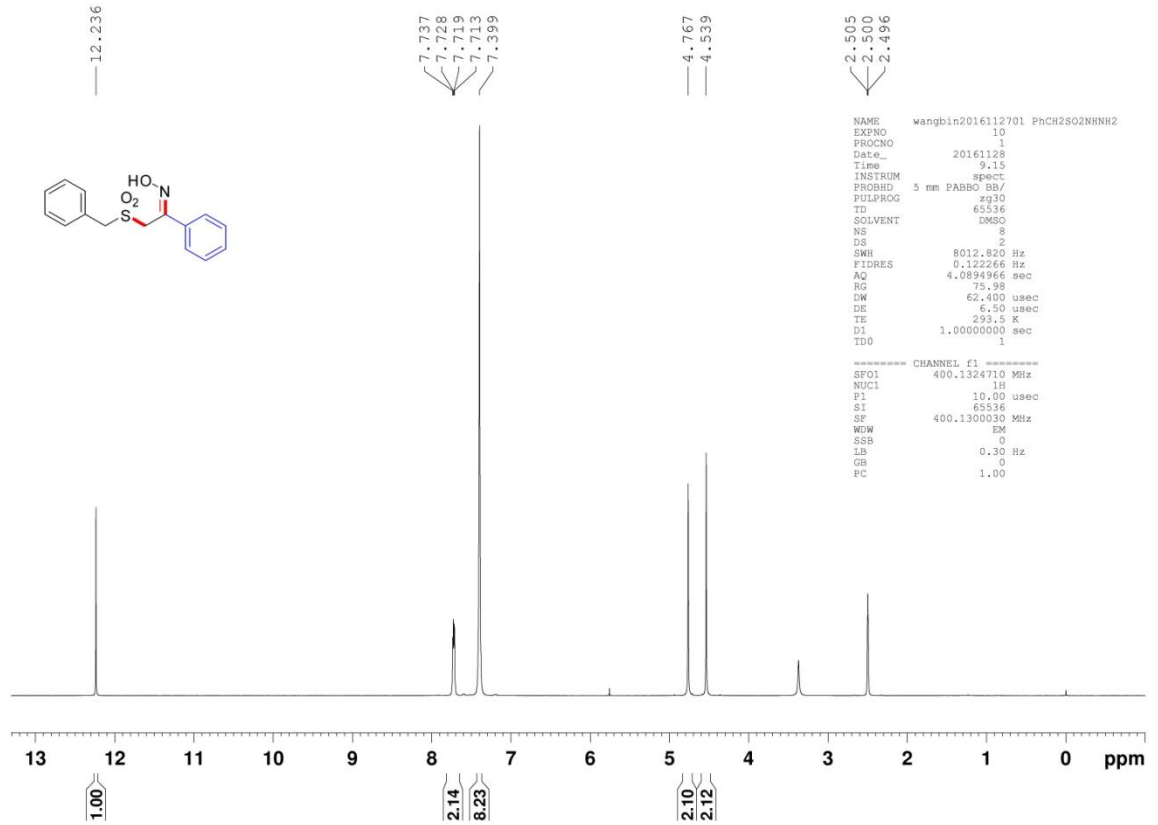


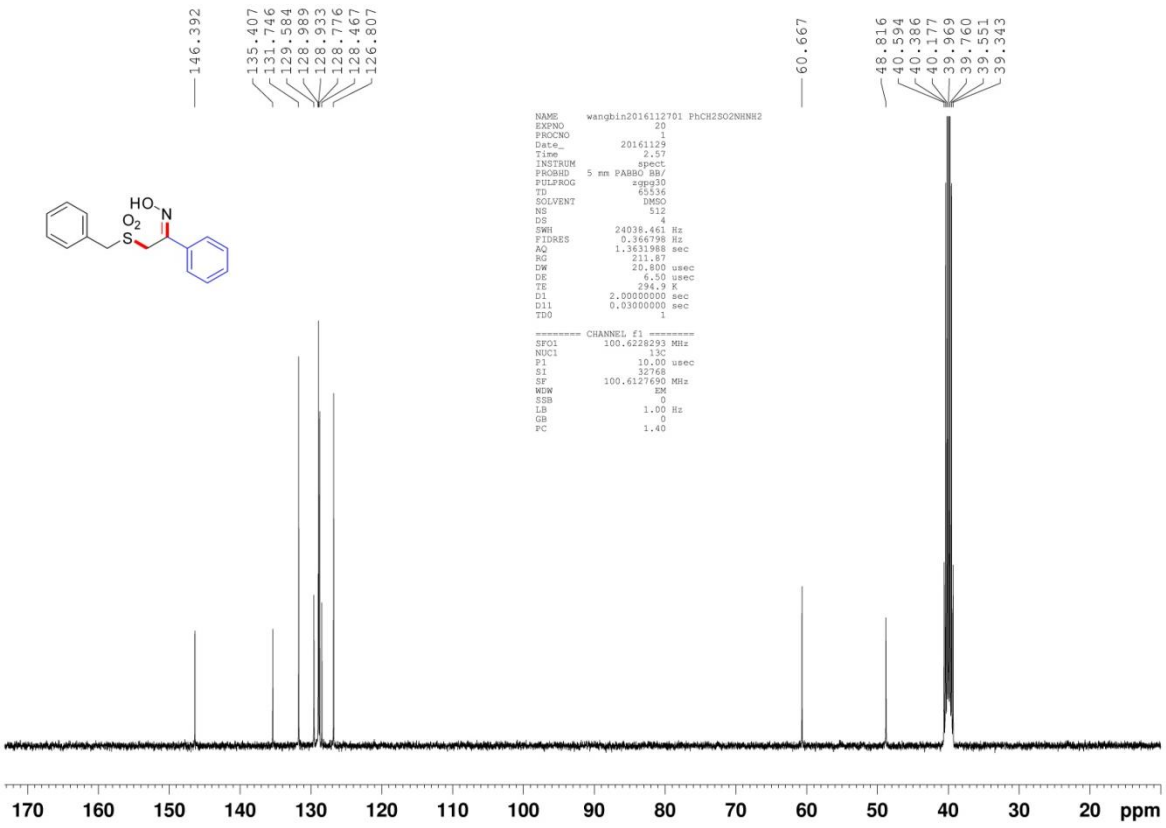
1-phenyl-2-(thiophen-2-ylsulfonyl)ethan-1-one oxime (**3as**).



