

Electronic Supplementary Material (ESI)

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Supplementary data

Nickel-catalyzed sulfonylative coupling of 2-chlorobenzothiazoles with sulfinates at room temperature

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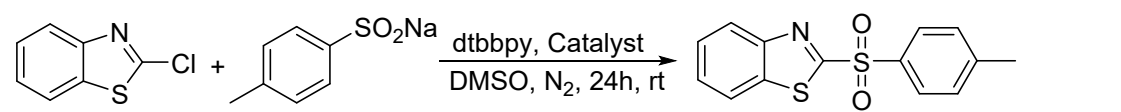
1. General

All commercial reagents were used directly without further purification, unless otherwise stated. Dimethyl sulfoxide (DMSO) was purchased from J & K chemical, stored over 4 Å molecular sieves and handled under N₂. 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. 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 of reaction conditions.

Table S1. Nickel Catalyst and additive Screening.^a



Entry	Catalyst (mol%)	Ligand (mol%)	Yield (%) ^b
1	Ni(OTf) ₂ (10 mol%)	L1 (10 mol%)	94
2	Cu(OAc) ₂ (10 mol%)	L1 (10 mol%)	64
3	CuBr (10 mol%)	L1 (10 mol%)	76
4	CuCl ₂ (10 mol%)	L1 (10 mol%)	82
5	Cu(OTf) ₂ (10 mol%)	L1 (10 mol%)	60
6	Fe(OTf) ₃ (10 mol%)	L1 (10 mol%)	75
7	FeCl ₂ (10 mol%)	L1 (10 mol%)	83
8	FeCl ₃ (10 mol%)	L1 (10 mol%)	58
9	Ni(OTf) ₂ (8 mol%)	L1 (10 mol%)	80
10	Ni(OTf) ₂ (5 mol%)	L1 (10 mol%)	78
11	Ni(OTf) ₂ (2 mol%)	L1 (10 mol%)	72
12	Ni(OTf) ₂ (10 mol%)	L1 (5 mol%)	48
13	Ni(OTf) ₂ (10 mol%)	L1 (2 mol%)	20

^a Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.) in 1 mL DMSO under an atmosphere of N₂ for 24 h. ^b Isolated yield.

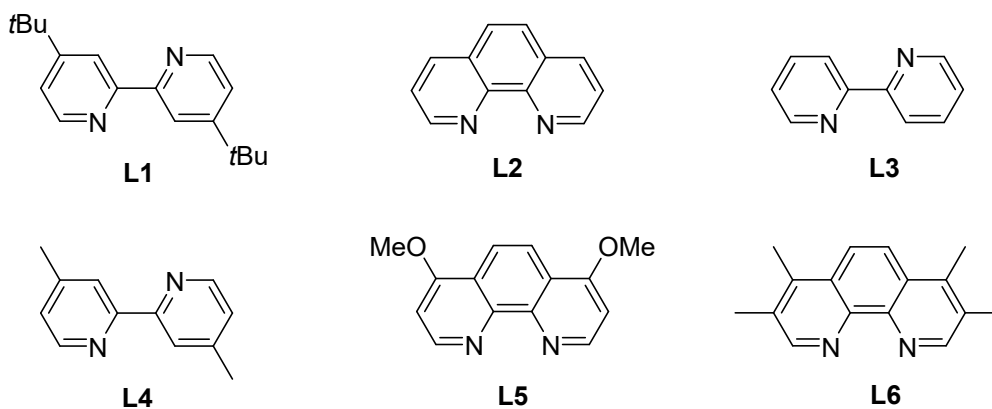
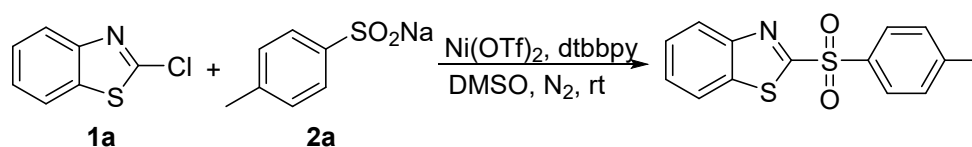


Table S2. Variation of time and molar ratio in optimization of reaction conditions.^a

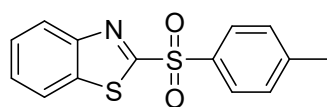


Entry	1a (equiv.)	2a (equiv.)	Time/h	Yield (%) ^b
1	1.0	2.0	24	94
2	1.0	3.0	24	81
3	1.0	4.0	24	90
4	1.0	1.0	24	83
5	2.0	1.0	24	70
6	3.0	1.0	24	60
7	1.0	2.0	18	72
8	1.0	2.0	12	70
9	1.0	2.0	6	65

^a Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.) Ni(OTf)₂ (10 mol%), dtbbpy (10 mol%), in 1 mL DMSO under an atmosphere of N₂ for 24 h.

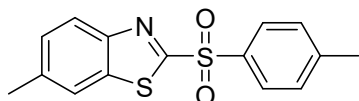
^b Isolated yield.

3. Data for the benzyl sulfone products.



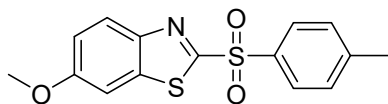
2-tosylbenzo[d]thiazole

3a¹: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 130.2 -132.6 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.58 - 7.51 (m, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 2.43 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.65, 152.90, 145.98, 137.02, 135.42, 130.25, 129.03, 127.84, 127.49, 125.52, 122.23, 21.81.



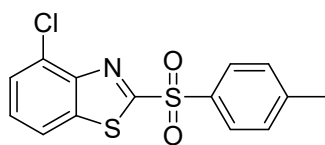
6-methyl-2-tosylbenzo[d]thiazole

3b: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 138.6-139.1 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.02 (t, *J* = 8.5 Hz, 3H), 7.73 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 3H), 2.51 (s, 3H), 2.43 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.33, 151.09, 145.82, 138.55, 137.32, 135.60, 130.21, 129.32, 128.95, 124.97, 121.66, 21.84, 21.80; HRMS (ESI) *m/z*: calcd for C₁₅H₁₃NO₂S₂ [M + H]⁺ 304.0460, found 304.0442.



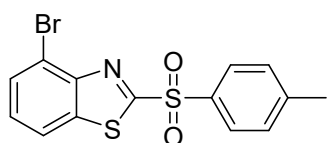
6-methoxy-2-tosylbenzo[d]thiazole

3c: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 145.7-149.1 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.02 (dd, *J* = 9.0, 6.5 Hz, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.15 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.89 (s, 3H), 2.43 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 164.28, 159.57, 147.43, 145.69, 138.96, 135.73, 130.16, 128.82, 126.14, 117.98, 103.32, 55.90, 21.76; HRMS (ESI) *m/z*: calcd for C₁₅H₁₃NO₃S₂ [M + H]⁺ 320.0410, found 320.0393.



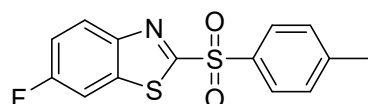
4-chloro-2-tosylbenzo[d]thiazole

3d: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 124.9-125.5 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.41, 150.23, 146.21, 138.29, 135.05, 130.41, 130.28, 129.19, 128.36, 127.73, 120.76, 21.85; HRMS (ESI) *m/z*: calcd for C₁₄H₁₀ClNO₂S₂ [M + H]⁺ 323.9914, found 323.9916.



4-bromo-2-tosylbenzo[d]thiazole

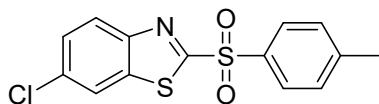
3e: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 143.5-143.7 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.37 (dd, *J* = 14.5, 8.0 Hz, 3H), 2.43 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.16, 151.41, 146.18, 137.68, 135.08, 131.00, 130.25, 129.19, 128.58, 121.40, 119.04, 21.84; HRMS (ESI) *m/z*: calcd for C₁₄H₁₀BrNO₂S₂ [M + H]⁺ 367.9409, found 367.9395.



6-fluoro-2-tosylbenzo[d]thiazole

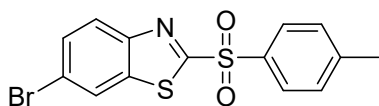
3f: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 166.7-167.0 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.11 (dd, *J* = 9.5, 5.0 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.63 (dd, *J* = 8.0, 3.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.31 (td, *J* = 9.0, 2.5 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.38 (d, *J* = 251.4 Hz), 161.75 (s) (d, *J* = 3.5 Hz), 149.56 (s), 146.14 (s), 138.22 (d, *J* = 11.2 Hz), 135.22 (s), 130.31 (s), 129.03 (s), 126.90 (d, *J* = 9.9 Hz), 116.89 (d, *J* = 25.3 Hz), 108.39 (d, *J* = 26.8 Hz), 21.82 (s); ¹⁹F NMR (CDCl₃, 376 MHz, 298 K) δ = -110.50.

HRMS (ESI) *m/z*: calcd for C₁₄H₁₀FNO₂S₂ [M + H]⁺ 308.0210, found 308.0212.



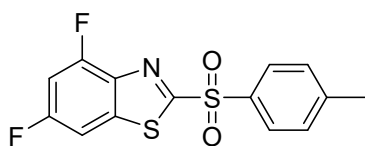
6-chloro-2-tosylbenzo[d]thiazole

3g: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 182.2-184.0 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.04 (dd, *J* = 8.5, 6.0 Hz, 3H), 7.93 (d, *J* = 1.5 Hz, 1H), 7.52 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.20, 151.38, 146.23, 138.06, 135.09, 134.08, 130.33, 129.07, 128.59, 126.27, 121.78, 21.84; HRMS (ESI) *m/z*: calcd for C₁₄H₁₀ClNO₂S₂ [M + H]⁺ 323.9914, found 323.9916.



6-bromo-2-tosylbenzo[d]thiazole

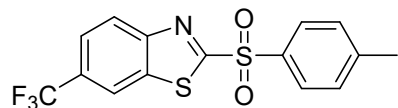
3h: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 189.3-189.6 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.09 (d, *J* = 1.5 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.65 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.22, 151.69, 146.24, 138.44, 135.07, 131.25, 130.34, 129.08, 126.53, 124.76, 121.90, 21.85; HRMS (ESI) *m/z*: calcd for C₁₄H₁₀BrNO₂S₂ [M + H]⁺ 367.9409, found 367.9408.



4,6-difluoro-2-tosylbenzo[d]thiazole

3i: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 162.1-163.0 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 9.5 Hz, 1H), 2.45 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.92 (d, *J* = 3.3 Hz), 162.77 (d, *J* = 10.1 Hz), 160.75 (d, *J* = 10.2 Hz), 157.75 (d, *J* = 13.6 Hz), 155.64 (d, *J*

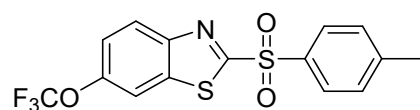
= 13.7 Hz), 146.39 (s), 139.77 - 139.10 (m), 134.81 (s), 130.36 (s), 129.18 (s), 104.46 - 103.61(m), 21.85 (s); ^{19}F NMR (CDCl_3 , 376 MHz, 298 K) δ = -106.61, -113.17.
HRMS (ESI) m/z : calcd for $\text{C}_{14}\text{H}_9\text{F}_2\text{NO}_2\text{S}_2$ [$\text{M} + \text{H}$] $^+$ 326.0116, found 326.0110.



2-tosyl-6-(trifluoromethyl)benzo[d]thiazole

3j: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 137.9-138.0 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.29 – 8.23 (m, 2H), 8.05 (d, J = 8.5 Hz, 2H), 7.80 (dd, J = 9.0, 1.5 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.05 (s), 154.67 (s), 146.49 (s), 136.91 (s), 134.74 (s), 130.40 (s), 129.82 (q, $J_{\text{C-F}}$ = 33.4 Hz), 129.21 (s), 126.87 (q, $J_{\text{C-F}}$ = 273.2 Hz), 126.06 (s), 124.36 (q, $J_{\text{C-F}}$ = 3.3 Hz), 120.46 (q, $J_{\text{C-F}}$ = 4.3 Hz), 21.85 (s); ^{19}F NMR (CDCl_3 , 376 MHz, 298 K) δ = -61.85.

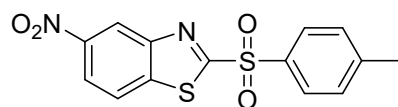
HRMS (ESI) m/z : calcd for $\text{C}_{15}\text{H}_{10}\text{F}_3\text{NO}_2\text{S}_2$ [$\text{M} + \text{H}$] $^+$ 358.0178, found 358.0158.



2-tosyl-6-(trifluoromethoxy)benzo[d]thiazole

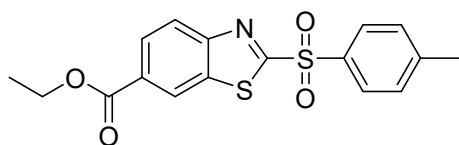
3k: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 124.3-124.7 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, J = 9.5 Hz, 1H), 8.04 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 1.0 Hz, 1H), 7.44 (dd, J = 9.0, 1.5 Hz, 1H), 7.39 (d, J = 8.5 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.97 (s), 151.22 (s), 148.20 (s), 146.31 (s), 137.90 (s), 135.00 (s), 130.35 (s), 129.09 (s), 126.69 (s), 120.36 ($J_{\text{C-F}}$ = 259.4 Hz), 121.59 (s), 114.38 (s), 21.82 (s); ^{19}F NMR (CDCl_3 , 376 MHz, 298 K) δ = -57.94.

HRMS (ESI) m/z : calcd for $\text{C}_{15}\text{H}_{10}\text{F}_3\text{NO}_3\text{S}_2$ [$\text{M} + \text{H}$] $^+$ 374.0127, found 374.0115.



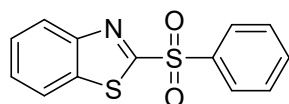
5-nitro-2-tosylbenzo[d]thiazole

3l: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 205.9-208.4 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.99 (d, *J* = 2.0 Hz, 1H), 8.40 (dd, *J* = 9.0, 2.0 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 171.91, 152.53, 147.50, 146.76, 142.73, 134.40, 130.47, 129.32, 123.19, 121.98, 121.01, 21.89; HRMS (ESI) *m/z*: calcd for C₁₄H₁₀N₂O₄S₂ [M + H]⁺ 335.0155, found 335.0140.



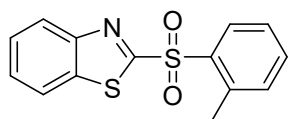
ethyl 2-tosylbenzo[d]thiazole-6-carboxylate

3m: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 148.5-150.6 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.69 (s, 1H), 8.23 (dd, *J* = 9.0, 1.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 4.43 (q, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 1.43 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 170.93, 165.42, 155.45, 146.35, 136.77, 134.88, 130.36, 129.74, 129.19, 128.34, 125.23, 124.46, 61.77, 21.85, 14.34; HRMS (ESI) *m/z*: calcd for C₁₇H₁₅NO₄S₂ [M + H]⁺ 362.0515, found 362.0502.



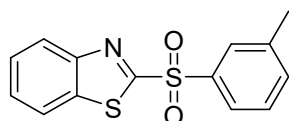
2-(phenylsulfonyl)benzo[d]thiazole

4a⁴: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 157.8-158.6 °C; ¹³C NMR (126 MHz, CDCl₃) δ 167.22, 152.91, 138.41, 137.06, 134.67, 129.61, 128.98, 127.97, 127.60, 125.58, 122.29.



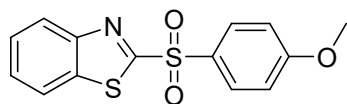
2-(o-tolylsulfonyl)benzo[d]thiazole

4b: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 116.8-116.9 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.29 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.59 - 7.52 (m, 3H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 2.74 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.63, 152.66, 139.75, 136.88, 136.62, 134.82, 132.99, 130.78, 127.91, 127.52, 126.91, 125.56, 122.22, 20.90; HRMS (ESI) *m/z*: calcd for C₁₄H₁₁NO₂S₂ [M + H]⁺ 290.0304, found 290.0296.



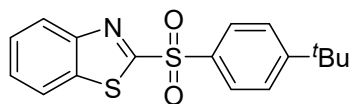
2-(*m*-tolylsulfonyl)benzo[*d*]thiazole

4c: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 140.9-141.1 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 3H), 7.60 – 7.52 (m, 2H), 7.50 – 7.43 (m, 2H), 2.44 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.43, 152.92, 139.97, 138.25, 137.08, 135.49, 129.44, 129.18, 127.89, 127.53, 126.14, 125.57, 122.25, 21.38; HRMS (ESI) *m/z*: calcd for C₁₄H₁₁NO₂S₂ [M + H]⁺ 290.0304, found 290.0293.



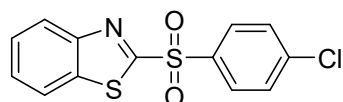
2-((4-methoxyphenyl)sulfonyl)benzo[*d*]thiazole

4d: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 118.1-119.7 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.54 (dt, *J* = 22.0, 7.5 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.02, 164.59, 152.88, 136.94, 131.35, 129.59, 127.76, 127.46, 125.45, 122.23, 114.88, 55.83; HRMS (ESI) *m/z*: calcd for C₁₄H₁₁NO₃S₂ [M + H]⁺ 306.0253, found 306.0237.



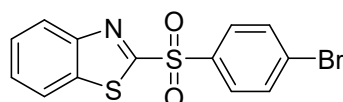
2-((4-(*tert*-butyl)phenyl)sulfonyl)benzo[*d*]thiazole

4e: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 204.5-206.4 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.42 (m, 4H), 1.32 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 167.62, 158.78, 152.92, 137.08, 135.29, 128.85, 127.85, 127.52, 126.71, 125.55, 122.27, 35.43, 31.00; HRMS (ESI) *m/z*: calcd for C₁₇H₁₇NO₂S₂ [M + H]⁺ 332.0773, found 332.0756.



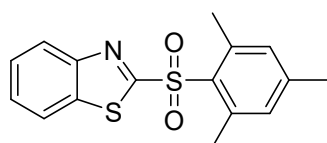
2-((4-chlorophenyl)sulfonyl)benzo[*d*]thiazole

4f: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 160.7-161.0 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 9.0 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.63 – 7.52 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 166.75, 152.90, 141.61, 137.02, 136.82, 130.45, 129.97, 128.12, 127.71, 125.58, 122.31.



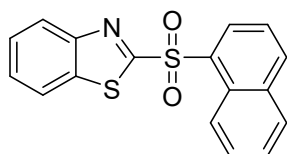
2-((4-bromophenyl)sulfonyl)benzo[*d*]thiazole

4g: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 166.9-168.8 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 7.5 Hz, 1H), 8.02 (dd, *J* = 8.9, 2.0 Hz, 2H), 7.99 – 7.95 (m, 1H), 7.72 (dd, *J* = 9.0, 2.0 Hz, 2H), 7.62 - 7.53 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 166.71, 152.90, 137.42, 137.01, 132.94, 130.45, 130.30, 128.11, 127.71, 125.60, 122.30; HRMS (ESI) *m/z*: calcd for C₁₃H₈BrNO₂S₂ [M + H]⁺ 353.9253, found 353.9248.



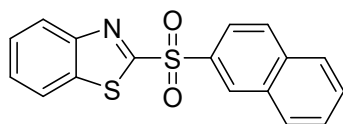
2-(mesitylsulfonyl)benzo[*d*]thiazole

4h: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 133.6-134.7 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.55 (dt, *J* = 19.5, 7.5 Hz, 2H), 7.00 (s, 2H), 2.78 (s, 6H), 2.31 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 168.93, 152.58, 144.79, 141.63, 136.47, 132.47, 132.35, 127.67, 127.34, 125.47, 122.14, 23.27, 21.22; HRMS (ESI) *m/z*: calcd for C₁₆H₁₅NO₂S₂ [M + H]⁺ 318.0617, found 318.0612.



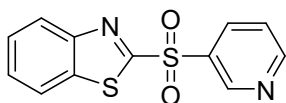
2-(naphthalen-1-ylsulfonyl)benzo[d]thiazole

4i: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 202.6 - 204.9 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.99 (d, *J* = 9.0 Hz, 1H), 8.65 (dd, *J* = 7.5, 1.0 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 8.10 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.93 (dd, *J* = 7.0, 1.0 Hz, 2H), 7.71 – 7.65 (m, 2H), 7.60 – 7.49 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.44, 152.56, 137.05, 136.53, 134.22, 133.65, 131.68, 129.10, 128.92, 128.91, 127.88, 127.46, 127.26, 125.61, 124.86, 124.61, 122.17; HRMS (ESI) *m/z*: calcd for C₁₇H₁₁NO₂S₂ [M + H]⁺ 326.0304, found 326.0308.



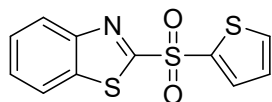
2-(naphthalen-2-ylsulfonyl)benzo[d]thiazole

4j⁵: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 153.9-156.4 °C; ¹³C NMR (126 MHz, CDCl₃) δ 167.31, 152.92, 137.06, 135.68, 135.18, 132.18, 131.17, 129.96, 129.91, 129.73, 128.06, 127.94, 127.92, 127.57, 125.57, 123.15, 122.26.



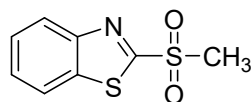
2-(pyridin-3-ylsulfonyl)benzo[d]thiazole

4k: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 172.1-172.6 °C; ¹H NMR (500 MHz, CDCl₃) δ 9.36 (s, 1H), 8.90 (s, 1H), 8.47 (d, *J* = 7.5 Hz, 1H), 8.18 – 8.14 (m, 1H), 8.02 – 7.97 (m, 1H), 7.63-7.54 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.24, 154.87, 152.89, 149.76, 137.01, 136.64, 135.36, 128.32, 127.84, 125.68, 124.14, 122.37; HRMS (ESI) *m/z*: calcd for C₁₂H₈N₂O₂S₂ [M + H]⁺ 277.0100, found 277.0086.



