Supporting Information for

Sulfonylation/cyclization of alkynes with sulfonyl chlorides by copper catalysis

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Table of Contents for Supporting Information

1. General considerations

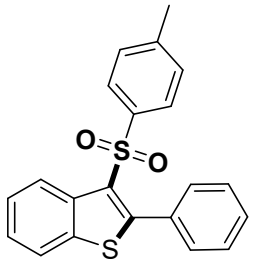
^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (600 MHz/151 MHz/565 NMR) in $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (J are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet).

2. General procedure for the synthesis of 3a

A mixture of 2-alkynylthioanisole **1a** (0.2 mmol), 4-methoxybenzenesulfonyl chloride **2a** (2 equiv), CuBr (10 mol%), K_2CO_3 (2 equiv), THF (2 mL), was heated at 90 ^{o}C oil bath for 12 h. After completion of reaction as monitored by TLC analysis, the reaction mixture was concentrated on a rotary evaporator and the residue was directly subjected to flash column chromatography on silica gel with (Petroleum ether/EtOAc = 15/1) as eluate to afford the desired product **3a** (88%).

3. Characterization data of all products

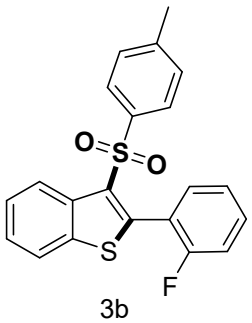
2-phenyl-3-tosylbenzo[*b*]thiophene (3a)



3a

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3a** as a yellow solid (64mg, 88% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.62 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.55 – 7.51 (m, 3H), 7.48 – 7.44 (m, 1H), 7.44 – 7.38 (m, 5H), 7.11 (d, J = 8.1 Hz, 2H), 2.32 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 152.5, 143.9, 139.4, 138.1, 136.1, 131.7, 130.5, 130.3, 129.4, 129.4, 127.6, 127.0, 125.9, 125.6, 124.6, 121.7, 21.5.

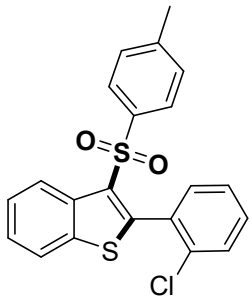
2-(2-fluorophenyl)-3-tosylbenzo[*b*]thiophene (3b)



3b

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3b** as a yellow solid (64.9mg, 85% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.47 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.52 – 7.38 (m, 4H), 7.25 – 7.11 (m, 4H), 2.33 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 160.7, 159.0, 145.0, 144.1, 138.9(d, J = 23.9 Hz), 135.5, 132.4, 131.8, 129.5, 127.1, 125.9, 125.8, 124.3,123.5 (d, J = 4.1 Hz), 121.9, 119.8, 119.7, 115.6, 115.4, 77.3, 77.0, 76.8, 21.5.

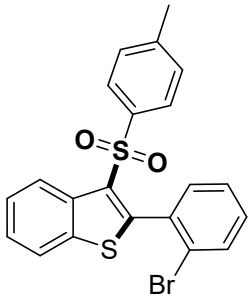
2-(2-chlorophenyl)-3-tosylbenzo[*b*]thiophene (3c)



3c

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3c** as a yellow solid (53.3mg, 67% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.53 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.38 (m, 4H), 7.35 (dd, J = 7.5, 1.5 Hz, 1H), 7.16 (d, J = 8.1 Hz, 2H), 2.32 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 148.4, 144.2, 138.8, 138.8, 135.3, 134.2, 132.5, 131.6, 130.9, 130.9, 129.5, 129.4, 127.3, 126.0, 125.9, 125.8, 124.4, 122.0, 21.6.

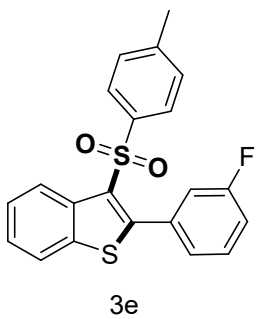
2-(2-bromophenyl)-3-tosylbenzo[*b*]thiophene (3d)



3d

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3d** as a yellow solid (60mg, 85% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.45 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.41 (s, 1H), 7.36 – 7.28 (m, 2H), 7.26 – 7.19 (m, 1H), 7.08 (d, J = 8.1 Hz, 2H), 2.24 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 150.1, 144.2, 138.7, 135.3, 132.9, 132.5, 131.4, 131.0, 129.5, 127.5, 126.6, 125.9, 125.9, 124.5, 124.2, 122.0, 21.6.

2-(3-fluorophenyl)-3-tosylbenzo[*b*]thiophene (3e)

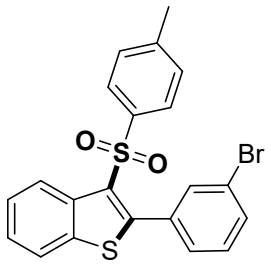


3e

The product purified by flash column chromatography on silica

gel (petroleum ether/ethyl acetate = 15/1) to afford the **3e** as a yellow solid (39.7mg, 52% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.62 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.55 (dd, J = 24.3, 8.0 Hz, 3H), 7.45 (t, J = 7.6 Hz, 1H), 7.38 (td, J = 8.0, 5.7 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.17 (t, J = 7.6 Hz, 3H), 7.09 (dt, J = 9.2, 2.1 Hz, 1H), 2.35 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 162.6, 144.1, 139.2, 138.1, 135.9, 133.6, 130.9, 129.5, 129.2 (d, J = 8.6 Hz), 127.0, 126.5 (d, J = 3.2 Hz), 126.1, 125.8, 124.7, 121.8, 117.6 (d, J = 22.9 Hz), 116.5, 116.3, 21.5.

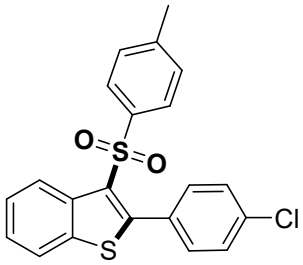
2-(3-bromophenyl)-3-tosylbenzo[*b*]thiophene (3f)



3f

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3f** as a yellow solid (64.5mg, 73% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.65 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.60 – 7.51 (m, 4H), 7.46 – 7.37 (m, 3H), 7.28 (d, J = 7.8 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 149.9, 144.2, 139.2, 138.1, 135.9, 133.6, 132.9, 132.4, 131.2, 129.5, 129.4, 129.2, 127.1, 126.1, 125.9, 124.7, 121.8, 121.6, 21.6.

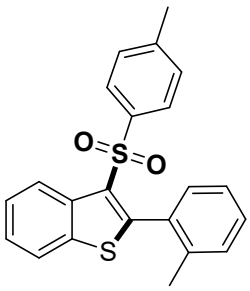
2-(4-chlorophenyl)-3-tosylbenzo[*b*]thiophene (3g)



3g

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3g** as a yellow solid (58.1mg, 73% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.60 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.60 – 7.51 (m, 2H), 7.44 (s, 0H), 7.38 (d, J = 4.3 Hz, 3H), 7.26 (s, 1H), 7.16 (d, J = 8.1 Hz, 2H), 2.35 (s,3H).^{13}C NMR (151 MHz, CDCl3) δ 150.8, 144.1, 139.3, 138.1, 136.0, 135.8, 131.8, 130.7, 130.1, 129.5, 127.9, 127.0, 126.0, 125.7, 124.6, 121.7, 21.5.

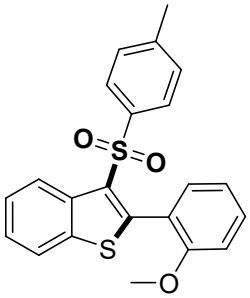
2-(*o*-tolyl)-3-tosylbenzo[*b*]thiophene (3h)



3h

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3h** as a yellow solid (66.5mg, 88% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.66 (d, J = 8.3 Hz, 1H), 7.57 – 7.52 (m, 4H), 7.44 (td, J = 7.6, 7.1, 1.2 Hz, 1H), 7.37 (td, J = 7.5, 1.4 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.17 – 7.12 (m, 4H), 2.35 (s, 3H), 2.09 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 151.6, 143.9, 138.5, 138.1, 135.8, 131.2, 131.0, 130.2, 129.8, 129.6, 129.4, 127.3, 125.8, 125.5, 124.9, 124.5, 121.8, 21.5, 20.2.

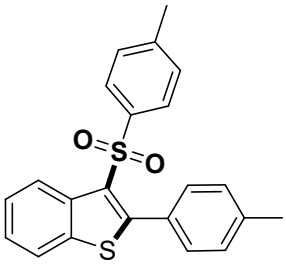
2-(2-methoxyphenyl)-3-tosylbenzo[*b*]thiophene (3i)



3i

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3i** as a yellow solid (67.8mg, 86% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.49 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.39 – 7.35 (m, 1H), 7.30 (dd, J = 7.4, 1.7 Hz, 1H), 7.12 (d, J = 8.1 Hz, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 3.61 (s, 3H), 2.31 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 157.2, 149.0, 143.6, 139.4, 138.8, 135.9, 132.0, 131.2, 130.7, 129.2, 127.1, 125.6, 125.3, 124.3, 121.9, 120.5, 119.8, 110.6, 55.3, 21.5.

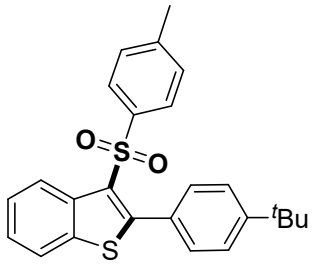
2-(*p*-tolyl)-3-tosylbenzo[*b*]thiophene (3j)



3j

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3j** as a yellow solid (69.6mg, 92% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.58 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 8.2 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.44 – 7.39 (m, 1H), 7.34 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H), 2.33 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 152.9, 143.8, 139.6, 139.5, 138.1, 136.2, 130.3, 129.9, 129.4, 128.7, 128.4, 127.0, 125.8, 125.4, 124.5, 121.7, 21.5, 21.4.

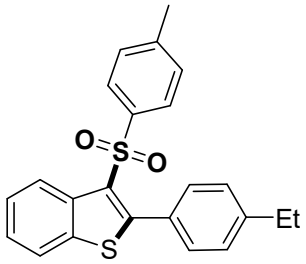
2-(4-(*tert*-butyl)phenyl)-3-tosylbenzo[*b*]thiophene (3k)



3k

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3k** as a yellow solid (75.6mg, 90% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.63 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.53 – 7.47 (m, 3H), 7.44 – 7.37 (m, 3H), 7.36 – 7.32 (m, 2H), 7.26 (s, 1H), 7.09 (d, J = 8.1 Hz, 2H), 2.32 (s, 3H), 1.38 (s, 9H).^{13}C NMR (151 MHz, CDCl3) δ 152.7, 152.6, 143.6, 139.4, 136.3, 130.2, 130.0, 129.2, 128.6, 127.1, 125.8, 125.4, 124.6, 124.6, 121.6, 31.3, 21.5.

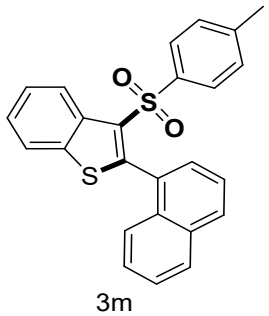
2-(4-ethylphenyl)-3-tosylbenzo[*b*]thiophene (3l)



3l

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3l** as a yellow solid (68.2mg,87% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.60 (d, J = 8.4 Hz, 0H), 7.78 (d, J = 8.0 Hz, 0H), 7.56 – 7.53 (m, 1H), 7.52 – 7.48 (m, 0H), 7.41 (d, J = 8.3, 7.2, 1.2 Hz, 0H), 7.36 – 7.33 (m, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 8.1 Hz, 1H), 2.73 (d, J = 7.6 Hz, 0H), 2.33 (s, 1H), 1.31 (t, J = 7.6 Hz, 1H).^{13}C NMR (151 MHz, CDCl3) δ 152.9, 145.8, 143.7, 139.5, 138.1, 136.2, 130.4, 129.9, 129.3, 128.9, 127.1, 127.0, 125.8, 125.4, 124.6, 121.7, 28.7, 21.5, 15.4.

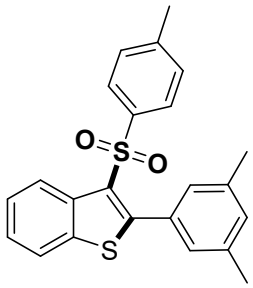
2-(naphthalen-1-yl)-3-tosylbenzo[*b*]thiophene (3m)



3m

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3m** as a yellow solid (53.8mg, 65% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.60 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.55 – 7.53 (m, 2H), 7.52 – 7.48 (m, 1H), 7.43 – 7.37 (m, 3H), 7.13 (d, J = 8.1 Hz, 2H), 6.95 – 6.91 (m, 2H).^{13}C NMR (151 MHz, CDCl3) δ 160.6, 152.8, 143.7, 139.5, 138.0, 131.9, 129.8, 129.4, 126.9, 125.85, 125.4, 124.5, 123.7, 121.6, 113.1, 55.3, 21.5.

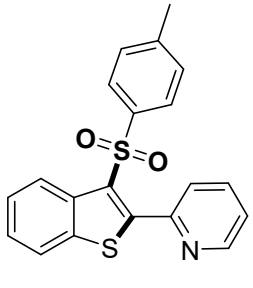
2-(3,5-dimethylphenyl)-3-tosylbenzo[*b*]thiophene (3n)



3n

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3n** as a yellow solid (59.6mg, 76% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.64 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.3 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 8.1 Hz, 2H), 6.96 (s, 2H), 2.34 (d, J = 6.4 Hz, 9H).^{13}C NMR (151 MHz, CDCl3) δ 152.9, 143.7, 139.6, 138.0, 137.1, 136.2, 131.4, 131.0, 130.1, 129.2, 128.1, 127.1, 125.8, 125.4, 124.64, 121.7,21.5, 21.2.

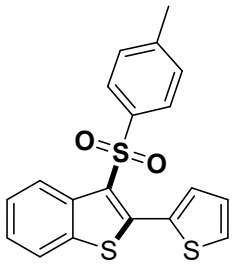
2-(3-tosylbenzo[*b*]thiophen-2-yl)pyridine (3o)



3o

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3o** as a yellow solid (60.6mg, 83% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.70 (dd, J = 4.9, 1.4 Hz, 1H), 8.45 (d, J = 8.3 Hz, 1H), 7.88 – 7.76 (m, 5H), 7.49 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.46 – 7.35 (m, 2H), 7.20 (d, J = 8.1 Hz, 2H), 2.33 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 151.1, 150.8, 149.0, 144.0, 138.9, 138.6, 135.8, 135.6, 130.3, 129.6, 127.3, 126.96, 125.95, 125.9, 124.5, 123.9, 122.0, 21.5.

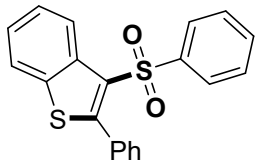
2-(thiophen-2-yl)-3-tosylbenzo[*b*]thiophene (3p)



3p

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3p** as a yellow solid (52.5mg, 71% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.67 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.50 (d, J = 4.4 Hz, 2H), 7.42 (d, J = 1.1 Hz, 1H), 7.26 (s, 1H), 7.18 – 7.09 (m, 3H), 2.33 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 144.6, 143.9, 139.1, 138.2, 136.5, 132.2, 131.0, 130.7, 129.4, 129.2, 127.4, 126.9, 126.0, 125.8, 124.8, 121.5, 21.5.

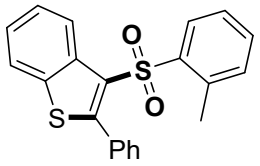
2-phenyl-3-(phenylsulfonyl)benzo[*b*]thiophene (3q)



3q

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3q** as a yellow solid (52.5mg, 75% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.64 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.9 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.48 – 7.38 (m, 7H), 7.33 (t, J = 7.7 Hz, 2H).^{13}C NMR (151 MHz, CDCl3) δ 152.9, 142.3, 138.1, 136.2, 132.9, 131.5, 130.5, 129.9, 129.5, 128.7, 127.7, 126.9, 126.0, 125.6, 124.6, 121.7.

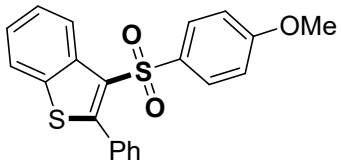
2-phenyl-3-(*o*-tolylsulfonyl)benzo[*b*]thiophene (3r)



3r

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3r** as a yellow solid (58.2mg, 80% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.53 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.48 (dd, J = 8.0, 1.3 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.38 – 7.33 (m, 1H), 7.24 (t, J = 7.3 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.16 (d, J = 7.6 Hz, 2H), 6.96 (d, J = 7.5 Hz, 1H), 6.88 (t, J = 7.7 Hz, 1H), 2.10 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 150.8, 138.9, 136.8, 136.4, 135.7, 131.7, 130.9, 130.1, 129.3, 128.6, 128.3, 127.5, 126.6, 126.6, 124.8, 124.4, 123.8, 120.7, 18.5.

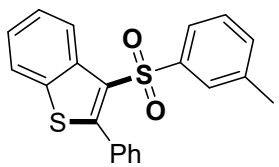
3-((4-methoxyphenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (3s)



3s

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3s** as a yellow solid (62.3mg, 82% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.63 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.48 – 7.37 (m, 6H), 6.81 – 6.75 (m, 2H), 3.77 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 163.1, 152.0, 138.1, 136.1, 134.0, 131.8, 130.7, 130.5, 129.4, 129.2, 127.6, 125.9, 125.5, 124.6, 121.7, 114.0, 55.6.

2-phenyl-3-(*m*-tolylsulfonyl)benzo[*b*]thiophene (3t)

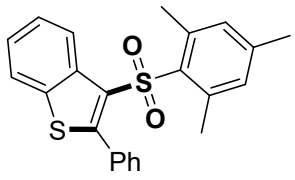


3t

The product purified by flash column chromatography on silica

gel (petroleum ether/ethyl acetate = 15/1) to afford the **3t** as a yellow solid (63.3mg, 87% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.67 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.52 (s, 1H), 7.46 – 7.36 (m, 8H), 7.23 (d, J = 7.9 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 2.25 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 152.6, 142.1, 138.9, 138.1, 136.2, 133.8, 131.6, 130.6, 130.3, 129.5, 128.6, 127.6, 127.4, 126.0, 125.6, 124.7, 124.1, 121.7, 21.2.

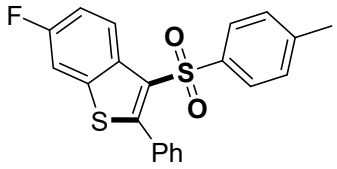
3-(mesitylsulfonyl)-2-phenylbenzo[*b*]thiophene (3u)



3u

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3u** as a yellow solid (57.2mg, 73% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.62 (d, J = 8.3 Hz, 1H), 7.82 (s, 0H), 7.50 (s, 0H), 7.44 (s, 0H), 7.28 (s, 0H), 7.17 (d, J = 6.6 Hz, 4H), 6.63 (s, 2H), 2.22 (s, 6H), 2.18 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 149.7, 142.5, 139.2, 137.8, 136.7, 136.3, 132.9, 131.5, 131.2, 129.7, 129.0, 127.5, 125.8, 125.3, 124.9, 121.7, 21.9.

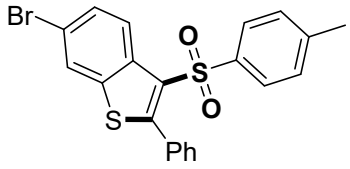
6-fluoro-2-phenyl-3-tosylbenzo[*b*]thiophene (3v)



3v

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3v** as a yellow solid (68mg, 89% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.61 (dd, J = 9.1, 5.1 Hz, 1H), 7.53 – 7.44 (m, 4H), 7.40 (d, J = 4.4 Hz, 4H), 7.30 – 7.26 (m, 1H), 7.12 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 161.6, 160.0, 152.0, 144.0, 139.2, 130.5, 129.6, 129.4, 127.7, 127.0, 126.1 (d, J = 8.8 Hz), 114.9 (d, J = 23.9 Hz), 107.9 (d, J = 25.1 Hz), 21.5.

6-bromo-2-phenyl-3-tosylbenzo[*b*]thiophene (3w)

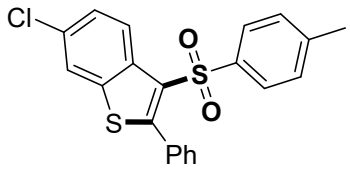


3w

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford

the **3w** as a yellow solid (75.1mg, 85% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.51 (d, J = 8.8 Hz, 1H), 7.95 (d, J = 1.8 Hz, 1H), 7.62 (dd, J = 8.9, 1.9 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.40 (d, J = 4.4 Hz, 4H), 7.26 (s, 1H), 7.12 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 152.7, 144.1, 139.4, 139.1, 135.0, 131.1, 130.5, 130.3, 129.7, 129.4, 129.4, 127.7, 127.0, 125.8, 124.2, 119.7, 21.5.

