

Electronic supplementary information for

## **Regulable Cross-Coupling of Alcohols and Benzothiazoles via Noble-Metal-Free Photocatalyst under Visible Light**

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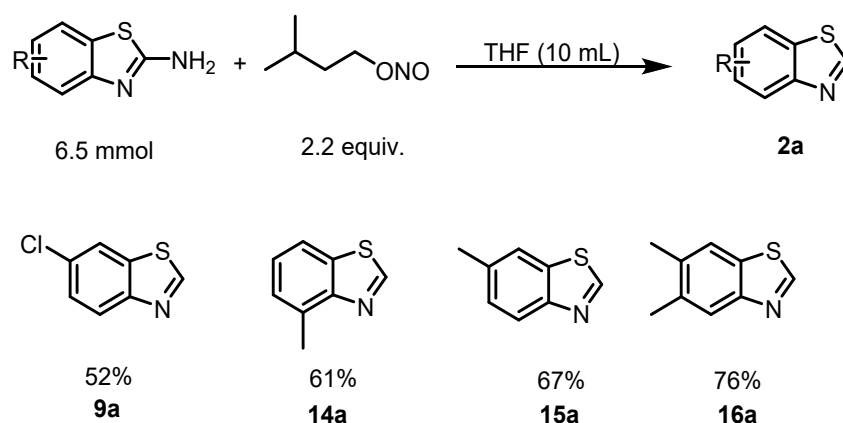
## 1. Experimental section

### 1) General information

All chemicals, unless otherwise noted, were purchased from commercial sources and were used without further purification. Unless stated otherwise, all reactions were carried out under nitrogen atmosphere. The substrates were synthesized according to the literature methods<sup>1</sup>. Irradiation with visible light was performed using blue LEDs ( $\lambda = 450 \pm 10$  nm) illumination instruments (The instruments were designed by ourselves and the actual output power density of the LEDs at 0.5 cm distance is 33.70 mW/cm<sup>2</sup> detected by CEL-NP2000-10 (Beijing Ceau Light Co. Ltd., China) light power meter). For irradiation, the material of the reaction vessel is common glass; the distance from the light source is about 0.5 cm.

The nuclear magnetic resonance spectra were recorded on the Bruker Ascend™ 400 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. High resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA).

## 2) Preparation of 2- 2- substituted benzothiazole



### Scheme S1. Synthesis of benzothiazoles.

Substituted benzothiazoles (**9a**, **14a**, **15a**, **16a**) were not commercially available: **7a**, **8a** were prepared following a procedure previously reported<sup>1-2</sup> in the literature (Scheme S1), In particular, a 50 mL round-bottom flask was charged with 10 mL of freshly distilled THF and the chosen 2-aminobenzothiazole derivative (6.5 mmol, 0.65 M). Stirring was applied and isoamyl nitrite (1.9 mL, 14.3 mmol, 2.2 equiv.,  $\rho = 0.872$  g/mL) was added dropwise. The resulting mixture was then refluxed, depending on the substrate, for a period of time ranging from 1 to 6 hours. The solution was then poured into a mixture of ice and water, then the aqueous phase was extracted with ethyl acetate (3×30 mL). Organic phases were combined and washed with brine, dried on Na<sub>2</sub>SO<sub>4</sub>, filtered, then solvent was removed under reduced pressure. Purification was performed by means of column chromatography (SiO<sub>2</sub>; n-hexane/ethyl acetate 95:5). Products were obtained with yields ranging from 52% to 76% (see above).

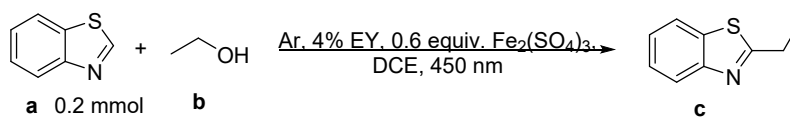
**9a**, **14a**, **15a**, **16a** were prepared according to the above procedure.

### 3) General procedure for the reactions

The benzothiazoles substrates (0.2 mmol, 1.1 eq.), ethyl alcohol (1 mL, 85.0 equiv.), 5 mol% Esoin Y and 0.6 equiv.  $\text{Fe}_2(\text{SO}_4)_3$  were dissolved in 4.0 mL DCE in a 15 mL reaction tube equipped with magnetic stirring bar, the reaction tube was sealed, and the resulting mixture was degassed with nitrogen for 15 min, then the reaction tube was irradiated by blue LEDs ( $\lambda = 450 \pm 10$  nm) at room temperature for 8-36 h. After reaction, the solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (200:3) as the eluent.

#### 4) Optimization of the reaction conditions

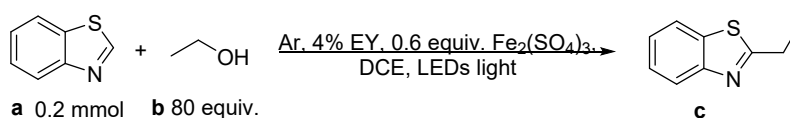
**Table S1. Substrate ratio effect**



Entry	a / b (equiv.)	Yield (%)
1	1/5	0
2	1/10	trace
3	1/25	20
4	1/50	58
5	1/85	99

Yields of isolated products.

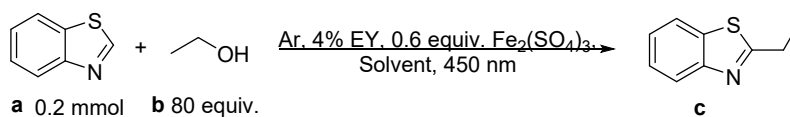
**Table S2. LED light effect**



Entry	LED light	Yield (%)
1	3W 380 nm	0
2	3W 450 nm	99
3	3W 510 nm	0

Yields of isolated products.

**Table S3. Solvent effect**

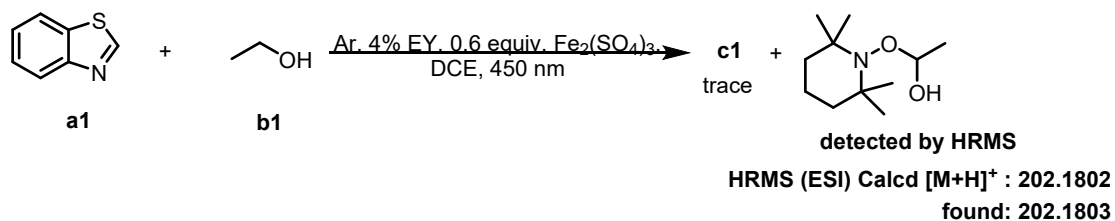


Entry	Solvent (4 mL)	Yield (%)
1	MeCN	41
2	1,4-Dioxane	80
3	DCE	99
4	DMF	0
5	DMSO	0

Yields of isolated products.



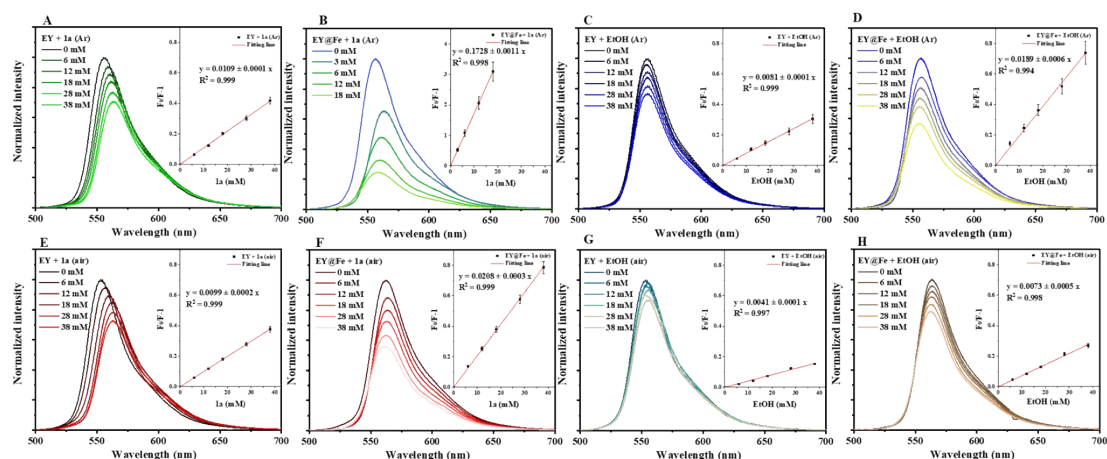
## 5) Radical-trapping experiment



Benzothiazole **a1** (0.2 mmol), ethanol **b1** (1.0 mL), 2 mol% Eosin Y, 60 mol%  $\text{Fe}_2(\text{SO}_4)_3$  and TEMPO (0.4 mmol) were dissolved in 4.0 mL DCE in a 15 mL reaction tube equipped with a magnetic stirring bar, the tube was sealed and degassed with nitrogen for 15 min, and then the reaction tube was irradiated with blue LED ( $\lambda = 450 \pm 10$  nm) at room temperature.



## 6) Quenching experiments



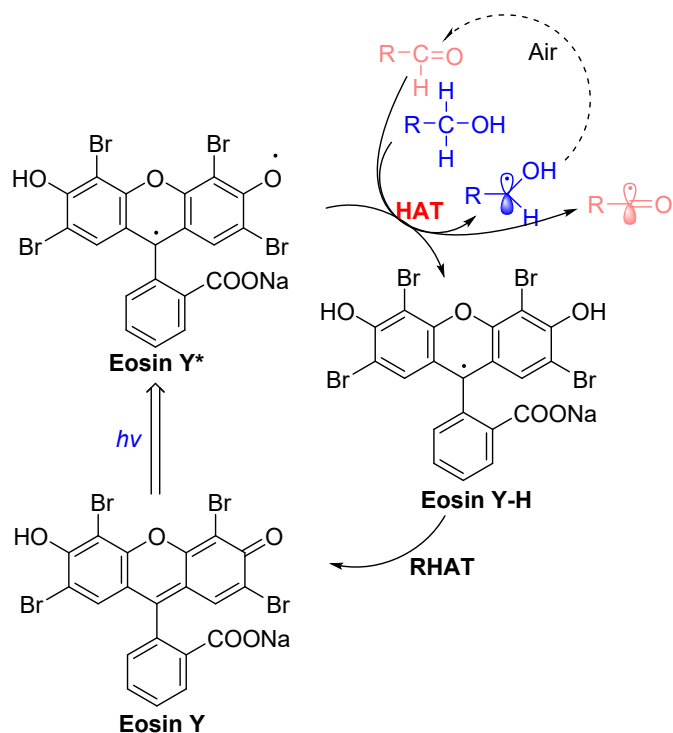
**Figure S1.** Photoluminescence quenching spectra of **EY** (Eosin Y) ( $1.0 \times 10^{-5}$  M) by **1a** and EtOH, in Ar or air atmosphere, and inset figures shows the Stern-Volmer plots. (A) **EY** + **1a** in Ar, (B) **EY** with iron salt (**EY@Fe**) + **1a** in Ar, (C) **EY** + EtOH in Ar, (D) **EY@Fe** + EtOH in Ar, (E) **EY** + **1a** in air, (F) **EY@Fe** + **1a** in air, (G) **EY** + EtOH in air, (H) **EY@Fe** + EtOH in air.

**Table S6.** Quenching constants with different additive in **EY** solvent

Entry	ATM	<b>EY</b> solvent	Quencher	K ( $M^{-1}$ )
1	Ar	<b>EY</b>	<b>1a</b>	$10.9 \pm 0.1$
2	Ar	<b>EY</b>	EtOH	$8.1 \pm 0.1$
3	Ar	<b>EY</b> + iron salt	<b>1a</b>	$172.8 \pm 1.1$
4	Ar	<b>EY</b> + iron salt	EtOH	$18.9 \pm 0.6$
5	Air	<b>EY</b>	<b>1a</b>	$9.9 \pm 0.2$
6	Air	<b>EY</b>	EtOH	$4.1 \pm 0.1$
7	Air	<b>EY</b> + iron salt	<b>1a</b>	$20.8 \pm 0.3$
8	Air	<b>EY</b> + iron salt	EtOH	$7.3 \pm 0.5$

**General procedure:** The fluorescence quenching experiments were measured with excitation at 450 nm. A degassed MeCN solution of  $1 \times 10^{-5}$  M **EY** and  $3.0 \times 10^{-1}$  M **1a** respectively were prepared. The experiments were conducted in 1.25 cm x 1.25 cm x 4.5 cm quartz cuvette at room temperature. Appropriate volume (the whole solution volume change < 5% ) of the quencher **1a** or EtOH was respectively injected to the MeCN solution (3 mL) of  $1 \times 10^{-5}$  M **EY** in the sealed quartz cuvette by microsyringe. For the **EY** solution with iron salt additive, 10 mg ferric sulfate solid was added.

## 7) Transformation Cycle of Eosin Y

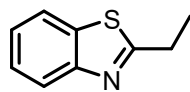


**Scheme S2.** The chemical structure of Eosin Y and its HAT cycles with alcohol and aldehyde to form alkyl radicals.

## 8) References

- 1 (a) Q. Q. Zhao, M. Li, X. S. Xue, J. R. Chen and W. J. Xiao, *Org. Lett.*, 2019, **21**, 3861;  
(b) C. Y. Zhao, K. Li, Y. Pang, J. Q. Li, C. Liang, G. F. Su and D. L. Mo, *Adv. Synth. Cat.*, 2018, **360**, 1919; (c) X. S. Ning, X. Liang, K. F. Hu, C. Z. Yao, J. P. Qu and Y. B. Kang, *Adv. Synth. Cat.*, 2018, **360**, 1590.
- 2 L. Capaldo, L. L. Quadri, D. Merli and D. Ravelli, *Chem. Commun.*, 2021, **57**, 4424.

## 2. Characterization data of the products

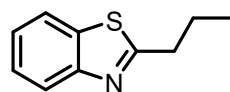


**2-ethylbenzo[d]thiazole (1c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.97 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 3.15 (q, *J* = 7.6 Hz, 2H), 1.47 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 173.57, 153.28, 135.07, 125.88, 124.62, 122.50, 121.50, 27.77, 13.80.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>10</sub>NS: 164.0534, found: 164.0534.

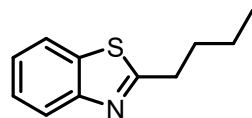


**2-propylbenzo[d]thiazole (2c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.99 (s, 1H), 7.85 (s, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.08 (s, 2H), 1.98 – 1.86 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 125.81, 124.64, 122.53, 121.51, 36.31, 23.04, 13.73.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>10</sub>H<sub>12</sub>NS: 178.0690, found: 178.0690.

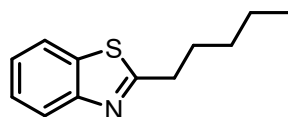


**2-butylbenzo[d]thiazole (3c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.97 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.37 – 7.30 (m, 1H), 3.16 – 3.07 (m, 2H), 1.90 – 1.83 (m, 2H), 1.54 – 1.42 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 172.41, 153.26, 135.14, 125.85, 124.61, 122.50, 121.47, 34.06, 31.78, 22.31, 13.76.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>11</sub>H<sub>14</sub>NS: 192.0847, found: 192.0854.

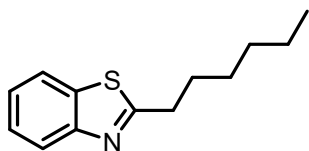


**2-pentylbenzo[d]thiazole (4c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.97 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 3.11 (t, *J* = 7.7 Hz, 2H), 1.88 (q, *J* = 7.4 Hz, 2H), 1.41 (s, 4H), 0.91 (t, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 172.55, 153.24, 135.16, 125.91, 124.66, 122.52, 121.53, 34.38, 31.38, 29.50, 22.44, 14.02.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>12</sub>H<sub>15</sub>NS: 206.1003, found: 206.1013.

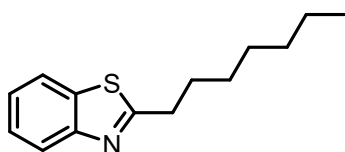


**2-hexylbenzo[d]thiazole (5c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.96 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 3.16 – 3.07 (m, 2H), 1.88 (p, *J* = 7.6 Hz, 2H), 1.44 (p, *J* = 6.6 Hz, 2H), 1.27 (s, 4H), 0.88 (t, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 172.49, 153.17, 135.10, 125.85, 124.61, 122.47, 121.46, 34.35, 31.80, 29.72, 29.12, 22.63, 14.07.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>13</sub>H<sub>17</sub>NS: 220.1115, found: 220.1108.

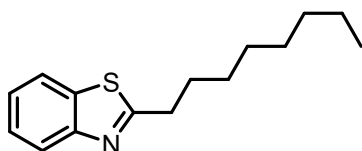


**2-heptylbenzo[d]thiazole (6c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.97 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.15 – 3.09 (m, 2H), 1.91 – 1.85 (m, 2H), 1.35 (ddd, *J* = 20.6, 18.2, 5.5 Hz, 8H), 0.88 (t, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 172.50, 153.21, 135.12, 125.86, 124.62, 122.49, 121.48, 34.36, 31.67, 29.74, 29.14, 28.97, 22.61, 14.06.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>14</sub>H<sub>19</sub>NS: 234.1316, found: 234.1319.

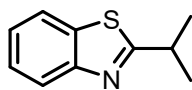


**2-octylbenzo[d]thiazole (7c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.97 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.16 – 3.05 (m, 2H), 1.88 (p, *J* = 7.6 Hz, 2H), 1.44 (p, *J* = 7.0, 6.5 Hz, 2H), 1.33 – 1.23 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 172.45, 153.25, 135.13, 125.83, 124.59, 122.49, 121.46, 34.37, 31.81, 29.73, 29.26, 29.18, 29.13, 22.64, 14.08.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>15</sub>H<sub>21</sub>NS: 248.1473, found: 248.1464.

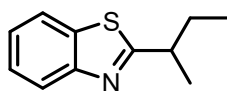


**2-isopropylbenzo[d]thiazole (9c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.98 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.43 (p, *J* = 6.9 Hz, 1H), 1.48 (d, *J* = 6.9 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 178.76, 153.13, 134.71, 125.91, 124.65, 122.62, 121.61, 34.15, 22.98.

**HRMS** (ESI-TOF) (*m/z*) for [M+Na]<sup>+</sup> calculated for C<sub>10</sub>H<sub>11</sub>NS: 178.0646, found: 178.0654.

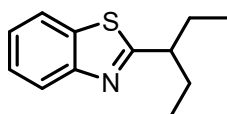


**2-(sec-butyl)benzo[d]thiazole (10c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.88 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 3.08 (h, *J* = 6.9 Hz, 1H), 1.78 (dd, *J* = 14.2, 6.9 Hz, 1H), 1.65 (dq, *J* = 13.9, 7.1 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 177.74, 153.12, 134.68, 124.53, 122.59, 121.52, 41.05, 30.59, 20.68, 11.82.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>11</sub>H<sub>13</sub>NS: 192.0847, found: 192.0843.

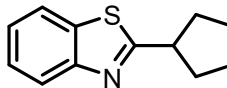


**2-(pentan-3-yl)benzo[d]thiazole (11c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.99 (d, *J* = 8.0 Hz, 1H), 7.85 (dd, *J* = 7.9, 0.4 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.38 – 7.31 (m, 1H), 3.00 (tt, *J* = 8.5, 5.8 Hz, 1H), 1.90 – 1.79 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 176.86, 153.07, 134.74, 125.73, 124.53, 122.62, 121.54, 48.72, 28.94, 11.90.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>12</sub>H<sub>16</sub>NS: 206.1003, found: 206.1008.

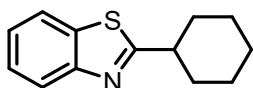


**2-cyclopentylbenzo[d]thiazole (12c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.97 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 3.56 (p, *J* = 8.1 Hz, 1H), 2.32 – 2.20 (m, 2H), 2.00 – 1.83 (m, 4H), 1.80 – 1.70 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 177.29, 153.14, 134.80, 125.90, 124.61, 122.51, 121.55, 44.83, 34.14, 25.66.

**HRMS** (ESI-TOF) (*m/z*) for [M+Na]<sup>+</sup> calculated for C<sub>12</sub>H<sub>13</sub>NS: 204.0802, found: 204.0806.

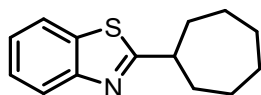


**2-cyclohexylbenzo[d]thiazole (13c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.97 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.35 – 7.27 (m, 1H), 3.09 (tt, *J* = 11.7, 3.6 Hz, 1H), 2.20 (dd, *J* = 13.3, 2.1 Hz, 2H), 1.92 – 1.83 (m, 2H), 1.80 – 1.72 (m, 1H), 1.63 (ddd, *J* = 24.6, 12.3, 3.1 Hz, 2H), 1.50 – 1.37 (m, 2H), 1.36 – 1.24 (m, 1H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 177.57, 153.14, 134.56, 125.79, 124.50, 122.57, 121.55, 43.45, 33.43, 26.08, 25.81.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>13</sub>H<sub>16</sub>NS: 218.1003, found: 218.1002.

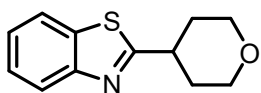


**2-cycloheptylbenzo[d]thiazole (14c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.96 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.36 – 7.29 (m, 1H), 3.35 – 3.21 (m, 1H), 2.22 (dd, *J* = 8.8, 5.1 Hz, 2H), 1.87 (dt, *J* = 13.0, 4.9 Hz, 4H), 1.73 – 1.57 (m, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 178.71, 153.02, 134.69, 125.78, 124.49, 122.54, 121.51, 45.52, 35.37, 28.08, 26.55.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>14</sub>H<sub>18</sub>NS: 232.1160, found: 232.1165.

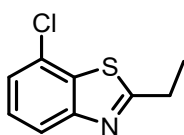


**2-(tetrahydro-2H-pyran-4-yl)benzo[d]thiazole (15c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.99 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.42 (m, 1H), 7.40 – 7.33 (m, 1H), 4.16 – 4.06 (m, 2H), 3.58 (t, *J* = 12.8 Hz, 2H), 3.42 – 3.30 (m, 1H), 2.05 (ddd, *J* = 29.3, 24.7, 12.1 Hz, 4H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 175.35, 153.06, 134.51, 126.01, 124.81, 122.73, 121.62, 67.51, 40.50, 32.83.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>12</sub>H<sub>14</sub>NS: 220.0796, found: 220.0796.

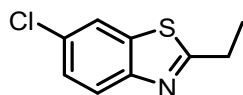


**7-chloro-2-ethylbenzo[d]thiazole (16c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.72 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.46 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 3.20 (q, *J* = 7.6 Hz, 2H), 1.47 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 175.00, 150.21, 136.52, 127.25, 126.15, 125.14, 120.07, 27.98, 14.07.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>9</sub>ClNS: 198.0144, found: 198.0151.

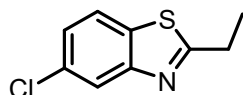


**6-chloro-2-ethylbenzo[d]thiazole (17c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.85 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.39 (dd, *J* = 8.7, 2.0 Hz, 1H), 3.13 (q, *J* = 7.6 Hz, 2H), 1.46 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 174.04, 151.81, 136.25, 130.51, 126.62, 123.20, 121.09, 27.74, 13.62.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>8</sub>ClNS: 198.0144, found: 198.0141.

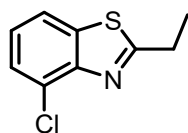


**5-chloro-2-ethylbenzo[d]thiazole (18c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.85 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.39 (dd, *J* = 8.7, 2.0 Hz, 1H), 3.13 (q, *J* = 7.6 Hz, 2H), 1.46 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 174.05, 151.83, 136.27, 130.52, 126.64, 123.22, 121.10, 27.74, 13.62.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>9</sub>ClNS: 198.0144, found: 198.0148.

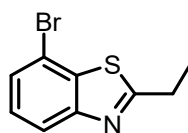


**4-chloro-2-ethylbenzo[d]thiazole (19c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.72 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.46 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.26 (t, *J* = 7.9 Hz, 1H), 3.20 (q, *J* = 7.6 Hz, 2H), 1.47 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 174.98, 150.19, 136.50, 127.23, 126.14, 125.12, 120.05, 27.98, 14.07.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>9</sub>ClNS: 198.0144, found: 198.0141.

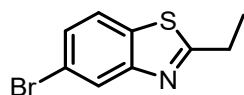


**7-bromo-2-ethylbenzo[d]thiazole (20c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.92 – 7.86 (m, 1H), 7.47 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 3.14 (q, *J* = 7.6 Hz, 2H), 1.47 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 173.86, 153.11, 137.96, 127.45, 127.07, 121.33, 113.86, 27.87, 13.70.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>9</sub>BrNS: 241.9639, found: 241.9647.

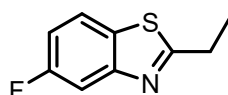


**5-bromo-2-ethylbenzo[d]thiazole (21c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.11 (d, *J* = 1.6 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.14 (q, *J* = 7.6 Hz, 2H), 1.46 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 154.49, 133.88, 127.73, 125.46, 122.53, 119.47, 27.83, 13.68.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>9</sub>BrNS: 241.9639, found: 241.9647.



**2-ethyl-5-fluorobenzo[d]thiazole (22c)**

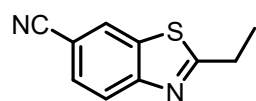
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.96 (d, *J* = 8.9 Hz, 1H), 7.71 (s, 1H), 7.31 (s, 1H), 3.16 (q, *J* = 7.6 Hz, 2H), 1.48 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 176.21, 161.73 (d, *J* = 242.7 Hz), 154.29, 130.41, 122.10 (d, *J* = 9.7 Hz), 113.24 (d, *J* = 24.9 Hz), 108.79 (d, *J* = 23.7 Hz), 27.90, 13.69.



**<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ ppm = -116.46.

**HRMS** (ESI-TOF) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>9</sub>FNS: 182.0440, found: 182.0437.

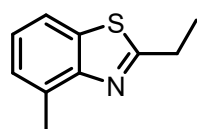


**2-ethylbenzo[d]thiazole-6-carbonitrile (23c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.18 (d, *J* = 1.2 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.70 (dd, *J* = 8.5, 1.6 Hz, 1H), 3.20 (q, *J* = 7.6 Hz, 2H), 1.50 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 129.18, 126.29, 123.31, 108.24, 28.03, 13.49.

**HRMS** (ESI-TOF) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>10</sub>H<sub>9</sub>N<sub>2</sub>S: 189.0486, found: 189.0486.

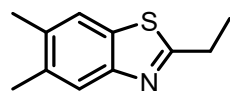


**2-ethyl-4-methylbenzo[d]thiazole (24c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.66 (dd, *J* = 5.3, 3.9 Hz, 1H), 7.23 (dd, *J* = 6.3, 3.0 Hz, 2H), 3.16 (q, *J* = 7.6 Hz, 2H), 2.73 (s, 3H), 1.46 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 172.32, 152.62, 134.99, 132.43, 126.45, 124.43, 118.88, 27.88, 18.46, 14.07.

**HRMS** (ESI-TOF) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>10</sub>H<sub>12</sub>NS: 178.0690, found: 178.0697.

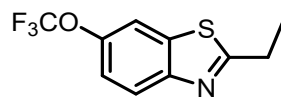


**2-ethyl-5,6-dimethylbenzo[d]thiazole (25c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.73 (s, 1H), 7.57 (s, 1H), 3.11 (q, *J* = 7.6 Hz, 2H), 2.37 (d, *J* = 5.9 Hz, 6H), 1.45 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 172.38, 152.03, 134.99, 133.92, 122.72, 121.44, 27.66, 20.12, 20.01, 13.80.

**HRMS** (ESI-TOF) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>11</sub>H<sub>14</sub>NS: 192.0847, found: 192.0846.



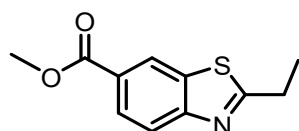
**2-ethyl-6-(trifluoromethoxy)benzo[d]thiazole (26c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.96 (d, *J* = 8.9 Hz, 1H), 7.71 (s, 1H), 7.31 (s, 1H), 3.16 (q, *J* = 7.6 Hz, 2H), 1.48 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 174.09, 151.83, 136.27, 130.53, 126.65, 123.22, 121.12, 13.64.

**<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ ppm = -58.07.

**HRMS** (ESI-TOF) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>10</sub>H<sub>8</sub>F<sub>3</sub>NOS: 248.0357, found: 203.0358.

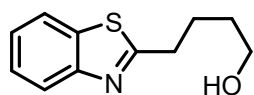


**methyl 2-ethylbenzo[d]thiazole-6-carboxylate (27c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.57 (d, *J* = 1.3 Hz, 1H), 8.12 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 3.96 (s, 3H), 3.17 (t, *J* = 7.6 Hz, 2H), 1.49 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 166.67, 156.22, 135.02, 127.15, 126.49, 123.72, 122.18, 28.02, 13.59.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>11</sub>H<sub>11</sub>NO<sub>2</sub>S: 222.0583, found: 222.0584.

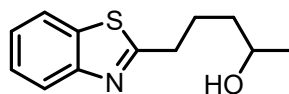
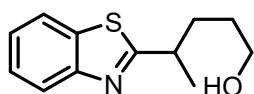


**4-(benzo[d]thiazol-2-yl)butan-1-ol (28c)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.96 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.70 (t, *J* = 6.3 Hz, 2H), 3.16 (t, *J* = 7.5 Hz, 2H), 2.15 (s, 1H), 2.04 – 1.94 (m, 2H), 1.78 – 1.66 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 172.04, 153.10, 135.06, 125.95, 124.75, 122.48, 121.49, 62.10, 33.81, 31.99, 25.67.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>11</sub>H<sub>14</sub>NOS: 208.0796, found: 208.0789.



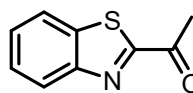
**4-(benzo[d]thiazol-2-yl)pentan-1-ol (29c) 5-(benzo[d]thiazol-2-yl)pentan-2-ol (29c')**

(29c and 29c' are the compounds that we had not been isolated, because their polarities are basically the same.)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.96 (d, *J* = 8.1 Hz, 1H), 7.83 (dd, *J* = 7.7, 4.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 1H), 3.36 – 3.28 (m, 1H), 3.14 (t, *J* = 7.5 Hz, 1H), 2.38 (s, 1H), 2.04 – 1.80 (m, 2H), 1.63 (ddt, *J* = 33.0, 16.0, 7.9 Hz, 2H), 1.46 (d, *J* = 6.9 Hz, 2H), 1.20 (d, *J* = 6.2 Hz, 1H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 177.79, 172.13, 153.08, 152.88, 135.04, 134.57, 125.94, 125.90, 124.74, 124.70, 122.55, 122.47, 121.57, 121.49, 67.38, 62.32, 39.15, 38.45, 34.01, 33.67, 30.34, 25.59, 23.55, 21.32.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>12</sub>H<sub>15</sub>NOS: 222.0908, found: 222.0913.

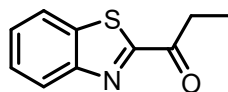


**1-(benzo[d]thiazol-2-yl)ethan-1-one (1d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.19 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.51 (m, 2H), 2.83 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 193.14, 166.50, 153.58, 137.44, 127.70, 126.98, 125.45, 122.45, 26.16.

**HRMS** (ESI-TOF) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>7</sub>NOS: 178.0321, found: 178.0322.

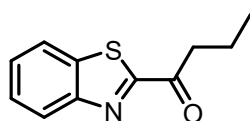


**1-(benzo[d]thiazol-2-yl)propan-1-one (2d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.18 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.61 – 7.49 (m, 2H), 3.31 (q, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 196.08, 166.42, 153.63, 137.25, 127.64, 127.00, 125.42, 122.50, 32.15, 7.94.

**HRMS** (ESI-TOF) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>10</sub>H<sub>9</sub>NOS: 192.0478, found: 192.0485.

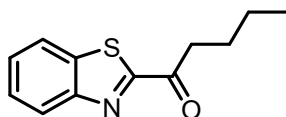


**1-(benzo[d]thiazol-2-yl)butan-1-one (3d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.18 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.50 (m, 2H), 3.26 (t, *J* = 7.3 Hz, 2H), 1.86 (p, *J* = 7.4 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 195.57, 166.69, 153.63, 137.29, 127.65, 126.99, 125.43, 122.50, 40.55, 17.55, 13.85.

**HRMS** (ESI-TOF) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>11</sub>H<sub>11</sub>NOS: 206.0634, found: 206.0640.

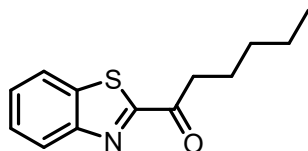


**1-(benzo[d]thiazol-2-yl)pentan-1-one (4d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.19 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.50 (m, 2H), 3.28 (t, *J* = 7.5 Hz, 2H), 1.80 (p, *J* = 7.5 Hz, 2H), 1.46 (h, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 195.73, 166.70, 153.64, 137.31, 127.65, 126.99, 125.44, 122.50, 38.40, 26.11, 22.43, 13.97.

**HRMS** (ESI-TOF) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>12</sub>H<sub>13</sub>NOS: 220.0791, found: 220.0793.

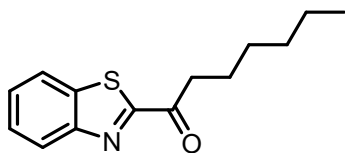


**1-(benzo[d]thiazol-2-yl)hexan-1-one (5d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.18 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.54 (dt, *J* = 20.8, 7.1 Hz, 2H), 3.27 (t, *J* = 7.5 Hz, 2H), 1.81 (q, *J* = 7.3 Hz, 2H), 1.44 – 1.35 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 195.70, 166.70, 153.65, 137.31, 127.62, 126.97, 125.44, 122.49, 38.62, 31.43, 23.72, 22.52, 14.00.

**HRMS** (ESI-TOF) (m/z) for [M+H]<sup>+</sup> calculated for C<sub>13</sub>H<sub>15</sub>NOS: 234.0908, found: 234.0911.

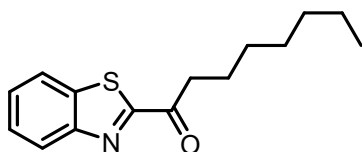


**1-(benzo[d]thiazol-2-yl)heptan-1-one (6d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.19 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.50 (m, 2H), 3.27 (t, *J* = 7.4 Hz, 2H), 1.81 (p, *J* = 7.4 Hz, 2H), 1.47 – 1.40 (m, 2H), 1.34 (dt, *J* = 7.3, 3.7 Hz, 4H), 0.90 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 195.73, 166.71, 153.65, 137.32, 127.63, 126.97, 125.44, 122.49, 38.68, 31.64, 28.94, 24.00, 22.57, 14.11.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>14</sub>H<sub>17</sub>NOS: 248.1104, found: 248.1104.

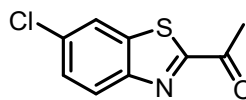


**1-(benzo[d]thiazol-2-yl)octan-1-one (7d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.19 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.55 (dt, *J* = 20.2, 7.2 Hz, 2H), 3.27 (t, *J* = 7.4 Hz, 2H), 1.82 (q, *J* = 7.3 Hz, 2H), 1.44 – 1.39 (m, 2H), 1.31 – 1.28 (m, 6H), 0.89 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 195.74, 166.71, 153.69, 137.32, 127.63, 126.97, 125.44, 122.49, 38.67, 31.74, 29.23, 24.04, 22.68, 14.15.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>15</sub>H<sub>19</sub>NOS: 262.1260, found: 262.1263.

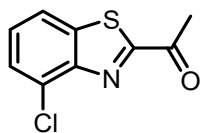


**1-(6-chlorobenzo[d]thiazol-2-yl)ethan-1-one (8d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.09 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.81 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 192.87, 166.96, 152.09, 138.58, 134.08, 128.11, 126.27, 122.05, 26.16.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>6</sub>ClNOS: 211.9931, found: 211.9927.



**1-(4-chlorobenzo[d]thiazol-2-yl)ethan-1-one (9d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.87 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 2.87 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 193.10, 167.06, 150.70, 138.92, 130.43, 128.21, 127.21, 121.03, 26.14.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>6</sub>ClNOS: 211.9931, found: 211.9935.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.12 (d, *J* = 1.8 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.67 (dd, *J* = 8.8, 1.8 Hz, 1H), 2.81 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 192.88, 166.92, 152.39, 138.98, 130.78, 126.54, 125.06, 121.98, 26.17.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>6</sub>BrNOS: 255.9426, found: 255.9428.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.33 (d, *J* = 1.7 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.62 (dd, *J* = 8.6, 1.8 Hz, 1H), 2.81 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 192.87, 167.96, 154.67, 136.17, 130.90, 128.17, 123.54, 120.63, 26.18.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>6</sub>BrNOS: 255.9426, found: 255.9427.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.92 (dd, *J* = 8.9, 5.0 Hz, 1H), 7.85 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.32 (td, *J* = 8.8, 2.5 Hz, 1H), 2.82 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 192.94, 168.81, 160.88, 154.51, 133.03, 123.34, 117.12, 116.87, 111.19, 110.96, 26.18.

**<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ ppm = -114.04.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>9</sub>H<sub>6</sub>FNOS: 196.0227, found: 196.0228.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = ppm = 7.78 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 2.83 (s, 3H), 2.80 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 193.48, 165.17, 153.19, 137.56, 135.85, 127.76, 127.22, 119.79, 26.08, 18.21.

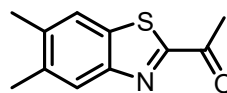
**HRMS** (ESI-TOF) (*m/z*) for [M+Na]<sup>+</sup> calculated for C<sub>10</sub>H<sub>9</sub>NOS: 214.0297, found: 214.0298.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.06 (d, *J* = 8.5 Hz, 1H), 7.76 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 2.81 (s, 3H), 2.53 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 193.29, 165.59, 151.81, 138.47, 128.95, 124.98, 122.05, 77.39, 26.19, 21.88.

