Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoredox-Catalyzed reaction of thianthrenium salts, sulfur dioxide and hydrazines

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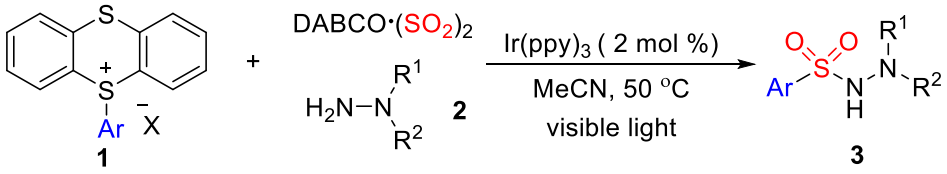
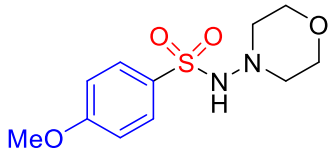
1. General Information

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates precoated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H, ^{13}C NMR spectra were recorded in $CDCl_3$ or Acetone-d6 on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument. Sulfonium salts were prepared according to literature procedures.[1,2]Some HRMS spectra deta can be found in the references. [3,4,5]

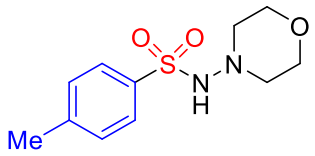
2. General Experimental Procedure and Characterization Data



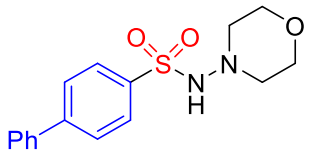
To an oven-dried flask was charged with thianthrenium salts **1** (0.2 mmol), DABCO $(SO_2)_2$ (0.24 mmol), hydrazine **2** (0.3 mmol) and $Ir(ppy)_3$ (2 mol%) under nitrogen atmosphere. Then anhydrous CH_3CN (2 mL) were added to the flask. The mixture was placed around a 30 W blue LEDs and stirred under blue light irradiation for 18 hours at 50 ℃. After completion of reaction as as monitored by TLC analysis, the solvent was evaporated and the residue was purified directly by flash column chromatography on silica gel (petroleum ether /ethyl acetate = 2:1) to give the corresponding product **3**.



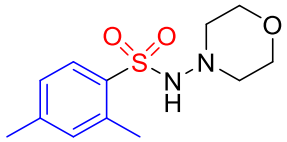
4-Methoxy-*N*-morpholinobenzenesulfonamide (3a)[5]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 5.49 (s, 1H), 3.87 (d, J = 4.6 Hz, 3H), 3.72 – 3.46 (m, 4H), 2.73 – 2.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 130.4, 130.2, 114.1, 66.8, 56.8, 55.8.



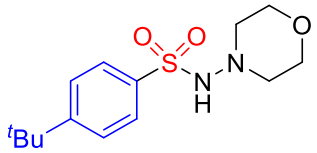
4-methyl-*N*-morpholinobenzenesulfonamide (3b)[5]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.60 (s, 1H), 3.77 – 3.43 (m, 4H), 2.75 – 2.52 (m, 4H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 135.8, 129.6, 128.2, 66.7, 56.7, 21.7.



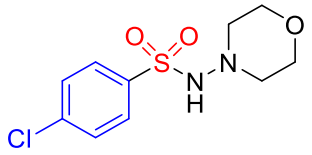
***N*-morpholino-[1,1'-biphenyl]-4-sulfonamide (3c)**[3]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.66 – 7.59 (m, 2H), 7.49 (t, J = 7.3 Hz, 2H), 7.45 – 7.39 (m, 1H), 5.63 (s, 1H), 3.69 – 3.53 (m, 4H), 2.75 – 2.57 (m, 4H);^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 139.2, 137.3, 129.2, 128.8, 127.5, 127.5, 66.8, 57.0.



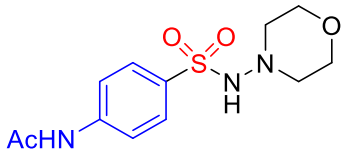
2,4-dimethyl-*N*-morpholinobenzenesulfonamide (3d) [6]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1H), 7.17 – 7.03 (m, 2H), 5.74 (s, 1H), 3.69 – 3.46 (m, 4H), 2.77 – 2.57 (d, J = 5.7 Hz, 7H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 138.0, 133.7, 133.1, 131.3, 126.9, 66.7, 56.8, 21.5, 20.7.



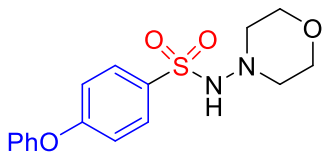
4-(*tert*-butyl)-*N*-morpholinobenzenesulfonamide (3e)[5]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 5.68 (s, 1H), 3.85 – 3.34 (m, 4H), 2.94 – 2.29 (m, 4H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 135.7, 128.1, 125.92, 66.7, 56.8, 35.3, 31.2.



4-chloro-*N*-morpholinobenzenesulfonamide (3f) [5]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 5.82 (s, 1H), 3.77 – 3.34 (m, 4H), 2.88 – 2.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 137.2, 129.7, 129.3, 66.7, 56.8.

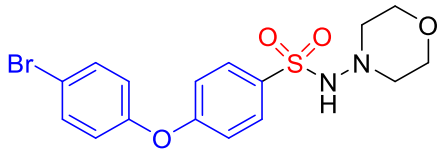


***N*-(4-(*N*-morpholinosulfamoyl)phenyl)acetamide (3g):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 8.6 Hz, 2H), 7.44 (s, 1H), 5.33 (s, 1H), 3.70 – 3.48 (m, 4H), 2.79 – 2.49 (m, 4H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 189.2, 136.8, 135.7, 134.7, 134.1, 129.6, 129.2, 129.0, 128.5, 59.8, 55.0, 28.0, 21.0; IR (KBr, cm^{-1}): 3441, 1645, 1325, 1045; HRMS (ESI) calcd for $C_{12}H_{17}N_3O_4NaS^+$ ($M+Na^+$): 322.0837, found: 322.0843.

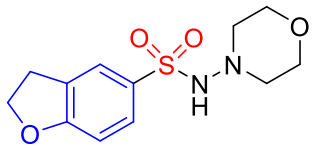


***N*-morpholino-4-phenoxybenzenesulfonamide (3h):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.8 Hz, 2H), 7.42 (t, J = 7.9 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 7.05 (dd, J

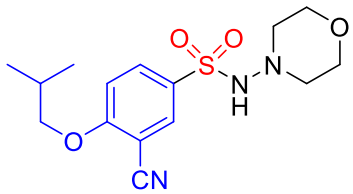
= 12.8, 8.5 Hz, 4H), 5.54 (s, 1H), 3.80 – 3.42 (m, 4H), 2.97 – 2.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 155.1, 132.1, 130.5, 130.4, 125.2, 120.5, 117.4, 66.8, 56.9; IR (KBr, cm^{-1}): 3198, 1582, 1334, 1155; HRMS (ESI) calcd for $C_{16}H_{19}N_2O_4S^+$ ($M+H^+$): 335.1066, found: 335.1066.



4-(4-bromophenoxy)-*N*-morpholinobenzenesulfonamide (3i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.7 Hz, 2H), 5.80 (s, 1H), 3.85 – 3.40 (m, 4H), 2.81 – 2.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 154.3, 133.3, 132.7, 130.6, 122.1, 117.9, 117.5, 66.7, 56.8; IR (KBr, cm^{-1}): 3192, 1576, 1265, 1155; HRMS (ESI) calcd for $C_{16}H_{18}N_2O_4SBr^+$ ($M+H^+$): 413.0171, found: 413.0170.

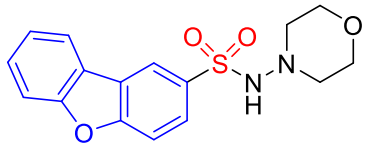


***N*-morpholino-2,3-dihydrobenzofuran-5-sulfonamide (3j):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.66 (m, 2H), 6.84 (d, J = 8.4 Hz, 1H), 5.56 (s, 1H), 4.68 (t, J = 8.8 Hz, 2H), 3.68 – 3.49 (m, 4H), 3.27 (t, J = 8.8 Hz, 2H), 2.72 – 2.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 130.1, 130.0, 128.2, 125.5, 109.5, 72.5, 66.8, 56.9, 29.1; IR (KBr, cm^{-1}): 3158, 1486, 1242, 1100; HRMS (ESI) calcd for $C_{12}H_{16}N_2O_4NaS^+$ ($M+Na^+$): 307.0728, found: 307.0736.

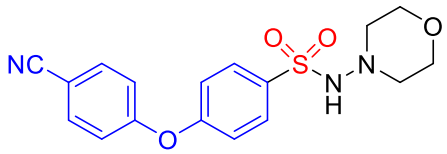


3-cyano-4-isobutoxy-*N*-morpholinobenzenesulfonamide (3k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 2.2 Hz, 1H), 8.09 (dd, J = 8.9, 2.2 Hz, 1H), 7.06 (d, J = 9.0 Hz, 1H), 5.96 (s, 1H), 3.91 (d, J = 6.5 Hz, 2H), 3.73 – 3.42 (m, 4H), 2.86 – 2.39 (m, 4H), 2.35 – 1.92 (m, 1H), 1.08 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9,

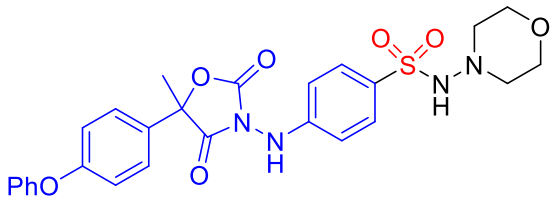
134.6, 134.3, 130.9, 114.8, 112.2, 102.7, 76.1, 66.7 56.8, 28.2, 19.1; IR (KBr, cm^{-1}): 3153, 2231, 1600, 1284; HRMS (ESI) calcd for $C_{15}H_{22}N_3O_4S^+$ ($M+H^+$): 340.1331, found: 340.1333.



***N*-morpholinodibenzo[b,d]furan-2-sulfonamide (3l):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 1.5 Hz, 1H), 8.09 (dd, J = 8.7, 1.8 Hz, 1H), 8.02 (d, J = 7.7 Hz, 1H), 7.69 (d, J = 8.7 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 7.56 (dd, J = 11.4, 4.1 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 5.58 (s, 1H), 3.67 – 3.47 (m, 4H), 2.89 – 2.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 157.1, 133.2, 128.8, 127.4, 124.9, 123.9, 123.2, 121.9, 121.3, 112.3, 66.8, 56.9; IR (KBr, cm^{-1}): 3560, 1592, 1445, 1123; HRMS (ESI) calcd for $C_{16}H_{16}N_2O_4NaS^+$ ($M+Na^+$): 355.0728, found: 355.0732.

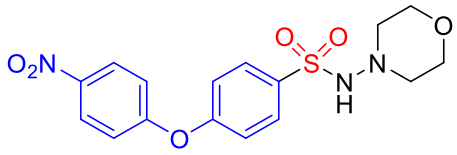


4-(4-cyanophenoxy)-*N*-morpholinobenzenesulfonamide (3m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.7 Hz, 2H), 7.69 (d, J = 8.7 Hz, 2H), 7.12 (dd, J = 12.4, 8.8 Hz, 4H), 5.50 (s, 1H), 3.88 – 3.39 (m, 4H), 2.94 – 2.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 159.5, 134.6, 134.4, 130.9, 119.8, 119.2, 118.4, 108.1, 66.8, 57.0; IR (KBr, cm^{-1}): 3124, 2921, 1501, 1244; HRMS (ESI) calcd for $C_{17}H_{18}N_3O_4S^+$ ($M+H^+$): 360.1018, found: 360.1026.

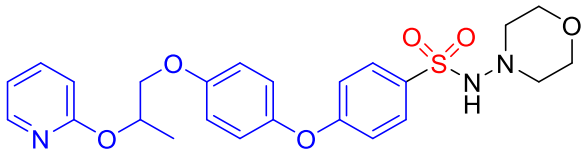


4-((5-methyl-2,4-dioxo-5-(4-phenoxyphenyl)oxazolidin-3-yl)amino)-N-morpholinobenzenesulfonamide (3n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.37 (t, J = 7.9 Hz, 2H), 7.16 (t, J = 7.4 Hz, 1H), 7.03 (dd, J = 8.8, 1.9 Hz, 5H), 6.68 (d, J = 8.5 Hz, 2H), 5.92 (s, 1H), 3.54 (m, 4H),

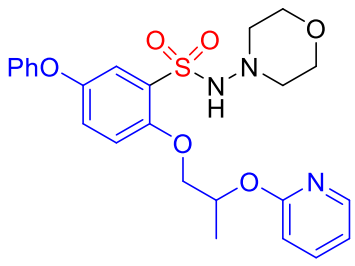
2.56 (m, 4H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 158.9, 156.1, 152.64, 148.6, 131.6, 130.2, 130.1, 129.9, 126.2, 124.3, 119.7, 118.7, 112.8, 85.6, 66.7, 56.6, 25.4; IR (KBr, cm^{-1}): 3201, 1759, 1245, 1159; HRMS (ESI) calcd for $C_{26}H_{27}N_4O_7S^+$ ($M+H^+$): 539.1600, found: 539.1596.



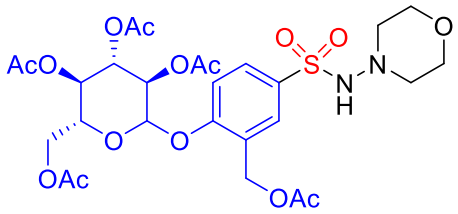
***N*-morpholino-4-(4-nitrophenoxy)benzenesulfonamide (3o):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 9.1 Hz, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.15 (dd, J = 21.3, 9.0 Hz, 4H), 5.54 (s, 1H), 3.82 – 3.28 (m, 4H), 2.90 – 2.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 159.4, 144.0, 134.8, 130.9, 126.3, 119.5, 119.0, 66.8, 57.0; IR (KBr, cm^{-1}): 3138, 1578, 1345, 1160; HRMS (ESI) calcd for $C_{16}H_{18}N_3O_6S^+$ ($M+H^+$): 380.0916, found: 380.0919.



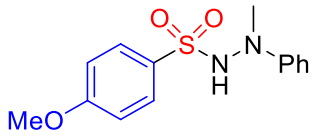
***N*-morpholino-4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)benzenesulfonamide (3p):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 4.8 Hz, 1H), 7.87 (d, J = 8.7 Hz, 2H), 7.58 (t, J = 7.7 Hz, 1H), 6.97 (d, J = 10.0 Hz, 6H), 6.92 – 6.81 (m, 1H), 6.75 (d, J = 8.3 Hz, 1H), 5.70 – 5.36 (m, 2H), 4.21 (dd, J = 9.8, 5.3 Hz, 1H), 4.09 (dd, J = 9.8, 4.7 Hz, 1H), 3.62 (d, J = 3.8 Hz, 4H), 2.78 – 2.44 (m, 4H), 1.49 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 163.0, 156.4, 148.3, 146.9, 138.9, 131.6, 130.4, 121.8, 117.0, 116.6, 116.2, 111.8, 71.1, 69.3, 66.8, 56.9, 17.1; IR (KBr, cm^{-1}): 3460, 1594, 1228, 1154; HRMS (ESI) calcd for $C_{24}H_{28}N_3O_6S^+$ ($M+H^+$): 486.1699, found: 486.1705.



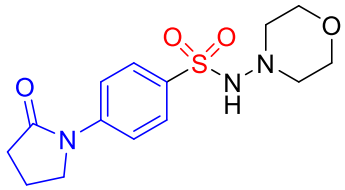
***N*-morpholino-5-phenoxy-2-(2-(pyridin-2-yloxy)propoxy)benzenesulfonamide (3q):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.08 (m, 1H), 7.87 (d, J = 8.9 Hz, 2H), 7.62 – 7.47 (m, 1H), 7.06 – 6.92 (m, 6H), 6.87 (dd, J = 6.5, 5.6 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 5.58 (d, J = 4.0 Hz, 2H), 4.21 (dd, J = 9.9, 5.3 Hz, 1H), 4.09 (dd, J = 9.9, 4.8 Hz, 1H), 3.80 – 3.43 (m, 4H), 2.76 – 2.48 (m, 4H), 1.49 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 163.0, 156.4, 148.3, 146.8, 138.9, 131.6, 130.4, 121.8, 117.0, 116.6, 116.2, 111.8, 71.1, 69.3, 66.8, 56.9, 17.1; IR (KBr, cm^{-1}): 3460, 1503, 1276, 1175; HRMS (ESI) calcd for $C_{24}H_{28}N_3O_6S^+$ ($M+H^+$): 486.1699, found: 486.1706.



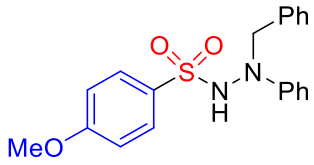
(2R,3R,4S,5R,6S)-2-(acetoxymethyl)-6-(2-(acetoxymethyl)-4-(*N*-morpholinosulfamoyl)phenoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (3r): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 1.6 Hz, 1H), 7.91 – 7.83 (m, 1H), 7.15 (d, J = 8.7 Hz, 1H), 5.68 (s, 1H), 5.37 – 5.25 (m, 2H), 5.16 (dd, J = 27.6, 10.4 Hz, 3H), 5.02 (d, J = 13.7 Hz, 1H), 4.29 (dd, J = 12.4, 5.2 Hz, 1H), 4.19 (dd, J = 12.3, 1.9 Hz, 1H), 4.00 – 3.88 (m, 1H), 3.66 – 3.54 (m, 4H), 2.76 – 2.48 (m, 4H), 2.16 – 1.95 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.3, 169.5, 169.4, 157.5, 133.3, 129.7, 129.2, 127.1, 114.7, 98.6, 72.4, 72.4, 70.8, 68.1, 66.7 61.9, 60.3, 56.8, 21.0, 20.8, 20.7; IR (KBr, cm^{-1}): 3469, 1751, 12345, 1041; HRMS (ESI) calcd for $C_{27}H_{37}N_2O_{15}S^+$ ($M+H^+$): 661.1915, found: 661.1915.



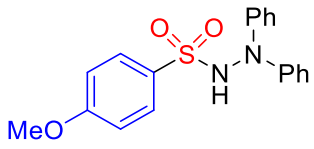
4-methoxy-*N'*-methyl-*N'*-phenylbenzenesulfonohydrazide (3s): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.8 Hz, 2H), 7.09 (t, J = 7.9 Hz, 2H), 6.90 – 6.72 (dd, J = 29.7, 8.6 Hz, 5H), 6.27 (s, 1H), 3.77 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 149.9, 130.5, 130.0, 129.0, 120.9, 114.5, 114.4, 55.7, 42.6.