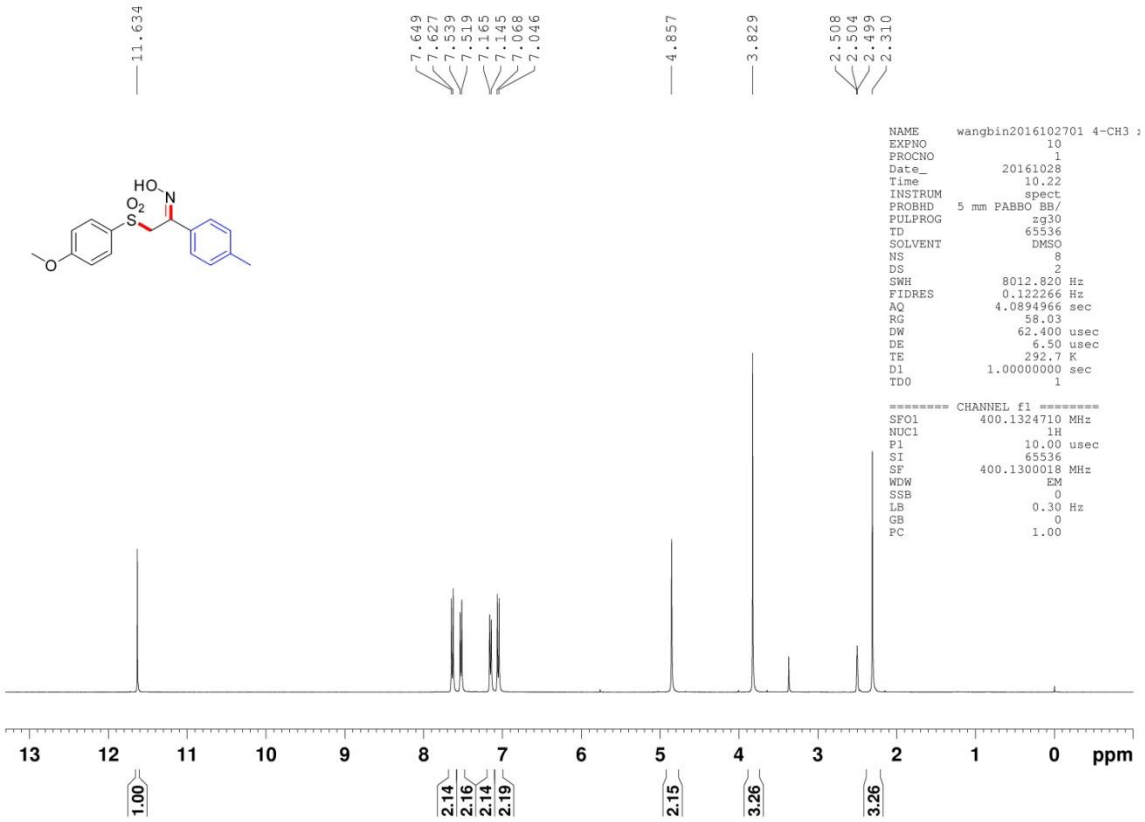


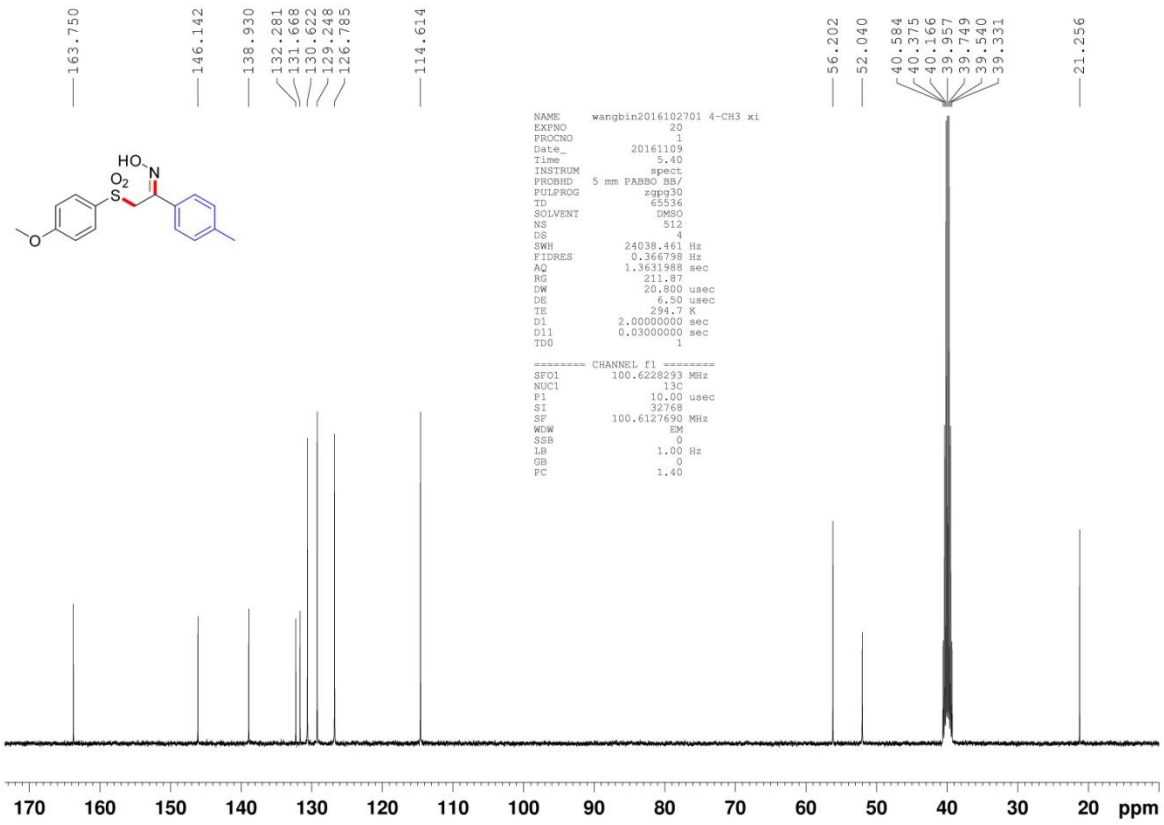
2-(benzylsulfonyl)-1-phenylethan-1-one oxime (**3at**).



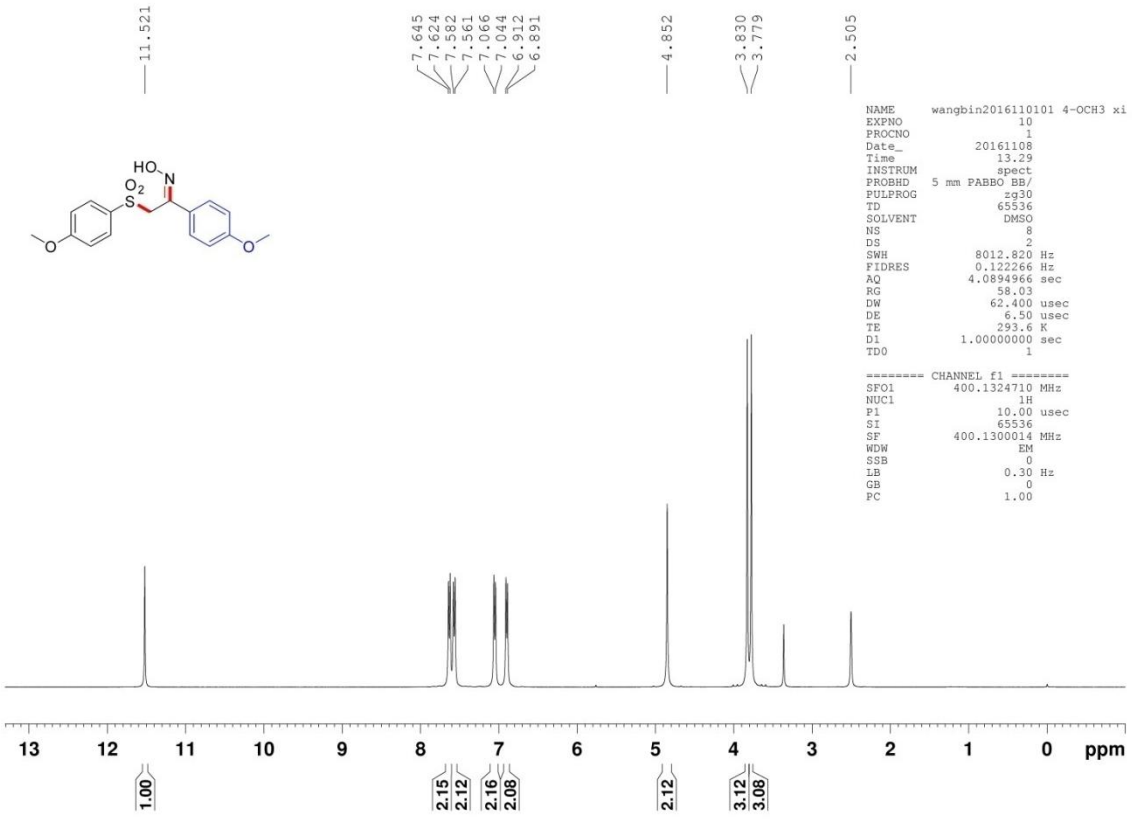


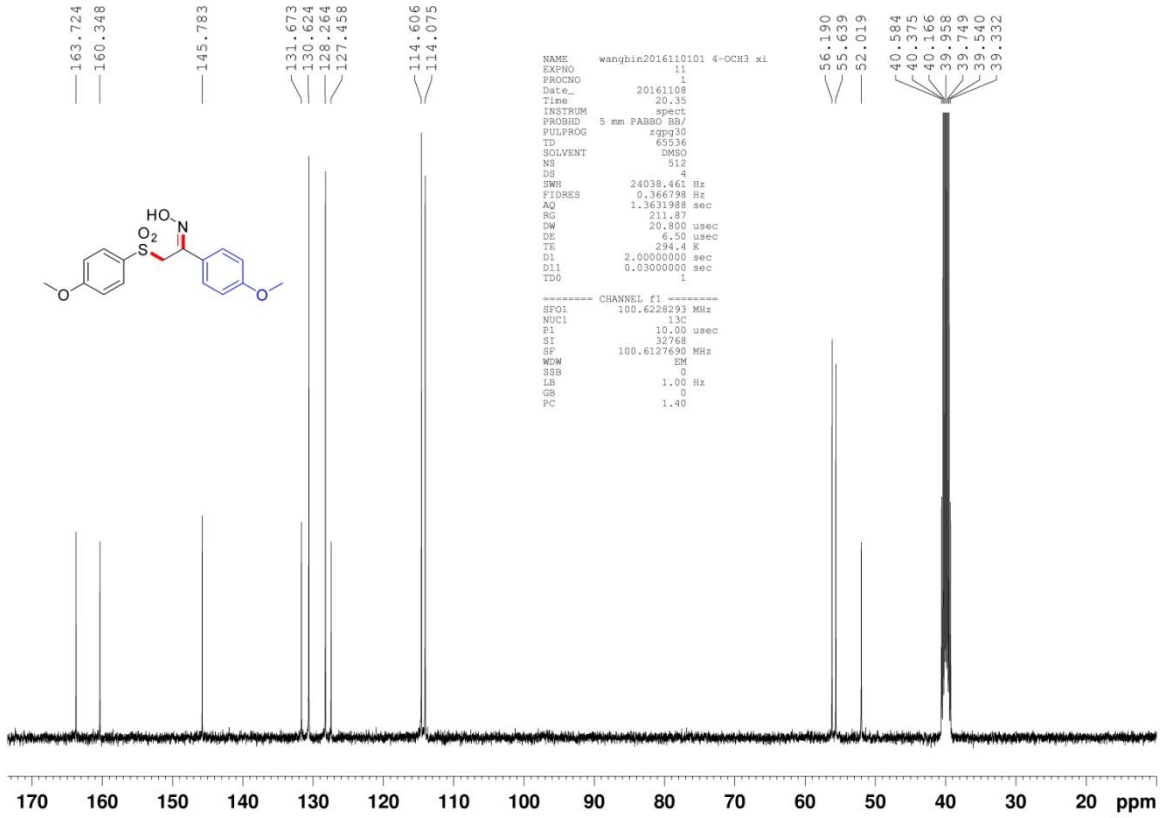
2-((4-methoxyphenyl)sulfonyl)-1-(p-tolyl)ethan-1-one oxime (**4aa**).



