Supporting Information

Electrochemical Reductive Cross-coupling of Acyl chlorides and Sulfinic Acids towards the Synthesis of Thioesters

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General information

Unless otherwise noted, materials were obtained from commercial suppliers (Leyan and so on) and used without further purification. The instrument for electrolysis was dual display potentiostat (DJS-292B) (made in China). The anodic electrode was zinc plate (20 mm×15 mm×0.3 mm) and cathodic electrode was stainless steel plate (20 mm×15 mm×1.0 mm). Thin-layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 300-400 mesh silica gel in petroleum (boiling point was between 60-90^{o}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they were listed as volume/volume ratios. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), 376 MHz (^{19}F NMR). Chemical shifts were reported relative to tetramethylsilane, dimethyl sulfoxide (2.50 ppm for ^{1}H, 39.6 ppm for ^{13}C), chloroform (7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C). And all ^{1}H, ^{13}C and ^{19}F NMR data spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants (*J*) are reported in Hertz (Hz). GC-MS spectra were recorded on a Shimadzu GC-MS QP2010 Ultra. High resolution mass spectra (HRMS) were measured with Bruker UltiMate3000 & Compact, accurate masses are reported for the molecular ion + hydrogen ([M+H^{+}])， the molecular ion + sodium ([M+Na^{+}]) and the molecular ion + potassium ([M+K^{+}]).

Experimental procedure

General procedure for the preparation of sulfinic acids:[1]

Benzenesulfinic acid and *p*-toluenesulfinic acid were obtained by acidification of the commercially available sodium benzenesulfinate and sodium *p*-toluenesulfinate, then the mixture was extracted by Et_2O. After dried by Na_2SO_4, the solvent was removed under vacuum at 0 ℃ to provide pure product. Other arylsulfinic acids, heteroaromatic sulfinic acids were prepared by the following procedures: arylsulfonyl chloride (10 mmol) and anhydrous sodium sulfite (30 mmol) were added into 20 mL of water. The reaction mixture was kept at 70-80 ℃ for 5 h. After the reaction was complete, the mixture was washed with chloroform. The water phase was acidified with excess concentrated HCl solution at 0 ℃, then extracted by Et_2O. After dried by Na_2SO_4, the organic solvent was removed under vacuum at 0 ℃ to provide pure products.

General procedure for the preparation of 3aa-3zad：

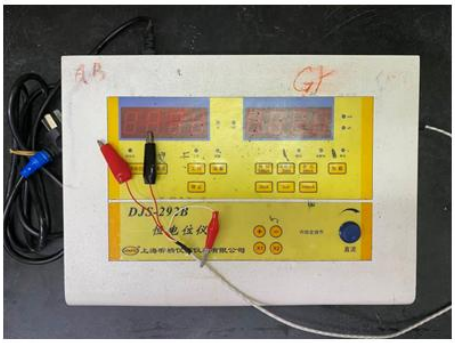


Fig S1 Instrument for electrolysis

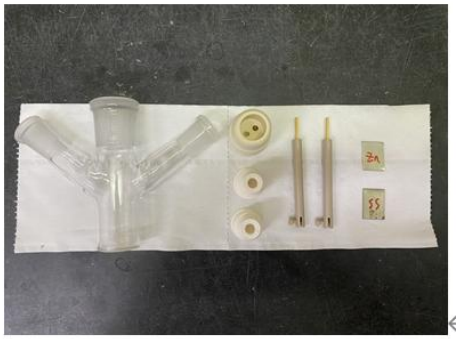


Fig S2 Electrode materials

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, Acyl chlorides **1** (1.5 mmol), benzenesulfinic acid **2a** (0.5 mmol), $^{n}Bu_4NBF_4$ (0.5 mmol, 164.6 mg), PPh_3 (0.5 mmol, 131.1 mg), Tf_2O (0.5 mmol, 84 μL), MeCN (12 mL) were added. The bottle was equipped with zinc plate (20 mm×15 mm×0.3 mm) as the anode and stainless steel plate (20 mm×15 mm×1.0 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 6 mA under Ar atmosphere at room temperature for 2 h. After completion of the reaction, as indicated by TLC and GC-MS, the pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 400: 1).

General procedure for the preparation of 3ab-3ak：

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 4-Methylbenzoyl

chloride **1a** (1.5 mmol), sulfinic acids **2** (0.5 mmol), $^{n}Bu_4NBF_4$ (0.5 mmol, 164.6 mg), PPh_3 (0.5 mmol, 131.1 mg), Tf_2O (0.5 mmol, 84 μL), MeCN (12 mL) were added. The bottle was equipped with zinc plate (20 mm×15 mm×0.3 mm) as the anode and stainless steel plate (20 mm×15 mm×1.0 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 6 mA under Ar atmosphere at room temperature for 2 h. After completion of the reaction, as indicated by TLC and GC-MS, the pure product was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 400: 1).

Procedure for gram scale synthesis of 3aa:

In an oven-dried undivided three-necked bottle (250 mL) equipped with a stir bar, 4-Methylbenzoyl chloride **1a** (15.0 mmol, 1.98 mL), benzenesulfinic acid **2a** (5 mmol, 711 mg), $^{n}Bu_4NBF_4$ (5.0 mmol, 1646.4 mg), PPh_3 (5.0 mmol, 1311.1 mg), Tf_2O (5.0 mmol, 840 μL), MeCN (120 mL) were added. The bottle was equipped with zinc plate (20 mm×15 mm×0.3 mm) as the anode and stainless steel plate (20 mm×15 mm×1.0 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under Ar atmosphere at room temperature for 6 h. After completion of the reaction, as indicated by TLC and GC-MS, the pure product (yield 75%, white solid, 0.85 g) was obtained by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 400: 1).

Procedure for the preparation of 5a:[2]

To a solution of **3aa** in DMF (0.1 M) was added phenylboronic acid (1.5 equiv.), CuI (20 mol%), $Pd(OAc)_2$ (5 mol%). After the mixture was stirred at 120 ℃ for 15 h. Upon completion of the reaction, the resulting mixture was diluted with EtOAc and washed with H_2O, dried over Na_2SO_4. The solvent was then removed under vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product **5a** in 35% yield.

Procedure for the preparation of 6a:[3]

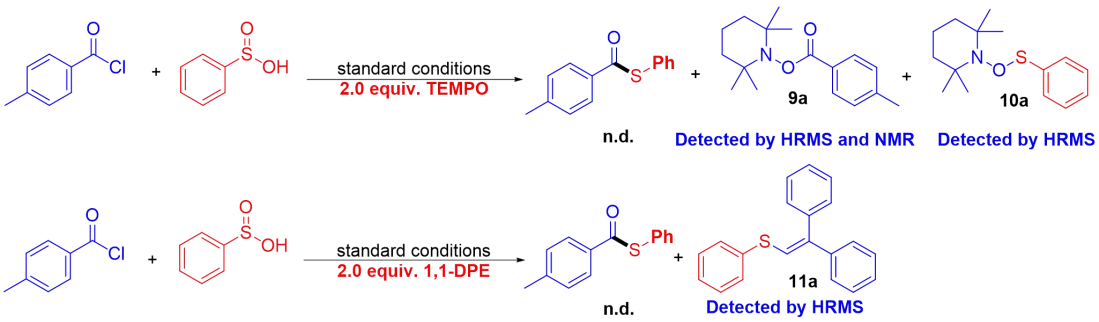
To a solution of **3aa** in 1,4-dioxane (0.2 M) was added $Ni(dppp)Cl_2$ (10 mol%), Na_2CO_3 (1.5 equiv.). After the mixture was stirred at 160 ℃ for 15 h. After completion of the reaction, as indicated by TLC and GC-MS. The solvent was then removed under vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product **6a** in 48% yield.

Procedure for the preparation of 7a/8a:[4]

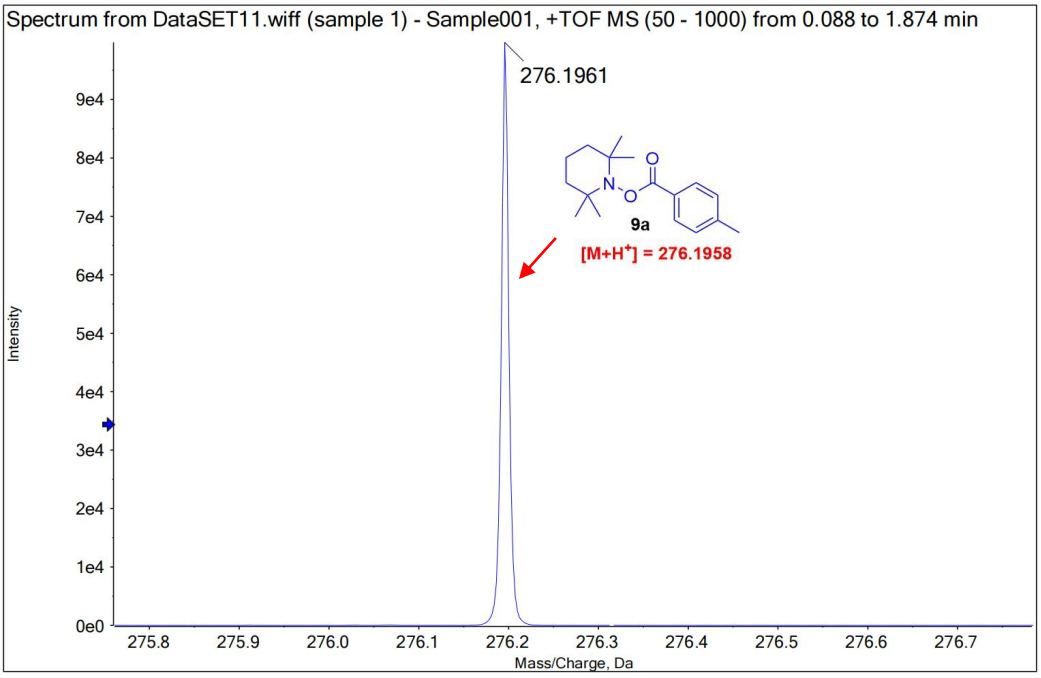
To a solution of **3aa** in DMF (0.05 M) was added $BnNH_2$ (2.5 equiv.). After the mixture was stirred at room temperature for 1 h. Upon completion of the reaction, the resulting mixture was diluted with EtOAc and washed with H_2O, dried over Na_2SO_4. The solvent was then removed under vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product **7a** (76% yield) and **8a** (73% yield).

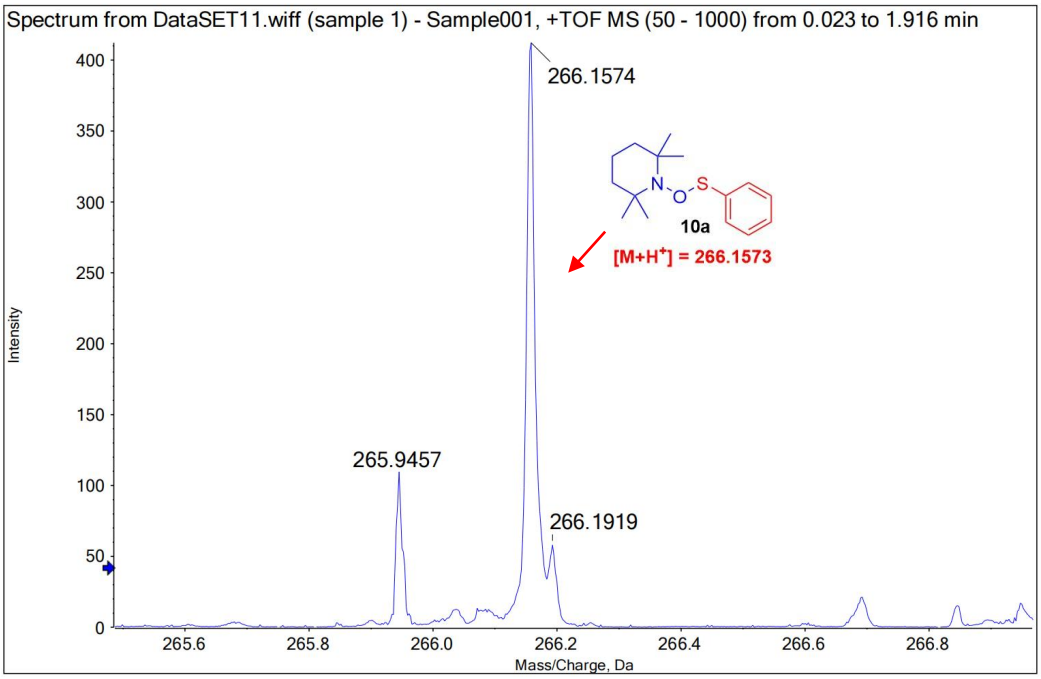
Mechanism research

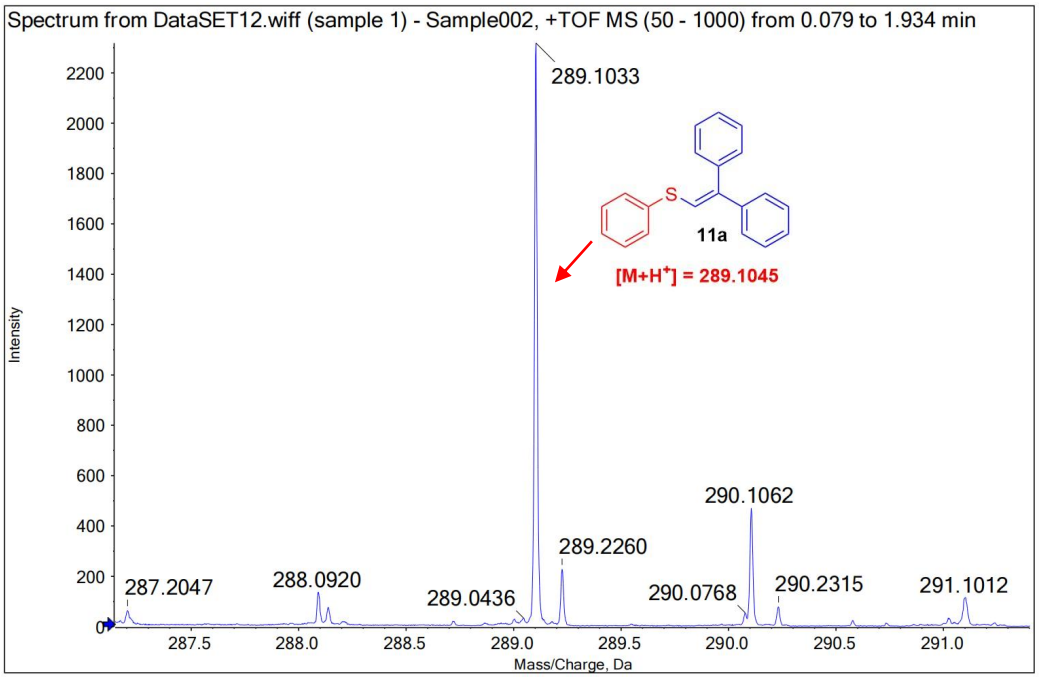
Radical trapping experiments:



In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, 4-Methylbenzoyl chloride **1a** (1.5 mmol), benzenesulfinic acid **2a** (0.5 mmol), $^{n}Bu_4NBF_4$ (0.5 mmol, 164.6 mg), PPh_3 (0.5 mmol, 131.1 mg), Tf_2O (0.5 mmol, 84 μL), MeCN (12 mL), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) or 1,1-diphenylethene (DPE) were added. The bottle was equipped with zinc plate (20 mm×15 mm×0.3 mm) as the anode and stainless steel plate (20 mm×15 mm×1.0 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 6 mA under Ar atmosphere at room temperature for 2 h. After completion of the reaction, as indicated by TLC and HRMS, The **9a**, **10a** and **11a** adducts was detected by HRMS in the reaction system. These results indicated this reaction probably underwent a radical pathway, and thiyl radical and acyl radical might be involved in the transformation.







CV experiments:

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under Ar at room temperature. The working electrode was a glassy carbon electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 10 mL of CH_3CN containing 0.01 M $^nBu_4NBF_4$ were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 3.0 V. The peak potentials *vs.* Ag/AgCl for used. The reduction peak of benzoyl chloride observed at -1.45 V and two relatively

reduction peaks of benzenesulfinic acid were observed at -2.21 V and -1.66 V. The CV of Tf_2O in acetonitrile exhibits two oxidation waves, one at -1.14 V and the other at -1.95 V. It demonstrated that the reduction of Tf_2O occurred preferentially during the reaction process.

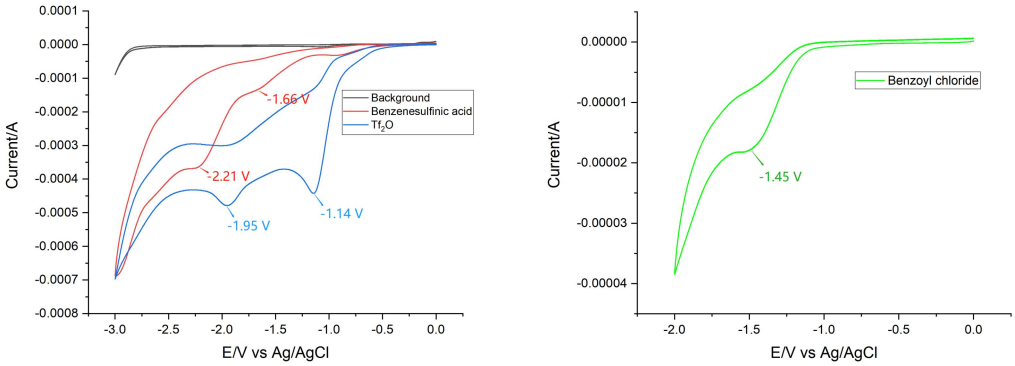
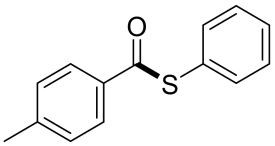
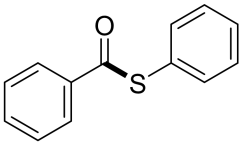


Figure S3 Cyclic voltammogram

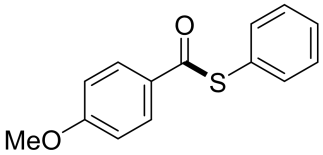
Detail descriptions for products



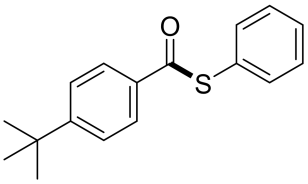
***S*-phenyl 4-methylbenzothioate (3aa)[5]** (White solid was obtained in 80% isolated yield, 91.2 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.88 (d, J = 8.0 Hz, 2H), 7.50 (s, 5H), 7.38 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.7, 145.0, 135.1, 133.4, 129.8, 129.7, 129.5, 127.3, 126.9, 21.4.



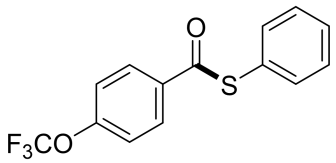
***S*-phenyl benzothioate (3ba)[5]** (White solid was obtained in 80% isolated yield, 85.7 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.98 (d, J = 8.0 Hz, 2H), 7.72 (t, J = 8.0 Hz, 1H), 7.58 (t, J = 8.0 Hz, 2H), 7.51 (s, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 189.4, 136.0, 135.2, 134.5, 129.9, 129.6, 129.4, 127.2, 126.8.



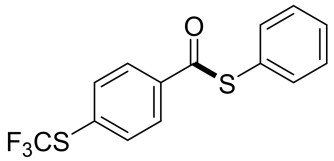
***S*-phenyl 4-methoxybenzothioate (3ca)[5]** (White solid was obtained in 87% isolated yield, 106.1 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.95 (d, J = 8.0 Hz, 2H), 7.49 (s, 5H), 7.09 (d, J = 8.0 Hz, 2H), 3.84 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 187.6, 164.1, 135.3, 129.8, 129.6, 129.5, 128.6, 127.2, 114.6, 55.9.



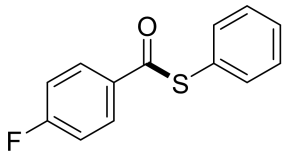
***S*-phenyl 4-(tert-butyl)benzothioate (3da)[6]** (White solid was obtained in 82% isolated yield, 111.3 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.91 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.49 (s, 5H), 1.28 (s, 9H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.7, 157.6, 135.1, 133.4, 129.8, 129.5, 127.2, 126.9, 126.2, 35.1, 30.8.



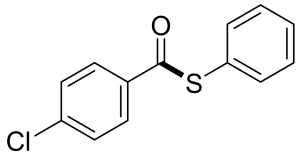
***S*-phenyl 4-(trifluoromethoxy)benzothioate (3ea)[7]** (White solid was obtained in 50% isolated yield, 74.5 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.08 (d, J = 8.0 Hz, 2H), 7.52 (s, 1H), 7.49 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.1, 152.4, 135.1, 134.7, 130.0, 129.7, 129.6, 126.5, 121.3, 120.1 (q, J =262.6 Hz); ^{19}F NMR (376 MHz, DMSO-d_6) δ -56.90.



***S*-phenyl 4-((trifluoromethyl)thio)benzothioate (3fa).** (White solid was obtained in 56% isolated yield, 88.1 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.04 (d, J = 12.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.48 (s, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.8, 137.9, 136.3, 135.1, 130.1, 129.9 (q, J =10.1 Hz), 129.7, 129.5 (q, J =313.1Hz), 128.4, 126.4; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -41.36. HRMS (ESI) calcd for $C_{14}H_{10}F_3OS_2$: 315.0120 ($M+H^+$), found: 315.0114.

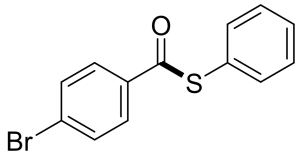


***S*-phenyl 4-fluorobenzothioate (3ga)[5]** (White solid was obtained in 79% isolated yield, 91.8 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.06–8.02 (m, 2H), 7.50 (s, 5H), 7.40 (t, J = 8.0 Hz, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.1, 165.8 (d, J =252.5 Hz), 135.3, 132.7 (d, J =10.1 Hz), 130.4 (d, J =10.1 Hz), 130.1, 129.7, 126.7, 116.6 (d, J =20.2 Hz); **^{19}F NMR** (376 MHz, DMSO-d_6) δ -104.12.

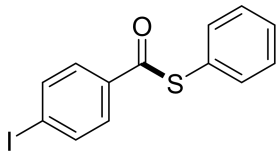


***S*-phenyl 4-chlorobenzothioate (3ha)[5]** (White solid was obtained in 46% isolated yield, 56.8 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.97 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 12.0 Hz, 2H), 7.50 (s, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.5, 139.4, 135.3,

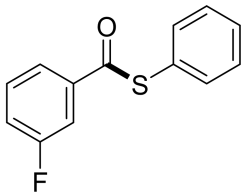
134.7, 130.2, 129.8, 129.7, 129.2, 126.5.



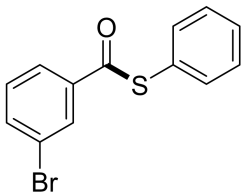
***S*-phenyl 4-bromobenzothioate (3ia)[6]** (White solid was obtained in 54% isolated yield, 78.6 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.89 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.51 (s, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.6, 135.2, 135.0, 132.5, 130.1, 129.7, 129.2, 128.5, 126.4.



***S*-phenyl 4-iodobenzothioate (3ja)** (White solid was obtained in 43% isolated yield, 73.9 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.96 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.50 (s, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 189.1, 138.5, 135.3, 135.3, 130.2, 129.8, 128.9, 126.5, 103.3.

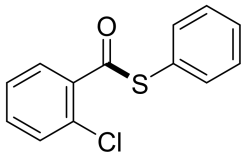


***S*-phenyl 3-fluorobenzothioate (3ka)** (White solid was obtained in 70% isolated yield, 81.2 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.84 (d, J = 8.0 Hz, 1H), 7.69–7.55 (m, 3H), 7.51 (s, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.4, 162.6 (d, J = 252.5 Hz), 138.1 (d, J = 10.1 Hz), 135.1, 131.8 (d, J = 10.1 Hz), 130.1, 129.7, 126.4, 123.6, 121.4 (d, J = 20.2 Hz), 113.7 (d, J = 20.2 Hz); **^{19}F NMR** (376 MHz, DMSO-d_6) δ -111.12.

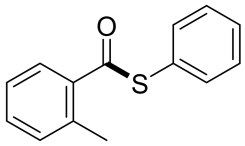


***S*-phenyl 3-bromobenzothioate (3la)[5]** (White solid was obtained in 85% isolated yield, 123.8 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.02 (s, 1H), 7.97 (d, J = 8.0 Hz,

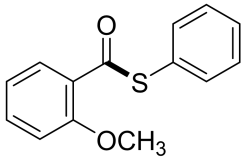
1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.51 (s, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.2, 137.9, 137.0, 135.1, 131.6, 130.1, 129.7, 129.4, 126.4, 126.3, 122.6.



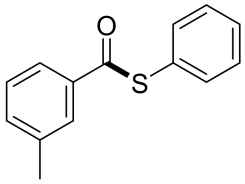
***S*-phenyl 2-chlorobenzothioate (3ma)[5]** (White solid was obtained in 68% isolated yield, 83.9 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.61–7.58 (m, 2H), 7.53–7.48 (m, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 190.0, 136.8, 134.9, 133.6, 131.0, 130.3, 129.9, 129.5, 129.3, 127.9, 126.9.



***S*-phenyl 2-methylbenzothioate (3na)[8]** (White solid was obtained in 85% isolated yield, 96.9 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.54–7.50 (m, 6H), 7.40–7.35 (m, 2H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 191.5, 136.5, 136.4, 134.9, 132.5, 131.9, 129.9, 129.6, 128.2, 127.6, 126.5, 20.2.

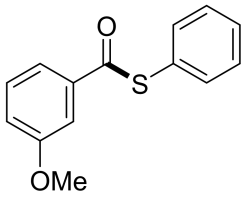


***S*-phenyl 2-methoxybenzothioate (3oa)[5]** (White solid was obtained in 89% isolated yield, 108.3 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.74–7.72 (m, 1H), 7.61–7.57 (m, 1H), 7.48 (t, *J* = 8.0 Hz, 5H), 7.21 (d, *J* = 12.0 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 3.88 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.5, 157.7, 135.1, 134.8, 129.7, 129.5, 129.3, 128.3, 125.8, 120.7, 113.0, 56.1.

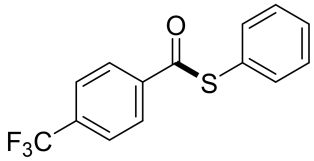


***S*-phenyl 3-methylbenzothioate (3pa)[7]** (White solid was obtained in 84% isolated yield, 95.8 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.77 (d, *J* = 8.0 Hz, 2H),

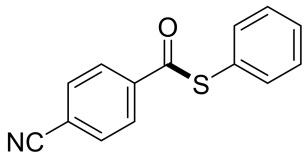
7.52–7.43 (m, 7H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 189.4, 139.0, 136.1, 135.2, 135.1, 129.9, 129.6, 129.3, 127.5, 126.9, 124.5, 21.0.



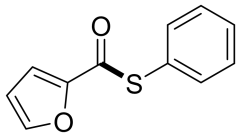
***S*-phenyl 3-methoxybenzothioate (3qa)[8]** (White solid was obtained in 72% isolated yield, 88.0 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.58 (d, J = 4.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 6H), 7.39 (s, 1H), 7.29–7.26 (m, 1H), 3.79 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 189.4, 159.8, 137.5, 135.3, 130.8, 130.1, 129.7, 126.9, 120.4, 119.8, 111.7, 55.7.



***S*-phenyl 4-(trifluoromethyl)benzothioate (3ra)[9]** (White solid was obtained in 78% isolated yield, 110.5 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.13 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.51 (s, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.9, 139.3, 135.0, 133.7 (q, J =30.3 Hz), 130.1, 129.7, 128.1, 126.4, 126.3, 123.7 (q, J =272.7 Hz); **^{19}F NMR** (376 MHz, DMSO-d_6) δ -61.88.

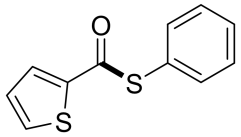


***S*-phenyl 4-cyanobenzothioate (3sa)[5]** (White solid was obtained in 77% isolated yield, 92.1 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.08 (d, J = 8.0 Hz, 2H), 8.02 (d, J = 8.0 Hz, 2H), 7.51 (s, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.9, 139.2, 135.1, 133.5, 130.3, 129.8, 128.0, 126.1, 118.2, 116.4.

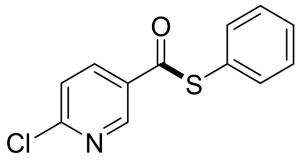


***S*-phenyl furan-2-carbothioate (3ta)[5]** (White solid was obtained in 82% isolated yield, 84.1 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.08 (s, 1H), 7.50 (s, 5H),

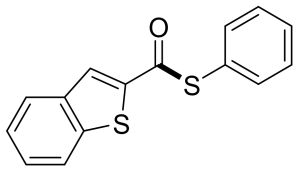
7.49–7.47 (m, 1H), 7.80–7.78 (m, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 177.7, 149.4, 148.7, 135.4, 130.1, 129.7, 125.8, 117.8, 113.4.



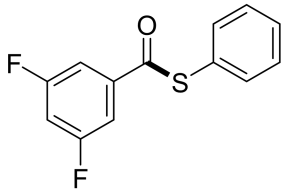
***S*-phenyl thiophene-2-carbothioate (3ua)[5]** (White solid was obtained in 78% isolated yield, 85.3 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.11–8.09 (m, 1H), 8.03–8.01 (m, 1H), 7.53–7.48 (m, 5H), 7.30–7.28 (m, 1H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 181.4, 140.3, 135.5, 135.2, 132.9, 130.1, 129.7, 129.2, 126.4.



***S*-phenyl 6-chloropyridine-3-carbothioate (3va)** (White solid was obtained in 80% isolated yield, 99.7 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.92 (d, J = 4.0 Hz, 1H), 8.34–8.31 (m, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.51 (s, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 187.5, 155.2, 148.5, 138.3, 135.1, 131.1, 130.3, 129.8, 125.8, 125.3. HRMS (ESI) calcd for $C_{12}H_9ClNOS$: 250.0088 ($M+H^+$), found: 250.0089.

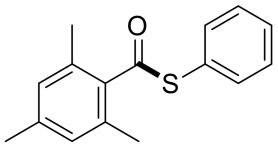


***S*-phenyl benzo[b]thiophene-2-carbothioate (3wa)** (Yellow solid was obtained in 50% isolated yield, 67.5 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.43 (s, 1H), 8.07 (t, J = 8.0 Hz, 2H), 7.57–7,47 (m, 7H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 182.9, 141.3, 139.8, 138.7, 135.1, 130.2, 130.0, 129.7, 128.2, 126.7, 126.2, 125.7, 123.3. HRMS (ESI) calcd for $C_{15}H_{10}NaOS_2$: 293.0065 ($M+Na^+$), found: 293.0059.

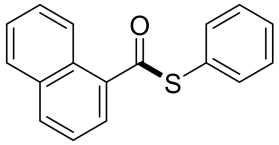


***S*-phenyl 3,5-difluorobenzothioate (3xa)[10]** (White solid was obtained in 88%

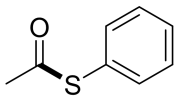
isolated yield, 116.4 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.68–7.56 (m, 3H), 7.53–7.49 (m, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 187.5 (t, J = 3.0 Hz), 162.7 (dd, J = 250.5, 13.1 Hz), 139.0 (t, J = 10.1 Hz), 135.0, 130.3, 129.7, 126.0, 110.6 (dd, J = 20.2, 10.1 Hz), 109.7 (t, J = 20.2 Hz); **^{19}F NMR** (376 MHz, DMSO-d_6) δ -107.11.



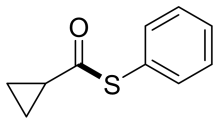
***S*-phenyl 2,4,6-trimethylbenzothioate (3ya)[11]** (White solid was obtained in 95% isolated yield, 121.5 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.55–7.50 (m, 5H), 6.93 (s, 2H) , 2.31 (s, 6H) , 2.25 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 195.1, 139.5, 136.8, 134.4, 133.1, 129.9, 129.6, 128.4, 127.2, 20.8, 18.6.



***S*-phenyl naphthalene-1-carbothioate (3za)[9]** (White solid was obtained in 88% isolated yield, 116.4 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.35 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.0 Hz, 2H), 8.02 (d, J = 8.0 Hz, 1H), 7.64–7.52 (m, 8H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 191.6, 135.0, 134.2, 133.6, 133.6, 130.0, 129.6, 128.8, 128.5, 128.5, 128.0, 127.7, 127.1, 125.1, 124.6.

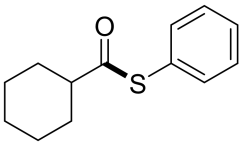


***S*-phenyl ethanethioate (3zaa)[6]** (White solid was obtained in 48% isolated yield, 36.2 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.47–7.45 (m, 3H), 7.44–7.40 (m, 2H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 193.8, 134.6, 129.8, 129.6, 127.8, 30.4.

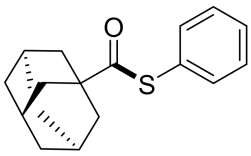


***S*-phenyl cyclopropanecarbothioate (3zab)[12]** (White solid was obtained in 89% isolated yield, 78.9 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.46–7.40 (m, 5H), 2.25–2.19 (m, 1H), 1.06–1.02 (m, 4H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 196.7,

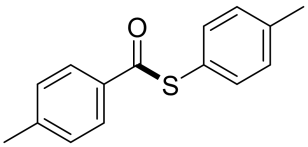
134.6, 129.6, 129.4, 127.4, 22.1, 11.1.



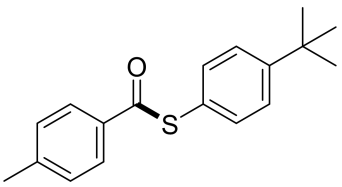
***S*-phenyl cyclohexanecarbothioate (3zac)[13]** (White solid was obtained in 91% isolated yield, 100.5 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.45–7.42 (m, 3H), 7.40–7.36 (m, 2H), 2.67–2.60 (m, 1H), 1.90 (d, J = 8.0 Hz, 2H), 1.73–1.68 (m, 2H), 1.61–1.57 (m, 1H), 1.44–1.13 (m, 5H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 199.8, 134.6, 129.5, 129.4, 127.5, 51.7, 29.2, 25.3, 25.0.



***S*-phenyl (3r,5r,7r)-adamantane-1-carbothioate (3zad)[14]** (White solid was obtained in 85% isolated yield, 115.6 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.43 (t, J = 4.0 Hz, 3H), 7.36–7.33 (m, 2H), 2.02 (s, 3H), 1.91 (s, 6H), 1.72–1.65 (m, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 202.9, 135.0, 129.4, 129.4, 127.5, 48.6, 38.9, 35.9, 27.8.

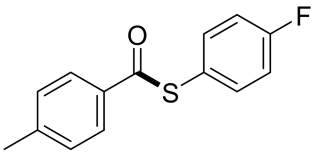


***S*-(p-tolyl) 4-methylbenzothioate (3ab)[6]** (White solid was obtained in 74% isolated yield, 89.0 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.86 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 4H), 7.29 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.8, 144.7, 139.4, 134.7, 133.5, 129.9, 129.6, 127.0, 123.4, 21.1, 20.7.

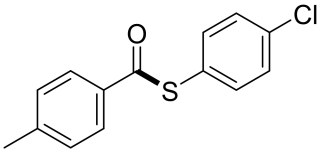


***S*-(4-(tert-butyl)phenyl) 4-methylbenzothioate (3ac)[15]** (White solid was obtained in 63% isolated yield, 88.9 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.86 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.40–7.35 (m, 4H), 2.37 (s, 3H), 1.27 (s, 9H); **^{13}C**

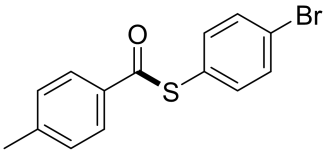
NMR (101 MHz, DMSO-d_6) δ 189.1, 152.5, 145.0, 134.9, 133.5, 129.9, 127.3, 126.5, 123.6, 34.7, 31.1, 21.4.



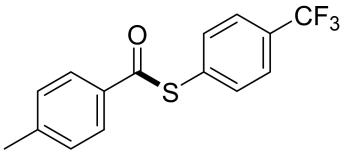
***S*-(4-fluorophenyl) 4-methylbenzothioate (3ad)[16]** (White solid was obtained in 73% isolated yield, 89.4 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.86 (d, J = 8.0 Hz, 2H), 7.56–7.51 (m, 2H), 7.38–7.31 (m, 4H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.8, 163.2 (d, J = 252.5 Hz), 145.2, 137.7 (d, J = 10.1 Hz), 133.3, 129.9, 127.3, 122.7, 116.7 (d, J = 20.2 Hz), 21.4; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -111.32.



***S*-(4-chlorophenyl) 4-methylbenzothioate (3ae)[6]** (White solid was obtained in 75% isolated yield, 98.3 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.86 (d, J = 8.0 Hz, 2H), 7.55–7.50 (m, 4H), 7.38 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.1, 144.9, 136.4, 134.7, 133.2, 129.6, 129.2, 127.1, 126.0, 21.1.

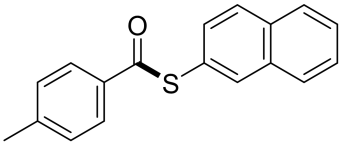


***S*-(4-bromophenyl) 4-methylbenzothioate (3af)[16]** (White solid was obtained in 88% isolated yield, 135.2 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.86 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 187.8, 144.8, 136.6, 133.1, 132.1, 129.6, 127.0, 126.5, 123.2, 21.0.

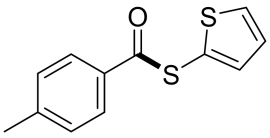


***S*-(4-(trifluoromethyl)phenyl) 4-methylbenzothioate (3ag)** (White solid was obtained in 49% isolated yield, 73.2 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.89–7.84 (m, 4H), 7.75 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H);

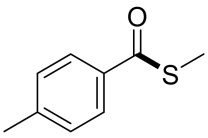
^{13}C NMR (101 MHz, DMSO-d_6) δ 187.8, 145.5, 135.8, 133.1, 132.5, 130.1 (q, J =30.3 Hz), 130.0, 127.5, 126.2, 124.2 (q, J =272.7 Hz), 21.4; **^{19}F NMR** (376 MHz, DMSO-d_6) δ -61.39. HRMS (ESI) calcd for $C_{15}H_{12}F_3OS$: 297.0555 ($M+H^+$), found: 297.0555.



