

# Supporting Information

## Z-Selective Radical Difunctionalization of Aromatic Alkynes:

### Synthesis of Multi-substituted Triarylethenes

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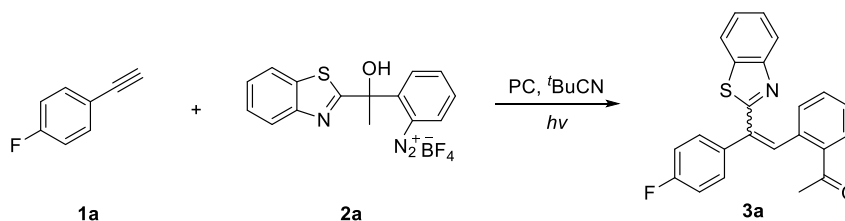
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## 1. General experimental details

Commercially available reagents were used without further purification. Infrared (FT-IR) spectra were recorded on a BRUKER VERTEX 70,  $\nu_{\max}$  in  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra were recorded on a BRUKER AVANCE III HD (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ( $\text{CDCl}_3$ :  $\delta$  7.26). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, br = broad, m = multiplet), coupling constants (Hz) and integration.  $^{13}\text{C-NMR}$  spectra were recorded on a BRUKER AVANCE III HD (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ( $\text{CDCl}_3$ :  $\delta$  77.16).  $^{19}\text{F-NMR}$  spectra were recorded on a BRUKER AVANCE III HD (376 MHz) spectrometer. Mass spectra were measured with an Agilent Technologies 6120 Quadrupole LC/MS. High resolution mass spectrometry (HRMS) were measured with a GCT Premier<sup>TM</sup> and BRUKER micrOTF-Q III. Melting points were measured using INESA WRR and values are uncorrected.

## 2. Optimization of reaction conditions

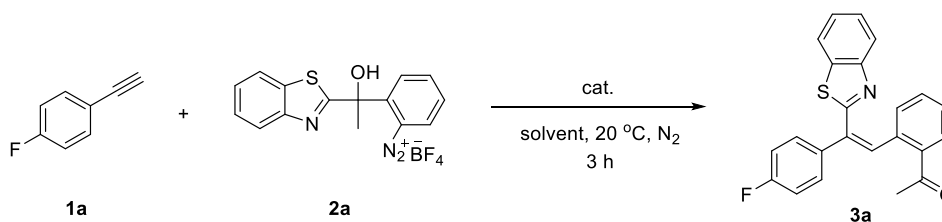
Supplementary Table 1 Examination of light sources and photocatalysts<sup>a</sup>



Entry	Light source	Photocatalyst	Yield (%) <sup>b</sup>	Z/E ratio <sup>c</sup>
1	5 W blue LEDs	None	40	1:1
2	5 W blue LEDs	$\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	85	1:1
3	30 W green LEDs	$\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$	49	7:1
4	45 W CFL	$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$	83	3:1
5	16 W purple LEDs	<i>fac</i> - $\text{Ir}(\text{ppy})_3$	28	3:1

<sup>a</sup>All reactions were carried out with **1a** (0.4 mmol, 2.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.) and photocatalyst (2 mol %) in  $t\text{BuCN}$  (1 mL) at r.t. under  $\text{N}_2$ . <sup>b</sup>Yields were determined by  $^1\text{H NMR}$  using 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup>The Z/E ratio was determined by  $^1\text{H NMR}$  or  $^{19}\text{F NMR}$ .

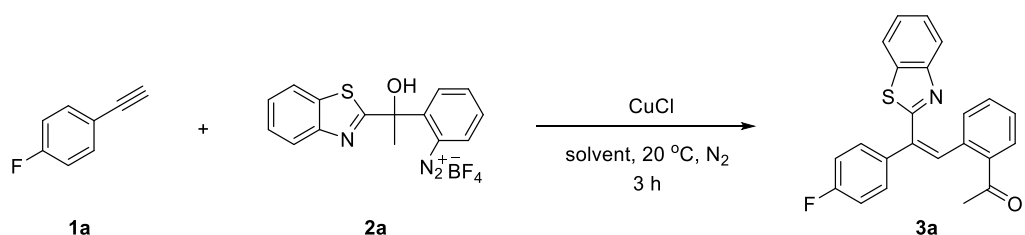
Supplementary Table 2 Examination of transition-metal catalysts<sup>a</sup>



Entry	Catalysts	Yield (%) <sup>b</sup>	Z/E ratio <sup>c</sup>
1	CuCl	74	>20:1
2	CuBr	24	>20:1
3	CuI	33	>20:1
4	CuCN	42	>20:1
5	Cu <sub>2</sub> O	59	>20:1
6	CuCl <sub>2</sub>	58	>20:1
7	CuF <sub>2</sub>	22	>20:1
8	Cu(OTf) <sub>2</sub>	19	>20:1
9	Cu(AcO) <sub>2</sub>	21	>20:1
10	Fe(acac) <sub>2</sub>	<10	-
11	FeBr <sub>2</sub>	17	>20:1
12	FeCl <sub>2</sub>	22	>20:1
13	Mn(OTf) <sub>2</sub>	14	>20:1
14	MnCl <sub>2</sub>	<10	-
15	MnO <sub>2</sub>	<10	-
16	CoBr <sub>2</sub>	<10	-
17	Co(acac) <sub>2</sub>	<10	-
18	AgOTf	0	-
19	NiCl <sub>2</sub>	<10	-
20	Ni(acac) <sub>2</sub>	0	-
21	GaCl <sub>3</sub>	0	-
22	AuCl <sub>3</sub>	<10	-

<sup>a</sup>All reactions were carried out with **1a** (0.5 mmol, 2.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), H<sub>2</sub>O (15 equiv.) and catalyst (10 mol %) in DMSO (1.2 M) at 20 °C under N<sub>2</sub>. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup>The Z/E ratio was determined by <sup>1</sup>H NMR or <sup>19</sup>F NMR.

**Supplementary Table 3** Examination of solvents<sup>a</sup>

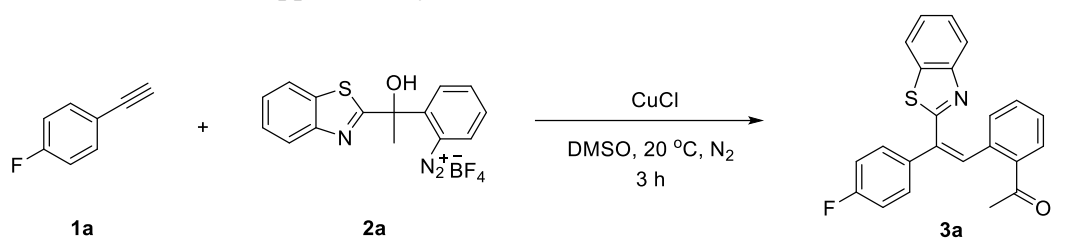


Entry	Solvent	Yield (%) <sup>b</sup>	Z/E ratio <sup>c</sup>
1	DMSO	43	> 20:1
2	MeCN	0	-
3	DCM	0	-
4	Acetone	0	-
5	(CF <sub>3</sub> ) <sub>2</sub> CHOH	<10	-
6	MeOH	<10	-
7	H <sub>2</sub> O	<10	-
8	DMF	14	>20:1

9	DMA	15	>20:1
10	EA	0	-
11	PhCF <sub>3</sub>	0	-
12	MeCN	0	-
13	DMSO+DCM	21	18:1
14	DMSO+MeCN	25	16:1
15	DMSO+Acetone	29	>20:1

<sup>a</sup>All reactions were carried out with **1a** (0.4 mmol, 2.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.) and CuCl (10 mol %) in solvent (1.2 M) at 20 °C under N<sub>2</sub>. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup>The *Z/E* ratio was determined by <sup>1</sup>H NMR or <sup>19</sup>F NMR.

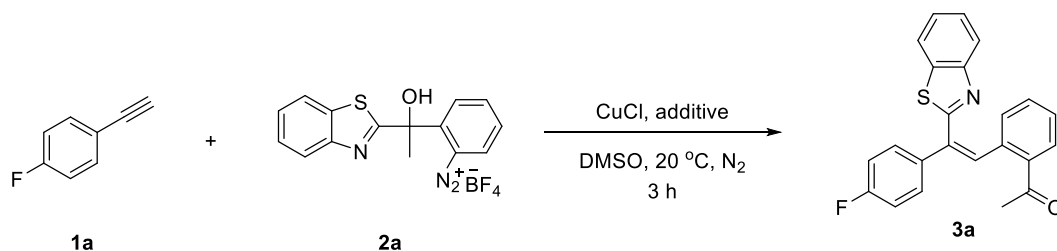
**Supplementary Table 4** Examination of concentration<sup>a</sup>



Entry	DMSO (x M)	Yield (%) <sup>b</sup>	<i>Z/E</i> ratio <sup>c</sup>
1	0.1	17	16:1
2	0.2	26	>20:1
3	0.4	44	>20:1
4	0.6	46	>20:1
5	0.8	49	>20:1
6	1.0	56	>20:1
7	1.2	64	>20:1
8	1.5	64	>20:1
9	2.0	63	>20:1

<sup>a</sup>All reactions were carried out with **1a** (0.4 mmol, 2.0 equiv.), **2a** (0.2 mmol, 1.0 equiv.), H<sub>2</sub>O (15 equiv.) and CuCl (10 mol %) in DMSO (1.2 M) at 20 °C under N<sub>2</sub>. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup>The *Z/E* ratio was determined by <sup>1</sup>H NMR or <sup>19</sup>F NMR.

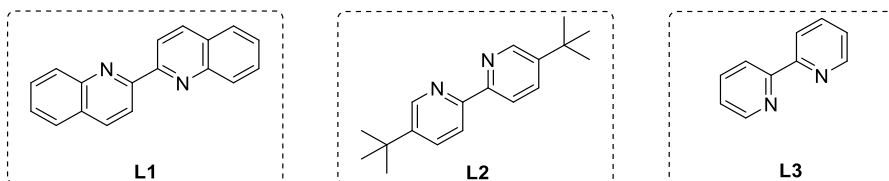
**Supplementary Table 5** Examination of bases and ligands<sup>a</sup>



Entry	Additive	Yield (%) <sup>b</sup>	<i>Z/E</i> ratio <sup>c</sup>
1	Na <sub>2</sub> HPO <sub>4</sub>	53	18:1
2	Na <sub>3</sub> PO <sub>4</sub>	64	>20:1

3	Na <sub>2</sub> CO <sub>3</sub>	64	18:1
4	2,6-Lutidine	48	>20:1
5	DBU	32	>20:1
6	Na <sub>2</sub> HPO <sub>4</sub>	53	18:1
7	L1	61	>20:1
8	L2	59	19:1
9	L3	65	>20:1

<sup>a</sup>All reactions were carried out with **1a** (0.5 mmol, 2.5 equiv.), **2a** (0.2 mmol, 1.0 equiv.), H<sub>2</sub>O (15 equiv.) and CuCl (10 mol %) in DMSO (1.2 M) at 20 °C under N<sub>2</sub>. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as an internal standard. <sup>c</sup>The *Z/E* ratio was determined by <sup>1</sup>H NMR or <sup>19</sup>F NMR.



### 3. General procedure for the difunctionalization of aromatic alkynes

Aryldiazonium tetrafluoroborate **2** (0.2 mmol, 1.0 equiv.) and CuCl (10 mol %) were loaded in a 4 mL reaction vial which was subjected to evacuation/flushing with N<sub>2</sub> three times, H<sub>2</sub>O (15 equiv.) and alkyne **1** (0.5 mmol, 2.5 equiv.) along with DMSO (1.2 M, 0.167 mL) were added to the mixture via syringe, then the reaction was stirred at 20 °C. After the reaction completion by TLC monitoring, the reaction mixture was extracted with dichloromethane (3×5 mL). The combined organic extract was washed by brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified by flash column chromatography on silica gel (eluent: acetone/dichloromethane/petroleum ether) to give the desired product **3** or **4**.

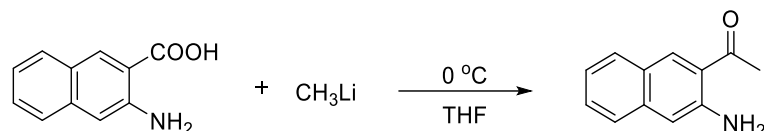
### 4. Gram-scale preparation

Aryldiazonium tetrafluoroborate **2a** (1.8457 g, 5.0 mmol) and CuCl (49.5 mg) were loaded in a 50 mL round bottom flask which was subjected to evacuation/flushing with N<sub>2</sub> three times, H<sub>2</sub>O (1.4 mL) and phenylacetylene **1b** (1.2767 g) along with DMSO (4.2 mL) were slowly and partially added under vigorously stirring at 0 °C, stirring at this temperature for 10 minutes, then the mixture was stirred at 20 °C for 3 h. After the reaction completion by TLC monitoring, the residue was diluted by dichloromethane (30 mL) and water (30 mL). The aqueous layer was extracted with dichloromethane (3×20 mL). The combined organic layers were washed with water and brine, dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude product was purified by silica gel column chromatography (acetone/dichloromethane/petroleum ether = 2/50/250 to 4/50/250, v/v/v) to afford the desired product **3b** (1.23 g, 70% isolated yield), as a white solid.

## 5. Synthesis of aryldiazonium tetrafluoroborate 2

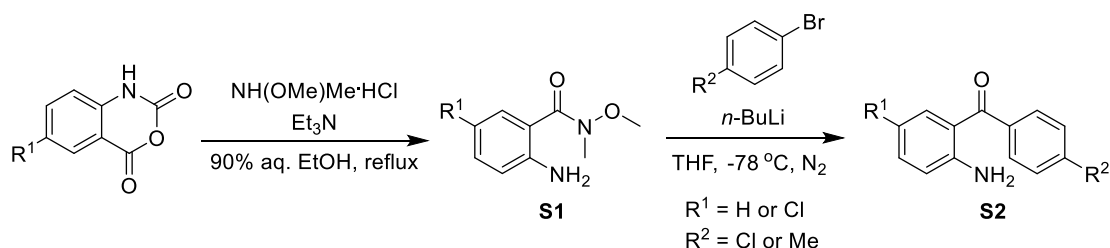
Aryldiazonium tetrafluoroborates were prepared according to the reported procedures. **2a-g**, **2p**, **2i-k** and **2o-s** are known compounds, whose spectrum data are in line with *ref. 1*. Other aryldiazonium tetrafluoroborates were prepared according to the following procedures:

### 5.1 Synthesis of substituted 2-aminoacetophenone



To a solution of 3-amino-2-naphthoic acid (15 mmol, 1.0 equiv.) in THF (100 mL) was slowly added  $\text{CH}_3\text{Li}$  (1.6 M in diethoxymethane, 45 mmol, 3.0 equiv.) at  $0\text{ }^\circ\text{C}$  under  $\text{N}_2$ , then the mixture was stirred for 16 h. After the reaction completion by TLC monitoring, the reaction mixture was quenched by saturated  $\text{NH}_4\text{Cl}$  solution. Then the mixture was warmed to room temperature and extracted with ethyl acetate ( $3 \times 20\text{ mL}$ ). The combined organic extracts were washed by saturated  $\text{NaHCO}_3$  solution and brine, dried with  $\text{Na}_2\text{SO}_4$ , filtered, concentrated, and purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1/15) to give the product as yellow solid.

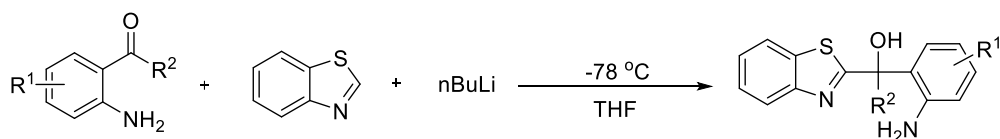
### 5.2 Synthesis of 2-aminoarylphenone



**Step 1:** To a solution of *N, O*-dimethylhydroxylamine hydrochloride (1.5 equiv.) in 90% aqueous ethanol was added triethylamine (1.5 equiv.). After 10 min of stirring at room temperature, isatoic anhydride (1.0 equiv.) was added in portions. The reaction mixture was heated under reflux for 1.5 h and poured onto an equal volume of ice and saturated aq.  $\text{NaHCO}_3$  solution. The ethanol was then removed by rotary evaporation, and the resulting aqueous mixture was extracted with ethyl acetate ( $3 \times 150\text{ mL}$ ), and the combined extracts were washed with water and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and activated charcoal, and concentrated to an orange oily product. The oily residue was purified by flash column chromatography on silica gel (diethyl ether/petroleum ether = 1/1, then acetone) to give **S1** as a yellow oil.

**Step 2:** To a mixture of **S1** (1.0 equiv.) and aryl bromide (1.0 equiv.) in anhydrous THF at  $-78\text{ }^\circ\text{C}$  under nitrogen was added, with vigorous stirring,  $n\text{-BuLi}$  in hexanes (2.0 equiv.) at 0.6 mL/min. The resulting solution was stirred for 30 min, and then aqueous hydrochloric acid was added. The mixture was extracted with ethyl acetate ( $3 \times 150\text{ mL}$ ), and the combined extracts were washed with water and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1 to 10/1) to afford compounds **S2** as a yellow solid.

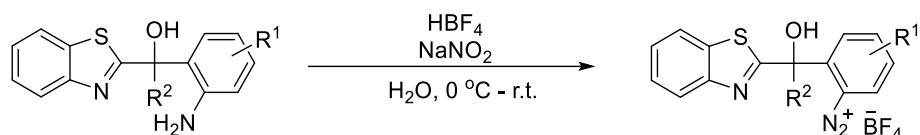
### 5.3 Synthesis of tertiary alcohol-substituted aniline



To a solution of benzothiazole (31 mmol, 3.1 equiv.) in THF (30 mL) was slowly added *n*BuLi (2.5 M in hexane, 31 mmol, 3.1 equiv.) at -78 °C under N<sub>2</sub>, then the mixture was stirred for 1 h, to which was added 2-aminoacetophenone (10 mmol, 1.0 equiv.) diluted with THF (10 mL) followed by further stirring at -78 °C for 4 h. After the reaction completion by TLC monitoring, the reaction mixture was quenched by saturated aq. NH<sub>4</sub>Cl solution. Then the mixture was warmed to room temperature and extracted with ethyl acetate (3×20 mL). The combined organic extracts were washed by saturated NaHCO<sub>3</sub> solution and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated, and purified by flash column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:15 to 1:5) to give the aniline product.

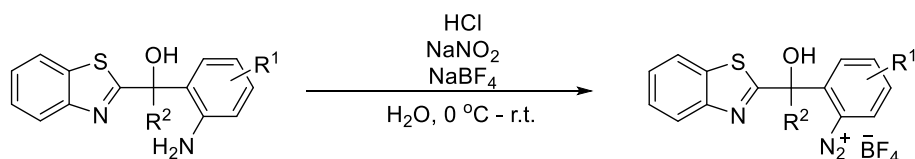
### 5.4 Synthesis of aryldiazonium tetrafluoroborates

#### General procedure A



The substituted aniline (1 mmol, 1.0 equiv.) was loaded in a 50 mL round-bottom flask containing a stirrer. Aqueous fluoroboric acid (0.5 mL, 48 wt%) was added to the mixture. After 0.5 h, the mixture became homogenous transparent liquid and was placed in an ice bath. Sodium nitrite (1.07 mmol, 1.07 equiv.) diluted with 0.5 mL of distilled water was added dropwise. After 10 min, the mixture was warmed to room temperature and then a lot of precipitate could be observed. After filtration, the cake was washed by distilled water (5 mL×3) and ether (5 mL×3) and evaporated to dryness under reduced pressure giving the substituted benzenediazonium tetrafluoroborate.

#### General procedure B

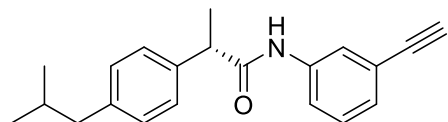


The substituted aniline (1 mmol, 1.0 equiv.) was loaded in a 100 mL round-bottom flask containing a stirrer. Concentrated hydrochloric acid (2 mL) was added portion wise to the mixture. After 1 h, the mixture became homogenous white viscous liquid and was placed in an ice bath. Sodium nitrite (1.1 mmol, 1.1 equiv.) in 1.0 mL of distilled water was added drop wise. After 15 min, a yellow clear solution was obtained. Sodium Tetrafluoroborate (10 mmol, 10 equiv.) was added to this solution, and then a lot of precipitate can be observed. After filtration, the cake was washed by distilled water (5 mL×3) and ether (5 mL×3) and evaporated to dryness under reduced pressure giving the substituted benzenediazonium tetrafluoroborate.

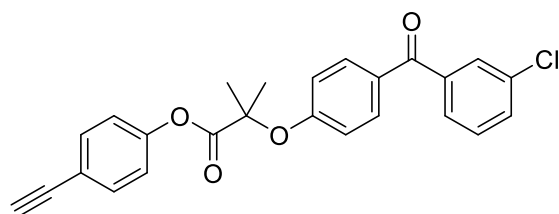
**Note:** the aryldiazonium tetrafluoroborate **2l**, **2m** and **2n** are soluble in ether, so it can not be washed by ether. The aryldiazonium tetrafluoroborate **2h** is soluble in water, so it can not be washed by

water, and more to the point, the equivalent of sodium tetrafluoroborate need to be reduced to 3 equiv. because excess sodium tetrafluoroborate can't be removed by water washing.

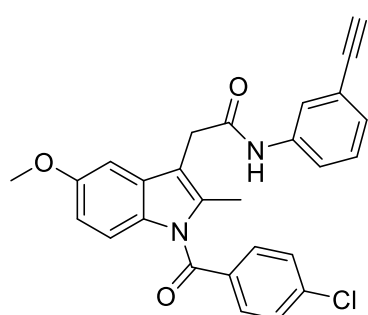
## 6. Characterization of starting materials



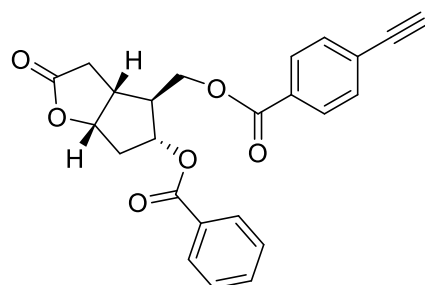
**1ae:** white solid, m.p. 113-114 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (s, 1H), 7.50-7.44 (m, 1H), 7.28-7.12 (m, 7H), 3.69 (q,  $J = 7.2$  Hz, 1H), 3.03 (s, 1H), 2.48 (d,  $J = 7.2$  Hz, 2H), 1.93-1.80 (m, 1H), 1.58 (d,  $J = 6.8$  Hz, 3H), 0.91 (d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 141.2, 138.0, 137.9, 129.9, 128.9, 127.9, 127.4, 123.1, 122.7, 120.3, 83.1, 77.4, 47.7, 45.0, 30.2, 22.4, 18.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3306, 3285, 3048, 3024, 2977, 1942, 1873, 1766, 1658, 1511. HRMS [ESI] calcd for  $\text{C}_{21}\text{H}_{23}\text{NO}$ Na  $[\text{M}+\text{Na}]^+$  328.1672, found 328.1662.



**1af:** white solid, m.p. 126-127 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82-7.76 (m, 2H), 7.74-7.68 (m, 2H), 7.51-7.42 (m, 4H), 7.01-6.93 (m, 4H), 3.07 (s, 1H), 1.82 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  194.1, 172.1, 159.4, 150.5, 138.5, 136.3, 133.4, 132.2, 131.2, 130.8, 128.6, 121.3, 120.3, 117.3, 82.6, 79.4, 77.7, 25.4. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3280, 3059, 3001, 2555, 2039, 1747, 1572, 1418, 1395. HRMS [ESI] calcd for  $\text{C}_{25}\text{H}_{19}\text{ClO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  441.0864, found 441.0860.

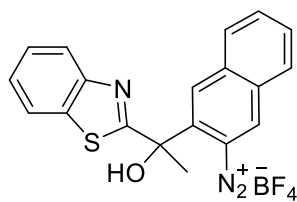


**1ag:** white solid, m.p. 211-212 °C.  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  10.31 (s, 1H), 7.81 (s, 1H), 7.72-7.56 (m, 5H), 7.32 (t,  $J = 8.0$  Hz, 1H), 7.20-7.13 (m, 2H), 6.94 (d,  $J = 8.8$  Hz, 1H), 6.72 (dd,  $J = 8.8, 2.4$  Hz, 1H), 4.16 (s, 1H), 3.77 (s, 2H), 3.75 (s, 3H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  169.2, 168.3, 156.1, 139.8, 138.1, 135.9, 134.7, 131.6, 131.3, 130.8, 129.7, 129.5, 127.0, 122.6, 122.5, 120.3, 115.1, 114.3, 111.6, 102.4, 83.8, 81.0, 55.9, 32.5, 13.9. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3271, 3054, 3004, 2964, 2835, 1916, 1729, 1667, 1621, 1527, 1462, 1397. HRMS [EI] calcd for  $\text{C}_{27}\text{H}_{21}\text{ClN}_2\text{O}_3$   $[\text{M}]^+$  456.1241, found 456.1250.

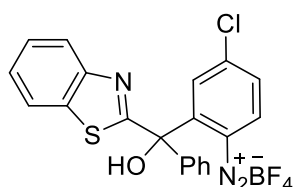


**1ah:** white solid, m.p. 142-143 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00-7.91 (m, 4H), 7.58-7.38 (m, 5H), 5.49-5.42 (m, 1H), 5.11 (t,  $J = 6.4$  Hz, 1H), 4.44-4.32 (m, 2H), 3.26 (s, 1H), 3.00-2.82 (m, 2H), 2.68-2.52 (m, 3H), 2.43-2.32 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1, 165.9, 165.6, 133.4, 132.2, 129.7, 129.5, 129.4, 128.5, 127.3, 83.9, 82.6, 80.5, 77.4, 64.7, 51.6, 40.6, 38.2, 35.7. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3071, 2993, 2949, 1766, 1625, 1581, 1449, 1402, 1378. HRMS [ESI] calcd for  $\text{C}_{24}\text{H}_{20}\text{O}_6\text{Na}$   $[\text{M}+\text{Na}]^+$  427.1152, found 427.1155.

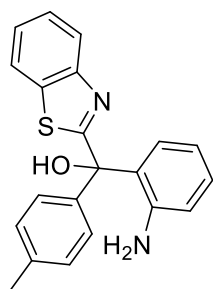




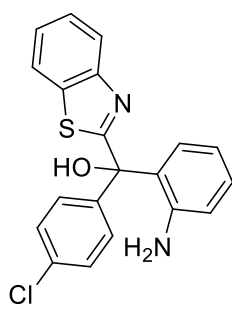
**2h**: following general procedure A, 347.9 mg, 83%, yellow solid, m.p. 114-115 °C (decomp.). <sup>1</sup>H NMR (400 MHz, DMSO) δ 9.71 (s, 1H), 8.68 (s, 1H), 8.34 (t, *J* = 7.2 Hz, 2H), 8.19-7.87 (m, 4H), 7.56-7.43 (m, 2H), 3.82 (br, 1H), 2.32 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO) δ 177.4, 153.4, 142.7, 138.9, 136.9, 135.4, 135.3, 130.9, 130.7, 130.3, 129.9, 129.8, 126.9, 126.1, 123.5, 123.0, 109.7, 76.2, 29.9. FT-IR: ν (cm<sup>-1</sup>) 3454, 3073, 1996, 1826, 1615, 1584, 1510, 1450. HRMS [EI] calcd for C<sub>19</sub>H<sub>14</sub>NOS<sup>+</sup> [M-N<sub>2</sub>BF<sub>4</sub>]<sup>+</sup> 304.0791, found 304.0798.



**2l**: following general procedure B, 353.9 mg, 76%, yellow solid, m.p. 101-102 °C (decomp.). <sup>1</sup>H NMR (400 MHz, DMSO) δ 9.48 (s, 1H), 8.87 (d, *J* = 8.8 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 8.15 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.00-7.92 (m, 1H), 7.62-7.38 (m, 6H), 4.05 (br, 1H); <sup>13</sup>C NMR (100 MHz, DMSO) δ 175.6, 153.4, 150.0, 146.2, 141.9, 137.9, 135.3, 131.9, 131.7, 130.1, 129.5, 128.2, 127.2, 126.4, 123.8, 123.1, 112.7, 80.3. FT-IR: ν (cm<sup>-1</sup>) 3606, 3391, 3097, 1626, 1577, 1493, 1435, 1391. HRMS [EI] calcd for C<sub>20</sub>H<sub>13</sub>ClNOS<sup>+</sup> [M-N<sub>2</sub>BF<sub>4</sub>]<sup>+</sup> 350.0401, found 350.0409.



**2m'**: 1.9 g, 56%, yellow solid, m.p. 115-116 °C (due to the instability of compound **2m**, the precursor aniline **2m'** was characterized.). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.51-7.45 (m, 1H), 7.43-7.35 (m, 3H), 7.22-7.12 (m, 3H), 6.81-6.75 (m, 1H), 6.72-6.64 (m, 2H), 5.38 (br, 1H), 4.21 (br, 2H), 2.38 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 178.1, 152.9, 145.3, 140.7, 138.2, 136.1, 129.5, 129.3, 129.2, 129.0, 127.1, 126.1, 125.2, 123.4, 121.7, 118.2, 118.2, 81.6, 21.23. FT-IR: ν (cm<sup>-1</sup>) 3457, 3370, 3061, 2950, 2866, 1730, 1576, 1454, 1472. HRMS [ESI] calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>OSNa [M+Na]<sup>+</sup> 369.1032, found 369.1026.

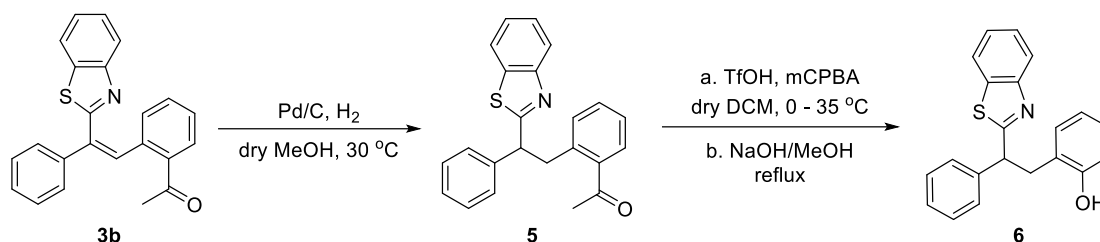


**2n'**: 2.6 g, 71%, yellow solid, m.p. 102-103 °C (due to the instability of compound **2n**, the precursor aniline **2n'** was characterized.). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.53-7.30 (m, 6H), 7.21-7.14 (m, 1H), 6.78-6.64 (m, 3H), 5.68 (br, 1H), 4.17 (br, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 177.5, 152.8, 145.2, 142.2, 136.0, 134.3, 129.8, 129.0, 128.9, 128.8, 128.6, 126.3, 125.5, 123.4, 121.8, 118.5, 118.4, 81.3. FT-IR: ν (cm<sup>-1</sup>) 3458, 3371, 3227, 3063, 2952, 2867, 1910, 1729, 1613, 1575, 1487. HRMS [ESI] calcd for C<sub>20</sub>H<sub>15</sub>ClN<sub>2</sub>OSNa [M+Na]<sup>+</sup> 389.0486, found 389.0488.

## References

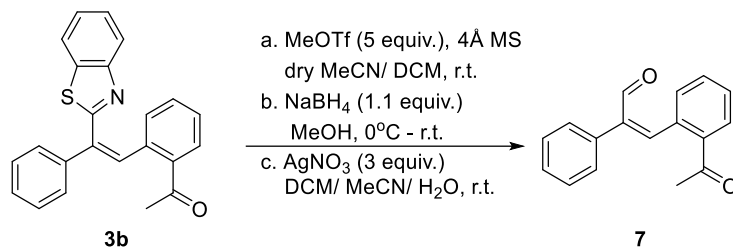
[1] M. Ji, X. Wang, J. Liu, X. Wu and C. Zhu, *Sci. China Chem.*, 2021, **64**, 1073-1078

## 7. Product transformations

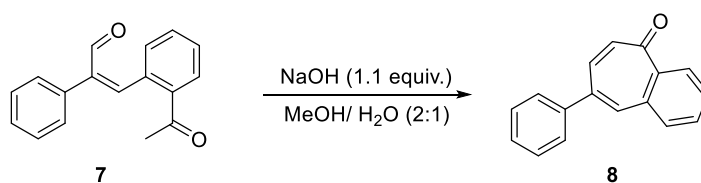


An oven-dried vial was charged with **3b** (0.5 mmol), Pd/C (2 mol%) and MeOH (3.0 mL) under nitrogen. The reaction mixture was stirred under a balloon of H<sub>2</sub> (1 atm.) for 12 h at room temperature. After reaction completion, the reaction mixture was filtered, the organic layers were combined and concentrated. Purification by flash column chromatography on silica gel (acetone/dichloromethane/petroleum ether = 2/50/250) afforded the pure product **5** as a yellow oil. (139.4 mg, 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73-7.68 (m, 1H), 7.51-7.45 (m, 1H), 7.42-7.20 (m, 8H), 7.11-7.05 (m, 1H), 4.84 (t, *J* = 7.2 Hz, 1H), 4.05 (dd, *J* = 12.8, 7.2 Hz, 1H), 3.74 (dd, *J* = 12.8, 7.2 Hz, 1H), 2.56 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.9, 173.9, 153.2, 141.5, 139.4, 137.8, 135.3, 132.5, 131.3, 129.6, 128.6, 128.4, 127.2, 126.4, 125.8, 124.7, 123.0, 121.5, 52.2, 40.3, 29.6. FT-IR: ν (cm<sup>-1</sup>) 3081, 2910, 1699, 1635, 1589, 1538, 1442, 1395, 1321. HRMS [ESI] calcd for C<sub>23</sub>H<sub>19</sub>NOSNa [M+Na]<sup>+</sup> 380.1080, found 380.1079.

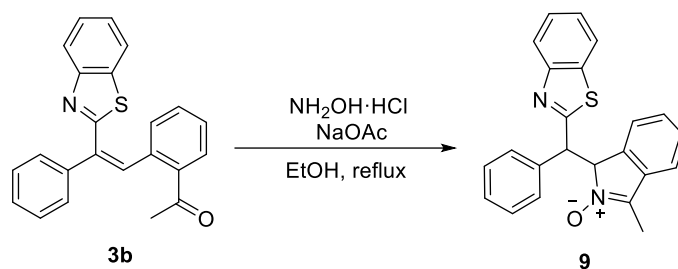
Ketone **5** (0.2 mmol) was dissolved in dry DCM (2 mL) and 3-chloroperoxybenzoic acid (2.0 equiv.) was added. The suspension was cooled to 0 °C and trifluoromethanesulfonic acid (10 mol%) was added dropwise. Then, the mixture was warmed to 35 °C. After completion of reaction, the mixture was diluted with DCM (4 mL) and saturated aq. Na<sub>2</sub>SO<sub>4</sub> solution (10 mL) was added and stirred for 30 min. The suspension was extracted with DCM (3×15 mL), washed with 10% NaHCO<sub>3</sub> solution (10 mL), the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated to give the crude ester. Aqueous 1.0 M NaOH solution (6 mL) was added in a 25 mL three-neck bottle. The crude ester (0.2 mmol) in 6.0 mL MeOH was added gradually and refluxed for 4 h. After completion of reaction, the mixture was neutralized with 1M HCl solution (10 mL) and extracted with EtOAc (3×15 mL). The residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/30 to 1/10) to afford **6** as a white solid (47.1 mg, 71% for 2 steps, m.p. 155-156 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.09 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.54-7.47 (m, 1H), 7.41-7.29 (m, 6H), 7.17-7.09 (m, 2H), 6.98-6.92 (m, 1H), 6.89-6.82 (m, 1H), 4.74 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.94 (dd, *J* = 14.0, 10.8 Hz, 1H), 3.19 (dd, *J* = 14.0, 2.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 175.7, 155.0, 150.9, 142.9, 135.5, 131.2, 129.1, 128.2, 127.8, 127.7, 126.9, 126.4, 125.5, 122.6, 121.6, 120.5, 118.7, 53.7, 35.9. FT-IR: ν (cm<sup>-1</sup>) 3059, 3026, 2955, 2755, 1970, 1600, 1511, 1486. HRMS [ESI] calcd for C<sub>21</sub>H<sub>18</sub>NOS [M+H]<sup>+</sup> 332.1104, found 332.1115.



**3b** (0.5 mmol, 1.0 equiv.), activated 4 Å powdered molecular sieves (1.5 g), and anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and MeCN (5 mL) was stirred at r.t. for 10 min, and then MeOTf (5 equiv.) was added. The suspension was stirred at r.t. for 4 h and then concentrated to dryness without filtering off the molecular sieves. To a cooled (0 °C), stirred suspension of the crude *N*-methyl benzothiazolium salt in MeOH (5 mL) was added NaBH<sub>4</sub> (1.2 equiv.). The mixture was stirred at r.t. for an additional 30 min, diluted with acetone, filtered through a pad of Celite, and concentrated. To a vigorously stirred solution of the crude benzothiazolines in CH<sub>2</sub>Cl<sub>2</sub> (1.6 mL) and MeCN (8.0 mL) were added H<sub>2</sub>O (1.0 mL) and then AgNO<sub>3</sub> (3 equiv.). The mixture was stirred at r.t. until the benzothiazolines were completely consumed as determined by TLC, and then diluted with 1 M phosphate buffer at pH 7 (0.5 mL). Stirring was continued for an additional 15 min, and the suspension was extracted with EtOAc (3×15 mL), and the combined organic layers were dried with Na<sub>2</sub>SO<sub>4</sub>, filtered through a pad of Celite, and concentrated. The residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:20) to afford product **7** as a yellow oil (63.8 mg, 51% for 3 steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.86 (s, 1H), 7.87 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.28-7.18 (m, 4H), 7.12-7.04 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 1H), 2.61 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.9, 193.8, 151.9, 141.3, 137.1, 135.4, 132.4, 131.8, 131.1, 130.1, 129.8, 128.8, 128.2, 127.9, 28.3. FT-IR: ν (cm<sup>-1</sup>) 3393, 3185, 2956, 2919, 1676, 1594, 1538, 1493, 1423. HRMS [EI] calcd for C<sub>17</sub>H<sub>14</sub>O<sub>2</sub> [M]<sup>+</sup> 250.0994, found 250.0990.



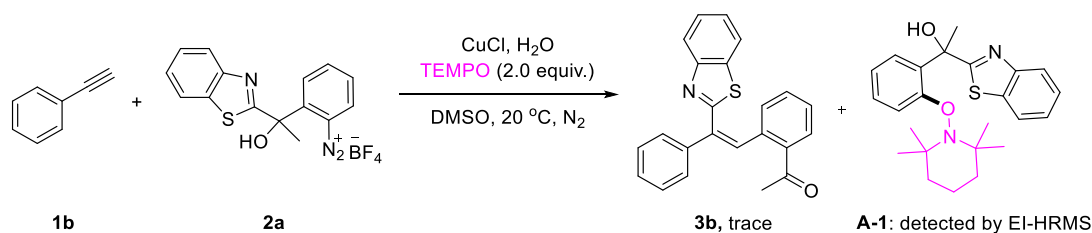
To a solution of NaOH (1.1 equiv.) in H<sub>2</sub>O (1.0 mL), compound **7** (0.2 mmol, 1.0 equiv.) in 2.0 mL ethanol at 0 °C was added gradually and stirred at 0 °C. After the reaction completion by TLC monitoring, the mixture was neutralized with 1M HCl solution (10 mL) and extracted with EtOAc (3×15 mL). The crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:5) to afford product **8** as an orange oil (29.3 mg, 63% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.55-8.50 (m, 1H), 7.78-7.63 (m, 3H), 7.60-7.36 (m, 7H), 7.07-7.02 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 187.9, 142.9, 139.9, 138.3, 137.9, 137.7, 136.0, 135.7, 134.5, 132.5, 130.6, 130.3, 128.9, 128.1, 127.3. FT-IR: ν (cm<sup>-1</sup>) 3425, 3059, 3025, 2925, 2889, 1675, 1450, 1373, 1293. HRMS [ESI] calcd for C<sub>17</sub>H<sub>13</sub>O [M+H]<sup>+</sup> 233.0961, found 233.0968



To a mixture of hydroxylamine hydrochloride (2.3 equiv.), NaOAc (2.5 equiv.), MeOH (1 mL) and H<sub>2</sub>O (0.5 ml) was added **3b** (0.5 mmol, 1.0 equiv.), and the mixture was stirred at 70 °C. The reaction was monitored by TLC. Once **3b** was completely consumed, the reaction was cooled down to room temperature, and then MeOH was removed under reduced pressure. The resulting mixture was extracted with Et<sub>2</sub>O (3×15 mL). The organic layer was then washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum. The crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:2 to 1:1) to afford product **9** as yellow solid (165.2 mg, 89% yield, m.p. 121-122 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.78-7.72 (m, 1H), 7.58-7.51 (m, 1H), 7.48-7.38 (m, 1H), 7.29-7.18 (m, 2H), 7.14-7.07 (m, 1H), 7.06-6.98 (m, 3H), 6.97-6.91 (m, 2H), 6.08 (s, 1H), 5.79 (d, *J* = 3.6 Hz, 1H), 2.16 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.2, 152.7, 144.8, 136.4, 136.1, 135.8, 134.6, 129.7, 128.5, 128.1, 127.6, 127.5, 126.1, 125.3, 124.6, 123.2, 121.6, 118.7, 77.4, 52.0, 9.1. FT-IR: ν (cm<sup>-1</sup>) 3300, 3058, 3025, 2953, 1676, 1586, 1484, 1426. HRMS [EI] calcd for C<sub>15</sub>H<sub>15</sub>ClFN [M]<sup>+</sup> 370.1140, found 370.1147.

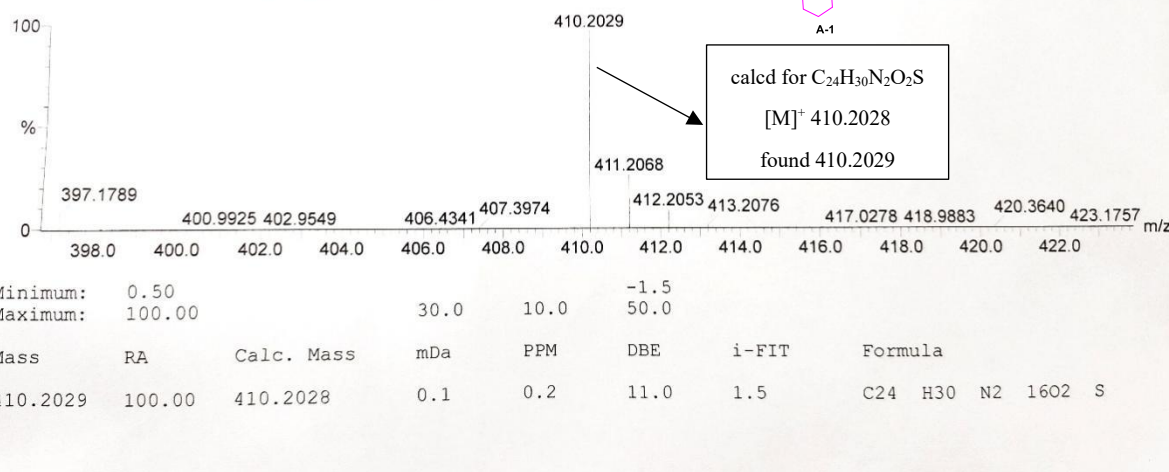
## 8. Radical trapping experiments

Aryldiazonium tetrafluoroborate **2a** (0.2 mmol, 1.0 equiv.), TEMPO (0.4 mmol, 2.0 equiv.) and CuCl (10 mol%) were loaded in a 4 mL reaction vial which was subjected to evacuation/flushing with N<sub>2</sub> three times, H<sub>2</sub>O (15 equiv.) and phenylacetylene **1b** (2.5 equiv.) along with DMSO (1.2 M) were added to the mixture via syringe, then the reaction was stirred at 20 °C. Then, the mixture was stirred for 3 h. As expected, only trace amount of product **3b** were generated, and the TEMPO-added byproduct **A-1** was detected by EI-HRMS.



**Multiple Mass Analysis: 7 mass(es) processed - displaying only valid results**  
 Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0  
 Element prediction: Off

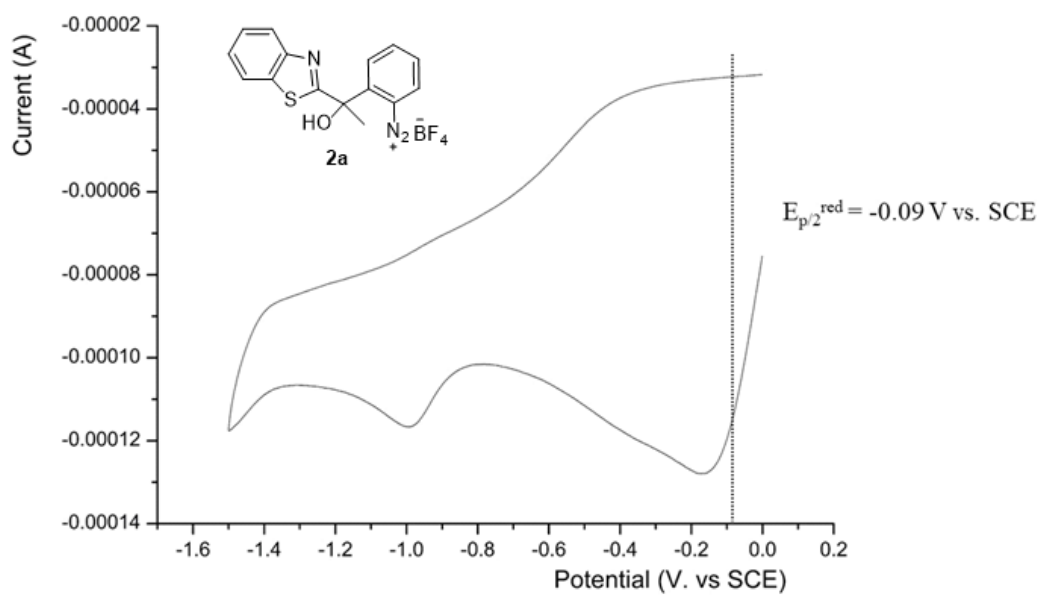
Monoisotopic Mass, Odd and Even Electron Ions  
 92 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)  
 Elements Used:  
 C: 0-24 H: 0-30 N: 0-2 16O: 0-2 S: 0-1  
 DEFAULT  
 20220714 301 (5.017) Cm (301:304-(222:229+214:218))



**Figure S1.** EI-HRMS spectrum

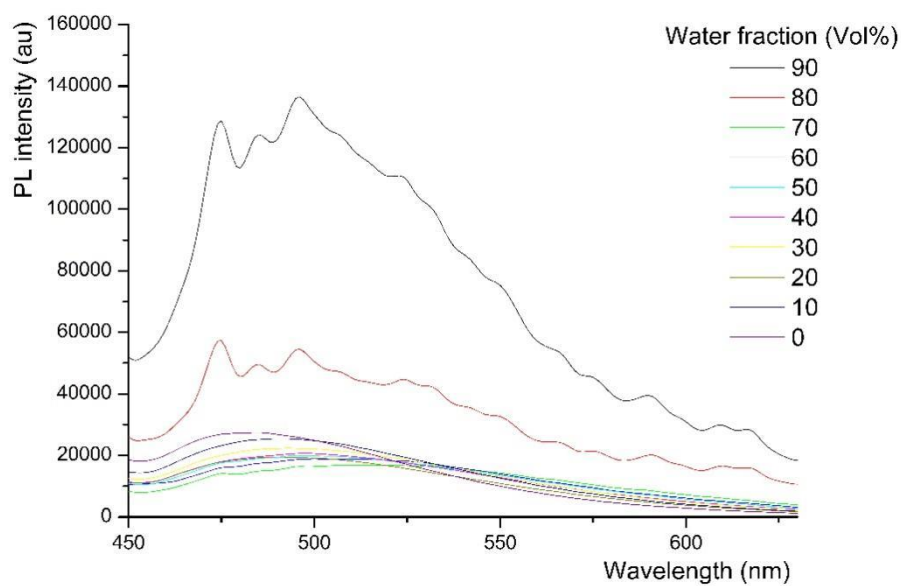
## 9. Cyclic voltammograms

All voltammograms were taken at room temperature using a meshplatinum (Pt) counter electrode, a glassy carbon working electrode (3 mm diameter), and a saturated KCl Ag/AgCl reference electrode. The conditions of the experiments were the following: an acetonitrile solution of 0.1 M tetrabutylammonium tetrafluoroborate ( $\text{Bu}_4\text{NBF}_4$ ) and 0.01 M diazonium salt **2a**, a scan rate of 0.1 V/s, and a negative initial scan direction. The reported potentials were averages over segments, and was taken at half-height of the cathodic peak ( $E_{p/2}$ ) of diazonium salt **2a**, since the reduction was nonreversible. To convert the potentials from SCE to  $\text{Fc}/\text{Fc}^+$  reference, 380 mV were subtracted from the measured values. The positive peaks on the return sweep of most substrates were thought to signify an ECE-type mechanism.

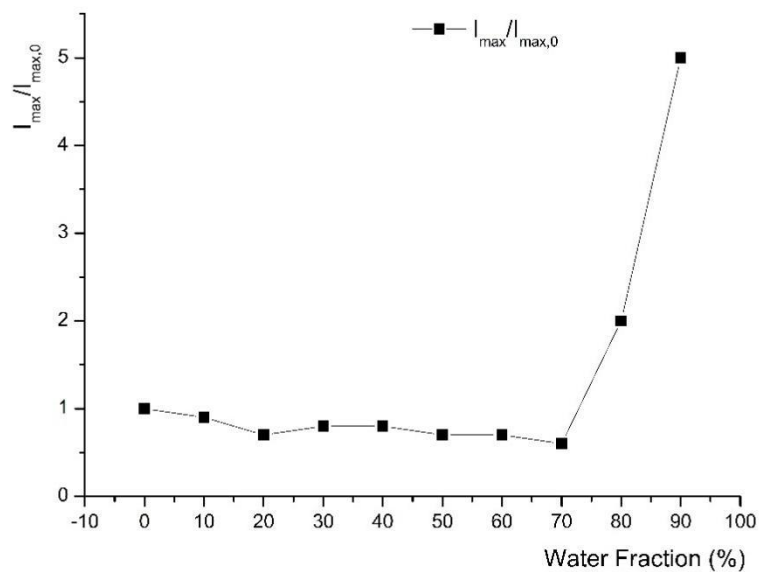


**Fig. S2** Cyclic voltammogram of diazonium salt **2a** in MeCN.

## 10. AIE studies of **3y**



(a)

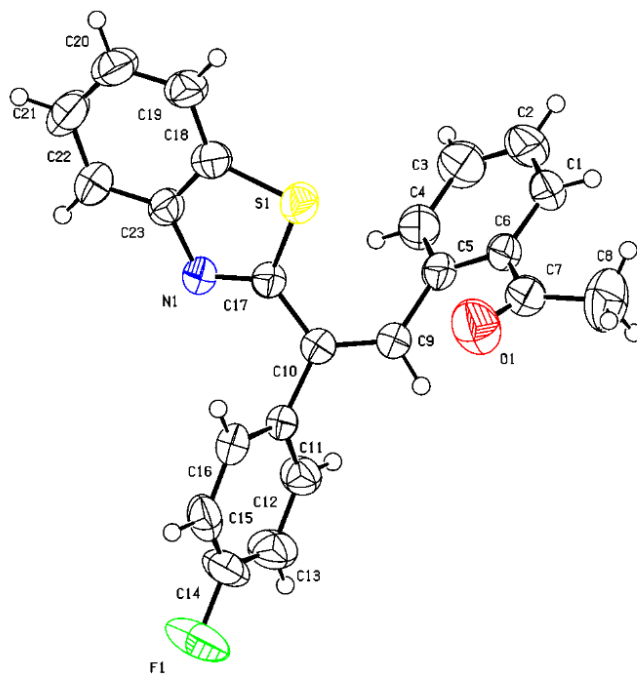


(b)

**Fig. S3 (a)** PL spectra of **3y** solutions in THF-water mixtures. **(b)** Photoluminescence of **3y** versus solvent composition of the THF-water mixture.

## 11. Single-crystal X-ray diffraction data

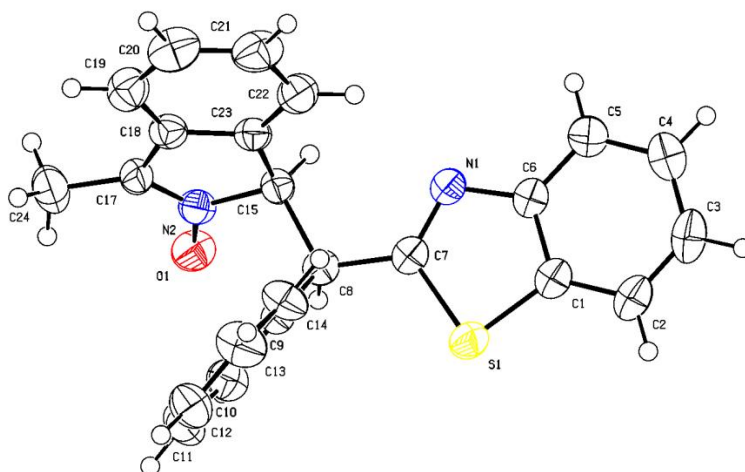
**3a**: (CCDC No:2202409)



Bond precision:	C-C = 0.0044 Å	Wavelength=0.71073	
Cell:	a=12.5347(7)	b=15.7748(8)	c=19.3093(10)

	alpha=90	beta=98.0108(16)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	3780.8(3)	3780.8(3)	
Space group	C 2/c	C 1 2/c 1	
Hall group	-C 2yc	-C 2yc	
Moiety formula	C <sub>23</sub> H <sub>16</sub> F N O S	C <sub>23</sub> H <sub>16</sub> F N O S	
Sum formula	C <sub>23</sub> H <sub>16</sub> F N O S	C <sub>23</sub> H <sub>16</sub> F N O S	
Mr	373.43	373.43	
Dx,g cm <sup>-3</sup>	1.312	1.312	
Z	8	8	
Mu (mm <sup>-1</sup> )	0.193	0.193	
F000	1552.0	1552.0	
F000'	1553.67		
h,k,lmax	16,20,25	16,20,25	
Nref	4364	4346	
Tmin,Tmax	0.933,0.962	0.675,0.746	
Tmin'	0.926		
Correction method = # Reported T Limits: Tmin=0.675 Tmax=0.746			
AbsCorr = MULTI-SCAN			
Data completeness = 0.996		Theta(max) = 27.547	
R(reflections) = 0.0674 (3222)		wR2(reflections) = 0.2219 (4346)	
S = 1.050		Npar = 245	

9: (CCDC: 2202373)



Bond precision:	C-C = 0.0034 Å	Wavelength=0.71073	
Cell:	a=8.2520 (7)	b=14.7387 (13)	c=15.4992 (13)
	alpha=90	beta=96.548 (2)	gamma=90



Temperature:	296 K	
	Calculated	Reported
Volume	1872.8 (3)	1872.8 (3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C23 H18 N2 O S	C23 H18 N2 O S
Sum formula	C23 H18 N2 O S	C23 H18 N2 O S
Mr	370.45	370.45
Dx,g cm-3	1.314	1.314
Z	4	4
Mu (mm-1)	0.188	0.188
F000	776.0	776.0
F000'	776.77	
h,k,lmax	9,17,18	9,17,18
Nref	3297	3296
Tmin,Tmax	0.947,0.978	0.556,0.746
Tmin'	0.945	

Correction method= # Reported T Limits: Tmin=0.556 Tmax=0.746

AbsCorr = NONE

Data completeness = 1.000

Theta(max) = 25.000

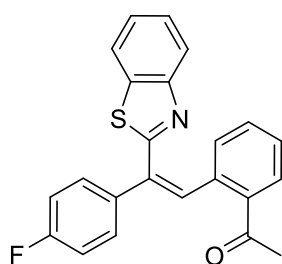
R(reflections) = 0.0447 (2187)

wR2(reflections) = 0.1045 (3296)

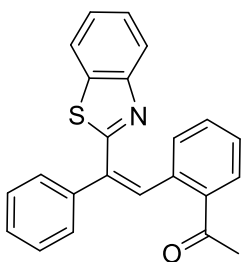
S = 1.023

Npar = 245

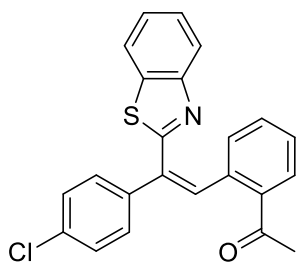
## 12. Characterization of products



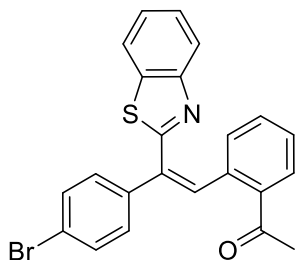
**3a:** 54.5 mg, 73%, *Z/E*>20:1, white solid, m.p. 124-125 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.83-7.78 (m, 1H), 7.71-7.66 (m, 1H), 7.60 (s, 1H), 7.52-7.46 (m, 2H), 7.44-7.38 (m, 1H), 7.35-7.27 (m, 2H), 7.25-7.19 (m, 2H), 7.07-6.99 (m, 2H), 2.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 166.8, 164.1, 161.6, 153.2, 137.0 (d, *J*<sub>C-F</sub> = 54.1 Hz), 136.5 (d, *J*<sub>C-F</sub> = 3.4 Hz), 136.1, 135.5, 134.0, 131.8 (d, *J*<sub>C-F</sub> = 37.5 Hz), 129.9, 129.8 (d, *J*<sub>C-F</sub> = 2.3 Hz), 128.0, 126.0, 125.3, 123.6, 121.4, 115.5, 115.2, 28.8; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -113.86. FT-IR: ν (cm<sup>-1</sup>) 3066, 3046, 2955, 2441, 1990, 1506, 1295, 1220. HRMS [ESI] calcd for C<sub>23</sub>H<sub>16</sub>FNOSNa [M+Na]<sup>+</sup> 396.0829, found 396.0826.