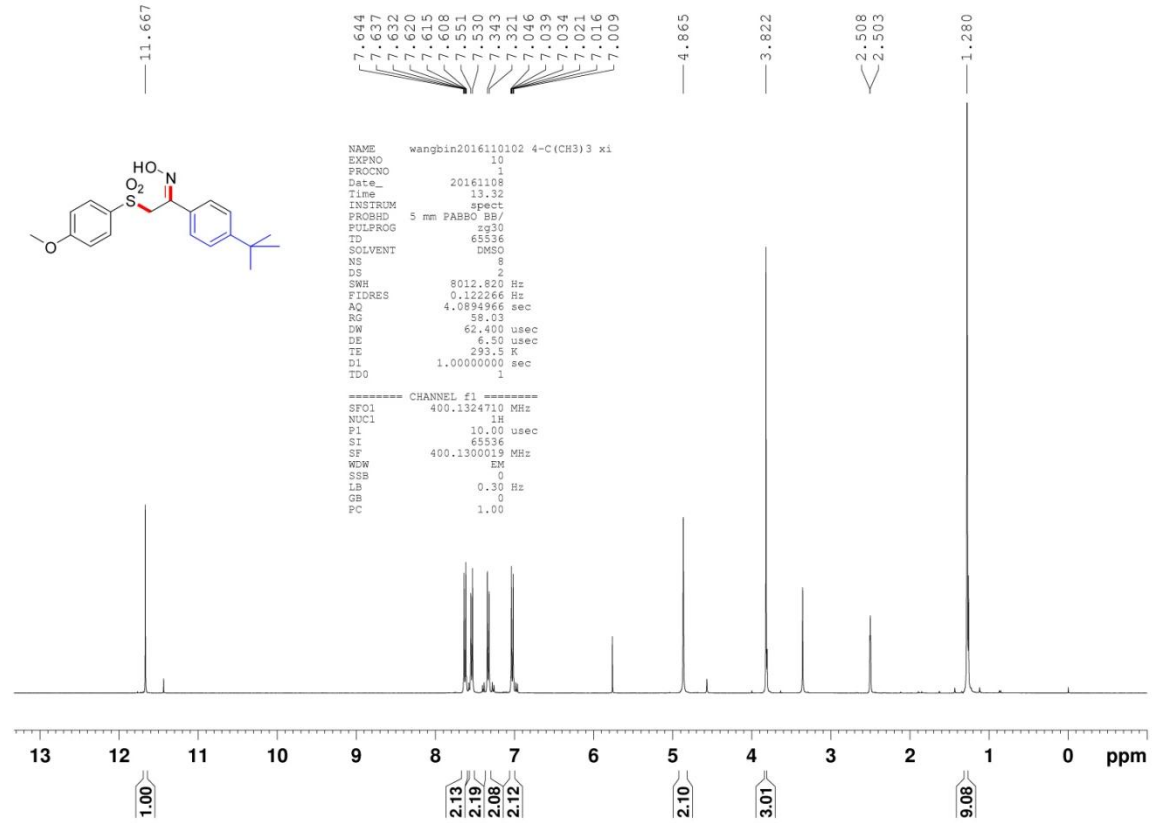


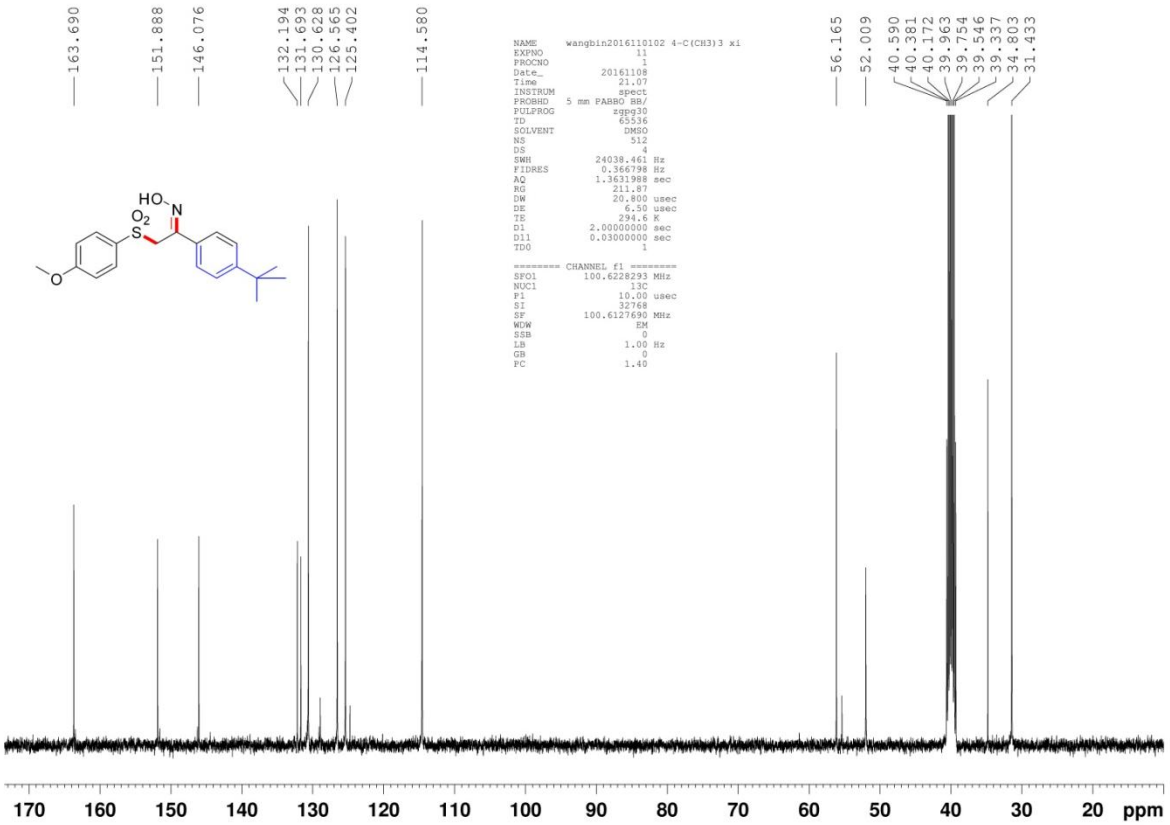
1-(4-methoxyphenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-one oxime (4ab).