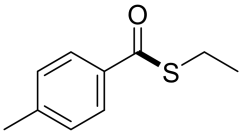
***S*-(naphthalen-2-yl) 4-methylbenzothioate (3ah)[17]** (White solid was obtained in 74% isolated yield, 102.8 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.12 (s, 1H), 8.00–7.93 (m, 3H), 7.90 (d, J = 8.0 Hz, 2H), 7.62–7.52 (m, 3H), 7.36 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.8, 144.8, 134.6, 133.5, 133.2, 132.9, 131.3, 129.7, 128.6, 127.8, 127.6, 127.3, 127.1, 126.7, 124.4, 21.1.



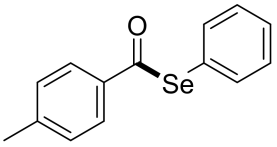
***S*-(thiophen-2-yl) 4-methylbenzothioate (3ai)** (White solid was obtained in 41% isolated yield, 47.4 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.92–7.90 (m, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.34–7.33 (m, 1H), 7.24–7.21 (m, 1H), 2.39 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 188.4, 145.4, 136.8, 133.4, 132.7, 130.0, 128.3, 127.4, 123.3, 21.4. HRMS (ESI) calcd for $C_{12}H_{11}OS_2$: 235.0246 ($M+H^+$), found: 235.0238.



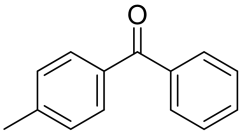
***S*-methyl 4-methylbenzothioate (3aj)[18]** (Colorless oil was obtained in 75% isolated yield, 62.3 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.81 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 191.2, 144.4, 134.0, 129.7, 126.9, 21.3, 11.3.



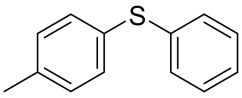
***S*-ethyl 4-methylbenzothioate (3ak)[6]** (Colorless oil was obtained in 65% isolated yield, 58.6 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.81 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 3.04–2.99 (m, 2H), 2.37 (s, 3H), 1.26 (t, J = 8.0 Hz, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 190.8, 144.4, 134.1, 129.7, 126.9, 22.9, 21.3, 14.9.



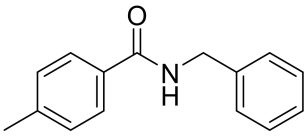
***Se*-phenyl 4-methylbenzoselenoate (4a)[19]** (White solid was obtained in 93% isolated yield, 128.5 mg). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.80 (d, J = 8.0 Hz, 2H), 7.57–7.55 (m, 2H), 7.50–7.42 (m, 3H), 7.38 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 191.9, 145.4, 136.3, 135.3, 130.1, 129.6, 129.2, 127.2, 125.5, 21.4.



phenyl(p-tolyl)methanone (5a)[20] (White solid was obtained in 35% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.2, 143.1, 137.7, 134.7, 132.1, 130.2, 129.8, 128.9, 128.1, 21.5.

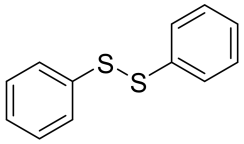


phenyl(p-tolyl)sulfane (6a)[21] (Colorless oil was obtained in 48% isolated yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.29 (d, J = 8.0 Hz, 2H), 7.26 - 7.21 (m, 4H), 7.19 - 7.14 (m, 1H), 7.11 (d, J = 8.0 Hz, 2H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 137.7, 137.2, 132.4, 131.4, 130.2, 129.9, 129.1, 126.5, 21.2.

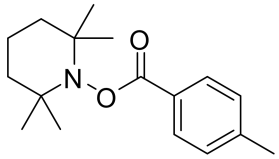


***N*-benzyl-4-methylbenzamide (7a)[22]** (White solid was obtained in 76% isolated

yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.29–7.27 (m, 4H), 7.26–7.23 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.80 (s, 1H), 4.56 (d, *J* = 4.0 Hz, 2H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.5, 141.9, 138.4, 131.5, 129.2, 128.7, 127.8, 127.4, 127.1, 44.0, 21.5.



1,2-diphenyldisulfane (8a)[23] (White solid was obtained in 73% isolated yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.51 (d, *J* = 8.0 Hz, 4H), 7.35 (t, *J* = 8.0 Hz, 4H), 7.26 (t, *J* = 8.0 Hz, 2H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 135.9, 129.5, 127.5, 127.1.



2,2,6,6-tetramethylpiperidin-1-yl 4-methylbenzoate (9a) (Colorless oil was obtained). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 1.61–1.48 (m, 5H), 1.32 (d, *J* = 12.0 Hz, 1H), 1.13 (s, 6H), 0.93 (s, 6H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 165.5, 143.7, 129.6, 129.2, 126.5, 59.8, 38.9, 31.6, 21.3, 20.5, 16.7. HRMS (ESI) calcd for $C_{17}H_{26}NO_2$: 276.1958 ($M+H^+$), found: 276.1961.

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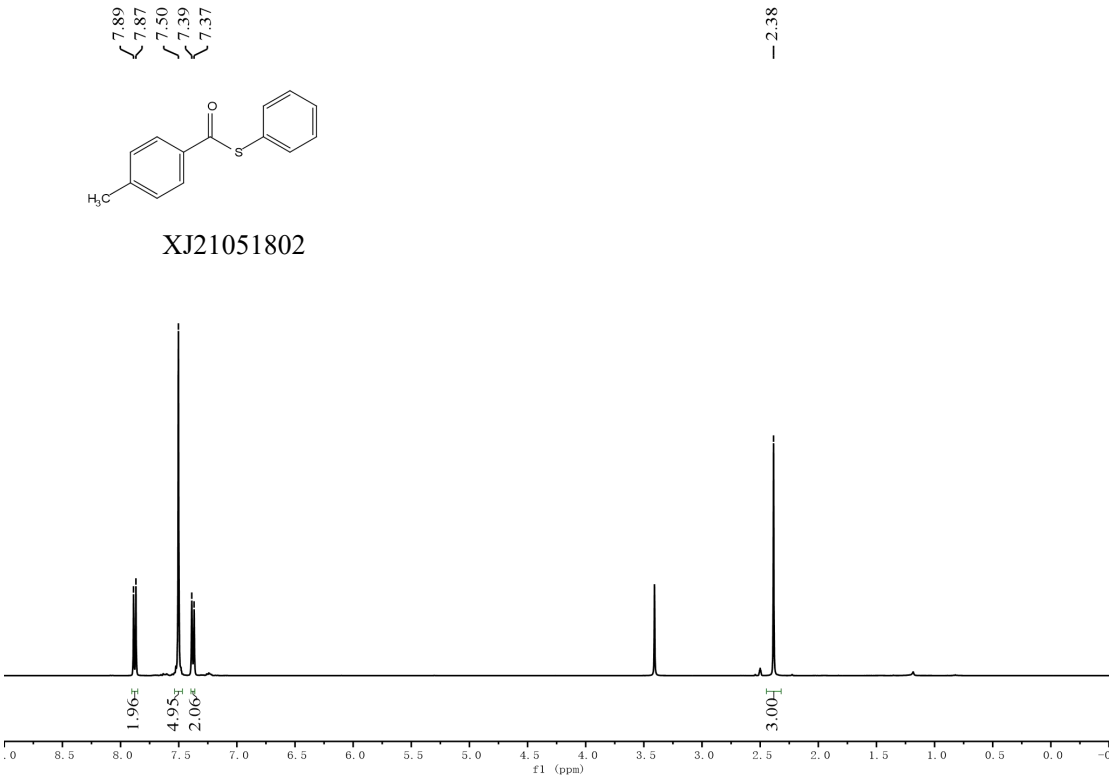
Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

^{1}H NMR (400 MHz, DMSO-d_6) of compound **3aa**



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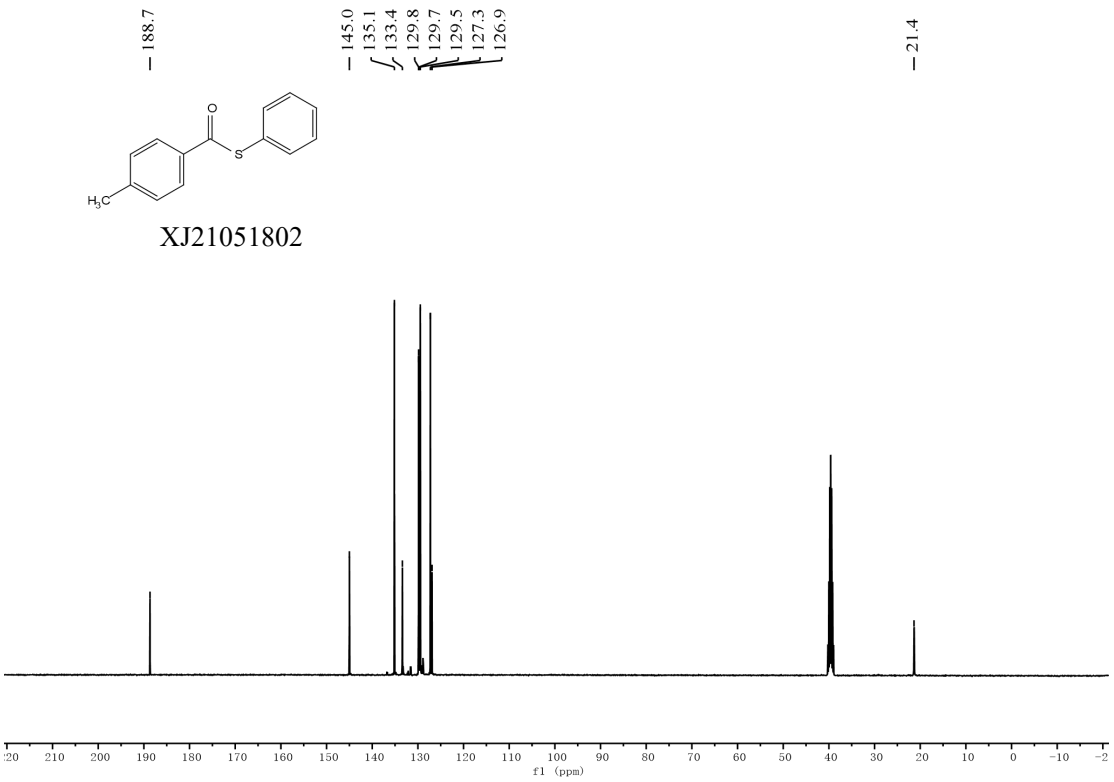

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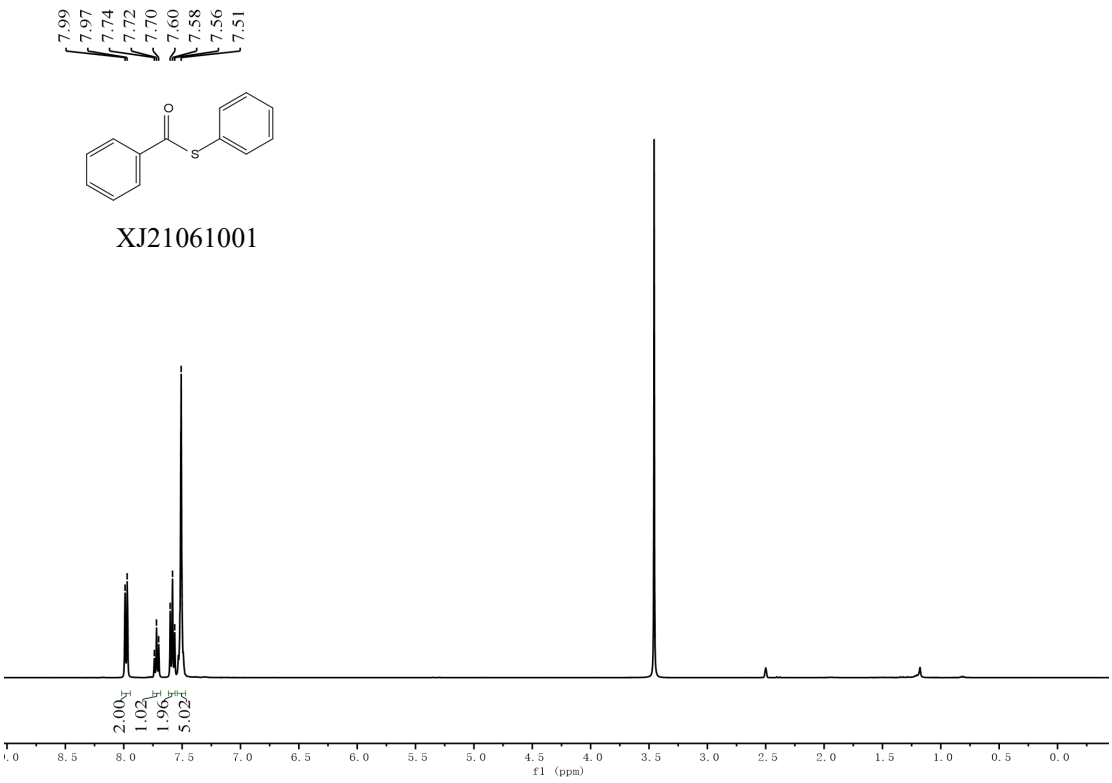

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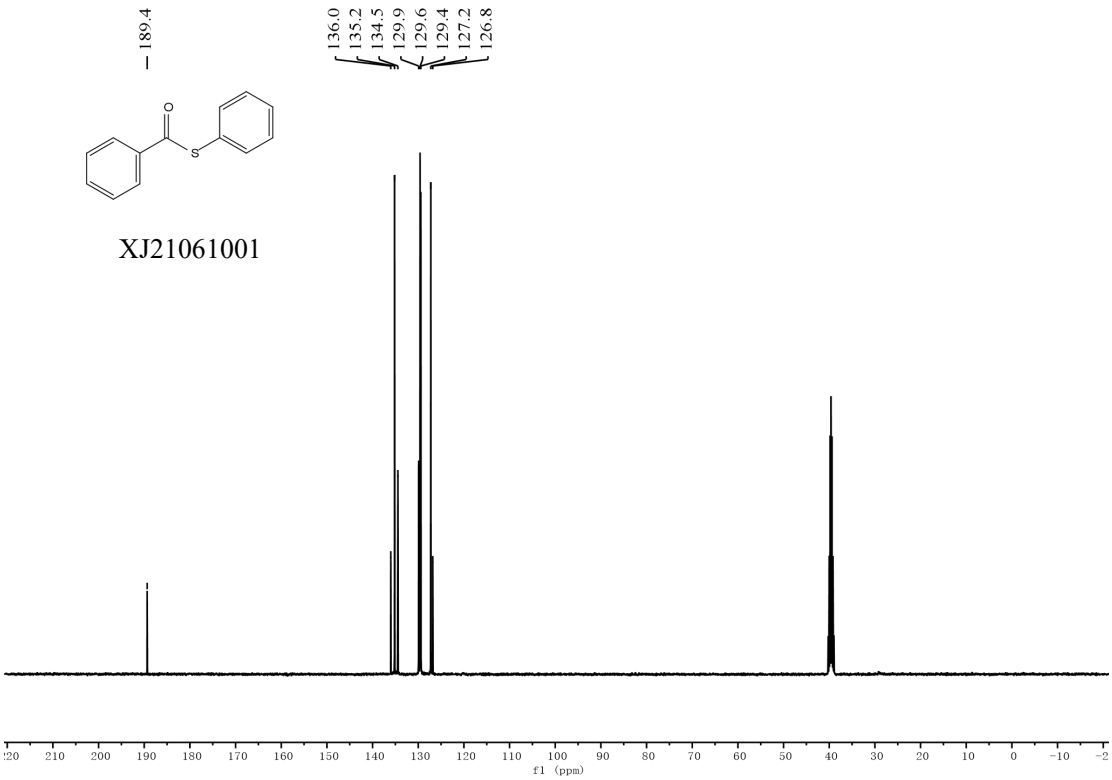

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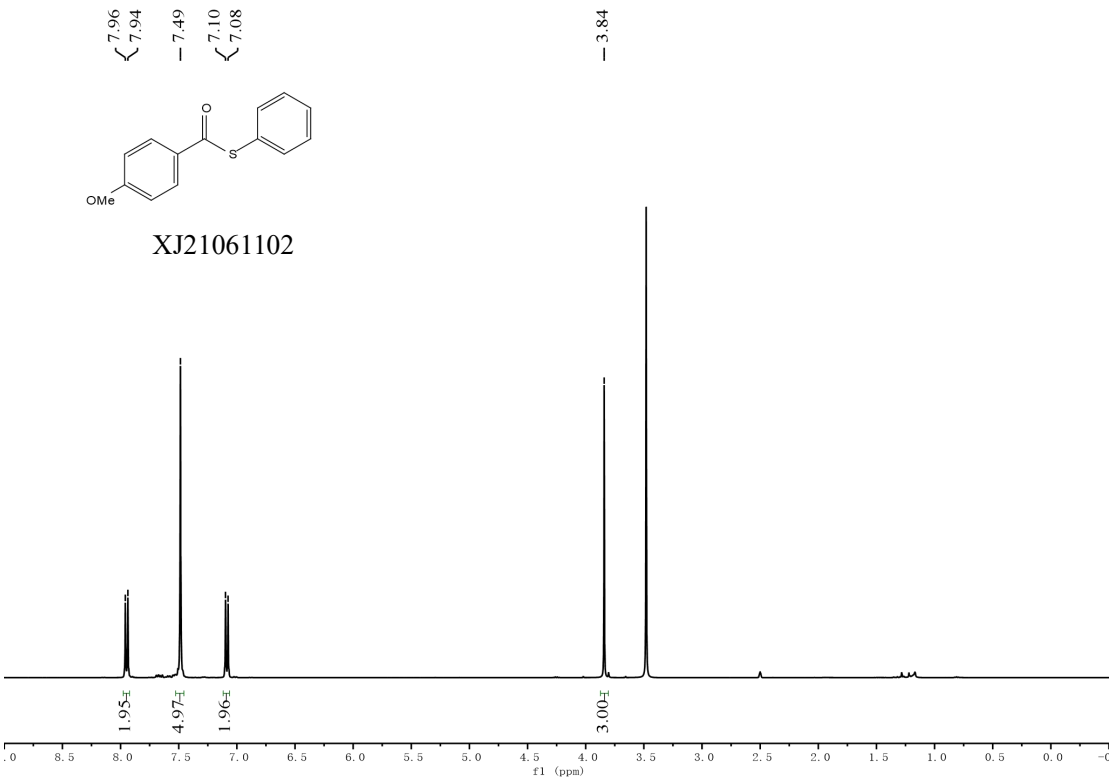

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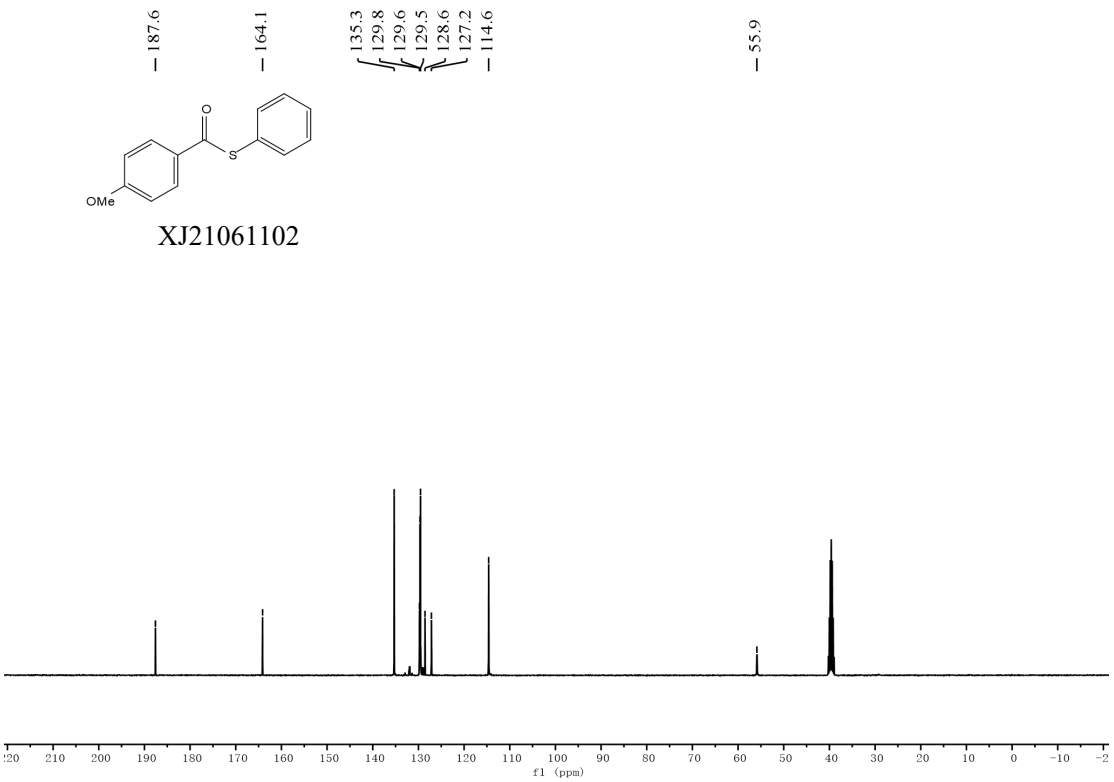

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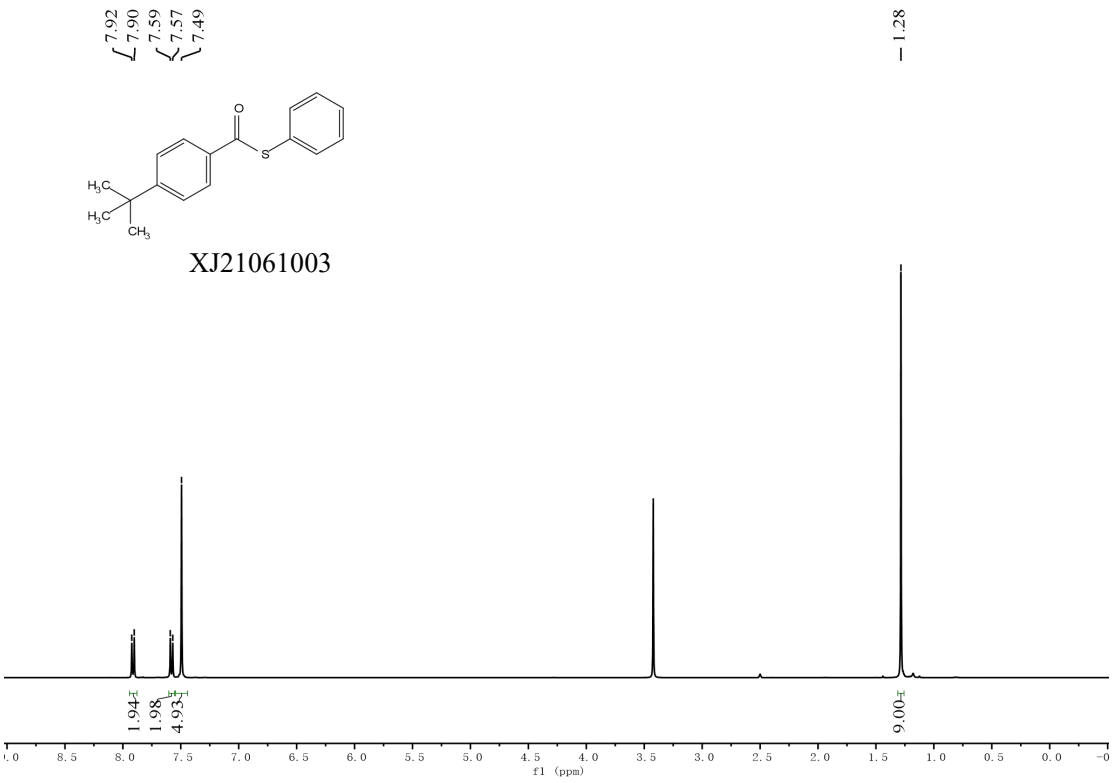

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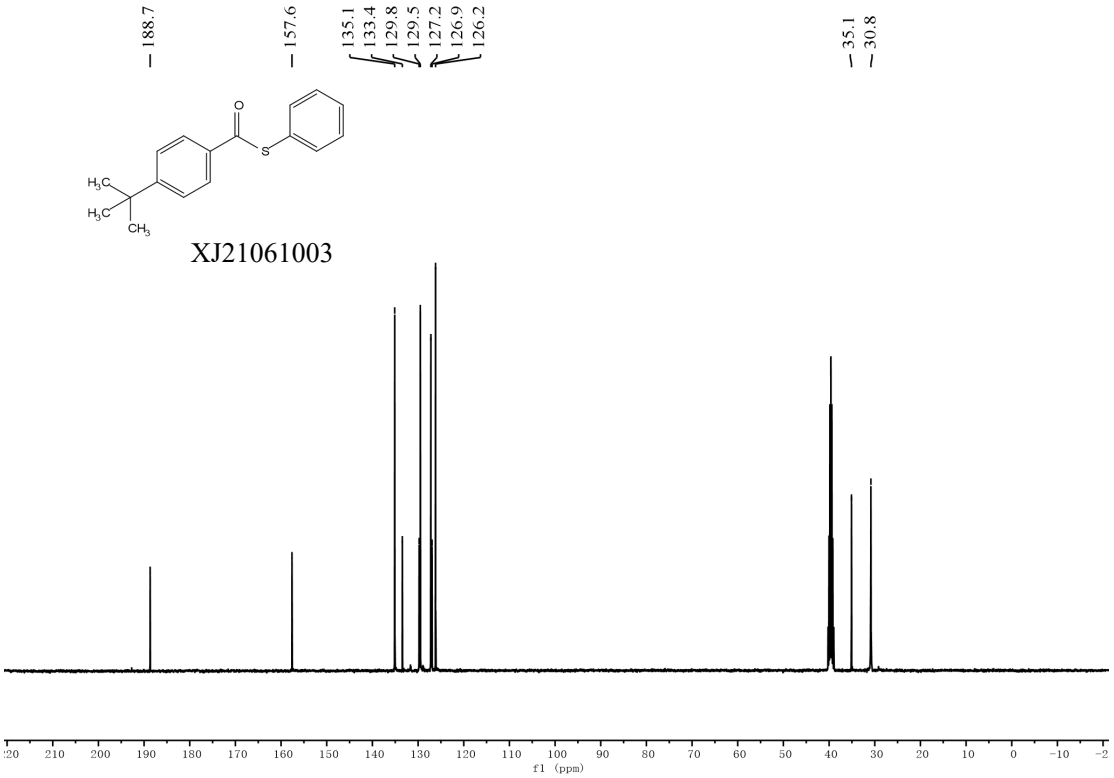

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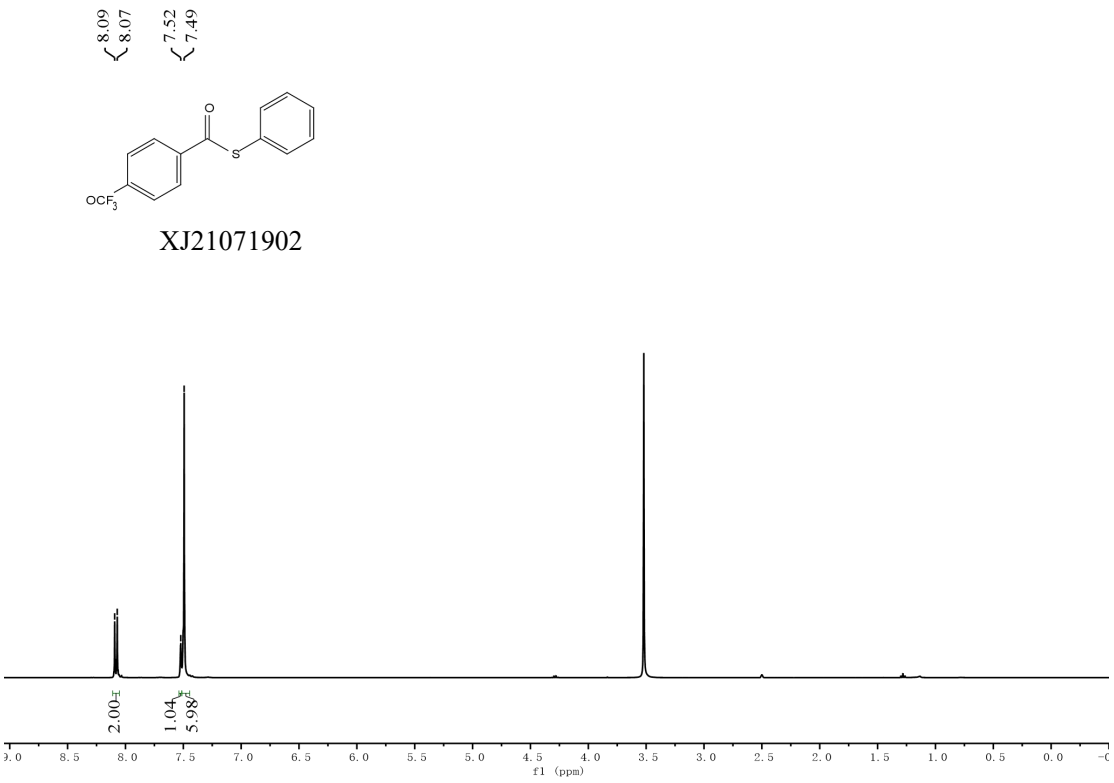

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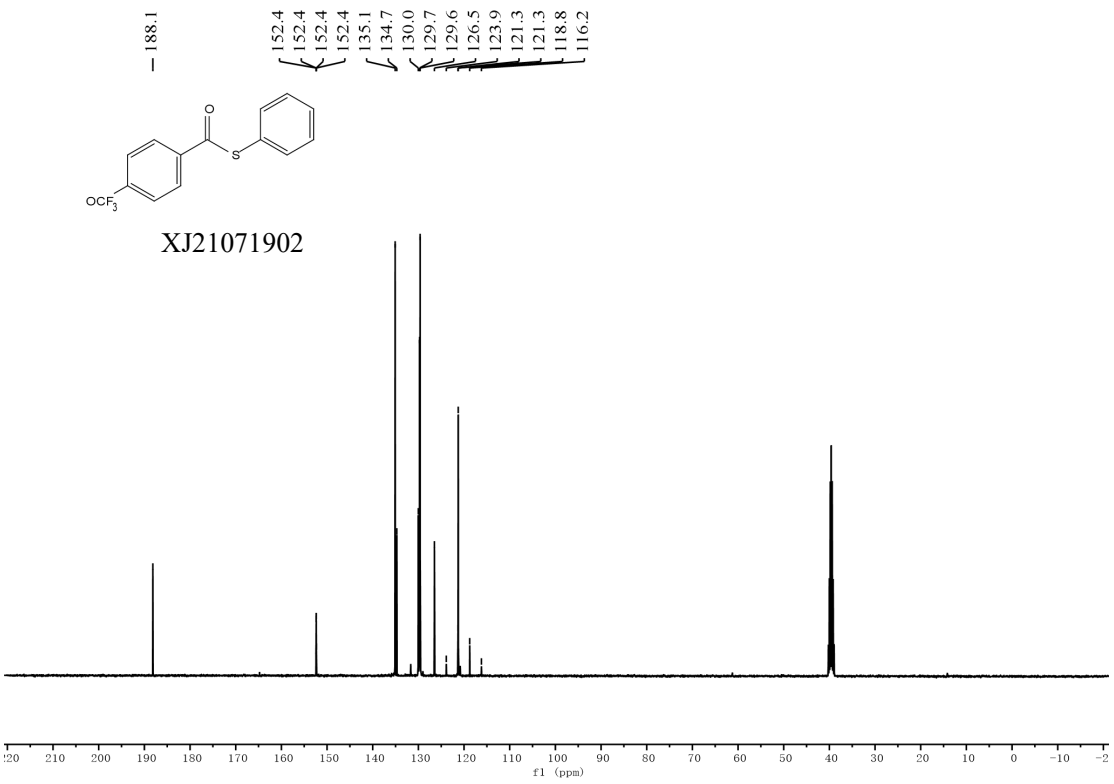
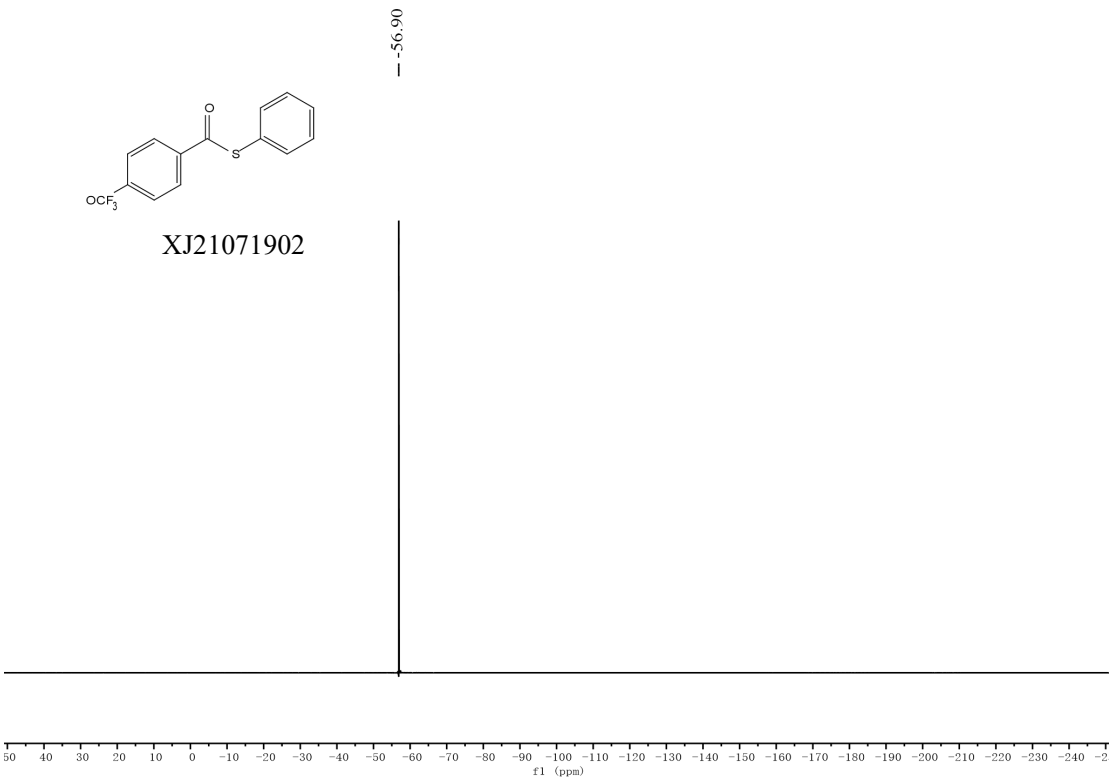


^{19}F NMR (376 MHz, DMSO-d_6) of compound **3ea**



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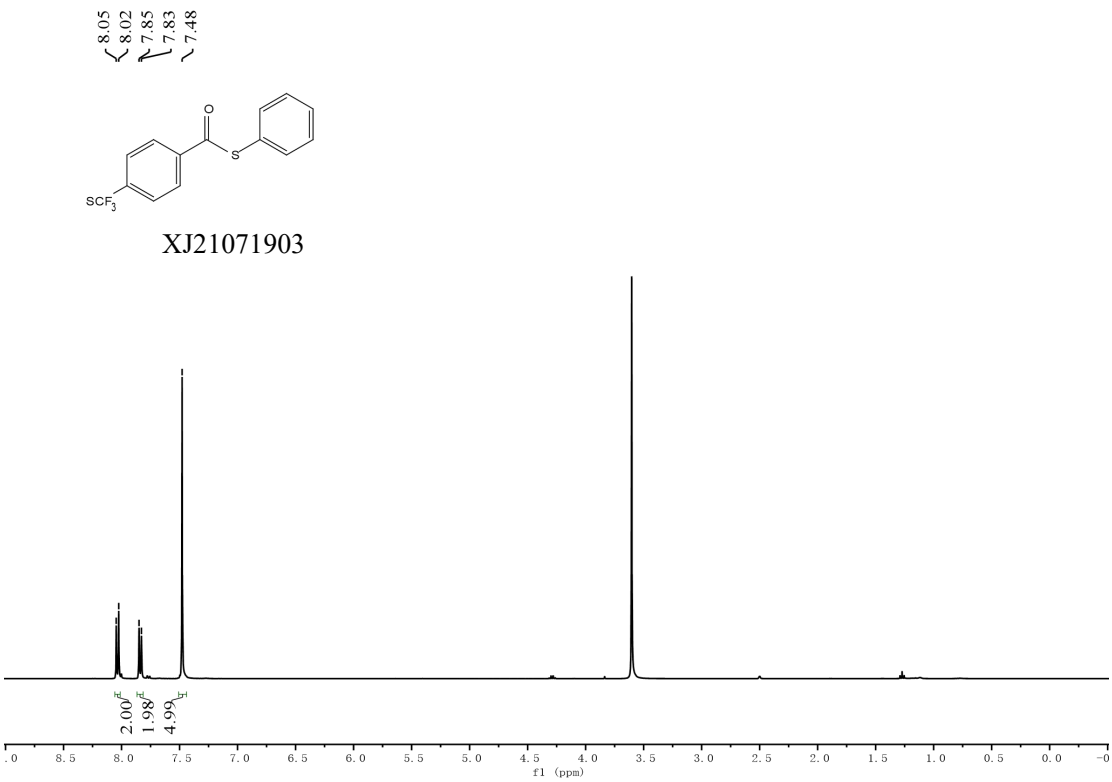

