

Supporting Information

Deep eutectic solvents as sustainable media for multicomponent sulfonylation: an efficient strategy to synthesize (hetero)aryl sulfones

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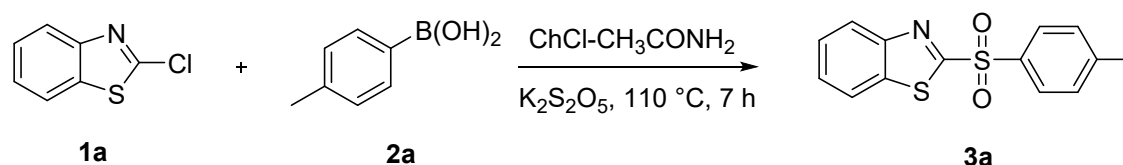
1. General

All commercial reagents were used directly without further purification, unless otherwise stated. DMSO-*d*₆ and CDCl₃ were purchased from Shanghai aladdin Biochemical Technology Co., Ltd. All Schlenk tubes and sealed vessels (50 mL) were purchased from Beijing Synthware Glass. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance III-500 spectrometer (Swiss Bruker, Switzerland). The following abbreviations were used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, q = quartet.

2. Experimental sections

2.1 Optimization studies

Table S1 Optimization of reaction conditions^a



Entry	1a (mmol)	2a (mmol)	DES (molar ratio)	Temperature (°C)	Time (h)	Yield(%) ^b
1	0.4	0.2	ChCl:Acetamide (1:2)	100	4	31
2	0.3	0.2	ChCl:Acetamide (1:2)	100	4	30
3	0.2	0.2	ChCl:Acetamide(1:2)	100	4	28
4	0.2	0.3	ChCl:Acetamide (1:2)	100	4	34
5	0.2	0.4	ChCl:Acetamide (1:2)	100	4	58
6	0.2	0.5	ChCl:Acetamide (1:2)	100	4	61
7	0.2	0.4	ChCl:Acetamide (1:2)	90	4	45
8	0.2	0.4	ChCl:Acetamide (1:2)	100	4	58
9	0.2	0.4	ChCl:Acetamide (1:2)	110	4	74
10	0.2	0.4	ChCl:Acetamide (1:2)	120	4	76
11	0.2	0.4	ChCl:Acetamide (1:2)	110	3	52
12	0.2	0.4	ChCl:Acetamide (1:2)	110	5	77
13	0.2	0.4	ChCl:Acetamide (1:2)	110	7	81
14	0.2	0.4	ChCl:Acetamide (1:2)	110	9	79
15	0.2	0.4	Betaine:Acetamide (1:2)	110	7	32
16	0.2	0.4	ChCl:Glucose (1:2)	110	7	0
17	0.2	0.4	ChCl:Oxalate (1:2)	110	7	0
18	0.2	0.4	ChCl:Citrate (1:2)	110	7	0
19	0.2	0.4	ChCl:Glycol (1:2)	110	7	0

20	0.2	0.4	ChCl:Urea (1:2)	110	7	0
20	0.2	0.4	ChCl:Glycerin (1:2)	110	7	25
21	0.2	0.4	ChCl:Sorbitol (1:2)	110	7	0
22	0.2	0.4	ChCl:SnCl ₄ (1:2)	110	7	18
23	0.2	0.4	ChC: Tartaric (1:2)	110	7	0
24	0.2	0.4	ZnCl ₂ :Acetamide (1:2)	110	7	45
25	0.2	0.4	ZnCl ₂ :Urea (1:2)	110	7	0

^a Reaction conditions: 2-chlorobenzothiazole **1a** (0.2 mmol), 4-methylbenzeneboronic acid **2a** (0.4 mmol) and K₂S₂O₅ (0.2 mmol) in 1 mL DES were heated to 110 °C with stirring for 7 h. ^b Isolated yield.

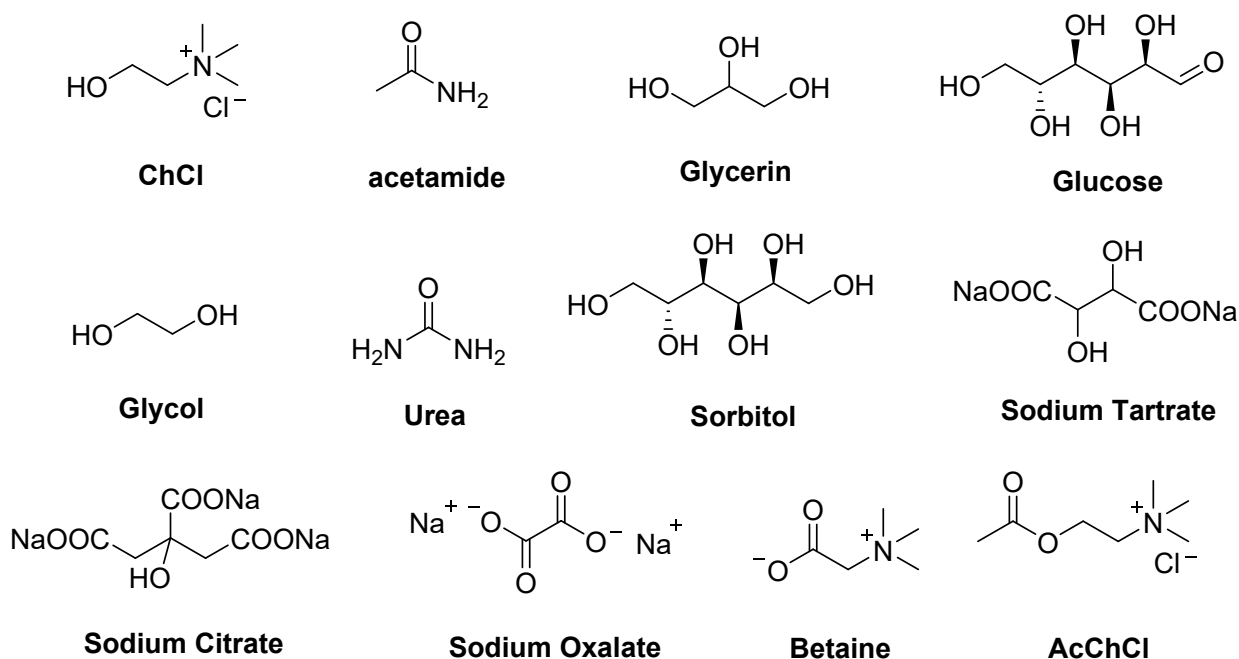
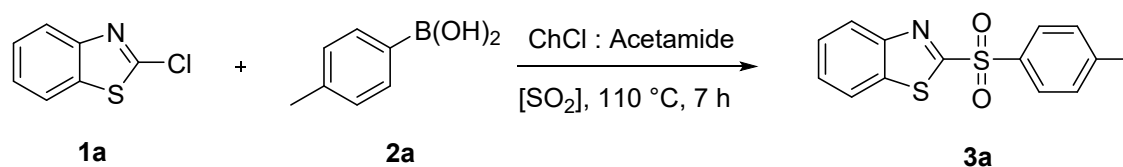


Table S2 Study of SO₂ surrogates^a

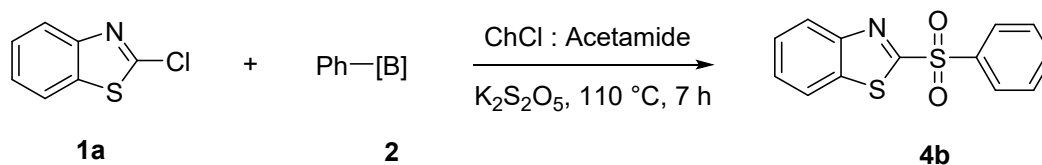


Entry	SO ₂ source	Yield (%) ^b
1	K ₂ S ₂ O ₅	81
2	Na ₂ S ₂ O ₅	75
3	DABSO	32
4	NaO ₂ SCH ₂ OH	trace
5	Na ₂ SO ₃	54
6	NaHSO ₃	42

^a Reaction conditions: 2-chlorobenzothiazole **1a** (0.2 mmol), 4-methylbenzeneboronic acid **2a** (0.4 mmol) and SO₂ surrogate (0.2 mmol) in 1 mL DES were heated to 110 °C with stirring for 7 h. ^b Isolated

yield.

Table S3 Study of aryl boron reagents^a



Entry	Boron reagents	Yield (%) ^b
1	Ph-B(OH) ₂	78
2	Ph-Bpin	35
3	Ph-BF ₃ K	12

^a Reaction conditions: 2-chlorobenzothiazole **1a** (0.2 mmol), phenyl boron reagent **2** (0.4 mmol) and K₂S₂O₅ (0.2 mmol) in 1 mL DES were heated to 110 °C with stirring for 7 h. ^b Isolated yield.

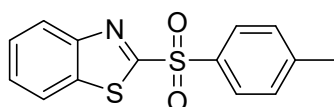
2.2 Preparation of DES.

A 1:2 molar ratio of ChCl/acetamide was heated with stirring until a clear colorless liquid was obtained. The mixture was used without further purification.^[1]

2.3 General procedures for sulfones in deep eutectic solvents.

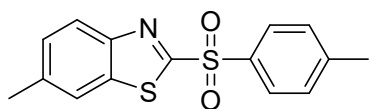
To a 50 mL test tube containing ChCl/acetamide (1 mL) was added 2-chlorobenzothiazole (**1a**) (0.2 mmol), *p*-methylphenylboronic acid (**2a**) (2.0 equiv.) and K₂S₂O₅ (2.0 equiv.). The resulting mixture was stirred at 110 °C for 7 h. The progress of the reaction was monitored by TLC (PE/EtOAc 4:1 v/v). After completion of the reaction, the mixture was cooled to room temperature and diluted with water (5 mL) and extracted with ethyl acetate (2×5 mL). The organic phases were dried over sodium sulfate. Filtration of the drying agent, and removal of all volatiles in vacuo gave a residue. Directly purified by flash chromatography to give the desired product.

3. Characterization of compounds



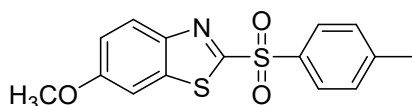
(**3a**) Light yellow solid, mp: 130.5-132.8 °C

^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 9.3$ Hz, 1H), 8.04 (d, $J = 8.3$ Hz, 2H), 7.95 (d, $J = 8.6$ Hz, 1H), 7.54 (dt, $J = 15.0, 7.8$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 2.43 (s, 3H).; ^{13}C NMR (126 MHz, CDCl_3) δ 167.66, 152.90, 145.97, 137.02, 135.43, 130.24, 129.03, 127.83, 127.49, 125.52, 122.23, 21.80.



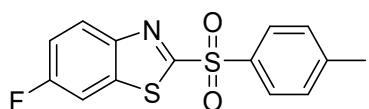
(3b) Light yellow solid, mp: 138.9-139.8 °C

^1H NMR (500 MHz, CDCl_3) δ 8.02 (t, $J = 8.1$ Hz, 3H), 7.73 (s, 1H), 7.37 (d, $J = 8.1$ Hz, 3H), 2.51 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.34, 151.08, 145.82, 138.55, 137.31, 135.64, 130.20, 129.31, 128.94, 124.96, 121.65, 21.82, 21.78.



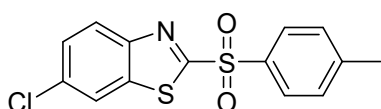
(3c) Light yellow solid, mp: 146.0-149.3 °C

^1H NMR (500 MHz, CDCl_3) δ 8.01 (dd, $J = 8.7, 7.4$ Hz, 3H), 7.36 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 2.5$ Hz, 1H), 7.15 (dd, $J = 9.1, 2.5$ Hz, 1H), 3.88 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 164.32, 159.62, 147.46, 145.72, 139.00, 135.79, 130.19, 128.85, 126.16, 118.01, 103.38, 55.93, 21.78.



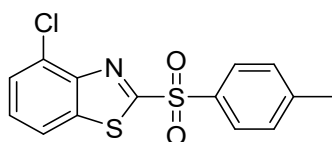
(3d) Light yellow solid, mp: 165.3-167.1 °C

^1H NMR (500 MHz, CDCl_3) δ 8.11 (dd, $J = 9.5, 5.0$ Hz, 1H), 8.03 (d, $J = 8.5$ Hz, 2H), 7.63 (dd, $J = 8.0, 3.0$ Hz, 1H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.31 (td, $J = 9.0, 2.5$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.30, 167.27, 162.68, 160.68, 149.45, 146.09, 135.65, 135.10, 130.24, 128.94, 126.85, 126.78, 116.92, 116.72, 108.31, 108.09, 21.73. ^{19}F NMR (CDCl_3 , 376 MHz, 298 K) $\delta = -110.41$.



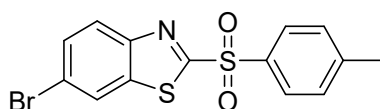
(3e) Light yellow solid, mp: 181.9-183.6 °C

^1H NMR (500 MHz, CDCl_3) δ 8.04 (dd, $J = 8.5, 7.4$ Hz, 3H), 7.93 (d, $J = 2.0$ Hz, 1H), 7.52 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.39 (d, $J = 8.4$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.22, 151.39, 146.21, 138.07, 135.13, 134.09, 130.32, 129.08, 128.59, 126.28, 121.77, 21.82.



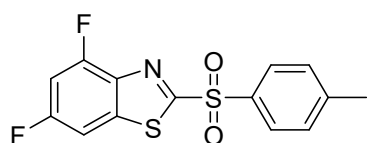
(3f) Light yellow solid, mp: 124.7-126.2 °C

^1H NMR (500 MHz, CDCl_3) δ 8.06 (d, $J = 8.1$ Hz, 2H), 7.83 (d, $J = 8.1$ Hz, 1H), 7.57 (d, $J = 7.7$ Hz, 1H), 7.44 (t, $J = 8.0$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.34, 150.16, 146.11, 138.21, 134.98, 130.34, 130.18, 129.11, 128.26, 127.64, 120.65, 21.75.



(3g) Light yellow solid, mp: 189.1-189.9 °C

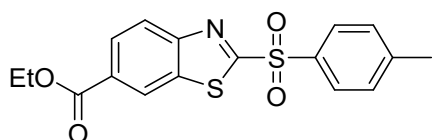
^1H NMR (500 MHz, CDCl_3) δ 8.10 (d, $J = 1.1$ Hz, 1H), 8.03 (d, $J = 8.2$ Hz, 2H), 7.99 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.8$ Hz, 1H), 7.39 (d, $J = 8.1$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.13, 151.58, 146.18, 138.35, 135.65, 134.96, 130.26, 130.00, 128.73, 126.44, 124.68, 121.84, 21.75.



(3h) Light yellow solid, mp: 161.8-163.3 °C

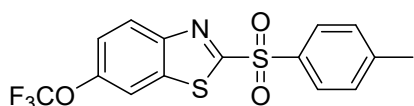
^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 7.3$ Hz, 1H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.07 (t, $J = 8.4$ Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.85, 162.72, 160.65, 157.61, 155.52, 146.31, 139.65, 139.07, 134.73, 130.27, 129.10, 104.10, 103.80, 21.80.

^{19}F NMR (CDCl_3 , 376 MHz, 298 K) $\delta = -106.53, -113.18$.



(3i) Light yellow solid, mp: 148.1-150.7 °C

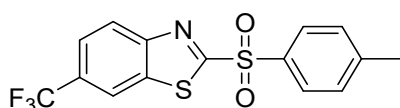
^1H NMR (500 MHz, CDCl_3) δ 8.61 (d, $J = 1.3$ Hz, 1H), 8.15 (dd, $J = 8.7, 1.5$ Hz, 1H), 8.09 (d, $J = 8.7$ Hz, 1H), 7.98 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.3$ Hz, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 2.37 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.89, 164.37, 154.41, 145.28, 135.72, 133.86, 129.29, 128.70, 128.15, 127.28, 124.19, 123.40, 60.70, 20.78, 13.28.



(3j) White solid, mp: 124.0-125.1 °C

^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, $J = 9.1$ Hz, 1H), 8.03 (d, $J = 8.2$ Hz, 2H), 7.82 (s, 1H), 7.44 (d, $J = 9.0$ Hz, 1H), 7.39 (d, $J = 7.9$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.89, 151.13, 148.13, 146.24, 137.82, 134.91, 130.27, 129.01, 126.61, 121.52, 114.30, 21.73.

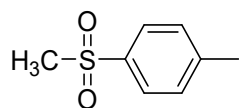
^{19}F NMR (CDCl_3 , 376 MHz, 298 K) $\delta = -57.94$.



(3k) Light yellow solid, mp: 137.6-138.5 °C

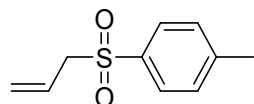
^1H NMR (500 MHz, CDCl_3) δ 8.30-8.23 (m, 2H), 8.05 (d, $J = 8.2$ Hz, 2H), 7.80 (d, $J = 8.6$ Hz, 1H), 7.40 (d, $J = 8.1$ Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.06, 154.67, 146.44, 136.90, 134.78, 130.37, 129.83 (q, $J_{\text{C-F}} = 32.76$ Hz), 129.20, 126.05, 124.33 (q, $J_{\text{C-F}} = 3.78$ Hz), 123.60 (q, $J_{\text{C-F}} = 273.42$ Hz), 120.14 (q, $J_{\text{C-F}} = 3.78$ Hz), 21.82.

^{19}F NMR (CDCl_3 , 376 MHz, 298 K) $\delta = -61.80$



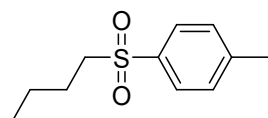
(3m) Light yellow solid, mp: 87.8-88.3 °C

¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 3.04 (s, 3H), 2.46 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 144.69, 137.67, 129.96, 127.36, 44.61, 21.62.



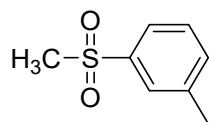
(3n) Light yellow solid, mp: 50.2-51.3 °C

¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 5.79 (td, *J* = 17.1, 7.5 Hz, 1H), 5.33 (d, *J* = 10.1 Hz, 1H), 5.15 (d, *J* = 17.1 Hz, 1H), 3.80 (d, *J* = 7.2 Hz, 2H), 2.45 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 144.78, 135.19, 129.70, 128.45, 124.76, 124.62, 60.88, 21.63.



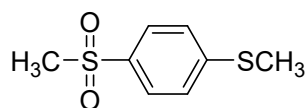
(3o) Light yellow liquid

¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 3.07 (dd, *J* = 9.7, 6.5 Hz, 2H), 2.46 (s, 3H), 1.71-1.64 (m, 2H), 1.42-1.34 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 144.58, 136.22, 129.88, 128.09, 56.18, 24.72, 21.65, 21.56, 13.54.



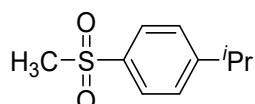
(3p) Light yellow solid, mp: 34.1-35.5 °C

¹H NMR (500 MHz, CDCl₃) δ 7.82-7.68 (m, 2H), 7.52-7.40 (m, 2H), 3.05 (s, 3H), 2.46 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 140.39, 139.71, 134.51, 129.27, 127.67, 124.45, 44.52, 21.36.



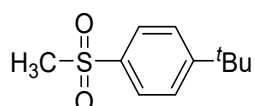
(3q) White solid, mp: 98.0-99.4 °C

^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 2H), 3.04 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 147.25, 136.16, 127.67, 125.48, 44.71, 14.78.



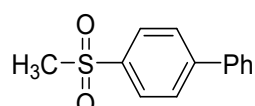
(3r) Light yellow liquid

^1H NMR (500 MHz, CDCl_3) δ 7.86 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H), 3.05 (s, 3H), 1.28 (d, $J = 7.0$ Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 155.37, 137.91, 127.52, 127.49, 44.60, 34.27, 23.66.



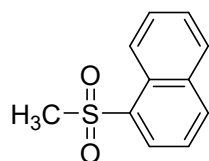
(3s) Light yellow solid, mp: 94.2-96.3 °C

^1H NMR (500 MHz, CDCl_3) δ 7.87 (d, $J = 8.3$ Hz, 2H), 7.58 (d, $J = 8.3$ Hz, 2H), 3.05 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 157.65, 137.57, 127.24, 126.39, 44.60, 35.29, 31.09.



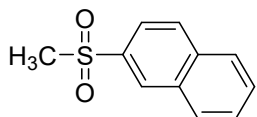
(3t) Light yellow solid, mp: 143.7-144.5 °C

^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, $J = 8.1$ Hz, 2H), 7.78 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 7.6$ Hz, 2H), 7.50 (t, $J = 7.3$ Hz, 2H), 7.46-7.42 (m, 1H), 3.10 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.75, 139.14, 139.07, 129.15, 128.73, 128.03, 127.96, 127.43, 44.67.



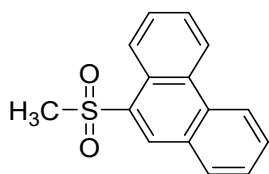
(3u) Light yellow solid, mp: 218.1-219.5 °C

^1H NMR (500 MHz, CDCl_3) δ 8.72 (d, $J = 8.6$ Hz, 1H), 8.33 (d, $J = 7.3$ Hz, 1H), 8.12 (d, $J = 8.2$ Hz, 1H), 7.97 (d, $J = 8.2$ Hz, 1H), 7.77-7.68 (m, 1H), 7.67-7.51 (m, 2H), 3.21 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 135.53, 135.25, 134.21, 129.68, 129.39, 128.83, 128.64, 127.09, 124.51, 123.90, 44.29.



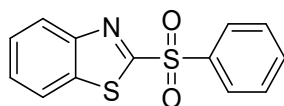
(3v) Light yellow solid, mp: 100.4-102.3 °C

^1H NMR (500 MHz, CDCl_3) δ 8.53 (s, 1H), 8.01 (t, $J = 9.3$ Hz, 2H), 7.92 (dd, $J = 15.3, 8.3$ Hz, 2H), 7.66 (dt, $J = 14.8, 7.0$ Hz, 2H), 3.13 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 137.40, 135.31, 132.18, 129.80, 129.45, 129.34, 129.10, 128.04, 127.84, 122.16, 44.60.



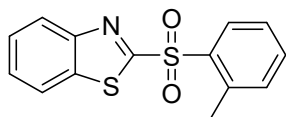
(3w) Light yellow solid, mp: 118.3-119.7 °C

^1H NMR (500 MHz, CDCl_3) δ 8.78 (s, 2H), 8.69 (s, 2H), 8.03 (d, $J = 6.8$ Hz, 1H), 7.86-7.66 (m, 4H), 3.27 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 134.17, 132.78, 132.65, 131.33, 130.79, 130.24, 129.24, 128.17, 127.82, 127.77, 126.19, 124.92, 123.73, 122.83, 44.17.



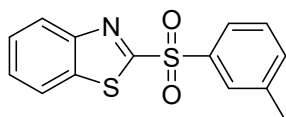
(4b) Light yellow solid, mp: 157.5-158.9 °C

^1H NMR (500 MHz, CDCl_3) δ 8.17 (t, $J = 6.8$ Hz, 3H), 7.96 (d, $J = 8.1$ Hz, 1H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.61-7.52 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.26, 152.93, 138.47, 137.07, 134.63, 129.58, 128.98, 127.94, 127.57, 125.59, 122.26.



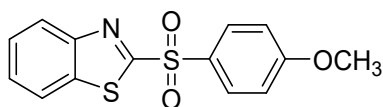
(4c) Light yellow solid, mp: 116.4-117.2 °C

^1H NMR (500 MHz, CDCl_3) δ 8.29 (d, $J = 8.0$ Hz, 1H), 8.14 (d, $J = 8.7$ Hz, 1H), 7.96 (d, $J = 7.5$ Hz, 1H), 7.61-7.51 (m, 3H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.70, 152.67, 139.76, 136.89, 136.71, 134.76, 132.96, 130.78, 127.86, 127.48, 126.87, 125.55, 122.19, 20.85.



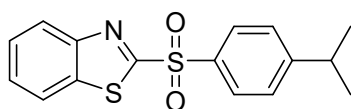
(4d) Light yellow solid, mp: 140.4-142.1 °C

^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.2$ Hz, 3H), 7.56 (dt, $J = 20.6, 7.4$ Hz, 2H), 7.46 (d, $J = 5.4$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.41, 152.89, 139.93, 138.24, 137.05, 135.44, 129.40, 129.14, 127.85, 127.49, 126.10, 125.53, 122.21, 21.33.



(4e) Light yellow solid, mp: 117.4-118.9 °C

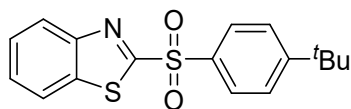
^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.1$ Hz, 1H), 8.09 (d, $J = 8.9$ Hz, 2H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.54 (dt, $J = 21.4, 7.3$ Hz, 2H), 7.03 (d, $J = 8.9$ Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.03, 164.60, 152.96, 136.94, 131.35, 129.61, 127.75, 127.45, 125.45, 122.22, 114.88, 55.82.



(4f) White solid, mp: 126.3-127.8 °C

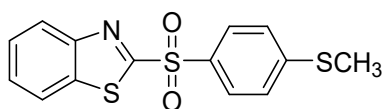
^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, $J = 8.1$ Hz, 1H), 8.08 (d, $J = 8.3$ Hz, 2H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.55 (dt, $J = 21.2, 7.3$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H), 3.02-2.93 (m, 1H), 1.25 (d, $J = 6.9$ Hz,

6H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.66, 156.52, 152.93, 137.07, 135.67, 129.16, 127.83, 127.78, 127.50, 125.54, 122.25, 34.39, 23.57.



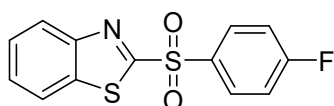
(4g) Light yellow solid, mp: 203.2-205.9 °C

^1H NMR (500 MHz, CDCl_3) δ 8.17 (d, $J = 8.1$ Hz, 1H), 8.08 (d, $J = 8.4$ Hz, 2H), 7.96 (d, $J = 7.9$ Hz, 1H), 7.62-7.50 (m, 4H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.67, 158.77, 152.94, 137.09, 135.35, 128.86, 127.82, 127.49, 126.68, 125.54, 122.24, 35.41, 31.00.



(4h) White solid, mp: 127.5-128.9 °C

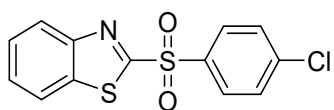
^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 8.2$ Hz, 1H), 8.02 (d, $J = 8.6$ Hz, 2H), 7.96 (d, $J = 8.1$ Hz, 1H), 7.55 (dt, $J = 14.5, 6.8$ Hz, 2H), 7.34 (d, $J = 8.6$ Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.55, 152.88, 148.87, 136.96, 133.61, 129.15, 127.82, 127.49, 125.48, 125.45, 122.20, 14.62.



(4i) White solid, mp: 151.5-153.1 °C

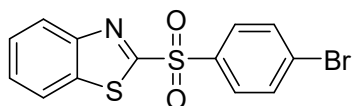
^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.23-8.13 (m, 3H), 7.97 (d, $J = 7.7$ Hz, 1H), 7.62 – 7.52 (m, 2H), 7.26 (t, $J = 8.5$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.01, 165.38 (d, $J = 259.56$ Hz), 152.86, 134.40 (d, $J = 2.52$ Hz), 132.06 (d, $J = 5.04$ Hz), 128.00, 127.62, 125.53, 122.25, 117.08, 116.89.

^{19}F NMR (CDCl_3 , 376 MHz, 298 K) $\delta = -101.40$.



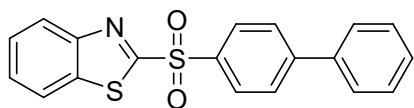
(4j) Light yellow solid, mp: 160.3-162.1 °C

^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 7.9$ Hz, 1H), 8.10 (d, $J = 8.7$ Hz, 2H), 7.97 (d, $J = 8.1$ Hz, 1H), 7.61-7.54 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.77, 152.90, 141.60, 137.01, 136.86, 130.44, 129.96, 128.11, 127.70, 125.60, 122.30.



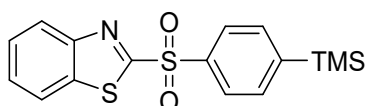
(4k) Light yellow solid, mp: 166.2-168.7 °C

^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, $J = 8.5$ Hz, 1H), 8.02 (d, $J = 8.7$ Hz, 2H), 7.97 (d, $J = 8.6$ Hz, 1H), 7.73 (d, $J = 8.7$ Hz, 2H), 7.57 (dt, $J = 15.0, 6.7$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.69, 152.88, 137.40, 136.99, 132.90, 130.42, 130.26, 128.06, 127.66, 125.57, 122.25.



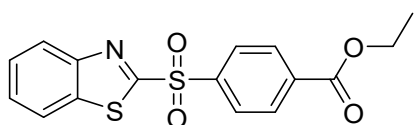
(4l) White solid, mp: 185.2-187.5 °C

^1H NMR (500 MHz, CDCl_3) δ 8.22 (d, $J = 8.4$ Hz, 2H), 8.17 (d, $J = 8.3$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 8.5$ Hz, 2H), 7.61-7.52 (m, 4H), 7.47 (t, $J = 7.3$ Hz, 2H), 7.44-7.40 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.43, 152.97, 147.62, 138.93, 137.09, 136.84, 129.54, 129.15, 128.89, 128.20, 127.93, 127.57, 127.46, 125.59, 122.27.



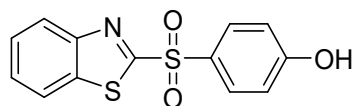
(4m) White solid, mp: 142.1-144.9 °C

^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, $J = 7.7$ Hz, 1H), 8.11 (d, $J = 7.5$ Hz, 2H), 7.96 (d, $J = 7.5$ Hz, 1H), 7.72 (d, $J = 7.5$ Hz, 2H), 7.55 (dd, $J = 13.1, 7.9$ Hz, 2H), 0.28 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.83, 154.39, 151.16, 139.96, 138.55, 135.79, 129.33, 129.09, 128.97, 127.02, 123.69, 0.00.



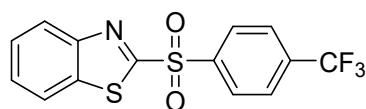
(4n) Light yellow solid, mp: 133.1-135.2 °C

^1H NMR (500 MHz, CDCl_3) δ 8.24 (s, 4H), 8.16 (d, $J = 8.1$ Hz, 1H), 7.98 (d, $J = 7.8$ Hz, 1H), 7.62-7.53 (m, 2H), 4.41 (q, $J = 7.1$ Hz, 2H), 1.40 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.49, 164.82, 152.93, 142.11, 137.09, 135.85, 130.59, 129.02, 128.16, 127.72, 125.65, 122.30, 61.92.



(4o) White solid, mp: 191.6-194.0 °C

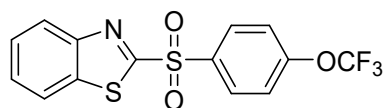
^1H NMR (500 MHz, CDCl_3) δ 11.04 (s, 1H), 8.25 (d, $J = 54.5$ Hz, 2H), 7.81 (d, $J = 144.3$ Hz, 4H), 7.16-6.93 (m, 2H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 168.89, 164.14, 152.70, 136.63, 131.83, 128.49, 128.39, 127.20, 125.20, 123.92, 117.12.



(4p) White solid, mp: 160.8-163.2 °C

^1H NMR (500 MHz, CDCl_3) δ 8.31 (d, $J = 8.2$ Hz, 2H), 8.17 (d, $J = 8.1$ Hz, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.86 (d, $J = 8.3$ Hz, 2H), 7.64-7.55 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.14, 152.94, 142.04, 137.07, 136.05 (d, $J_{\text{C-F}}=34.02$ Hz), 129.59, 128.25, 127.78, 126.66 (d, $J_{\text{C-F}}=3.78$ Hz), 122.97 (d, $J_{\text{C-F}}=273.42$ Hz), 125.68, 122.30.

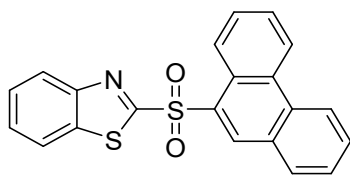
^{19}F NMR (CDCl_3 , 376 MHz, 298 K) $\delta = -63.30$.



(4q) White solid, mp: 123.6-124.5 °C

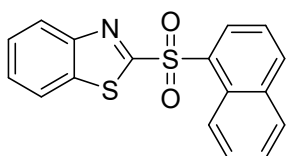
^1H NMR (500 MHz, CDCl_3) δ 8.23 (d, $J = 8.7$ Hz, 2H), 8.17 (d, $J = 8.1$ Hz, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 7.58 (dt, $J = 15.0, 7.2$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.67, 153.65, 152.94, 137.05, 136.58, 131.36, 128.13, 127.71, 125.63, 122.30, 121.13, 120.15 (q, $J=260.82$ Hz).

^{19}F NMR (CDCl_3 , 376 MHz, 298 K) $\delta = -57.61$.



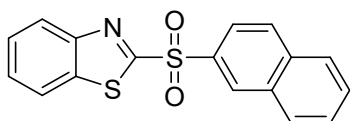
(4r) Light yellow solid, mp: 181.1-182.9 °C

^1H NMR (500 MHz, CDCl_3) δ 9.02 (s, 1H), 8.98 (dd, $J = 5.9, 3.7$ Hz, 1H), 8.68 (dd, $J = 6.1, 3.4$ Hz, 1H), 8.64 (d, $J = 8.4$ Hz, 1H), 8.08 (dd, $J = 14.0, 7.8$ Hz, 2H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.81 (t, $J = 7.7$ Hz, 1H), 7.73-7.66 (m, 3H), 7.53-7.45 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.34, 152.51, 137.05, 135.12, 133.23, 132.39, 131.26, 131.18, 130.80, 129.22, 128.03, 127.93, 127.87, 127.84, 127.49, 125.96, 125.82, 125.58, 123.37, 122.87, 122.18.



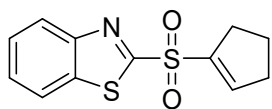
(4s) Light yellow solid, mp: 201.1-204.3 °C

^1H NMR (500 MHz, CDCl_3) δ 8.99 (d, $J=8.5$ Hz, 1H), 8.65 (d, $J=7.5$ Hz, 1H), 8.17 (d, $J=8.0$ Hz, 1H), 8.10 (d, $J=7.5$, 1H), 7.92 (d, $J = 8.0$ Hz, 2H), 7.70-7.65 (m, 2H), 7.58 (t, $J=7.5$ Hz, 1H), 7.54-7.48 (m, 2H); ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 167.37, 152.49, 136.98, 136.46, 134.15, 133.58, 131.61, 129.03, 128.84, 127.82, 127.39, 127.19, 125.54, 124.79, 124.53, 122.10.



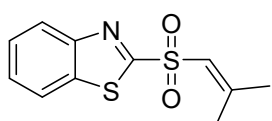
(4t) Light yellow solid, mp: 153.1-155.9 °C

^1H NMR (500 MHz, CDCl_3) δ 8.77 (s, 1H), 8.17-8.07 (m, 2H), 8.00 (t, $J = 10.0$ Hz, 2H), 7.94 (d, $J = 7.9$ Hz, 1H), 7.89 (d, $J = 8.1$ Hz, 1H), 7.64 (dt, $J = 14.9, 7.2$ Hz, 2H), 7.58-7.49 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.31, 152.88, 137.02, 135.63, 135.20, 132.15, 131.11, 129.87, 129.84, 129.67, 127.99, 127.87, 127.85, 127.50, 125.51, 123.11, 122.19.



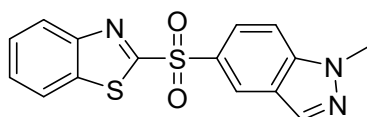
(4u) Light yellow solid, mp: 113.5-114.1 °C

¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.61 (dt, *J* = 22.7, 7.3 Hz, 2H), 7.11 (s, 1H), 2.79 (t, *J* = 6.6 Hz, 2H), 2.69-2.61 (m, 2H), 2.16-2.08 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 166.37, 152.96, 148.73, 142.24, 137.05, 127.91, 127.56, 125.56, 122.30, 33.49, 31.24, 23.69.



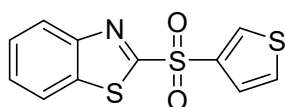
(4v) Light yellow solid, mp: 98.1-98.5 °C

¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.60 (dt, *J* = 16.3, 7.6 Hz, 2H), 6.42 (s, 1H), 2.30 (s, 3H), 2.01 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.31, 160.62, 152.87, 136.79, 127.79, 127.51, 125.43, 123.64, 122.28, 27.62, 20.15.



(4w) White solid, mp: 176.9-178.5 °C

¹H NMR (500 MHz, CDCl₃) δ 8.65 (s, 1H), 8.17 (s, 1H), 8.12 (t, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.58-7.49 (m, 3H), 4.11 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.87, 152.88, 141.56, 136.93, 135.06, 130.34, 127.82, 127.50, 125.53, 125.46, 125.16, 123.58, 122.23, 110.24, 36.00.