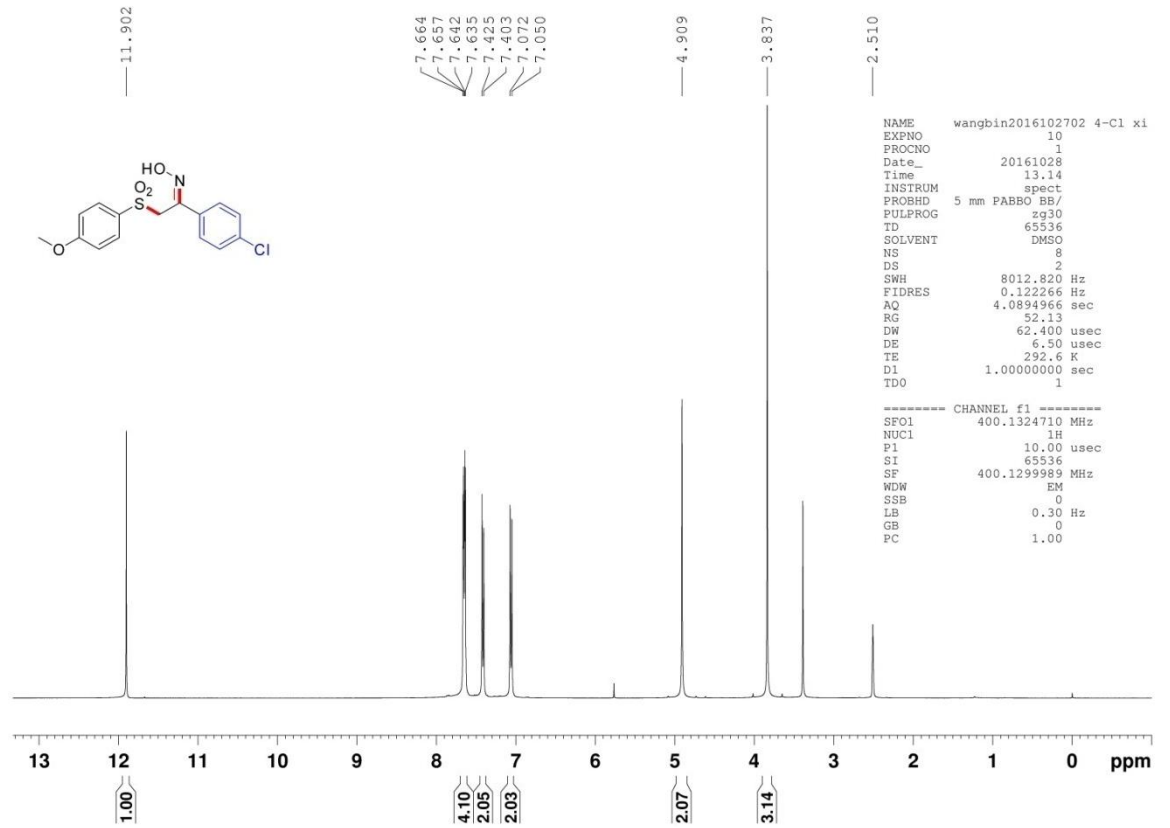


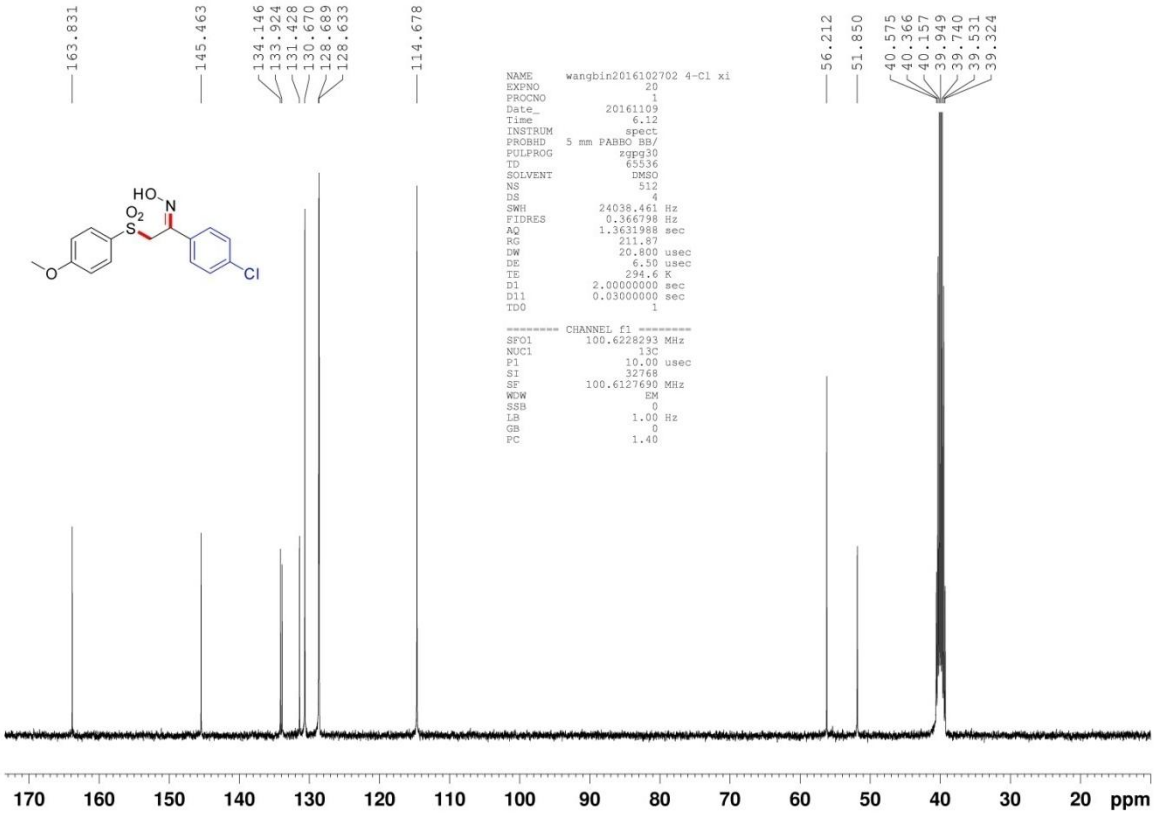
1-(4-(tert-butyl)phenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-one oxime (**4ac**).





1-(4-chlorophenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-one oxime (**4ad**).