2-(thiophen-2-ylsulfonyl)benzo[d]thiazole

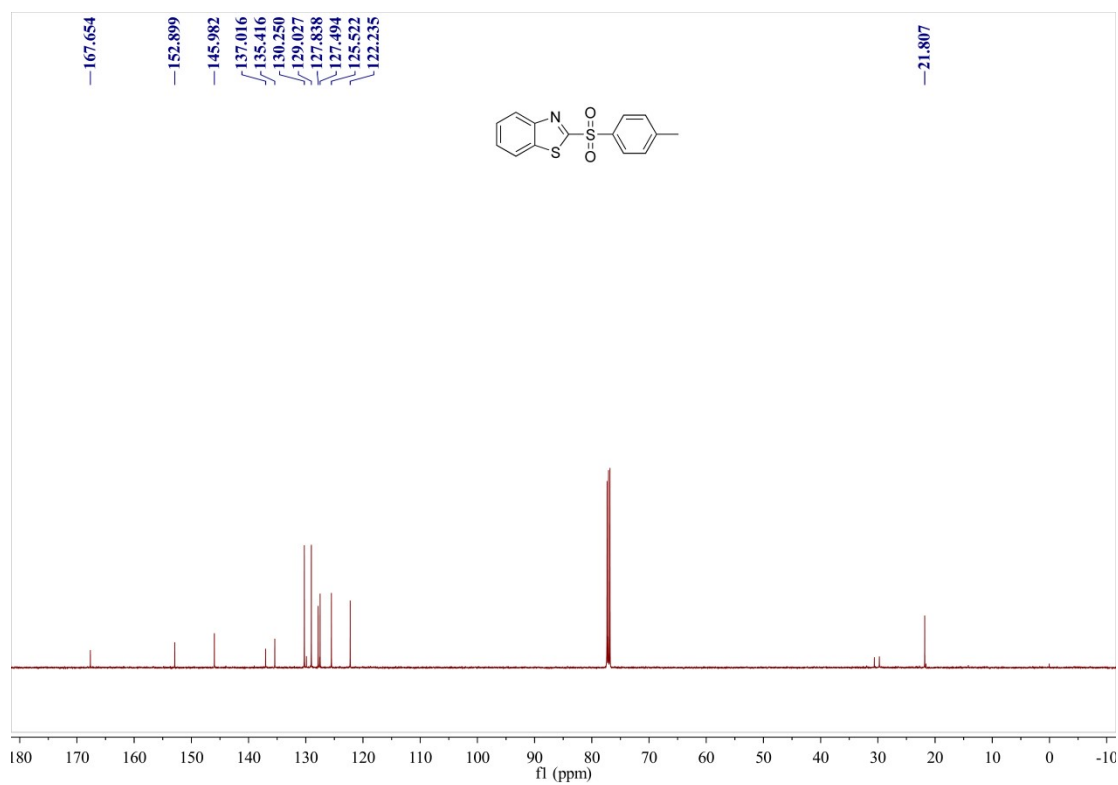
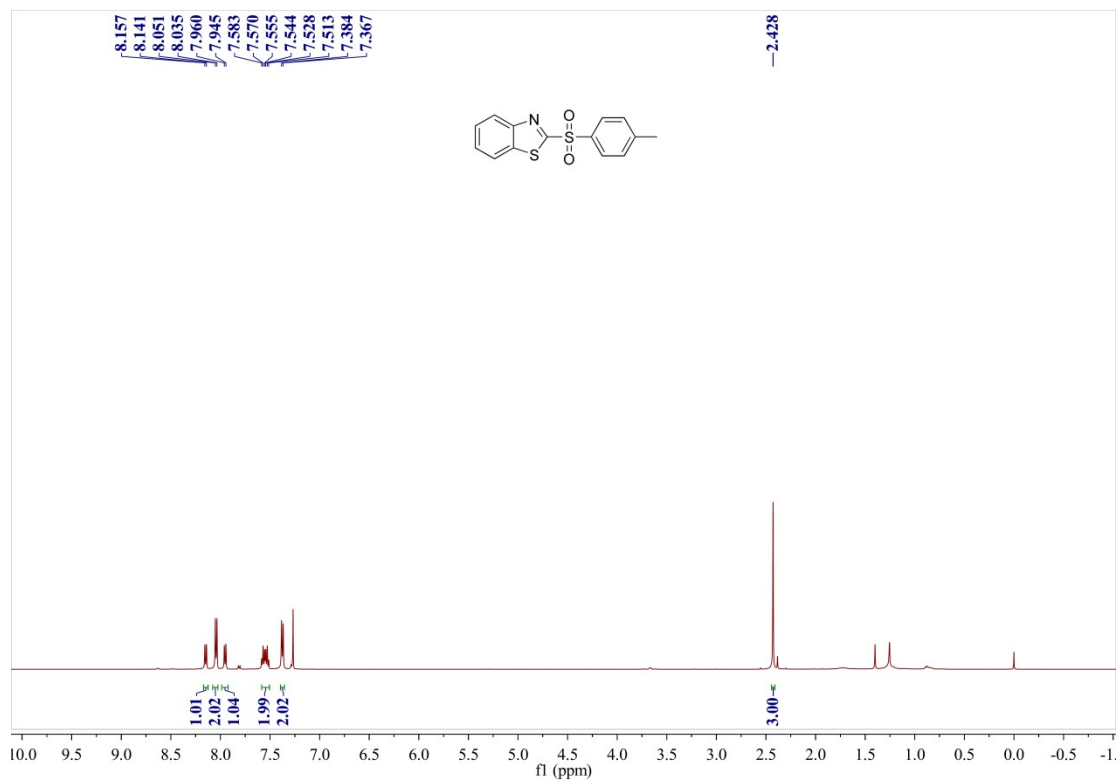
4l: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 173.6-174.0 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.99 - 7.95 (m, 2H), 7.81 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.63 - 7.52 (m, 2H), 7.18 (dd, *J* = 5.0, 4.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 167.18, 152.73, 138.89, 137.10, 136.52, 136.21, 128.50, 128.03, 127.64, 125.62, 122.29; HRMS (ESI) *m/z*: calcd for C₁₁H₇NO₂S₃ [M + H]⁺ 281.9712, found 281.9717.

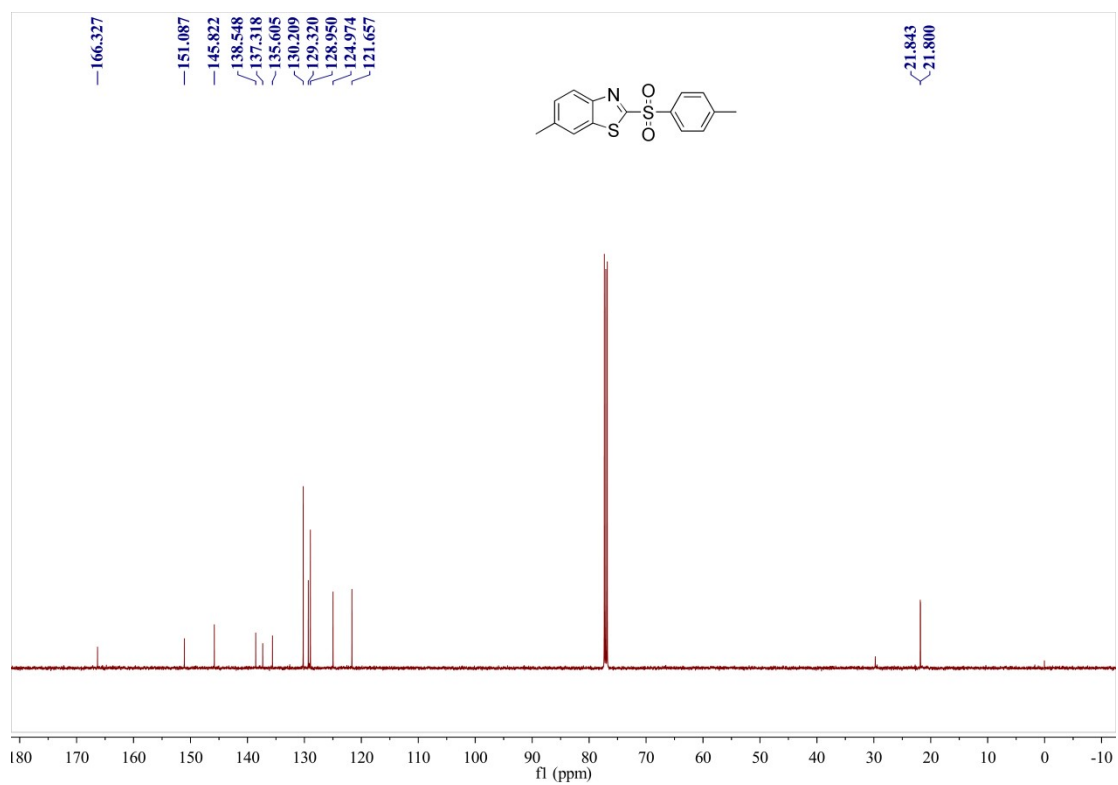
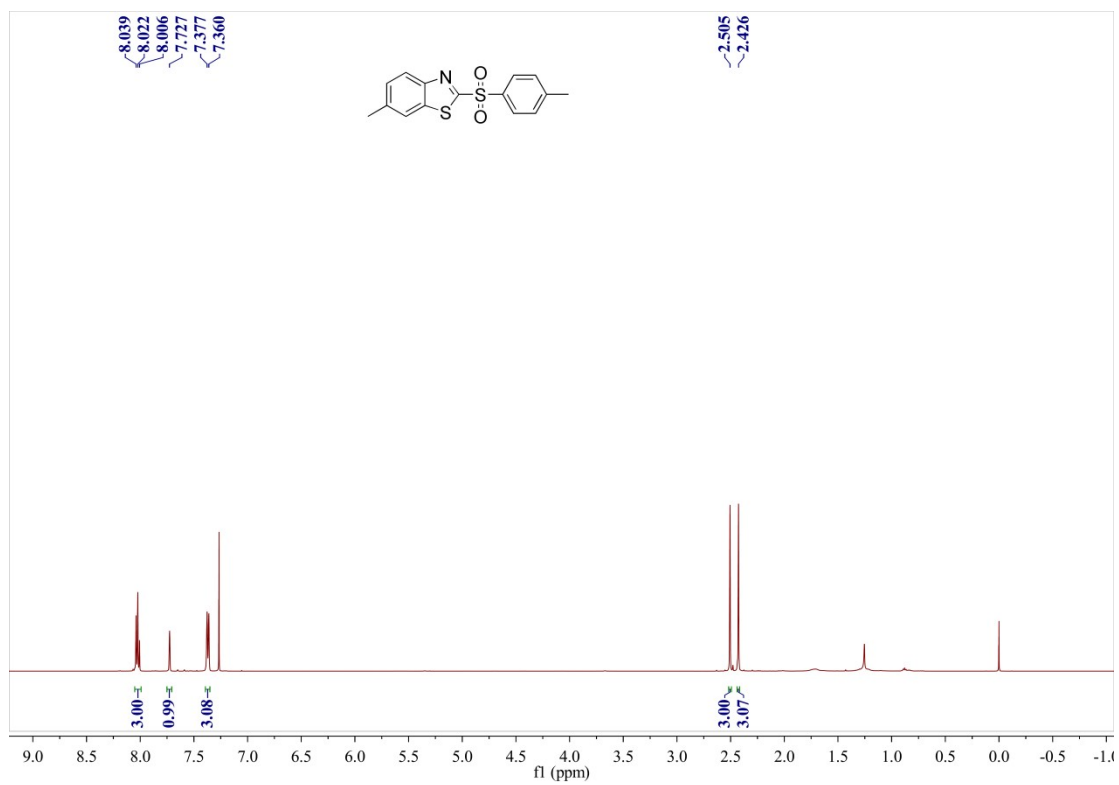


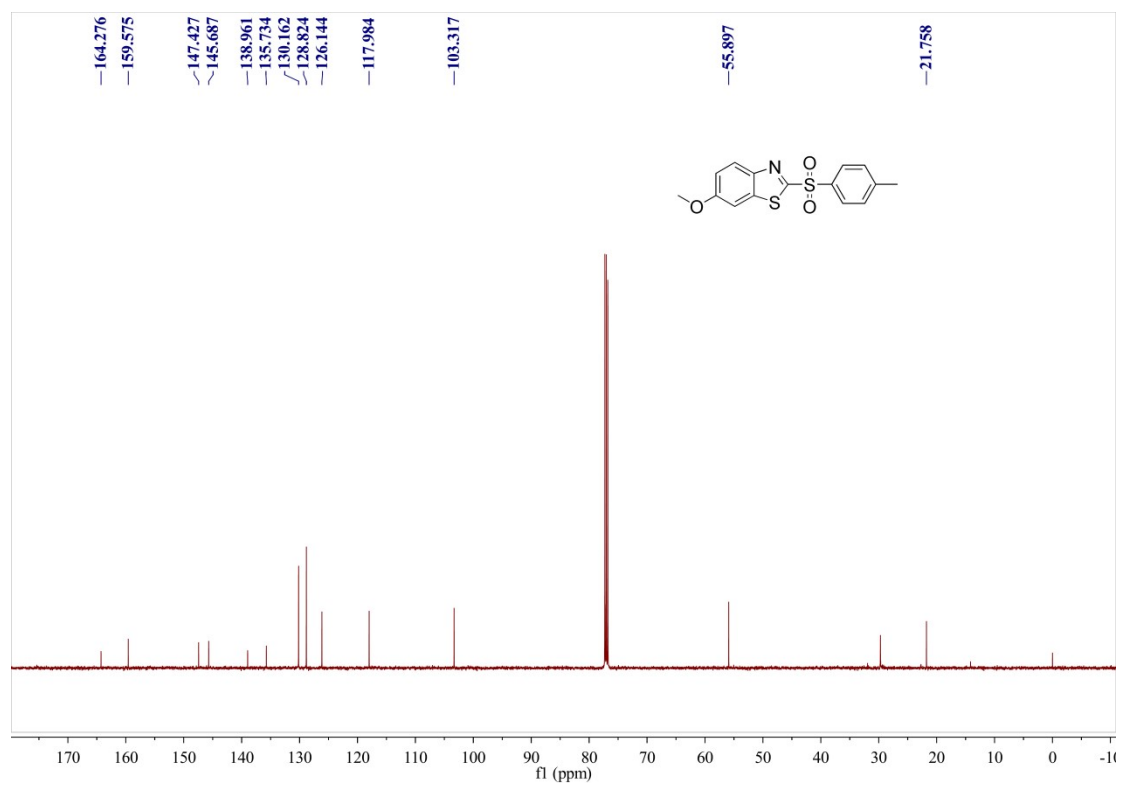
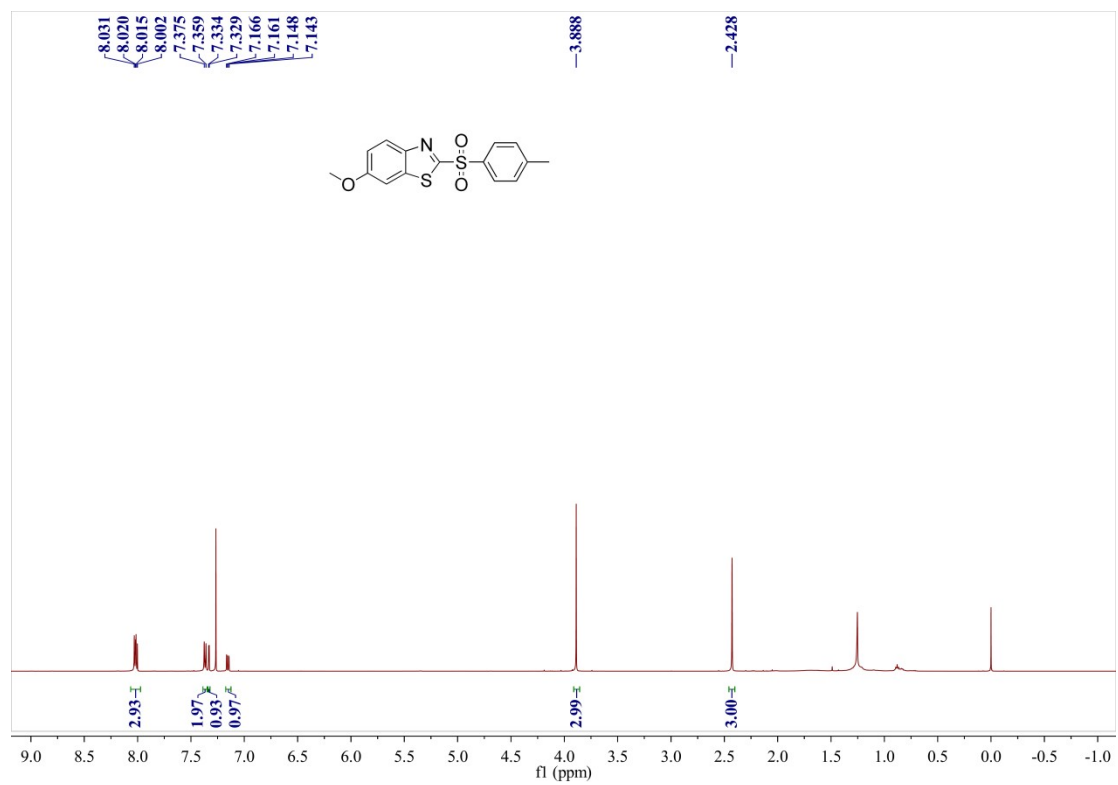
2-(methylsulfonyl)benzo[d]thiazole

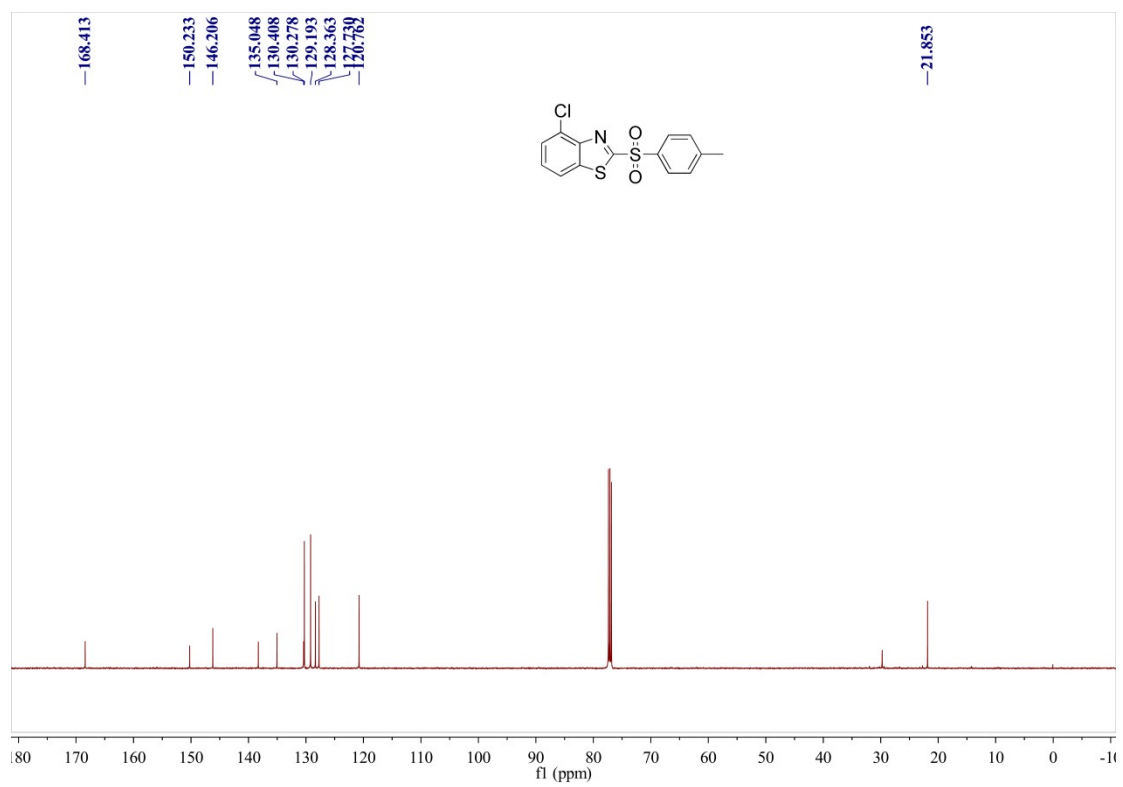
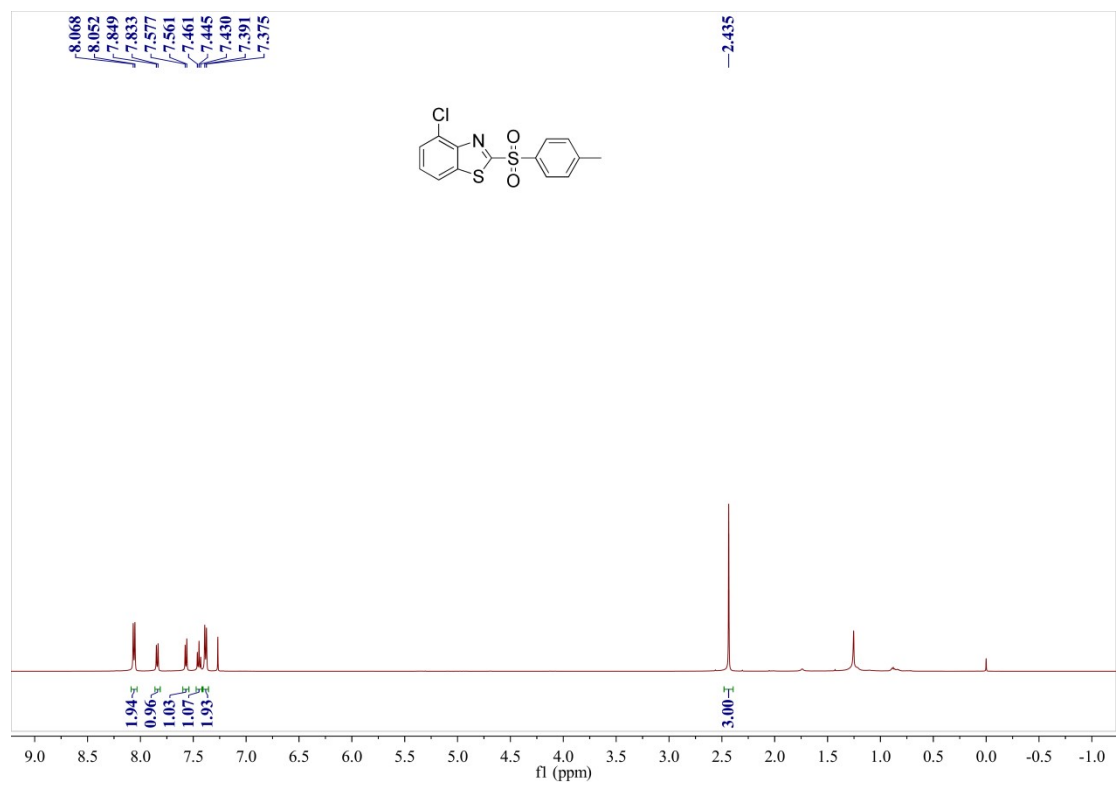
4m²: Flash column chromatography (petroleum/ethyl acetate 4:1) afforded the titled sulfone as a light yellow solid; mp 166.7-167.0 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.63 (dt, *J* = 24.0, 7.0 Hz, 2H), 3.42 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 166.36, 152.46, 136.62, 128.16, 127.77, 125.43, 122.44, 42.48.

