

# Supporting Information

## Lewis/Brønsted Acid-Mediated Cyclization/Amidation of 1,6-Enynes with Nitriles: Access to 3-Enamide Substituted Dihydrobenzofurans

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### List of Contents

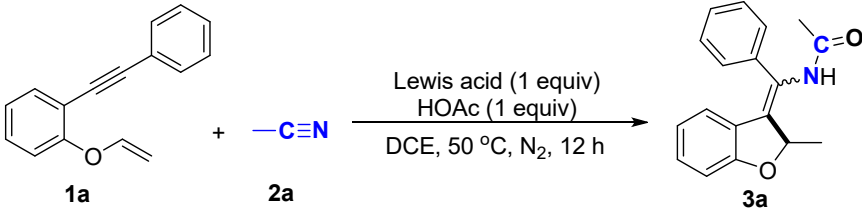
<b>General Information.....</b>	<b>S1</b>
<b>Condition Optimization.....</b>	<b>S1</b>
<b>General Experimental Procedure.....</b>	<b>S4</b>
<b>Characterization Data for Substrates and All Products.....</b>	<b>S11</b>
<b>X-ray Crystallographic Data.....</b>	<b>S38</b>
<b>References.....</b>	<b>S41</b>
<b>NMR Spectra for All the Compounds.....</b>	<b>S42</b>

## General Information

Melting points were determined with a Buchi Melting Point B-545 instrument.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker DRX-400 spectrometer with Dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) and chloroform- $d$  ( $\text{CDCl}_3$ ) as solvent. The peaks were internally referenced to residual solvent signal (2.5 and 39.5 ppm for dimethyl sulfoxide- $d_6$ ) and TMS (0.00 ppm) or residual solvent signal (7.26 and 77.0 ppm for chloroform- $d$ ). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMSIT-TOF). TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was affected at 254 nm. Data collections for crystal structure were performed at room temperature (170 K) using MoK $\alpha$  radiation on a 'Bruker D8 VENTURE' diffractometer. Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification.

## Condition Optimization

**Table S1.** Screening of Lewis Acid<sup>a</sup>

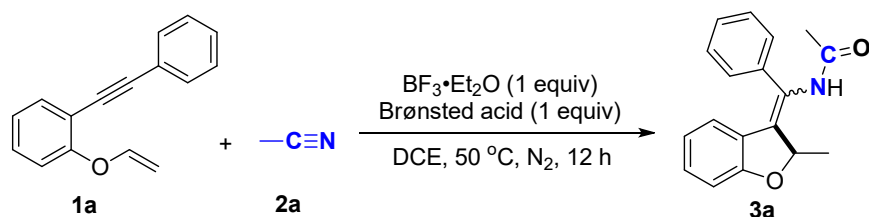


Entry	Lewis acid	Yield of <b>3a</b> (%) <sup>b</sup>	Z/E <sup>c</sup>
1	$\text{BF}_3 \cdot \text{Et}_2\text{O}$	<b>51</b>	2:1
2	AgOTf	n.d.	--
3	$\text{Cu}(\text{OTf})_2$	trace	--
4	$\text{CuCl}_2$	n.d.	--
5	$\text{Zn}(\text{OTf})_2$	n.d.	--
6	$\text{ZnCl}_2$	n.d.	--

7	Fe(OTf) <sub>3</sub>	trace	--
8	FeCl <sub>3</sub>	n.d.	--
9	FeCl <sub>2</sub>	n.d.	--
10	Y(OTf) <sub>3</sub>	trace	--
11	SnCl <sub>4</sub>	trace	--
12	AlCl <sub>3</sub>	trace	--
13	BPh <sub>3</sub>	n.d.	--
14	B(C <sub>6</sub> F <sub>6</sub> ) <sub>3</sub>	n.d.	--
15	BCl <sub>3</sub>	trace	--
16	MeOTf	trace	--

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (10 equiv), Lewis acid (1 equiv), HOAc (1 equiv), DCE (0.5 mL), under nitrogen at 50 °C for 12 h. n.d. = not detected. <sup>b</sup>Determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>c</sup>Z/E Determined by <sup>1</sup>H NMR.

**Table S2.** Screening of Brønsted Acid<sup>a</sup>

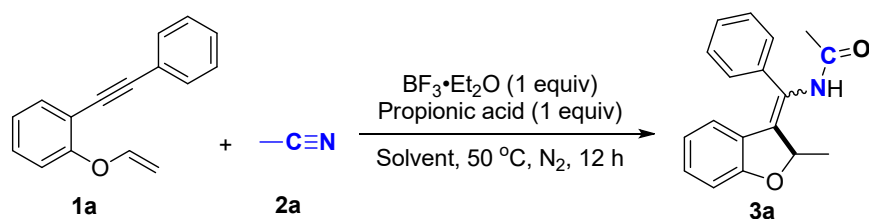


Entry	Brønsted acid	Yield of <b>3a</b> (%) <sup>b</sup>	Z/E <sup>c</sup>
1	Formic acid	24	5:1
2	Propionic acid	72	5:1
3	<i>n</i> -Butyric acid	32	2:1
4	<i>n</i> -Pentanoic acid	57	2:1
5	TfOH	13	2:1
6	H <sub>3</sub> BO <sub>3</sub>	trace	--
7	Malonic acid	trace	--
8	Lactic acid	trace	--
9	CF <sub>3</sub> CO <sub>2</sub> H	n.d.	--
10	(CH <sub>3</sub> ) <sub>3</sub> CCO <sub>2</sub> H	62	4:1

11	PhCO <sub>2</sub> H	53	4:1
12	Tartaric acid	trace	--
13	TsOH	n.d.	--
14	Salicylic acid	n.d.	--

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (10 equiv), Lewis acid (1 equiv), Brønsted acid (1 equiv), DCE (0.5 mL), under nitrogen at 50 °C for 12 h. n.d. = not detected. <sup>b</sup>Determined by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>c</sup>Z/E Determined by <sup>1</sup>H NMR.

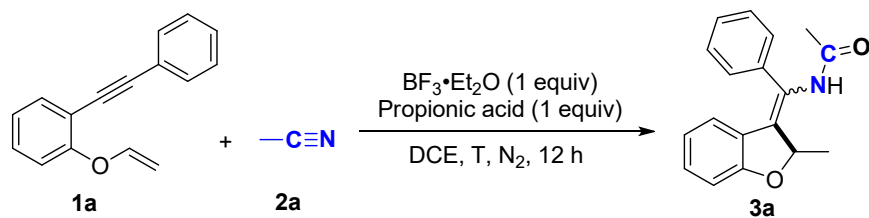
**Table S3.** Screening of Solvent<sup>a</sup>



Entry <sup>a</sup>	Solvent	Yield of <b>3a</b> (%) <sup>b</sup>	Z/E <sup>c</sup>
1	DCM	39	3:1
2	DMF	n.d.	--
3	DMA	n.d.	--
4	THF	n.d.	--
5	Dioxane	n.d.	--

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (10 equiv), BF<sub>3</sub>·Et<sub>2</sub>O (1 equiv), propionic acid (1 equiv), solvent (0.5 mL), under nitrogen at 50 °C for 12 h. n.d. = not detected; <sup>b</sup>Detected by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>c</sup>Z/E Determined by <sup>1</sup>H NMR.

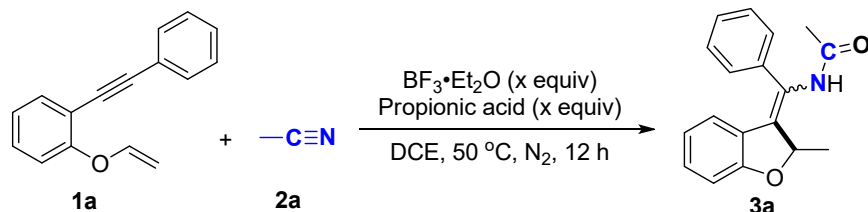
**Table S4.** Screening of Temperature<sup>a</sup>



Entry	T (°C)	Yield of <b>3a</b> (%) <sup>b</sup>	Z/E <sup>c</sup>
1	40	68	3:1
2	60	63	3:1

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (10 equiv), BF<sub>3</sub>·Et<sub>2</sub>O (1 equiv), propionic acid (1 equiv), DCE (0.5 mL), under nitrogen for 12 h. n.d. = not detected; <sup>b</sup>Detected by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>c</sup>Z/E Determined by <sup>1</sup>H NMR.

**Table S5.** Screening of Equivalents of Lewis acid and Brønsted acid<sup>a</sup>

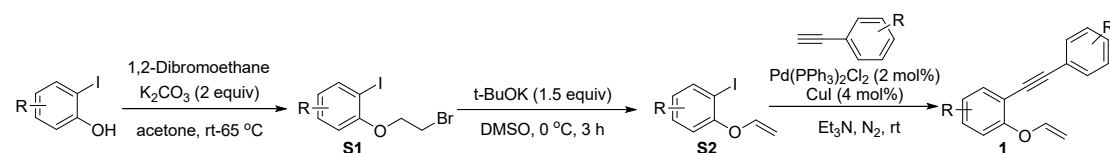


Entry <sup>a</sup>	BF <sub>3</sub> ·Et <sub>2</sub> O (x equiv)	Propionic Acid (x equiv)	Yield of <b>3a</b> (%) <sup>b</sup>	Z/E <sup>c</sup>
1	0.5	1	36	3:1
2	1.5	1	72	6:1
3	2	1	80	6:1
4	2.5	1	81	6:1
5	2	1.5	68	6:1

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (10 equiv), BF<sub>3</sub>·Et<sub>2</sub>O (x equiv), propionic acid (x equiv), DCE (0.5 mL), under nitrogen at 50 °C for 12 h. n.d. = not detected; <sup>b</sup>Detected by <sup>1</sup>H NMR using CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>c</sup>Z/E Determined by <sup>1</sup>H NMR.

## General Experimental Procedure

### A. General Procedure for the Preparation of 1,6-Enynes [1-6]

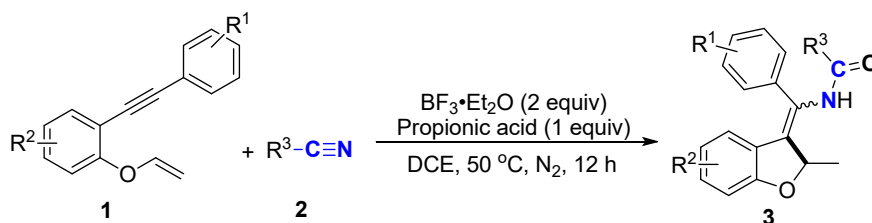


**Synthesis of S1:** To a stirred solution of 2-iodophenol (1 equiv) and 1,2-dibromoethane (10 equiv) in acetone (0.1 M) was added K<sub>2</sub>CO<sub>3</sub> (2 equiv). After the reaction was finished, the reaction was quenched with water (10 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL × 3). The organic layer was washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporator under reduced pressure. The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt (100/1) as the eluent to give product **S1**.

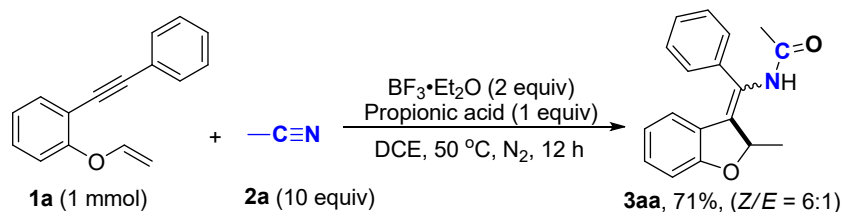
**Synthesis of S2:** A solution of **S1** (2.9329 g, 9.0 mmol) in DMSO (50 mL) was stirred at room temperature. Then KO<sup>t</sup>Bu (1.5124 g, 13.5 mmol) in portions was added. The resulting mixture was stirred at room temperature for 2 h. After the reaction was finished, The reaction was quenched with water (10 mL) and extracted with EtOAc (20 mL × 3), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporator under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether as the eluent to give product **S2**.

**Synthesis of 1:** To a solution of **S2** (1.4831 g, 6.03 mmol) and substituted phenylacetylene (0.7099 g, 7.24 mmol) in trimethylamine (30 mL) was added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.0847 g, 0.12 mmol) and CuI (0.0458 g, 0.24 mmol) under nitrogen. The resulting mixture was stirred at room temperature for 12 h. Upon completion, the reaction mixture was filtered with a pad of Celite. The filtrate was then concentrated under vacuum. The residue was purified by silica gel column chromatography using a petroleum ether as the eluent to give product **1**.

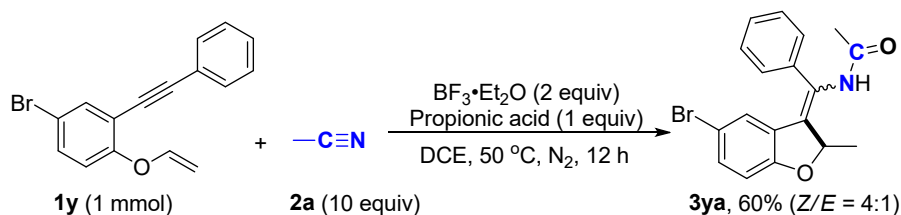
## B. General Procedure for the Preparation of 3-Enamide Substituted Dihydrobenzofurans



To a Schlenk tube was added enyne **1** (0.1 mmol, 0.1 M), nitrile **2** (1 mmol, 10 equiv), BF<sub>3</sub>·Et<sub>2</sub>O (24.7 uL, 2 equiv), propionic acid (7.5 uL, 1 equiv) and dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL). Then the tube was stirred at 50 °C (oil bath temperature) in nitrogen atmosphere for 12 h until complete consumption of starting materials as monitored by TLC. The mixture was cooled to room temperature and quenched with aqueous NaHCO<sub>3</sub> (10 mL), and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 3). Collected organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1~3/1) to give product **3**.

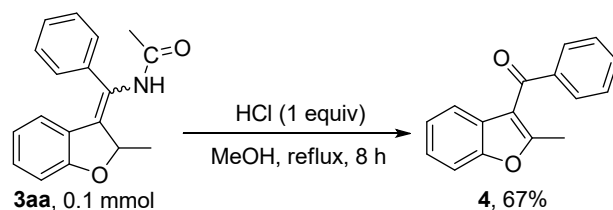


**Scale-up reaction of 3aa:** To a Schlenk tube was added enyne **1a** (220 mg, 1 mmol), nitrile **2a** (522  $\mu\text{L}$ , 10 equiv),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (250  $\mu\text{L}$ , 2 equiv), propionic acid (75  $\mu\text{L}$ , 1 equiv) and dry  $\text{CH}_2\text{Cl}_2$  (10 mL). Then the tube was stirred at 50  $^\circ\text{C}$  (oil bath temperature) in nitrogen atmosphere for 12 h until complete consumption of starting materials as monitored by TLC. The mixture was cooled to room temperature and quenched with aqueous  $\text{NaHCO}_3$  (30 mL), and extracted with  $\text{CH}_2\text{Cl}_2$  (30 mL  $\times$  3). Collected organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1~3/1) to give the *Z/E* mixed product **3aa** (198.1 mg, 71% yield, *Z/E* = 6:1).

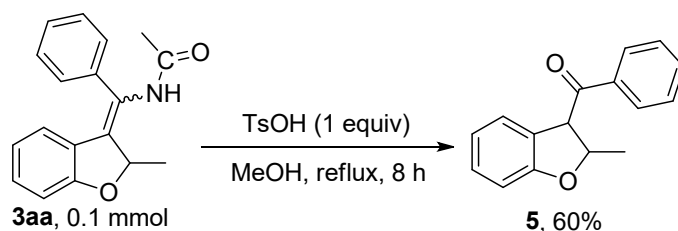


**Scale-up reaction of 3ya:** To a Schlenk tube was added enynes **1y** (297 mg, 1 mmol), nitrile **2a** (522  $\mu\text{L}$ , 10 equiv),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (250  $\mu\text{L}$ , 2 equiv), propionic acid (75  $\mu\text{L}$ , 1 equiv) and dry  $\text{CH}_2\text{Cl}_2$  (10 mL). Then the tube was stirred at 50  $^\circ\text{C}$  (oil bath temperature) in nitrogen atmosphere for 12 h until complete consumption of starting materials as monitored by TLC. The mixture was cooled to room temperature and quenched with aqueous  $\text{NaHCO}_3$  (30 mL), and extracted with  $\text{CH}_2\text{Cl}_2$  (30 mL  $\times$  3). Collected organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1~3/1) to give the *Z/E* mixed product **3ya** (214.2 mg, 60% yield, *Z/E* = 4:1). Then *Z/E* mixed product **3ya** was purified by flash chromatography on silica gel ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) to give **Z-3ya** (171.4 mg, 48% yield).

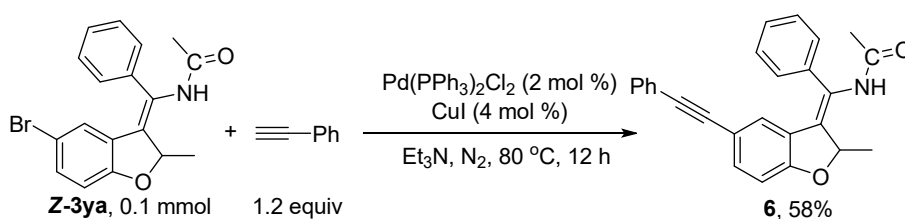
### C. Synthetic Utility



**Synthesis of 4:** To a Schlenk tube was added **3aa** (27.9 mg, 0.1 mmol), HCl (3.2  $\mu$ L, 1 equiv) and MeOH (1 mL). Then the tube was stirred at reflux for 12 h until complete consumption of starting materials as monitored by TLC. The mixture was cooled to room temperature and quenched with aqueous  $\text{NaHCO}_3$  (10 mL), and extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times$  3). The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt (20/1) as the eluent to give product **4** (15.8 mg, 67% yield).



**Synthesis of 5:** To a Schlenk tube was added **3aa** (27.9 mg, 0.1 mmol), TsOH (17.2 mg, 1 equiv) and MeOH (1 mL). Then the tube was stirred at reflux for 12 h until complete consumption of starting materials as monitored by TLC. The mixture was cooled to room temperature and quenched with aqueous  $\text{NaHCO}_3$  (10 mL), and extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times$  3). The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt (20/1) as the eluent to give product **5** (14.3 mg, 60% yield).

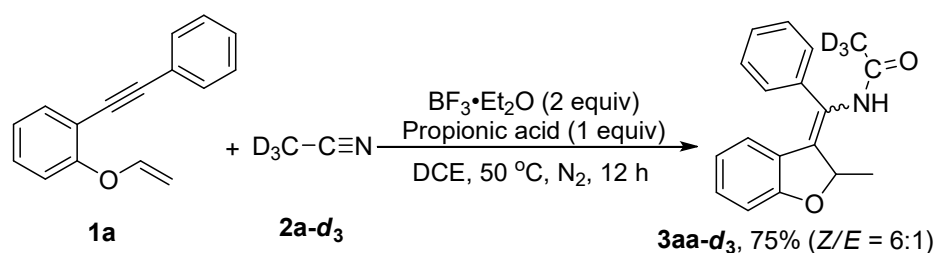


**Synthesis of 6:** To a Schlenk tube was added **Z-3ya** (35.7 mg, 0.1 mmol), phenylacetylene (13.2  $\mu$ L, 1.2 equiv),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (1.4 mg, 2 mol %), CuI (0.8 mg, 4 mol %) and  $\text{Et}_3\text{N}$  (1 mL). The reaction vessel was fitted with a rubber septum, and

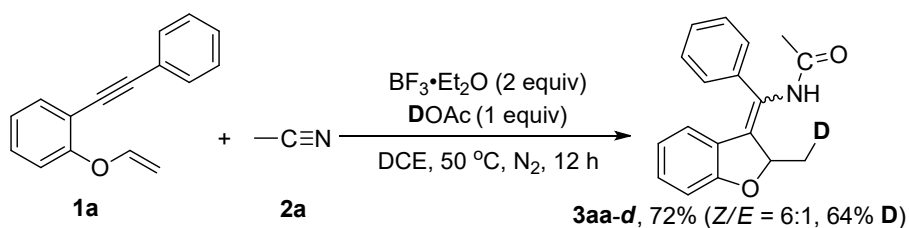
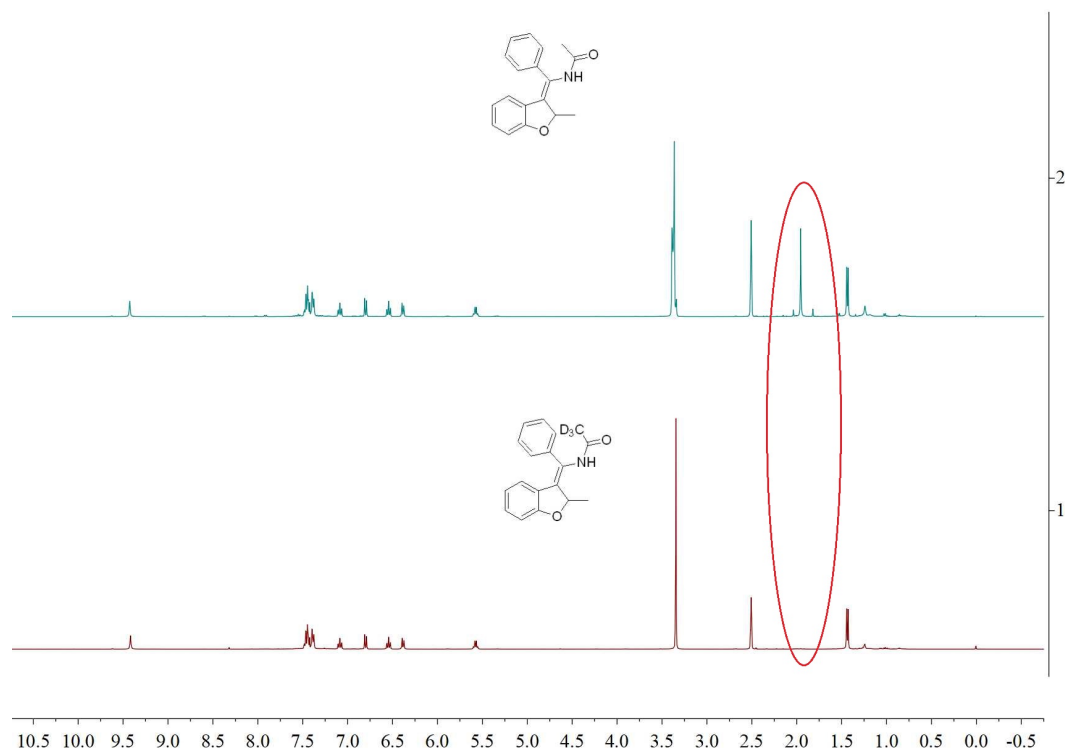


evacuated and back-filled with nitrogen. Then the mixture was stirred at 80 °C for 12 h. After the reaction was cooled to room temperature, the resulting mixture was extracted with ethyl acetate and the combined organic layers were evaporated under vacuum. The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt (5/1) as the eluent to give product **6** (22.0 mg, 58% yield).

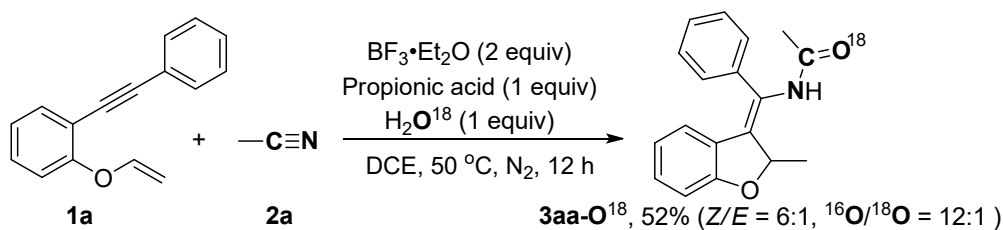
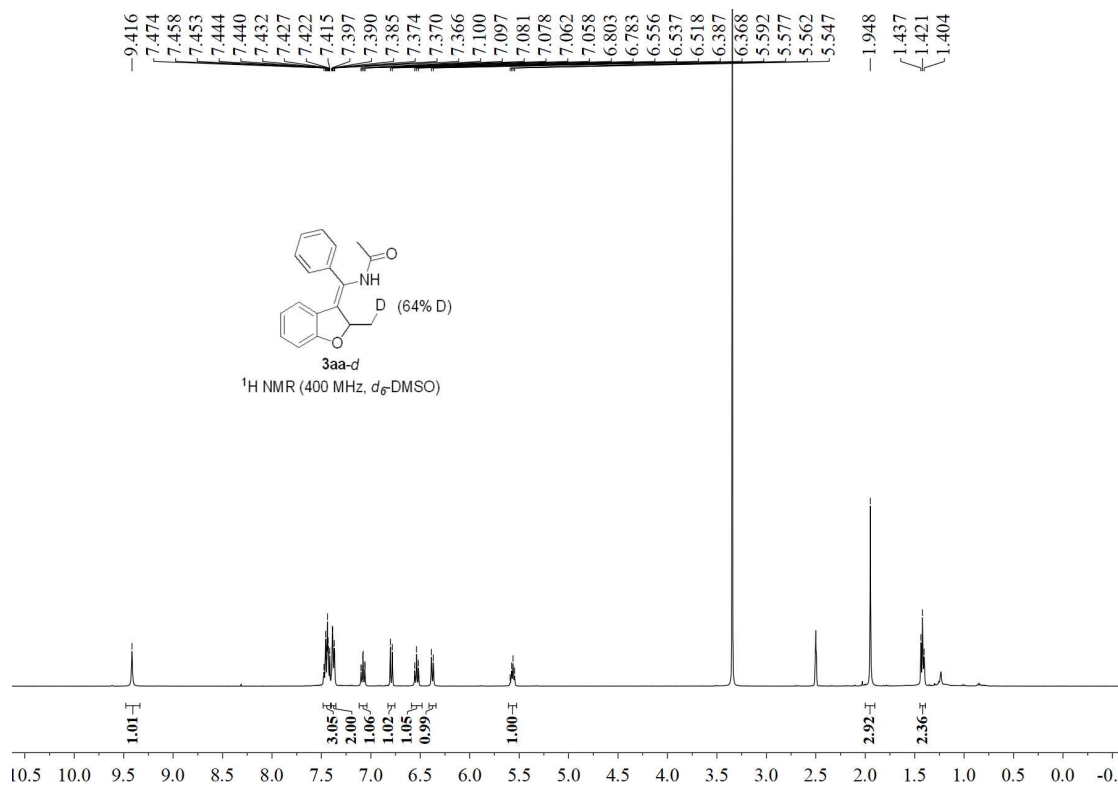
#### D. Control Experiments



**Synthesis of 3aa-d<sub>3</sub>:** To a Schlenk tube was added enyne **1a** (22.0 mg, 0.1 mmol), CD<sub>3</sub>CN **2a-d<sub>3</sub>** (52 uL, 10 equiv), BF<sub>3</sub>·Et<sub>2</sub>O (25 uL, 2 equiv), propionic acid (7.5 uL, 1 equiv) and dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL). Then the tube was stirred at 50 °C (oil bath temperature) in nitrogen atmosphere for 12 h until complete consumption of starting material as monitored by TLC. The mixture was cooled to room temperature and quenched with aqueous NaHCO<sub>3</sub> (10 mL), and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 3). Collected organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1~3/1) to give the *Z/E* mixture product **3aa-d<sub>3</sub>** (21.2 mg, 75% yield, *Z/E* = 6:1). Then *Z/E* mixture product **3aa-d<sub>3</sub>** was purified by flash chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) to give **Z-3aa-d<sub>3</sub>** (18.2 mg, 64% yield, white solid).

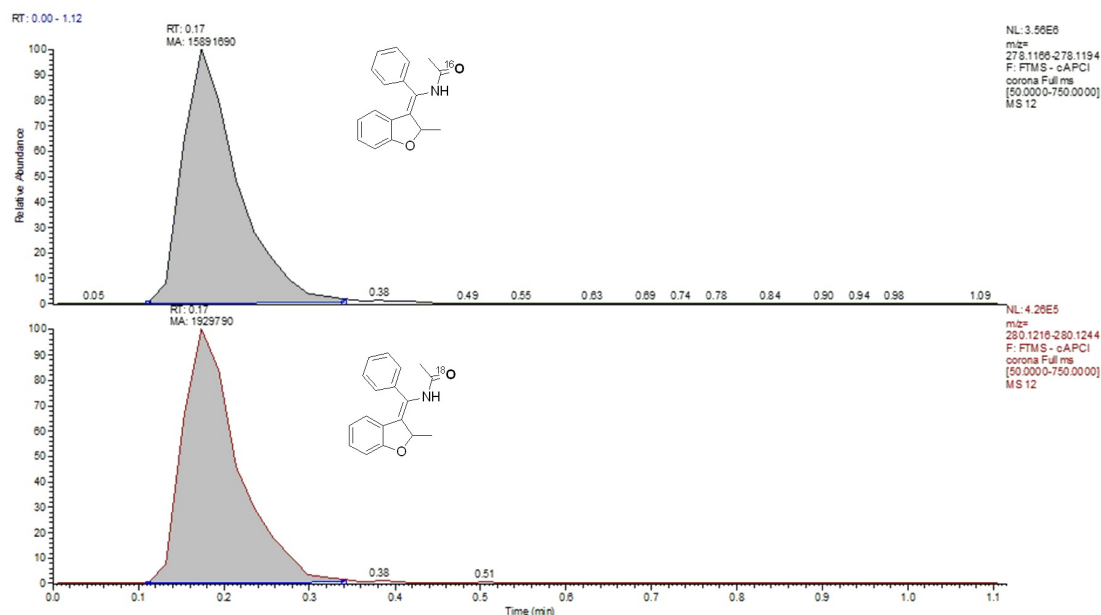


**Synthesis of 3aa-d:** To a Schlenk tube was added enyne **1a** (22.0 mg, 0.1 mmol),  $\text{CH}_3\text{CN}$  **2a** (52  $\mu\text{L}$ , 10 equiv),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (25  $\mu\text{L}$ , 2 equiv), acetic acid-D (5.8  $\mu\text{L}$ , DOAc, 1 equiv) and dry  $\text{CH}_2\text{Cl}_2$  (1 mL). Then the tube was stirred at 50  $^\circ\text{C}$  (oil bath temperature) in nitrogen atmosphere for 12 h until complete consumption of starting material as monitored by TLC. The mixture was cooled to room temperature and quenched with aqueous  $\text{NaHCO}_3$  (10 mL), and extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times$  3). Collected organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1~3/1) to give the *Z/E* mixture product **3aa-d** (19.9 mg, 71% yield, *Z/E* = 6:1). The *Z/E* mixture product **3aa-d** was purified by flash chromatography on silica gel ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) to give **Z-3aa-d** (17.1 mg, 61% yield, white solid).

