Supporting Information

for

Photoredox-Catalyzed Cascade Annulation of Methyl(2-(phenylethynyl)phenyl)sulfanes and Methyl(2-(phenylethynyl)phenyl)selanes with Sulfonyl Chlorides: Synthesis of Benzothiophenes and Benzoselenophenes

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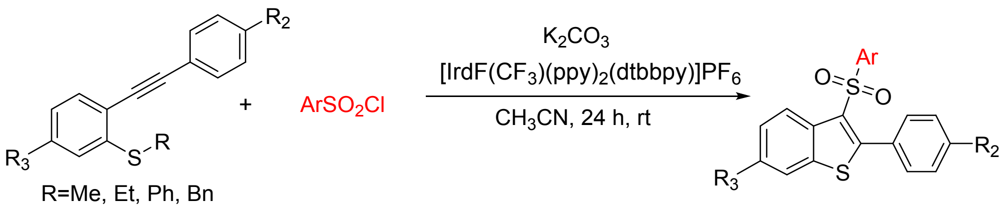
1. General information

All chemicals were purchased from Adamas Reagent, energy chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd and Tansoole. CH_3CN was dried by CaH prior to use. Unless otherwise stated, all experiments were conducted in a Schlenk tube under N_2 atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 500 spectrometer (500 MHz ^{1}H, 125 MHz ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR , δ = 77.00 for ^{13}C-NMR) as an internal reference. High resolution mass spectra were recorded using a Thermo Fisher Scientific LTQ FT Ultra or Waters Micromass GCT Premier instrument. Coupling constants (J) were reported in Hertz (Hz).

2. Experimental procedures

General procedure for the preparation of 3a-3af

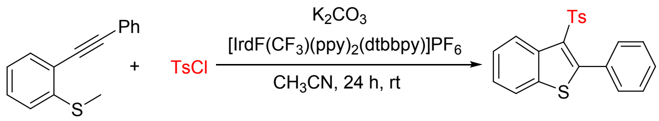


1 **2** **3**

To a flame dried transparent Schlenk tube equipped with a stirring bar was added methyl(2-(phenylethynyl)phenyl)sulfane (0.2 mmol), Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6 (2 mol %), benzenesulfonyl chloride (0.4 mmol) and K_2CO_3 (0.4 mmol). Then dry CH_3CN (2 mL) was added under N_2. The reaction mixture was stirred under the irradiation of a 5 W blue LEDs at room temperature for 24 h. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt (50:1) to afford the corresponding products

3. Optimization of the reaction conditions

Table S1. Optimization of reaction conditions.[a]



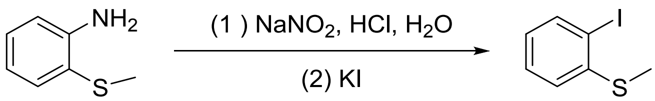
1a **2a** **3a**

entry	K_2CO_3 (equiv)	TsCl (equiv)	yield (%)[b]
1	1.2	1.2	50
2	1.5	1.5	69
3	1.8	1.8	75
4	2.0	2.0	**(83)**[c]
5	2.5	2.5	78
6	2.0	2.2	69
7	2.0	2.5	60
8	2.0	1.8	66
9	2.5	2.0	76
10	2.2	2.0	71
11	1.8	2.0	76

[a] Reaction conditions: **1a** (0.2 mmol), photocatalyst (2 mol %), solvent (2 mL).
[b] Deremined by GC. [c] isolated yields

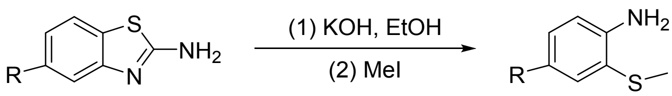
4. General procedure for starting materials

General experimental procedures for substrates 1o-v [1-2]



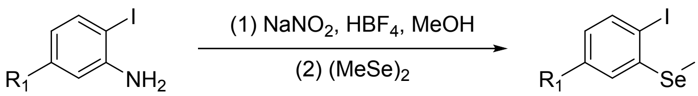
A mixture of 2-(methylthio)aniline (149 mg, 1.5 mmol), aqueous HCl (37%, 0.3 mL) and water (1.3 mL) was cooled to 0 °C. A solution of $NaNO_2$ (113 mg, 1.6 mmol) in water (0.3 mL) was added dropwise and stirred for 10 min. The resulting diazonium salt was treated with a solution of KI (285 mg, 1.7 mmol) in water (0.3 mL). The resulting brown foamy mixture was stirred for 30 min at room temperature and heated at reflux for 15 min. After cooling to ambient temperature, the reaction was diluted with water (10 mL) and neutralized by slow addition of aquesou $Na_2S_2O_3$. The mixture was extracted with dichloromethane (10 mL x 2). The combined organic layer was dried over $NaSO_4$, filtered and evaporated in vacuo. The residue was purified by silica gel column chromatographyto afford (2-iodophenyl)(methyl)sulfane as colorless oil (260 mg, 81%).

General experimental procedures for substrates 1w-aa [1-3]



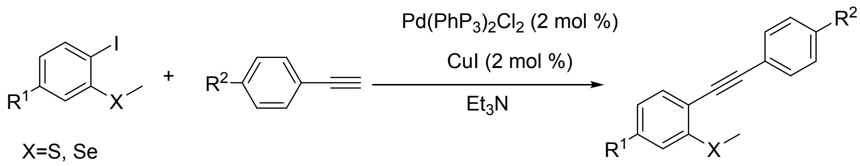
To the stirred solution of KOH (6 g) in 24 mL of water, benzothioazole (3 mmol) was added and refluxed for 17 h. After cooling to room temperature, MeI (3 mmol) was added drop wise and stirring was continued for an additional 1 h. The resultant reaction mixture extracted with diethyl ether (3 x 25 mL) combined organic layers dried over Na_2SO_4, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate (15:1) as eluent.

General experimental procedures for substrates 1ab-af [2, 4]



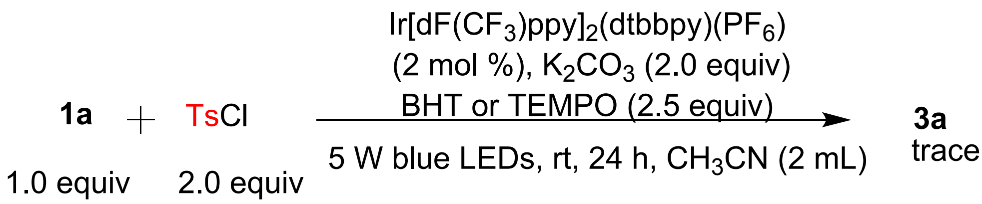
To a stirred solution of methanol (30 mL) and 10 mmol of the 2-iodoaniline, 20 mmol of HBF_4 (36 mL, 48% solution) was added dropwise. After the addition was complete, the solution was allowed to cool to 0 °C. To this solution an aqueous solution of $NaNO_2$ (12 mmol in 5 mL of water) was added dropwise to the reaction mixture, which turned a pale yellow to red brown. The mixture was allowed to warm to room temperature and methanol was removed under vacuum at room temperature. The mixture was filtered and washed with cold methanol. The diazonium salt was dried under vacuum and used for the next step without purification. A suspension of 8 mmol of the crude diazonium salt in 25 mL of $CHCl_3$ containing 10 mol % of 18-

crown-6 and 9 mmol of dimethyl diselenide was stirred at 0 °C. To this mixture, 16 mmol of KOAc was added in small portions over a period of 10 min and the resulting solution was allowed to stir for 4 h and then filtered. The solid residue was washed with chloroform and the resulting filtrate was washed with water (2 x 5 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude product obtained was then purified by flash chromatography on silica gel using ethyl acetate/hexanes as the eluent.

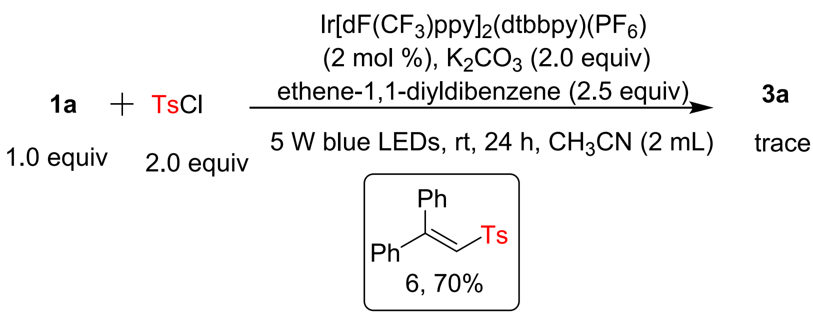


To a solution of (2-iodophenyl)(methyl)sulfane (5 mmol), CuI (2 mol %), and $Pd(Ph_3P)_2Cl_2$ (2 mol %) in triethylamine (100 mL) was added drop-wise an alkyne (6 mmol) under N_2. The reaction mixture was stirred for 5-10 h at room temperature. Upon completion, the mixture was diluted with diethyl ether and then washed with water and brine successively. The organic phase was dried with anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified through silica gel flash chromatography to give the desired product in mostly > 90% yield

Experiments on Mechanism



To a flame dried transparent Schlenk tube equipped with a stirring bar was added **1a** (0.2mmol), **TsCl** (0.4 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol %), K_2CO_3 (0.4 mmol) and BHT or TEMPO (2.5 equiv). Then dry CH_3CN (2 mL) was added under N_2. The reaction mixture was stirred under the irradiation of a 5 W blue LEDs at room temperature for 24 h. After that, the mixture was diluted with ethyl acetate. The amount of **3aa** was detected by TLC and GC-MS.



To a flame dried transparent Schlenk tube equipped with a stirring bar was added **1a** (0.2mmol), **TsCl** (0.4 mmol), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol %), K_2CO_3 (0.4 mmol) and and ethene-1,1-diyldibenzene (2.5 equiv). Then dry CH_3CN (2 mL) was added under N_2. The reaction mixture was stirred under the irradiation of a 5 W blue

LEDs at room temperature for 24 h. After that, the mixture was diluted with ethyl acetate. The amount of **3aa** was detected by TLC and GC-MS. The radical addition elimination product **6** in 70% yield.

5. References

[1] Z. He and Y. Huang, *ACS Catal*. 2016, **6**, 7814−7823

[2] B. Lu, Y. Luo, L. Liu, L. Ye, Y. Wang, and L. Zhang, *Angew. Chem. Int. Ed*. 2011, **50**, 8358 –8362

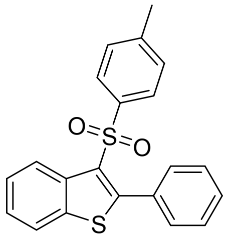
[3] D. Hari, T. Hering, and B. Köning, *Org. Lett*. 2012, **14**, 5334

[4] T. Kesharwani, S. A. Worlikar, and R. C. Larock, *J. Org. Chem*. 2006, **71**, 2307-2312

[5] W. Kong, H. An, and Q. Song, *Chem. Commun*., 2017, **53**, 8968—8971

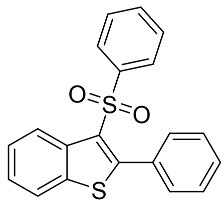
6. Experimental characterization data for products

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



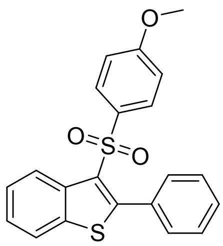
60.4 mg, 83% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.49 – 7.39 (m, 6H), 7.13 (d, *J* = 8.1 Hz, 2H), 2.33 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5 (s), 143.9 (s), 139.4 (s), 138.2 (s), 136.2 (s), 131.7 (s), 130.5 (s), 130.3 (s), 129.5 (s), 127.7 (s), 127.0 (s), 125.9 (s), 125.6 (s), 124.6 (s), 121.8 (s), 21.6 (s).

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



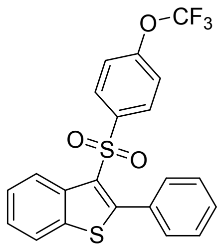
64.4 mg, 92% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.50 – 7.39 (m, 7H), 7.37 – 7.29 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9 (s), 142.3 (s), 138.2 (s), 136.2 (s), 132.9 (s), 131.6 (s), 130.5 (s), 129.9 (s), 129.5 (s), 128.8 (s), 127.7 (s), 126.9 (s), 126.0 (s), 125.7 (s), 124.6 (s), 121.8 (s).

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



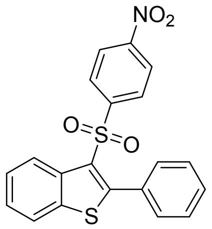
72.2 mg, 95% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 – 8.62 (m, 1H), 7.82 – 7.77 (m, 1H), 7.61 – 7.57 (m, 2H), 7.55 – 7.51 (m, 1H), 7.49 – 7.39 (m, 6H), 6.84 – 6.74 (m, 2H), 3.78 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 (s), 152.1 (s), 138.2 (s), 136.1 (s), 133.9 (s), 131.8 (s), 130.8 (s), 130.5 (s), 129.5 (s), 129.2 (s), 127.7 (s), 125.9 (s), 125.6 (s), 124.6 (s), 121.8 (s), 113.9 (s), 55.6 (s).

2-phenyl-3-((4-(trifluoromethoxy)phenyl)sulfonyl)benzo[b]thiophene (3d)



59.5 mg, 69% yield, white solid. 1H NMR (500 MHz, CDCl3) δ 8.67 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.59 – 7.53 (m, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.35 (m, 4H), 7.12 (d, *J* = 8.2 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1 (s), 152.3 (q, *J*=6.7 Hz), 140.5 (s), 138.1 (s), 136.1 (s), 131.3 (s), 130.5 (s), 129.7 (d, J = 8.7 Hz), 129.2 (s), 127.8 (s), 126.2 (s), 125.8 (s), 124.6 (s), 121.9 (s), 121.2 (s), 120.5 (s), 119.1 (s). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{14}F_3O_2S_2^+$, 435.0331; Found: 435.0331.
^{19}F NMR (471 MHz, $CDCl_3$) δ -57.67 (s).

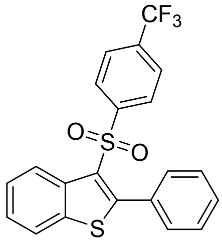
3-((4-nitrophenyl)sulfonyl)-2-phenylbenzo[b]thiophene (3e)



45.0 mg, 57% yield, white solid. [1]H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.53 – 7.46 (m, 2H), 7.45 – 7.36 (m, 4H).

[13]C NMR (126 MHz, $CDCl_3$) δ 154.3 (s), 150.1 (s), 147.7 (s), 138.2 (s), 135.9 (s), 131.0 (s), 130. (s), 129.9 (s), 128.6 (s), 128.3 (s), 127.9 (s), 126.4 (s), 126.0 (s), 124.3 (s), 123.9 (s), 122.0 (s).

2-phenyl-3-((4-(trifluoromethyl)phenyl)sulfonyl)benzo[b]thiophene (3f)

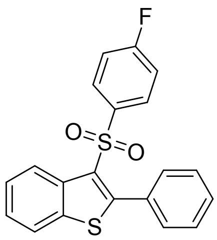


60.2 mg, 72% yield, white solid. [1]H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.52 (m, 3H), 7.51 – 7.43 (m, 2H), 7.43 – 7.36 (m, 4H).

[13]C NMR (126 MHz, $CDCl_3$) δ 153.7 (s), 145.6 (s), 138.2 (s), 136.0 (s), 134.765 (s), 134.4 (s), 131.2 (s), 130.5 (s), 129.8 (s), 129.2 (s), 127.8 (s), 127.5 (s), 126.3 (s), 125.7 (q, *J*=5.3 Hz), 124.5 (s), 124.2 (s), 121.9 (d, J = 12.7 Hz).

[19]F NMR (471 MHz, $CDCl_3$) δ -63.17 (s).

3-((4-fluorophenyl)sulfonyl)-2-phenylbenzo[b]thiophene (3g)

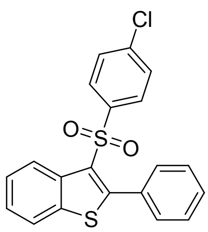


64.0mg, 87% yield, white solid. [1]H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.44 (m, 2H), 7.43 – 7.38 (m, 4H), 7.03 – 6.95 (m, 2H).

[13]C NMR (126 MHz, $CDCl_3$) δ 165.2 (d, *J* = 255.6 Hz), 152.9 (s), 138.3 (d, *J* = 3.1 Hz), 138.2 (s), 136.1 (s), 131.5 (s), 130.5 (s), 130.0 (s), 129.9 (s), 129.8 (s), 129.6 (s), 127.8 (s), 126.1 (s), 125.7 (s), 124.5 (s), 121.8 (s), 116.0 (d, *J* = 22.6 Hz).

[19]F NMR (471 MHz, $CDCl_3$) δ -104.41 (s).

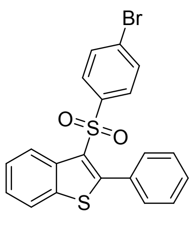
3-((4-chlorophenyl)sulfonyl)-2-phenylbenzo[b]thiophene (3h)



52.2 mg, 68% yield, white solid. [1]H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.53 (m, 3H), 7.50 – 7.38 (m, 6H), 7.28 (d, *J* = 8.5 Hz, 2H).

[13]C NMR (126 MHz, $CDCl_3$) δ 153.1 (s), 140.7 (s), 139.7 (s), 138.2 (s), 136.0 (s), 131.4 (s), 130.5 (s), 129.7 (s), 129.1 (s), 128.5 (s), 127.8 (s), 126.2 (s), 125.9 (s), 124.5 (s), 121.9 (s).

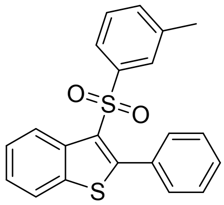
3-((4-bromophenyl)sulfonyl)-2-phenylbenzo[b]thiophene (3i)



65.2 mg, 76% yield, white solid. [1]H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.50 – 7.43 (m, 6H), 7.43 – 7.39 (m, 4H).

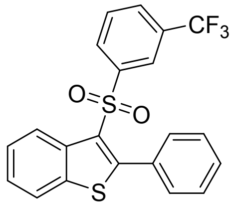
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2 (s), 141.3 (s), 138.2 (s), 136.0 (s), 132.0 (s), 131.4 (s), 130.5 (s), 129.7 (s), 128.5 (s), 128.1 (s), 127.8 (s), 126.2 (s), 125.8 (s), 124.5 (s), 121.9 (s).

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



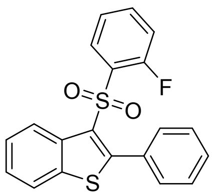
45.9 mg, 63% yield, white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.48 – 7.44 (m, 3H), 7.42 – 7.38 (m, 5H), 7.25 – 7.18 (m, 2H), 2.27 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6 (s), 142.1 (s), 138.9 (s), 138.1 (s), 136.2 (s), 133.8 (s), 131.6 (s), 130.6 (s), 130.3 (s), 129.5 (s), 128.7 (s), 127.6 (s), 127.4 (s), 125.9 (s), 125.6 (s), 124.7 (s), 124.2 (s), 121.7 (s), 21.2 (s).

2-phenyl-3-((3-(trifluoromethyl)phenyl)sulfonyl)benzo[b]thiophene (3k)



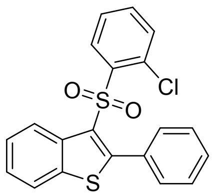
70.2 mg, 84% yield, white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.72 – 8.65 (m, 1H), 7.85 – 7.75 (m, 3H), 7.68 (d, J = 7.7 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.51 – 7.43 (m, 3H), 7.41 – 7.32 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6 (s), 143.4 (s), 138.2 (s), 136.0 (s), 131.3 (d, J = 33.6 Hz), 131.2 (s), 130.4 (s), 130.3 (s), 129.9 (s), 129.7 (s), 129.4 (s), 127.9 (s), 126.3 (s), 125.2 (d, J = 178.1 Hz), 124.2 (q, J = 3.9 Hz), 121.9 (s).
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.73 (s).
HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{14}F_3O_2S_2^+$, 419.0382; Found: 419.0388

3-((2-fluorophenyl)sulfonyl)-2-phenylbenzo[b]thiophene (3l)



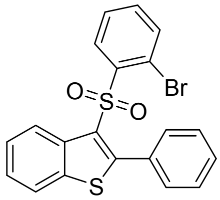
50.8 mg, 69% yield, white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.53 – 7.30 (m,8H), 7.11 – 7.04 (m, 1H), 7.01 – 6.94 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.53 (s), 158.49 (s), 153.49 (s), 137.9 (s), 136.1 (s), 135.5 (s), 135.4 (s), 131.3 (s), 130.5 (s), 129.5 (s), 129.5 (s), 129.2 (s), 127.6 (s), 125.9 (s), 125.6 (s), 124.5 (s), 123.9 (d, J = 3.8 Hz), 121.7 (s), 116.9 (s), 116.8 (s).
^{19}F NMR (471 MHz, $CDCl_3$) δ -108.47 (s).

3-((2-chlorophenyl)sulfonyl)-2-phenylbenzo[b]thiophene (3m)



56.7 mg, 77% yield, white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.55 – 7.49 (m, 1H), 7.48 – 7.42 (m, 1H), 7.34 – 7.25 (m, 5H), 7.25 – 7.19 (m, 2H), 7.09 – 7.02 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2 (s), 139.2 (s), 137.8 (s), 136.6 (s), 133.8 (s), 133.0 (s), 131.2 (s), 131.1 (s), 130.4 (s), 130.4 (s), 129.4 (s), 128.9 (s), 127.7 (s), 126.3 (s), 125.9 (s), 125.5 (s), 124.9 (s), 121.8 (s). HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{14}NaClO_2S_2^+$, 406.9938; Found: 406.9942.

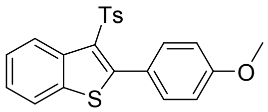
3-((2-bromophenyl)sulfonyl)-2-phenylbenzo[b]thiophene (3n)



59.9 mg, 70% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.56 – 7.52 (m, 1H), 7.49 – 7.43 (m, 2H), 7.32 – 7.23 (m, 3H), 7.21 – 7.16 (m, 3H), 7.08 – 7.03 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7 (s), 140.7 (s), 137.8 (s), 137.3 (s), 134.6 (s), 133.6 (s), 131.0 (s), 130.8 (s), 130.3 (s), 129.4 (s), 128.8 (s), 127.7 (s), 126.8 (s), 125.9 (s), 125.5 (s), 125.2 (s), 121.7 (s), 121.1 (s).

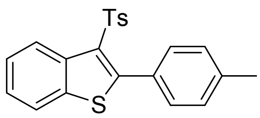
2-(4-methoxyphenyl)-3-tosylbenzo[b]thiophene (3o)



59.1 mg, 75% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.59 – 7.48 (m, 3H), 7.39 (d, J = 7.6 Hz, 3H), 7.13 (d, J = 7.1 Hz, 2H), 6.94 (d, *J* = 7.6 Hz, 2H), 3.88 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6 (s), 152.9 (s), 143.8 (s), 139.6 (s), 138.0 (s), 136.3 (s), 131.9 (s), 129.8 (s), 129.4 (s), 126.9 (s), 125.8 (s), 125.4 (s), 124.6 (s), 123.7 (s), 121.7 (s), 113.2 (s), 77.3 (s), 77.1 (s), 76.8 (s), 55.4 (s), 21.5 (s).

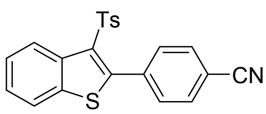
2-(p-tolyl)-3-tosylbenzo[b]thiophene (3p)



66.5 mg, 88% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.45 – 7.39 (m, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9 (s), 143.8 (s), 139.6 (s), 138.1 (s), 136.2 (s), 130.4 (s), 129.9 (s), 129.4 (s), 128.8 (s), 128.4 (s), 127.0 (s), 125.9 (s), 125.5 (s), 124.6 (s), 121.7 (s), 21.5 (s).

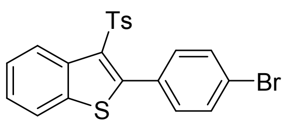
4-(3-tosylbenzo[b]thiophen-2-yl)benzonitrile (3q)



53.7 mg, 69% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.61 – 7.52 (m, 5H), 7.50 – 7.42 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3 (s), 144.5 (s), 139.0 (s), 138.4 (s), 136.7 (s), 135.8 (s), 131.4 (s), 131.3 (s), 129.7 (s), 126.9 (s), 126.3 (s), 126.2 (s), 124.7 (s), 121.9 (s), 118.3 (s), 113.3 (s), 21.6 (s).

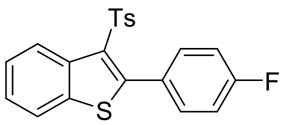
2-(4-bromophenyl)-3-tosylbenzo[b]thiophene (3r)



60.2 mg, 68% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.51 (m, 5H), 7.47 – 7.41 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.80 (s), 144.2 (s), 139.3 (s), 138.2 (s), 136.0 (s), 132.1 (s), 130.9 (s), 130.7 (s), 130.7 (s), 129.6 (s), 127.0 (s), 126.1 (s), 125.8 (s), 124.7 (s), 124.1 (s), 121.8 (s), 21.6 (s).

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

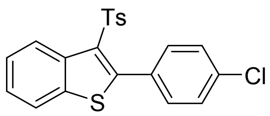


64.9 mg, 85% yield, white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.60 – 7.48 (m, 3H), 7.43 (d, J = 6.4 Hz, 3H), 7.19 – 7.05 (m, 4H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.52 (d, J = 250.0 Hz), 151.2 (s), 144.1 (s), 139.4 (s), 138.1 (s), 136.1 (s), 132.5 (d, J = 8.5 Hz), 130.6 (s), 129.51 (s), 127.6 (s), 127.0 (s), 126.1 (s), 125.7 (s), 124.7 (s), 121.778 (s), 114.9 (d, J = 21.9 Hz), 21.6 (s).

^{19}F NMR (471 MHz, $CDCl_3$) δ -111.19 (s).

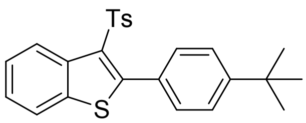
2-(4-chlorophenyl)-3-tosylbenzo[b]thiophene (3t)



63.7 mg, 80% yield, white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.62 – 7.50 (m, 3H), 7.48 – 7.35 (m, 5H), 7.16 (d, J = 7.6 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9 (s), 144.2 (s), 139.3 (s), 138.2 (s), 136.0 (s), 135.8 (s), 131.8 (s), 130.7 (s), 130.2 (s), 129.6 (s), 128.0 (s), 127.0 (s), 126.1 (s), 125.8 (s), 124.6 (s), 121.8 (s), 21.6 (s).