**HRMS** (ESI-TOF) (*m/z*) for [M+Na]<sup>+</sup> calculated for C<sub>10</sub>H<sub>9</sub>NOS: 192.0438, found: 192.0438.

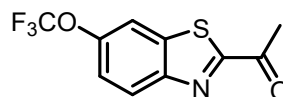


**1-(5,6-dimethylbenzo[d]thiazol-2-yl)ethan-1-one (15d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 7.94 (s, 1H), 7.72 (s, 1H), 2.80 (s, 3H), 2.42 (d, *J* = 2.6 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 193.29, 165.48, 152.51, 138.06, 136.71, 135.22, 125.26, 122.15, 26.19, 20.33.

**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>11</sub>H<sub>11</sub>NOS: 206.0634, found: 206.0636.



**1-(6-(trifluoromethoxy)benzo[d]thiazol-2-yl)ethan-1-one (16d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ ppm = 8.20 (d, *J* = 9.0 Hz, 1H), 7.84 (s, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 2.83 (s, 3H).

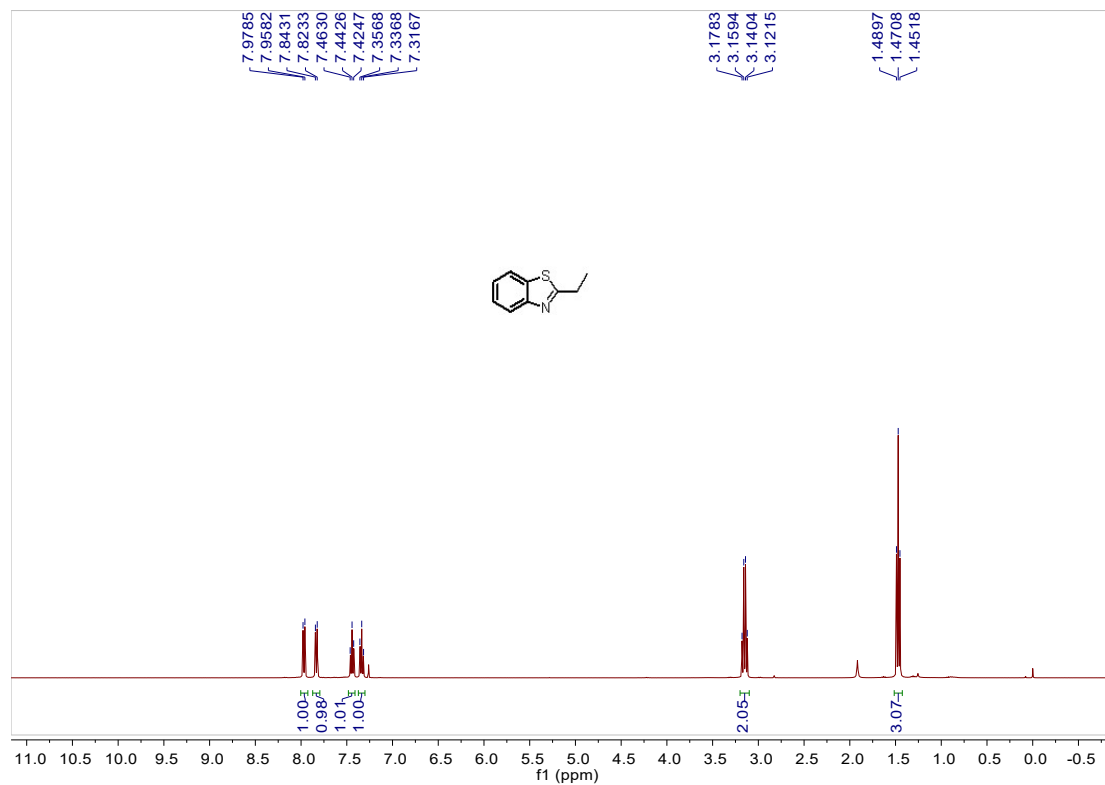
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ ppm = 192.73, 167.66, 151.93, 148.37, 138.39, 126.62, 121.02, 114.49, 29.74, 26.12.

**<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ ppm = -57.88.

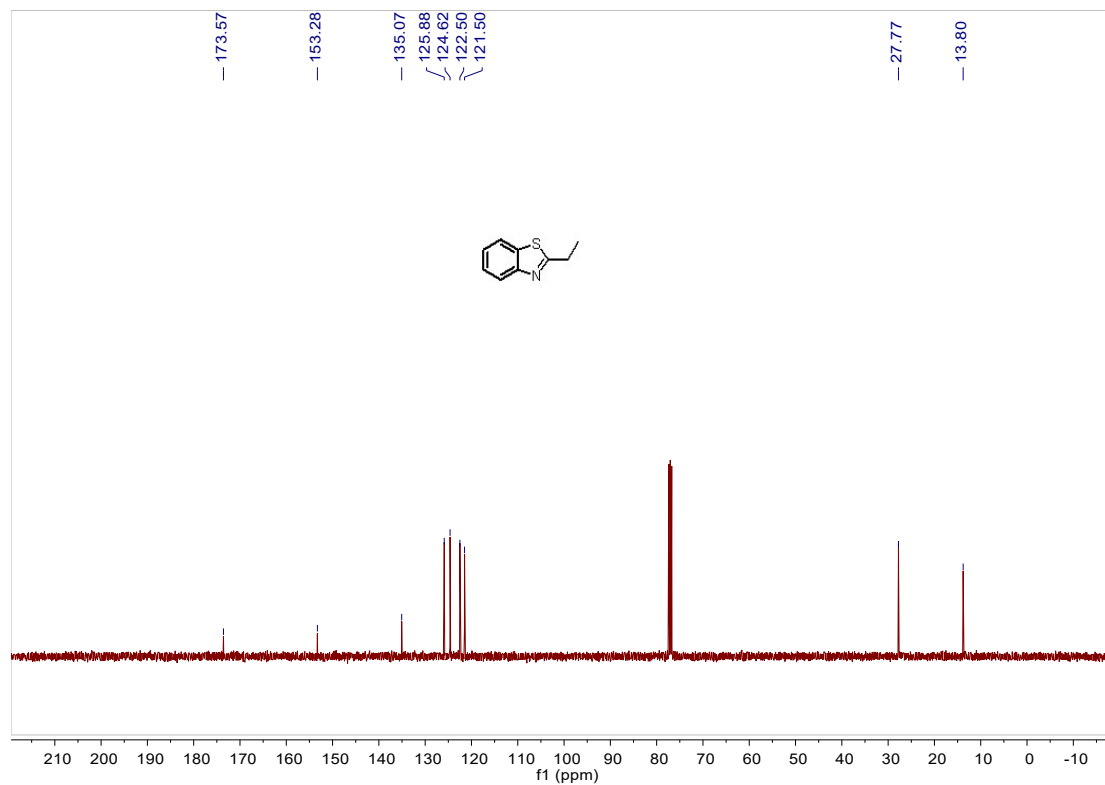
**HRMS** (ESI-TOF) (*m/z*) for [M+H]<sup>+</sup> calculated for C<sub>10</sub>H<sub>6</sub>F<sub>3</sub>NO<sub>2</sub>S: 262.0144, found: 262.0145

### 3. NMR spectra for the products

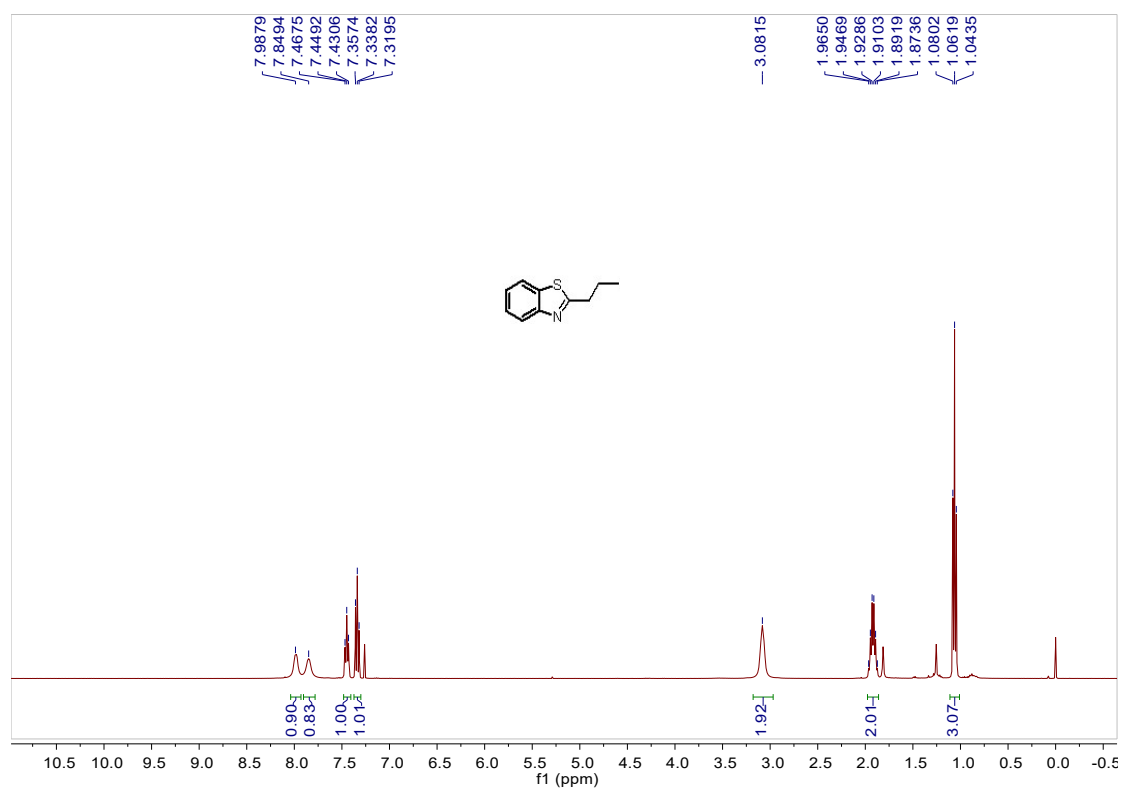
$^1\text{H}$  NMR spectrum of compound **1c** in  $\text{CDCl}_3$  (400 MHz):



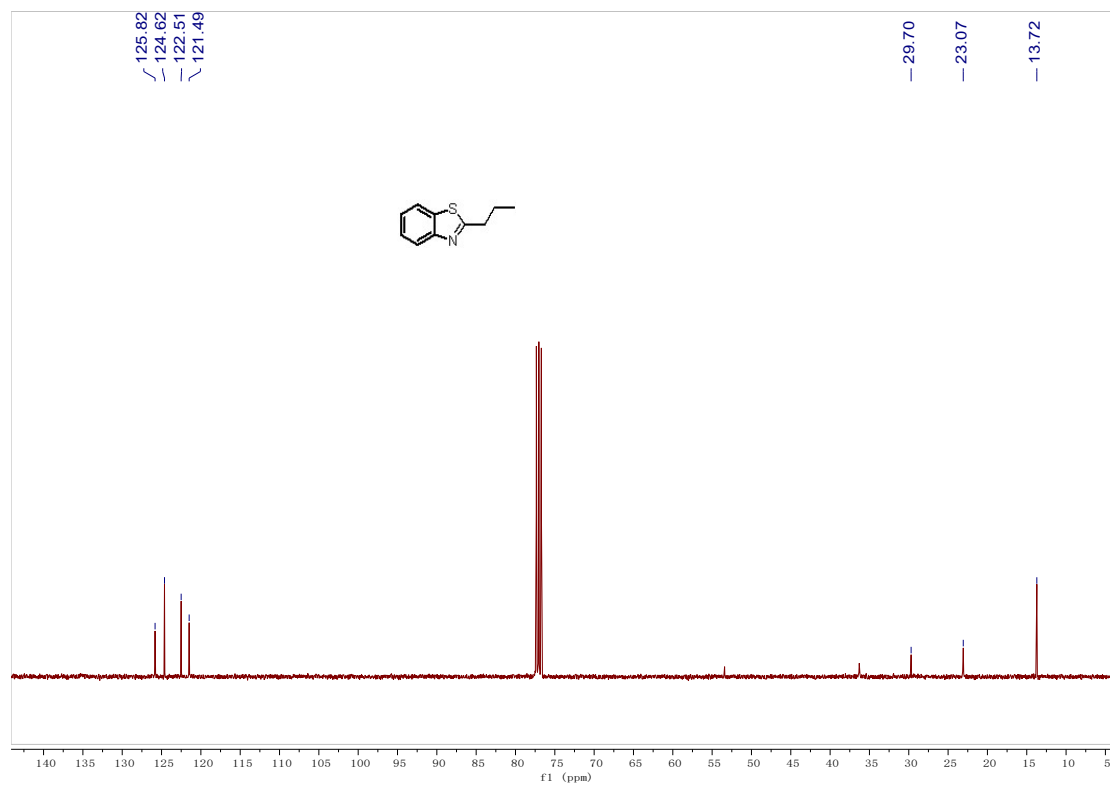
$^{13}\text{C}$  NMR spectrum of compound **1c** in  $\text{CDCl}_3$  (101 MHz):



$^1\text{H}$  NMR spectrum of compound **2c** in  $\text{CDCl}_3$  (400 MHz):

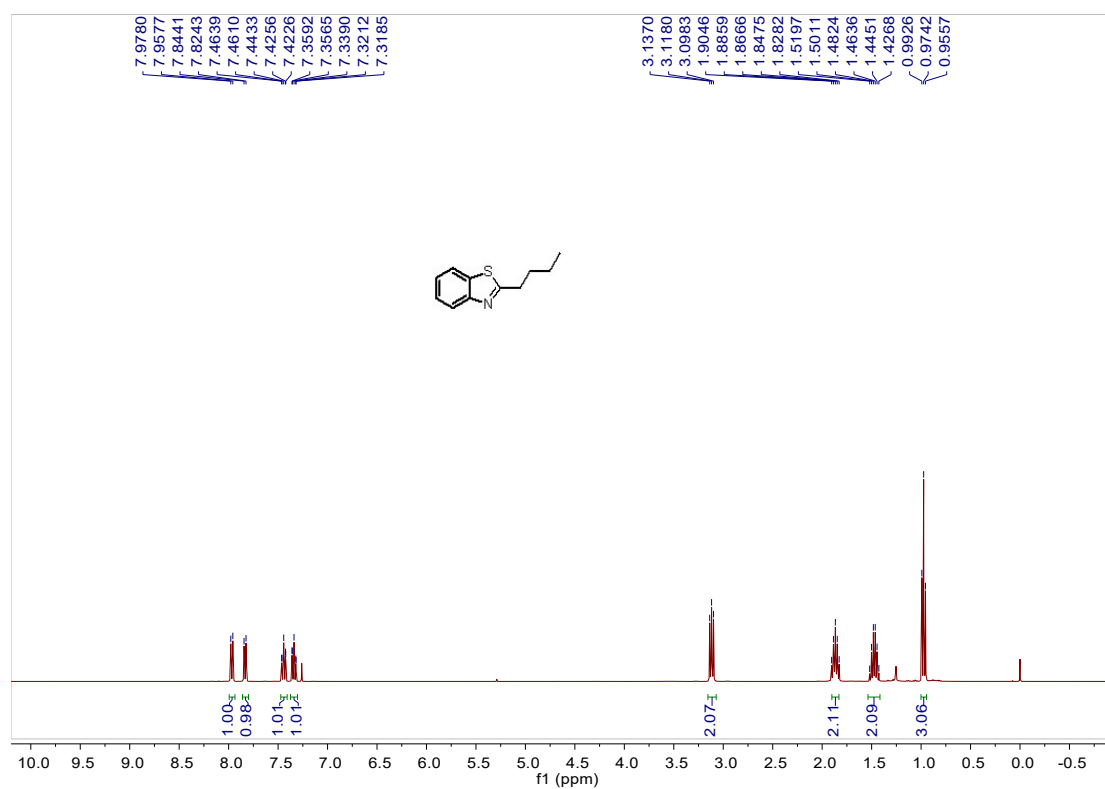


$^{13}\text{C}$  NMR spectrum of compound **2c** in  $\text{CDCl}_3$  (101 MHz):

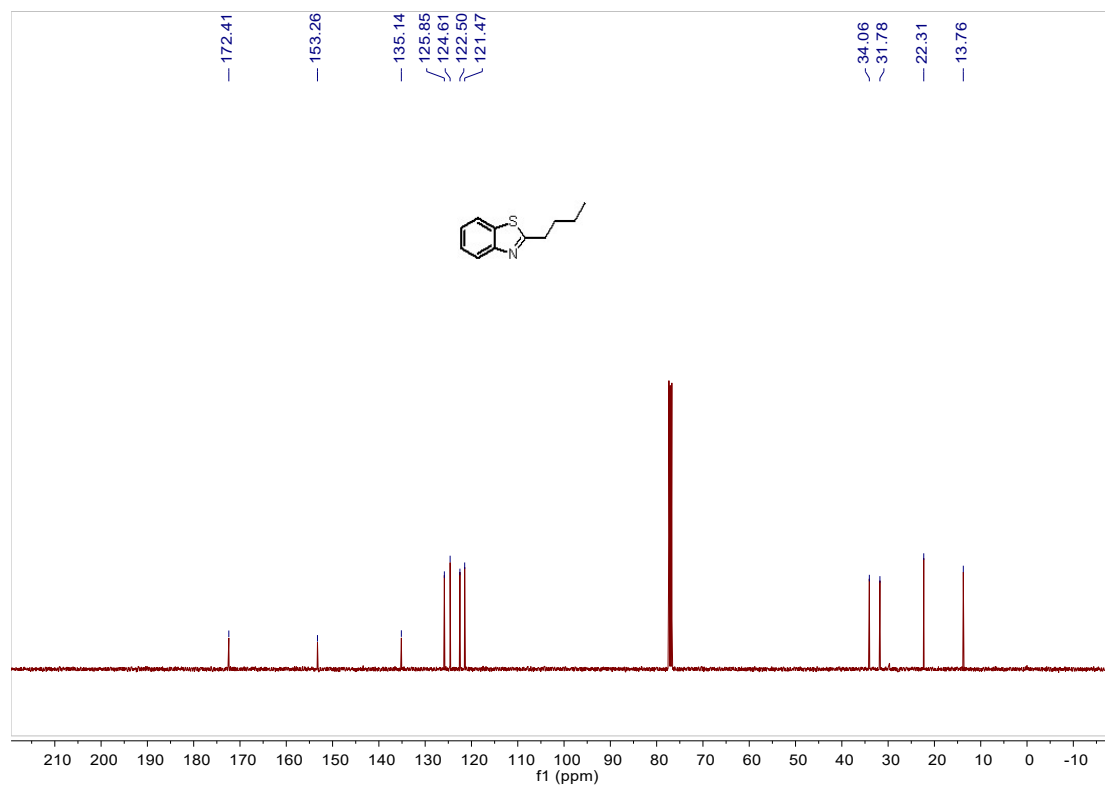




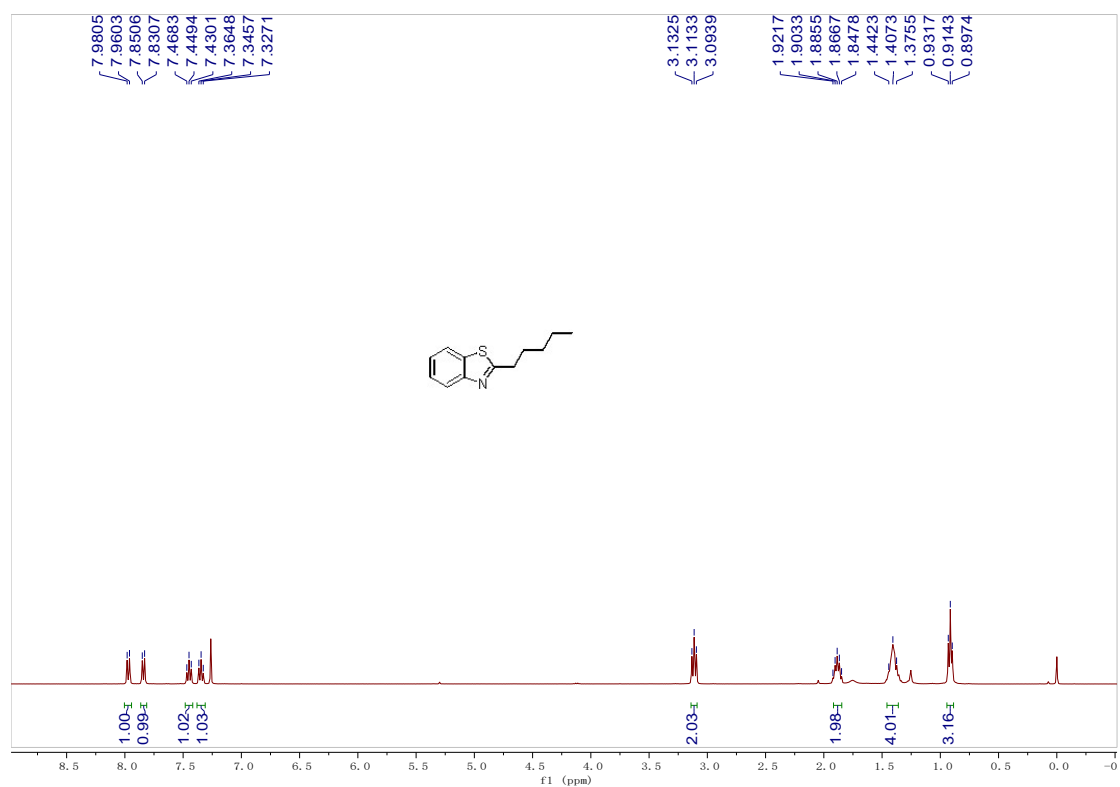
$^1\text{H}$  NMR spectrum of compound **3c** in  $\text{CDCl}_3$  (400 MHz):



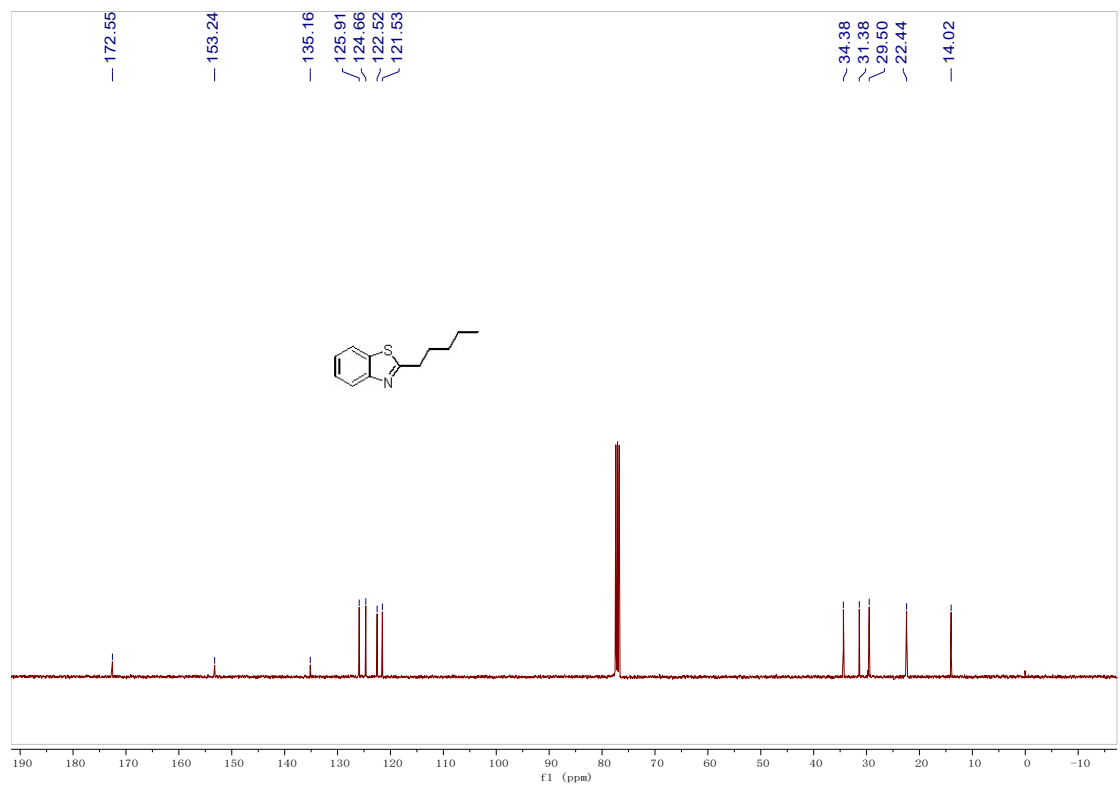
$^{13}\text{C}$  NMR spectrum of compound **3c** in  $\text{CDCl}_3$  (101 MHz):



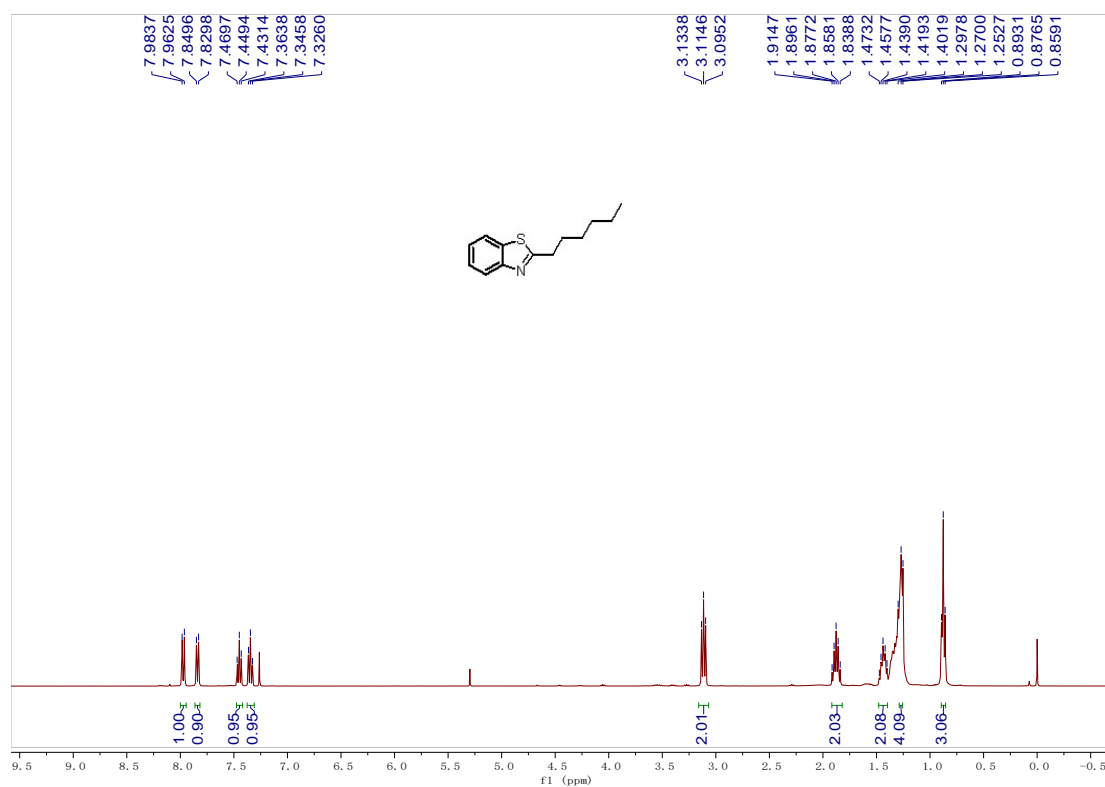
$^1\text{H}$  NMR spectrum of compound **4c** in  $\text{CDCl}_3$  (400 MHz):



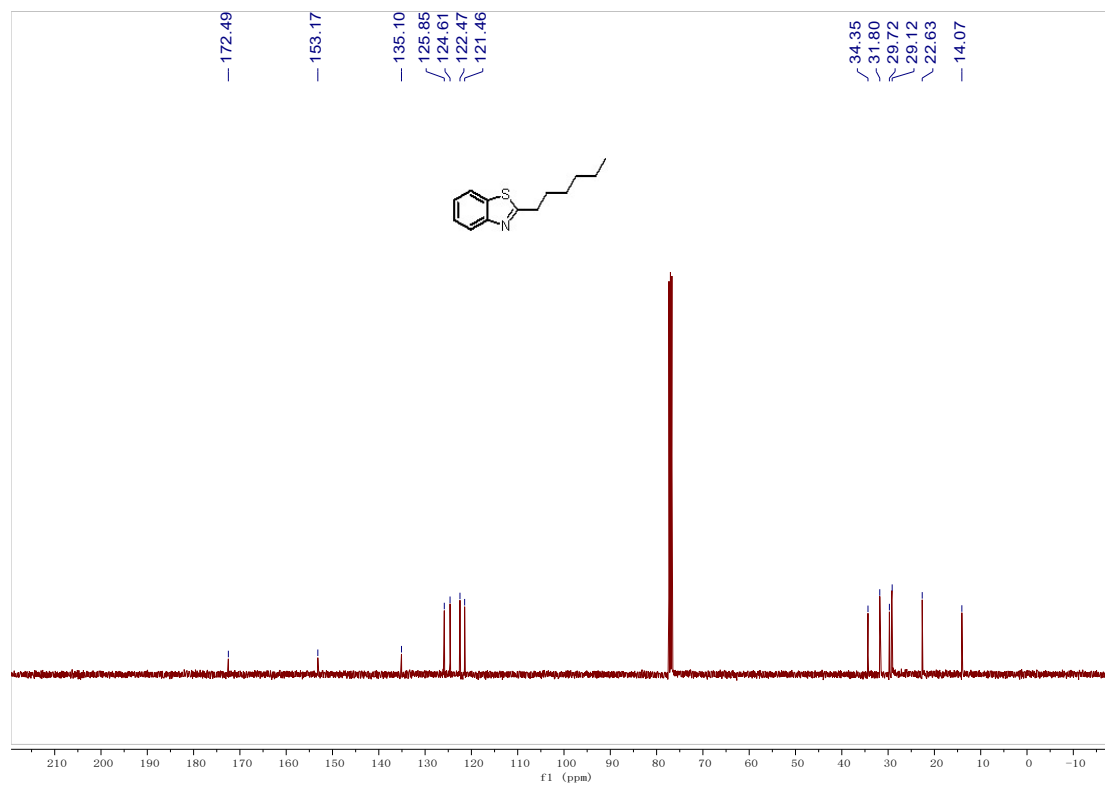
$^{13}\text{C}$  NMR spectrum of compound **4c** in  $\text{CDCl}_3$  (101 MHz):



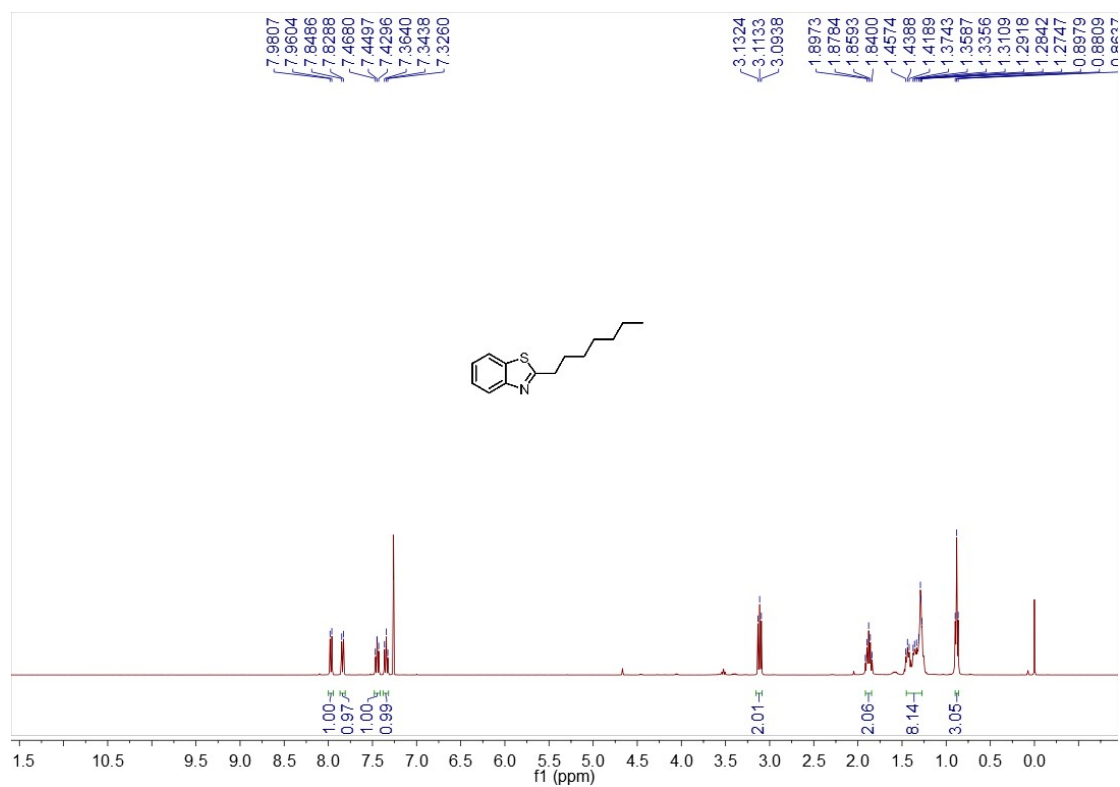
$^1\text{H}$  NMR spectrum of compound **5c** in  $\text{CDCl}_3$  (400 MHz):



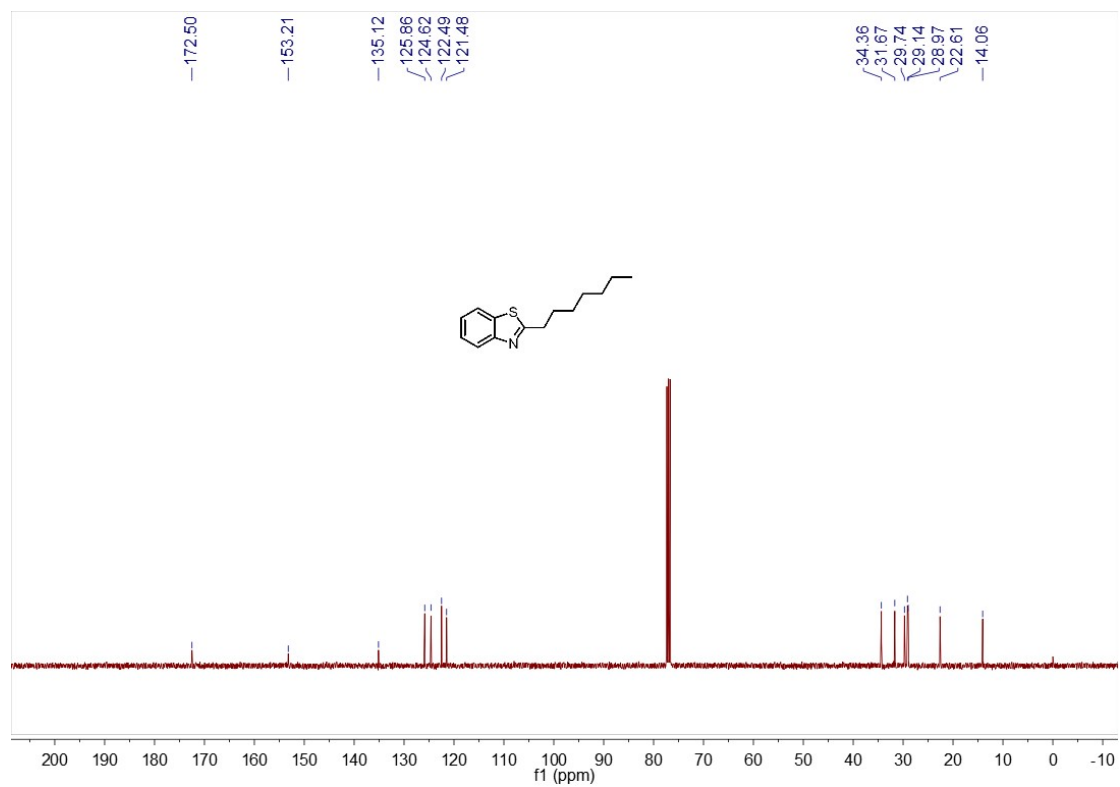
$^{13}\text{C}$  NMR spectrum of compound **5c** in  $\text{CDCl}_3$  (101 MHz):