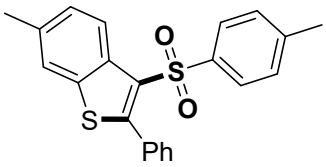
6-chloro-2-phenyl-3-tosylbenzo[*b*]thiophene (3x)



3x

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3x** as a yellow solid (64.5mg, 81% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.57 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 2.0 Hz, 1H), 7.52 – 7.45 (m, 4H), 7.40 (d, J = 4.4 Hz, 4H), 7.12 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 152.7, 144.1, 139.1, 139.1, 134.6, 131.9, 131.2, 130.5, 130.3, 129.6, 129.4, 127.7, 127.0, 126.8, 125.6, 121.3, 21.5.

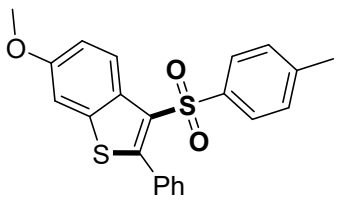
6-methyl-2-phenyl-3-tosylbenzo[*b*]thiophene (3y)



3y

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3y** as a yellow solid (63.5 mg, 84% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.48 (d, J = 8.5 Hz, 1H), 7.57 (s, 1H), 7.53 (d, J = 7.9 Hz, 2H), 7.47 – 7.36 (m, 5H), 7.33 (d, J = 8.5 Hz, 1H), 7.11 (d, J = 7.9 Hz, 2H), 2.47 (s, 3H), 2.31 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 151.3, 143.8, 139.5, 138.5, 135.8, 133.9, 131.8, 130.5, 130.0, 129.4, 129.3, 127.6, 127.6, 127.0, 124.2, 121.4, 721.5, 21.4.

6-methoxy-2-phenyl-3-tosylbenzo[*b*]thiophene (3z)

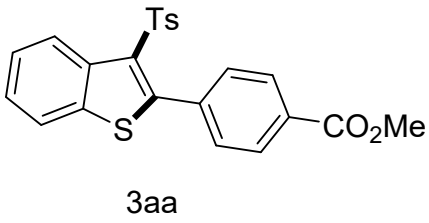


3z

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford

the **3z** as a yellow solid (58 mg, 74% yield).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.49 (d, J = 9.1 Hz, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 7.0 Hz, 1H), 7.43 – 7.37 (m, 4H), 7.24 (d, J = 2.4 Hz, 1H), 7.13 (td, J = 6.8, 3.1 Hz, 3H), 3.87 (s, 3H), 2.33 (s, 3H).^{13}C NMR (151 MHz, CDCl3) δ 158.0, 149.6, 143.8, 139.7, 139.5, 131.8, 130.6, 130.0, 129.9, 129.3, 129.3, 127.6, 127.0, 125.4, 115.8, 104.0, 55.6, 21.5.

Methyl 4-(3-tosylbenzo[*b*]thiophen-2-yl)benzoate (3aa)



3aa

The product purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the **3aa** as a yellow solid (43 mg, 51% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.49 (m, 5H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 3.98 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.58 (s), 150.82 (s), 144.20 (s), 139.27 (s), 138.32 (s), 136.45 (s), 135.96 (s), 130.98 (s), 130.63 (s), 129.58 (s), 128.82 (s), 127.02 (s), 126.15 (s), 125.88 (s), 124.69 (s), 121.83 (s), 52.38 (s), 21.55 (s).

4. Biological Assays

We assessed the antibacterial activity of the compounds. A preliminary antibacterial activity screening experiment was conducted on 3-sulfonylbenzothiophene derivatives, against the pathogen responsible for *Pectobacterium carotovorum* subsp. *Carotovorum* (Pcc) indicated that some compounds exhibited moderate to excellent inhibitory activity against bacterial growth at a concentration of 100 mg/L. Notably, compounds **3f**, **3r**, and **3y** demonstrated average inhibition rates against *Pectobacterium carotovorum* subsp. *carotovorum* pathogen ranging from 74.20% to 82.65% (**Table S1**). Compound **3f**, which possesses a -Br substituent on the aromatic ring connected to the alkyne and other -Br substituents or substituents at the meta position, did not exhibit prominent antibacterial activity. This might be associated with the position and type of the substituents. Compounds **3r**

and **3y**, which bear methyl groups on the aromatic rings connected to the sulfonyl group and the thiomethyl group, respectively, showed lower antibacterial activity compared to other compounds with methyl groups. This could be related to the position and quantity of the methyl groups in these types of compounds.

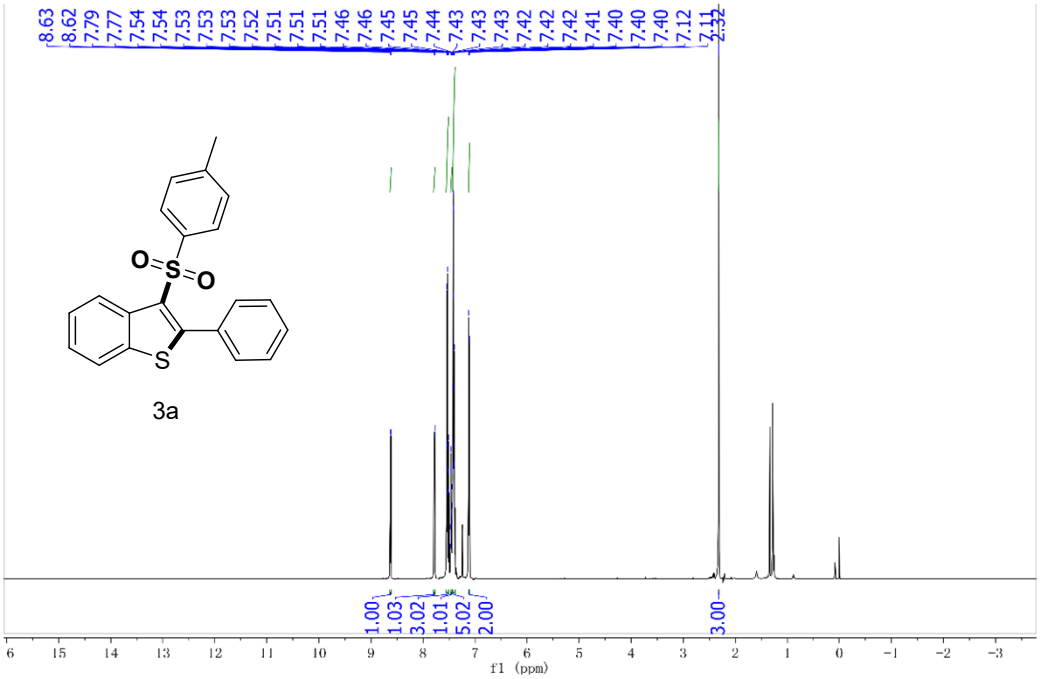
Table S1. Antibacterial activity test results of benzothiophene derivatives against Pcc (inhibitory rate, %)

Compd	Inhibition rate I/%	Compd	Inhibition rate I/%
3a	35.04 ± 1.35	**3o**	5.75 ± 4.55
3b	3.58 ± 3.58	**3p**	36.25 ± 3.97
3c	/	**3q**	/
3d	20.54 ± 1.03	**3r**	74.20 ± 1.37
3e	42.32 ± 2.81	**3s**	/
3f	82.65 ± 1.07	**3t**	12.08 ± 2.15
3g	35.98 ± 2.83	**3u**	44.35 ± 2.25
3h	11.68 ± 4.14	**3v**	/
3i	/	**3w**	/
3j	24.28 ± 3.15	**3x**	33.03 ± 2.37
3k	26.29 ± 1.79	**3y**	80.33 ± 0.82
3l	48.27 ± 3.29	**3z**	/
3m	/	**kasugamycin**	95.69 ± 0.28
3n	/	**CK**	--

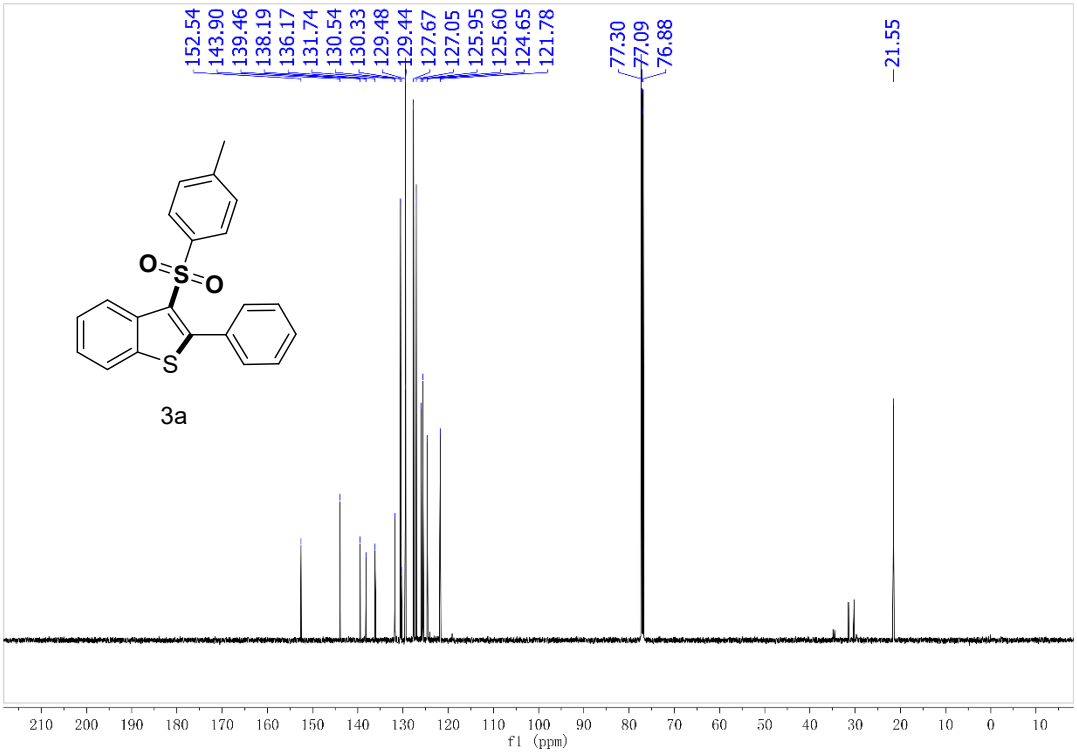
"/": The compound has no bacteriostatic activity at all or the error is too large, which is not statistically significant.

5. NMR spectra of compounds

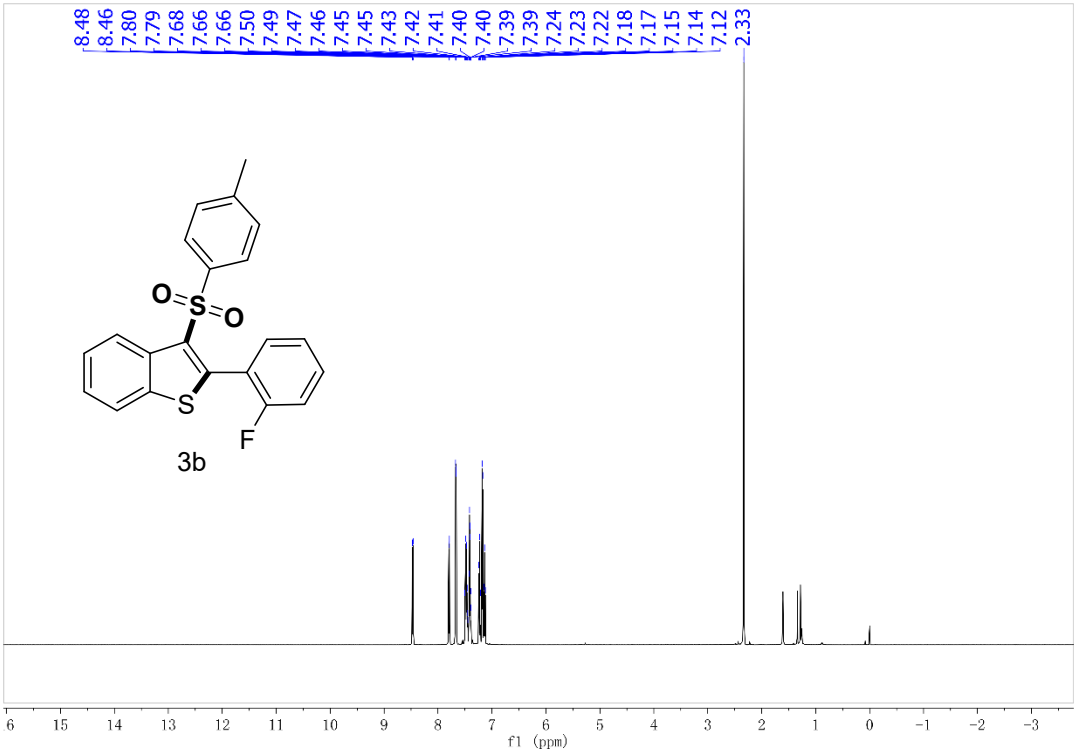
^{1}H NMR of **3a** in Chloroform-*d* (600 MHz, Chloroform-*d*)



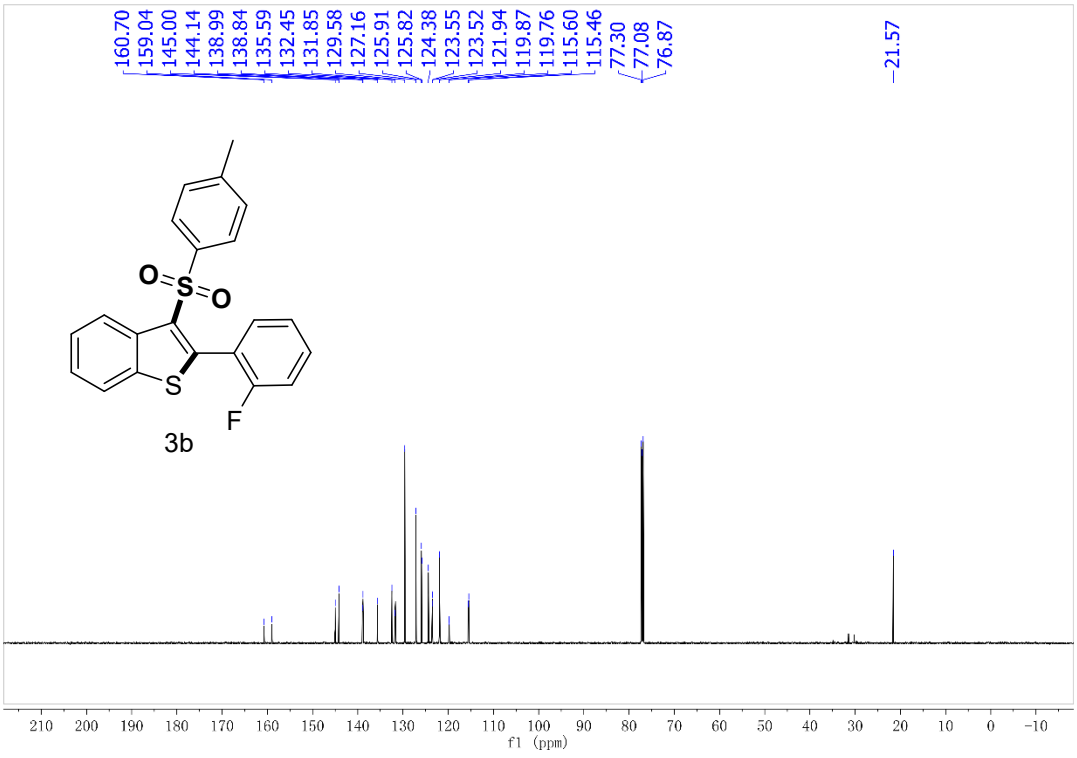
^{13}C NMR of **3a** in $CDCl_3$ (151 MHz, $CDCl_3$)



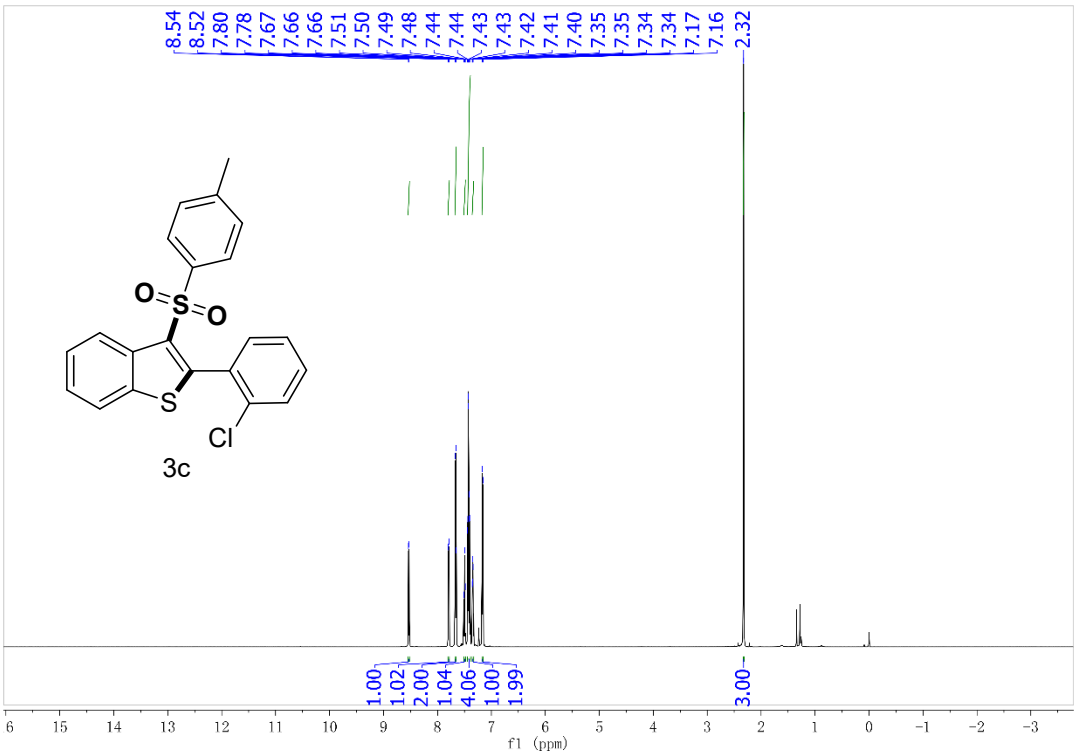
^{1}H NMR of **3b** in Chloroform-*d* (600 MHz, Chloroform-*d*)



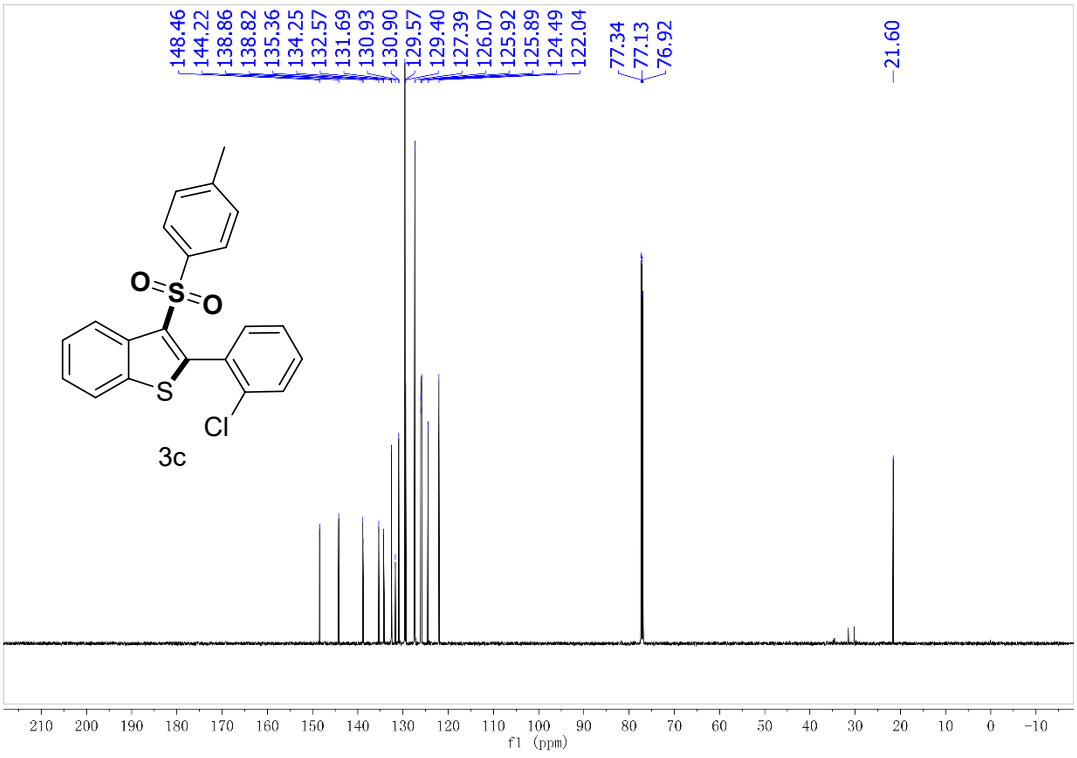
^{13}C NMR of **3b** in $CDCl_3$ (151 MHz, $CDCl_3$)