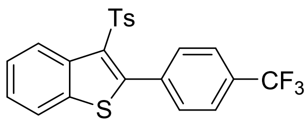
2-(4-(tert-butyl)phenyl)-3-tosylbenzo[b]thiophene (3u)



72.2 mg, 86% yield, white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.52 (d, J = 7.7 Hz, 3H), 7.45 – 7.33 (m, 5H), 7.09 (d, J = 7.8 Hz, 2H), 2.32 (s, 3H), 1.39 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8 (s), 152.7 (s), 143.7 (s), 139.4 (s), 138.1 (s), 136.4 (s), 130.3 (s), 130.1 (s), 129.3 (s), 128.7 (s), 127.1 (s), 125.8 (s), 125.4 (s), 124.7 (s), 124.6 (s), 121.7 (s), 34.8 (s), 31.4 (s), 21.5 (s). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{25}O_2S_2^+$, 421.1290; Found: 421.1294.

3-tosyl-2-(4-(trifluoromethyl)phenyl)benzo[b]thiophene (3v)

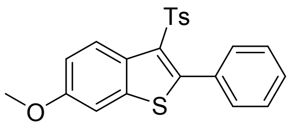


71.7 mg, 83% yield, white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.66 – 8.57 (m, 1H), 7.82 (d, J = 7.3 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.60 – 7.52 (m, 5H), 7.47 (d, J = 6.7 Hz, 1H), 7.15 (d, J = 6.8 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0 (s), 144.3 (s), 139.1 (s), 138.3 (s), 135.9 (s), 135.5 (s), 131.8 (s), 131.6 (s), 131.3 (d, J = 7.8 Hz), 131.0 (s), 129.6 (s), 127.0 (s), 126.2 (s), 126.0 (s), 125.0 (s), 124.6 (q, J = 8.5 Hz), 121.9 (s), 21.5 (s).

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.68 (s).

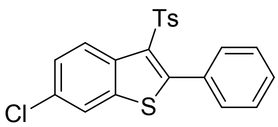
6-methoxy-2-phenyl-3-tosylbenzo[b]thiophene (3w)



72.5 mg, 92% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, J = 9.1 Hz, 1H), 7.53 (d, J = 7.9 Hz, 2H), 7.47 – 7.37 (m, 5H), 7.24 (s, 1H), 7.12 (d, J = 7.2 Hz, 3H), 3.87 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0 (s), 149.7 (s), 143.8 (s), 139.8 (s), 139.5 (s), 131.8 (s), 130.6 (s), 130.0 (s), 129.9 (s), 129.4 (s), 129.3 (s), 127.6 (s), 127.0 (s), 125.4 (s), 115.8 (s), 104.1 (s), 55.7 (s), 21.5 (s).

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

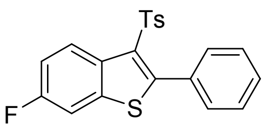


62.9 mg, 79% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 1.7 Hz, 1H), 7.53 – 7.46 (m, 4H), 7.41 (d, J = 4.4 Hz, 4H), 7.13 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8 (s), 144.1 (s), 139.1 (s), 139.1 (s), 134.7 (s), 131.9 (s), 131.4 (s), 130.5 (s), 130.3 (s), 129.7 (s), 129.5 (s), 127.8 (s), 127.0 (s), 126.8 (s), 125.6 (s), 121.3 (s), 21.6 (s).

. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{16}O_2S_2^+$, 399.0275; Found: 399.0275.

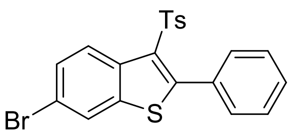
6-fluoro-2-phenyl-3-tosylbenzo[b]thiophene (3y)



60 mg, 78.5% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 – 8.58 (m, 1H), 7.55 – 7.45 (m, 4H), 7.41 (d, J = 4.4 Hz, 4H), 7.30 – 7.27 (m, 1H), 7.13 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (s), 159.8 (s), 152.1 (d, J = 3.5 Hz), 144.1 (s), 139.2 (s), 139.1 (s), 132.6 (s), 131.4 (s), 130.5 (s), 130.1 (s), 129.6 (s), 129.5 (s), 127.7 (s), 127.0 (s), 126.2 (s), 126.1 (s), 115.1 (s), 114.9 (s), 108.0 (s), 107.8 (s), 21.6 (s).

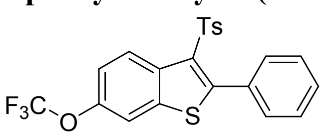
^{19}F NMR (471 MHz, $CDCl_3$) δ -114.86 (s).

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



71.8 mg, 81% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, J = 8.3 Hz, 1H), 7.93 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.54 – 7.35 (m, 8H), 7.12 (d, J = 6.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 152.8 (s), 144.1 (s), 139.5 (s), 139.2 (s), 135.0 (s), 131.2 (s), 130.5 (s), 130.4 (s), 129.7 (s), 129.5 (s), 129.4 (s), 127.8 (s), 127.0 (s), 125.9 (s), 124.3 (s), 119.7 (s), 21.6 (s).

2-phenyl-3-tosyl-6-(trifluoromethyl)benzo[b]thiophene (3aa)

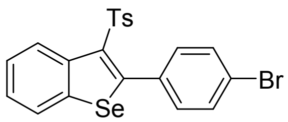


74.4 mg, 83% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 – 8.66 (m, 1H), 7.67 (s, 1H), 7.50 (d, J = 8.3 Hz, 3H), 7.45 – 7.38 (m, 5H), 7.13 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5 (s), 147.0 (s), 144.2 (s), 139.1 (s), 138.8 (s),

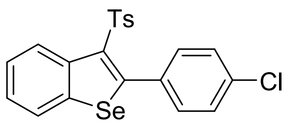
134.7 (s), 131.2 (s), 130.5 (s), 130.3 (s), 129.7 (s), 129.5 (s), 127.8 (s), 127.1 (s), 126.0 (s), 121.5 (s), 119.8 (s), 119.5 (s), 114.0 (s), 21.5 (s).
^{19}F NMR (471 MHz, $CDCl_3$) δ -57.82 (s). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{16}F_3O_3S_2^+$, 449.0487; Found: 449.0491.

2-(4-bromophenyl)-3-tosylbenzo[b]selenophene (5ab)



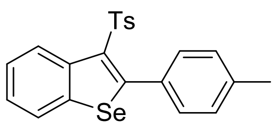
73.5 mg, 75% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.55 – 7.48 (m, 3H), 7.42 – 7.35 (m, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 2.35 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6 (s), 144.1 (s), 140.6 (s), 139.2 (s), 137.7 (s), 133.1 (s), 133.0 (s), 131.3 (s), 130.8 (s), 129.6 (s), 127.0 (s), 126.8 (s), 126.0 (s), 124.8 (s), 123.6 (s), 21.6 (s).

2-(4-chlorophenyl)-3-tosylbenzo[b]selenophene (5ac)



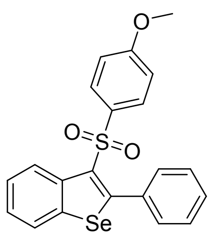
51.6 mg, 58% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 – 8.61 (m, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.46 – 7.34 (m, 3H), 7.16 (d, J = 8.0 Hz, 2H), 7.12 – 7.05 (m, 2H), 2.34 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (s), 162.2 (s), 157.1 (s), 144.1 (s), 140.5 (s), 139.3 (s), 137.8 (s), 133.1 (s), 131.7 (s), 131.6 (s), 129.9 (s), 129.9 (s), 129.6 (s), 127.0 (s), 126.8 (s), 126.0 (s), 125.9 (s), 124.8 (s), 114.8 (s), 114.7 (s), 21.6 (s).

2-(p-tolyl)-3-tosylbenzo[b]selenophene (5ad)



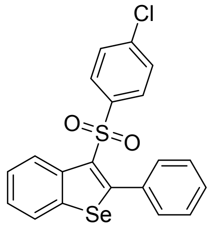
60.0 mg, 67% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.52 – 7.45 (m, 1H), 7.39 – 7.30 (m, 3H), 7.23 – 7.12 (m, 4H), 2.43 (s, 3H), 2.34 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9 (s), 143.8 (s), 140.4 (s), 139.5 (s), 139.2 (s), 138.0 (s), 132.4 (s), 131.0 (s), 129.6 (s), 129.4 (s), 128.3 (s), 127.0 (s), 126.7 (s), 125.8 (s), 125.6 (s), 124.7 (s), 21.5 (s), 21.5 (s).

3-((4-methoxyphenyl)sulfonyl)-2-phenylbenzo[b]selenophene (5ae)



40.2 mg, 47% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.54 – 7.47 (m, 1H), 7.48 – 7.35 (m, 6H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1 (s), 157.9 (s), 140.5 (s), 137.9 (s), 134.06 (s), 133.9 (s), 133.1 (s), 129.7 (s), 129.3 (s), 129.1 (s), 127.6 (s), 126.7 (s), 125.8 (s), 125.7 (s), 124.8 (s), 114.0 (s), 55.6 (s).

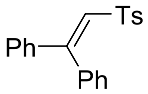
3-((4-chlorophenyl)sulfonyl)-2-phenylbenzo[b]selenophene (5af)



48.3 mg, 56% yield, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 7.0 Hz, 1H), 7.88 (d, *J* = 6.4 Hz, 1H), 7.68 – 7.51 (m, 3H), 7.51 – 7.37 (m, 6H), 7.36 – 7.27 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1 (s), 140.8 (s), 140.6 (s), 139.5 (s), 137.8 (s), 133.7 (s), 132.215 (s), 129.7 (s), 129.3 (s), 129.1 (s), 128.5 (s), 127.7 (s), 126.6 (s), 126.0 (s), 125.9 (s), 124.9 (s).

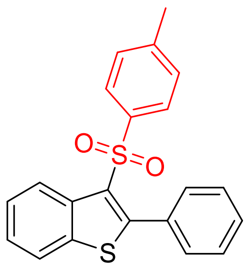
(2-tosylethene-1,1-diyl)dibenzene (6)



93.5 mg, 70% yield , Oily liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 4H), 7.23 – 7.18 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.08 (m, 2H), 7.00 (s, 1H), 2.38 (s, 3H).

13C NMR (126 MHz, CDCl3) δ 152.9 (s), 142.3 (s), 138.2 (s), 136.2 (s), 133.0 (s), 131.6 (s), 130.5 (s), 130.0 (s), 129.5 (s), 128.8(s), 127.7 (s), 127.0 (s), 126.0 (s), 125.7 (s), 124.6 (s), 121.8 (s). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{19}O_2S^+$, 335.1100; Found:335.1103

7. Copies for ^{1}H NMR and ^{13}C NMR spectra



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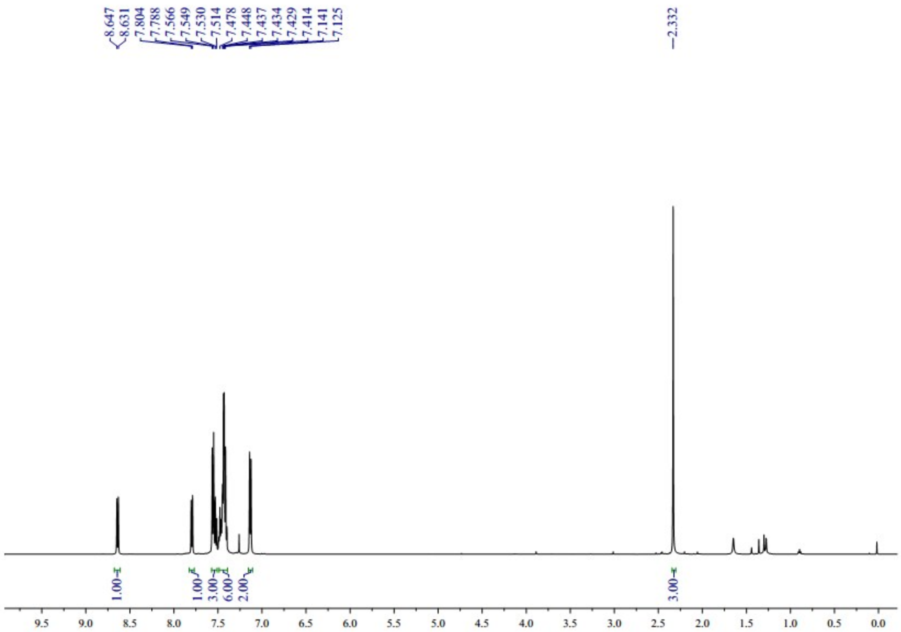

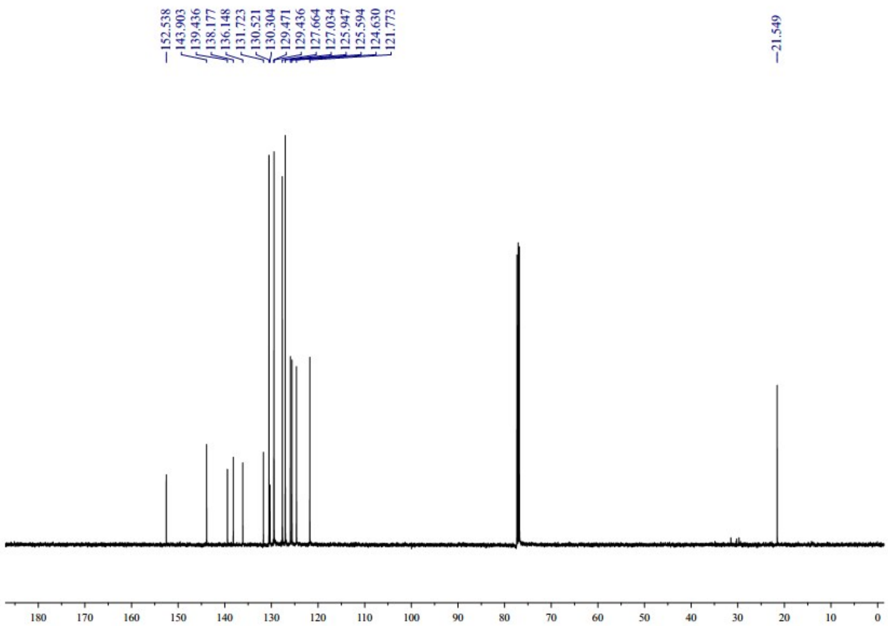

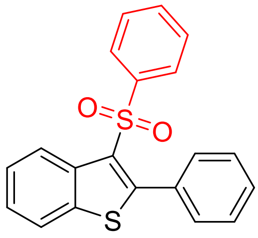

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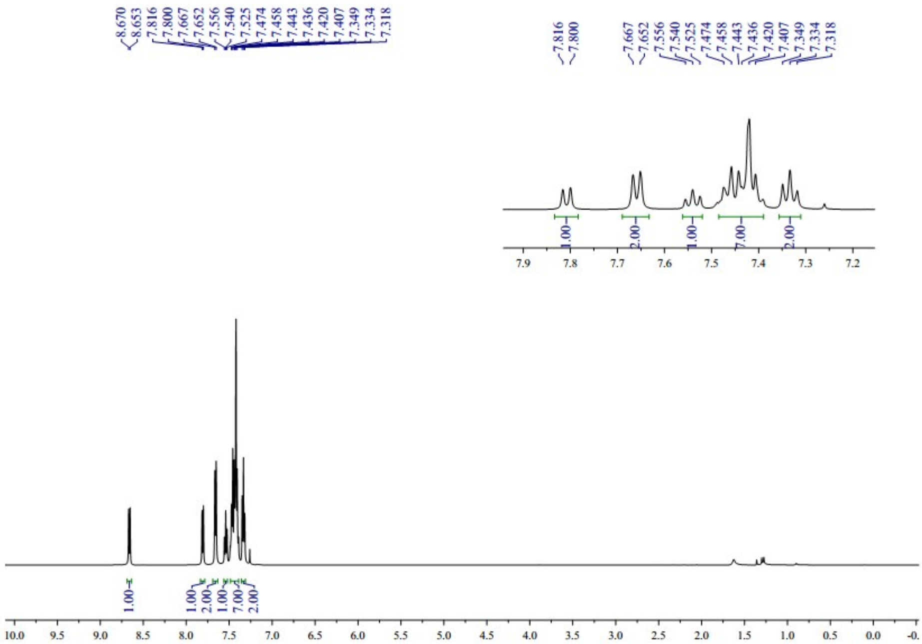
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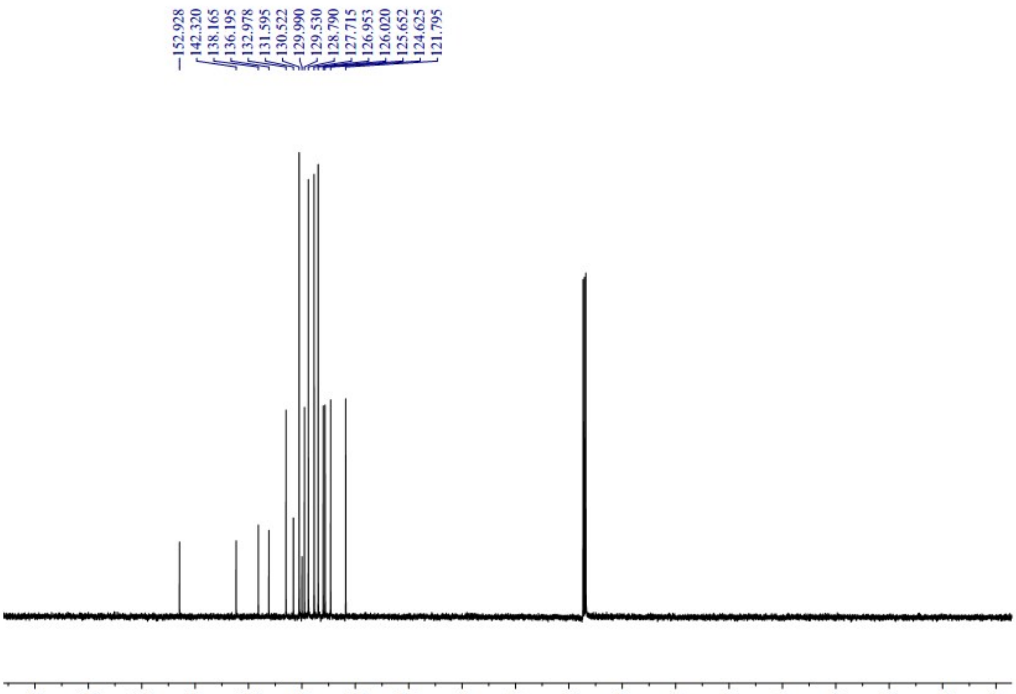
2.00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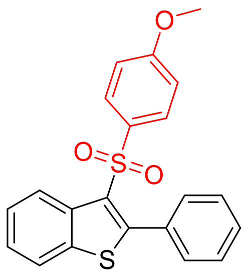
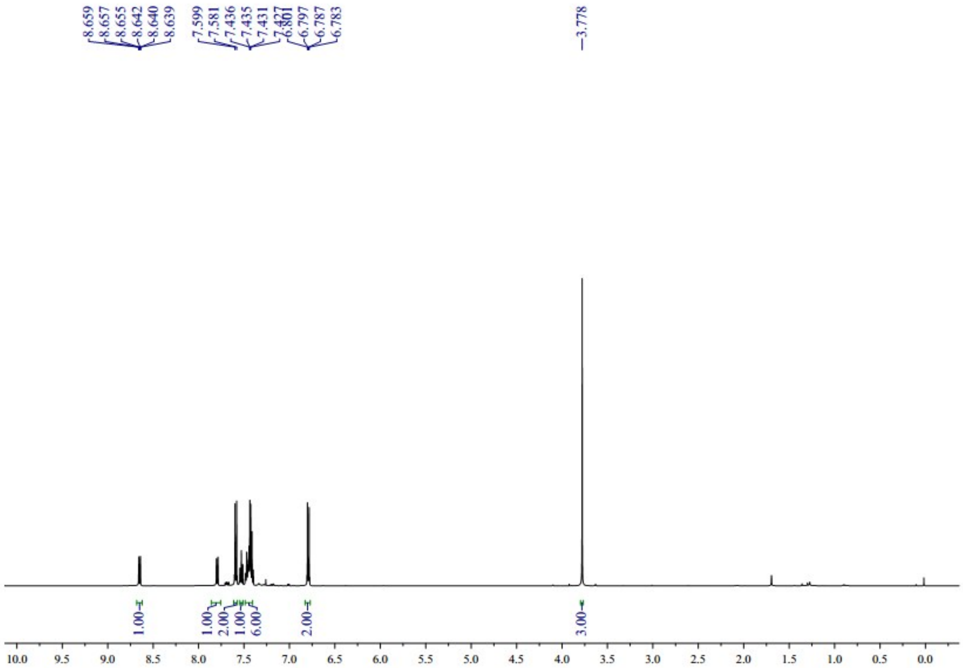

O
O
S
O
S

3c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3.778
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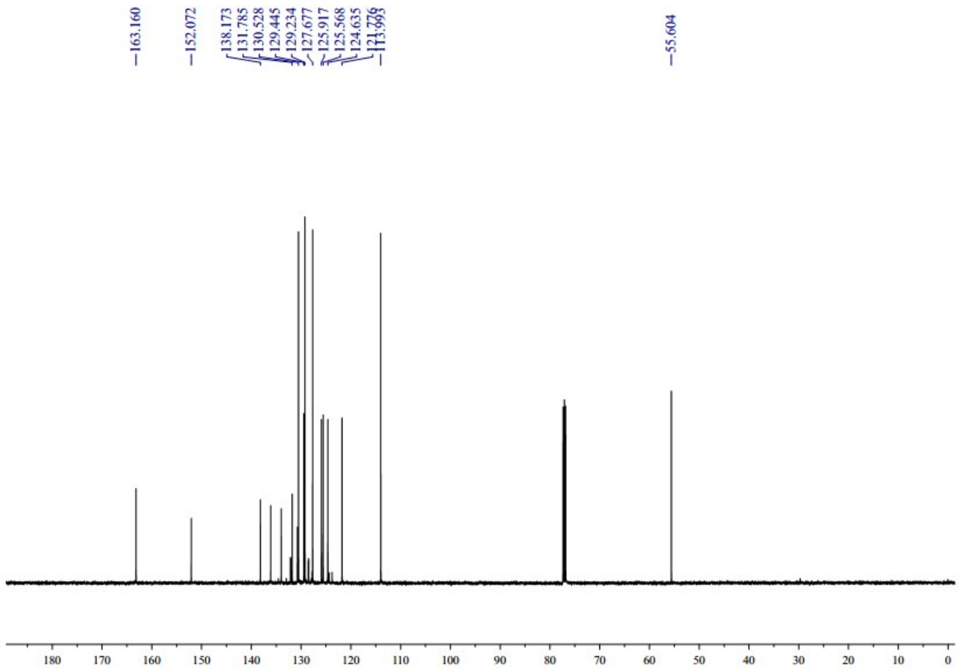
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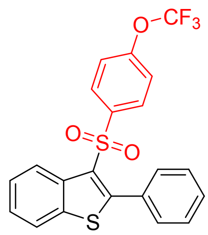

