Photocatalyzed Transfer Hydrogenation and Deuteriation of Cyclic *N*-Sulfonylimines

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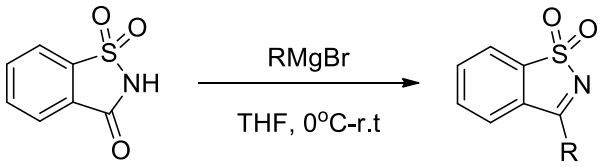
Table of contents

Part I General Method

The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox (Mikrouna, Supper 1220/750). Anhydrous THF (Tetrahydrofuran) and dioxane were distilled from sodium benzophenone ketyl prior to use. Anhydrous CH_3CN and DCE (Dichloroethane) was distilled from calcium hydride and stored under argon. Cyclic *N*-sulfonylimines **1a-u** were prepared according to the reported references.[1-4] ^{1}HNMR and ^{13}C NMR spectra were recorded on Bruker-Avance 400 MHz spectrometer. $CDCl_3$ was used as solvent. Chemical shifts (δ) were reported in ppm with tetramethylsilane as internal standard, and J values were given in Hz. Melting points were measured on X-4 melting point apparatus and uncorrected. High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer. Column chromatography was performed with silica gel (200-300 mesh) with petroleum ether and ethyl acetate as eluents.

Part II Procedure for the reactions

Typical procedure for the preparation of cyclic *N*-sulfonylimines[1-3].



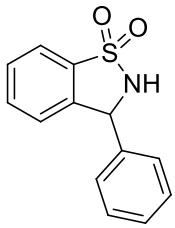
The Grignard reagent was typically prepared using flame-dried magnesium turnings (2.0 equiv) with a few crystals of I_2 in anhydrous THF (10 mL). The aryl halide (1.0 equiv) was added to the solution until initiation of the Grignard reagent, after which the remaining aryl halide was added dropwise at 0 °C. The reaction was stirred 2 h at room temperature, then titrated. The Grignard reagent (2.0 equiv) was then slowly added to a solution of saccharin (1.0 equiv) in THF (6 mL) at 0 °C. The reaction was allowed to warm and stirred at 22 °C overnight. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) and extracted with EtOAc (3 x 20 mL). The solvent was removed under reduced pressure and the crude product was dissolved in toluene (30 mL), followed by the addition of TsOH (200 mg, 1.2 mmol). The resulting solution was heated to reflux for 2h. The solvent was removed and then a saturated aqueous NH_4Cl solution (20 mL) was added. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuum. The product was purified by recrystallization from hot absolute ethanol and chloroform or by flash column chromatography using silica gel to obtain the corresponding *N*-sulfonylimines. Compounds **1a-t** were prepared in similar methods.

Typical procedure for the preparation of *N*-sulfonylimine 1u[4]:
A 50 mL Schlenck flask containing CH_2Cl_2 (30 mL) was charged with benzenesulfinamide (314 mg, 2.0 mmol), acetophenone (1.2 mL, 10 mmol) and $Ti(OEt)_4$ (1.7 mL, 8.0 mmol). The resulting solution was refluxed and monitored by TLC until complete consumption of benzenesulfinamide. Then, CH_3OH (6 mL) and a few drops of $NaHCO_3$ were added. The solution was filtered through anhydrous Na_2SO_4 and washed with EtOAc. The solvent was removed under reduced pressure and the crude product was dissolved in CH_2Cl_2 (10 mL) followed by the addition of *m*-CPBA (0.7 mg, 3.0 mmol). After the completion of the reaction, the solution was washed with saturated solution of $NaHCO_3$ and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using hexanes and EtOAc (10:1) to obtain the corresponding *N*-sulfonylimine **1u** in 66% yield.

Typical procedure for the transfer hydrogenation of cyclic *N*-sulfonylimines:
N-Sulfonylimines **1a** (24.3 mg, 0.1 mmol), catalyst $Ir(ppy)_3$ (1.3 mg, 0.02 mmol), PhSSPh (8.7 mg, 0.04 mmol) and 2.0 mL THF were added to a Schlenk tube under argon atmosphere, and then DIEDA (8.7 μL, 0.05 mmol) and H_2O (180 μL, 10mmol) was injected using a micro-syringe. The mixture was placed under a 30 W blue LED light source and stirred at room temperature. Upon completion of the reaction, the reaction mixture was concentrated, and the residue was purified by chromatography on a silica gel column to afford the desired product **2a** (24.3 mg, 99% yield).

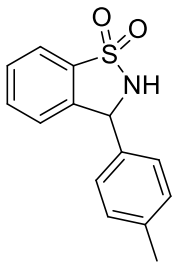
Part III Characterization Data of the products

3-phenyl-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2a)[2]



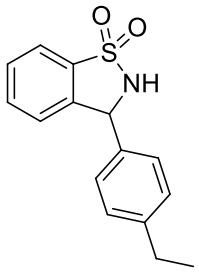
White solid, 99% yield, Mp 128-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.8, 3.0 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.40 (s, 5H), 7.16 (dd, *J* = 5.3, 2.9 Hz, 1H), 5.74 (d, *J* = 4.1 Hz, 1H), 5.14 (d, *J* = 3.2 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ139.8, 138.7, 134.7, 133.4, 129.5, 129.3, 129.1, 127.6, 125.4, 121.2, 61.4.

3-(p-tolyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2b)[2]



White solid, 98% yield, Mp 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.7, 3.0 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.30 – 7.24 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.15 (dd, *J* = 5.4, 2.9 Hz, 1H), 5.71 (d, *J* = 3.6 Hz, 1H), 5.01 (s, 1H), 2.37 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 139.1, 135.8, 134.8, 133.4, 129.9, 129.4, 127.6, 125.4, 121.1, 61.2, 21.2.

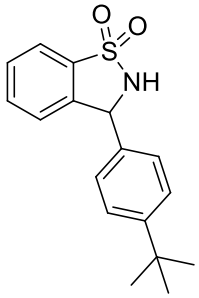
3-(4-ethylphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2c)



White solid, 89% yield, Mp 120-123°C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.40 (m, 2H), 7.19 (d, *J* = 7.1 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 6.6 Hz, 1H), 5.62 (d, *J* = 3.7 Hz, 1H), 4.91 (d, *J* = 2.3 Hz, 1H), 2.57 (q, *J* = 7.5 Hz, 2H), 1.15 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 140.1, 135.9, 134.9, 133.3, 129.4, 128.8, 127.6, 125.4, 121.1, 61.3, 28.6, 15.4. HRMS calcd for $C_{15}H_{15}NO_2S$ $[M]^+$: 273.0824. Found: 273.0827.

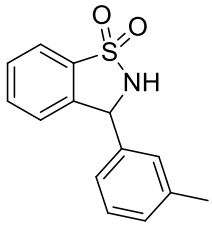
3-(4-(*tert*-butyl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole

1,1-dioxide(2d)



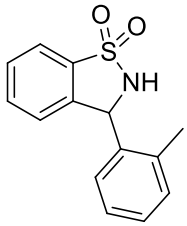
White solid, 98% yield, Mp 128-130°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 1H), 7.58 – 7.50 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.16 (d, *J* = 7.0 Hz, 1H), 5.70 (d, *J* = 3.9 Hz, 1H), 5.04 (d, *J* = 3.6 Hz, 1H), 1.30 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 140.1, 135.6, 134.9, 133.3, 129.4, 127.4, 126.2, 125.5, 121.1, 61.2, 34.7, 31.3. HRMS calcd for $C_{17}H_{19}NO_2S$ $[M]^+$: 301.1137. Found: 301.1140.

3-(*m*-tolyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2e) [2]



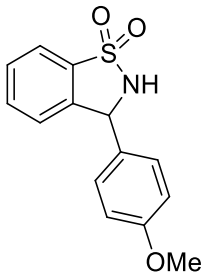
White solid, 98% yield, Mp 155-158 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.27 (dd, *J* = 9.7, 5.6 Hz, 1H), 7.16 (t, *J* = 9.9 Hz, 4H), 5.68 (d, *J* = 3.7 Hz, 1H), 5.05 (d, *J* = 2.1 Hz, 1H), 2.34 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 138.2, 137.5, 133.7, 132.3, 128.9, 128.4, 128.1, 127.1, 124.4, 123.7, 120.1, 60.4, 20.37.

3-(*o*-tolyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2f) [2]



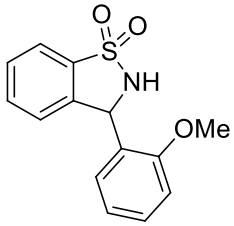
White solid, 98% yield, Mp 67-69 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 1H), 7.65 – 7.54 (m, 2H), 7.30 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 7.17 – 7.12 (m, 2H), 6.03 (d, *J* = 4.5 Hz, 1H), 4.86 (d, *J* = 4.1 Hz, 1H), 2.48 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 136.8, 136.2, 135.7, 133.3, 131.3, 129.5, 129.1, 128.1, 127.1, 125.2, 121.3, 58.3, 19.4 .

3-(4-methoxyphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2g)[2]



White solid, 98% yield, Mp 150-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.76 (m, 1H), 7.65 – 7.47 (m, 2H), 7.30 – 7.19 (m, 2H), 7.13 (d, *J* = 6.7 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.68 (d, *J* = 3.9 Hz, 1H), 5.00 (d, *J* = 3.5 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 140.3, 135.0, 133.3, 130.6, 129.4, 129.0, 125.4, 121.1, 114.6, 61.0, 55.4.

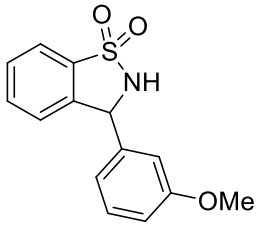
3-(2-methoxyphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2h)[6]



White solid, 93% yield, Mp 168-170 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 6.5, 2.1 Hz, 1H), 7.53 (m, 2H), 7.34 (m, 1H), 7.25 (ddd, *J* = 8.3, 7.0, 2.2 Hz, 2H), 6.99 – 6.92 (m, 2H),

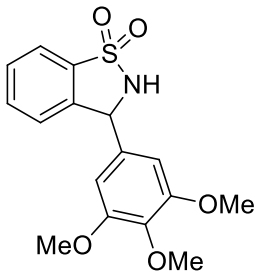
6.15 (d, *J* = 5.0 Hz, 1H), 5.14 (d, *J* = 4.7 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 140.4, 135.3, 133.1, 130.2, 129.2, 128.7, 126.4, 125.2, 121.3, 121.1, 111.1, 56.4, 55.6 .

3-(3-methoxyphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2i)



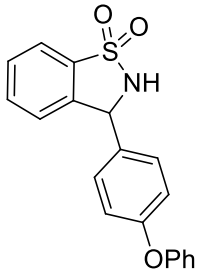
White solid, 94% yield, Mp 133-135 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 1H), 7.62 – 7.49 (m, 2H), 7.33 – 7.25 (m, 1H), 7.18 (t, *J* = 6.3 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.93 – 6.86 (m, 2H), 5.69 (d, *J* = 3.9 Hz, 1H), 5.10 (d, *J* = 3.0 Hz, 1H), 3.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3 , 140.2, 139.7, 134.7, 133.4, 130.3, 129.5, 125.4, 121.2, 119.7, 114.6, 112.9, 61.3, 55.4. HRMS calcd for $C_{14}H_{13}NO_3S$ $[M]^+$: 275.0616. Found: 275.0609.

3-(3,4,5-trimethoxyphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2j)[5]



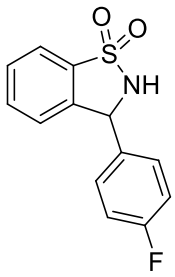
Yellow solid , 78% yield, Mp 189-191 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.75 (m, 1H), 7.68 – 7.49 (m, 2H), 7.24 – 7.15 (m, 1H), 6.57 (s, 2H), 5.63 (d, *J* = 2.3 Hz, 1H), 5.24 (s, 1H), 3.81 (d, *J* = 3.2 Hz, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 139.6, 138.3, 134.7, 134.3, 133.4, 129.6, 125.3, 121.2, 104.4, 61.6, 60.8, 56.2.

3-(4-phenoxyphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2k)



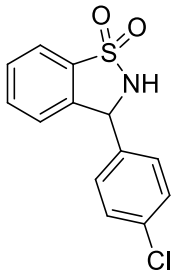
White solid, 91% yield, Mp 91-93°C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.82 (m, 1H), 7.67 – 7.53 (m, 2H), 7.41 – 7.30 (m, 4H), 7.17 (dd, *J* = 14.9, 7.4 Hz, 2H), 7.09 – 6.95 (m, 4H), 5.74 (d, *J* = 3.9 Hz, 1H), 5.03 (d, *J* = 3.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 156.4, 139.9, 134.9, 133.4, 133.1, 129.9, 129.6, 129.2, 125.4, 123.9, 121.2, 119.4, 119.0, 60.9. HRMS calcd for $C_{19}H_{15}NO_3S$ $[M]^+$: 337.0773. Found: 337.0781.

3-(4-fluorophenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2l)[2]



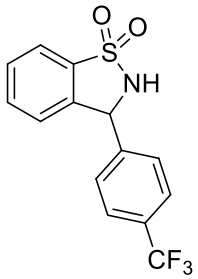
White solid, 98% yield, Mp 163-166 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (m, 1H), 7.62 – 7.49 (m, 2H), 7.41 – 7.29 (m, 2H), 7.15 – 7.10 (m, 1H), 7.06 (t, *J* = 8.6 Hz, 2H), 5.72 (d, *J* = 4.1 Hz, 1H), 5.22 (d, *J* = 3.6 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 161.8, 139.6, 134.7, 134.6, 134.6, 133.5, 129.7, 129.5, 129.4, 125.3, 121.2, 116.4, 116.2, 60.6.

3-(4-chlorophenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2m)[5]



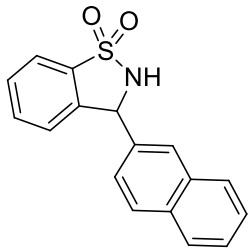
Light yellow solid, 98% yield, Mp 179-181 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 1H), 7.61 – 7.53 (m, 2H), 7.40 – 7.28 (m, 4H), 7.17 – 7.02 (m, 1H), 5.71 (d, *J* = 3.9 Hz, 1H), 5.18 (d, *J* = 3.4 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 137.3, 135.1, 134.6, 133.5, 129.8, 129.5, 128.9, 125.3, 121.3, 60.6.

3-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2n)



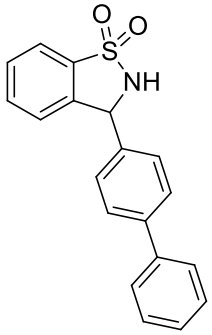
Yellow solid , 98% yield, Mp 134-136 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.2, 2.0 Hz, 1H), 7.68 – 7.50 (m, 6H), 7.18 – 7.09 (m, 1H), 5.81 (s, 1H), 5.42 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 138.7, 134.4, 133.6, 129.9, 127.9, 126.3, 126.2, 125.3, 121.4, 60.6. HRMS calcd for $C_{14}H_{10}F_3NO_2S$ $[M]^+$: 313.0384. Found: 313.0382.

3-(naphthalen-2-yl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2o)



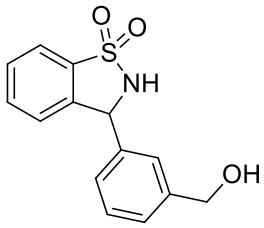
White solid, 90% yield, Mp 135-138°C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.70 (m, 5H), 7.45 (dd, *J* = 8.7, 3.5 Hz, 4H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.11 – 6.99 (m, 1H), 5.80 (d, *J* = 3.9 Hz, 1H), 5.11 (d, *J* = 3.1 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 135.9, 134.8, 133.5, 133.4, 133.1, 129.6, 127.9, 127.3, 126.9, 126.8, 125.5, 124.4, 121.2, 61.59. HRMS calcd for $C_{17}H_{13}NO_2S$ $[M]^+$: 295.0667. Found: 295.0670.

3-([1,1'-biphenyl]-4-yl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2p)



White solid, 94% yield, Mp 203-205 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 1H), 7.61 – 7.51 (m, 6H), 7.43 (dd, *J* = 11.8, 5.1 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 5.76 (d, *J* = 4.0 Hz, 1H), 5.22 (d, *J* = 3.9 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 140.2, 139.8, 137.7, 134.7, 133.5, 129.7, 129.6, 128.9, 128.9, 128.1, 127.9, 127.8, 127.5, 127.1, 126.9, 125.5, 121.2, 61.1. HRMS calcd for $C_{19}H_{15}NO_2S$ $[M]^+$: 321.0824. Found: 321.0820.

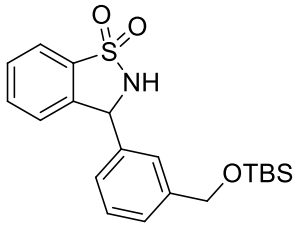
3-(3-(hydroxymethyl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2q)[2]



Colorless oil, 95% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 5.7, 3.1 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.26 (s, 1H), 7.23 – 7.14 (m, 3H), 7.05 (dd, *J* = 5.7, 2.7 Hz, 1H), 5.61 (d, *J* = 3.5 Hz, 1H), 5.58 (d, *J* = 3.7 Hz, 1H), 4.51 (s, 2H), 2.76 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$)

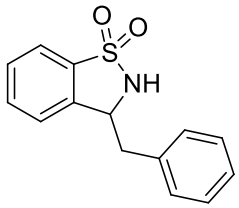
δ 142.11, 139.7, 139.1, 134.5, 133.4, 129.5, 129.3, 127.6, 126.7, 125.9, 125.4, 121.1, 64.6, 61.3.

3-(3-(((tert-butyldimethylsilyl)oxy)methyl)phenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (2r)[2]



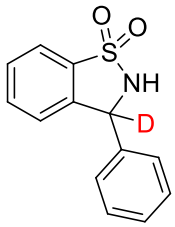
Yellow solid, 95% yield, Mp 57-59ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.78 (m, 1H), 7.55 (dd, *J* = 6.1, 2.7 Hz, 2H), 7.34 (t, *J* = 10.9 Hz, 3H), 7.26 – 7.22 (m, 1H), 7.18 – 7.07 (m, 1H), 5.72 (d, *J* = 4.0 Hz, 1H), 5.00 (d, *J* = 3.9 Hz, 1H), 4.73 (s, 2H), 0.91 (s, 9H), 0.08 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 142.2, 139.8, 139.1, 138.6, 134.8, 133.3, 129.4, 127.6 , 126.7, 126.2, 125.9, 125.4, 125.1, 121.1, 64.6, 25.9, 18.6 , -3.6, -5.3.

3-benzyl-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2s)[2]



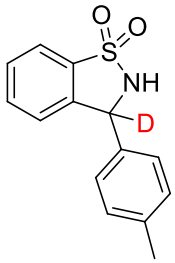
White solid, 25% yield, Mp 145-148 oC 1H NMR (400 MHz, CDCl3) δ 7.75 (d, J = 7.7 Hz, 1H), 7.60 – 7.48 (m, 2H), 7.35 – 7.22 (m, 6H), 4.84 (dt, J = 9.3, 4.5 Hz, 1H), 4.64 (s, 1H), 3.23 (dd, J = 13.8, 4.8 Hz, 1H), 2.96 (dd, J = 13.8, 9.6 Hz, 1H).13C NMR (101 MHz, CDCl3) δ 139.4, 136.4, 135.6, 133.0, 129.6, 129.4, 129.0, 127.5, 124.4, 121.5, 58.8, 42.4.

3-phenyl-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3a)



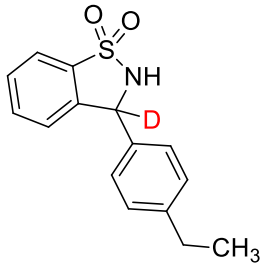
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 1H), 7.65 – 7.52 (m, 2H), 7.48 – 7.33 (m, 5H), 7.23 – 7.08 (m, 1H), 5.09 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 138.7, 134.8, 133.4, 129.6, 129.3, 129.1, 127.6, 125.4, 121.2, 61.3, 60.1 (t, *J* = 22 Hz).

3-(*p*-tolyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3b)[2]



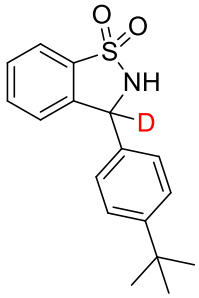
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 1H), 7.61 – 7.49 (m, 2H), 7.28 – 7.22 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 1H), 4.95 (s, 1H), 2.35 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 139.2, 135.6, 134.9, 133.4, 129.9, 129.5, 127.6, 125.4, 121.1, 60.9 (t, *J* = 22 Hz), 21.2.

3-(4-ethylphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3c)



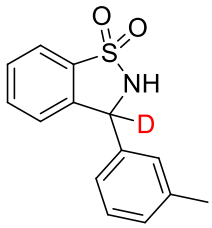
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 1H), 7.48 (ddd, *J* = 6.3, 5.3, 1.0 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.09 – 7.04 (m, 1H), 4.90 (s, 1H), 2.57 (q, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 140.1, 135.8, 135.0, 133.3, 129.4, 128.8, 127.6, 125.4, 121.1, 60.9 (t, *J* = 23Hz), 28.6, 15.4.

3-(4-(*tert*-butyl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3d)



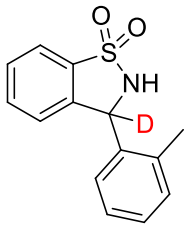
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 6.2, 2.7 Hz, 1H), 7.54 (ddd, *J* = 5.9, 5.2, 3.4 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.19 – 7.12 (m, 1H), 5.02 (s, 1H), 1.30 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 140.0, 135.6, 135.0, 133.3, 129.4, 127.4, 126.2, 125.5, 121.1, 60.8 (t, *J* = 22Hz), 34.7, 31.3 .

3-(*m*-tolyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3e)



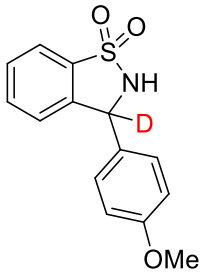
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 1H), 7.63 – 7.50 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.15 (m, 4H), 4.92 (s, 1H), 2.34 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 139.3, 138.5, 134.9, 133.4, 129.9, 129.5, 129.2, 128.1, 125.4, 124.7, 121.1, 61.1 (t, *J* = 22 Hz), 21.4.

3-(*o*-tolyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3f)



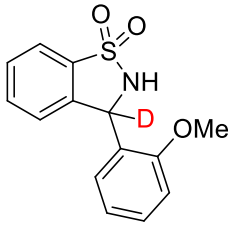
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.5, 3.3 Hz, 1H), 7.57 (dd, *J* = 6.1, 2.6 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.21 – 7.15 (m, 1H), 7.12 (d, *J* = 7.0 Hz, 2H), 4.86 (s, 1H), 2.45 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 136.8, 136.2, 135.7, 133.4, 131.3, 129.5, 129.1, 128.1, 127.1, 125.3, 121.3, 57.9 (t, *J* = 24 Hz), 19.4.

3-(4-methoxyphenyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (4g)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.73 (m, 1H), 7.66 – 7.49 (m, 2H), 7.33 – 7.20 (m, 2H), 7.13 (d, *J* = 6.3 Hz, 1H), 6.89 (dd, *J* = 8.6, 1.9 Hz, 2H), 5.02 (s, 1H), 3.81 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 140.2, 135.1, 133.3, 130.6, 129.4, 128.9, 125.4, 121.1, 114.6, 60.7 (t, *J* = 22 Hz), 55.4.

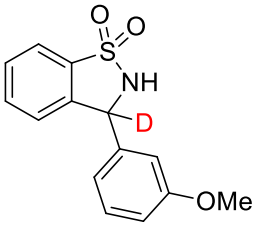
3-(2-methoxyphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3h)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.51 – 7.40 (m, 2H), 7.31 – 7.23 (m, 1H), 7.19 (d, *J* = 1.8 Hz, 1H), 7.17 – 7.12 (m, 1H), 6.91 – 6.83 (m, 2H), 4.97 (s, 1H), 3.77 (s,

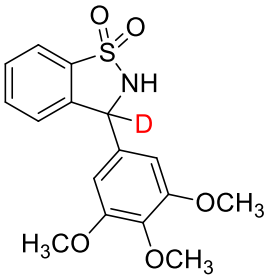
3H).[13]C NMR (101 MHz, $CDCl_3$) δ 157.0, 140.4, 135.4, 133.1, 130.3, 129.2, 128.8, 126.3, 125.2, 121.3, 121.1, 111.1, 55.6.

3-(3-methoxyphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3i)



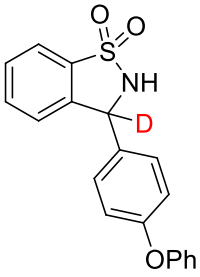
[1]H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.71 (m, 1H), 7.63 – 7.51 (m, 2H), 7.30 (td, *J* = 7.6, 1.2 Hz, 1H), 7.22 – 7.14 (m, 1H), 6.99 – 6.93 (m, 1H), 6.93 – 6.86 (m, 2H), 5.06 (s, 1H), 3.78 (s, 3H).[13]C NMR (101 MHz, $CDCl_3$) δ 160.3, 140.2, 139.6, 134.8, 133.4, 130.4, 129.5, 125.4, 121.2, 119.7, 114.6, 112.9, 60.9 (t, *J* = 22 Hz), 55.4.

3-(3,4,5-trimethoxyphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3j)



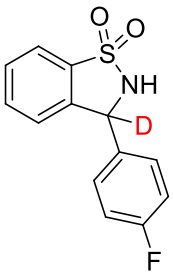
[1]H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 1H), 7.64 – 7.51 (m, 2H), 7.20 (dd, *J* = 6.4, 1.9 Hz, 1H), 6.58 (s, 2H), 5.11 (s, 1H), 3.82 (d, *J* = 3.6 Hz, 9H).[13]C NMR (101 MHz, $CDCl_3$) δ 153.8, 139.6, 138.4, 134.8, 134.2, 133.4, 129.6, 125.3, 121.2, 104.4, 61.1 (t, *J* = 22Hz), 60.9, 56.3.

3-(4-phenoxyphenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3k)



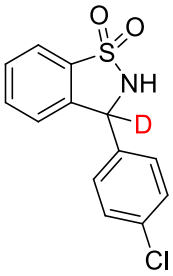
[1]H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 6.7, 1.8 Hz, 1H), 7.59 (dd, *J* = 7.3, 1.3 Hz, 2H), 7.43 – 7.30 (m, 4H), 7.22 – 7.13 (m, 2H), 7.07 – 6.97 (m, 4H), 5.05 (s, 1H).[13]C NMR (101 MHz, $CDCl_3$) δ 158.3, 156.4, 139.8, 135.0, 133.4, 133.0, 129.9, 129.6, 129.2, 125.4, 123.9, 121.2, 119.4, 119.0, 60.5 (t, *J* = 17Hz).

3-(4-fluorophenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3l)



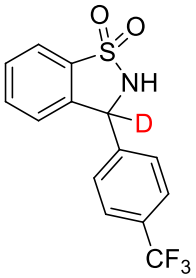
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.9, 2.4 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.44 – 7.31 (m, 2H), 7.22 – 6.95 (m, 3H), 5.16 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 161.8, 139.5, 134.7, 134.6, 134.5, 133.5, 129.7, 129.5, 129.4, 125.3, 121.2, 116.4, 116.2, 60.4 (t, *J* = 23 Hz).

3-(4-chlorophenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3m)



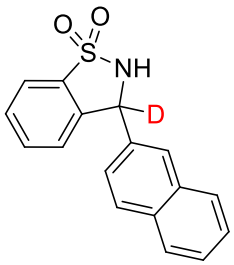
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 1H), 7.59 – 7.50 (m, 2H), 7.33 (ddd, *J* = 17.9, 5.0, 1.5 Hz, 4H), 7.16 – 7.04 (m, 1H), 5.05 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 137.2, 135.1, 134.7, 133.5, 129.8, 129.5, 128.9, 125.3, 121.3, 60.4 (t, *J* = 46 Hz).