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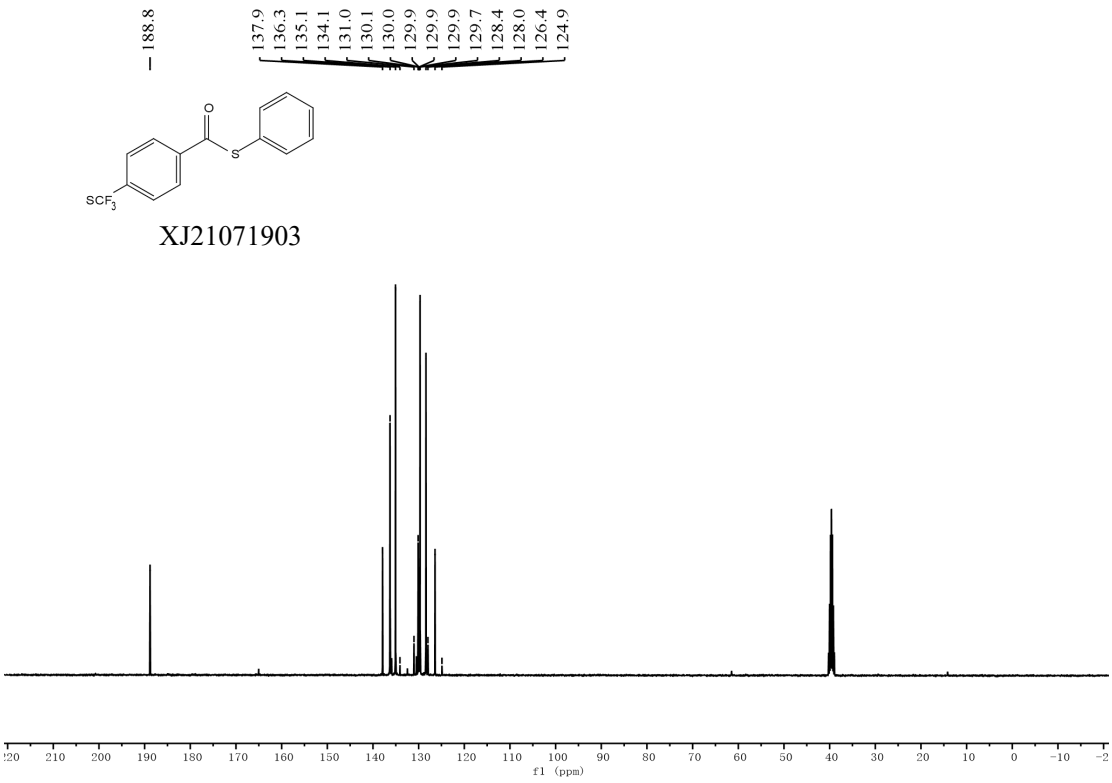

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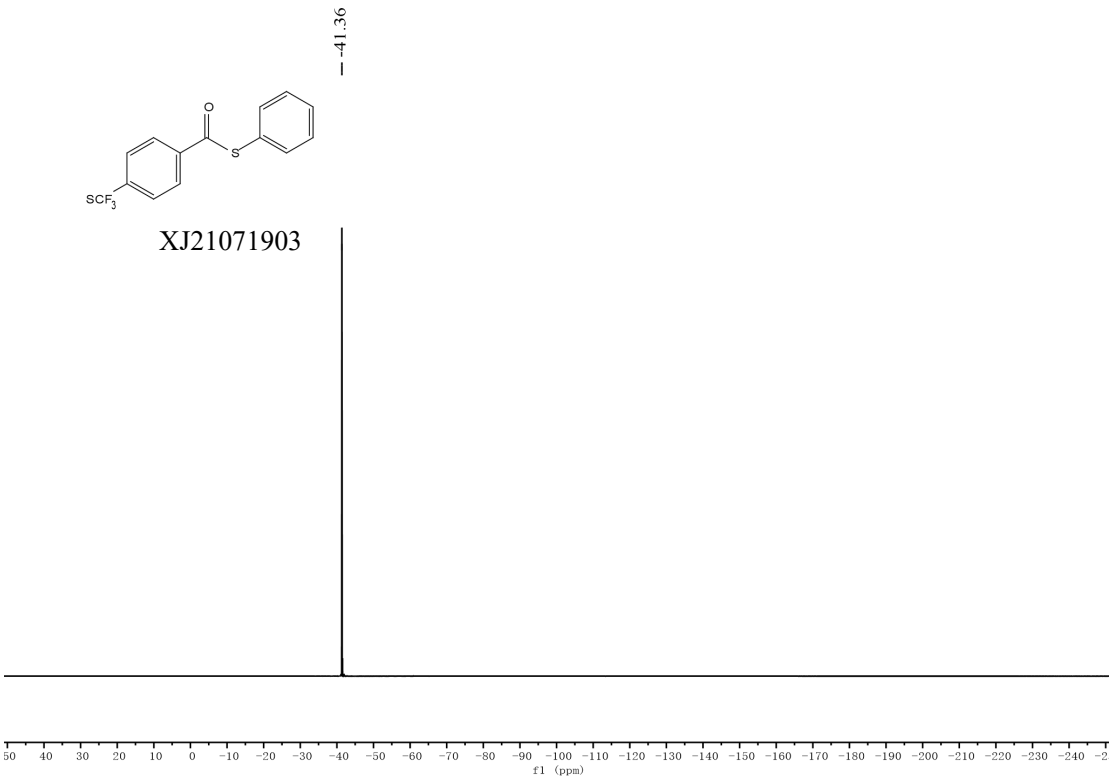

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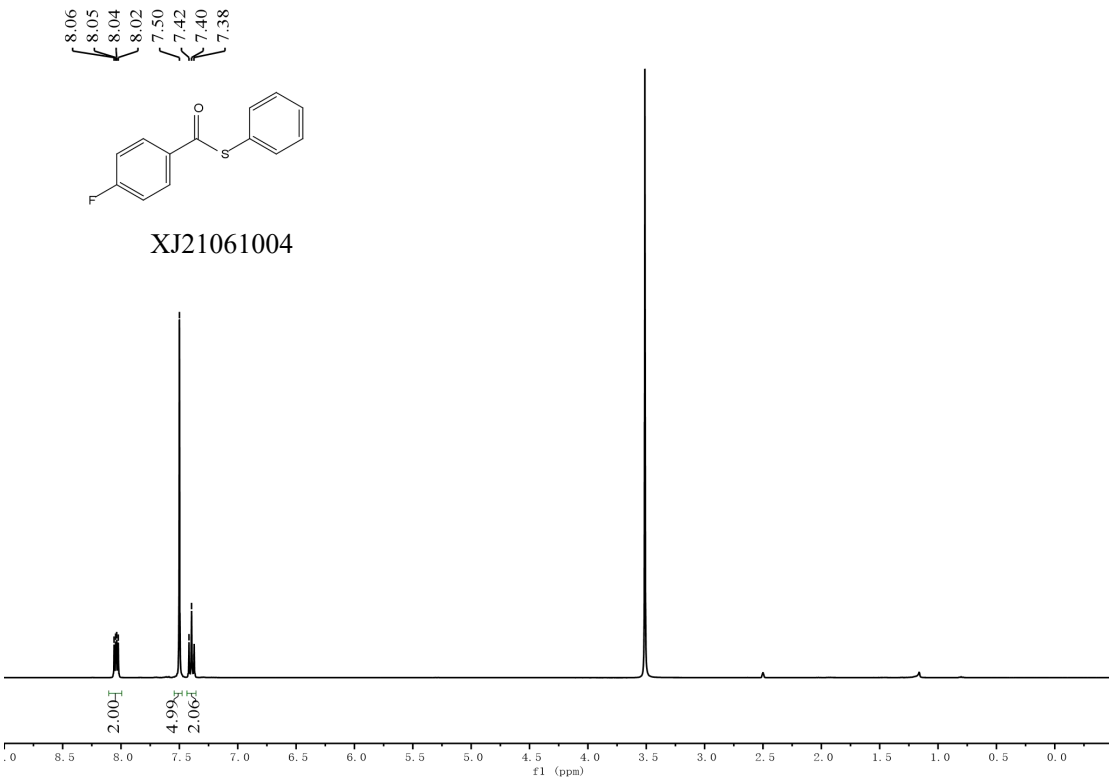

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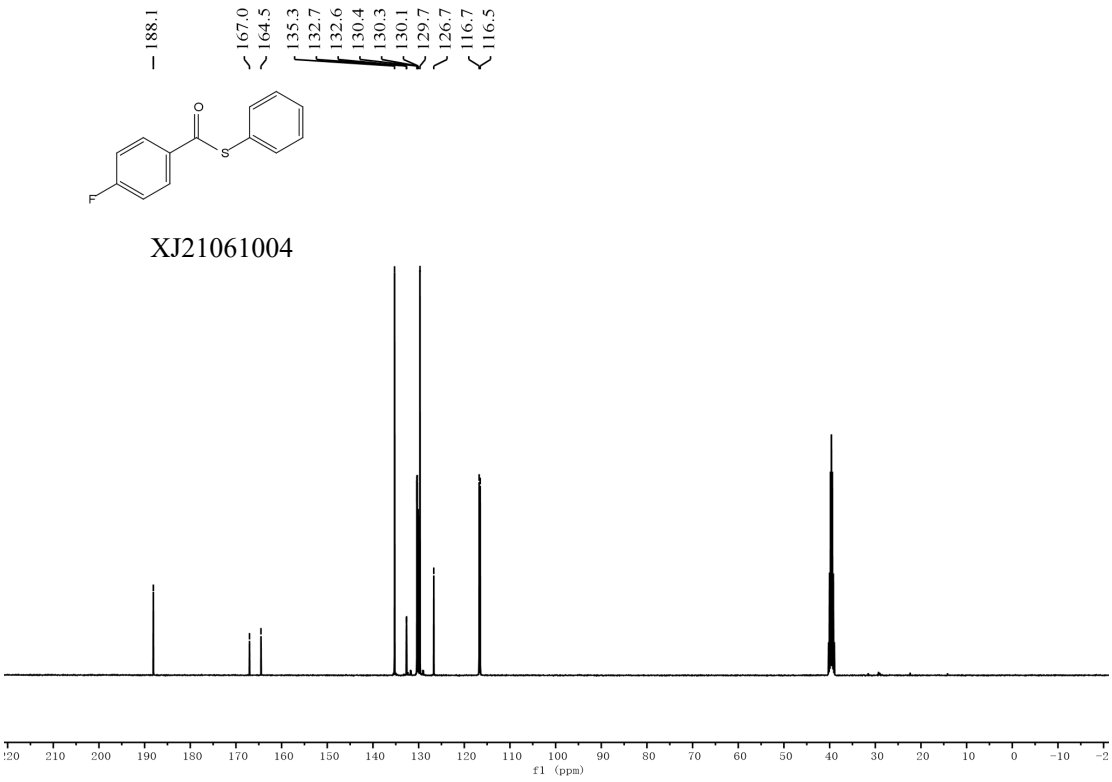

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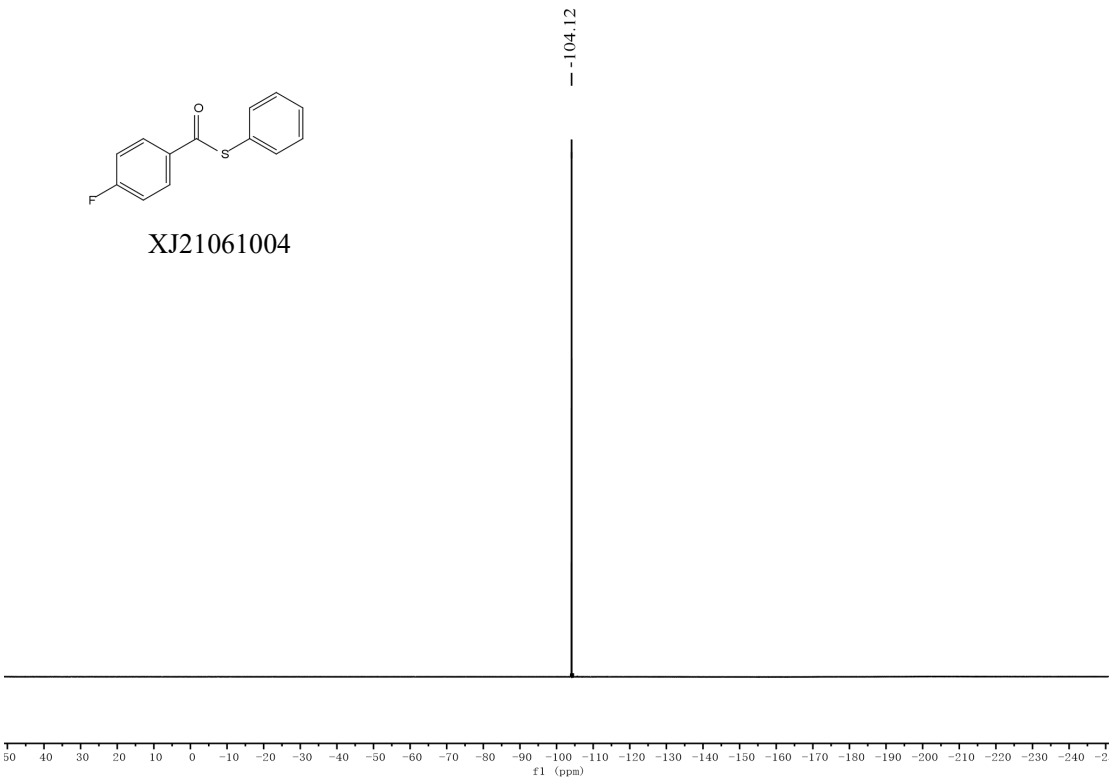

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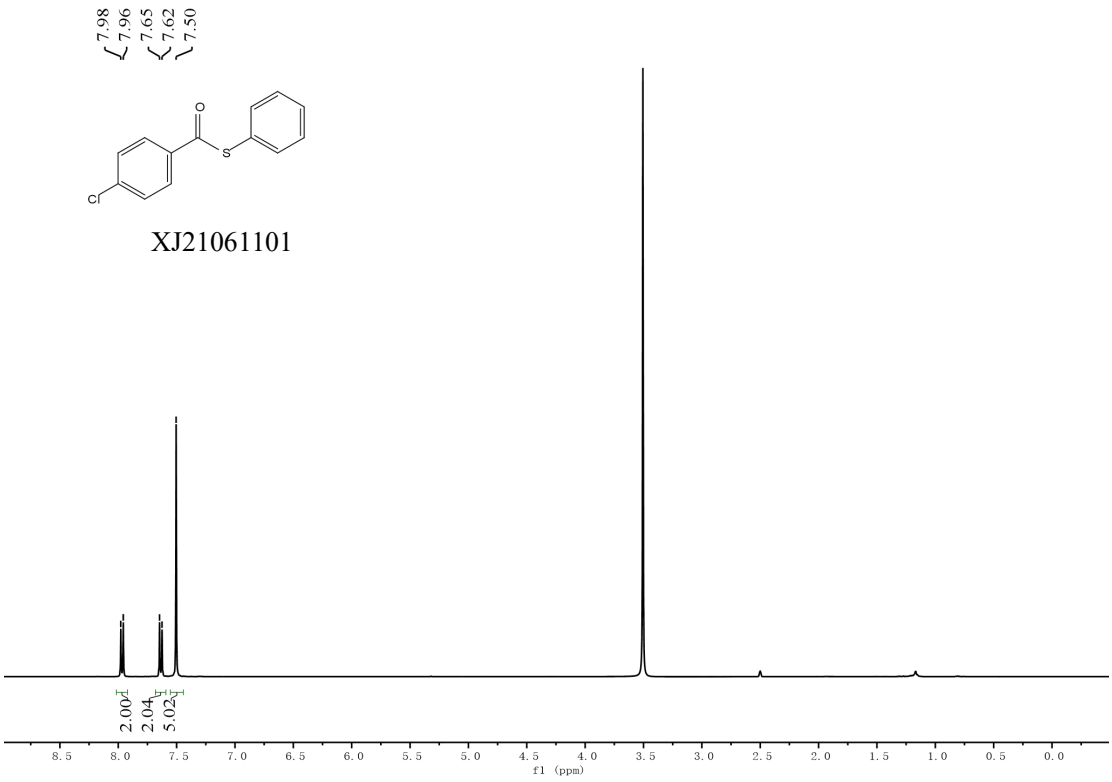

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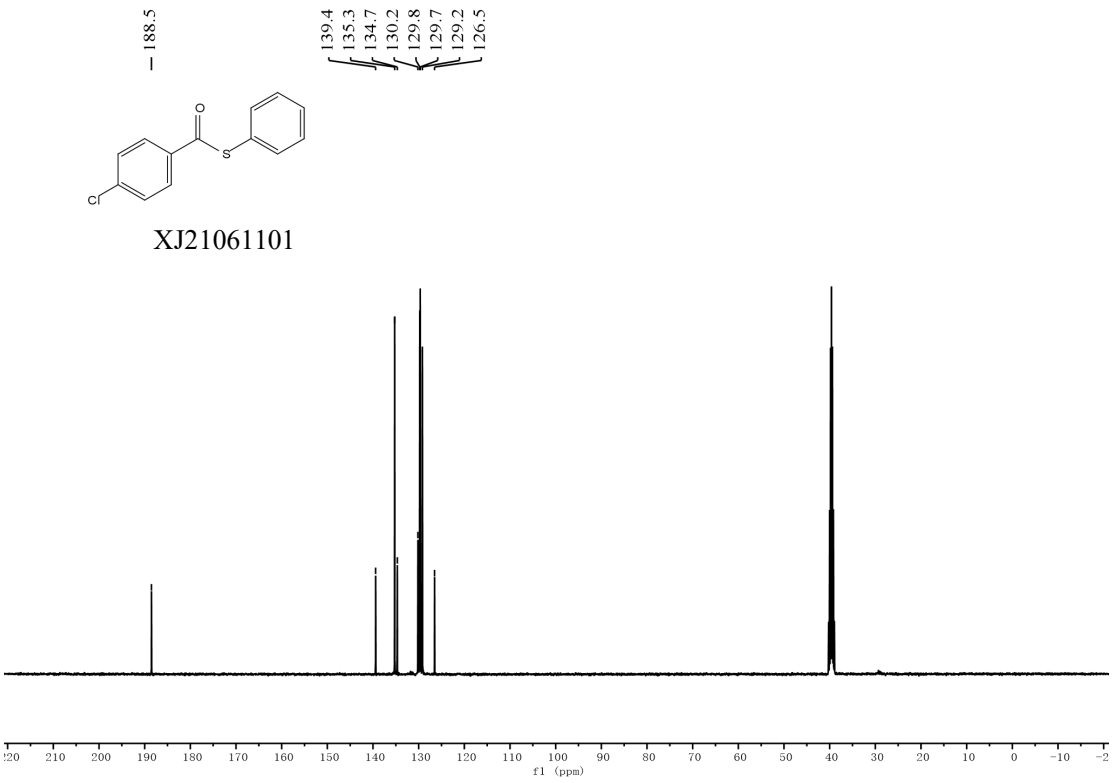

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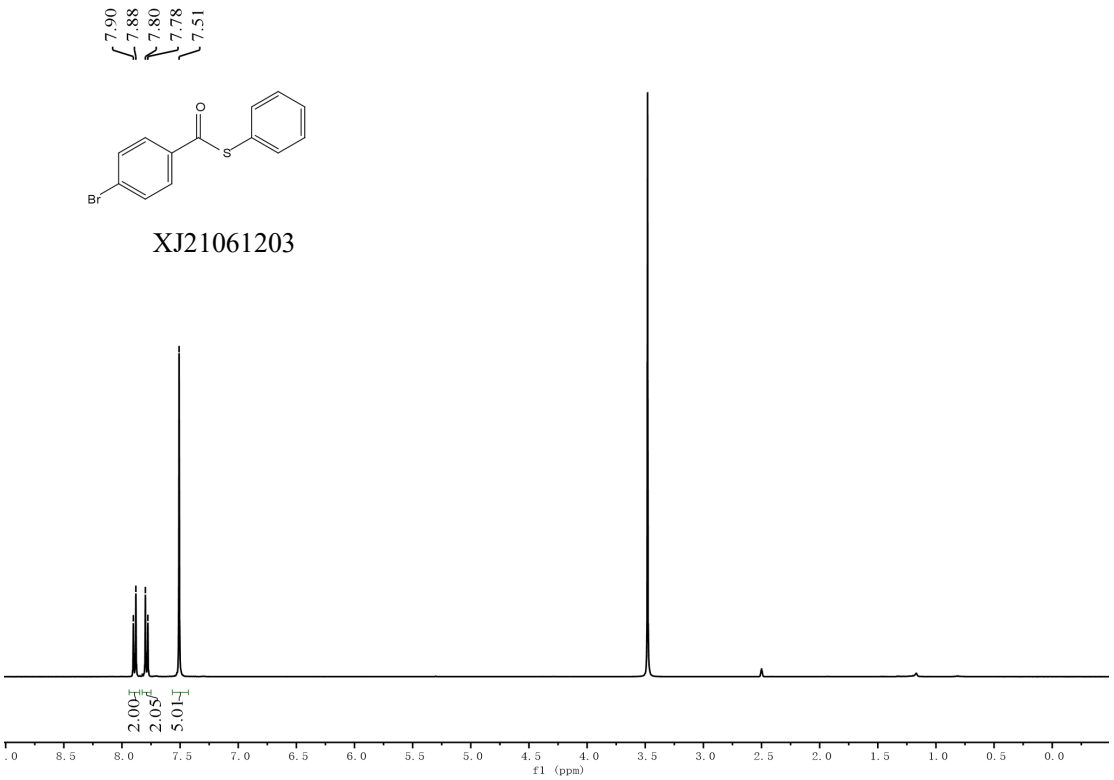

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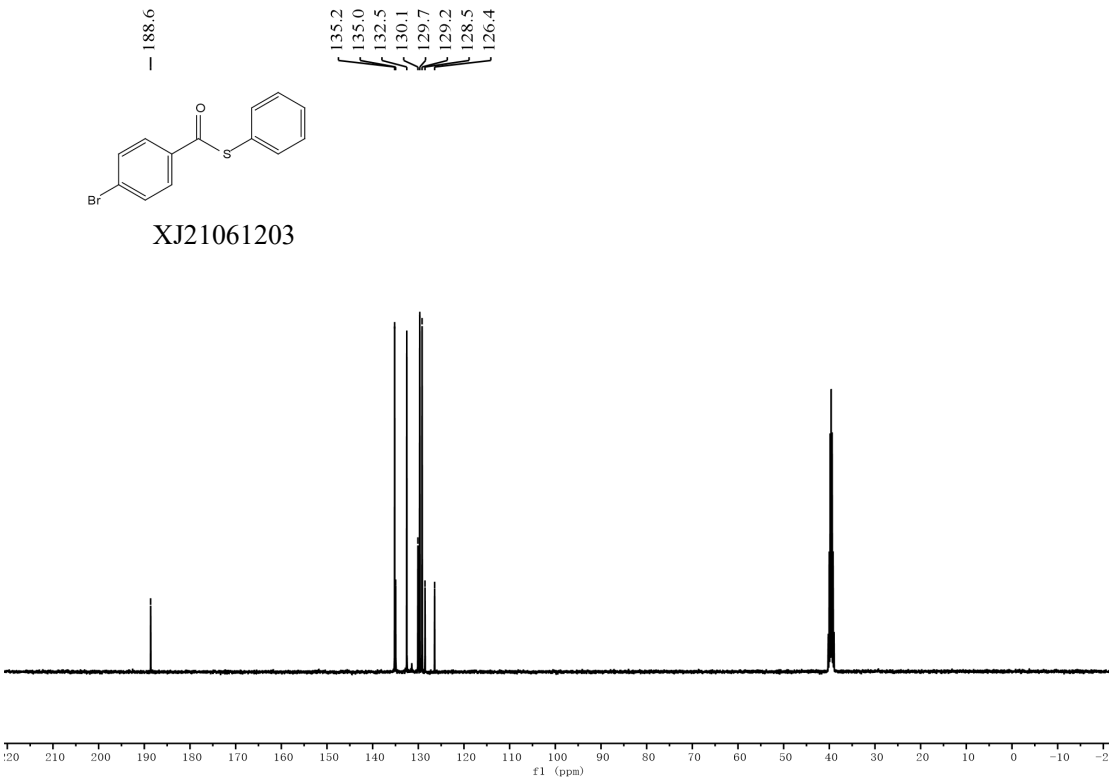

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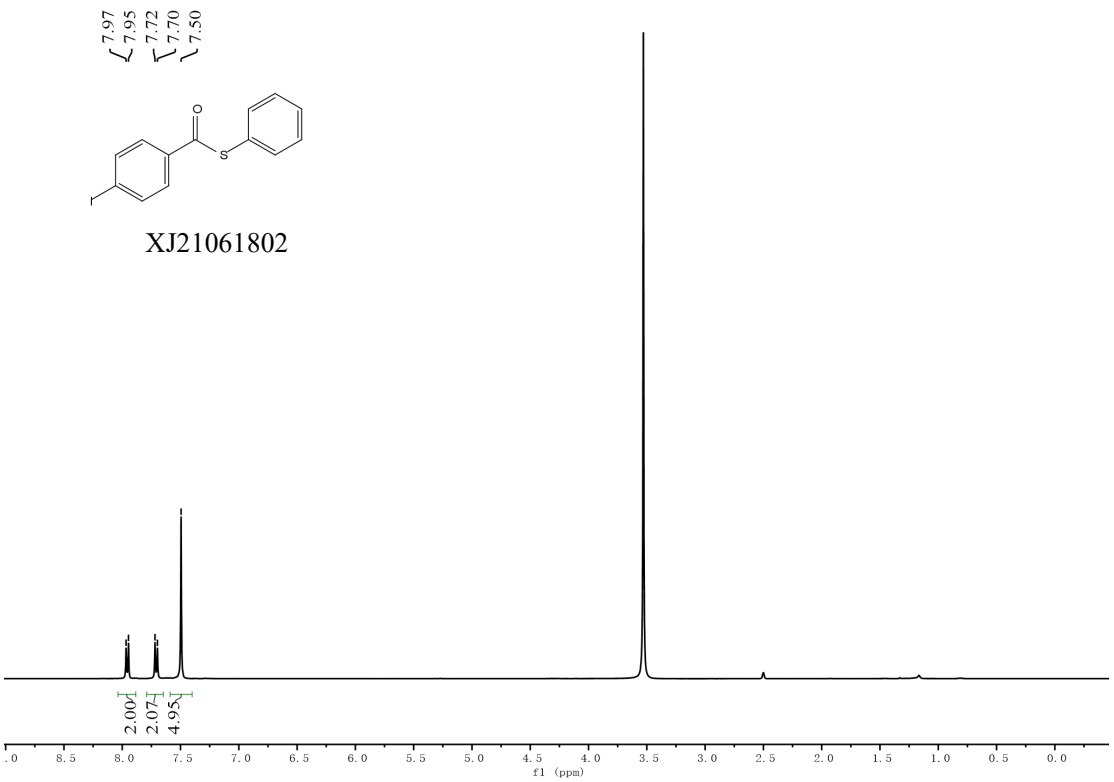

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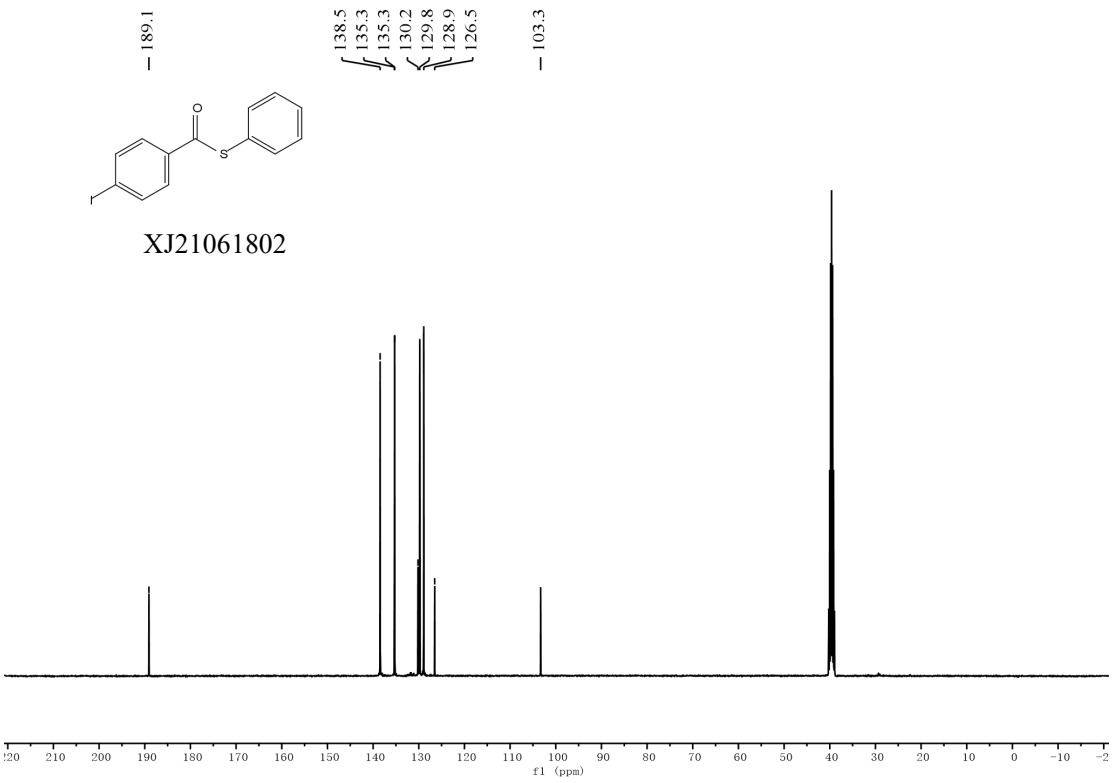

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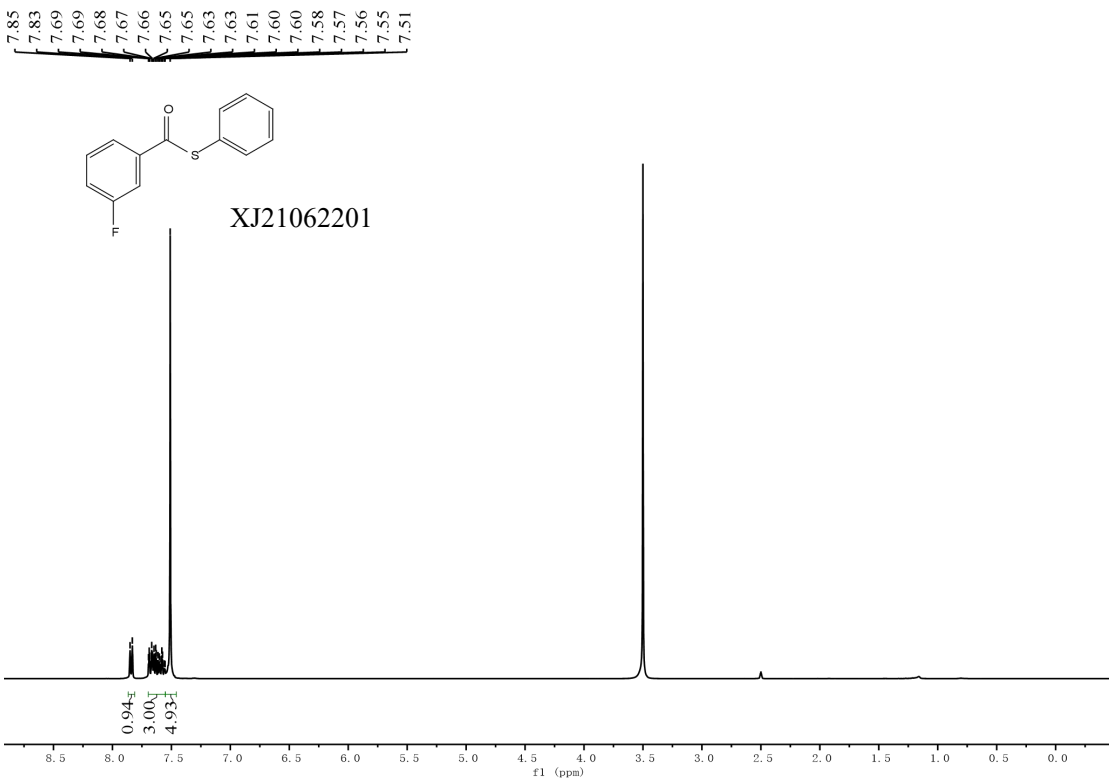

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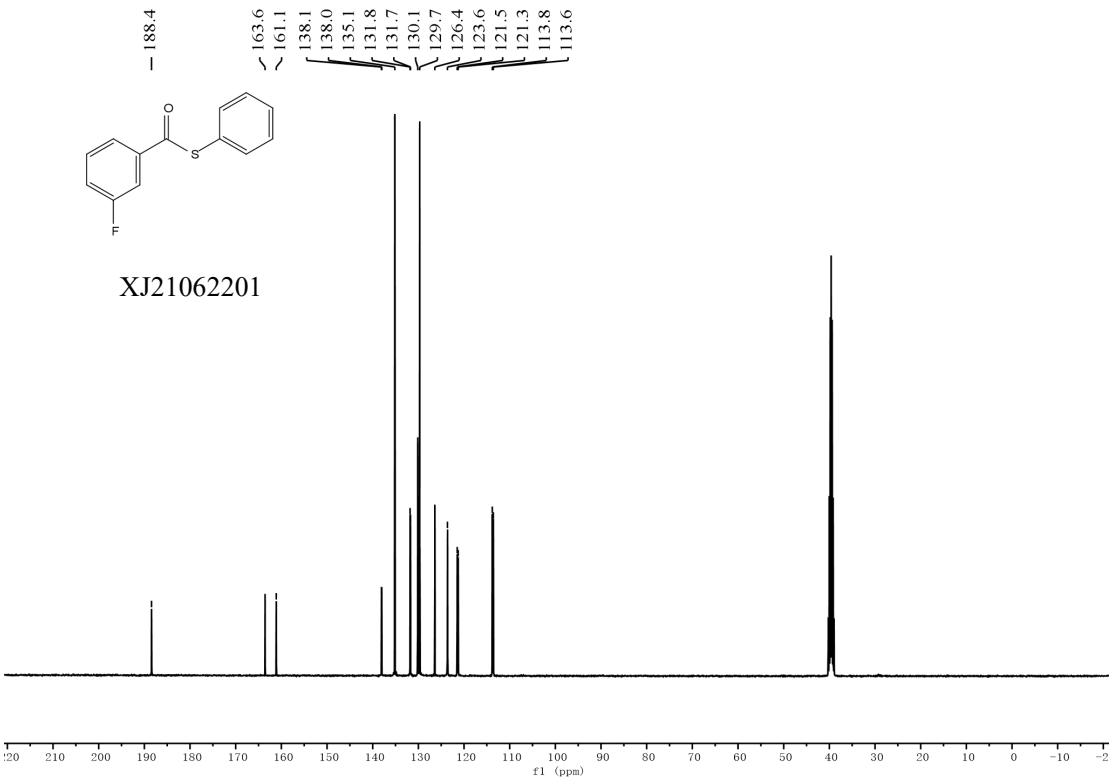
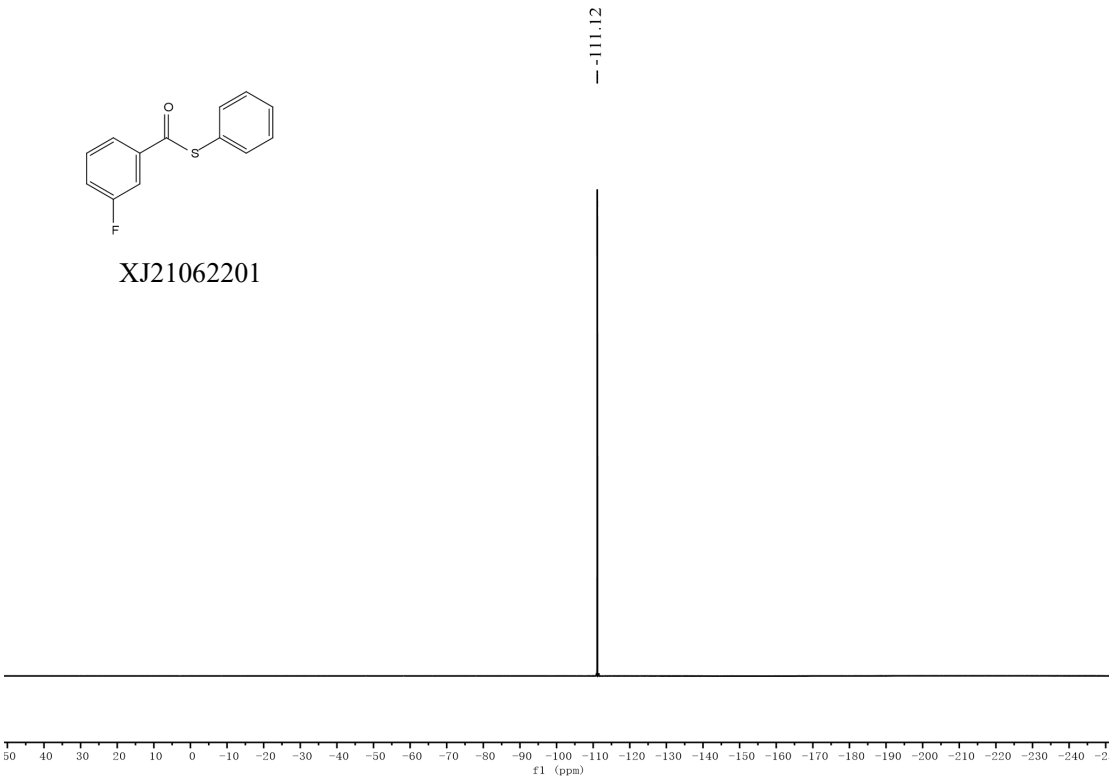