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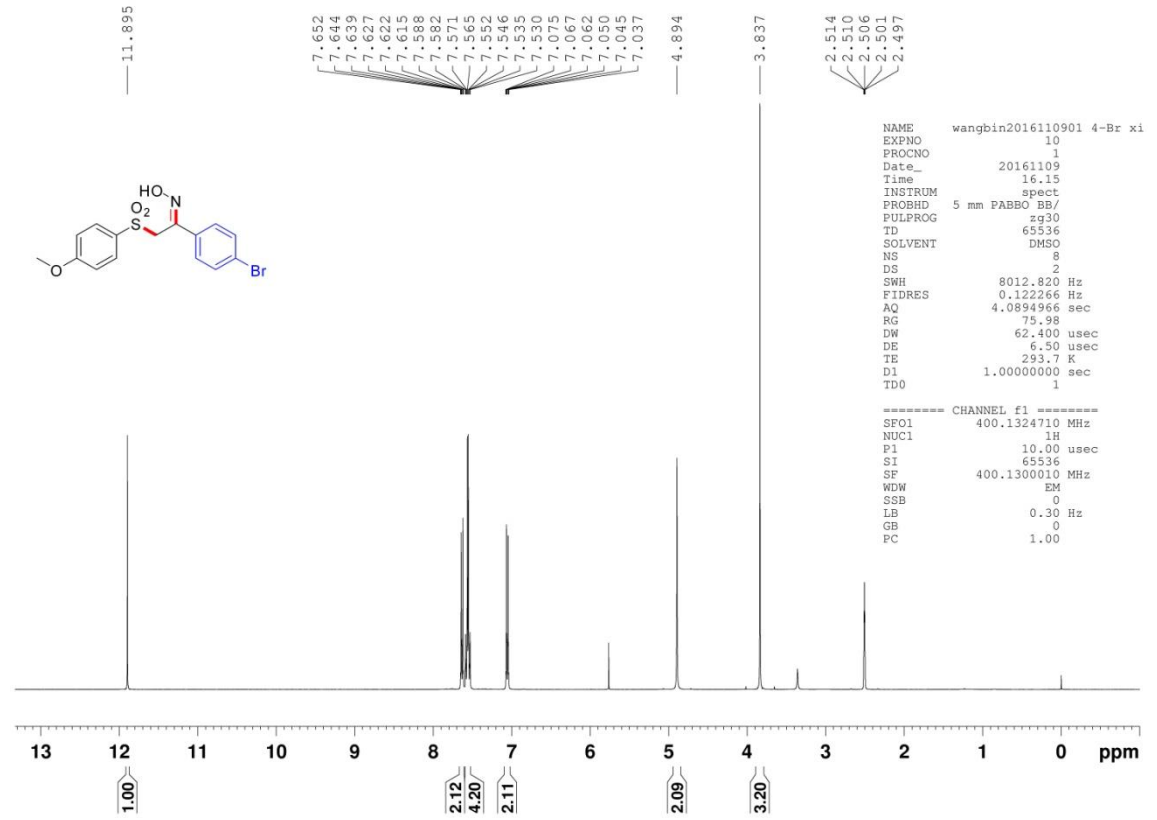
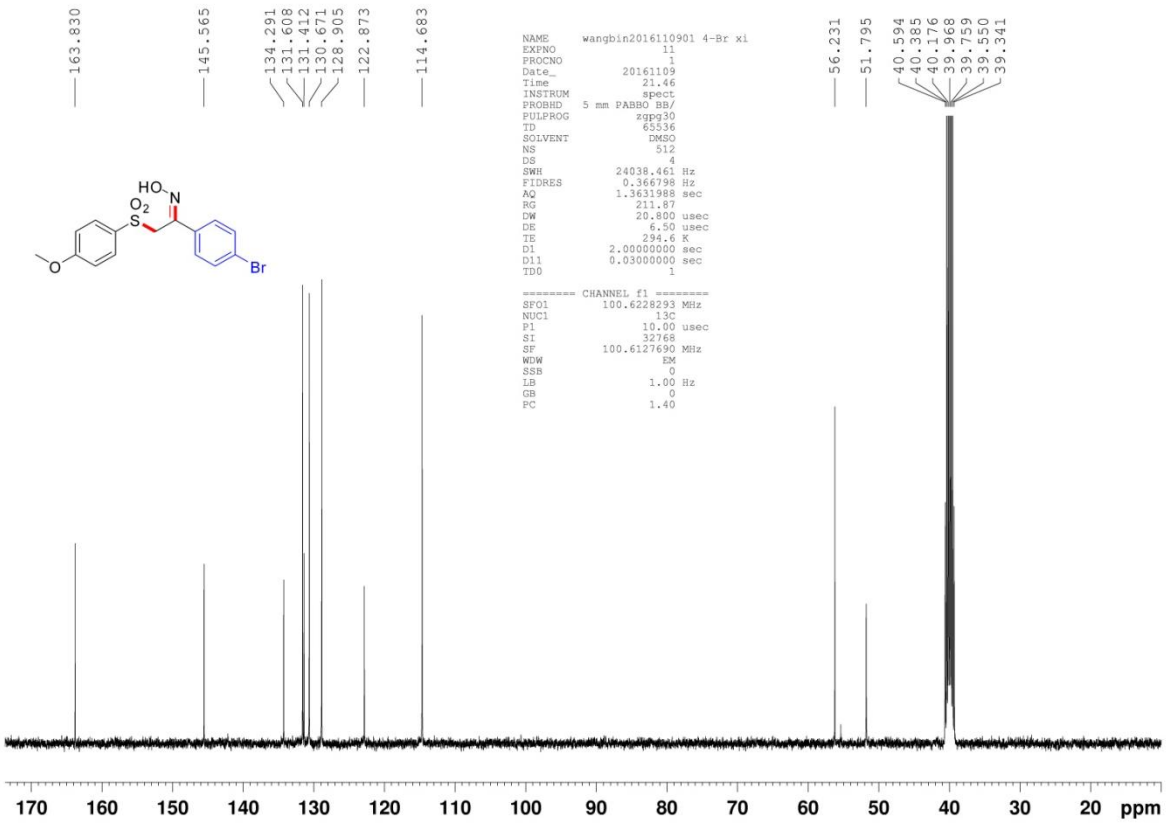
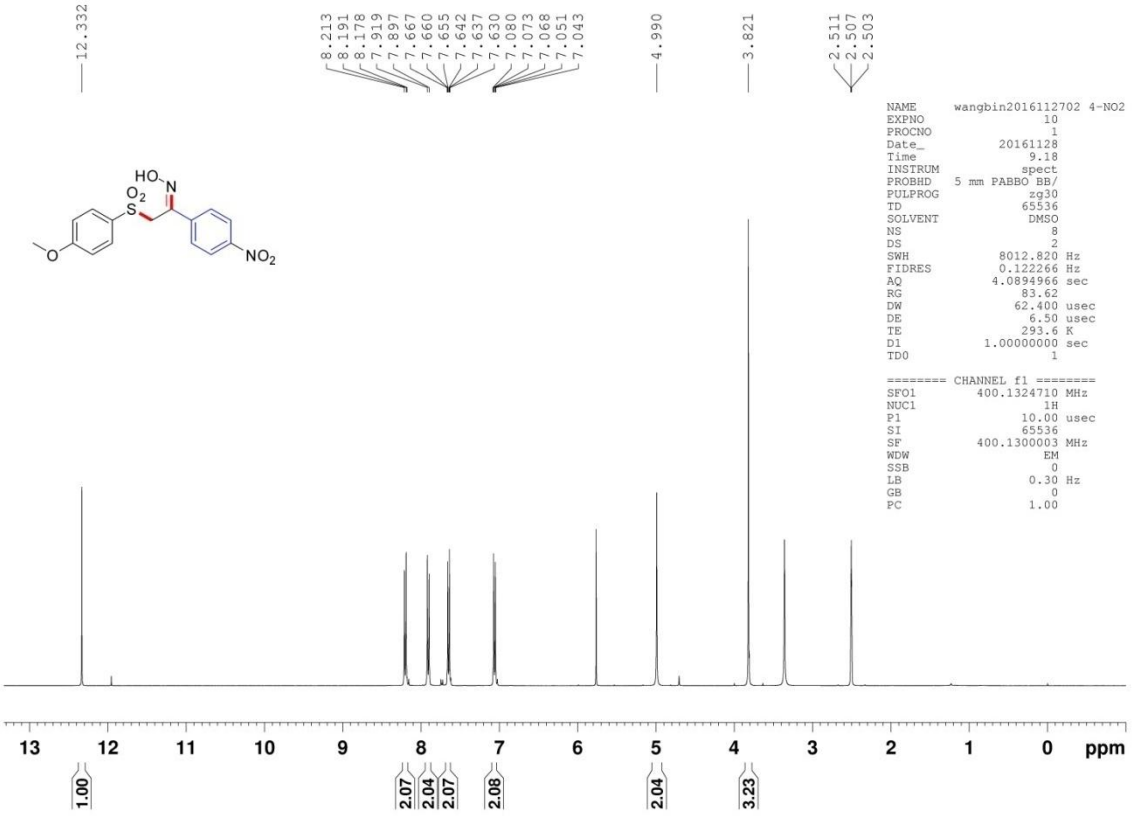
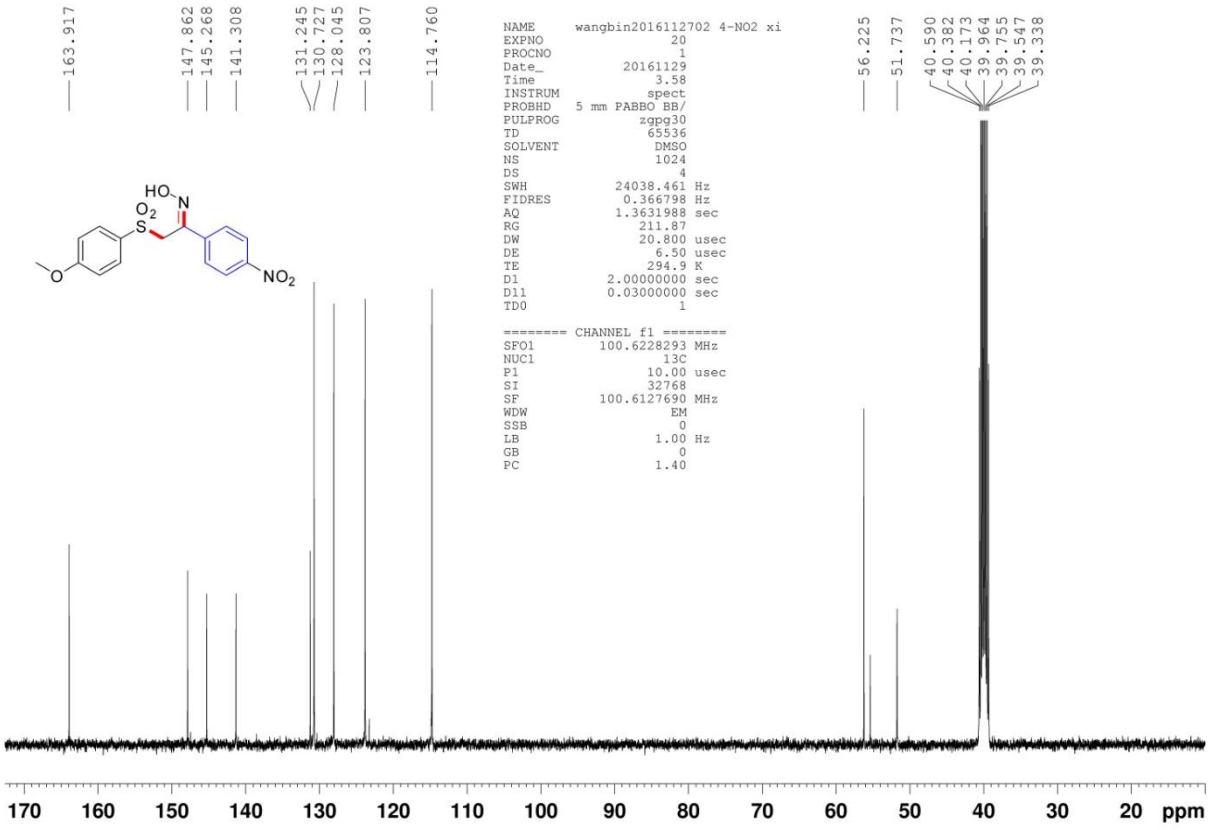


