Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Electrochemical synthesis of sulfonated benzothiophenes using 2-alkynylthioanisoles and sodium sulfinates

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Table of Contents for Supporting Information

1. General considerations

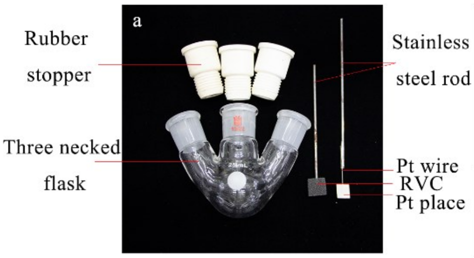
All reactions were carried out under air. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz/100 MHz; 600 MHz/151 MHz respectively) in $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. 1H NMR data are reported as follows: 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), m (multiplet), and br (broad singlet). High resolution mass spectroscopic data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI.

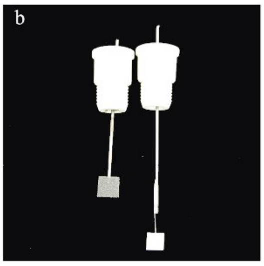
2. Preparation of the starting materials

Sodium sulfinates and 2-alkynylthioanisoles derivatives were prepared according to reported methods (W. Kim, H. Y. Kim and K. Oh, *Org. Lett.,* 2020, **22**, 6319-6323; W.-C. Yang, P. Dai, K. Luo, Y.-G. Ji and L. Wu, *Adv. Synth. Catal.,* 2017, **359**, 2390-2395; W. Liu, Y.-Q. Hu, X.-Y. Hong, G.-X. Li, X.-B. Huang, W.-X. Gao, M.-C. Liu, Y. Xia, Y.-B. Zhou and H.-Y. Wu, *Chem. Commun.,* 2018, **54**, 14148-14151). The chemicals and solvents were purchased from commercial supplierseither Aldrich (USA), Energy-Chemical (Shanghai) or Shanghai Chemical Company (P. R. China). All solvents were dried and freshly distilled in N_2 prior to use. Products were purified by flash chromatographyon 200–300 mesh silica gel.

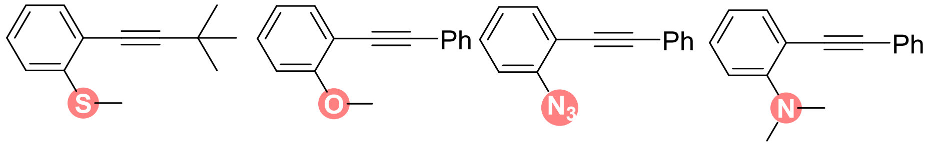
3. General procedure for the synthesis of 3a

A 50 mL vial was charged with 2-alkynylthioanisole (**1a**, 0.20 mmol), sodium sulfinate (**2a**, 0.40 mmol), TBAB (2.0 equiv, 0.40 mmol), CH_3CN:H_2O (1:1, 2.0 mL) and a magnetic stir bar. The vial was equipped with platinum electrode (1.5 cm×1.5 cm×0.3 mm) as cathode, RVC (1.2 cm×1.0 cm×1.0 mm) as the anode at constant current = 2.0 mA, at room temperature for 10 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30 : 1) to give the desired product **3a**.





4. Failed substrates:



5. Cyclic voltammetry study

The cyclic voltammetries were determined in an electrolyte of TBAB (0.20 M) in MeCN/H_2O (1:1, 10 mL) under air using a glassy carbon disk working electrode, a Pt wire and Ag/AgCl as counter and reference electrode. The scan rate is 100 mV/s.

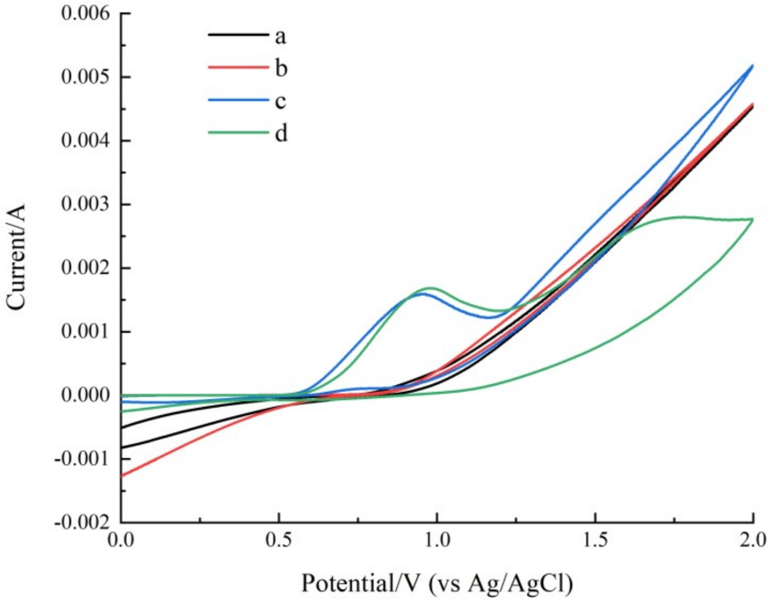
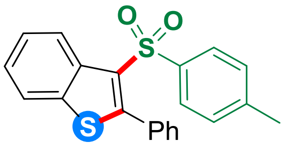


Figure S1. Cyclic voltammograms of **1a**, **2a** in 0.20 M TBAB in a mixed solvent of H_2O/CH_3CN (v:v = 1:1, 10 mL) using glassy carbon electrode, Pt wire and Ag/AgCl as counter and reference electrode at 100 mV/s scan rate.
(a) TBAB (0.20 M) (black line)
(b) TBAB (0.20 M) + **1a** (0.10 M) (red line)
(c) TBAB (0.20 M) + **2a** (0.20 M) (blue line)
(d) TBAB (0.20 M) + **1a** (0.10 M) + **2a** (0.20 M) (green line)

As shown in Figure S1, the mixture of **1a** and TBAB had no obvious oxidation peak (red curve b) in the range of 0.0−2.0 V vs Ag/AgCl, which revealed that compound **1a** could not be oxidized within the examined potential window. Meanwhile, TsNa readily underwent the anodic oxidation, and its oxidative peak appears at 0.95 V vs Ag/AgCl (blue curve c). The same oxidative peak at 0.98 V vs Ag/AgCl was observed (green curve d) when the mixture of **1a**, **2a** and TBAB was employed. These results implied that radical intermediates are possibly involved in this electrochemical oxidation system, and TsNa was likely to be first oxidized at the anode.

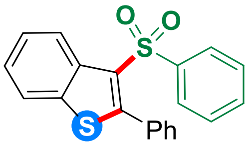
6. Characterization data of products

2-Phenyl-3-tosylbenzo[*b*]thiophene (3a)[1]



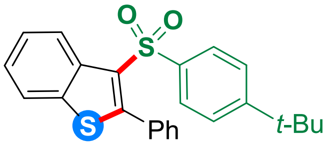
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt = 30:1) to afford the **3a** as a white solid (56.06 mg, 77% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.54 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.47–7.43(m, 3H), 7.41–7.37 (m, 1H), 7.37–7.31 (m, 5H), 7.05 (d, *J* = 8.2 Hz, 2H), 2.25 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 152.5, 143.8, 139.4, 138.1, 136.1, 131.7, 130.5, 130.3, 129.4, 129.4, 127.6, 127.0, 125.9, 125.5, 124.6, 121.7, 21.5. The characterization data matched the literature.[1]

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



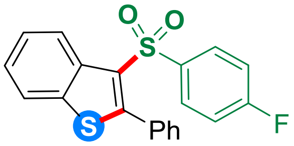
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt = 30:1) to afford the **3b** as a yellow solid (55.3 mg, 79% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.56 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.28 (m, 7H), 7.23 (t, *J* = 7.8 Hz, 2H).**^{13}C NMR (151 MHz, CDCl$_3$)** δ 152.9, 142.3, 138.1, 136.2, 132.9, 131.6, 130.5, 130.0, 129.54, 128.8, 127.7, 126.9, 126.0, 125.6, 124.6, 121.8. The characterization data matched the literature.[2]

3-((4-(*tert*-butyl)Phenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (3c)[1]



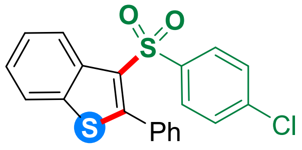
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt = 30:1) to afford the **3c** as a yellow solid (52.53 mg, 77% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.58 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.47–7.44 (m, 1H), 7.39–7.29 (m, 6H), 7.26 (d, *J* = 8.6 Hz, 2H), 1.19 (s, 9H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 156.7, 152.4, 139.2, 138.1, 136.2, 131.7, 130.5, 130.4, 129.40, 127.6, 126.9, 125.9, 125.7, 125.5, 124.7, 121.7, 35.1, 31.0. The characterization data matched the literature.[1]

3-((4-Fluorophenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (3d)[1]



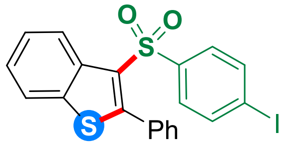
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt = 30:1) to afford the **3d** as a yellow solid (41.22 mg, 56% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.57 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.56–7.51 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.40–7.36 (m, 2H), 7.35–7.30 (m, 4H), 6.93–6.86 (m, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 165.2 (d, *J* = 255.3 Hz), 152.8, 138.3, 138.1, 136.0, 131.4, 130.5, 130.0, 129.8 (d, *J* = 9.7 Hz), 129.6, 127.7, 126.1, 125.7, 124.5, 121.8, 115.9 (d, *J* = 22.6 Hz). The characterization data matched the literature.[1]

3-((4-Chlorophenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (3e)[1]



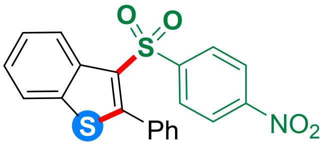
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt = 30:1) to afford the **3e** as a yellow solid (26.11 mg, 34% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.55 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.48–7.43 (m, 3H), 7.41–7.34 (m, 2H), 7.34–7.30 (m, 4H), 7.20–7.17 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.1, 140.7, 139.5, 138.1, 136.0, 131.4, 130.5, 129.7, 129.6, 129.0, 128.4, 127.7, 126.1, 125.7, 124.5, 121.8. The characterization data matched the literature.[1]

3-((4-Iodophenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (3f)



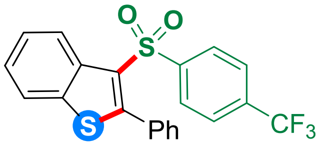
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt = 30:1) to afford the **3f** as a yellow solid (64.74 mg, 68% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.54 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.60–7.57 (dt, 2H), 7.48–7.45 (m, 1H), 7.42–7.31 (m, 6H), 7.25–7.22 (dt, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.1, 141.9, 138.1, 138.0, 136.0, 131.4, 130.5, 129.6, 129.6, 128.3, 127.7, 126.1, 125.7, 124.5, 121.8, 100.7.

3-((4-Nitrophenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (3g)[1]



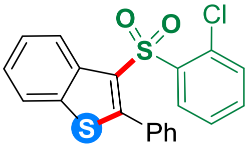
The sulfonylation product was purified by flash column chromatography on silica gel (PE/ AcOEt = 30:1) to afford the **3g** as a yellow solid (39.5 mg, 50% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.56 (d, *J* = 8.4 Hz, 1H), 8.06–8.04 (m, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.68–7.66 (m, 2H), 7.51–7.47 (m, 1H), 7.43–7.38(m, 2H), 7.35–7.29 (m, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 154.3, 150.1, 147.7, 138.1, 135.9, 131.0, 130.5, 130.3, 129.9, 128.6, 128.2, 128.0, 127.9, 126.4, 126.0, 124.3, 123.9, 122.0. The characterization data matched the literature.[1]

2-Phenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)benzo[*b*]thiophene (3h)[1]



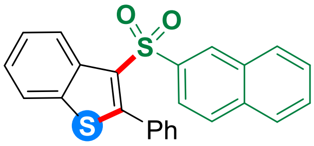
The sulfonylation product was purified by flash column chromatography on silica gel (PE) to afford the **3h** as a yellow solid (51 mg, 61% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.58 (d, J = 8.3 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.50–7.47(m, 3H), 7.42–7.37 (m, 2H), 7.34–7.29 (m, 4H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.71, 145.66, 138.17, 136.04, 134.53 (dd, *J* = 66.3, 33.0 Hz), 131.2, 130.5, 129.7, 129.1, 127.8, 127.5, 126.2, 125.8 (d, *J* = 6.5 Hz), 124.4, 123.3 (d, *J* = 271.8 Hz), 121.9. The characterization data matched the literature.[1]

2,6-Dimethyl-4-((*m*-tolylsulfonyl)methyl)phenol (3i)[2]



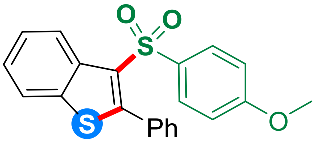
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3i** as a yellow solid (40.7mg, 53% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.63 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.66–7.64(m, 1H), 7.53–7.50 (m, 1H), 7.47–7.42 (m, 1H), 7.32–7.24 (m, 5H), 7.23–7.19 (m, 2H), 7.06–7.03(m, 1H).**^{13}C NMR (151 MHz, CDCl$_3$)** δ 152.1, 139.2, 137.8, 136.9, 133.7, 132.9, 131.1, 131.0, 130.4, 130.4, 129.3, 127.6, 126.3, 125.9, 125.5, 124.9, 121.7. The characterization data matched the literature.[2]

2-Phenyl-3-(phenylsulfonyl)benzo[*b*]thiophene (3j)[1]



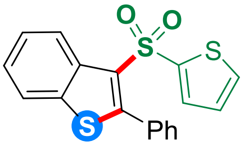
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3j** as a yellow solid (68.8 mg, 86% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 1.5 Hz, 1H), 7.73–7.66 (m, 4H), 7.53–7.43 (m, 4H), 7.37–7.32 (m, 2H), 7.31–7.30 (m, 2H), 7.27–7.25 (m, 2H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 152.9, 138.9, 138.1, 136.2, 134.9, 131.8, 131.5, 130.5, 130.1, 129.5, 129.4, 129.1, 128.9, 128.5, 127.8, 127.6, 127.3, 126.0, 125.6, 124.7, 122.1, 121.7. The characterization data matched the literature.[1]

3-((4-Methoxyphenyl)sulfonyl)-2-phenylbenzo[*b*]thiophene (3k)[1]



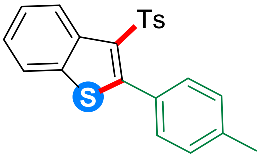
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 15:1) to afford the **3k** as a yellow liquid (40.1 mg, 53% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.55 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.52–7.47 (m, 2H), 7.46–7.42 (m, 1H), 7.40 – 7.30 (m, 6H), 6.74–6.66 (m, 2H), 3.69 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.1, 151.01, 137.1, 135.1, 133.0, 130.7, 129.7, 129.4, 128.3, 128.1, 126.6, 124.8, 124.5, 123.6, 120.7, 112.9, 54.5. The characterization data matched the literature.[1]

2-phenyl-3-(thiophen-2-ylsulfonyl)benzo[*b*]thiophene (3m)



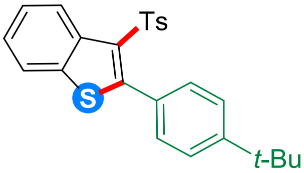
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3m** as a yellow solid (25.2 mg, 35% yield).^{1}H NMR (600 MHz, CDCl$_3$) δ 8.52 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.50–7.34 (m, 9H), 6.86 (t, *J* = 4.3 Hz, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 151.8, 142.8, 137.0, 134.6, 132.1, 131.7, 130.5, 129.2, 129.0, 128.5, 126.7, 126.2, 124.9, 124.6, 123.50, 120.80. The characterization data matched the literature.[3]

2-(*p*-Tolyl)-3-tosylbenzo[*b*]thiophene (3n)[1]



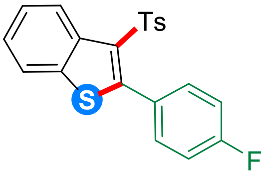
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3n** as a yellow solid (54.4 mg, 72% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.50 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 2.34 (s, 3H), 2.23 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 153.0, 143.8, 139.6, 138.1, 136.2, 130.4, 129.9, 129.4, 128.7, 128.4, 127.0, 125.8, 125.4, 124.5, 121.7, 21.5, 21.4. The characterization data matched the literature.[1]

2,6-Di-*tert*-butyl-4-(1-(phenylsulfonyl)ethyl)phenol (3o)[2]



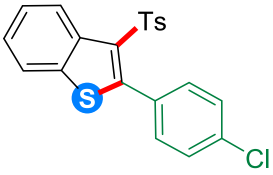
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3o** as a yellow solid (56.3 mg, 67% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.55 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 6.9 Hz, 3H), 7.35–7.31(m, 3H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 7.7 Hz, 2H), 2.24 (s, 3H), 1.30 (s, 9H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 152.8, 152.6, 143.6, 139.3, 138.1, 136.3, 130.2, 130.0, 129.2, 128.6, 127.1, 125.8, 125.4, 124.6, 121.7, 34.8, 31.3, 21.5. The characterization data matched the literature.[2]

2-(4-Fluorophenyl)-3-tosylbenzo[*b*]thiophene (3p)[1]



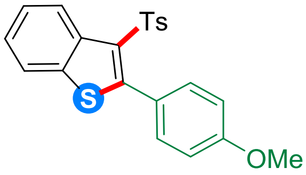
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3p** as a yellow solid (52.72 mg, 69% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.53 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.48–7.42 (m, 3H), 7.37–7.31 (m, 3H), 7.06 (d, *J* = 8.2 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 2.25 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 162.4 (d, *J* = 250.0 Hz), 150.1, 143.0, 138.3, 137.0, 135.0, 131.4 (d, *J* = 8.3 Hz), 129.6, 128.4, 126.5 (d, *J* = 3.5 Hz), 125.9, 125.0, 124.6, 123.6, 120.7, 113.8 (d, *J* = 21.8 Hz), 20.4. The characterization data matched the literature.[1]

2-(4-Chlorophenyl)-3-tosylbenzo[*b*]thiophene (3q)[2]



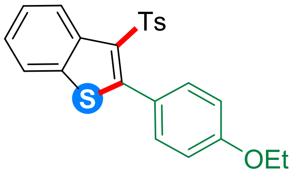
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3q** as a yellow solid (50.1 mg, 63% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.52 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.31–7.27 (m, 4H), 7.07 (d, *J* = 8.3 Hz, 2H), 2.25 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** 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, 125.8, 124.6, 121.8, 21.5. The characterization data matched the literature.[2]

2-(4-Methoxyphenyl)-3-tosylbenzo[*b*]thiophene (3r)[1]



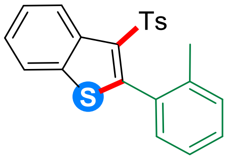
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 15:1) to afford the **3r** as a yellow solid (60.68 mg, 77% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.60 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.41–7.37(m, 3H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 2.32 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 160.6, 152.8, 143.8, 139.6, 138.0, 136.3, 131.9, 129.8, 129.4, 126.9, 125.8, 125.4, 124.5, 123.7, 121.7, 113.2, 55.4, 21.5. The characterization data matched the literature.[1]

2-(4-Ethoxyphenyl)-3-tosylbenzo[*b*]thiophene (3s)



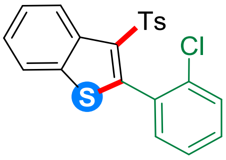
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3s** as a yellow solid (60.38 mg, 74% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.60 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.50–7.48(m, 1H), 7.41–7.38(m, 1H), 7.37–7.33 (m, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.94–6.89 (m, 2H), 4.11–4.08(m, 2H), 2.31 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 160.0, 153.0, 143.7, 139.6, 138.0, 136.3, 131.9, 129.7, 129.3, 126.9, 125.8, 125.4, 124.5, 123.5, 121.6, 113.6, 63.6, 21.5, 14.8.

2-(*o*-Tolyl)-3-tosylbenzo[*b*]thiophene (3t)



The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3t** as a yellow solid (36.29 mg, 48% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.58 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.47–7.43 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.17–7.11 (m, 2H), 7.06–7.04 (m, 3H), 2.25 (s, 3H), 2.00 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 151.7, 144.0, 139.2, 138.5, 138.1, 135.8, 131.2, 130.2, 129.8, 129.6, 129.4, 127.3, 125.8, 125.5, 124.9, 124.5, 121.8, 21.5, 20.2. HRMS (ESI) calcd for $C_{22}H_{19}O_2S_2$ $[M+H]^+$ 379.0826, found 379.0825. The characterization data matched the literature.[3]

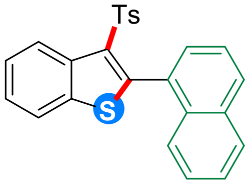
2-(2-Chlorophenyl)-3-tosylbenzo[*b*]thiophene (3u)[3]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3u** as a white liquid (33.43 mg, 42% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.53 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.53–7.50(m, 1H), 7.47–7.40 (m, 4H), 7.38–7.33 (m, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 2.35 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 148.4, 144.1, 138.8, 138.8, 135.3, 134.2, 132.5, 131.6, 130.8, 129.5, 129.3, 127.3, 126.0, 125.8, 125.8, 124.4, 121.9, 21.5.

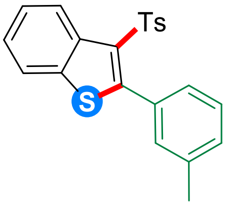
HRMS (ESI) calcd for $C_{21}H_{16}ClO_2S_2$ $[M+H]^+$ 399.0280, found 399.0279. The characterization data matched the literature.[3]

2-(Naphthalen-1-yl)-3-tosylbenzo[*b*]thiophene(3v)



The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3v** as a yellow solid (45.5 mg, 55% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.68 (d, *J* = 8.4 Hz, 1H), 7.85 (t, *J* = 4.7 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.45–7.31 (m, 4H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.21–7.11 (m, 2H), 6.77 (d, *J* = 7.9 Hz, 2H), 2.10 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 149.7, 143.7, 138.8, 138.4, 135.9, 133.0, 132.9, 132.3, 130.0, 129.3, 129.0, 128.7, 128.0, 127.3, 126.3 , 125.9, 125.9, 125.7, 125.7, 124.7, 124.5, 121.8, 21.3.

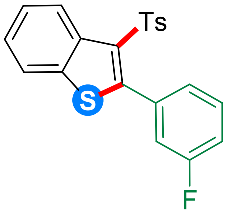
2-(*m*-Tolyl)-3-tosylbenzo[*b*]thiophene (3w)



The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3w** as a yellow solid (63.5 mg, 84% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.63 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.30–7.25 (m, 2H), 7.22 (d, *J* = 7.3 Hz, 1H), 7.16–7.10 (m, 3H), 2.37 (s, 3H), 2.34 (s, 3H). **^{13}C NMR (151 MHz,**

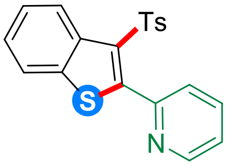
CDCl$_3$) δ 152.7, 143.8, 139.5, 138.1, 137.2, 136.2, 131.5, 131.0, 130.1, 129.3, 127.5, 127.1, 125.8, 125.5, 124.6, 121.7, 21.5, 21.3. HRMS (ESI) calcd for $C_{22}H_{19}O_2S_2$ $[M+H]^+$ 379.0826, found 379.0828. The characterization data matched the literature.[3]

2-(3-Fluorophenyl)-3-tosylbenzo[*b*]thiophene (3x)



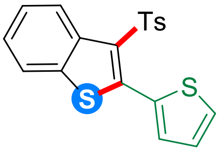
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3x** as a yellow solid (59.59mg, 78% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.62 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.37 (dd, *J* = 14.3, 7.3 Hz, 1H), 7.26–7.21 (m, 1H), 7.16 (t, *J* = 8.1 Hz, 3H), 7.10 (d, *J* = 9.2 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 161.7 (d, *J* = 247.3 Hz), 150.3, 144.2, 139.2, 138.1, 135.9, 133.6 (d, *J* = 8.5 Hz), 130.8, 129.5, 129.2 (d, *J* = 8.4 Hz), 127.0, 126.5 (d, *J* = 3.1 Hz), 126.1, 125.8, 124.7, 121.8, 117.6 (d, *J* = 22.9 Hz), 116.4 (d, *J* = 20.9 Hz), 21.5. HRMS (ESI) calcd for $C_{21}H_{16}FO_2S_2$ $[M+H]^+$ 383.0576, found 383.0576. The characterization data matched the literature.[3]

4-(3-Tosylbenzo[*b*]thiophen-2-yl)pyridine (3y)



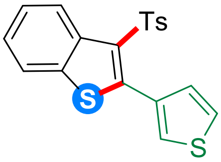
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 7:1) to afford the **3y** as a colorless liquid (43.8 mg, 60% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.62 (d, *J* = 4.8 Hz, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 5H), 7.43–7.30 (m, 3H), 7.13 (d, *J* = 7.8 Hz, 2H), 2.25 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 151.1, 150.8, 148.9, 144.0, 139.0, 138.6, 135.8, 135.6, 130.4, 129.6, 127.3, 126.9, 125.9, 125.9, 124.5, 123.9, 122.0, 21.5. HRMS (ESI) calcd for $C_{20}H_{16}NO_2S_2$ $[M+H]^+$ 366.0622, found 366.0620.