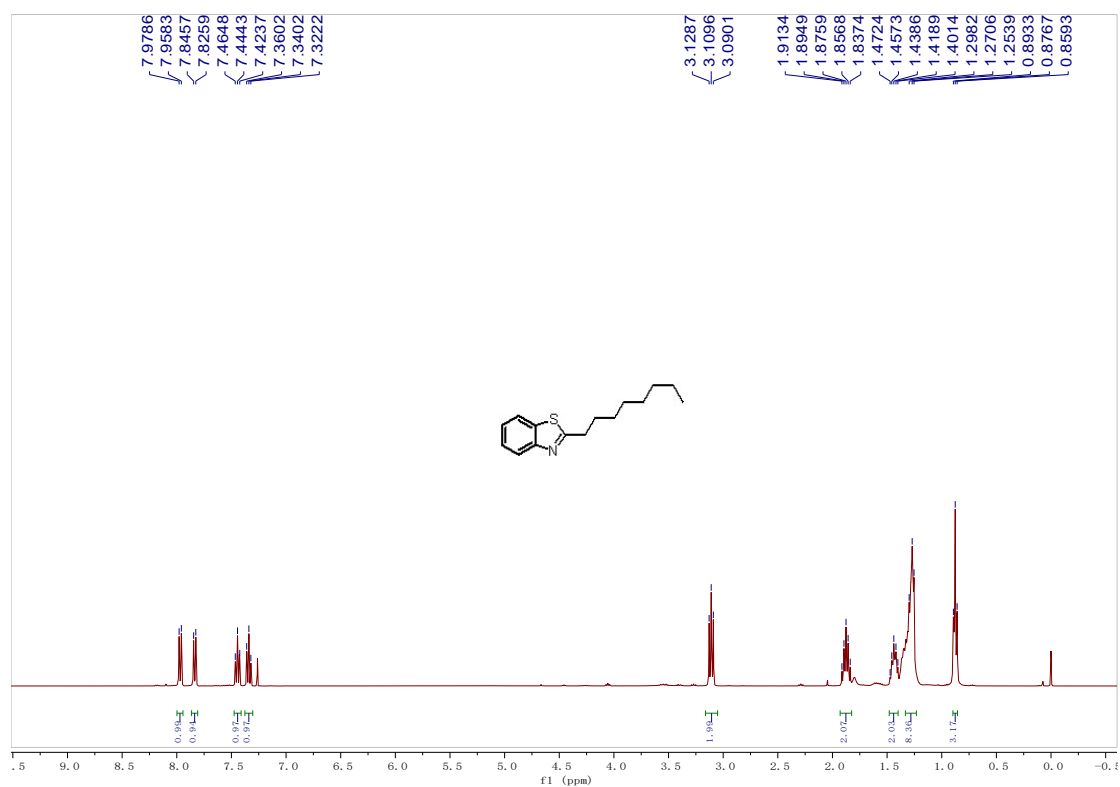
$^1\text{H}$  NMR spectrum of compound **6c** in  $\text{CDCl}_3$  (400 MHz):



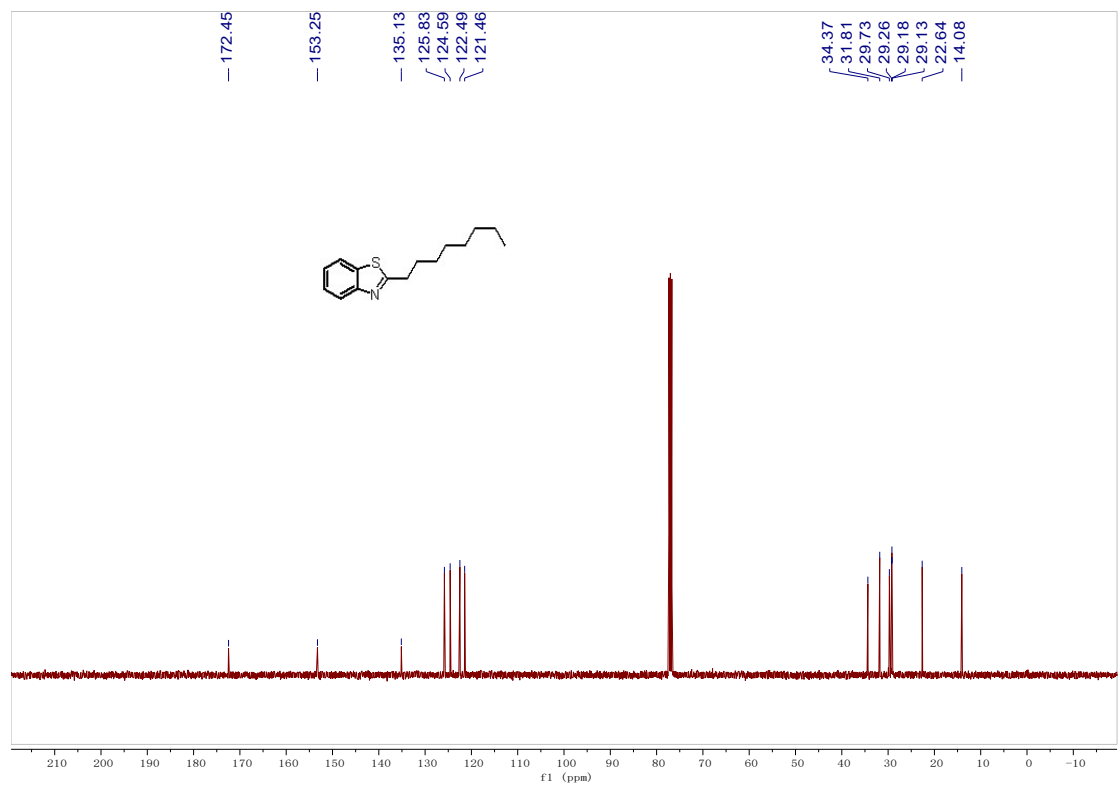
$^{13}\text{C}$  NMR spectrum of compound **6c** in  $\text{CDCl}_3$  (101 MHz):



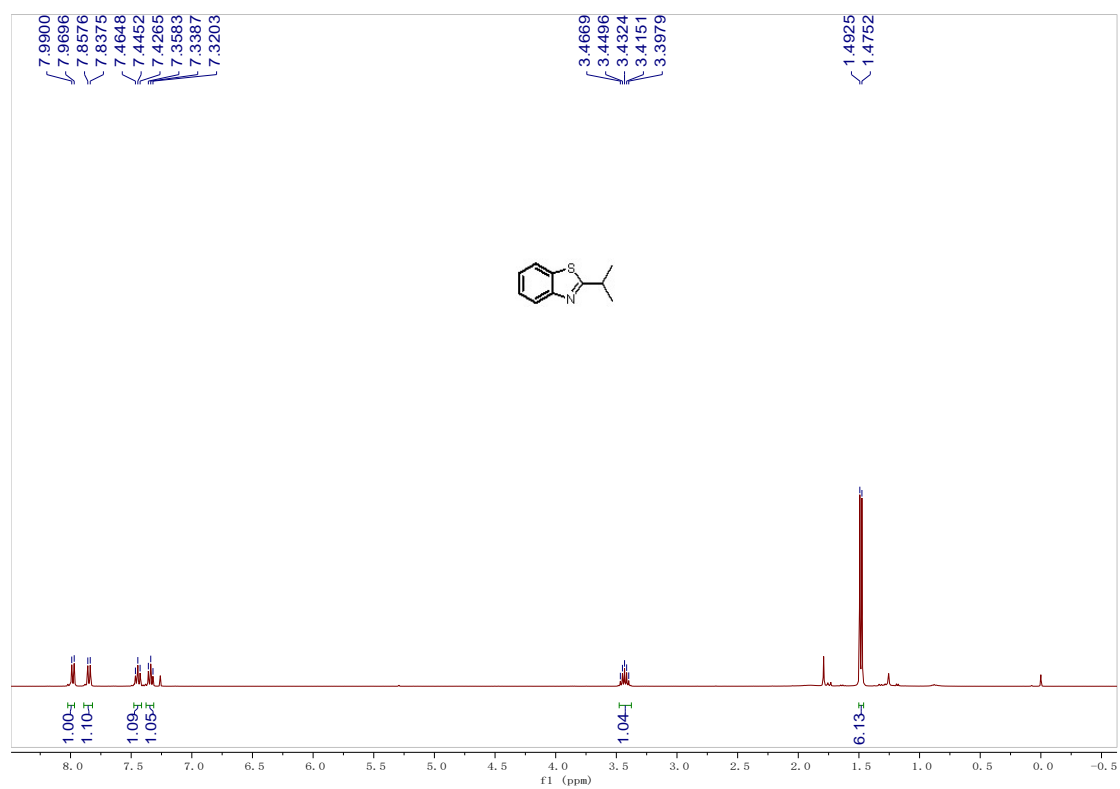
$^1\text{H}$  NMR spectrum of compound **7c** in  $\text{CDCl}_3$  (400 MHz):



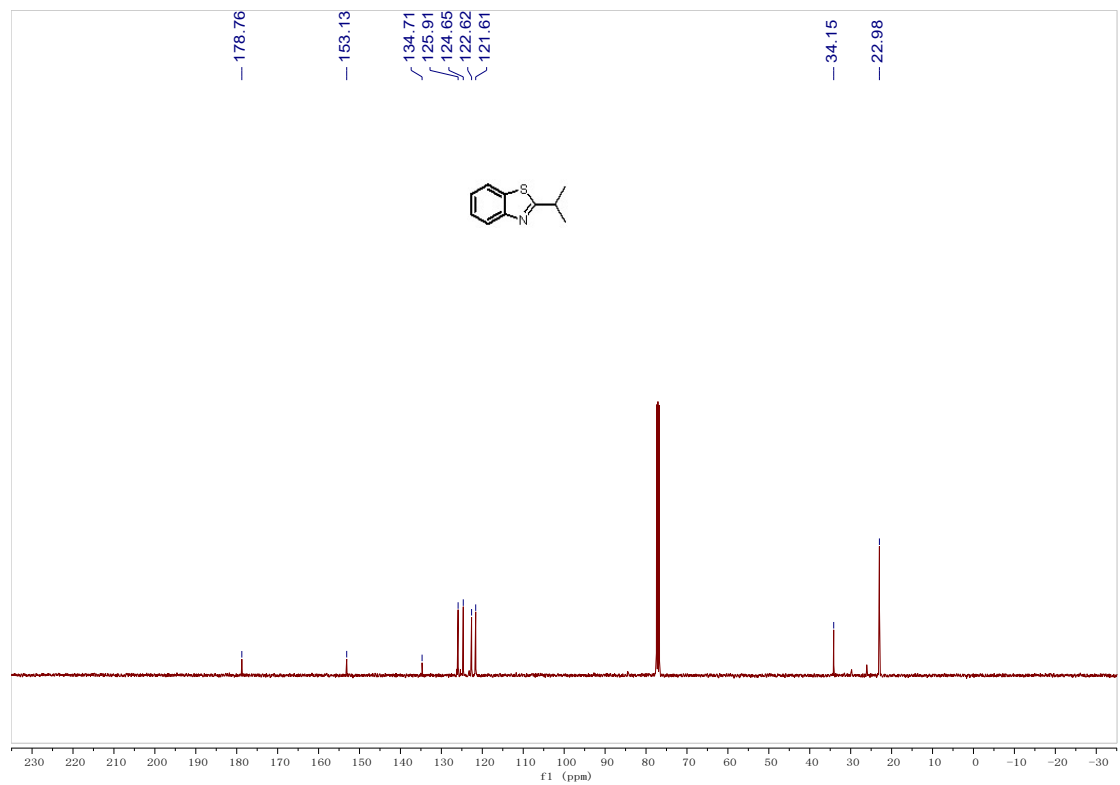
$^{13}\text{C}$  NMR spectrum of compound **7c** in  $\text{CDCl}_3$  (101 MHz):



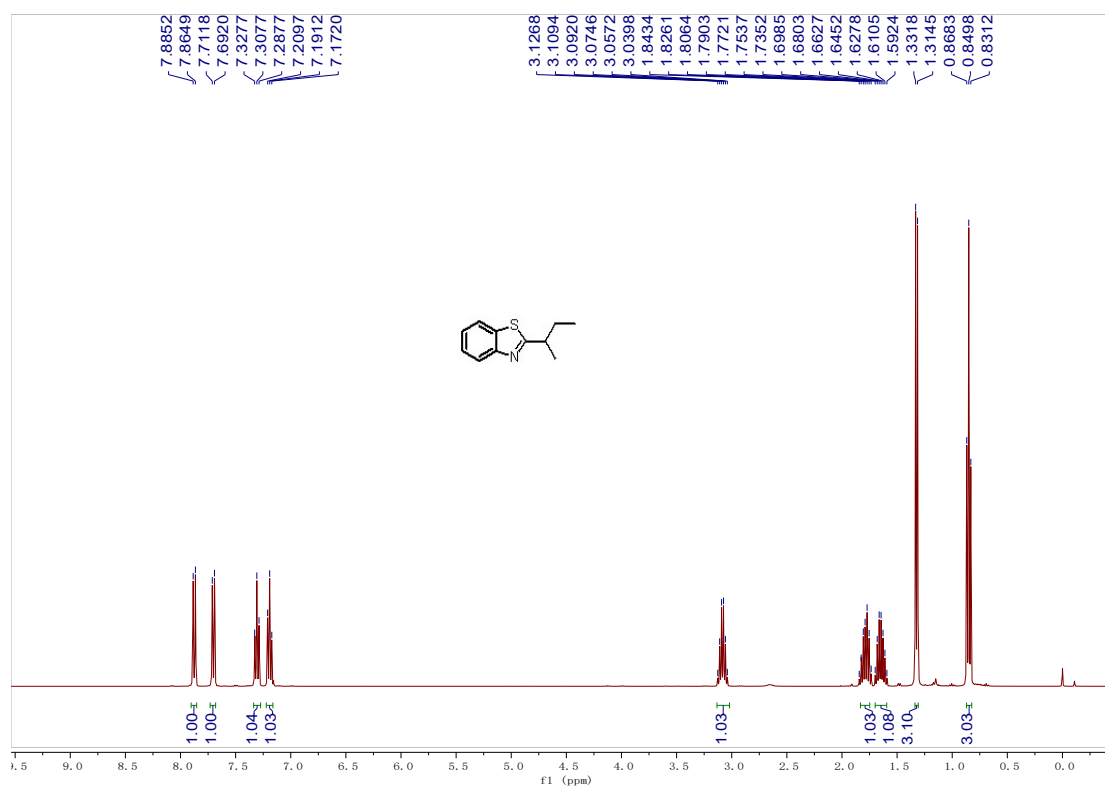
$^1\text{H}$  NMR spectrum of compound **9c** in  $\text{CDCl}_3$  (400 MHz):



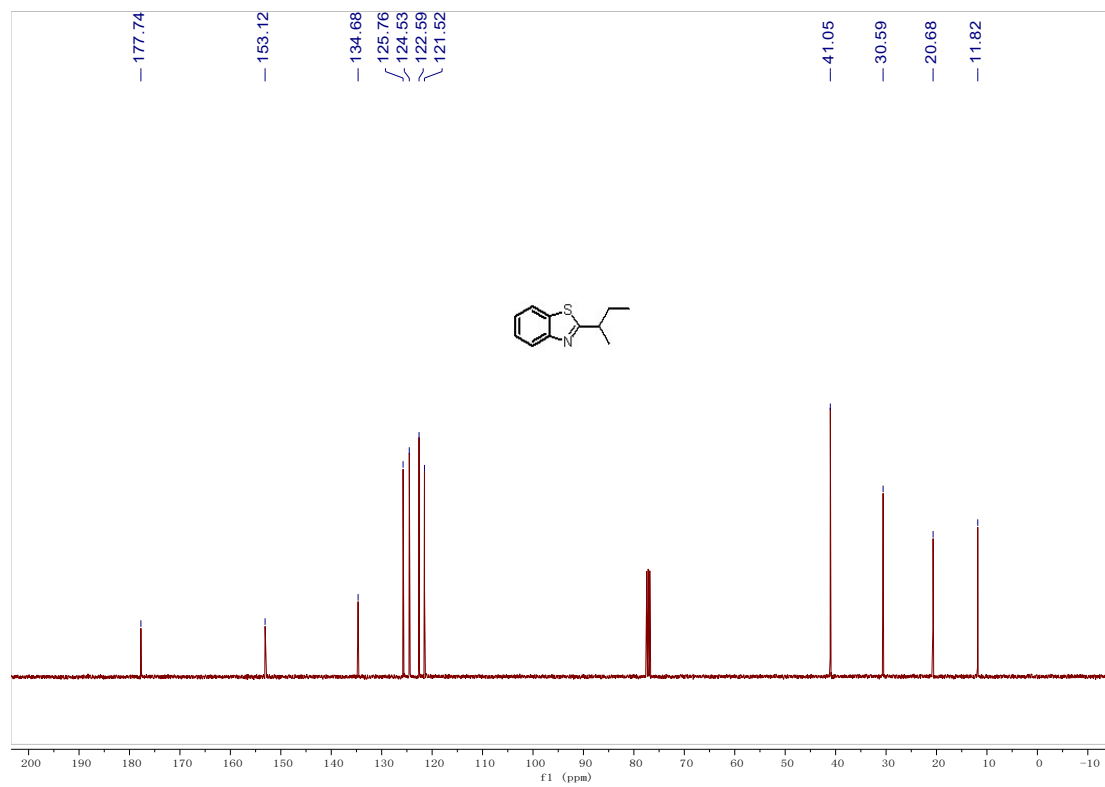
$^{13}\text{C}$  NMR spectrum of compound **9c** in  $\text{CDCl}_3$  (101 MHz):



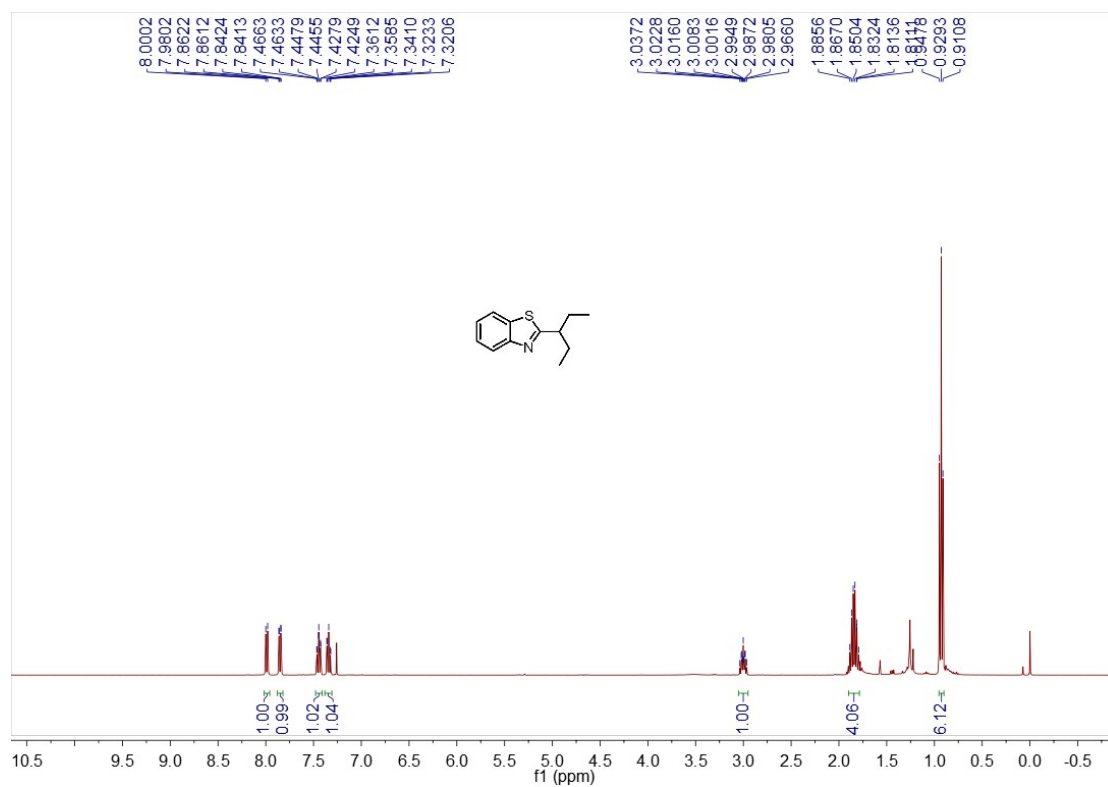
$^1\text{H}$  NMR spectrum of compound **10c** in  $\text{CDCl}_3$  (400 MHz):



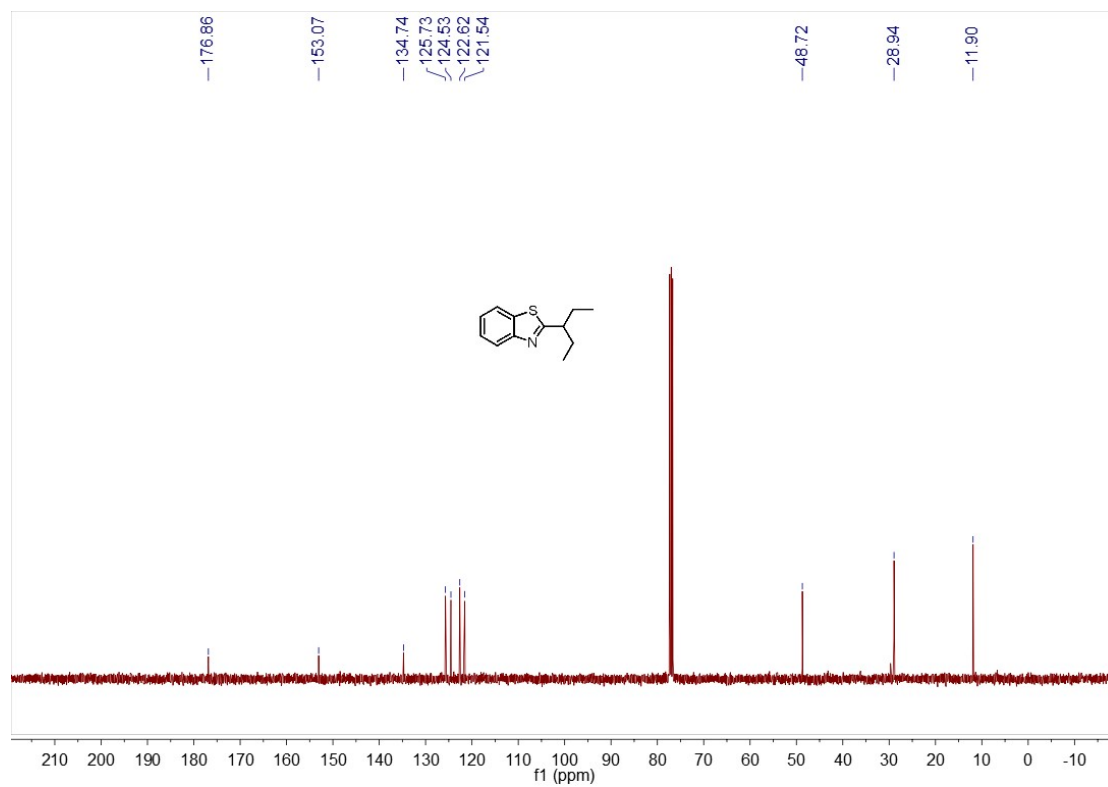
$^{13}\text{C}$  NMR spectrum of compound **10c** in  $\text{CDCl}_3$  (101 MHz):



$^1\text{H}$  NMR spectrum of compound **11c** in  $\text{CDCl}_3$  (400 MHz):

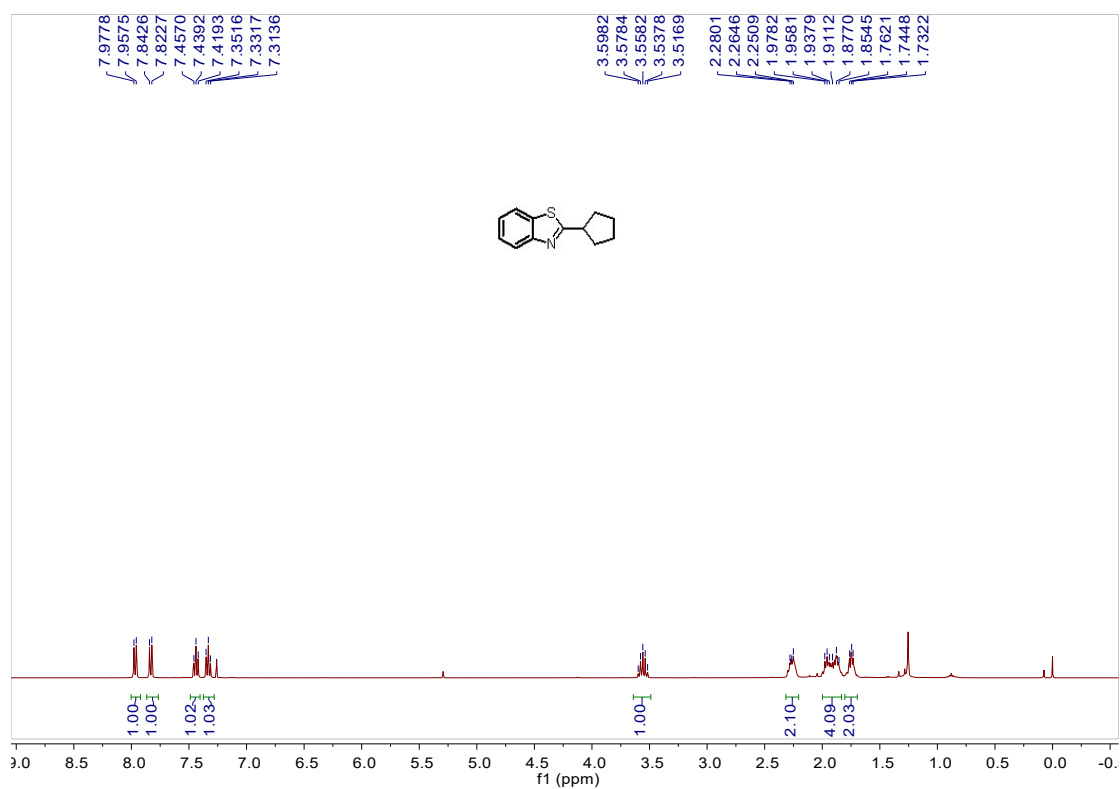


$^{13}\text{C}$  NMR spectrum of compound **11c** in  $\text{CDCl}_3$  (101 MHz):

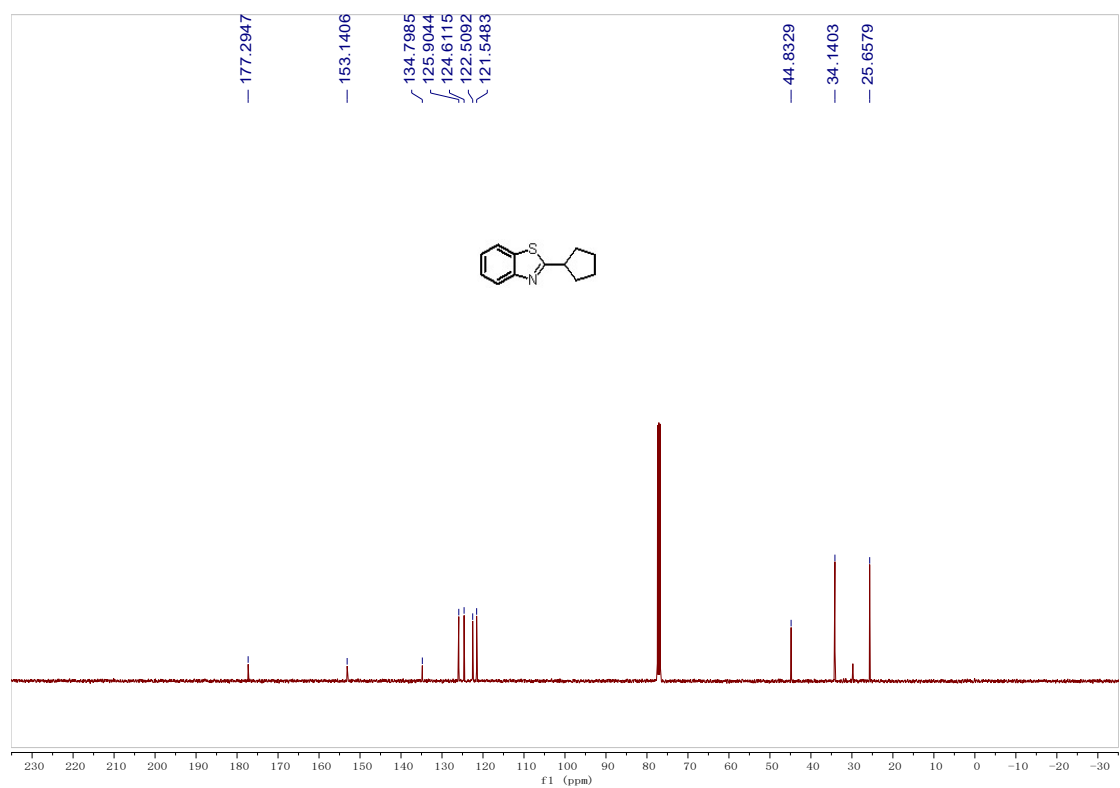




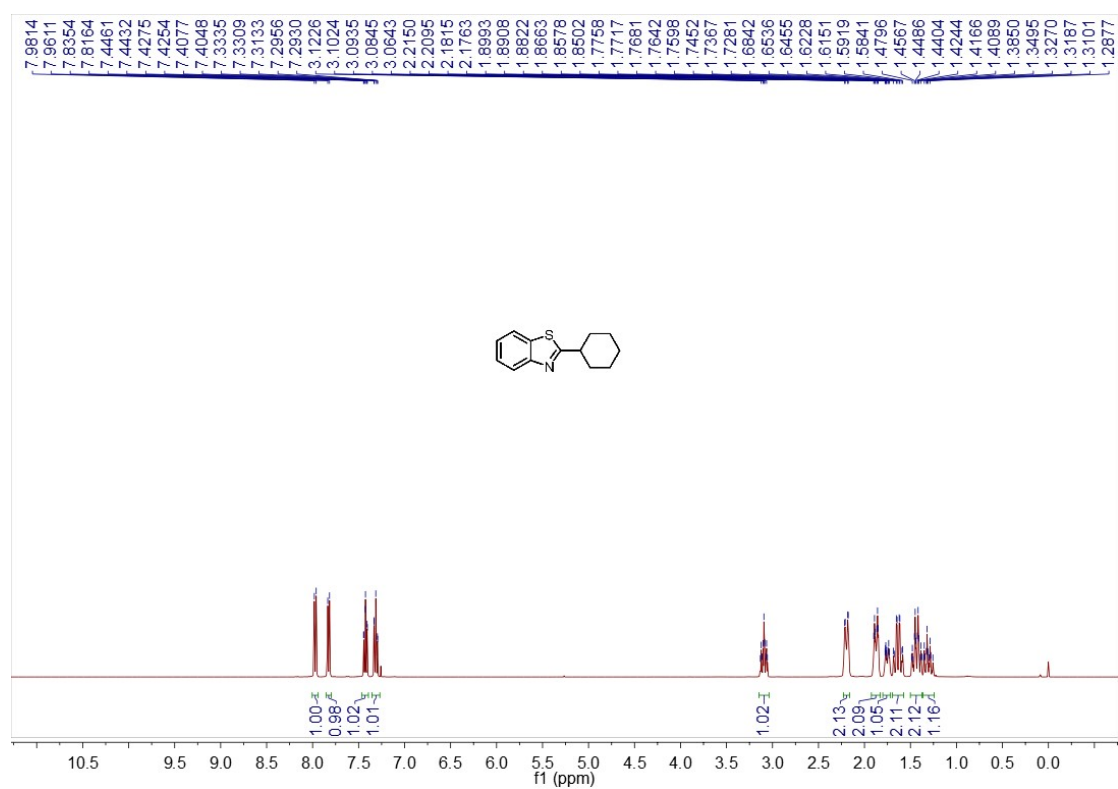
<sup>1</sup>H NMR spectrum of compound **12c** in CDCl<sub>3</sub> (400 MHz):



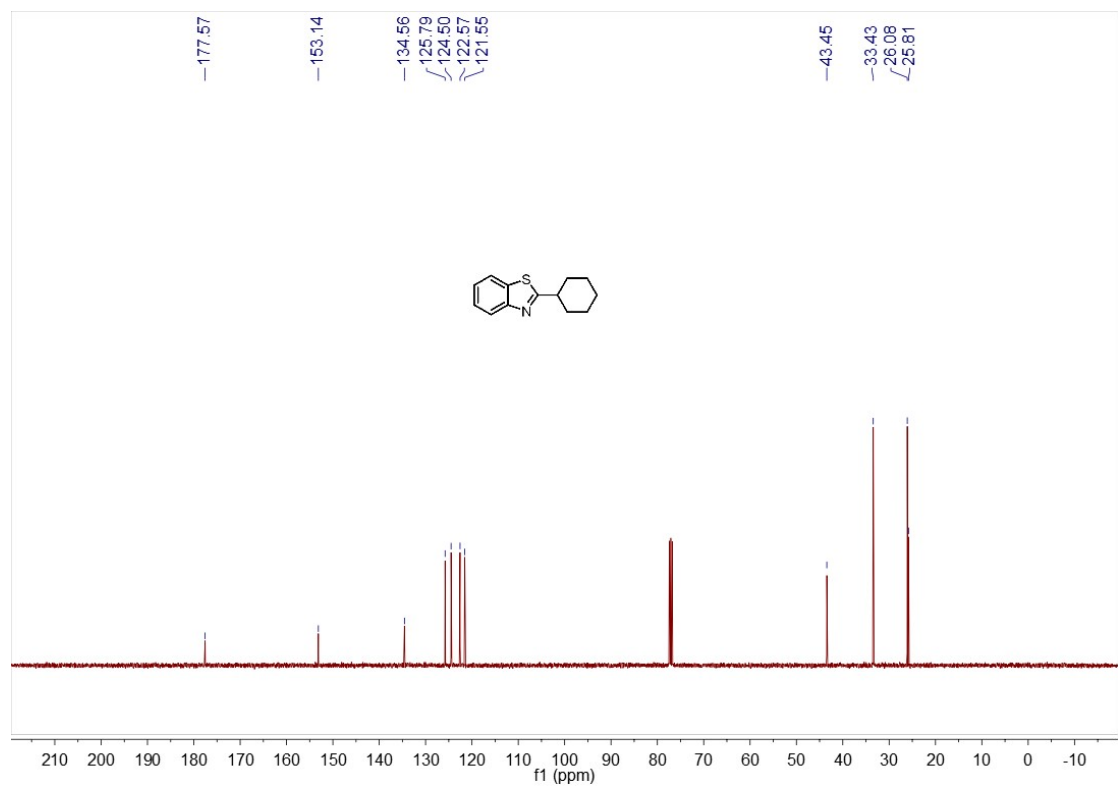
<sup>13</sup>C NMR spectrum of compound **12c** in CDCl<sub>3</sub> (101 MHz):



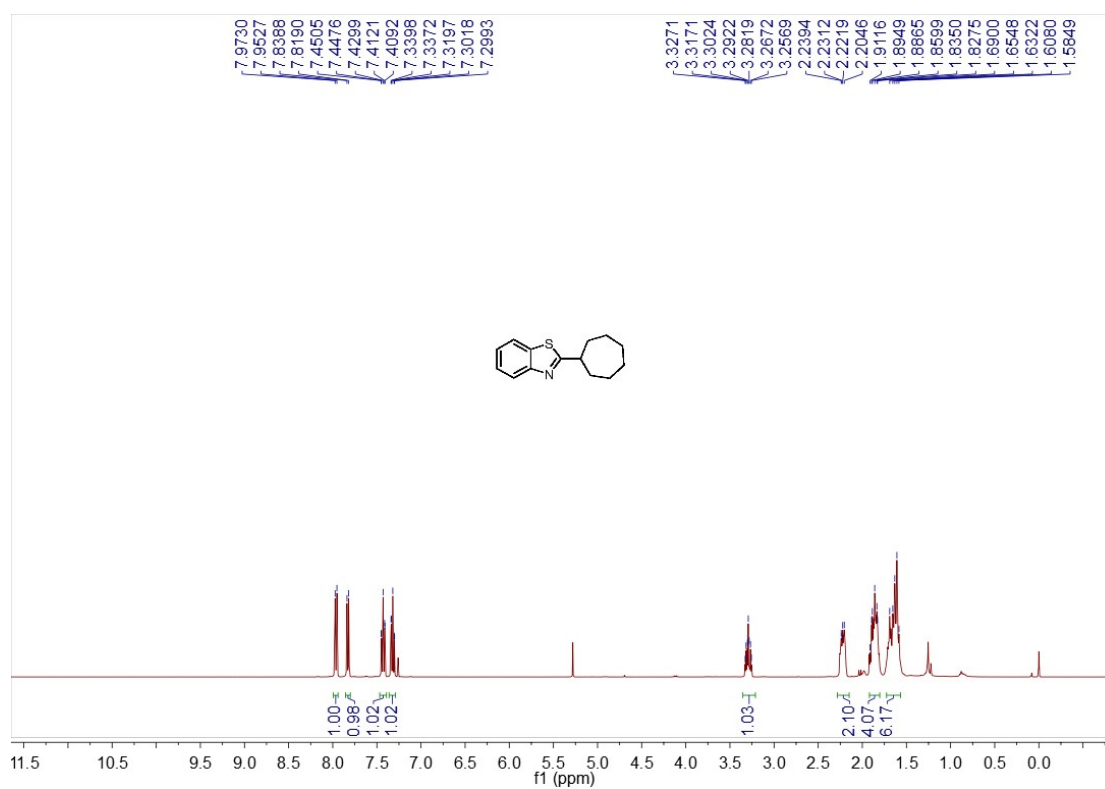
$^1\text{H}$  NMR spectrum of compound **13c** in  $\text{CDCl}_3$  (400 MHz):