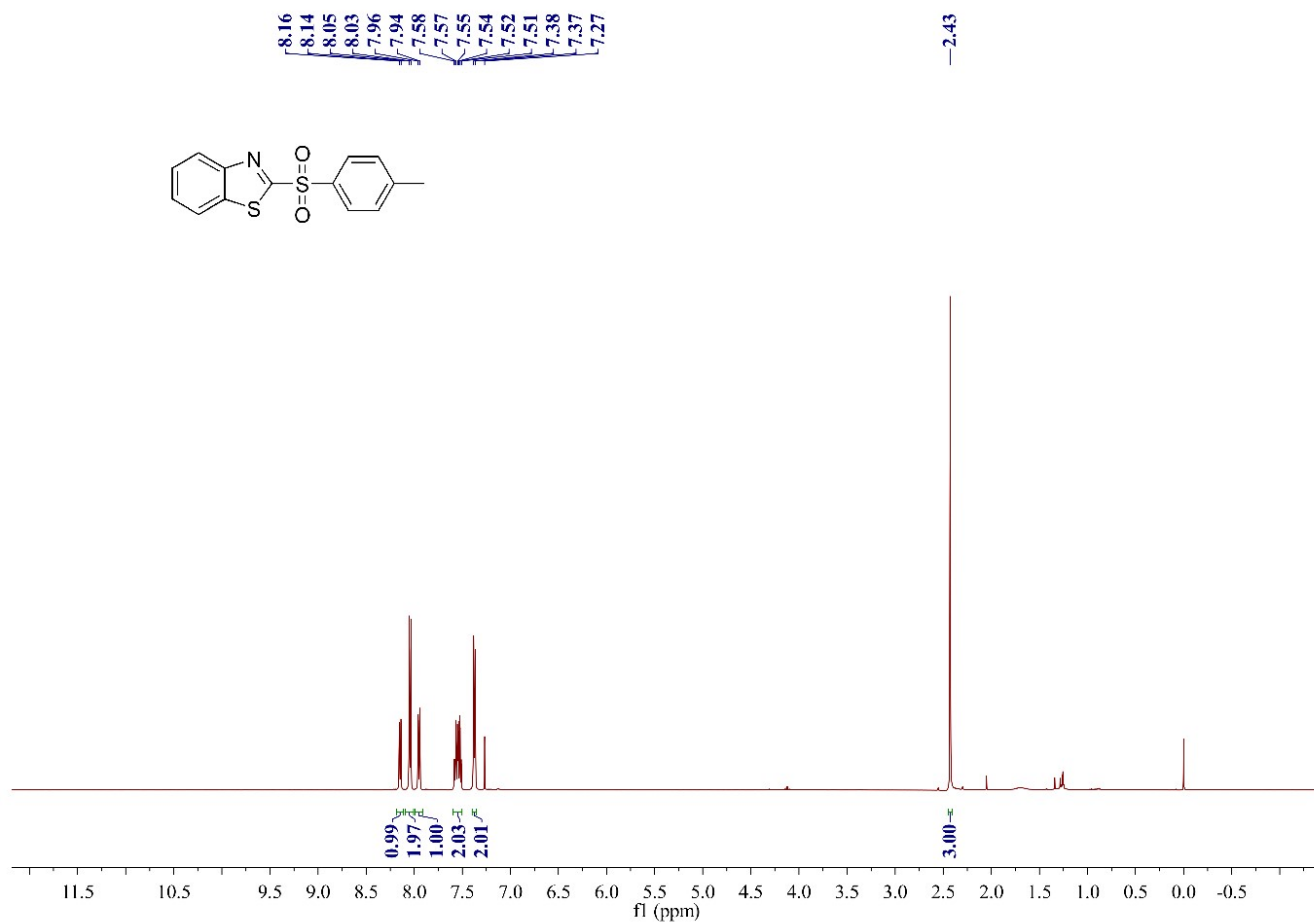


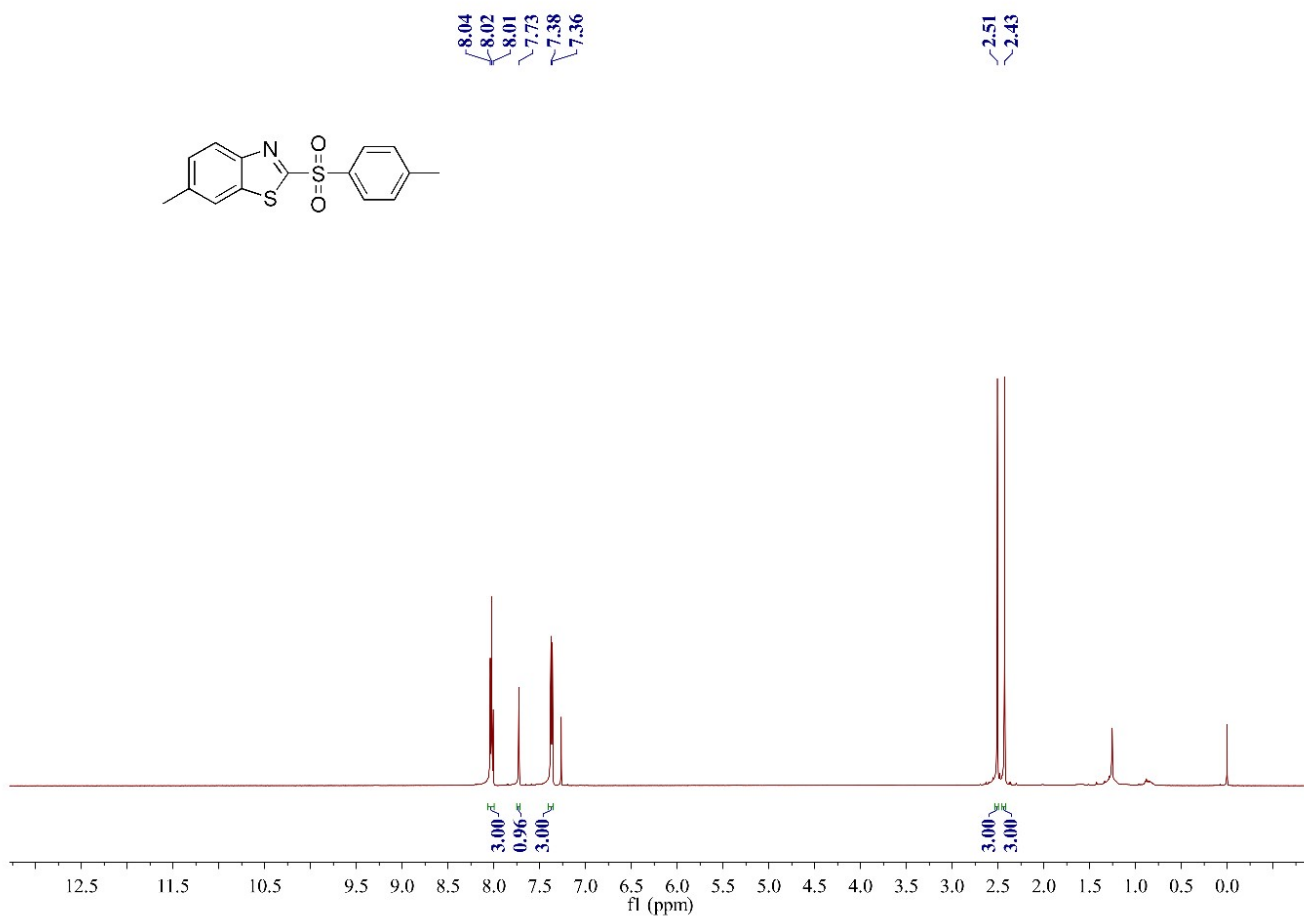
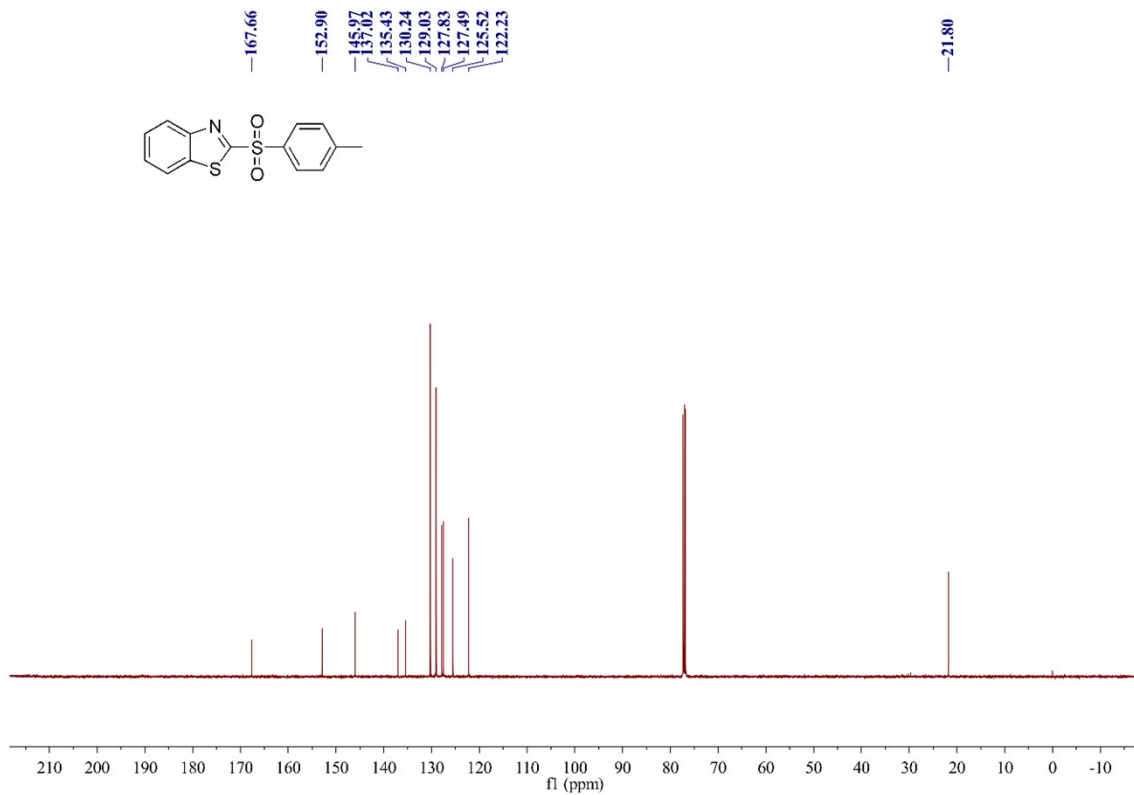
(4x) Light yellow solid, mp: 173.2-175.1 °C

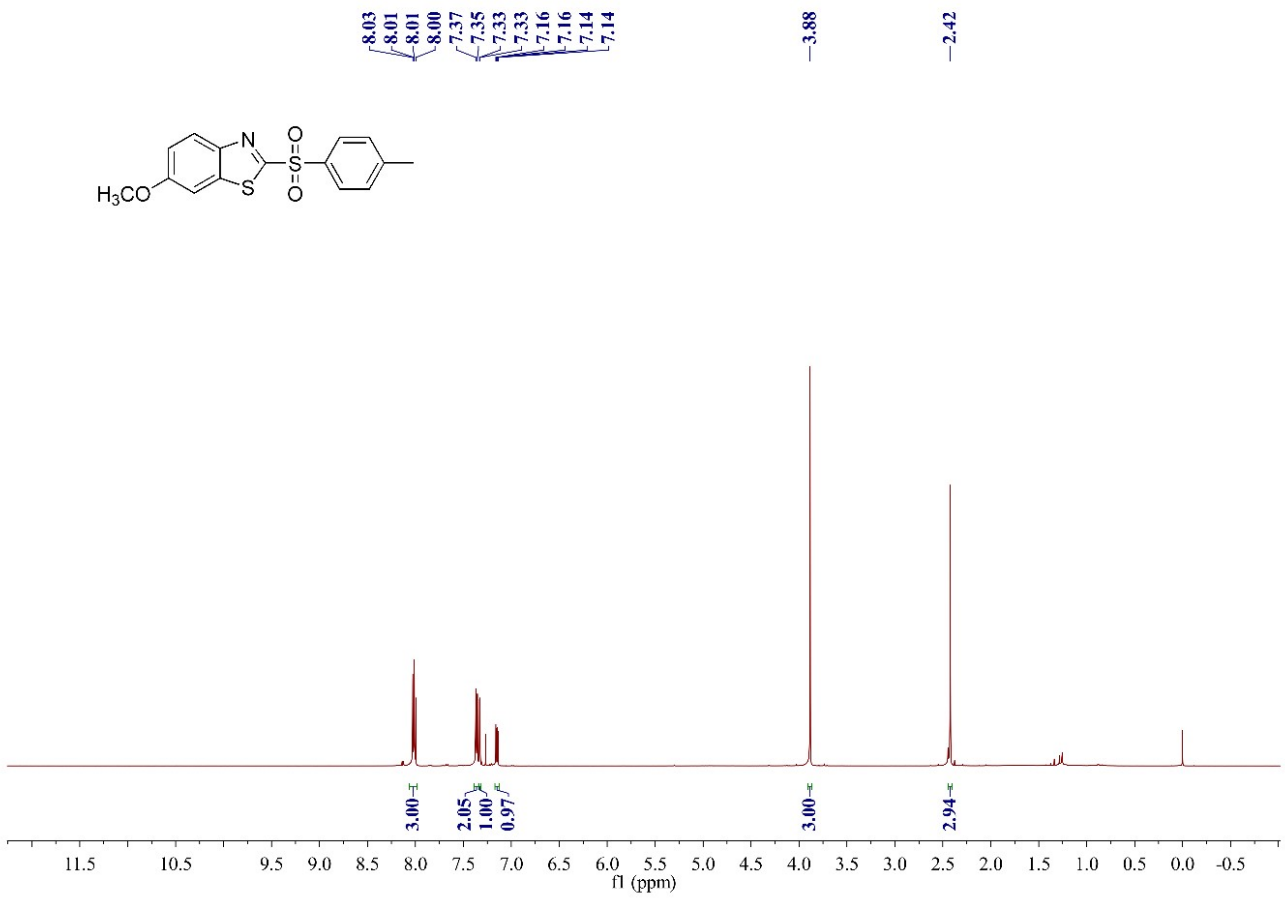
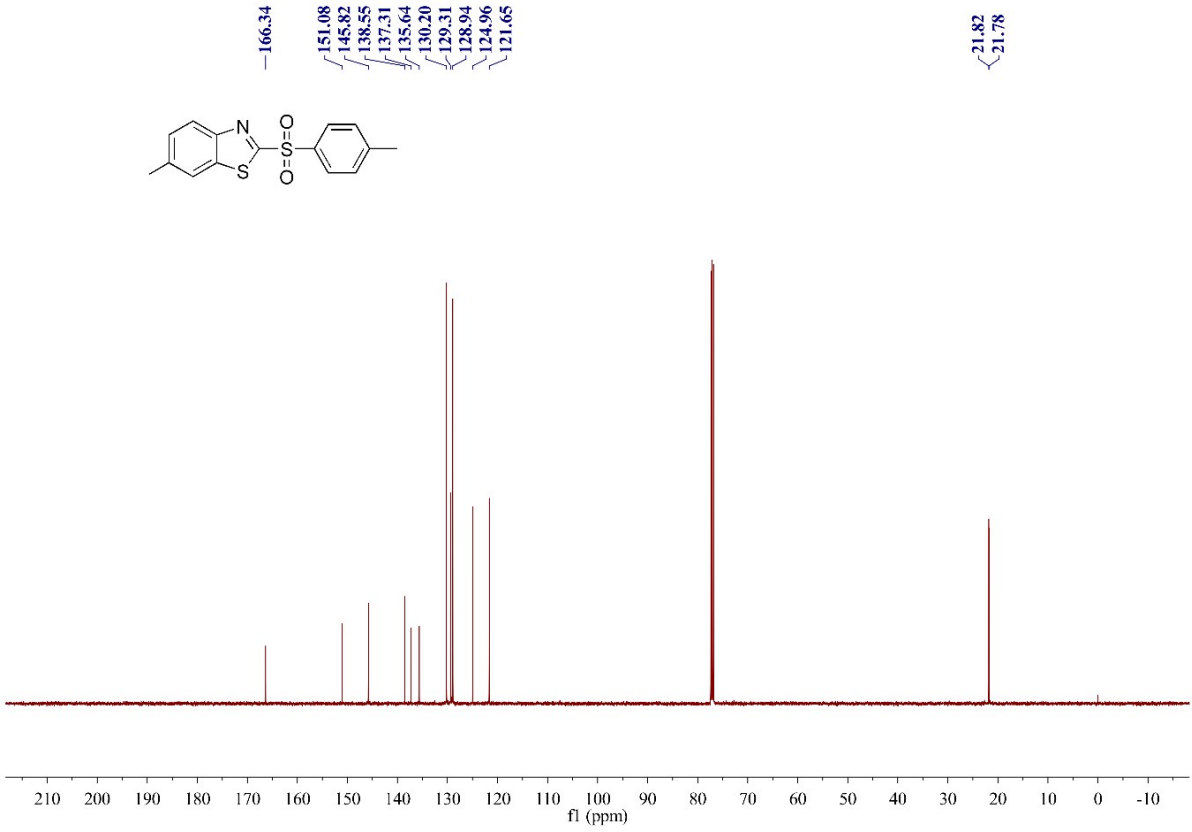
¹H NMR (500 MHz, CDCl₃) δ 8.37 (dd, *J* = 3.0, 1.0 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.61-7.54 (m, 3H), 7.47 (dd, *J* = 5.0, 3.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 167.20,

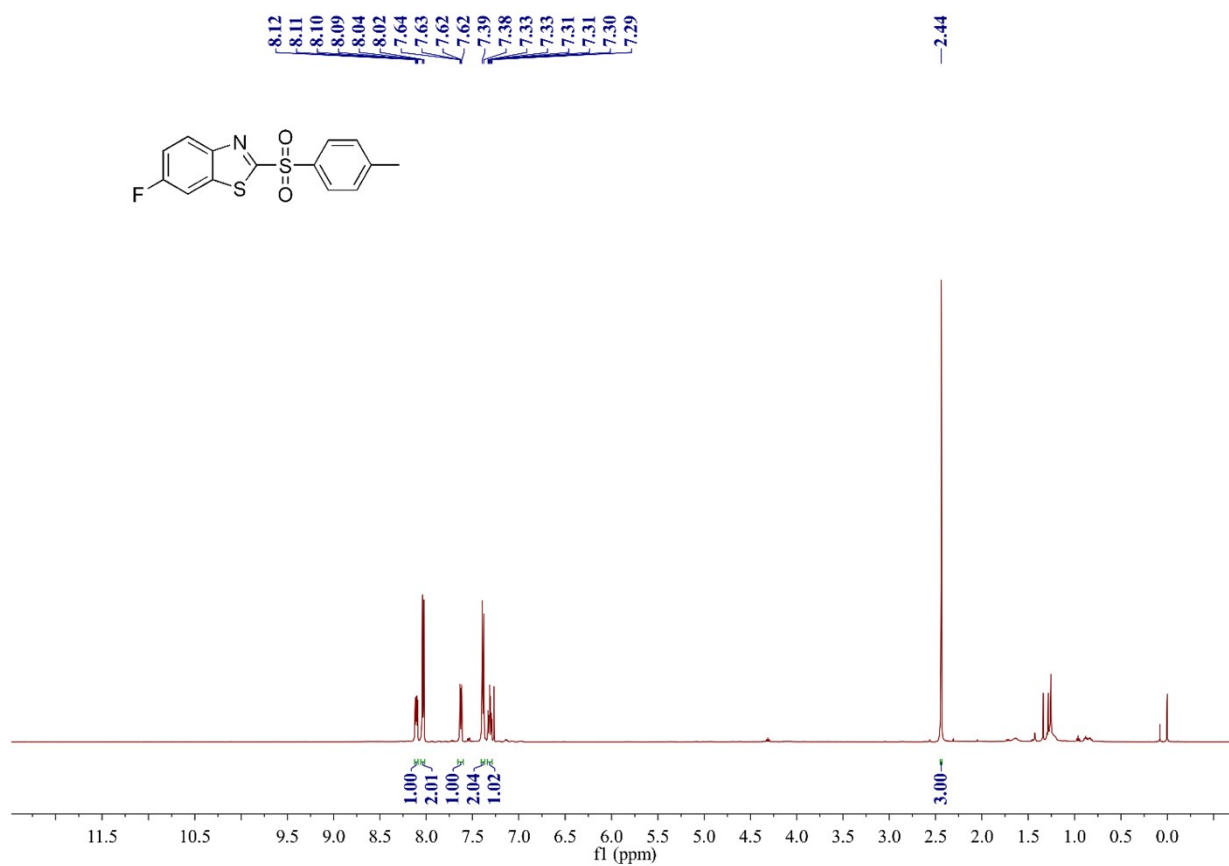
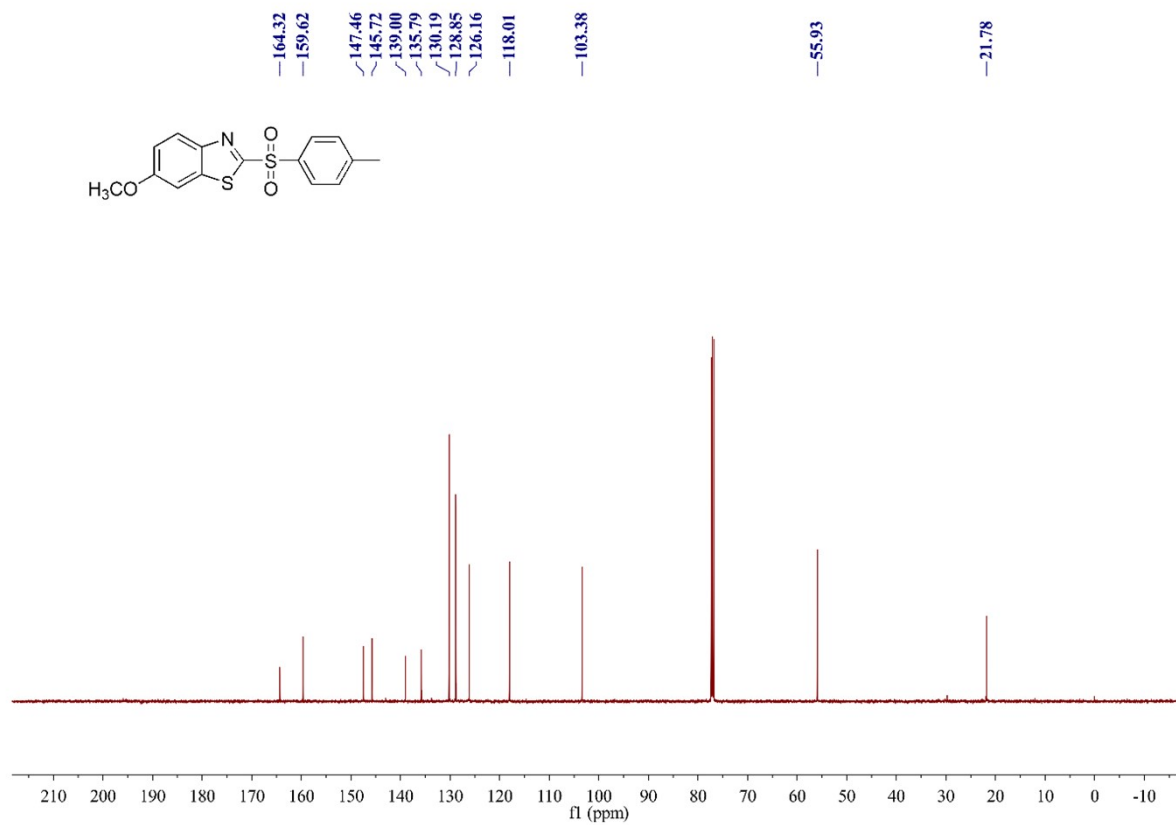
152.86, 138.52, 137.04, 134.68, 128.74, 127.99, 127.62, 126.61, 125.58, 122.29.

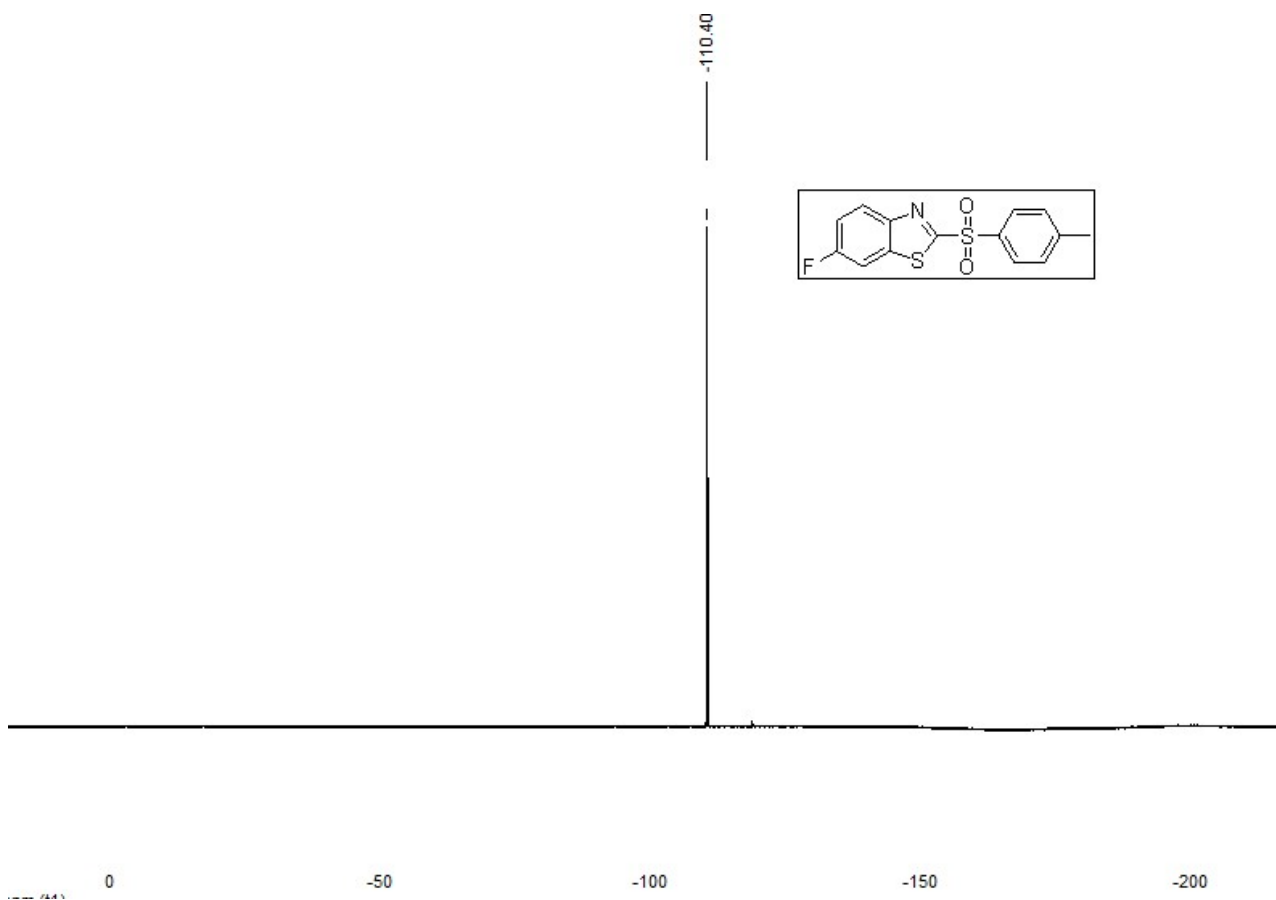
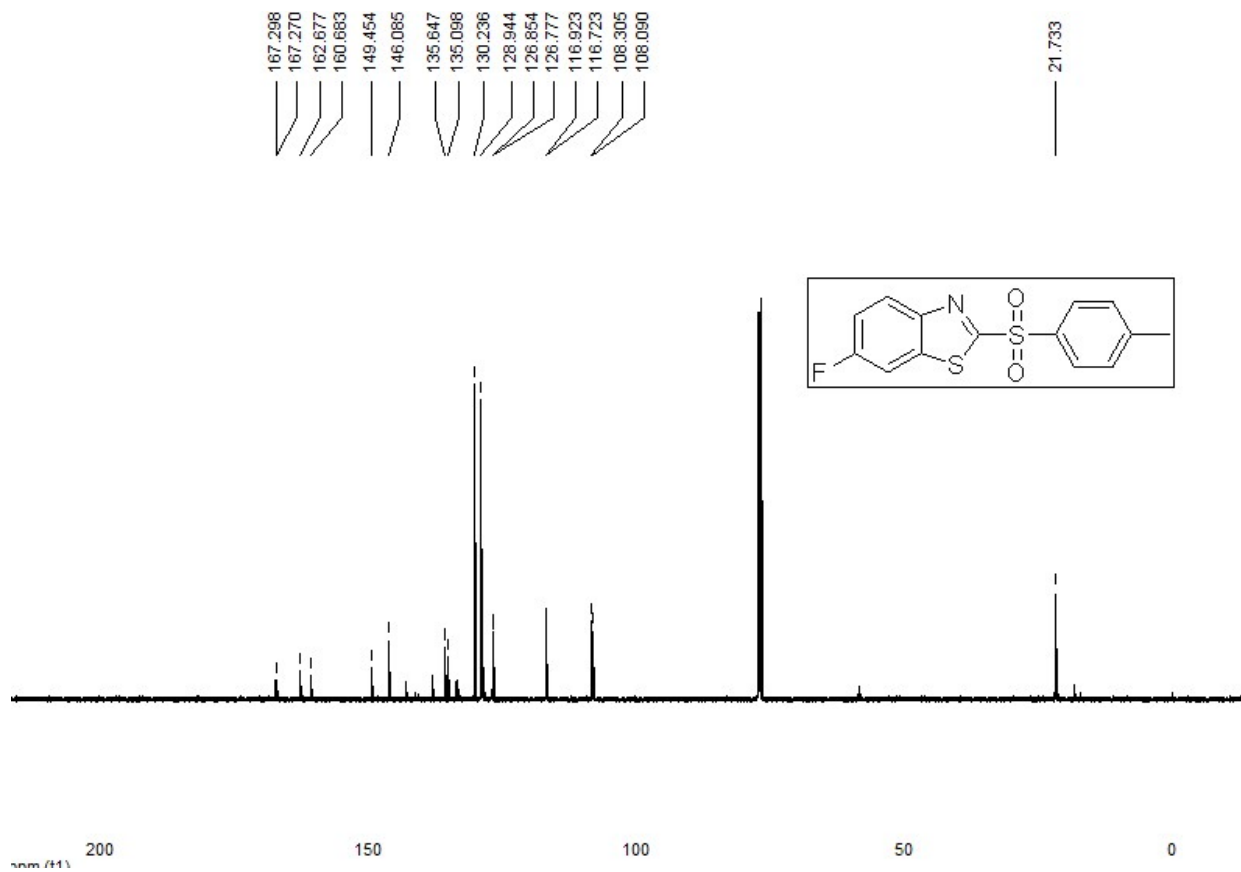
4. ^1H NMR spectra and ^{13}C NMR spectra for compounds

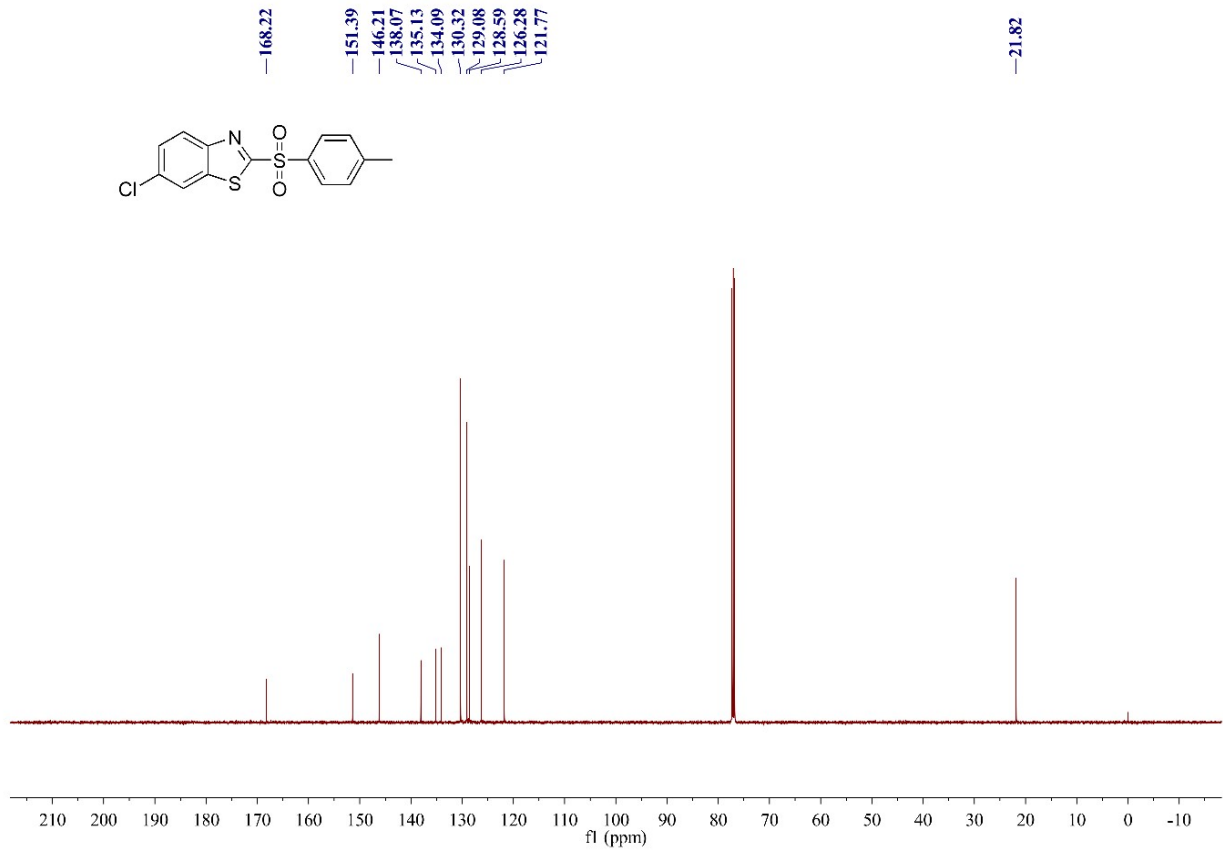
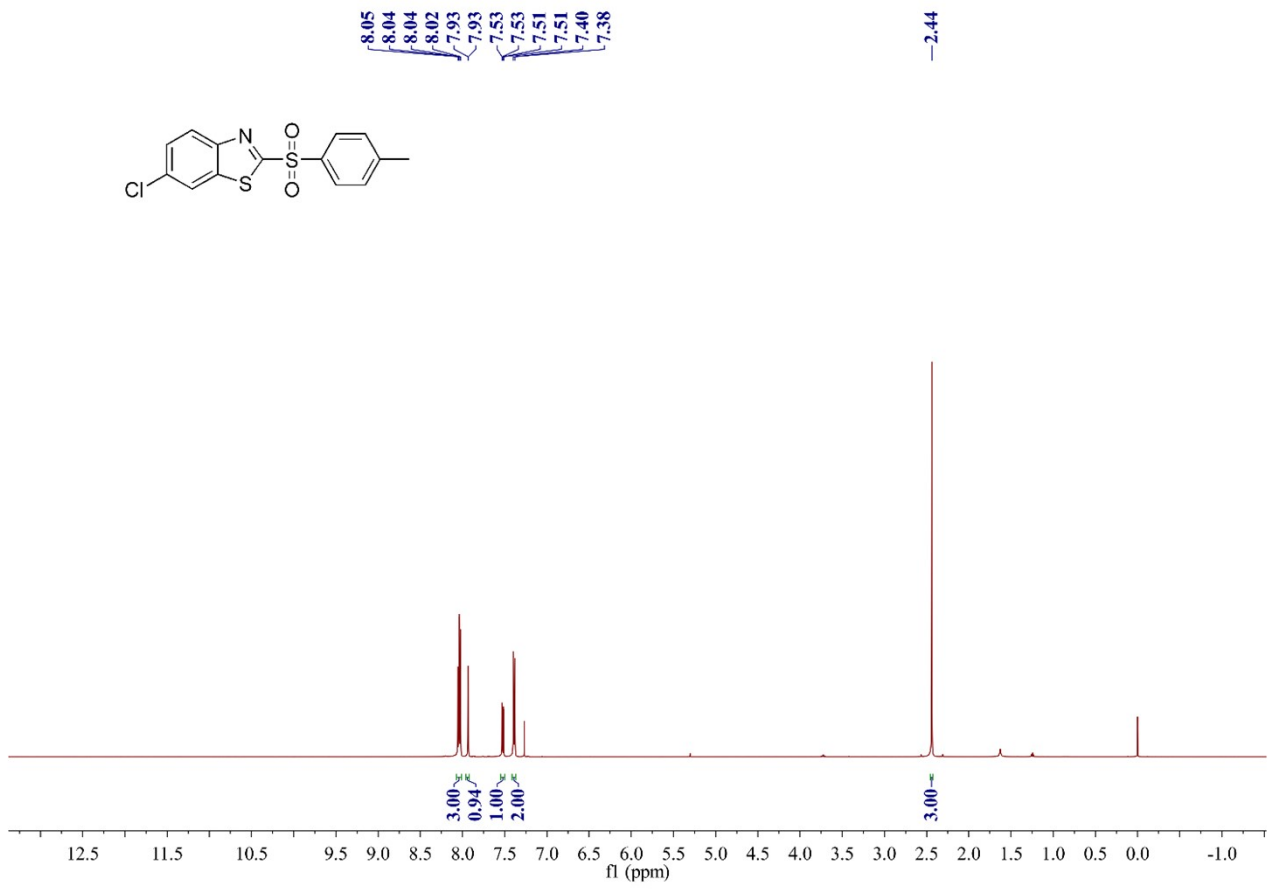


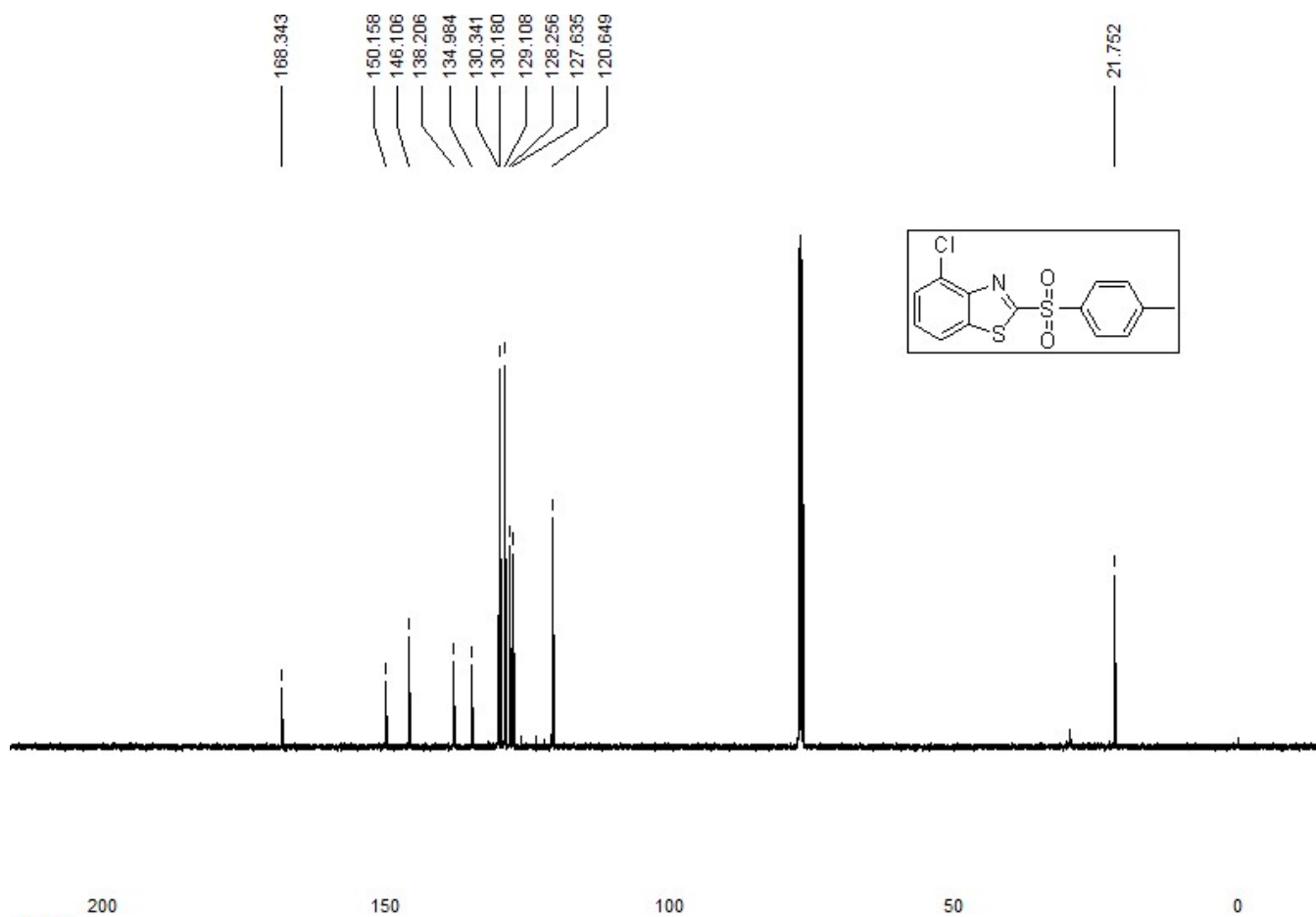
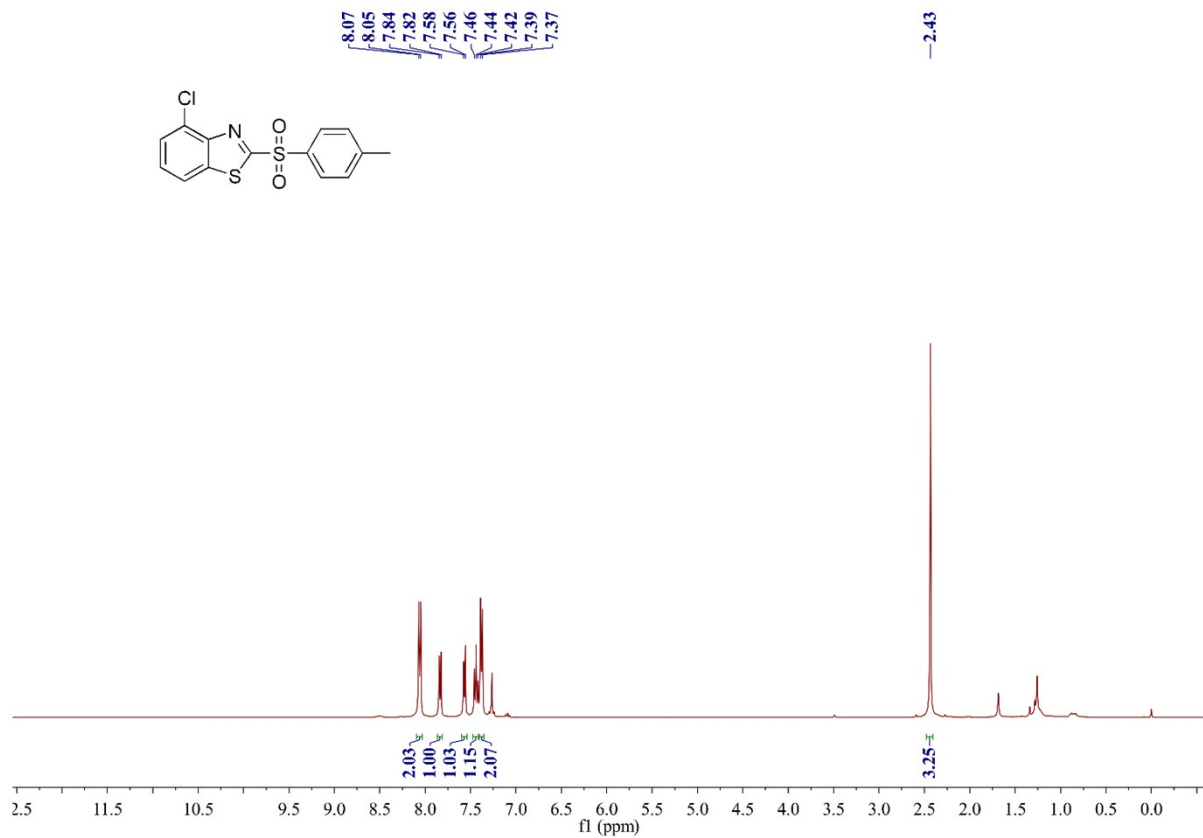


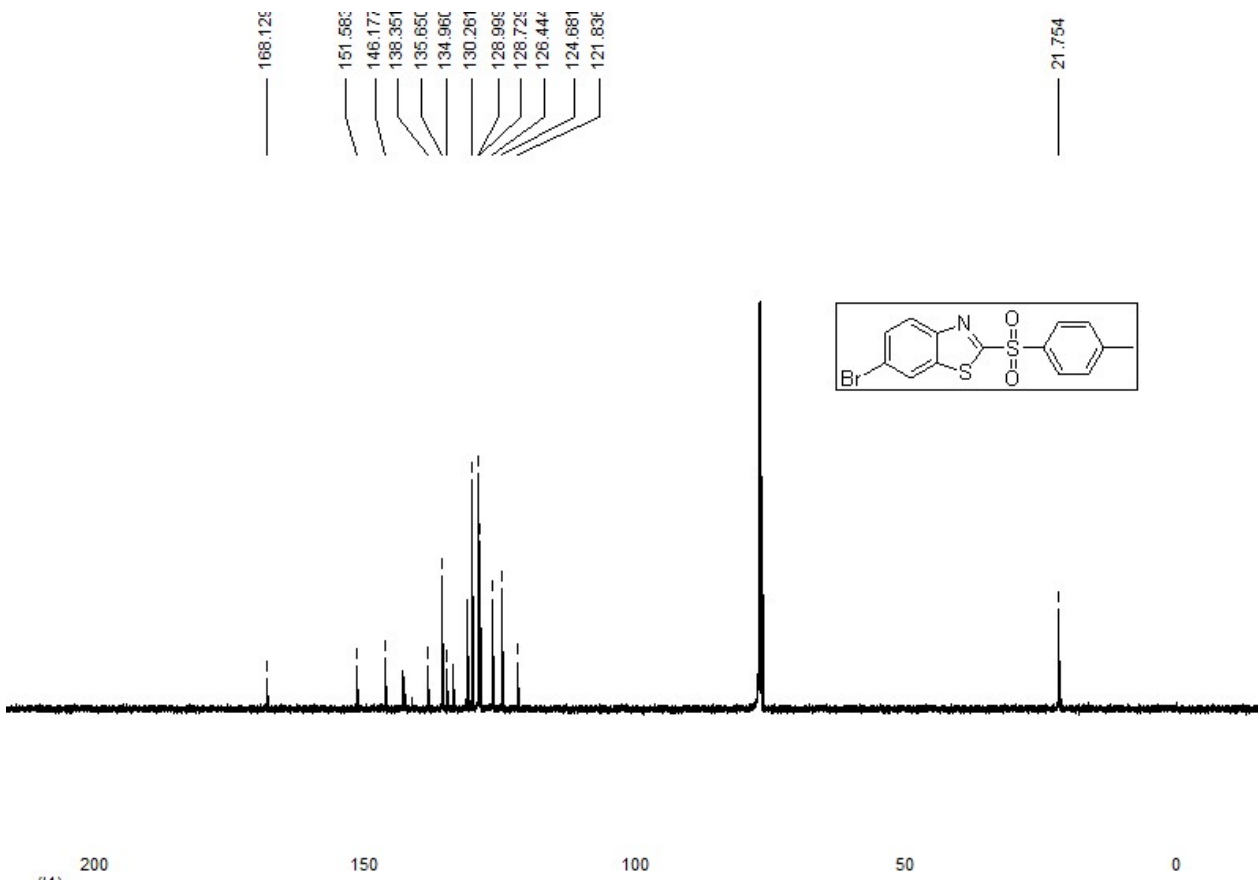
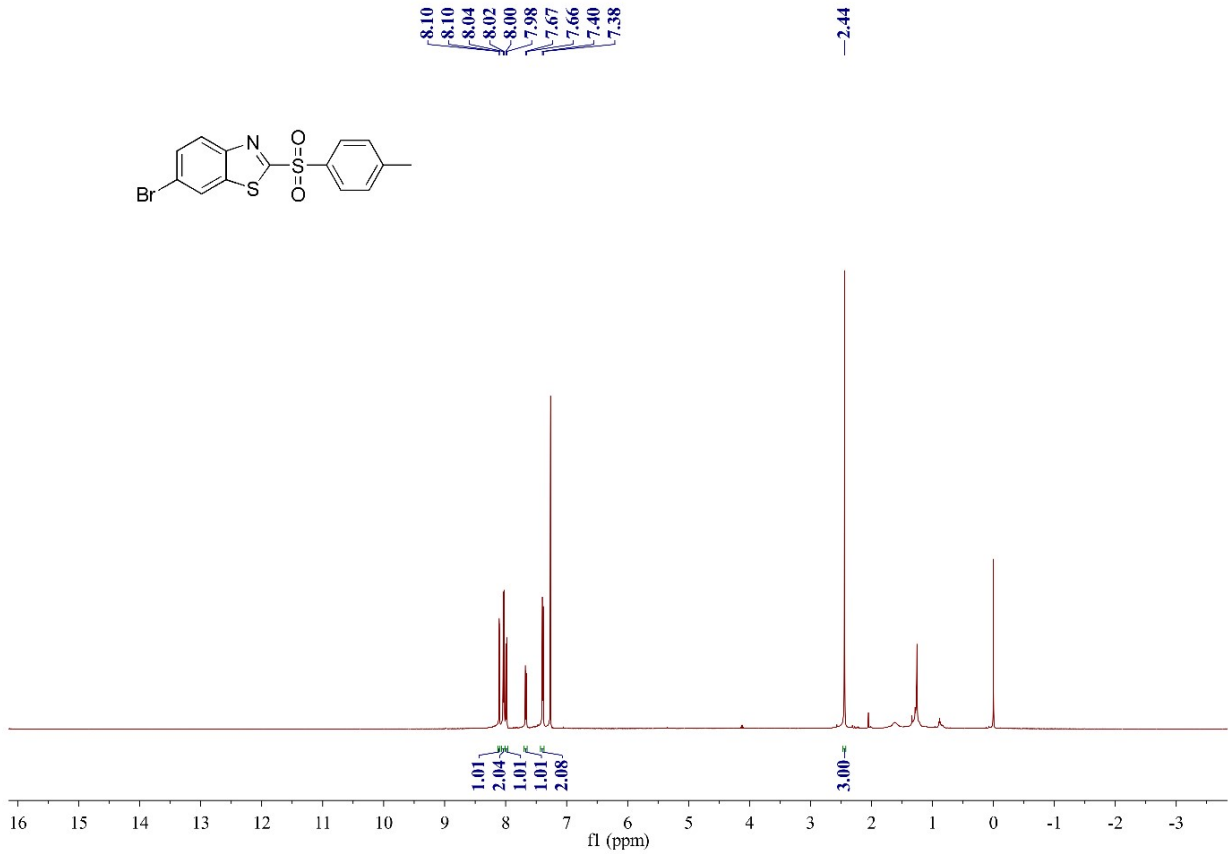
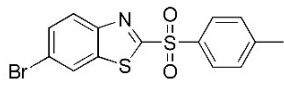