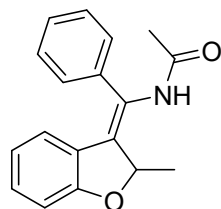


**Synthesis of 3aa-O<sup>18</sup>:** To a Schlenk tube was added enyne **1a** (22.0 mg, 0.1 mmol),  $\text{CH}_3\text{CN}$  **2a** (52  $\mu\text{L}$ , 10 equiv),  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (25  $\mu\text{L}$ , 2 equiv), propionic acid (7.5  $\mu\text{L}$ , 1 equiv),  $\text{H}_2\text{O}^{18}$  (1.8  $\mu\text{L}$ , 1 equiv) and dry  $\text{CH}_2\text{Cl}_2$  (1 mL). Then the tube was stirred at 50 °C (oil bath temperature) in nitrogen atmosphere for 12 h until complete consumption of starting material as monitored by TLC. The mixture was cooled to room temperature and quenched with aqueous  $\text{NaHCO}_3$  (10 mL), and extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times$  3). Collected organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1~3/1) to give the  $Z/E$  mixture product **3aa-O<sup>18</sup>** (14.6 mg, 52% yield,  $Z/E = 6:1$ ). The  $Z/E$  mixture product **3aa-O<sup>18</sup>** was purified by flash chromatography on silica gel ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) to give **Z**-

**3aa-O<sup>18</sup>** (12.5 mg, 45%, white solid). The ratio of <sup>16</sup>O/<sup>18</sup>O = 12/1 was detected by HRMS.



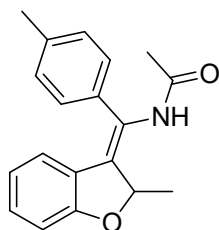
## Characterization Data for Substrates and All Products



**(Z)-N-((2-Methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-3aa):**

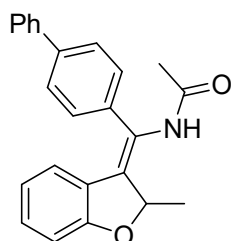
Following the general procedure B, the *Z/E* mixed product **3aa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (22.3 mg, 80% yield, *Z/E* = 6:1), then **Z-3aa** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (19.1 mg; 69% yield; mp 165.2-165.7 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.41 (s, 1H), 7.47-7.41 (m, 3H), 7.37 (dt, *J* = 7.7, 2.0 Hz, 2H), 7.10-7.02 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.53 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 1H), 5.56

(q,  $J = 6.4$  Hz, 1H), 1.94 (s, 3H), 1.42 (d,  $J = 6.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  ppm 167.5, 162.5, 138.2, 133.6, 130.3, 129.5, 129.2, 129.0, 126.5, 124.4, 122.9, 120.4, 110.6, 82.4, 23.4, 19.2;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3320, 2924, 2855, 2370, 1702, 1530, 1270, 1167, 947, 816, 751; HRMS (ESI)  $m/z$ :  $\text{C}_{18}\text{H}_{16}\text{NO}_2$   $[\text{M} - \text{H}]^-$  calcd for 278.1187, Found 278.1188.



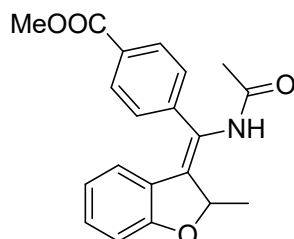
**(Z)-N-((2-Methylbenzofuran-3(2H)-ylidene)(p-tolyl)methyl)acetamide (Z-3ba):**

Following the general procedure B, the *Z/E* mixed product **3aa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (24.0 mg, 82% yield, *Z/E* = 4:1), then **Z-3ba** was obtained after purification by column chromatography ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) as a white solid (19.2 mg; 66% yield; mp 180.3-180.8 °C);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  ppm 9.35 (s, 1H), 7.25 (s, 4H), 7.08-7.04 (m, 1H), 6.77 (d,  $J = 8.0$  Hz, 1H), 6.54 (t,  $J = 7.6$  Hz, 1H), 6.46 (d,  $J = 8.0$  Hz, 1H), 5.54 (q,  $J = 6.4$  Hz, 1H), 2.35 (s, 3H), 1.93 (s, 3H), 1.40 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  ppm 167.5, 162.4, 138.4, 135.2, 133.2, 130.2, 129.7, 129.4, 126.5, 124.5, 122.9, 120.4, 110.5, 82.4, 23.4, 21.5, 19.3;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3382, 2924, 2833, 1608, 1459, 1361, 1269, 1069, 722; HRMS (ESI)  $m/z$ :  $\text{C}_{19}\text{H}_{18}\text{NO}_2$   $[\text{M} - \text{H}]^-$  calcd for 292.1343, Found 292.1346.



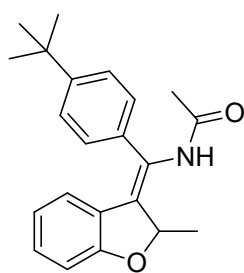
**(Z)-N-([1,1'-Biphenyl]-4-yl(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide**

**(Z-3ca):** Following the general procedure B, the *Z/E* mixed product **3aa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (26.6 mg, 75% yield, *Z/E* = 4:1), then **Z-3ca** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (21.3 mg; 60% yield; mp 234.3-234.9 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.44 (s, 1H), 7.75 (t, *J* = 8.4 Hz, 4H), 7.51-7.46 (m, 4H), 7.41-7.36 (m, 1H), 7.11-7.07 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.62-6.55 (m, 2H), 5.59 (q, *J* = 6.4 Hz, 1H), 1.96 (s, 3H), 1.44 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.7, 162.6, 140.5, 140.0, 137.1, 133.7, 130.4, 130.1, 129.5, 128.2, 127.3, 127.1, 126.1, 124.3, 123.0, 120.5, 110.6, 82.4, 23.4, 19.3.; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3264, 2920, 2854, 1702, 1659, 1515, 1327, 1275, 1159, 1056, 945, 841, 745; HRMS (ESI) *m/z*: C<sub>24</sub>H<sub>20</sub>NO<sub>2</sub> [M - H]<sup>-</sup> calcd for 354.1500, Found 354.1501.



**(Z)-Methyl 4-(Acetamido(2-methylbenzofuran-3(2H)-ylidene)methyl)benzoate**

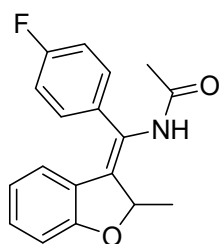
**(Z-3da):** Following the general procedure B, the *Z/E* mixed product **3aa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (24.9 mg, 74% yield, *Z/E* = 3:1), then **Z-3da** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (18.9 mg; 56% yield; mp 215.6-216.3 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.48 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.13-7.08 (m, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.57 (t, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 5.59 (q, *J* = 6.4 Hz, 1H), 3.87 (s, 3H), 1.94 (s, 3H), 1.44 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 168.1, 166.5, 162.8, 142.9, 134.9, 130.9, 130.1, 129.9, 129.8, 125.6, 123.7, 123.0, 120.7, 110.8, 82.4, 52.8, 23.4, 19.3; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3154, 2921, 2837, 1720, 1600, 1457, 1365, 1278, 1104, 750; HRMS (ESI) *m/z*: C<sub>20</sub>H<sub>18</sub>NO<sub>4</sub> [M - H]<sup>-</sup> calcd for 336.1241, Found 336.1244.



**(Z)-N-((4-(tert-Butyl)phenyl)(2-methylbenzofuran-3(2H)-**

**ylidene)methyl)acetamide (Z-3ea):** Following the general procedure B, the *Z/E* mixed product **3aa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (23.8 mg, 71% yield, *Z/E* = 6:1), then **Z-3ea** was obtained after purification by column chromatography

(CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (20.4 mg; 61% yield; mp 163.3-163.8 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.36 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08-7.04 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.53 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 5.54 (q, *J* = 6.4 Hz, 1H), 1.93 (s, 3H), 1.40 (d, *J* = 6.4 Hz, 3H), 1.32 (s, 9H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.3, 162.4, 151.6, 135.2, 133.2, 130.2, 129.2, 126.3, 125.9, 124.5, 122.9, 120.4, 110.5, 82.5, 35.0, 31.6, 23.4, 19.2; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2957, 2857, 1609, 1517, 1462, 1361, 1279, 834, 753; HRMS (ESI) *m/z*: C<sub>22</sub>H<sub>24</sub>NO<sub>2</sub> [M - H]<sup>-</sup> calcd for 334.1813, Found 334.1815.

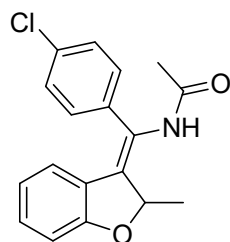


**(Z)-N-((4-Fluorophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide**

**(Z-3fa):** Following the general procedure B, the *Z/E* mixed product **3aa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (19.3 mg, 65% yield, *Z/E* = 4:1), then **Z-3fa** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (15.4 mg; 52% yield; mp 181.1-181.7 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.41 (s, 1H), 7.43-7.39 (m, 2H), 7.29-7.24 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.57 (t, *J* = 7.6 Hz, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 5.56 (q, *J* = 6.4 Hz, 1H), 1.94 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.7, 162.5 (d, *J* = 143.8 Hz), 162.5, 134.5 (d, *J* = 3.0 Hz), 133.8, 131.7 (d, *J* =

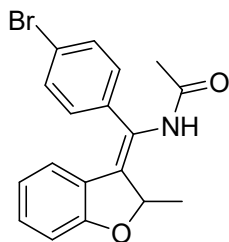


8.0 Hz), 130.4, 125.5, 124.2, 122.8, 120.5, 116.1 (d,  $J = 21.3$  Hz), 110.6, 82.3, 23.4, 19.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm -112.95;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2926, 2832, 1601, 1510, 1461, 1363, 1227, 1151, 1064, 839, 766; HRMS (ESI)  $m/z$ :  $\text{C}_{18}\text{H}_{15}\text{FNO}_2$   $[\text{M} - \text{H}]^-$  calcd for 296.1092, Found 296.1093.



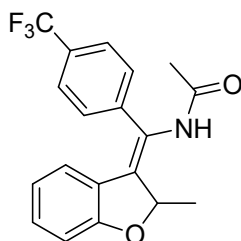
**(Z)-N-((4-Chlorophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide**

**(Z-3ga):** Following the general procedure B, the *Z/E* mixed product **3aa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (21.3 mg, 68% yield, *Z/E* = 4:1), then **Z-3ga** was obtained after purification by column chromatography ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) as a white solid (16.9 mg; 54% yield; mp 232.3-233.8 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 9.41 (s, 1H), 7.50-7.48 (m, 2H), 7.40-7.38 (m, 2H), 7.10 (t,  $J = 8.0$  Hz, 1H), 6.80 (d,  $J = 8.0$  Hz, 1H), 6.59 (t,  $J = 7.6$  Hz, 1H), 6.46 (d,  $J = 7.6$  Hz, 1H), 5.57 (q,  $J = 6.4$  Hz, 1H), 1.93 (s, 3H), 1.42 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 167.9, 162.6, 137.0, 134.2, 133.4, 131.4, 130.6, 129.2, 125.4, 123.9, 122.9, 120.6, 110.7, 82.3, 23.4, 19.3;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2903, 1635, 1506, 1311, 741; HRMS (ESI)  $m/z$ :  $\text{C}_{18}\text{H}_{15}\text{ClNO}_2$   $[\text{M} - \text{H}]^-$  calcd for 312.0797, Found 312.0799.



**(Z)-N-((4-Bromophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide**

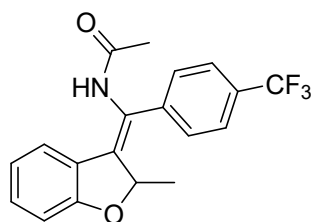
**(Z-3ha):** Following the general procedure B, the *Z/E* mixed product **3ha** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (25.7 mg, 72% yield, *Z/E* = 4:1), then **Z-3ha** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (20.7 mg; 58% yield; mp 218.4-218.9 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.40 (s, 1H), 7.65-7.62 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12-7.08 (m, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.56 (q, *J* = 6.4 Hz, 1H), 1.93 (s, 3H), 1.41 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.9, 162.6, 137.3, 134.1, 132.1, 131.7, 130.6, 125.5, 123.9, 122.8, 122.0, 120.6, 110.7, 82.3, 23.3, 19.3; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3124, 2926, 2832, 1602, 1362, 769; HRMS (ESI) *m/z*: C<sub>18</sub>H<sub>15</sub>BrNO<sub>2</sub> [M - H]<sup>-</sup> calcd for 356.0292, Found 356.0293.



**(Z)-N-((2-Methylbenzofuran-3(2H)-ylidene)(4-**

**(trifluoromethyl)phenyl)methyl)acetamide (Z-3ia):** Following the general procedure B, the *Z/E* mixed product **3ia** was obtained after purification by column

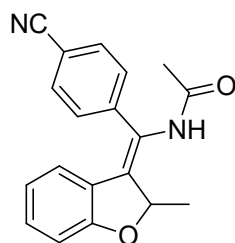
chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (18.0 mg, 52% yield, *Z/E* = 2:1), then **Z-3ia** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (12.1 mg; 35% yield; mp 246.2-246.7 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.47 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 7.6 Hz, 1H), 5.61 (q, *J* = 6.4 Hz, 1H), 1.94 (s, 3H), 1.44 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 168.2, 162.8, 142.3, 135.0, 130.9, 130.4, 129.1 (q, *J* = 31.5 Hz), 126.1 (q, *J* = 3.6 Hz), 125.3, 123.6, 123.4, 122.8, 120.7, 110.9, 82.3, 23.3, 19.3; <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ ppm -60.32; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2922, 2830, 1612, 1461, 1360, 1124, 1068, 763; HRMS (ESI) *m/z*: C<sub>19</sub>H<sub>15</sub>F<sub>3</sub>NO<sub>2</sub> [M - H]<sup>-</sup> calcd for 346.1060, Found 346.1062.



**(E)-N-((2-Methylbenzofuran-3(2H)-ylidene)(4-**

**(trifluoromethyl)phenyl)methyl)acetamide (E-3ia):** Following the general procedure B, the *Z/E* mixed product **3ia** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (18.0 mg, 52% yield, *Z/E* = 2:1), then **Z-3ia** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (6.0 mg; 17% yield; mp 246.3-246.8 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.76 (s, 1H), 7.70

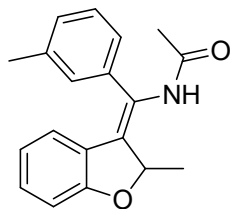
(q,  $J = 8.4$  Hz, 4H), 7.62 (d,  $J = 7.8$  Hz, 1H), 7.27-7.25 (m, 1H), 6.98-6.94 (m, 1H), 6.88 (d,  $J = 8.4$  Hz, 1H), 5.93 (q,  $J = 6.0$  Hz, 1H), 2.04 (s, 3H), 1.02 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  ppm 168.7, 161.8, 142.9, 136.2, 130.8, 128.4, 127.6 (q,  $J = 31.5$  Hz), 125.4 (q,  $J = 3.9$  Hz), 125.1, 125.0, 124.4, 122.9, 120.7, 110.1, 80.2, 22.8, 19.8;  $^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ )  $\delta$  ppm -61.00;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  2912, 2841, 1655, 1468, 1356, 1115, 1071, 772; HRMS (ESI)  $m/z$ :  $\text{C}_{19}\text{H}_{15}\text{F}_3\text{NO}_2$   $[\text{M} - \text{H}]^-$  calcd for 346.1060, Found 346.1061.



**(Z)-N-((4-Cyanophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide**

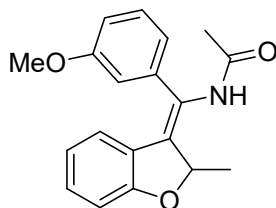
**(Z-3ja):** Following the general procedure B, the *Z/E* mixed product **3ja** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (14.9 mg, 49% yield, *Z/E* = 2:1), then **Z-3ja** was obtained after purification by column chromatography ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) as a white solid (10.0 mg; 33% yield; mp 202.3-202.8 °C);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  ppm 9.48 (s, 1H), 7.89 (d,  $J = 8.0$  Hz, 2H), 7.58 (d,  $J = 8.1$  Hz, 2H), 7.15-7.11 (m, 1H), 6.82 (d,  $J = 8.4$  Hz, 1H), 6.60 (t,  $J = 7.6$  Hz, 1H), 6.48 (d,  $J = 7.6$  Hz, 1H), 5.61 (q,  $J = 6.4$  Hz, 1H), 1.94 (s, 3H), 1.44 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  ppm 168.3, 162.9, 142.9, 135.4, 133.1, 131.1, 130.5, 125.1, 123.4, 122.9, 120.8, 119.3, 111.2, 110.9, 82.3, 23.3, 19.3;  $\nu_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$  2924, 2834, 1611, 1461,

1361, 772; HRMS (ESI)  $m/z$ : C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> [M - H]<sup>-</sup> calcd for 303.1139, Found 303.1140.



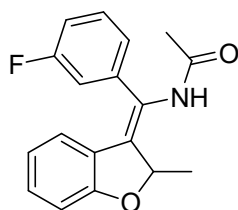
**(Z)-N-((2-Methylbenzofuran-3(2H)-ylidene)(*m*-tolyl)methyl)acetamide (Z-3ka):**

Following the general procedure B, the *Z/E* mixed product **3ka** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (22.3 mg, 76% yield, *Z/E* = 4:1), then **Z-3ka** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (17.9 mg; 61% yield; mp 165.5-166.0 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.38 (s, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 9.6 Hz, 1H), 7.08-7.04 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.53 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 5.55 (q, *J* = 6.4 Hz, 1H), 2.33 (s, 3H), 1.94 (s, 3H), 1.41 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.4, 162.4, 138.4, 138.1, 133.3, 130.2, 129.8, 129.6, 129.1, 126.6, 126.5, 124.5, 123.0, 120.4, 110.5, 82.4, 23.4, 21.4, 19.2;  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 2922, 1647, 1523, 1313, 748; HRMS (ESI)  $m/z$ : C<sub>19</sub>H<sub>18</sub>NO<sub>2</sub> [M - H]<sup>-</sup> calcd for 292.1343, Found 292.1345.



**(Z)-N-((3-Methoxyphenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide**

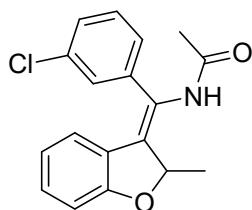
**(Z-3la):** Following the general procedure B, the *Z/E* mixed product **3la** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (21.0 mg, 68% yield, *Z/E* = 4:1), then **Z-3la** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (16.7 mg; 54% yield; mp 141.6-142.1 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.38 (s, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.00-6.94 (m, 2H), 6.87 (s, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.56 (t, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 5.54 (q, *J* = 6.4 Hz, 1H), 3.75 (s, 3H), 1.94 (s, 3H), 1.41 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.6, 162.5, 160.0, 139.5, 133.7, 130.4, 130.4, 126.2, 124.3, 123.2, 121.8, 120.5, 114.7, 114.6, 110.6, 82.4, 55.7, 23.4, 19.2; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3487, 2927, 2849, 2356, 1654, 1590, 1464, 1374, 1283, 1225, 1046, 754, 697; HRMS (ESI) *m/z*: : C<sub>19</sub>H<sub>18</sub>NO<sub>3</sub> [M - H]<sup>-</sup> calcd for 308.1292, Found 308.1293.



**(Z)-N-((3-Fluorophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide**

**(Z-3ma):** Following the general procedure B, the *Z/E* mixed product **3ma** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (19.3 mg, 65% yield, *Z/E* = 3.5:1), then **Z-3ma** was

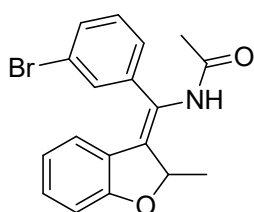
obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (15.1 mg; 51% yield; mp 210.3-210.8 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.43 (s, 1H), 7.49-7.46 (m, 1H), 7.27-7.22 (m, 2H), 7.17-7.14 (m, 1H), 7.12-7.08 (m, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.58 (t, *J* = 7.6 Hz, 1H), 6.43 (d, *J* = 7.6 Hz, 1H), 5.57 (q, *J* = 6.4 Hz, 1H), 1.94 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 165.2 (d, *J* = 502.4 Hz), 162.8 (d, *J* = 242.9 Hz) 140.5 (d, *J* = 7.6 Hz), 134.3, 131.2 (d, *J* = 8.4 Hz), 130.6, 125.8 (d, *J* = 2.7 Hz), 125.2 (d, *J* = 2.2 Hz), 123.9, 122.9, 120.6, 116.2, 115.9 (d, *J* = 8.4 Hz), 115.7, 110.7, 82.3, 23.4, 19.2; <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ ppm -112.90; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3367, 2924, 2831, 1598, 1459, 1364, 769; HRMS (ESI) *m/z*: C<sub>18</sub>H<sub>15</sub>FNO<sub>2</sub> [M - H]<sup>-</sup> calcd for 296.1092, Found 296.1093.



**(*Z*)-*N*-((3-Chlorophenyl)(2-methylbenzofuran-3(*2H*))-ylidene)methyl)acetamide**

**(*Z*-3na):** Following the general procedure B, the *Z/E* mixed product **3na** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (21.9 mg, 70% yield, *Z/E* = 4:1), then ***Z*-3na** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (17.5 mg; 56% yield; mp 198.3-198.8 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.44 (s, 1H), 7.48-7.46 (m, 2H), 7.38-7.34 (m, 2H), 7.13-7.08 (m, 1H), 6.81

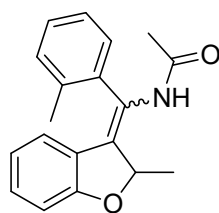
(d,  $J = 8.0$  Hz, 1H), 6.59 (t,  $J = 7.6$  Hz, 1H), 6.41 (d,  $J = 7.6$  Hz, 1H), 5.58 (q,  $J = 6.4$  Hz, 1H), 1.94 (s, 3H), 1.42 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  ppm 167.9, 162.7, 140.3, 134.5, 133.7, 131.1, 130.7, 129.1, 128.8, 128.3, 125.1, 123.8, 122.8, 120.6, 110.8, 82.3, 23.3, 19.2;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3115, 2924, 2830, 1601, 1362, 770; HRMS (ESI)  $m/z$ :  $\text{C}_{18}\text{H}_{15}\text{ClNO}_2$   $[\text{M} - \text{H}]^-$  calcd for 312.0797, Found 312.0800.



**(Z)-N-((3-Bromophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide**

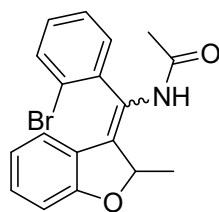
**(Z-30a):** Following the general procedure B, the *Z/E* mixed product **30a** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (20.3 mg, 65% yield, *Z/E* = 4:1), then **Z-30a** was obtained after purification by column chromatography ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) as a white solid (16.3 mg; 52% yield; mp 205.6-206.1 °C);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  ppm 9.43 (s, 1H), 7.62-7.59 (m, 1H), 7.51 (s, 1H), 7.43-7.39 (m, 2H), 7.11 (t,  $J = 7.6$  Hz, 1H), 6.81 (d,  $J = 8.4$  Hz, 1H), 6.59 (t,  $J = 7.6$  Hz, 1H), 6.40 (d,  $J = 8.0$  Hz, 1H), 5.57 (q,  $J = 6.4$  Hz, 1H), 1.94 (s, 3H), 1.42 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  ppm 167.9, 162.7, 140.5, 134.6, 131.9, 131.7, 131.4, 130.7, 128.7, 125.0, 123.8, 122.8, 122.2, 120.6, 110.8, 82.3, 23.3, 19.2;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3167, 2925, 2831, 1598, 1364, 1070, 765; HRMS (ESI)  $m/z$ :  $\text{C}_{18}\text{H}_{15}\text{BrNO}_2$   $[\text{M} - \text{H}]^-$  calcd for 312.0797, Found 356.0294.





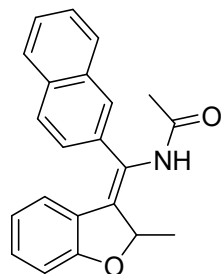
***N*-((2-Methylbenzofuran-3(2*H*)-ylidene)(*o*-tolyl)methyl)acetamide (3pa):**

Following the general procedure B, the *Z/E* inseparable isomers product **3pa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (19.0 mg, 65% yield, *Z/E* = 1:1, mp 205.2-205.7 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.40 (s, 1H), 9.33 (s, 1H), 7.37-7.35 (m, 2H), 7.32-7.24 (m, 5H), 7.11-7.01 (m, 3H), 6.77 (t, *J* = 8.4 Hz, 2H), 6.51 (t, *J* = 7.6 Hz, 1H), 6.46 (t, *J* = 7.6 Hz, 1H), 5.85 (d, *J* = 7.6 Hz, 1H), 5.76 (d, *J* = 7.6 Hz, 1H), 5.67-5.60 (m, 2H), 2.25 (s, 3H), 2.11 (s, 3H), 1.94 (d, *J* = 6.4 Hz, 6H), 1.41 (t, *J* = 6.4 Hz, 6H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 166.8, 166.0, 161.7, 161.5, 137.4, 136.9, 136.7, 136.6, 132.3, 132.2, 130.6, 130.4, 130.0, 129.7, 129.3, 128.8, 128.3, 126.7, 126.2, 125.8, 124.6, 124.3, 124.0, 122.4, 121.8, 120.3, 120.0, 109.9, 109.8, 81.5, 22.9, 18.9, 18.6, 18.3; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3239, 2924, 2853, 2373, 1777, 1660, 1520, 1460, 1382, 1272, 996, 751; HRMS (ESI) *m/z*: C<sub>19</sub>H<sub>18</sub>NO<sub>2</sub> [M - H]<sup>-</sup> calcd for 292.1343, Found 292.1345.



***N*-((2-Bromophenyl)(2-methylbenzofuran-3(2*H*)-ylidene)methyl)acetamide**

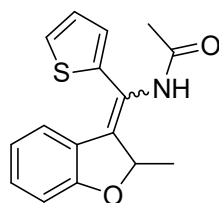
**(3qa):** Following the general procedure B, the *Z/E* inseparable isomer product **3pa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (19.3 mg, 54% yield, *Z/E* = 1:1.1, mp 205.3-205.8 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.42 (s, 0.9H), 9.38 (s, 1H), 7.76-7.72 (m, 2.2H), 7.53-7.44 (m, 3.4H), 7.41-7.36 (m, 2.2H), 7.30-7.27 (m, 1H), 7.10-7.04 (m, 2.2H), 6.81 (d, *J* = 3.6 Hz, 1H), 6.79 (d, *J* = 3.2 Hz, 0.9H), 6.56-6.48 (m, 2.2H), 5.86 (d, *J* = 8.0 Hz, 1H), 5.79 (d, *J* = 8.0 Hz, 1.1H), 5.73 (q, *J* = 6.4 Hz, 1.1H), 5.64 (q, *J* = 6.4 Hz, 1H), 1.95 (d, *J* = 4.1 Hz, 6.2H), 1.45 (d, *J* = 6.4 Hz, 3H), 1.42 (d, *J* = 6.4 Hz, 3.2H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 166.8, 166.6, 161.8, 161.7, 138.2, 137.6, 133.4, 133.2, 133.1, 132.8, 132.5, 130.6, 130.5, 130.2, 129.8, 129.7, 128.7, 127.9, 125.6, 124.2, 124.0, 123.8, 123.5, 122.5, 122.3, 122.2, 120.3, 120.2, 110.0, 110.0, 81.6, 81.4, 22.9, 18.4, 18.3; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3439, 2923, 2863, 2361, 2252, 1668, 1524, 1464, 1292, 1015, 826, 757; HRMS (ESI) *m/z*: C<sub>18</sub>H<sub>15</sub>BrNO<sub>2</sub> [M - H]<sup>-</sup> calcd for 352.0292, Found 356.0292.



***(Z)*-*N*-((2-Methylbenzofuran-3(2*H*)-ylidene)(naphthalen-2-yl)methyl)acetamide**

**(Z-3ra):** Following the general procedure B, the *Z/E* mixed product **3ra** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1)

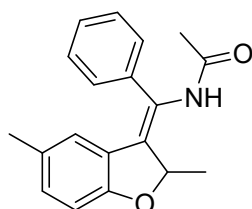
as a white solid (22.3 mg, 68% yield, *Z/E* = 3:1), then **Z-3ra** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (16.8 mg; 51% yield; mp 171.2-171.7 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.51 (s, 1H), 7.98-7.94 (m, 4H), 7.54 (dt, *J* = 6.0, 2.4 Hz, 2H), 7.48 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.47 (t, *J* = 7.5 Hz, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 5.63 (q, *J* = 6.4 Hz, 1H), 1.97 (s, 3H), 1.47 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.7, 162.6, 135.5, 133.8, 133.5, 133.3, 130.4, 128.6, 128.4, 128.1, 127.5, 127.7, 127.0, 126.5, 124.4, 122.8, 120.5, 110.6, 82.5, 23.5, 19.3;  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 3441, 2922, 2850, 1651, 1516, 1459, 1372, 1231, 1060, 817, 749; HRMS (ESI) *m/z*: C<sub>22</sub>H<sub>18</sub>NO<sub>2</sub> [M - H]<sup>-</sup> calcd for 328.1343, Found 328.1344.



***N*-((2-Methylbenzofuran-3(2*H*)-ylidene)(thiophen-2-yl)methyl)acetamide (**3sa**):**

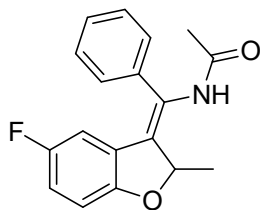
Following the general procedure B, the *Z/E* inseperable isomers product **3sa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (22.2 mg, 78% yield, *Z/E* = 4:1, mp 205.3-205.8 °C); **Z-3sa**: <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.52 (s, 1H), 7.67-7.66 (m, 1H), 7.23-7.20 (m, 1H), 7.14-7.12 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.66-6.64 (m, 2H), 5.52 (q, *J* = 6.4 Hz, 1H), 1.95 (s, 3H), 1.41 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.0, 162.2, 139.7, 136.2, 130.4, 128.1, 127.5, 127.3, 123.5, 122.7, 120.2,

118.3, 110.2, 81.9, 22.8, 18.6;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3444, 2926, 1656, 1517, 1460, 1369, 1319, 1264, 996, 841, 750; HRMS (ESI)  $m/z$ :  $\text{C}_{16}\text{H}_{14}\text{NO}_2\text{S}$   $[\text{M} - \text{H}]^-$  calcd for 284.0751, Found 284.0752.



