Supporting Information

Transition-Metal-Free Sulfonylation of Methylthiolated Alkynones to Synthesize 3-Sulfonylated Thioflavones

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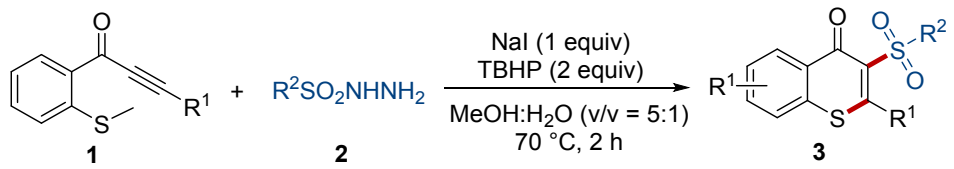
Table of Contents

1. General information

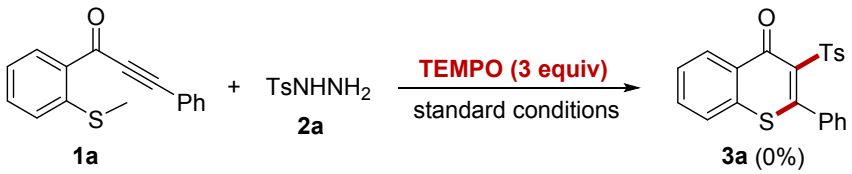
1.1 Materials and instruments

Tert-butyl hydroperoxide (TBHP), sodium iodide (NaI) were purchased from Tansoole, Shanghai, China. Other reagents were purchased from Bidepharm.com. Unless otherwise stated, all commercially available reagents were directly used without further purification. All solvents were purified by standard methods prior to use. All reactions were monitored by thin layer chromatography (TLC), and column chromatography was carried out on 100-200 mesh of silica gel purchased from Damas-beta. All nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 600 MHz in $CDCl_3$ at room temperature (20 ± 3 °C), using tetramethylsilane as internal standard. High resolution mass spectra (HRMS) were conducted on a 3000-mass spectrometer, using Bruker compact Qq TOF MS/MS system with the ESI technique.

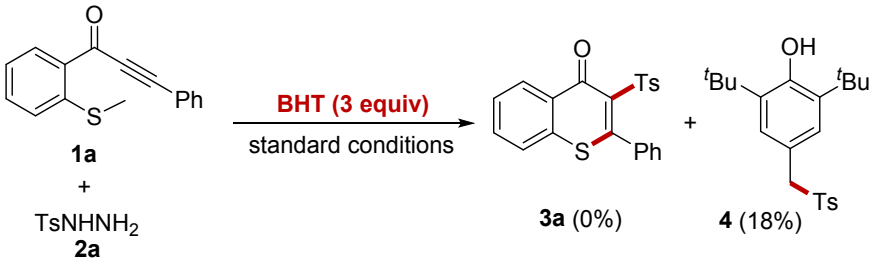
2. Experimental procedures



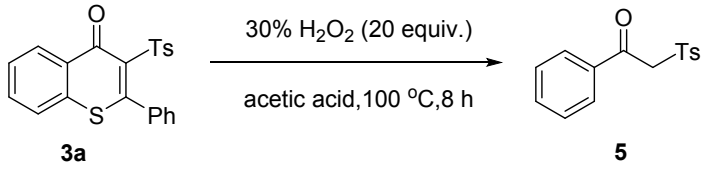
General experimental procedures for 3-sulfonylated thioflavones: In a 25 mL flask, 1-(2-(methylthio)phenyl)-3-phenylprop-2-yn-1-ones **1** (0.2 mmol) and arylsulfonyl hydrazides **2** (3.0 equiv) were dissolved in MeOH/H_2O (v/v = 5/1) (2 mL), and then TBHP (2.0 equiv), NaI (1.0 equiv) were added. The mixture was stirred at 70 ^oC for 2 h. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the ethyl acetate (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford the desired product.



Control experiments with TEMPO: In a 25 mL flask, 1-(2-(methylthio)phenyl)-3-phenylprop-2-yn-1-one (**1a**) (0.2 mmol) and $TsNHNH_2$ (**2a**) (3.0 equiv) were dissolved in MeOH/H_2O (v/v = 5/1) (2 mL) and TBHP (3.0 equiv), NaI (1.0 equiv) were added. Afterward, ((2,2,6,6-tetramethylpiperidin1-yl)oxidanyl) (TEMPO, 3.0 equiv) was added in the mixture. The mixture was allowed to stir at 70 °C for 2h. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the ethyl acetate (15 mL) was added three times for extraction. The reaction mixture was tested using HRMS and product **4** was successfully detected. Furthermore, product **4** was isolated in 18% yield.

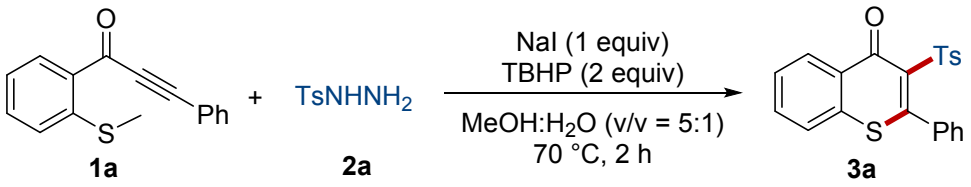


Control experiments with BHT: In a 25 mL flask, 1-(2-(methylthio)phenyl)-3-phenylprop-2-yn-1-one (**1a**) (0.2 mmol) and $TsNHNH_2$ (**2a**) (3.0 equiv) were dissolved in MeOH/H_2O (v/v = 5/1) (2 mL) and TBHP (3.0 equiv), NaI (1.0 equiv) were added. Afterward, (2,6-ditert-butyl-4-methylphenol) (BHT, 3.0 equiv) was added in the mixture. The mixture was allowed to stir at 70 °C for 2 h. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (5 mL), and then the ethyl acetate (15 mL) was added three times for extraction. The reaction mixture was tested using HRMS and no desired product was detected.



3a **5**

Transformation of the product 3a: In a 25 mL flask, 2-phenyl-3-tosyl-4H-thiochromen-4-one (**3a**) (0.2 mmol) was dissolved in acetic acid (5 mL), and then 30% H_2O_2 (20 equiv) was added. The mixture was refluxed at 100 °C for 8 h. After the reaction was completed, the solvent was quenched with saturated sodium carbonate solution (8 mL). Then, the ethyl acetate (15 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 7/1) to afford product **5** in 43% yield.

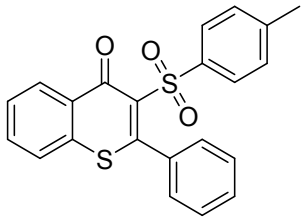


1a **2a** **3a**

Gram-scale synthesis of 3a: In a 250 mL flask, 1-(2-(methylthio)phenyl)-3-phenylprop-2-yn-1-ones (**1a**) (4 mmol) and $TsNHNH_2$ **(2a)** (3.0 equiv) were dissolved in $MeOH/H_2O$ (v/v = 5/1) (40 mL), and then TBHP (2.0 equiv), NaI (1.0 equiv) were added. The mixture was stirred at 70 °C for 2 h. After the reaction was completed, the solvent was evaporated under vacuum. Then, the residue was quenched with water (50 mL), and then the ethyl acetate (150 mL) was added three times for extraction. The combined organic layers were dried over anhydrous Na_2SO_4. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 6/1) to afford product **3a** in 33% yield.

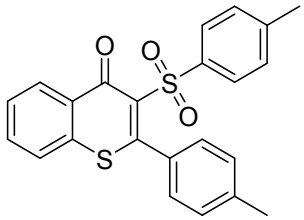
3. Characterization of compounds

*2-phenyl-3-tosyl-4H-thiochromen-4-one (**3a**)*



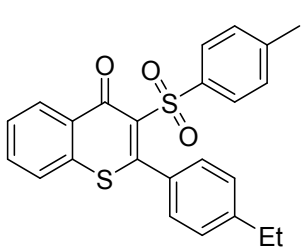
66.6 mg, 85%; White solid, m.p. 171-172°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.63 (t, *J* = 8.4 Hz, 1H), 7.56-7.49 (m, 7H), 7.27 (d, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.2, 162.5, 144.0, 138.9, 135.8, 134.8, 133.2, 132.7, 131.8, 130.4, 129.2, 129.1, 128.9, 128.8, 128.2, 128.1, 125.4, 21.7. HRMS Calcd for $C_{22}H_{17}O_3S_2$ $[M + H]^+$: m/z 393.0614, Found: 393.0604.

*2-(p-tolyl)-3-tosyl-4H-thiochromen-4-one (**3b**)*



56.8 mg, 70%; White solid, m.p. 179-180 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 162.8, 144.0, 140.9, 139.1, 136.0, 133.3, 132.6, 132.1, 132.0, 129.4, 129.2, 129.0, 128.9, 128.8, 128.2, 125.4, 21.8, 21.7. HRMS Calcd for $C_{23}H_{19}O_3S_2$ $[M + H]^+$: m/z 407.0770, Found: 407.0765.

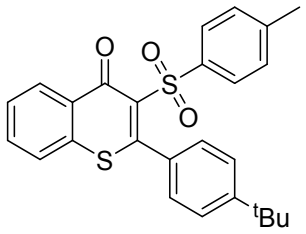
*2-(4-ethylphenyl)-3-tosyl-4H-thiochromen-4-one (**3c**)*



58.8 mg, 70%; White solid, m.p. 158-159 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 6.0 Hz, 1H), 7.53-7.48 (m, 4H),

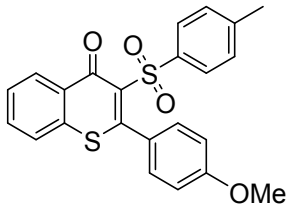
7.34 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 2.76 (q, *J* = 15.0, 7.2 Hz, 2H), 2.39 (s, 3H), 1.31 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 162.8, 146.9, 144.0, 139.1, 136.0, 133.2, 132.6, 132.2, 132.0, 129.4, 129.2, 128.9, 128.8, 128.3, 127.8, 125.4, 28.9, 21.8, 15.2. HRMS Calcd for $C_{24}H_{21}O_3S_2$ $[M + H]^+$: m/z 421.0927, Found: 421.0933.

*2-(4-(tert-butyl)phenyl)-3-tosyl-4H-thiochromen-4-one (**3d**)*



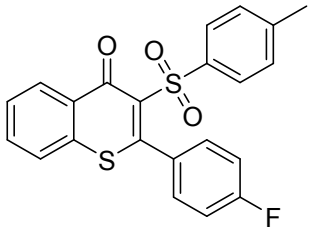
79.8 mg, 89%; White solid, m.p. 238-239°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.54-7.50 (m, 6H), 7.27 (d, *J* = 1.2 Hz, 2H), 2.40 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 162.9, 153.9, 143.9, 139.2, 136.1, 133.1, 132.6, 132.0, 131.9, 129.4, 129.1, 128.8, 128.7, 128.2, 125.4, 125.3, 35.1, 31.4, 21.8. HRMS Calcd for $C_{26}H_{25}O_3S_2$ $[M + H]^+$: m/z 449.1240, Found: 449.1220.

*2-(4-methoxyphenyl)-3-tosyl-4H-thiochromen-4-one (**3e**)*



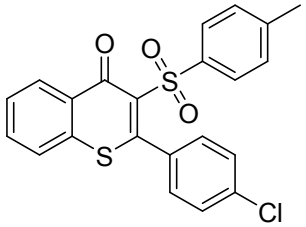
66.7 mg, 79%; White solid, m.p. 183-184°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.55-7.50 (m, 4H), 7.26 (d, *J* = 3.6 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.5, 162.5, 161.7, 143.9, 139.2, 136.0, 133.2, 132.6, 132.1, 130.1, 129.4, 129.1, 128.9, 128.7, 127.0, 125.3, 113.9, 55.6, 21.8. HRMS Calcd for $C_{23}H_{19}O_4S_2$ $[M + H]^+$: m/z 423.0719, Found: 423.0710.

*2-(4-fluorophenyl)-3-tosyl-4H-thiochromen-4-one (**3f**)*



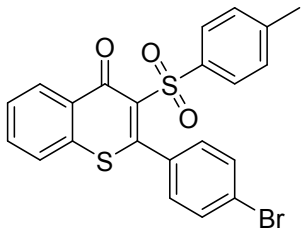
64.1 mg, 78%; White solid, m.p. 221-222 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.56-7.51 (m, 4H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.24 (t, *J* = 8.4 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.2, 164.1 (d, *J* = 249.0 Hz), 161.2, 144.2, 138.8, 135.6, 133.6, 132.7, 131.9, 130.8 (d, *J* = 4.5 Hz), 130.3 (d, *J* = 9.0 Hz), 129.4, 129.2, 128.9, 128.8, 125.4, 115.6 (d, *J* = 22.5 Hz), 21.7. ^{19}F NMR (564 MHz, $CDCl_3$) δ -109.6. HRMS Calcd for $C_{22}H_{16}FO_3S_2$ $[M + H]^+$: m/z 411.0519, Found: 411.0509.

*2-(4-chlorophenyl)-3-tosyl-4H-thiochromen-4-one (**3g**)*



52.9 mg, 62%; White solid, m.p. 204-205°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.56-7.49 (m, 6H), 7.28 (d, *J* = 7.8 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.1, 161.0, 144.3, 138.8, 136.9, 135.6, 133.6, 133.3, 132.8, 131.9, 129.6, 129.5, 129.3, 129.0, 128.9, 128.7, 125.4, 21.8. HRMS Calcd for $C_{22}H_{16}ClO_3S_2$ $[M + H]^+$: m/z 427.0224, Found: 427.0224.

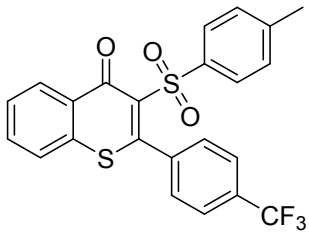
*2-(4-bromophenyl)-3-tosyl-4H-thiochromen-4-one (**3h**)*



89.3 mg, 95%; White solid, m.p. 189-190°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J*

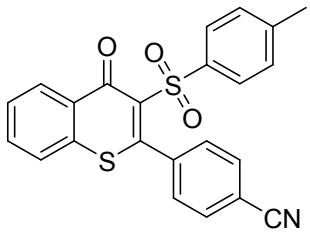
= 8.4 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.67-7.65 (m, 3H), 7.56-7.52 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.1, 161.0, 144.3, 138.8, 135.6, 133.8, 133.6, 132.8, 131.9, 131.6, 129.8, 129.5, 129.3, 129.0, 128.9, 125.4, 125.1, 21.8. HRMS Calcd for $C_{22}H_{15}BrNaO_3S_2$ $[M + Na]^+$: m/z 492.9536, Found: 492.9514.

*3-tosyl-2-(4-(trifluoromethyl)phenyl)-4H-thiochromen-4-one (**3i**)*



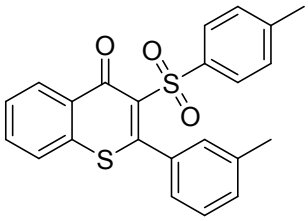
81.9 mg, 89%; White solid, m.p. 242-243 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.69-7.65 (m, 3H), 7.58-7.53 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.0, 160.4, 144.5, 138.5, 135.4, 133.7, 132.9, 132.3 (q, *J* = 31.5 Hz), 131.9, 129.5, 129.3, 129.2, 129.0, 128.6, 125.5, 125.4 (q, *J* = 3.0 Hz), 123.9 (q, *J* = 271.5 Hz), 21.8. ^{19}F NMR (564 MHz, $CDCl_3$) δ -62.8. HRMS Calcd for $C_{23}H_{16}F_3O_3S_2$ $[M + H]^+$: m/z 461.0487, Found: 461.0481.

*4-(4-oxo-3-tosyl-4H-thiochromen-2-yl)benzonitrile (**3j**)*



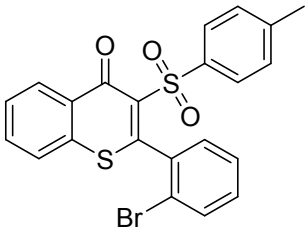
53.4 mg, 64%; White solid, m.p. 240-242°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.69-7.66 (m, 3H), 7.59-7.53 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.8, 159.6, 144.7, 139.4, 138.3, 135.2, 133.8, 133.0, 132.1, 131.8, 129.6, 129.4, 129.3, 129.1, 128.9, 125.5, 118.2, 114.2, 21.82. HRMS Calcd for $C_{23}H_{16}NO_3S_2$ $[M + H]^+$: m/z 418.0566, Found: 418.0557.

*2-(m-tolyl)-3-tosyl-4H-thiochromen-4-one (**3k**)*



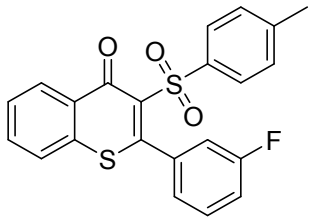
66.6 mg, 82%; White solid, m.p. 170-171°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.53 (q, *J* = 15.6, 7.8 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.37-7.32 (m, 3H), 7.27 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 162.8, 144.0, 139.1, 138.0, 135.9, 134.9, 133.2, 132.6, 132.0, 131.3, 129.4, 129.2, 129.0, 128.8, 128.7, 128.2, 125.5, 125.4, 21.8, 21.6. HRMS Calcd for $C_{23}H_{19}O_3S_2$ $[M + H]^+$: m/z 407.0770, Found: 407.0766.

*2-(2-bromophenyl)-3-tosyl-4H-thiochromen-4-one (**3l**)*



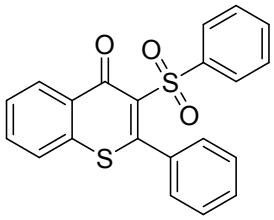
51.7 mg, 55%; White solid, m.p. 150-151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.56-7.53 (m, 2H), 7.49 (t, *J* = 3.0 Hz, 2H), 7.40-7.37 (m, 1H), 7.29 (d, *J* = 4.2 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 160.6, 144.3, 138.7, 135.9, 135.6, 133.9, 133.0, 132.7, 131.9, 131.3, 129.8, 129.5, 129.3, 129.1, 128.9, 127.3, 125.6, 121.8, 21.8. HRMS Calcd for $C_{22}H_{16}BrO_3S_2$ $[M + H]^+$: m/z 470.9719, Found: 470.9705.

*2-(3-fluorophenyl)-3-tosyl-4H-thiochromen-4-one (**3m**)*



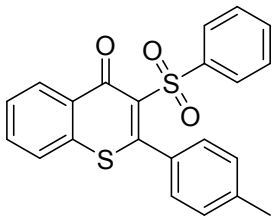
64.0 mg, 78%; White solid, m.p. 188-189°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.66 (t, *J* = 8.4 Hz, 1H), 7.56-7.47 (m, 3H), 7.34 (d, *J*=7.8 Hz, 1H), 7.29 (d, *J*=7.8 Hz, 2H), 7.23 (d, *J*=11.4 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.1, 162.2 (d, *J* = 246.0 Hz), 160.6, 160.5, 144.3, 138.7, 136.6 (d, *J* = 9.0 Hz), 135.6, 133.6, 132.8, 131.9, 130.0 (d, *J* = 9.0 Hz), 129.5, 129.3, 129.0, 125.4, 124.3 (d, *J* = 4.5 Hz), 117.4 (d, *J* = 21.0 Hz), 115.6 (d, *J* = 24.0 Hz), 21.8. ^{19}F NMR (564 MHz, $CDCl_3$) δ -112.0. HRMS Calcd for $C_{22}H_{16}FO_3S_2$ $[M + H]^+$: m/z 411.0519, Found: 411.0505.

*2-phenyl-3-(phenylsulfonyl)-4H-thiochromen-4-one (**3n**)*



67.3 mg, 89%; White solid, m.p. 194-195°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.57-7.52 (m, 8H), 7.48 (t, *J* = 7.6 Hz, 2H) ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.3, 162.9, 142.0, 135.9, 134.8, 133.2, 133.1, 132.7, 131.9, 130.5, 129.4, 128.9, 128.8, 128.5, 128.3, 128.2, 125.4. HRMS Calcd for $C_{21}H_{15}O_3S_2$ $[M + H]^+$: m/z 379.0457, Found: 379.0443.

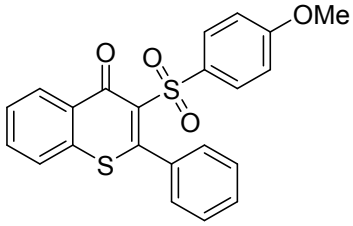
*3-(phenylsulfonyl)-2-(p-tolyl)-4H-thiochromen-4-one (**3o**)*



45.5 mg, 58%; White solid, m.p. 150-152 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J*

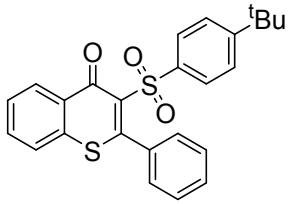
= 8.4 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 8.4 Hz, 1H), 7.56-7.51 (m, 3H), 7.49-7.46 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.3, 163.2, 142.1, 141.0, 136.0, 133.1, 132.9, 132.7, 131.9, 131.8, 129.3, 129.1, 128.8, 128.7, 128.5, 128.3, 125.4, 21.7. HRMS Calcd for $C_{22}H_{17}O_3S_2$ $[M + H]^+$: m/z 393.0614, Found: 393.0621.

*3-((4-methoxyphenyl)sulfonyl)-2-phenyl-4H-thiochromen-4-one (**3p**)*



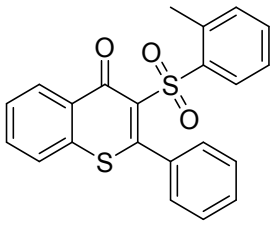
77.5 mg, 95%; White solid, m.p. 169-170°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.55-7.51 (m, 7H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 163.4, 162.1, 135.9, 135.1, 133.6, 133.4, 132.6, 132.0, 131.5, 130.4, 129.4, 128.8, 128.3, 128.2, 125.4, 113.7, 55.72. HRMS Calcd for $C_{22}H_{17}O_4S_2$ $[M + H]^+$: m/z 409.0563, Found: 409.0557.