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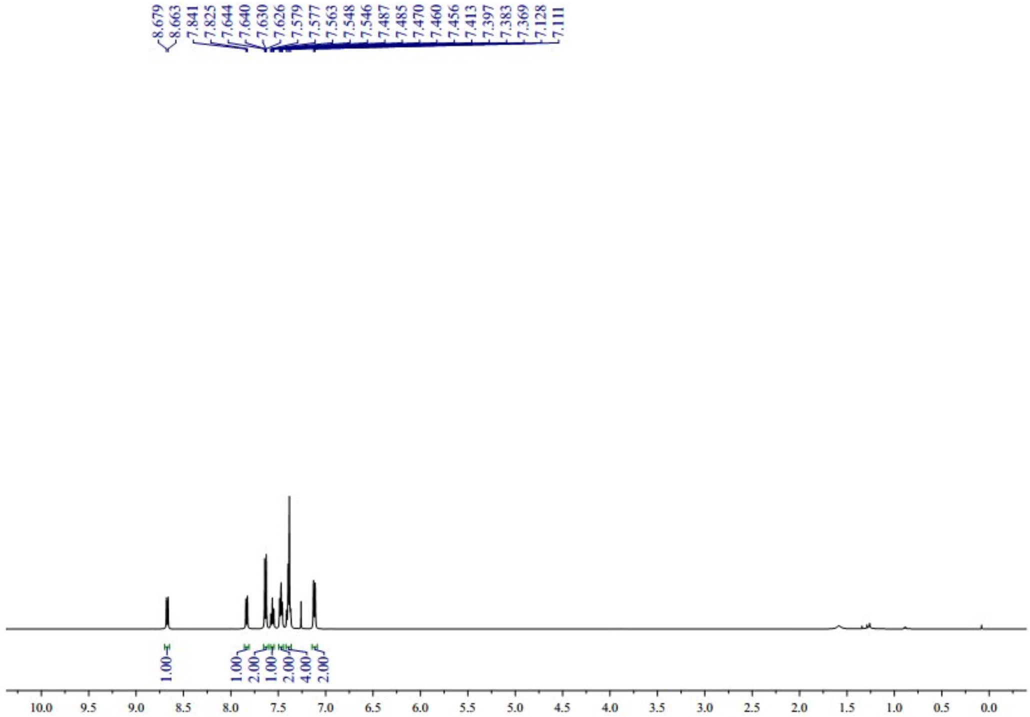
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7.546
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7.485
7.470
7.460
7.456
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7.397
7.383
7.369
7.128
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1.00
2.00
1.00
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4.00
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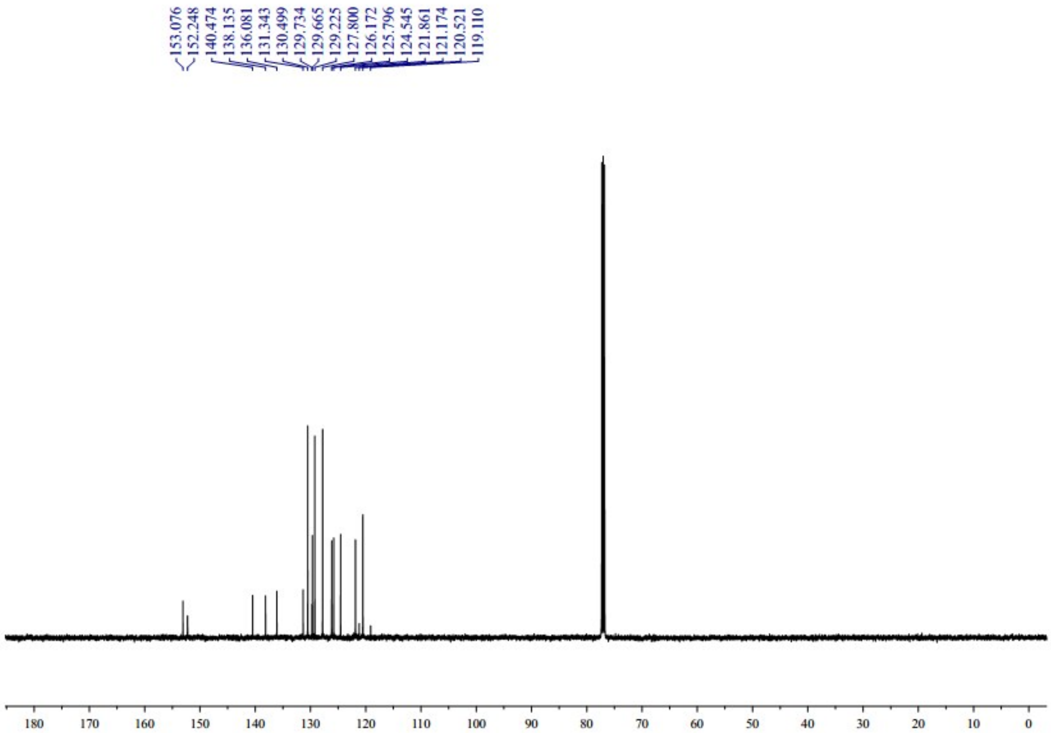
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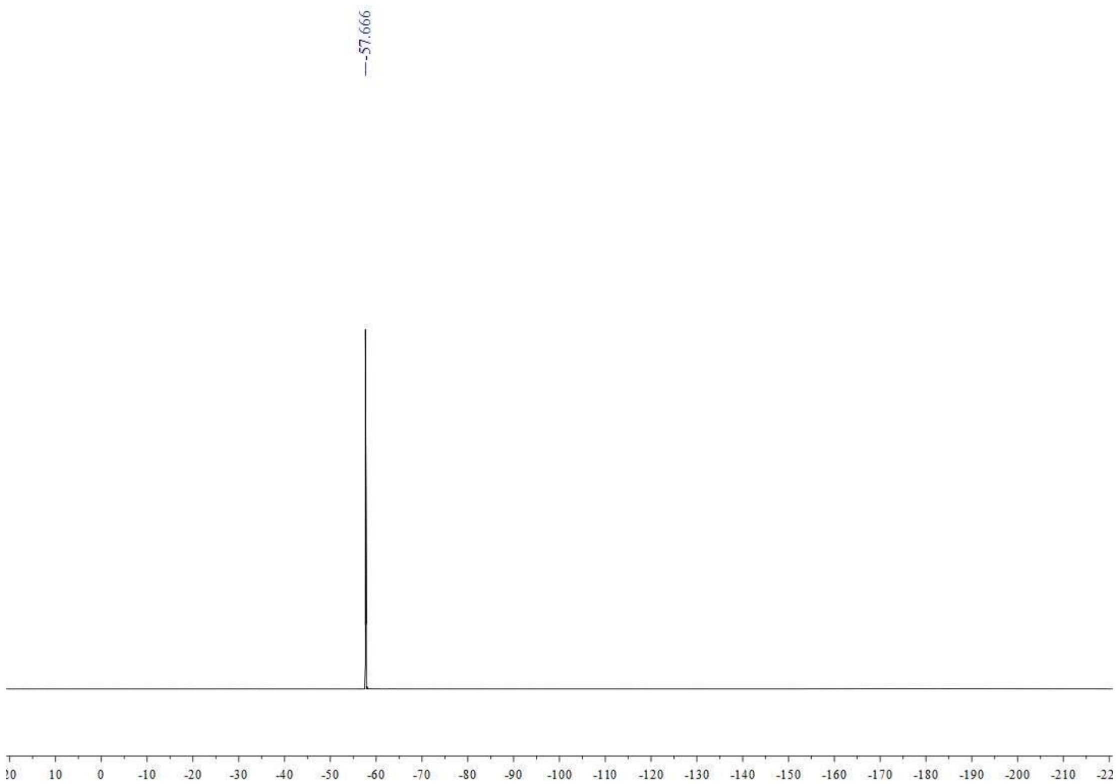
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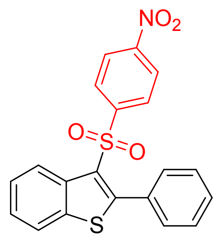
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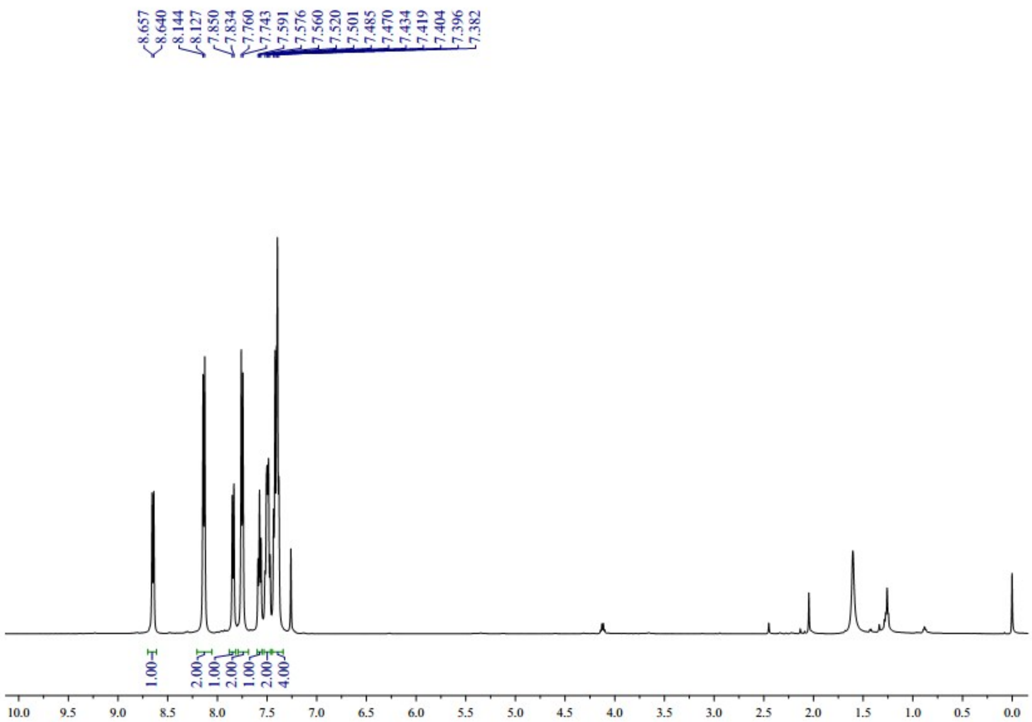
O
S

3e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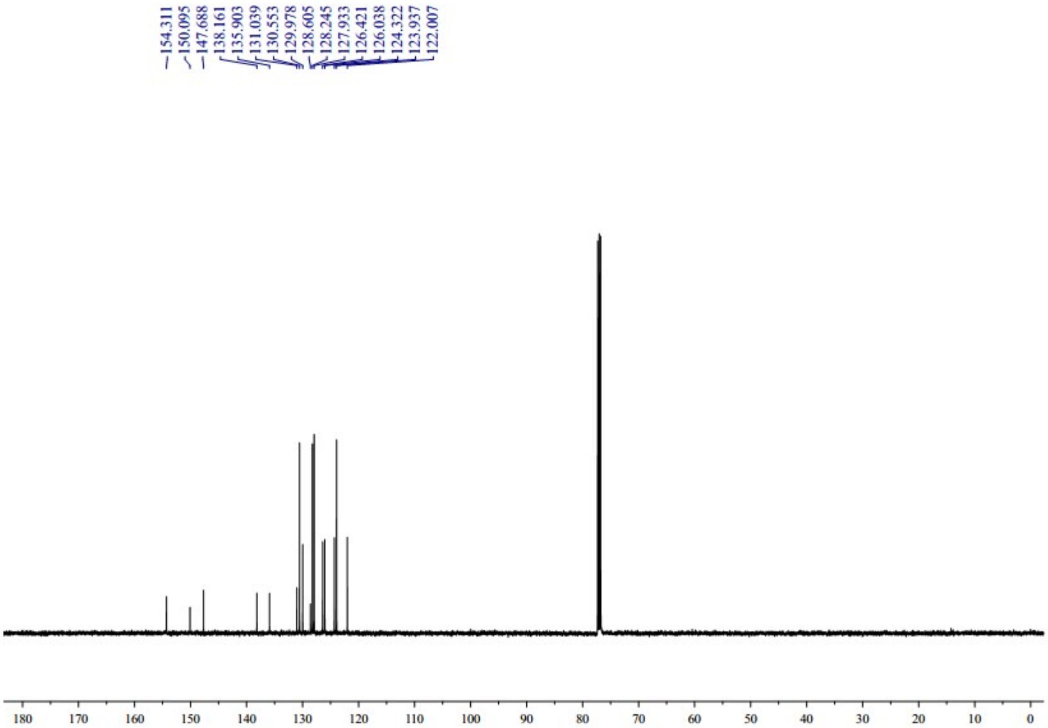
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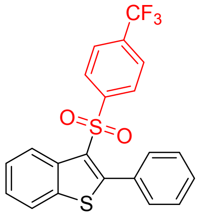
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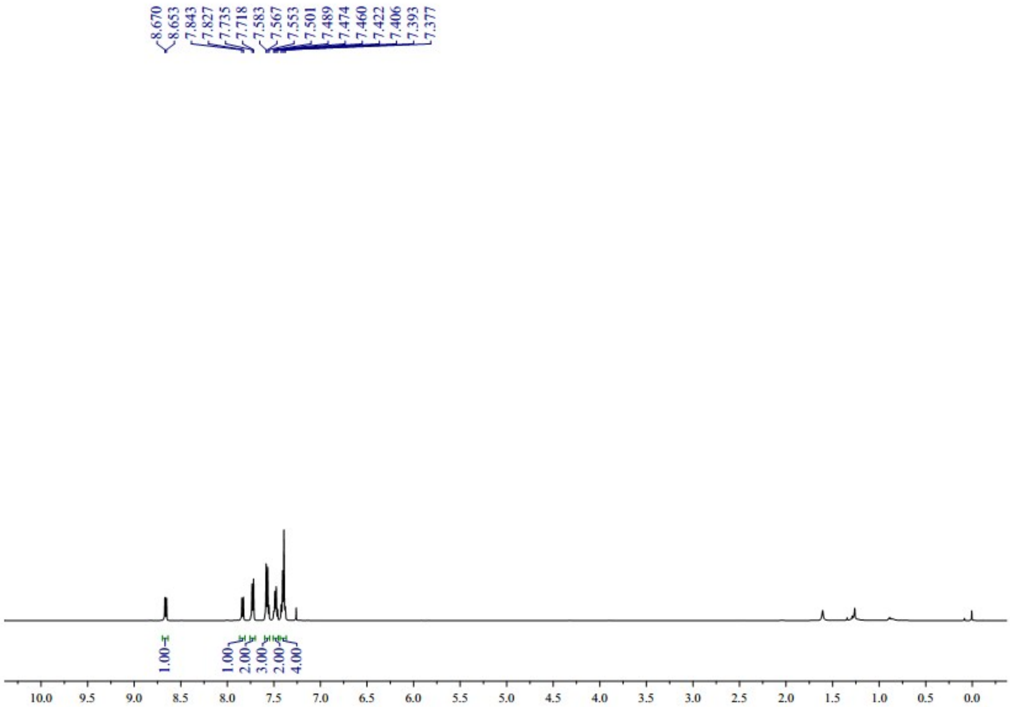
O
S

3f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7.406
7.393
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4.00
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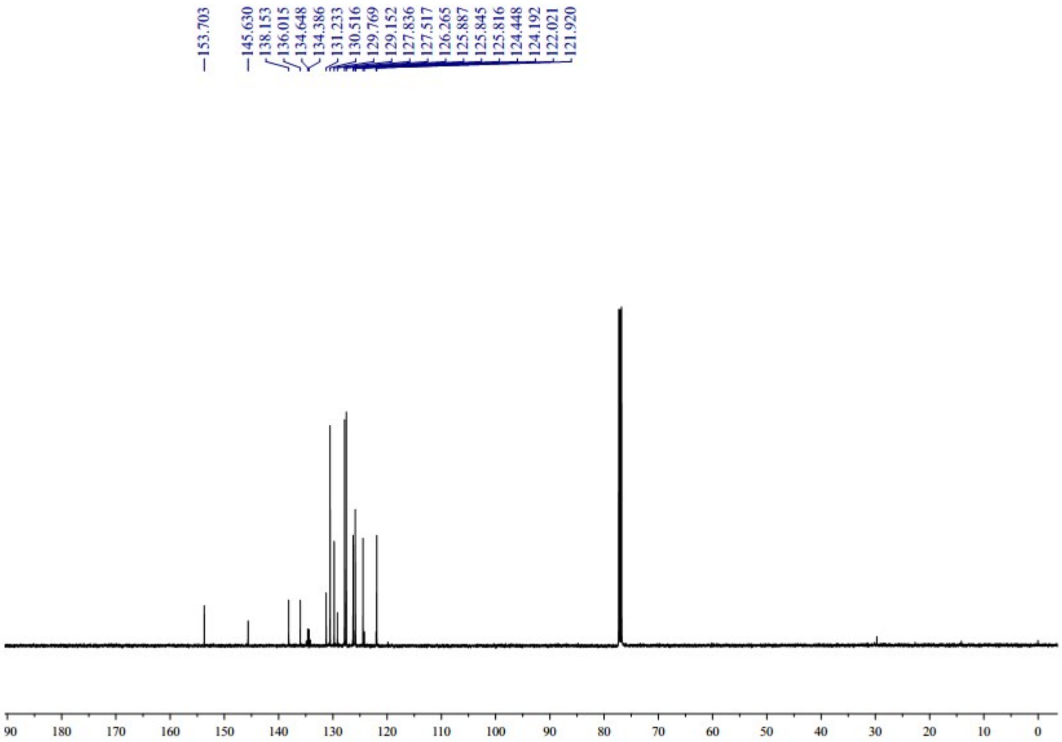
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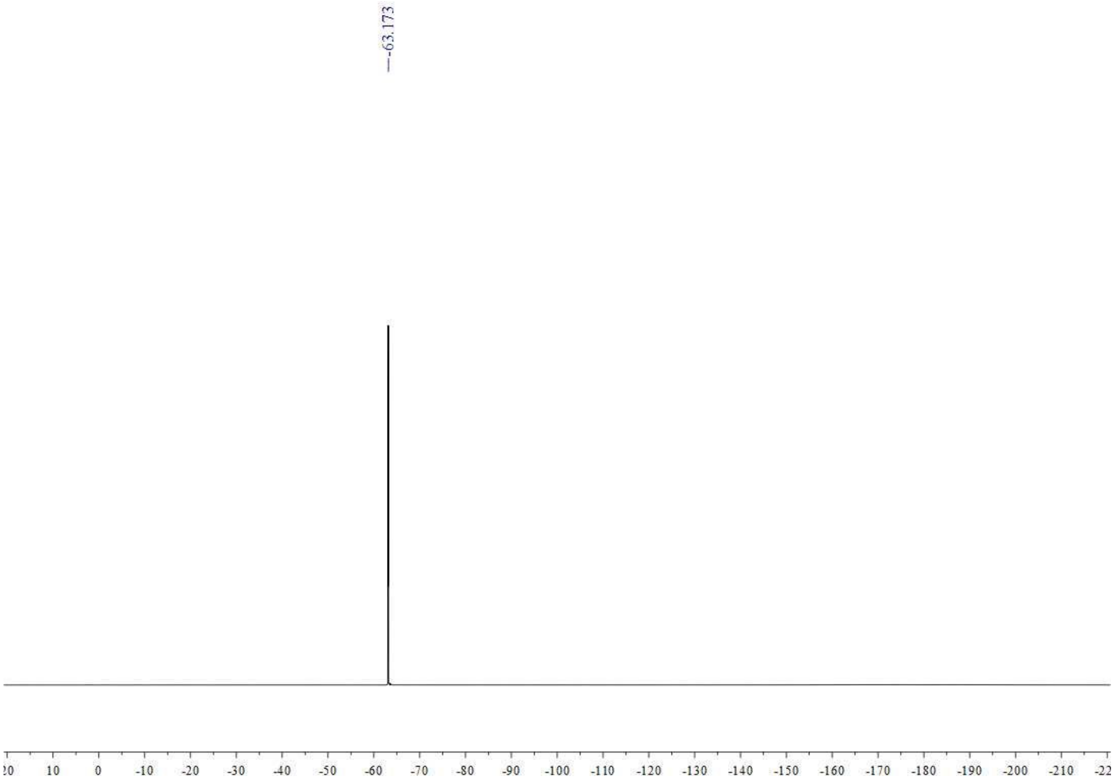
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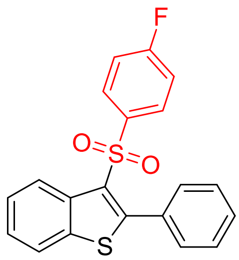
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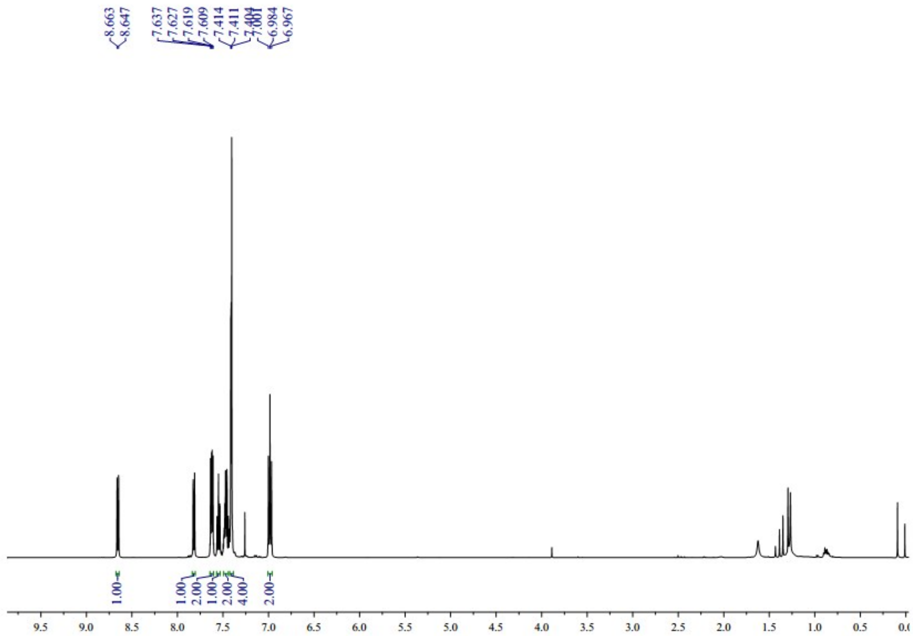
O
S

3g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2.00
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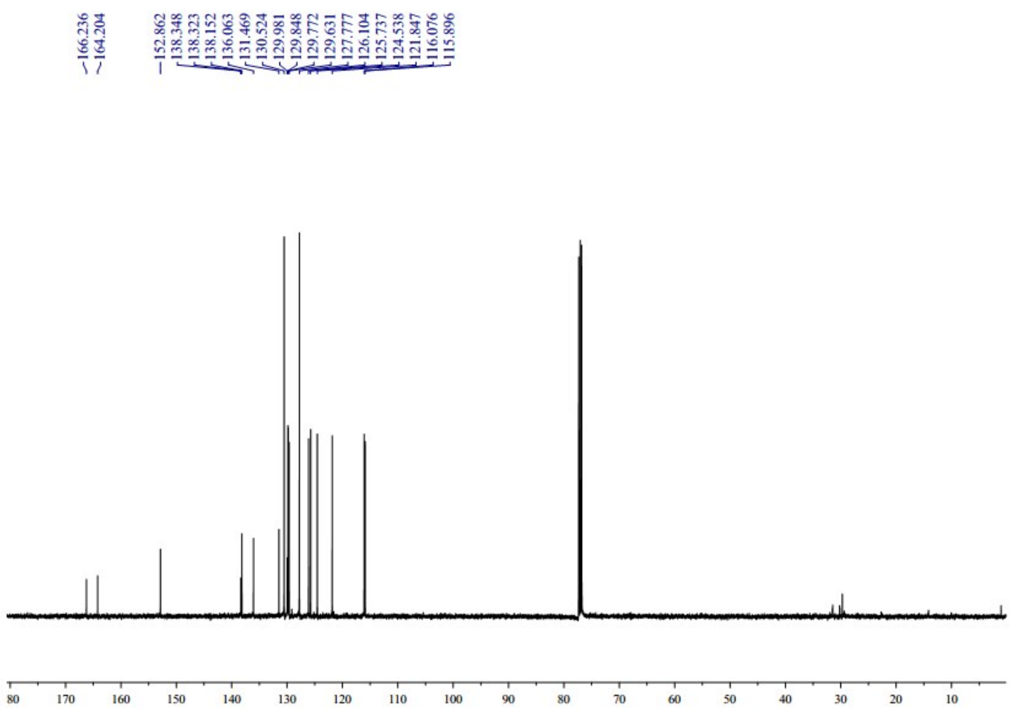
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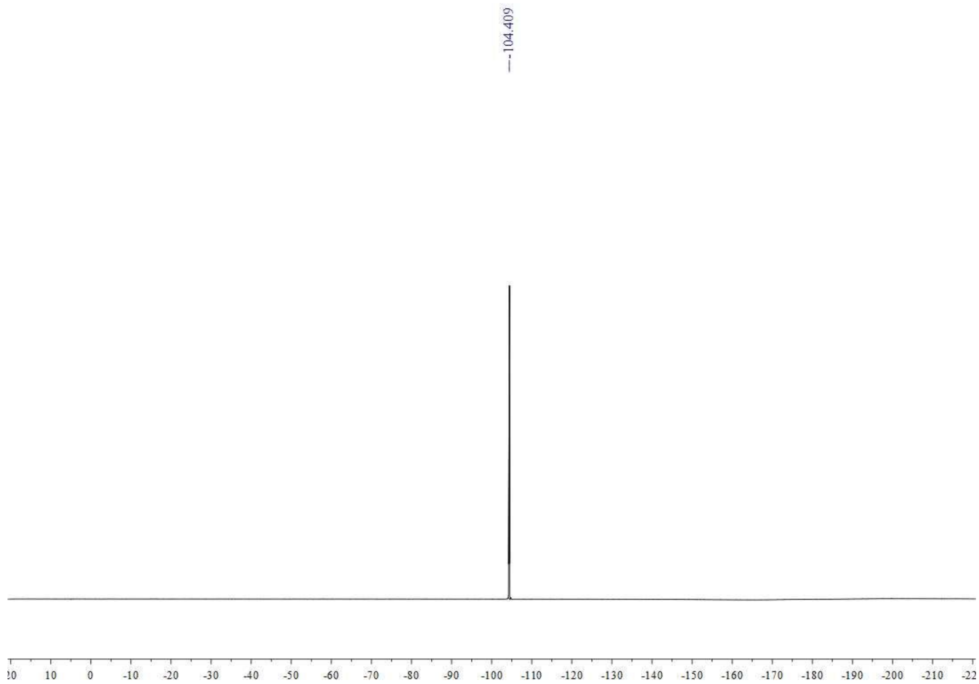
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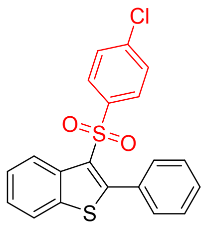

