

Supporting Information

Visible-Light-Promoted Photocatalyst-Free Alkylation and Acylation of Benzothiazoles

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1. General Methods

All reactions were carried out in 5 mL glass bottle. The reactions were monitored by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates. Visualization was accomplished by UV light (254 nm). The crude products were purified by flash column chromatography using silica gel (normal phase, 200-300 mesh). ^1H NMR spectra were recorded on a 400 MHz spectrometer at ambient temperature. Data were reported as follows: (1) chemical shift in parts per million (δ , ppm) from CDCl_3 (7.26 ppm); (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, and m = multiplet); (3) coupling constants (Hz). ^{13}C NMR spectra were recorded on a 100 MHz spectrometer at ambient temperature. Chemical shifts were reported in ppm from CDCl_3 (77.10 ppm). UV-VIS measurements were carried out on a Shimadzu UV-2501PC spectrophotometer. HR-MS analyses were carried out using a time-of-flight (TOF)-MS instrument with an electrospray ionization (ESI) source. All commercial materials were used as received unless otherwise noted.

Synthesis of 1,4-Dihydropyridines

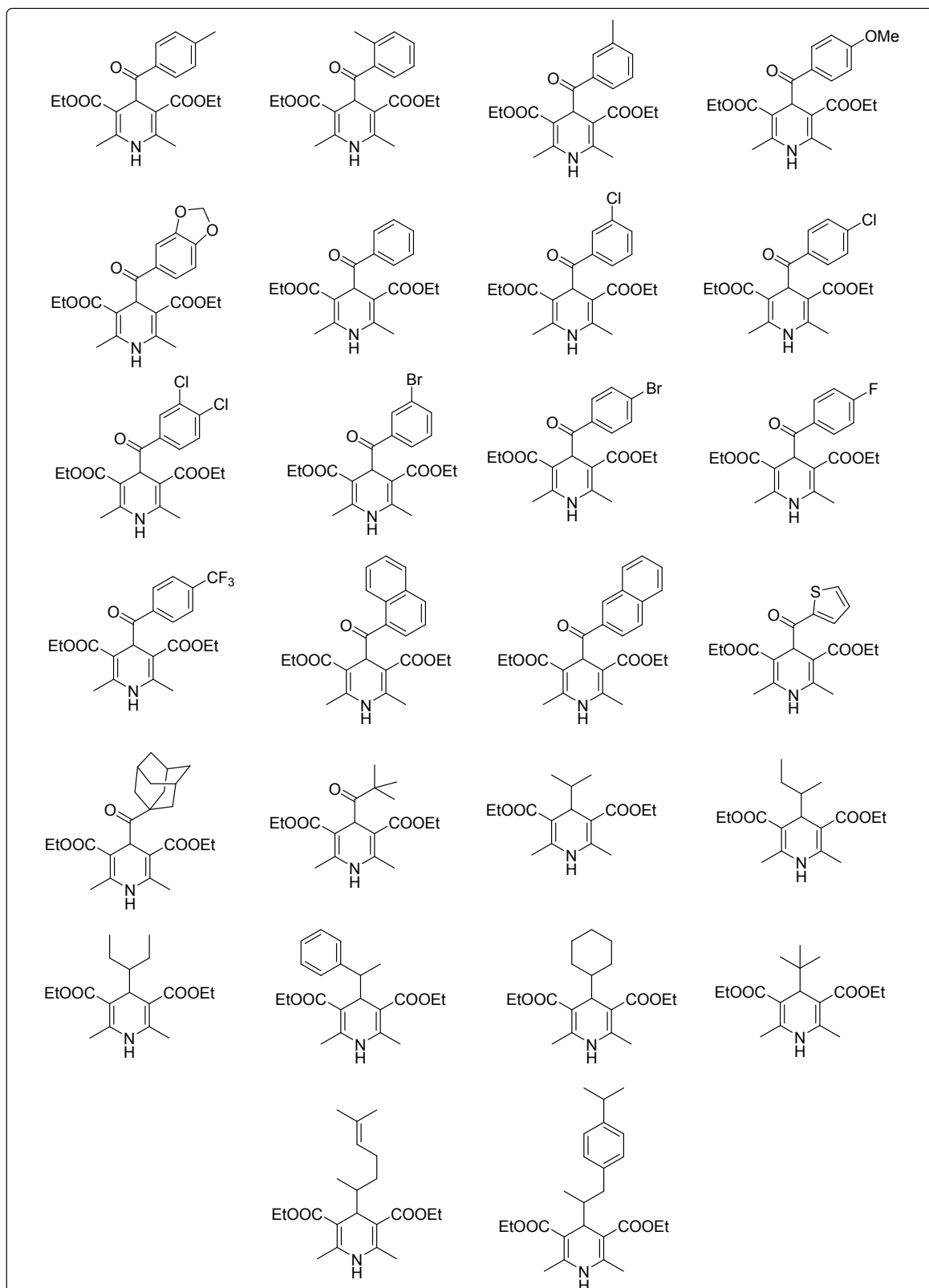
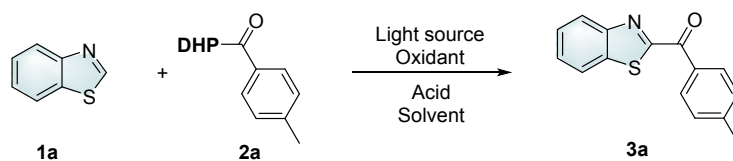


Figure S1 Hantzsch esters used in this study.^[1-6]

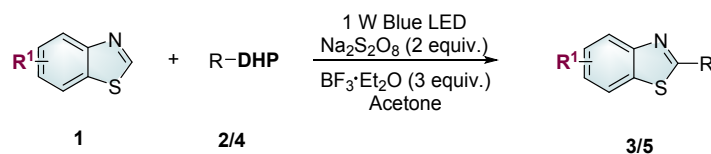
Compounds were synthesized via reported procedures.^[1-6]

Table S1 Optimization studies^a

Entry	Oxidant	Light source	Acid (equiv.)	Solvent	Yield ^b
1	Na ₂ S ₂ O ₈	Blue LED	TFA (3)	Dioxane	16
2	Na ₂ S ₂ O ₈	Blue LED	TFA (3)	DCM	37
3	Na ₂ S ₂ O ₈	Blue LED	TFA (3)	MeOH	36
4	Na ₂ S ₂ O ₈	Blue LED	TFA (3)	Acetone	43
5	BPO	Blue LED	TFA (3)	Acetone	23
6	DTBP	Blue LED	TFA (3)	Acetone	31
7	Na ₂ S ₂ O ₈	Blue LED	CH ₃ COOH (3)	Acetone	15
8	Na ₂ S ₂ O ₈	Blue LED	TsOH·H ₂ O (3)	Acetone	29
9	Na ₂ S ₂ O ₈	Blue LED	BF ₃ ·Et ₂ O (3)	Acetone	67(66) ^c
10	Na ₂ S ₂ O ₈	Green LED	BF ₃ ·Et ₂ O (3)	Acetone	18
11	Na ₂ S ₂ O ₈	White LED	BF ₃ ·Et ₂ O (3)	Acetone	22
12	Na ₂ S ₂ O ₈	-	BF ₃ ·Et ₂ O (3)	Acetone	trace
13 ^d	Na ₂ S ₂ O ₈	-	BF ₃ ·Et ₂ O (3)	Acetone	19
14	-	Blue LED	BF ₃ ·Et ₂ O (3)	Acetone	trace
15	Na ₂ S ₂ O ₈	Blue LED	BF ₃ ·Et ₂ O (2)	Acetone	55
16	Na ₂ S ₂ O ₈	Blue LED	BF ₃ ·Et ₂ O (4)	Acetone	47
17 ^e	Na ₂ S ₂ O ₈	Blue LED	BF ₃ ·Et ₂ O (3)	Acetone	58
18 ^f	Na ₂ S ₂ O ₈	Blue LED	BF ₃ ·Et ₂ O (3)	Acetone	61
19	(NH ₄) ₂ S ₂ O ₈	Blue LED	BF ₃ ·Et ₂ O (3)	Acetone	27
20	K ₂ S ₂ O ₈	Blue LED	BF ₃ ·Et ₂ O (3)	Acetone	27
21 ^g	Na ₂ S ₂ O ₈	-	BF ₃ ·Et ₂ O (3)	Acetone	trace

^a**1a** (0.1 mmol), **2a** (0.2 mmol), oxidant (0.2 mmol), acid (0.3 mmol), and solvent (0.5 mL) under 1 W blue LED at room temperature for 2 hours. ^bYield determined by ¹H NMR with 1,3,5-trimethoxybenzene as the internal standard. ^cIsolated yields. ^dat 70 °C. ^e1 equiv. **2a** used. ^f3 equiv. **2a** used. ^g0.4 equiv. AgNO₃ was added. TFA = trifluoroacetic acid. BPO = benzoyl peroxide. DTBP = di-*tert*-butyl peroxide.

2. General Procedure for the Acyl/Alkylation of Benzothiazoles



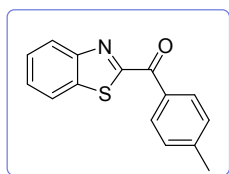
The 5 mL glass bottle was charged with benzothiazole (**1a**, 0.2 mmol, 27 mg), acyl-DHP reagent (**2a**, 0.4 mmol, 149 mg), $\text{Na}_2\text{S}_2\text{O}_8$ (2.0 equiv., 92 mg), and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (3.0 equiv., 85 mg) in acetone (1 mL), and the reaction mixture was stirred at blue LED ($\lambda_{\text{max}} = 465 \text{ nm}$) for 15 hours. After completion, the solvent was evaporated on the rotary evaporator. Then the reaction mixture was extracted with ethyl acetate, and the organic phase was washed with brine, dried over anhydrous Na_2SO_4 . After evaporating the solvent under reduced pressure, the crude product was purified by column chromatography using petroleum ether/ethyl acetate as the eluents.



Figure S2 Substrates that failed to react under the reaction conditions.



Figure S3 Detailed set-up and illumination system.



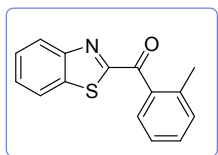
benzo[d]thiazol-2-yl(p-tolyl)methanone (**3a**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3a** (34 mg, 66% yield) as a yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.48 (d, $J = 8.3$ Hz, 2H), 8.25 – 8.23 (m, 1H), 8.02 – 8.00 (m, 1H), 7.60 – 7.52 (m, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 2.47 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 184.9, 167.4, 153.9, 145.0, 136.9, 132.4, 131.4, 129.2, 127.5, 126.8, 125.6, 122.1, 21.8.

HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{12}\text{NOS}^+$ $[\text{M}+\text{H}]^+$ 254.0634, found 254.0628.



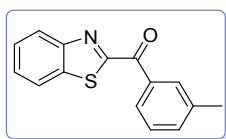
benzo[d]thiazol-2-yl(o-tolyl)methanone (**3b**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3b** (29 mg, 57% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 6.7 Hz, 1H), 8.01 (t, *J* = 7.5 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 6.4 Hz, 2H), 2.52 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 189.2, 167.5, 153.8, 139.1, 137.2, 135.1, 132.0, 131.5, 131.3, 127.7, 126.9, 125.8, 125.3, 122.2, 20.6.

HRMS (ESI): Calcd for C₁₅H₁₂NOS⁺ [M+H]⁺ 254.0634, found 254.0628.



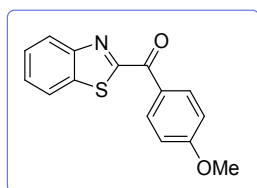
benzo[d]thiazol-2-yl(m-tolyl)methanone (**3c**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3c** (29 mg, 57% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.38 (d, *J* = 7.1 Hz, 1H), 8.28 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.49 – 7.42 (m, 2H), 2.48 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 185.7, 167.2, 153.8, 138.3, 137.0, 135.0, 134.7, 131.4, 128.6, 128.4, 127.5, 126.8, 125.7, 122.1, 21.4.

HRMS (ESI): Calcd for C₁₅H₁₂NOS⁺ [M+H]⁺ 254.0634, found 254.0631.



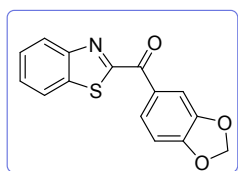
benzo[d]thiazol-2-yl(4-methoxyphenyl)methanone (3d)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3d** (35 mg, 64% yield) as a white solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.65 – 8.62 (m, 2H), 8.22 – 8.20 (m, 1H), 7.99 – 7.97 (m, 1H), 7.57 – 7.48 (m, 2H), 7.04 – 7.00 (m, 2H), 3.90 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 183.3, 167.9, 164.4, 153.9, 136.9, 133.8, 127.7, 127.3, 126.8, 125.5, 122.1, 113.9, 55.5.

HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{12}\text{NO}_2\text{S}^+$ $[\text{M}+\text{H}]^+$ 270.0583, found 270.0572.



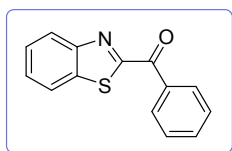
benzo[d][1,3]dioxol-5-yl(benzo[d]thiazol-2-yl)methanone (3e)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3e** (39 mg, 68% yield) as a yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.42 – 8.39 (m, 1H), 8.23 (d, $J = 7.6$ Hz, 1H), 8.07 (d, $J = 1.7$ Hz, 1H), 8.01 (d, $J = 7.0$ Hz, 1H), 7.60 – 7.52 (m, 2H), 6.98 (d, $J = 8.3$ Hz, 1H), 6.11 (s, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 182.9, 167.6, 153.8, 152.7, 148.0, 136.9, 129.3, 128.7, 127.4, 126.8, 125.6, 122.1, 110.7, 108.2, 102.0.

HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{10}\text{NO}_3\text{S}^+$ $[\text{M}+\text{H}]^+$ 284.0376, found 284.0370.



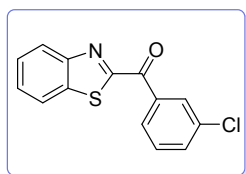
benzo[d]thiazol-2-yl(phenyl)methanone (3f)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3f** (20 mg, 40% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, *J* = 7.6 Hz, 2H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.61 – 7.54 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 185.4, 167.1, 153.9, 137.0, 135.0, 133.9, 131.3, 128.5, 127.6, 126.9, 125.7, 122.1.

HRMS (ESI): Calcd for C₁₄H₁₀NOS⁺ [M+H]⁺ 240.0478, found 240.0476.



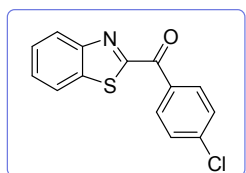
benzo[d]thiazol-2-yl(3-chlorophenyl)methanone (**3g**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3g** (19 mg, 35% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.56 (s, 1H), 8.48 (d, *J* = 7.8 Hz, 1H), 8.27 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.49 (m, 4H).

¹³C NMR (100 MHz, CDCl₃) δ 184.0, 166.4, 153.8, 137.1, 136.4, 134.7, 133.8, 131.1, 129.8, 129.4, 127.9, 127.1, 125.9, 122.2.

HRMS (ESI): Calcd for C₁₄H₉ClNOS⁺ [M+H]⁺ 274.0088, found 274.0084.



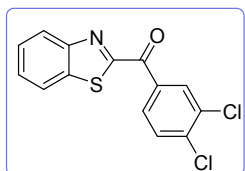
benzo[d]thiazol-2-yl(4-chlorophenyl)methanone (**3h**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3h** (22 mg, 40% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.57 – 8.54 (m, 2H), 8.25 – 8.22(m, 1H), 8.03 – 8.01 (m, 1H), 7.62 – 7.58 (m, 1H), 7.57 – 7.55 (m, 1H), 7.55 – 7.52 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 184.0, 166.8, 153.8, 140.6, 137.0, 133.2, 132.7, 128.8, 127.8, 127.0, 125.7, 122.2.

HRMS (ESI): Calcd for C₁₄H₉ClNOS⁺ [M+H]⁺ 274.0088, found 274.0083.



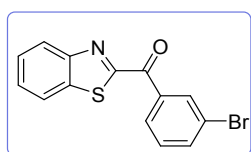
benzo[d]thiazol-2-yl(3,4-dichlorophenyl)methanone (3i)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3i** (24 mg, 39% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, *J* = 2.0 Hz, 1H), 8.48 – 8.45 (m, 1H), 8.27 – 8.25 (m, 1H), 8.03 – 8.01 (m, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.55 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 182.9, 166.2, 153.7, 138.7, 137.1, 134.4, 133.1, 133.1, 130.6, 130.3, 128.0, 127.1, 125.9, 122.2.

HRMS (ESI): Calcd for C₁₄H₈Cl₂NOS⁺ [M+H]⁺ 307.9698, found 307.9694.



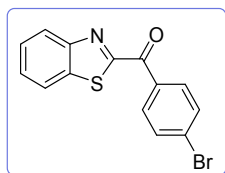
benzo[d]thiazol-2-yl(3-bromophenyl)methanone (3j)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3j** (23 mg, 36% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.70 (t, *J* = 1.7 Hz, 1H), 8.54 – 8.52 (m, 1H), 8.26 (d, *J* = 7.7 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.5 Hz, 2H), 7.44 (t, *J* = 7.9 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 183.9, 166.4, 153.8, 137.0, 136.7, 134.0, 131.9, 130.0, 129.9, 127.9, 127.1, 125.9, 122.6, 122.2.

HRMS (ESI): Calcd for $\text{C}_{14}\text{H}_8\text{BrNNaOS}^+$ $[\text{M}+\text{Na}]^+$ 339.9402, found 339.9397.



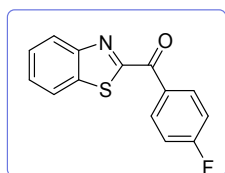
benzo[d]thiazol-2-yl(4-bromophenyl)methanone (**3k**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3k** (32 mg, 50% yield) as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 8.48 (d, $J = 7.7$ Hz, 2H), 8.24 (d, $J = 7.8$ Hz, 1H), 8.02 (d, $J = 7.5$ Hz, 1H), 7.71 (d, $J = 7.6$ Hz, 2H), 7.62 – 7.54 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 184.3, 166.7, 153.8, 137.0, 133.7, 132.7, 131.8, 129.5, 127.8, 127.0, 125.8, 122.2.

HRMS (ESI): Calcd for $\text{C}_{14}\text{H}_9\text{BrNOS}^+$ $[\text{M}+\text{H}]^+$ 317.9583, found 317.9581.



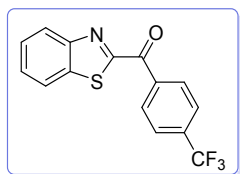
benzo[d]thiazol-2-yl(4-fluorophenyl)methanone (**3l**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3l** (29 mg, 61% yield) as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 8.48 (d, $J = 7.7$ Hz, 2H), 8.24 (d, $J = 7.8$ Hz, 1H), 8.02 (d, $J = 7.5$ Hz, 1H), 7.71 (d, $J = 7.6$ Hz, 2H), 7.62 – 7.54 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 183.5, 167.3 (d, $J = 64.8$ Hz, 1C), 165.1, 153.8, 137.0, 134.2 (d, $J = 9.4$ Hz, 1C), 131.3 (d, $J = 2.9$ Hz, 1C), 127.7, 127.0, 125.7, 122.2, 115.7 (d, $J = 21.7$ Hz, 1C).

HRMS (ESI): Calcd for $C_{14}H_9FNOS^+$ $[M+H]^+$ 258.0383, found 258.0381.



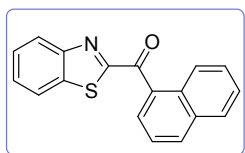
benzo[d]thiazol-2-yl(4-(trifluoromethyl)phenyl)methanone (3m)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3m** (21 mg, 34% yield) as a yellow solid.

1H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, $J = 8.1$ Hz, 2H), 8.26 – 8.24 (m, 1H), 8.05 – 8.03 (m, 1H), 7.83 (d, $J = 8.3$ Hz, 2H), 7.64 – 7.56 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 184.5, 166.2, 153.8, 137.8, 137.1, 134.7 (q, $J = 32.9$ Hz, 1C), 131.5, 128.0, 127.2, 125.9, 125.4 (q, $J = 3.7$ Hz, 1C), 123.7 (q, $J = 272.7$ Hz, 1C), 122.2.

HRMS (ESI): Calcd for $C_{15}H_9F_3NOS^+$ $[M+H]^+$ 308.0351, found 208.0347.



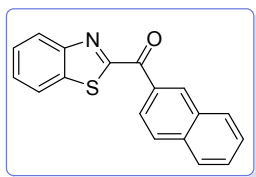
benzo[d]thiazol-2-yl(naphthalen-1-yl)methanone (3n)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3n** (23 mg, 40% yield) as a yellow solid.

1H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, $J = 8.3$ Hz, 1H), 8.36 (d, $J = 7.2$ Hz, 1H), 8.20 – 8.17 (m, 1H), 8.11 (d, $J = 8.2$ Hz, 1H), 8.05 – 8.03 (m, 1H), 7.94 (d, $J = 7.7$ Hz, 1H), 7.63 – 7.55 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 168.0, 153.7, 137.3, 133.9, 133.5, 132.2, 131.9, 131.1, 128.6, 128.0, 127.7, 126.9, 126.5, 125.8, 125.4, 124.3, 122.2.

HRMS (ESI): Calcd for $C_{18}H_{11}NNaOS^+$ $[M+Na]^+$ 312.0454, found 312.0448.



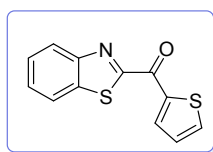
benzo[d]thiazol-2-yl(naphthalen-2-yl)methanone (**3o**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3o** (31 mg, 53% yield) as a yellow solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.38 (s, 1H), 8.48 (d, $J = 8.6$ Hz, 1H), 8.33 (d, $J = 7.9$ Hz, 1H), 8.08 – 8.03 (m, 2H), 8.01 (d, $J = 8.6$ Hz, 1H), 7.95 (d, $J = 8.1$ Hz, 1H), 7.66 – 7.54 (m, 4H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 185.1, 167.4, 153.9, 137.0, 135.9, 134.3, 132.4, 132.2, 130.2, 129.0, 128.3, 127.8, 127.6, 126.9, 126.7, 125.8, 125.7, 122.2.

HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{12}\text{NOS}^+$ $[\text{M}+\text{H}]^+$ 290.0634, found 290.0625.



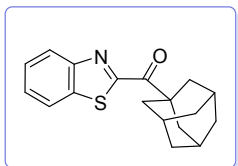
benzo[d]thiazol-2-yl(thiophen-2-yl)methanone (**3p**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3p** (20 mg, 40% yield) as a white solid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.77 (d, $J = 3.9$ Hz, 1H), 8.25 (d, $J = 8.2$ Hz, 1H), 8.01 (d, $J = 7.7$ Hz, 1H), 7.84 (d, $J = 4.9$ Hz, 1H), 7.61 – 7.52 (m, 2H), 7.27 (d, $J = 4.1$ Hz, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 177.0, 166.6, 153.7, 139.7, 137.4, 137.0, 136.8, 128.4, 127.5, 126.9, 125.5, 122.2.

HRMS (ESI): Calcd for $\text{C}_{12}\text{H}_8\text{NOS}_2^+$ $[\text{M}+\text{H}]^+$ 246.0042, found 246.0038.



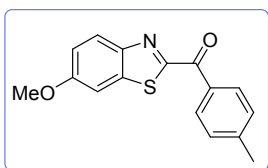
((1*r*,3*R*,5*S*)-adamantan-1-yl)(benzo[d]thiazol-2-yl)methanone (3q)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3q** (31 mg, 51% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.47 (m, 2H), 2.31 (d, *J* = 2.6 Hz, 6H), 2.14 (s, 3H), 1.84 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 199.3, 166.2, 153.8, 136.5, 127.2, 126.5, 125.5, 122.0, 46.9, 38.3, 36.7, 28.1.

HRMS (ESI): Calcd for C₁₈H₁₉NNaOS⁺ [M+Na]⁺ 320.1080, found 320.1075.



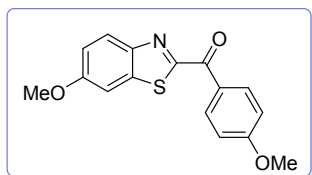
(6-methoxybenzo[d]thiazol-2-yl)(p-tolyl)methanone (3s)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3s** (45 mg, 75% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 8.1 Hz, 2H), 8.09 (d, *J* = 9.1 Hz, 1H), 7.39 (d, *J* = 2.3 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.14 (m, 1H), 3.91 (s, 3H), 2.45 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 184.7, 164.9, 159.6, 148.5, 144.7, 139.0, 132.6, 131.3, 129.2, 126.4, 117.5, 103.4, 55.8, 21.8.

HRMS (ESI): Calcd for C₁₆H₁₄NO₂S⁺ [M+H]⁺ 284.0740, found 284.0734.



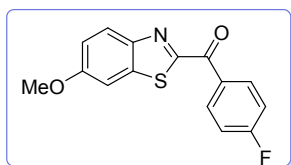
(6-methoxybenzo[d]thiazol-2-yl)(4-methoxyphenyl)methanone (3t)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3t** (43 mg, 72% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.63 (d, *J* = 9.0 Hz, 2H), 8.09 (d, *J* = 9.1 Hz, 1H), 7.40 (d, *J* = 2.5 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.04 – 7.01 (m, 2H), 3.91 (d, *J* = 1.3 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 183.2, 165.4, 164.2, 159.5, 148.5, 138.9, 133.7, 127.9, 126.2, 117.4, 113.8, 103.4, 55.8, 55.5.

HRMS (ESI): Calcd for C₁₆H₁₄NO₃S⁺ [M+H]⁺ 300.0689, found 300.0693.



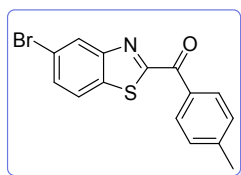
(4-fluorophenyl)(6-methoxybenzo[d]thiazol-2-yl)methanone (3u)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3u** (45 mg, 90% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.66 – 8.63 (m, 2H), 8.09 (d, *J* = 9.1 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.24 – 7.17 (m, 3H), 3.92 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 183.3, 167.5, 164.7 (d, *J* = 48.17 Hz, 1C), 159.8, 148.4, 139.1, 133.9 (d, *J* = 9.3 Hz, 1C), 131.4 (d, *J* = 2.9 Hz, 1C), 117.7, 115.7, 115.5, 103.3, 55.8.

HRMS (ESI): Calcd for C₁₅H₁₁FNO₂S⁺ [M+H]⁺ 288.0489, found 288.0482.



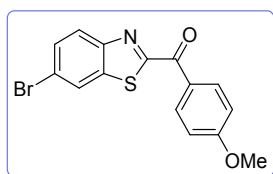
(5-bromobenzo[d]thiazol-2-yl)(p-tolyl)methanone (3v)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3v** (21 mg, 32% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.47 (d, *J* = 8.2 Hz, 2H), 8.16 (d, *J* = 1.6 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 184.4, 169.0, 154.9, 145.3, 135.7, 132.1, 131.4, 130.6, 129.3, 128.3, 123.2, 120.4, 21.8.

HRMS (ESI): Calcd for C₁₅H₁₀BrNNaOS⁺ [M+Na]⁺ 353.9559, found 353.9552.



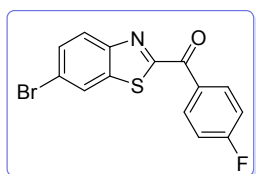
(6-bromobenzo[d]thiazol-2-yl)(4-methoxyphenyl)methanone (3w)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3w** (21 mg, 32% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.64 (d, *J* = 9.0 Hz, 2H), 8.16 (d, *J* = 1.8 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.68 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.06 – 7.02 (m, 2H), 3.93 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 182.9, 164.6, 152.7, 143.8, 138.5, 133.9, 130.6, 127.6, 126.7, 124.8, 121.7, 114.0, 55.7.

HRMS (ESI): Calcd for C₁₅H₁₁BrNO₂S⁺ [M+H]⁺ 347.09688, found 347.9685.



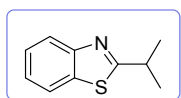
(6-bromobenzo[d]thiazol-2-yl)(4-fluorophenyl)methanone (**3x**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **3x** (38 mg, 57% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.68 – 8.64 (m, 2H), 8.17 (d, *J* = 1.8 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.23 (d, *J* = 8.7 Hz, 2H)

¹³C NMR (100 MHz, CDCl₃) δ 183.1, 167.7 (d, *J* = 23.4 Hz, 1C), 165.2, 152.6, 138.5, 134.1 (d, *J* = 9.3 Hz, 1C), 131.0, 130.7, 126.7, 124.8, 122.0, 115.8 (d, *J* = 2.1 Hz, 1C).

HRMS (ESI): Calcd for C₁₄H₈BrFNOS⁺ [M+H]⁺ 335.9489, found 335.9478.



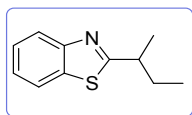
2-isopropylbenzo[d]thiazolen (**5a**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5a** (21 mg, 58% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.35 – 7.31 (m, 1H), 3.47 – 3.37 (m, 1H), 1.48 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 178.6, 153.1, 134.7, 125.8, 124.5, 122.5, 121.5, 34.1, 22.9.

HRMS (ESI): Calcd for C₁₀H₁₂NS⁺ [M+H]⁺ 178.0685, found 178.0684.



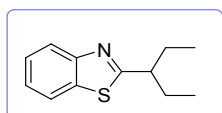
2-(sec-butyl)benzo[d]thiazole (**5b**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5b** (20 mg, 52% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.35 – 7.31 (m, 1H), 3.25 – 3.17 (m, 1H), 1.97 – 1.86 (m, 1H), 1.83 – 1.72 (m, 1H), 1.45 (d, *J* = 6.9 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 177.9, 153.1, 134.6, 125.8, 124.5, 122.6, 121.5, 41.0, 30.6, 20.7, 11.8.

HRMS (ESI): Calcd for C₁₁H₁₄NS⁺ [M+H]⁺ 192.0841, found 192.0839.



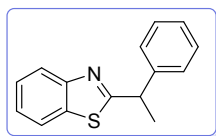
2-(pentan-3-yl)benzo[d]thiazole (**5c**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5c** (21 mg, 51% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.38 – 7.34 (m, 1H), 3.06 – 2.99 (m, 1H), 1.92 – 1.80 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 176.8, 153.0, 134.7, 125.7, 124.5, 122.6, 121.5, 48.7, 28.9, 11.9.

HRMS (ESI): Calcd for C₁₂H₁₆NS⁺ [M+H]⁺ 206.0998, found 206.0996.



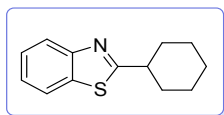
2-(1-phenylethyl)benzo[d]thiazole (**5d**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5d** (17 mg, 35% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.25 (m, 7H), 4.58 (q, *J* = 7.2 Hz, 1H), 1.87 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 176.3, 153.1, 143.1, 135.3, 128.7, 127.6, 127.2, 125.8, 124.7, 122.8, 121.4, 44.8, 21.2.

HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{14}\text{NS}^+$ $[\text{M}+\text{H}]^+$ 240.0841, found 240.0832.