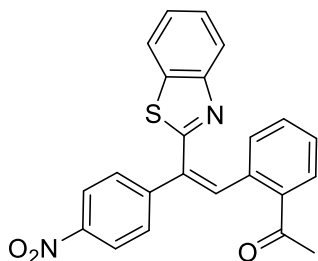
**3b:** 53.1 mg, 75%, *Z/E*>20:1, yellow solid, m.p. 136-137 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.58-7.52 (m, 2H), 7.48-7.42 (m, 1H), 7.42-7.30 (m, 5H), 7.26 (d, *J* = 3.6 Hz, 2H), 2.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.2, 167.0, 153.3, 140.3, 137.5, 136.8, 136.1, 135.3, 135.2, 131.9, 131.6, 129.6, 128.4, 128.3, 128.0, 127.9, 125.9, 125.2, 123.6, 121.4, 29.0. FT-IR: ν (cm<sup>-1</sup>) 3098, 3058, 2957, 2852, 2158, 1954, 1727, 1456. HRMS [ESI] calcd for C<sub>23</sub>H<sub>16</sub>NOSNa [M+Na]<sup>+</sup> 378.0923, found 378.0931.



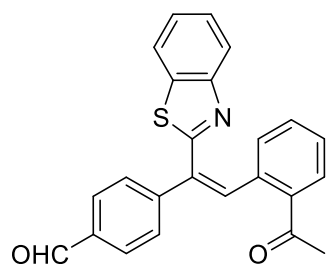
**3c:** 60.3 mg, 77%, *Z/E*>20:1, yellow solid, m.p. 165-166 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.50-7.42 (m, 3H), 7.38-7.31 (m, 4H), 7.30-7.22 (m, 2H), 2.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.9, 166.5, 153.1, 138.8, 137.2, 136.7, 136.1, 136.0, 134.1, 133.8, 132.0, 131.6, 129.8, 129.4, 128.6, 128.1, 126.0, 125.3, 123.5, 121.4, 28.8. FT-IR: ν (cm<sup>-1</sup>) 3053, 2958, 2921, 2852, 2162, 1592, 1458. HRMS [ESI] calcd for C<sub>23</sub>H<sub>16</sub>ClNOS [M+Na]<sup>+</sup> 412.0533, found 412.0533.



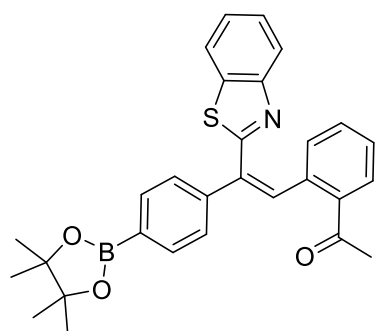
**3d:** 60.7 mg, 70%, *Z/E*>20:1, white solid, m.p. 161-162 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.53-7.40 (m, 5H), 7.38-7.22 (m, 4H), 2.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.9, 166.4, 153.2, 139.3, 137.2, 136.7, 136.1, 136.0, 133.9, 132.1, 131.6, 131.5, 129.9, 129.7, 128.2, 126.0, 125.3, 123.6, 122.4, 121.4, 28.8. FT-IR: ν (cm<sup>-1</sup>) 3058, 3027, 2953, 2922, 2163, 1731, 1677, 1561. HRMS [EI] calcd for C<sub>23</sub>H<sub>16</sub>BrNOS [M]<sup>+</sup> 433.0136, found 433.0138.



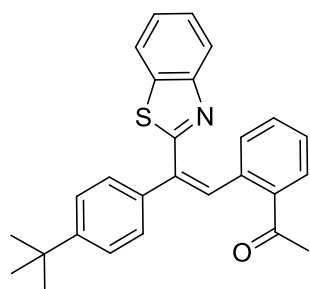
**3e:** 31.2 mg, 39%, *Z/E*>20:1, yellow solid, m.p. 112-113 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27-8.22 (m, 2H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.92 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.82 (s, 1H), 7.76-7.70 (m, 3H), 7.50-7.27 (m, 5H), 2.66 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.6, 165.4, 153.0, 147.4, 146.8, 139.2, 136.9, 136.3, 135.9, 132.8, 132.4, 131.5, 130.2, 128.9, 128.7, 126.2, 125.6, 123.7, 123.6, 121.4, 28.5. FT-IR: ν (cm<sup>-1</sup>) 3071, 2921, 2848, 2160, 1615, 1433, 1342, 1207. HRMS [ESI] calcd for C<sub>23</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>SNa [M+Na]<sup>+</sup> 423.0774, found 423.0764.



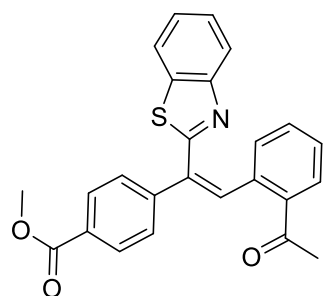
**3f:** 32.2 mg, 42%, *Z/E*=14:1, white solid, m.p. 144-145 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/Petroleum ether = 1/25). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.03 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 3H), 7.81 (s, 1H), 7.77-7.67 (m, 3H), 7.51-7.23 (m, 5H), 2.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.8, 191.9, 166.0, 153.1, 146.3, 138.1, 137.0, 136.5, 136.0, 135.7, 133.8, 132.2, 131.5, 130.0, 129.9, 128.6, 128.4, 126.1, 125.4, 123.6, 121.4, 28.6. FT-IR: ν (cm<sup>-1</sup>) 3057, 2999, 2760, 2163, 1602, 1489, 1431, 1353. HRMS [ESI] calcd for C<sub>24</sub>H<sub>17</sub>NO<sub>2</sub>SNa [M+Na]<sup>+</sup> 406.0872, found 406.0868.



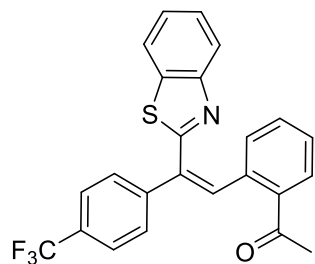
**3g:** 29.8 mg, 31%, *Z/E*>20:1, yellow oil. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 3H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.55-7.50 (m, 2H), 7.46-7.40 (m, 1H), 7.36-7.30 (m, 2H), 7.27-7.23 (m, 2H), 2.62 (s, 3H), 1.35 (s, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.1, 166.7, 153.3, 143.1, 137.5, 136.7, 136.1, 135.9, 135.2, 134.9, 134.5, 131.8, 131.5, 129.6, 128.0, 127.3, 125.9, 125.2, 123.6, 121.4, 83.8, 29.0, 24.9. FT-IR: ν (cm<sup>-1</sup>) 3062, 3033, 2977, 1937, 1680, 1562, 1508. HRMS [ESI] calcd for C<sub>29</sub>H<sub>28</sub>BNO<sub>3</sub>SNa [M+Na]<sup>+</sup> 504.1775, found 504.1779.



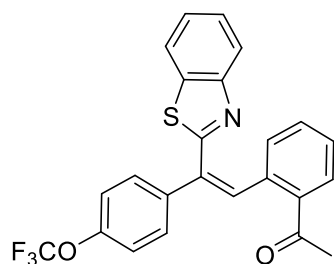
**3h:** 31.4 mg, 38%, *Z/E*>20:1, white solid, m.p. 125-126 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.62 (s, 1H), 7.44-7.33 (m, 5H), 7.32-7.25 (m, 2H), 7.24-7.18 (m, 2H), 2.59 (s, 3H), 1.30 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.3, 167.2, 153.3, 151.3, 137.7, 137.3, 136.9, 136.1, 135.2, 134.3, 131.7, 131.6, 129.4, 127.8, 127.6, 125.8, 125.4, 125.1, 123.5, 121.4, 34.6, 31.3, 29.1. FT-IR: ν (cm<sup>-1</sup>) 3086, 3057, 3025, 2920, 2856, 1679, 1508, 1356. HRMS [ESI] calcd for C<sub>27</sub>H<sub>25</sub>NOSNa [M+Na]<sup>+</sup> 434.1549, found 434.1555.



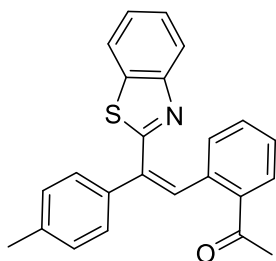
**3i:** 31.4 mg, 32%, *Z/E*>20:1, white solid, m.p. 137-138 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08-7.99 (m, 3H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.77 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 6.8 Hz, 1H), 7.40-7.32 (m, 2H), 7.31-7.23 (m, 2H), 3.93 (s, 3H), 2.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.8, 166.9, 166.2, 153.1, 144.7, 137.4, 137.1, 136.6, 136.0, 134.0, 132.1, 131.6, 129.9, 129.7, 129.6, 128.3, 128.0, 126.0, 125.4, 123.6, 121.4, 52.1, 28.7. FT-IR: ν (cm<sup>-1</sup>) 3059, 3031, 2949, 2849, 1672, 1509, 1431. HRMS [ESI] calcd for C<sub>25</sub>H<sub>19</sub>NO<sub>3</sub>SNa [M+Na]<sup>+</sup> 436.0978, found 436.0985.



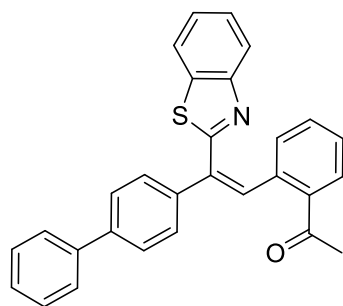
**3j:** 65.0 mg, 77%, *Z/E*>20:1, white solid, m.p. 119-120 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/Petroleum ether = 1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.74 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.70-7.65 (m, 4H), 7.48-7.26 (m, 5H), 2.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.8, 166.1, 153.1, 143.9, 137.7, 137.1, 136.5, 136.0, 133.7, 132.2, 131.6, 130.0, 128.4, 128.4, 126.1, 125.4, 125.4 (q, *J*<sub>C-F</sub> = 3.7 Hz), 124.2 (q, *J*<sub>C-F</sub> = 270.3 Hz), 123.6, 121.4, 28.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.5 (s, CF<sub>3</sub>). FT-IR: ν (cm<sup>-1</sup>) 3057, 2955, 2922, 2852, 1680, 1595, 1562, 1354, 1251. HRMS [ESI] calcd for C<sub>29</sub>H<sub>21</sub>NOSNa [M+Na]<sup>+</sup> 446.0797, found 446.0798.



**3k:** 49.2 mg, 56%, *Z/E*>20:1, yellow solid, m.p. 109-110 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.69 (s, 1H), 7.61-7.55 (m, 2H), 7.48-7.41 (m, 1H), 7.39-7.28 (m, 3H), 7.27-7.20 (m, 3H), 2.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 199.9, 166.4, 153.1, 149.1 (d, *J*<sub>C-F</sub> = 1.8 Hz), 139.0, 137.2, 136.6, 136.5, 136.0, 133.6, 132.1, 131.6, 129.9, 129.5, 128.2, 126.0, 125.3, 123.6, 121.4, 120.9, 120.5 (q, *J*<sub>C-F</sub> = 255.7 Hz), 28.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -57.7 (s, OCF<sub>3</sub>). FT-IR: ν (cm<sup>-1</sup>) 3021, 3000, 2957, 2922, 1912, 1561, 1507, 1434. HRMS [ESI] calcd for C<sub>24</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>2</sub>SNa [M+Na]<sup>+</sup> 462.0746, found 462.0737.

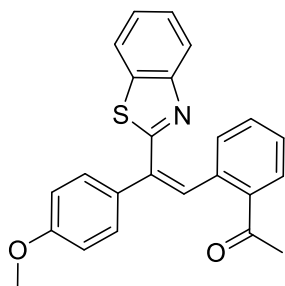


**3l:** 40.1 mg, 54%, *Z/E*>20:1, yellow solid, m.p. 133-134 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.43-7.36 (m, 3H), 7.33-7.25 (m, 2H), 7.23-7.19 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.59 (s, 3H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.3, 167.2, 153.3, 138.2, 137.6, 137.5, 136.9, 136.1, 135.2, 134.3, 131.8, 131.6, 129.5, 129.1, 127.9, 127.8, 125.9, 125.1, 123.5, 121.4, 29.1, 21.3. FT-IR: ν (cm<sup>-1</sup>) 3199, 3058, 3028, 2976, 2854, 2160, 1899, 1510. HRMS [ESI] calcd for C<sub>24</sub>H<sub>19</sub>NOSNa [M+Na]<sup>+</sup> 392.1080, found 392.1087.

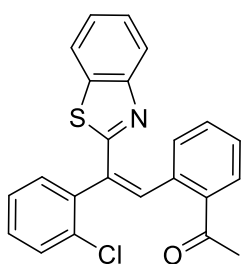


**3m:** 35.4 mg, 43%, *Z/E*=14/1, yellow oil. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.78 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.68-7.55 (m, 6H), 7.50-7.42 (m, 3H), 7.41-7.32 (m, 3H), 7.31-7.24 (m, 2H), 2.66 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.1, 167.0, 153.3, 141.1, 140.8, 139.3, 137.5, 136.8, 136.1, 135.2, 134.8, 131.9, 131.6, 129.6, 128.8, 128.4, 127.9, 127.4, 127.2, 127.1, 125.9, 125.2, 123.6, 121.4, 29.0. FT-IR: ν (cm<sup>-1</sup>) 3057, 3028, 2959, 2921, 2850, 1677, 1594. HRMS [ESI] calcd for C<sub>29</sub>H<sub>21</sub>NOSNa [M+Na]<sup>+</sup> 454.1236, found

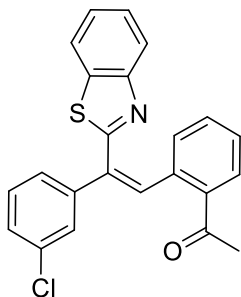
454.1226.



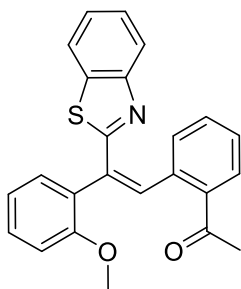
**3n:** 36.2 mg, 47%, *Z/E*>20:1, white solid, m.p. 117-118 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/Petroleum ether = 1/50). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.60 (s, 1H), 7.49-7.41 (m, 3H), 7.36-7.27 (m, 2H), 7.23 (d, *J* = 4.0 Hz, 2H), 6.93-6.88 (m, 2H), 3.83 (s, 3H), 2.63 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.3, 167.4, 159.8, 153.3, 137.6, 136.9, 136.1, 134.8, 133.5, 133.0, 131.8, 131.6, 129.5, 129.3, 127.7, 125.9, 125.1, 123.5, 121.4, 113.9, 55.4, 29.1. FT-IR: ν (cm<sup>-1</sup>) 3064, 3030, 2934, 2161, 1672, 1605, 1560. HRMS [ESI] calcd for C<sub>25</sub>H<sub>19</sub>NO<sub>3</sub>SNa [M+Na]<sup>+</sup> 408.1029, found 408.1036.



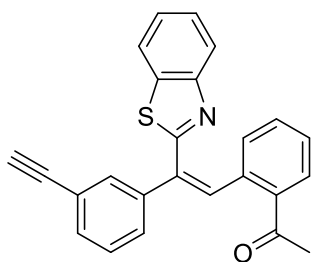
**3o:** 55.3 mg, 71%, *Z/E*>20:1, white solid, m.p. 133-134 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/5/25). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93-7.86 (m, 2H), 7.69-7.61 (m, 2H), 7.50-7.42 (m, 5H), 7.41-7.32 (m, 3H), 7.30-7.24 (m, 1H), 2.61 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.7, 165.8, 152.9, 140.3, 139.2, 137.5, 136.3, 135.9, 134.0, 133.6, 132.1, 131.8, 131.7, 129.8, 129.4, 128.5, 127.0, 125.8, 125.1, 123.6, 121.1, 28.7. FT-IR: ν (cm<sup>-1</sup>) 3054, 2987, 2923, 1951, 1723, 1618, 1564. HRMS [ESI] calcd for C<sub>23</sub>H<sub>16</sub>ClNOSNa [M+Na]<sup>+</sup> 412.0533, found 412.0523.



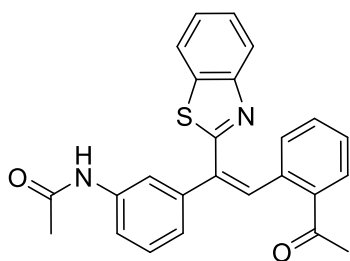
**3p:** 58.5 mg, 75%, *Z/E*>20:1, white solid, m.p. 126-127 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.53 (s, 1H), 7.46-7.38 (m, 2H), 7.37-7.20 (m, 6H), 2.62 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 166.2, 153.2, 142.2, 137.2, 136.8, 136.6, 136.0, 134.3, 133.7, 132.1, 131.6, 129.9, 129.6, 128.2, 128.2, 128.1, 126.3, 126.0, 125.3, 123.6, 121.4, 28.8. FT-IR: ν (cm<sup>-1</sup>) 3057, 3025, 2920, 1944, 1879, 1675, 1592, 1453. HRMS [ESI] calcd for C<sub>23</sub>H<sub>16</sub>ClNOSNa [M+Na]<sup>+</sup> 412.0533, found 412.0524.



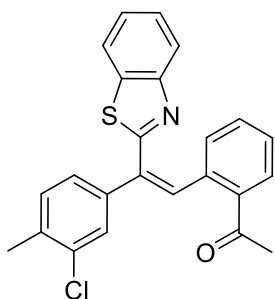
**3q:** 23.1 mg, 30%, *Z/E*=12:1, white solid, m.p. 143-144 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/5/25). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.46 (s, 1H), 7.40-7.24 (m, 6H), 7.08-7.02 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.59 (s, 3H), 2.59 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.3, 167.8, 157.5, 153.1, 137.9, 136.8, 136.7, 136.0, 133.5, 131.7, 131.6, 131.1, 130.7, 129.8, 129.3, 127.8, 125.5, 124.7, 123.3, 121.2, 120.9, 111.6, 55.7, 29.2. FT-IR: ν (cm<sup>-1</sup>) 3052, 2921, 2836, 1673, 1593, 1561, 1490, 1459. HRMS [ESI] calcd for C<sub>24</sub>H<sub>19</sub>NO<sub>2</sub>SNa [M+Na]<sup>+</sup> 408.1029, found 408.1020.



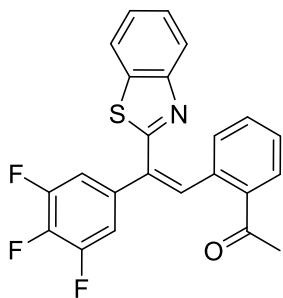
**3r:** 40.9 mg, 54%, *Z/E*=10:1, yellow solid, m.p. 114-115 °C. Purification by flash column chromatography on silica gel (eluent: eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.69-7.66 (m, 2H), 7.56-7.40 (m, 3H), 7.39-7.30 (m, 3H), 7.30-7.18 (m, 2H), 3.05 (s, 1H), 2.64 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 166.4, 153.2, 140.6, 137.3, 136.7, 136.4, 136.1, 134.1, 132.0, 131.8, 131.7, 131.6, 129.8, 128.6, 128.5, 128.1, 126.0, 125.3, 123.6, 122.3, 121.4, 83.6, 77.2, 28.8. FT-IR: ν (cm<sup>-1</sup>) 3288, 3059, 3026, 2954, 2922, 2105, 1676, 1593, 1562, 1433, 1354. HRMS [ESI] calcd for C<sub>25</sub>H<sub>17</sub>NOSNa [M+Na]<sup>+</sup> 402.0923, found 402.0910.



**3s:** 47.8 mg, 58%, *Z/E*=14:1, yellow solid, m.p. 119-120 °C. Purification by flash column chromatography on silica gel (eluent: eluent: Acetone/Petroleum ether = 1/25). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.65-7.59 (m, 2H), 7.44-7.36 (m, 1H), 7.35-7.19 (m, 5H), 7.17-7.11 (m, 1H), 2.60 (s, 3H), 2.05 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.1, 168.5, 167.2, 152.7, 140.7, 138.5, 137.4, 136.6, 135.9, 135.8, 134.5, 132.0, 131.4, 129.7, 129.2, 128.1, 126.0, 125.2, 123.3, 123.2, 121.5, 119.9, 118.9, 28.9, 24.5. FT-IR: ν (cm<sup>-1</sup>) 3264, 3205, 3136, 3059, 2957, 2851, 1941, 1673, 1586, 1455. HRMS [ESI] calcd for C<sub>25</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>SNa [M+Na]<sup>+</sup> 435.1138, found 435.1148.

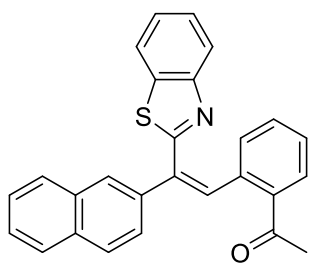


**3t:** 36.4 mg, 45%, *Z/E*>20:1, yellow solid, m.p. 113-114 °C. Purification by flash column chromatography on silica gel (eluent: eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.84 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.74-7.70 (m, 1H), 7.64 (s, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.47-7.41 (m, 1H), 7.37-7.19 (m, 6H), 2.64 (s, 3H), 2.39 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 166.5, 153.2, 139.6, 137.3, 136.6, 136.1, 136.0, 135.8, 134.4, 133.8, 132.0, 131.6, 130.8, 129.8, 128.5, 128.1, 126.3, 126.0, 125.3, 123.6, 121.4, 28.9, 19.9. FT-IR: ν (cm<sup>-1</sup>) 3051, 2999, 2921, 1954, 1841, 1673, 1486, 1429. HRMS [ESI] calcd for C<sub>24</sub>H<sub>18</sub>ClNOSNa [M+Na]<sup>+</sup> 426.0690, found 426.0680.

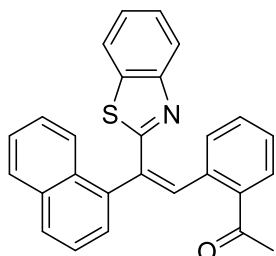


**3u:** 49.9 mg, 61%, *Z/E*>20:1, white solid, m.p. 147-148 °C. Purification by flash column chromatography on silica gel (eluent: eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.71 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.68 (s, 1H), 7.49-7.28 (m, 4H), 7.26-7.18 (m, 3H), 2.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.7, 165.3, 153.0, 152.3 (dd, *J*<sub>C-F</sub> = 9.8, 4.3 Hz), 149.8 (dd, *J*<sub>C-F</sub> = 10.1, 4.3 Hz), 137.9, 136.8, 136.2, 135.9, 132.3, 131.9 (d, *J*<sub>C-F</sub> = 1.8 Hz), 131.5, 130.2, 128.6, 126.2, 125.6, 123.6, 121.4, 112.4 (d, *J*<sub>C-F</sub> = 22.1 Hz), 112.4 (d, *J*<sub>C-F</sub> = 10.2 Hz), 28.5; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -134.49 (d, *J* = 19.9 Hz), -161.02 (t, *J* = 20.3 Hz). FT-IR: ν (cm<sup>-1</sup>) 3064, 2923, 2852,

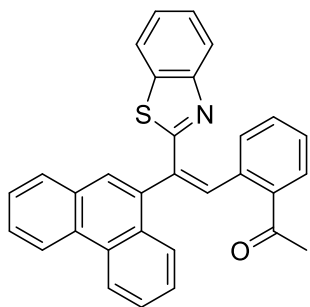
1953, 1884, 1675, 1561, 1481, 1356. HRMS [ESI] calcd for  $C_{23}H_{14}F_3NOSNa$   $[M+Na]^+$  432.0640, found 432.0629.



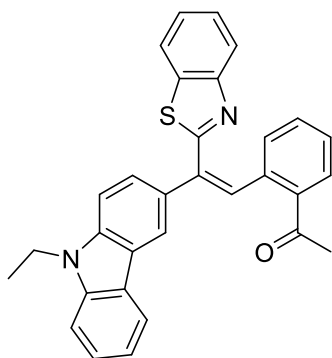
**3v:** 49.5 mg, 61%, *Z/E*=17:1, white solid, m.p. 135-136 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.04 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 7.88-7.79 (m, 5H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.51-7.43 (m, 3H), 7.40-7.27 (m, 4H), 2.65 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  200.1, 167.0, 153.3, 137.8, 137.5, 136.8, 136.2, 135.8, 135.2, 133.4, 133.2, 131.9, 131.6, 129.7, 128.4, 128.0, 128.0, 127.6, 127.4, 126.3, 126.2, 125.9, 125.8, 125.2, 123.6, 121.4, 29.0. FT-IR:  $\nu$  ( $cm^{-1}$ ) 3054, 3032, 2956, 2921, 1980, 1791, 1679, 1452, 1355. HRMS [ESI] calcd for  $C_{27}H_{19}NOSNa$   $[M+Na]^+$  428.1080, found 428.1070.



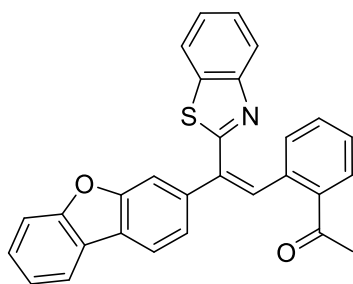
**3w:** 58.0 mg, 72%, *Z/E*>20:1, white solid, m.p. 135-136 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/50/250).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.08 (d, *J* = 8.0 Hz, 1H), 7.94-7.86 (m, 3H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.75 (dd, *J* = 6.8, 0.8 Hz, 1H), 7.65 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.67-7.62 (m, 1H), 7.54-7.39 (m, 6H), 7.36-7.30 (m, 1H), 7.28-7.22 (m, 1H), 2.60 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  199.8, 167.2, 153.2, 139.1, 138.9, 137.6, 136.8, 135.9, 134.0, 133.8, 132.2, 132.0, 131.6, 129.6, 128.8, 128.3, 128.1, 127.7, 126.4, 126.0, 125.9, 125.8, 125.5, 125.0, 123.6, 121.2, 28.7. FT-IR:  $\nu$  ( $cm^{-1}$ ) 3057, 3005, 2922, 2852, 1947, 1678, 1505, 1477. HRMS [ESI] calcd for  $C_{27}H_{19}NOSNa$   $[M+Na]^+$  428.1080, found 428.1070.



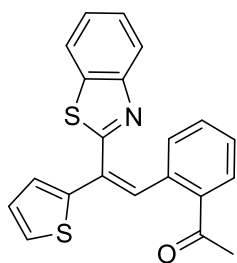
**3x:** 49.2 mg, 54%, *Z/E*>20:1, yellow solid, m.p. 112-113 °C. Purification by flash column chromatography on silica gel (eluent: eluent: Acetone/DCM/Petroleum ether = 2/50/250).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.78-8.68 (m, 2H), 8.13 (d, *J* = 7.6 Hz, 1H), 8.08 (s, 1H), 8.04-7.98 (m, 1H), 7.94-7.88 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.74-7.43 (m, 9H), 7.36-7.29 (m, 1H), 7.28-7.22 (m, 1H), 2.62 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  199.9, 167.0, 153.2, 138.8, 137.9, 137.7, 136.8, 135.9, 134.2, 132.0, 131.6, 131.2, 130.7, 129.6, 129.1, 128.6, 128.2, 127.0, 126.9, 126.8, 126.5, 125.8, 125.1, 123.5, 122.9, 122.6, 121.2, 28.7. FT-IR:  $\nu$  ( $cm^{-1}$ ) 3027, 2956, 2922, 1955, 1677, 1562, 1491, 1450, 1354. HRMS [EI] calcd for  $C_{31}H_{21}NOS$   $[M]^+$  455.1344, found 455.1347.



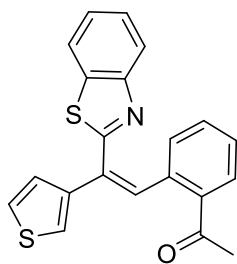
**3y:** 43.7 mg, 46%, *Z/E*=16:1, yellow solid, m.p. 217-218 °C. Purification by flash column chromatography on silica gel (eluent: eluent: Acetone/Petroleum ether = 1/60). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21 (d, *J* = 1.6 Hz, 1H), 8.05-7.97 (m, 2H), 7.78-7.70 (m, 2H), 7.67 (s, 1H), 7.59 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.46-7.27 (m, 6H), 7.26-7.12 (m, 3H), 4.34 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.6, 168.0, 153.4, 140.4, 140.0, 137.8, 137.1, 136.2, 136.2, 133.5, 131.7, 131.6, 129.4, 127.6, 126.1, 125.8, 125.8, 125.1, 123.6, 123.1, 123.1, 121.4, 120.7, 120.3, 119.0, 108.6, 108.3, 37.7, 29.3, 13.9. FT-IR: ν (cm<sup>-1</sup>) 3062, 2905, 2822, 2810, 1966, 1889, 1770, 1694, 1590. HRMS [EI] calcd for C<sub>31</sub>H<sub>24</sub>N<sub>2</sub>OS [M]<sup>+</sup> 472.1609, found 472.1613.



**3z:** 65.9 mg, 74%, *Z/E*=12:1, white solid, m.p. 126-127 °C. Purification by flash column chromatography on silica gel (eluent: eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.98-7.91 (m, 2H), 7.86-7.83 (m, 1H), 7.82 (s, 1H), 7.77 (d, *J* = 1.2 Hz, 1H), 7.76-7.73 (m, 1H), 7.59-7.54 (m, 2H), 7.49-7.42 (m, 2H), 7.39-7.20 (m, 5H), 2.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.1, 167.0, 156.8, 156.4, 153.3, 139.8, 137.4, 136.8, 136.2, 136.0, 134.9, 132.0, 131.6, 129.8, 128.1, 127.3, 126.0, 125.3, 124.3, 124.0, 123.6, 123.0, 122.8, 121.5, 120.8, 120.4, 111.7, 111.4, 28.9. FT-IR: ν (cm<sup>-1</sup>) 3059, 2955, 2922, 2852, 1946, 1789, 1676, 1594, 1493. HRMS [ESI] calcd for C<sub>29</sub>H<sub>19</sub>NO<sub>2</sub>SNa [M+Na]<sup>+</sup> 468.1029, found 468.1030.

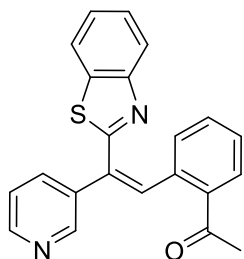


**3aa:** 47.8 mg, 66%, *Z/E*=11:1, yellow solid, m.p. 106-107 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 2/5/25). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.79 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.52-7.44 (m, 1H), 7.40-7.27 (m, 3H), 7.25-7.06 (m, 3H), 7.04-6.95 (m, 1H), 2.66 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.1, 165.7, 153.1, 143.3, 137.3, 136.2, 136.0, 132.9, 131.8, 131.6, 129.7, 129.0, 127.9, 127.6, 126.8, 126.0, 125.8, 125.4, 123.6, 121.5, 29.0. FT-IR: ν (cm<sup>-1</sup>) 3111, 3036, 2919, 2034, 1906, 1789, 1594, 1496. HRMS [ESI] calcd for C<sub>21</sub>H<sub>15</sub>NOS<sub>2</sub>Na [M+Na]<sup>+</sup> 384.0487, found 384.0494.

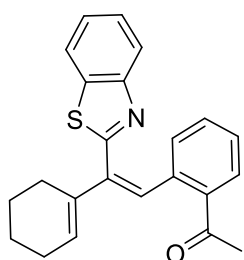


**3ab:** 38.3 mg, 53%, *Z/E*=14:1, yellow solid, m.p. 105-106 °C. Purification by flash column chromatography on silica gel (eluent: eluent: Acetone/DCM/Petroleum ether = 2/5/25). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.78 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.50-7.43 (m, 1H), 7.41-7.27 (m, 5H), 7.26-7.17 (m, 2H), 2.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.2, 166.6, 153.2, 141.0, 137.3, 136.5, 136.0, 133.6, 131.8, 131.7, 130.0, 129.7, 127.8, 126.5, 125.9, 125.8, 125.2, 123.8, 123.5, 121.4, 29.0. FT-IR: ν (cm<sup>-1</sup>) 3111, 3057, 2960, 2922, 1994, 1916, 1886, 1675, 1523. HRMS [ESI] calcd for C<sub>21</sub>H<sub>15</sub>NOS<sub>2</sub>Na [M+Na]<sup>+</sup> 384.0487, found 384.0494.

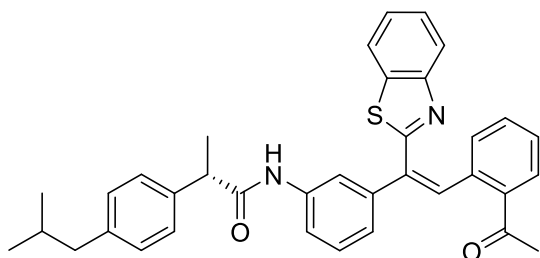




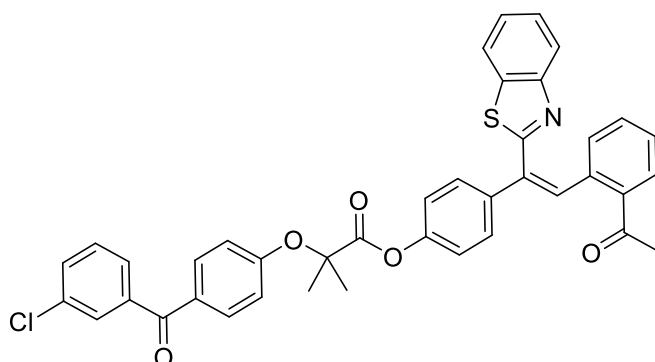
**3ac:** 48.5 mg, 68%, *Z/E*>20:1, yellow solid, m.p. 130-131 °C. Purification by flash column chromatography on silica gel (Acetone/Petroleum ether = 1/25). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.83 (s, 1H), 8.57 (d, *J* = 4.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.85-7.80 (m, 1H), 7.76-7.67 (m, 2H), 7.47-7.36 (m, 2H), 7.35-7.24 (m, 4H), 2.63 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 165.8, 153.0, 149.1, 149.1, 137.6, 137.1, 136.4, 136.3, 135.9, 135.6, 132.2, 131.9, 131.6, 130.0, 128.5, 126.1, 125.4, 123.5, 123.1, 121.4, 28.6. FT-IR: ν (cm<sup>-1</sup>) 3065, 3019, 2920, 2526, 1965, 1801, 1673, 1581, 1499. HRMS [ESI] calcd for C<sub>22</sub>H<sub>17</sub>N<sub>2</sub>OS [M+H]<sup>+</sup> 357.1056, found 357.1049.



**3ad:** 15.8 mg, 22%, *Z/E*>20:1, white solid, m.p. 133-134 °C. Purification by flash column chromatography on silica gel (eluent: eluent: Acetone/DCM/Petroleum ether = 2/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08-8.05 (m, 1H), 7.73-7.70 (m, 2H), 7.48-7.42 (m, 1H), 7.35 (s, 1H), 7.34-7.29 (m, 1H), 7.21-7.16 (m, 1H), 7.13-7.05 (m, 2H), 5.79-5.74 (m, 1H), 2.62 (s, 3H), 2.50-2.43 (m, 2H), 2.18-2.11 (m, 2H), 1.84-1.76 (m, 2H), 1.69-1.62 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.6, 167.1, 153.1, 137.2, 137.1, 136.6, 136.4, 136.1, 131.5, 131.4, 130.3, 129.8, 129.3, 127.2, 125.7, 124.9, 123.3, 121.4, 29.3, 26.2, 26.1, 22.8, 22.0. FT-IR: ν (cm<sup>-1</sup>) 3056, 2925, 2855, 1670, 1594, 1475, 1382, 1309. HRMS [ESI] calcd for C<sub>23</sub>H<sub>21</sub>NOSNa [M+Na]<sup>+</sup> 382.1236, found 382.1226.

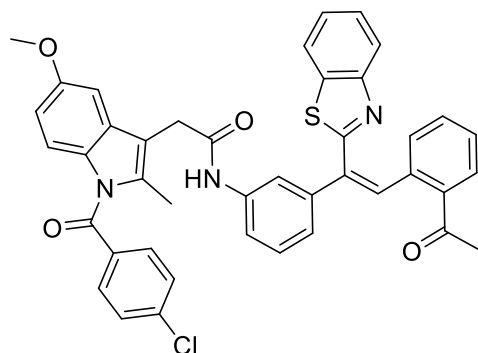


**3ae:** 36.8 mg, 33%, *Z/E*=15:1, white solid, m.p. 117-118 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.64-7.37 (m, 5H), 7.36-7.27 (m, 3H), 7.26-7.15 (m, 5H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.65 (q, *J* = 6.8 Hz, 1H), 2.61 (s, 3H), 2.44 (d, *J* = 6.8 Hz, 2H), 1.89-1.77 (m, 1H), 1.55 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 172.5, 166.7, 153.1, 141.1, 141.0, 138.2, 138.1, 137.4, 136.7, 136.1, 136.0, 134.6, 131.9, 131.5, 129.8, 129.6, 129.0, 128.0, 127.4, 125.9, 125.2, 124.0, 123.5, 121.4, 119.6, 118.9, 47.8, 45.0, 30.2, 28.9, 22.4, 18.6. FT-IR: ν (cm<sup>-1</sup>) 3293, 3059, 2953, 1768, 1677, 1510, 1455, 1355, 1299. HRMS [EI] calcd for C<sub>36</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>S [M]<sup>+</sup> 558.2341, found 558.2340.

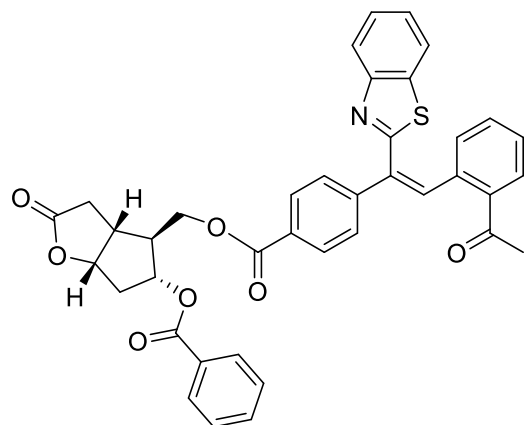


**3af:** 61.8 mg, 46%, *Z/E*=10:1, white solid, m.p. 108-109 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.81-7.75 (m, 2H), 7.74-7.68 (m, 3H), 7.65 (s, 1H),

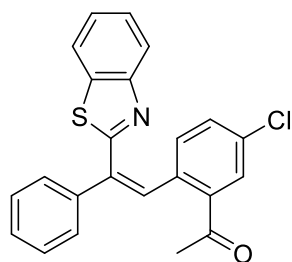
7.58-7.51 (m, 2H), 7.48-7.40 (m, 3H), 7.37-7.19 (m, 4H), 7.04-6.96 (m, 4H), 2.63 (s, 3H), 1.84 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.0, 194.2, 172.3, 166.6, 159.6, 153.1, 150.3, 138.5, 138.4, 137.2, 136.7, 136.3, 136.1, 136.0, 133.9, 132.2, 132.0, 131.6, 131.2, 130.7, 129.8, 129.3, 128.6, 128.1, 126.0, 125.3, 123.5, 121.4, 121.1, 117.4, 79.5, 28.8, 25.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3060, 2994, 2922, 1754, 1678, 1503, 1355, 1302. HRMS [EI] calcd for  $\text{C}_{40}\text{H}_{30}\text{ClNO}_5\text{S}$  [M] $^+$  671.1533, found 671.1532.



**3ag:** 32.7 mg, 23%,  $Z/E=18:1$ , yellow solid, m.p. 161-162 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.4$  Hz, 1H), 7.81 (d,  $J = 7.2$  Hz, 1H), 7.72-7.62 (m, 3H), 7.61-7.55 (m, 2H), 7.51-7.37 (m, 5H), 7.36-7.27 (m, 3H), 7.25-7.14 (m, 3H), 6.93 (d,  $J = 2.0$  Hz, 1H), 6.87 (d,  $J = 8.8$  Hz, 1H), 6.68 (dd,  $J = 8.8, 2.4$  Hz, 1H), 3.78-3.75 (m, 5H), 2.60 (s, 3H), 2.41 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.0, 168.3, 168.2, 166.7, 156.4, 153.1, 141.2, 139.5, 137.7, 137.3, 136.7, 136.6, 136.3, 136.0, 134.4, 133.6, 132.0, 131.5, 131.2, 130.9, 130.2, 129.7, 129.2, 129.1, 128.0, 126.0, 125.2, 124.4, 123.5, 121.4, 120.1, 119.5, 115.2, 112.6, 112.4, 100.7, 55.8, 33.3, 28.8, 13.4. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3300, 3060, 2956, 2922, 1675, 1588, 1476, 1400, 1355. HRMS [EI] calcd for  $\text{C}_{42}\text{H}_{32}\text{ClN}_3\text{O}_4\text{S}$  [M] $^+$  709.1802, found 709.1798.

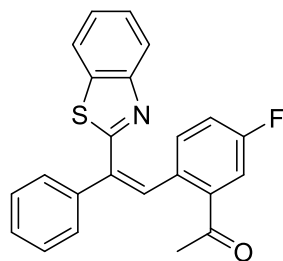


**3ah:** 34.2 mg, 26%,  $Z/E=10:1$ , white solid, m.p. 110-111 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/Petroleum ether = 1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07-7.95 (m, 5H), 7.87 (d,  $J = 7.6$  Hz, 1H), 7.77 (s, 1H), 7.72 (d,  $J = 7.6$  Hz, 1H), 7.60 (d,  $J = 8.4$  Hz, 2H), 7.55-7.49 (m, 1H), 7.48-7.22 (m, 7H), 5.50-5.43 (m, 1H), 5.15-5.08 (m, 1H), 4.41 (d,  $J = 6.4$  Hz, 2H), 3.01-2.85 (m, 2H), 2.64 (s, 3H), 2.65-2.54 (m, 3H), 2.43-2.35 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.8, 176.2, 166.1, 165.9, 153.1, 145.3, 137.7, 137.1, 136.5, 136.0, 133.8, 133.4, 132.2, 131.6, 130.0, 129.8, 129.7, 129.4, 128.8, 128.5, 128.4, 128.2, 126.1, 125.4, 123.6, 121.4, 84.1, 77.5, 64.5, 51.8, 40.6, 38.4, 35.8, 28.7. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3061, 2953, 2895, 1769, 1713, 1604, 1492, 1357, 1313. HRMS [ESI] calcd for  $\text{C}_{39}\text{H}_{31}\text{NO}_7\text{SNa}$  [M+Na] $^+$  680.1713, found 680.1717.

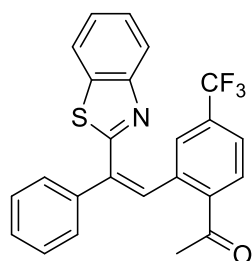


**4a:** 59.2 mg, 76%,  $Z/E>20:1$ , white solid, m.p. 141-142 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 8.0$  Hz, 1H), 7.79-7.74 (m, 2H), 7.58 (s, 1H), 7.55-7.50 (m, 2H), 7.49-7.42 (m, 1H), 7.41-7.30 (m, 4H), 7.24-7.16 (m, 2H), 2.61 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  198.9, 166.5, 153.3, 140.0, 138.8, 136.0, 136.0, 135.1, 133.7, 133.6, 132.8, 131.7, 129.5,

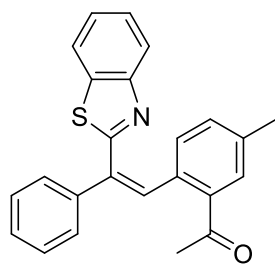
128.5, 128.0, 126.1, 125.4, 123.6, 121.5, 29.1. FT-IR:  $\nu$  (cm<sup>-1</sup>) 3058, 2921, 1846, 1686, 1589, 1455, 1352. HRMS [ESI] calcd for C<sub>23</sub>H<sub>16</sub>ClNOSNa [M+Na]<sup>+</sup> 412.0533, found 412.0538.



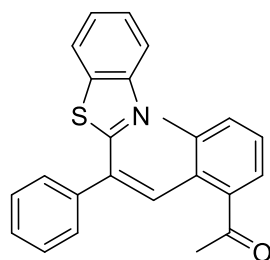
**4b**: 55.7 mg, 75%, *Z/E*=12:1, white solid, m.p. 133-134 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.54-7.42 (m, 4H), 7.41-7.29 (m, 4H), 7.26-7.20 (m, 1H), 7.00-6.93 (m, 1H), 2.61 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.9, 166.7, 161.8 (d, *J*<sub>C-F</sub> = 247.9 Hz), 153.2, 140.1, 139.1 (d, *J*<sub>C-F</sub> = 5.8 Hz), 135.9 (d, *J*<sub>C-F</sub> = 25.7 Hz), 133.8, 133.4 (d, *J*<sub>C-F</sub> = 7.7 Hz), 132.7 (d, *J*<sub>C-F</sub> = 3.5 Hz), 130.1, 128.5, 128.4, 128.0, 126.0, 125.3, 123.6, 121.4, 118.9 (d, *J*<sub>C-F</sub> = 21.0 Hz), 116.3 (d, *J*<sub>C-F</sub> = 22.3 Hz), 29.0; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -112.4. FT-IR:  $\nu$  (cm<sup>-1</sup>) 3192, 3052, 3002, 1887, 1687, 1572, 1455. HRMS [ESI] calcd for C<sub>23</sub>H<sub>16</sub>FNOSNa [M+Na]<sup>+</sup> 396.0829, found 396.0819.



**4c**: 49.1 mg, 58%, *Z/E*=7:1, white solid, m.p. 113-114 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.99-7.95 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.77-7.73 (m, 1H), 7.62 (s, 1H), 7.60-7.53 (m, 4H), 7.48-7.31 (m, 5H), 2.62 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  199.7, 165.8, 153.1, 140.5, 139.8, 137.2, 136.9, 135.9, 132.8 (q, *J*<sub>C-F</sub> = 32.6 Hz), 132.7, 129.3, 128.7, 128.6 (q, *J*<sub>C-F</sub> = 3.6 Hz), 128.5, 128.1, 126.1, 125.4, 124.4 (q, *J*<sub>C-F</sub> = 3.6 Hz), 123.6, 123.2 (q, *J*<sub>C-F</sub> = 271.4 Hz), 121.3, 29.3; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.4. FT-IR:  $\nu$  (cm<sup>-1</sup>) 3123, 3082, 3030, 1804, 1681, 1574, 1493, 1444, 1353. HRMS [ESI] calcd for C<sub>24</sub>H<sub>16</sub>F<sub>3</sub>NOSNa [M+Na]<sup>+</sup> 446.0797, found 446.0785.

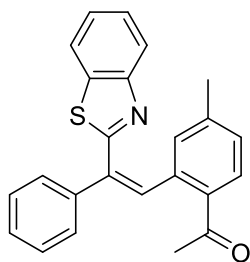


**4d**: 47.0 mg, 64%, *Z/E*>20:1, white solid, m.p. 126-127 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.62 (s, 1H), 7.56-7.50 (m, 2H), 7.49-7.41 (m, 1H), 7.40-7.30 (m, 4H), 7.17-7.12 (m, 1H), 7.09-7.04 (m, 1H), 2.63 (s, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.4, 167.2, 153.3, 140.4, 137.9, 137.5, 136.1, 135.3, 134.9, 133.8, 132.6, 131.5, 130.2, 128.4, 128.2, 128.0, 125.9, 125.1, 123.5, 121.4, 29.1, 21.2. FT-IR:  $\nu$  (cm<sup>-1</sup>) 3049, 3031, 2989, 2958, 1827, 1795, 1683, 1555, 1468, 1353. HRMS [ESI] calcd for C<sub>24</sub>H<sub>19</sub>NOSNa [M+Na]<sup>+</sup> 392.1080, found 392.1083.



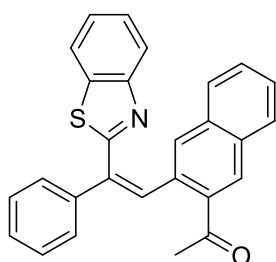
**4e**: 42.2 mg, 57%, *Z/E*>20:1, yellow solid, m.p. 114-115 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.65-7.57 (m, 3H), 7.47-7.26 (m, 8H), 2.48 (s, 3H), 2.33 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  200.7, 165.8, 152.8, 140.6, 139.3, 138.1, 136.0, 135.8, 135.4, 135.4, 133.7, 128.6, 128.3, 128.1, 127.9, 126.7, 125.8, 125.1, 123.6,

121.1, 29.1, 20.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3023, 2946, 2921, 1948, 1797, 1677, 1589, 1492, 1427. HRMS [ESI] calcd for  $\text{C}_{24}\text{H}_{19}\text{NOSNa}$  [ $\text{M}+\text{Na}$ ] $^{+}$  392.1080, found 392.1081.



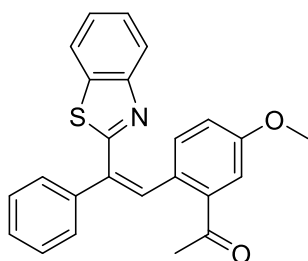
**4f:** 47.3 mg, 64%,  $Z/E > 20:1$ , white solid, m.p. 143-144 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/Petroleum ether = 1/50).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.0$  Hz, 1H), 7.76-7.70 (m, 2H), 7.67 (s, 1H), 7.58-7.51 (m, 2H), 7.47-7.28 (m, 5H), 7.17-7.09 (m, 2H), 2.60 (s, 3H), 2.15 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.5, 167.0, 153.2, 142.6, 140.4, 137.1, 136.1, 135.9, 134.8, 134.7, 132.3, 123.0, 128.6, 128.4, 128.1, 128.0, 125.8, 125.1, 123.4, 121.3, 28.7, 21.3.

FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3069, 2944, 2920, 2566, 1790, 1680, 1625, 1453, 1366. HRMS [ESI] calcd for  $\text{C}_{24}\text{H}_{19}\text{NOSNa}$  [ $\text{M}+\text{Na}$ ] $^{+}$  392.1080, found 392.1086.



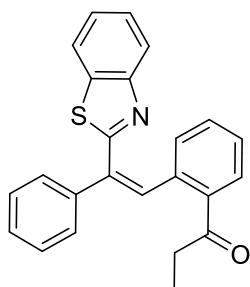
**4g:** 43.1 mg, 53%,  $Z/E > 20:1$ , white solid, m.p. 169-170 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (s, 1H), 7.98 (d,  $J = 8.0$  Hz, 1H), 7.88-7.82 (m, 1H), 7.75 (s, 2H), 7.60 (d,  $J = 8.0$  Hz, 1H), 7.58-7.53 (m, 3H), 7.50-7.41 (m, 2H), 7.40-7.29 (m, 4H), 7.27-7.20 (m, 1H), 2.71 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.8, 167.2, 153.2, 140.5, 136.0, 135.6, 135.6, 134.8, 134.4,

133.1, 131.8, 131.1, 131.1, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.1, 125.8, 125.1, 123.4, 121.4, 28.7. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3144, 3006, 2944, 2879, 2011, 1848, 1676, 1595, 1489, 1350. HRMS [ESI] calcd for  $\text{C}_{27}\text{H}_{19}\text{NOSNa}$  [ $\text{M}+\text{Na}$ ] $^{+}$  428.1080, found 428.1070.



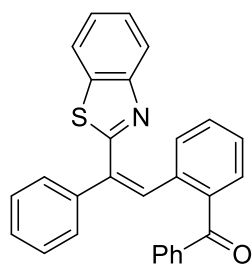
**4h:** 46.5 mg, 60%,  $Z/E = 5:1$ , yellow oil. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (d,  $J = 8.0$  Hz, 1H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.59 (s, 1H), 7.53-7.41 (m, 3H), 7.40-7.27 (m, 5H), 7.17 (d,  $J = 8.8$  Hz, 1H), 6.78 (dd,  $J = 8.4, 2.8$  Hz, 1H), 3.80 (s, 3H), 2.62 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  200.2, 167.3, 159.1, 153.3, 140.5, 139.0, 136.1, 134.7, 132.9, 130.9, 128.8, 128.4,

128.1, 127.9, 125.9, 125.2, 123.5, 121.4, 116.6, 115.4, 55.5, 29.2. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3057, 3002, 2959, 1952, 1678, 1600, 1559, 1455, 1354. HRMS [ESI] calcd for  $\text{C}_{24}\text{H}_{19}\text{NO}_2\text{SNa}$  [ $\text{M}+\text{Na}$ ] $^{+}$  408.1029, found 408.1029.

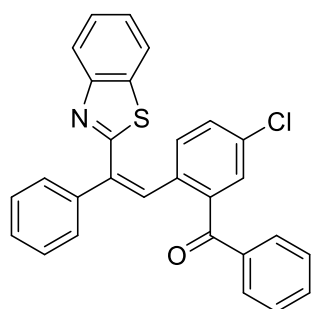


**4i:** 40.5 mg, 55%,  $Z/E > 20:1$ , yellow solid, m.p. 135-136 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.0$  Hz, 1H), 7.79 (d,  $J = 7.6$  Hz, 1H), 7.73 (d,  $J = 7.6$  Hz, 1H), 7.65 (s, 1H), 7.54-7.49 (m, 2H), 7.47-7.41 (m, 1H), 7.40-7.28 (m, 5H), 7.27-7.22 (m, 2H), 3.00 (q,  $J = 7.2$  Hz, 2H), 1.21 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  203.2, 167.1, 153.3, 140.4, 137.6, 136.7, 136.1, 135.2, 131.6, 131.5, 128.8, 128.4, 128.3, 128.0, 127.9, 125.9, 125.2, 123.5,

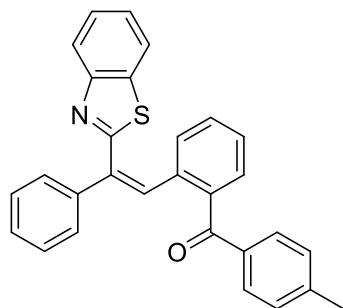
121.4, 34.1, 8.4. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3053, 2920, 2333, 1938, 1859, 1660, 1594, 1491. HRMS [ESI] calcd for  $\text{C}_{24}\text{H}_{19}\text{NOSNa}$  [ $\text{M}+\text{Na}$ ] $^{+}$  392.1080, found 392.1075.



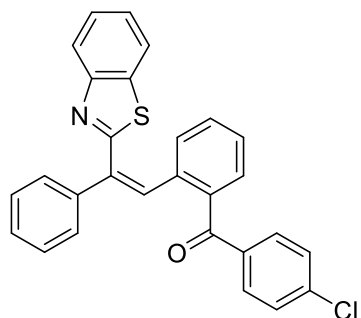
**4j:** 36.5 mg, 44%,  $Z/E > 20:1$ , yellow oil. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.0$  Hz, 1H), 7.83-7.74 (m, 3H), 7.59-7.51 (m, 1H), 7.50-7.23 (m, 14H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.4, 166.6, 153.3, 140.2, 140.2, 138.8, 137.6, 136.8, 136.1, 136.1, 133.1, 132.8, 130.7, 130.5, 130.2, 129.3, 128.4, 128.3, 127.8, 127.3, 125.9, 125.3, 123.6, 121.5. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3137, 3008, 2942, 1933, 1755, 1653, 1438. HRMS [ESI] calcd for  $\text{C}_{28}\text{H}_{19}\text{NOSNa}$  [ $\text{M}+\text{Na}$ ] $^{+}$  440.1080, found 440.1077.