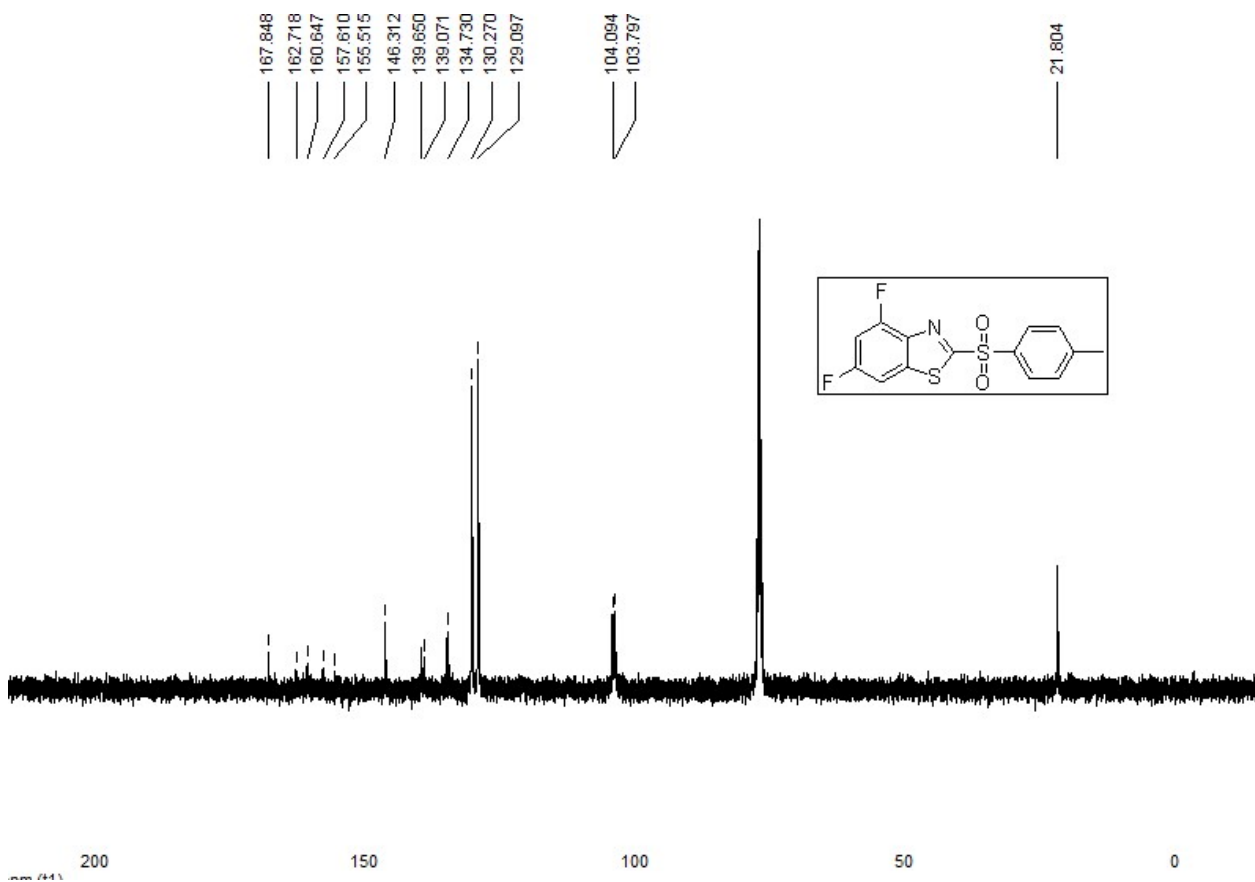
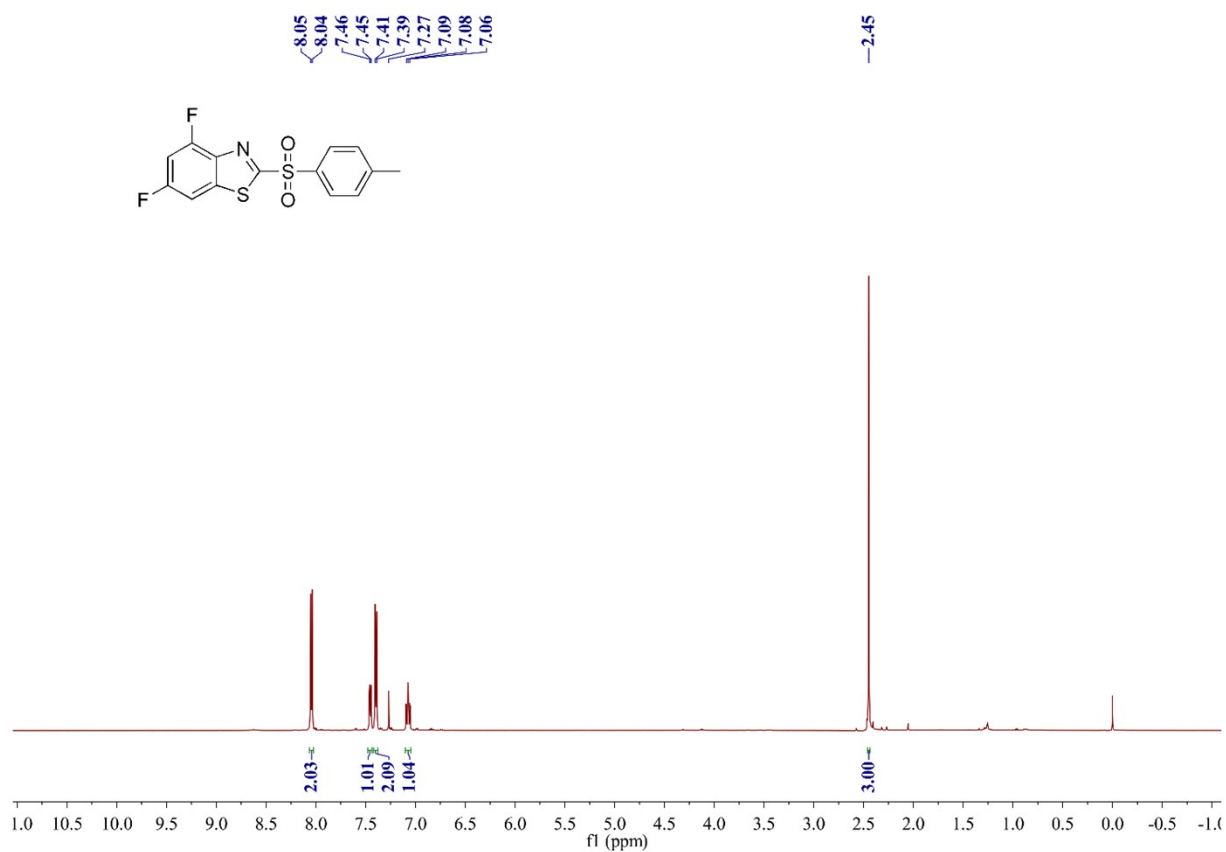
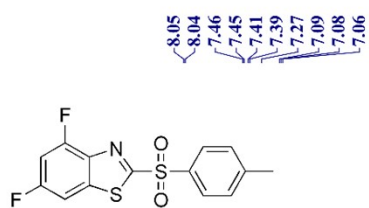


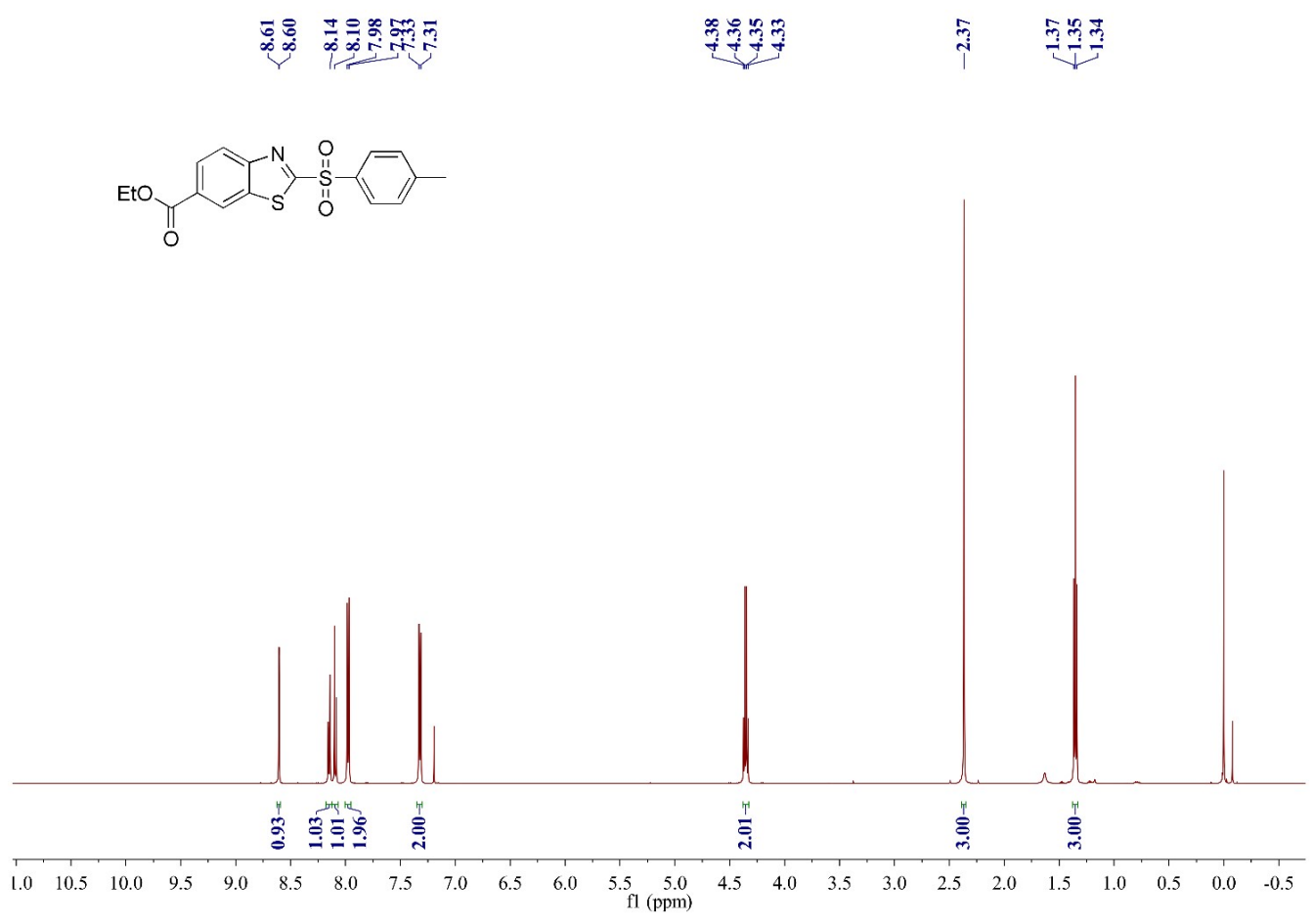
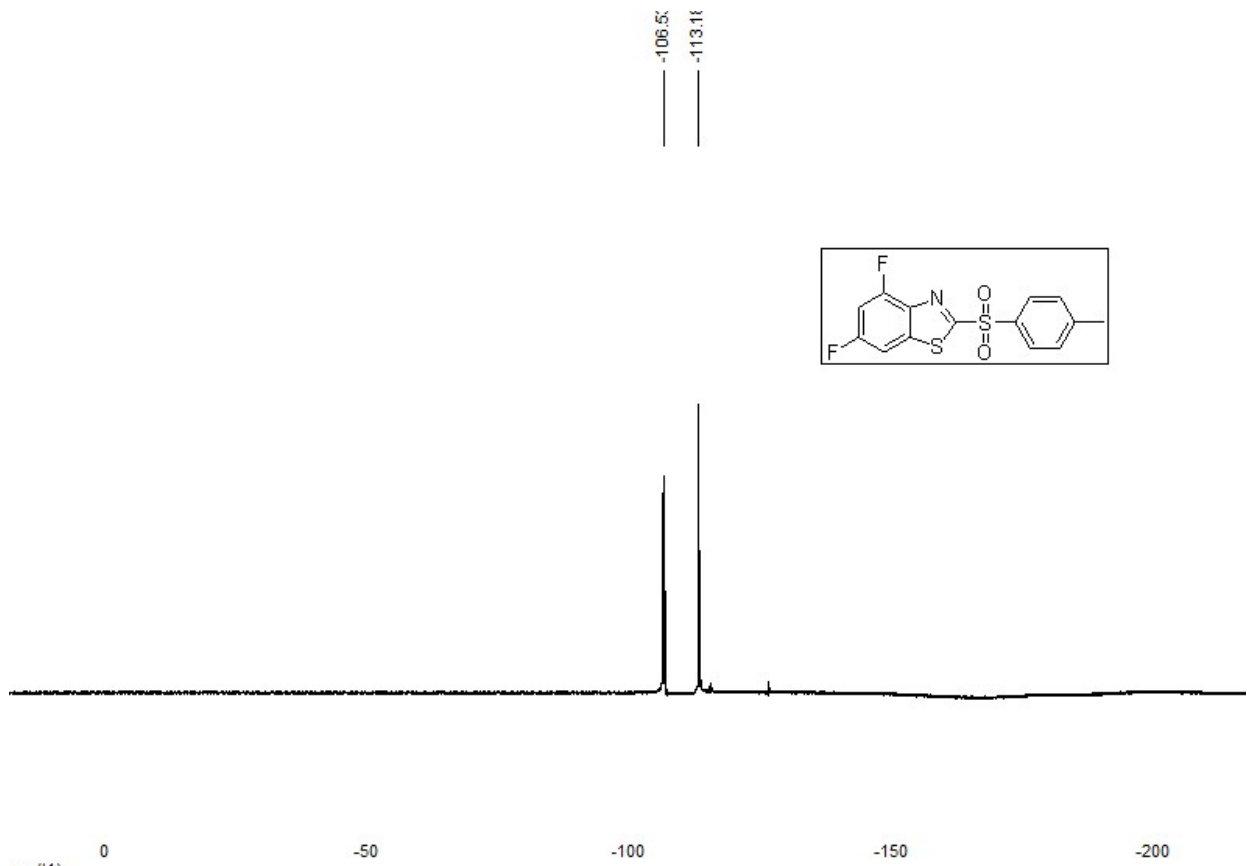


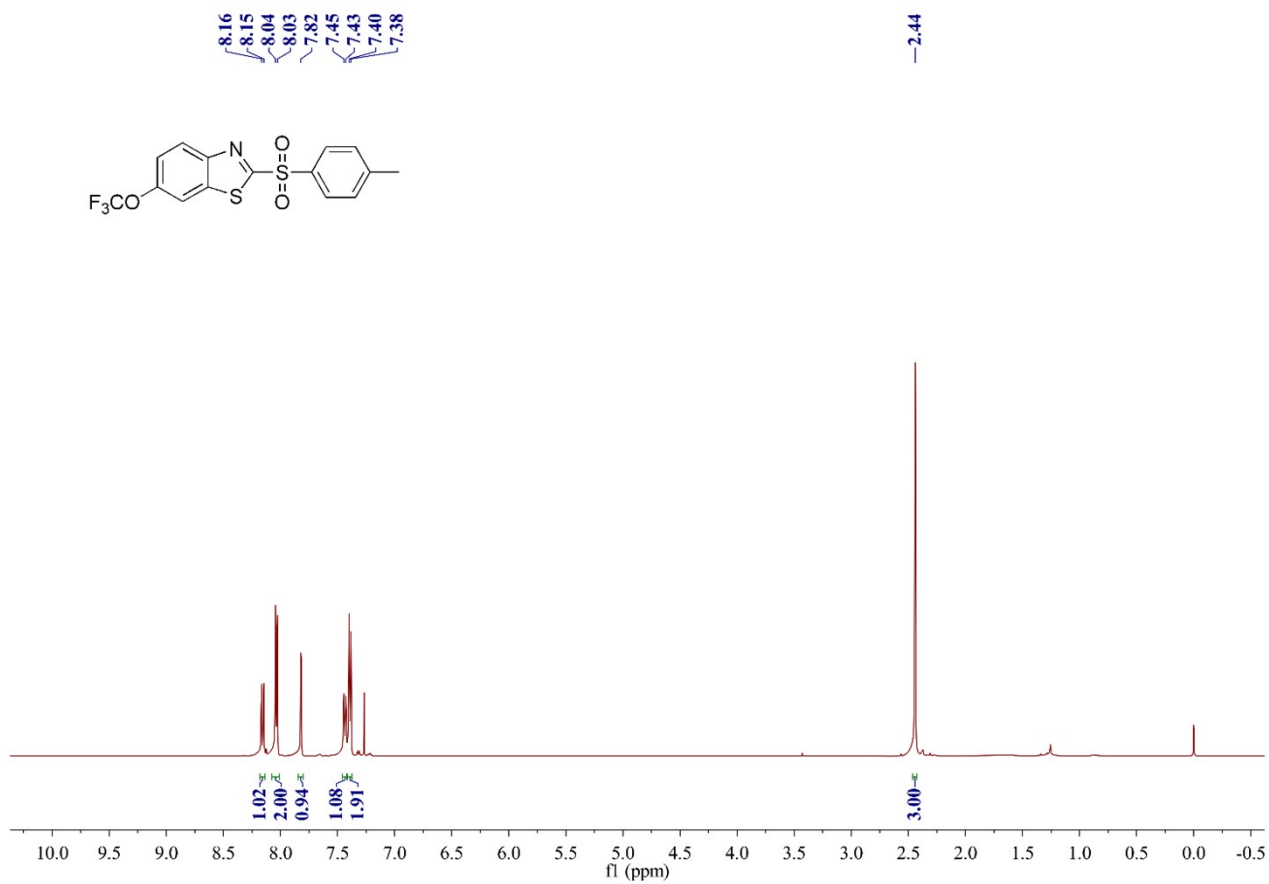
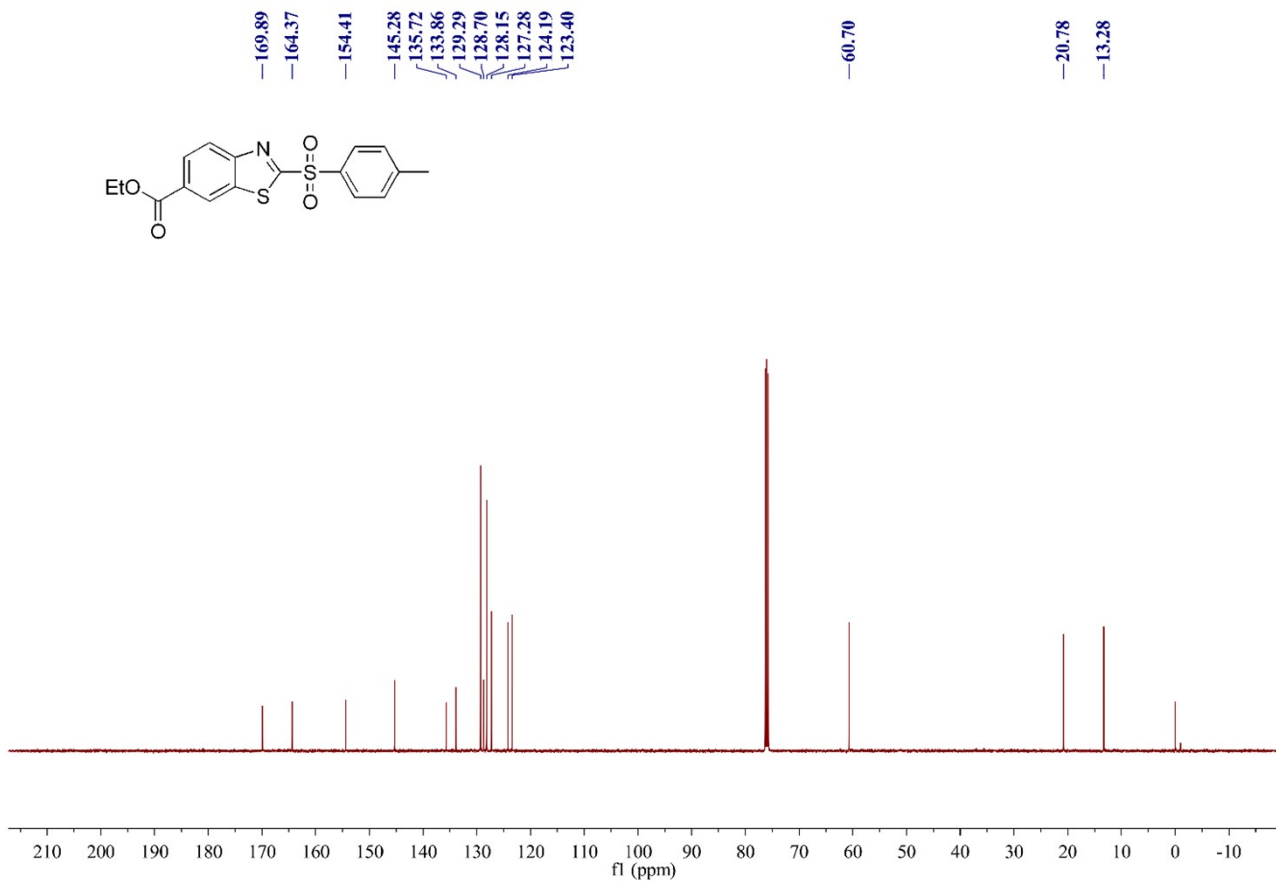


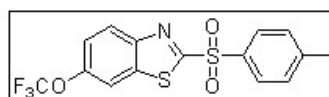
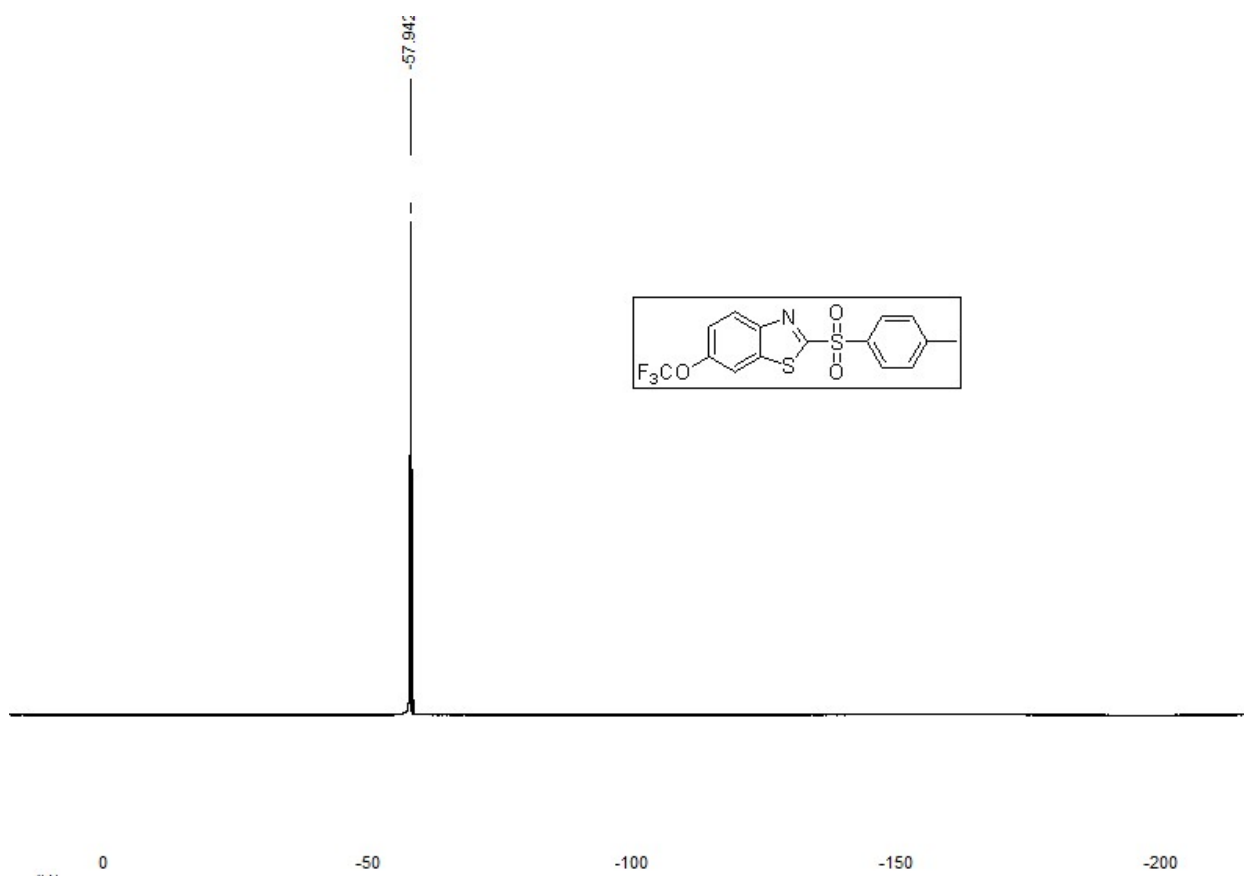
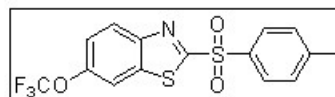
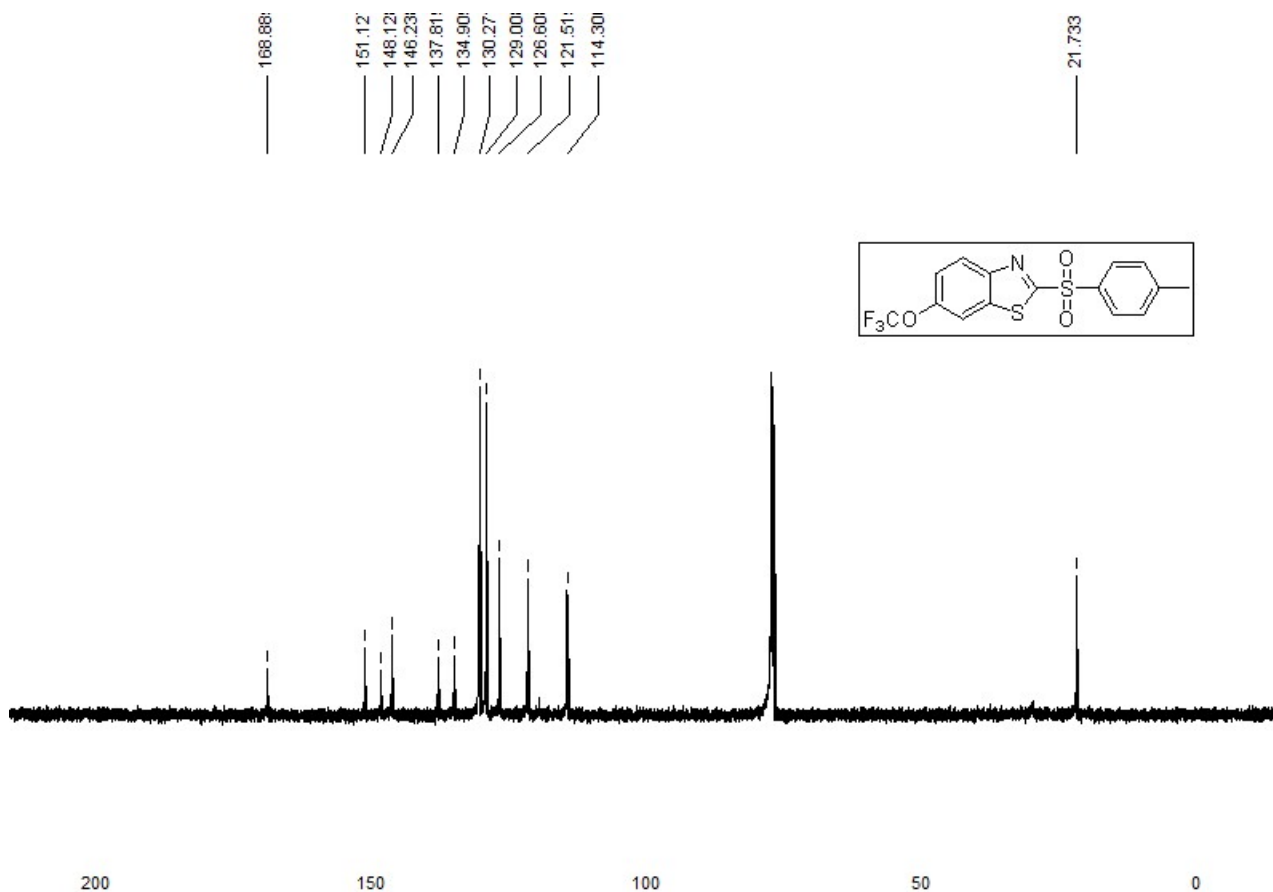


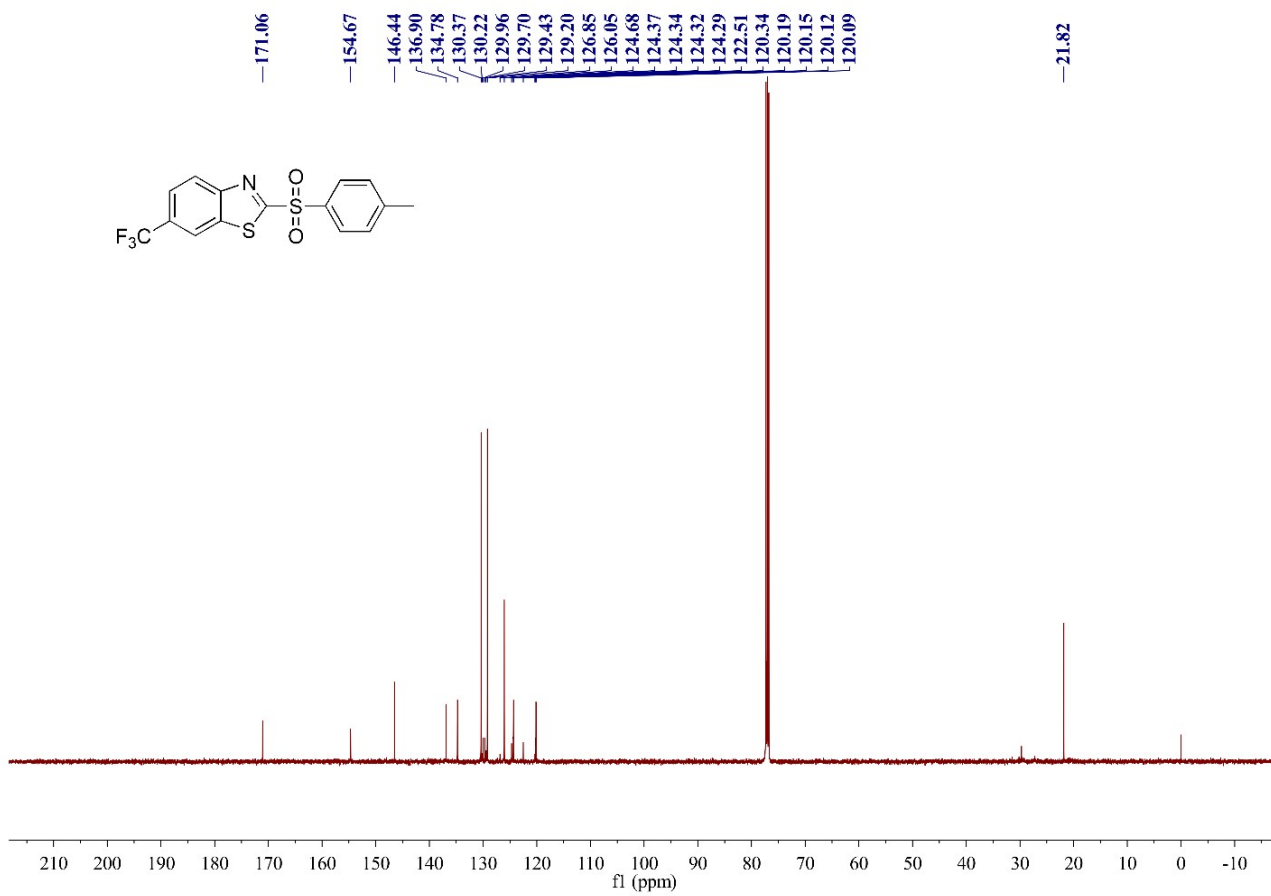
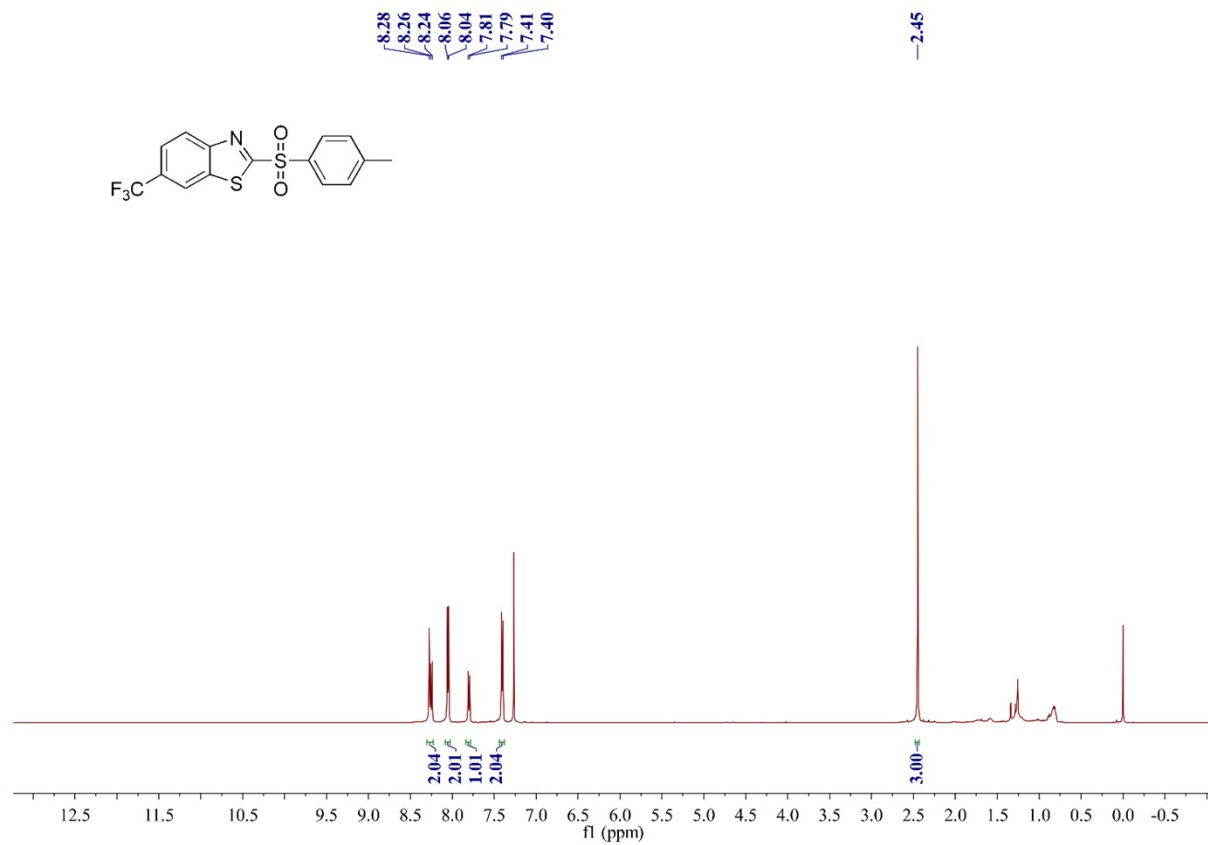


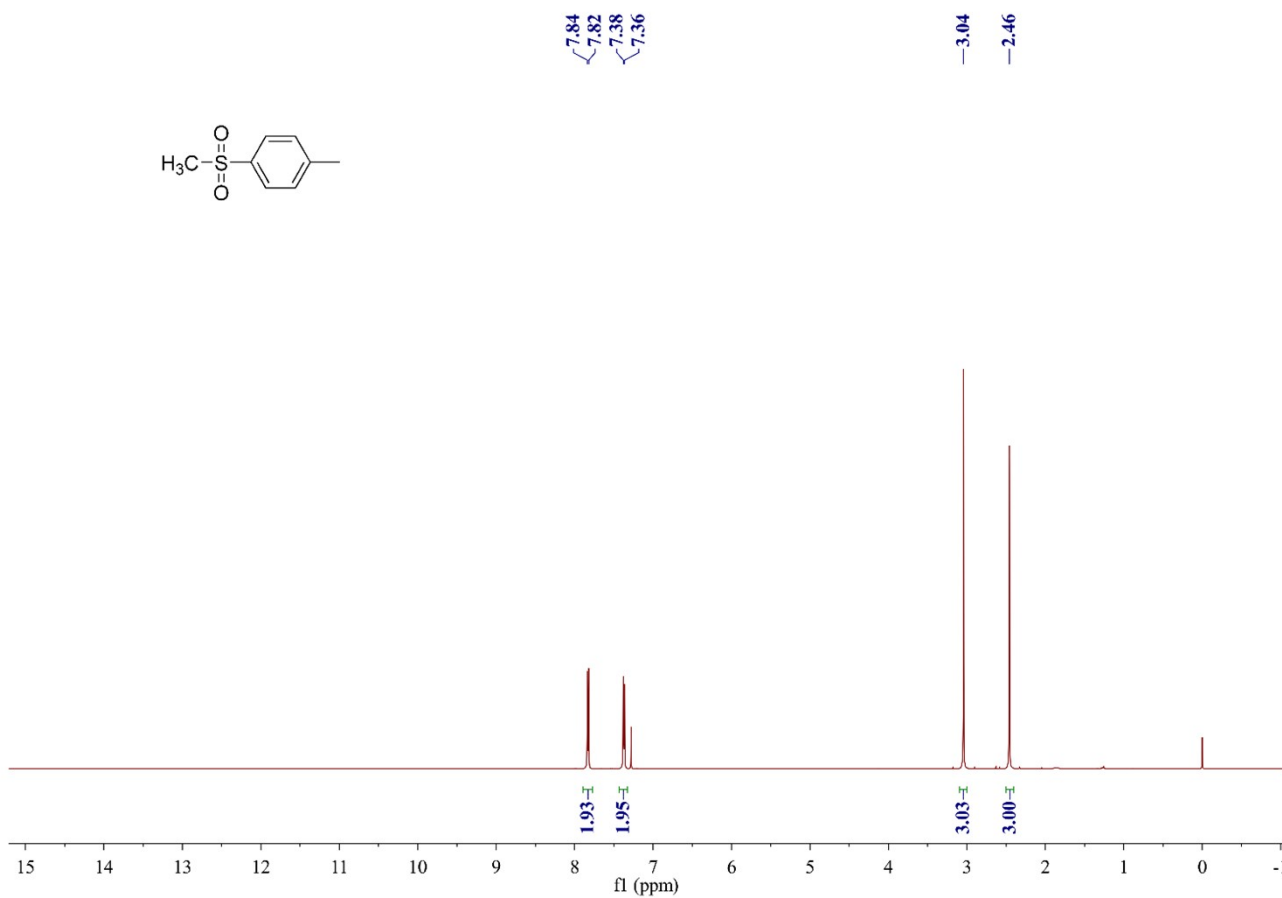
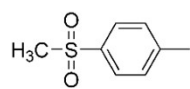
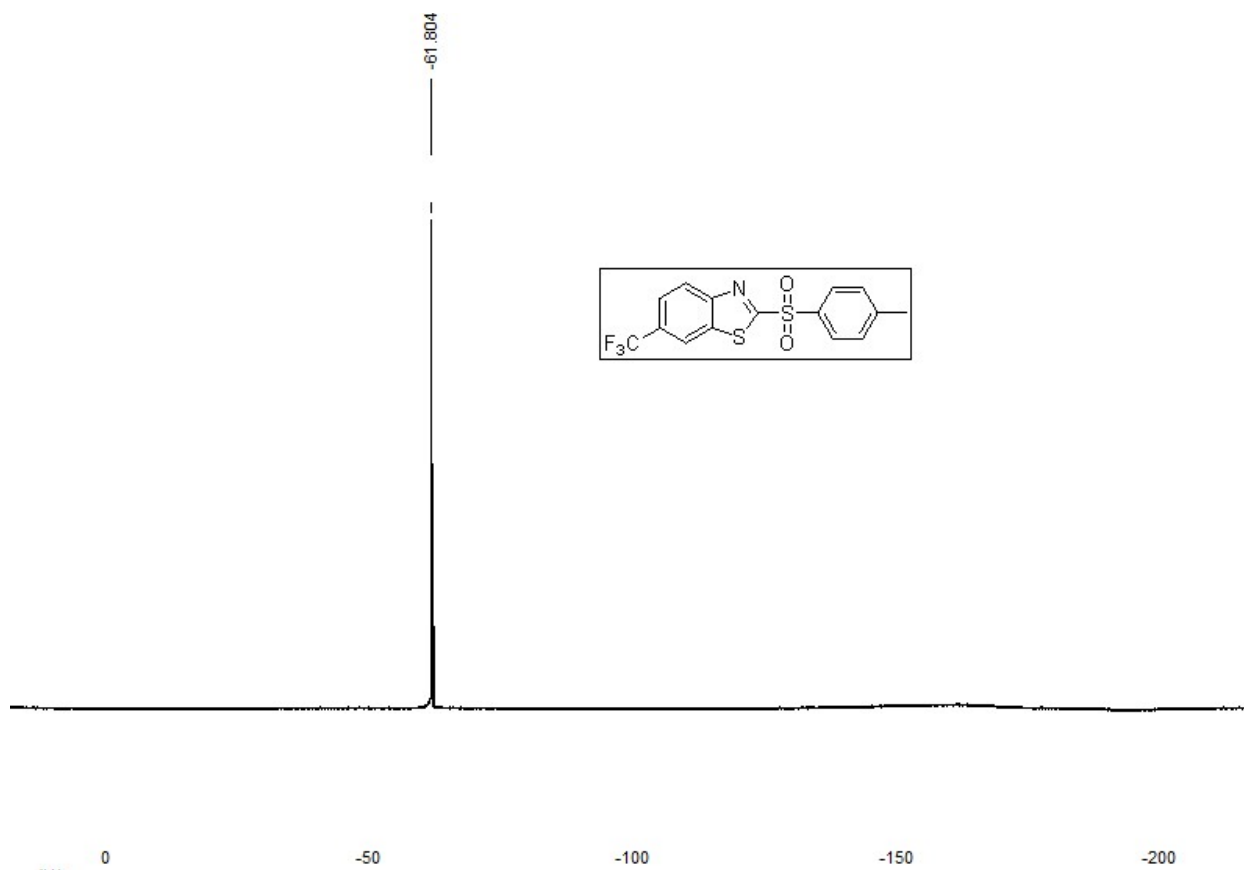