***N*-morpholino-4-(2-oxopyrrolidin-1-yl)benzenesulfonamide (3t):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 5.63 (s, 1H), 3.91 (t, J = 7.0 Hz, 2H), 3.59 (m, 4H), 2.81 – 2.48 (m, 6H), 2.34 – 2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 143.7, 133.4, 129.3, 118.8, 66.8, 56.9, 48.6, 33.0, 17.9; IR (KBr, cm^{-1}): 3445, 1677, 1334, 1162; HRMS (ESI) calcd for $C_{14}H_{19}N_3O_4NaS^+$ ($M+Na^+$): 348.0994, found: 348.1000.



***N'*-benzyl-4-methoxy-*N'*-phenylbenzenesulfonohydrazide (3u):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.9 Hz, 2H), 7.33 – 7.19 (m, 3H), 7.15 (t, J = 8.0 Hz, 2H), 7.09 – 6.97 (m, 2H), 6.90 (t, J = 8.7 Hz, 4H), 6.84 (t, J = 7.3 Hz, 1H), 6.28 (s, 1H), 4.53 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 148.9, 134.7, 130.41, 130.3, 129.1, 128.9, 128.3, 128.0, 121.0, 115.4, 114.3, 58.1, 55.7; IR (KBr, cm^{-1}): 3216, 1596, 1326, 1151; HRMS (ESI) calcd for $C_{20}H_{20}N_2O_3NaS^+$ ($M+Na^+$): 391.1092, found: 391.1089.



4-methoxy-*N',N'*-diphenylbenzenesulfonohydrazide (3v): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.8 Hz, 2H), 7.17 (t, J = 7.8 Hz, 4H), 7.04 – 6.92 (m, 7H), 6.75 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 147.0, 130.6, 130.1, 129.2, 124.0, 120.9, 114.1, 55.8; IR (KBr, cm^{-1}): 3225, 1590, 1339, 1092; HRMS (ESI) calcd for $C_{19}H_{18}N_2O_3NaS^+$ ($M+Na^+$): 377.0936, found: 377.0936.

3. Mechanistic Studies

3.1 Stern-Volmer fluorescence quenching experiments.

Stern-Volmer fluorescence quenching experiments were performed with freshly prepared solutions of 0.1 mM fac-Ir(ppy)$_3$ in degassed dry CH_3CN added with the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. The solution was irradiated at 395 nm and fluorescence was measured from 450 nm to 650 nm.[7]

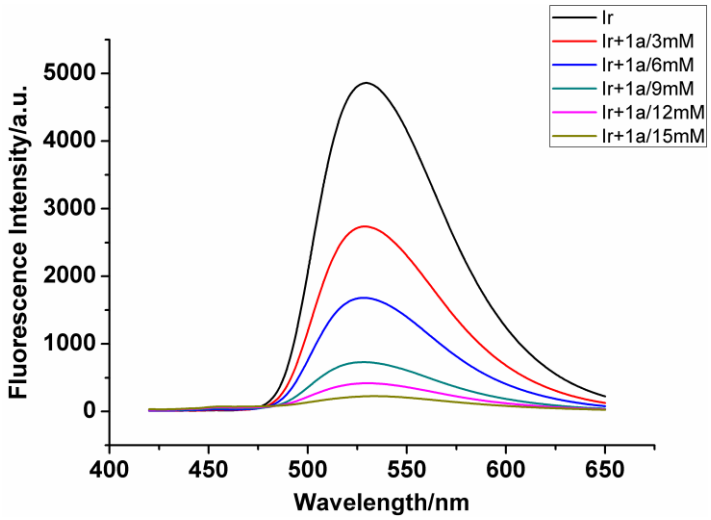


Figure S1. Fluorescence quenching experiments of fac-Ir(ppy)$_3$ and **1a.**

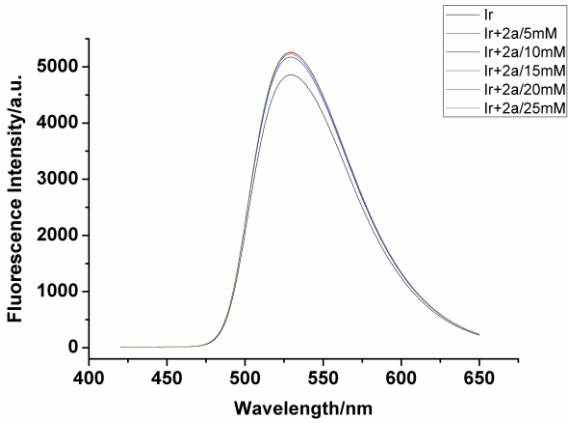


Figure S2. Fluorescence quenching experiments of fac-Ir(ppy)$_3$ and **2a**.

3.2 Measurement of quantum yield

Determination of photon flux of LED blue light by standard potassium ferric oxalate photometric method. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (328mg,) in 5 mL of H_2SO_4 (0.20 M) solution. A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10- phenanthroline (54.1 mg) and sodium acetate (1.23 g) in 20 mL of H_2SO_4 (0.20 M) solution.

Add 0.50 mL of ferric oxalate solution to a vial. then the small The bottle is sealed and placed 2.0 cm away from the 25 W LED blue light. After 10 seconds of irradiation, add to the vial 1.5 mL of aqueous sulfuric acid and 2.0 mL of buffer solution. The solution was then allowed to stand for 1 hour to allow the resulting ferrous ions Complete reaction with 1,10-phenanthroline. Take 50 μL of the resulting solution as an aliquot and add 3.0 mL of 0.20 M sulfur Diluted with aqueous acid. The absorbance of the resulting solution at 510 nm (l = 1.0 cm) was measured with a UV-Vis spectrometer. luminosity. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. The calculation method of the amount of ferrous ions generated is as follows:

$$\text{n } Fe^{2+} = \frac{V \times \Delta A}{l \times \varepsilon}$$

where V is the total volume (0.24L) of the measurement sample, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions [ΔA = 0.23, l is the optical path of the sample in the spectrophotometer (1 cm), and ε is the extinction coefficient of the complex $Fe^{II}(phen)_3^{2+}$ at 510 nm (11100 L mol^{-1} cm^{-1})

$$\text{photon flux} = \frac{n\ Fe^{2+}}{\Phi \times t \times f}$$

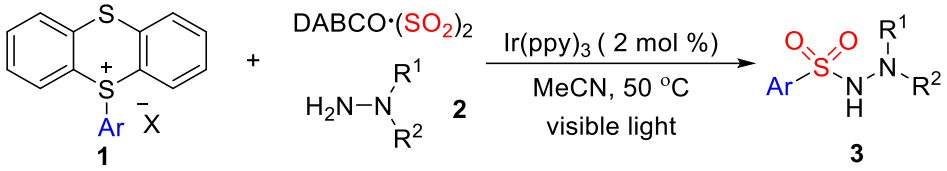
where Φ is the quantum yield for the ferrioxalate actinometer (0.845 at λ_{ex} = 457.9 nm), t is the irradiation time (10 s), and f is the fraction of light absorbed at λ_{ex} = 450 nm by the ferrioxalate actinometer.

$$f = 1\text{-}10^{-A\ (450nm)} = 1\text{-}10^{-2.148} = 0.9929$$

$$\text{n } Fe^{2+} = \frac{V \times \Delta A}{l \times \varepsilon} = \frac{0.24L \times 0.23}{1cm \times 11100L\ mol^{-1}cm^{-1}} = 4.97 \times 10^{-6} \text{ mol}$$

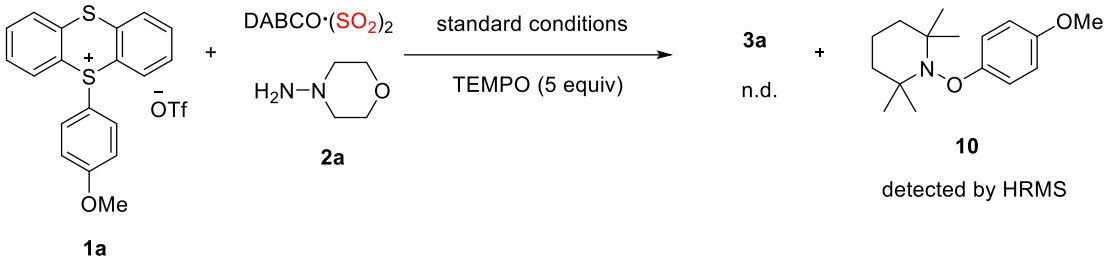
$$photon\ flux = \frac{n\ Fe^{2+}}{\Phi \times t \times f} = \frac{4.97 \times 10^{-6}}{0.845 \times 10 \times 0.9929} = 5.93 \times 10^{-7} \text{ einstein } s^{-1}$$

Under nitrogen, a dry quartz vial equipped with a magnetic stir bar was charged with **1** (0.2 mmol), **2** (0.3 mmol), DABSO (0.24 mmol) and $Ir(ppy)_3$ (2 mol%). Then dry MeCN (2 mL) was added. The reaction mixture was placed in a water bath, stirred for 1 hour at 900 rpm under 35 W blue LED light. After the completion of reaction, the solvent was removed under reduced pressure. 1,3,5-tris Methoxybenzene was used as the internal standard, and the yield was 40.2% (4.02×10^{-5} mol) by ^{1}H NMR

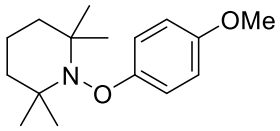


$$\Phi\ (\mathbf{3}) = \frac{Mol\ product}{flux*t*f} = \frac{4.02\times10^{-5}}{5.93\times10^{-7}\times3600\times0.9929} = 0.0198$$

3.3 Radical trapping experiments

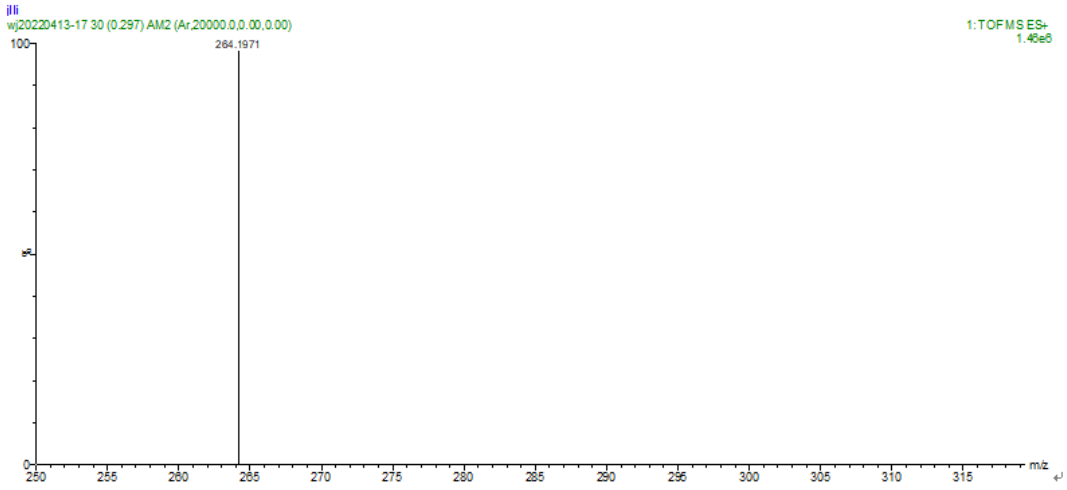


An oven-dried flask was charged with thianthrenium salts **1a** (0.2 mmol, 1.0 equiv), DABCO $(SO_2)_2$ (0.24 mmol, 1.2 equiv), hydrazine **2a** (0.3 mmol, 1.5 equiv), fac-Ir(ppy)3 (0.004 mmol, 0.02 equiv) and TEMPO (1.0 mmol, 5.0 equiv) under nitrogen atmosphere. Then anhydrous CH_3CN (2 mL) was added into the flask. The mixture was stirred under 35 W blue light irradiation for 18 hours at 50°C. As a result, significant inhibition of the reactivity was observed, and the corresponding trapping product **10** was detected by HRMS.



10

HRMS (ESI) calcd for $C_{16}H_{26}NO_2^+$ (M+H+): 264.1964, found: 264.1971.



4.References

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(2) Florian, M.; Plutschack, J.; Yu, W.; Samira, S.; Matthem Ho.; Nils, F.; Tobias, R. *Nature*. **2019**, *567*, 223-228.

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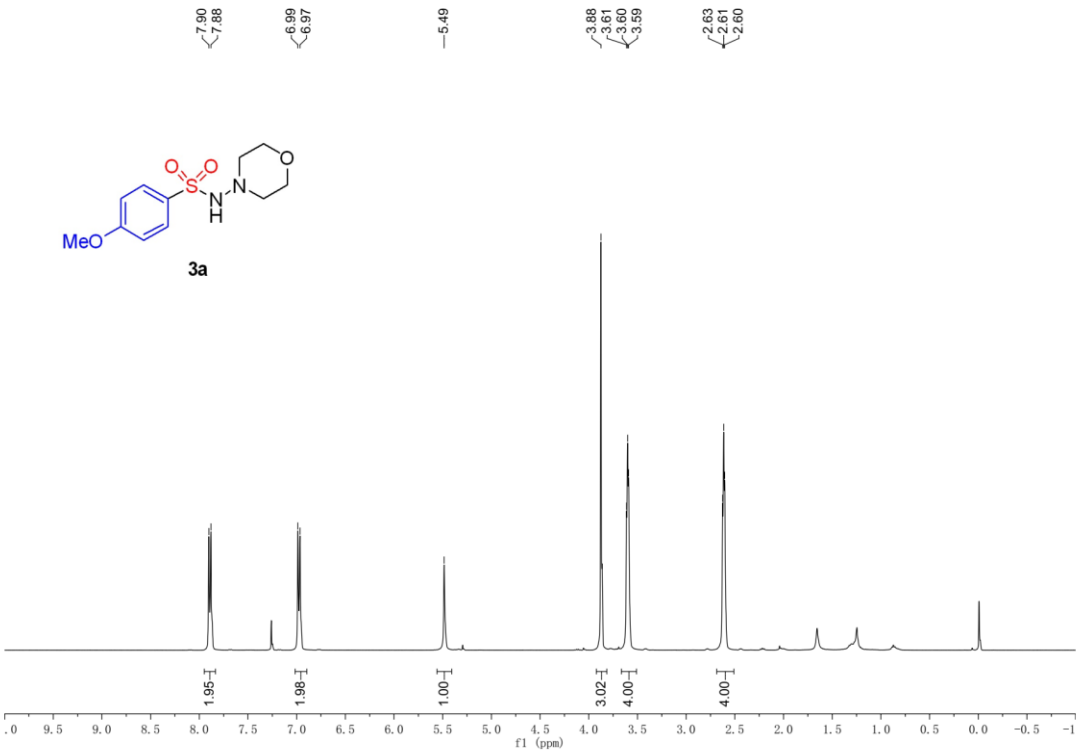
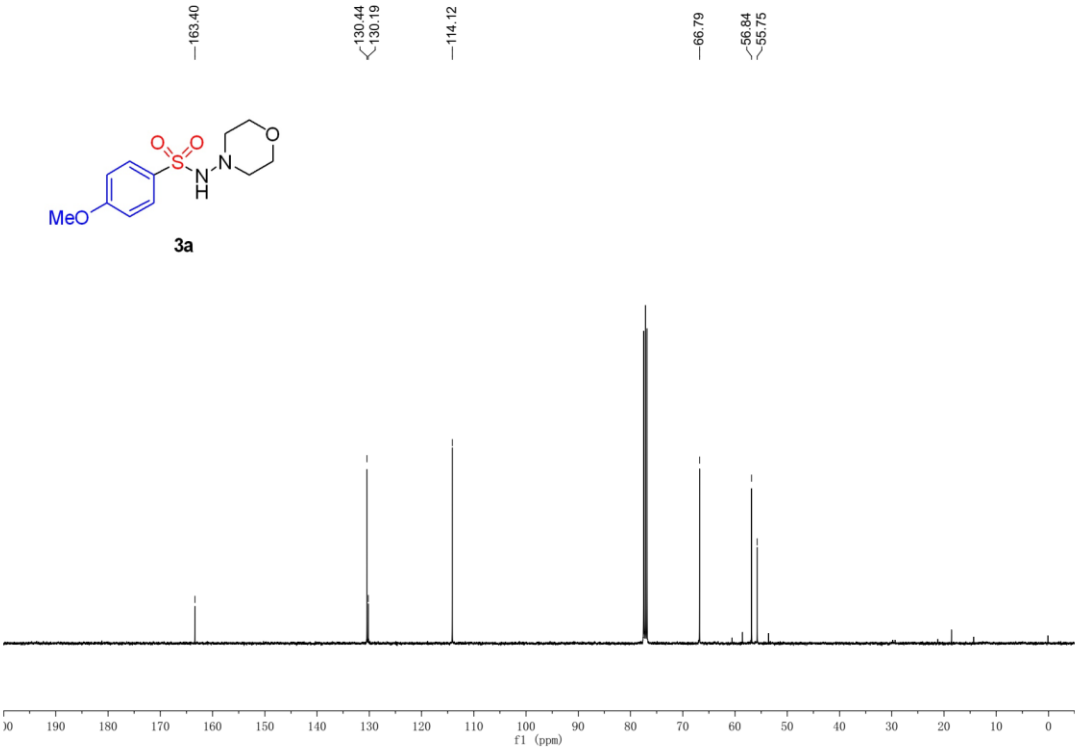
(7) He, F-S; Bao, P; Tang, Z; Yu, F; Deng, W-P; Wu, J. *Org. Lett*. **2022**, *24*, 2955-2960.

5.Copies of ^{1}H ,^{13}C NMR Spectra.