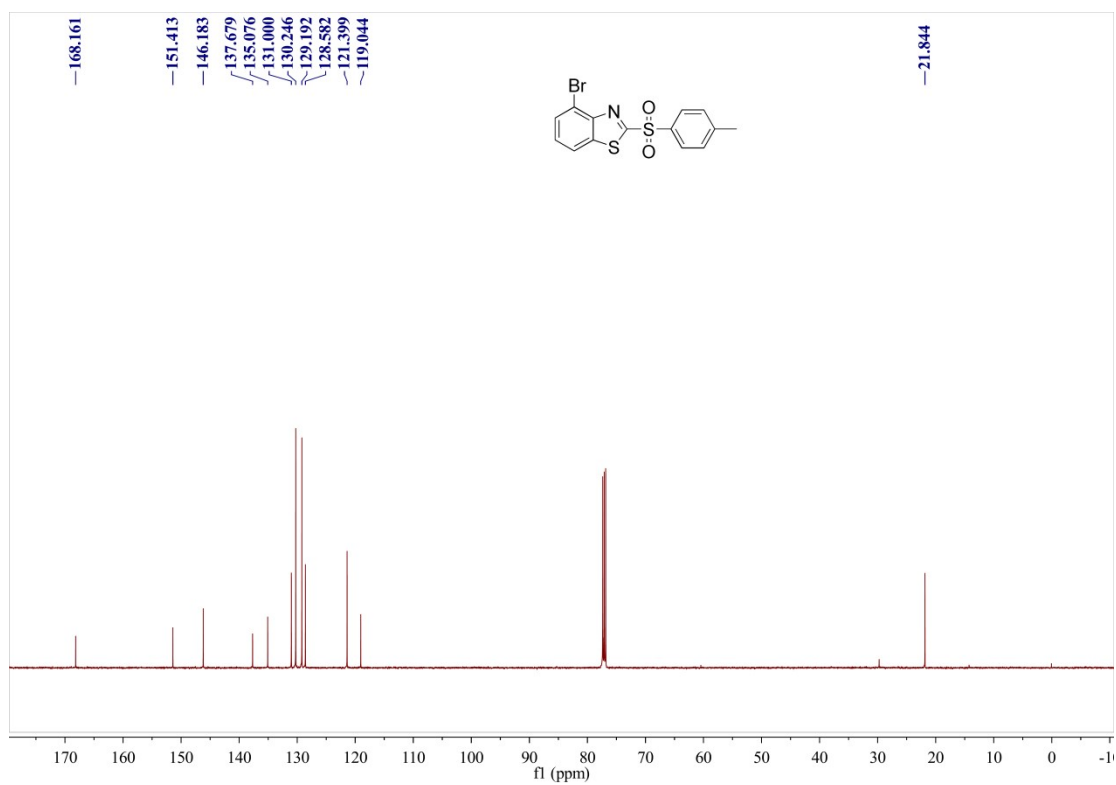
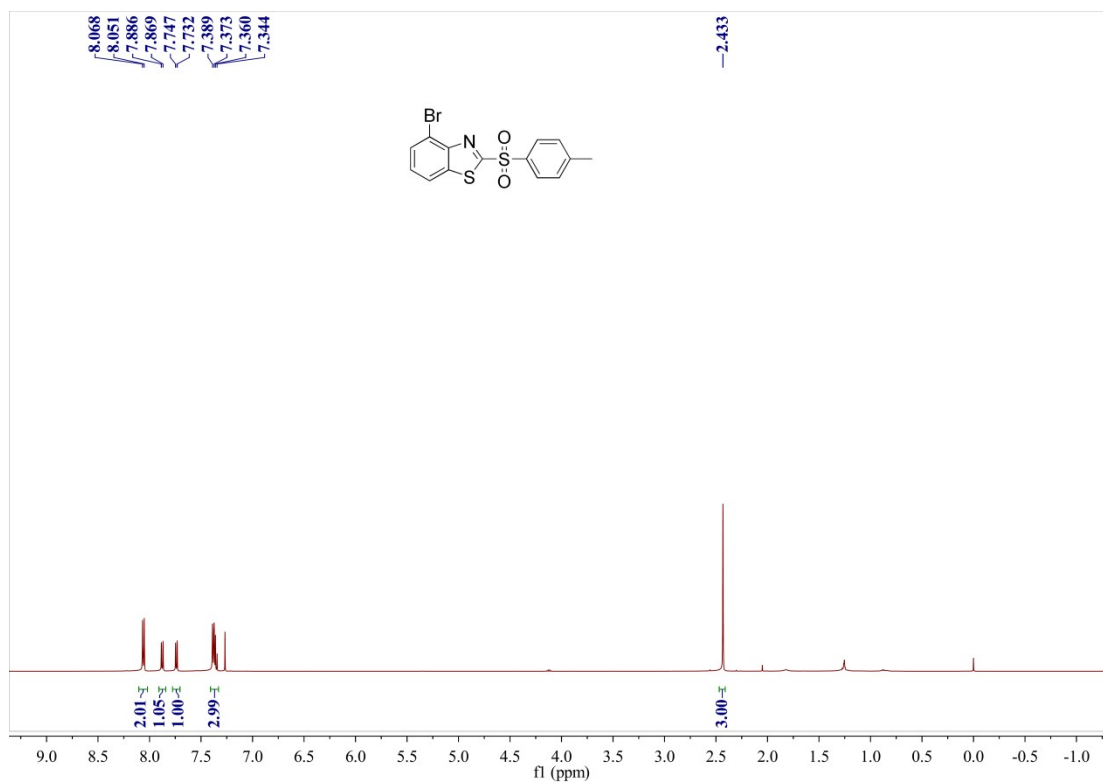
4. ^1H NMR, ^{13}C NMR and ^{19}F NMR for the sulfone products.

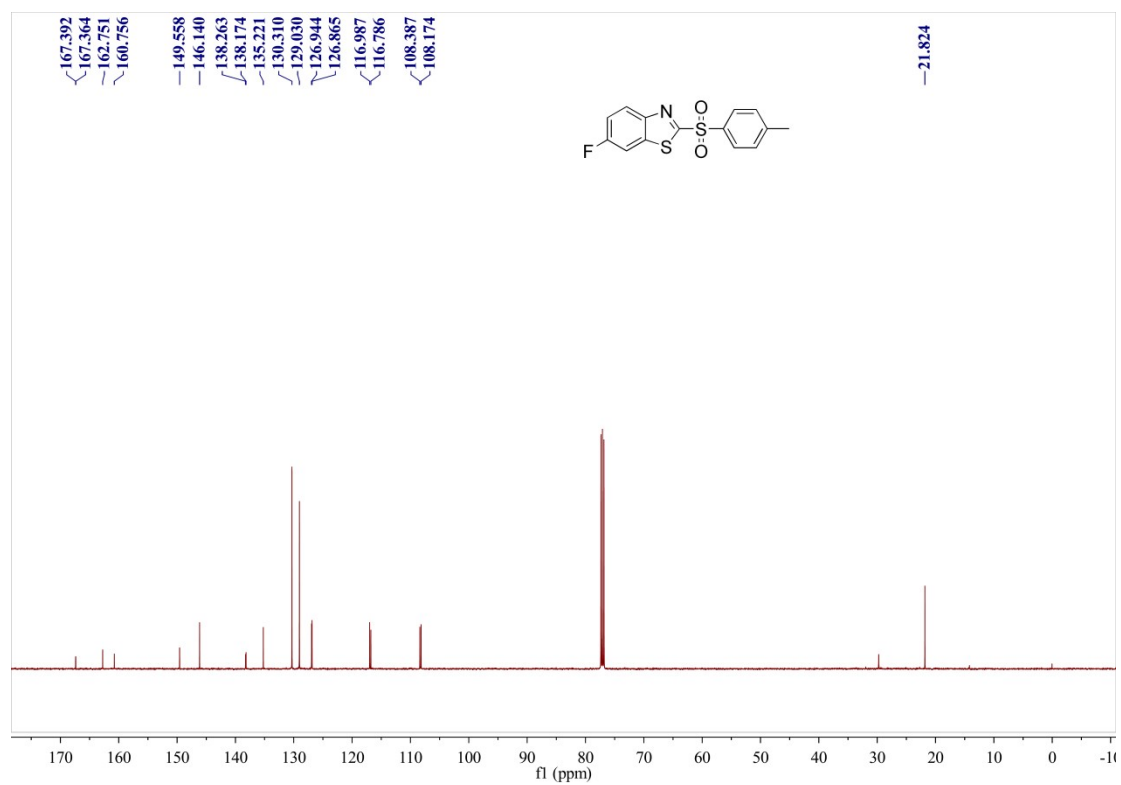
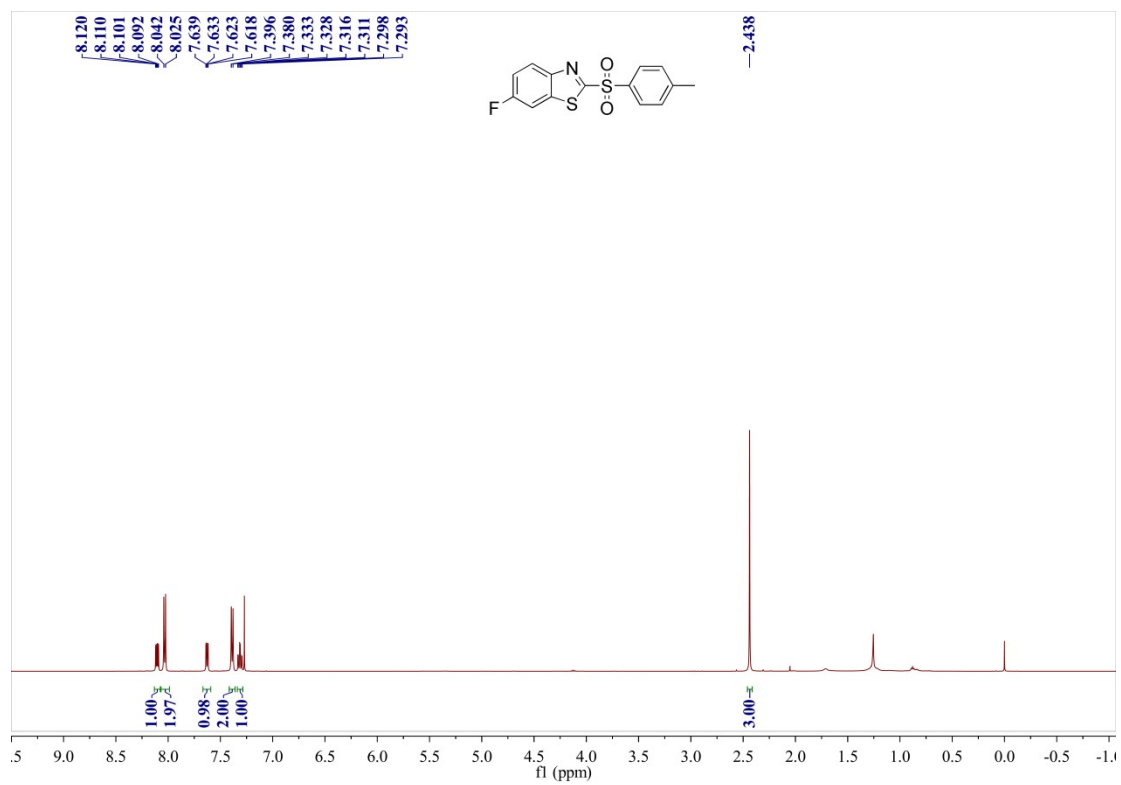


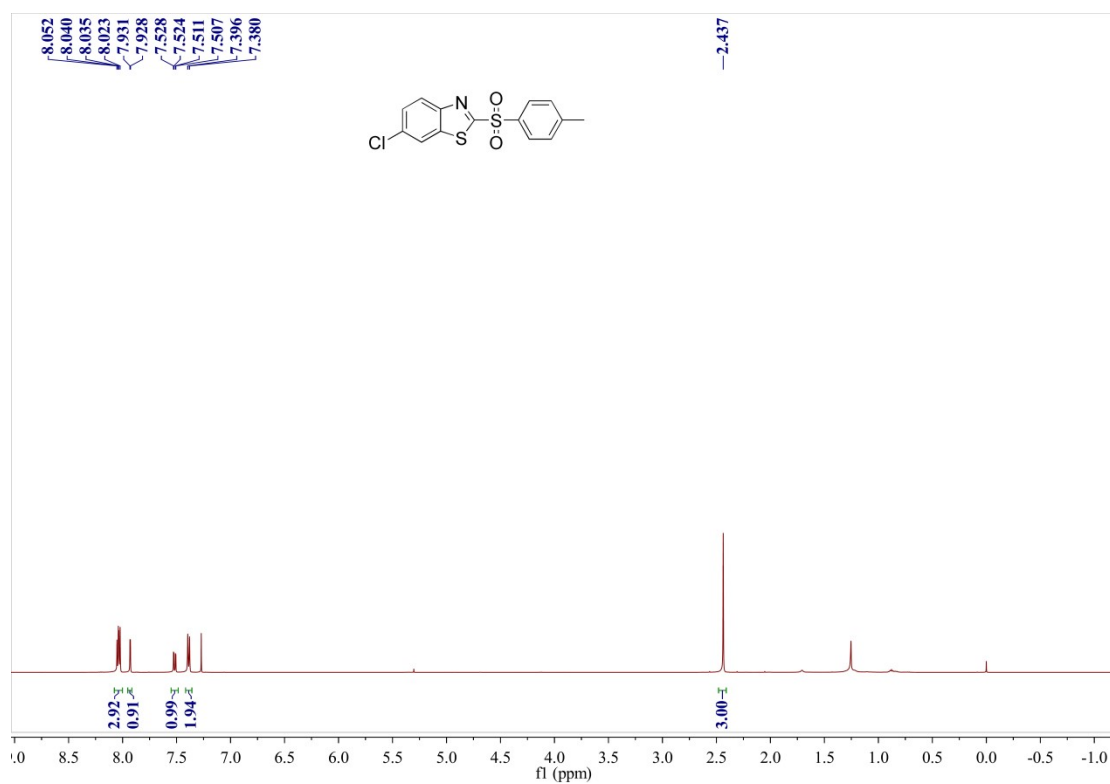
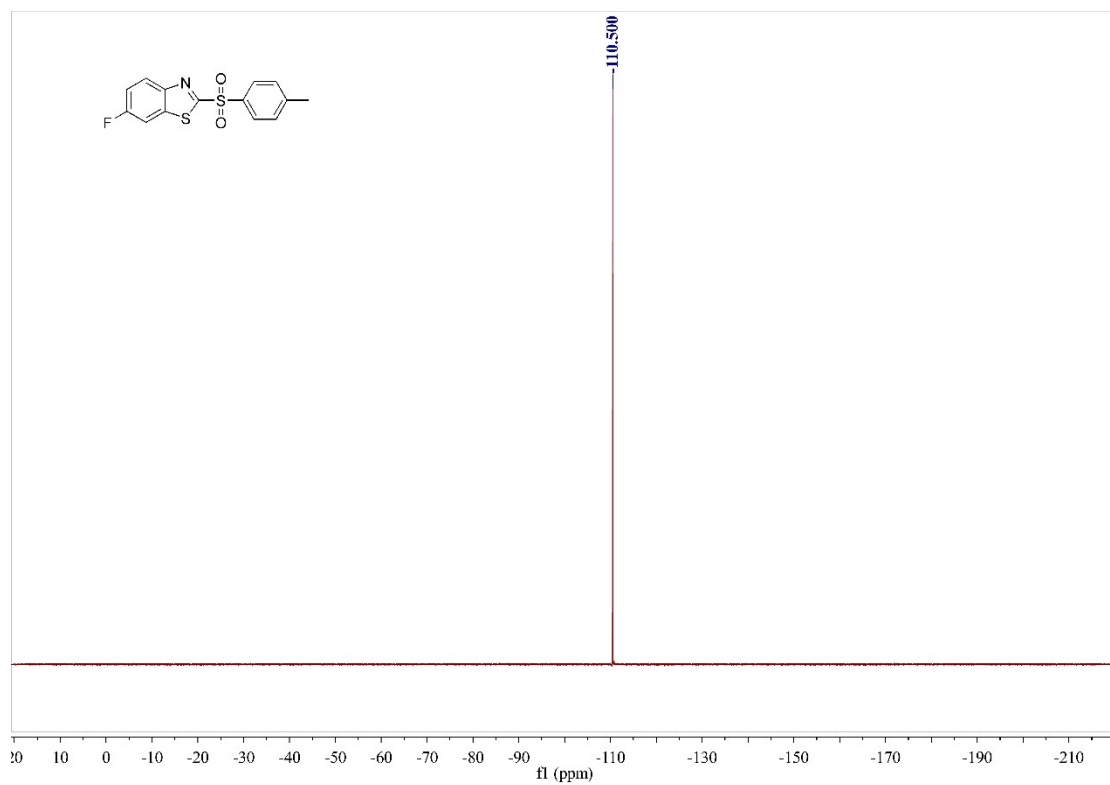


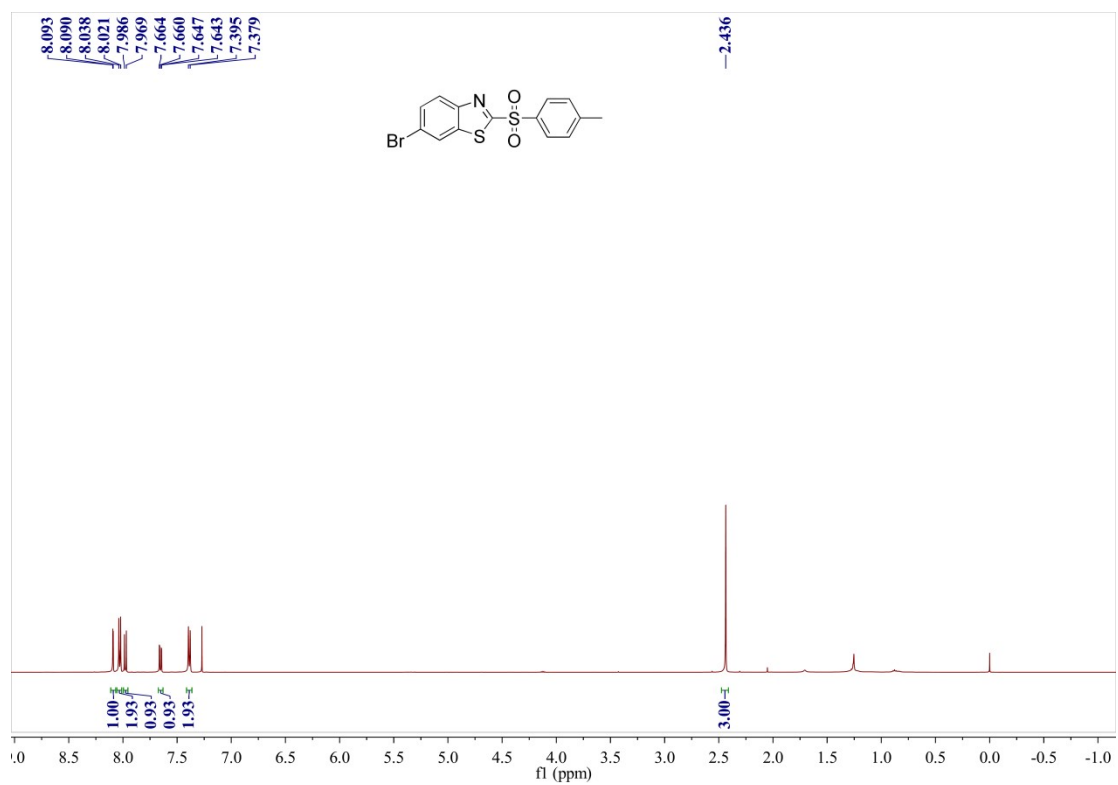
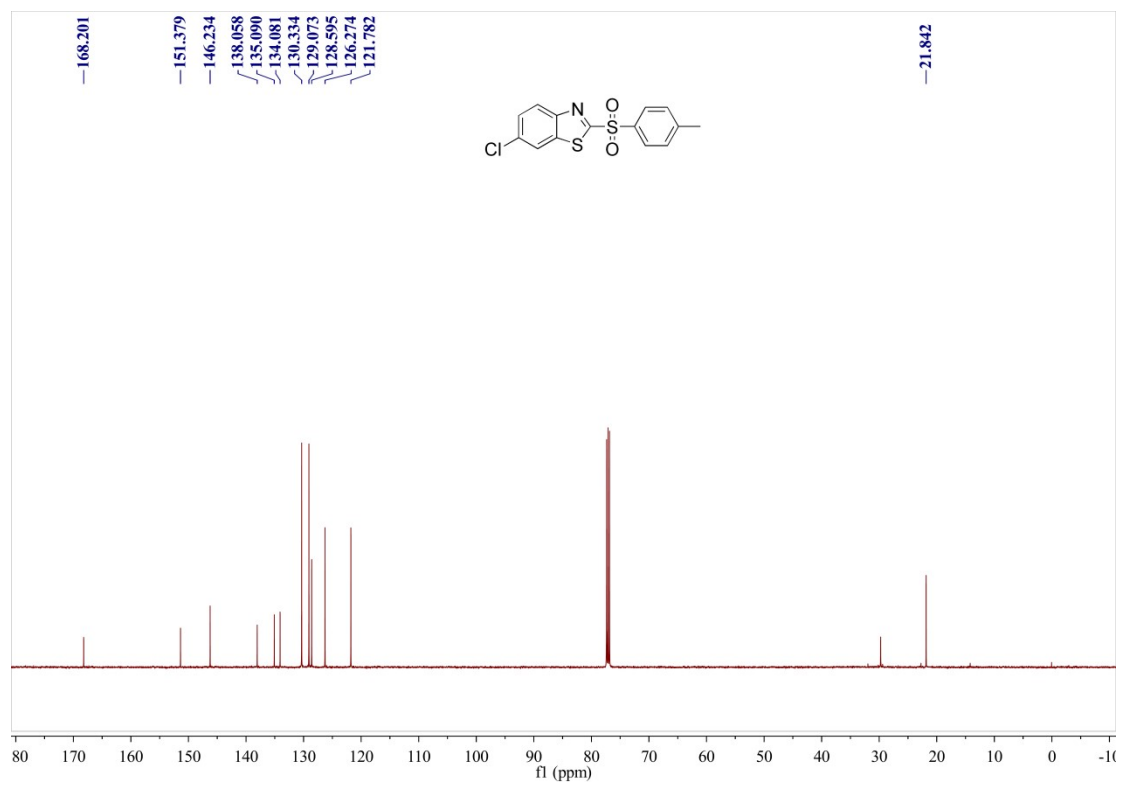