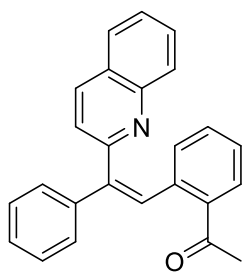
**4k:** 47.5 mg, 53%,  $Z/E > 20:1$ , yellow solid, m.p. 120-121  $^{\circ}\text{C}$ . Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 8.4$  Hz, 1H), 7.88-7.79 (m, 3H), 7.67-7.58 (m, 1H), 7.56-7.37 (m, 5H), 7.37-7.25 (m, 8H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.9, 166.2, 153.4, 140.3, 139.9, 137.5, 136.9, 136.1, 134.4, 133.5, 133.5, 132.0, 131.2, 130.5, 130.2, 129.0, 128.6, 128.6, 128.4, 127.8, 126.1, 125.5, 123.7, 121.6. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3057, 3025, 2921, 1977, 1663, 1552, 1490, 1388. HRMS [ESI] calcd for  $\text{C}_{28}\text{H}_{18}\text{ClNOSNa}$  [ $\text{M}+\text{Na}$ ] $^{+}$  474.0690, found 474.0703.



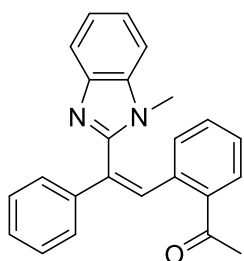
**4l:** 28.5 mg, 33%,  $Z/E > 20:1$ , yellow solid, m.p. 162-163  $^{\circ}\text{C}$ . Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 8.0$  Hz, 1H), 7.74 (d,  $J = 8.0$  Hz, 1H), 7.67 (d,  $J = 8.0$  Hz, 2H), 7.46-7.37 (m, 2H), 7.36-7.27 (m, 4H), 7.26-7.22 (m, 6H), 7.16 (d,  $J = 8.4$  Hz, 2H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.1, 166.7, 153.4, 144.1, 140.3, 139.1, 136.7, 136.2, 135.9, 135.0, 132.8, 130.6, 130.5, 130.3, 129.1, 128.3, 128.3, 127.8, 127.3, 125.9, 125.3, 123.6, 121.5, 21.7. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3152, 2921, 2162, 1934, 1853, 1650, 1489, 1445, 1351. HRMS [ESI] calcd for  $\text{C}_{29}\text{H}_{22}\text{NOS}$  [ $\text{M}+\text{H}$ ] $^{+}$  432.1417, found 432.1406.



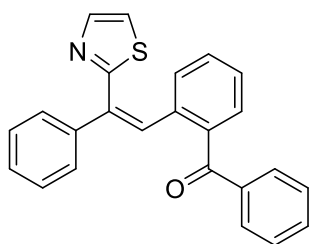
**4m:** 33.9 mg, 36%,  $Z/E > 20:1$ , yellow solid, m.p. 193-194  $^{\circ}\text{C}$ . Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.0$  Hz, 1H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.72-7.67 (m, 2H), 7.49-7.42 (m, 1H), 7.42-7.24 (m, 13H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 166.4, 153.3, 140.2, 139.6, 138.3, 137.1, 136.2, 135.7, 132.6, 131.6, 130.8, 130.7, 129.1, 128.6, 128.5, 128.4, 127.9, 127.4, 126.0, 125.4, 123.6, 121.4. FT-IR:  $\nu$  ( $\text{cm}^{-1}$ ) 3118, 3014, 2992, 1994, 1843, 1756, 1654, 1539, 1467. HRMS [ESI] calcd for  $\text{C}_{28}\text{H}_{18}\text{ClNOSNa}$  [ $\text{M}+\text{Na}$ ] $^{+}$  474.0690, found 474.0689.



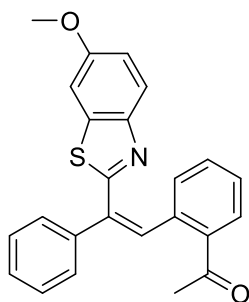
**4n:** 21.7 mg, 31%, *Z/E*>20:1, white solid, m.p. 136-137 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.72-7.65 (m, 2H), 7.58 (s, 1H), 7.54-7.48 (m, 1H), 7.45-7.40 (m, 2H), 7.36-7.28 (m, 3H), 7.21-7.15 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.08-7.02 (m, 1H), 7.01-6.97 (m, 1H), 2.63 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.0, 159.7, 148.1, 142.3, 141.2, 137.9, 137.5, 135.8, 131.9, 131.3, 130.8, 129.7, 129.3, 129.1, 128.3, 127.9, 127.7, 127.5, 127.0, 126.8, 126.5, 124.2, 29.3. FT-IR: ν (cm<sup>-1</sup>) 3073, 3055, 3037, 2920, 1954, 1672, 1557, 1474, 1351. HRMS [EI] calcd for C<sub>25</sub>H<sub>19</sub>NO [M]<sup>+</sup> 349.1467, found 349.1465.



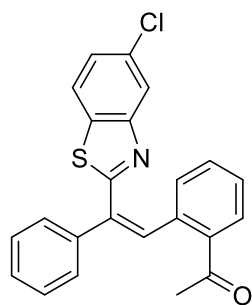
**4o:** 30.3 mg, 43%, *Z/E*>20:1, white solid, m.p. 144-145 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84-7.80 (m, 1H), 7.77 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.72 (s, 1H), 7.50-7.45 (m, 2H), 7.37-7.29 (m, 3H), 7.28-7.16 (m, 4H), 7.15-7.06 (m, 2H), 3.29 (s, 3H), 2.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.6, 152.1, 143.1, 139.6, 136.9, 136.7, 135.2, 134.8, 132.2, 130.6, 130.6, 129.5, 128.6, 128.1, 127.7, 127.1, 122.5, 122.1, 119.9, 109.5, 29.9, 28.8. FT-IR: ν (cm<sup>-1</sup>) 3057, 3022, 2920, 1976, 1727, 1673, 1596, 1491, 1445. HRMS [ESI] calcd for C<sub>24</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 353.1648, found 353.1643.



**4p:** 26.9 mg, 44%, *Z/E*>20:1, white solid, m.p. 113-114 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79-7.71 (m, 3H), 7.56-7.50 (m, 1H), 7.45-7.38 (m, 3H), 7.37-7.29 (m, 2H), 7.28-7.18 (m, 5H), 7.16-7.08 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.5, 165.9, 143.1, 140.7, 138.8, 137.9, 136.9, 136.4, 133.0, 131.8, 130.5, 130.5, 130.2, 129.4, 128.5, 128.2, 127.9, 127.3, 120.7. FT-IR: ν (cm<sup>-1</sup>) 3121, 3080, 3052, 2955, 2921, 1966, 1720, 1658, 1594, 1491, 1336. HRMS [ESI] calcd for C<sub>24</sub>H<sub>17</sub>NOSNa [M+Na]<sup>+</sup> 390.0923, found 390.0918.

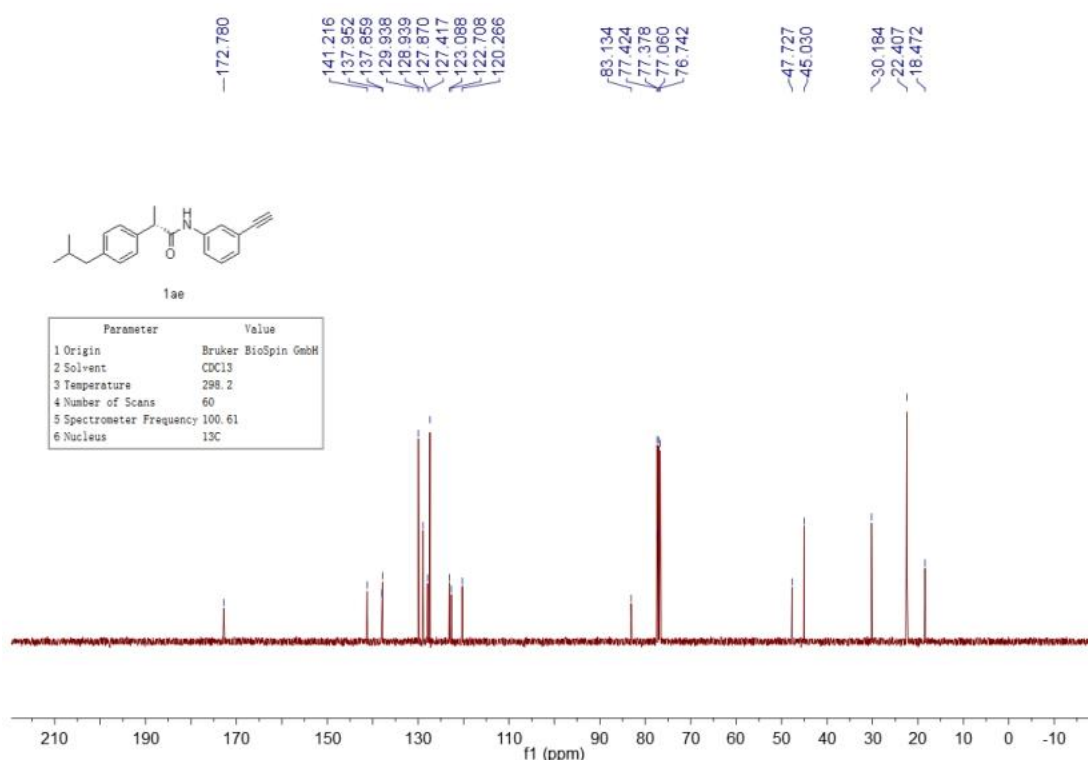
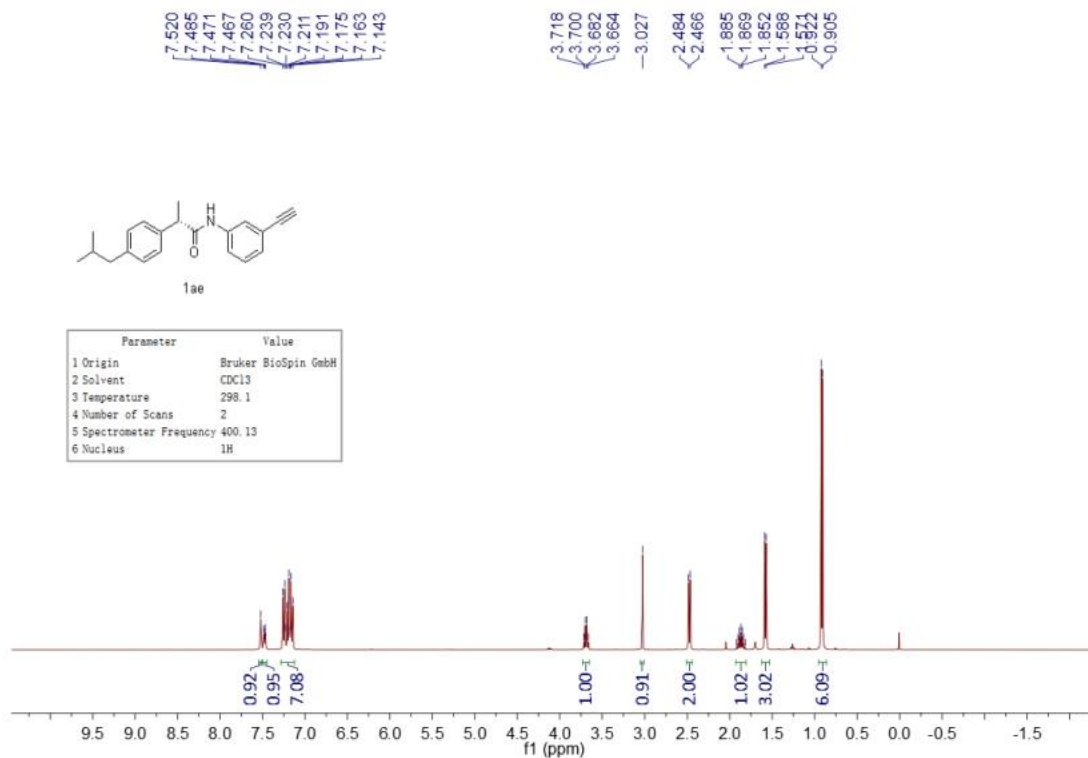


**4q:** 45.8 mg, 59%, *Z/E*=12:1, yellow solid, m.p. 111-112 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.62 (s, 1H), 7.55-7.50 (m, 2H), 7.41-7.23 (m, 6H), 7.17 (d, *J* = 2.8 Hz, 1H), 7.03 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.83 (s, 3H), 2.62 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.2, 164.3, 157.7, 147.8, 140.4, 137.6, 137.5, 136.9, 135.3, 134.8, 131.8, 131.6, 129.5, 128.4, 128.2, 128.1, 127.8, 124.0, 115.4, 103.7, 55.8, 29.1. FT-IR: ν (cm<sup>-1</sup>) 3064, 3001, 2920, 1975, 1855, 1674, 1553, 1462. HRMS [ESI] calcd for C<sub>24</sub>H<sub>19</sub>NO<sub>2</sub>SNa [M+Na]<sup>+</sup> 440.1029, found 440.1019.

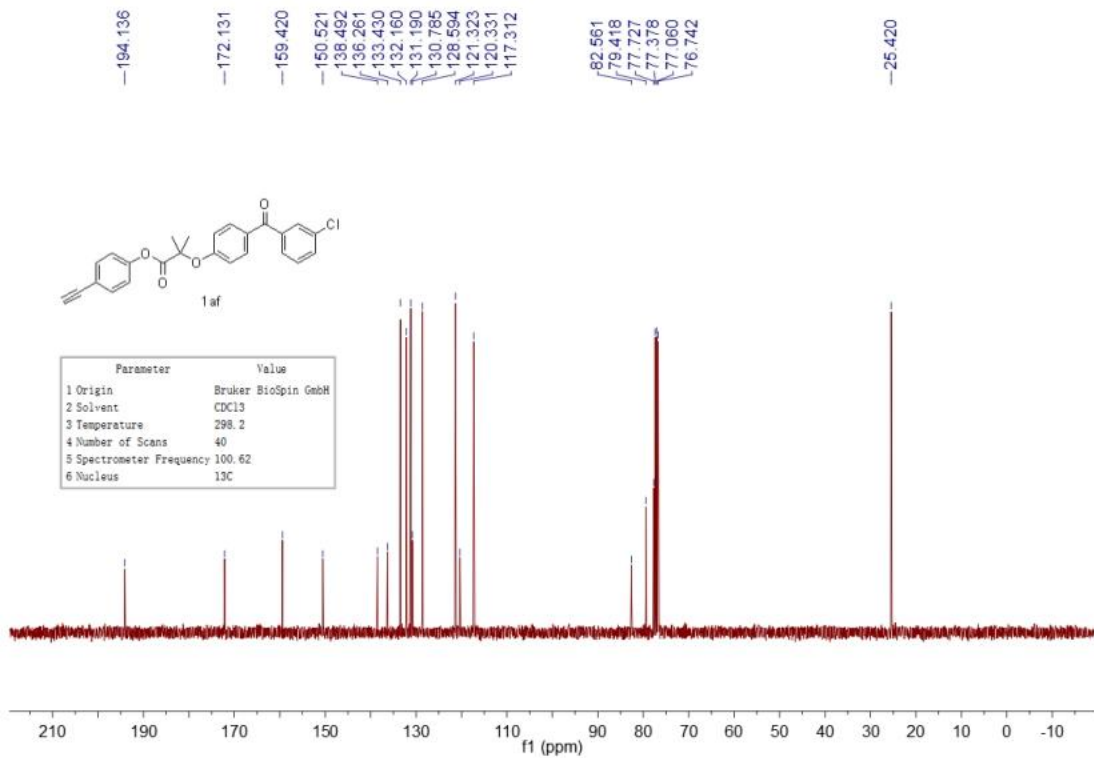
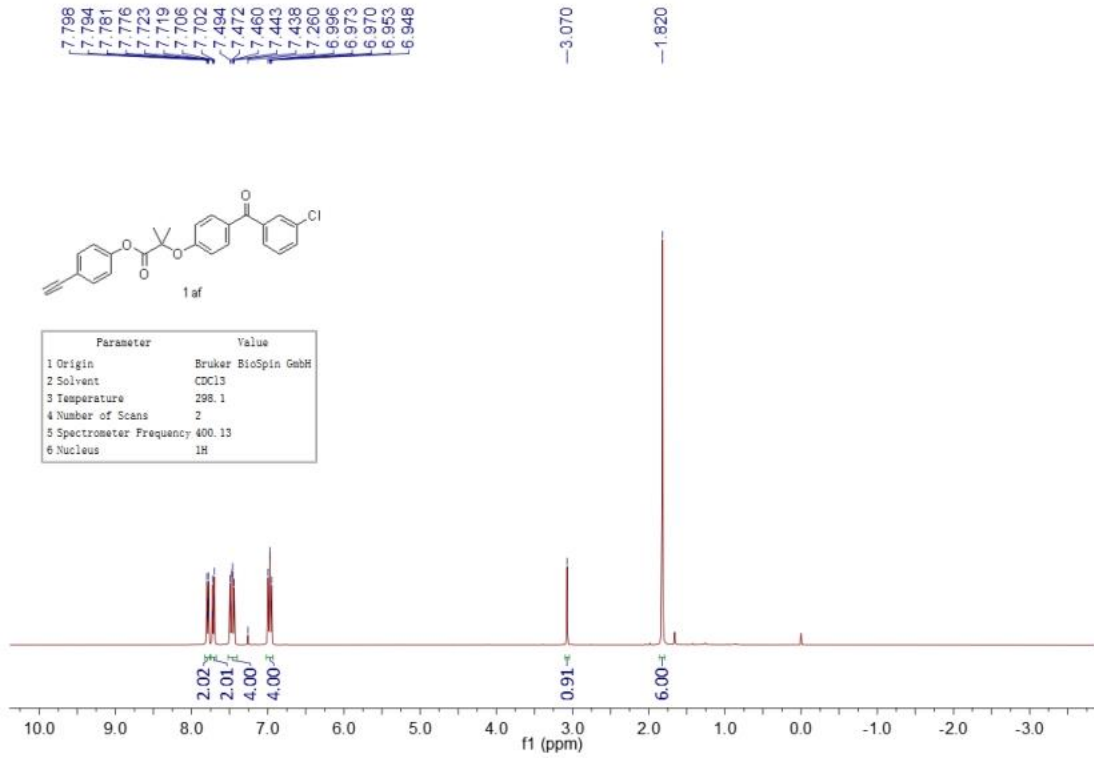


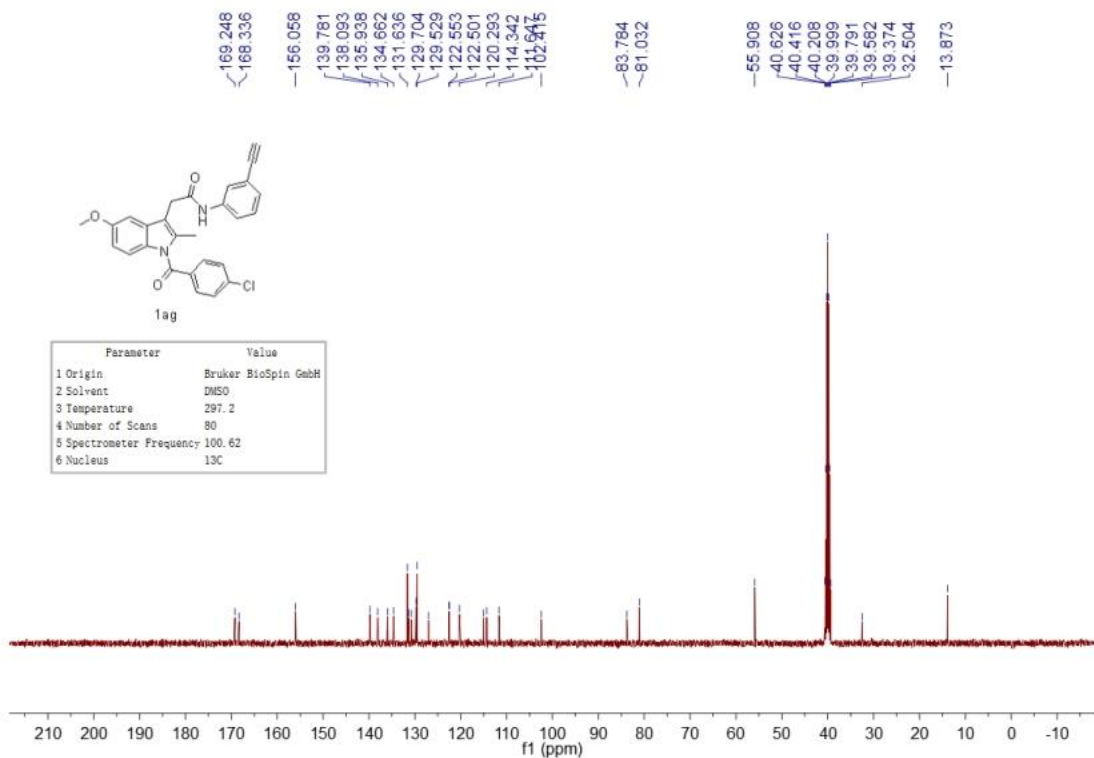
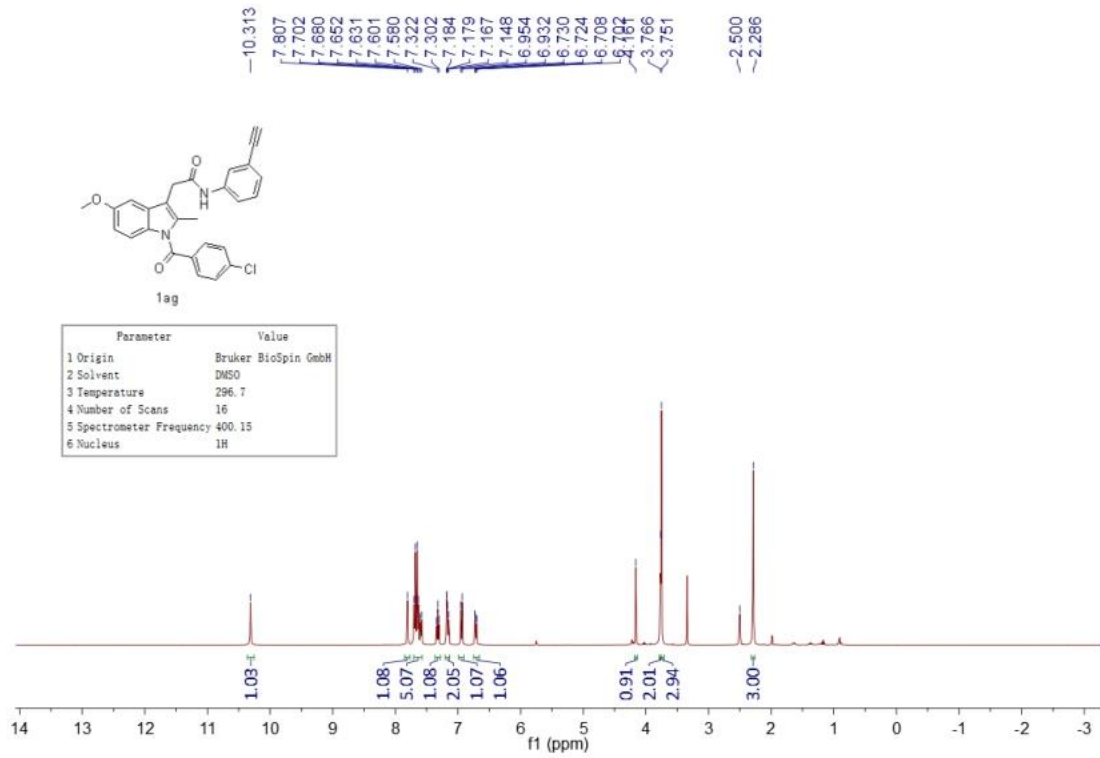
**4r**: 49.1 mg, 63%, *Z/E*=11:1, yellow solid, m.p. 168-169 °C. Purification by flash column chromatography on silica gel (eluent: Acetone/DCM/Petroleum ether = 1/50/250). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 2.0 Hz, 1H), 7.80 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.52-7.46 (m, 2H), 7.39-7.29 (m, 4H), 7.29-7.13 (m, 3H), 2.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 169.0, 154.1, 140.1, 137.4, 136.8, 136.0, 134.8, 134.3, 132.0, 131.5, 130.8, 129.7, 128.5, 128.4, 128.1, 128.0, 125.7, 123.3, 122.1, 28.9. FT-IR: ν (cm<sup>-1</sup>) 3089, 3038, 2920, 2849, 1954, 1715, 1674, 1560, 1432, 1353. HRMS [ESI] calcd for C<sub>23</sub>H<sub>16</sub>ClNOSNa [M+Na]<sup>+</sup> 412.0533, found 412.0538.

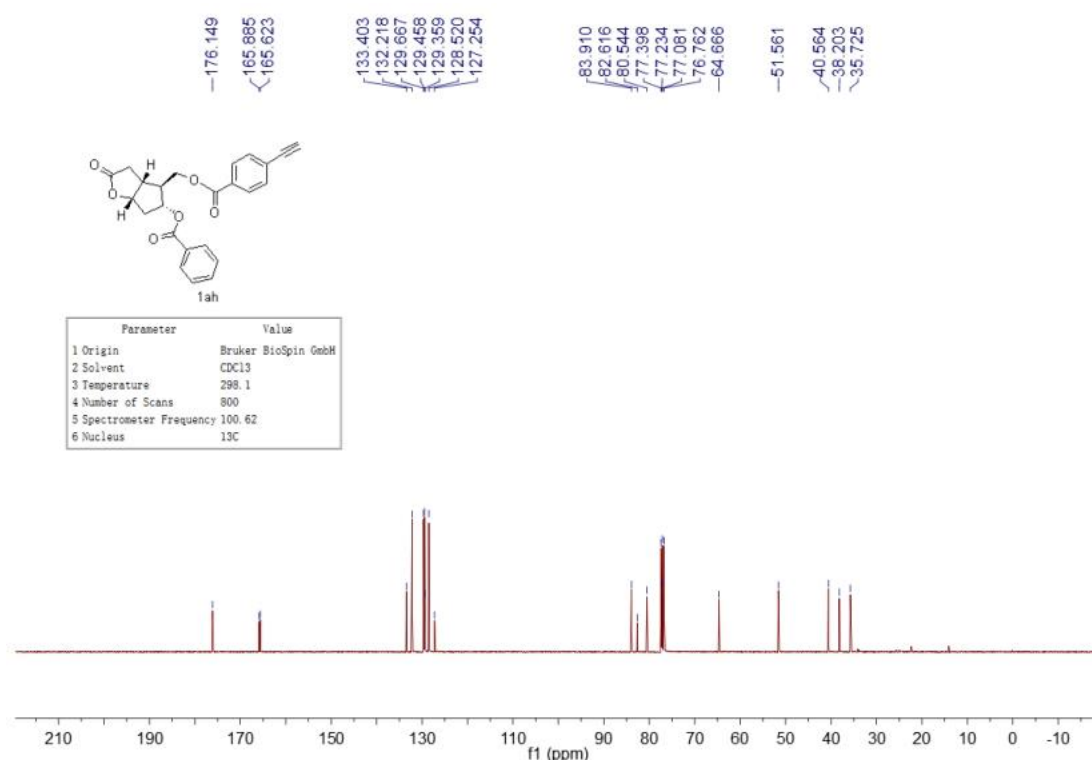
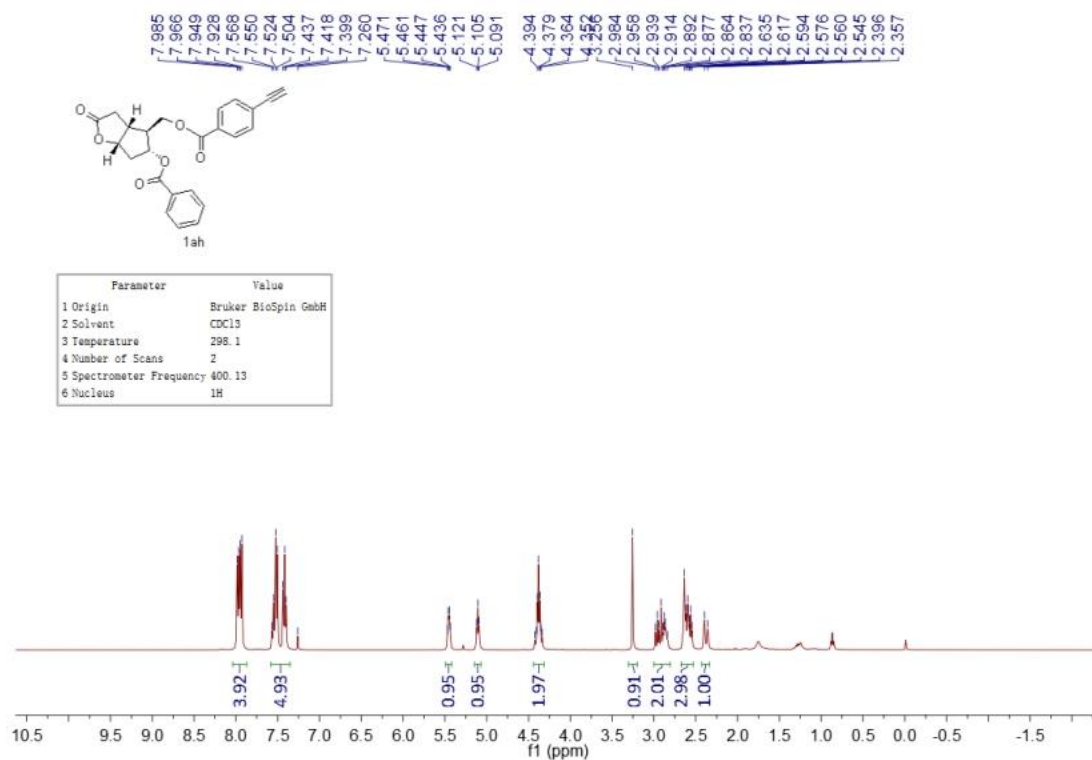
### 13. $^1\text{H}$ , $^{13}\text{C}$ , $^{19}\text{F}$ NMR spectra

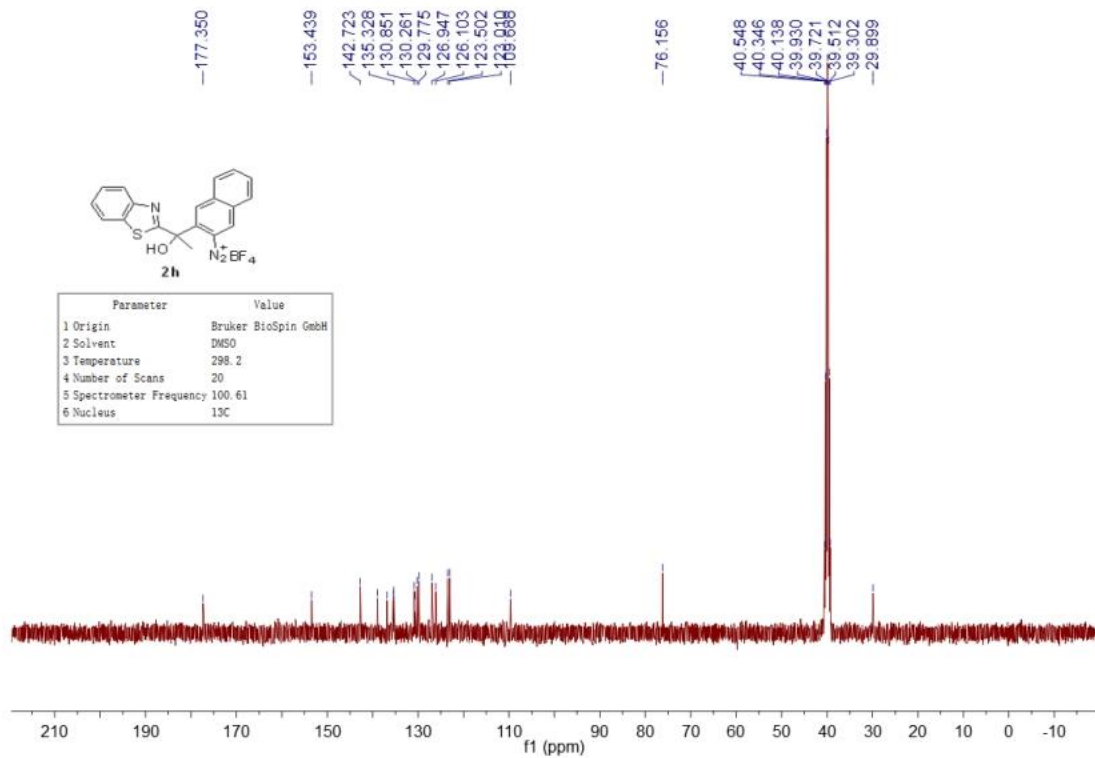
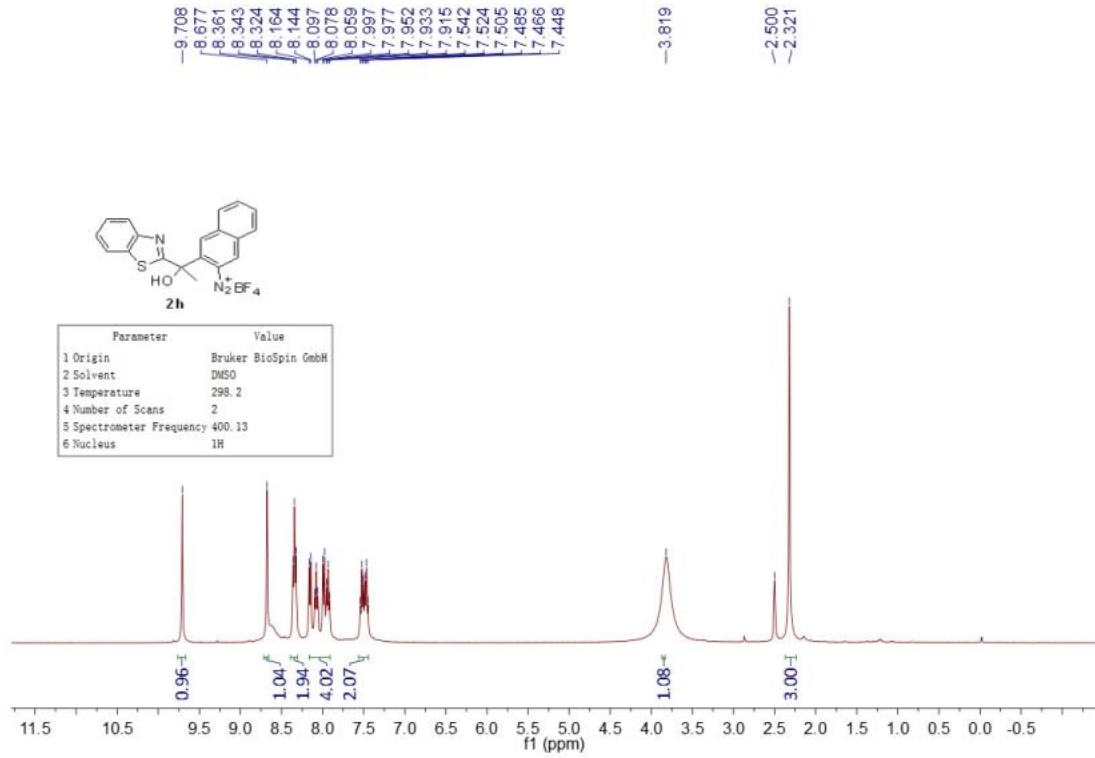


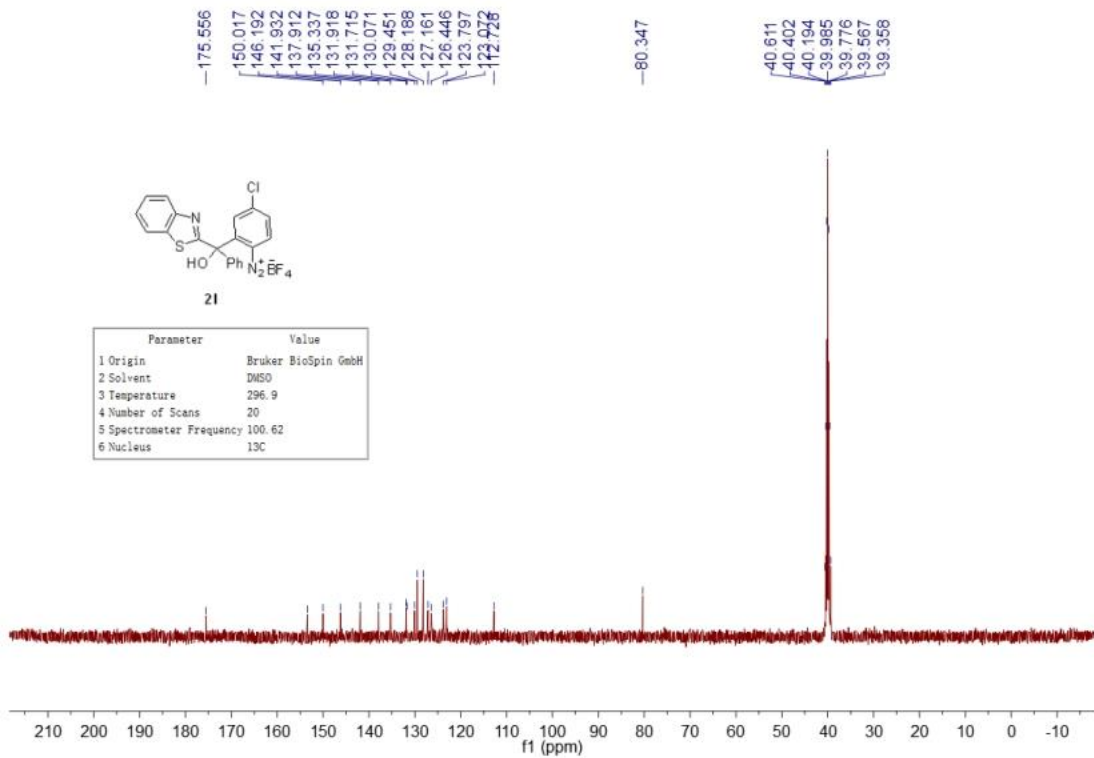
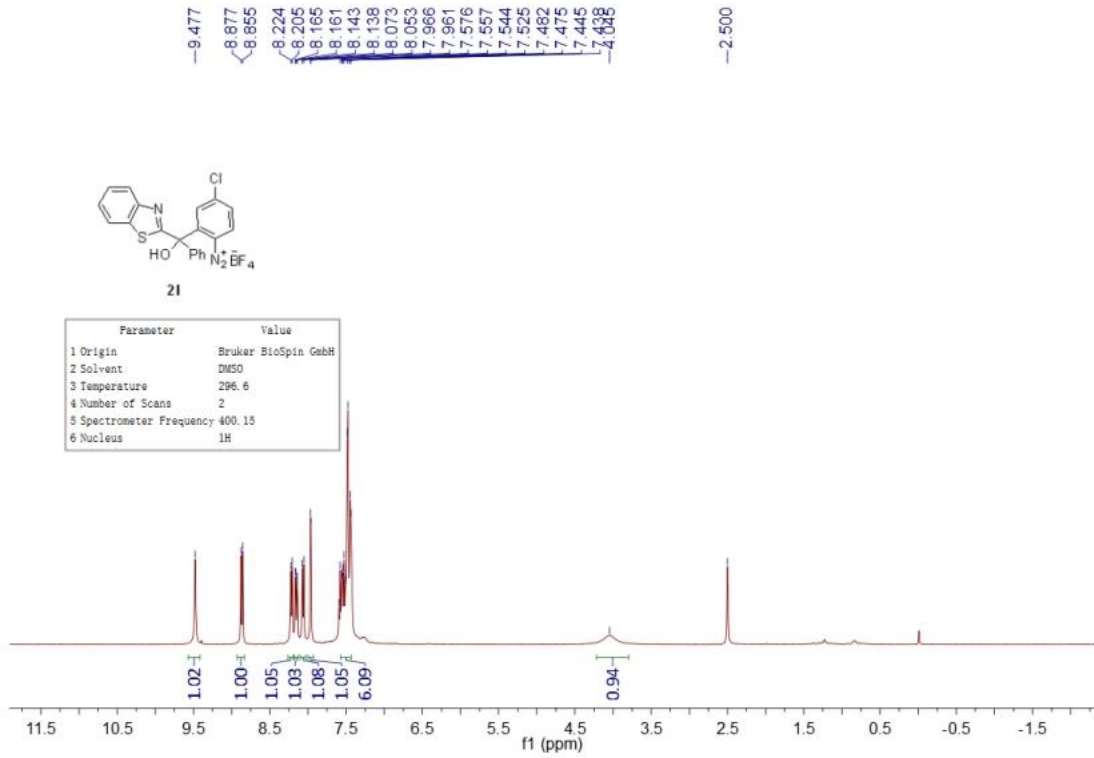


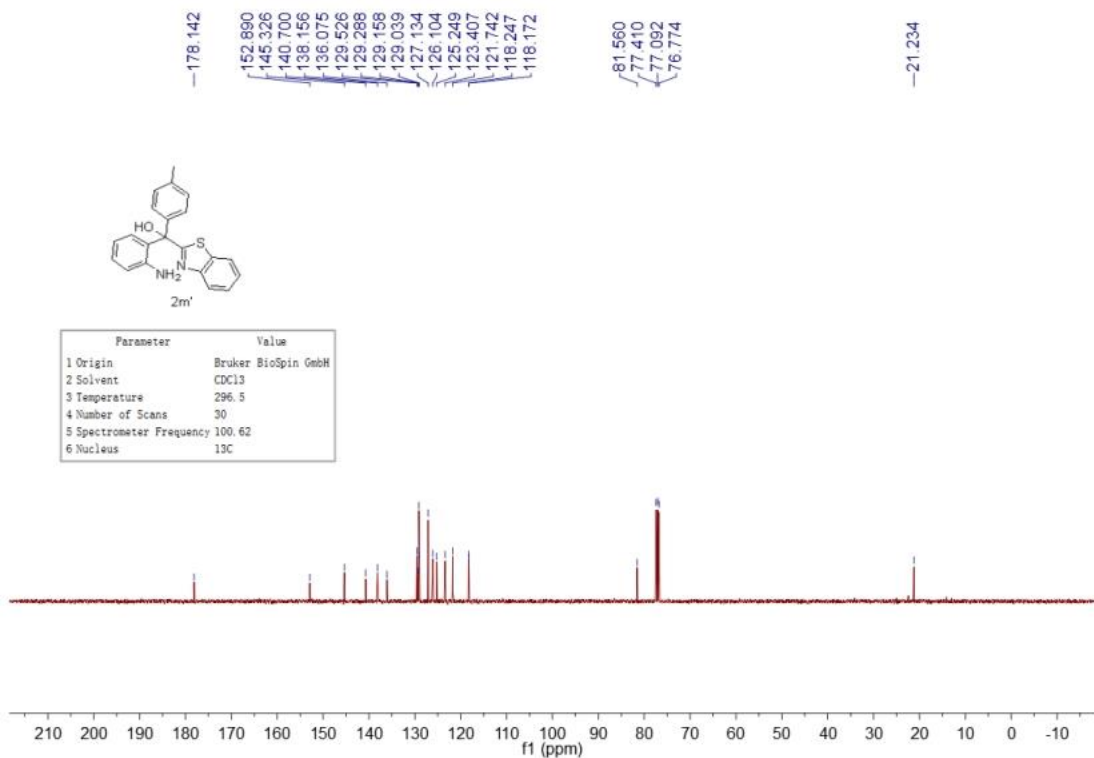
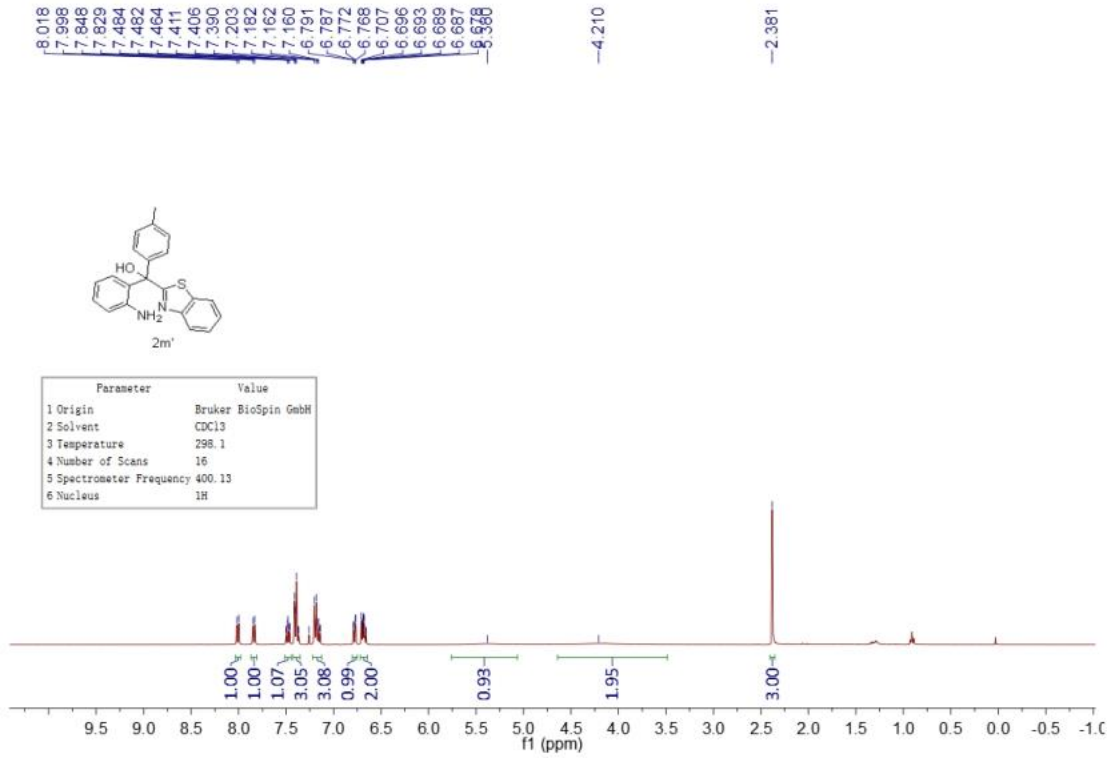


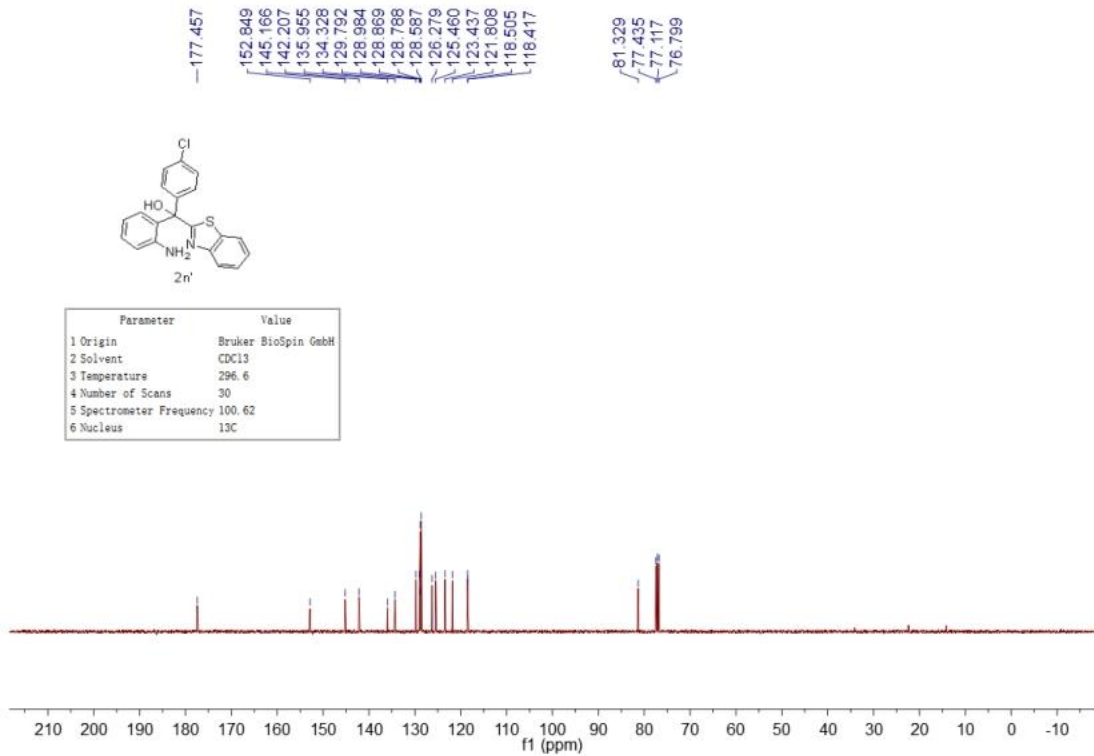
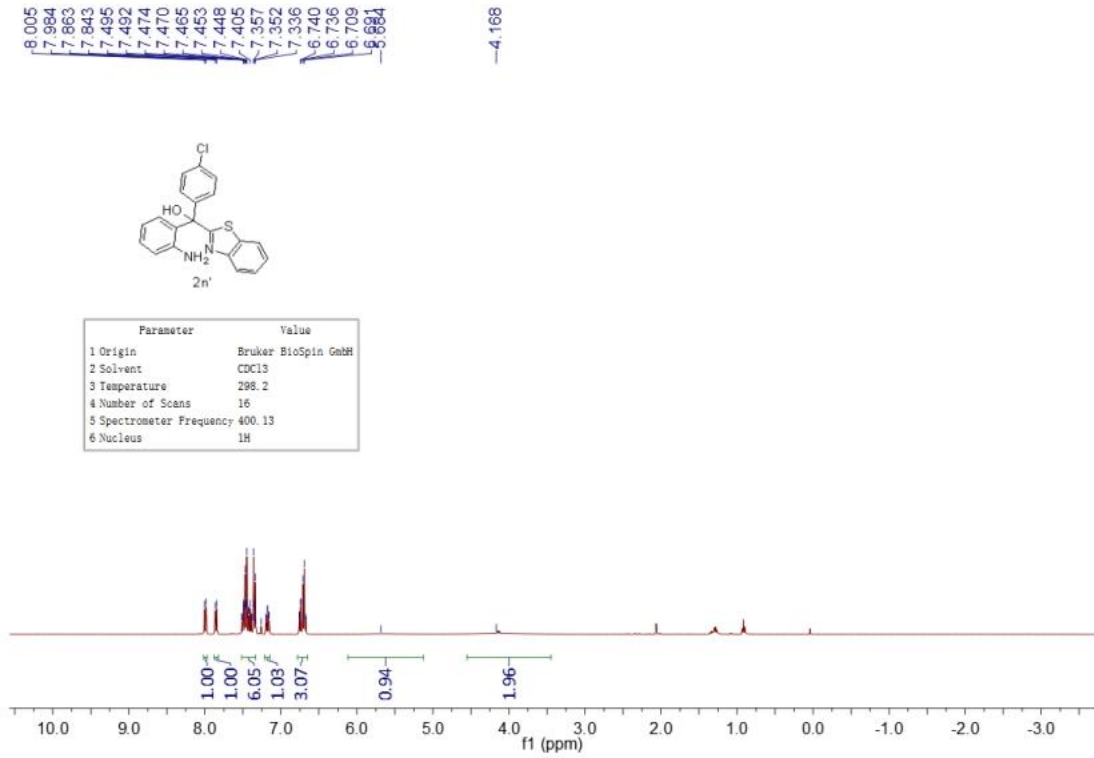




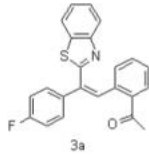




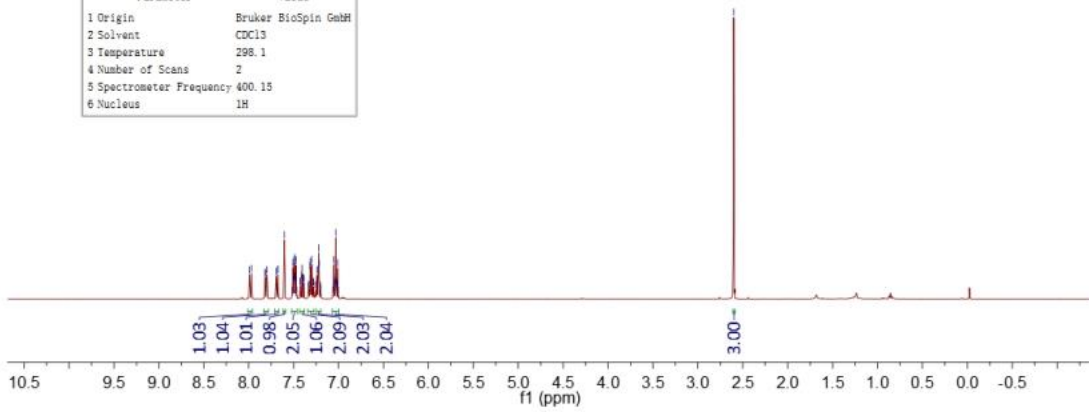




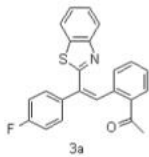
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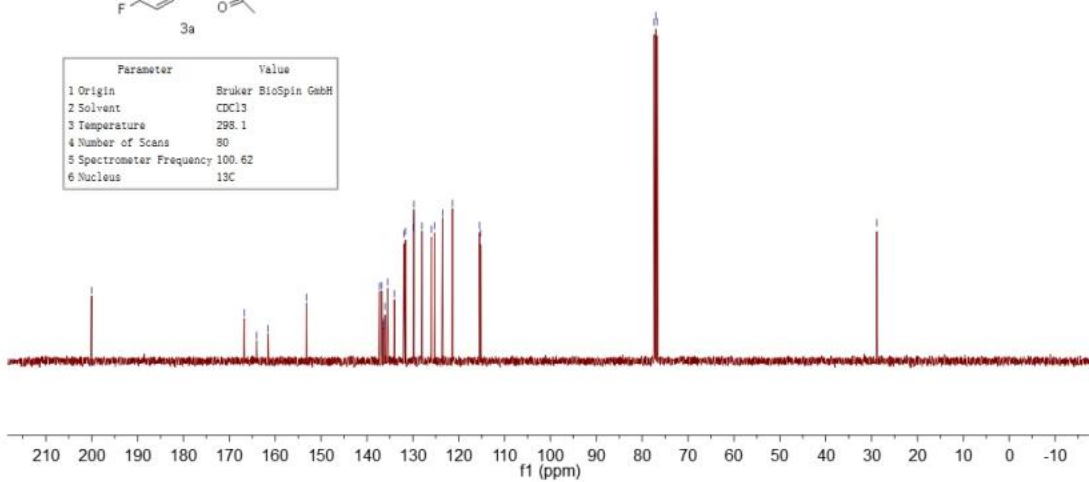
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3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H