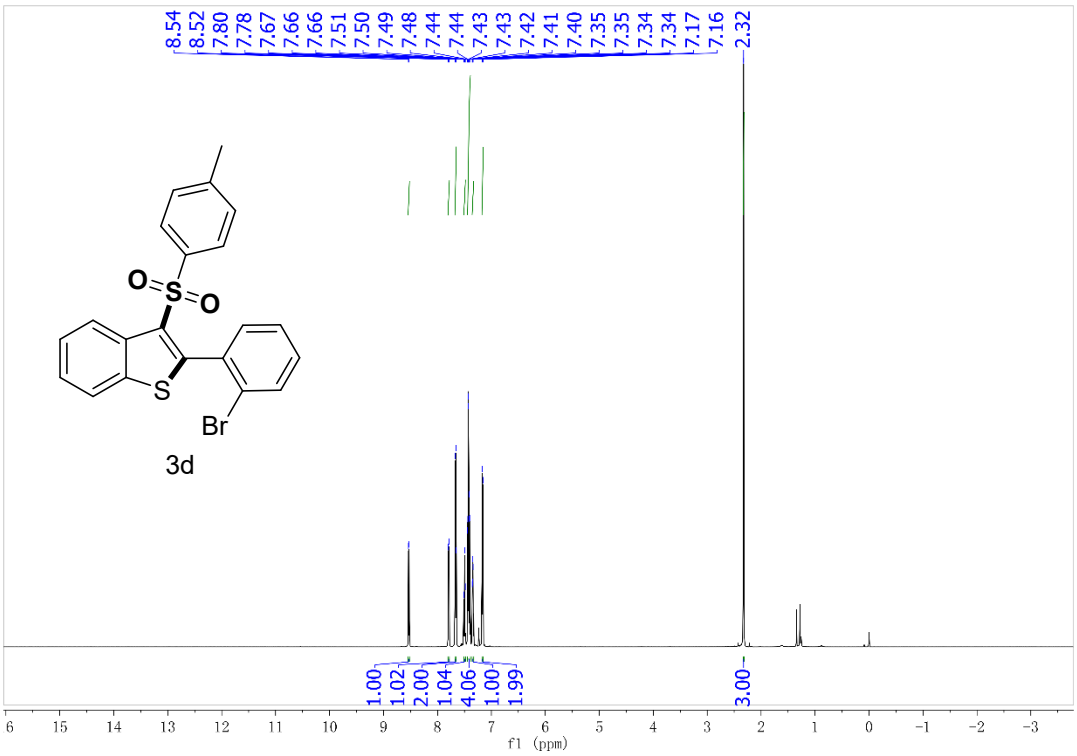
^{1}H NMR of **3c** in Chloroform-*d* (600 MHz, Chloroform-*d*)



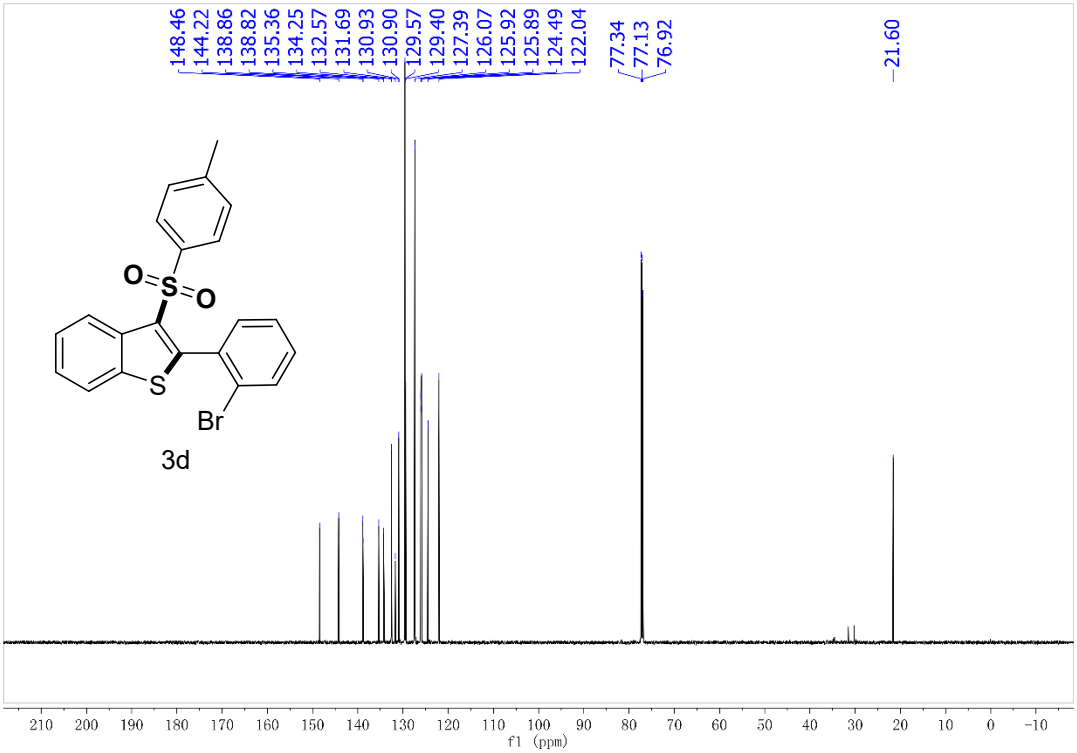
^{13}C NMR of **3c** in CDCl3 (151 MHz, $CDCl_3$)



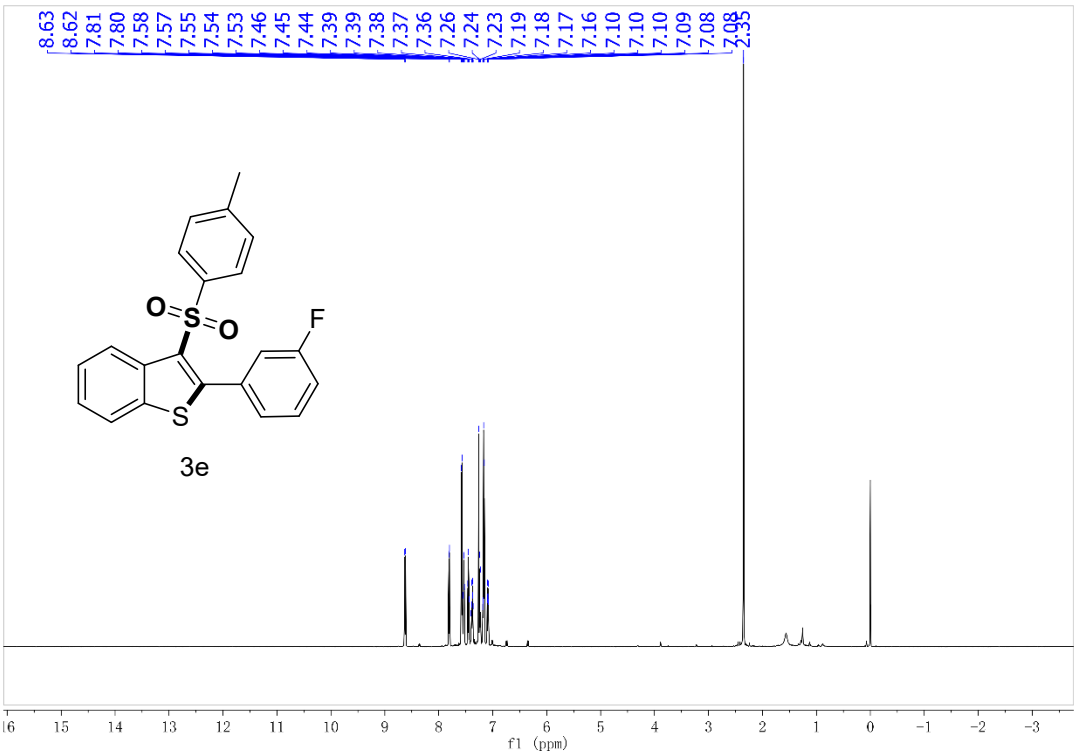
^{1}H NMR of **3d** in Chloroform-*d* (600 MHz, Chloroform-*d*)



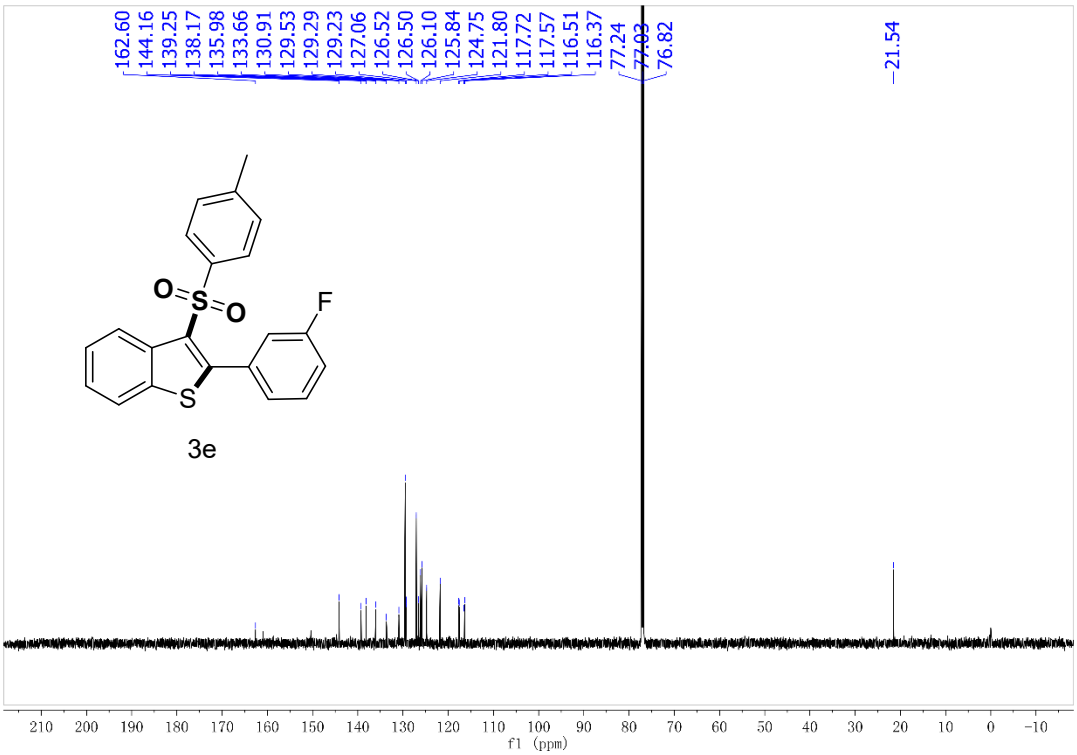
^{13}C NMR of **3d** in $CDCl_3$ (151 MHz, $CDCl_3$)



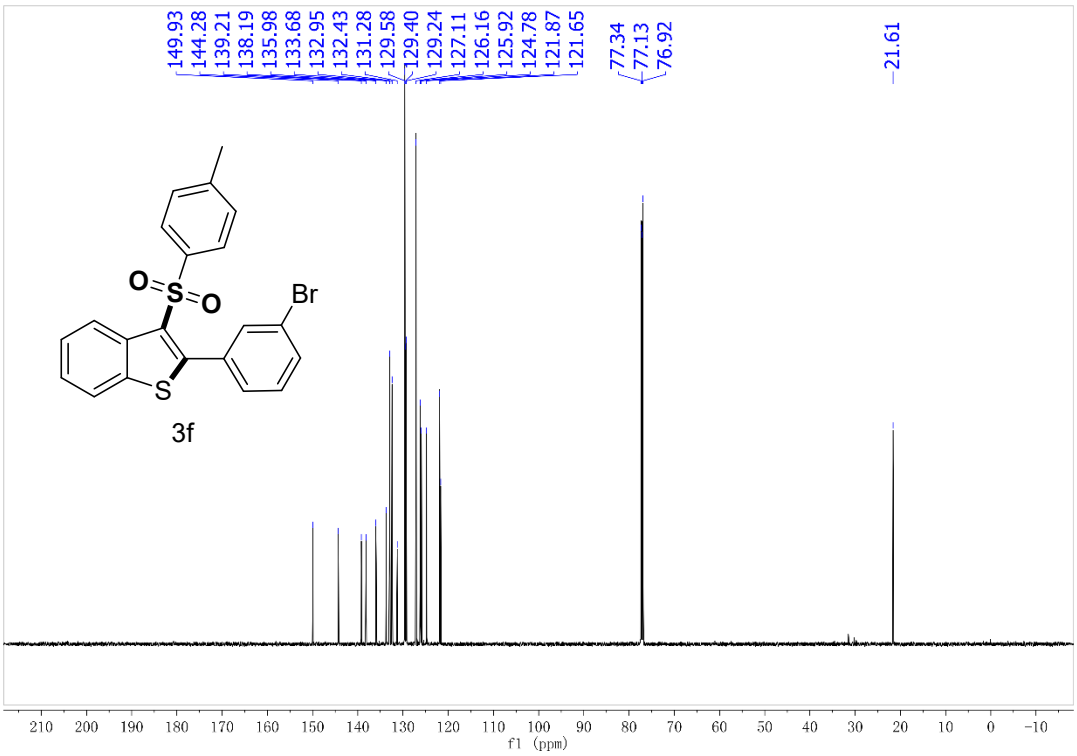
^{1}H NMR of **3e** in Chloroform-*d* (600 MHz, Chloroform-*d*)



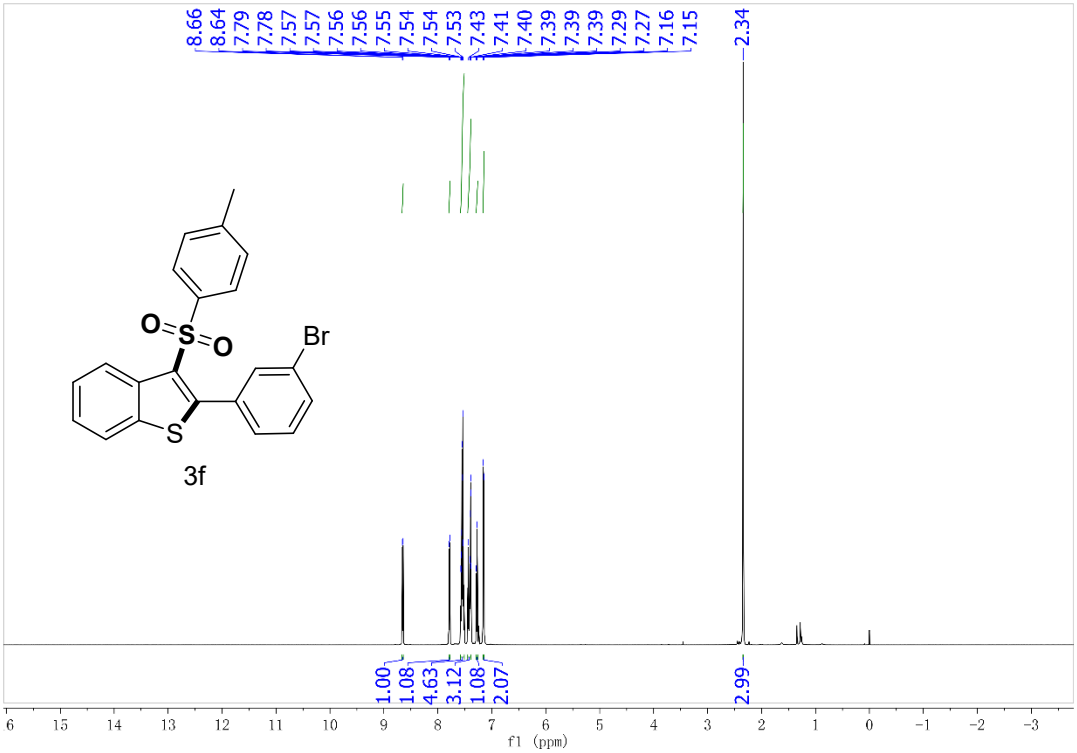
^{13}C NMR of **3e** in $CDCl_3$ (151 MHz, $CDCl_3$)



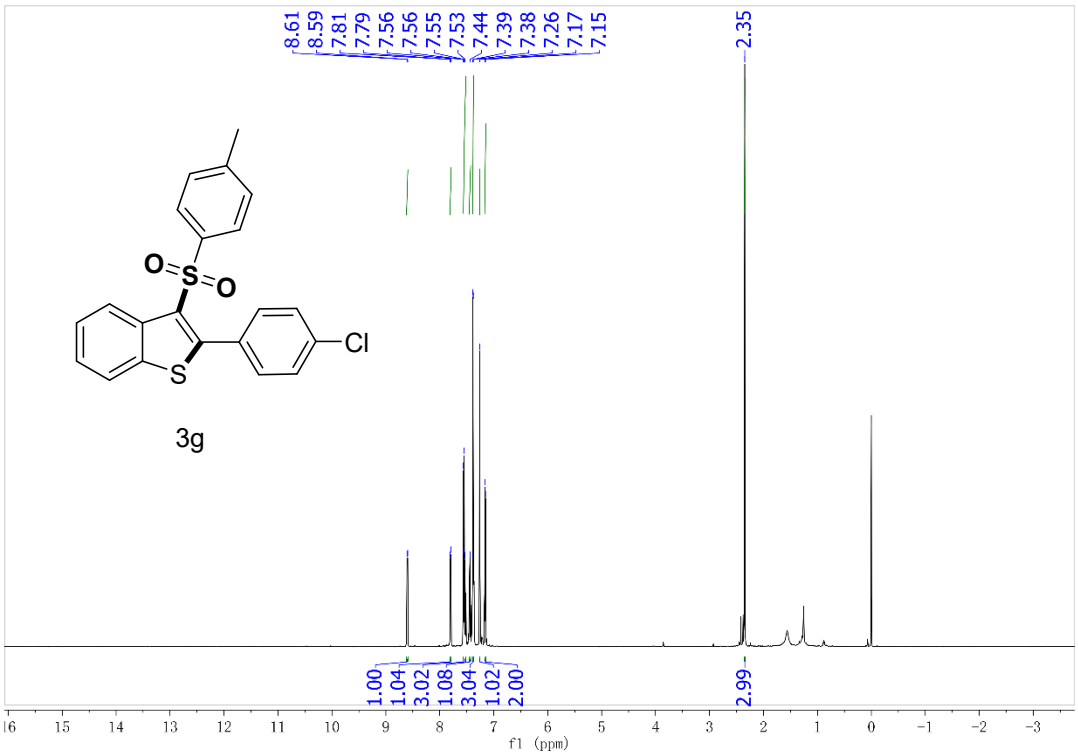
^{1}H NMR of **3f** in Chloroform-*d* (600 MHz, Chloroform-*d*)



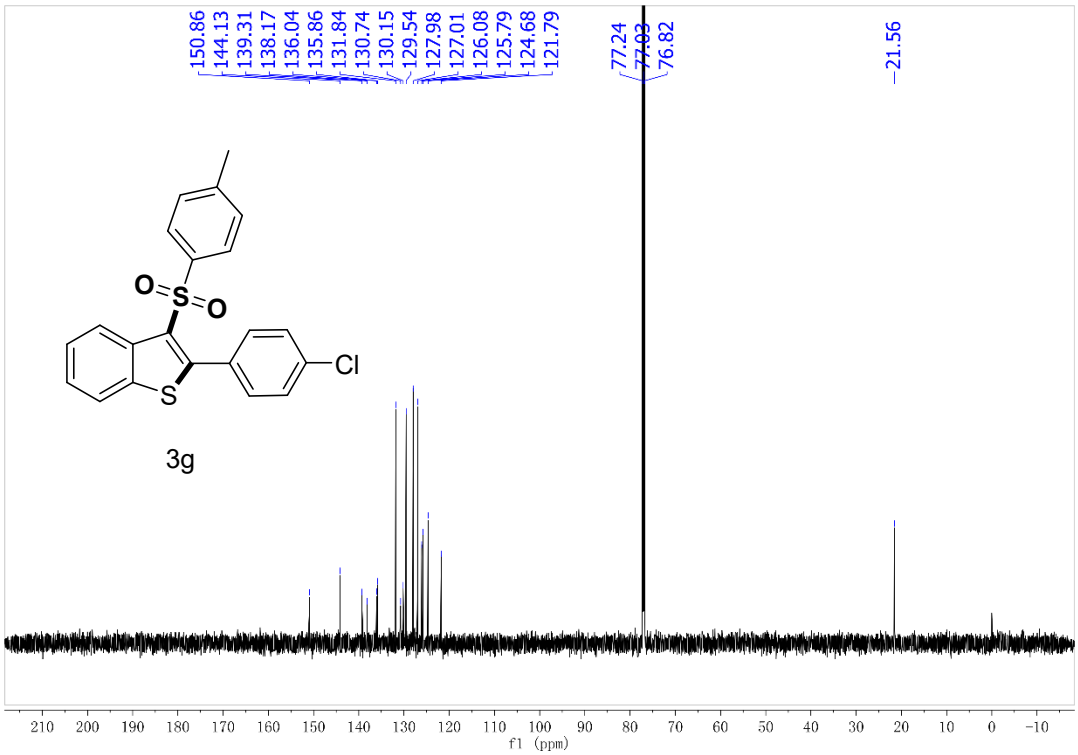
13C NMR of **3f** in $CDCl_3$ (151 MHz, CDCl3)