*3-((4-(tert-butyl)phenyl)sulfonyl)-2-phenyl-4H-thiochromen-4-one (**3q**)*



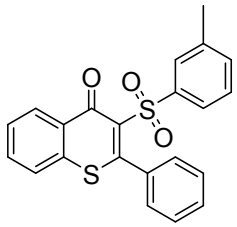
54.7 mg, 63%; White solid, m.p. 167-168 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.65 (t, *J* = 8.4 Hz, 1H), 7.56-7.48 (m, 9H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 162.5, 157.0, 138.8, 135.9, 134.9, 133.3, 132.7, 132.0, 130.4, 129.4, 128.9, 128.8, 128.2, 128.1, 125.7, 125.4, 35.3, 31.2. HRMS Calcd for $C_{22}H_{23}O_3S_2$ $[M + H]^+$: m/z 435.1083, Found: 435.1062.

*2-phenyl-3-(o-tolylsulfonyl)-4H-thiochromen-4-one (**3r**)*



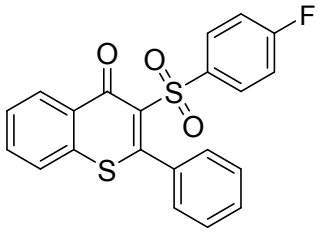
40.2 mg, 51%; White solid, m.p. 190-191°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.8 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.57-7.49 (m, 5H), 7.41-7.34 (m, 2H), 7.12 (d, *J* = 7.2 Hz 1H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 162.5, 140.5, 136.6, 136.0, 134.5, 133.0, 132.9, 132.7, 132.0, 131.6, 130.9, 130.4, 129.4, 128.9, 1286, 128.4, 126.1, 125.6, 19.9. HRMS Calcd for $C_{22}H_{17}O_3S_2$ $[M + H]^+$: m/z 393.0614, Found: 393.0604.

*2-phenyl-3-(m-tolylsulfonyl)-4H-thiochromen-4-one (**3s**)*



46.3 mg, 59%; White solid, m.p. 167-168 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 5.4 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.57-7.49 (m, 7H), 7.38-7.33 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.3, 162.7, 141.9, 138.6, 135.9, 134.8, 134.0, 133.1, 132.7, 132.0, 130.5, 129.5, 129.0, 128.9, 128.4, 128.3, 125.9, 125.4, 21.5. HRMS Calcd for $C_{22}H_{17}O_3S_2$ $[M + H]^+$: m/z 393.0614, Found: 393.0604.

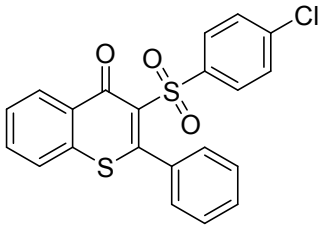
*3-((4-fluorophenyl)sulfonyl)-2-phenyl-4H-thiochromen-4-one (**3t**)*



62.6 mg, 79%; White solid, m.p. 184-185 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.8 Hz, 1H), 8.06 (q, *J* = 9.0, 4.8 Hz, 2H), 7.66 (t, *J* = 7.2 Hz, 1H), 7.57-7.50 (m, 7H),

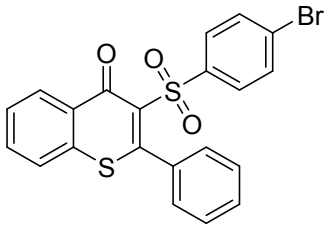
7.14 (t, *J* = 9.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.2, 165.5 (d, *J* = 253.5 Hz), 163.1, 137.8 (d, J = 3.0 Hz), 135.8, 134.7, 132.9, 132.8, 131.9 (d, *J* = 10.5 Hz), 131.9, 130.6, 129.3, 129.0, 128.3, 128.2, 125.5, 115.7 (d, *J* = 22.5 Hz). ^{19}F NMR (564 MHz, $CDCl_3$) δ -104.5. HRMS Calcd for $C_{21}H_{14}FO_3S_2$ $[M + H]^+$: m/z 397.0363, Found: 397.0327.

*3-((4-chlorophenyl)sulfonyl)-2-phenyl-4H-thiochromen-4-one (**3u**)*



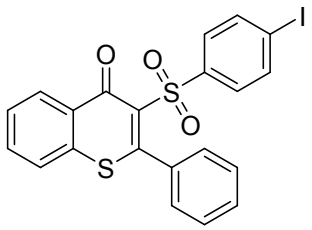
38.0 mg, 46%; White solid, m.p. 172-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.58-7.54 (m, 7H), 7.45 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.2, 163.3, 140.5, 139.8, 135.9, 134.7, 132.9, 132.8, 131.9, 130.7, 130.5, 129.4, 129.1, 128.8, 128.4, 128.2, 125.5. HRMS Calcd for $C_{21}H_{14}ClO_3S_2$ $[M + H]^+$: m/z 413.0067, Found: 413.0050.

*3-((4-bromophenyl)sulfonyl)-2-phenyl-4H-thiochromen-4-one (**3v**)*



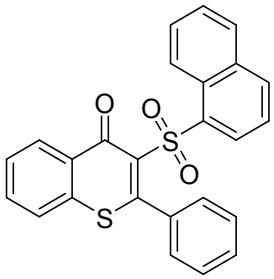
57.5 mg, 63%; White solid, m.p. 173-174 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 2H), 7.67 (t, *J* = 6.6 Hz, 1H), 7.61 (d, *J* =8.4 Hz, 2H), 7.58-7.51 (m, 7H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.2, 163.3, 141.0, 135.8, 134.6, 132.9, 132.7, 131.9, 131.8, 130.7, 130.5, 129.4, 129.1, 128.4, 128.3, 128.2, 125.5. HRMS Calcd for $C_{21}H_{14}BrO_3S_2$ $[M + H]^+$: m/z 456.9562, Found: 456.9552.

*3-((4-iodophenyl)sulfonyl)-2-phenyl-4H-thiochromen-4-one (**3w**)*



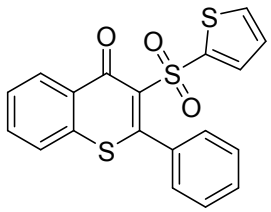
60.4 mg, 60%; White solid, m.p. 176-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.58-7.53 (m, 7H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.2, 163.3, 141.7, 137.8, 135.8, 134.6, 132.9, 132.7, 131.8, 130.7, 130.4, 129.4, 129.1, 128.4, 128.2, 125.5, 101.2. HRMS Calcd for $C_{21}H_{14}IO_3S_2$ $[M + H]^+$: m/z 504.9424, Found: 504.9443.

*3-(naphthalen-1-ylsulfonyl)-2-phenyl-4H-thiochromen-4-one (**3x**)*



42.8 mg, 50%; White solid, m.p. 196-197 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.2 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.70-7.67 (m, 2H), 7.61-7.52 (m, 5H), 7.50-7.40 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.8, 162.2, 136.7, 135.8, 134.5, 134.4, 133.9, 133.6, 132.6, 131.6, 131.3, 131.0, 129.4, 129.1, 128.8, 128.7, 128.5, 127.9, 126.3, 125.4, 124.5, 123.8. HRMS Calcd for $C_{25}H_{17}O_3S_2$ $[M + H]^+$: m/z 429.0614, Found: 429.0594.

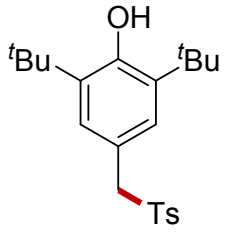
*2-phenyl-3-(thiophen-2-ylsulfonyl)-4H-thiochromen-4-one (**3y**)*



33.1 mg, 43%; White solid, m.p. 150-151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 3.6 Hz, 1H), 7.69-7.65 (m, 2H), 7.60 (t, *J* = 7.8 Hz, 1H),

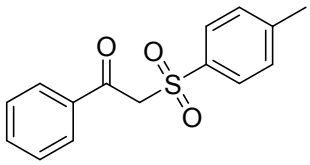
7.55-7.50 (m, 6H), 7.08 (t, J = 4.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.6, 162.7, 143.0, 135.8, 135.7, 134.9, 134.3, 133.1, 132.8, 132.0, 130.5, 129.5, 129.0, 128.3, 128.1, 127.1, 125.4. HRMS Calcd for $C_{19}H_{13}O_3S_3$ $[M + H]^+$: m/z 385.0021, Found: 384.9998.

*2,6-di-tert-butyl-4-(tosylmethyl)phenol (**4**)*



13.5 mg, 18%; White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 6.73 (s, 2H), 5.23 (s, 1H), 4.19 (s, 2H), 2.40 (s, 3H), 1.32 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.3, 144.4, 136.1, 135.1, 129.4, 129.0, 127.8, 119.1, 63.4, 34.3, 30.2, 21.7. HRMS Calcd for $C_{22}H_{30}NaO_3S$ $[M + Na]^+$: m/z 397.1808, Found:397.1784.

*1-phenyl-2-tosylethan-1-one (**5**)*[1]

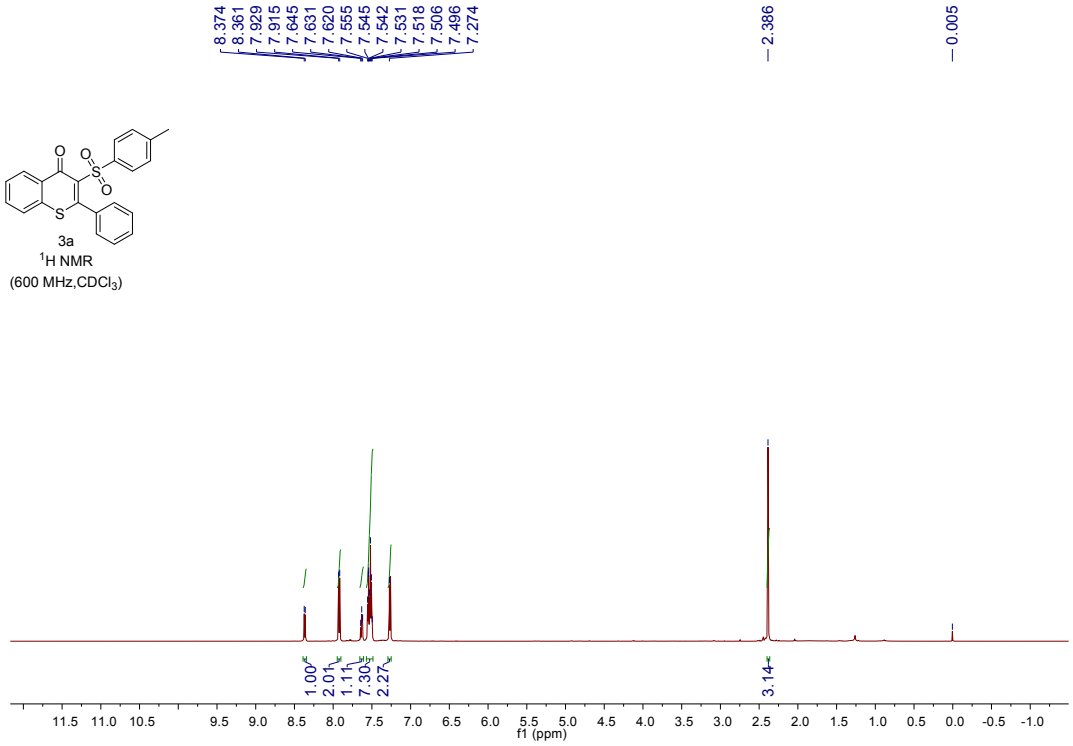


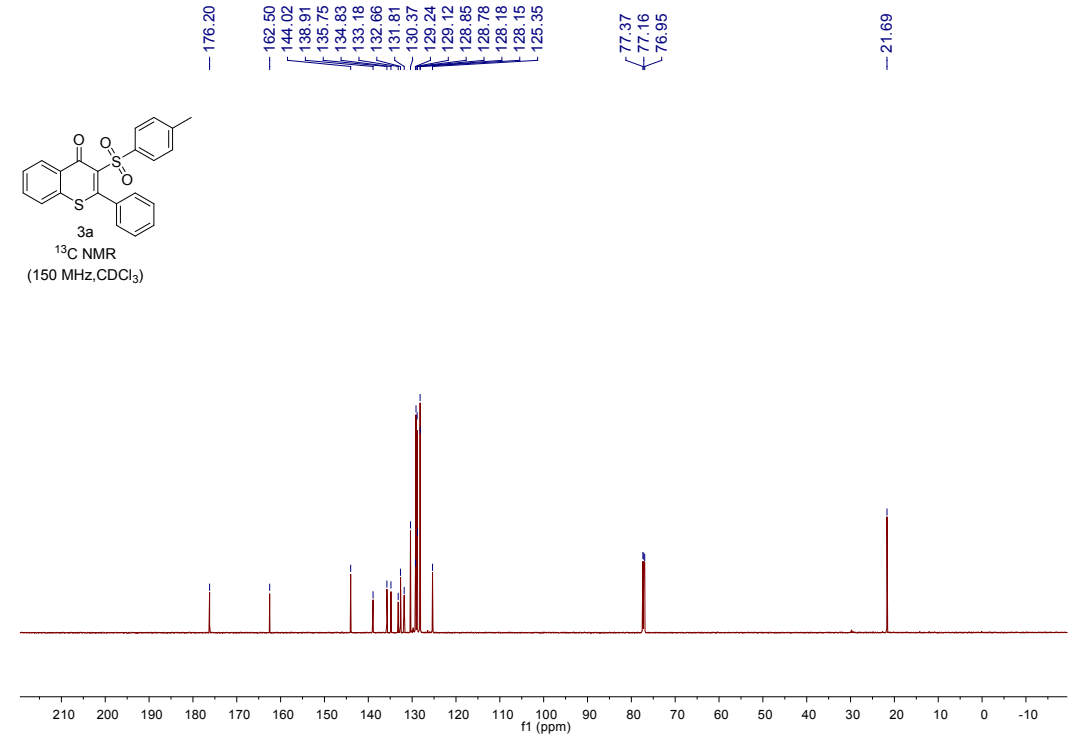
23.7 mg, 43%; White solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 7.2 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 4.71 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.3, 145.5, 136.0, 135.9, 134.5, 130.0, 129.5, 129.0, 128.8, 63.8, 21.9. HRMS Calcd for $C_{15}H_{15}O_3S$ $[M + H]^+$: m/z 275.0736, Found:275.0737.

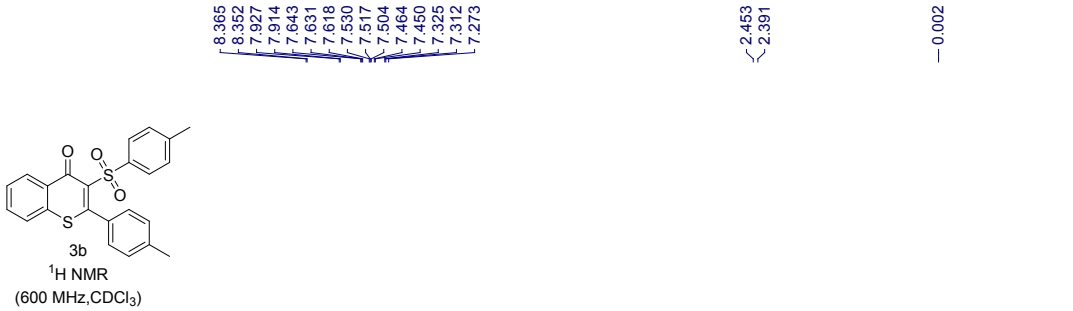
Reference

(1) Xie, L.; Zhen, X.; Huang, S.; Su, X.; Lin, M.; Li, Y. Photoinduced rearrangement of vinyl tosylates to β-ketosulfones. *Green Chemistry* **2017**, *19*, 3530-3534.

4. NMR copies of products






8.365
8.352
7.927
7.914
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7.517
7.504
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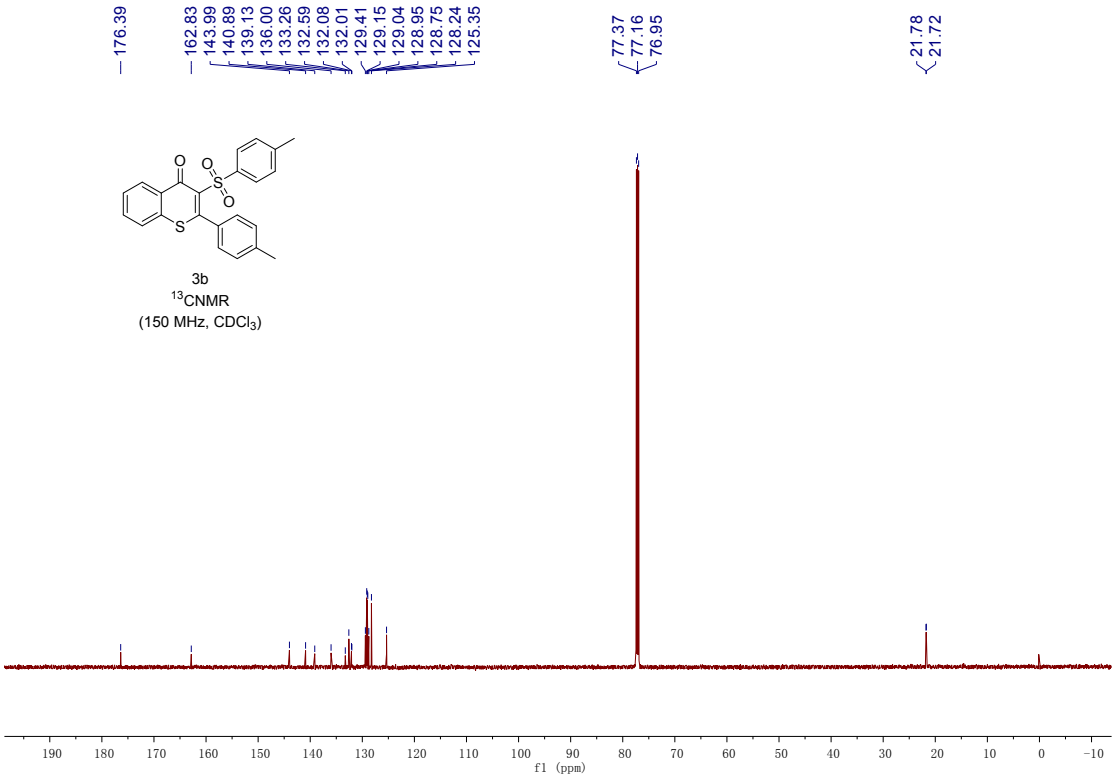
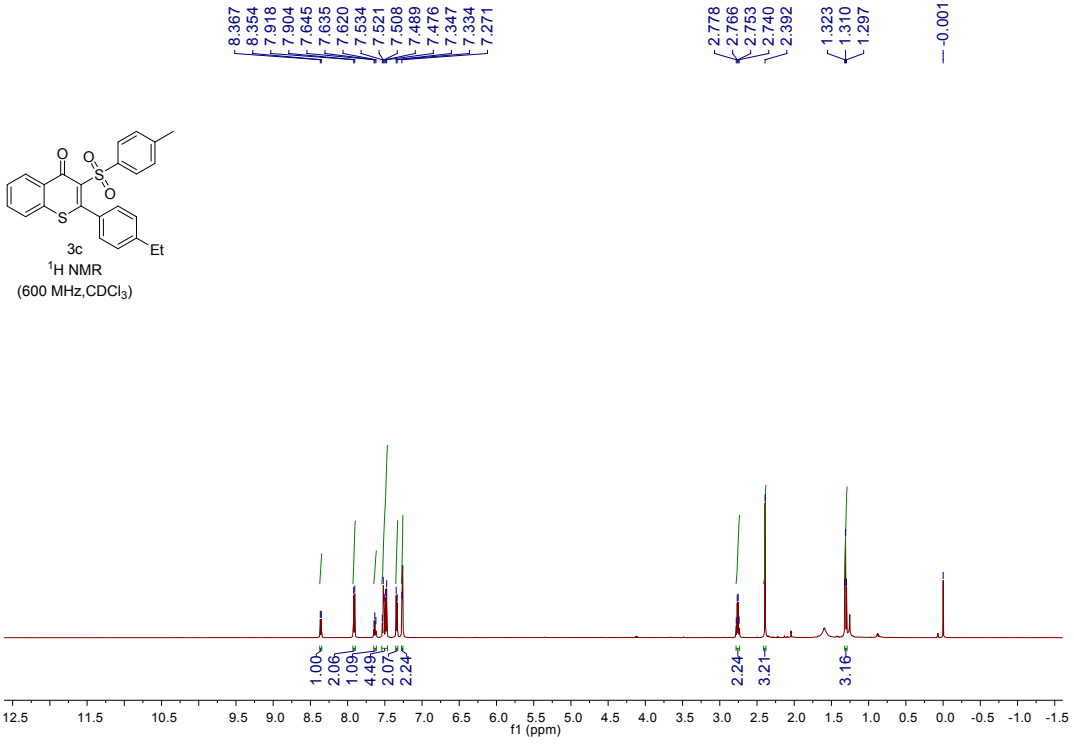
7.450
7.325
7.312
7.273
2.453
2.391
0.002
O
O
S
O
S
3b
1H NMR
(600 MHz,CDCl3)
1.00
2.01
1.05
2.06
2.05
2.17
2.02
3.05
3.06
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


