Supplementary Information

for

Palladium-Catalyzed Oxidative C–H/C–H Cross-Coupling of Benzothiazoles with Thiophenes and Thiazoles

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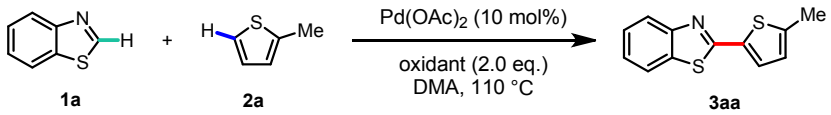
General information

Analytical thin layer chromatography (TLC) was HSGF 254 (0.15–0.2 mm thickness, Yantai Huiyou Company, China). Column chromatography was carried out on silica gel (200–300 mesh). NMR spectra were recorded at Varian Mercury-300 spectrometer, Varian Mercury-400 spectrometer and Varian Mercury-500 spectrometers (300 MHz or 400 MHz for ^{1}H NMR, 100 MHz or 125 MHz for ^{13}C NMR). Tetramethylsilane (TMS) was used as internal standard. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), heptet (hept), multipet (m) and broad (br). Low- and high-resolution mass spectra (LRMS and HRMS) were recorded on a Finnigan/MAT-95 (EI), Finnigan LCQ/DECA and Micromass Ultra Q-TOF (ESI) spectrometer. LC-MS was performed on an Agilent 1200-6110 instrument. Melting points (m.p.) were measured by Büchi 510 melting point apparatus and were uncorrected.

Optimization of reaction conditions

Table S1 Screening of Oxidants.[a]



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

Entry	Oxidant	Time (h)	Yield[b] (%)
1	$Cu(OAc)_2$	20	11
2	$CuBr_2$	20	Trace
3	$CuCl_2$	20	Trace
4	$Cu(OTf)_2$	20	Trace
5	AgOAc	20	18
6	AgTFA	20	6
7	Ag_2CO_3	20	21
8	Ag_2SO_4	20	Trace
9	Ag_2O	20	13
10	$AgNO_3$	12	28
11[c]	$AgNO_3$	12	27
12	O_2	20	0
13	BQ	20	Trace

[a] **1a** (1.0 mmol, 1.0 equiv), **2a** (4.0 mmol, 4.0 equiv), DMA (3.0 mL), all of reagents were mixed and stirred at r.t. for 5 minutes, then the sealed tubes were screw capped and heated at 110

°C for indicated time. [b] Yield Determined by ^{1}H NMR analysis of the crude product using dimethyl terephthalate as an internal standard. [c] The reaction was carried out under N_2 atmosphere.

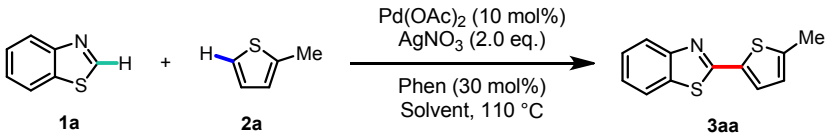
Table S2 Screening of Ligands.[a]

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

Entry	Ligand	Time (h)	Yield[b] (%)
1	–	12	28
2	AcOH	12	29
3	PivOH	10	36
4	Me-Gly-OH	5	18
5	$(Me)_2$-Gly-OH	5	17
6	Pro-OH	12	14
7	Boc-Me-Ala-OH	2	22
8	$PhCO_2H$	10	15
9	$p$$NO_2$-$PhCO_2H$	10	12
10	Bipy	10	45
11	Phen	10	50
12	Phen (15 mol%), Boc-Me-Ala-OH (15 mol%)	4	41
13	Phen (15 mol%), PivOH (15 mol%)	4	40

[a] **1a** (1.0 mmol, 1.0 equiv), **2a** (4.0 mmol, 4.0 equiv), DMA (3.0 mL), all of reagents were mixed and stirred at r.t. for 5 minutes, then the sealed tubes were screw capped and heated at 110 °C until **1a** disappeared. [b] Determined by ^{1}H NMR analysis of the crude product using dimethyl terephthalate as an internal standard.

Table S3 Screening of Solvents.[a]



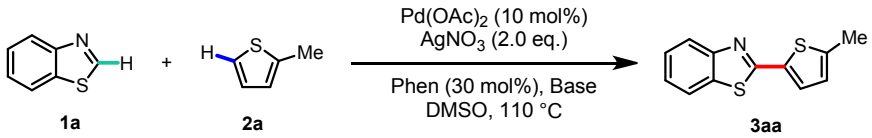
1a **2a** **3aa**

Entry	Solvent	Time (h)	Yield[b] (%)
1	DMA	10	50
2	DMF	10	31
3	NMP	10	27
4	DMSO	10	69(63)[c]
5	Dioxane	10	27
6	EtAc	10	8
7	DME	10	12
8	nBuOH	10	21

[a] **1a** (1.0 mmol, 1.0 equiv), **2a** (4.0 mmol, 4.0 equiv), solvent (3.0 mL), all of reagents were mixed and stirred at r.t. for 5 minutes, then the sealed tubes were screw capped and heated at 110 °C until **1a** disappeared. [b] Determined by ^{1}H NMR analysis of the crude product using dimethyl

terephthalate as an internal standard. [c] The isolated yield was given in parentheses.

Table S4 Screening of Bases.[a]

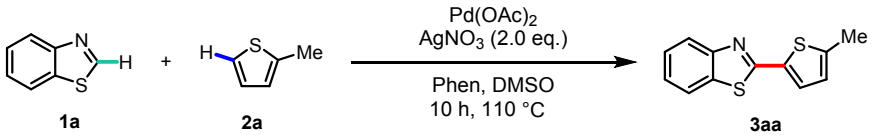


1a **2a** **3aa**

Entry	Base	Time (h)	Yield[b] (%)
1	–	10	69
2[c]	–	10	6
3	NaOAc	10	24
4	Na_2CO_3	10	32
5	K_2CO_3	10	33
6	KF	10	37
7	$Na_3PO_4·3H_2O$	10	15

[a] **1a** (1.0 mmol, 1.0 equiv), **2a** (4.0 mmol, 4.0 equiv), DMSO (3.0 mL), all of reagents were mixed and stirred at r.t. for 5 minutes, then the sealed tubes were screw capped and heated at 110 °C until **1a** disappeared. [b] Determined by ^{1}H NMR analysis of the crude product using dimethyl terephthalate as an internal standard. [c] TEMPO (30 mol%) was added.

Table S5 Screening of loadings of reagents.[a]

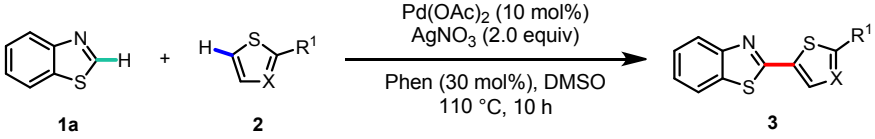


1a **2a** **3aa**

Entry	Reagent	Loading	Yield[b] (%)
1	$Pd(OAc)_2$	5 mol%	18
2	$Pd(OAc)_2$	2.5 mol%	trace
3	$Pd(OAc)_2$	0	0
4	Phen	1.0 equiv	42

[a] **1a** (1.0 mmol, 1.0 equiv), **2a** (4.0 mmol, 4.0 equiv), DMSO (3.0 mL), all of reagents were mixed and stirred at r.t. for 5 minutes, then the sealed tubes were screw capped and heated at 110 °C for 10 h. [b] Determined by ^{1}H NMR analysis of the crude product using dimethyl terephthalate as an internal standard.

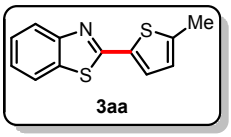
General procedure for cross-dehydrogenative coupling of benzothiazoles with thiophenes and thiazoles



1a **2** X = CH, N **3**

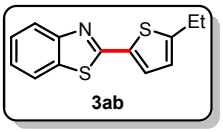
To a septum capped 25 mL of sealed tube were added $Pd(OAc)_2$ (10 mol%), $AgNO_3$ (2.0 equiv)

and 1,10-Phenanthroline hydrate (30 mol%) under air, followed by DMSO (3.0 mL) with stirring. Benzothiazoles **1** (1.0 mmol, 1.0 equiv) and thiophenes/thiazoles **2** (4.0 euqiv) were then added subsequently. The sealed tube was screw capped and heated to 110 °C. After being stirred for 10 h, the reaction mixture was cooled to room temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, washed with 80 mL of CH_2Cl_2. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (PE/EA) to provide the desired product.



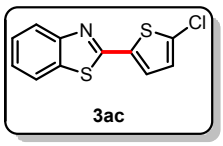
3aa

2-(5-Methylthiophen-2-yl)benzo[*d*]thiazole[1]**:** As a pale brown powder (PE:EA = 40:1 v:v); m.p. 95–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1 H), 7.83 (ddd, *J* = 8.0, 1.3, 0.6 Hz, 1 H), 7.48–7.42 (m, 2 H), 7.34 (ddd, *J* = 8.0, 7.3, 1.2 Hz, 1 H), 6.80 (dq, *J* = 3.4, 1.1 Hz, 1 H), 2.56 (d, *J* = 1.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.59, 153.66, 144.68, 134.79, 134.46, 128.84, 126.43, 126.27, 124.92, 122.70, 121.33, 15.67; HRMS (EI): *m*/*z* Calcd. For $C_{12}H_9NS_2$ $[M]^+$: 231.0176; Found: 231.0149.



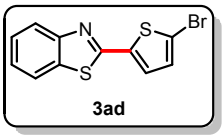
3ab

2-(5-Ethylthiophen-2-yl)benzo[*d*]thiazole: As brown oil which solidified at room temperature (PE:EA = 40:1 v:v); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1 H), 7.82 (ddd, *J* = 7.9, 1.3, 0.6 Hz, 1 H), 7.50–7.41 (m, 2 H), 7.34 (ddd, *J* = 7.9, 7.3, 1.2 Hz, 1 H), 6.82 (dt, *J* = 3.7, 1.0 Hz, 1 H), 2.91 (qd, *J* = 7.5, 0.8 Hz, 2 H), 1.36 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.69, 153.67, 152.37, 134.49, 134.40, 128.67, 126.27, 124.91, 124.62, 122.69, 121.34, 23.77, 15.69; HRMS (EI): *m*/*z* Calcd. For $C_{13}H_{11}NS_2$ $[M]^+$: 245.0333; Found: 245.0325.



3ac

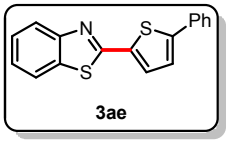
2-(5-Chlorothiophen-2-yl)benzo[*d*]thiazole[2]**:** As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 103–105 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1 H), 7.84 (ddd, *J* = 8.0, 1.2, 0.6 Hz, 1 H), 7.48 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 1 H), 7.43–7.32 (m, 2 H), 6.96 (d, *J* = 4.0 Hz, 1 H); ^{13}C NMR (100MHz, $CDCl_3$) δ 160.28, 153.41, 135.79, 134.43, 134.38, 127.62, 127.19, 126.52, 125.40, 122.96, 121.44; HRMS (EI): *m*/*z* Calcd. For $C_{11}H_6ClNS_2$ $[M]^+$: 250.9630; Found: 250.9621.



3ad

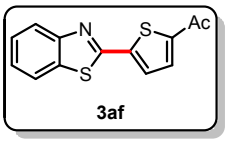
2-(5-Bromothiophen-2-yl)benzo[*d*]thiazole[3]**:** As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 110–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (ddd, *J* = 8.1, 1.3, 0.6 Hz, 1 H), 7.85 (ddd, *J* = 7.9, 1.4, 0.6 Hz, 1 H), 7.48

(ddd, J = 8.3, 7.2, 1.4 Hz, 1 H), 7.41–7.33 (m, 2 H), 7.10 (d, J = 4.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.15, 153.45, 138.66, 134.44, 130.88, 128.43, 126.53, 125.43, 122.99, 121.45, 117.10; HRMS (EI): *m*/*z* Calcd. For $C_{11}H_6BrNS_2$ $[M]^+$: 294.9125; Found: 294.9124.



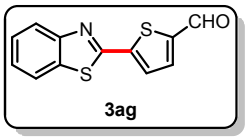
3ae

2-(5-Phenylthiophen-2-yl)benzo[*d*]thiazole[1]**:** As a yellow powder (PE:EA = 80:1 v:v); m.p. 156–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08–7.99 (m, 1 H), 7.90–7.80 (m, 1 H), 7.71–7.65 (m, 2 H), 7.62 (d, J = 3.9 Hz, 1 H), 7.52–7.32 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.28, 153.71, 148.19, 136.09, 134.66, 133.52, 129.55, 129.12, 128.49, 126.49, 125.97, 125.22, 123.92, 122.90, 121.47; HRMS (EI): *m*/*z* Calcd. For $C_{17}H_{11}NS_2$ $[M]^+$: 293.0333; Found: 293.0038.



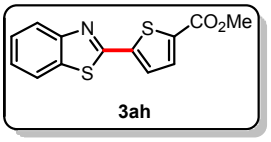
3af

1-(5-(Benzo[*d*]thiazol-2-yl)thiophen-2-yl)ethanone[4]**:** As a pale yellow powder (PE:EA = 30:1 v:v); m.p. 188–190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20–7.96 (m, 1 H), 7.93–7.86 (m, 1 H), 7.70 (d, J = 4.0 Hz, 1 H), 7.65 (d, J = 4.0 Hz, 1 H), 7.61–7.48 (m, 1 H), 7.50–7.36 (m, 1 H), 2.61 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.49, 160.05, 153.60, 146.01, 144.05, 135.12, 132.57, 128.47, 126.81, 125.97, 123.51, 121.62, 26.97; HRMS (EI): *m*/*z* Calcd. For $C_{13}H_9NOS_2$ $[M]^+$: 259.0126; Found: 259.0120.



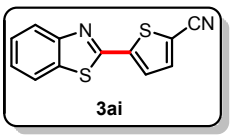
3ag

5-(Benzo[*d*]thiazol-2-yl)thiophene-2-carbaldehyde[4]**:** As a yellow powder (PE:EA = 10:1 v:v); m.p. 146–148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.96 (s, 1 H), 8.08 (ddd, J = 8.1, 1.2, 0.6 Hz, 1 H), 7.88 (ddd, J = 8.0, 1.2, 0.6 Hz, 1 H), 7.76 (d, J = 4.0 Hz, 1 H), 7.70 (d, J = 4.0 Hz, 1 H), 7.52 (ddd, J = 8.3, 7.2, 1.3 Hz, 1 H), 7.43 (ddd, J = 8.3, 7.2, 1.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.87, 159.65, 153.54, 145.48, 145.18, 136.19, 135.20, 128.41, 126.87, 126.13, 123.61, 121.61; HRMS (EI): *m*/*z* Calcd. For $C_{12}H_7NOS_2$ $[M]^+$: 244.9969; Found: 244.9961.



3ah

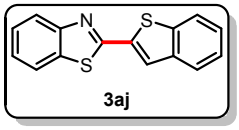
Methyl 5-(benzo[*d*]thiazol-2-yl)thiophene-2-carboxylate[5]**:** As a pale yellow powder (PE:EA = 20:1 v:v); m.p. 162–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (ddd, J = 8.2, 1.2, 0.6 Hz, 1 H), 7.88 (ddd, J = 8.0, 1.3, 0.6 Hz, 1 H), 7.79 (d, J = 4.0 Hz, 1 H), 7.61 (d, J = 4.0 Hz, 1 H), 7.51 (ddd, J = 8.2, 7.3, 1.3 Hz, 1 H), 7.41 (ddd, J = 8.3, 7.2, 1.2 Hz, 1 H), 3.93 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.18, 160.06, 153.52, 143.02, 135.72, 134.95, 133.75, 128.11, 126.69, 125.81, 123.38, 121.54, 52.46; HRMS (EI): *m*/*z* Calcd. For $C_{13}H_9NO_2S_2$ $[M]^+$: 275.0075; Found: 275.0066.



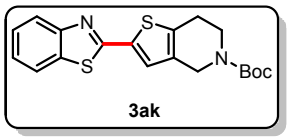
3ai

5-(Benzo[*d*]thiazol-2-yl)thiophene-2-carbonitrile[1]**:** As a pale yellow

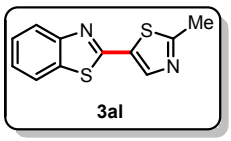
powder (PE:EA = 30:1 v:v); m.p. 176–178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (ddd, *J* = 8.2, 1.3, 0.6 Hz, 1 H), 7.90 (ddd, *J* = 7.9, 1.4, 0.7 Hz, 1 H), 7.63 (d, *J* = 4.0 Hz, 1 H), 7.59 (d, *J* = 4.0 Hz, 1 H), 7.54 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1 H), 7.45 (ddd, *J* = 7.9, 7.2, 1.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.64, 153.33, 143.79, 137.86, 134.96, 127.44, 126.99, 126.29, 123.59, 121.66, 113.67, 112.01; HRMS (EI): *m*/*z* Calcd. For $C_{12}H_6N_2S_2$ $[M]^+$: 241.9972; Found: 242.0001.



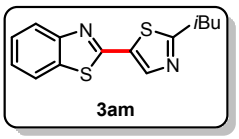
2-(Benzo[*b*]thiophen-2-yl)benzo[*d*]thiazole[6]: As a pale yellow powder (PE:EA = 100:1 v:v); m.p. 193–195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1 H), 7.95–7.73 (m, 4 H), 7.50 (td, *J* = 8.3, 7.7, 1.3 Hz, 1 H), 7.45–7.33 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.48, 153.68, 140.82, 139.53, 137.14, 135.01, 126.58, 126.17, 125.63, 125.33, 125.00, 124.59, 123.34, 122.62, 121.54; HRMS (EI): *m*/*z* Calcd. For $C_{15}H_9NS_2$ $[M]^+$: 267.0176; Found: 267.0169.



Tert-butyl 2-(benzo[*d*]thiazol-2-yl)-6,7-dihydrothieno[3,2-*c*]pyridine-5(4*H*)-carboxylate: As yellow oil which solidified at room temperature (PE:EA = 10:1 v:v); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1 H), 7.83 (ddd, *J* = 8.0, 1.3, 0.6 Hz, 1 H), 7.46 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1 H), 7.39–7.31 (m, 2 H), 4.52 (brs, 2 H), 3.76 (t, *J* = 5.5 Hz, 2 H), 2.90 (t, *J* = 5.5 Hz, 2 H), 1.50 (s, 9 H); **conformational isomer 1:** ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.26, 154.74, 153.62, 138.42, 134.76, 134.57, 133.38, 126.39, 125.13, 122.79, 121.41, 80.23, 44.12, 40.58, 28.47, 25.43; **conformational isomer 2:** ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.26, 154.74, 153.62, 137.95, 134.76, 134.57, 133.75, 126.39, 125.13, 122.79, 121.41, 80.23, 43.44, 41.80, 28.47, 25.31; HRMS (EI): *m*/*z* Calcd. For $C_{19}H_{20}N_2O_2S_2$ $[M]^+$: 372.0966; Found: 372.0965.

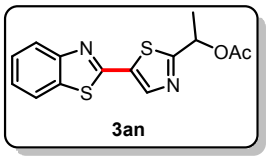


2-(2-Methylthiazol-5-yl)benzo[*d*]thiazole[7]: As a pale yellow powder (PE:EA = 20:1 v:v); m.p. 123–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1 H), 8.02 (ddd, *J* = 8.0, 1.2, 0.6 Hz, 1 H), 7.87 (ddd, *J* = 7.9, 1.3, 0.7 Hz, 1 H), 7.49 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1 H), 7.40 (ddd, *J* = 7.9, 7.2, 1.2 Hz, 1 H), 2.79 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.25, 158.37, 153.35, 142.78, 134.39, 132.60, 126.55, 125.59, 123.01, 121.49, 19.59; HRMS (EI): *m*/*z* Calcd. For $C_{11}H_8N_2S_2$ $[M]^+$: 232.0129; Found: 232.0121.



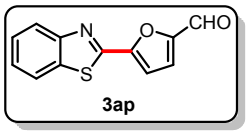
2-(2-Isobutylthiazol-5-yl)benzo[*d*]thiazole: As colorless oil which solidified at room temperature (PE:EA = 20:1 v:v); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 1 H), 8.02 (ddd, *J* = 8.2, 1.3, 0.7 Hz, 1 H), 7.86 (ddd, *J* =

7.9, 1.3, 0.6 Hz, 1 H), 7.48 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1 H), 7.39 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1 H), 2.93 (d, *J* = 7.2 Hz, 2 H), 2.17 (hept, *J* = 6.8 Hz, 1 H), 1.03 (d, *J* = 6.7 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.05, 169.31, 157.61, 152.92, 142.38, 134.12, 132.88, 126.26, 125.39, 122.74, 121.16, 69.39, 20.61, 20.34; HRMS (EI): *m*/*z* Calcd. For $C_{14}H_{14}N_2S_2$ $[M]^+$: 274.0598; Found: 274.0604.



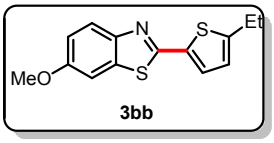
3an

1-(5-(Benzo[*d*]thiazol-2-yl)thiazol-2-yl)ethyl acetate: As a pale yellow powder (PE:EA = 8:1 v:v); m.p. 108–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1 H), 8.03 (ddd, *J* = 8.2, 1.2, 0.6 Hz, 1 H), 7.87 (ddd, *J* = 8.0, 1.3, 0.7 Hz, 1 H), 7.50 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1 H), 7.45 – 7.35 (m, 1 H), 6.18 (q, *J* = 6.6 Hz, 1 H), 2.18 (s, 3 H), 1.73 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.24, 158.10, 152.97, 142.35, 134.00, 131.82, 126.14, 125.17, 122.60, 121.10, 42.22, 29.44, 21.85; HRMS (EI): *m*/*z* Calcd. For $C_{14}H_{12}N_2O_2S_2$ $[M]^+$: 304.0340; Found: 304.0342.



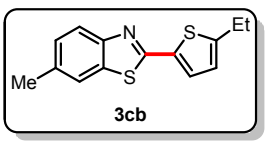
3ap

5-(Benzo[*d*]thiazol-2-yl)furan-2-carbaldehyde[8]: As a brown powder (PE:EA = 30:1 v:v); m.p. 180–182 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (s, 1 H), 8.10 (ddd, *J* = 8.2, 1.3, 0.7 Hz, 1 H), 7.95 (ddd, *J* = 8.0, 1.3, 0.7 Hz, 1 H), 7.54 (dd, *J* = 8.2, 1.4 Hz, 1 H), 7.46 (dd, *J* = 8.0, 1.3 Hz, 1 H), 7.39 (d, *J* = 3.8 Hz, 1 H), 7.35 (d, *J* = 3.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.87, 155.84, 153.63, 153.15, 152.78, 134.88, 126.92, 126.20, 123.69, 121.83, 121.60, 112.53; HRMS (EI): *m*/*z* Calcd. For $C_{12}H_7NO_2S$ $[M]^+$: 229.0197; Found: 229.0193.



3bb

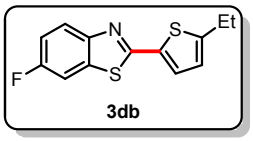
2-(5-Ethylthiophen-2-yl)-6-methoxybenzo[*d*]thiazole: As a brown powder (PE:EA = 20:1 v:v); m.p. 74–76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 1 H), 7.41 (d, *J* = 3.7 Hz, 1 H), 7.29 (d, *J* = 2.5 Hz, 1 H), 7.05 (dd, *J* = 8.9, 2.5 Hz, 1 H), 6.80 (dt, *J* = 3.7, 1.0 Hz, 1 H), 3.88 (s, 3 H), 2.90 (qd, *J* = 7.5, 1.0 Hz, 2 H), 1.36 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.33, 157.55, 151.64, 148.15, 135.85, 134.55, 127.93, 124.47, 123.18, 115.30, 104.15, 55.75, 23.73, 15.70; HRMS (EI): *m*/*z* Calcd. For $C_{14}H_{13}NOS_2$ $[M]^+$: 275.0439; Found: 275.0445.



3cb

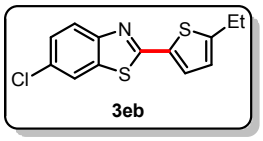
2-(5-Ethylthiophen-2-yl)-6-methylbenzo[*d*]thiazole: As brown oil which solidified at room temperature (PE:EA = 40:1 v:v); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 1 H), 7.61 (dd, *J* = 1.8, 1.0 Hz, 1 H), 7.45 (d, *J* = 3.7 Hz, 1 H), 7.26 (dd, *J* = 8.2, 1.9 Hz, 1 H), 6.81 (dt, *J* = 3.7, 1.0 Hz, 1 H), 2.90

(qd, J = 7.6, 1.0 Hz, 2 H), 2.47 (s, 3 H), 1.36 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.69, 151.99, 151.75, 135.06, 134.64, 134.56, 128.28, 127.80, 124.52, 122.19, 121.13, 23.75, 21.50, 15.71; HRMS (EI): *m*/*z* Calcd. For $C_{14}H_{13}NS_2$ $[M]^+$: 259.0489; Found: 259.0486.



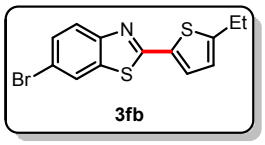
3db

2-(5-Ethylthiophen-2-yl)-6-fluorobenzo[*d*]thiazole: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 102–103 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 9.0, 4.8 Hz, 1 H), 7.51 (dd, J = 8.1, 2.6 Hz, 1 H), 7.45 (d, J = 3.7 Hz, 1 H), 7.18 (td, J = 9.0, 2.6 Hz, 1 H), 6.82 (dt, J = 3.7, 1.0 Hz, 1 H), 2.91 (qd, J = 7.5, 1.0 Hz, 2 H), 1.36 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.39 (d, J = 3.4 Hz, C–CH–CH–CF), 160.26 (d, J = 246.0 Hz, C–F), 152.48, 150.27, 135.46 (d, J = 10.8 Hz, C–CH–CF), 134.04, 128.69, 124.64, 123.50 (d, J = 9.4 Hz, CH–CH–CF), 114.76 (d, J = 24.7 Hz, CH–CF), 107.66 (d, J = 26.8 Hz, CH–CF), 23.75, 15.67; HRMS (EI): *m*/*z* Calcd. For $C_{13}H_{10}FNS_2$ $[M]^+$: 263.0239; Found: 263.0241.



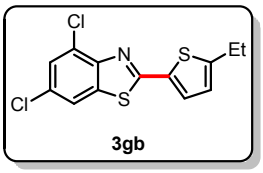
3eb

6-Chloro-2-(5-ethylthiophen-2-yl)benzo[*d*]thiazole: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 138–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 8.7 Hz, 1 H), 7.79 (d, J = 2.1 Hz, 1 H), 7.47 (d, J = 3.7 Hz, 1 H), 7.40 (dd, J = 8.7, 2.1 Hz, 1 H), 6.83 (dt, J = 3.7, 1.0 Hz, 1 H), 2.91 (qd, J = 7.5, 1.0 Hz, 2 H), 1.36 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.10, 152.88, 152.24, 135.66, 133.91, 130.62, 128.99, 127.02, 124.72, 123.32, 120.93, 23.78, 15.65; HRMS (EI): *m*/*z* Calcd. For $C_{13}H_{10}ClNS_2$ $[M]^+$: 278.9943; Found: 278.9925.