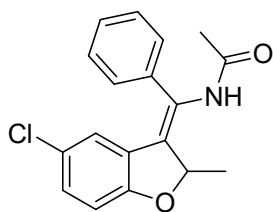
**(Z)-N-((2,5-Dimethylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-3va)**

**3va**): Following the general procedure B, the *Z/E* mixed product **3va** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (18.5 mg, 63% yield, *Z/E* = 5:1), then **Z-3va** was obtained after purification by column chromatography ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) as a white solid (15.5 mg; 53% yield; mp 185.2-185.6 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 9.39 (s, 1H), 7.46-7.41 (m, 3H), 7.37-7.35 (m, 2H), 6.92-6.83 (m, 1H), 6.67 (d,  $J$  = 8.0 Hz, 1H), 6.17 (s, 1H), 5.52 (q,  $J$  = 6.3 Hz, 1H), 1.92 (d,  $J$  = 6.8 Hz, 6H), 1.39 (d,  $J$  = 6.4 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 167.6, 160.7, 138.2, 133.9, 130.9, 129.5, 129.1, 129.0, 128.8, 126.3, 124.3, 123.4, 110.2, 82.4, 23.4, 21.1, 19.4;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3259, 2924, 2857, 1665, 1487, 1271, 1051, 963, 751, 701; HRMS (ESI)  $m/z$ :  $\text{C}_{19}\text{H}_{18}\text{NO}_2$   $[\text{M} - \text{H}]^-$  calcd for 292.1343, Found 292.1345.



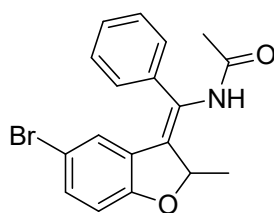
**(Z)-N-((5-Fluoro-2-methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide**

**(Z-3wa):** Following the general procedure B, the *Z/E* mixed product **3wa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (16.0 mg, 54% yield, *Z/E* = 3:1), then **Z-3wa** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (12.2 mg; 41% yield; mp 175.1-175.5 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.50 (s, 1H), 7.48-7.44 (m, 3H), 7.38-7.36 (m, 2H), 6.92-6.87 (m, 1H), 6.79-6.76 (m, 1H), 5.90 (d, *J* = 8.8 Hz, 1H), 5.62 (q, *J* = 6.4 Hz, 1H), 1.95 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 163.0 (d, *J* = 883.6 Hz), 156.4 (d, *J* = 232.2 Hz), 137.6, 132.4, 129.5, 129.4, 129.3, 128.0, 125.8 (d, *J* = 9.5 Hz), 116.5 (d, *J* = 24.5 Hz), 111.0 (d, *J* = 8.9 Hz), 109.1, 108.9, 83.3, 23.4, 19.0; <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ ppm -123.86; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2928, 2828, 1612, 1472, 1360, 771, 529; HRMS (ESI) *m/z*: C<sub>18</sub>H<sub>15</sub>FNO<sub>2</sub> [M - H]<sup>-</sup> calcd for 296.1092, Found 296.1093.



**(Z)-N-((5-Chloro-2-methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide**

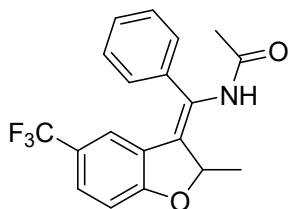
**(Z-3xa):** Following the general procedure B, the *Z/E* mixed product **3xa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (24.1 mg, 77% yield, *Z/E* = 3:1), then **Z-3xa** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (18.2 mg; 58% yield; mp 202.2-202.5 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.48 (s, 1H), 7.51-7.45 (m, 3H), 7.38-7.36 (m, 2H), 7.10-7.07 (m, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.16 (s, 1H), 5.63 (q, *J* = 6.3 Hz, 1H), 1.95 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.4, 161.1, 137.6, 131.6, 129.5, 129.4(2C), 129.4, 128.3, 126.7, 124.0, 122.3, 111.8, 83.4, 23.4, 19.0;  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 2923, 2833, 1624, 1532, 1363, 773, 699; HRMS (ESI) *m/z*: C<sub>18</sub>H<sub>15</sub>ClNO<sub>2</sub> [M - H]<sup>-</sup> calcd for 312.0797, Found 312.0800.



**(Z)-N-((5-Bromo-2-methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide**

**(Z-3ya):** Following the general procedure B, the *Z/E* mixed product **3ya** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (23.2 mg, 65% yield, *Z/E* = 4:1), then **Z-3ya** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (18.6 mg; 52% yield; mp 182.3-182.6 °C); <sup>1</sup>H NMR (400 MHz, DMSO-

$d_6$ )  $\delta$  ppm 9.50 (s, 1H), 7.49-7.46 (m, 3H), 7.38-7.36 (m, 2H), 7.21-7.18 (m, 1H), 6.76 (d,  $J = 8.4$  Hz, 1H), 6.30 (s, 1H), 5.63 (q,  $J = 6.4$  Hz, 1H), 1.95 (s, 3H), 1.42 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm 167.4, 161.4, 137.6, 132.3, 131.4, 129.4, 129.4 (2C), 128.3, 127.3, 125.3, 112.4, 111.6, 83.3, 23.4, 19.0;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2925, 2831, 1607, 1457, 1362, 1065, 772; HRMS (ESI)  $m/z$ :  $\text{C}_{18}\text{H}_{15}\text{BrNO}_2$   $[\text{M} - \text{H}]^-$  calcd for 356.0292, Found 356.0294.

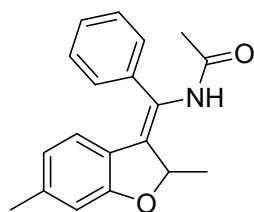


**(Z)-N-((2-Methyl-5-(trifluoromethyl)benzofuran-3(2H)-**

**ylidene)(phenyl)methyl)acetamide (Z-3za):** Following the general procedure B, the *Z/E* mixed product **3za** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (17.4 mg, 50% yield, *Z/E* = 3:1), then **Z-3za** was obtained after purification by column chromatography ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) as a white solid (13.2 mg; 38% yield; mp 209.1-209.5 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm 9.57 (s, 1H), 7.50-7.46 (m, 3H), 7.40-7.38 (m, 3H), 6.95 (d,  $J = 8.4$  Hz, 1H), 6.42 (s, 1H), 5.71 (q,  $J = 6.4$  Hz, 1H), 1.97 (s, 3H), 1.45 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm 166.1 (d,  $J = 270.4$  Hz), 137.4 (d,  $J = 5.8$  Hz), 130.6, 129.5, 129.5, 129.4, 128.9, 127.3 (d,  $J = 2.9$  Hz), 126.1, 125.8, 123.4, 121.3 (q,  $J = 31.5$  Hz), 119.8 (q,  $J = 4.1$  Hz), 111.0, 84.0, 23.5, 18.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO}-d_6$ )  $\delta$  ppm -60.32;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3237,

3023, 2918, 1648, 1500, 1449, 1333, 1277, 1159, 1107, 1001, 901, 822, 764, 708;

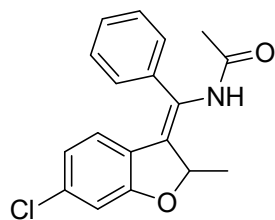
HRMS (ESI)  $m/z$ :  $C_{19}H_{15}F_3NO_2$   $[M - H]^-$  calcd for 346.1060, Found 346.1063.



**(Z)-N-((2,6-Dimethylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-**

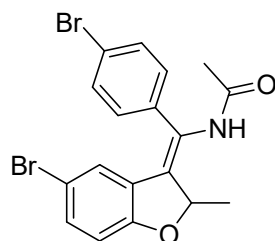
**3aaa)**: Following the general procedure B, the *Z/E* mixed product **3aaa** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (15.2 mg, 52% yield, *Z/E* = 3:1), then **Z-3aaa** was obtained after purification by column chromatography ( $CH_2Cl_2$ /petroleum ether = 8:1-10:1) as a white solid (11.4 mg; 39% yield; mp 165.1-165.5 °C);  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$  ppm 9.37 (s, 1H), 7.46-7.39 (m, 3H), 7.37-7.35 (m, 2H), 6.62 (s, 1H), 6.37 (d,  $J$  = 8.4 Hz, 1H), 6.30 (d,  $J$  = 8.0 Hz, 1H), 5.54 (q,  $J$  = 6.4 Hz, 1H), 2.18 (s, 3H), 1.93 (s, 3H), 1.41 (d,  $J$  = 6.0 Hz, 3H);  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ )  $\delta$  ppm 167.5, 162.8, 140.5, 138.3, 133.8, 129.5, 129.1, 128.9, 125.3, 122.6, 121.6, 121.3, 111.0, 82.5, 23.4, 21.6, 19.3;  $\nu_{max}(KBr)/cm^{-1}$  3485, 3262, 2923, 2854, 1657, 1521, 1442, 1376, 1278, 1129, 1055, 1003, 755, 707; HRMS (ESI)  $m/z$ :  $C_{19}H_{18}NO_2$   $[M - H]^-$  calcd for 292.1343, Found 292.1344.





**(Z)-N-((6-Chloro-2-methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide**

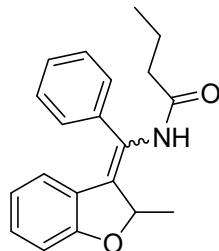
**(Z-3aba):** Following the general procedure B, the *Z/E* mixed product **3aba** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (21.9 mg, 70% yield, *Z/E* = 3:1), then **Z-3aba** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/ petroleum ether = 8:1-10:1) as a white solid (16.6 mg; 53% yield; mp 217.4-217.8 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.46 (s, 1H), 7.47-7.42 (m 3H), 7.37-7.35 (m, 2H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.61-6.59 (m, 1H), 6.29 (d, *J* = 8.4 Hz, 1H), 5.62 (q, *J* = 6.3 Hz, 1H), 1.94 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.5, 163.1, 137.8, 134.1, 131.7, 129.5, 129.4, 129.3, 127.4, 123.9, 123.6, 120.6, 110.8, 83.7, 23.4, 19.0; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 2924, 2832, 1599, 1363, 1070, 770; HRMS (ESI) *m/z*: C<sub>18</sub>H<sub>17</sub>ClNO<sub>2</sub> [M - H]<sup>-</sup> calcd for 312.0797, Found 312.0799.



**(Z)-N-((5-Bromo-2-methylbenzofuran-3(2H)-ylidene)(4-**

**bromophenyl)methyl)acetamide (Z-3aca):** Following the general procedure B, the *Z/E* mixed product **3aca** was obtained after purification by column chromatography

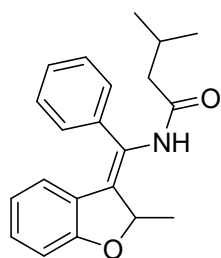
(petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (26.5 mg, 61% yield, *Z/E* = 3:1), then **Z-3aca** was obtained after purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether = 8:1-10:1) as a white solid (20.4 mg; 46% yield; mp 201.1-201.5 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.50 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.26-7.24 (m, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 5.64 (q, *J* = 6.4 Hz, 1H), 1.95 (s, 3H), 1.42 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ ppm 167.4, 161.1, 136.2, 132.2, 131.8, 131.5, 131.2, 126.8, 126.4, 124.6, 121.9, 112.2, 111.3, 82.8, 22.9, 18.5; ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3440, 3225, 2927, 2844, 2349, 1645, 1514, 1459, 1368, 1268, 1134, 1065, 826, 753; HRMS (ESI) *m/z*: C<sub>18</sub>H<sub>14</sub>Br<sub>2</sub>NO<sub>2</sub> [M - H]<sup>-</sup> calcd for 433.9397, Found 433.9400.



***N*-((2-Methylbenzofuran-3(2*H*)-ylidene)(phenyl)methyl)butyramide (3ab):**

Following the general procedure B, the *Z/E* inseparable isomer product **3ab** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (16.0 mg, 52% yield, *Z/E* = 2.5:1, mp 215.3-215.8 °C); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ ppm 9.59 (s, 0.4H), 9.38 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 0.4H), 7.48-7.41 (m, 3.8H), 7.39-7.37 (m, 2.8H), 7.31-7.27 (m, 0.5H), 7.22-7.18 (m, 0.4H), 7.10-7.06 (m, 1H), 6.92-6.89 (m, 0.4H), 6.84 (d, *J* = 8.0 Hz, 0.4H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.54 (t, *J* = 7.6 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 1H), 5.89 (q, *J* = 6.4 Hz,

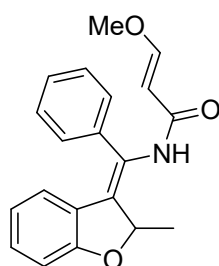
0.4H), 5.58 (q,  $J = 6.4$  Hz, 1H), 2.30 (t,  $J = 7.2$  Hz, 0.8H), 2.19 (t,  $J = 7.2$  Hz, 2H), 1.63-1.50 (m, 3H), 1.43 (d,  $J = 6.4$  Hz, 3H), 1.01 (d,  $J = 6.4$  Hz, 1.2H), 0.92-0.87 (m, 4.2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 171.1, 169.9, 162.0, 161.5, 138.8, 137.7, 134.5, 133.1, 130.1, 129.8, 129.0, 128.7, 128.5, 128.5, 127.7, 127.6, 126.4, 126.0, 124.8, 123.8, 122.39, 120.4, 119.9, 110.1, 109.9, 81.9, 80.4, 19.6, 18.8, 18.6, 18.4, 13.8, 13.7;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3248, 2962, 2866, 1764, 1657, 1596, 1513, 1462, 1374, 1320, 1278, 1208, 1150, 1055, 958, 883, 749, 701; HRMS (ESI)  $m/z$ :  $\text{C}_{20}\text{H}_{20}\text{NO}_2$   $[\text{M} - \text{H}]^-$  calcd for 306.1500, Found 306.1502.



**(Z)-3-Methyl-N-((2-methylbenzofuran-3(2H)-**

**ylidene)(phenyl)methyl)butanamide (Z-3ac):** Following the general procedure B, the  $Z/E$  mixed product **3ac** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (18.9 mg, 59% yield,  $Z/E = 1.3:1$ ), then **Z-3ac** was obtained after purification by column chromatography ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) as a white solid (10.7 mg; 33% yield; mp 201.1-201.5 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 9.37 (s, 1H), 7.48-7.42 (m, 3H), 7.37 (d,  $J = 7.2$  Hz, 2H), 7.08 (t,  $J = 7.6$  Hz, 1H), 6.79 (d,  $J = 8.0$  Hz, 1H), 6.54 (t,  $J = 7.2$  Hz, 1H), 6.40 (d,  $J = 7.6$  Hz, 1H), 5.58 (q,  $J = 6.4$  Hz, 1H), 2.10 (d,  $J = 6.8$  Hz, 2H), 2.06-1.99 (m, 1H), 1.43 (d,  $J = 6.4$  Hz, 3H), 0.90 (dd,  $J = 6.5, 2.1$

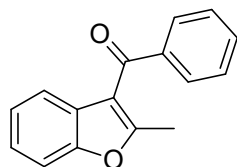
Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 169.4, 162.0, 137.7, 133.3, 129.8, 129.0, 128.7, 126.7, 126.0, 123.8, 122.4, 119.9, 110.1, 81.8, 44.6, 25.6, 22.4, 22.3, 18.9;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3371, 3251, 2930, 2340, 2250, 1652, 1510, 1459, 1280, 1014, 827, 756, 689; HRMS (ESI)  $m/z$ :  $\text{C}_{21}\text{H}_{22}\text{NO}_2$   $[\text{M} - \text{H}]^-$  calcd for 320.1656, Found 320.1657.



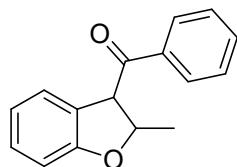
**(E)-3-Methoxy-N-((Z)-(2-methylbenzofuran-3(2H)-**

**ylidene)(phenyl)methyl)acrylamide (Z-3ae):** Following the general procedure B, the *Z/E* mixed product **3ae** was obtained after purification by column chromatography (petroleum ether/ethyl acetate = 5:1-3:1) as a white solid (18.6 mg, 58% yield, *Z/E* = 3:1), then **Z-3ae** was obtained after purification by column chromatography ( $\text{CH}_2\text{Cl}_2$ /petroleum ether = 8:1-10:1) as a white solid (14.1 mg; 44% yield; mp 165.1-165.4 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 9.23 (s, 1H), 7.49- 7.42 (m, 4H), 7.39-7.36 (m, 2H), 7.09-7.05 (m, 1H), 6.79 (d,  $J = 8.0$  Hz, 1H), 6.55-6.51 (m, 1H), 6.35 (d,  $J = 8.0$  Hz, 1H), 5.63 (q,  $J = 6.4$  Hz, 1H), 5.50 (d,  $J = 12.4$  Hz, 1H), 3.64 (s, 3H), 1.41 (d,  $J = 6.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 161.9, 160.3, 137.8, 129.6 (2C), 129.1 (2C), 128.7, 128.5, 126.1, 124.1, 122.4, 119.9, 110.0, 98.6, 82.0, 57.4, 18.6;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3256, 2093, 2385, 1774, 1704, 1499, 1336, 1161,

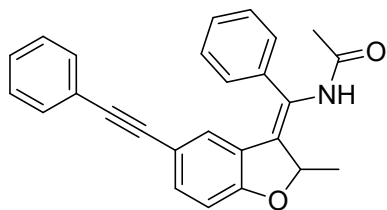
1039, 935, 750, 701, 616; HRMS (ESI)  $m/z$ :  $C_{20}H_{18}NO_3$   $[M - H]^-$  calcd for 320.1292, Found 320.1293.



**(2-Methylbenzofuran-3-yl)(phenyl)methanone (4)**<sup>[4]</sup>: Yield: 15.8 mg, 67%; yellow oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm 7.842-7.80 (m, 2H), 7.62-7.57 (m, 1H), 7.50-7.45 (m, 3H), 7.41 (d,  $J = 8.0$  Hz, 1H), 7.29-7.25 (m, 1H), 7.21-7.17 (m, 1H), 2.54 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  ppm 191.9, 161.9, 153.6, 139.3, 132.6, 129.1, 128.5, 126.9, 124.4, 123.5, 121.3, 116.9, 110.8, 14.7; HRMS (ESI)  $m/z$ :  $C_{16}H_{13}O_2$   $[M + H]^+$  calcd for 237.0910, Found 237.0907.



**(2-Methyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (5)**<sup>[7]</sup>: Yield: 14.3 mg, 60%; yellow oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm 8.07-8.04 (m, 2H), 7.68-7.64 (m, 1H), 7.57-7.53 (m, 2H), 7.17-7.13 (m, 1H), 6.90 (d,  $J = 7.6$  Hz, 1H), 6.83 (d,  $J = 8.4$  Hz, 1H), 6.74 (td,  $J = 7.5, 1.0$  Hz, 1H), 5.46 (d,  $J = 6.4$  Hz, 1H), 4.87 (d,  $J = 6.8$  Hz, 1H), 1.54 (d,  $J = 6.4$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  ppm 196.5, 159.4, 136.5, 133.7, 129.3, 129.1, 128.9, 125.4, 124.8, 120.3, 110.1, 81.2, 56.9, 21.1; HRMS (ESI)  $m/z$ :  $C_{16}H_{14}O_2$   $[M - H]^-$  calcd for 237.0921, Found 237.0918.



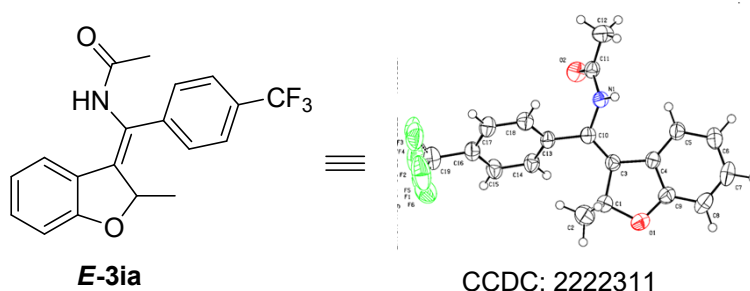
**(Z)-N-((2-Methyl-5-(phenylethynyl)benzofuran-3(2H)-**

**ylidene)(phenyl)methyl)acetamide (6):** Yield: 22.0 mg, 58%; yellow solid; mp 200.1-200.3 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 9.49 (s, 1H), 7.52-7.46 (m, 3H), 7.41-7.39 (m, 2H), 7.36 (s, 5H), 7.28 (dd,  $J = 8.4, 1.8$  Hz, 1H), 6.85 (d,  $J = 8.4$  Hz, 1H), 6.44 (s, 1H), 5.65 (q,  $J = 6.4$  Hz, 1H), 1.96 (s, 3H), 1.44 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  ppm 167.5, 162.7, 137.8, 133.8, 131.7, 131.6, 129.5, 129.4, 129.3, 129.2, 129.0, 128.0, 125.9, 125.3, 122.9, 114.1, 111.1, 90.1, 87.7, 83.4, 23.4, 19.1;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3495, 2929, 2852, 2358, 1648, 1590, 1392, 1267, 1112, 994, 754, 701; HRMS (ESI)  $m/z$ :  $\text{C}_{26}\text{H}_{22}\text{NO}_2$   $[\text{M} + \text{H}]^+$  calcd for 380.1645, Found 380.1639.

**X-ray Crystallographic Data of Products *E*-3ia and *Z*-3aca**

Compound *E*-3ia was dissolved in a mixed solvent (ethyl acetate: petroleum ether = 1:20), and the corresponding single crystals for X-ray diffraction were obtained by

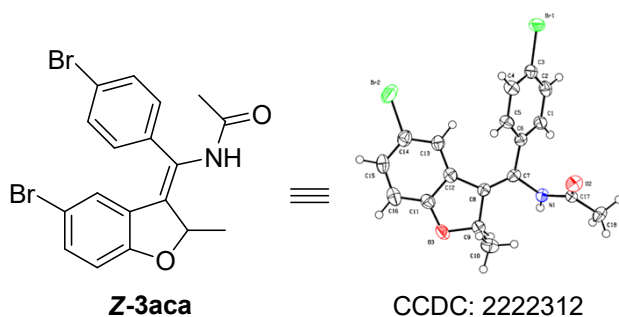
slowly natural volatilization crystallization. Data collections for this crystal structure were performed at 170 K using MoK $\alpha$  radiation on a 'Bruker D8 VENTURE' diffractometer. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. Displacement ellipsoids are drawn at the 50% probability level. Crystallographic data of ***E-3ia*** is shown in Table S6. Selected bond lengths and bond angles are listed in Table S6. CCDC reference number for ***E-3ia***: 2222311.



<b>Table S6 Crystal data and structure refinement for <i>E-3ia</i></b>	
Identification code	<b><i>E-3ia</i></b>
Empirical formula	C <sub>19</sub> H <sub>16</sub> F <sub>3</sub> NO <sub>2</sub>
Formula weight	347.33
Temperature/K	170
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	18.843(7)
b/Å	9.345(4)
c/Å	9.737(4)
$\alpha$ /°	90
$\beta$ /°	95.050(11)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	1707.9(12)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.351

$\mu/\text{mm}^{-1}$	0.110
F(000)	720.0
Crystal size/ $\text{mm}^3$	$0.12 \times 0.08 \times 0.05$
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	4.34 to 50.21
Index ranges	$-22 \leq h \leq 22, -11 \leq k \leq 9, -11 \leq l \leq 11$
Reflections collected	13067
Independent reflections	2960 [ $R_{\text{int}} = 0.0871, R_{\text{sigma}} = 0.0722$ ]
Data/restraints/parameters	2960/334/255
Goodness-of-fit on $F^2$	1.029
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0613, wR_2 = 0.1247$
Final R indexes [all data]	$R_1 = 0.1248, wR_2 = 0.1570$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.23/-0.22

Compound **Z-3aca** was dissolved in a mixed solvent (ethyl acetate: petroleum ether = 1:20), and the corresponding single crystals for X-ray diffraction were obtained by slowly natural volatilization crystallization. Data collections for this crystal structure were performed at 170 K using MoK $\alpha$  radiation on a 'Bruker D8 VENTURE' diffractometer. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. Displacement ellipsoids are drawn at the 50% probability level. Crystallographic data of **Z-3aca** is shown in Table S7. Selected bond lengths and bond angles are listed in Table S7. CCDC reference numbers for **Z-3aca**: 2222312.





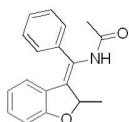
<b>Table S7 Crystal data and structure refinement for Z-3aca</b>	
Identification code	<b>Z-3aca</b>
Empirical formula	C <sub>18</sub> H <sub>15</sub> Br <sub>2</sub> NO <sub>2</sub>
Formula weight	437.13
Temperature/K	170.0
Crystal system	monoclinic
Space group	Pc
a/Å	9.1676(10)
b/Å	4.8980(6)
c/Å	19.342(2)
α/°	90
β/°	92.437(3)
γ/°	90
Volume/Å <sup>3</sup>	867.74(17)
Z	2
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.673
μ/mm <sup>-1</sup>	4.679
F(000)	432.0
Crystal size/mm <sup>3</sup>	0.19 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.216 to 52.73
Index ranges	-9 ≤ h ≤ 11, -6 ≤ k ≤ 5, -23 ≤ l ≤ 24
Reflections collected	4773
Independent reflections	2713 [R <sub>int</sub> = 0.0360, R <sub>sigma</sub> = 0.0752]
Data/restraints/parameters	2713/2/210
Goodness-of-fit on F <sup>2</sup>	0.978
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0359, wR <sub>2</sub> = 0.0714
Final R indexes [all data]	R <sub>1</sub> = 0.0518, wR <sub>2</sub> = 0.0793
Largest diff. peak/hole / e Å <sup>-3</sup>	0.33/-0.53

## References

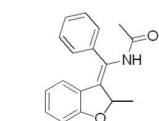
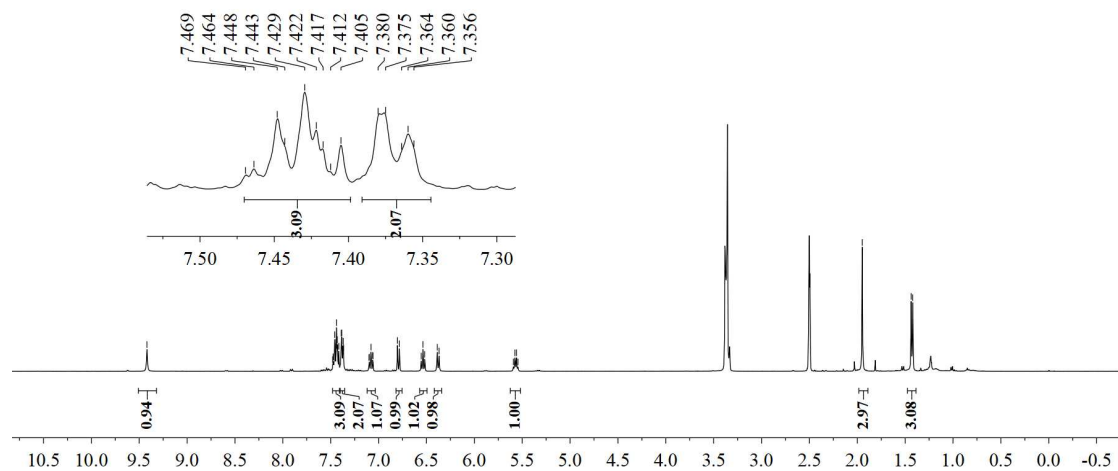
- [1] Hu, M.; Song, R.-J.; Li, J.-H. *Angew. Chem., Int. Ed.* **2015**, *53*, 608–612.
- [2] Wu, W.; Yi, S.; Huang, W.; Luo, D.; Jiang, H. *Org. Lett.* **2017**, *19*, 2825–2828.
- [3] Jana, S.; Verma, A.; Kadu, R.; Kumar, S. *Chem. Sci.* **2017**, *8*, 6633–6644.
- [4] Xia, X.-F.; He, W.; Zhang, G.-W.; Wang, D.-W. *Org. Chem. Front.* **2019**, *6*, 342–346.
- [5] Zhao, M.-M.; He, W.; Zou, L.-H.; Wang, D.-W.; Sun, T.-Y.; Xia, X.-F. *Org. Chem. Front.* **2021**, *8*, 643–652.
- [6] Zhang, P.-B.; Wang, C.; Cui, M.-C.; Du, M.-S.; Li, W.-W.; Jia, Z.-X.; Zhao, Q. *Org. Lett.* **2020**, *22*, 1149–1154.
- [7] Meng, Q.-Y.; Lezius, L.; Studer, A. *Nat Commun* **2021**, *12*, 2068–2075.