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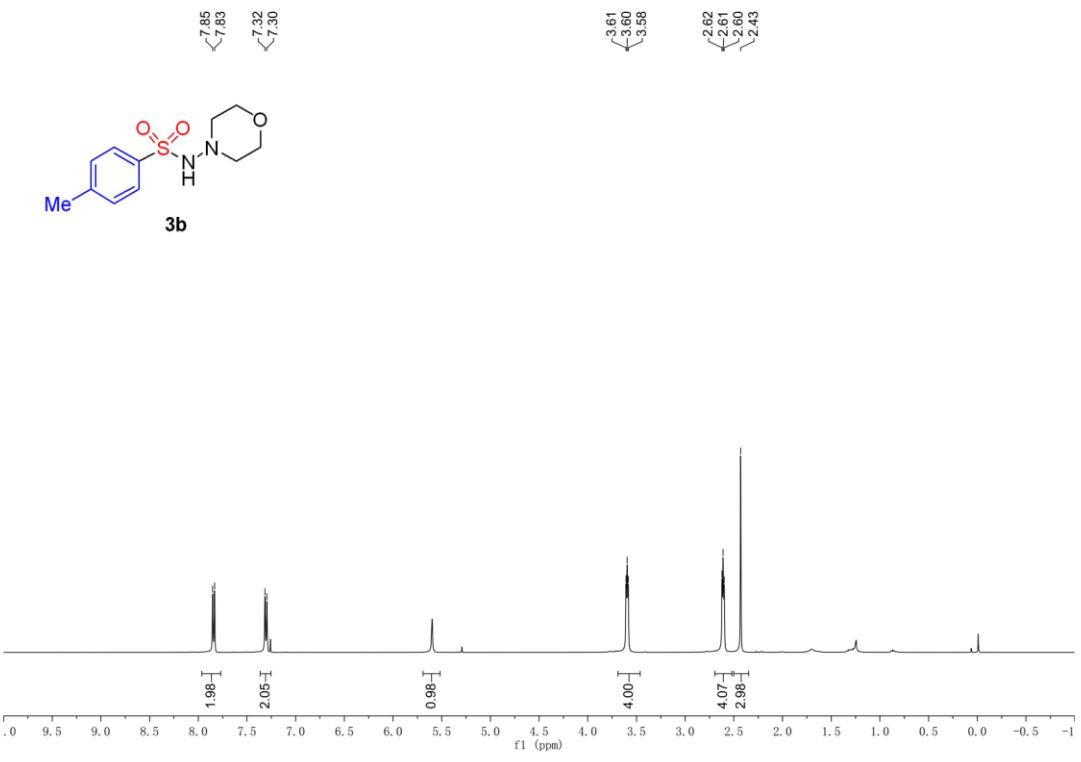
114.12
66.79
56.84
55.75
MeO
3a
f1 (ppm)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7.32
7.30
3.61
3.60
3.58
2.62
2.61
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2.43
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3b
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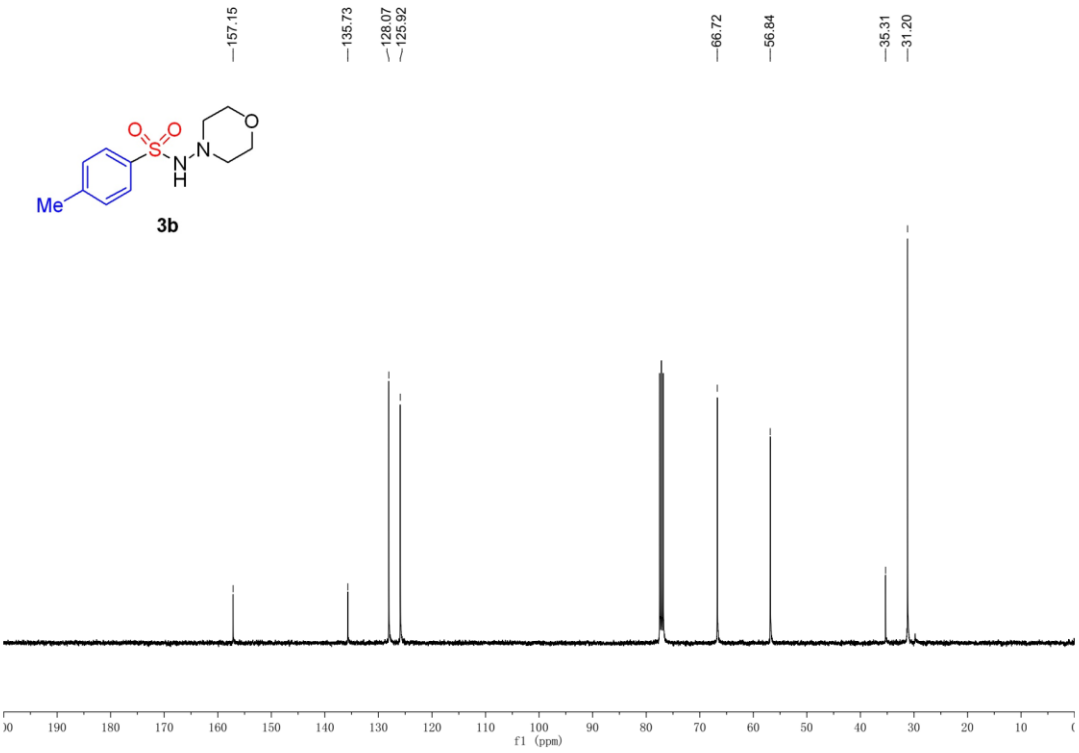
4.00
4.07
2.98
f1 (ppm)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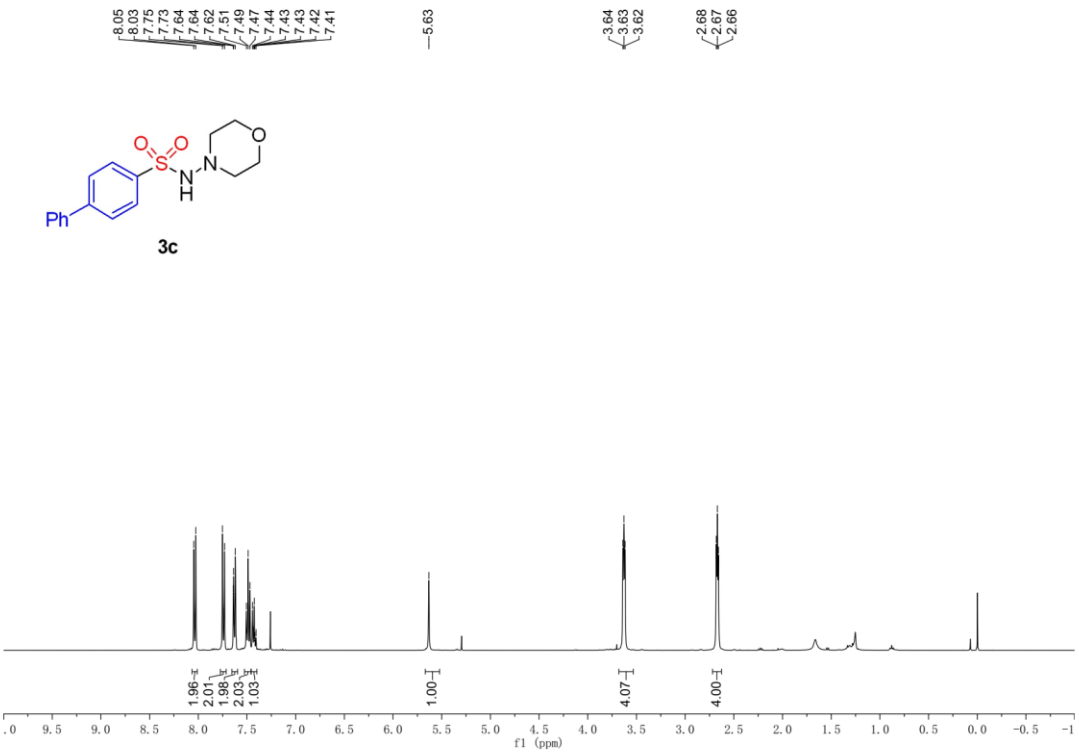
35.31
31.20
Me
3b
f1 (ppm)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7.47
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7.43
7.42
7.41
5.63
3.64
3.63
3.62
2.68
2.67
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Ph
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1.98
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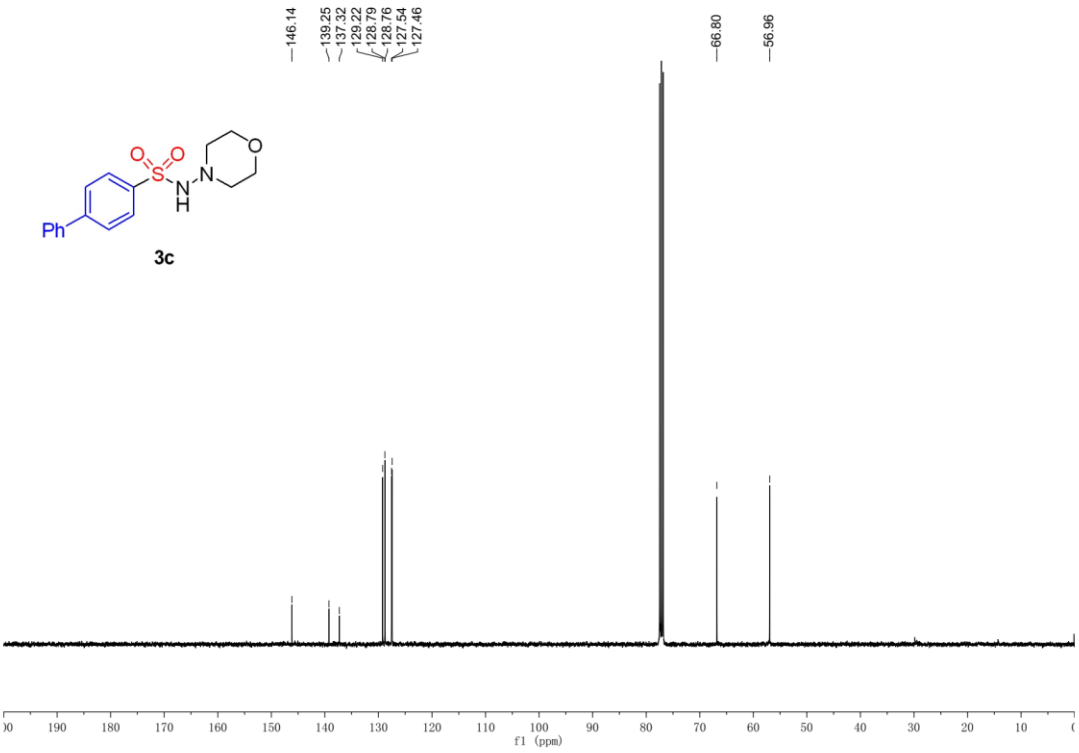
1.00
4.07
4.00
f1 (ppm)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56.96
Ph
3c
f1 (ppm)


7.93
7.91
7.12
7.10
7.09
5.74
3.57
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3.55
2.77
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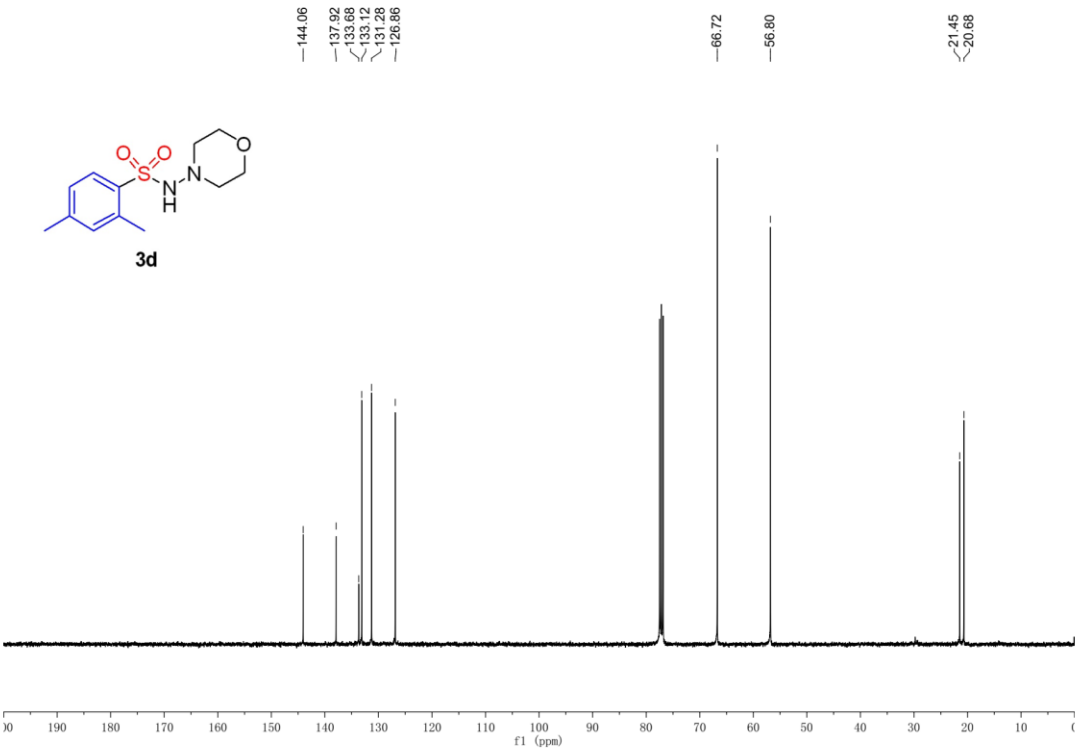
f1 (ppm)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N
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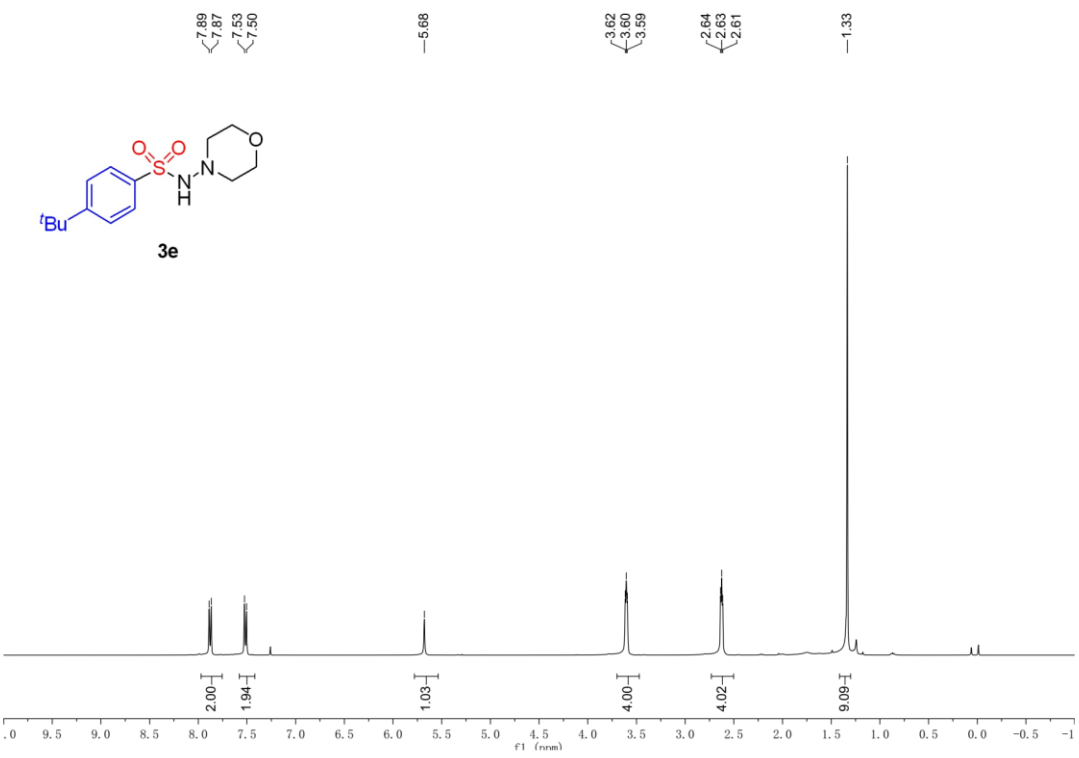
O
N
f1 (ppm)

3d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H
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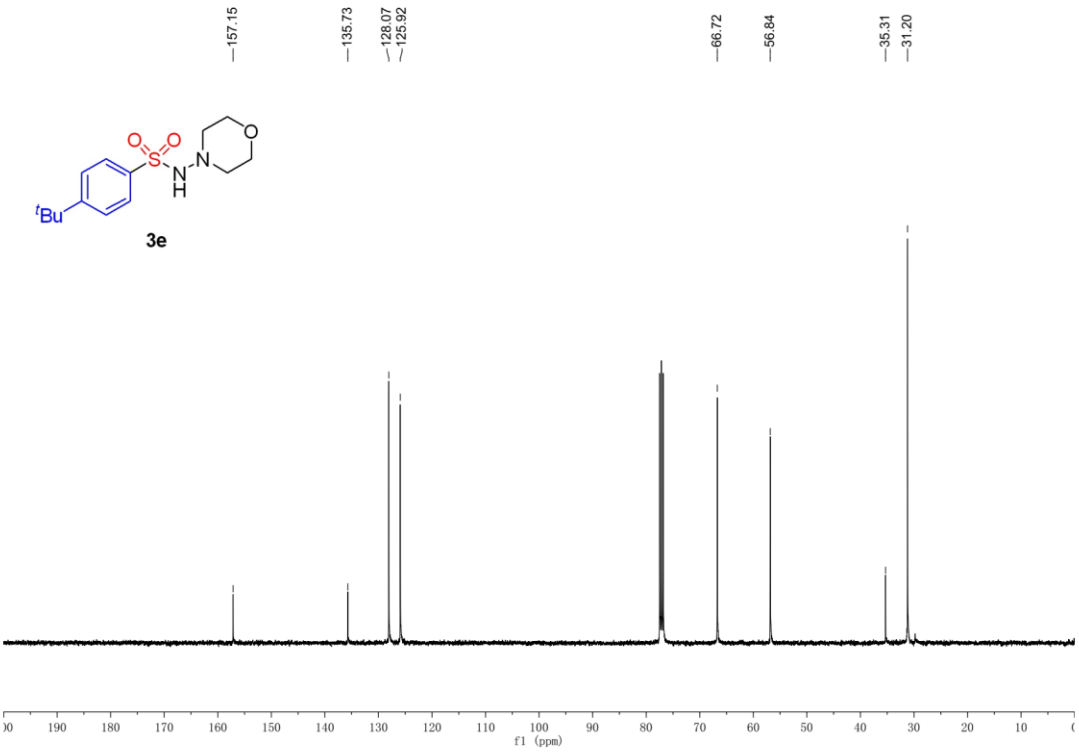
9.09
f1 (ppm)