3-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (2n)



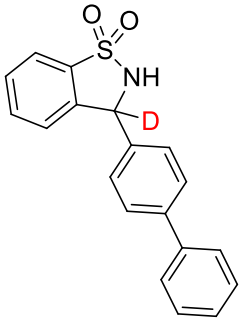
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.51 (m, 4H), 7.17 – 7.11 (m, 1H), 5.31 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 138.7, 134.5, 133.6, 129.9, 127.9, 126.3, 126.2, 125.3, 121.4, 60.3 (t, *J* = 23 Hz).

3-(naphthalen-2-yl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3o)



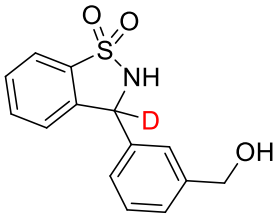
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 12.8, 8.3 Hz, 5H), 7.51 (m, 4H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.11 (dd, *J* = 4.8, 2.3 Hz, 1H), 5.03 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 135.8, 134.8, 133.5, 133.1, 133.0, 129.7, 128.0, 127.9, 127.3, 126.9, 126.9, 125.5, 124.4, 121.3, 61.7.

3-([1,1'-biphenyl]-4-yl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3p)



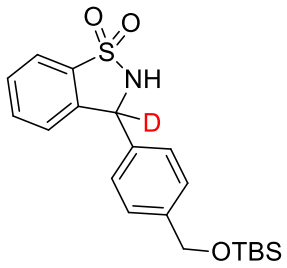
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 1H), 7.60 – 7.53 (m, 6H), 7.47 – 7.41 (m, 4H), 7.39 – 7.34 (m, 1H), 7.21 – 7.14 (m, 1H), 5.17 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 140.2, 139.7, 137.6, 134.8, 133.5, 132.9, 129.6, 128.9, 128.9, 128.1, 127.9, 127.8, 127.5, 127.1, 126.9, 125.5, 121.2, 60.8 (t, *J* = 22 Hz).

3-(3-(hydroxymethyl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3q)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 1H), 7.50 – 7.42 (m, 2H), 7.22 (ddd, *J* = 16.9, 8.9, 2.5 Hz, 4H), 7.10 – 7.02 (m, 1H), 5.45 (s, 1H), 4.54 (s, 2H), 2.54 (s, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 139.6, 139.0, 134.6, 133.4, 129.6, 129.4, 127.6, 126.8, 125.9, 125.4, 121.2, 64.6, 60.9 (t, *J* = 28 Hz).

3-(3-(((*tert*-butyldimethylsilyl)oxy)methyl)phenyl)-2,3-dihydrobenzo[*d*]isothiazole 1,1-dioxide (3r)

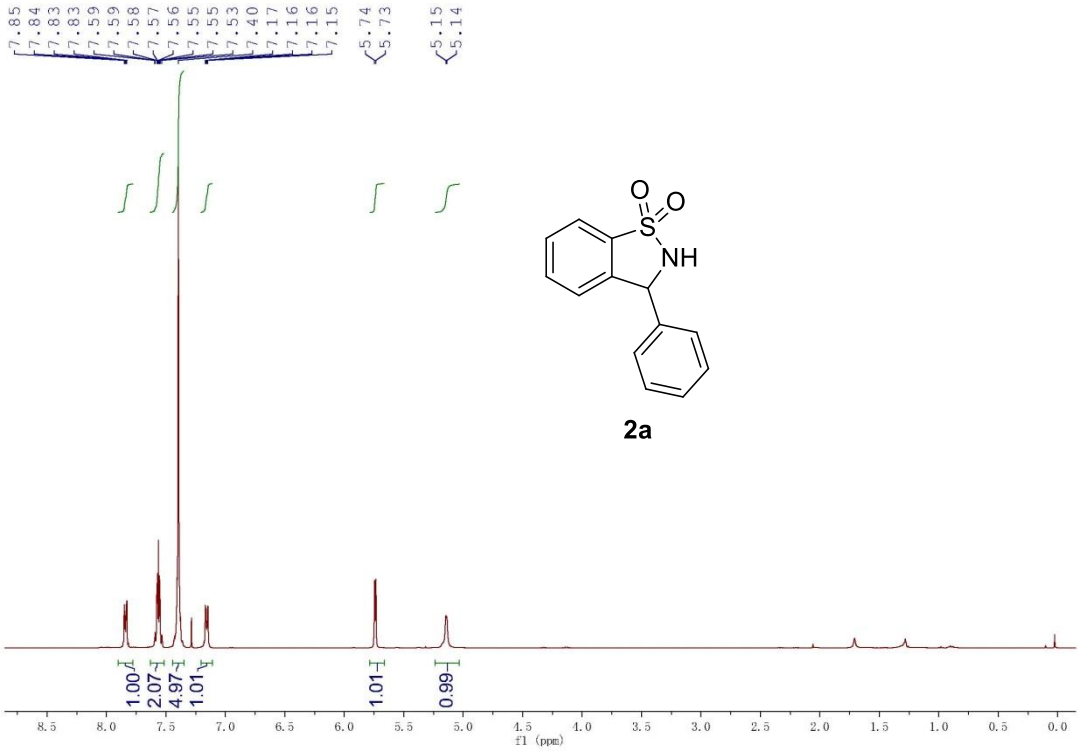


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 6.2, 2.8 Hz, 1H), 7.56 (dd, *J* = 9.1, 4.9 Hz, 2H), 7.39 – 7.28 (m, 3H), 7.25 (dd, *J* = 7.7, 5.7 Hz, 1H), 7.17 – 7.11 (m, 1H), 4.98 (s, 1H), 4.73 (s, 2H), 0.91 (s, 9H), 0.08 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 139.6, 139.0, 133.4, 129.6, 129.4, 127.6, 126.7, 125.9, 125.4, 121.2, 64.7, 61.1 (t, *J* = 17Hz), 25.9, 25.7, 17.9, -3.6, -5.3.

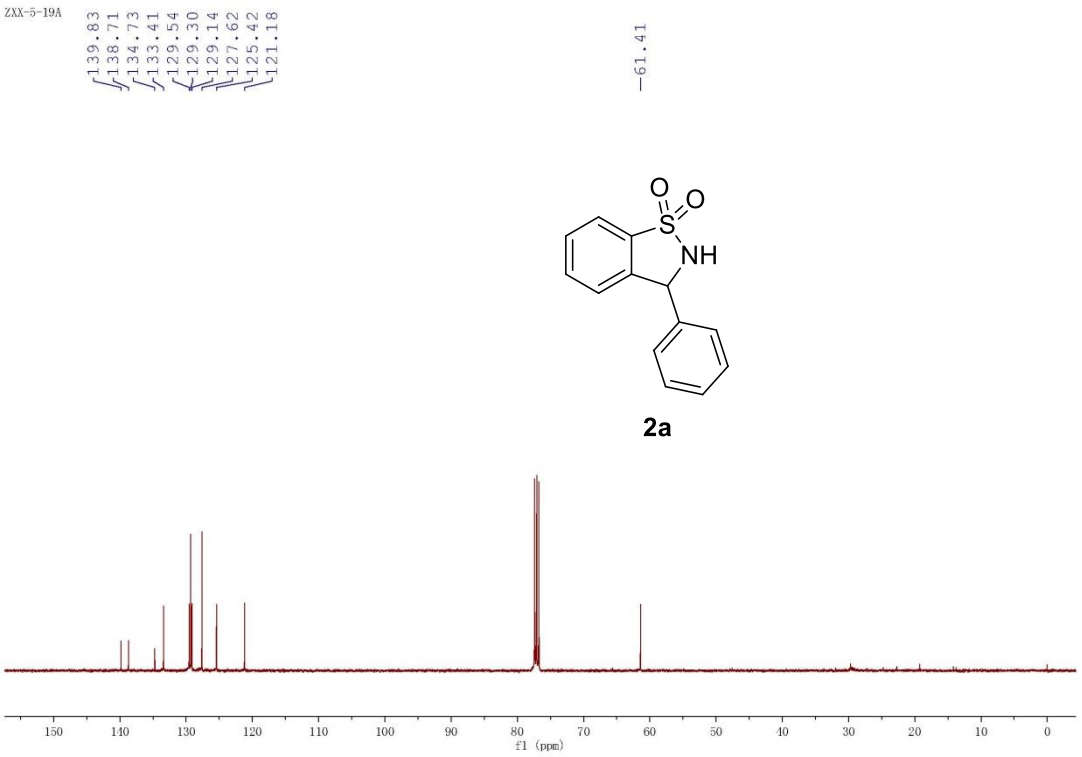
Notes and references:

[1] B. Song, C.-B. Yu,W.-X. Huang, M.-W. Chen and Y.-G. Zhou, *Org. Lett*., 2015, **17**, 190.
(b) C. A. Osborne, T. B. D. Endean and E. R. Jarvo, *Org. Lett*., 2015, **17**, 5340.
[2] C.-B. Yu, D.-W. Wang and Y.-G. Zhou, *J. Org. Chem.*, 2009, **74**, 5633.
[3] Y. Li, M. Lei, W. Yuan, E. Meggers and L. Gong, *Chem. Commun.*, 2017, **53**, 8089.
[4] Q. Yang, G. Shang, W.-Z. Gao, J.-G. Deng and X.-M. Zhang, *Angew. Chem. Int. Ed*., 2006, **45**, 3832.
[5] Y.-H. Dong, Q.-W. Ni, S.-T. Ma and Z.-P. Liu, *Heterocycles*, 2010, **81**, 637.
[6] B. Song, C.-B. Yu, W.-X. Huang, M.-W. Chen, Y.-G. Zhou, *Org. Lett.*, 2015, **17**, 190.
[7] The University of Tennesseee Research Corporation - US6458962, 2002, B1.

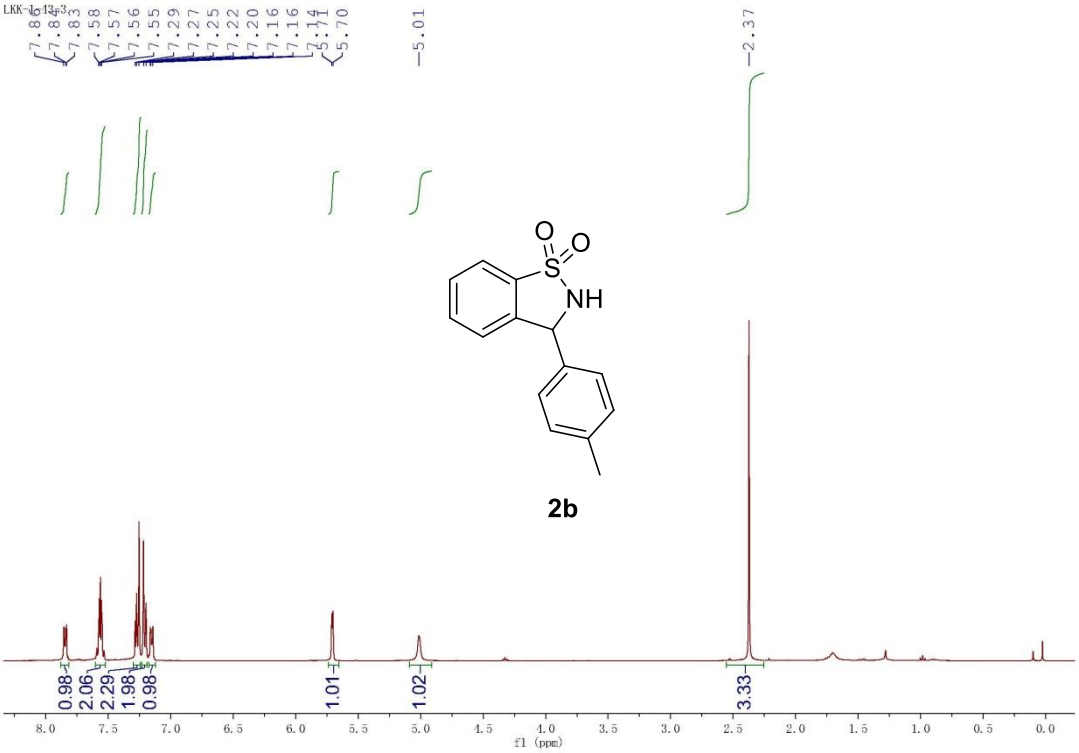
Part IV NMR spectra



2a



2a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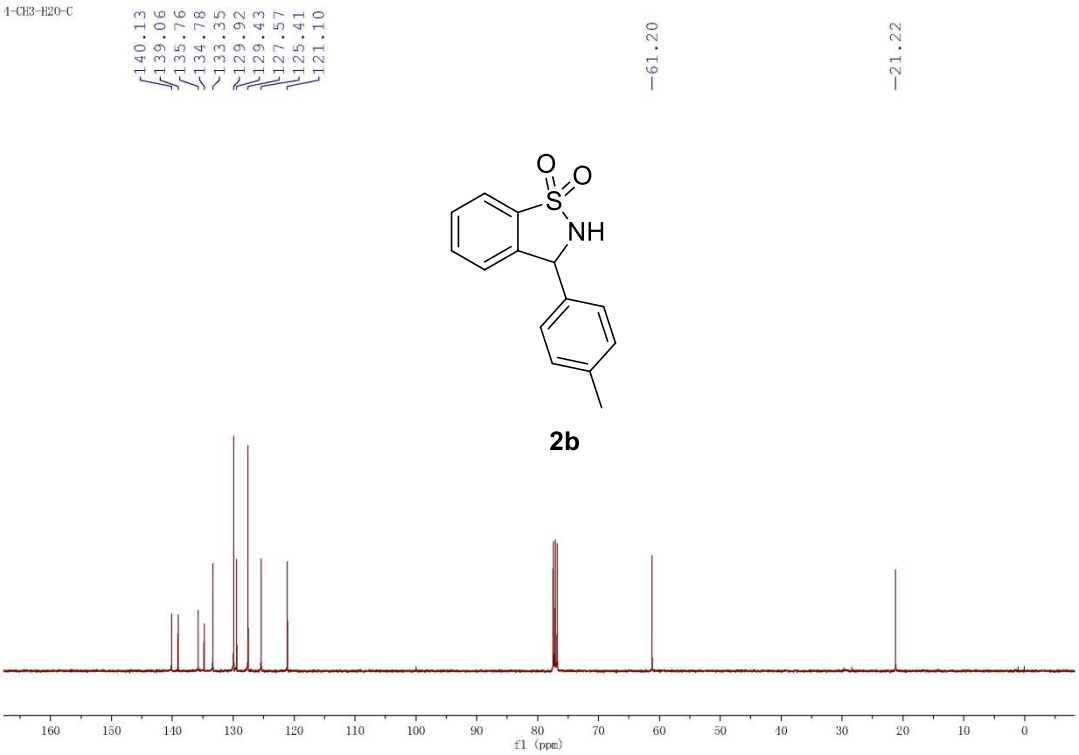
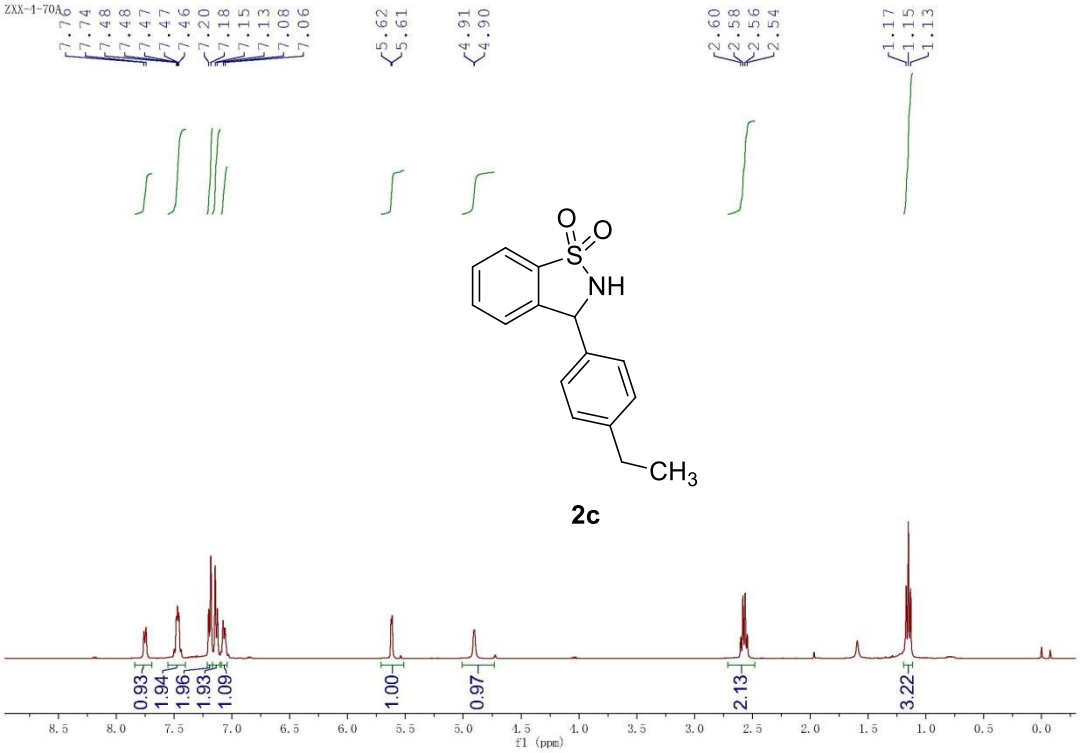
7.84
7.83
7.58
7.57
7.56
7.55
7.29
7.27
7.25
7.22
7.20
7.16
7.16
5.71
5.70
5.01
2.37
O
O
S
NH
0.98
2.06
2.29
1.98
0.98
1.01
1.02
3.33
f1 (ppm)

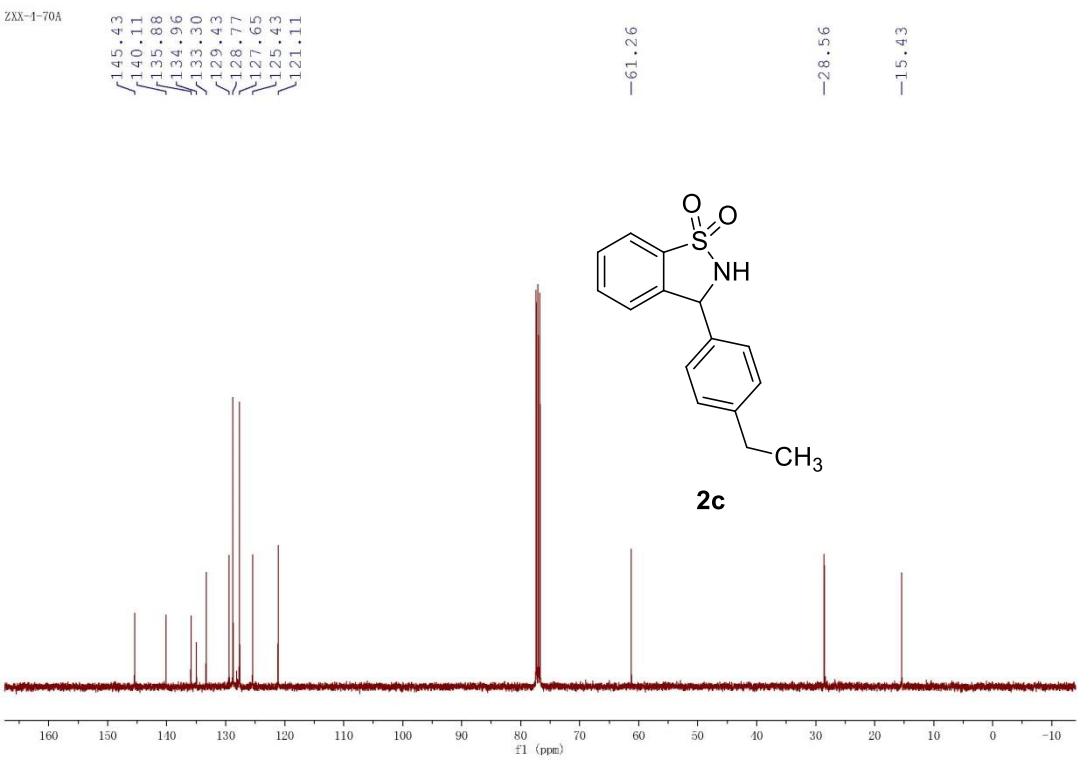
2b


1-CH3-H2O-C
140.13
139.06
135.76
134.78
133.35
129.92
129.43
127.57
125.41
121.10
61.20
21.22
O
O
S
NH
f1 (ppm)

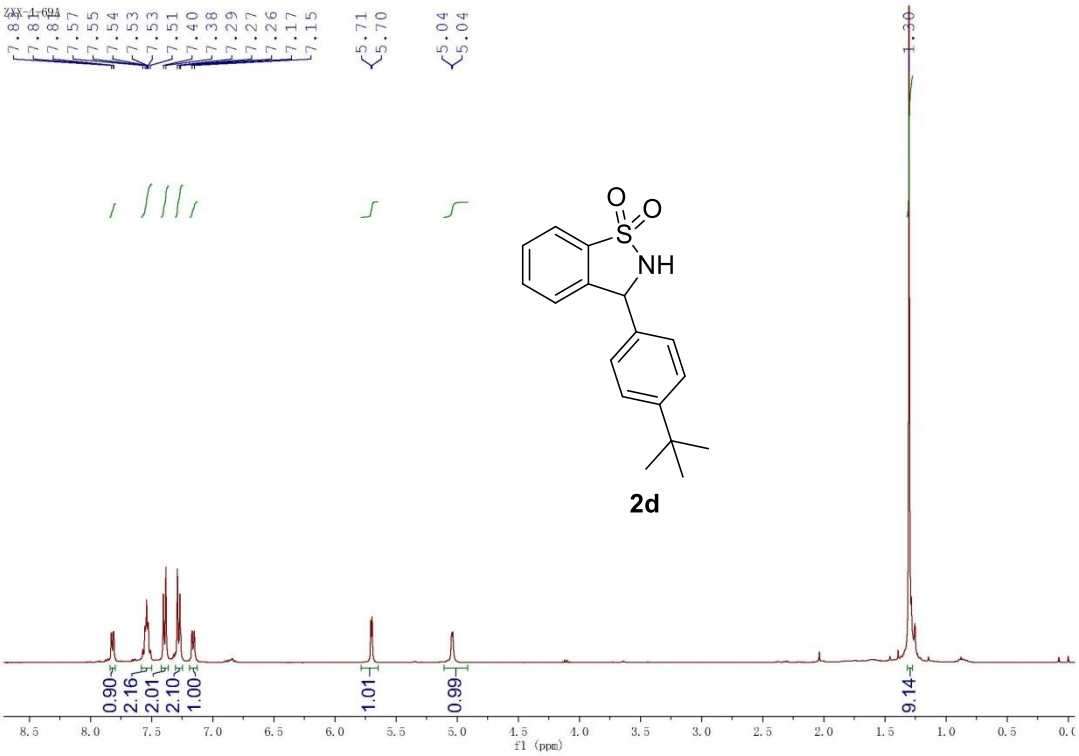
2b

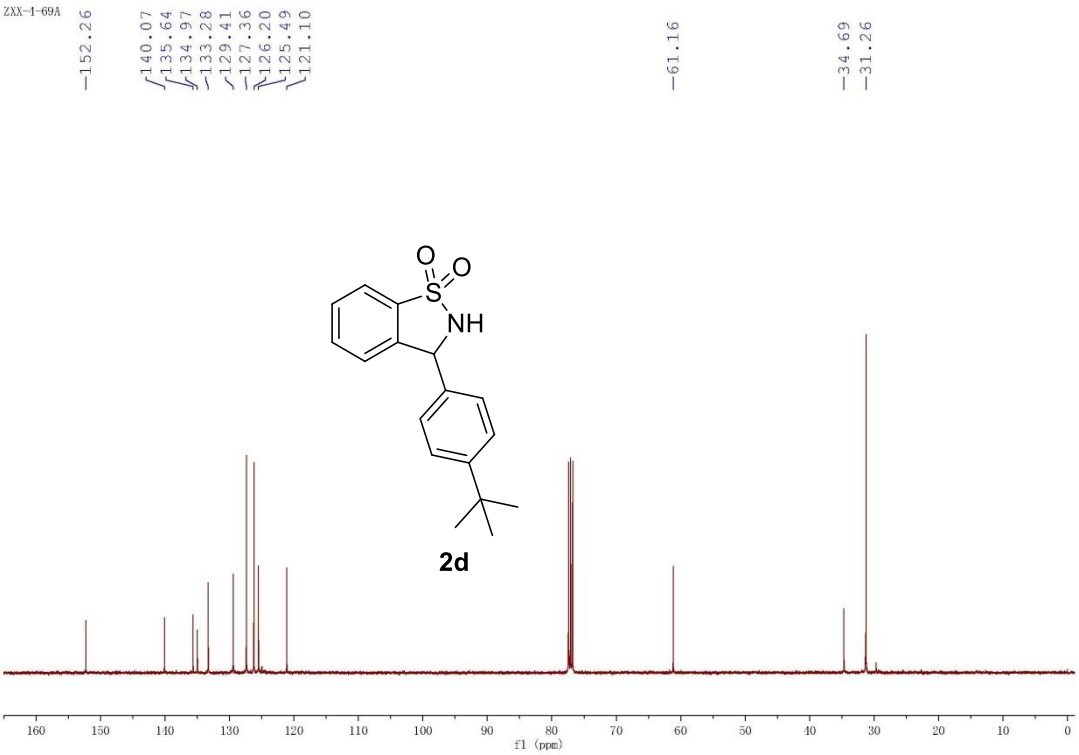

ZXX-4-70A
7.76
7.74
7.48
7.48
7.47
7.47
7.46
7.20
7.18
7.15
7.13
7.08
7.06
5.62
5.61
4.91
4.90
2.60
2.58
2.56
2.54
1.17
1.15
1.13
O
O
S
NH
CH3
0.93
1.94
1.96
1.93
1.09
1.00
0.97
2.13
3.22
f1 (ppm)

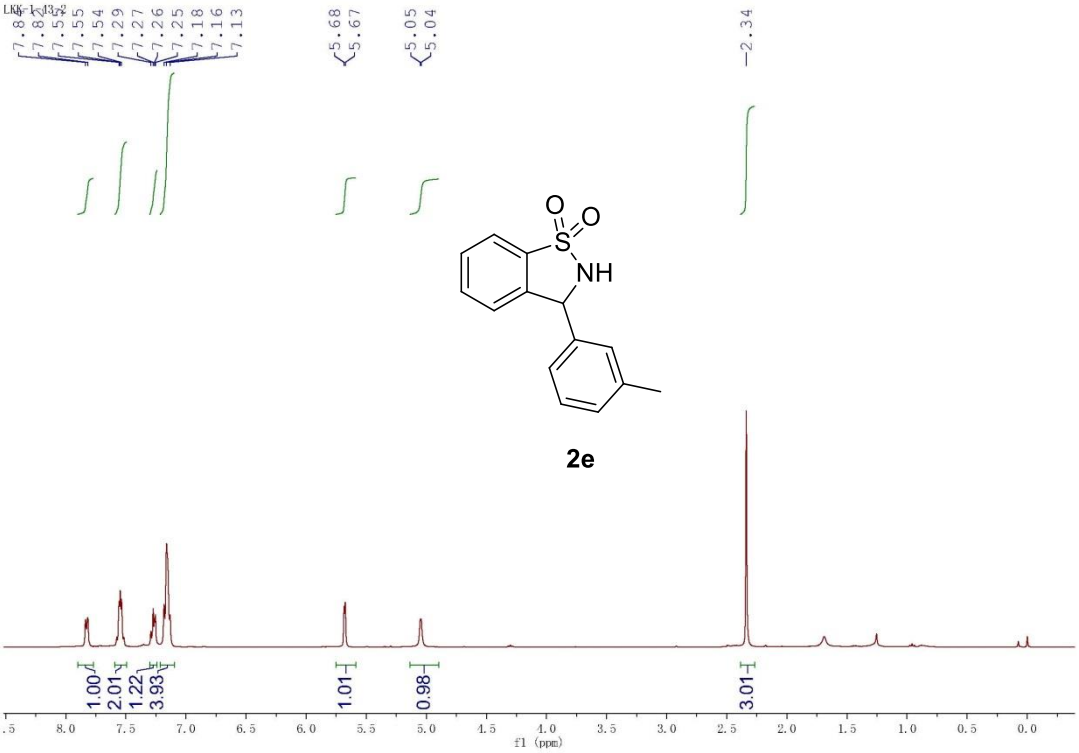
2c


ZXX-4-70A
145.43
140.11
135.88
134.96
133.30
129.43
128.77
127.65
125.43
121.11
61.26
28.56
15.43
O
O
S
NH
CH3
f1 (ppm)