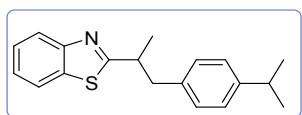
2-cyclohexylbenzo[d]thiazole (5e)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5e** (34 mg, 75% yield) as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.45 – 7.40 (m, 1H), 7.34 – 7.29 (m, 1H), 3.12 – 3.06 (m, 1H), 2.21 – 2.18 (m, 2H), 1.90 – 1.85 (m, 2H), 1.77 – 1.74 (m, 1H), 1.68 – 1.58 (m, 2H), 1.49 – 1.38 (m, 2H), 1.36 – 1.28 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 176.5, 152.0, 133.5, 124.7, 123.4, 121.5, 120.5, 42.4, 32.3, 25.0, 24.7.

HRMS (ESI): Calcd for $\text{C}_{13}\text{H}_{16}\text{NS}^+$ $[\text{M}+\text{H}]^+$ 218.0998, found 218.0996.



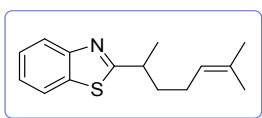
2-(1-(4-isopropylphenyl)propan-2-yl)benzo[d]thiazole (5f)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5f** (24 mg, 52% yield) as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 7.7$ Hz, 1H), 7.46 – 7.42 (m, 1H), 7.35 – 7.31 (m, 1H), 7.13 (s, 4H), 3.60 – 3.51 (m, 1H), 3.32 – 3.27 (m, 1H), 2.92 – 2.84 (m, 2H), 1.42 (d, $J = 6.9$ Hz, 3H), 1.22 (d, $J = 6.9$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 177.1, 153.1, 146.9, 136.5, 134.7, 129.0, 126.4, 125.8, 124.6, 122.6, 121.6, 43.0, 41.1, 33.7, 24.0, 20.3.

HRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{22}\text{NS}^+$ $[\text{M}+\text{H}]^+$ 296.1467, found 296.1462.



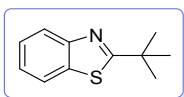
2-(6-methylhept-5-en-2-yl)benzo[d]thiazole (**5g**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5g** (16 mg, 34% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.35 – 7.31 (m, 1H), 5.12 (t, *J* = 7.1 Hz, 1H), 3.34 – 3.26 (m, 1H), 2.11 – 2.00 (m, 2H), 1.98 – 1.89 (m, 1H), 1.79 – 1.72 (m, 1H), 1.66 (s, 3H), 1.56 (s, 3H), 1.45 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 177.9, 153.1, 134.7, 132.3, 125.7, 124.5, 123.5, 122.6, 121.5, 39.0, 37.6, 25.8, 25.7, 21.2, 17.7.

HRMS (ESI): Calcd for C₁₅H₂₀NS⁺ [M+H]⁺ 246.1311, found 246.1307.



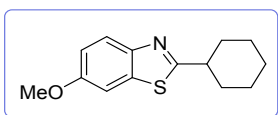
2-(tert-butyl)benzo[d]thiazole (**5h**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5h** (23 mg, 63% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.89 (m, 1H), 7.76 – 7.73 (m, 1H), 7.36 – 7.32 (m, 1H), 7.25 – 7.21 (m, 1H), 1.43 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 181.8, 153.2, 134.9, 125.7, 124.5, 122.6, 121.4, 38.3, 30.7.

HRMS (ESI): Calcd for C₁₁H₁₄NS⁺ [M+H]⁺ 192.0841, found 192.0839.



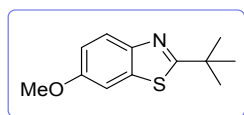
2-cyclohexyl-6-methoxybenzo[d]thiazole (**5i**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5i** (45 mg, 90% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.9 Hz, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 7.04 – 7.02 (m, 1H), 3.85 (s, 3H), 3.08 – 3.01 (m, 1H), 2.20 – 2.16 (m, 2H), 1.89 – 1.85 (m, 2H), 1.77 – 1.72 (m, 1H), 1.66 – 1.56 (m, 2H), 1.48 – 1.37 (m, 2H), 1.35 – 1.24 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 175.0, 157.2, 147.6, 135.7, 122.9, 114.9, 104.3, 55.7, 43.3, 33.4, 26.0, 25.8.

HRMS (ESI): Calcd for C₁₄H₁₈NOS⁺ [M+H]⁺ 248.1104, found 248.1098.



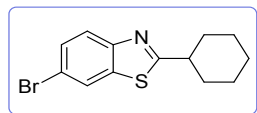
2-(tert-butyl)-6-methoxybenzo[d]thiazole (**5j**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5j** (39 mg, 88% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.9 Hz, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.04 – 7.02 (m, 1H), 3.85 (s, 3H), 1.50 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 179.2, 157.2, 147.7, 136.2, 123.1, 114.8, 104.1, 55.7, 38.1, 30.7.

HRMS (ESI): Calcd for C₁₂H₁₆NOS⁺ [M+H]⁺ 222.0947, found 222.0941.



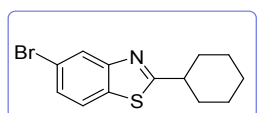
6-bromo-2-cyclohexylbenzo[d]thiazole (**5k**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5k** (33 mg, 56% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 1.8 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.44 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.12 – 3.05 (m, 1H), 2.20 – 2.17 (m, 2H), 1.90 – 1.86 (m, 2H), 1.78 – 1.74 (m, 1H), 1.69 – 1.57 (m, 2H), 1.49 – 1.38 (m, 2H), 1.36 – 1.28 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 178.4, 153.3, 132.3, 126.5, 124.4, 121.5, 118.3, 42.4, 32.3, 24.9, 24.7.

HRMS (ESI): Calcd for C₁₃H₁₅BrNS⁺ [M+H]⁺ 296.0103, found 296.0099.



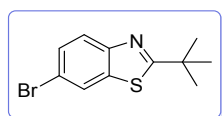
5-bromo-2-cyclohexylbenzo[d]thiazole (**5l**)

Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5l** (29 mg, 55% yield) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 1.9 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.53 (dd, *J* = 8.7, 1.9 Hz, 1H), 3.11 – 3.03 (m, 1H), 2.21 – 2.17 (m, 2H), 1.90 – 1.86 (m, 2H), 1.78 – 1.74 (m, 1H), 1.67 – 1.60 (m, 2H), 1.49 – 1.38 (m, 2H), 1.36 – 1.28 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 178.4, 153.3, 132.3, 126.5, 124.4, 121.5, 118.3, 42.4, 32.3, 24.9, 24.7.

HRMS (ESI): Calcd for C₁₃H₁₅BrNS⁺ [M+H]⁺ 296.0103, found 296.0099.



6-bromo-2-(tert-butyl)benzo[d]thiazole (**5m**)

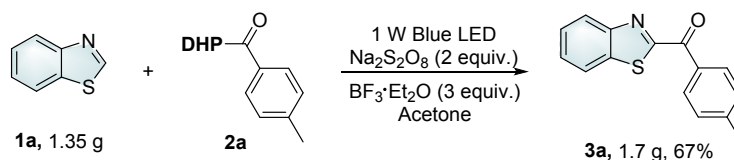
Following the general procedure, the crude product was purified by silica gel flash chromatography (PE: EA=200:1 as the eluent) to give **5m** (30 mg, 55% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 1.9 Hz, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.52 (m, 1H), 1.51 (s, 9H).

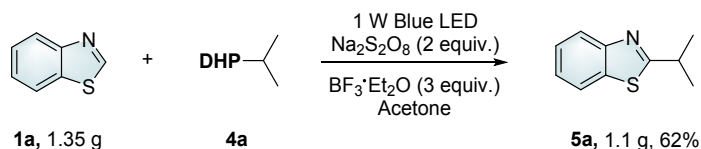
¹³C NMR (100 MHz, CDCl₃) δ 182.4, 152.1, 136.7, 129.2, 123.9, 123.8, 117.9, 38.4, 30.6.

HRMS (ESI): Calcd for $C_{11}H_{13}BrNS^+$ $[M+H]^+$ 296.9947, found 296.9943.

3. Scale-up Synthesis

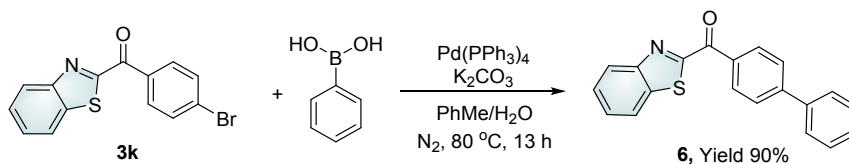


The 50 mL glass bottle was charged with benzothiazole (**1a**, 10 mmol, 1.35 g), acyl-DHP reagent (**2a**, 20 mmol, 7.43 g), $Na_2S_2O_8$ (2.0 equiv., 4.76 g), and $BF_3 \cdot Et_2O$ (3.0 equiv., 4.26 g) in acetone (10 mL), and the reaction mixture was stirred at blue LED (25 W) for 20 hours. After completion, 50 mL water was added and the mixture was extracted with 50 mL ethyl acetate for three times. The combined organic layer was dried over Na_2SO_4 and then evaporated under reduced pressure. After evaporating the solvent under reduced pressure, the crude product was purified by column chromatography using petroleum ether/ethyl acetate as the eluents. The product was obtained as a yellow solid (1.7 g, 67%).

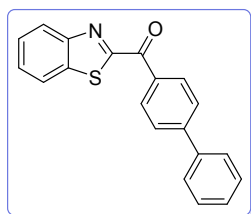


The 50 mL glass bottle was charged with benzothiazole (**1a**, 10 mmol, 1.35 g), alkyl-DHP reagent (**4a**, 20 mmol, 5.91 g), $Na_2S_2O_8$ (2.0 equiv., 4.76 g), and $BF_3 \cdot Et_2O$ (3.0 equiv., 4.26 g) in acetone (10 mL), and the reaction mixture was stirred at blue LED (25 W) for 15 hours. After completion, 50 mL water was added and the mixture was extracted with 50 mL ethyl acetate for three times. The combined organic layer was dried over Na_2SO_4 and then evaporated under reduced pressure. After evaporating the solvent under reduced pressure, the crude product was purified by column chromatography using petroleum ether/ethyl acetate as the eluents. The product was obtained as a yellow oil. (1.1 g, 62%).

4. Synthetic Application



Under nitrogen atmosphere, **3k** (0.3 mmol, 95.46 mg), phenylboronic acid (0.45 mmol, 54.87 mg), tetrakis(triphenylphosphine)palladium (0.015 mmol, 1.73 mg), potassium carbonate (1.2 mmol, 165.85 mg), toluene (1 mL) and water (0.2 mL) were added successively to a 10 mL reaction flask. The mixture was stirred at $80\text{ }^\circ\text{C}$ for 8 hours. The mixture was cooled to room temperature. Then 20 mL water was added to the mixture and extracted with 20 mL ethyl acetate for three times. The combined organic layer was dried over Na_2SO_4 and then evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether: ethyl acetate = 20:1). Compound **6** was obtained as yellow solid (85 mg, 90%).



[1,1'-biphenyl]-4-yl(benzo[d]thiazol-2-yl)methanone (**6**)

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.63 (d, $J = 8.2$ Hz, 2H), 8.23 (d, $J = 8.1$ Hz, 1H), 7.96 (d, $J = 7.9$ Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 2H), 7.63 (d, $J = 7.7$ Hz, 2H), 7.56 – 7.42 (m, 2H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.38 (t, $J = 7.1$ Hz, 1H).

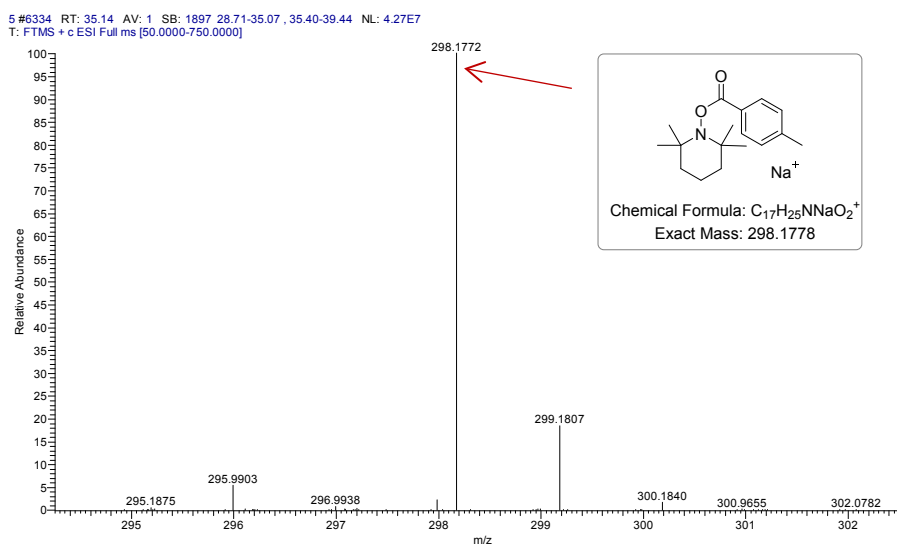
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 184.8, 167.3, 153.9, 146.5, 139.9, 137.0, 133.7, 131.9, 129.0, 128.4, 127.6, 127.4, 127.2, 126.9, 125.7, 122.2.

HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{14}\text{NOS}^+$ $[\text{M}+\text{H}]^+$ 316.0791, found 316.0795.

5. Control Experiment



The 5 mL glass bottle was charged with benzothiazole (**1a**, 0.2 mmol), acyl-DHP reagent (**2a**, 0.4 mmol, 149 mg), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (3.0 equiv., 85 mg), $\text{Na}_2\text{S}_2\text{O}_8$ (2.0 equiv., 92 mg) and TEMPO (3.0 equiv., 94 mg) in acetone (1 mL), and the reaction mixture was stirred at blue LED for 15 hours. According to the detected result by LC-MS, the benzoyl radical could be trapped by TEMPO to produce the 1-(*p*-toluoyl)-2,2,6,6-tetramethylpiperidine (**A**).



HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{25}\text{NNaO}_2^+$ $[\text{M}+\text{Na}]^+$ 298.1778, found 298.1772.

6. UV-VIS Absorption Spectra

Solutions of **2a** ($[\mathbf{2a}] = 0.15$ mM in CH_3COH_3) were introduced into a 1 cm path length quartz cuvette equipped with a Teflon® septum (Figure S4). Solutions at different concentrations of **2a**, obtained by opportunely diluting an original stock solution ($[\mathbf{2a}] = 0.3$ mM in CH_3COH_3), were introduced to a 1 cm path length quartz

cuvette (Figure S5). The solution was analyzed using a Shimadzu 2501 PC UV-VIS spectrophotometer. The absorption spectra show a typical Lambert-Beer linear correlation with the concentrations (Figure S6). Ultraviolet-visible spectroscopy (UV-VIS) measurements were conducted. No obvious change of the absorption was observed when different components were mixed under standard reaction conditions (Figure S7).

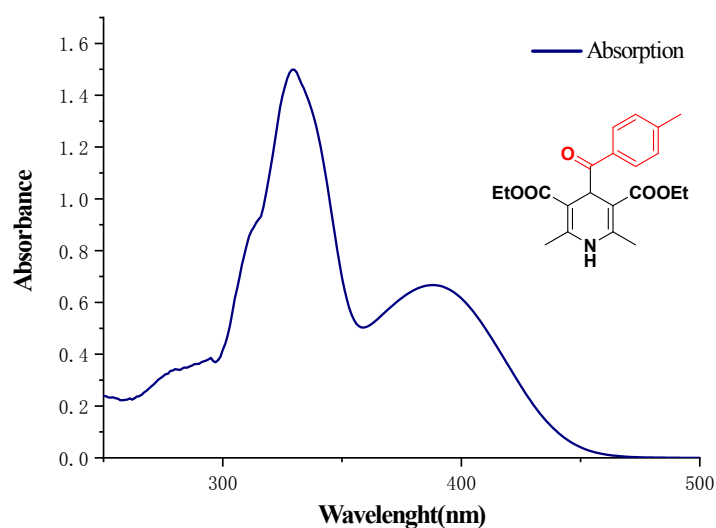


Figure S4 Absorption spectrum of **2a** in CH_3COCH_3

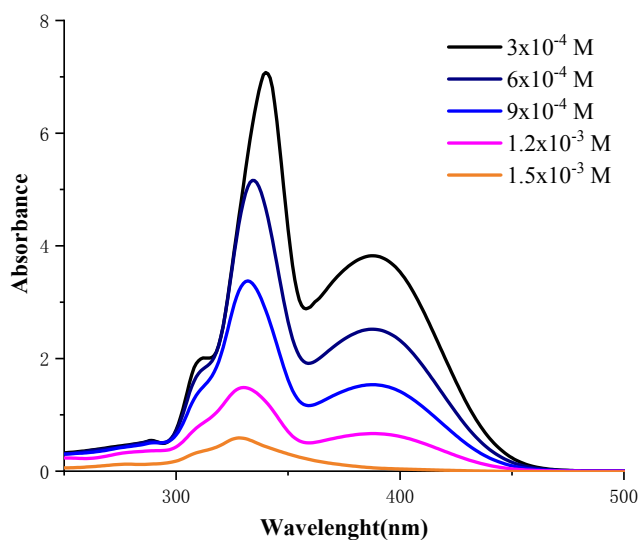


Figure S5. Absorption spectra of **2a** at different concentrations in CH_3COCH_3 . The tail wavelength of absorption was considered at 475 nm.

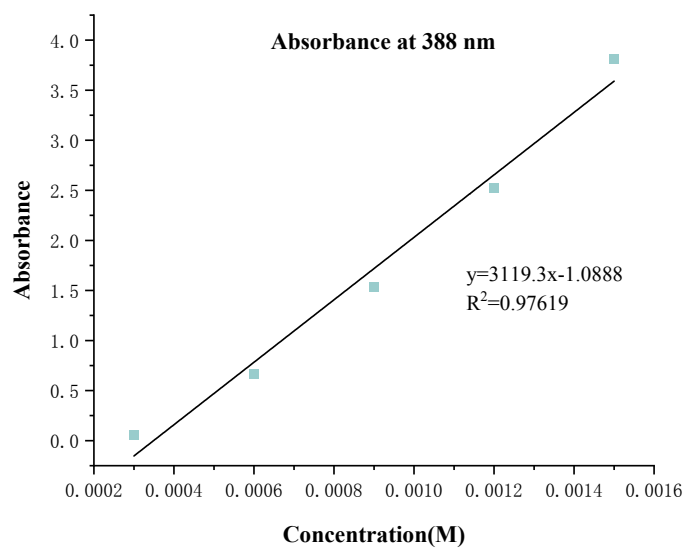


Figure S6. Lambert-Beer linear correlation between absorbance and concentration at 388 nm for **2a**. The slope of the line is the molar extinction coefficient ϵ at 388 nm ($M^{-1} \text{ cm}^{-1}$).

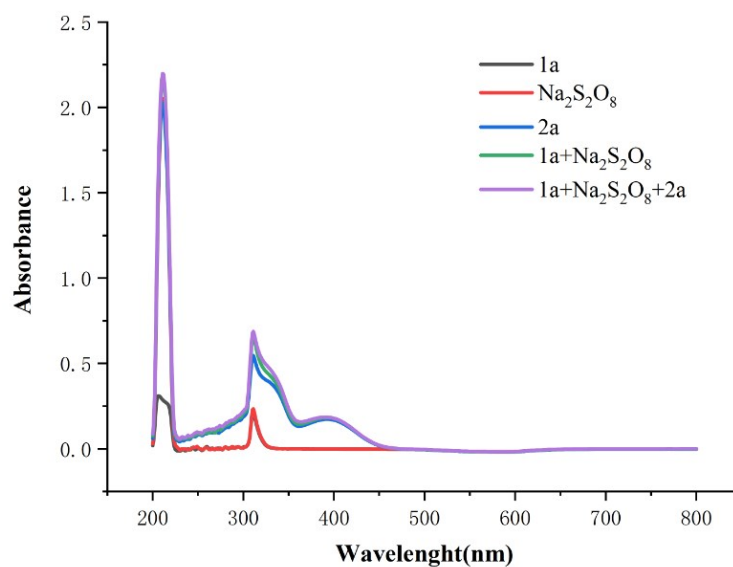


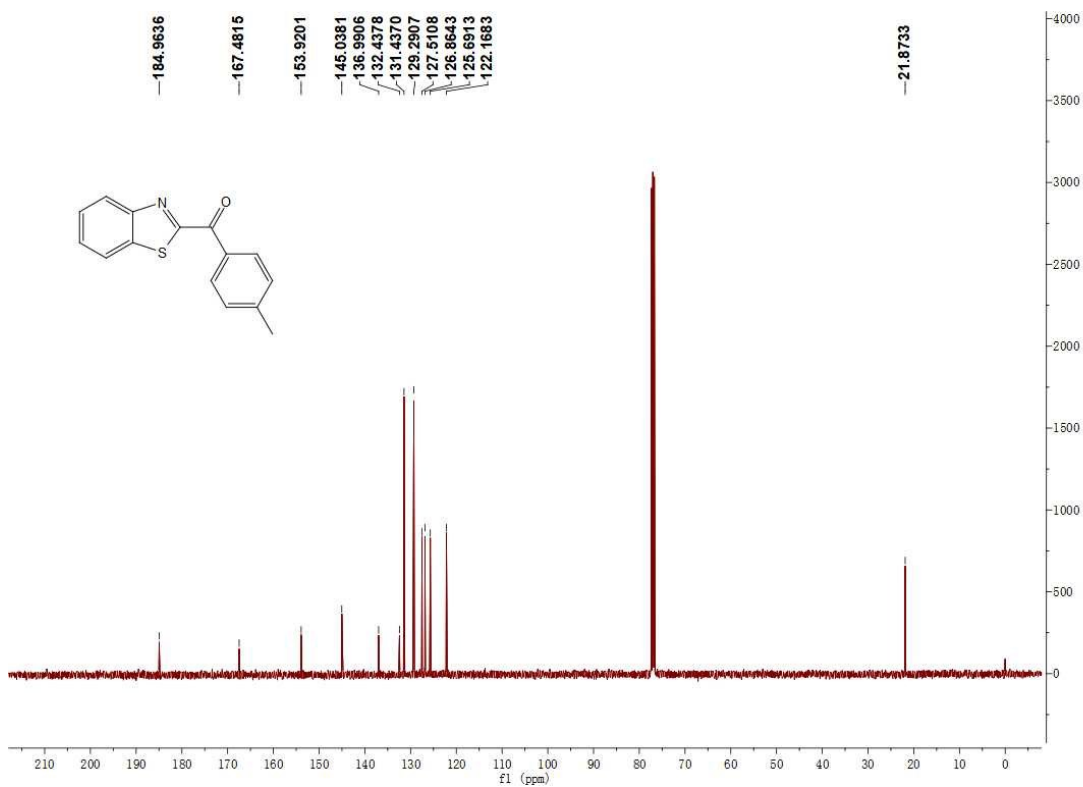
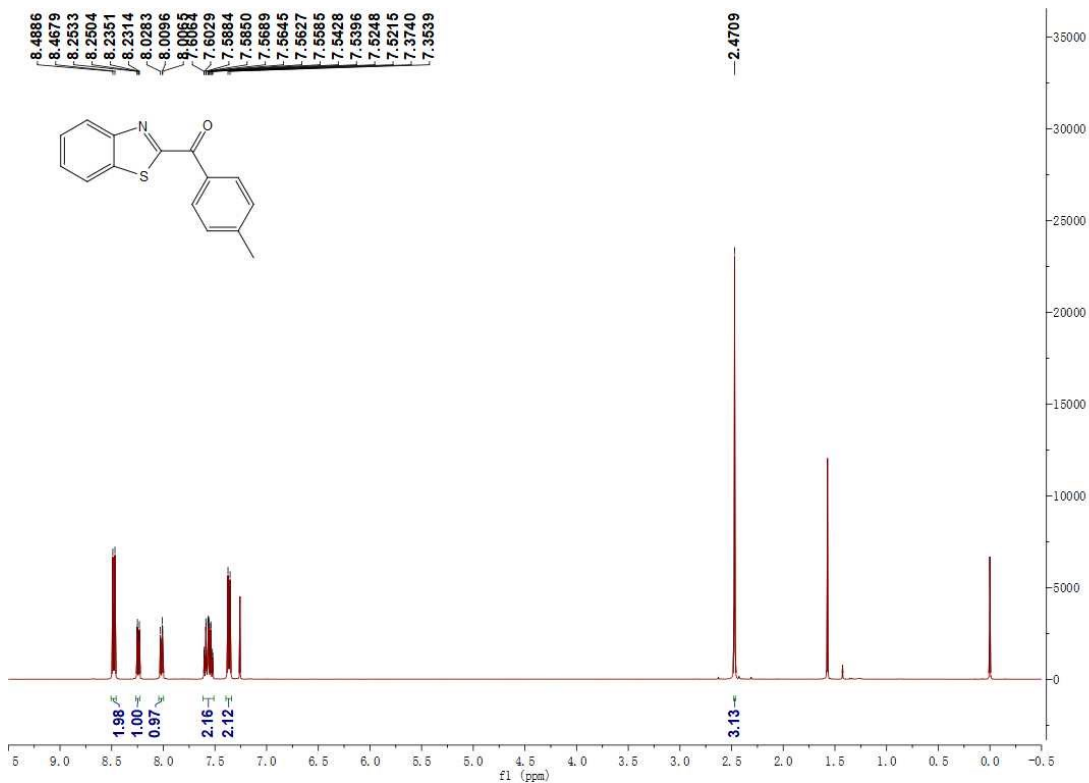
Figure S7 Spectroscopic studies UV-VIS absorption spectra ($\lambda = 465 \text{ nm}$; $\text{CH}_3\text{COCH}_3/\text{H}_2\text{O} = 1/1$; $C=0.2 \text{ mM}$)

7. References

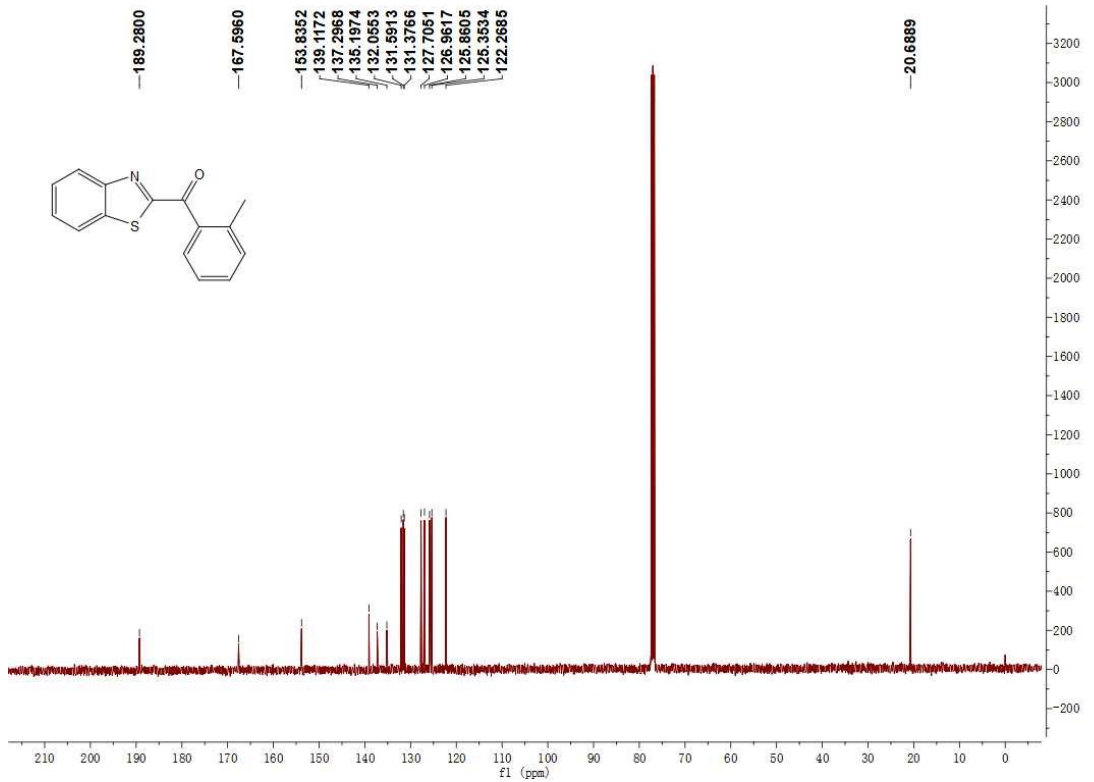
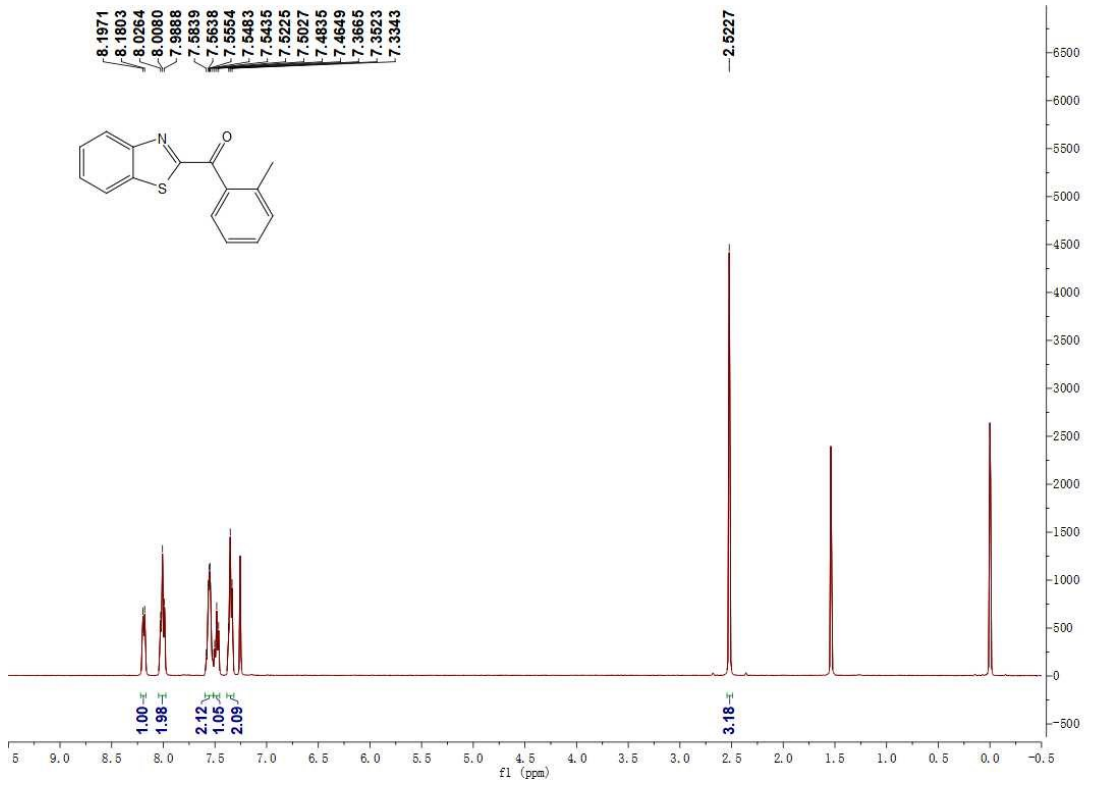
- [1] Á. Gutiérrez-Bonet, C. Remeur, J. K. Matsui, G. A. Molander, *J. Am. Chem. Soc.*, 2017, **139**, 12251-12258.
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- [4] G. Li, R. Chen, L. Wu, Q. Fu, X. Zhang, Z. Tang, *Angew. Chem., Int. Ed.*, 2013, **52**, 8432-8436.
- [5] B. Bieszczad, L. A. Perego, P. Melchiorre, *Angew. Chem., Int. Ed.*, 2019, **58**, 16878-16883.
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8. ¹H NMR and ¹³C NMR Spectra of the Products