3fb

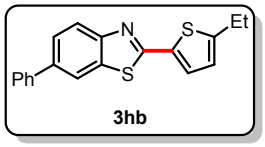
6-Bromo-2-(5-ethylthiophen-2-yl)benzo[*d*]thiazole: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 136–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 1.9 Hz, 1 H), 7.83 (d, J = 8.7 Hz, 1 H), 7.54 (dd, J = 8.7, 2.0 Hz, 1 H), 7.48 (d, J = 3.7 Hz, 1 H), 6.83 (dt, J = 3.8, 1.0 Hz, 1 H), 2.91 (qd, J = 7.5, 0.9 Hz, 2 H), 1.36 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.12, 152.99, 152.58, 136.12, 133.86, 129.75, 129.05, 124.75, 123.85, 123.71, 118.24, 23.79, 15.66; HRMS (EI): *m*/*z* Calcd. For $C_{13}H_{10}BrNS_2$ $[M]^+$: 322.9438; Found: 322.9440.



3gb

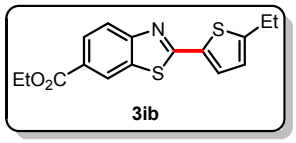
4,6-Dichloro-2-(5-ethylthiophen-2-yl)benzo[*d*]thiazole: As a brown powder (PE:EA = 40:1 v:v); m.p. 103–105 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 2.0 Hz, 1 H), 7.50 (d, J = 3.8 Hz, 1 H), 7.47 (d, J = 2.0 Hz, 1 H), 6.83 (dt, J = 3.7, 1.0 Hz, 1 H), 2.91 (qd, J = 7.7,

1.1 Hz, 2 H), 1.36 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.66, 153.67, 149.54, 136.56, 133.55, 130.42, 129.51, 127.80, 126.97, 124.82, 119.53, 23.82, 15.64; HRMS (EI): *m*/*z* Calcd. For $C_{13}H_9Cl_2NS_2$ $[M]^+$: 312.9553; Found: 312.9555.



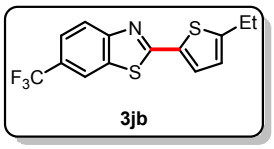
3hb

2-(5-Ethylthiophen-2-yl)-6-phenylbenzo[*d*]thiazole: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 126–128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10–8.01 (m, 2 H), 7.75–7.62 (m, 3 H), 7.54–7.44 (m, 3 H), 7.39 (t, *J* = 7.3 Hz, 1 H), 6.85 (dt, *J* = 3.7, 1.0 Hz, 1 H), 2.94 (dt, *J* = 7.4, 1.1 Hz, 2 H), 1.39 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.84, 153.02, 152.49, 140.54, 138.33, 135.29, 134.43, 128.86, 128.70, 127.42, 127.28, 125.94, 124.66, 122.73, 119.60, 23.79, 15.70; HRMS (EI): *m*/*z* Calcd. For $C_{19}H_{15}NS_2$ $[M]^+$: 321.0646; Found: 321.0645.



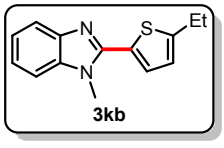
3ib

Ethyl 2-(5-ethylthiophen-2-yl)benzo[*d*]thiazole-6-carboxylate: As a pale yellow powder (PE:EA = 20:1 v:v); m.p. 122–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 1.7, 0.6 Hz, 1 H), 8.13 (dd, *J* = 8.6, 1.7 Hz, 1 H), 7.99 (dd, *J* = 8.6, 0.6 Hz, 1 H), 7.54 (d, *J* = 3.8 Hz, 1 H), 6.85 (dt, *J* = 3.7, 1.0 Hz, 1 H), 4.42 (q, *J* = 7.1 Hz, 2 H), 2.92 (qd, *J* = 7.4, 0.8 Hz, 2 H), 1.43 (t, *J* = 7.1 Hz, 3 H), 1.37 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.08, 164.85, 156.64, 153.54, 134.39, 133.97, 129.59, 127.59, 126.88, 124.89, 123.43, 122.17, 61.19, 23.81, 15.63, 14.34; HRMS (EI): *m*/*z* Calcd. For $C_{16}H_{15}NO_2S_2$ $[M]^+$: 317.0544; Found: 317.0546.



3jb

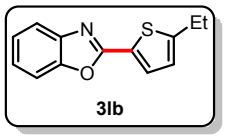
2-(5-Ethylthiophen-2-yl)-6-(trifluoromethyl)benzo[*d*]thiazole: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 139–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13–8.09 (m, 1 H), 8.05 (dd, *J* = 8.8, 1.0 Hz, 1 H), 7.71–7.65 (m, 1 H), 7.54 (d, *J* = 3.7 Hz, 1 H), 6.86 (dt, *J* = 3.8, 0.9 Hz, 1 H), 2.92 (qd, *J* = 7.6, 0.9 Hz, 2 H), 1.37 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.53 , 155.69 , 153.67 , 134.56 , 133.69 , 129.69 , 126.87 (q, *J* = 32.4 Hz, C–CF_3), 123.90 (q, *J* = 272.2 Hz, C–F_3) , 124.90 , 123.31 (q, *J* = 3.5 Hz, CH–C–CF_3), 122.80 , 118.95 (q, *J* = 4.2 Hz, CH–C–CF_3), 23.80, 15.61; HRMS (EI): *m*/*z* Calcd. For $C_{14}H_{10}F_3NS_2$: $[M]^+$: 313.0207; Found: 313.0201.



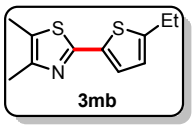
3kb

2-(5-Eethylthiophen-2-yl)-1-methyl-1*H*-benzo[*d*]imidazole: As brown oil which solidified at room temperature (PE:EA = 8:1 v:v); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81–7.75 (m, 1 H), 7.39 (d, *J* = 3.7 Hz, 1 H), 7.37–7.32 (m, 1 H), 7.32–7.26 (m, 2 H), 6.88 (dt, *J* = 3.7, 0.8 Hz, 1 H), 3.98 (s, 3 H), 2.92 (qd, *J* = 7.5, 0.8 Hz, 2

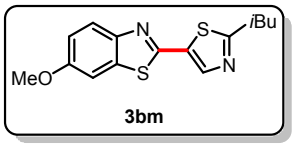
H), 1.37 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.17, 148.17, 142.85, 136.51, 129.69, 127.78, 124.29, 122.59, 122.42, 119.53, 109.19, 31.58, 23.50, 15.80; HRMS (EI): *m*/*z* Calcd. For $C_{14}H_{14}N_2S$: $[M]^+$: 242.0878; Found: 242.0885.



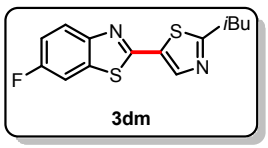
2-(5-Ethylthiophen-2-yl)benzo[*d*]oxazole: As brown oil which solidified at room temperature (PE:EA = 30:1 v:v); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J* = 3.7 Hz, 1 H), 7.72–7.68 (m, 1 H), 7.55–7.49 (m, 1 H), 7.34–7.29 (m, 2 H), 6.88 (d, *J* = 3.7 Hz, 1 H), 2.93 (q, *J* = 7.4 Hz, 2 H), 1.37 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.20, 153.43, 150.34, 142.08, 130.06, 126.61, 124.87, 124.71, 124.54, 119.56, 110.25, 23.71, 15.66; HRMS (EI): *m*/*z* Calcd. For $C_{13}H_{11}NS$: $[M]^+$: 229.0561; Found: 229.0558.



2-(5-Ethylthiophen-2-yl)-4,5-dimethylthiazole: As brown oil which solidified at room temperature (PE:EA = 40:1 v:v); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 3.6 Hz, 1 H), 6.71 (dt, *J* = 3.6, 1.0 Hz, 1 H), 2.84 (qd, *J* = 7.5, 1.1 Hz, 2 H), 2.34 (s, 3 H), 2.32 (s, 3 H), 1.31 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.53, 149.36, 148.51, 134.96, 125.40, 125.06, 124.09, 23.60, 15.77, 14.69, 11.37. HRMS (EI): *m*/*z* Calcd. For $C_{11}H_{13}NS_2$: $[M]^+$: 223.0489; Found: 223.0480.

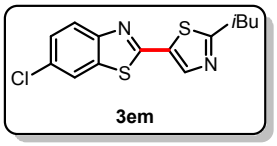


2-(2-Isobutylthiazol-5-yl)-6-methoxybenzo[*d*]thiazole: As pale yellow oil which solidified at room temperature (PE:EA = 15:1 v:v); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (s, 1 H), 7.89 (d, *J* = 8.9 Hz, 1 H), 7.31 (d, *J* = 2.5 Hz, 1 H), 7.07 (dd, *J* = 9.0, 2.5 Hz, 1 H), 3.88 (s, 3 H), 2.92 (d, *J* = 7.2 Hz, 2 H), 2.16 (hept, *J* = 13.5, 6.8 Hz, 1 H), 1.03 (dd, *J* = 6.6, 0.7 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.01, 158.01, 155.97, 147.90, 142.06, 135.88, 132.35, 123.50, 115.79, 104.03, 55.77, 42.60, 29.83, 22.25; HRMS (EI): *m*/*z* Calcd. For $C_{15}H_{16}N_2OS_2$: $[M]^+$: 304.0704; Found: 304.0701.



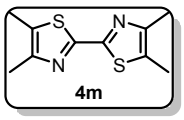
6-Fluoro-2-(2-isobutylthiazol-5-yl)benzo[*d*]thiazole: As a pale yellow powder (PE:EA = 20:1 v:v); m.p. 68–69 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1 H), 7.96 (dd, *J* = 9.0, 4.8 Hz, 1 H), 7.55 (dd, *J* = 8.0, 2.6 Hz, 1 H), 7.22 (td, *J* = 9.0, 2.6 Hz, 1 H), 2.93 (d, *J* = 7.2 Hz, 2 H), 2.17 (hept, *J* = 13.6, 6.8 Hz, 1 H), 1.03 (d, *J* = 6.6 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.73, 160.59 (d, *J* = 246.7 Hz), 158.22 (d, *J* = 3.6 Hz), 150.02, 142.78, 135.45 (d, *J* = 11.3 Hz), 131.88, 123.91 (d, *J* = 9.3 Hz), 115.19 (d, *J* = 24.7 Hz), 107.81 (d, *J* = 27.0 Hz), 42.62, 29.83, 22.24; HRMS (EI): *m*/*z* Calcd. For

$C_{14}H_{13}FN_2S_2$: $[M]^+$: 292.0504; Found: 292.0508.



3em

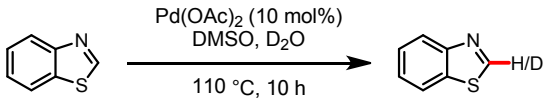
6-Chloro-2-(2-isobutylthiazol-5-yl)benzo[*d*]thiazole: As a pale yellow powder (PE:EA = 20:1 v:v); m.p. 90–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1 H), 7.92 (dd, *J* = 8.7, 0.5 Hz, 1 H), 7.84 (dd, *J* = 2.1, 0.5 Hz, 1 H), 7.45 (dd, *J* = 8.7, 2.1 Hz, 1 H), 2.94 (d, *J* = 7.2 Hz, 2 H), 2.17 (hept, *J* = 13.6, 6.7 Hz, 1 H), 1.04 (d, *J* = 6.6 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.00, 158.91, 151.92, 143.04, 135.57, 131.78, 131.41, 127.35, 123.65, 121.09, 42.63, 29.83, 22.25; HRMS (EI): *m*/*z* Calcd. For $C_{14}H_{13}ClN_2S_2$: $[M]^+$: 308.0209; Found: 308.0204.



4m

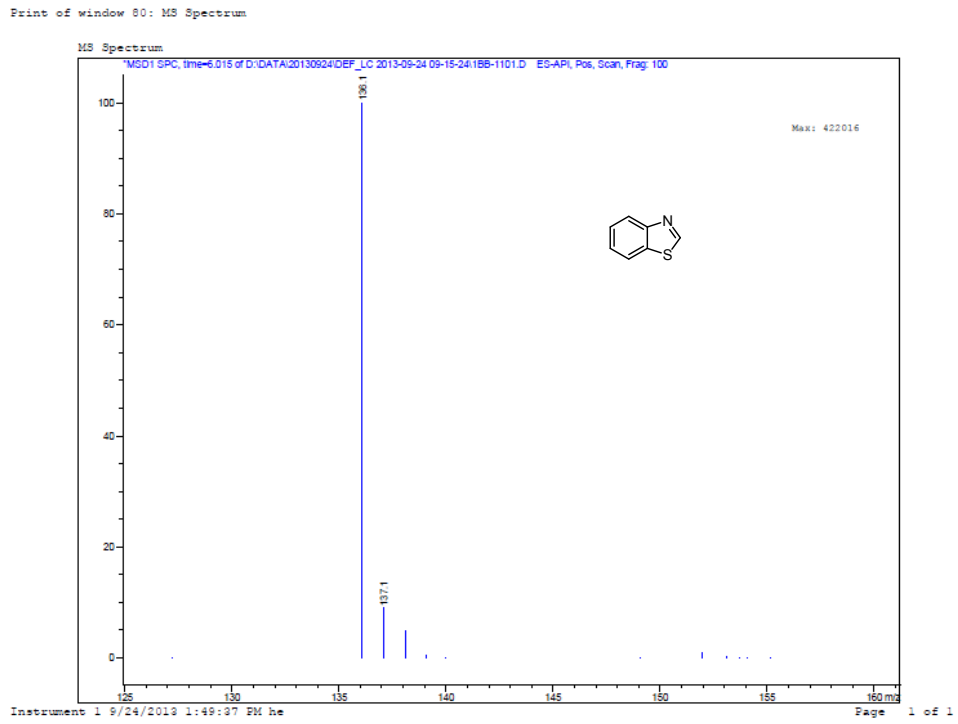
4,4',5,5'-Tetramethyl-2,2'-bithiazole[9]: As a pale yellow powder (PE:EA = 40:1 v:v); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (q, *J* = 0.8 Hz, 6 H), 2.36 (q, *J* = 0.7 Hz, 6 H); LRMS (ESI): m/z 225 $[M+H]^+$.

The H/D exchange experiment for 1a

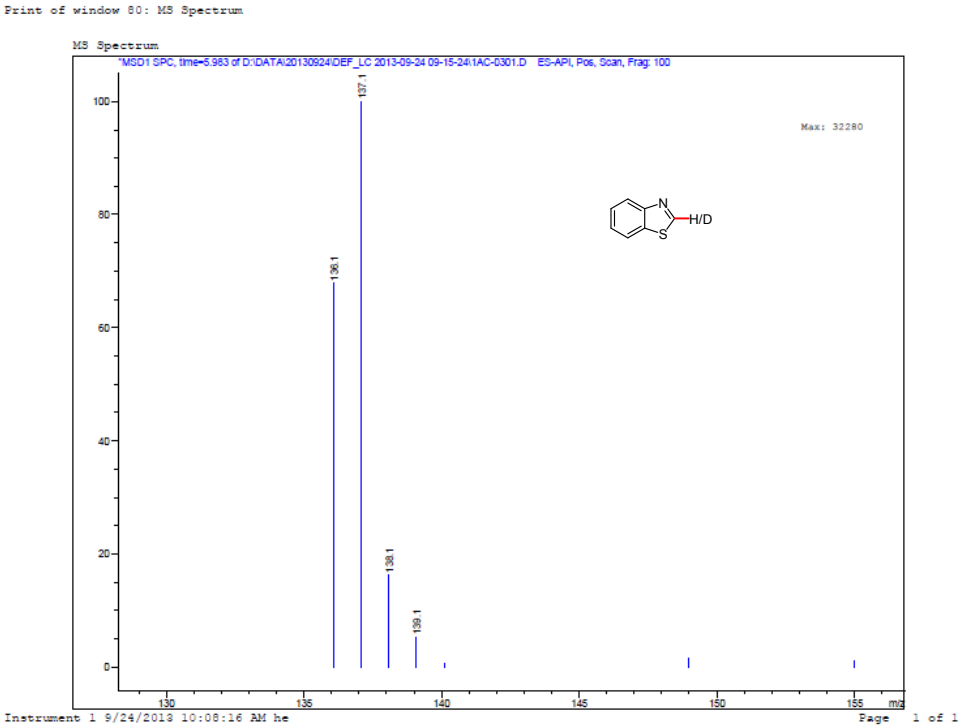


1a **1a/1a-[D$_1$]** = 2:3

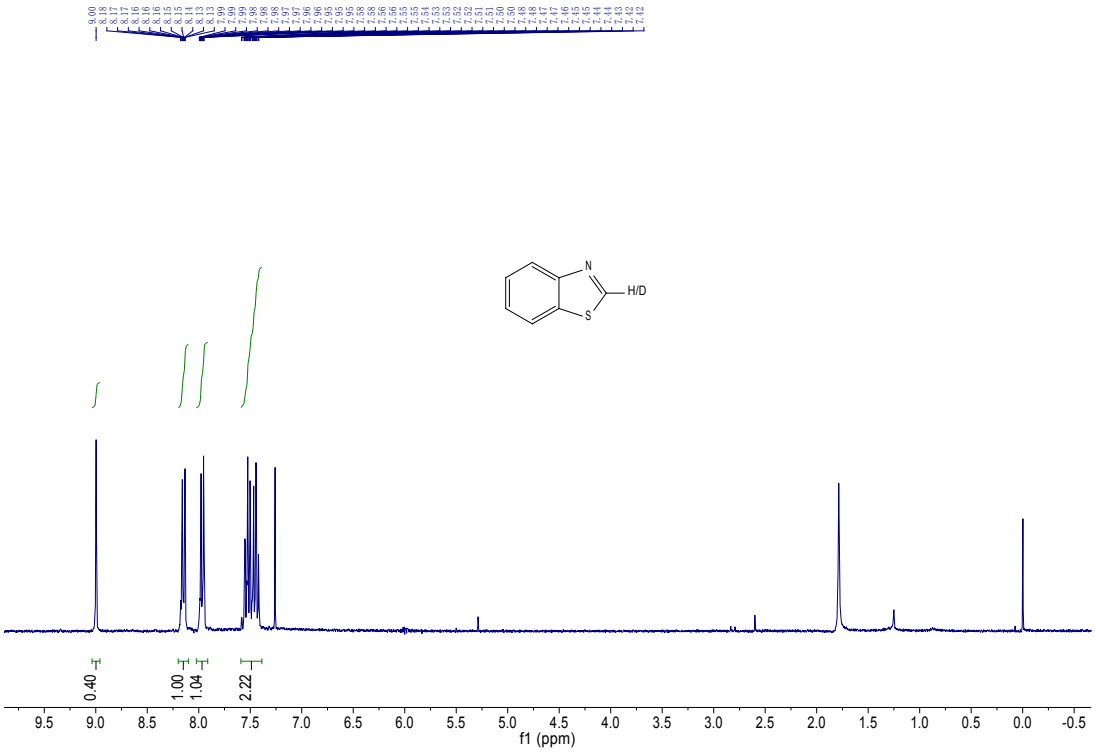
To a solution of **1a** (1.0 mmol, 1.0 equiv) in DMSO (2.0 mL), $Pd(OAc)_2$ (10 mol%) and D_2O (1.0 mL) was added, and the mixture was heated at 110 °C for 10 h. After cooling, the reaction solution was washed with saturated brine and extracted with ethyl acetate three times. The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product. **1a-[D$_1$]** was detected by LC-MS, and the ratio of **1a** and **1a-[D$_1$]** was determined by ^{1}H NMR analysis of the crude product.



Copy of low-resolution mass spectrum (ESI) of **1a**

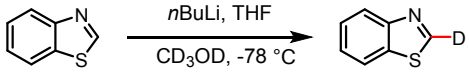


Copy of low-resolution mass spectrum (ESI) of the crude product



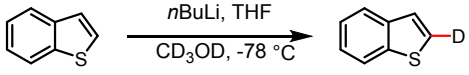
H^1 NMR spectrum of the crude product

Kinetic isotope experiments



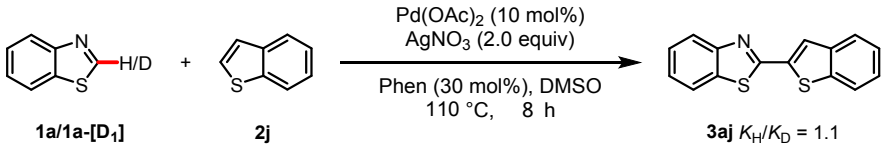
1a **1a-[D_1]**

Preparation of 2-deutero-benzothiazole (1a-[D_1])[10]: A stirred solution of benzothiazole **1a** (10 mmol) in dry THF (10 mL) under nitrogen was cooled to –78 °C and 12 mmol *n*BuLi in hexane was added dropwise. 2-Lithiobenzothiazole was immediately formed. This orange-colored anion solution was quickly quenched at –78 °C with CD_3OD (1.0 mL) after the addition of *n*BuLi. The suspension was extracted with water and ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuum. After purification by column chromatography on silica gel with petroleum ether /ethyl acetate (PE:EA = 20:1 v:v), the desired products were obtained in 95% yield as pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (ddd, *J* = 7.9, 1.3, 0.7 Hz, 1 H), 7.97 (ddd, *J* = 7.9, 1.4, 0.7 Hz, 1 H), 7.57–7.49 (m, 1 H), 7.48–7.41 (m, 1 H); MS (ESI): m/z 137 $[M+H]^+$.

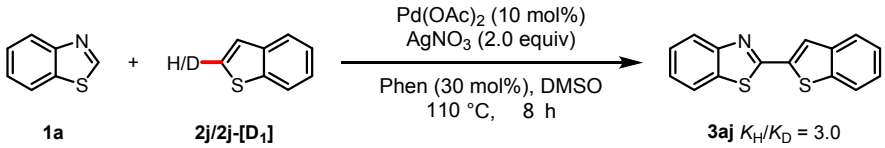


2j **2j-[D_1]**

Preparation of 2-deutero-benzothiophene (2j-[D_1])[11]**:** A stirred solution of benzothiophene **2j** (10 mmol) in dry THF (10 mL) under nitrogen was cooled to –78 °C and 12 mmol *n*BuLi in hexane was added dropwise. CD_3OD (1.0 mL) was added to the reaction system after reacting for 1 h. The suspension was extracted with water extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuum. After purification by column chromatography on silica gel with petroleum ether /ethyl acetate (PE:EA = 20:1 v:v), the desired products were obtained in 97% yield as colorless oil which solidified at room temperature; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92–7.79 (m, 2 H), 7.41–7.30 (m, 3 H); MS (EI): m/z 135 $[M]^+$.



Two sets of reactions were carried out in a parallel manner. In each case benzothiophene **2j** (4.0 mmol) was allowed to react with benzothiazole **1a** (1.0 mmol) and 2-deuterio-benzothiazole **1a-[D_1]** (1.0 mmol), respectively. The sealed tubes were screw capped and heated to 110 °C. After being stirred for 8 h, the reaction mixture was cooled to room temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, washed with 80 mL of CH_2Cl_2. The combined organic extracts were concentrated. The yield of **3aj** was determined by LC-MS.



Two sets of reactions were carried out in a parallel manner. In each case benzothiazole **1a** (4.0 mmol) was allowed to react with benzothiophene **2j** (1.0 mmol) and 2-deuterio-benzothiophene **2j-[D_1]** (1.0 mmol), respectively. The sealed tubes were screw capped and heated to 110 °C. After being stirred for 8 h, the reaction mixture was cooled to room temperature, diluted with 20 mL of CH_2Cl_2, filtered through a celite pad, washed with 80 mL of CH_2Cl_2. The combined organic extracts were concentrated. The yield of **3aj** was determined by LC-MS.