176.39
162.83
143.99
140.89
139.13
136.00
133.26
132.59
132.08
132.01
129.41
129.15
129.04
128.95
128.75
128.24
125.35
77.37
77.16
76.95
21.78
21.72
O
O
S
O
S
3b
13CNMR
(150 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.367
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7.347
7.334
7.271
2.778
2.766
2.753
2.740
2.392
1.323
1.310
1.297
-0.001
3c
1H NMR
(600 MHz,CDCl3)
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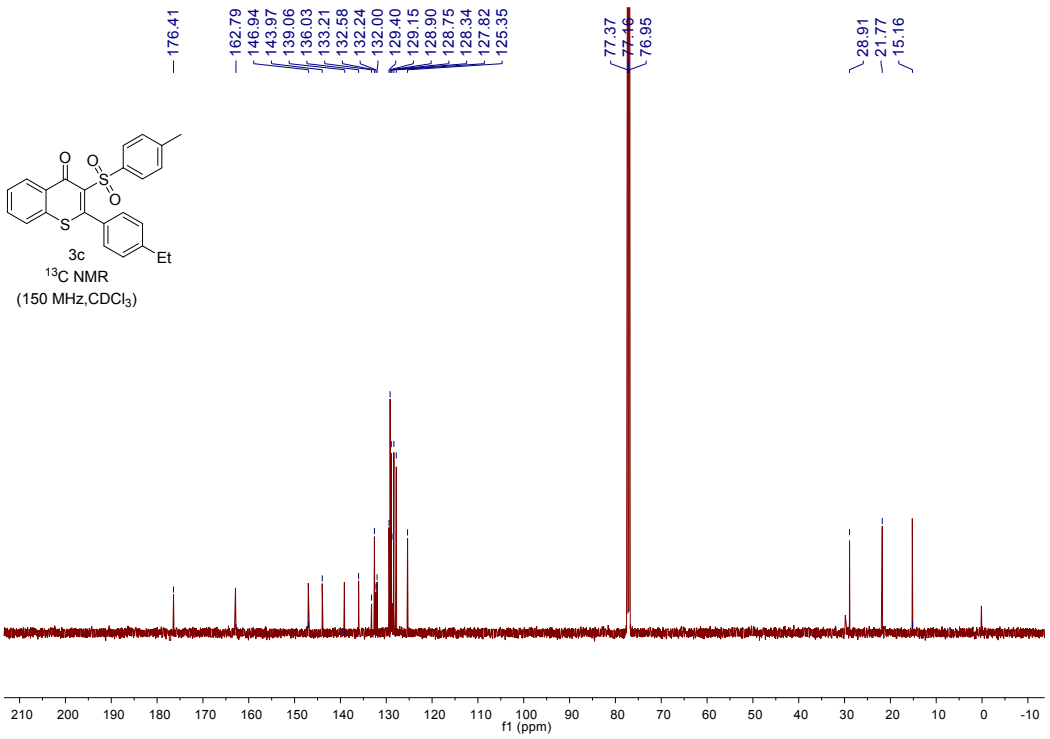
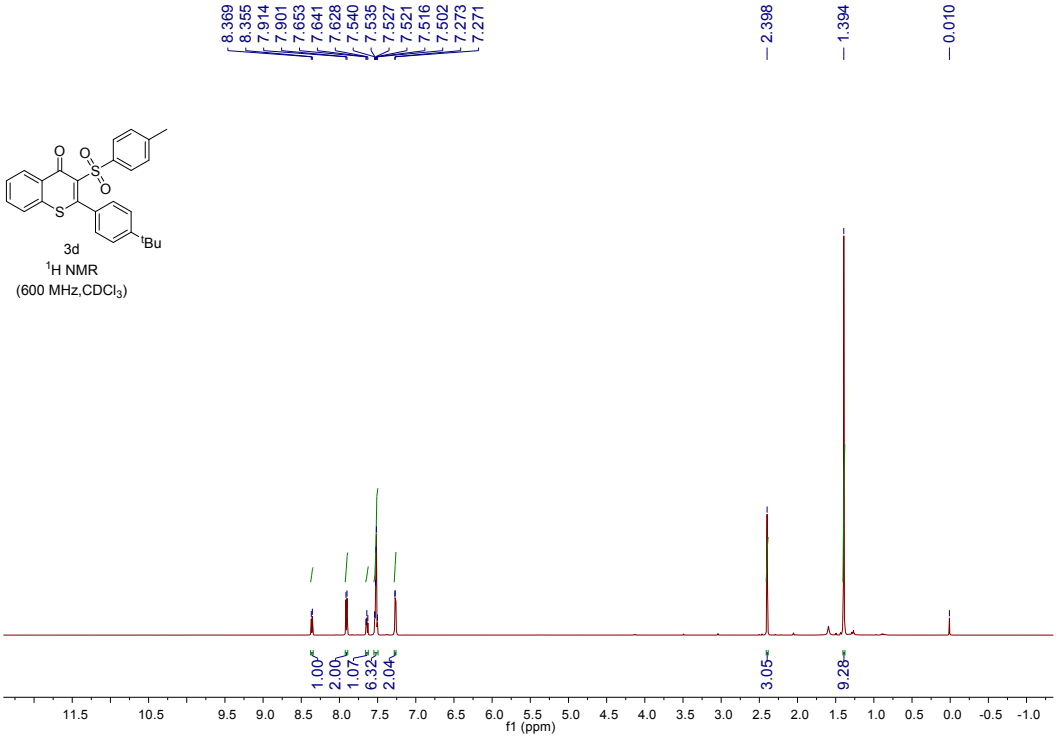
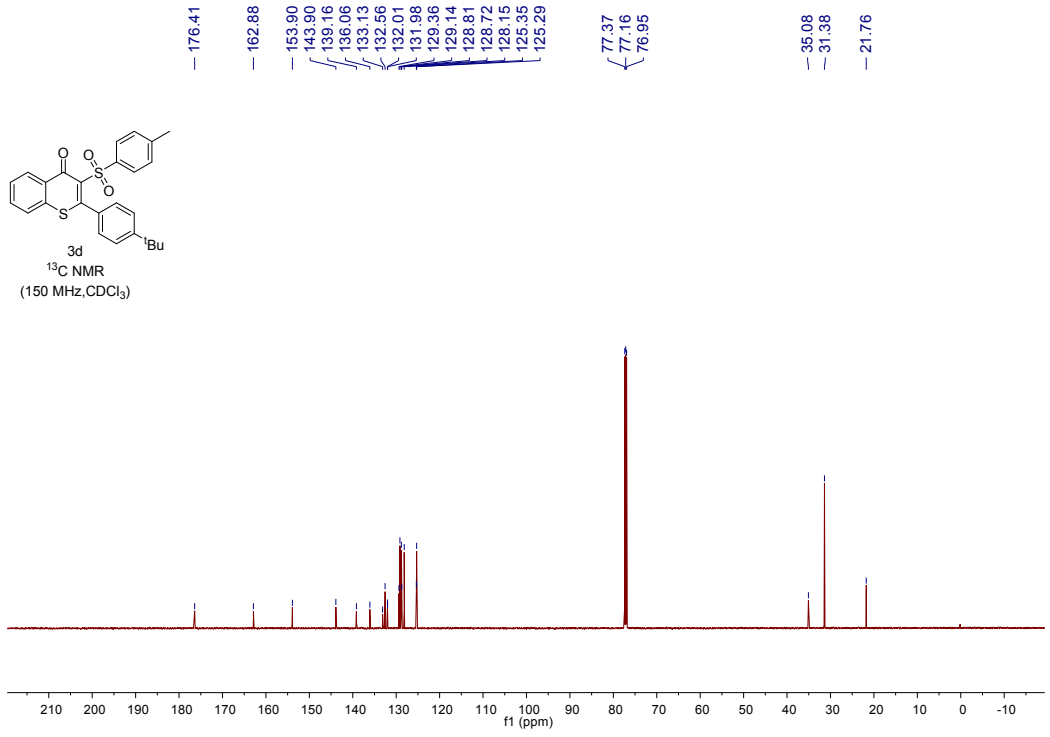
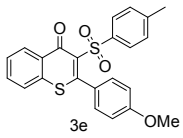
2.06
1.09
4.49
2.07
2.24
2.24
3.21
3.16
f1 (ppm)


176.41
162.79
146.94
143.97
139.06
136.03
133.21
132.58
132.24
132.00
129.40
129.15
128.90
128.75
128.34
127.82
125.35
77.37
77.16
76.95
28.91
21.77
15.16
3c
13C NMR
(150 MHz,CDCl3)
f1 (ppm)


8.369
8.355
7.914
7.901
7.653
7.641
7.628
7.540
7.535
7.527
7.521
7.516
7.502
7.273
7.271
2.398
1.394
0.010
3d
^{1}H NMR
(600 MHz,CDCl$_3$)
1.00
2.00
1.07
6.32
2.04
3.05
9.28
f1 (ppm)

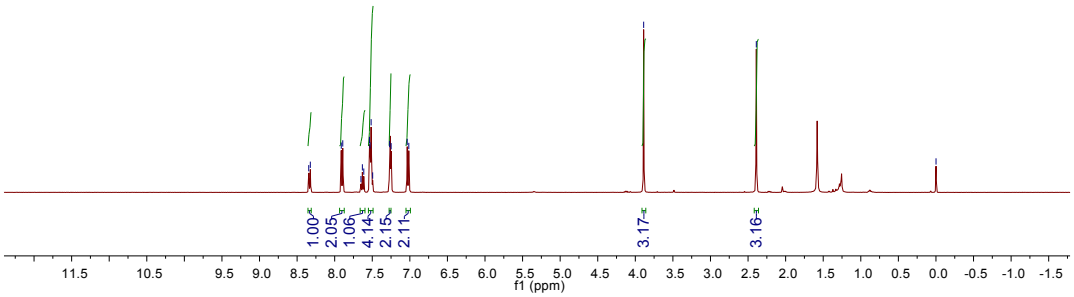

176.41
162.88
153.90
143.90
139.16
136.06
133.13
132.56
132.01
131.98
129.36
129.14
128.81
128.72
128.15
125.35
125.29
77.37
77.16
76.95
35.08
31.38
21.76
3d
^{13}C NMR
(150 MHz,CDCl$_3$)
f1 (ppm)

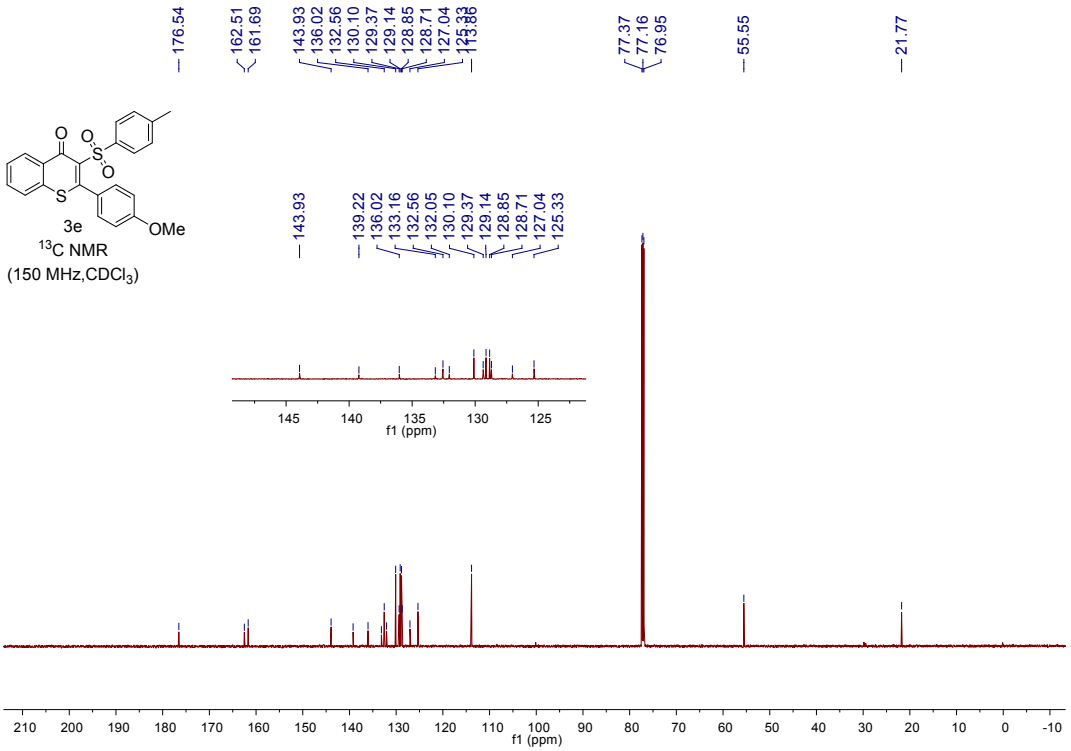


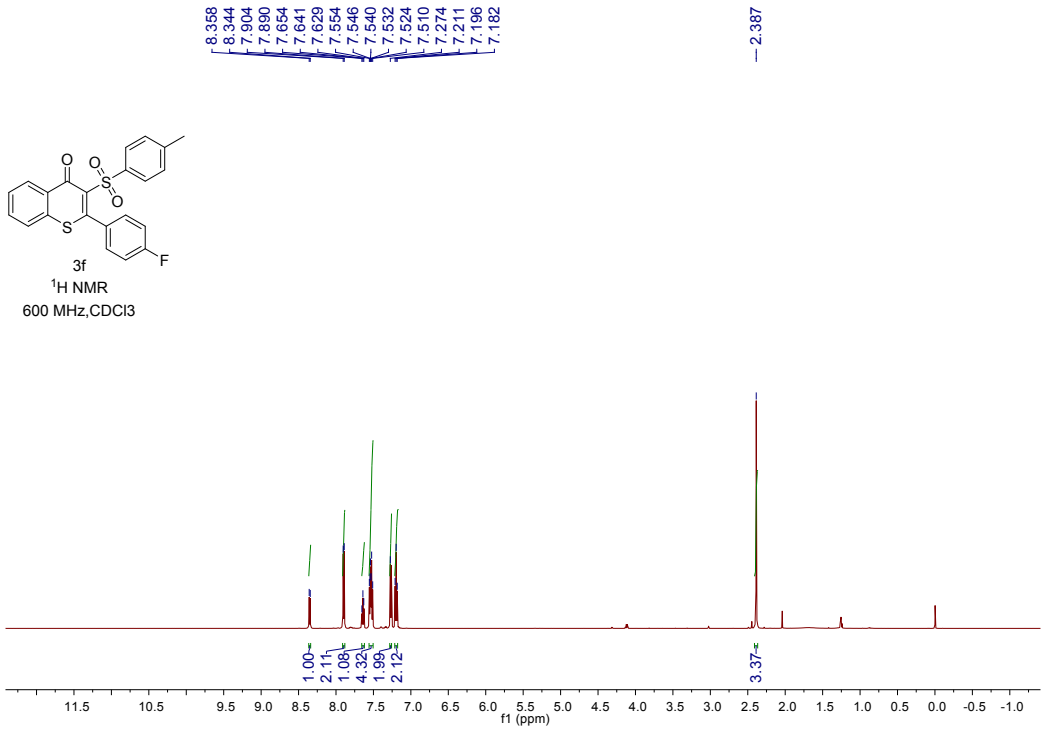
3e

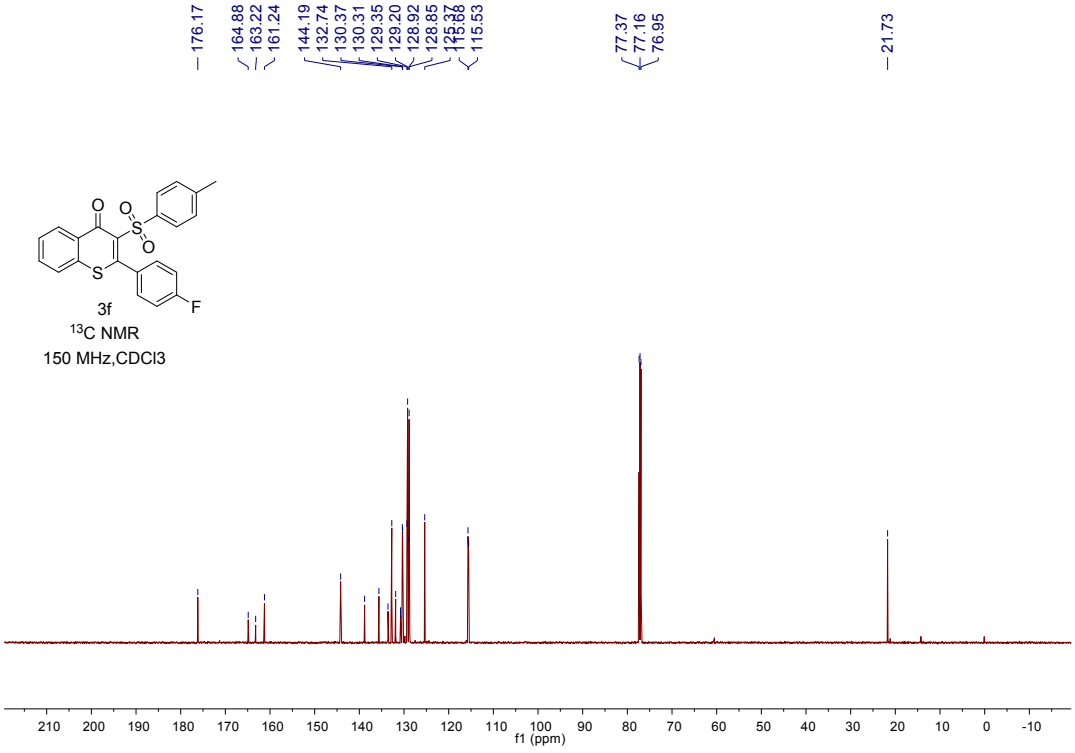
^{1}H NMR

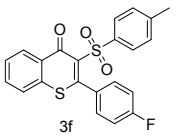
(400 MHz,$CDCl_3$)






8.358
8.344
7.904
7.890
7.654
7.641
7.629
7.554
7.546
7.540
7.532
7.524
7.510
7.274
7.211
7.196
7.182
2.387
3f
1H NMR
600 MHz,CDCl3
1.00
2.11
1.08
4.32
1.99
2.12
3.37
f1 (ppm)

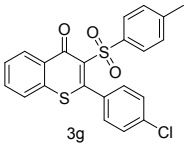

176.17
164.88
163.22
161.24
144.19
132.74
130.37
130.31
129.35
129.20
128.92
128.85
125.37
115.68
115.53
77.37
77.16
76.95
21.73
3f
13C NMR
150 MHz,CDCl3
f1 (ppm)