2-(Thiophen-2-yl)-3-tosylbenzo[*b*]thiophene (3z)[1]



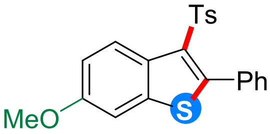
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3z** as a yellow liquid (40.7 mg, 55% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.67 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.53–7.47 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.16–7.11 (m 3H), 2.31 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 144.6, 144.0, 139.1, 138.2, 136.5, 132.2, 131.0, 130.7, 129.4, 129.3, 127.4, 126.5, 126.0, 125.8, 124.8, 121.6, 21.5. The characterization data matched the literature.[3]

2-(Thiophen-3-yl)-3-tosylbenzo[*b*]thiophene (3aa)



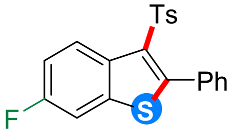
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3aa** as a yellow liquid (47.36 mg, 64% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.66 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.53–7.49 (m, 4H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.34 (s, 1H), 7.26 (d, *J* = 5.1 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 147.1, 143.9, 139.3, 137.9, 136.4, 131.1, 130.2, 130.1, 129.4, 127.8, 126.8, 125.9, 125.6, 125.0, 124.6, 121.6, 21.5. HRMS (ESI) calcd for $C_{19}H_{15}O_2S_3$ $[M+H]^+$ 371.0234, found 371.0235. The characterization data matched the literature.[3]

6-Methoxy-2-phenyl-3-tosylbenzo[*b*]thiophene (3ab)[1]



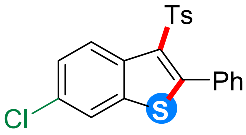
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 15:1) to afford the **3ab** as a yellow solid (63 mg, 80% yield). **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.49 (d, *J* = 9.1 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.44–7.38 (m, 5H), 7.22 (s, 1H), 7.12 (t, *J* = 7.5 Hz, 3H), 3.85 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 158.0, 149.7, 143.8, 139.7, 139.4, 131.8, 130.6, 130.0, 129.8, 129.4, 129.3, 127.6, 126.9, 125.3, 115.8, 104.0, 55.6, 21.5. The characterization data matched the literature.[1]

6-Fluoro-2-phenyl-3-tosylbenzo[*b*]thiophene (3ac)[2]



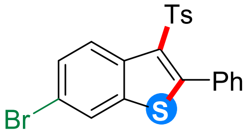
The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3ac** as a yellow solid (38.2 mg, 50% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.55 – 8.51 (m, 1H), 7.43 – 7.35 (m, 4H), 7.31 (d, *J* = 4.0 Hz, 4H), 7.20 – 7.16(m, 1H), 7.03 (d, *J* = 7.8 Hz, 2H), 2.24 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 160.8 (d, *J* = 247.9 Hz), 152.0 (d, J = 3.6 Hz), 144.0, 139.2, 139.1, 132.6, 131.3, 130.5, 130.1, 129.6, 129.4, 127.7, 127.0, 126.1 (d, J = 9.0 Hz), 114.9 (d, *J* = 23.7 Hz), 107.9 (d, *J* = 25.4 Hz), 21.5. The characterization data matched the literature.[2]

6-Chloro-2-phenyl-3-tosylbenzo[*b*]thiophene (3ad)[2]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3ad** as a yellow solid (57.6 mg, 72% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.48 (d, *J* = 8.9 Hz, 1H), 7.68 (s, 1H), 7.41–7.38(m, 4H), 7.31 (d, *J* = 3.7 Hz, 4H), 7.03 (d, *J* = 7.8 Hz, 2H), 2.24 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 152.7, 144.1, 139.1, 139.1, 134.7, 131.9, 131.2, 130.5, 129.6, 129.4, 127.7, 127.0, 126.7, 125.6, 121.3, 21.5. The characterization data matched the literature.[2]

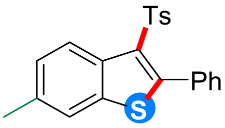
6-Bromo-2-phenyl-3-tosylbenzo[*b*]thiophene (3ae)[1]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3ae** as a yellow solid (67.03 mg, 76% yield). **^{1}H NMR**

(400 MHz, CDCl$_3$) δ 8.42 (d, *J* = 8.9 Hz, 1H), 7.84 (s, 1H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.41–7.37 (m, 3H), 7.32 (d, *J* = 4.2 Hz, 4H), 7.03 (d, *J* = 7.9 Hz, 2H), 2.24 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 152.7, 144.1, 139.5, 139.1, 135.0, 131.1, 130.5, 130.4, 129.7, 129.4, 129.4, 127.7, 127.0, 125.8, 124.3, 119.7, 21.5. The characterization data matched the literature.[1]

6-Methyl-2-phenyl-3-tosylbenzo[*b*]thiophene (3af)[1]



The sulfonylation product was purified by flash column chromatography on silica gel (PE/AcOEt = 30:1) to afford the **3af** as a yellow solid (54.43 mg, 72% yield). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.39 (d, *J* = 8.5 Hz, 1H), 7.47–7.43(m, 3H), 7.38–7.26 (m, 5H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H), 2.22 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** 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, 121.5, 21.5, 21.4. The characterization data matched the literature.[1]

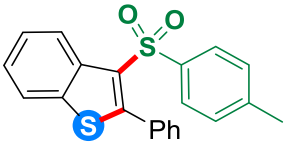
References for known compounds:

[1] J. Xu, X. Yu, J. Yan and Q. Song, *Org. Lett.,* 2017, **19**, 6292–6295.

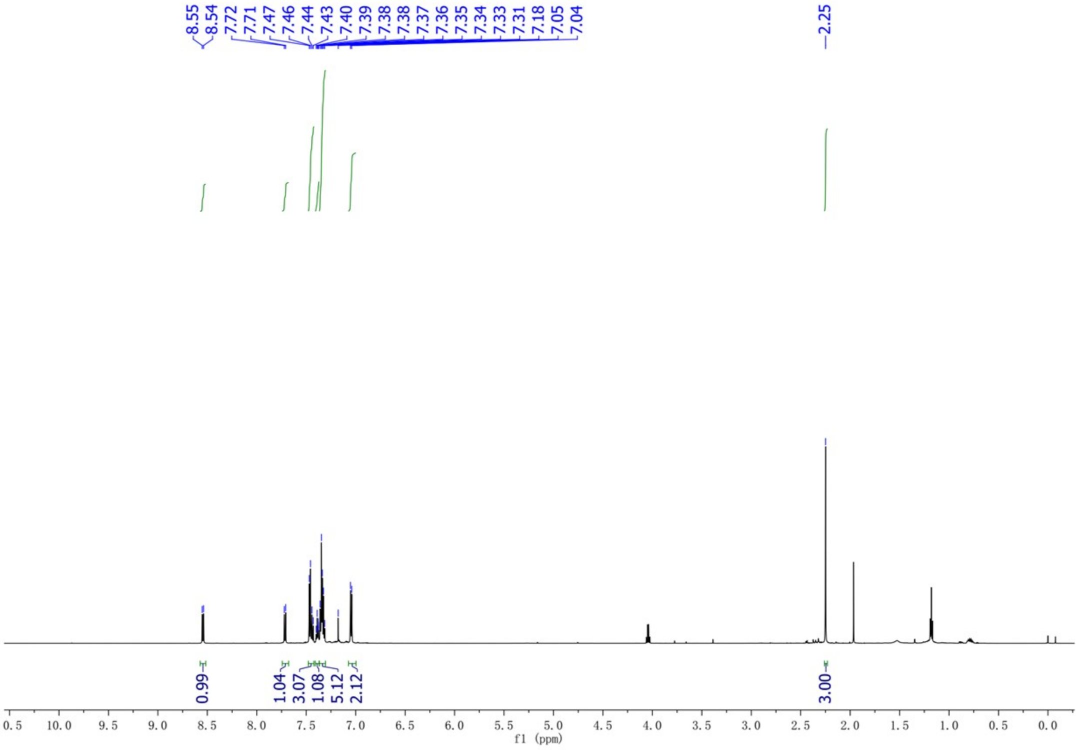
[2] J. Yan, J. Xu, Y. Zhou, J. Chen and Q. Song, *Org. Chem. Front.*, 2018, **5**, 1483–1487.

[3] D. Zhang, J. Cai, J. Du, X. Wang, W. He, Z. Yang, C. Liu, Z. Fang and K. Guo, *J. Org. Chem.*, 2021, **86**, 2593–2601.

7. ^{1}H and ^{13}C NMR spectra of the products



3a


8.55
8.54
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7.71
7.47
7.46
7.44
7.43
7.40
7.39
7.38
7.38
7.37
7.36
7.35
7.34
7.33
7.31
7.18
7.05
7.04
2.25
0.99
1.04
3.07
1.08
5.12
2.12
3.00
0.5
10.0
9.5
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8.5
8.0
7.5
7.0
6.5
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5.5
5.0
4.5
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3.5
3.0
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2.0
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1.0
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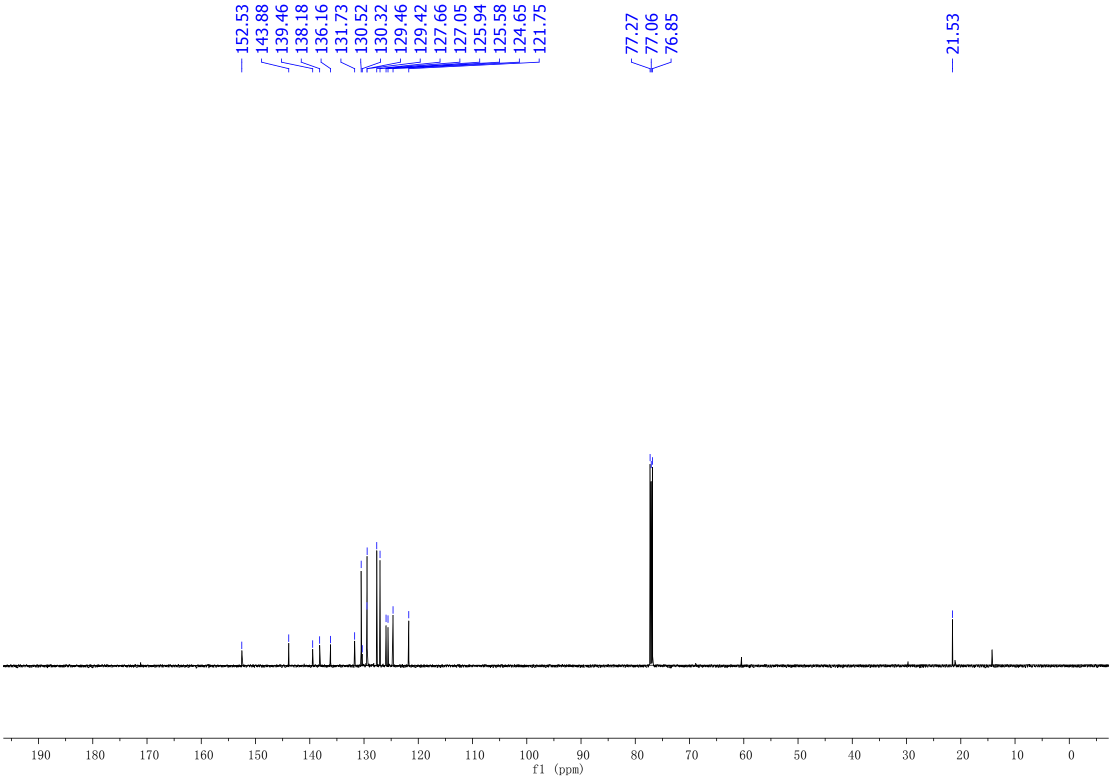
0.0
f1 (ppm)


152.53
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77.06
76.85
21.53
190
180
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50
40
30
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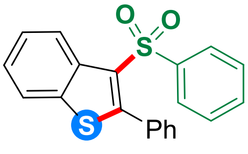
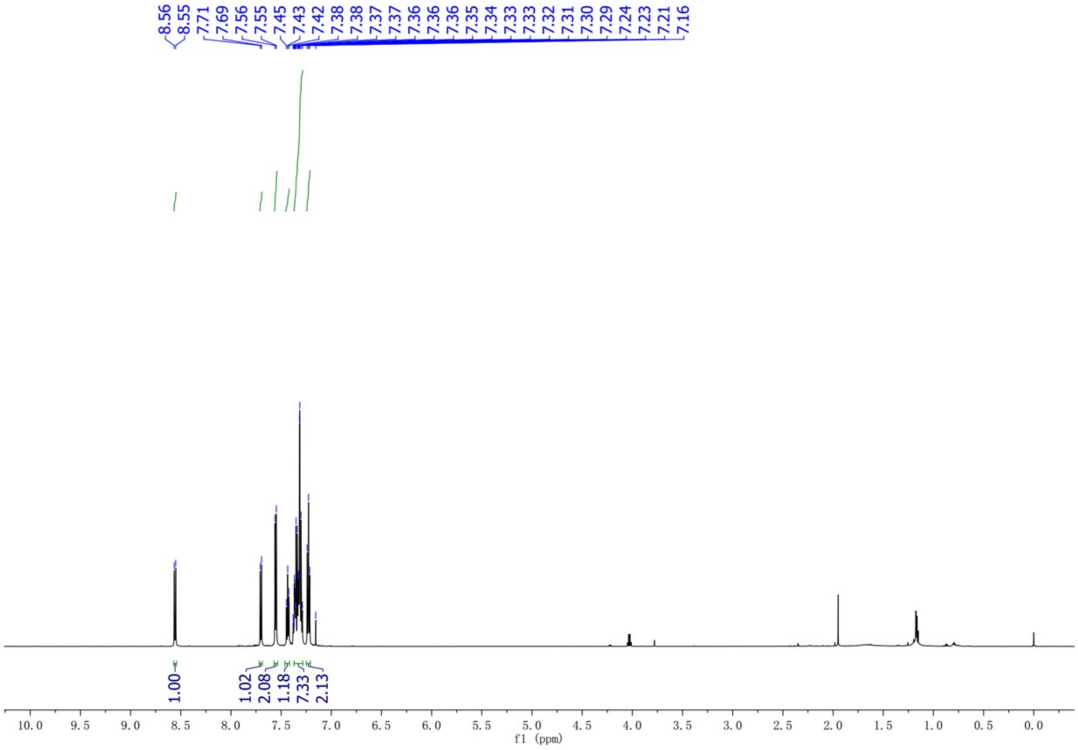
10
0
f1 (ppm)


O
O
S
S
Ph

3b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7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.24
7.23
7.21
7.16
1.00
1.02
2.08
1.18
7.33
2.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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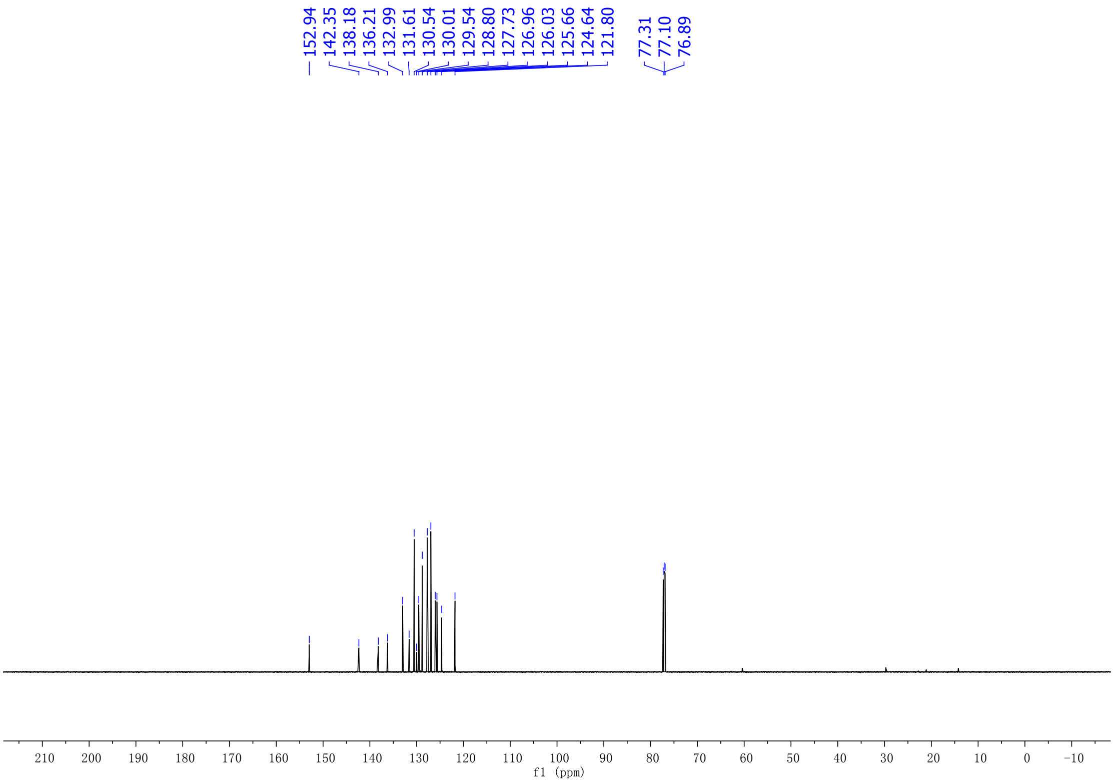
0.0
f1 (ppm)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130.01
129.54
128.80
127.73
126.96
126.03
125.66
124.64
121.80
77.31
77.10
76.89
210
200
190
180
170
160
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140
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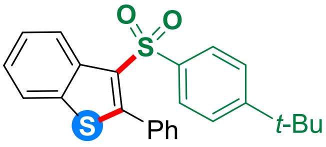
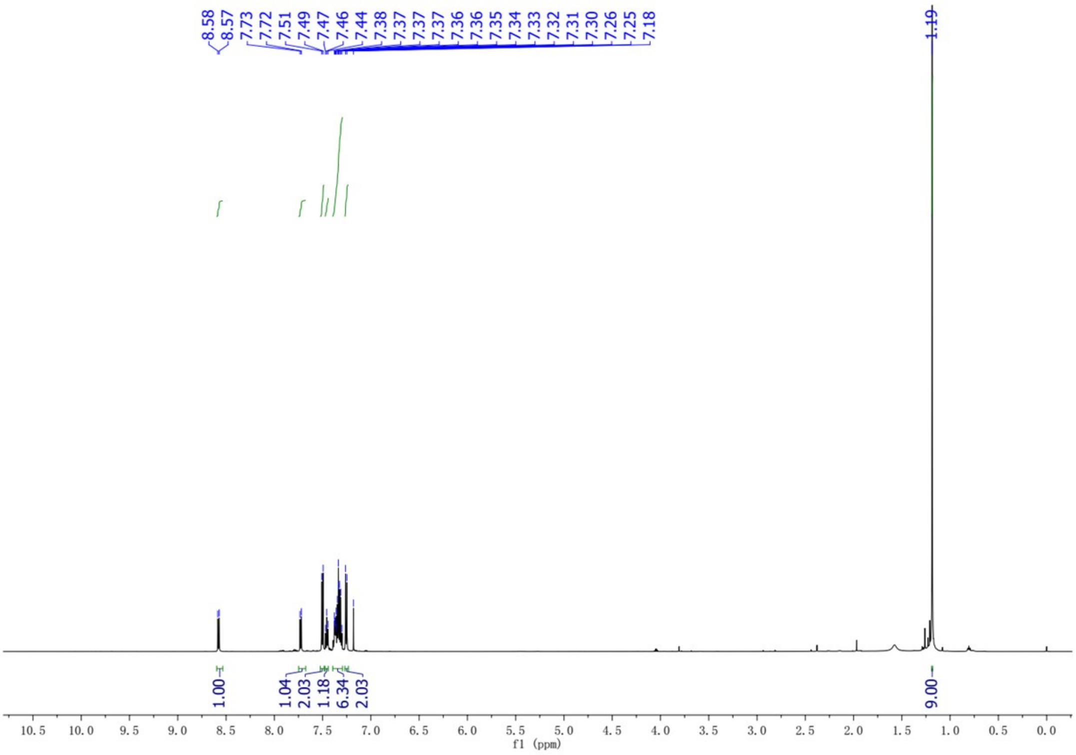
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
S
S
Ph
t-Bu

3c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7.36
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.26
7.25
7.18
1.19
1.00
1.04
2.03
1.18
6.34
2.03
9.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
5.5
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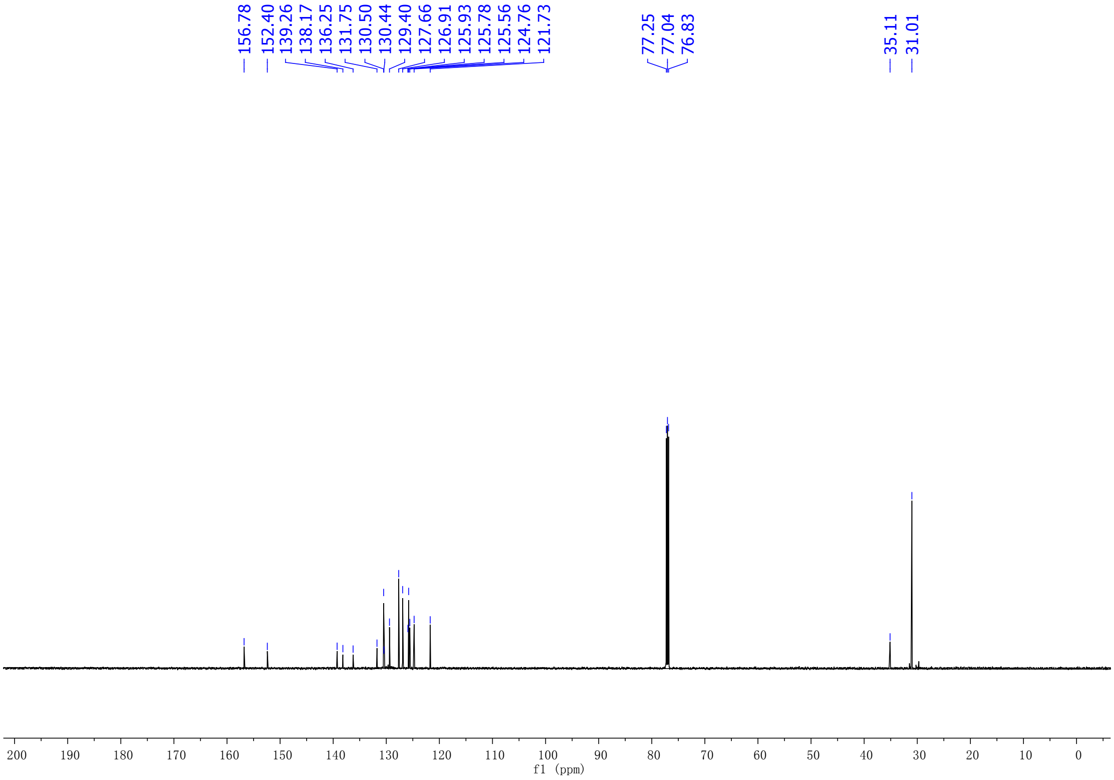
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125.93
125.78
125.56
124.76
121.73
77.25
77.04
76.83
35.11
31.01
200
190
180
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140
130
120
110
100
90
80
70
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50
40
30
20
10
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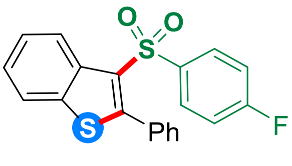
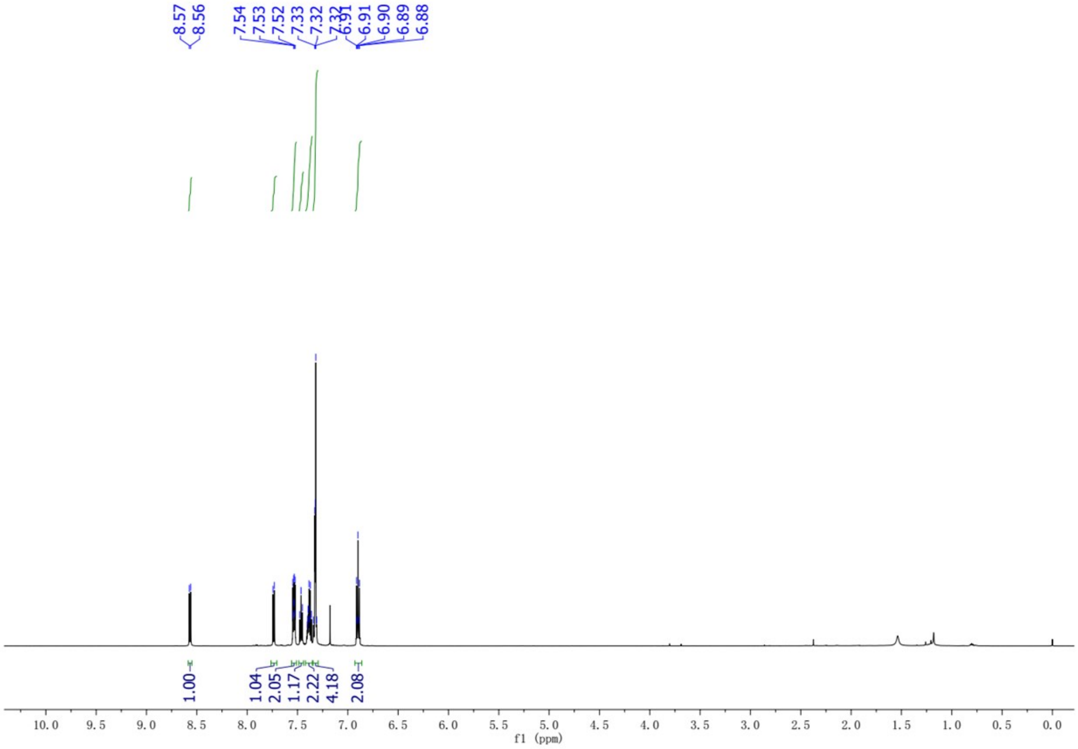
f1 (ppm)