^{19}F NMR (376 MHz, DMSO-d_6) of compound **3ka**



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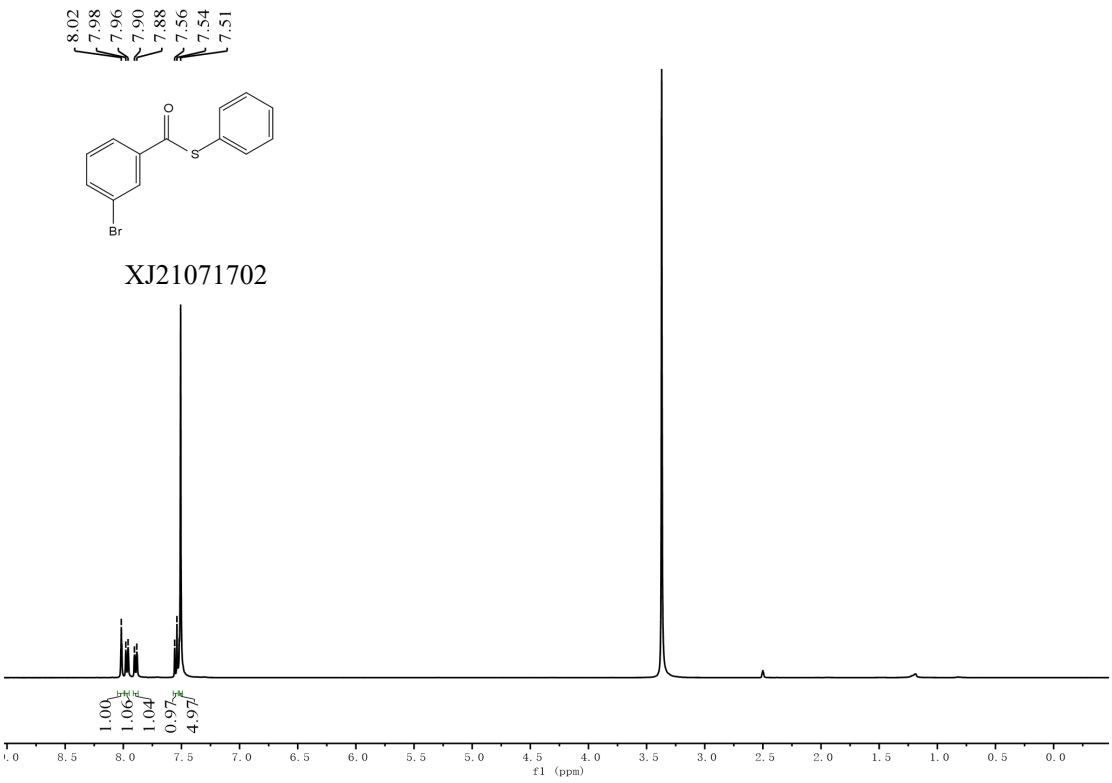

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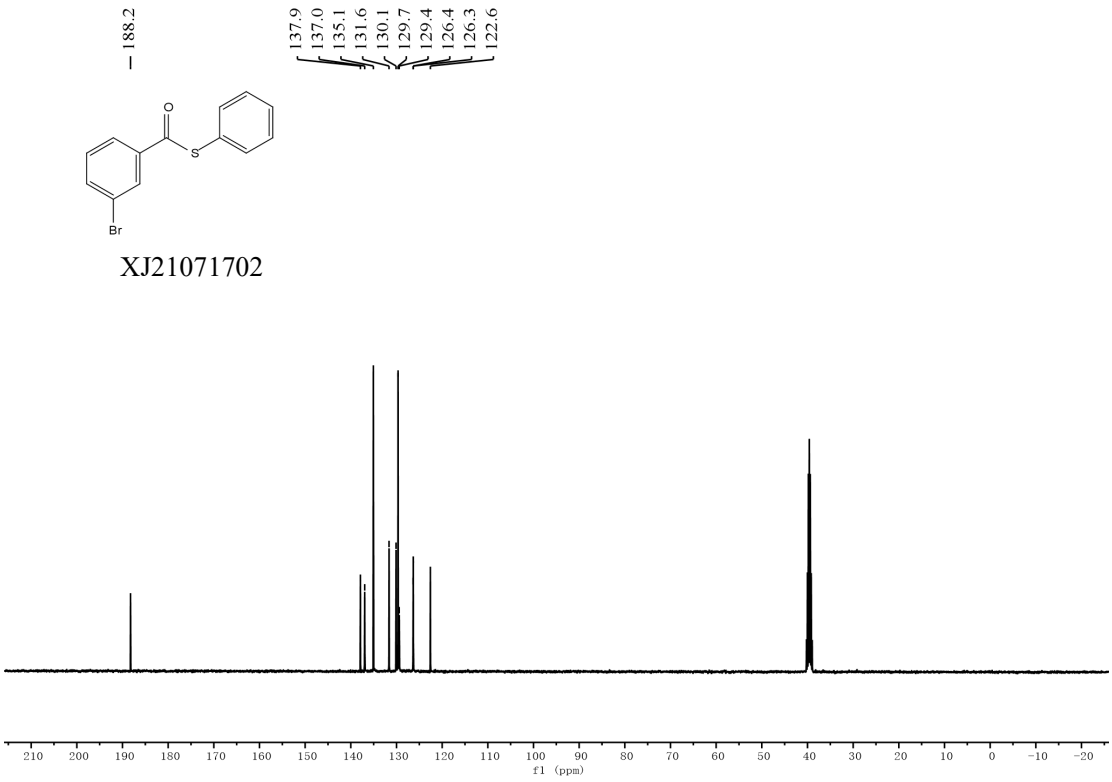

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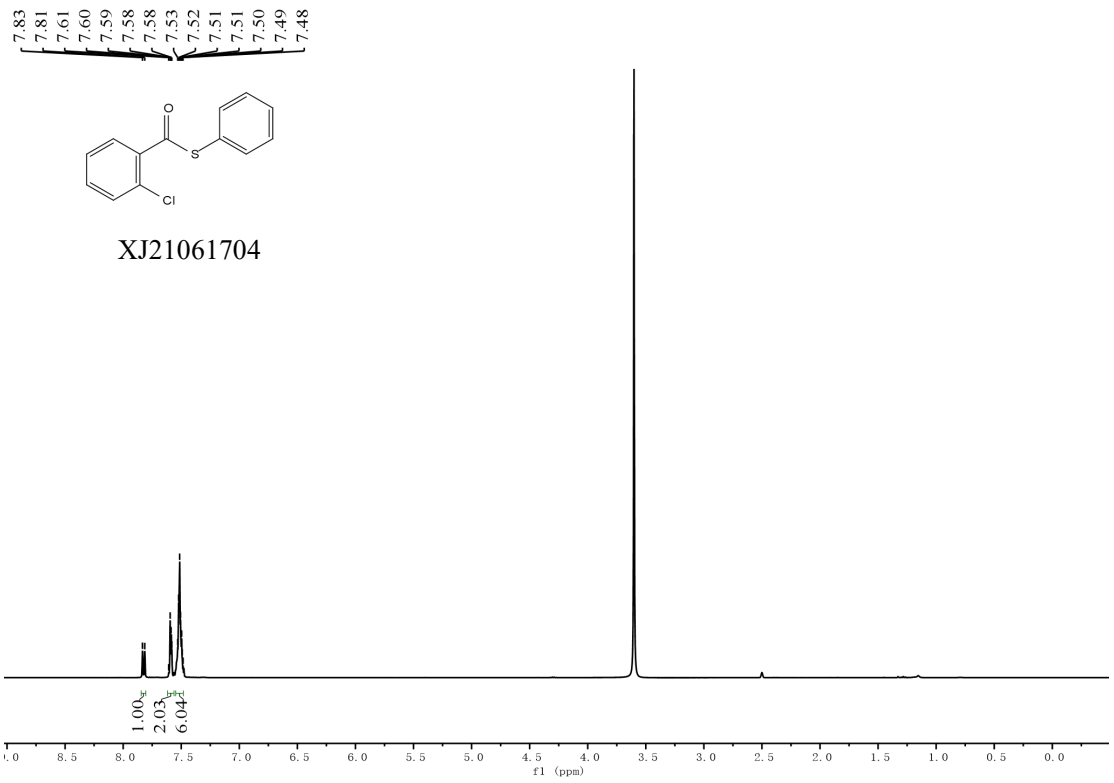

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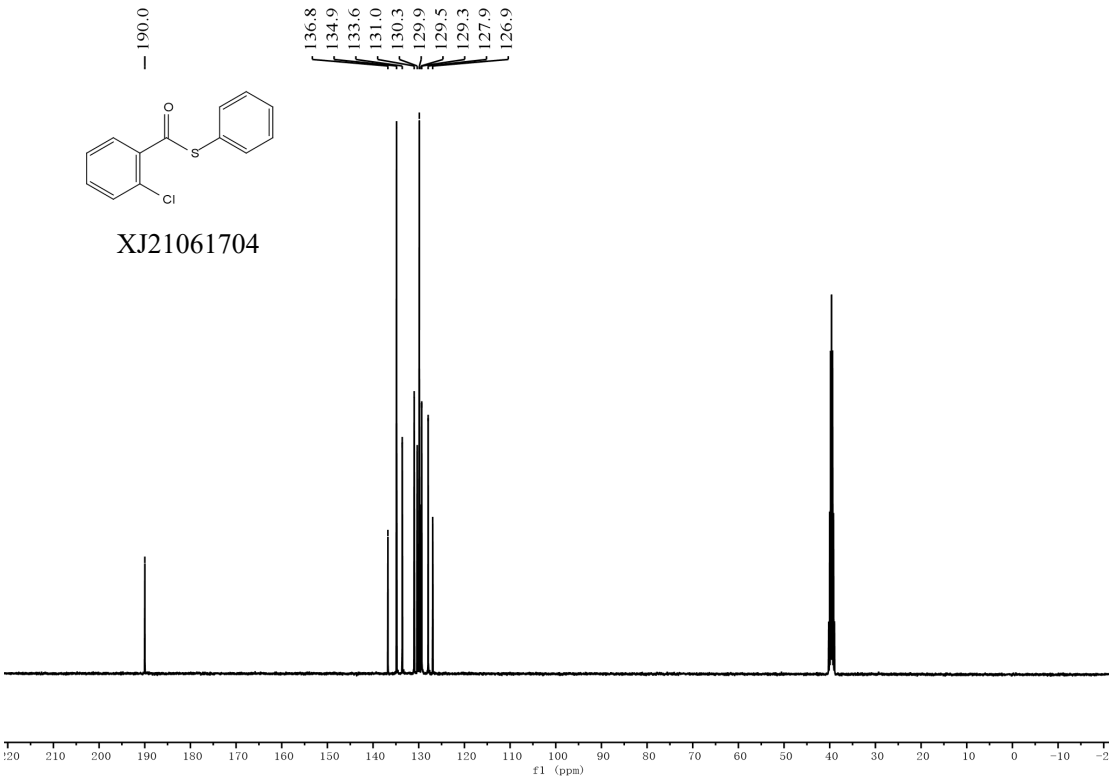
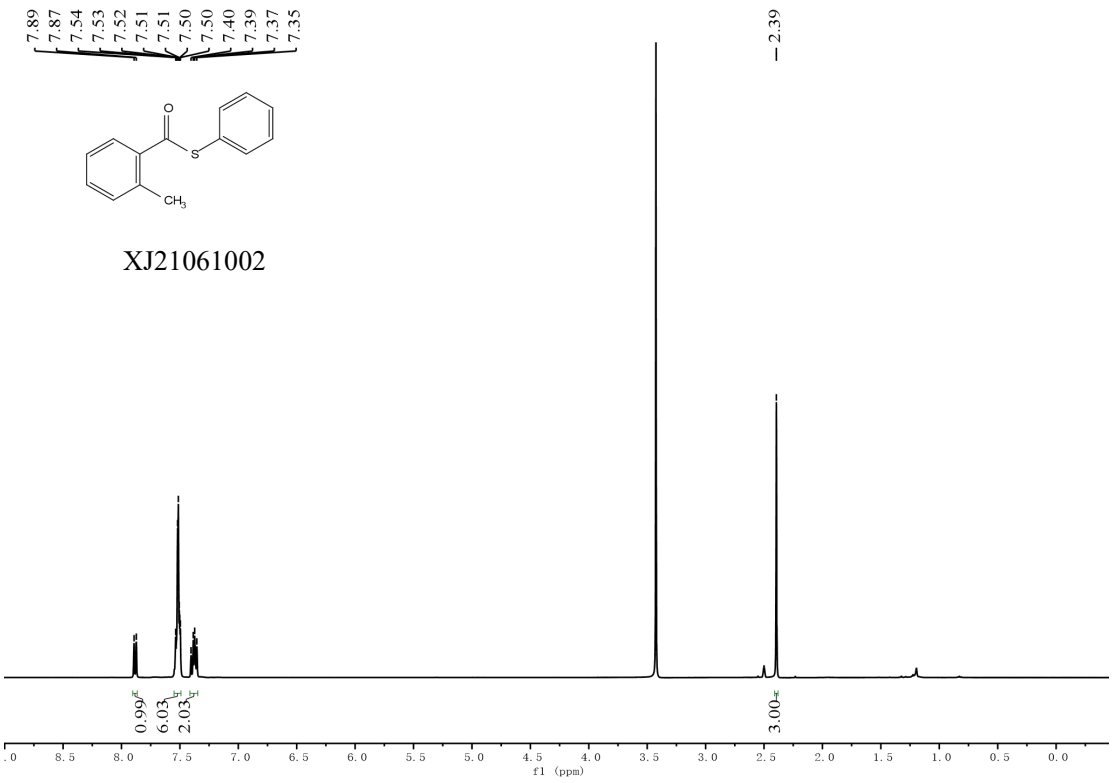
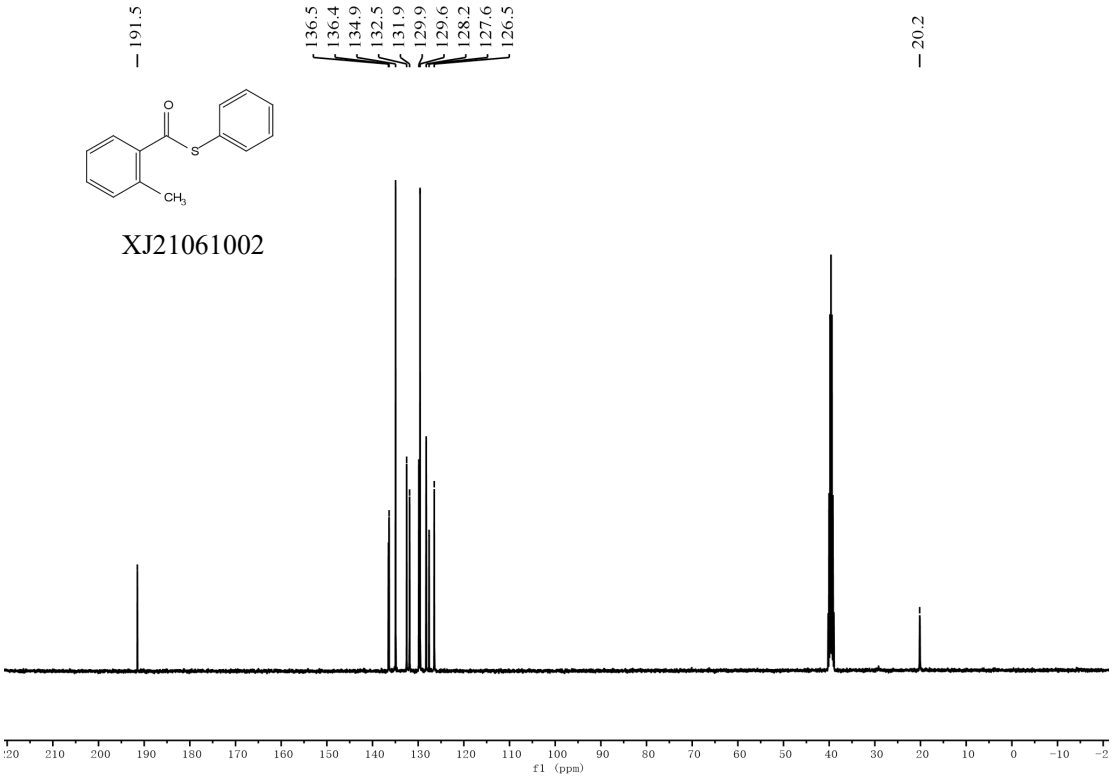


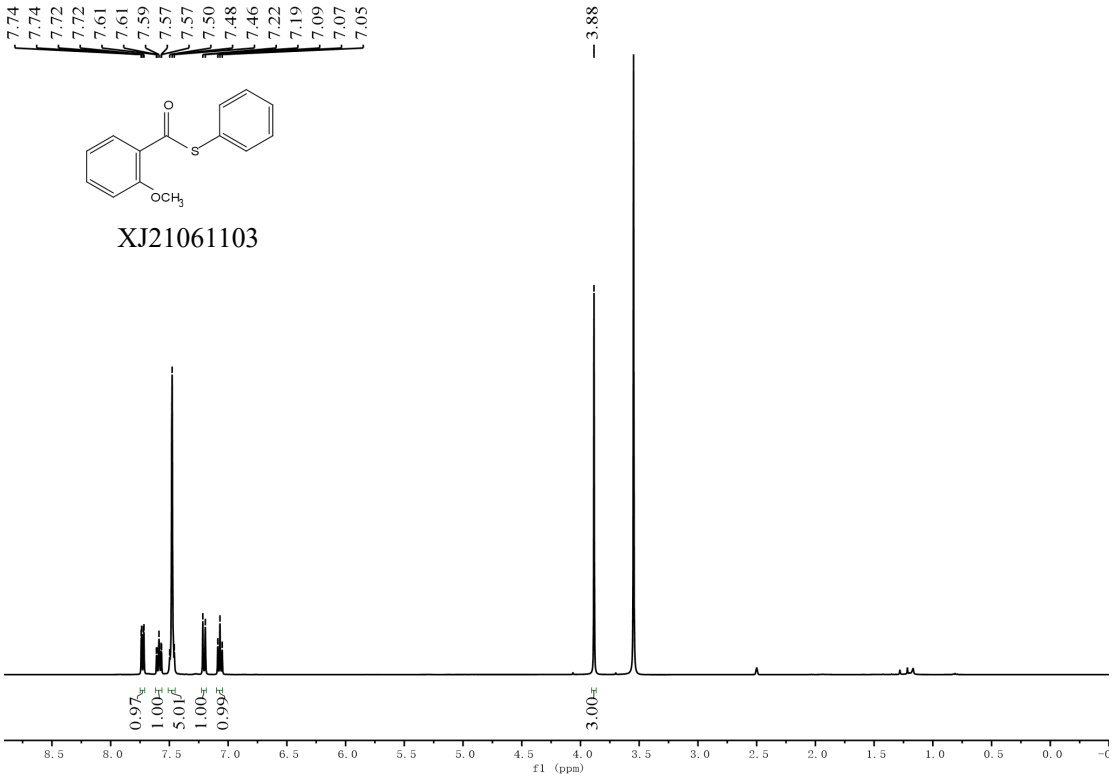
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3na**



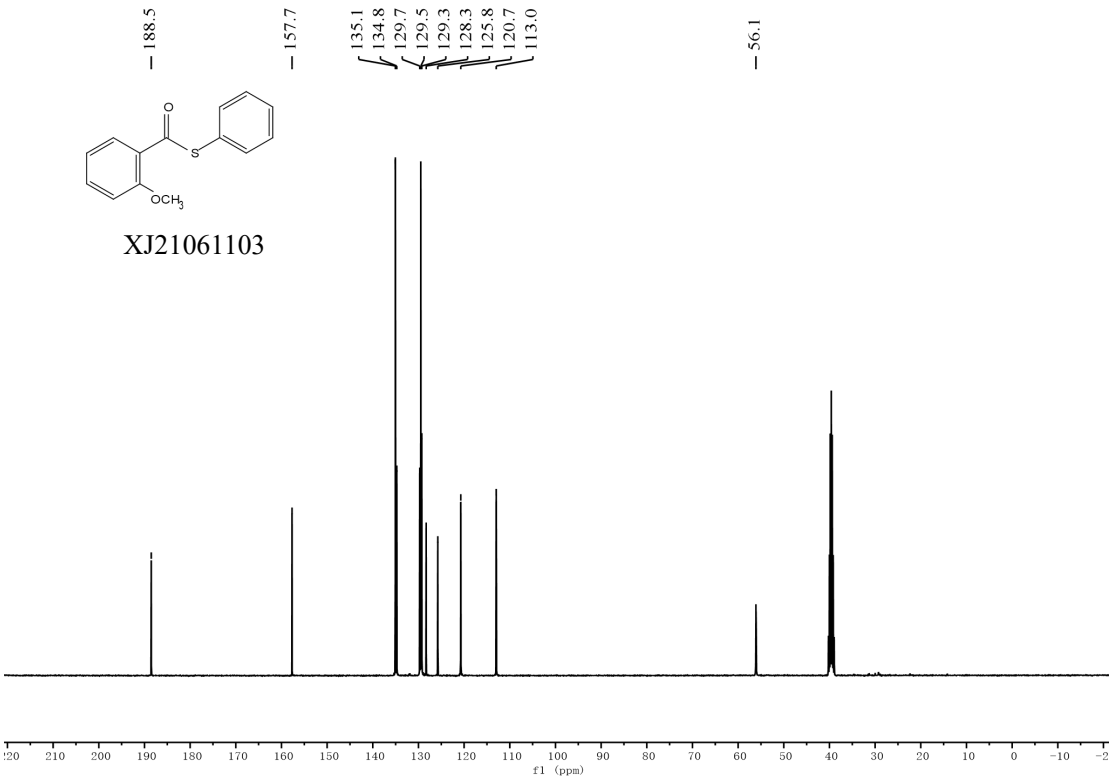
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3na**



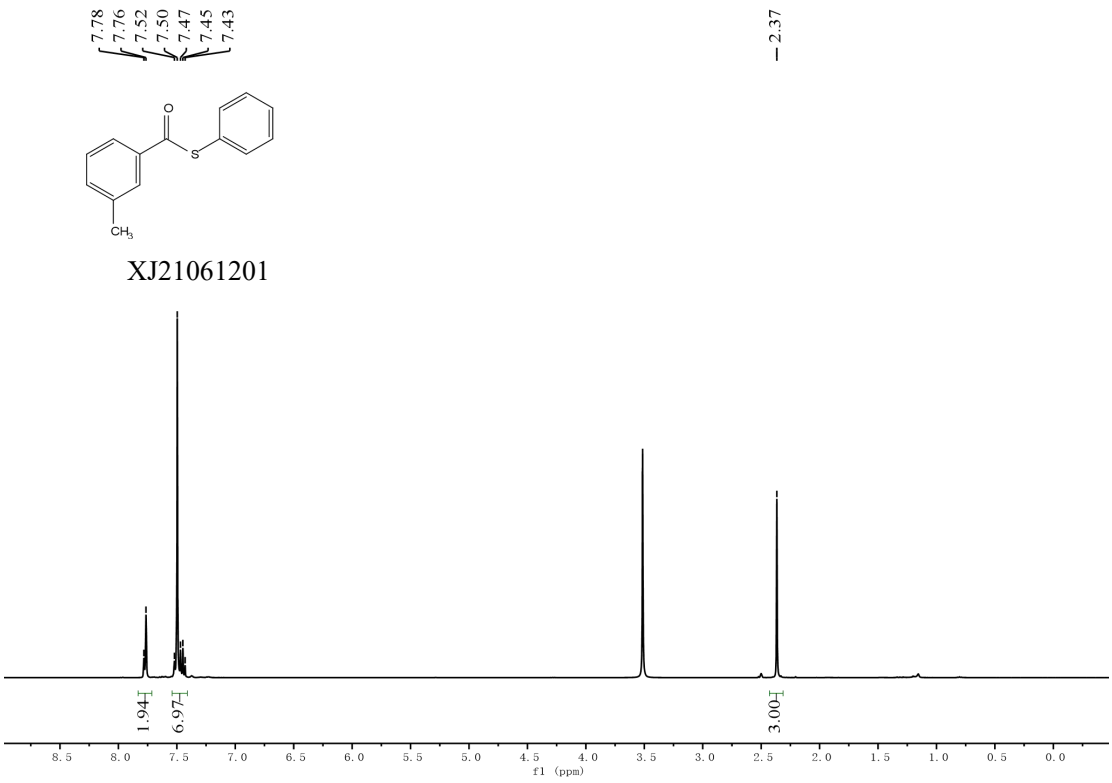
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3oa**



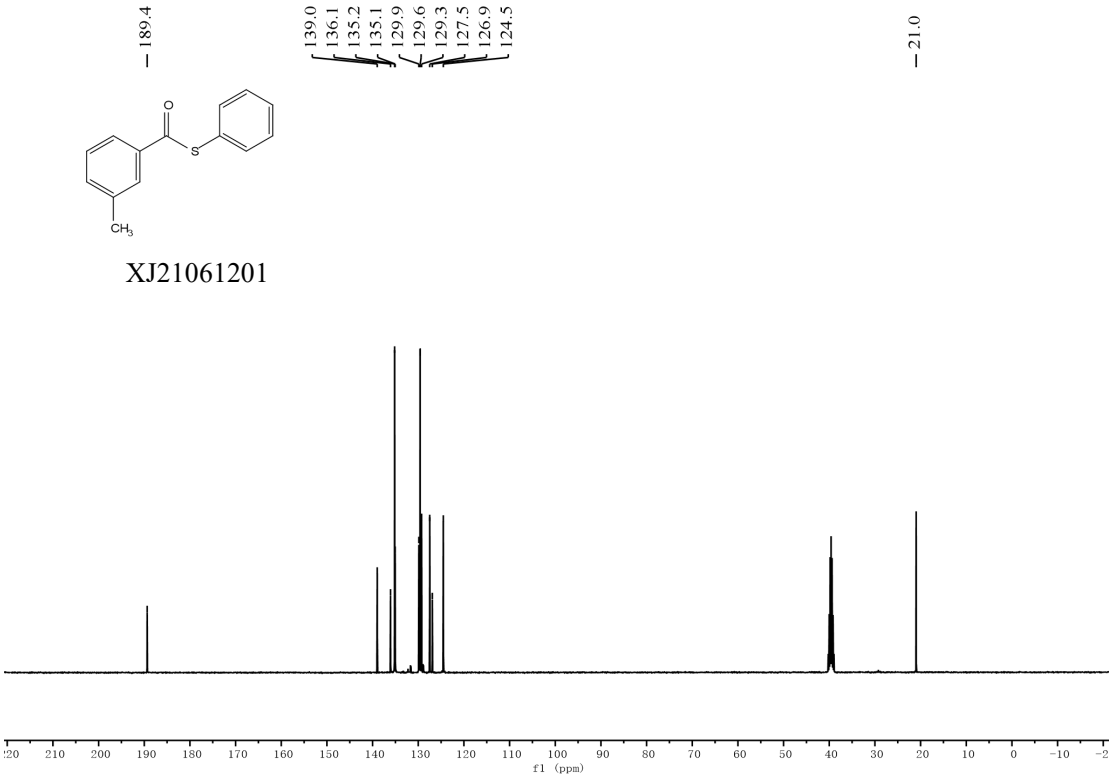
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3oa**



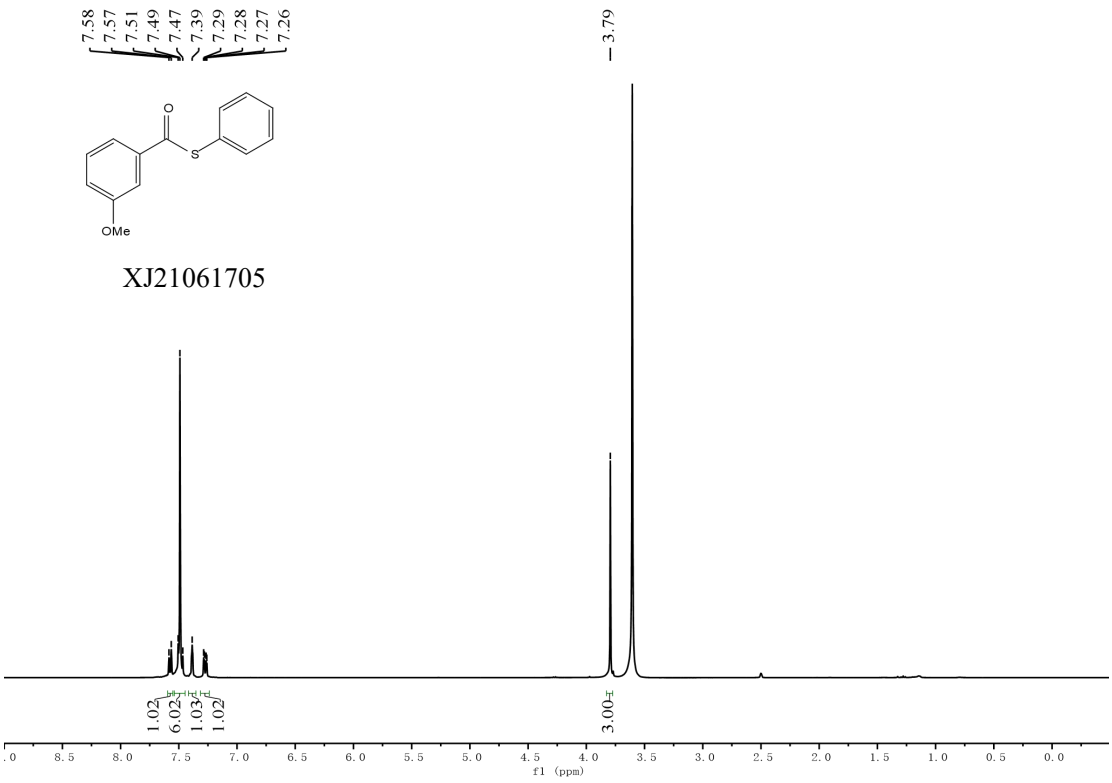
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3pa**



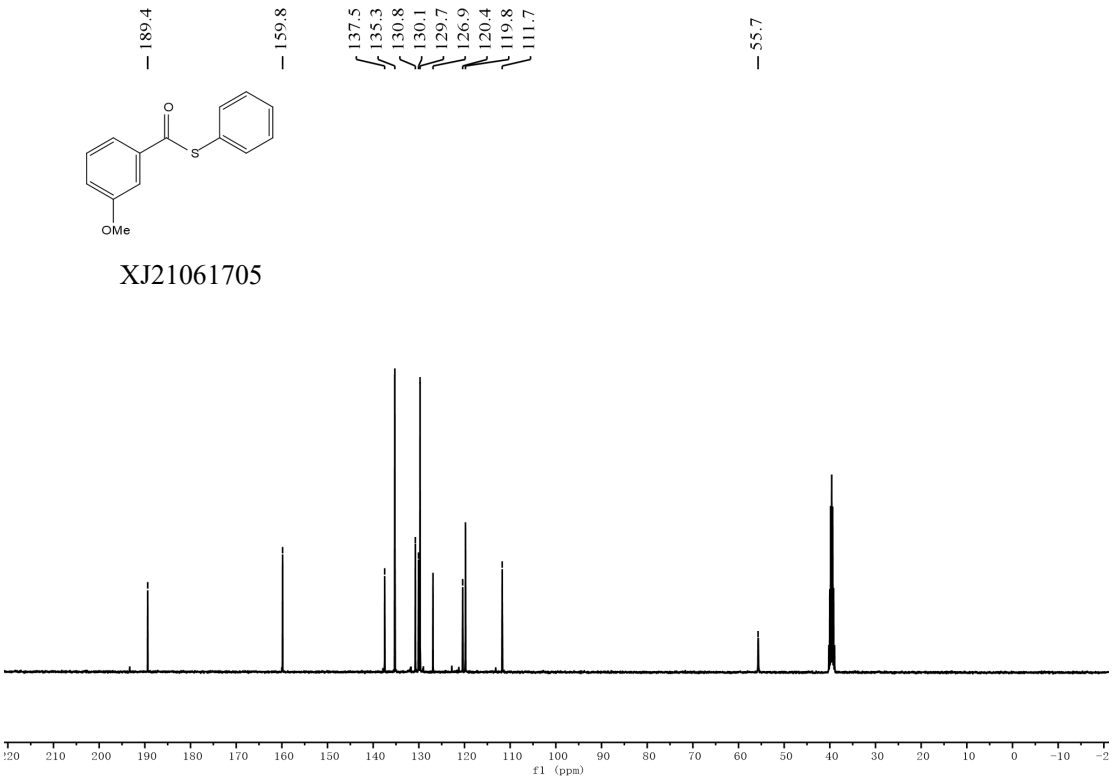
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3pa**



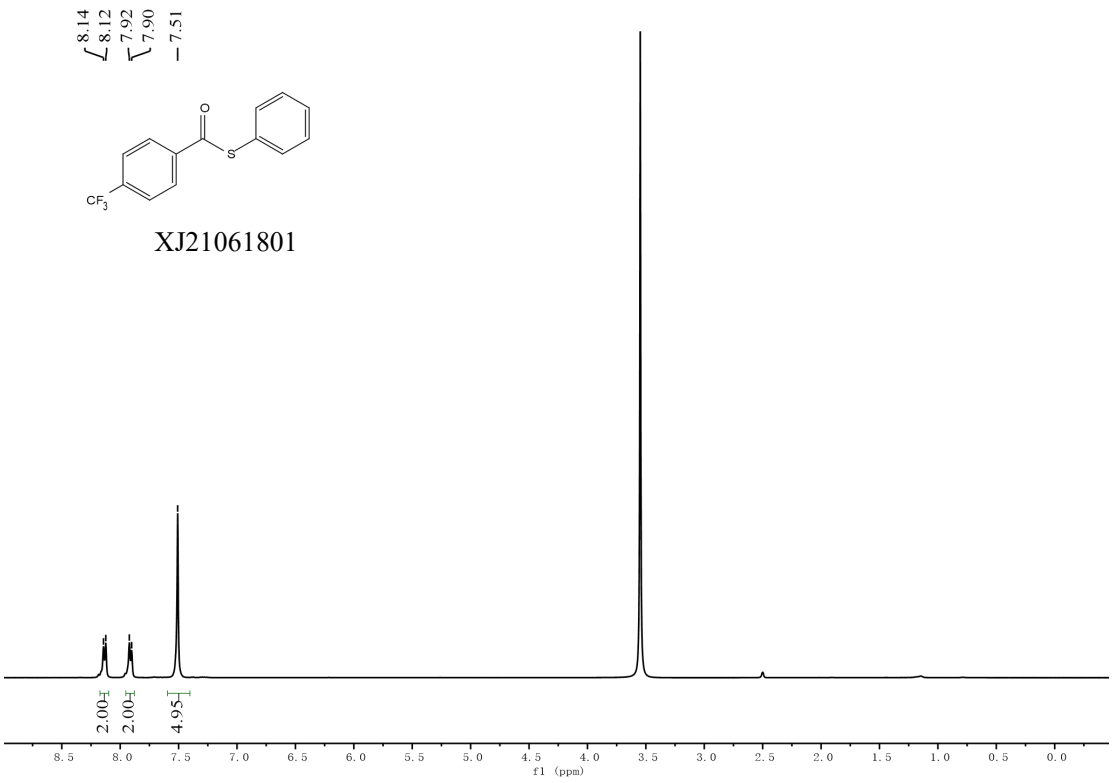
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3qa**



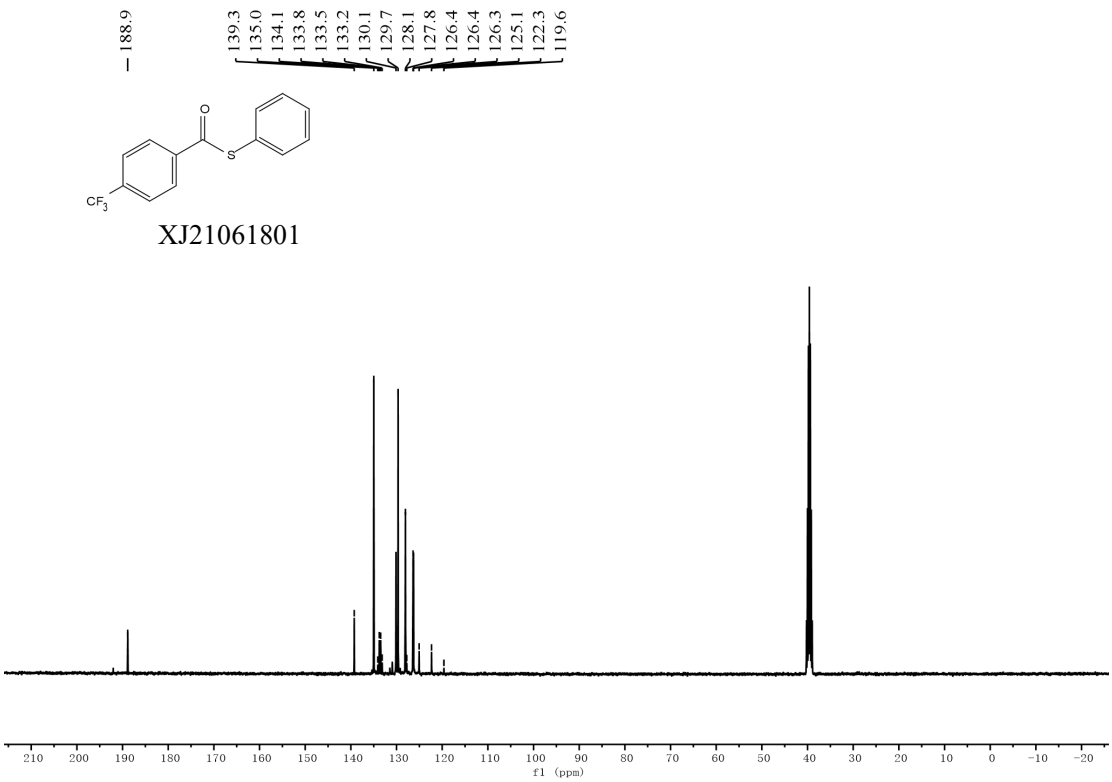
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3qa**



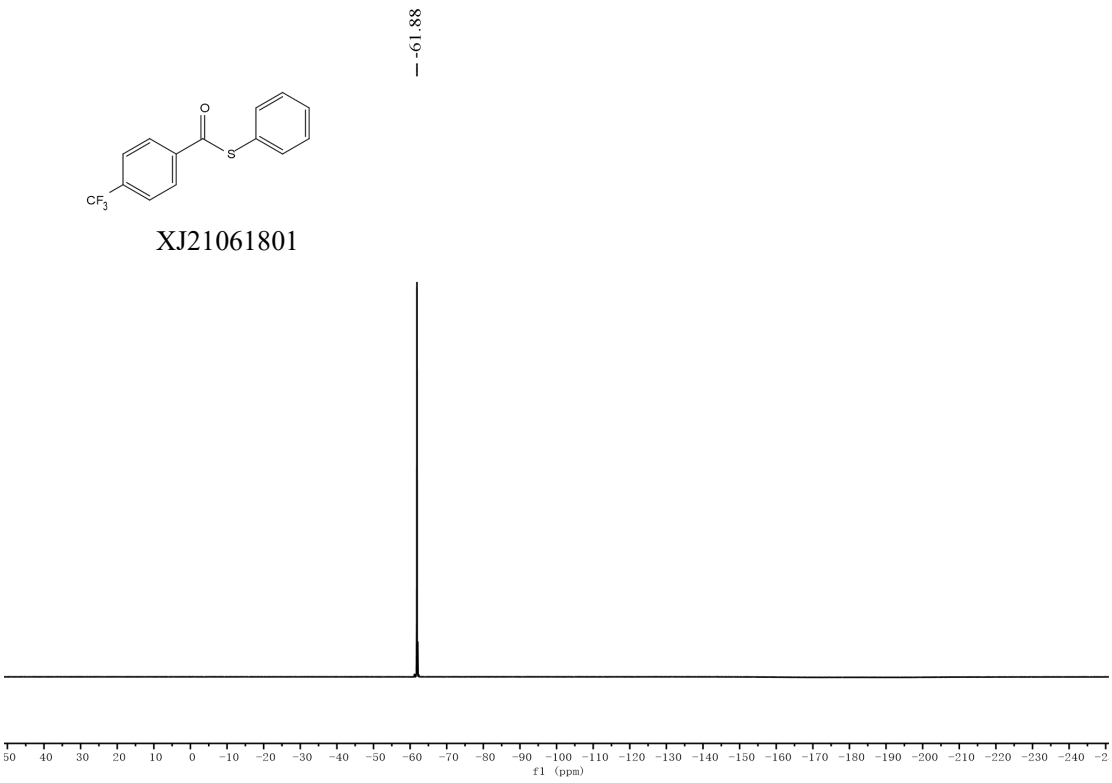
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ra**