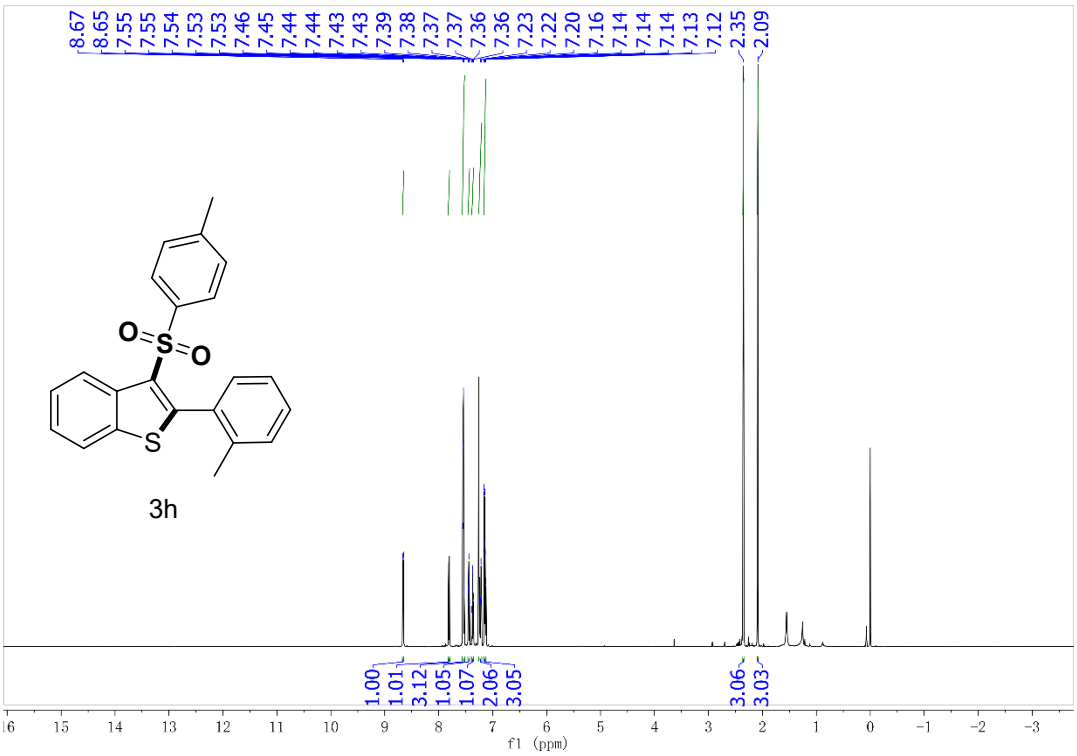
^{1}H NMR of **3g** in Chloroform-*d* (600 MHz, Chloroform-*d*)



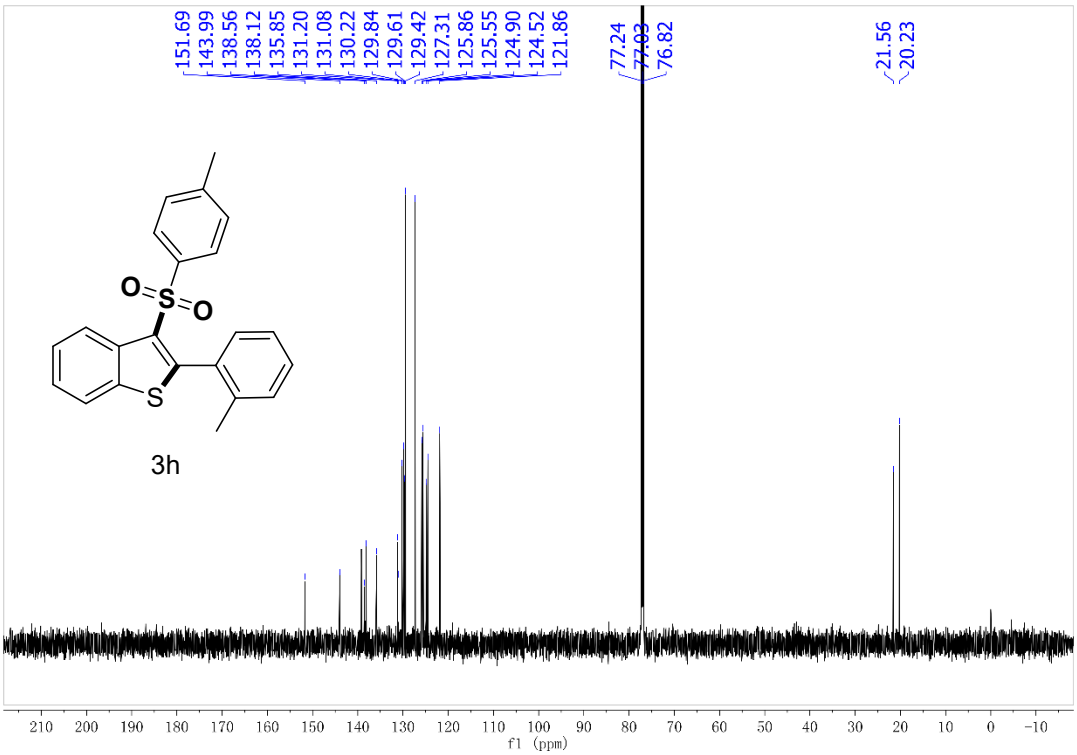
^{13}C NMR of **3g** in $CDCl_3$ (151 MHz, $CDCl_3$)



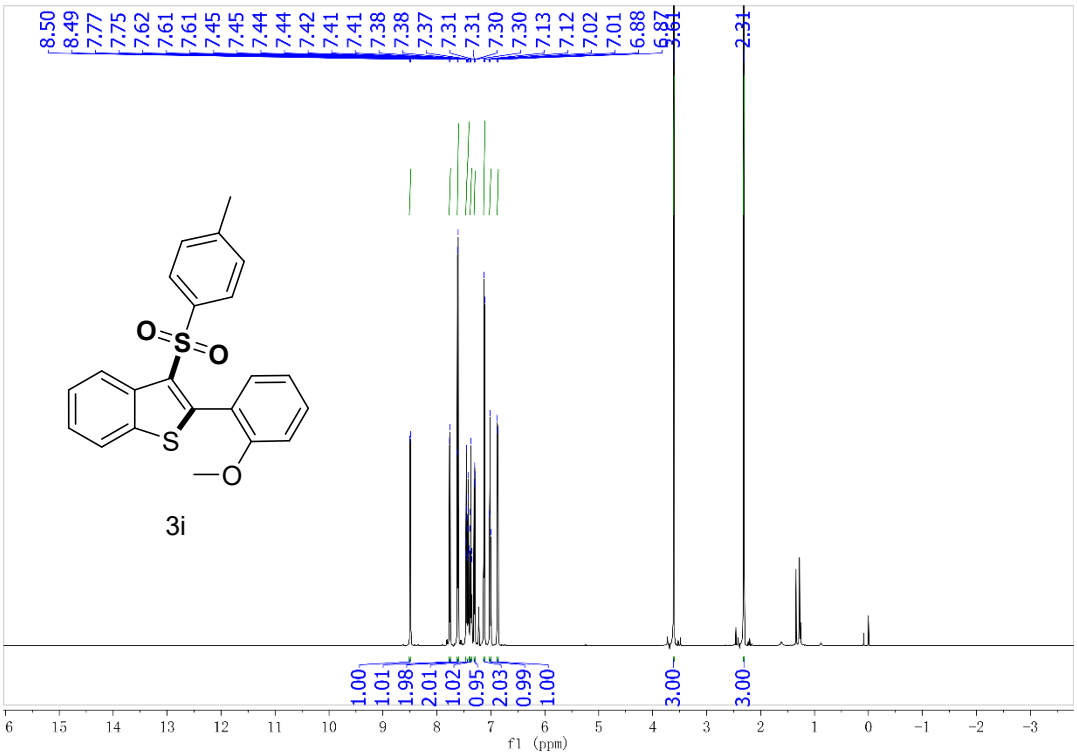
^{1}H NMR of **3h** in Chloroform-*d* (600 MHz, Chloroform-*d*)



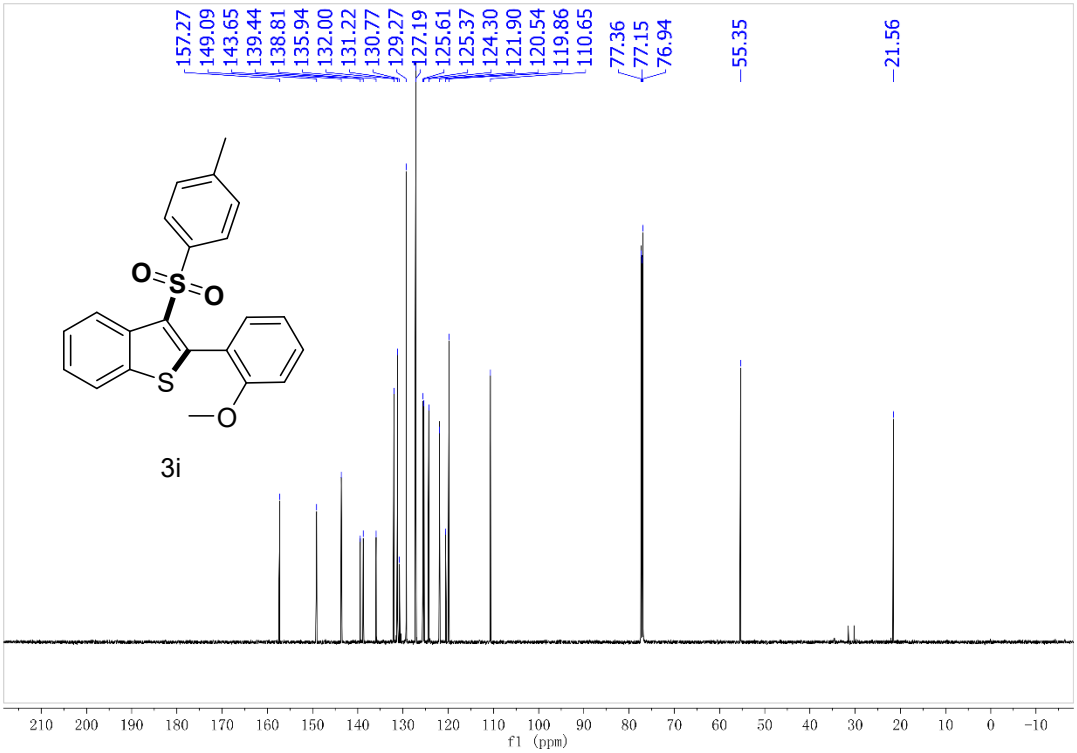
^{13}C NMR of **3h** in $CDCl_3$ (151 MHz, $CDCl_3$)



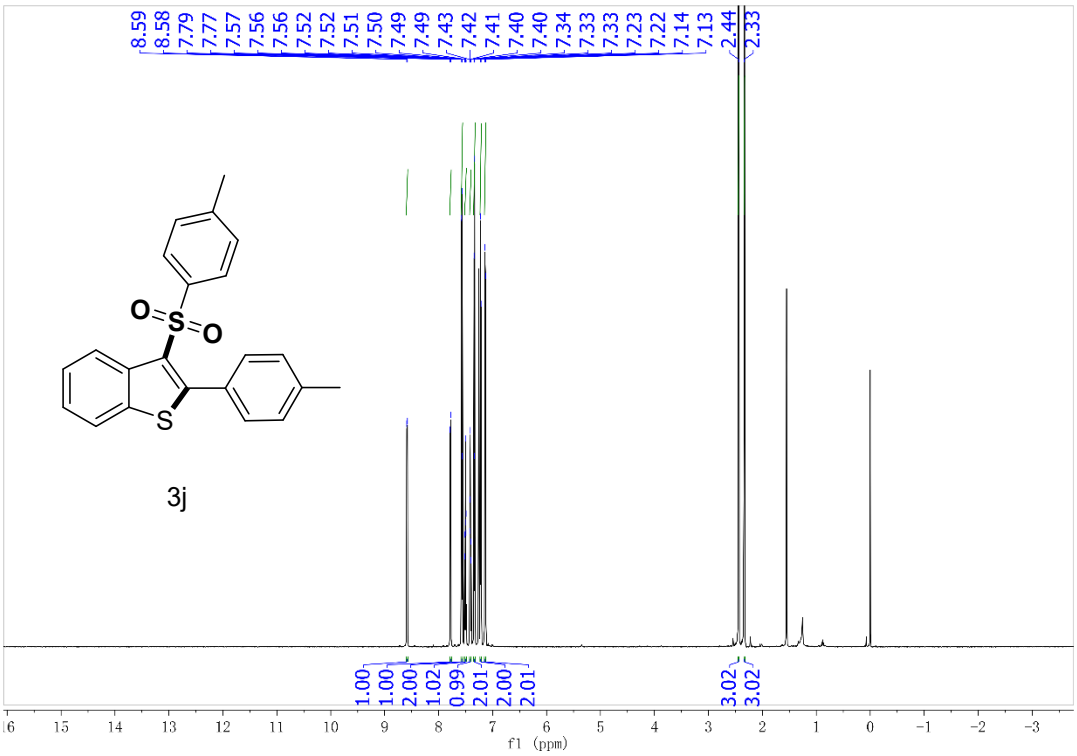
^{1}H NMR of **3i** in Chloroform-*d* (600 MHz, Chloroform-*d*)



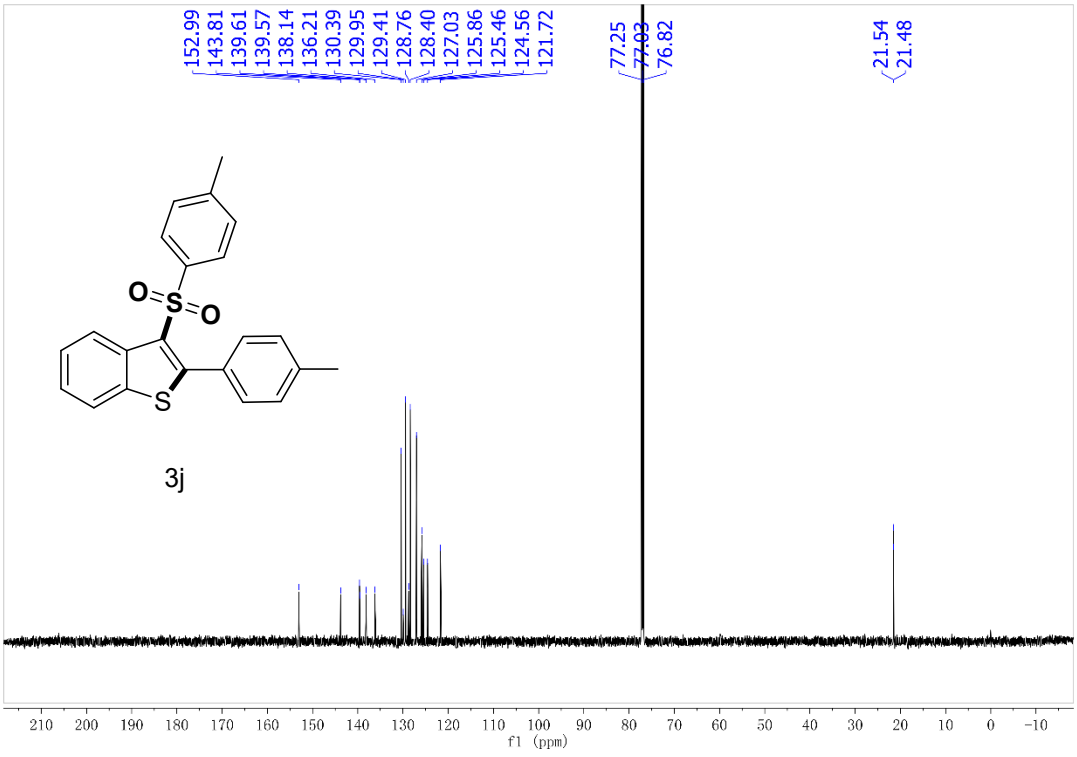
^{13}C NMR of **3i** in $CDCl_3$ (151 MHz, $CDCl_3$)



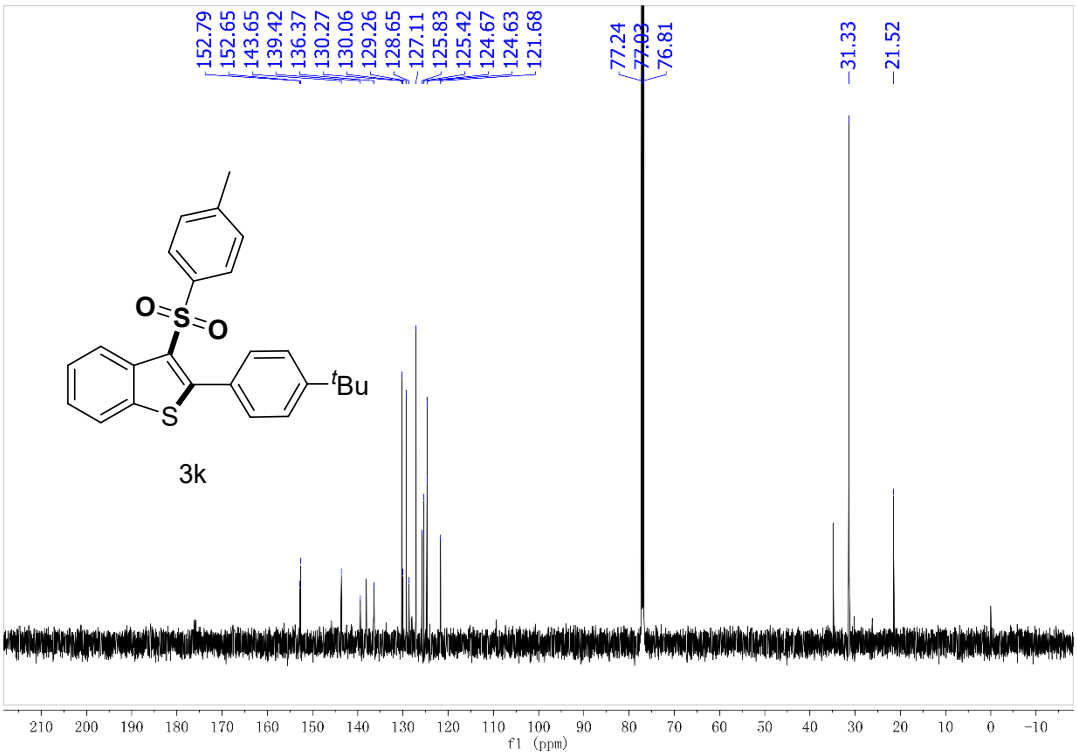
^{1}H NMR of **3j** in Chloroform-*d* (600 MHz, Chloroform-*d*)



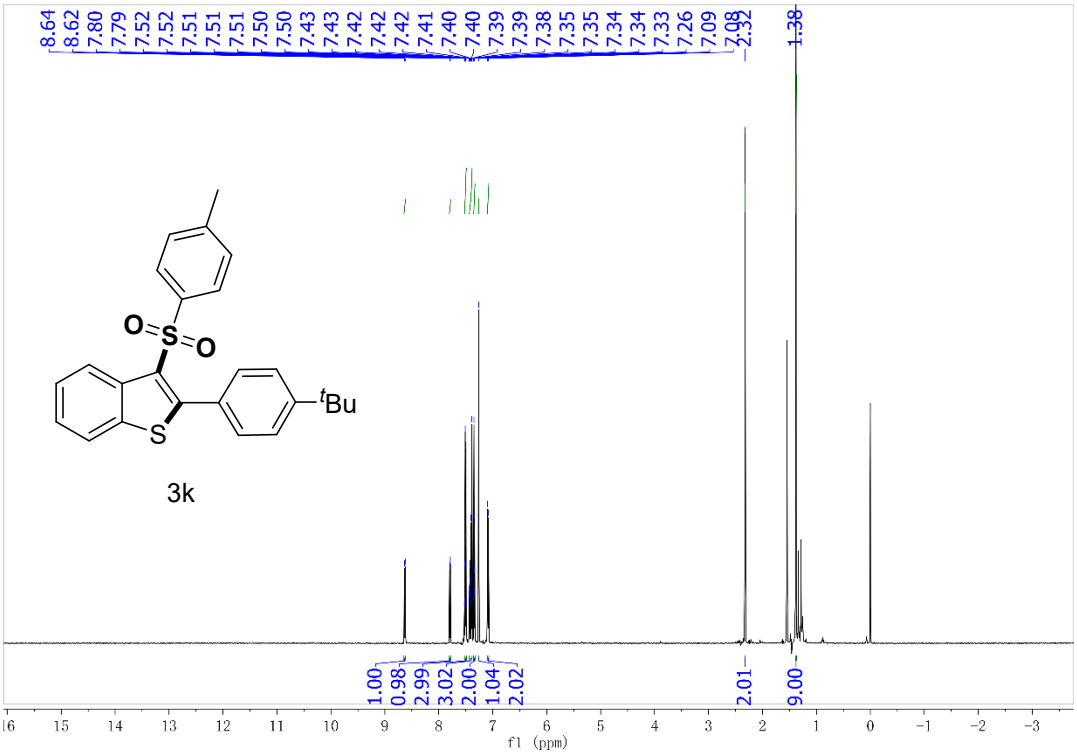
^{13}C NMR of **3j** in $CDCl_3$ (151 MHz, $CDCl_3$)