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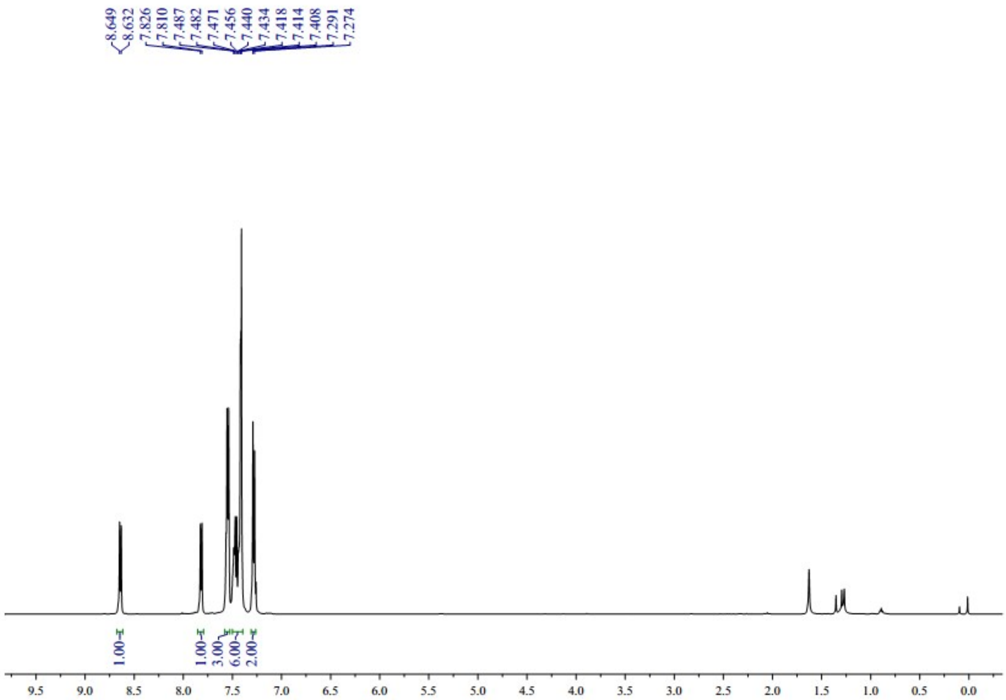
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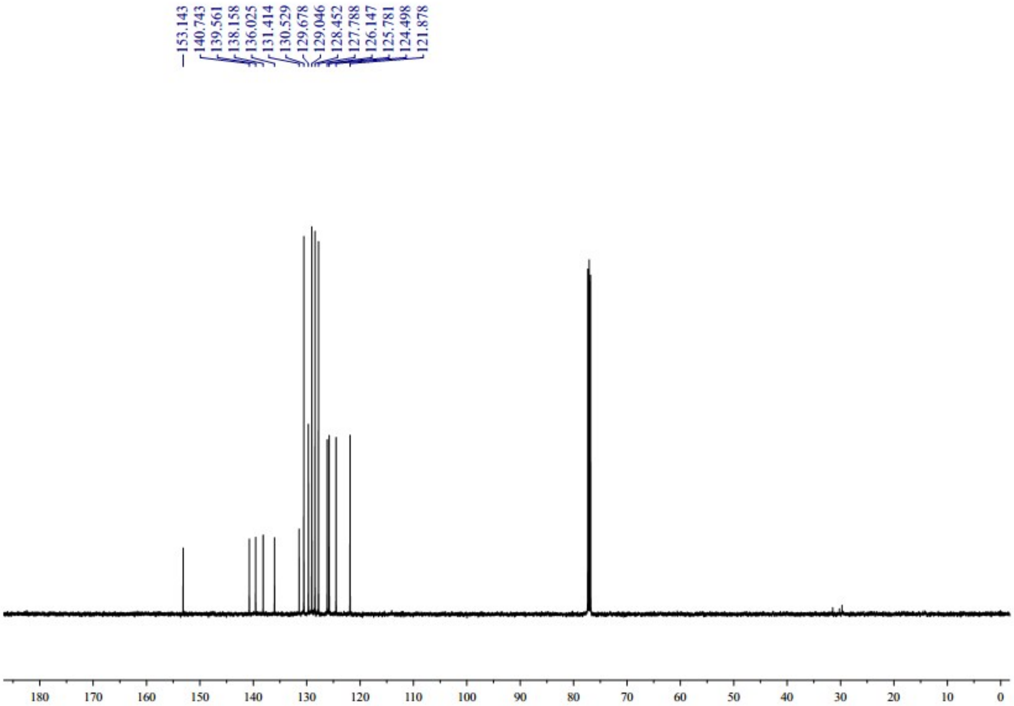
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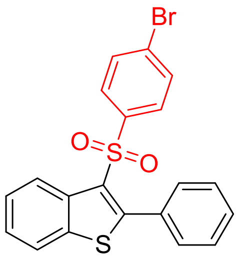
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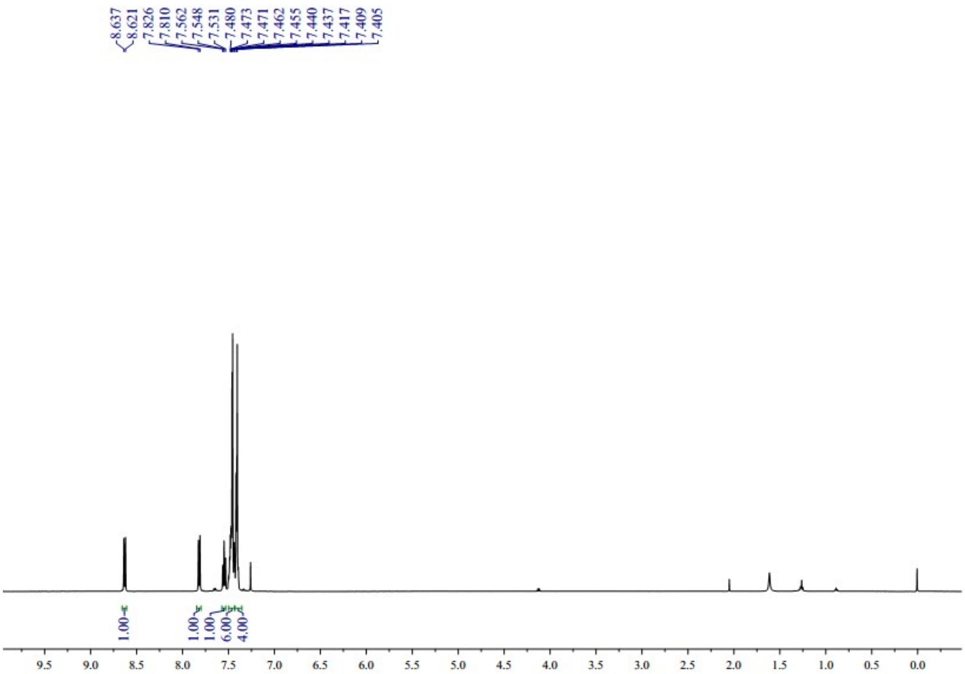
S
O
S

3i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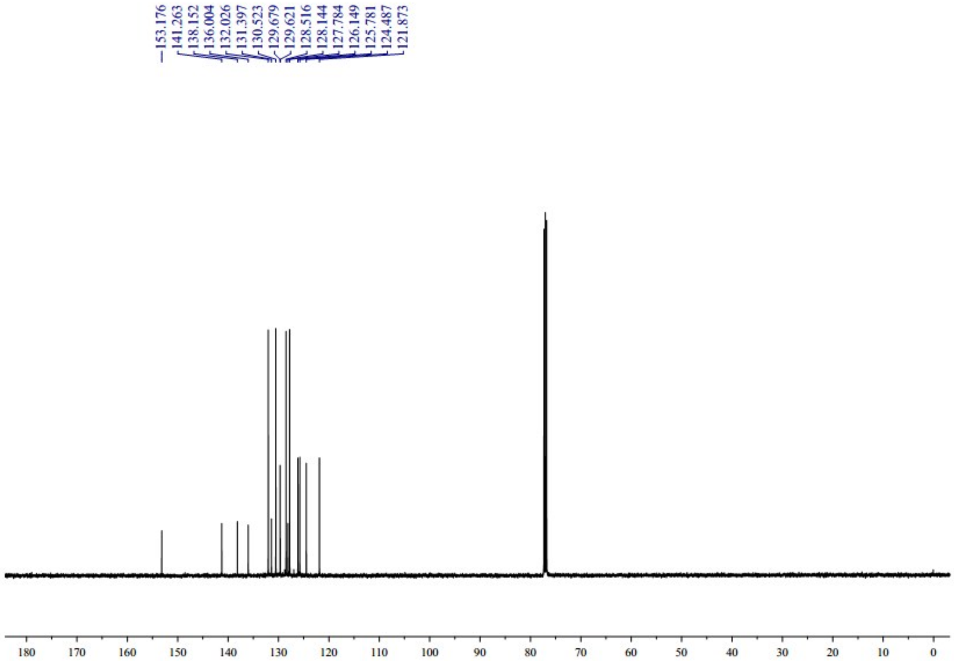
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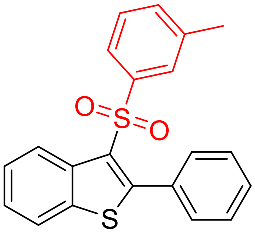
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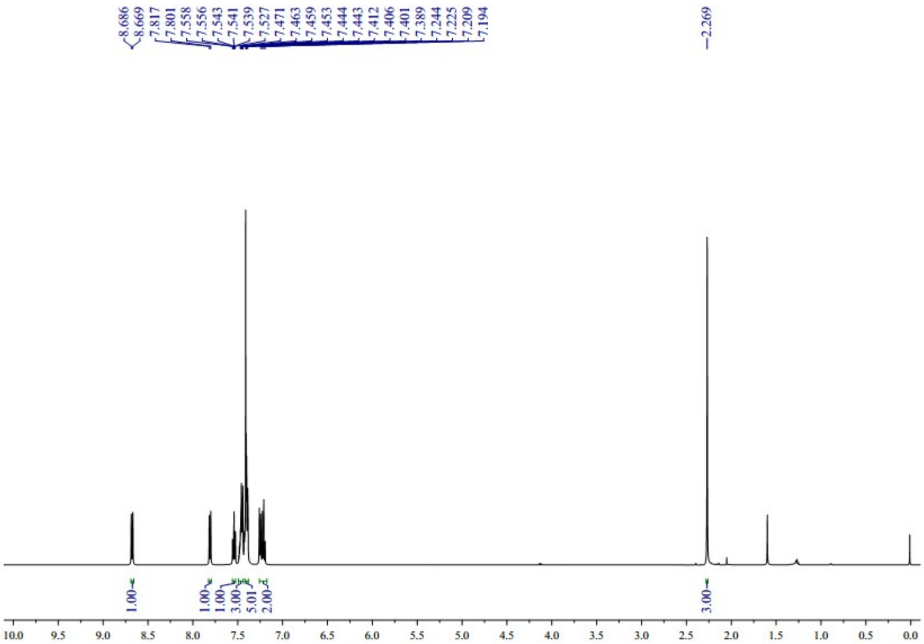
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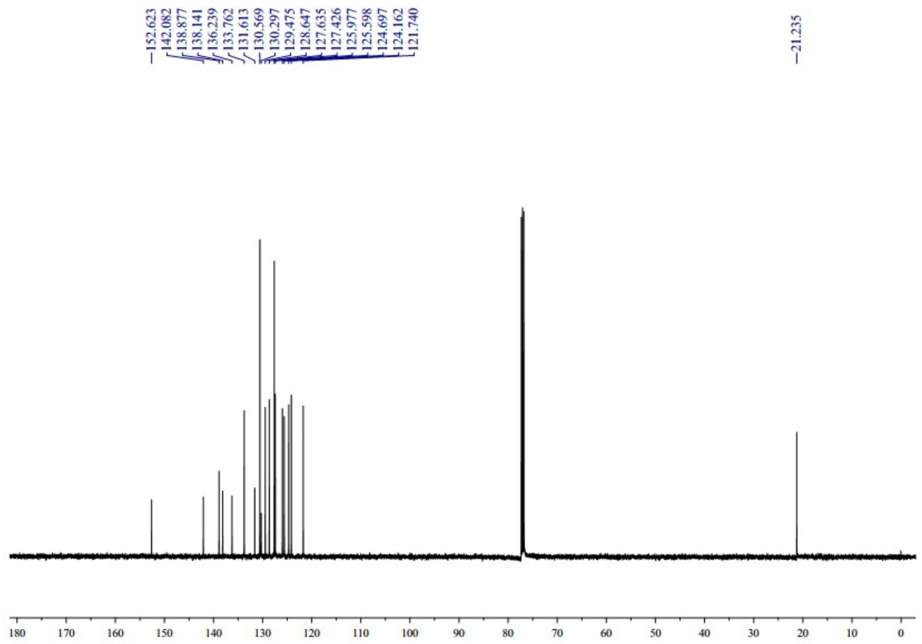
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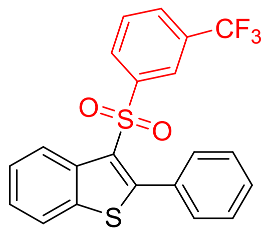
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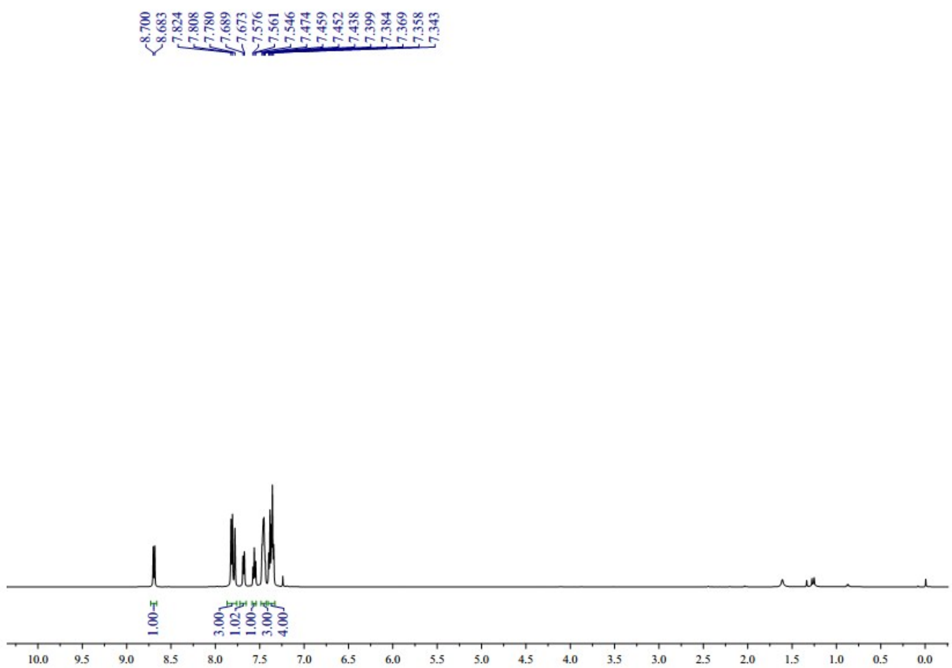
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1.02
1.00
3.00
4.00
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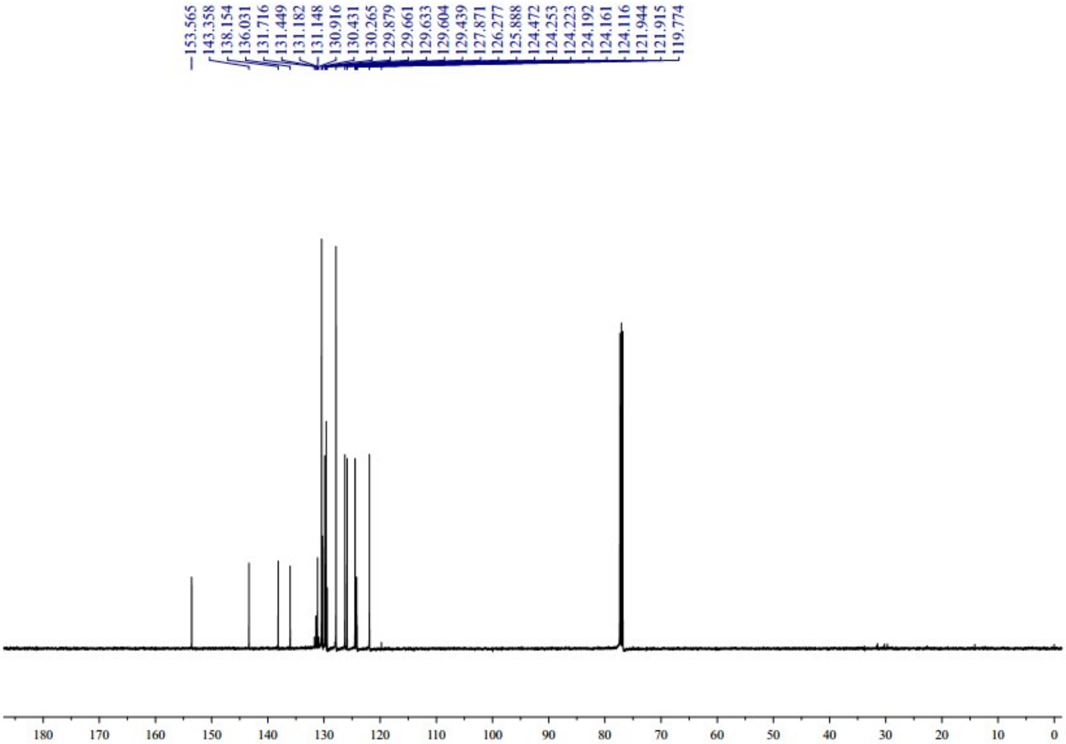
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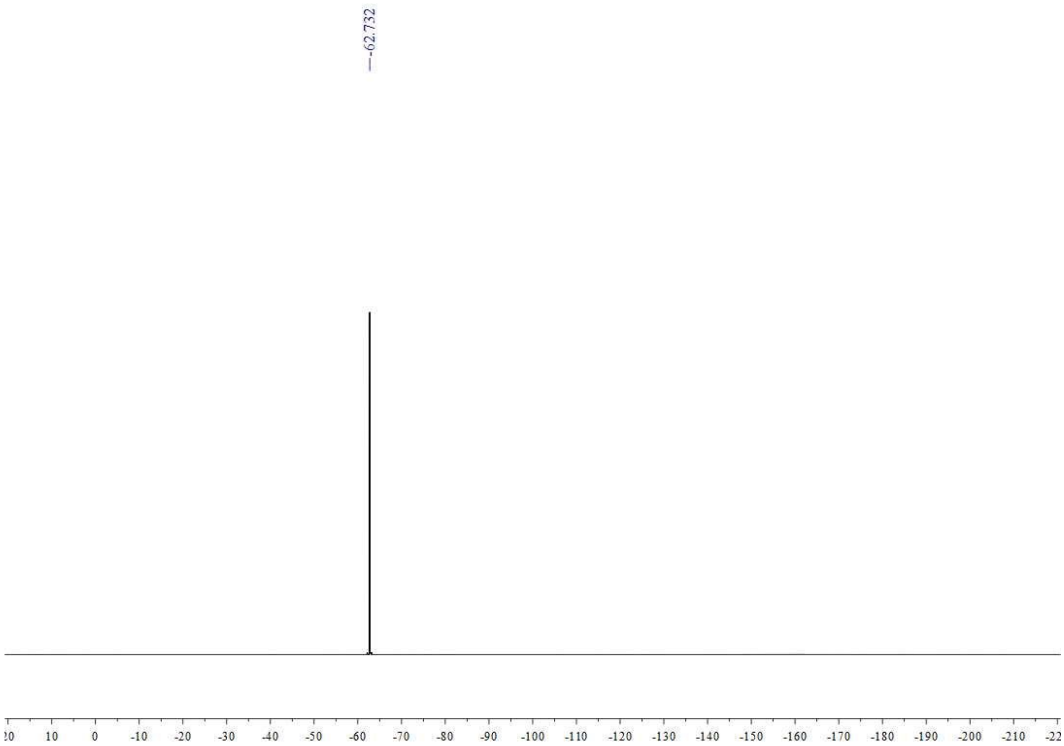
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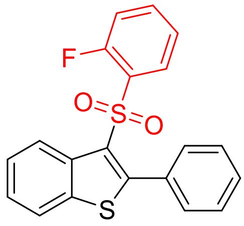
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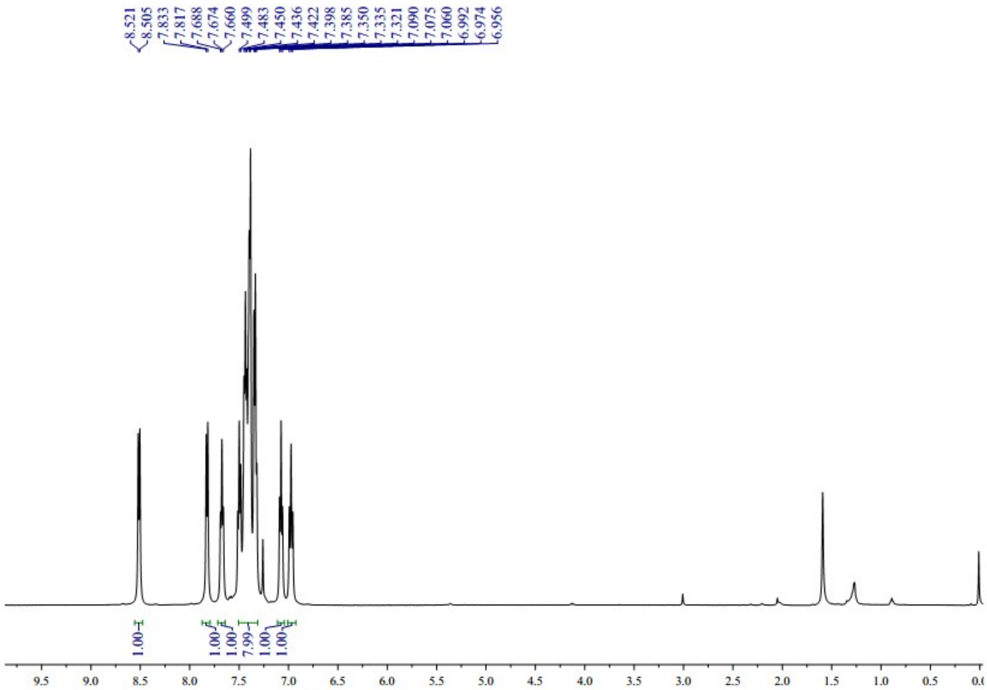
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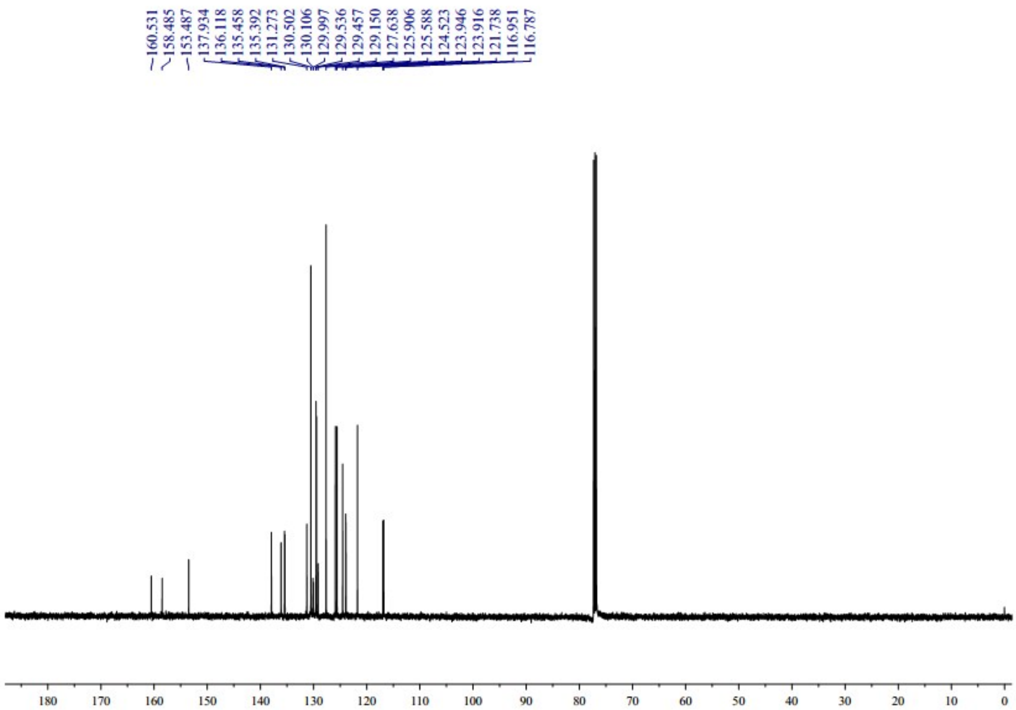
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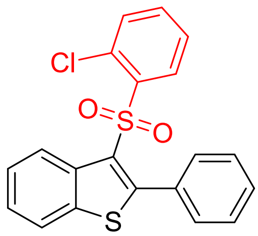

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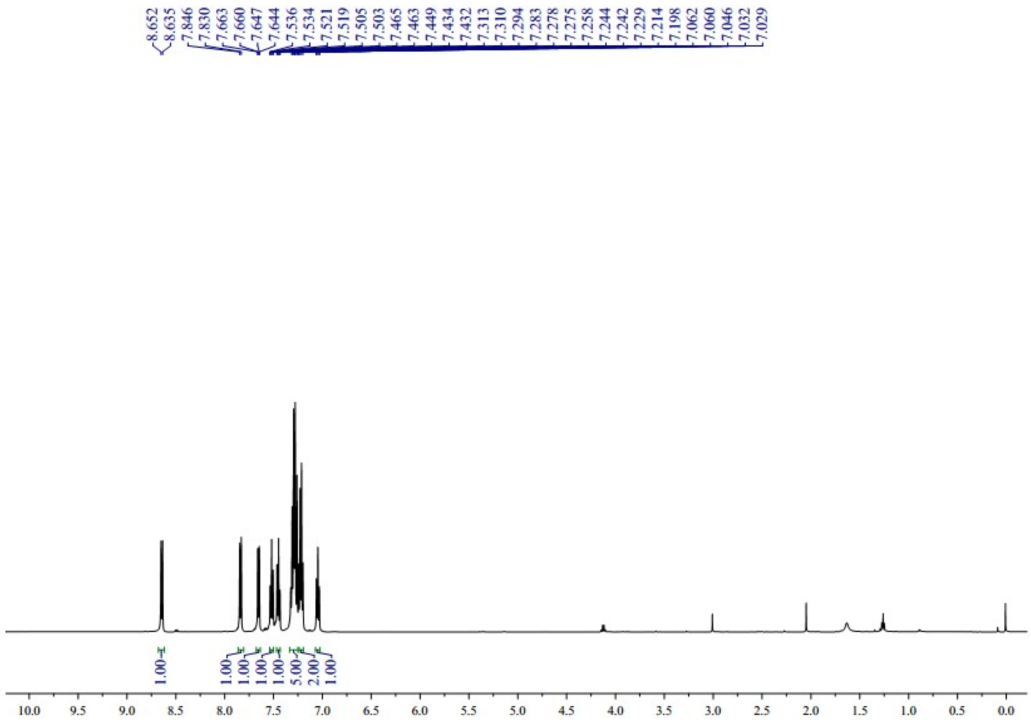

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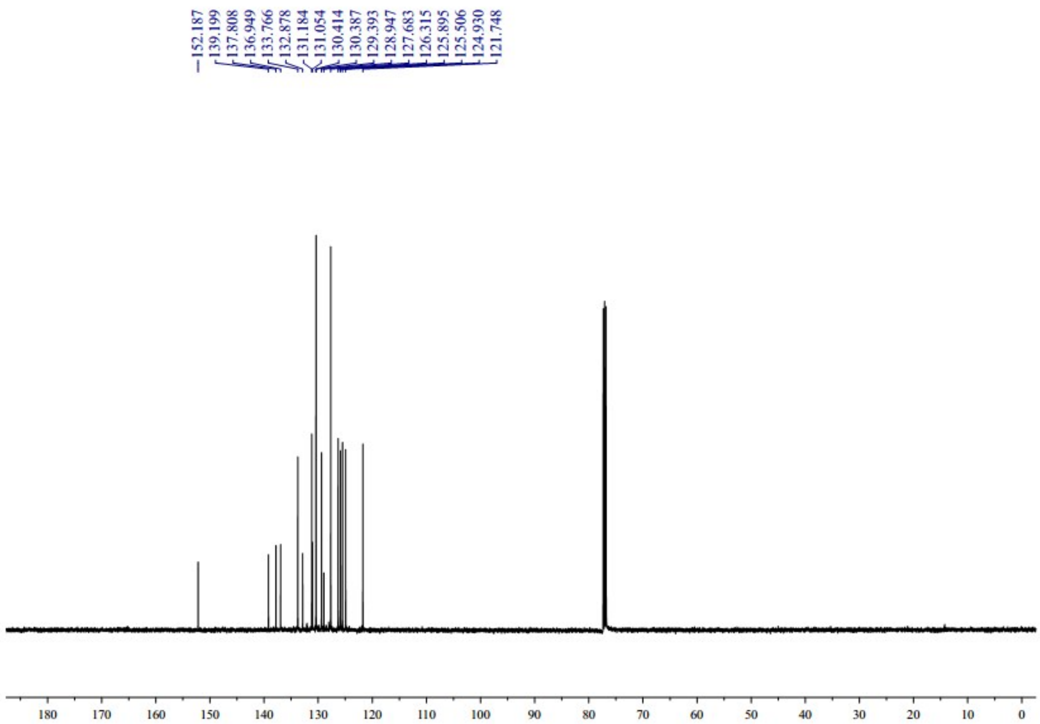