3e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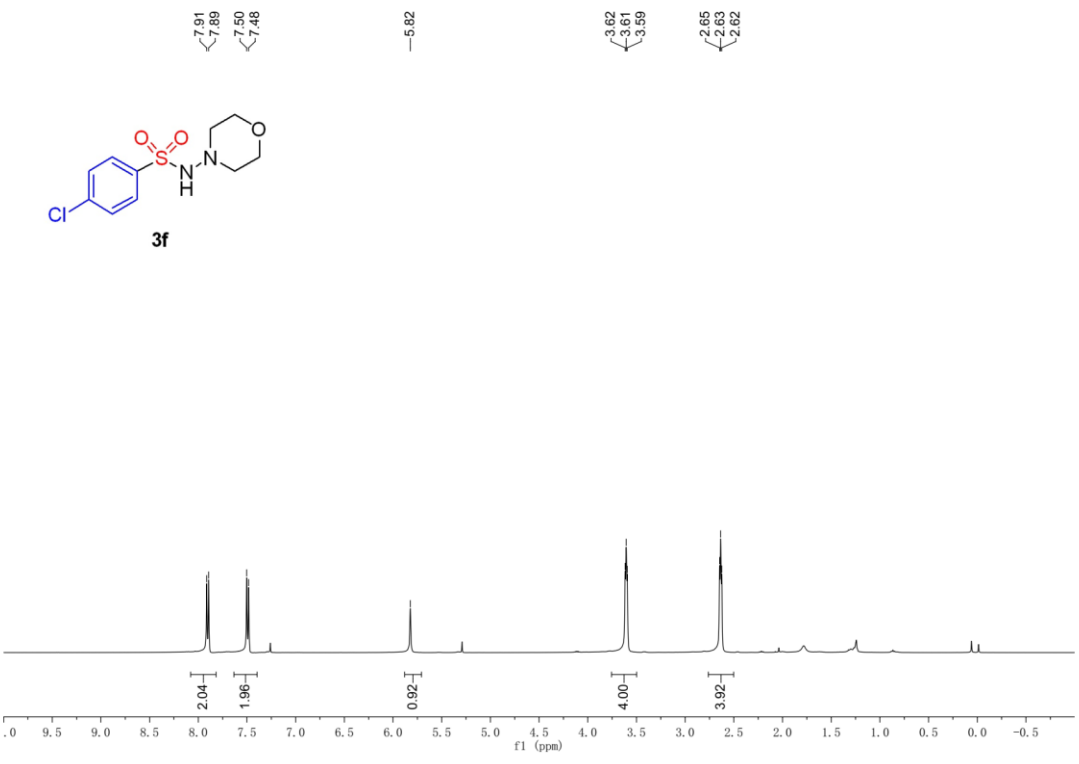
56.84
35.31
31.20
tBu
3e
f1 (ppm)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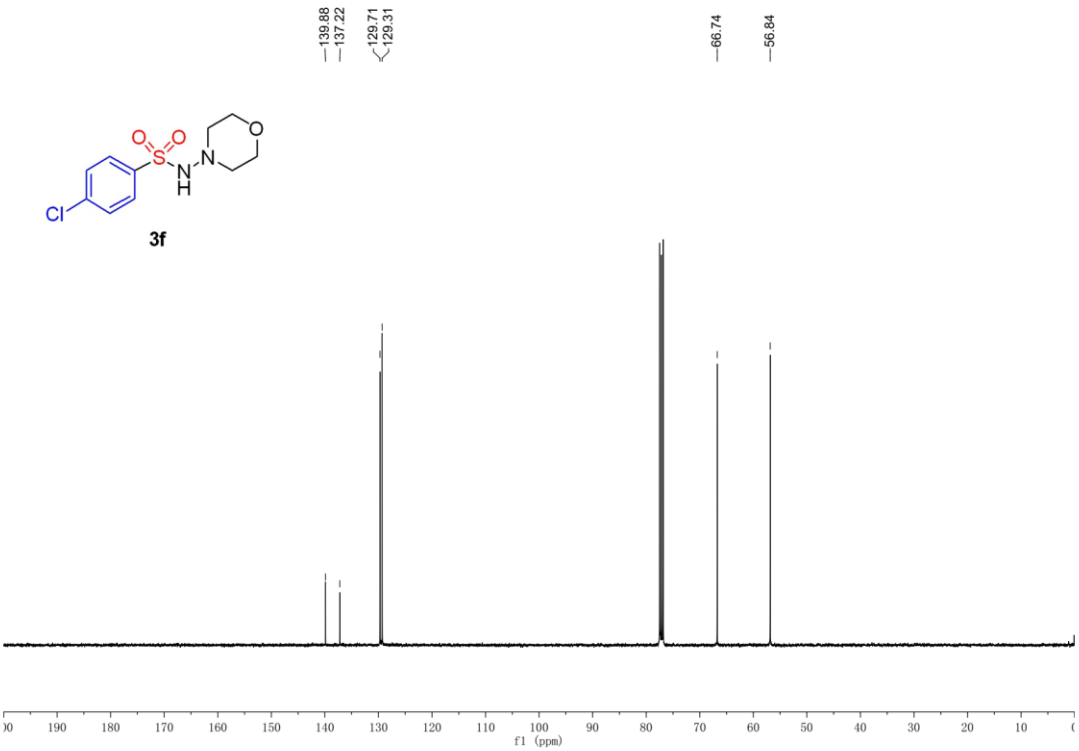
f1 (ppm)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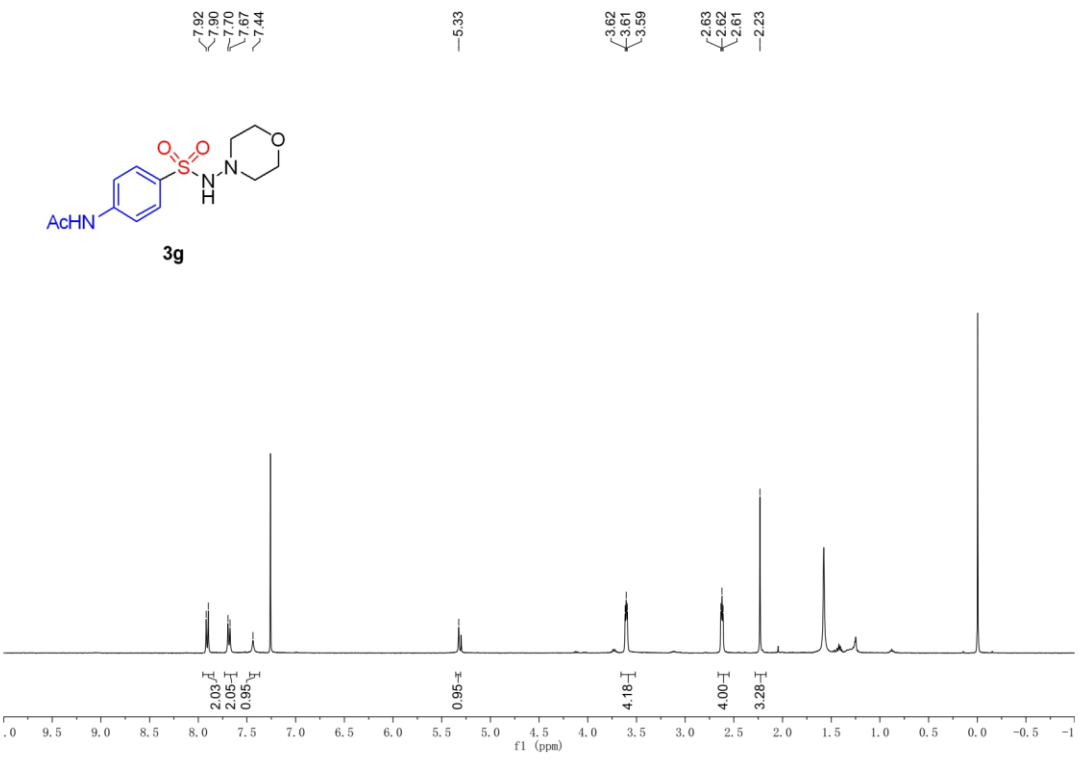
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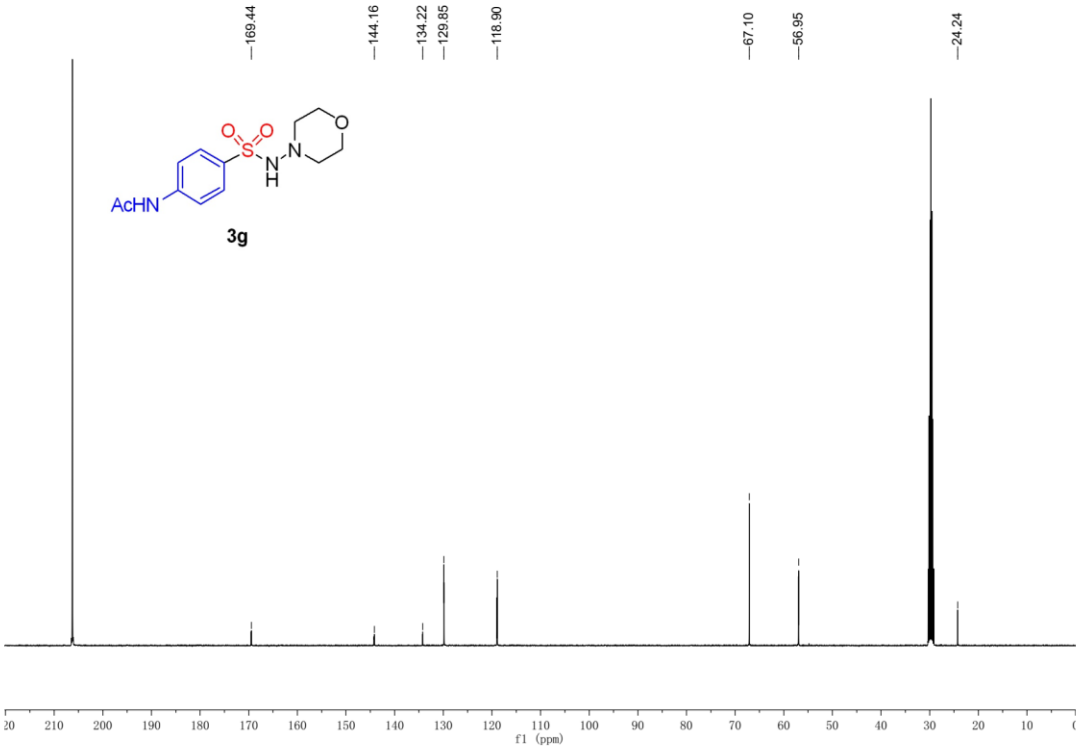
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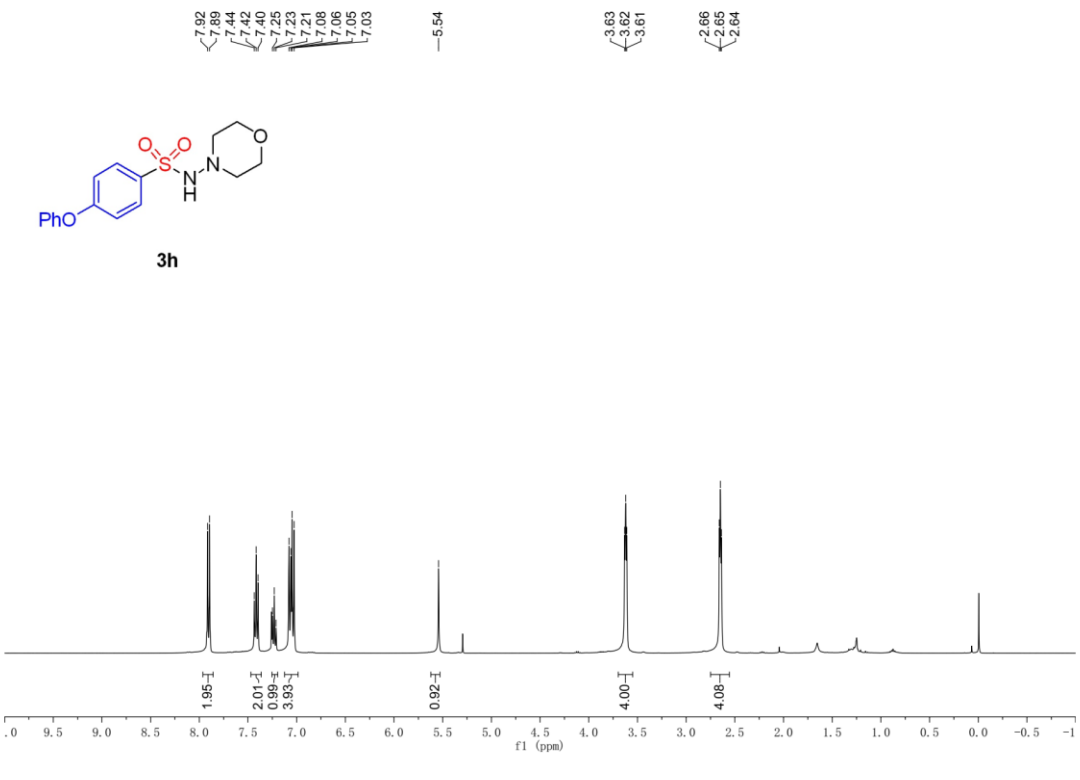
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3.63
3.62
3.61
2.66
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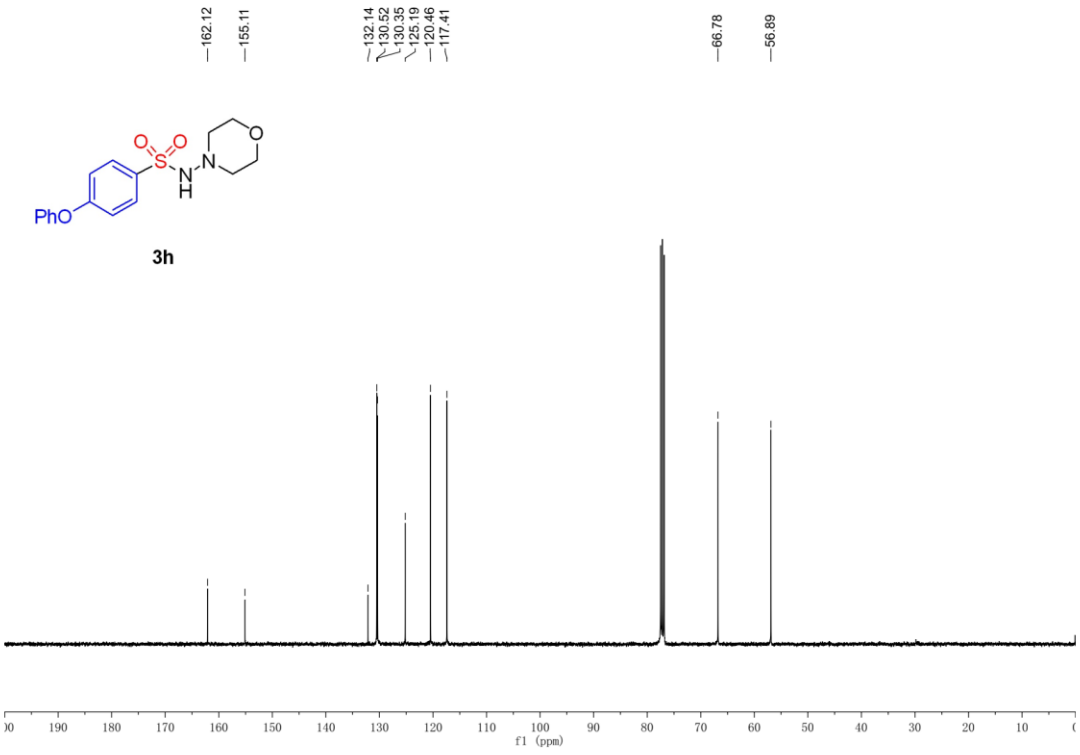
4.08
f1 (ppm)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PhO
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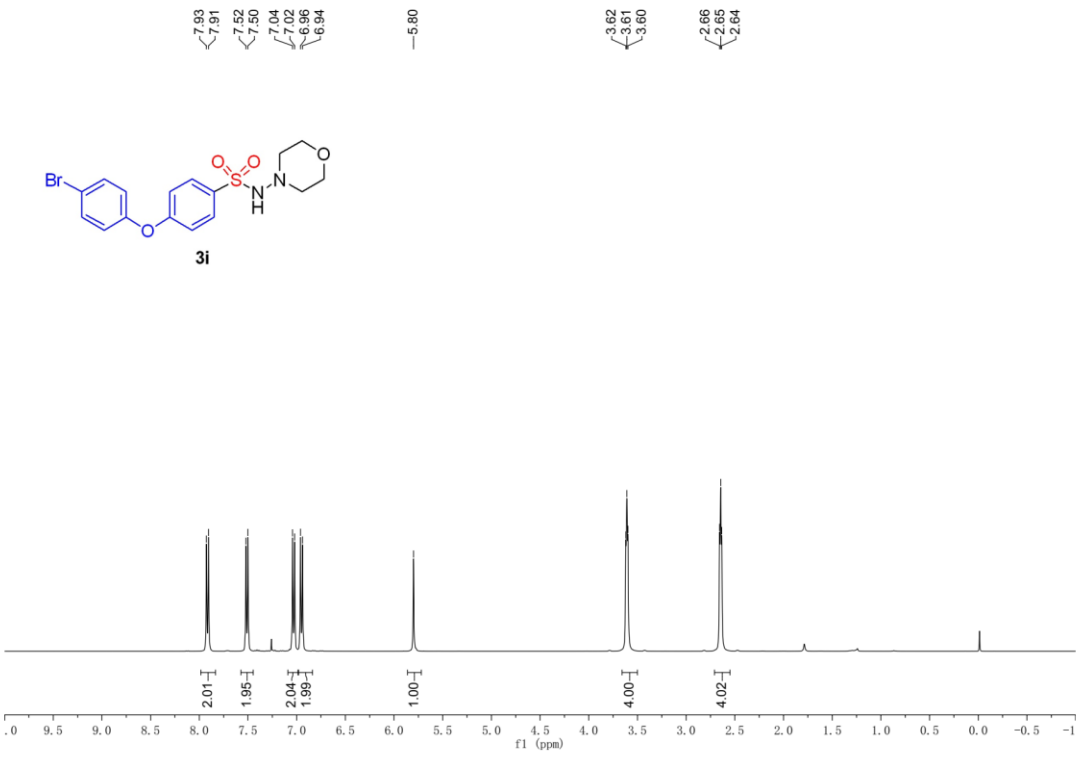
f1 (ppm)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2.66
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2.64
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O
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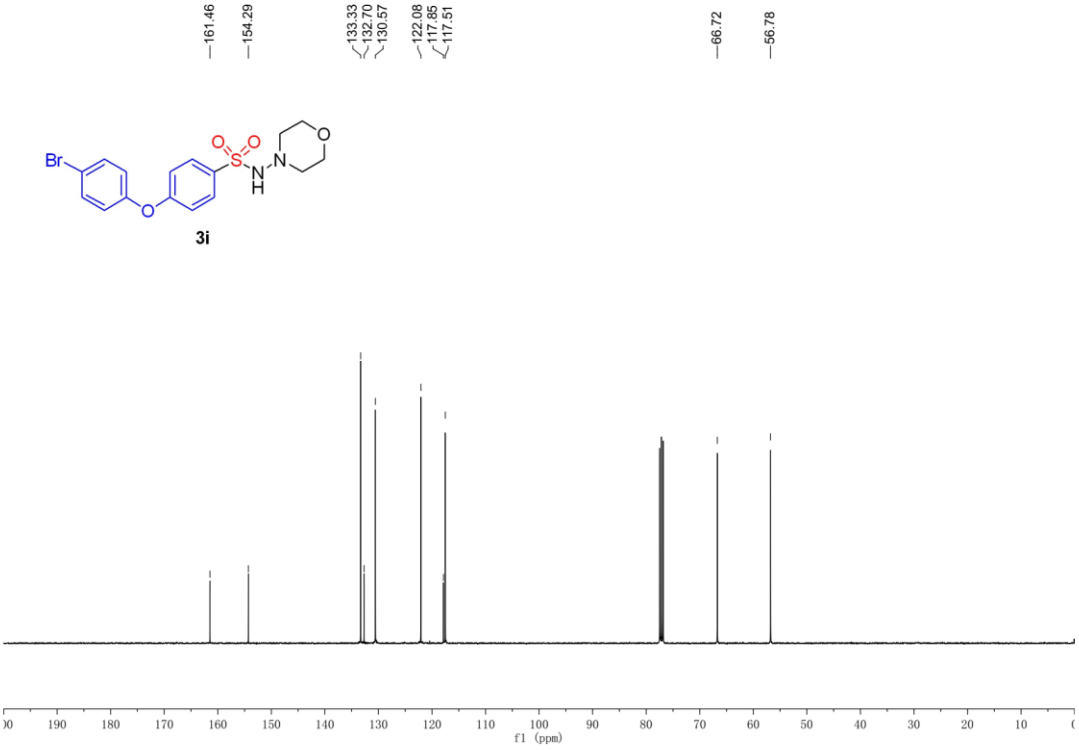
1.00
4.00
4.02
f1 (ppm)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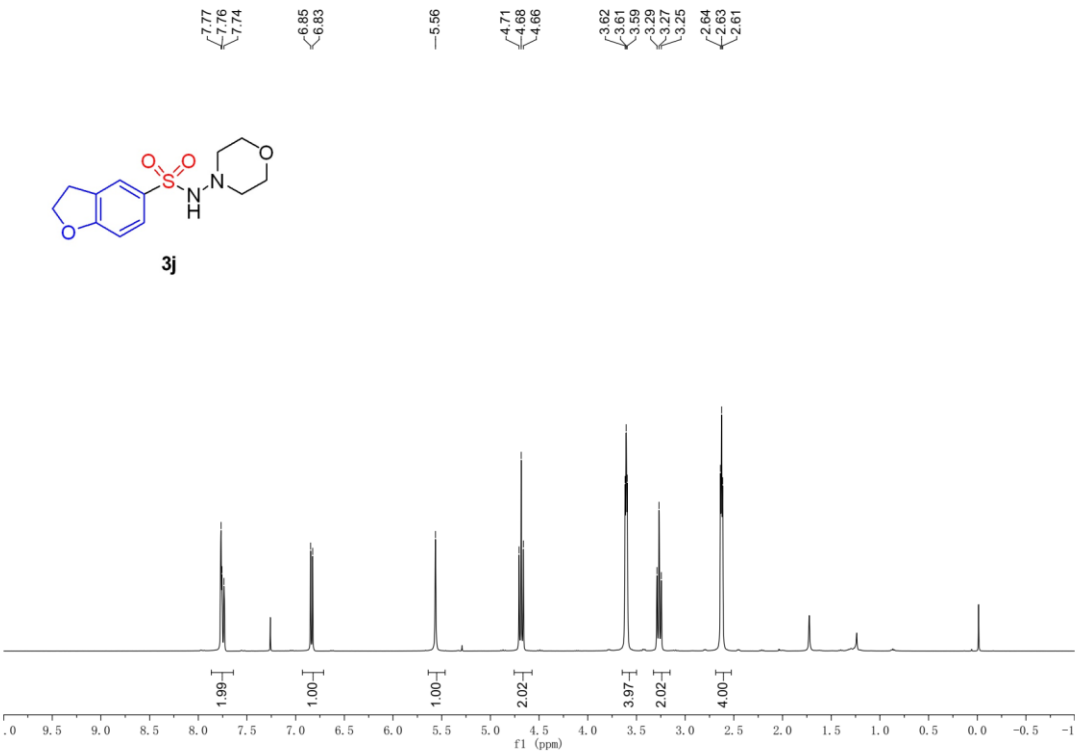
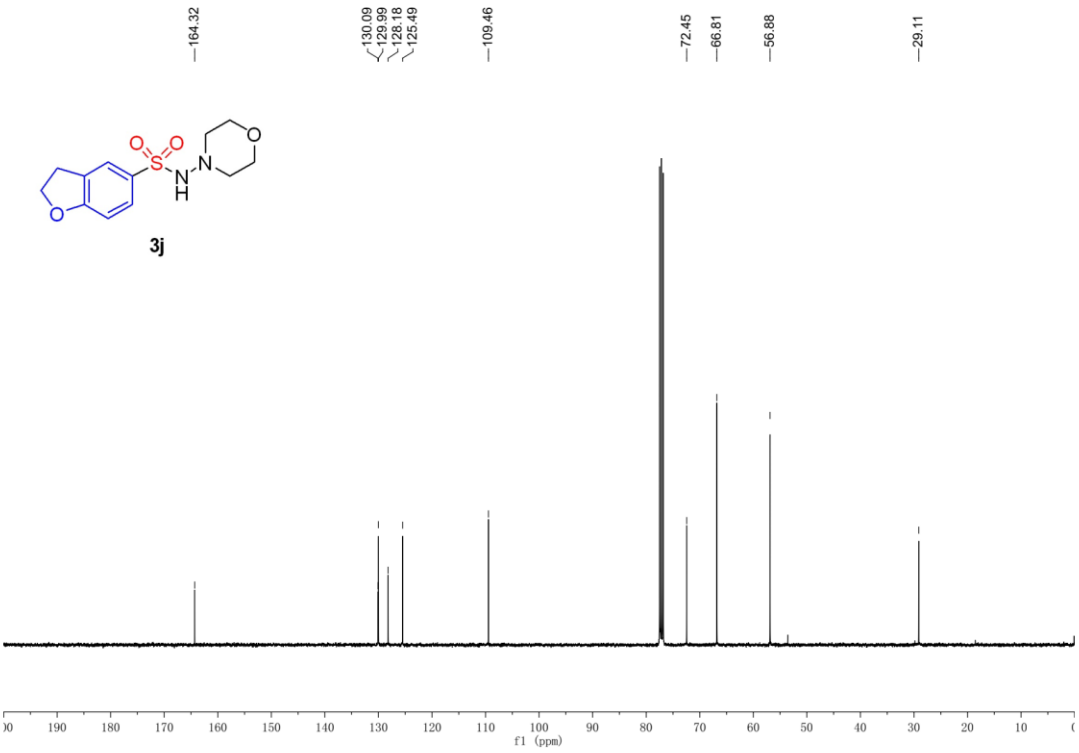
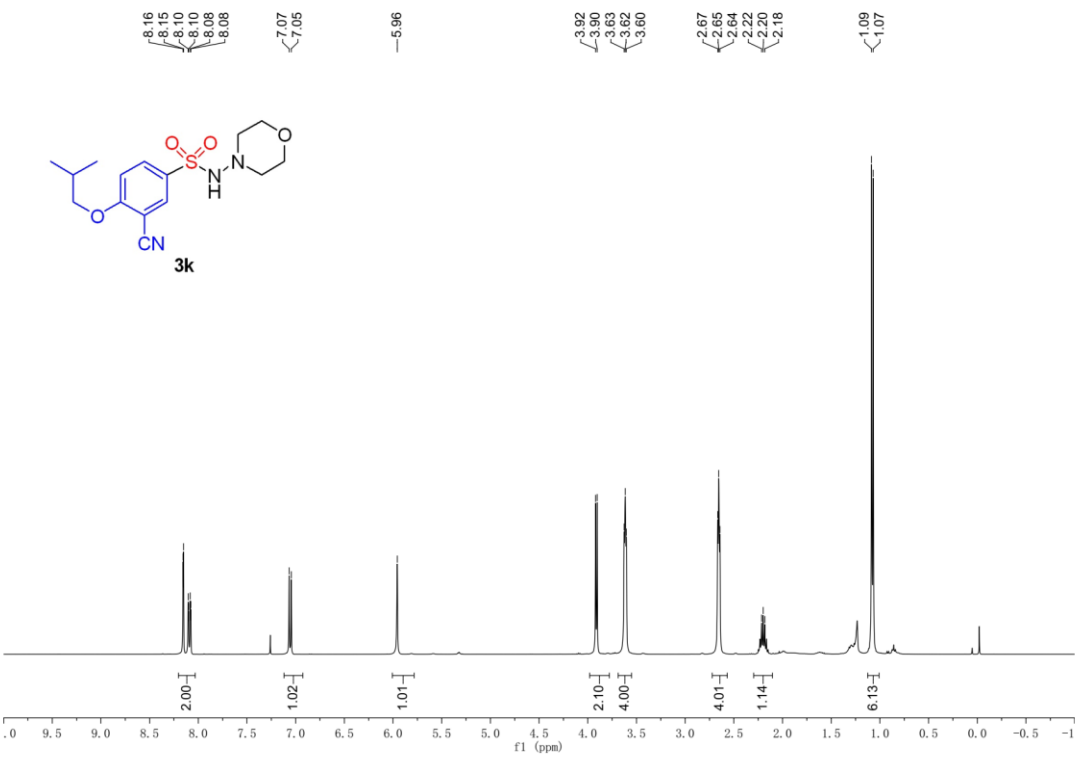
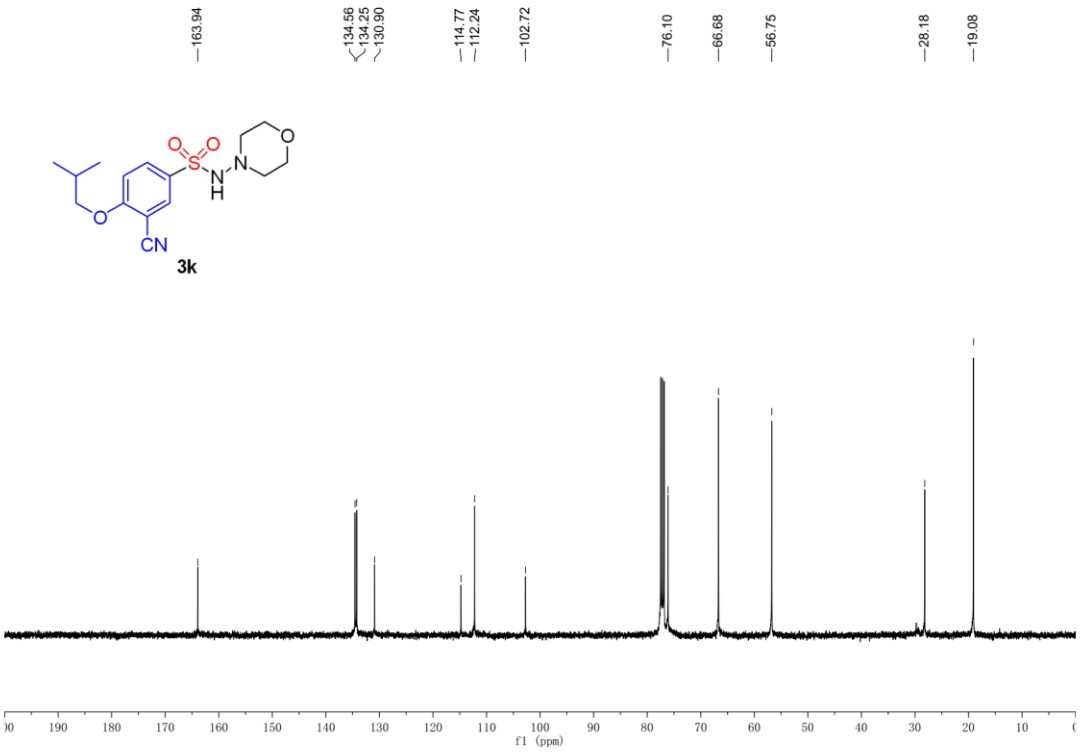
S
N
H
3i
f1 (ppm)