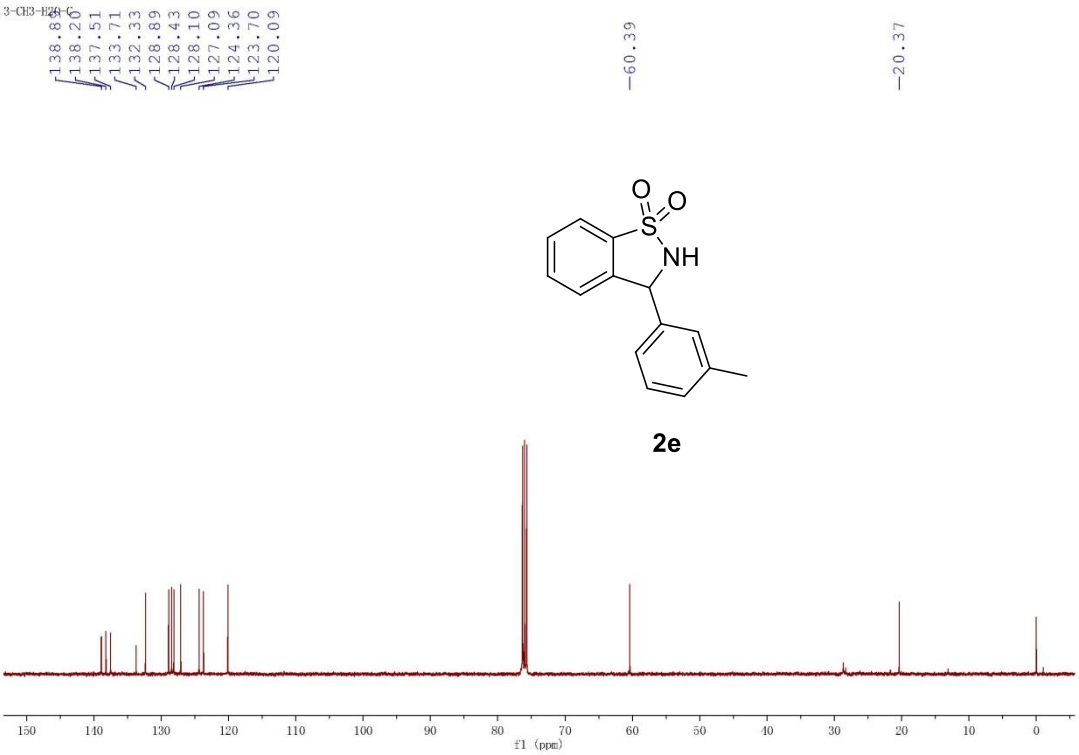
2c


ZXX-1-69A
7.85
7.84
7.83
7.57
7.55
7.54
7.53
7.53
7.51
7.40
7.38
7.29
7.27
7.26
7.17
7.15
5.71
5.70
5.04
5.04
1.30
O
O
S
NH
2d
0.90
2.16
2.01
2.10
1.00
1.01
0.99
9.14
f1 (ppm)

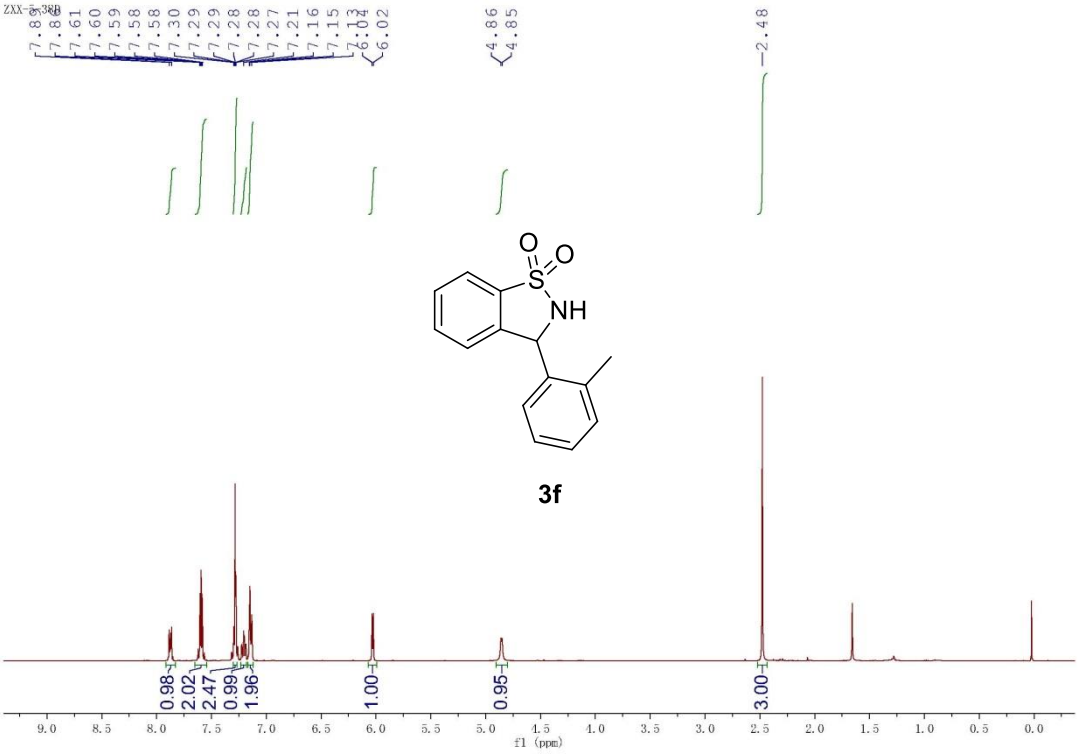

ZXX-1-69A
152.26
140.07
135.64
134.97
133.28
129.41
127.36
126.20
125.49
121.10
61.16
34.69
31.26
O
O
S
NH
2d
f1 (ppm)

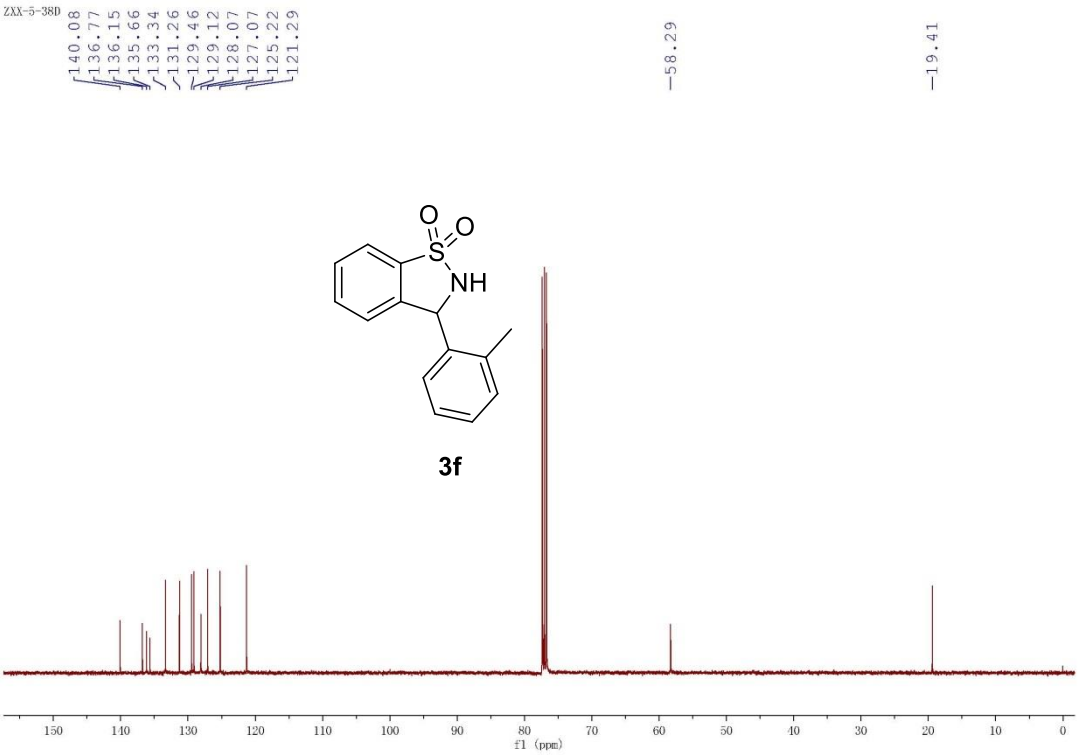

7.85
7.84
7.55
7.55
7.54
7.29
7.27
7.26
7.25
7.18
7.16
7.13
5.68
5.67
5.05
5.04
2.34
O
O
S
NH
1.00
2.01
1.22
3.93
1.01
0.98
3.01
f1 (ppm)

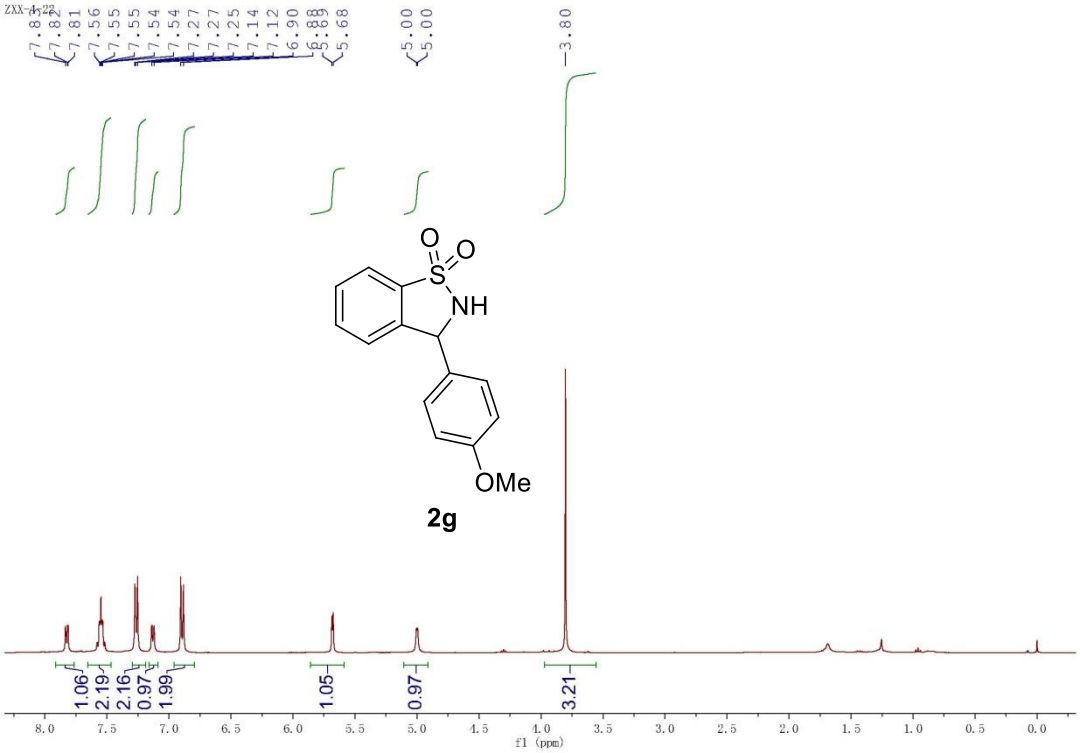
2e

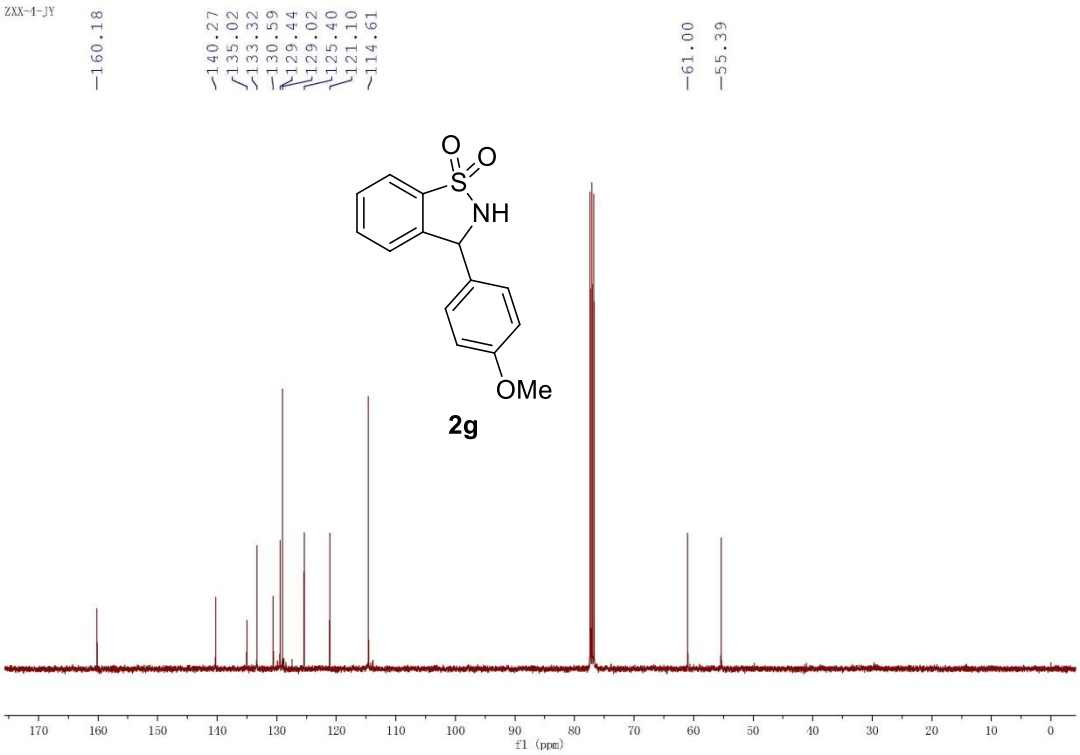

138.85
138.20
137.51
133.71
132.33
128.89
128.43
128.10
127.09
124.36
123.70
120.09
60.39
20.37
O
O
S
NH
f1 (ppm)

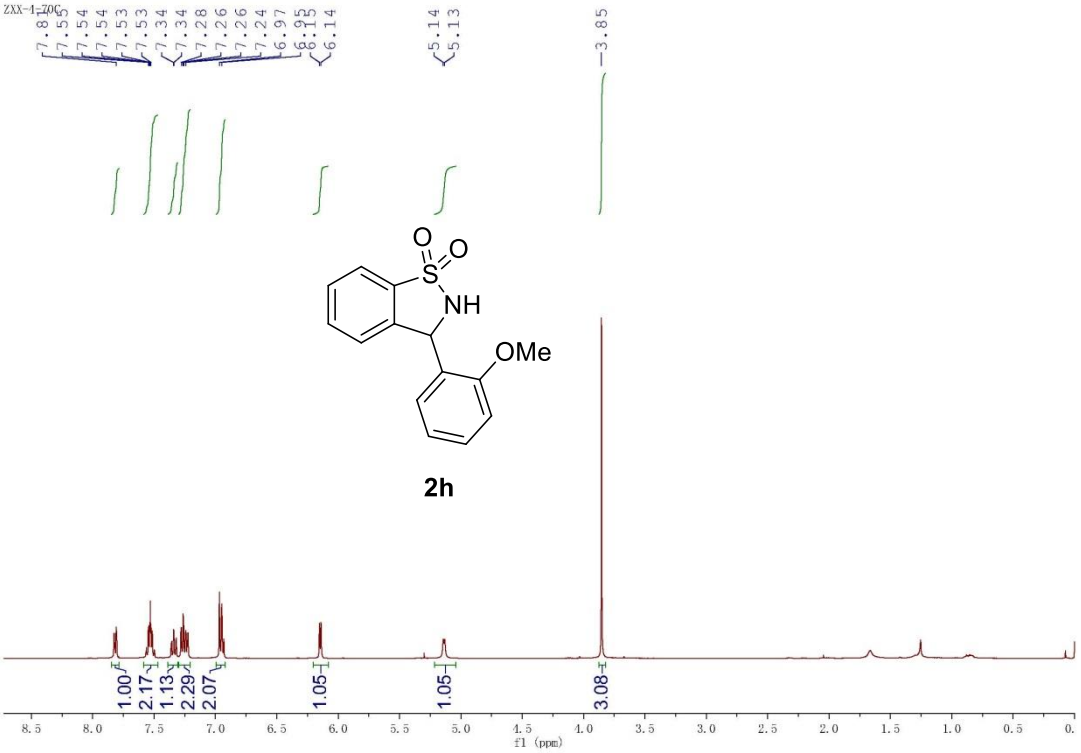
2e


ZXX-5-38D
7.88
7.88
7.61
7.60
7.59
7.58
7.58
7.30
7.29
7.29
7.28
7.28
7.27
7.21
7.16
7.15
7.13
7.04
6.02
4.86
4.85
2.48
O
O
S
NH
3f
0.98
2.02
2.47
0.99
1.96
1.00
0.95
3.00
f1 (ppm)

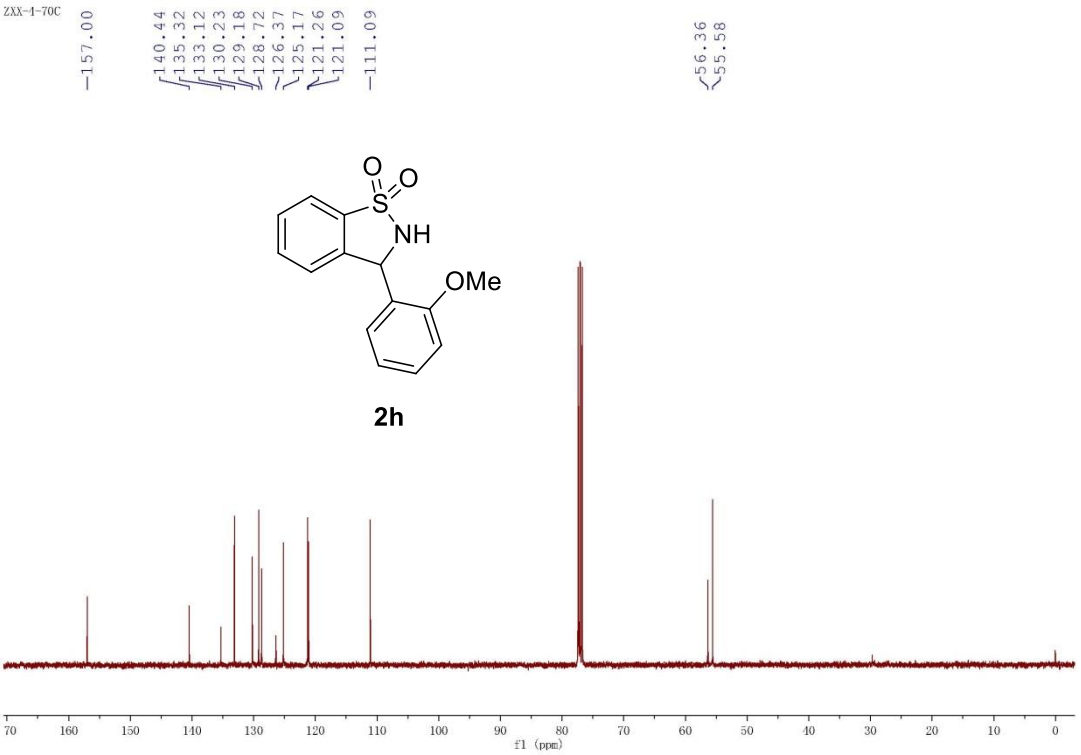

ZXX-5-38D
140.08
136.77
136.15
135.66
133.34
131.26
129.46
129.12
128.07
127.07
125.22
121.29
58.29
19.41
O
O
S
NH
3f
f1 (ppm)


7.83
7.82
7.81
7.56
7.55
7.55
7.54
7.54
7.27
7.27
7.25
7.14
7.12
6.90
6.88
6.89
5.68
5.00
5.00
3.80
O
O
S
NH
OMe
2g
1.06
2.19
2.16
0.97
1.99
1.05
0.97
3.21
f1 (ppm)

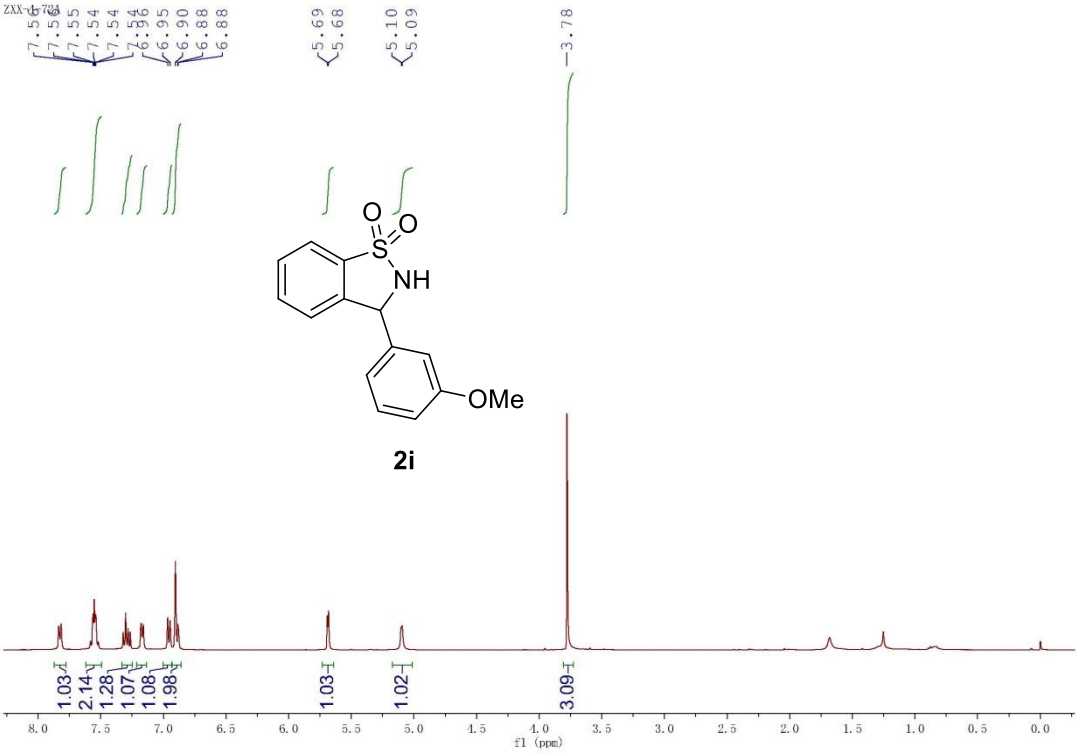

ZXX-4-JY
160.18
140.27
135.02
133.32
130.59
129.44
129.02
125.40
121.10
114.61
61.00
55.39
O
O
S
NH
OMe
2g
f1 (ppm)


ZXX-1-70C
7.85
7.55
7.54
7.54
7.54
7.53
7.53
7.34
7.34
7.28
7.26
7.26
7.24
6.97
6.95
6.15
6.14
5.14
5.13
3.85
O
O
S
NH
OMe
1.00
2.17
1.13
2.29
2.07
1.05
1.05
3.08
f1 (ppm)

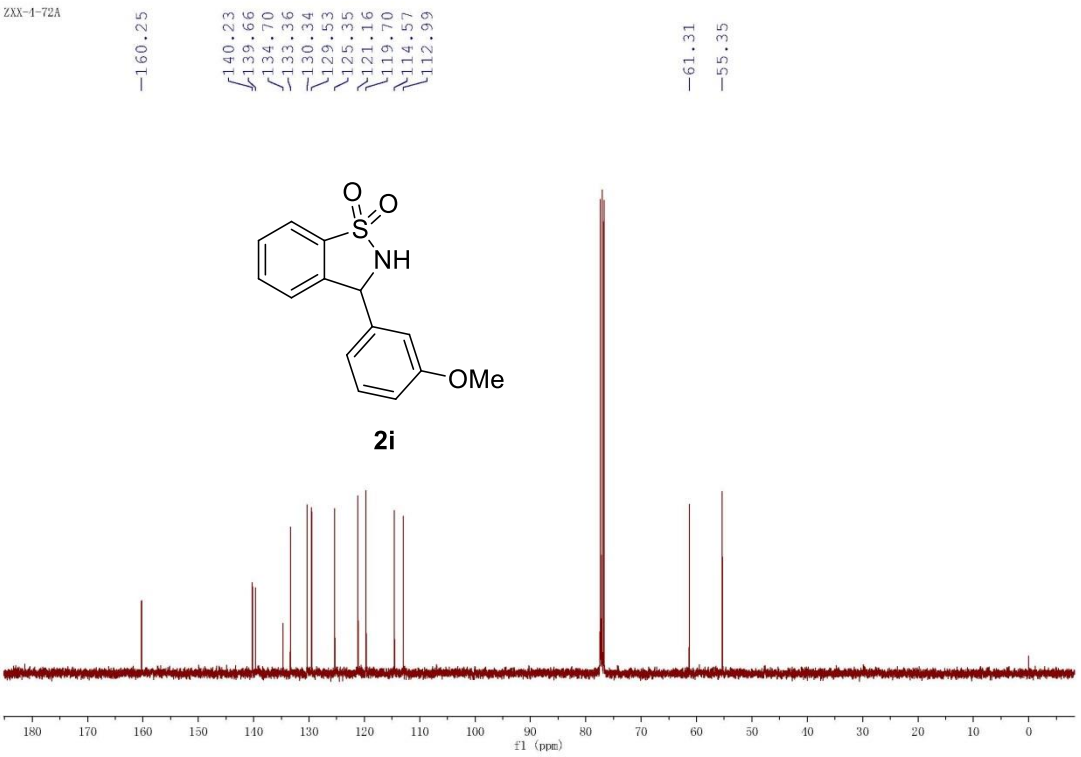
2h


ZXX-1-70C
157.00
140.44
135.32
133.12
130.23
129.18
128.72
126.37
125.17
121.26
121.09
111.09
56.36
55.58
O
O
S
NH
OMe
f1 (ppm)

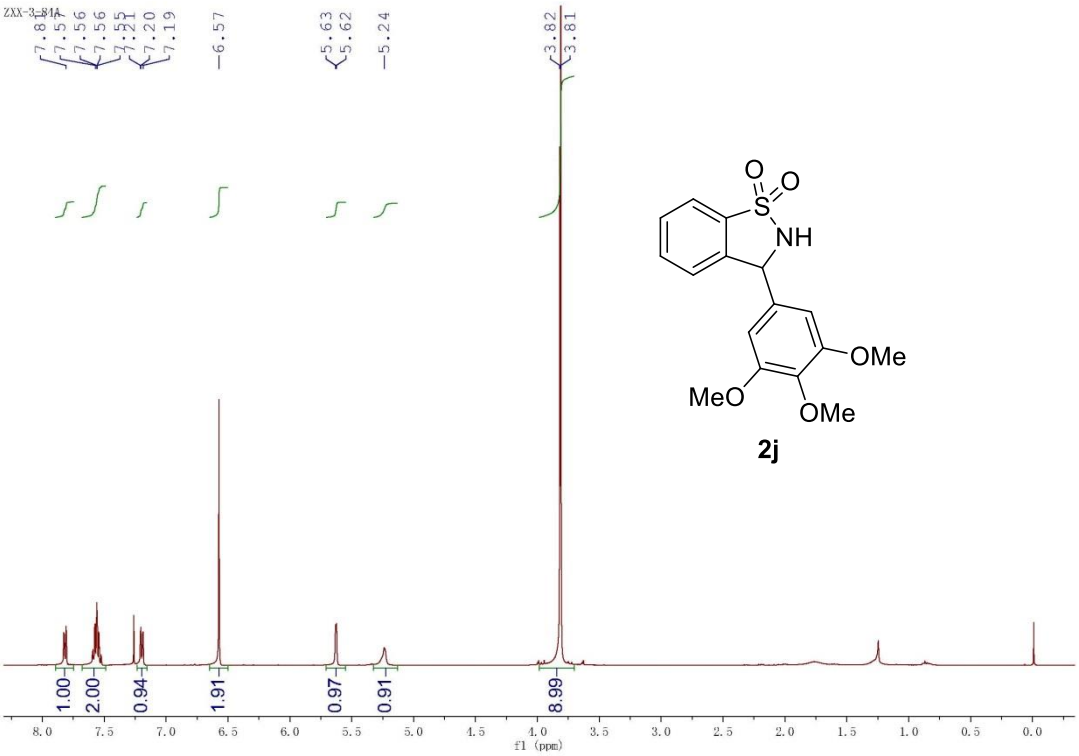
2h


7.56
7.55
7.55
7.54
7.54
7.54
6.96
6.95
6.90
6.88
6.88
5.69
5.68
5.10
5.09
3.78
O
O
S
NH
OMe
1.03
2.14
1.28
1.07
1.08
1.98
1.03
1.02
3.09
f1 (ppm)