# NMR Spectra for All the Compounds

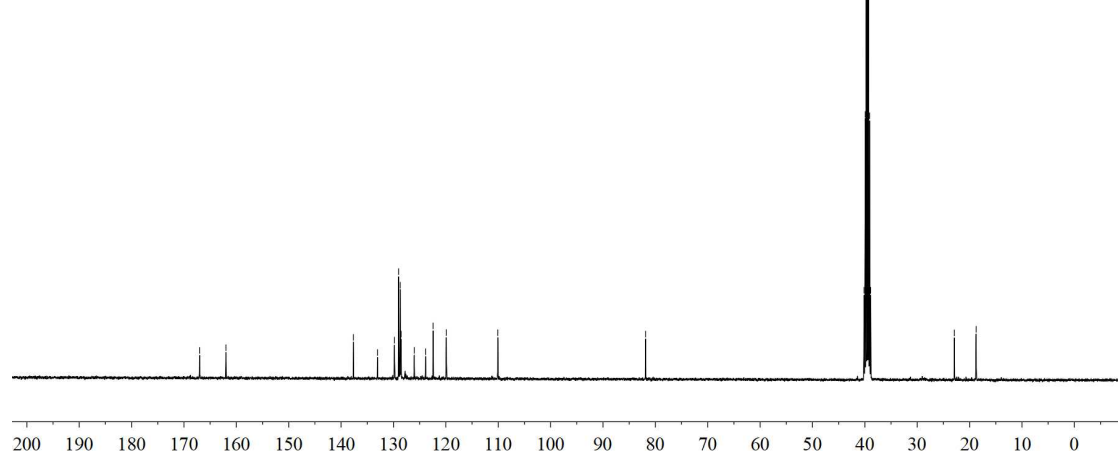
## (Z)-N-((2-Methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-3aa)



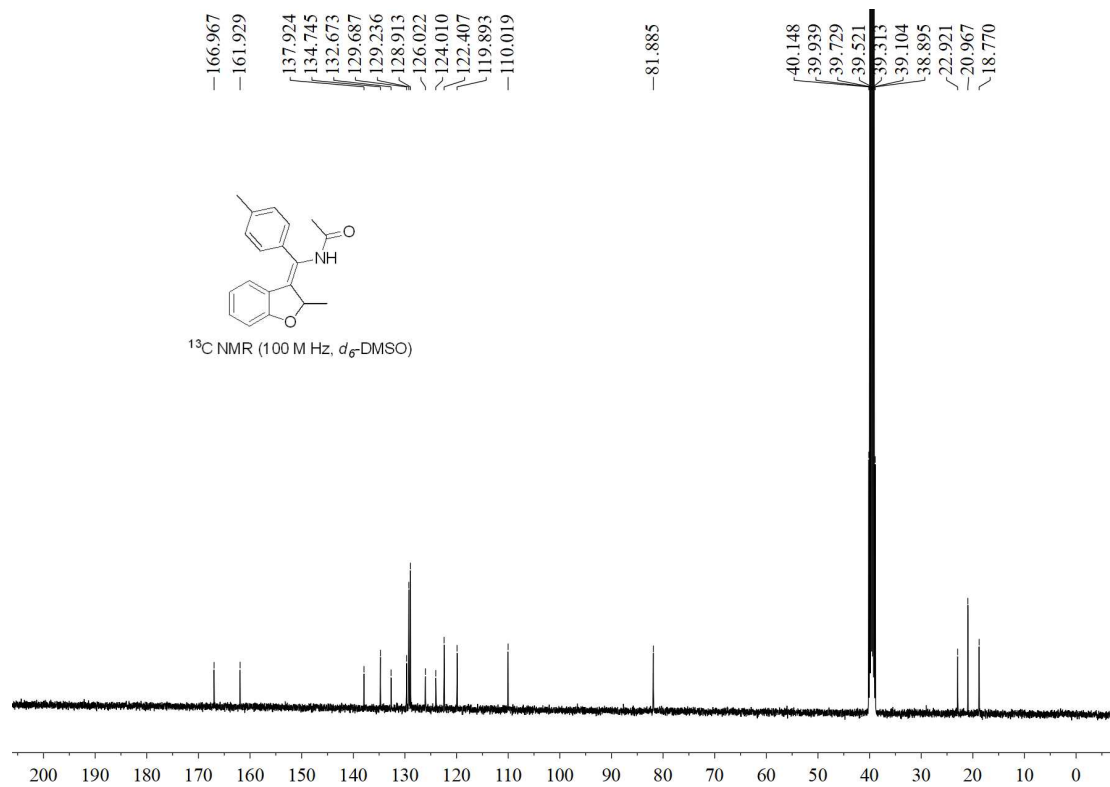
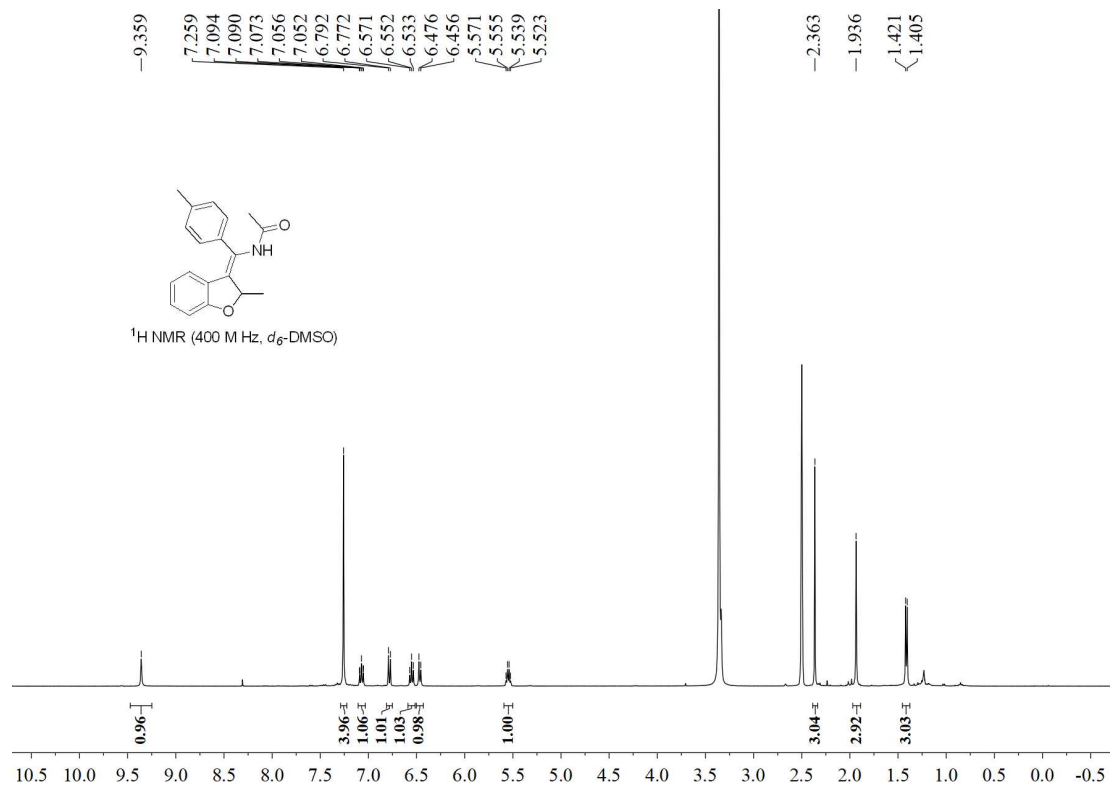
$^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)



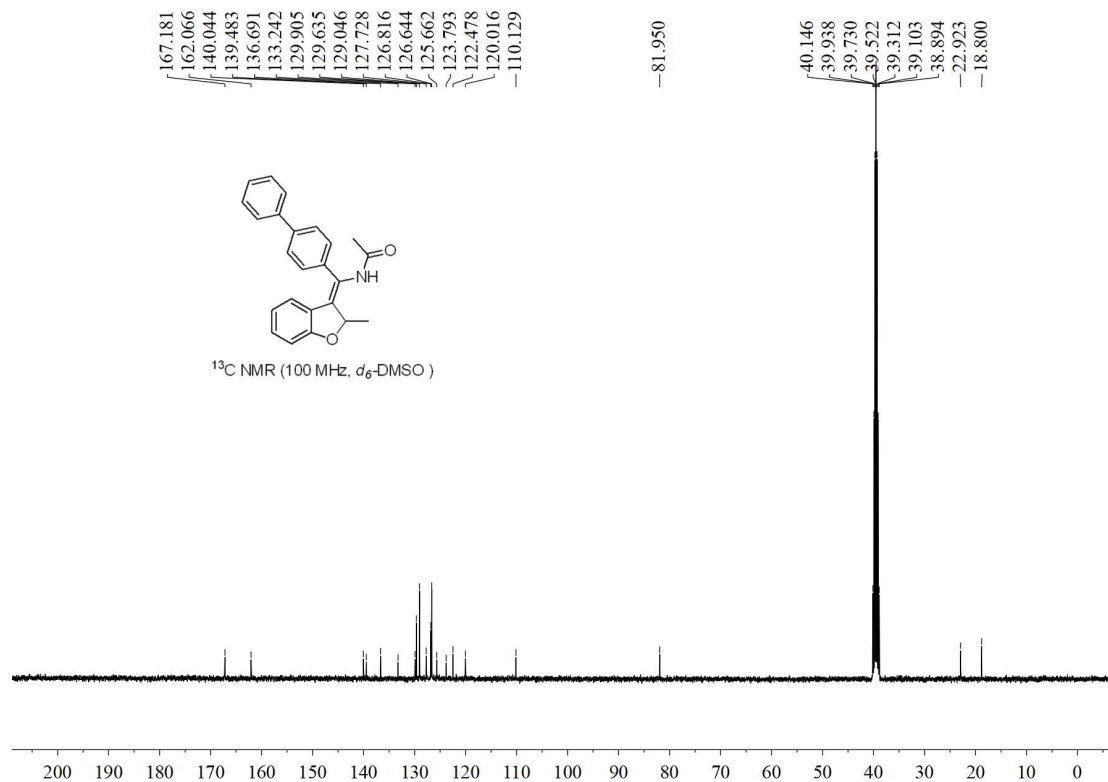
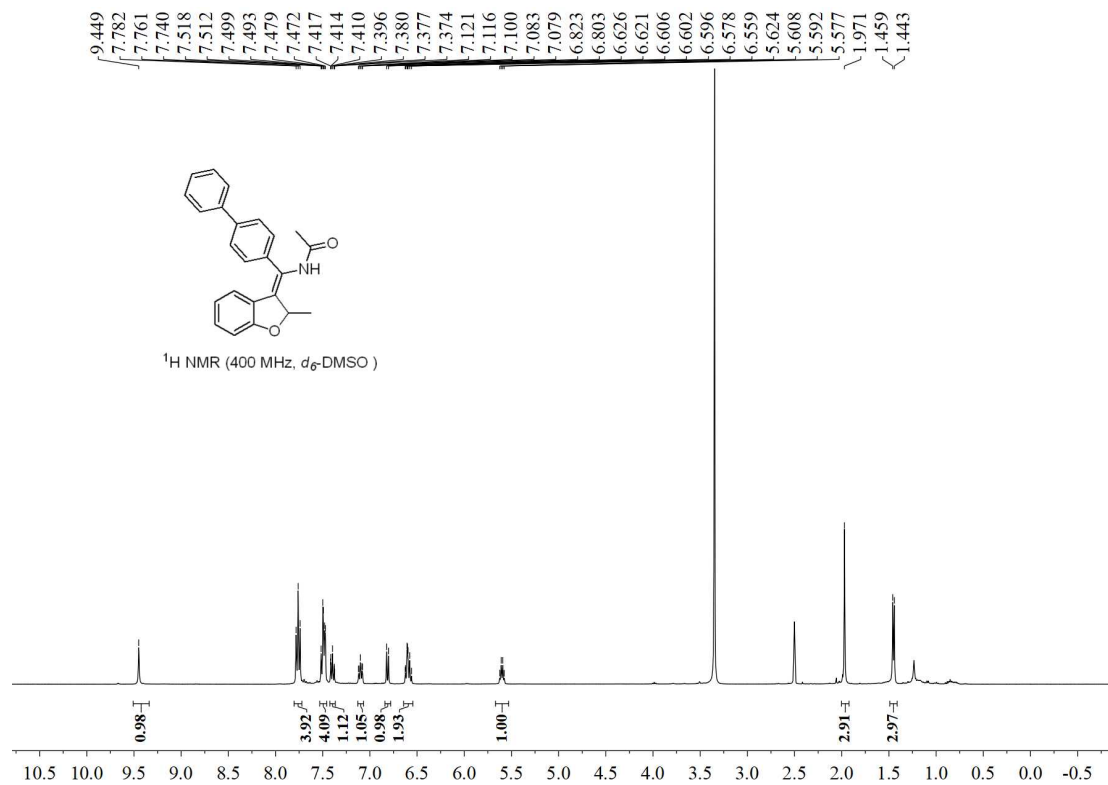
$^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)



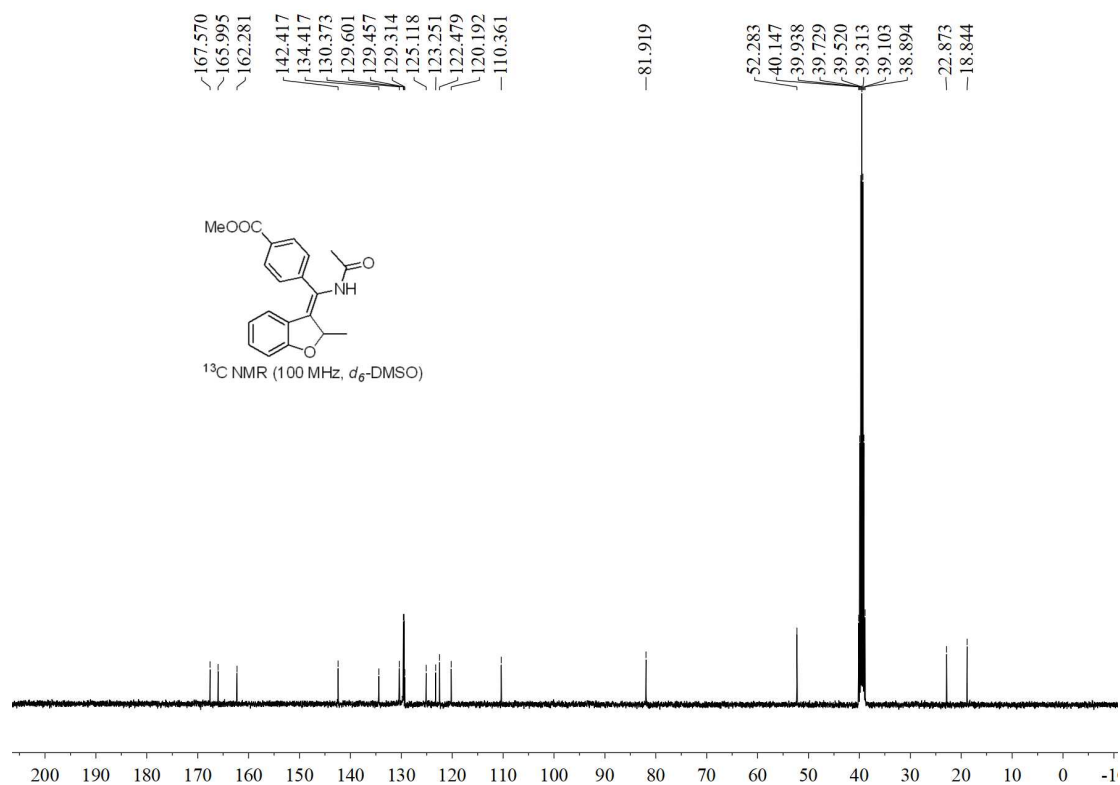
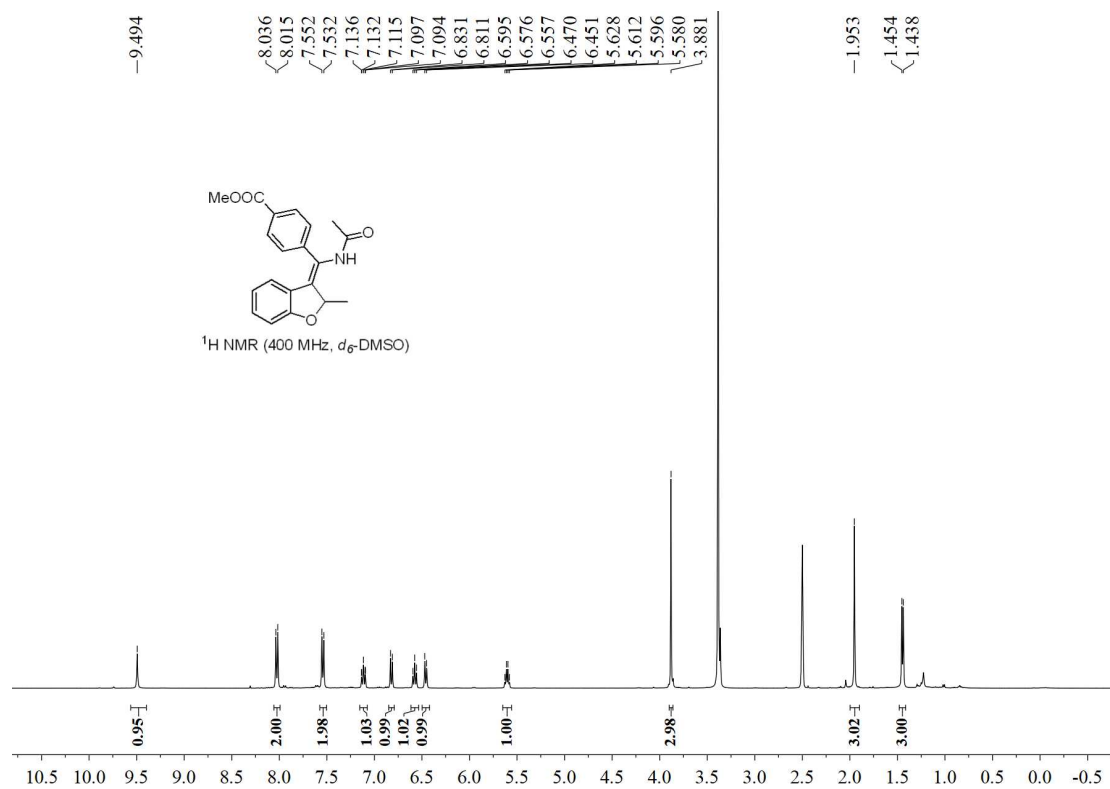
**(Z)-N-((2-Methylbenzofuran-3(2H)-ylidene)(p-tolyl)methyl)acetamide (Z-3ba)**



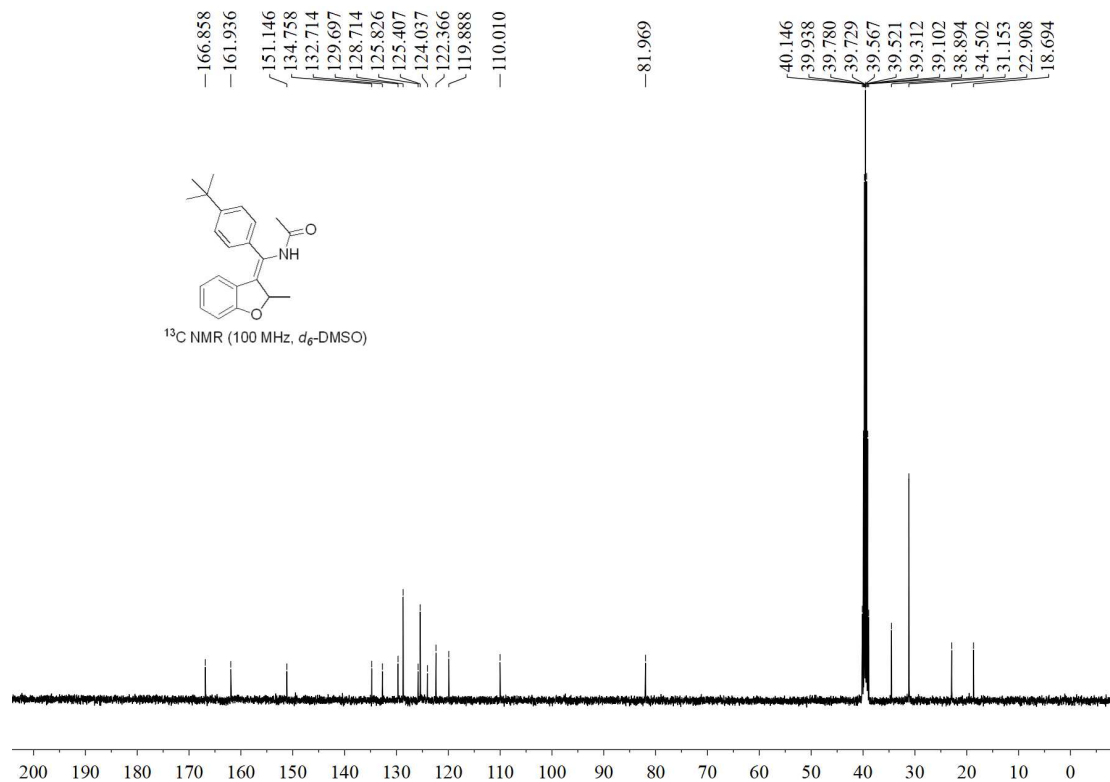
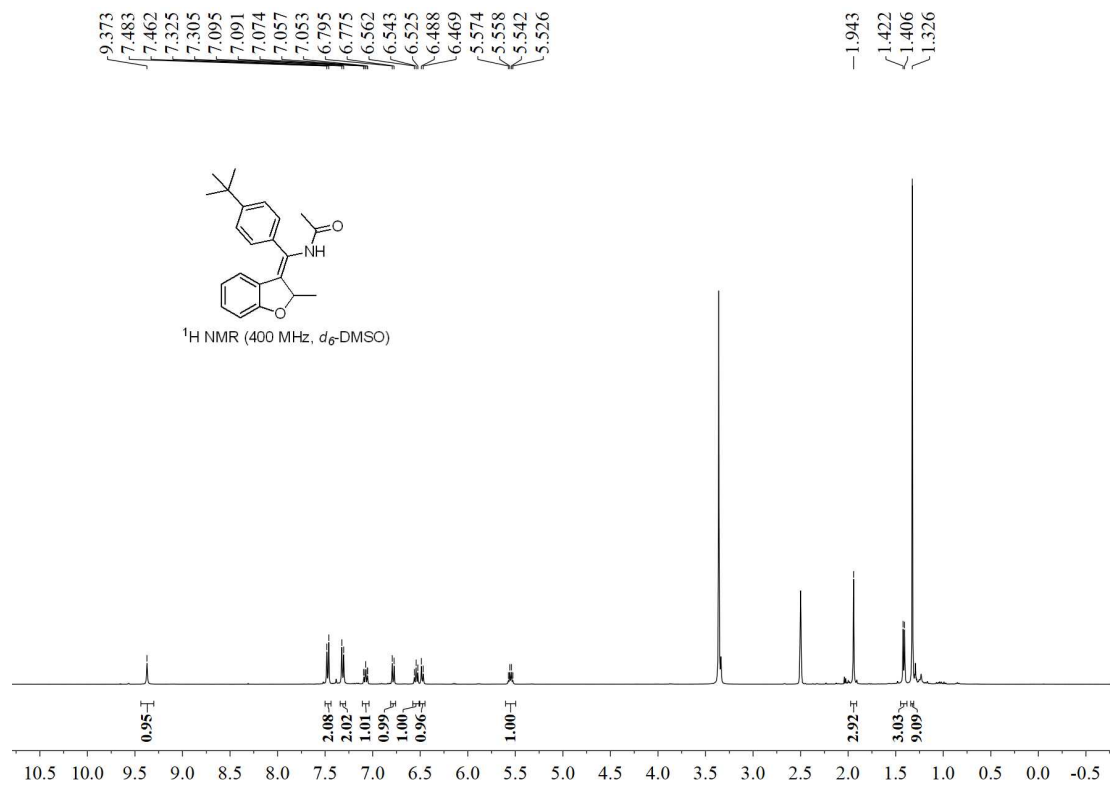
(Z)-N-([1,1'-Biphenyl]-4-yl(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide (Z-3ca)



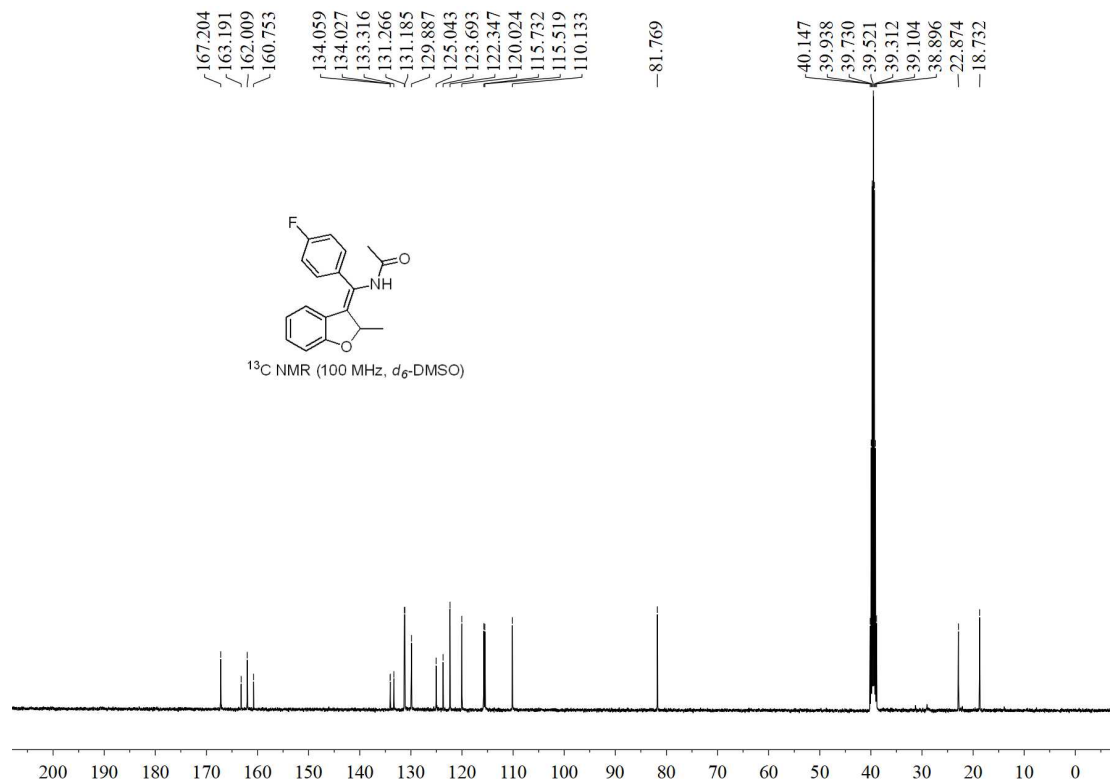
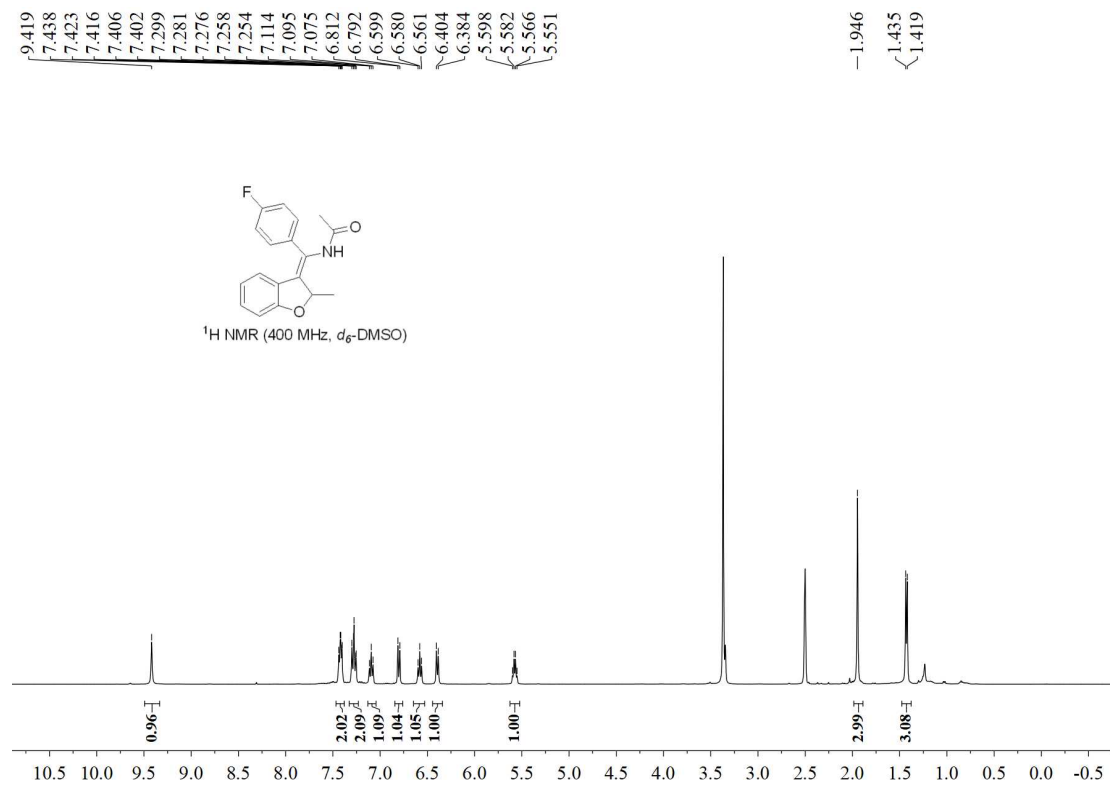
(Z)-Methyl 4-(Acetamido(2-methylbenzofuran-3(2H)-ylidene)methyl)benzoate (Z-3da)



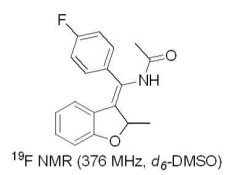
**(Z)-N-((4-*tert*-Butyl)phenyl)(2-methylbenzofuran-3(*H*)-ylidene)methyl)acetamide (Z-3ea)**



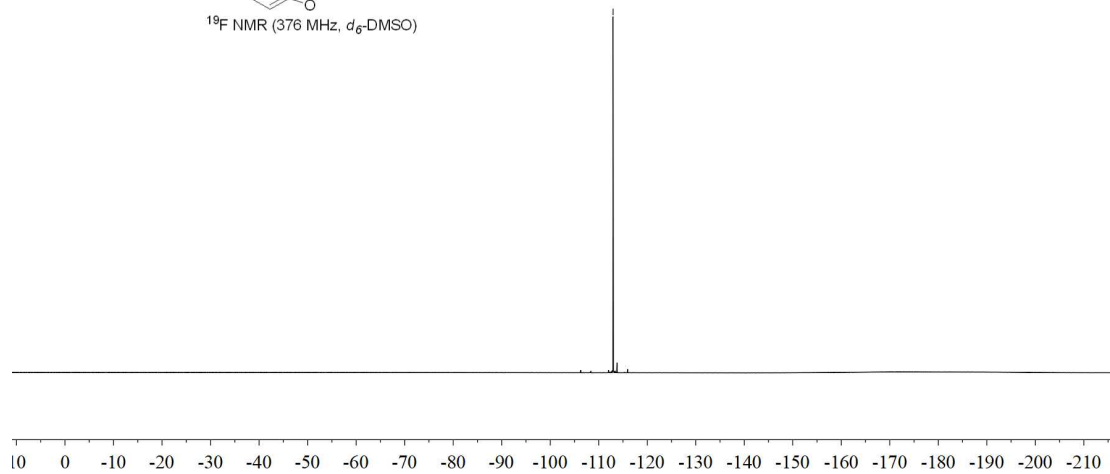
(Z)-N-((4-Fluorophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide (Z-3fa)