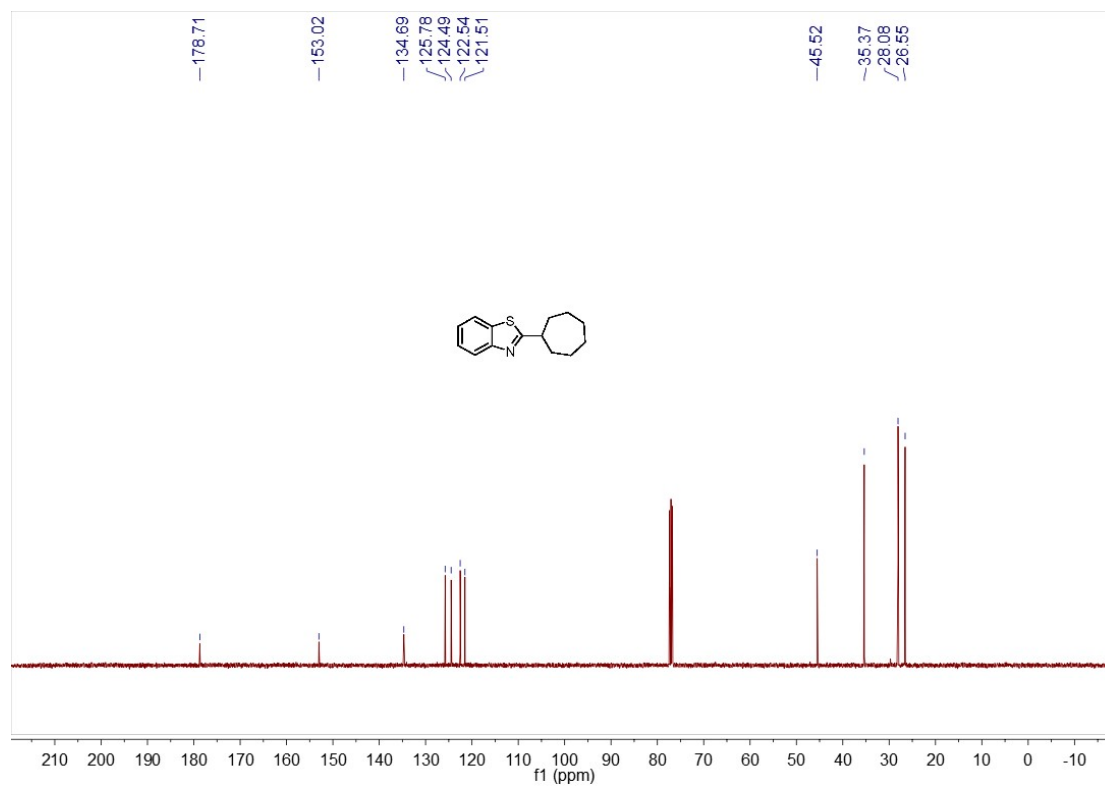
$^{13}\text{C}$  NMR spectrum of compound **13c** in  $\text{CDCl}_3$  (101 MHz):



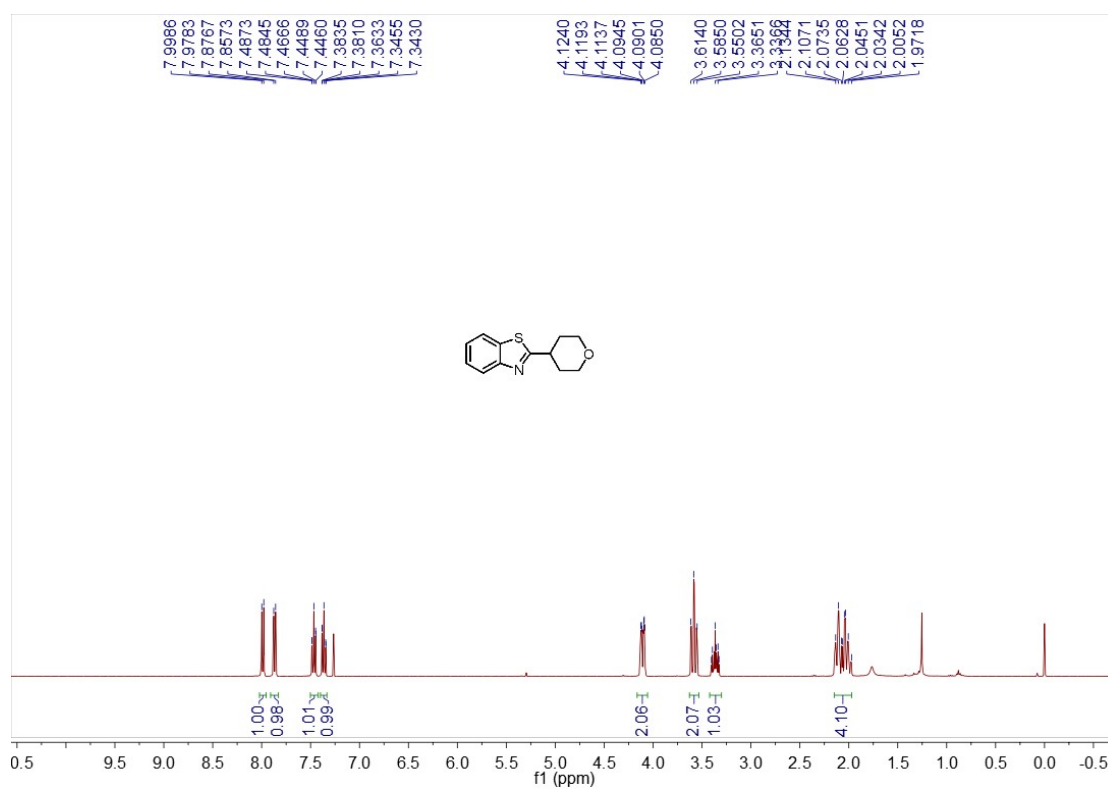
$^1\text{H}$  NMR spectrum of compound **14c** in  $\text{CDCl}_3$  (400 MHz):



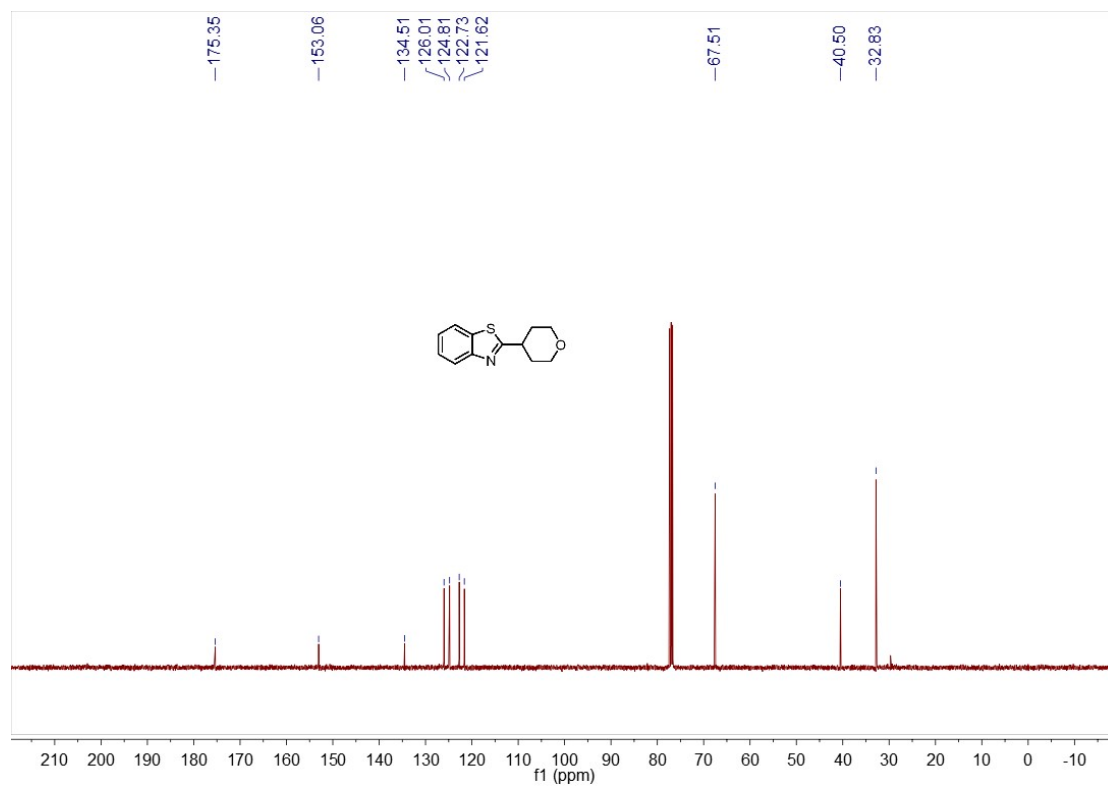
$^{13}\text{C}$  NMR spectrum of compound **14c** in  $\text{CDCl}_3$  (101 MHz):



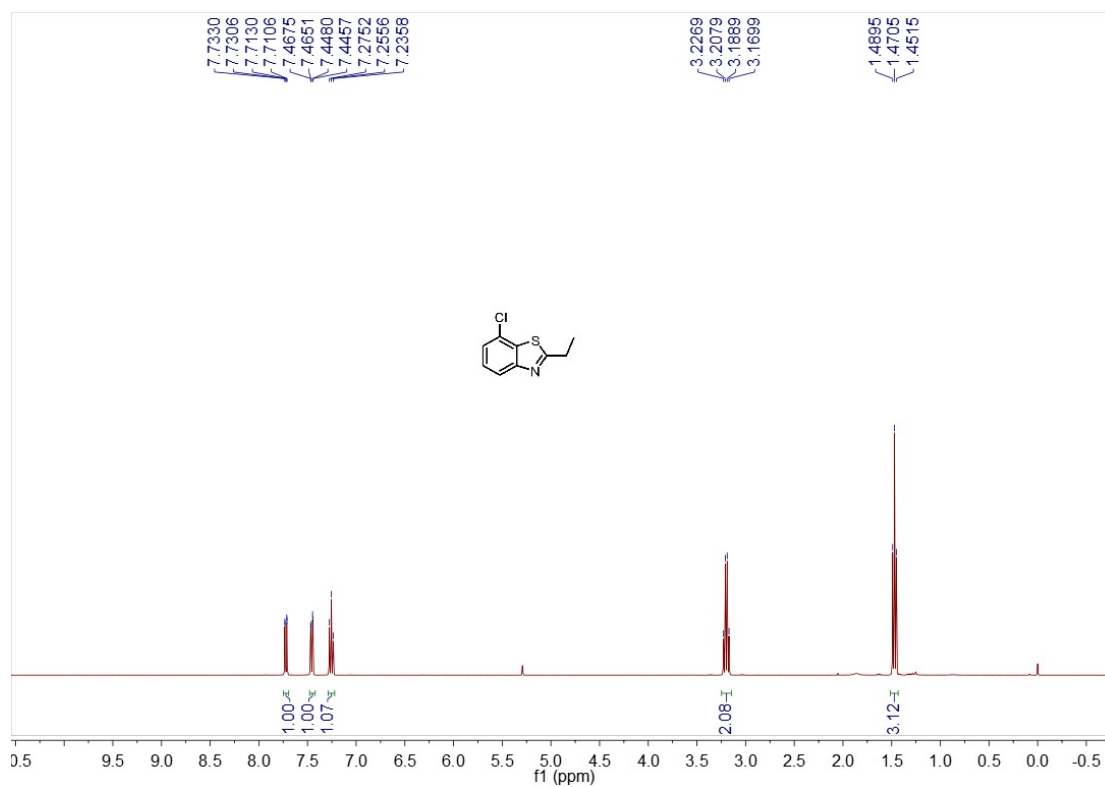
$^1\text{H}$  NMR spectrum of compound **15c** in  $\text{CDCl}_3$  (400 MHz):



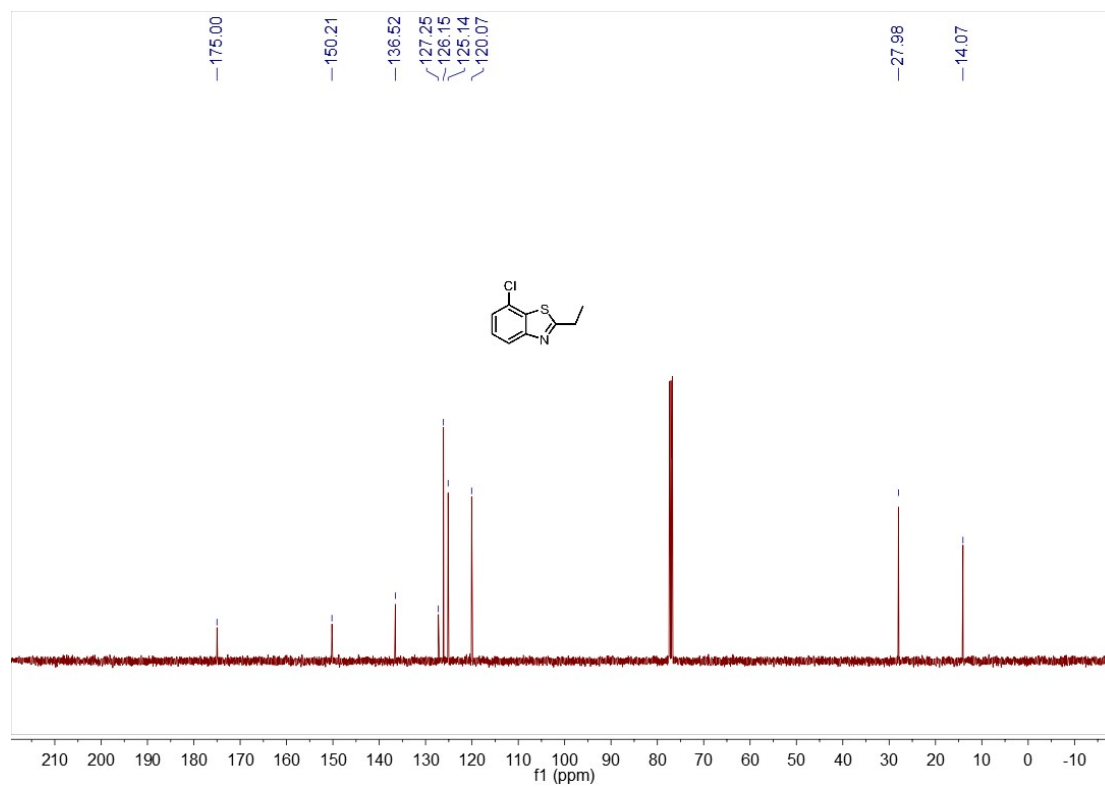
$^{13}\text{C}$  NMR spectrum of compound **15c** in  $\text{CDCl}_3$  (101 MHz):



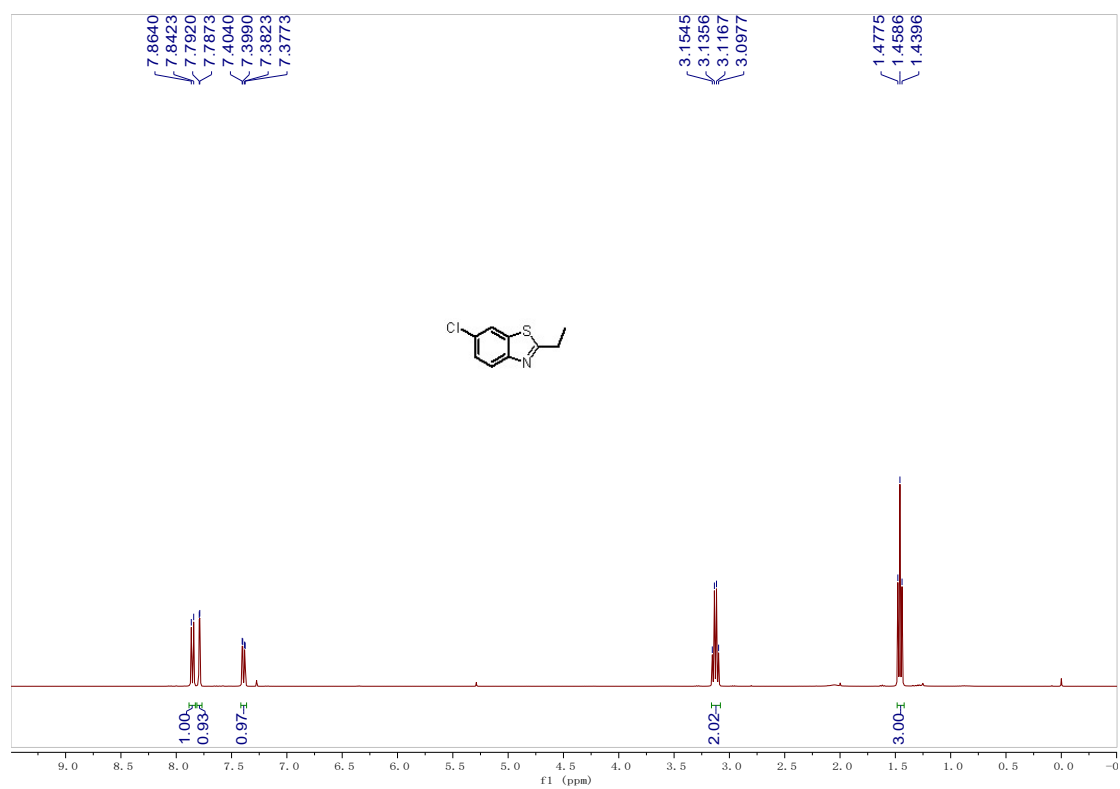
$^1\text{H}$  NMR spectrum of compound **16c** in  $\text{CDCl}_3$  (400 MHz):



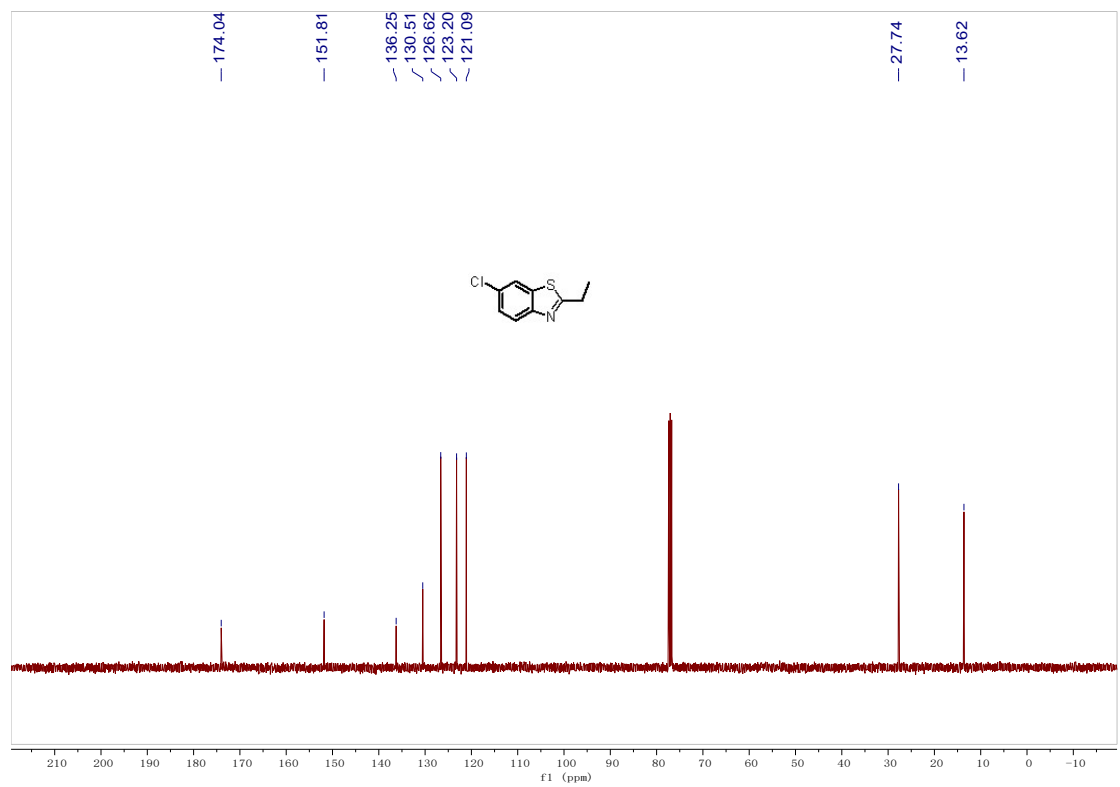
$^{13}\text{C}$  NMR spectrum of compound **16c** in  $\text{CDCl}_3$  (101 MHz):



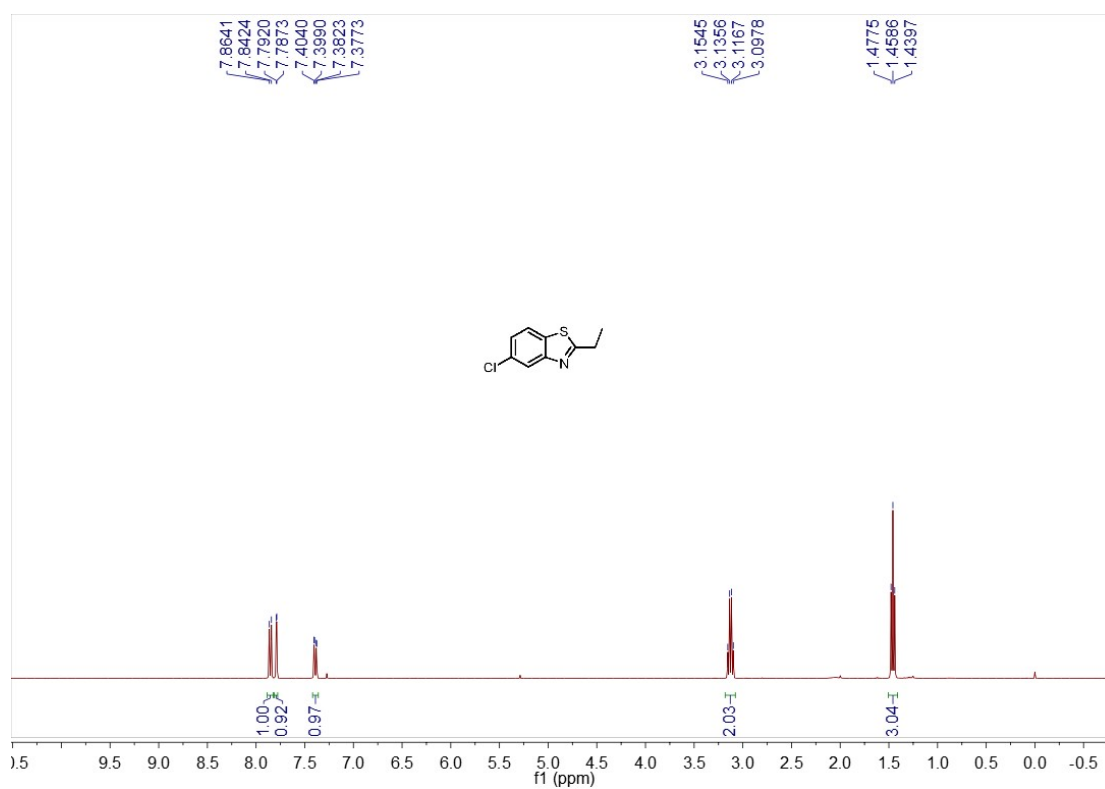
<sup>1</sup>H NMR spectrum of compound **17c** in CDCl<sub>3</sub> (400 MHz):



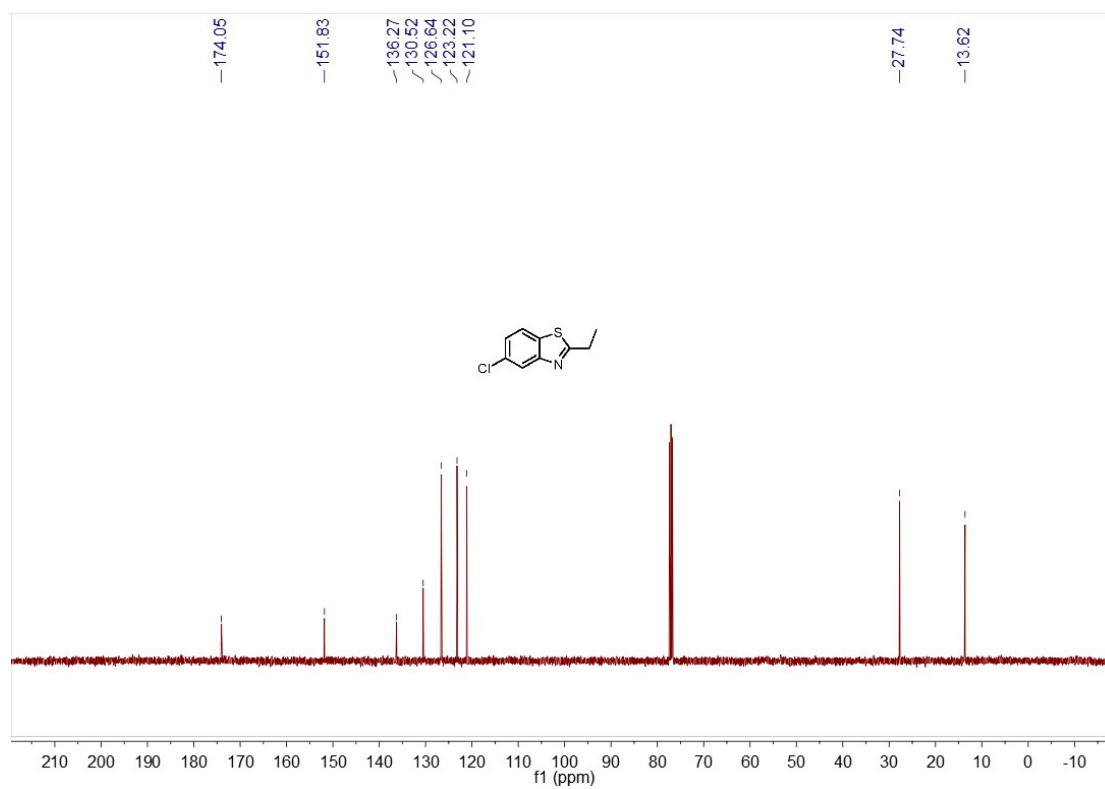
<sup>13</sup>C NMR spectrum of compound **17c** in CDCl<sub>3</sub> (101 MHz):



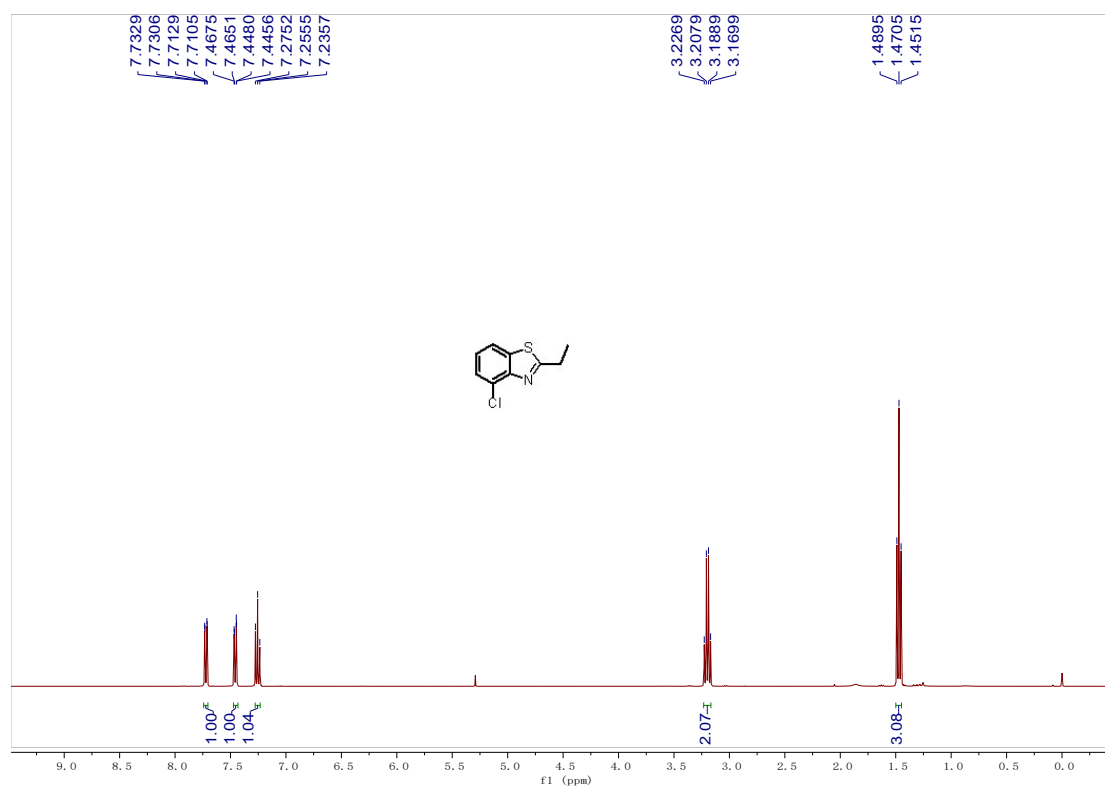
$^1\text{H}$  NMR spectrum of compound **18c** in  $\text{CDCl}_3$  (400 MHz):



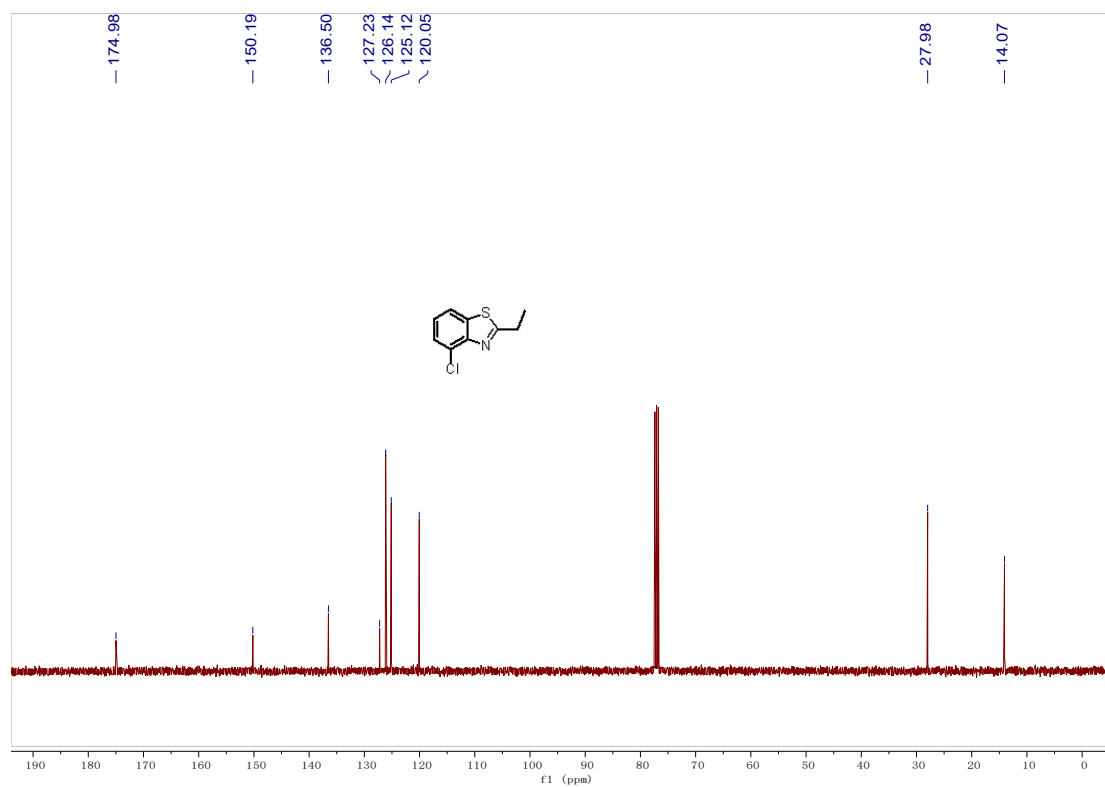
$^{13}\text{C}$  NMR spectrum of compound **18c** in  $\text{CDCl}_3$  (101 MHz):



$^1\text{H}$  NMR spectrum of compound **19c** in  $\text{CDCl}_3$  (400 MHz):

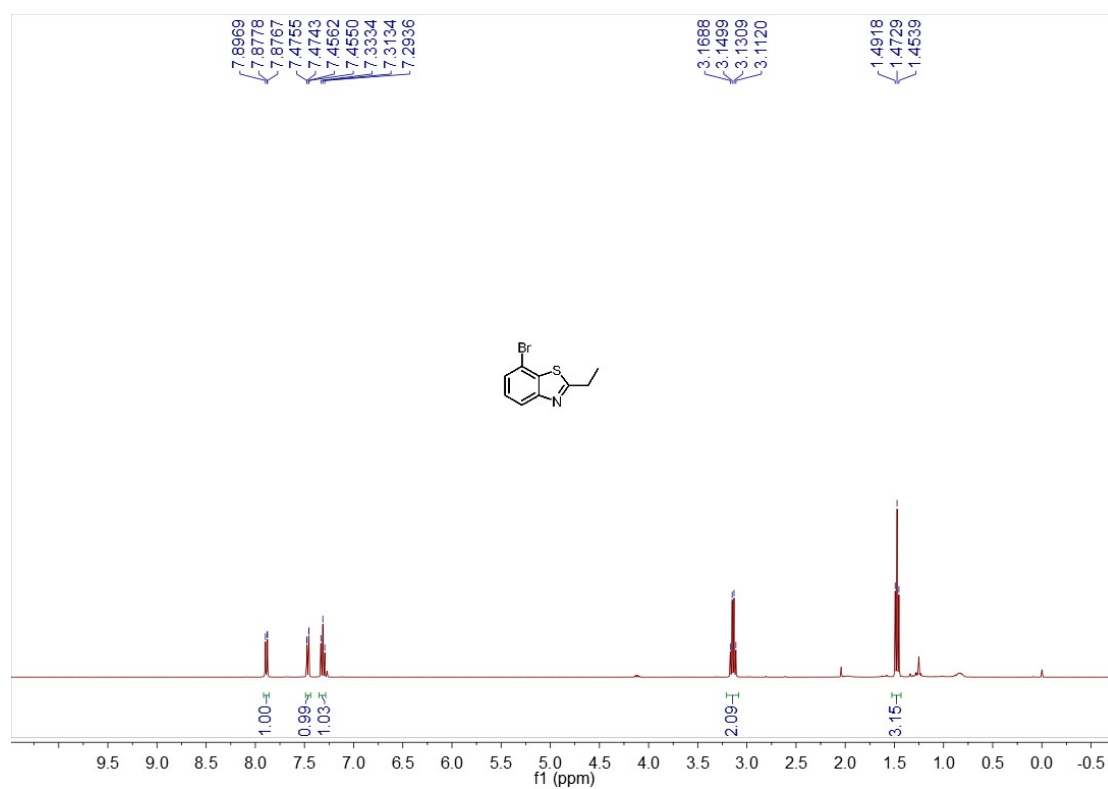


$^{13}\text{C}$  NMR spectrum of compound **19c** in  $\text{CDCl}_3$  (101 MHz):

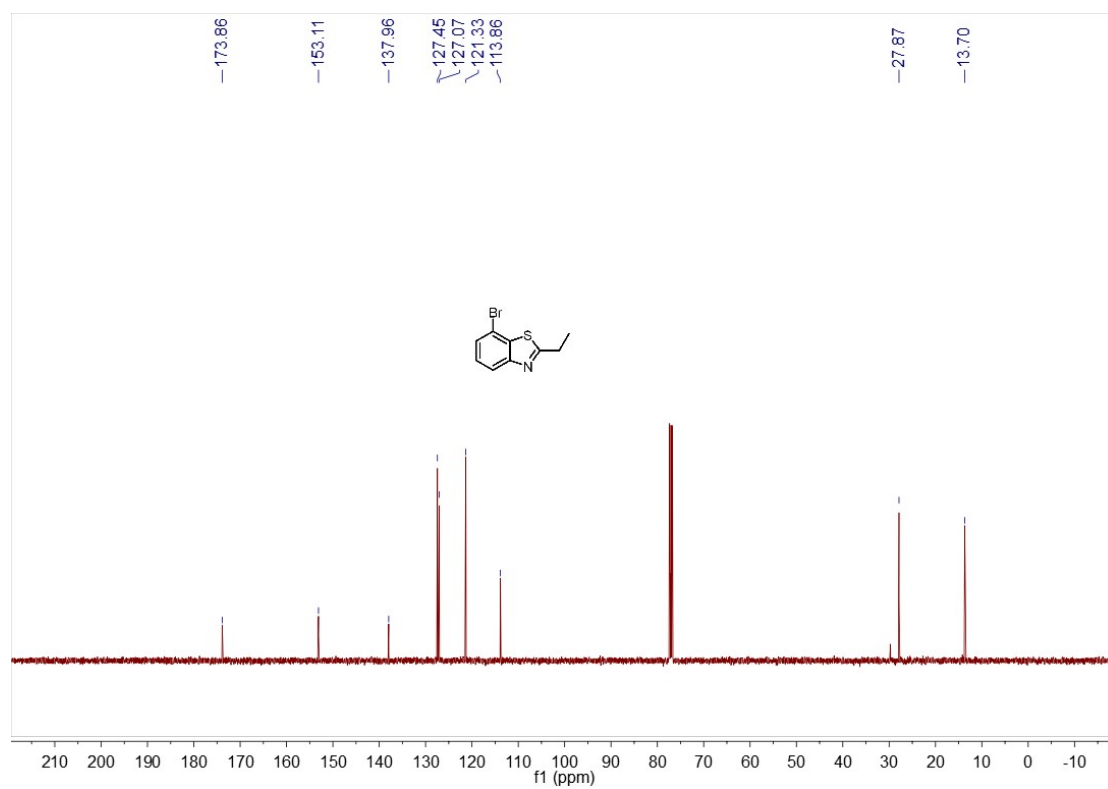




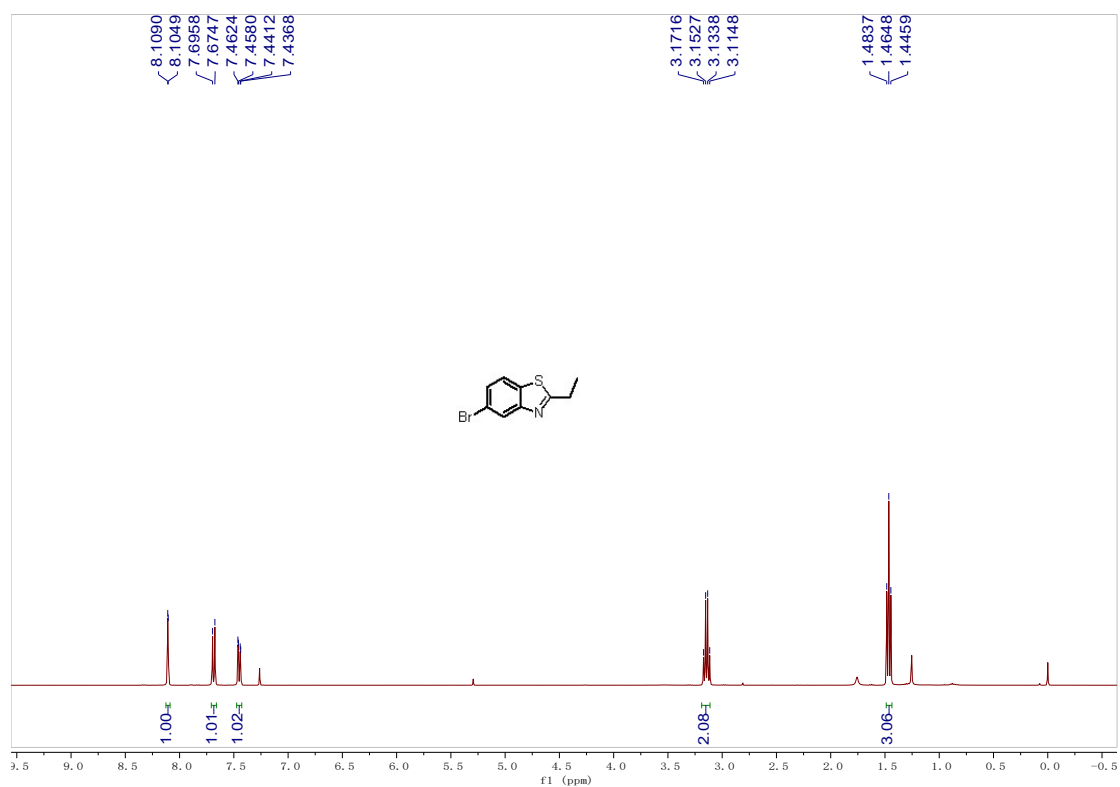
$^1\text{H}$  NMR spectrum of compound **20c** in  $\text{CDCl}_3$  (400 MHz):