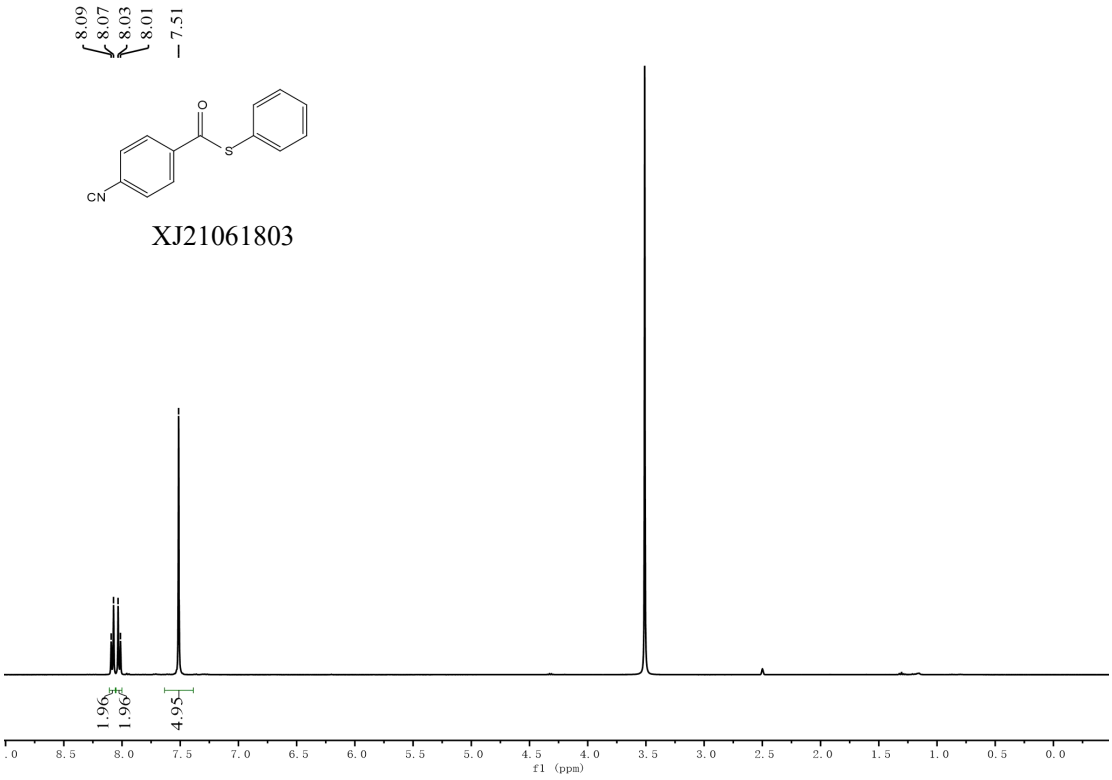
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ra**



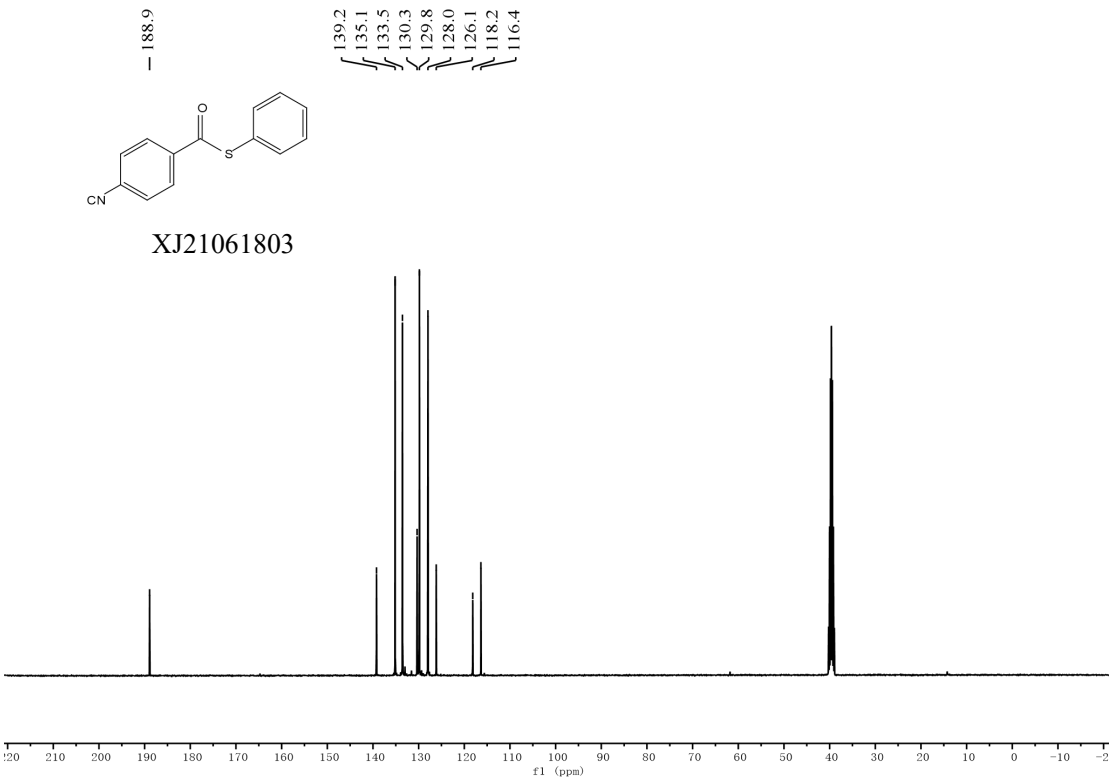
^{19}F NMR (376 MHz, DMSO-d_6) of compound **3ra**



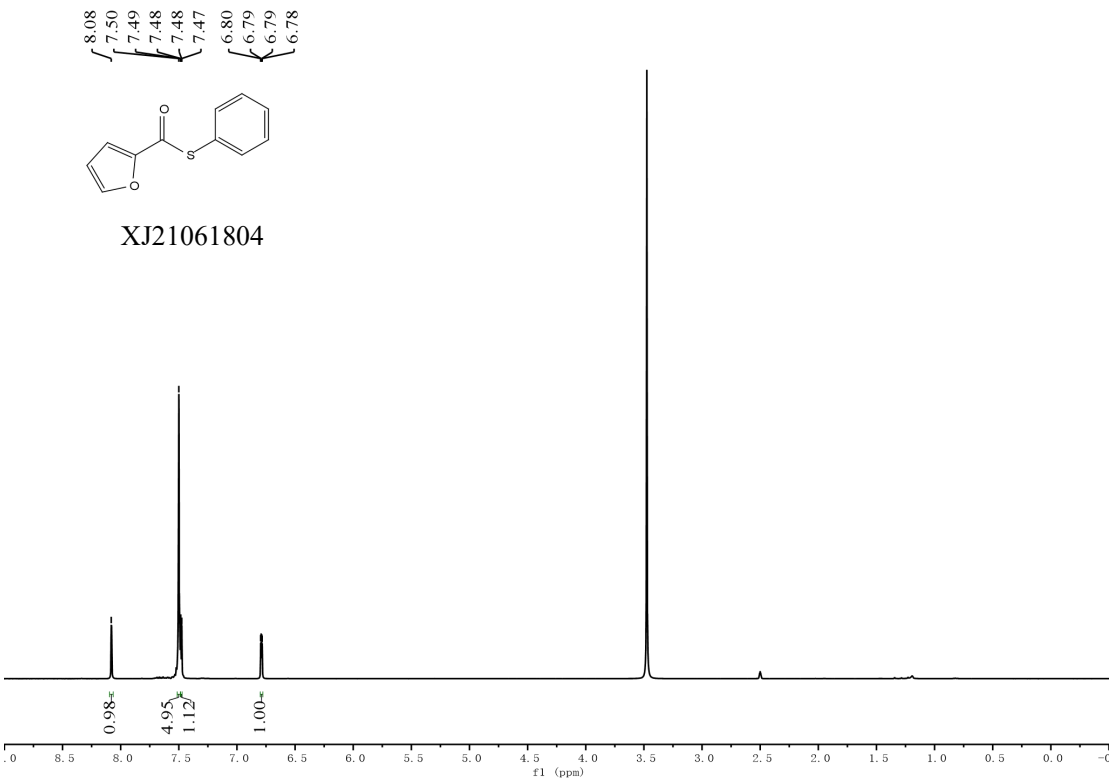
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3sa**



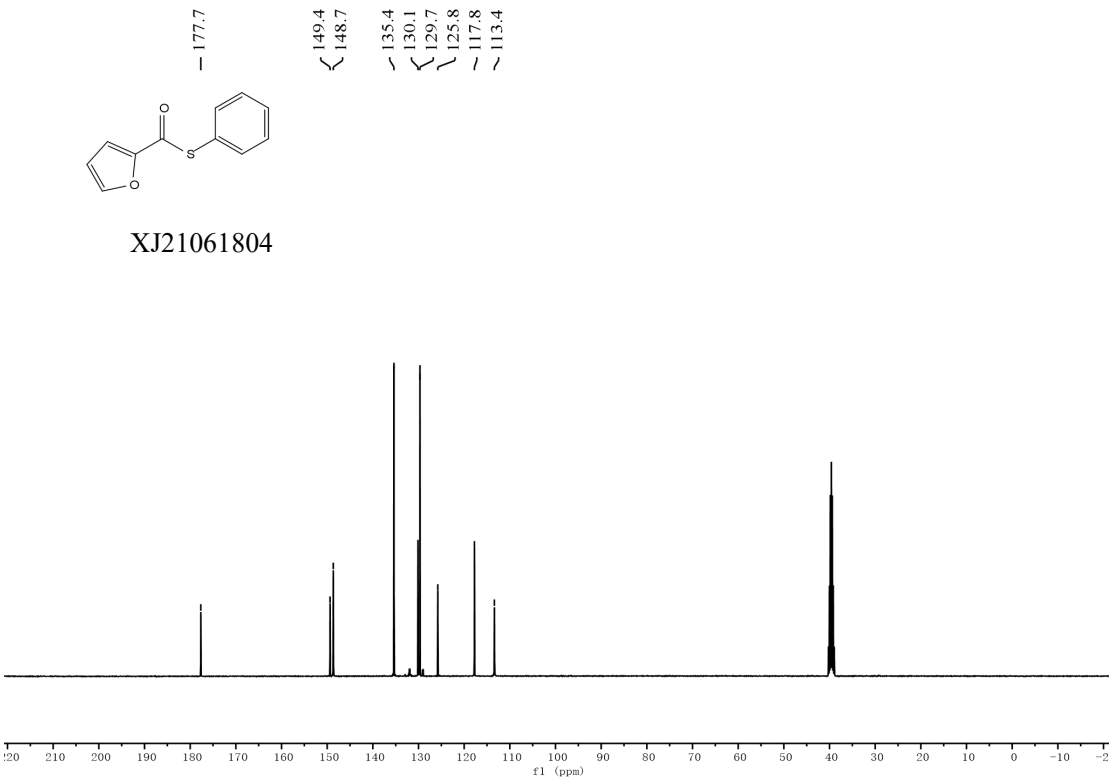
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3sa**



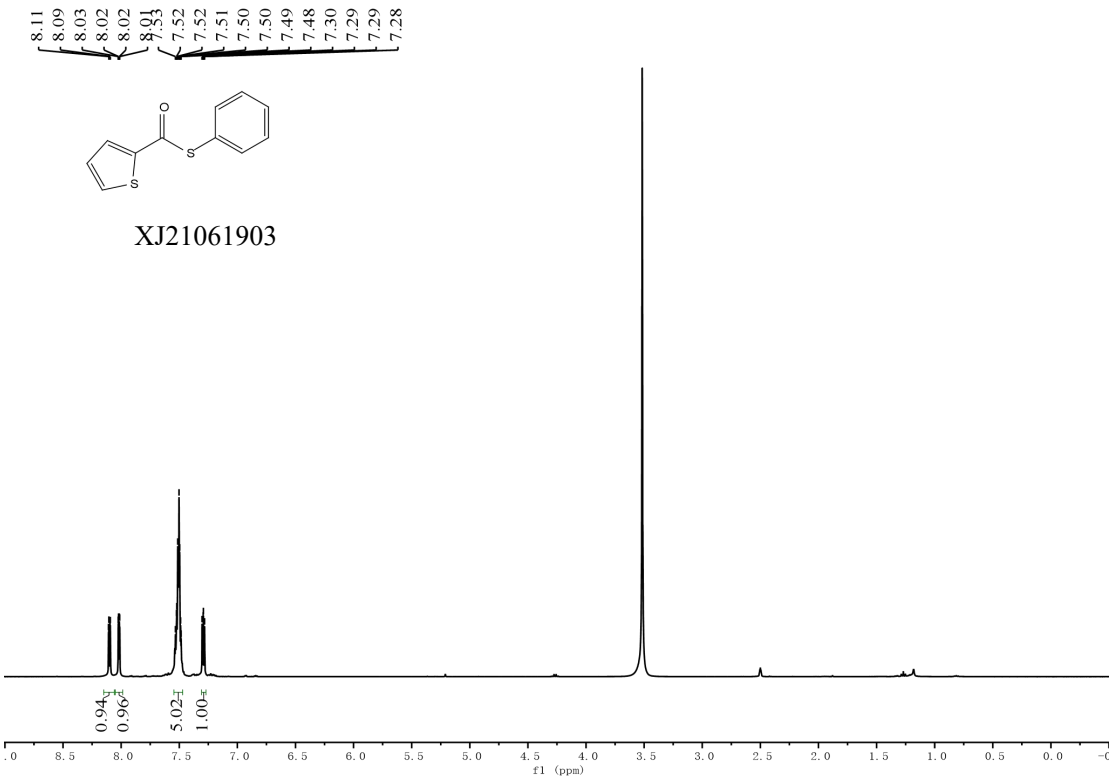
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ta**



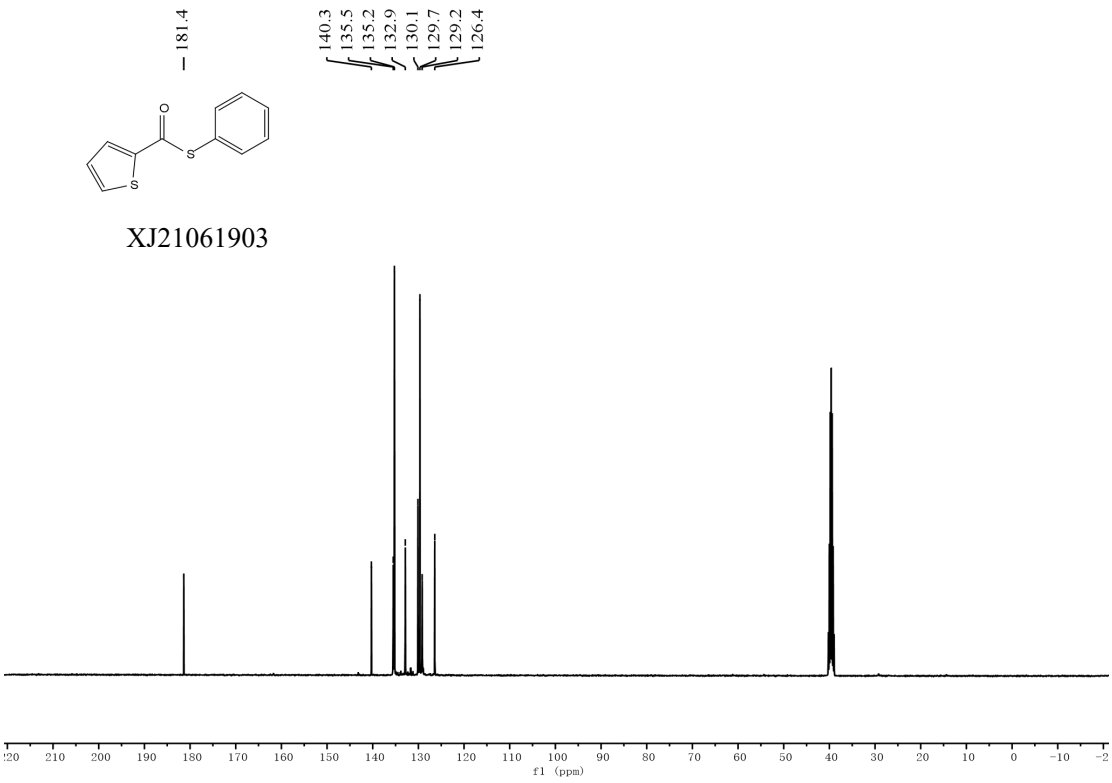
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ta**



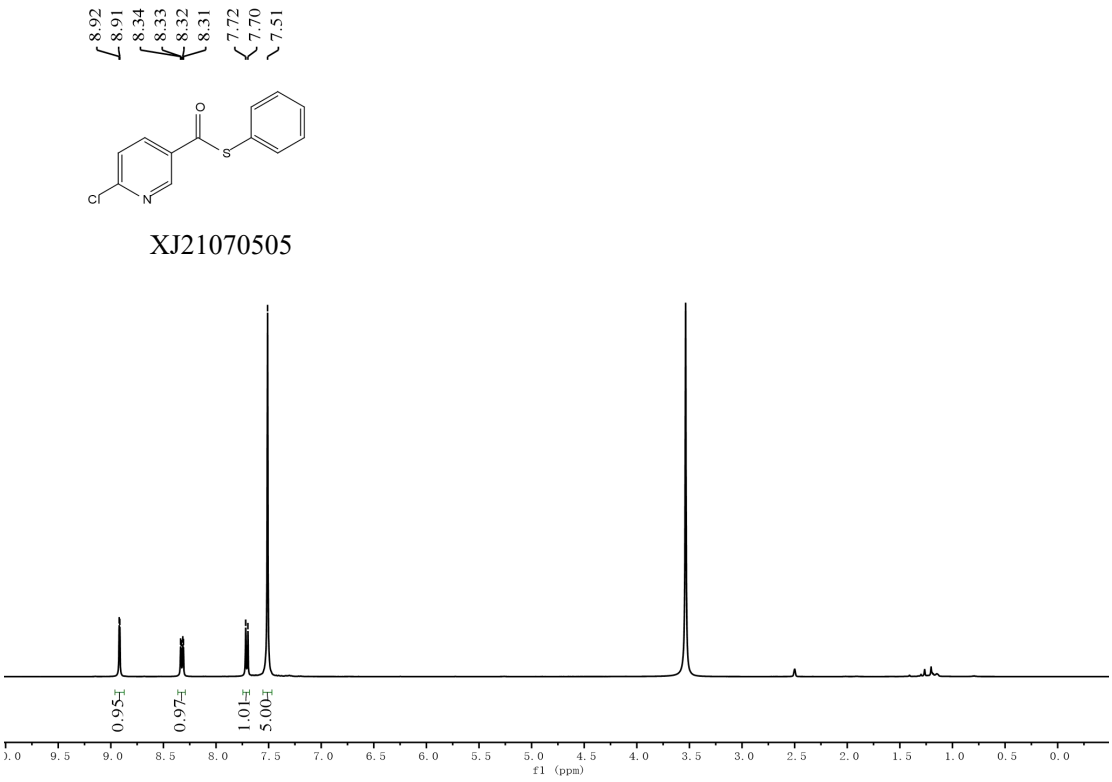
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ua**



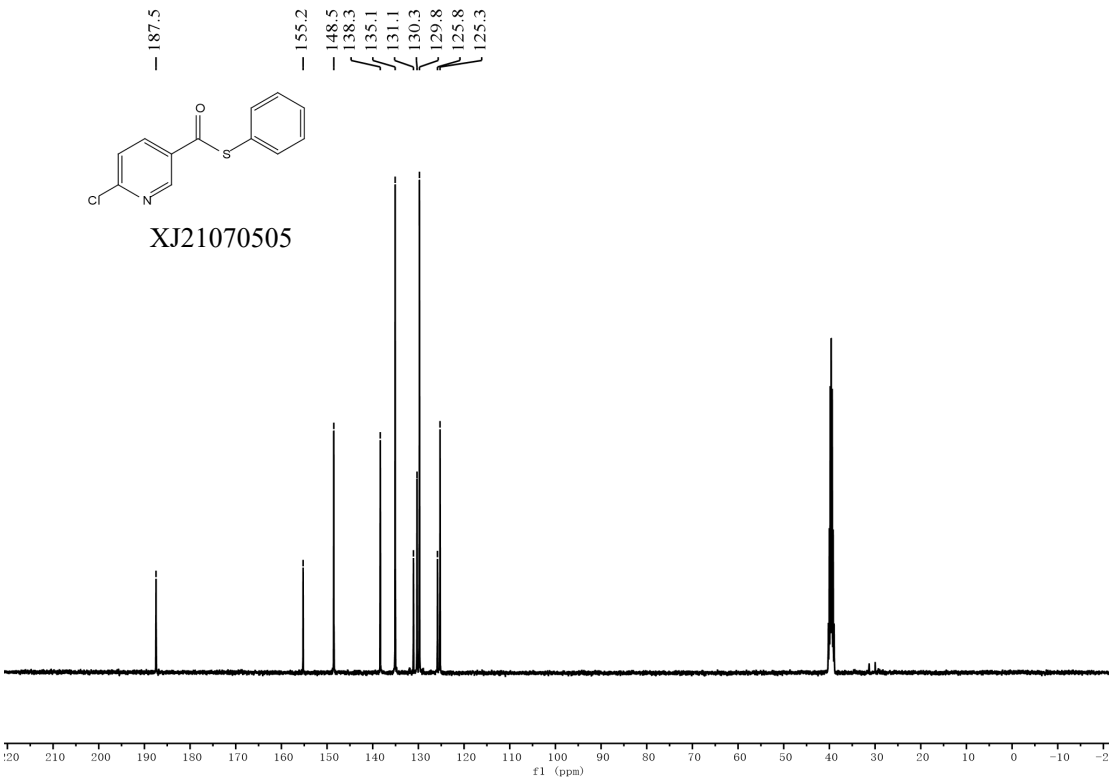
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ua**



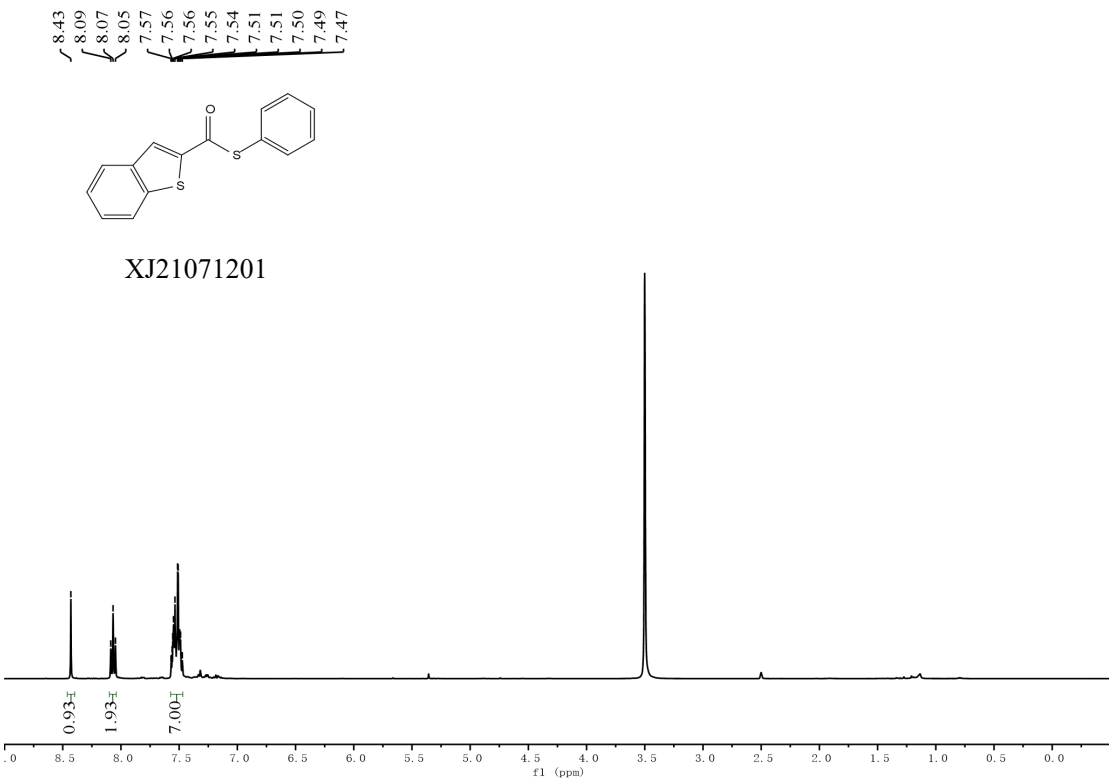
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3va**



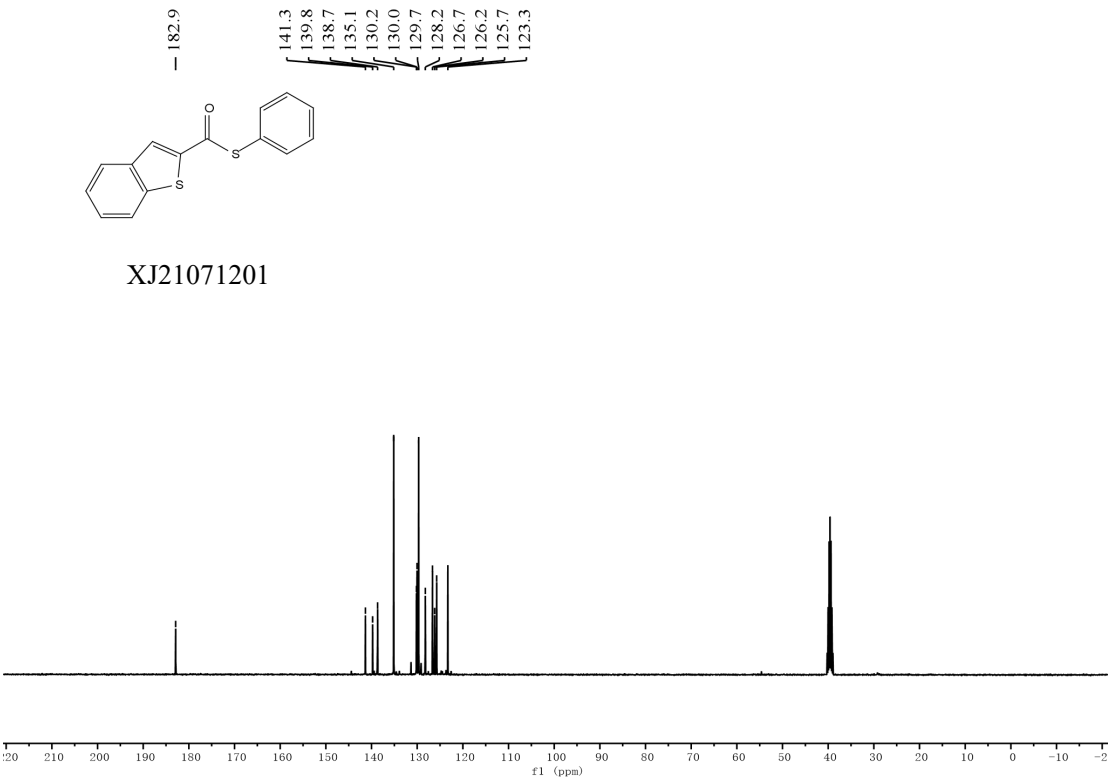
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3va**



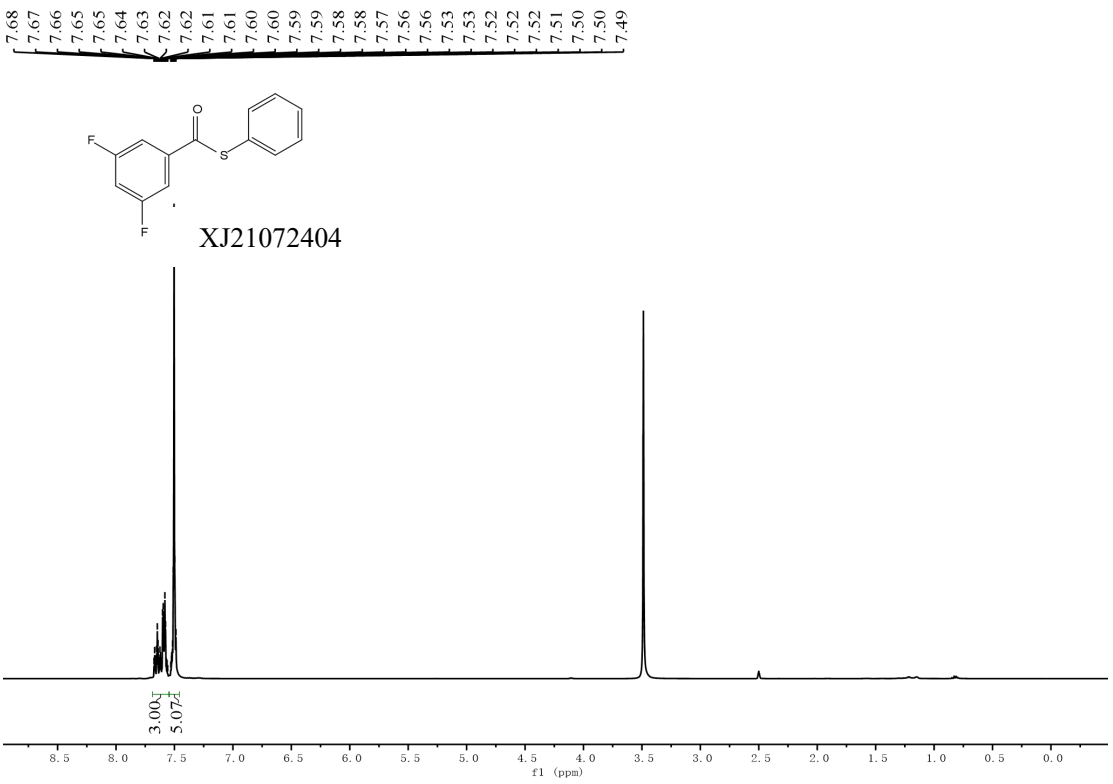
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3wa**



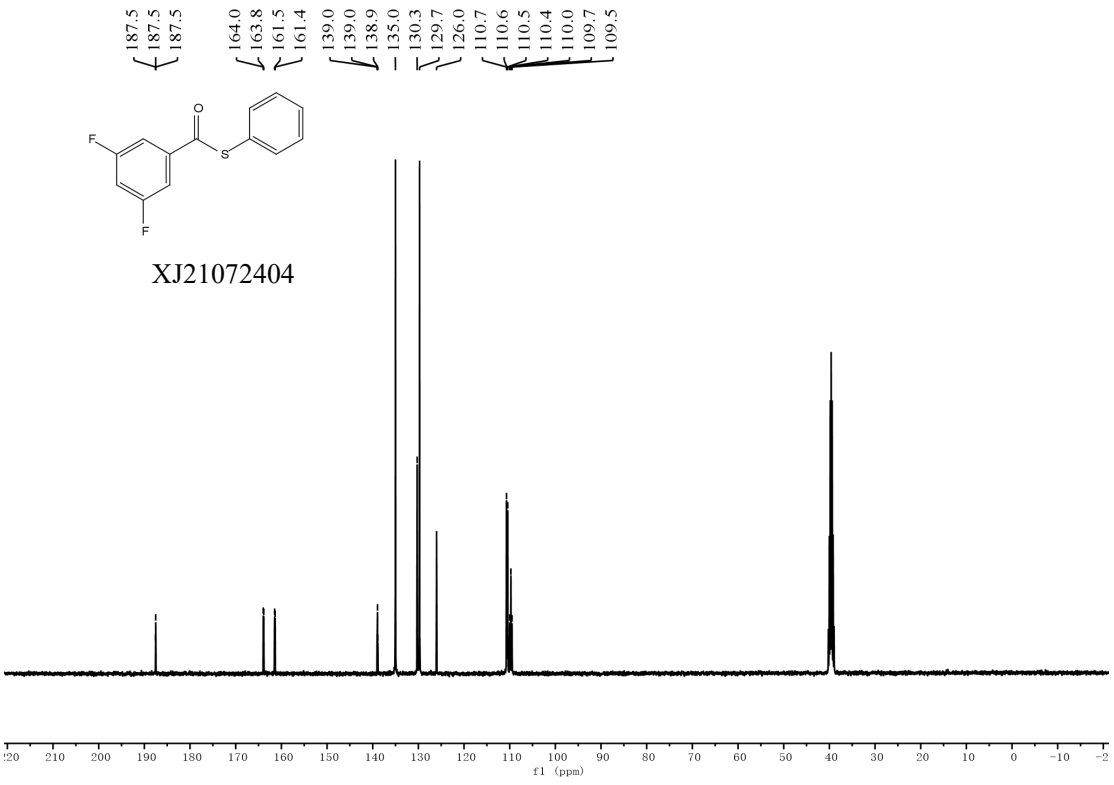
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3wa**



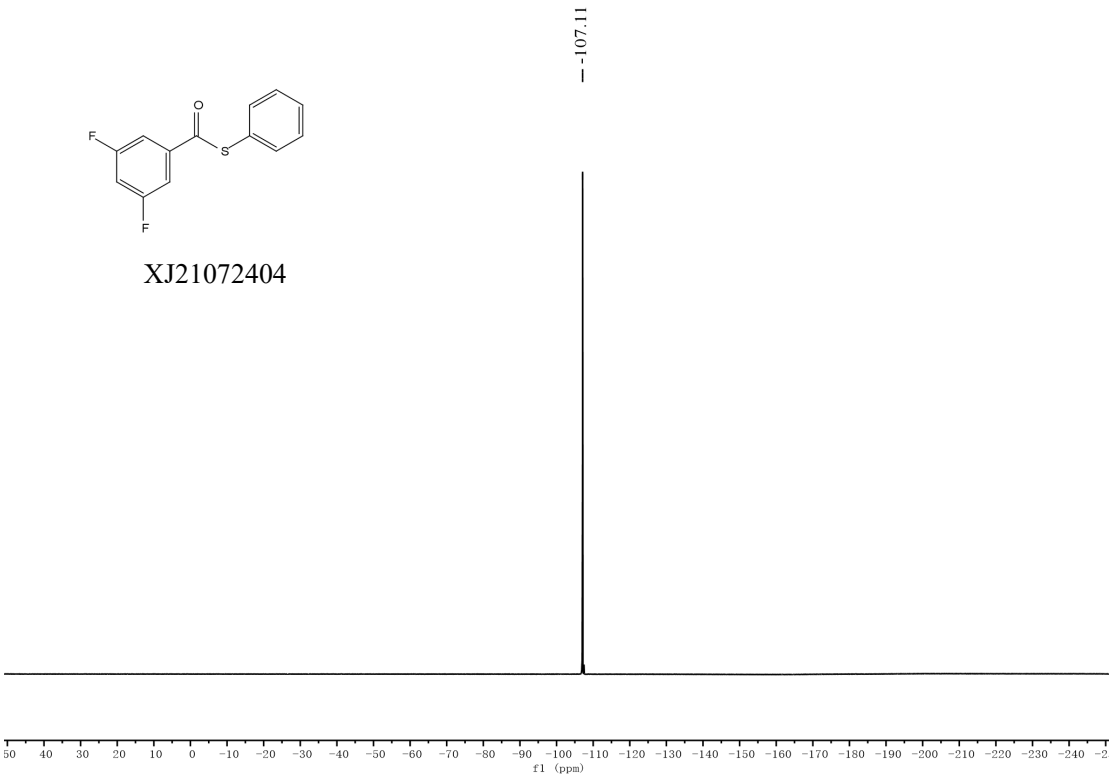
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3xa**



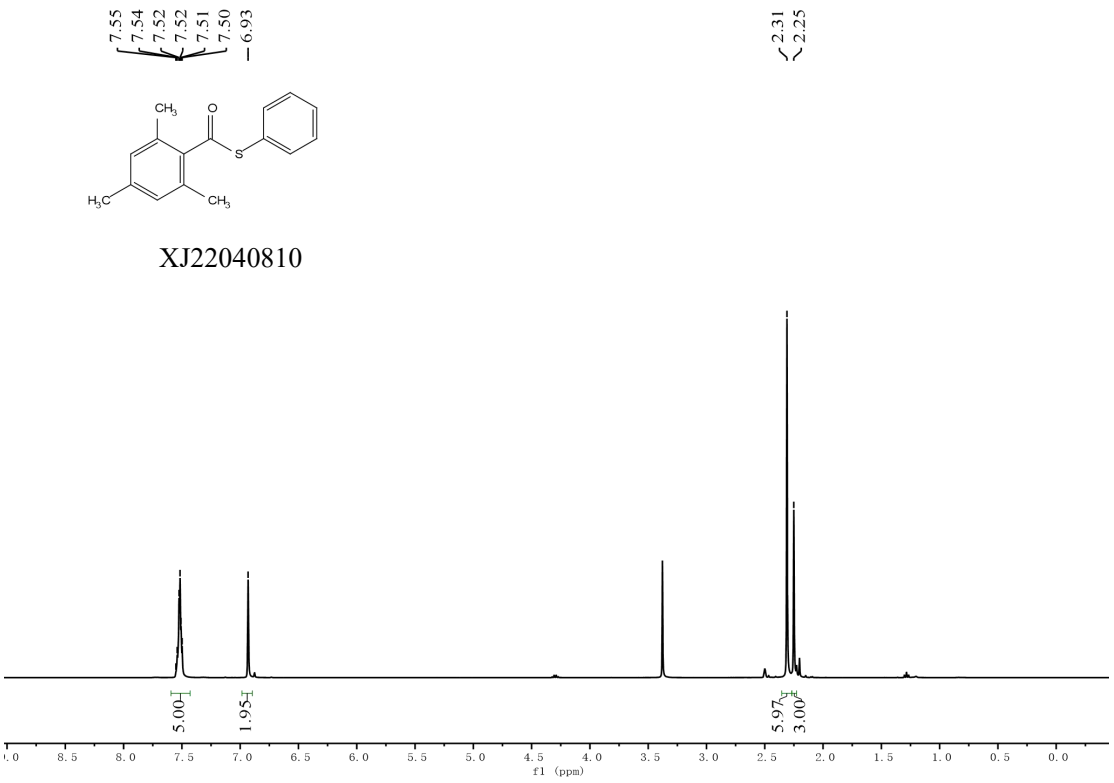
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3xa**