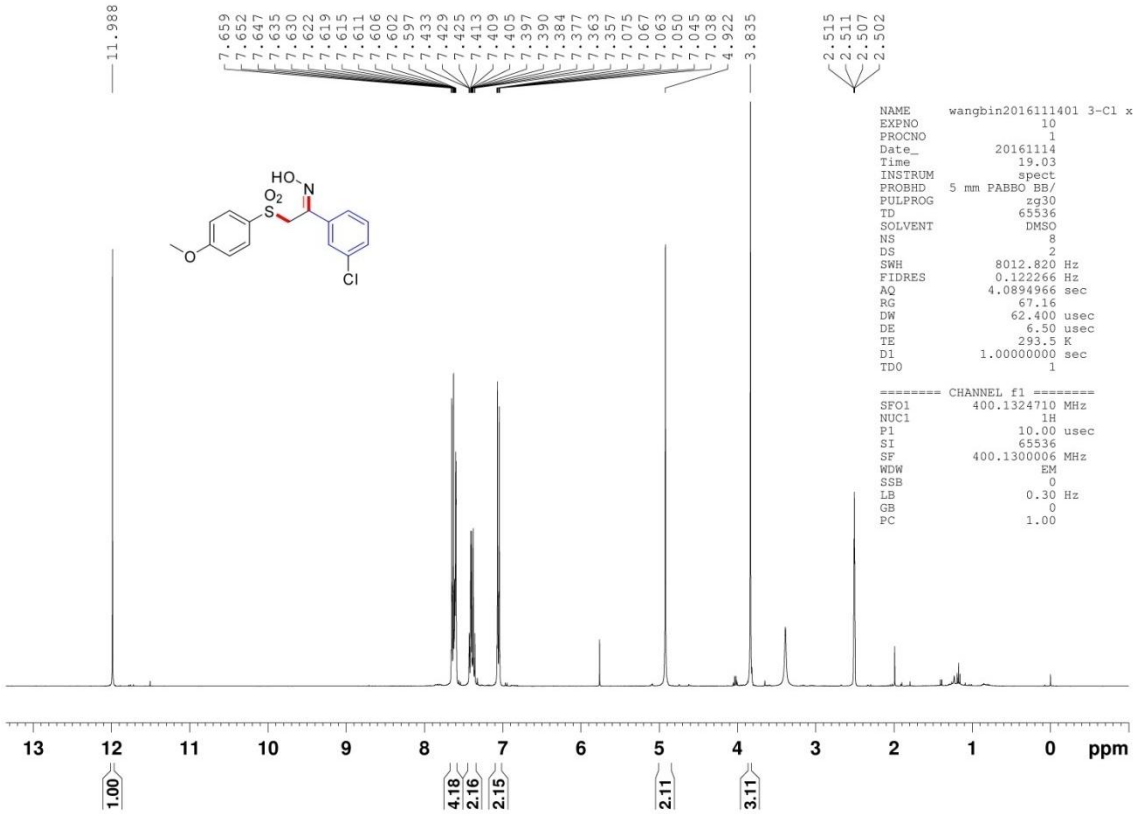


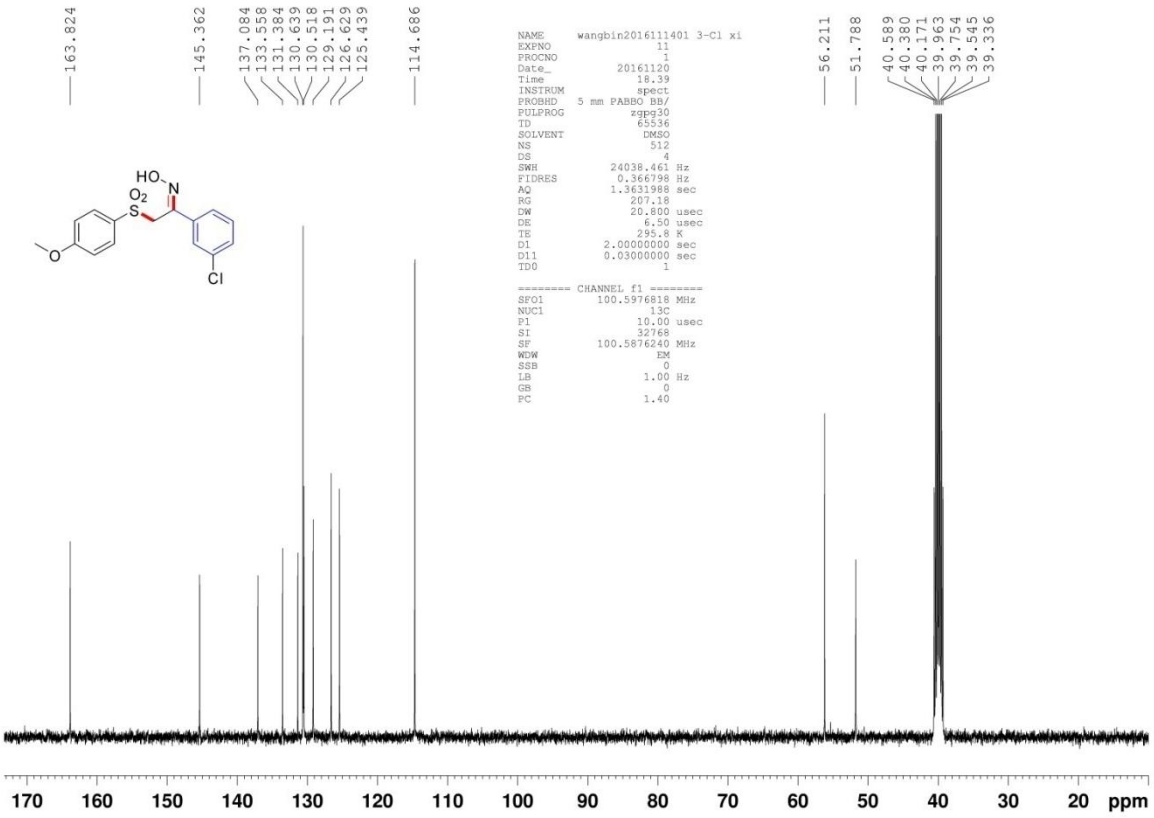
2-((4-methoxyphenyl)sulfonyl)-1-(4-nitrophenyl)ethan-1-one oxime (**4af**).



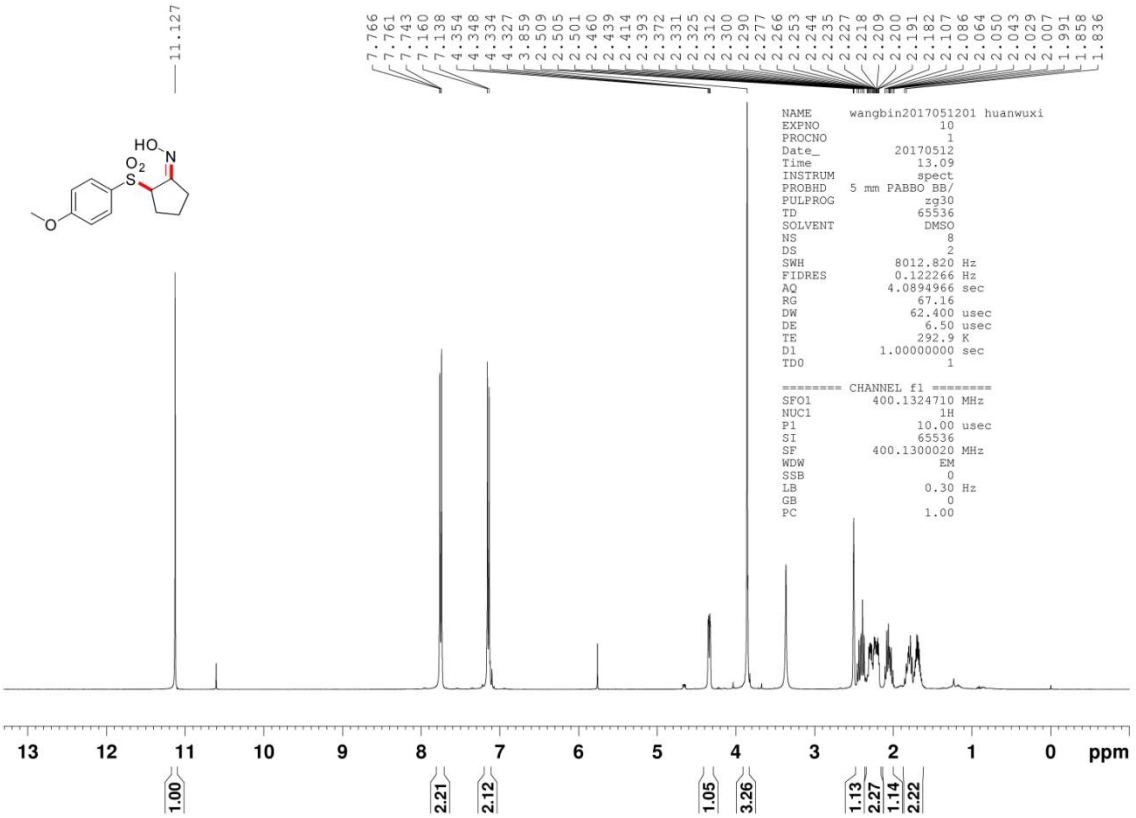


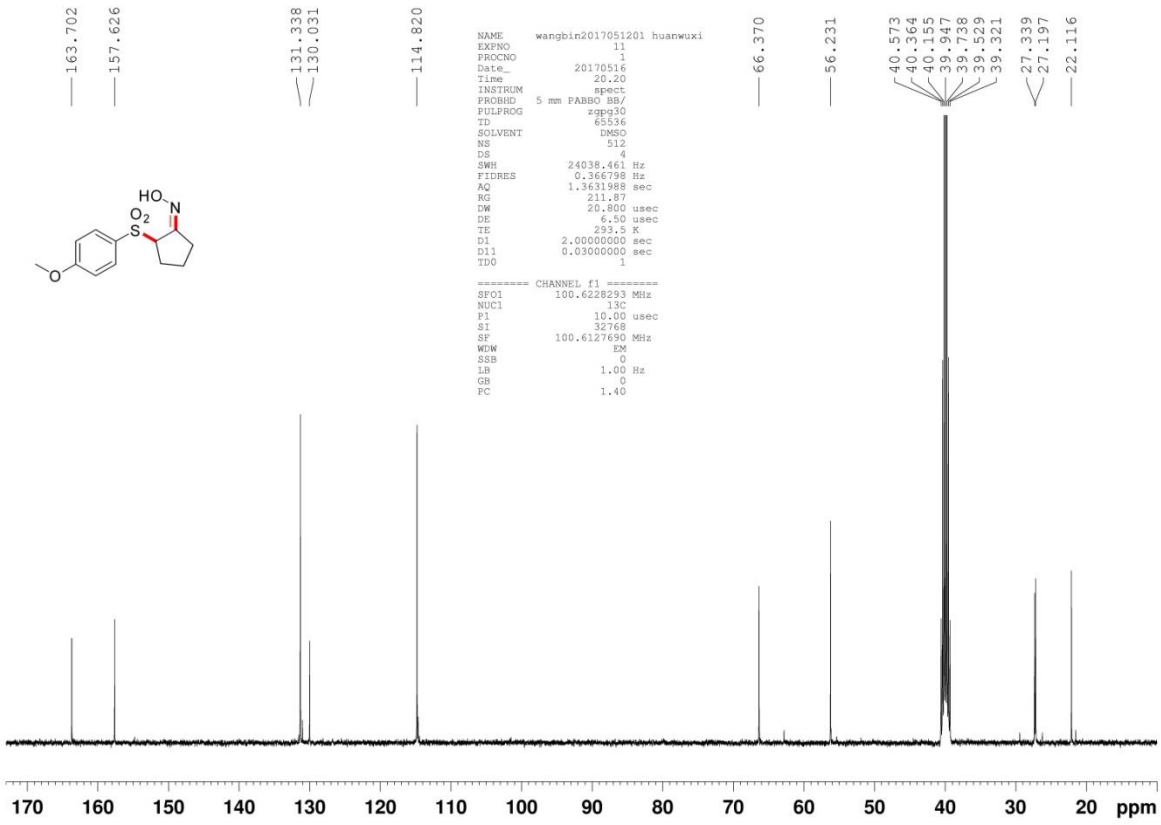
1-(3-chlorophenyl)-2-((4-methoxyphenyl)sulfonyl)ethan-1-one oxime (**4ag**).