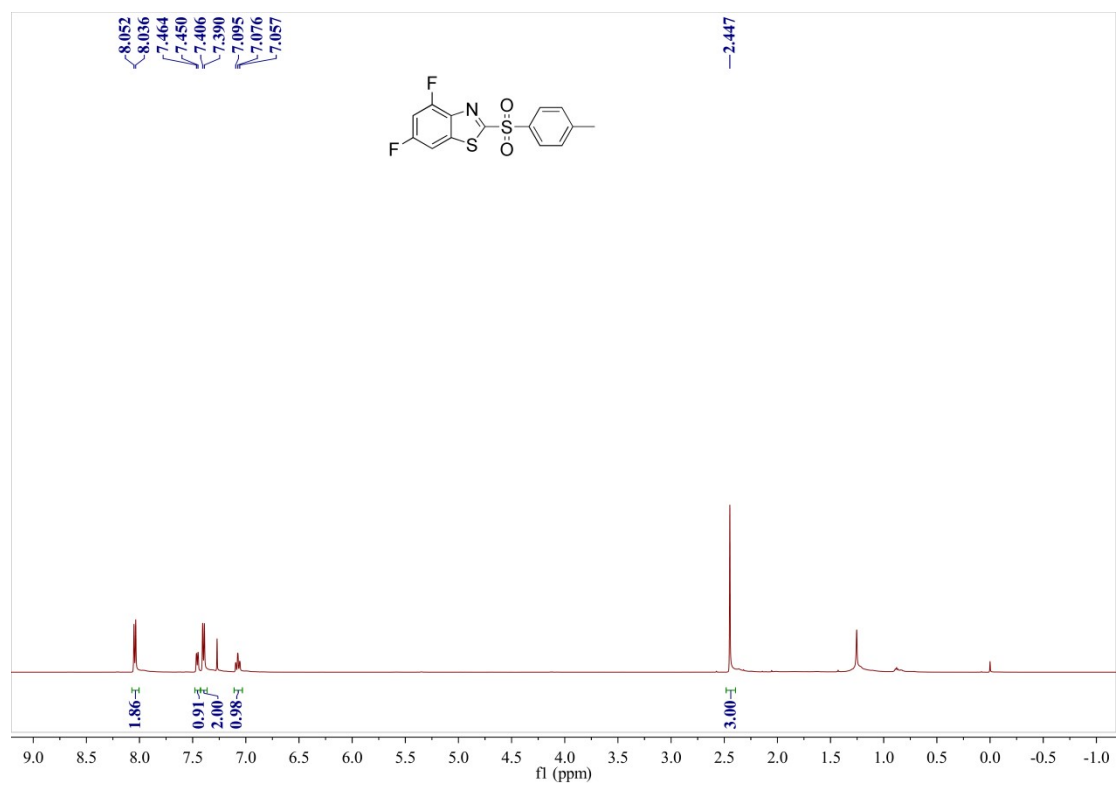
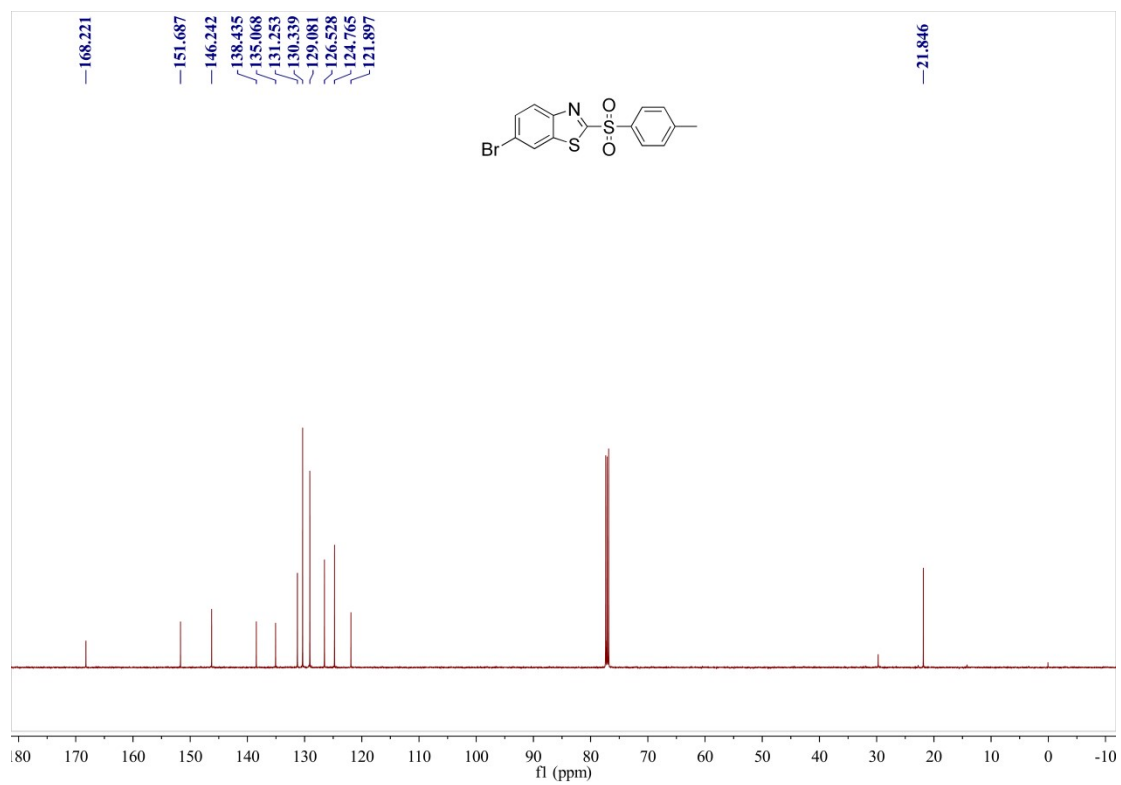


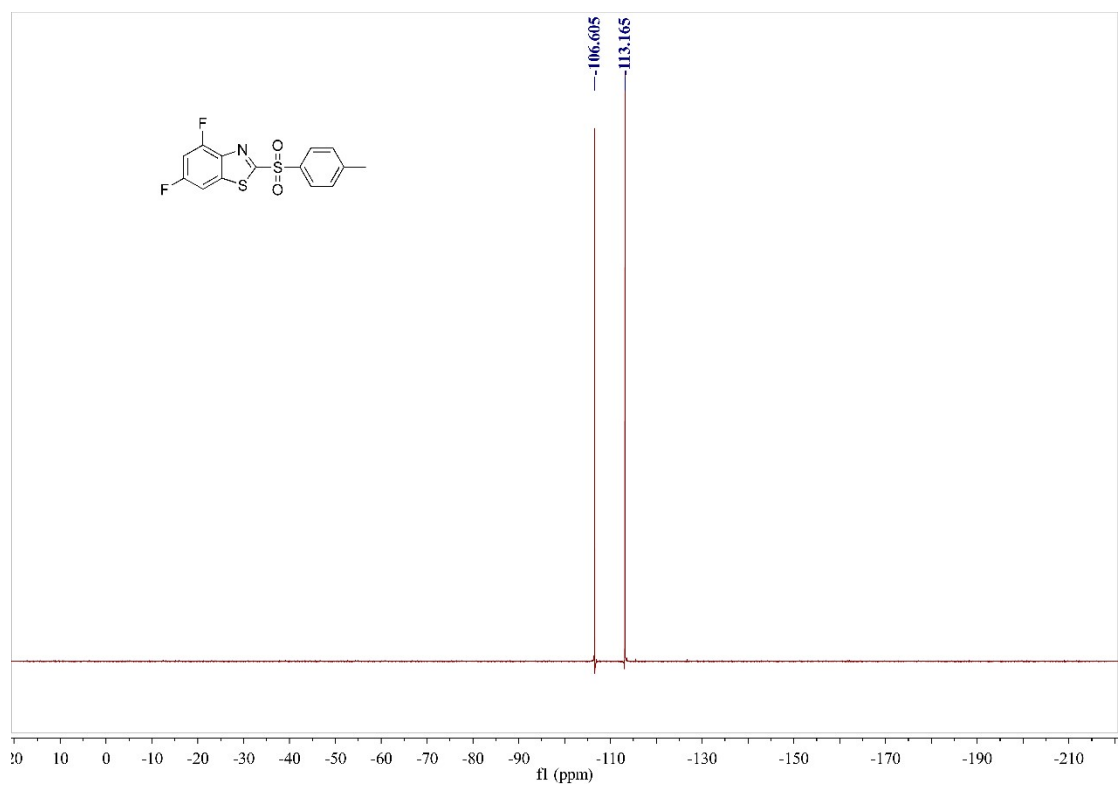
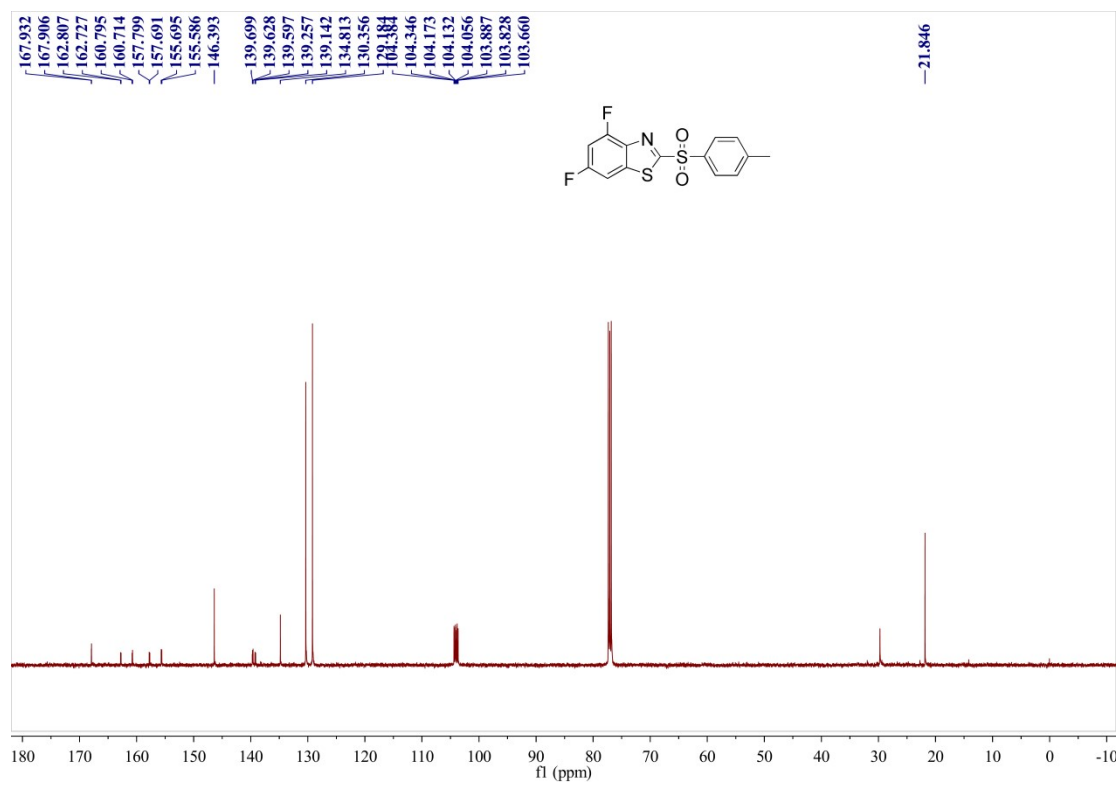


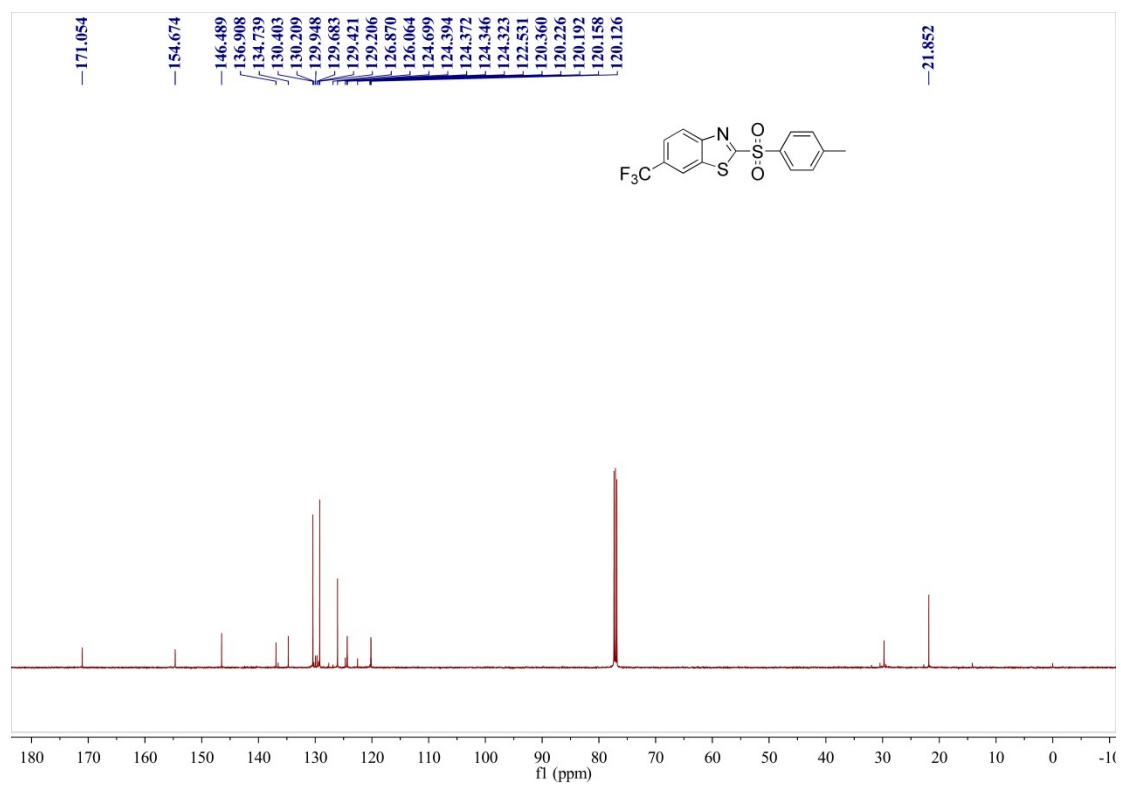
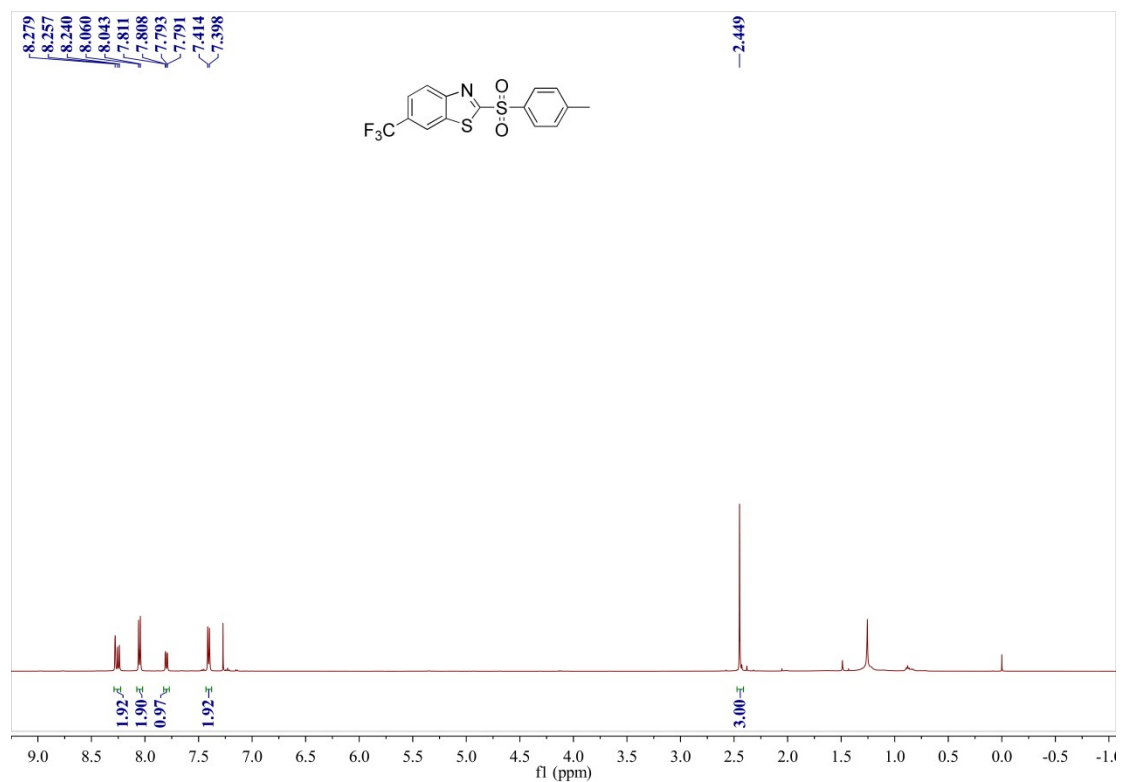


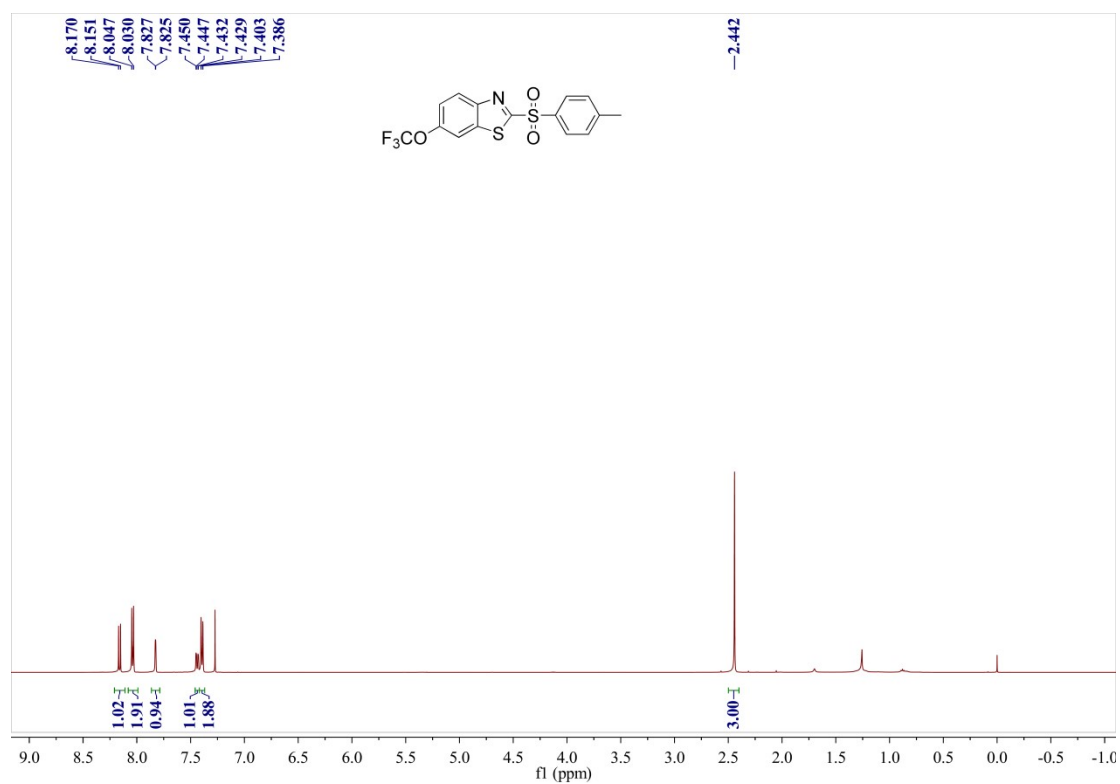
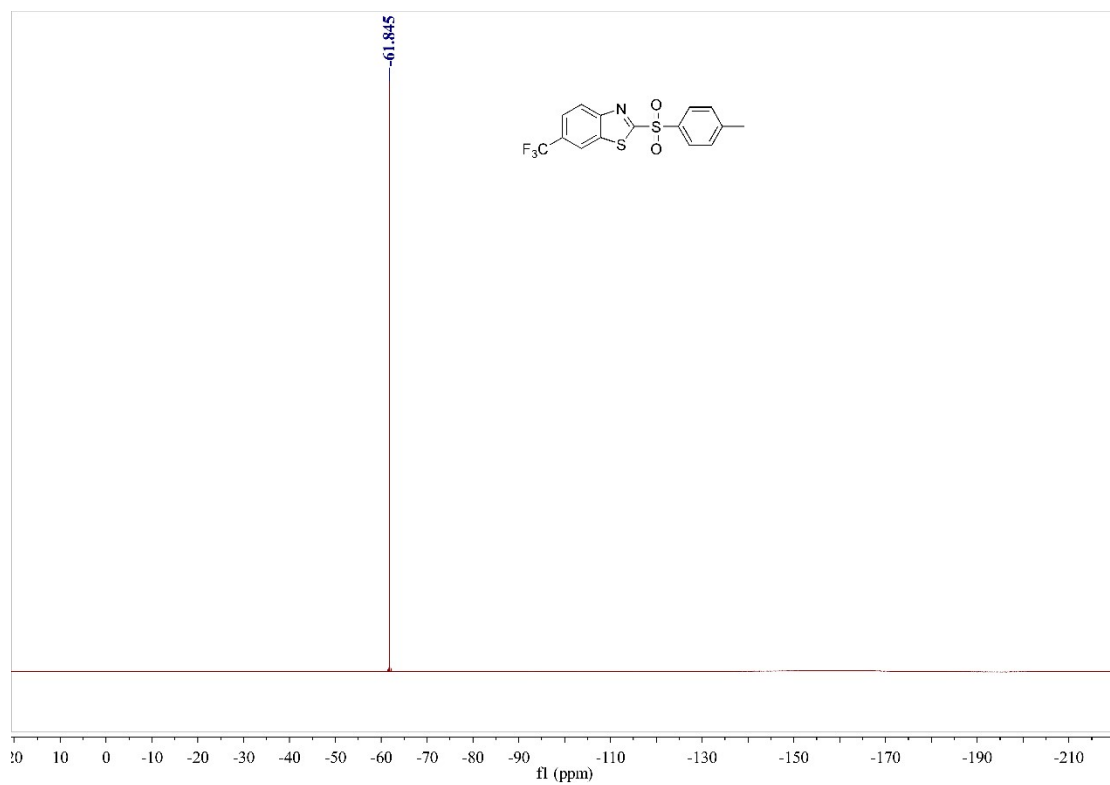