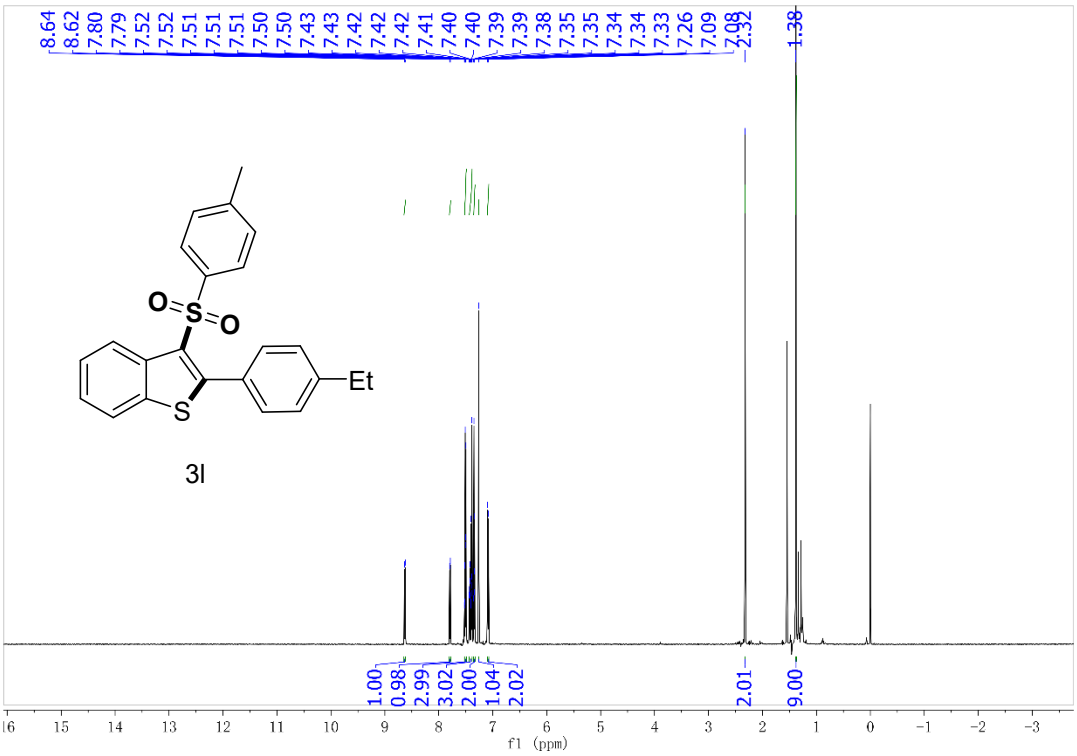
^{1}H NMR of **3k** in Chloroform-*d* (600 MHz, Chloroform-*d*)



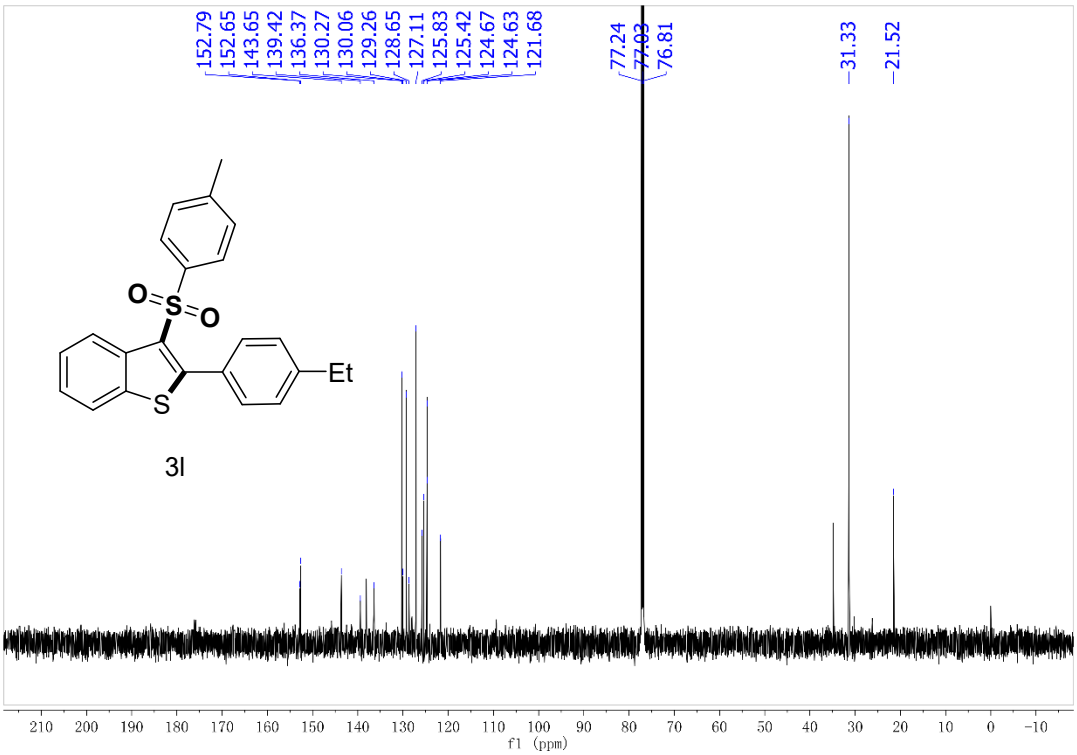
^{13}C NMR of **3k** in $CDCl_3$ (151 MHz, $CDCl_3$)



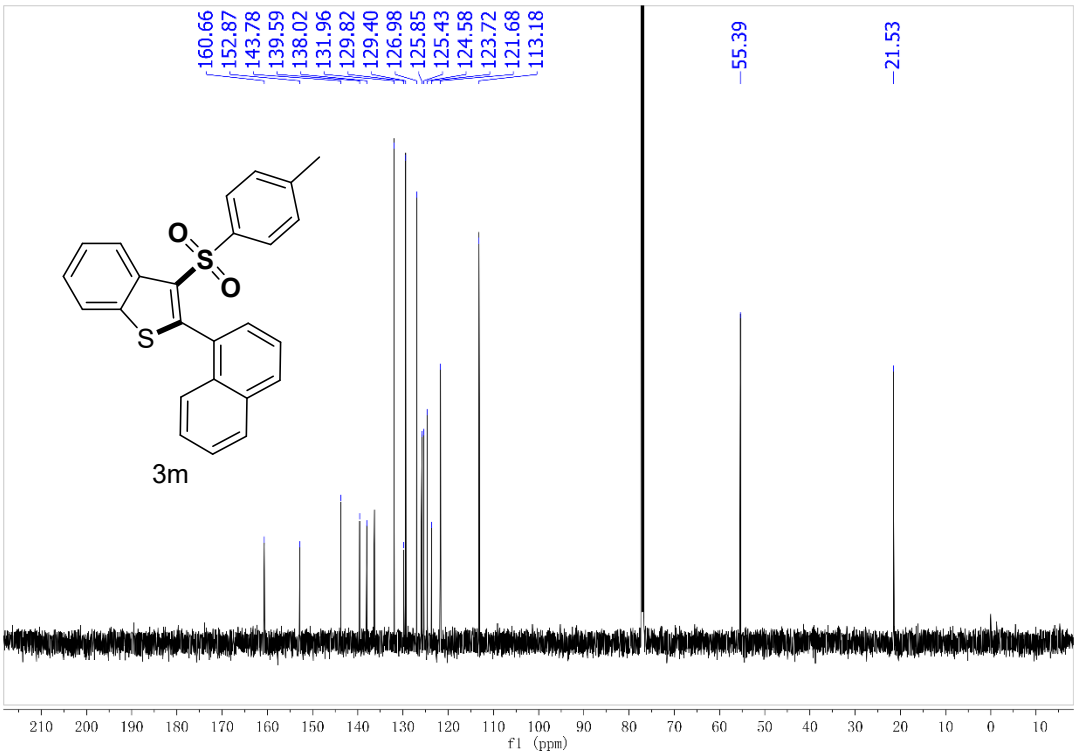
^{1}H NMR of **3l** in Chloroform-*d* (600 MHz, Chloroform-*d*)



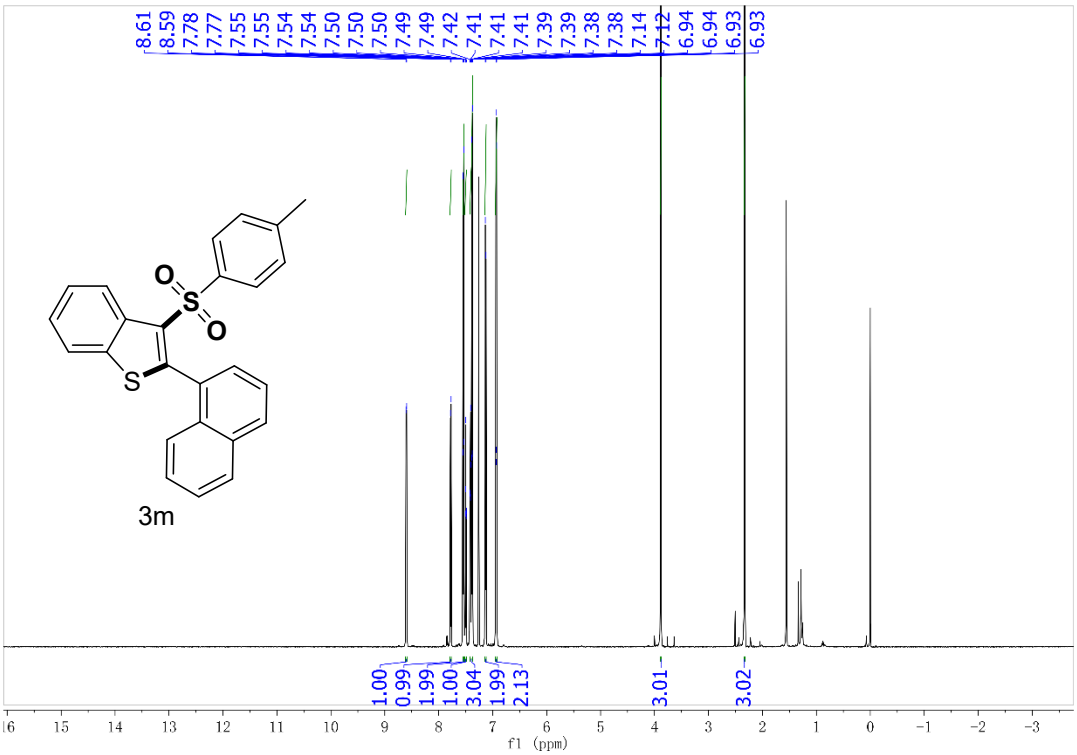
^{13}C NMR of **3l** in $CDCl_3$ (151 MHz, $CDCl_3$)



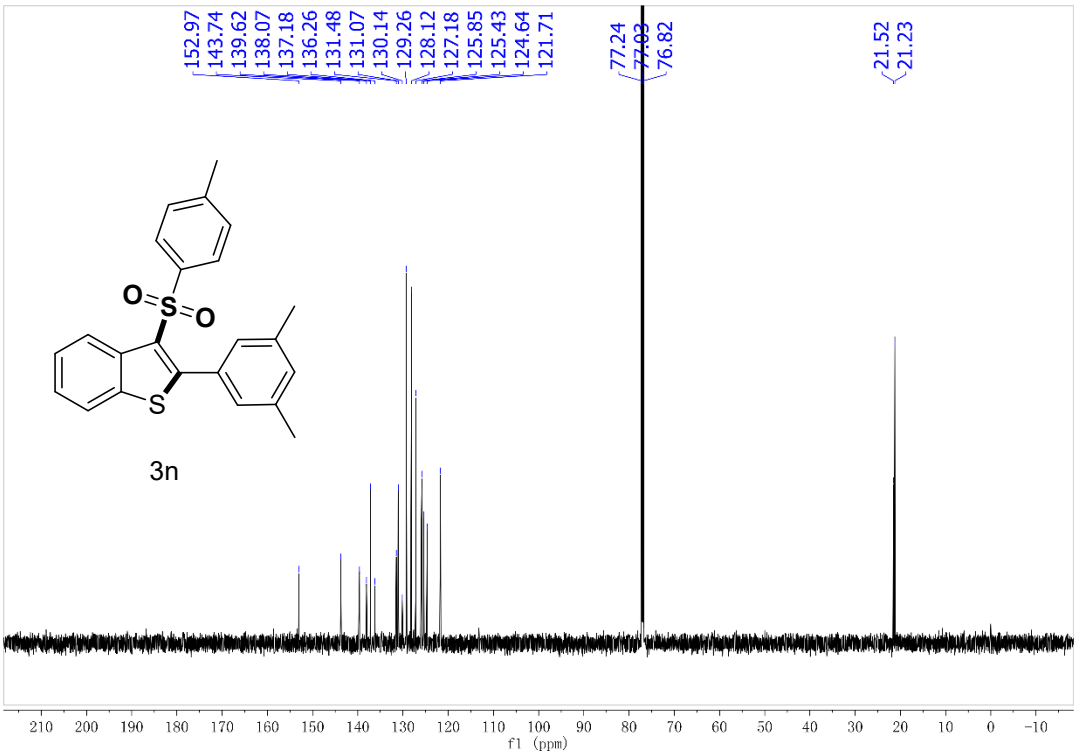
^{1}H NMR of **3m** in Chloroform-*d* (600 MHz, Chloroform-*d*)



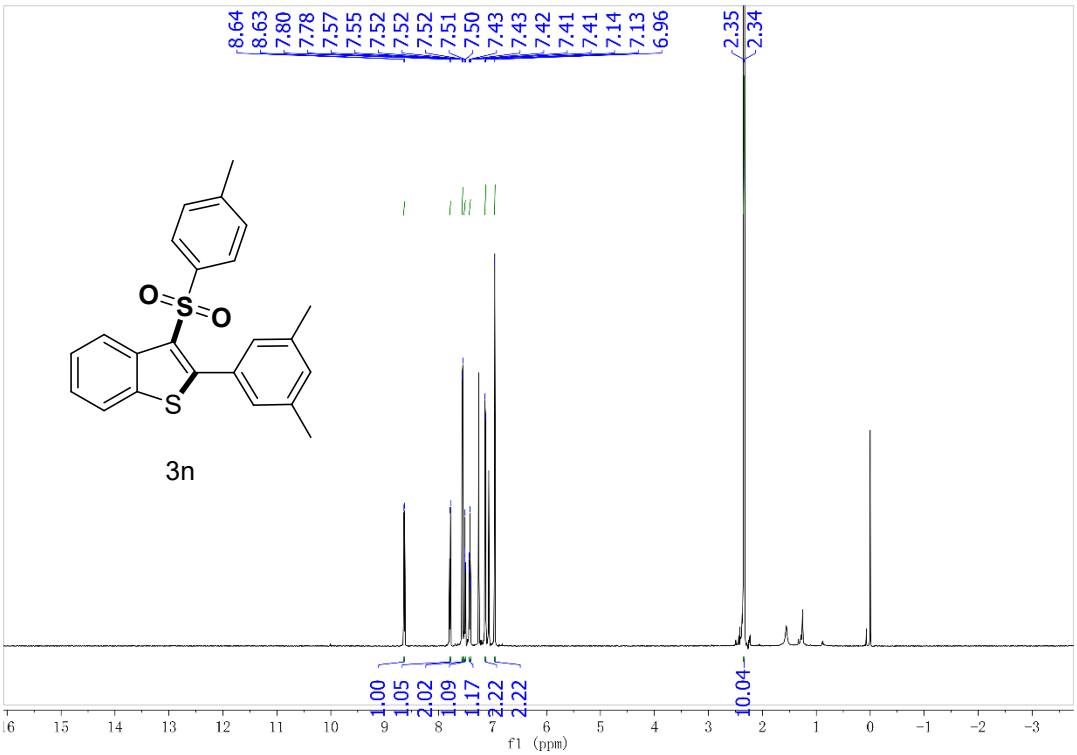
^{13}C NMR of **3m** in $CDCl_3$ (151 MHz, $CDCl_3$)



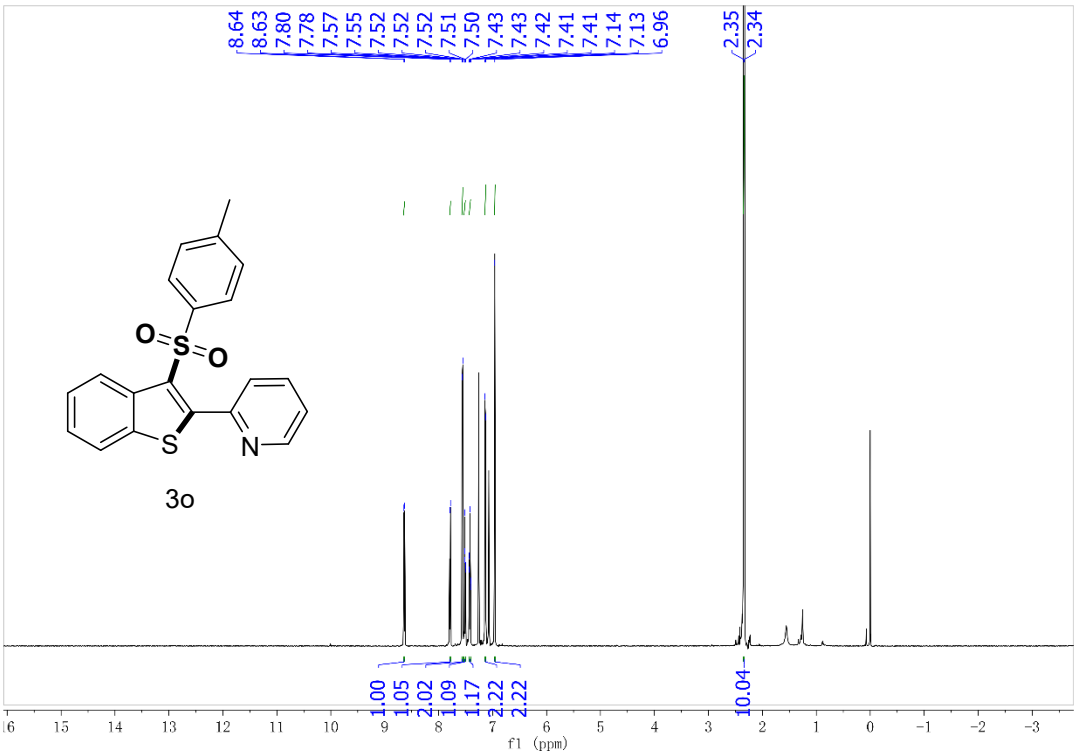
^{1}H NMR of **3n** in Chloroform-*d* (600 MHz, Chloroform-*d*)



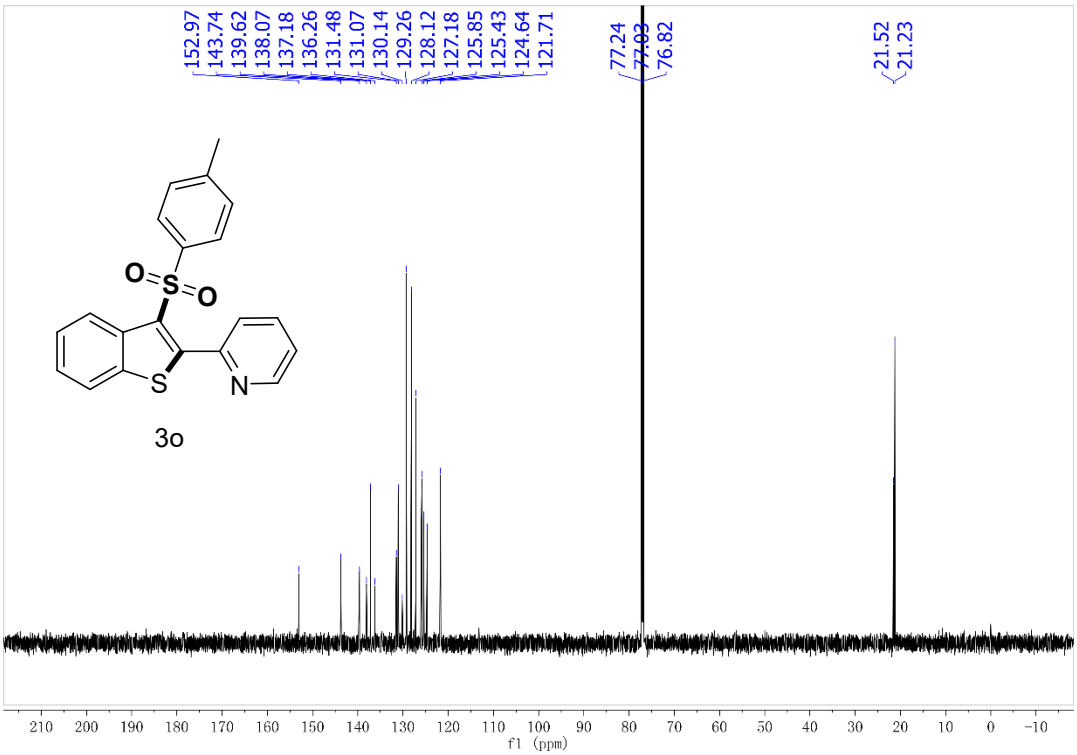
^{13}C NMR of **3n** in $CDCl_3$ (151 MHz, $CDCl_3$)