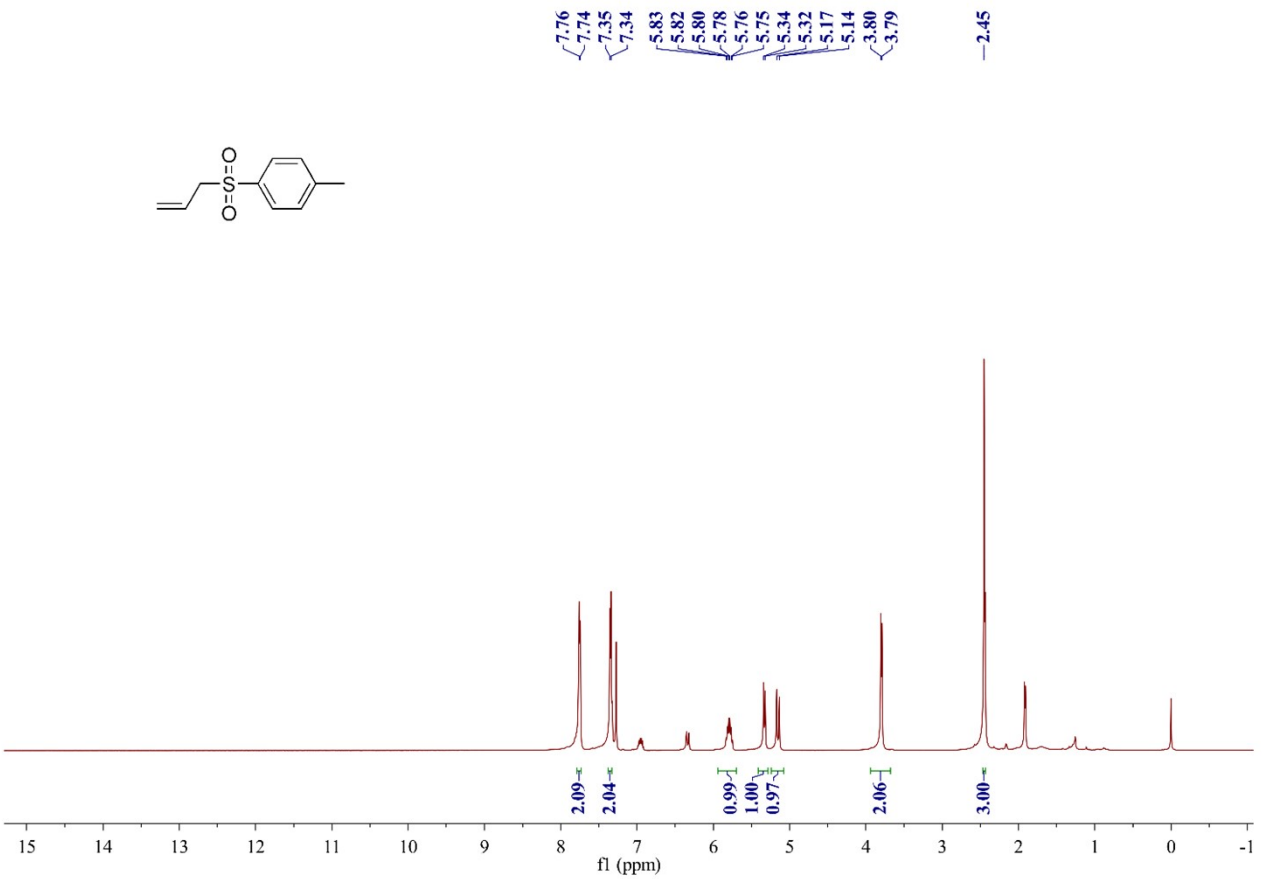
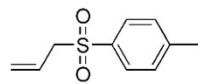
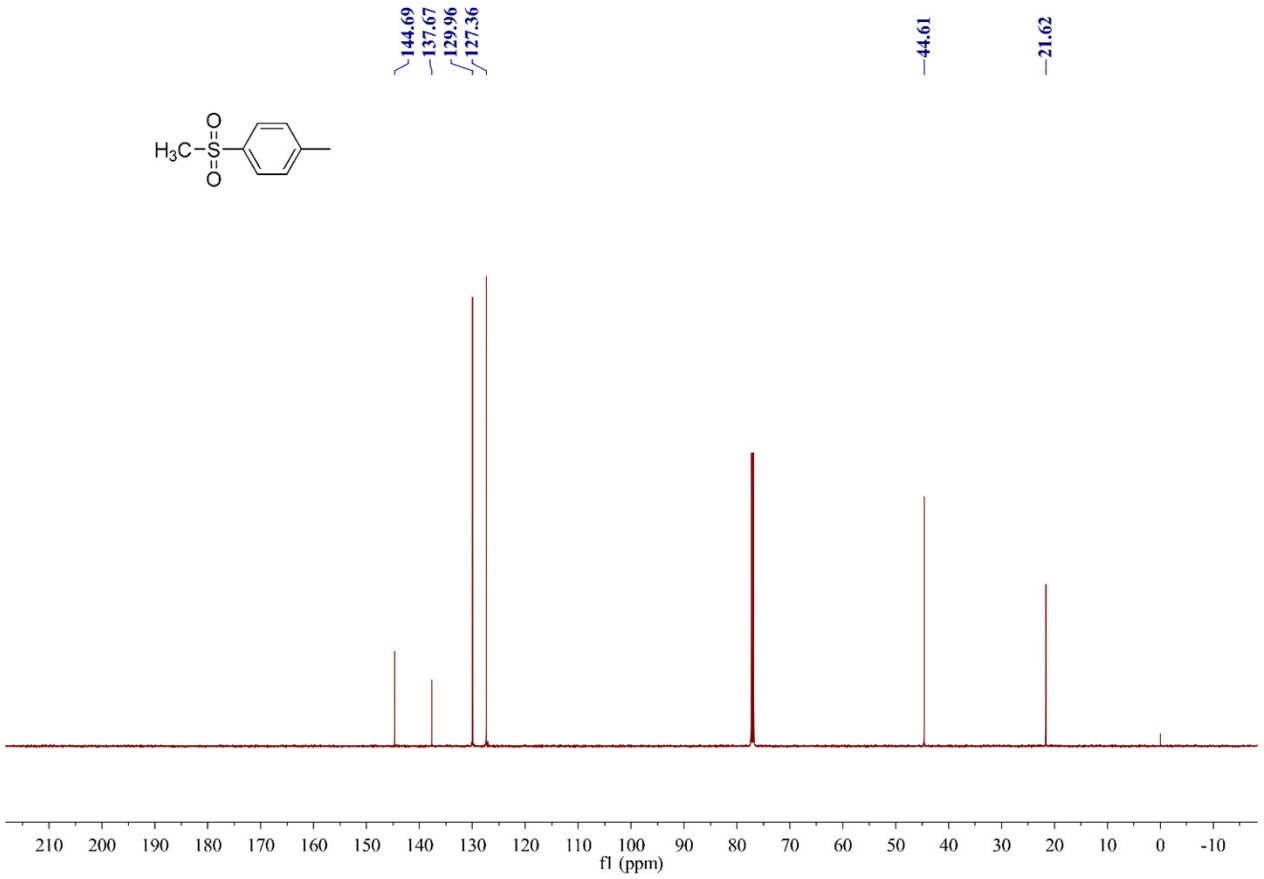
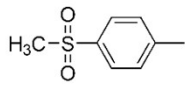


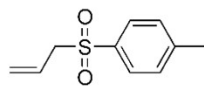








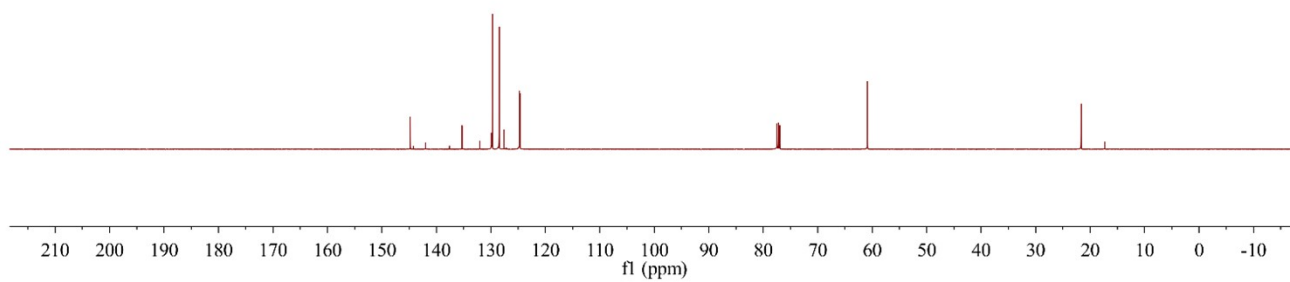


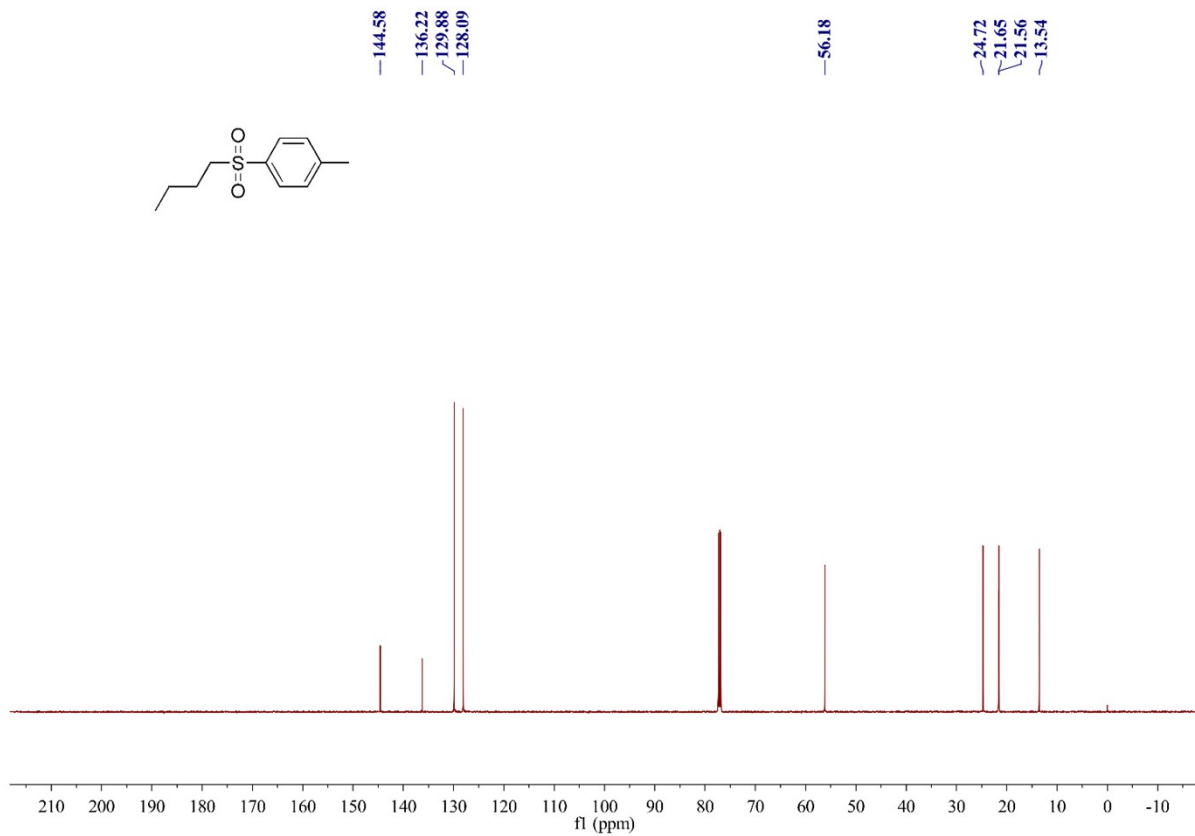
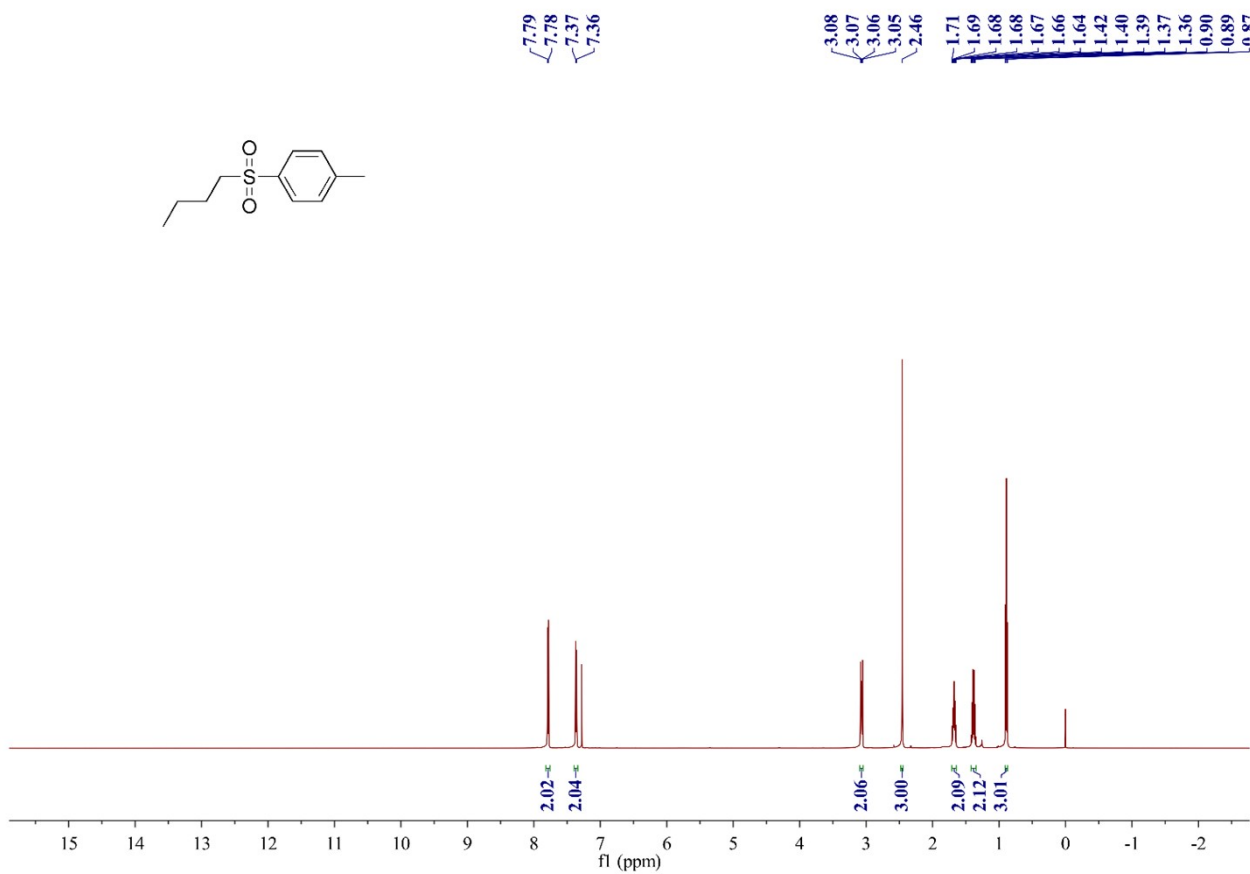


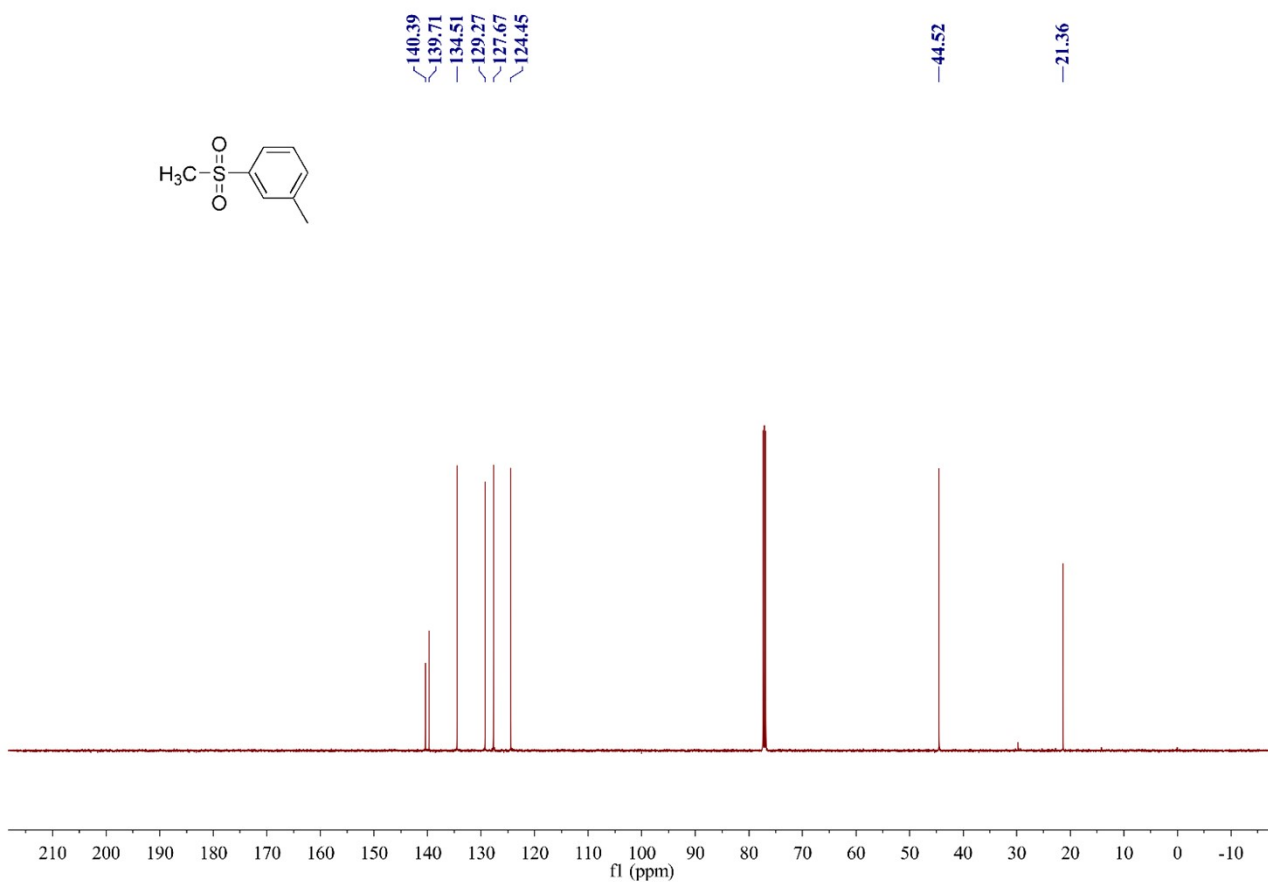
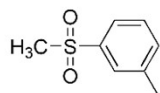
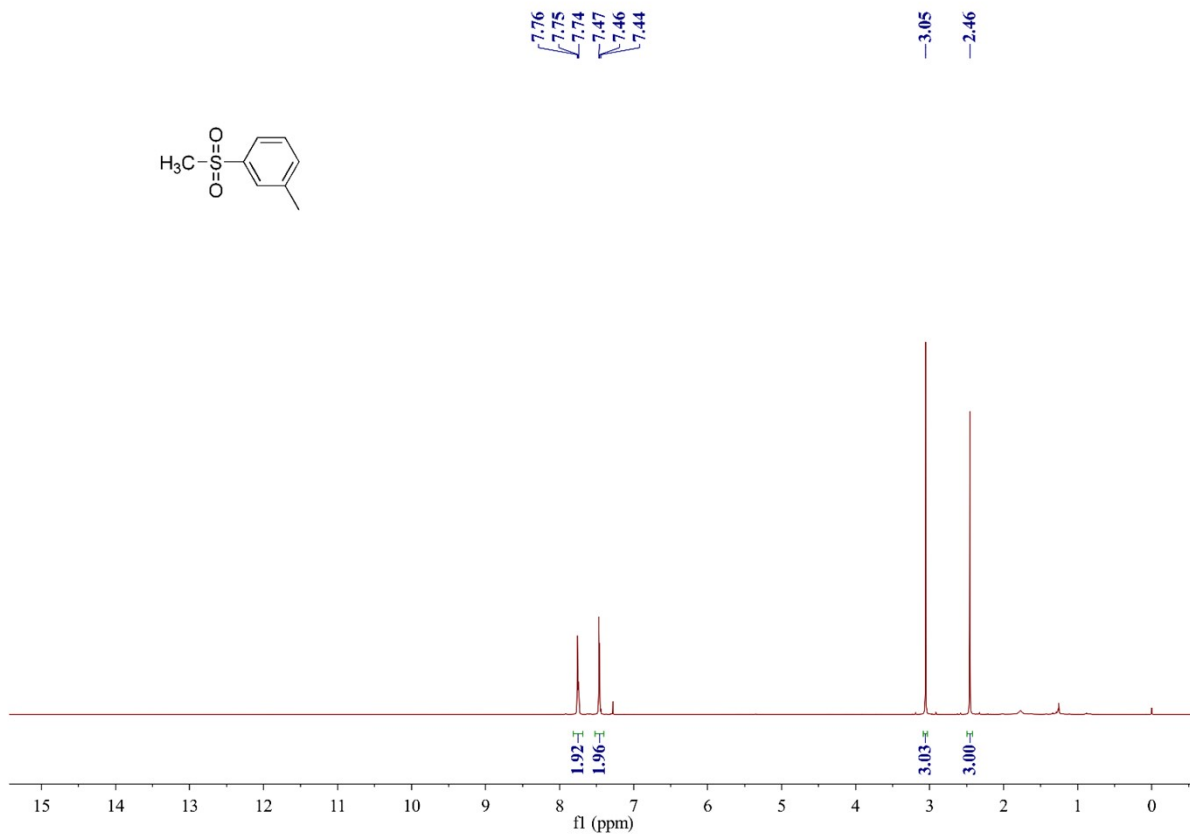
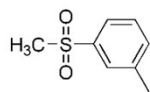
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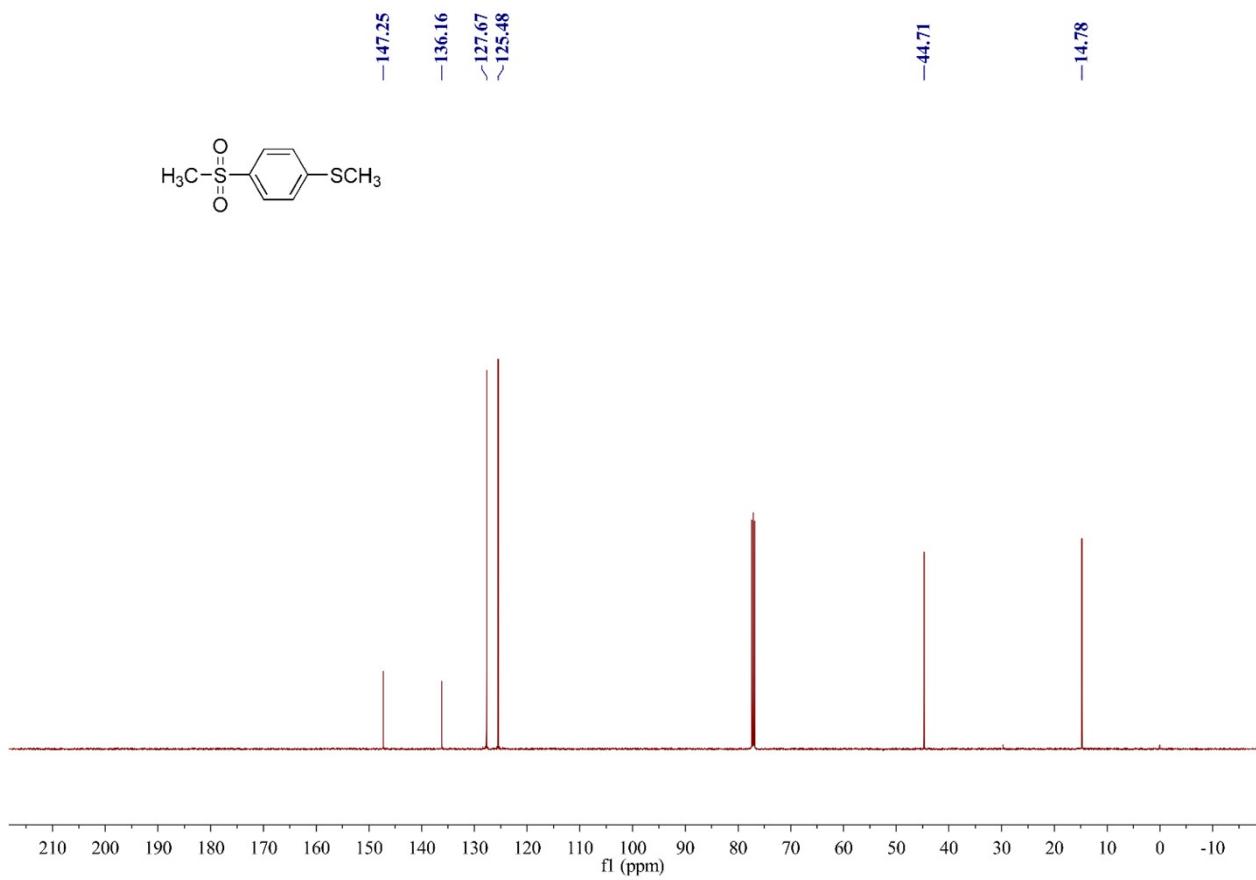
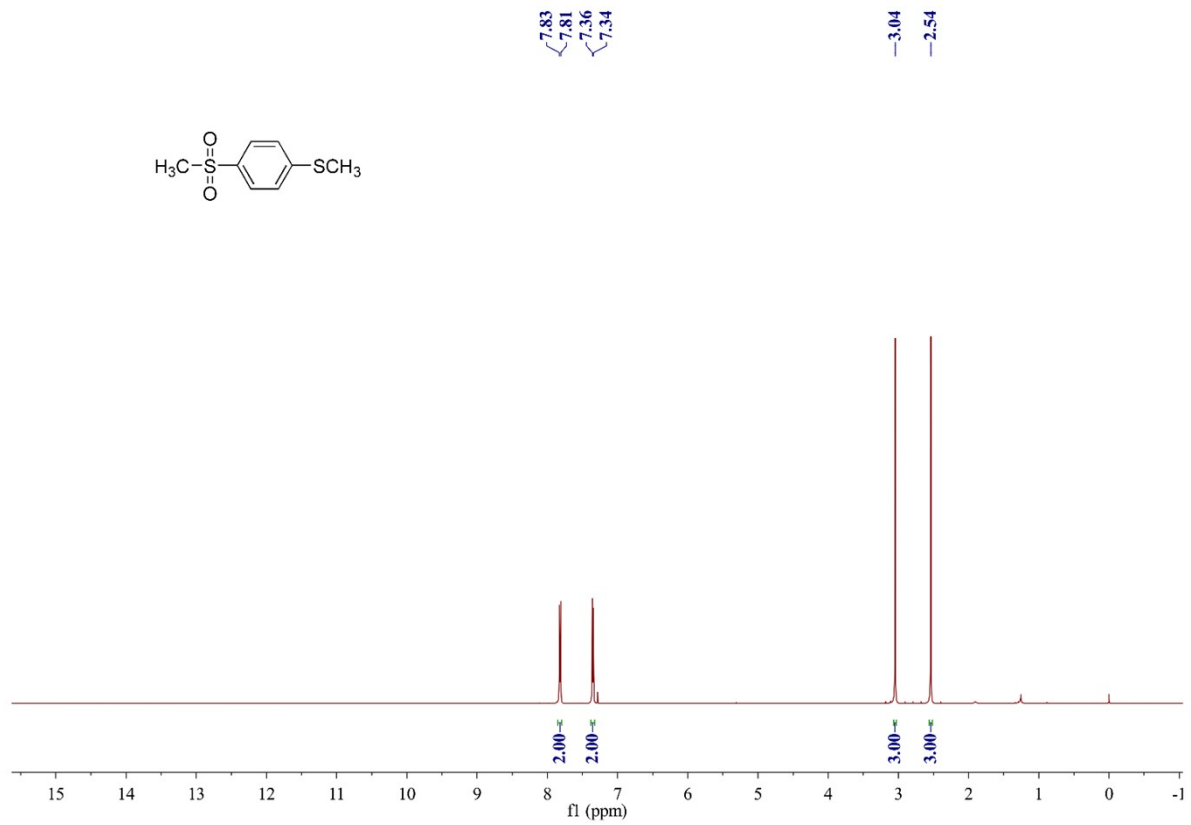
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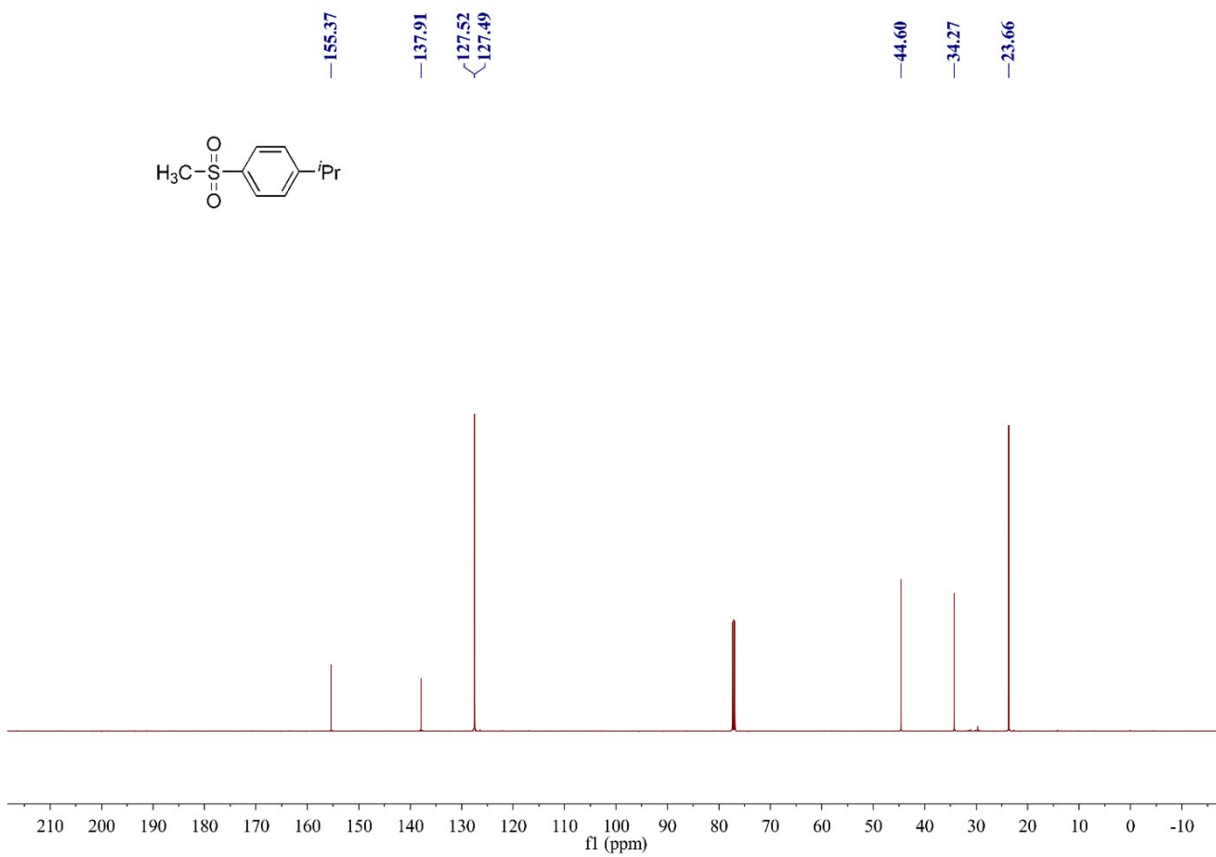
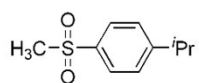
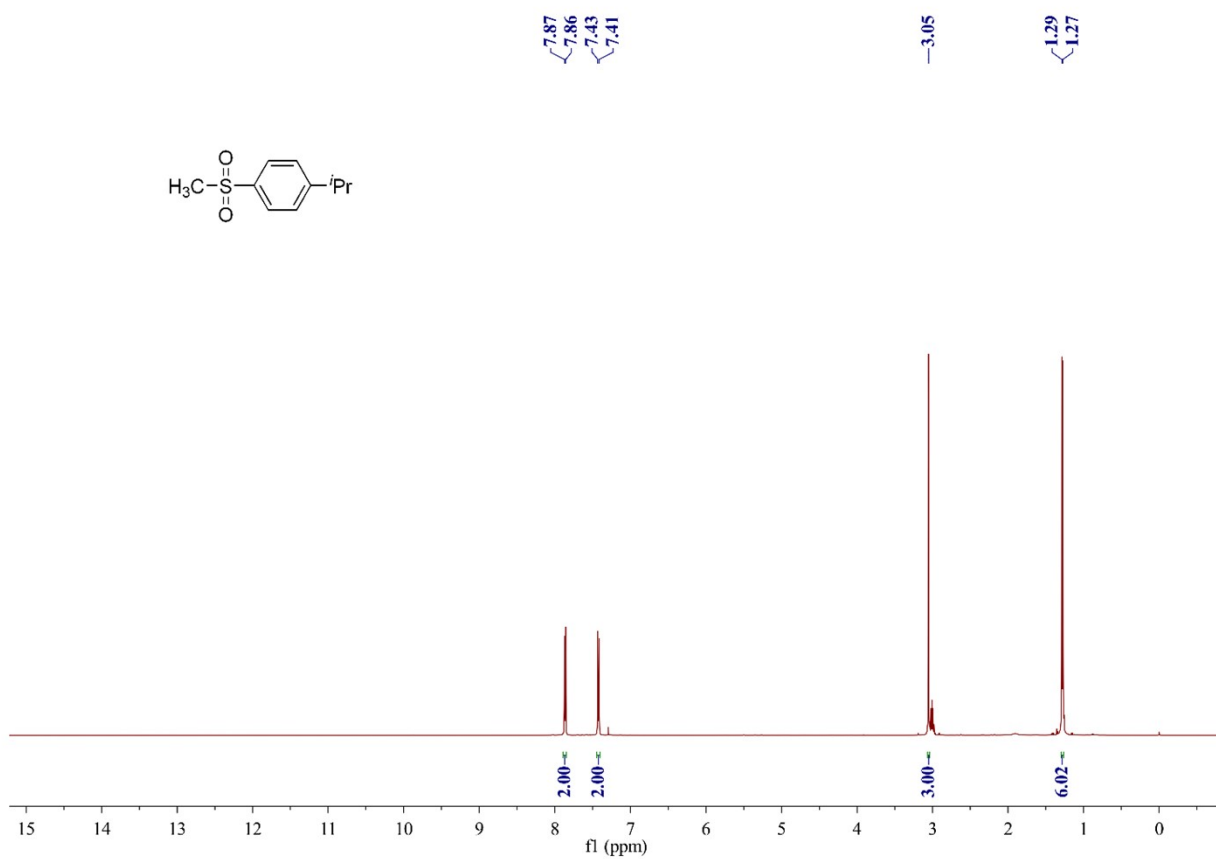
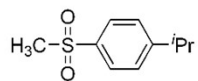
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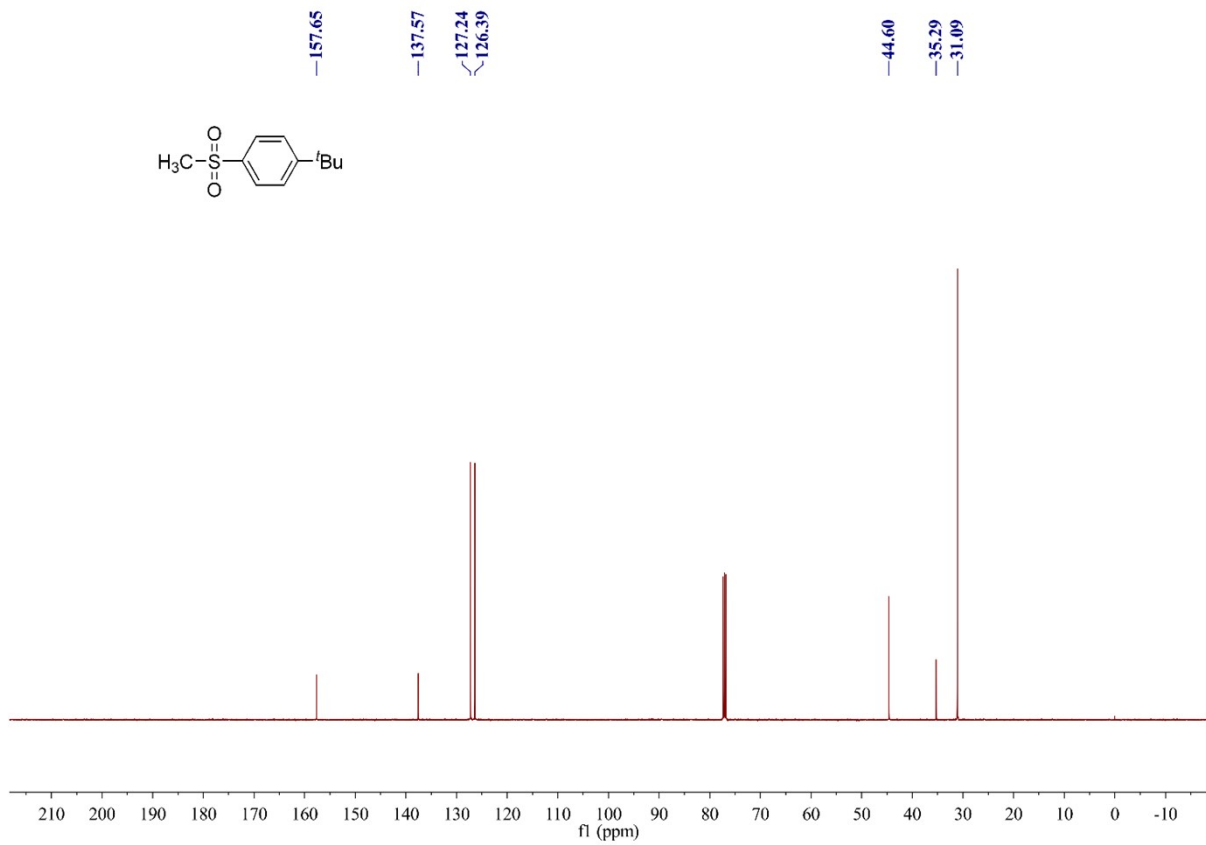
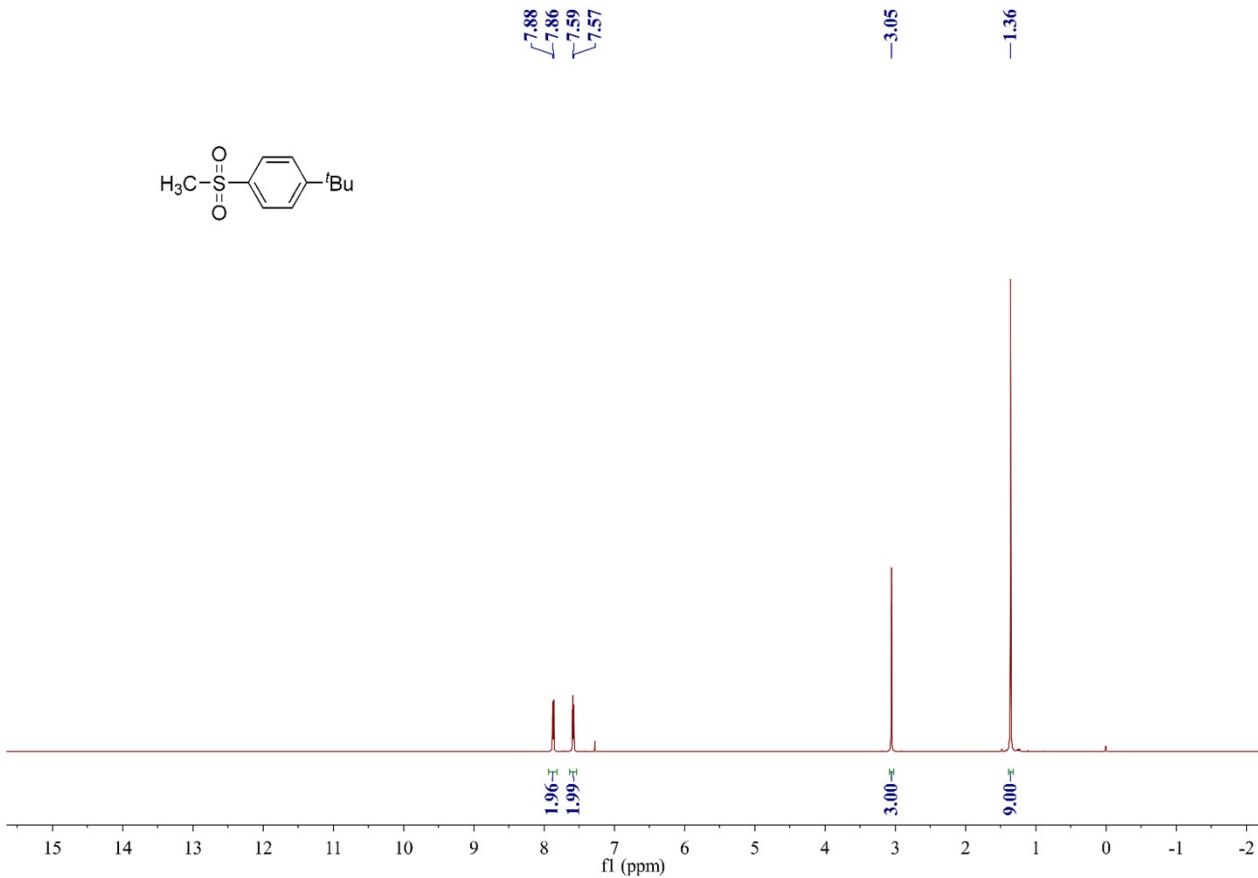