O
O
S
S
Ph
F

3d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7.33
7.32
7.32
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6.91
6.90
6.89
6.88
1.00
1.04
2.05
1.17
2.22
4.18
2.08
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
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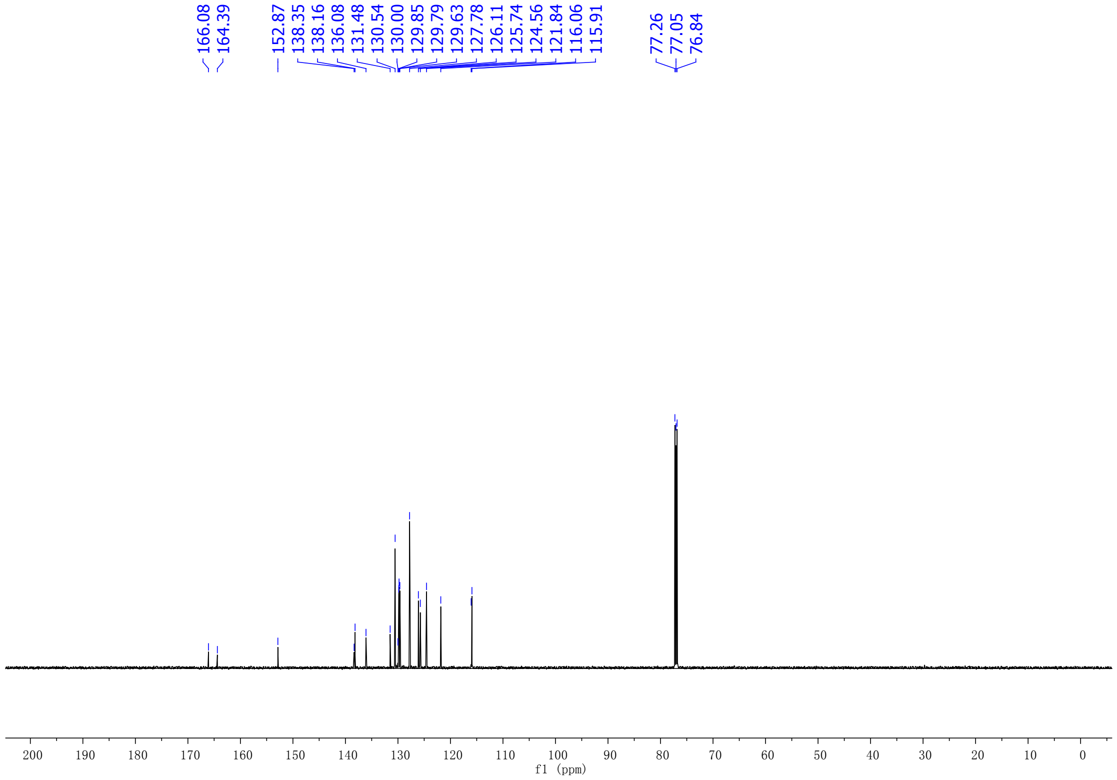
0.0
f1 (ppm)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129.63
127.78
126.11
125.74
124.56
121.84
116.06
115.91
77.26
77.05
76.84
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
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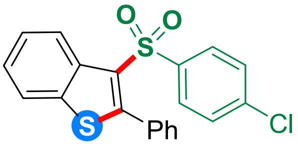
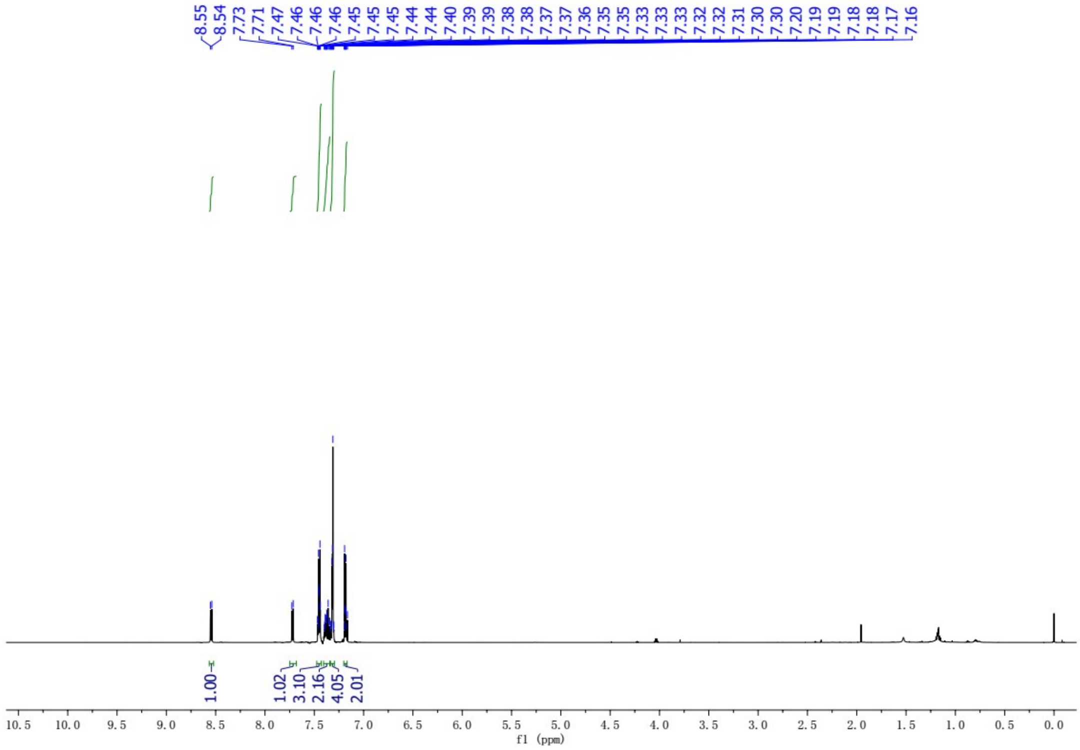
30
20
10
0
f1 (ppm)


O
O
S
S
Ph
Cl

3e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7.46
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7.45
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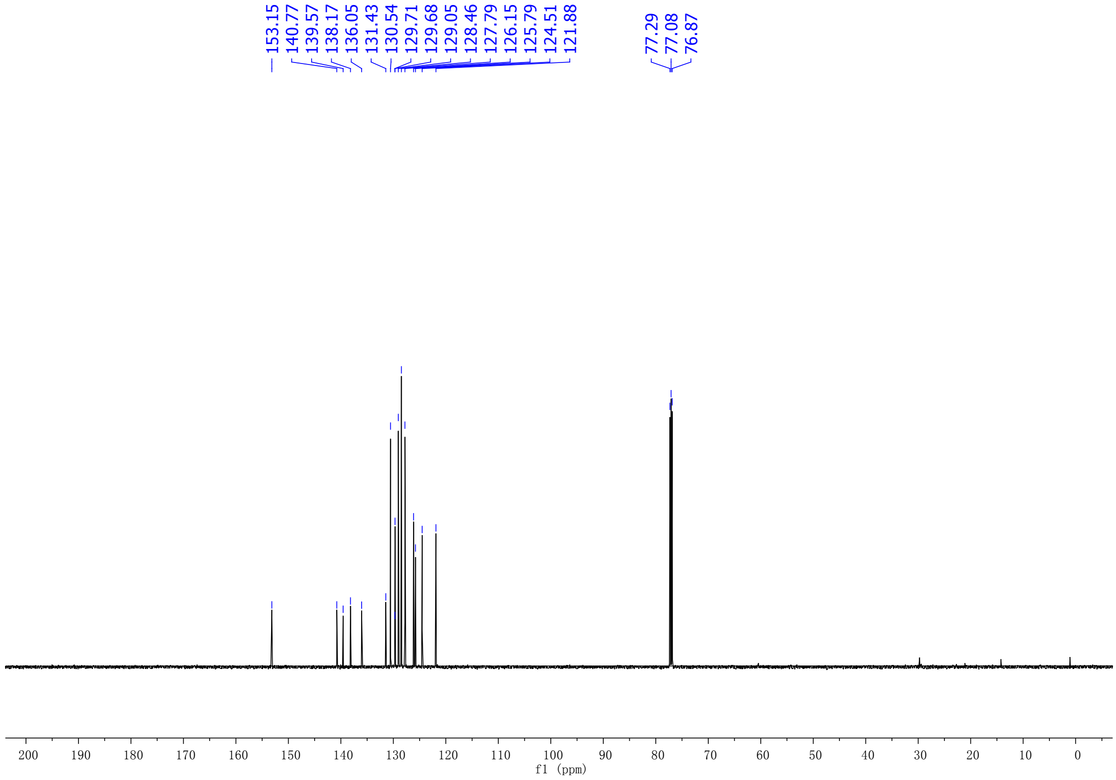
7.44
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.33
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.20
7.19
7.19
7.18
7.18
7.17
7.16
1.00
1.02
3.10
2.16
4.05
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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131.43
130.54
129.71
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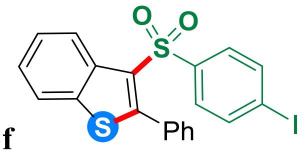
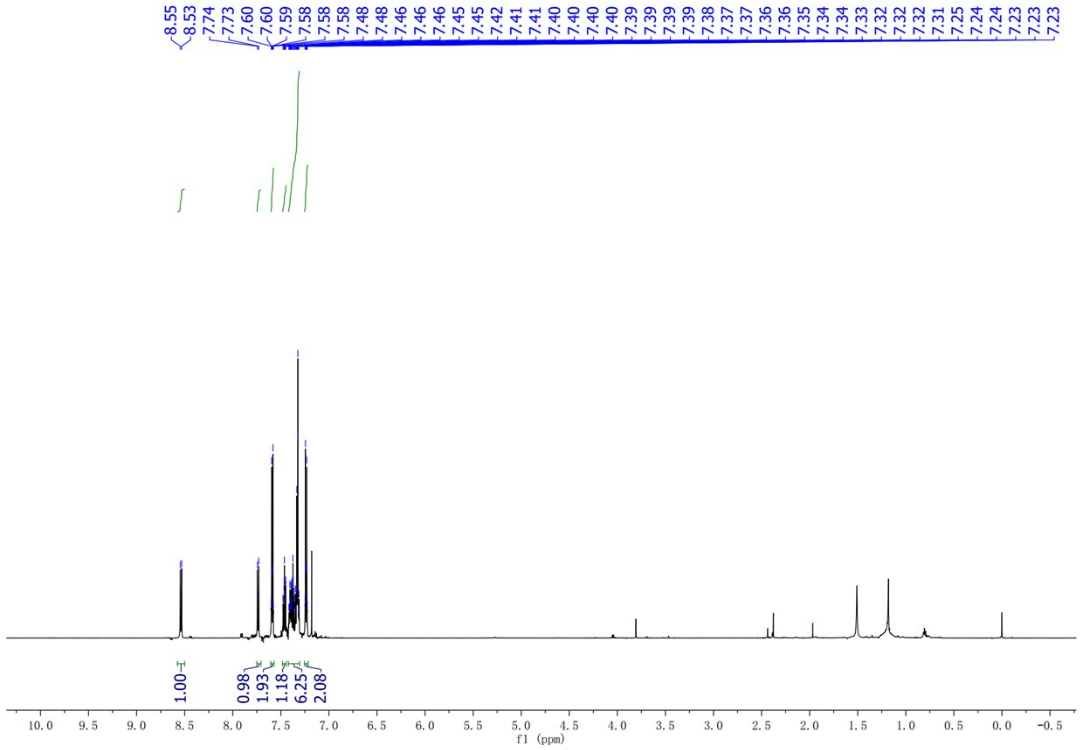
129.05
128.46
127.79
126.15
125.79
124.51
121.88
77.29
77.08
76.87
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
S
S
Ph
I

3f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7.58
7.58
7.58
7.48
7.48
7.46
7.46
7.46
7.45
7.45
7.42
7.41
7.41
7.40
7.40
7.40
7.40
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7.39
7.39
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7.38
7.37
7.37
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7.34
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7.33
7.32
7.32
7.32
7.31
7.25
7.24
7.24
7.23
7.23
7.23
1.00
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1.93
1.18
6.25
2.08
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
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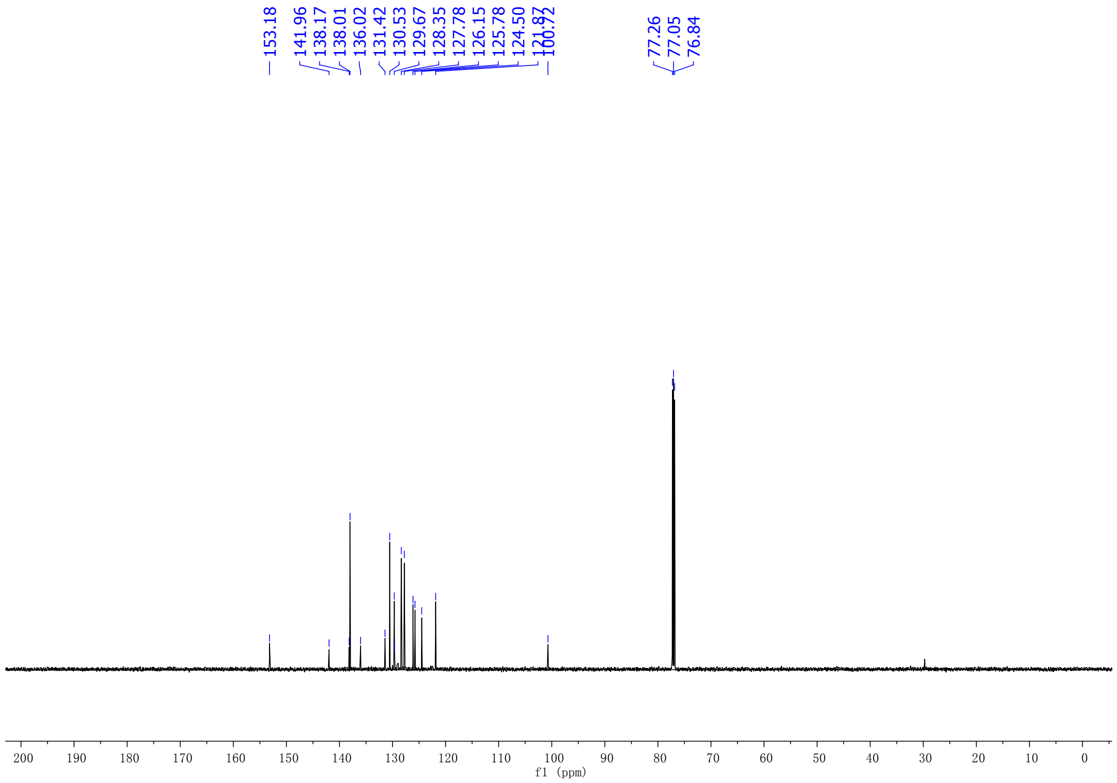
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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125.78
124.50
121.87
100.72
77.26
77.05
76.84
200
190
180
170
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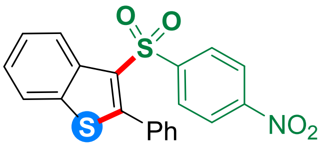
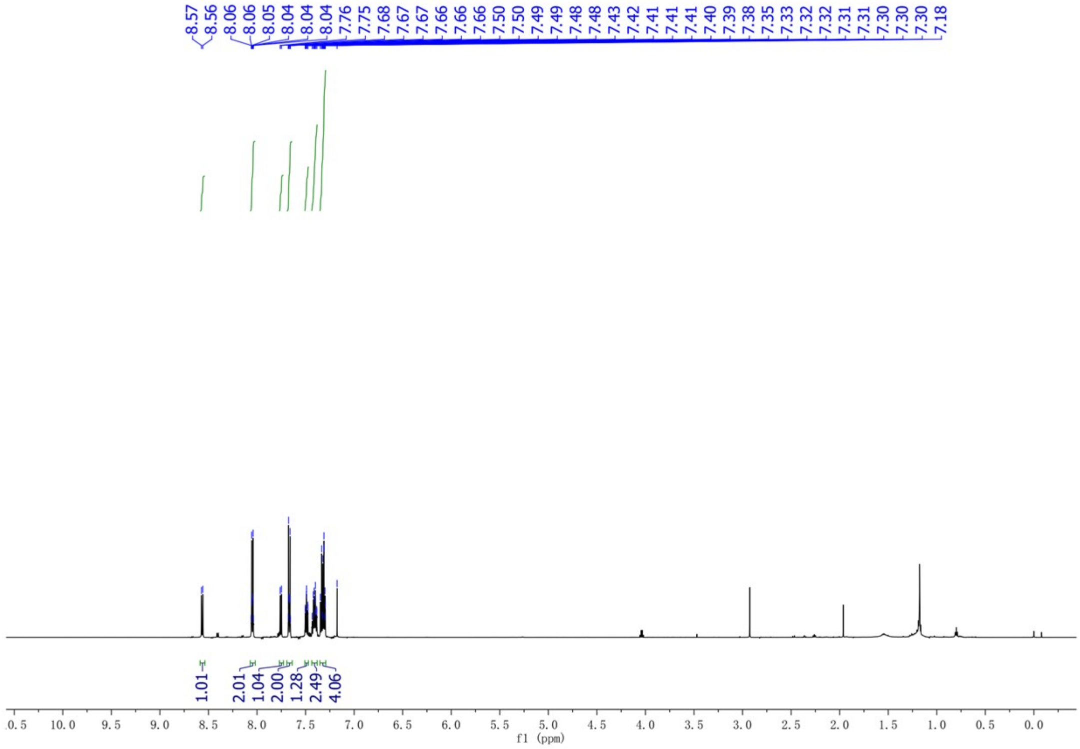
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
S
Ph
NO2

3g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8.04
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7.75
7.68
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7.67
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7.66
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7.50
7.49
7.49
7.48
7.48
7.43
7.42
7.41
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7.41
7.40
7.39
7.38
7.35
7.33
7.32
7.32
7.31
7.30
7.30
7.30
7.18
1.01
2.01
1.04
2.00
1.28
2.49
4.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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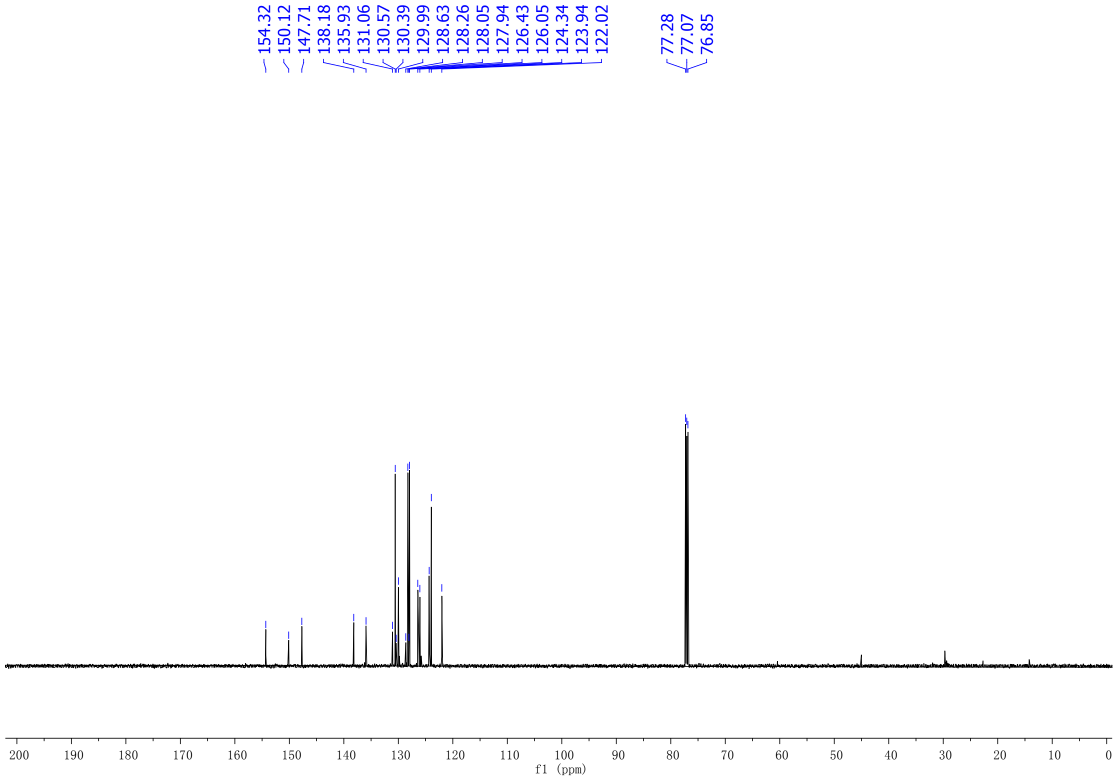
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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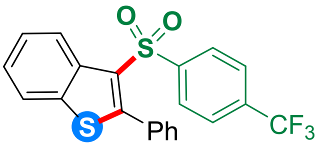
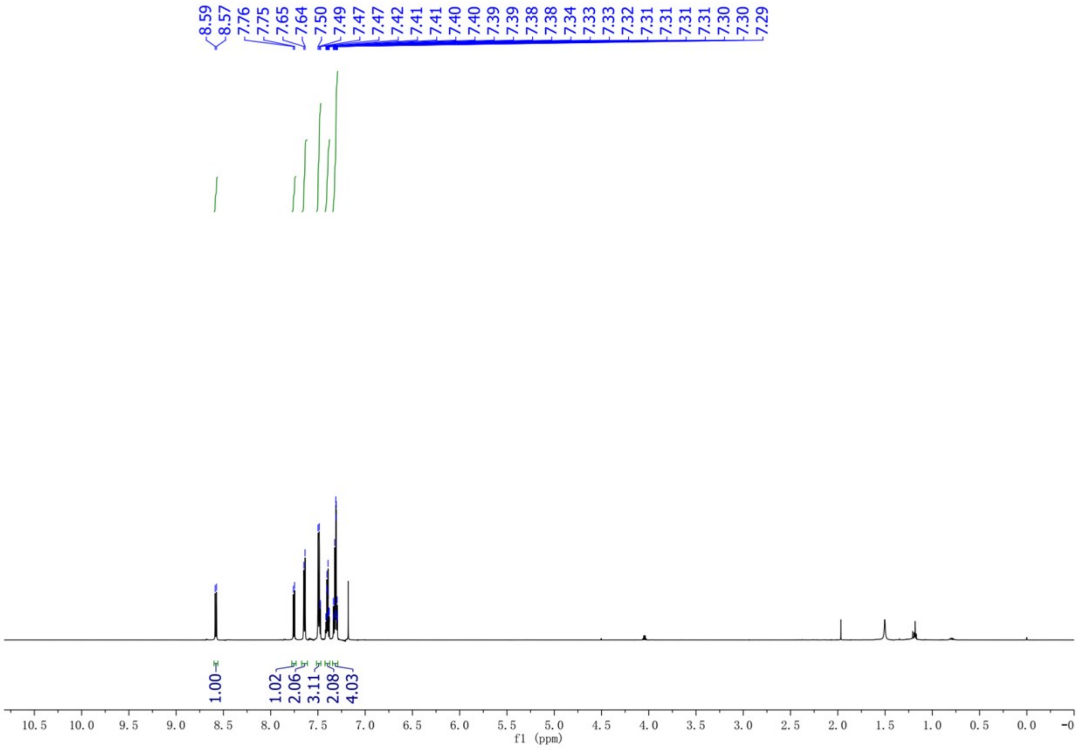
130.39
129.99
128.63
128.26
128.05
127.94
126.43
126.05
124.34
123.94
122.02
77.28
77.07
76.85
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
S
Ph
CF3

3h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7.33
7.33
7.32
7.31
7.31
7.31
7.31
7.30
7.30
7.29
1.00
1.02
2.06
3.11
2.08
4.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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1.0
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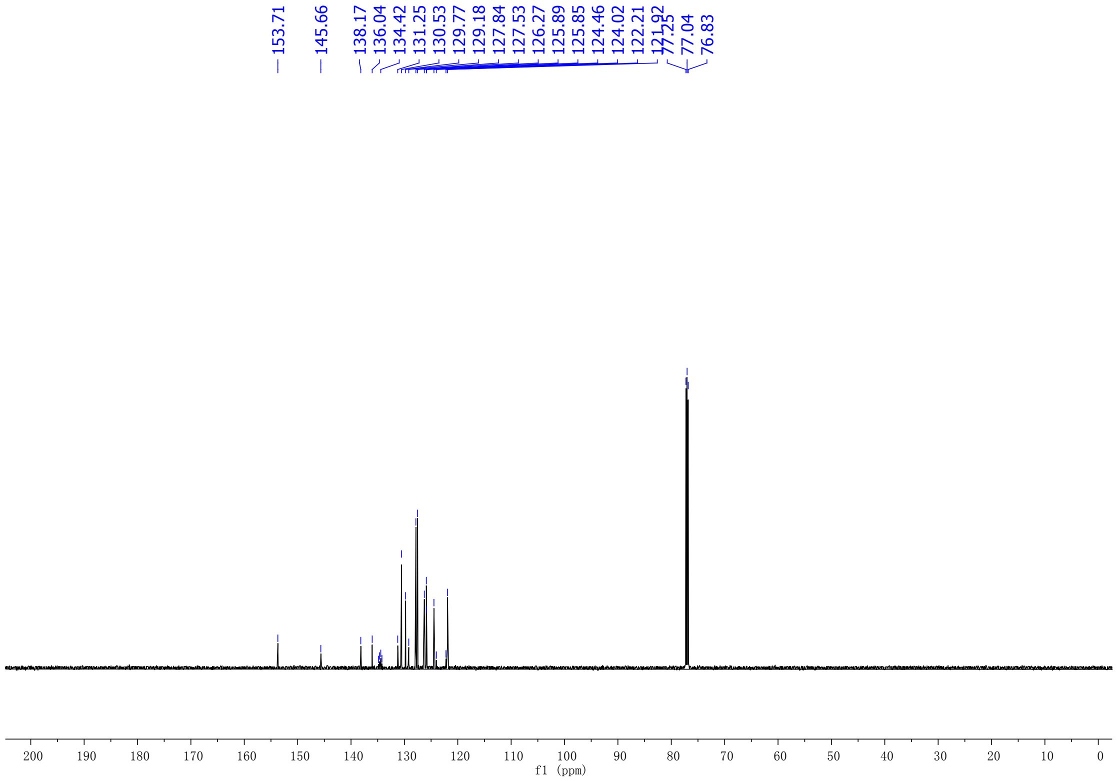
−0
f1 (ppm)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127.53
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125.89
125.85
124.46
124.02
122.21
121.92
77.25
77.04
76.83
200
190
180
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130
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110
100
90
80
70
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50
40
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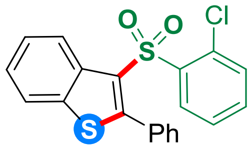
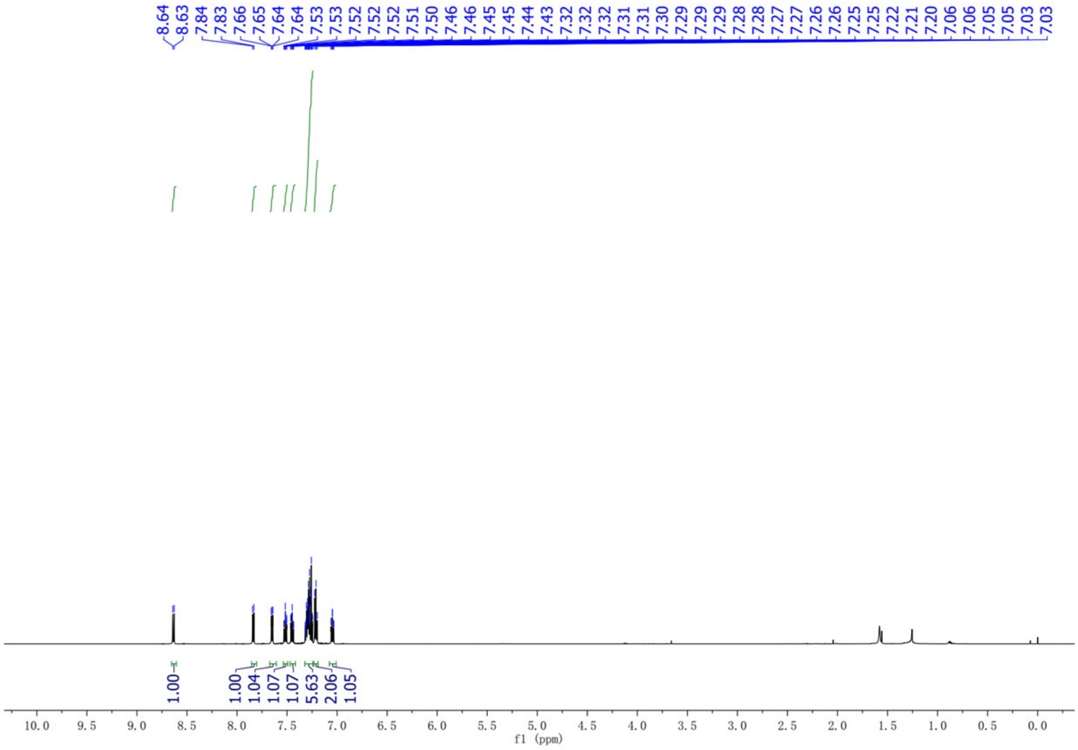
20
10
0
f1 (ppm)