References

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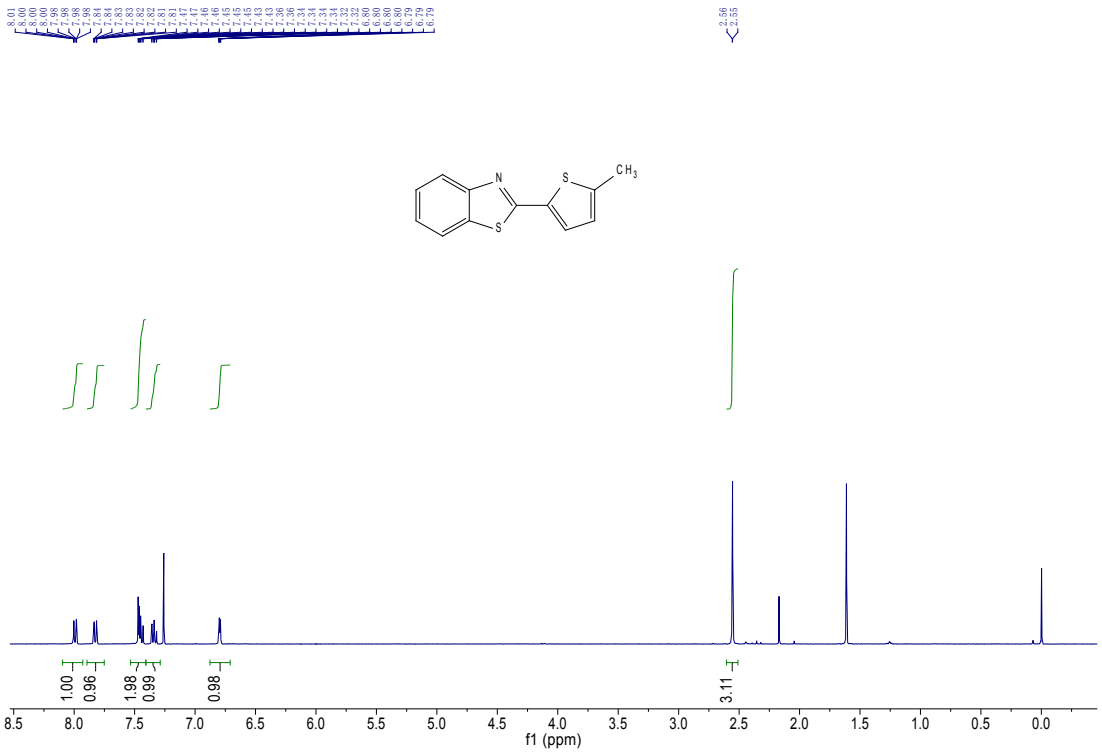
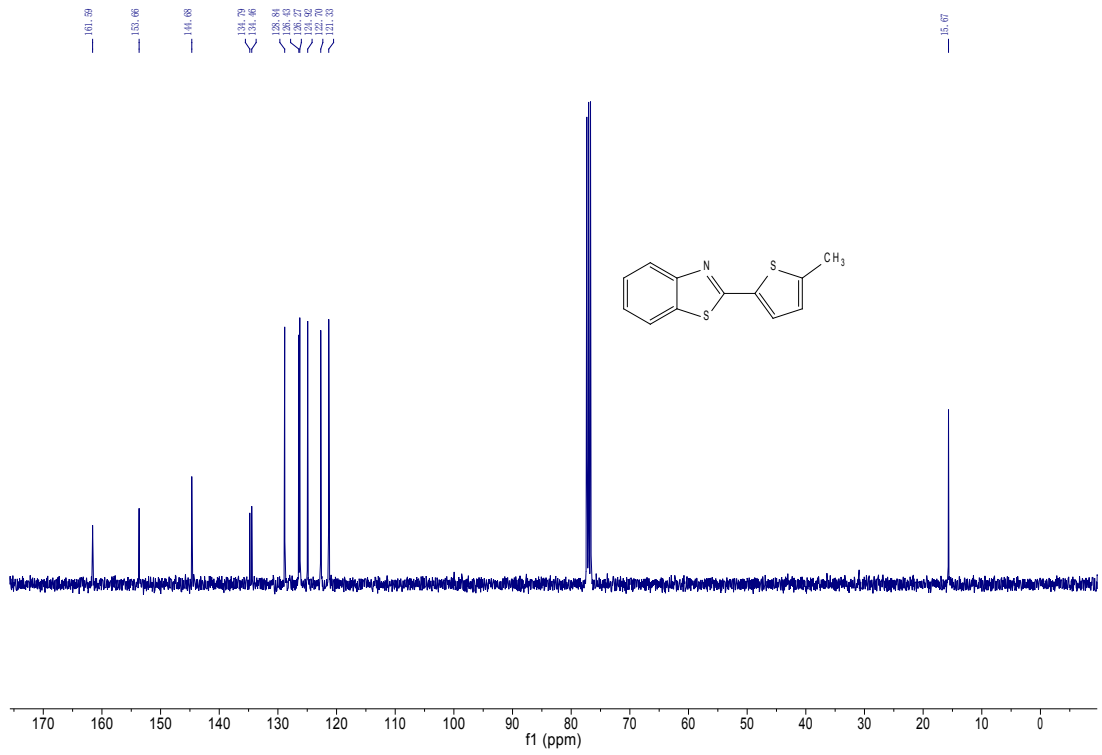
^{1}H NMR, ^{13}C NMR and HSQC spectra

3aa





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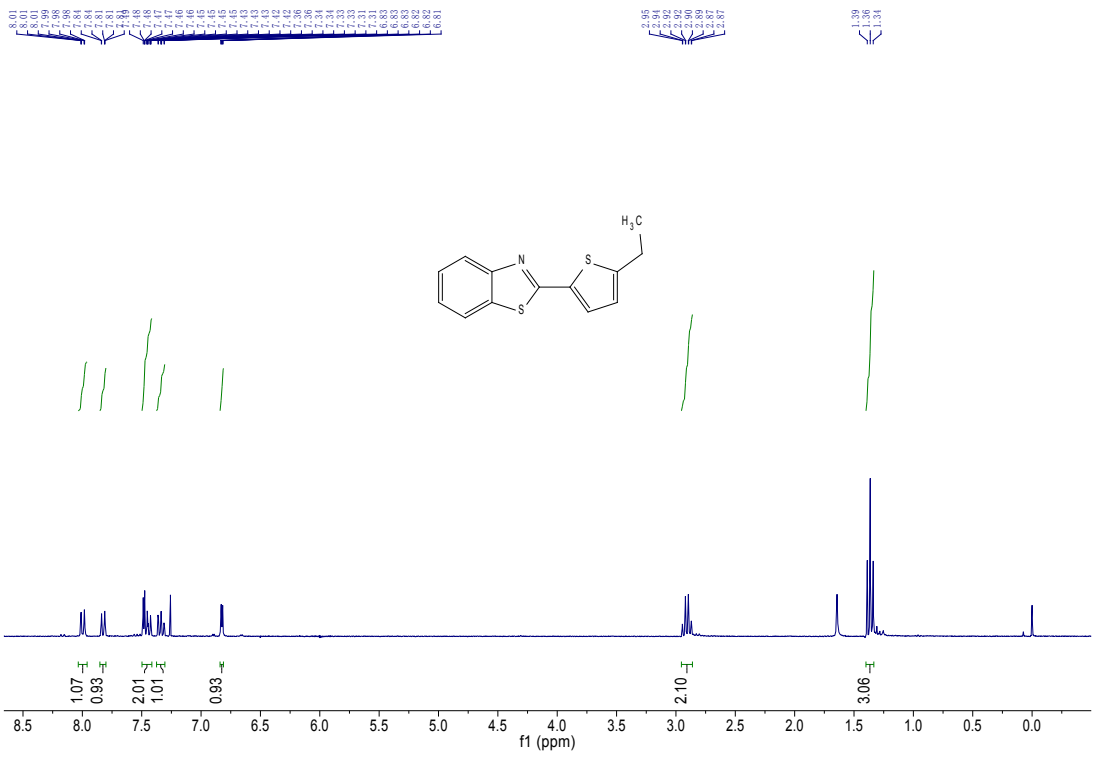
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2.92
2.90
2.89
2.87
2.87
1.39
1.36
1.34
H3C
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S
S
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1.01
0.93
2.10
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6.0
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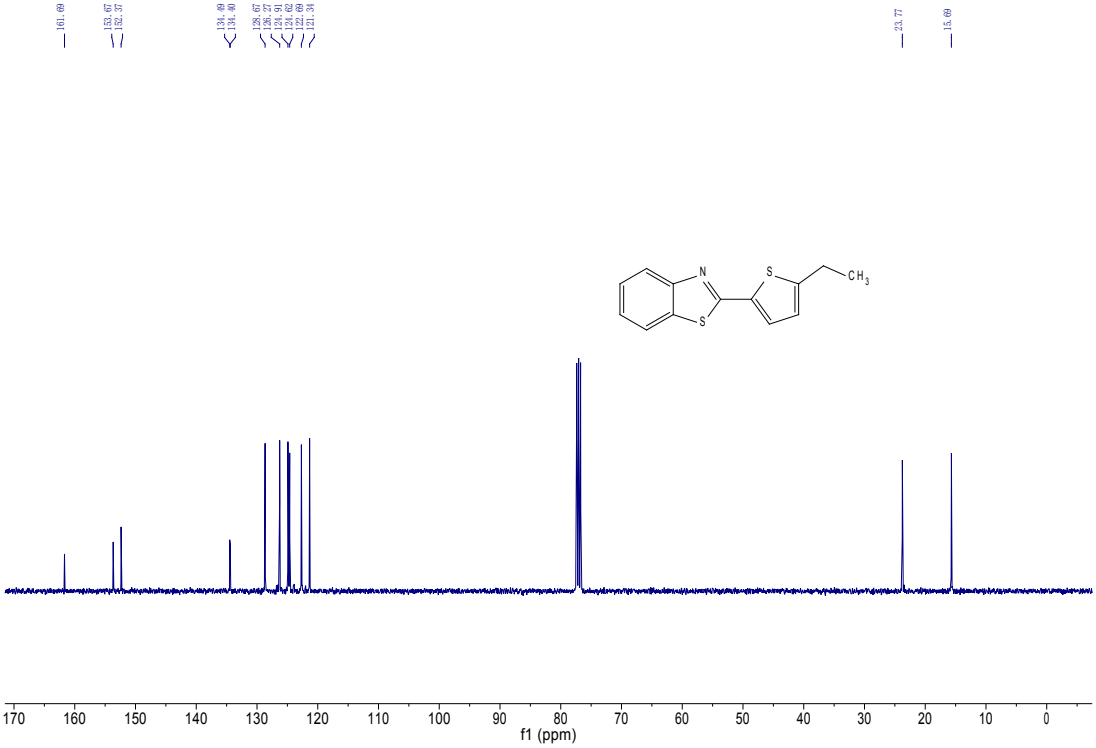
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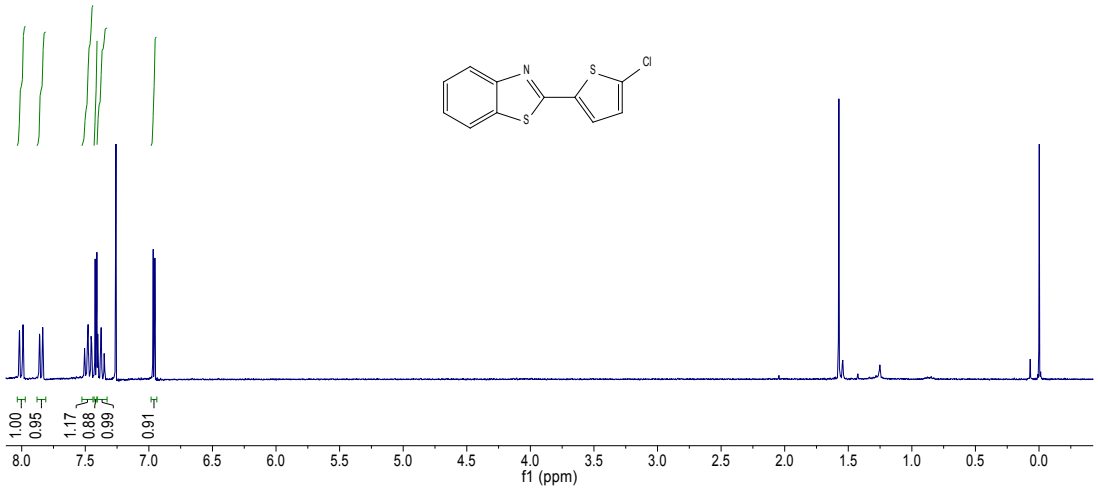
f1 (ppm)

3ac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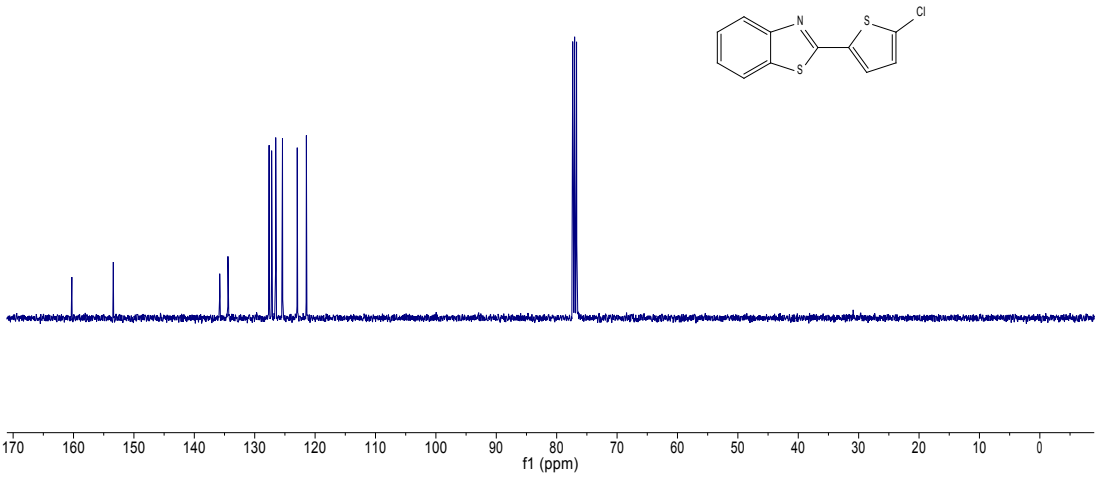
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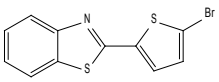
0
f1 (ppm)

3ad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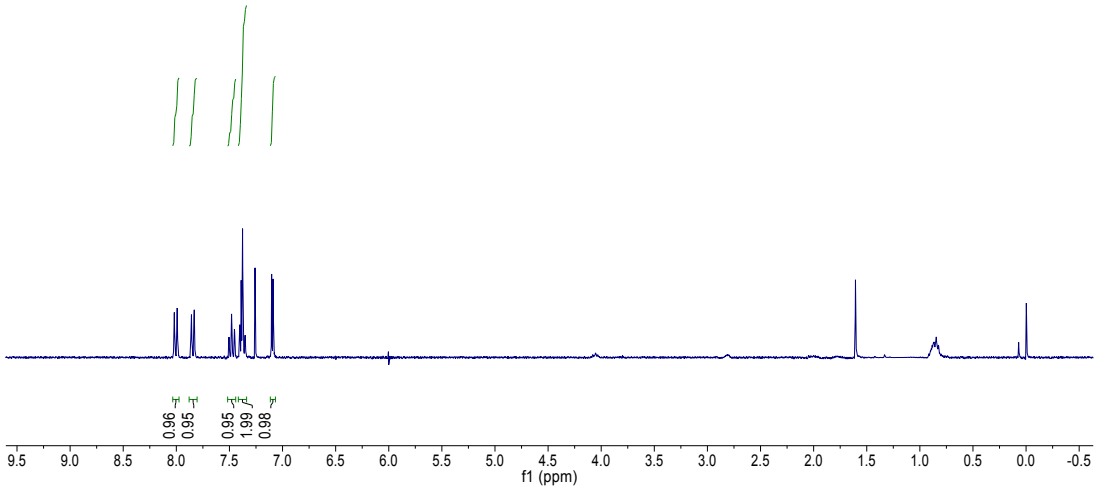
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f1 (ppm)


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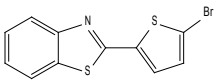
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S
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f1 (ppm)

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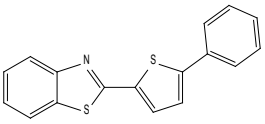

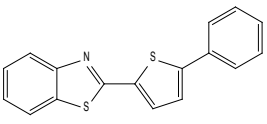

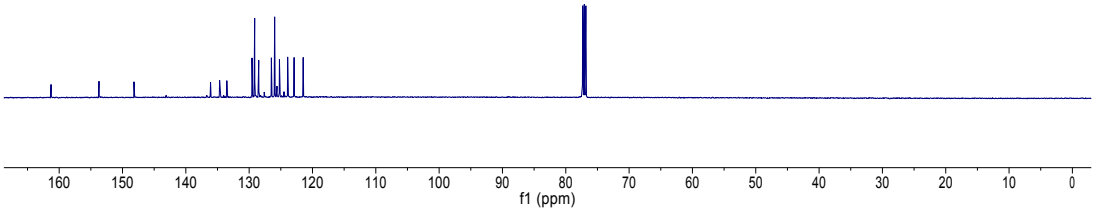

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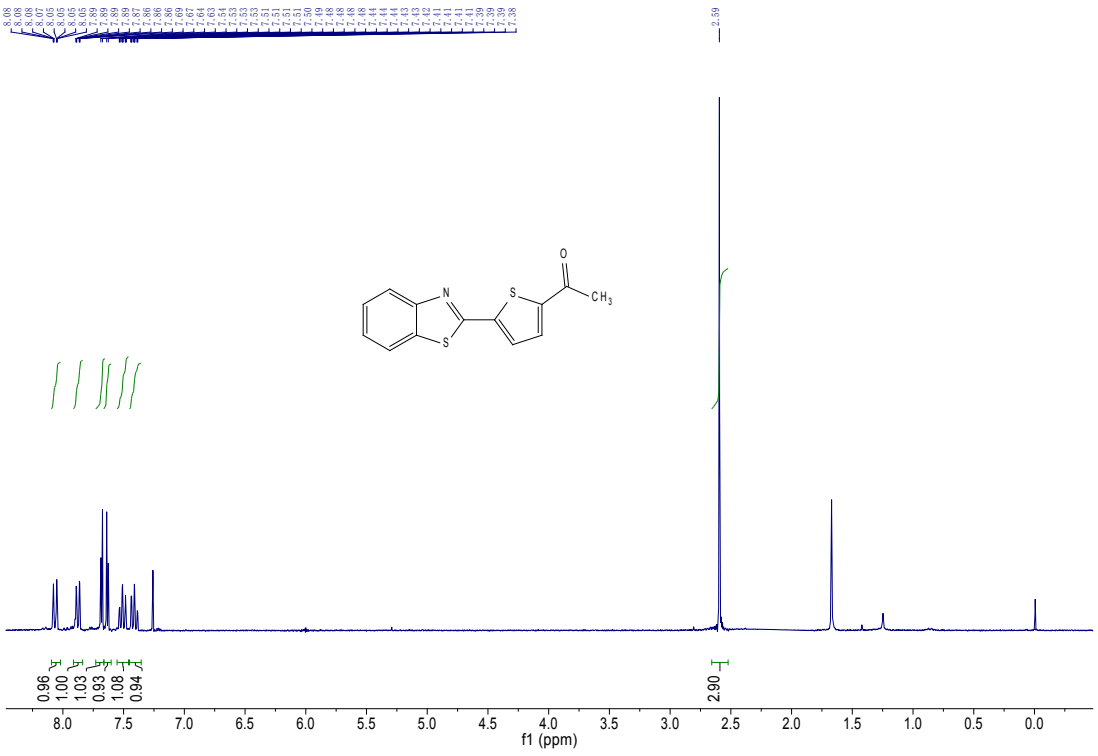
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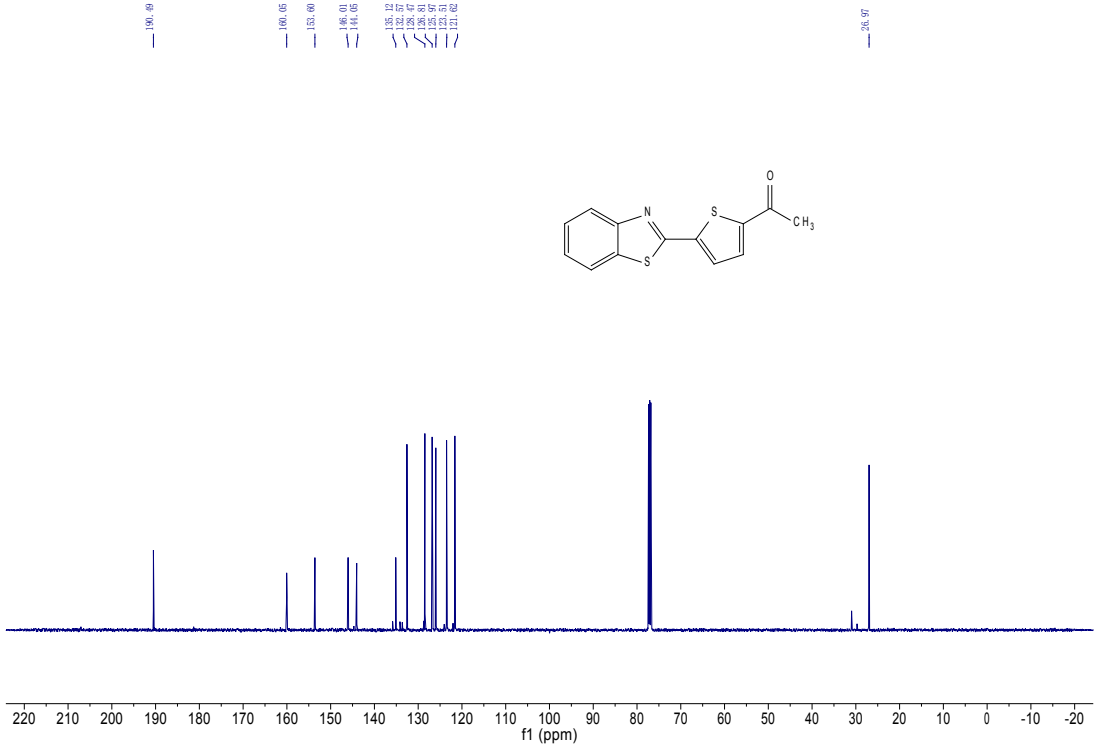
f1 (ppm)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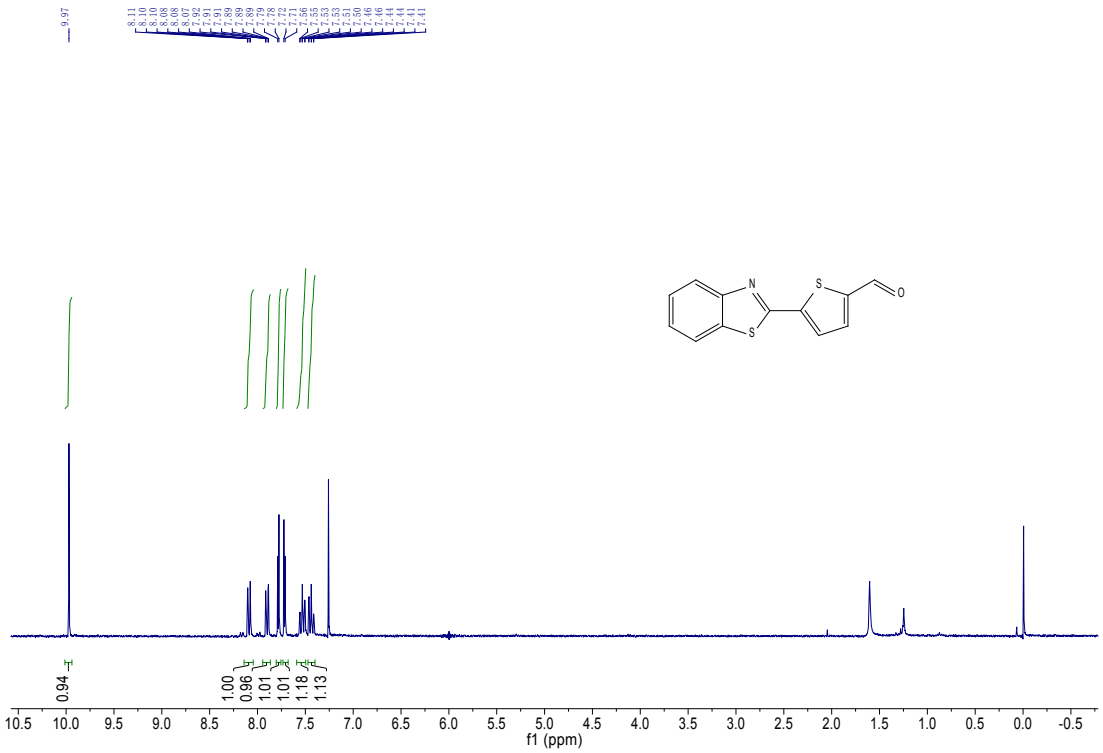
f1 (ppm)