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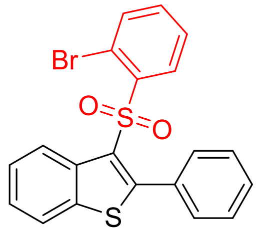
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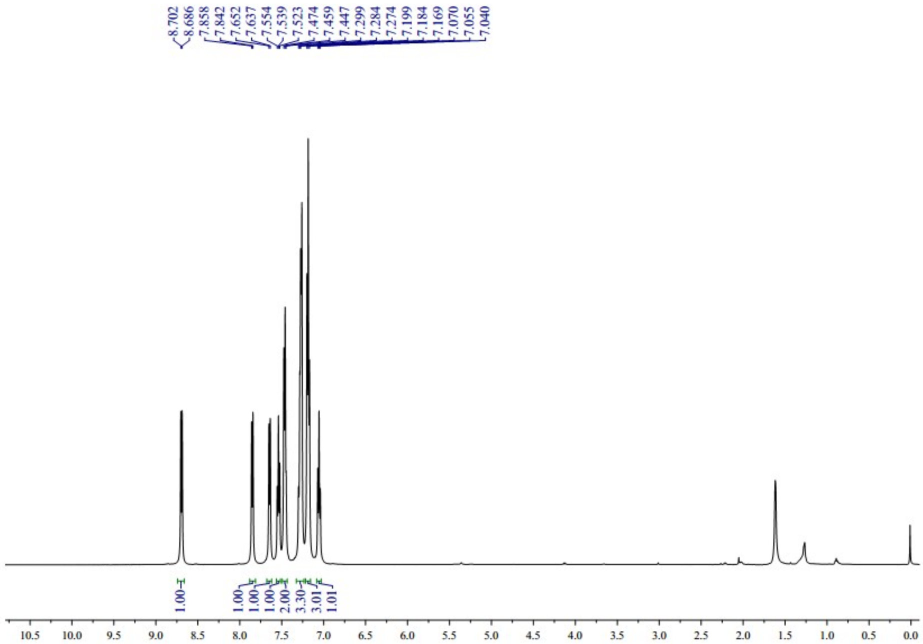
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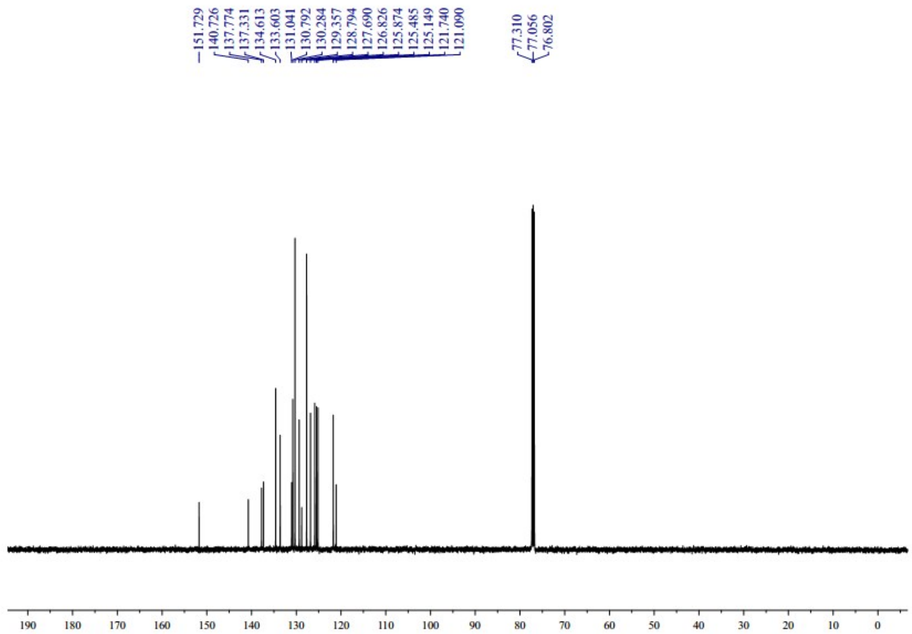
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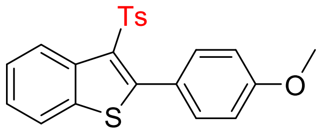
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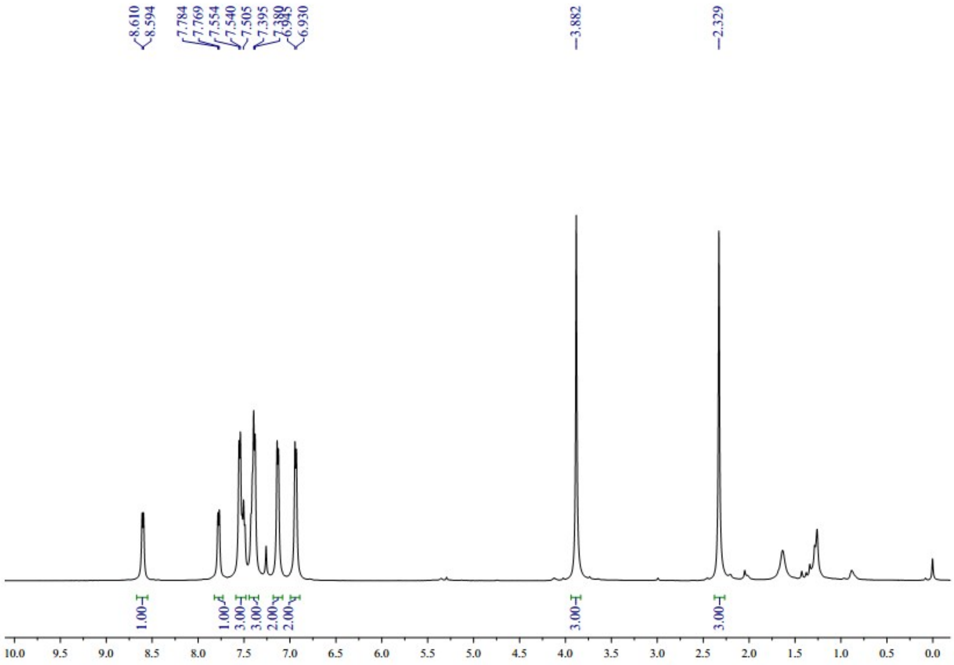
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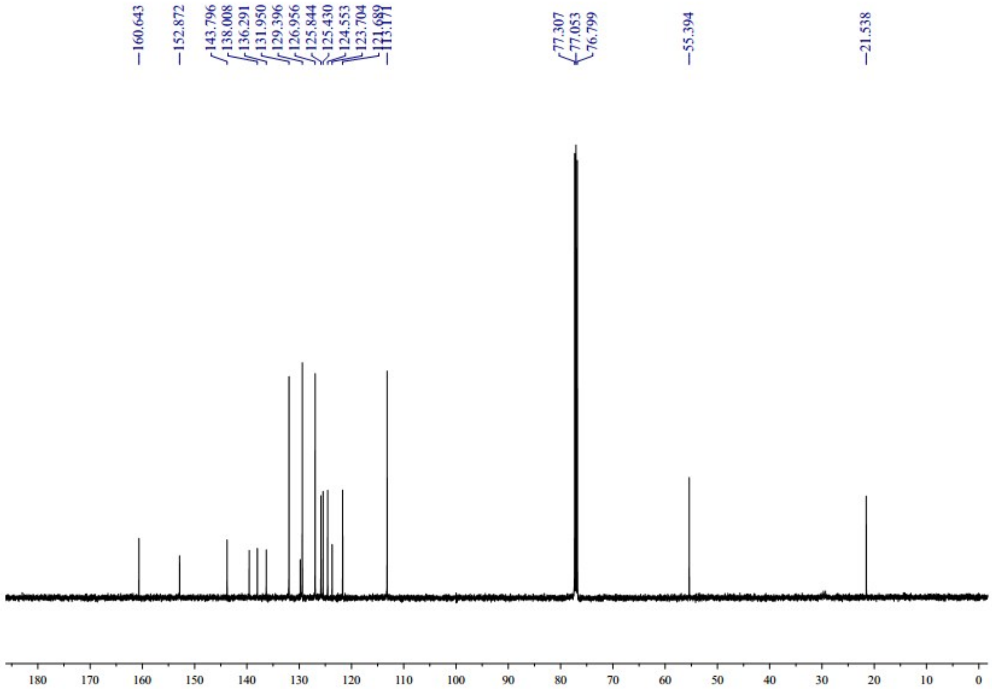
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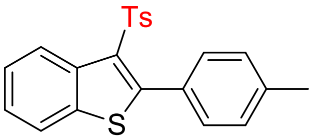
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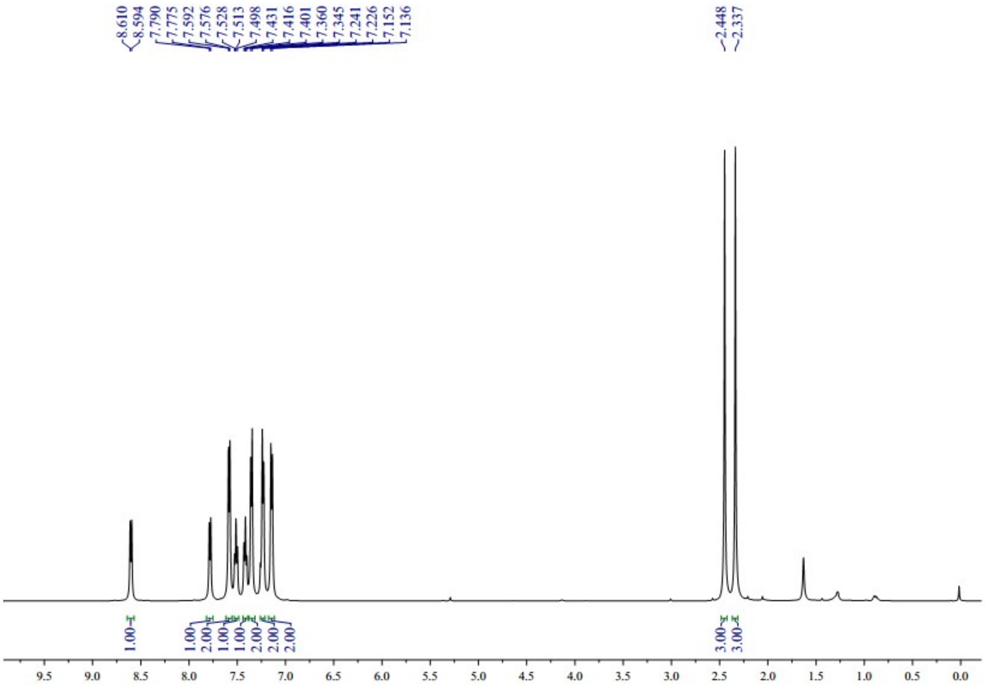
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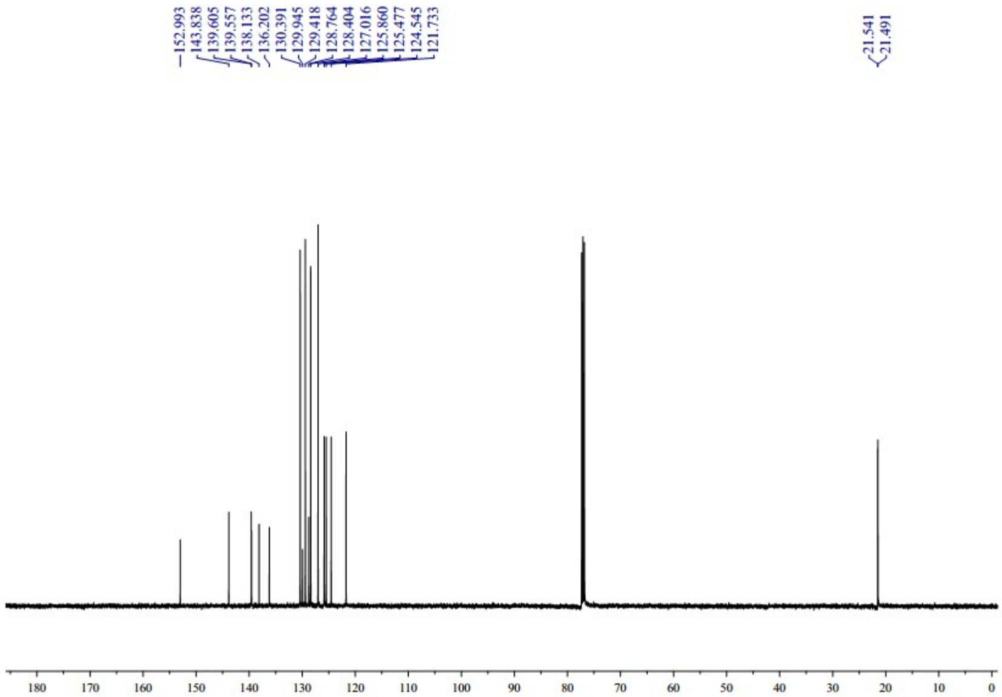
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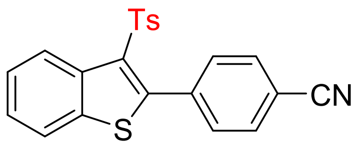
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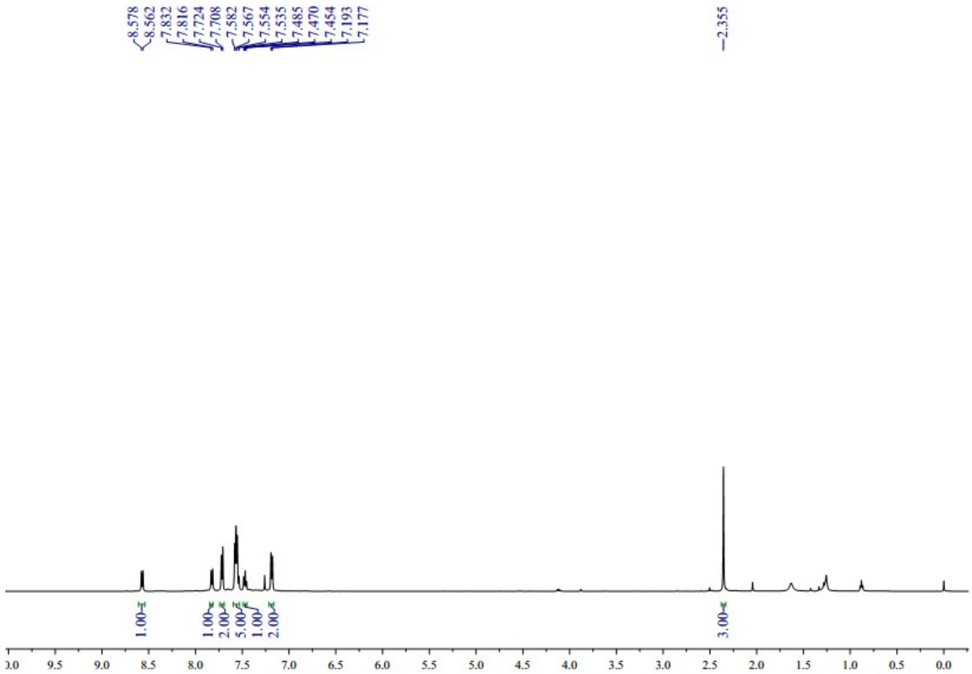
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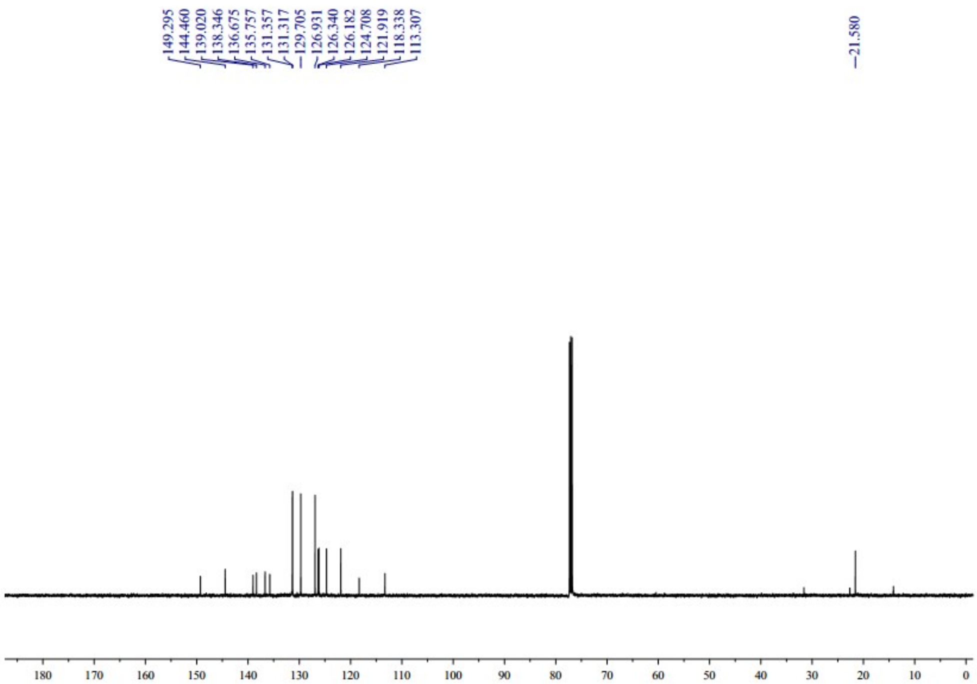
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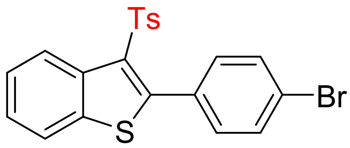

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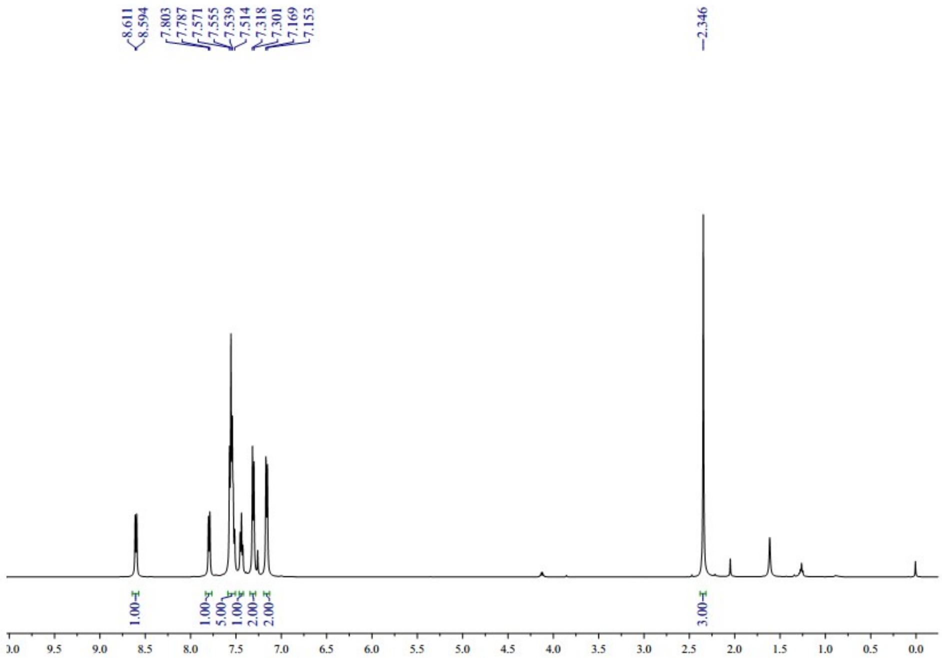

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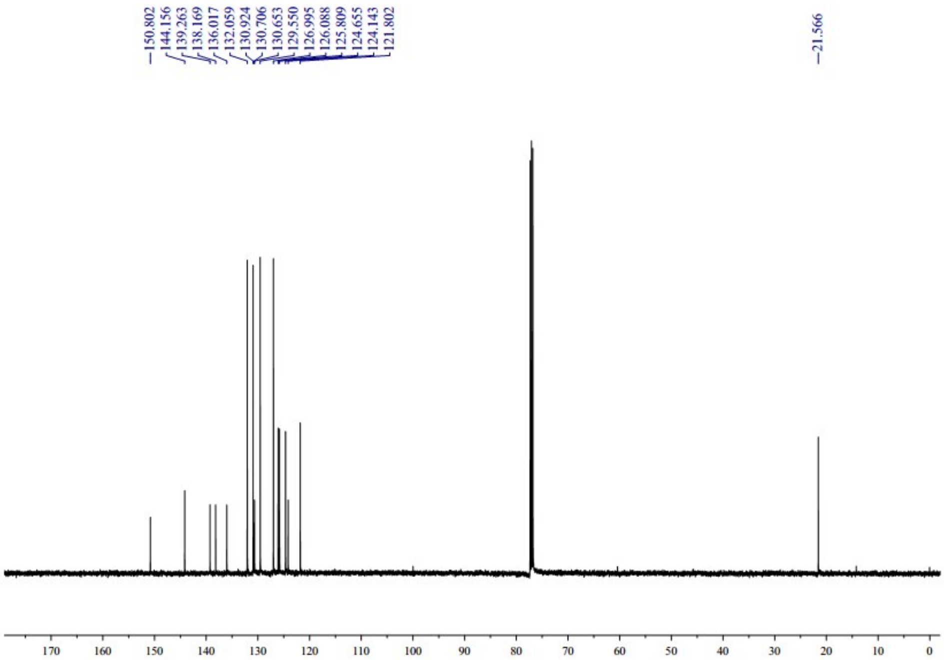