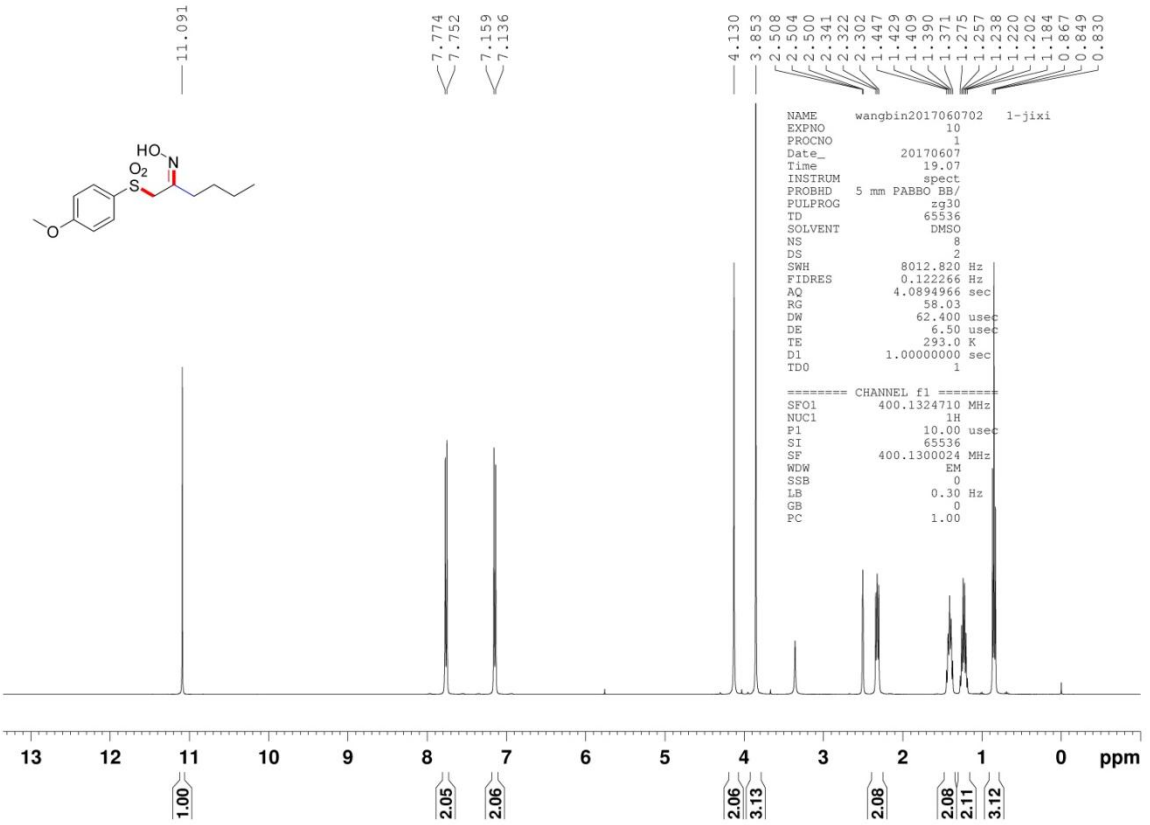


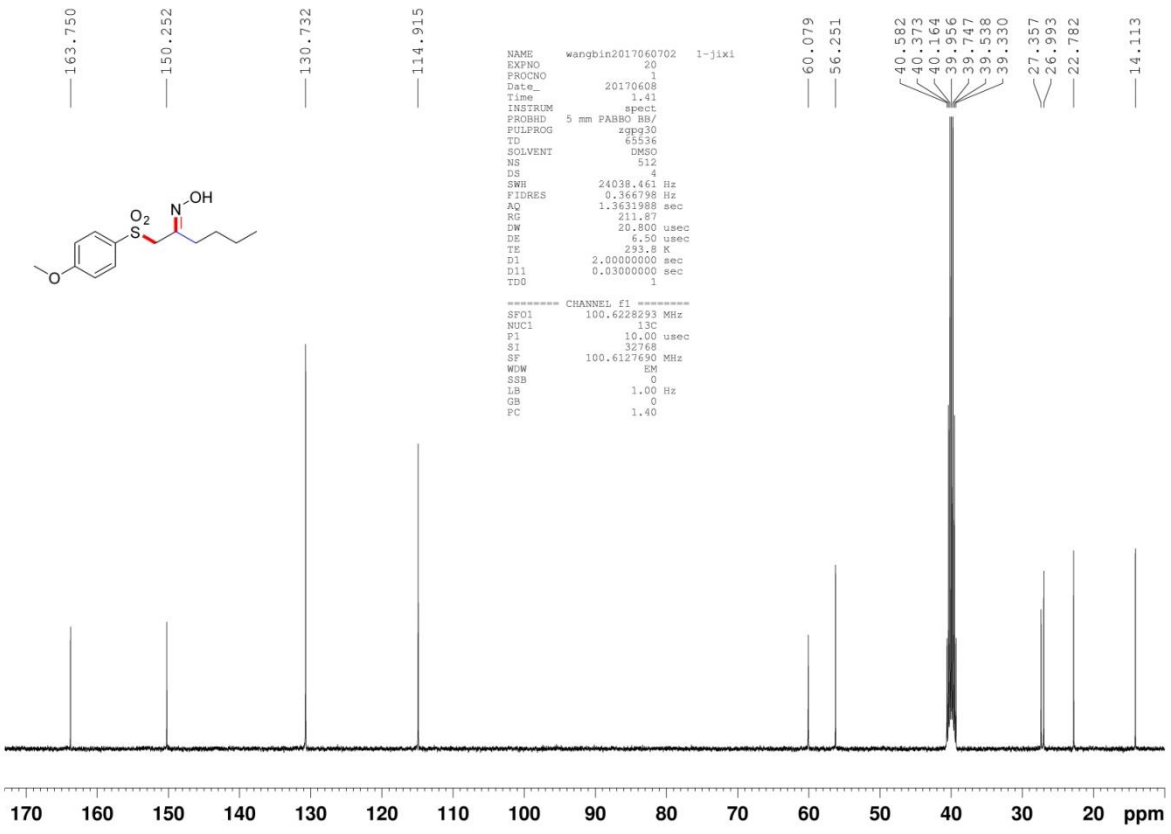
2-tosylcyclopentan-1-one oxime (**4ak**).