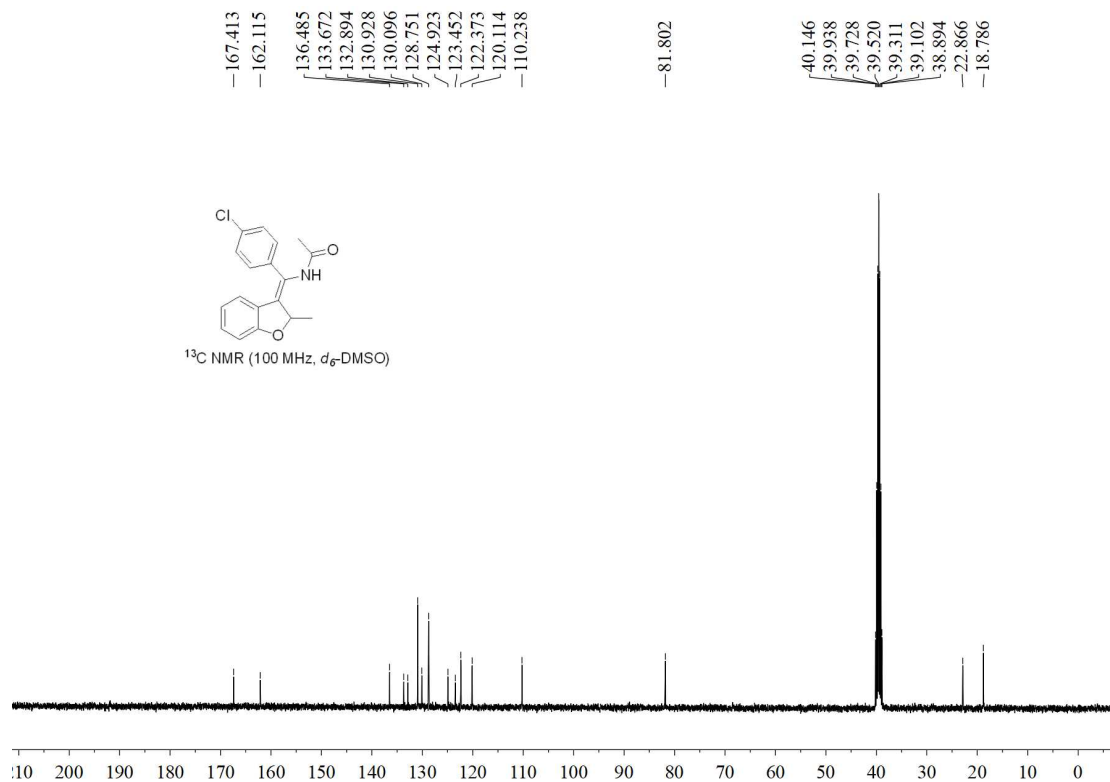
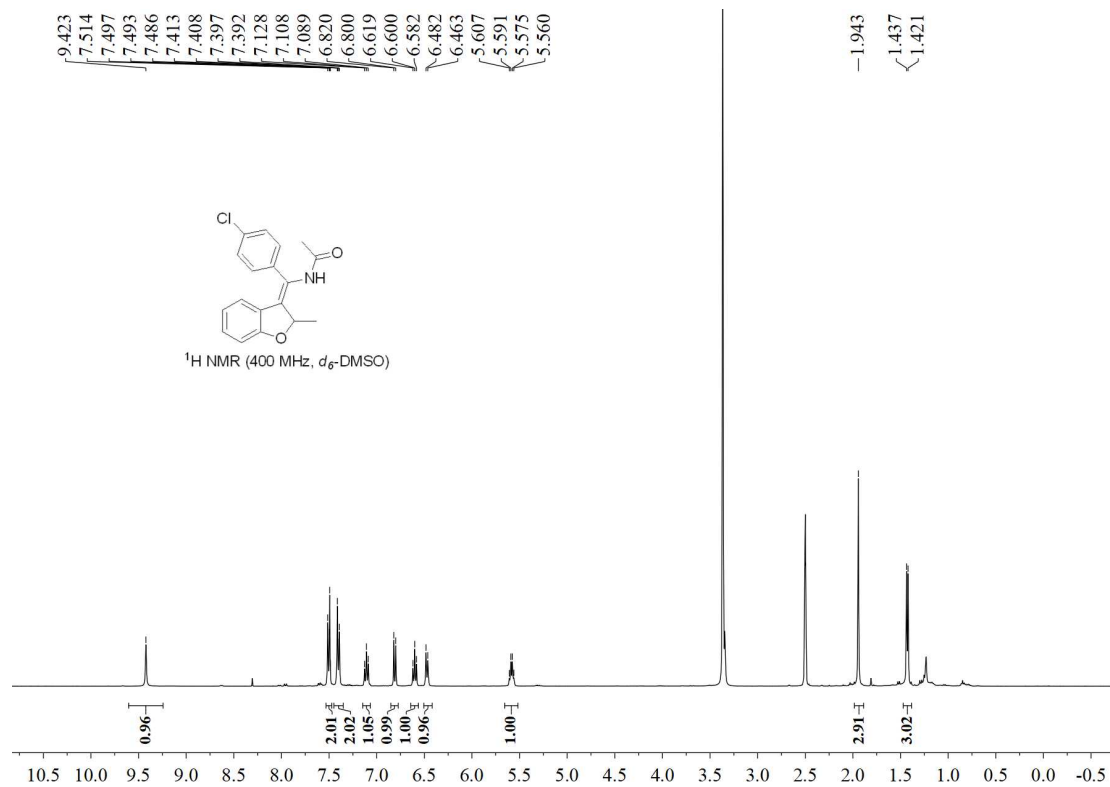




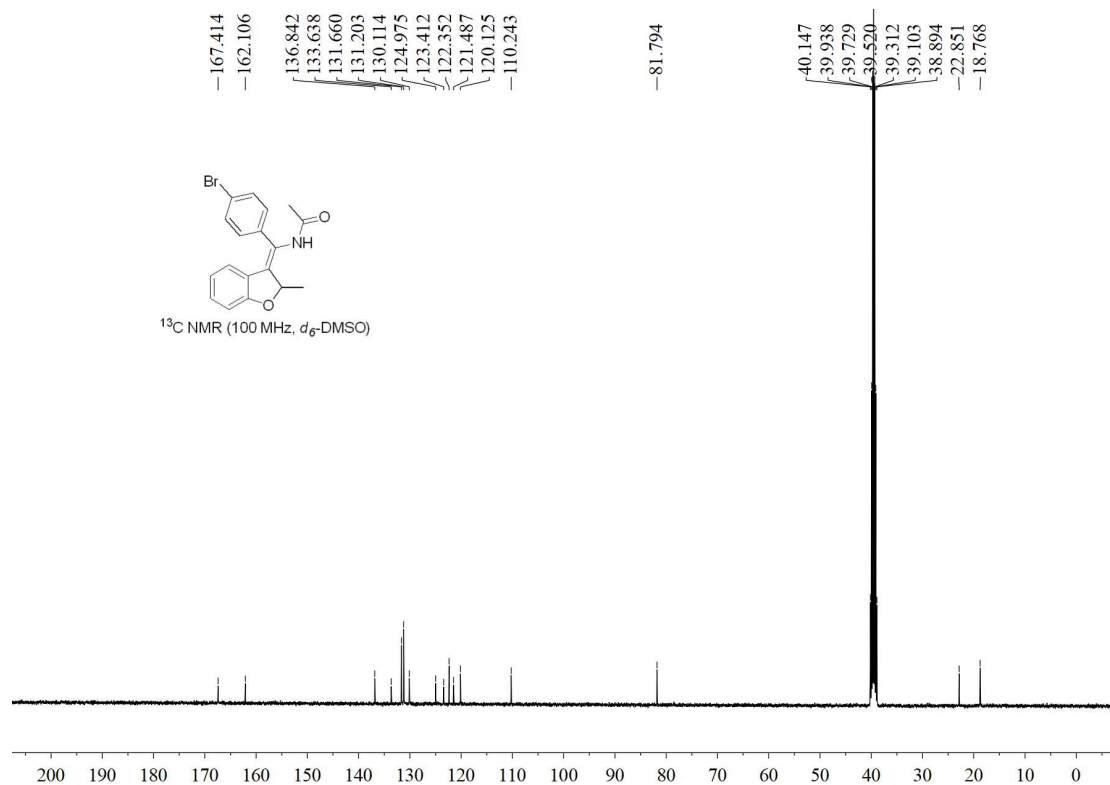
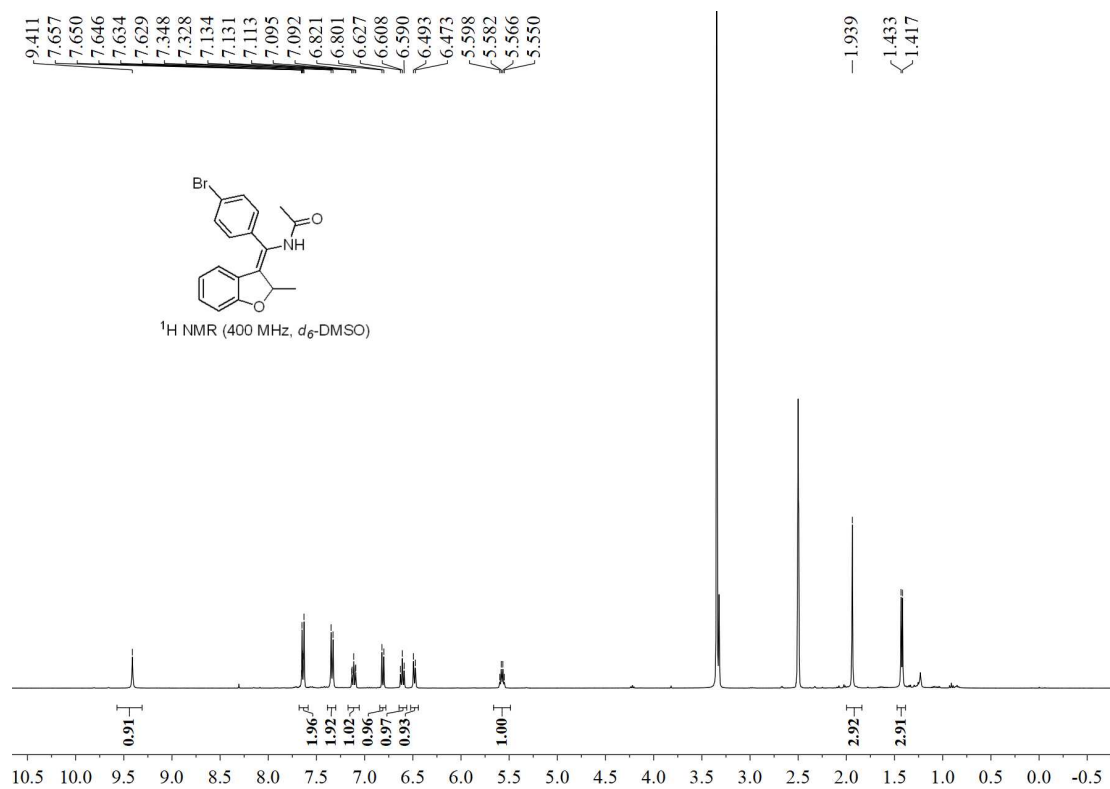
-112.954



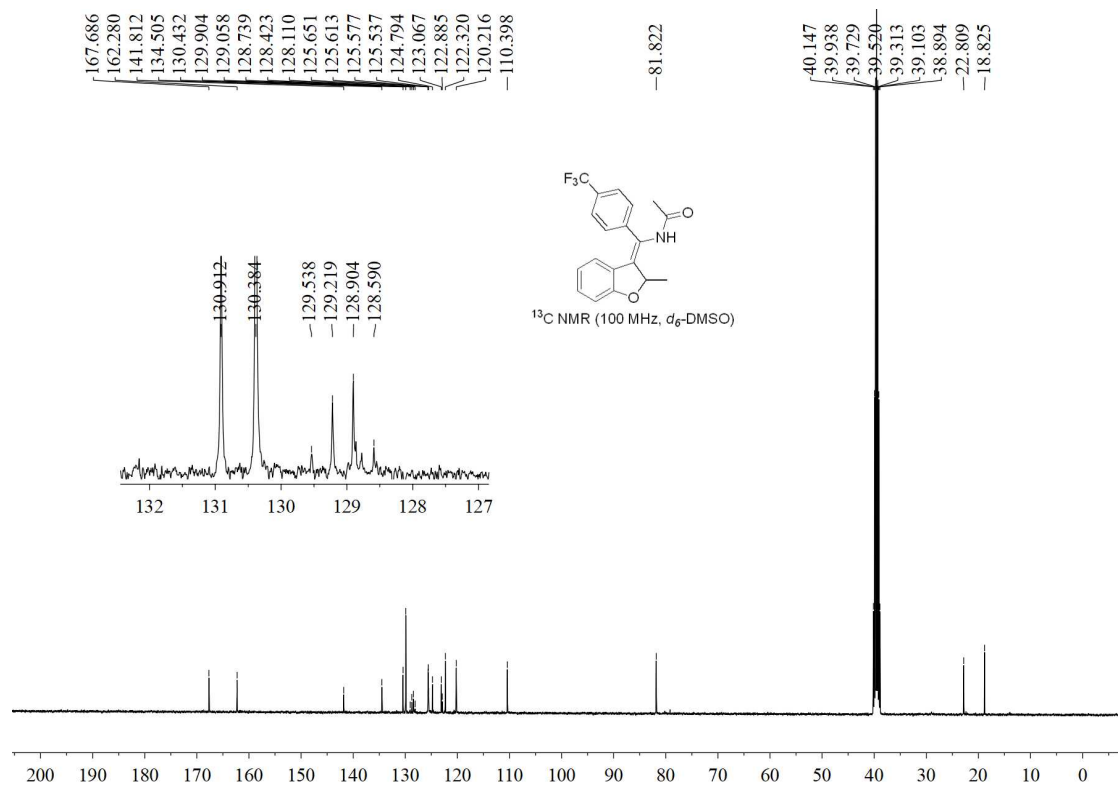
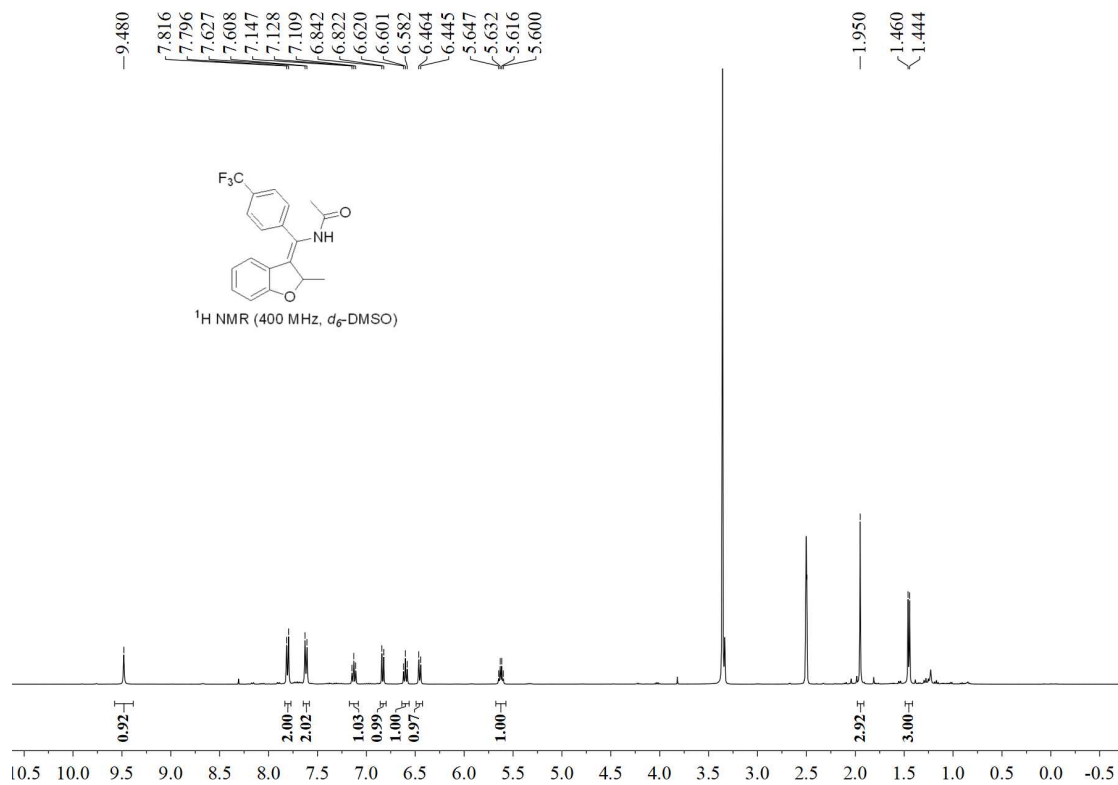
(Z)-N-((4-Chlorophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide (Z-3ga)

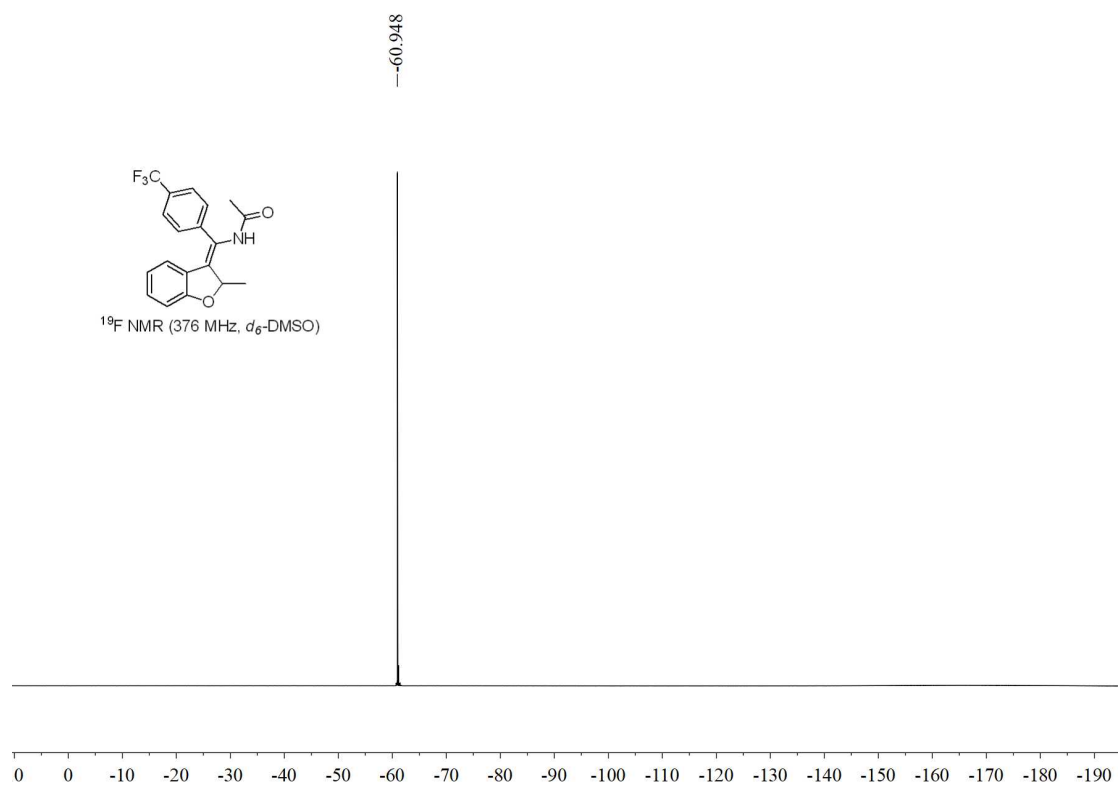


(Z)-N-((4-Bromophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide (Z-3ha)

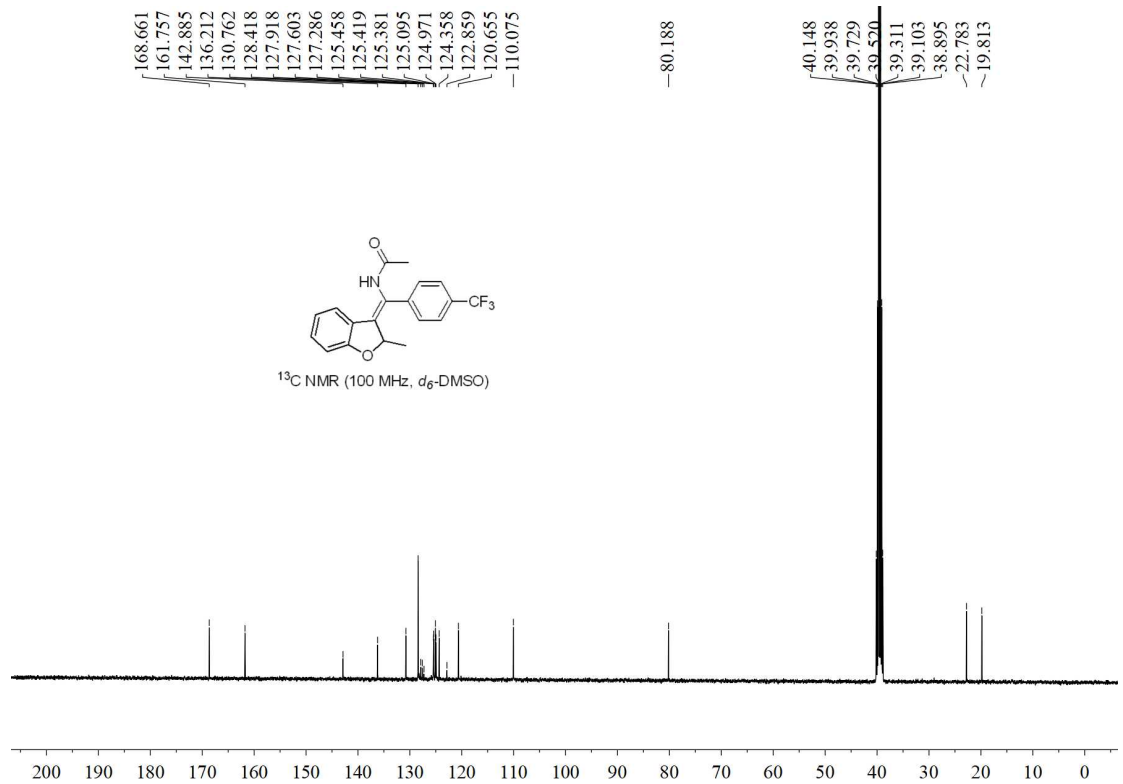
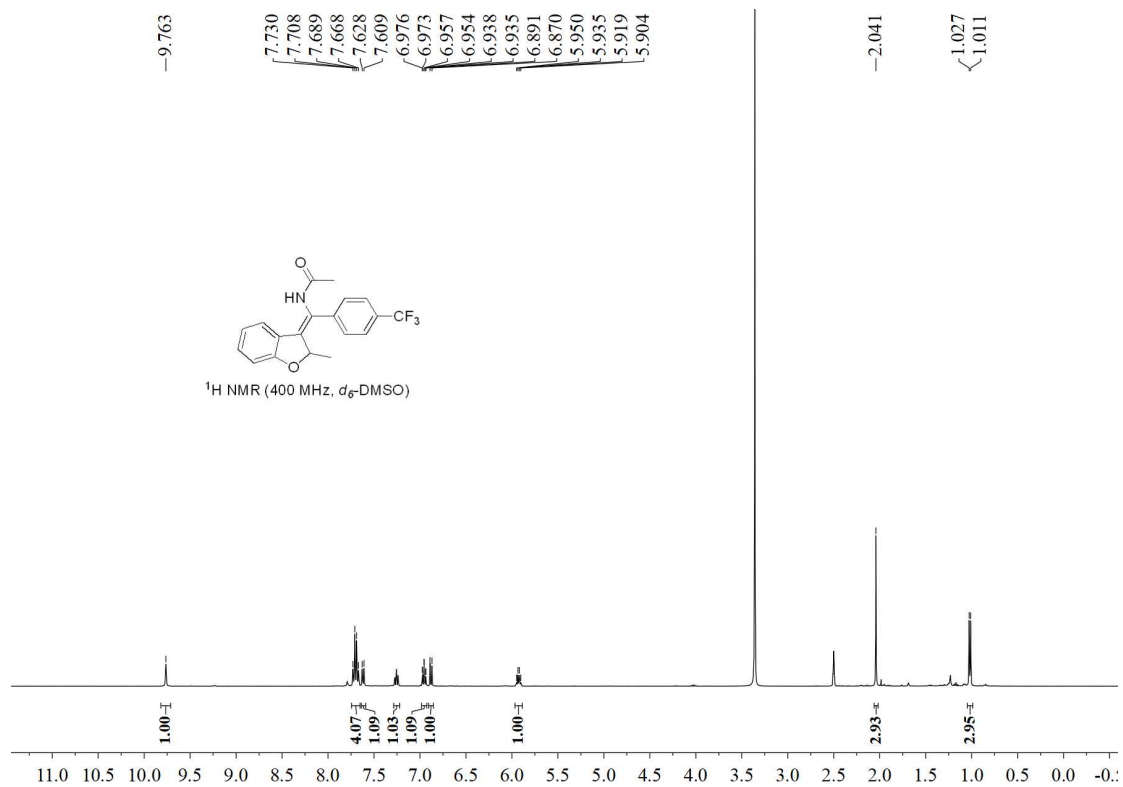


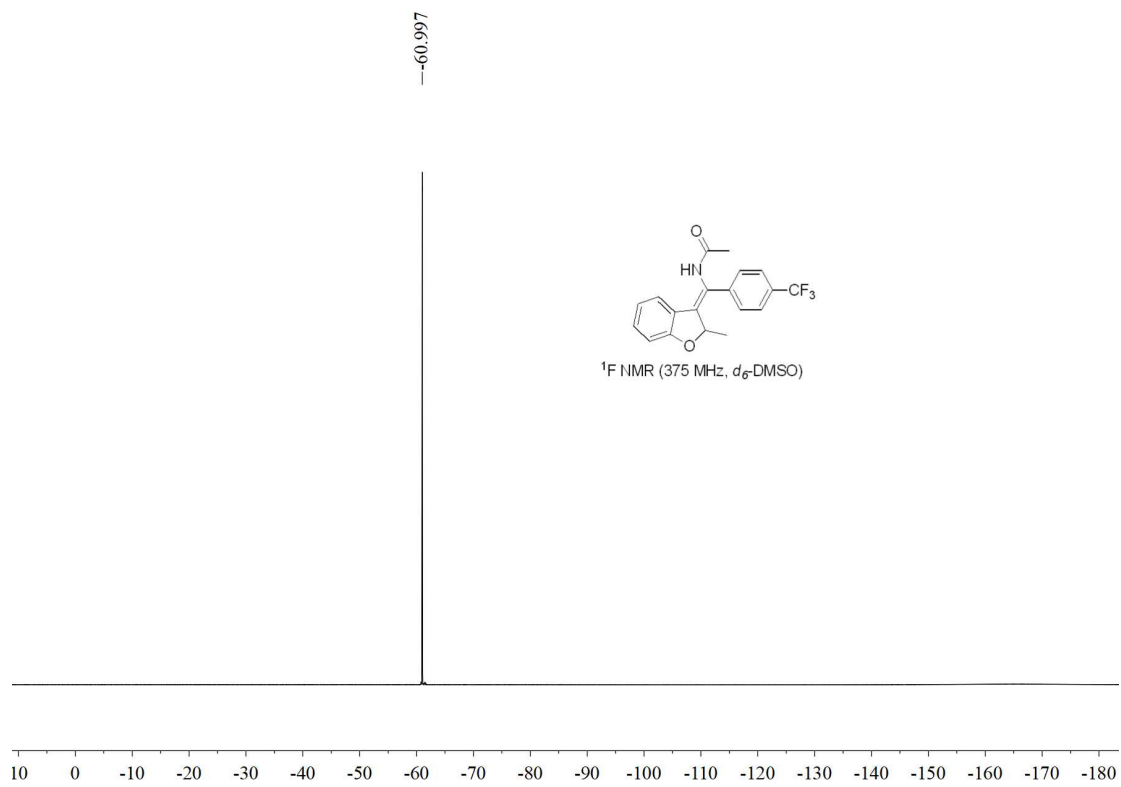
**(Z)-N-((2-Methylbenzofuran-3(2H)-ylidene)(4-(trifluoromethyl)phenyl)methyl)acetamide (Z-3ia)**



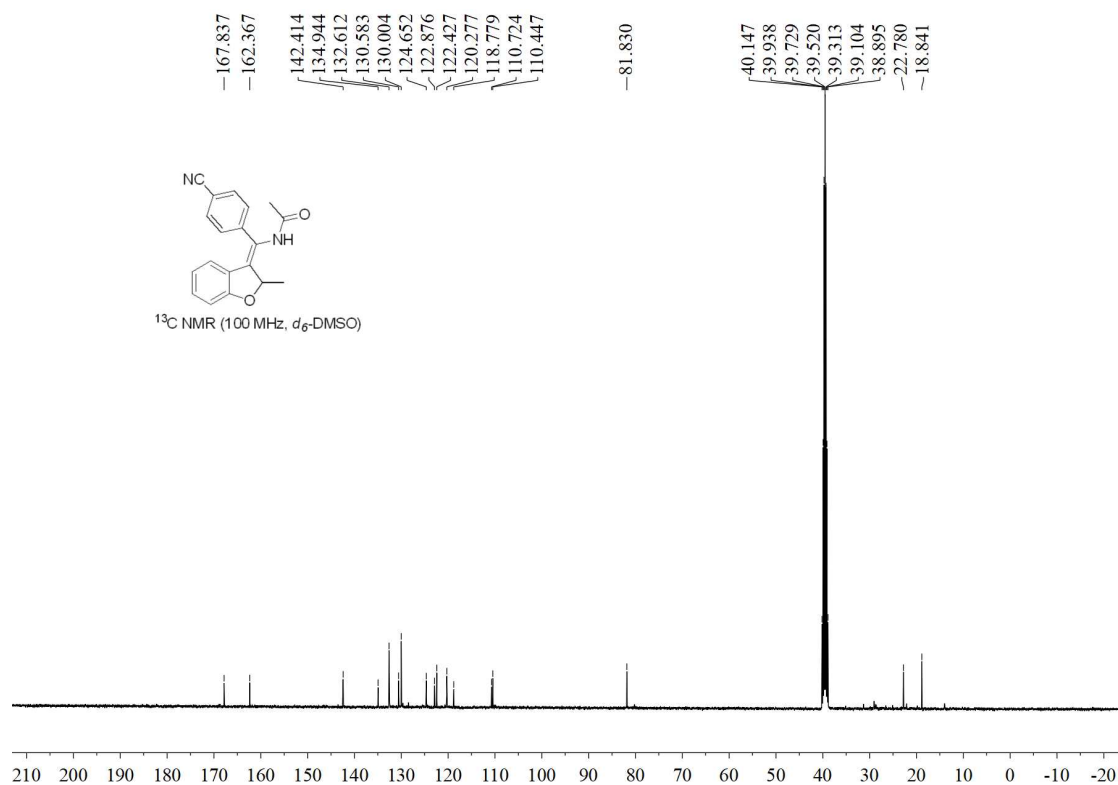
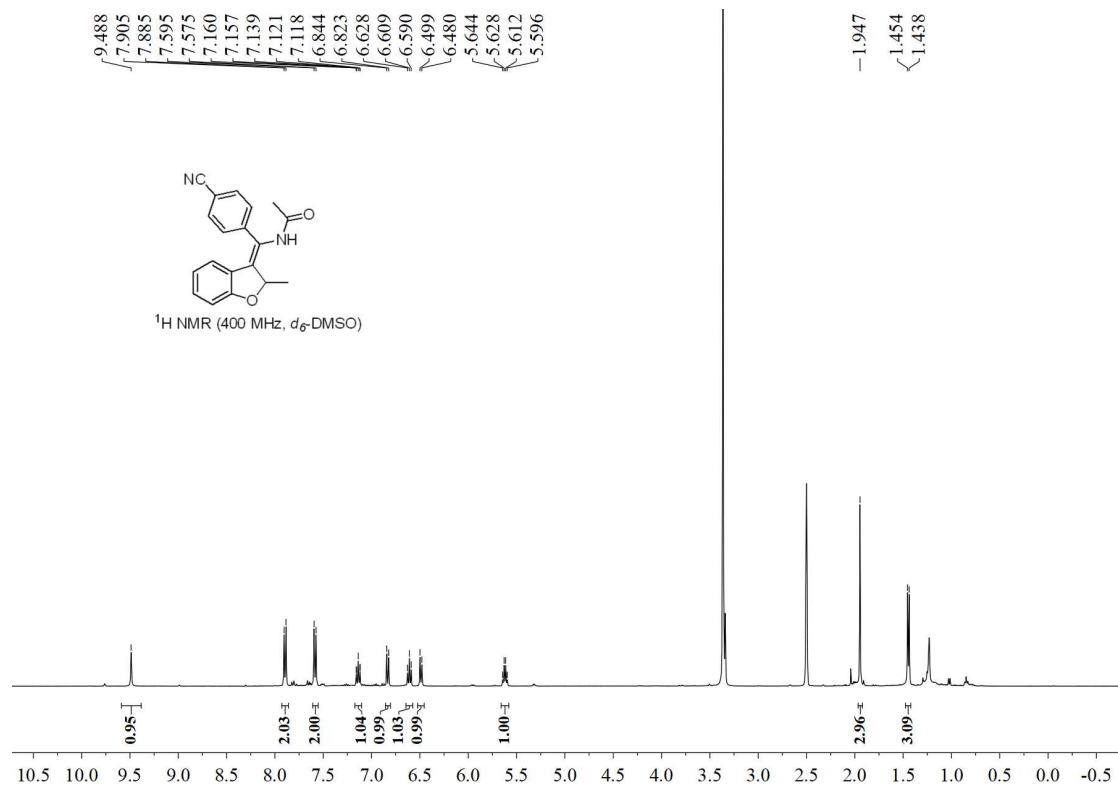