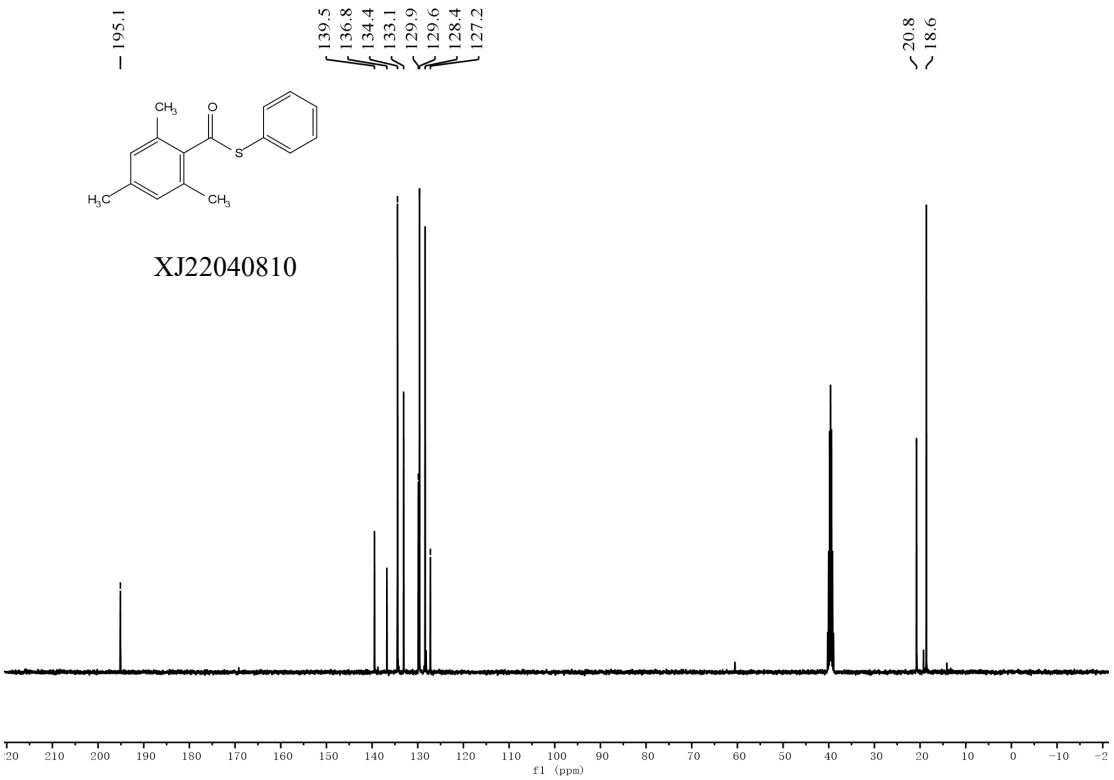
^{19}F NMR (376 MHz, DMSO-d_6) of compound **3xa**



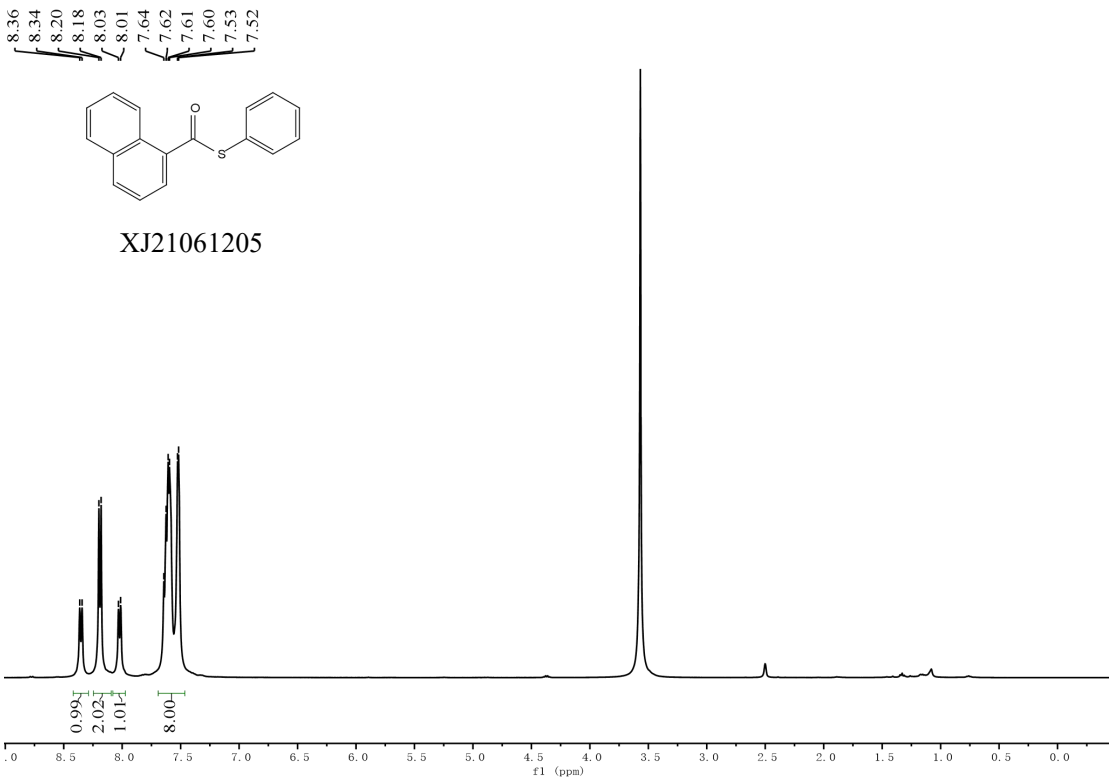
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ya**



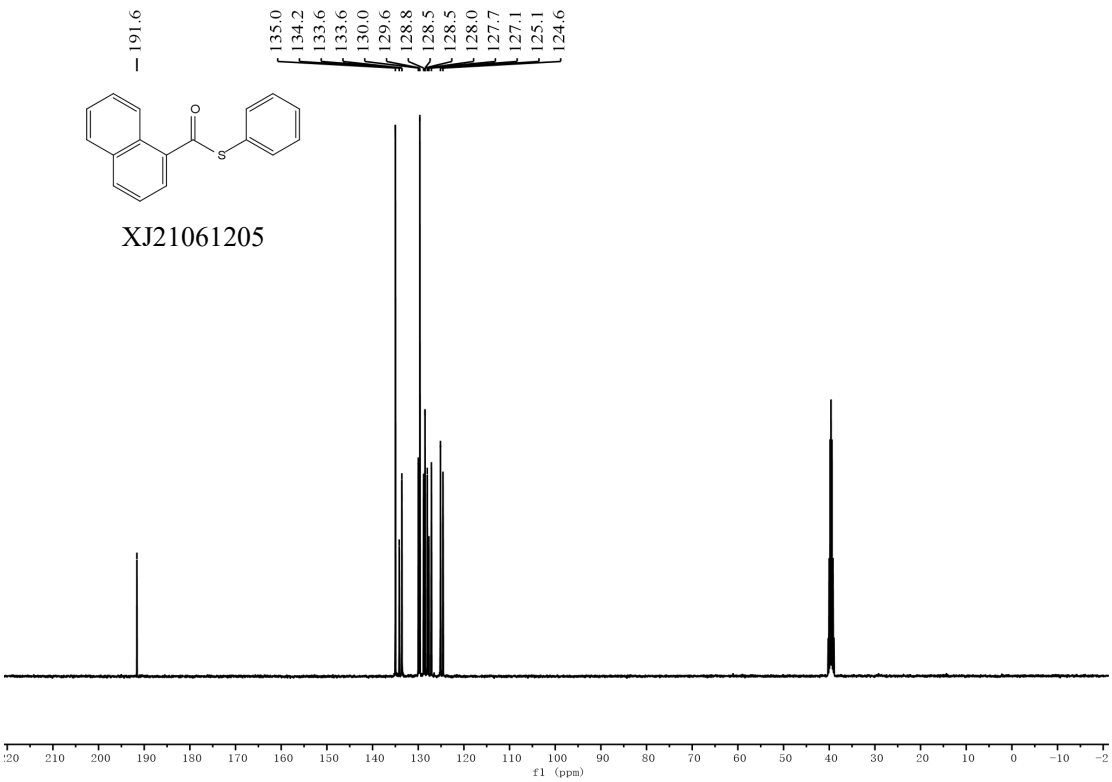
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ya**



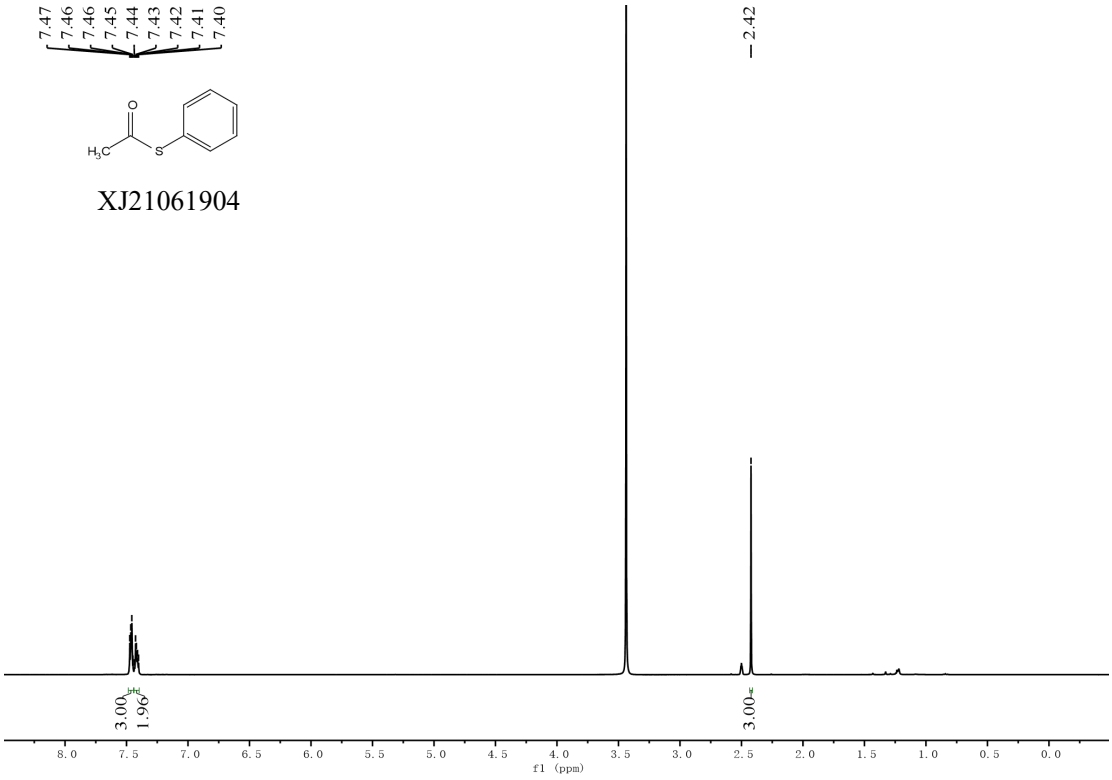
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3za**



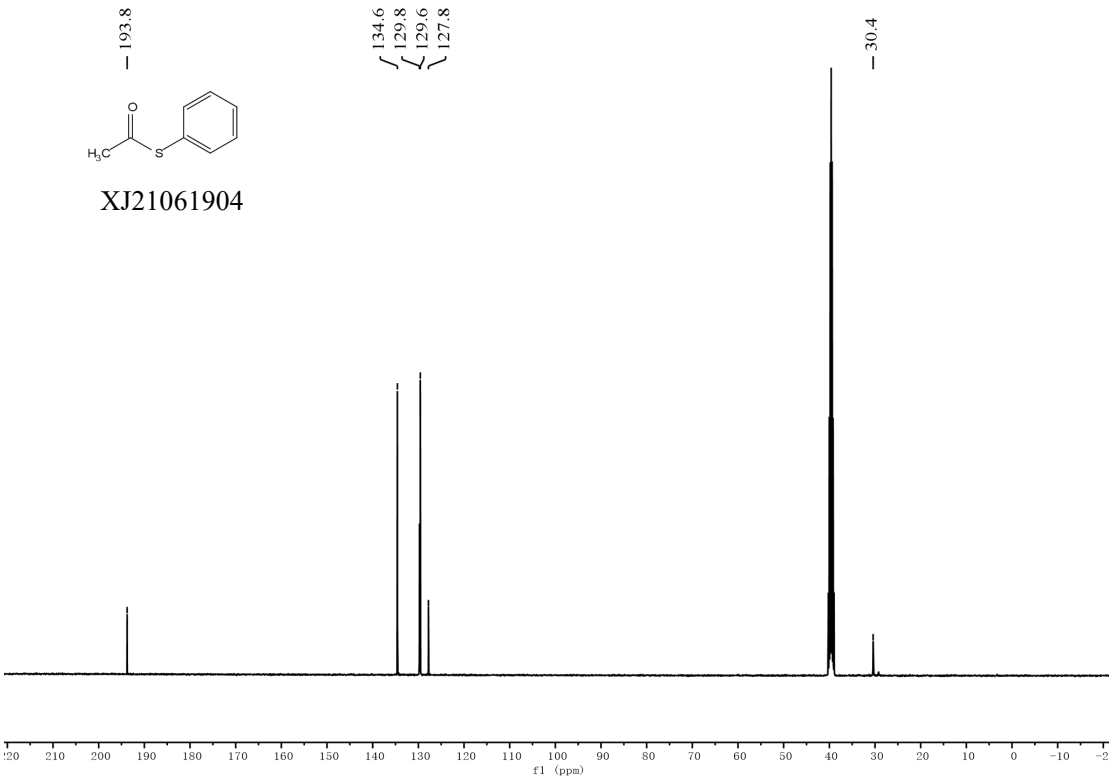
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3za**



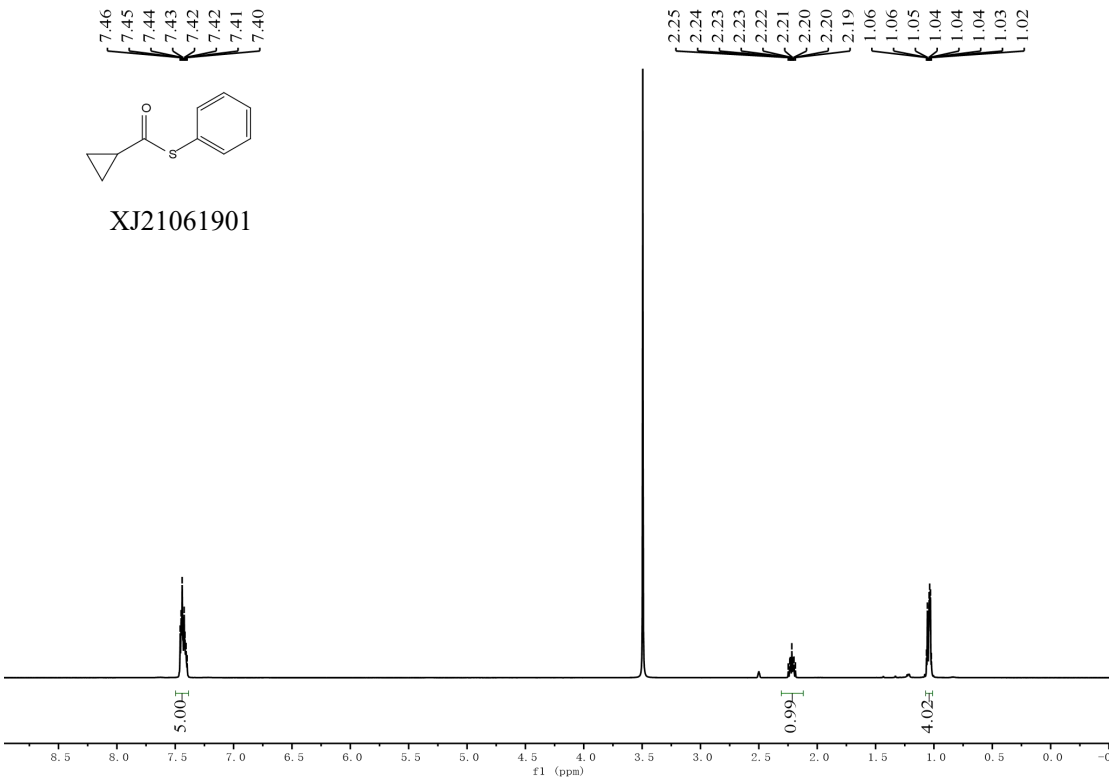
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3zaa**



^{13}C NMR (101 MHz, DMSO-d_6) of compound **3zaa**

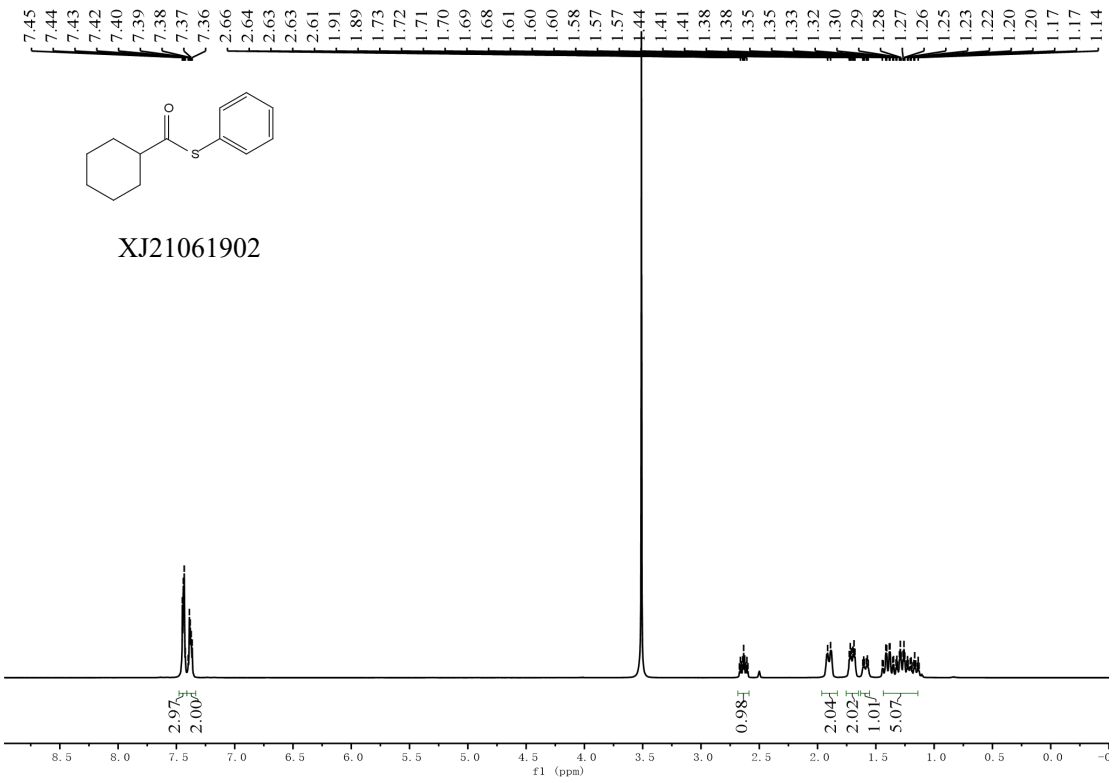


^{1}H NMR (400 MHz, DMSO-d_6) of compound **3zab**

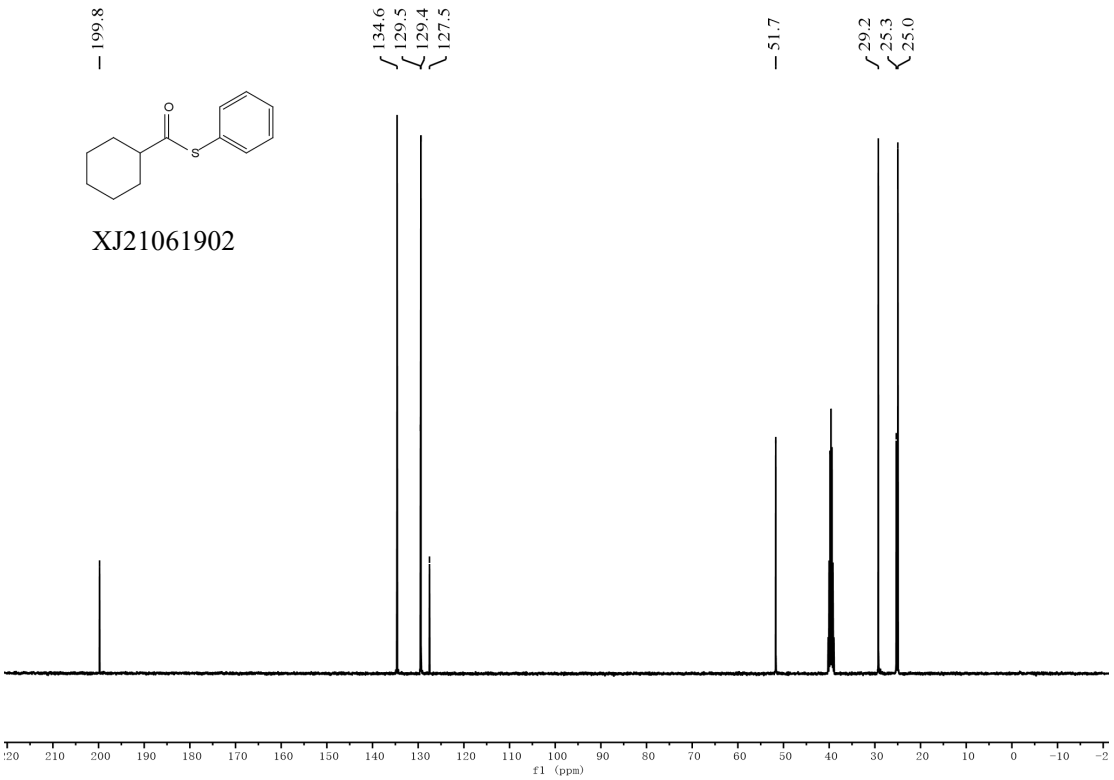


^{13}C NMR (101 MHz, DMSO-d_6) of compound **3zab**

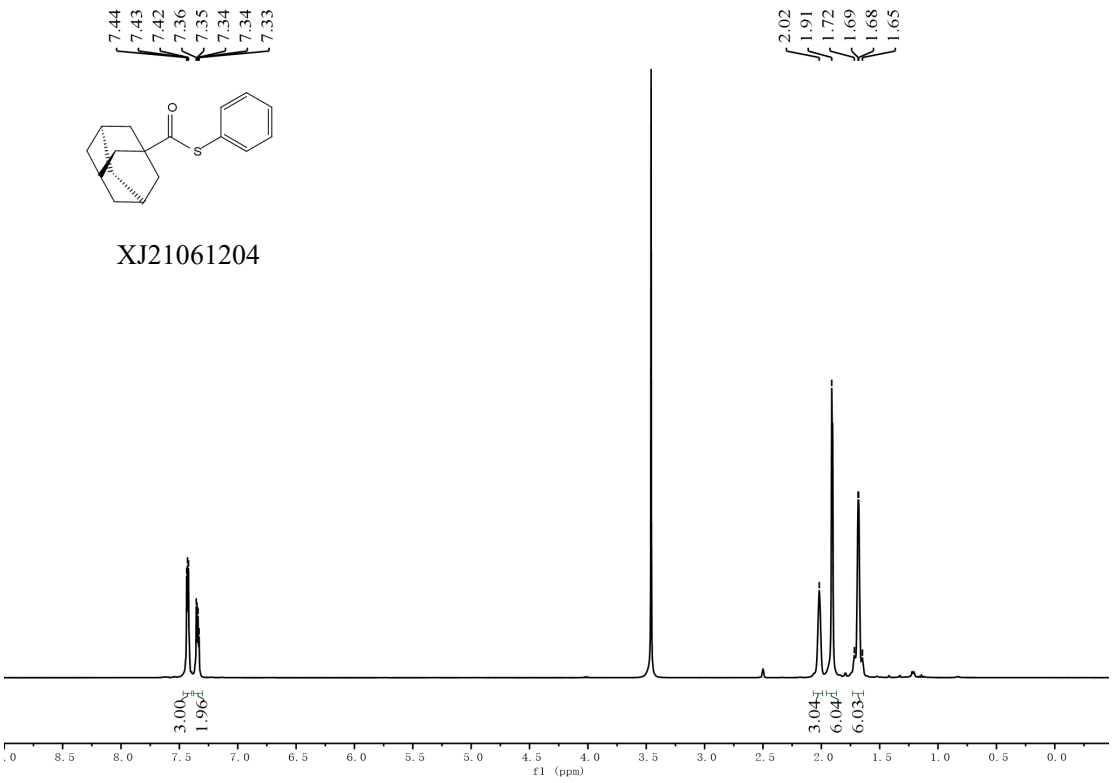
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3zac**



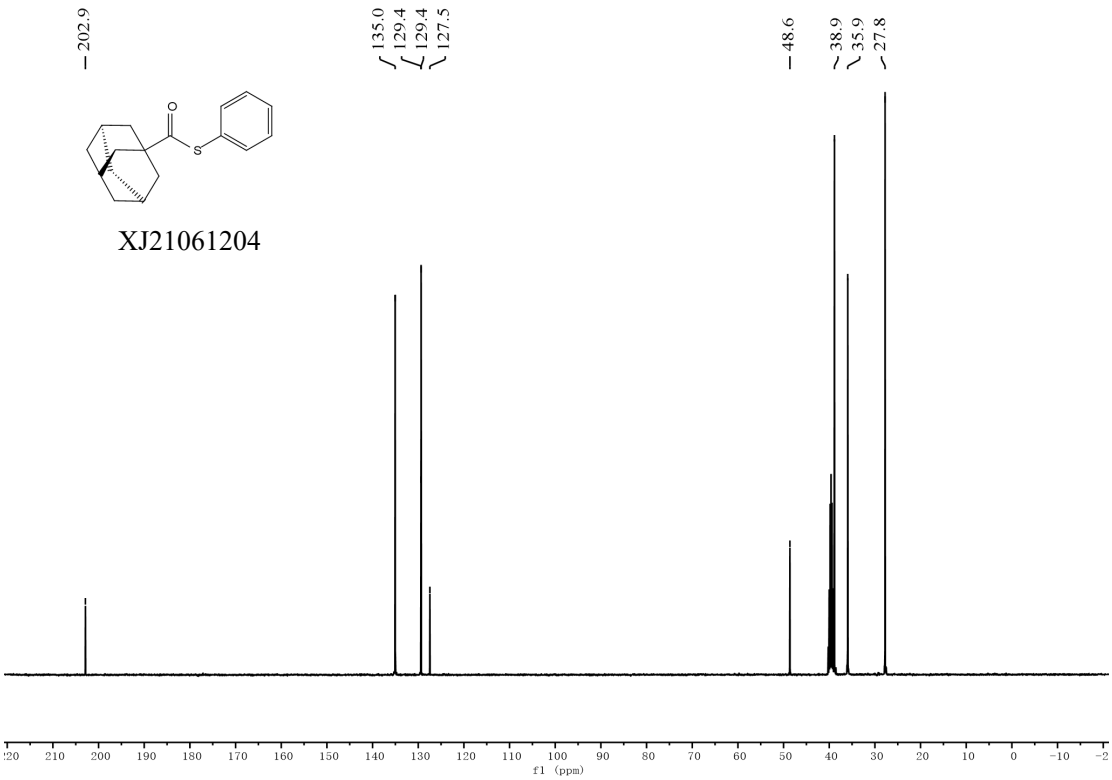
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3zac**



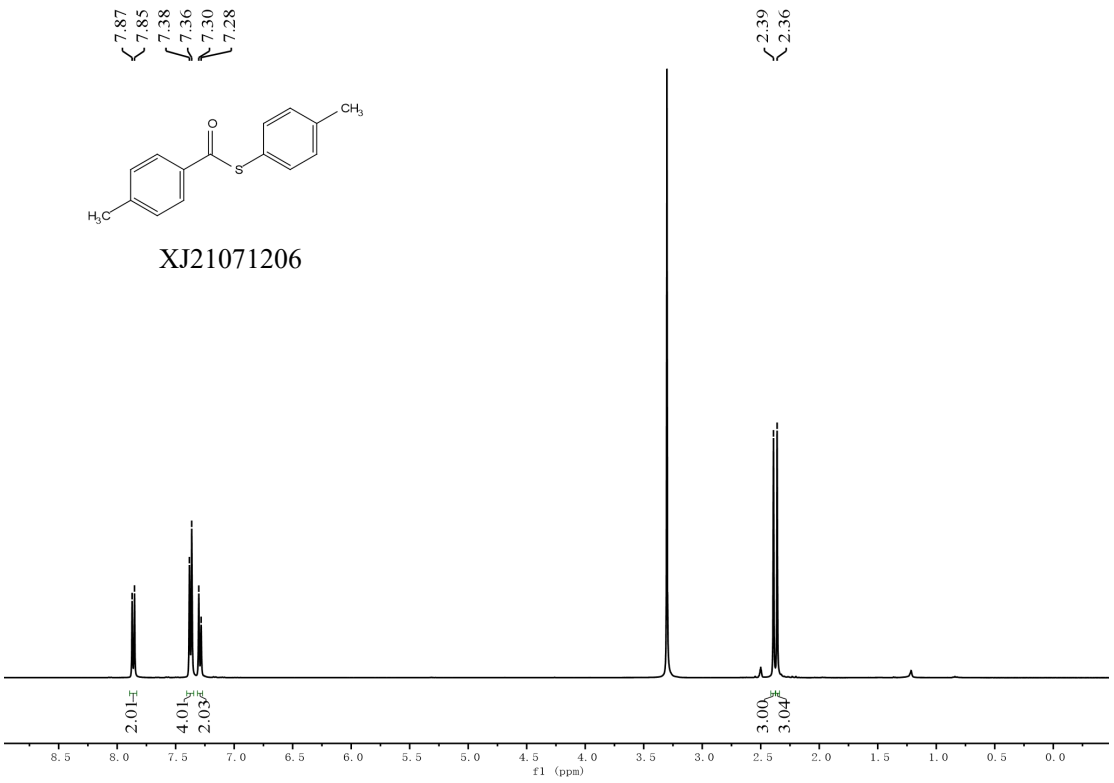
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3zad**



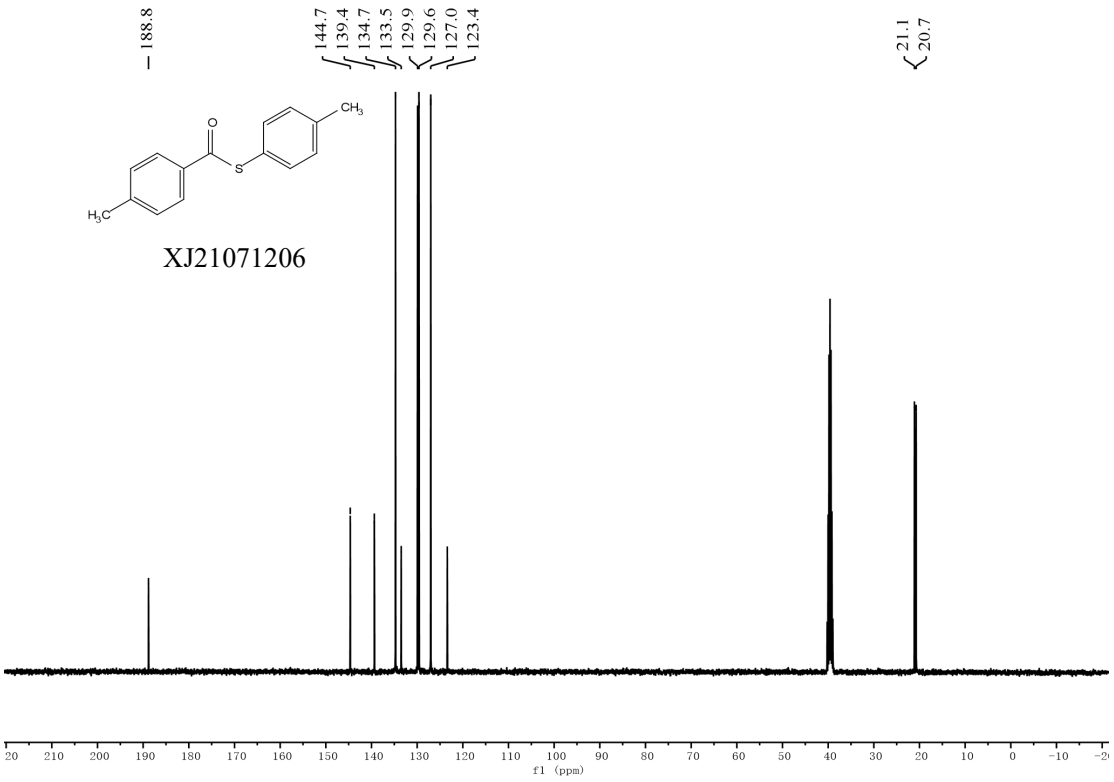
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3zad**



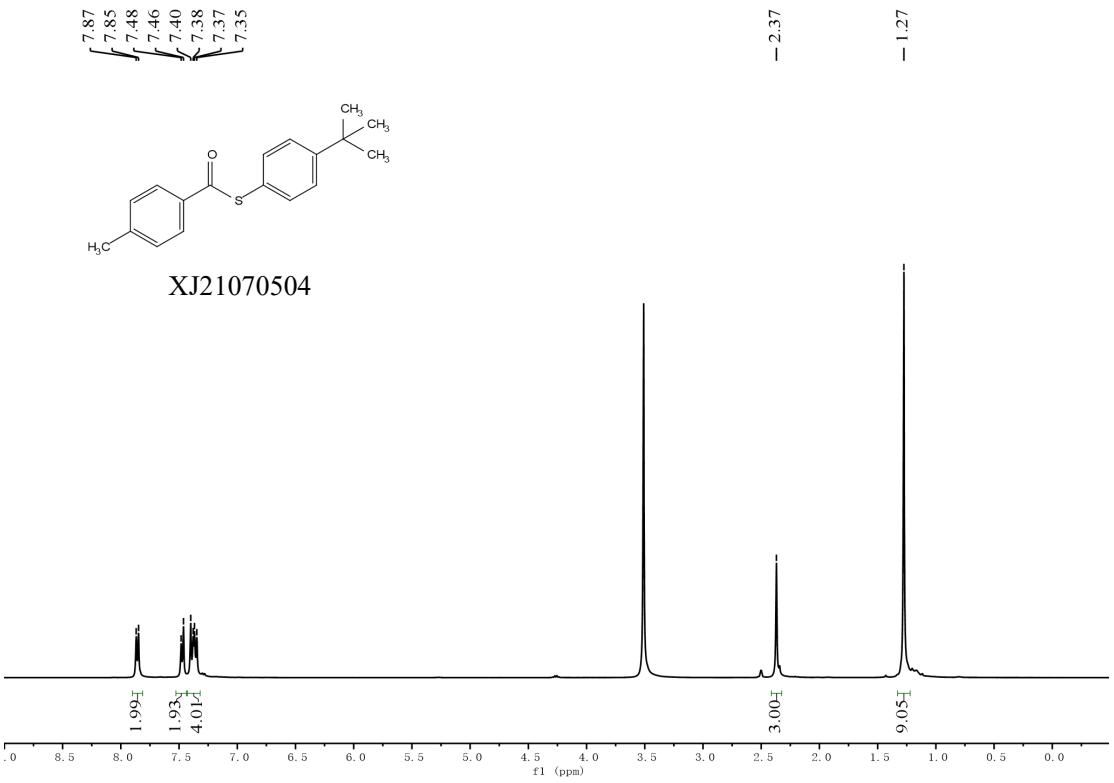
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ab**



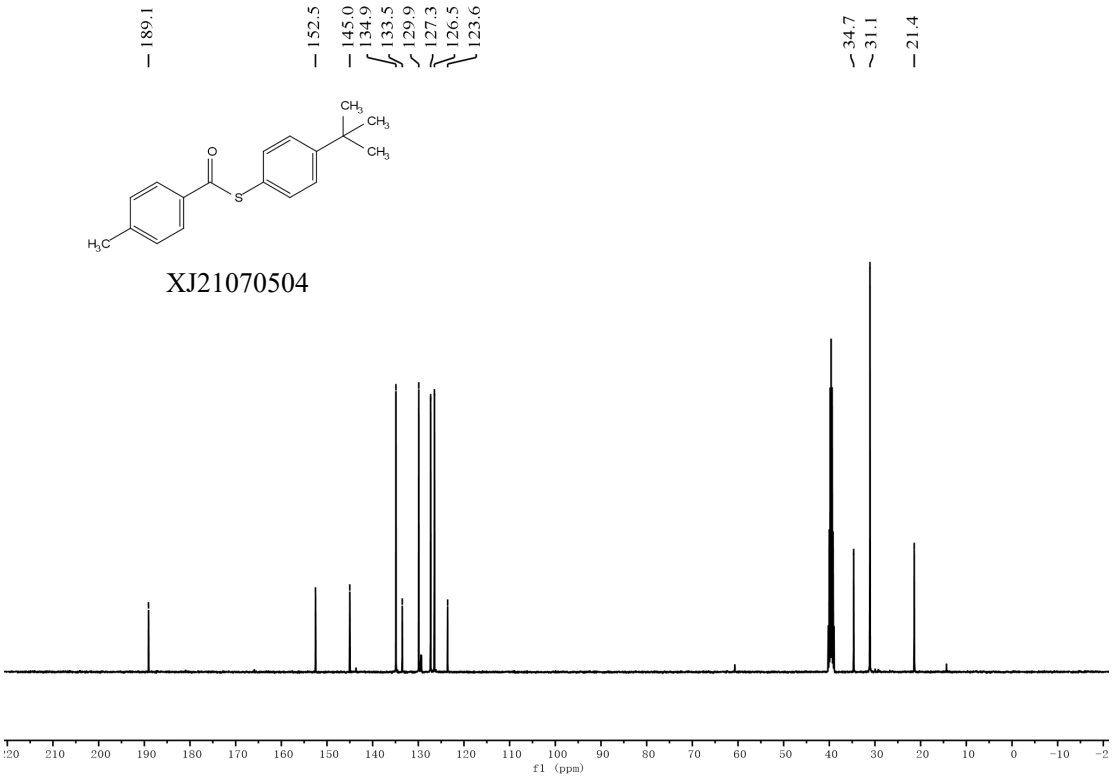
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ab**