3f

^{19}F NMR

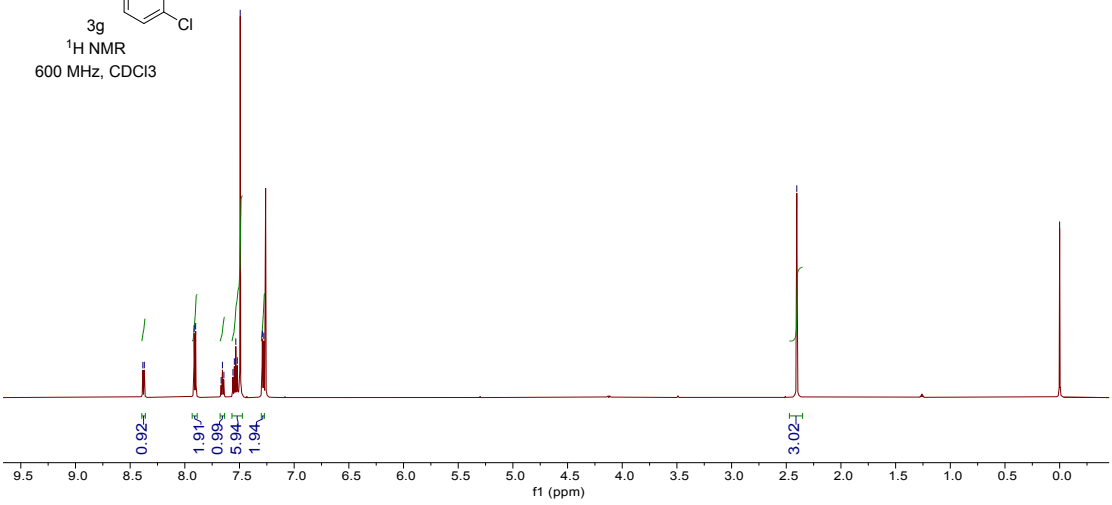
564 MHz,CDCl3

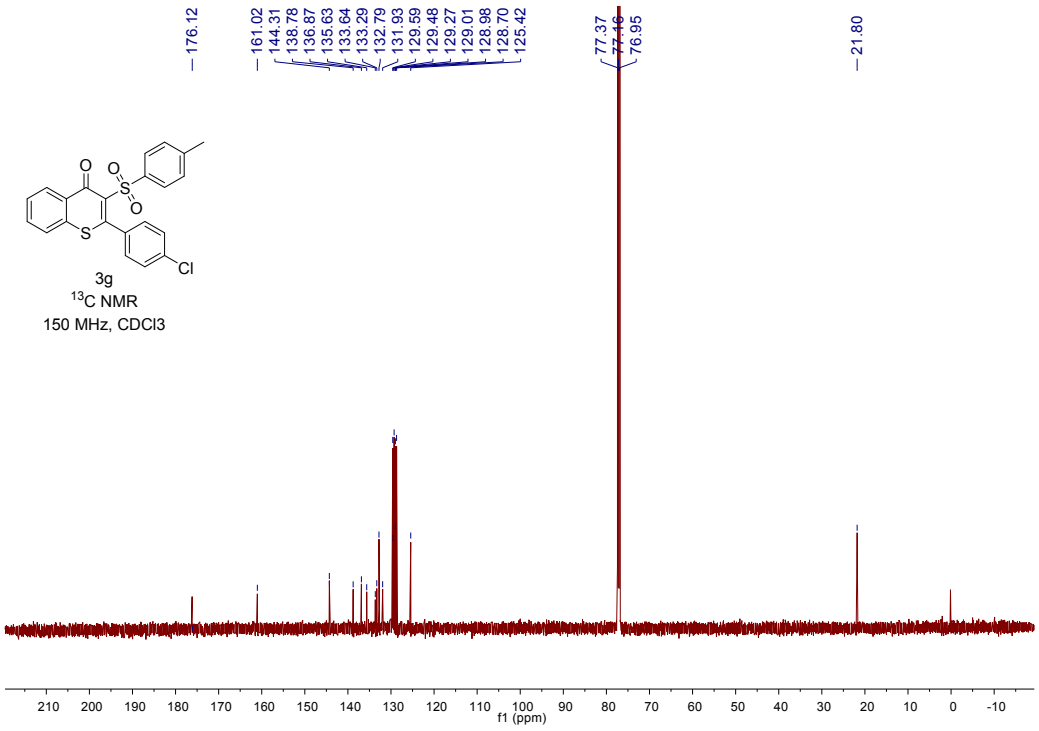


3g

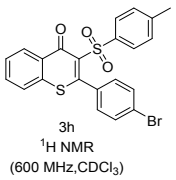
^{1}H NMR

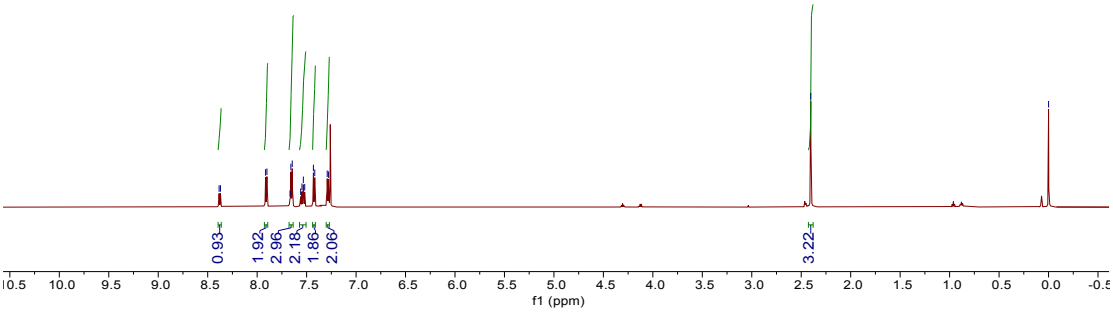
600 MHz, CDCl3

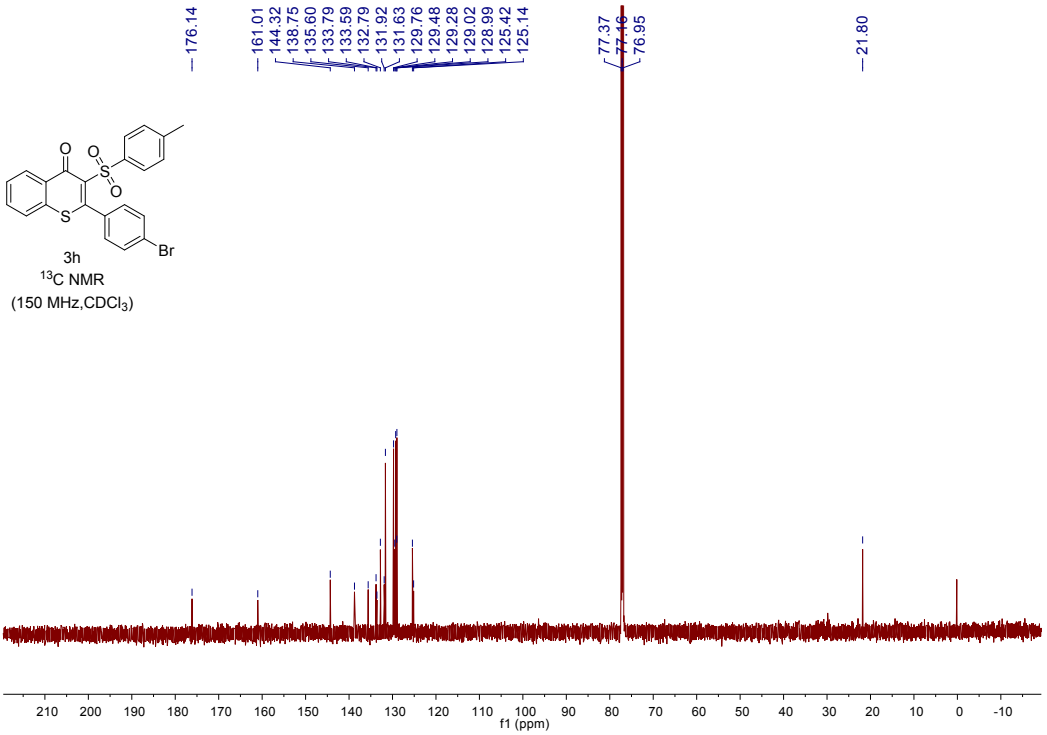


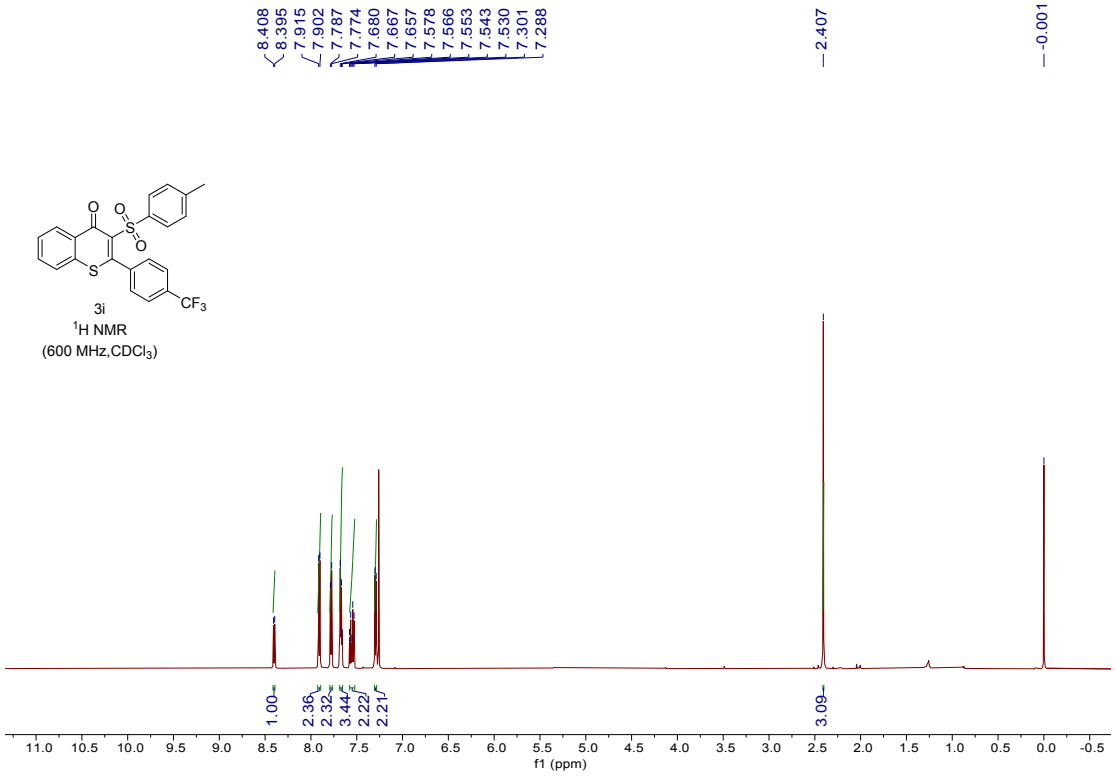

176.12
161.02
144.31
138.78
136.87
135.63
133.64
133.29
132.79
131.93
129.59
129.48
129.27
129.01
128.98
128.70
125.42
77.37
77.16
76.95
21.80
O
O
S
O
S
Cl
3g
13C NMR
150 MHz, CDCl3
f1 (ppm)

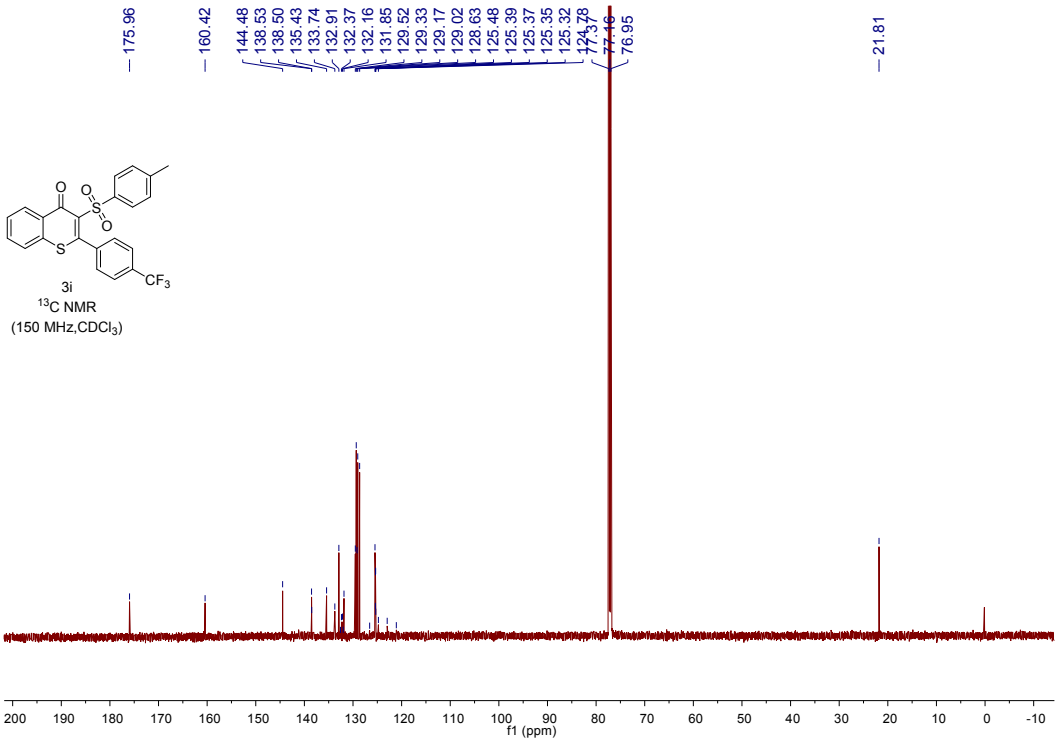

8.385
8.371
7.915
7.901
7.668
7.659
7.645
7.560
7.547
7.533
7.519
7.431
7.418
7.292
7.278
2.404
-0.000

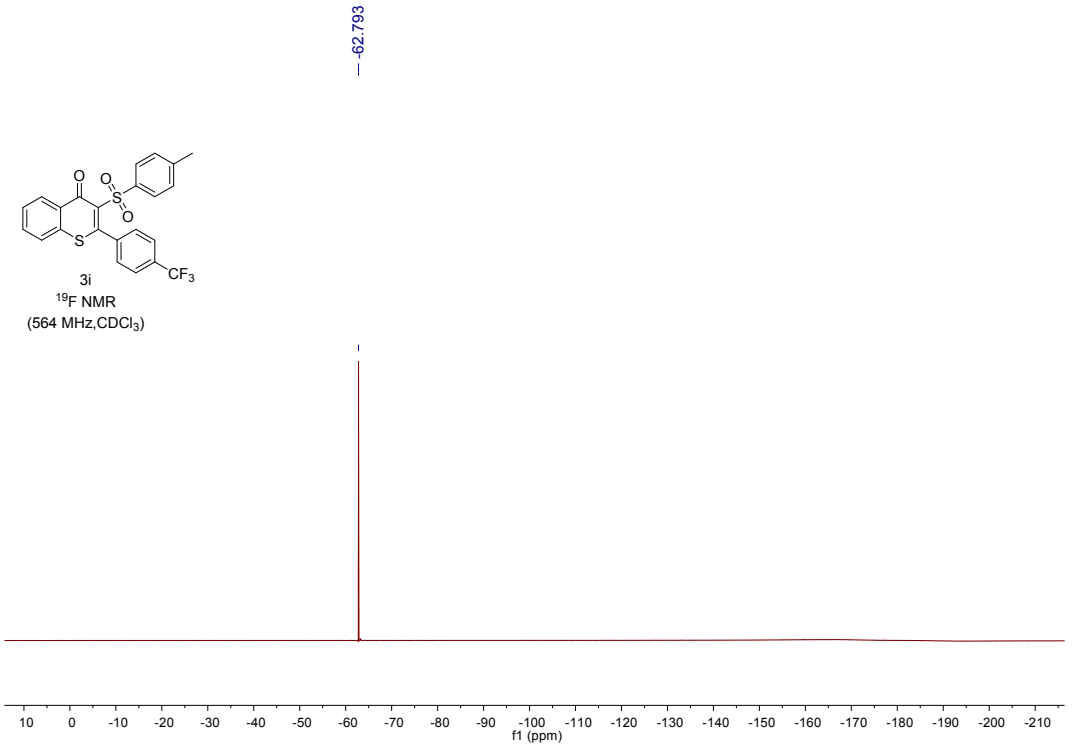

O
O
S
O
S
Br
3h
1H NMR
(600 MHz,CDCl3)

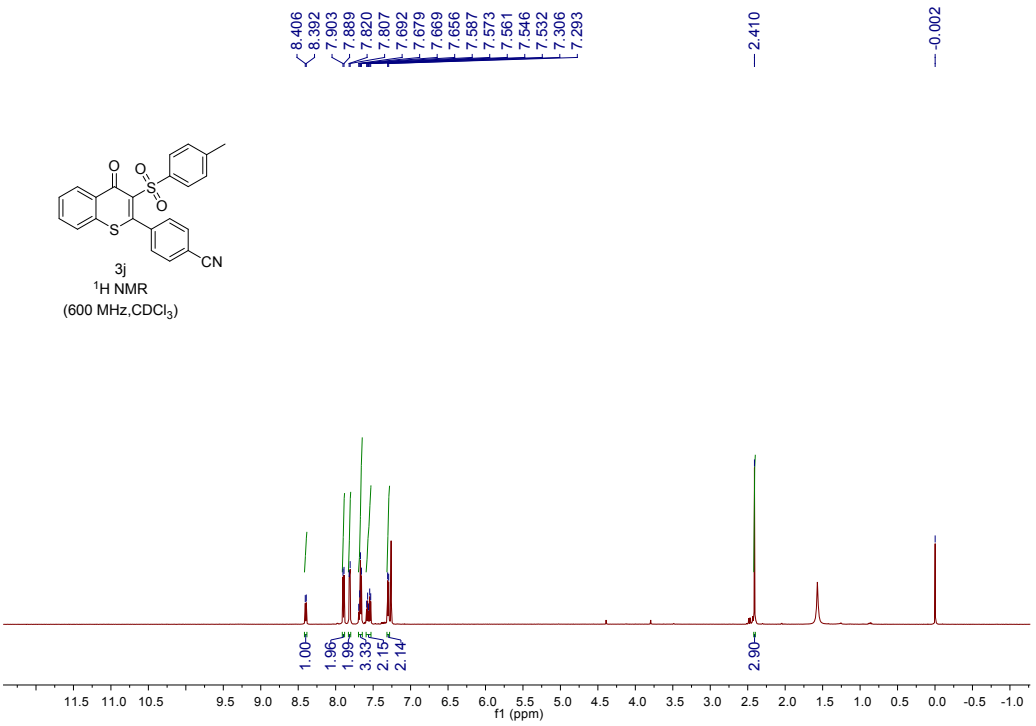

0.93
1.92
2.96
2.18
1.86
2.06
3.22
f1 (ppm)

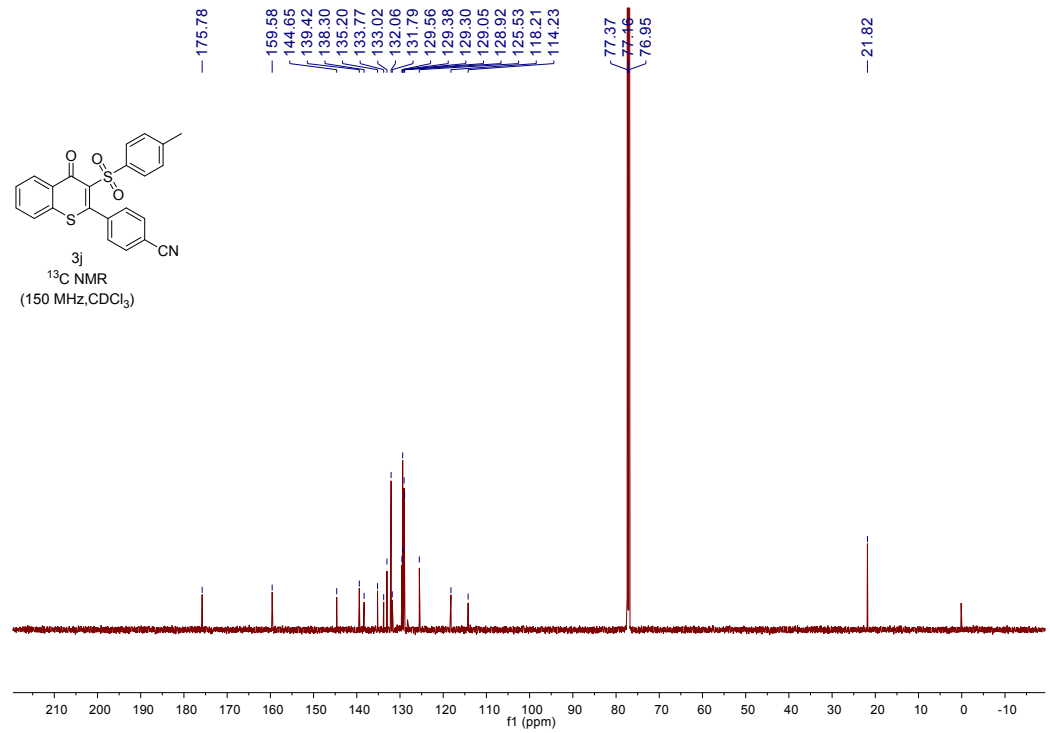

176.14
161.01
144.32
138.75
135.60
133.79
133.59
132.79
131.92
131.63
129.76
129.48
129.28
129.02
128.99
125.42
125.14
77.37
77.16
76.95
21.80
O
O
S
O
S
Br
3h
13C NMR
(150 MHz,CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.408
8.395
7.915
7.902
7.787
7.774
7.680
7.667
7.657
7.578
7.566
7.553
7.543
7.530
7.301
7.288
2.407
-0.001
O
O
S
O
S
CF3
3i
1H NMR
(600 MHz,CDCl3)
1.00
2.36
2.32
3.44
2.22
2.21
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


175.96
160.42
144.48
138.53
138.50
135.43
133.74
132.91
132.37
132.16
131.85
129.52
129.33
129.17
129.02
128.63
125.48
125.39
125.37
125.35
125.32
77.16
76.95
21.81
O
O
S
O
S
CF3
3i
13C NMR
(150 MHz,CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.793
O
O
S
O
S
CF3
3i
19F NMR
(564 MHz,CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.406
8.392
7.903
7.889
7.820
7.807
7.692
7.679
7.669
7.656
7.587
7.573
7.561
7.546
7.532
7.306
7.293
2.410
-0.002
O
O
S
O
S
CN
3j
1H NMR
(600 MHz,CDCl3)
1.00
1.96
1.99
3.33
2.15
2.14
2.90
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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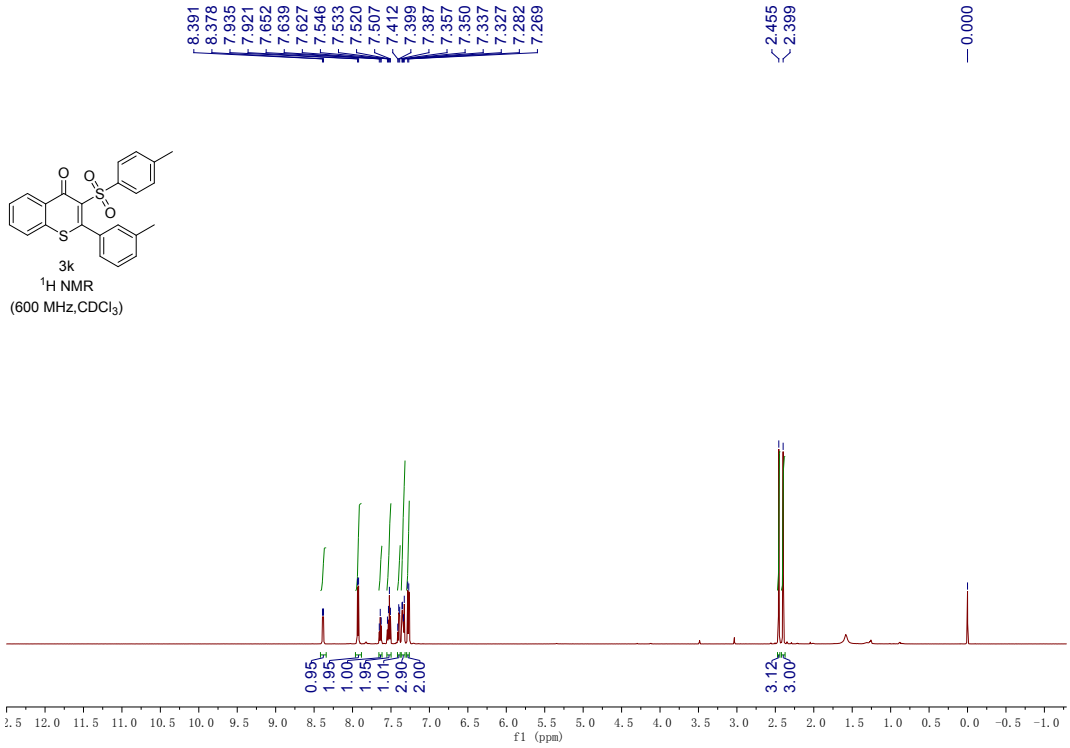
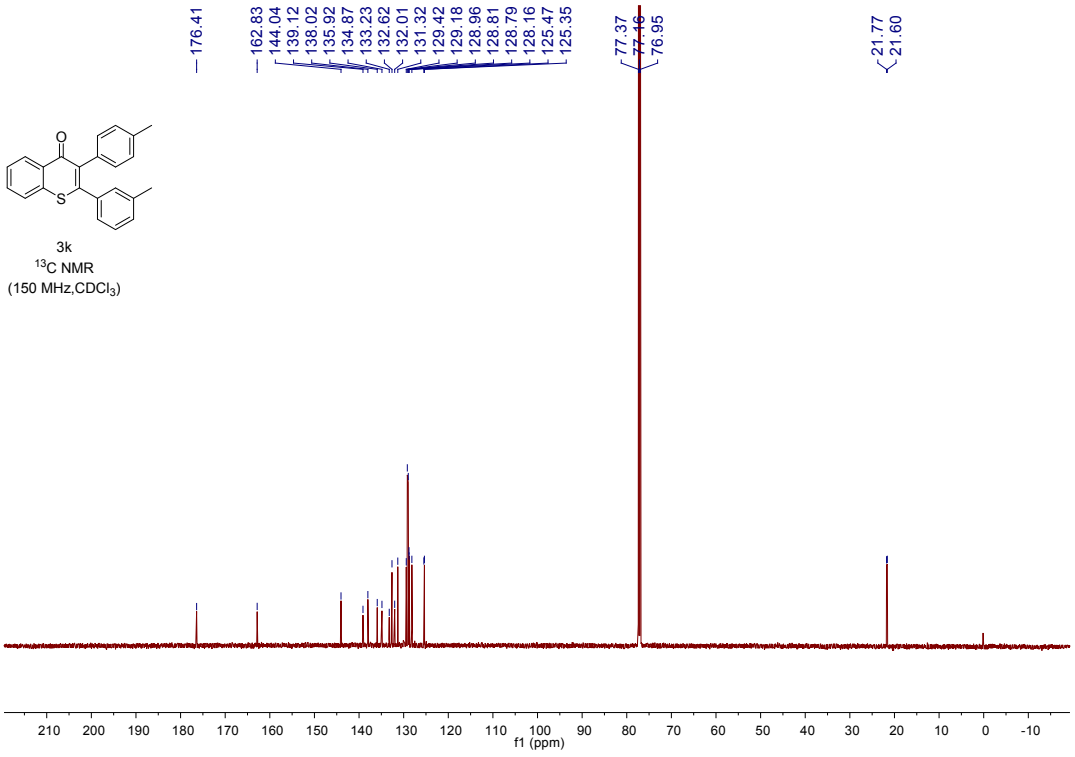
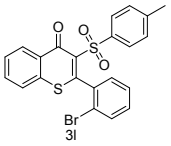
144.65
139.42
138.30
135.20
133.77
133.02
132.06
131.79
129.56
129.38
129.30
129.05
128.92
125.53
118.21
114.23
77.37
77.16
76.95
21.82
O
O
S
O
S
CN
3j
13C NMR
(150 MHz,CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.391
8.378
7.935
7.921
7.652
7.639
7.627
7.546
7.533
7.520
7.507
7.412
7.399
7.387
7.357
7.350
7.337
7.327
7.282
7.269
2.455
2.399
0.000
3k
1H NMR
(600 MHz,CDCl3)
0.95
1.95
1.00
1.95
1.01
2.90
2.00
3.12
3.00
f1 (ppm)