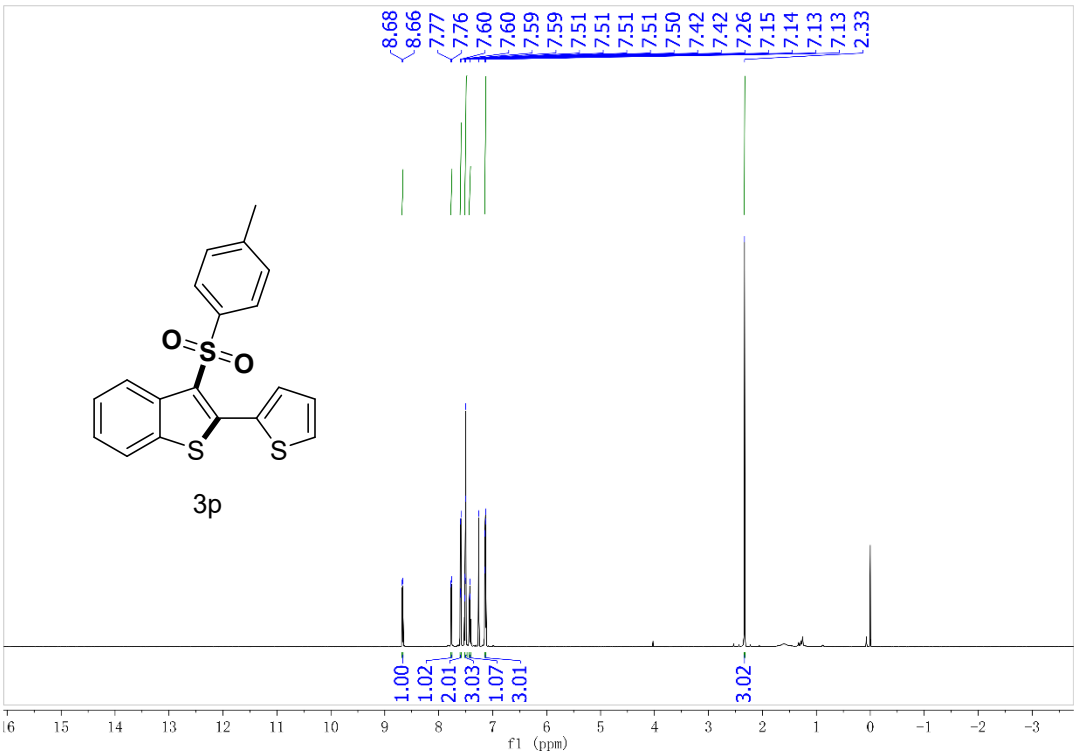
^{1}H NMR of **3o** in Chloroform-*d* (600 MHz, Chloroform-*d*)



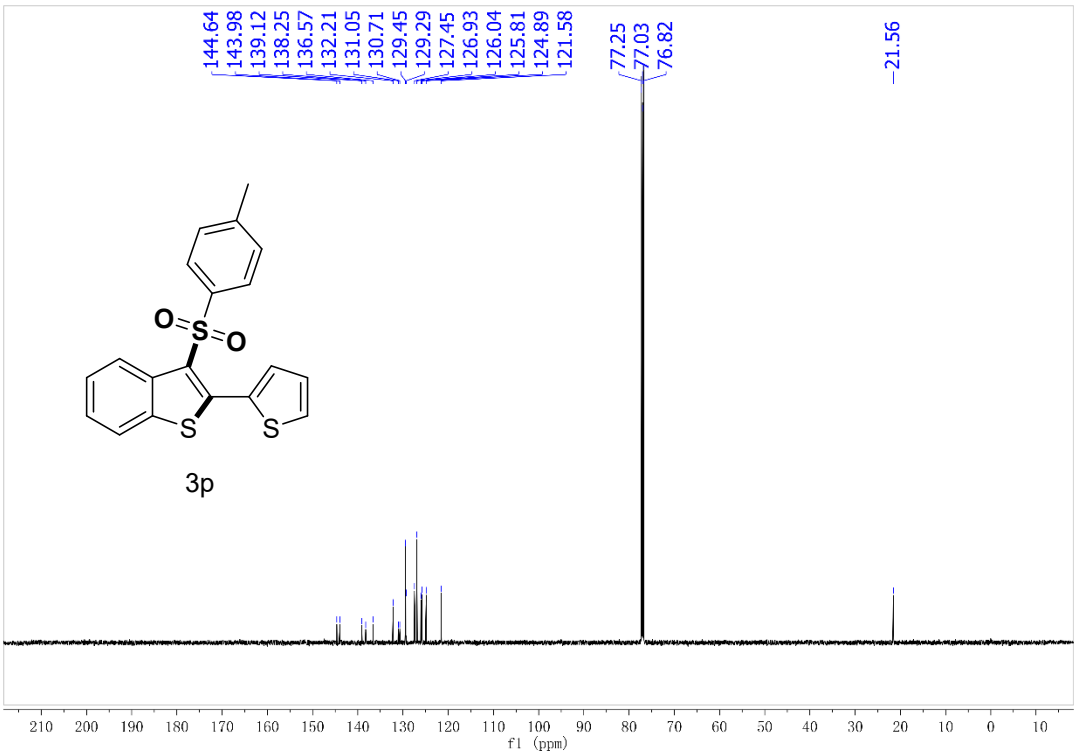
^{13}C NMR of **3o** in $CDCl_3$ (151 MHz, $CDCl_3$)



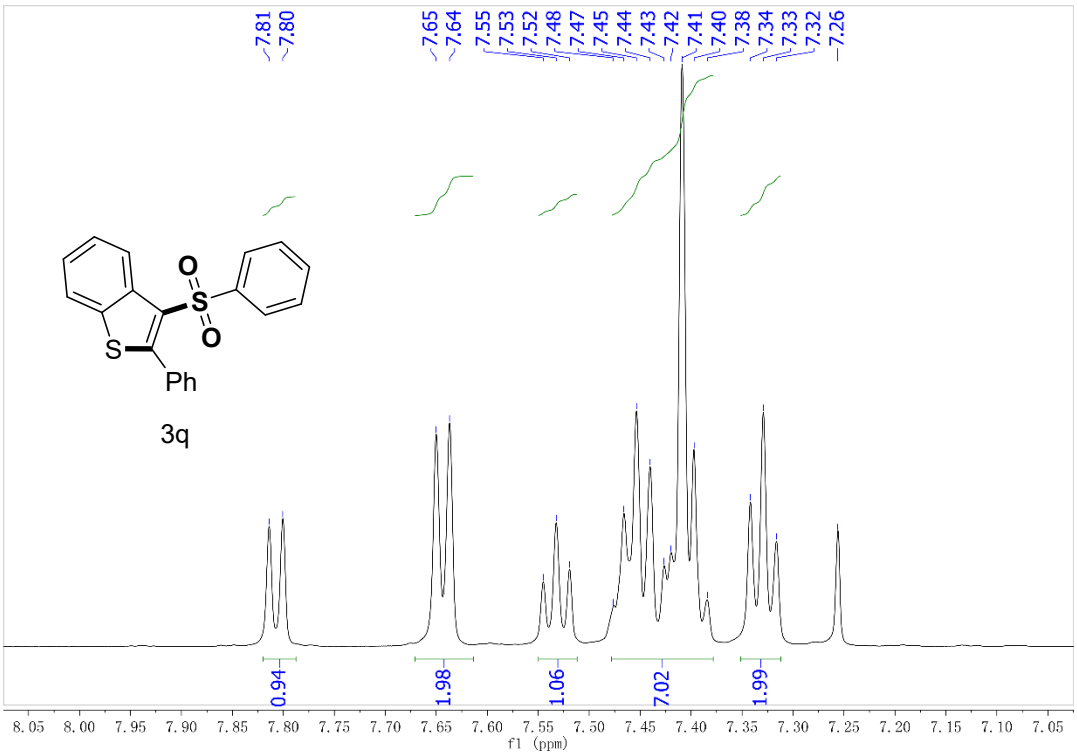
^{1}H NMR of **3p** in Chloroform-*d* (600 MHz, Chloroform-*d*)



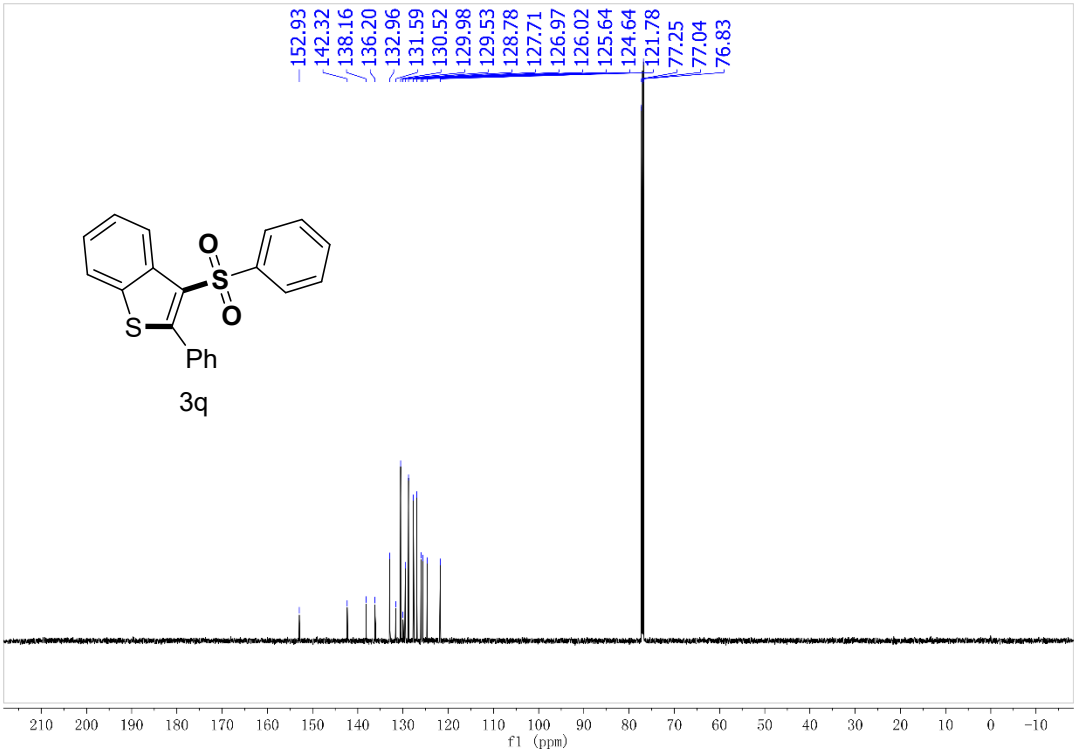
^{13}C NMR of **3p** in $CDCl_3$ (151 MHz, $CDCl_3$)



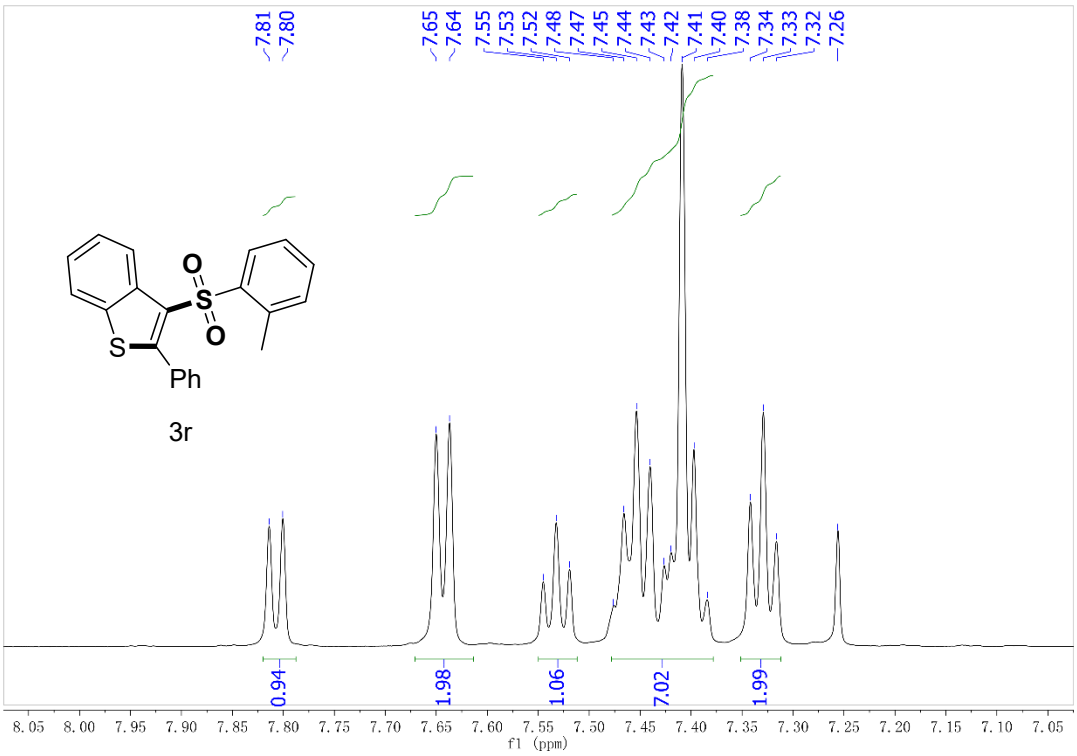
^{1}H NMR of **3q** in Chloroform-*d* (600 MHz, Chloroform-*d*)



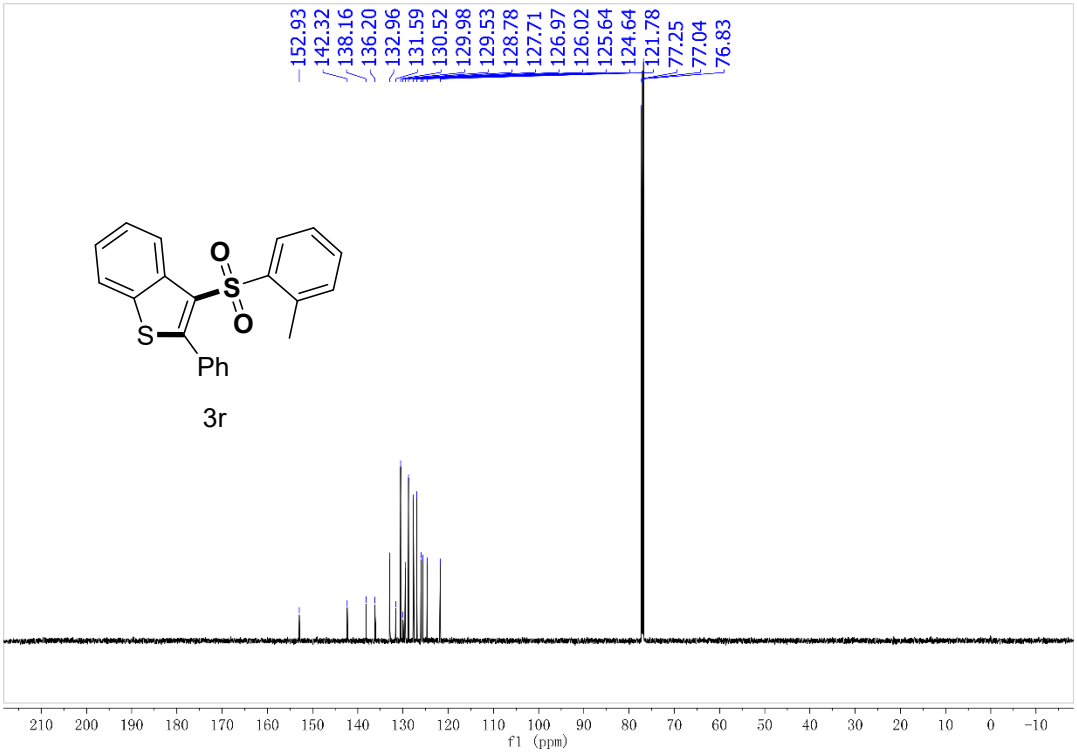
^{13}C NMR of **3q** in $CDCl_3$ (151 MHz, $CDCl_3$)



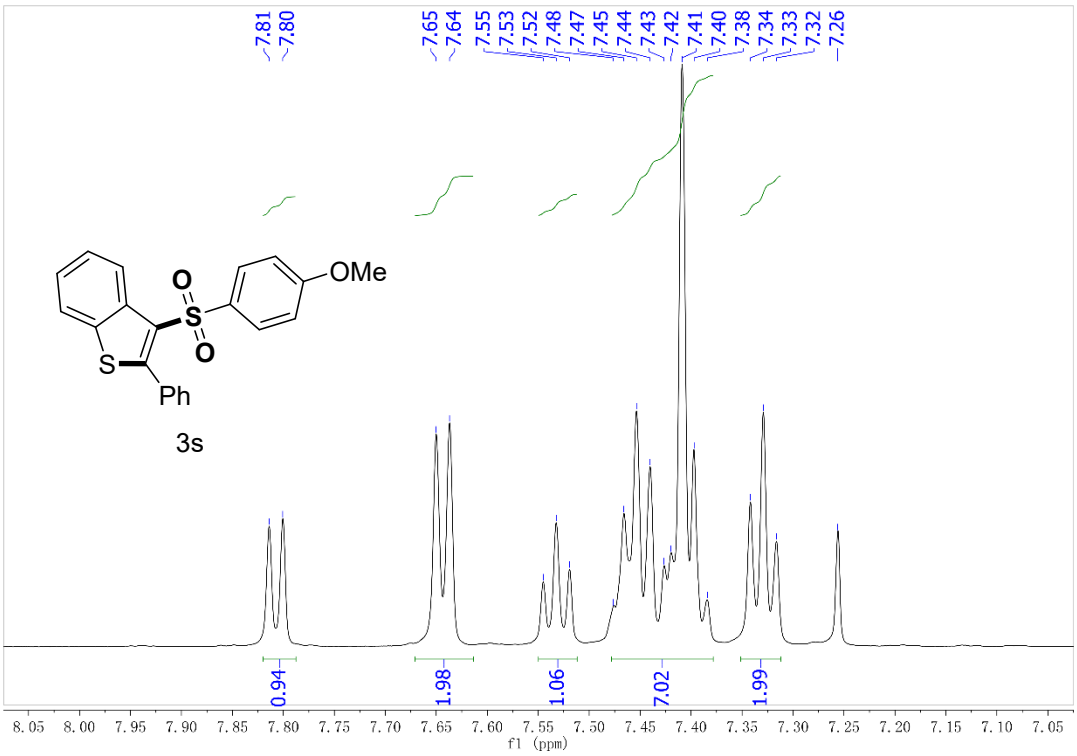
^{1}H NMR of **3r** in Chloroform-*d* (600 MHz, Chloroform-*d*)