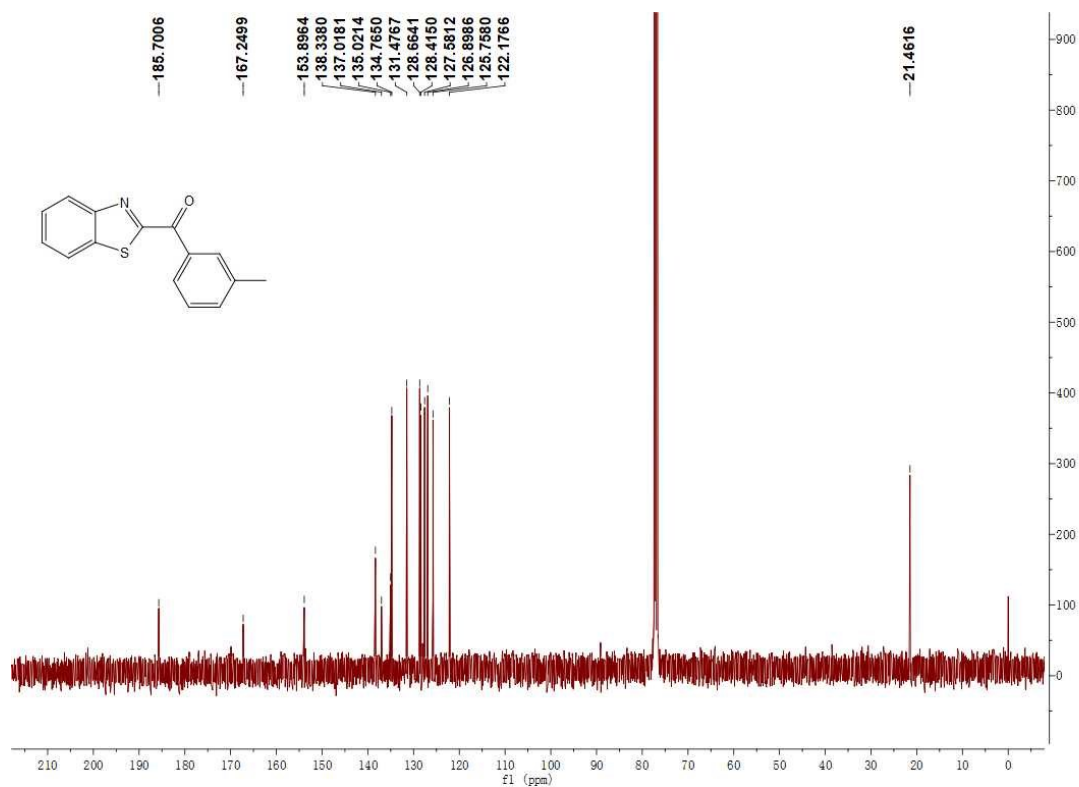
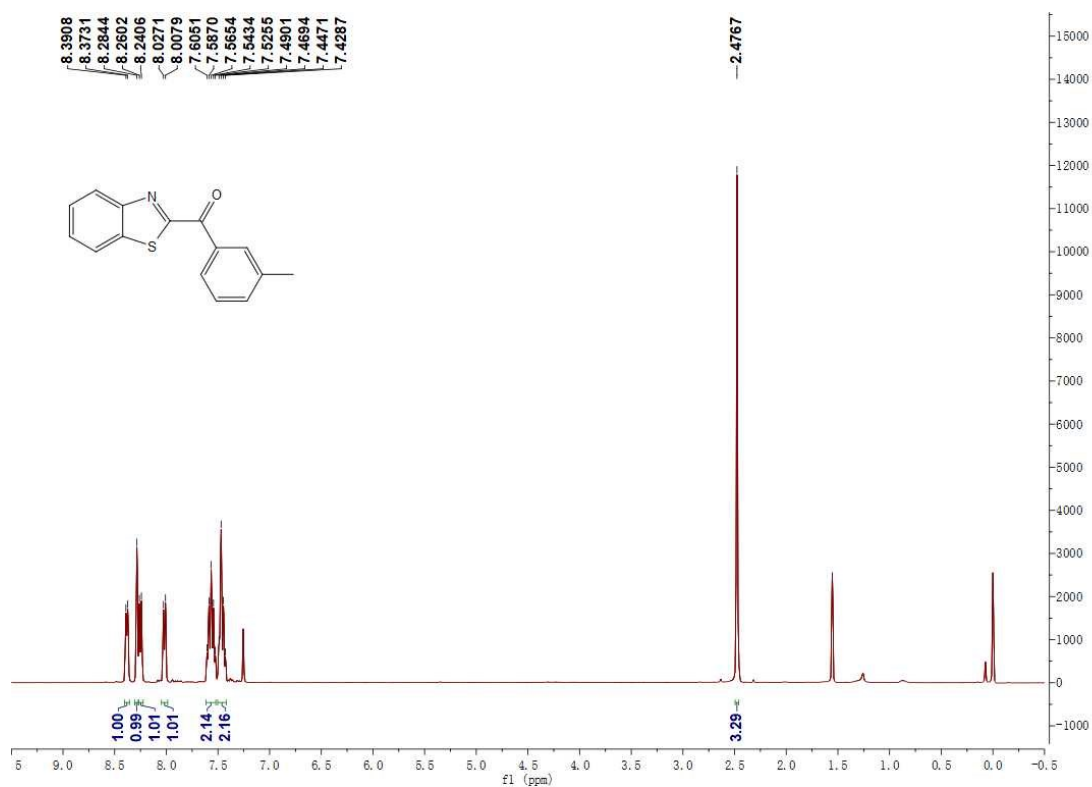
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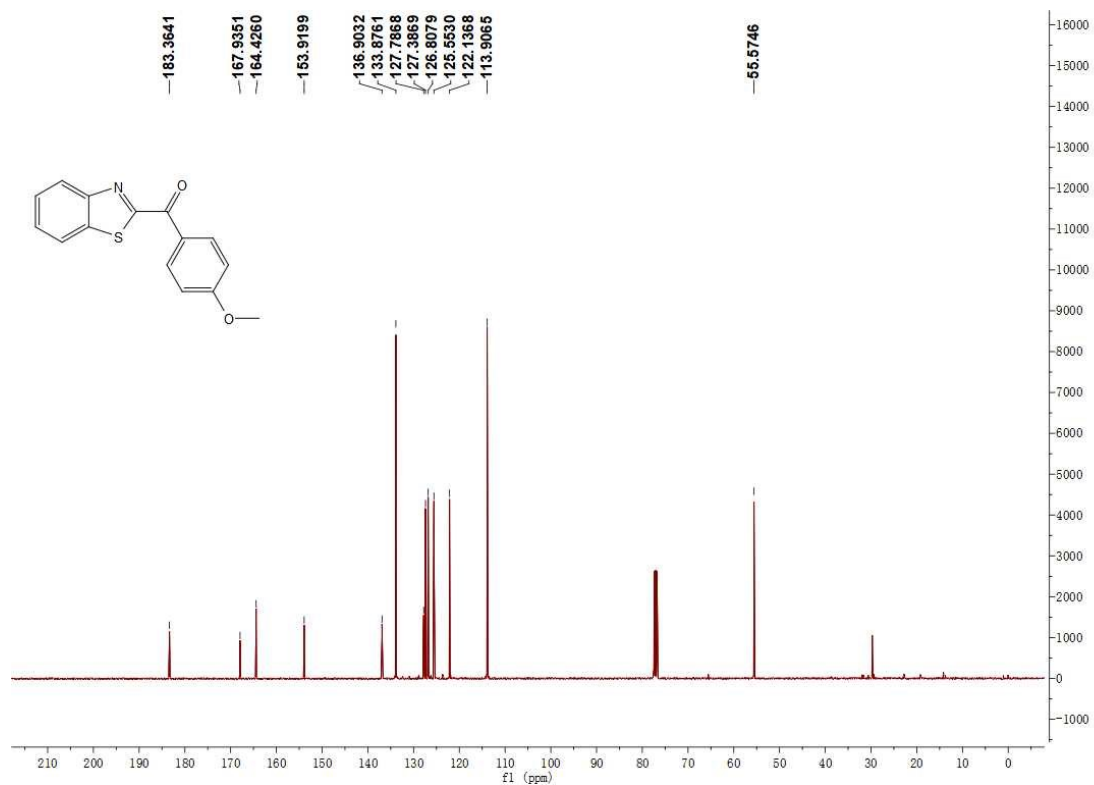
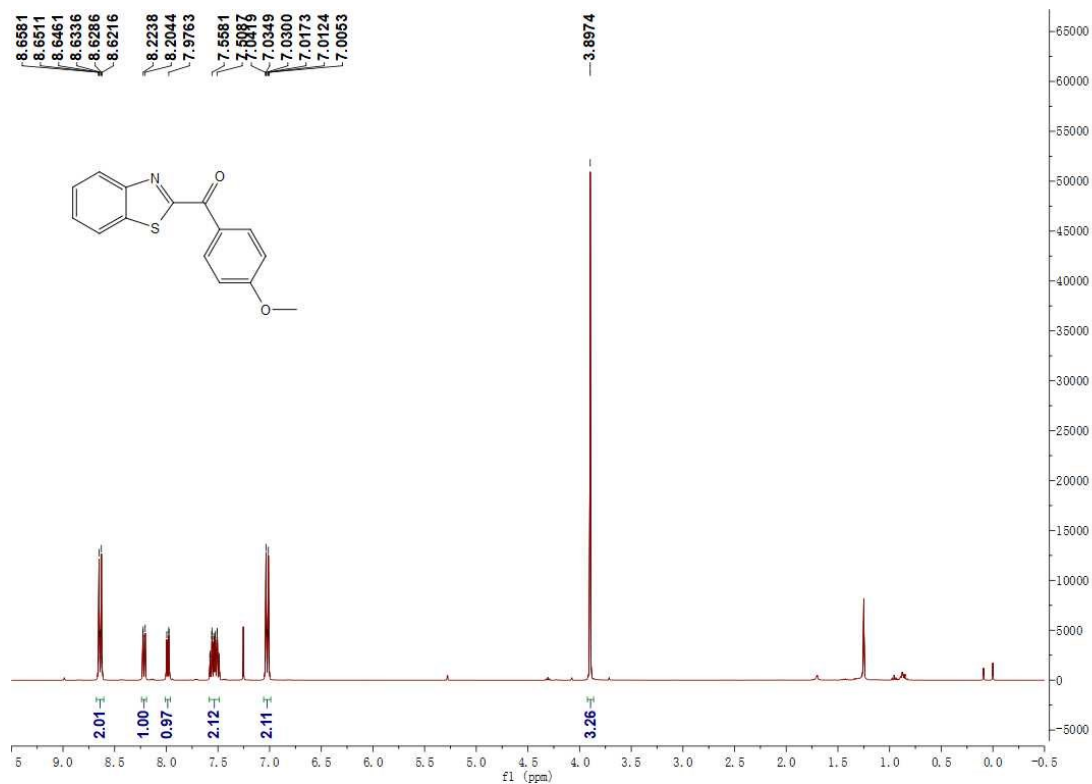
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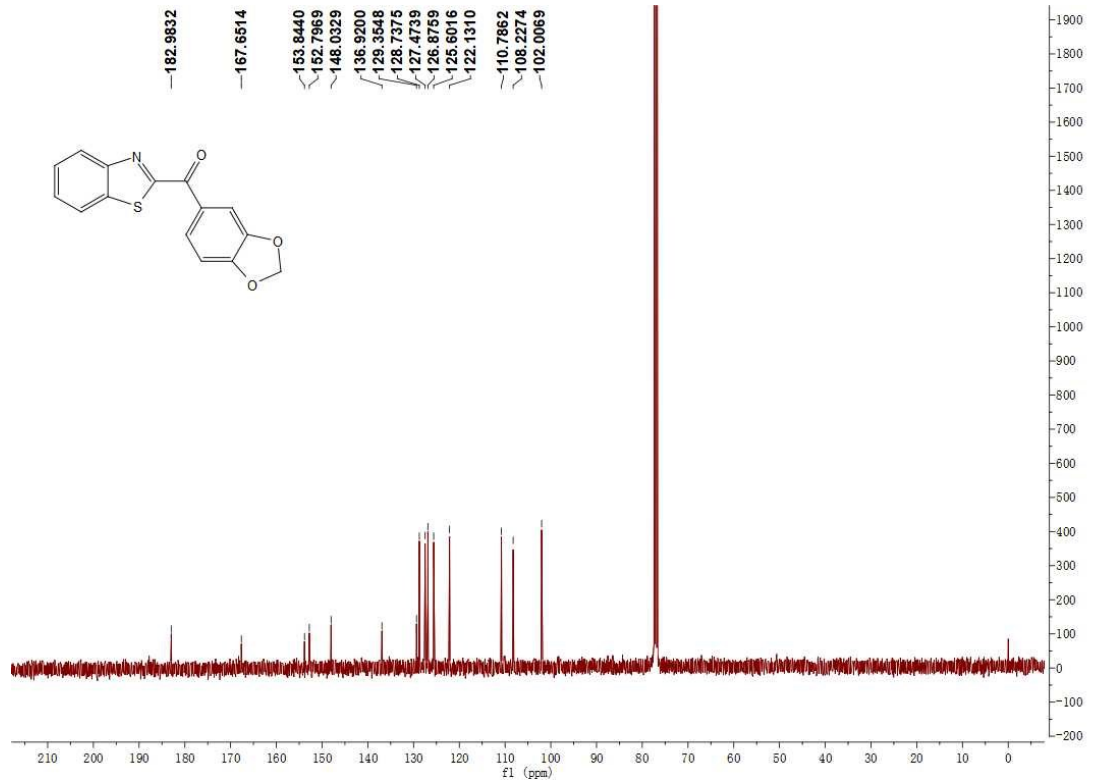
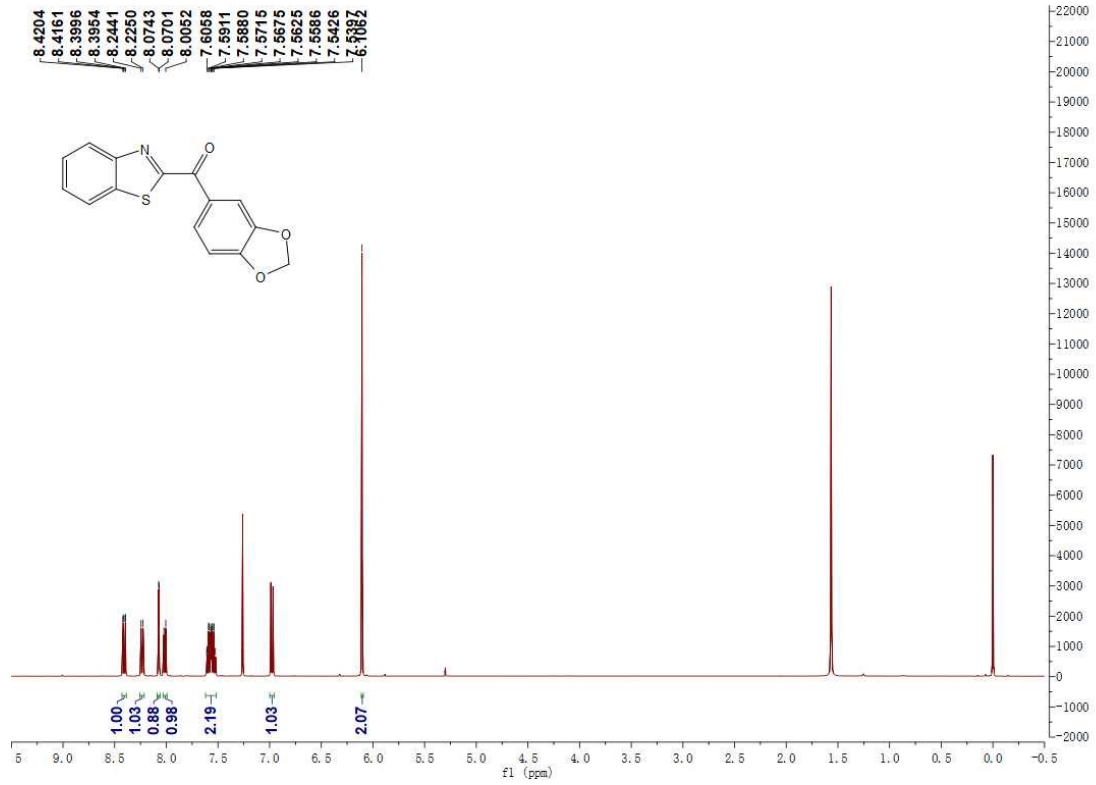
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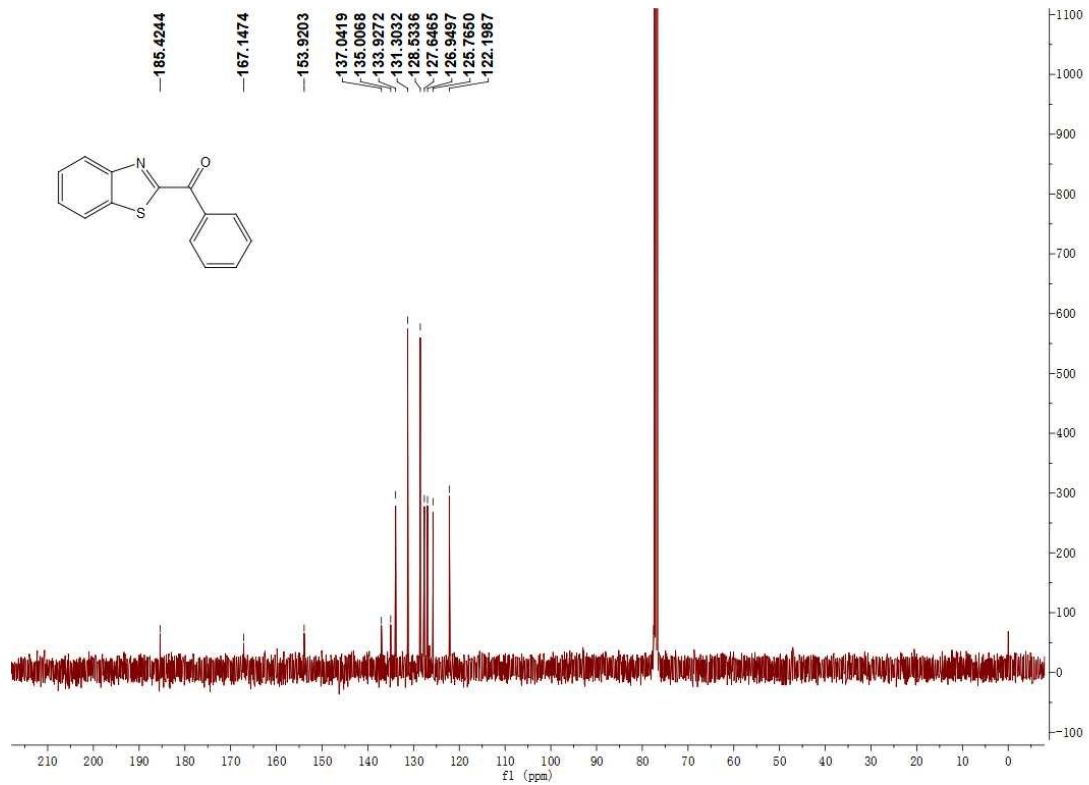
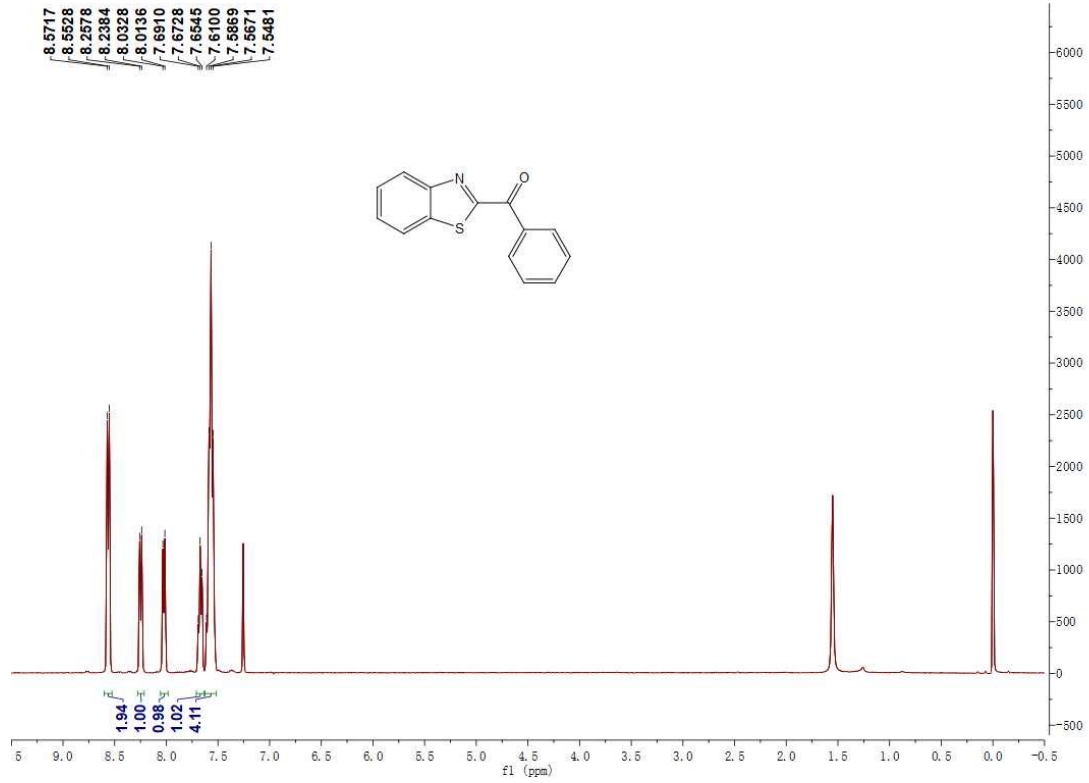
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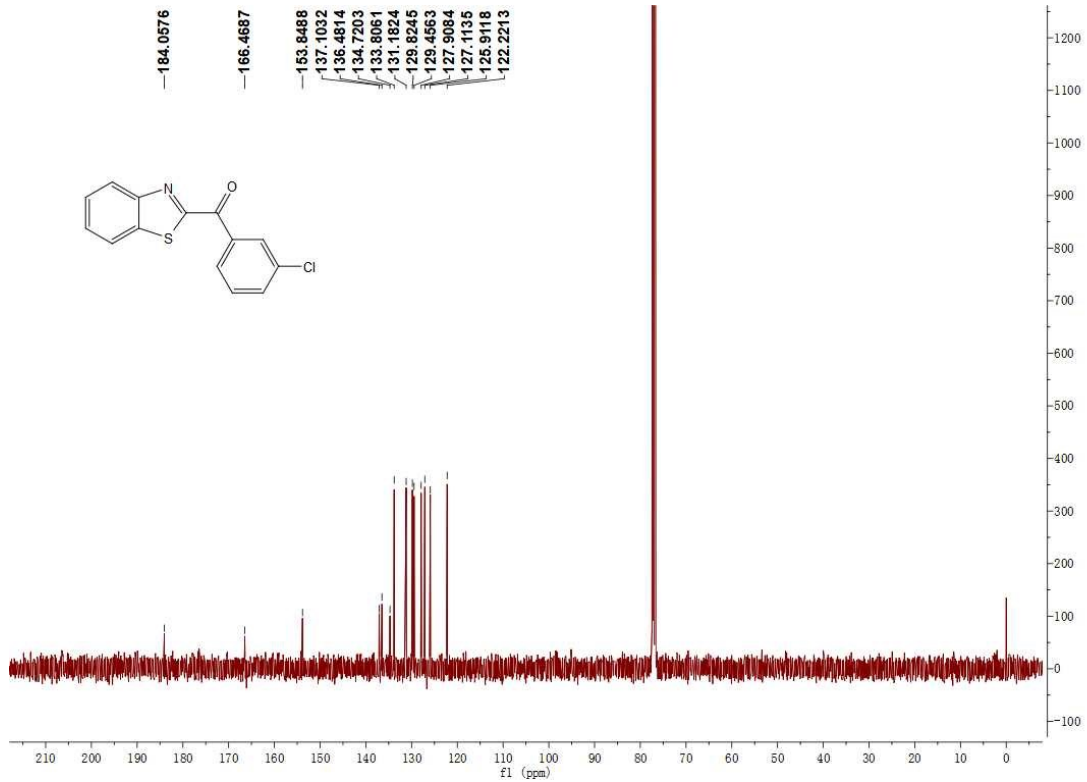
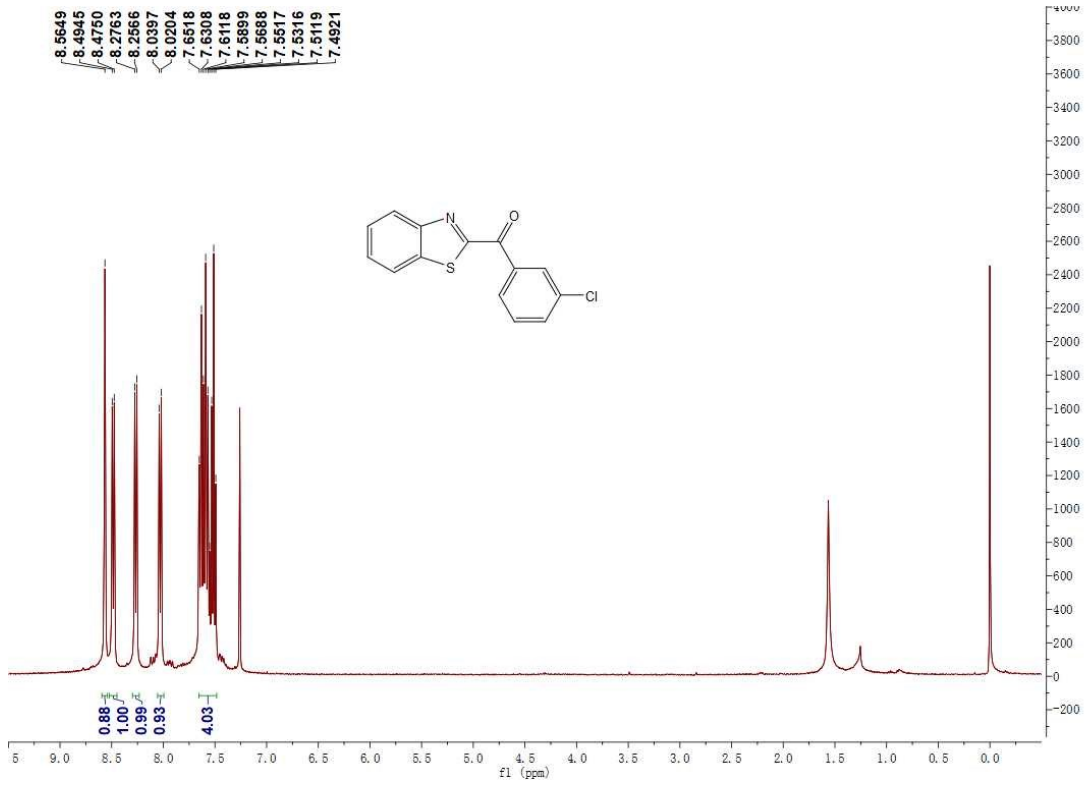
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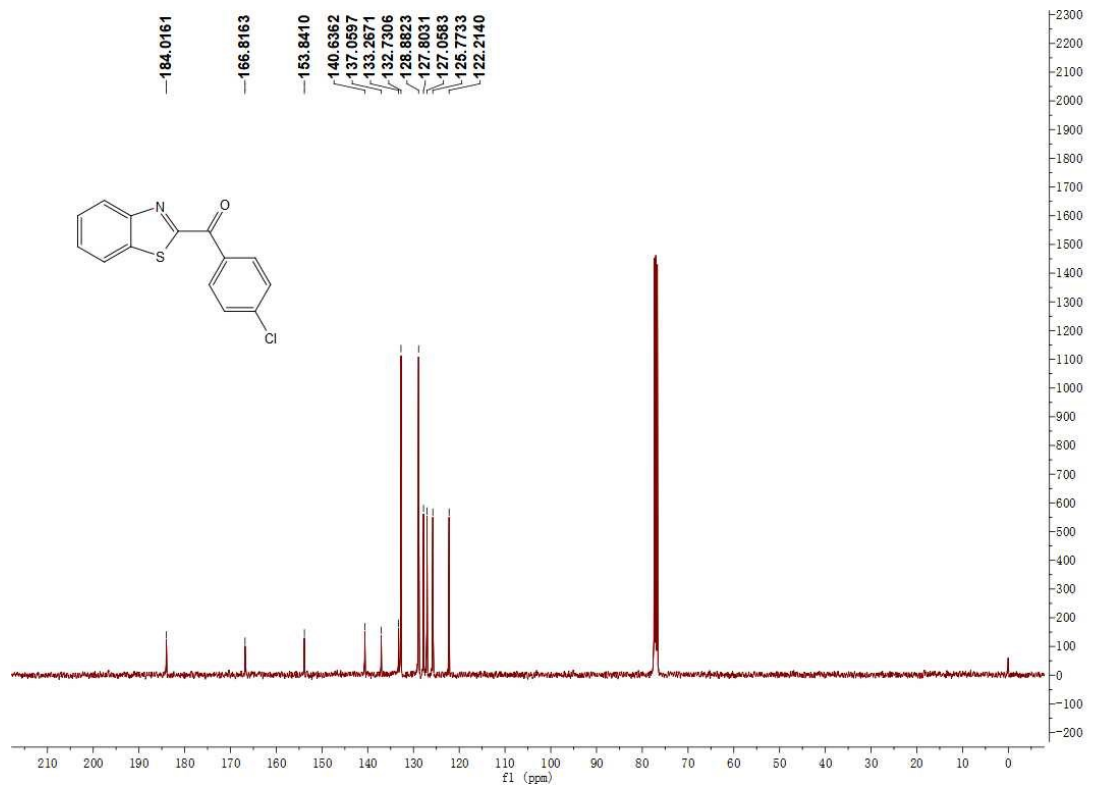
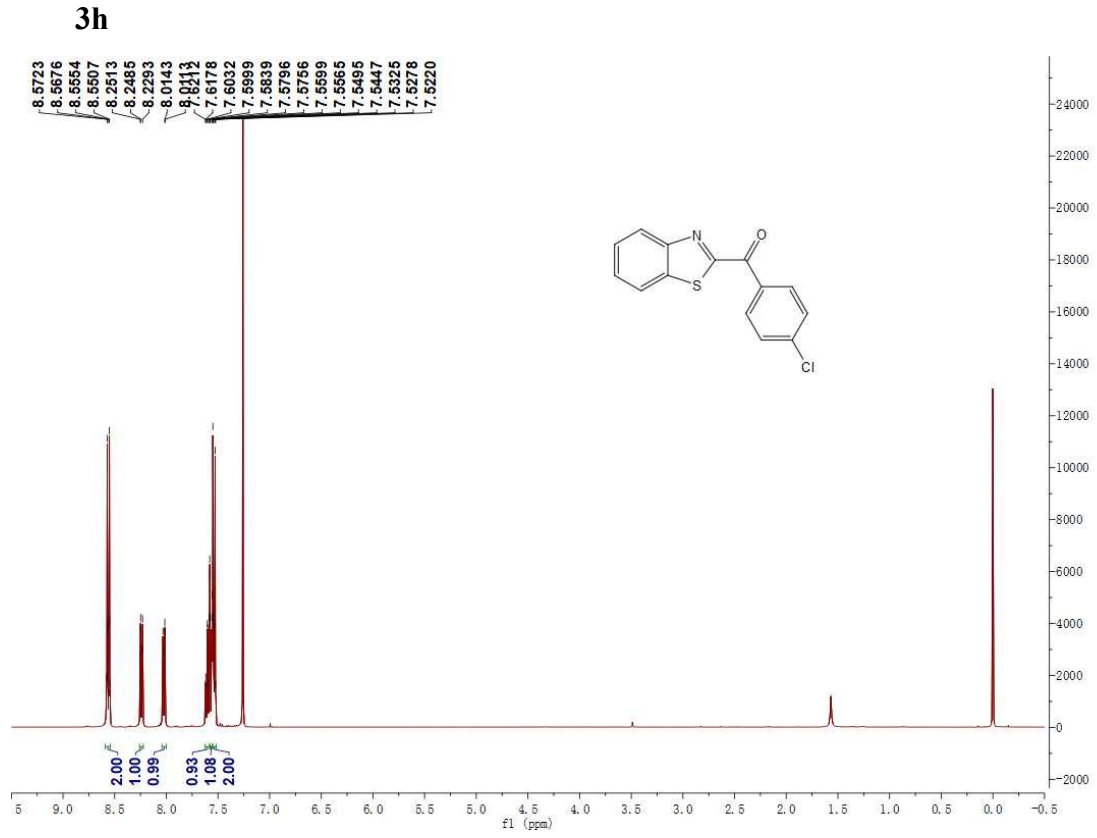