3ag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O
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1.18
1.13
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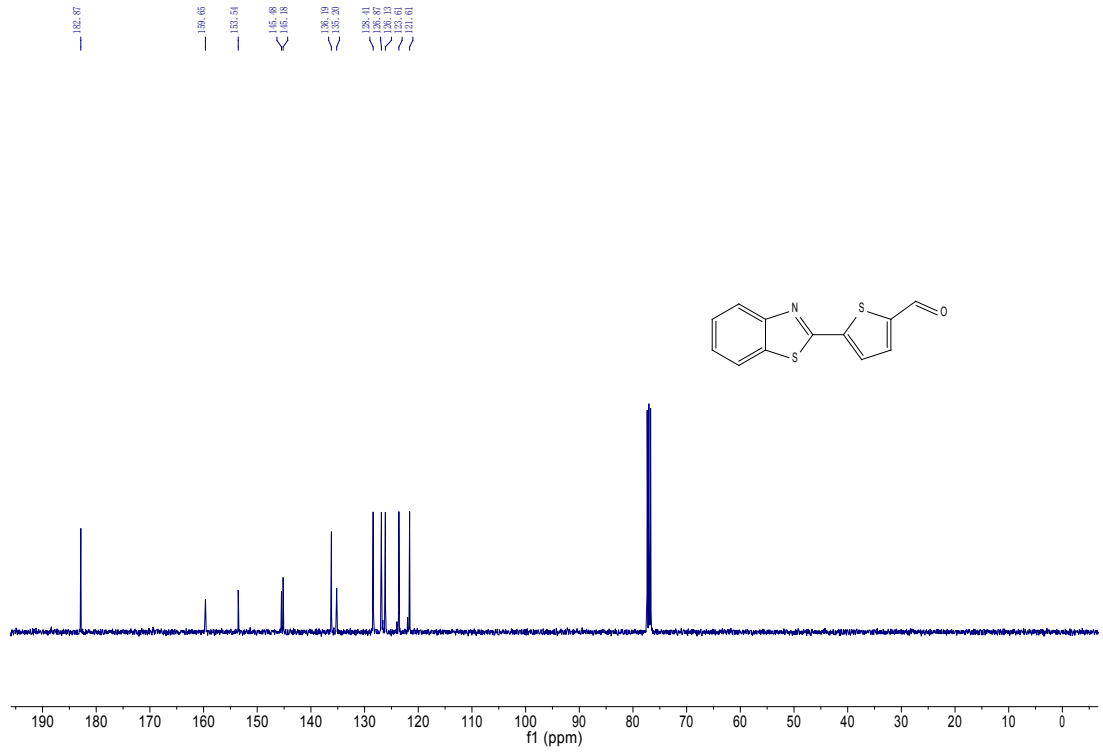
f1 (ppm)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S
S
O
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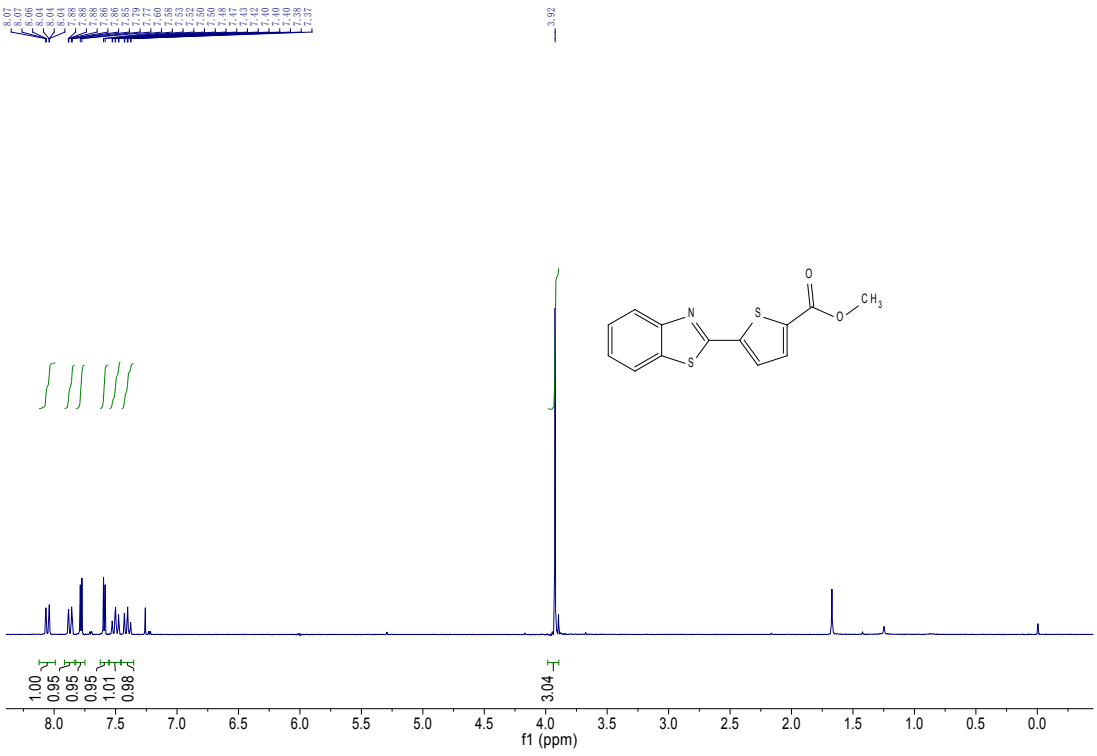
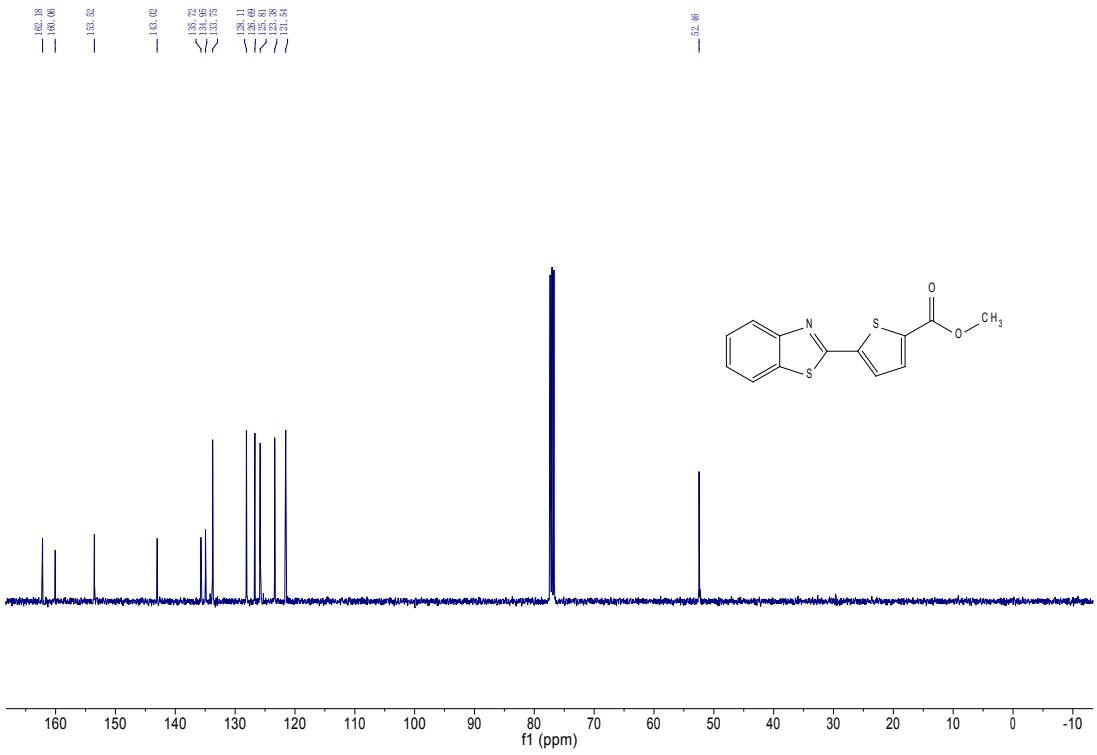
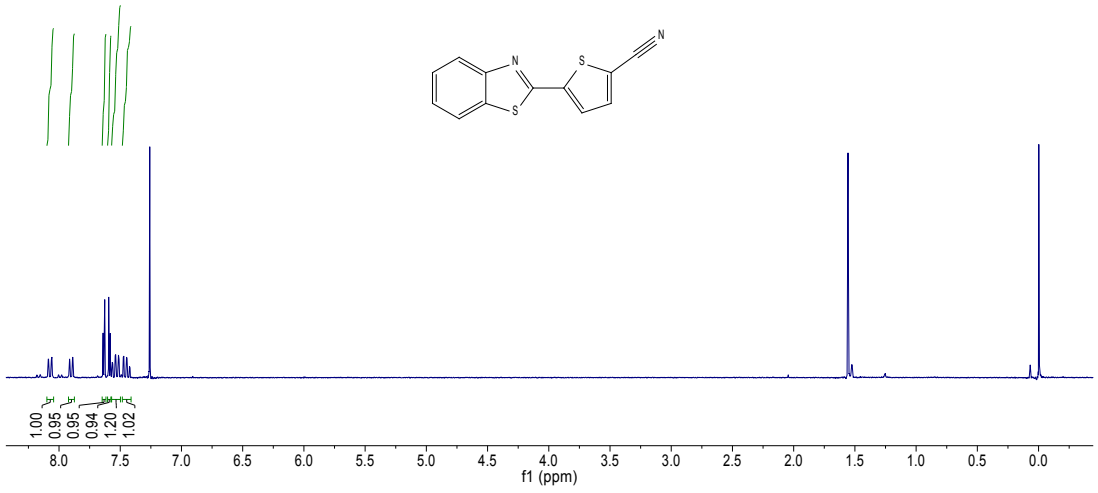
f1 (ppm)

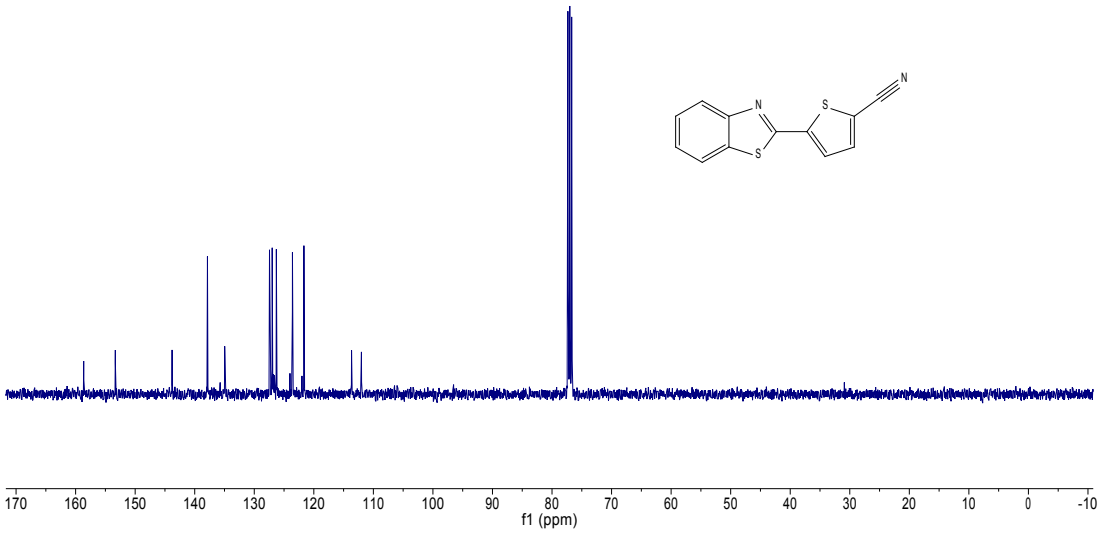
3ah


8.07
8.06
8.04
8.04
8.01
7.88
7.88
7.88
7.86
7.85
7.79
7.77
7.60
7.58
7.53
7.52
7.50
7.48
7.47
7.43
7.42
7.40
7.40
7.38
7.37
3.92
1.00
0.95
0.95
0.95
1.01
0.98
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
N
S
S
O
O
CH3

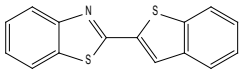

162.18
160.06
153.52
143.02
135.72
134.95
133.75
128.11
126.69
125.81
123.98
121.54
52.46
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
N
S
S
O
O
CH3

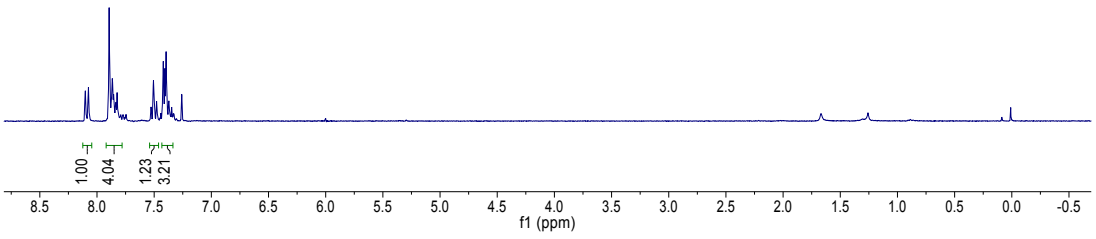
3ai

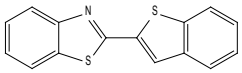

N
S
N
S
1.00
0.95
0.95
0.94
1.20
1.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

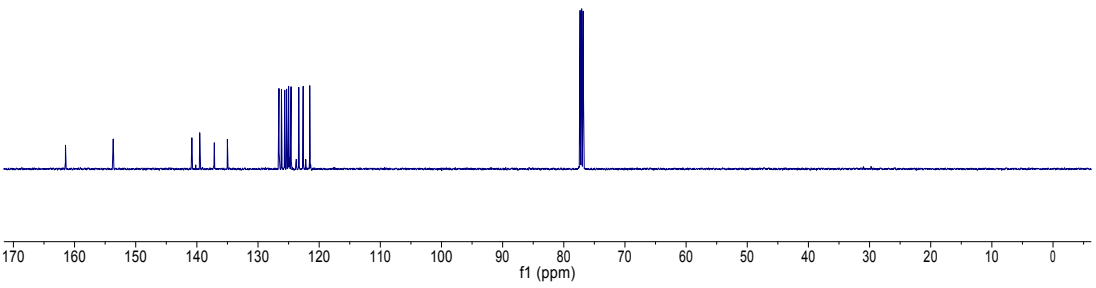

N
S
N
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3aj

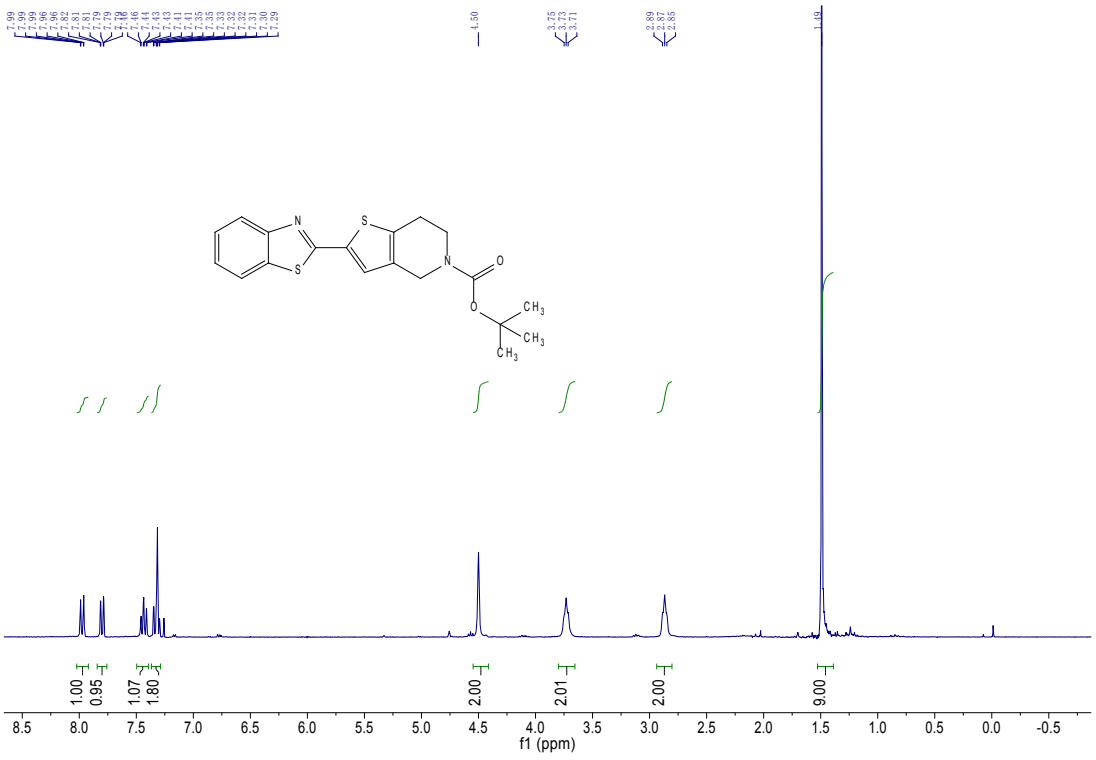


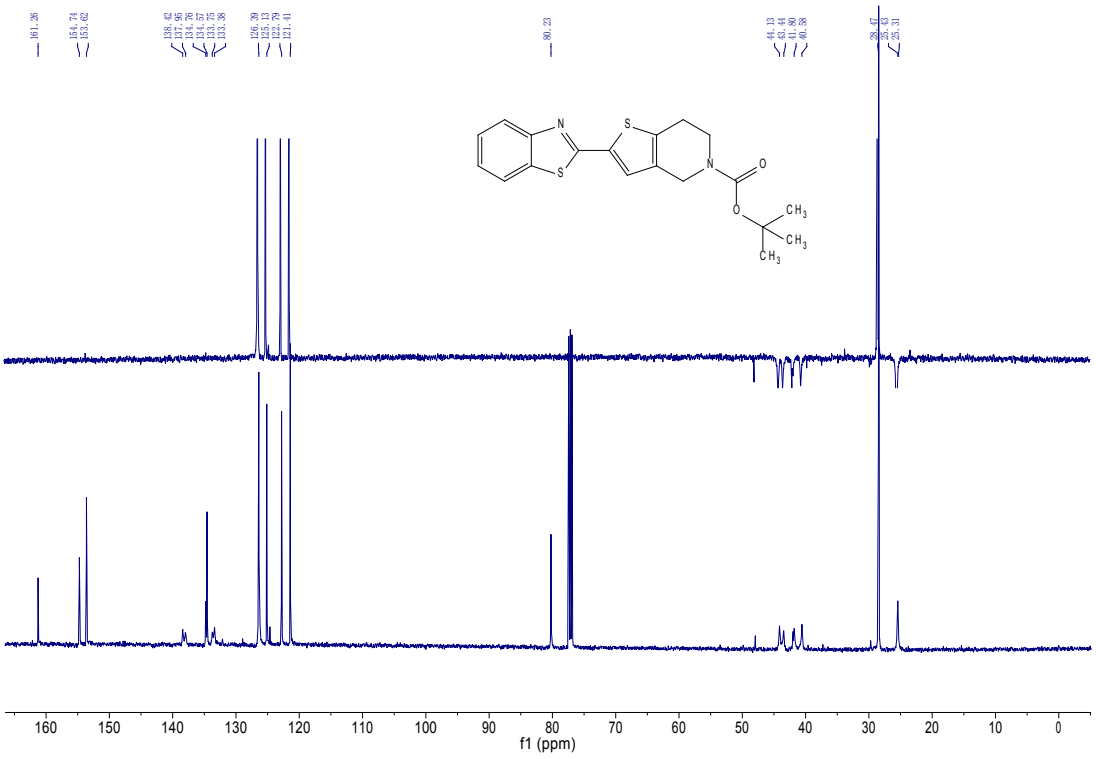

1.00
4.04
1.23
3.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

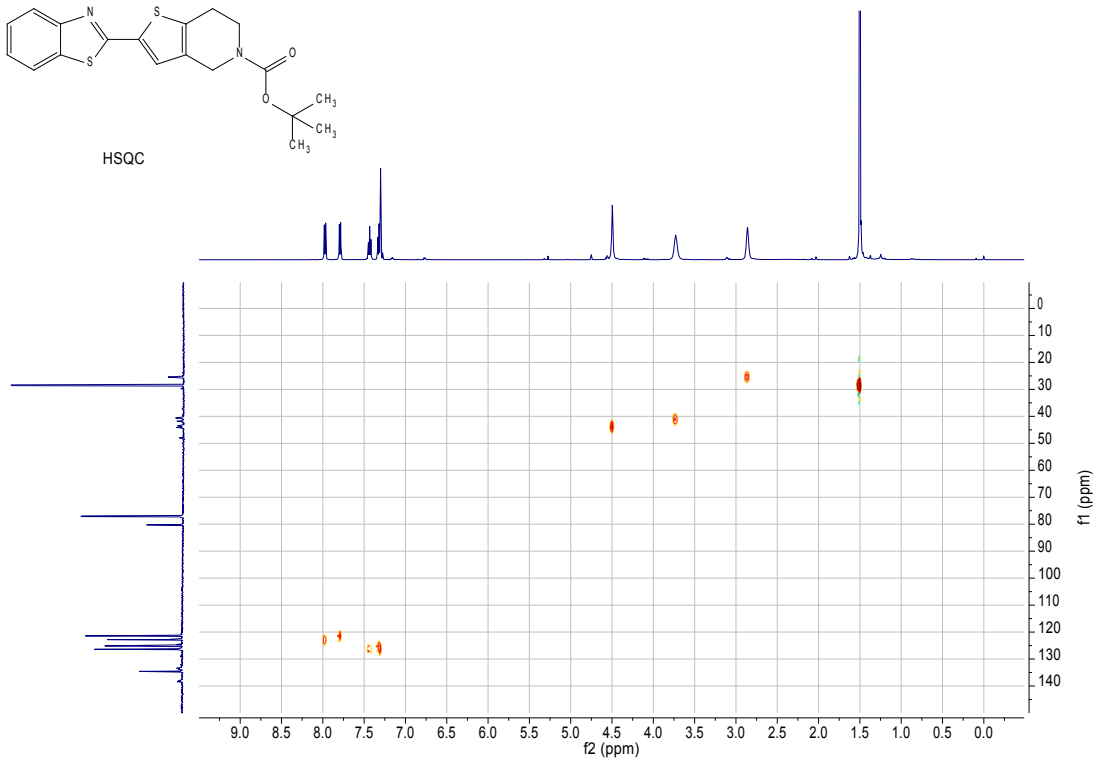



170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

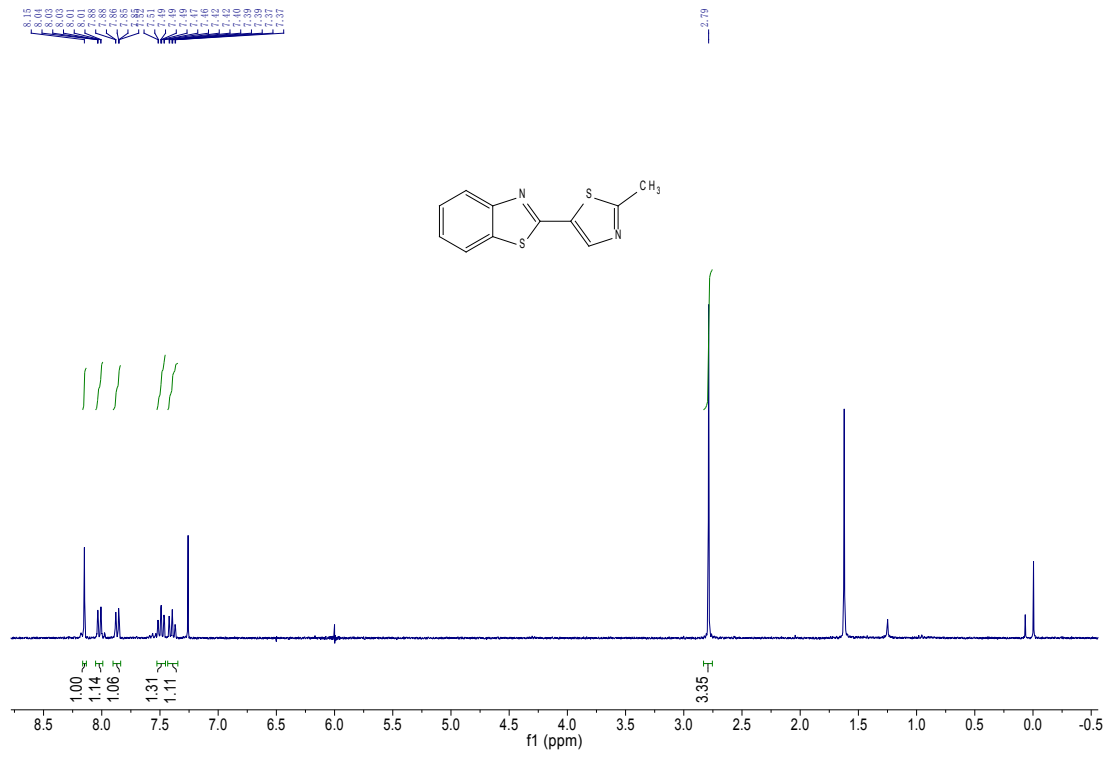
3ak

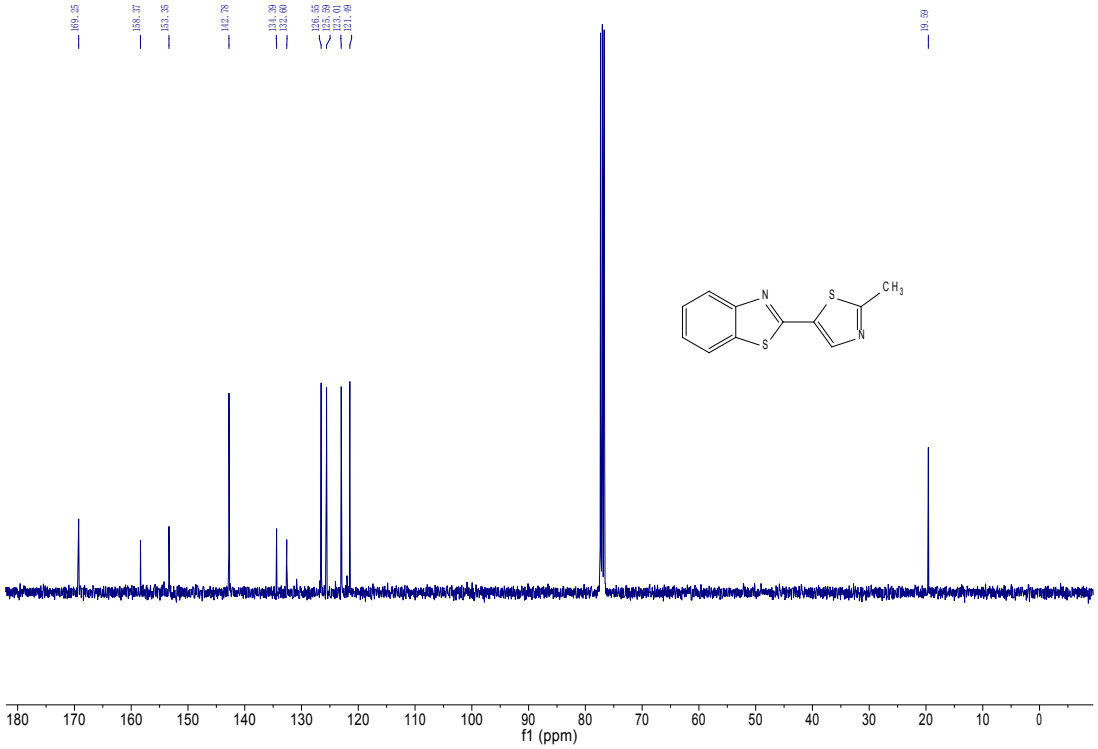

7.99
7.99
7.99
7.96
7.96
7.82
7.81
7.81
7.79
7.79
7.46
7.44
7.43
7.41
7.41
7.35
7.33
7.32
7.32
7.31
7.30
7.29
4.50
3.75
3.73
3.71
2.89
2.87
2.85
1.49
1.00
0.95
1.07
1.80
2.00
2.01
2.00
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


161.26
154.74
153.62
138.62
137.95
134.76
134.57
133.75
133.38
126.39
125.13
122.79
121.41
80.23
44.13
43.44
41.80
40.38
28.47
25.43
25.31
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