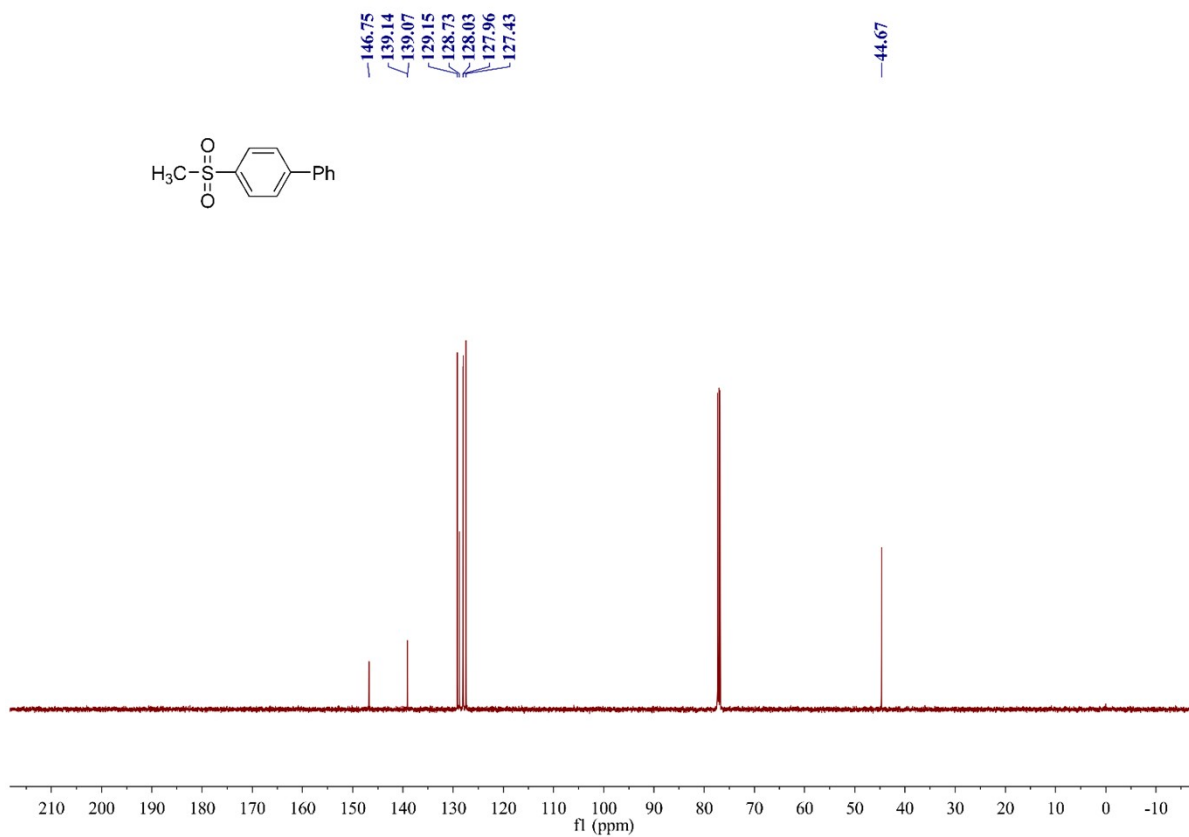
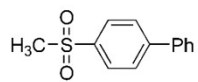
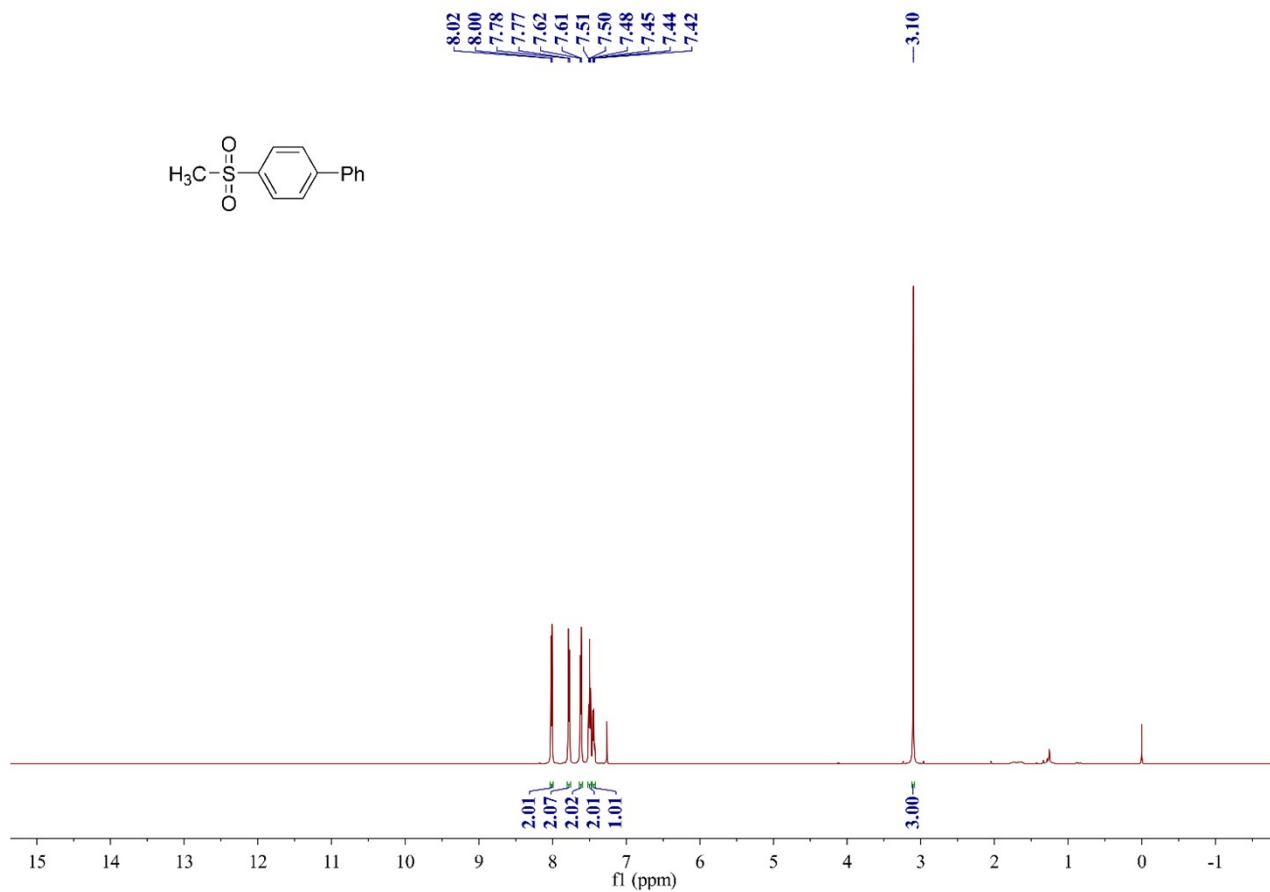
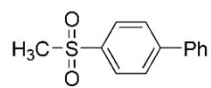


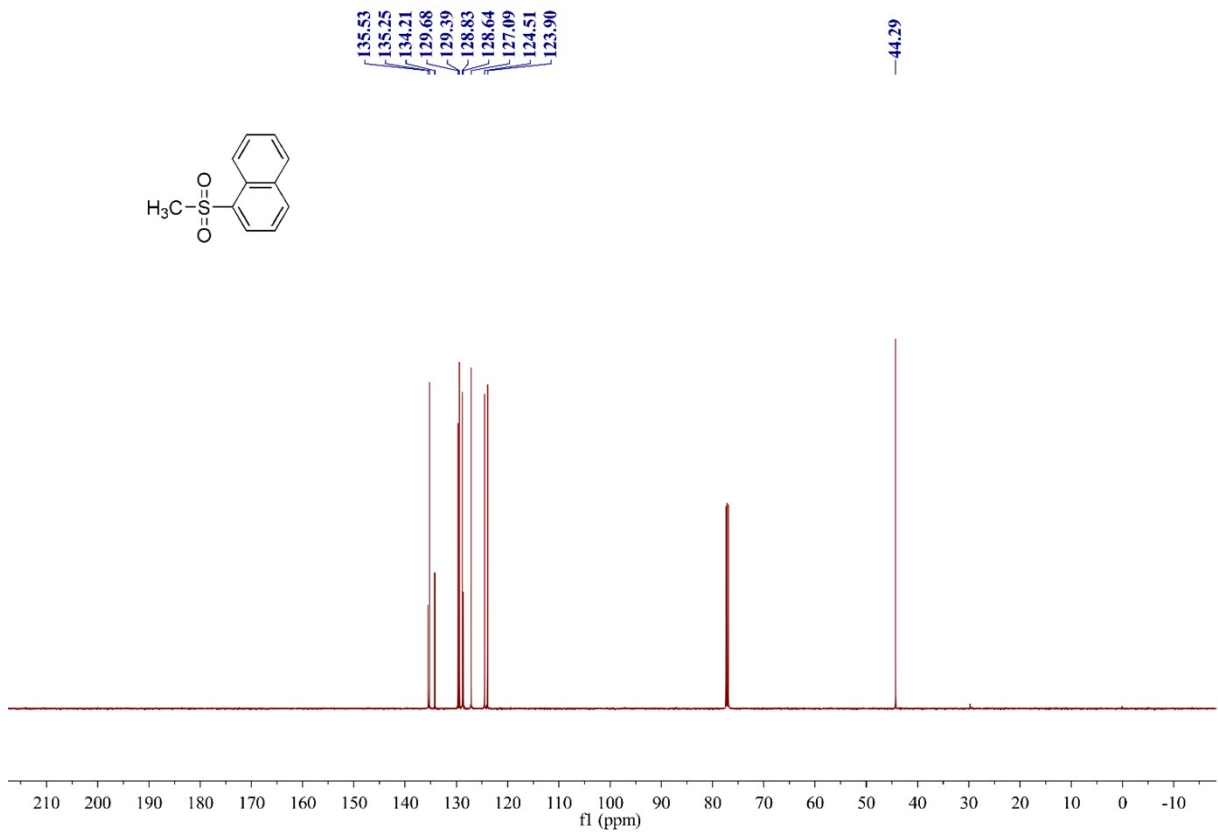
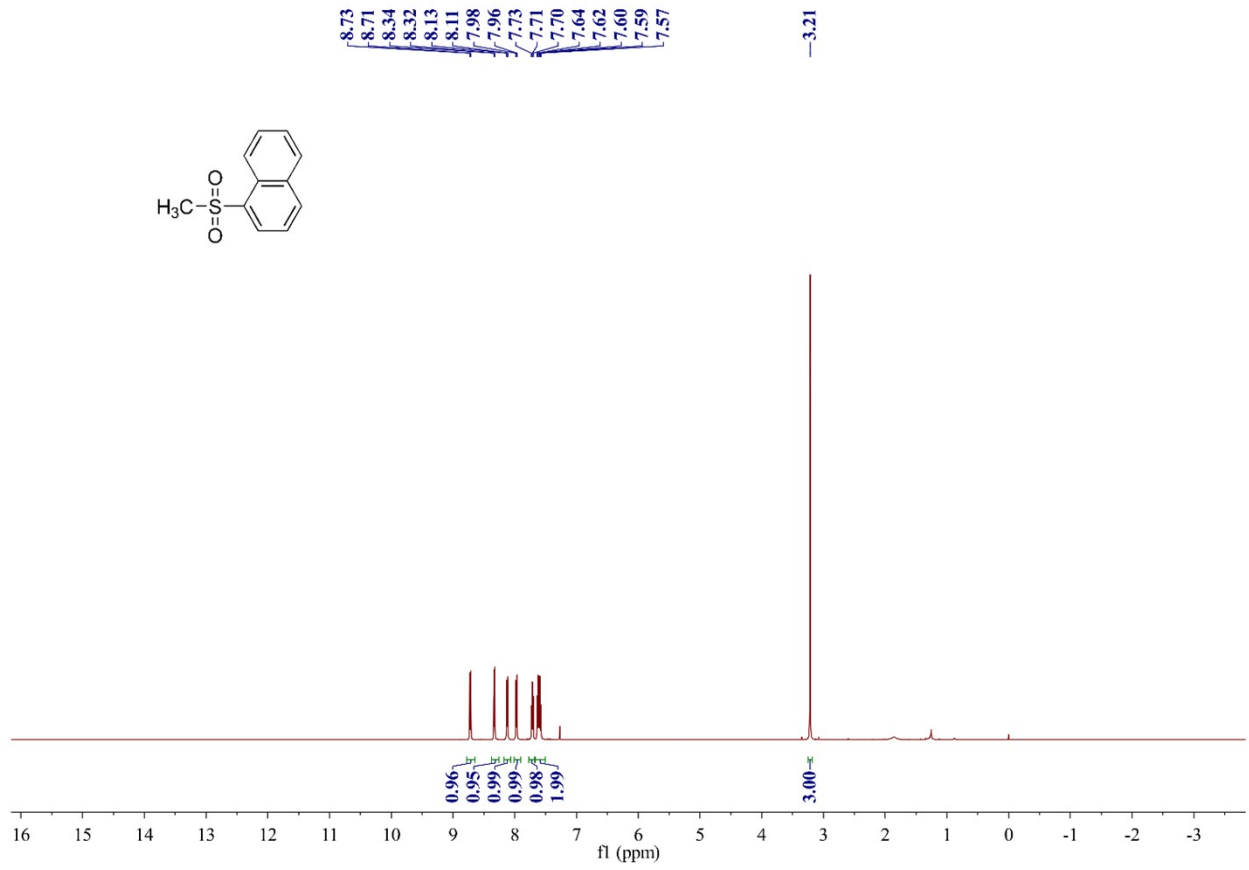


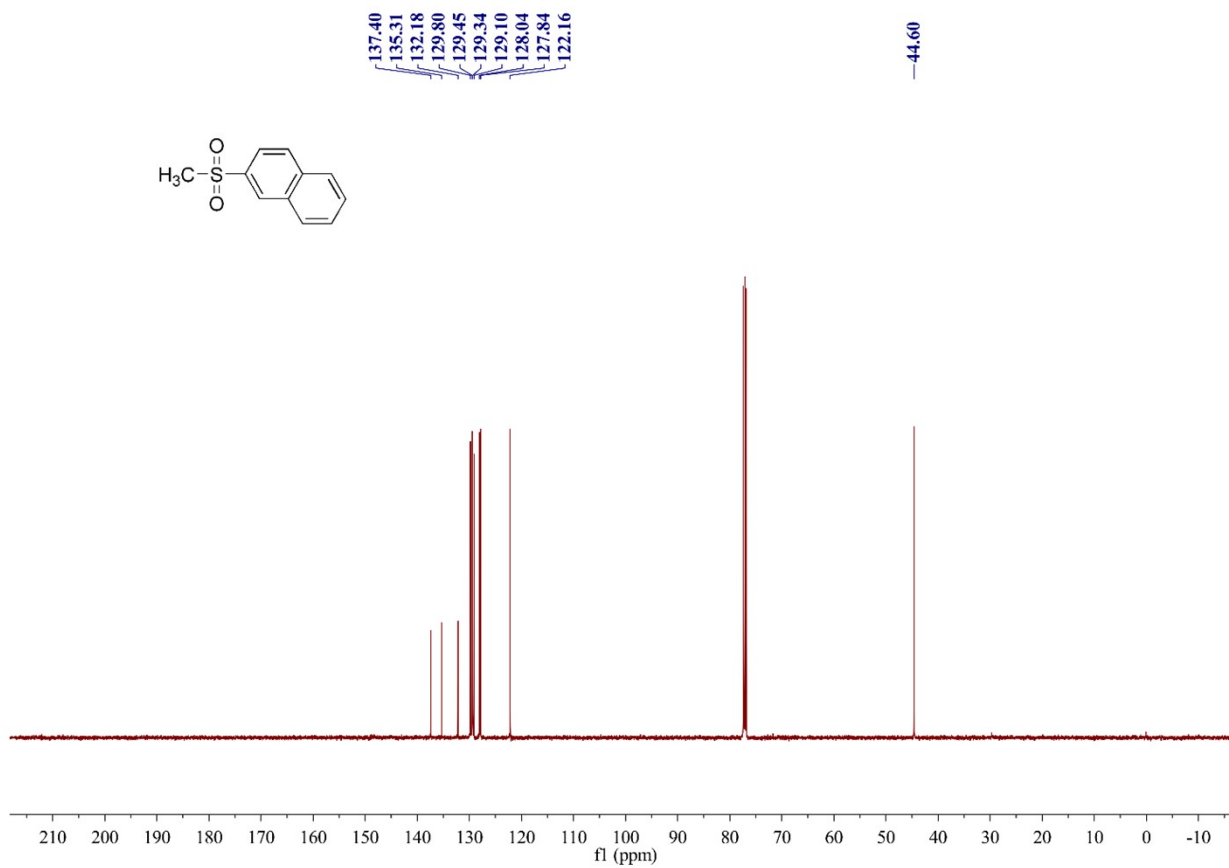
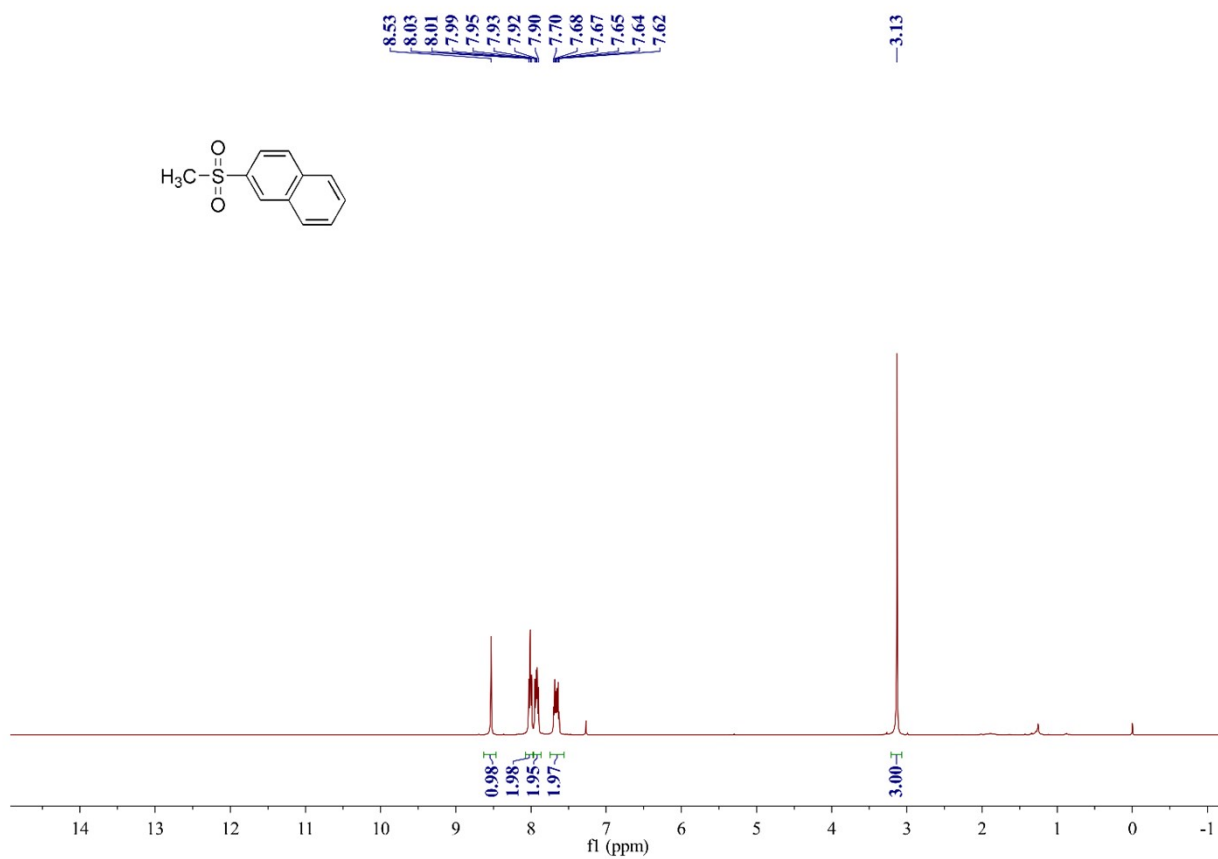


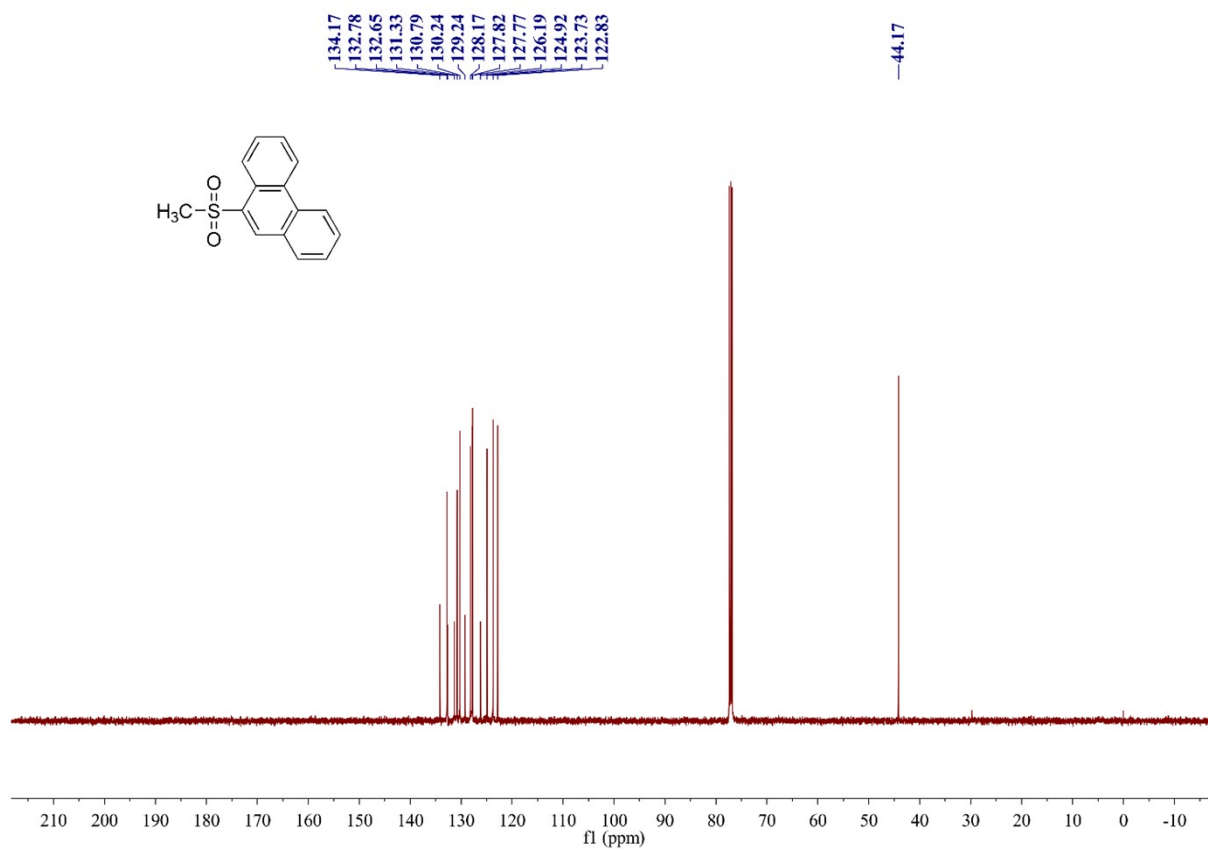
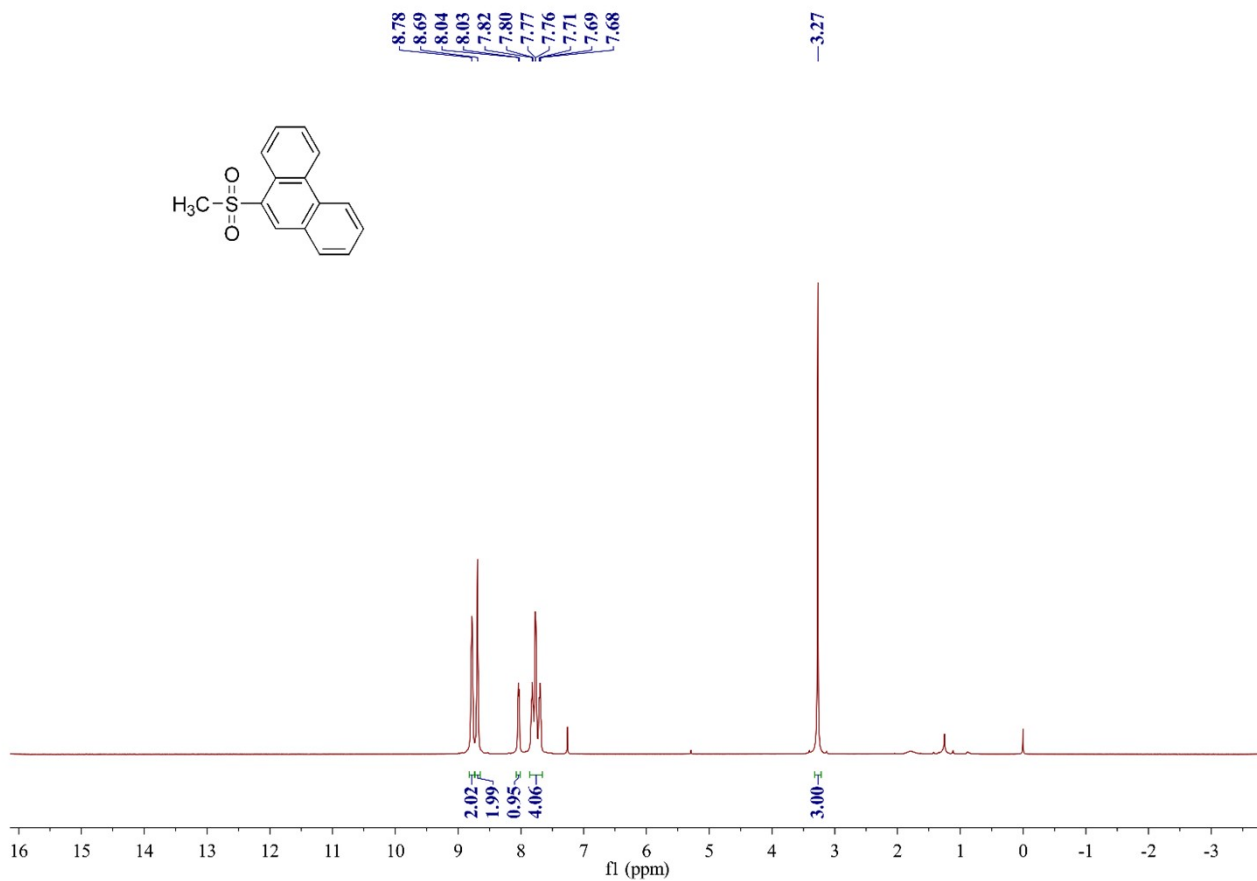




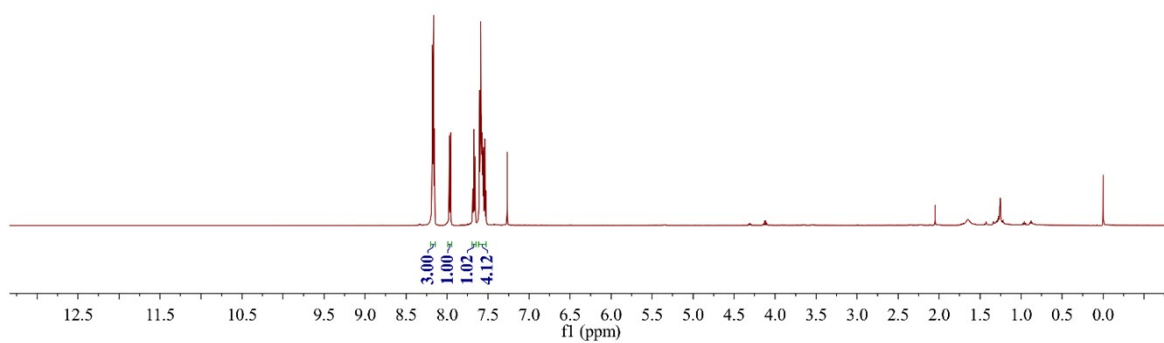
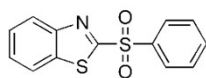




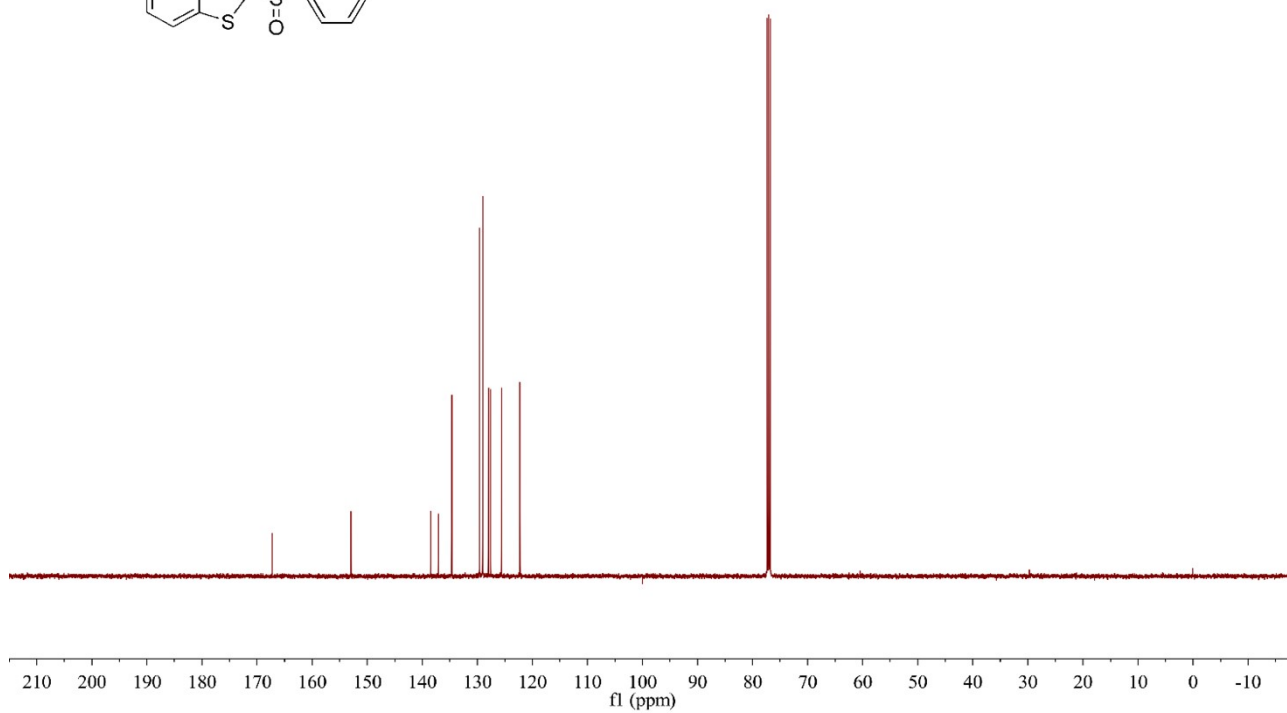
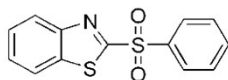


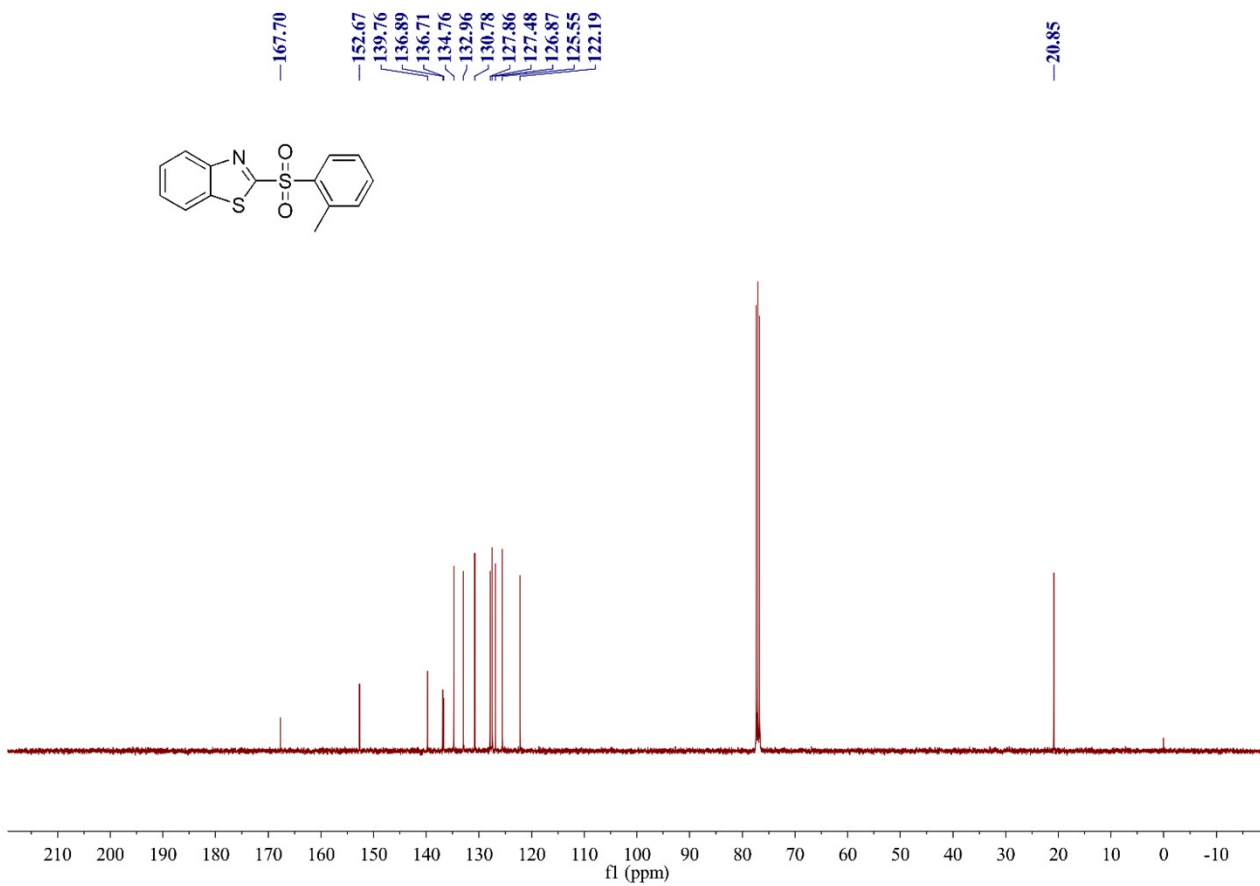
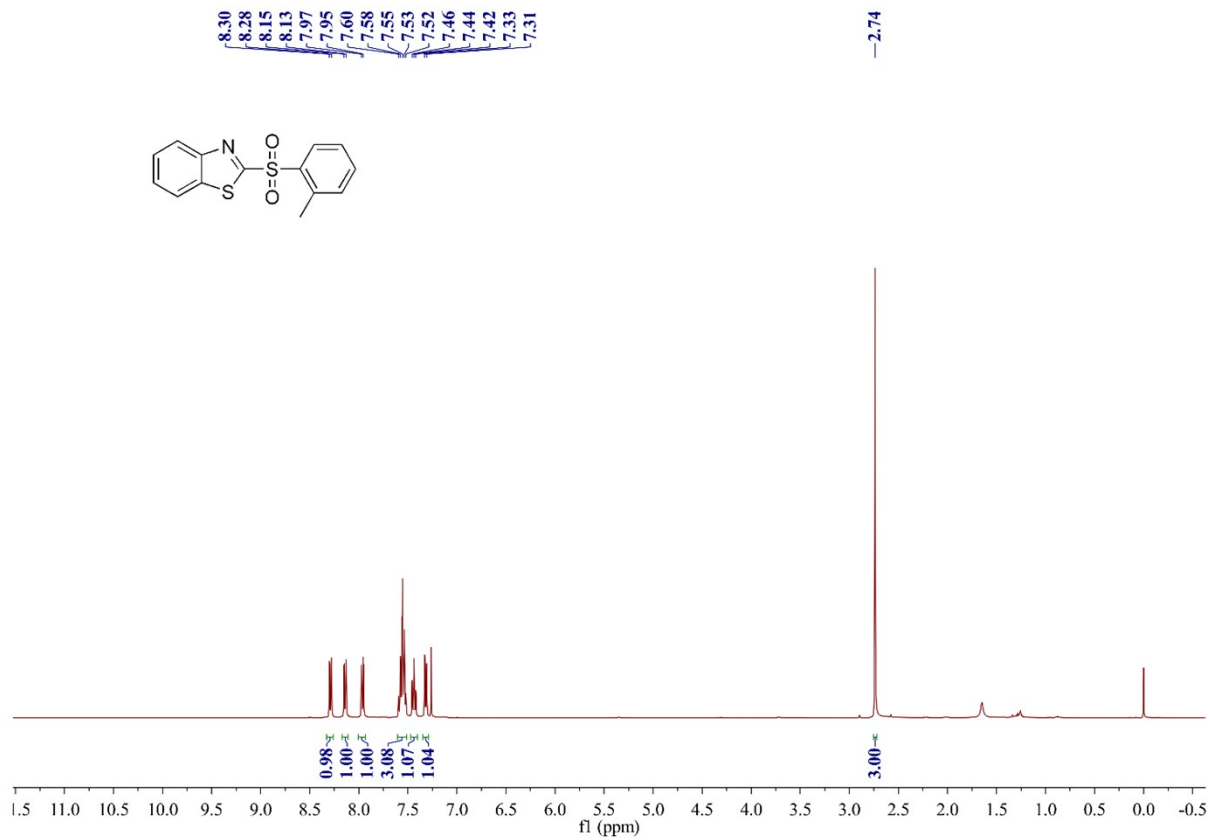


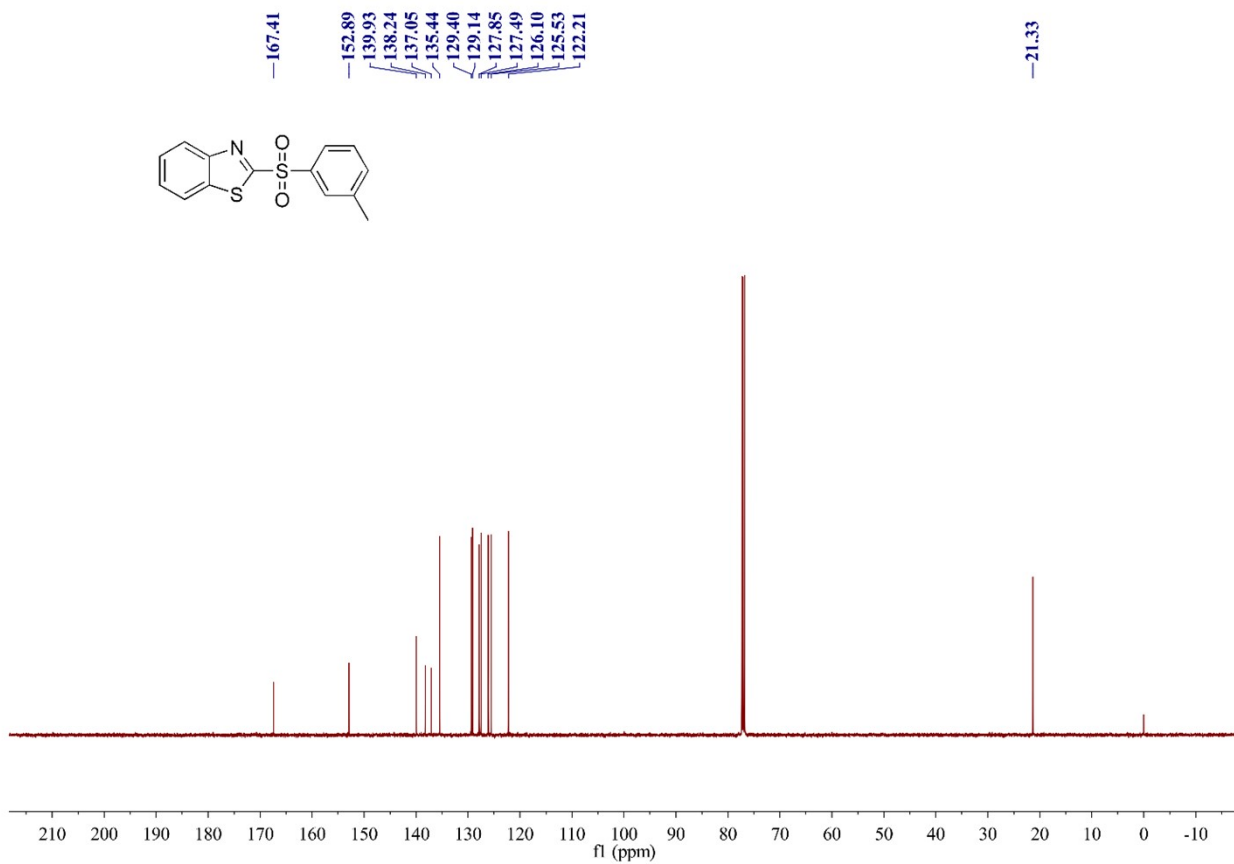
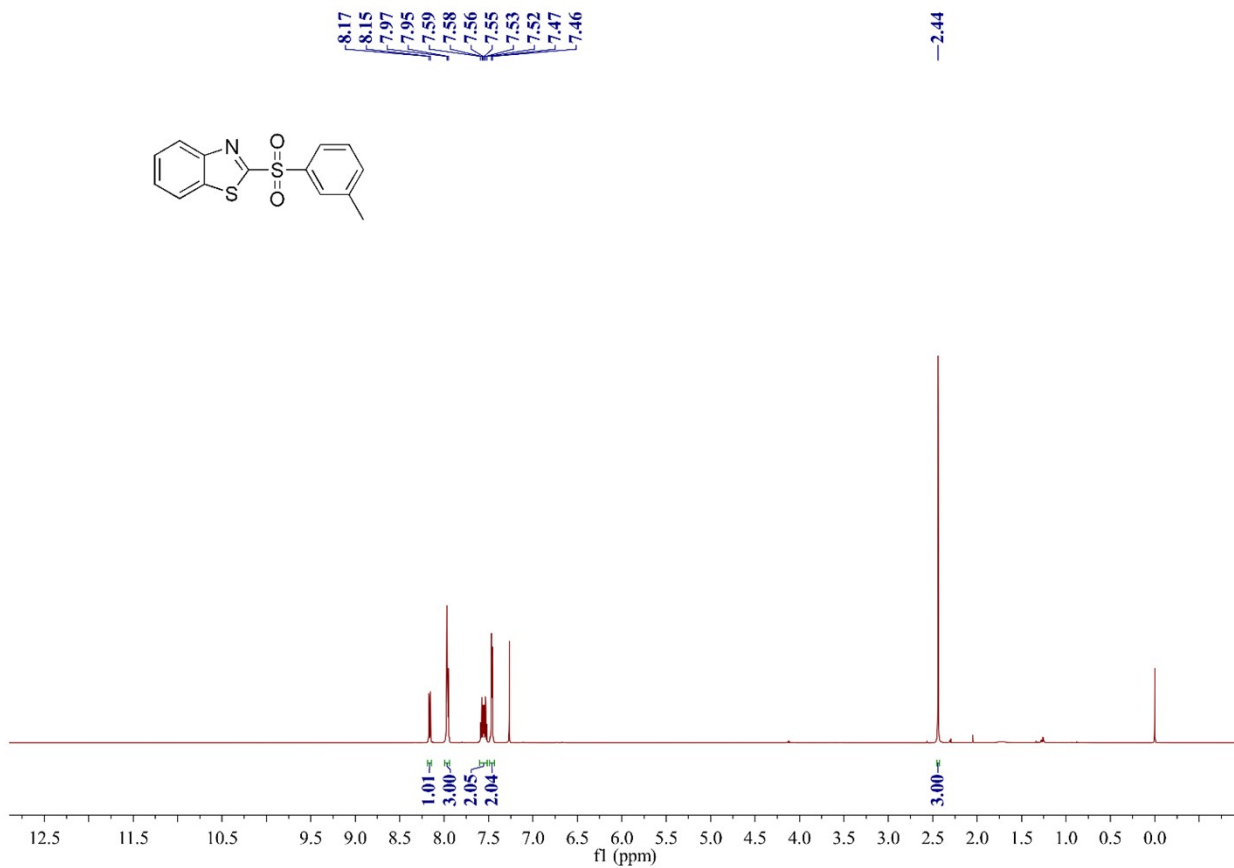
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8.17
8.15
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7.66
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7.53
7.52