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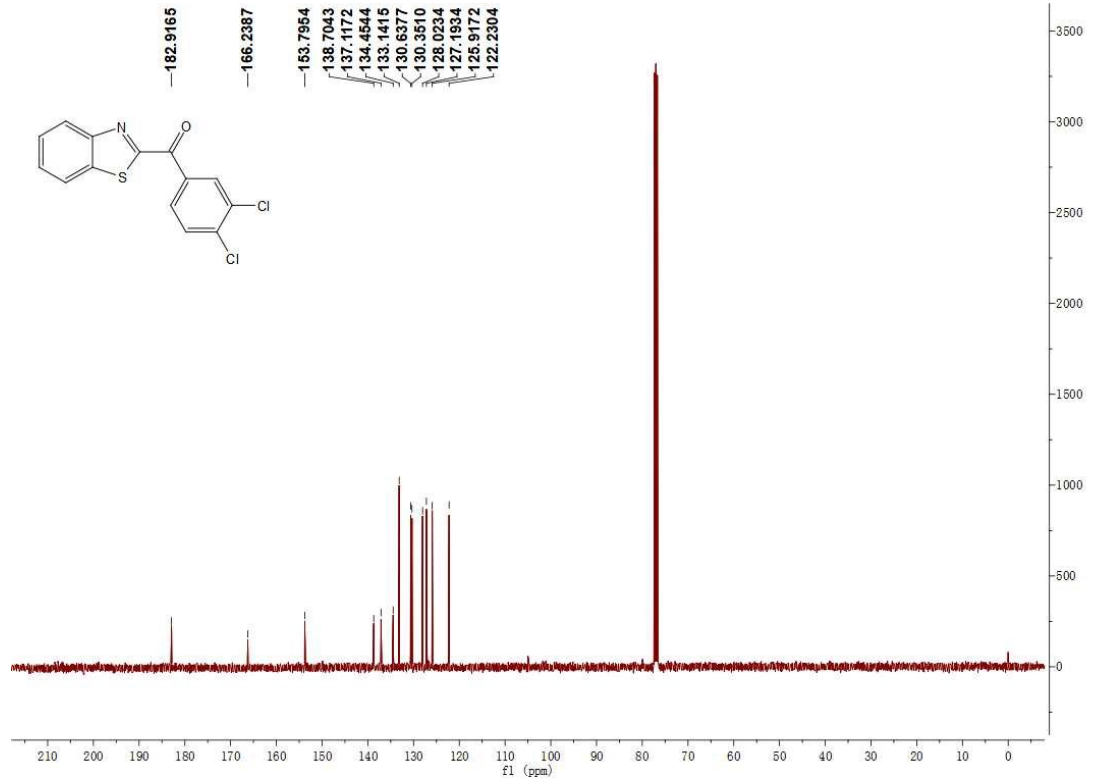
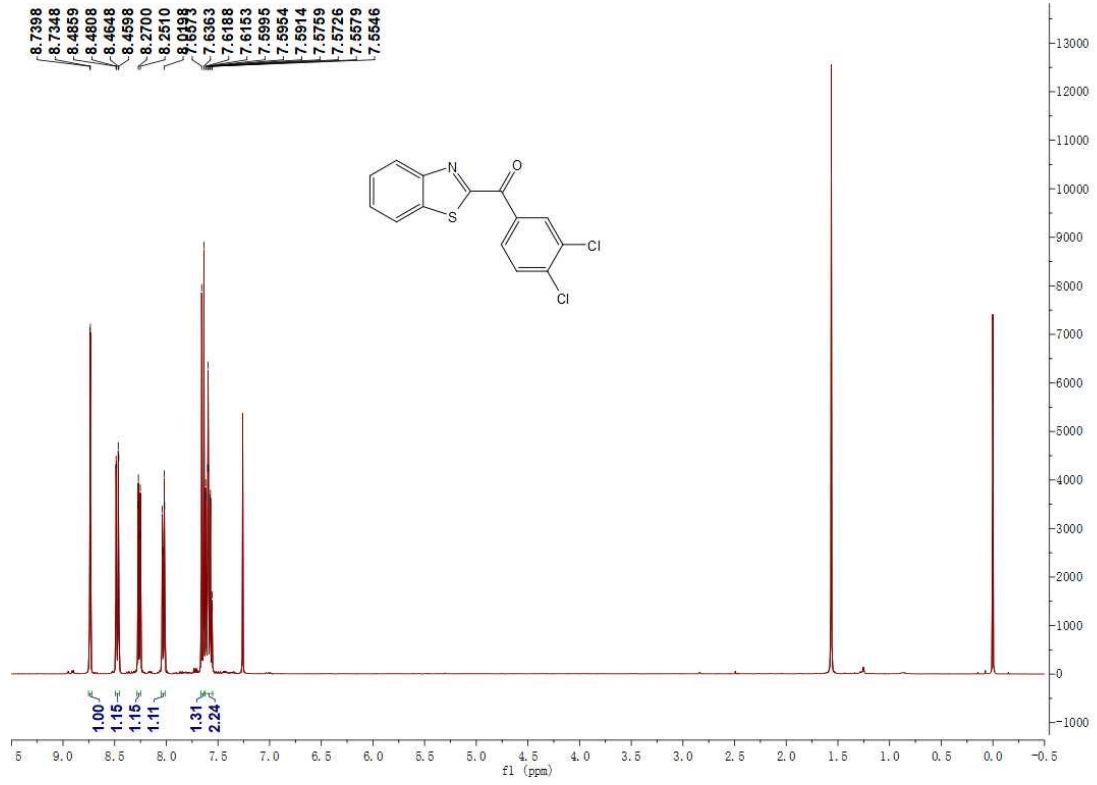


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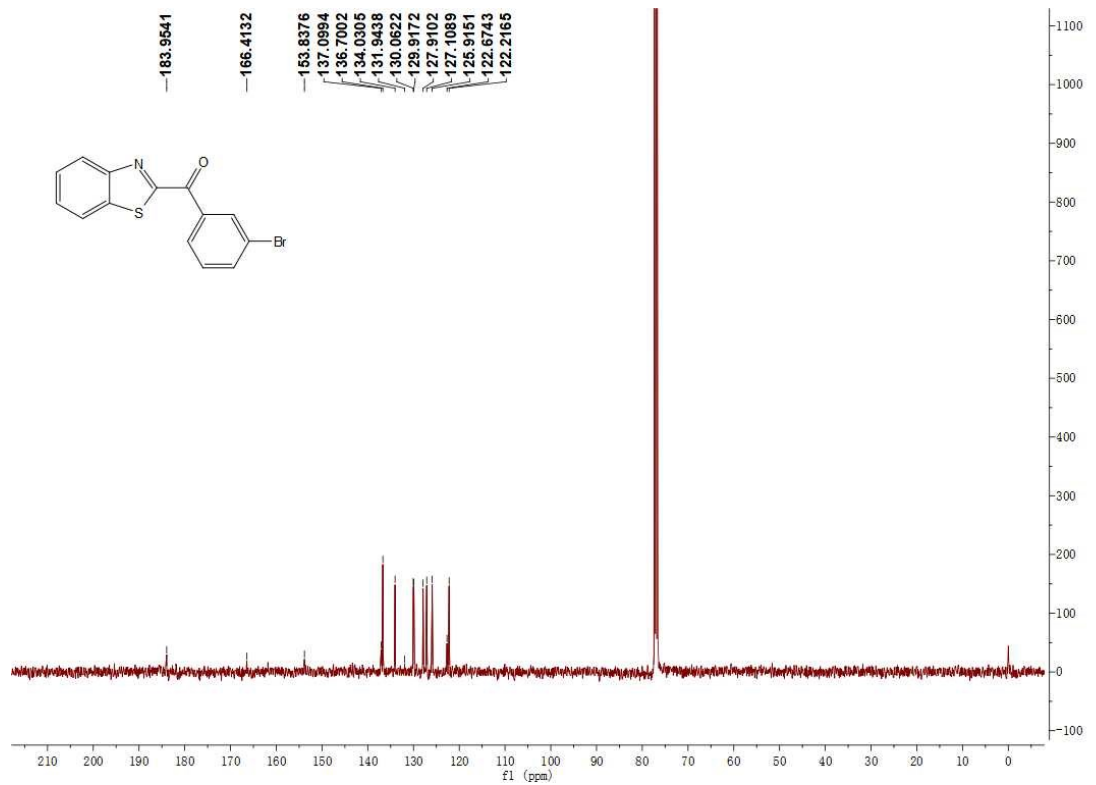
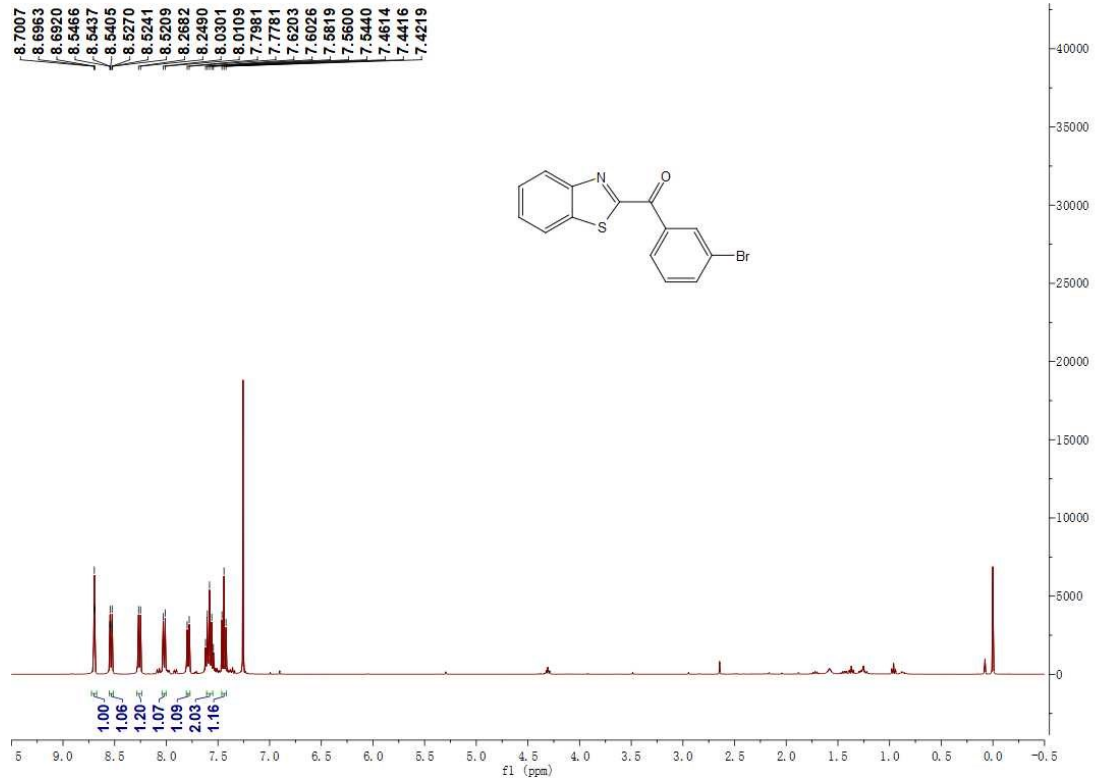




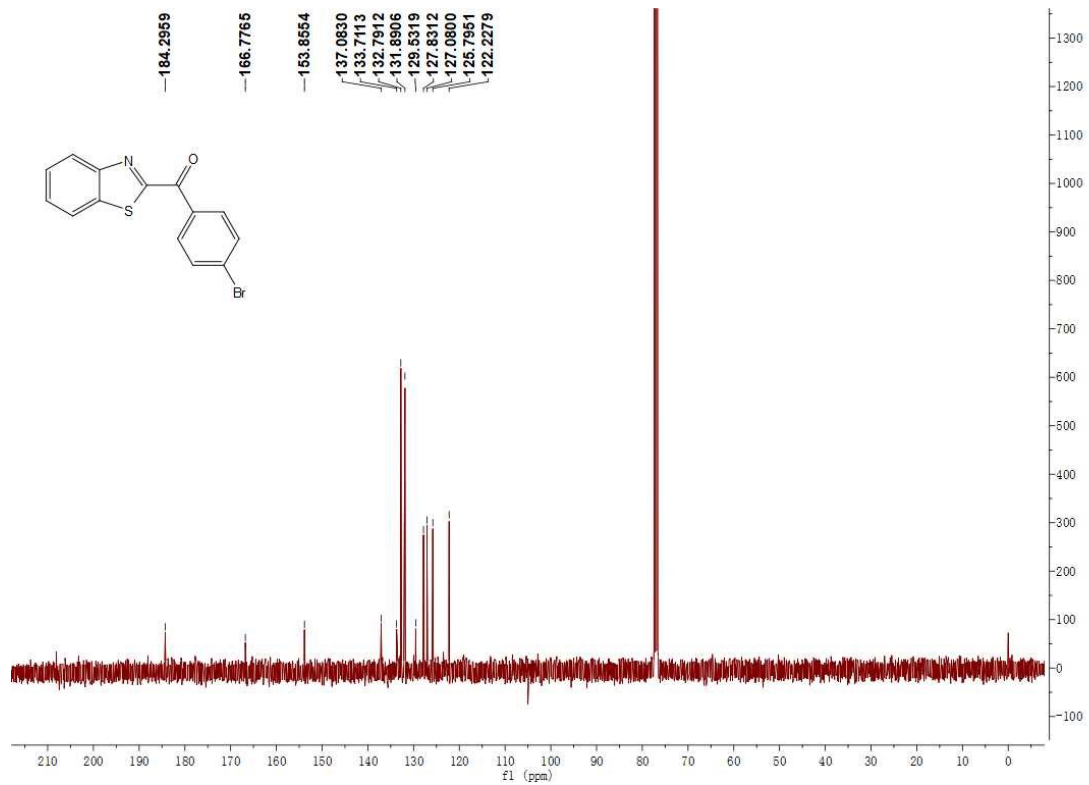
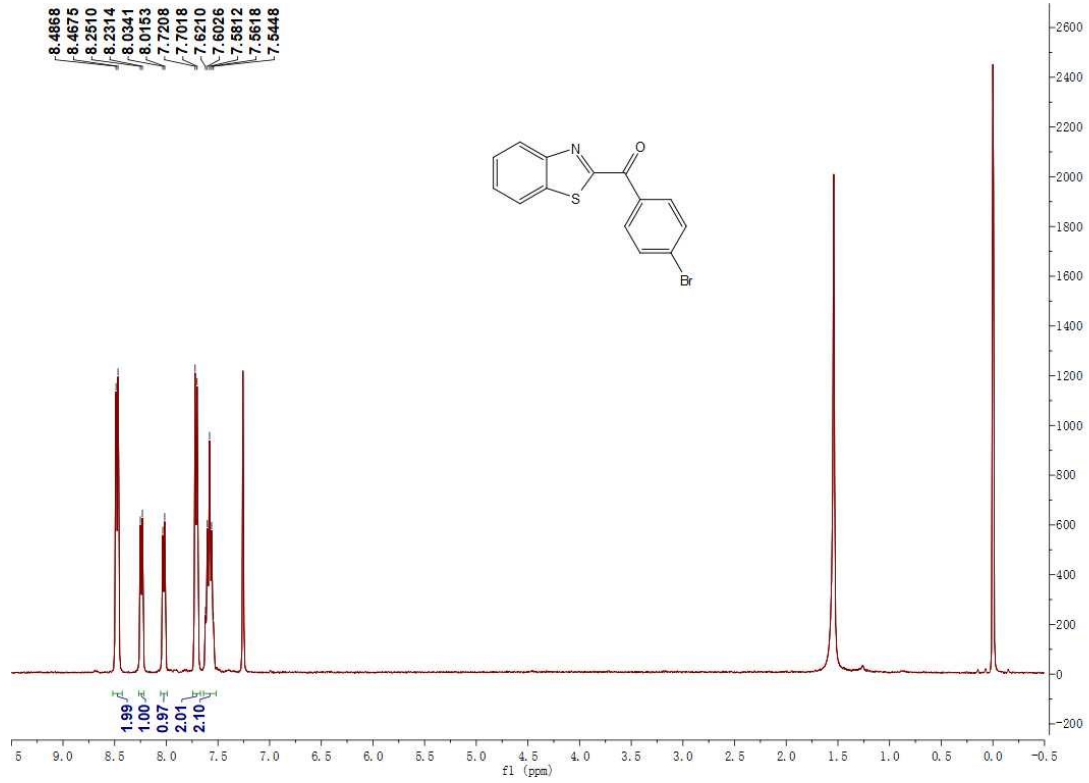
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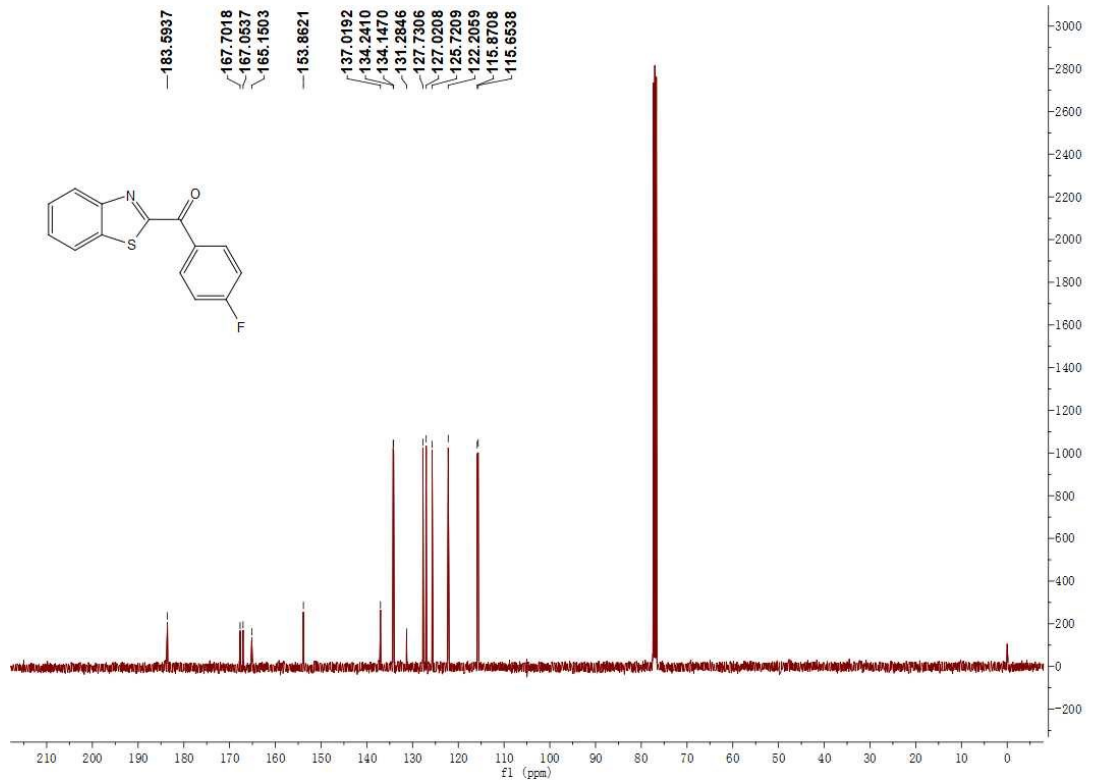
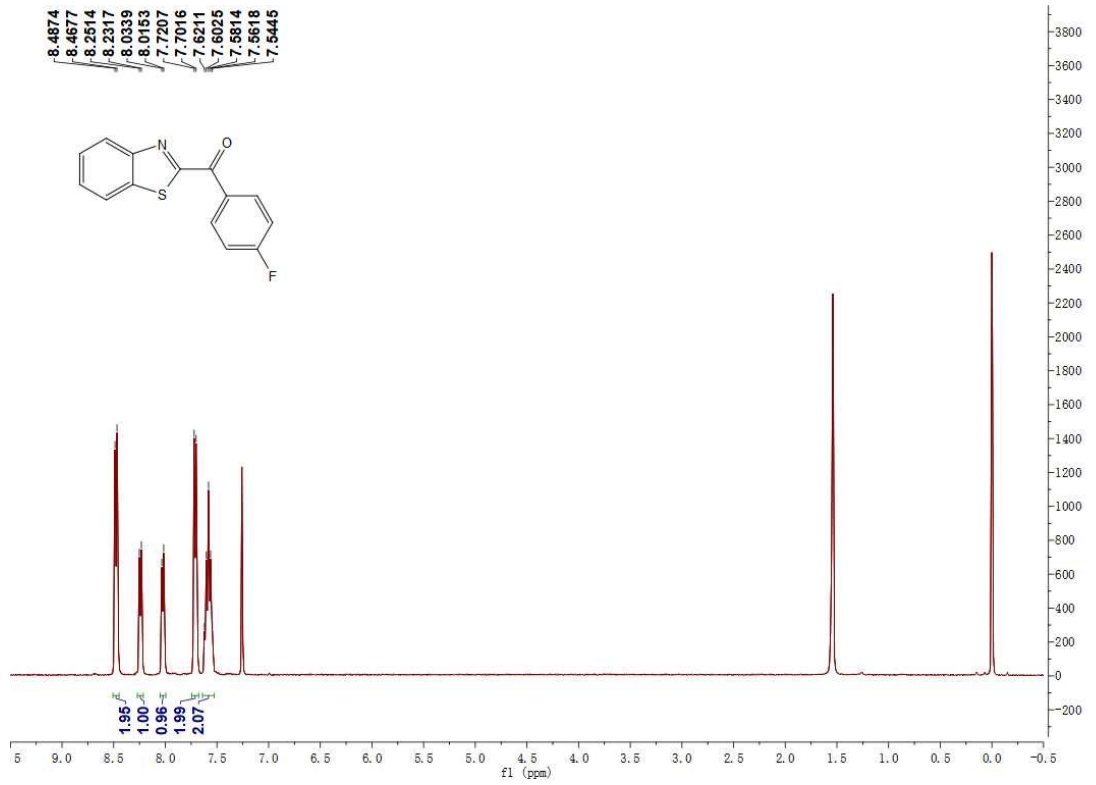
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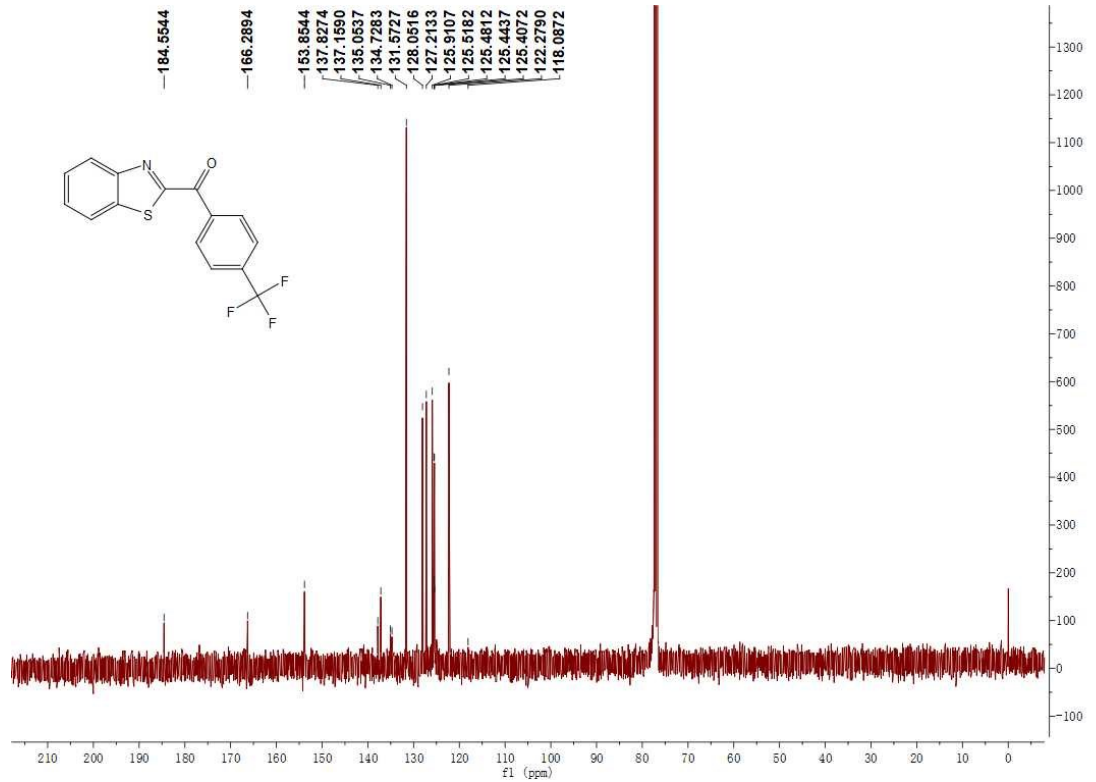
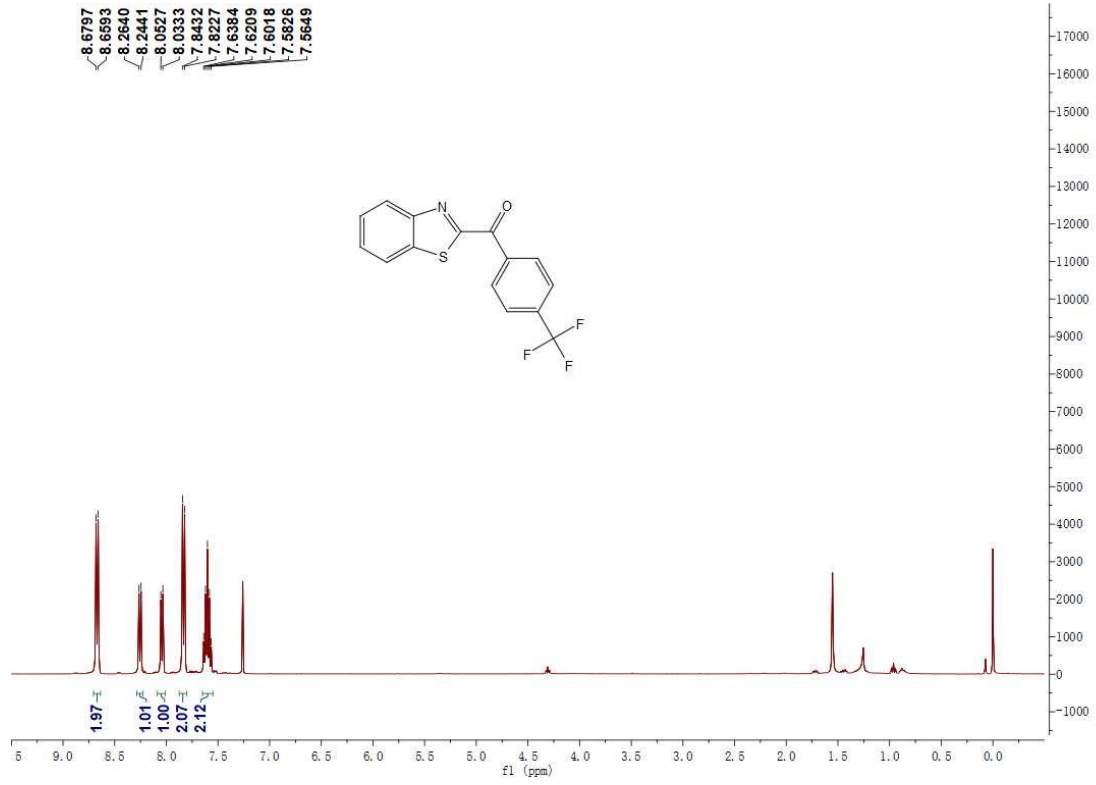
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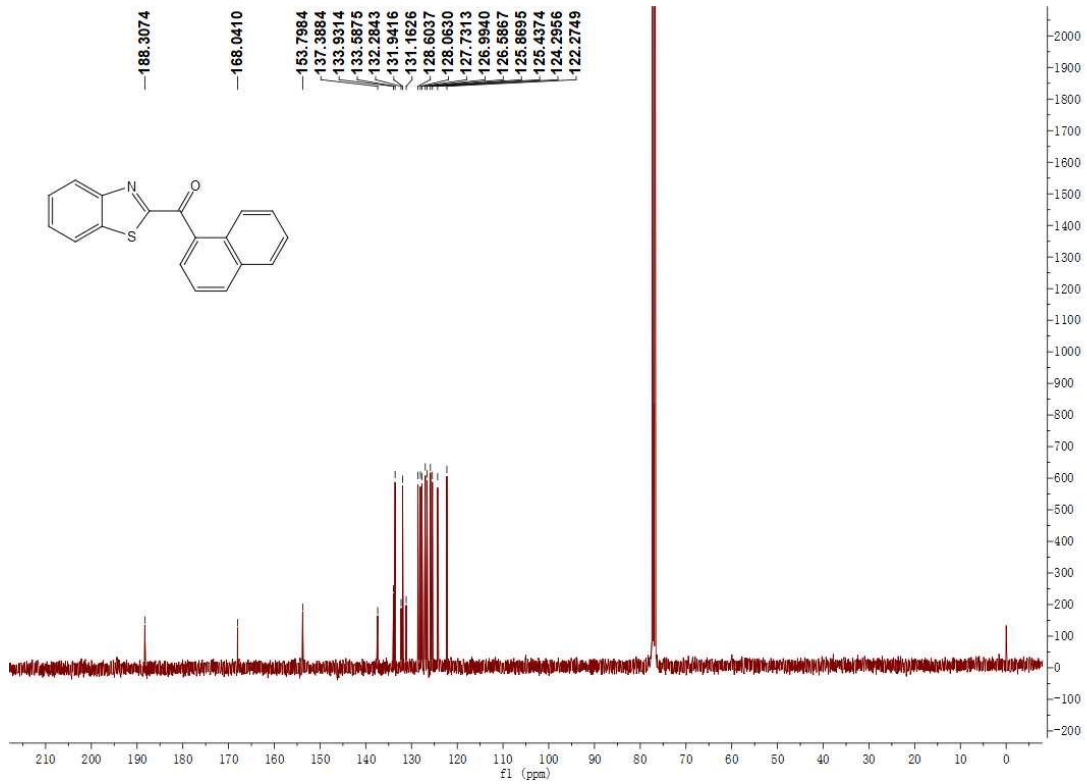
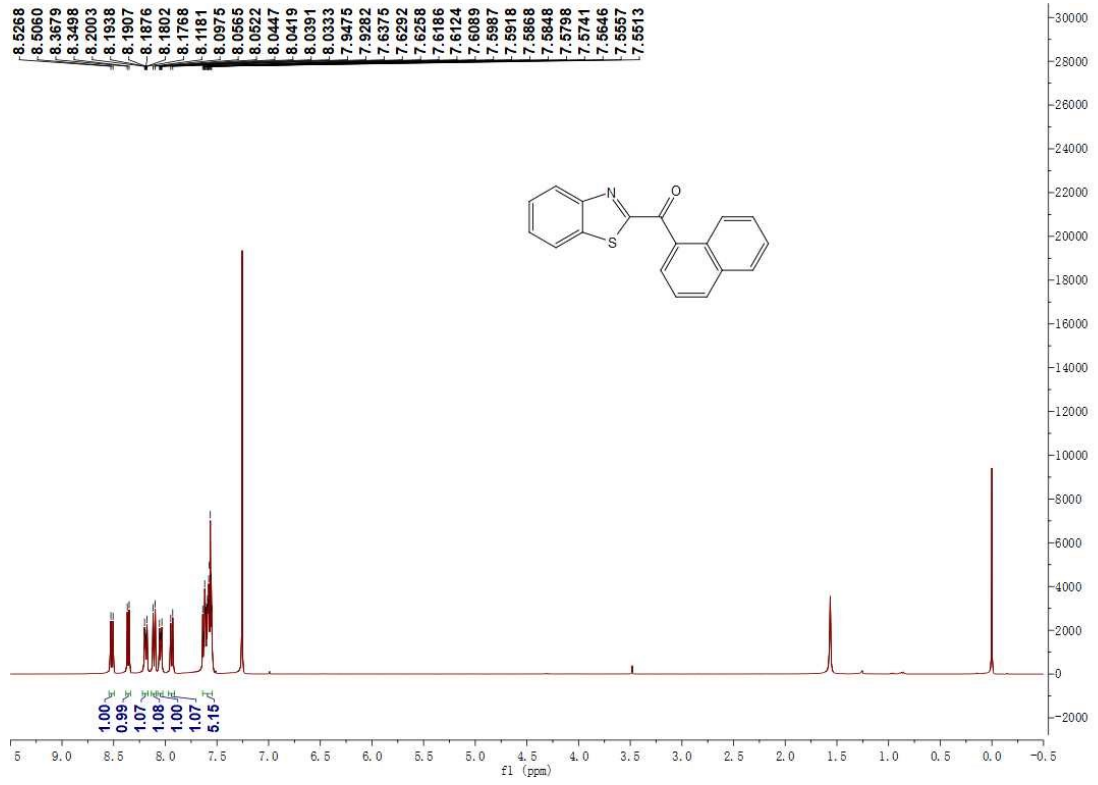
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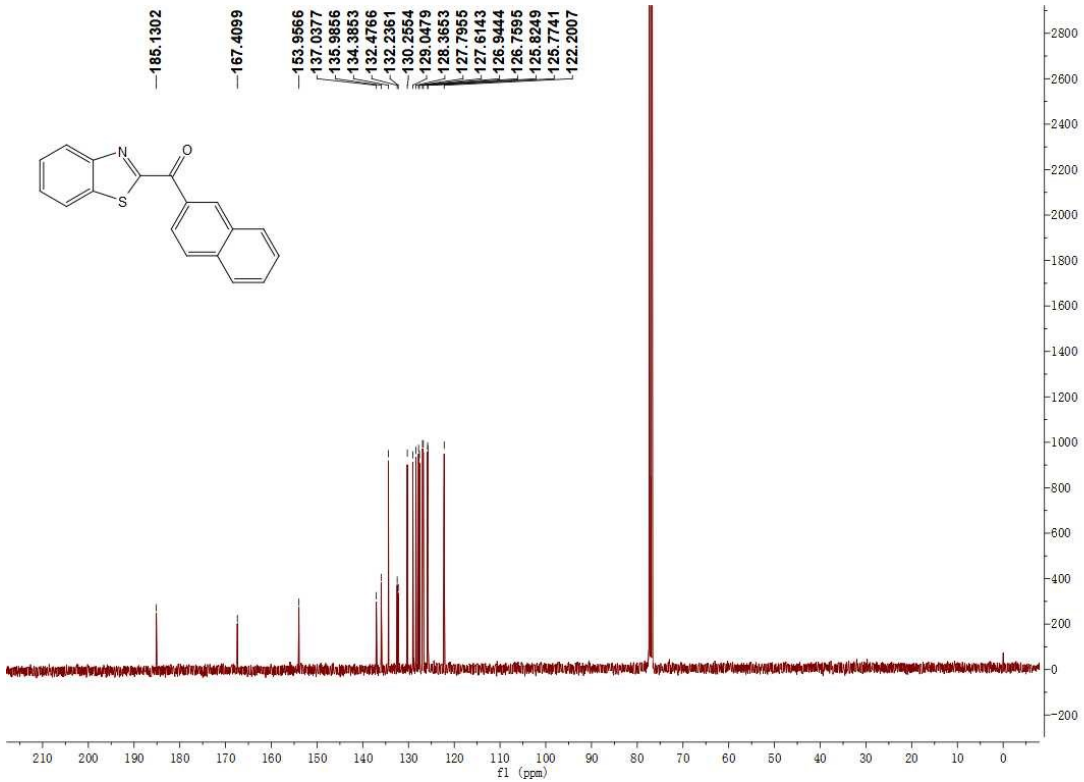
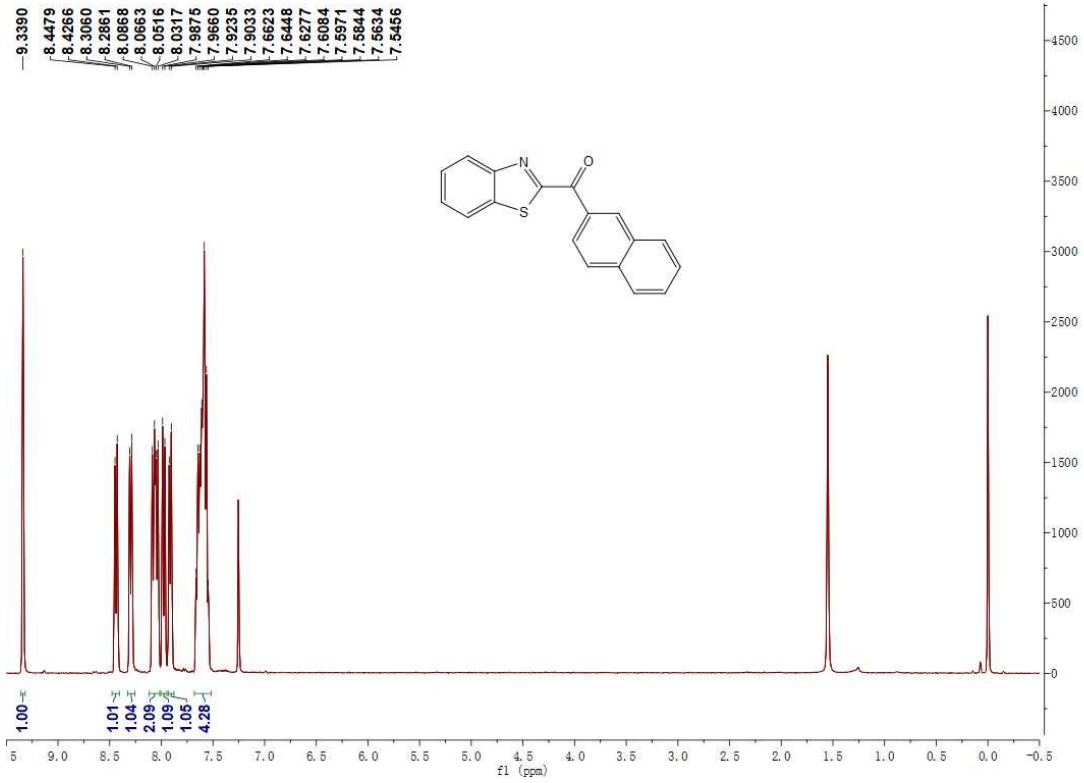
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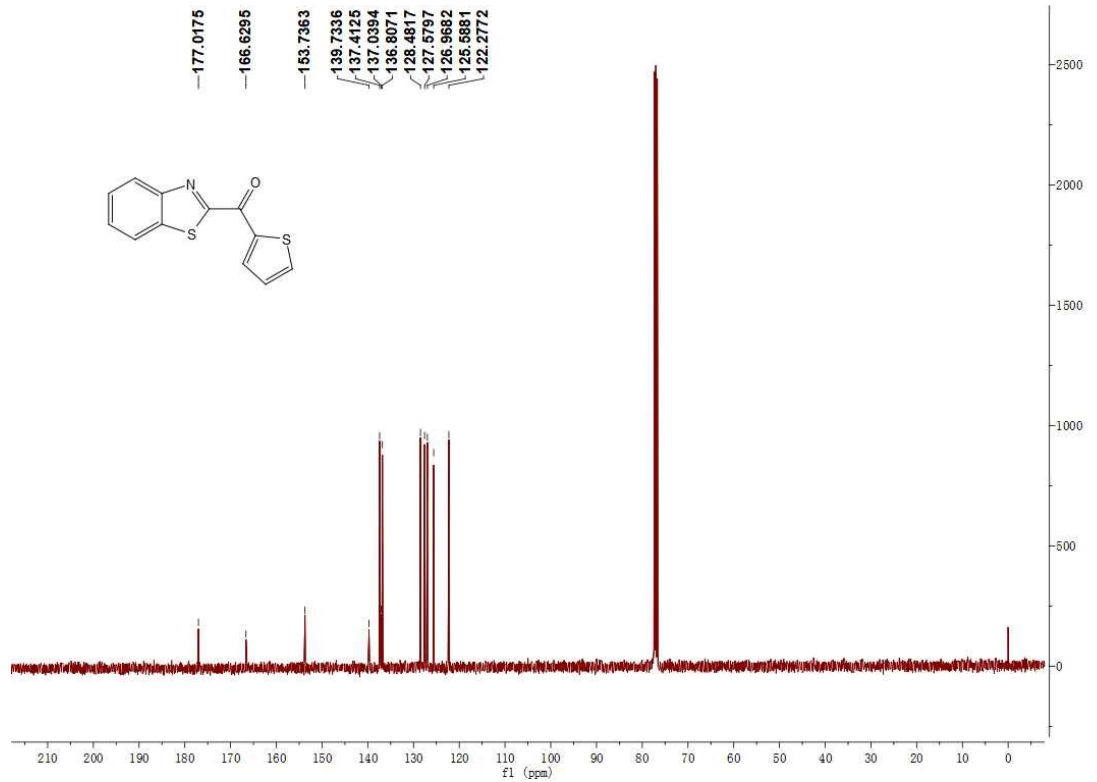
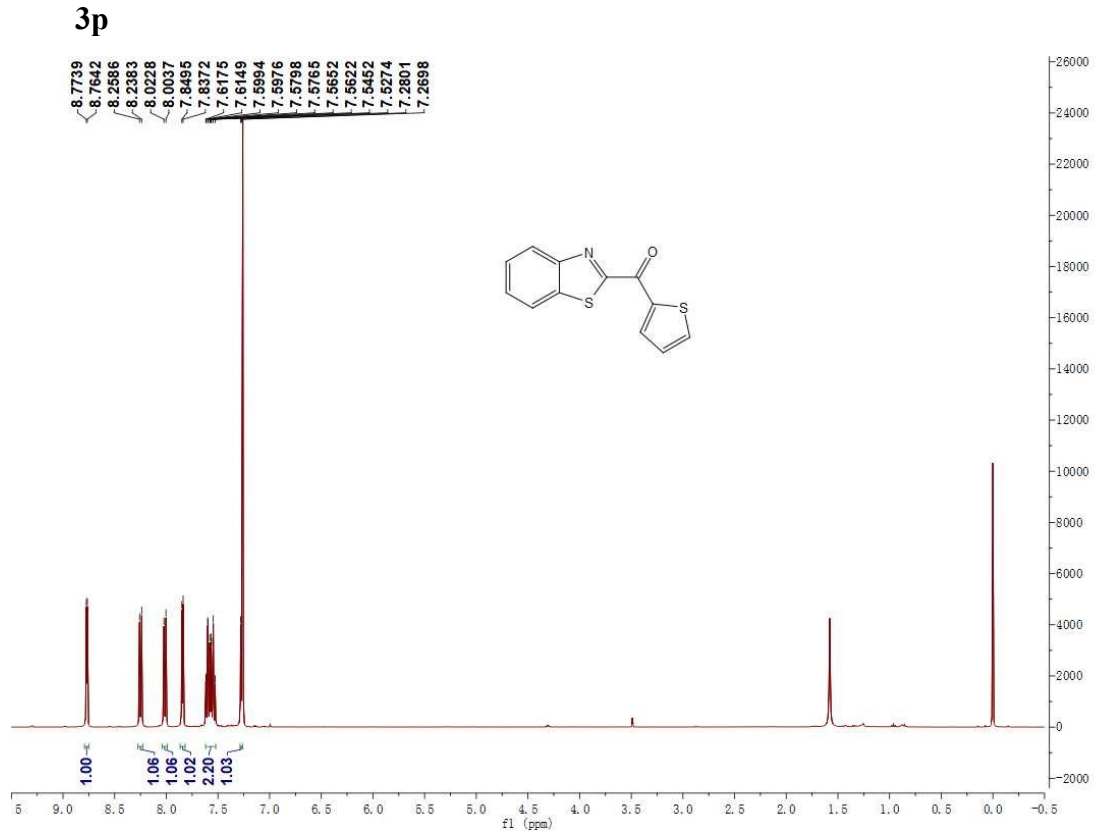