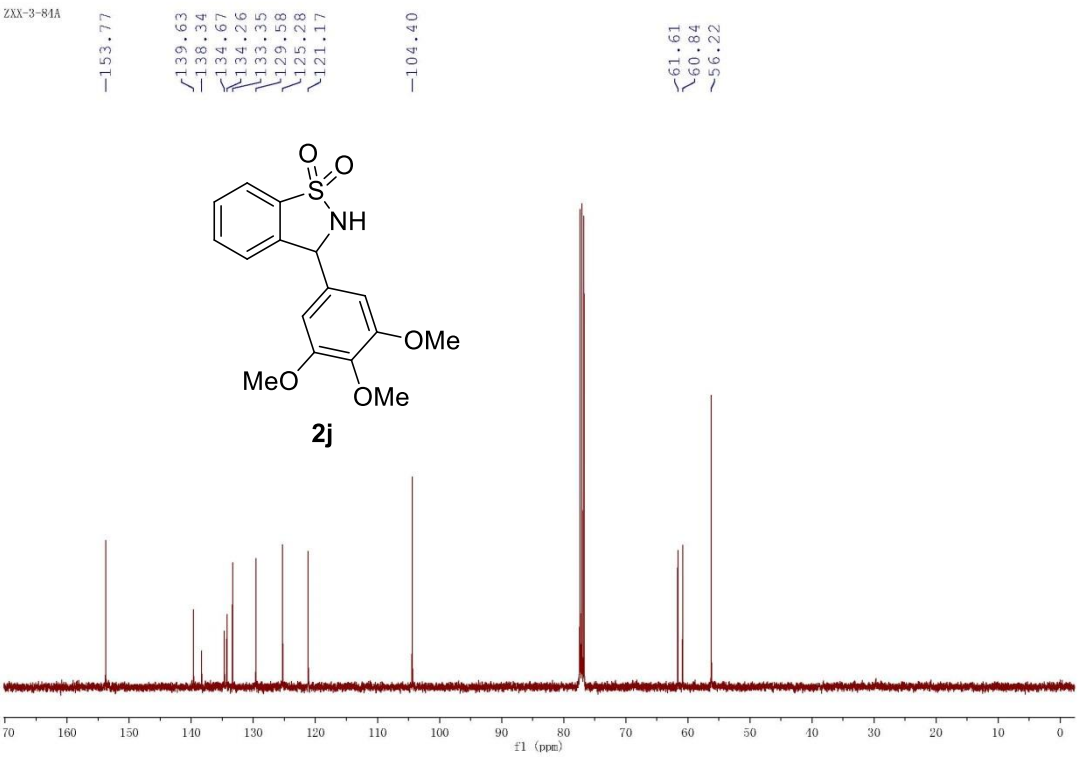
2i


ZXX-1-72A
160.25
140.23
139.66
134.70
133.36
130.34
129.53
125.35
121.16
119.70
114.57
112.99
61.31
55.35
O
O
S
NH
OMe
f1 (ppm)

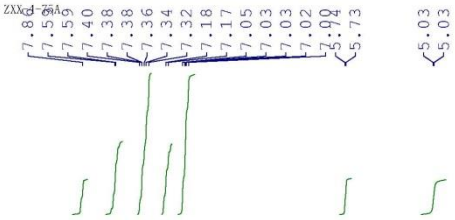
2i

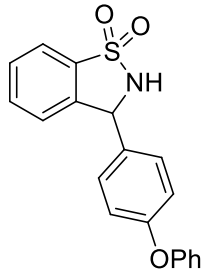

ZXX-3-84A
7.87
7.57
7.56
7.56
7.21
7.20
7.19
6.57
5.63
5.62
5.24
3.82
3.81
1.00
2.00
0.94
1.91
0.97
0.91
8.99
f1 (ppm)
O
O
S
NH
OMe
MeO
OMe

2j

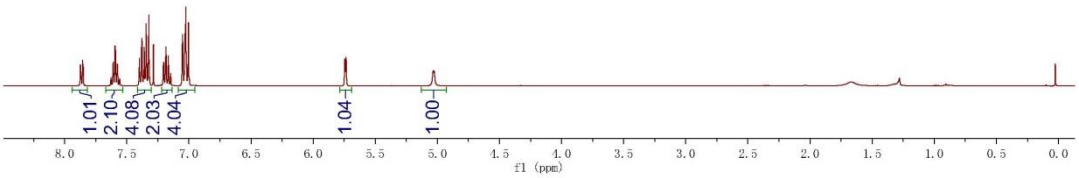

ZXX-3-84A
153.77
139.63
138.34
134.67
134.26
133.35
129.58
125.28
121.17
104.40
61.61
60.84
56.22
f1 (ppm)
O
O
S
NH
OMe
MeO
OMe

2j

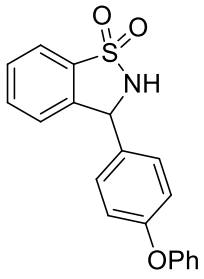

7.85
7.59
7.40
7.38
7.38
7.36
7.34
7.32
7.18
7.17
7.05
7.03
7.03
7.02
5.74
5.73
5.03
5.03


O
O
S
NH
OPh

2k

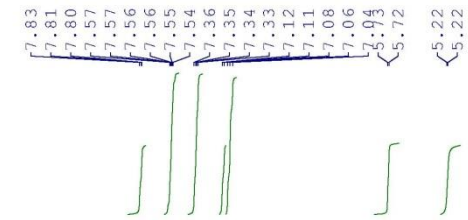

1.01
2.10
4.08
2.03
4.04
1.04
1.00
f1 (ppm)


158.27
156.40
139.90
134.97
133.38
133.06
129.92
129.56
129.19
125.41
123.94
121.19
119.41
119.00
60.89


O
O
S
NH
OPh

2k

f1 (ppm)


7.83
7.81
7.80
7.57
7.57
7.56
7.56
7.55
7.54
7.36
7.35
7.34
7.33
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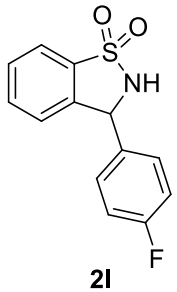
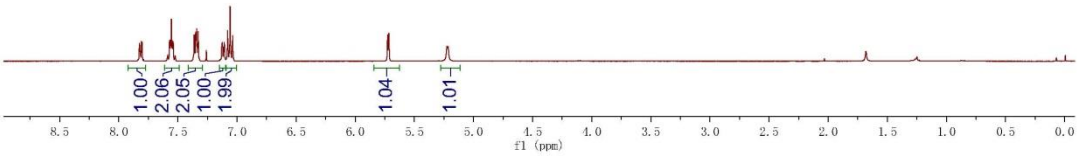
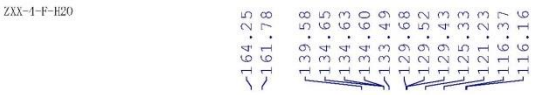
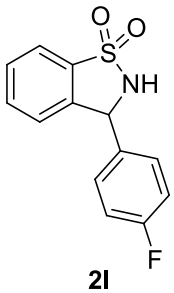
7.08
7.06
5.73
5.72
5.22
5.22


O
O
S
NH
F

2l

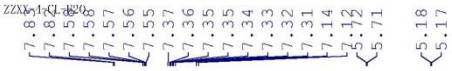

1.00
2.06
2.05
1.00
1.99
1.04
1.01
f1 (ppm)

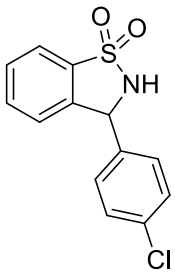

ZXX-4-F-H2O
164.25
161.78
139.58
134.65
134.63
134.60
133.49
129.68
129.52
129.43
125.33
121.23
116.37
116.16
60.62


O
O
S
NH
F

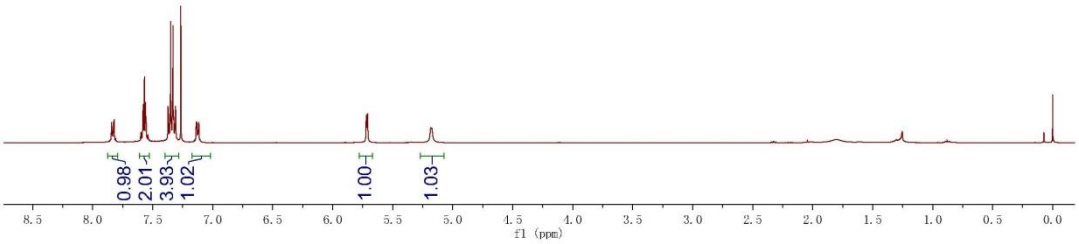
2l

f1 (ppm)


7.83
7.82
7.58
7.57
7.56
7.55
7.37
7.36
7.35
7.34
7.33
7.32
7.31
7.14
5.12
5.71
5.18
5.17

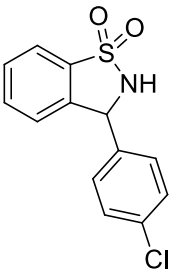

O
O
S
NH
Cl

2m


0.98
2.01
3.93
1.02
1.00
1.03
f1 (ppm)

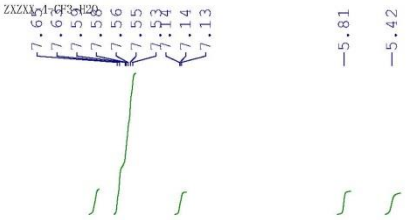

ZXX-4-CL-H2O
139.23
137.29
135.08
134.57
133.54
129.76
129.48
128.96
125.29
121.29

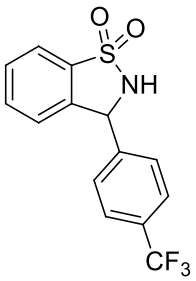

60.61


O
O
S
NH
Cl

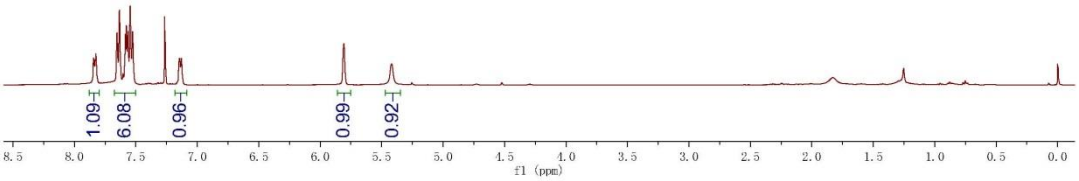
2m

f1 (ppm)


7.67
7.56
7.55
7.53
7.14
7.13
5.81
5.42

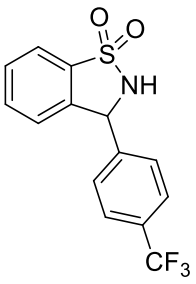

O
O
S
NH
CF3

2n

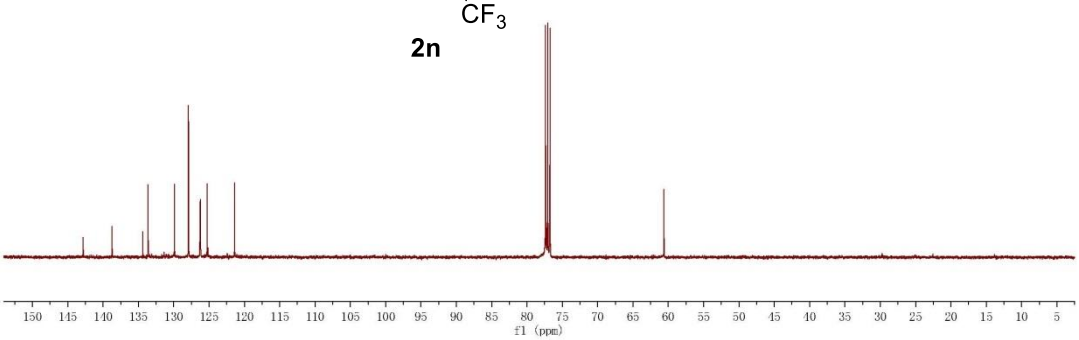

1.09
6.08
0.96
0.99
0.92
f1 (ppm)

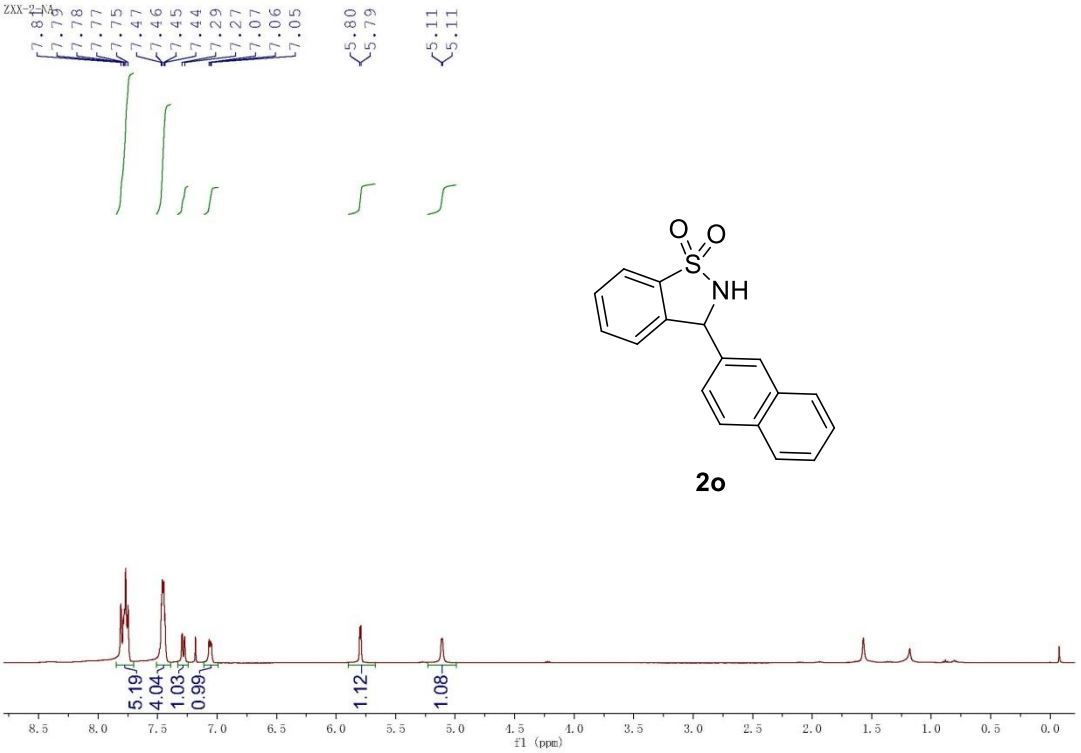

142.87
138.75
134.38
133.63
129.90
127.92
126.26
126.23
125.27
121.38


60.62

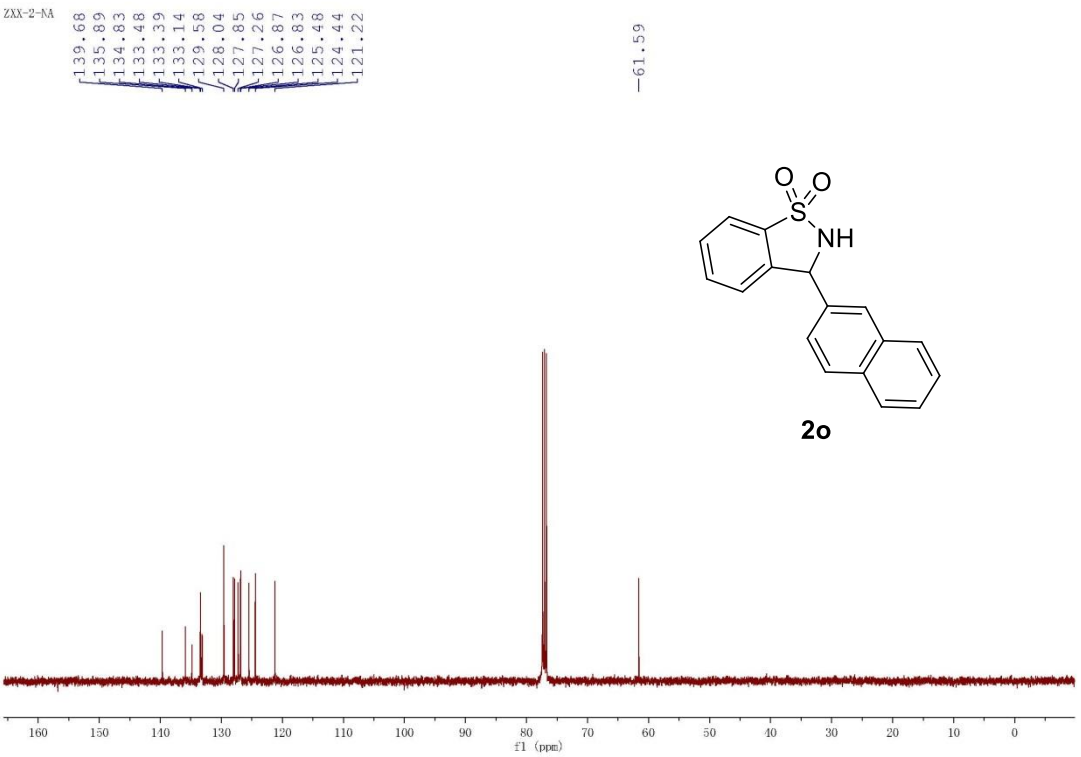

O
O
S
NH
CF3

2n

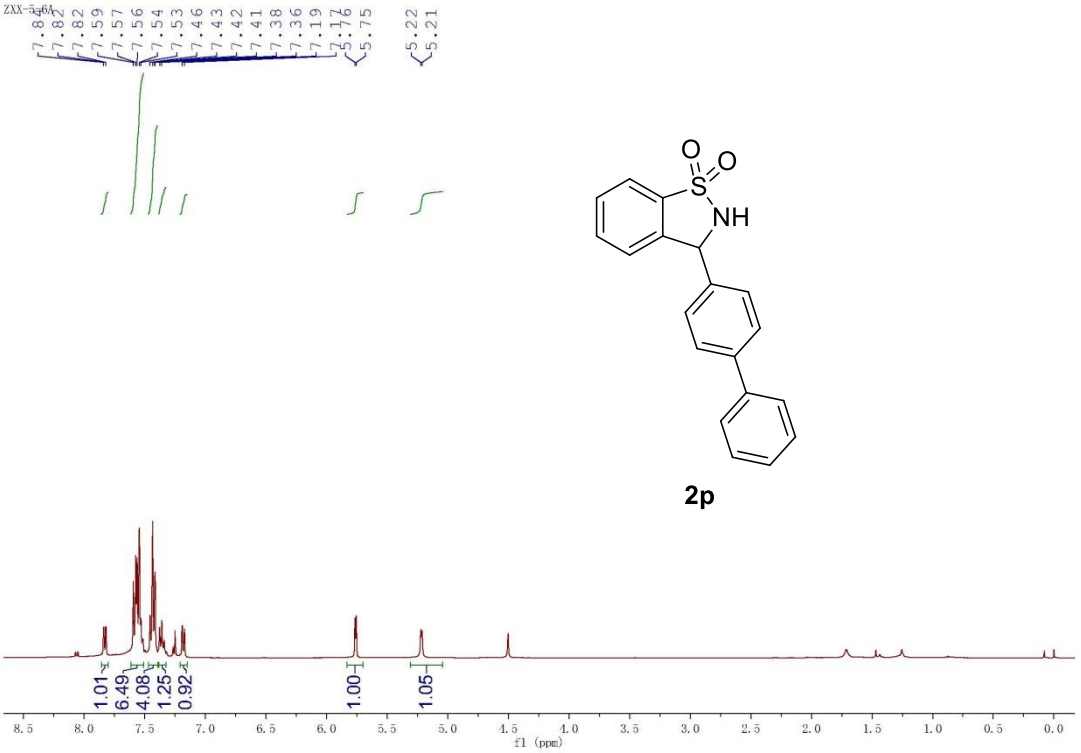

f1 (ppm)


ZXX-2-NA
7.81
7.79
7.78
7.77
7.75
7.47
7.46
7.45
7.44
7.29
7.27
7.07
7.06
7.05
5.80
5.79
5.11
5.11
O
O
S
NH
5.19
4.04
1.03
0.99
1.12
1.08
f1 (ppm)

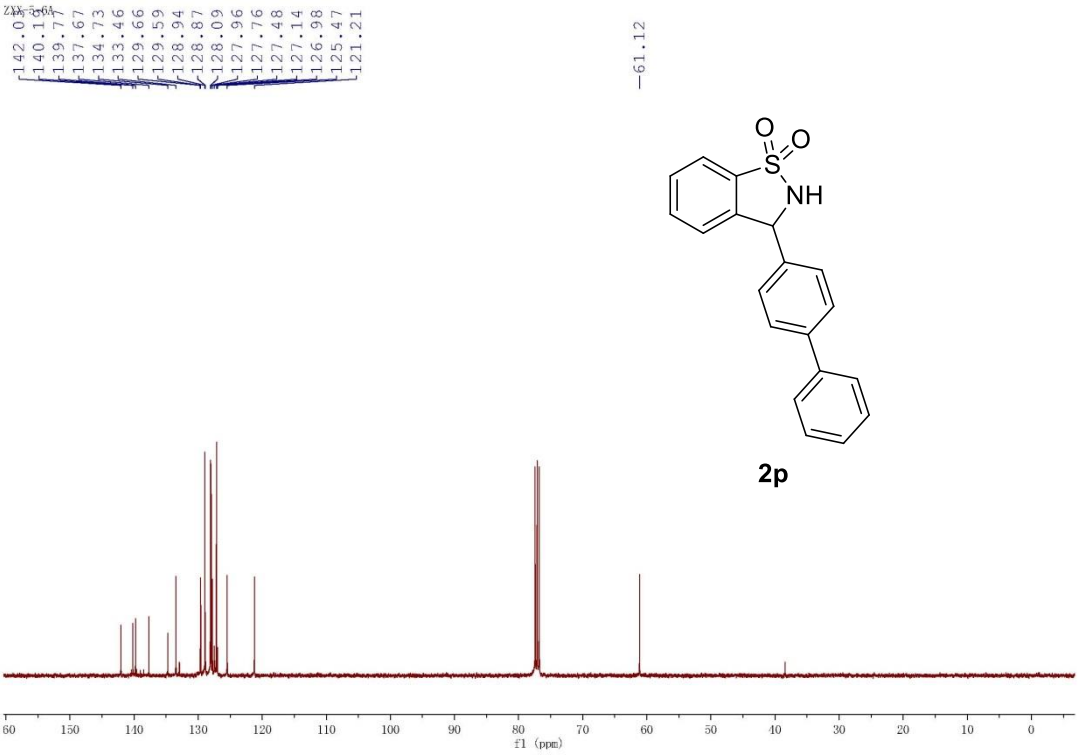
2o


ZXX-2-NA
139.68
135.89
134.83
133.48
133.39
133.14
129.58
128.04
127.85
127.26
126.87
126.83
125.48
124.44
121.22
61.59
O
O
S
NH
f1 (ppm)

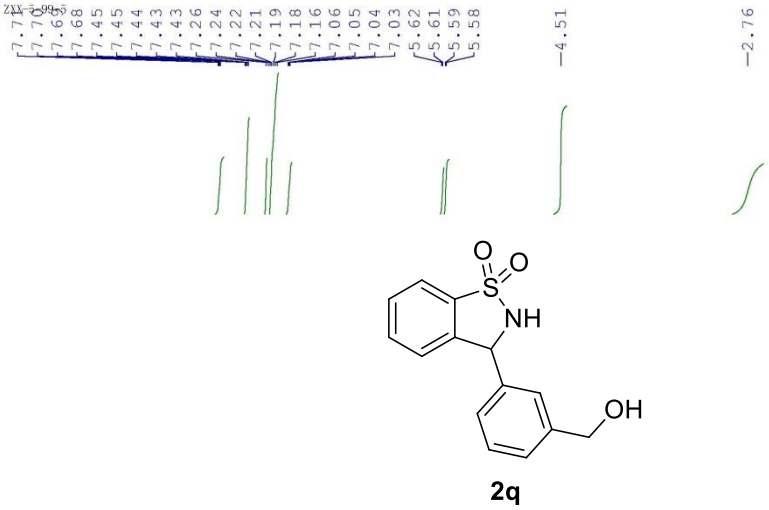
2o


ZXX-5-s6A
7.83
7.82
7.82
7.59
7.57
7.56
7.54
7.53
7.46
7.43
7.42
7.41
7.38
7.36
7.19
5.17
5.16
5.75
5.22
5.21
O
O
S
NH
1.01
6.49
4.08
1.25
0.92
1.00
1.05
f1 (ppm)

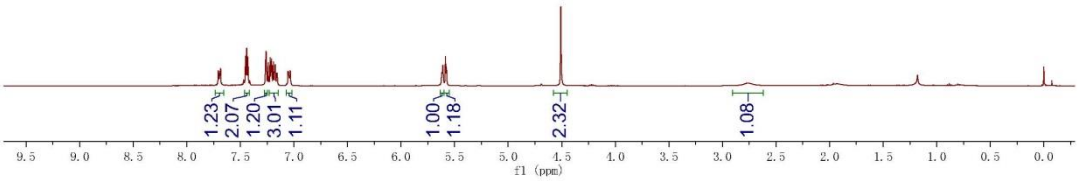
2p

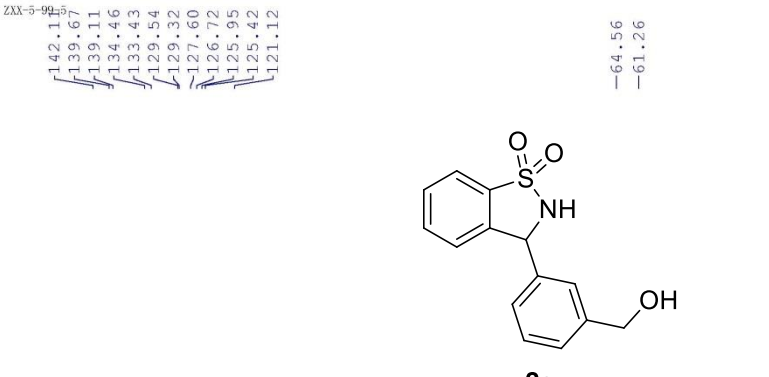

ZXX-5-s6A
142.03
140.17
139.77
137.67
134.73
133.46
129.66
129.59
128.94
128.87
128.09
127.96
127.76
127.48
127.14
126.98
125.47
121.21
61.12
O
O
S
NH
f1 (ppm)