O
O
S
Cl
S
Ph

3i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7.46
7.45
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7.29
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7.25
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7.20
7.06
7.06
7.05
7.05
7.03
7.03
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1.00
1.04
1.07
1.07
5.63
2.06
1.05
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9.5
9.0
8.5
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7.5
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6.5
6.0
5.5
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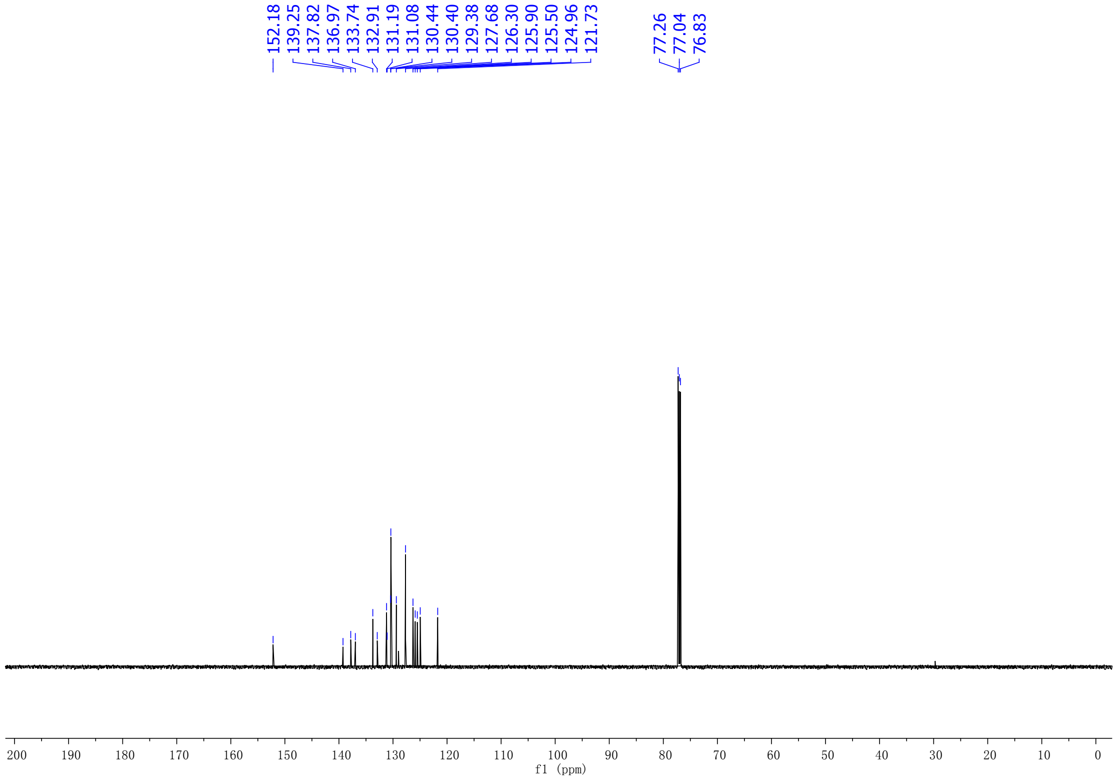
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.38
127.68
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125.90
125.50
124.96
121.73
77.26
77.04
76.83
200
190
180
170
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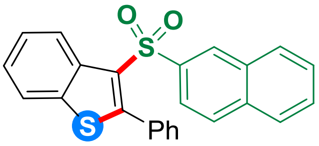
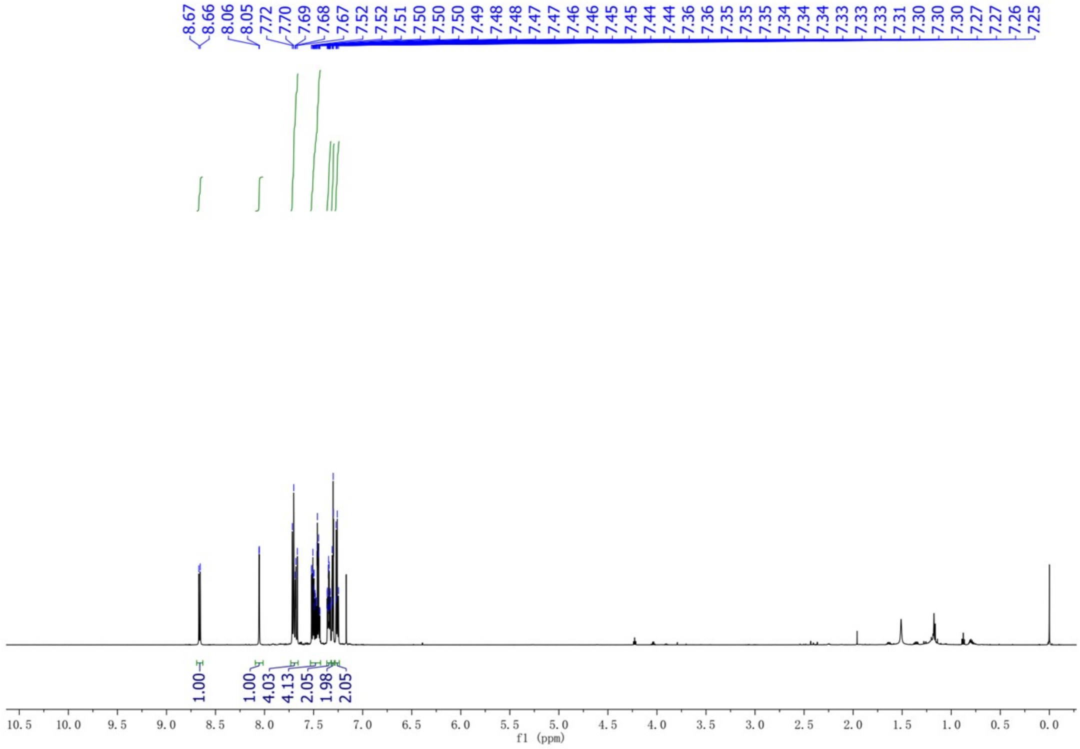
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
S
Ph

3j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7.45
7.44
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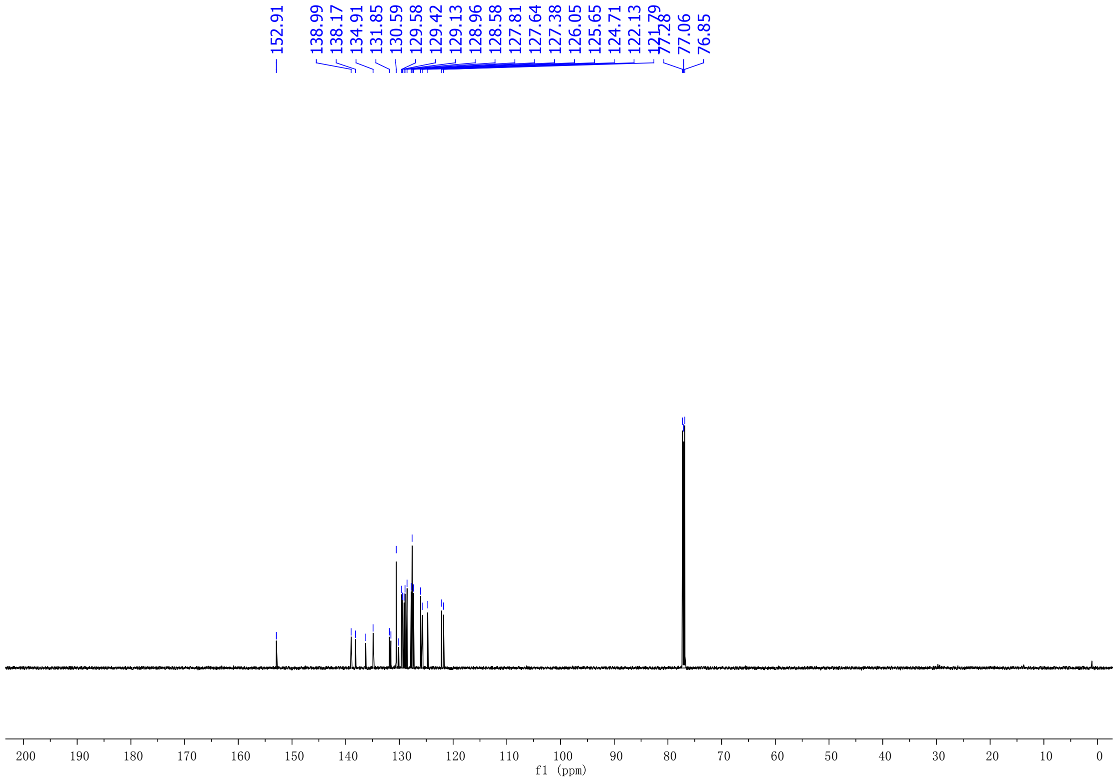
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.96
128.58
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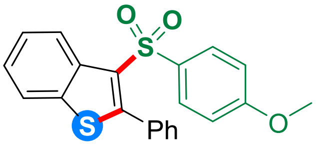
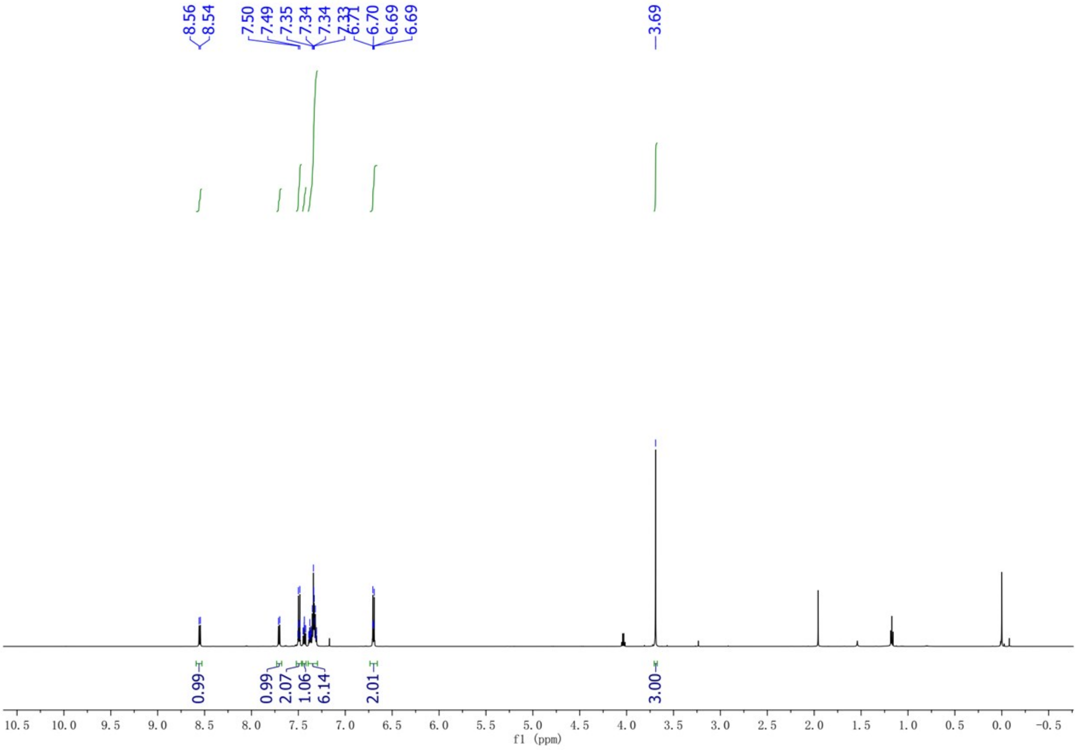
127.64
127.38
126.05
125.65
124.71
122.13
121.79
77.28
77.06
76.85
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
S
S
Ph
O

3k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7.50
7.49
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7.34
7.33
6.71
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6.69
6.69
3.69
0.99
0.99
2.07
1.06
6.14
2.01
3.00
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
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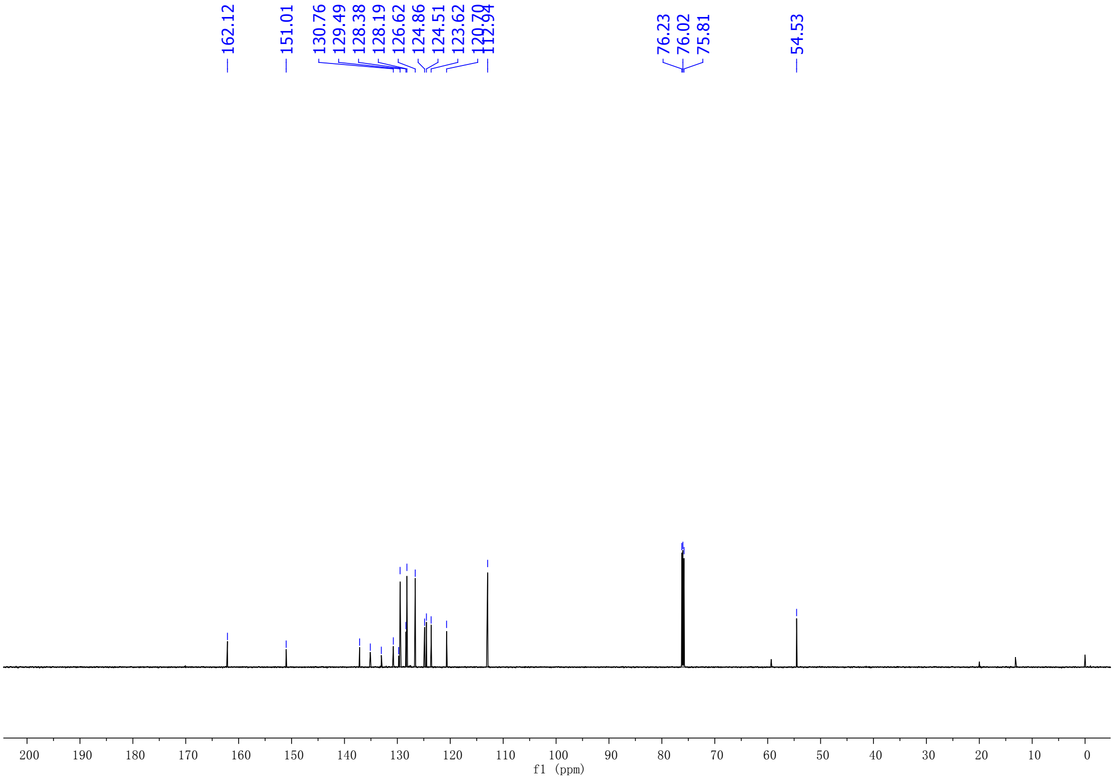
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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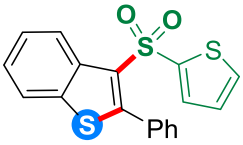
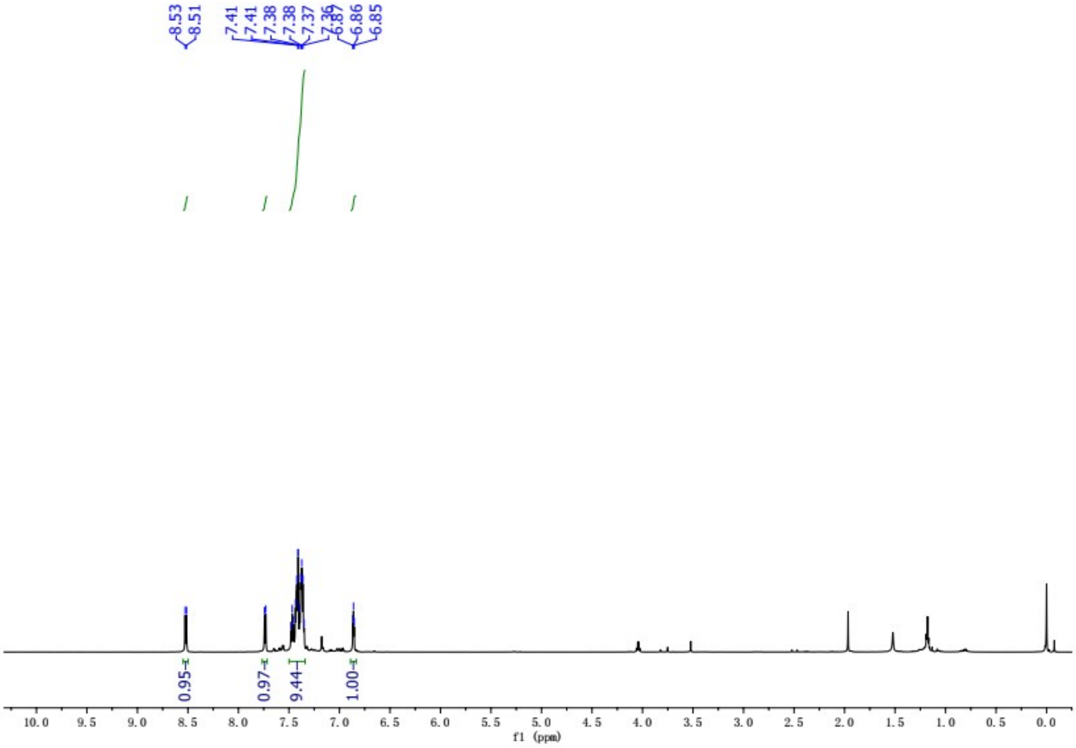
123.62
120.70
112.94
76.23
76.02
75.81
54.53
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3m


O
O
S
S
S
Ph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7.0
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6.0
5.5
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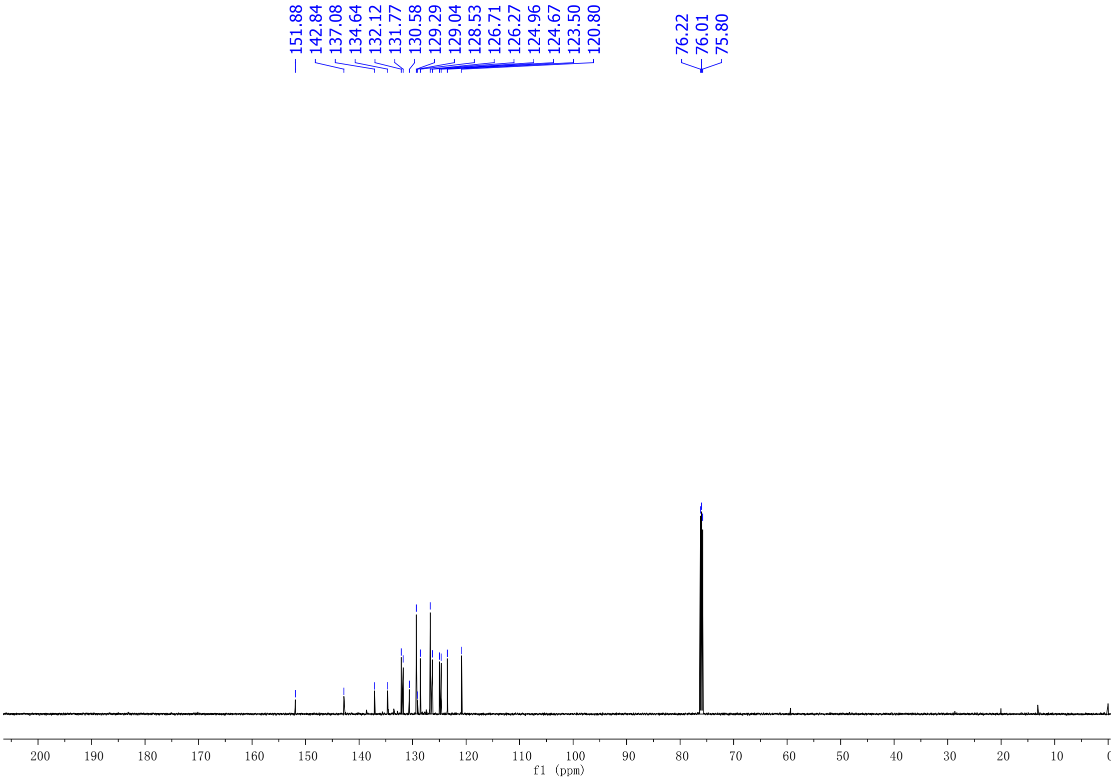
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124.67
123.50
120.80
76.22
76.01
75.80
200
190
180
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10
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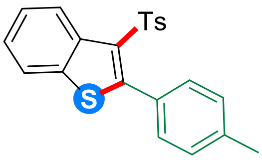
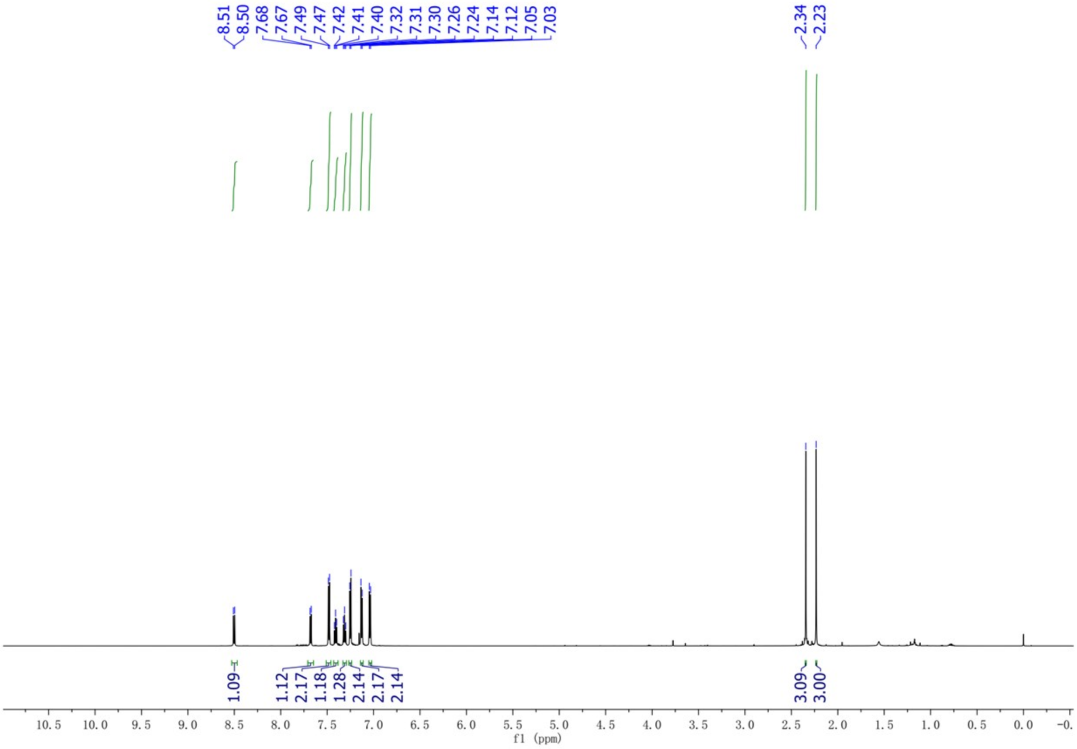
f1 (ppm)