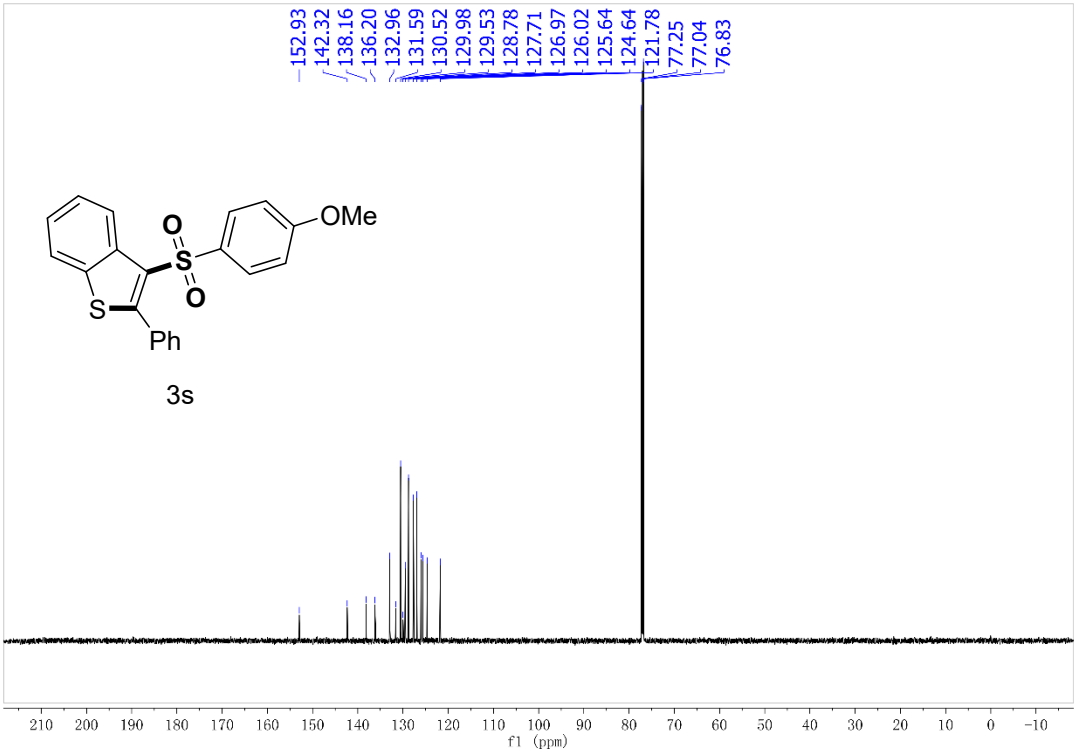
^{13}C NMR of **3r**in $CDCl_3$ (151 MHz, $CDCl_3$)



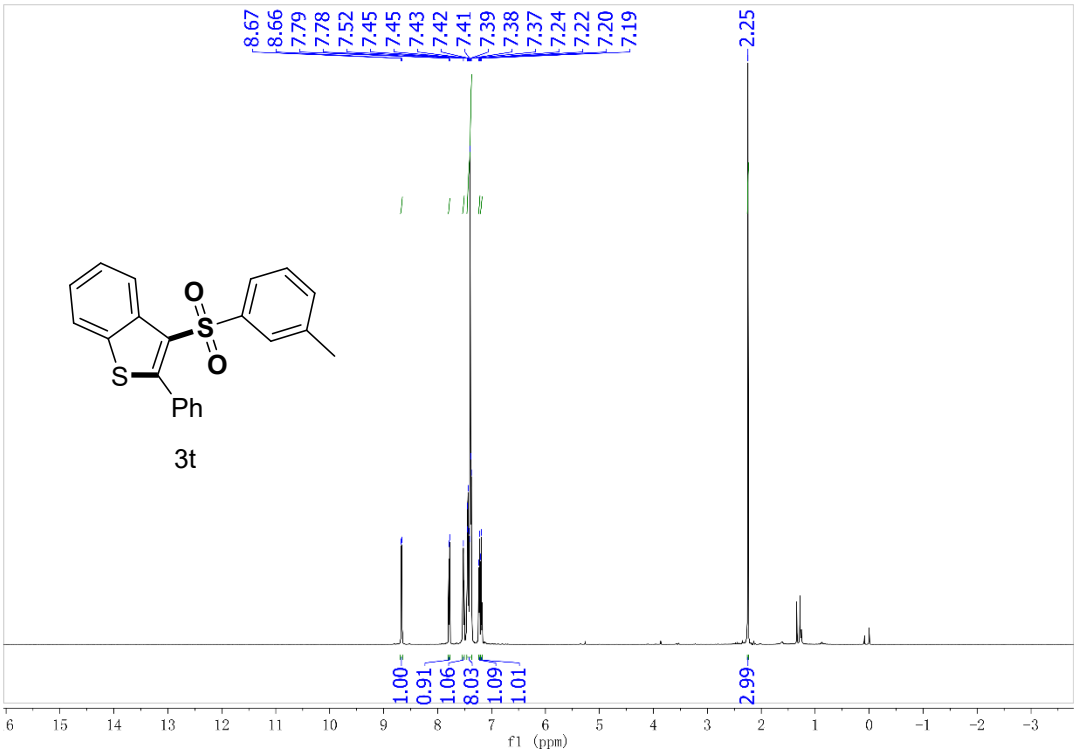
^{1}H NMR of **3s** in Chloroform-*d* (600 MHz, Chloroform-*d*)



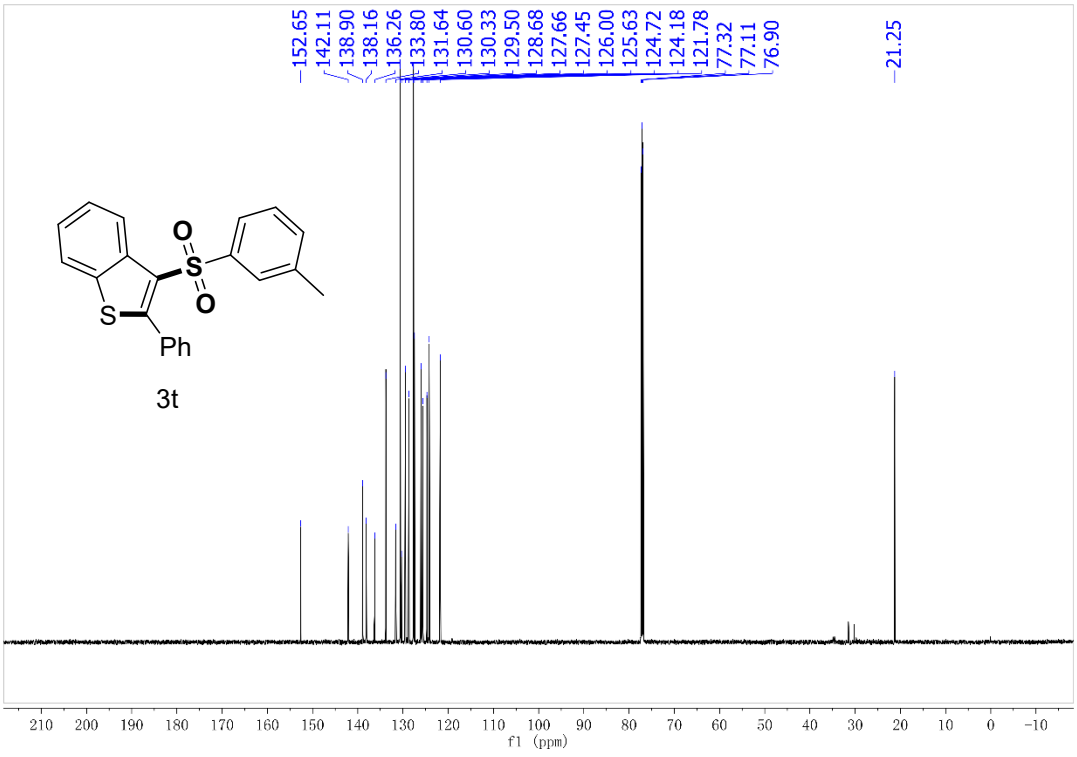
^{13}C NMR of **3s** in $CDCl_3$ (151 MHz, $CDCl_3$)



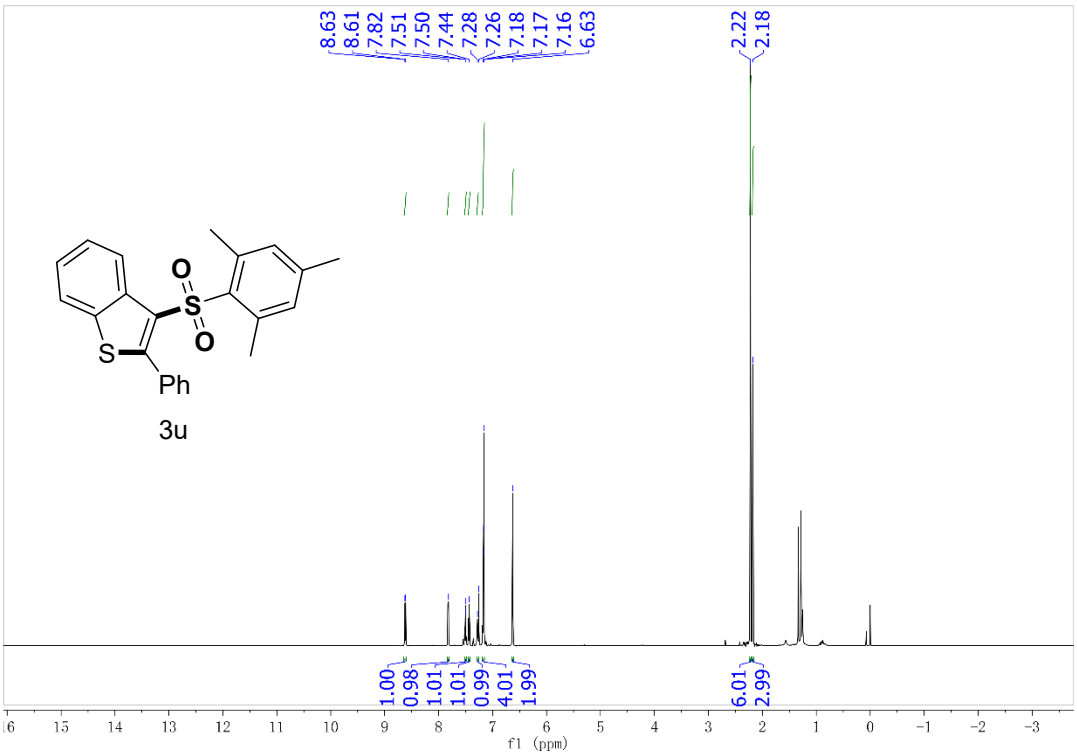
^{1}H NMR of **3t** in Chloroform-*d* (600 MHz, Chloroform-*d*)



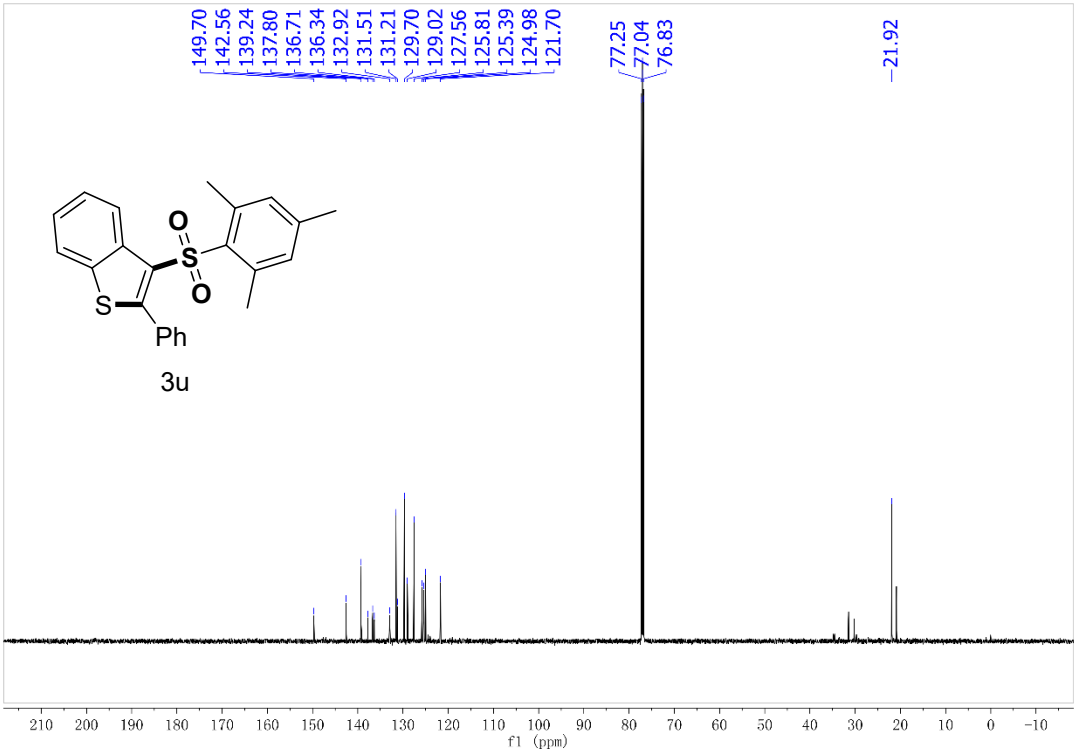
^{13}C NMR of **3t** in $CDCl_3$ (151 MHz, $CDCl_3$)



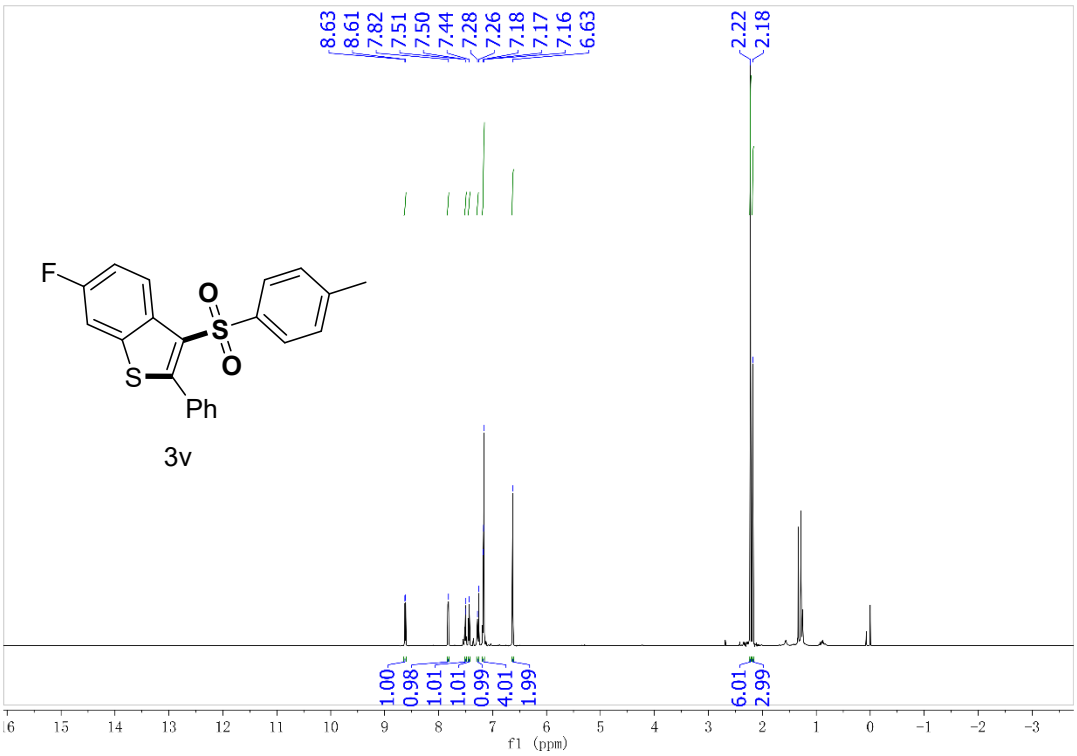
^{1}H NMR of **3u** in Chloroform-*d* (600 MHz, Chloroform-*d*)



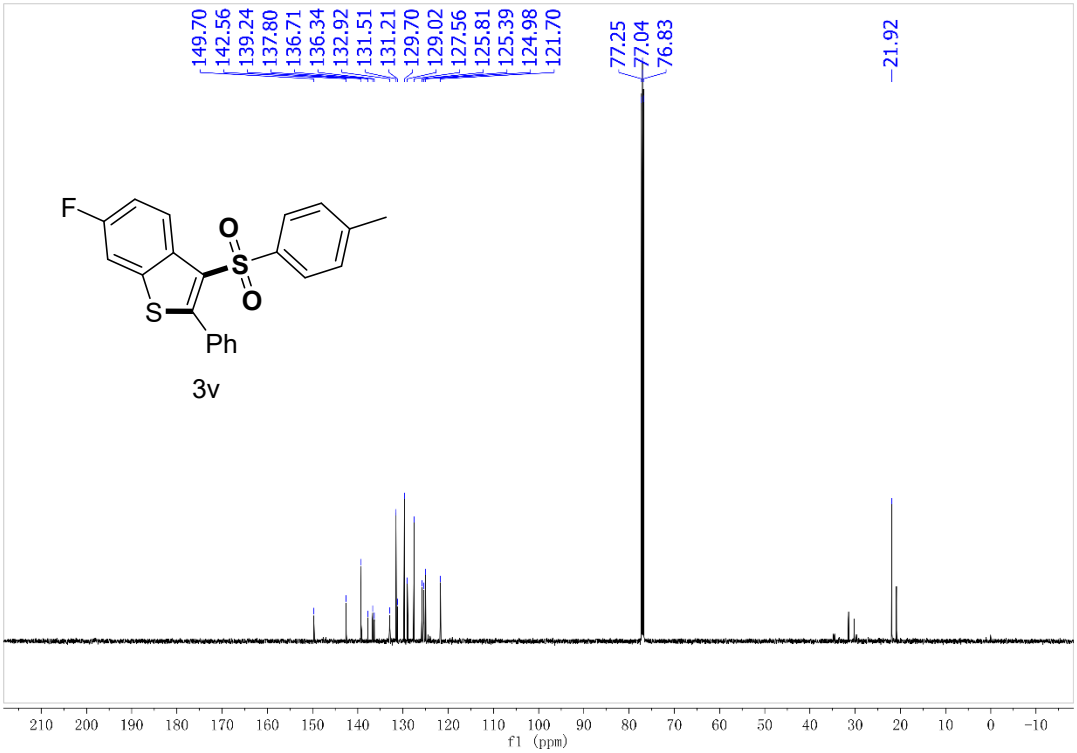
^{13}C NMR of **3u** in $CDCl_3$ (151 MHz, $CDCl_3$)



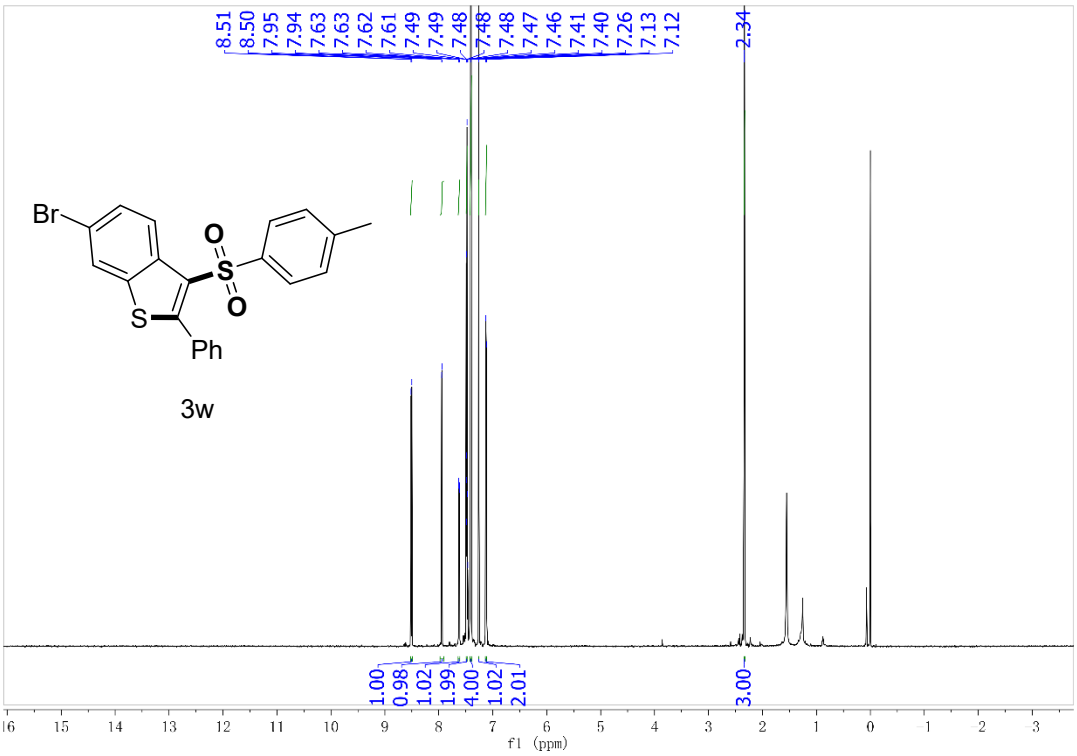
^{1}H NMR of **3v** in Chloroform-*d* (600 MHz, Chloroform-*d*)