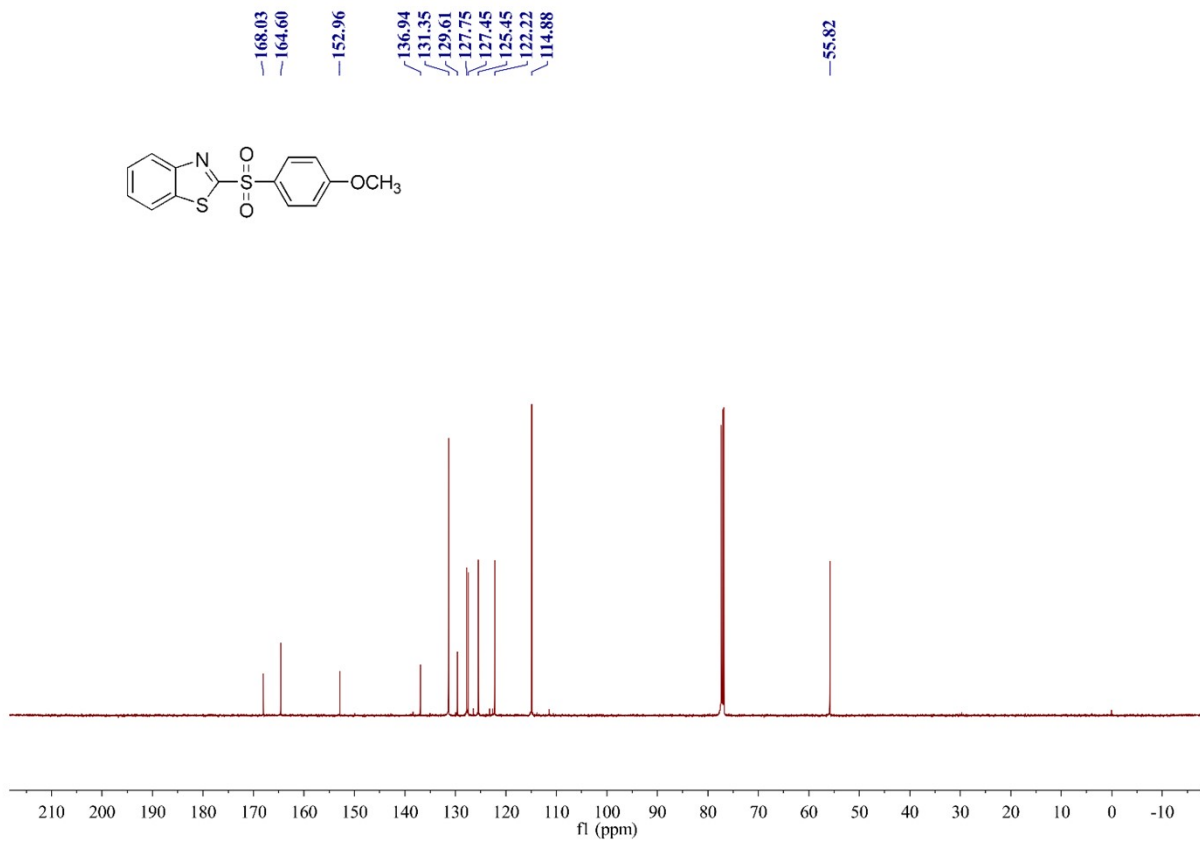
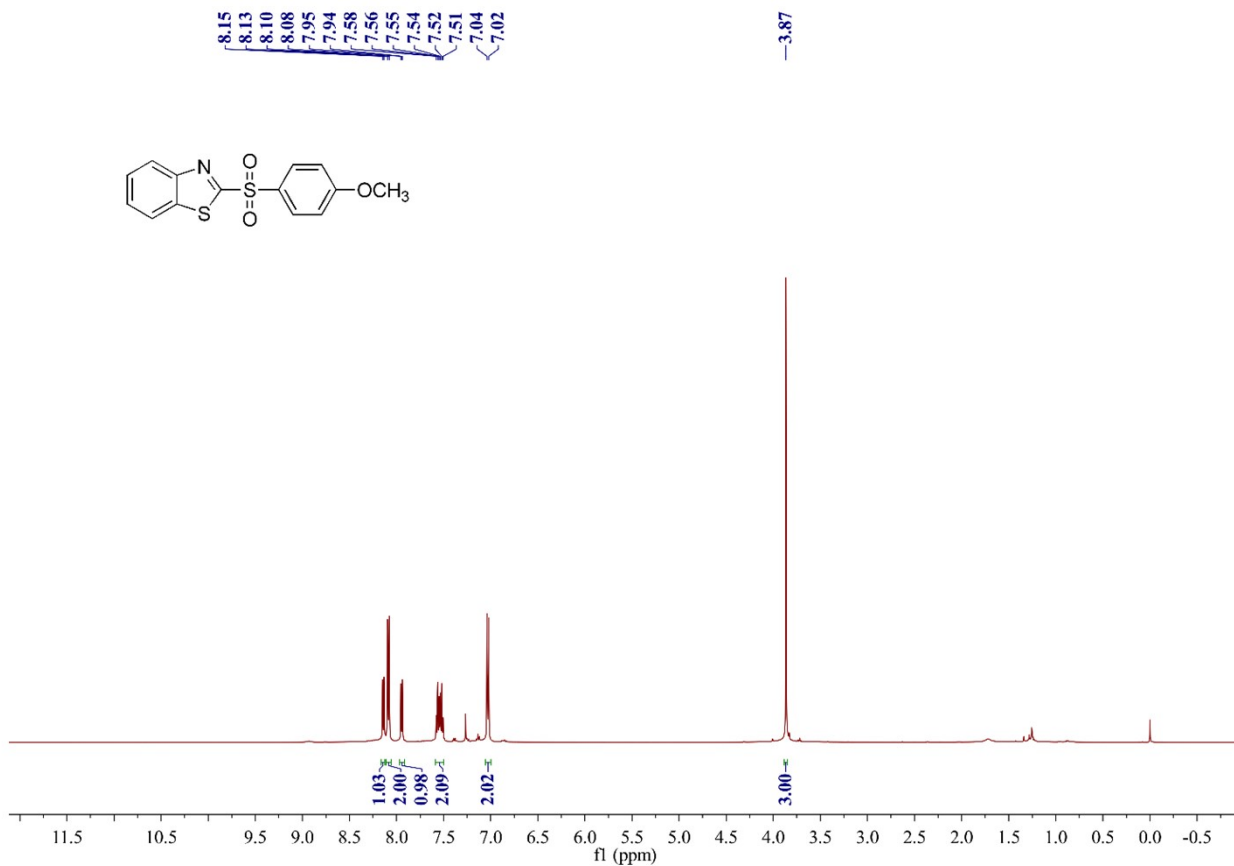


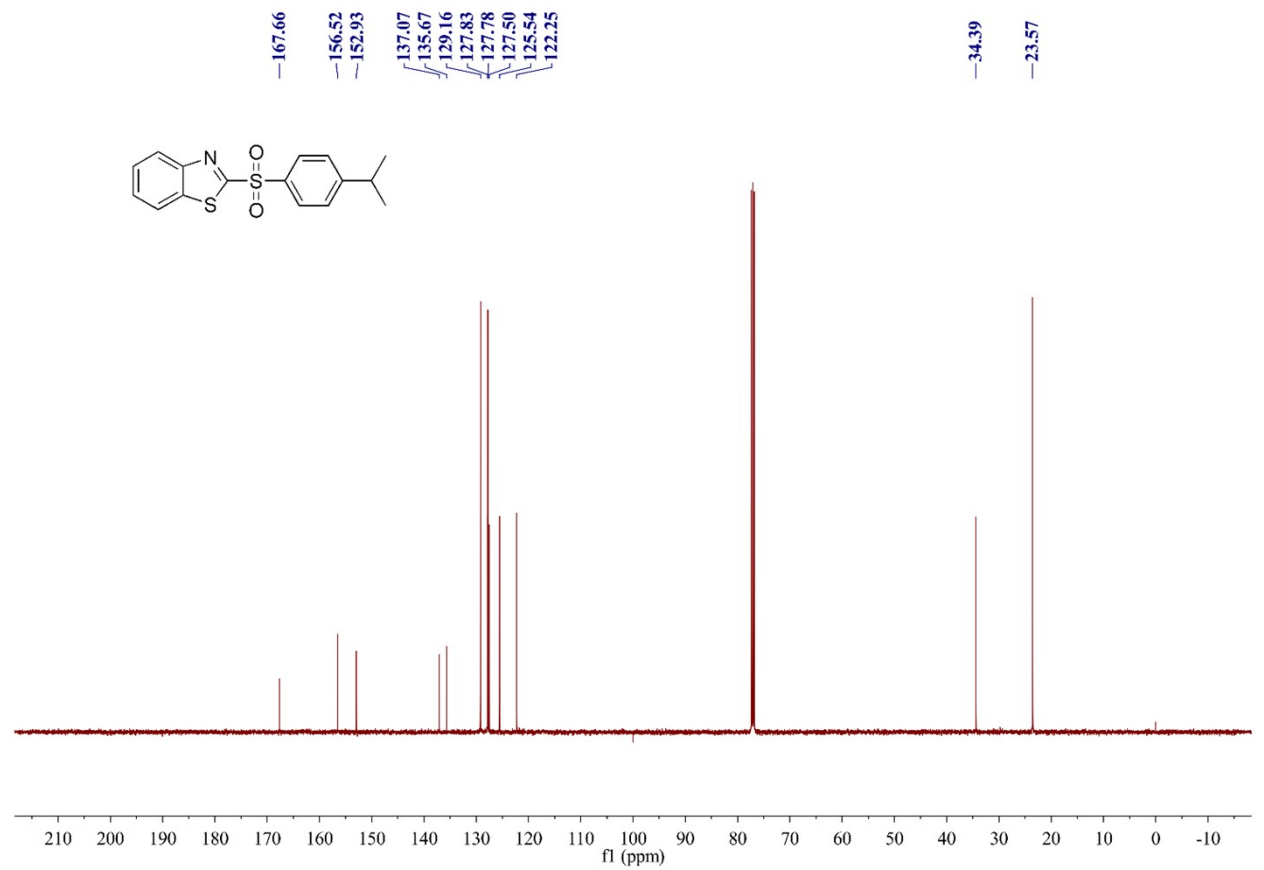
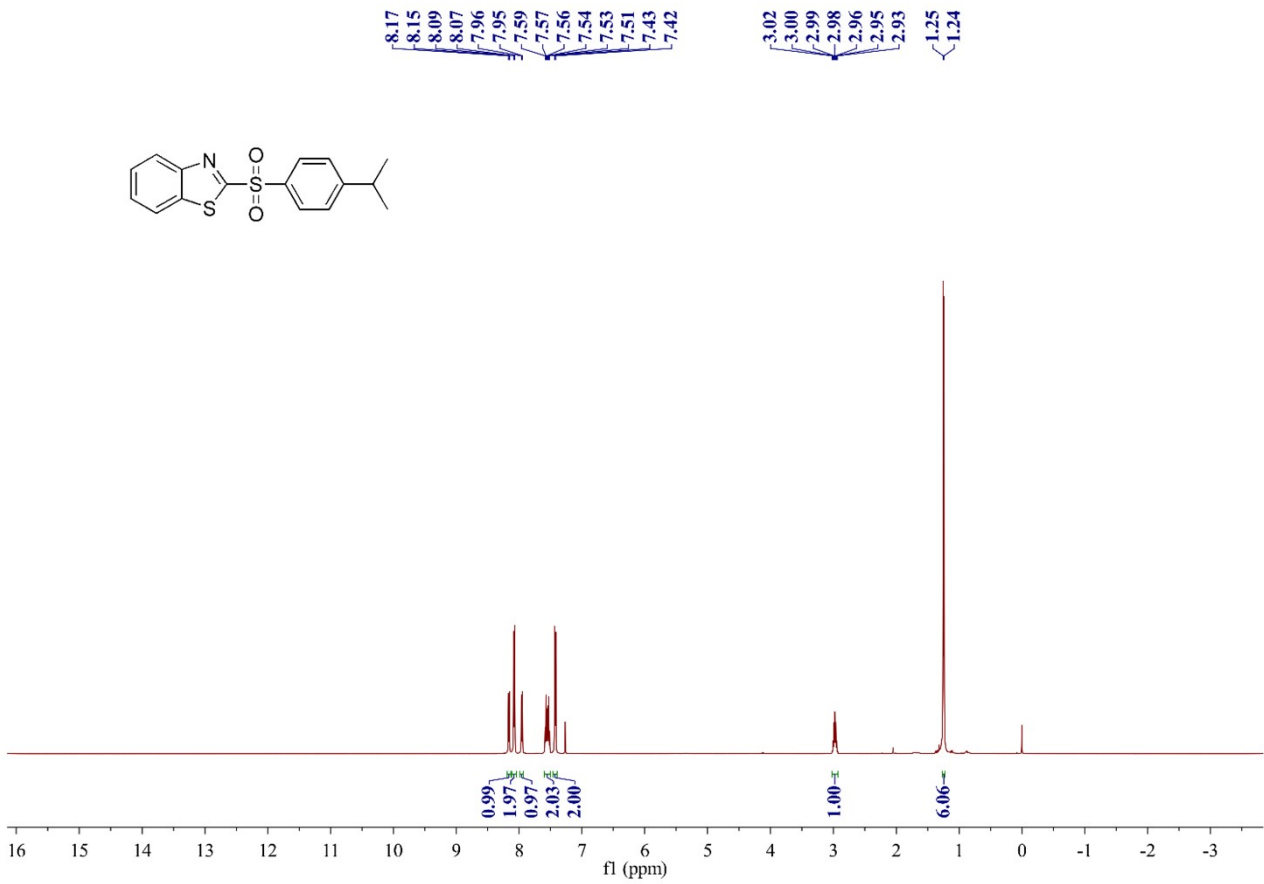
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122.26

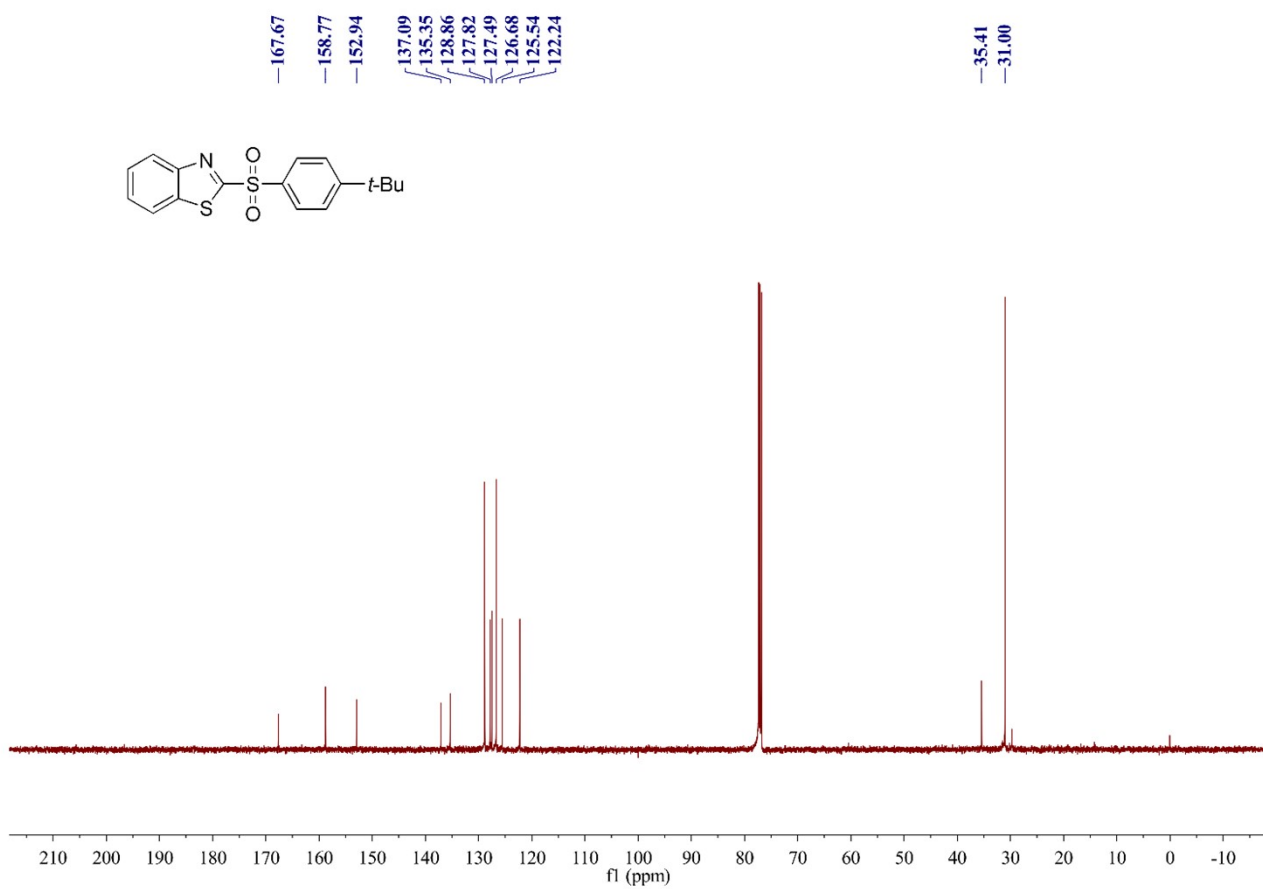
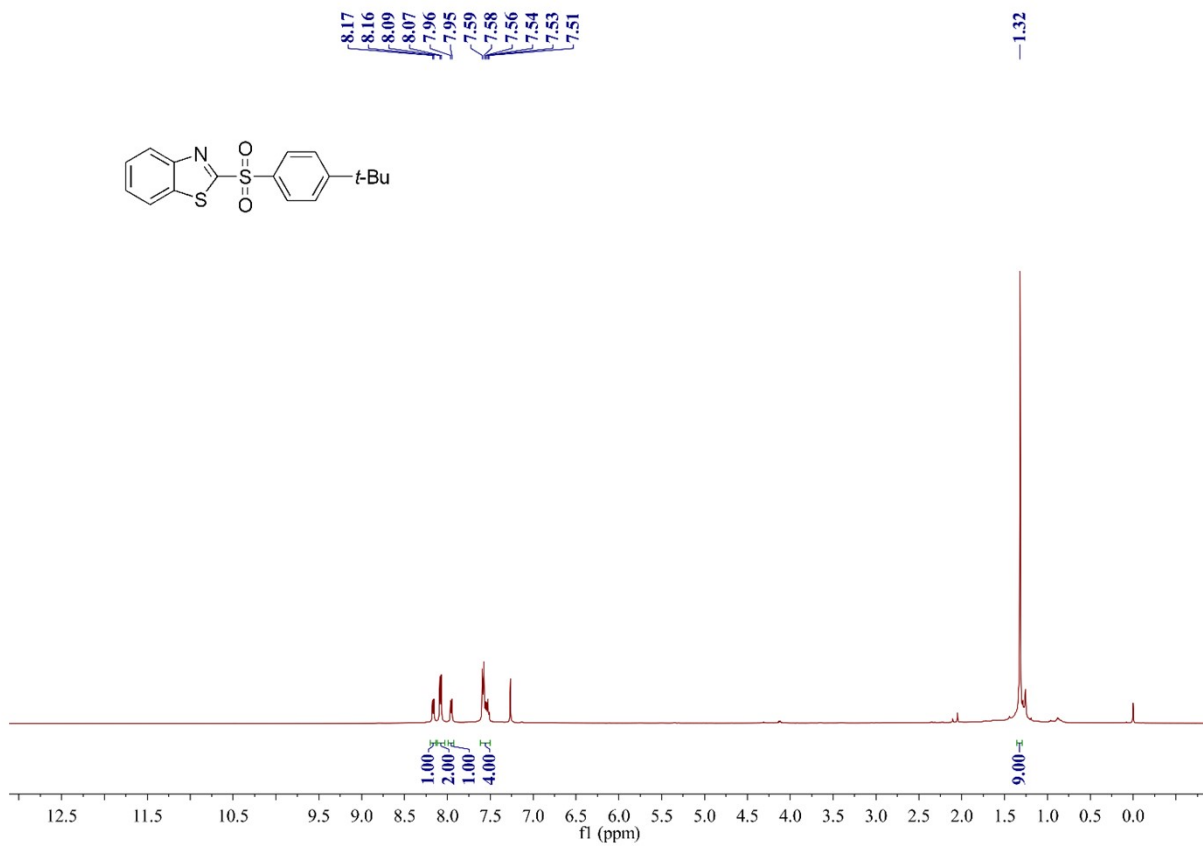


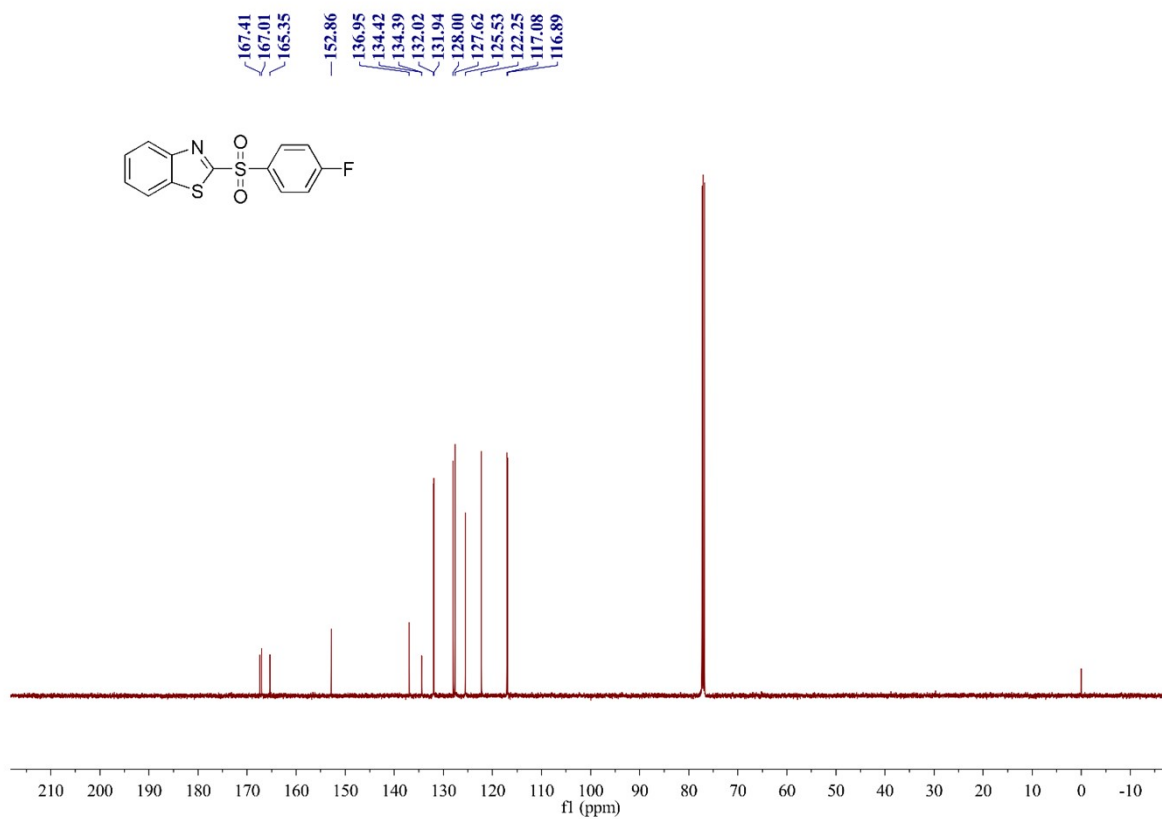
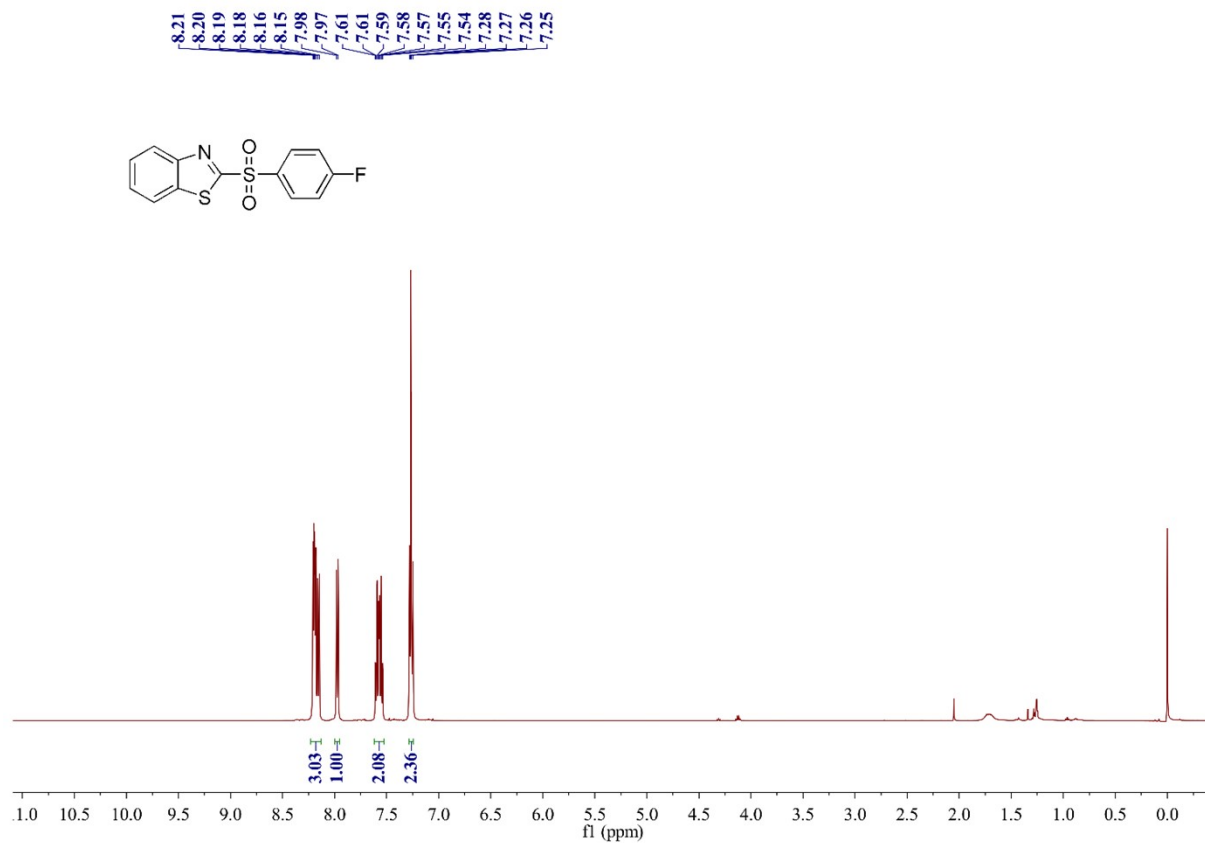


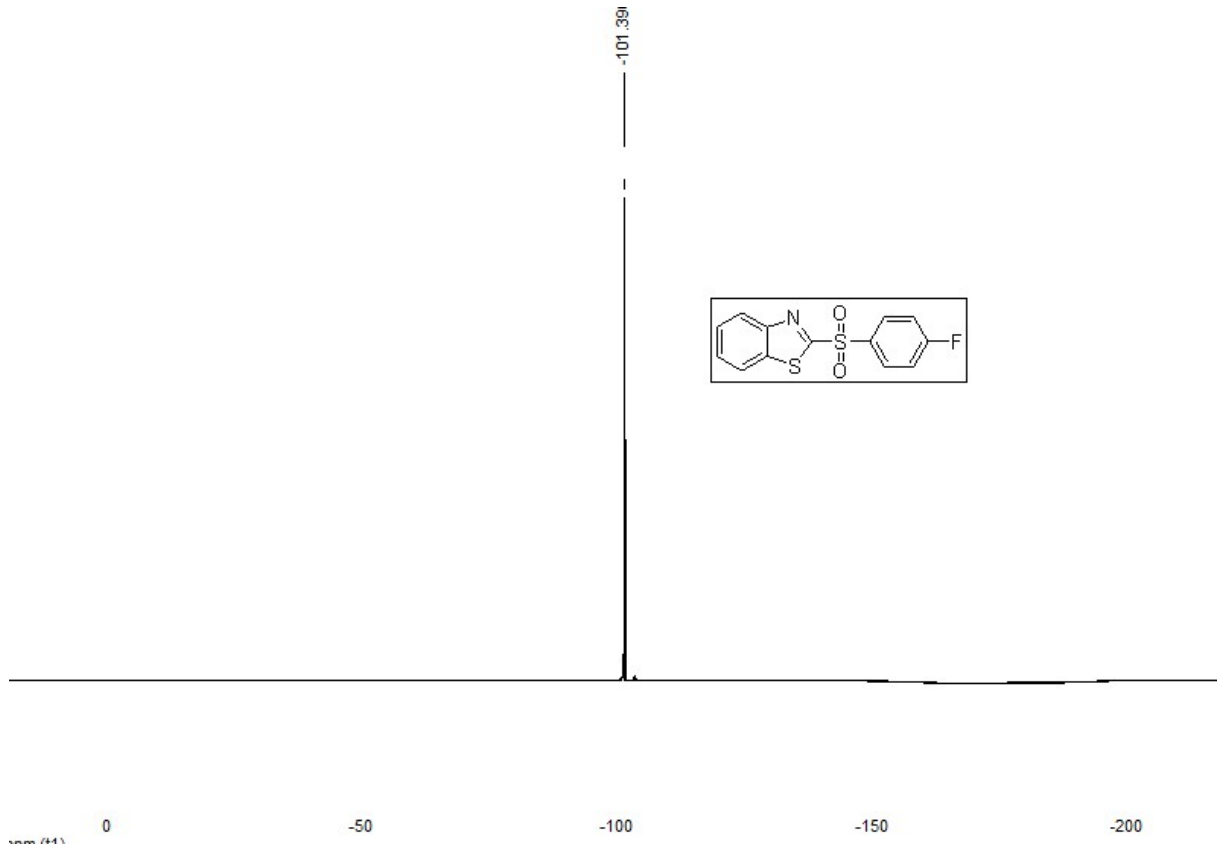




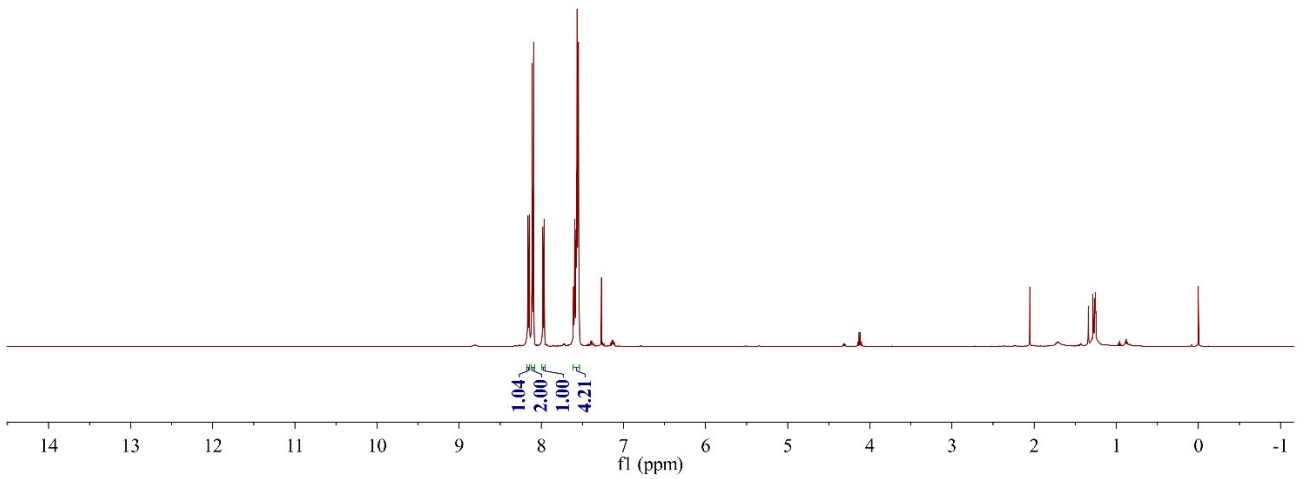
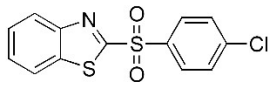


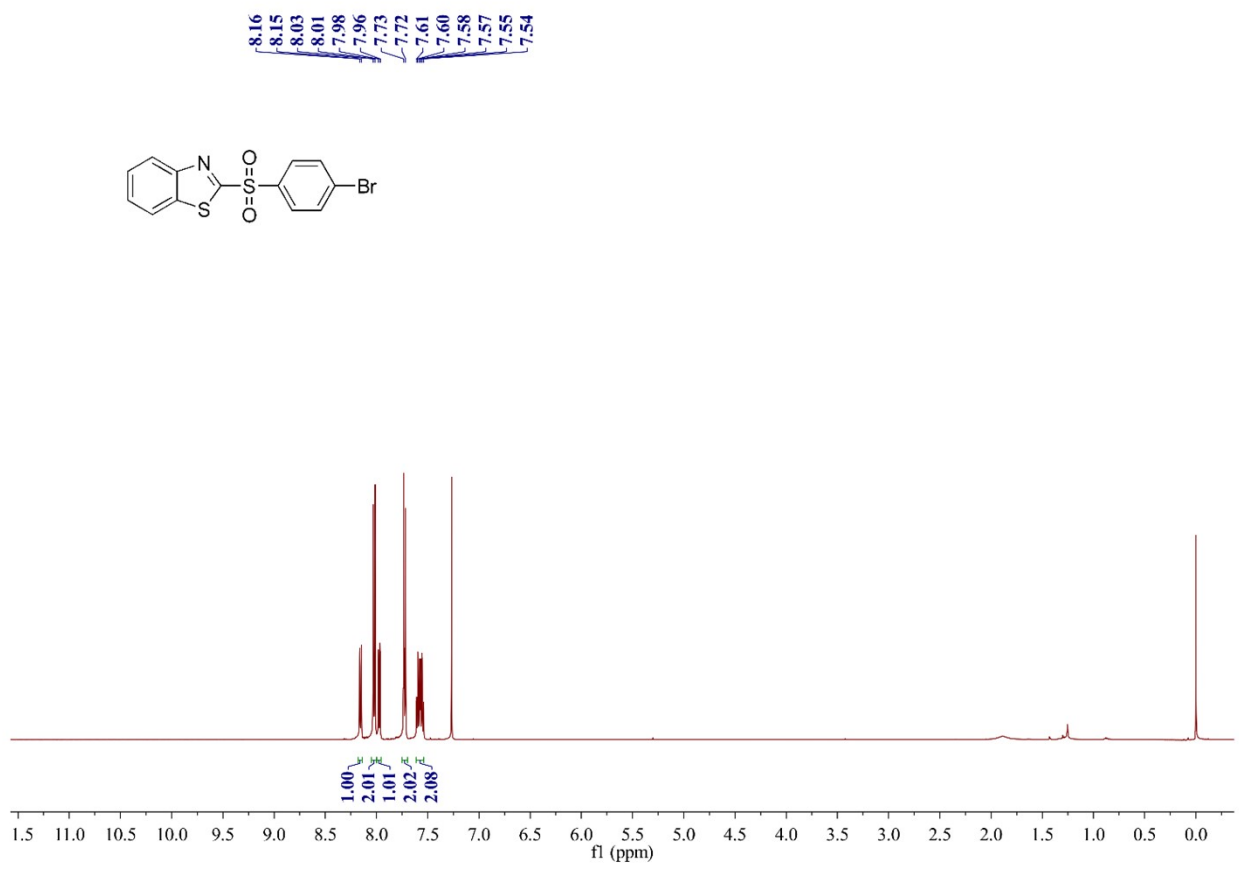
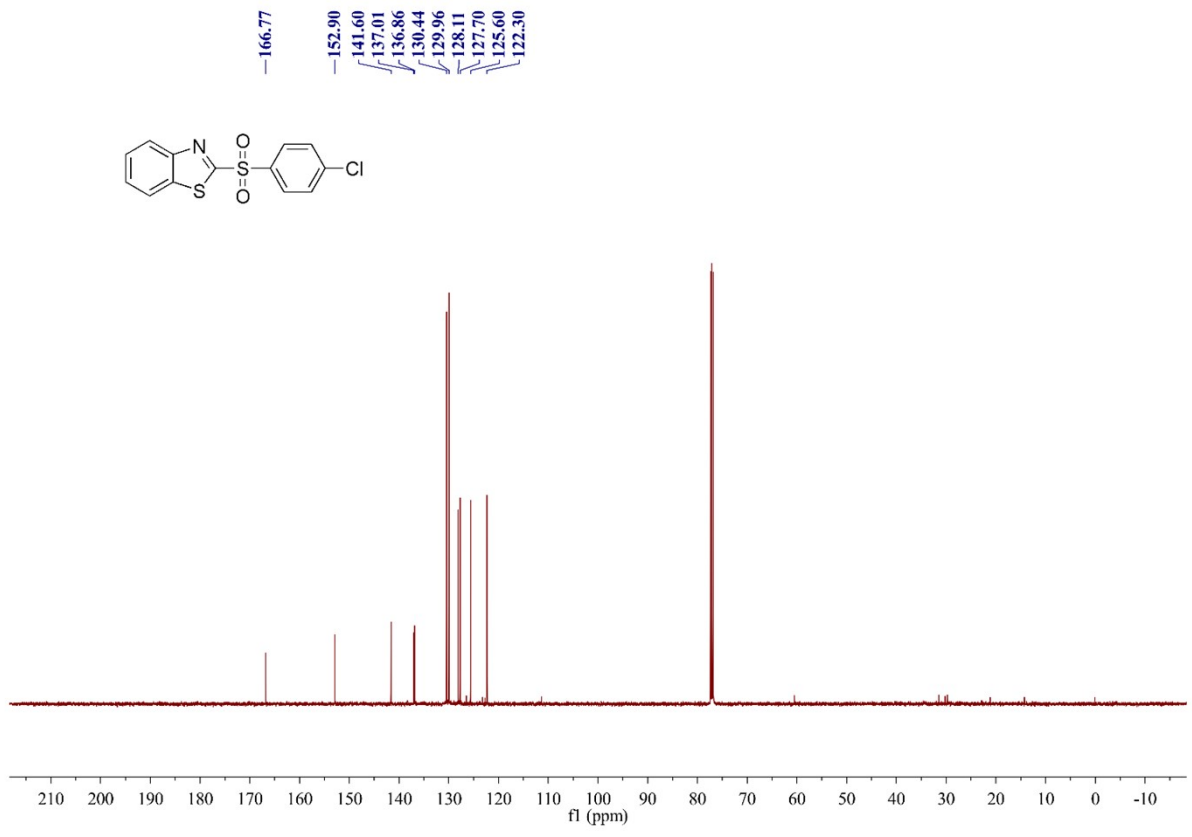


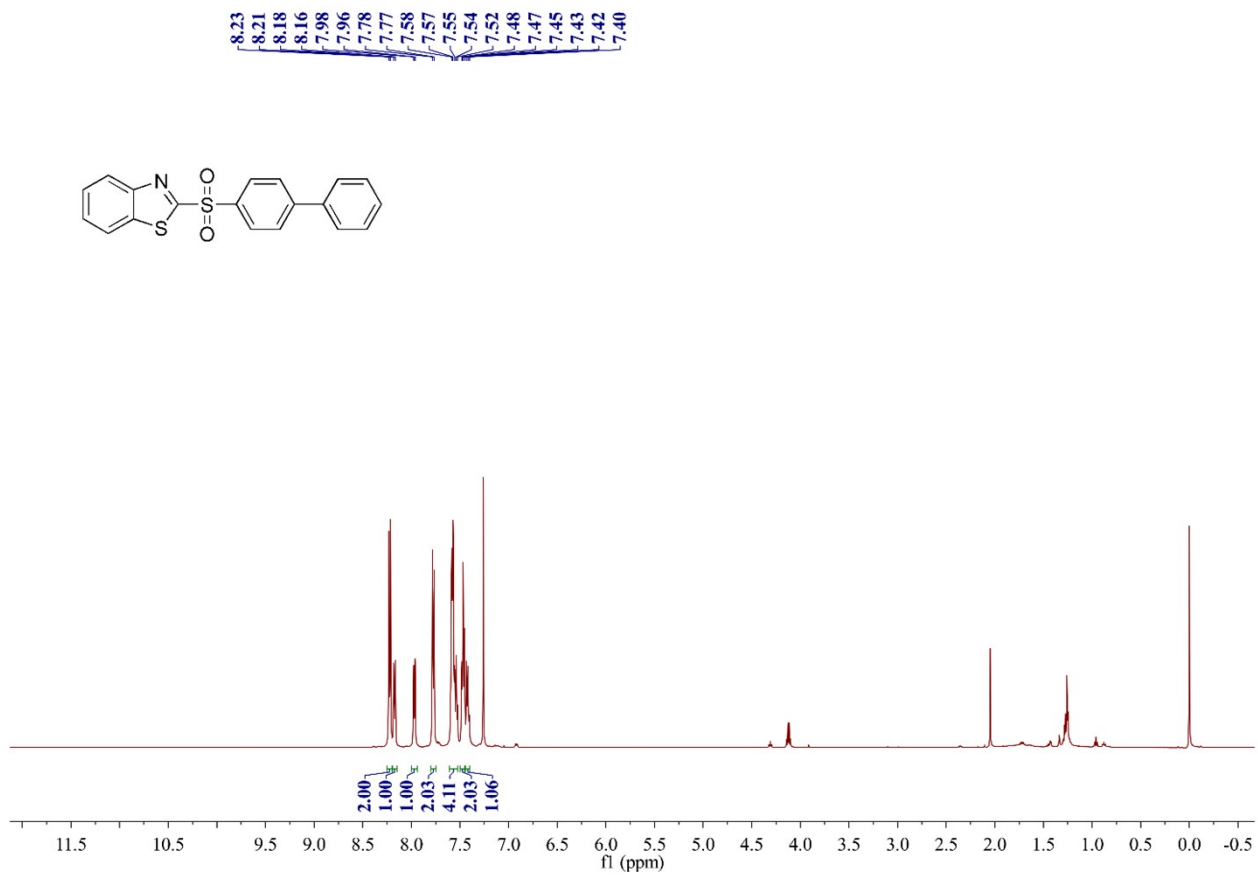
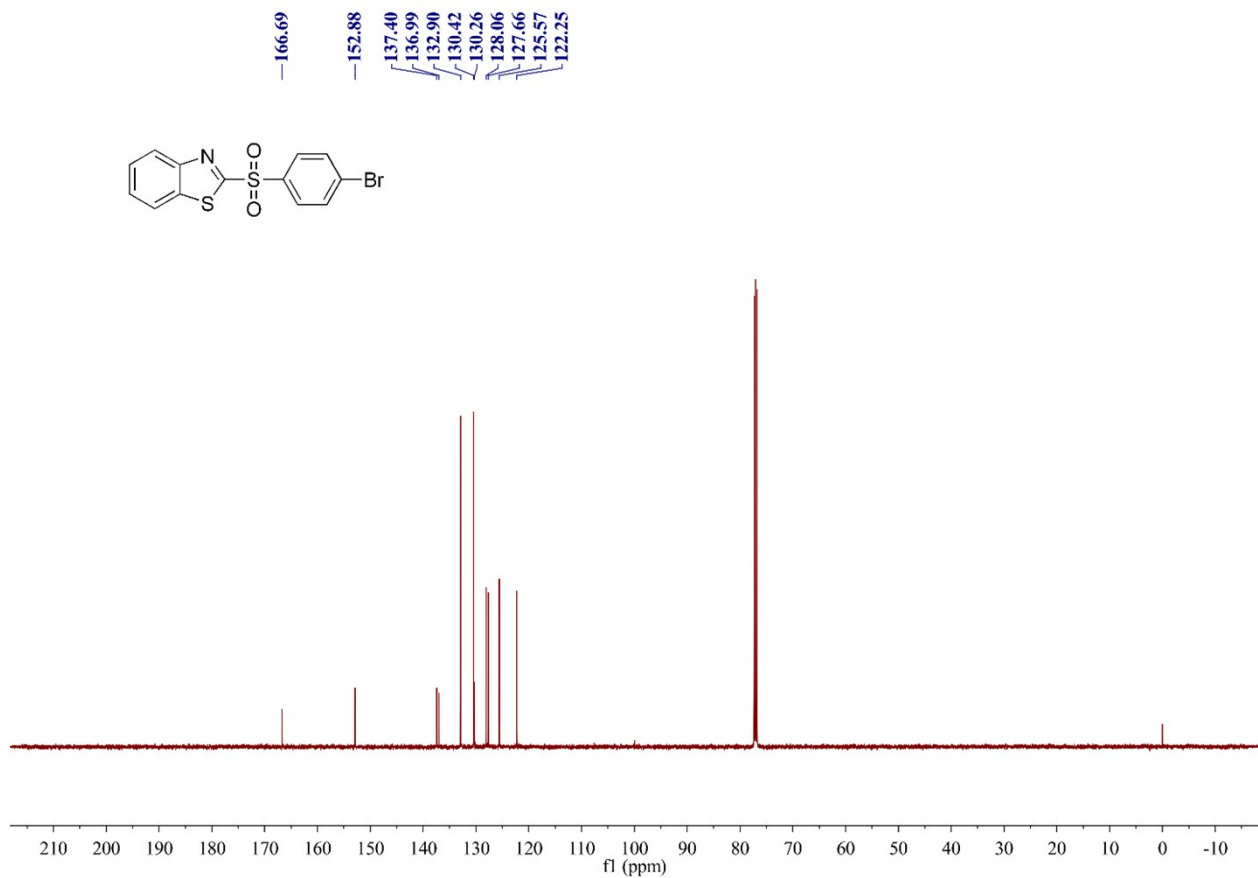