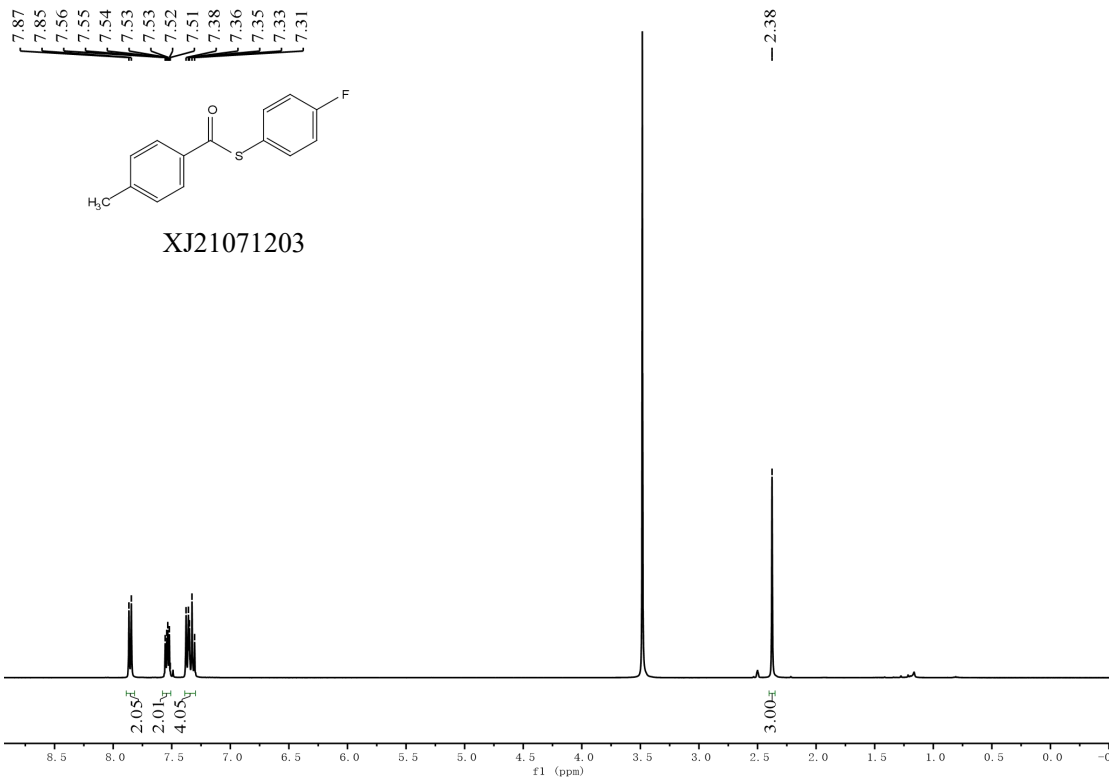
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ac**



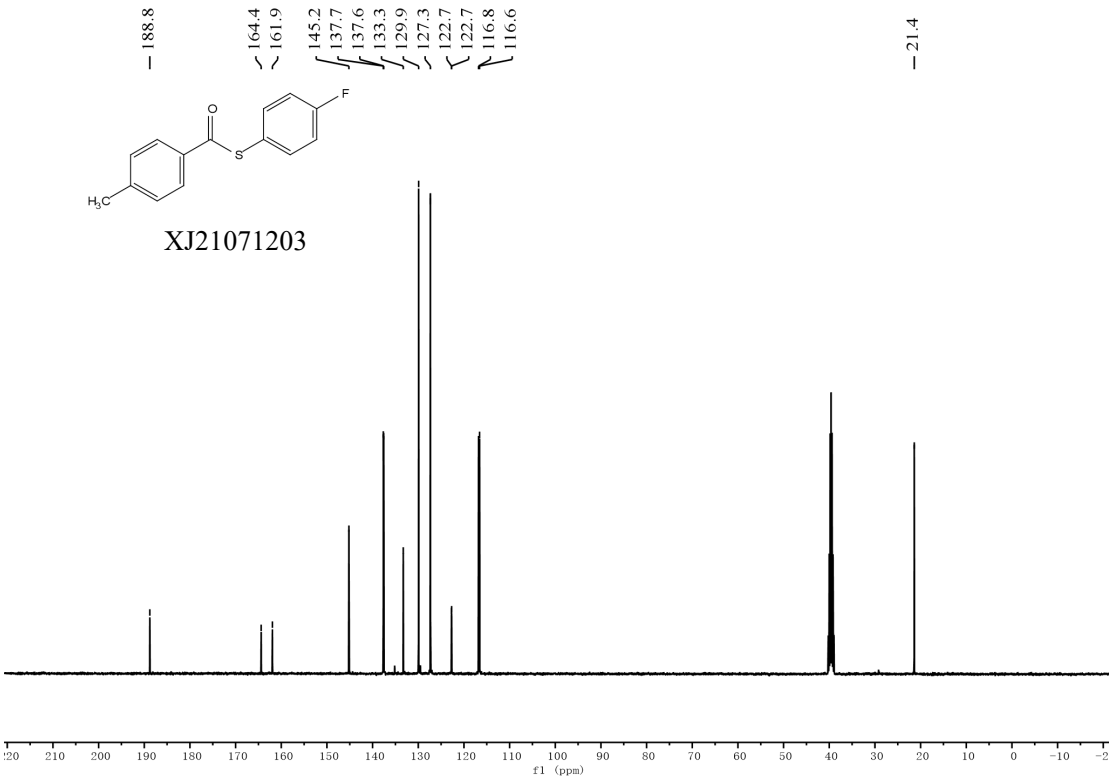
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ac**



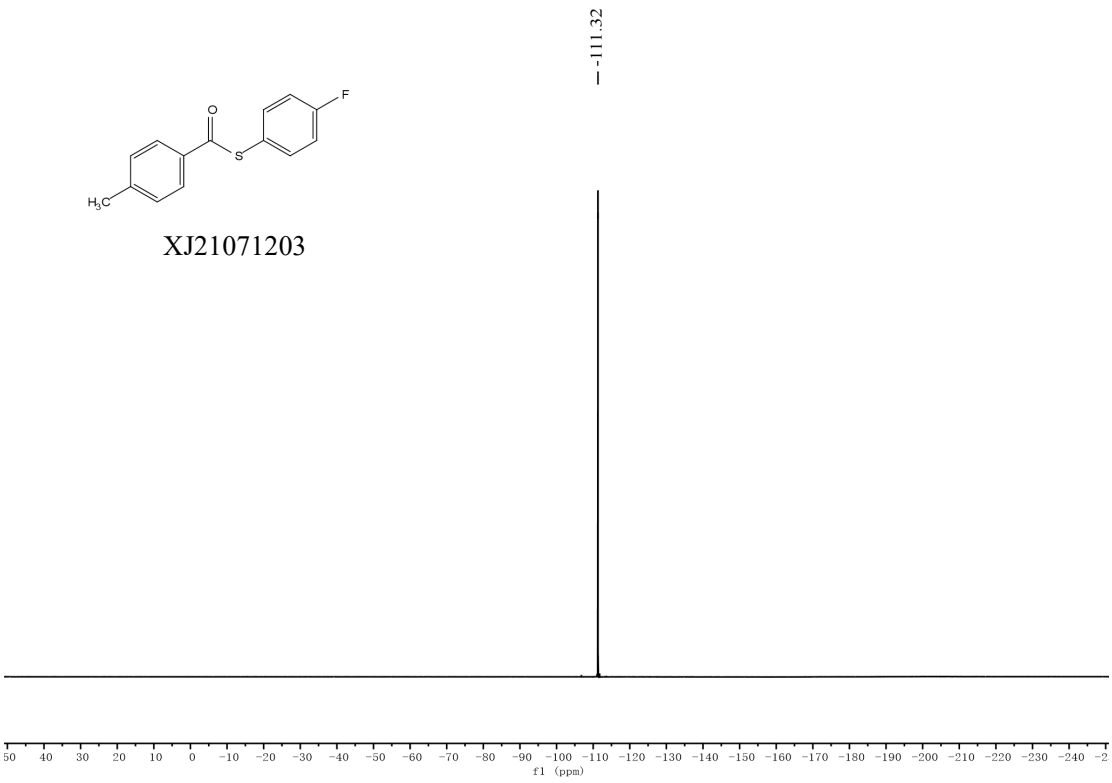
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ad**



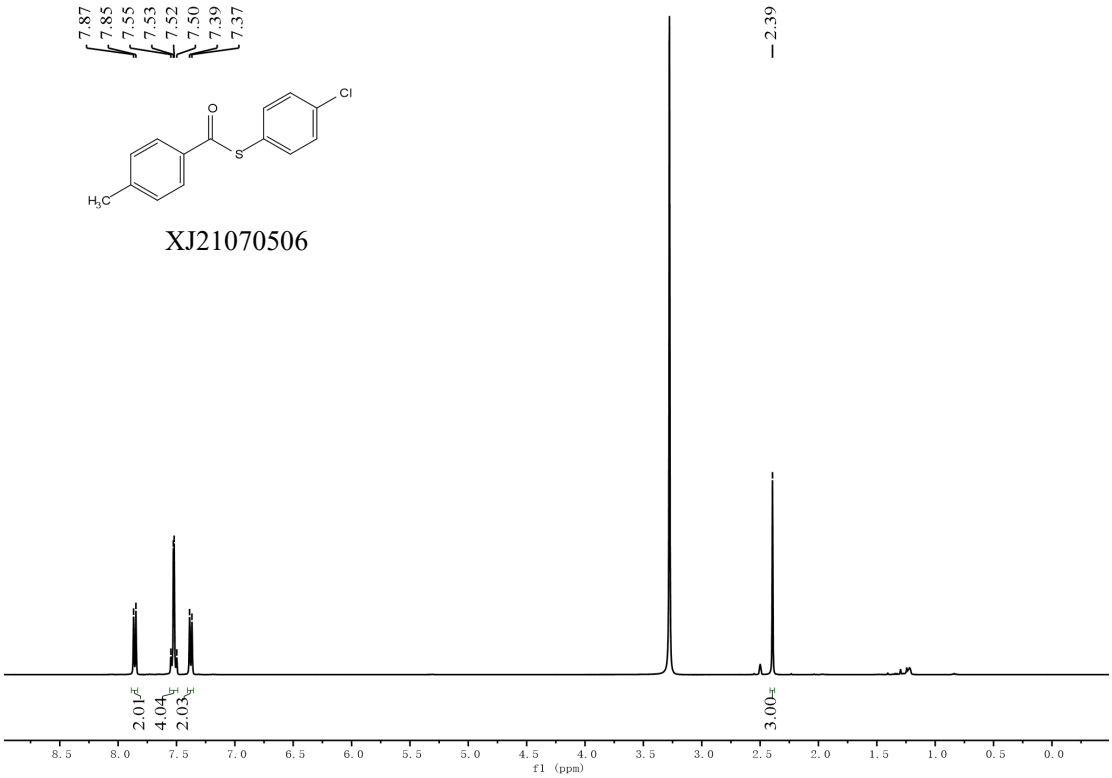
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ad**



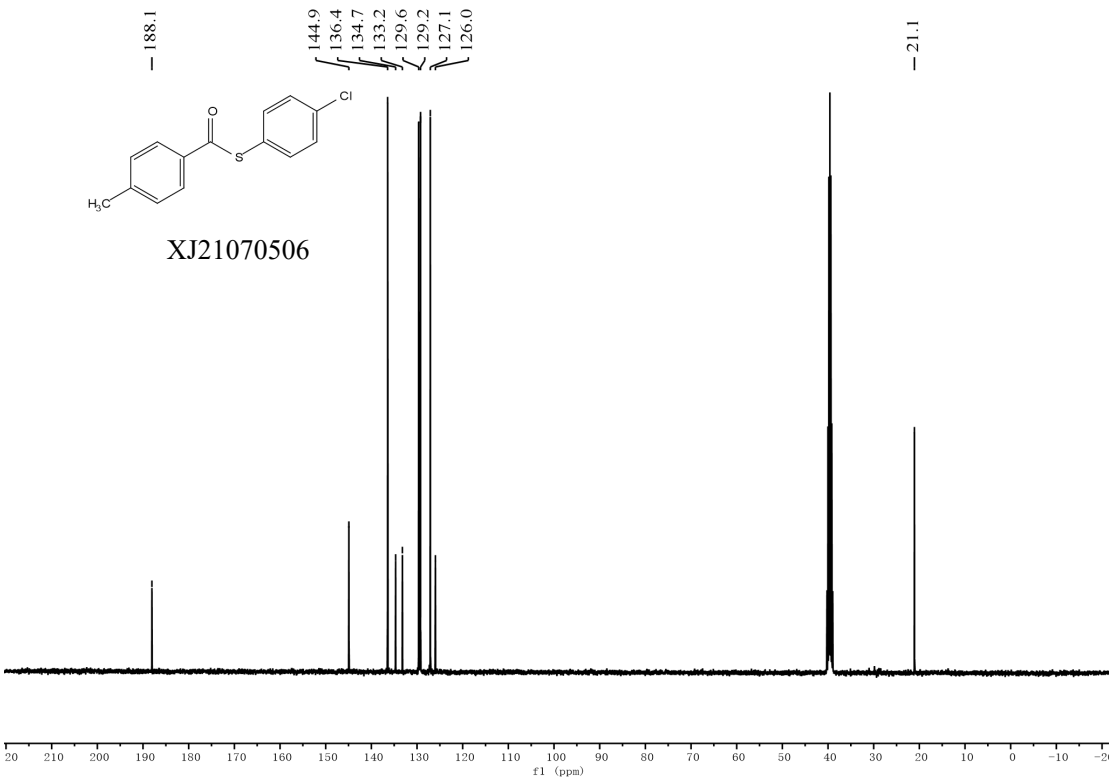
^{19}F NMR (376 MHz, DMSO-d_6) of compound **3ad**



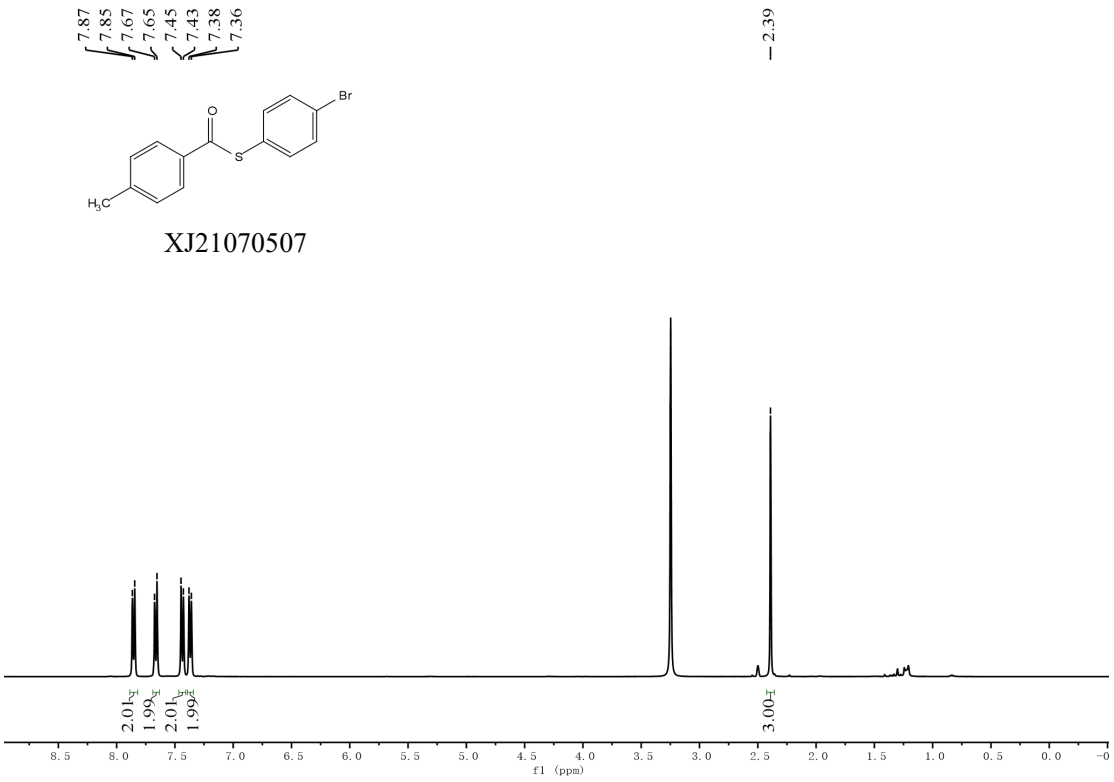
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ae**



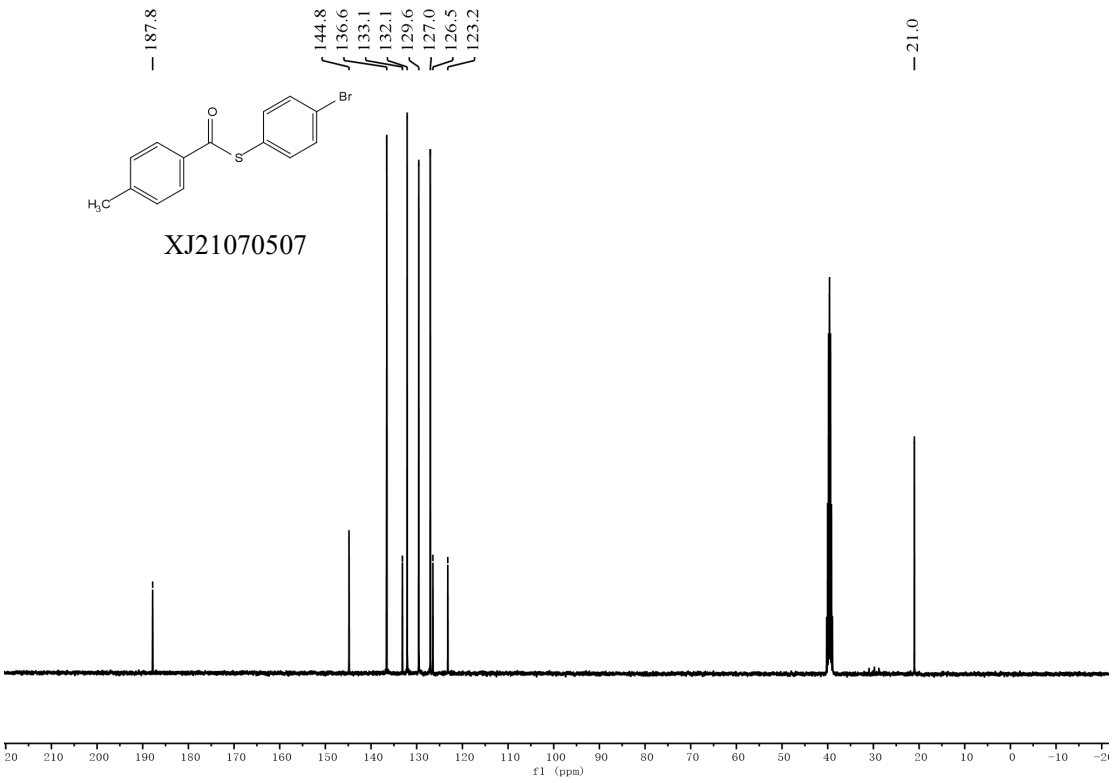
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ae**



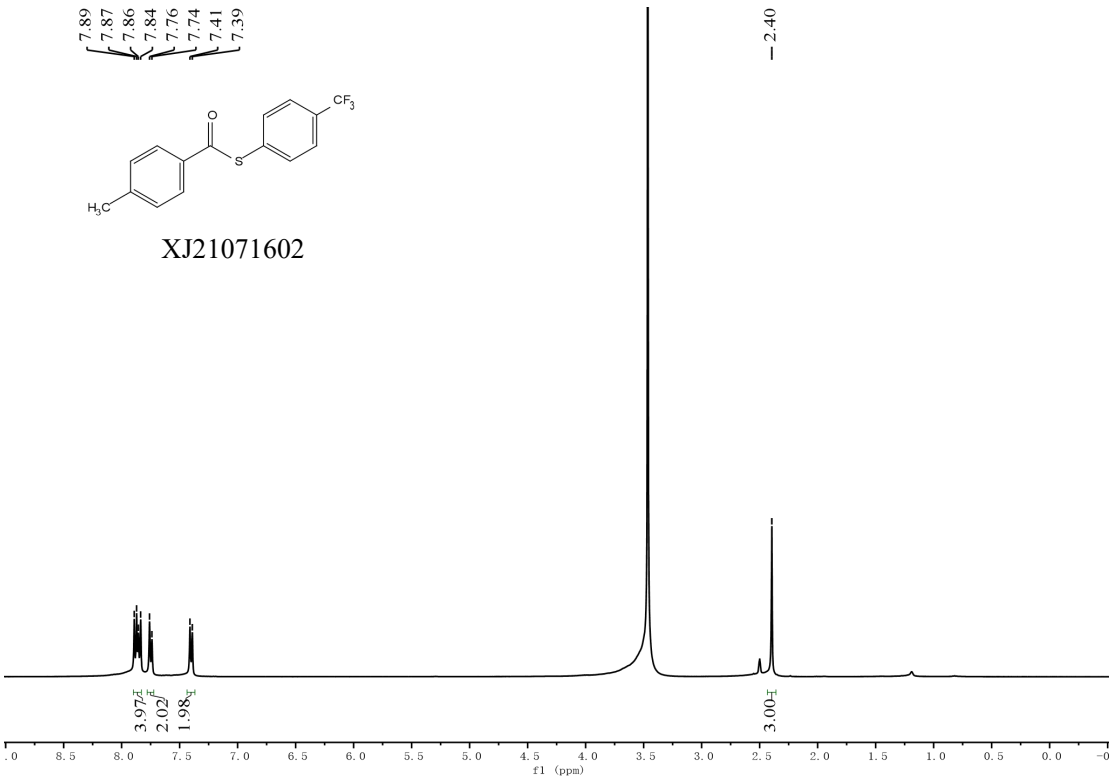
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3af**



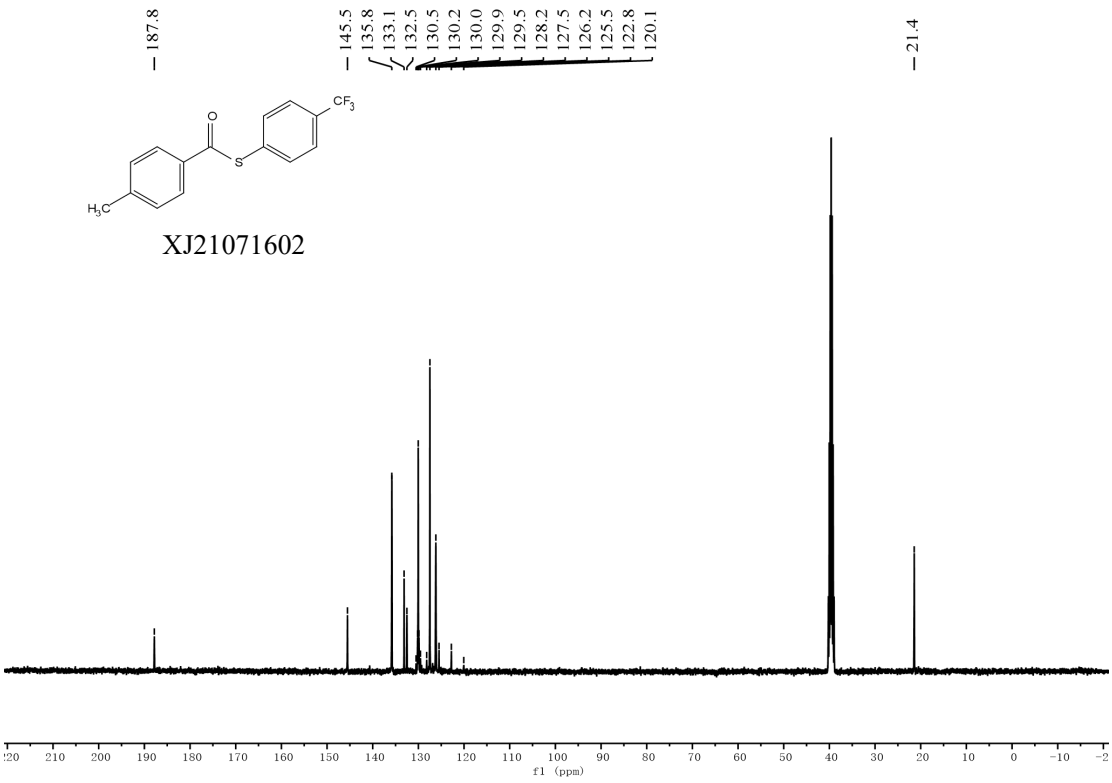
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3af**



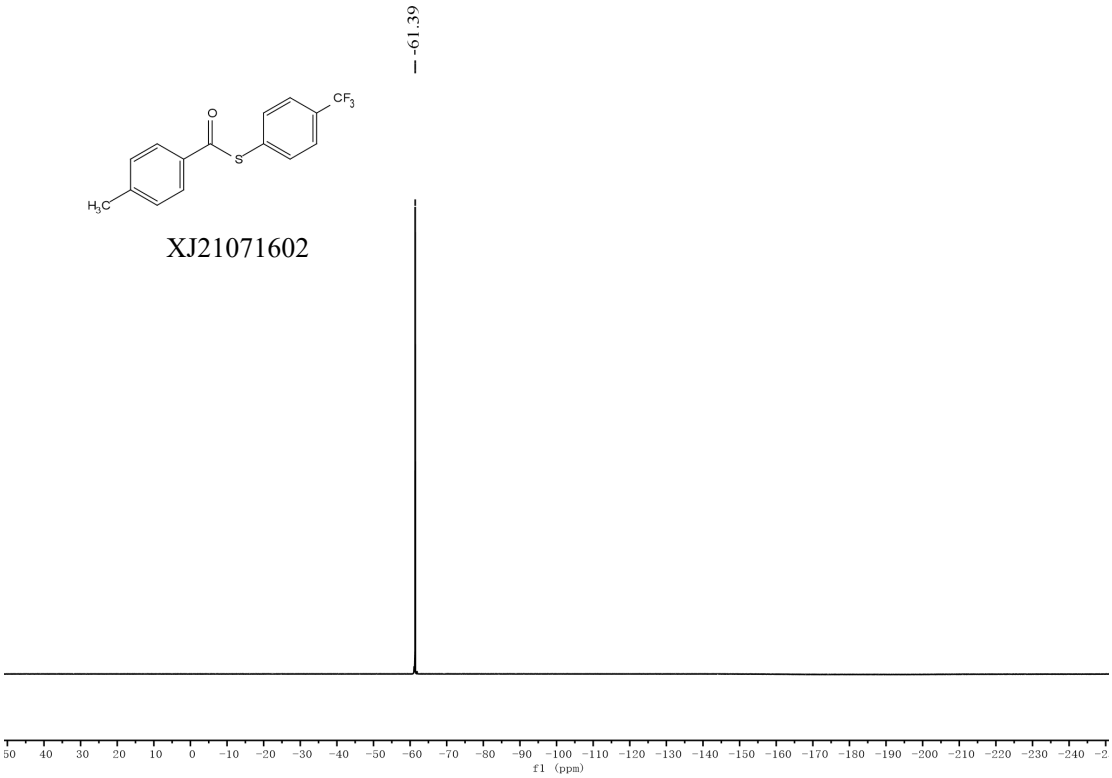
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ag**



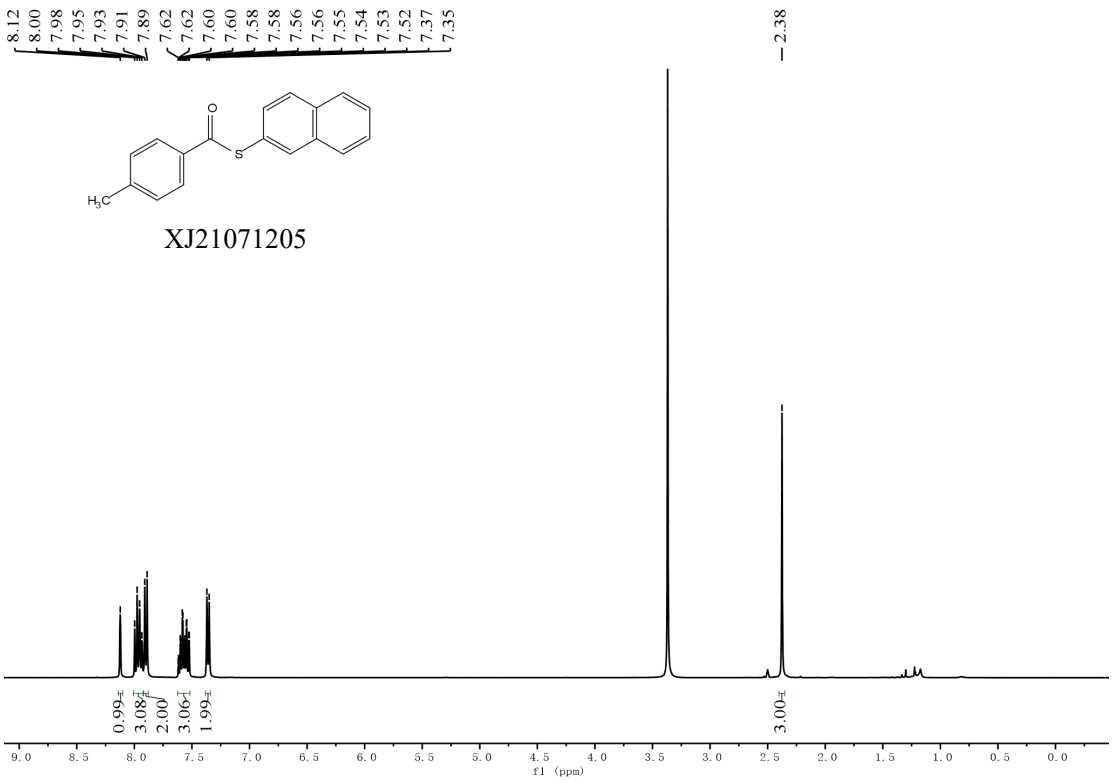
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ag**



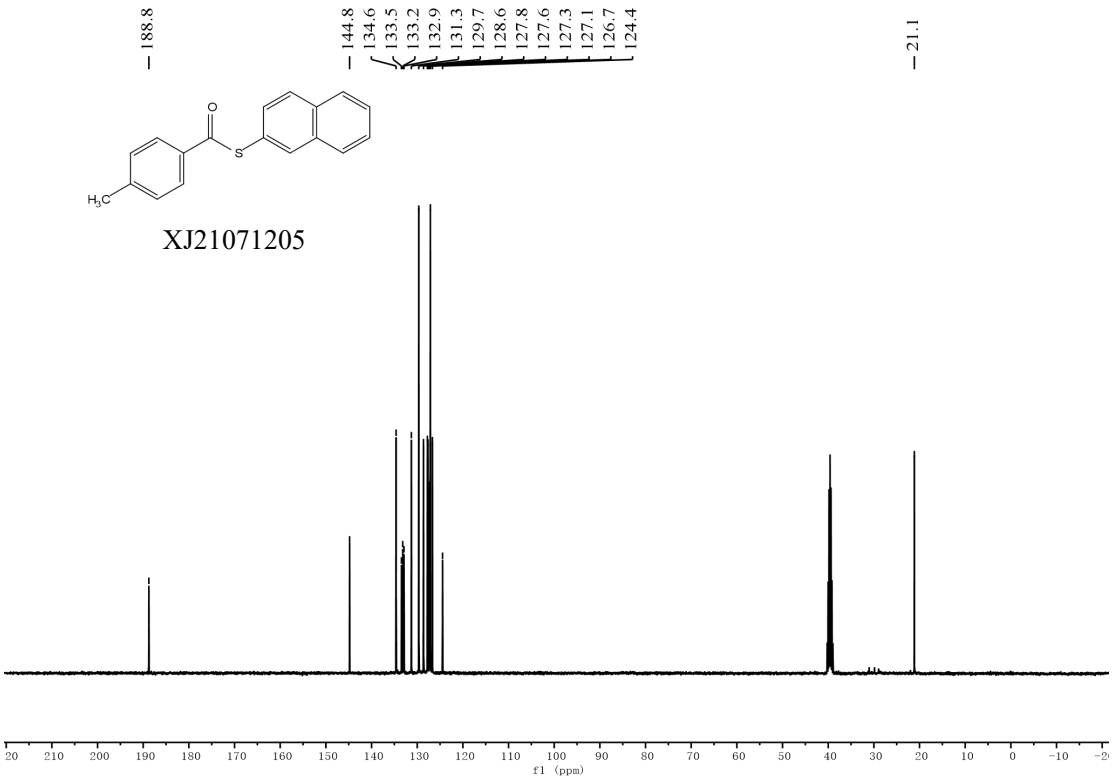
^{19}F NMR (376 MHz, DMSO-d_6) of compound **3ag**



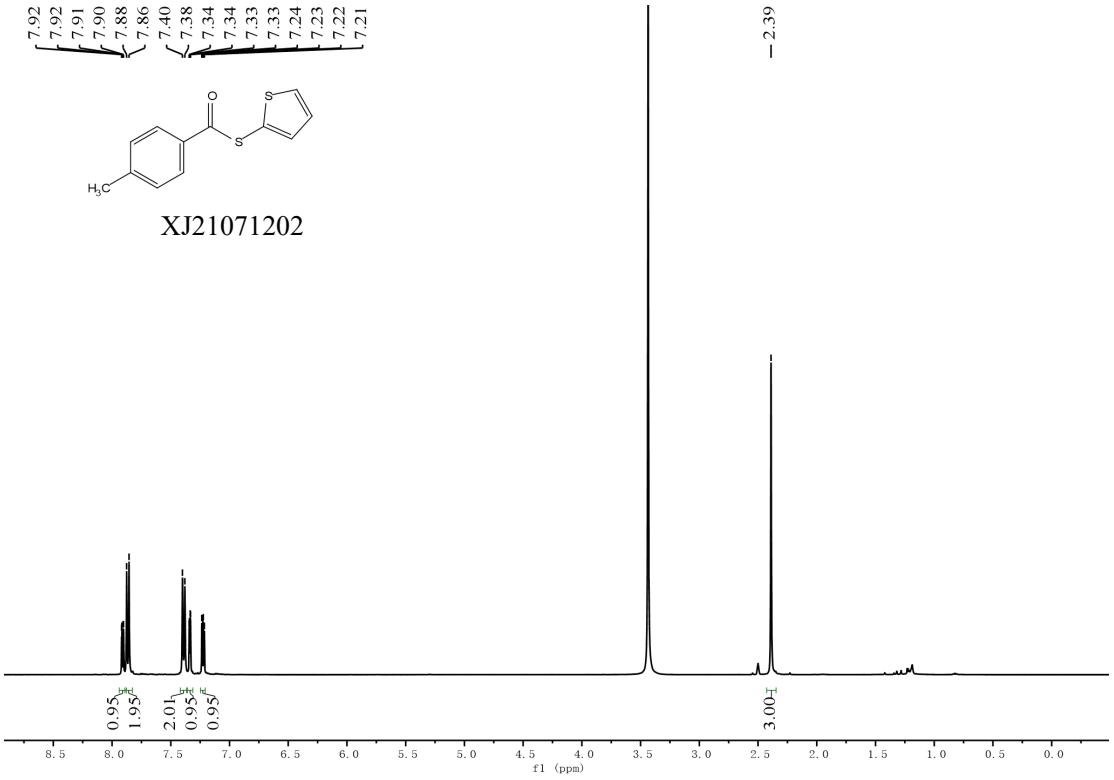
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ah**



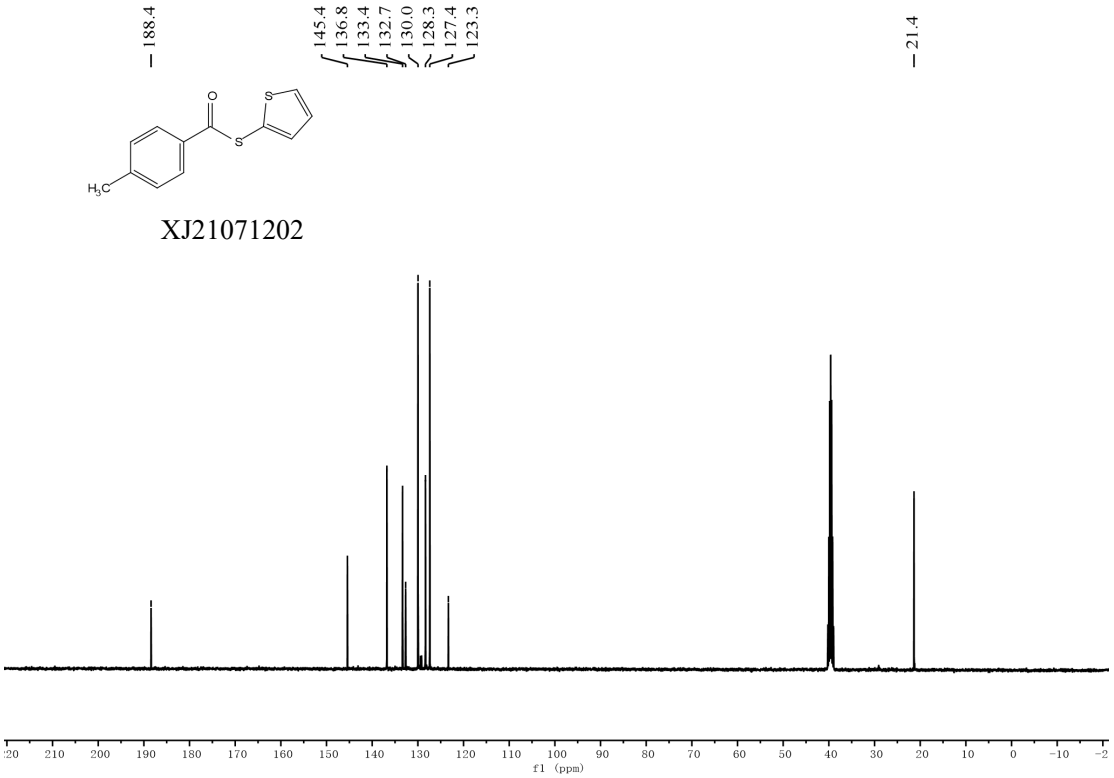
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ah**