Ts
S

3n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7.26
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7.14
7.12
7.05
7.03
2.34
2.23
1.09
1.12
2.17
1.18
1.28
2.14
2.17
2.14
3.09
3.00
10.5
10.0
9.5
9.0
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8.0
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7.0
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6.0
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5.0
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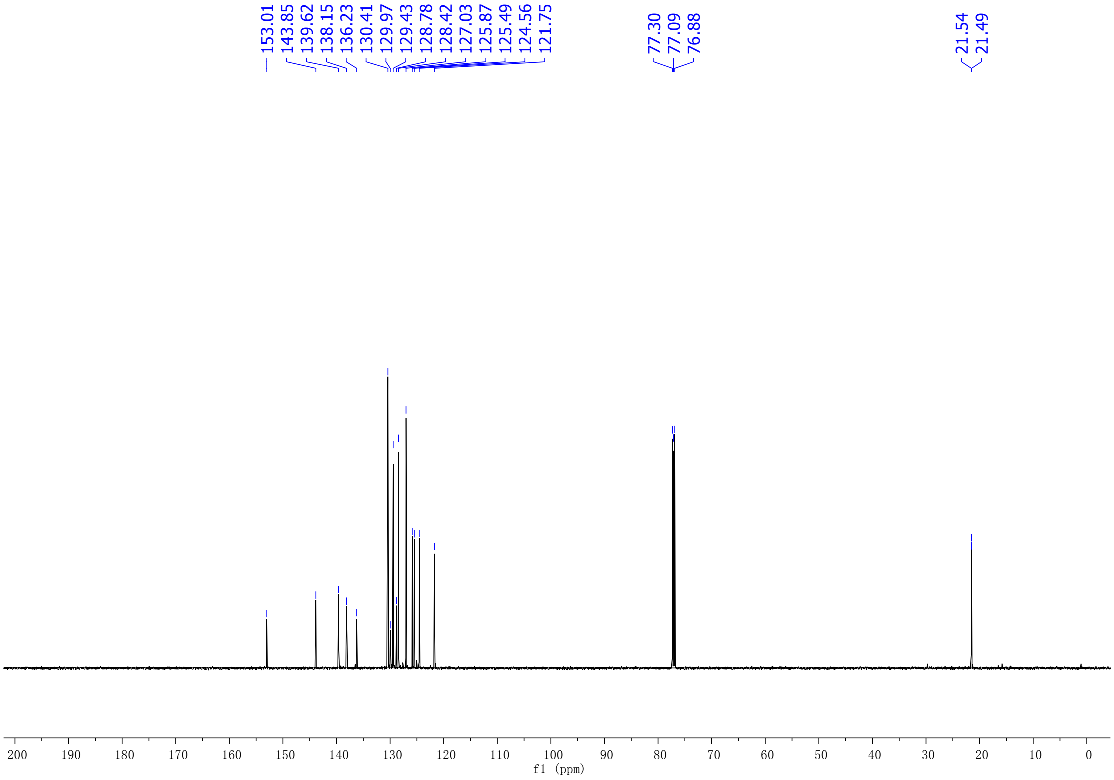
f1 (ppm)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128.42
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121.75
77.30
77.09
76.88
21.54
21.49
200
190
180
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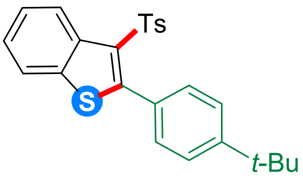
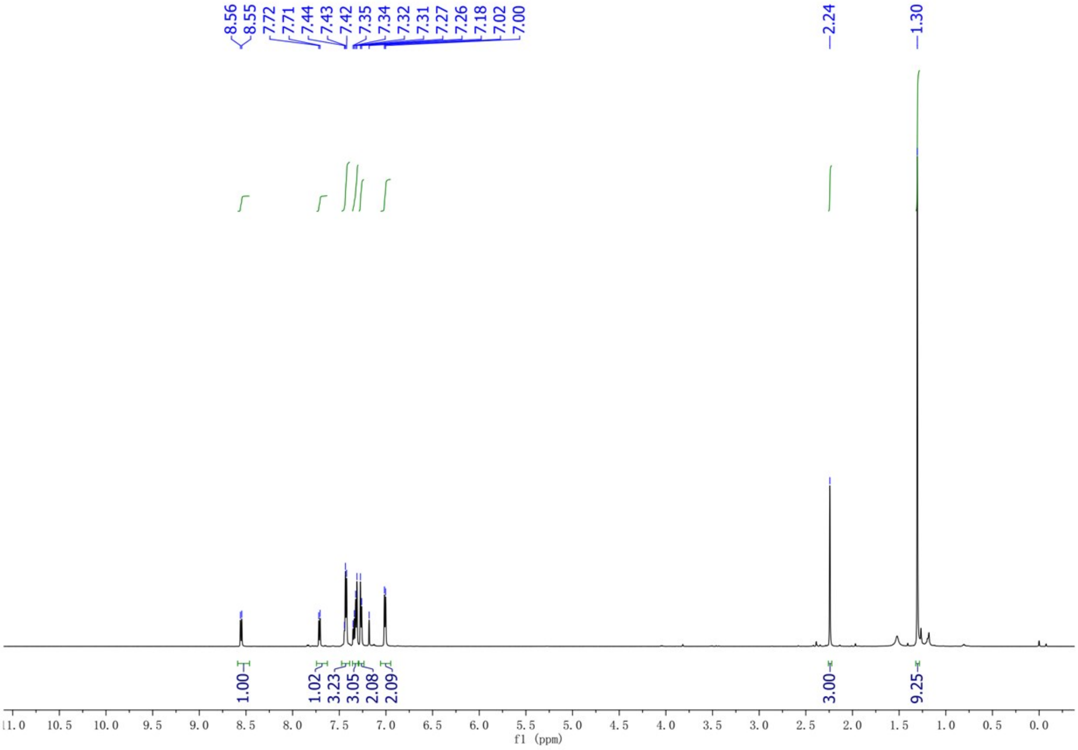

Ts
S
t-Bu

3o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7.32
7.31
7.27
7.26
7.18
7.02
7.00
2.24
1.30
1.00
1.02
3.23
3.05
2.08
2.09
3.00
9.25
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10.0
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1.0
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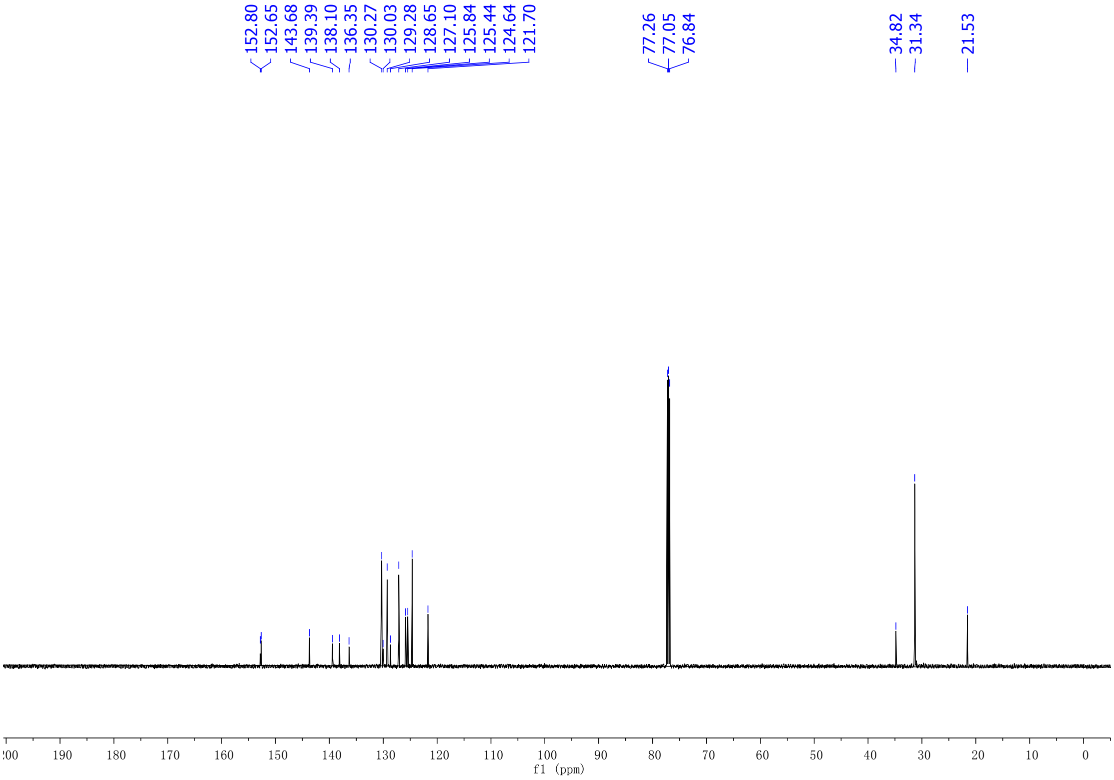
f1 (ppm)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77.26
77.05
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200
190
180
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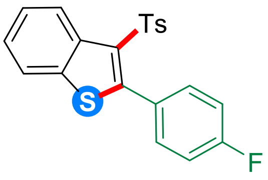
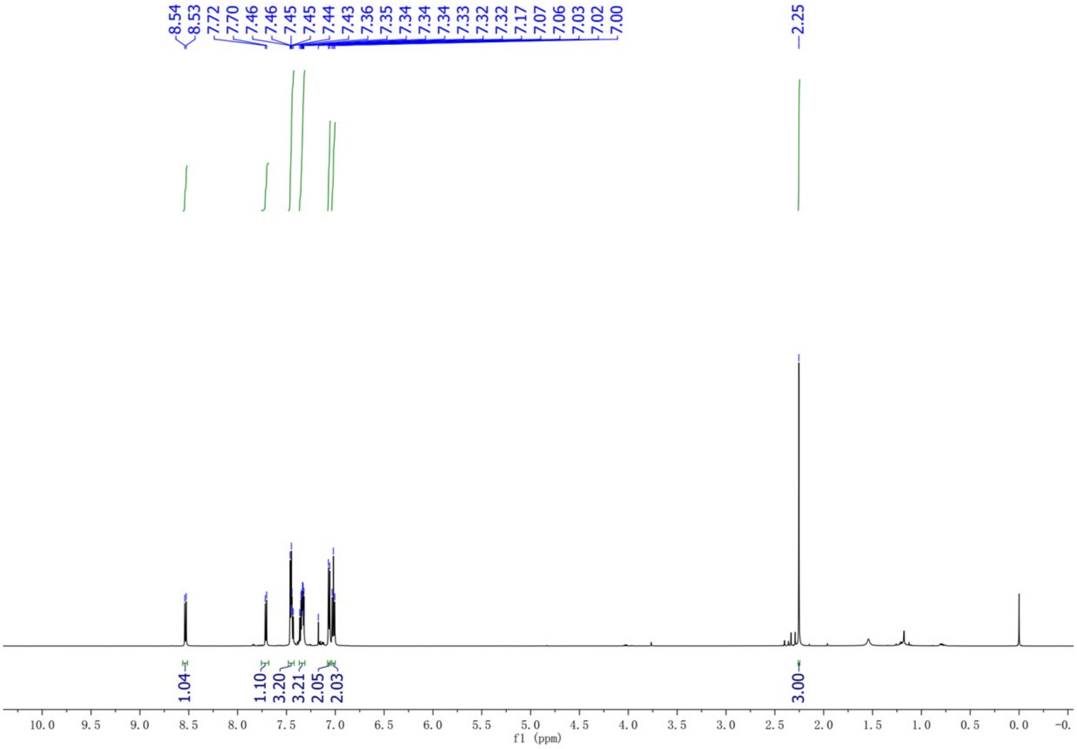

Ts
S
F

3p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7.45
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7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.17
7.07
7.06
7.03
7.02
7.00
2.25
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1.10
3.20
3.21
2.05
2.03
3.00
10.0
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9.0
8.5
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7.5
7.0
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6.0
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5.0
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2.0
1.5
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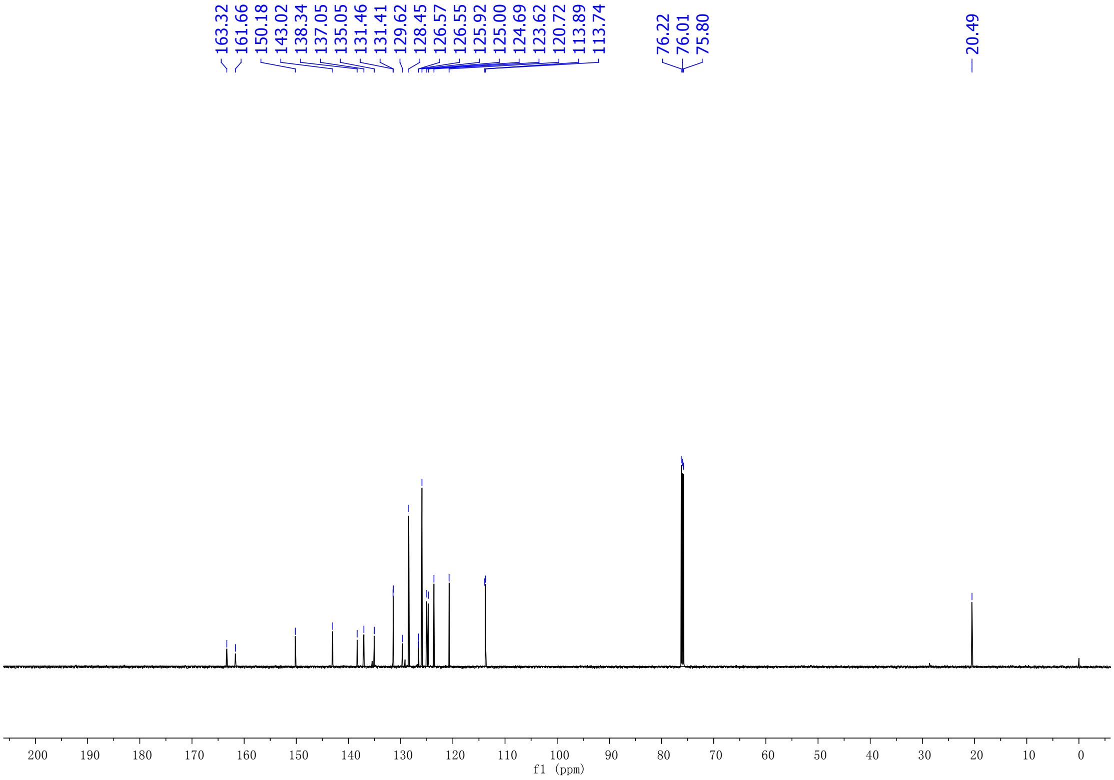
f1 (ppm)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129.62
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126.55
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125.00
124.69
123.62
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113.74
76.22
76.01
75.80
20.49
200
190
180
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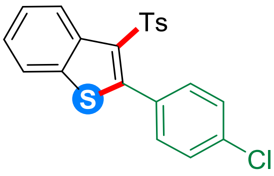
f1 (ppm)


Ts
S
Cl

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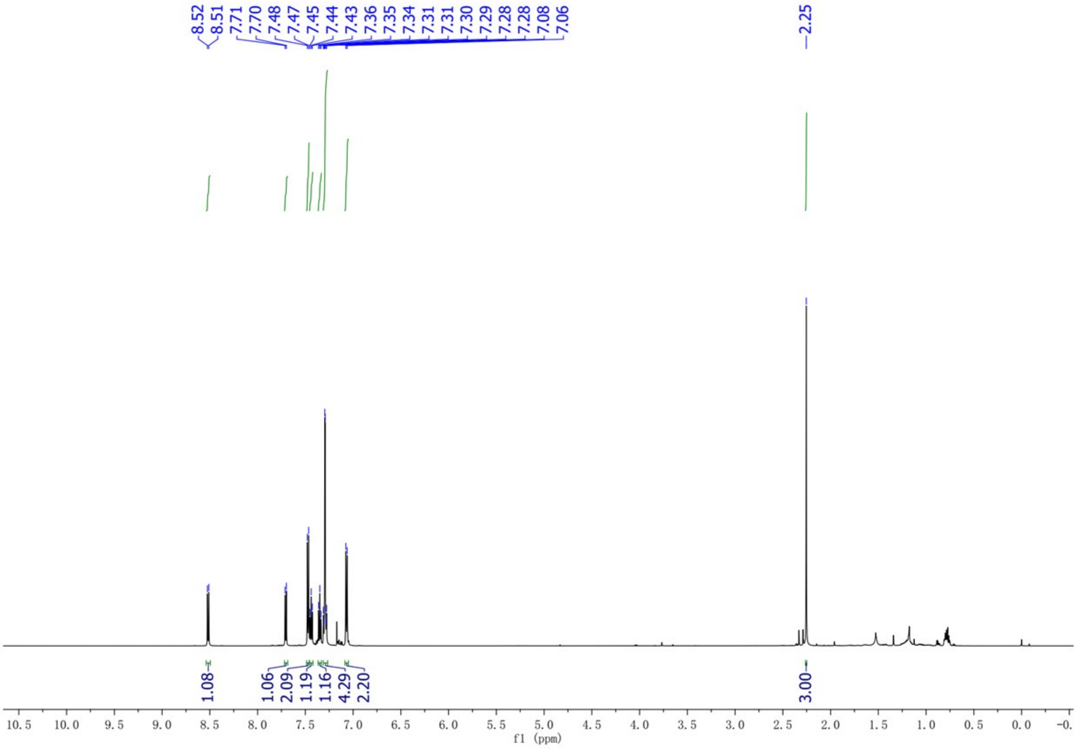
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7.45
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7.43
7.36
7.35
7.34
7.31
7.31
7.30
7.29
7.28
7.28
7.08
7.06
2.25
1.08
1.06
2.09
1.19
1.16
4.29
2.20
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.0
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5.0
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2.0
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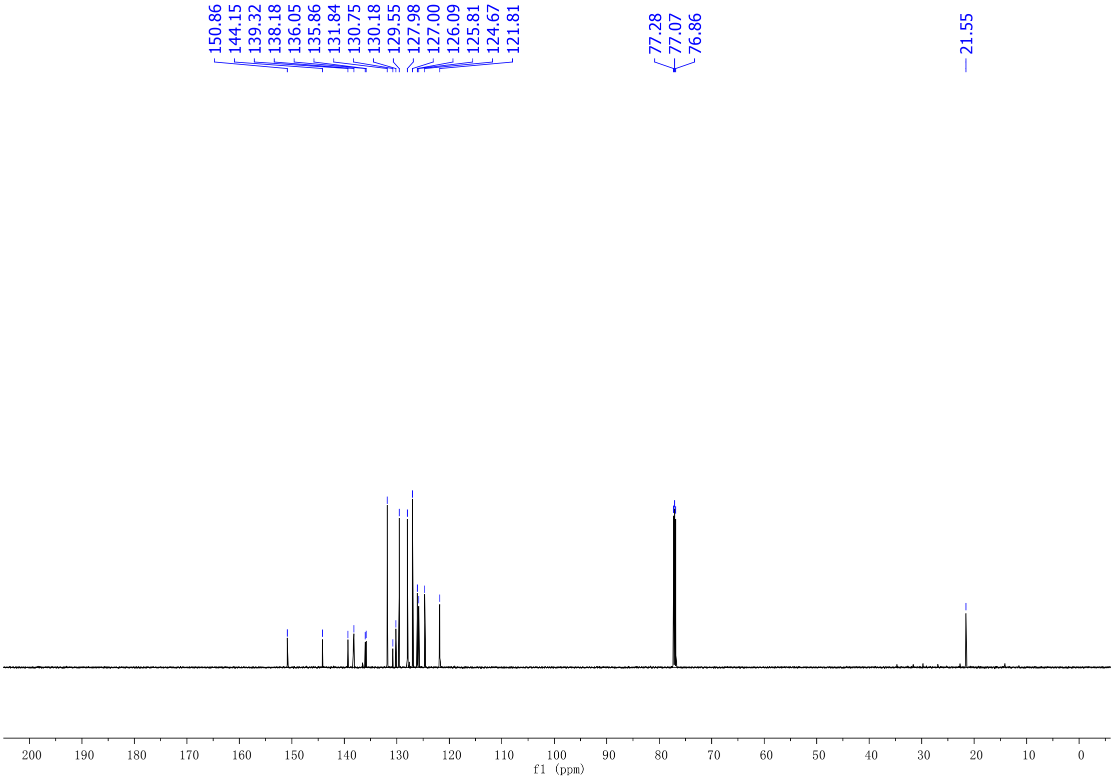
f1 (ppm)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126.09
125.81
124.67
121.81
77.28
77.07
76.86
21.55
200
190
180
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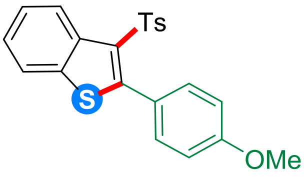
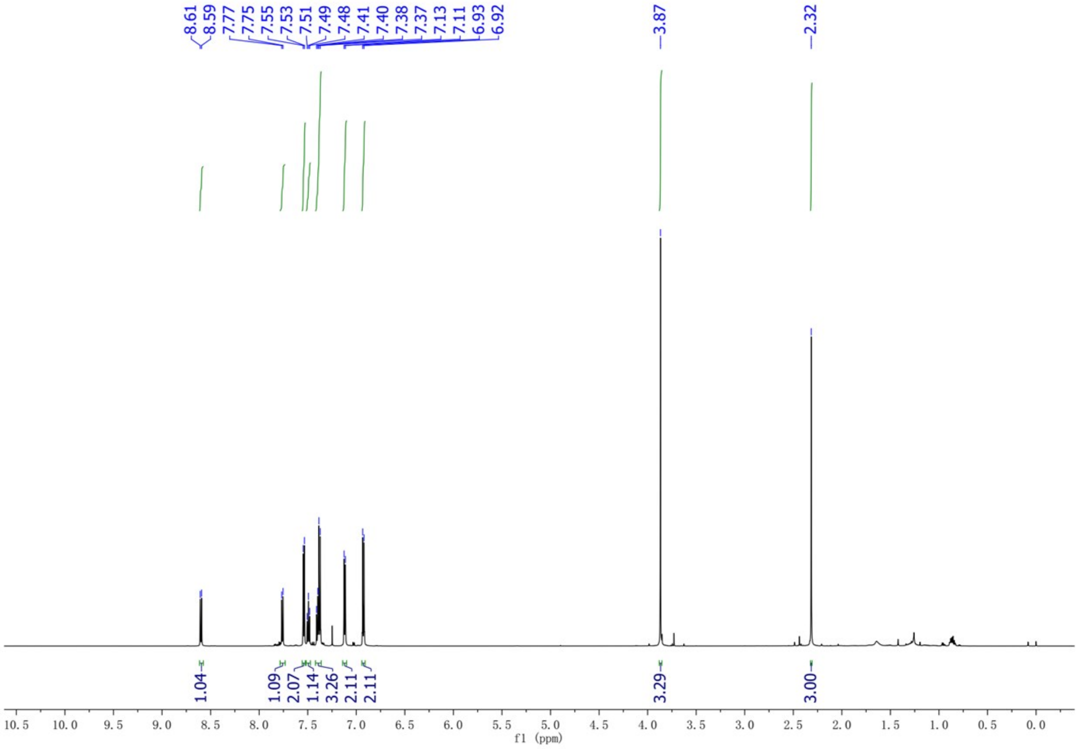
f1 (ppm)


Ts
S
OMe

3r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7.37
7.13
7.11
6.93
6.92
3.87
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1.04
1.09
2.07
1.14
3.26
2.11
2.11
3.29
3.00
10.5
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9.5
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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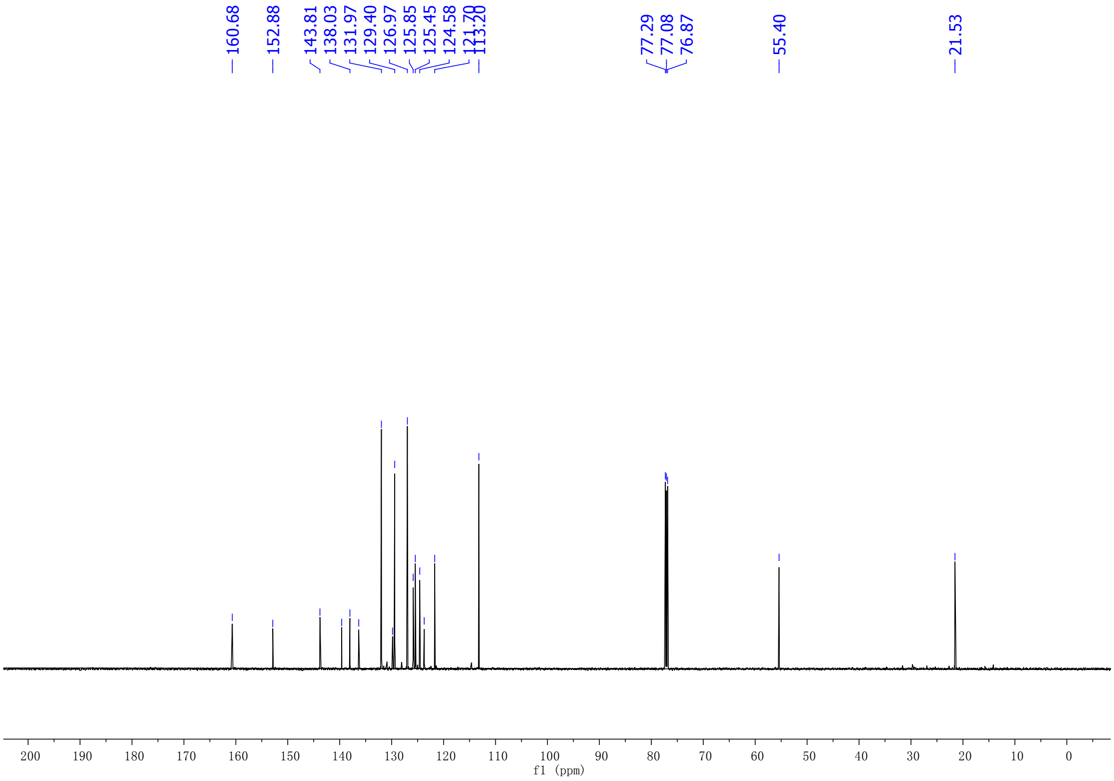
f1 (ppm)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113.20
77.29
77.08
76.87
55.40
21.53
200
190
180
170
160
150
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130
120
110
100
90
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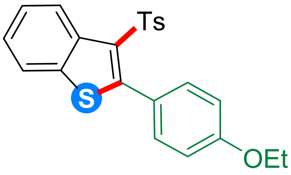
f1 (ppm)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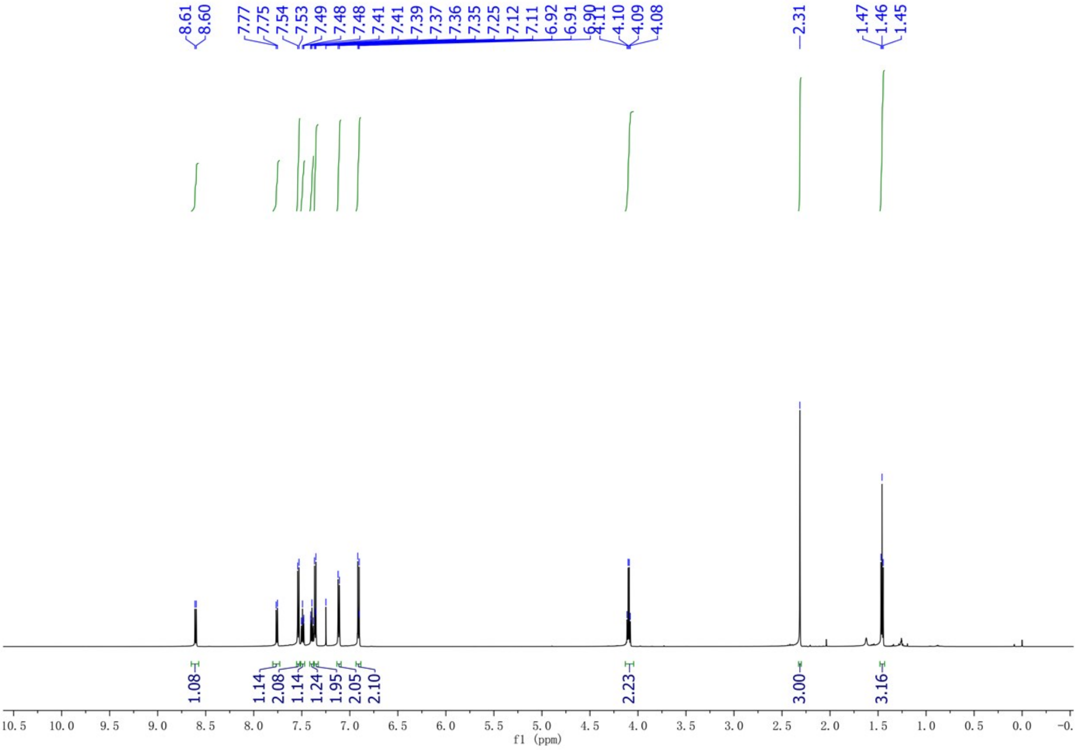
S
OEt