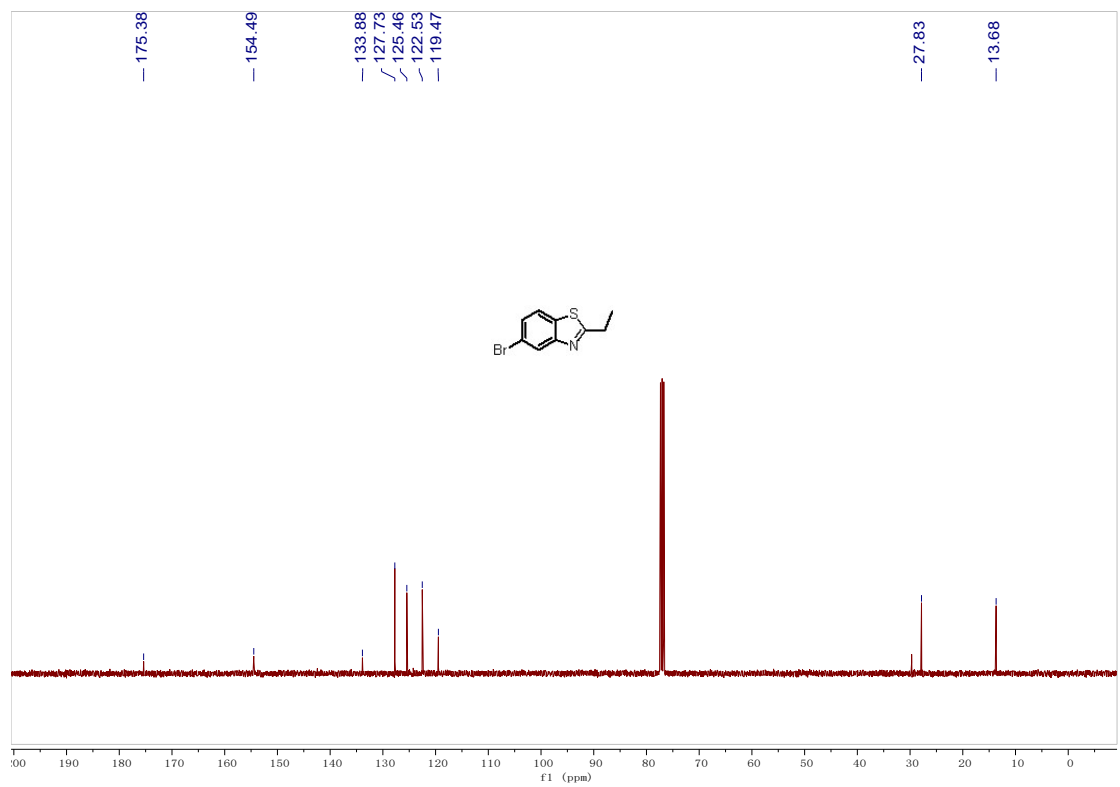
$^{13}\text{C}$  NMR spectrum of compound **20c** in  $\text{CDCl}_3$  (101 MHz):



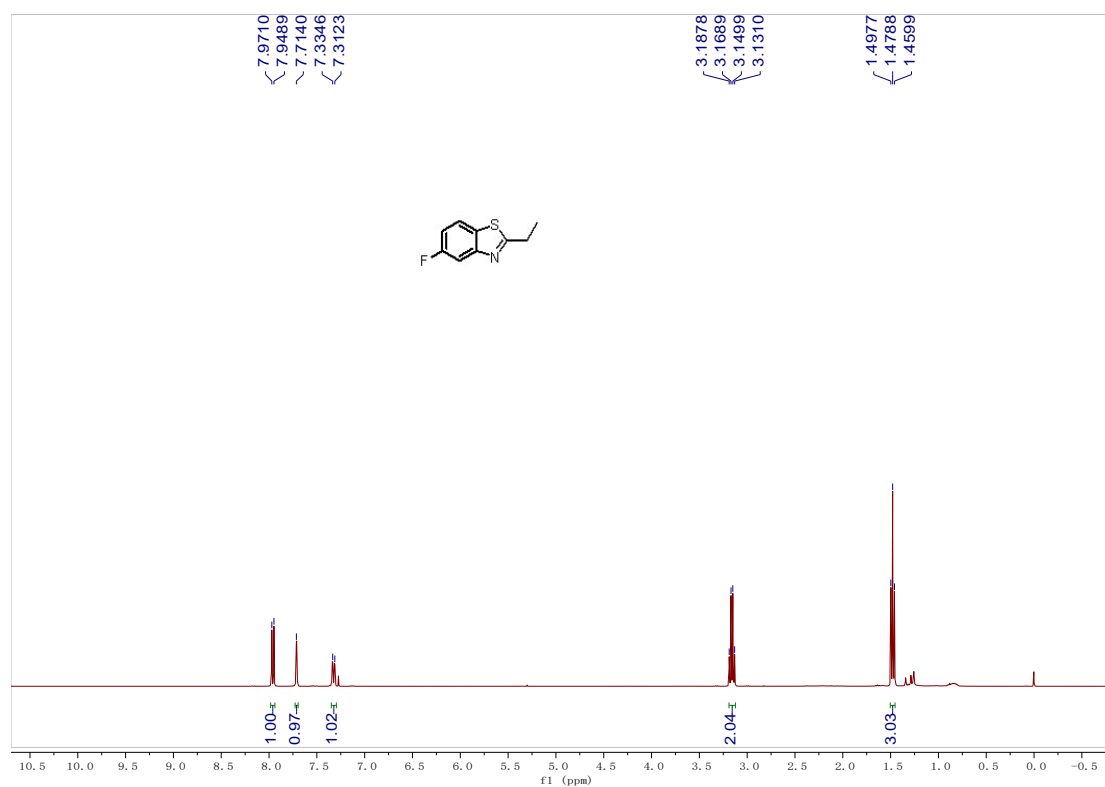
$^1\text{H}$  NMR spectrum of compound **21c** in  $\text{CDCl}_3$  (400 MHz):



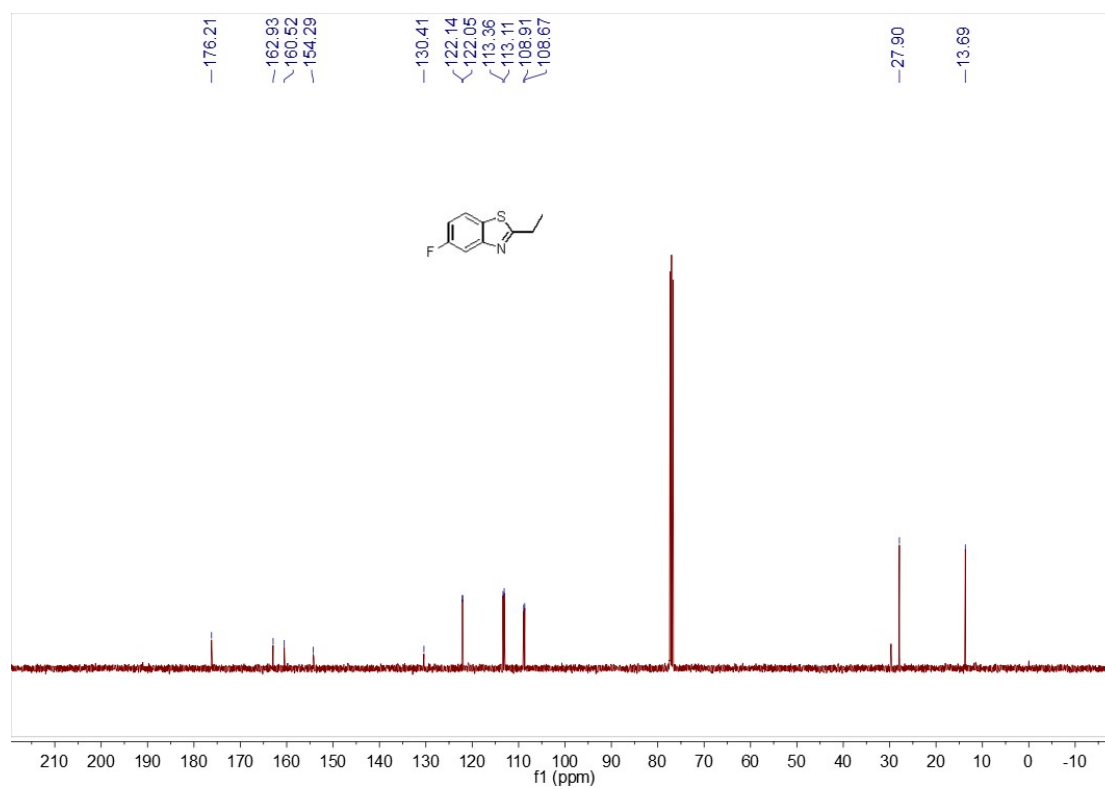
$^{13}\text{C}$  NMR spectrum of compound **21c** in  $\text{CDCl}_3$  (101 MHz):



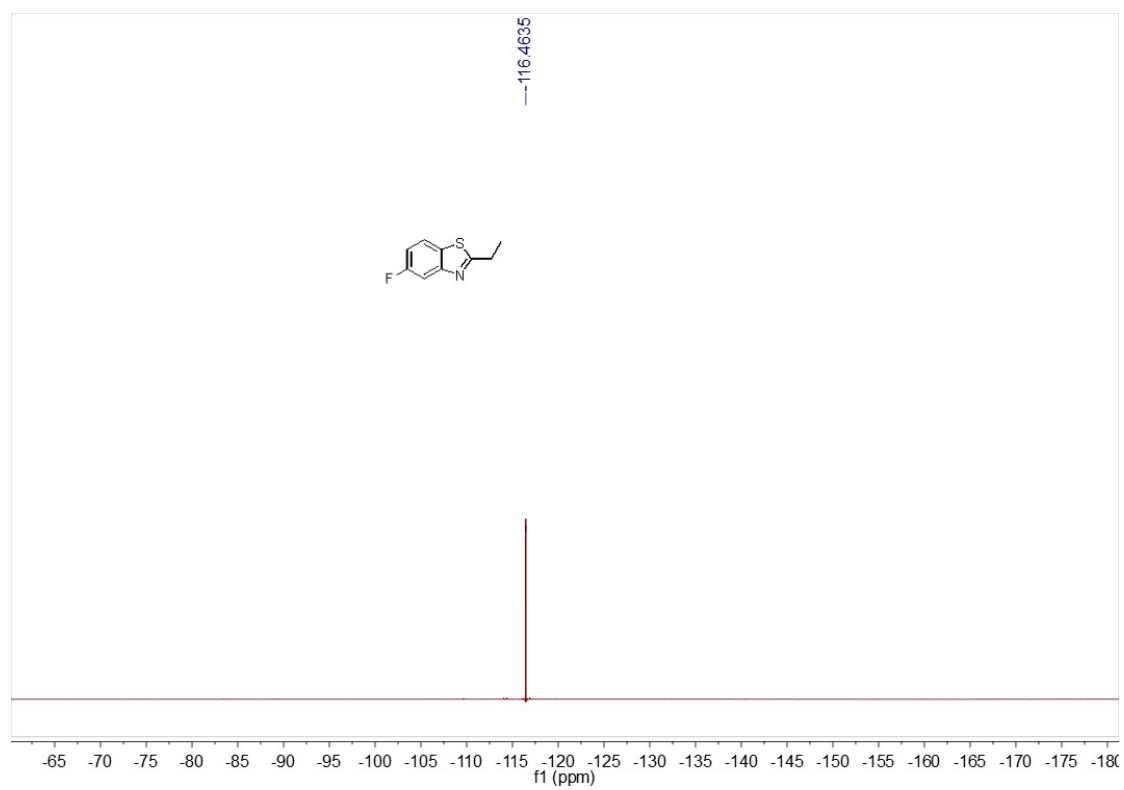
$^1\text{H}$  NMR spectrum of compound **22c** in  $\text{CDCl}_3$  (400 MHz):



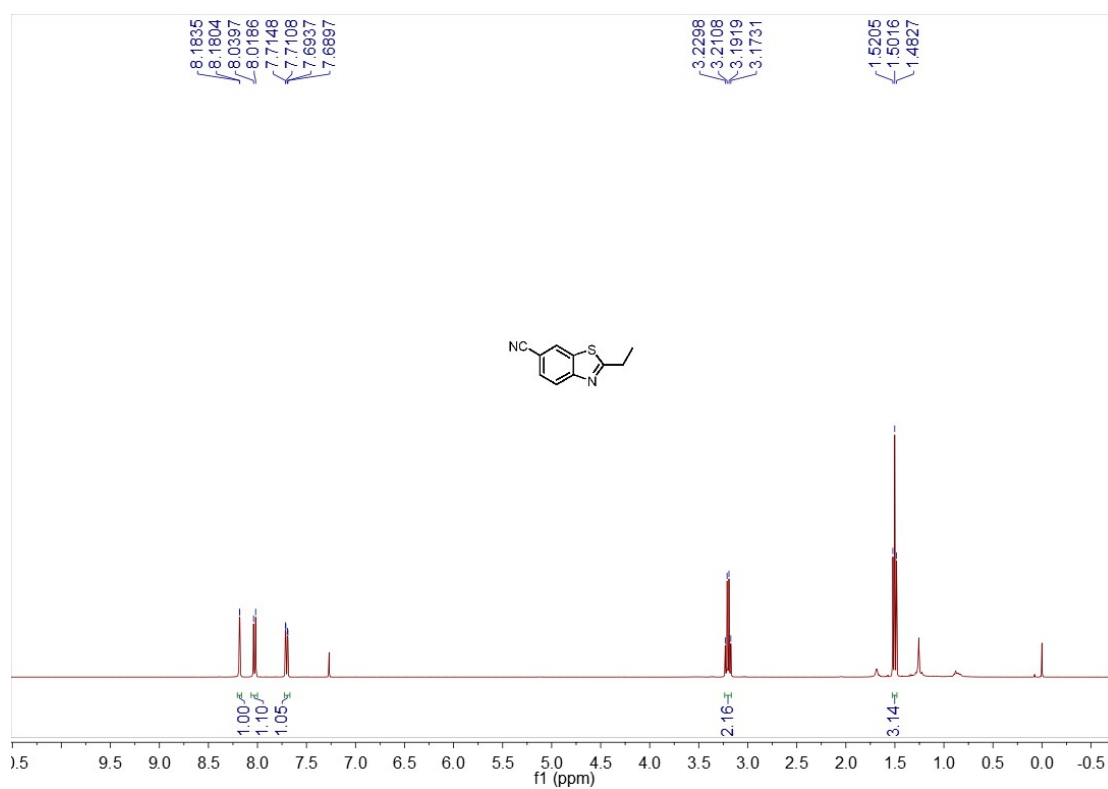
$^{13}\text{C}$  NMR spectrum of compound **22c** in  $\text{CDCl}_3$  (101 MHz):



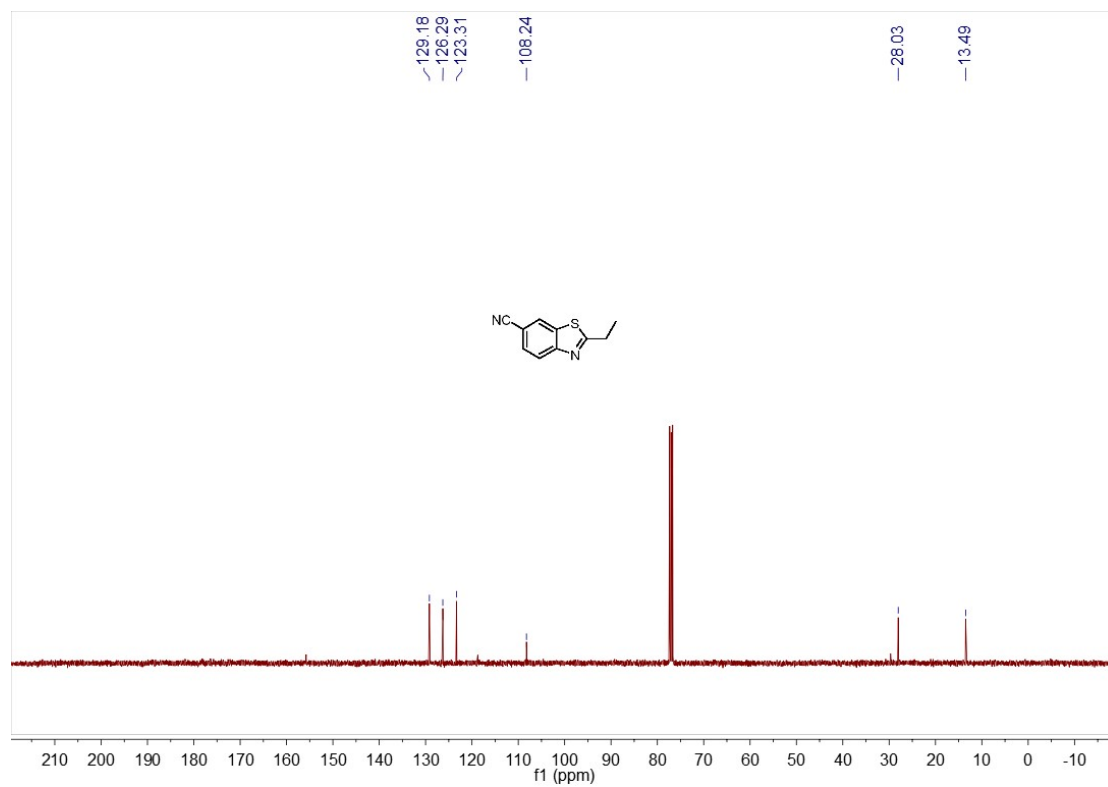
$^{19}\text{F}$  NMR spectrum of compound **22c** in  $\text{CDCl}_3$  (101 MHz):



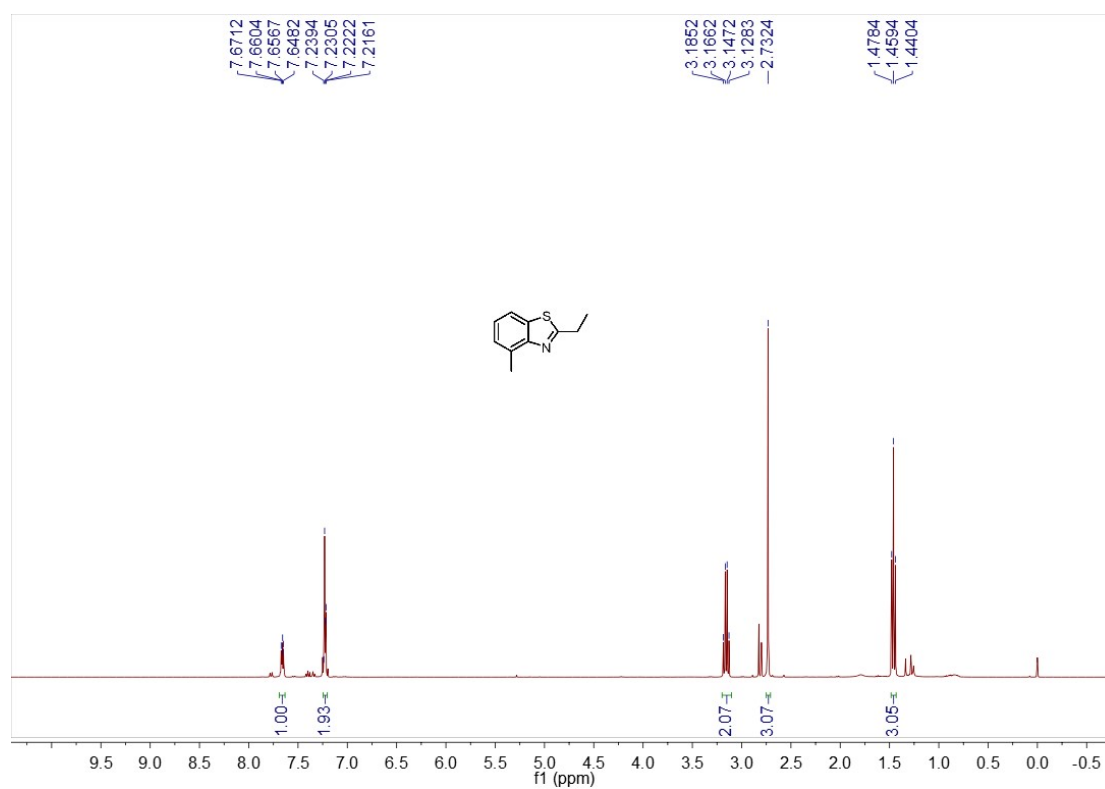
$^1\text{H}$  NMR spectrum of compound **23c** in  $\text{CDCl}_3$  (400 MHz):



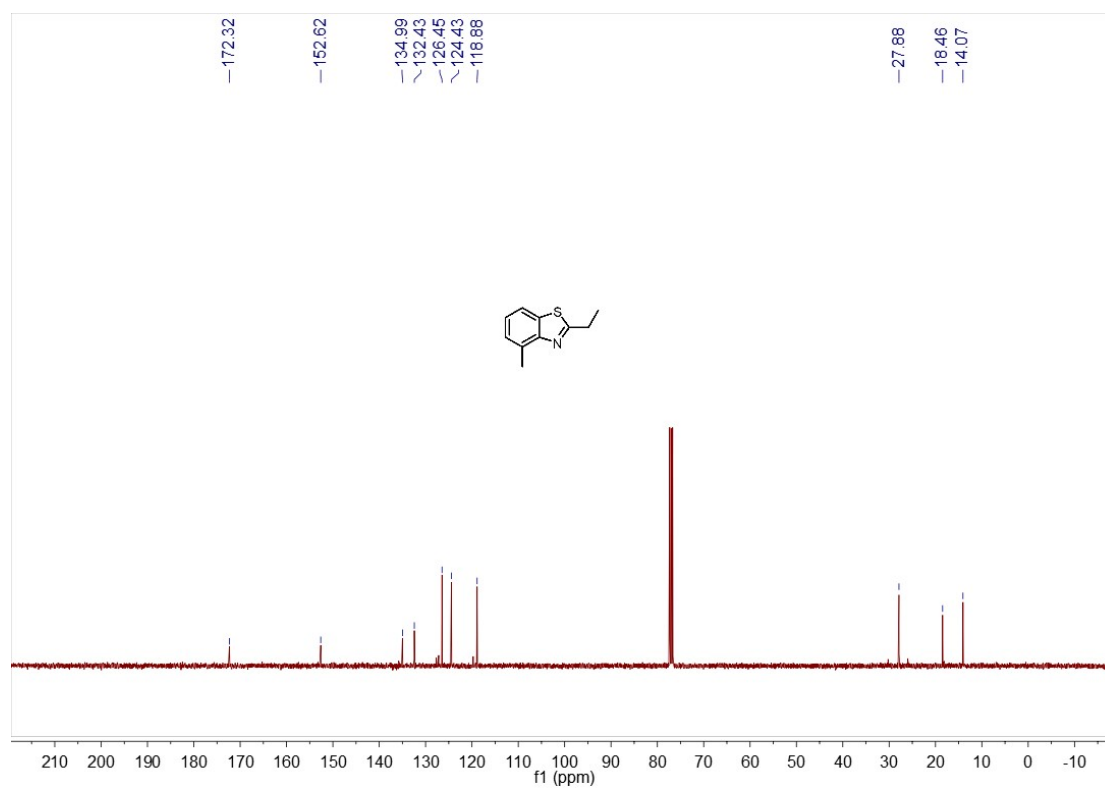
$^{13}\text{C}$  NMR spectrum of compound **23c** in  $\text{CDCl}_3$  (101 MHz):



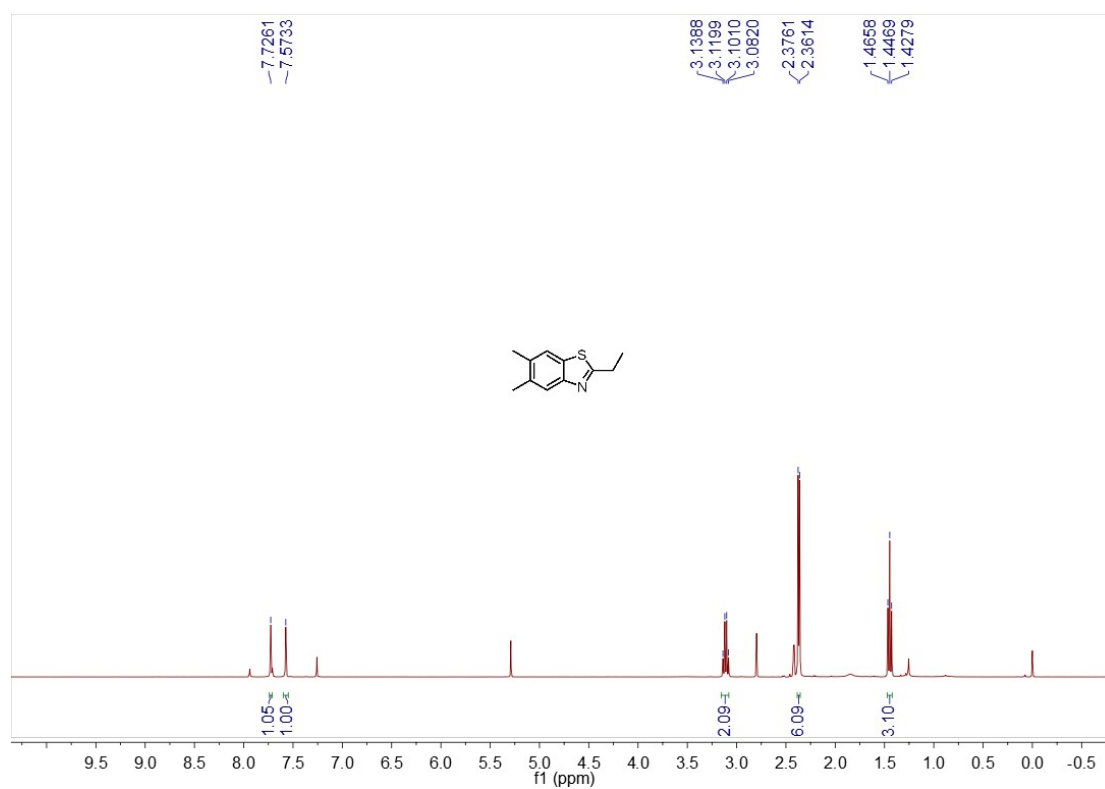
$^1\text{H}$  NMR spectrum of compound **24c** in  $\text{CDCl}_3$  (400 MHz):



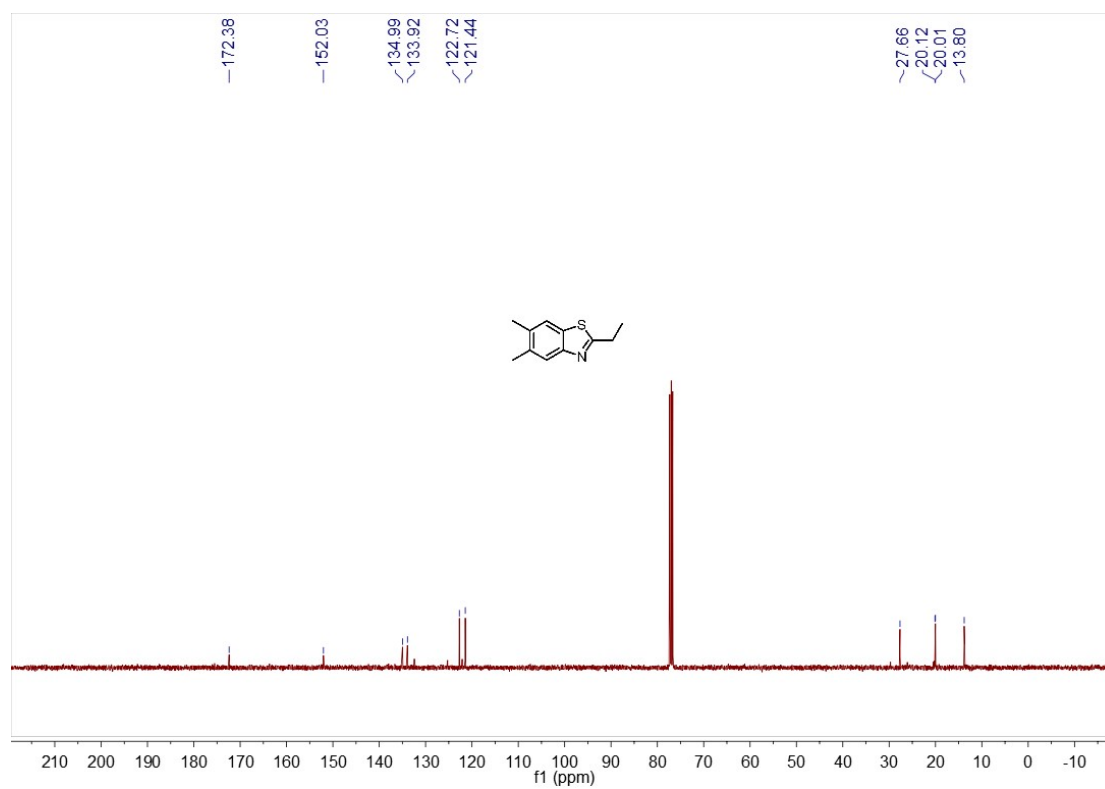
$^{13}\text{C}$  NMR spectrum of compound **24c** in  $\text{CDCl}_3$  (101 MHz):



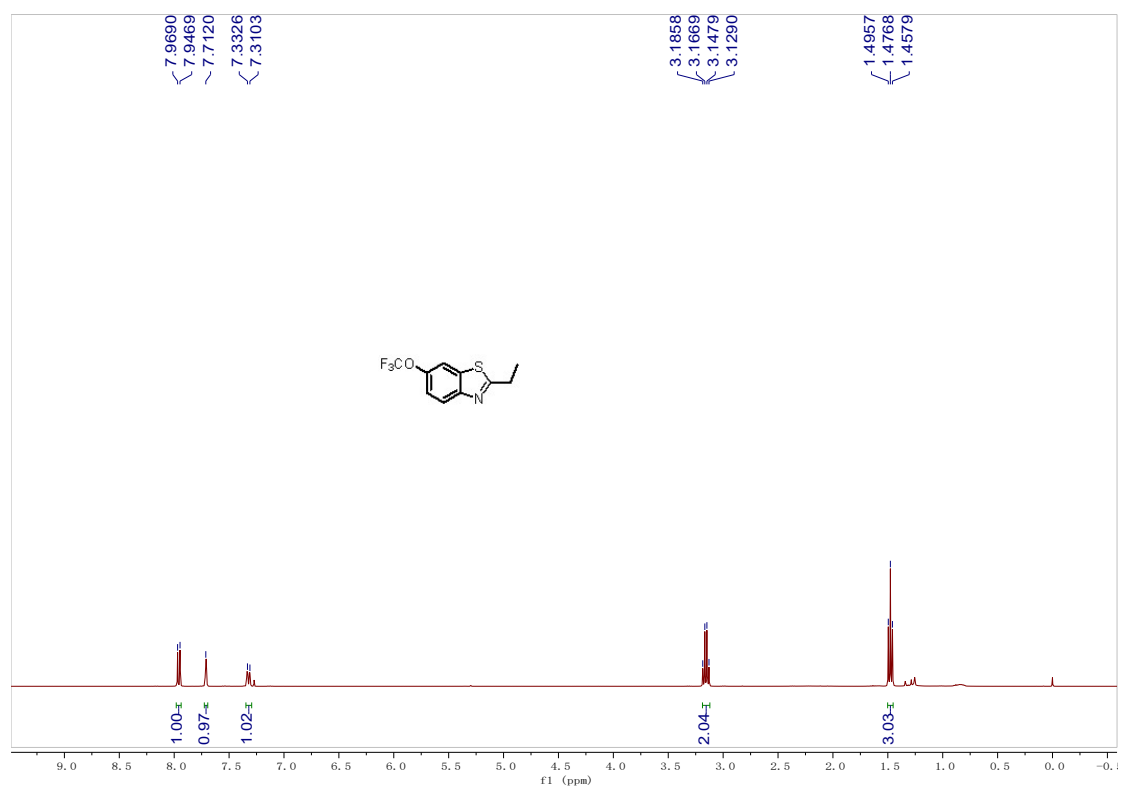
$^1\text{H}$  NMR spectrum of compound **25c** in  $\text{CDCl}_3$  (400 MHz):



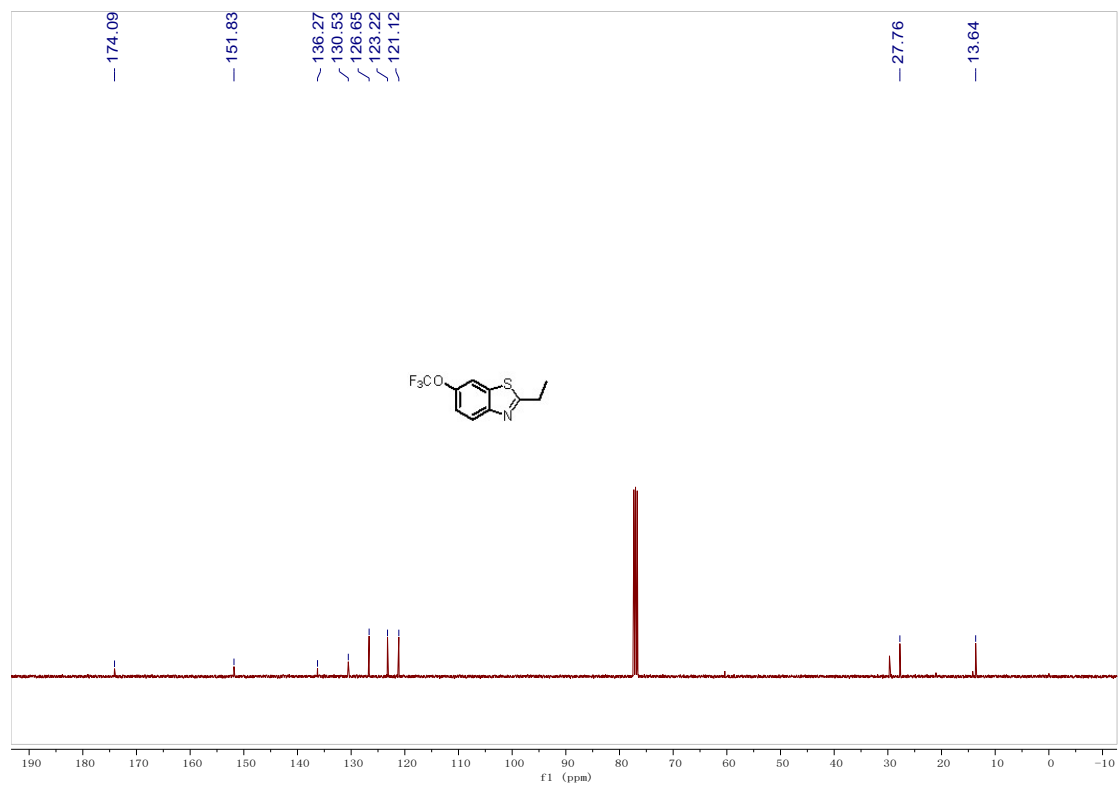
$^{13}\text{C}$  NMR spectrum of compound **25c** in  $\text{CDCl}_3$  (101 MHz):