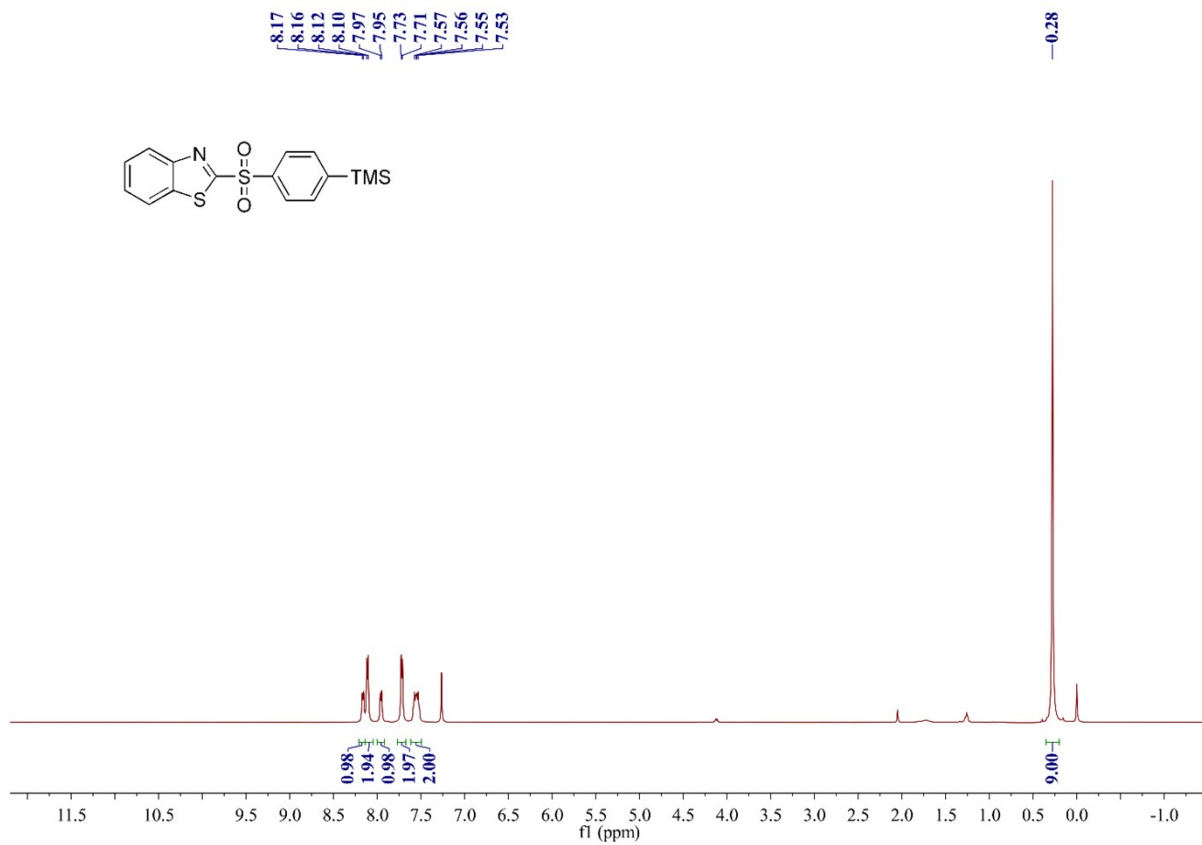
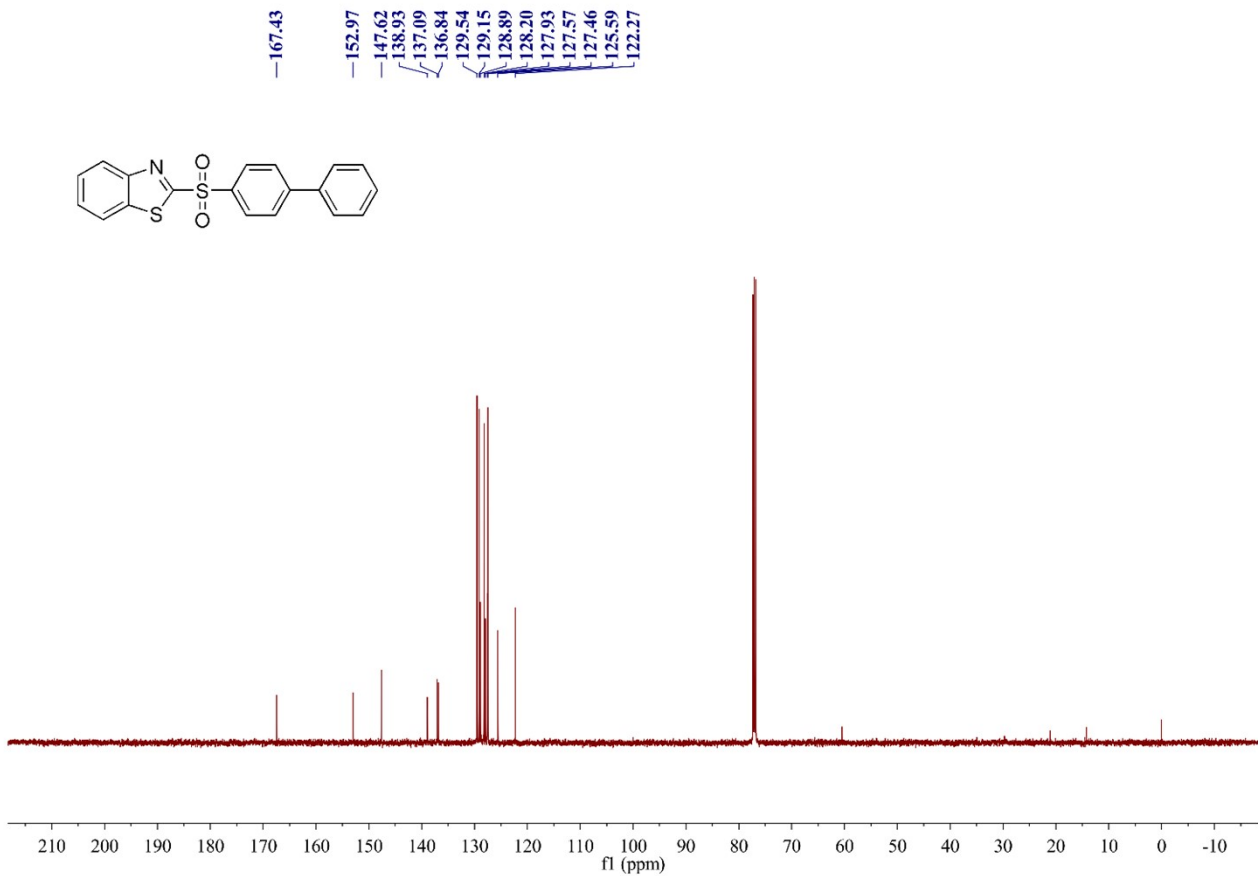


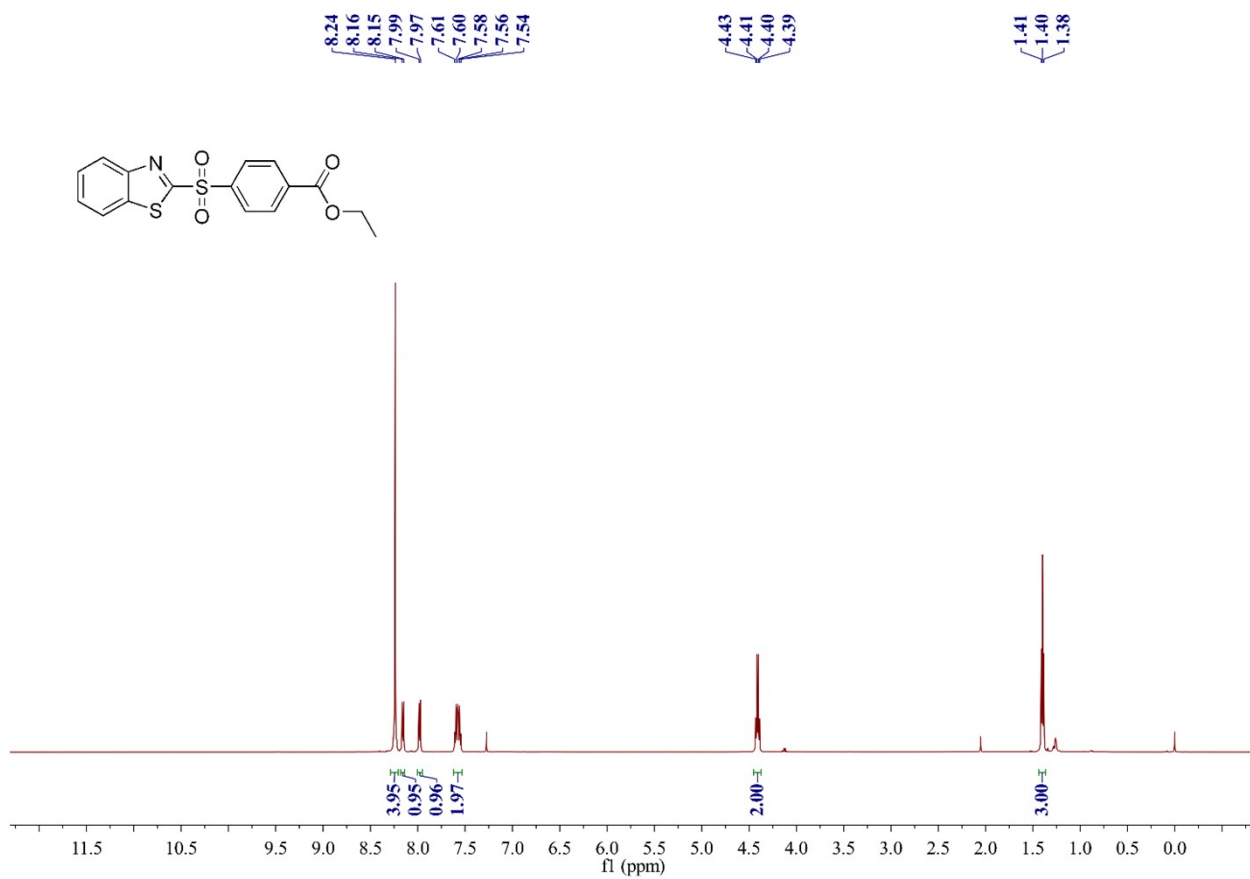
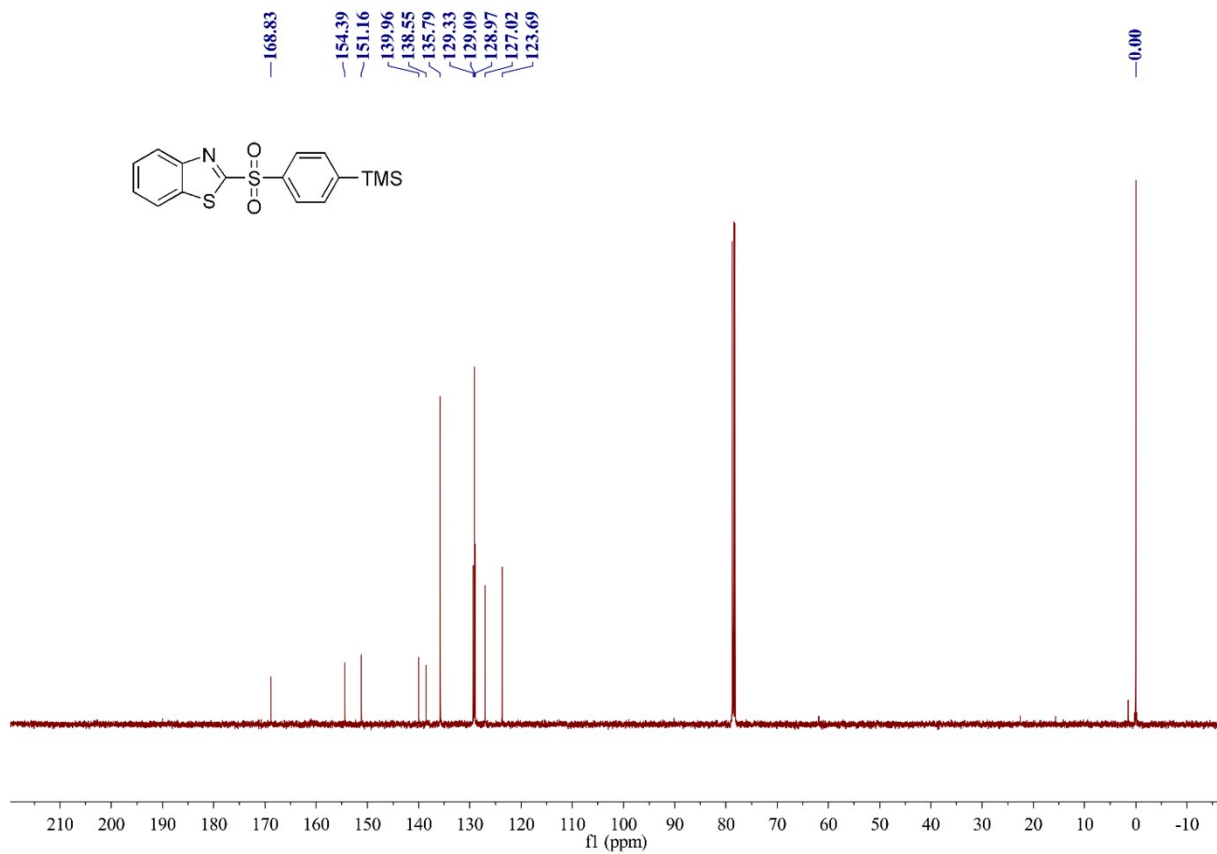
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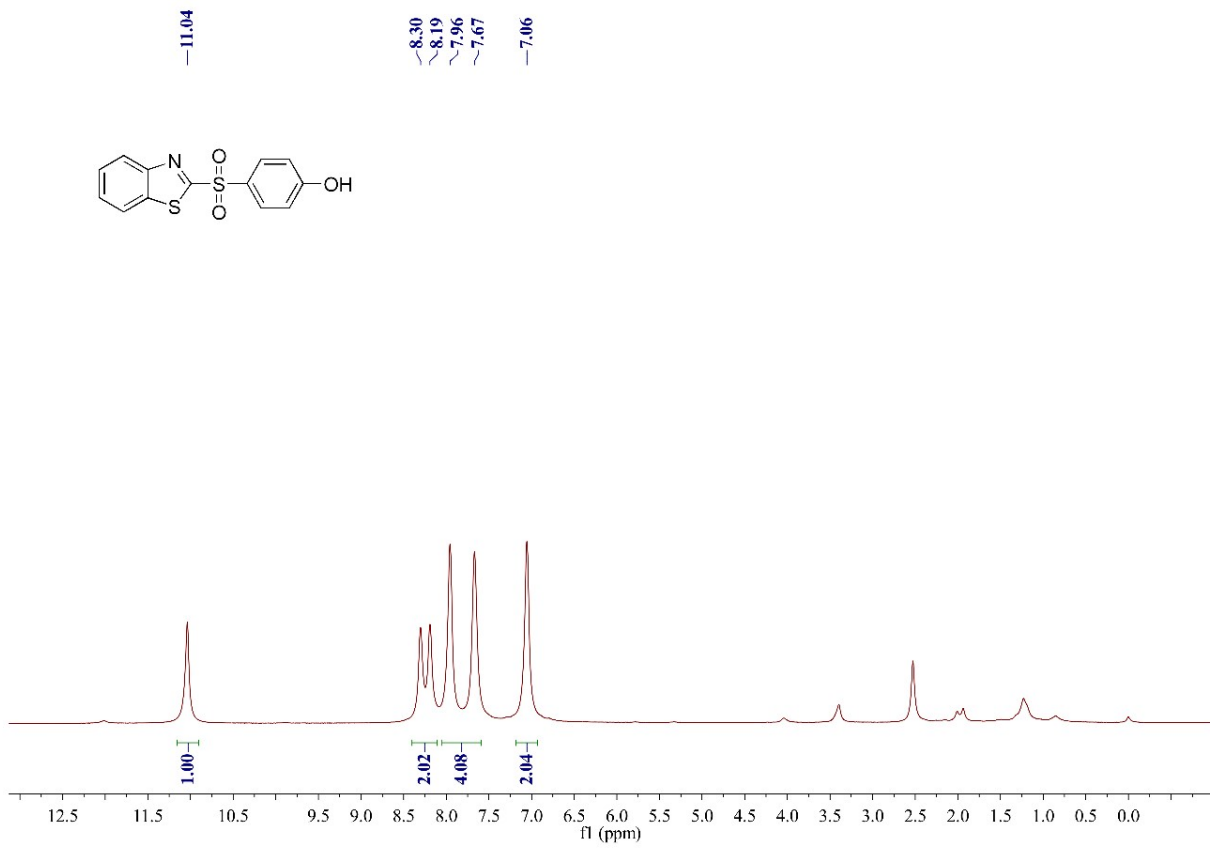
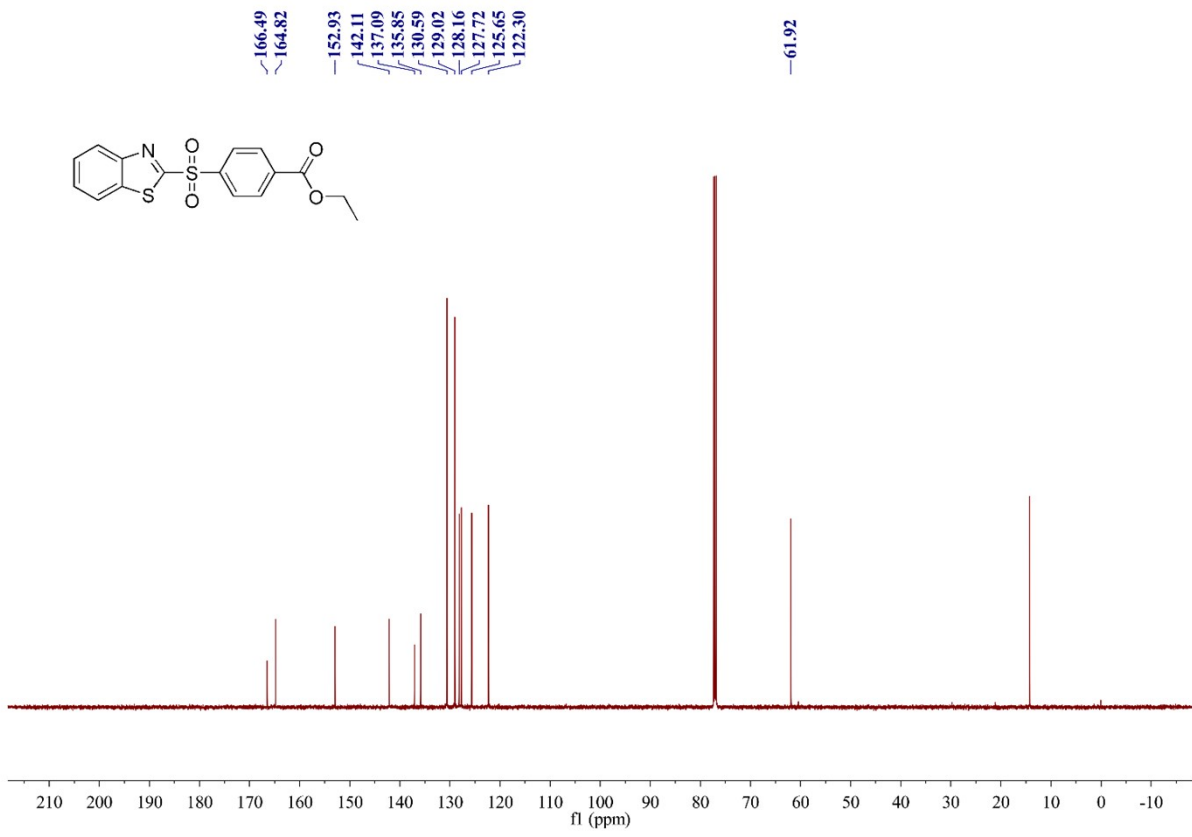


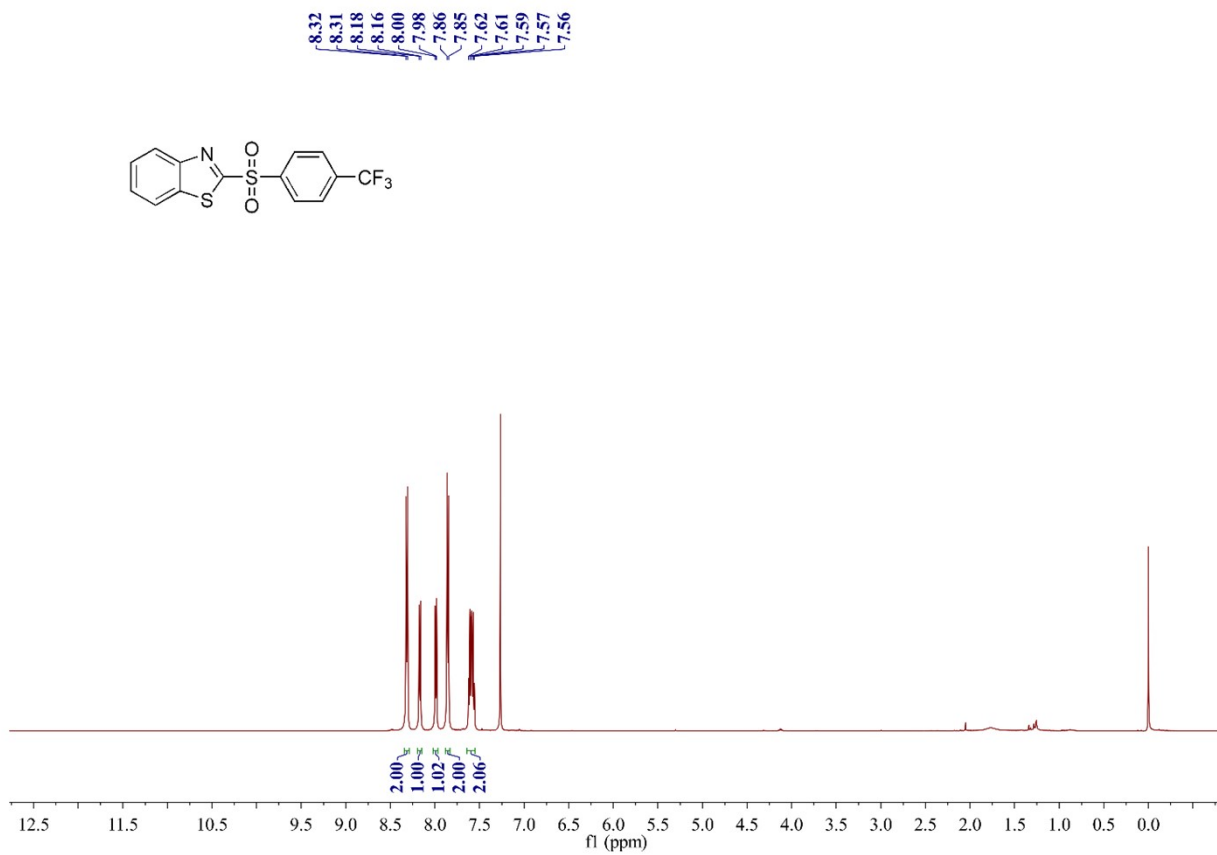
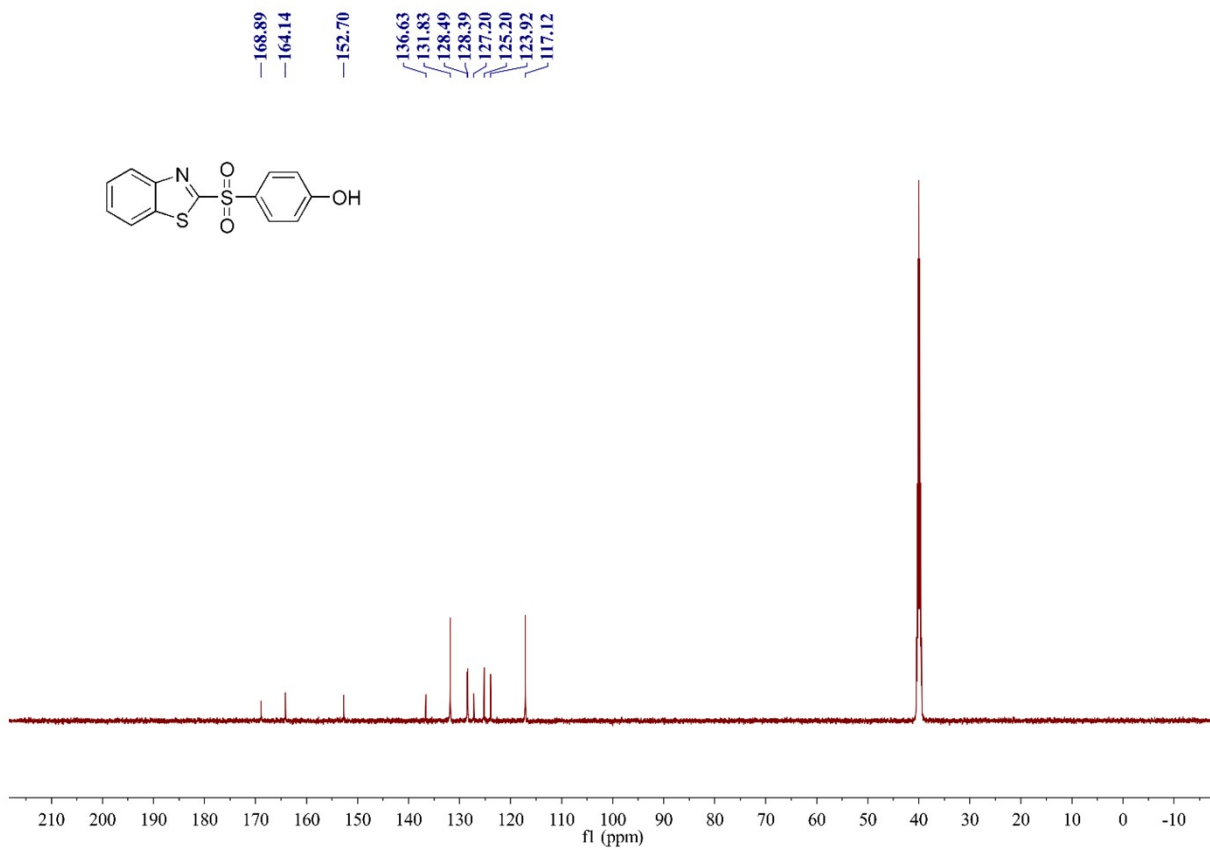


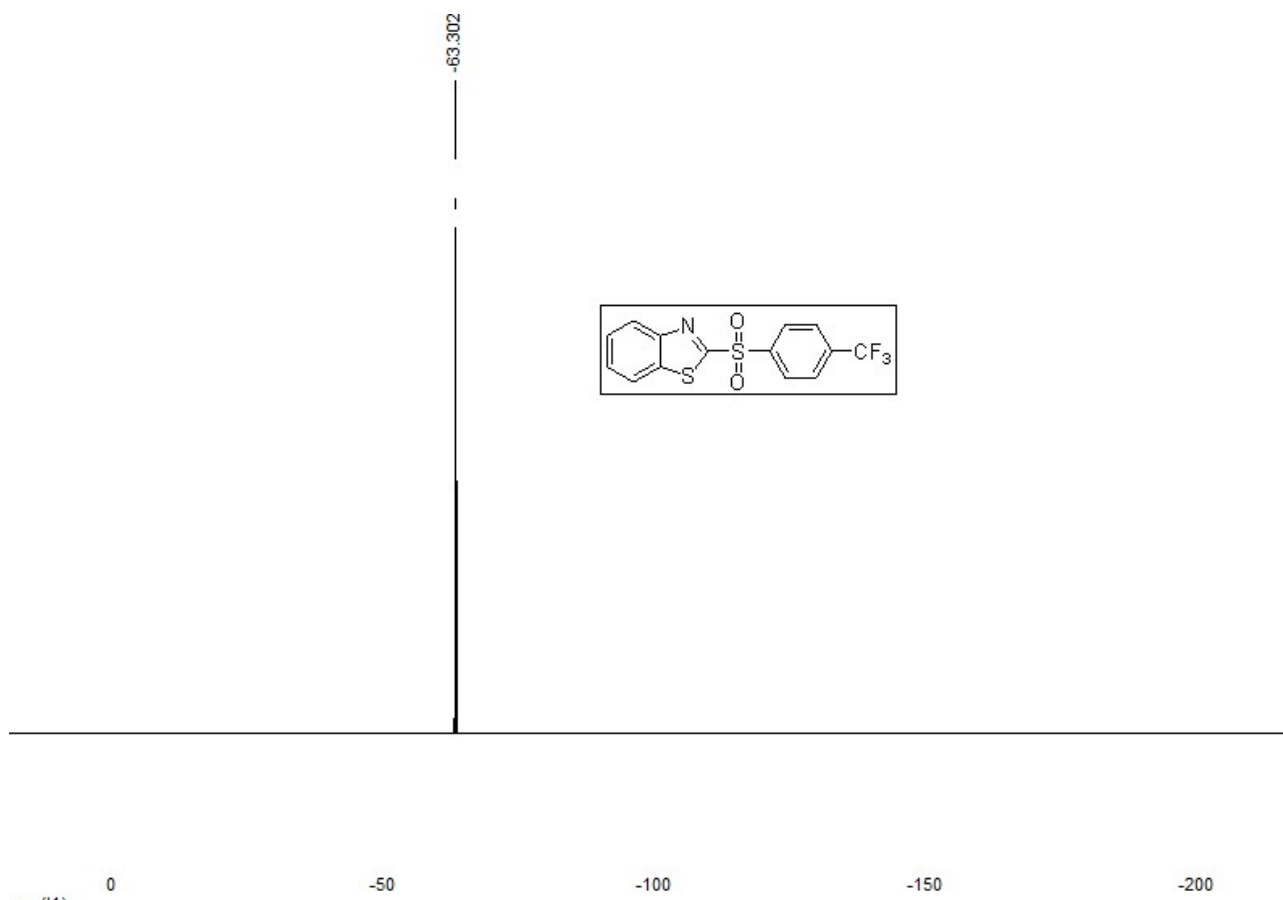
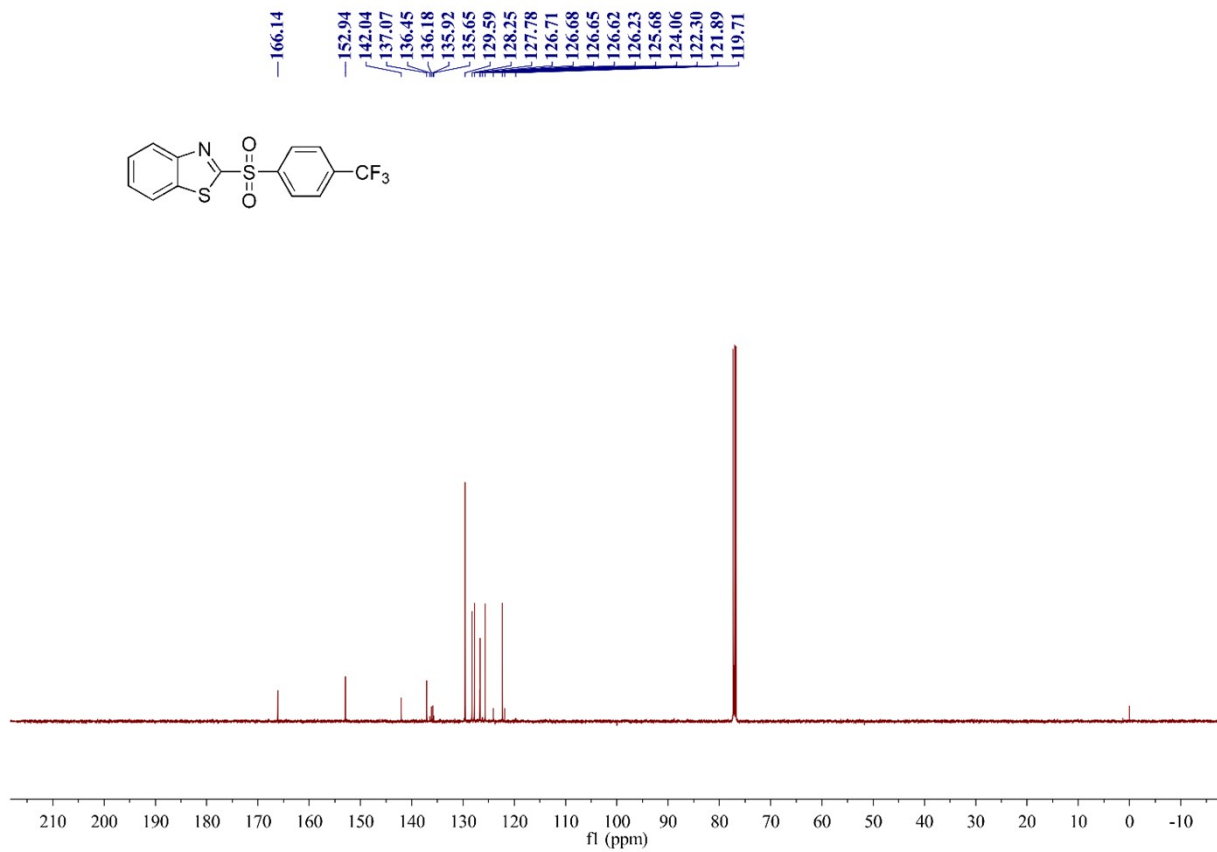


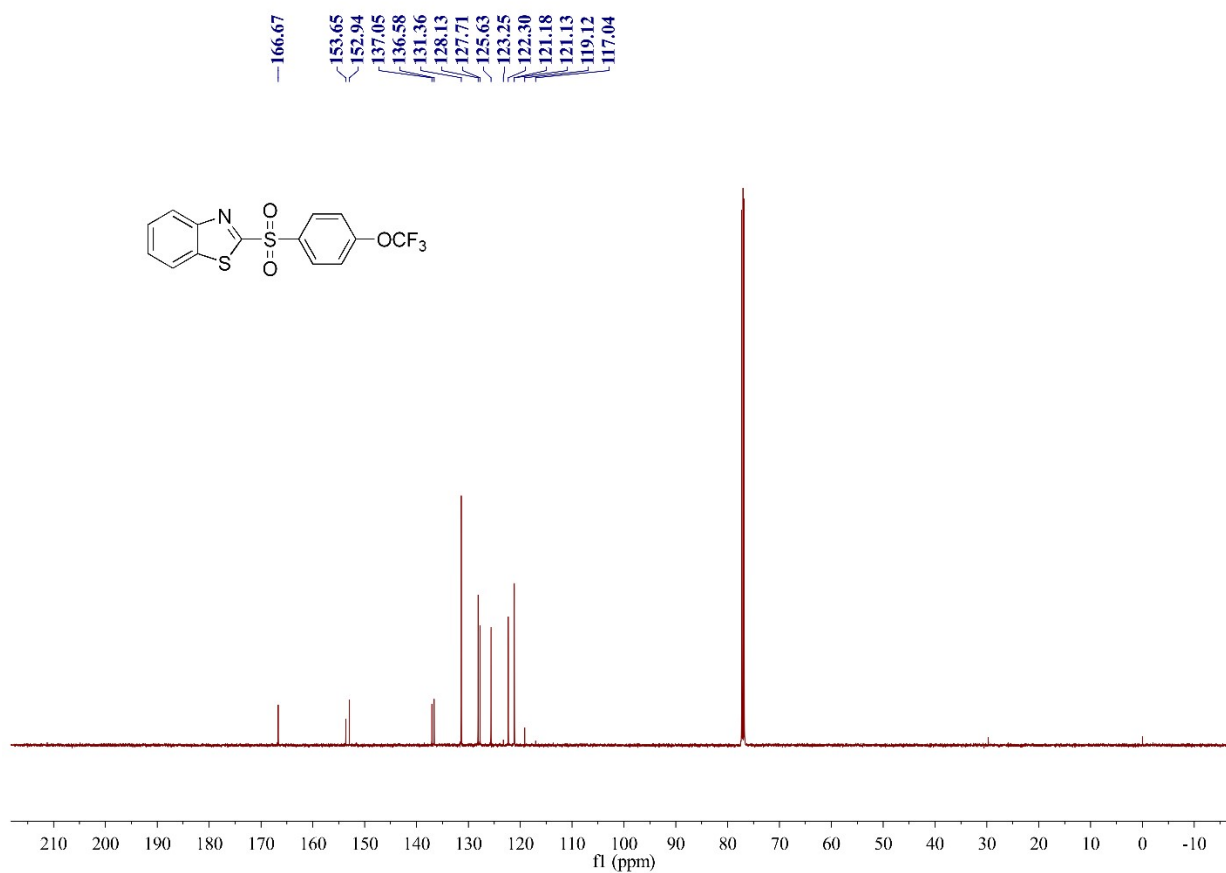
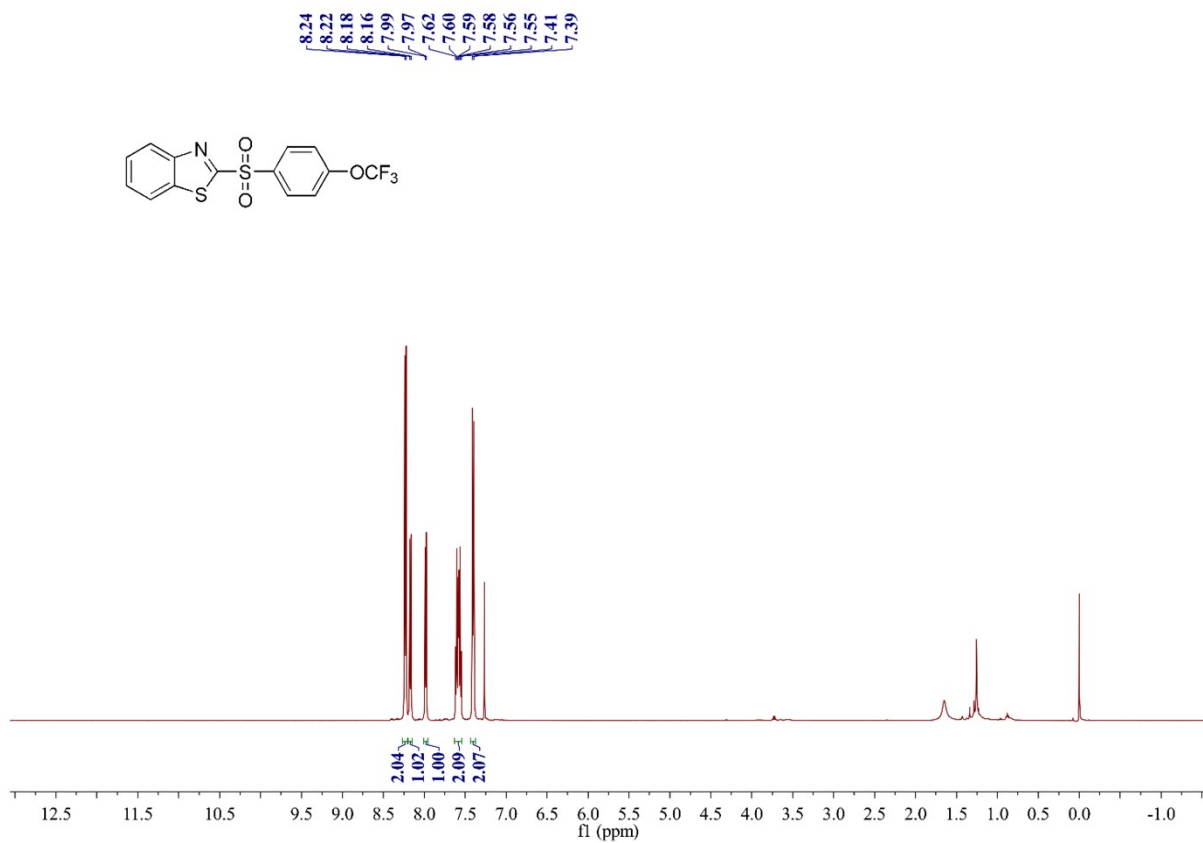