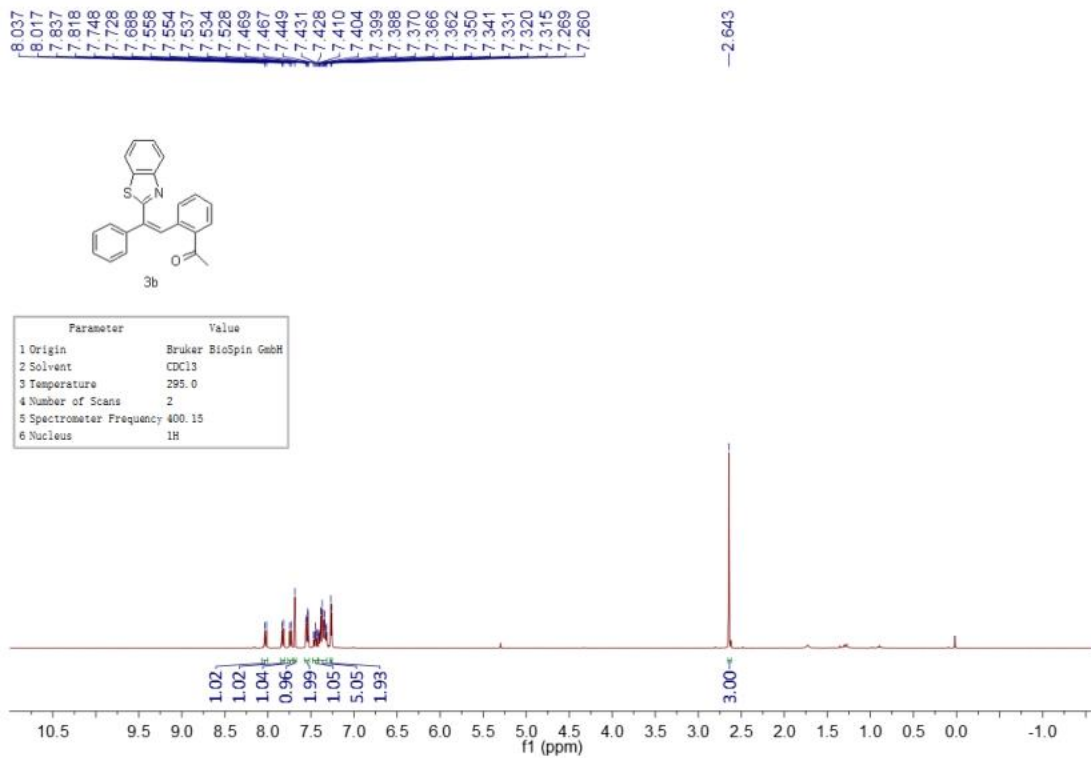
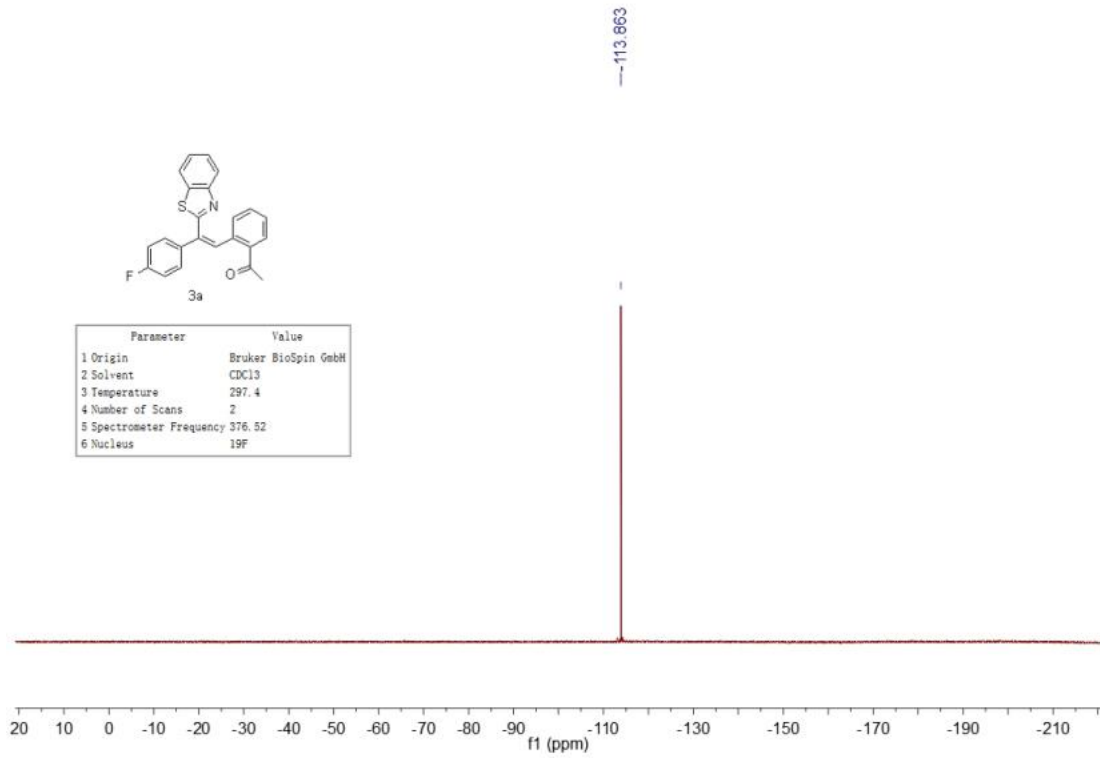
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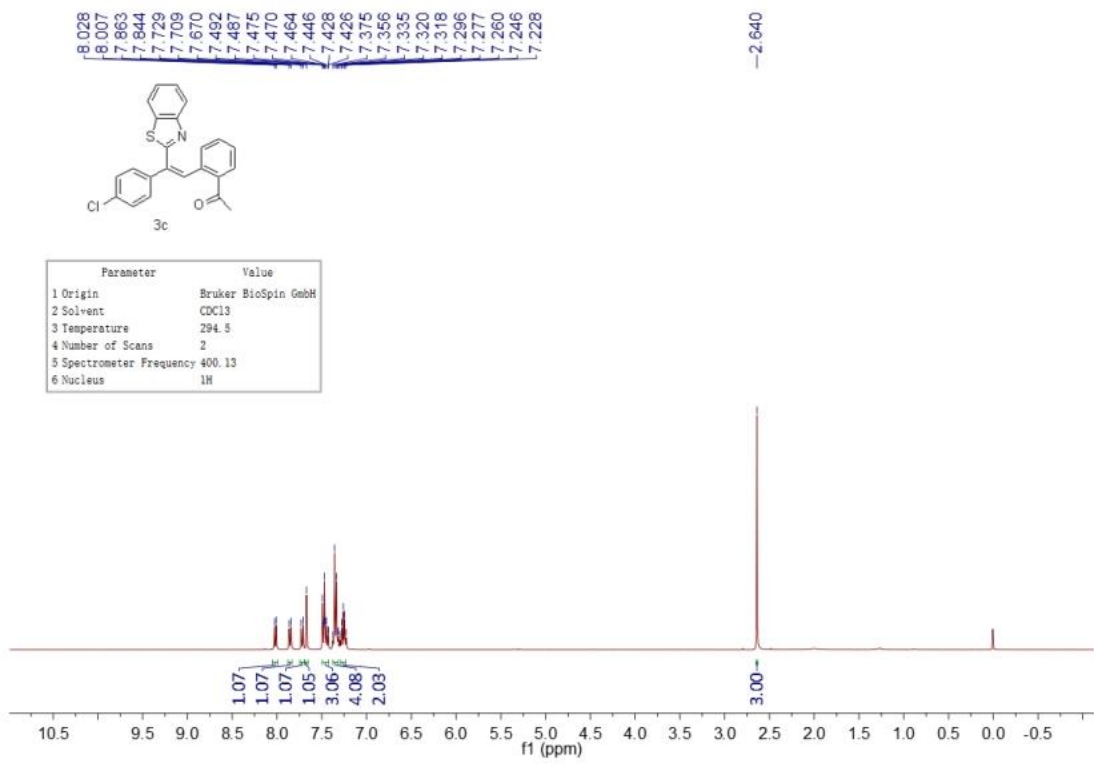
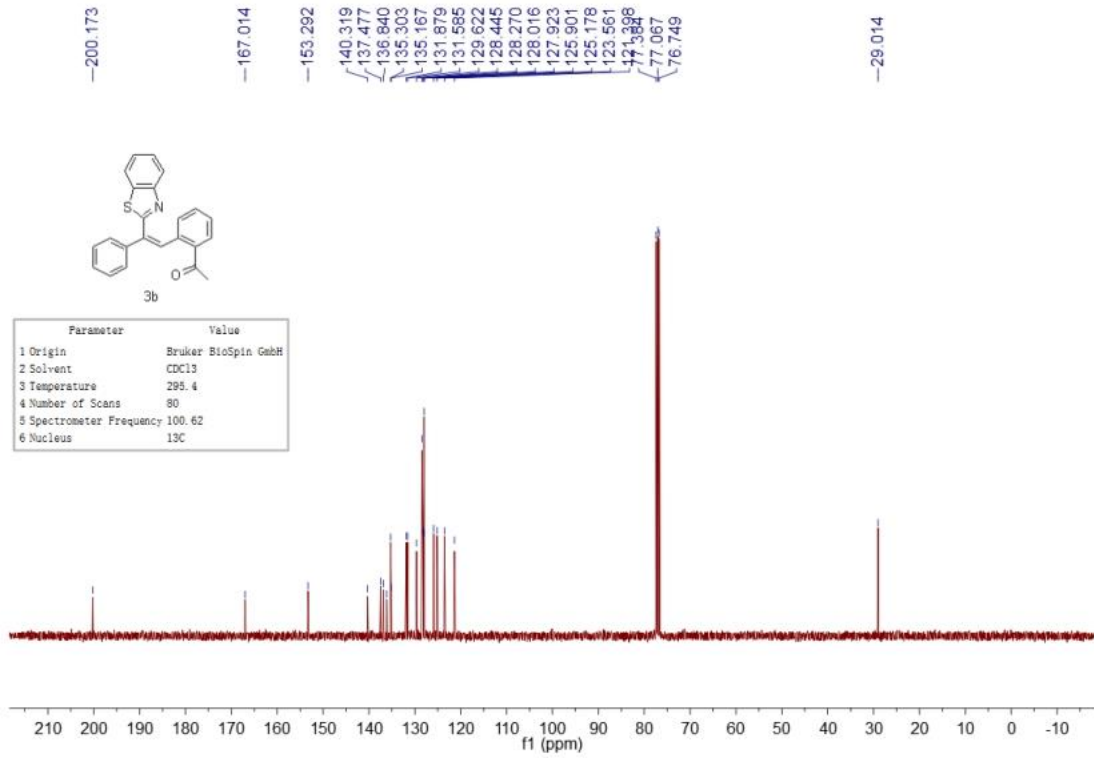


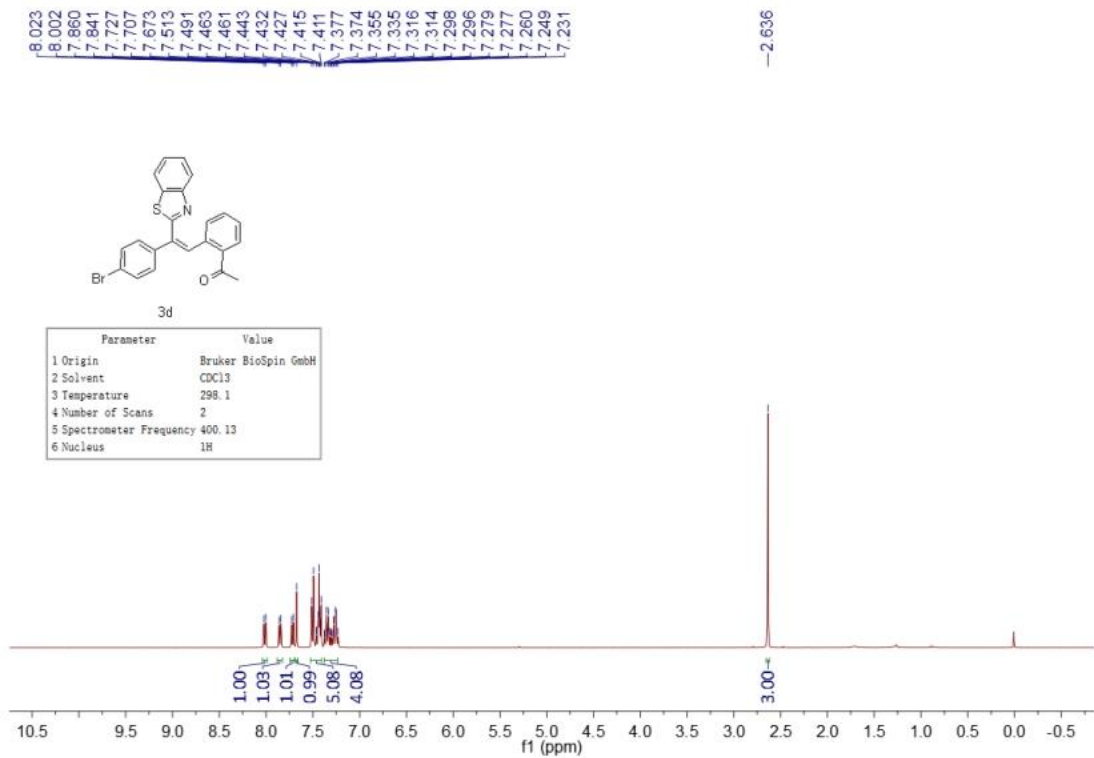
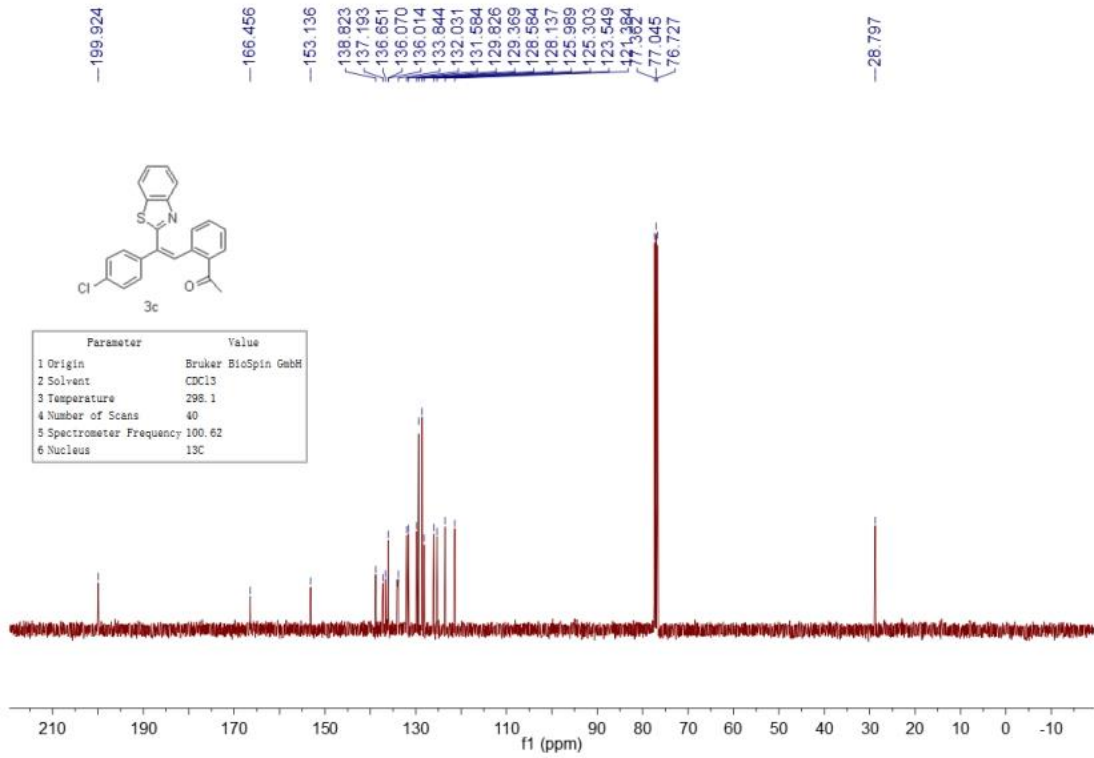
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2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	80
5 Spectrometer Frequency	100.62
6 Nucleus	13C

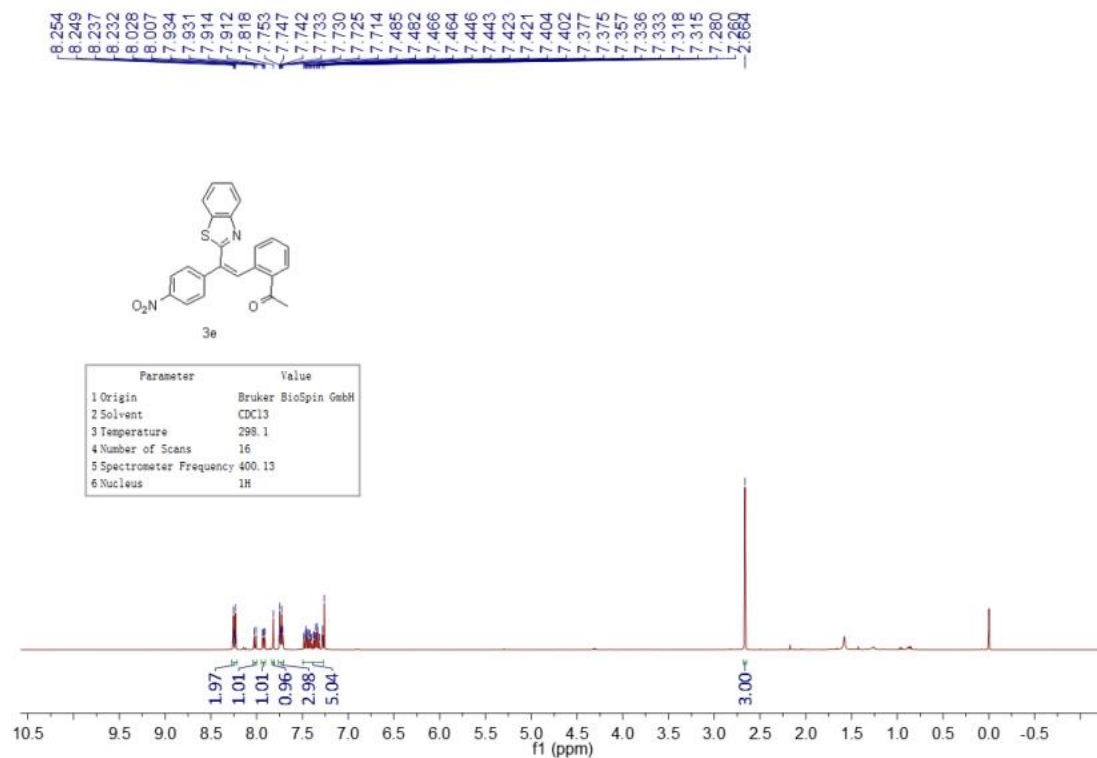
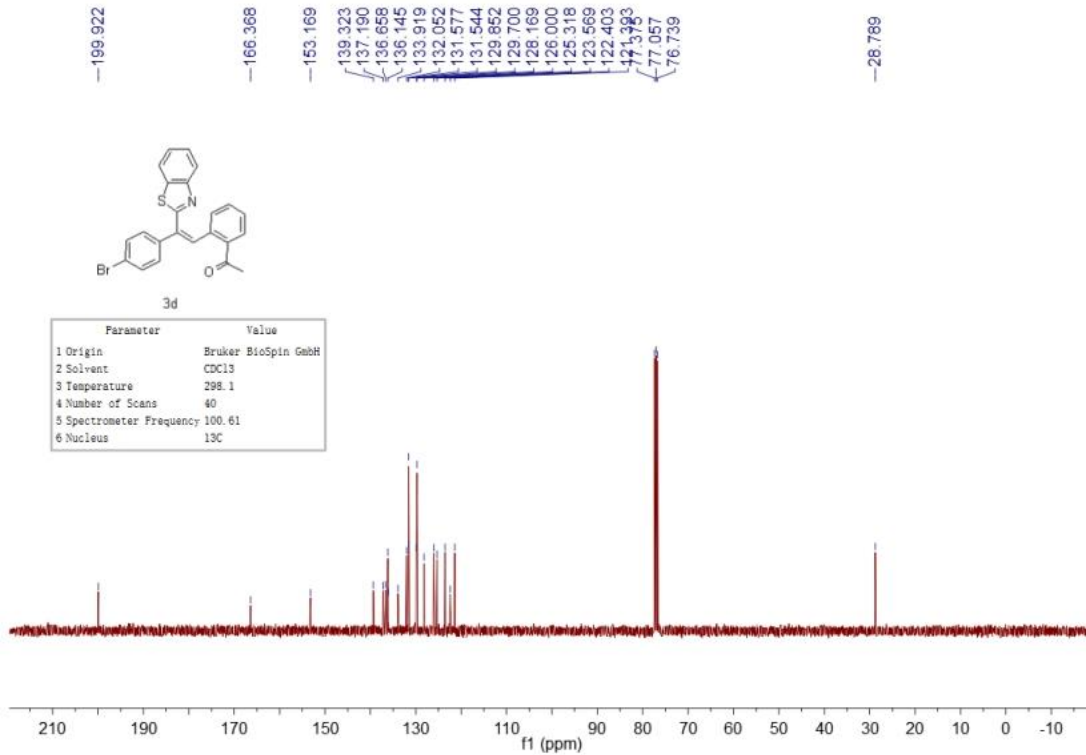


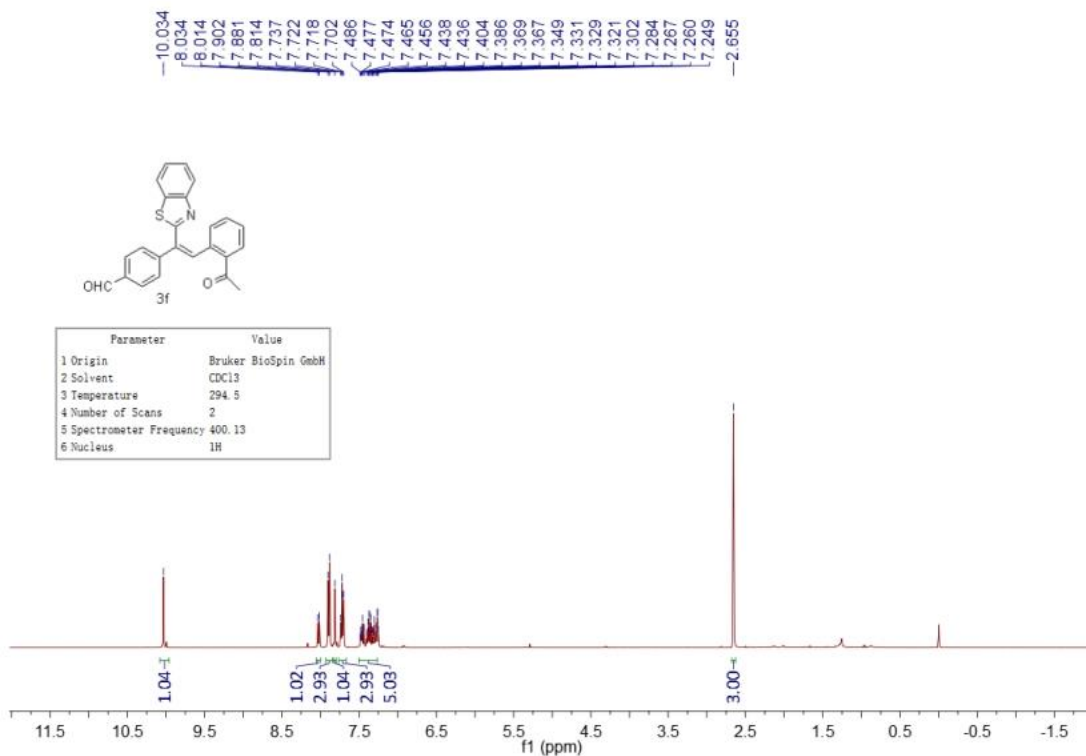
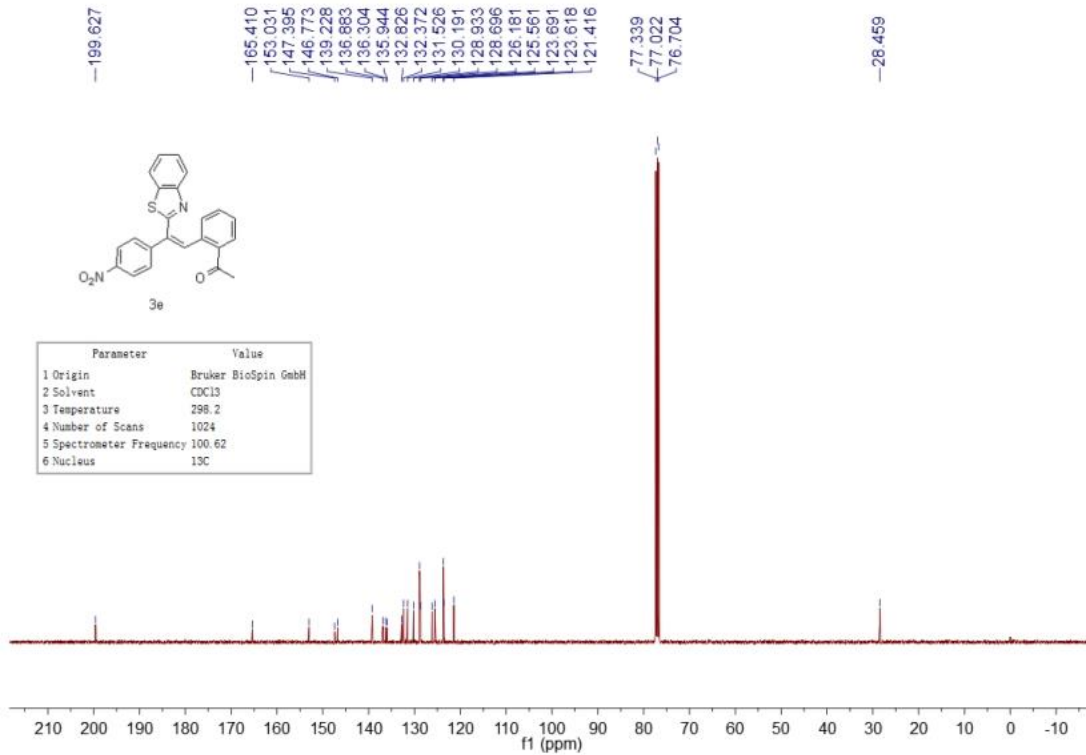


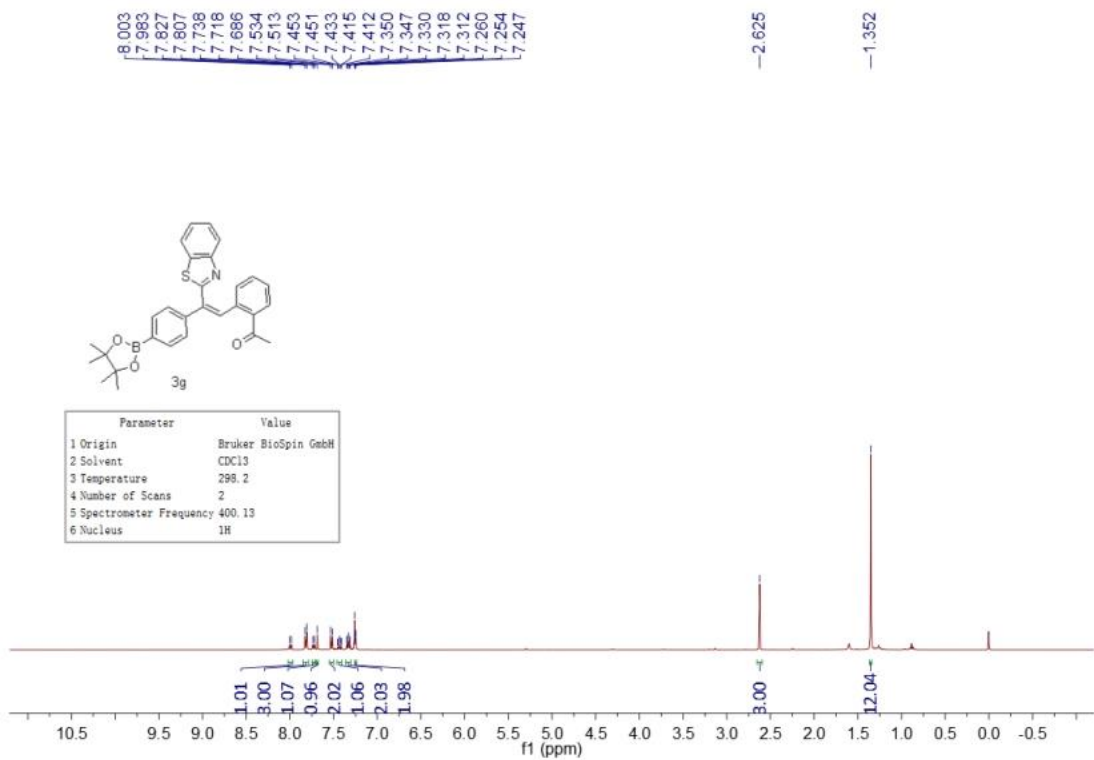
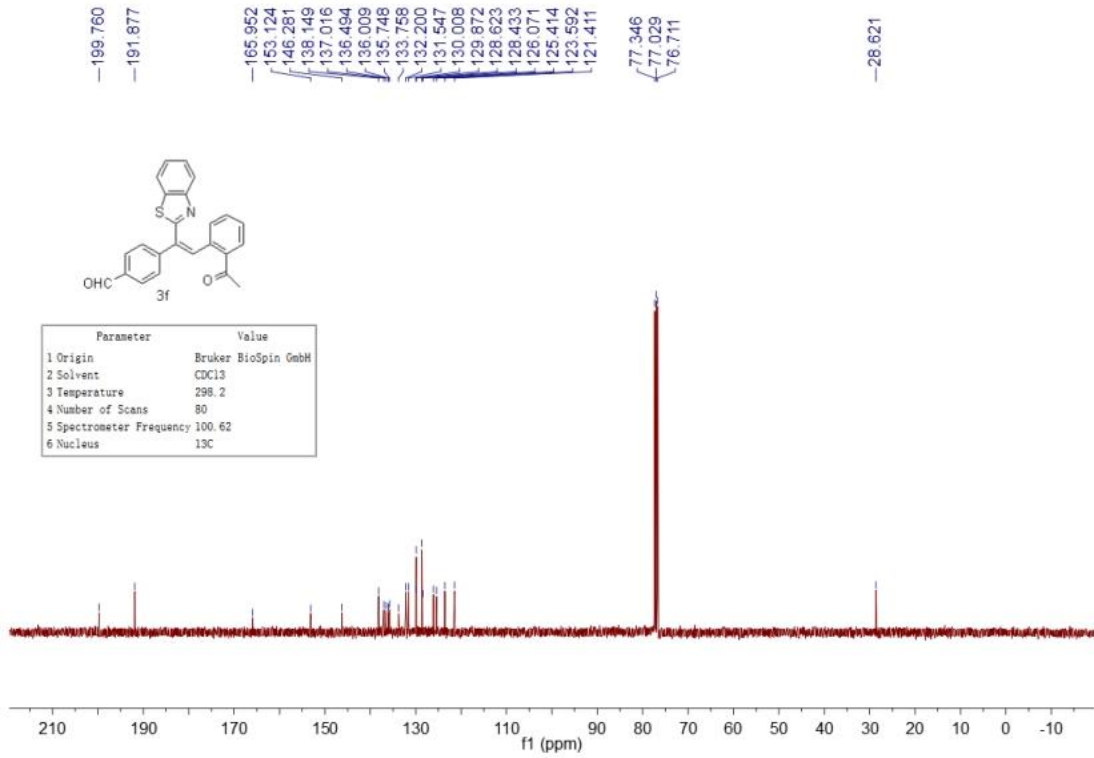


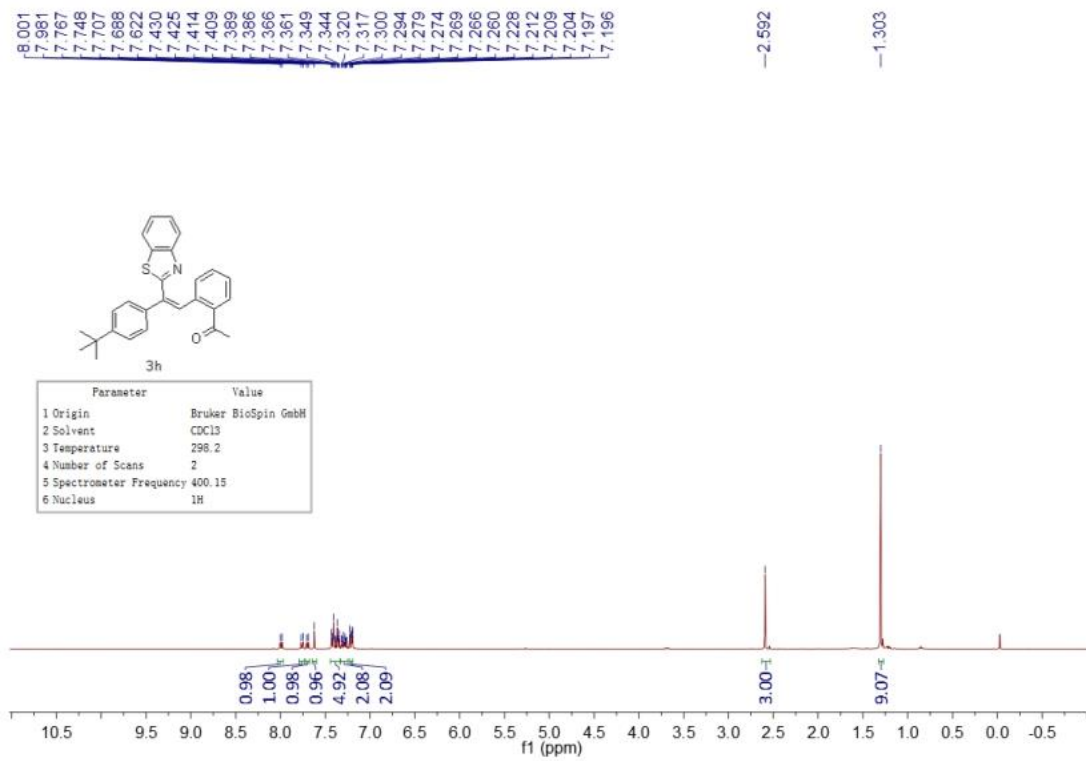
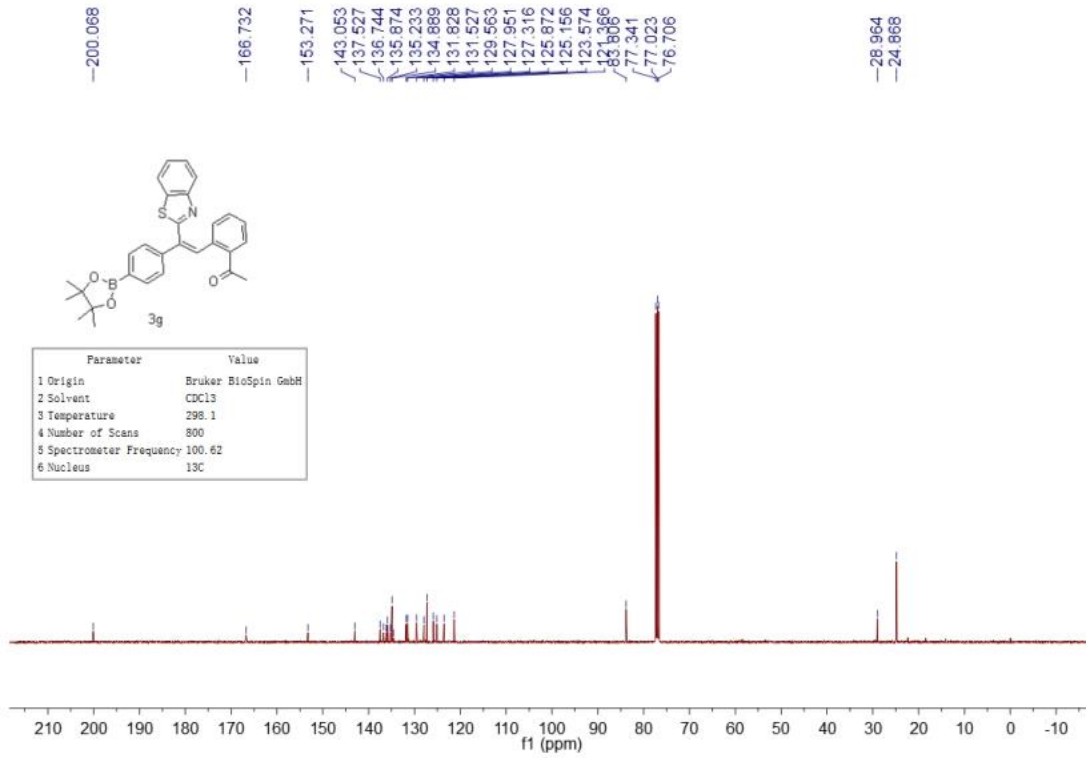


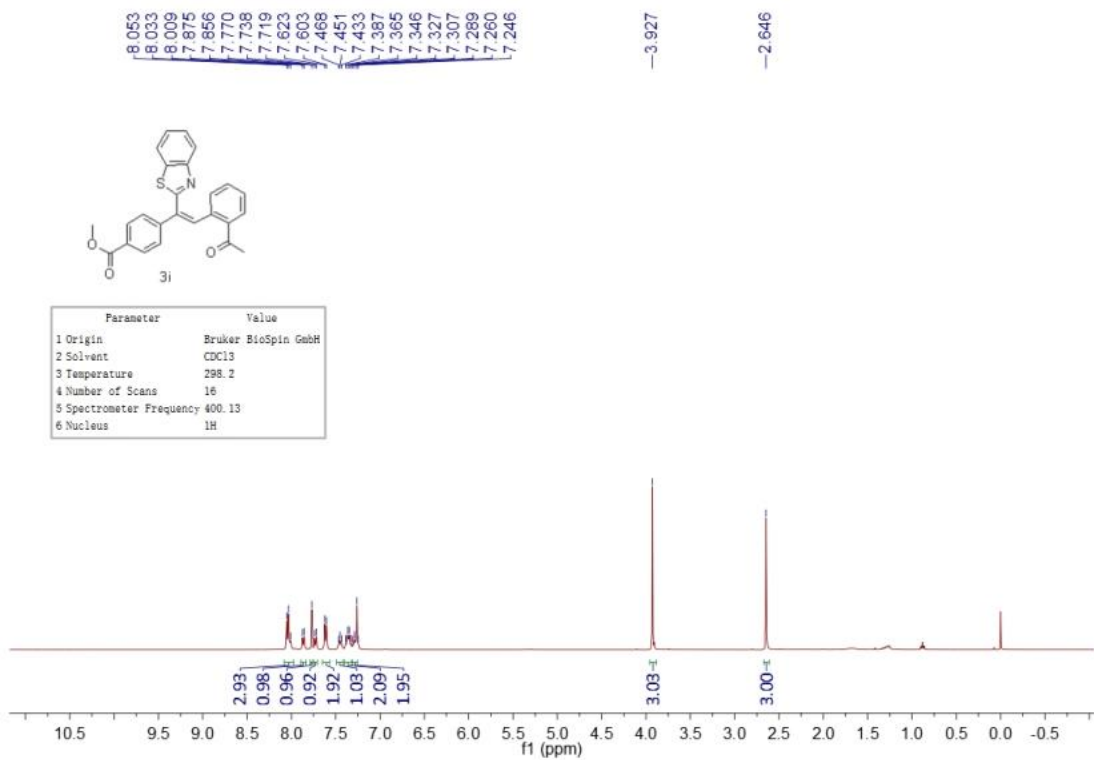
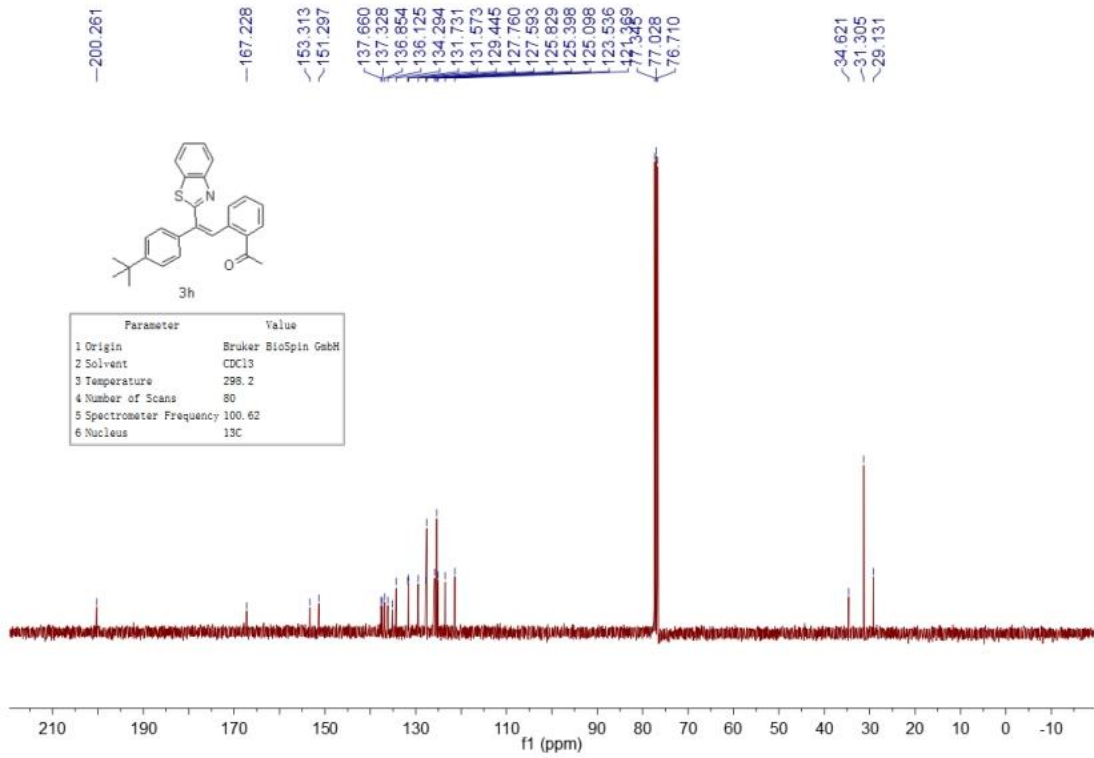




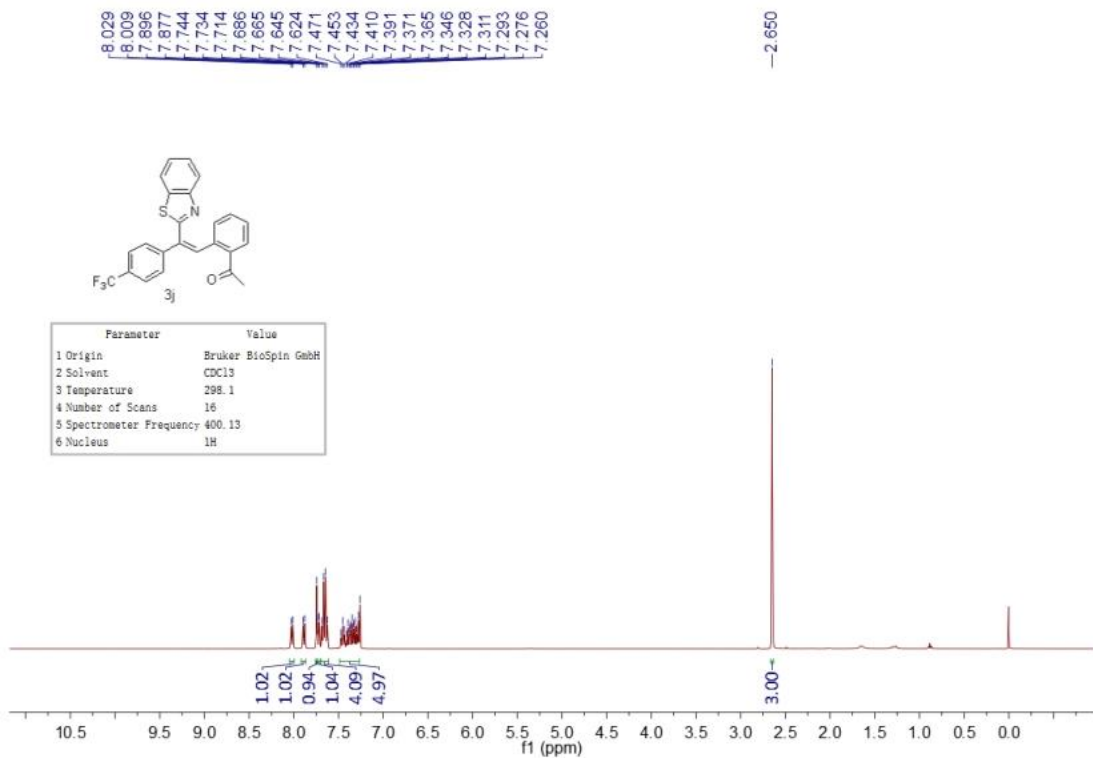
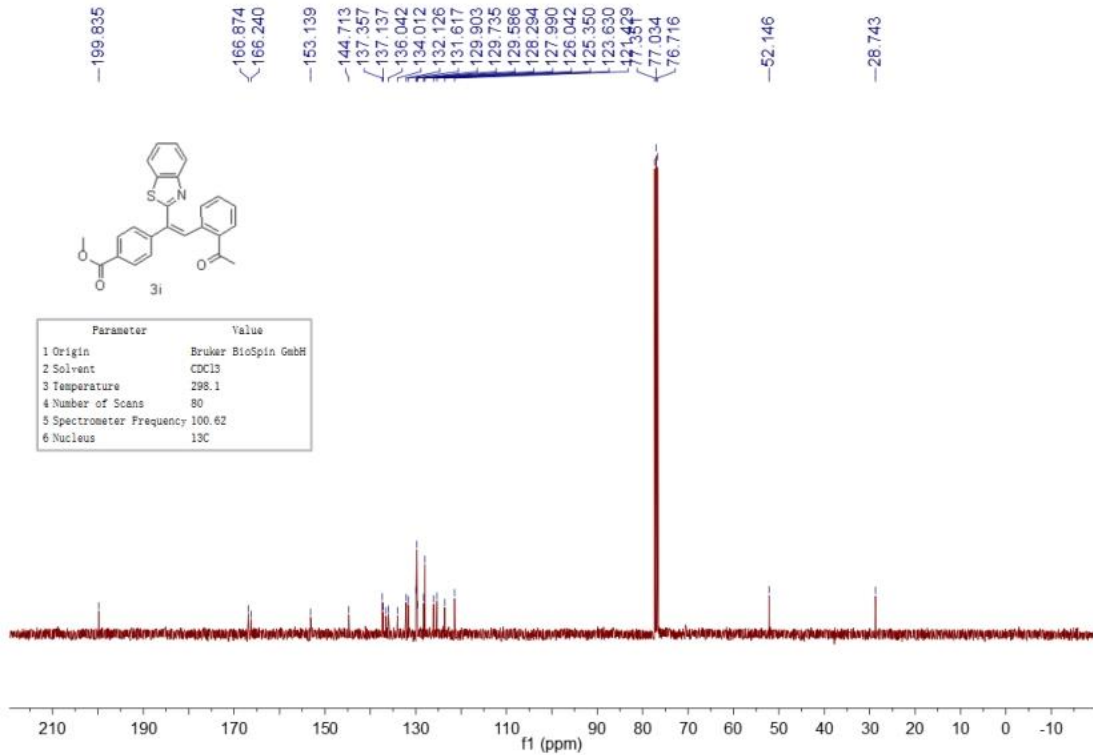


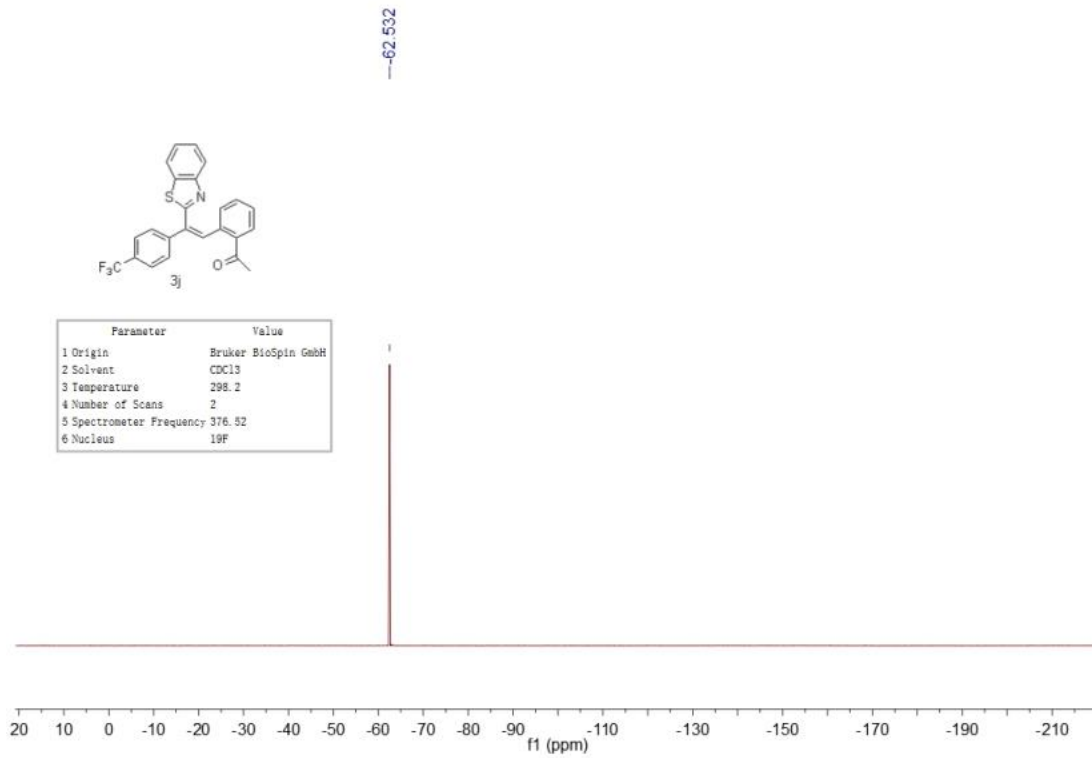
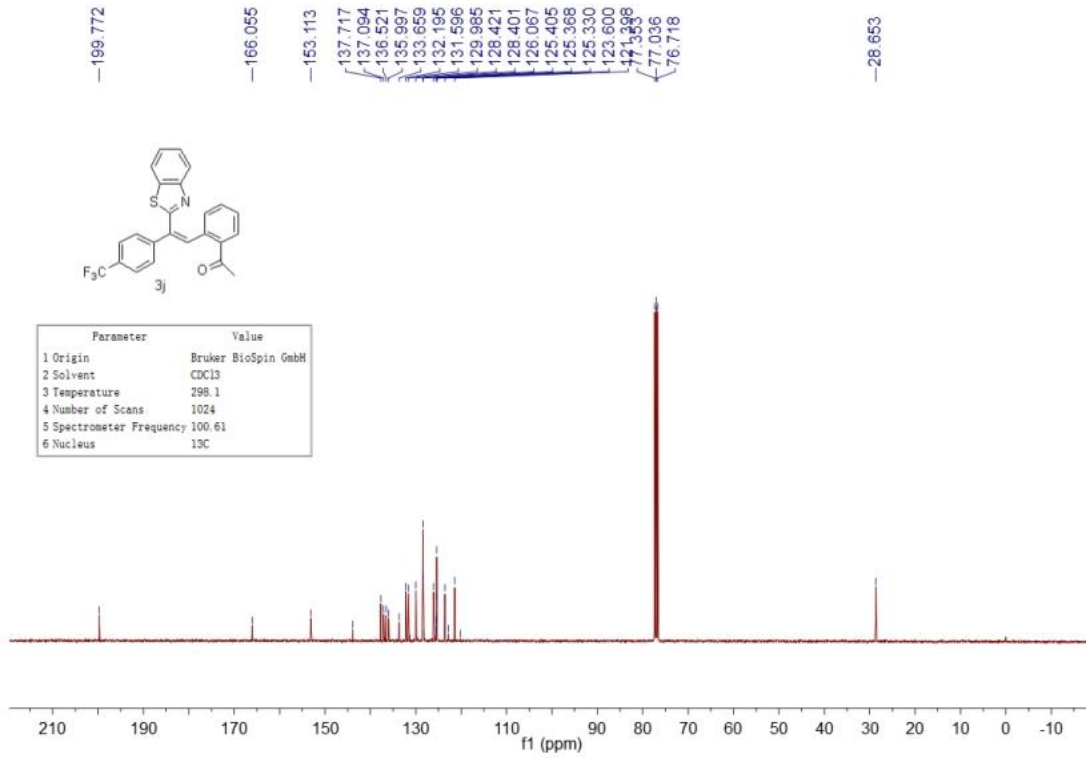


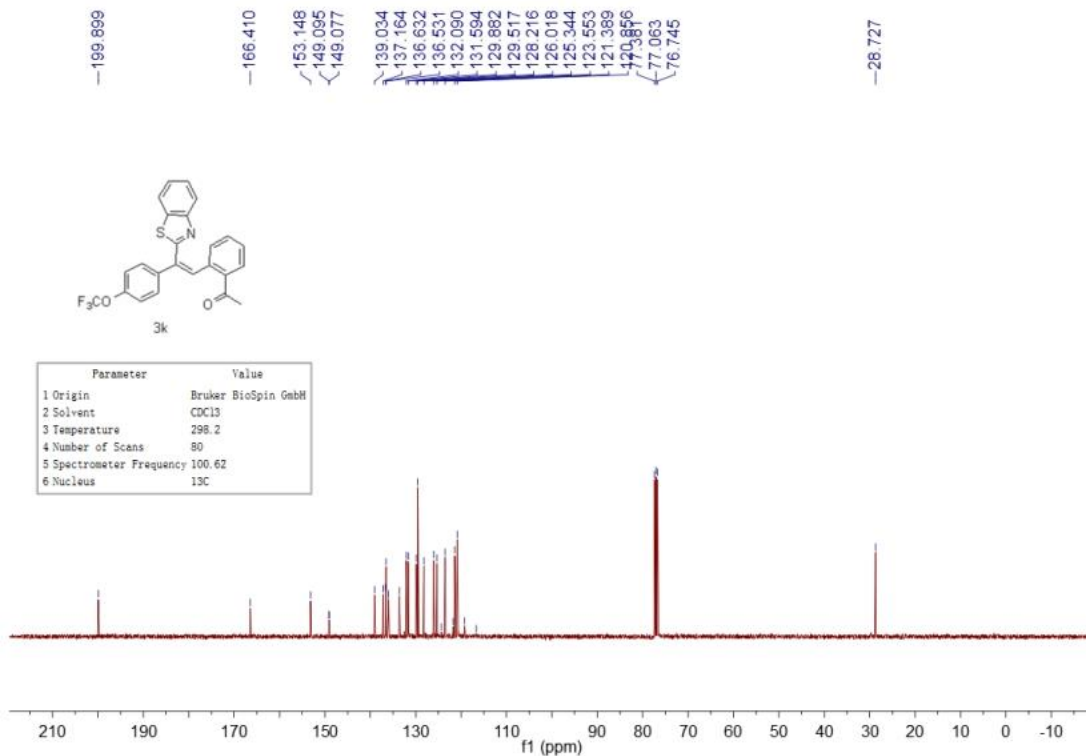
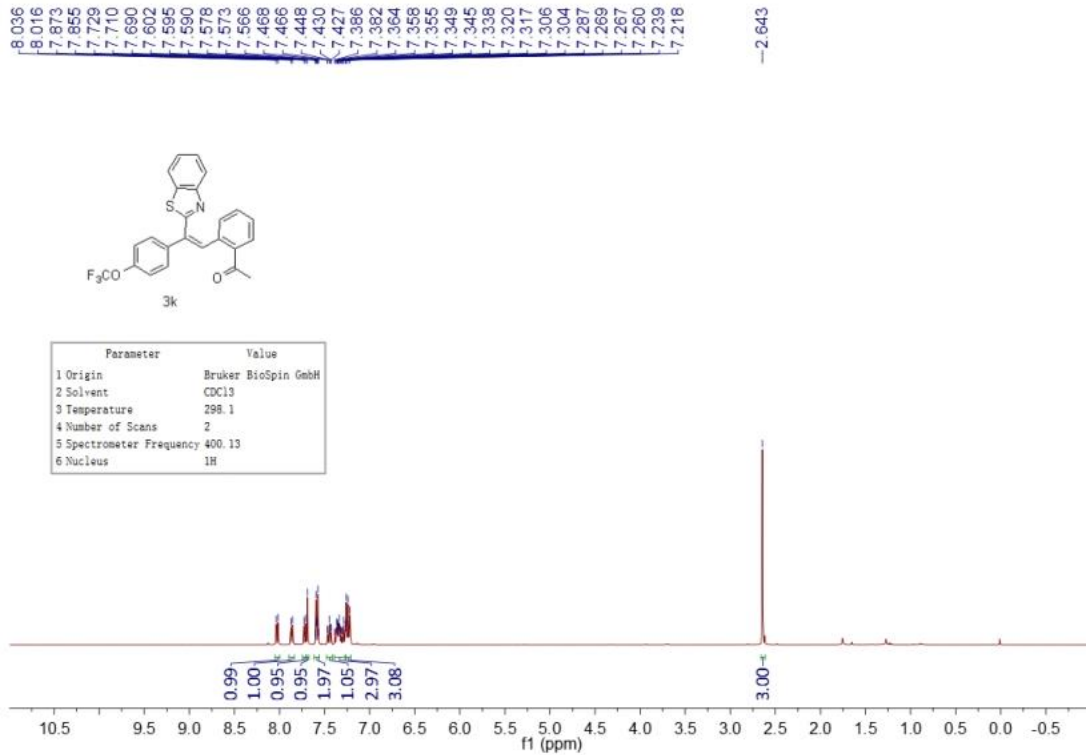