$^1\text{H}$  NMR spectrum of compound **26c** in  $\text{CDCl}_3$  (400 MHz):

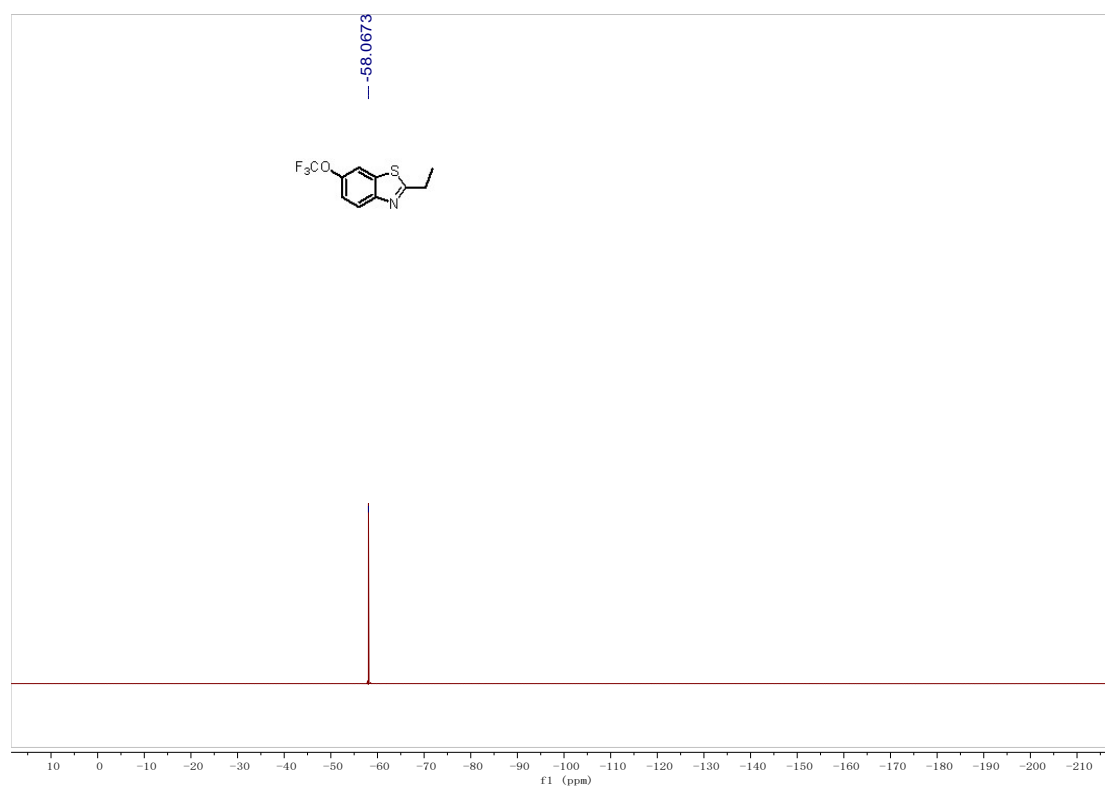


$^{13}\text{C}$  NMR spectrum of compound **26c** in  $\text{CDCl}_3$  (101 MHz):

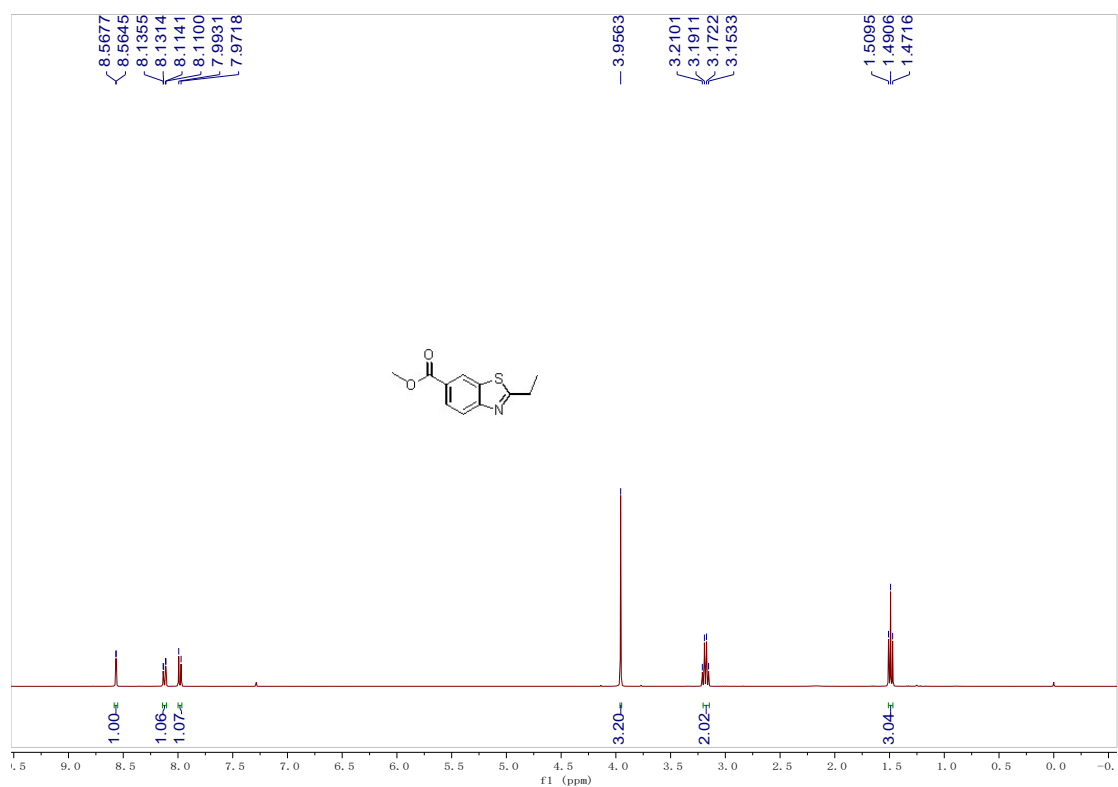




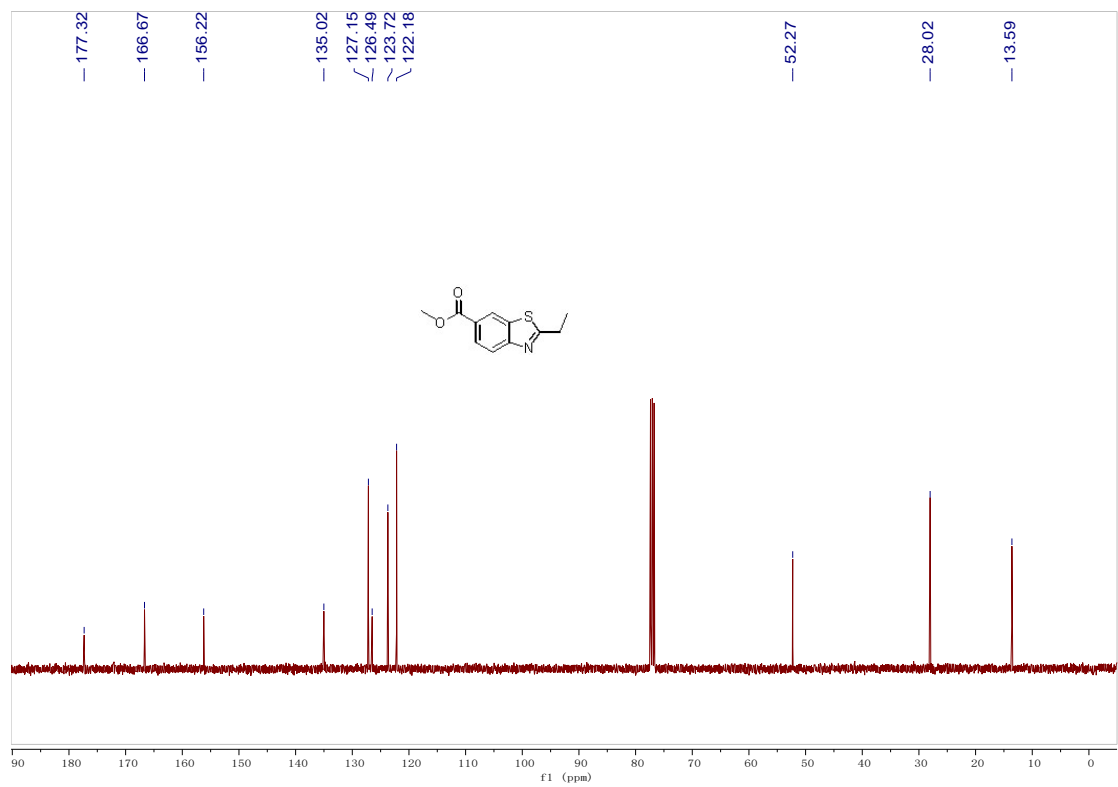
$^{19}\text{F}$  NMR spectrum of compound **26c** in  $\text{CDCl}_3$  (101 MHz):



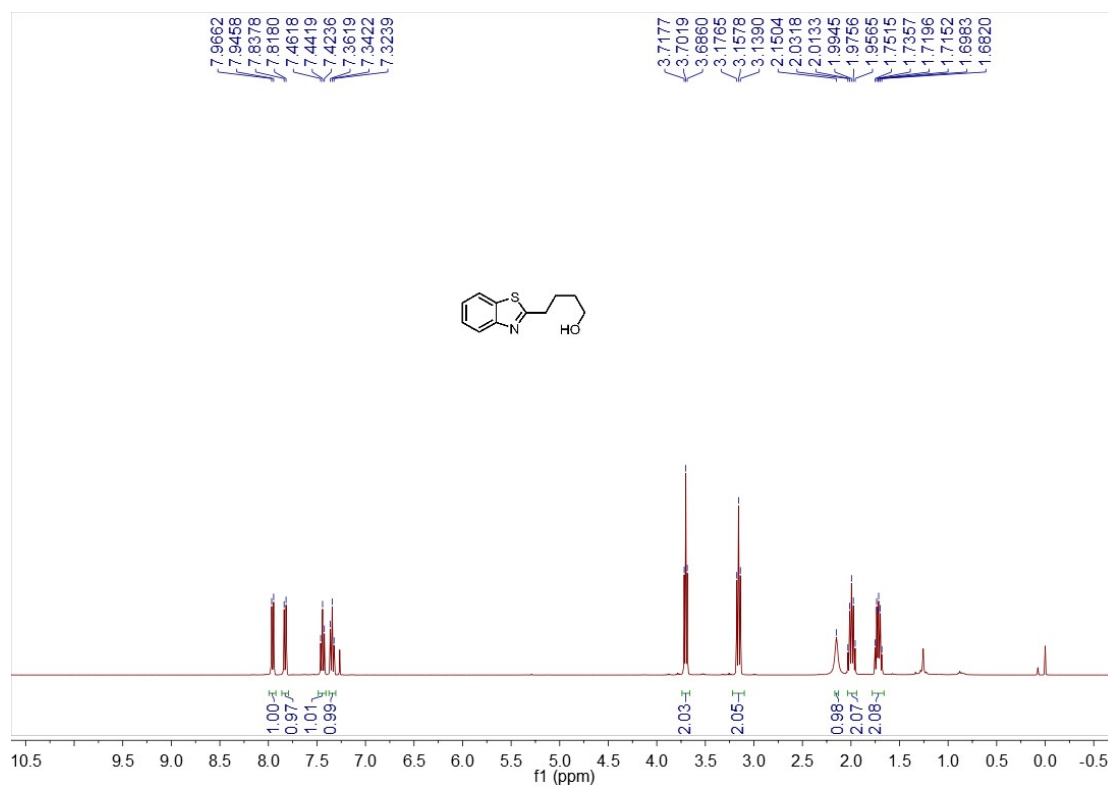
$^1\text{H}$  NMR spectrum of compound **27c** in  $\text{CDCl}_3$  (400 MHz):



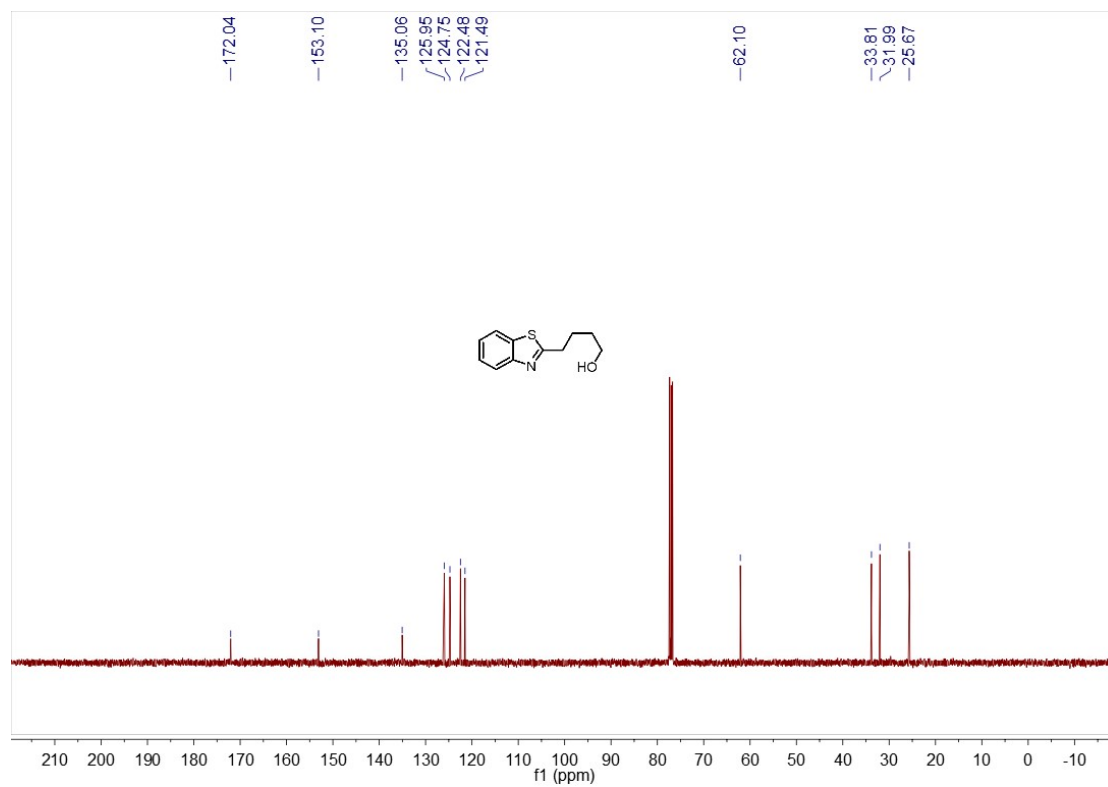
$^{13}\text{C}$  NMR spectrum of compound **27c** in  $\text{CDCl}_3$  (101 MHz):



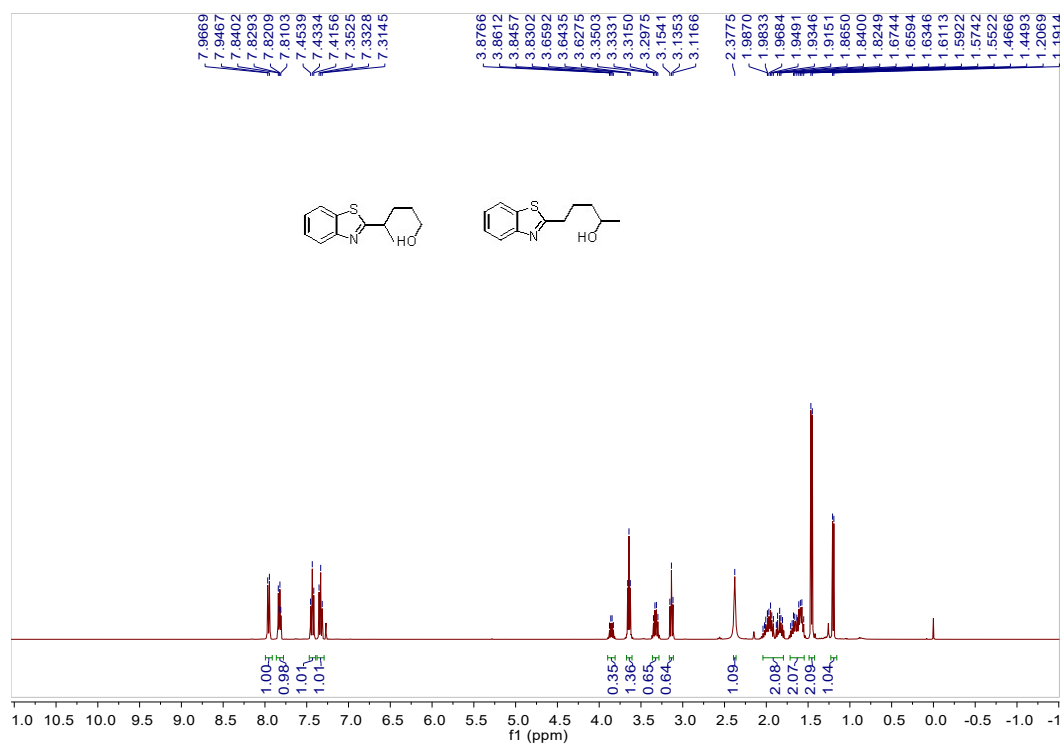
<sup>1</sup>H NMR spectrum of compound **28c** in CDCl<sub>3</sub> (400 MHz):



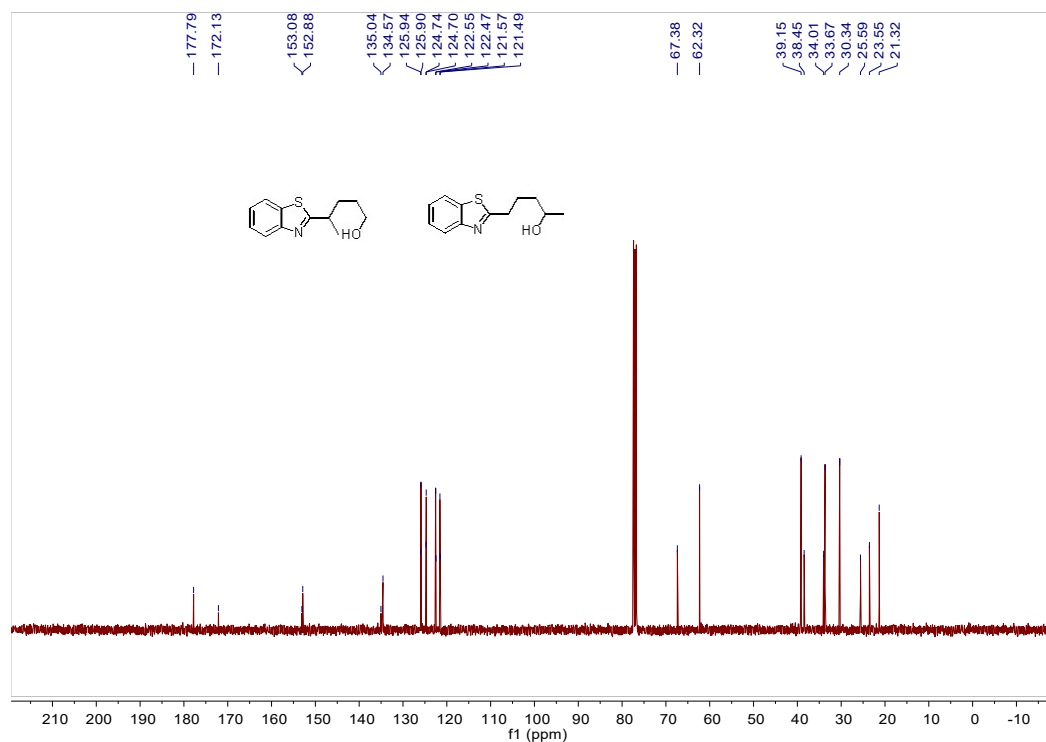
<sup>13</sup>C NMR spectrum of compound **28c** in CDCl<sub>3</sub> (101 MHz):



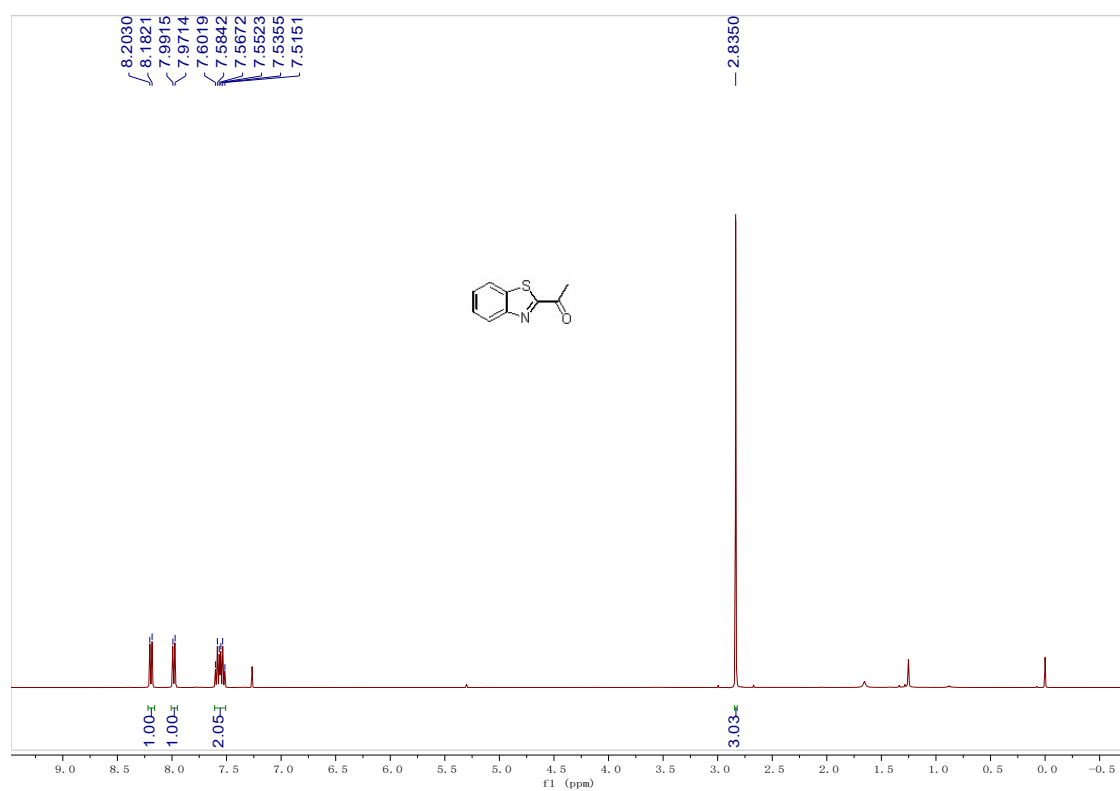
**<sup>1</sup>H NMR spectrum of compound 29c and 29c' in CDCl<sub>3</sub> (400 MHz):**



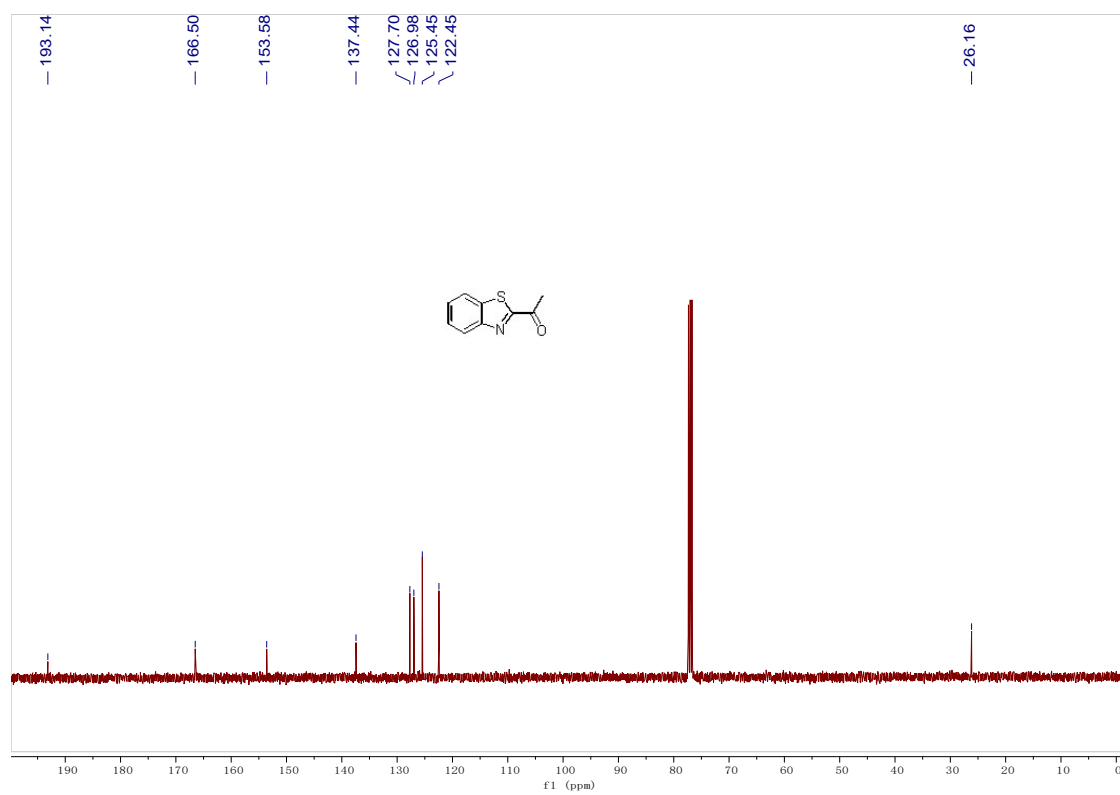
**<sup>13</sup>C NMR spectrum of compound 29c and 29c' in CDCl<sub>3</sub> (101 MHz):**



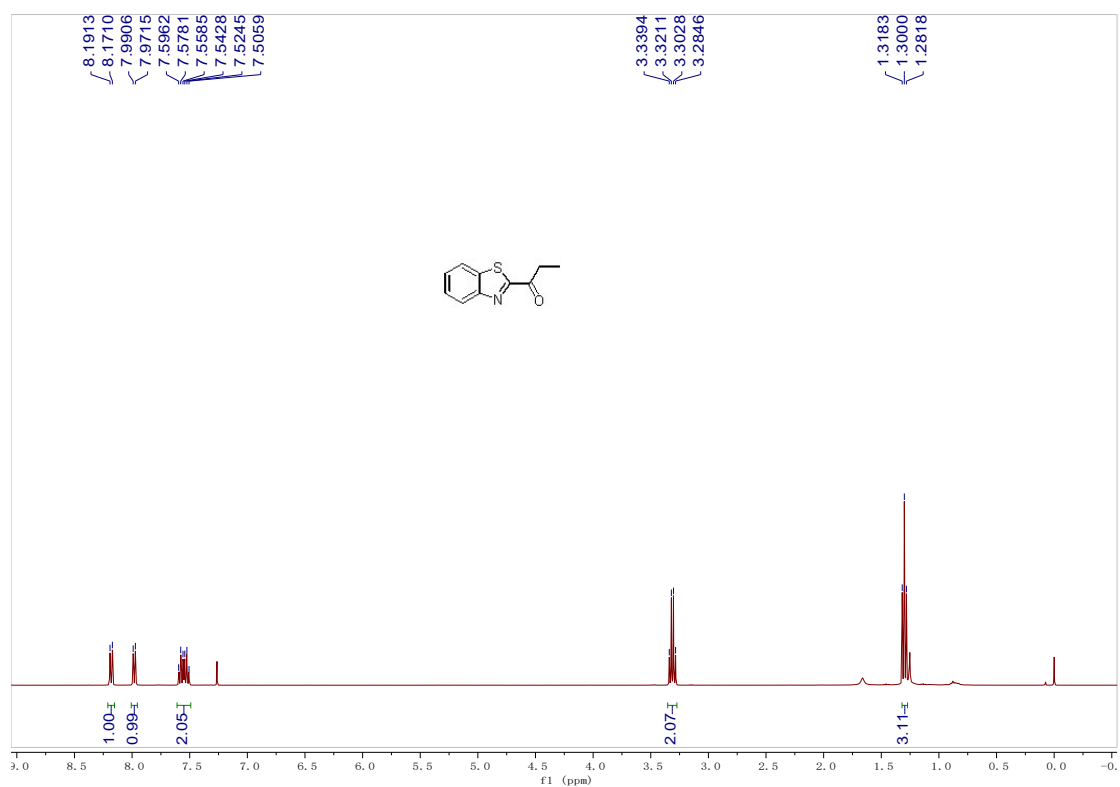
$^1\text{H}$  NMR spectrum of compound **1d** in  $\text{CDCl}_3$  (400 MHz):



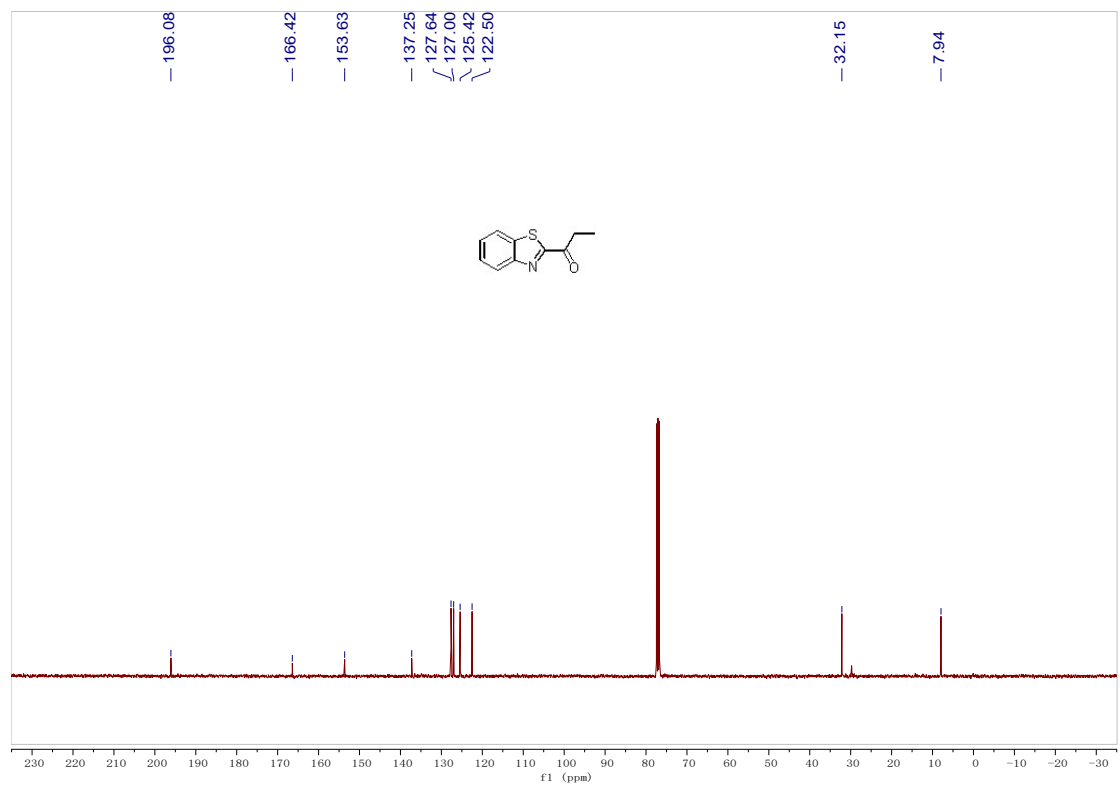
$^{13}\text{C}$  NMR spectrum of compound **1d** in  $\text{CDCl}_3$  (101 MHz):



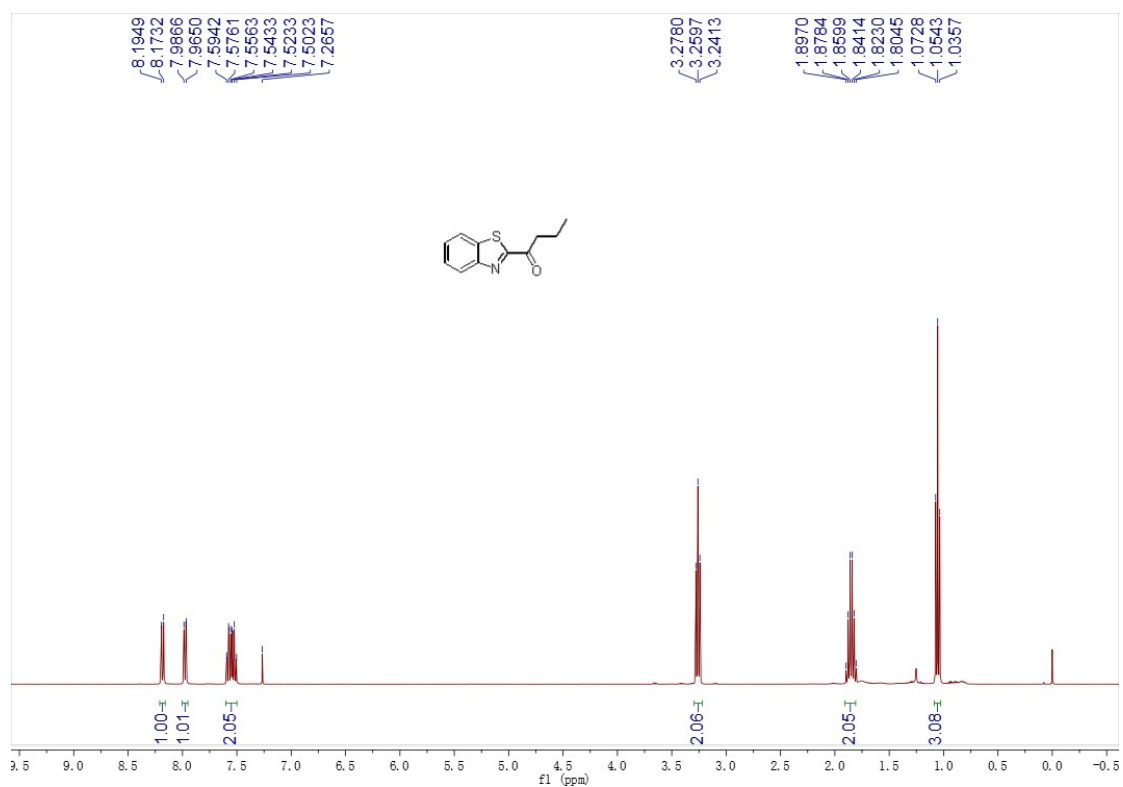
$^1\text{H}$  NMR spectrum of compound **2d** in  $\text{CDCl}_3$  (400 MHz):



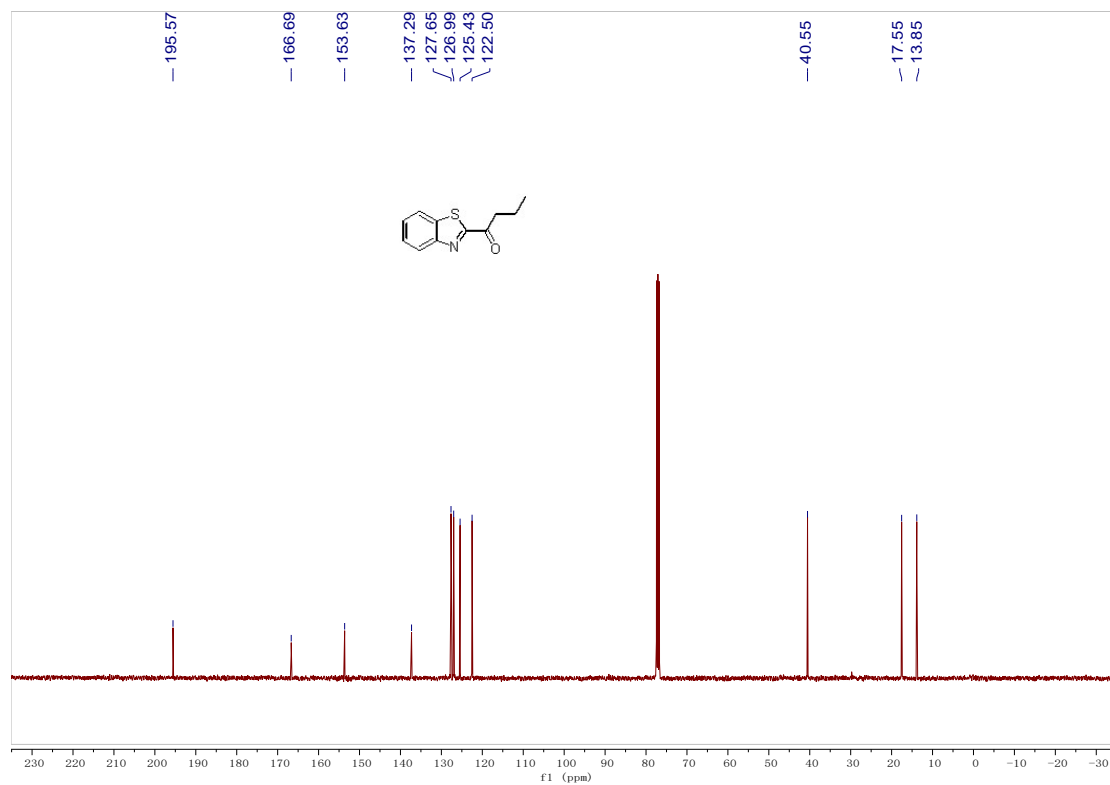
$^{13}\text{C}$  NMR spectrum of compound **2d** in  $\text{CDCl}_3$  (101 MHz):