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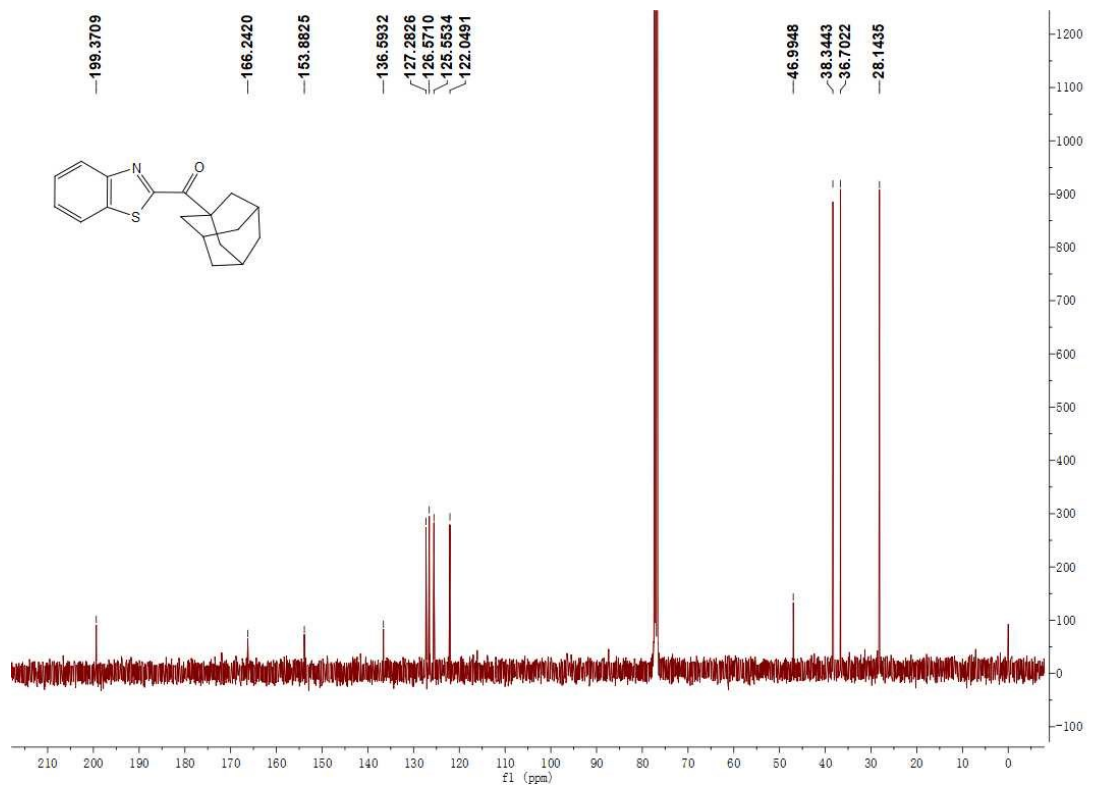
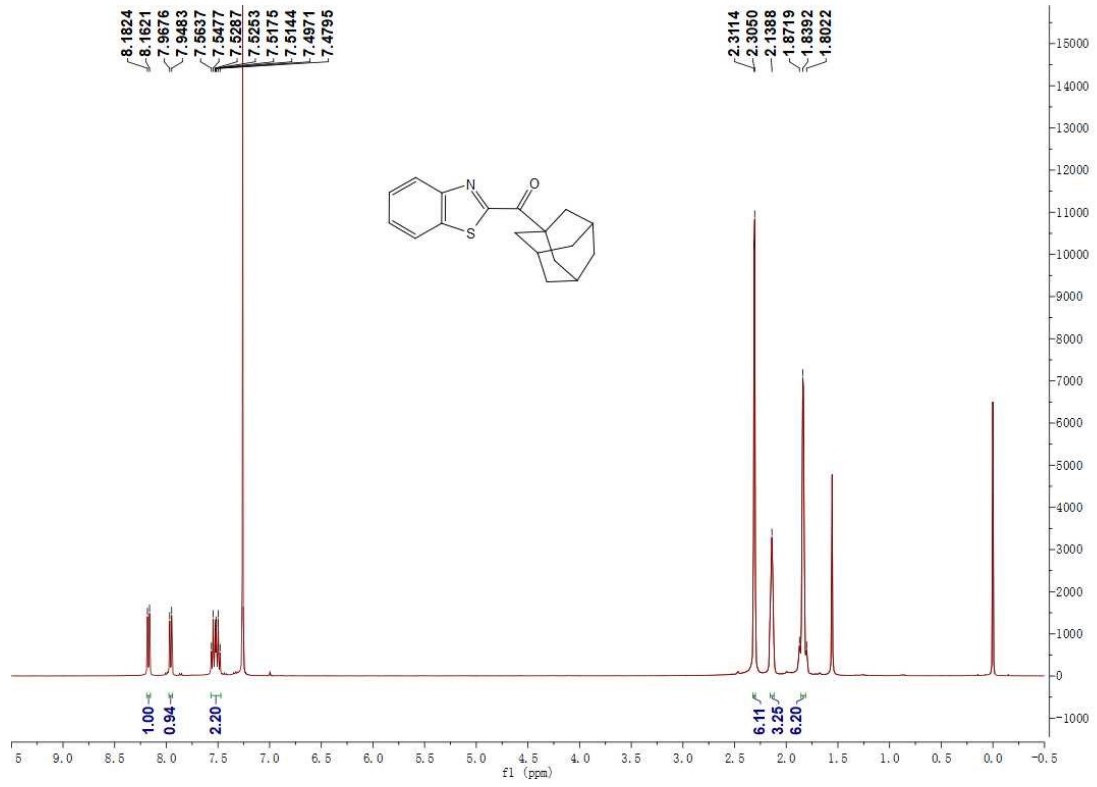


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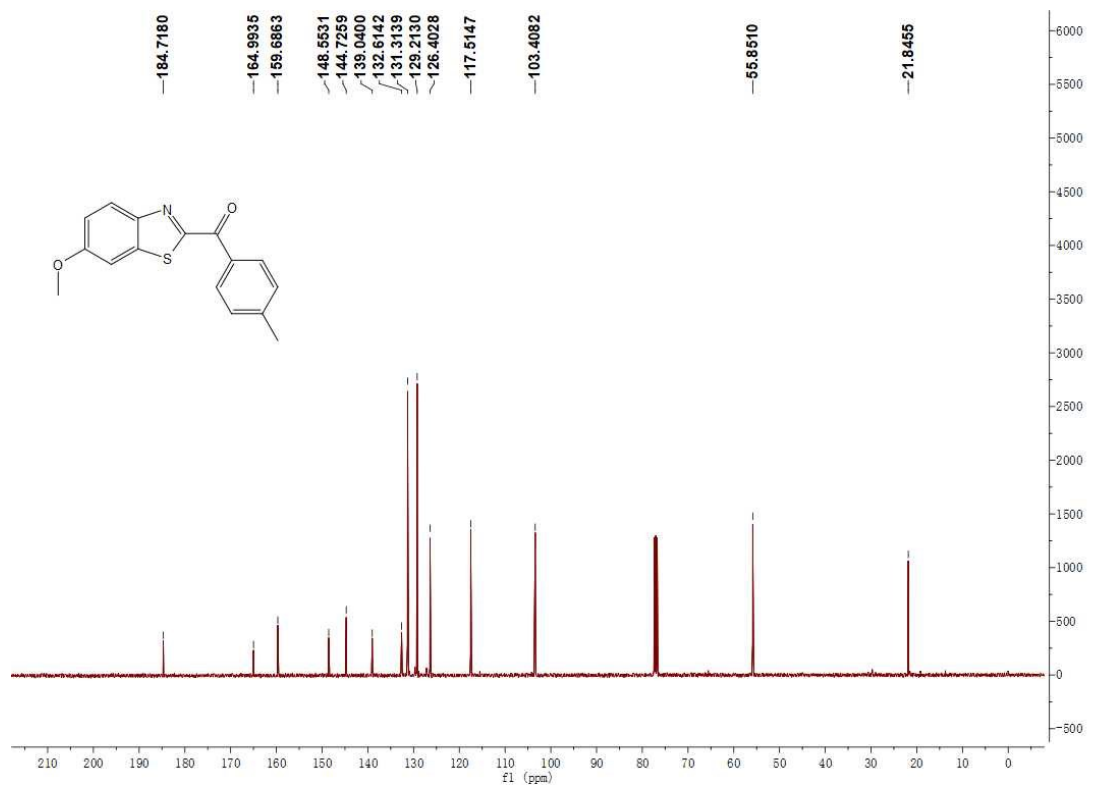
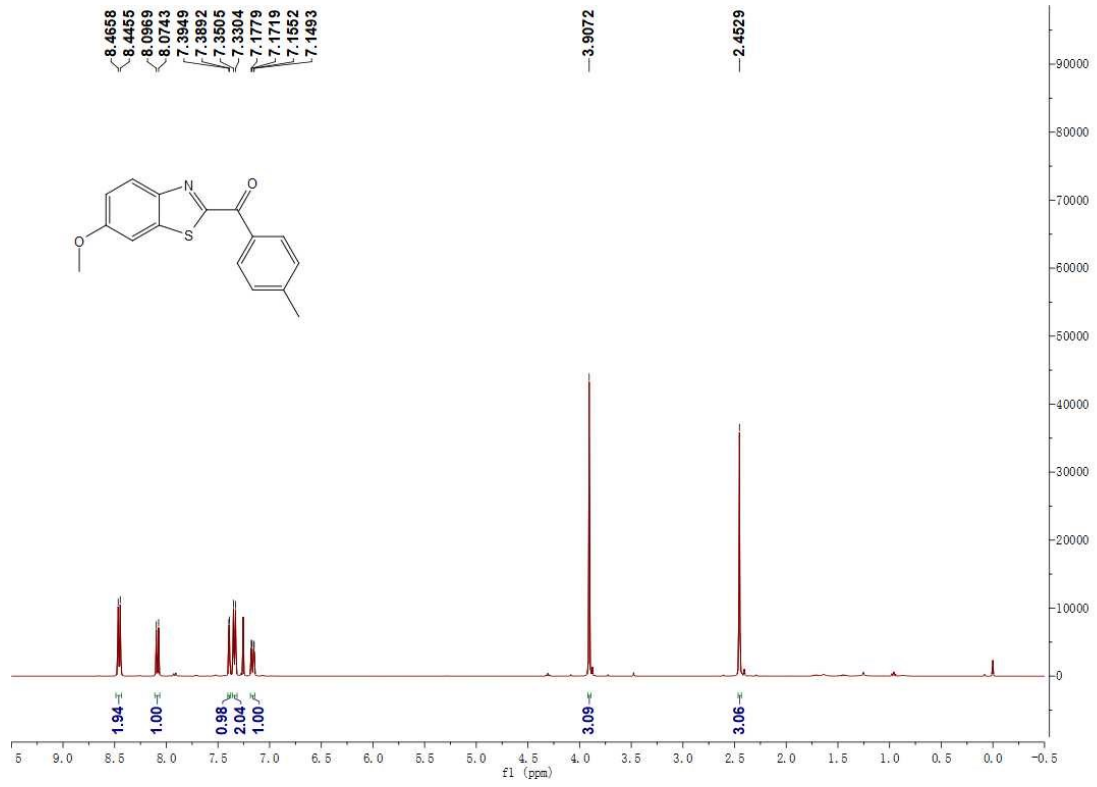