**(E)-N-((2-Methylbenzofuran-3(2H)-ylidene)(4-(trifluoromethyl)phenyl)methyl)acetamide (E-3ia)**



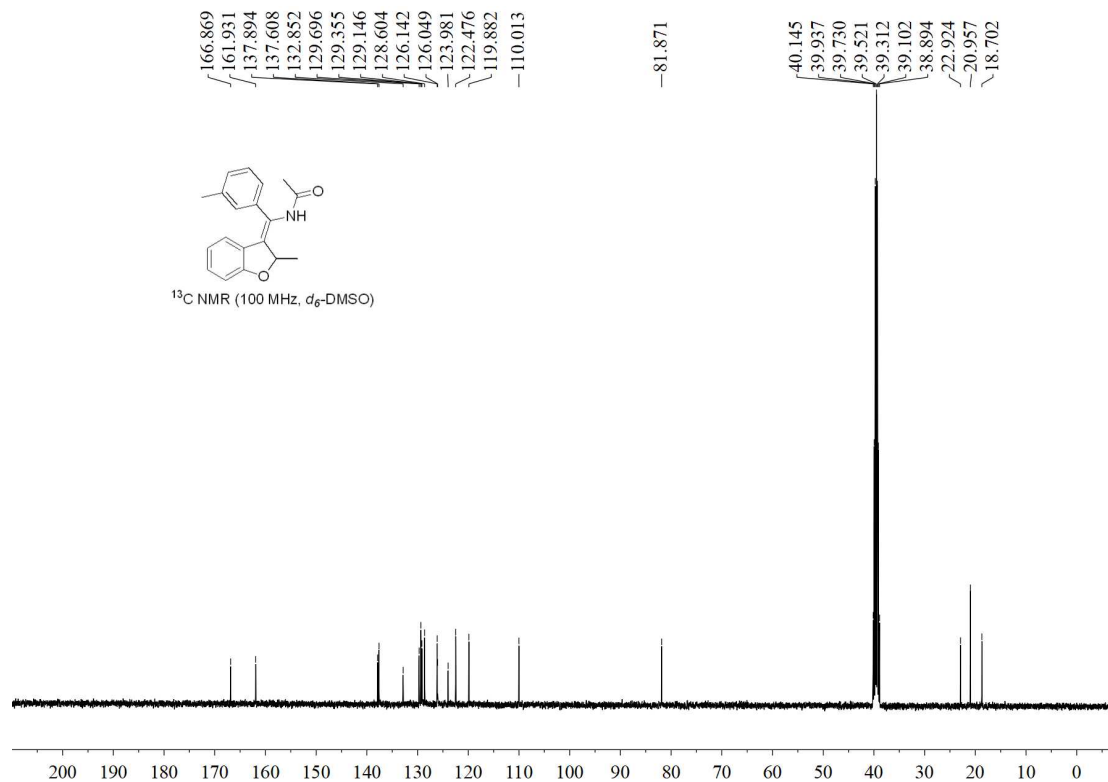
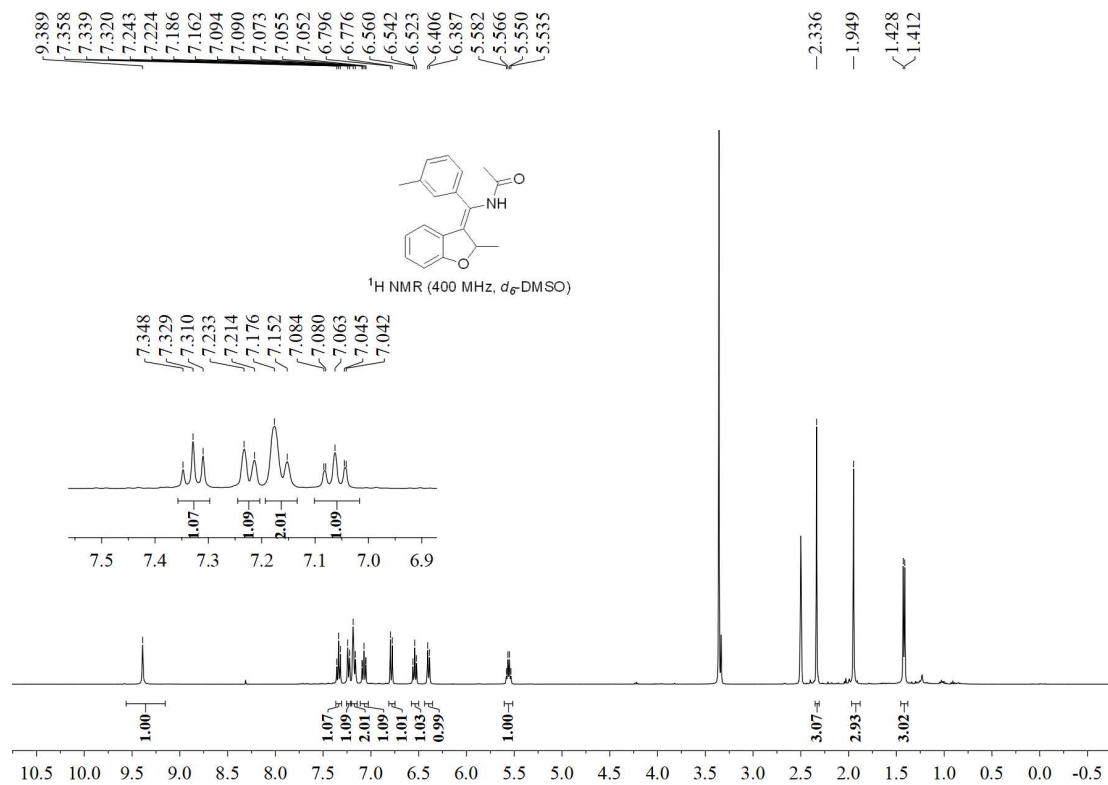


(Z)-N-((4-Cyanophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide (Z-3ja)

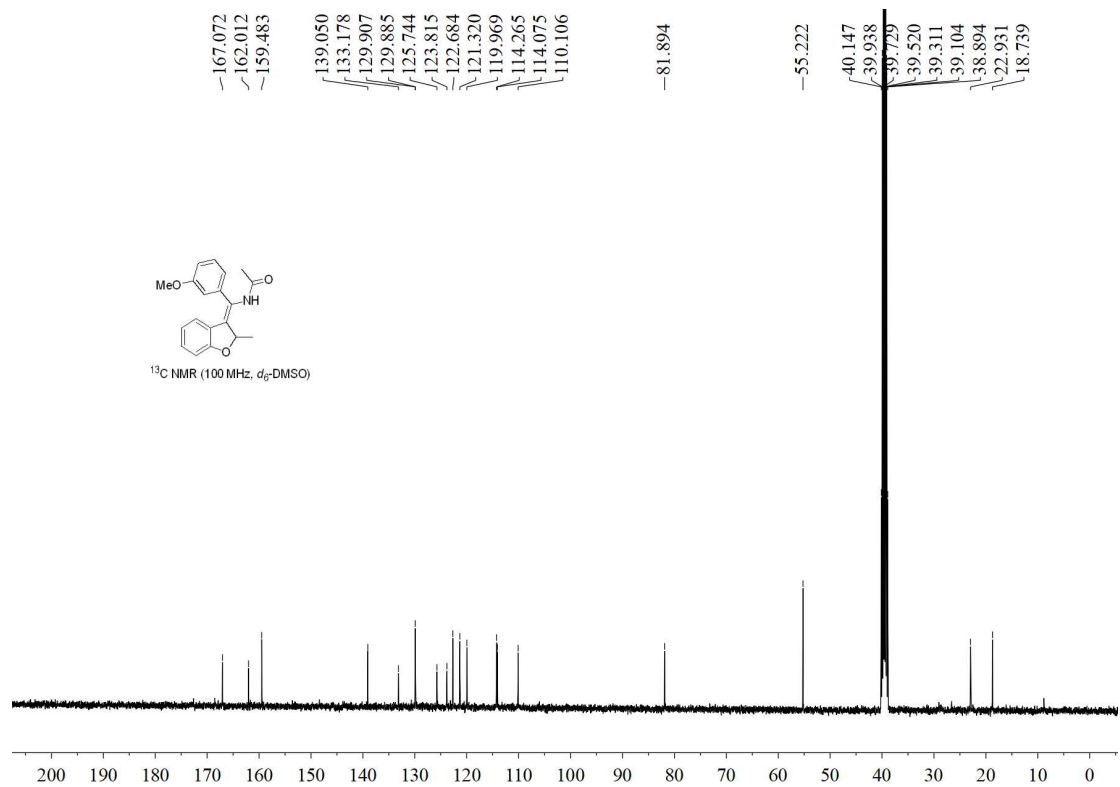
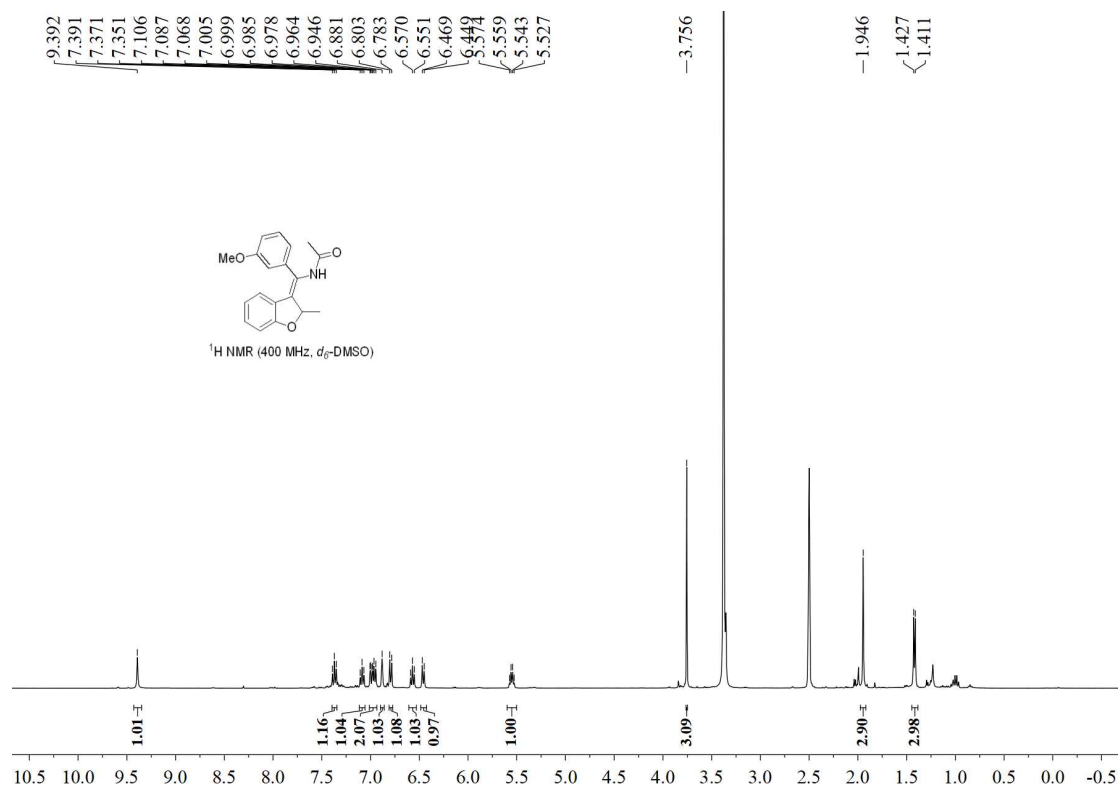




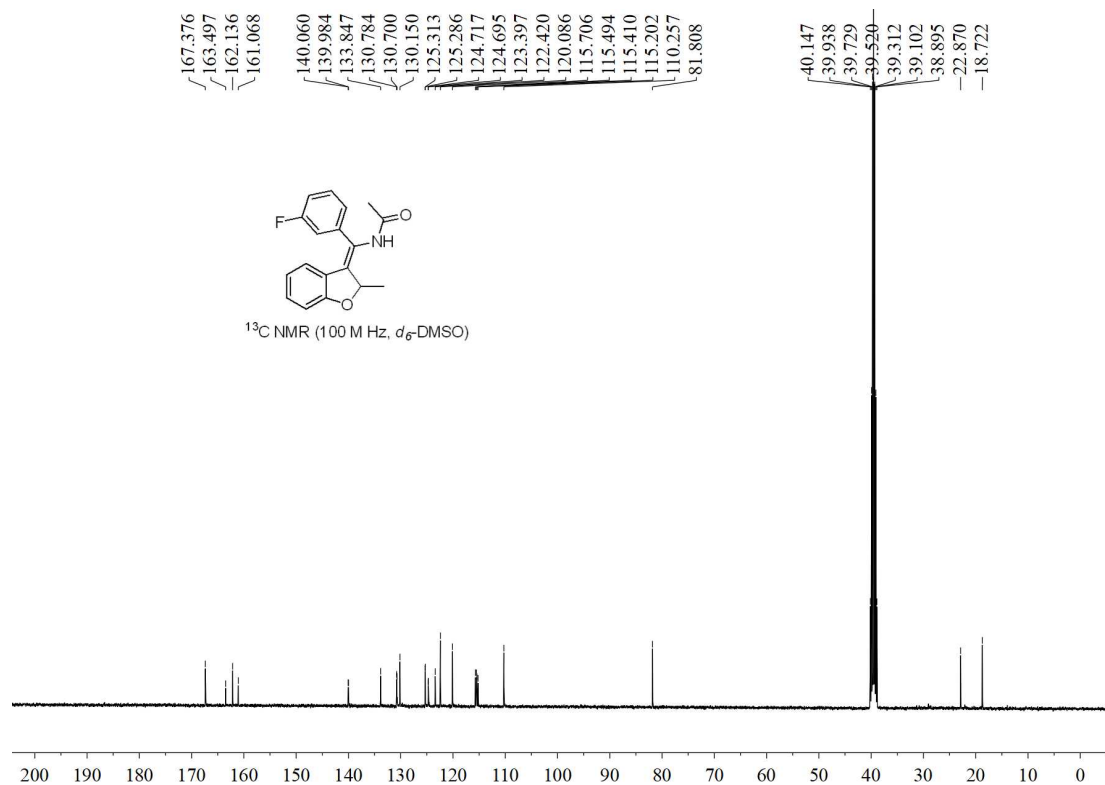
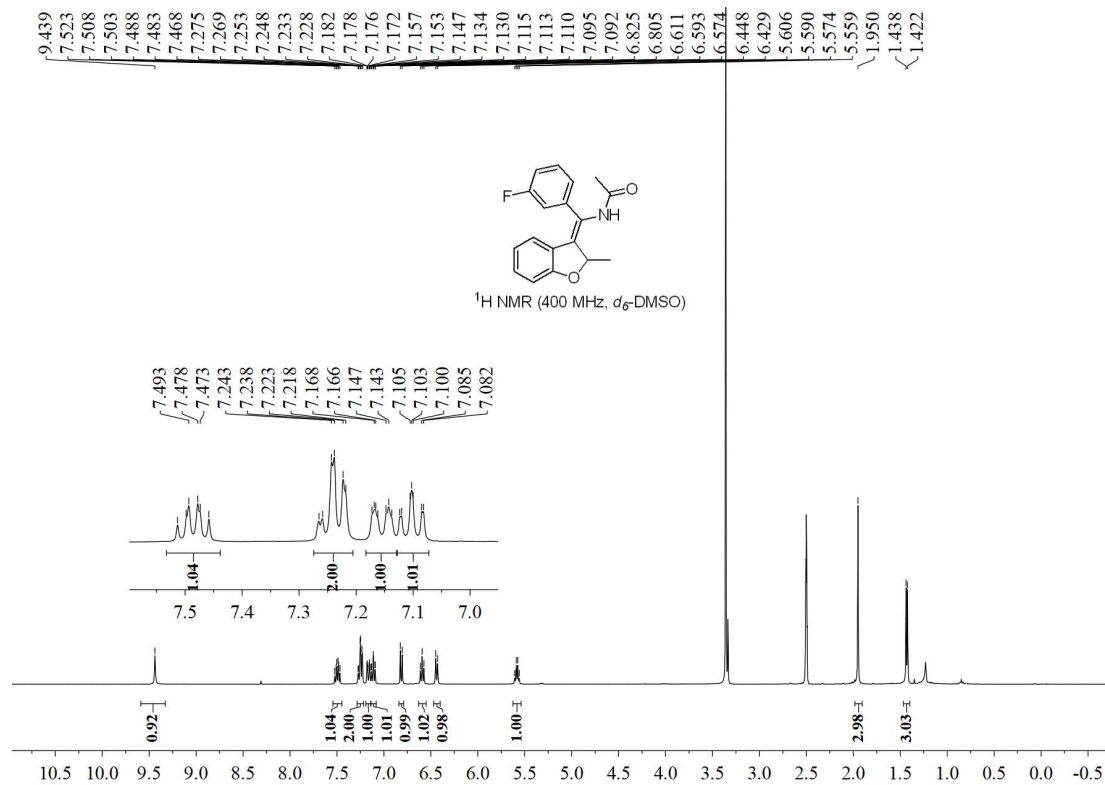
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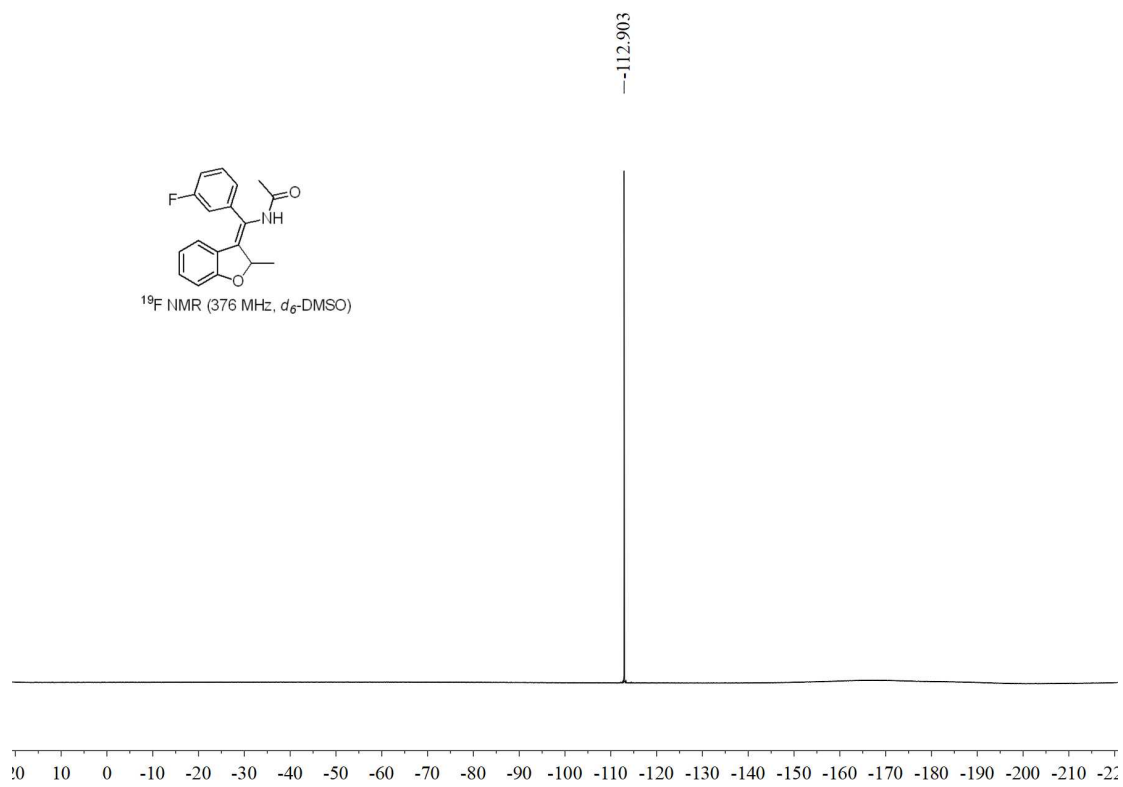


(Z)-N-((3-Methoxyphenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide (Z-31a)

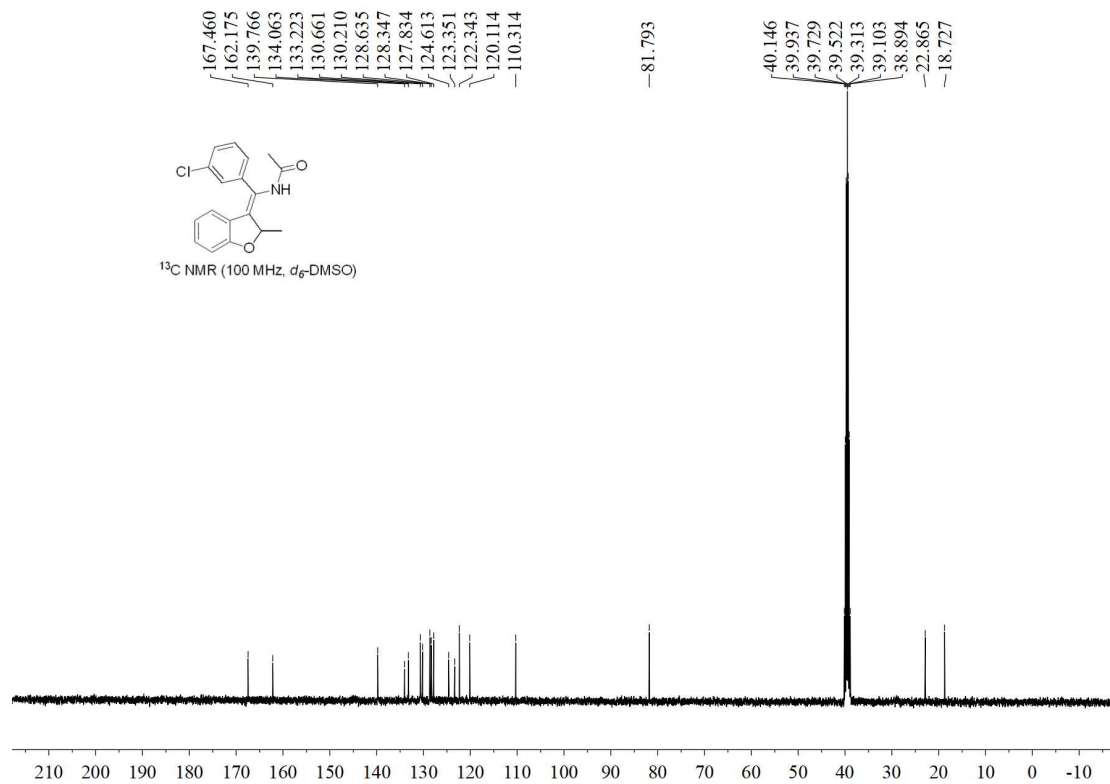
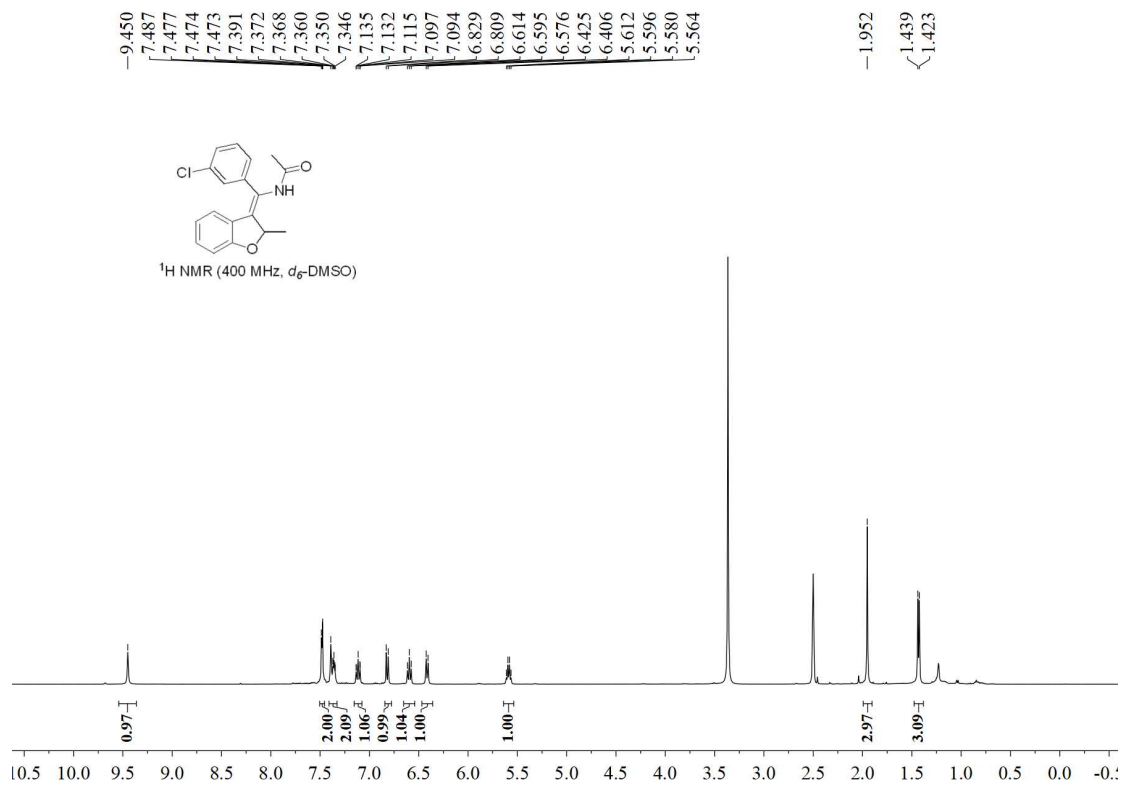


**(Z)-N-((3-Fluorophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide (Z-3ma)**

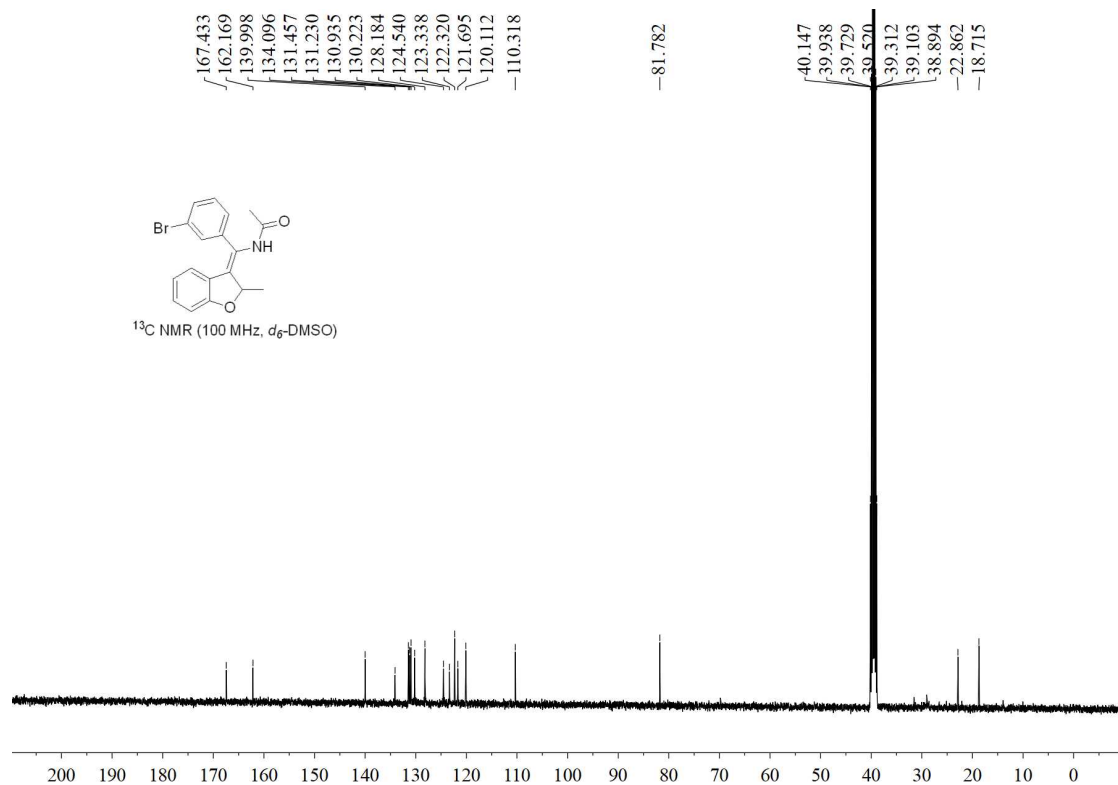
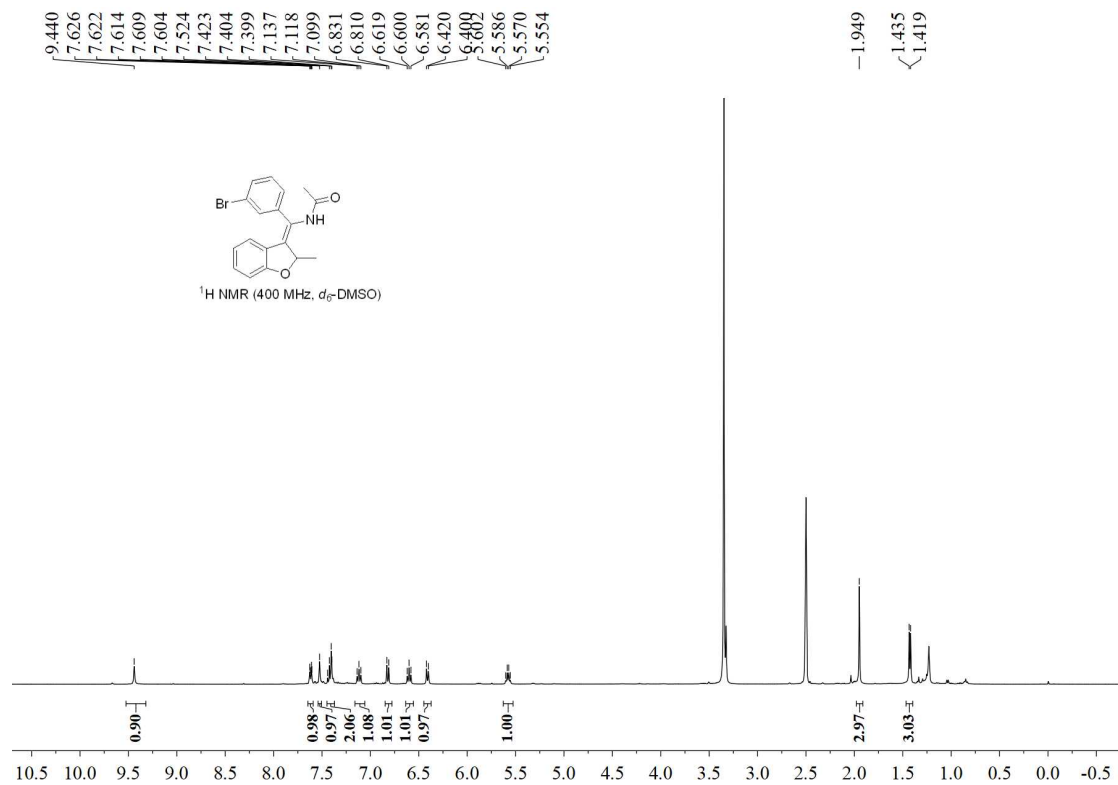