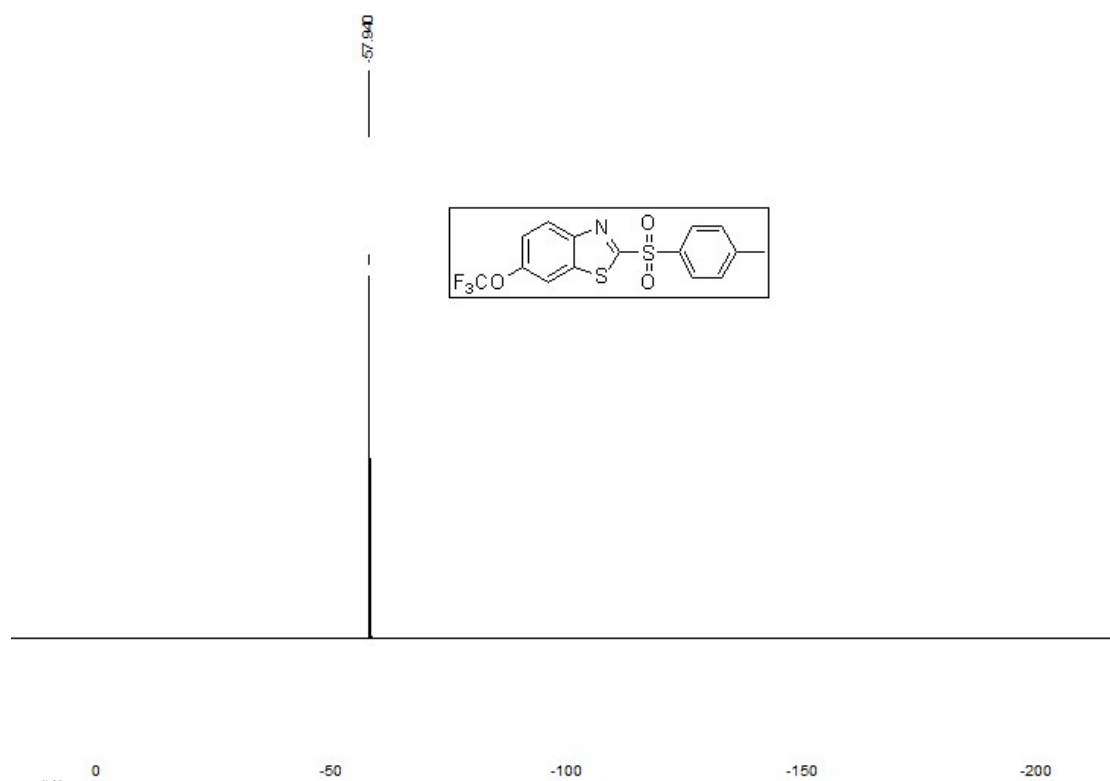
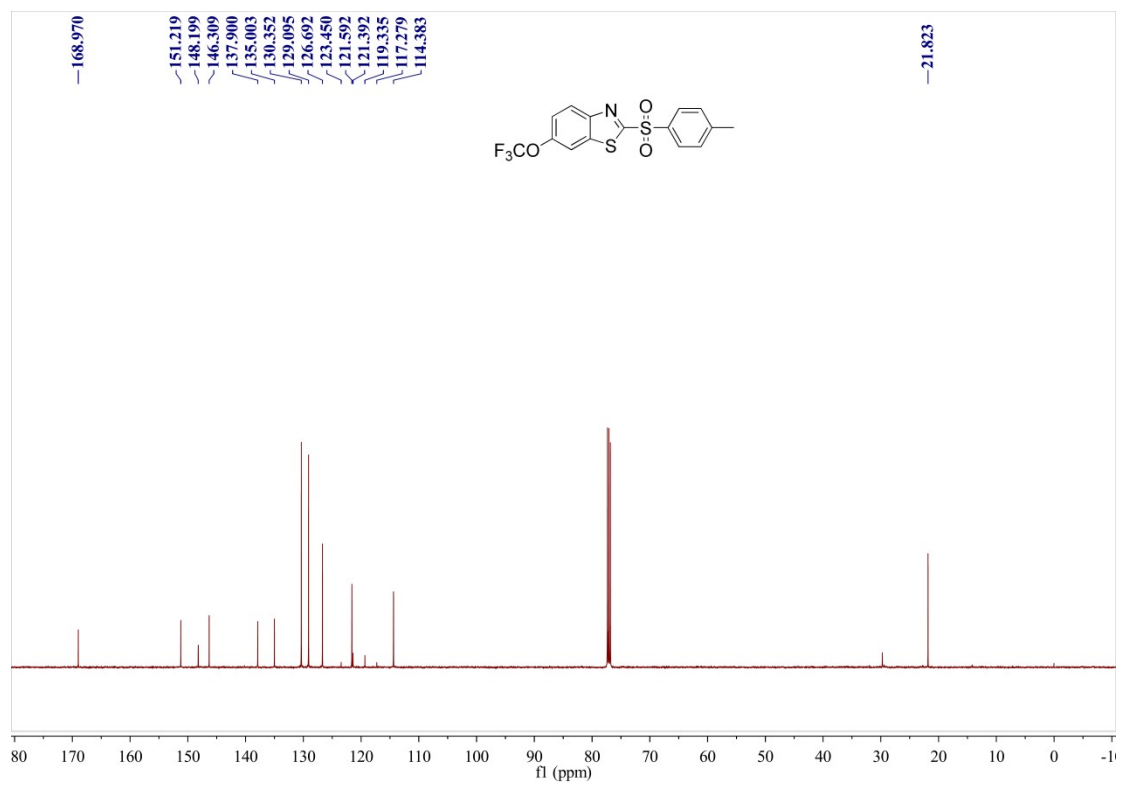


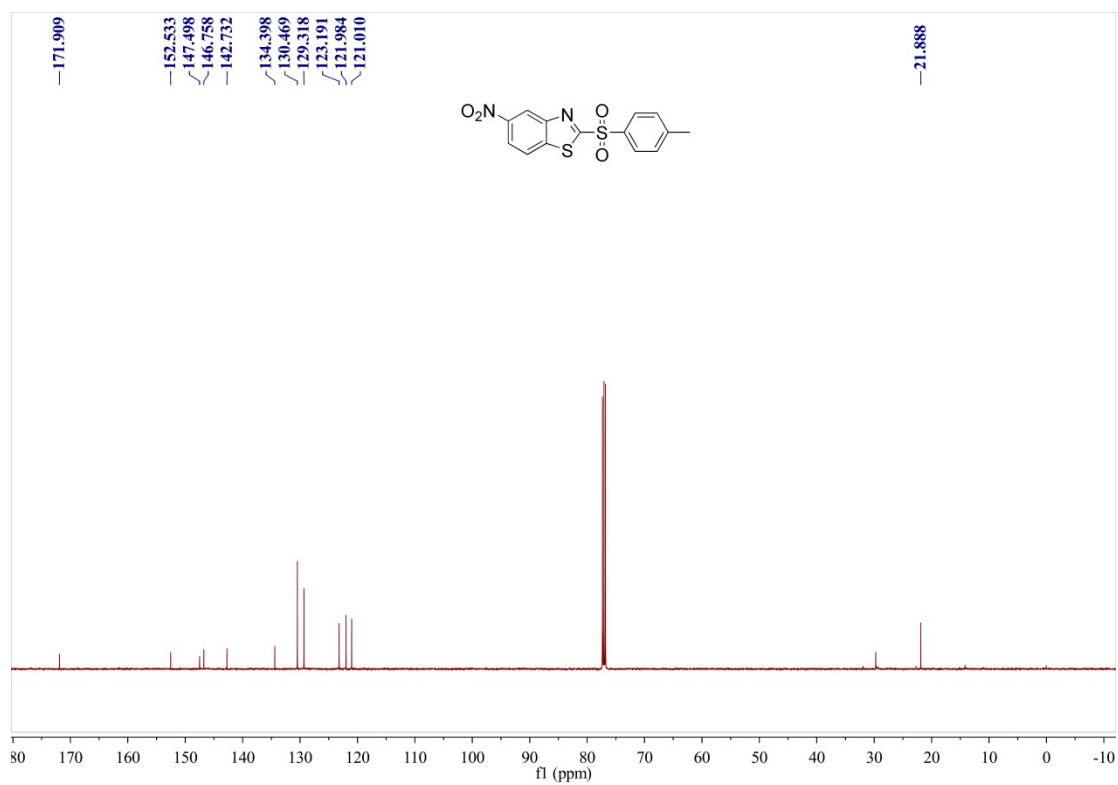
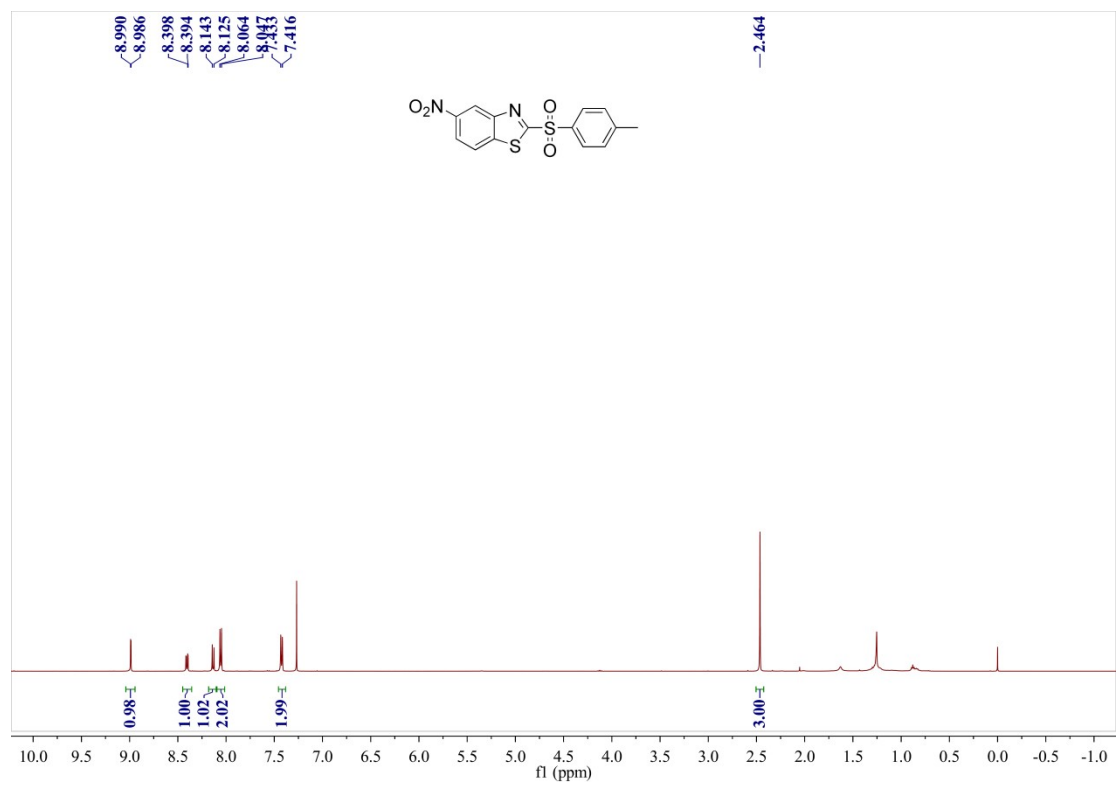


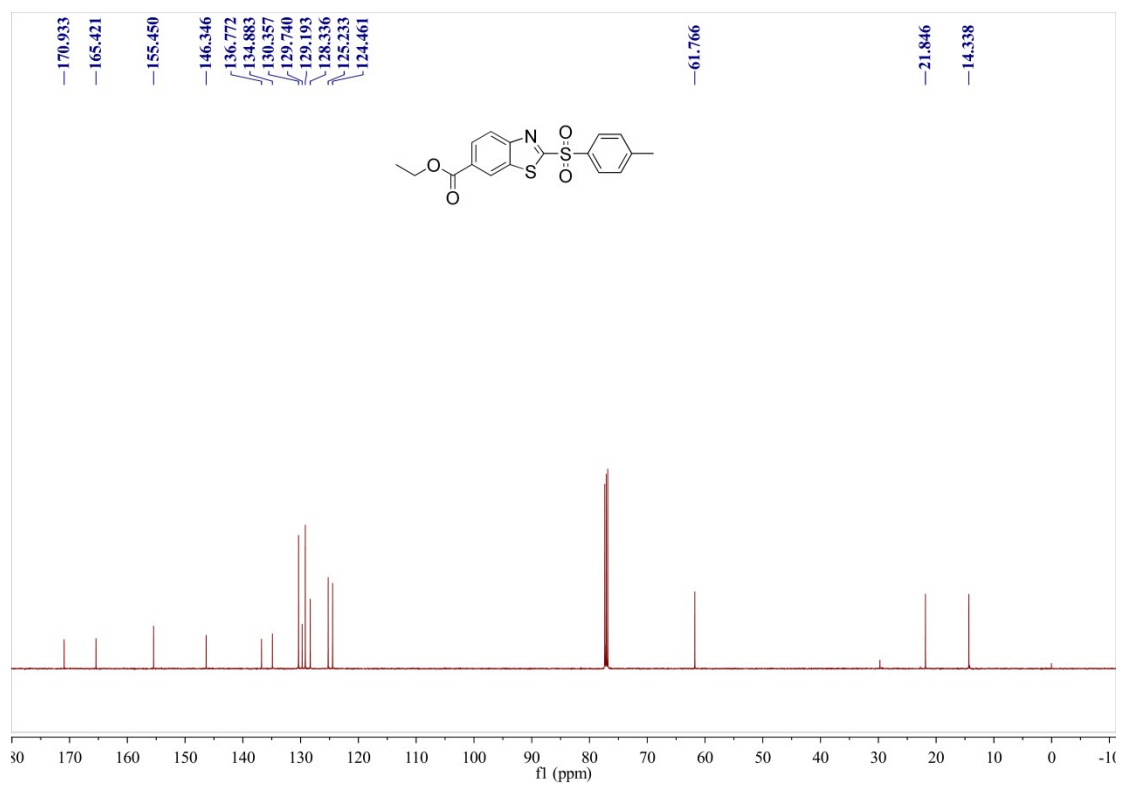
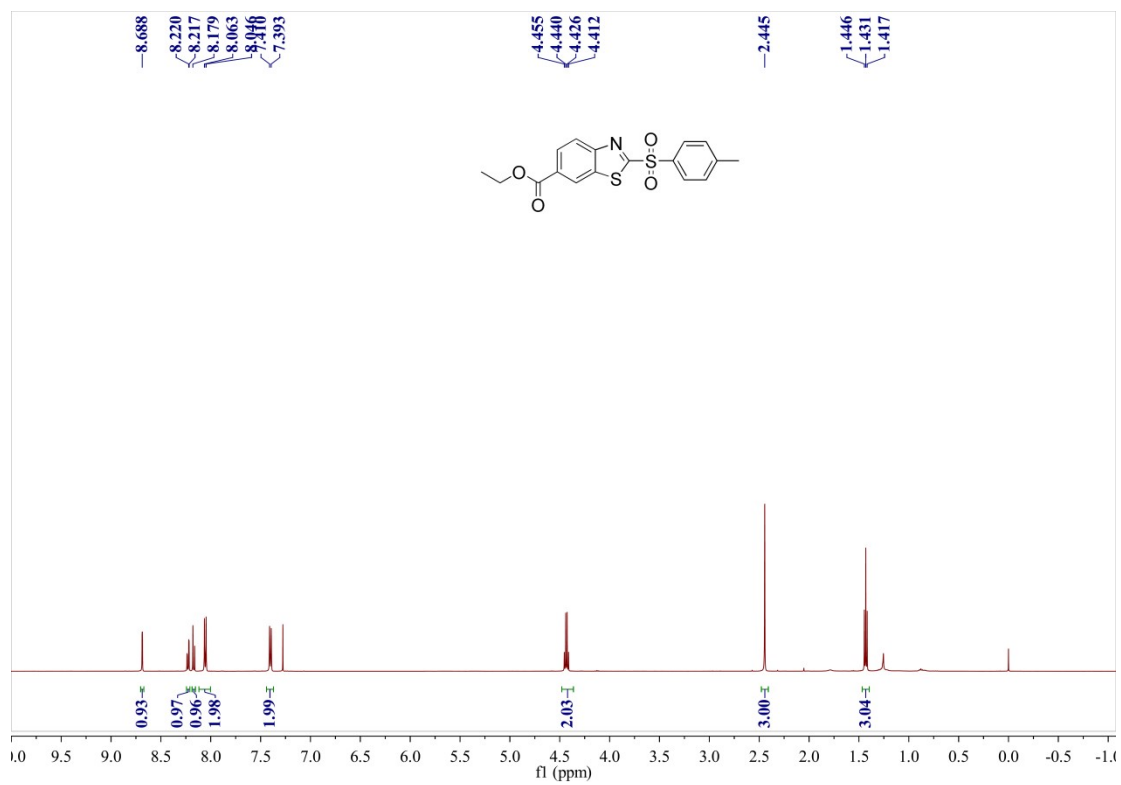


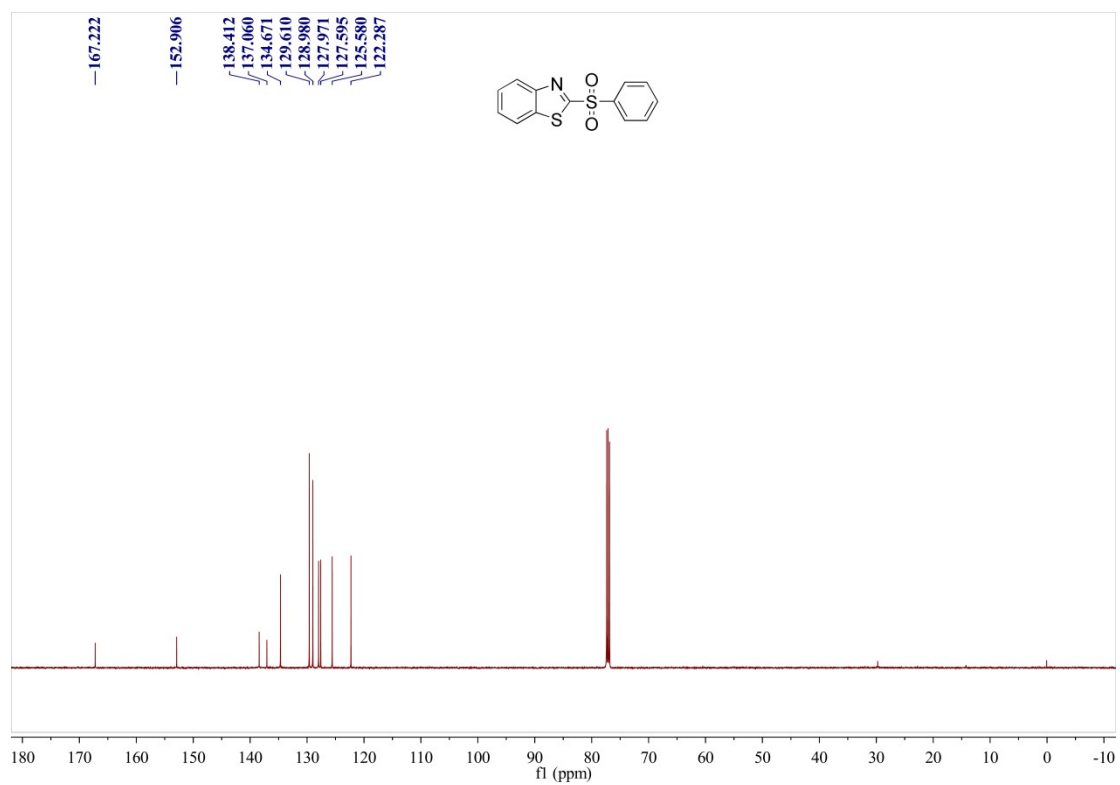
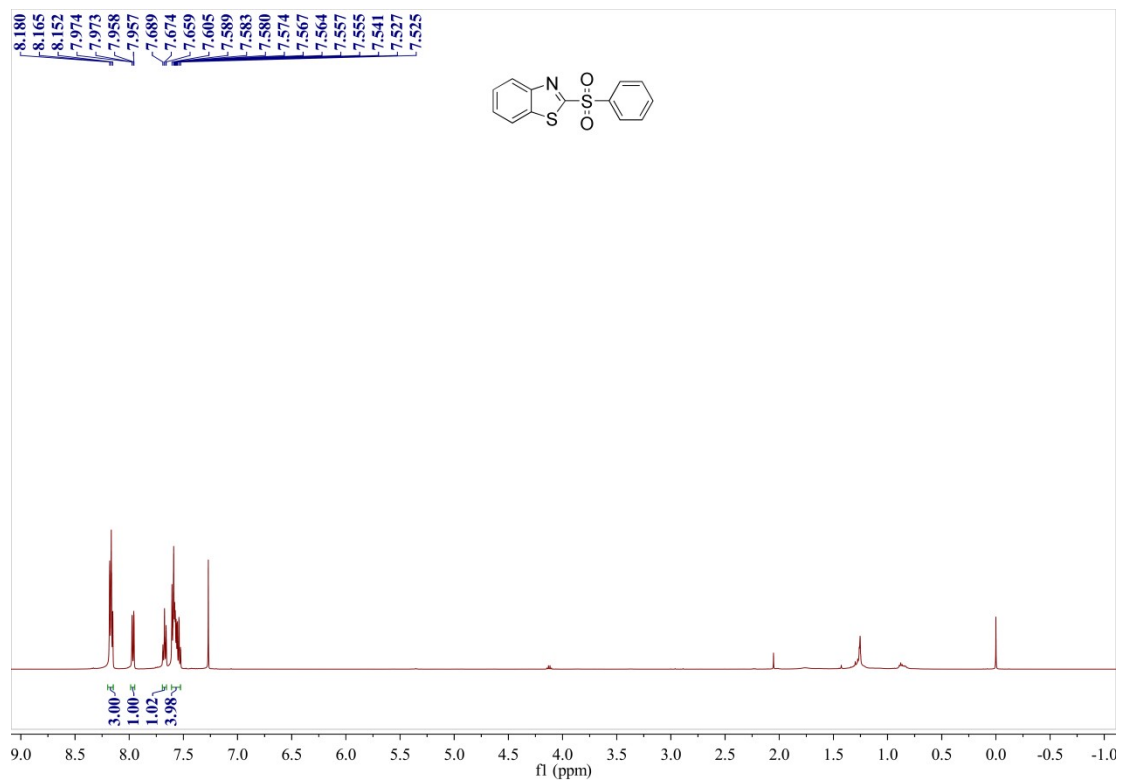