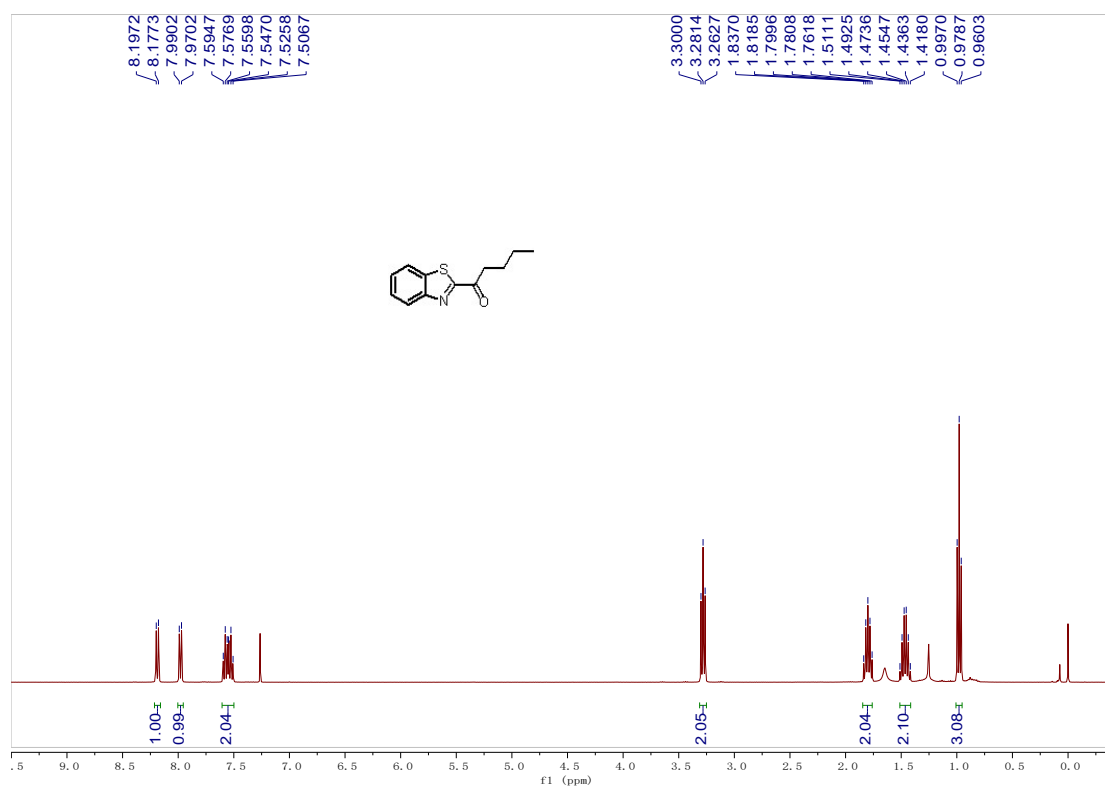
$^1\text{H}$  NMR spectrum of compound **3d** in  $\text{CDCl}_3$  (400 MHz):



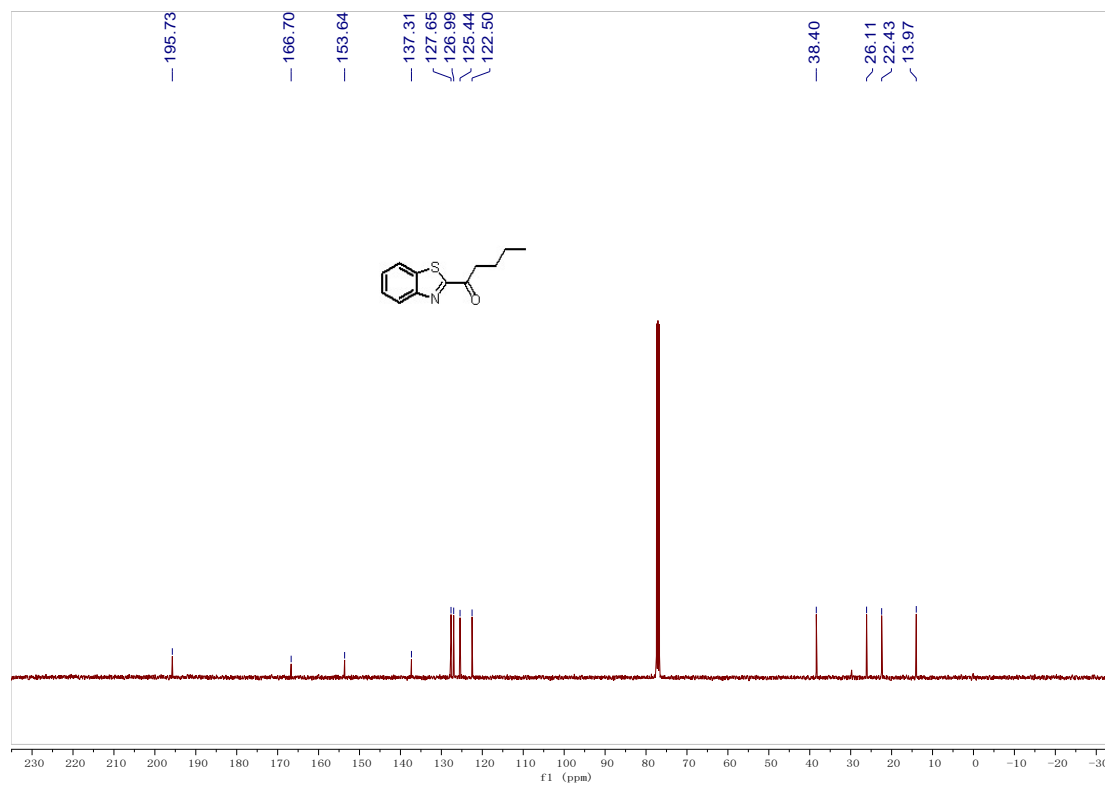
$^{13}\text{C}$  NMR spectrum of compound **3d** in  $\text{CDCl}_3$  (101 MHz):



$^1\text{H}$  NMR spectrum of compound **4d** in  $\text{CDCl}_3$  (400 MHz):

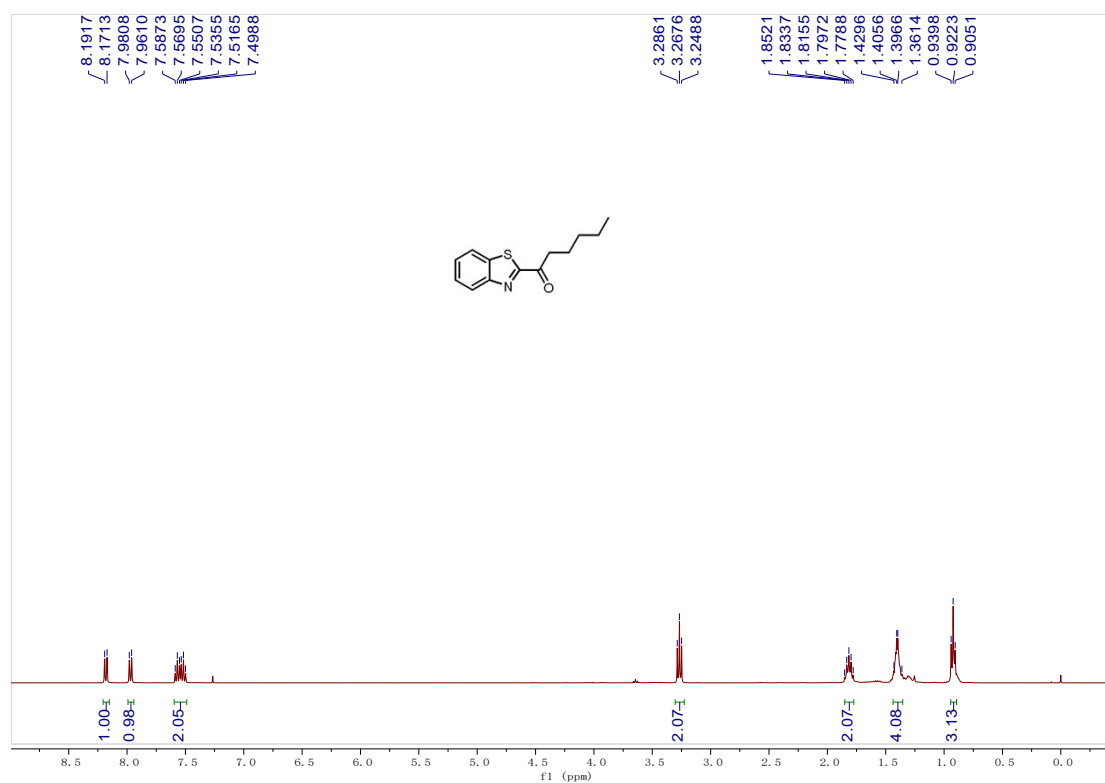


$^{13}\text{C}$  NMR spectrum of compound **4d** in  $\text{CDCl}_3$  (101 MHz):

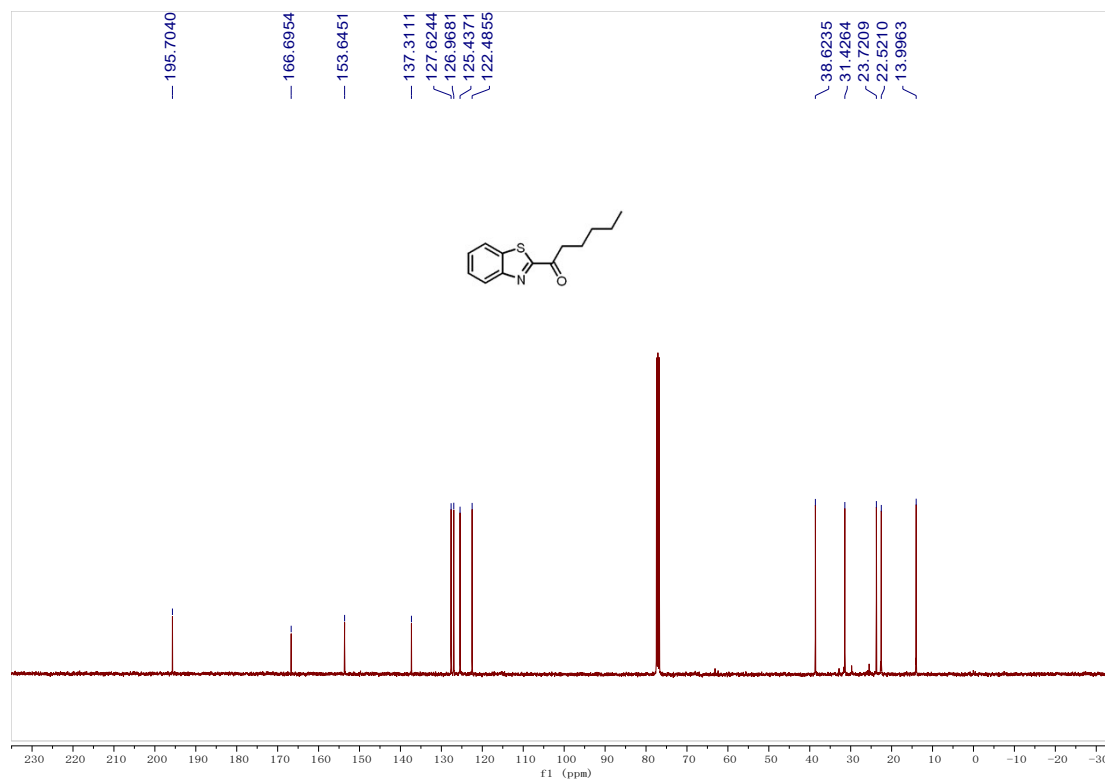




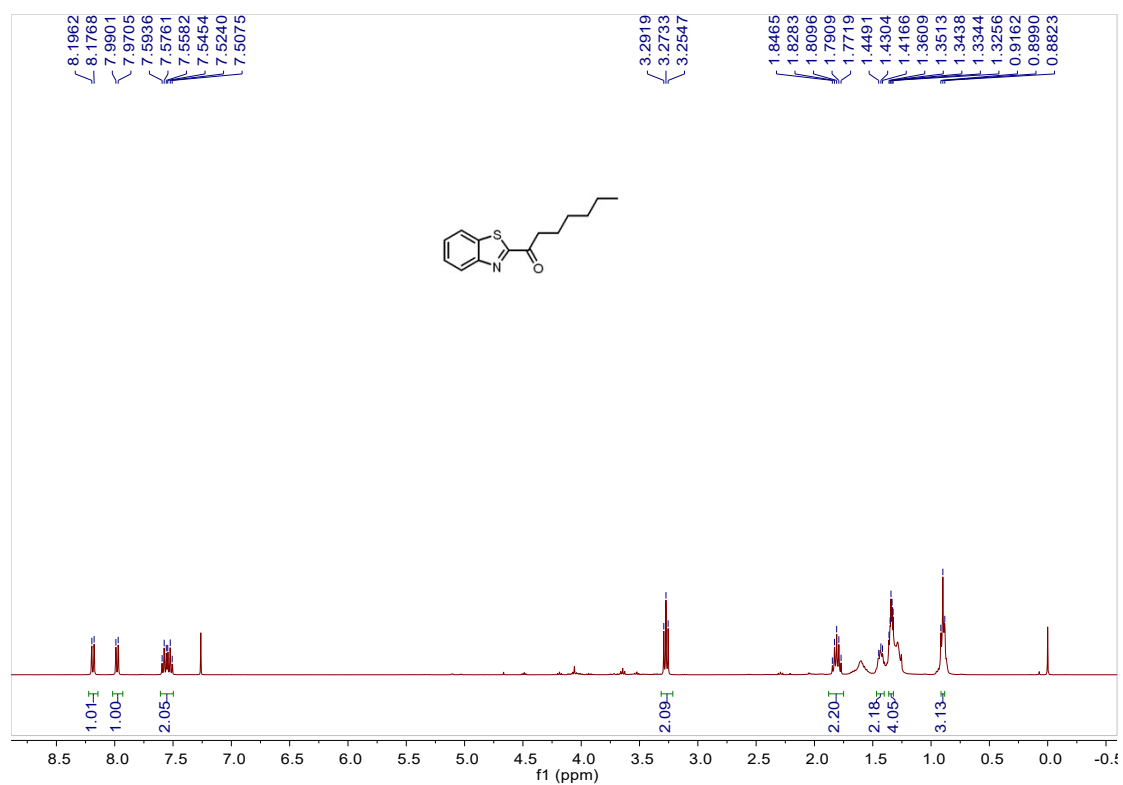
$^1\text{H}$  NMR spectrum of compound **5d** in  $\text{CDCl}_3$  (400 MHz):



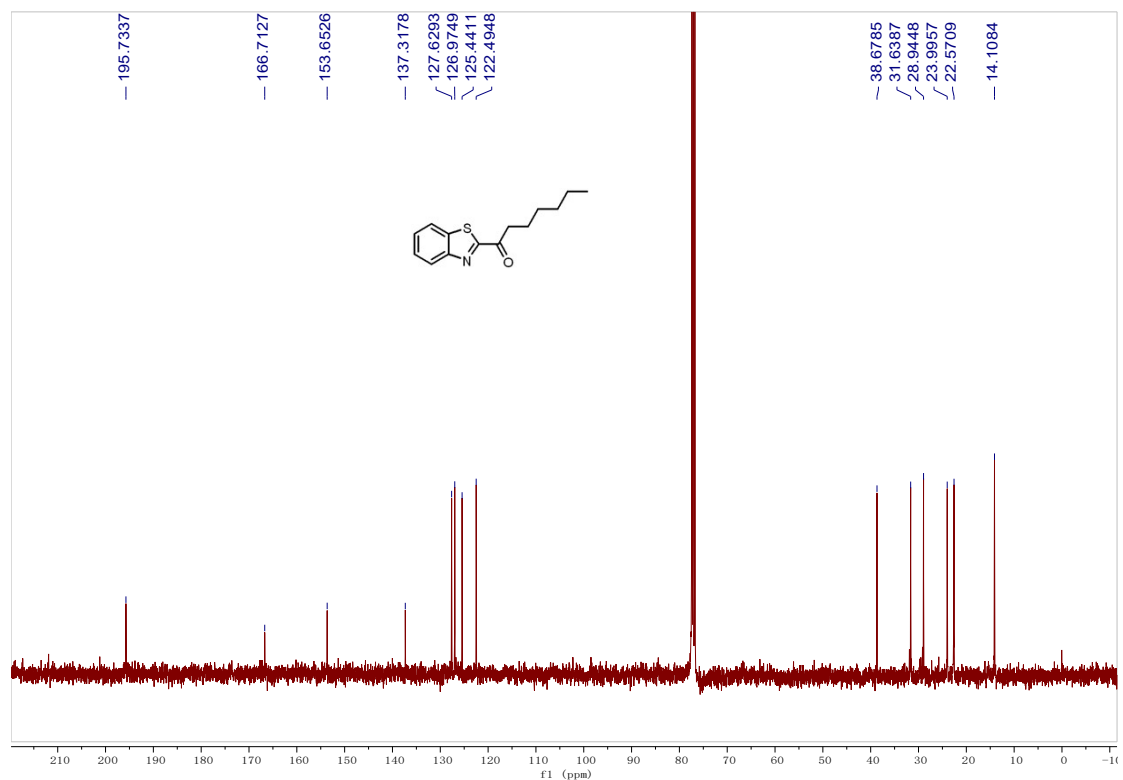
$^{13}\text{C}$  NMR spectrum of compound **5d** in  $\text{CDCl}_3$  (101 MHz):



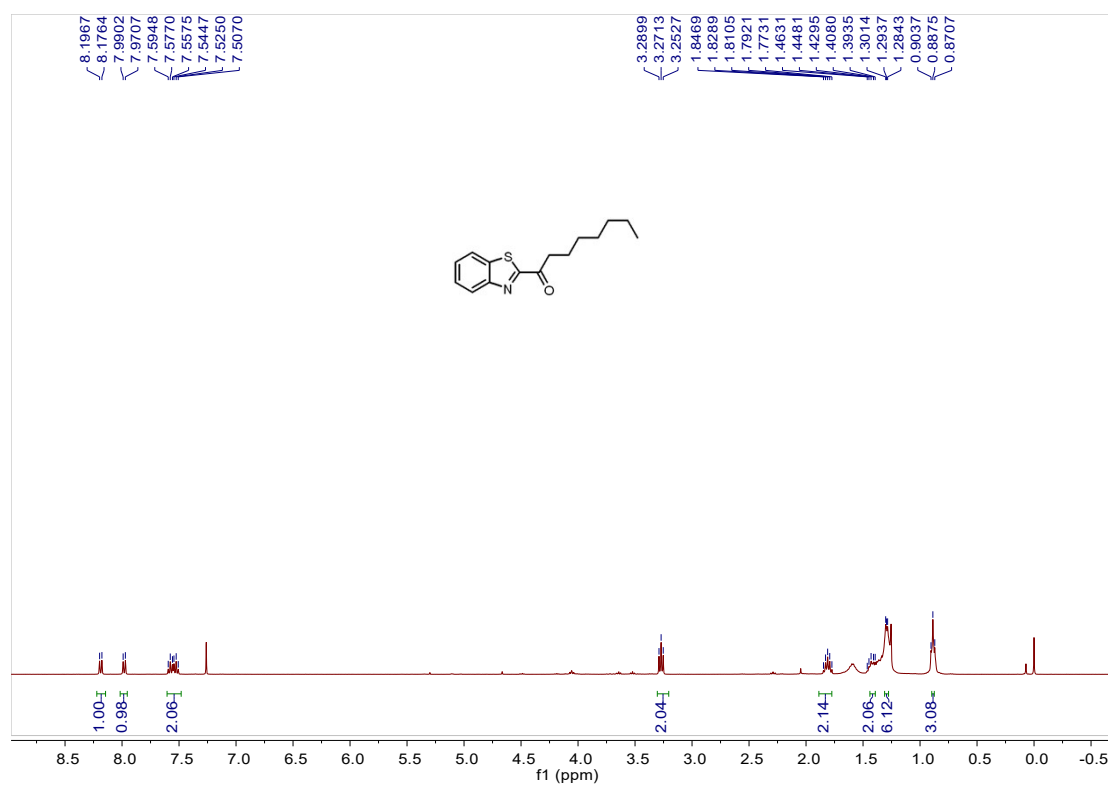
$^1\text{H}$  NMR spectrum of compound **6d** in  $\text{CDCl}_3$  (400 MHz):



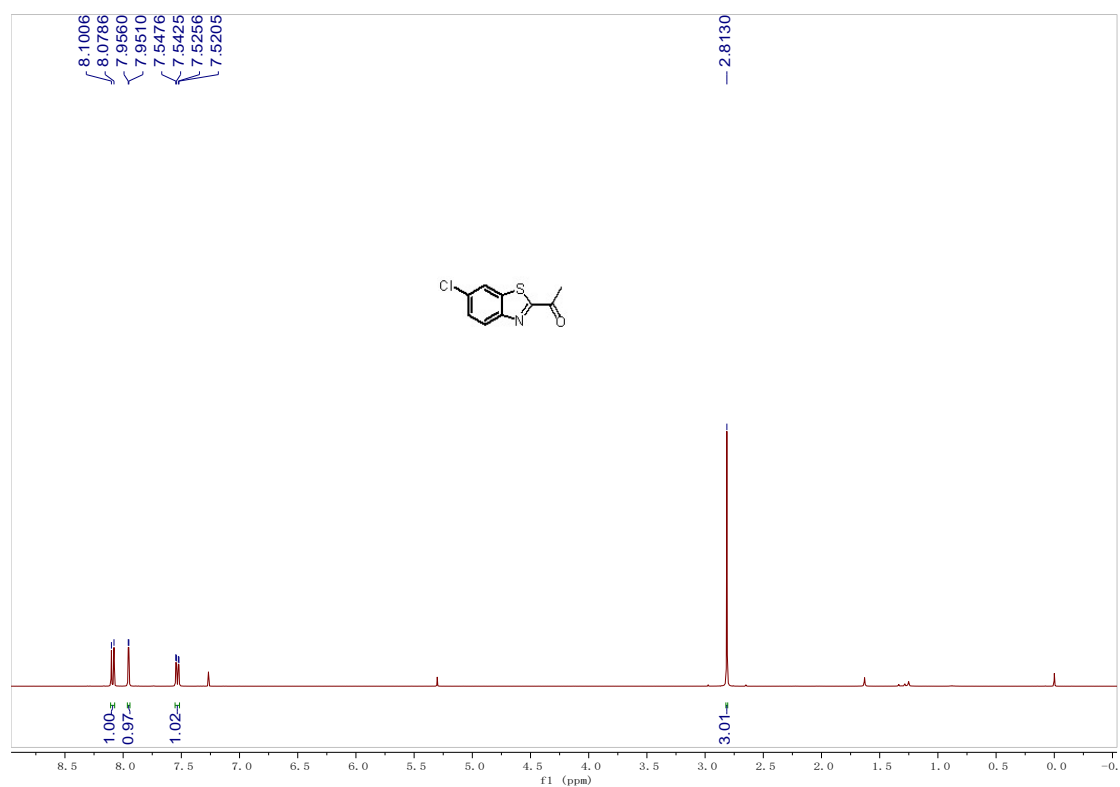
$^{13}\text{C}$  NMR spectrum of compound **6d** in  $\text{CDCl}_3$  (101 MHz):



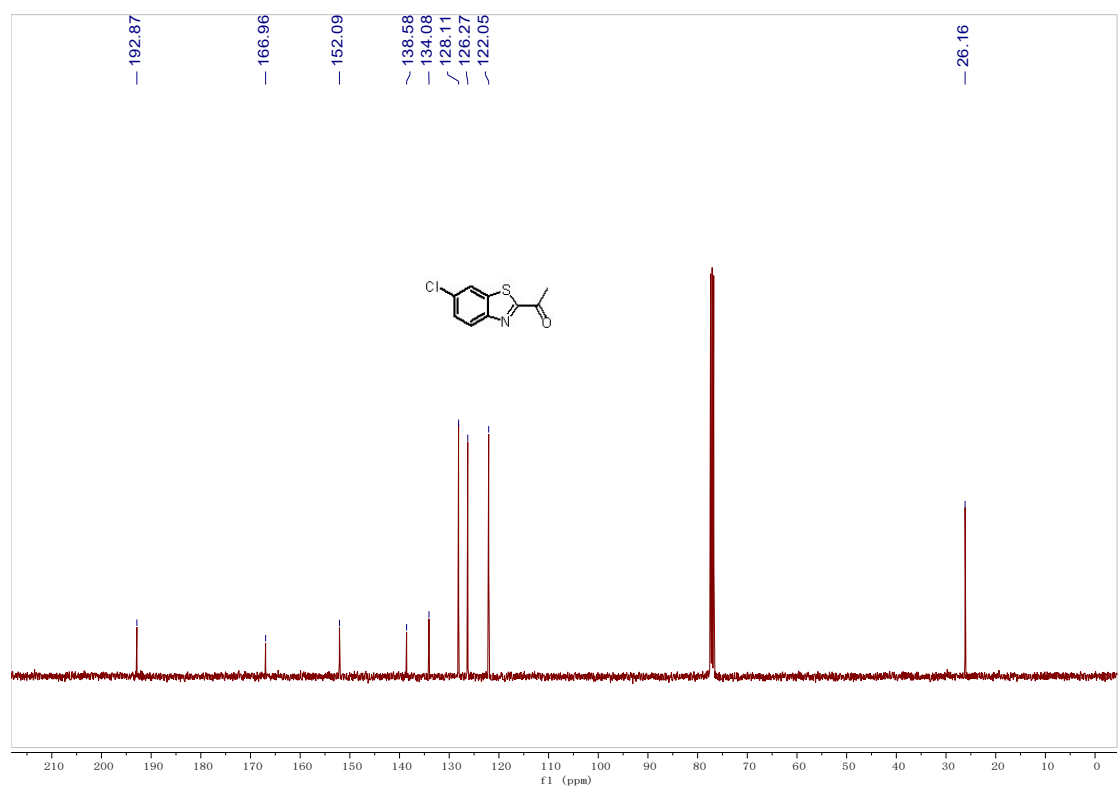
$^1\text{H}$  NMR spectrum of compound **7d** in  $\text{CDCl}_3$  (400 MHz):



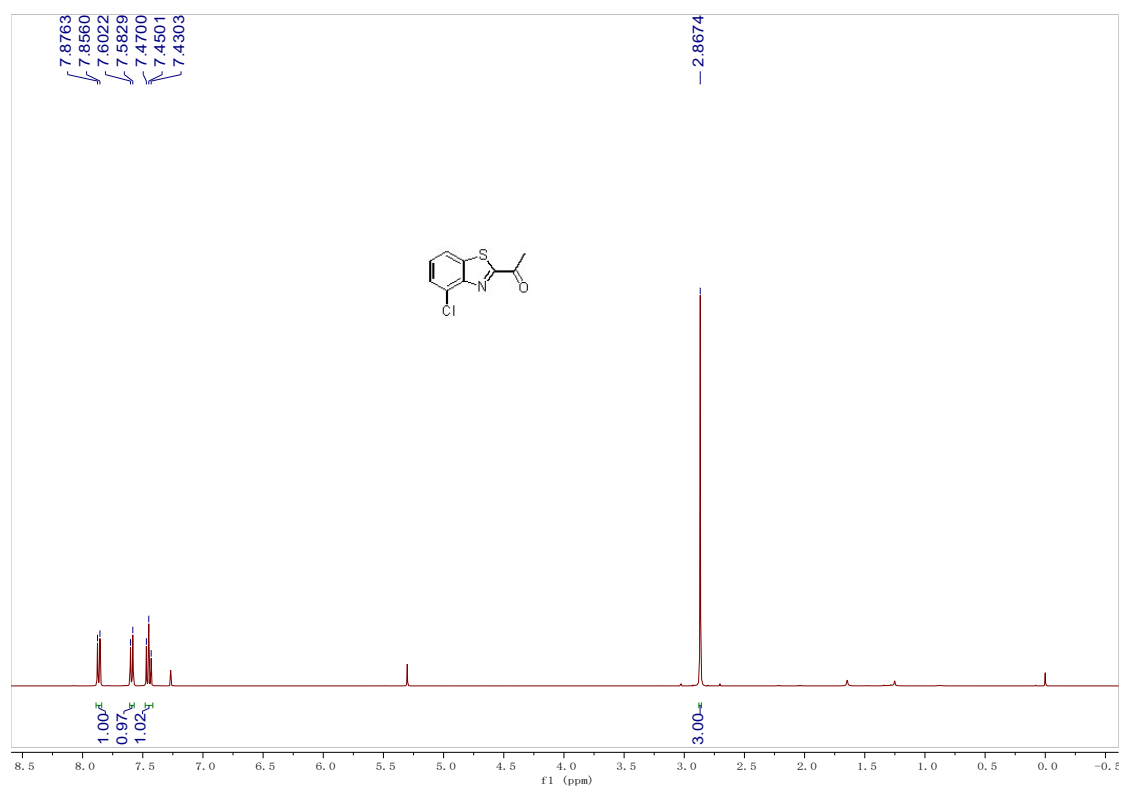
$^1\text{H}$  NMR spectrum of compound **8d** in  $\text{CDCl}_3$  (400 MHz):



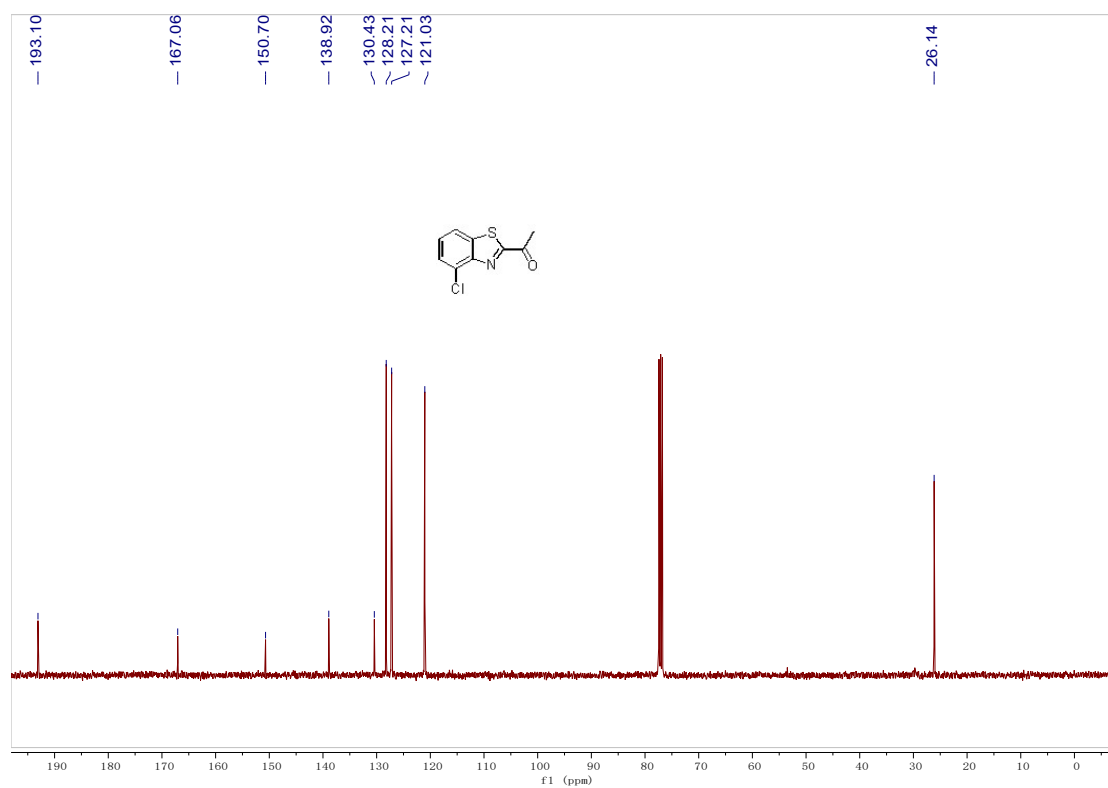
$^{13}\text{C}$  NMR spectrum of compound **8d** in  $\text{CDCl}_3$  (101 MHz):



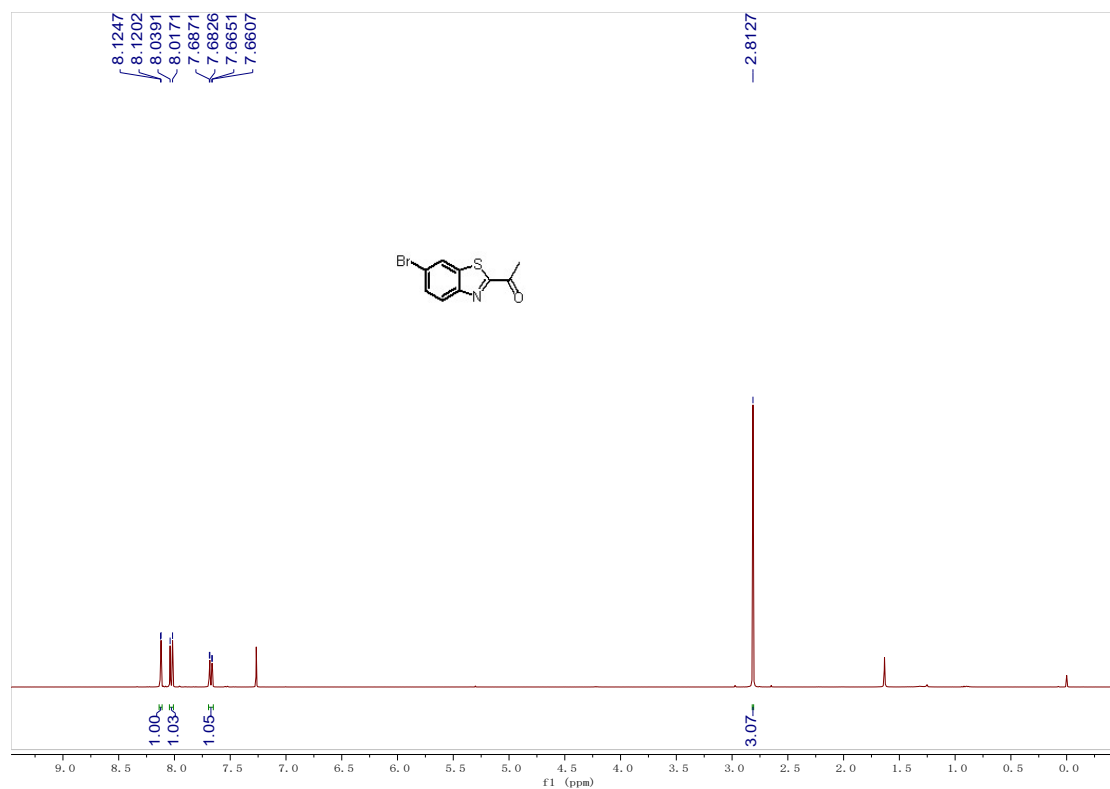
$^1\text{H}$  NMR spectrum of compound **9d** in  $\text{CDCl}_3$  (400 MHz):



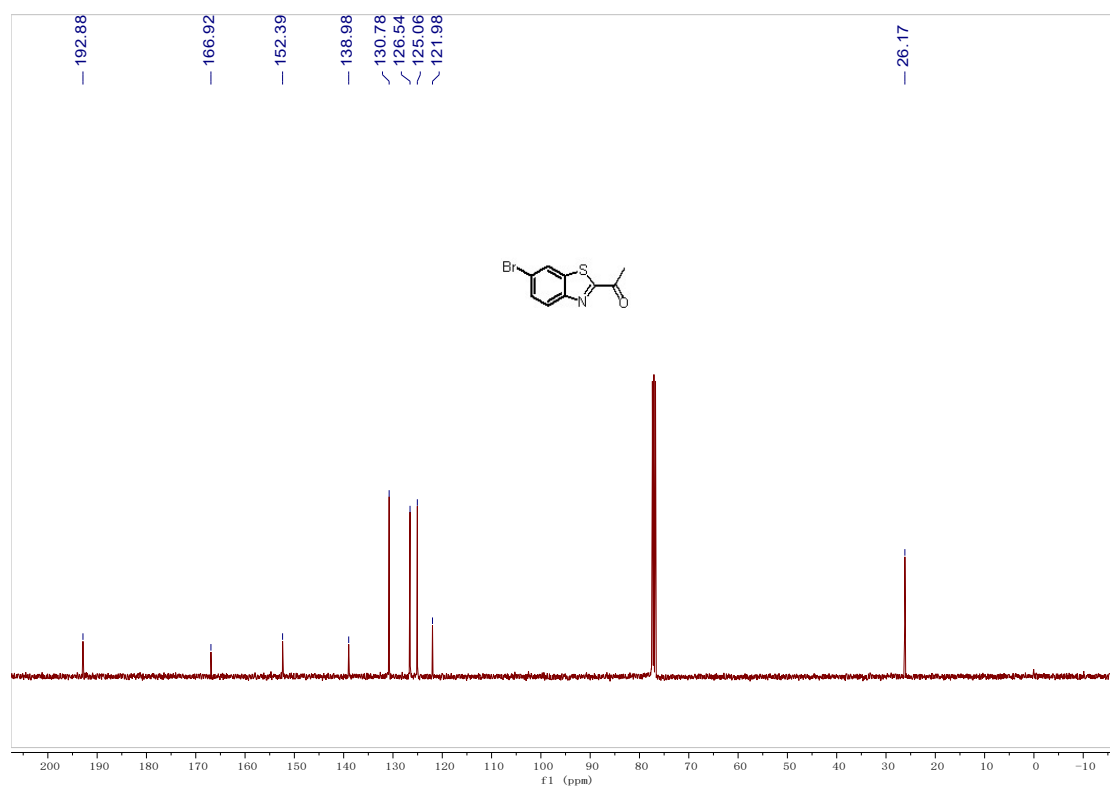
$^{13}\text{C}$  NMR spectrum of compound **9d** in  $\text{CDCl}_3$  (101 MHz):