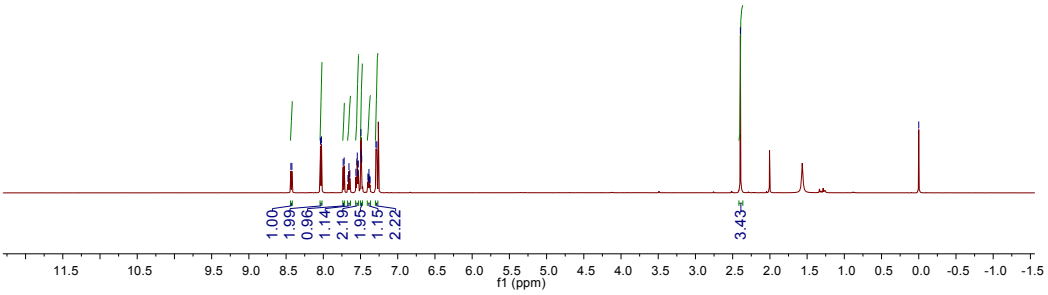

176.41
162.83
144.04
139.12
138.02
135.92
134.87
133.23
132.62
132.01
131.32
129.42
129.18
128.96
128.81
128.79
128.16
125.47
125.35
77.37
77.16
76.95
21.77
21.60
3k
13C NMR
(150 MHz,CDCl3)
f1 (ppm)

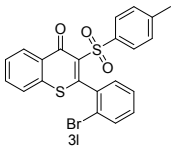


3l

^{1}H NMR

(600 MHz,$CDCl_3$)

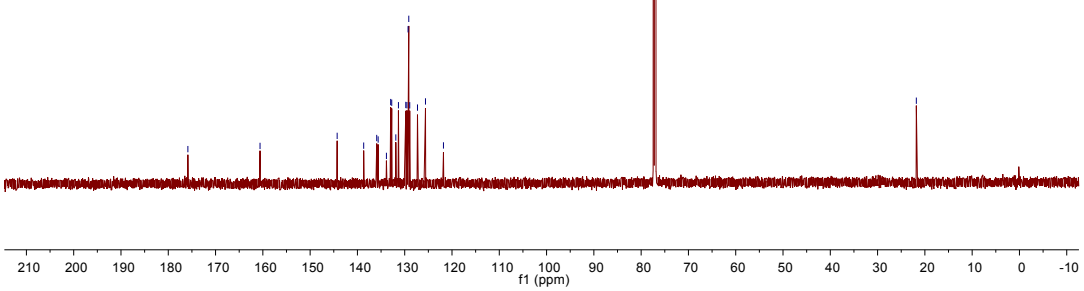


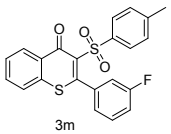


3l

^{13}C NMR

(150 MHz,$CDCl_3$)

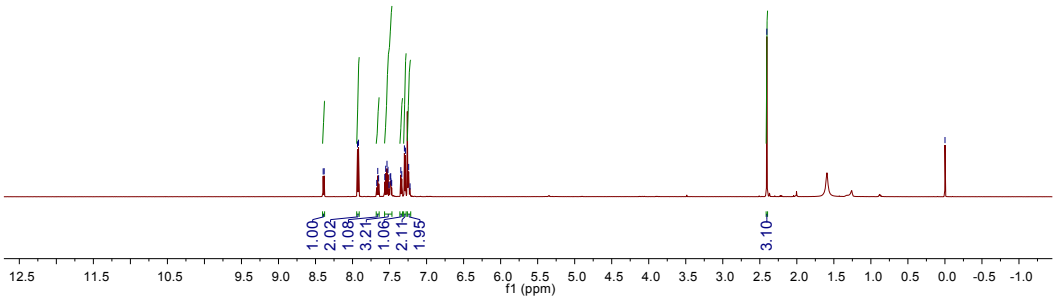


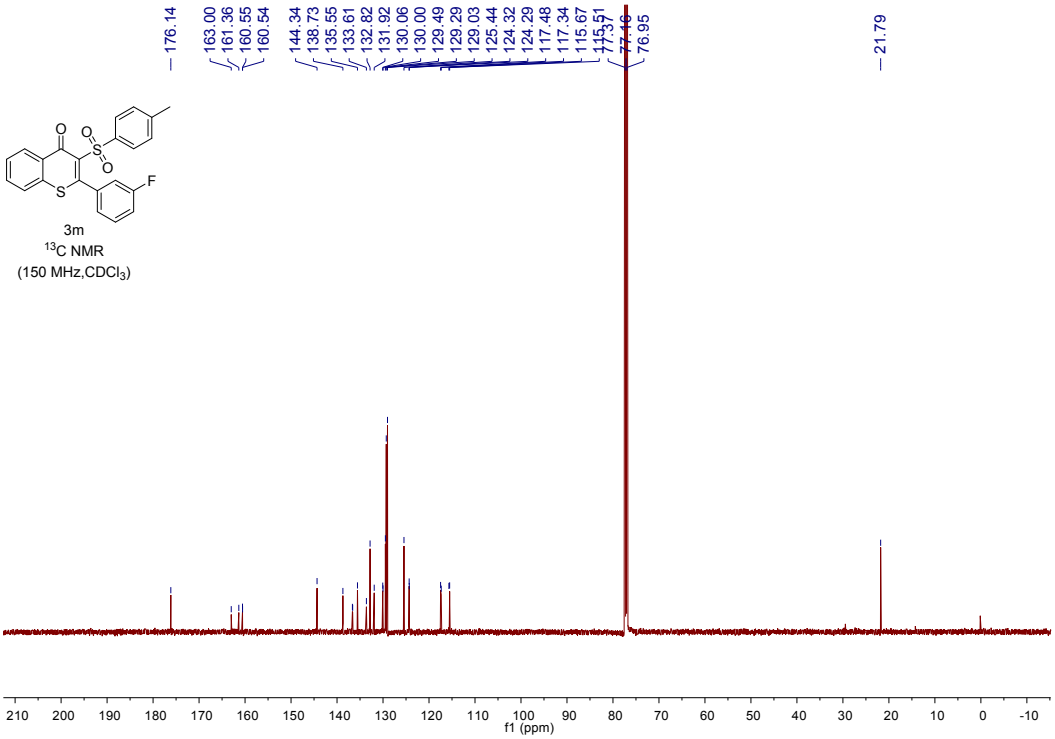


3m

^{1}H NMR

(600 MHz,$CDCl_3$)

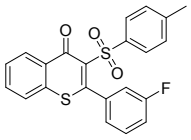




3m

^{13}C NMR

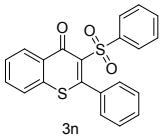
(150 MHz,$CDCl_3$)



3m

^{19}F NMR

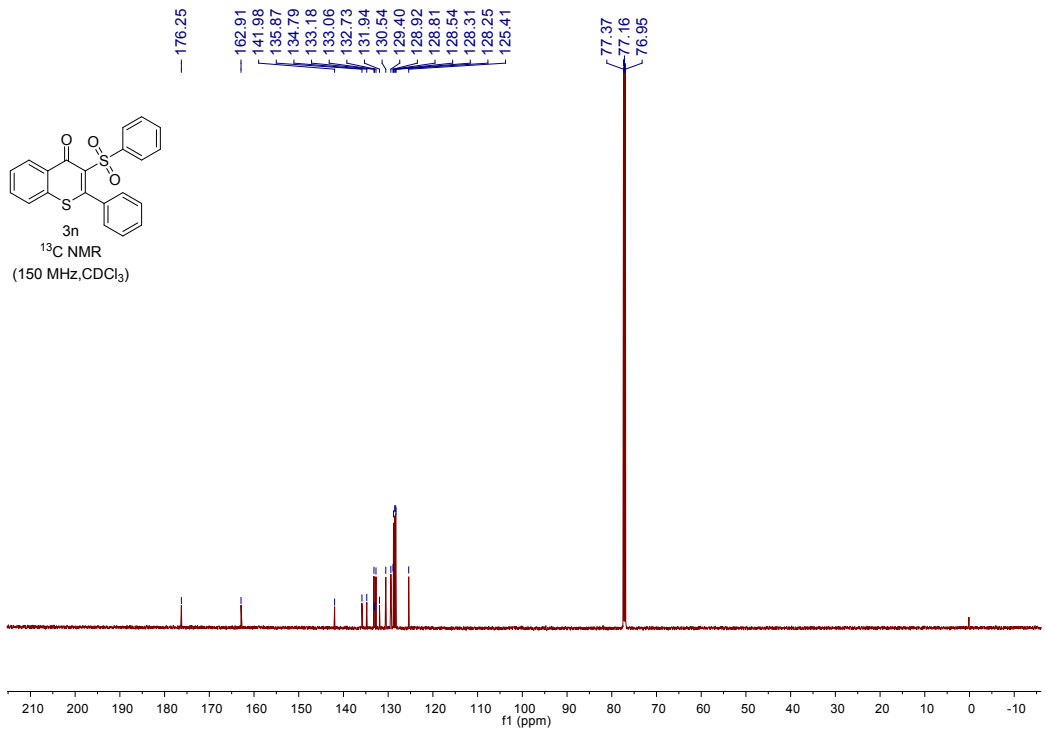
(564 MHz,$CDCl_3$)



3n

^{1}H NMR

(400 MHz,$CDCl_3$)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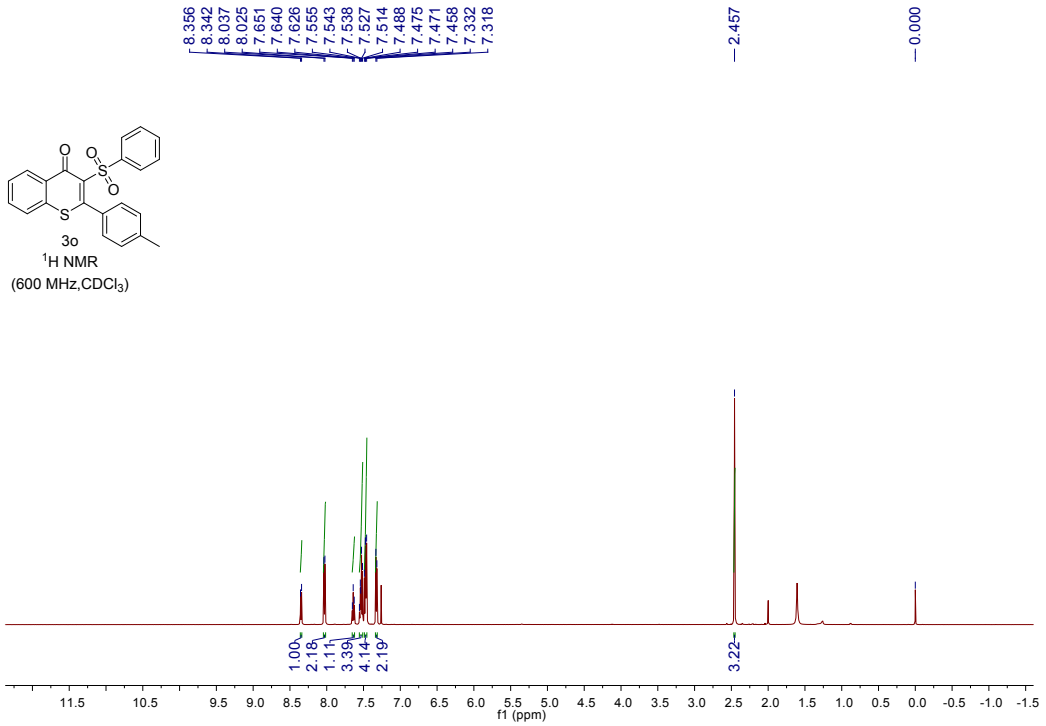
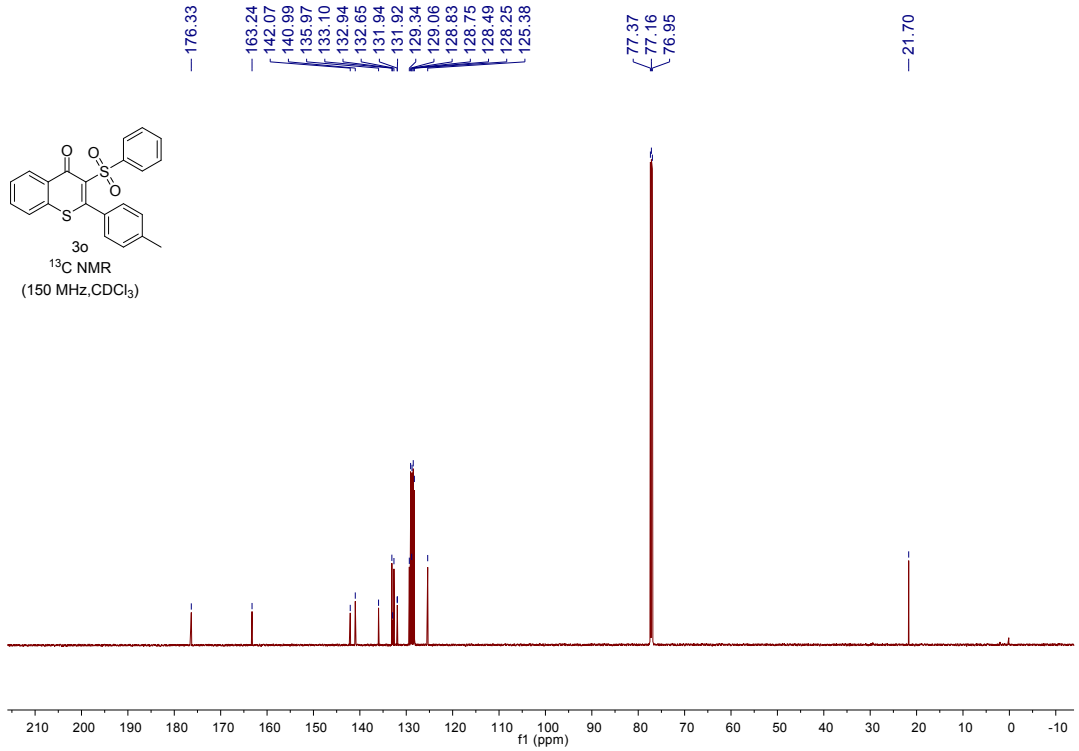
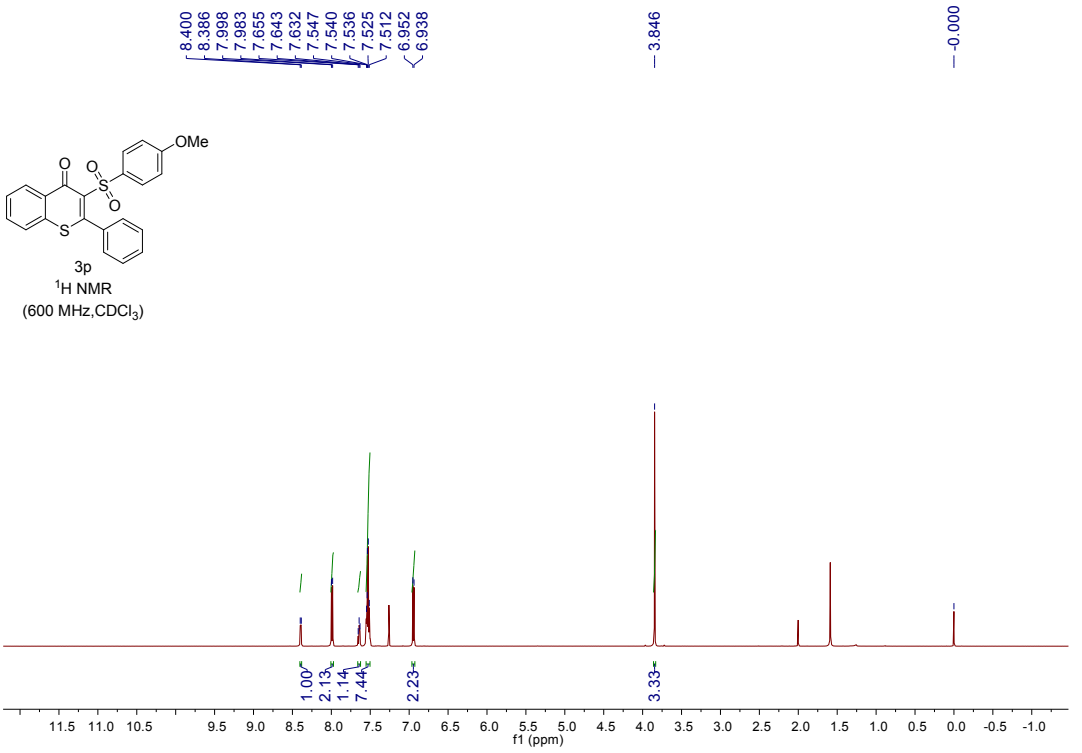
141.98
135.87
134.79
133.18
133.06
132.73
131.94
130.54
129.40
128.92
128.81
128.54
128.31
128.25
125.41
77.37
77.16
76.95
3n
13C NMR
(150 MHz,CDCl3)
f1 (ppm)


8.356
8.342
8.037
8.025
7.651
7.640
7.626
7.555
7.543
7.538
7.527
7.514
7.488
7.475
7.471
7.458
7.332
7.318
2.457
0.000
3o
1H NMR
(600 MHz,CDCl3)
1.00
2.18
1.11
3.39
4.14
2.19
3.22
f1 (ppm)