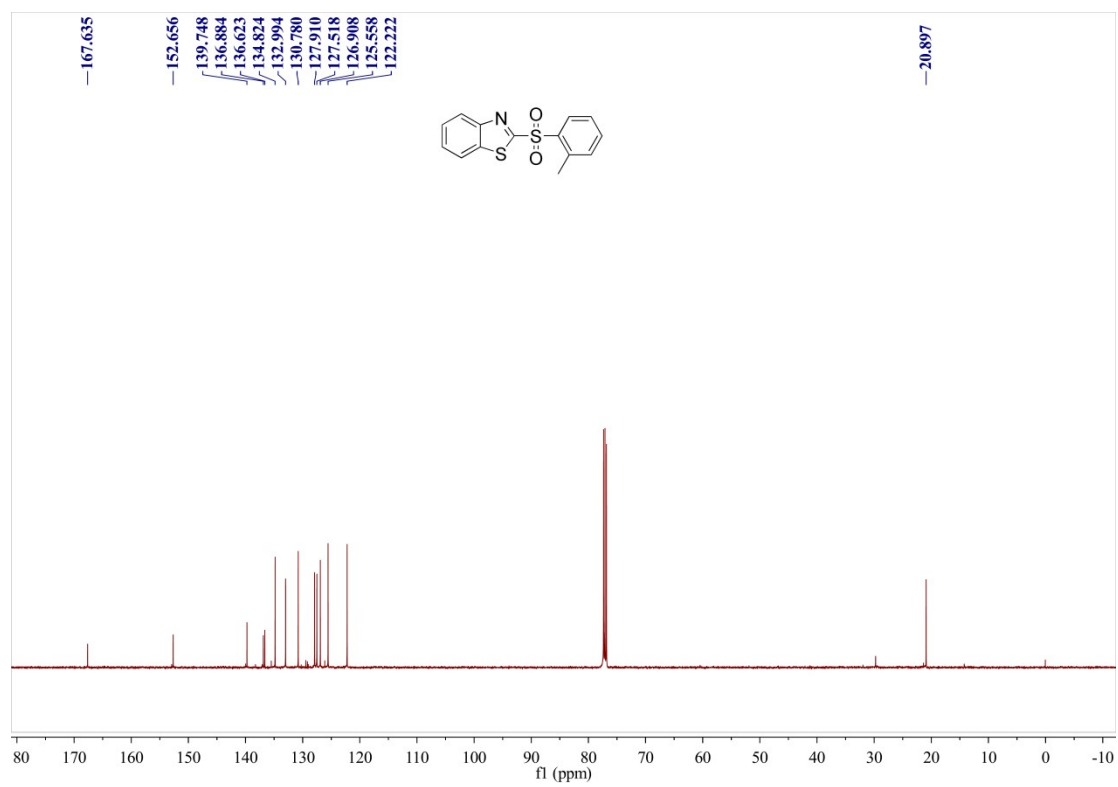
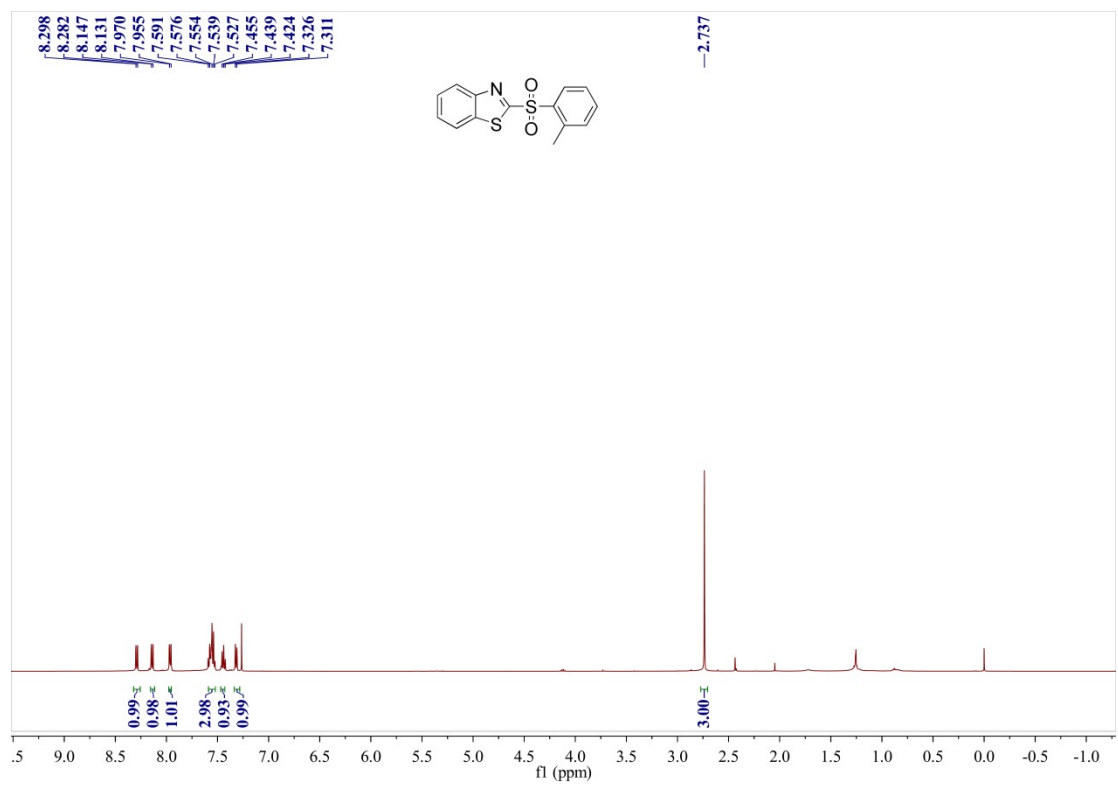


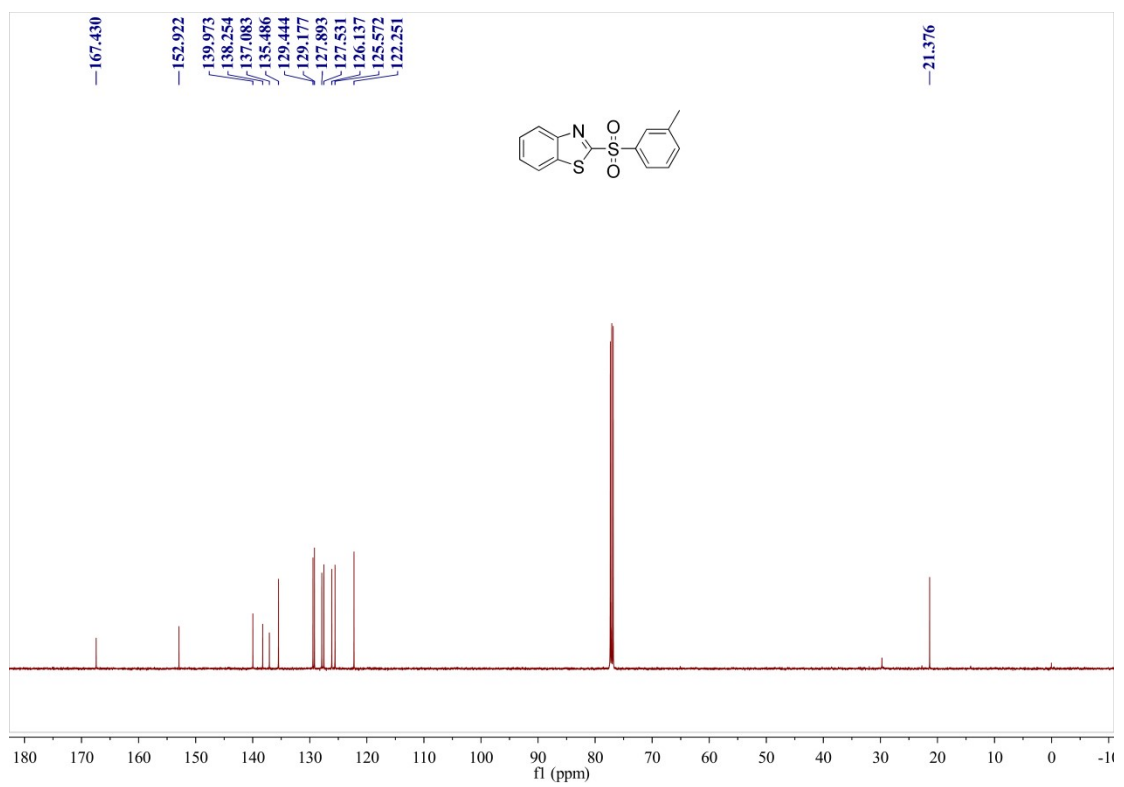
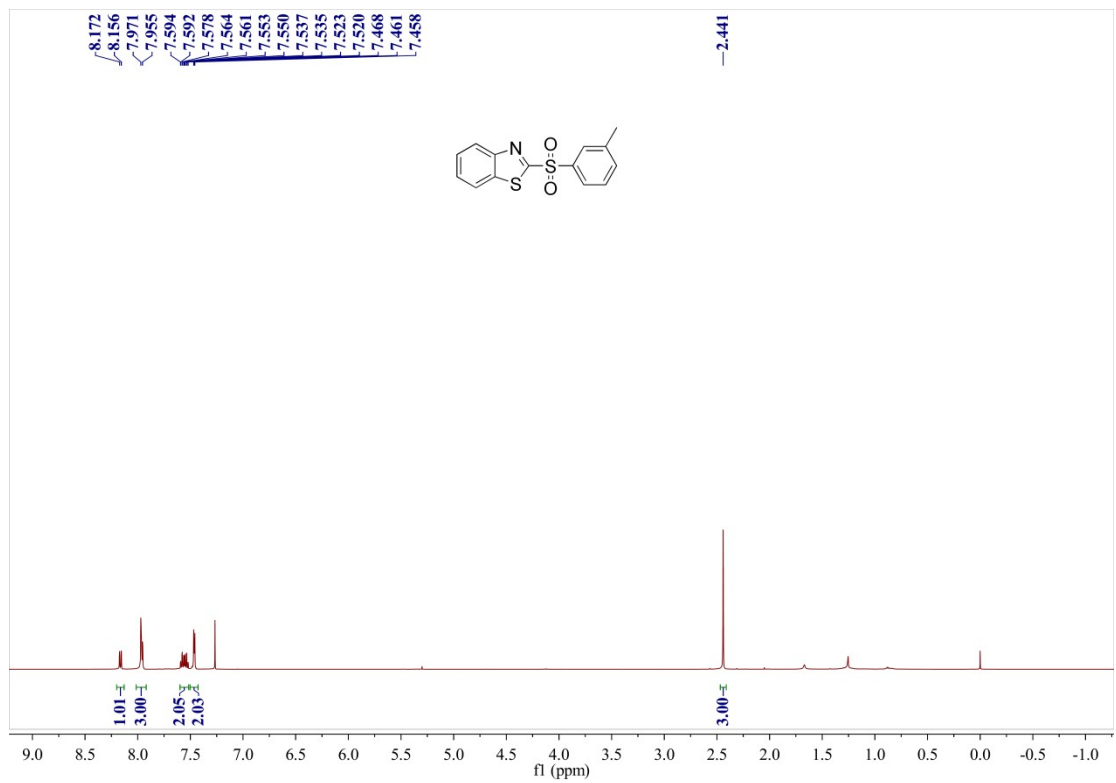


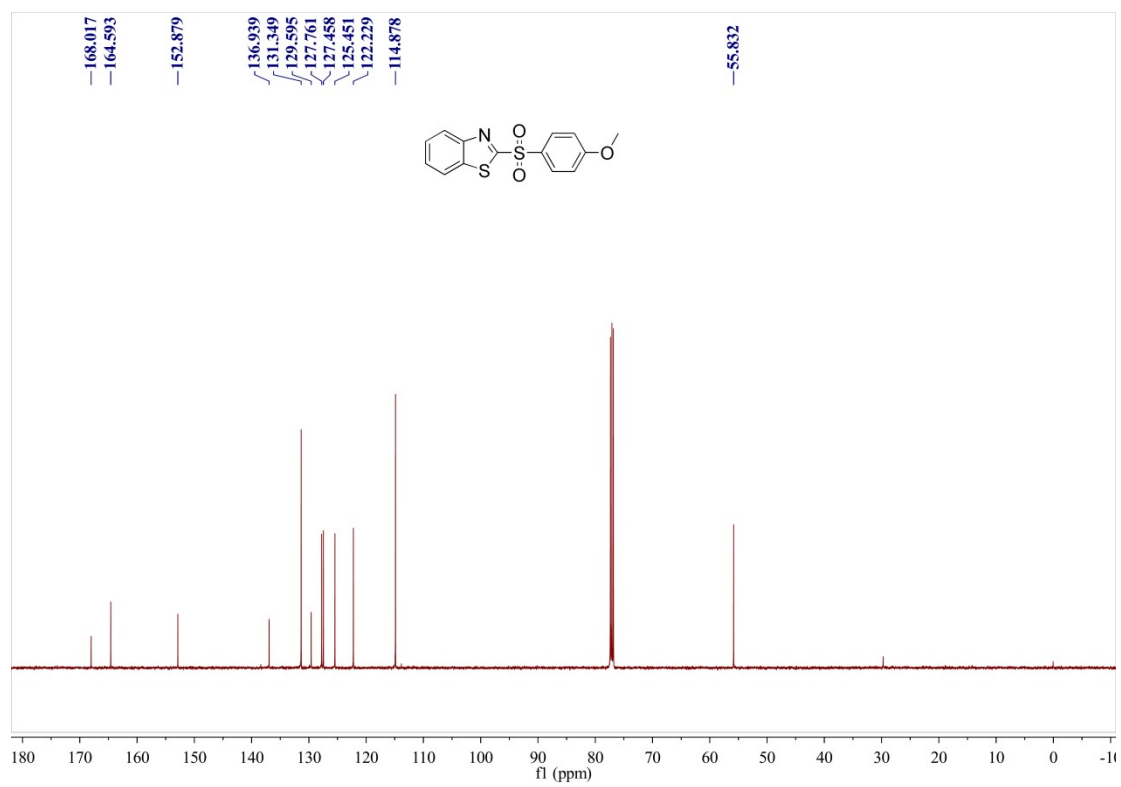
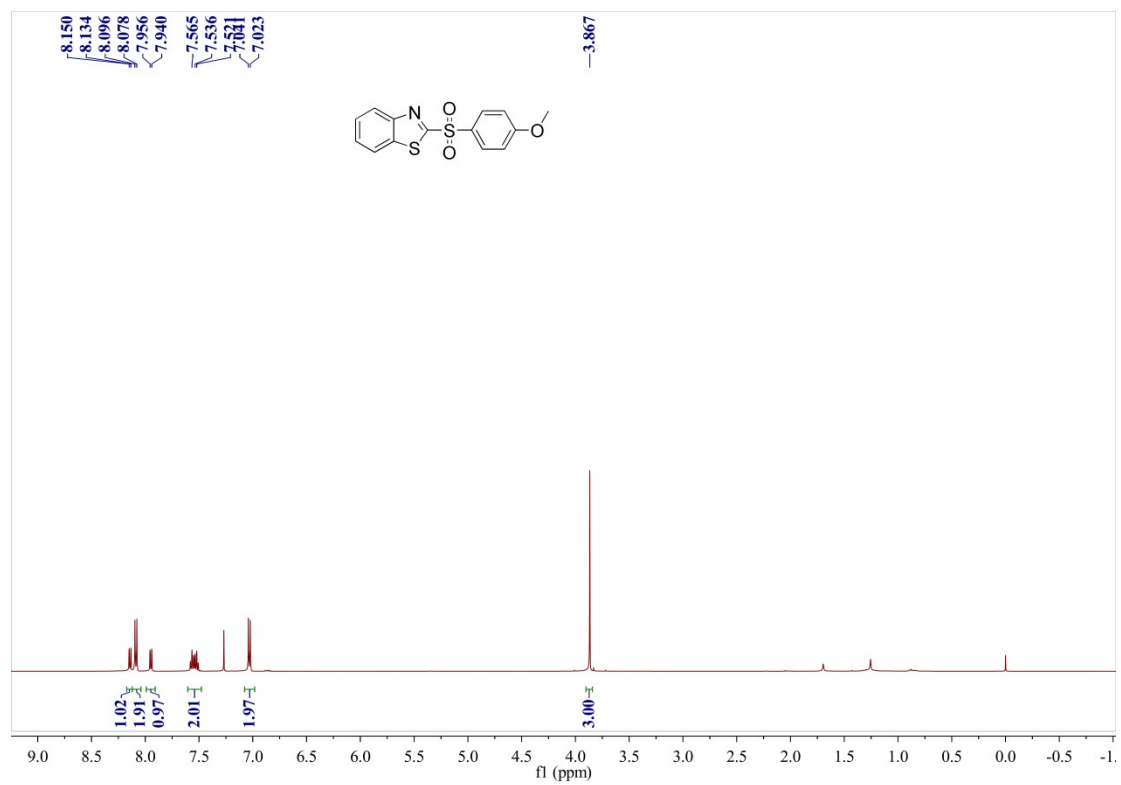


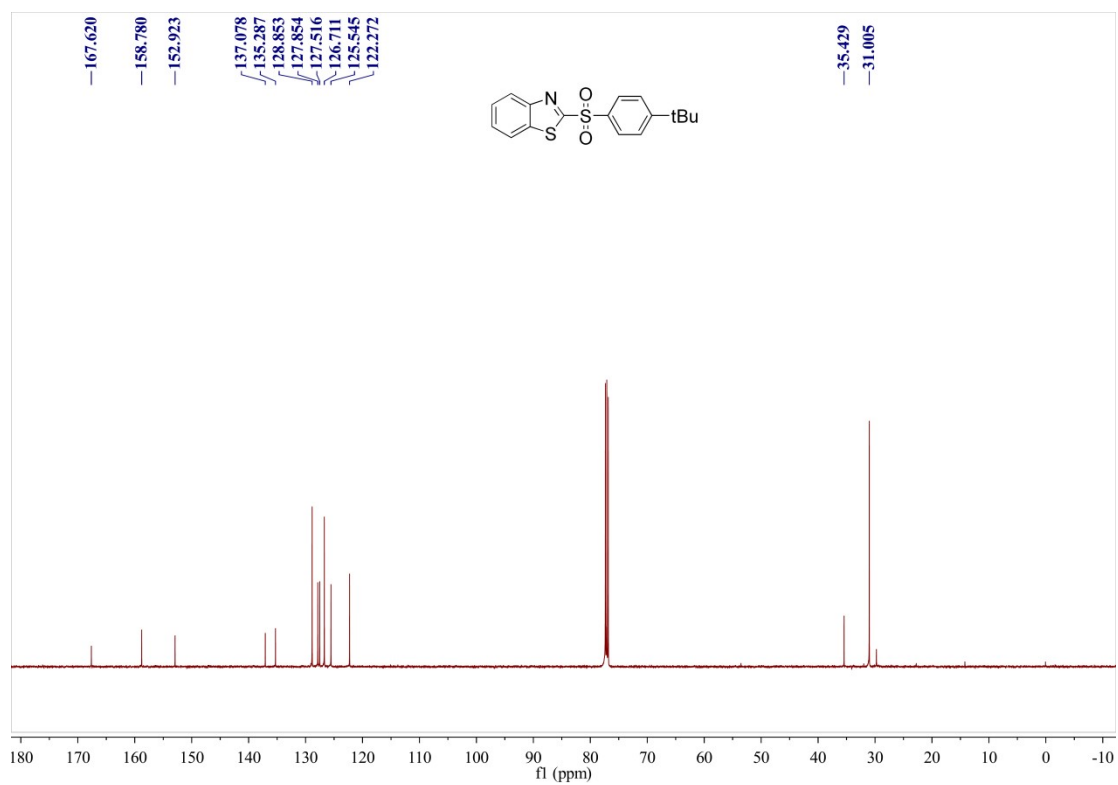
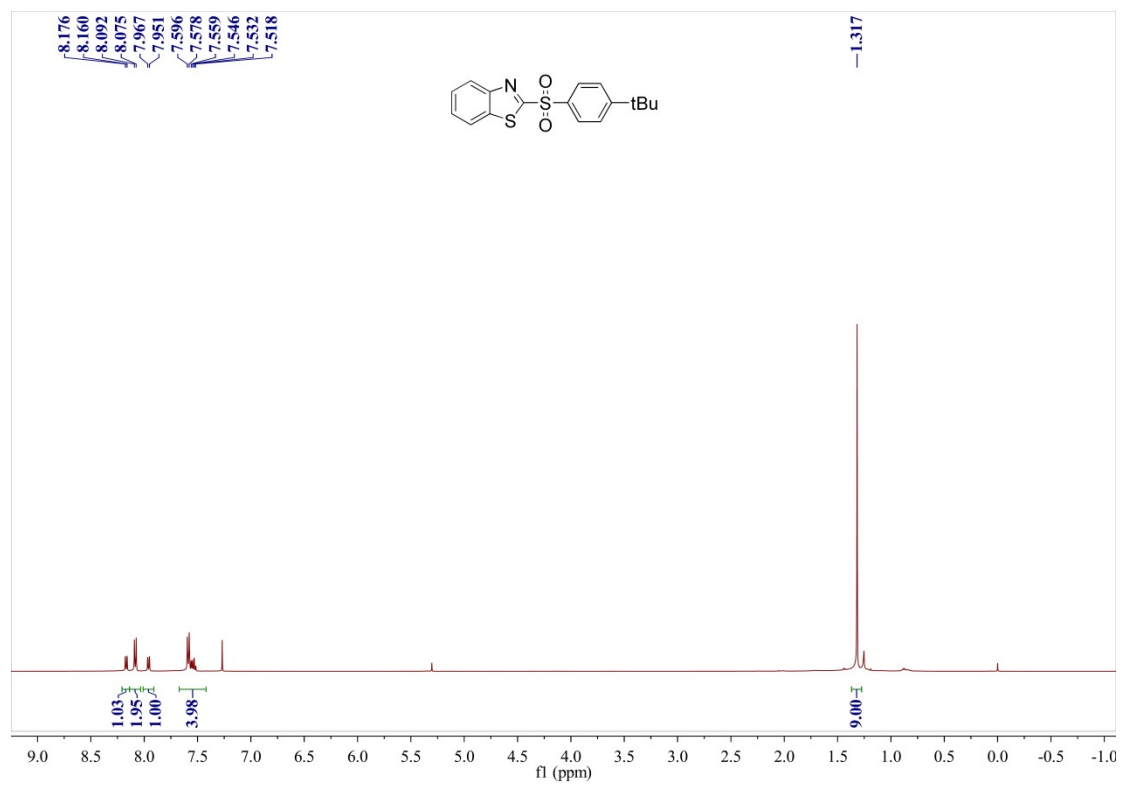