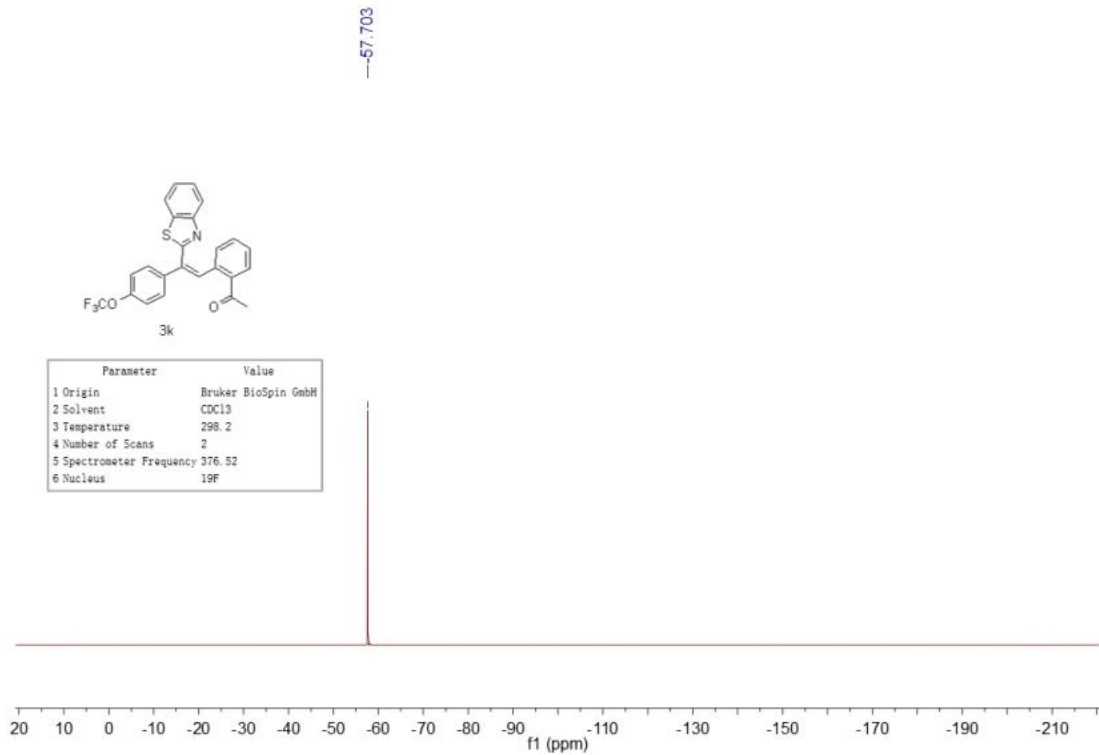






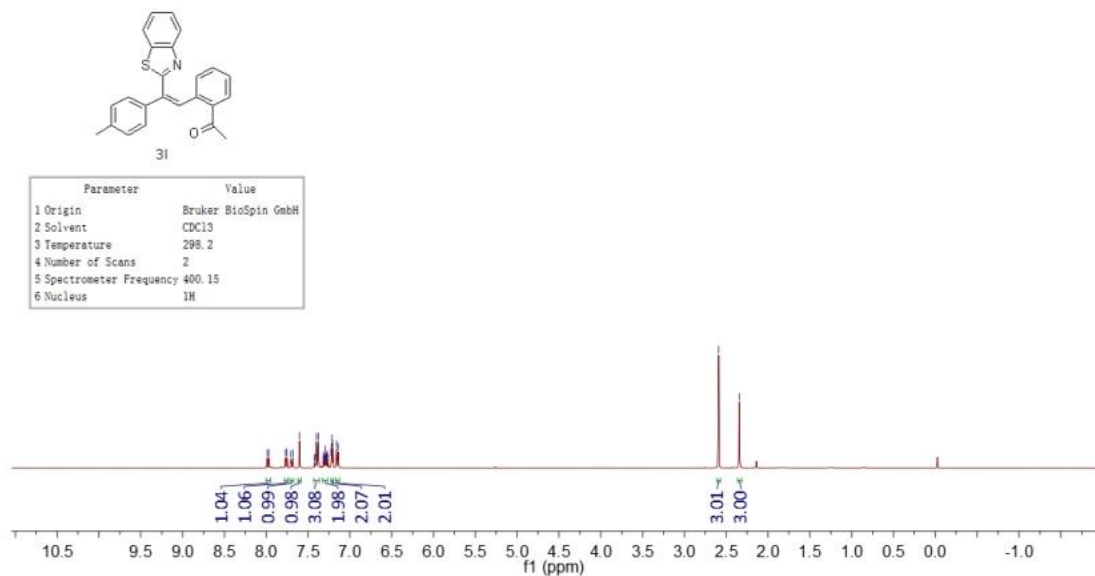


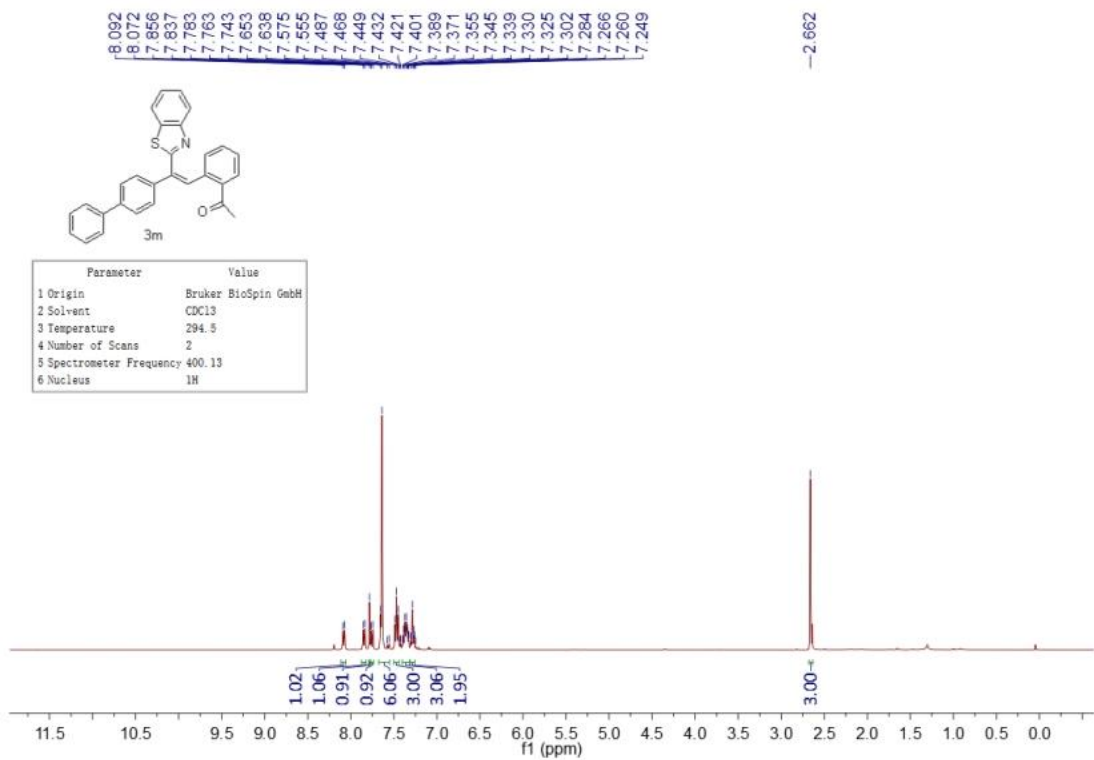
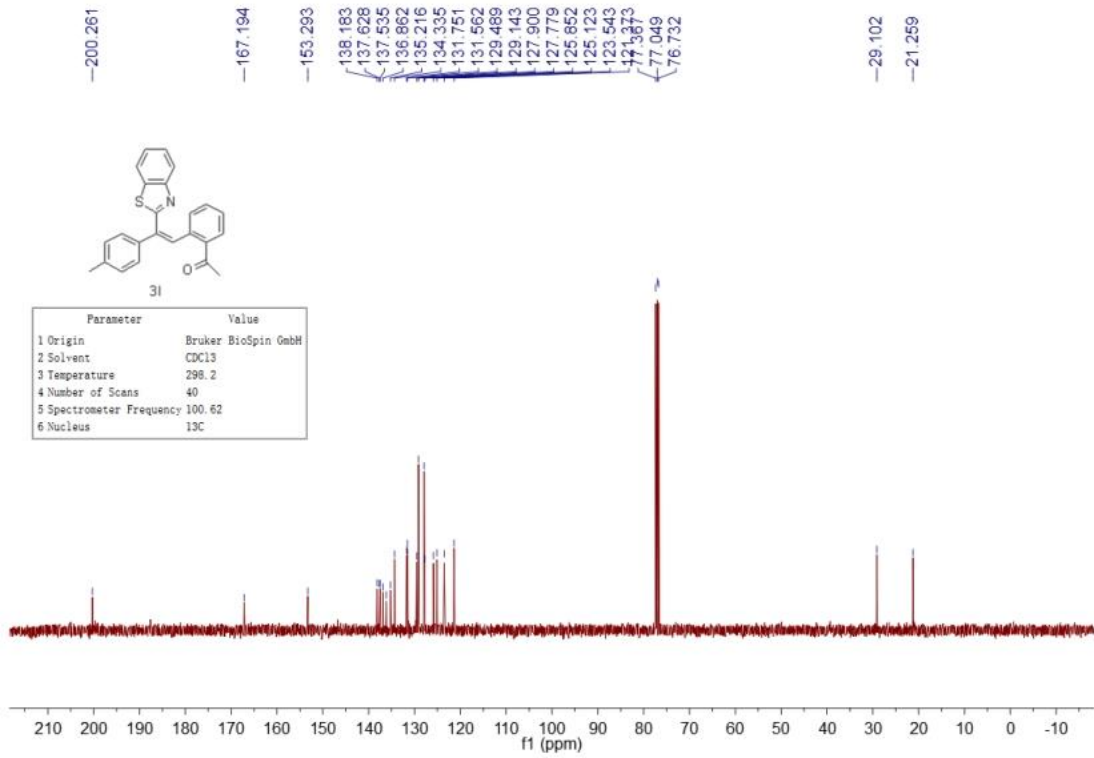


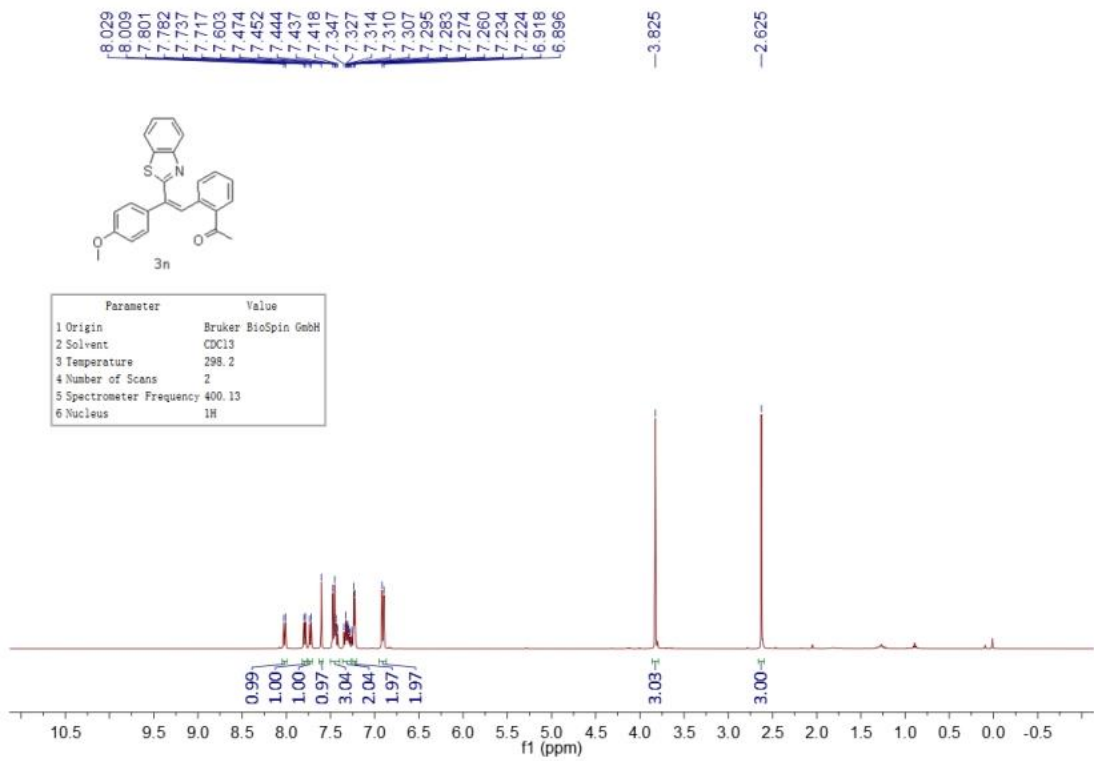
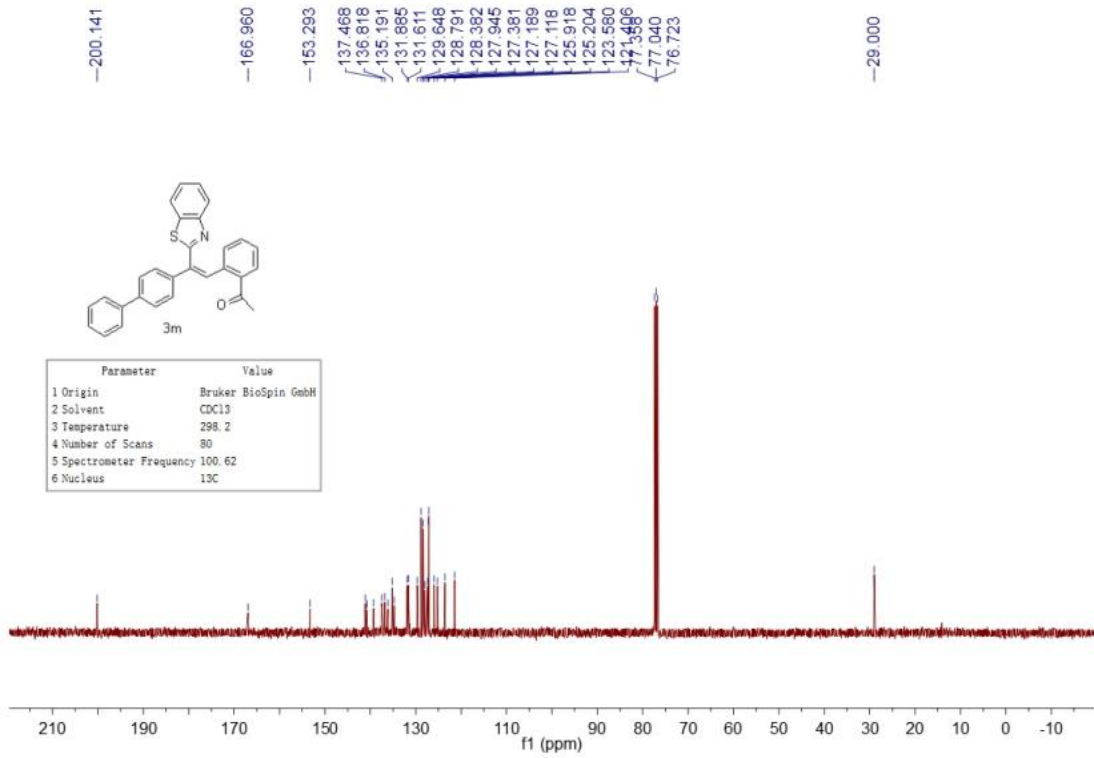


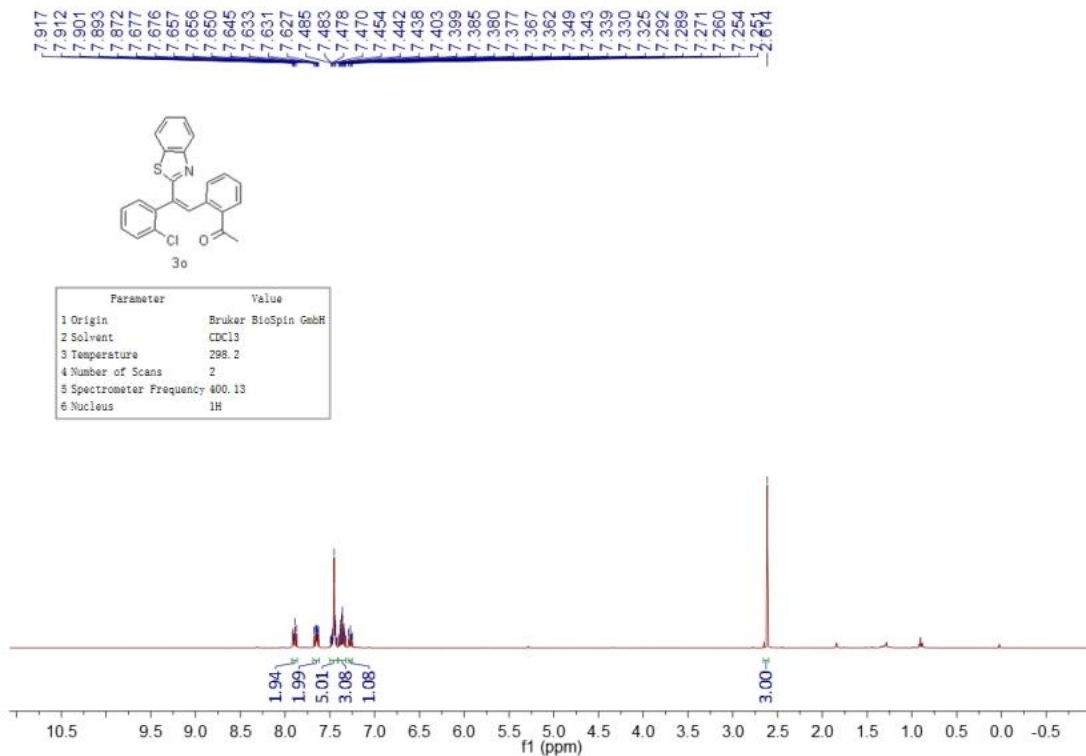
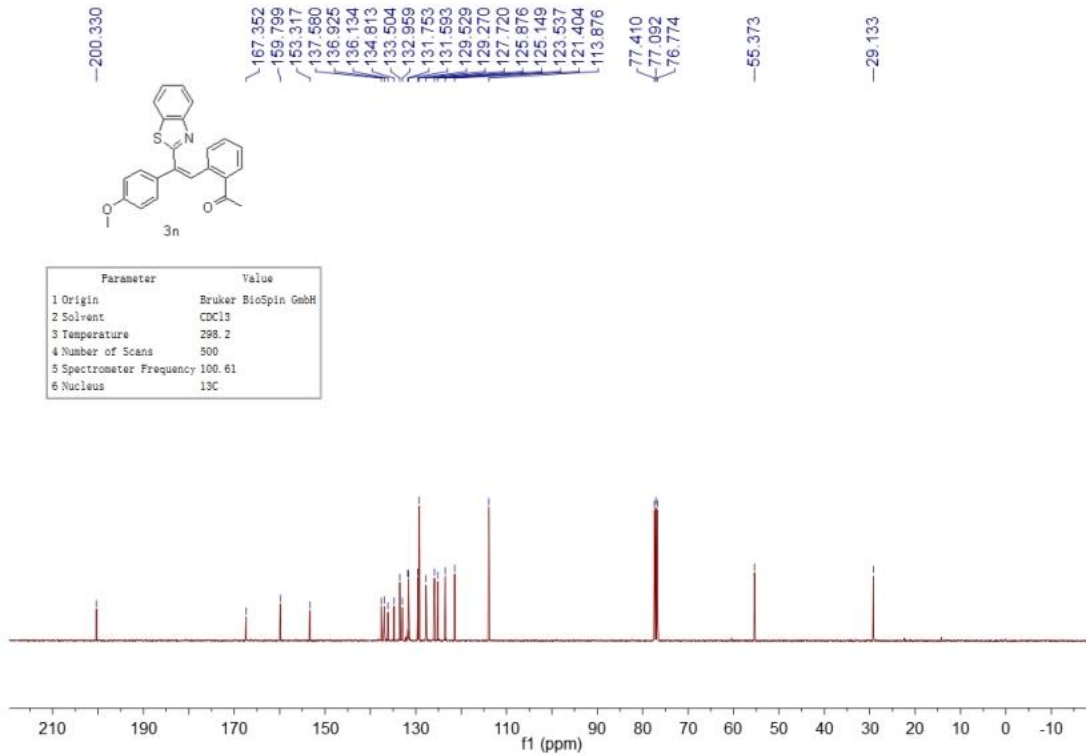
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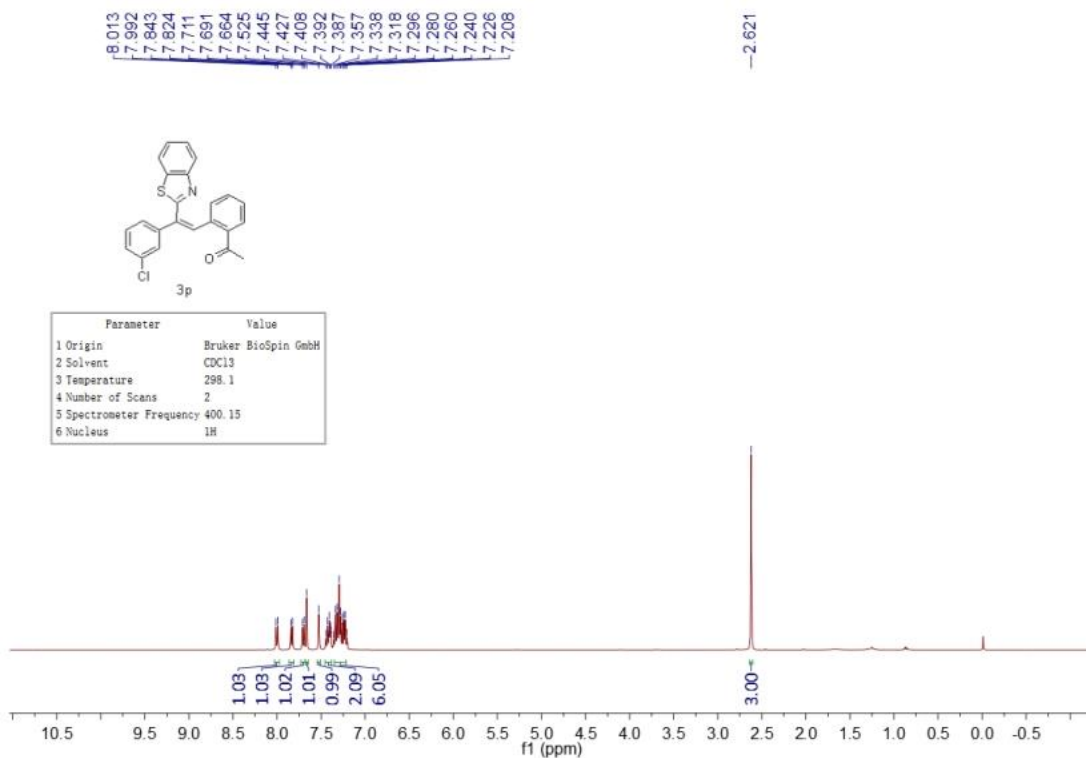
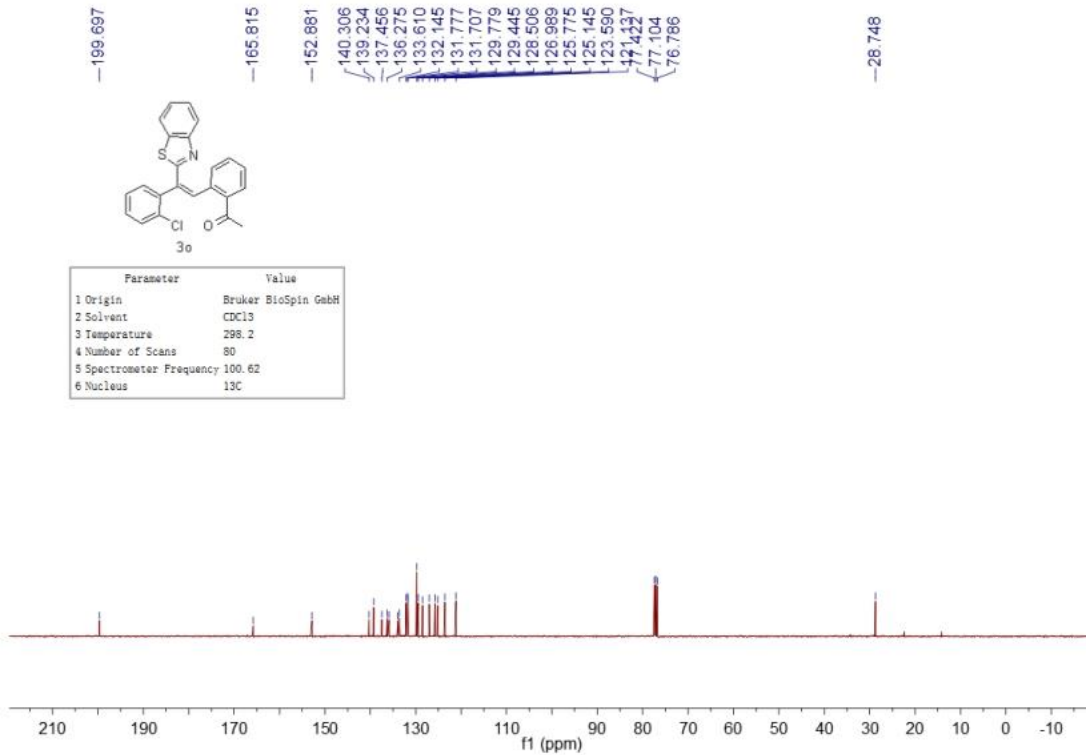
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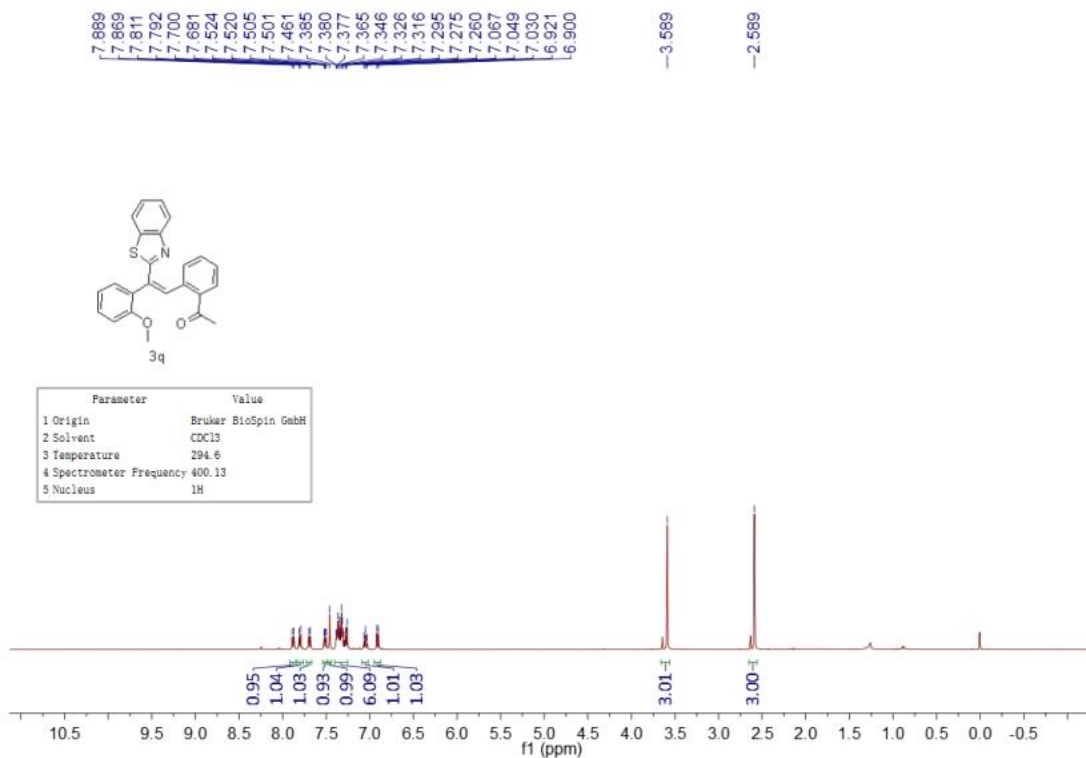
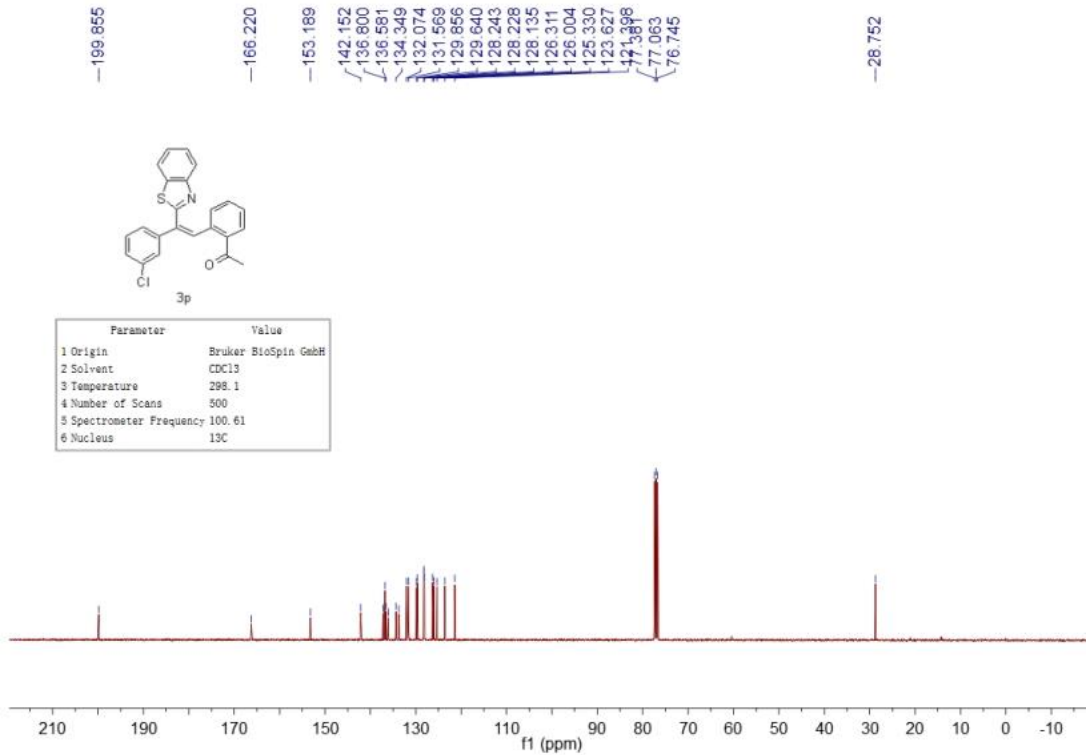


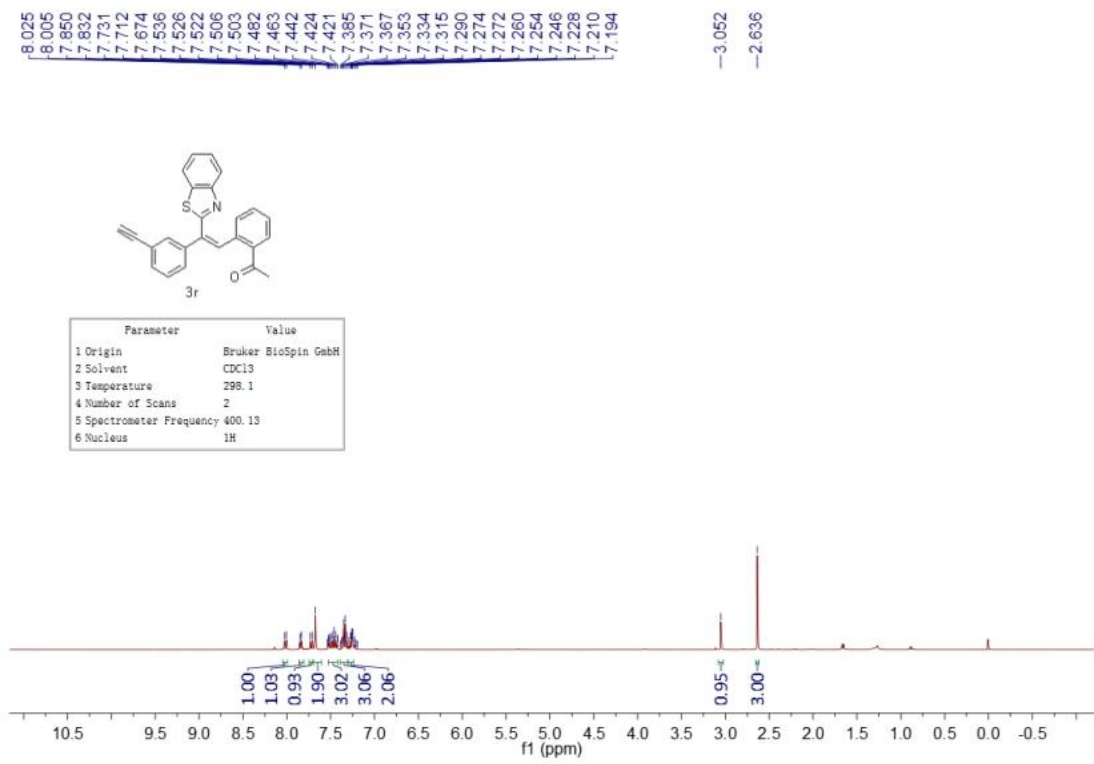
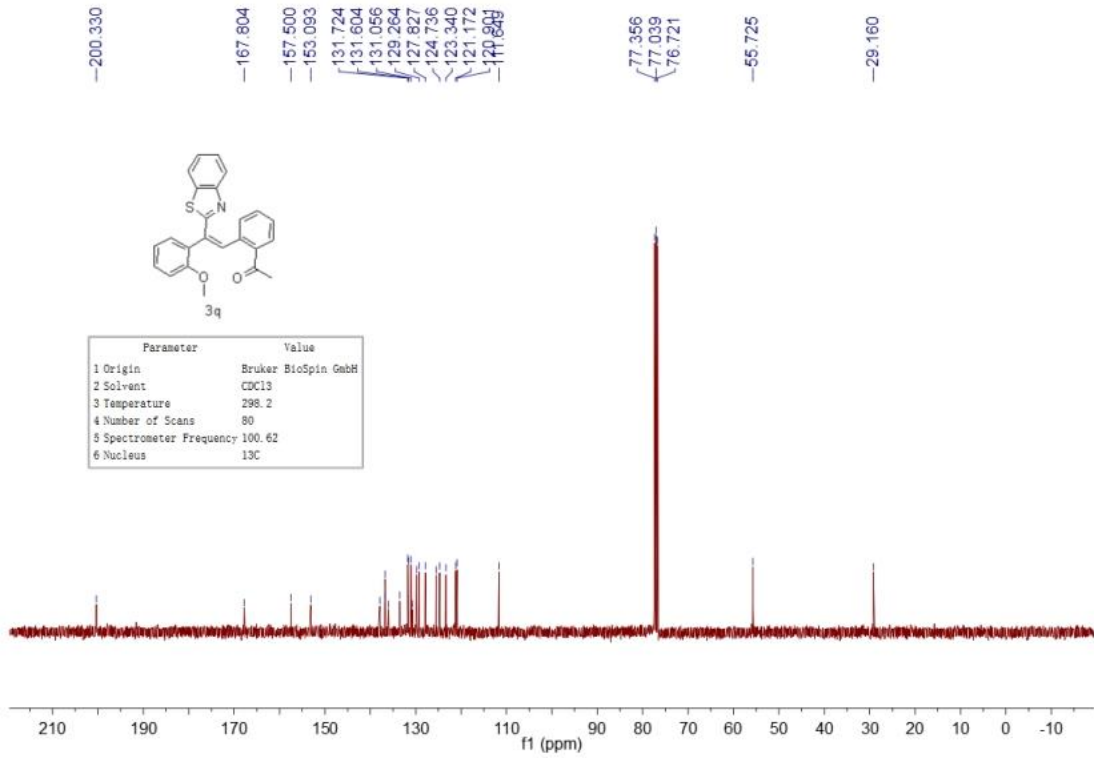


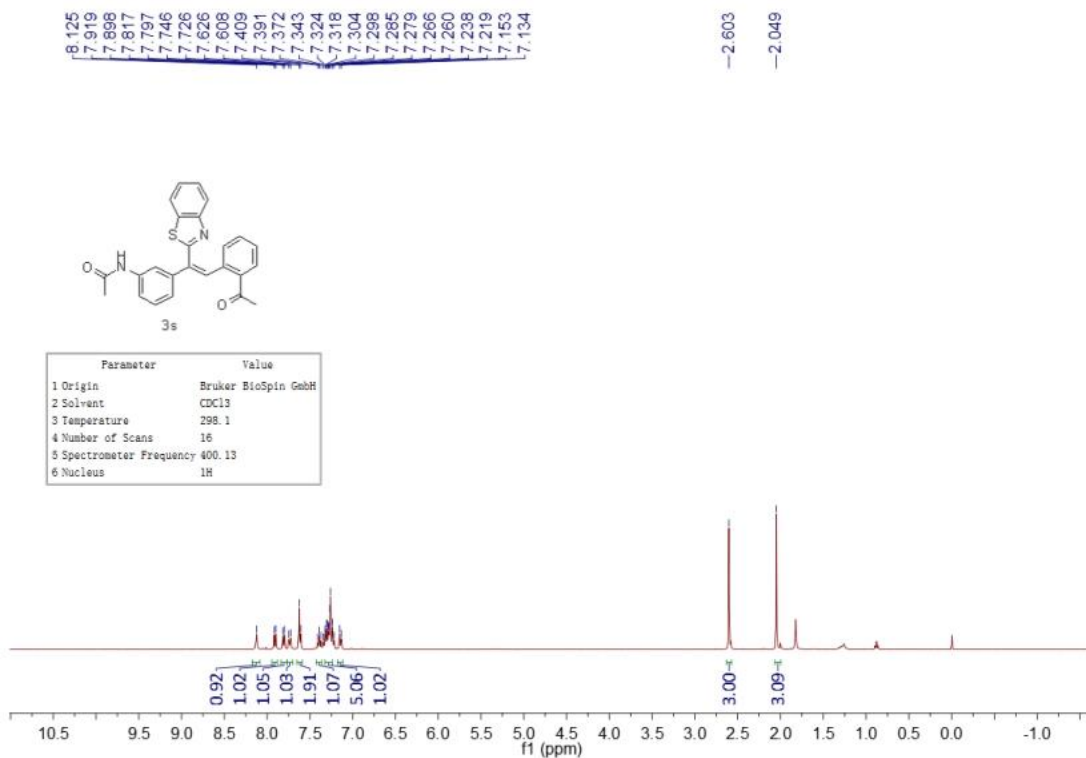
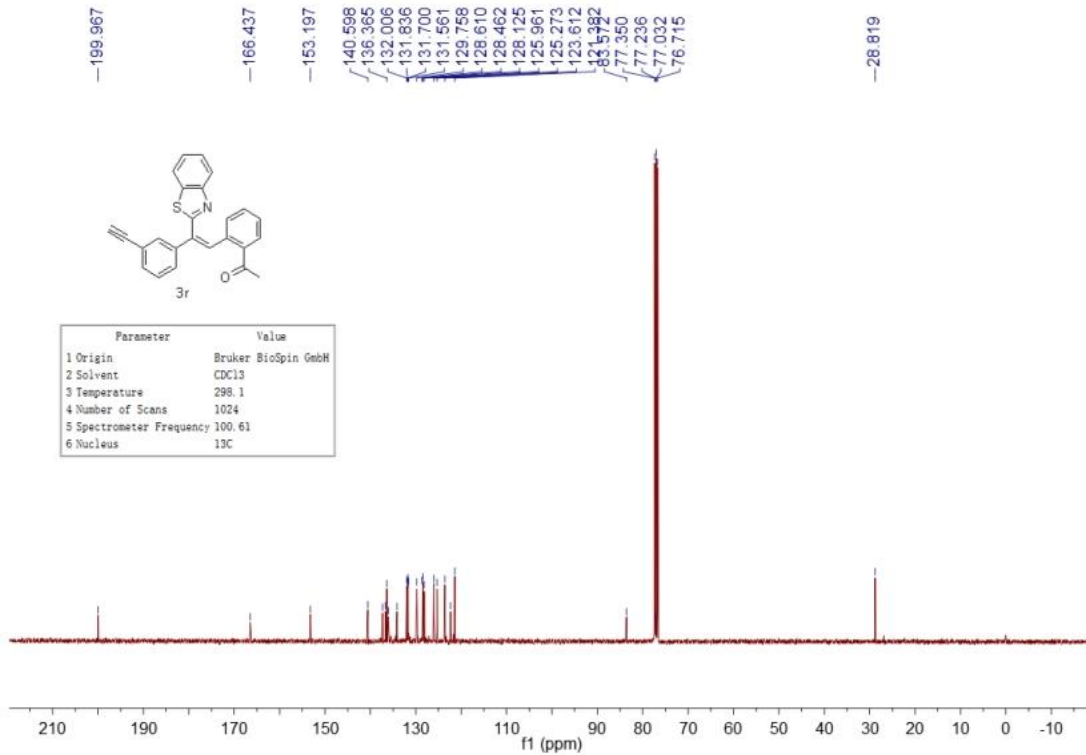


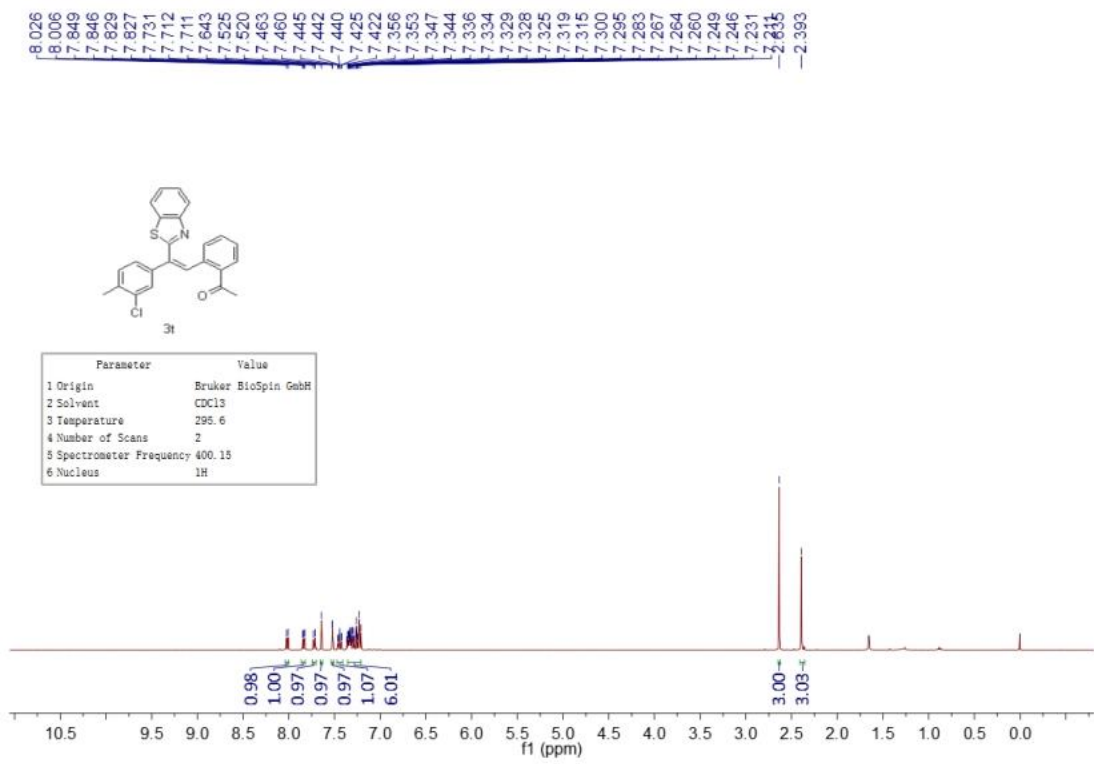
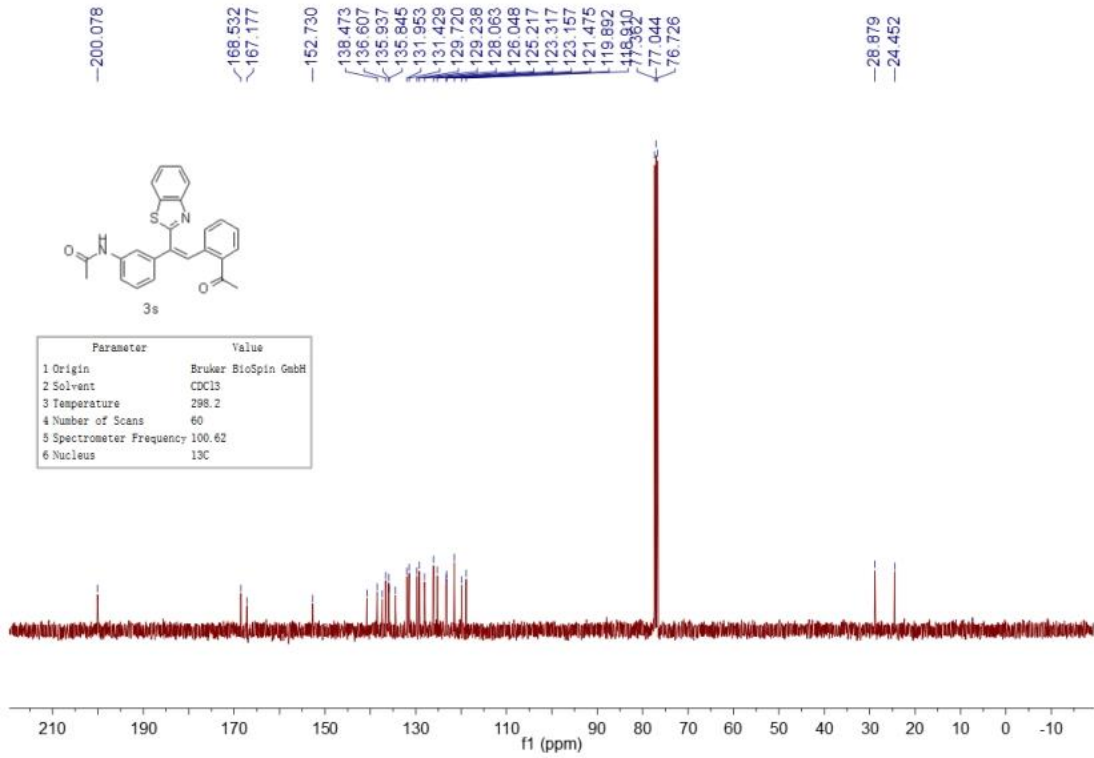


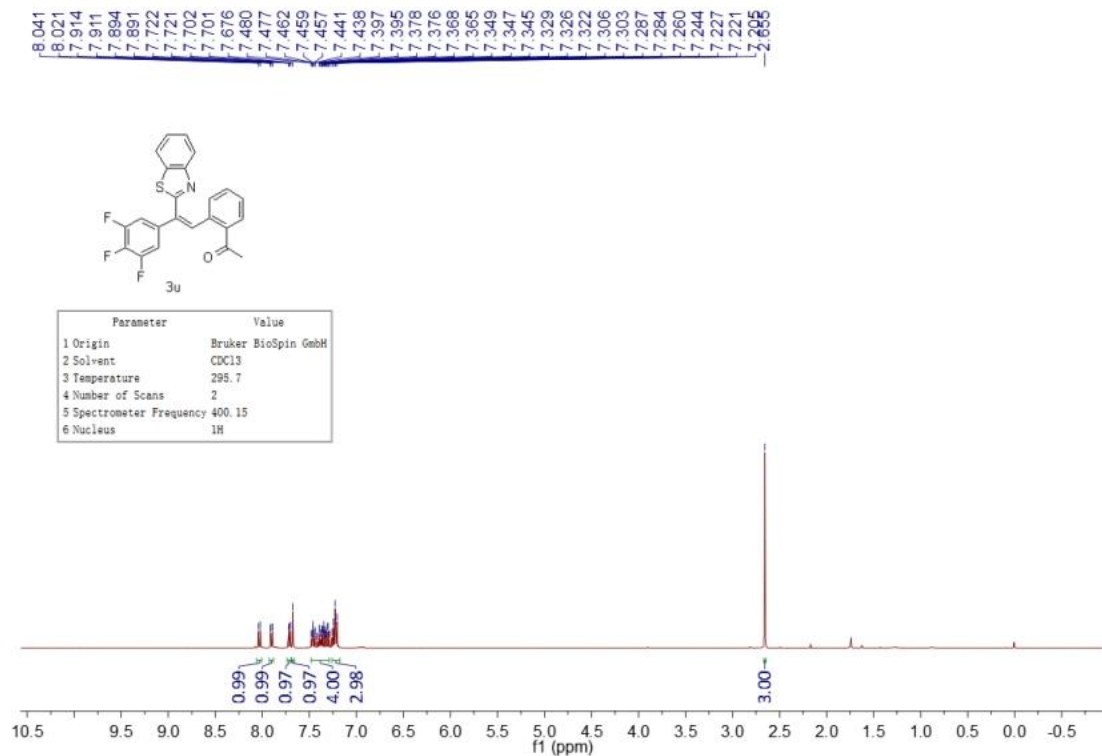
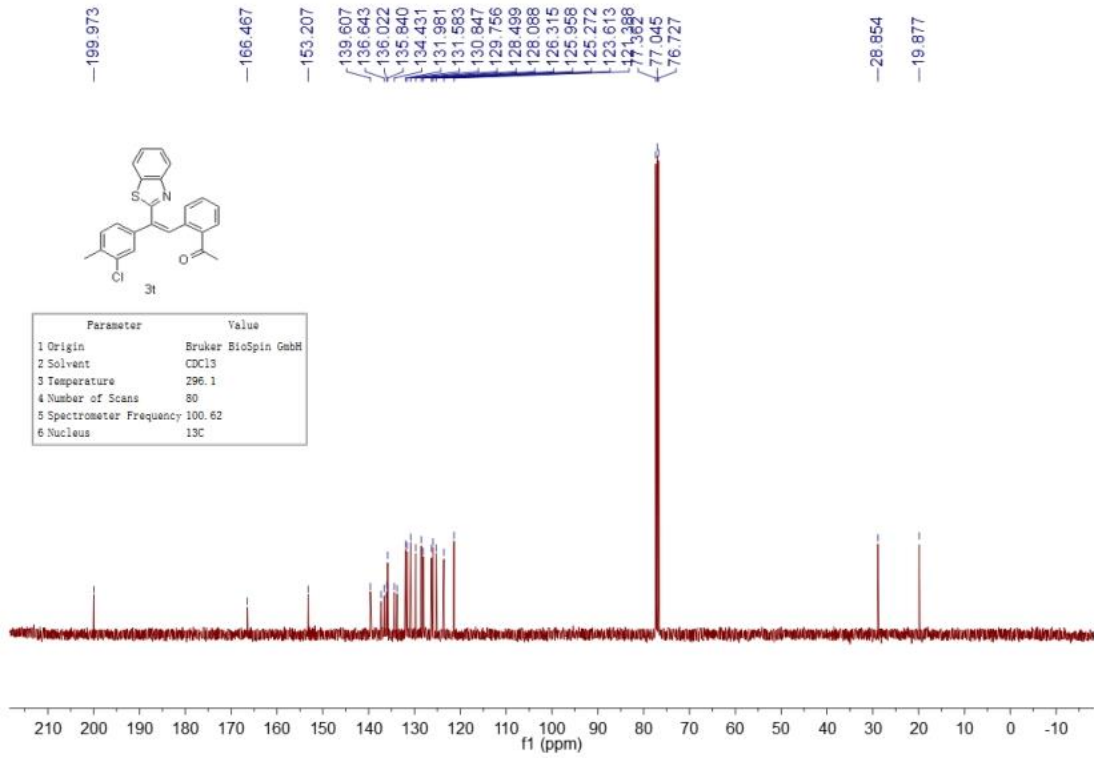


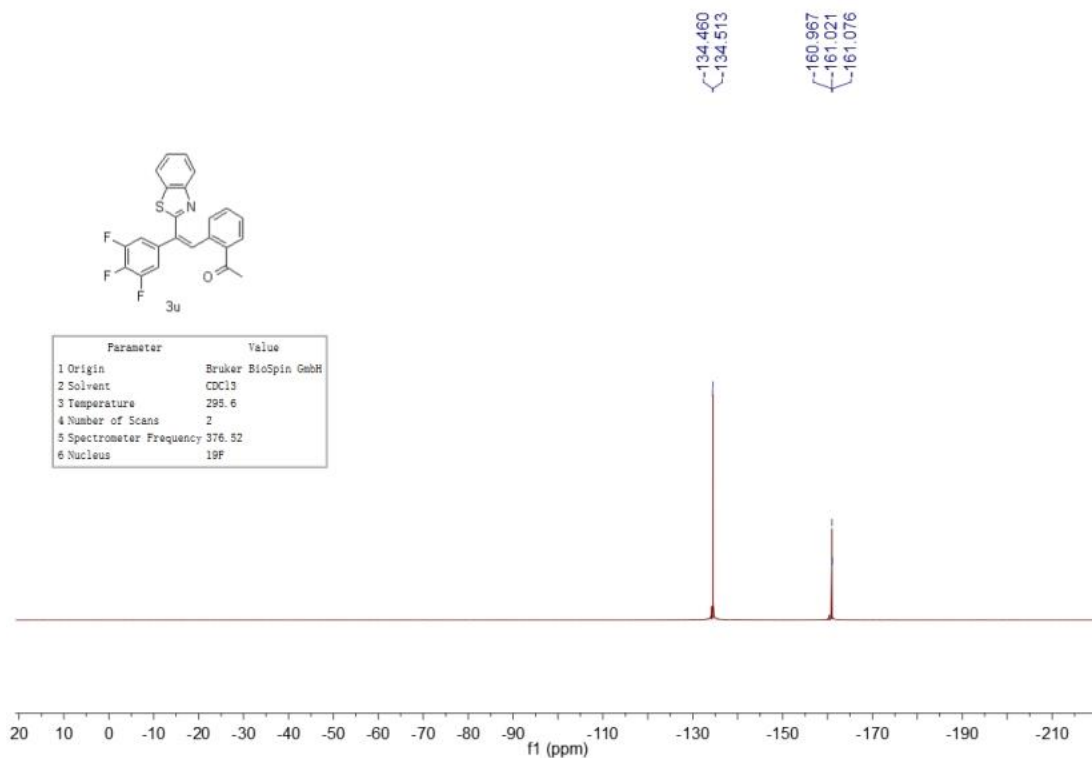
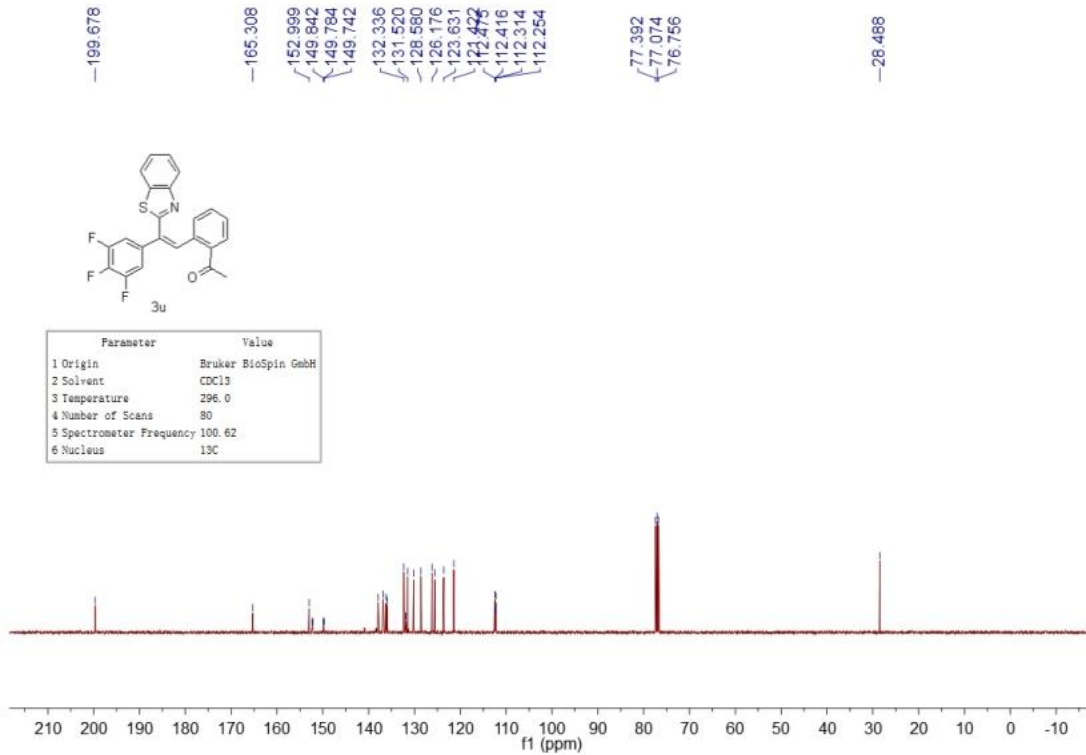