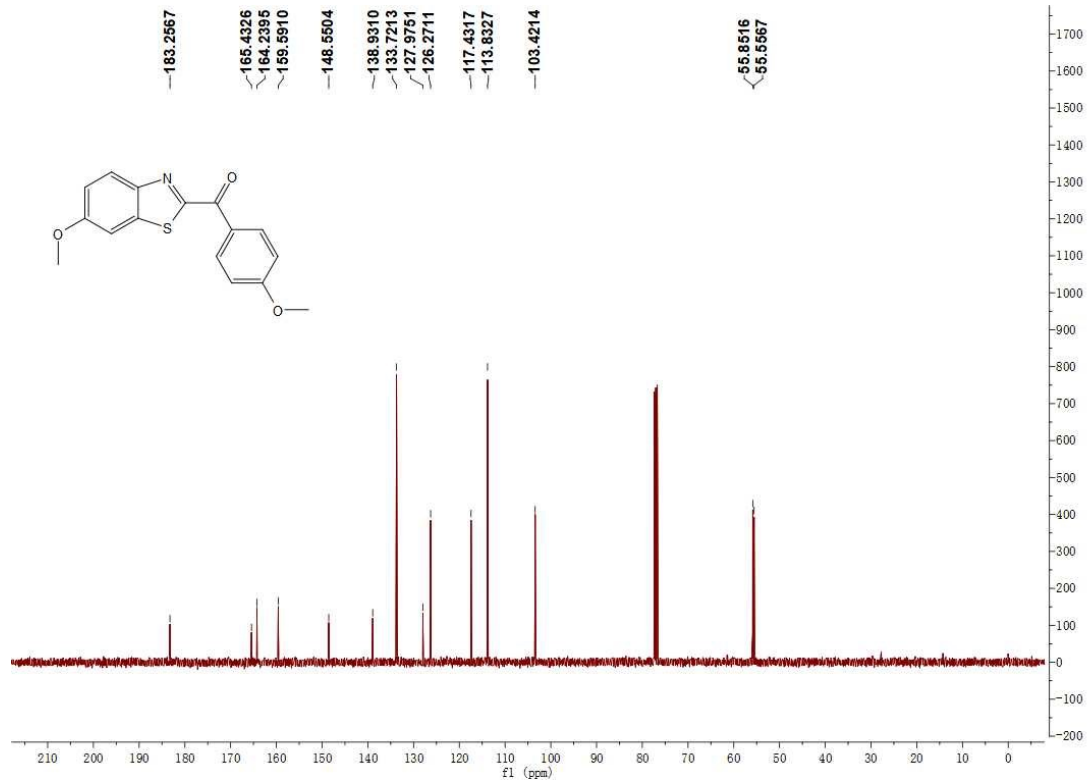
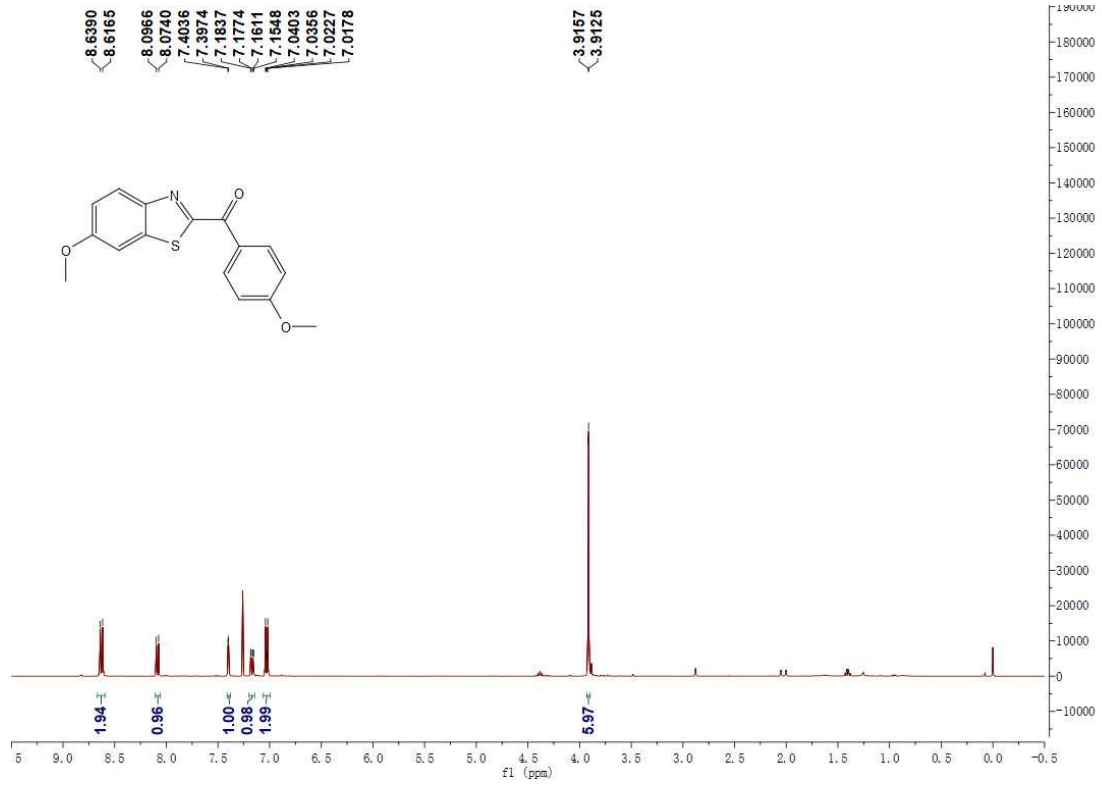
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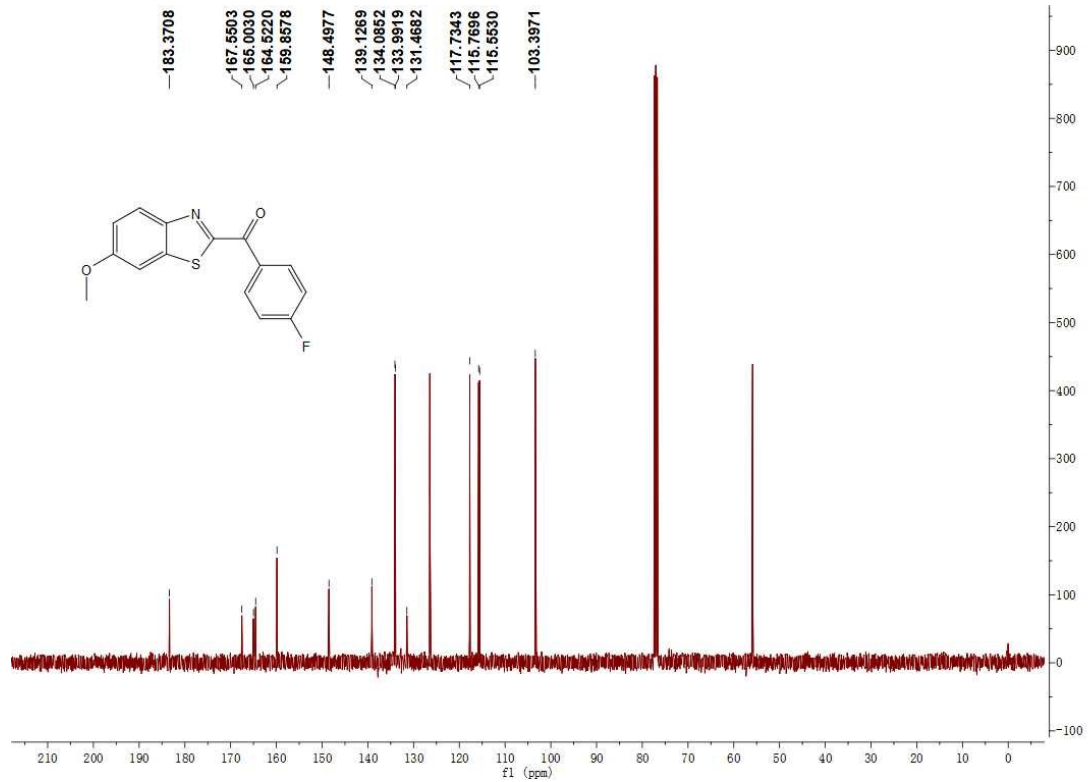
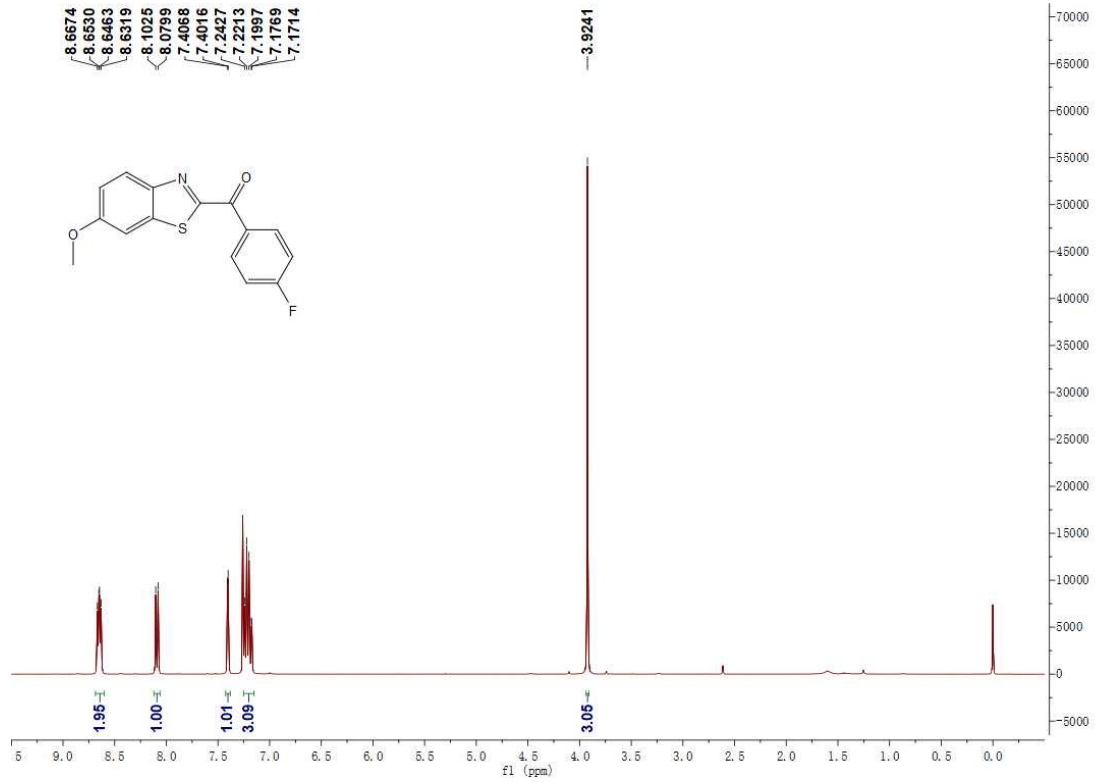
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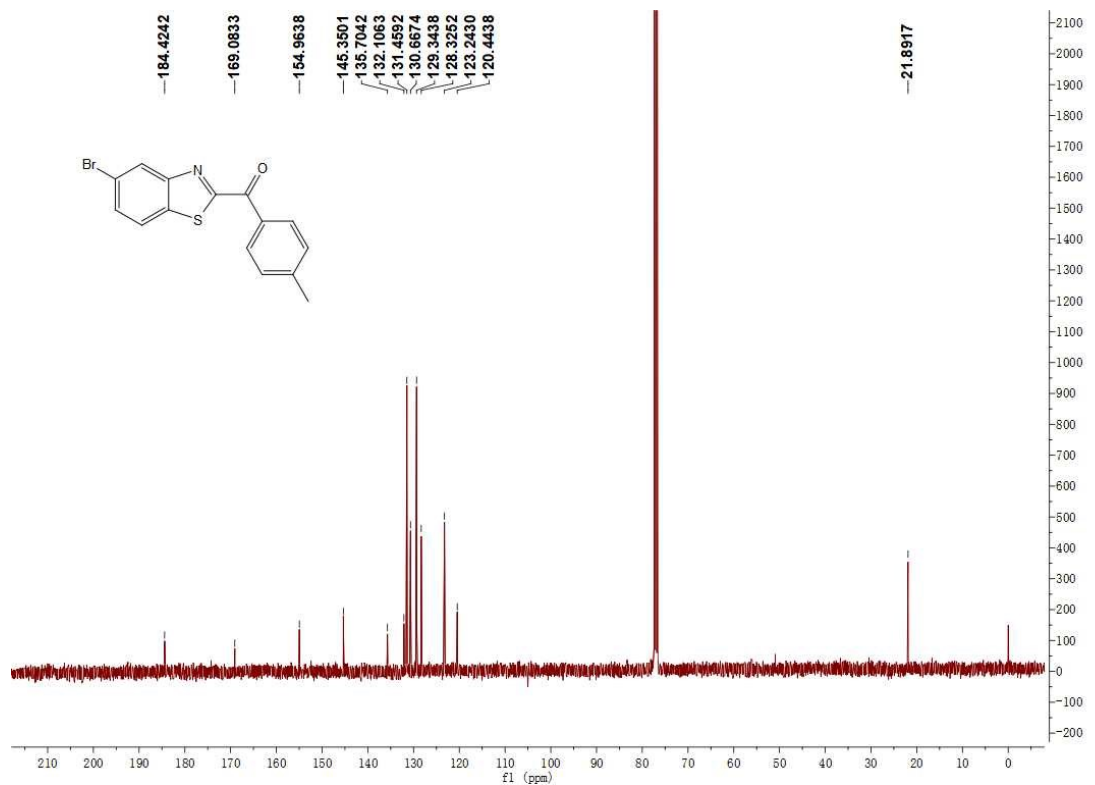
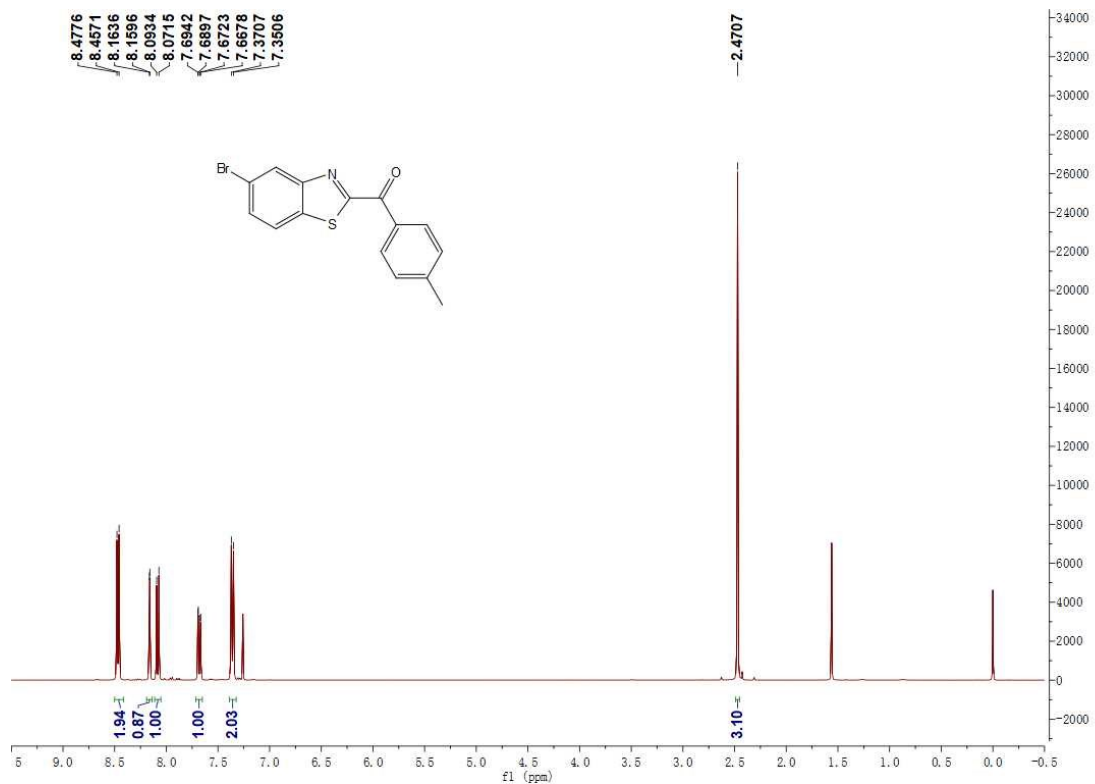
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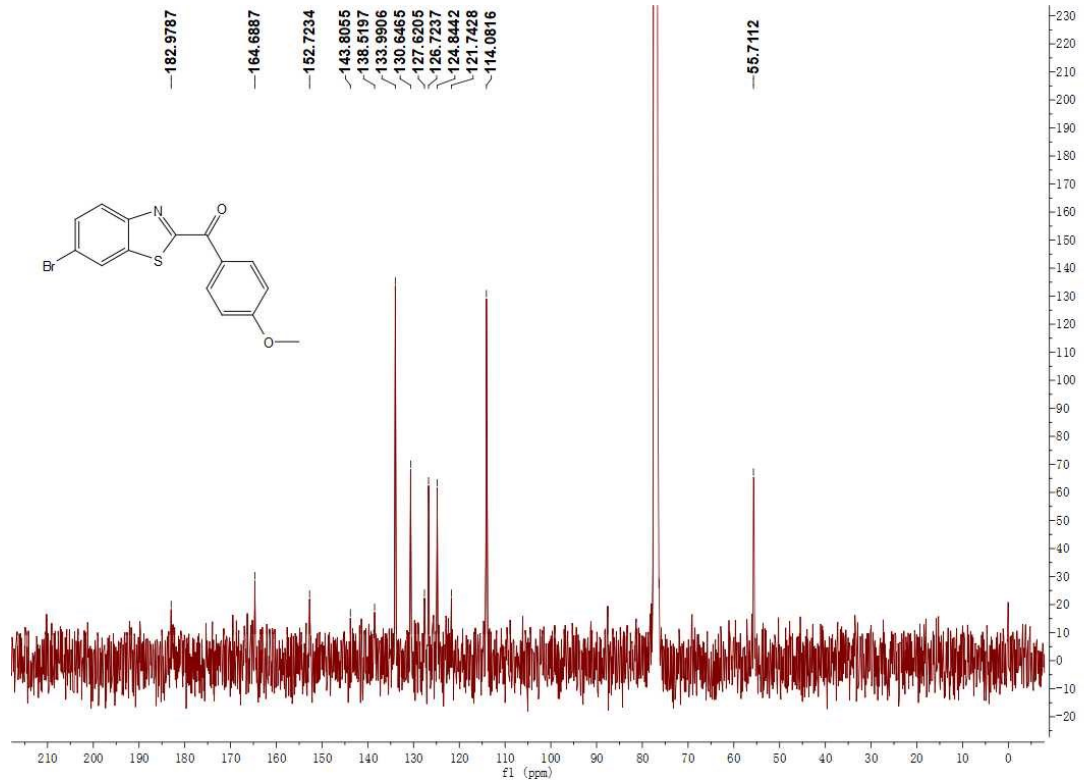
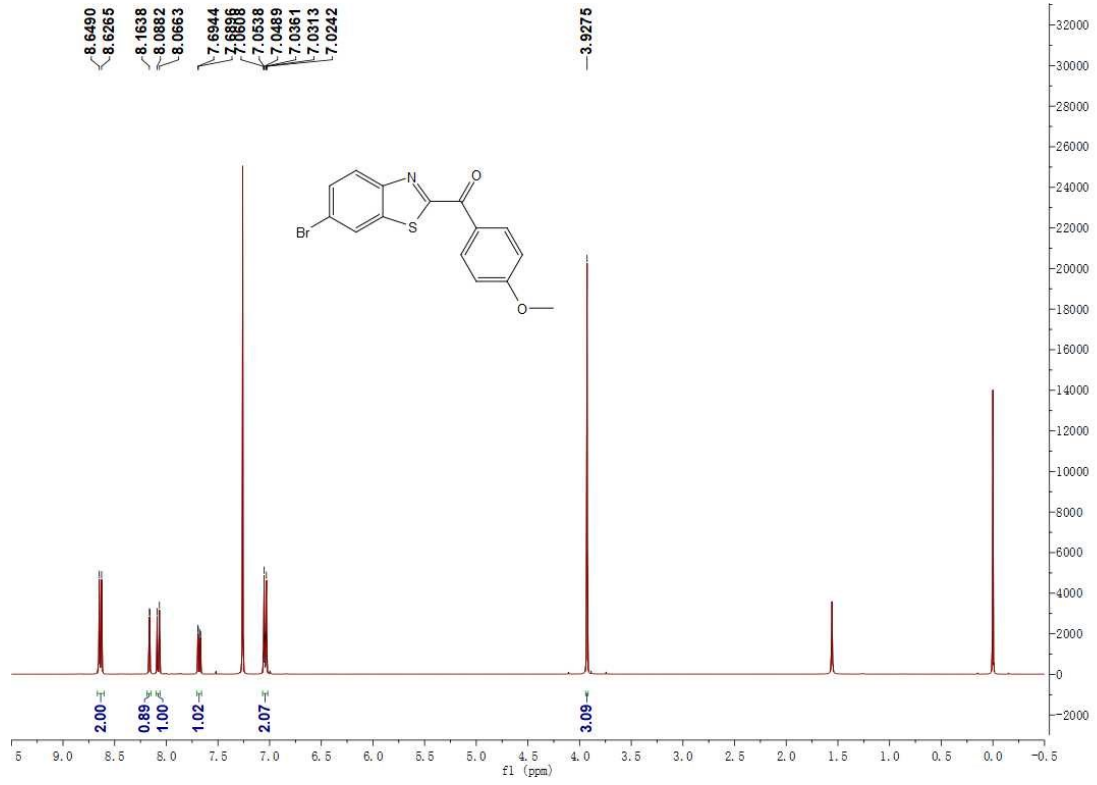
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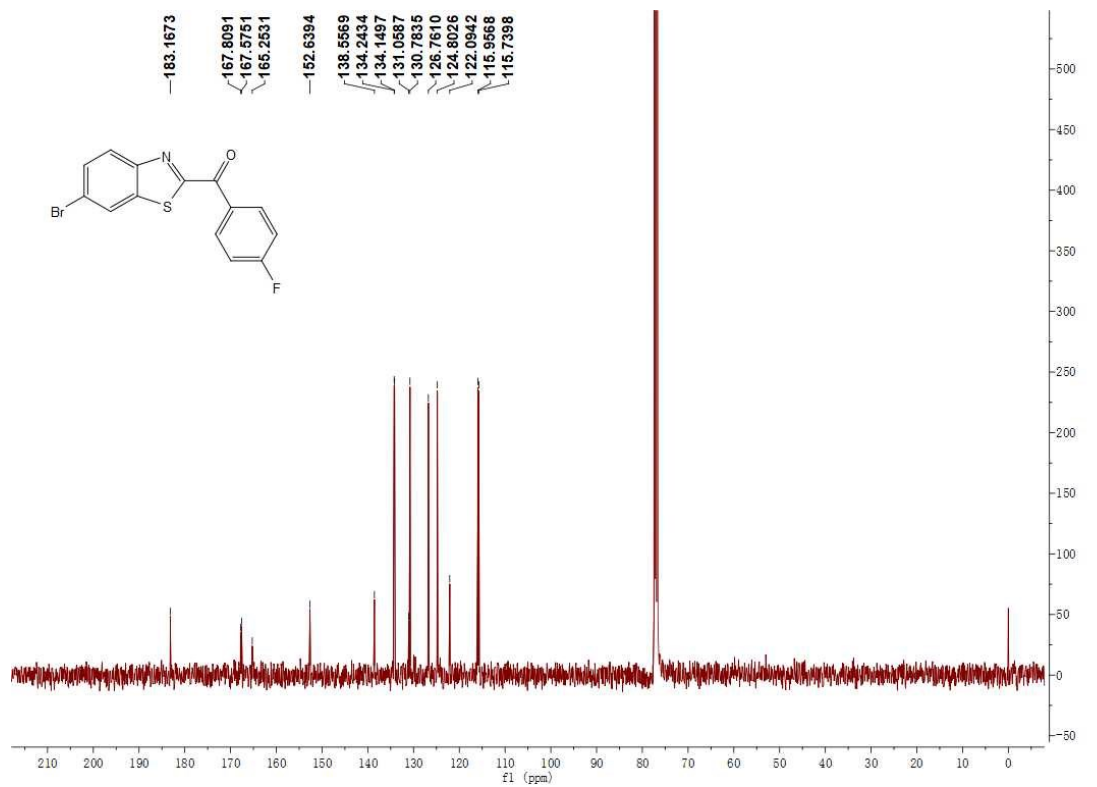
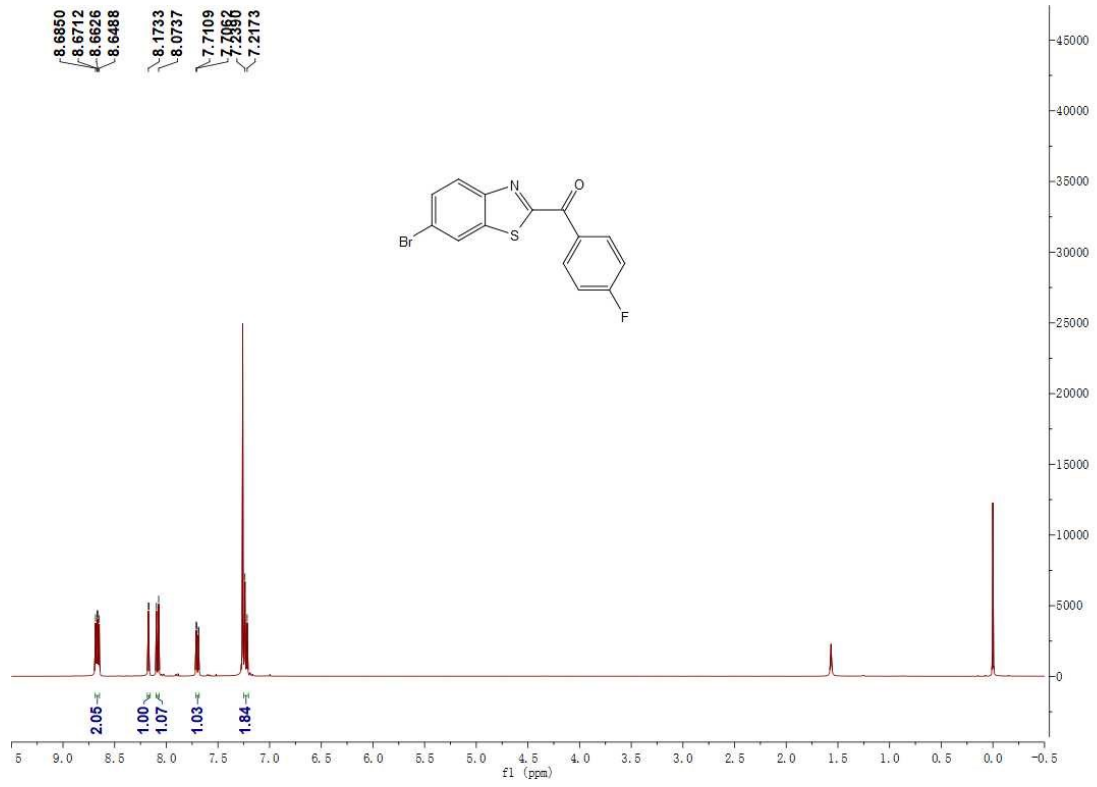
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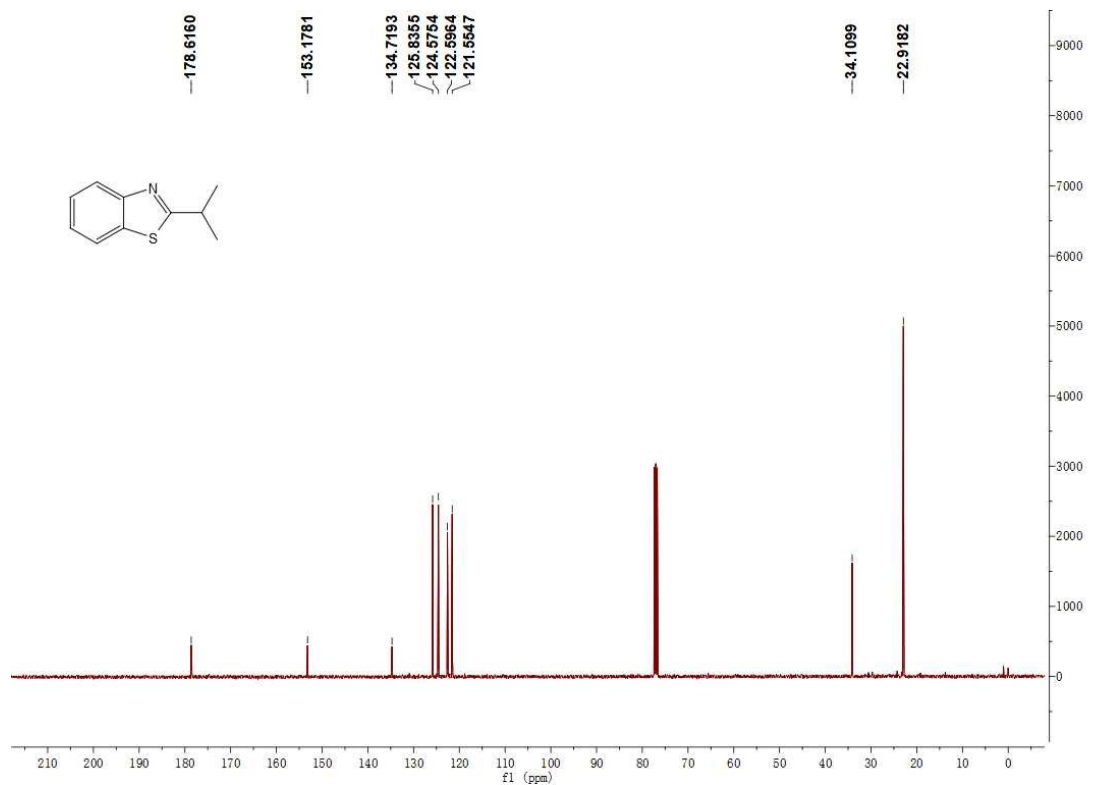
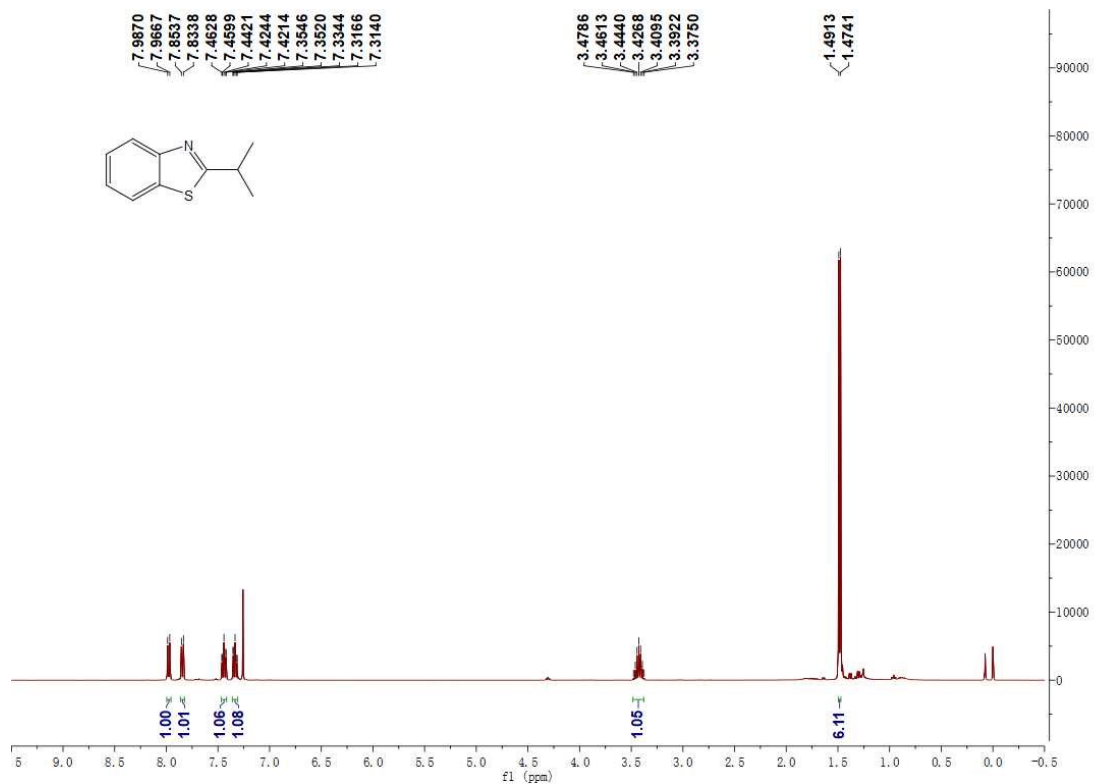