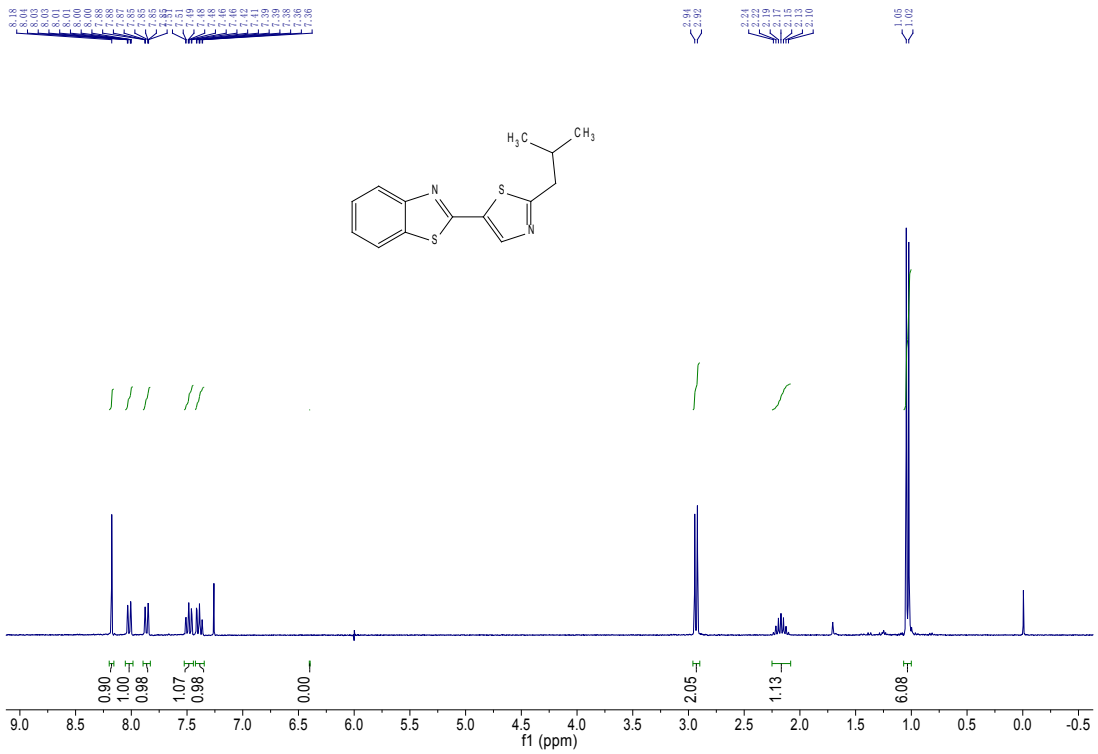


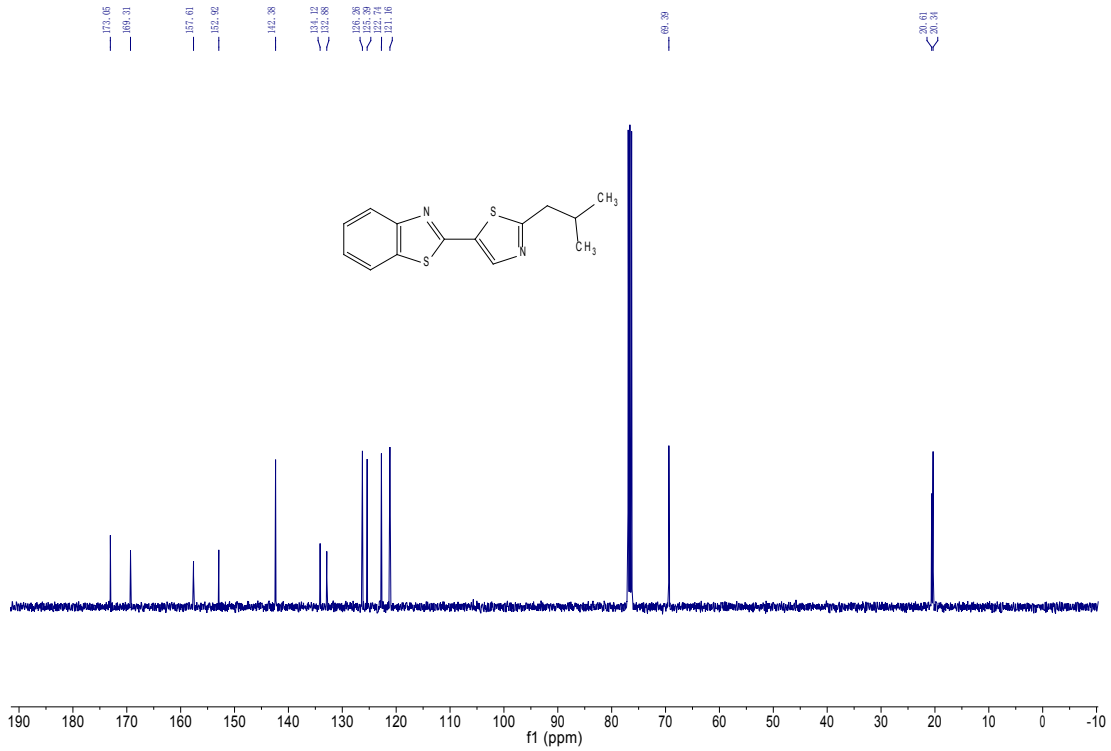
3al



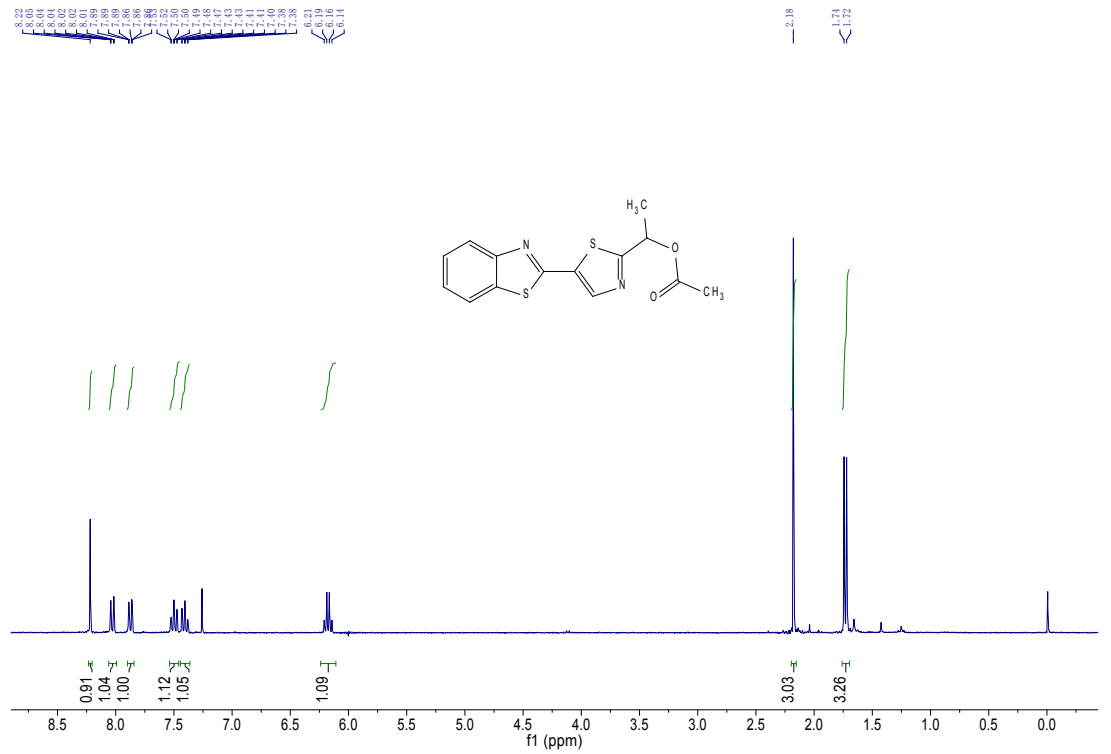

169.25
158.37
153.35
142.78
134.39
132.60
126.55
125.59
123.01
121.49
19.89
N
S
S
N
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

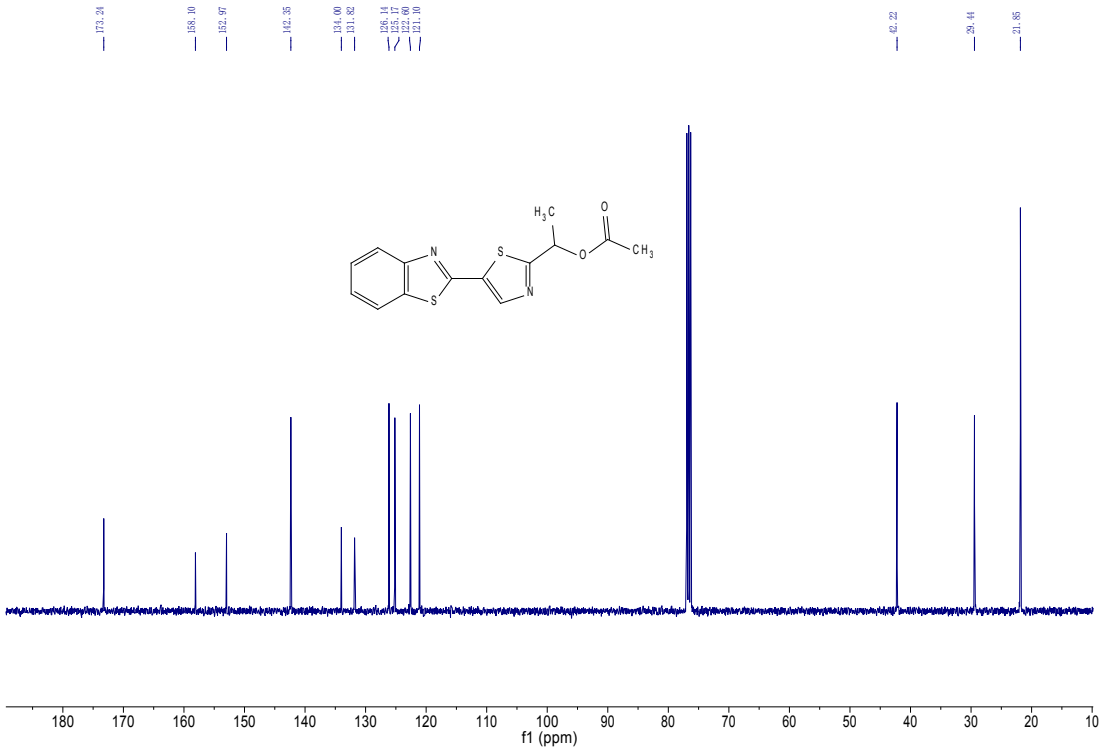
3am


8.18
8.04
8.03
8.01
8.00
7.88
7.87
7.85
7.51
7.49
7.48
7.46
7.42
7.41
7.39
7.38
7.36
2.94
2.92
2.24
2.22
2.19
2.17
2.15
2.13
2.10
1.05
1.02
H3C
CH3
N
S
S
N
0.90
1.00
0.98
1.07
0.98
0.00
2.05
1.13
6.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

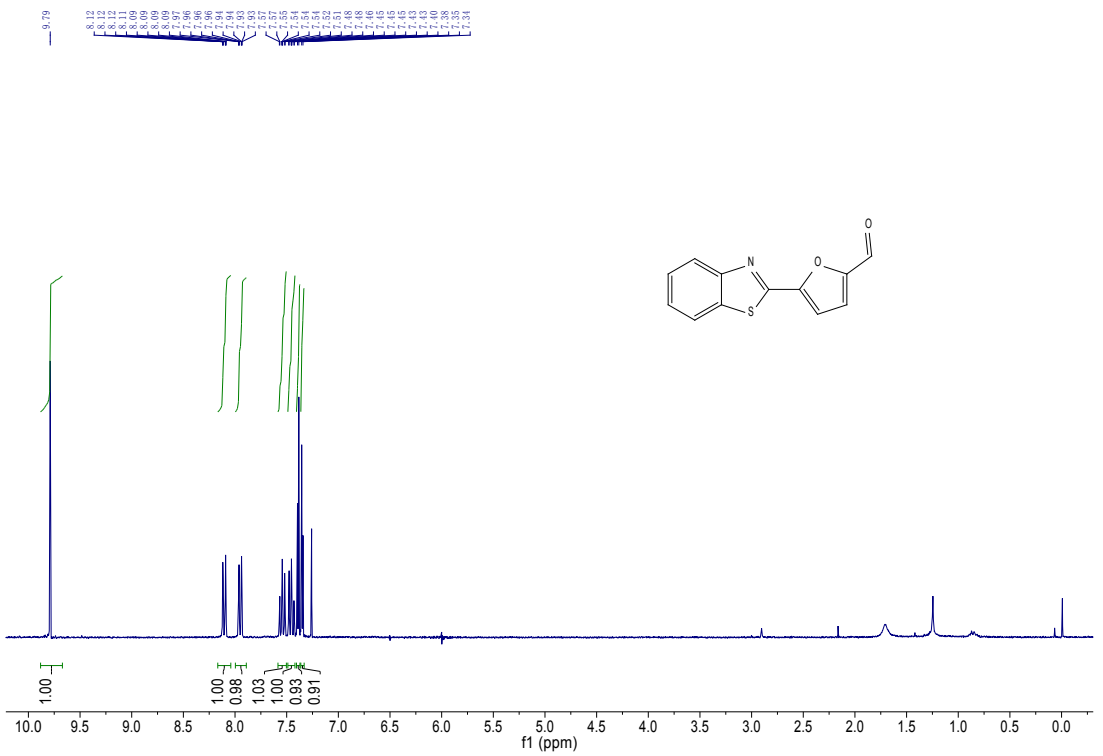

173.05
169.31
157.61
152.92
142.38
134.12
132.88
126.26
125.39
123.74
121.16
69.39
20.61
20.34
f1 (ppm)

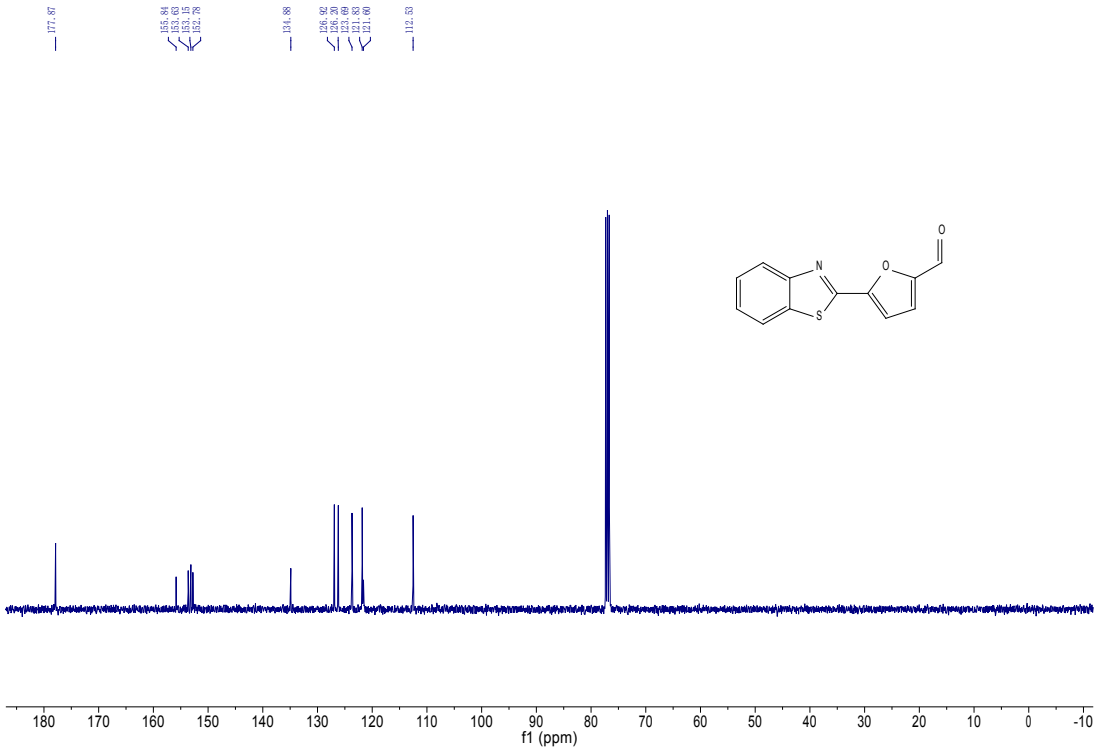
3an


2.18
1.74
1.72
0.91
1.04
1.00
1.12
1.05
1.09
3.03
3.26
f1 (ppm)

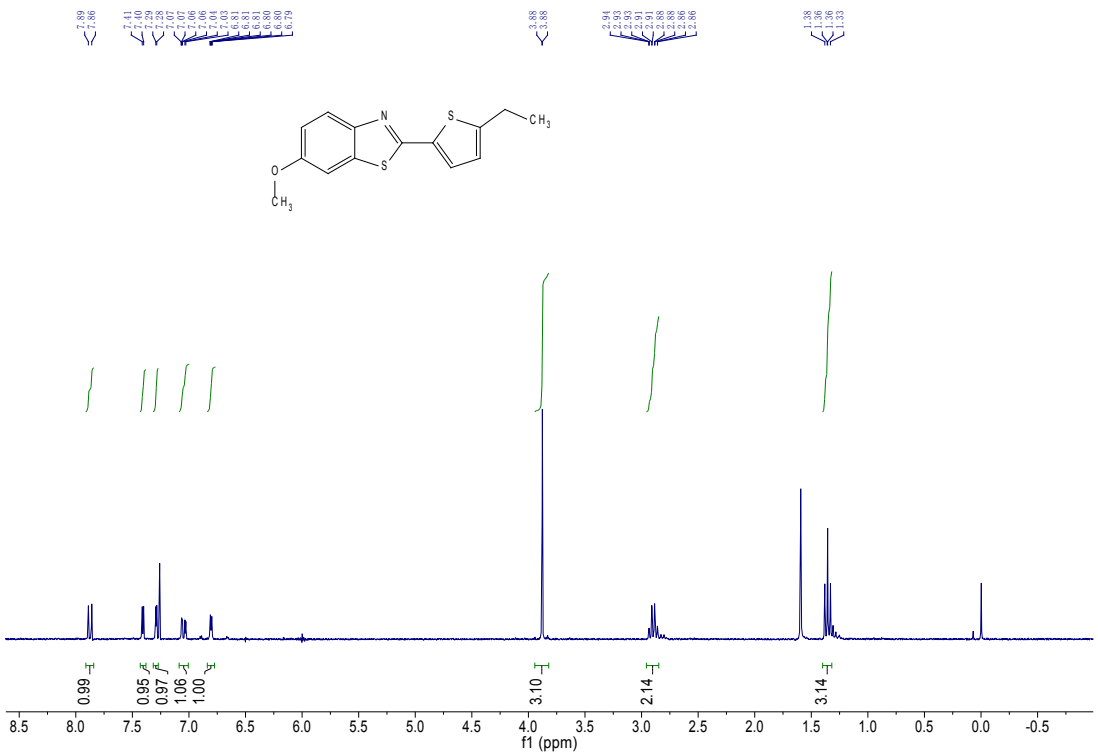

173.24
158.10
152.97
142.35
134.00
131.82
126.14
125.17
122.60
121.10
62.22
29.44
21.85
H3C
O
CH3
O
N
S
S
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

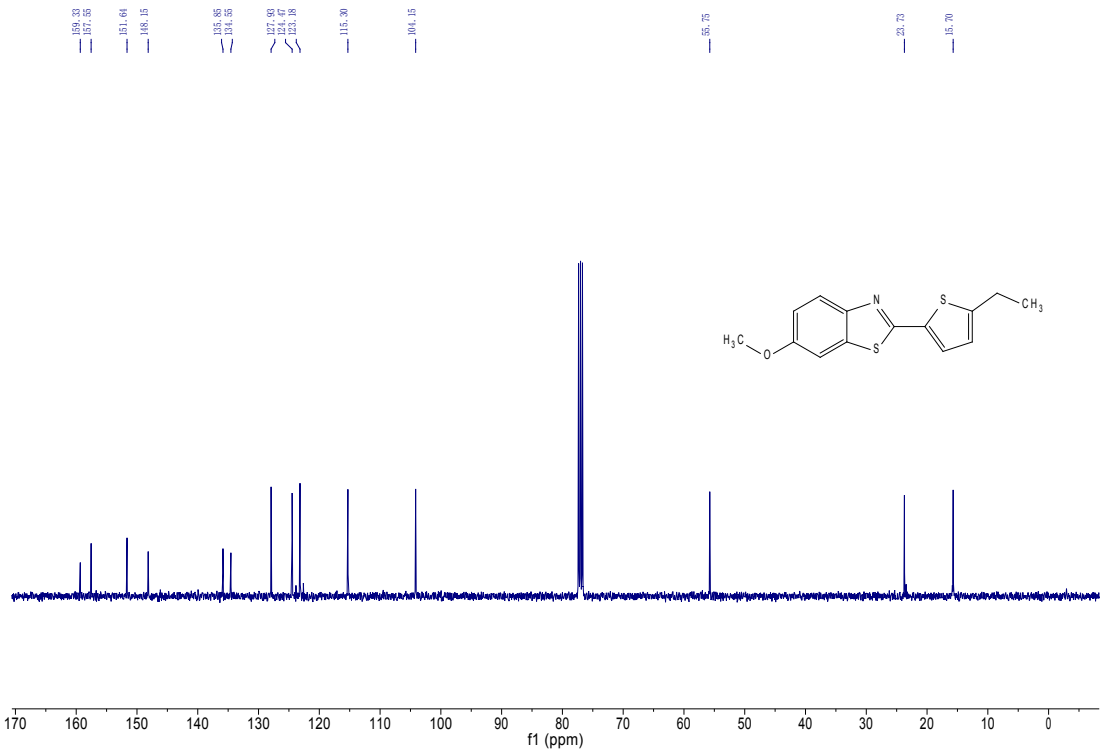
3ap


9.79
8.12
8.12
8.12
8.11
8.09
8.09
8.09
8.07
7.96
7.96
7.94
7.94
7.93
7.93
7.57
7.57
7.55
7.54
7.54
7.53
7.52
7.51
7.48
7.48
7.46
7.46
7.45
7.45
7.45
7.45
7.43
7.43
7.40
7.38
7.35
7.34
O
N
O
S
1.00
1.00
0.98
1.03
1.00
0.93
0.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

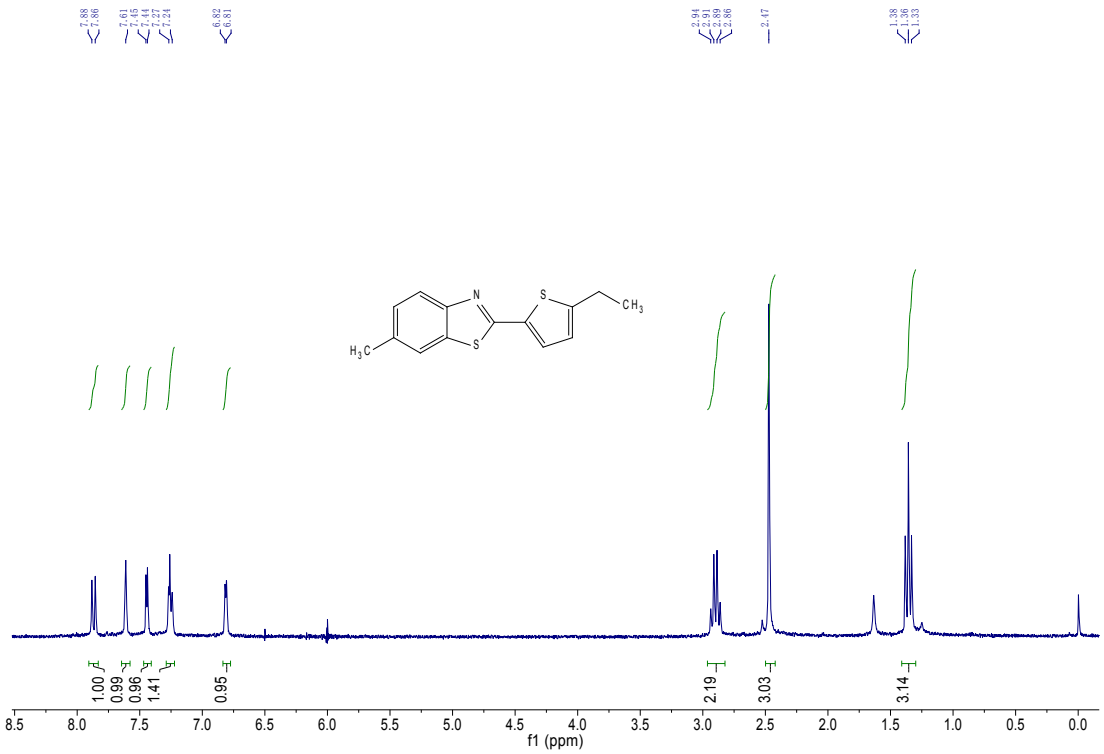

177.87
155.84
153.63
153.15
152.78
134.88
126.92
126.20
123.68
121.83
121.60
112.53
O
N
O
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

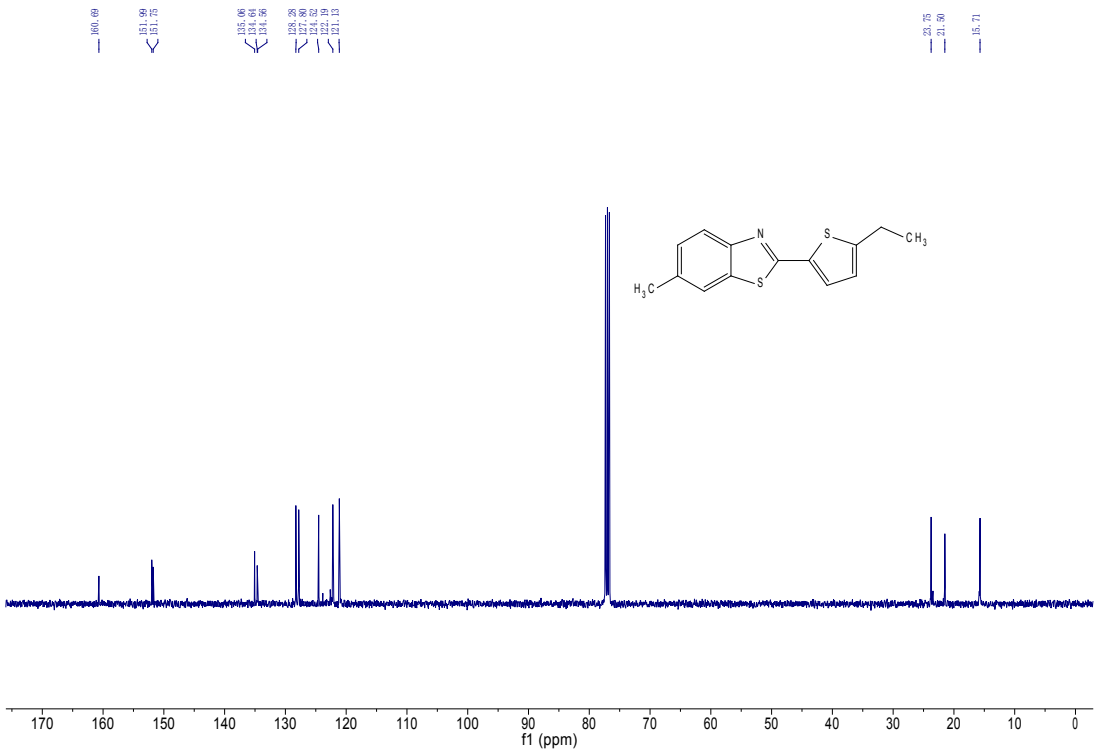
3bb


7.89
7.86
7.41
7.40
7.39
7.38
7.07
7.06
7.06
7.04
7.03
6.81
6.81
6.81
6.80
6.80
6.79
3.88
3.88
2.94
2.93
2.93
2.91
2.91
2.88
2.88
2.86
2.86
1.38
1.36
1.36
1.33
N
S
CH3
O
S
CH3
0.99
0.95
0.97
1.06
1.00
3.10
2.14
3.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

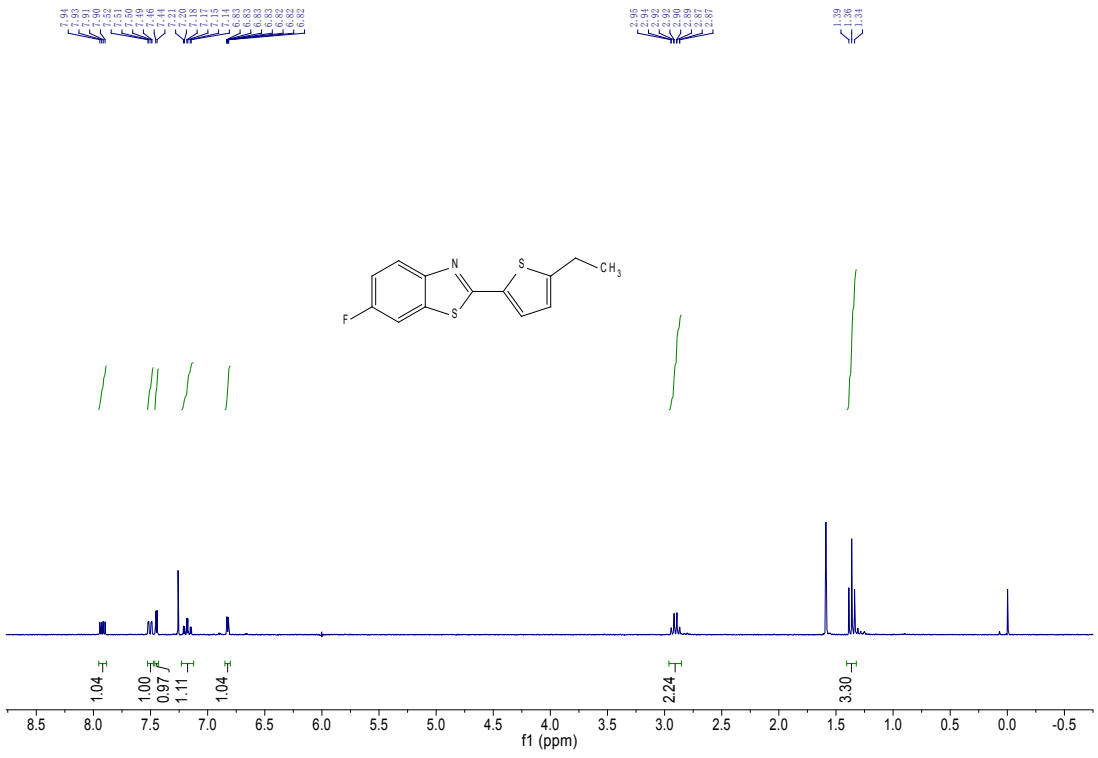

159.33
157.55
151.64
148.15
135.85
134.55
127.93
124.47
123.18
115.30
104.15
55.75
23.73
15.70
N
S
CH3
H3C
O
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