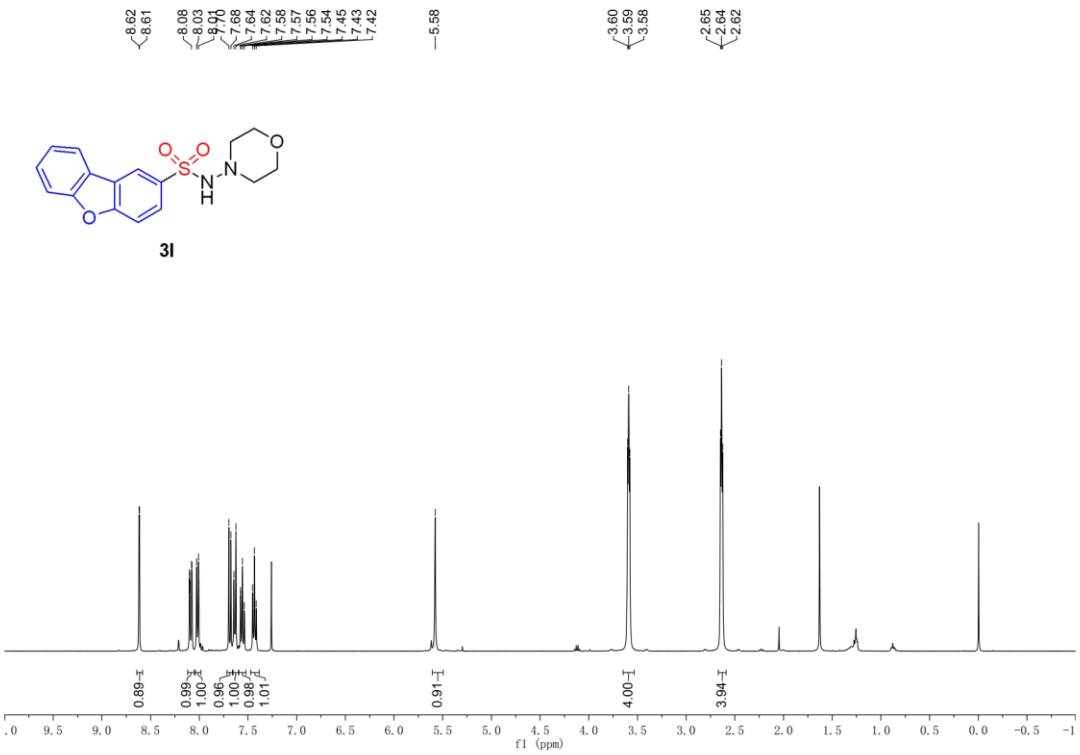

7.77
7.76
7.74
6.85
6.83
5.56
4.71
4.68
4.66
3.62
3.61
3.59
3.29
3.27
3.25
2.64
2.63
2.61
O
S
N
H
3j
1.99
1.00
1.00
2.02
3.97
2.02
4.00
f1 (ppm)


164.32
130.09
129.99
128.18
125.49
109.46
72.45
66.81
56.88
29.11
3j
f1 (ppm)

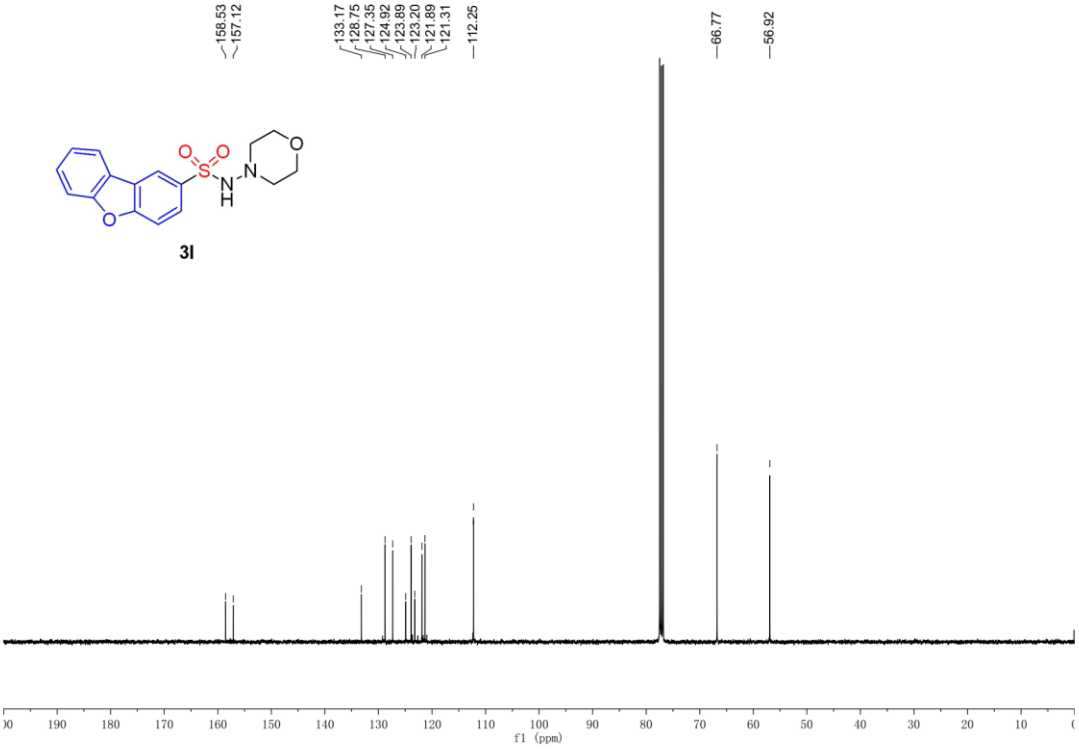

8.16
8.15
8.10
8.10
8.08
8.08
7.07
7.05
5.96
3.92
3.90
3.63
3.62
3.60
2.67
2.65
2.64
2.22
2.20
2.18
1.09
1.07
CN
3k
2.00
1.02
1.01
2.10
4.00
4.01
1.14
6.13
f1 (ppm)


163.94
134.56
134.25
130.90
114.77
112.24
102.72
76.10
66.68
56.75
28.18
19.08
O
S
O
N
H
N
O
O
CN
f1 (ppm)