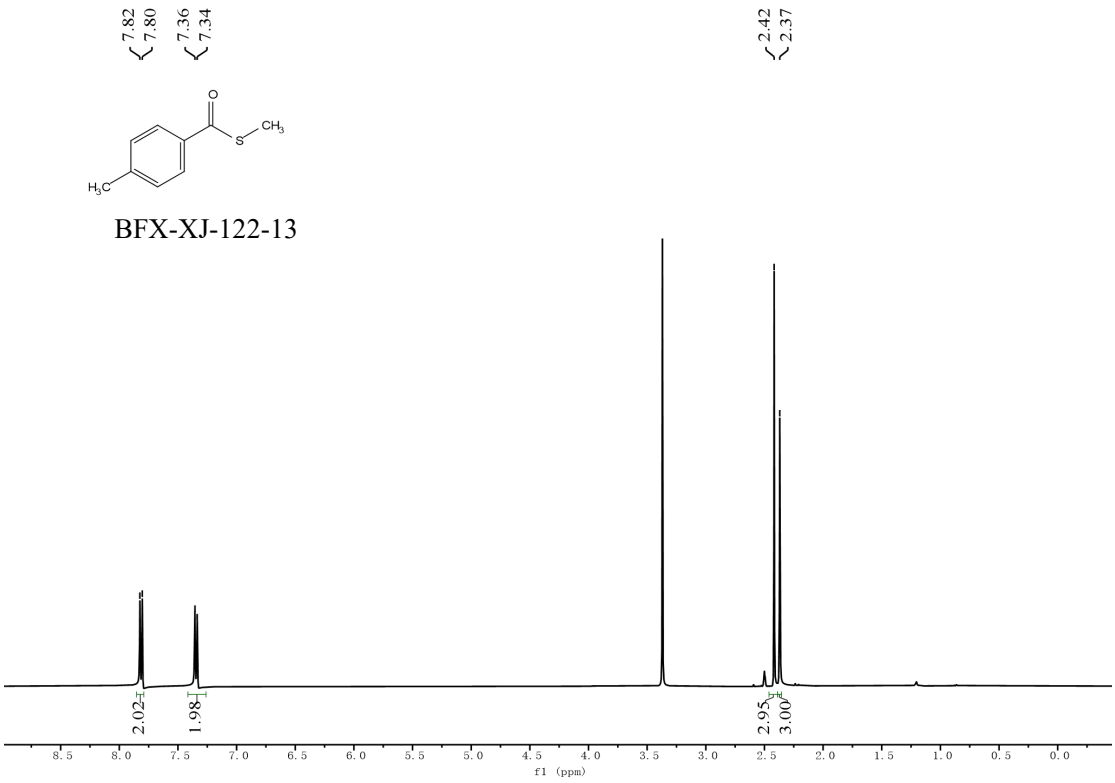
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ai**



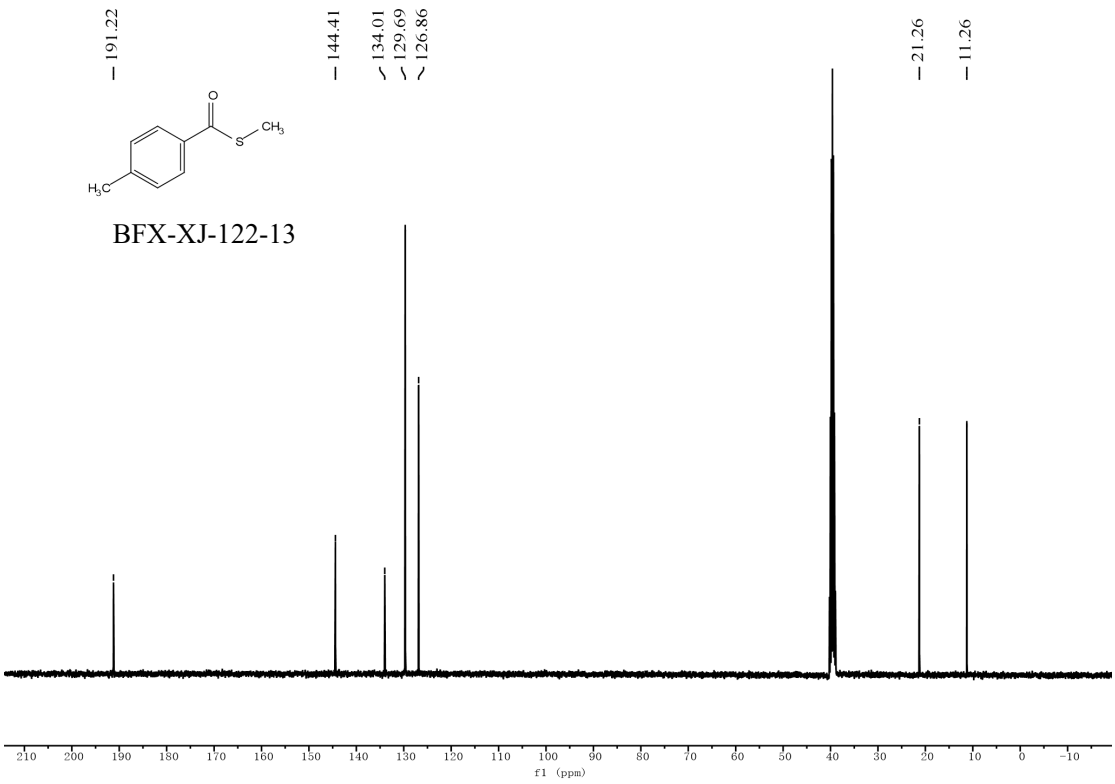
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ai**



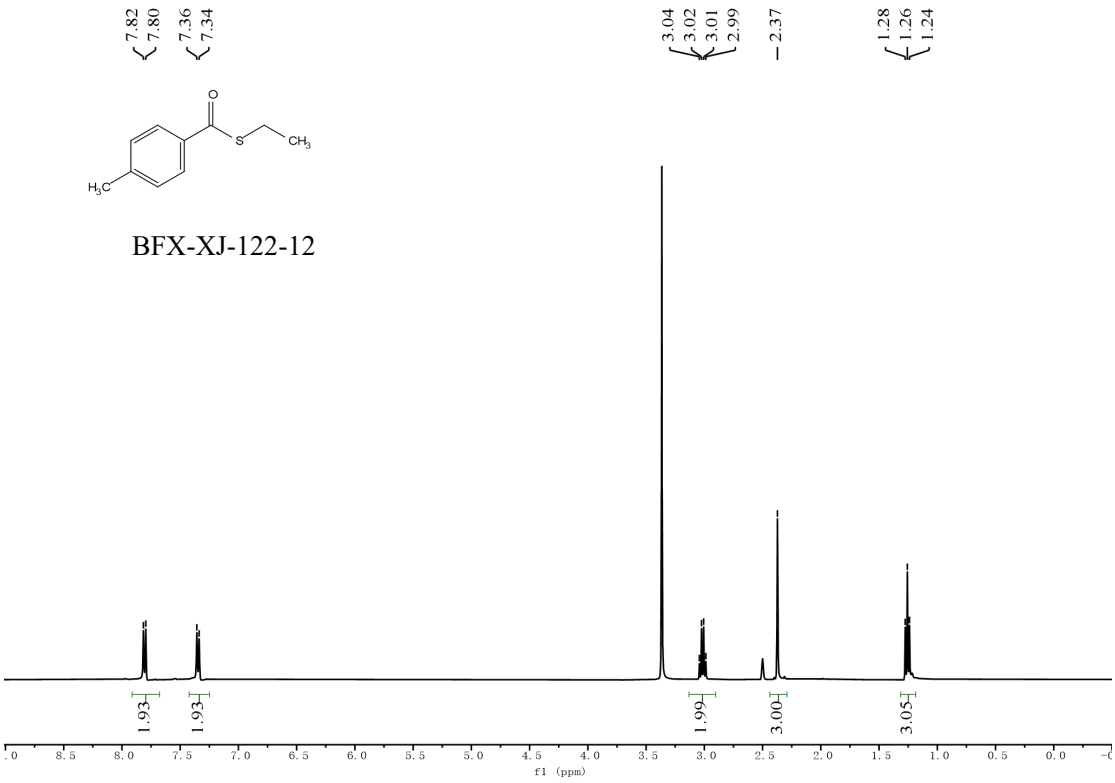
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3aj**



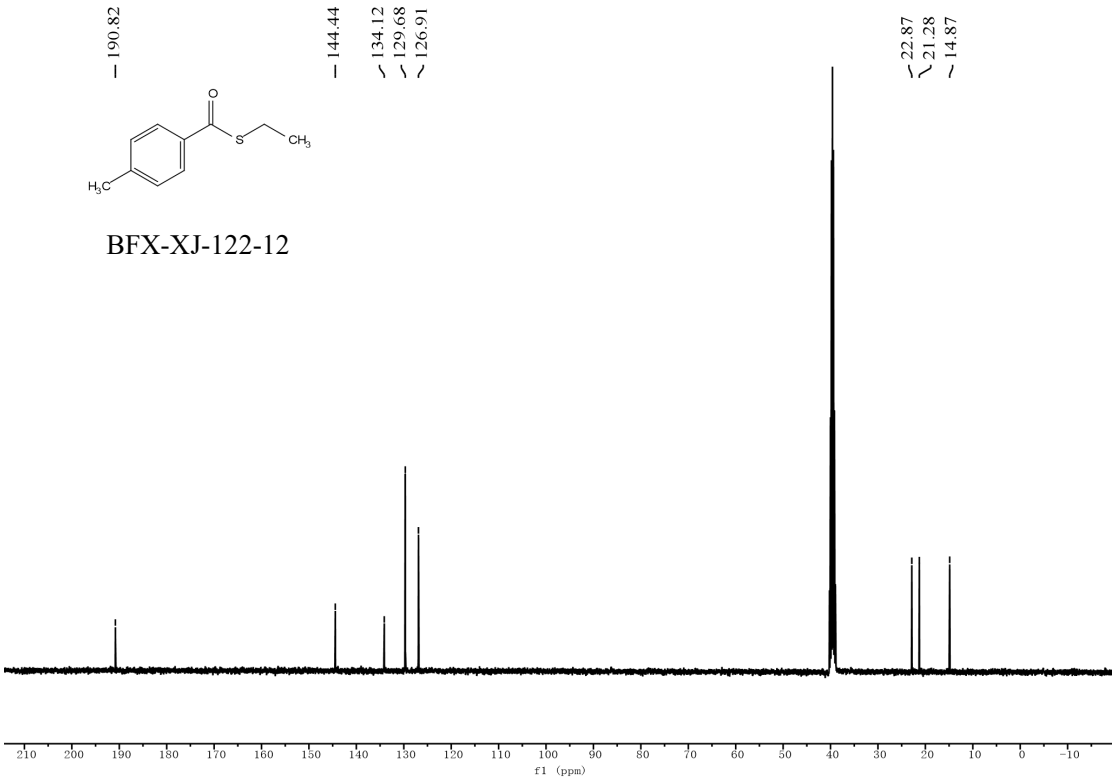
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3aj**



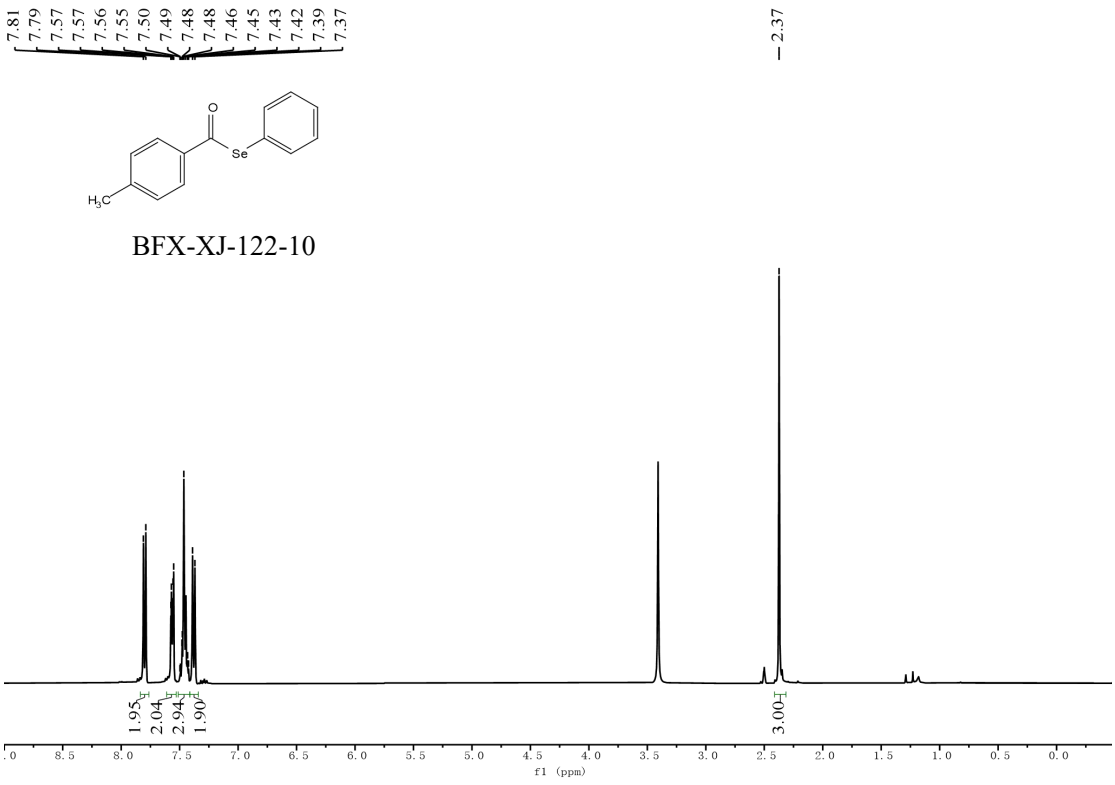
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3ak**



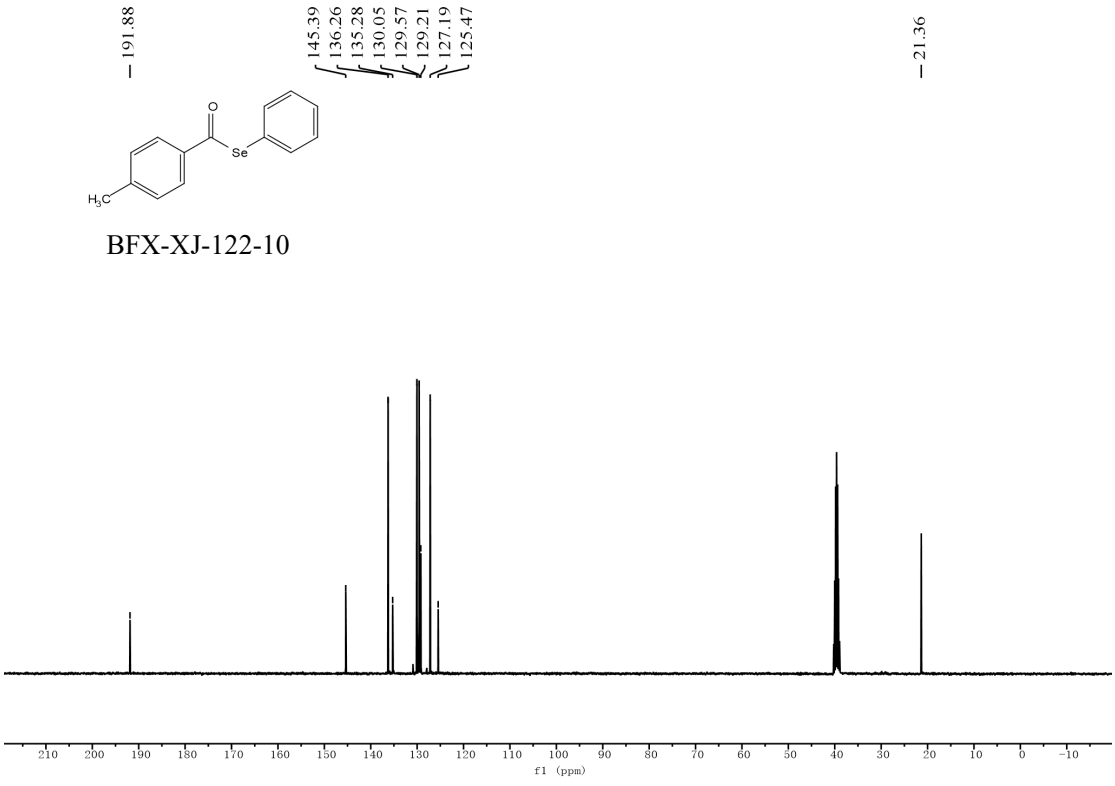
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3ak**



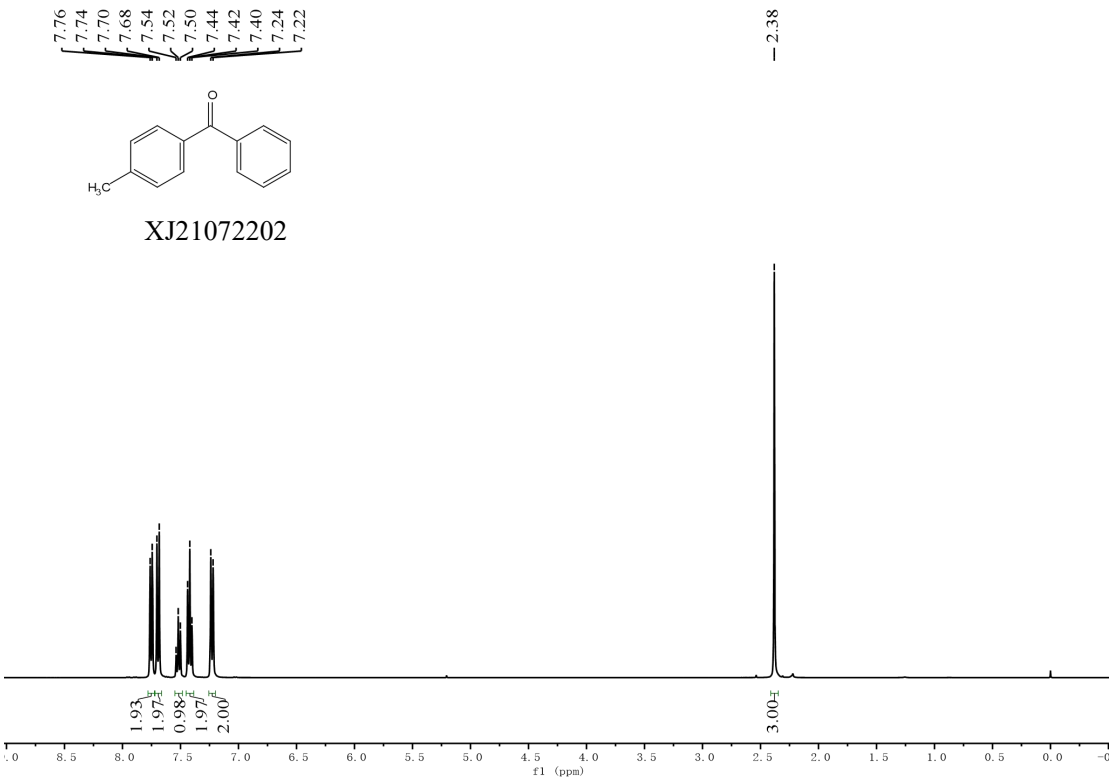
^{1}H NMR (400 MHz, DMSO-d_6) of compound **4a**



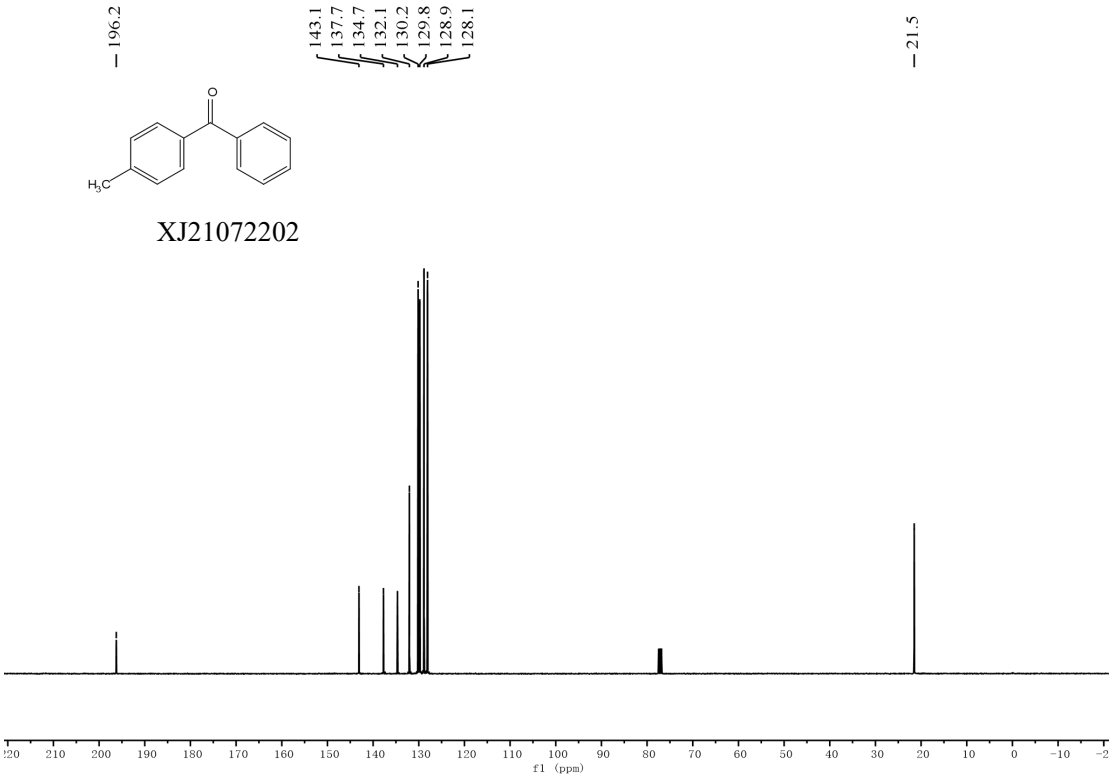
^{13}C NMR (101 MHz, DMSO-d_6) of compound **4a**



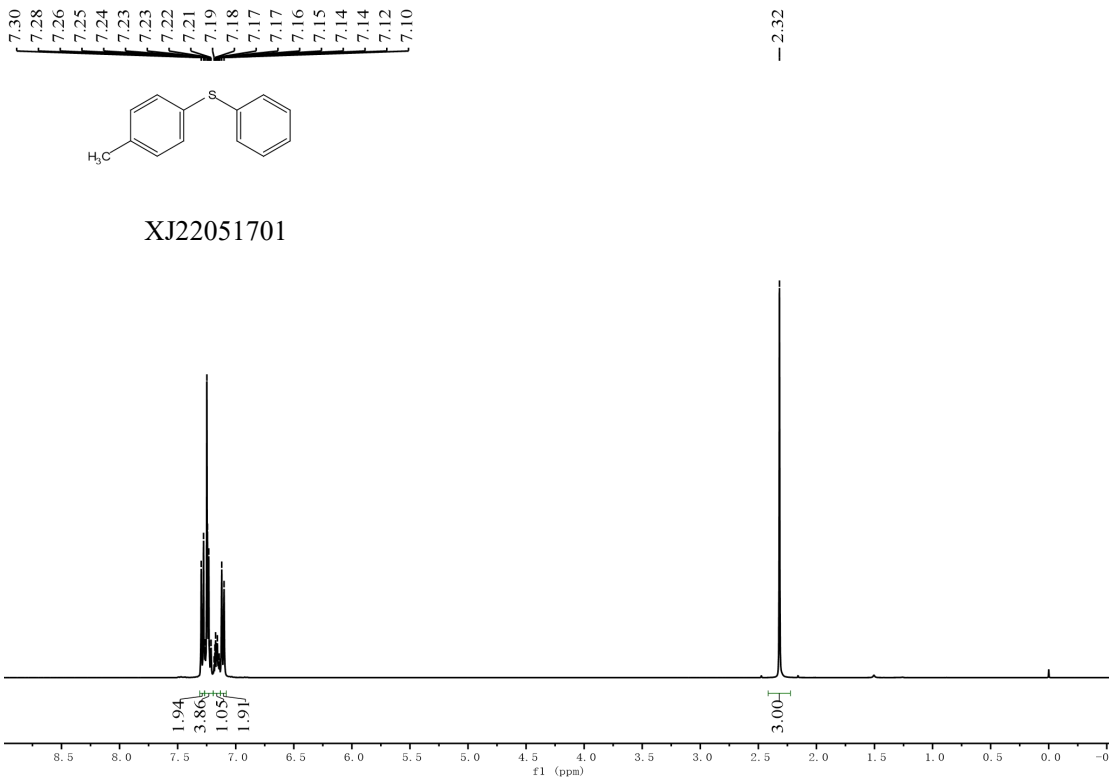
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5a**



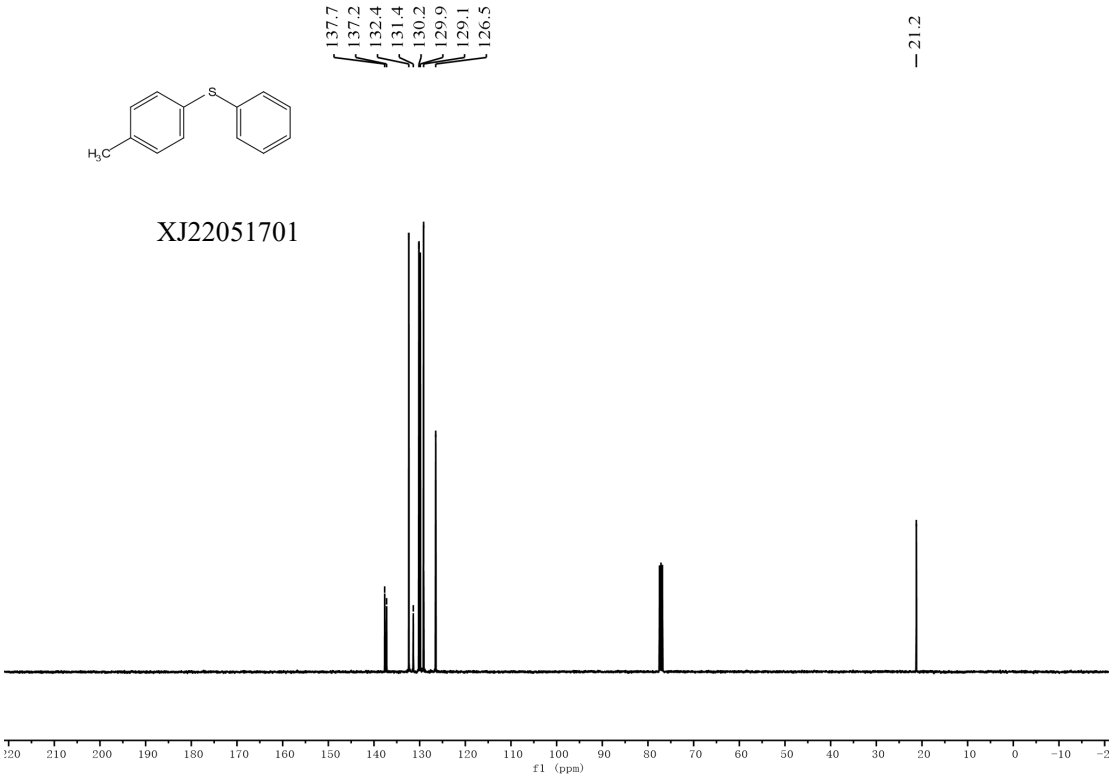
^{13}C NMR (101 MHz, $CDCl_3$) of compound **5a**



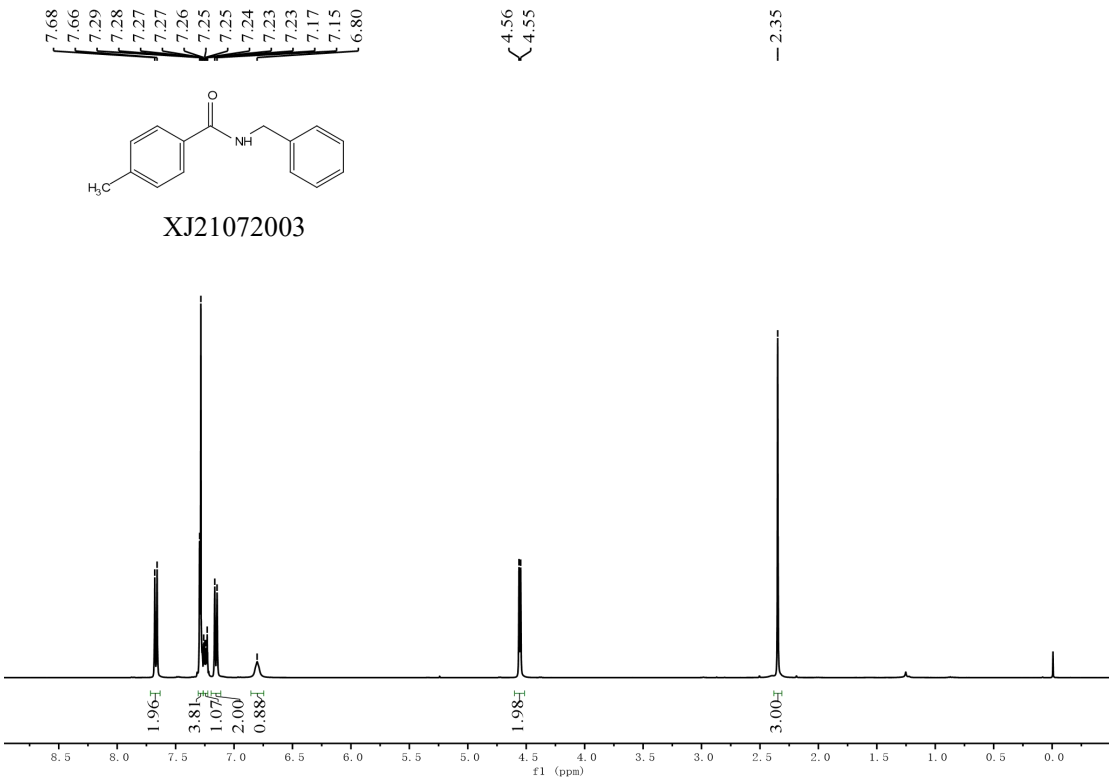
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6a**



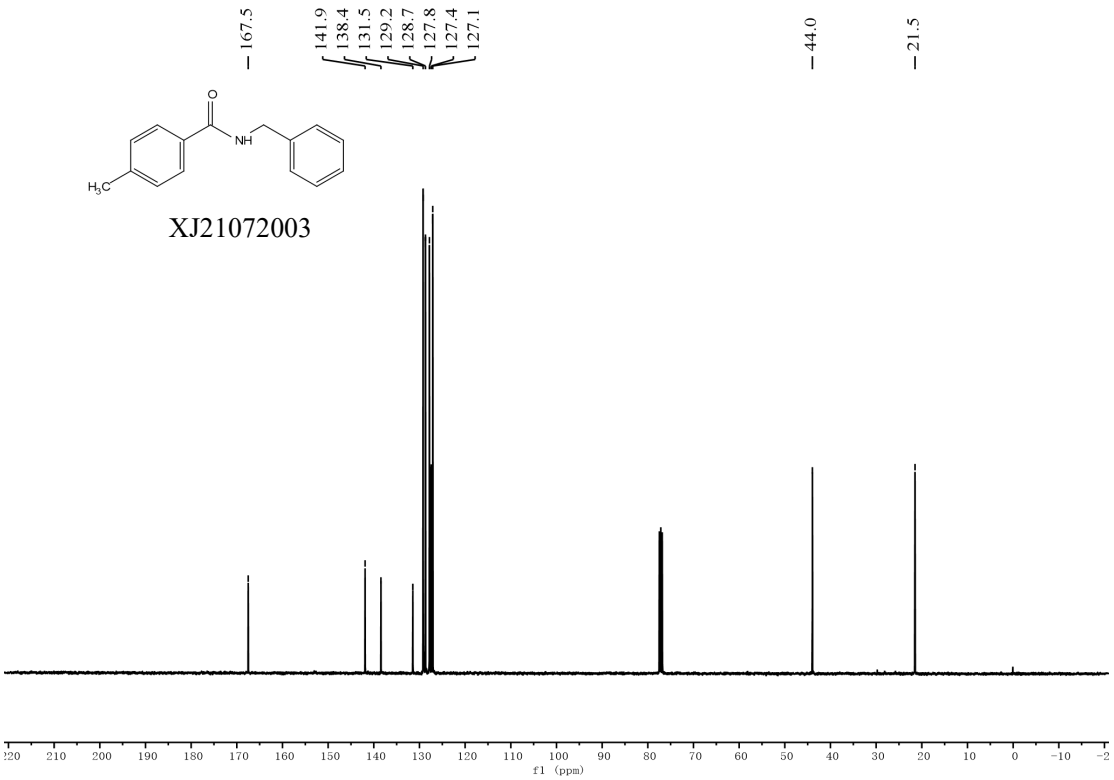
^{13}C NMR (101 MHz, $CDCl_3$) of compound **6a**



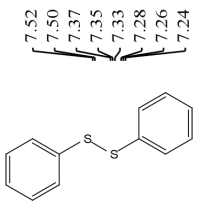
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7a**



^{13}C NMR (101 MHz, $CDCl_3$) of compound **7a**



^{1}H NMR (400 MHz, DMSO-d_6) of compound **8a**



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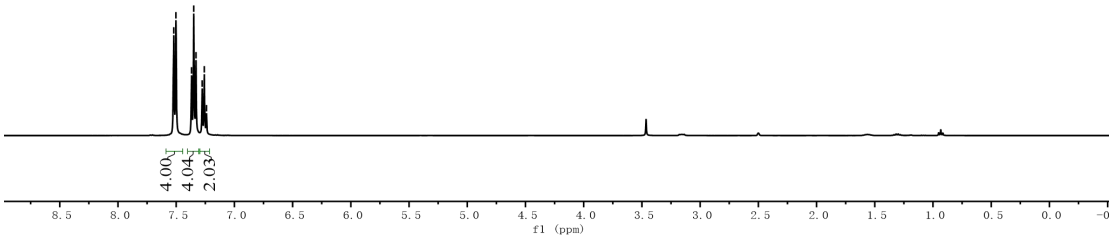
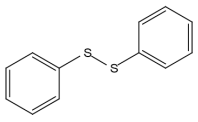
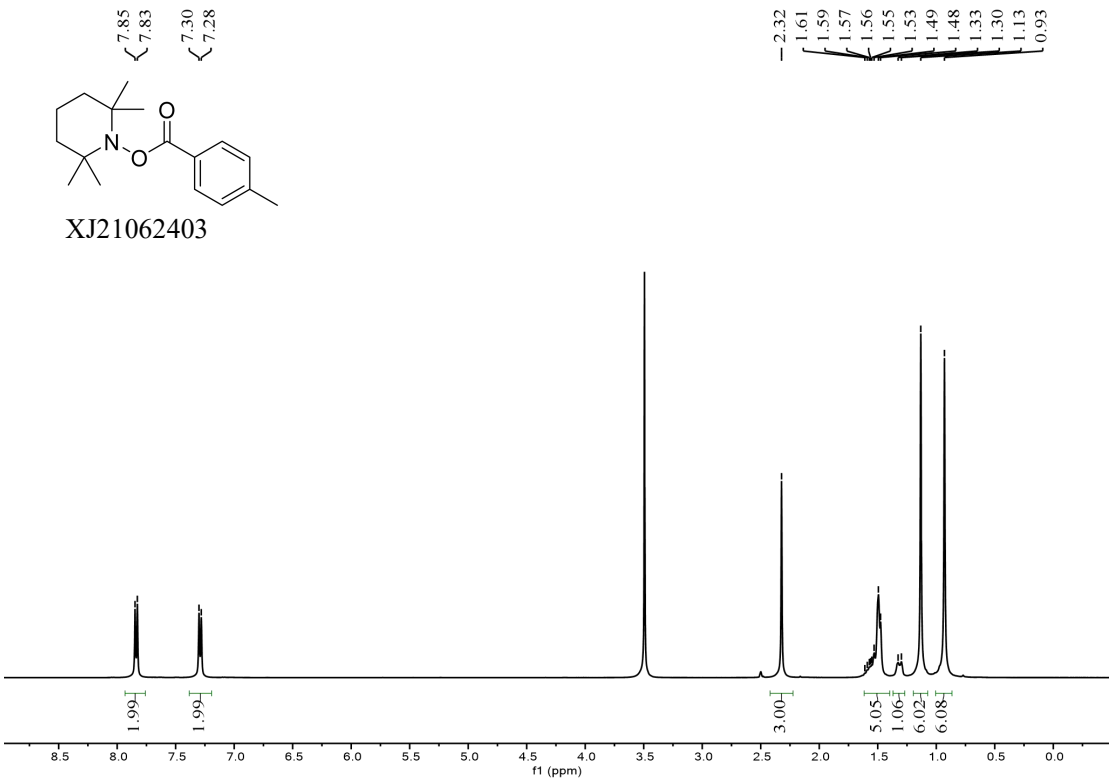


^{13}C NMR (101 MHz, DMSO-d_6) of compound **8a**



XJ21072402

^{1}H NMR (400 MHz, DMSO-d_6) of compound **9a**



^{13}C NMR (101 MHz, DMSO-d_6) of compound **9a**