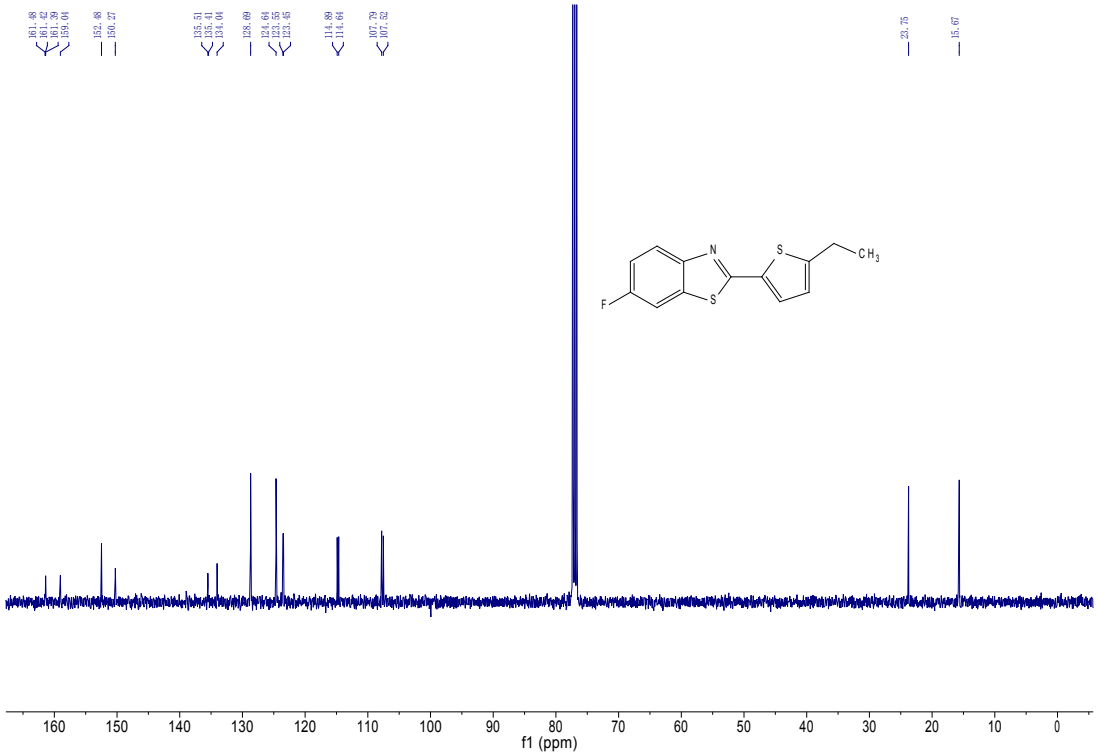
3cb


7.88
7.86
7.61
7.45
7.44
7.27
7.24
6.82
6.81
2.94
2.91
2.89
2.86
2.47
1.38
1.36
1.33
N
S
CH3
H3C
S
1.00
0.99
0.96
1.41
0.95
2.19
3.03
3.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

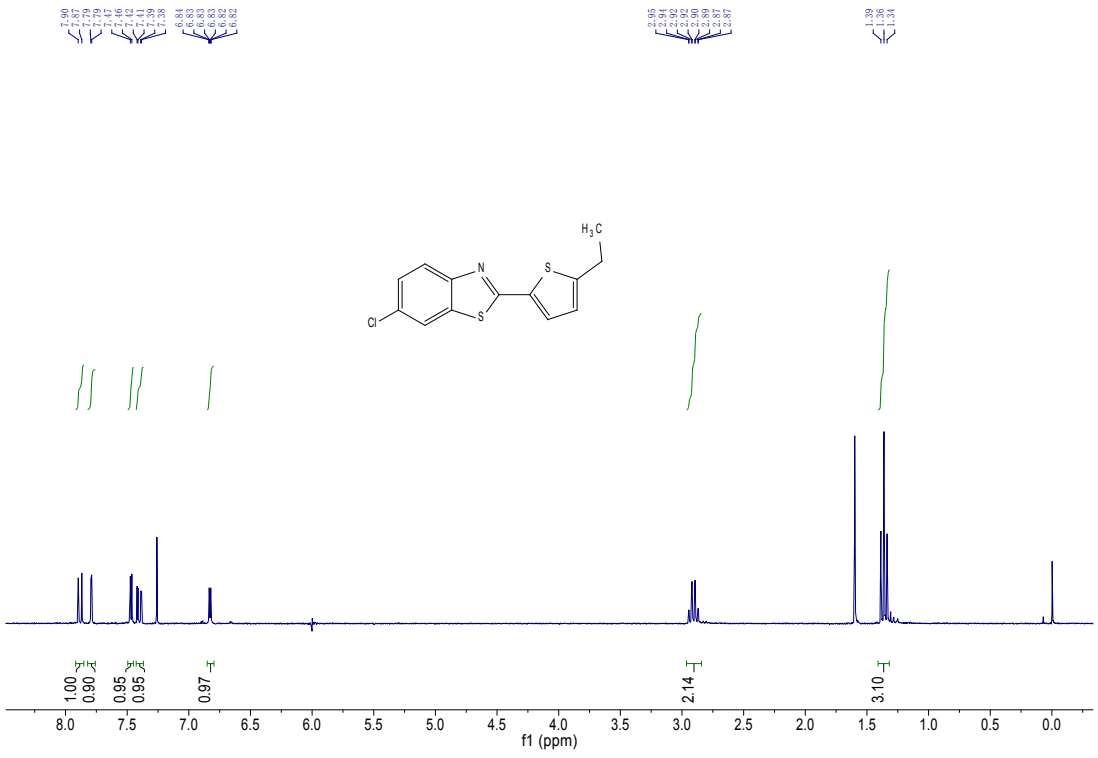

160.69
151.99
151.75
135.06
134.64
134.56
128.28
127.80
124.32
122.19
121.13
23.75
21.80
15.71
N
S
S
CH3
H3C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

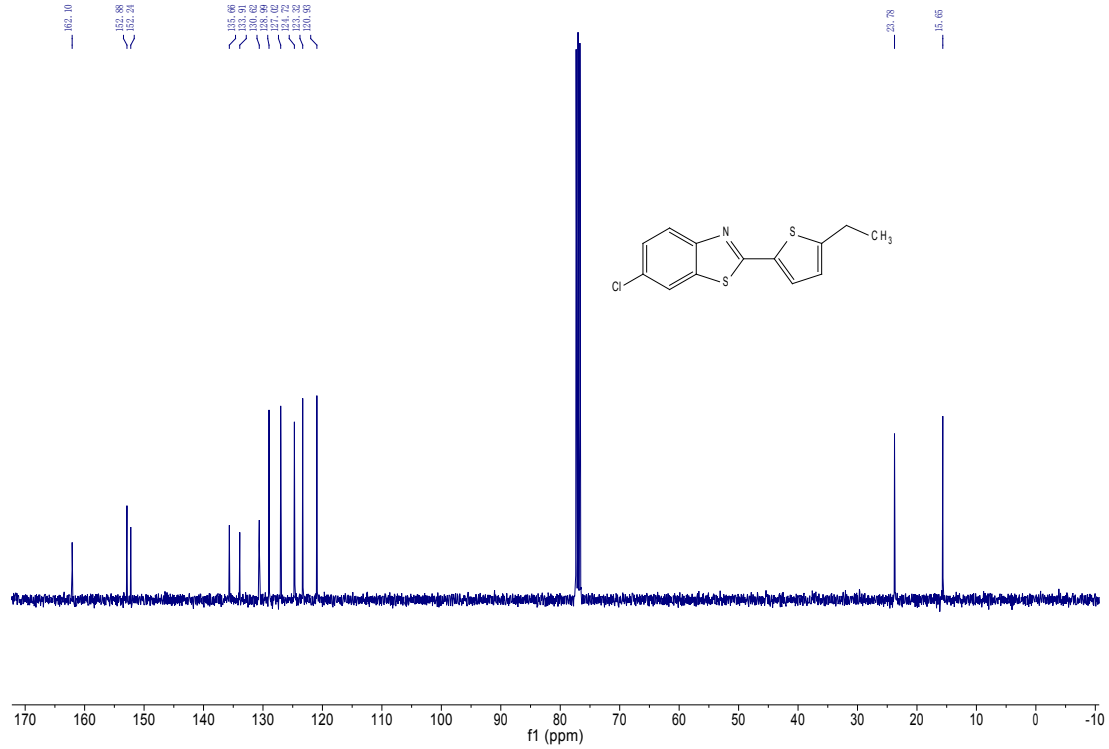
3db


7.94
7.93
7.91
7.90
7.52
7.51
7.50
7.49
7.46
7.44
7.41
7.21
7.20
7.18
7.17
7.15
7.14
6.83
6.83
6.83
6.82
6.82
6.82
2.95
2.94
2.92
2.92
2.90
2.89
2.87
2.87
1.39
1.36
1.34
N
S
S
CH3
F
1.04
1.00
0.97
1.11
1.04
2.24
3.30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

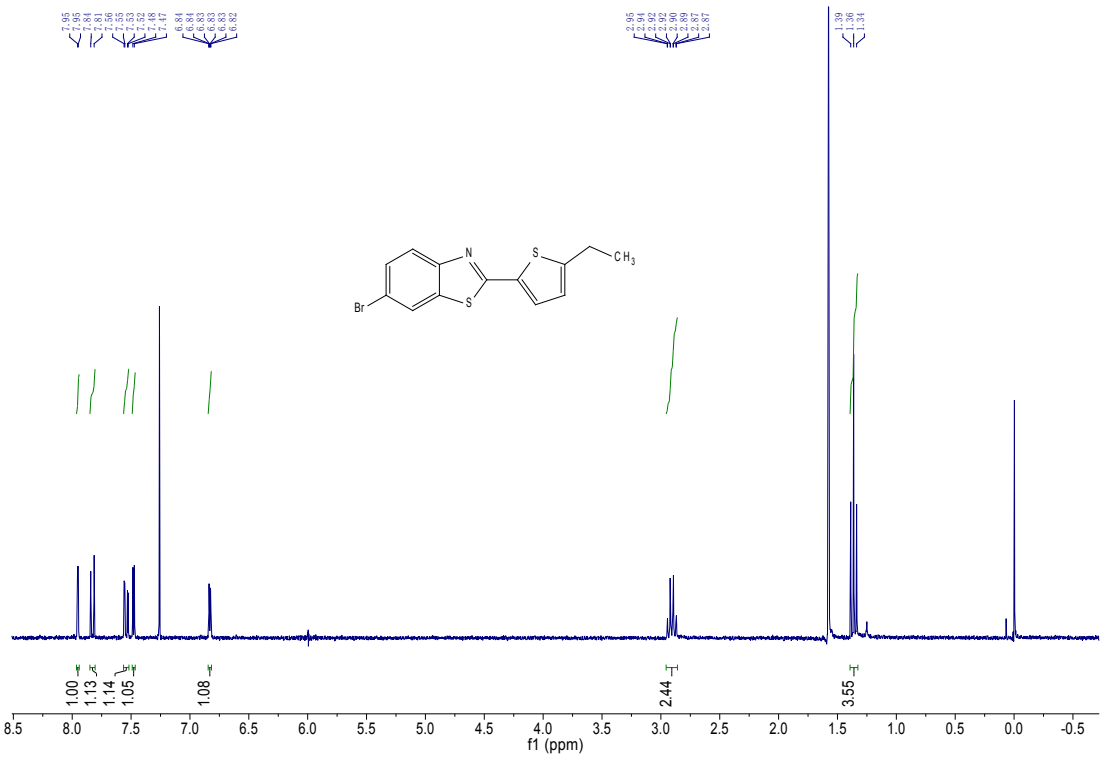

161.48
161.42
161.39
159.04
152.48
150.27
135.51
135.41
134.04
128.69
124.64
123.55
123.45
114.89
114.64
107.79
107.52
23.75
15.67
N
S
CH3
F
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

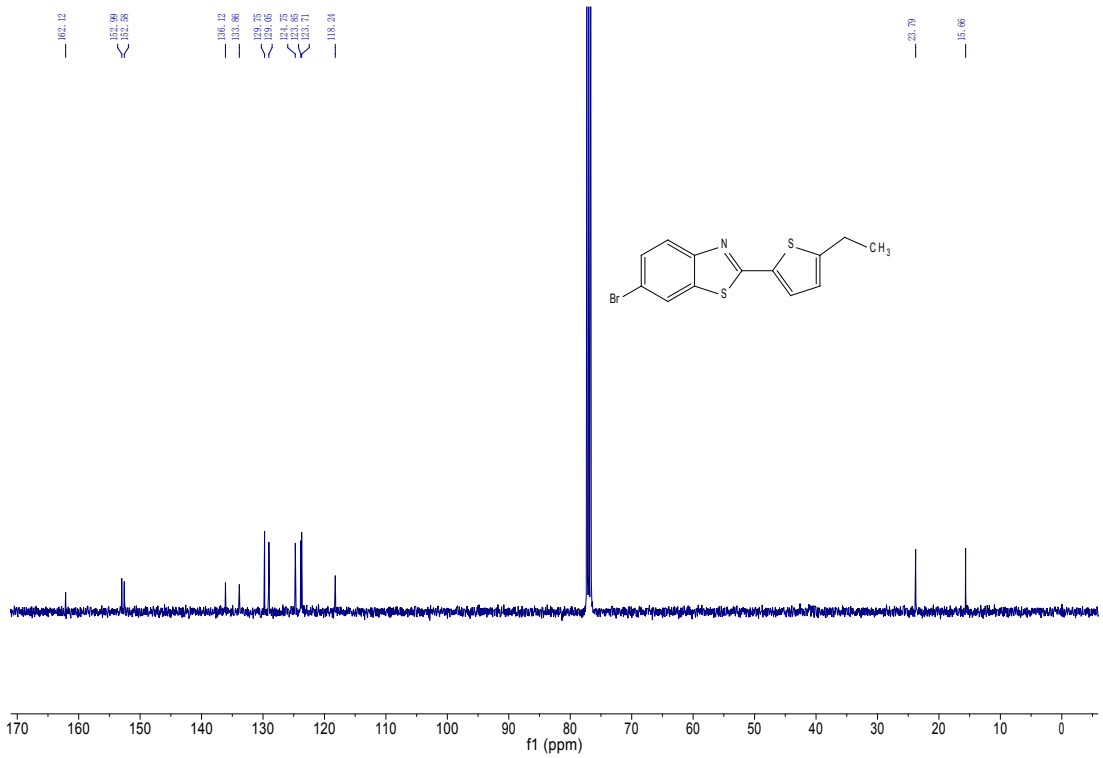
3eb


7.90
7.87
7.79
7.79
7.47
7.46
7.42
7.41
7.39
7.38
6.84
6.83
6.83
6.82
6.82
2.95
2.94
2.92
2.92
2.90
2.89
2.87
2.87
1.39
1.36
1.34
H3C
N
S
S
Cl
1.00
0.90
0.95
0.95
0.97
2.14
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

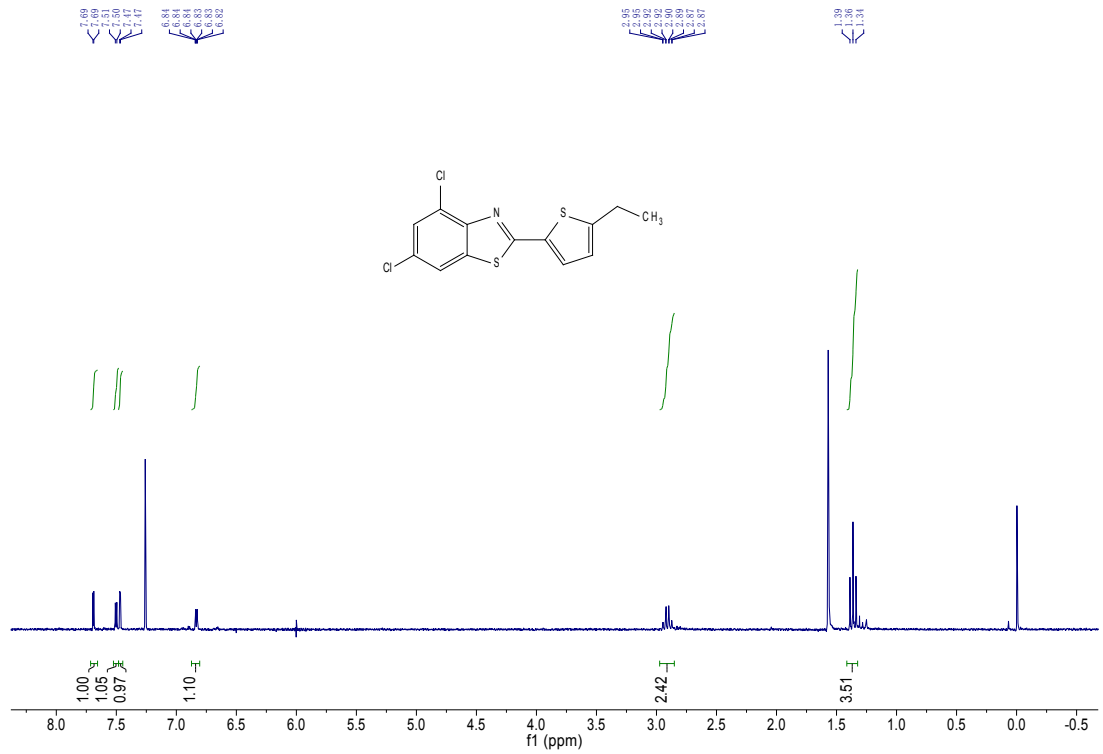

162.10
152.88
152.24
135.66
133.91
130.62
129.94
127.02
124.72
123.32
120.50
23.78
15.65
Cl
N
S
S
CH3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3fb


7.95
7.95
7.84
7.81
7.56
7.55
7.53
7.52
7.48
7.47
6.84
6.84
6.83
6.83
6.83
6.82
2.95
2.94
2.92
2.92
2.90
2.89
2.87
2.87
1.39
1.36
1.34
Br
N
S
S
CH3
1.00
1.13
1.14
1.05
1.08
2.44
3.55
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


162.12
152.99
152.38
136.12
133.86
129.75
129.05
124.75
123.85
123.71
118.24
23.79
15.66
N
S
CH3
Br
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3gb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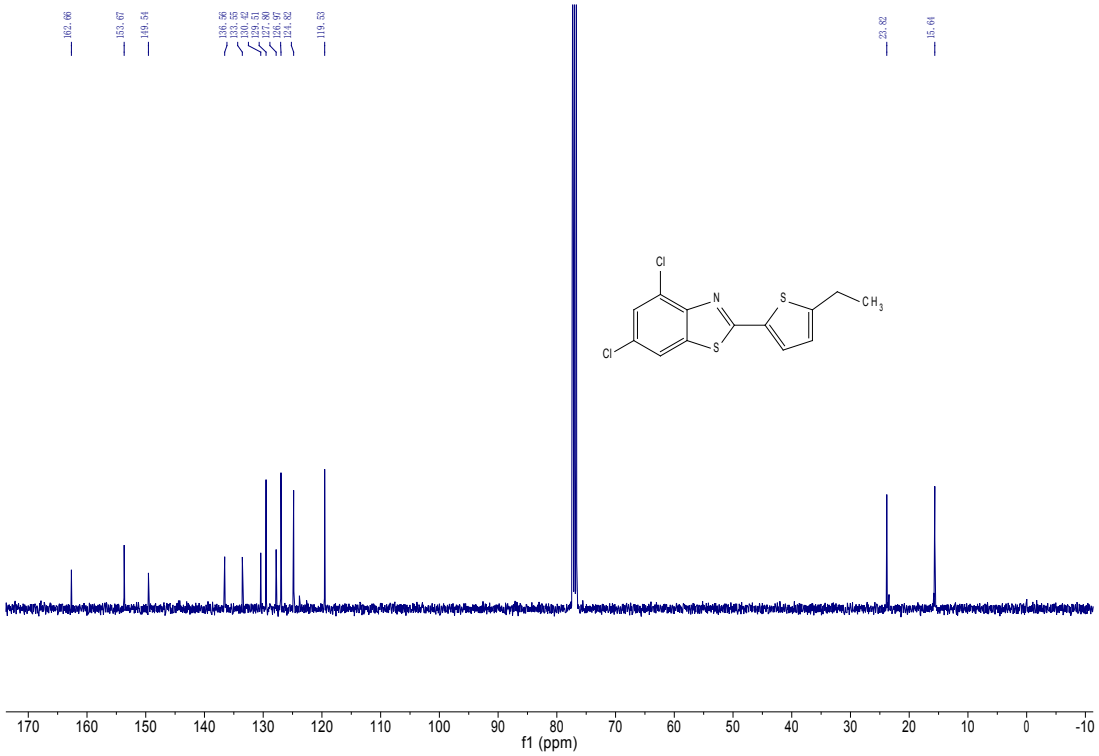
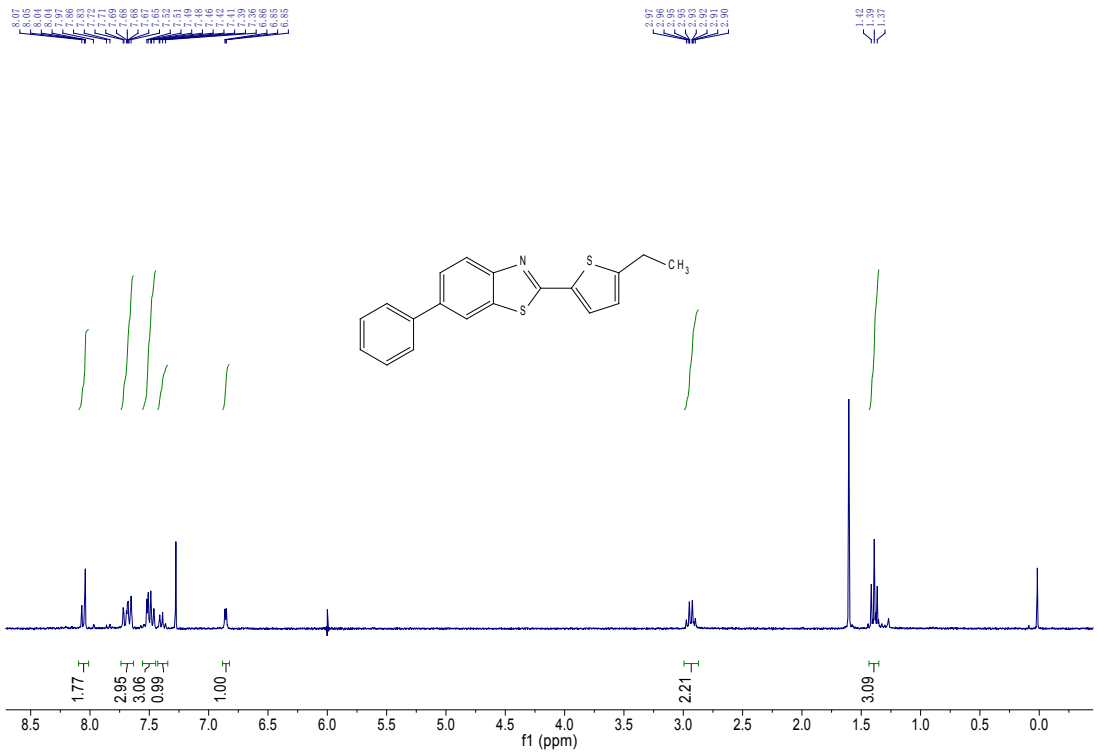
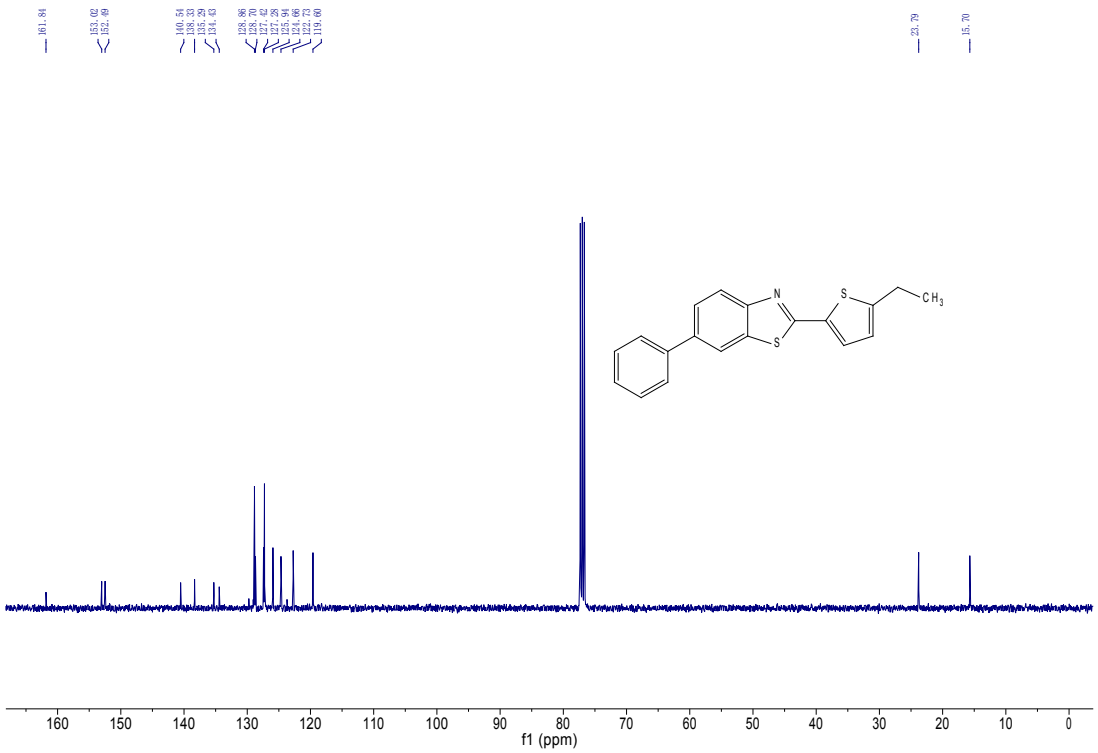
7.69
7.51
7.50
7.47
7.47
6.84
6.84
6.84
6.83
6.83
6.82
2.95
2.95
2.92
2.92
2.90
2.89
2.87
2.87
1.39
1.36
1.34
Cl
N
S
CH3
Cl
S
1.00
1.05
0.97
1.10
2.42
3.51
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