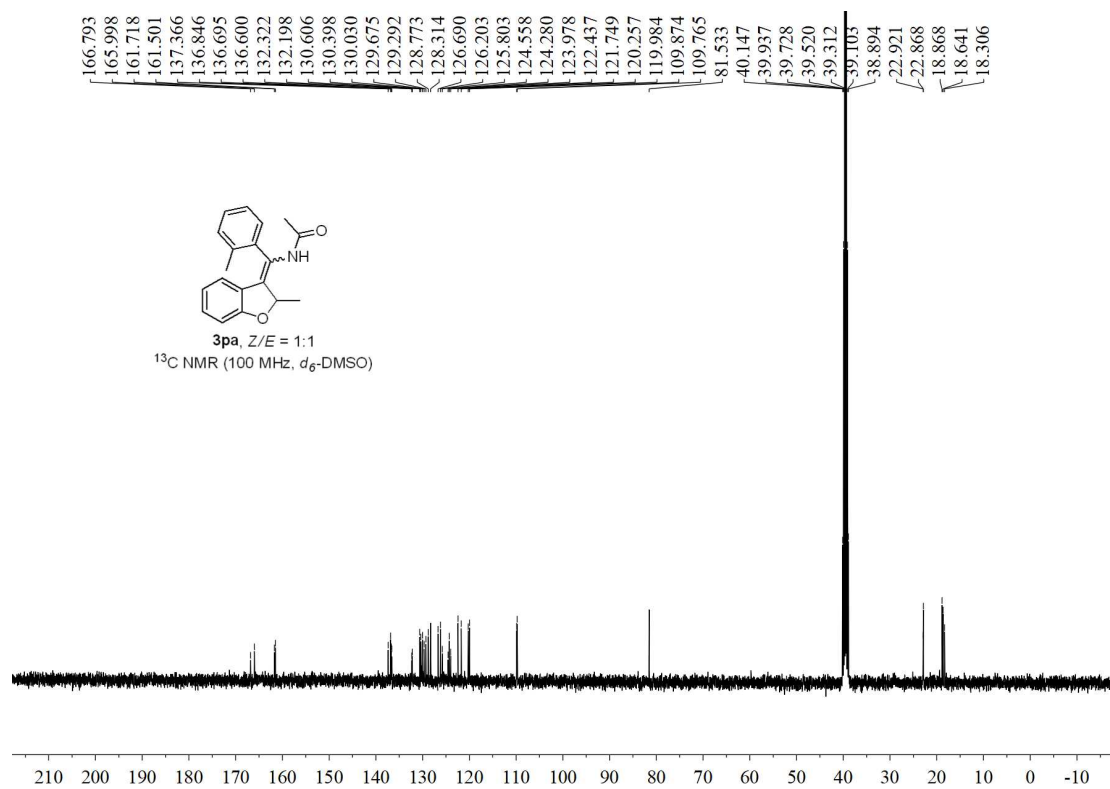
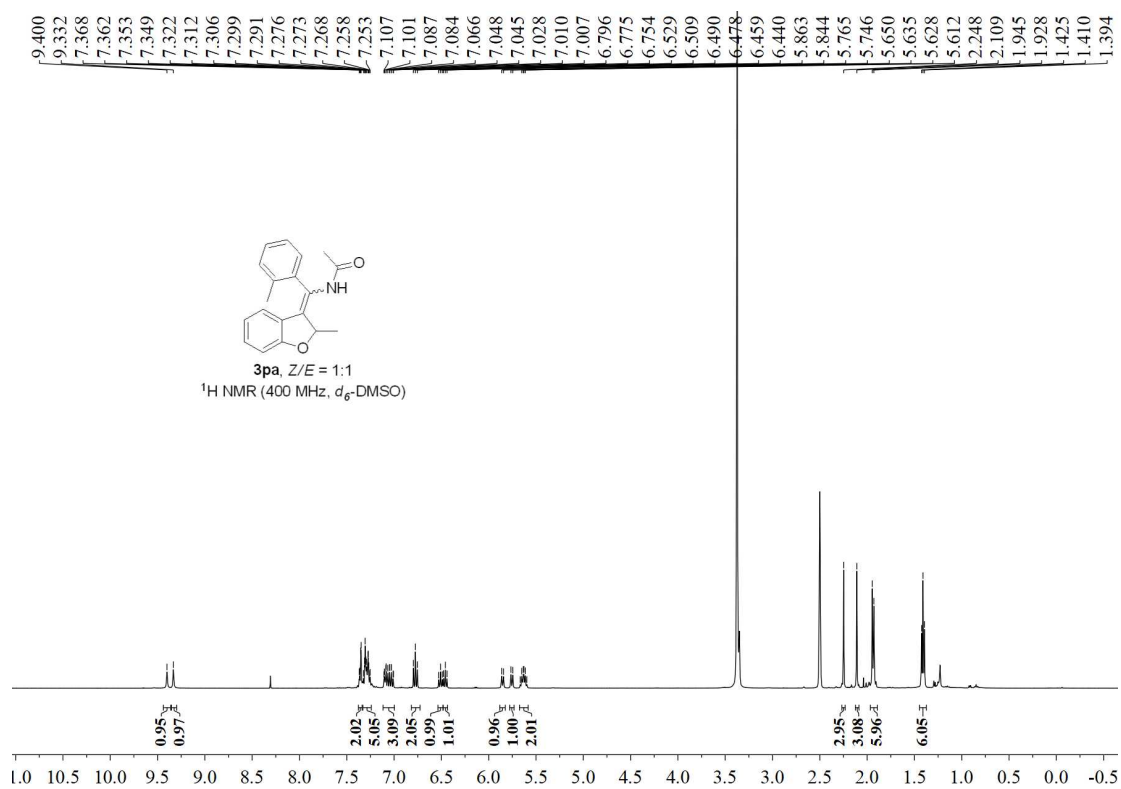
(Z)-N-((3-Chlorophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide (Z-3na)



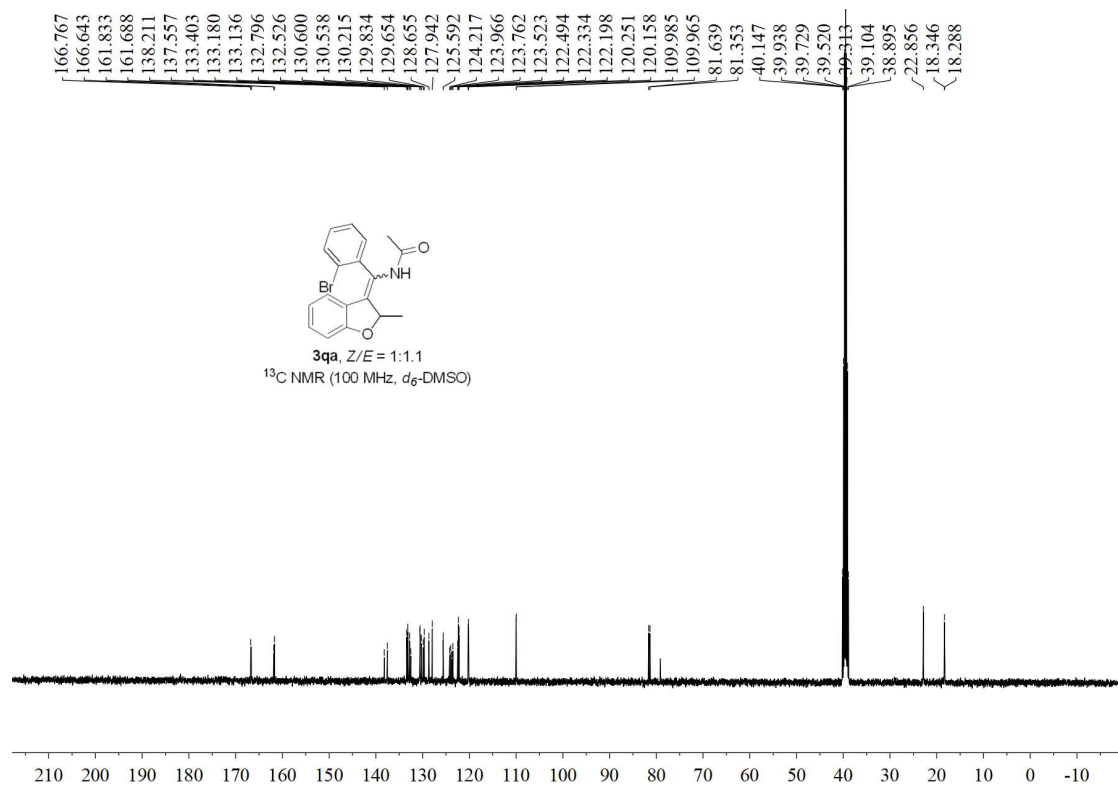
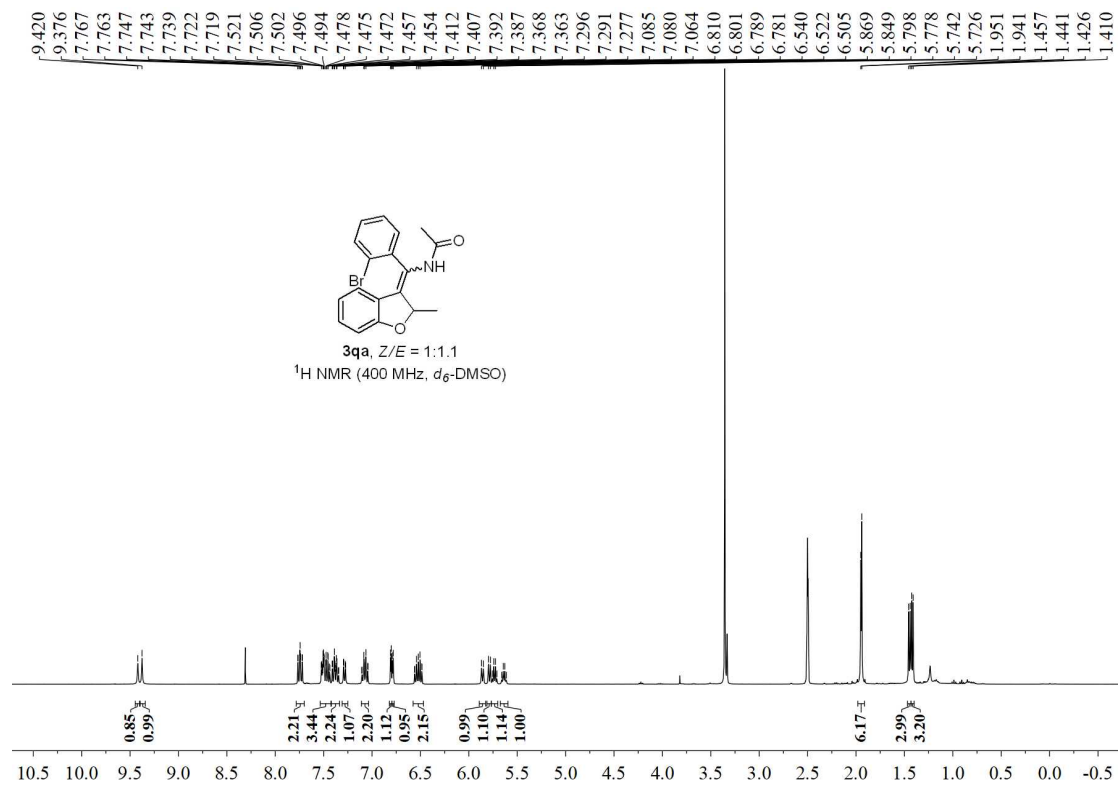
**(Z)-N-((3-Bromophenyl)(2-methylbenzofuran-3(2H)-ylidene)methyl)acetamide (Z-3oa)**



***N*-((2-Methylbenzofuran-3(2*H*)-ylidene)(*o*-tolyl)methyl)acetamide (3pa)**

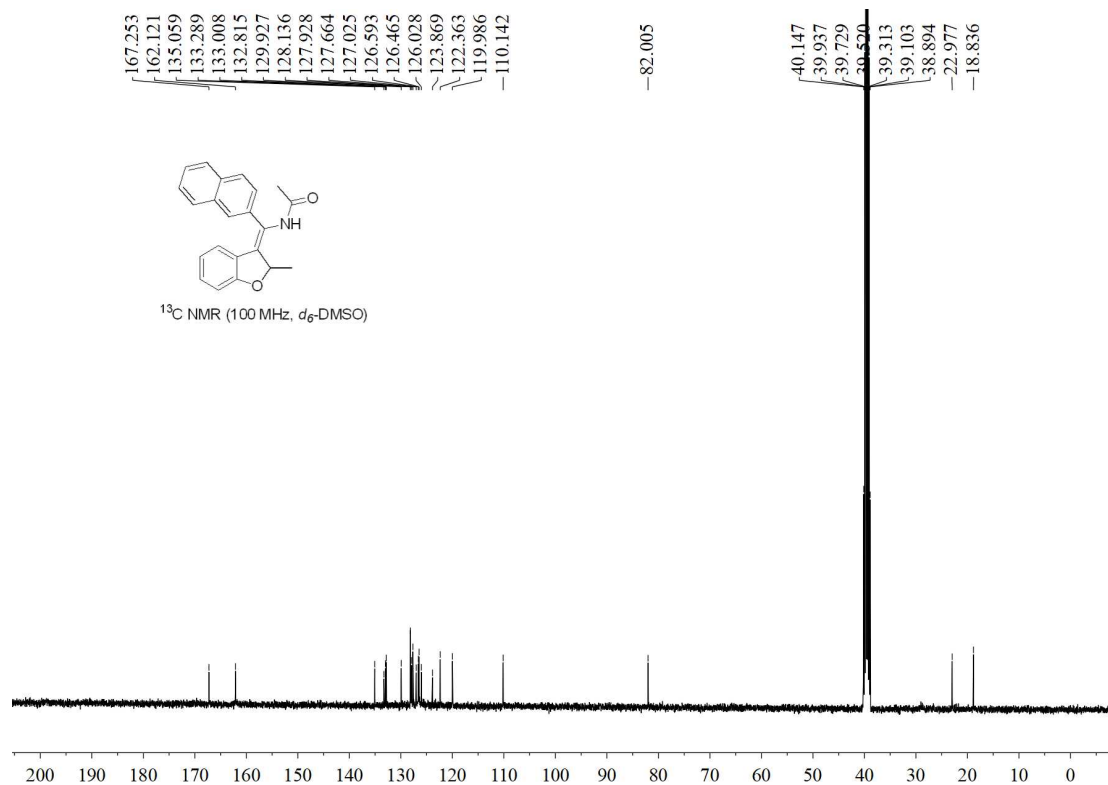
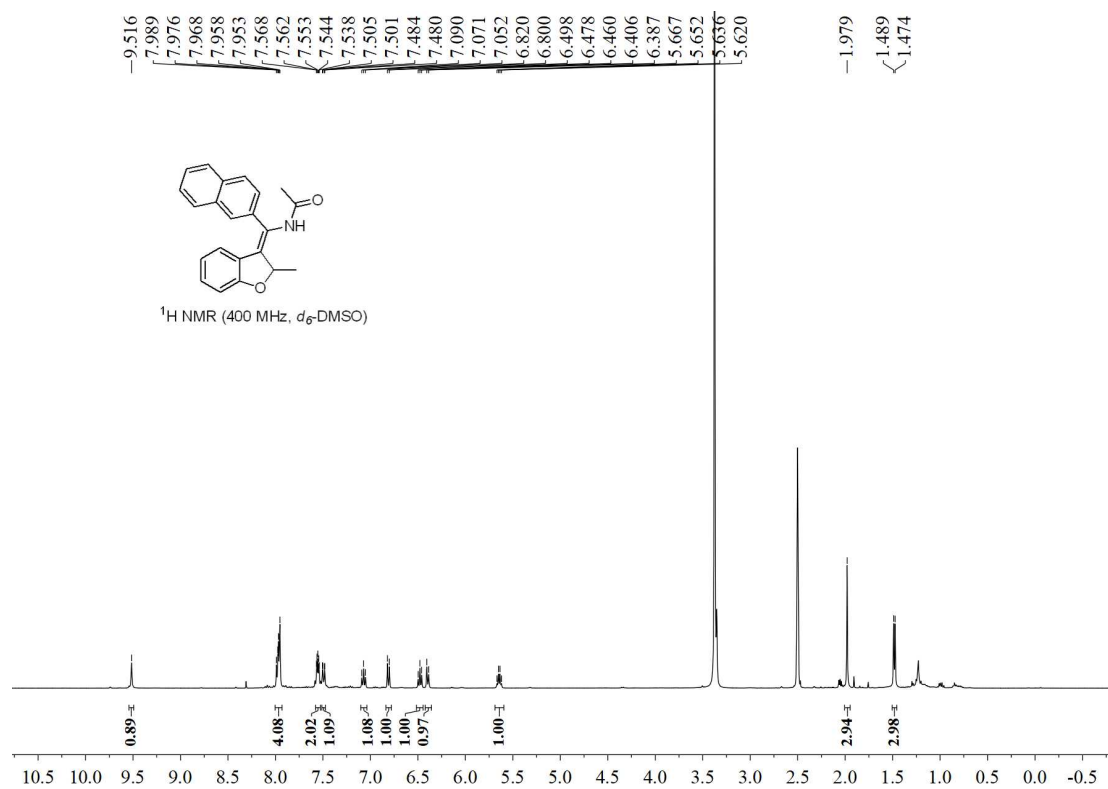


***N*-((2-Bromophenyl)(2-methylbenzofuran-3(2*H*)-ylidene)methyl)acetamide (3qa)**

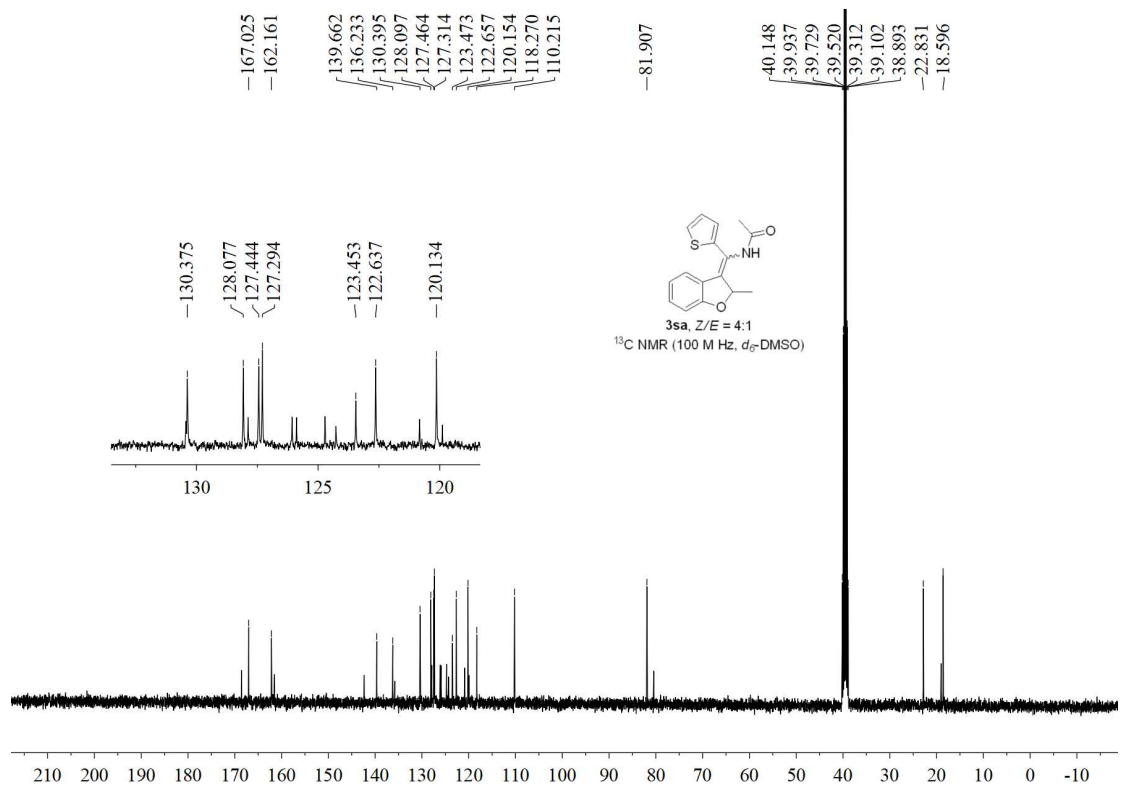
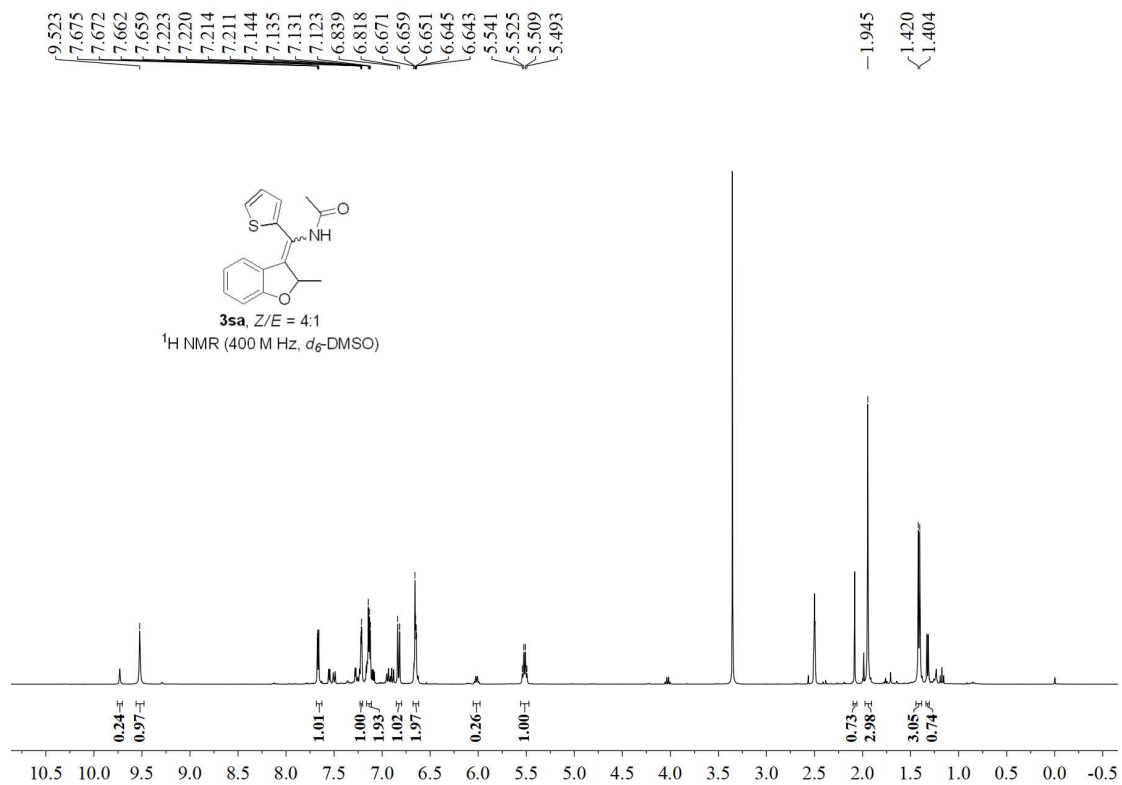




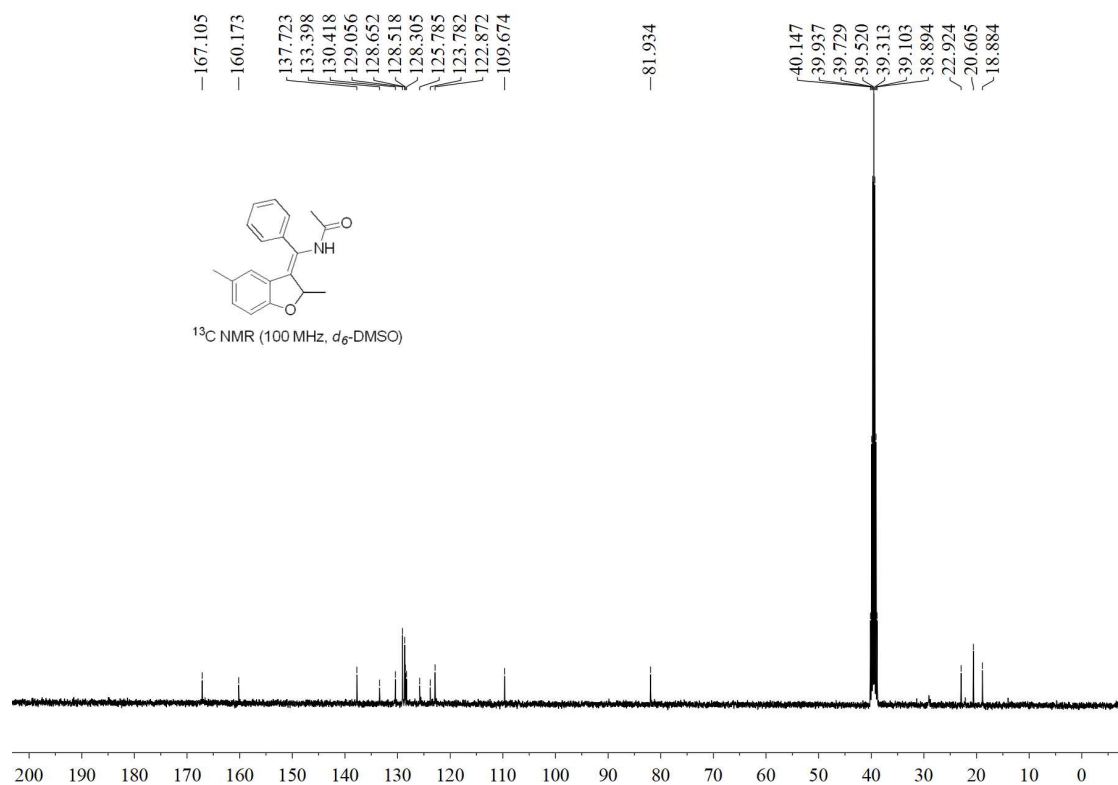
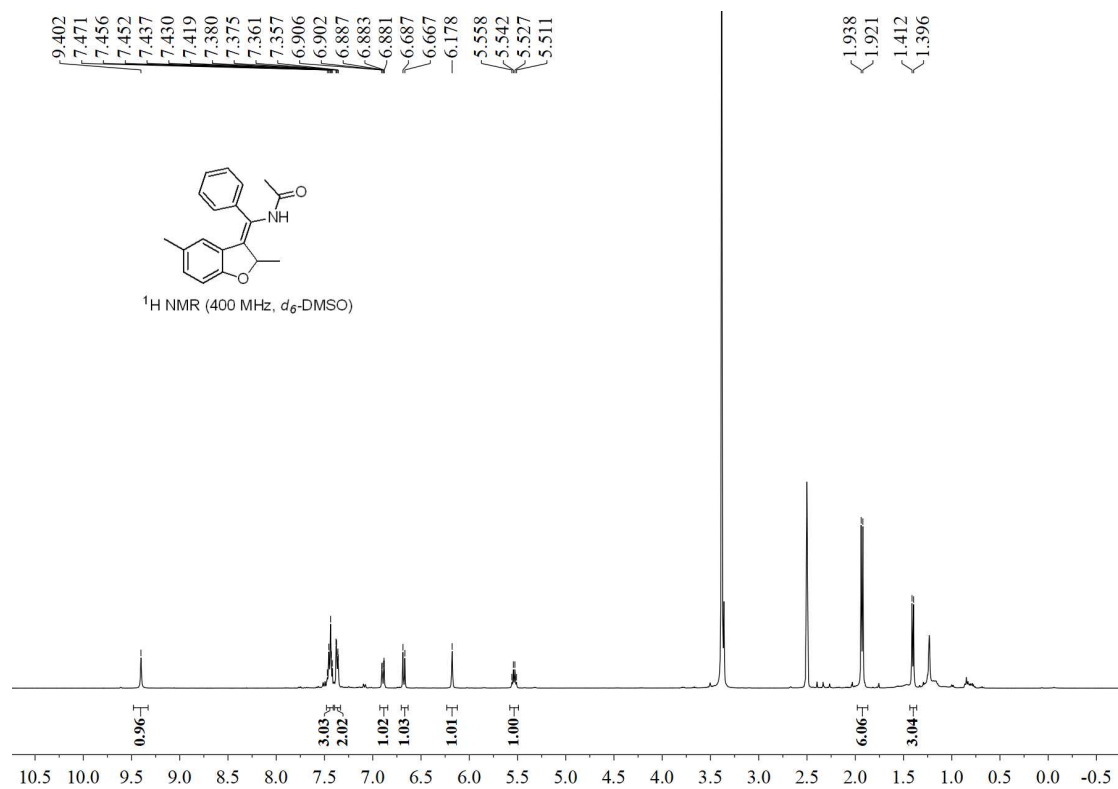
**(Z)-N-((2-Methylbenzofuran-3(2H)-ylidene)(naphthalen-2-yl)methyl)acetamide (Z-3ra)**