176.33
163.24
142.07
140.99
135.97
133.10
132.94
132.65
131.94
131.92
129.34
129.06
128.83
128.75
128.49
128.25
125.38
77.37
77.16
76.95
21.70
O
O
S
O
S
3o
13C NMR
(150 MHz,CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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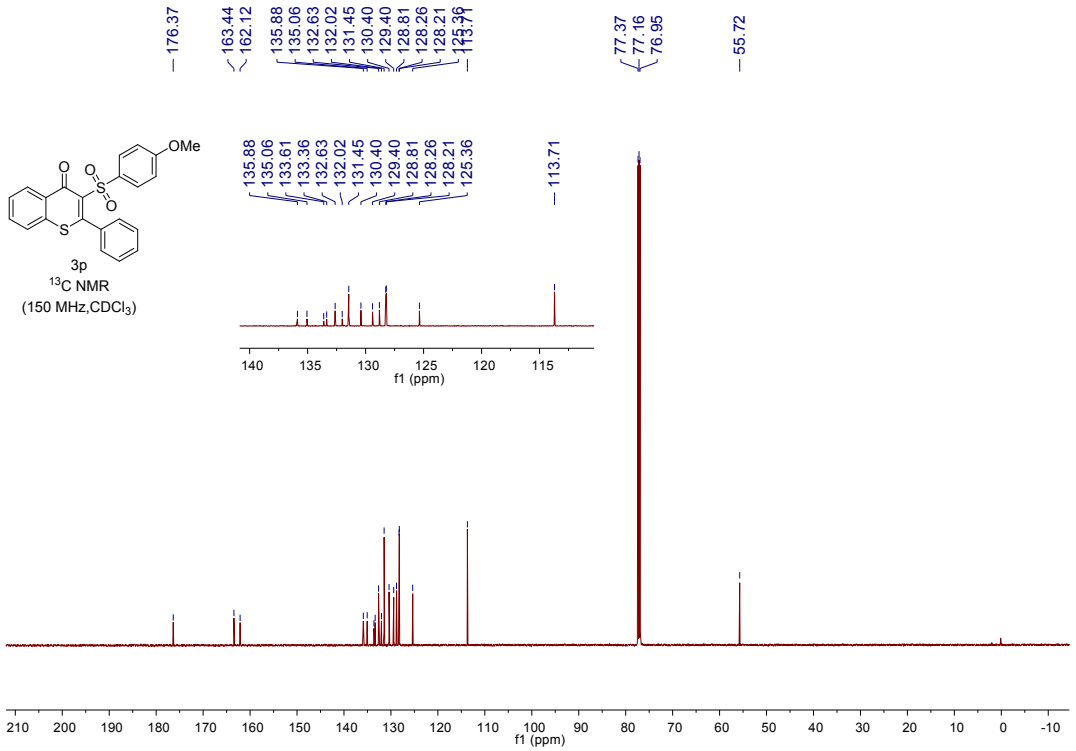
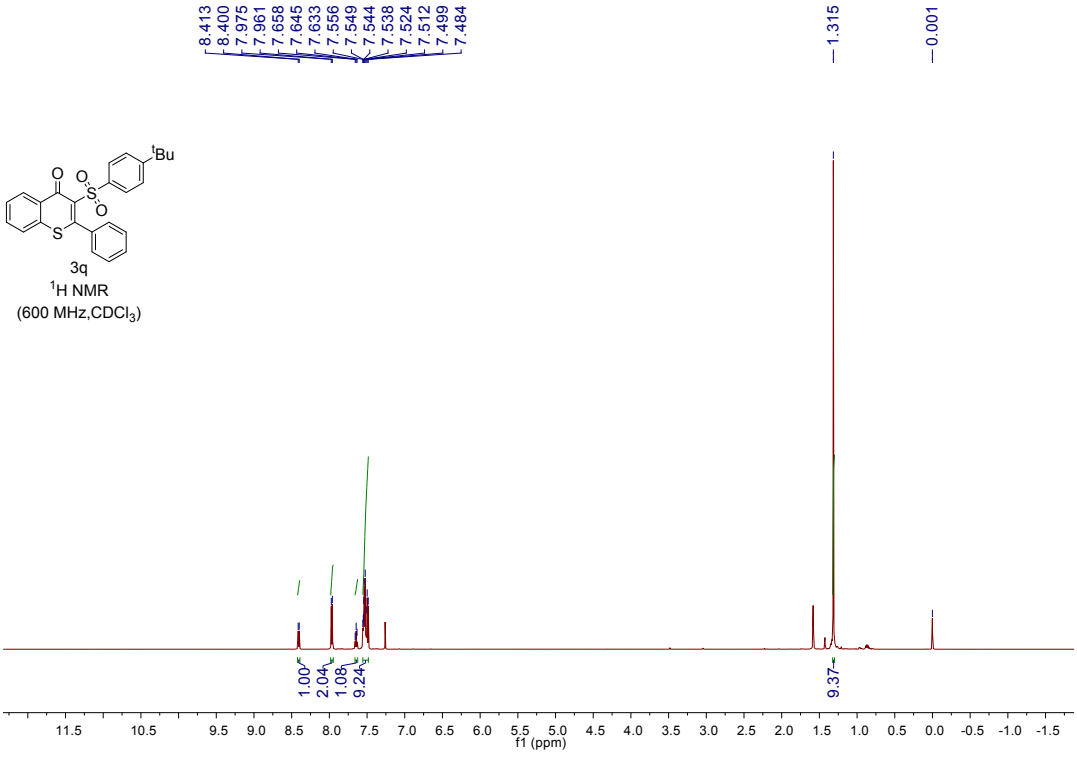
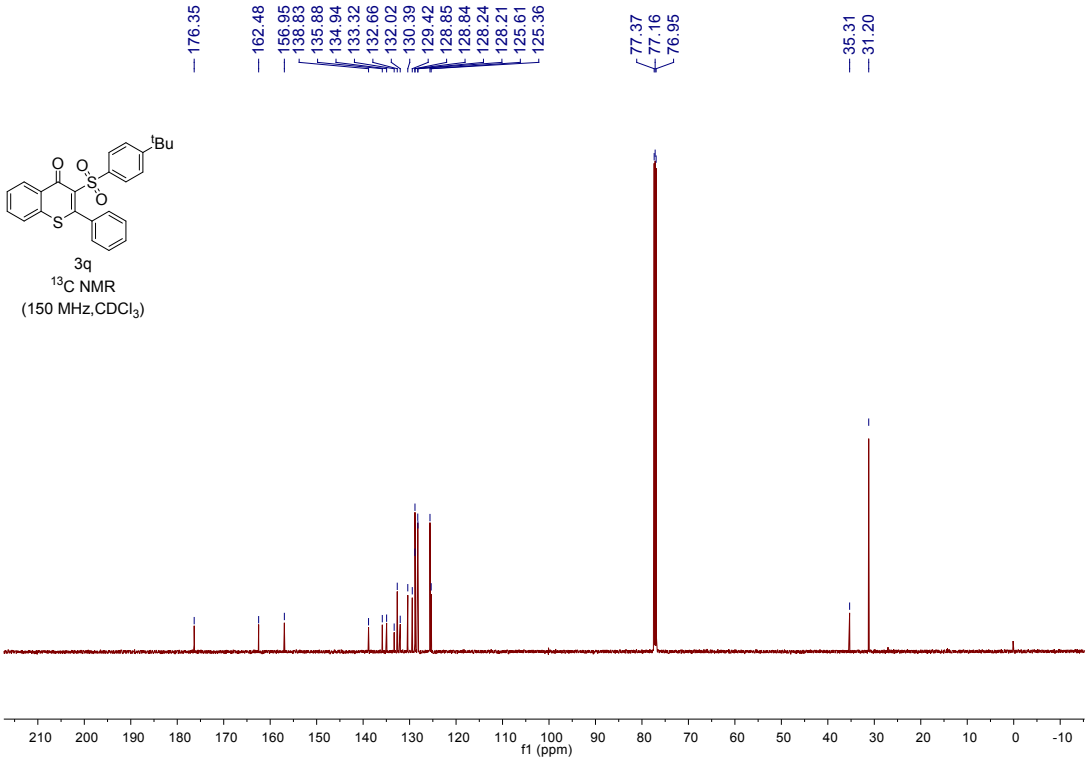
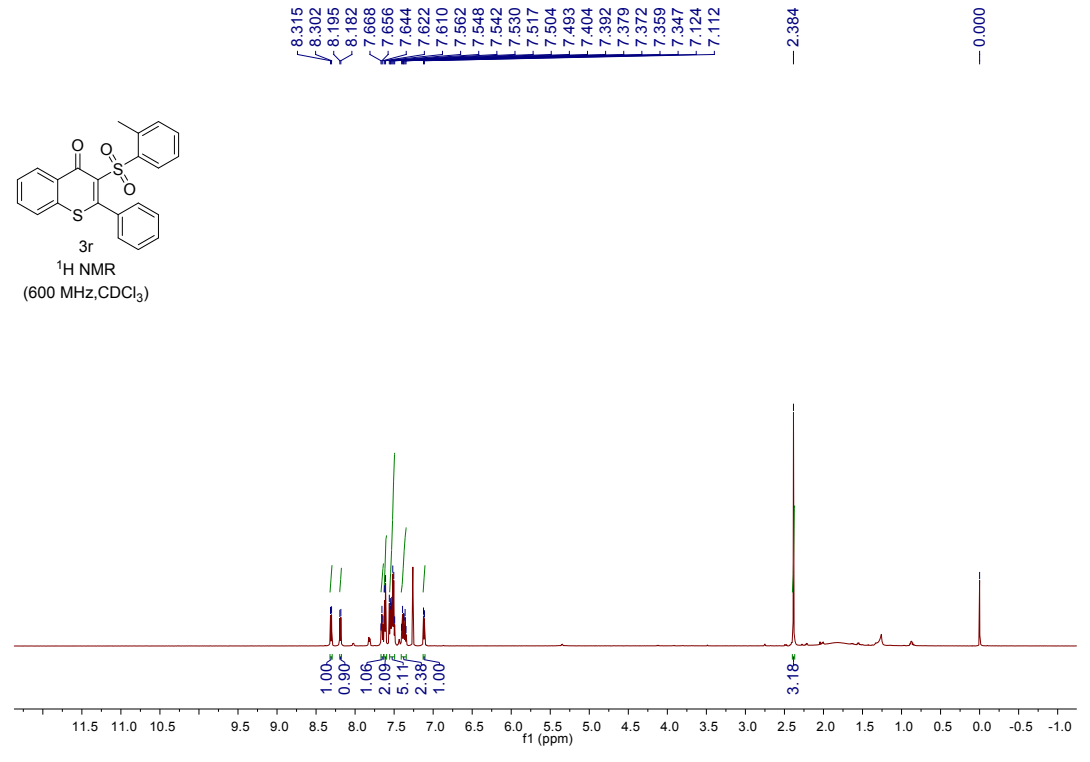
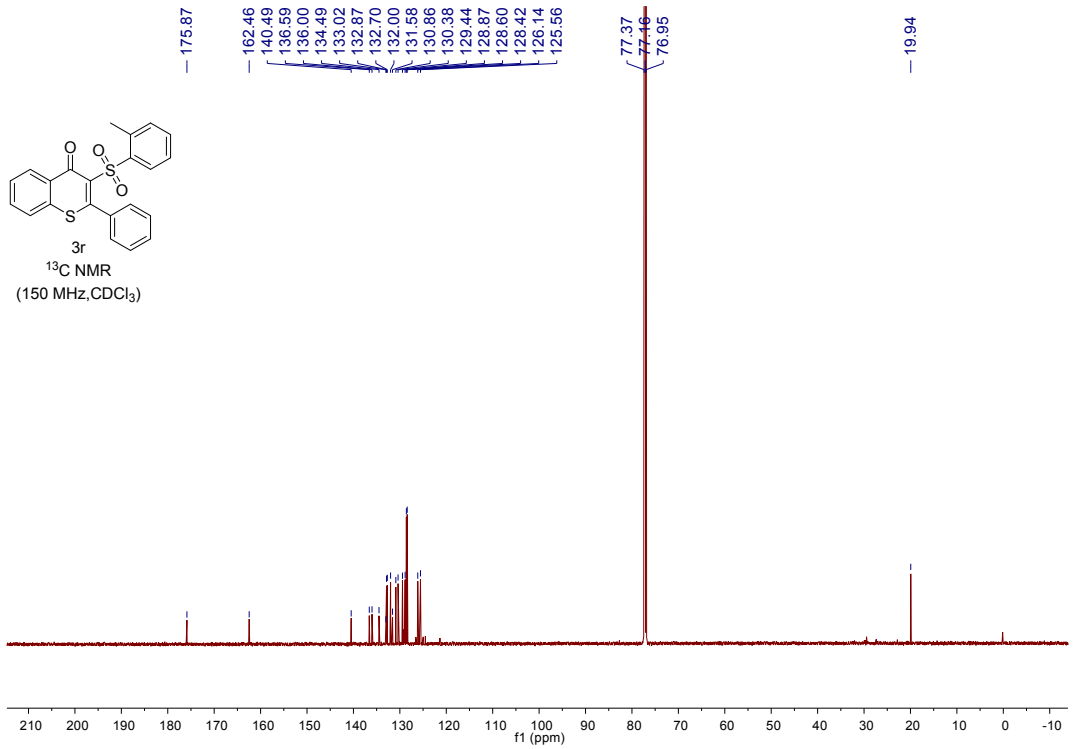
7.983
7.655
7.643
7.632
7.547
7.540
7.536
7.525
7.512
6.952
6.938
3.846
-0.000
OMe
O
O
S
O
S
3p
1H NMR
(600 MHz,CDCl3)
1.00
2.13
1.14
7.44
2.23
3.33
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


176.37
163.44
162.12
135.88
135.06
132.63
132.02
131.45
130.40
129.40
128.81
128.26
128.21
125.36
113.71
77.37
77.16
76.95
55.72
OMe
O
O
S
O
S
3p
13C NMR
(150 MHz,CDCl3)
135.88
135.06
133.61
133.36
132.63
132.02
131.45
130.40
129.40
128.81
128.26
128.21
125.36
113.71
140
135
130
125
120
115
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.413
8.400
7.975
7.961
7.658
7.645
7.633
7.556
7.549
7.544
7.538
7.524
7.512
7.499
7.484
1.315
0.001
tBu
O
O
S
O
S
3q
1H NMR
(600 MHz,CDCl3)
1.00
2.04
1.08
9.24
9.37
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


176.35
162.48
156.95
138.83
135.88
134.94
133.32
132.66
132.02
130.39
129.42
128.85
128.84
128.24
128.21
125.61
125.36
77.37
77.16
76.95
35.31
31.20
tBu
O
O
S
O
S
3q
13C NMR
(150 MHz,CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

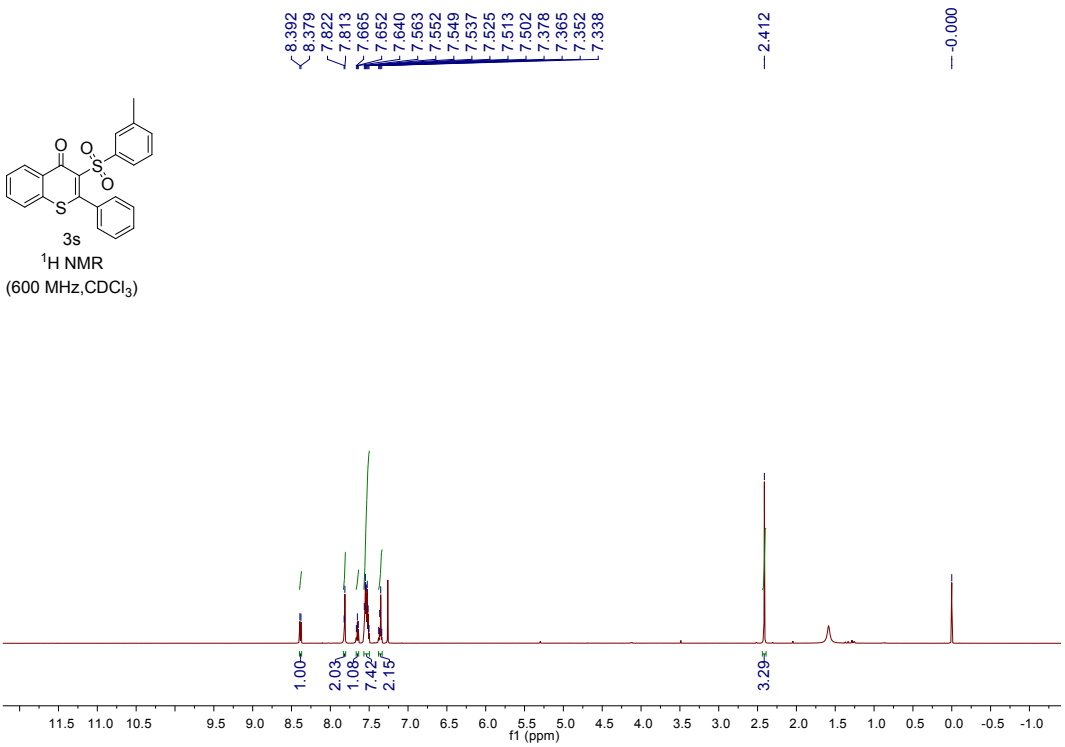

8.315
8.302
8.195
8.182
7.668
7.656
7.644
7.622
7.610
7.562
7.548
7.542
7.530
7.517
7.504
7.493
7.404
7.392
7.379
7.372
7.359
7.347
7.124
7.112
2.384
0.000
O
O
S
O
S
3r
1H NMR
(600 MHz,CDCl3)
1.00
0.90
1.06
2.09
5.11
2.38
1.00
3.18
11.5 11.0 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



3r

^{13}C NMR

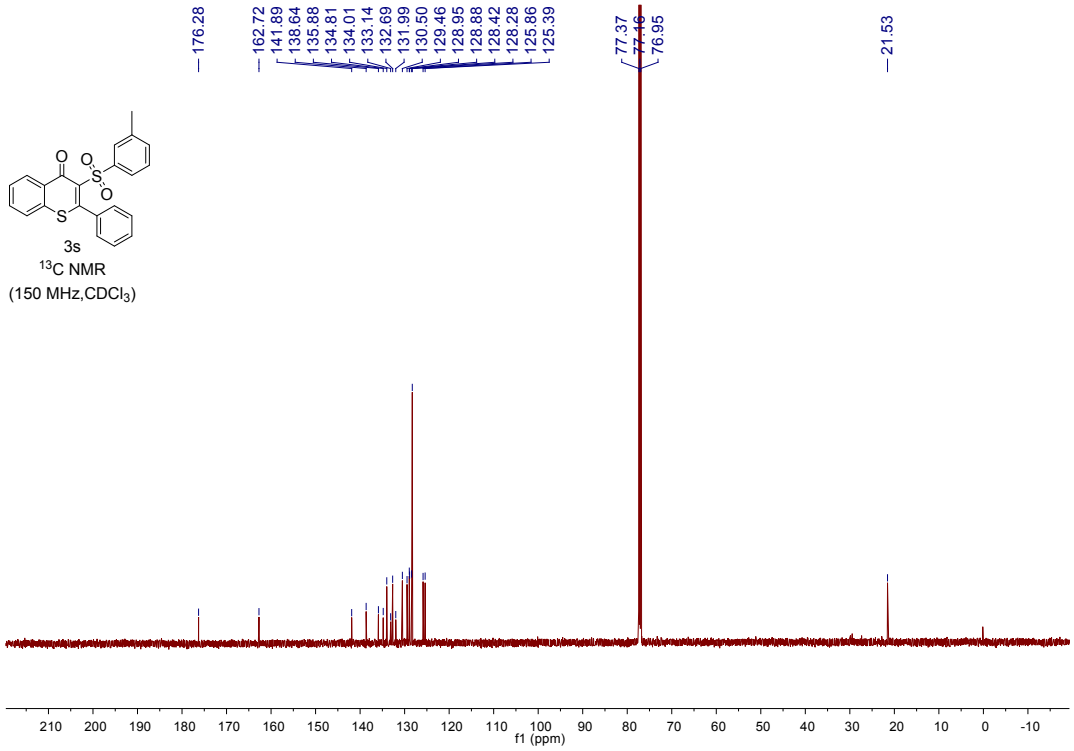
(150 MHz,$CDCl_3$)