2p

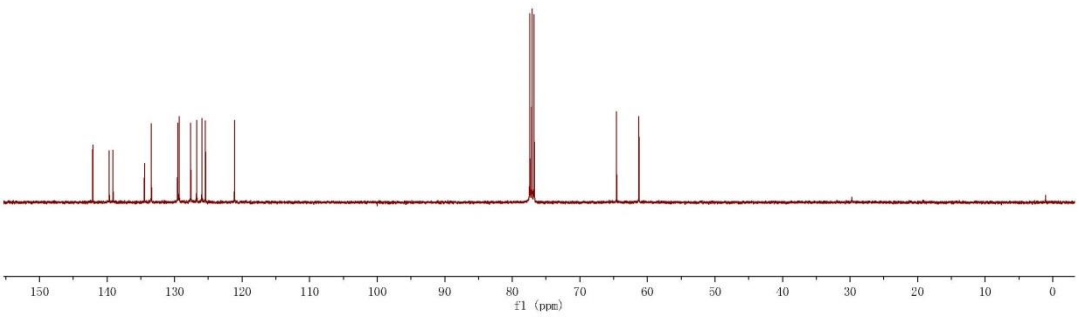

ZXX-5-99-5
7.77
7.76
7.68
7.45
7.44
7.43
7.26
7.24
7.22
7.21
7.19
7.18
7.16
7.06
7.05
7.04
7.03
5.62
5.61
5.59
5.58
4.51
2.76
O
O
S
NH
OH

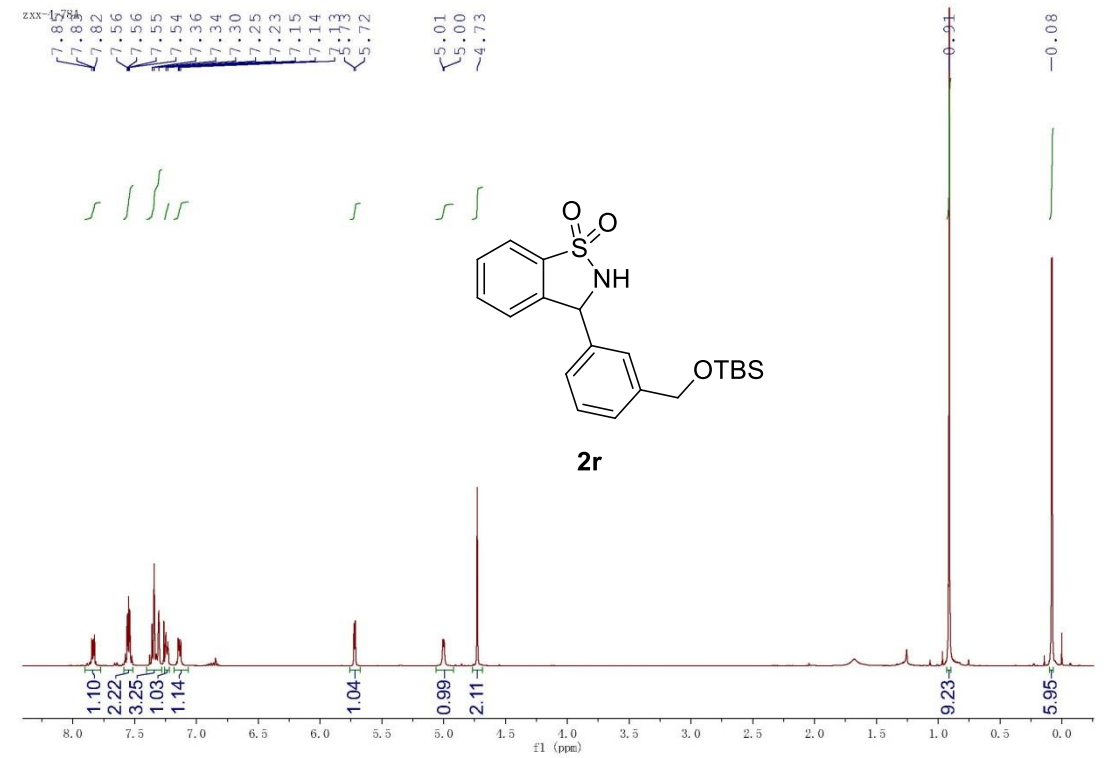
2q

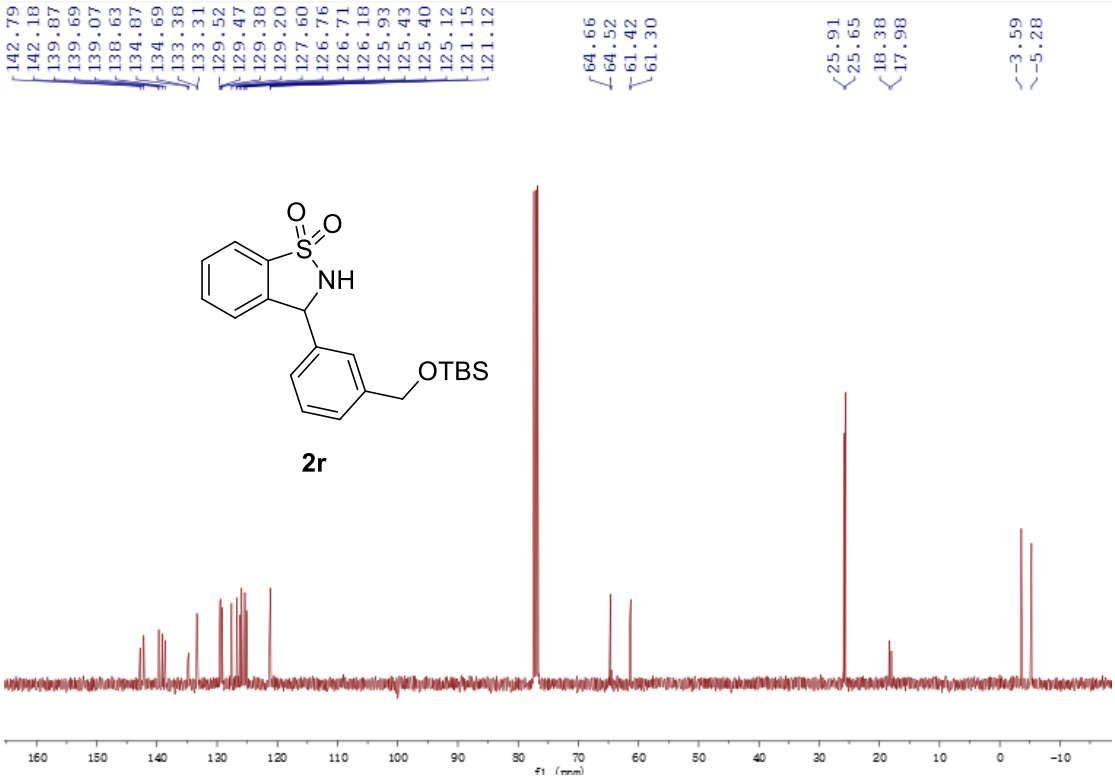

1.23
2.07
1.20
3.01
1.11
1.00
1.18
2.32
1.08
f1 (ppm)

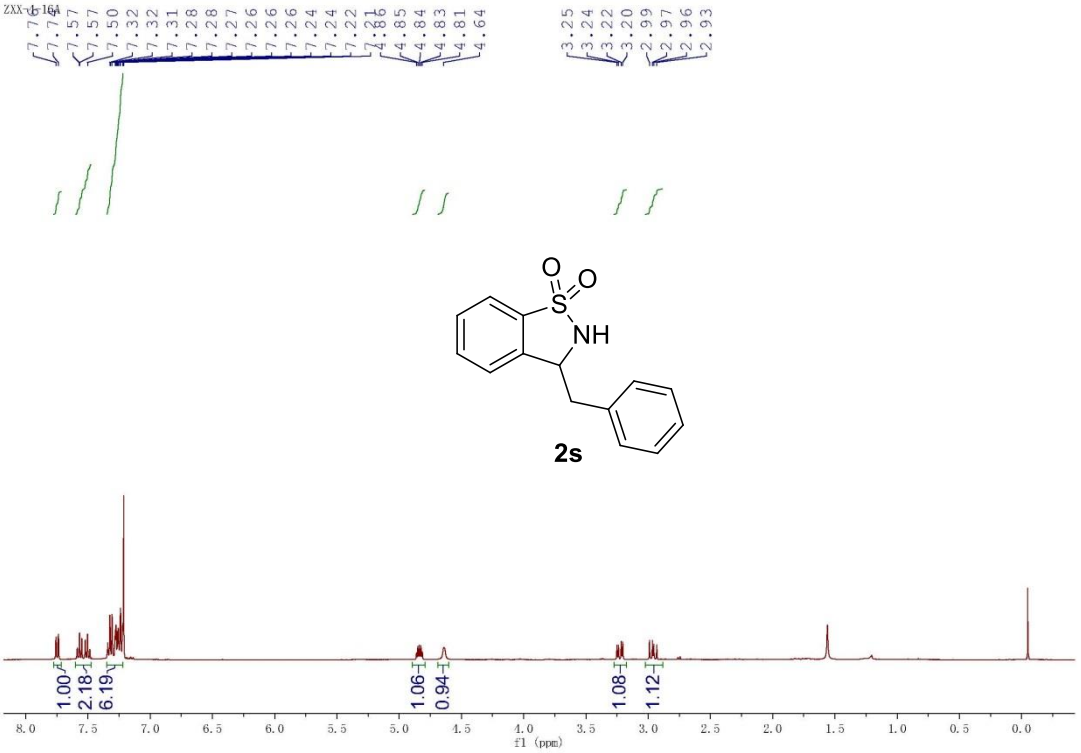

ZXX-5-99-5
142.11
139.67
139.11
134.46
133.43
129.54
129.32
127.60
126.72
125.95
125.42
121.12
64.56
61.26
O
O
S
NH
OH

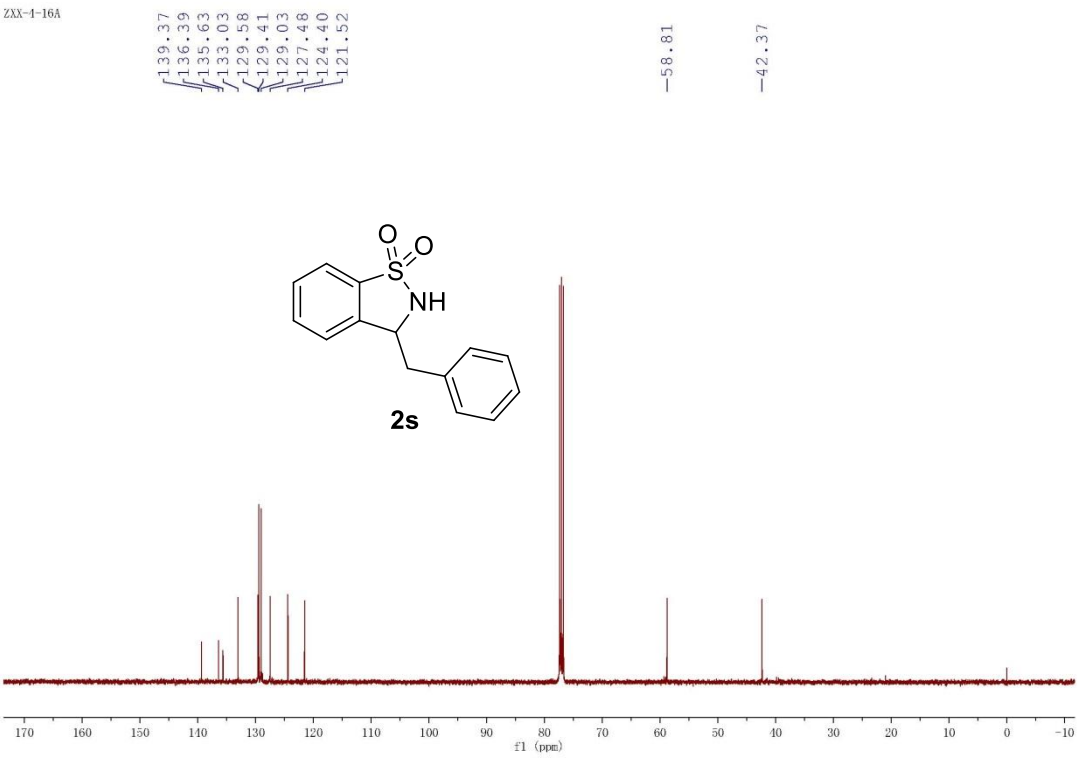
2q

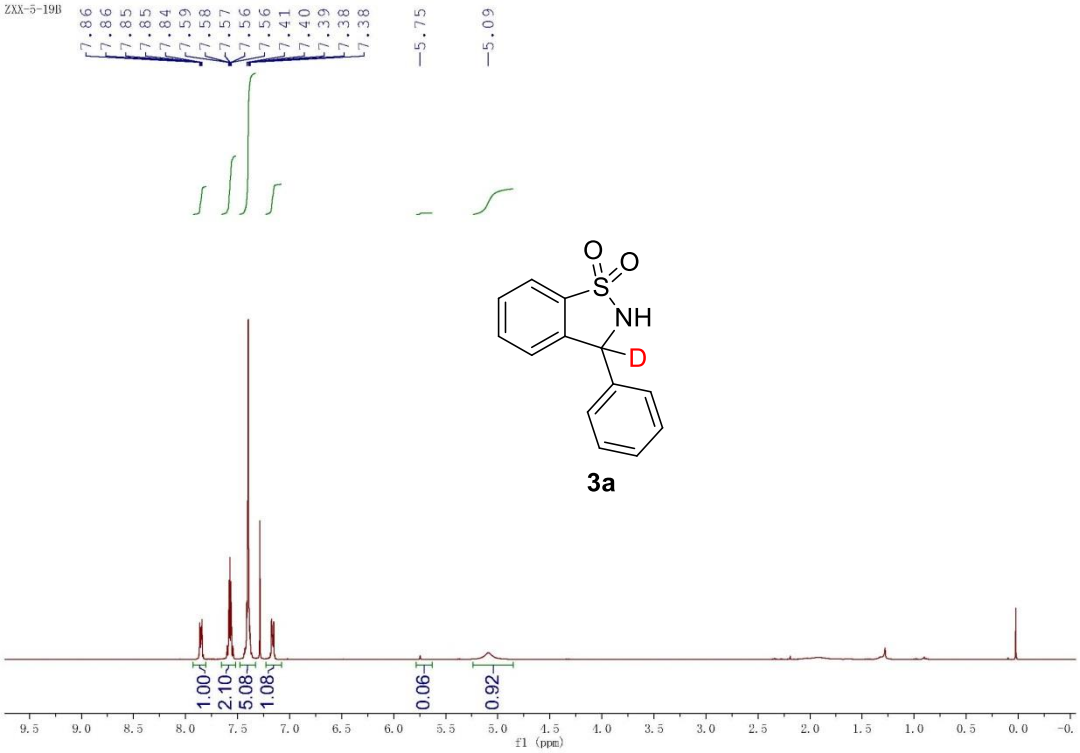

f1 (ppm)

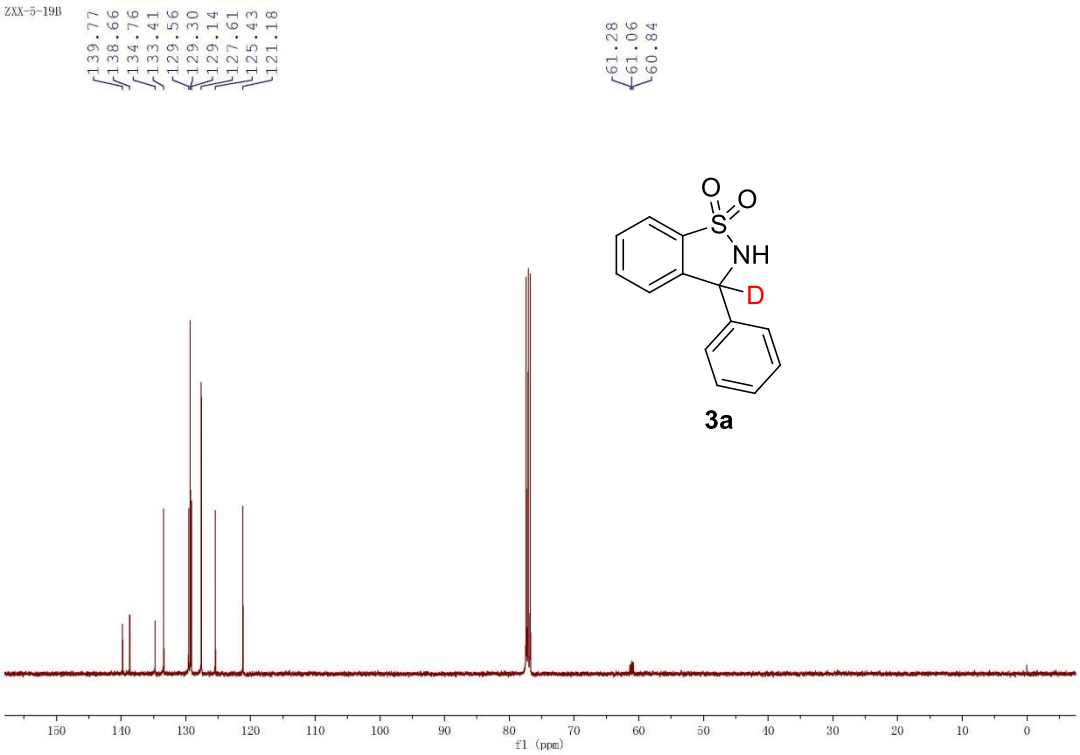

7.84
7.82
7.56
7.55
7.54
7.36
7.34
7.30
7.25
7.23
7.15
7.14
7.13
5.72
5.01
5.00
4.73
0.91
-0.08
O
O
S
NH
OTBS
2r
1.10
2.22
3.25
1.03
1.14
1.04
0.99
2.11
9.23
5.95
f1 (ppm)

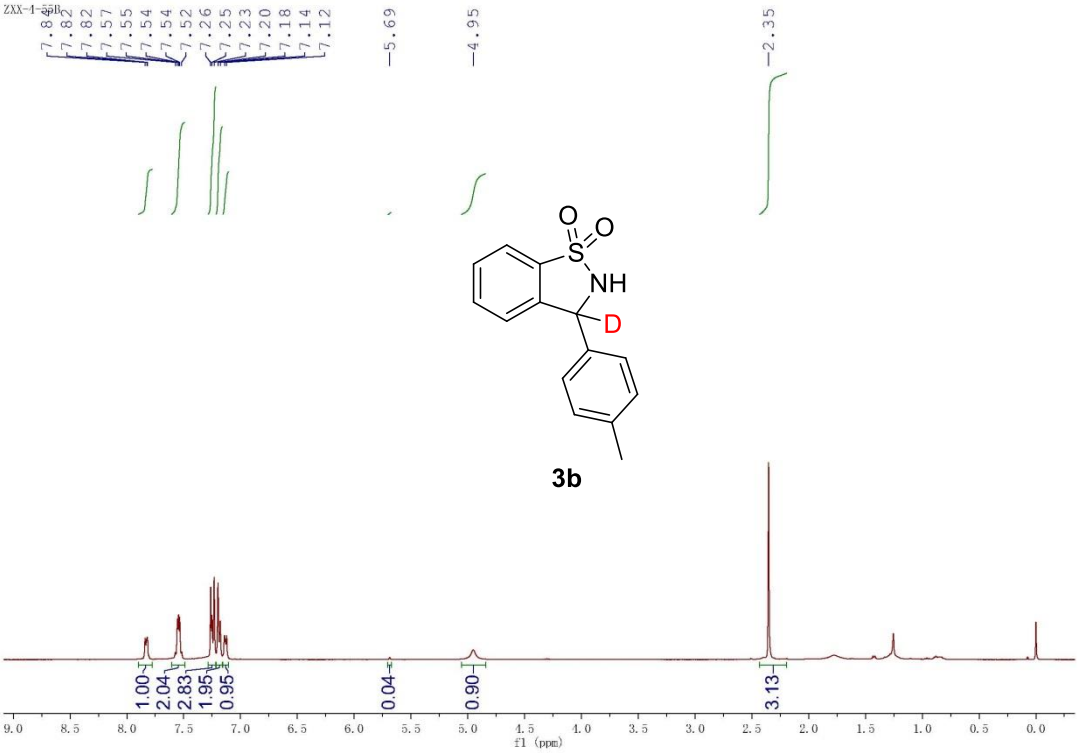

142.79
142.18
139.87
139.69
139.07
138.63
134.87
134.69
133.38
133.31
129.52
129.47
129.38
129.20
127.60
126.76
126.71
126.18
125.93
125.43
125.40
125.12
121.15
121.12
64.66
64.52
61.42
61.30
25.91
25.65
18.38
17.98
-3.59
-5.28
O
O
S
NH
OTBS
2r
f1 (ppm)

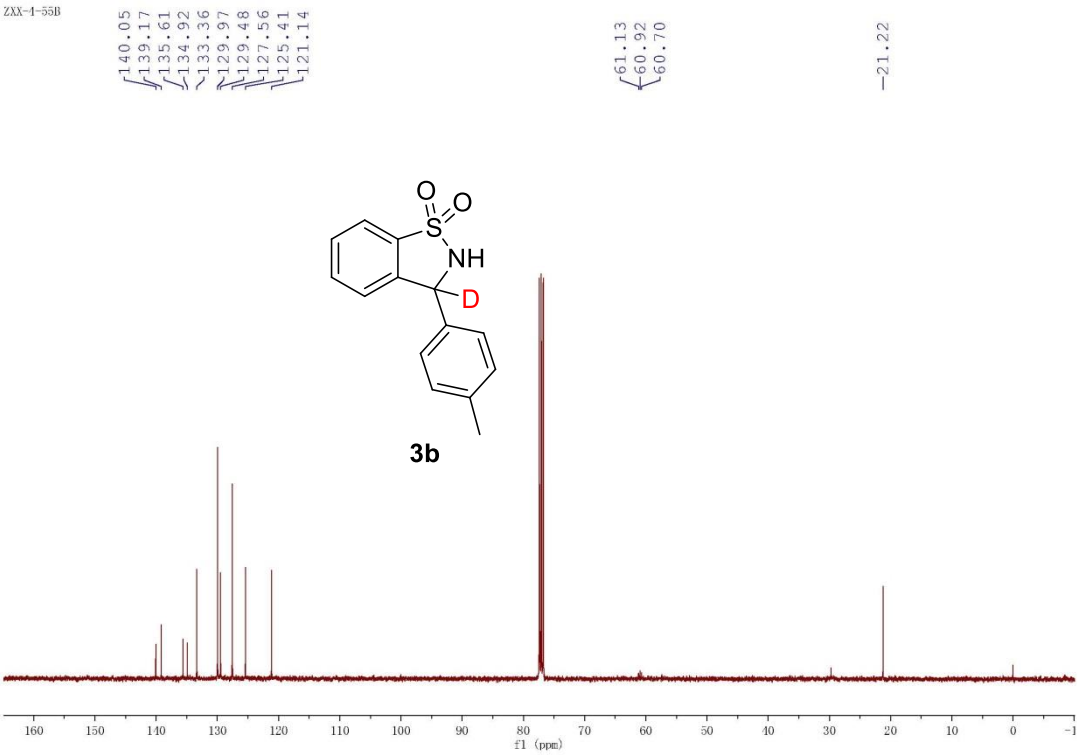

ZXX-1-16A
7.76
7.74
7.57
7.57
7.50
7.32
7.32
7.31
7.28
7.28
7.27
7.26
7.26
7.24
7.24
7.22
7.21
4.86
4.85
4.84
4.83
4.81
4.64
3.25
3.24
3.22
3.20
2.99
2.97
2.96
2.93
O
O
S
NH
2s
1.00
2.18
6.19
1.06
0.94
1.08
1.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

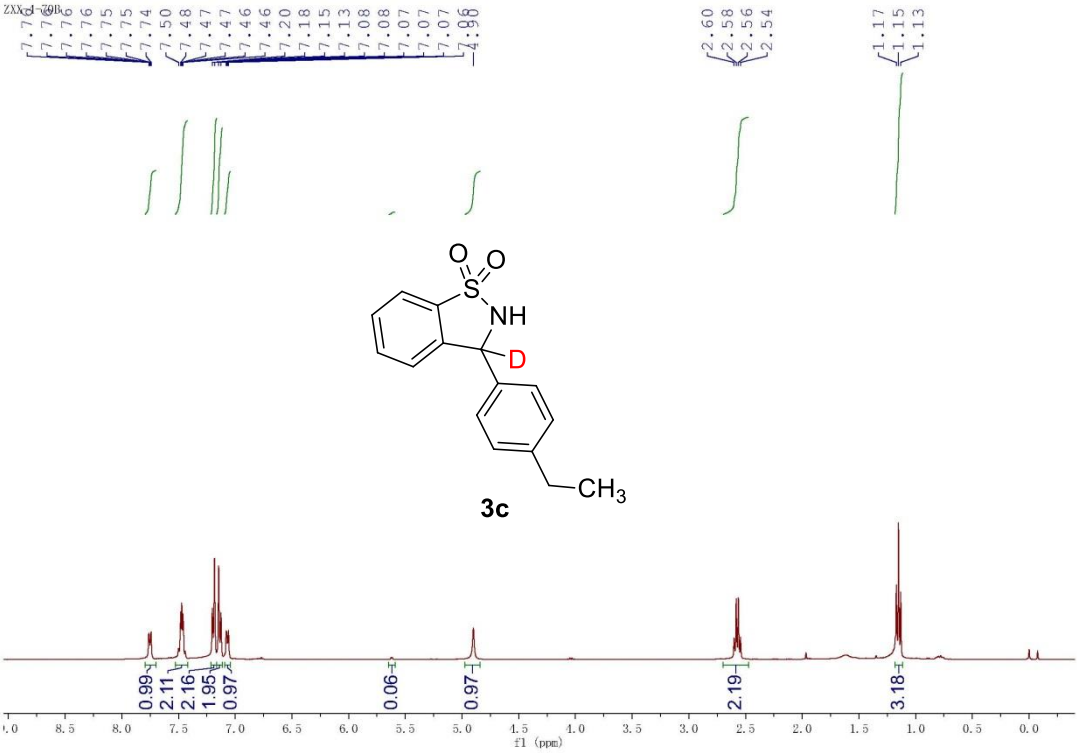

ZXX-1-16A
139.37
136.39
135.63
133.03
129.58
129.41
129.03
127.48
124.40
121.52
58.81
42.37
O
O
S
NH
2s
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

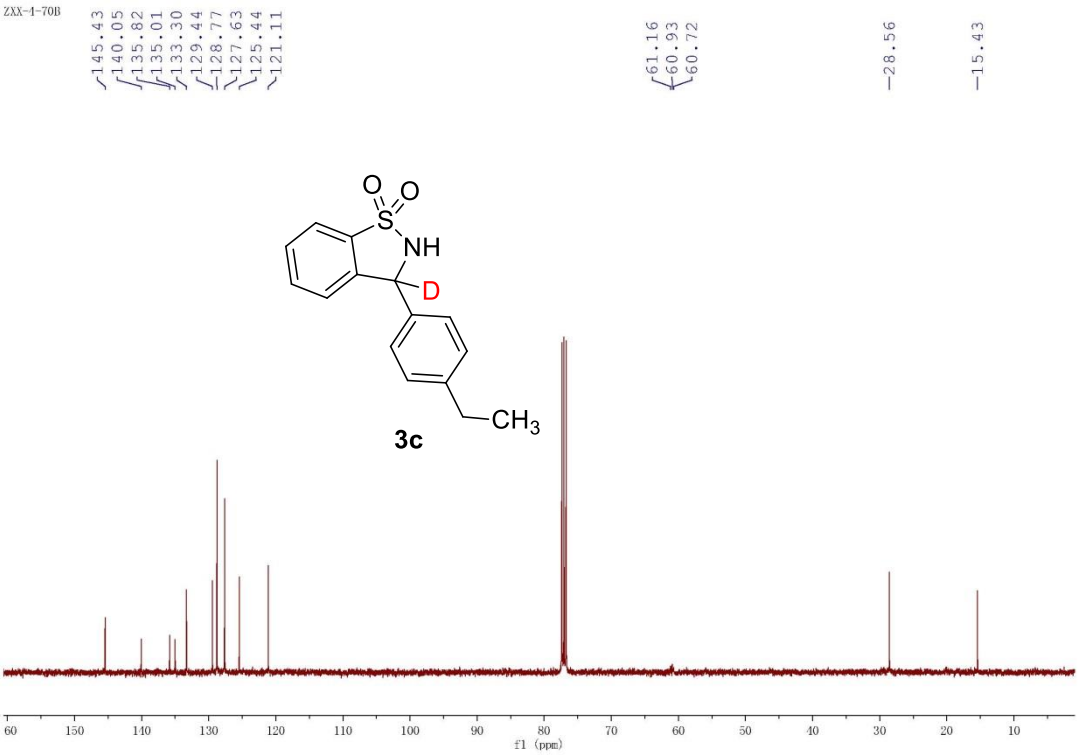

ZXX-5-19B
7.86
7.86
7.85
7.85
7.84
7.59
7.58
7.57
7.56
7.56
7.41
7.40
7.39
7.38
7.38
5.75
5.09
O
O
S
NH
D
3a
1.00
2.10
5.08
1.08
0.06
0.92
f1 (ppm)