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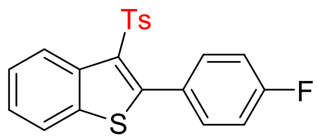
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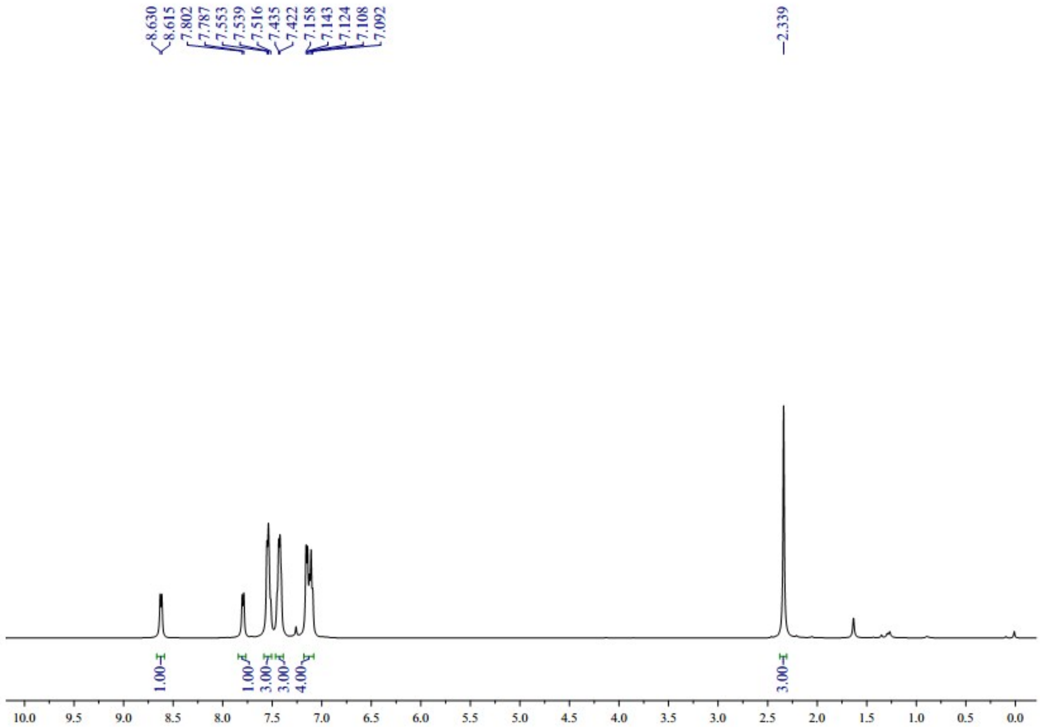
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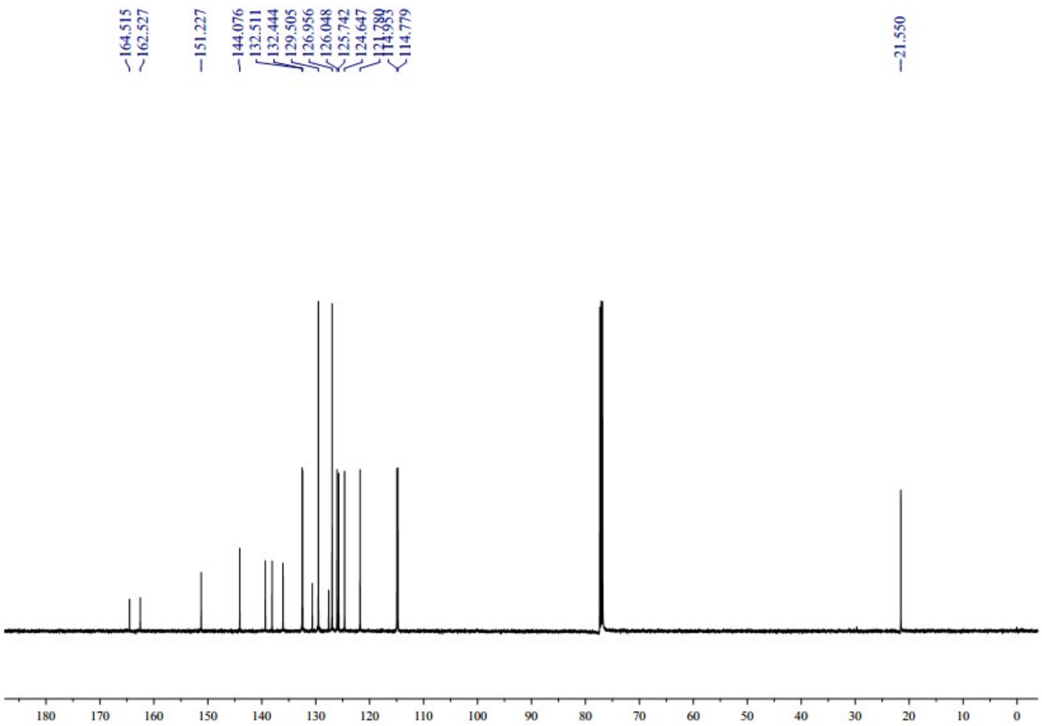
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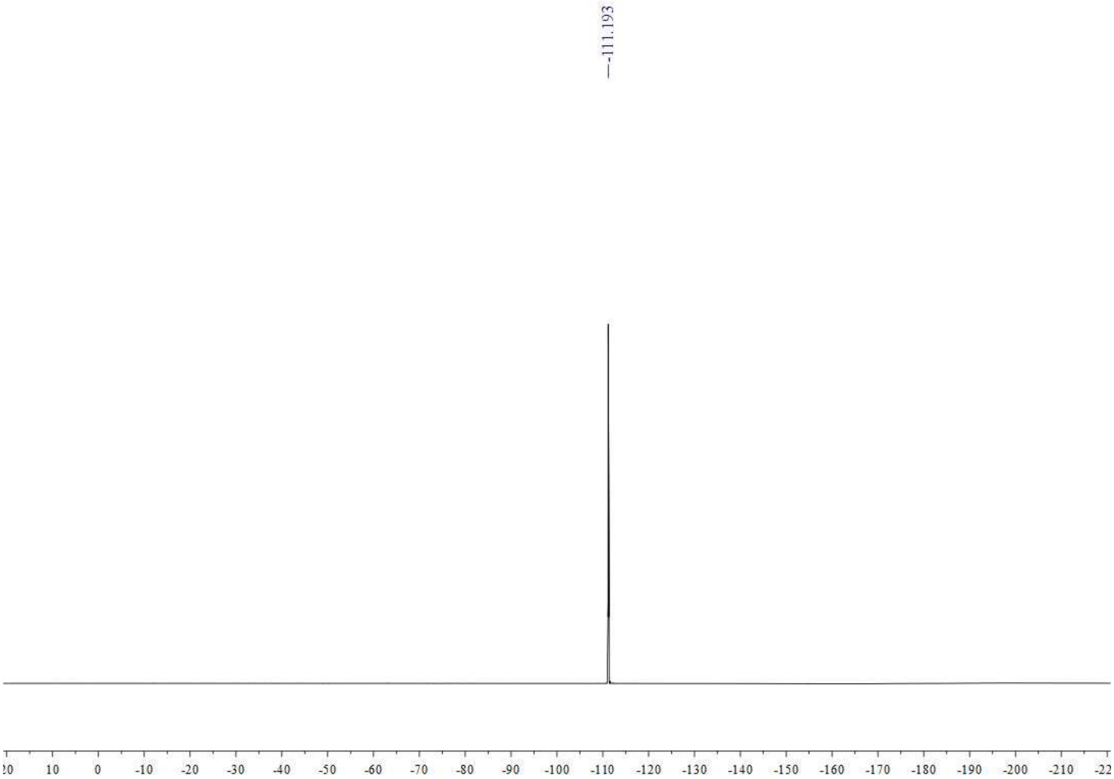
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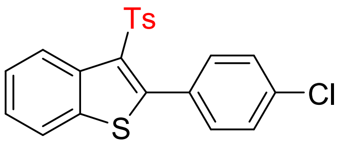
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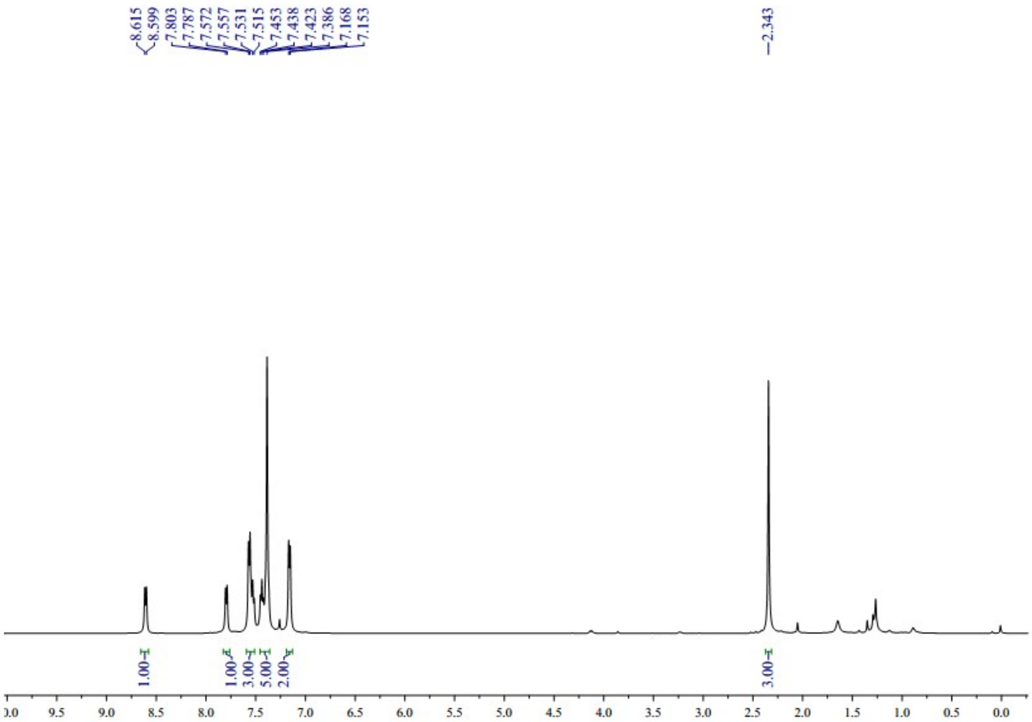
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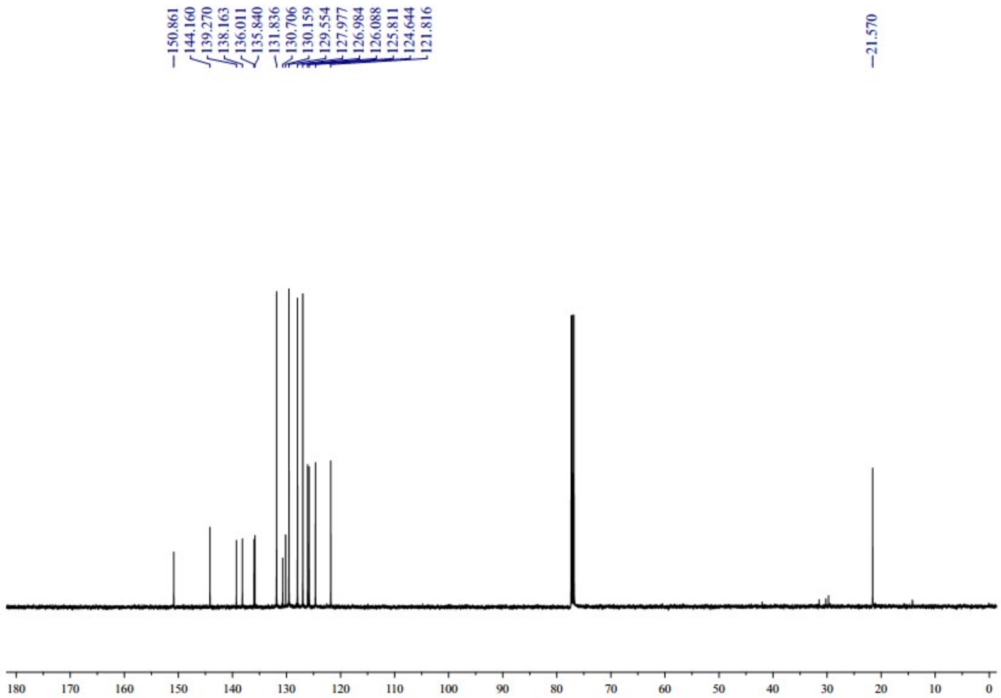
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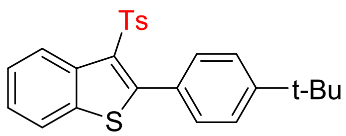
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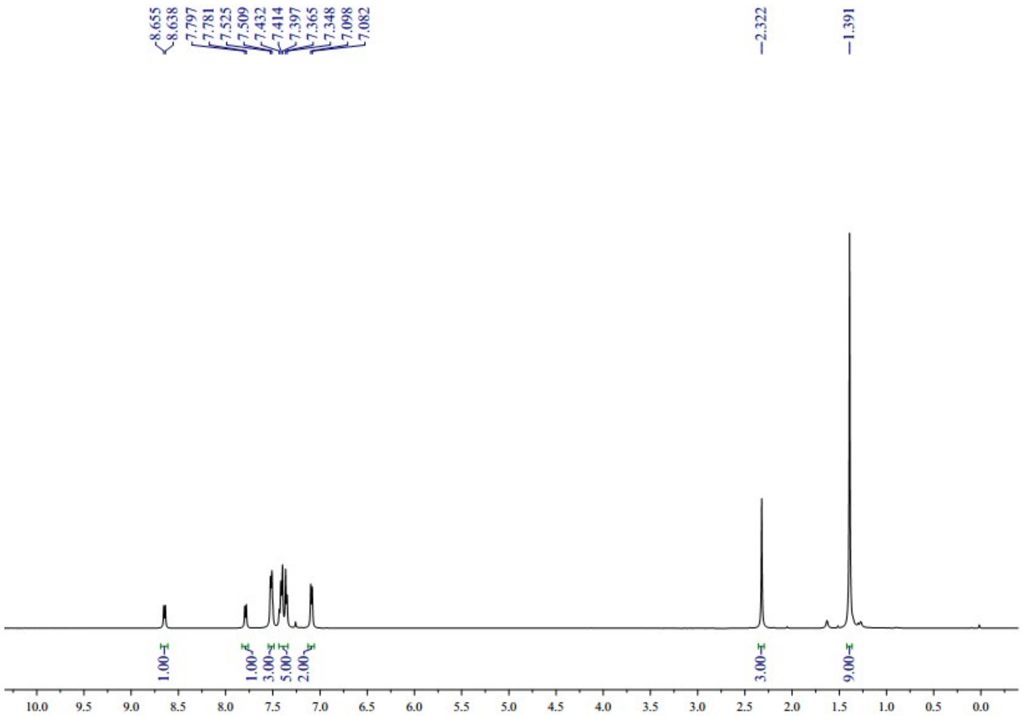
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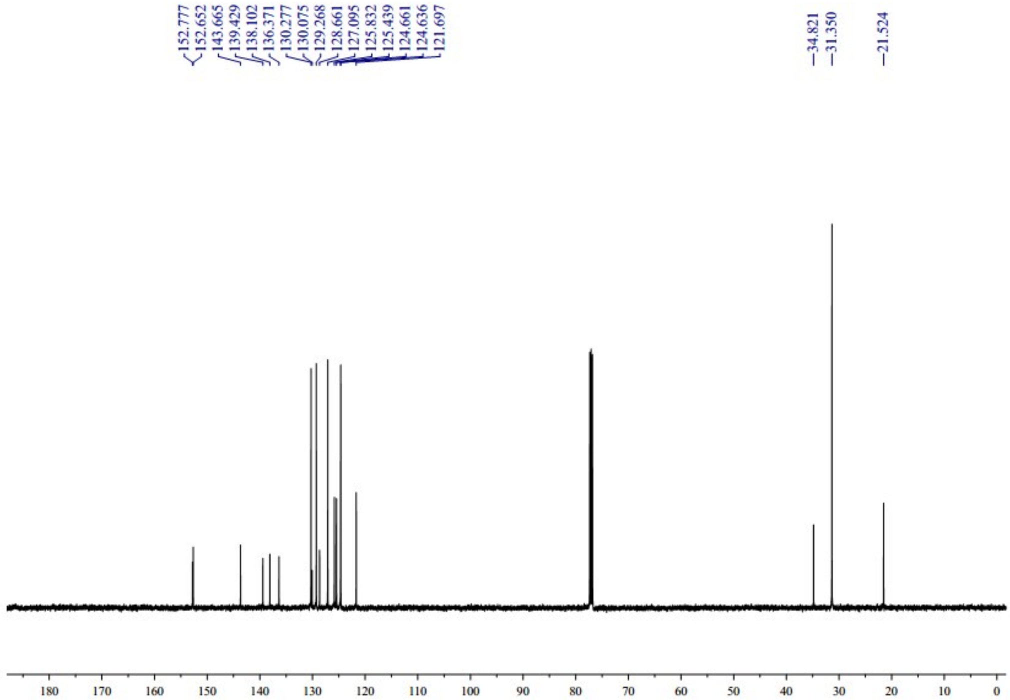
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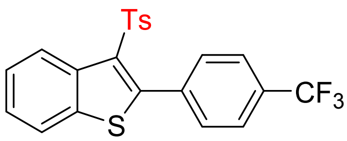
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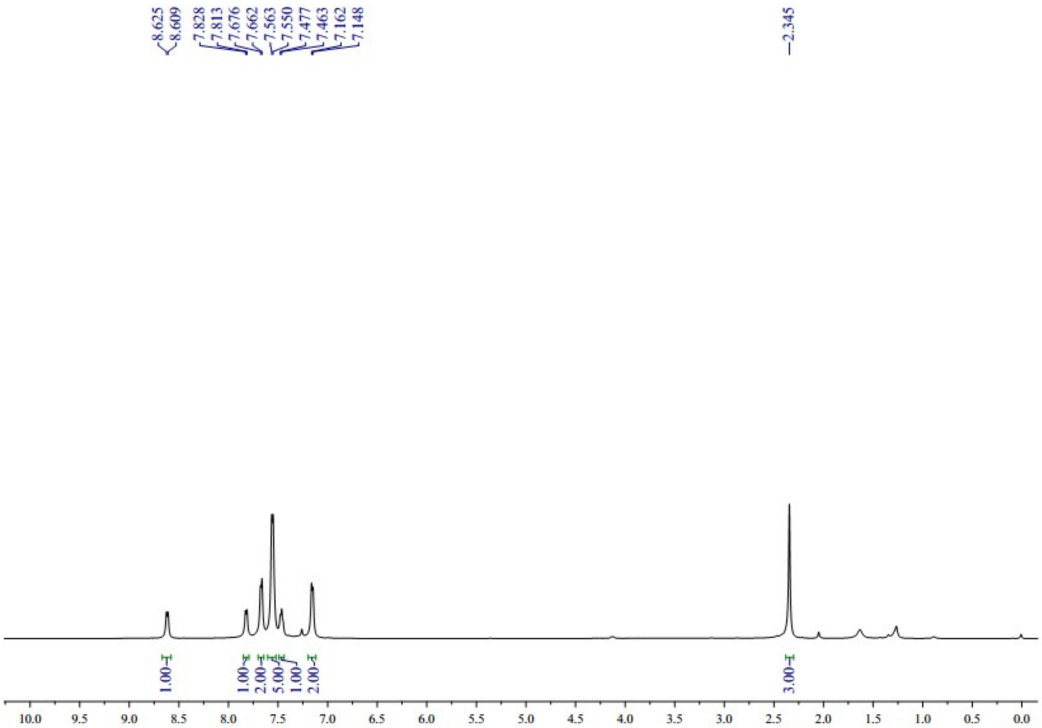
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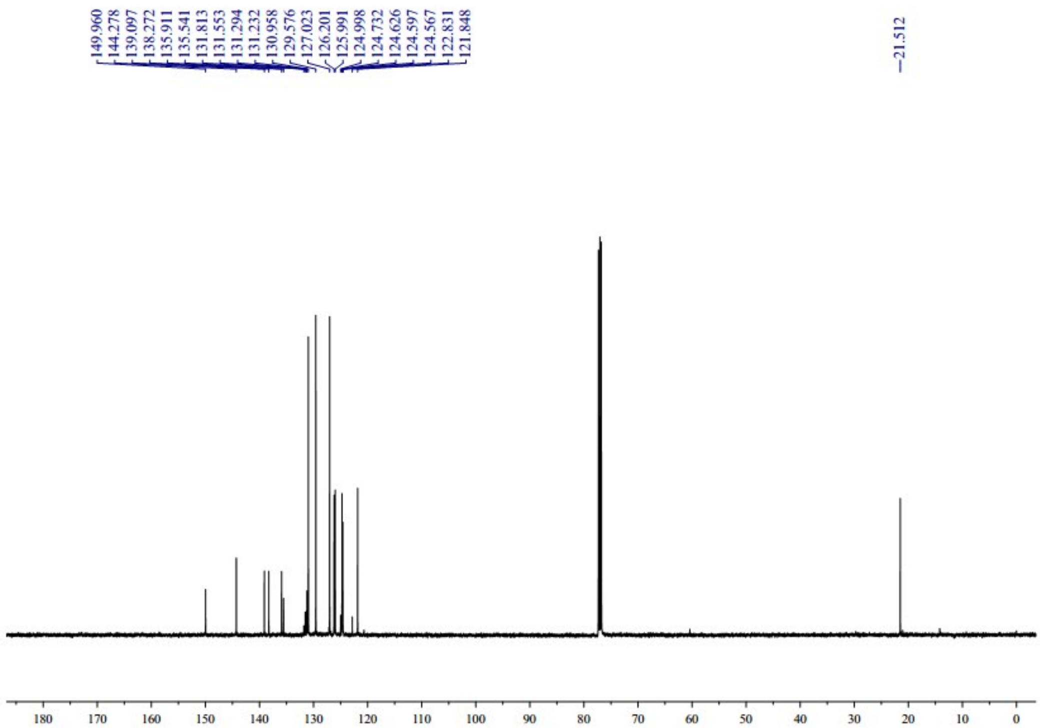
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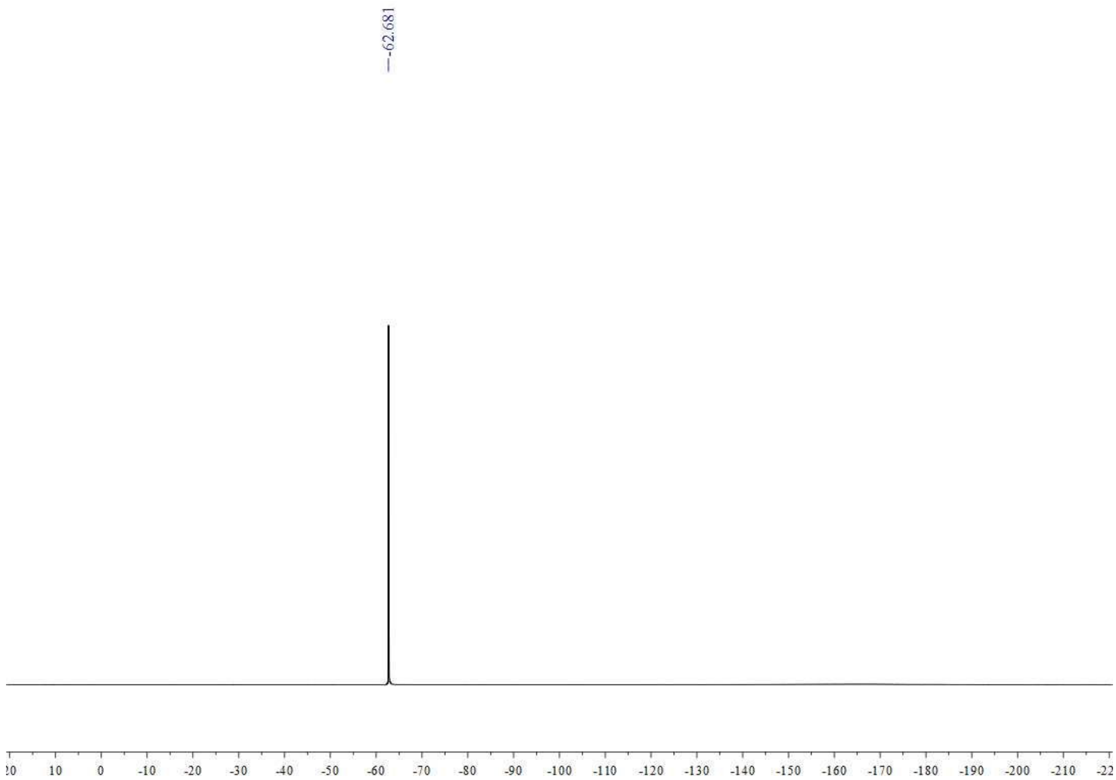
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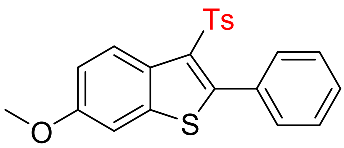
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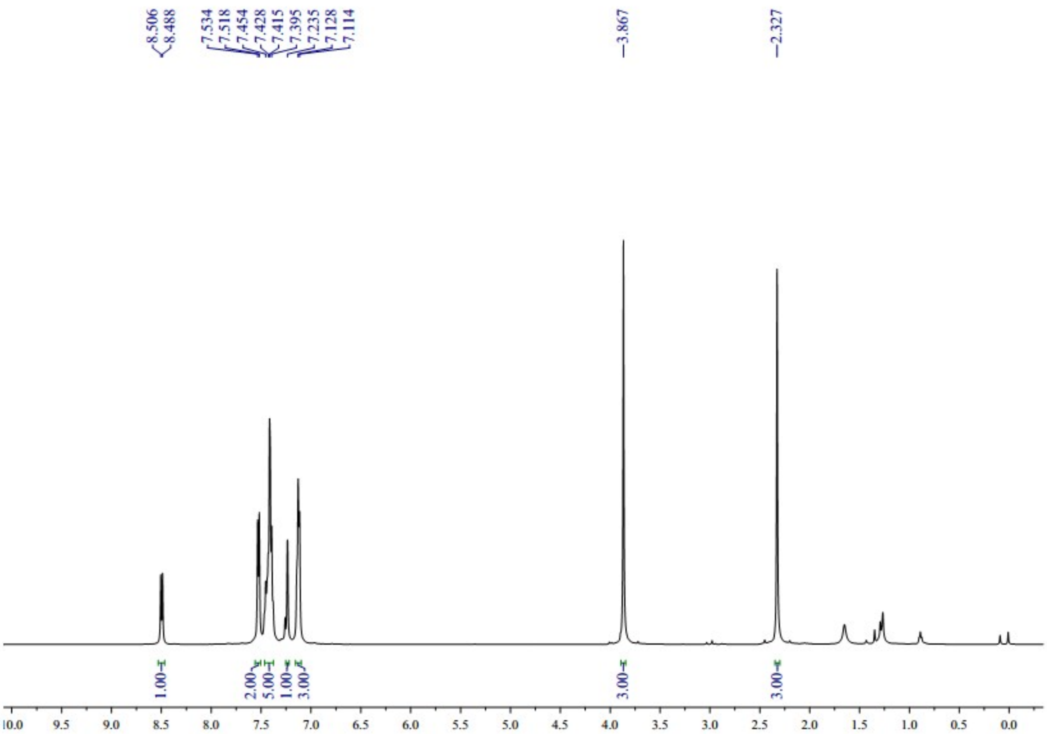
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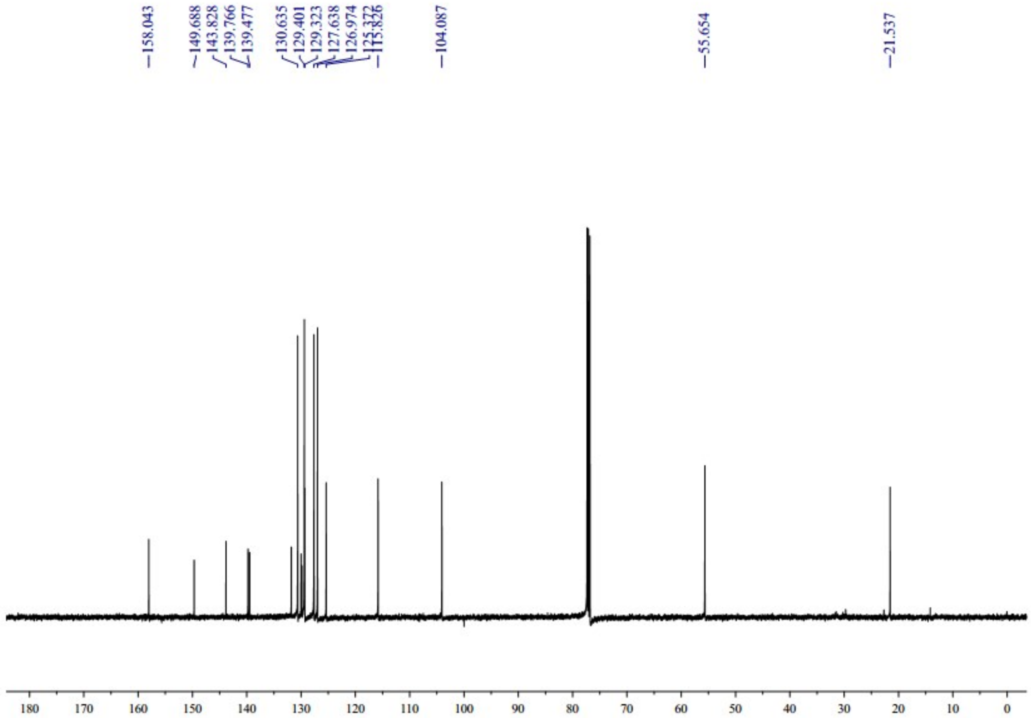
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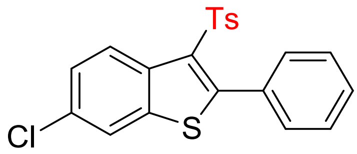
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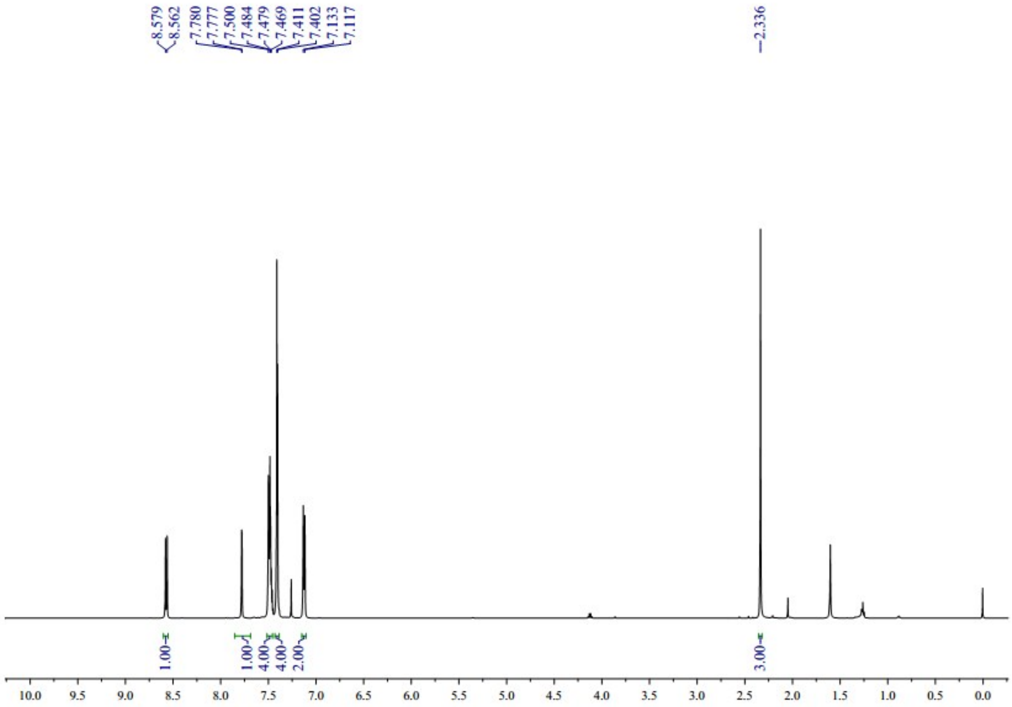
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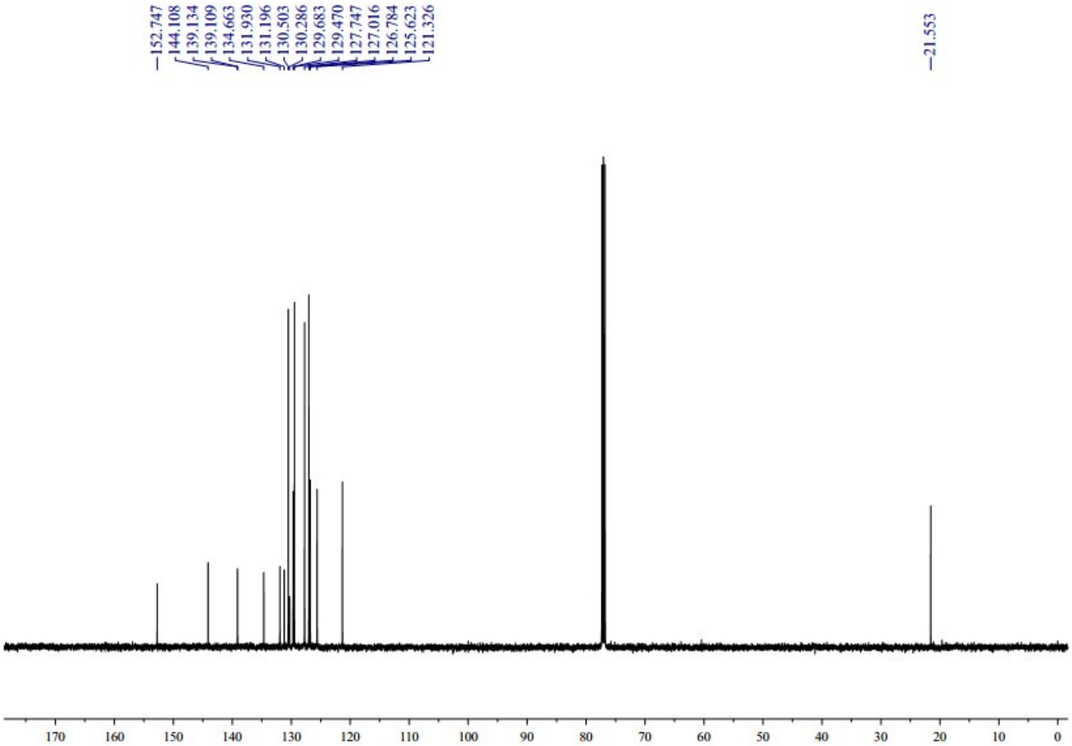
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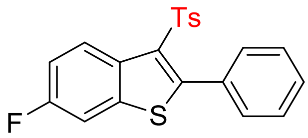
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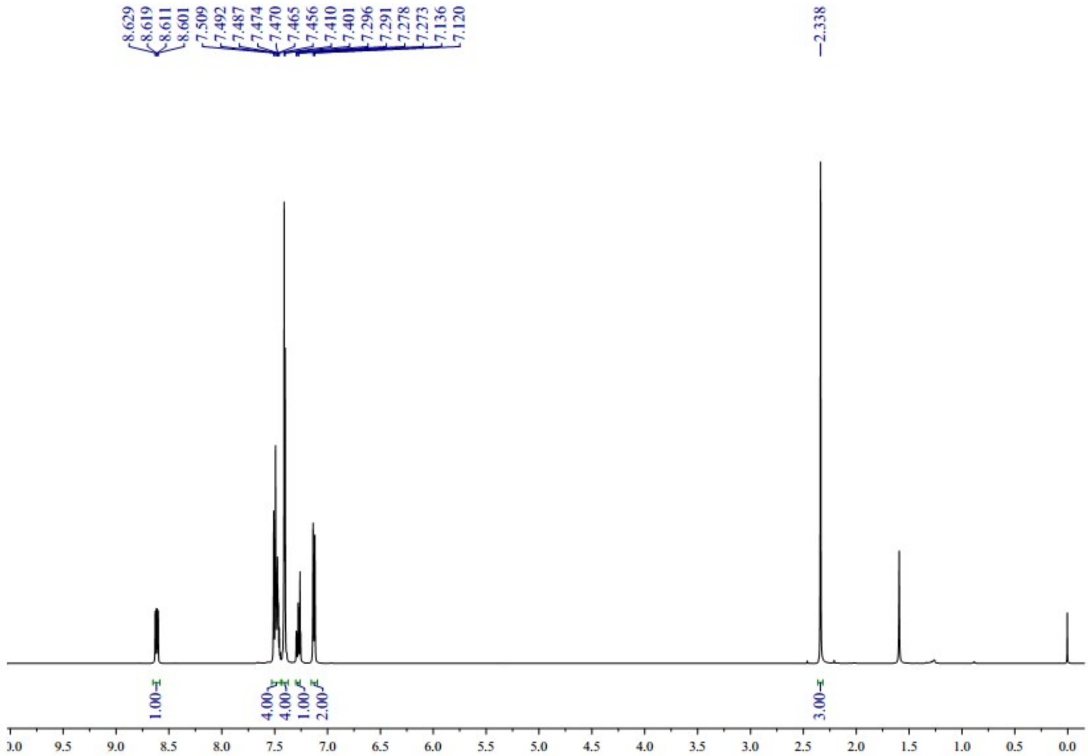
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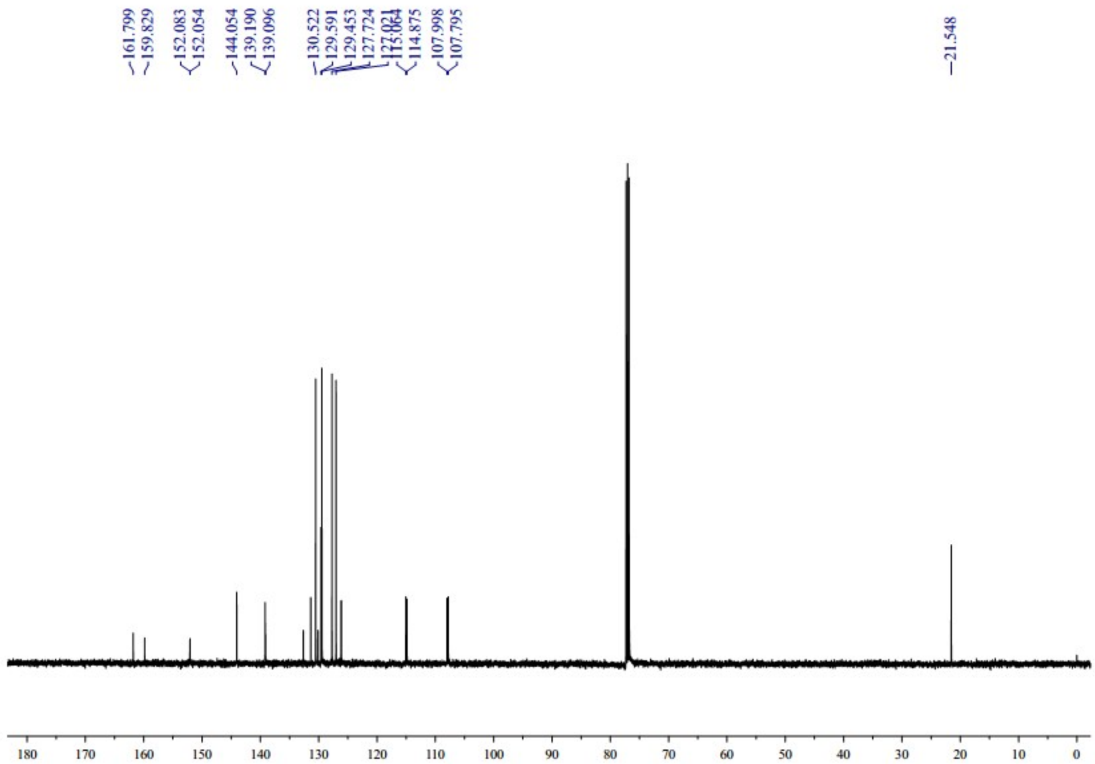
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127.021
114.875
107.998
107.795
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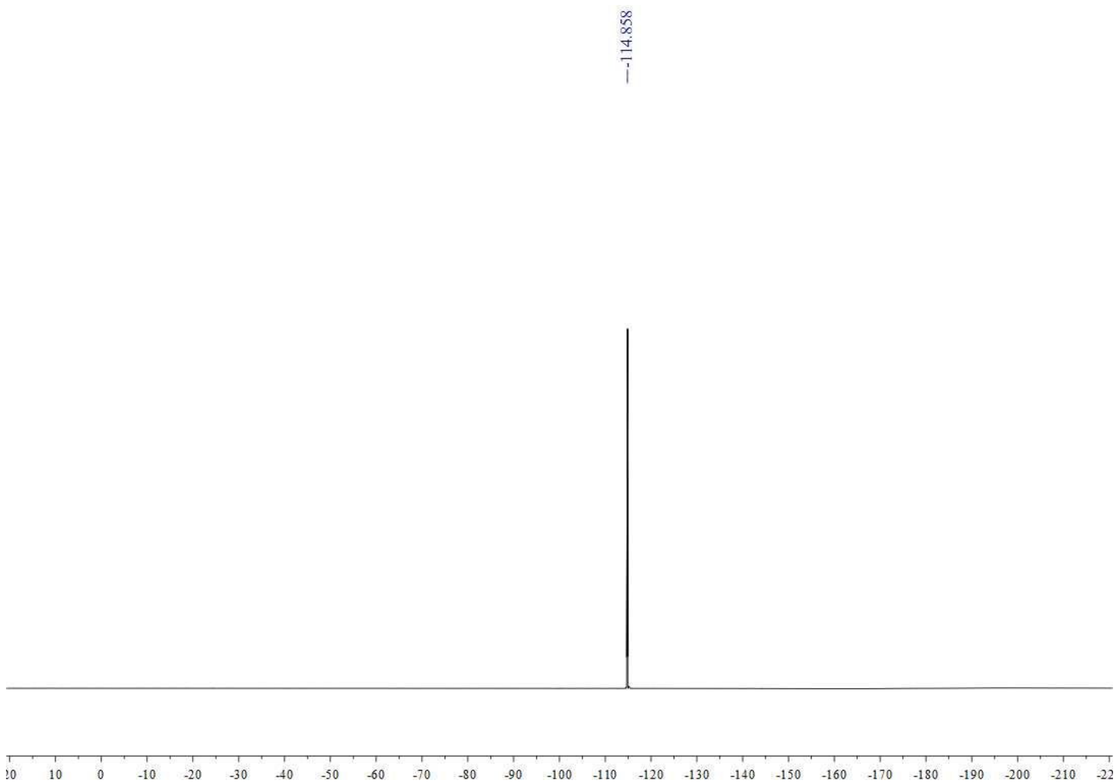
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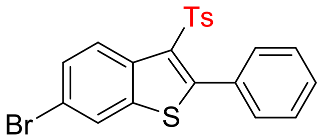
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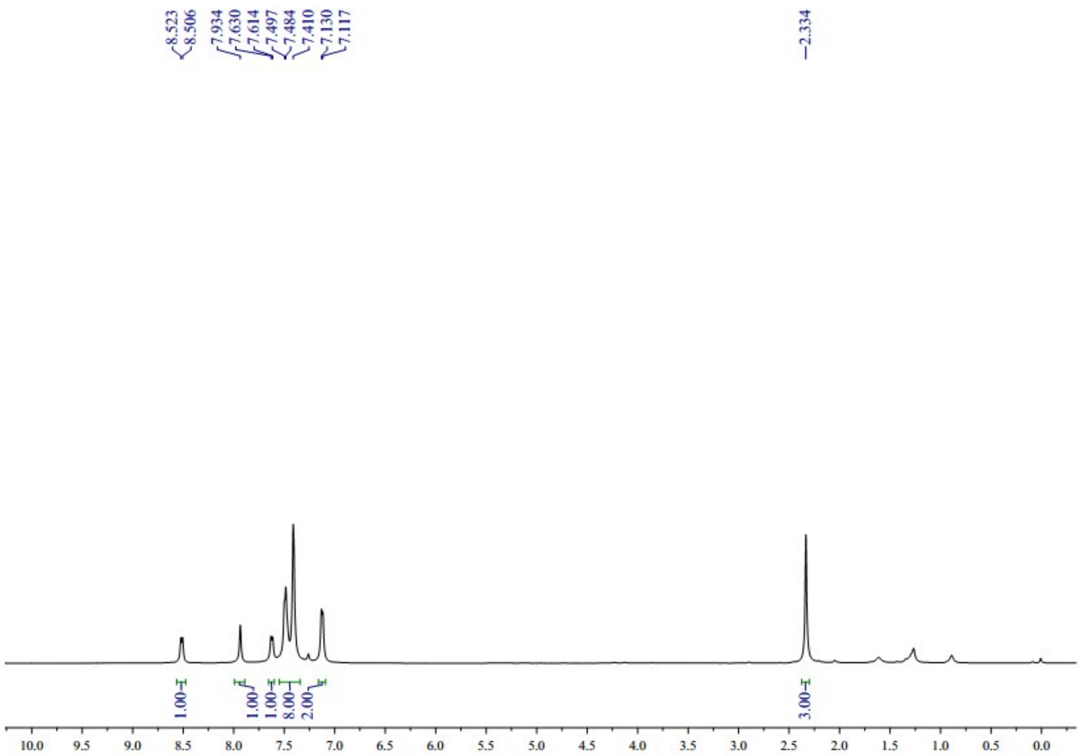
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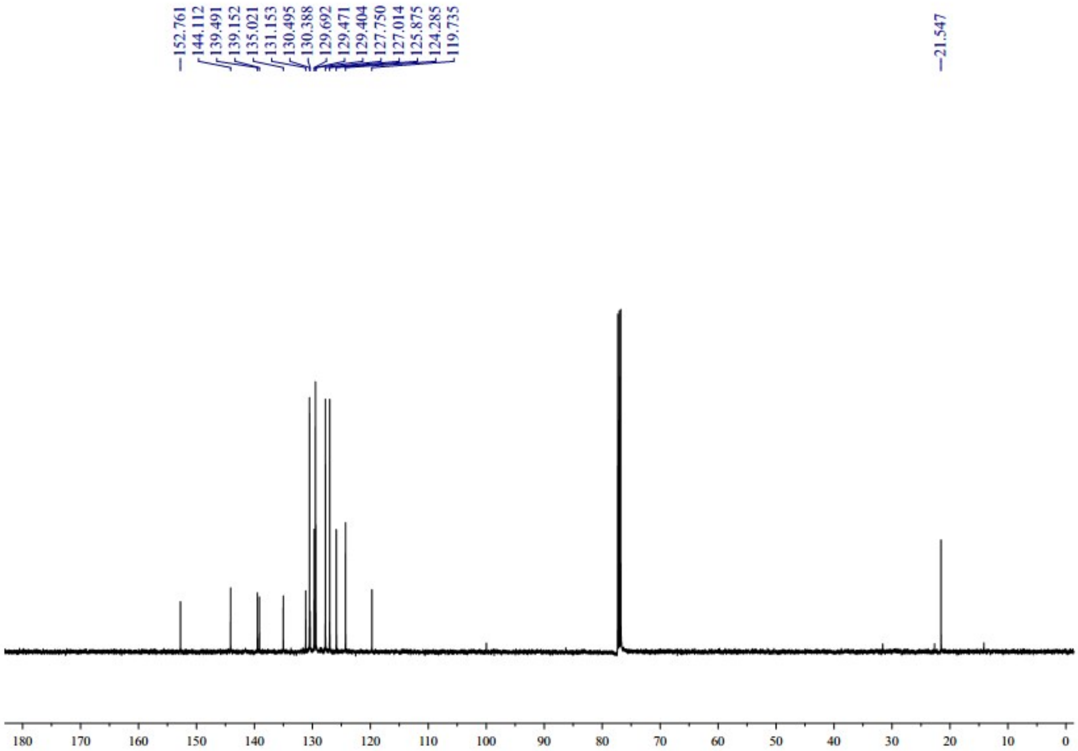
8.00
2.00
3.00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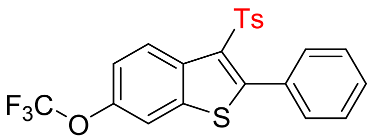
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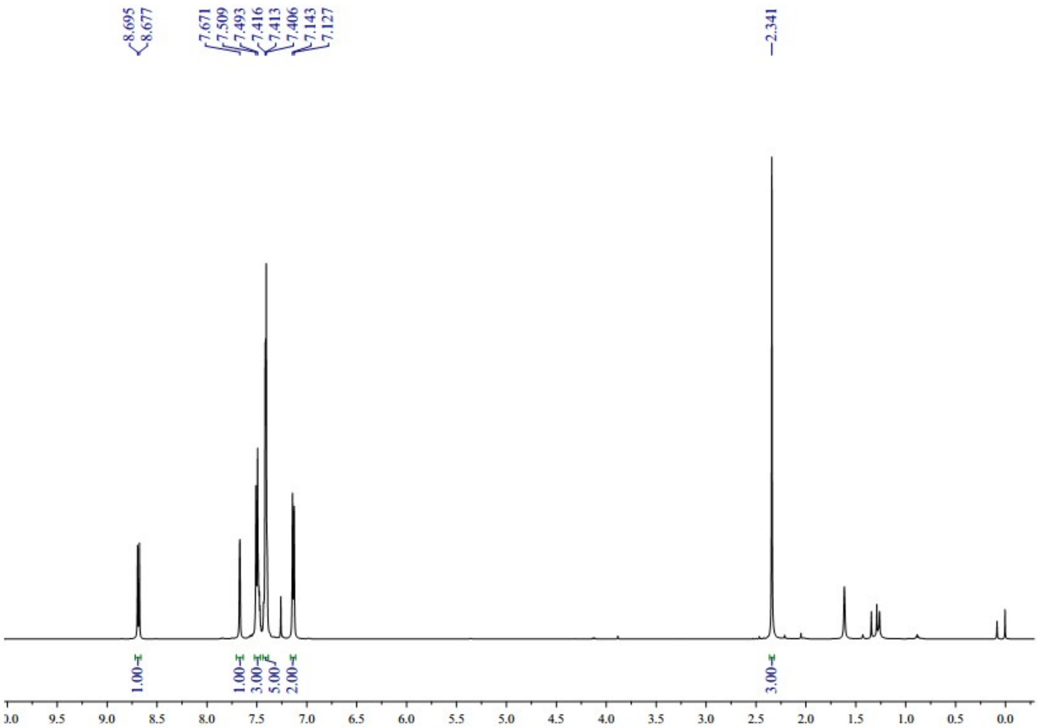
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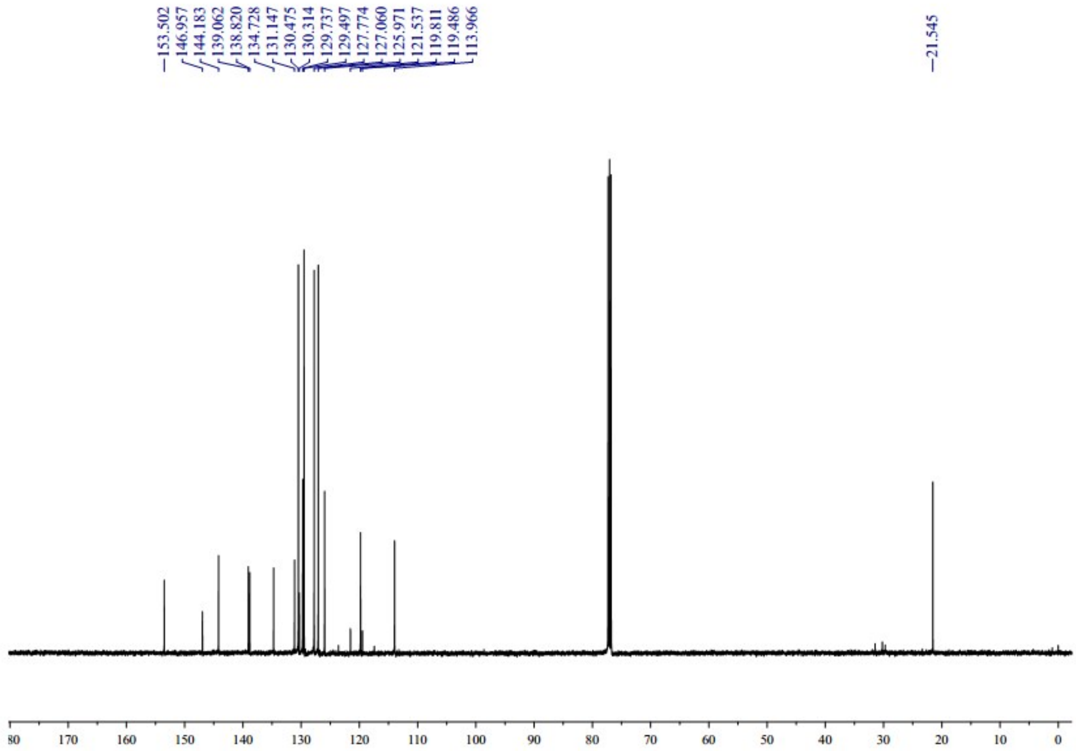
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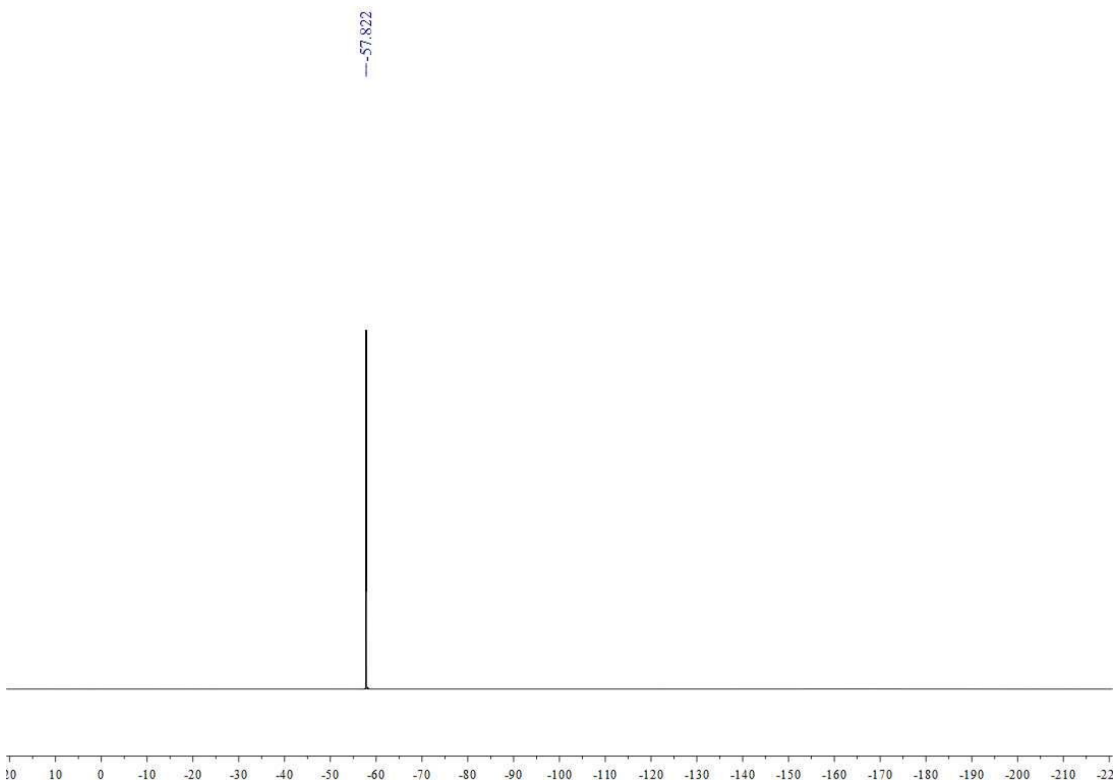
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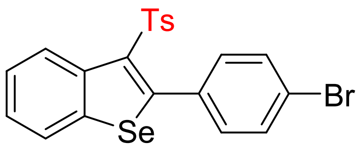
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Se
Br