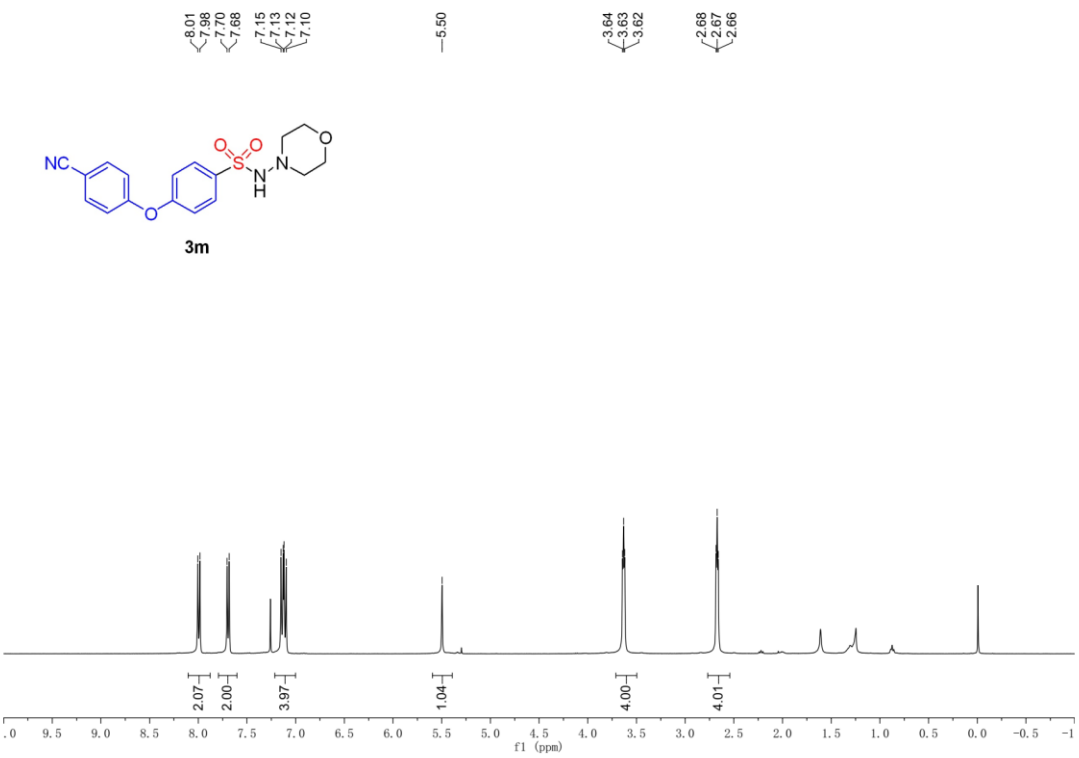
3k


8.62
8.61
8.08
8.03
7.68
7.64
7.62
7.58
7.57
7.56
7.54
7.45
7.43
7.42
5.58
3.60
3.59
3.58
2.65
2.64
2.62
O
S
O
N
H
N
O
O
0.89
0.99
1.00
0.96
1.00
0.98
1.01
0.91
4.00
3.94
f1 (ppm)

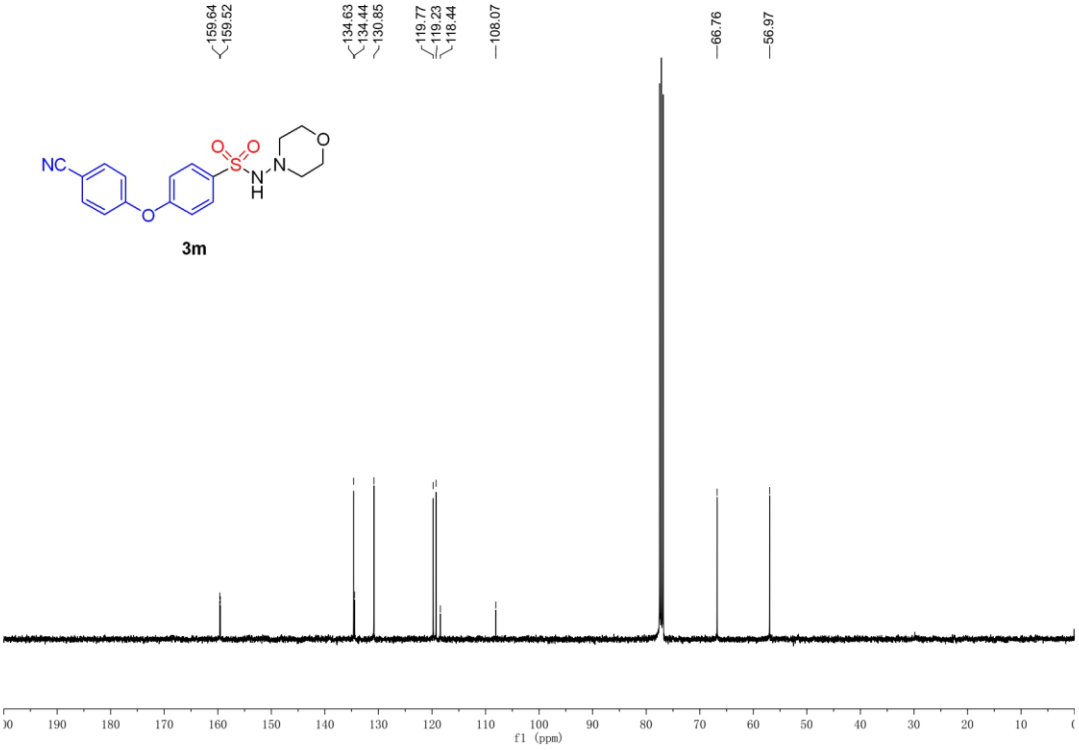
3l

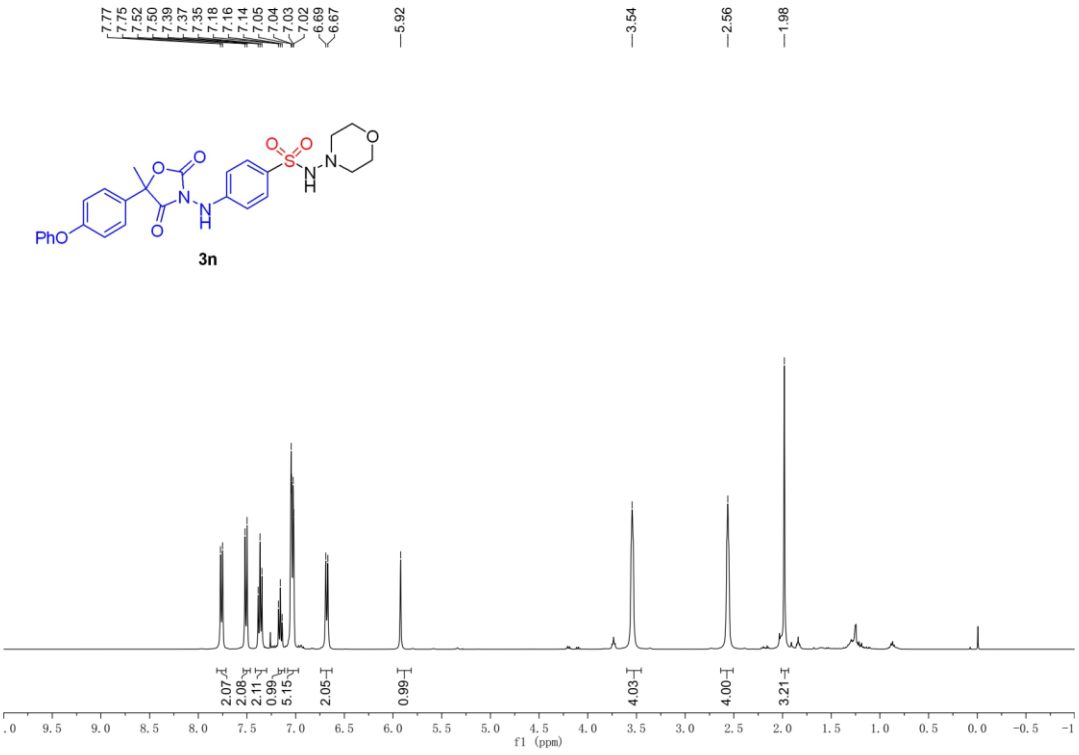

158.53
157.12
133.17
128.75
127.35
124.92
123.89
123.20
121.89
121.31
112.25
66.77
56.92
f1 (ppm)

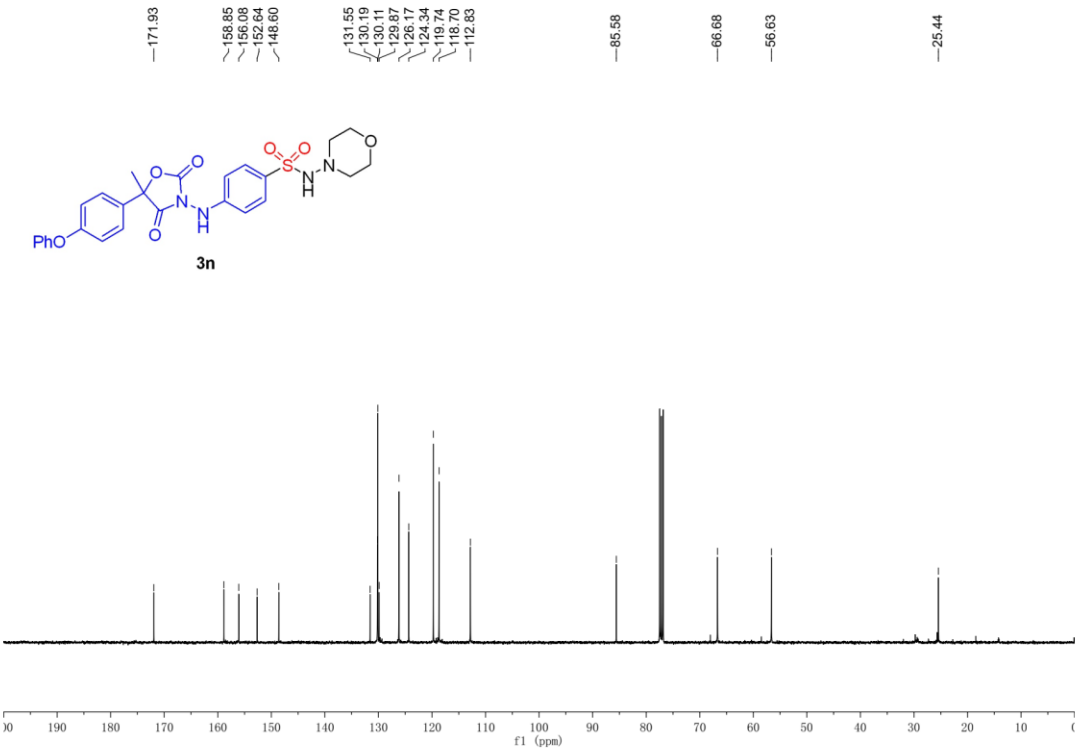
3l

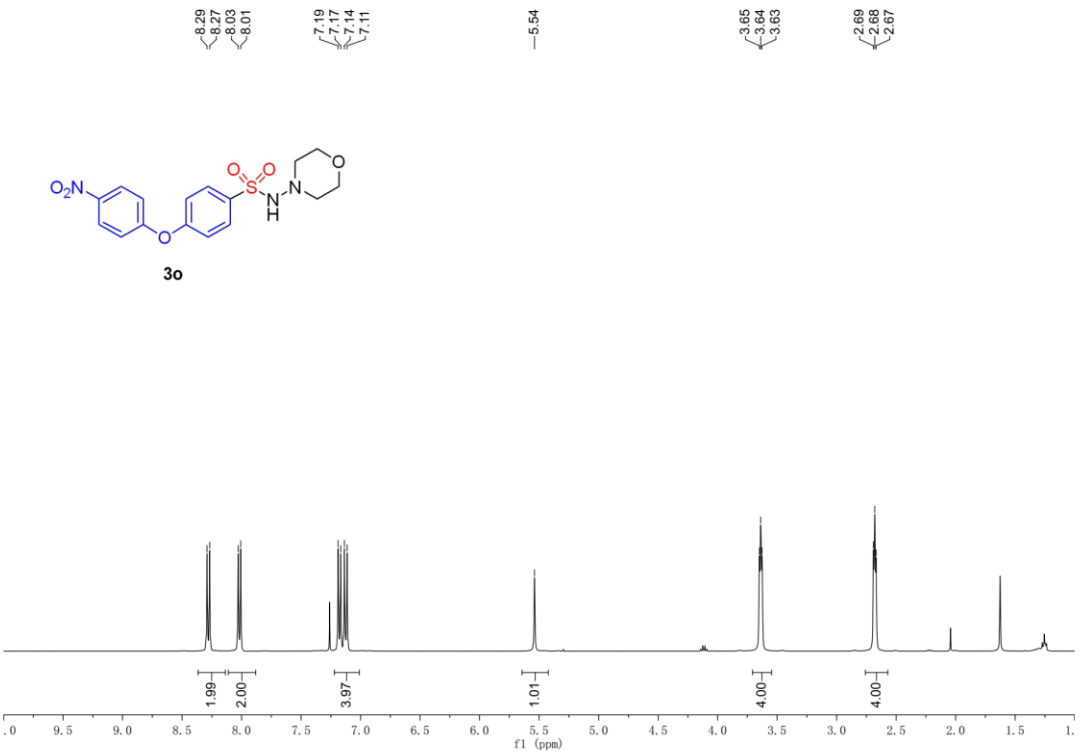

8.01
7.98
7.70
7.68
7.15
7.13
7.12
7.10
5.50
3.64
3.63
3.62
2.68
2.67
2.66
2.07
2.00
3.97
1.04
4.00
4.01
f1 (ppm)

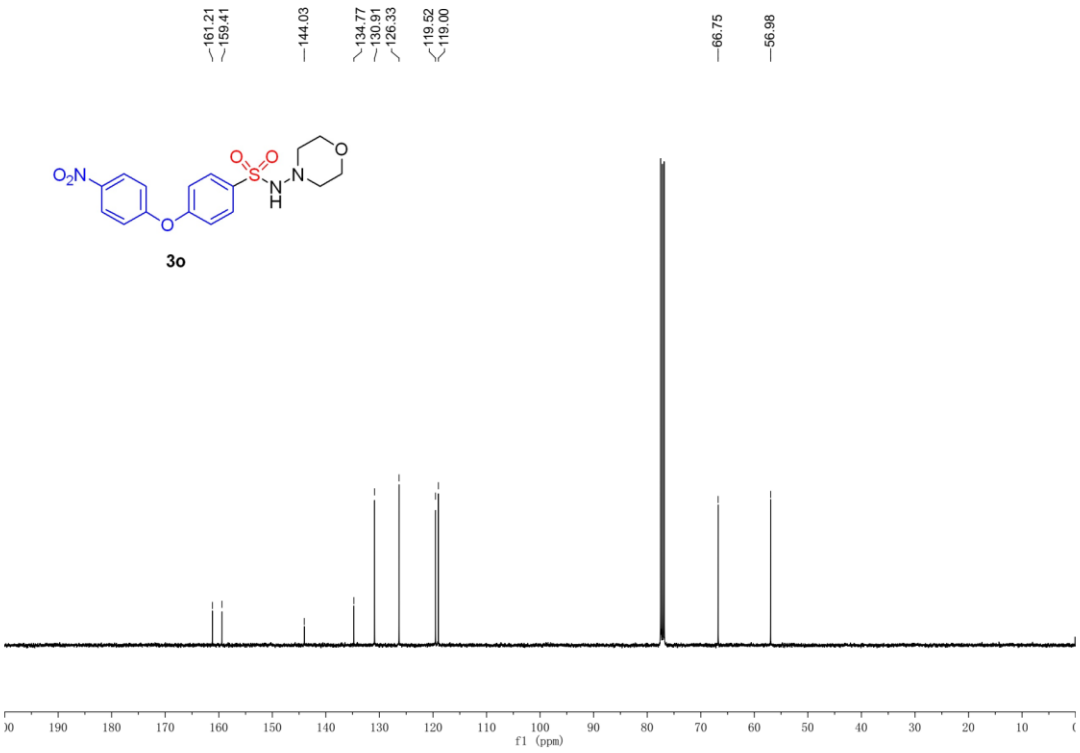
3m

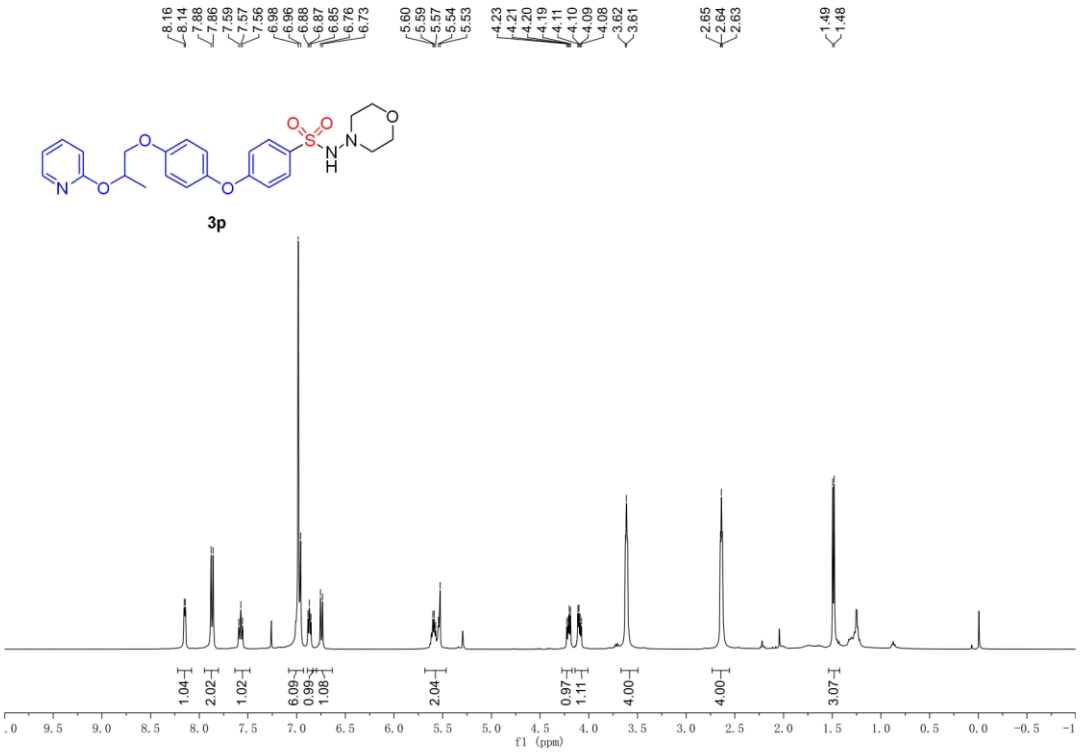

159.64
159.52
134.63
134.44
130.85
119.77
119.23
118.44
108.07
66.76
56.97
NC
O
S
O
N
N
H
O
3m
f1 (ppm)