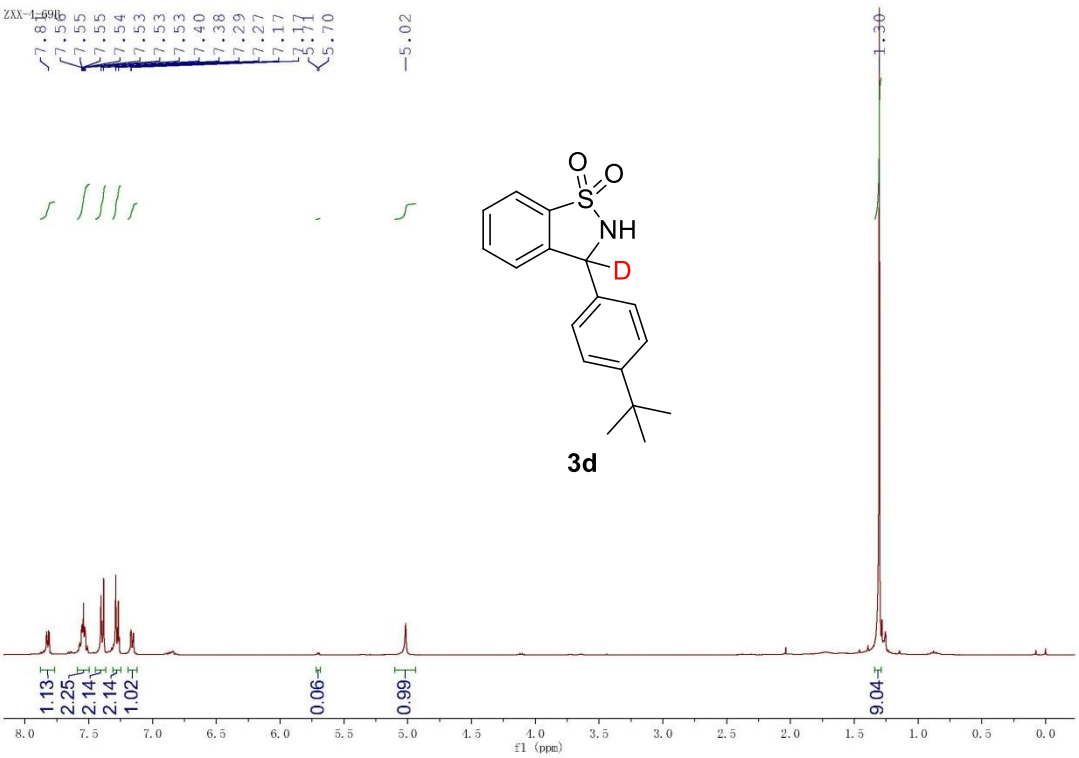

ZXX-5-19B
139.77
138.66
134.76
133.41
129.56
129.30
129.14
127.61
125.43
121.18
61.28
61.06
60.84
O
O
S
NH
D
3a
f1 (ppm)

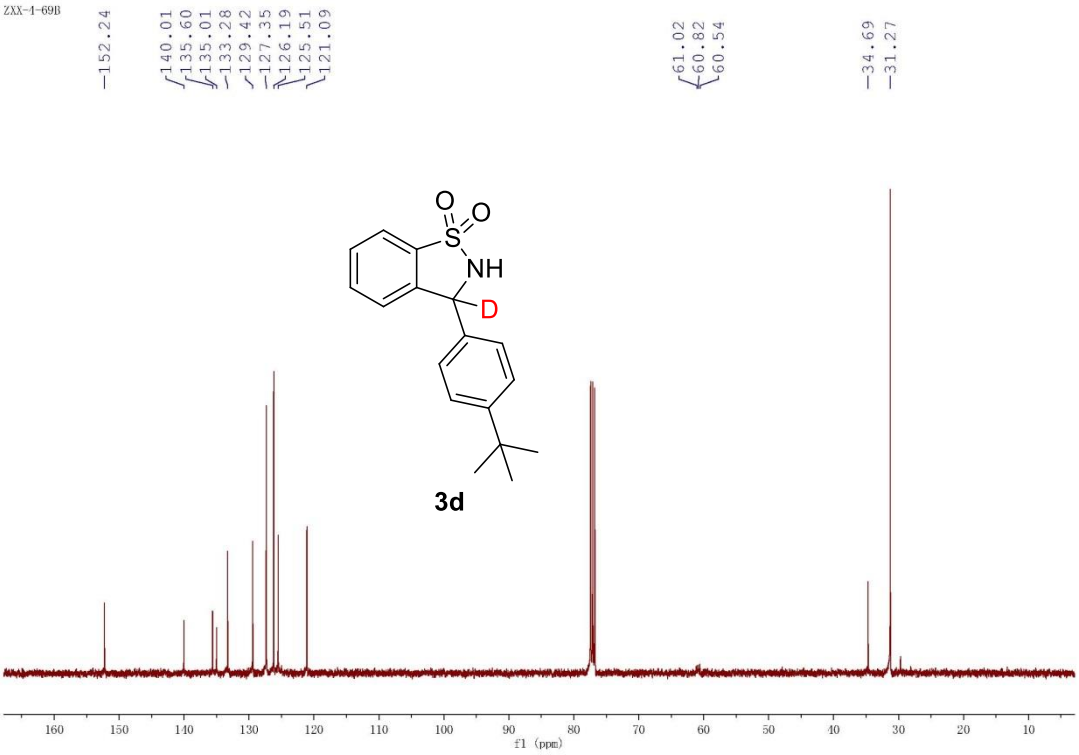

ZXX-1-55B
7.88
7.82
7.82
7.57
7.55
7.54
7.54
7.52
7.26
7.25
7.23
7.20
7.18
7.14
7.12
5.69
4.95
2.35
O
O
S
NH
D
3b
1.00
2.04
2.83
1.95
0.95
0.04
0.90
3.13
f1 (ppm)

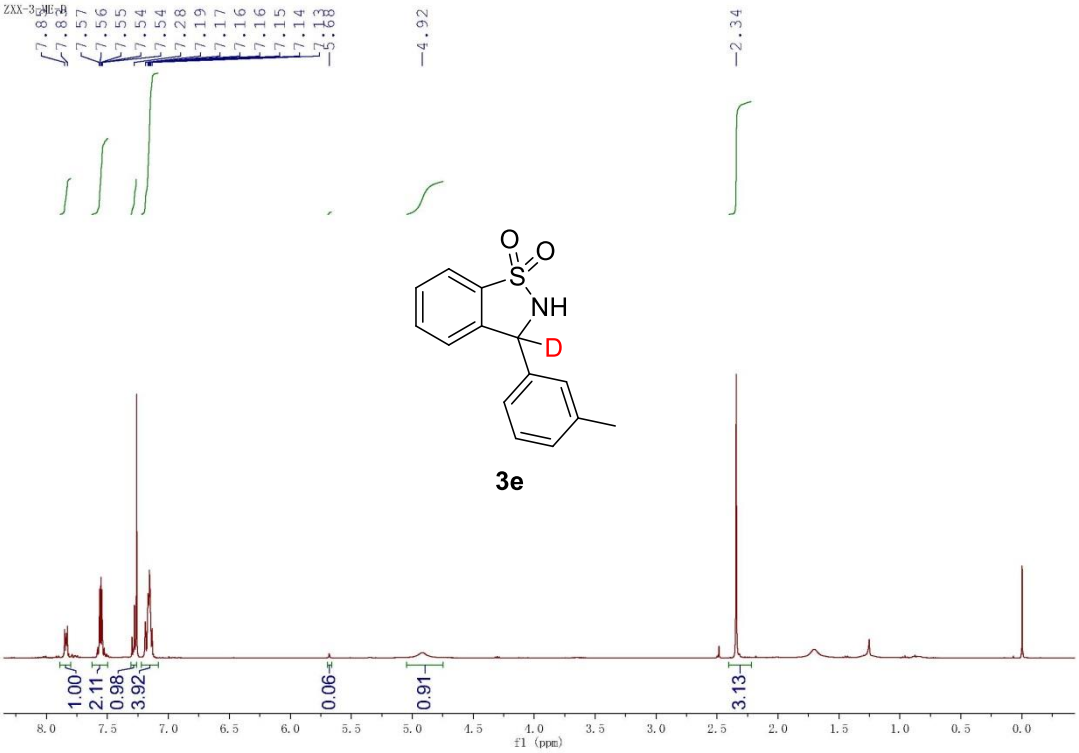

ZXX-1-55B
140.05
139.17
135.61
134.92
133.36
129.97
129.48
127.56
125.41
121.14
61.13
60.92
60.70
21.22
O
O
S
NH
D
3b
f1 (ppm)

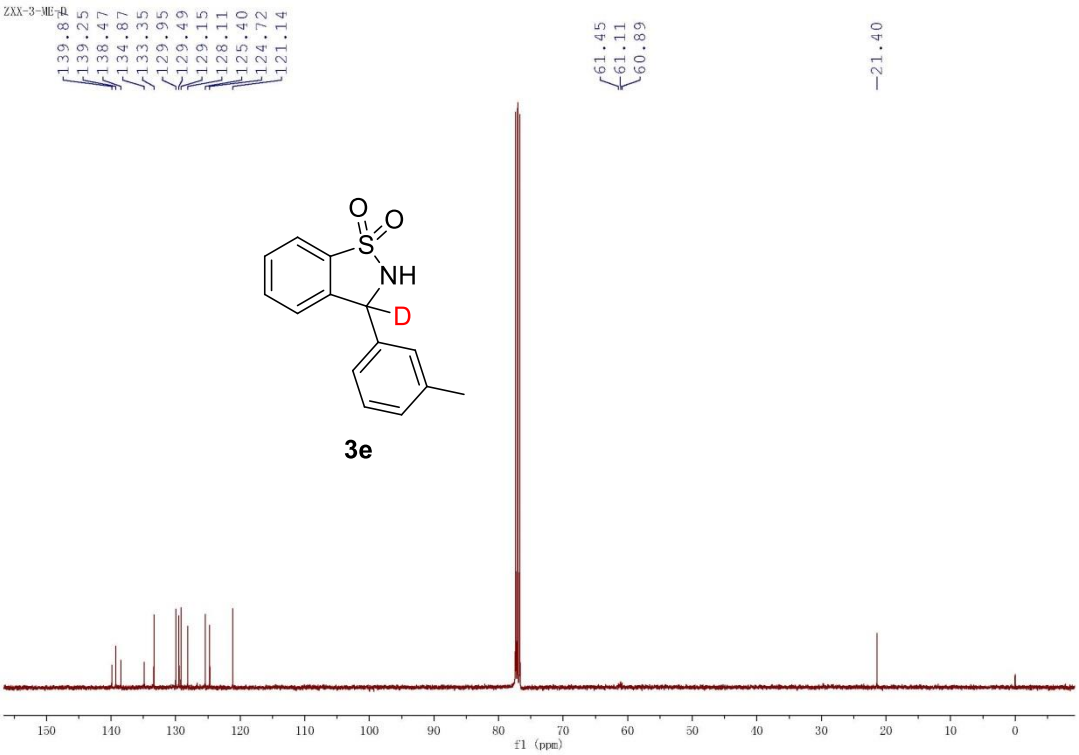

7.76
7.75
7.74
7.50
7.48
7.47
7.46
7.20
7.18
7.15
7.13
7.08
7.07
2.60
2.58
2.56
2.54
1.17
1.15
1.13
O
O
S
NH
D
CH3
3c
0.99
2.11
2.16
1.95
0.97
0.06
0.97
2.19
3.18
f1 (ppm)

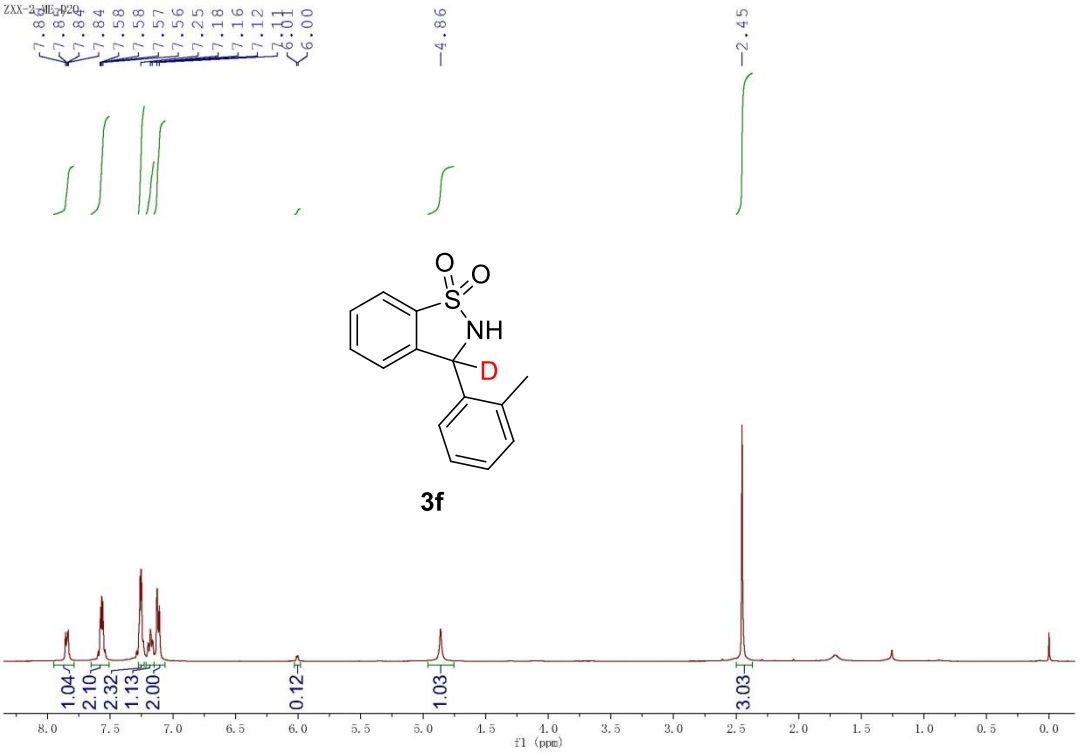

ZXX-1-70B
145.43
140.05
135.82
135.01
133.30
129.44
128.77
127.63
125.44
121.11
61.16
60.93
60.72
28.56
15.43
O
O
S
NH
D
CH3
3c
f1 (ppm)


ZXX-1-69D
7.81
7.56
7.55
7.55
7.54
7.53
7.53
7.53
7.40
7.38
7.29
7.27
7.17
5.71
5.70
5.02
1.30
O
O
S
NH
D
3d
1.13
2.25
2.14
2.14
1.02
0.06
0.99
9.04
f1 (ppm)

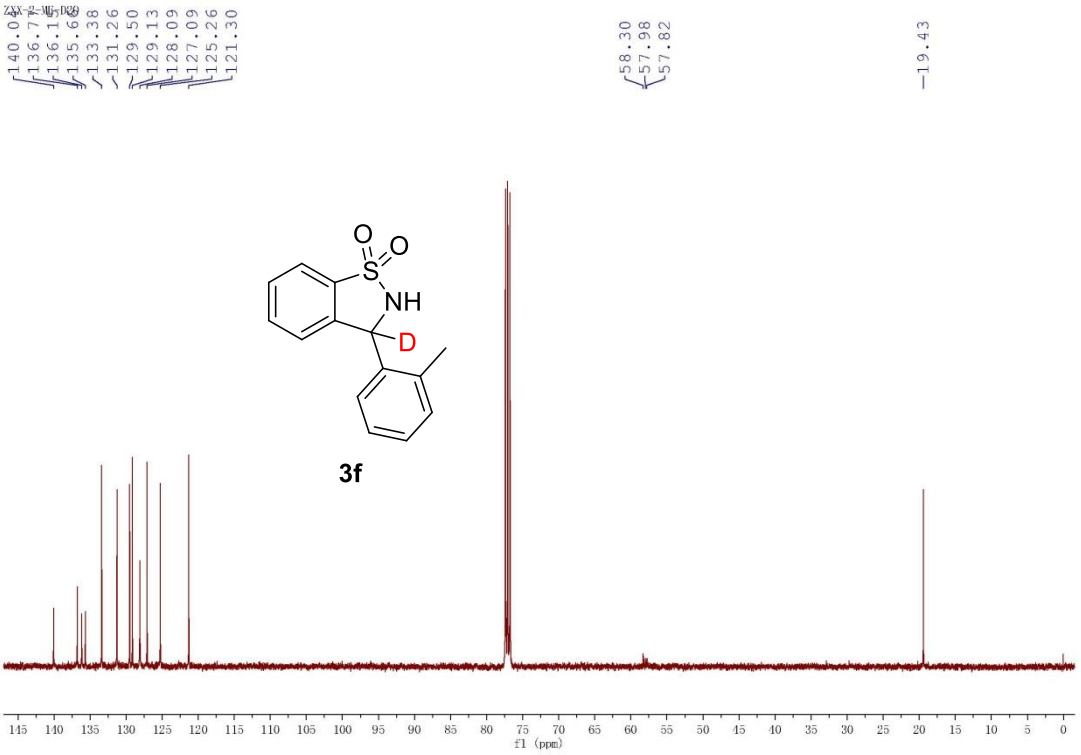

ZXX-1-69B
152.24
140.01
135.60
135.01
133.28
129.42
127.35
126.19
125.51
121.09
61.02
60.82
60.54
34.69
31.27
O
O
S
NH
D
3d
f1 (ppm)


7.83
7.82
7.57
7.56
7.55
7.54
7.54
7.28
7.19
7.17
7.16
7.16
7.15
7.14
7.13
5.08
4.92
2.34
O
O
S
NH
D
3e
1.00
2.11
0.98
3.92
0.06
0.91
3.13
f1 (ppm)

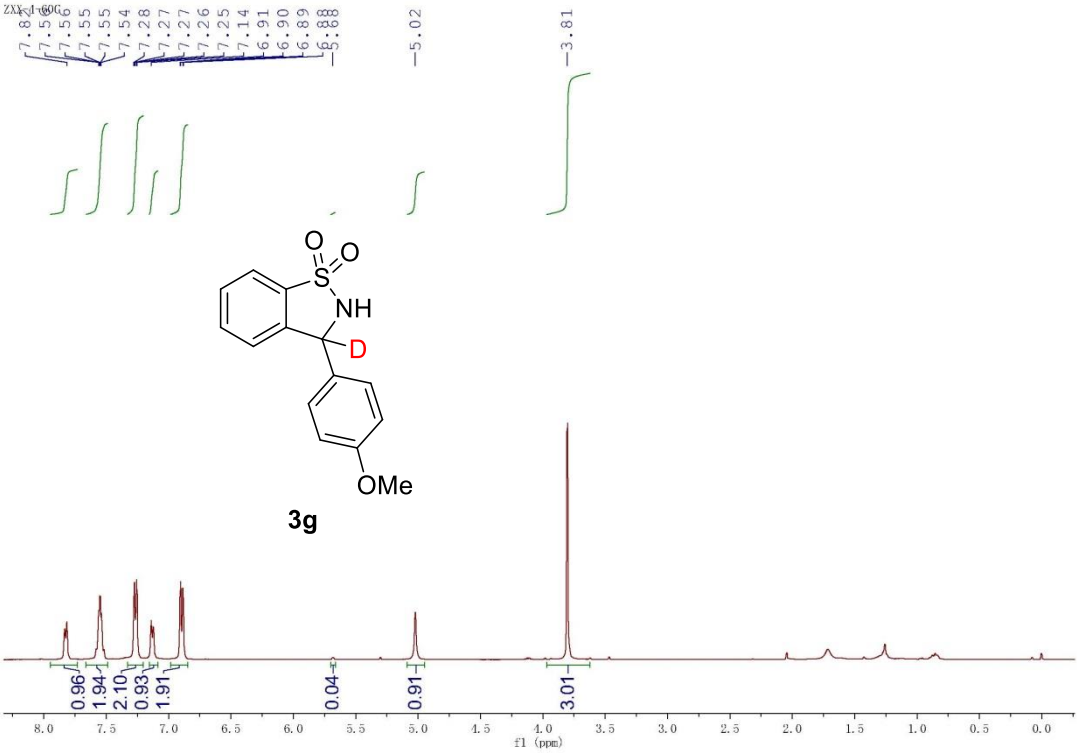

139.87
139.25
138.47
134.87
133.35
129.95
129.49
129.15
128.11
125.40
124.72
121.14
61.45
61.11
60.89
21.40
O
O
S
NH
D
3e
f1 (ppm)

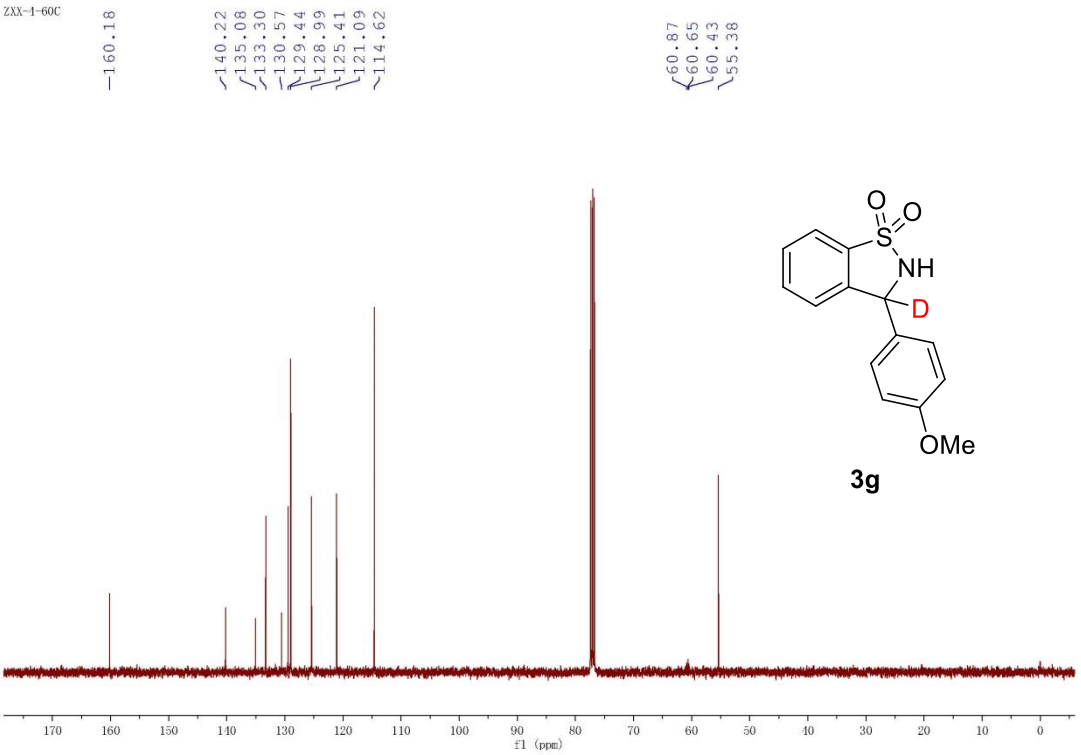

7.85
7.84
7.84
7.84
7.58
7.58
7.57
7.56
7.25
7.18
7.16
7.12
7.11
6.01
6.00
4.86
2.45
O
O
S
NH
D
1.04
2.10
2.32
1.13
2.00
0.12
1.03
3.03
f1 (ppm)

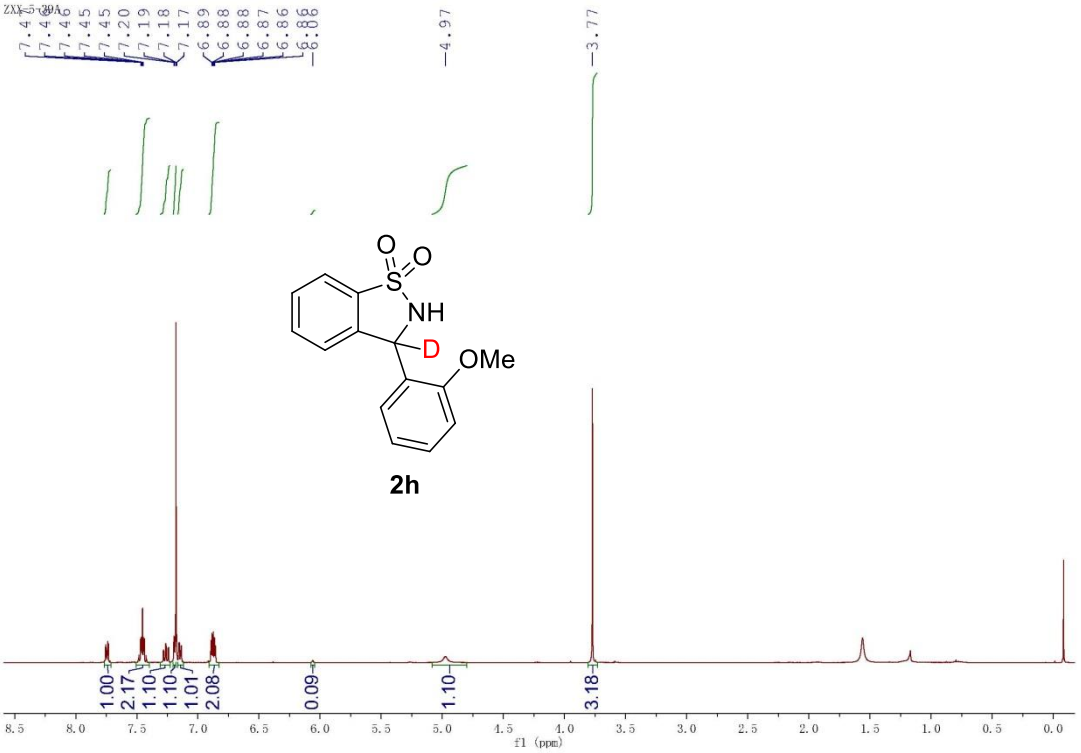
3f

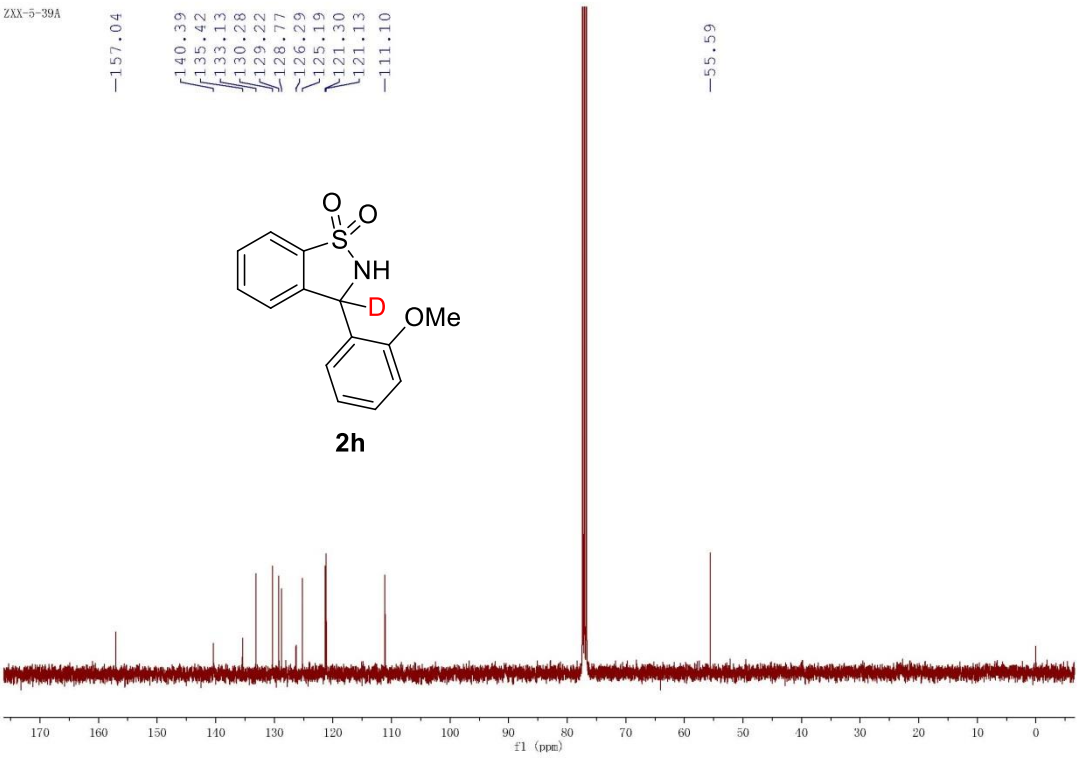

140.07
136.77
136.12
135.62
133.38
131.26
129.50
129.13
128.09
127.09
125.26
121.30
58.30
57.98
57.82
19.43
O
O
S
NH
D
f1 (ppm)