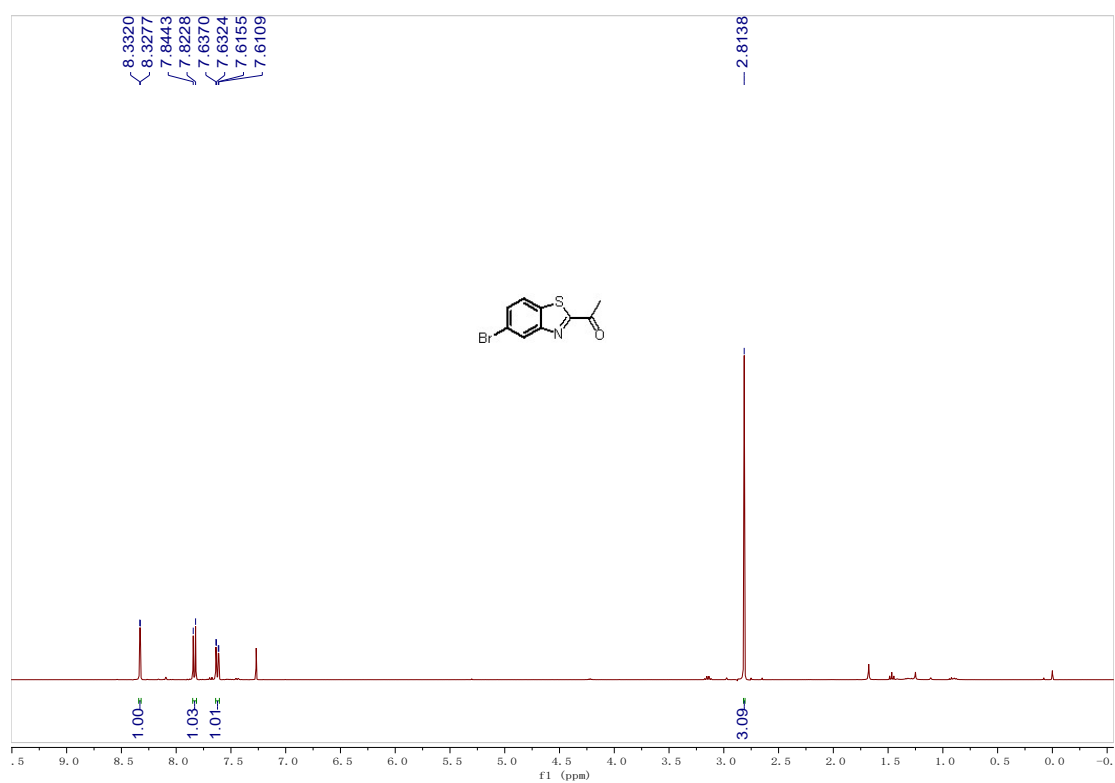
$^1\text{H}$  NMR spectrum of compound **10d** in  $\text{CDCl}_3$  (400 MHz):



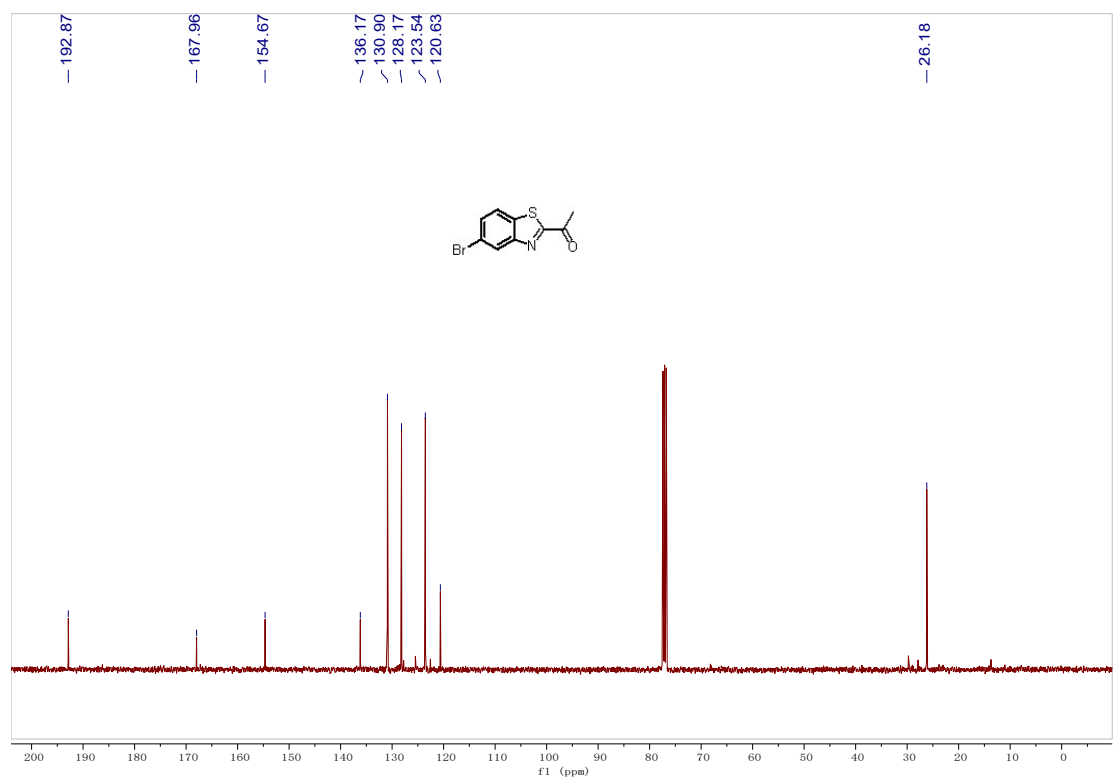
$^{13}\text{C}$  NMR spectrum of compound **10d** in  $\text{CDCl}_3$  (101 MHz):



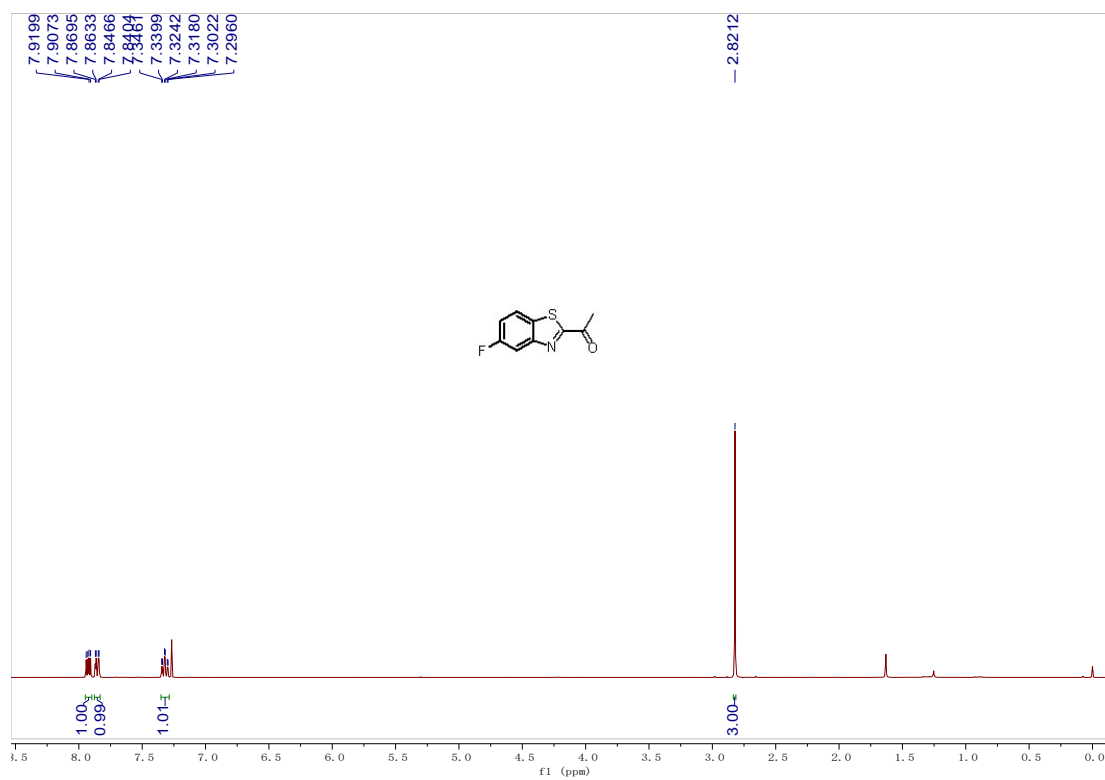
$^1\text{H}$  NMR spectrum of compound **11d** in  $\text{CDCl}_3$  (400 MHz):



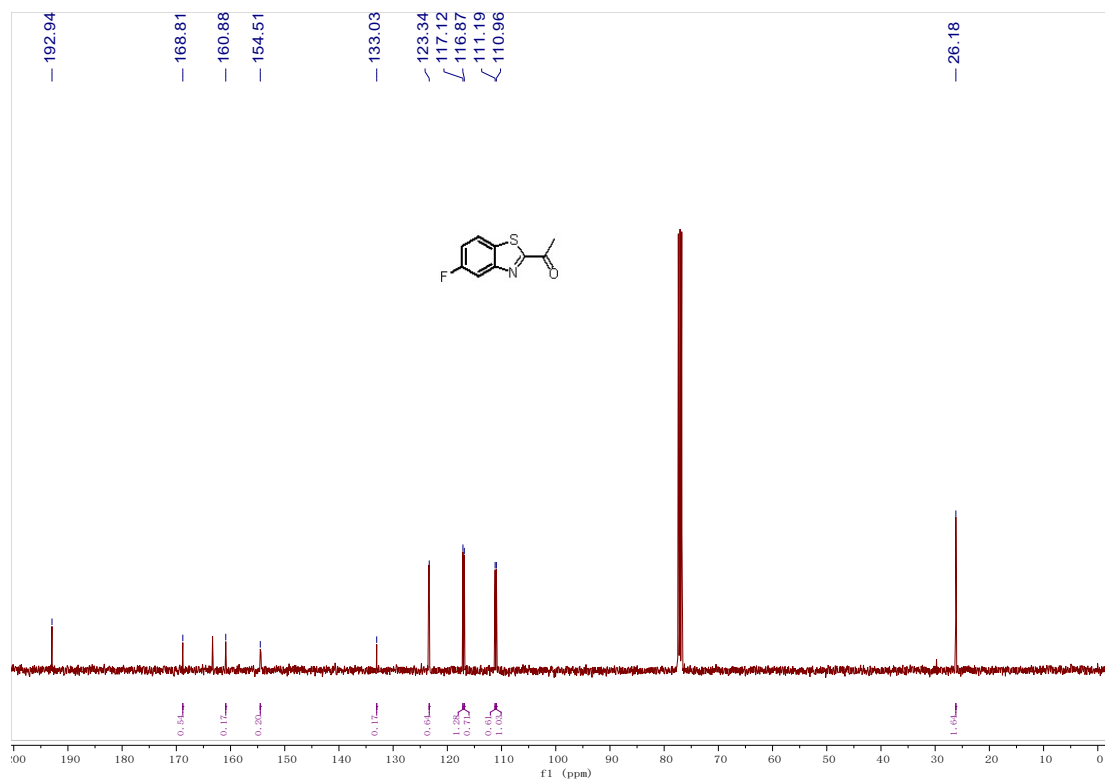
$^{13}\text{C}$  NMR spectrum of compound **11d** in  $\text{CDCl}_3$  (101 MHz):



$^1\text{H}$  NMR spectrum of compound **12d** in  $\text{CDCl}_3$  (400 MHz):

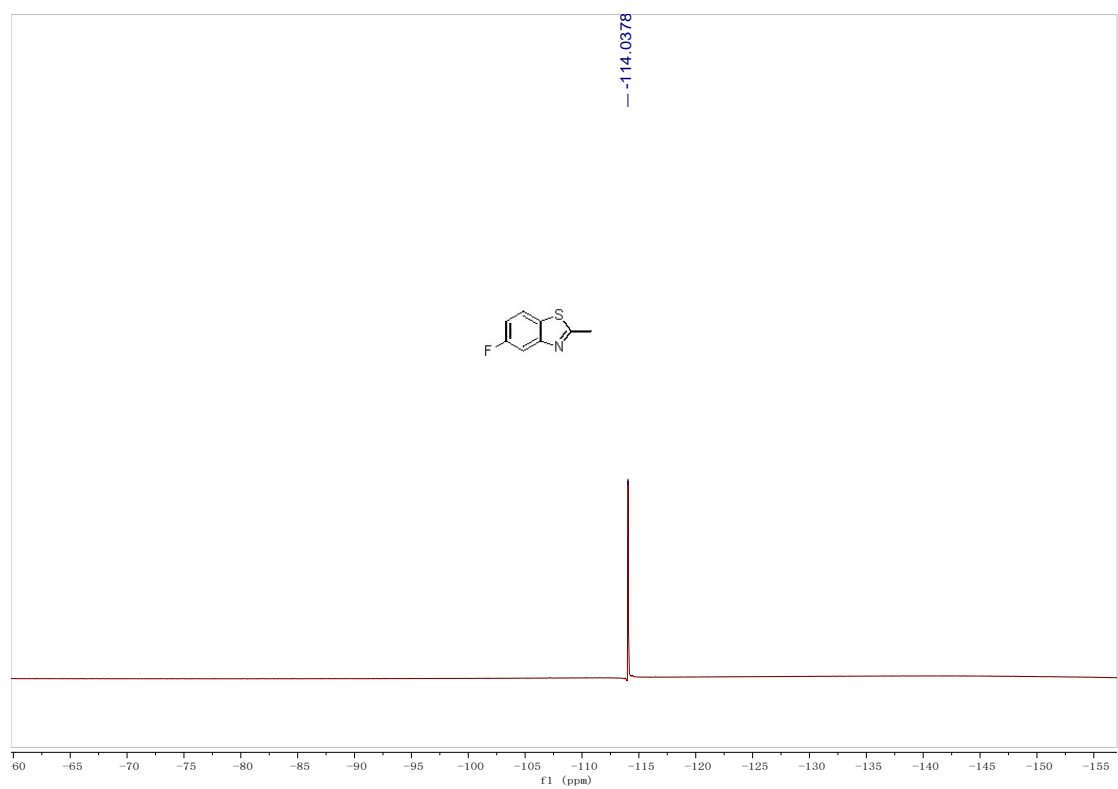


$^{13}\text{C}$  NMR spectrum of compound **12d** in  $\text{CDCl}_3$  (101 MHz):

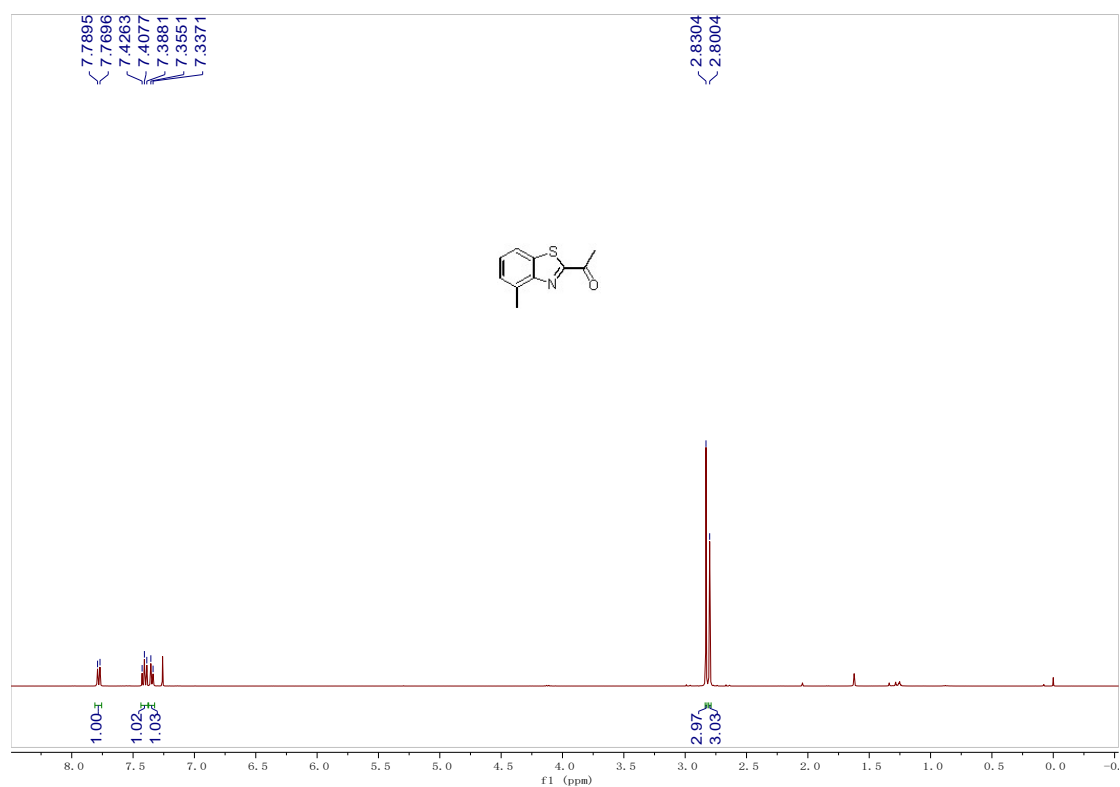




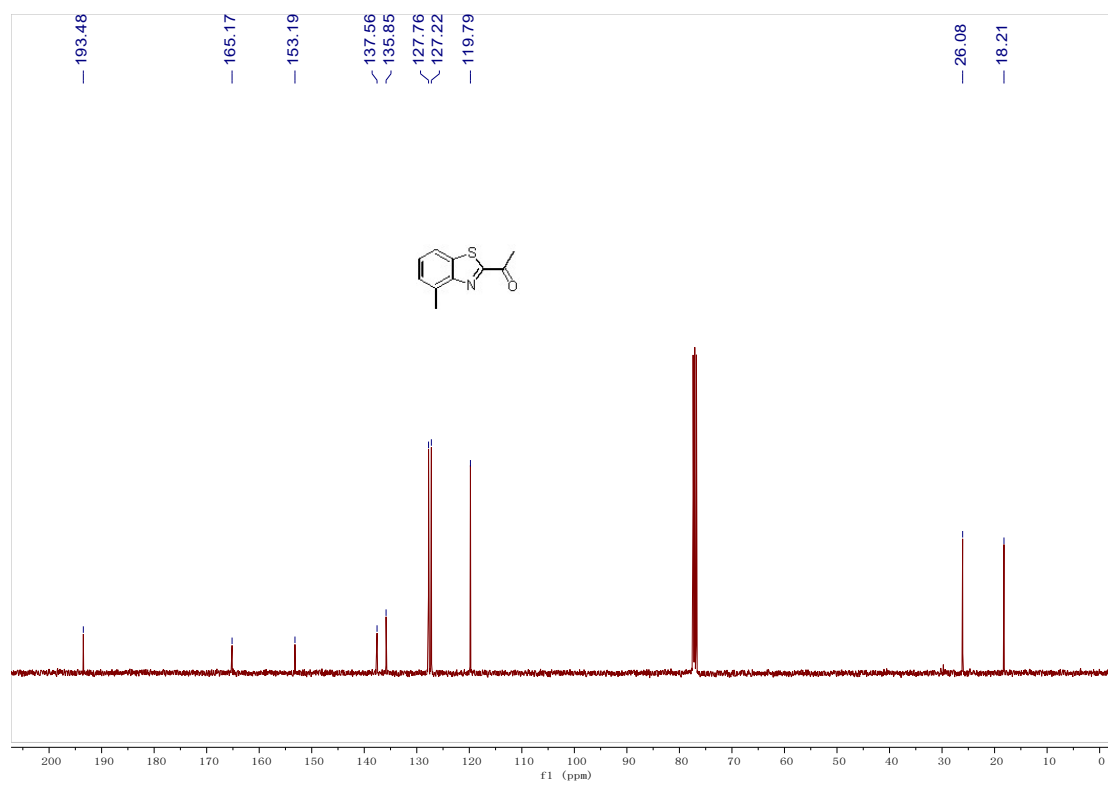
$^{19}\text{F}$  NMR spectrum of compound **12d** in  $\text{CDCl}_3$  (101 MHz):



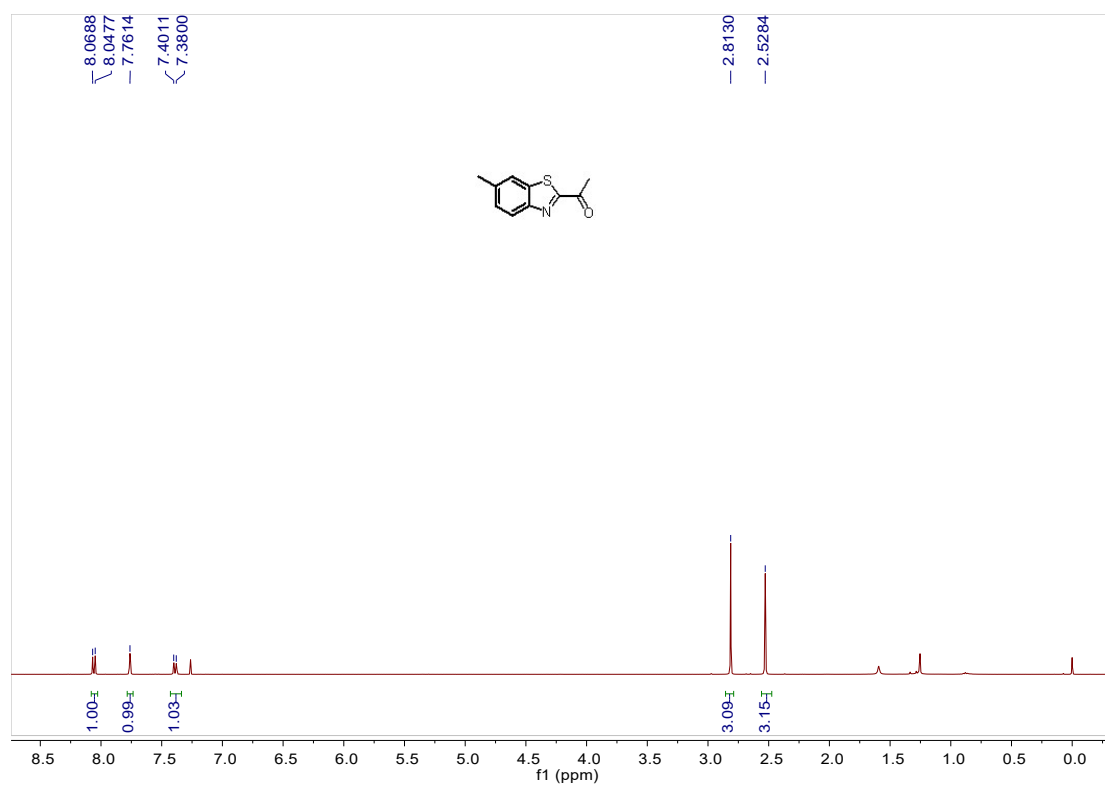
$^1\text{H}$  NMR spectrum of compound **13d** in  $\text{CDCl}_3$  (400 MHz):



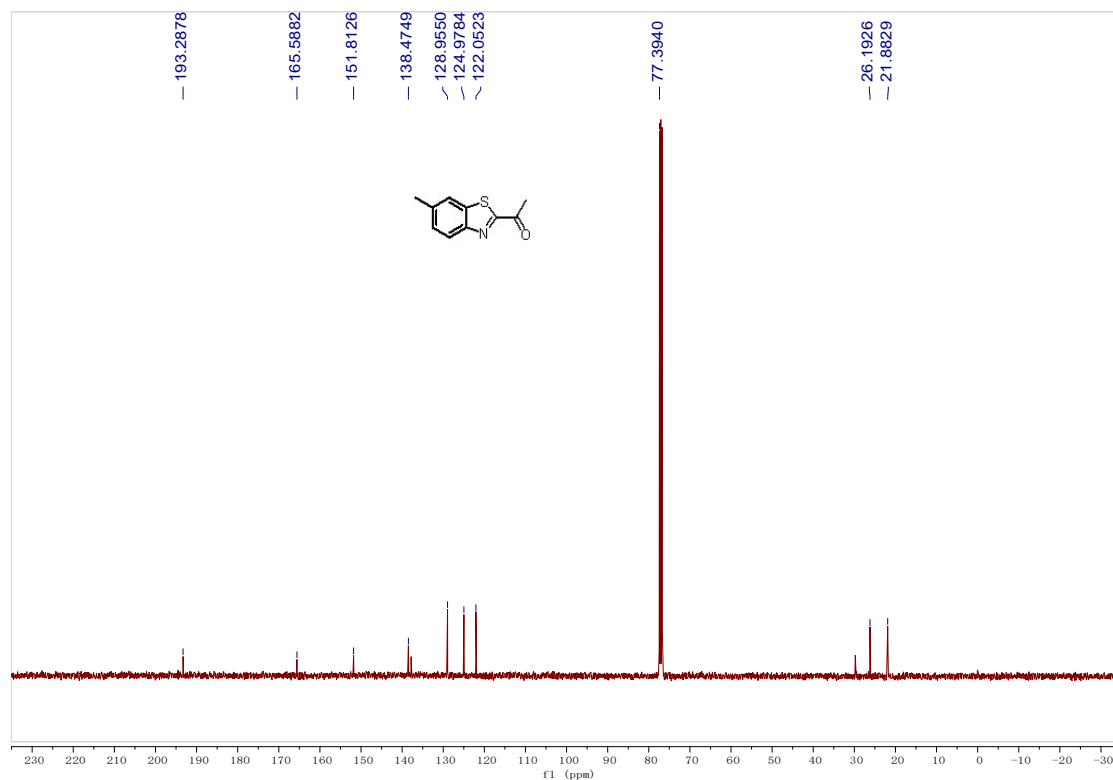
$^{13}\text{C}$  NMR spectrum of compound **13d** in  $\text{CDCl}_3$  (101 MHz):



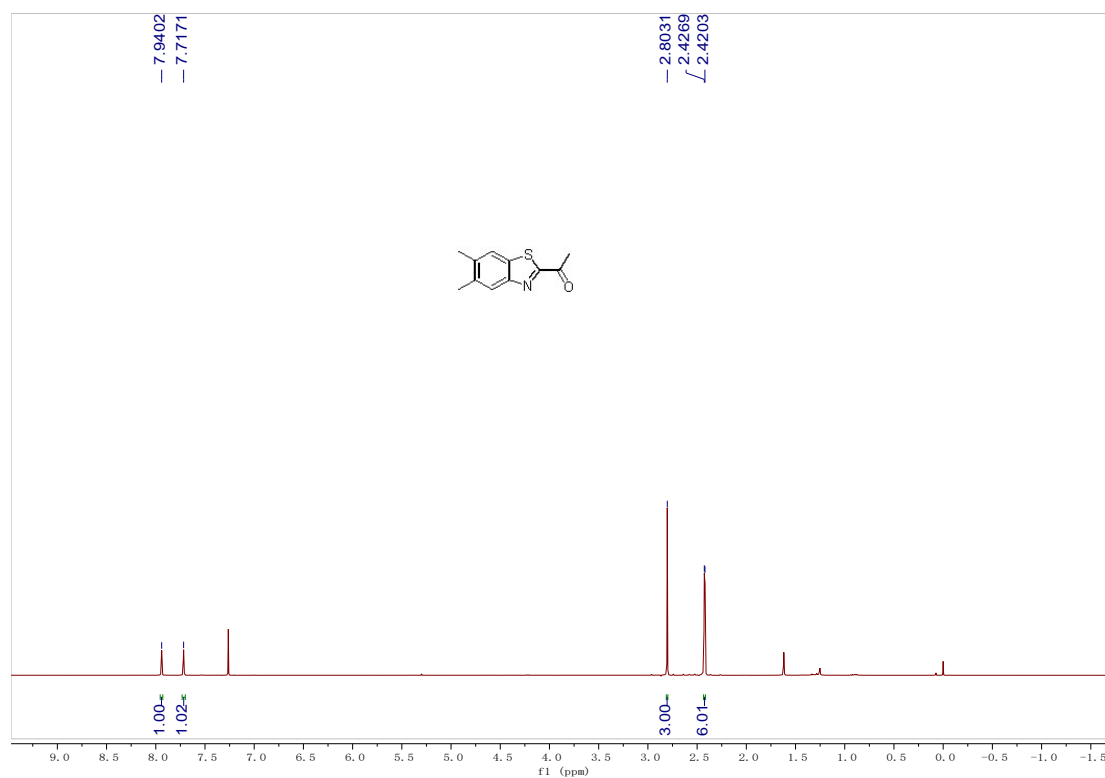
$^1\text{H}$  NMR spectrum of compound **14d** in  $\text{CDCl}_3$  (400 MHz):



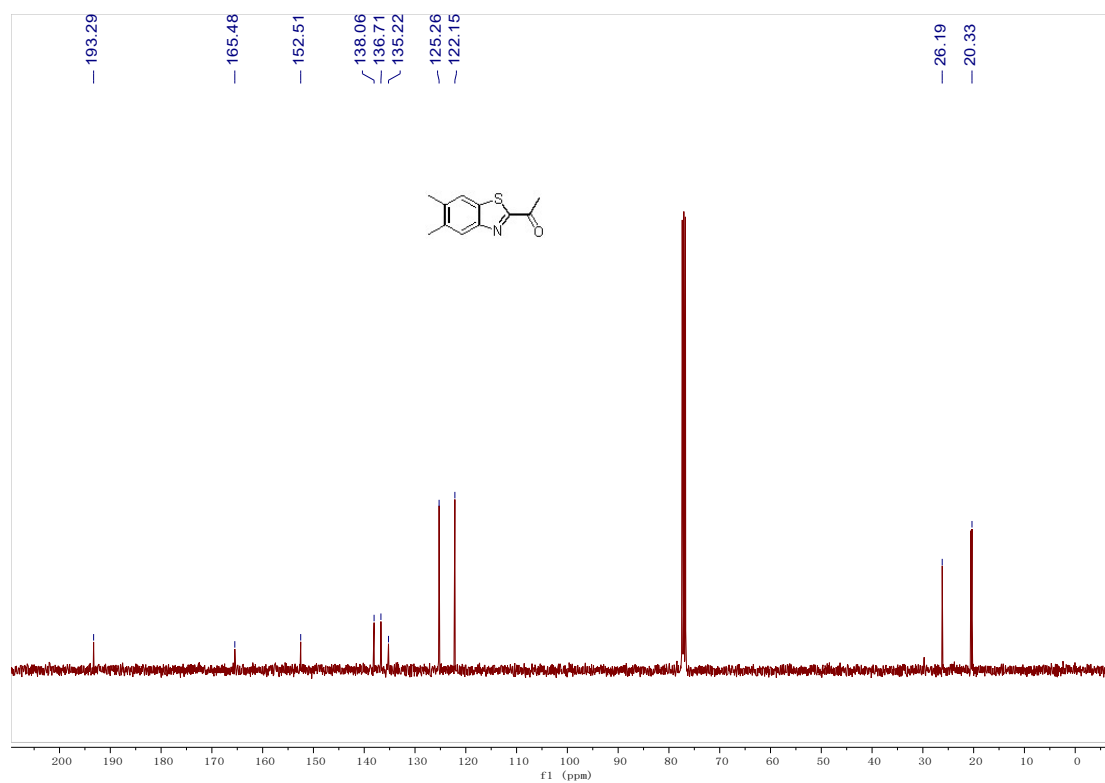
$^{13}\text{C}$  NMR spectrum of compound **14d** in  $\text{CDCl}_3$  (101 MHz):



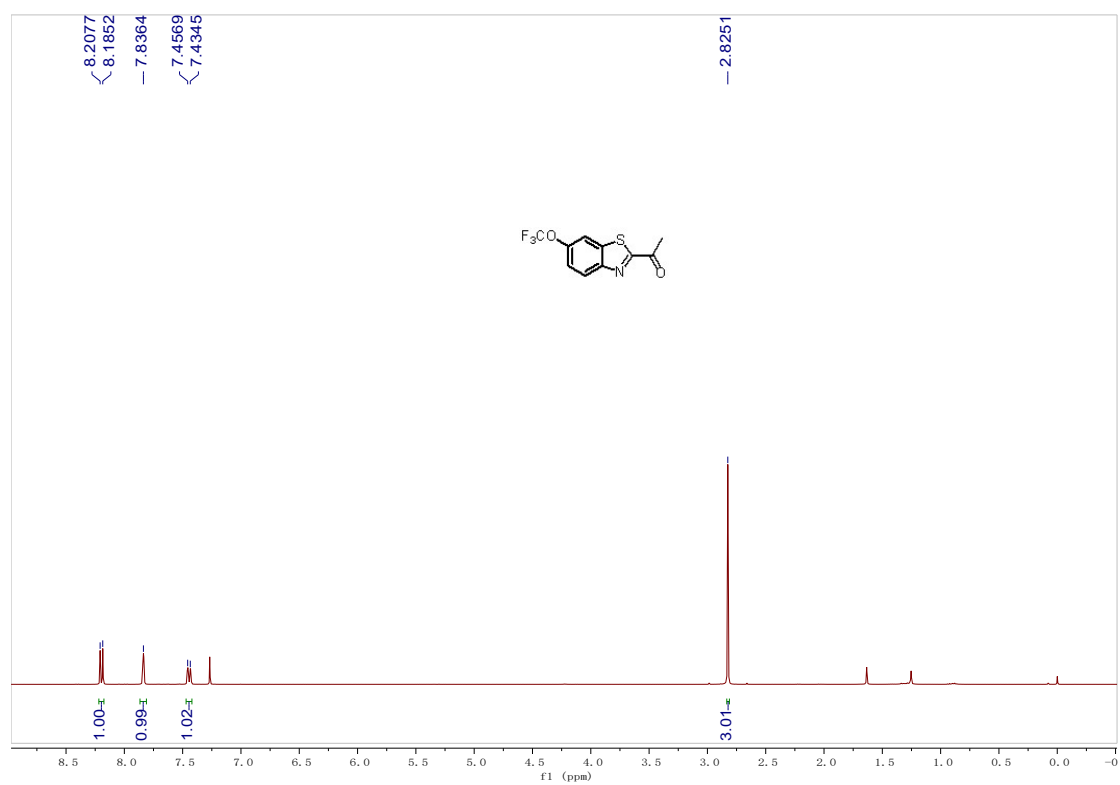
$^1\text{H}$  NMR spectrum of compound **15d** in  $\text{CDCl}_3$  (400 MHz):



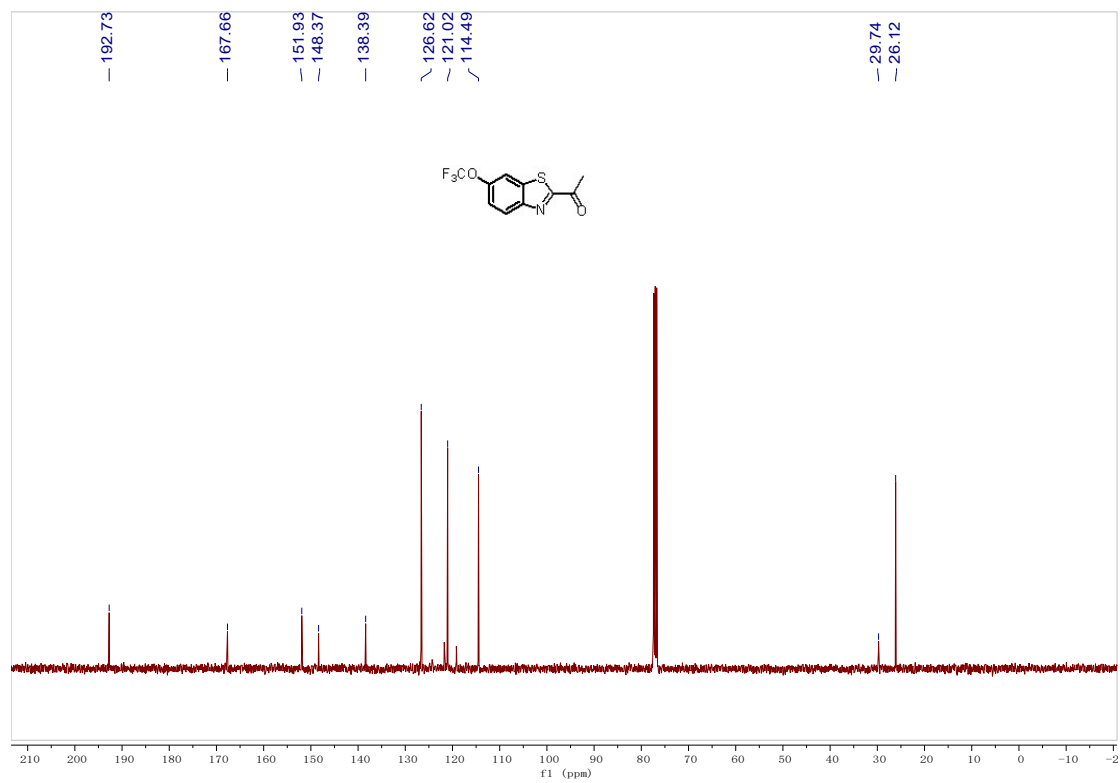
$^{13}\text{C}$  NMR spectrum of compound **15d** in  $\text{CDCl}_3$  (101 MHz):



$^1\text{H}$  NMR spectrum of compound **16d** in  $\text{CDCl}_3$  (400 MHz):



$^{13}\text{C}$  NMR spectrum of compound **16d** in  $\text{CDCl}_3$  (101 MHz):



$^{19}\text{F}$  NMR spectrum of compound **16d** in  $\text{CDCl}_3$  (101 MHz):