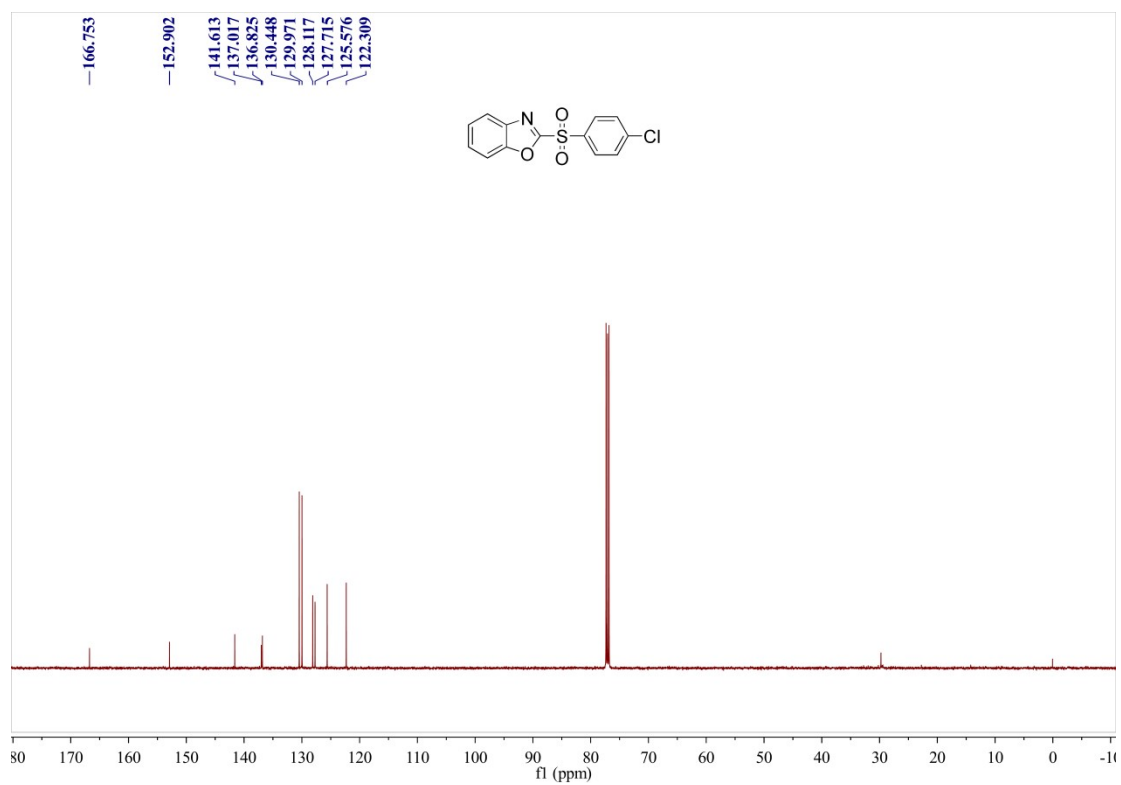
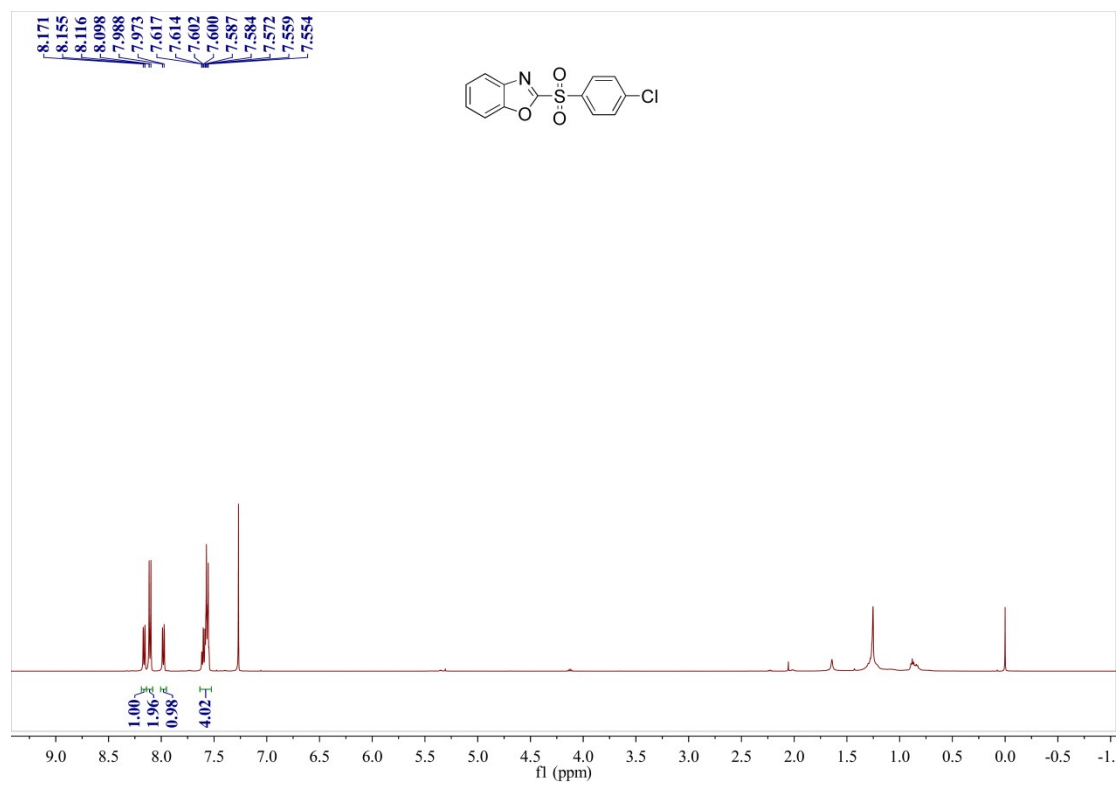


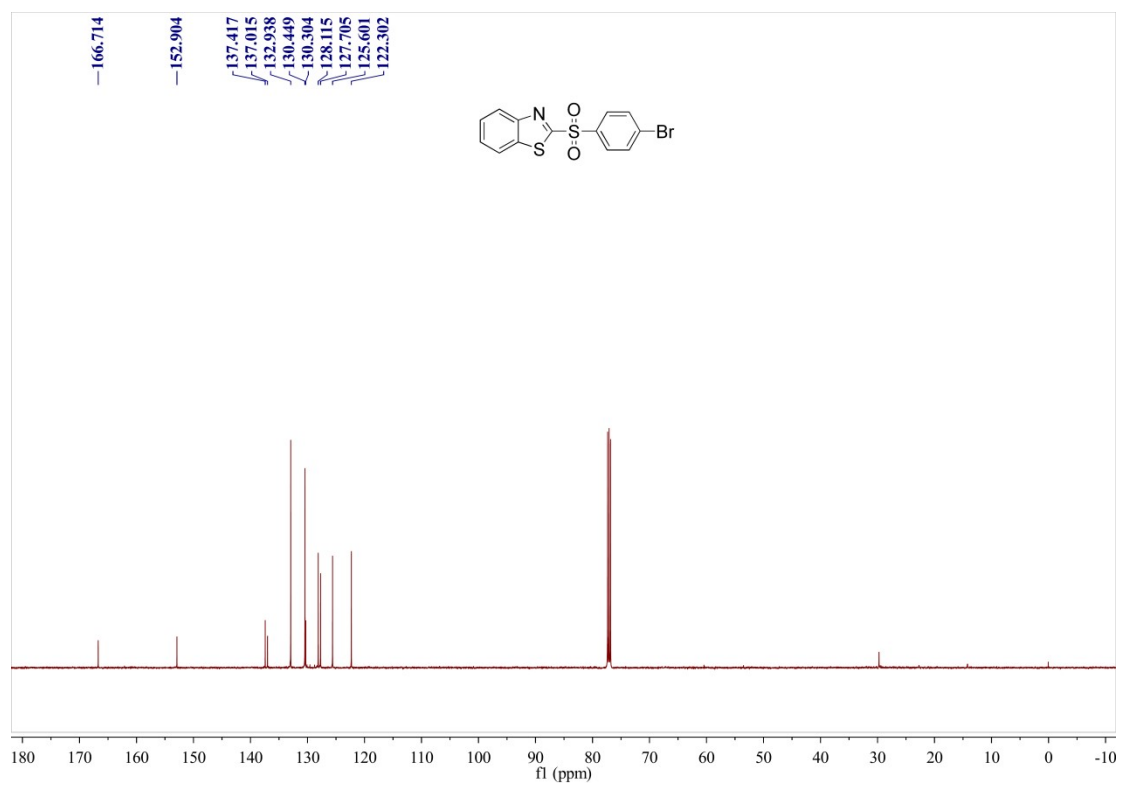
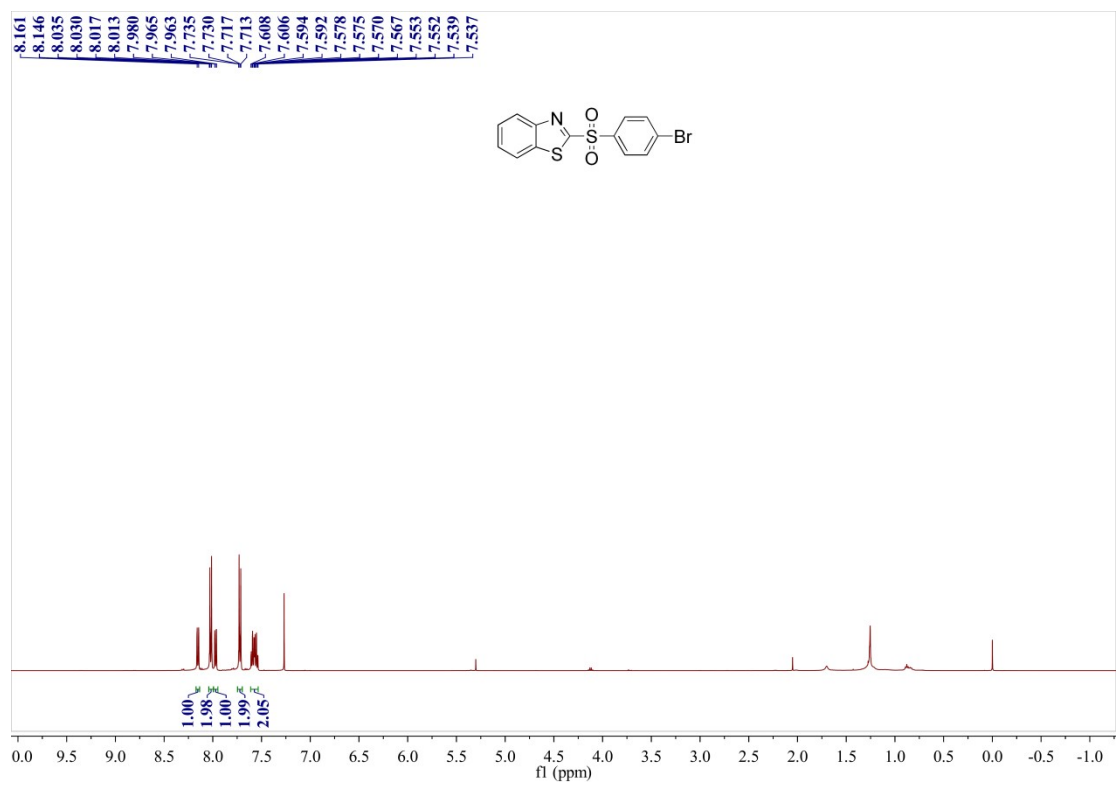


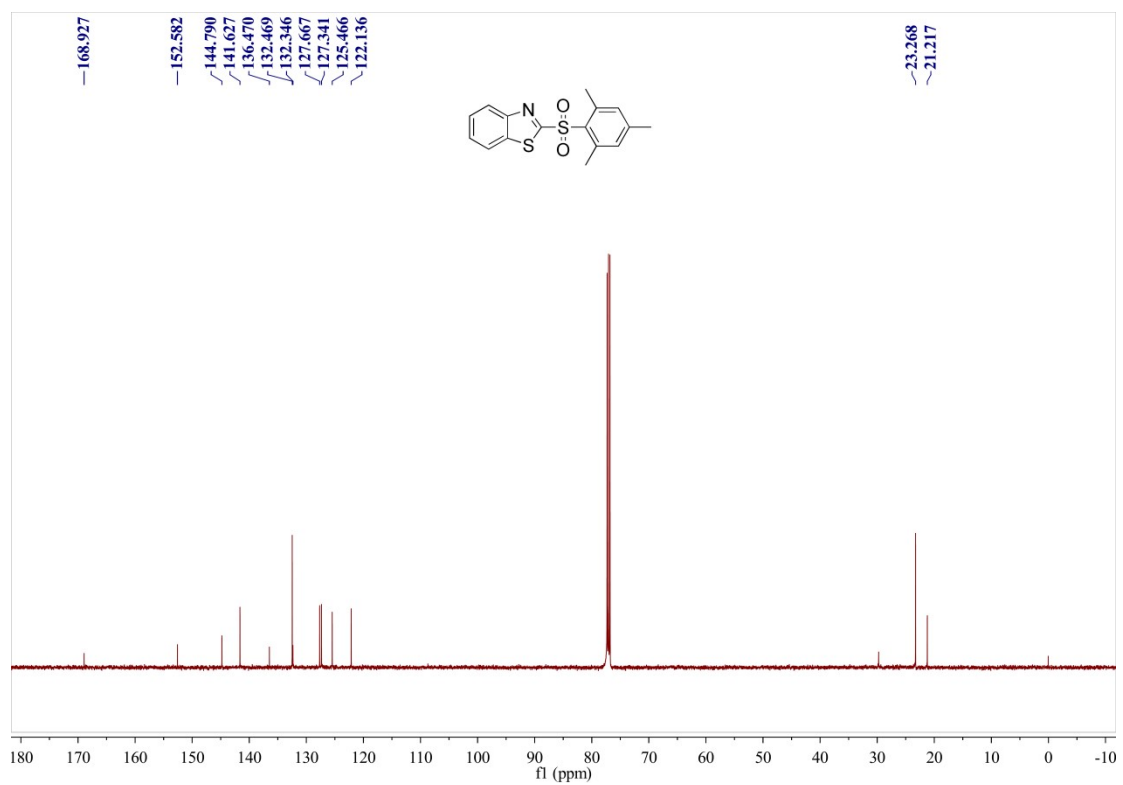
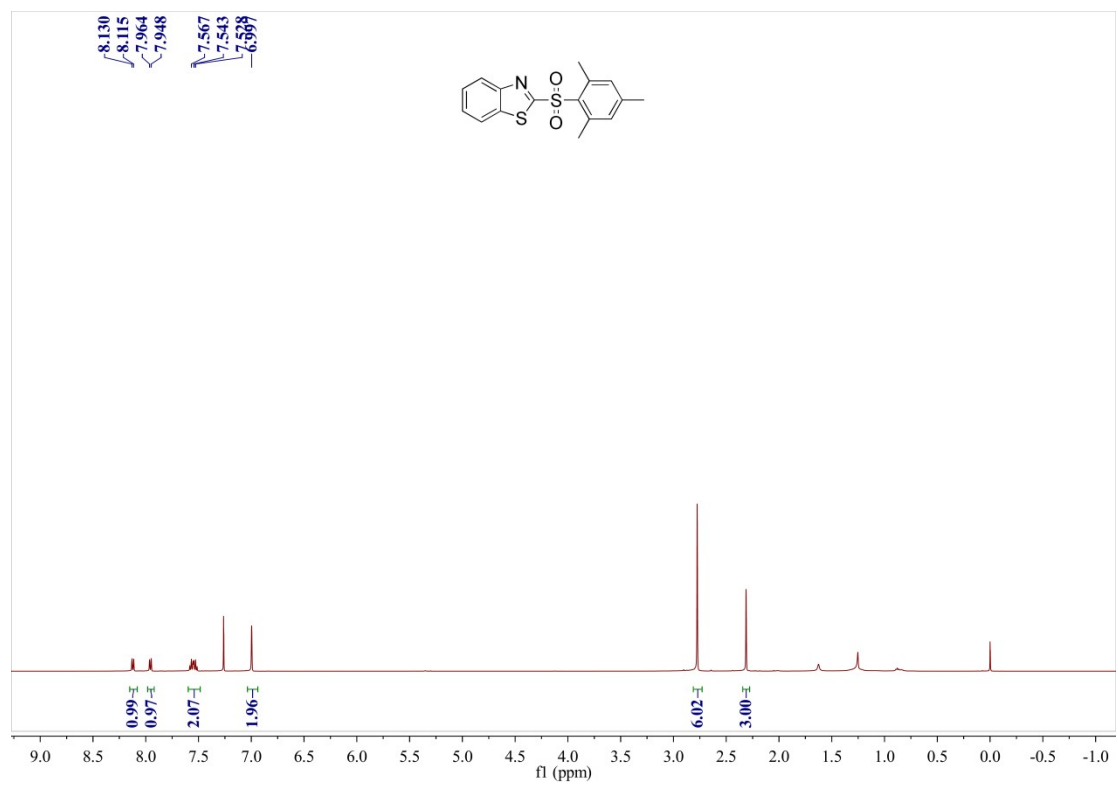


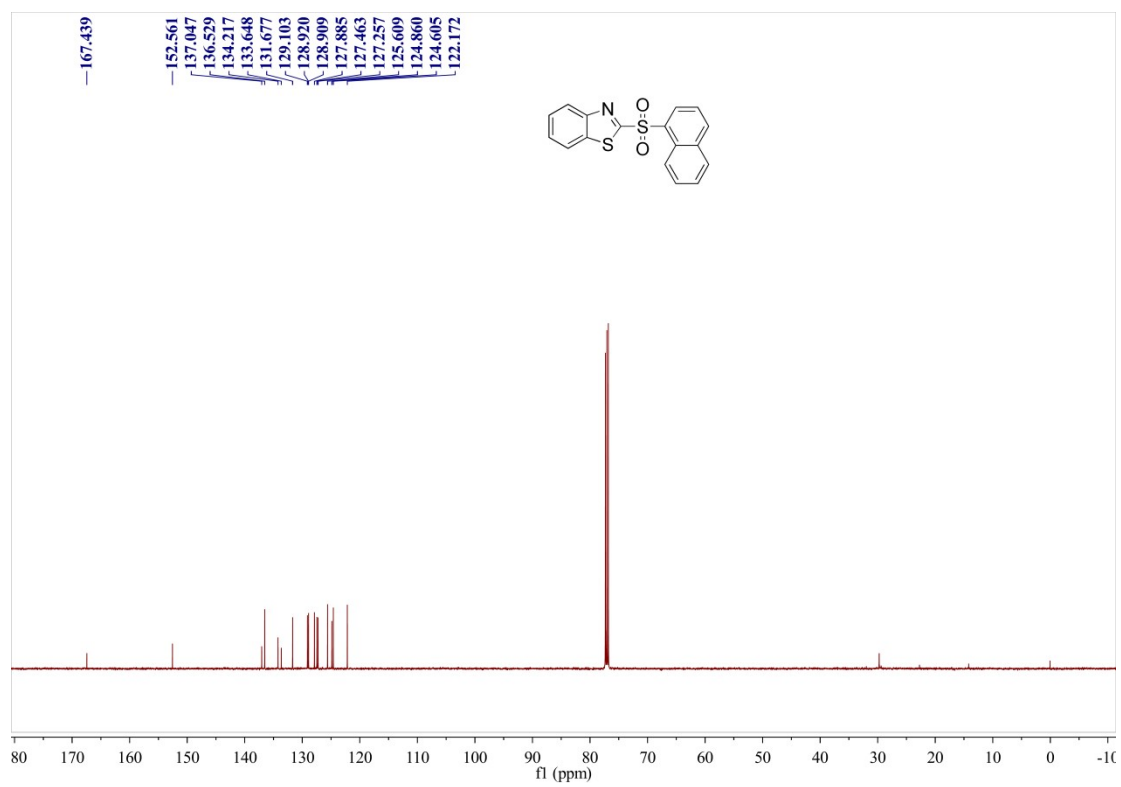
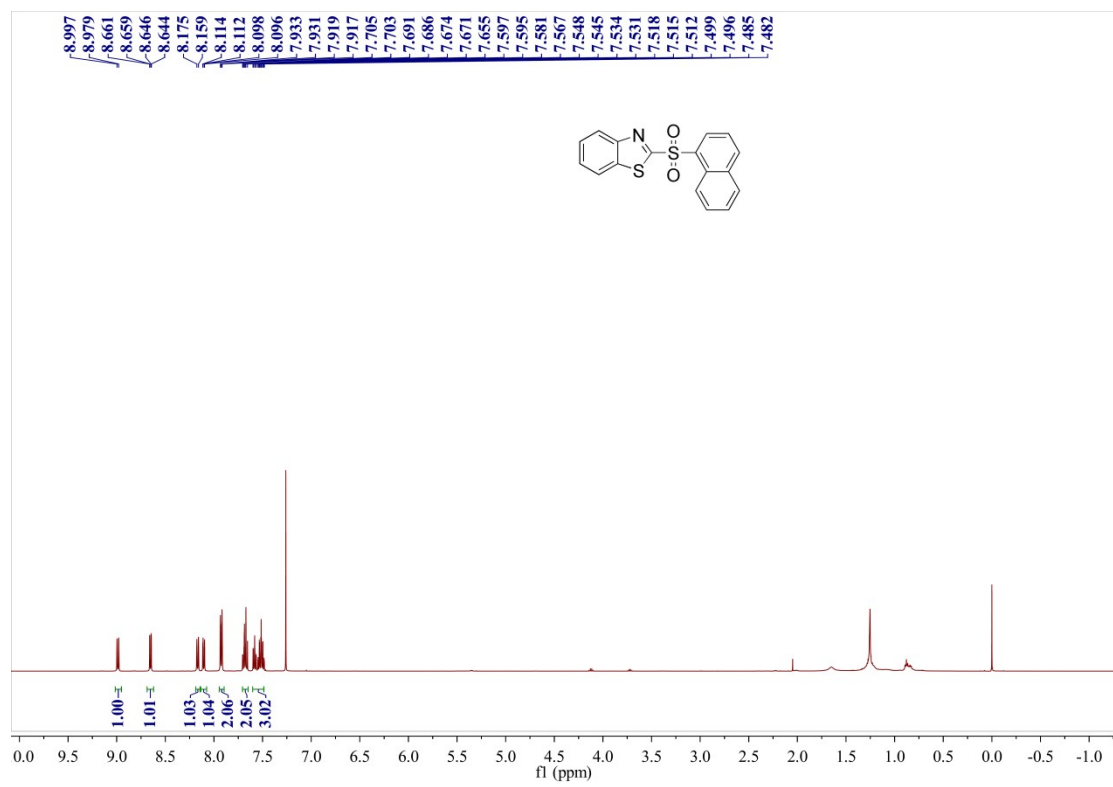