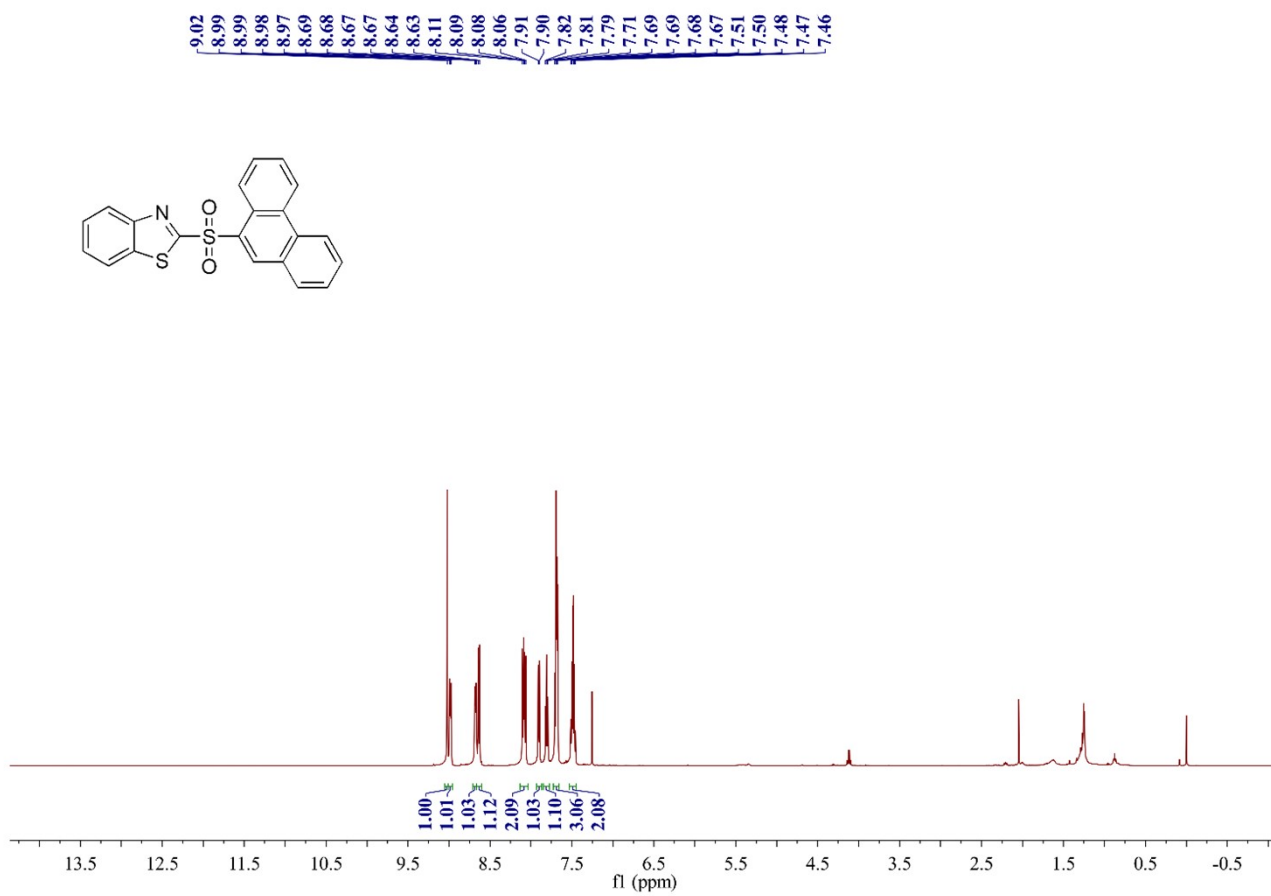
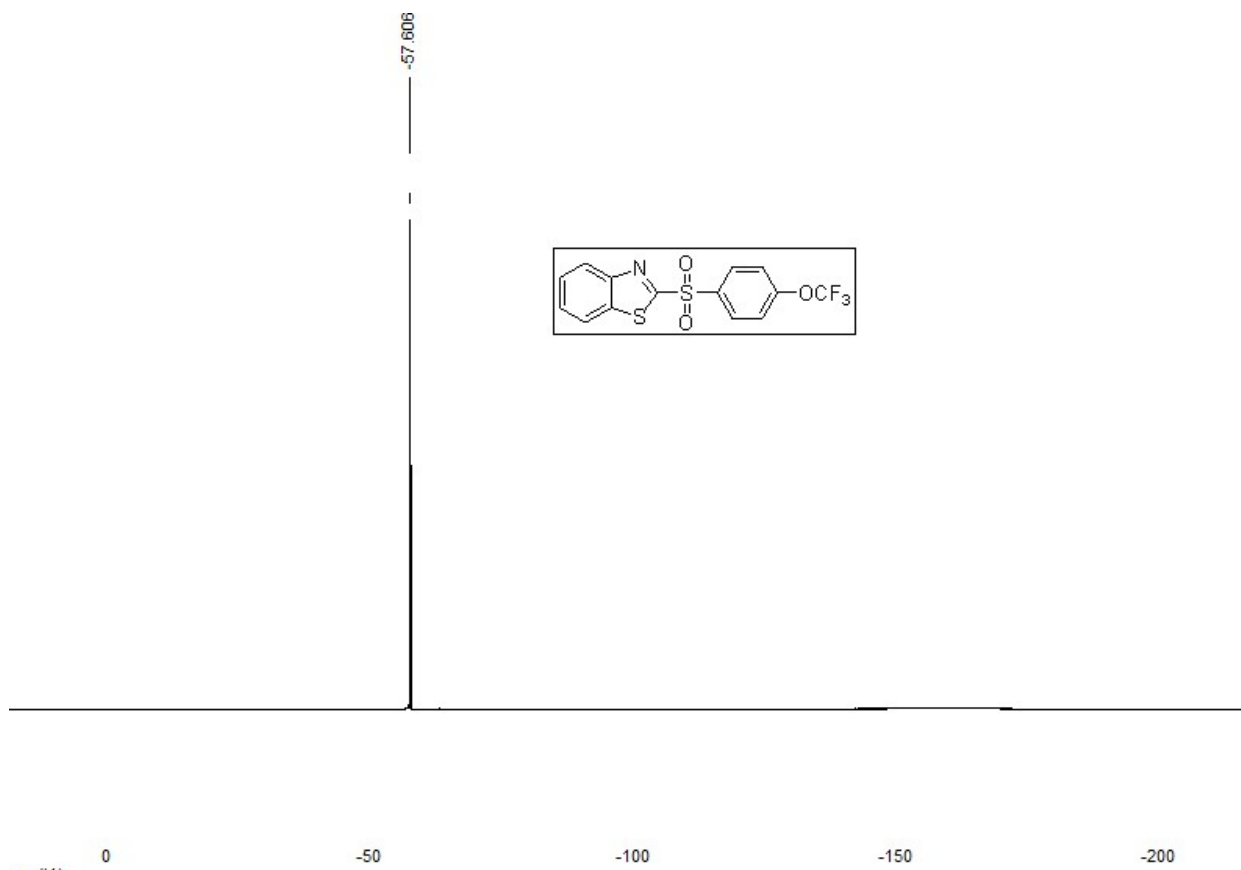


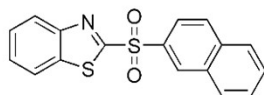
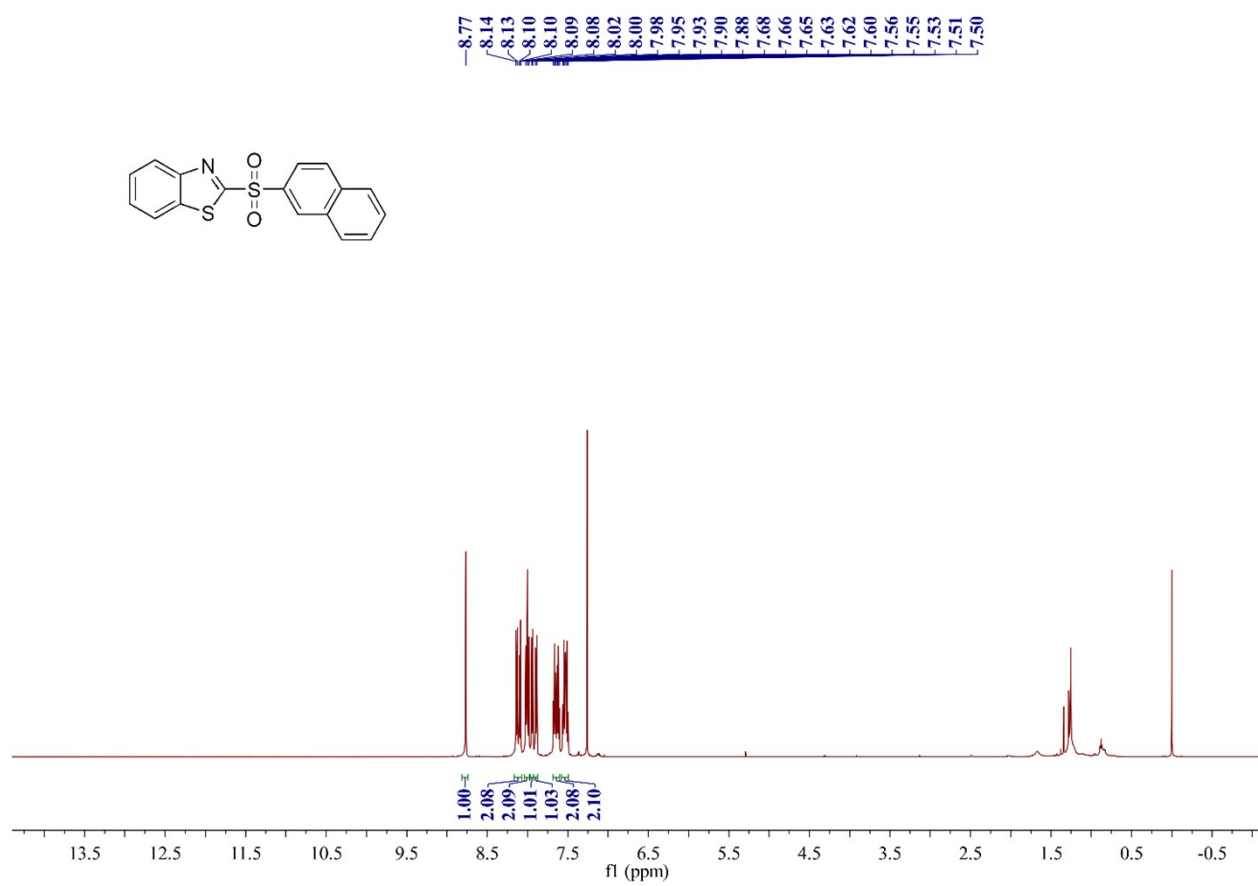
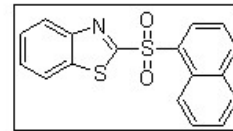
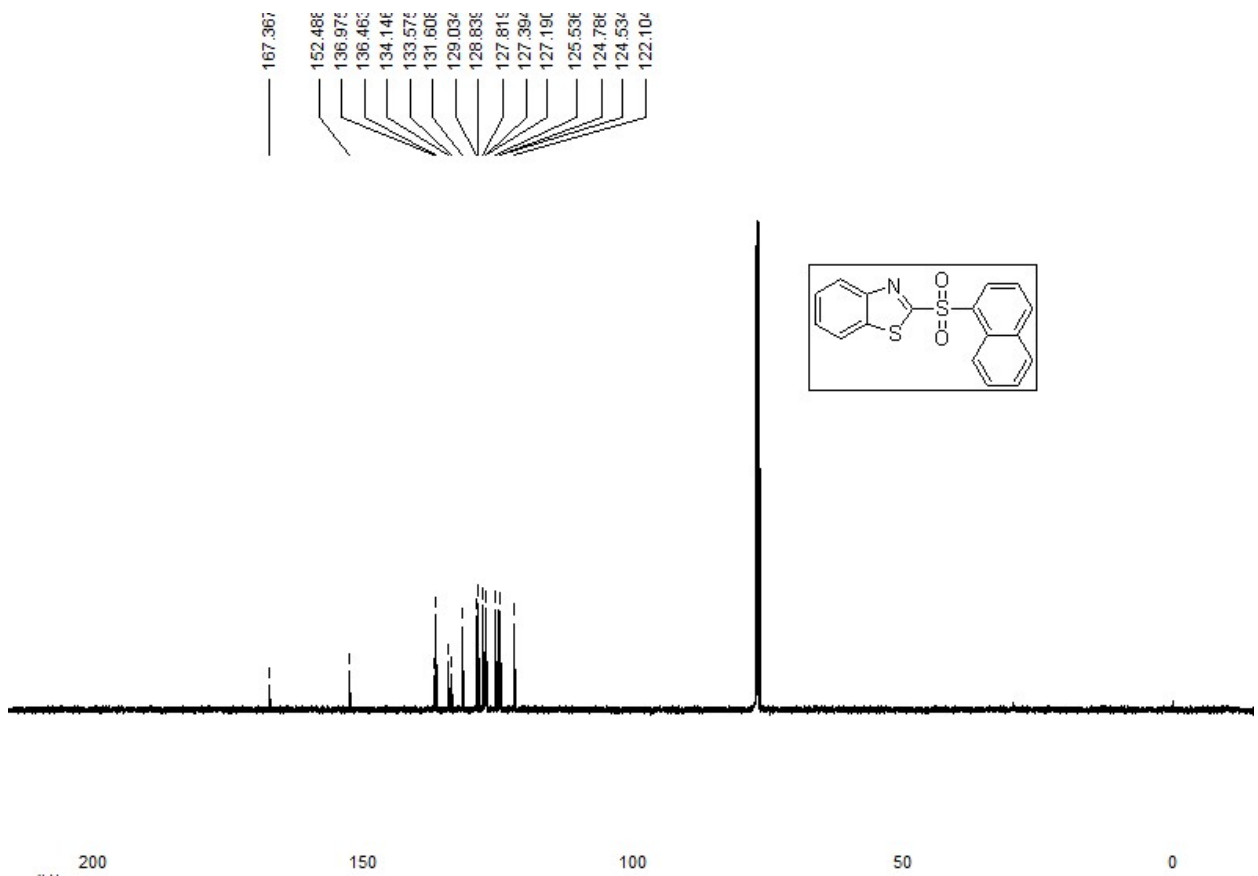


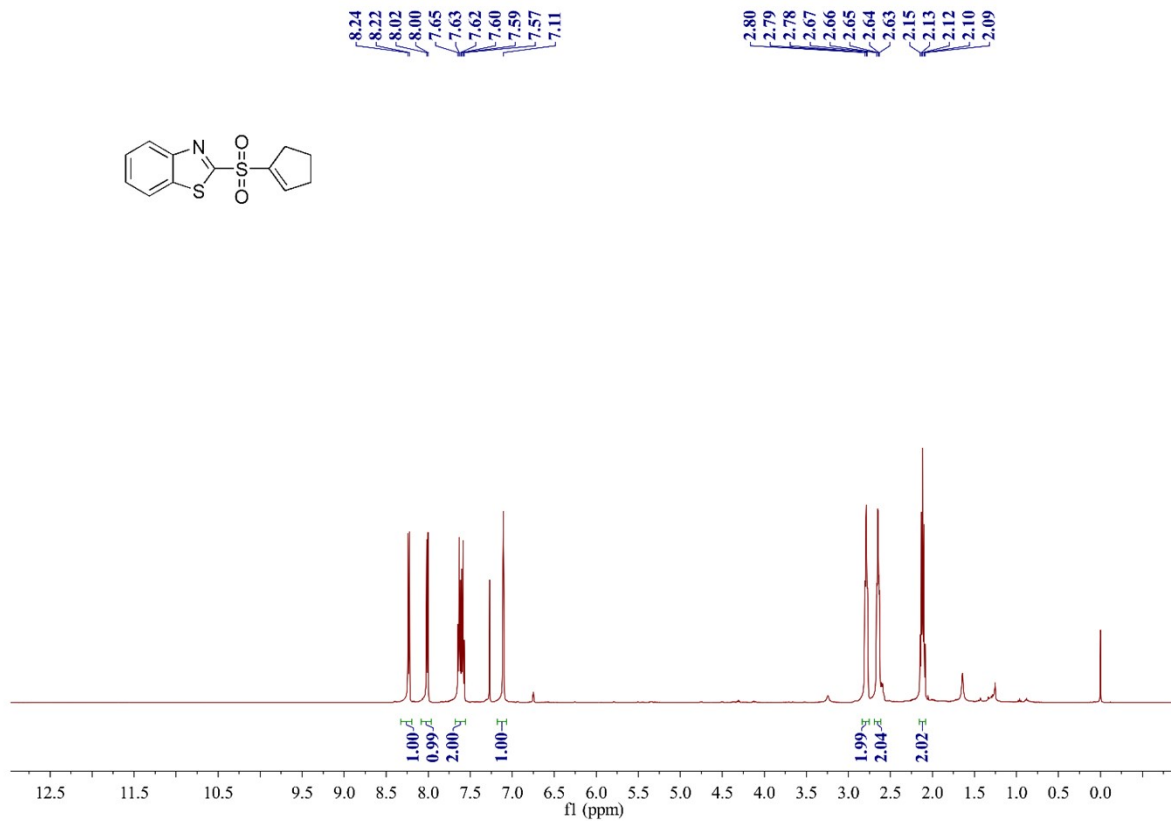
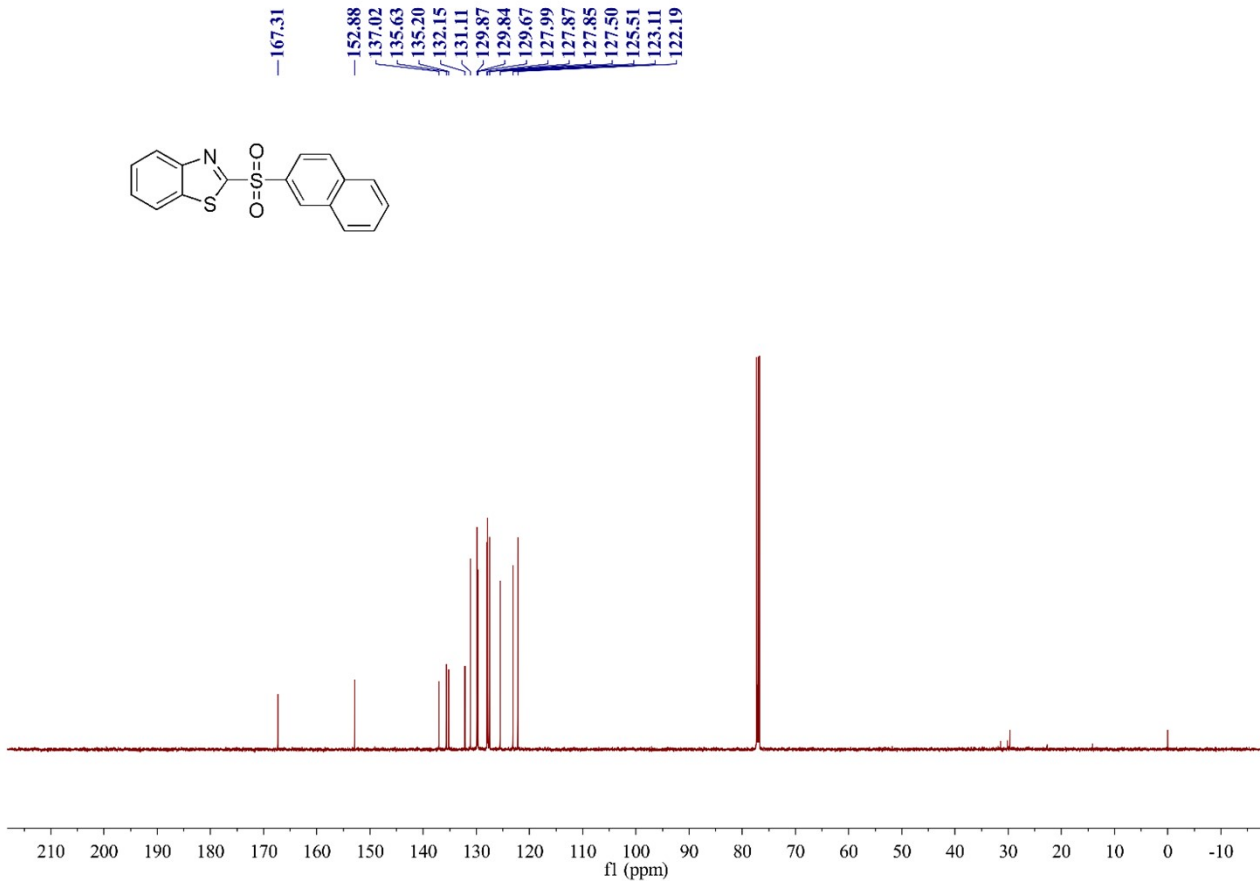


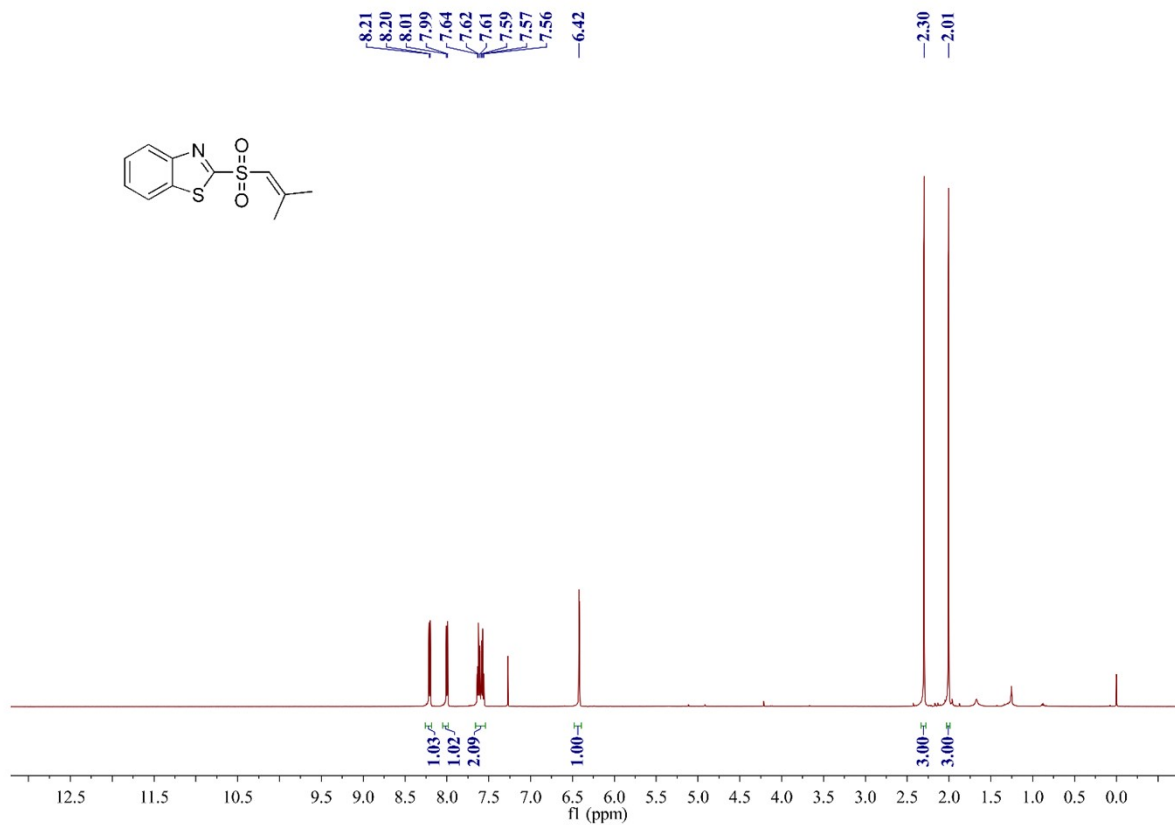
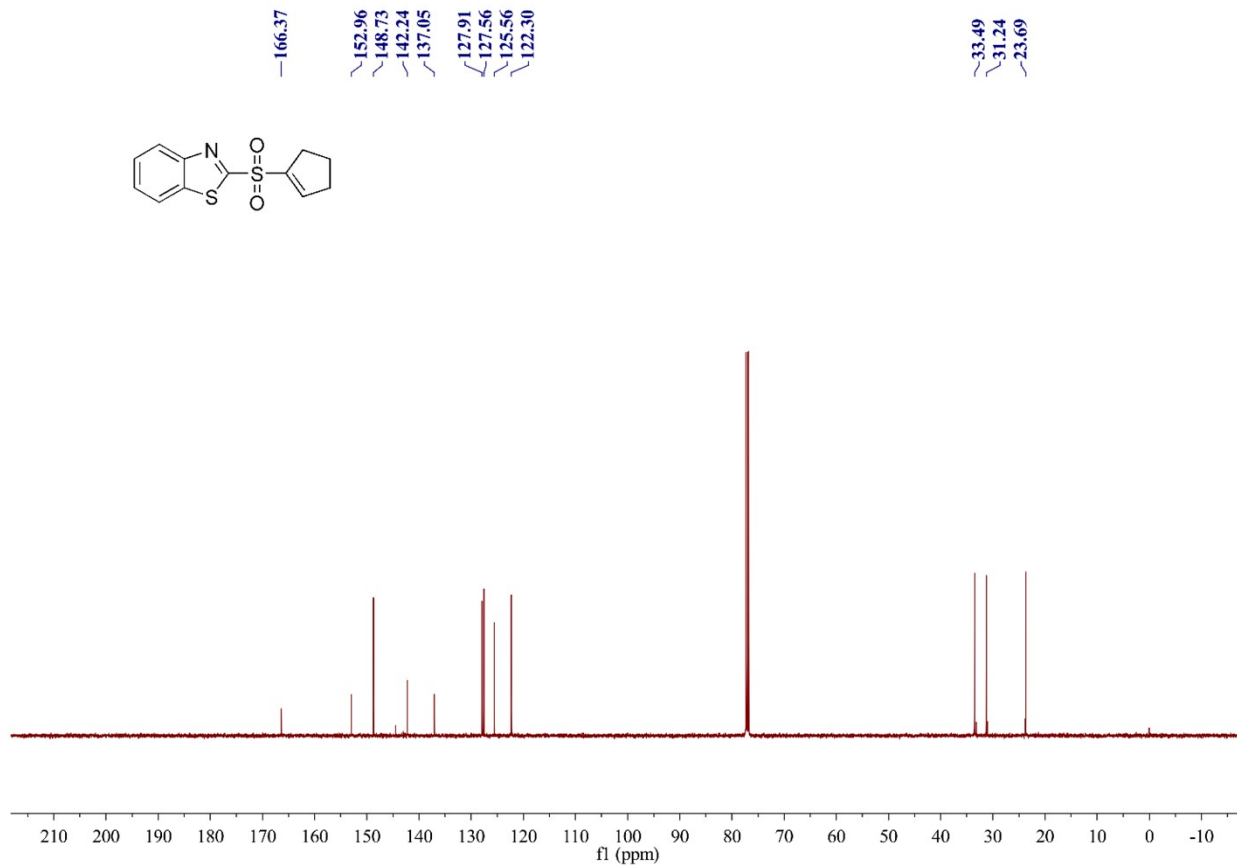


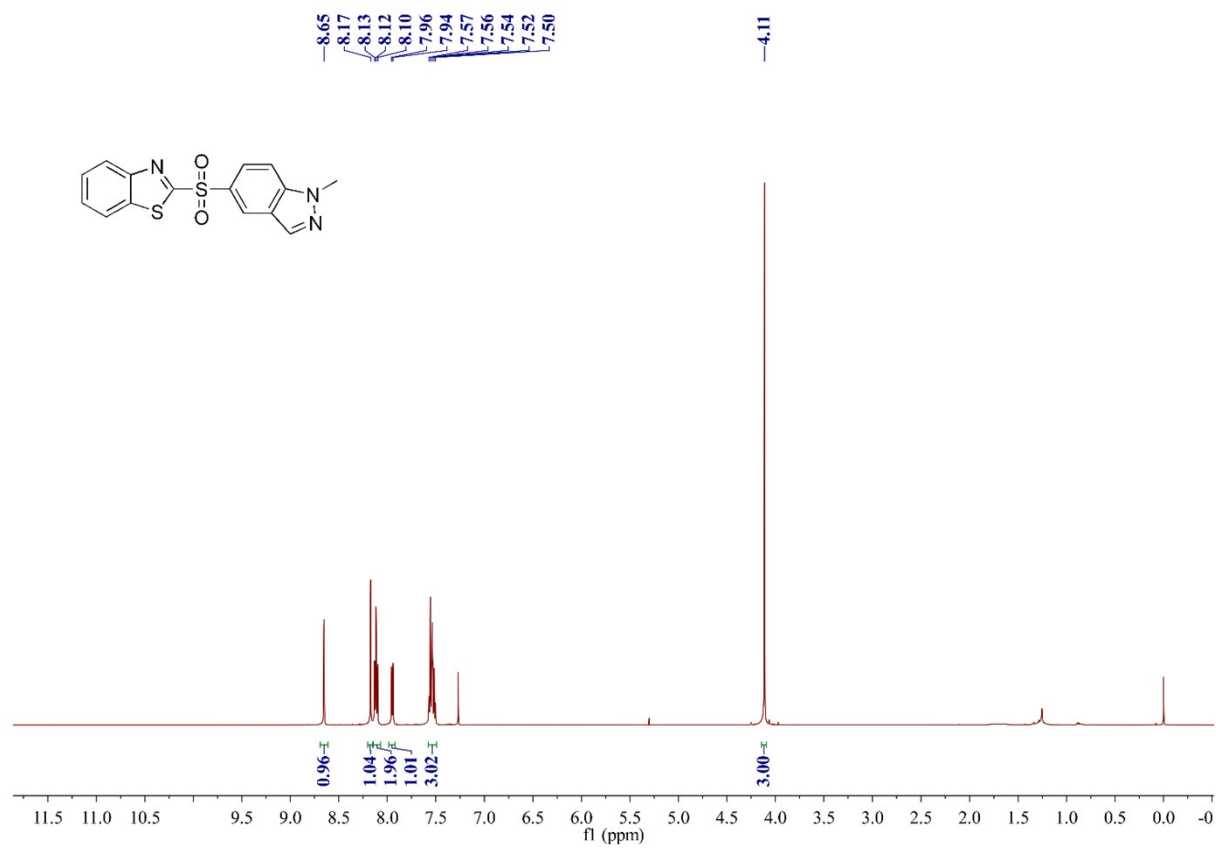
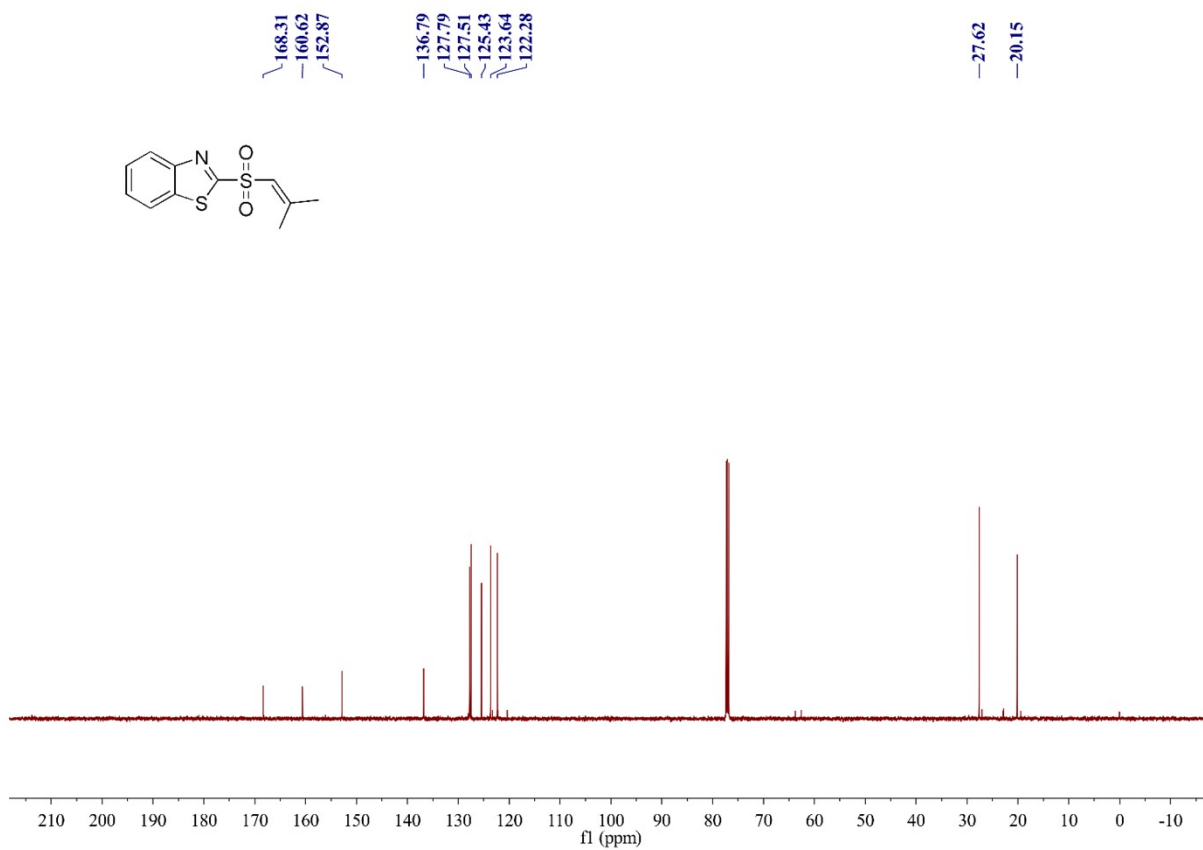


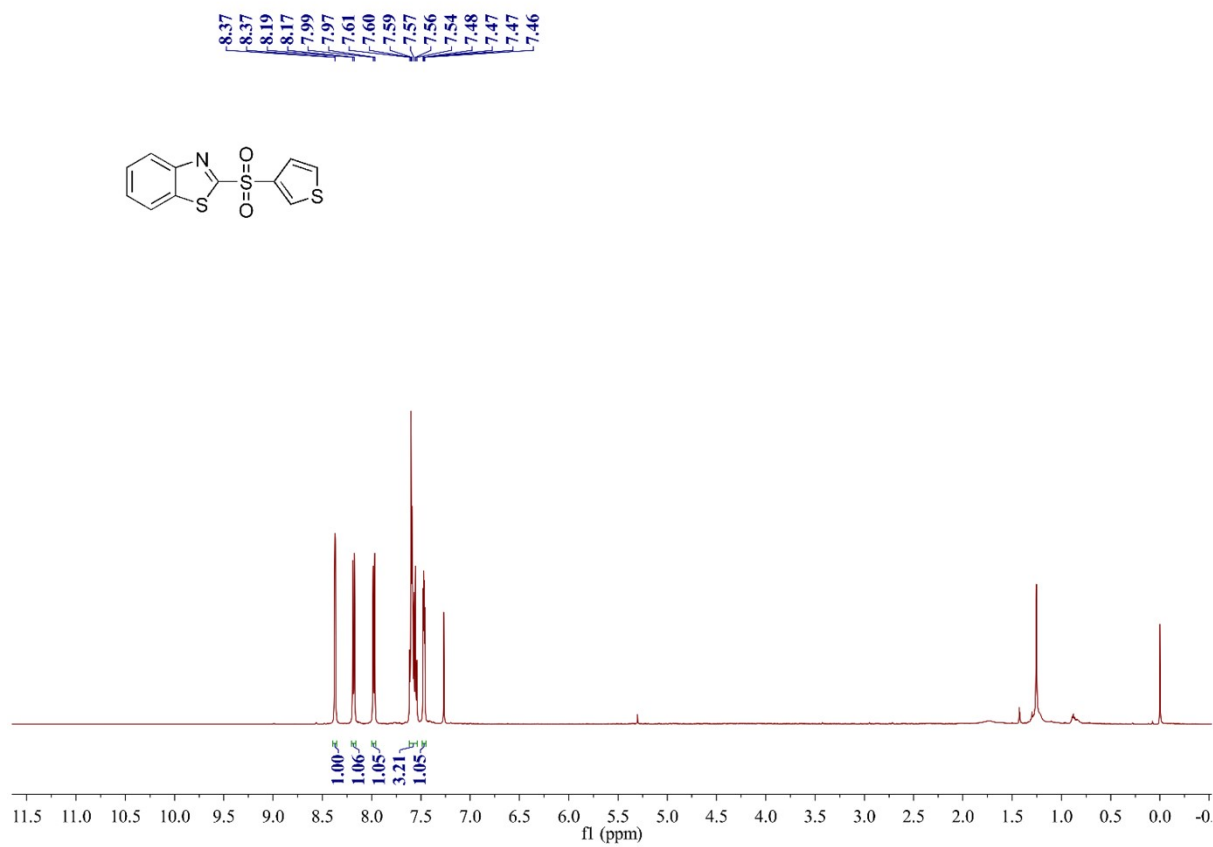
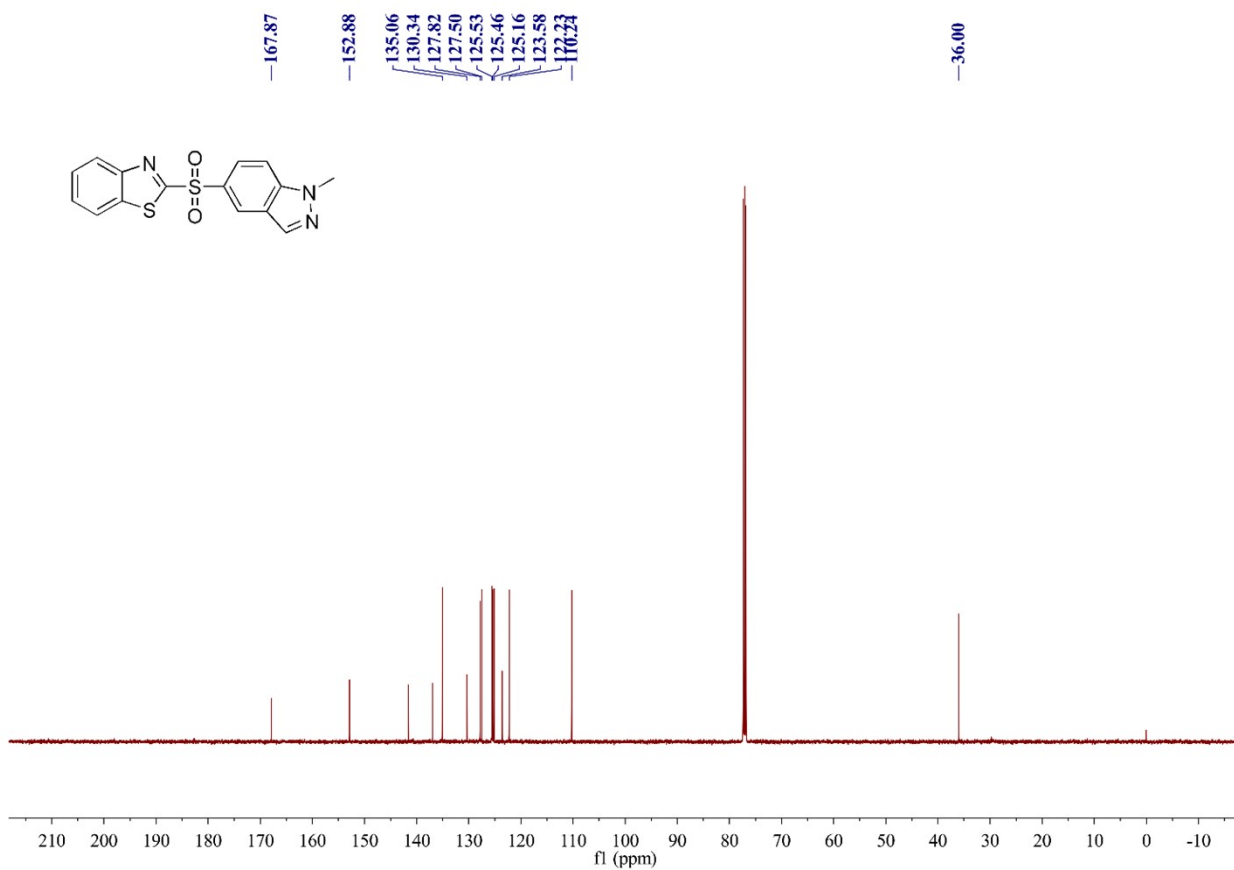


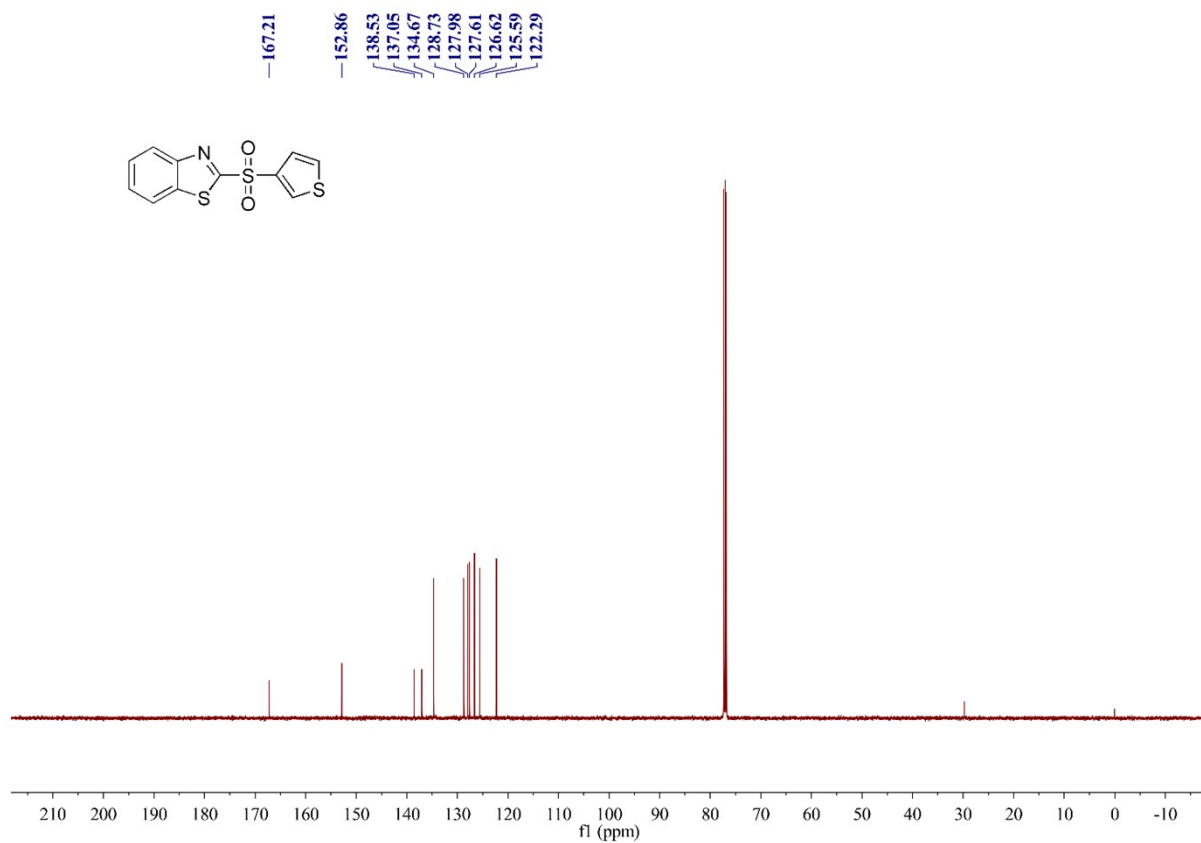












5. References

- [1] Z. Xie, H. Li, J. Yang, X. Zhu and Z. Le, *Synthesis*, 2022, **54**, 770-778.