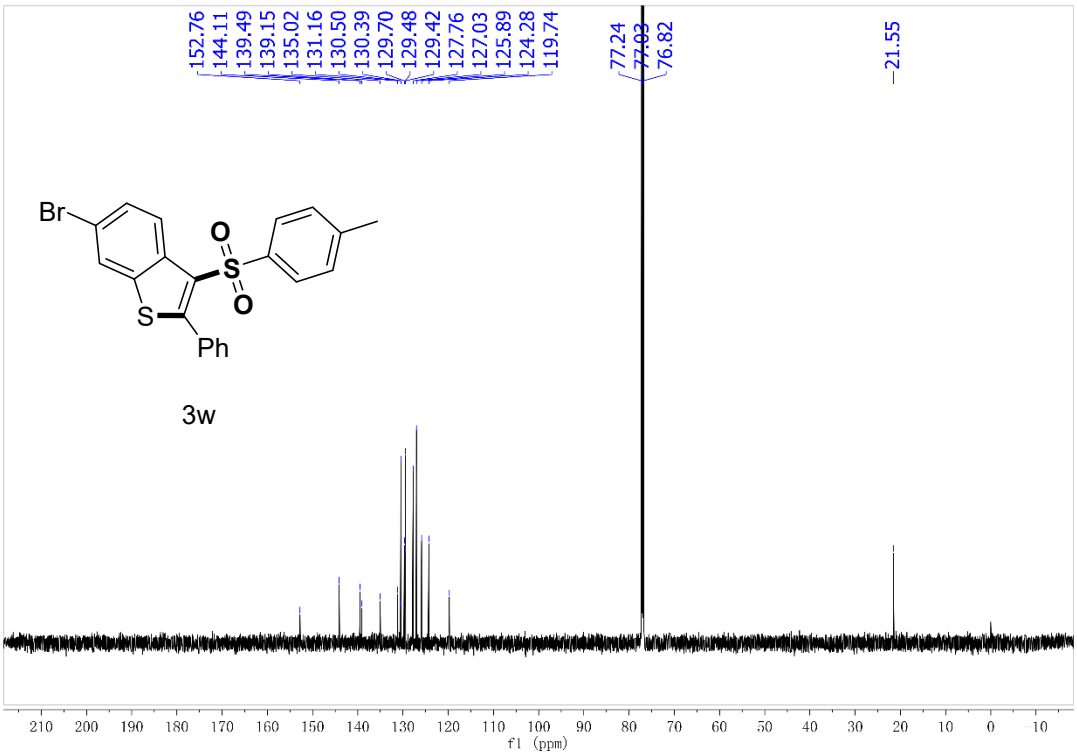
^{13}C NMR of **3v** in $CDCl_3$ (151 MHz, $CDCl_3$)



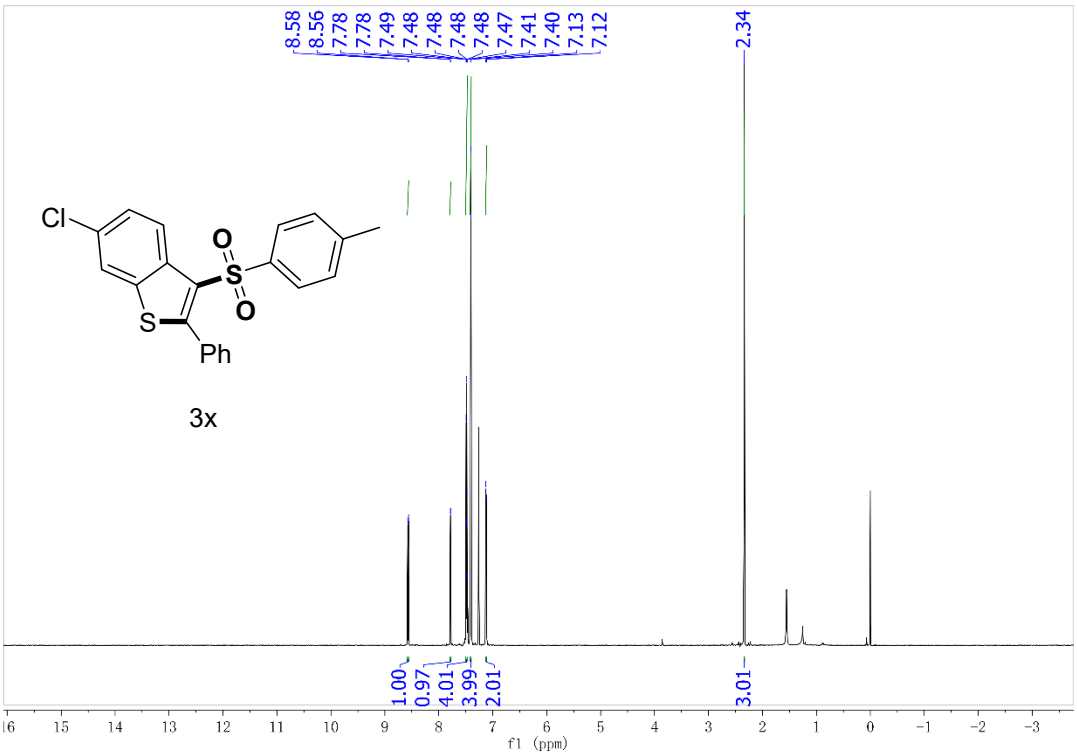
^{1}H NMR of **3w** in Chloroform-*d* (600 MHz, Chloroform-*d*)



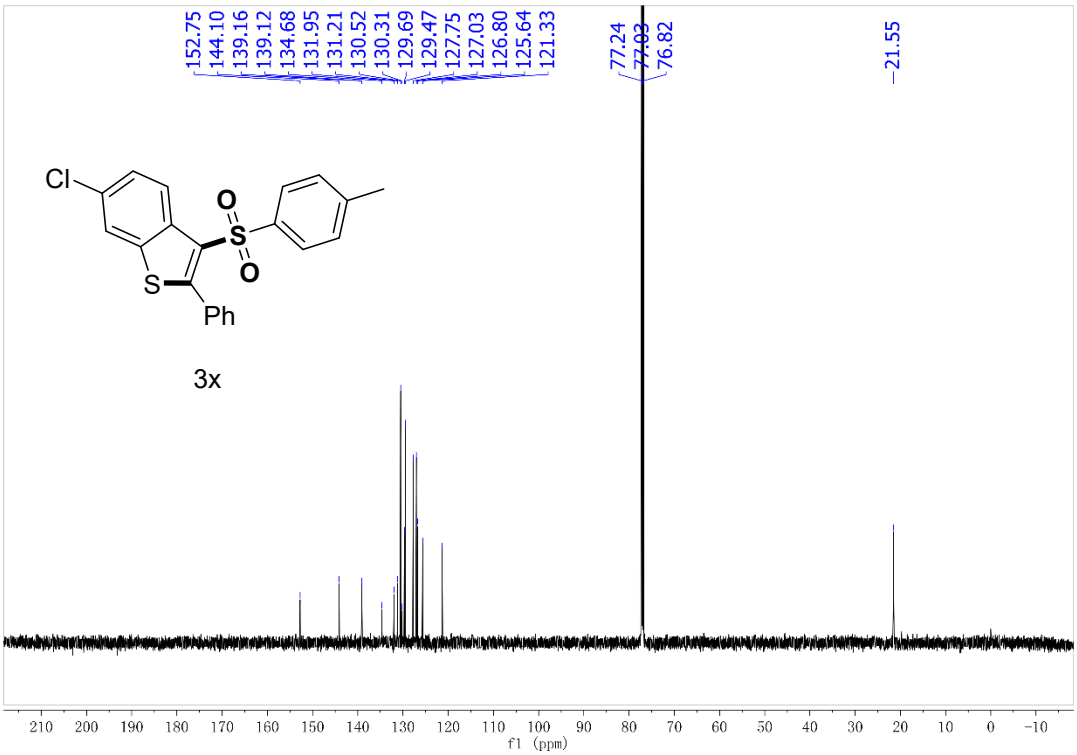
^{13}C NMR of 3w in $CDCl_3$ (151 MHz, $CDCl_3$)



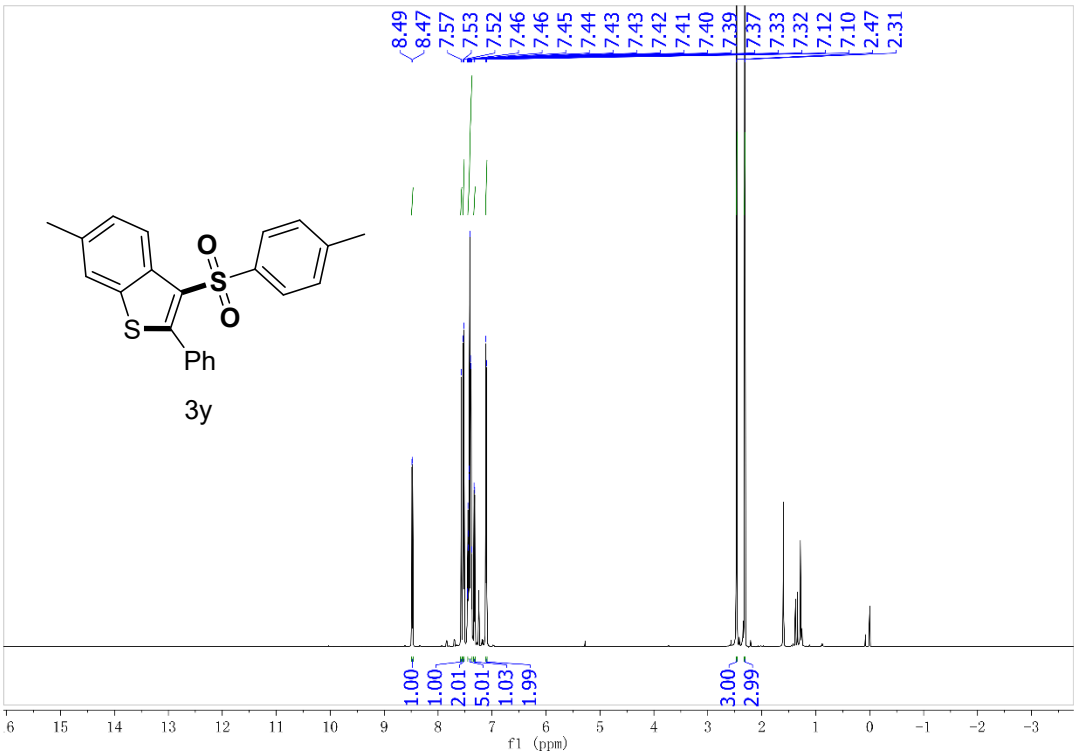
^{1}H NMR of **3x** in Chloroform-*d* (600 MHz, Chloroform-*d*)



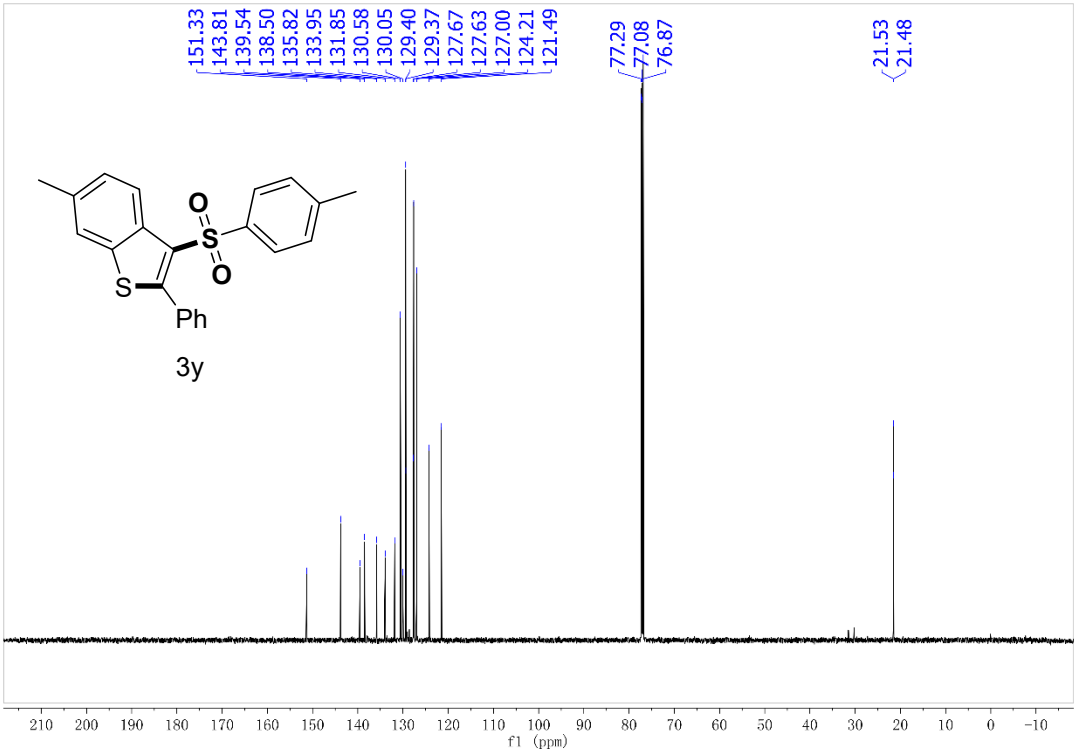
^{13}C NMR of **3x** in $CDCl_3$ (151 MHz, $CDCl_3$)



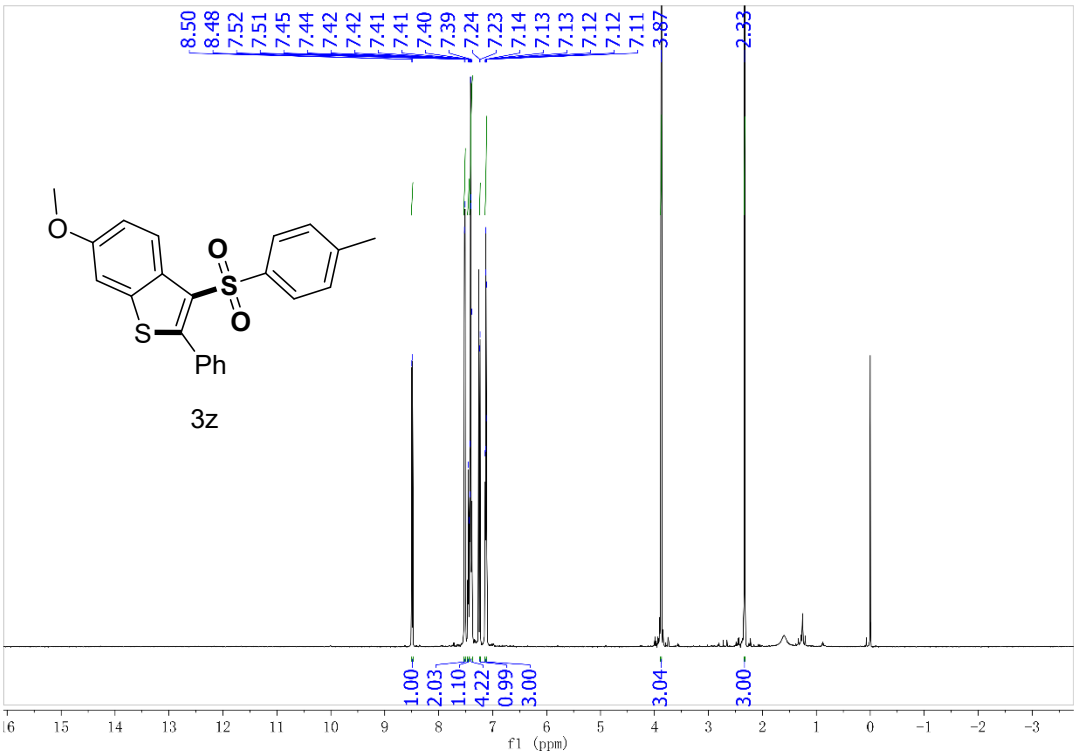
^{1}H NMR of **3y** in Chloroform-*d* (600 MHz, Chloroform-*d*)



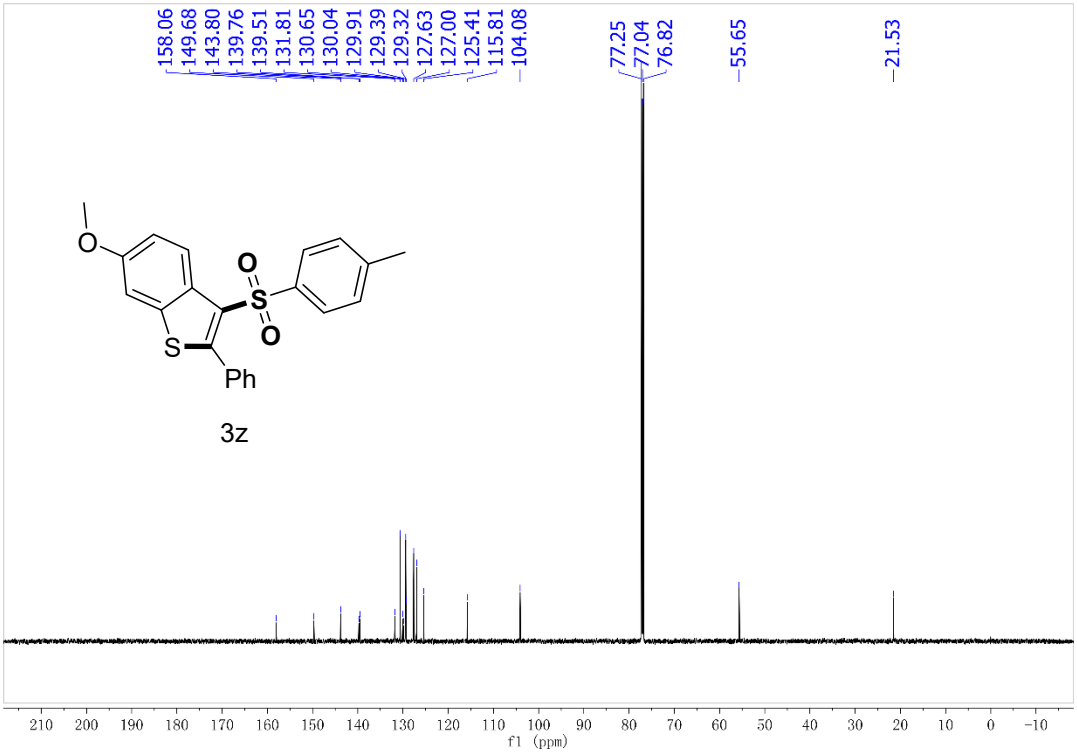
^{13}C NMR of **3y** in $CDCl_3$ (151 MHz, $CDCl_3$)



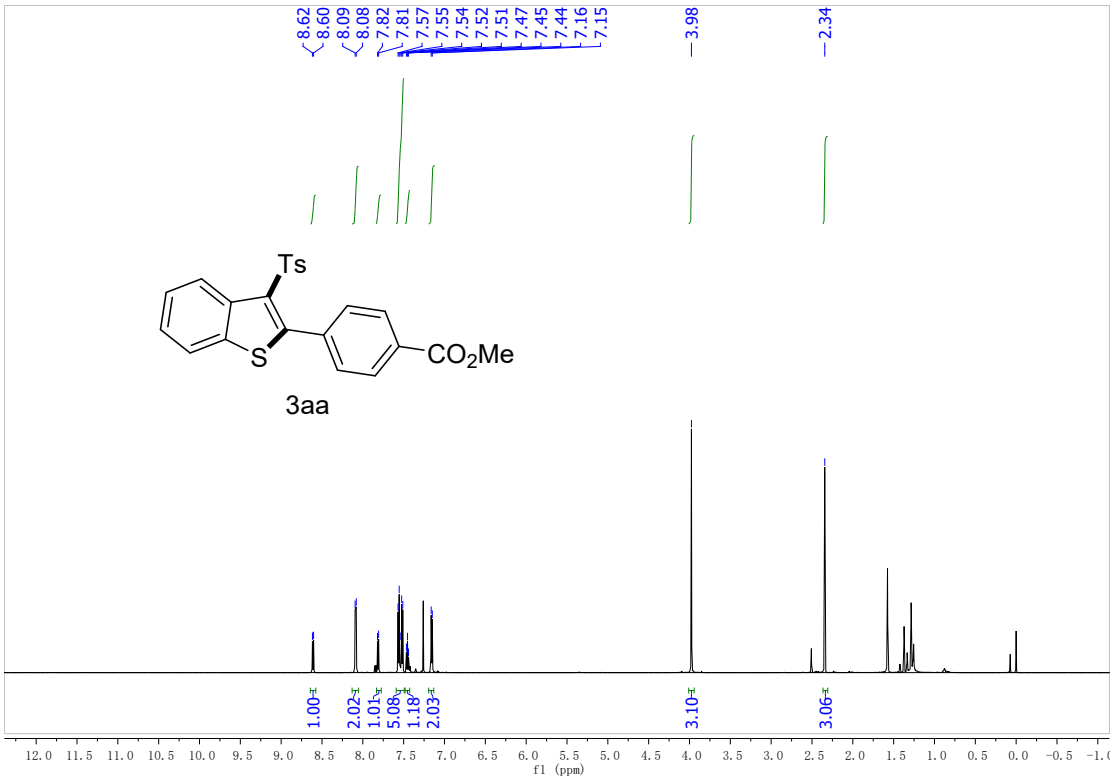
^{1}H NMR of **3z** in Chloroform-*d* (600 MHz, Chloroform-*d*)



^{13}C NMR of **3z** in $CDCl_3$ (151 MHz, $CDCl_3$)



^{1}H NMR of **3aa** in $CDCl_3$ (600 MHz, $CDCl_3$)



^{13}C NMR of **3aa** in $CDCl_3$ (151 MHz, $CDCl_3$)