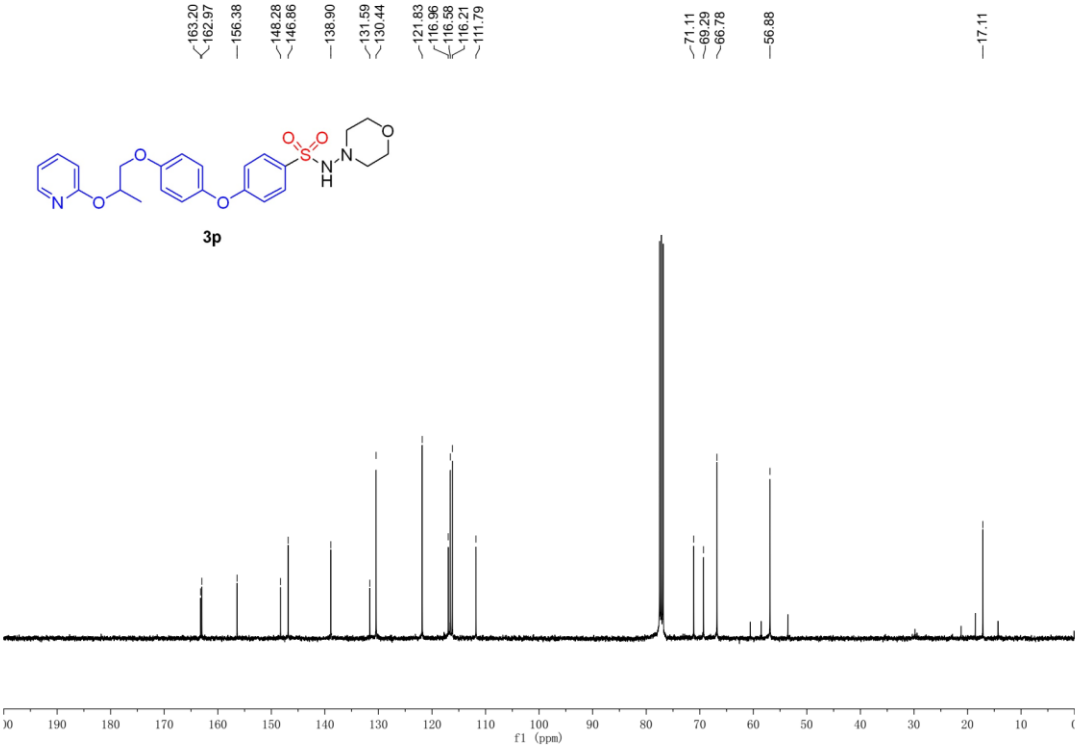

7.77
7.75
7.52
7.50
7.39
7.37
7.35
7.18
7.16
7.14
7.05
7.04
7.03
7.02
6.69
6.67
5.92
3.54
2.56
1.98
PhO
O
S
O
N
N
H
O
3n
2.07
2.08
2.11
0.99
5.15
2.05
0.99
4.03
4.00
3.21
f1 (ppm)

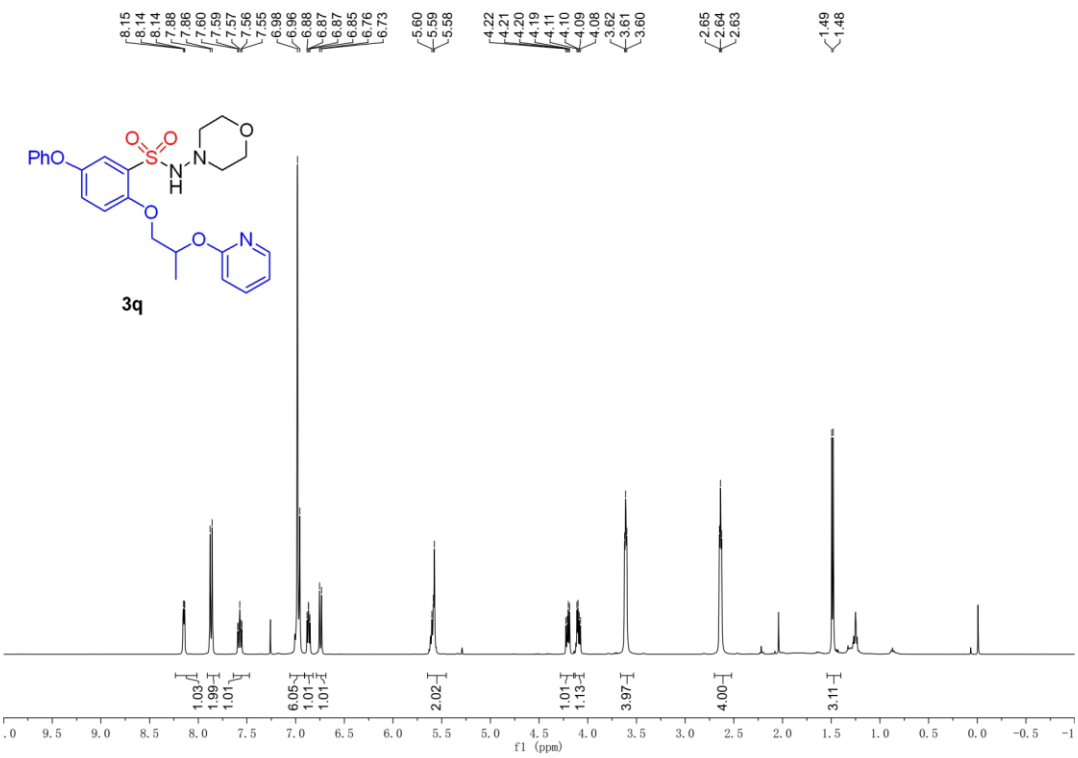

171.93
158.85
156.08
152.64
148.60
131.55
130.19
130.11
129.87
126.17
124.34
119.74
118.70
112.83
85.58
66.68
56.63
25.44
PhO
3n
f1 (ppm)

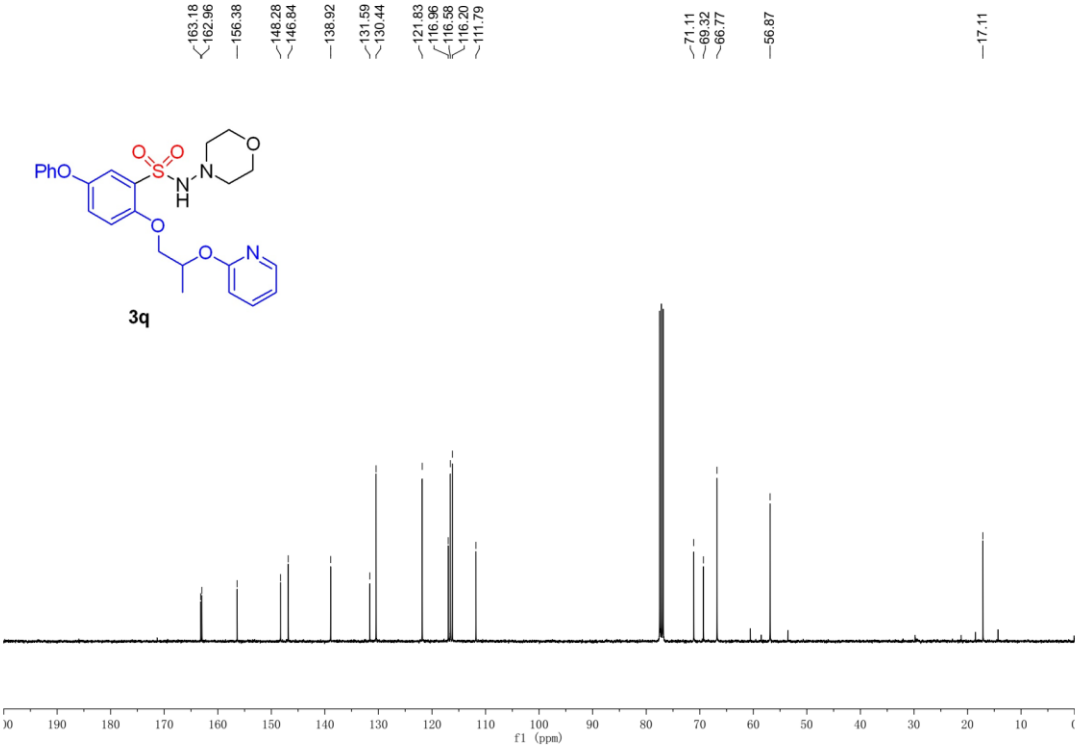

8.29
8.27
8.03
8.01
7.19
7.17
7.14
7.11
5.54
3.65
3.64
3.63
2.69
2.68
2.67
O2N
3o
1.99
2.00
3.97
1.01
4.00
4.00
f1 (ppm)

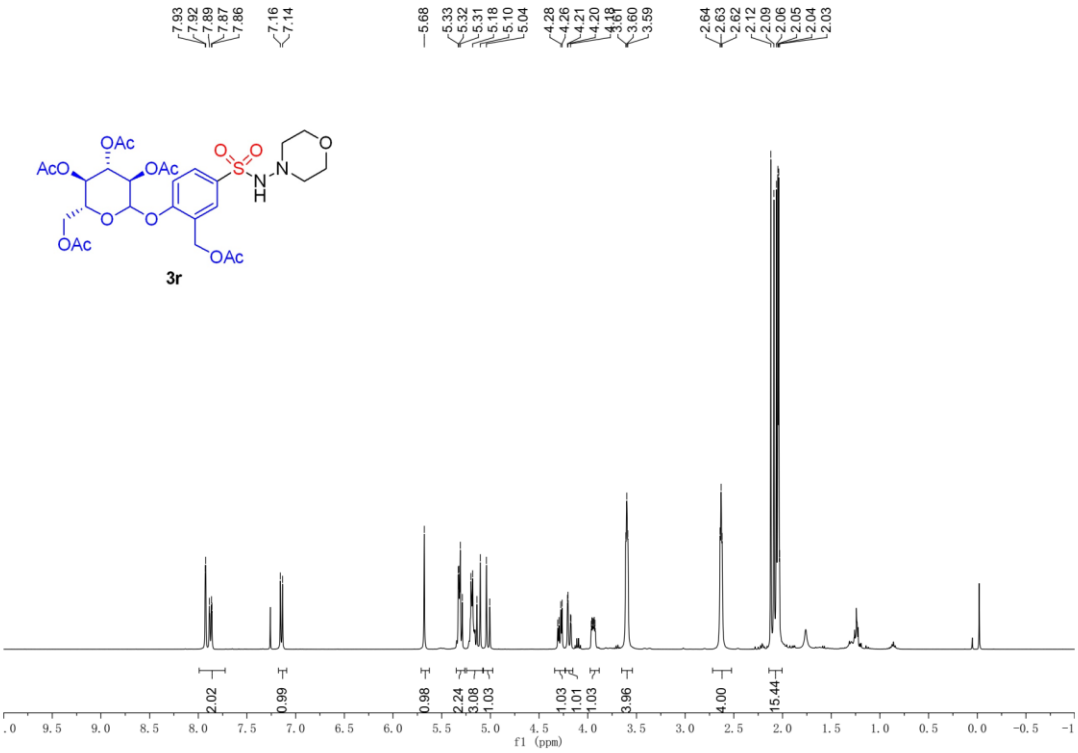

161.21
159.41
144.03
134.77
130.91
126.33
119.52
119.00
66.75
56.98
3o
f1 (ppm)


8.16
8.14
7.88
7.86
7.59
7.57
7.56
6.98
6.96
6.88
6.87
6.85
6.76
6.73
5.60
5.59
5.57
5.54
5.53
4.23
4.21
4.20
4.19
4.11
4.10
4.09
4.08
3.62
3.61
2.65
2.64
2.63
1.49
1.48
3p
1.04
2.02
1.02
6.09
0.99
1.08
2.04
0.97
1.11
4.00
4.00
3.07
f1 (ppm)


163.20
162.97
156.38
148.28
146.86
138.90
131.59
130.44
121.83
116.96
116.58
116.21
111.79
71.11
69.29
66.78
56.88
17.11
3p
f1 (ppm)


8.15
8.14
8.14
7.88
7.86
7.60
7.59
7.57
7.56
7.55
6.98
6.96
6.88
6.87
6.85
6.76
6.73
5.60
5.59
5.58
4.22
4.21
4.20
4.19
4.11
4.10
4.09
4.08
3.62
3.61
3.60
2.65
2.64
2.63
1.49
1.48
PhO
3q
1.03
1.99
1.01
6.05
1.01
1.01
2.02
1.01
1.13
3.97
4.00
3.11
f1 (ppm)


163.18
162.96
156.38
148.28
146.84
138.92
131.59
130.44
121.83
116.96
116.58
116.20
111.79
71.11
69.32
66.77
56.87
17.11
PhO
O
S
O
N
H
O
O
O
N
3q
f1 (ppm)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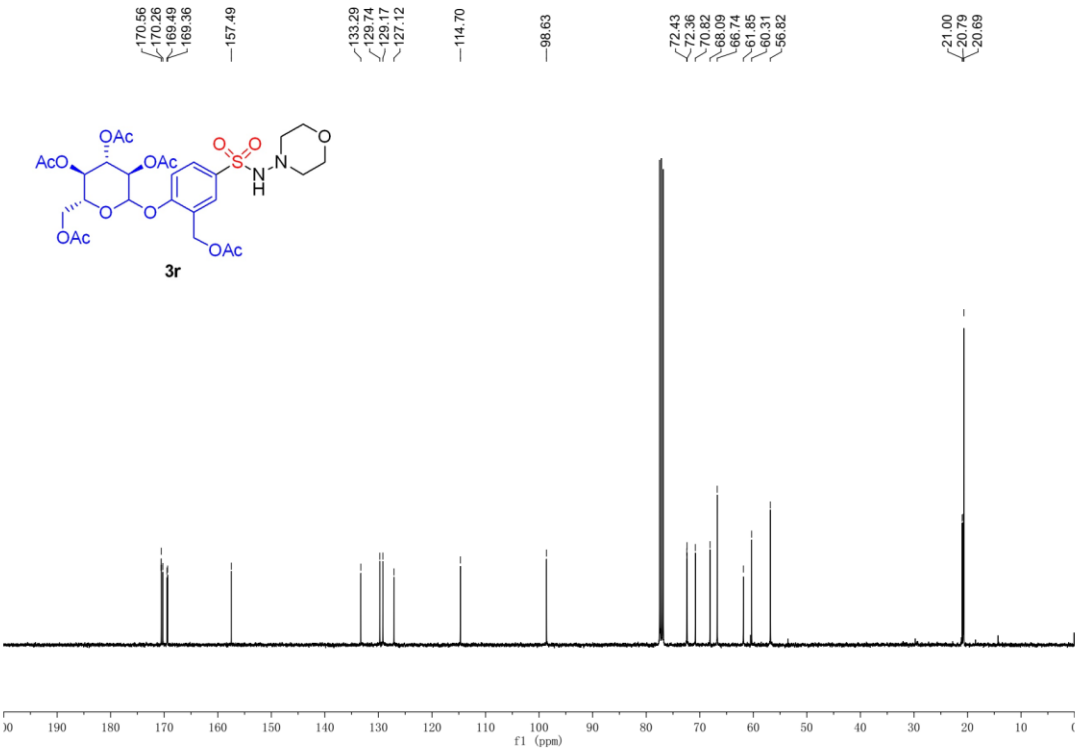
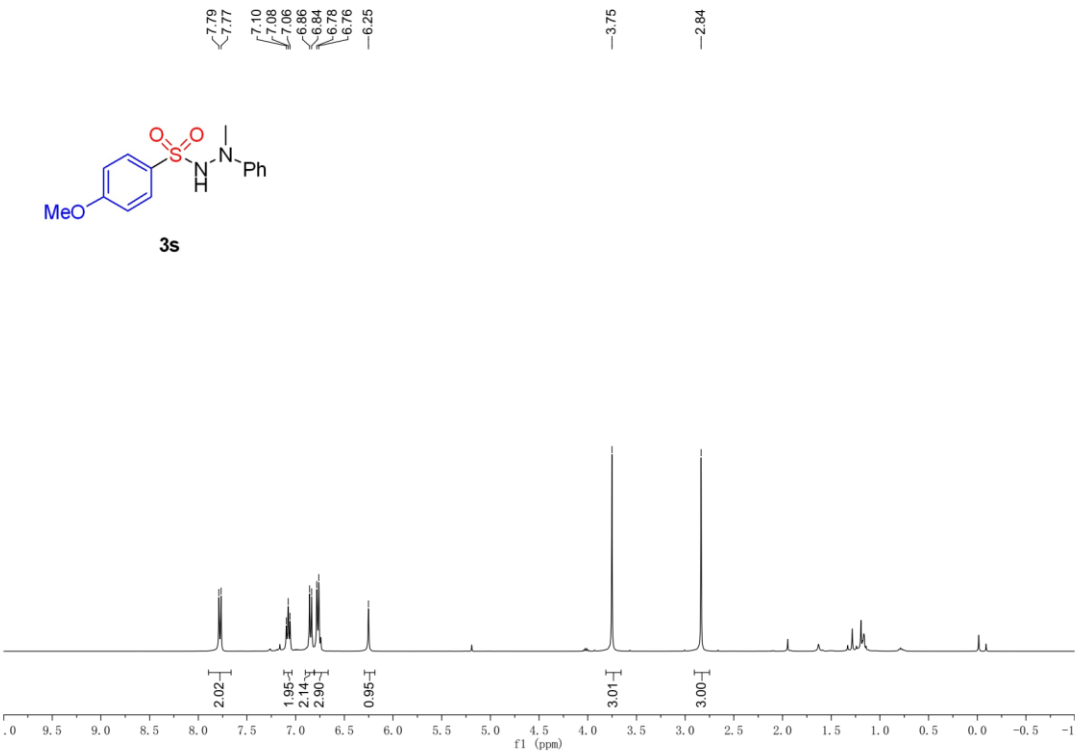
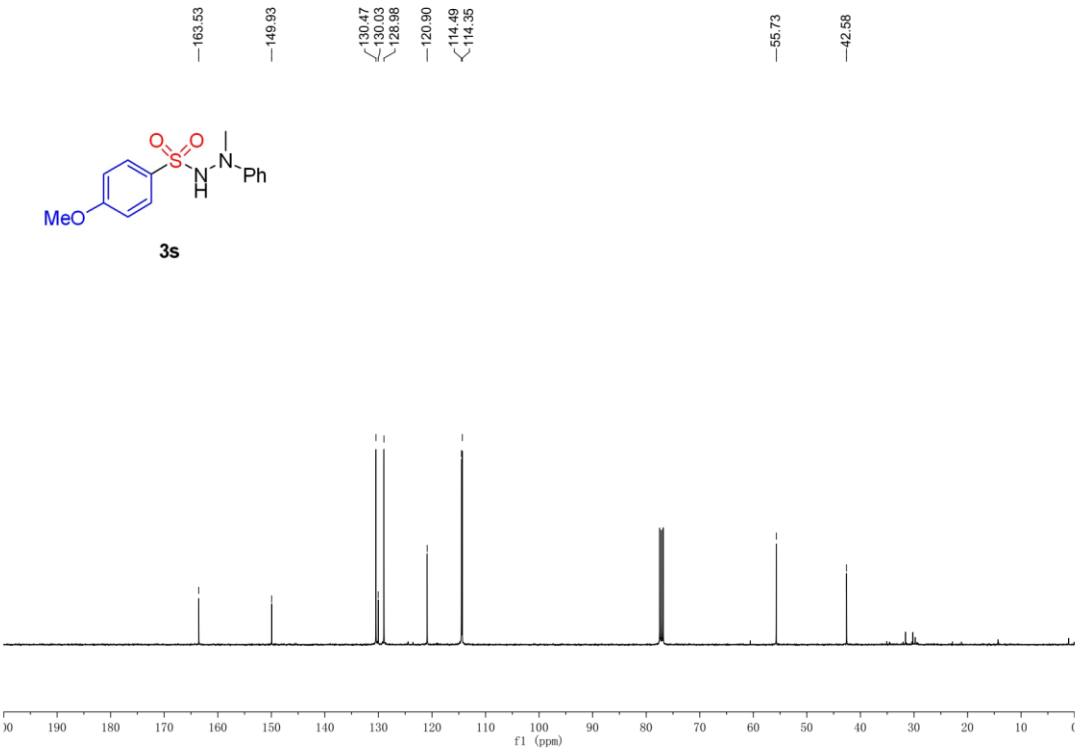
7.92
7.89
7.87
7.86
7.16
7.14
5.68
5.33
5.32
5.31
5.18
5.10
5.04
4.28
4.26
4.21
4.20
4.18
3.61
3.60
3.59
2.64
2.63
2.62
2.12
2.08
2.06
2.05
2.04
2.03
OAc
AcO
OAc
O
S
O
N
H
O
O
OAc
OAc
3r
2.02
0.99
0.98
2.24
3.08
1.03
1.03
1.01
1.03
3.96
4.00
15.44
f1 (ppm)