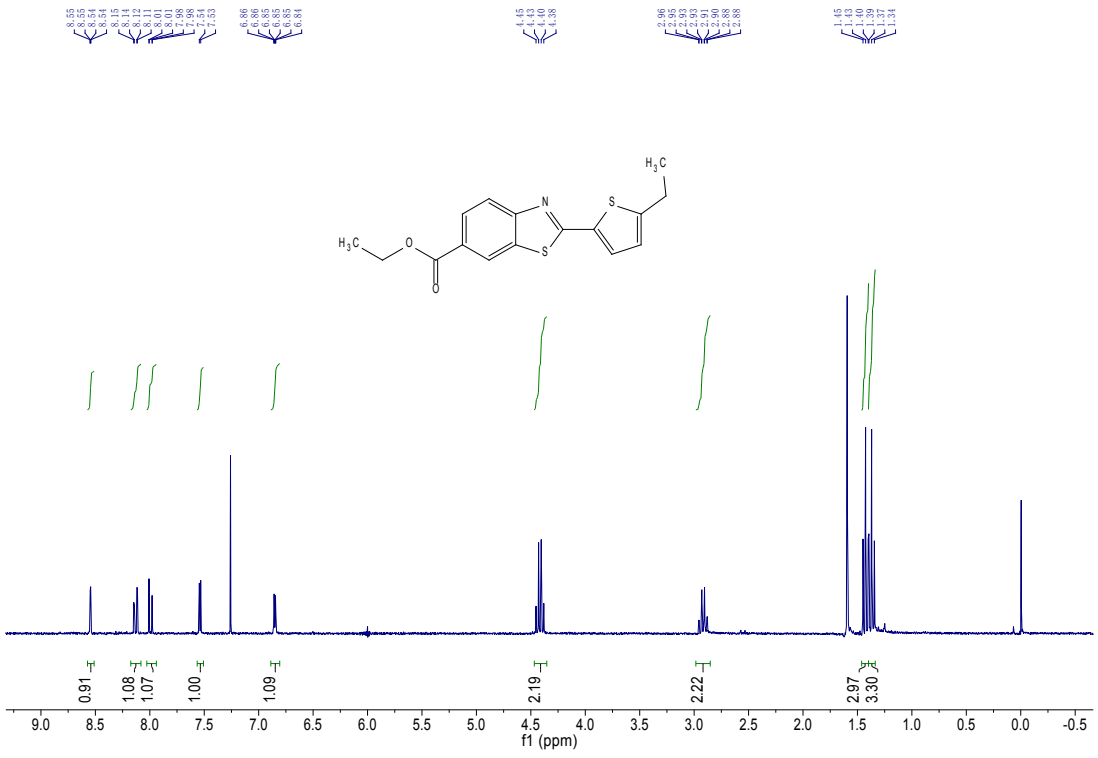

162.66
153.67
149.54
136.56
133.35
130.62
129.51
127.80
126.97
124.82
119.53
25.82
15.64
Cl
N
S
CH3
Cl
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3hb


8.07
8.05
8.04
8.04
7.97
7.86
7.83
7.72
7.71
7.69
7.68
7.68
7.67
7.65
7.52
7.51
7.49
7.48
7.46
7.42
7.41
7.39
7.36
6.86
6.85
6.85
2.97
2.96
2.95
2.95
2.93
2.92
2.91
2.90
1.42
1.39
1.37
N
S
S
CH3
1.77
2.95
3.06
0.99
1.00
2.21
3.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.84
153.02
152.49
140.54
138.33
135.29
134.43
128.86
128.70
127.42
125.94
124.66
122.73
119.60
23.79
15.70
N
S
S
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ib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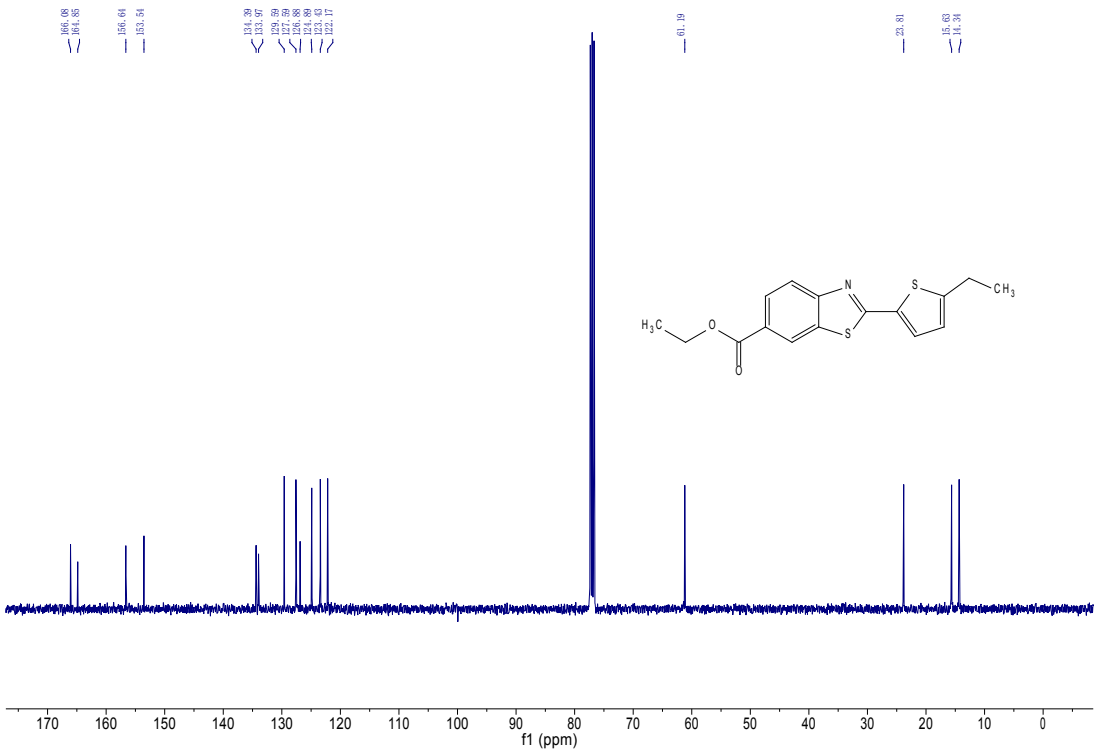
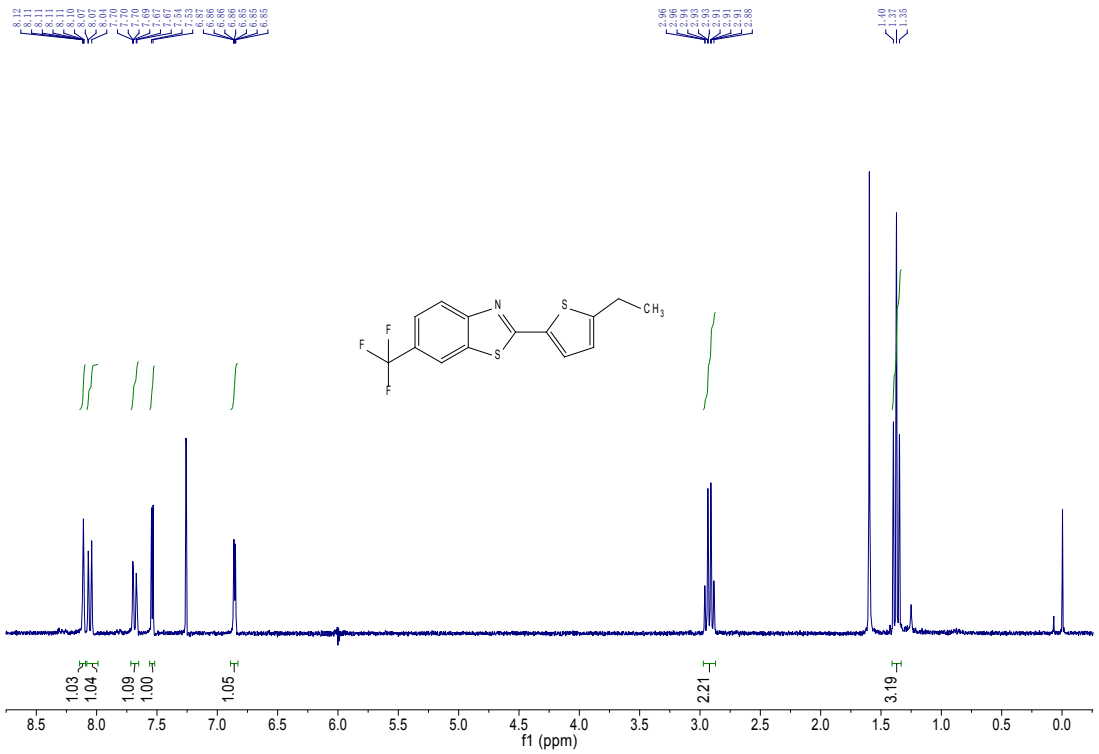
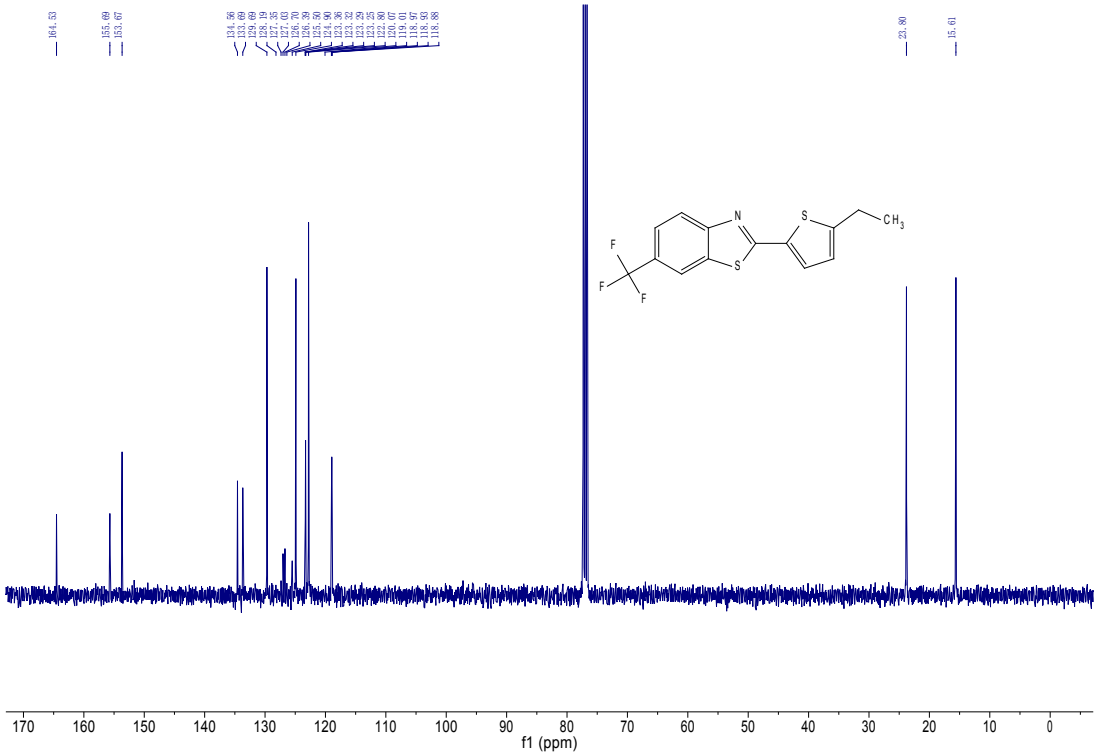
8.55
8.54
8.54
8.15
8.14
8.12
8.11
8.01
7.98
7.96
7.54
7.53
6.86
6.86
6.85
6.85
6.84
4.45
4.43
4.40
4.38
2.96
2.95
2.93
2.93
2.91
2.90
2.88
2.88
1.45
1.43
1.40
1.39
1.37
1.34
H3C
N
S
S
H3C
O
O
0.91
1.08
1.07
1.00
1.09
2.19
2.22
2.97
3.30
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

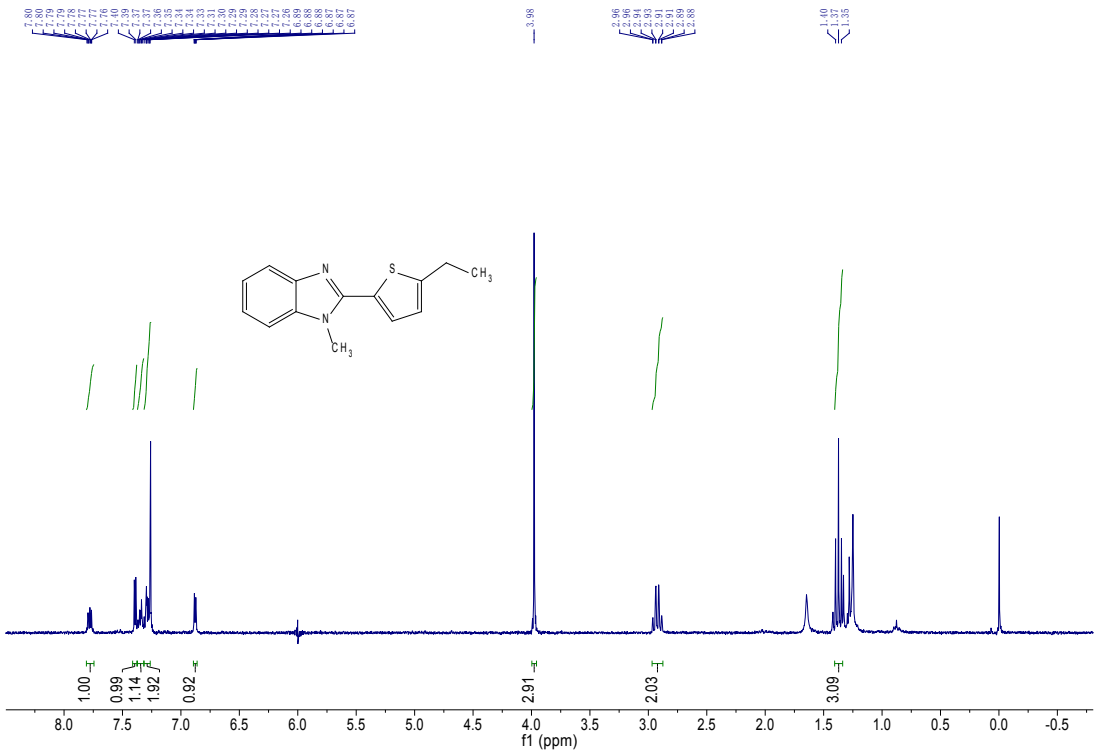

166.08
164.85
156.64
153.54
134.39
133.97
129.39
127.38
126.88
124.89
123.43
122.17
61.19
23.81
15.63
14.34
N
S
CH3
H3C
O
S
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3jb


8.12
8.11
8.11
8.11
8.11
8.10
8.07
8.07
8.07
8.04
7.70
7.70
7.70
7.69
7.67
7.67
7.67
7.54
7.53
6.87
6.86
6.86
6.85
6.85
6.85
6.85
2.96
2.96
2.94
2.93
2.93
2.91
2.91
2.91
2.91
2.88
1.40
1.37
1.35
N
S
CH3
F
F
F
S
1.03
1.04
1.09
1.00
1.05
2.21
3.19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.53
155.69
153.67
134.56
133.69
129.69
128.19
127.35
127.03
126.70
126.39
125.90
125.54
123.36
123.32
123.25
123.03
122.80
120.07
119.91
118.97
118.93
118.88
23.80
15.61
N
S
CH3
F
F
F
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3kb


7.80
7.80
7.79
7.79
7.78
7.77
7.77
7.76
7.40
7.39
7.37
7.37
7.36
7.35
7.34
7.34
7.33
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26
6.89
6.88
6.88
6.87
6.87
6.87
3.98
2.96
2.96
2.94
2.94
2.93
2.91
2.91
2.89
2.89
2.88
1.40
1.37
1.37
1.35
N
S
CH3
N
CH3
1.00
0.99
1.14
1.92
0.92
2.91
2.03
3.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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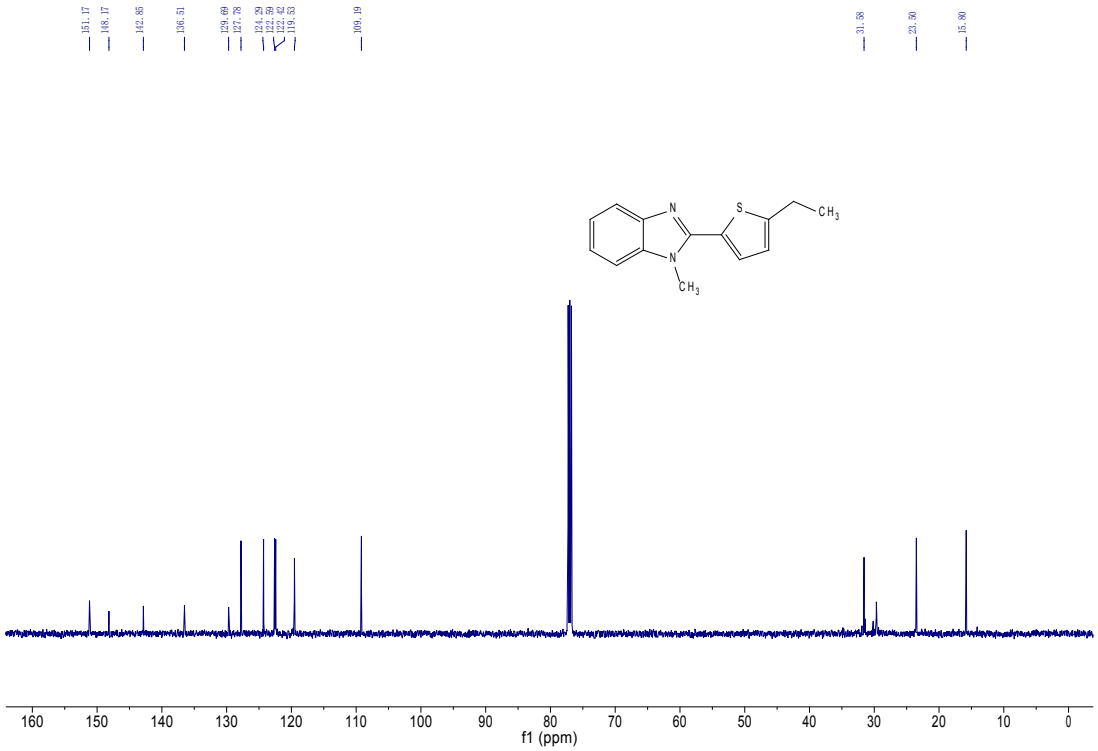
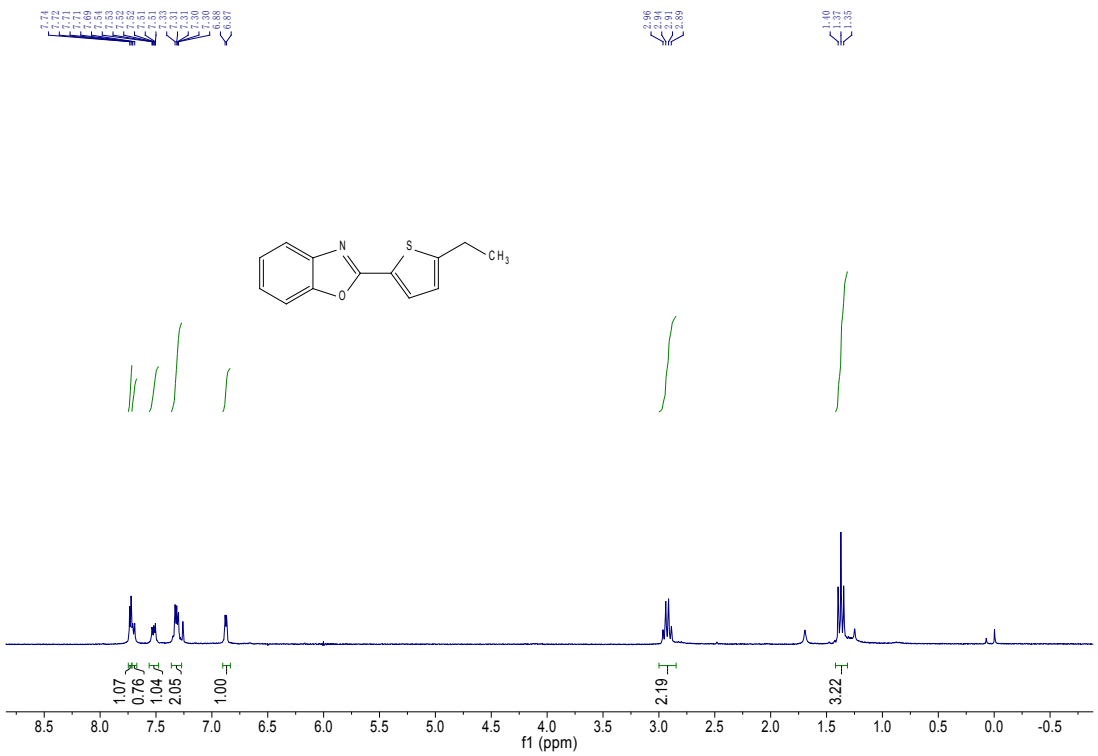
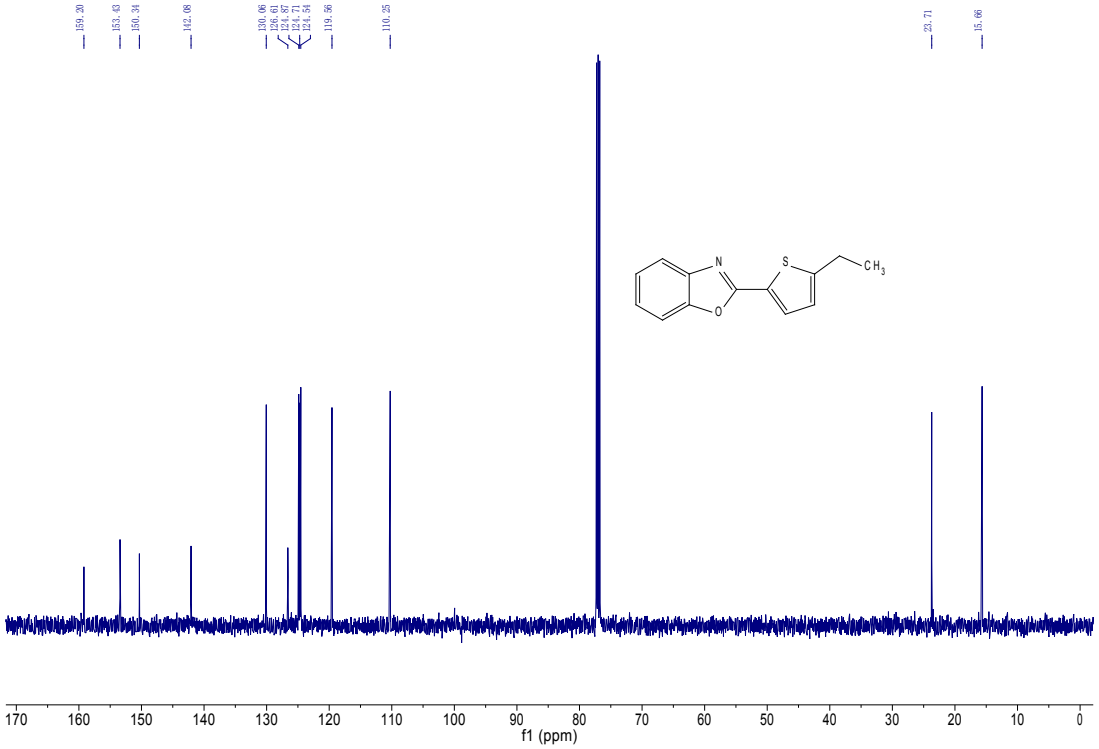
0.5
0.0
-0.5
f1 (ppm)

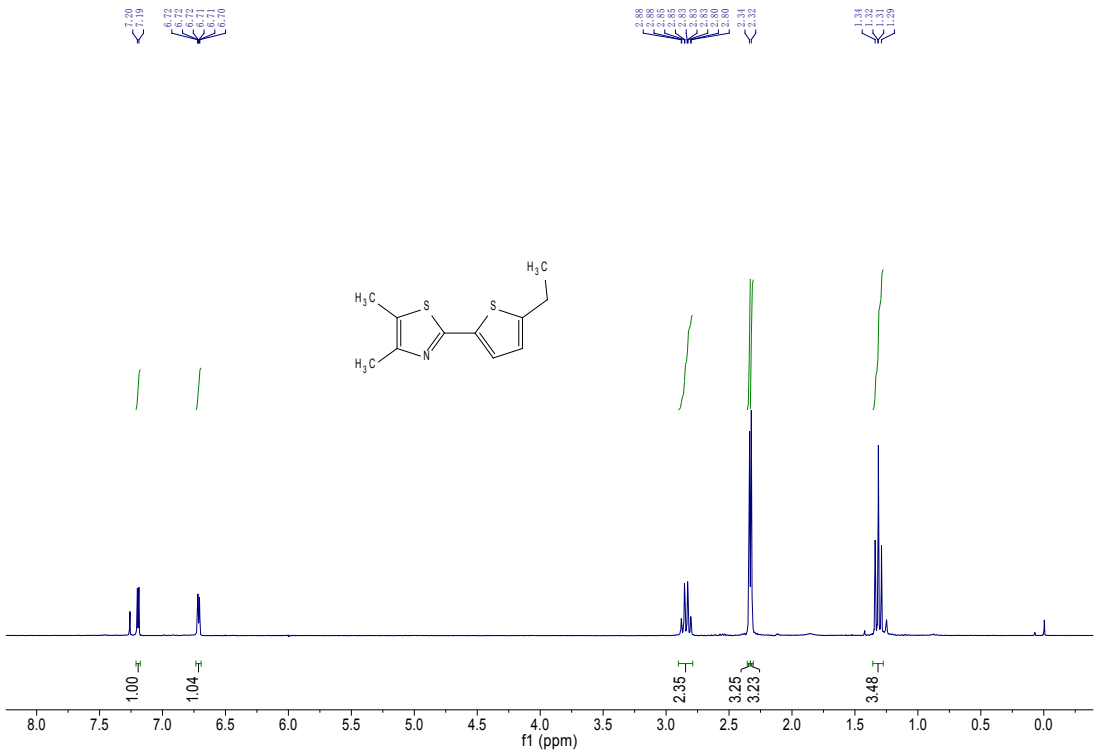

151.17
148.17
142.85
136.51
129.69
127.78
124.29
122.59
122.42
119.53
109.19
31.58
23.50
15.80
N
S
CH3
N
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