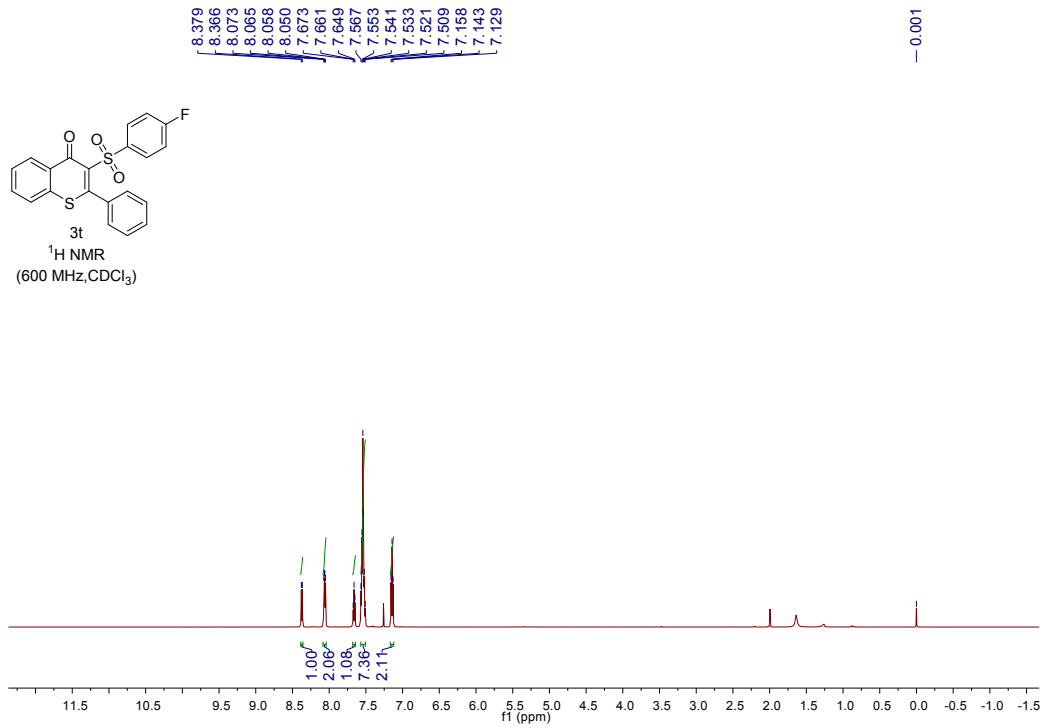


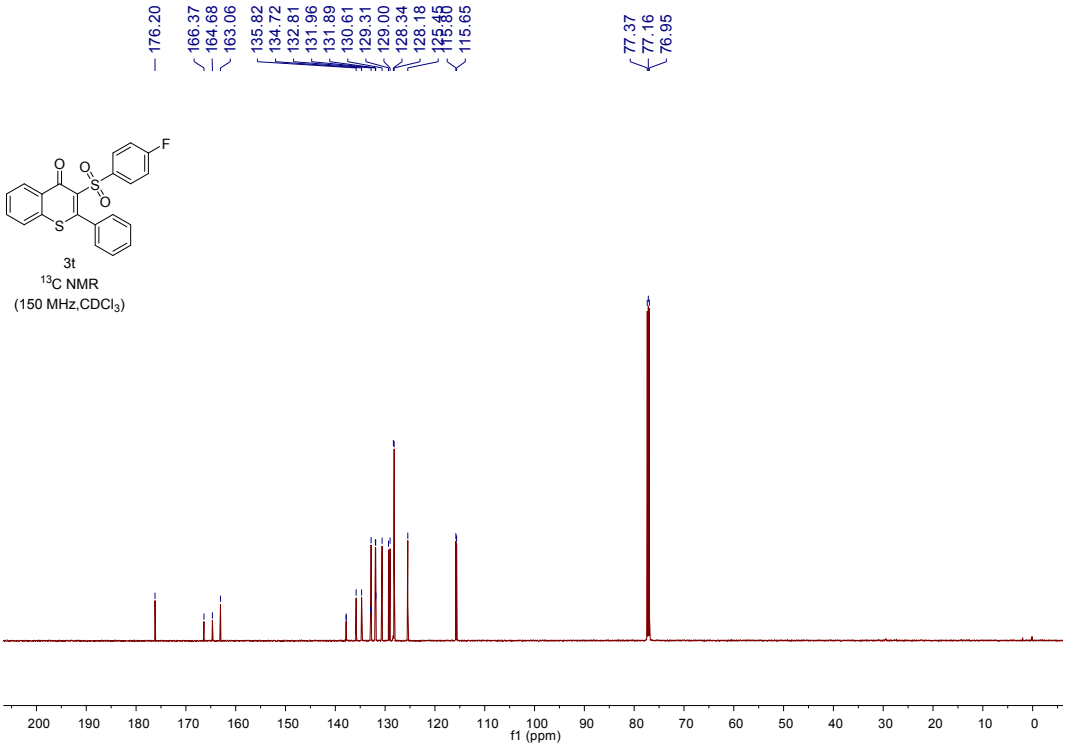
3s

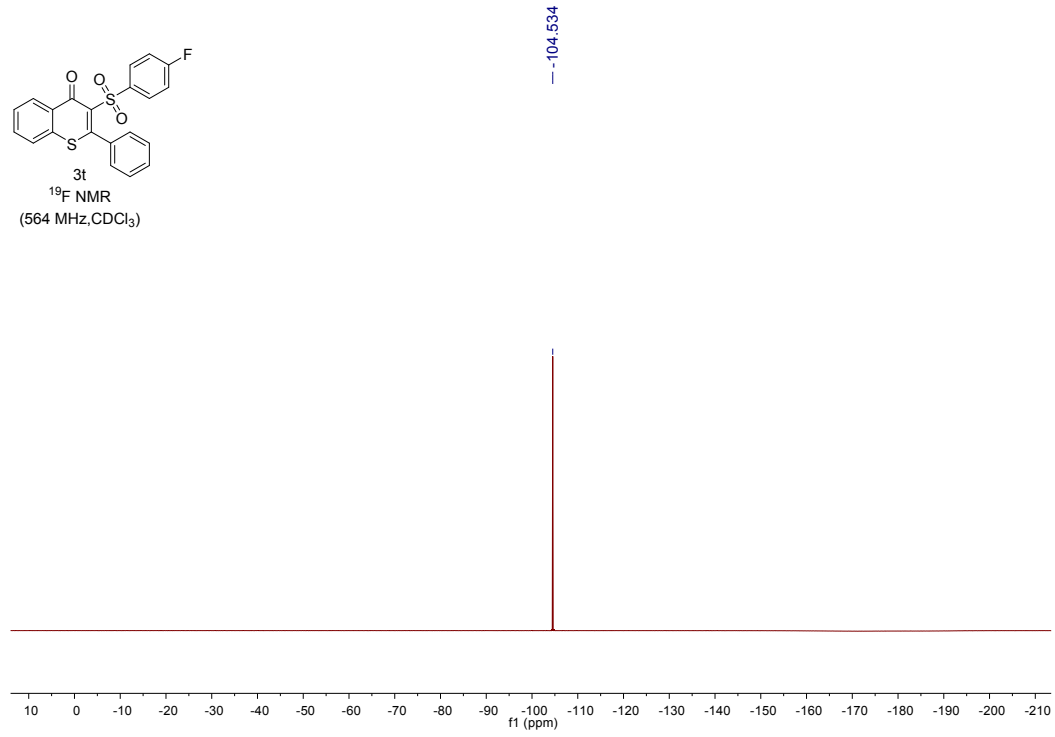
^{1}H NMR

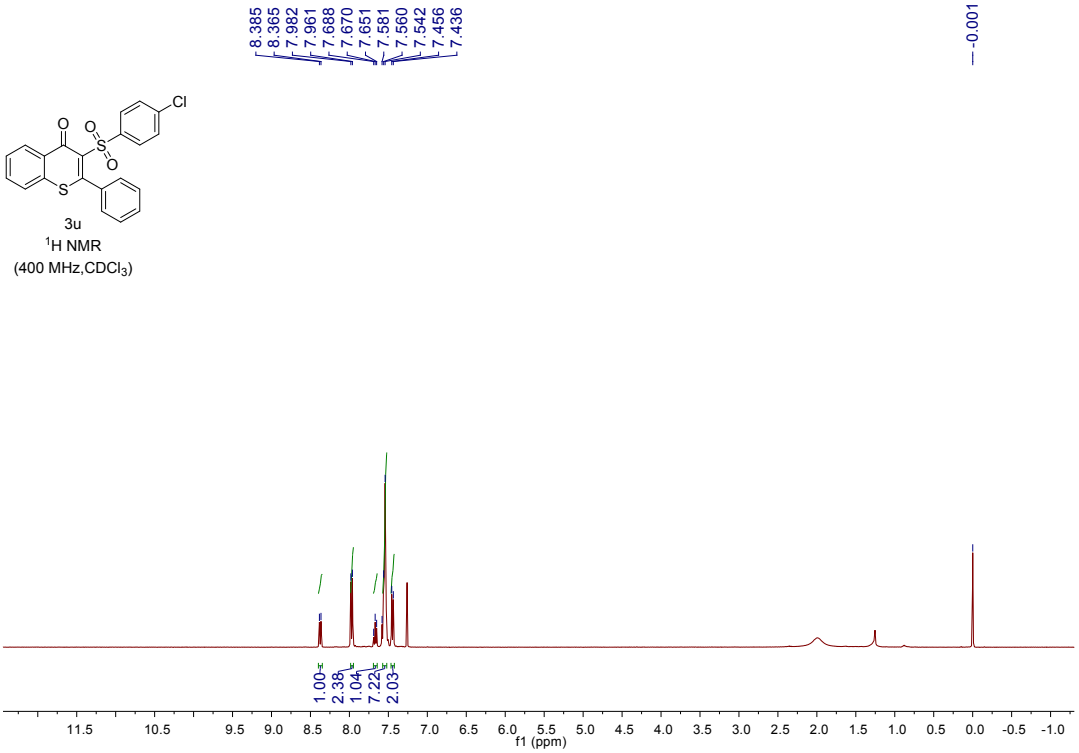
(600 MHz,$CDCl_3$)

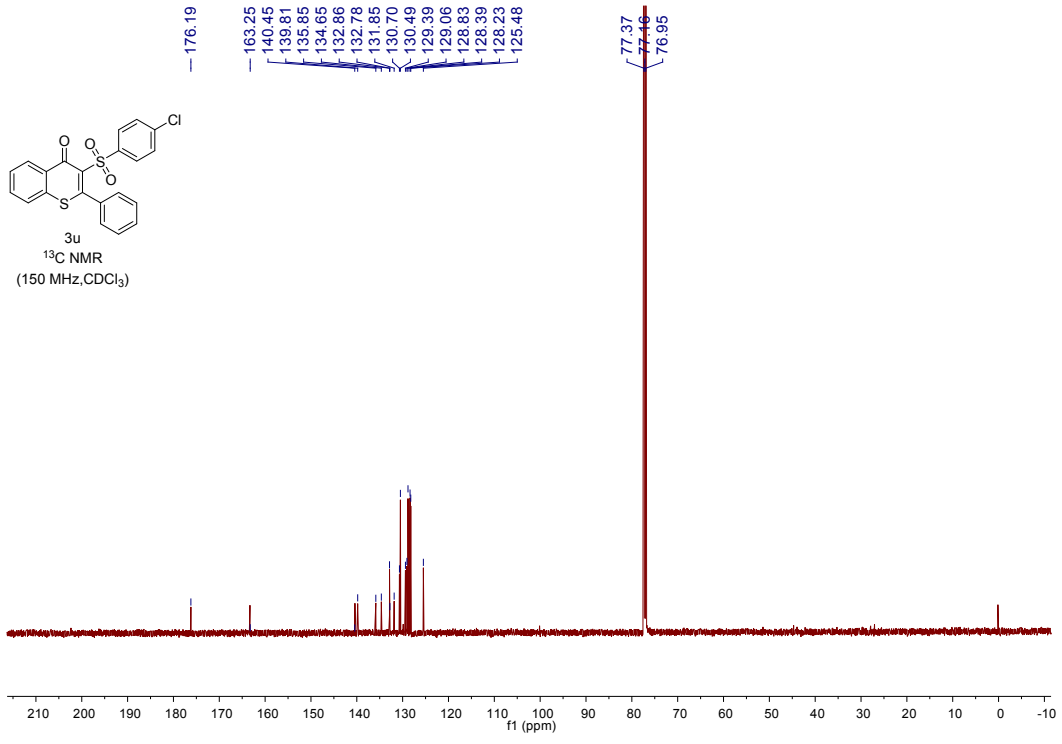

176.28
162.72
141.89
138.64
135.88
134.81
134.01
133.14
132.69
131.99
130.50
129.46
128.95
128.88
128.42
128.28
125.86
125.39
77.37
77.16
76.95
21.53
O
O
S
O
S
3s
13C NMR
(150 MHz,CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

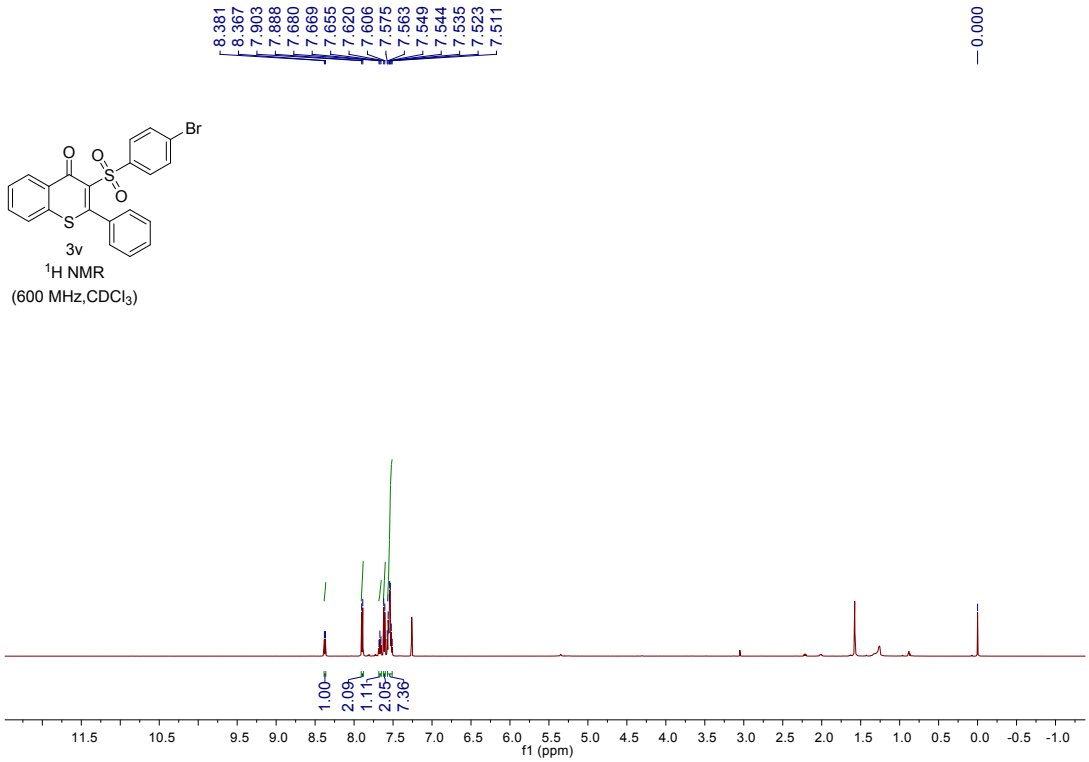

8.379
8.366
8.073
8.065
8.058
8.050
7.673
7.661
7.649
7.567
7.553
7.541
7.533
7.521
7.509
7.158
7.143
7.129
0.001
O
O
S
O
S
F
3t
1H NMR
(600 MHz,CDCl3)
1.00
2.06
1.08
7.36
2.11
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

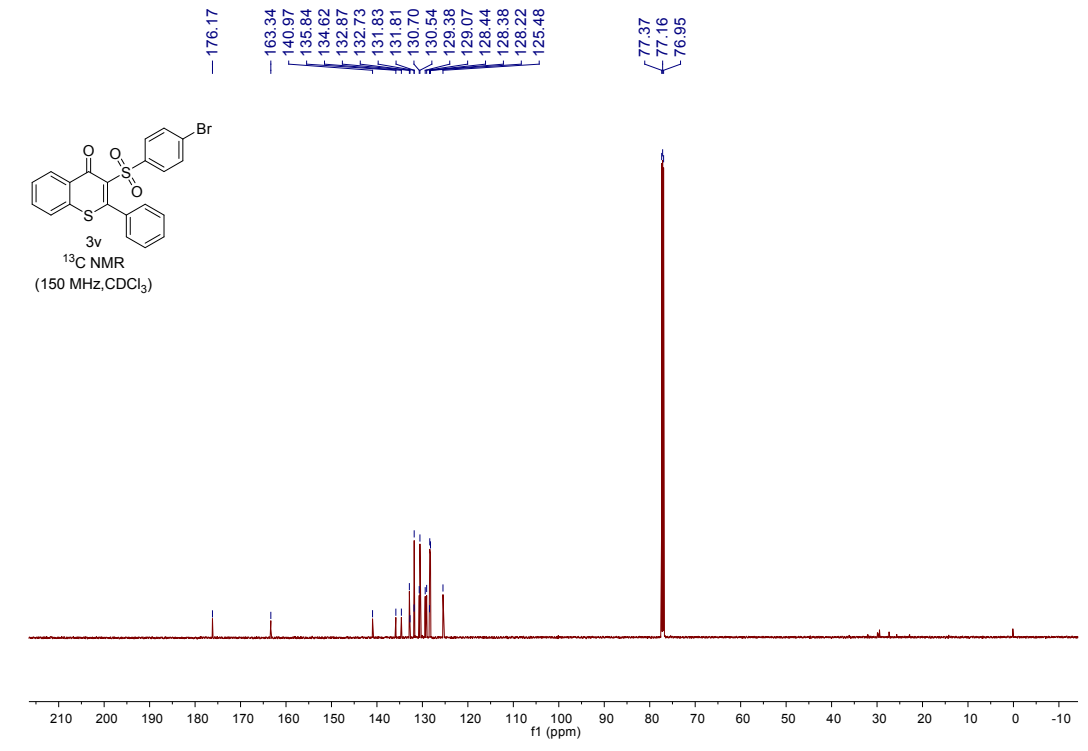

176.20
166.37
164.68
163.06
135.82
134.72
132.81
131.96
131.89
130.61
129.31
129.00
128.34
128.18
125.45
115.80
115.65
77.37
77.16
76.95
F
O
O
S
O
S
3t
^{13}C NMR
(150 MHz,CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

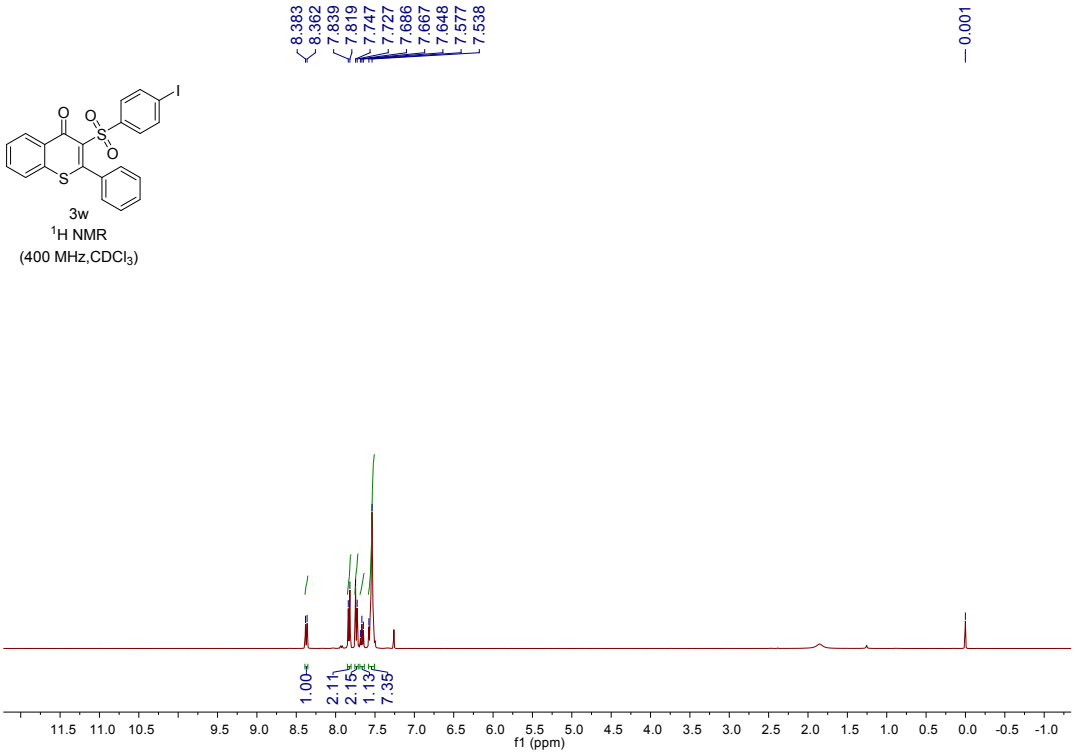

-104.534
F
O
O
S
O
S
3t
^{19}F NMR
(564 MHz,CDCl$_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

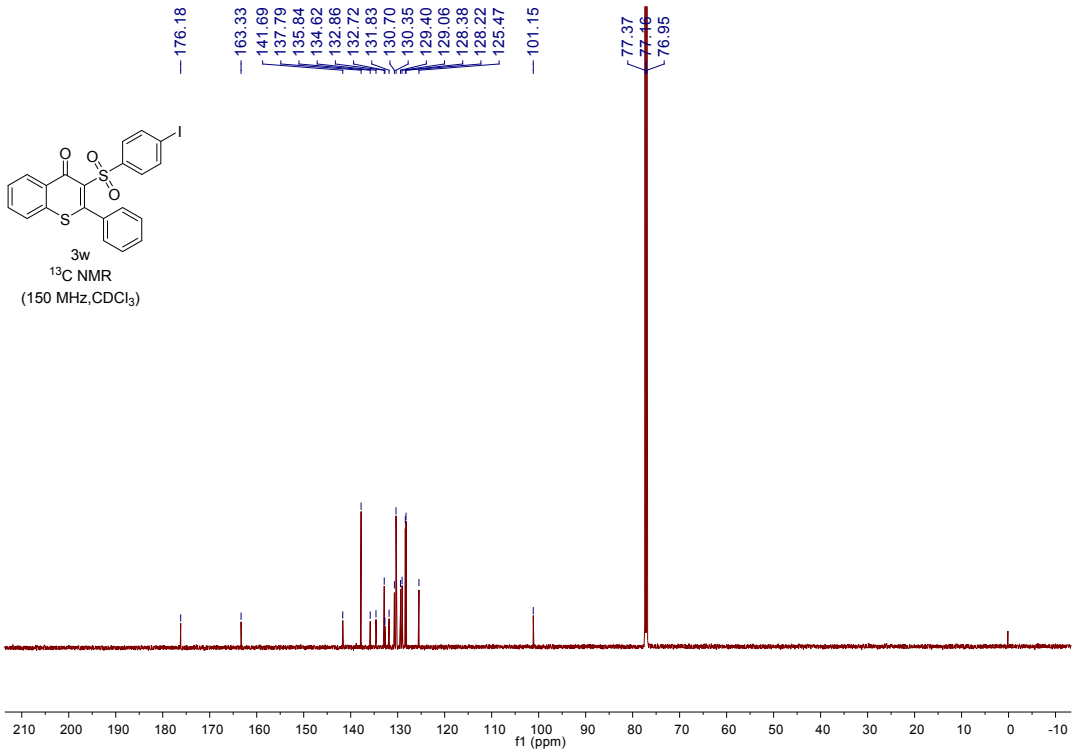

8.385
8.365
7.982
7.961
7.688
7.670
7.651
7.581
7.560
7.542
7.456
7.436
-0.001
Cl
O
O
S
O
S
3u
^{1}H NMR
(400 MHz,$CDCl_3$)
1.00
2.38
1.04
7.22
2.03
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

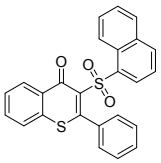

176.19
163.25
140.45
139.81
135.85
134.65
132.86
132.78
131.85
130.70
130.49
129.39
129.06
128.83
128.39
128.23
125.48
77.37
77.16
76.95
Cl
O
O
S
O
S
3u
^{13}C NMR
(150 MHz,$CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.381
8.367
7.903
7.888
7.680
7.669
7.655
7.620
7.606
7.575
7.563
7.549
7.544
7.535
7.523
7.511
0.000
Br
O
O
S
O
S
3v
^{1}H NMR
(600 MHz,CDCl$_3$)
1.00
2.09
1.11
2.05
7.36
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