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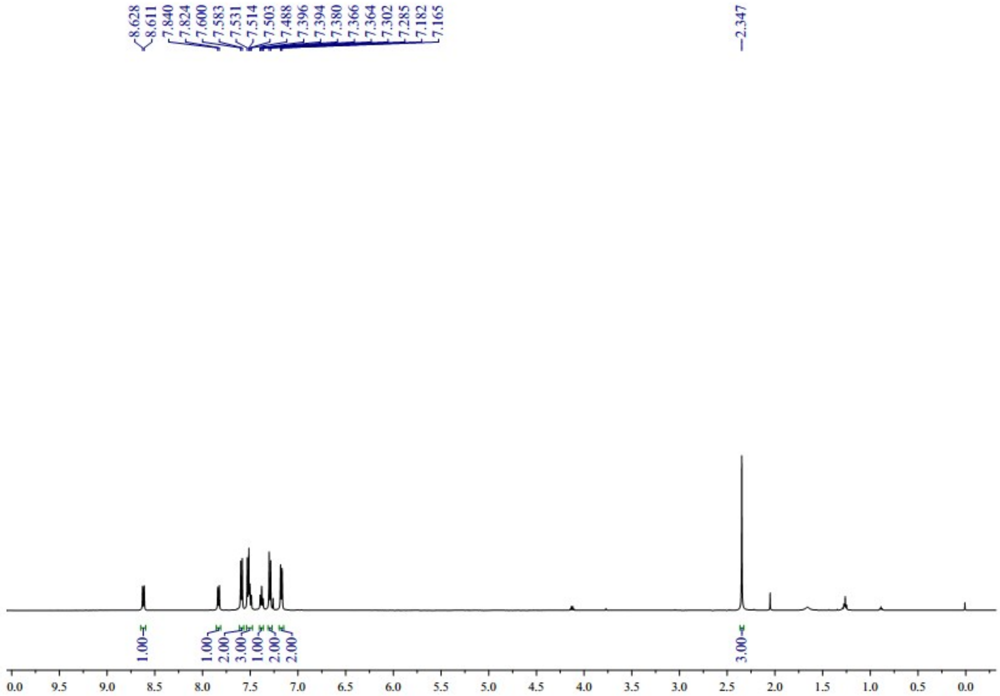
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7.394
7.380
7.366
7.364
7.302
7.285
7.182
7.165
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1.00
2.00
3.00
1.00
2.00
2.00
3.00
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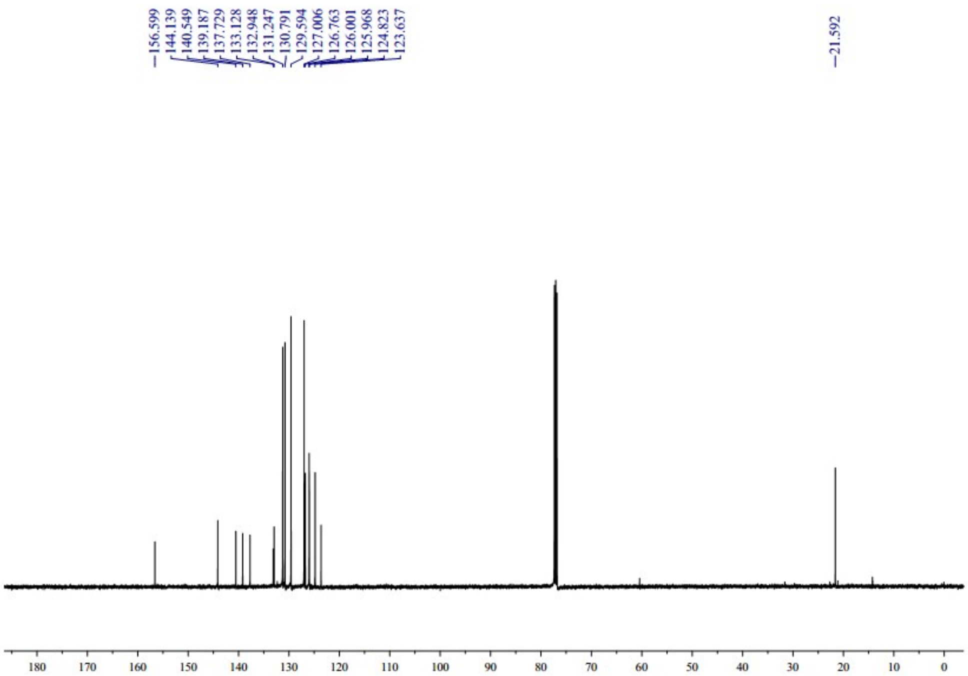
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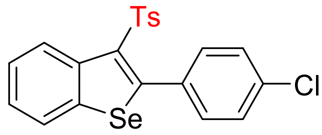
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Se
Cl