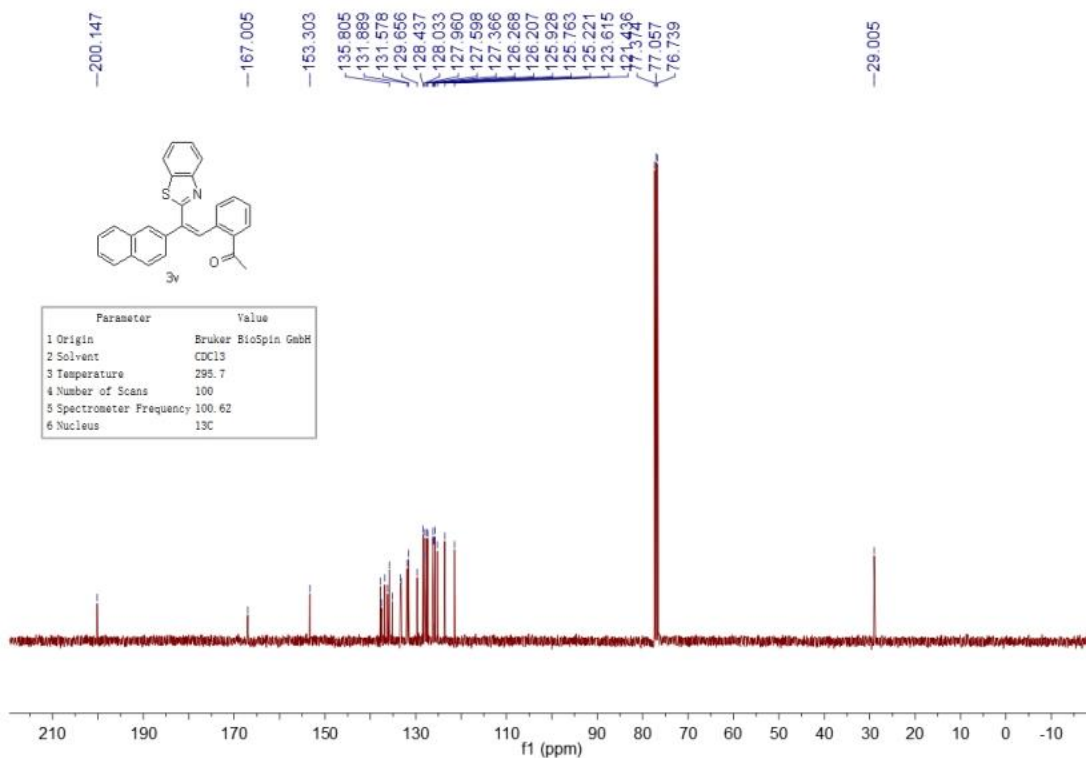
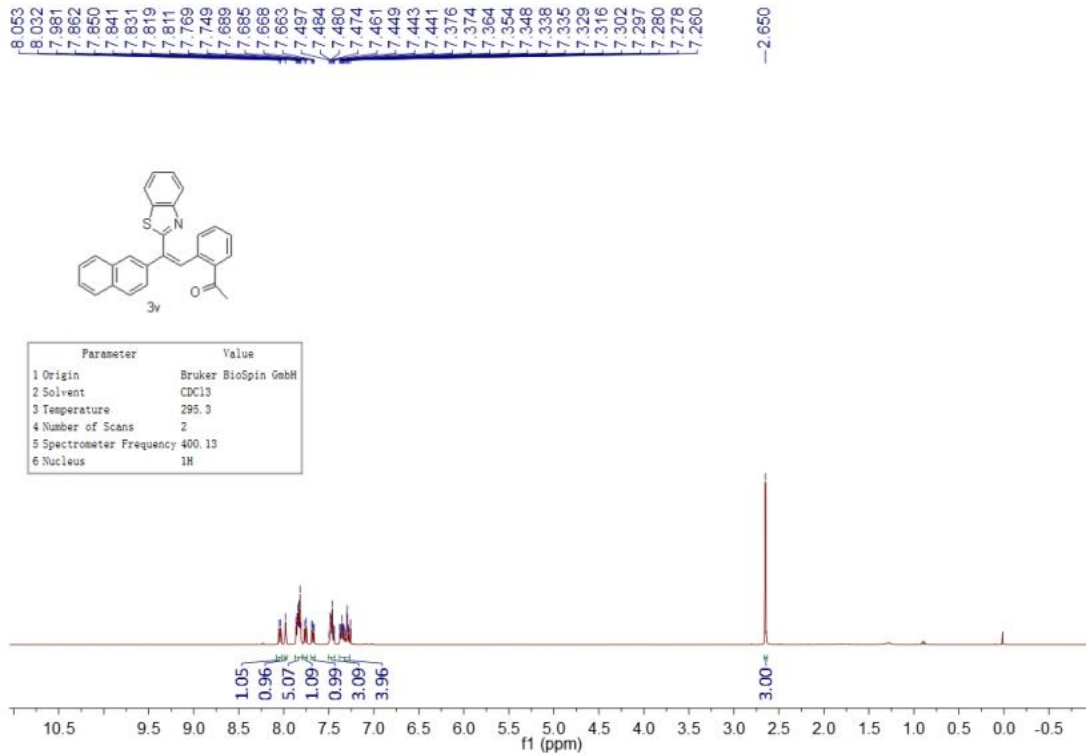


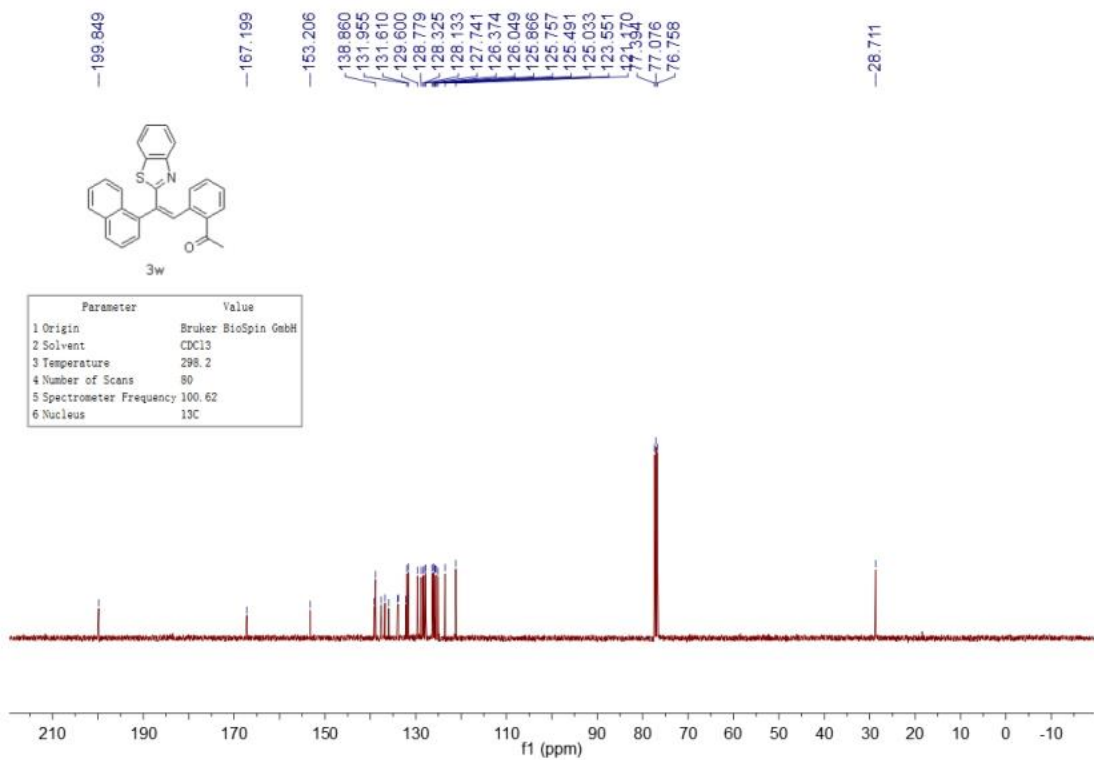
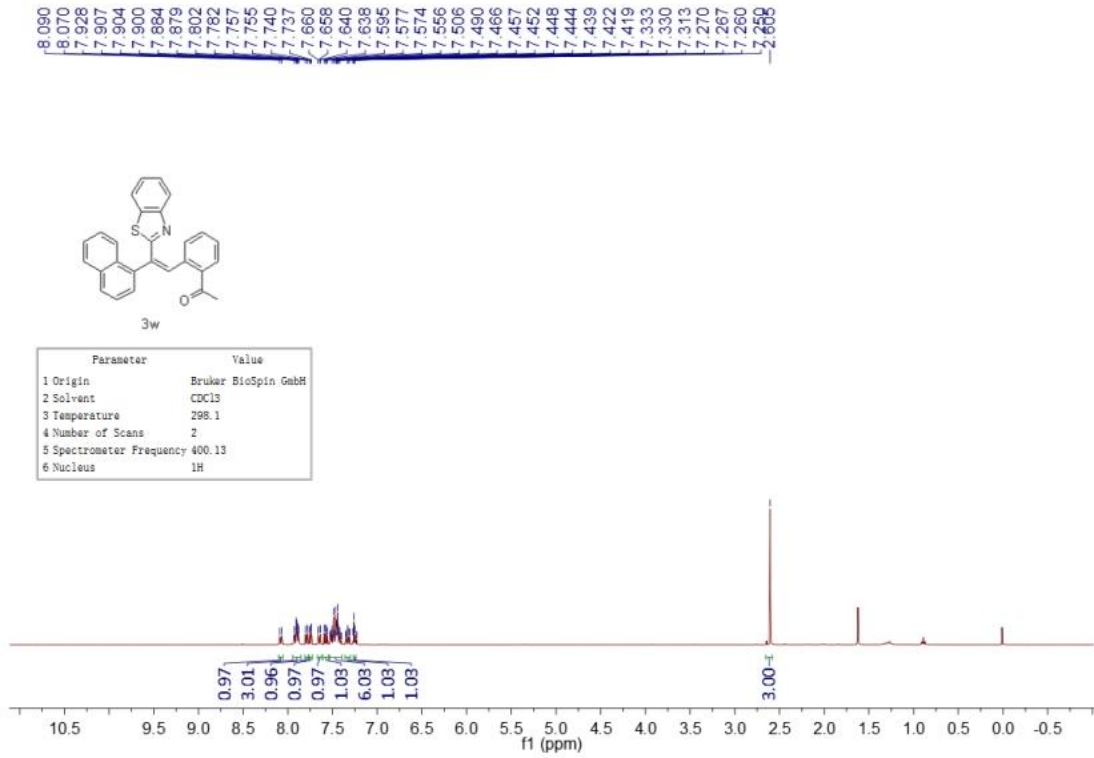




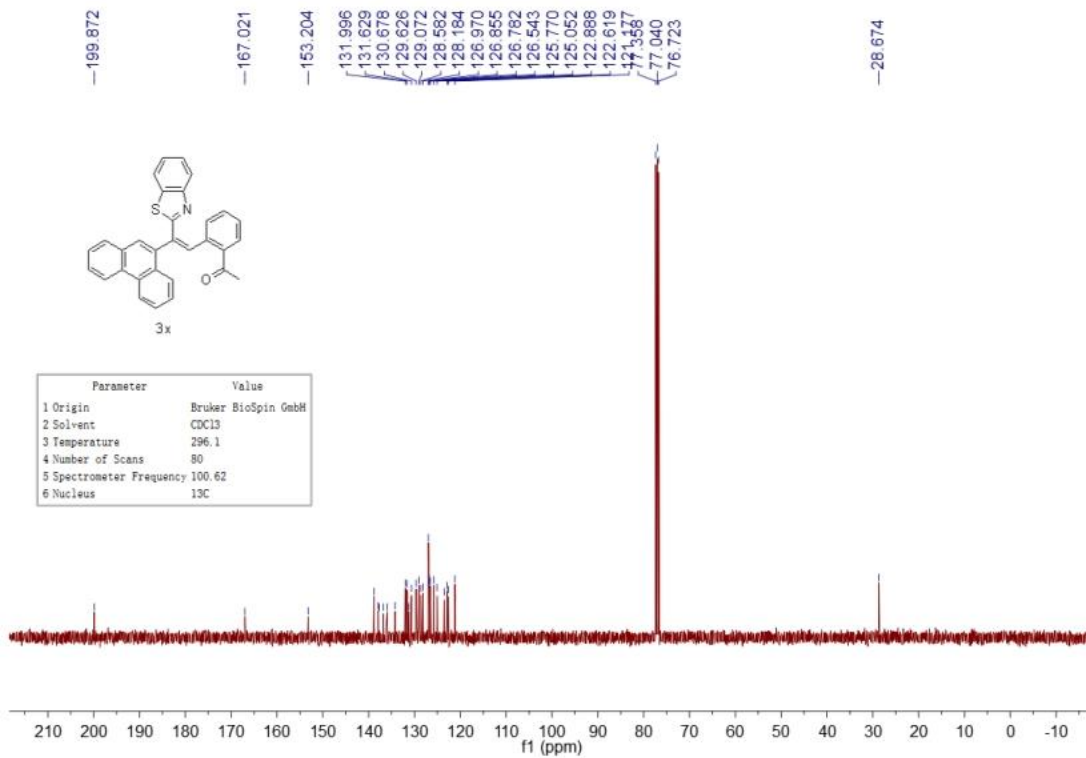
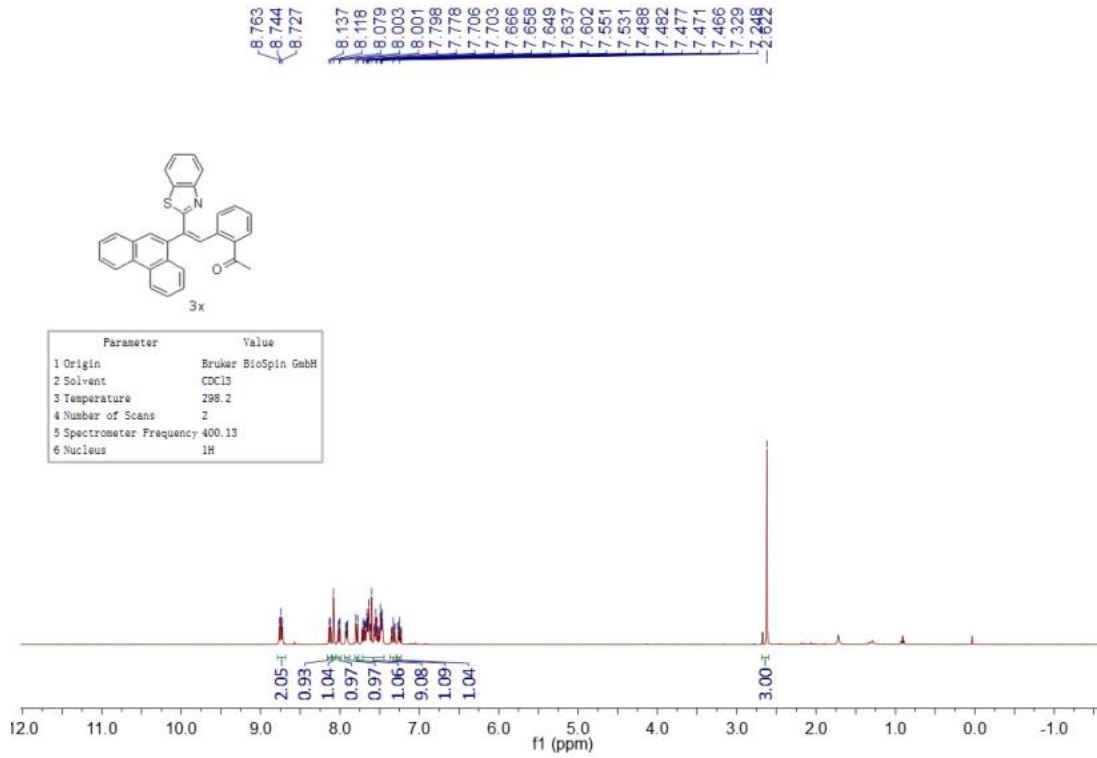




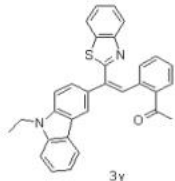






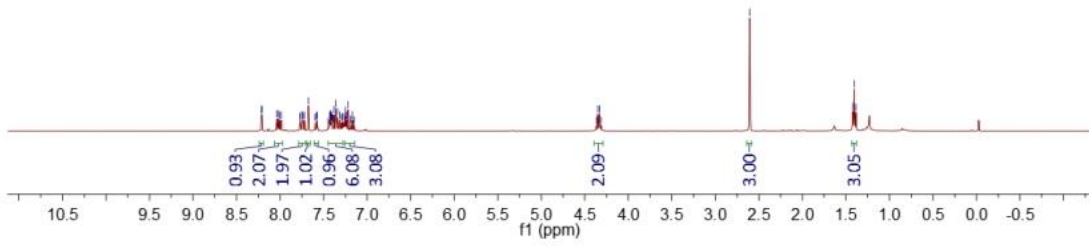


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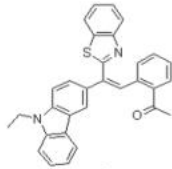


3y

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.2
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H

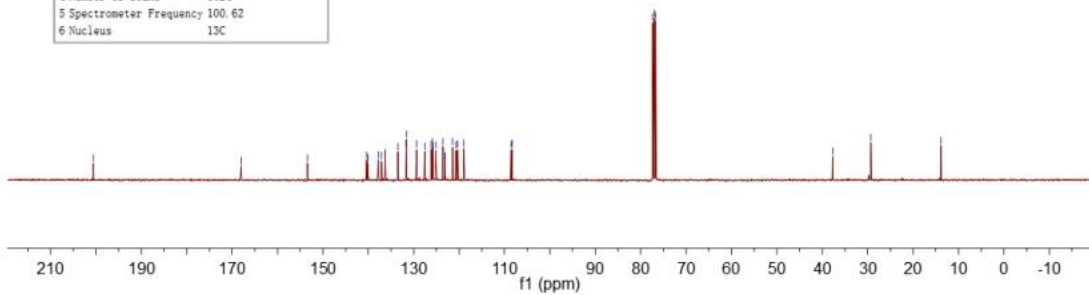


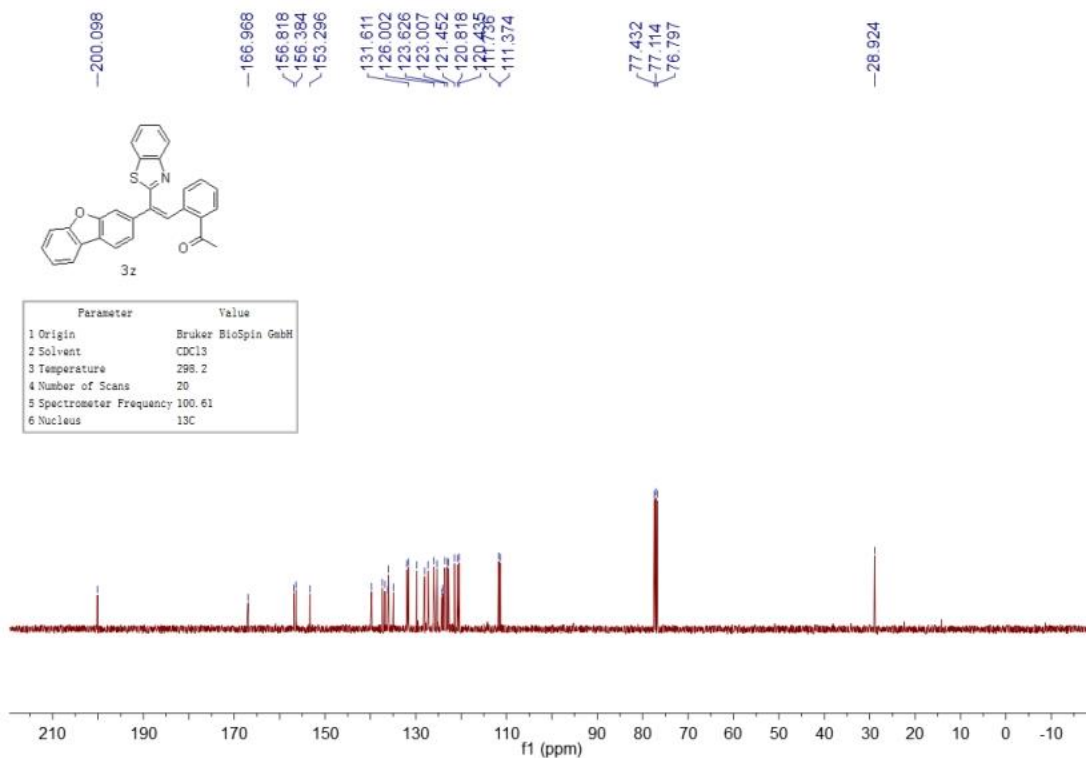
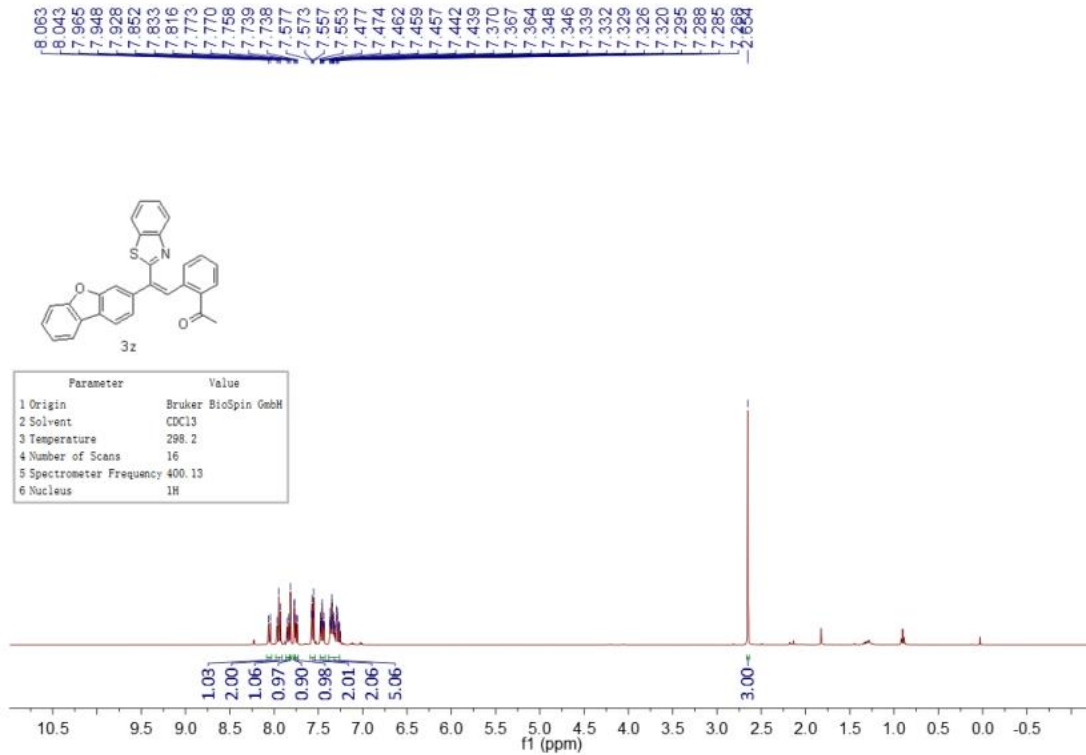
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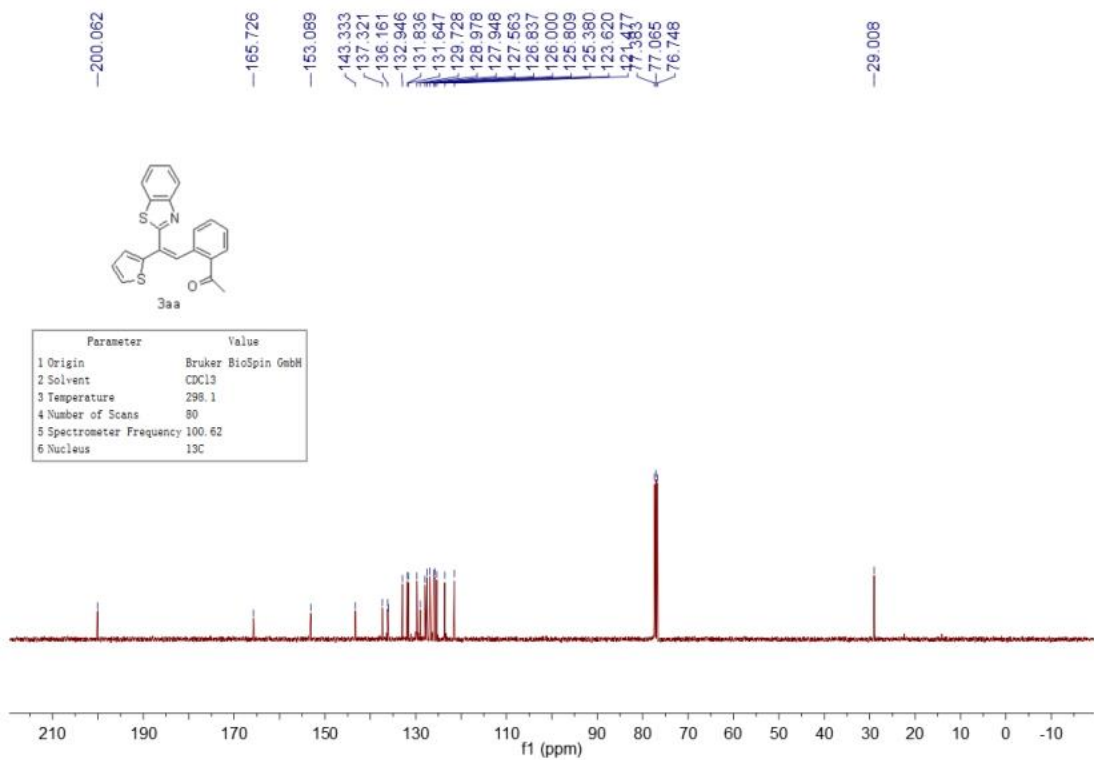
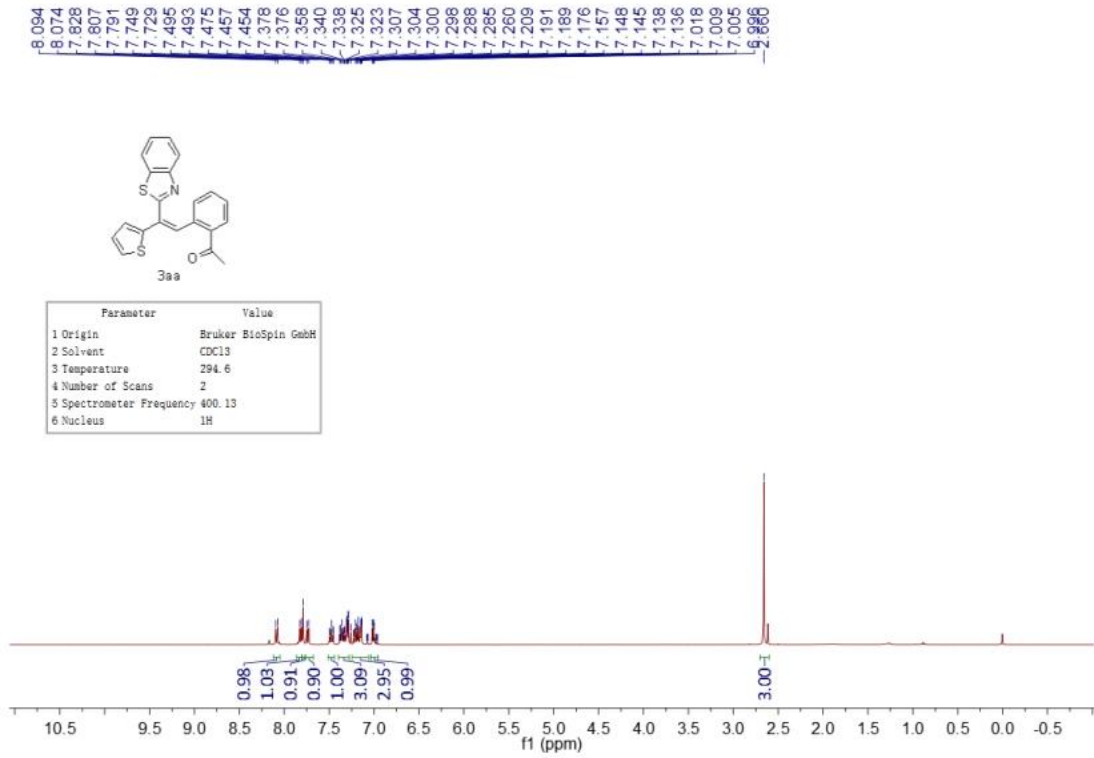


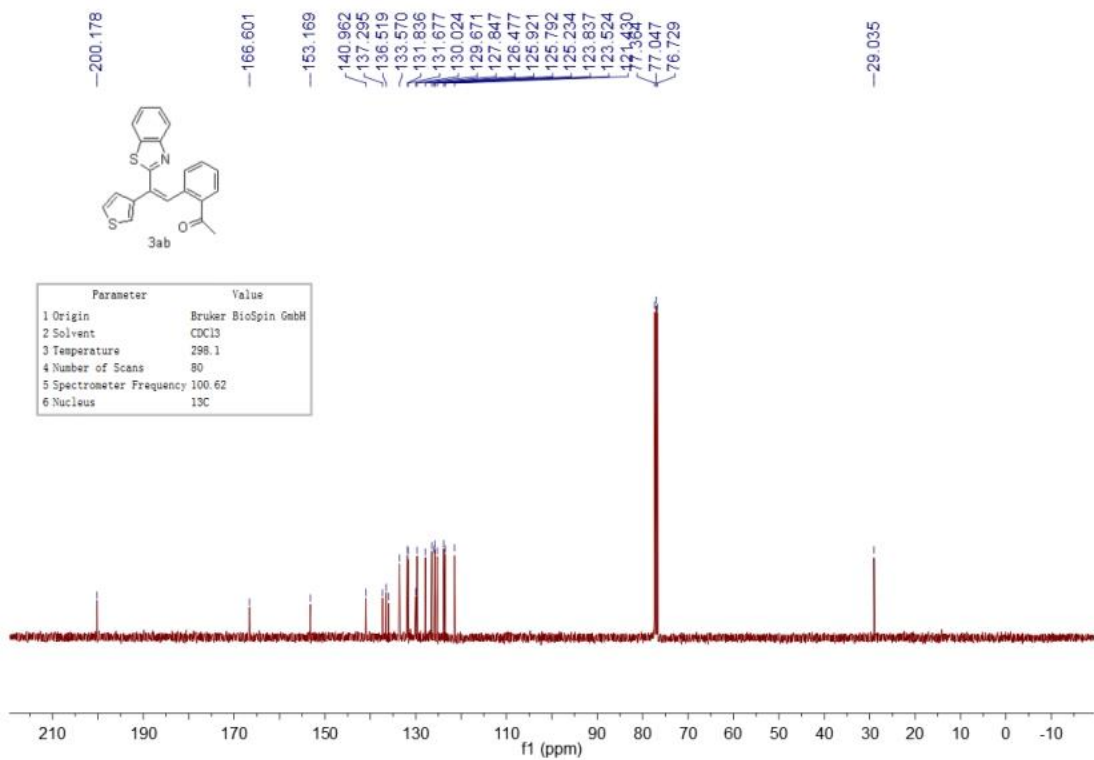
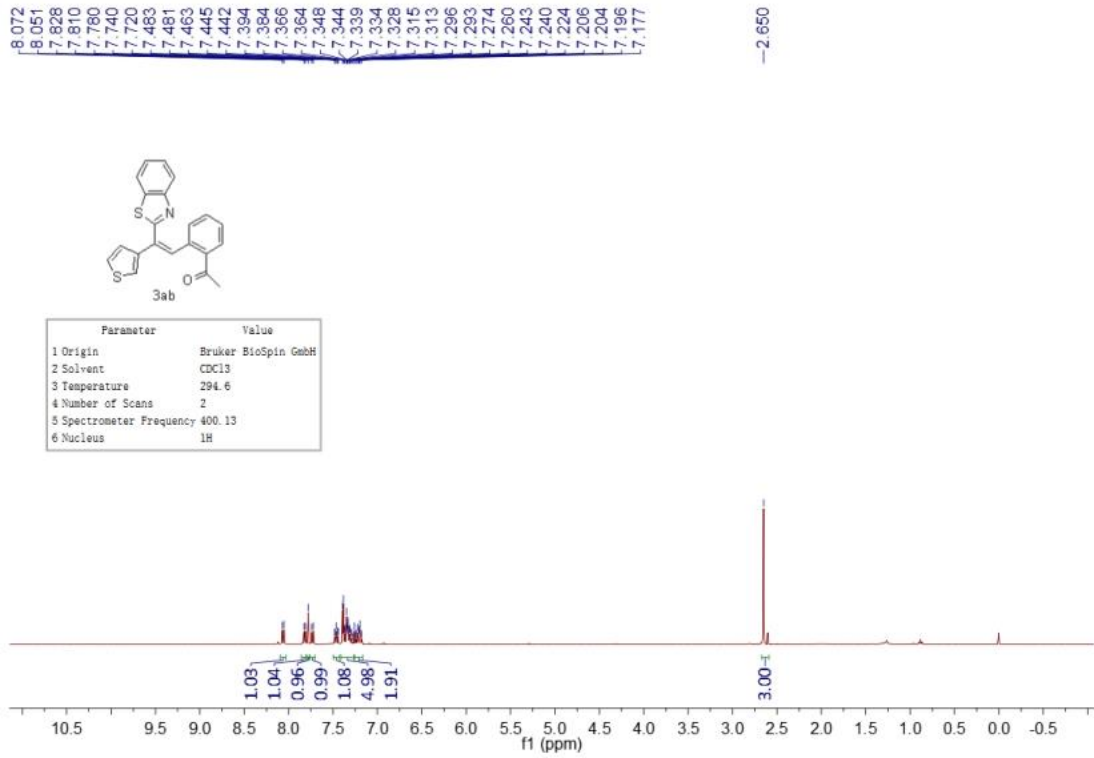
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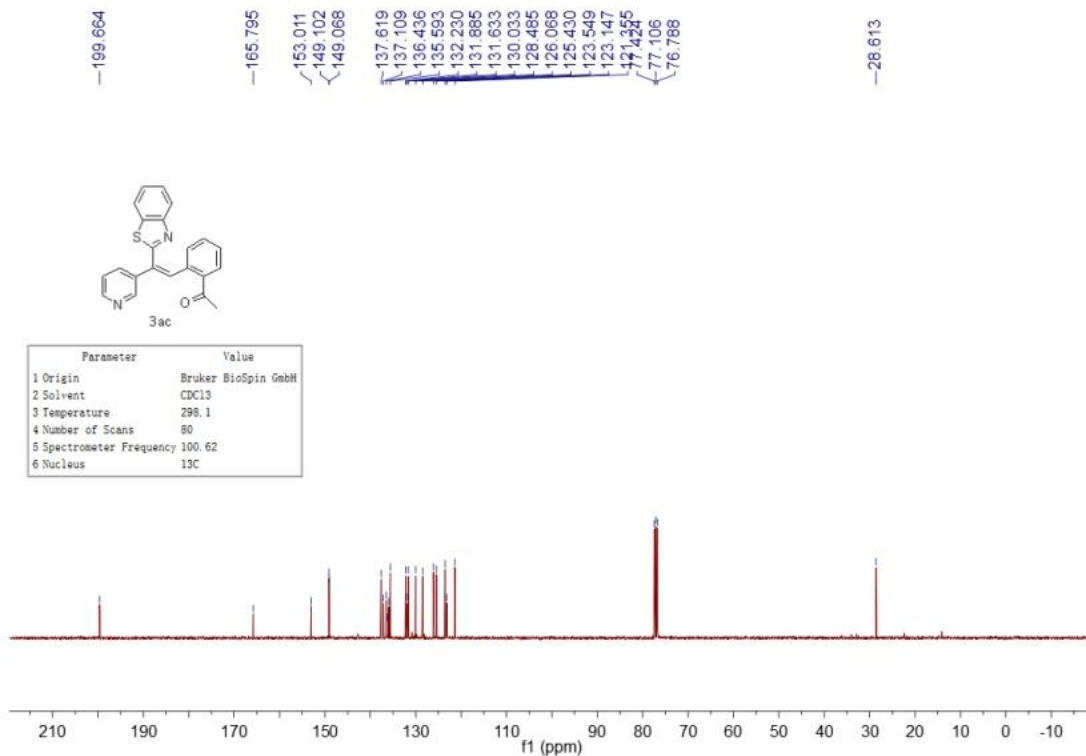
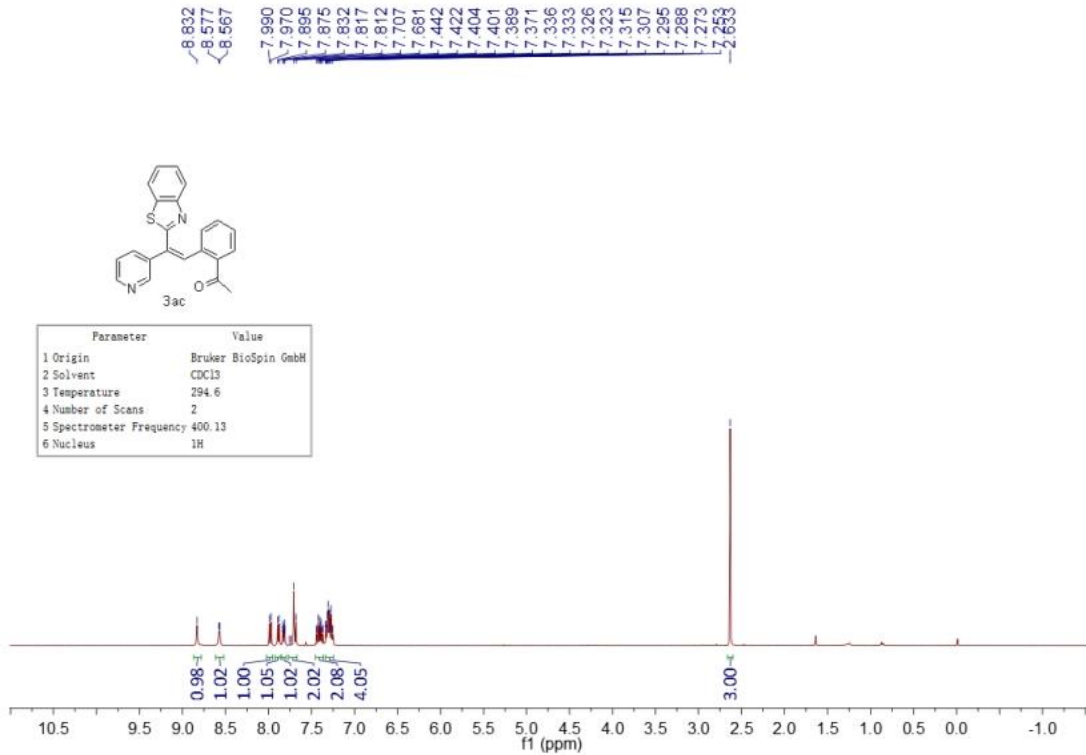
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	13C

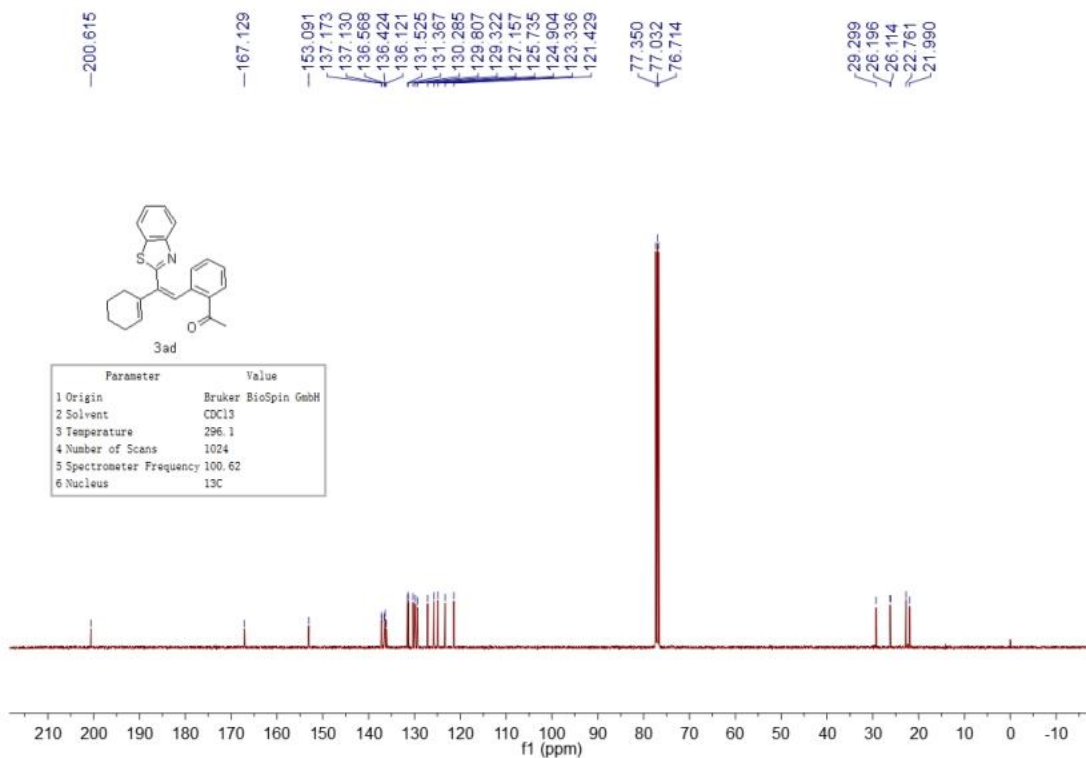
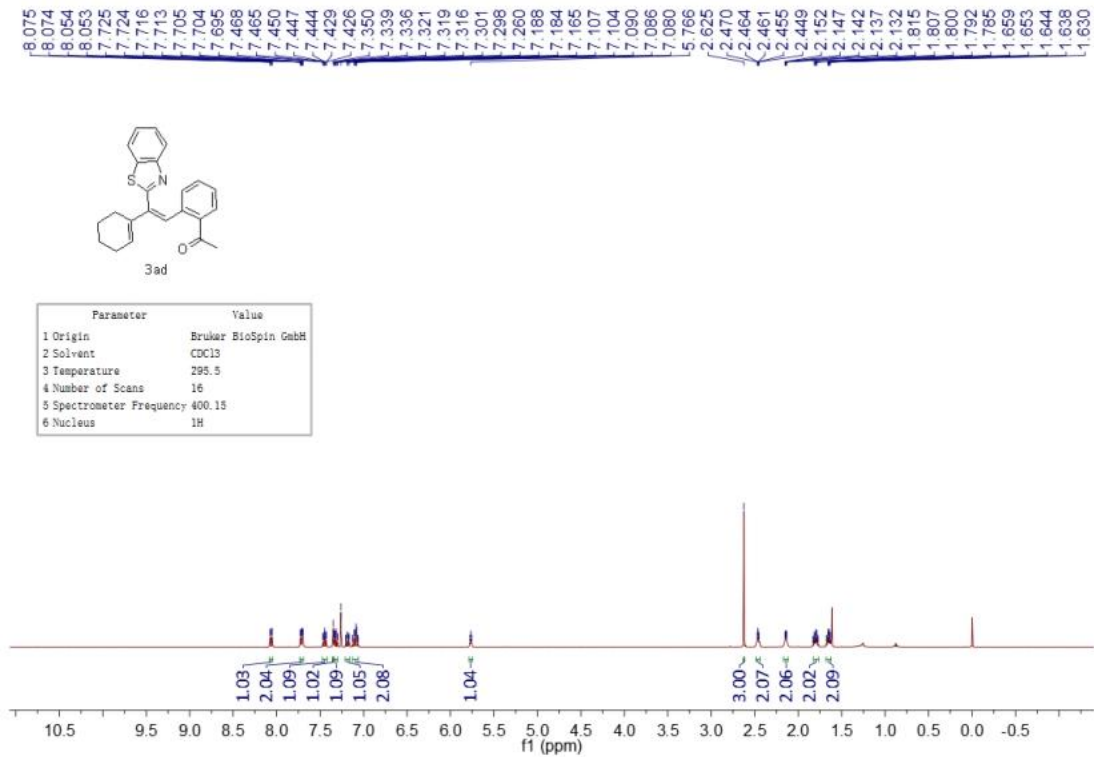


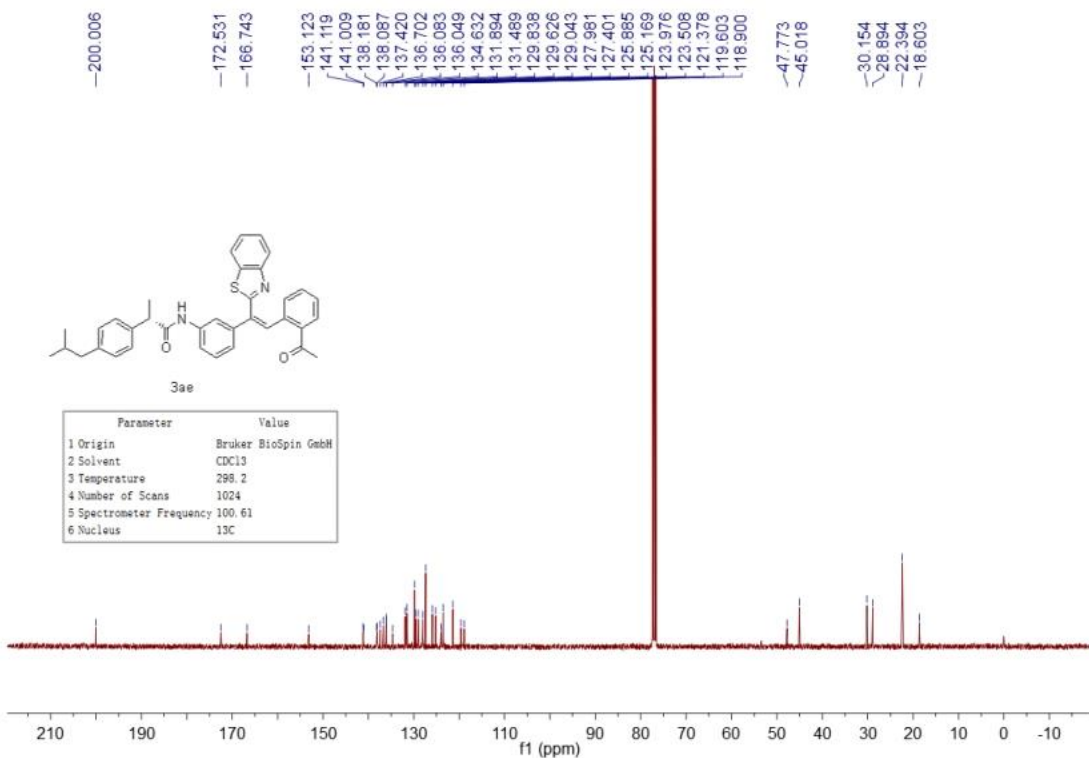
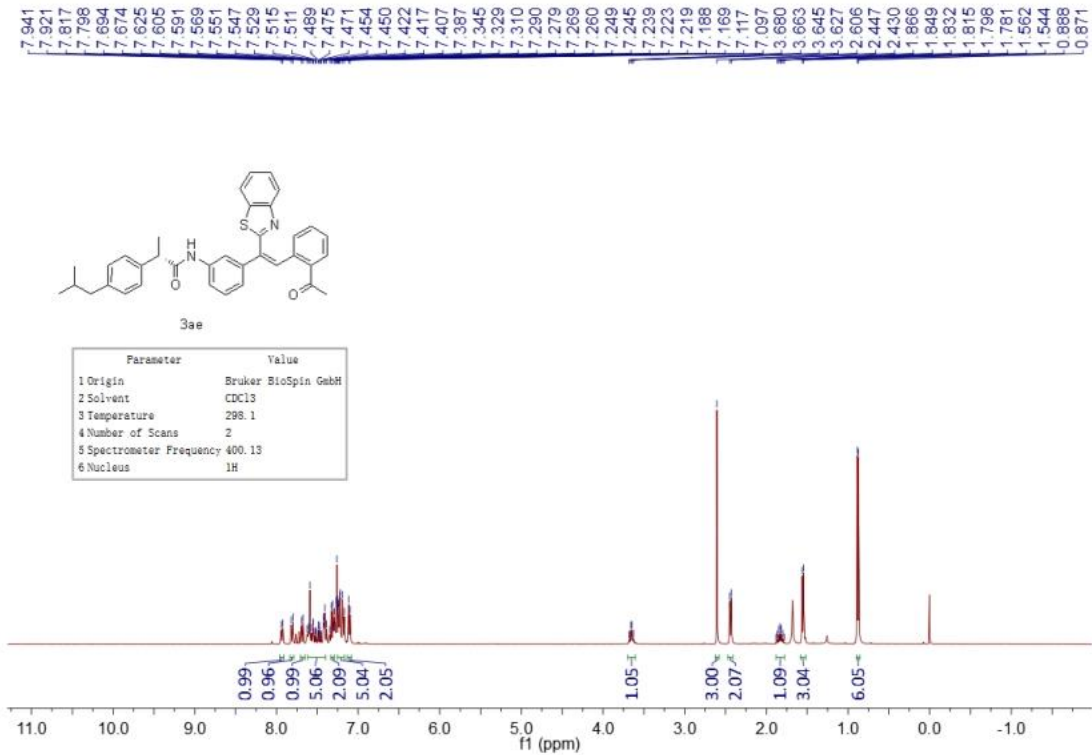




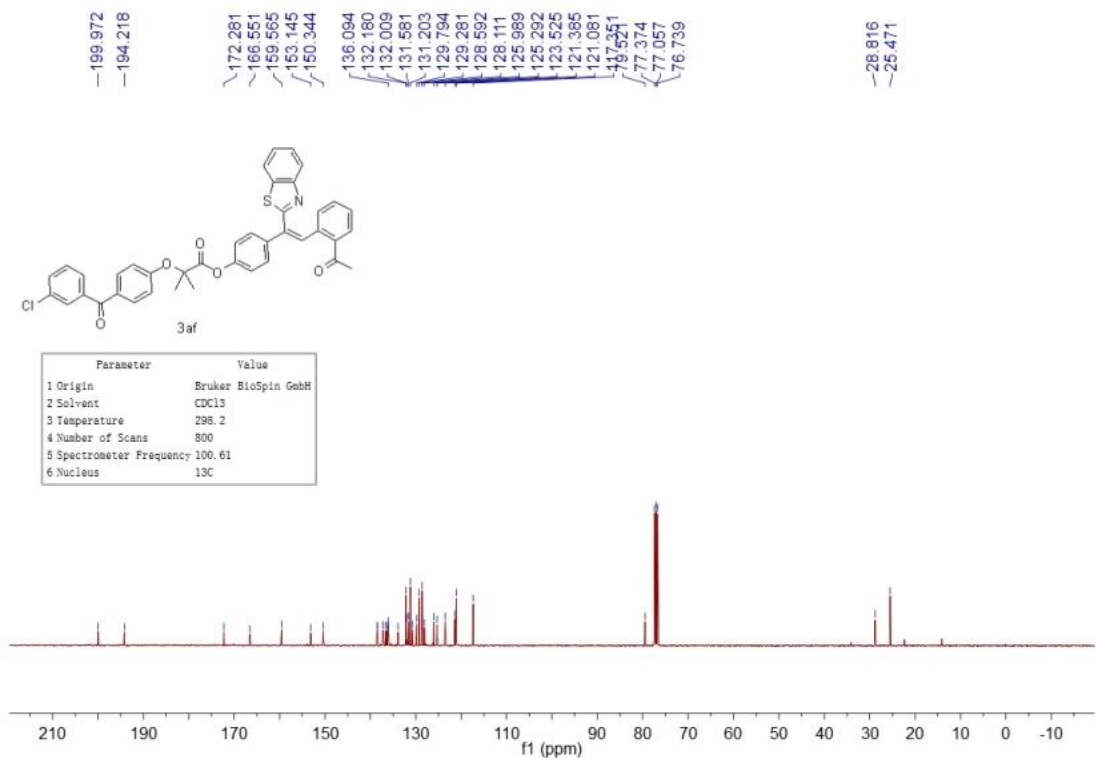
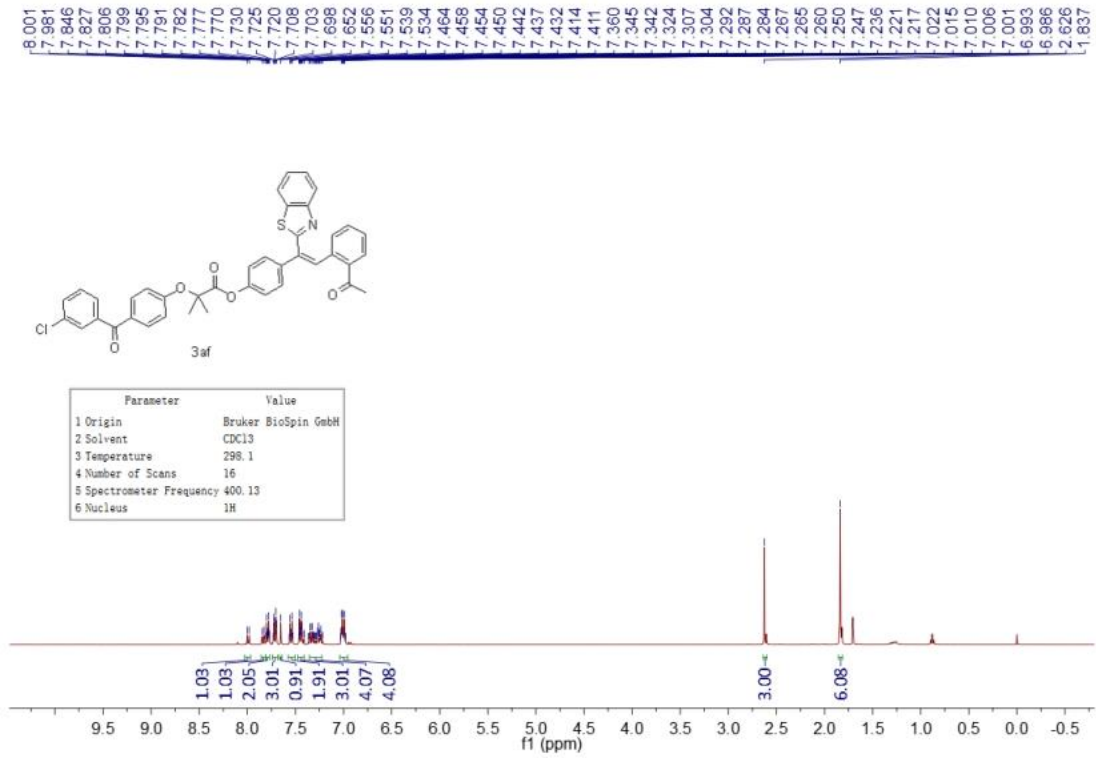