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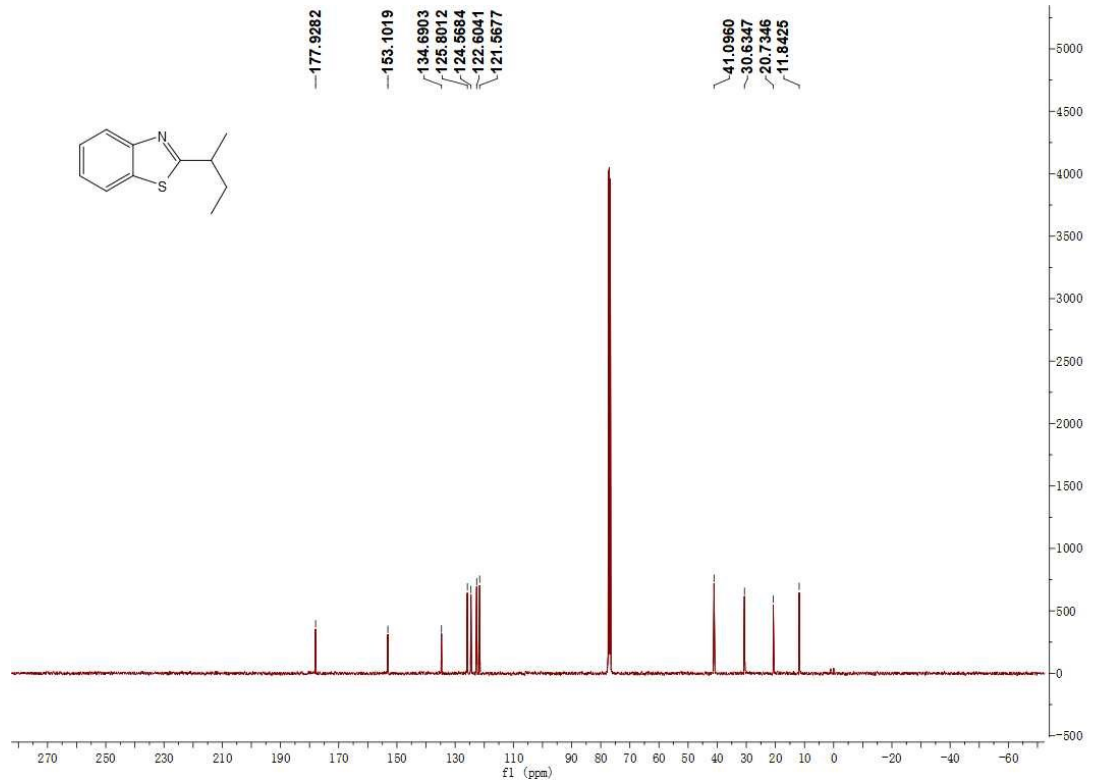
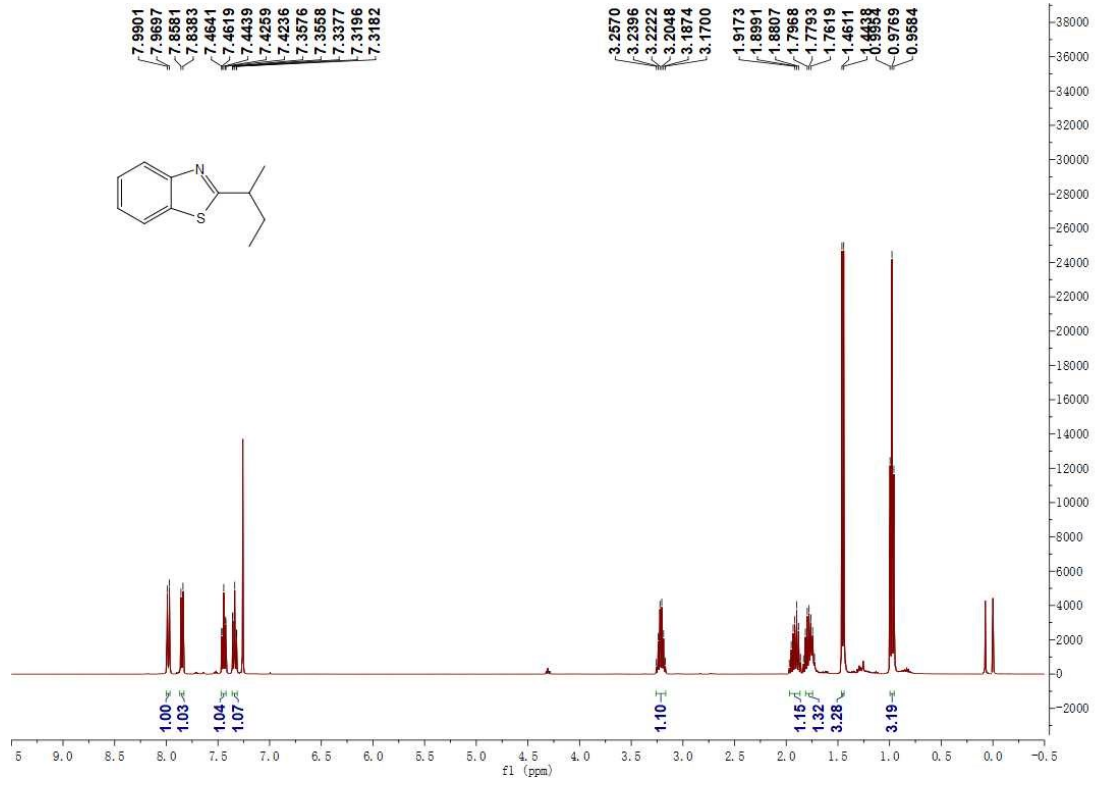
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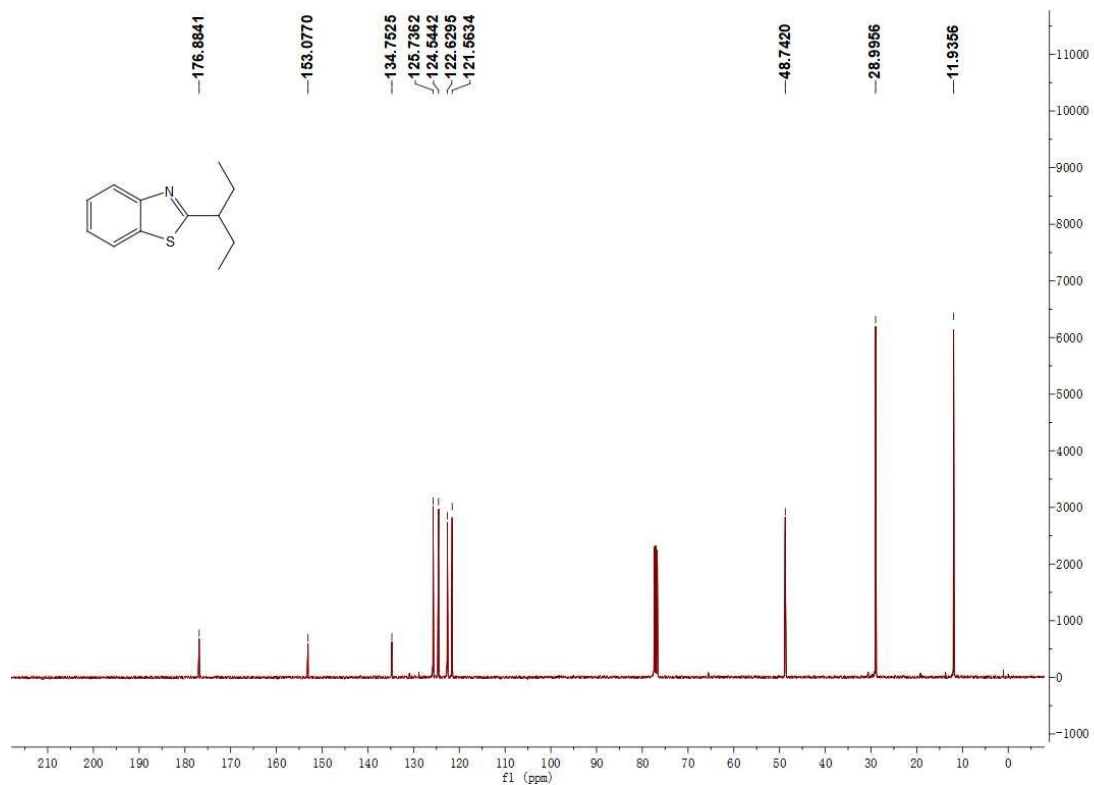
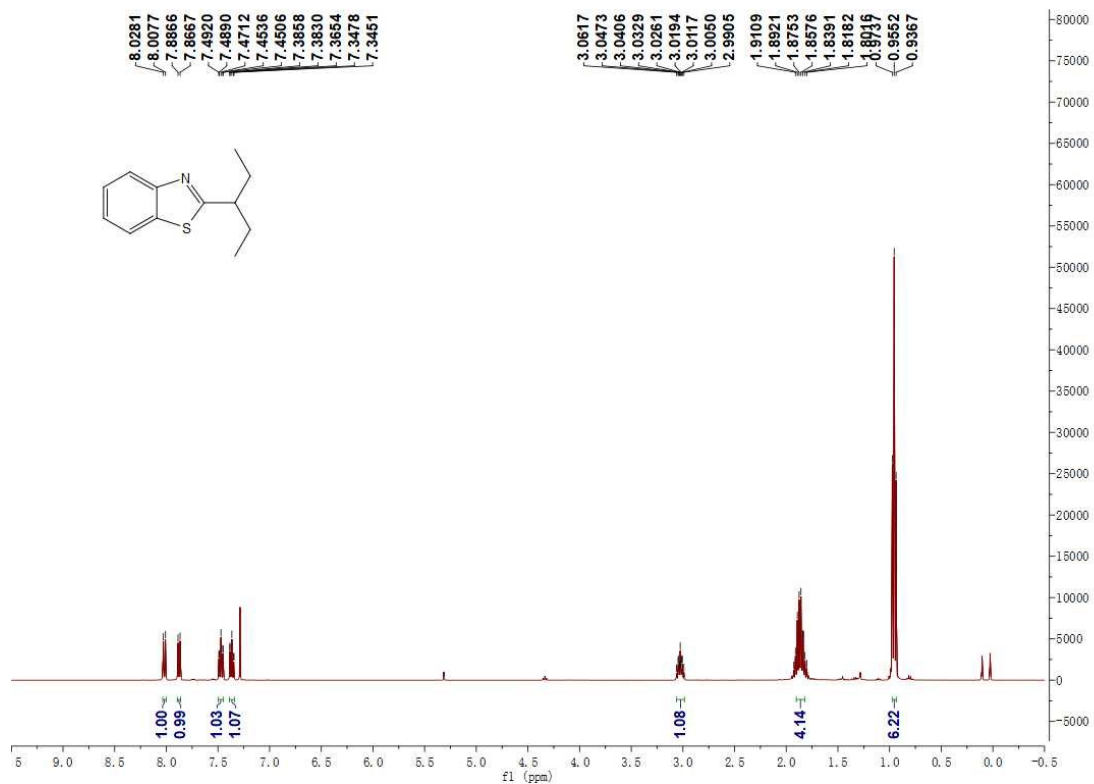
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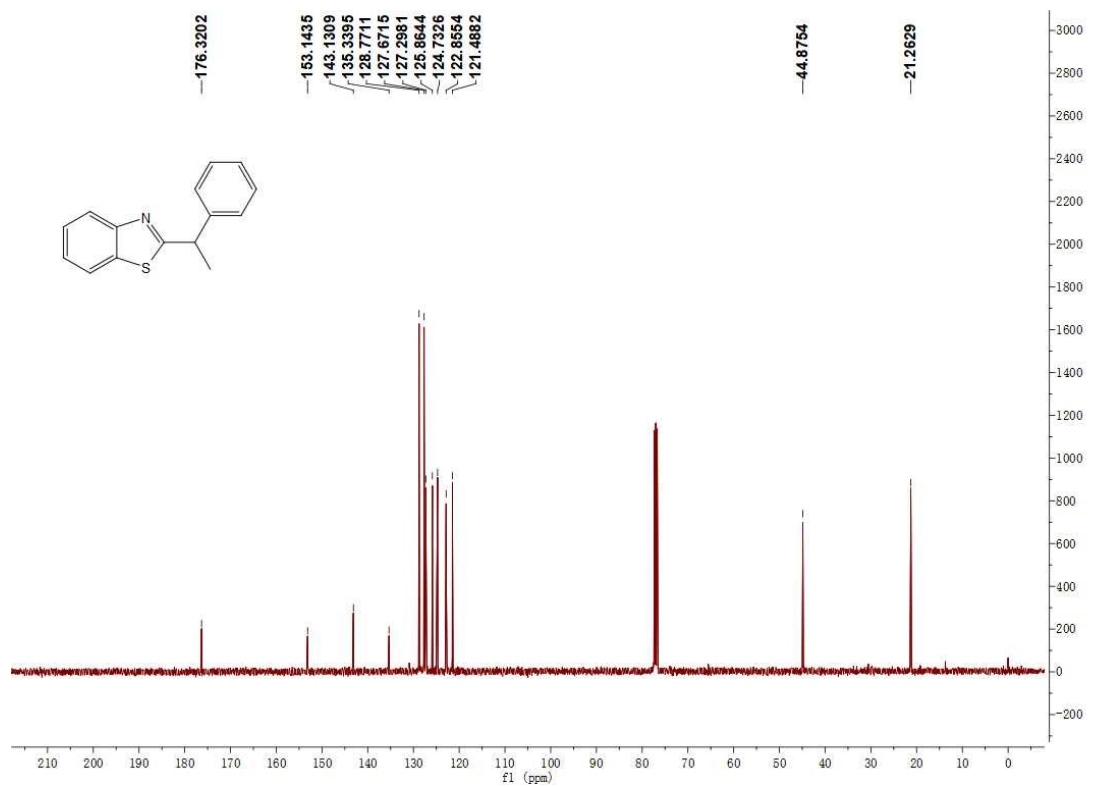
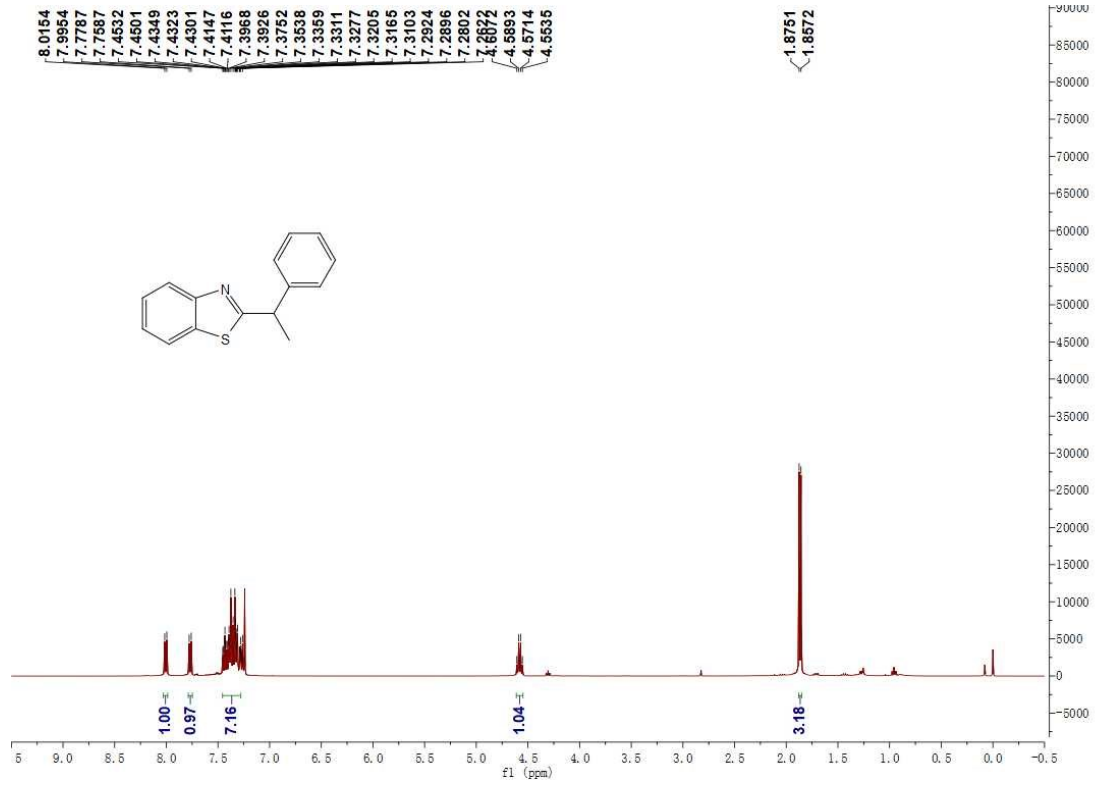
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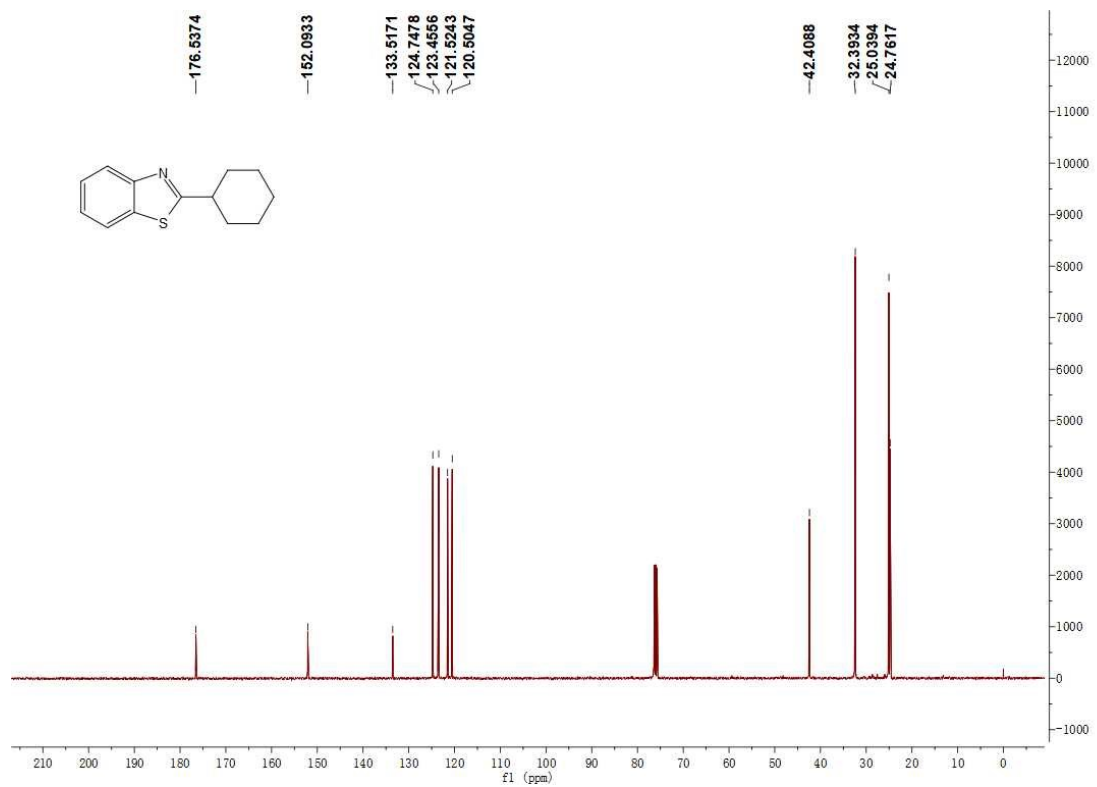
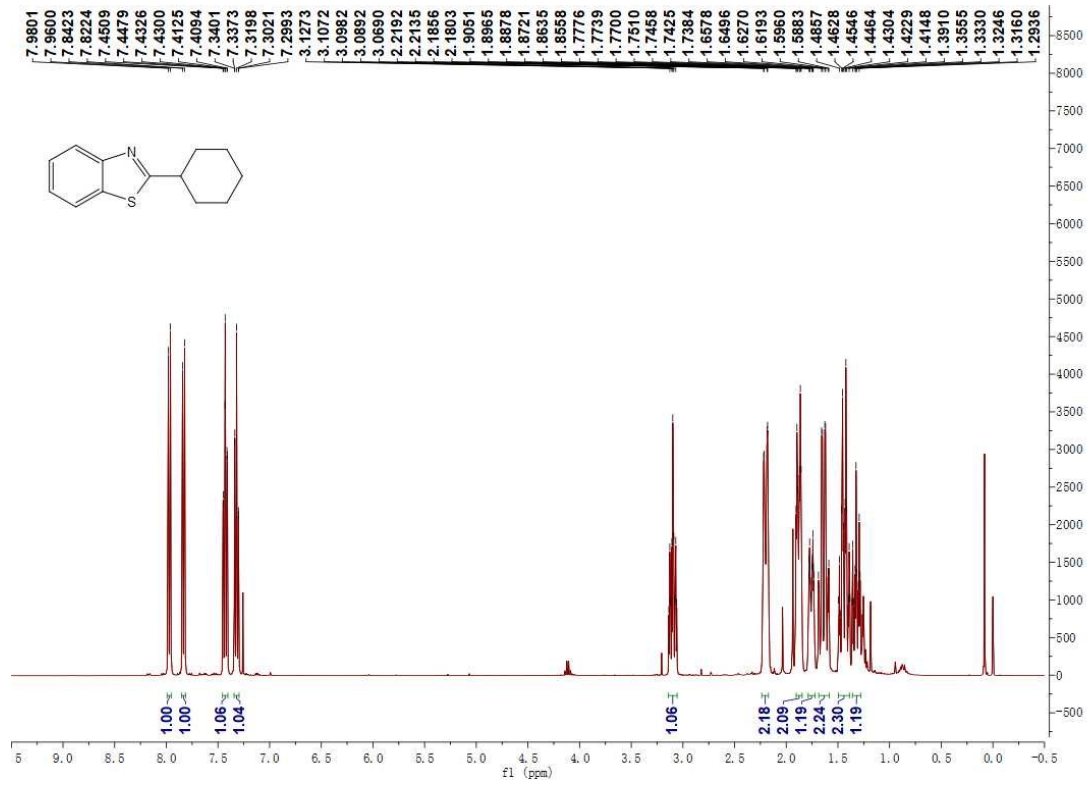
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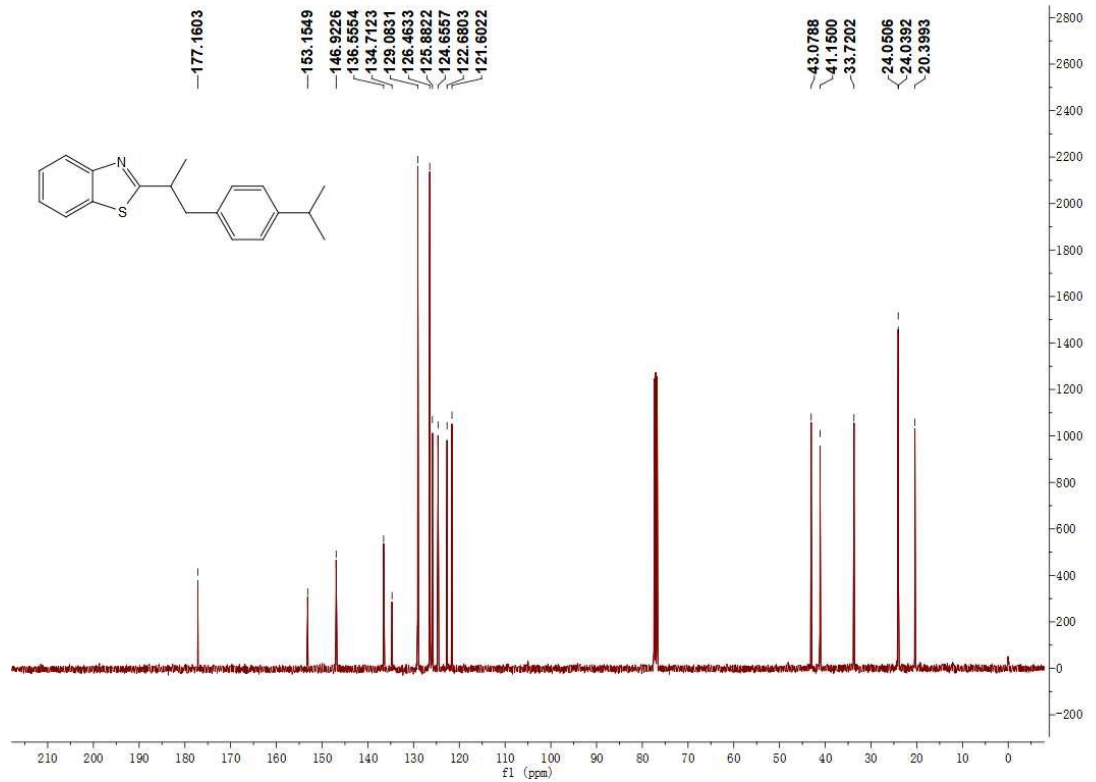
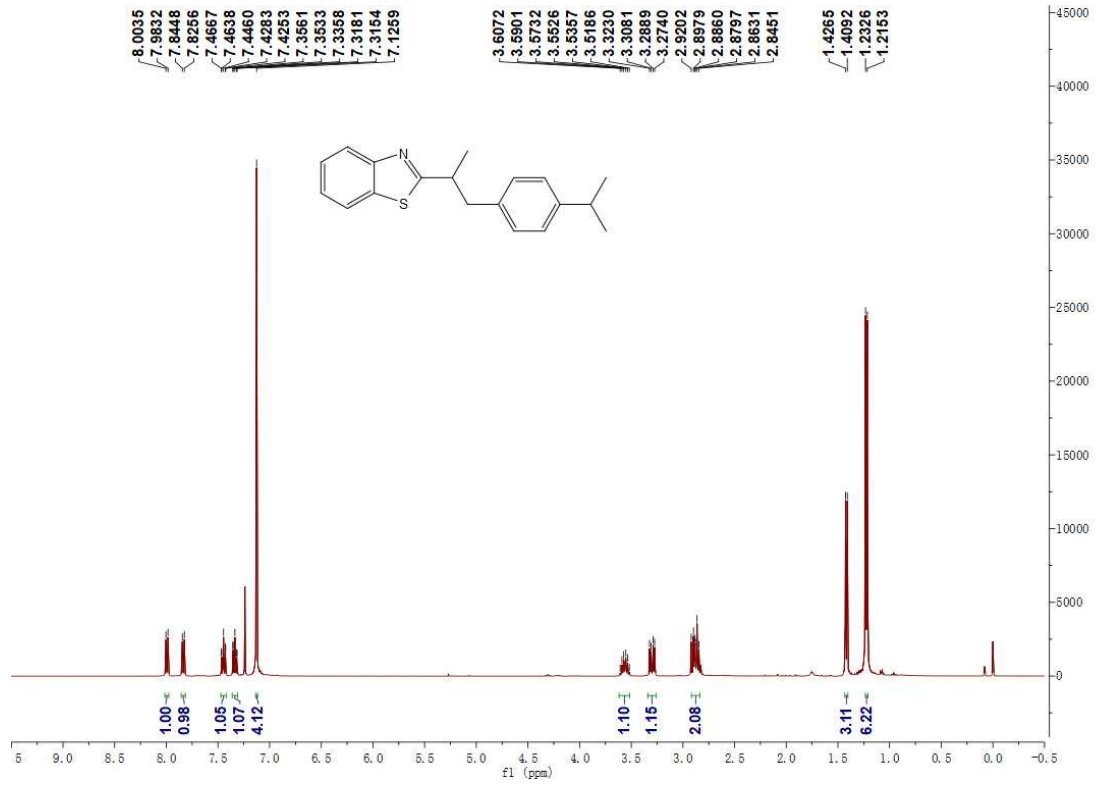
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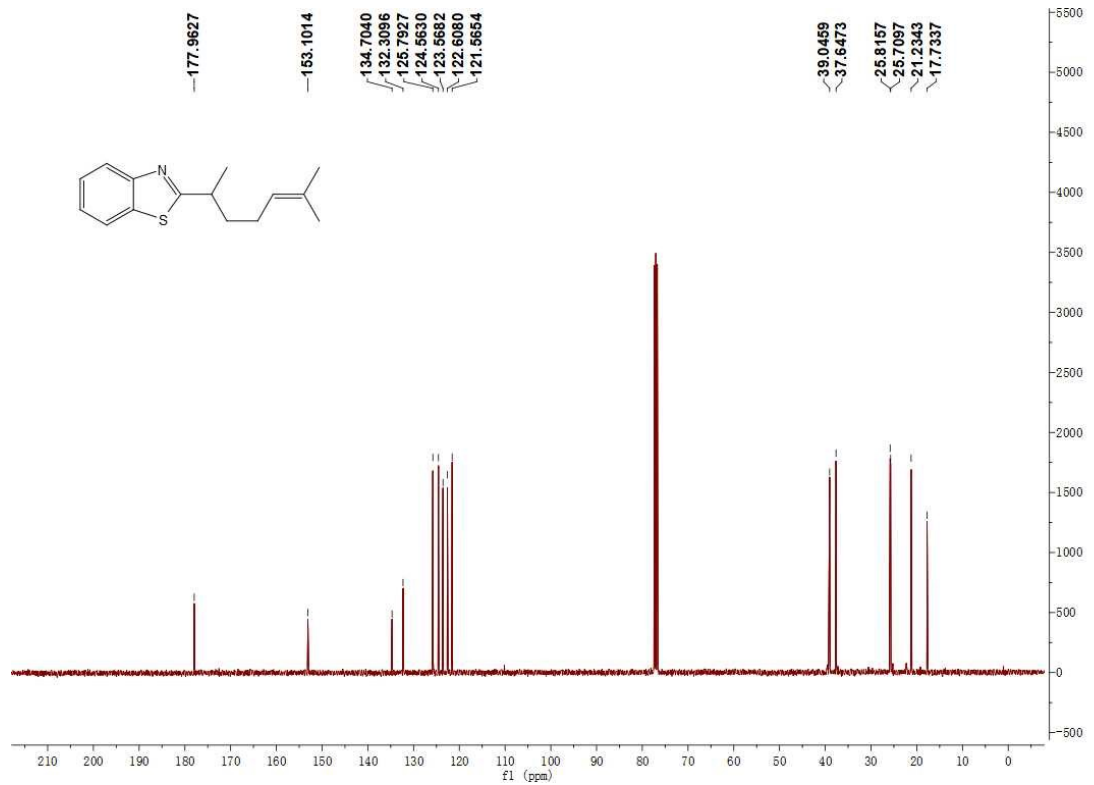
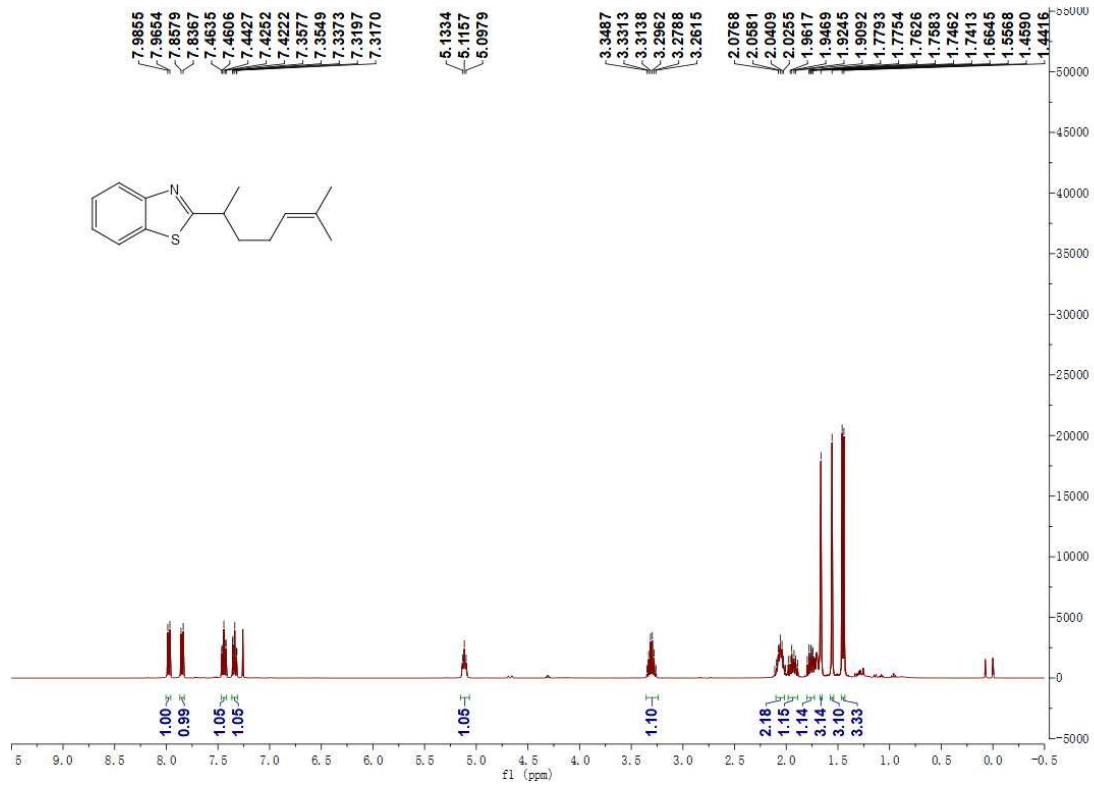