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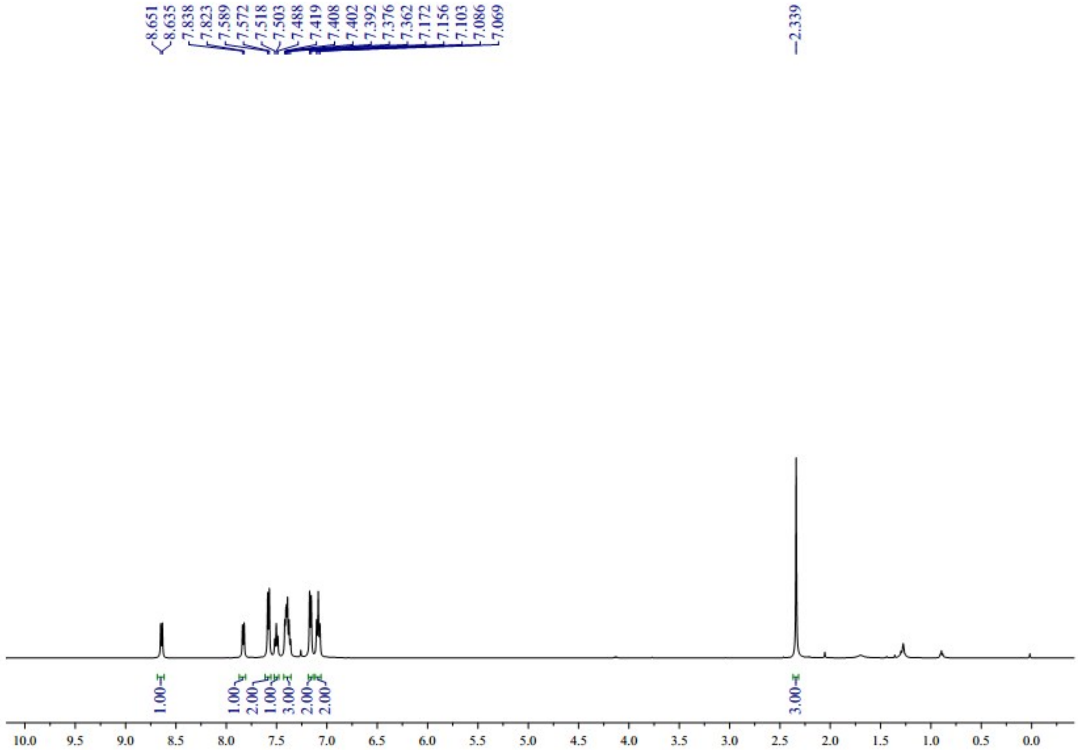
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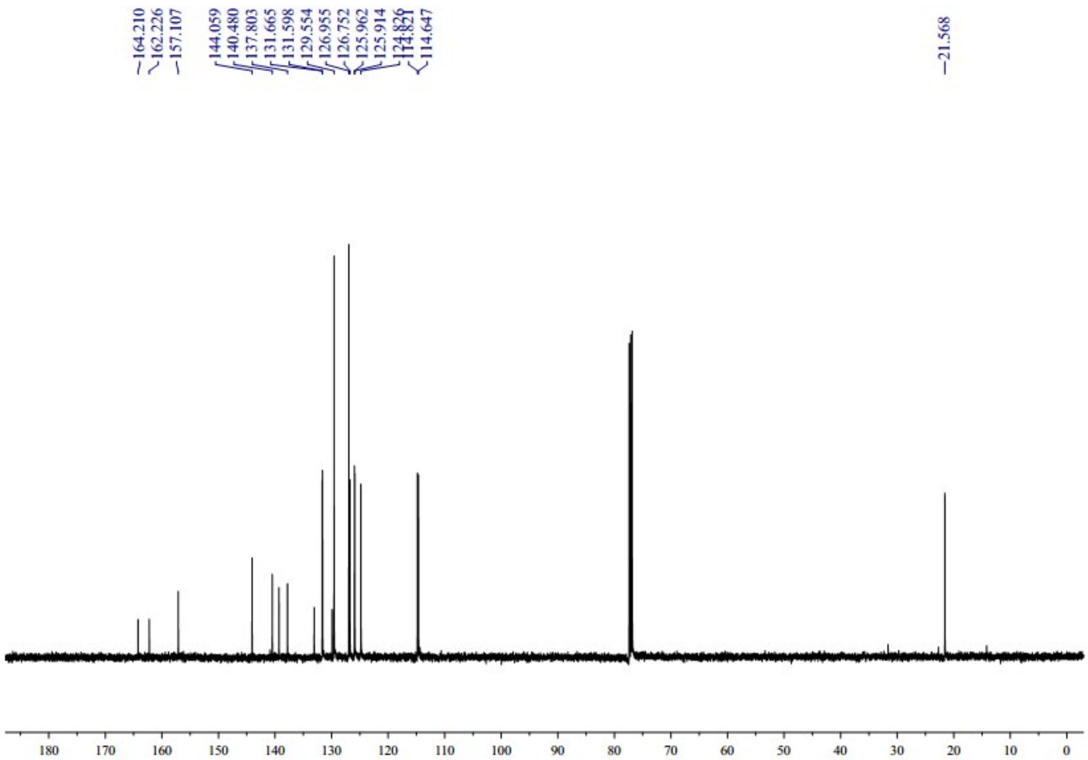
7.392
7.376
7.362
7.172
7.156
7.103
7.086
7.069
2.339
1.00
1.00
2.00
1.00
3.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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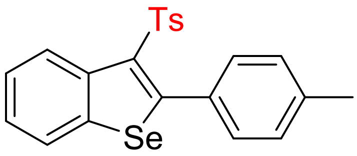

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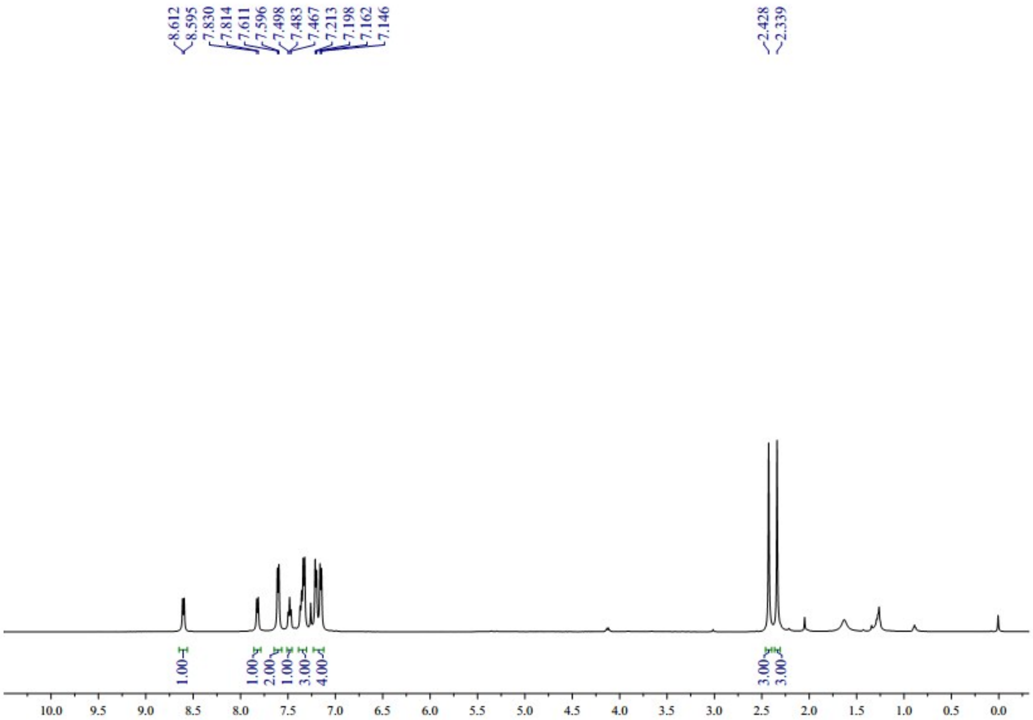
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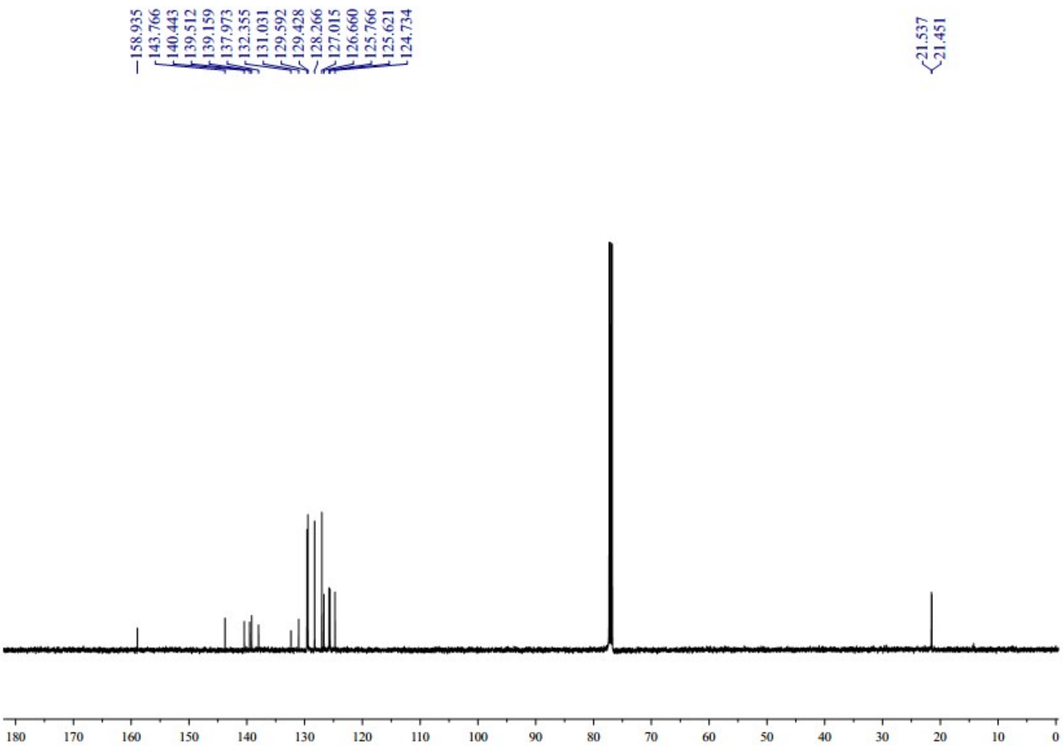
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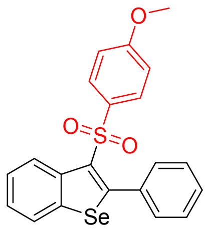
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Se

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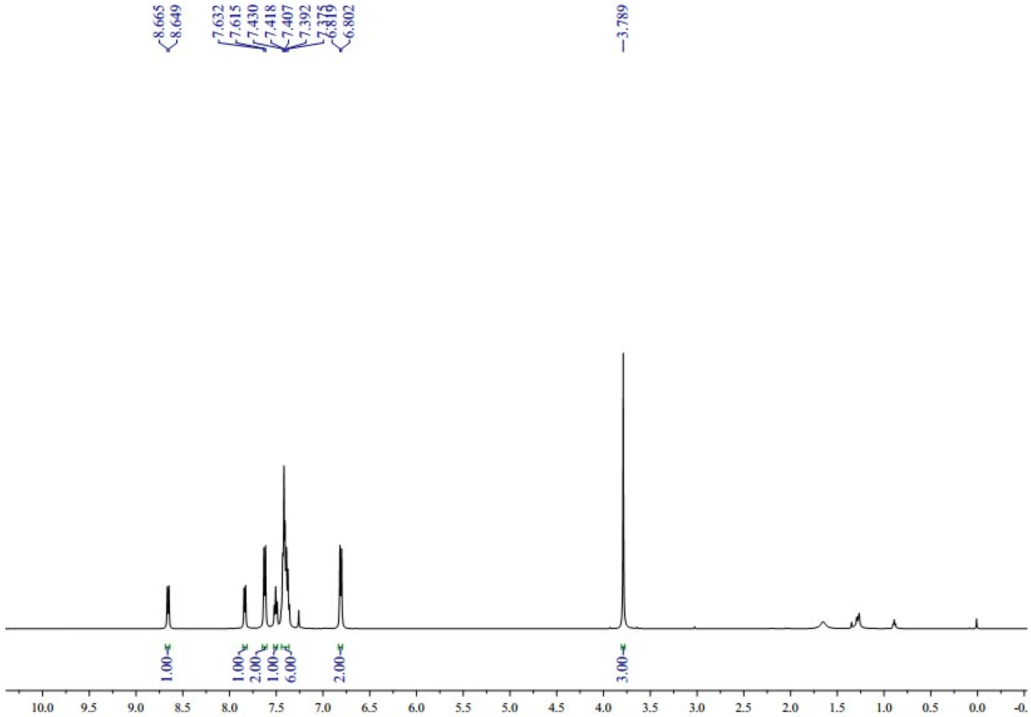
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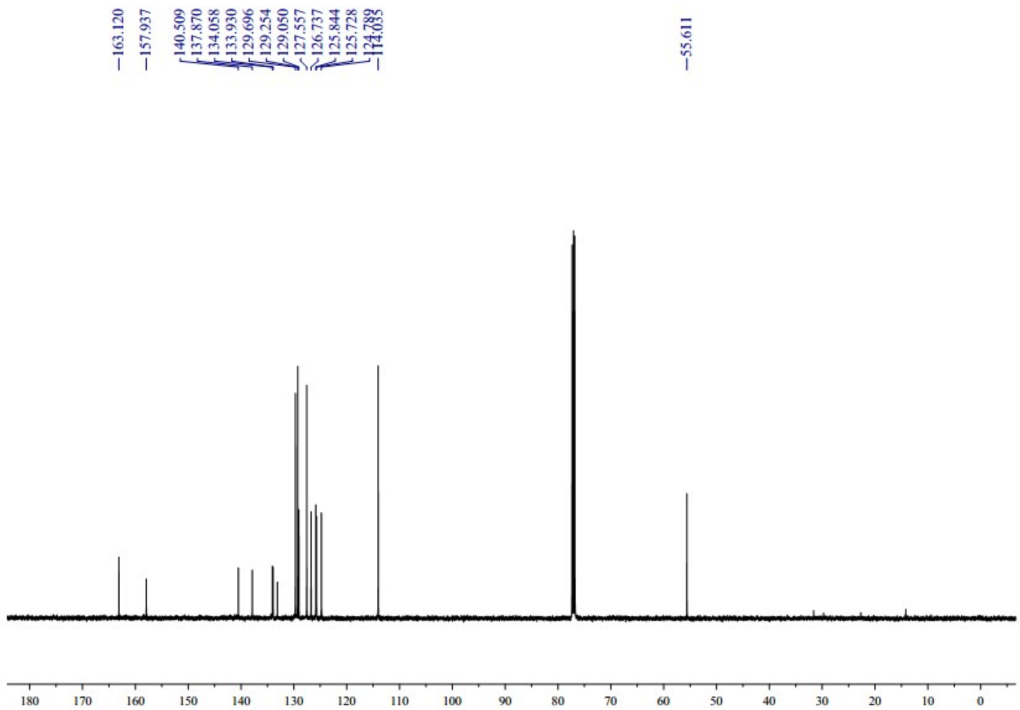
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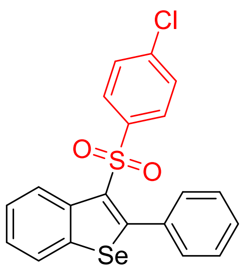

Cl
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S
O
Se

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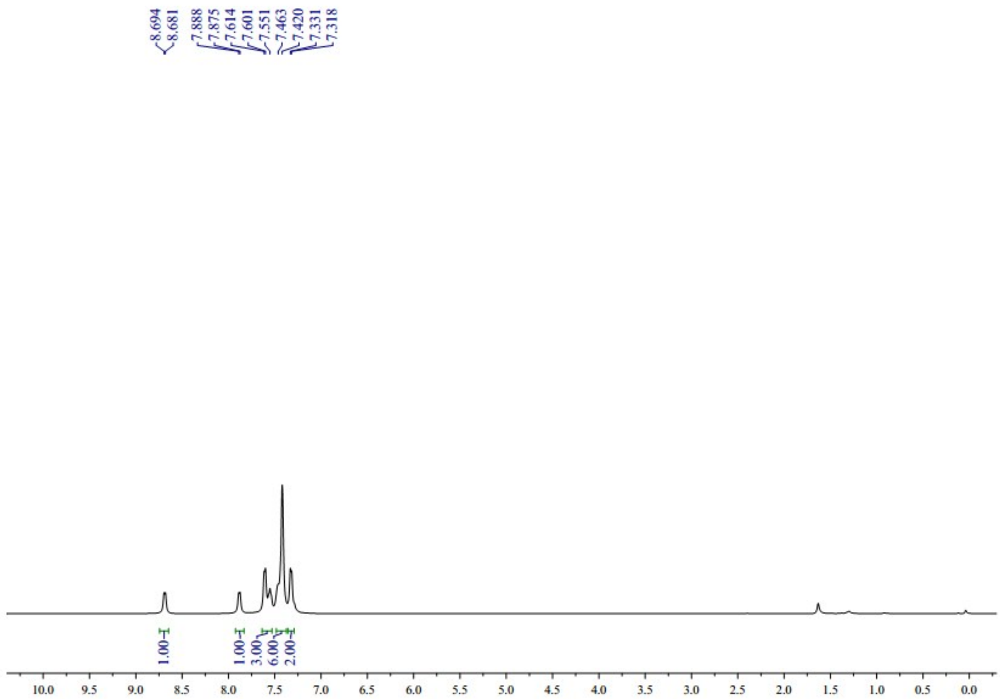

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2.00
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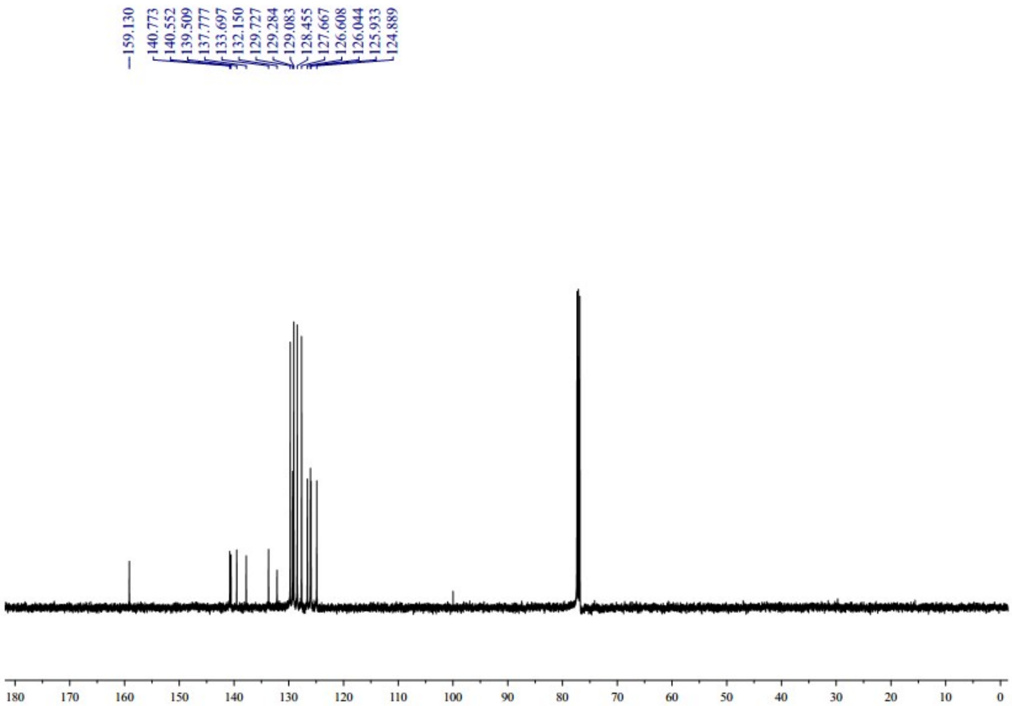

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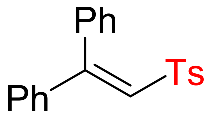
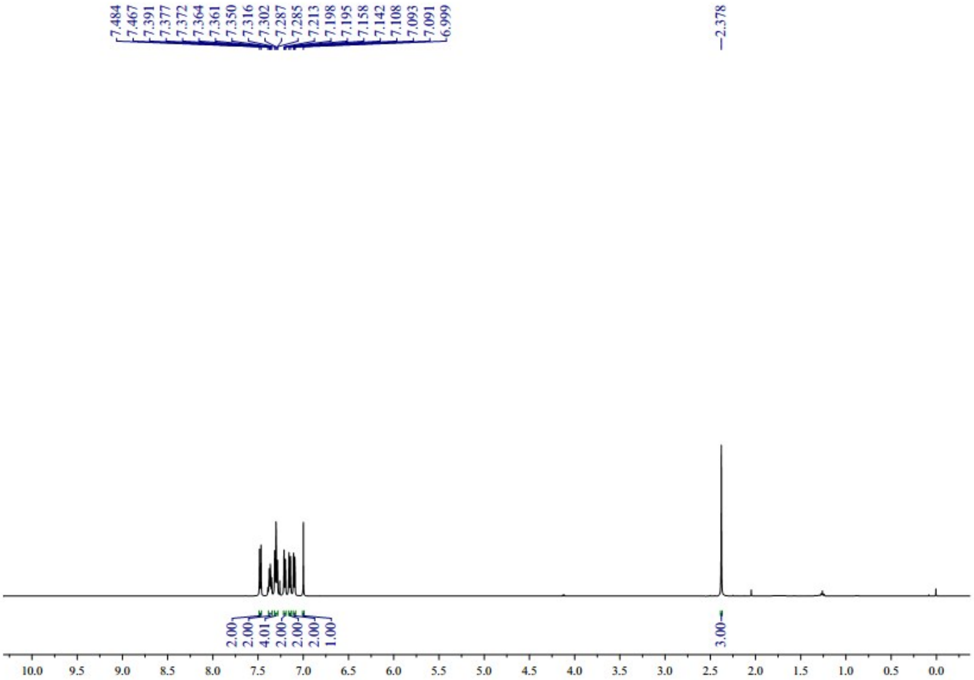

Ph
Ph
Ts

6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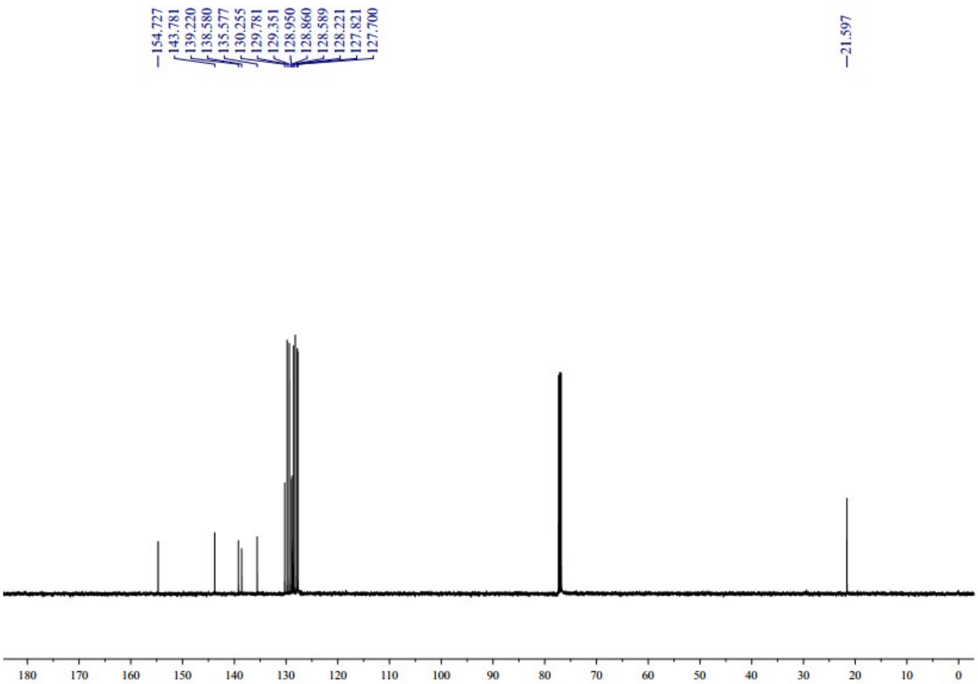
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