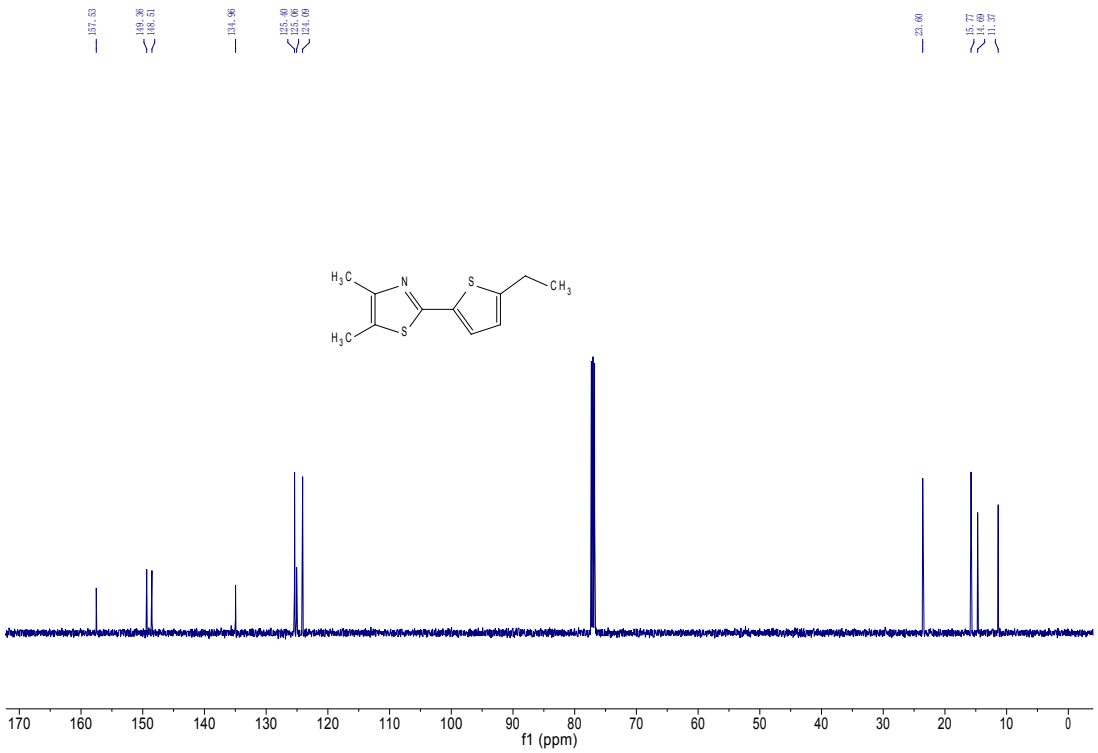
3lb


7.74
7.72
7.71
7.71
7.69
7.54
7.53
7.52
7.52
7.51
7.51
7.33
7.31
7.31
7.30
7.30
6.88
6.87
2.96
2.94
2.91
2.89
1.40
1.37
1.35
N
S
CH3
O
1.07
0.76
1.04
2.05
1.00
2.19
3.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

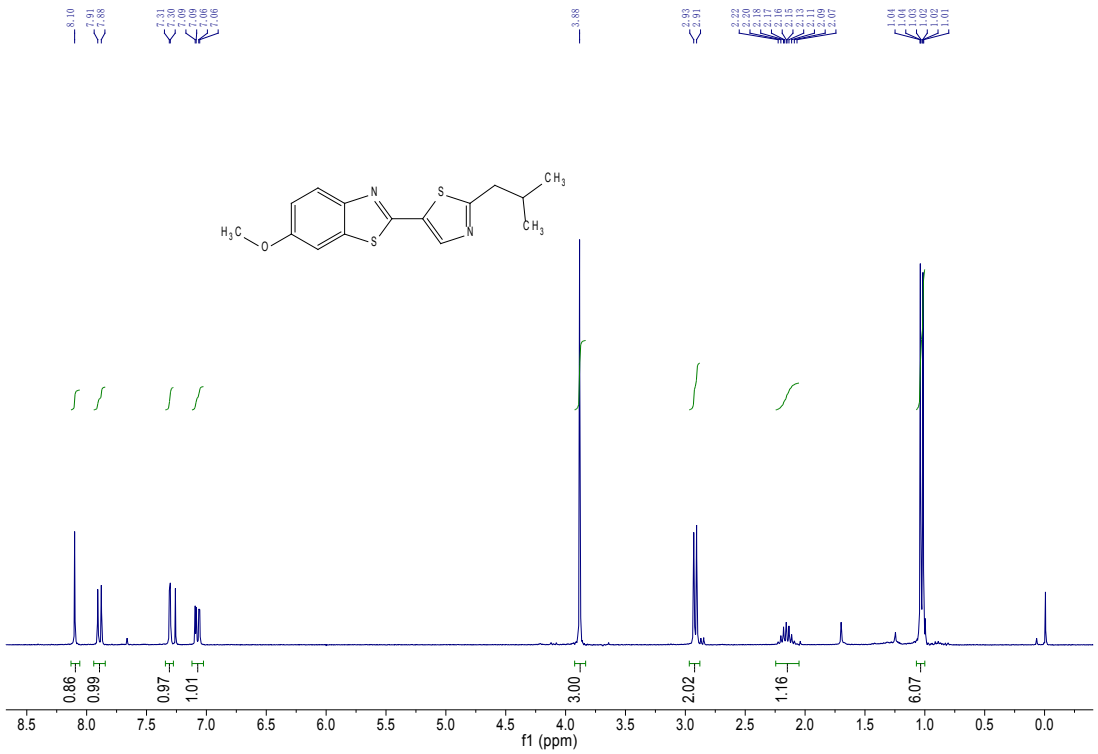

159.20
153.43
150.34
142.08
130.06
126.67
124.87
124.71
124.54
119.66
110.25
23.71
15.66
N
S
O
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

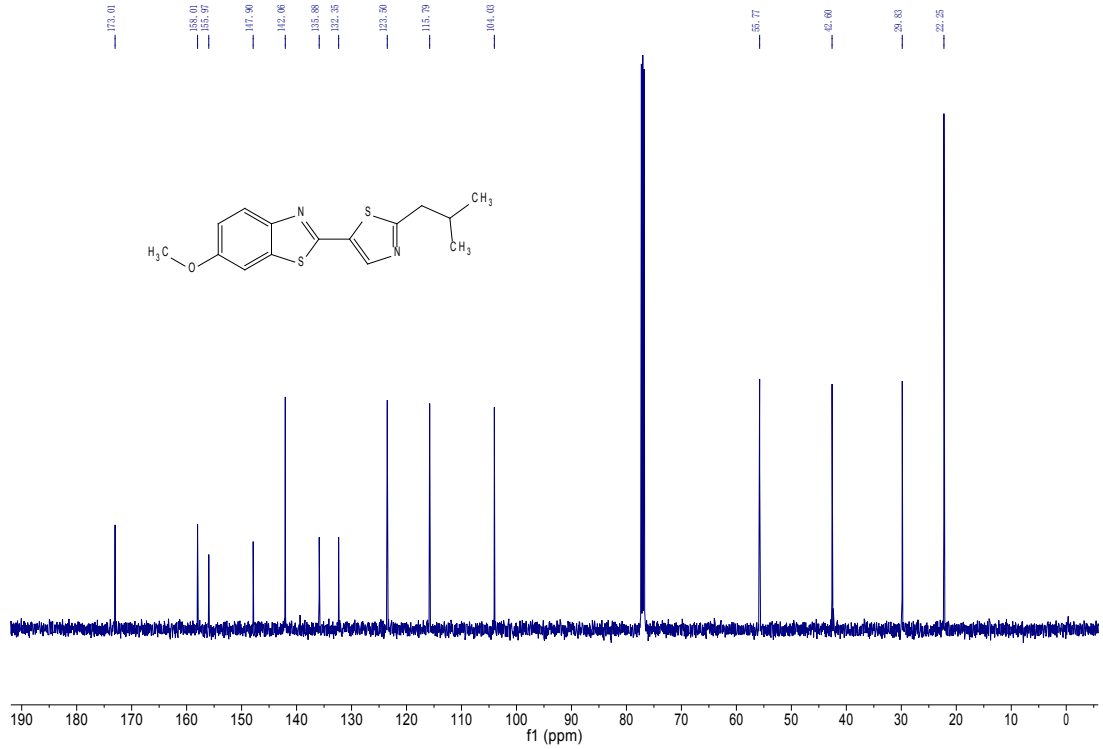
3mb


7.20
7.19
6.72
6.72
6.72
6.71
6.71
6.70
2.88
2.86
2.85
2.85
2.83
2.83
2.83
2.80
2.34
2.32
1.34
1.32
1.31
1.29
H3C
H3C
H3C
S
S
N
1.00
1.04
2.35
3.25
3.23
3.48
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

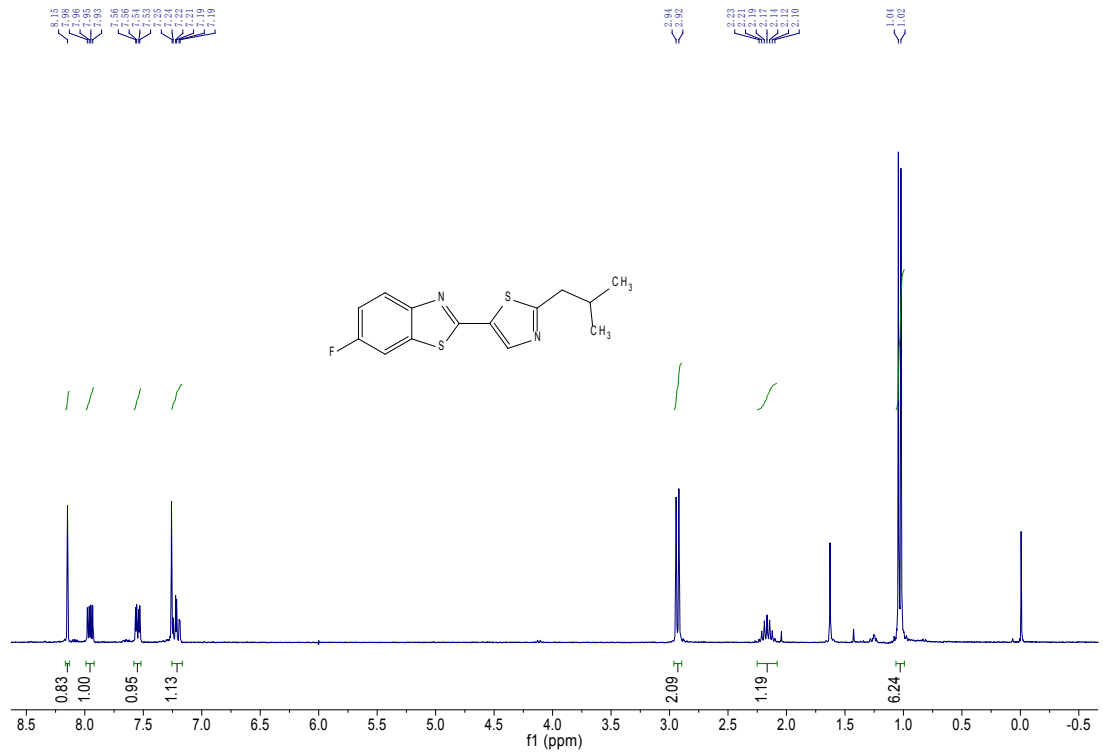

157.53
149.36
148.51
134.96
125.40
125.06
124.09
23.60
15.77
14.69
11.37
f1 (ppm)

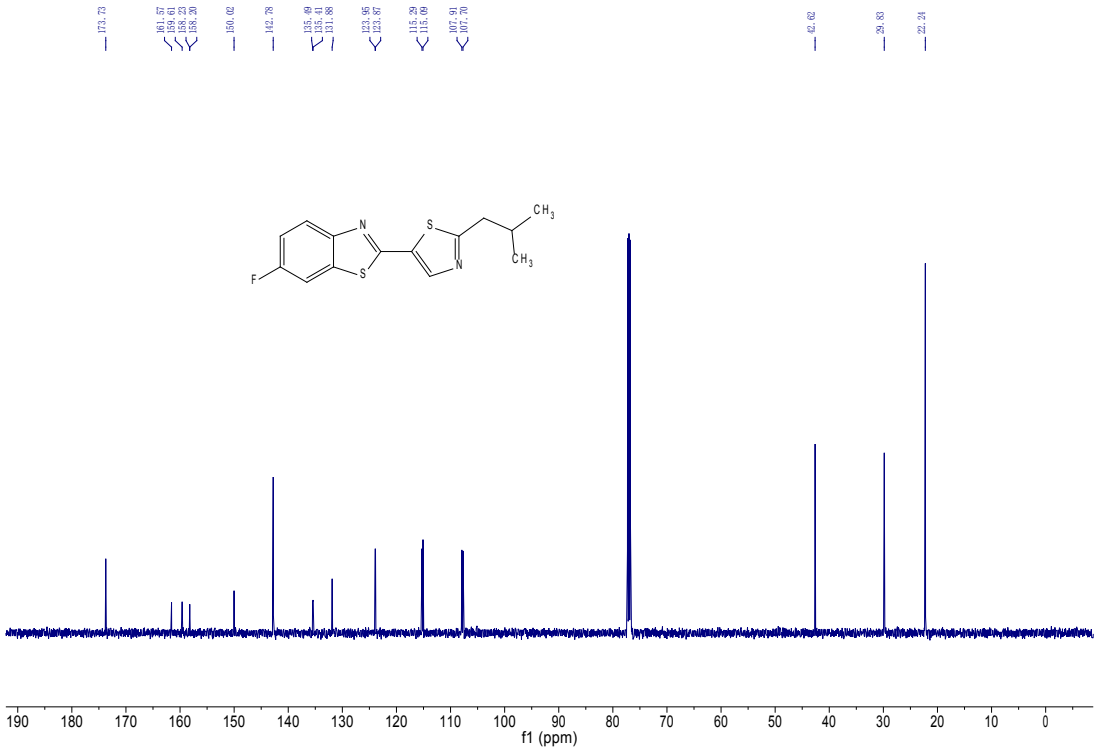
3bm


8.10
7.91
7.88
7.31
7.30
7.09
7.08
7.06
7.06
3.88
2.93
2.91
2.22
2.20
2.18
2.17
2.16
2.15
2.13
2.11
2.09
2.07
1.04
1.04
1.03
1.02
1.02
1.01
0.86
0.99
0.97
1.01
3.00
2.02
1.16
6.07
f1 (ppm)


173.01
168.01
155.97
147.90
142.06
135.88
122.35
123.50
115.79
104.03
55.77
42.60
29.83
22.25
f1 (ppm)

3dm


8.15
7.98
7.96
7.95
7.93
7.56
7.55
7.54
7.53
7.25
7.24
7.22
7.21
7.19
7.19
2.94
2.92
2.23
2.21
2.19
2.17
2.14
2.12
2.10
1.04
1.02
0.83
1.00
0.95
1.13
2.09
1.19
6.24
f1 (ppm)


173.73
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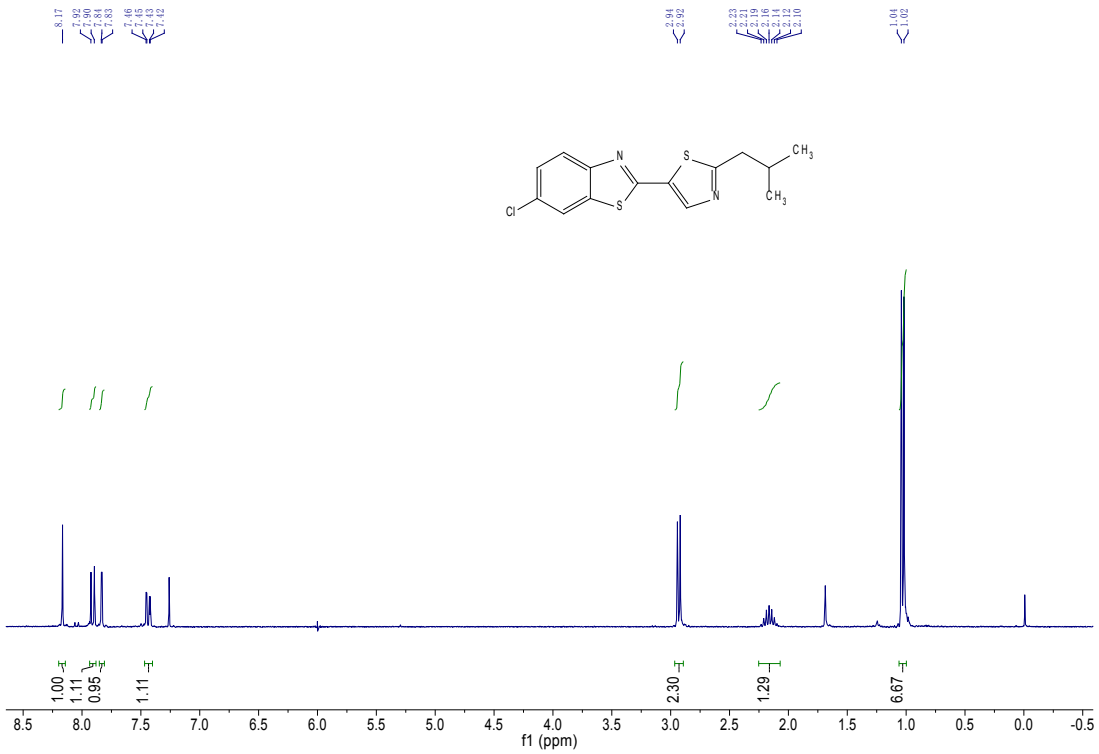
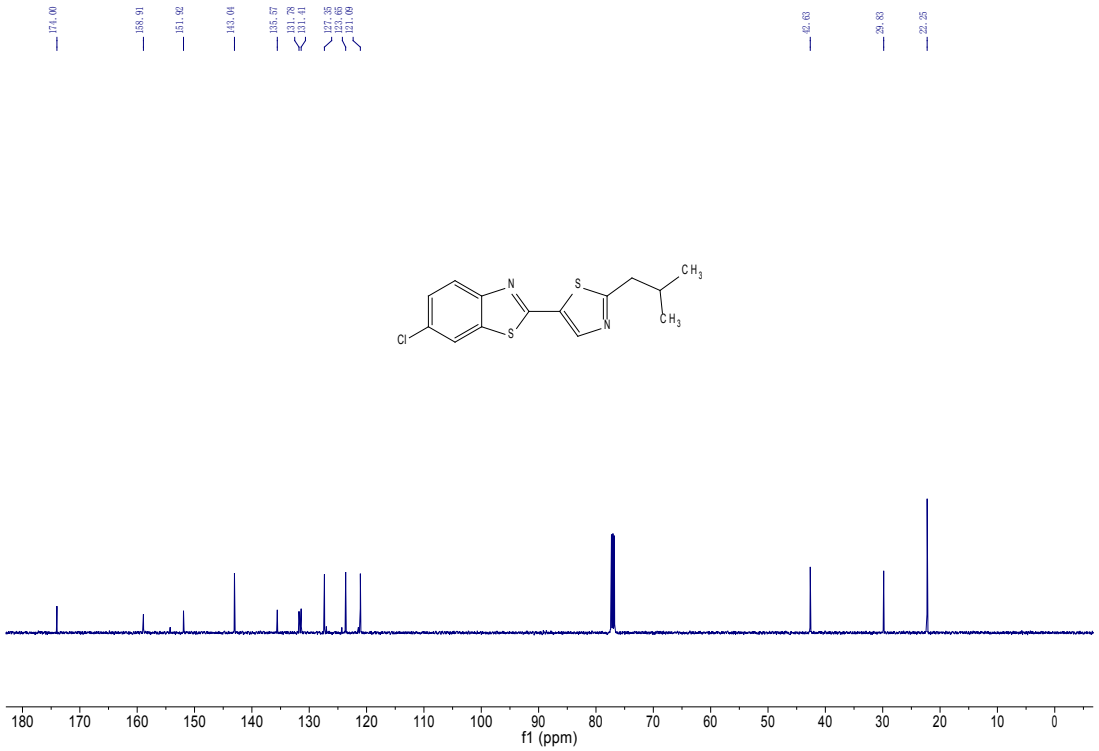
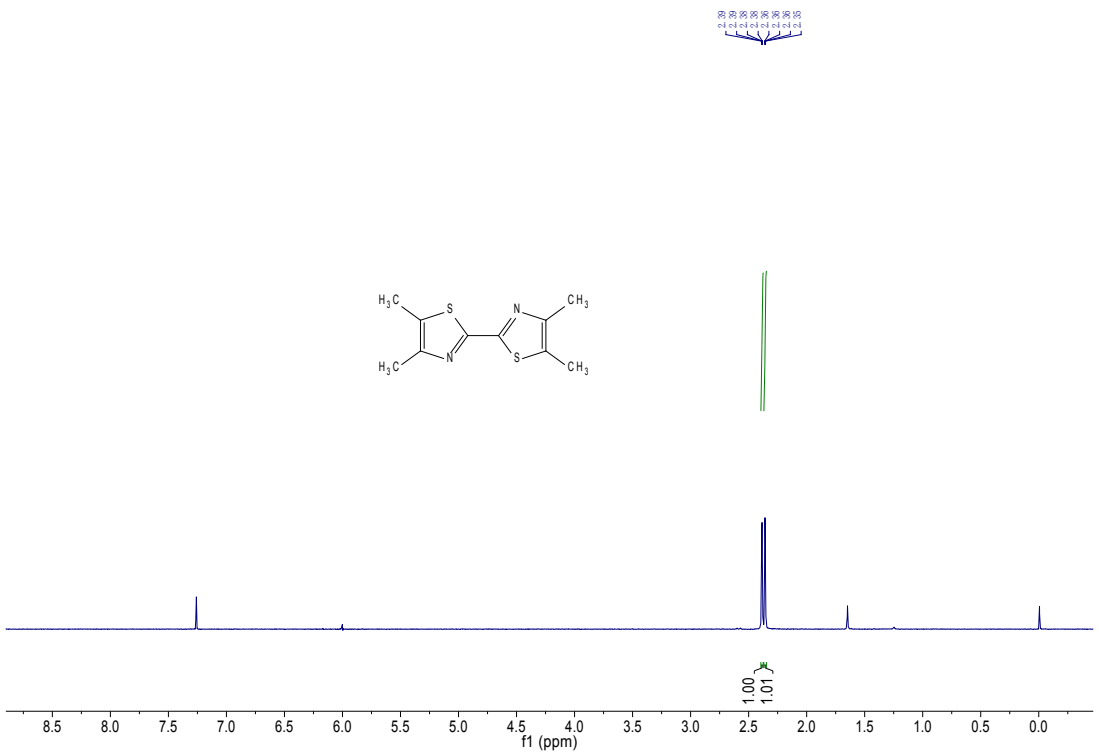
159.61
158.23
158.20
150.02
142.78
135.49
135.41
131.88
123.95
123.87
115.29
115.09
107.91
107.70
42.62
29.83
22.24
CH3
CH3
N
S
S
N
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3em

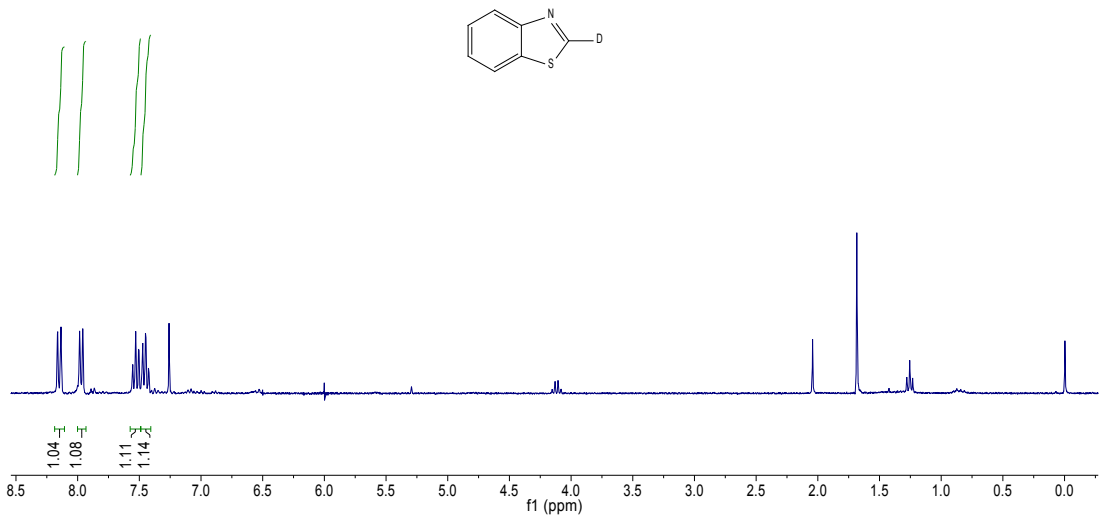

8.17
7.92
7.90
7.84
7.83
7.46
7.45
7.43
7.42
2.94
2.92
2.23
2.21
2.19
2.16
2.14
2.12
2.10
1.04
1.02
CH3
CH3
N
S
S
N
Cl
1.00
1.11
0.95
1.11
2.30
1.29
6.67
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


174.00
158.91
151.92
143.04
135.57
131.28
131.41
127.35
123.65
121.09
62.63
29.83
22.25
N
S
S
N
Cl
CH3
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

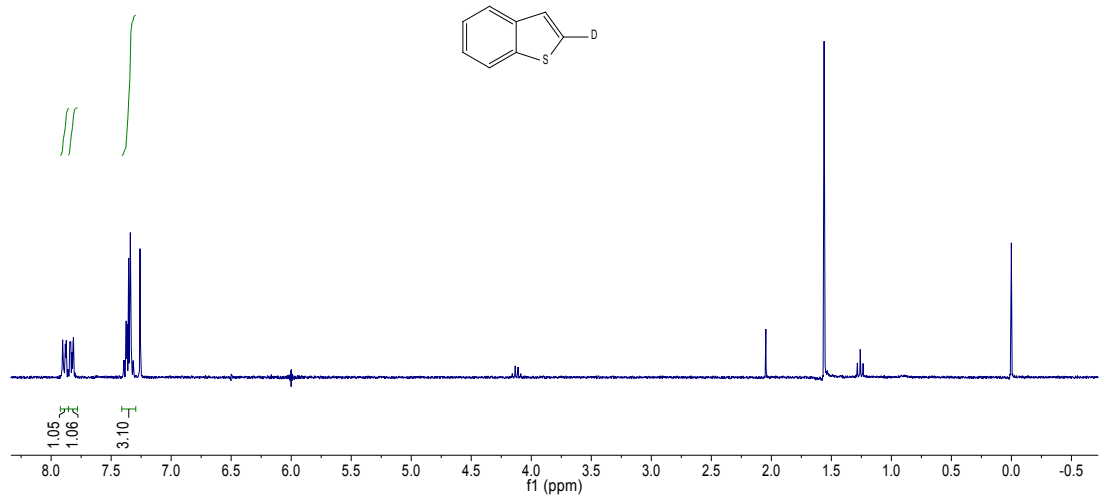
4m


2.39
2.39
2.38
2.38
2.36
2.36
2.36
2.35
H3C
S
N
CH3
H3C
N
S
CH3
1.00
1.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

1a-[D_1]


N
D
S
1.04
1.08
1.11
1.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2j-[D_1]


D
S
1.05
1.06
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)