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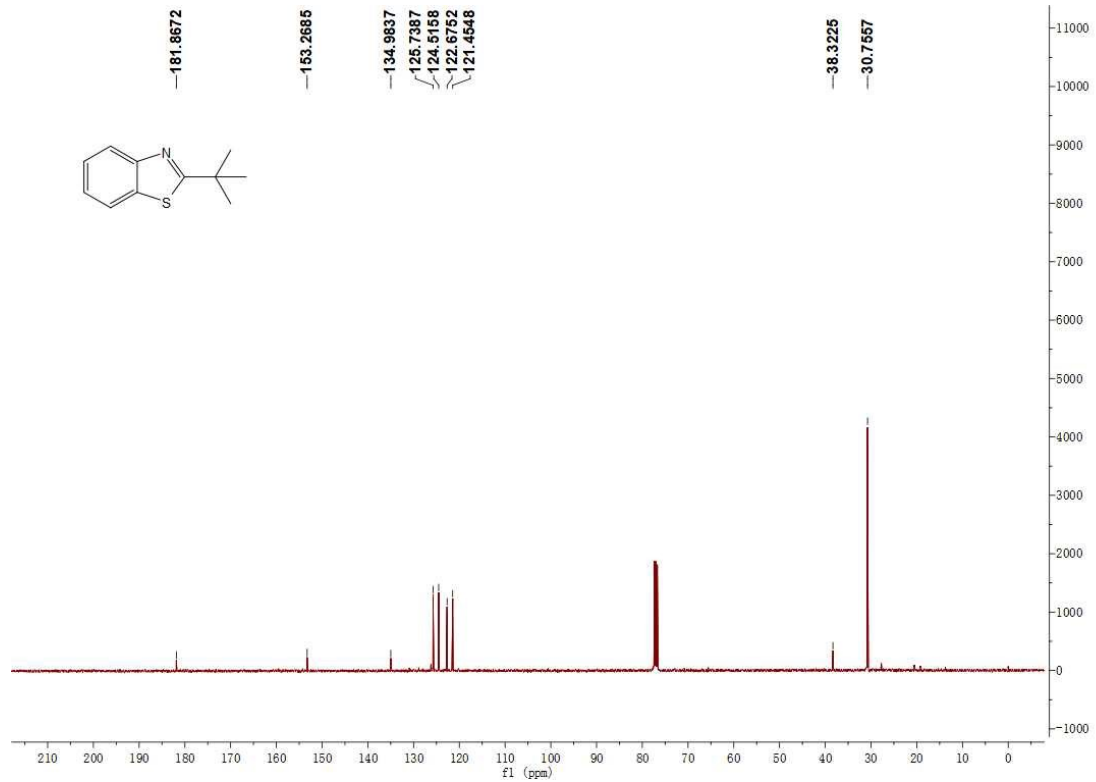
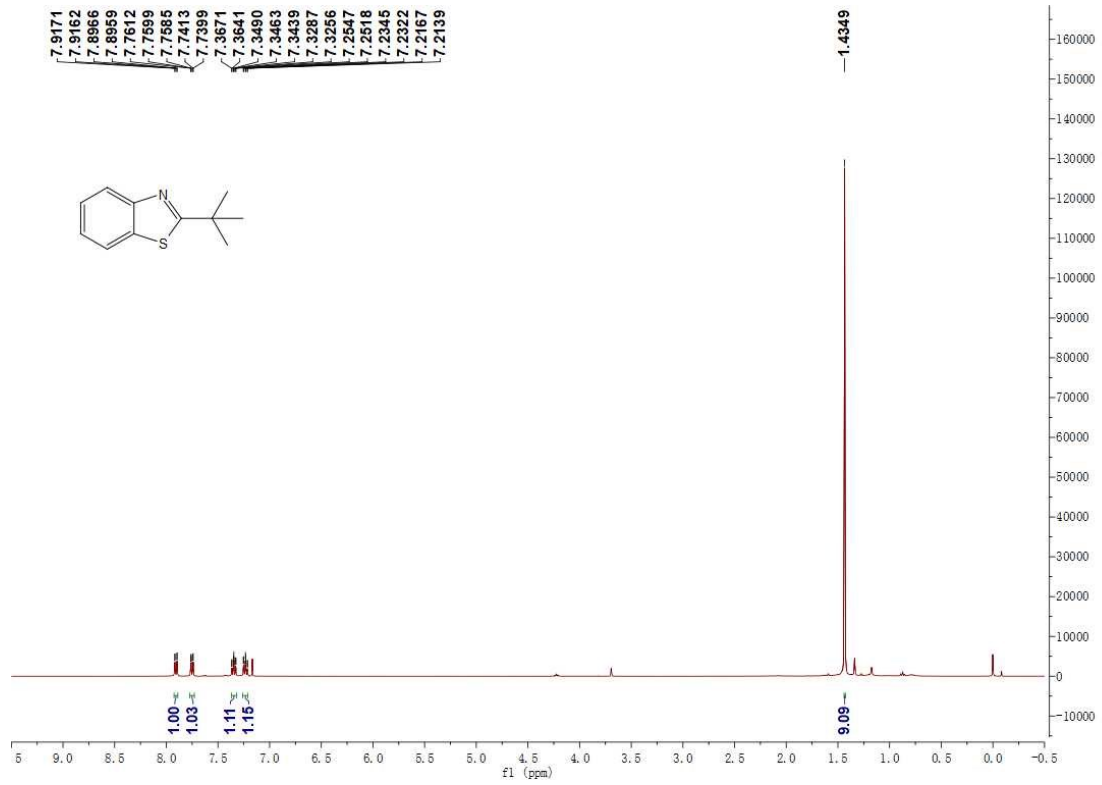
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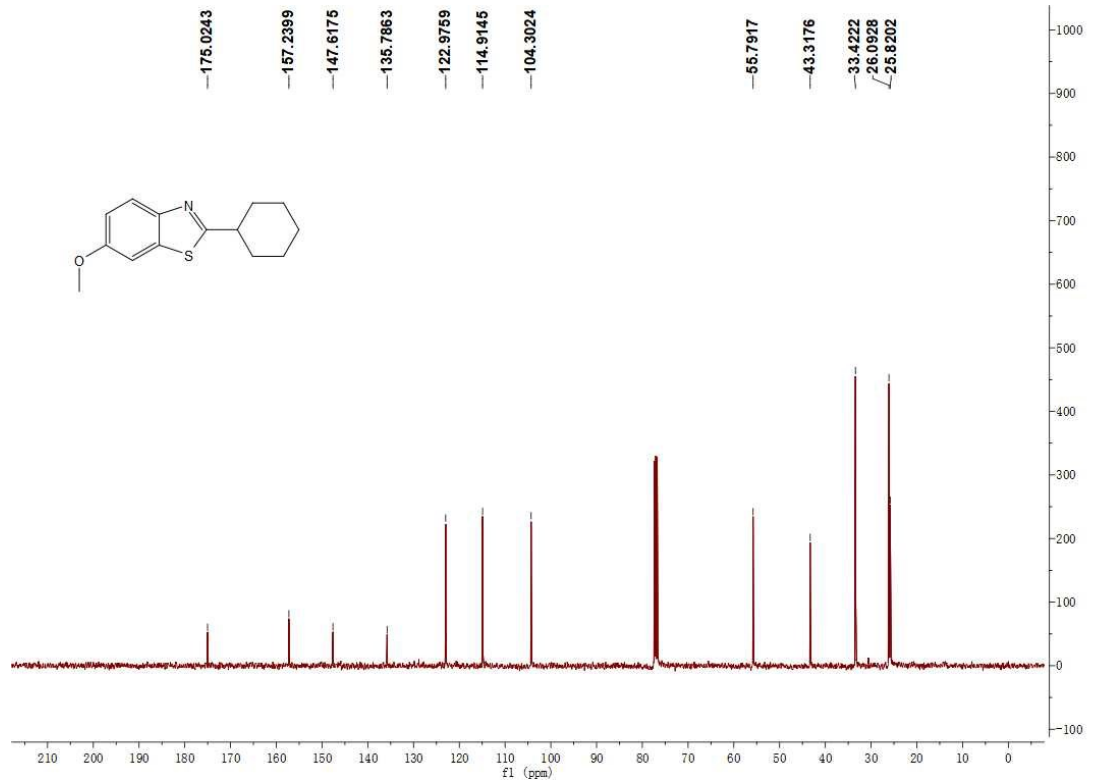
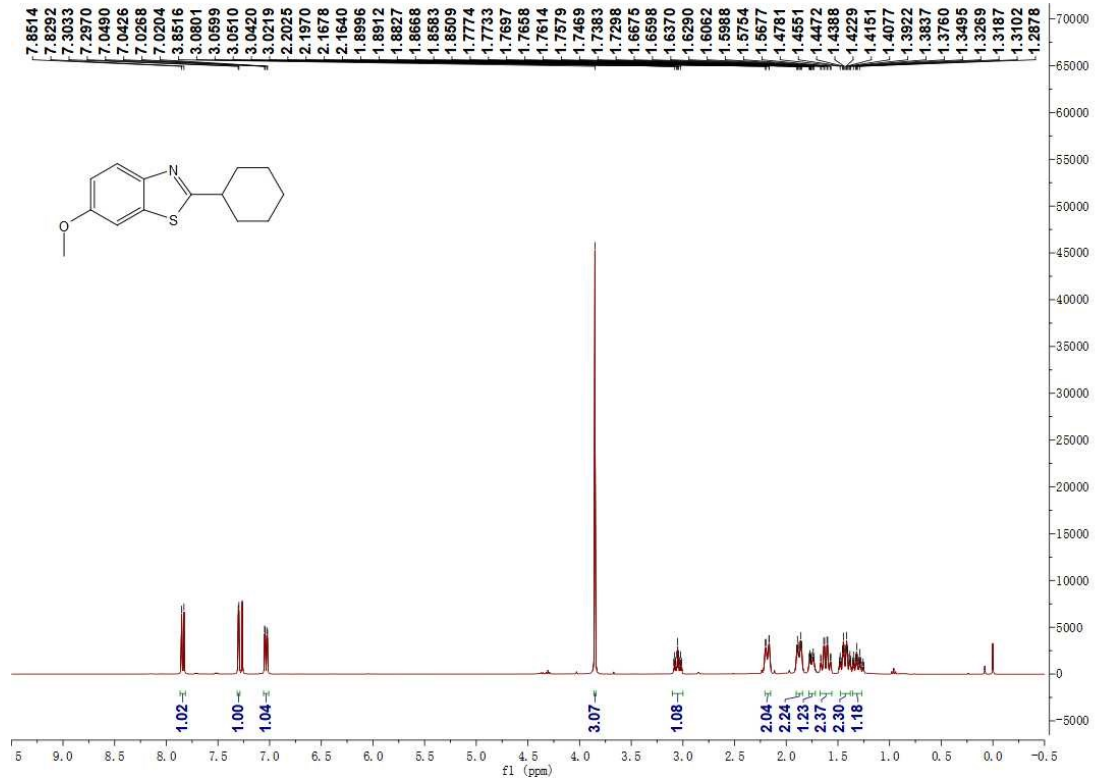
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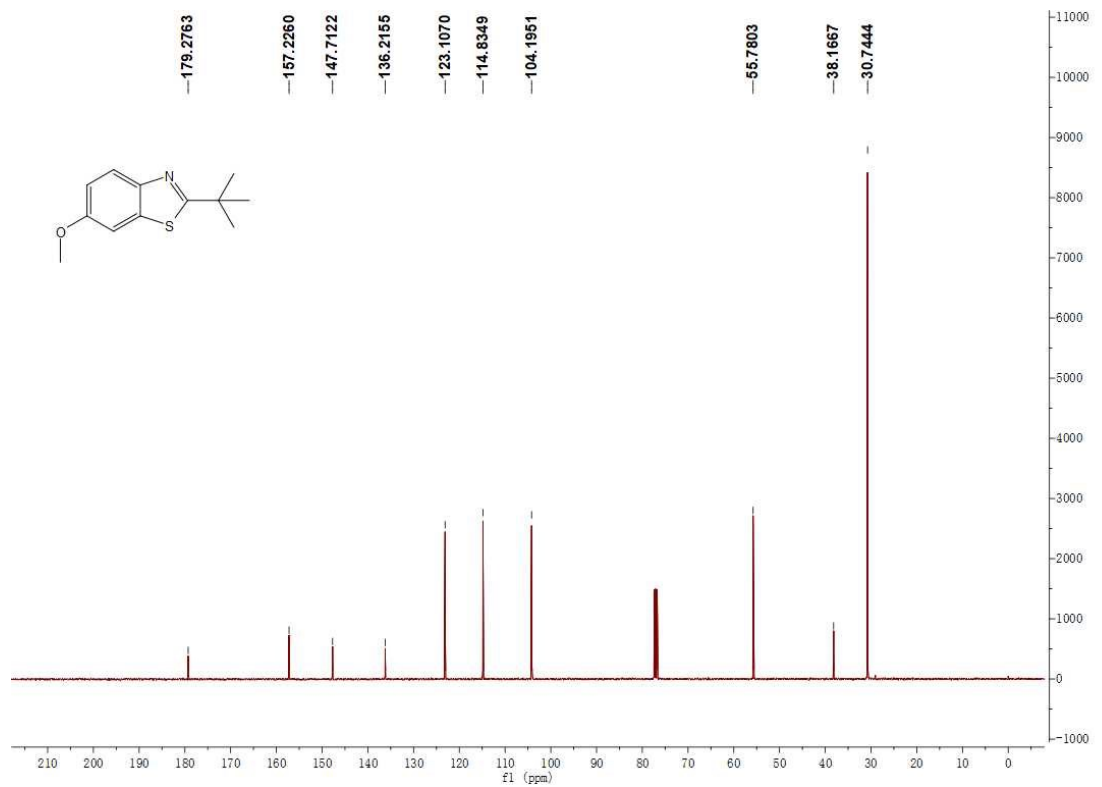
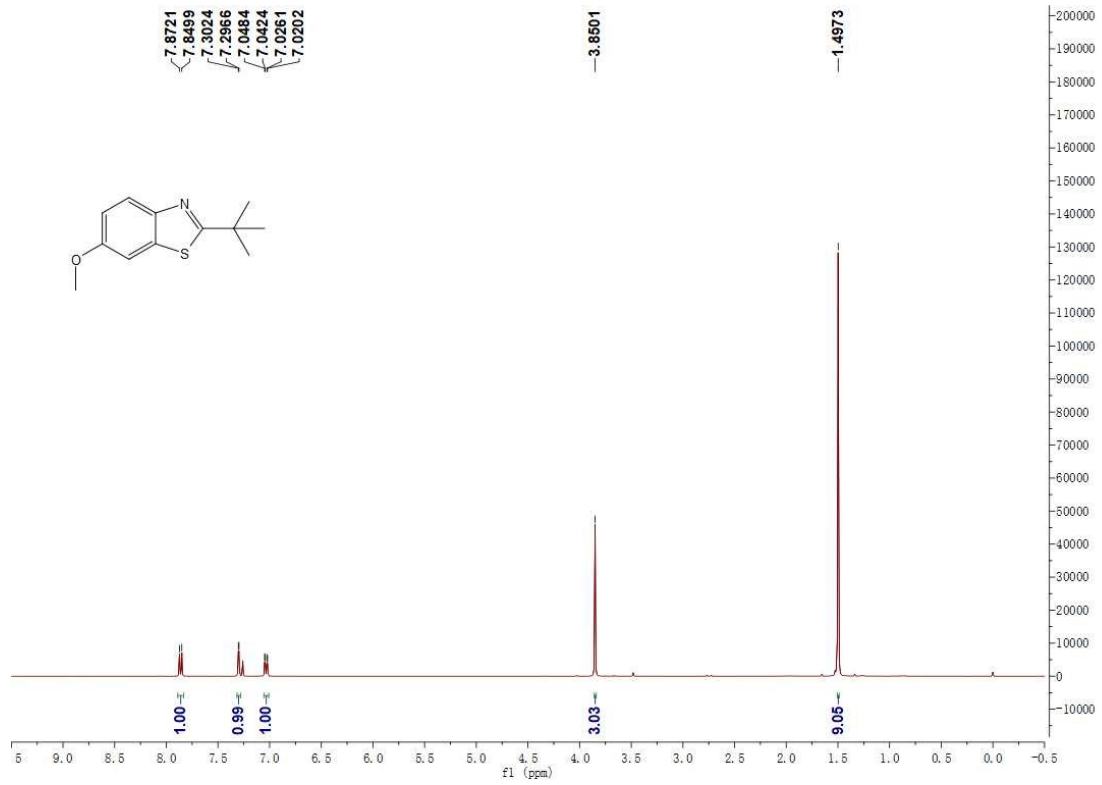
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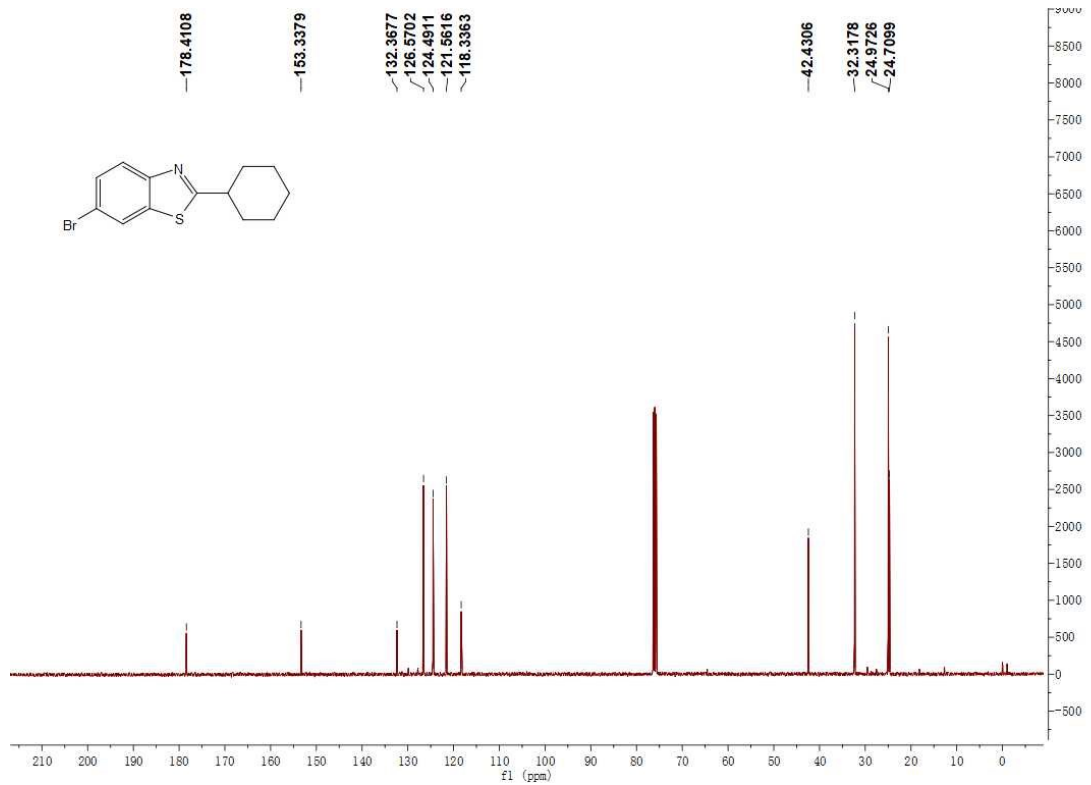
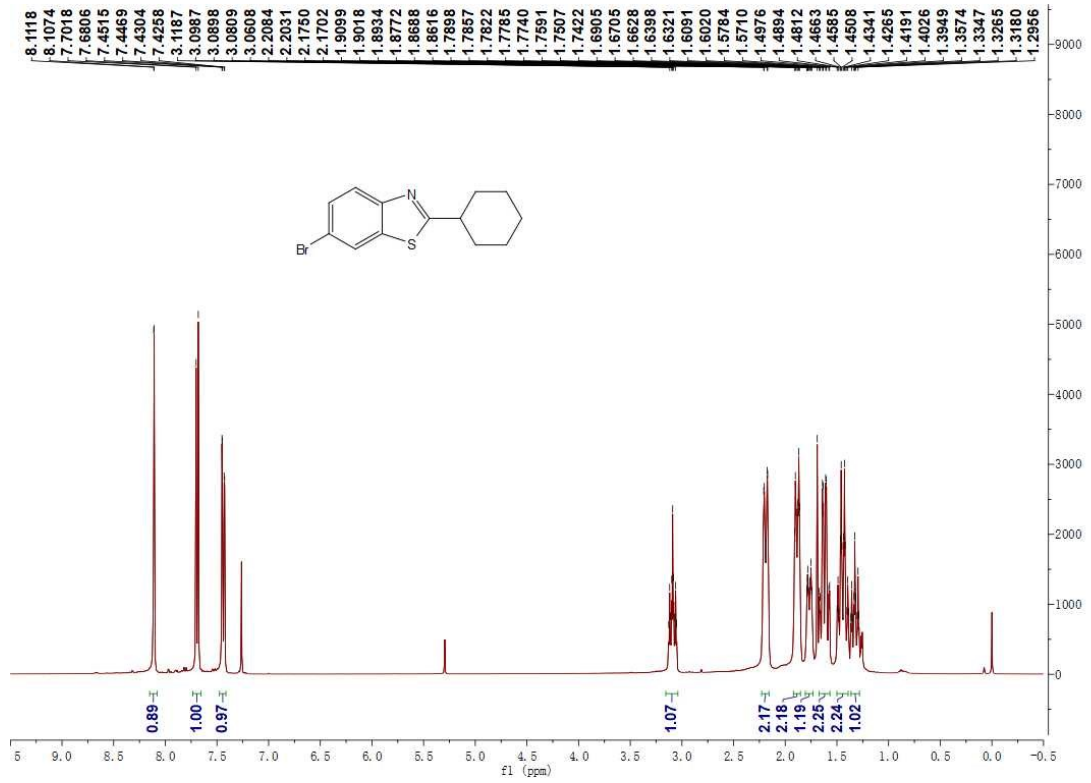
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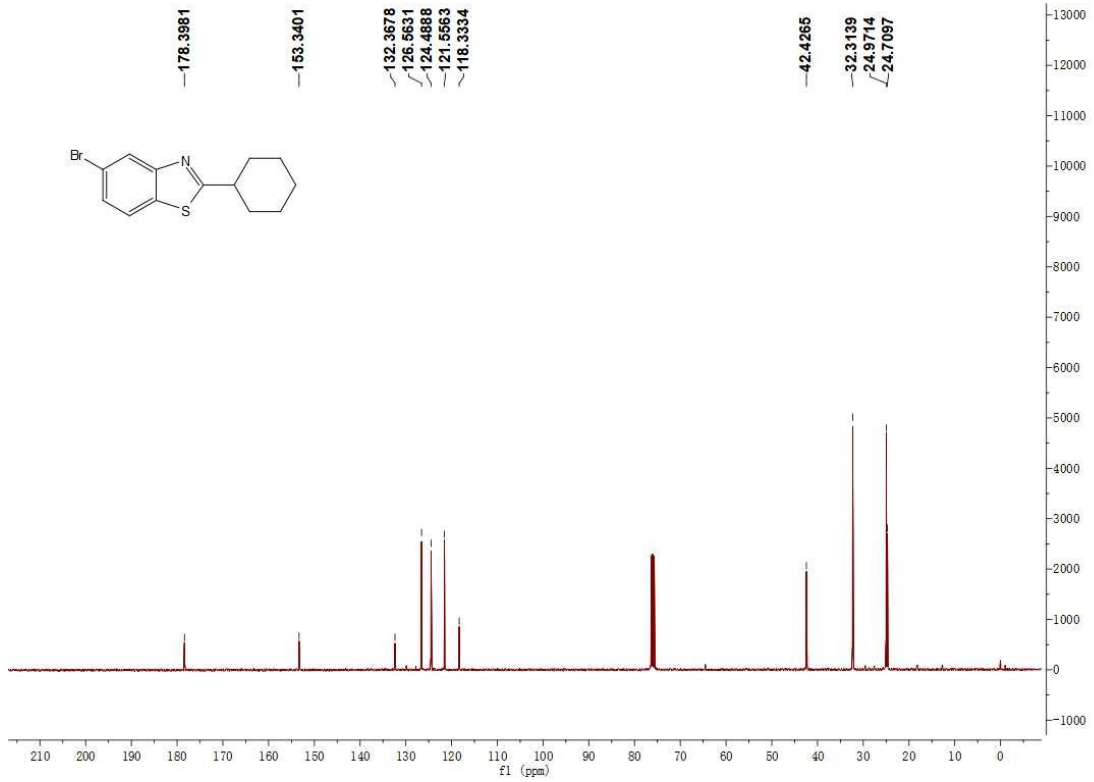
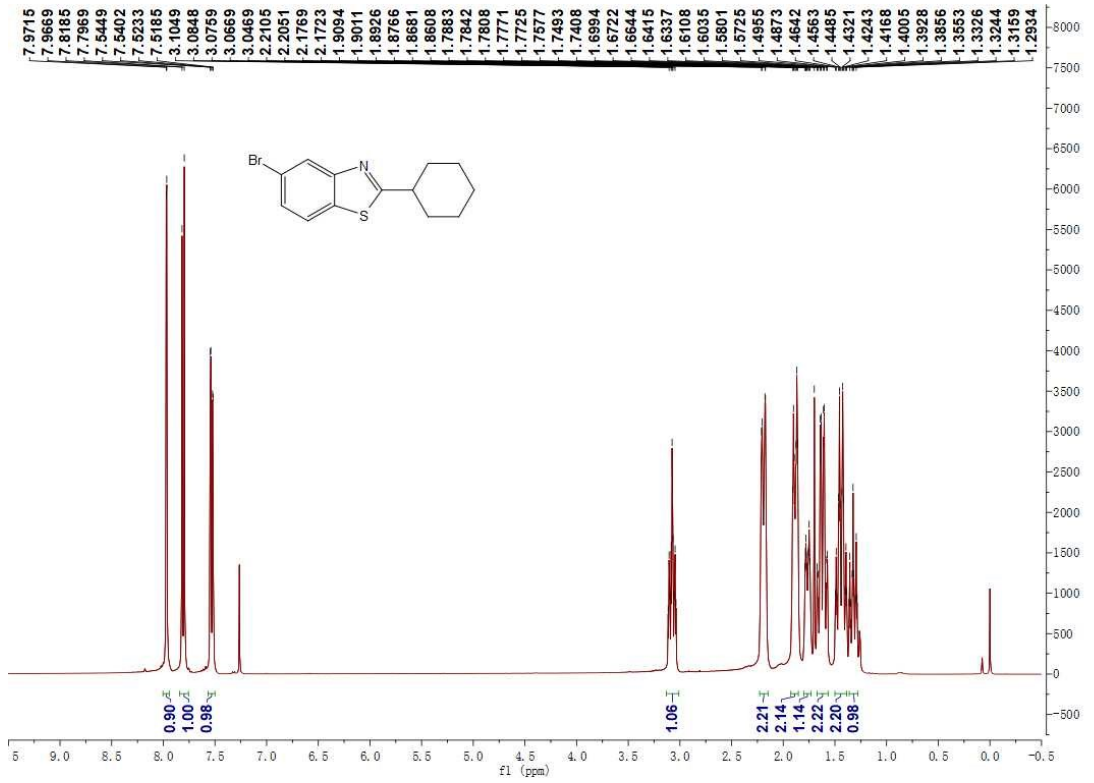
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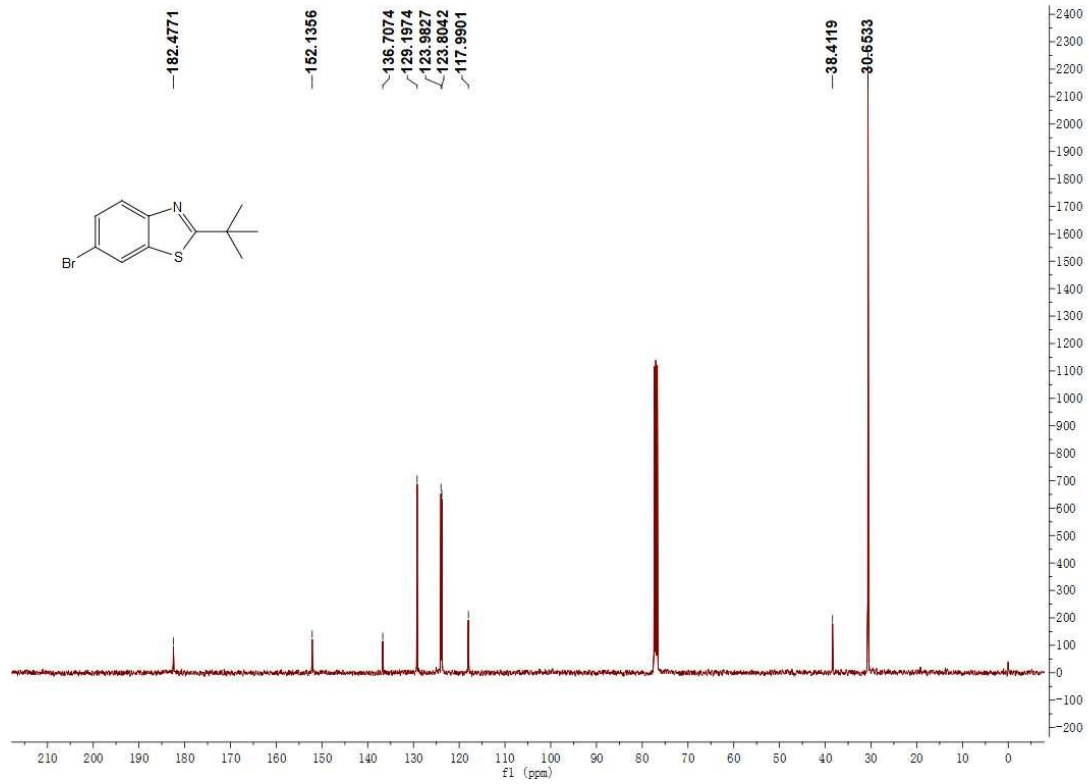
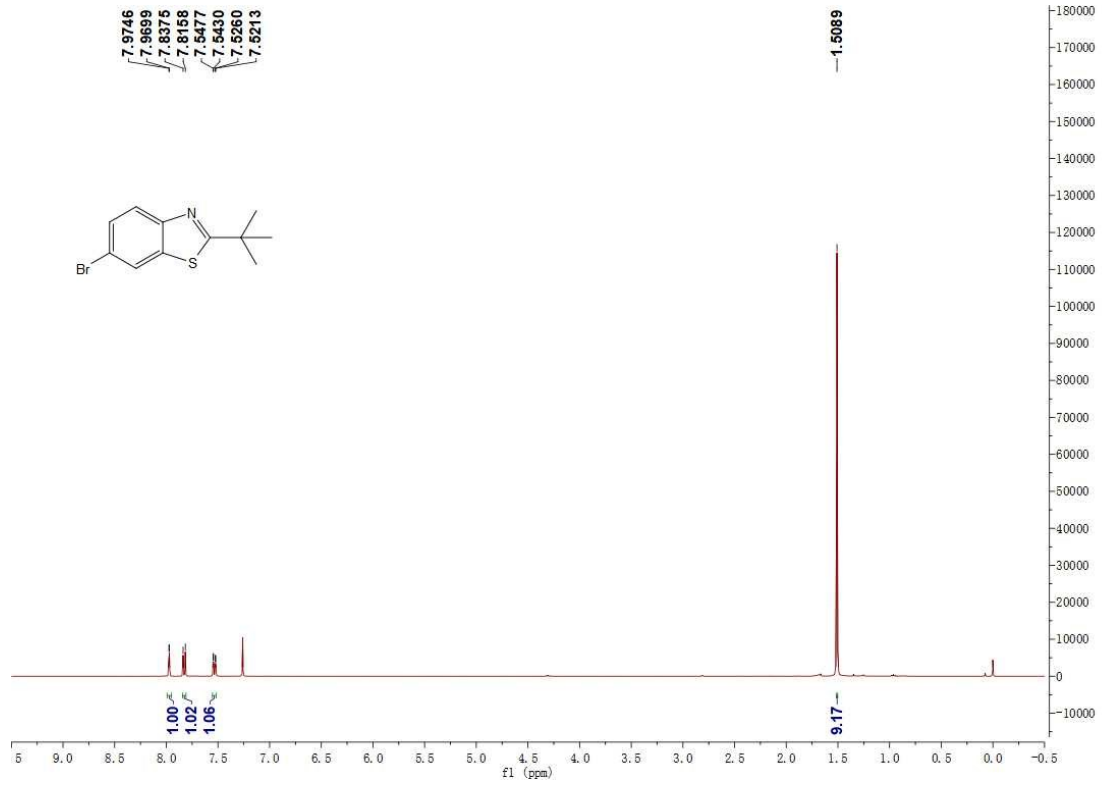
5k



51



5m



6