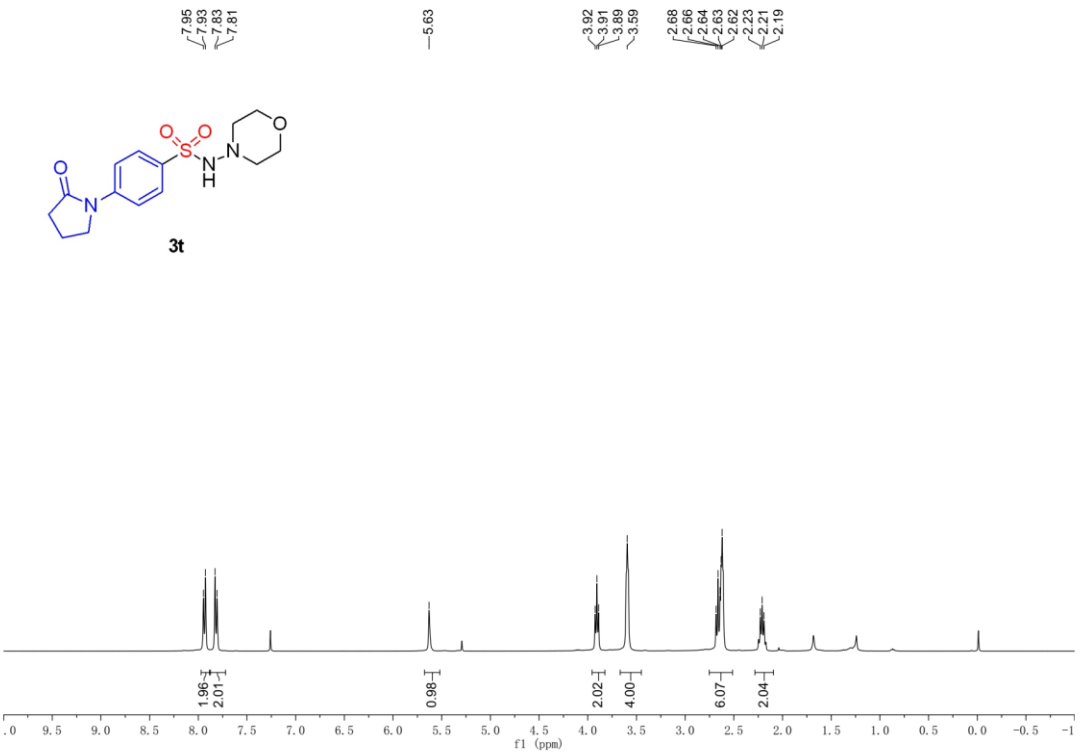

170.56
170.26
169.49
169.36
157.49
133.29
129.74
129.17
127.12
114.70
98.63
72.43
72.36
70.82
68.09
66.74
61.85
60.31
56.82
21.00
20.79
20.69
OAc
AcO
OAc
OAc
OAc
O
S
O
N
H
N
O
f1 (ppm)

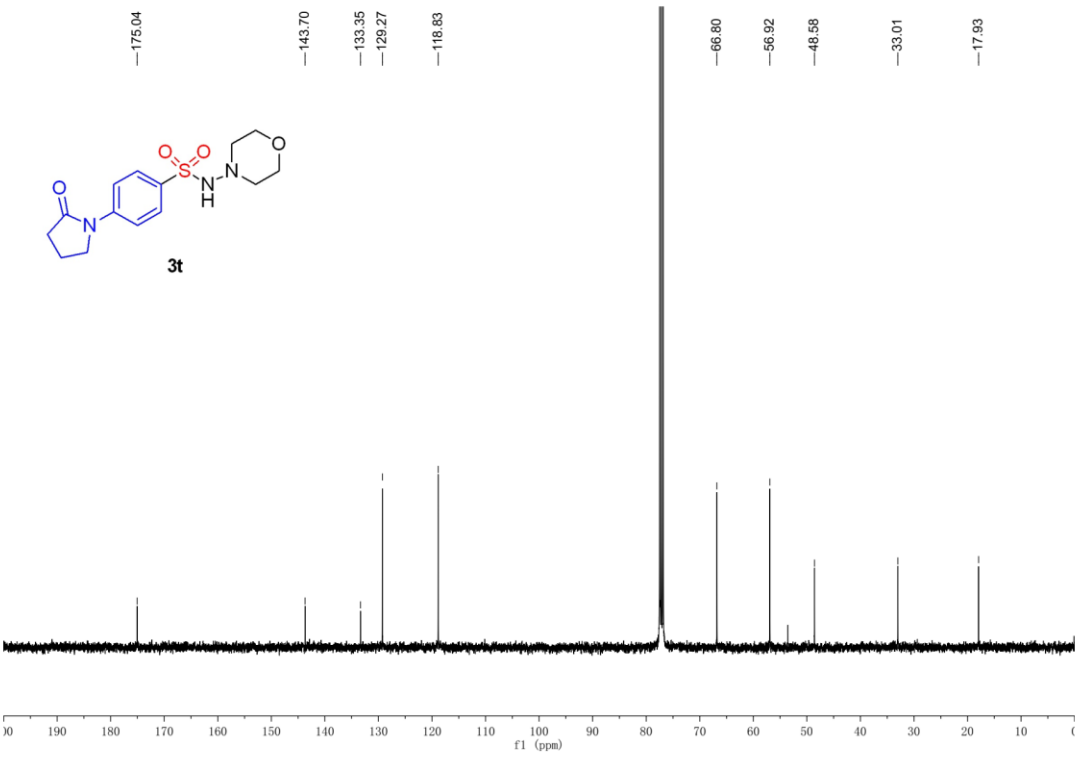
3r


7.79
7.77
7.10
7.08
7.06
6.86
6.84
6.78
6.76
6.25
3.75
2.84
O
S
O
N
N
Ph
H
MeO
2.02
1.95
2.14
2.90
0.95
3.01
3.00
f1 (ppm)

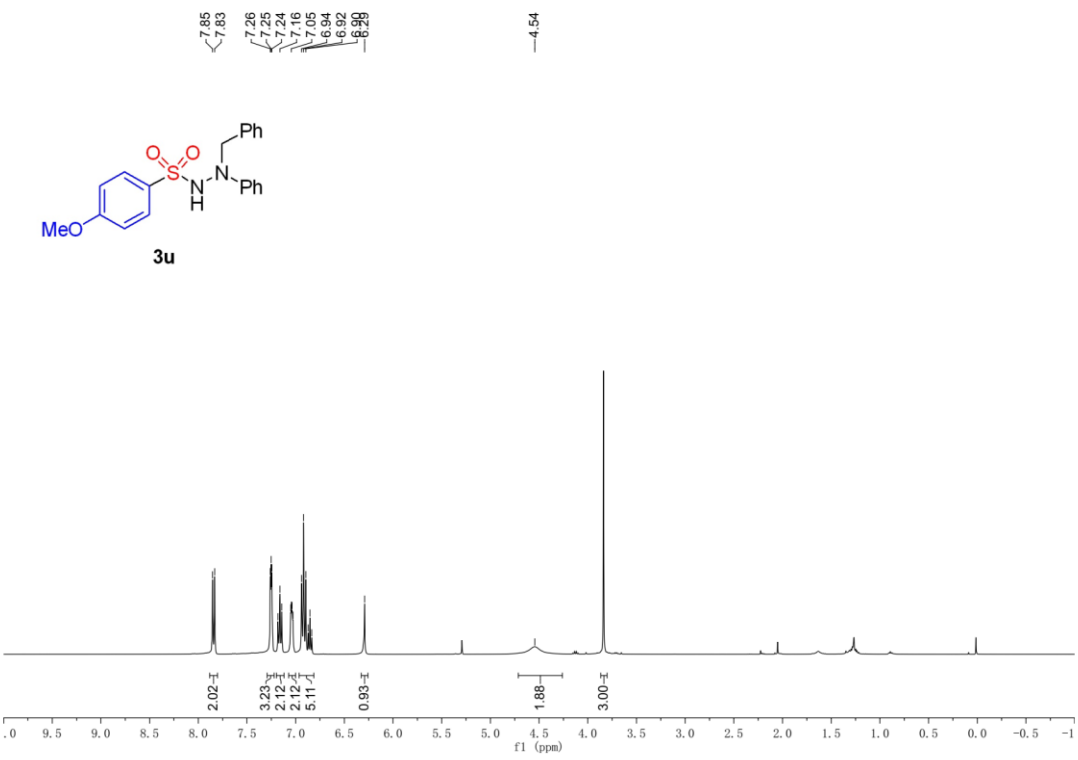
3s


163.53
149.93
130.47
130.03
128.98
120.90
114.49
114.35
55.73
42.58
MeO
Ph
3s
f1 (ppm)

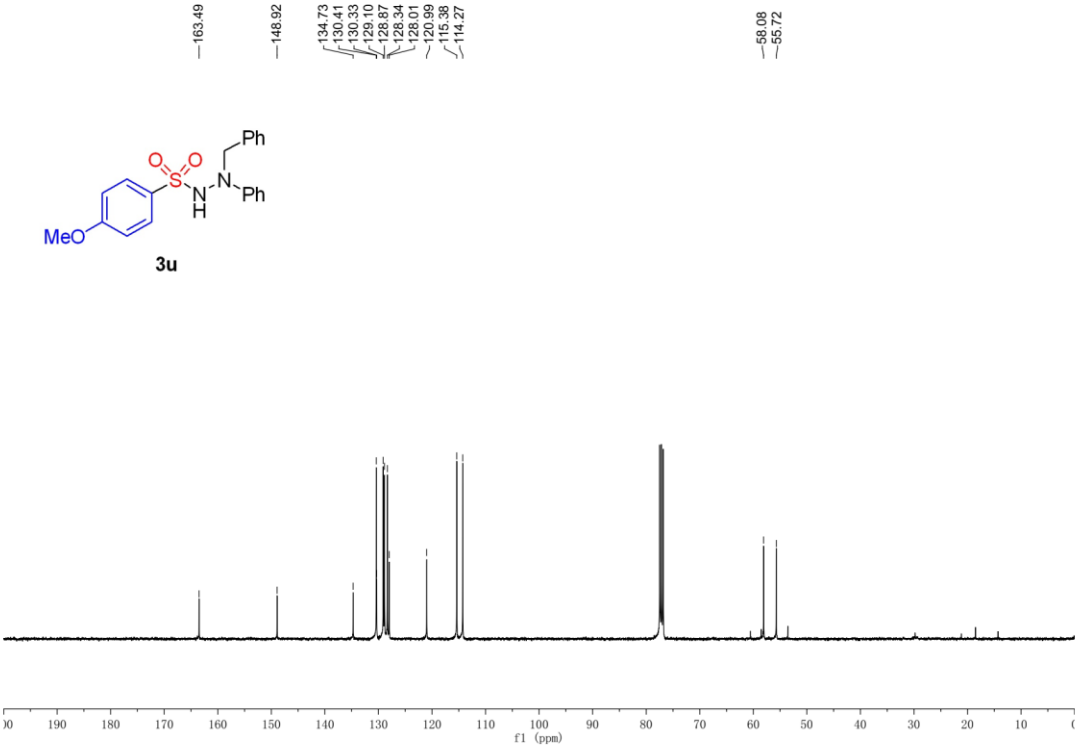

7.95
7.93
7.83
7.81
5.63
3.92
3.91
3.89
3.59
2.68
2.66
2.64
2.63
2.62
2.23
2.21
2.19
3t
1.96
2.01
0.98
2.02
4.00
6.07
2.04
f1 (ppm)

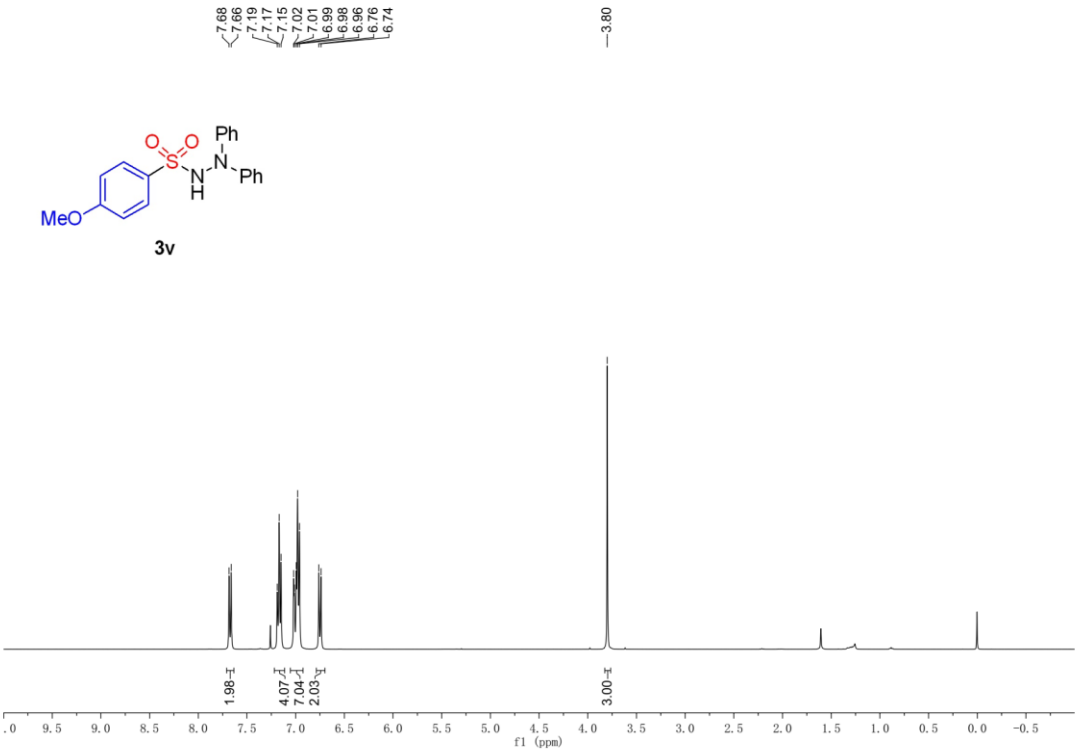

175.04
143.70
133.35
129.27
118.83
66.80
56.92
48.58
33.01
17.93
f1 (ppm)

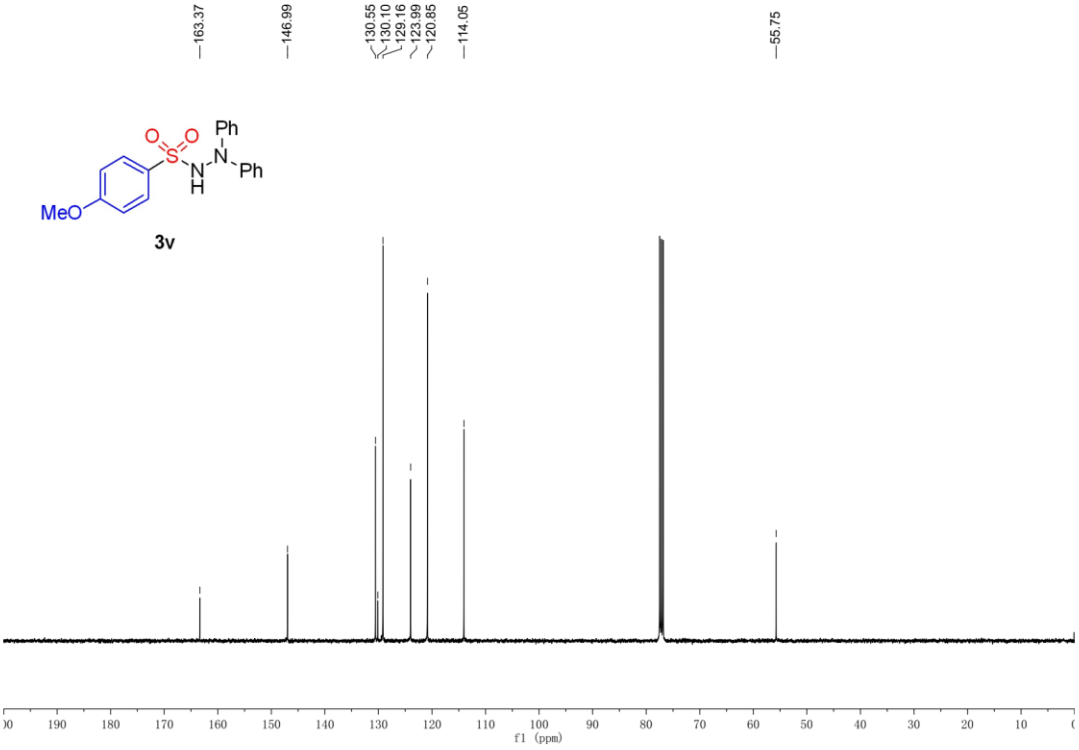
3t


7.85
7.83
7.26
7.25
7.24
7.16
7.05
6.94
6.92
6.90
6.89
4.54
2.02
3.23
2.12
2.12
5.11
0.93
1.88
3.00
f1 (ppm)

3u


163.49
148.92
134.73
130.41
130.33
129.10
128.87
128.34
128.01
120.99
115.38
114.27
58.08
55.72
Ph
Ph
Ph
MeO
3u
f1 (ppm)


7.68
7.66
7.19
7.17
7.15
7.02
7.01
6.99
6.98
6.96
6.76
6.74
3.80
Ph
Ph
Ph
MeO
3v
1.98
4.07
7.04
2.03
3.00
f1 (ppm)


163.37
146.99
130.55
130.10
129.16
123.99
120.85
114.05
55.75
O
O
S
N
H
N
Ph
Ph
MeO
3v
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)