3s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7.35
7.25
7.12
7.11
6.92
6.91
6.90
4.11
4.10
4.09
4.08
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1.47
1.46
1.45
1.08
1.14
2.08
1.14
1.24
1.95
2.05
2.10
2.23
3.00
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6.0
5.5
5.0
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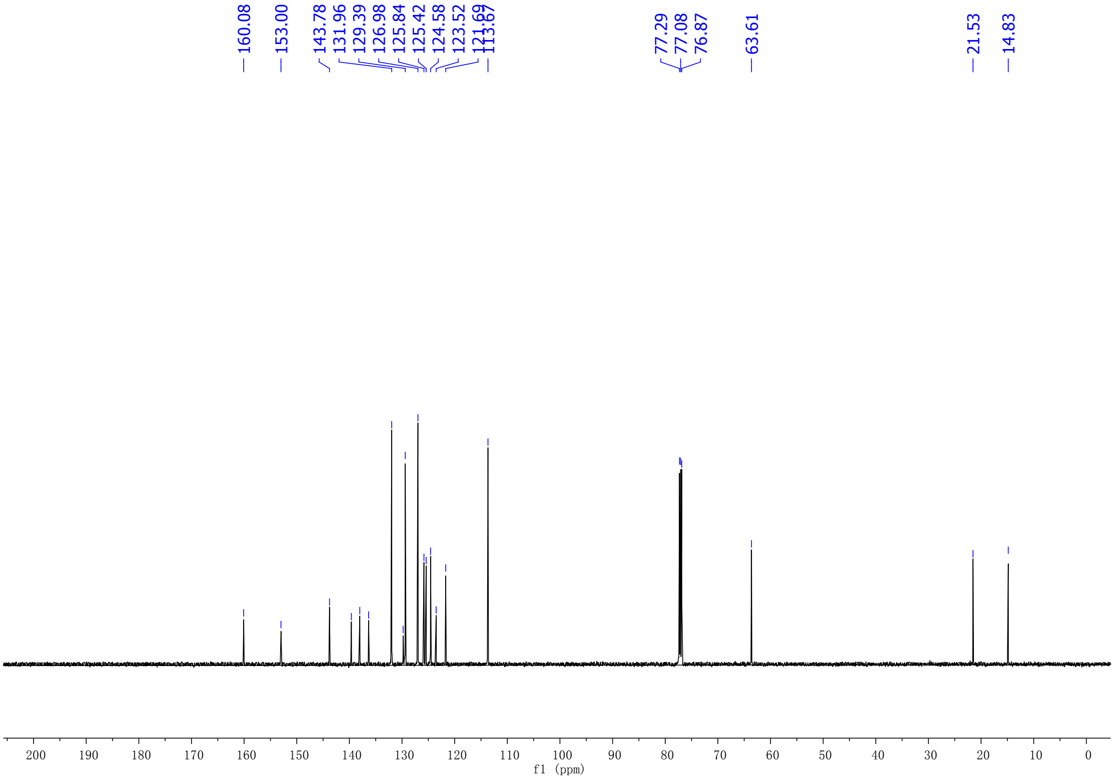
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113.67
77.29
77.08
76.87
63.61
21.53
14.83
200
190
180
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90
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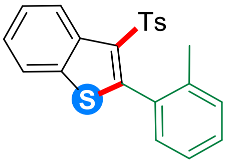
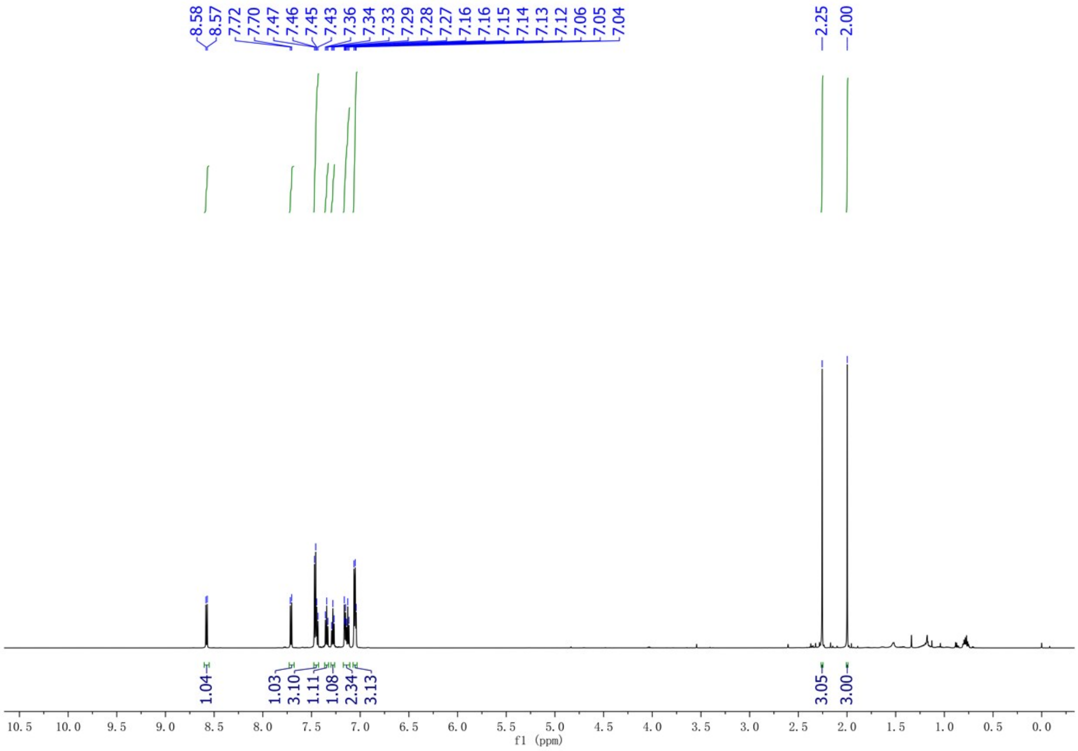
f1 (ppm)


Ts
S

3t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7.27
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7.15
7.14
7.13
7.12
7.06
7.05
7.04
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2.00
1.04
1.03
3.10
1.11
1.08
2.34
3.13
3.05
3.00
10.5
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7.0
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6.0
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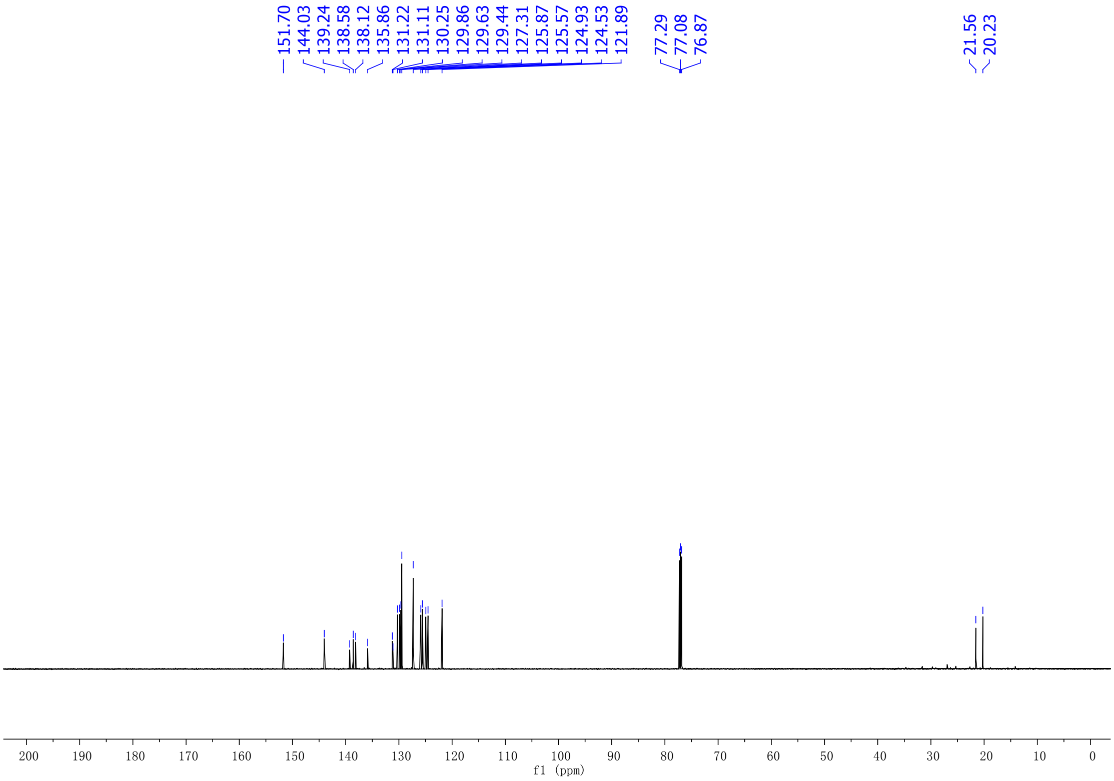
f1 (ppm)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129.86
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125.87
125.57
124.93
124.53
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77.29
77.08
76.87
21.56
20.23
200
190
180
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10
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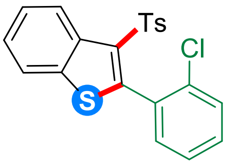
f1 (ppm)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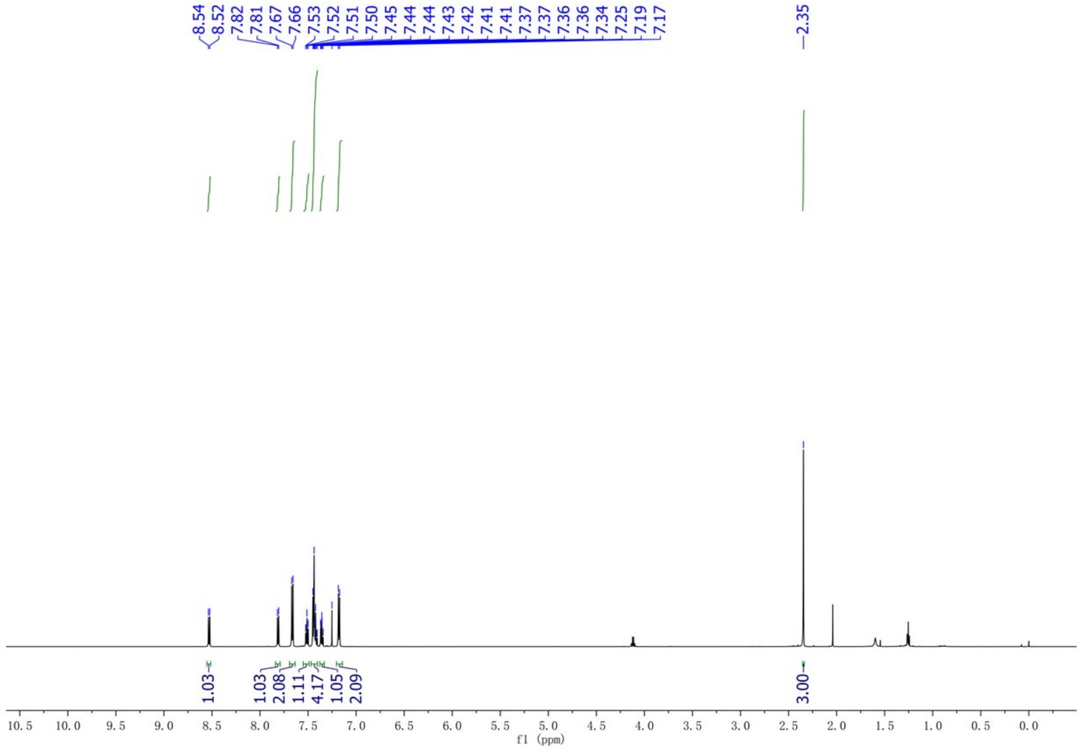
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7.36
7.34
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1.03
2.08
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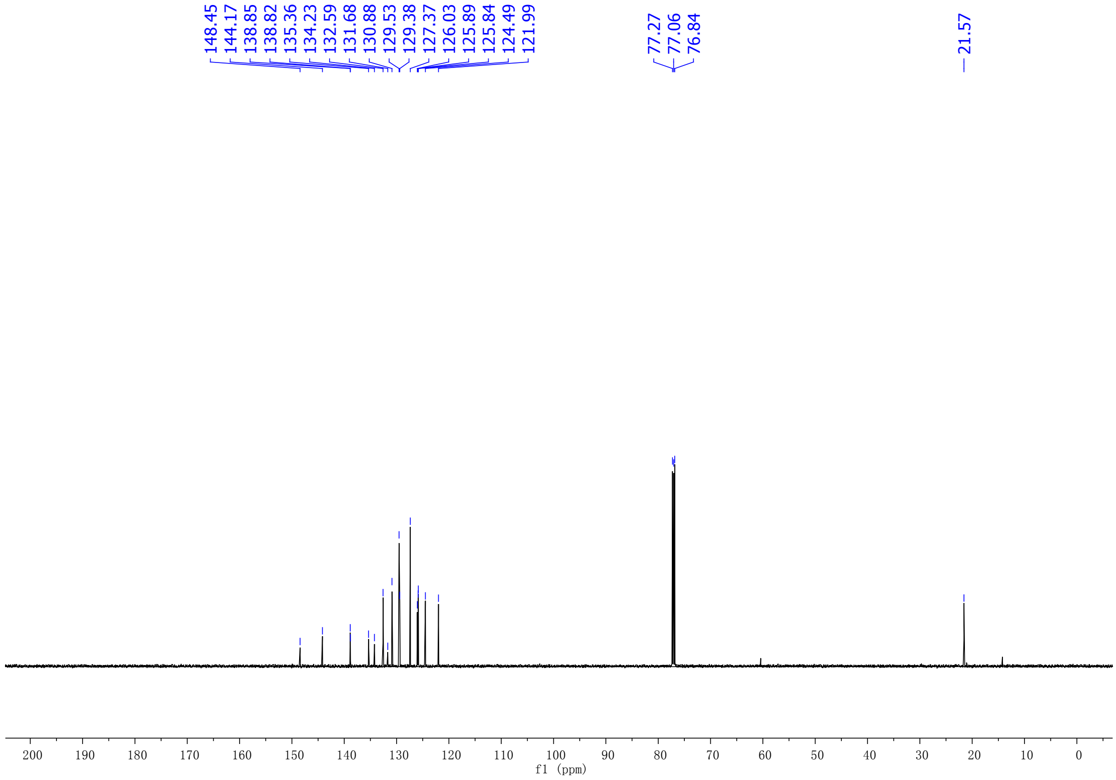
f1 (ppm)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126.03
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125.84
124.49
121.99
77.27
77.06
76.84
21.57
200
190
180
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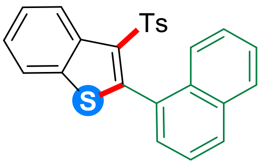
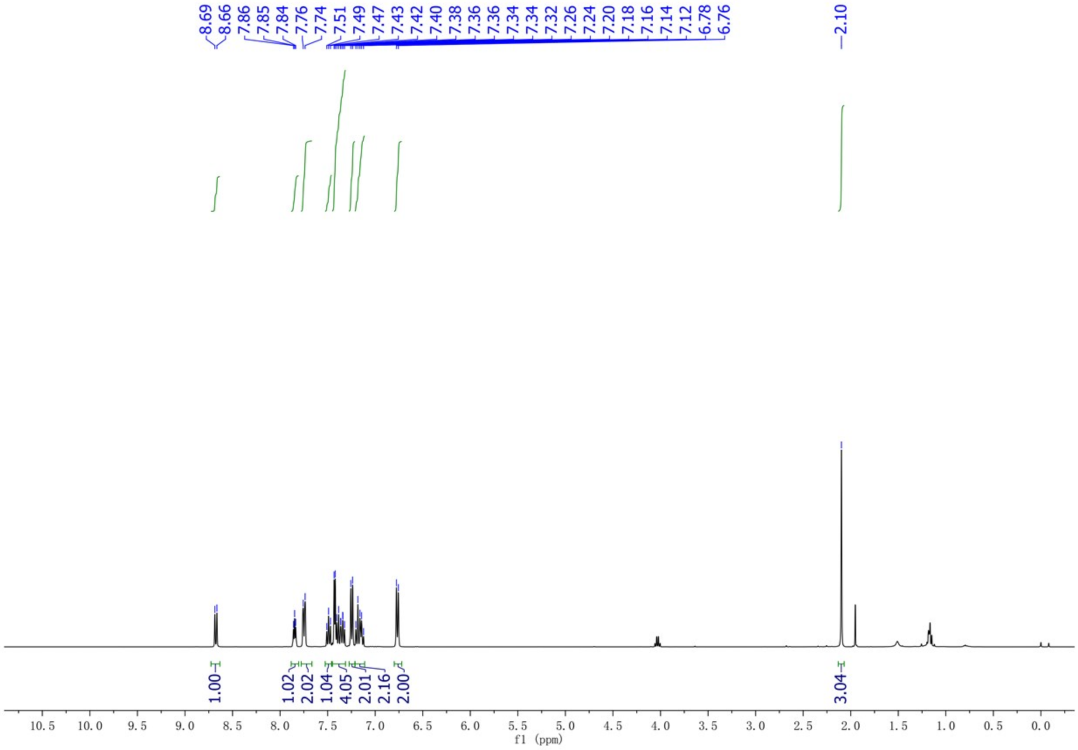
f1 (ppm)


Ts
S

3v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7.36
7.36
7.34
7.34
7.32
7.26
7.24
7.20
7.18
7.16
7.14
7.12
6.78
6.76
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1.00
1.02
2.02
1.04
4.05
2.01
2.16
2.00
3.04
10.5
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5.5
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1.0
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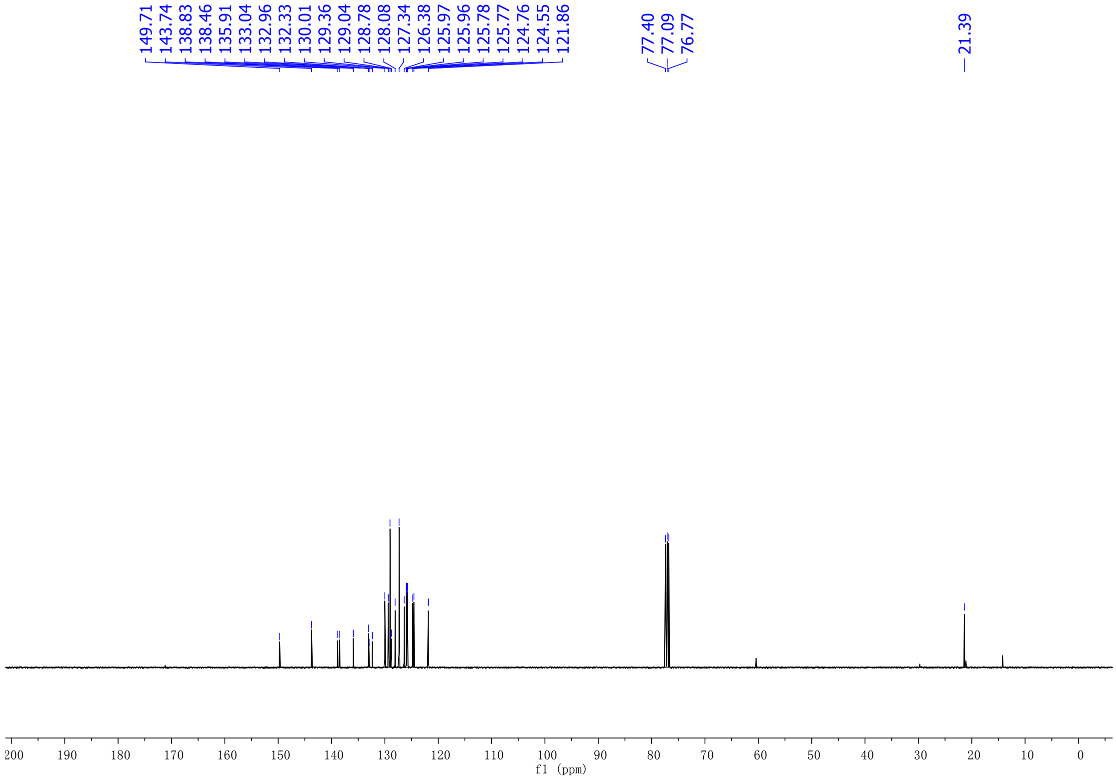
0.0
f1 (ppm)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200
190
180
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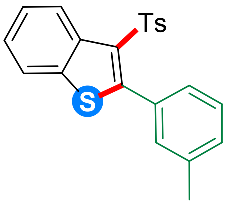
f1 (ppm)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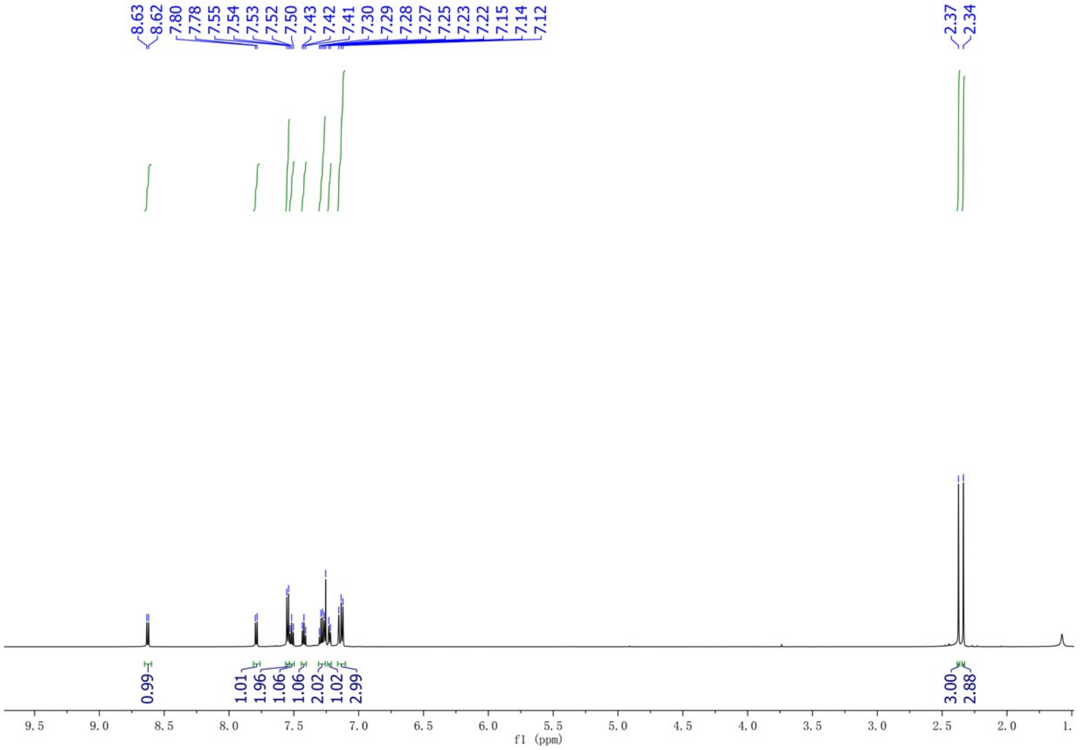
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7.27
7.25
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7.12
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1.96
1.06
1.06
2.02
1.02
2.99
3.00
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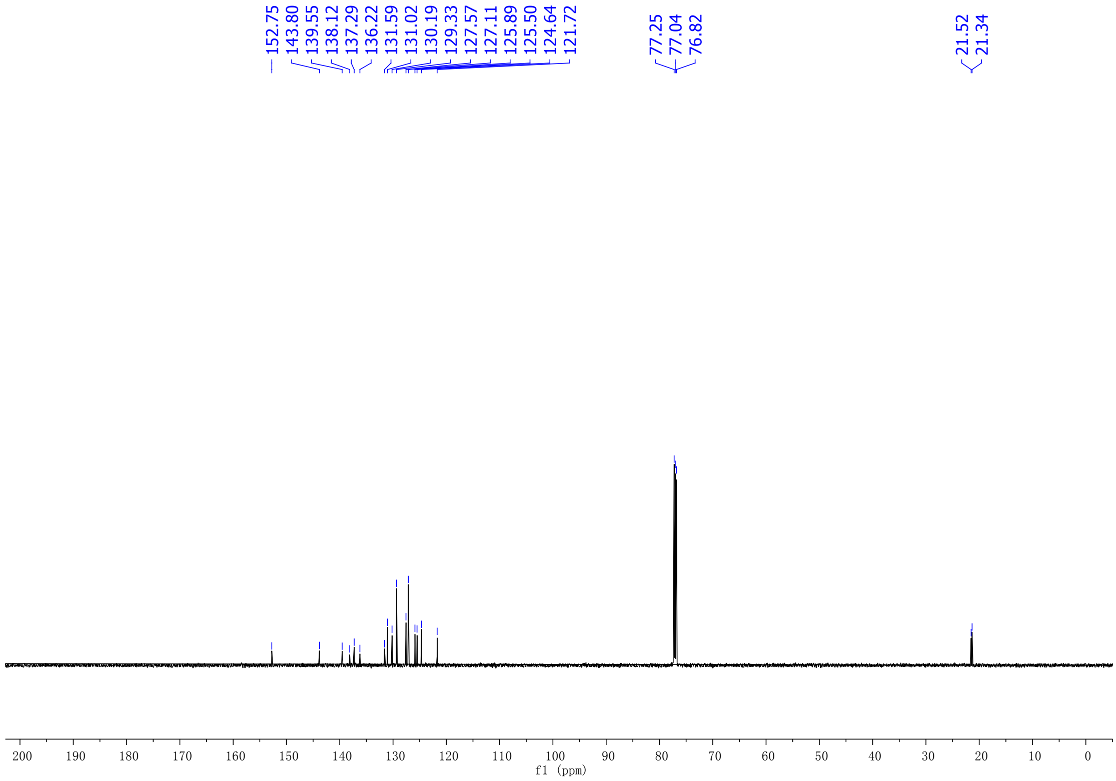
1.
f1 (ppm)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131.02
130.19
129.33
127.57
127.11
125.89
125.50
124.64
121.72
77.25
77.04
76.82
21.52
21.34
200
190
180
170
160
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140
130
120
110
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90
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70
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50
40
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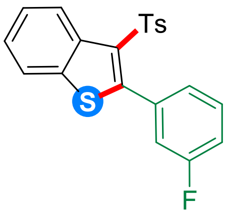
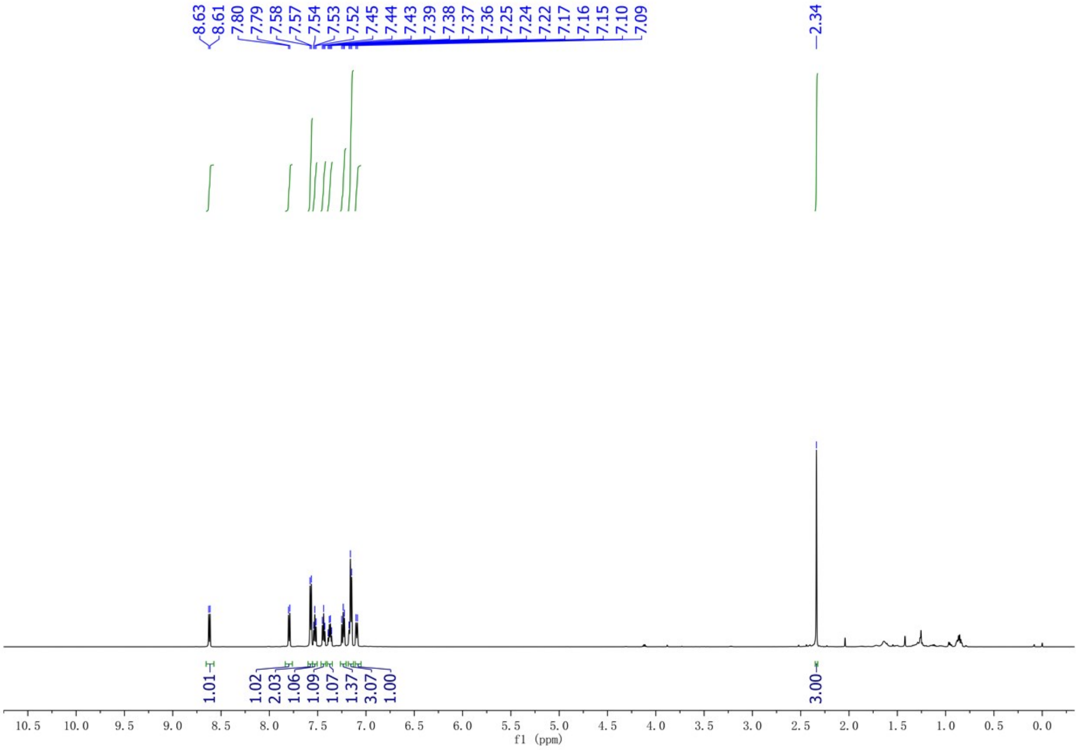
f1 (ppm)