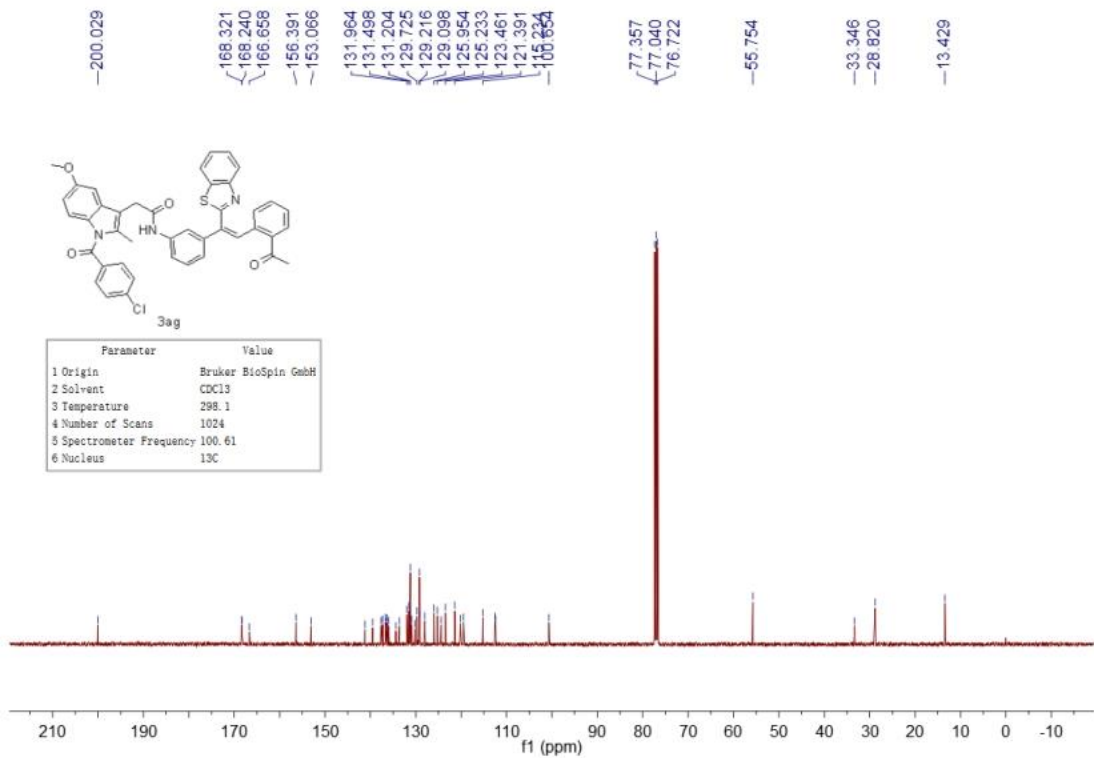
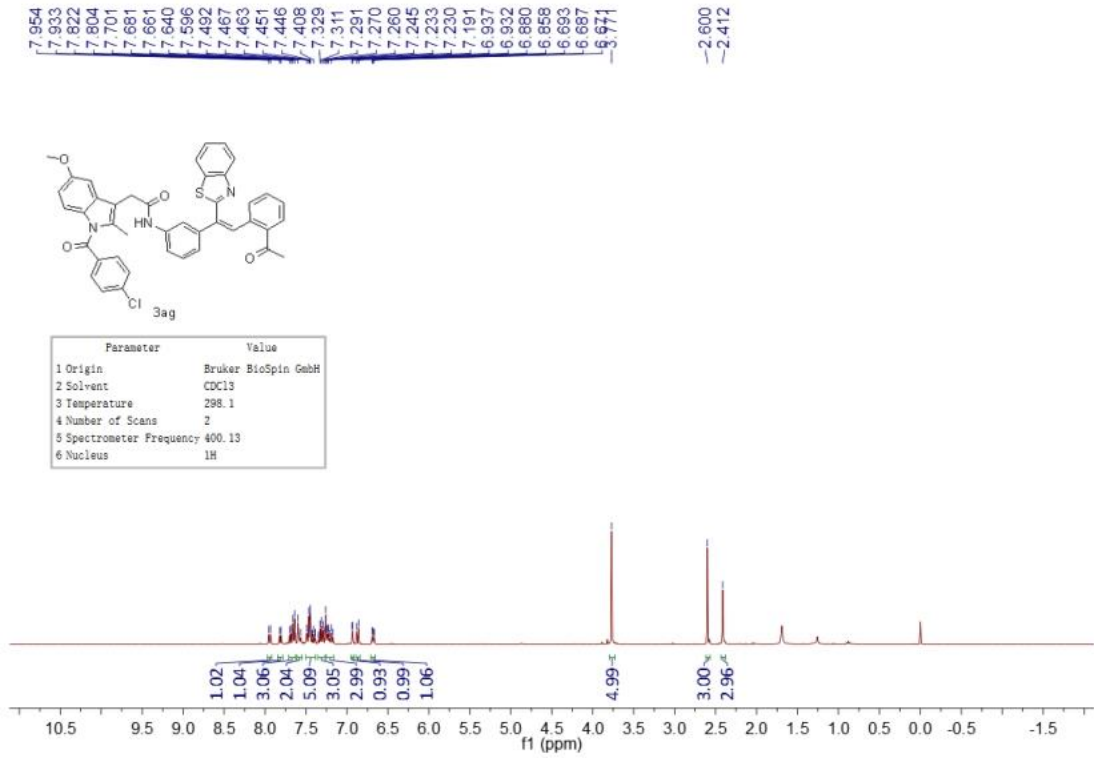


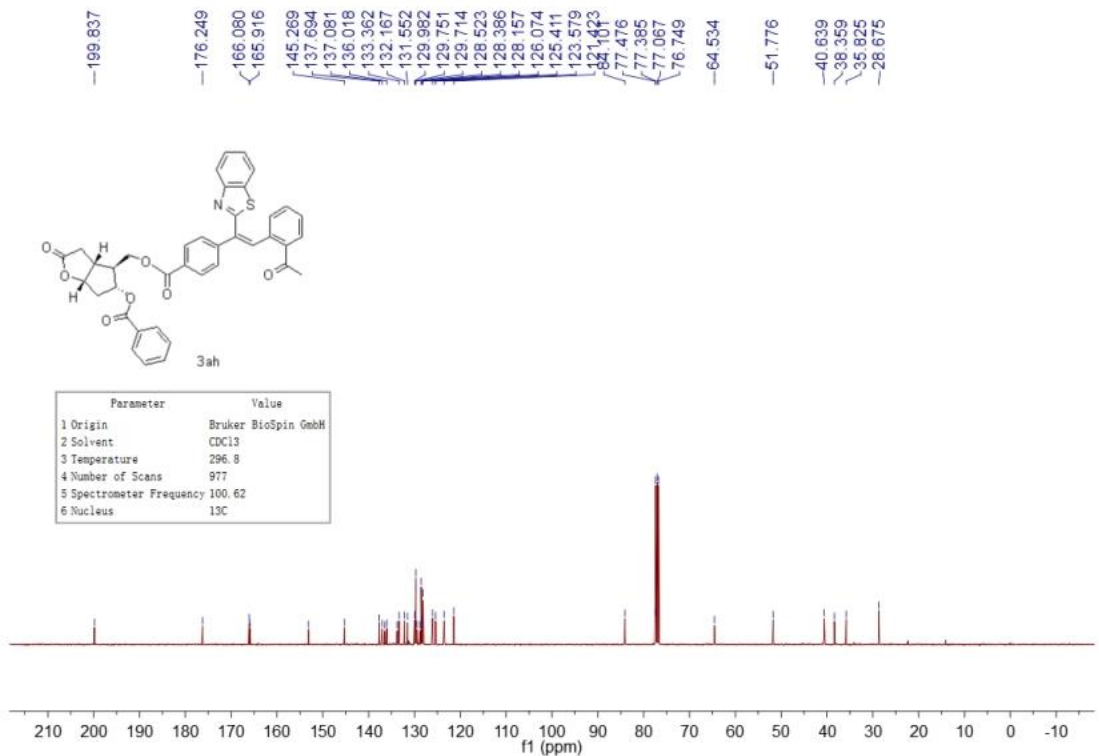
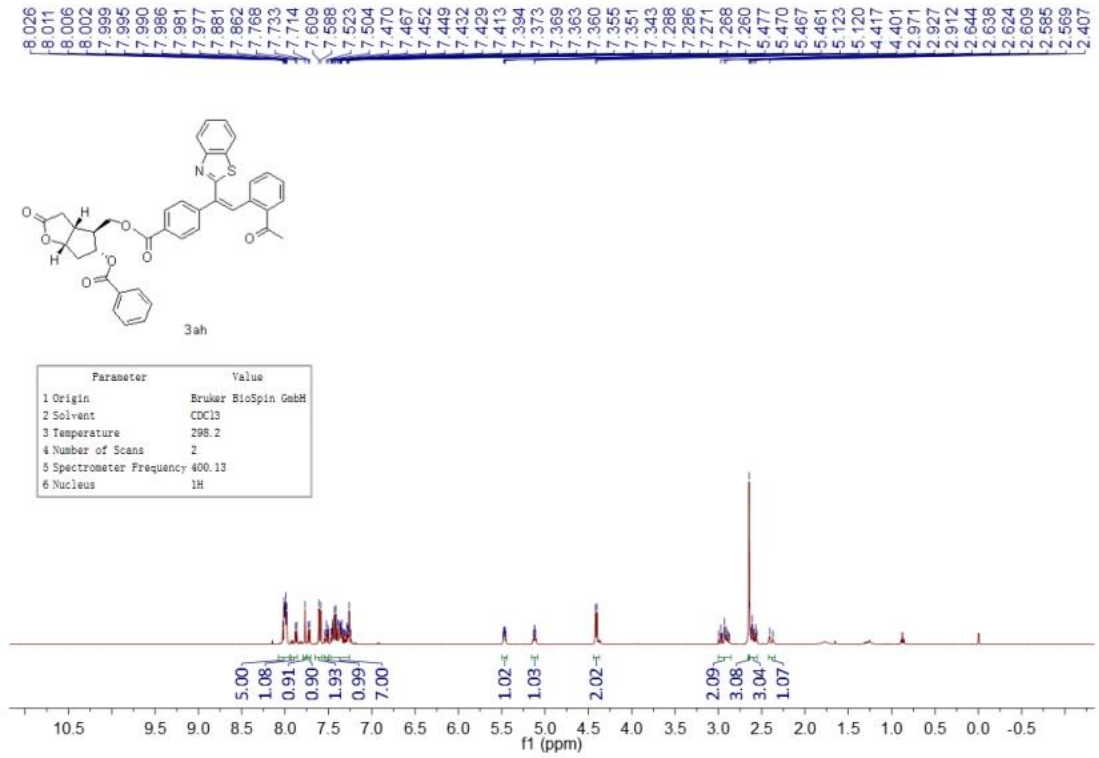


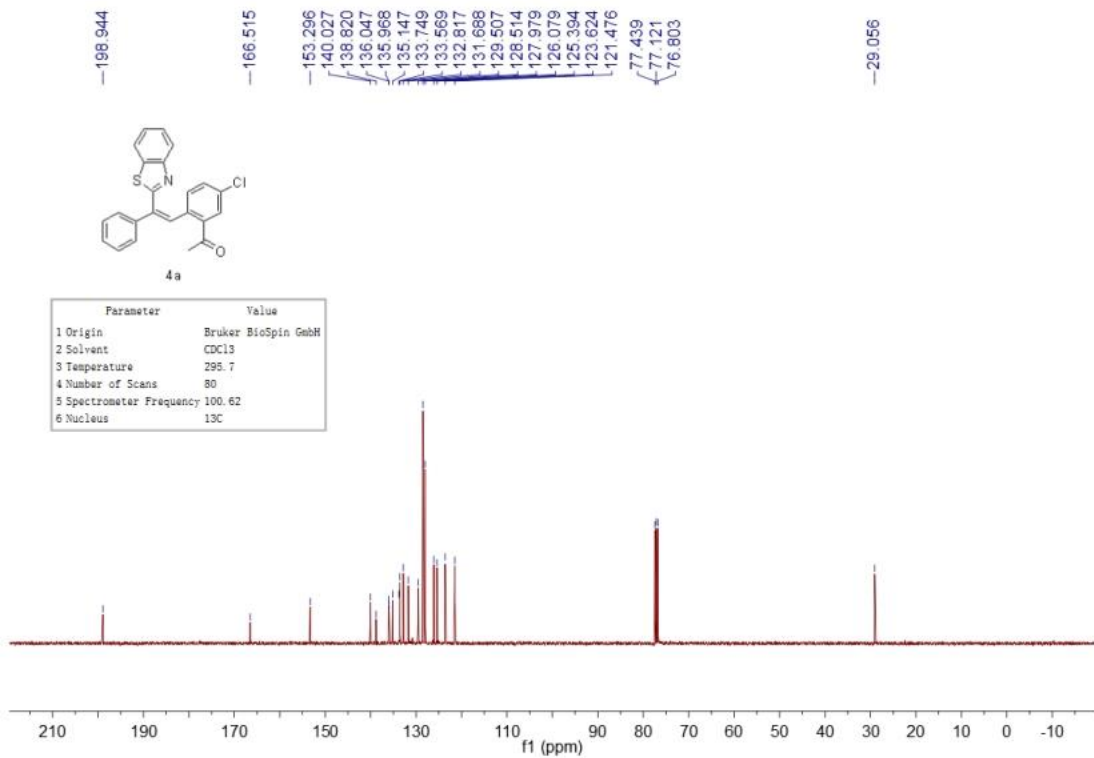
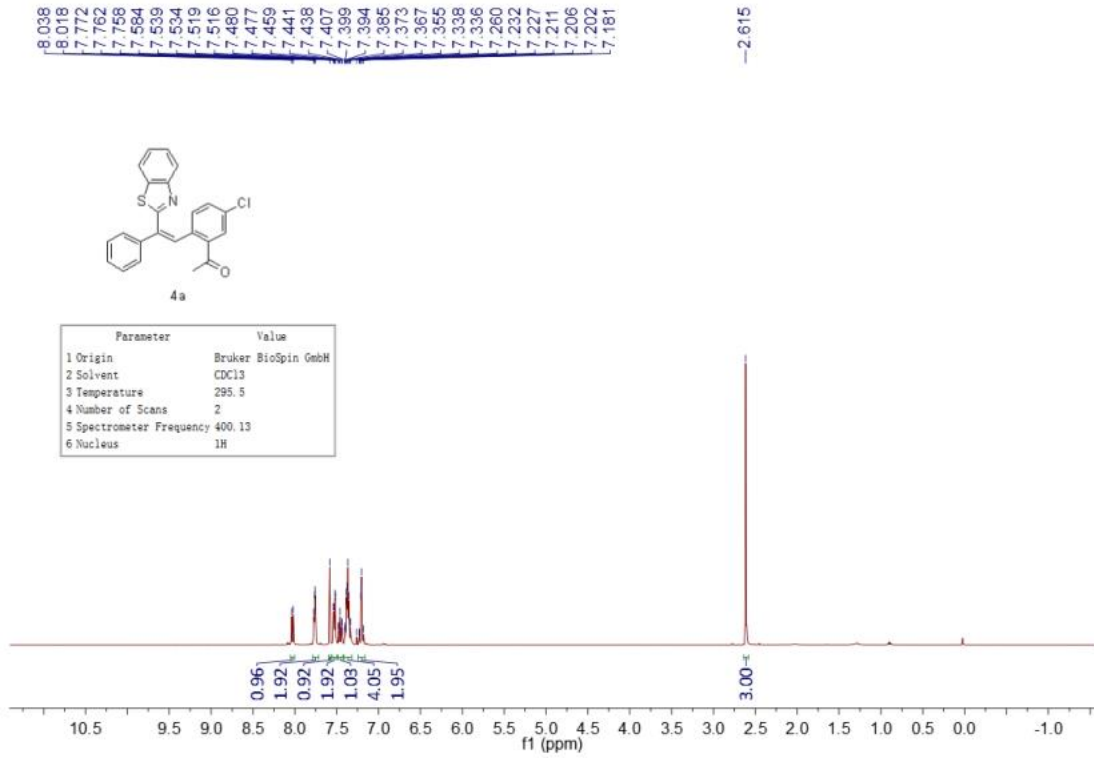




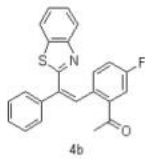




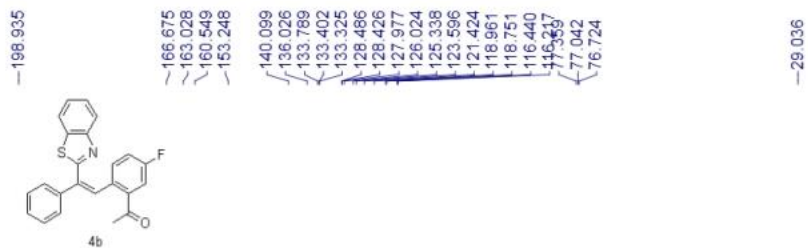
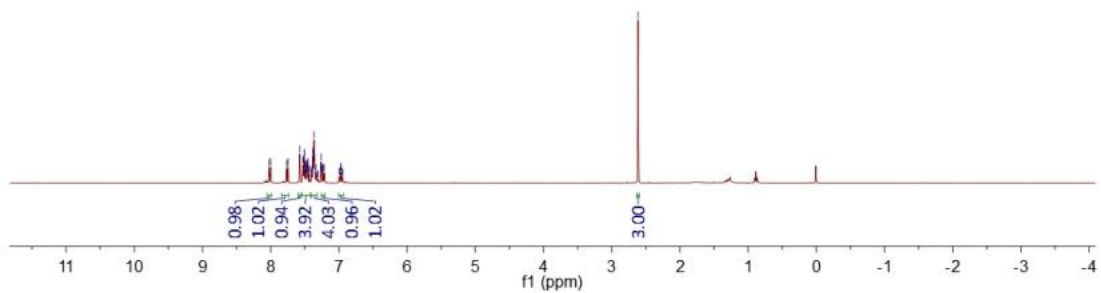




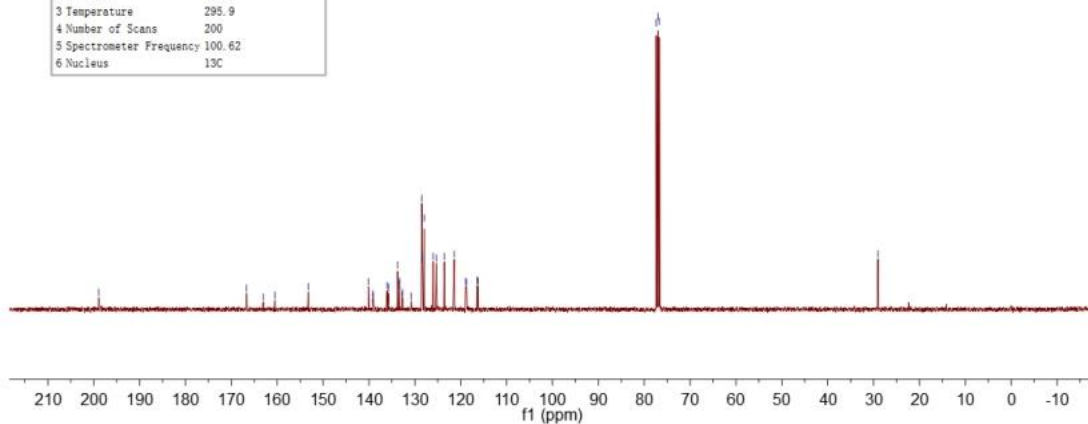
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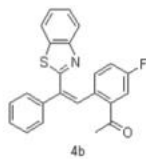


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	295.4
4 Number of Scans	2
5 Spectrometer Frequency	400.15
6 Nucleus	1H

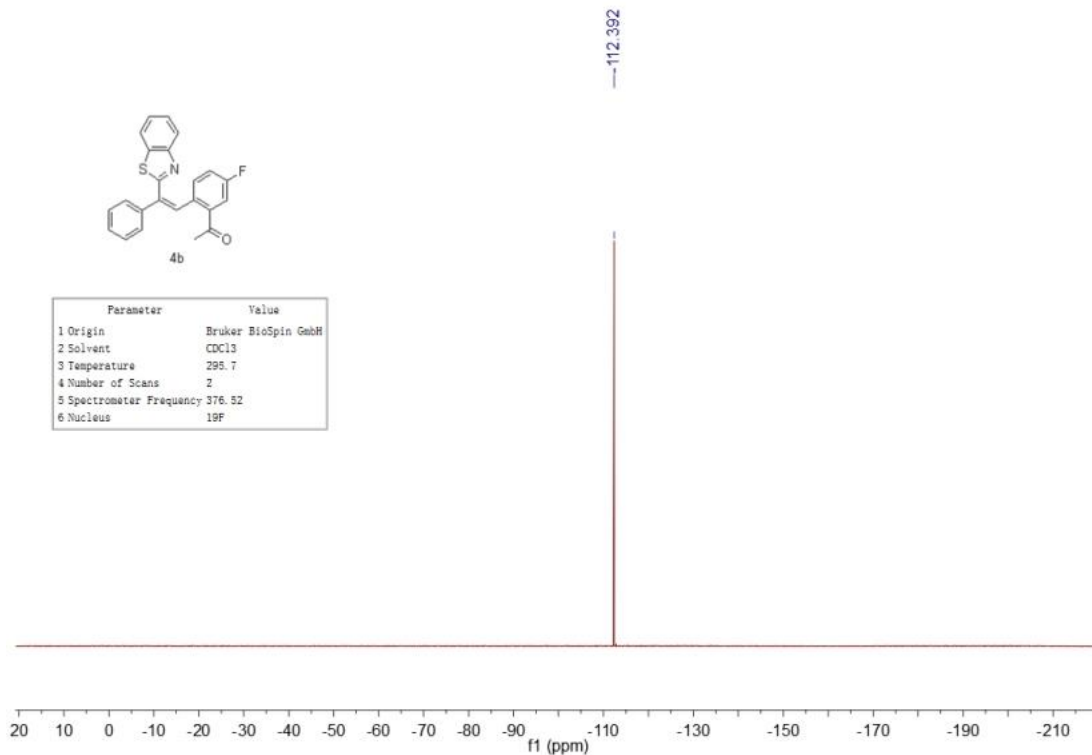


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	295.9
4 Number of Scans	200
5 Spectrometer Frequency	100.62
6 Nucleus	13C

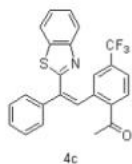




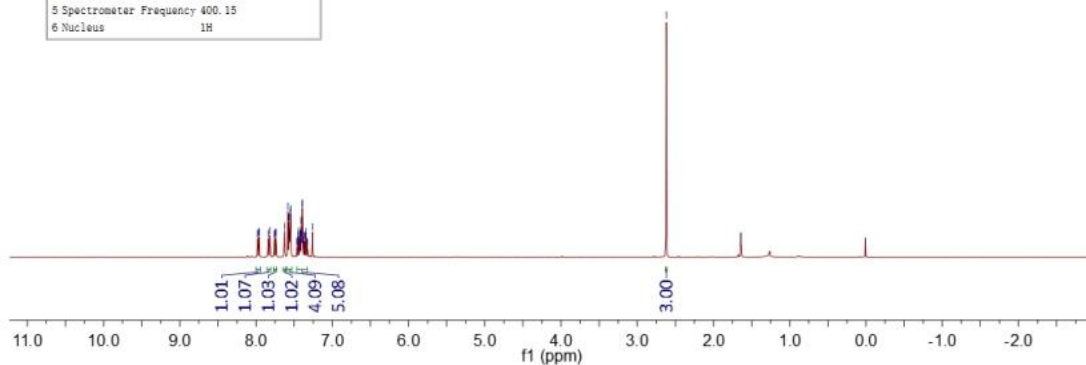
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1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	295.7
4 Number of Scans	2
5 Spectrometer Frequency	376.52
6 Nucleus	19F

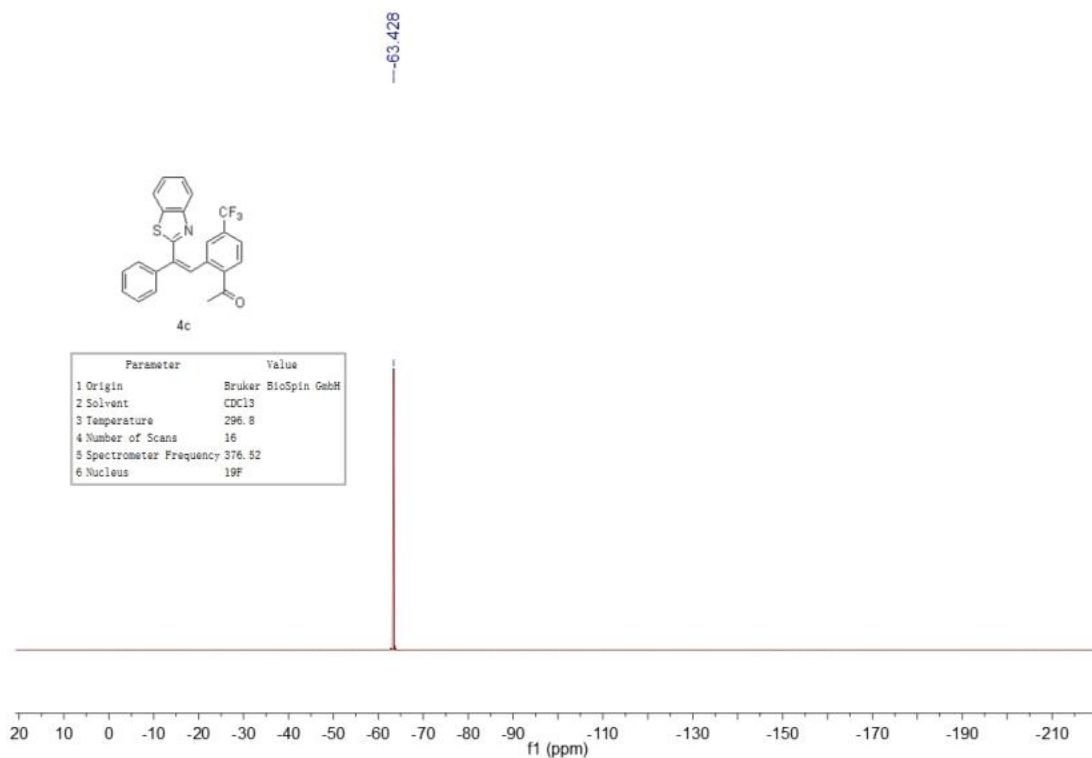
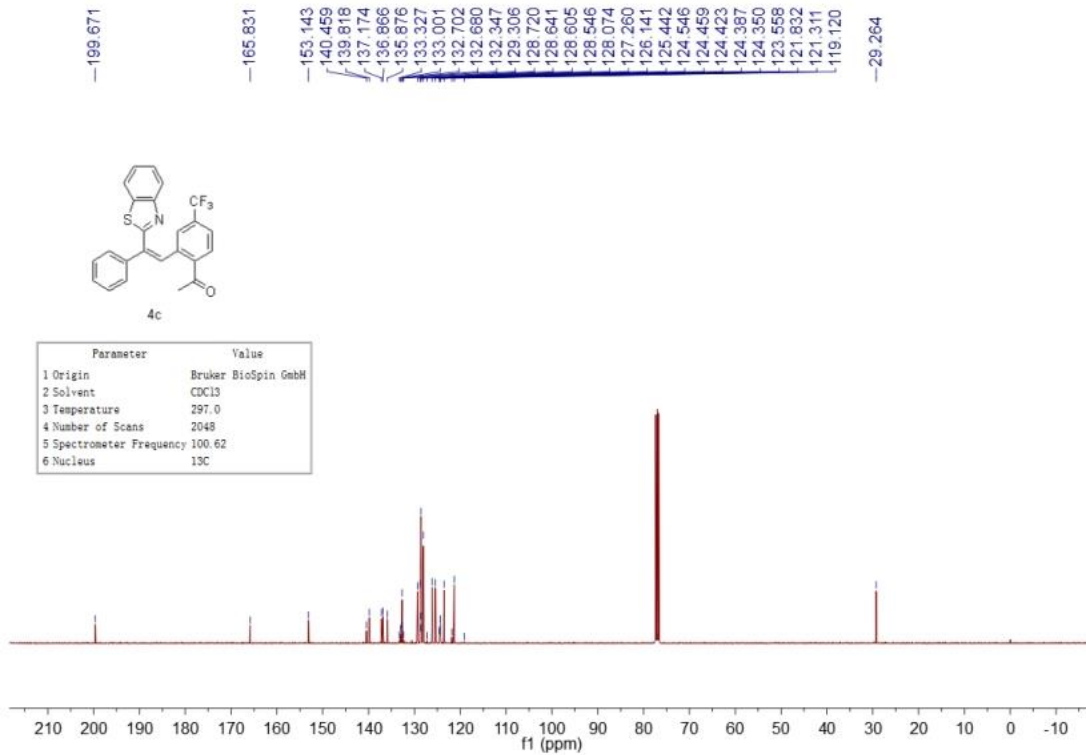


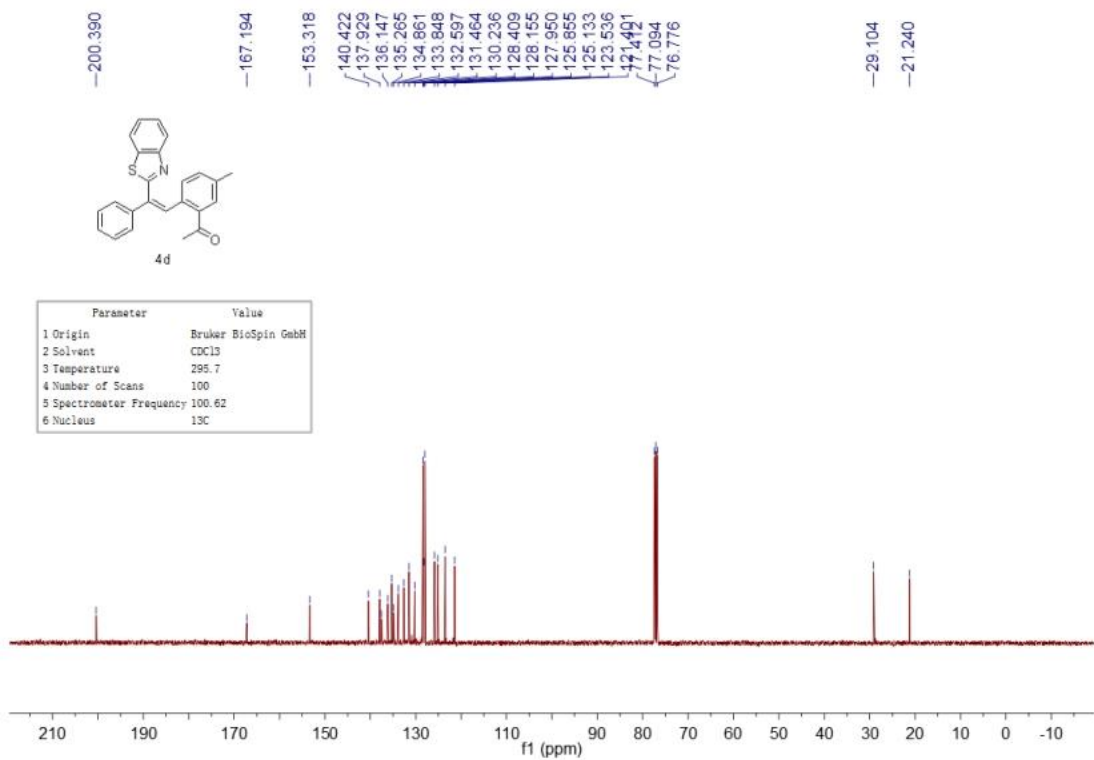
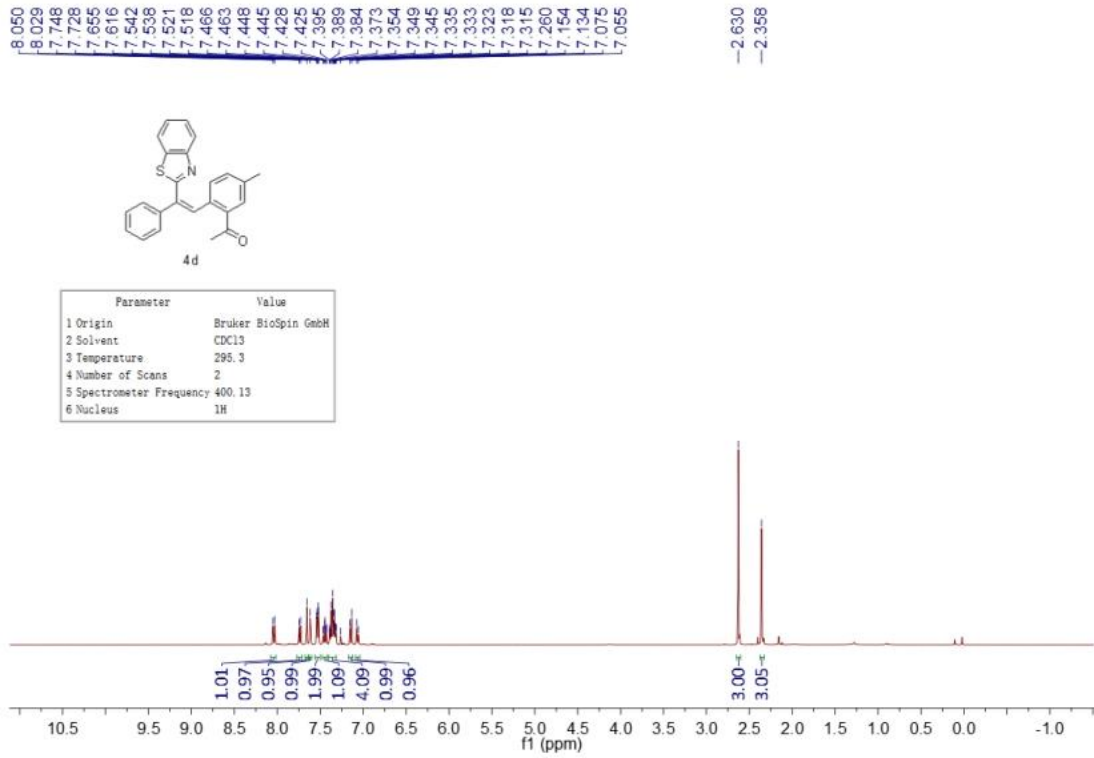
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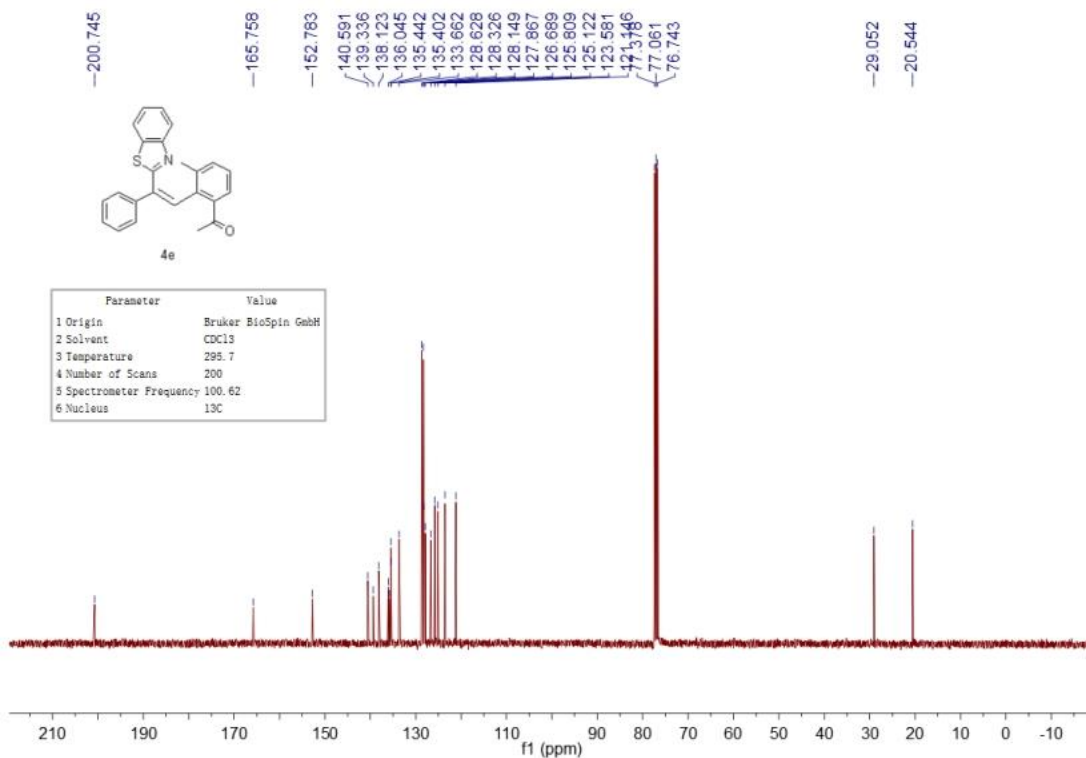
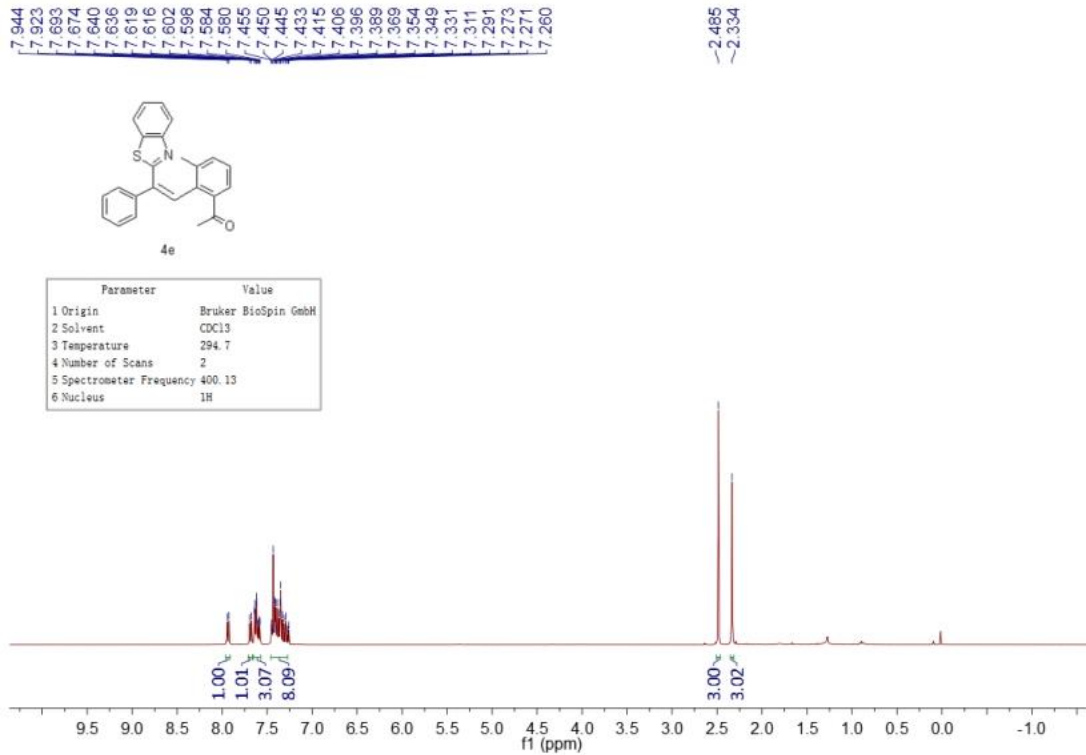
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.7
4 Number of Scans	16
5 Spectrometer Frequency	400.15
6 Nucleus	1H

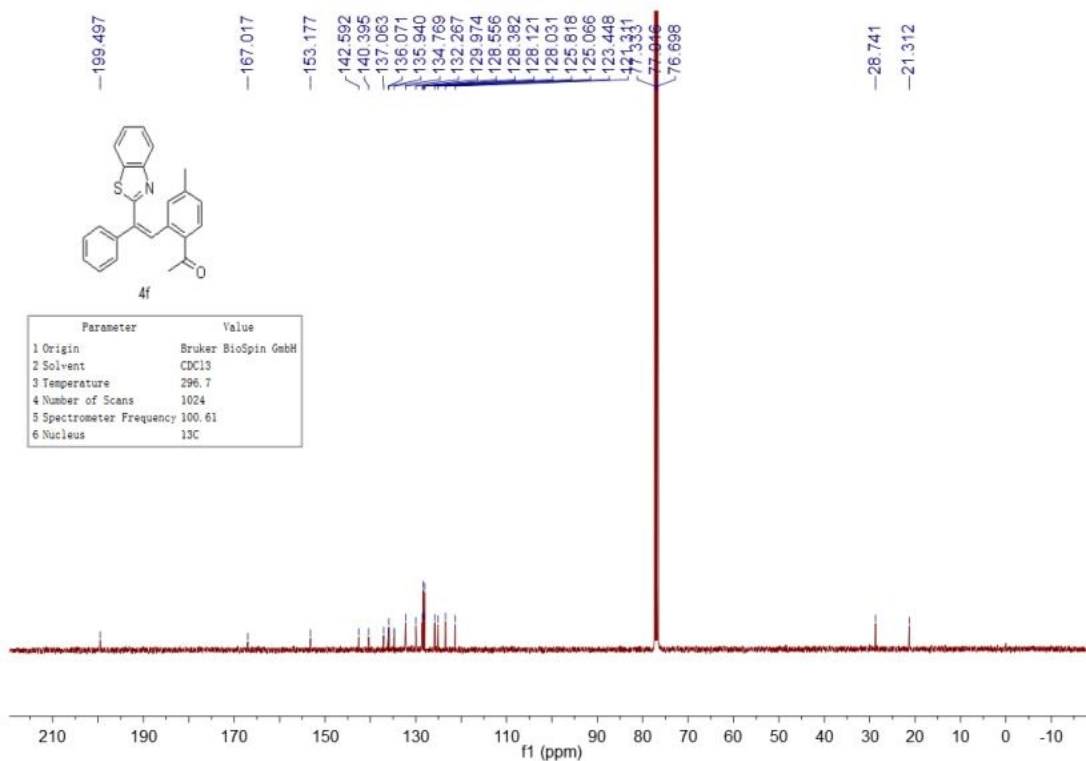
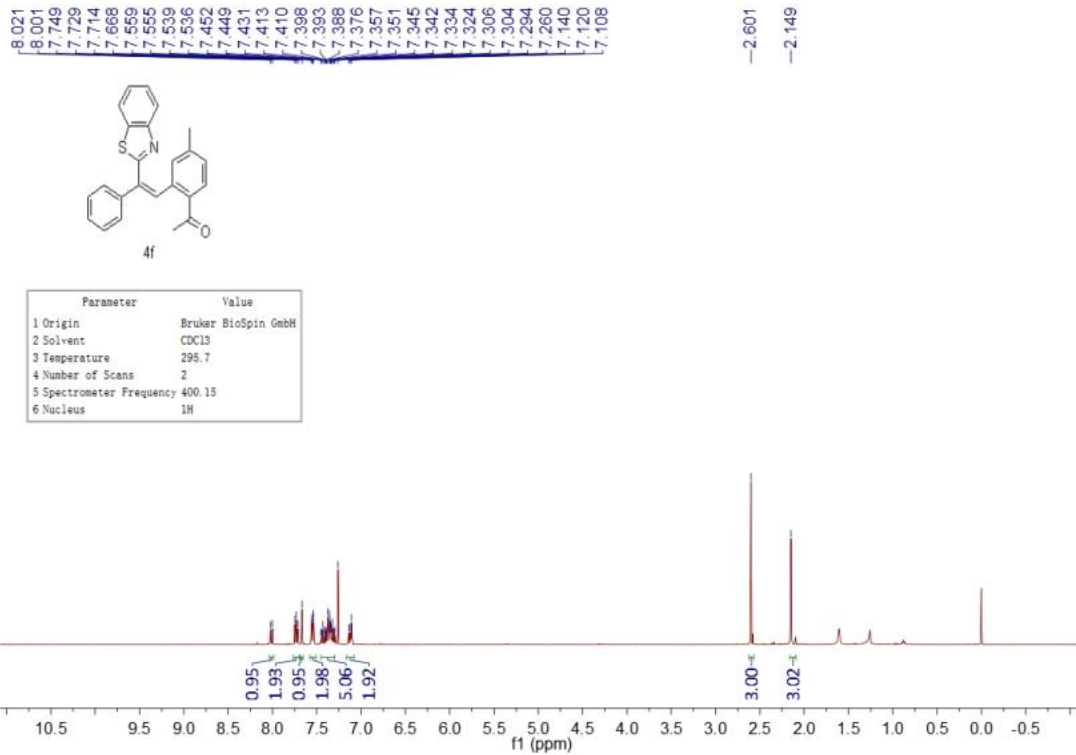


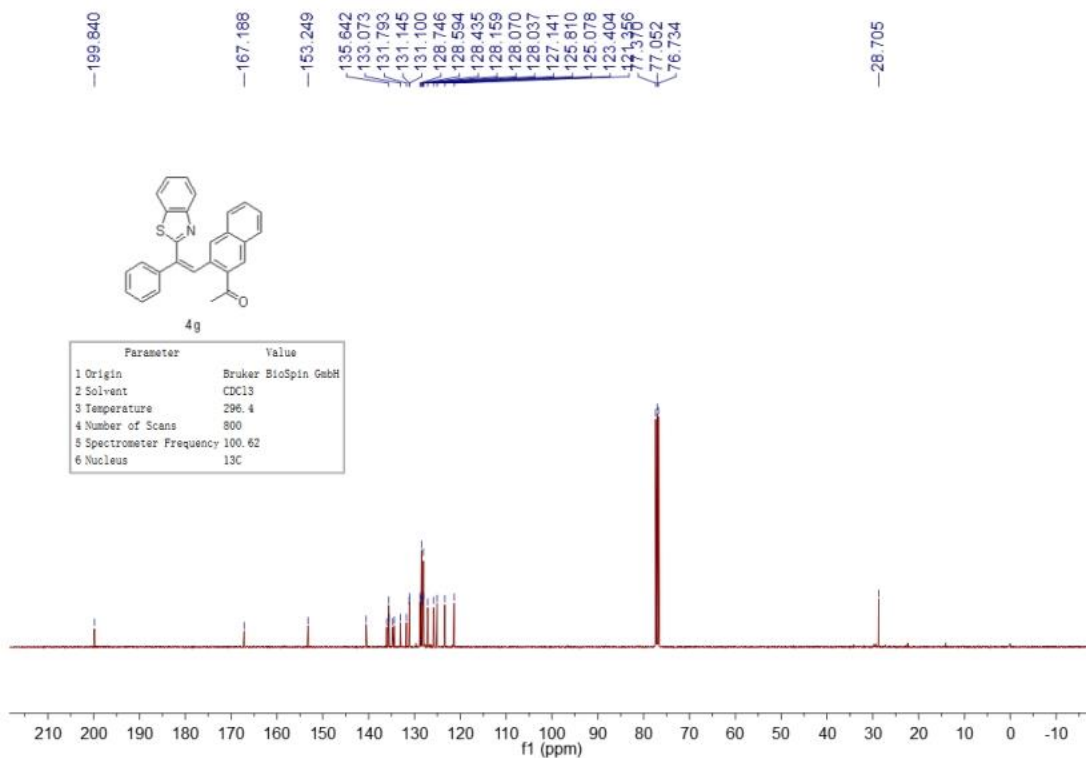
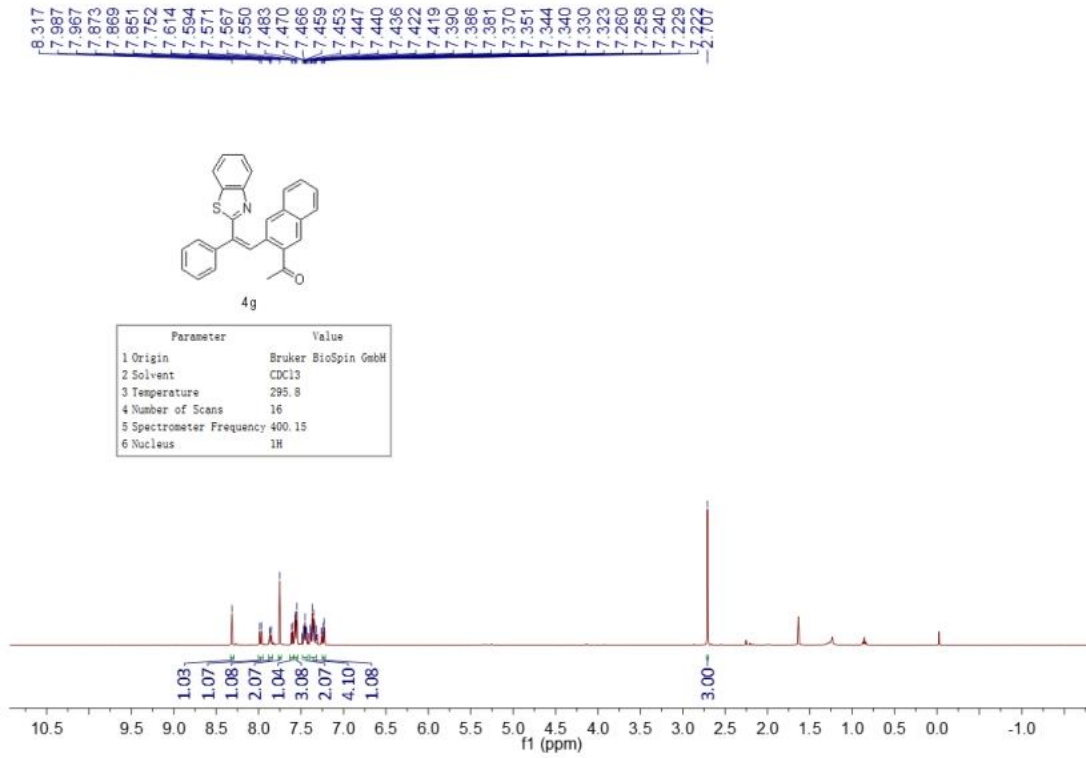


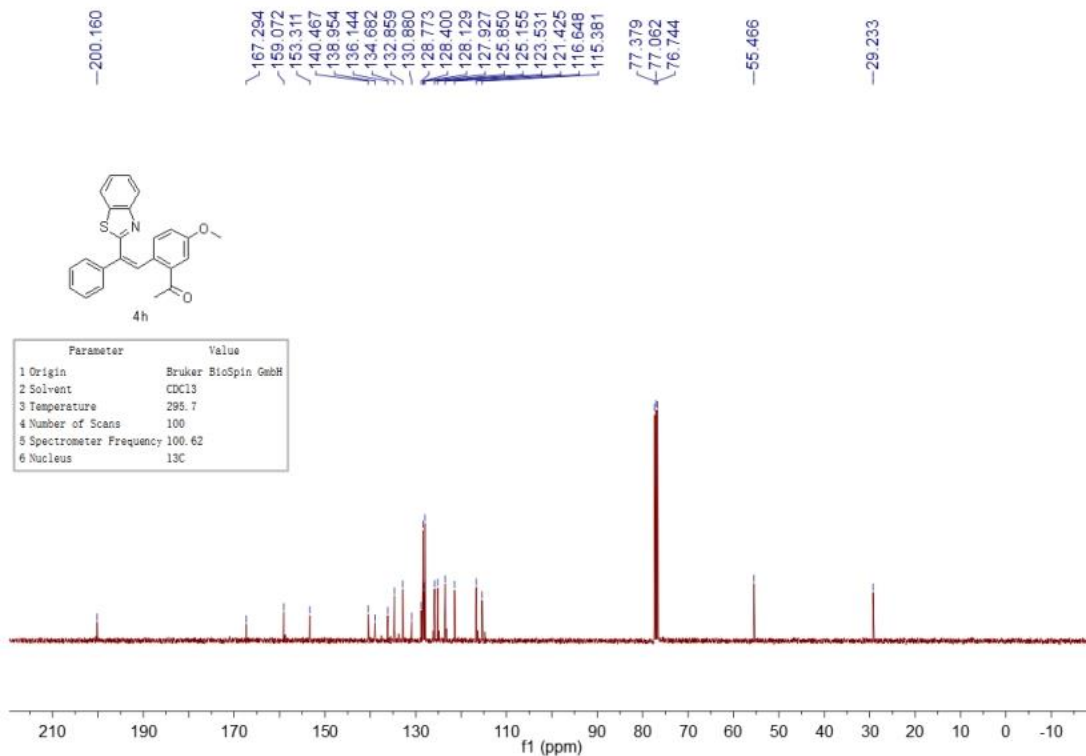
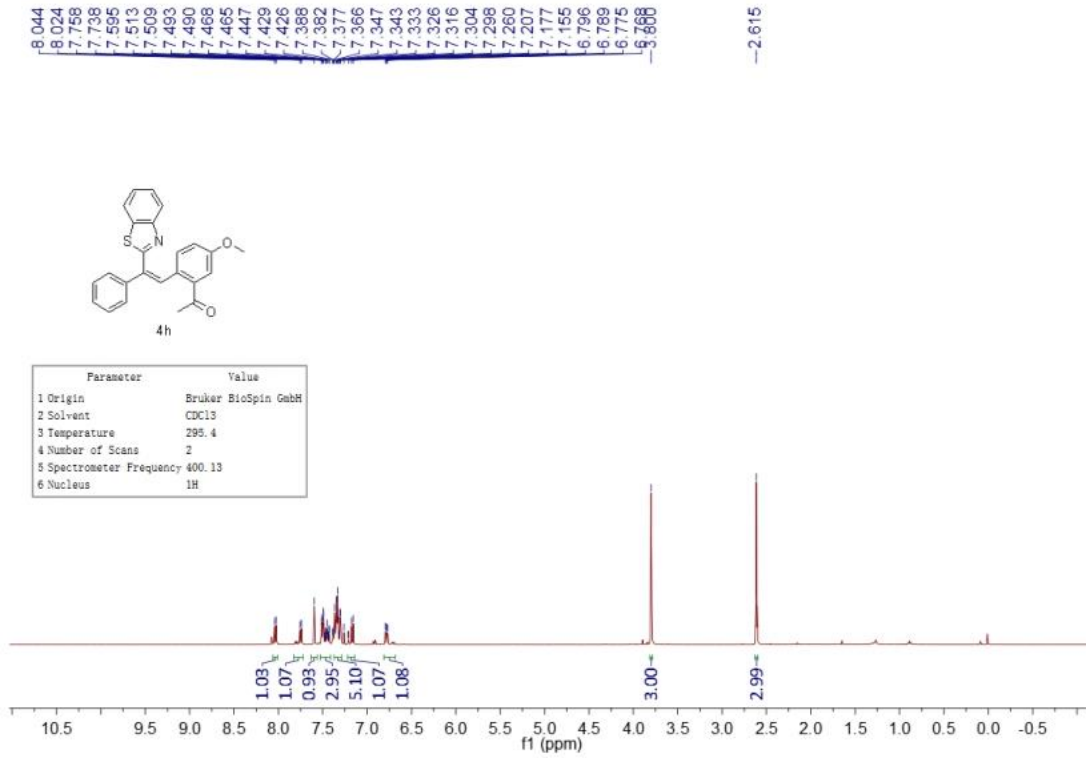


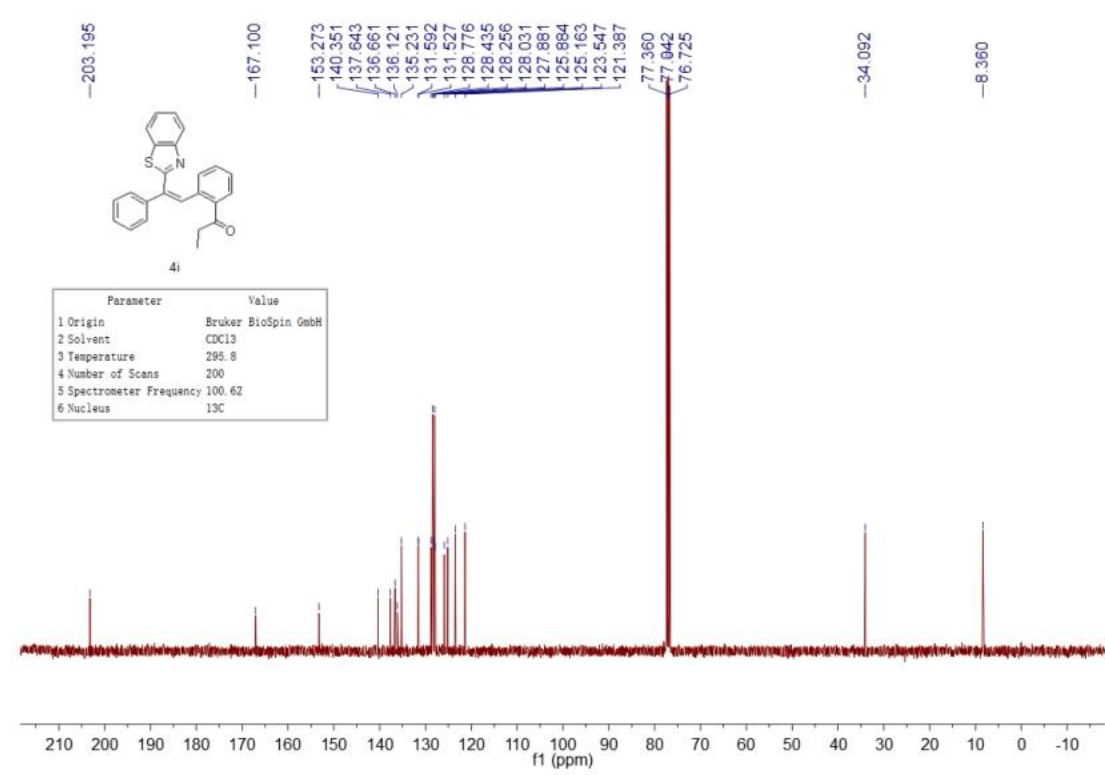
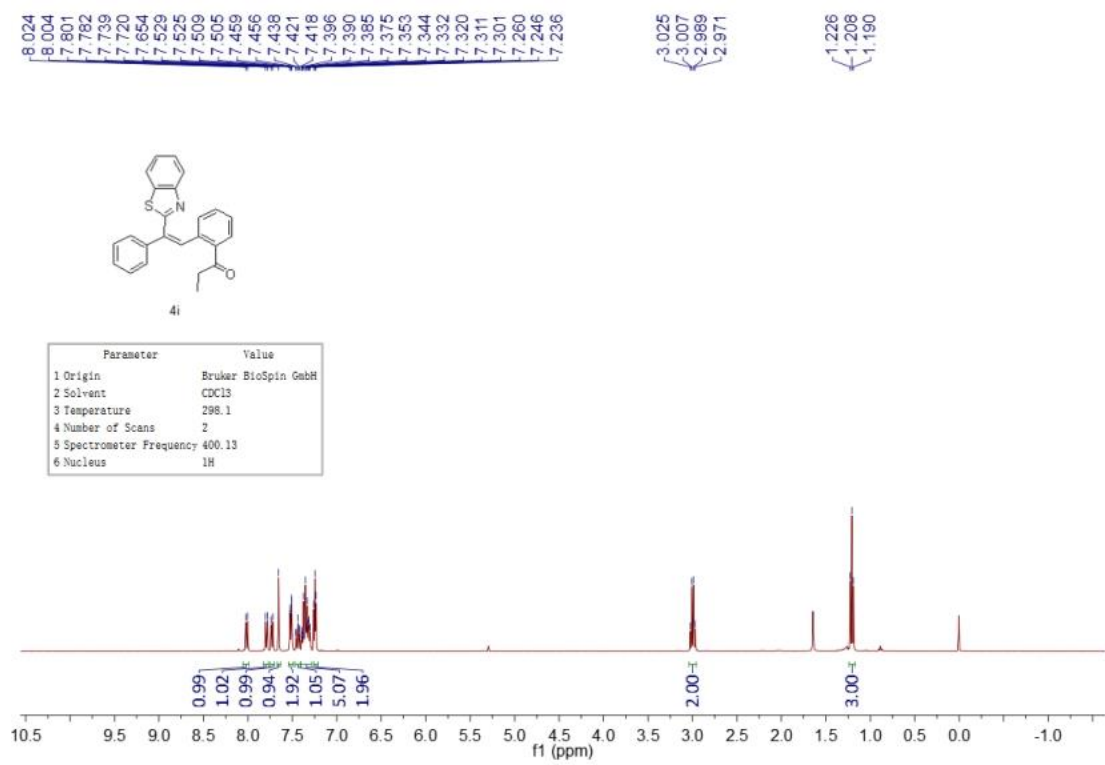