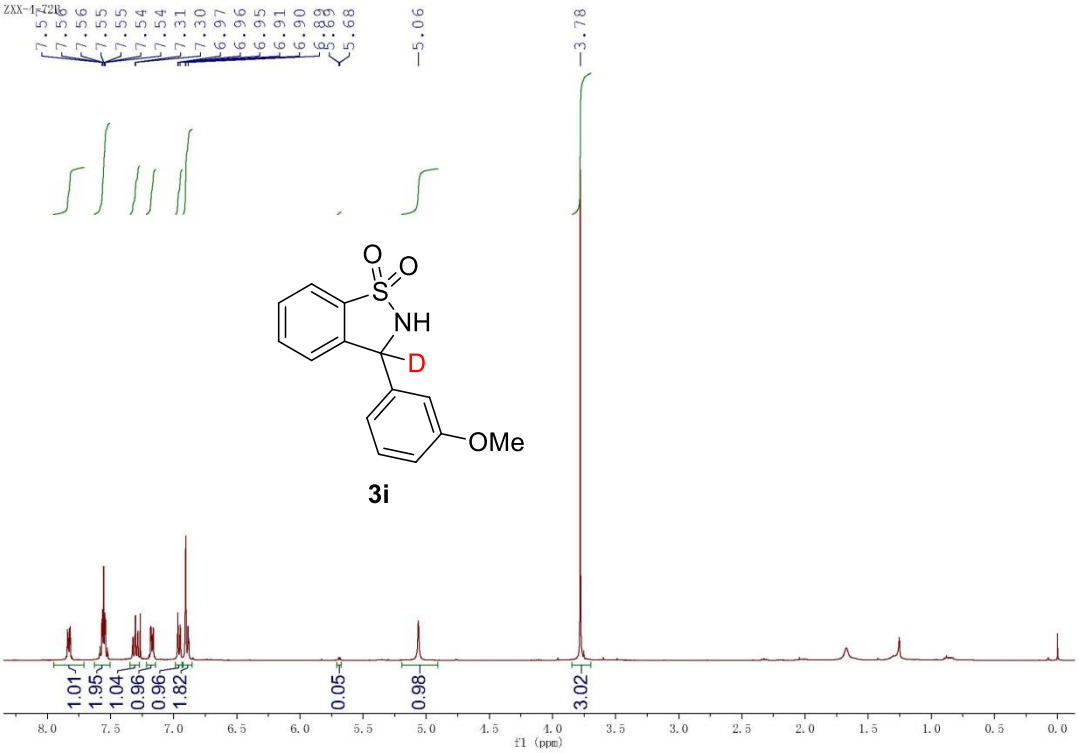
3f

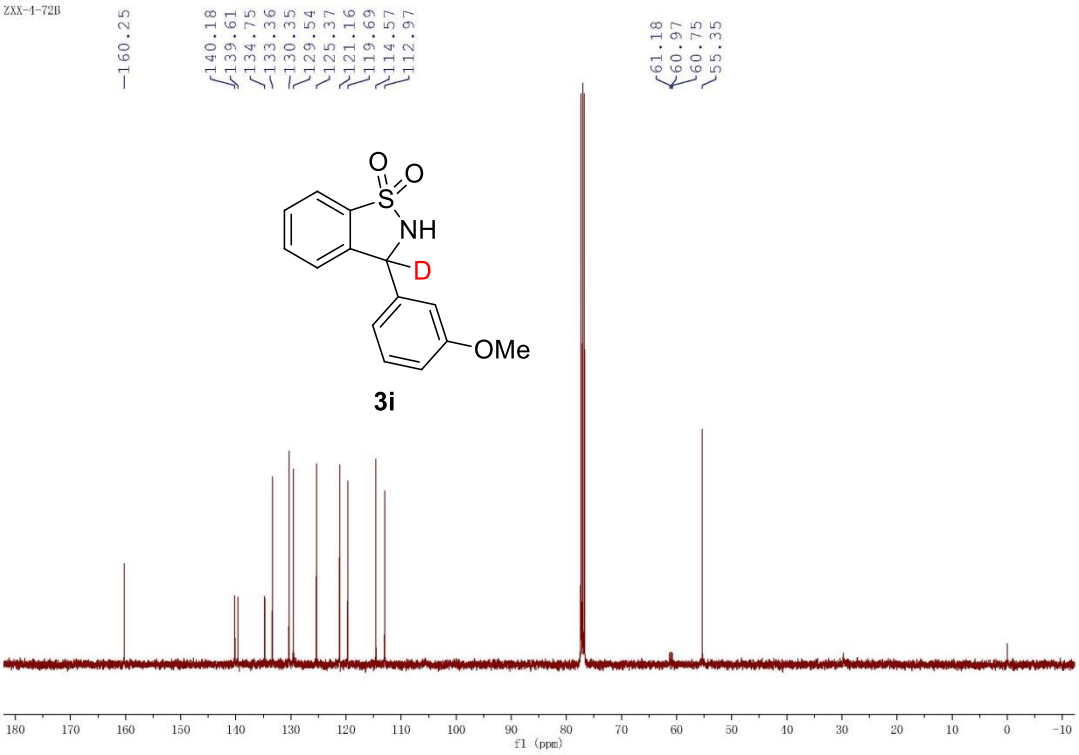

ZXX-1-60C
7.56
7.55
7.55
7.54
7.28
7.27
7.27
7.26
7.25
7.14
6.91
6.90
6.89
6.88
5.02
3.81
O
O
S
NH
D
OMe
3g
0.96
1.94
2.10
0.93
1.91
0.04
0.91
3.01
f1 (ppm)

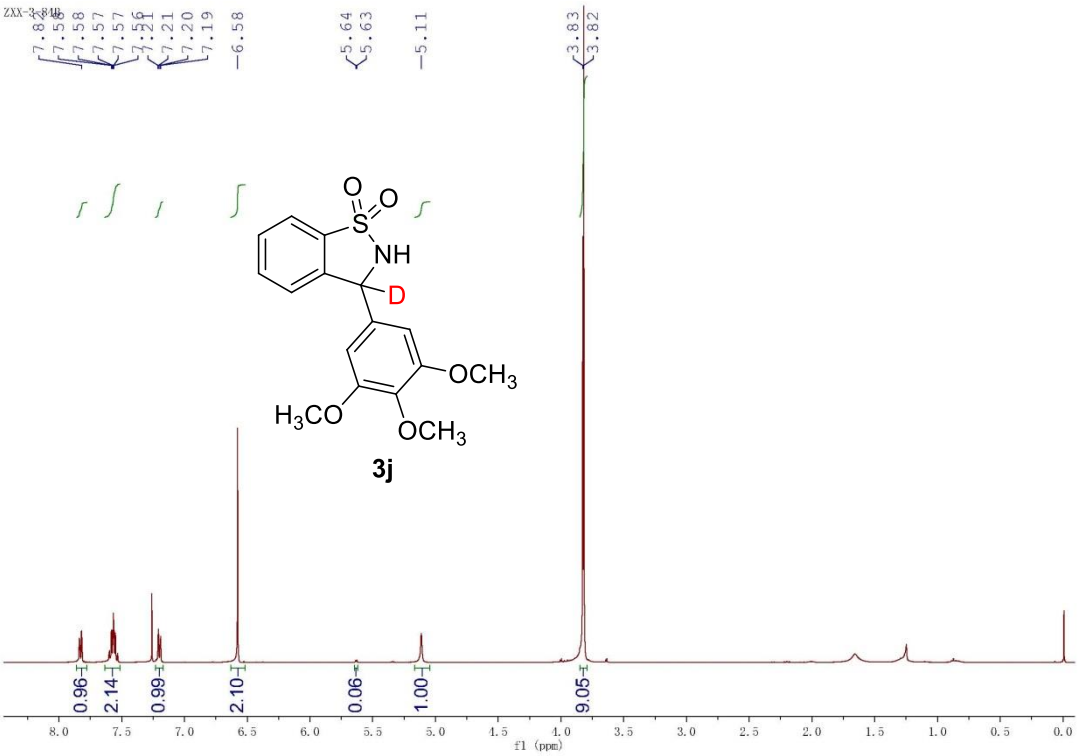

ZXX-1-60C
160.18
140.22
135.08
133.30
130.57
129.44
128.99
125.41
121.09
114.62
60.87
60.65
60.43
55.38
O
O
S
NH
D
OMe
3g
f1 (ppm)

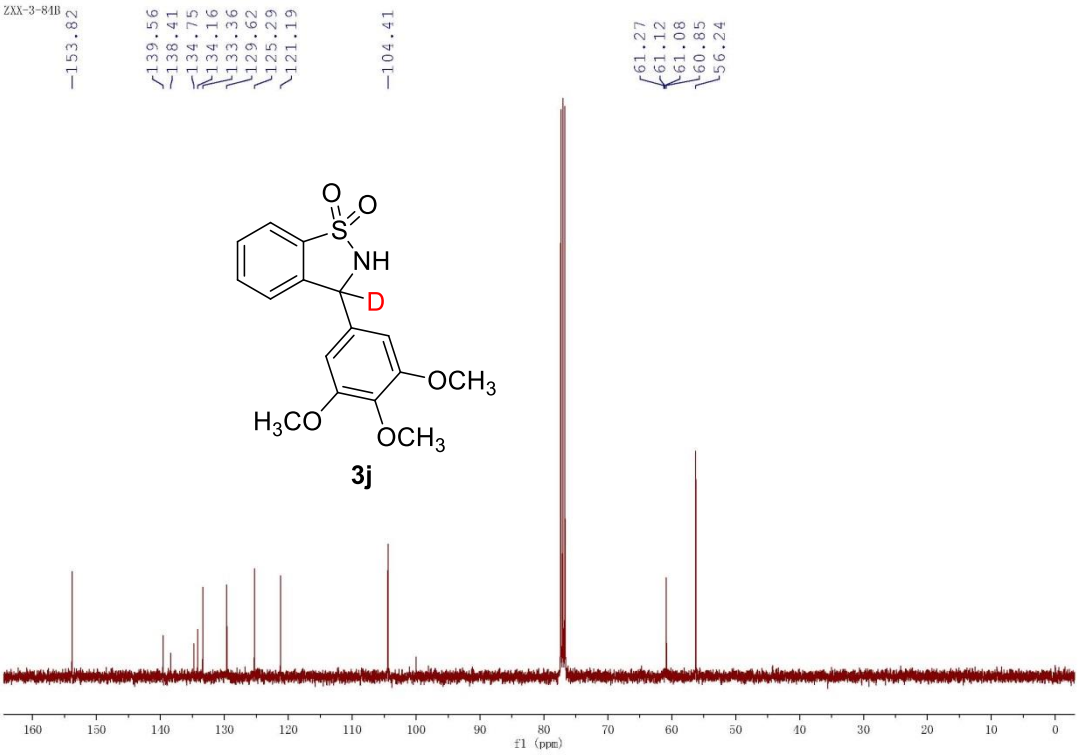

ZXX-5-39A
7.46
7.45
7.20
7.19
7.18
7.17
6.89
6.88
6.87
6.86
4.97
3.77
O
O
S
NH
D
OMe
2h
1.00
2.17
1.10
1.10
1.01
2.08
0.09
1.10
3.18
f1 (ppm)

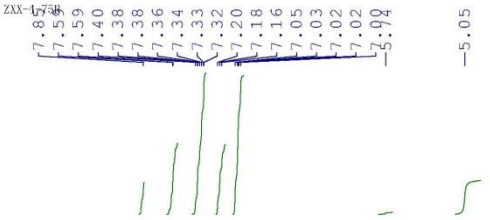

ZXX-5-39A
157.04
140.39
135.42
133.13
130.28
129.22
128.77
126.29
125.19
121.30
121.13
111.10
55.59
O
O
S
NH
D
OMe
2h
f1 (ppm)

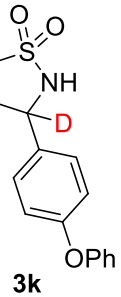

ZXX-1-72B
7.56
7.56
7.56
7.55
7.55
7.55
7.54
7.54
7.31
7.30
6.97
6.96
6.95
6.91
6.90
5.68
5.06
3.78
O
O
S
NH
D
OMe
3i
1.01
1.95
1.04
0.96
0.96
1.82
0.05
0.98
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


ZXX-1-72B
160.25
140.18
139.61
134.75
133.36
130.35
129.54
125.37
121.16
119.69
114.57
112.97
61.18
60.97
60.75
55.35
O
O
S
NH
D
OMe
3i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

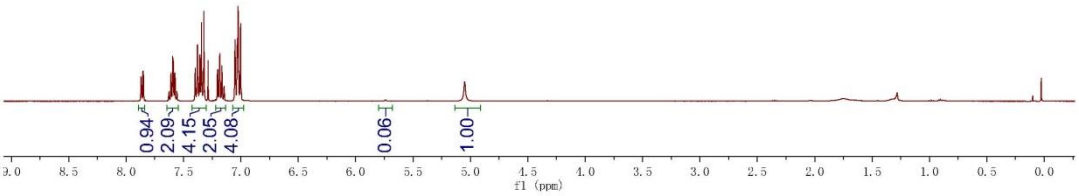

ZXX-3-84B
7.58
7.58
7.57
7.57
7.56
7.21
7.20
7.19
6.58
5.64
5.63
5.11
3.83
3.82
O
O
S
NH
D
OCH3
H3CO
OCH3
3j
0.96
2.14
0.99
2.10
0.06
1.00
9.05
f1 (ppm)

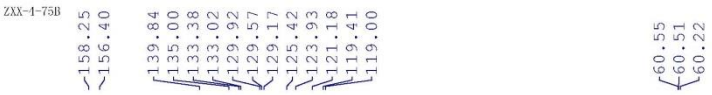

ZXX-3-84B
153.82
139.56
138.41
134.75
134.16
133.36
129.62
125.29
121.19
104.41
61.27
61.12
61.08
60.85
56.24
O
O
S
NH
D
OCH3
H3CO
OCH3
3j
f1 (ppm)