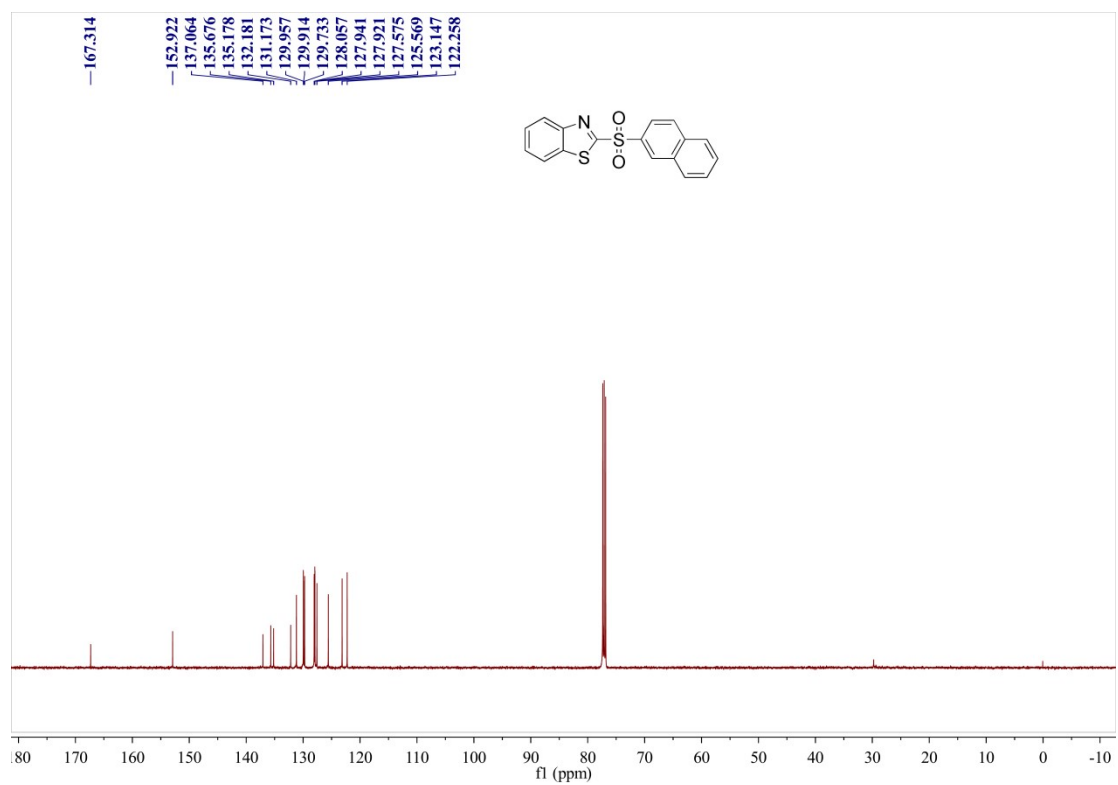
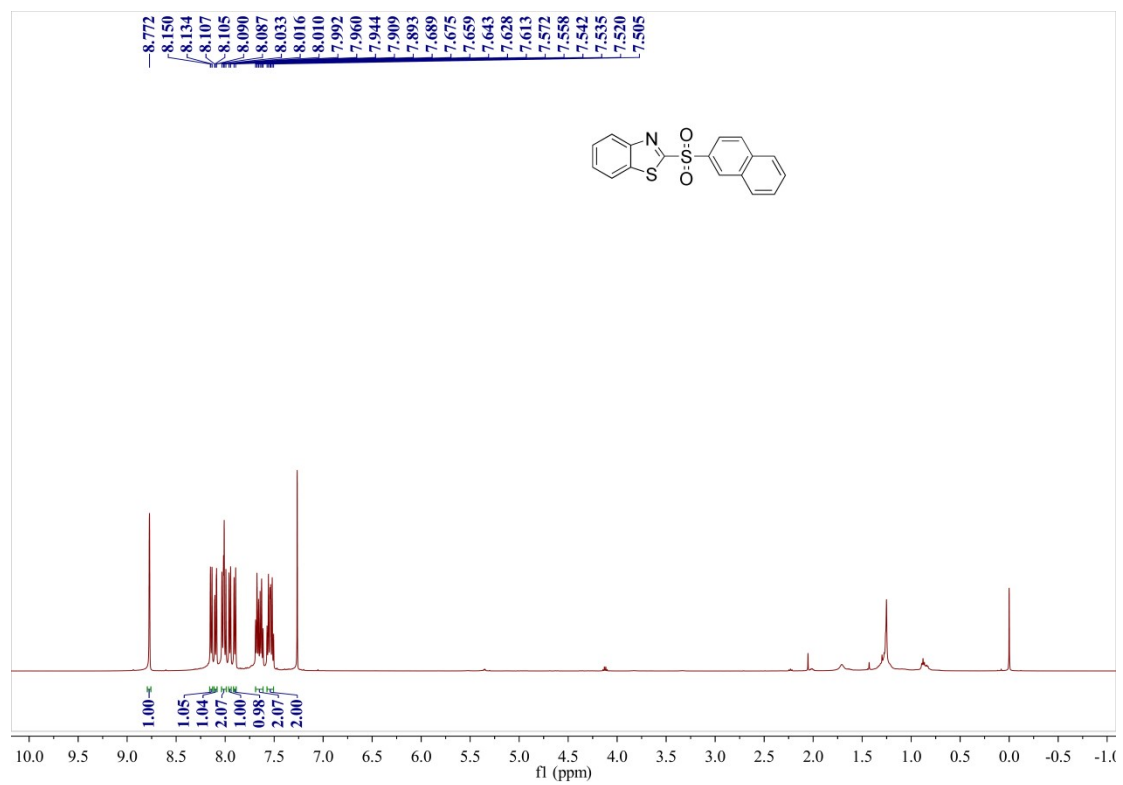


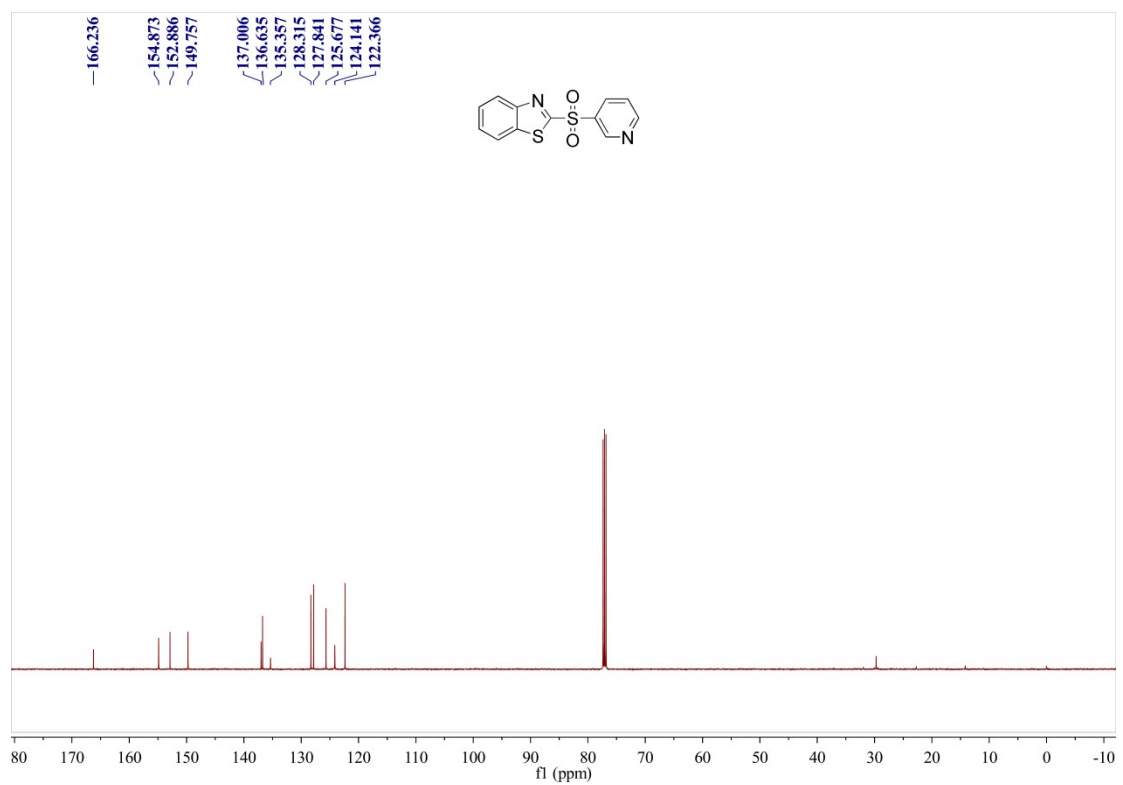
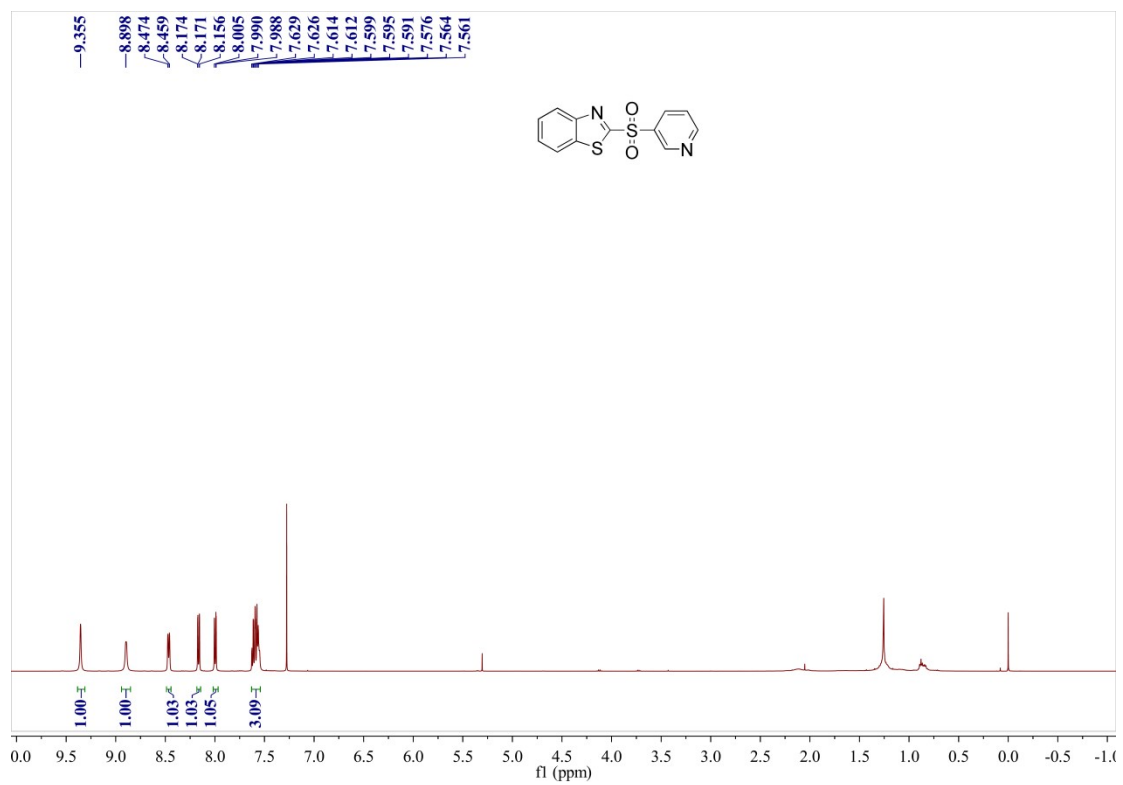


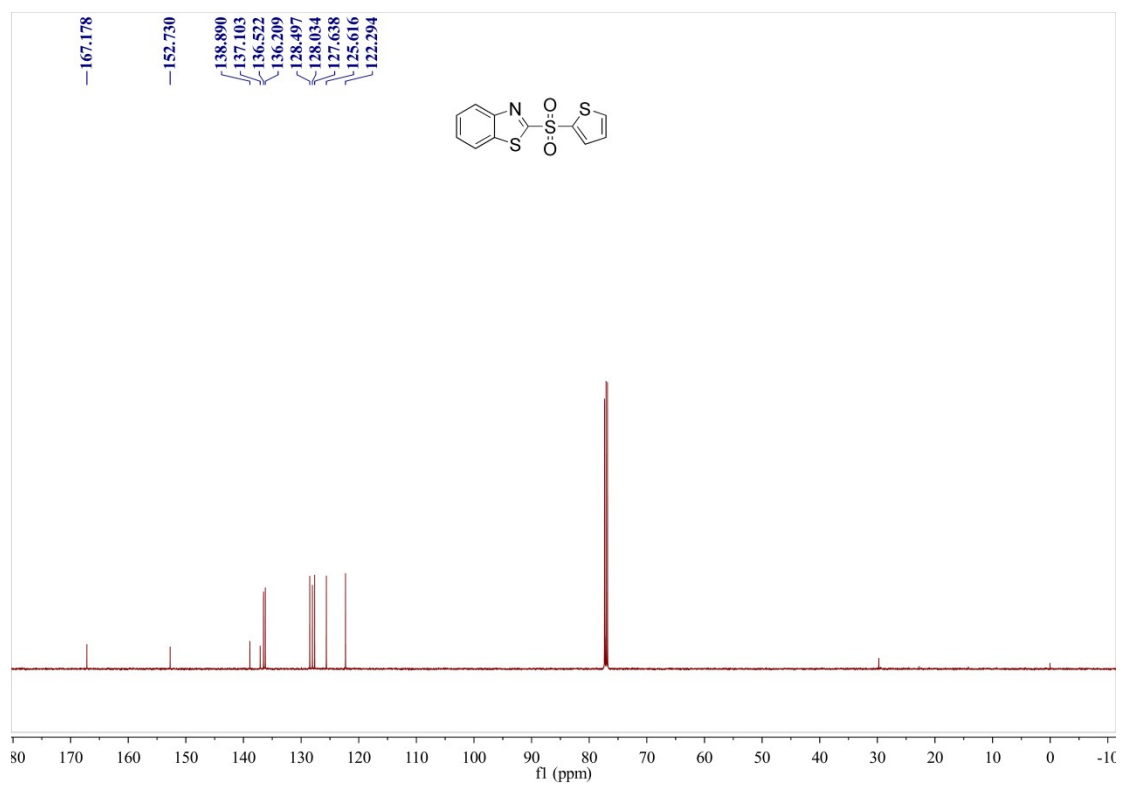
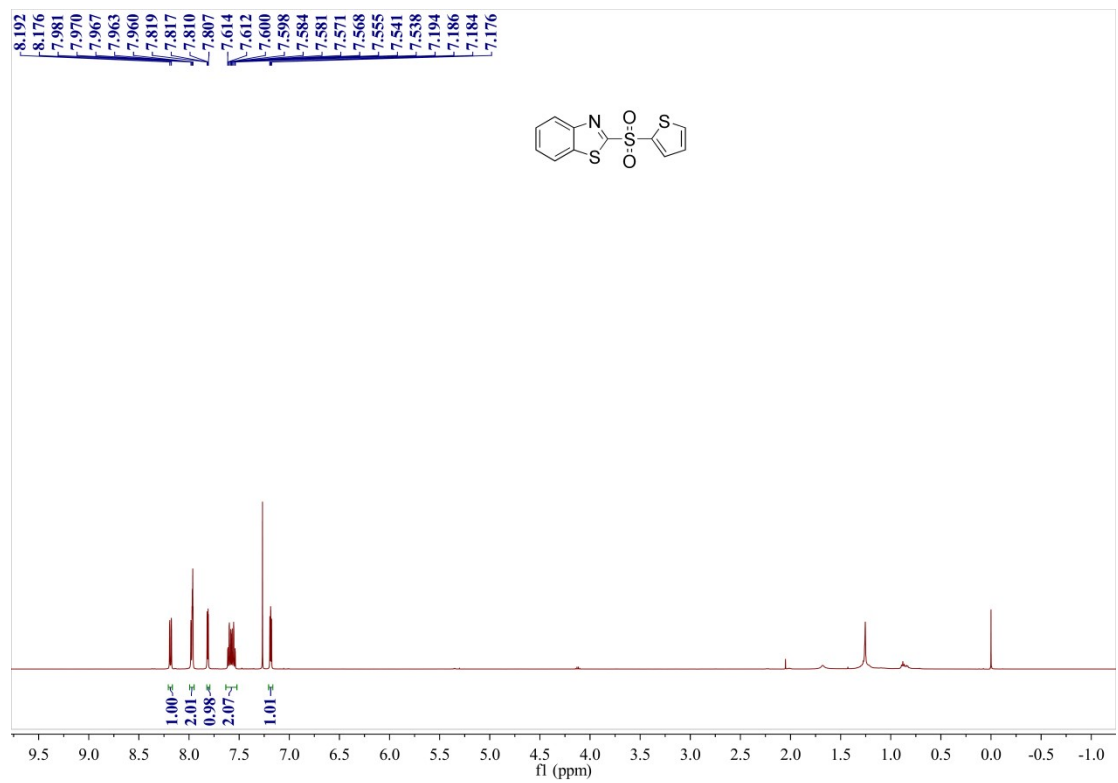


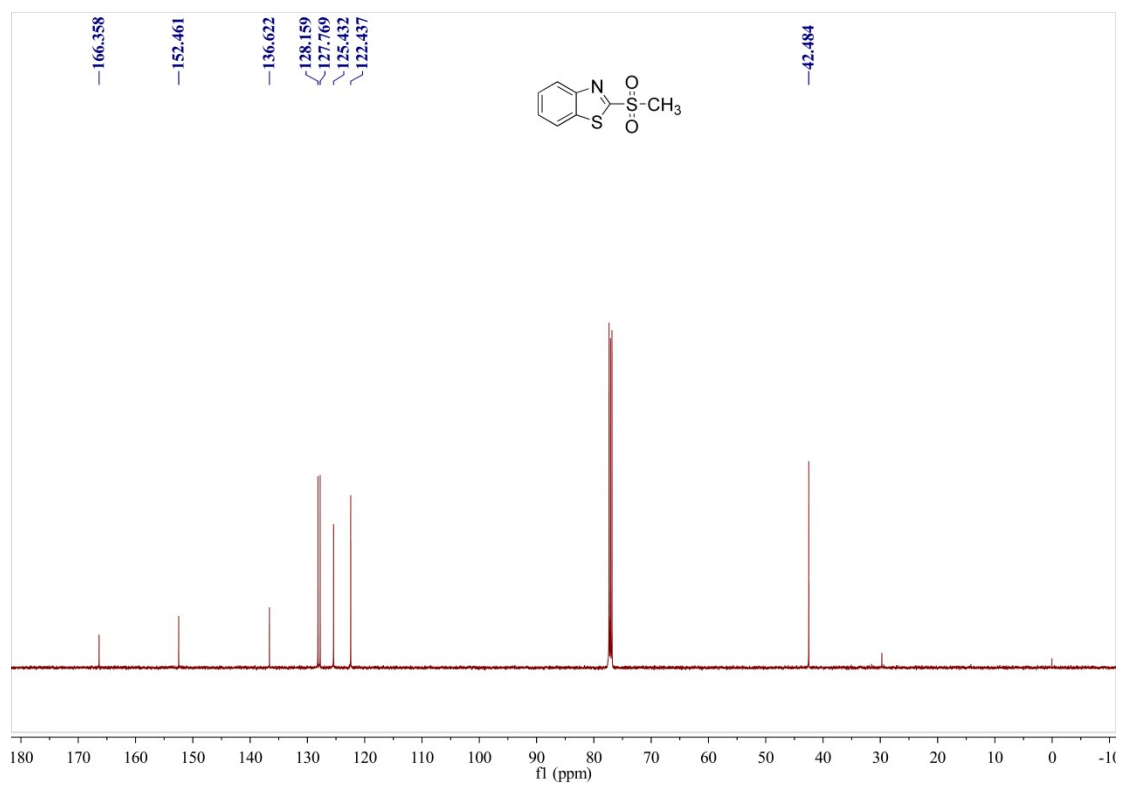
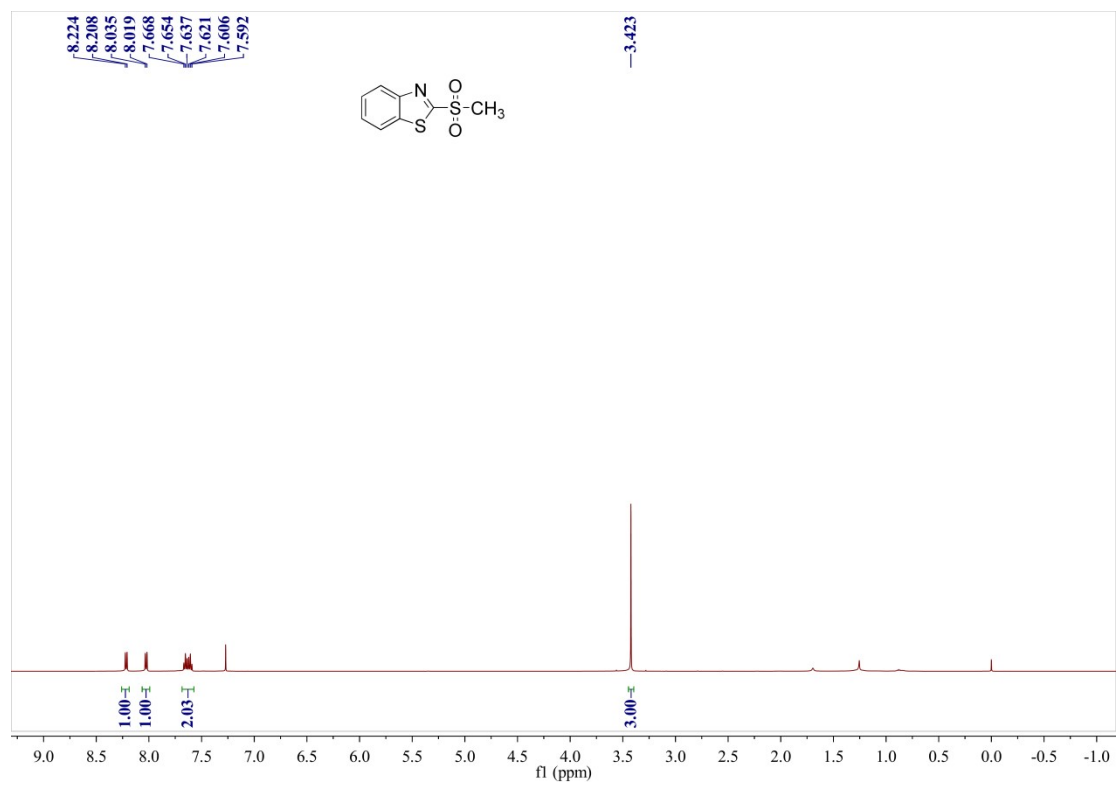












5. References.

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