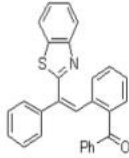






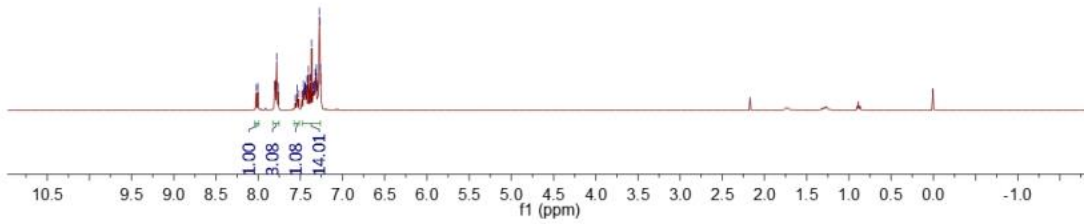


8.023  
7.803  
7.761  
7.763  
7.558  
7.540  
7.521  
7.482  
7.461  
7.455  
7.447  
7.443  
7.441  
7.433  
7.423  
7.403  
7.384  
7.365  
7.347  
7.340  
7.334  
7.323  
7.316  
7.309  
7.299  
7.294  
7.275  
7.271  
7.260

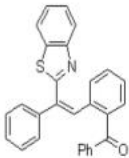


4j

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	295.4
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H

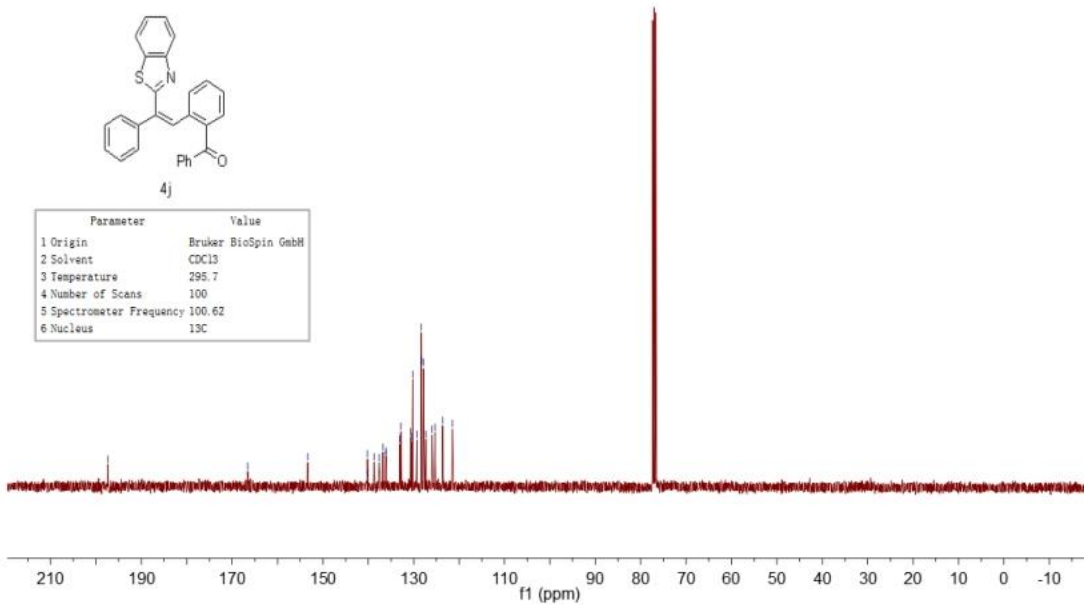


197.356  
166.556  
153.326  
140.180  
140.155  
138.760  
137.624  
136.793  
136.138  
136.107  
133.071  
132.822  
130.660  
130.534  
130.231  
129.329  
128.364  
128.318  
127.823  
127.349  
125.938  
125.282  
123.644  
121.463

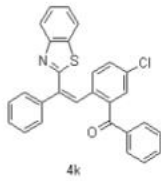


4j

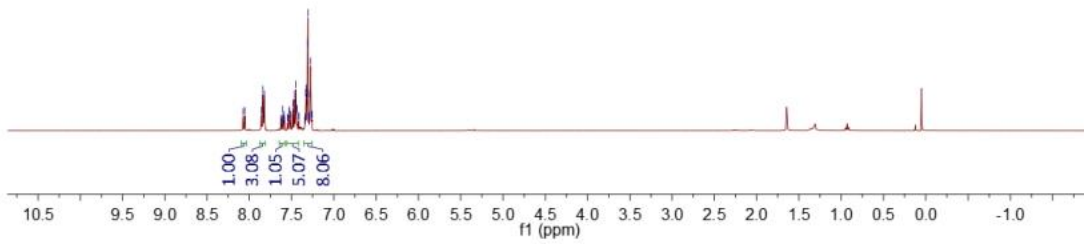
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	295.7
4 Number of Scans	100
5 Spectrometer Frequency	100.62
6 Nucleus	13C



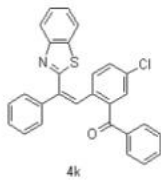
8.074  
8.053  
7.857  
7.840  
7.827  
7.823  
7.819  
7.629  
7.626  
7.622  
7.607  
7.592  
7.588  
7.585  
7.548  
7.545  
7.530  
7.527  
7.509  
7.506  
7.485  
7.485  
7.456  
7.451  
7.448  
7.436  
7.418  
7.415  
7.344  
7.339  
7.334  
7.329  
7.322  
7.316  
7.308  
7.305  
7.288  
7.288  
7.284  
7.277  
7.268  
7.266  
7.260



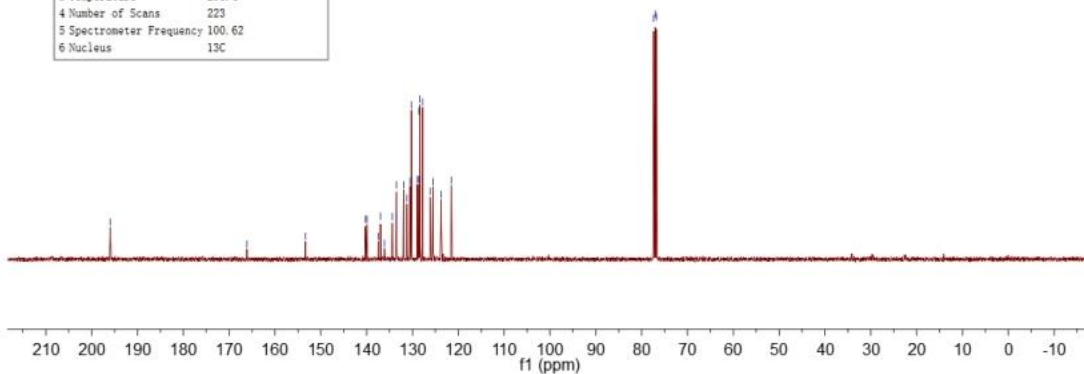
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H

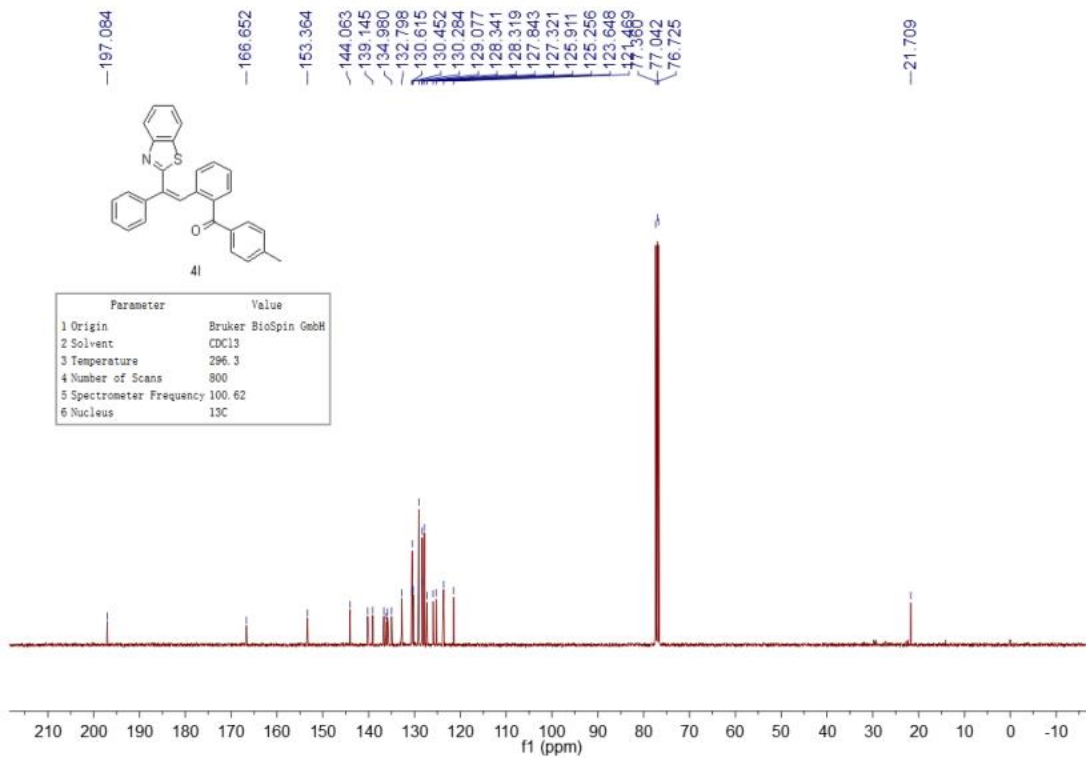
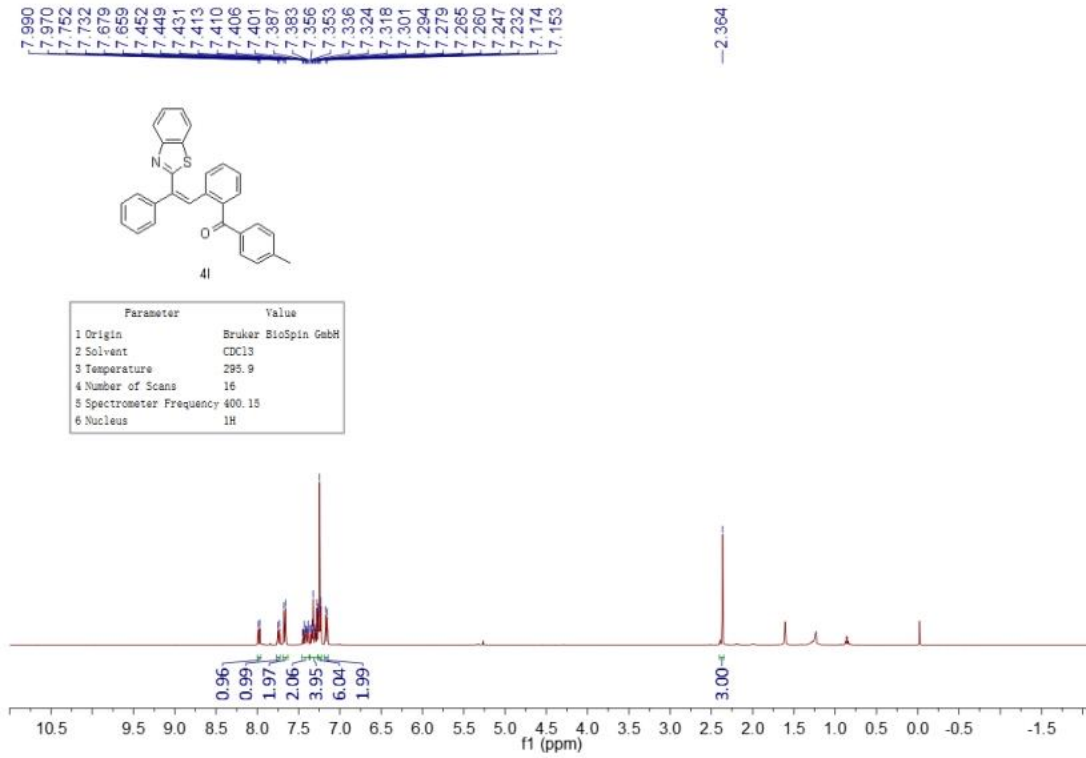


195.943  
166.153  
153.355  
136.946  
134.432  
133.529  
131.960  
131.210  
130.501  
130.241  
128.970  
128.609  
128.572  
128.393  
127.814  
126.133  
125.511  
123.727  
121.554  
121.382  
77.065  
76.747



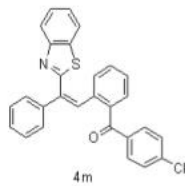
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.4
4 Number of Scans	223
5 Spectrometer Frequency	100.62
6 Nucleus	13C



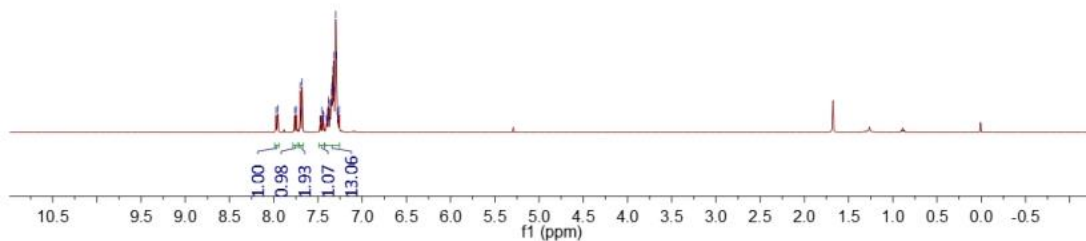




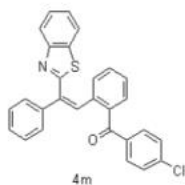
7.973  
7.953  
7.764  
7.744  
7.700  
7.695  
7.678  
7.476  
7.474  
7.456  
7.438  
7.435  
7.402  
7.394  
7.389  
7.382  
7.372  
7.364  
7.352  
7.347  
7.341  
7.336  
7.330  
7.320  
7.316  
7.298  
7.291  
7.282  
7.274  
7.260



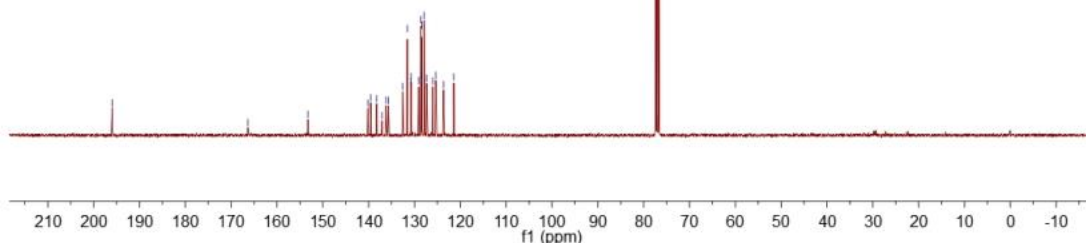
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H

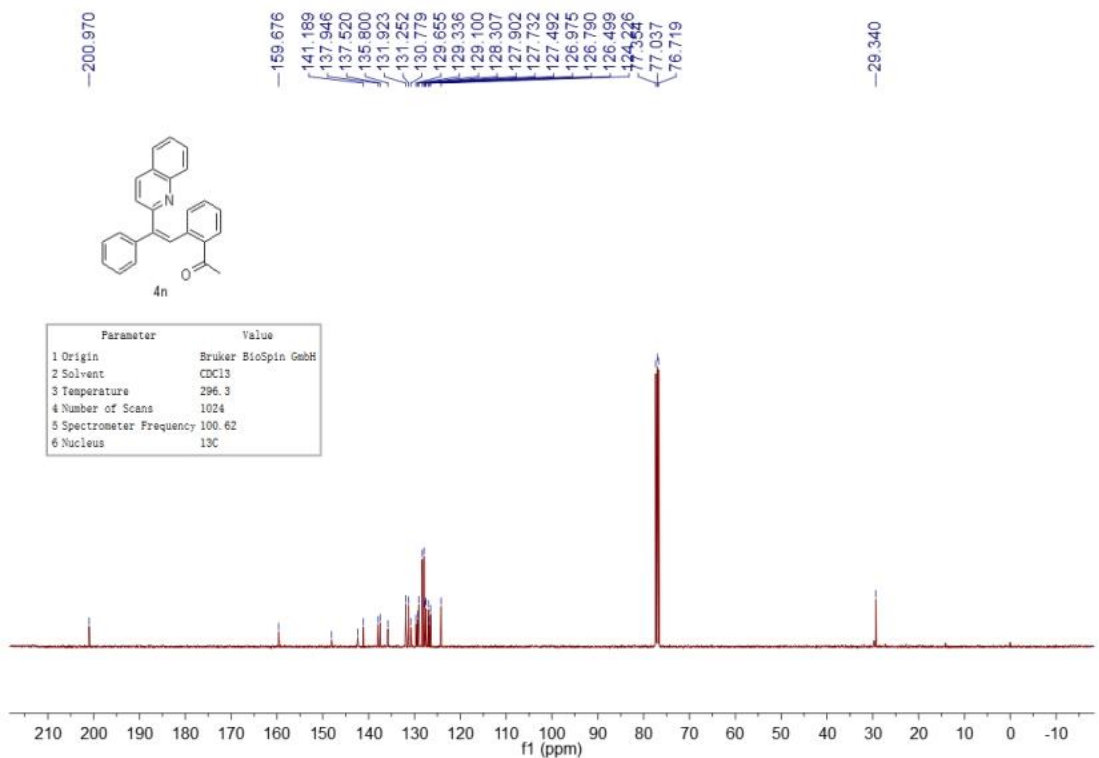
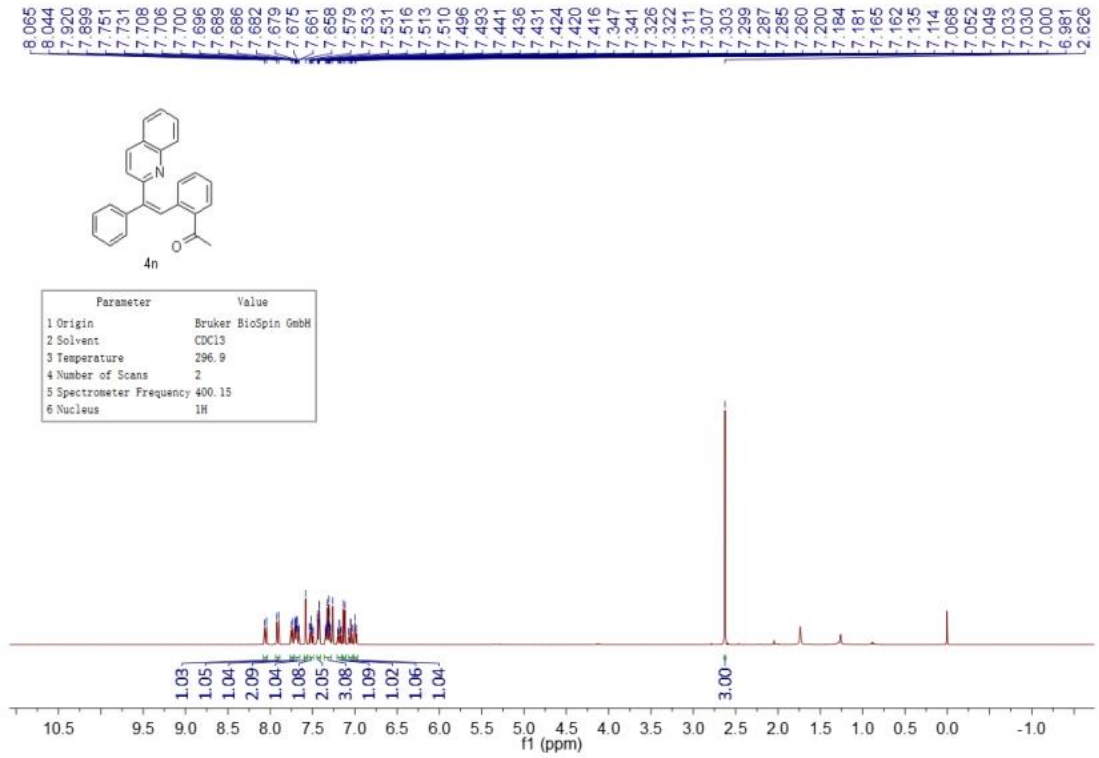


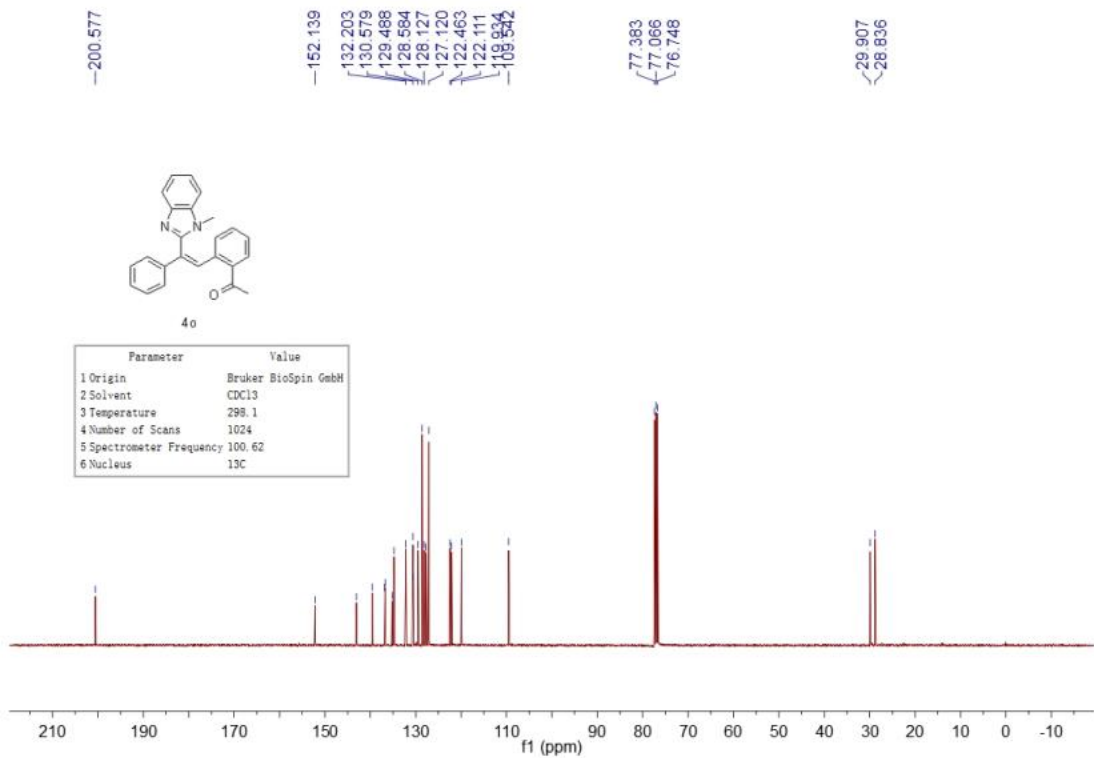
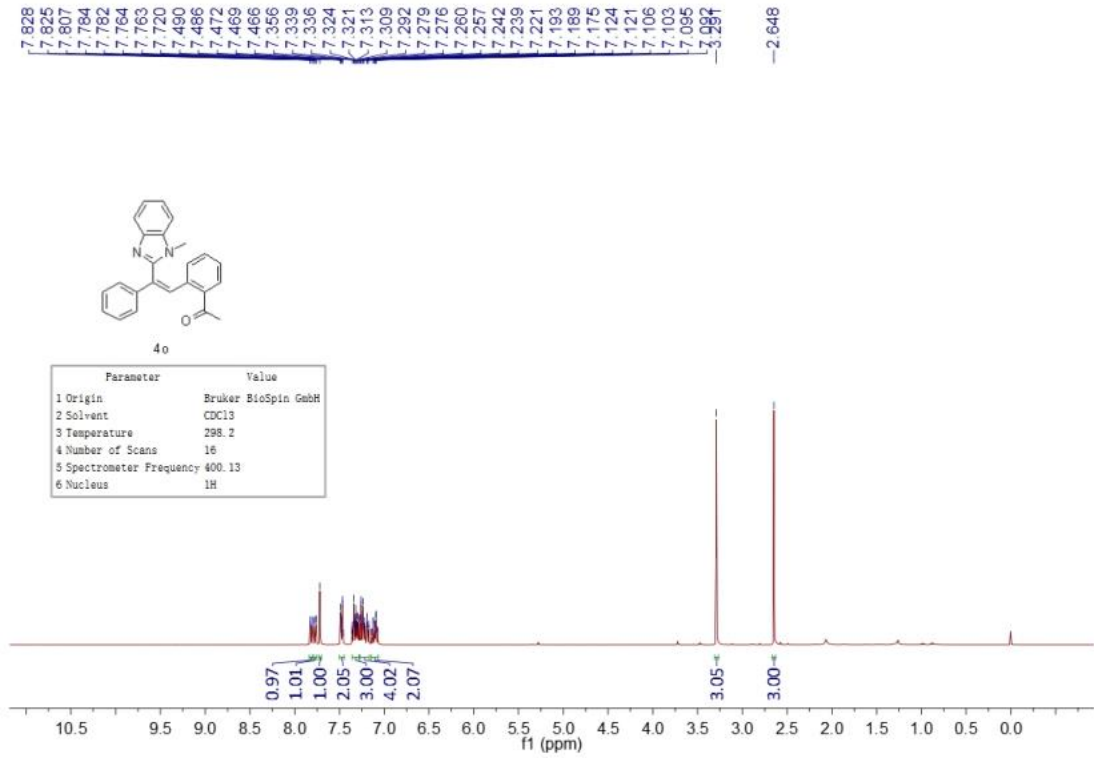
195.951  
166.380  
153.276  
139.564  
138.279  
132.572  
131.574  
130.801  
130.748  
128.120  
128.600  
128.523  
128.403  
127.901  
127.367  
126.025  
125.380  
123.649  
121.436  
77.044  
76.727



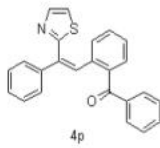
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.2
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	13C



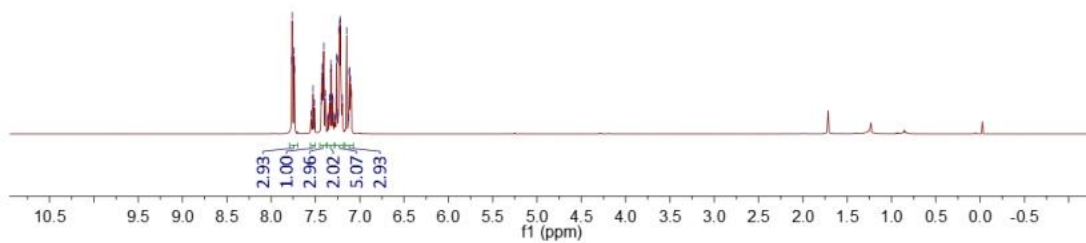




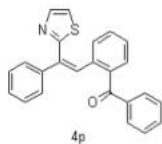
7.770  
7.761  
7.740  
7.737  
7.547  
7.529  
7.510  
7.436  
7.425  
7.419  
7.414  
7.406  
7.387  
7.360  
7.356  
7.342  
7.338  
7.325  
7.320  
7.307  
7.303  
7.288  
7.274  
7.260  
7.252  
7.243  
7.234  
7.228  
7.219  
7.198  
7.148  
7.128  
7.120  
7.115  
7.106  
7.096



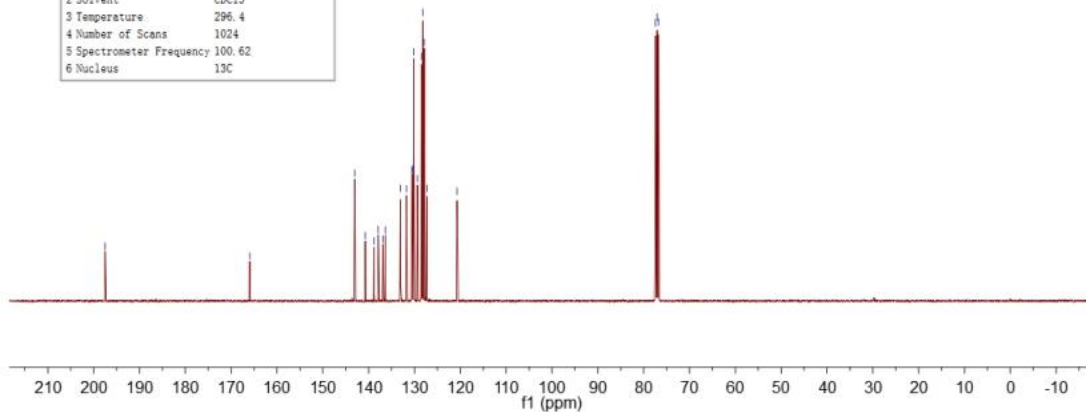
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	295.9
4 Number of Scans	16
5 Spectrometer Frequency	400.15
6 Nucleus	1H

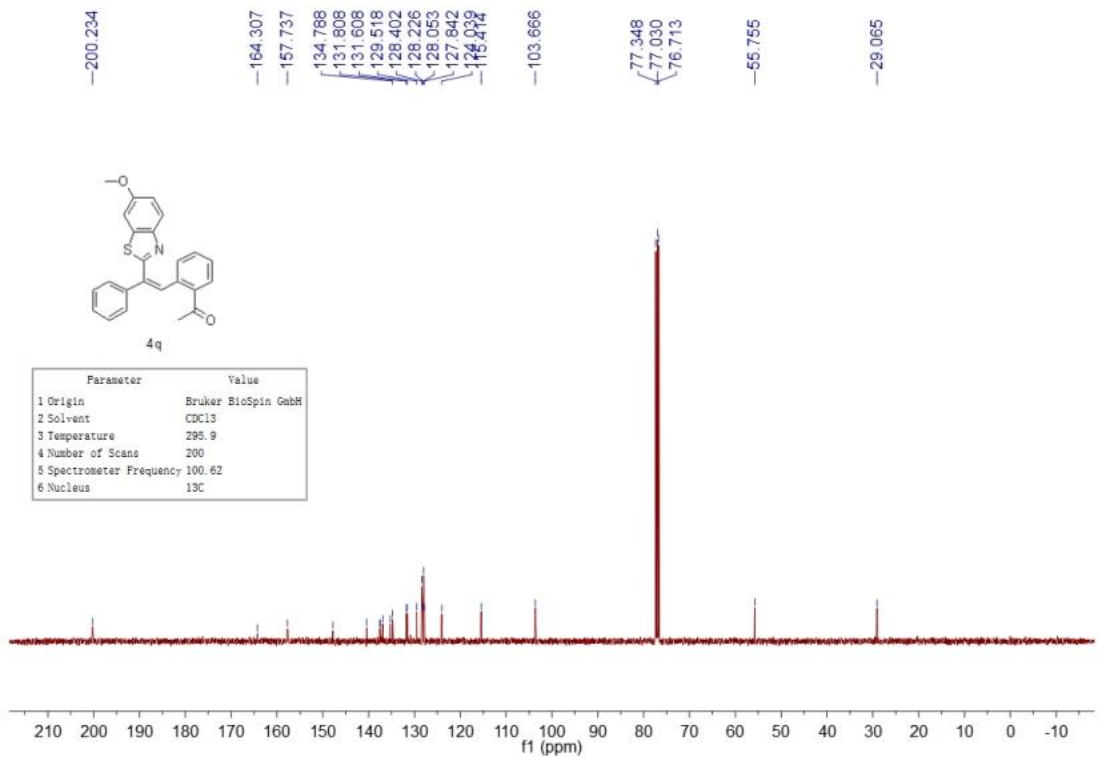
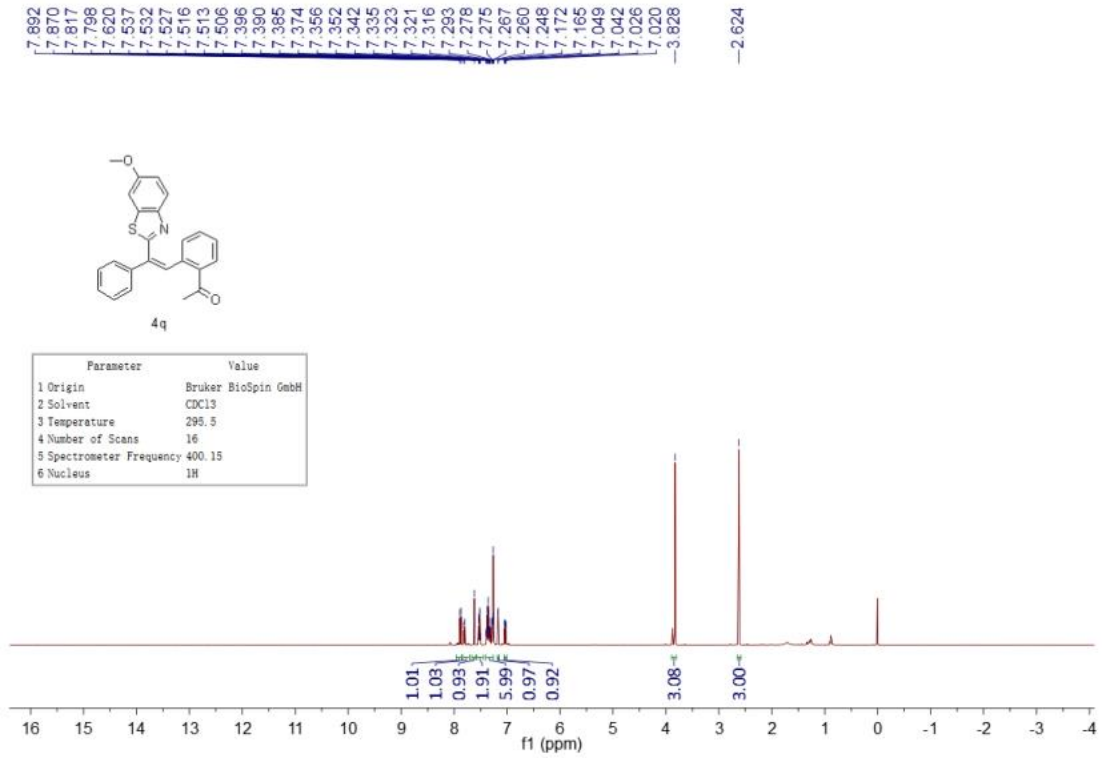


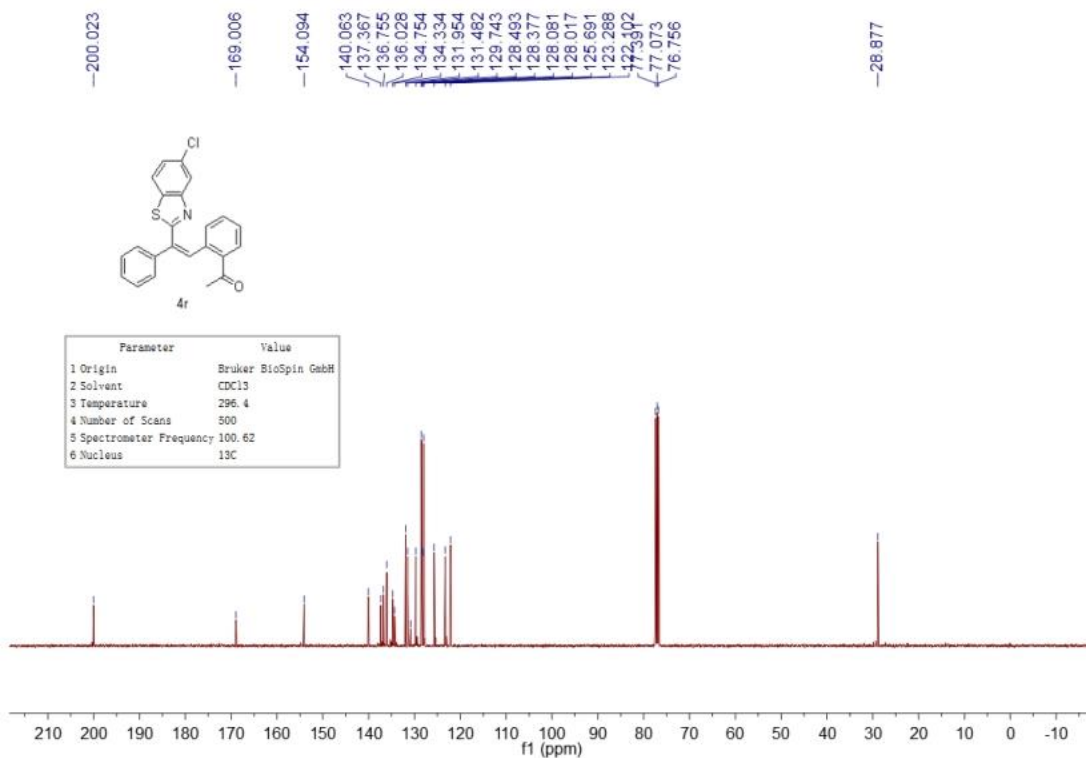
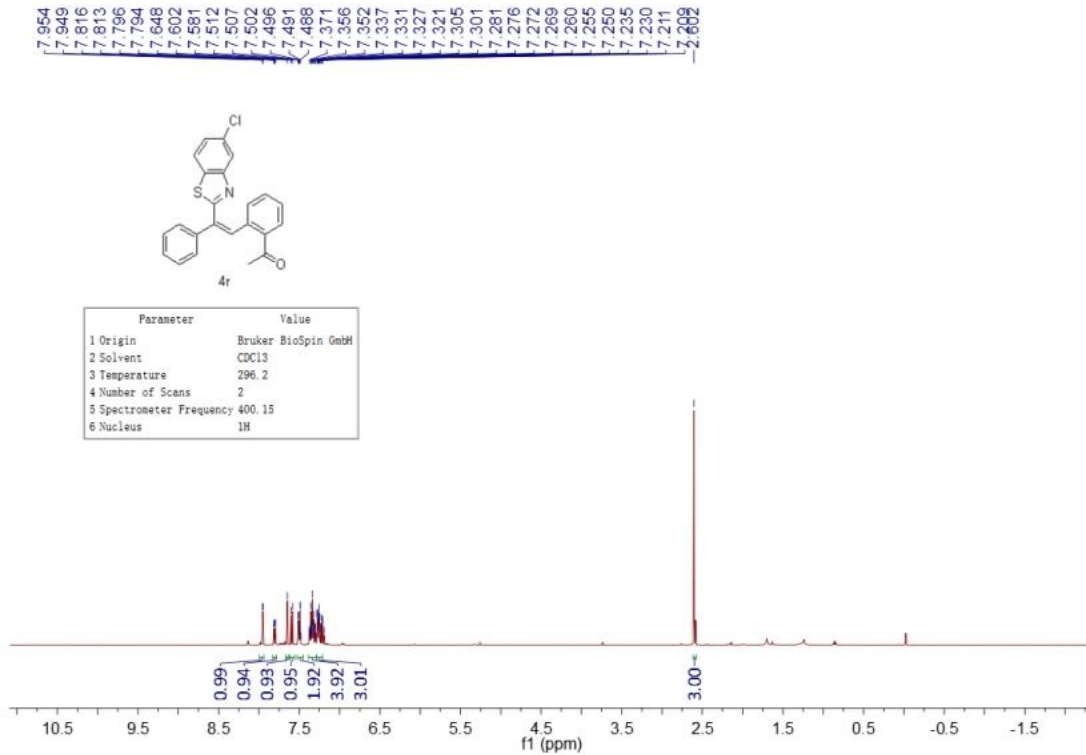
197.474  
165.924  
143.075  
140.720  
138.804  
137.889  
136.870  
136.380  
133.040  
131.778  
130.515  
130.472  
130.153  
128.368  
128.451  
128.220  
127.857  
127.325  
120.735  
77.397  
77.079  
76.762



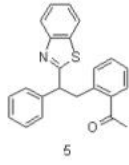
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.4
4 Number of Scans	1024
5 Spectrometer Frequency	100.62
6 Nucleus	13C



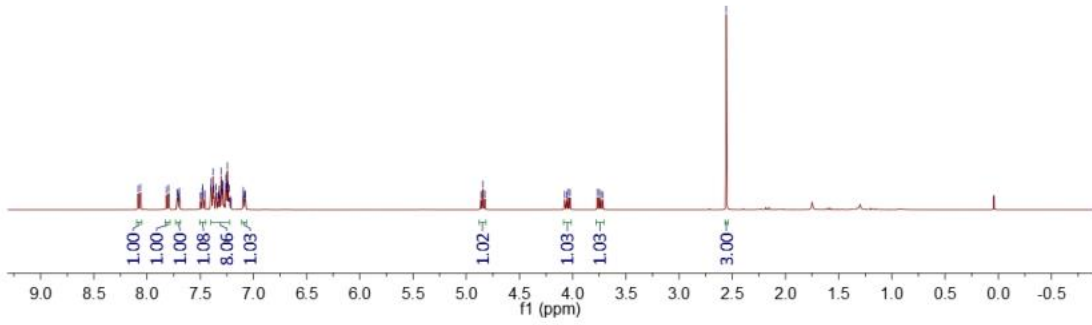




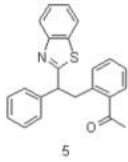
8.083  
8.062  
7.816  
7.796  
7.480  
7.477  
7.401  
7.397  
7.379  
7.372  
7.352  
7.321  
7.304  
7.300  
7.291  
7.285  
7.260  
7.255  
7.252  
7.244  
7.236  
7.229  
4.987  
4.844  
4.825  
4.074  
4.057  
4.042  
4.024  
3.768  
3.749  
3.735  
3.716  
-2.556



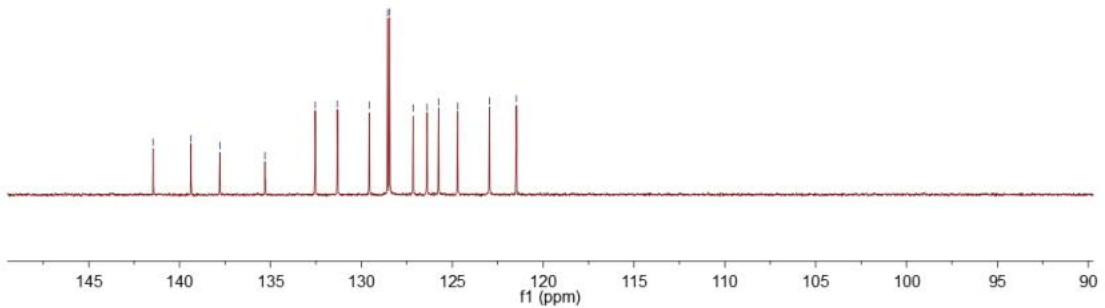
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H

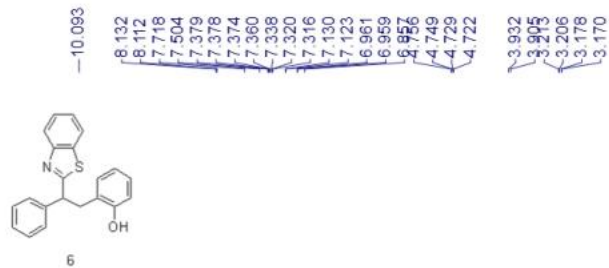


141.457  
139.384  
137.786  
-135.300  
132.545  
131.316  
129.568  
128.560  
128.444  
127.158  
126.388  
125.761  
124.703  
122.960  
121.478

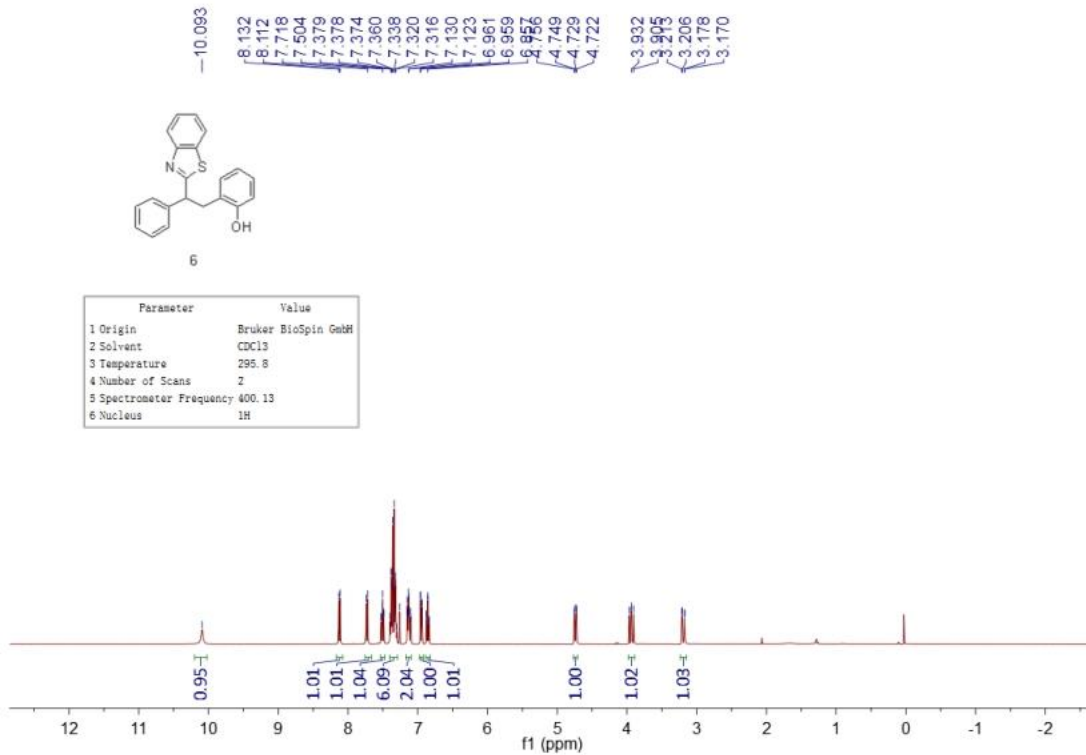


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.1
4 Number of Scans	1024
5 Spectrometer Frequency	100.61
6 Nucleus	13C

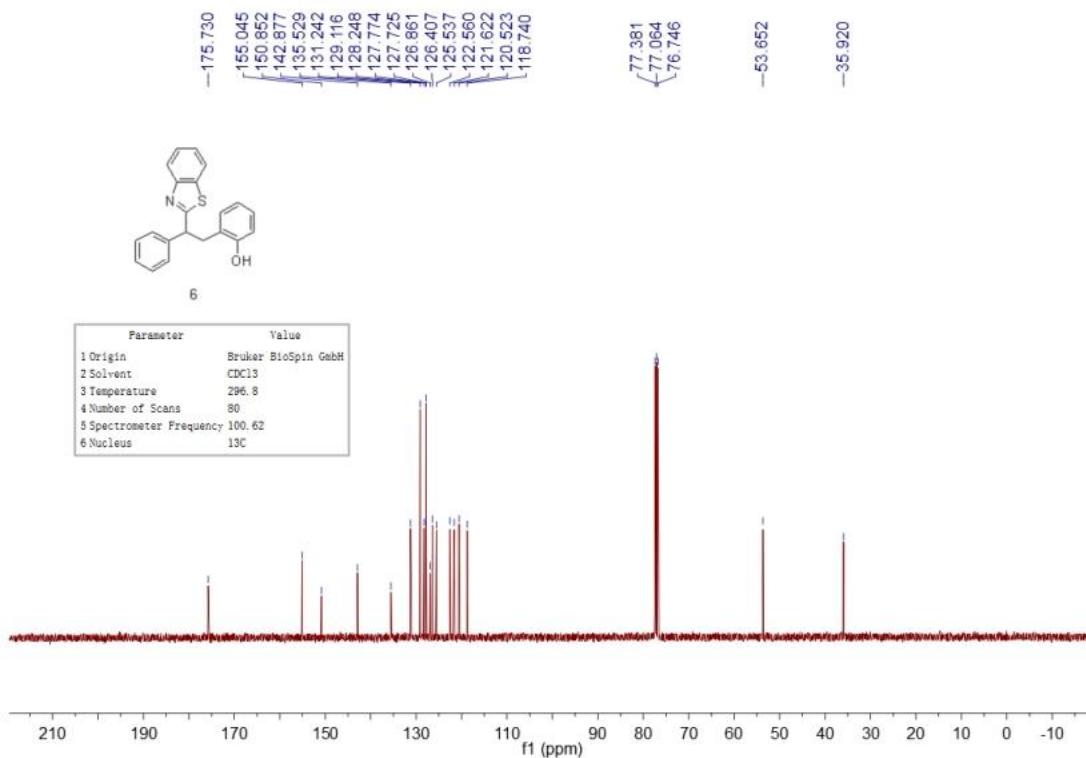




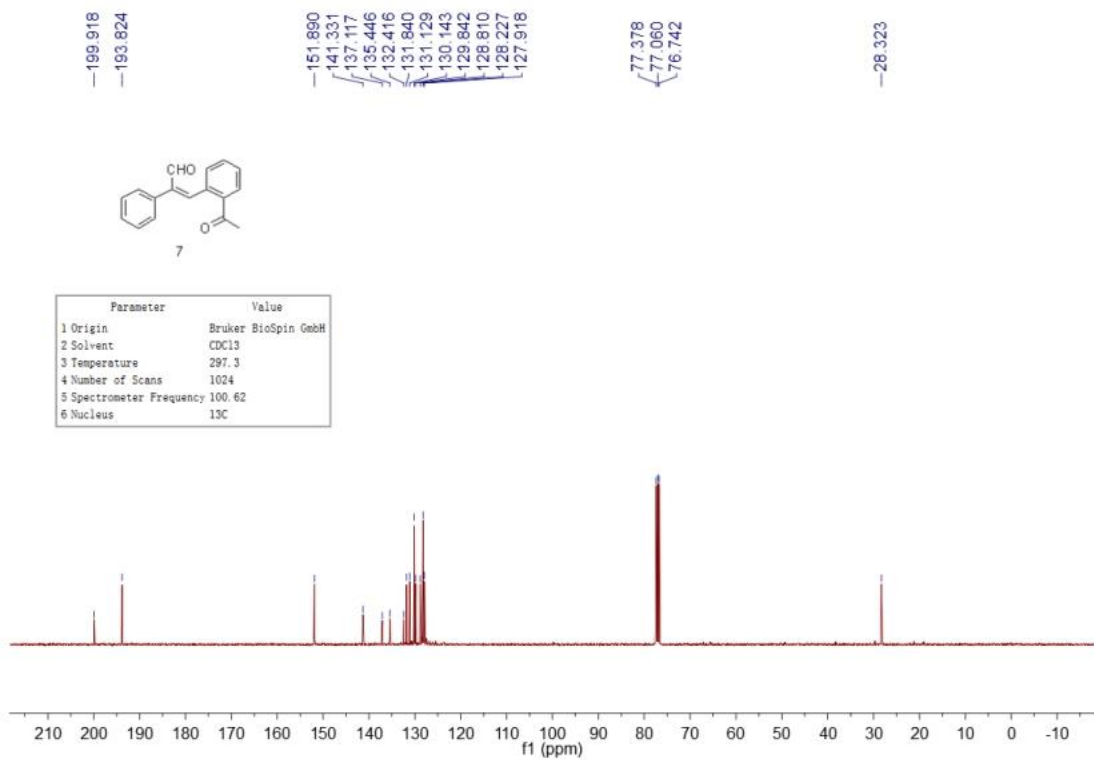
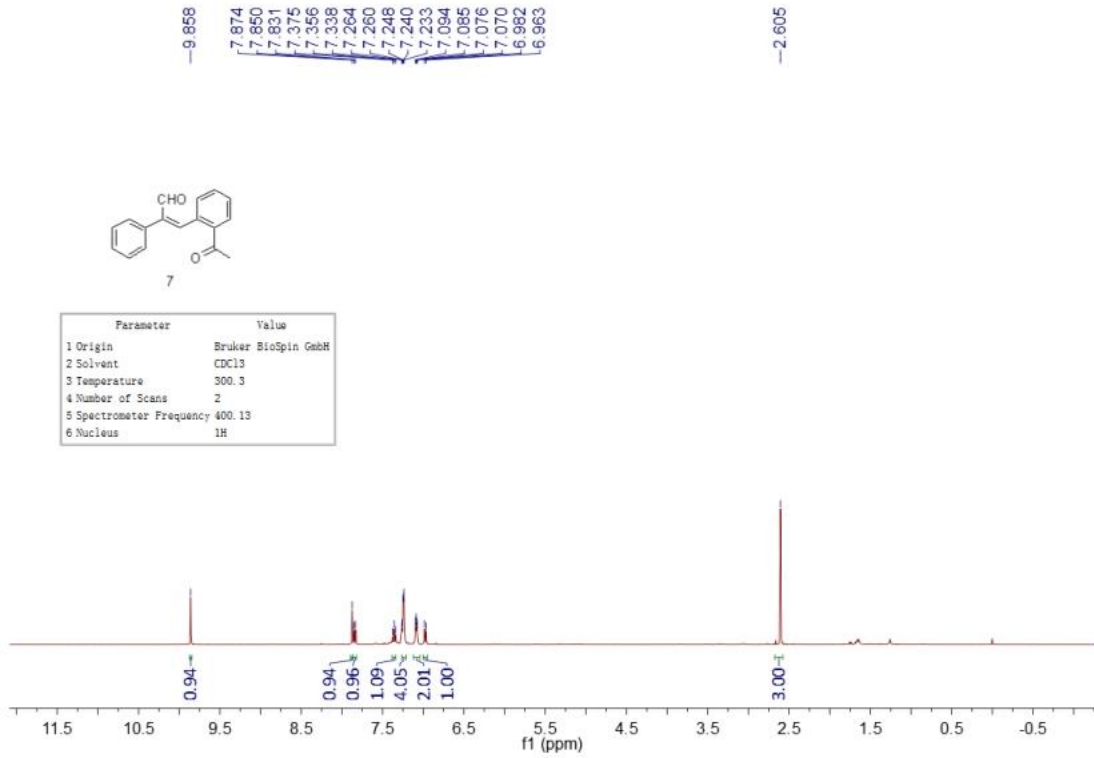
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	295.8
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	<sup>1</sup> H



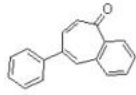
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	296.8
4 Number of Scans	80
5 Spectrometer Frequency	100.62
6 Nucleus	<sup>13</sup> C





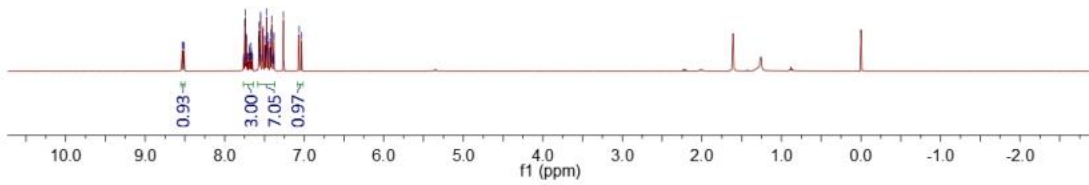


8.633  
8.515  
8.511  
7.766  
7.760  
7.745  
7.741  
7.729  
7.725  
7.709  
7.706  
7.691  
7.685  
7.675  
7.671  
7.666  
7.655  
7.650  
7.571  
7.568  
7.563  
7.550  
7.548  
7.542  
7.521  
7.518  
7.494  
7.491  
7.486  
7.473  
7.469  
7.458  
7.454  
7.430  
7.427  
7.424  
7.415  
7.410  
7.402  
7.394  
7.391  
7.387  
7.383  
7.378  
7.260  
7.065  
7.034

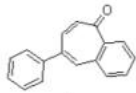


8

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	2
5 Spectrometer Frequency	400.13
6 Nucleus	1H



187.875  
142.851  
139.920  
138.318  
137.887  
137.692  
136.982  
135.706  
134.494  
132.502  
130.589  
130.312  
128.886  
128.067  
127.333  
77.341  
77.024  
76.706



8

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	1024
5 Spectrometer Frequency	100.61
6 Nucleus	13C