Ts
S
F

3x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7.54
7.53
7.52
7.45
7.44
7.43
7.39
7.38
7.37
7.36
7.25
7.24
7.22
7.17
7.16
7.15
7.10
7.09
2.34
1.01
1.02
2.03
1.06
1.09
1.07
1.37
3.07
1.00
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
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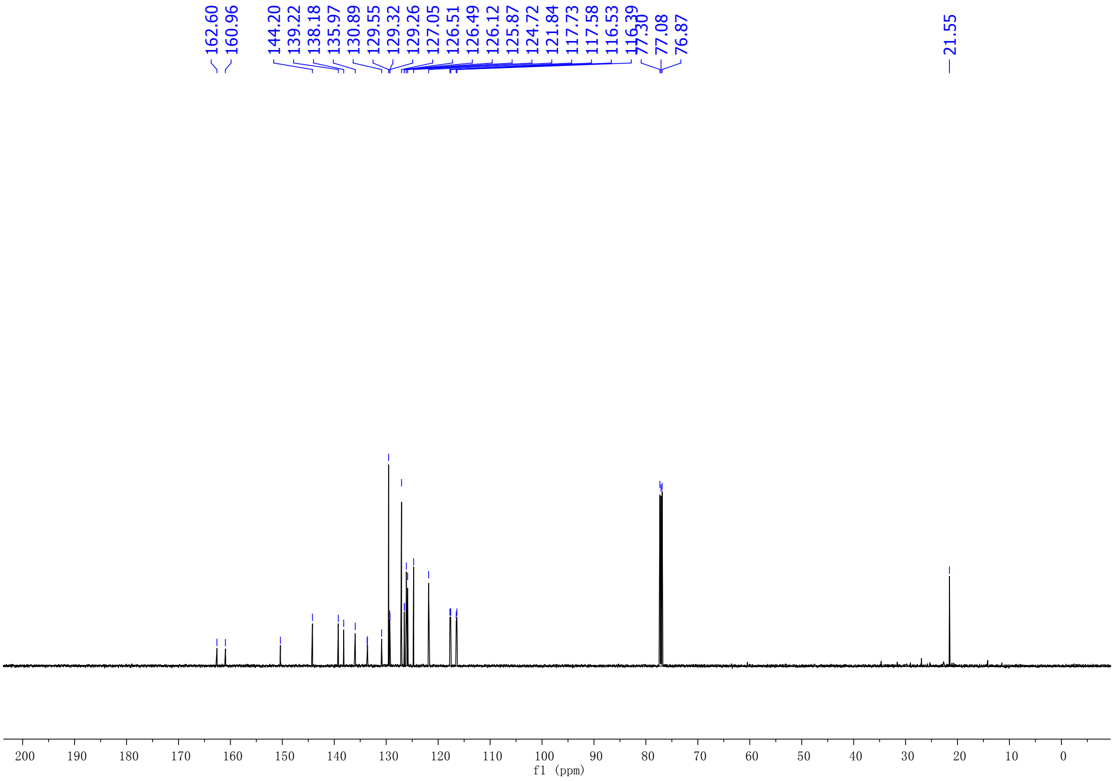
0.0
f1 (ppm)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138.18
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129.55
129.32
129.26
127.05
126.51
126.49
126.12
125.87
124.72
121.84
117.73
117.58
116.53
116.39
77.30
77.08
76.87
21.55
200
190
180
170
160
150
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120
110
100
90
80
70
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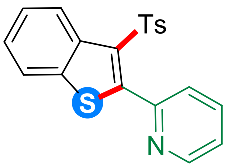
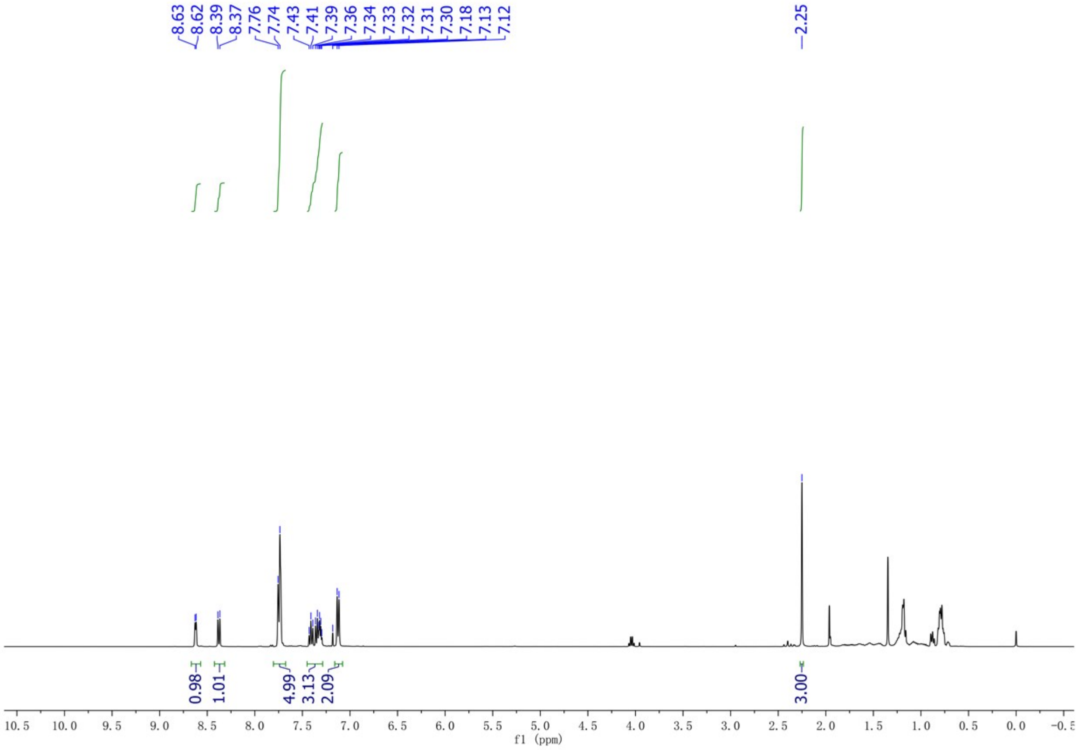
50
40
30
20
10
0
f1 (ppm)


Ts
S
N

3y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7.43
7.41
7.39
7.36
7.34
7.33
7.32
7.31
7.30
7.18
7.13
7.12
2.25
0.98
1.01
4.99
3.13
2.09
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
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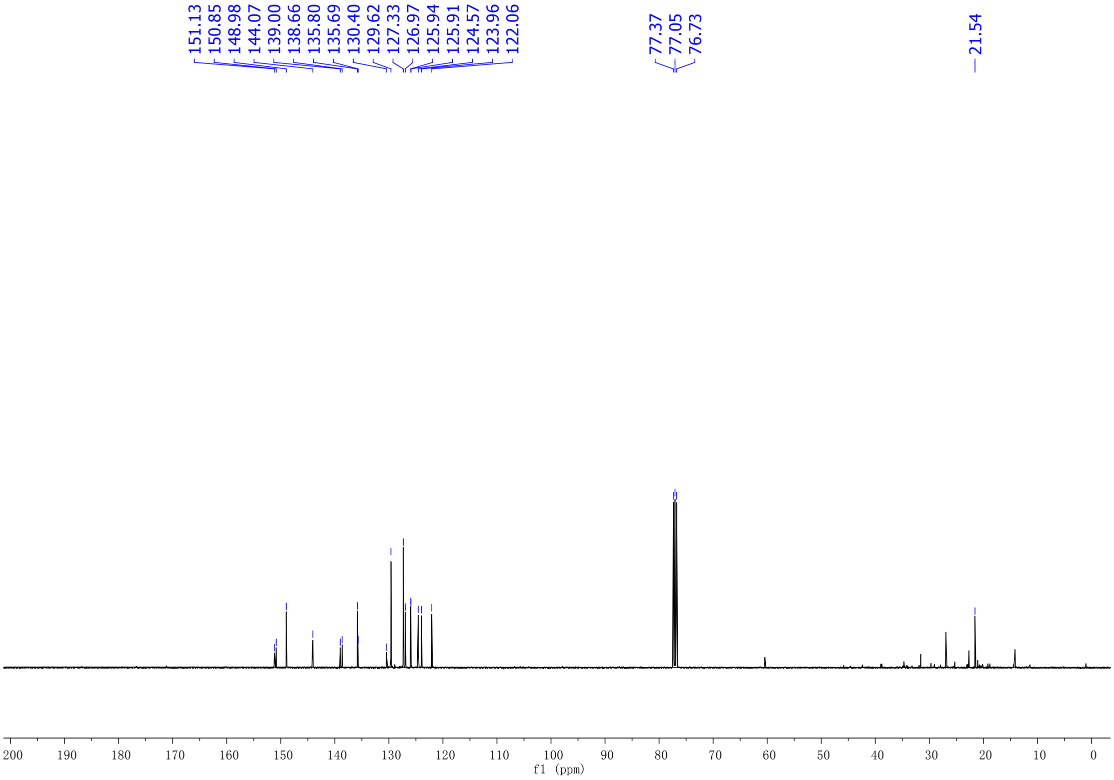
-0.5
f1 (ppm)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135.69
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129.62
127.33
126.97
125.94
125.91
124.57
123.96
122.06
77.37
77.05
76.73
21.54
200
190
180
170
160
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140
130
120
110
100
90
80
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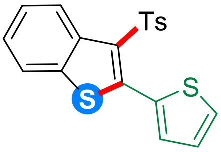
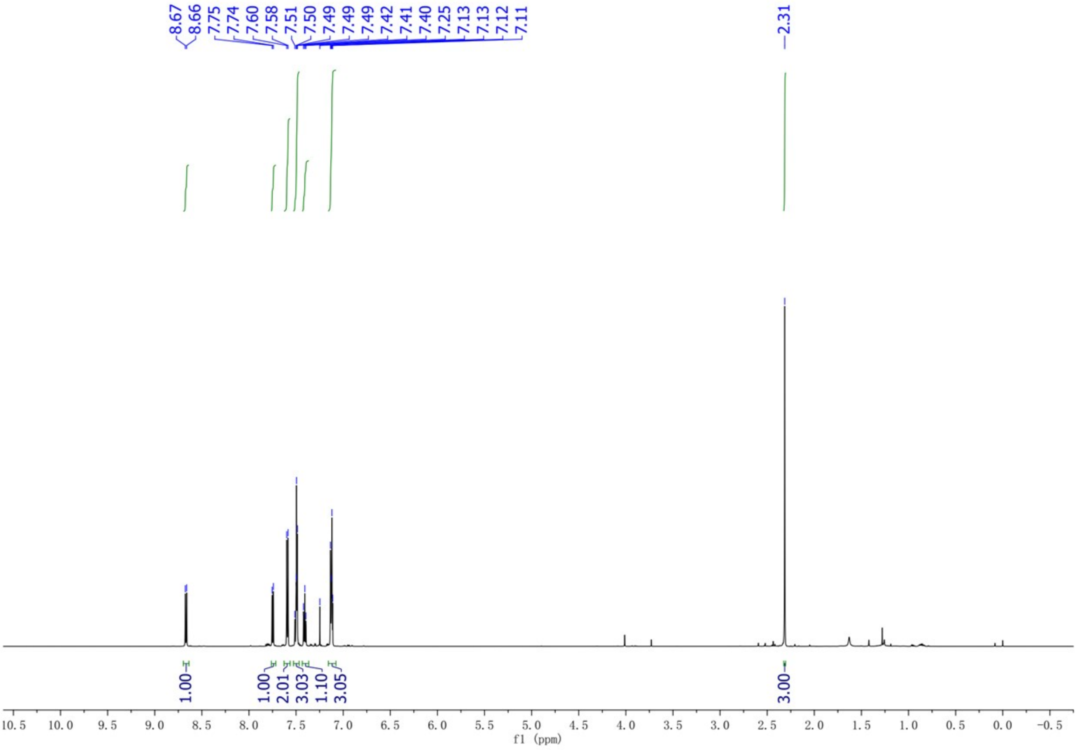
50
40
30
20
10
0
f1 (ppm)


Ts
S
S

3z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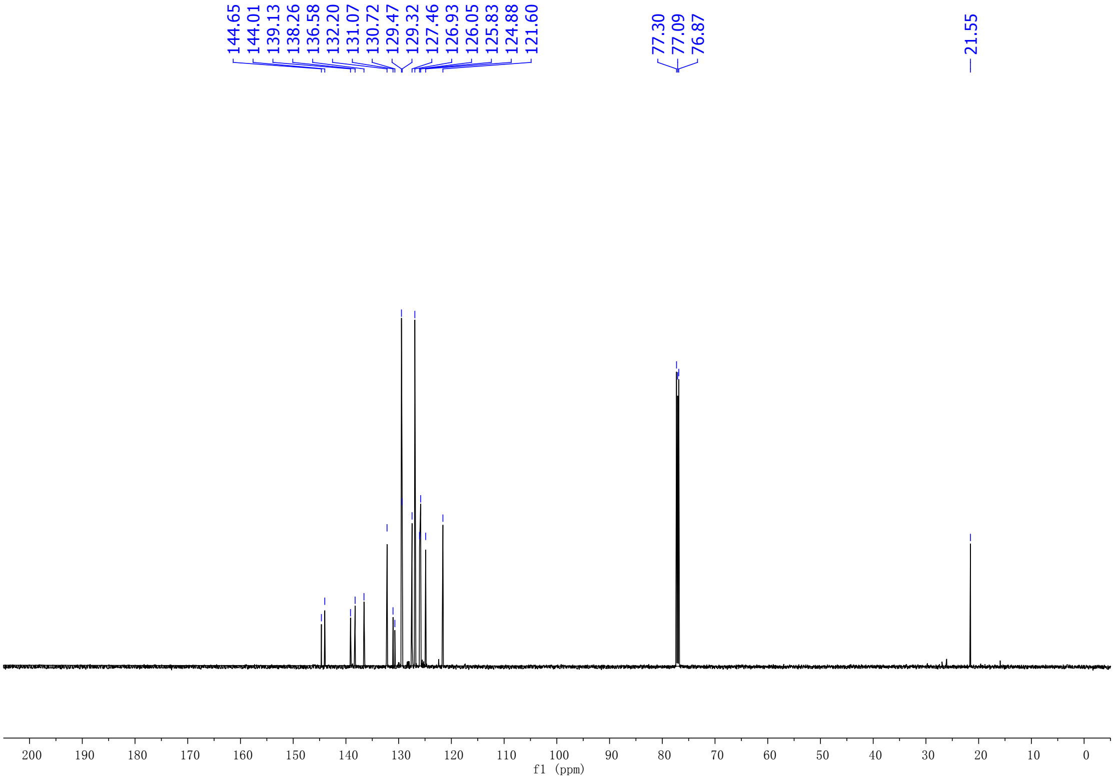
7.74
7.60
7.58
7.51
7.50
7.49
7.49
7.49
7.42
7.41
7.40
7.25
7.13
7.13
7.12
7.11
2.31
1.00
1.00
2.01
3.03
1.10
3.05
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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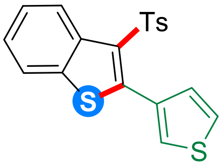
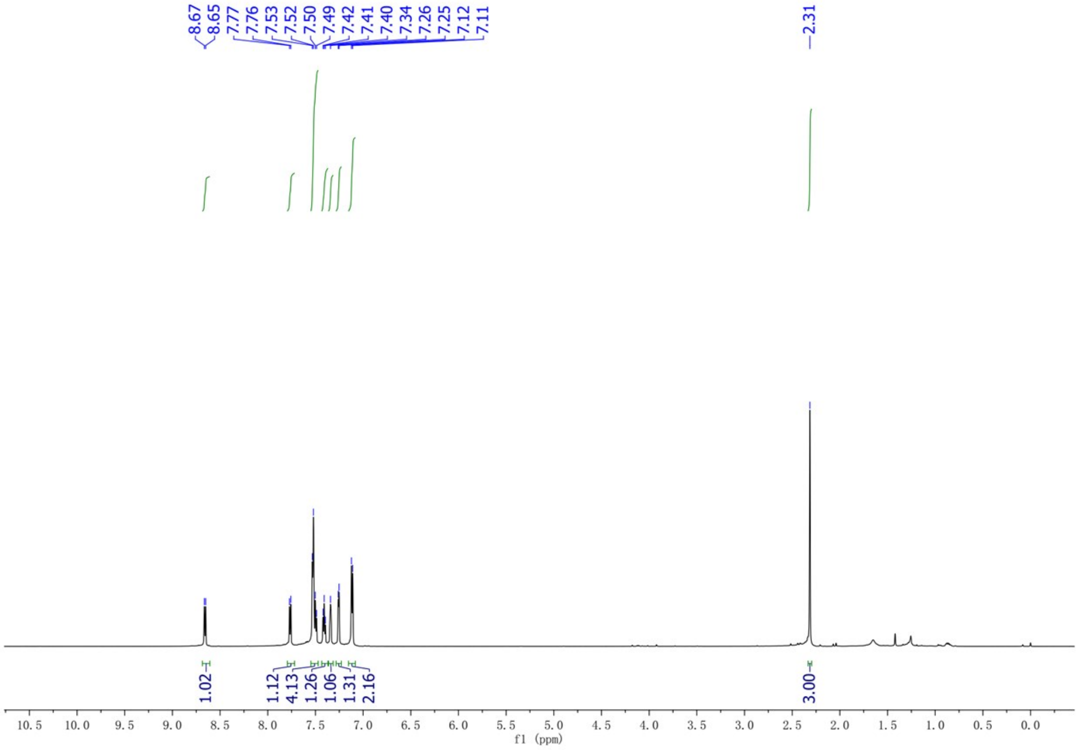
136.58
132.20
131.07
130.72
129.47
129.32
127.46
126.93
126.05
125.83
124.88
121.60
77.30
77.09
76.87
21.55
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ts
S
S

3aa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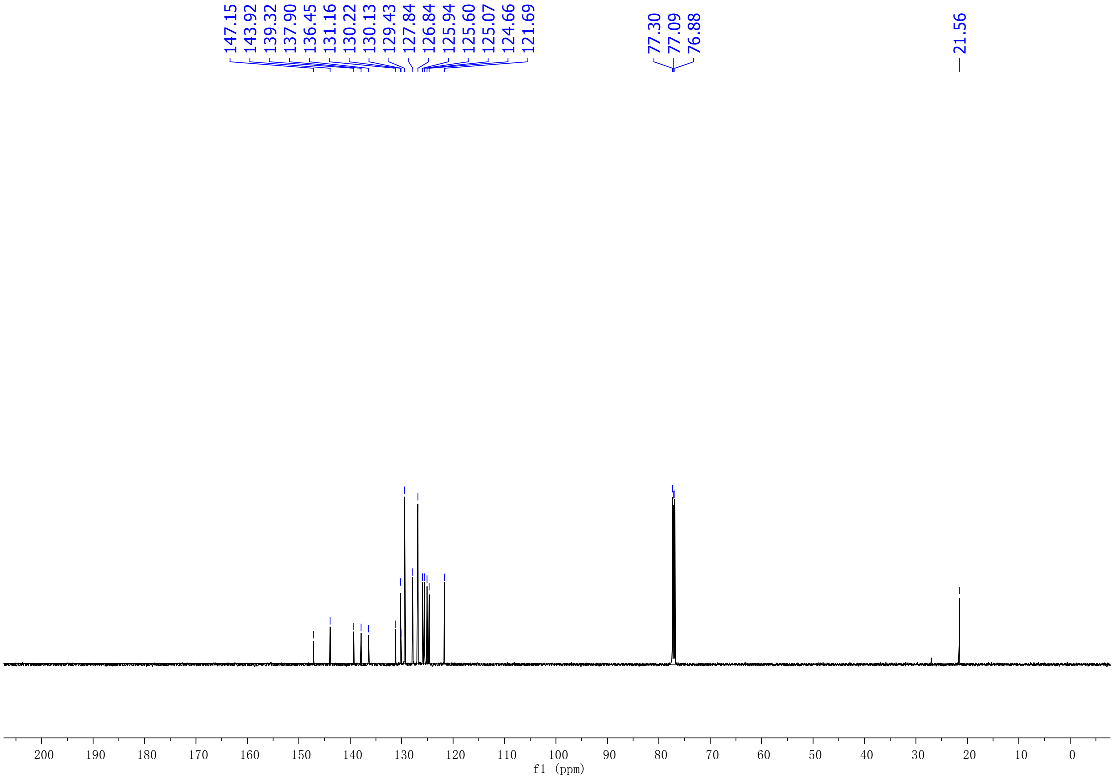
7.42
7.41
7.40
7.34
7.26
7.25
7.12
7.11
2.31
1.02
1.12
4.13
1.26
1.06
1.31
2.16
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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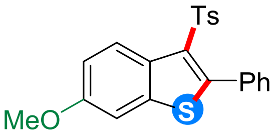
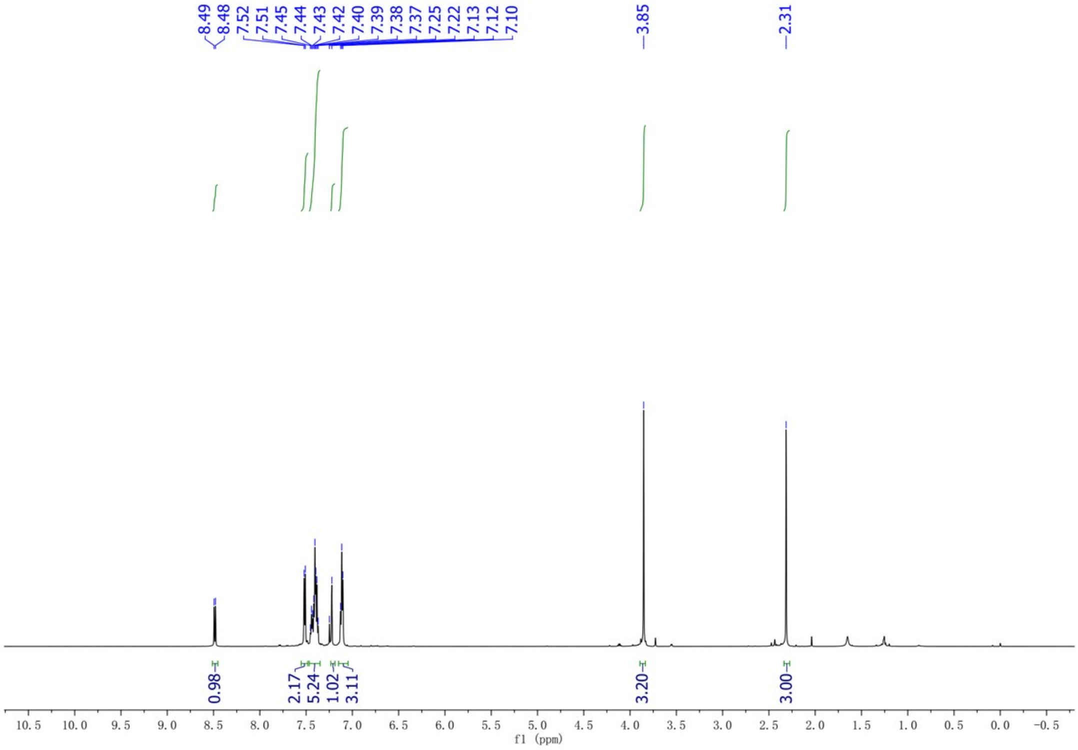
131.16
130.22
130.13
129.43
127.84
126.84
125.94
125.60
125.07
124.66
121.69
77.30
77.09
76.88
21.56
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
Ph
S
MeO