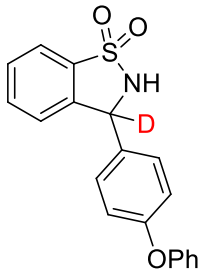




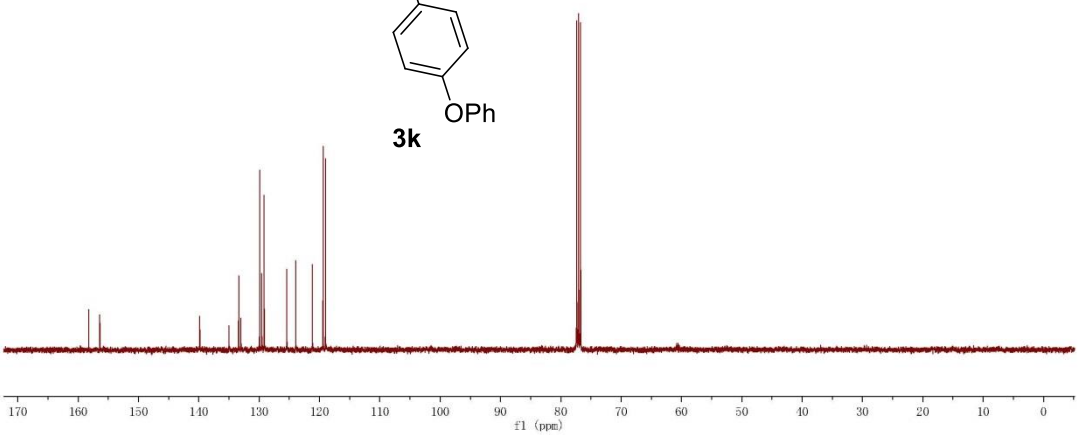
3k

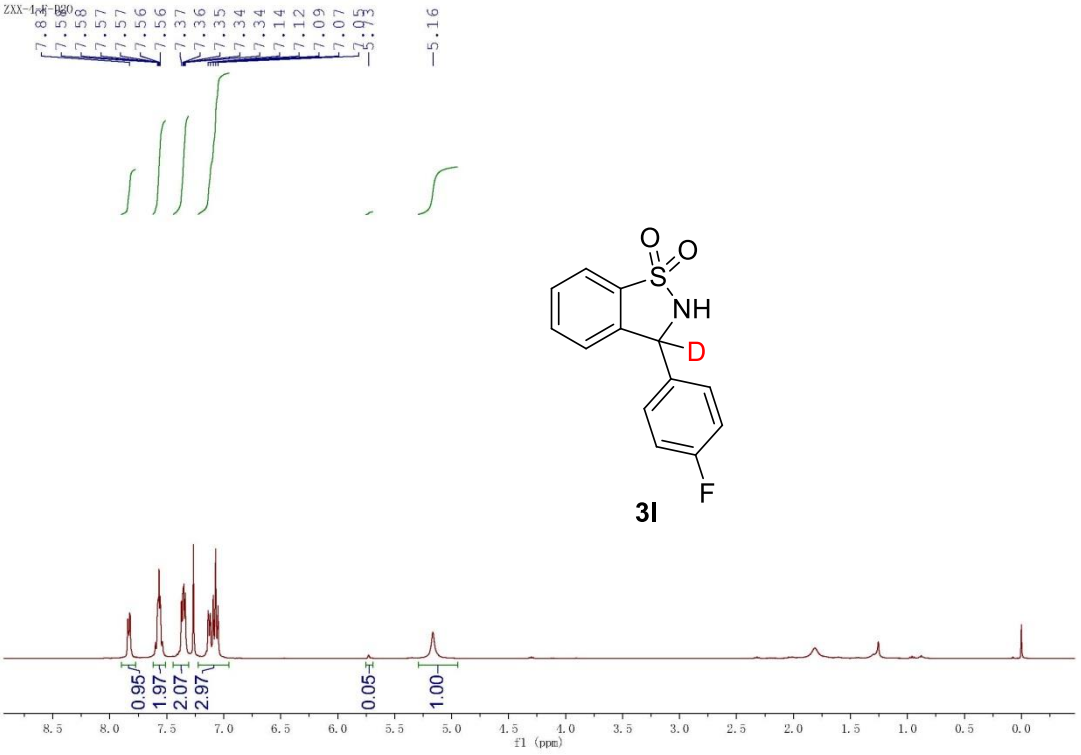


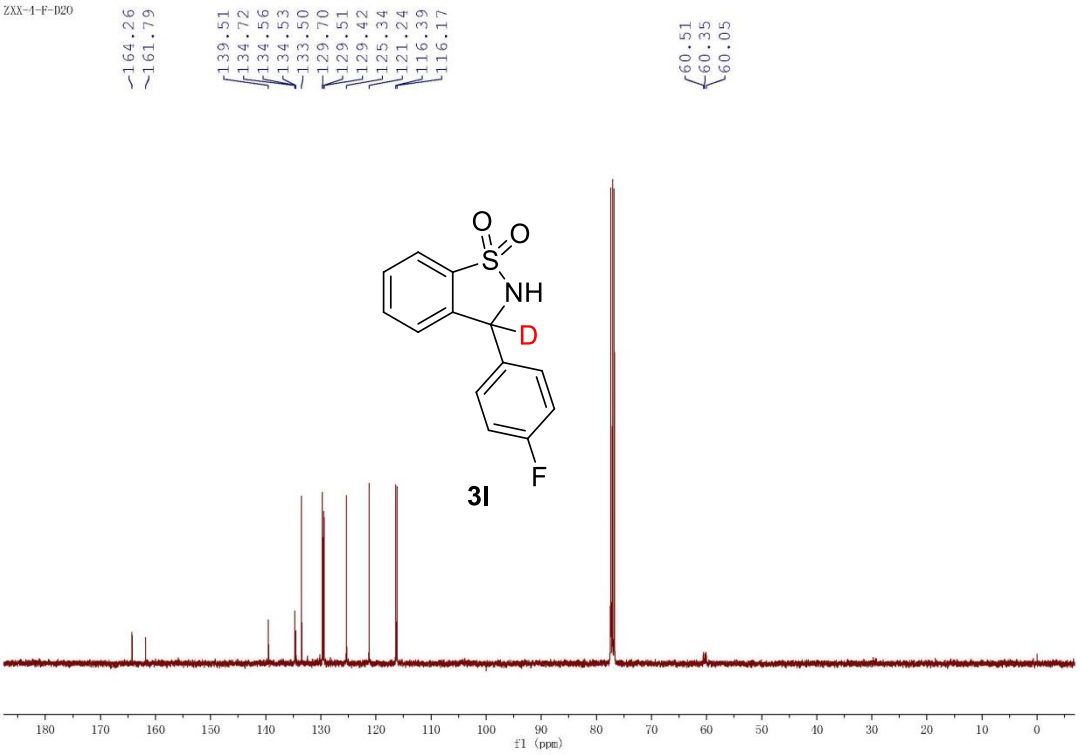


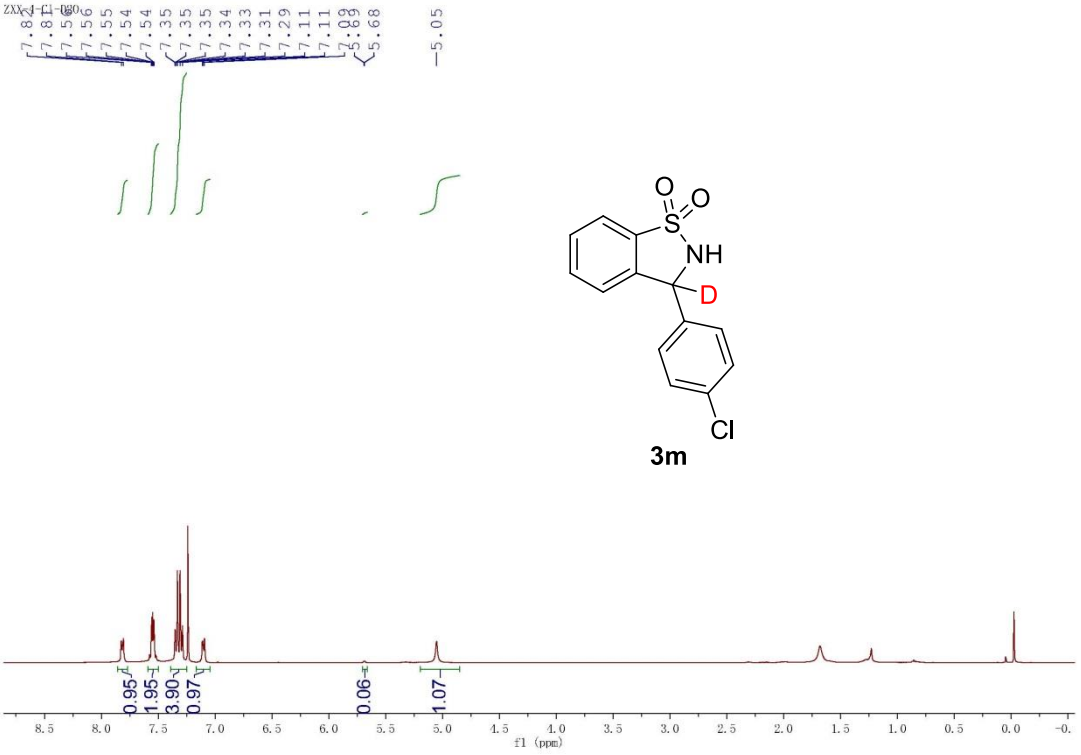


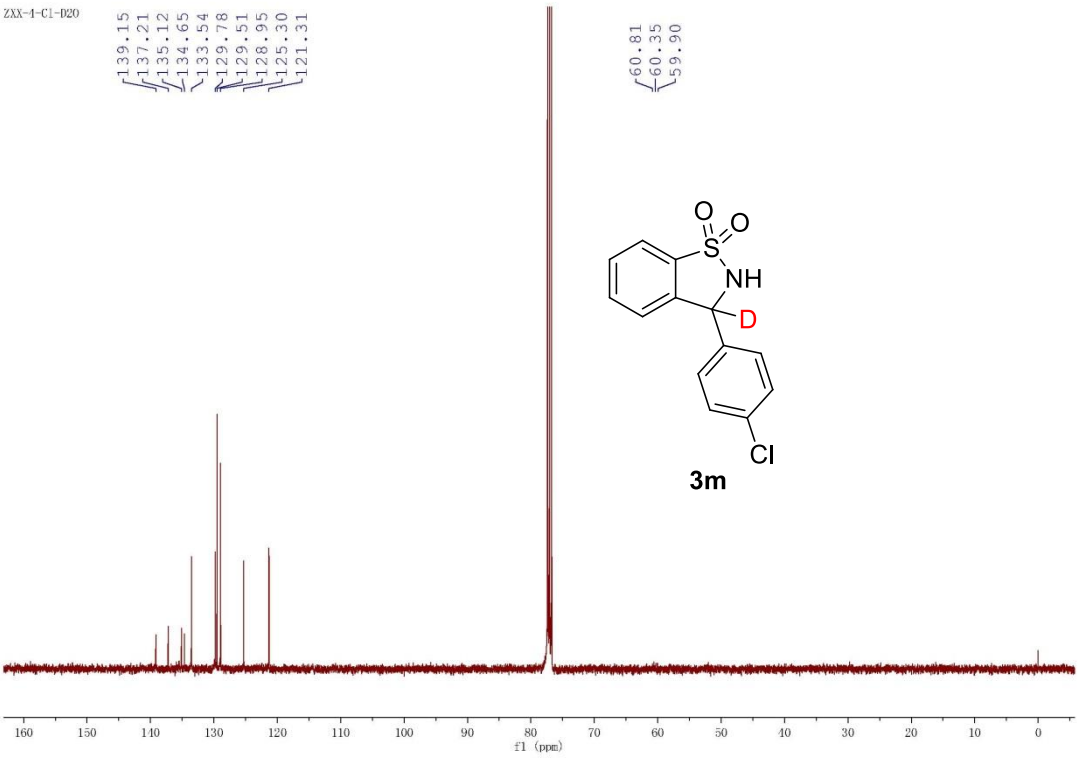
3k

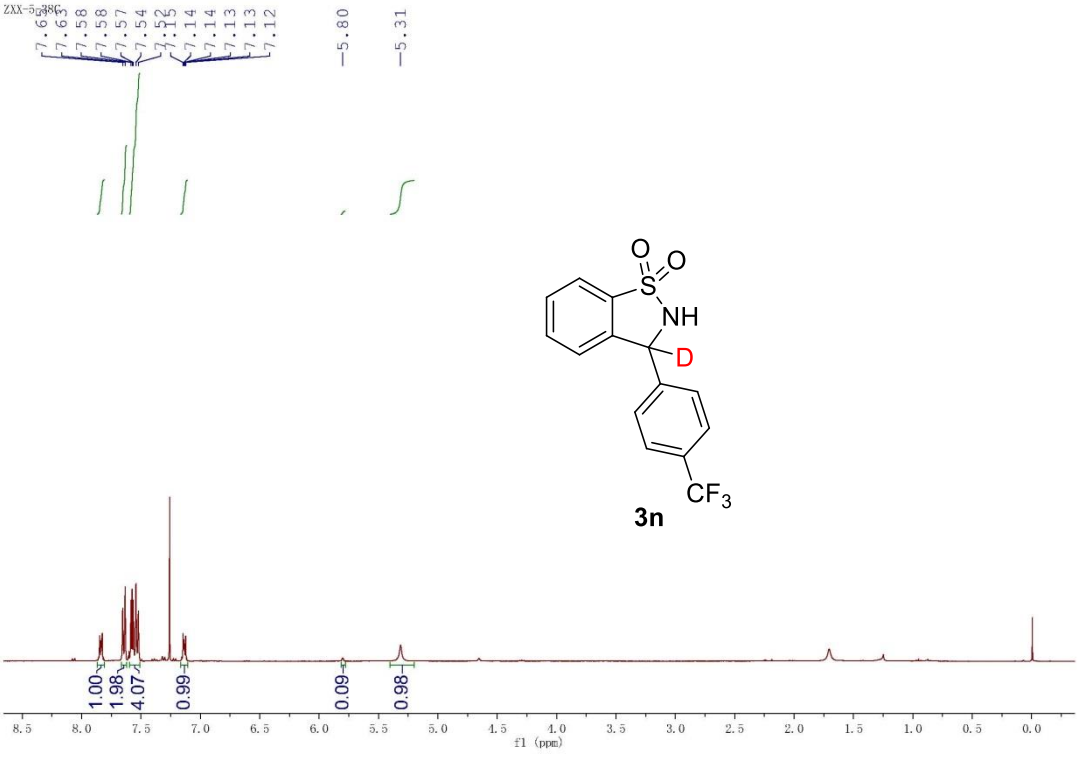


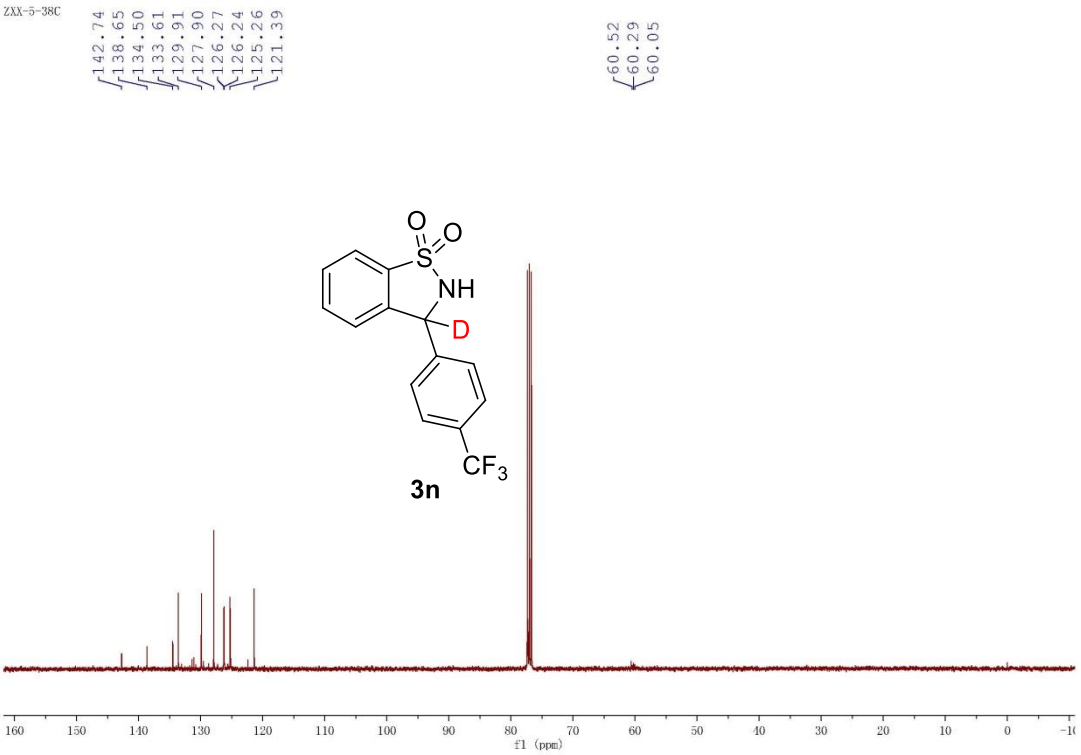

ZXX-1-F-D2O
7.58
7.57
7.56
7.37
7.35
7.34
7.14
7.12
7.09
7.07
5.16
O
O
S
NH
D
F
3l
0.95
1.97
2.07
2.97
0.05
1.00
f1 (ppm)

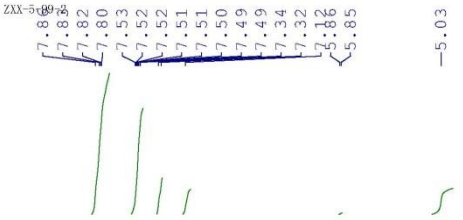

ZXX-1-F-D2O
164.26
161.79
139.51
134.72
134.56
134.53
133.50
129.70
129.51
129.42
125.34
121.24
116.39
116.17
60.51
60.35
60.05
O
O
S
NH
D
F
3l
f1 (ppm)

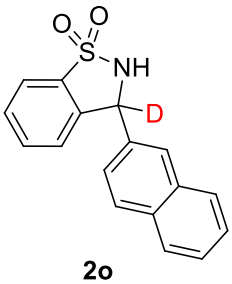

ZXX-3-C1-D2O
7.82
7.81
7.56
7.55
7.54
7.54
7.35
7.35
7.35
7.34
7.33
7.31
7.29
7.11
7.11
5.09
5.68
5.05
O
O
S
NH
D
Cl
3m
0.95
1.95
3.90
0.97
0.06
1.07
f1 (ppm)


ZXX-4-C1-D2O
139.15
137.21
135.12
134.65
133.54
129.78
129.51
128.95
125.30
121.31
60.81
60.35
59.90
O
O
S
NH
D
Cl
3m
f1 (ppm)

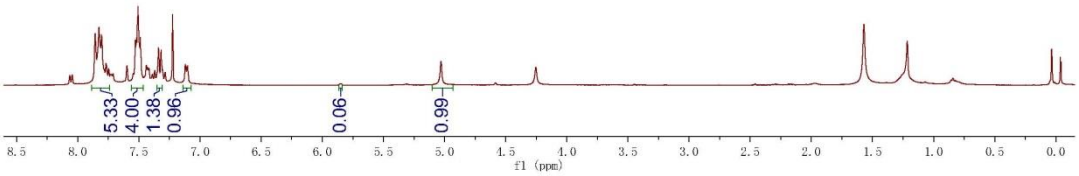

ZXX-5-38C
7.63
7.58
7.58
7.57
7.54
7.52
7.15
7.14
7.14
7.13
7.13
7.12
5.80
5.31
O
O
S
NH
D
CF3
3n
1.00
1.98
4.07
0.99
0.09
0.98
f1 (ppm)

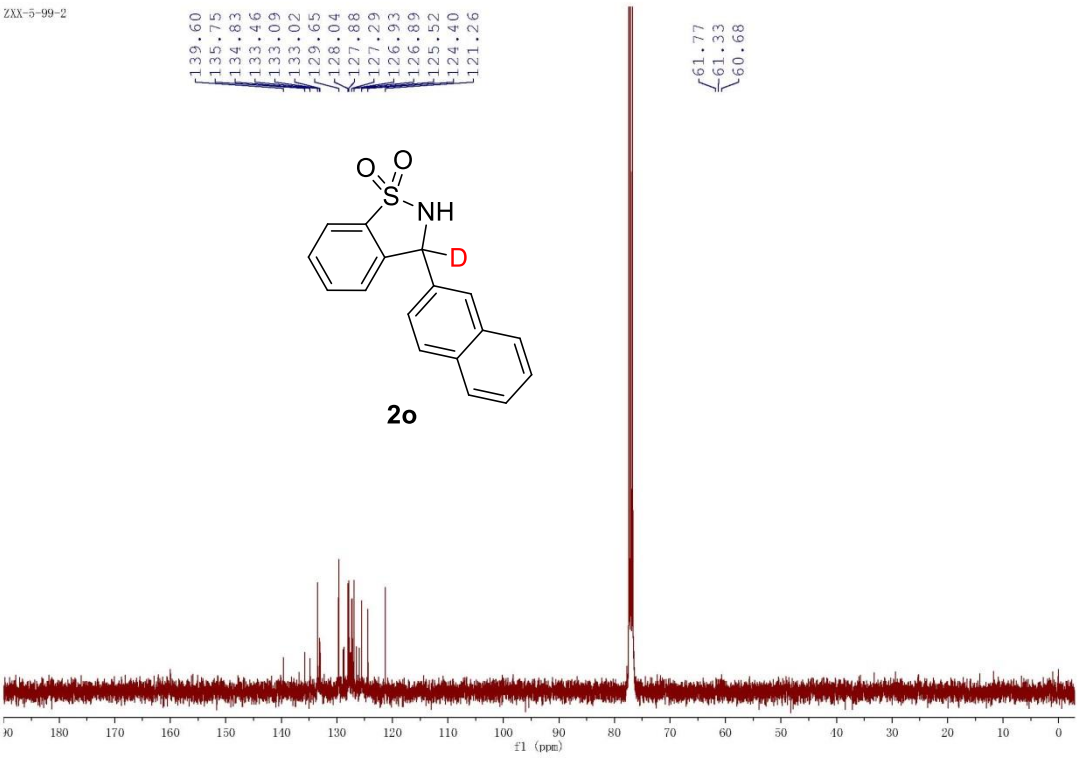

ZXX-5-38C
142.74
138.65
134.50
133.61
129.91
127.90
126.27
126.24
125.26
121.39
60.52
60.29
60.05
O
O
S
NH
D
CF3
3n
f1 (ppm)


ZXX-5-99-2
7.83
7.82
7.80
7.53
7.52
7.51
7.50
7.49
7.34
7.32
5.86
5.85
5.03

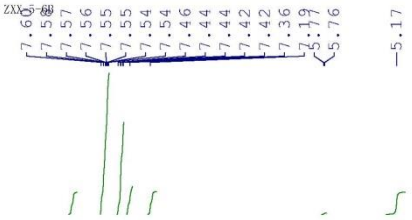

O
O
S
NH
D

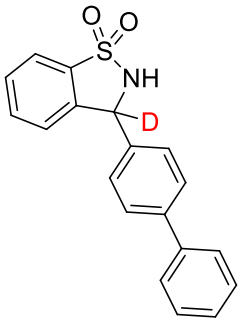
2o


5.33
4.00
1.38
0.96
0.06
0.99
f1 (ppm)

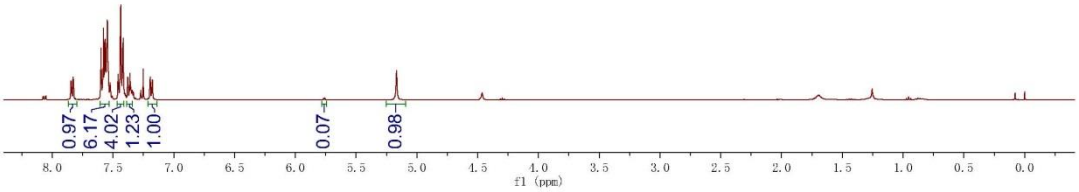

ZXX-5-99-2
139.60
135.75
134.83
133.46
133.09
133.02
129.65
128.04
127.88
127.29
126.93
126.89
125.52
124.40
121.26
61.77
61.33
60.68
O
O
S
NH
D
f1 (ppm)

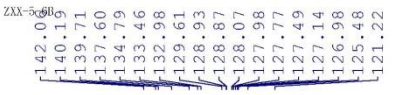
2o


7.60
7.58
7.57
7.56
7.55
7.55
7.54
7.54
7.46
7.44
7.44
7.42
7.42
7.36
5.19
5.17
5.76
5.17

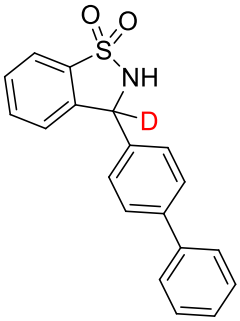

O
O
S
NH
D

3p

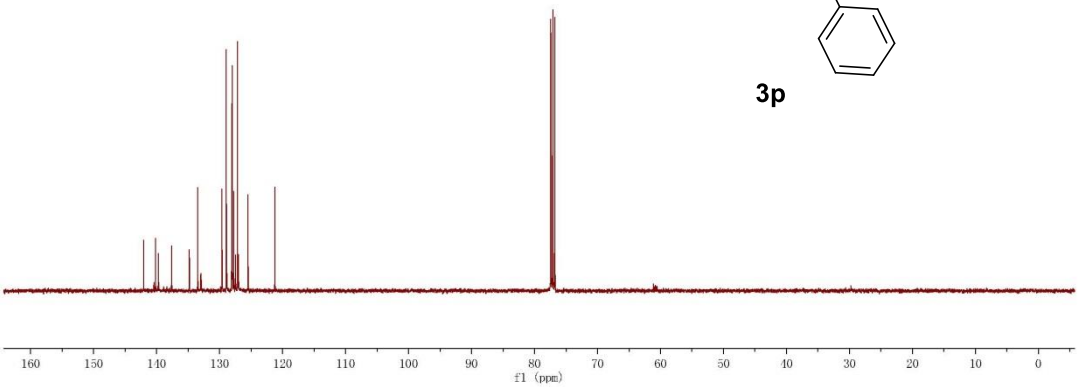

0.97
6.17
4.02
1.23
1.00
0.07
0.98
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

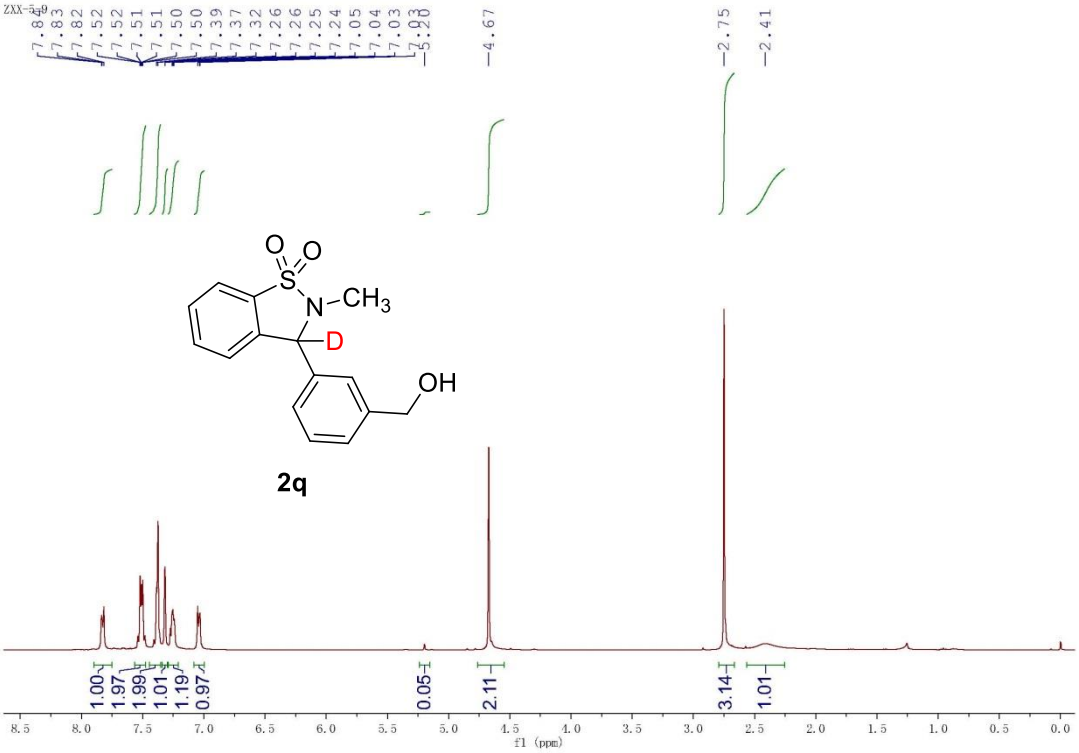

142.05
140.19
139.71
137.60
134.79
133.46
132.98
129.61
128.93
128.87
128.07
127.98
127.77
127.49
127.14
126.98
125.48
121.22


61.13
60.80
60.59

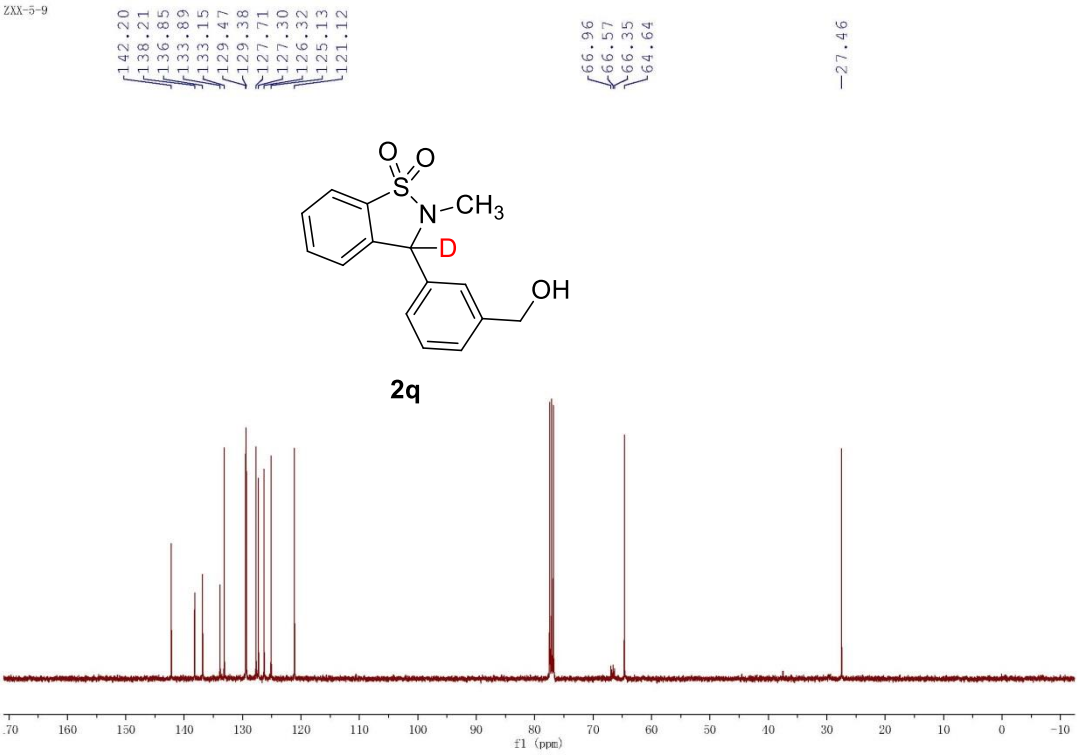

O
O
S
NH
D

3p

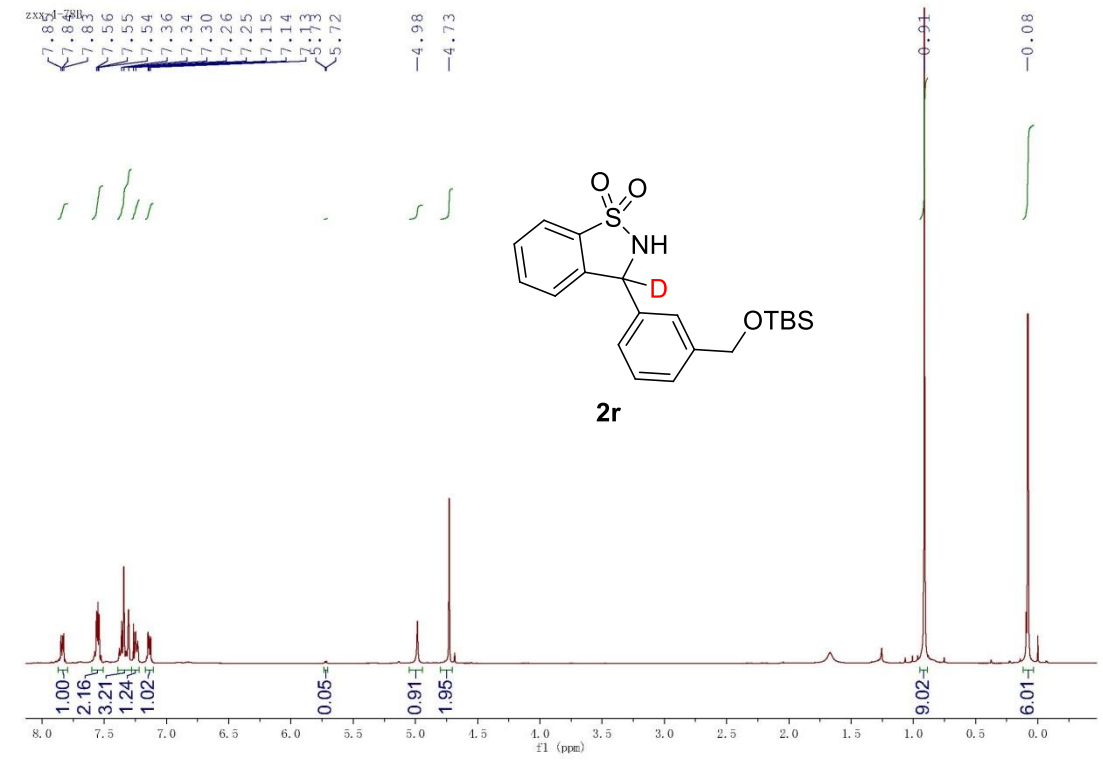

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

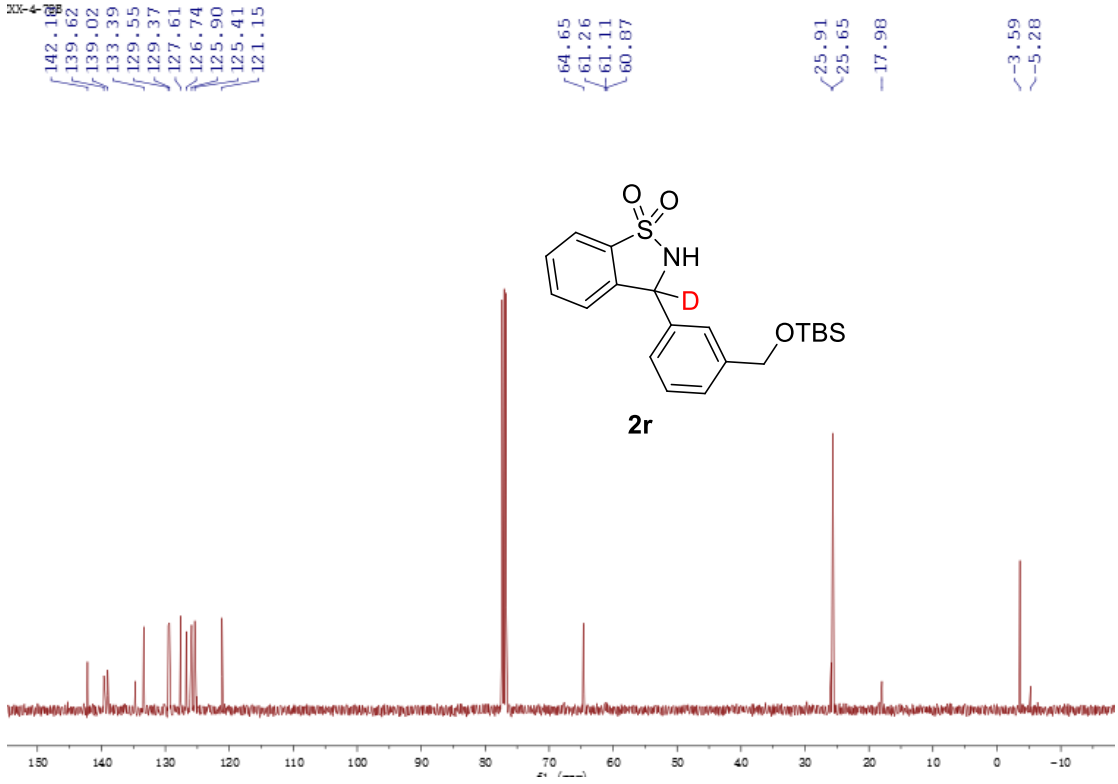

ZXX-5-9
7.83
7.82
7.52
7.51
7.50
7.39
7.37
7.32
7.26
7.25
7.24
7.05
7.04
7.03
4.67
2.75
2.41
O
O
S
N
CH3
D
OH
1.00
1.97
1.99
1.01
1.19
0.97
0.05
2.11
3.14
1.01
f1 (ppm)

2q

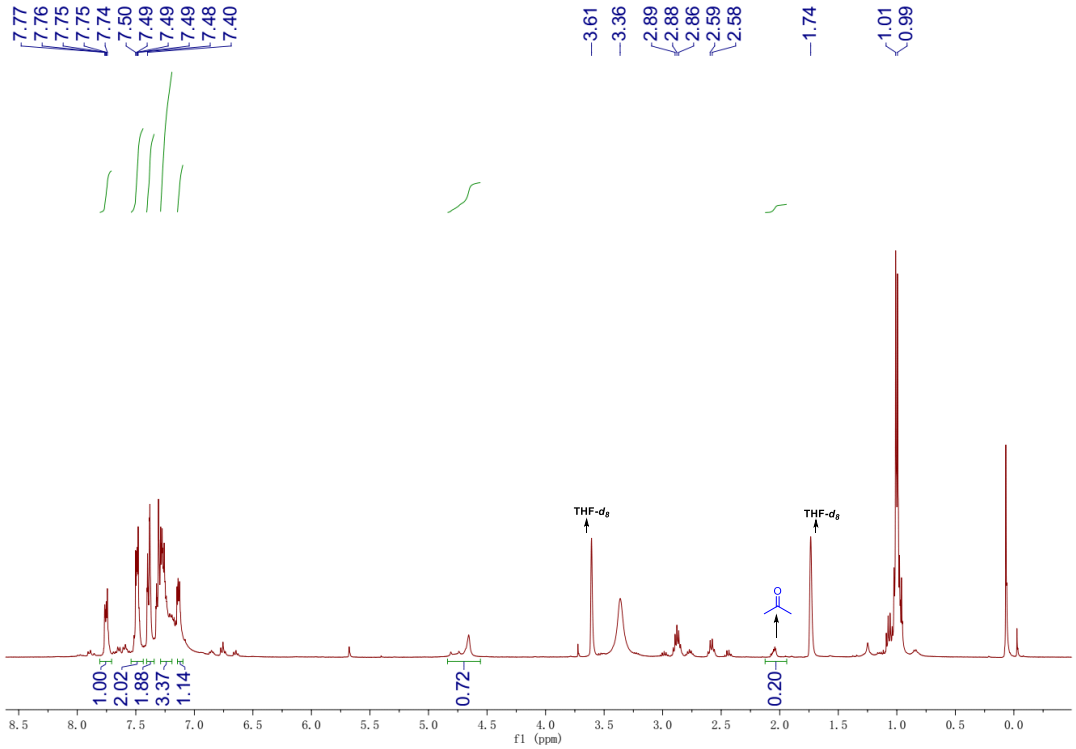

ZXX-5-9
142.20
138.21
136.85
133.89
133.15
129.47
129.38
127.71
127.30
126.32
125.13
121.12
66.96
66.57
66.35
64.64
27.46
O
O
S
N
CH3
D
OH
f1 (ppm)

2q


7.84
7.83
7.56
7.55
7.54
7.36
7.34
7.30
7.26
7.25
7.15
7.14
5.13
5.72
4.98
4.73
0.91
0.08
O
O
S
NH
D
OTBS
2r
1.00
2.16
3.21
1.24
1.02
0.05
0.91
1.95
9.02
6.01
f1 (ppm)


142.15
139.62
139.02
133.39
129.55
129.37
127.61
126.74
125.90
125.41
121.15
64.65
61.26
61.11
60.87
25.91
25.65
17.98
-3.59
-5.28
O
O
S
NH
D
OTBS
2r

^{1}H-NMR of the reaction mixtures that using THF-d_8 as solvent instead of THF after 24 hours



^{1}H-NMR of the products that using the mixture of H_2O and D_2O as reductant after 2 hours