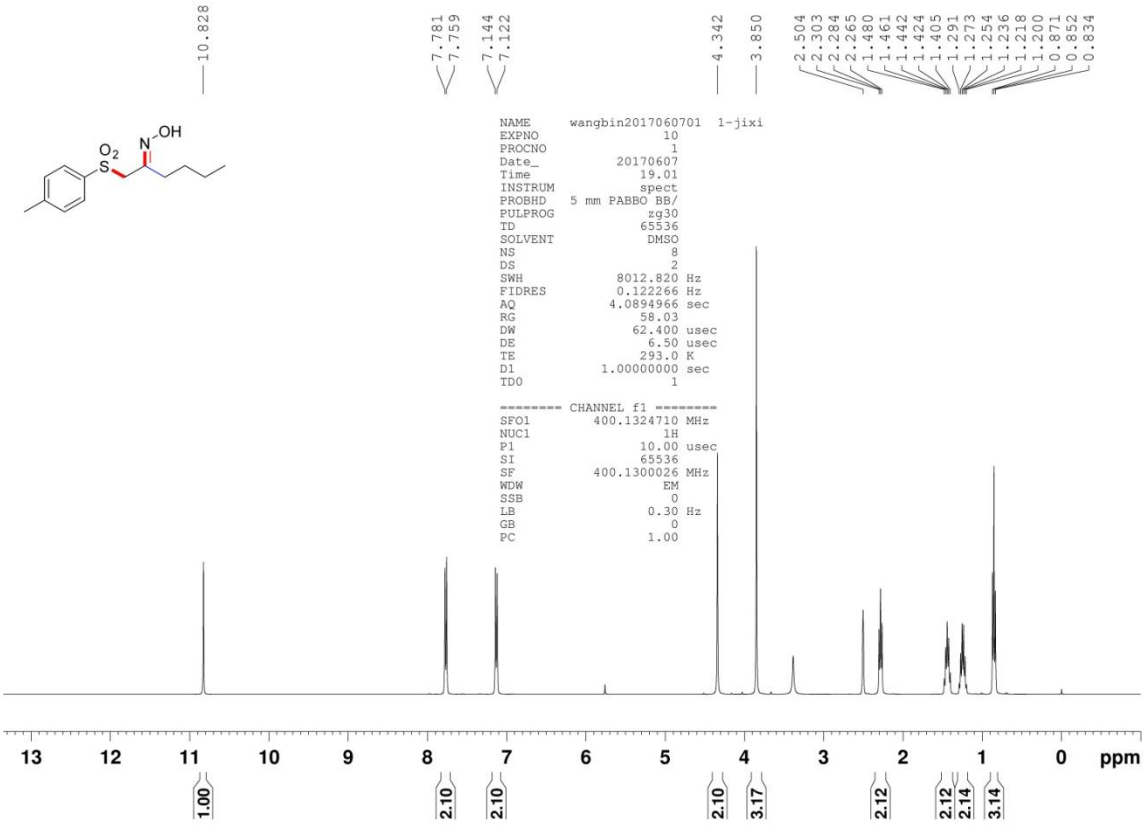


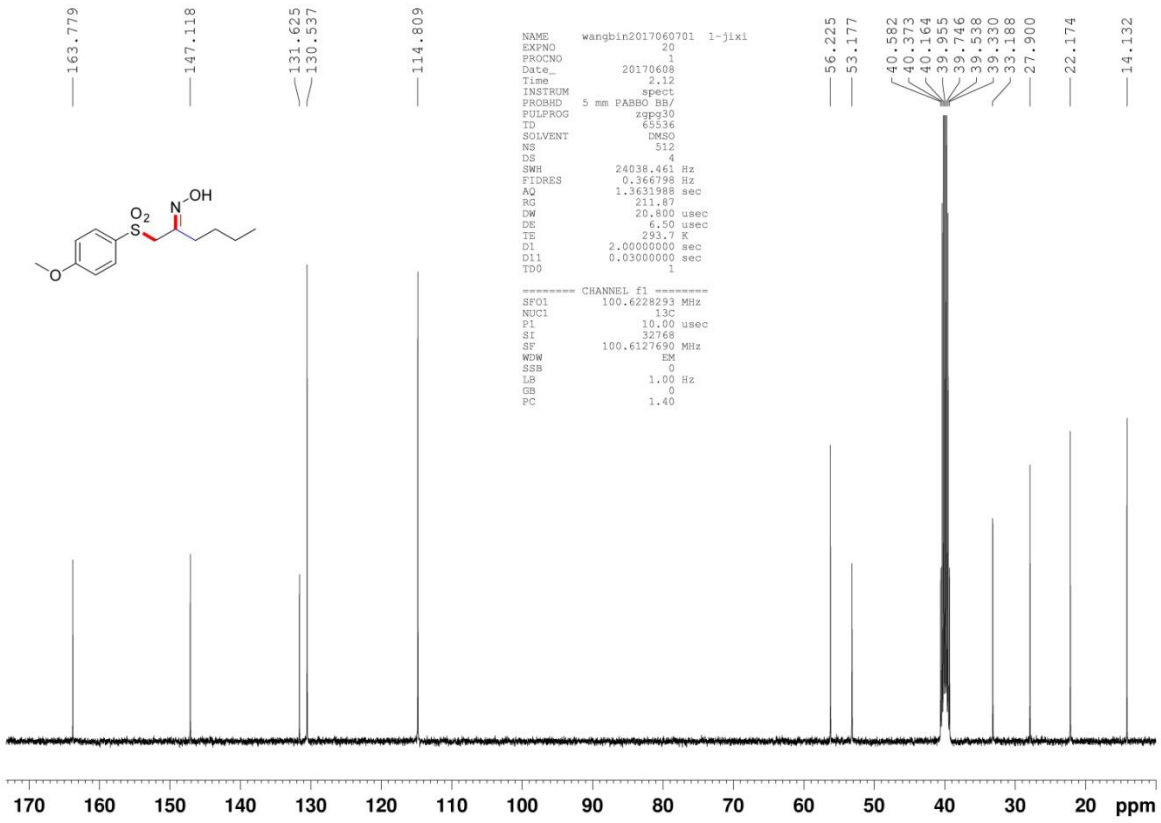
(Z)-1-tosylhexan-2-one oxime (**4al**).



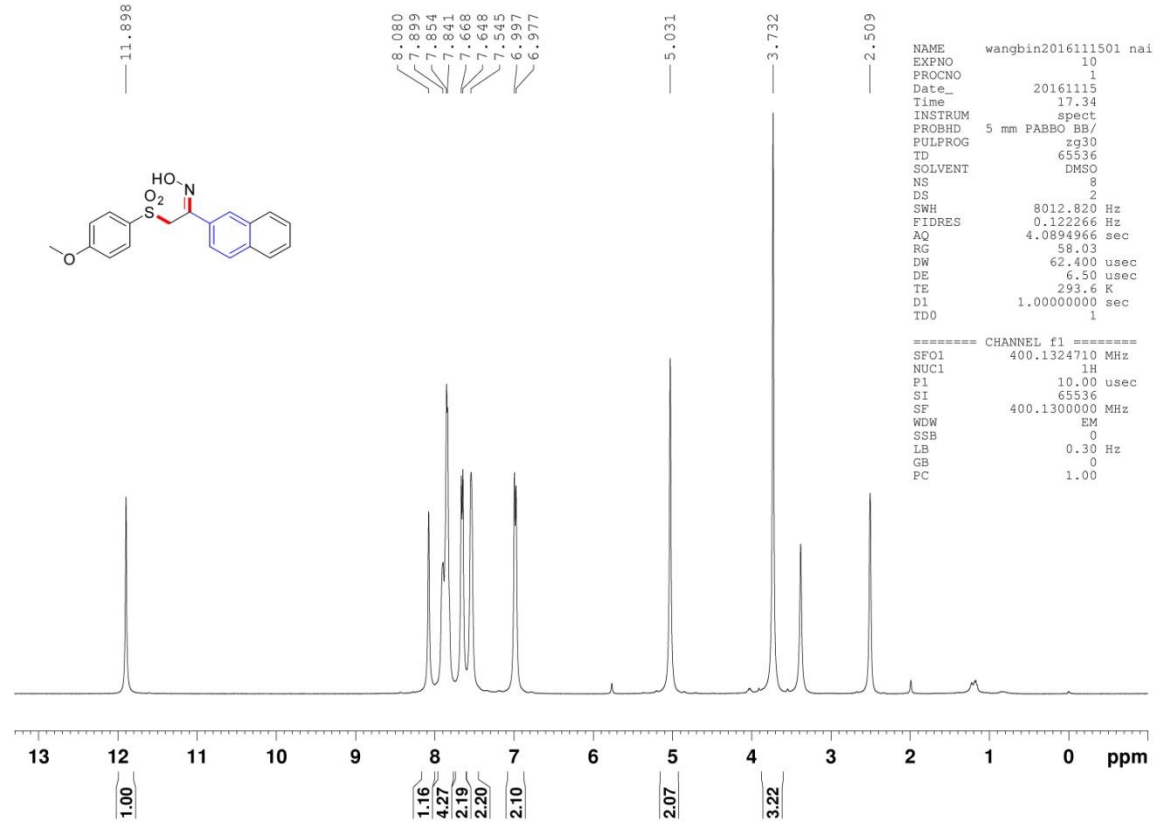


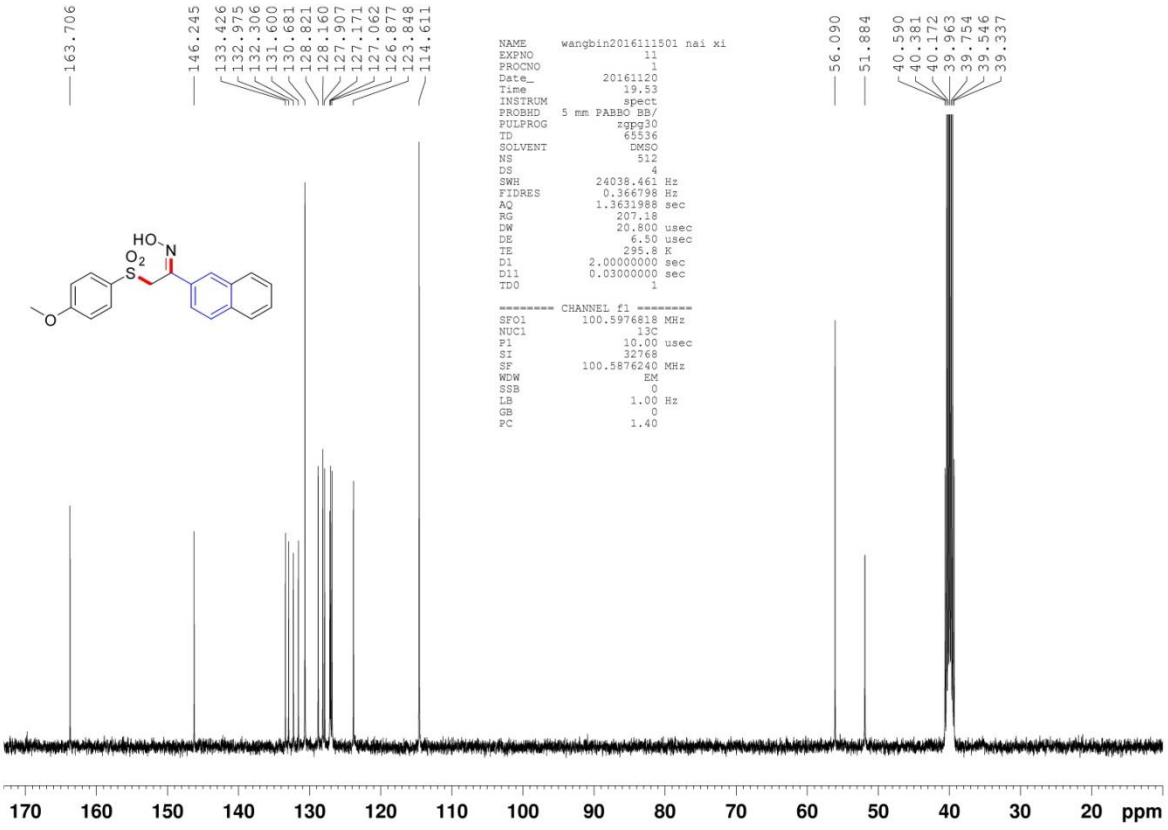
(E)-1-tosylhexan-2-one oxime (**4al'**).





2-((4-methoxyphenyl)sulfonyl)-1-(naphthalen-2-yl)ethan-1-one oxime (**4am**).

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39.337
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D1 2.00000000 sec
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P1 10.00 usec
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PC 1.40
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150
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ppm