3ab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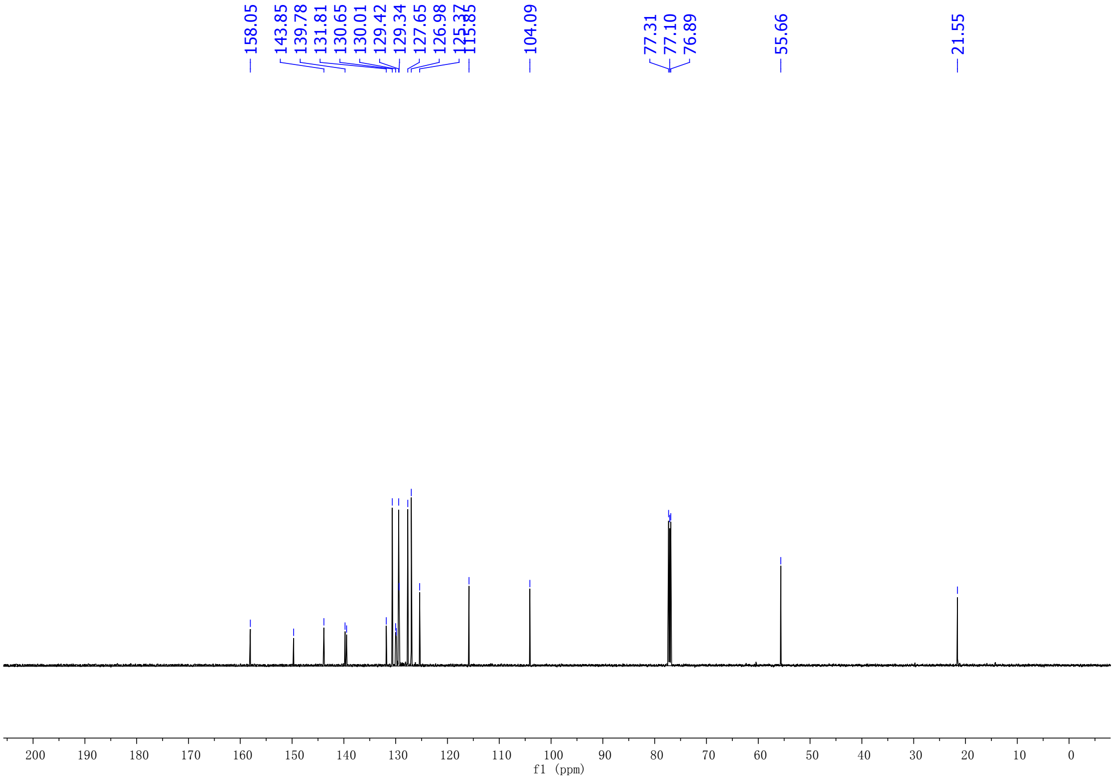
7.43
7.42
7.40
7.39
7.38
7.37
7.25
7.22
7.13
7.12
7.10
3.85
2.31
0.98
2.17
5.24
1.02
3.11
3.20
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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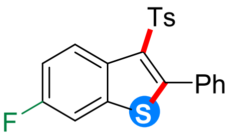
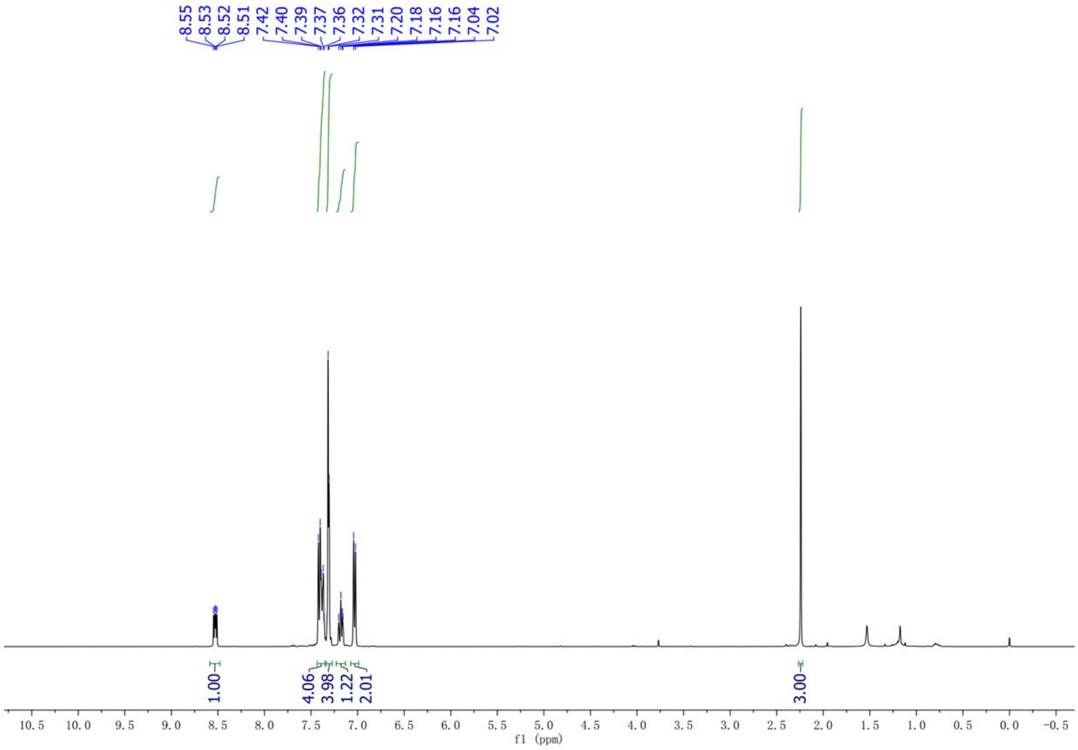
130.01
129.42
129.34
127.65
126.98
125.37
115.85
104.09
77.31
77.10
76.89
55.66
21.55
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ts
Ph
S
F

3ac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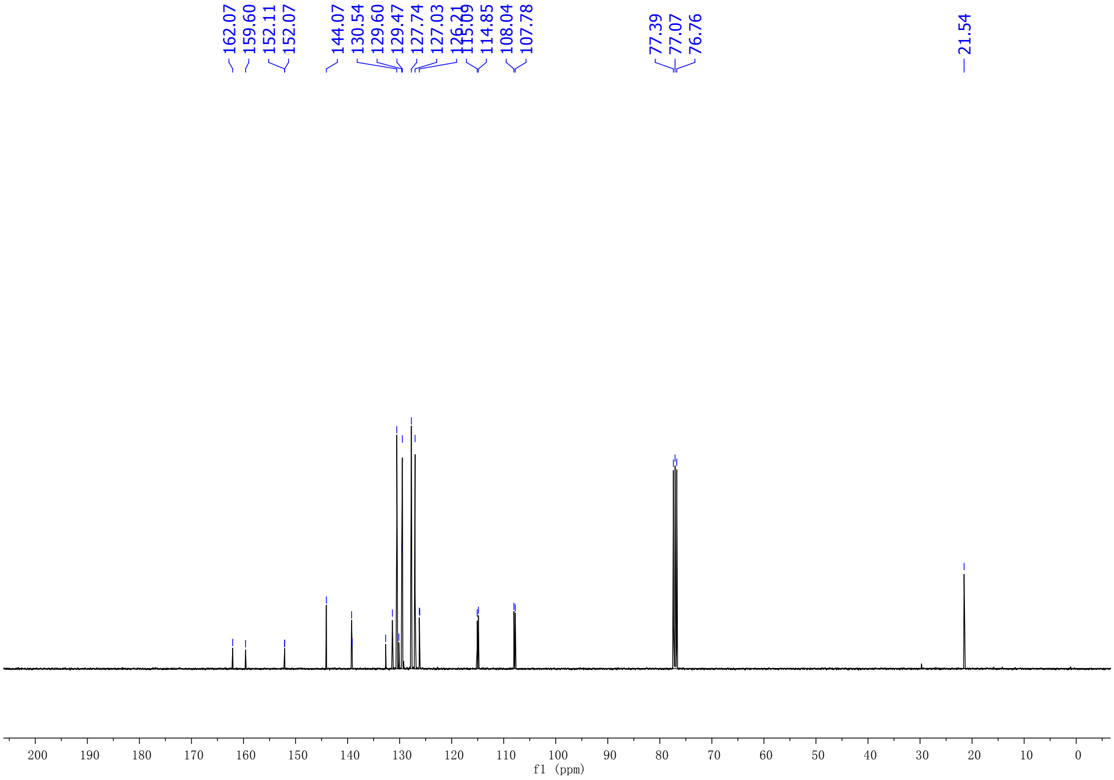
7.37
7.36
7.32
7.31
7.20
7.18
7.16
7.16
7.04
7.02
1.00
4.06
3.98
1.22
2.01
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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152.07
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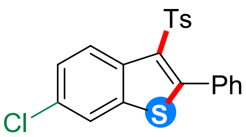
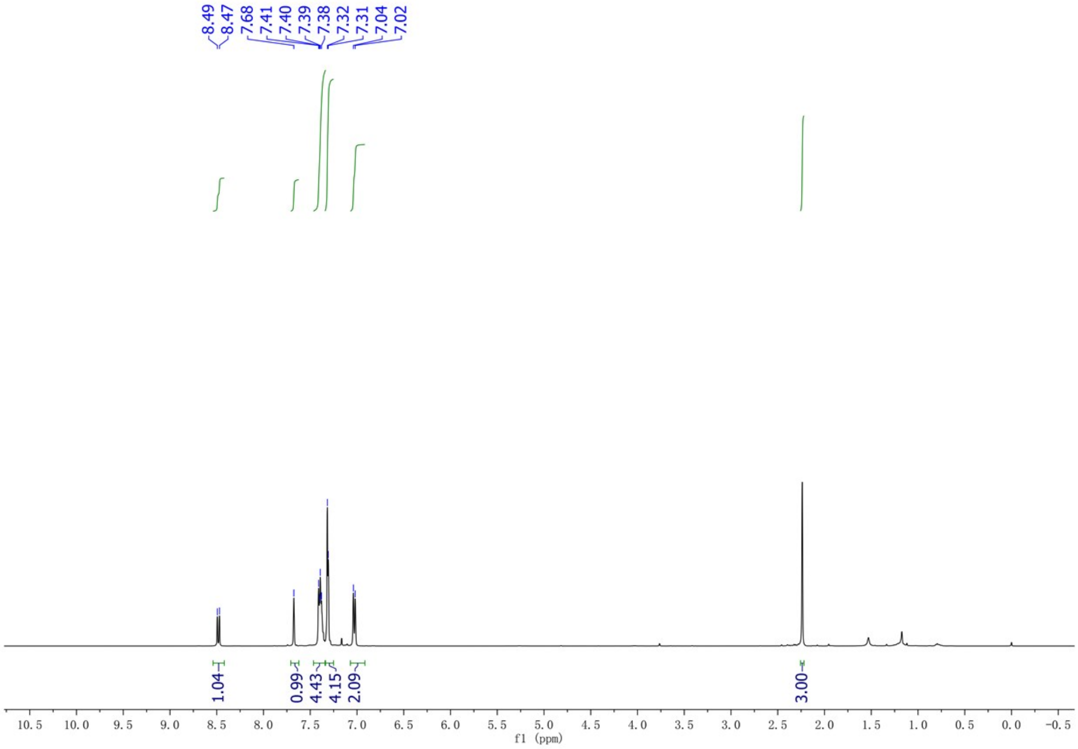
129.47
127.74
127.03
126.21
115.09
114.85
108.04
107.78
77.39
77.07
76.76
21.54
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
Ph
S
Cl

3ad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7.31
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7.02
1.04
0.99
4.43
4.15
2.09
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
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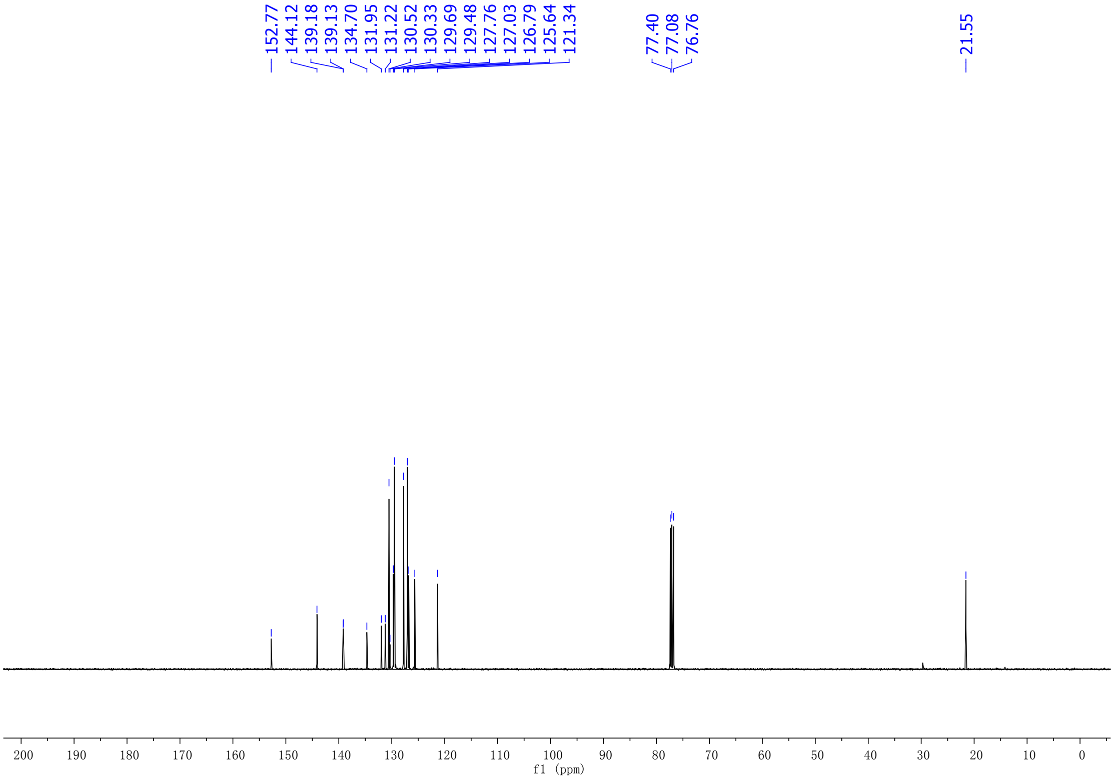
0.5
0.0
-0.5
f1 (ppm)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129.48
127.76
127.03
126.79
125.64
121.34
77.40
77.08
76.76
21.55
200
190
180
170
160
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120
110
100
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80
70
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30
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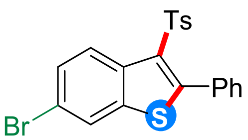
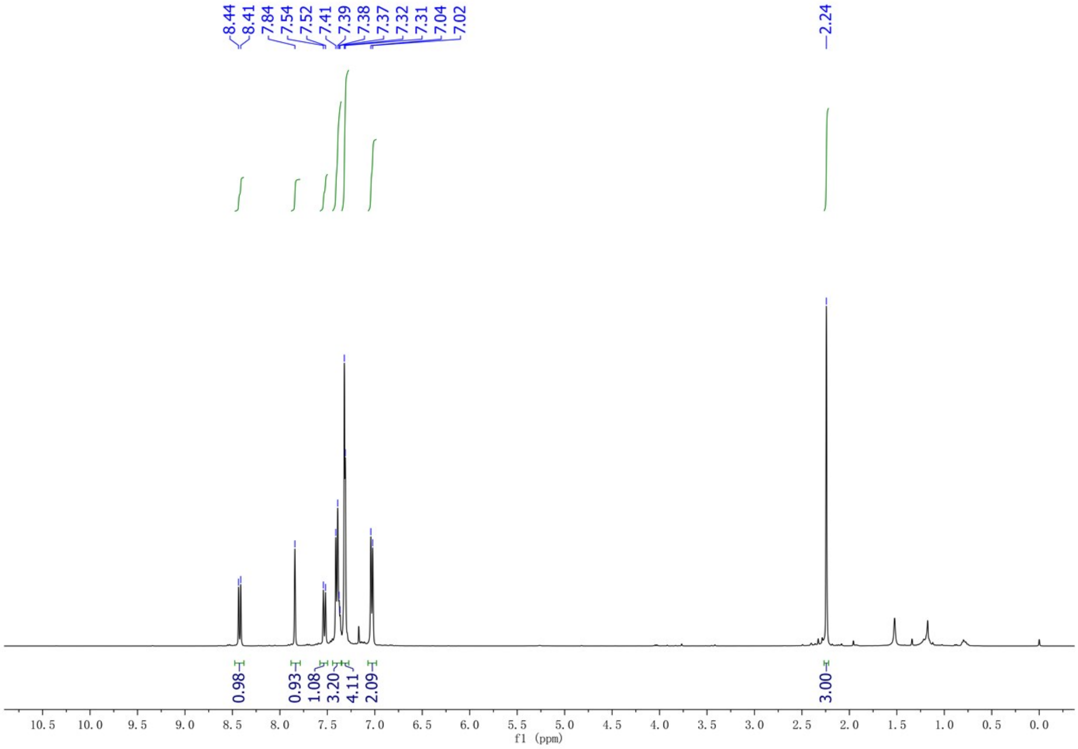
0
f1 (ppm)

3ae


Ts
Ph
S
Br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7.02
2.24
0.98
0.93
1.08
3.20
4.11
2.09
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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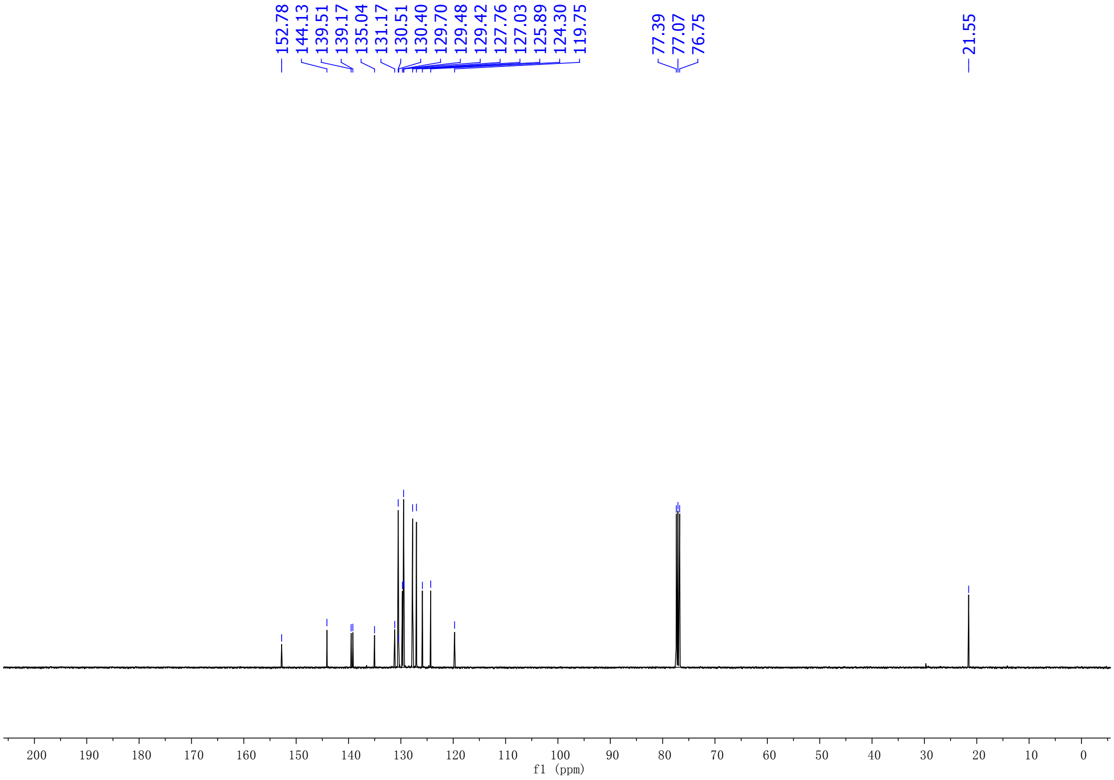
0.0
f1 (ppm)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125.89
124.30
119.75
77.39
77.07
76.75
21.55
200
190
180
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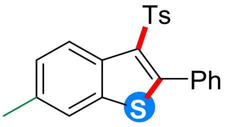
f1 (ppm)


Ts
Ph
S

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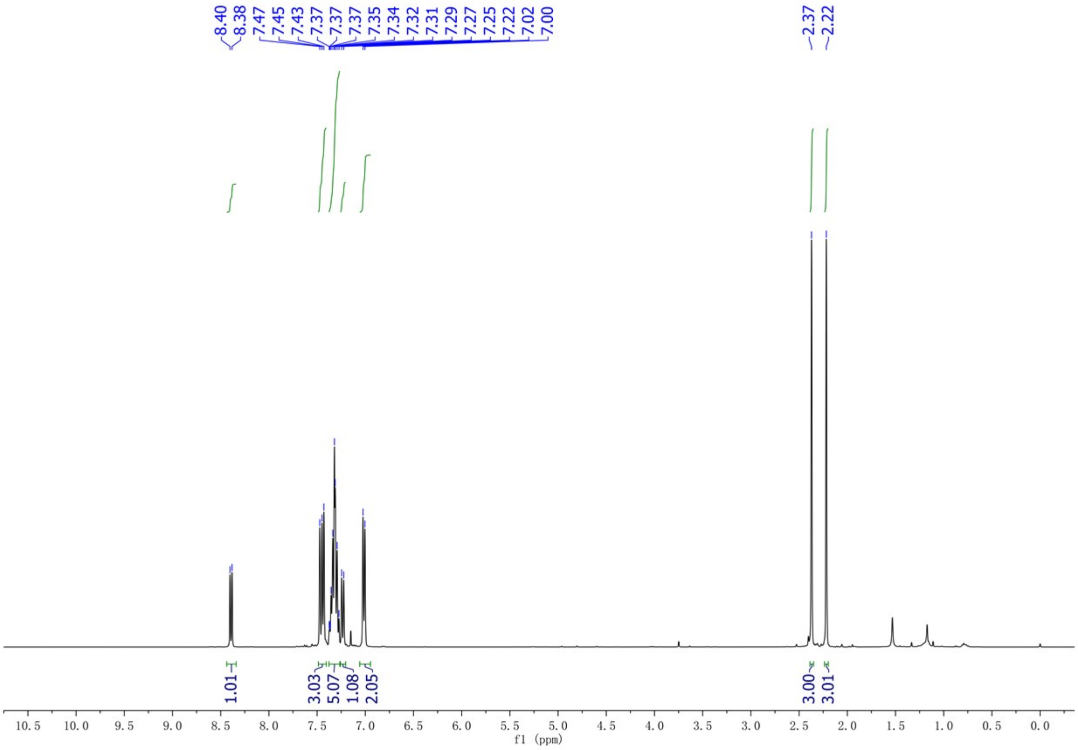
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7.25
7.22
7.02
7.00
2.37
2.22
1.01
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5.07
1.08
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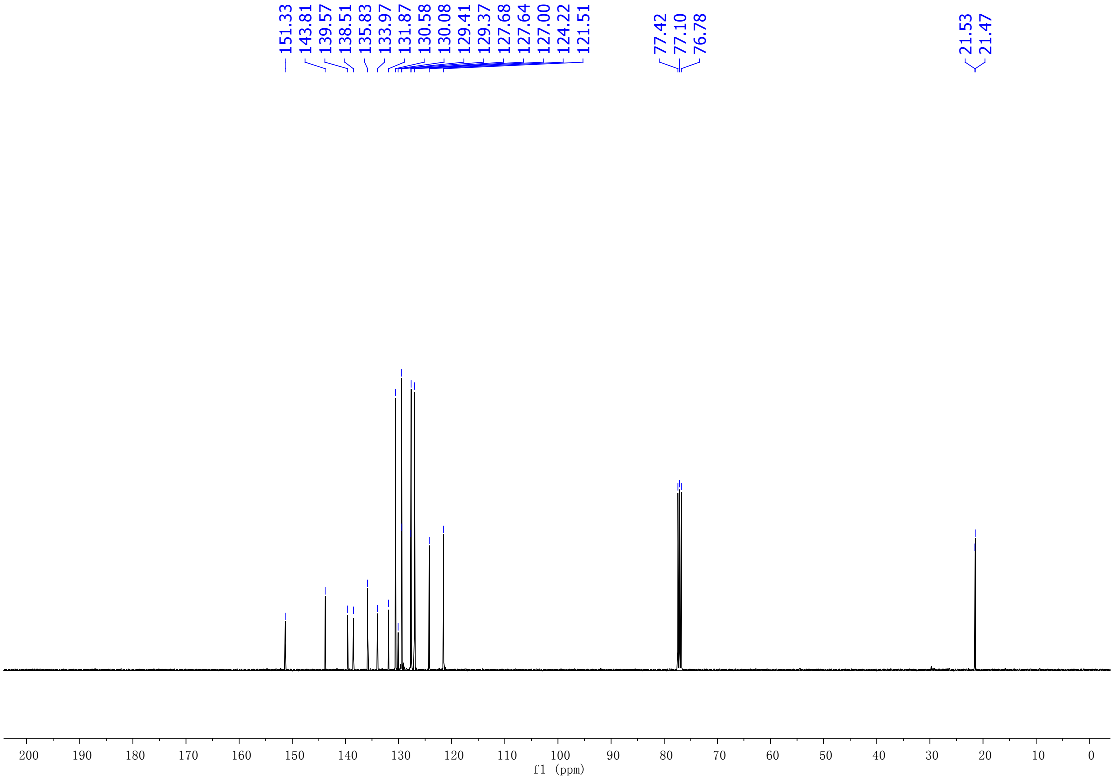
f1 (ppm)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77.42
77.10
76.78
21.53
21.47
200
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70
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30
20
10
0
f1 (ppm)