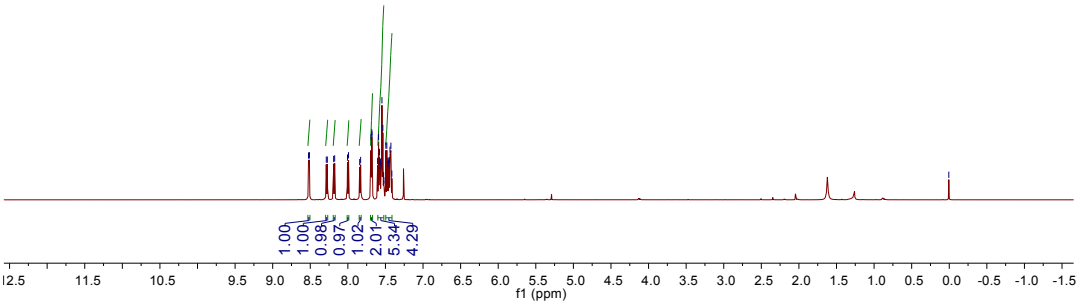

176.17
163.34
140.97
135.84
134.62
132.87
132.73
131.83
131.81
130.70
130.54
129.38
129.07
128.44
128.38
128.22
125.48
77.37
77.16
76.95
Br
O
O
S
O
S
3v
^{13}C NMR
(150 MHz,CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

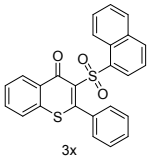

8.383
8.362
7.839
7.819
7.747
7.727
7.686
7.667
7.648
7.577
7.538
0.001
3w
1H NMR
(400 MHz,CDCl3)
1.00
2.11
2.15
1.13
7.35
f1 (ppm)


176.18
163.33
141.69
137.79
135.84
134.62
132.86
132.72
131.83
130.70
130.35
129.40
129.06
128.38
128.22
125.47
101.15
77.37
77.16
76.95
3w
13C NMR
(150 MHz,CDCl3)
f1 (ppm)

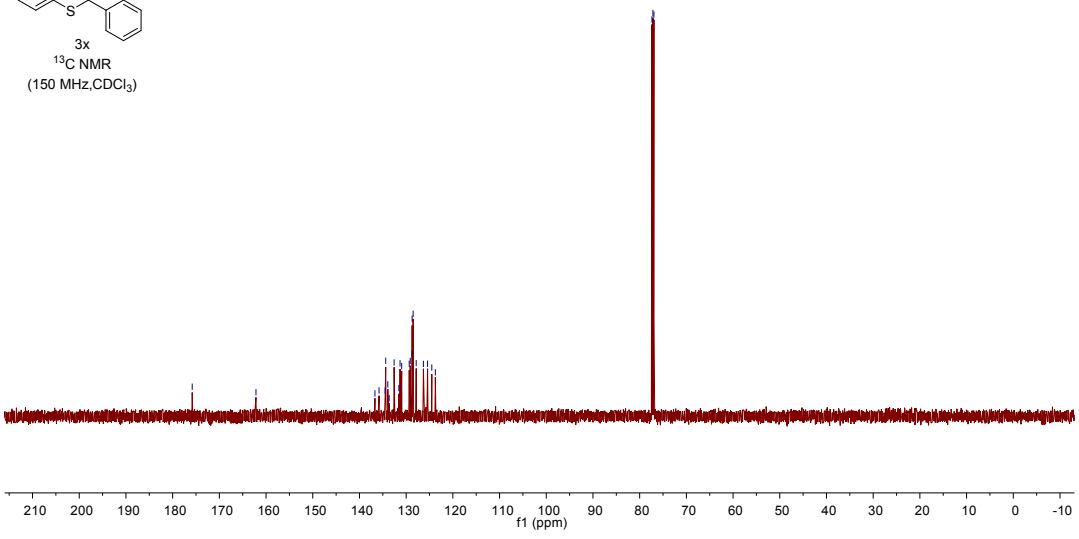


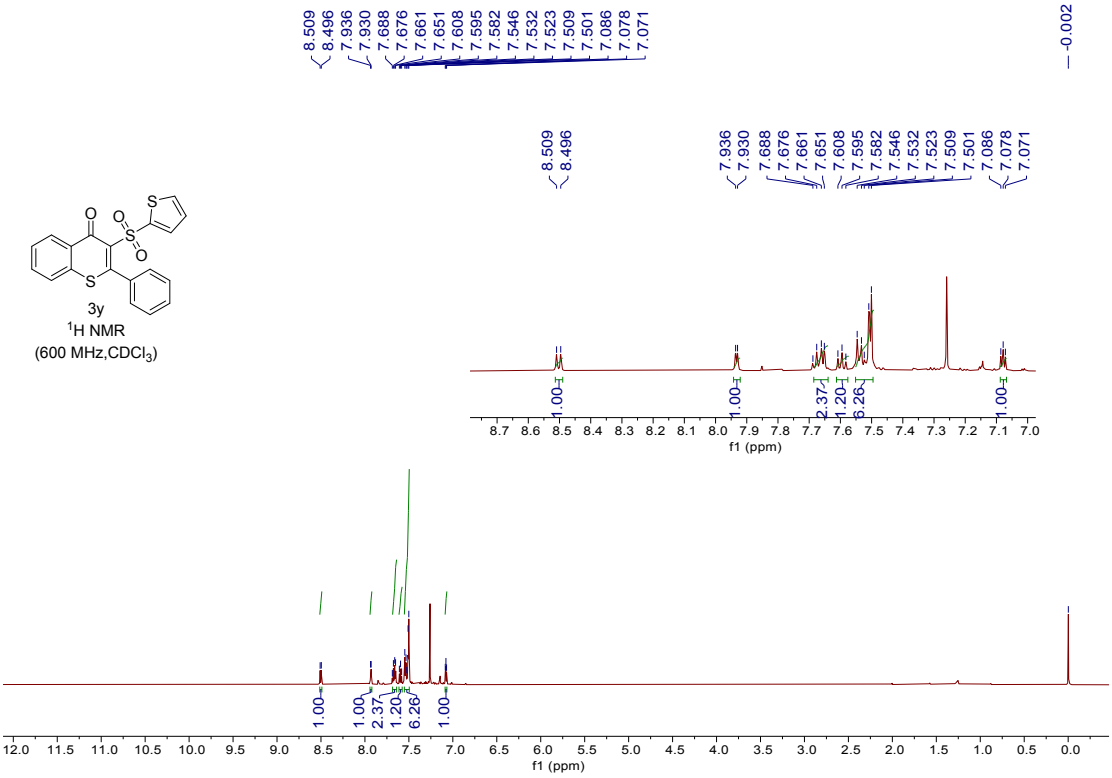
3x
^{1}H NMR
(600 MHz,$CDCl_3$)

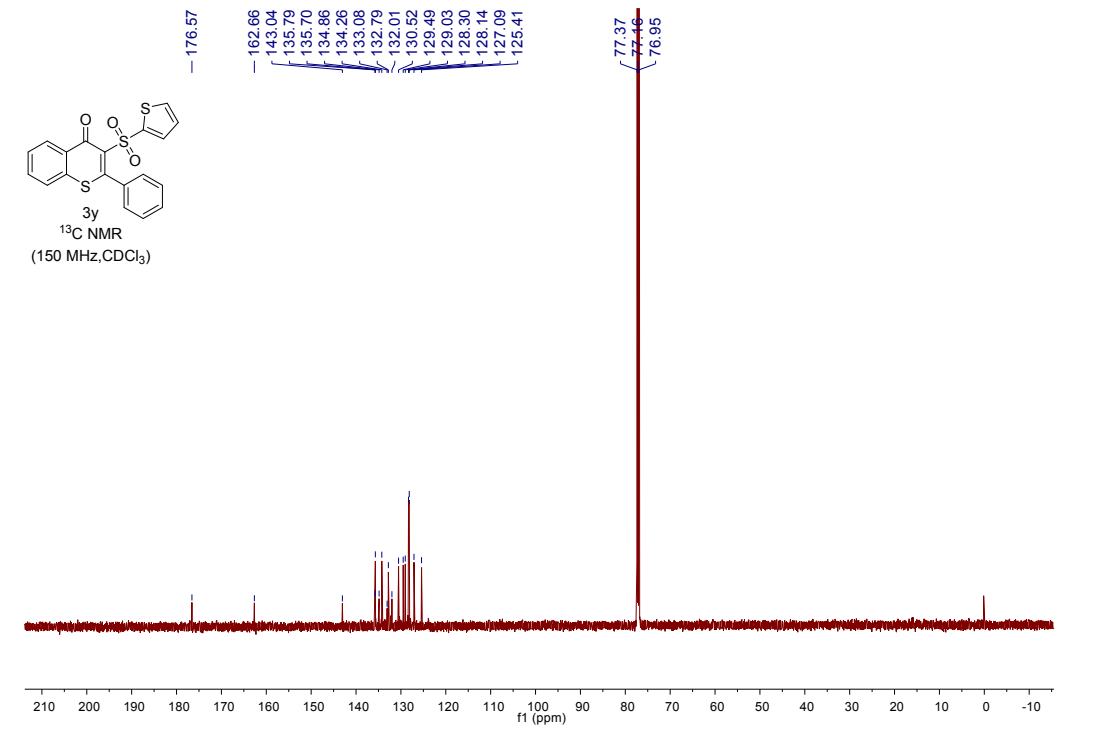


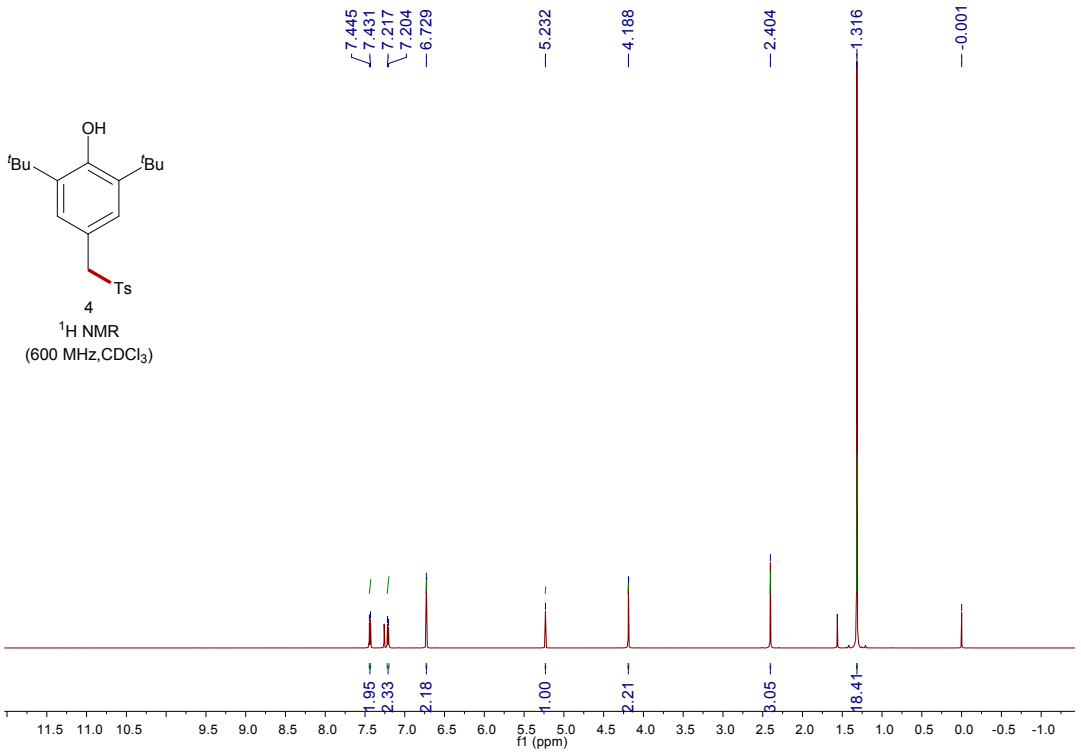


3x
^{13}C NMR
(150 MHz,$CDCl_3$)




8.509
8.496
7.936
7.930
7.688
7.676
7.661
7.651
7.608
7.595
7.582
7.546
7.532
7.523
7.509
7.501
7.086
7.078
7.071
-0.002
3y
1H NMR
(600 MHz,CDCl3)
1.00
1.00
2.37
1.20
6.26
1.00
f1 (ppm)

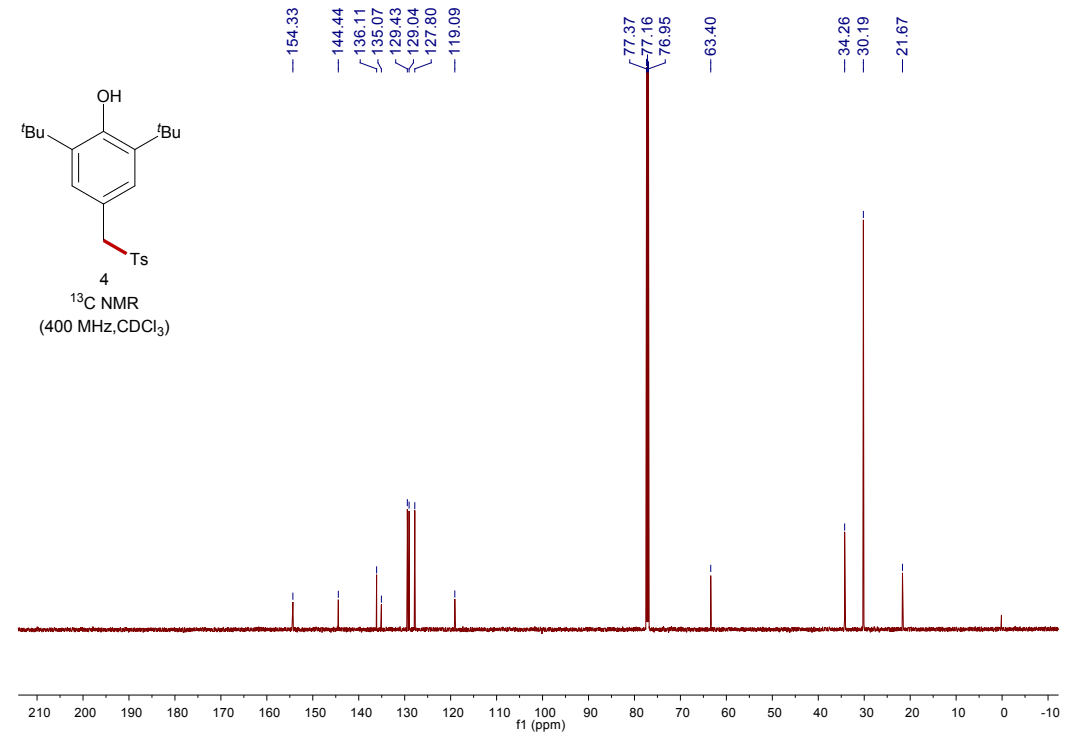

176.57
162.66
143.04
135.79
135.70
134.86
134.26
133.08
132.79
132.01
130.52
129.49
129.03
128.30
128.14
127.09
125.41
77.37
77.16
76.95
3y
13C NMR
(150 MHz,CDCl3)
f1 (ppm)



4

^{1}H NMR

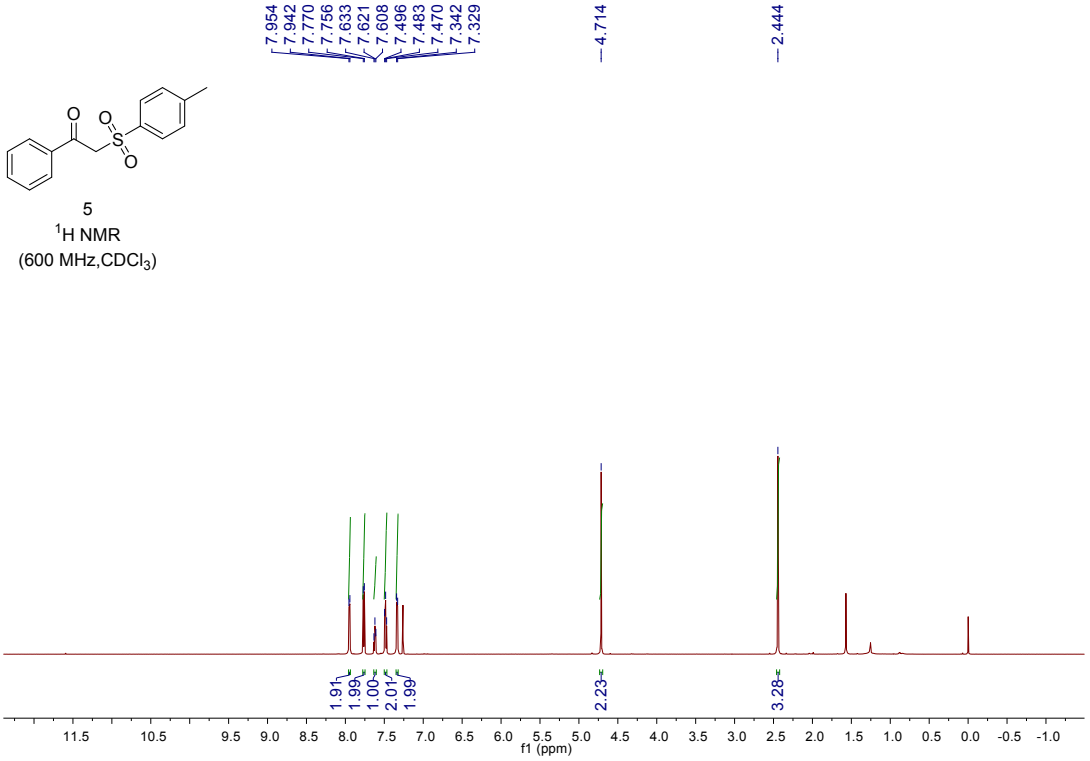
(600 MHz,$CDCl_3$)



4

^{13}C NMR

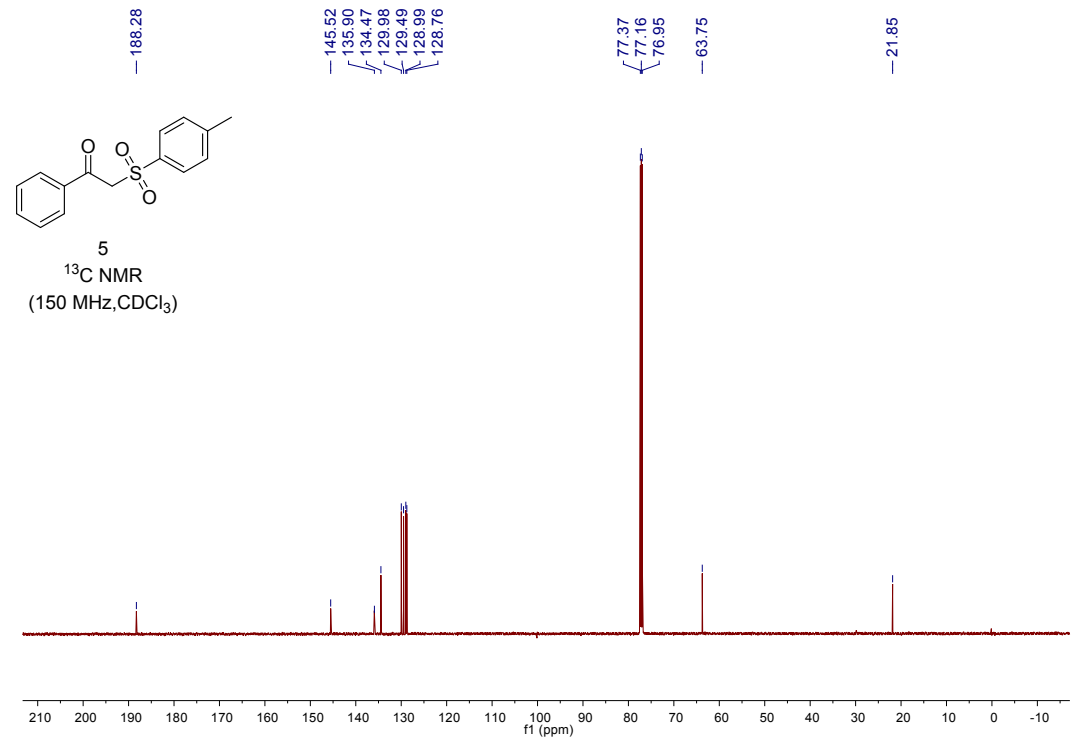
(400 MHz,$CDCl_3$)



5

^{1}H NMR

(600 MHz,$CDCl_3$)

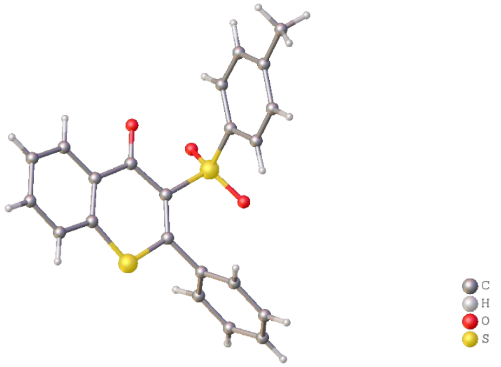


5

^{13}C NMR

(150 MHz,$CDCl_3$)

Table 1 Crystal data and structure refinement for **3a**.



Identification code	CCDC number: 1953609
Empirical formula	$C_{22}H_{16}O_3S_2$
Formula weight	392.47
Temperature/K	295.5(3)
Crystal system	triclinic
Space group	P-1
a/Å	5.3571(2)
b/Å	12.7753(6)
c/Å	13.8969(6)
α/°	74.461(4)
β/°	86.616(3)
γ/°	85.790(3)
Volume/Å^3	913.08(7)
Z	2
ρ_{calc}g/cm^3	1.427
μ/mm^{-1}	2.813
F(000)	408.0
Crystal size/mm^3	0.4 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.194 to 124.964
Index ranges	-6 ≤ h ≤ 4, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15
Reflections collected	7397
Independent reflections	2919 [R_{int} = 0.0279, R_{sigma} = 0.0342]
Data/restraints/parameters	2919/0/245
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.1029
Final R indexes [all data]	R_1 = 0.0420, wR_2 = 0.1055
Largest diff. peak/hole / e Å^{-3}	0.22/-0.29