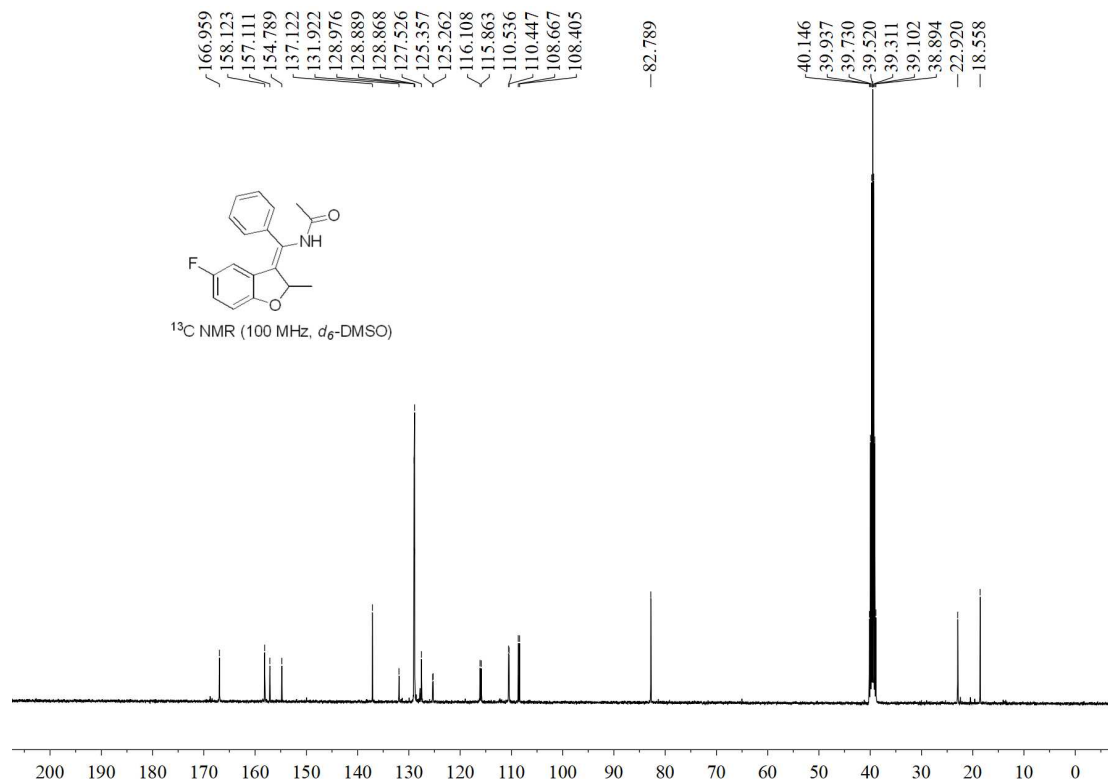
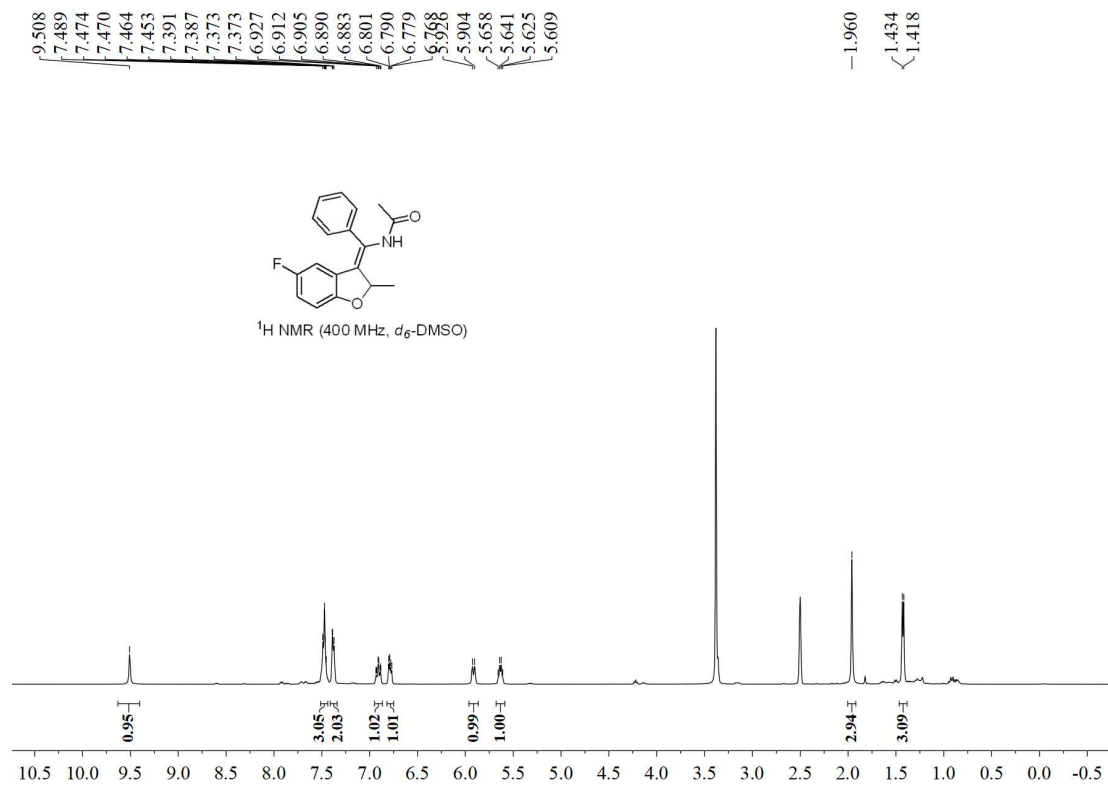
***N*-((2-Methylbenzofuran-3(*H*))-ylidene)(thiophen-2-yl)methyl)acetamide (3sa)**

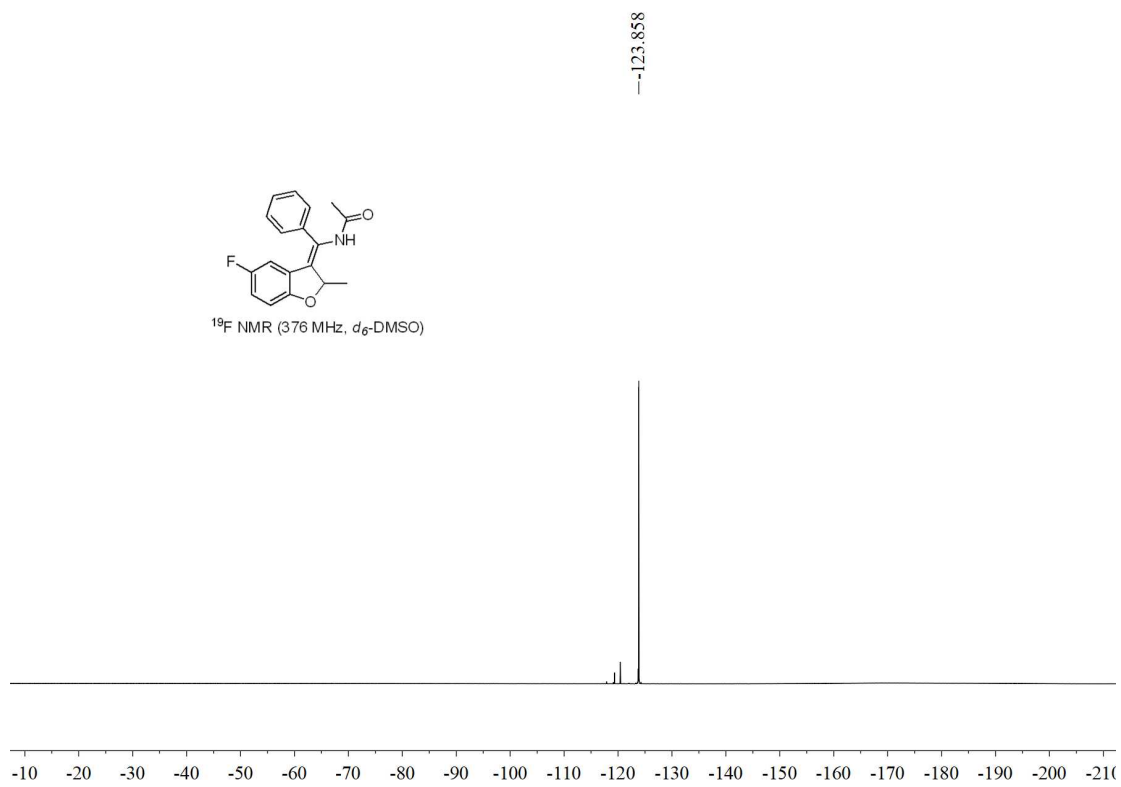


(Z)-N-((2,5-Dimethylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-3va)

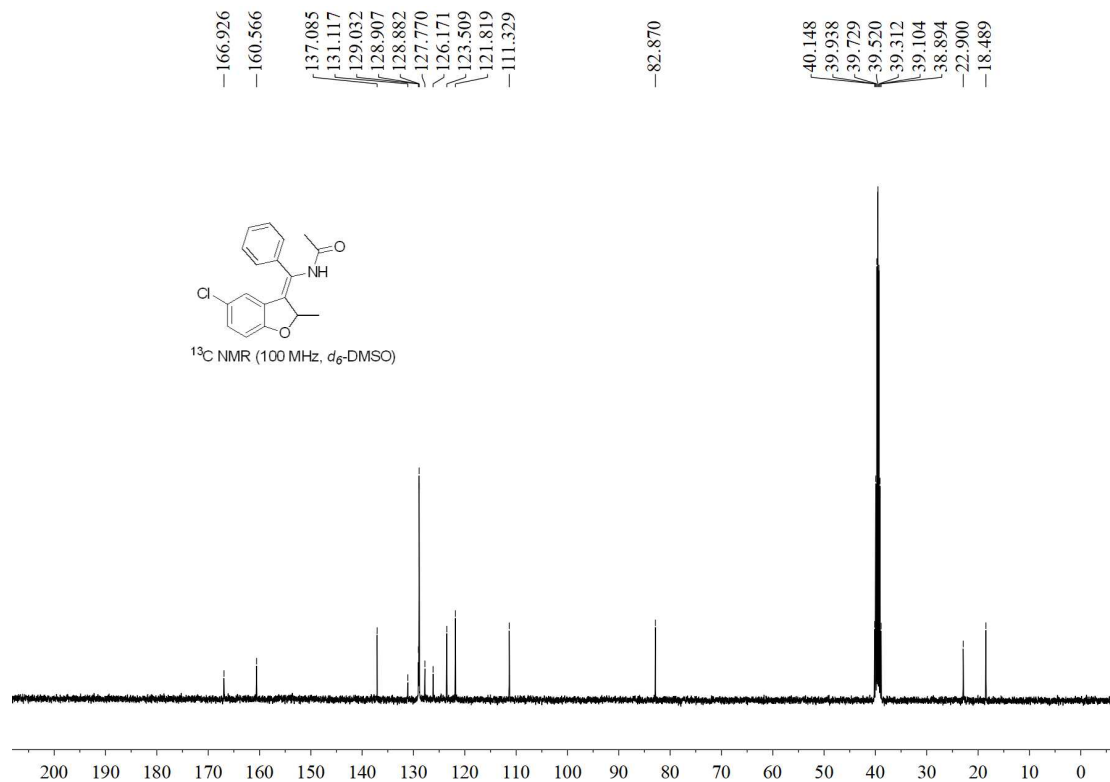
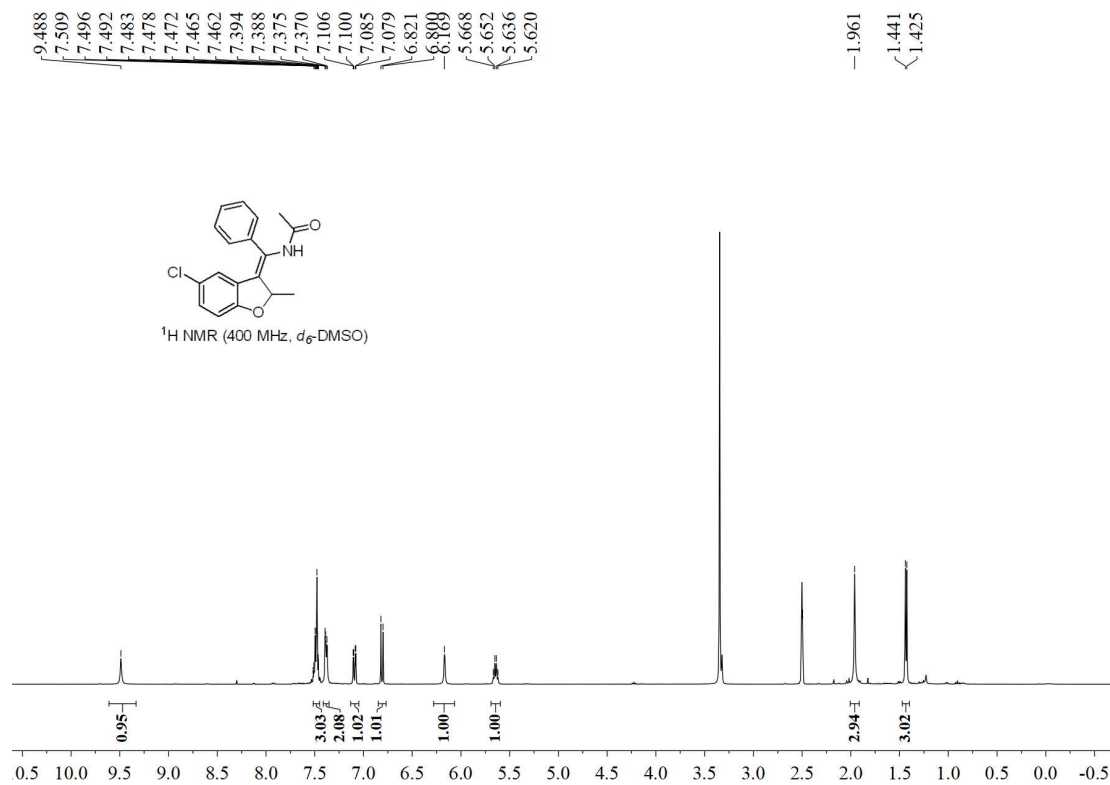


**(Z)-N-((5-Fluoro-2-methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-3wa)**

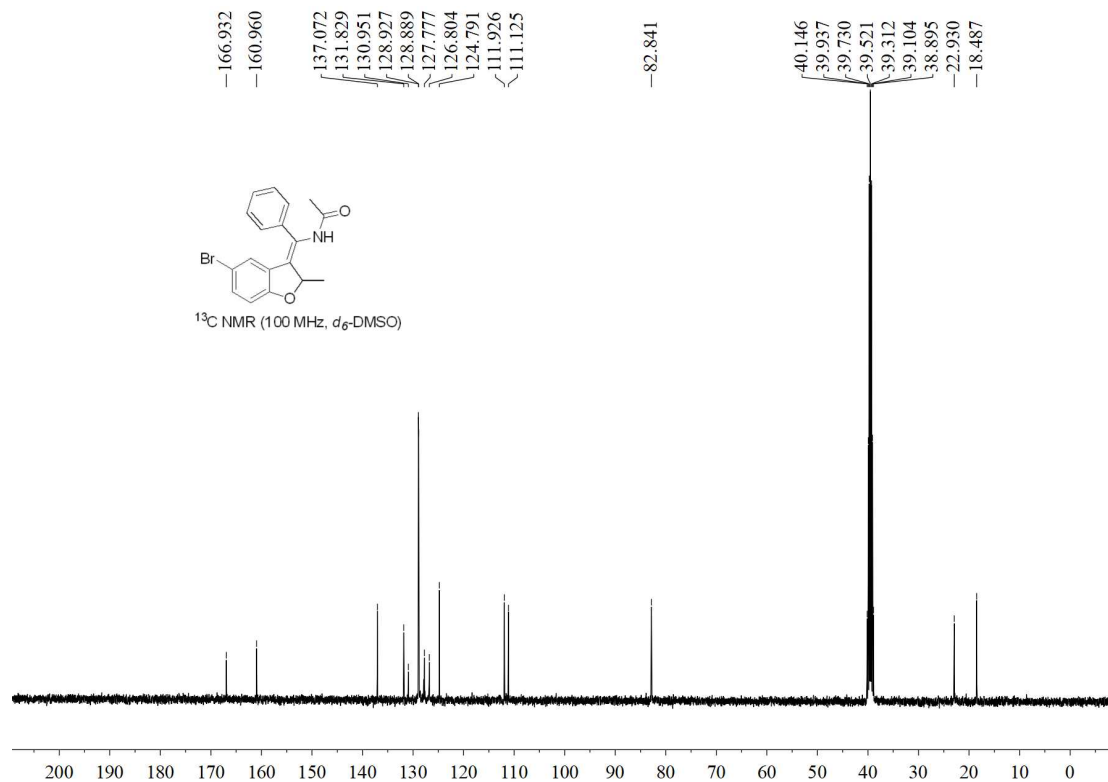
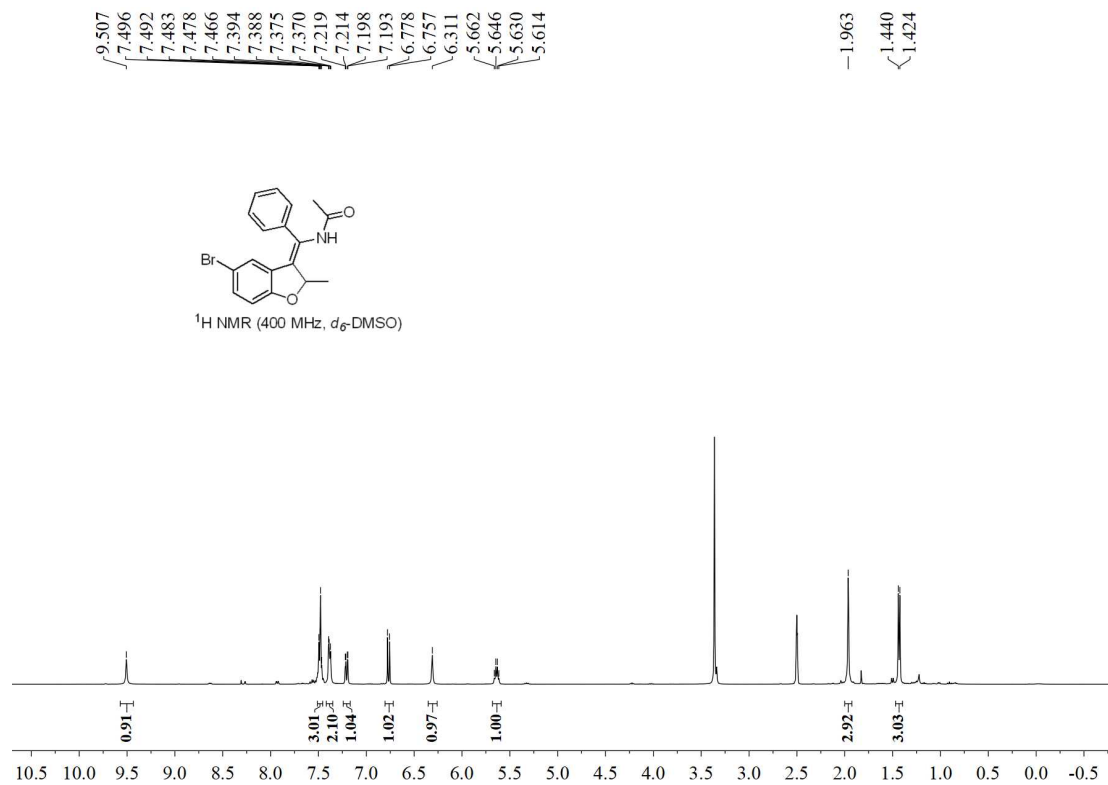




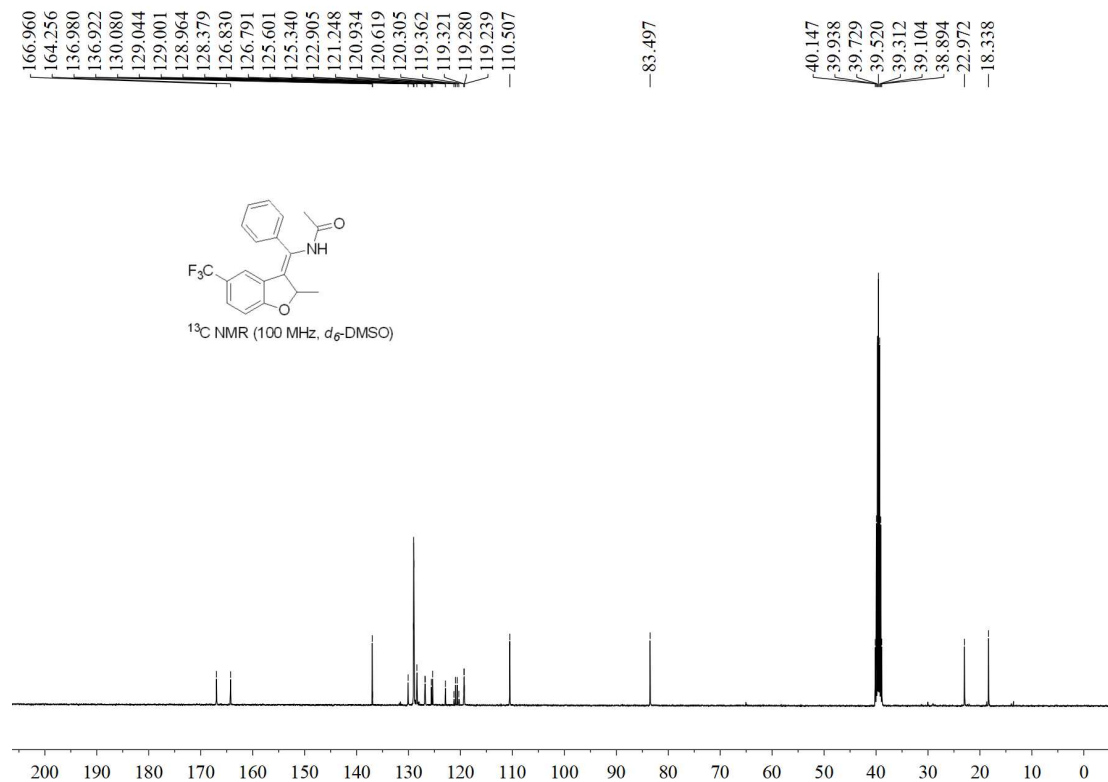
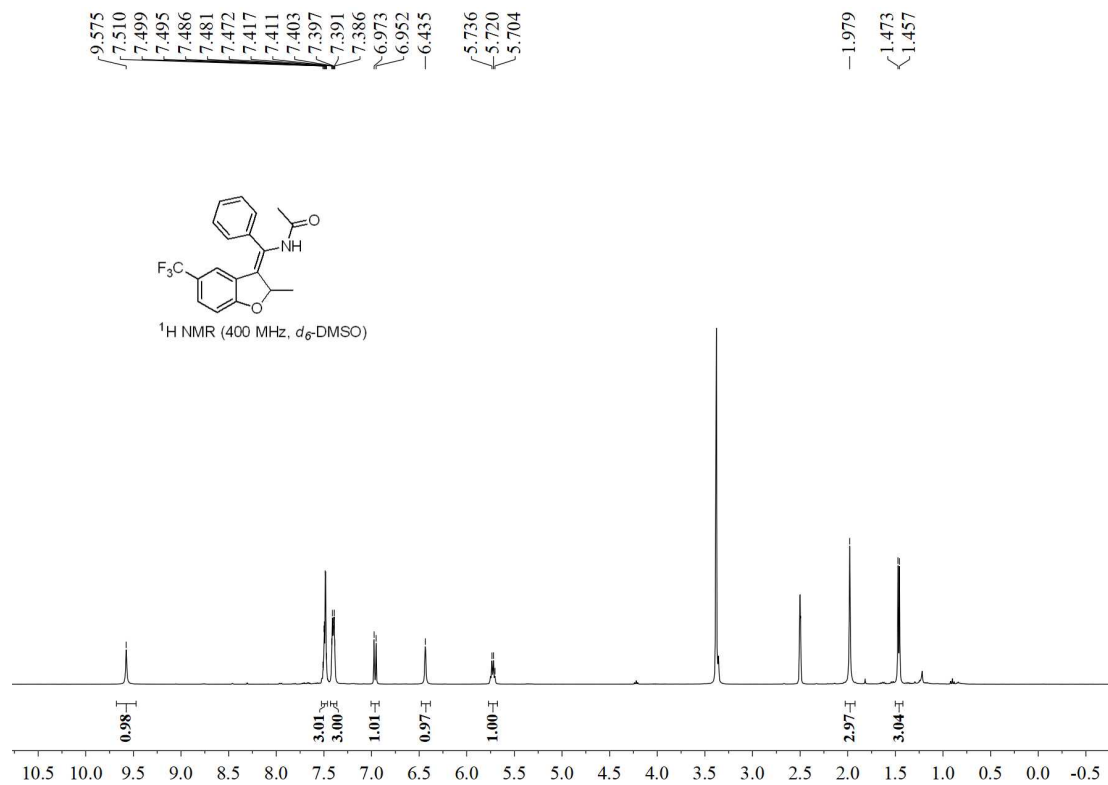
(Z)-N-((5-Chloro-2-methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-3xa)



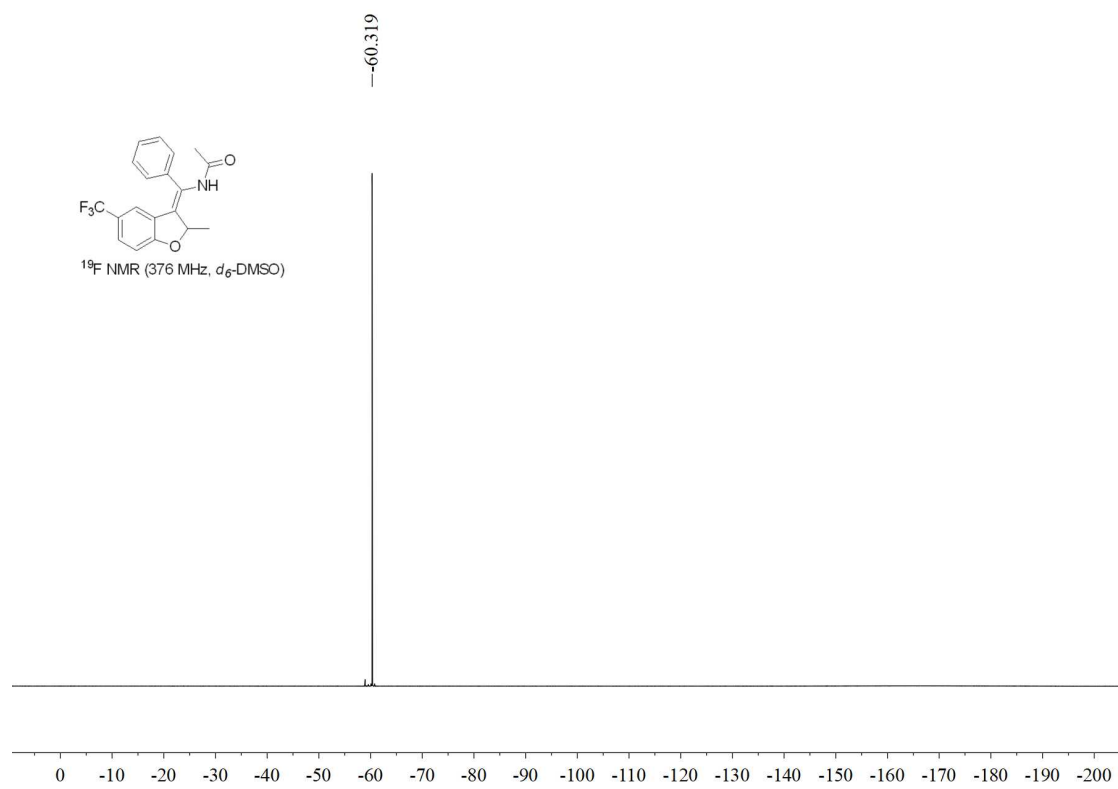
**(Z)-N-((5-Bromo-2-methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-3ya)**



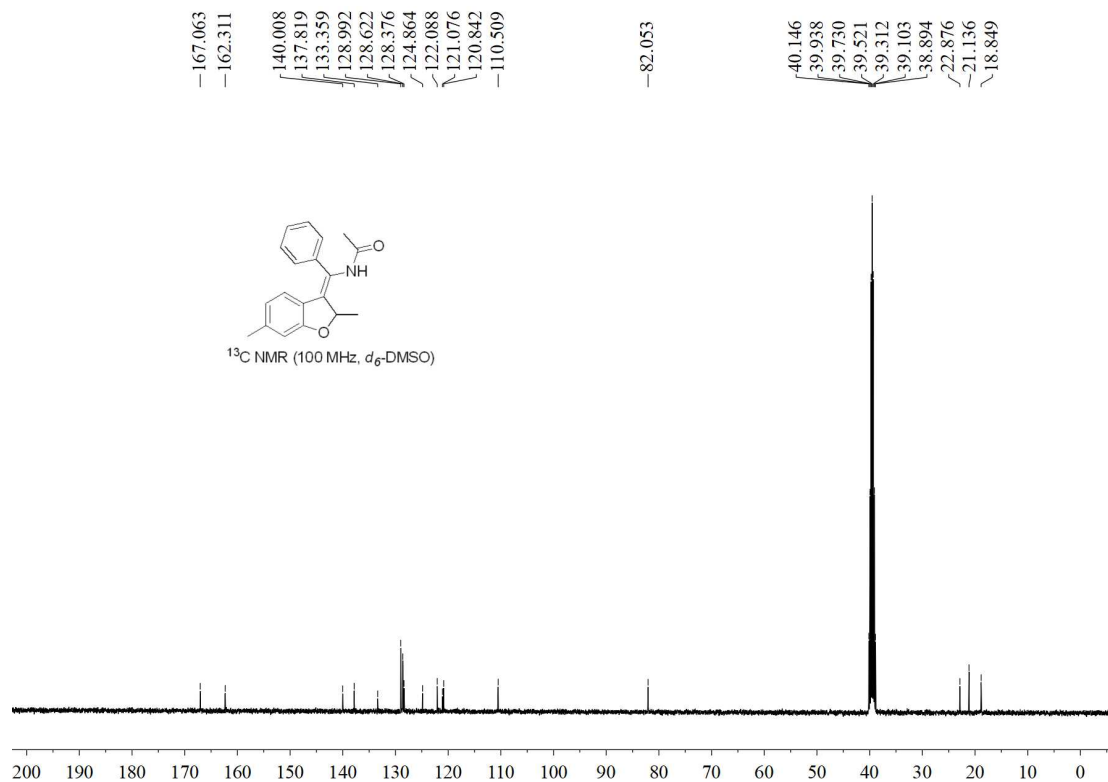
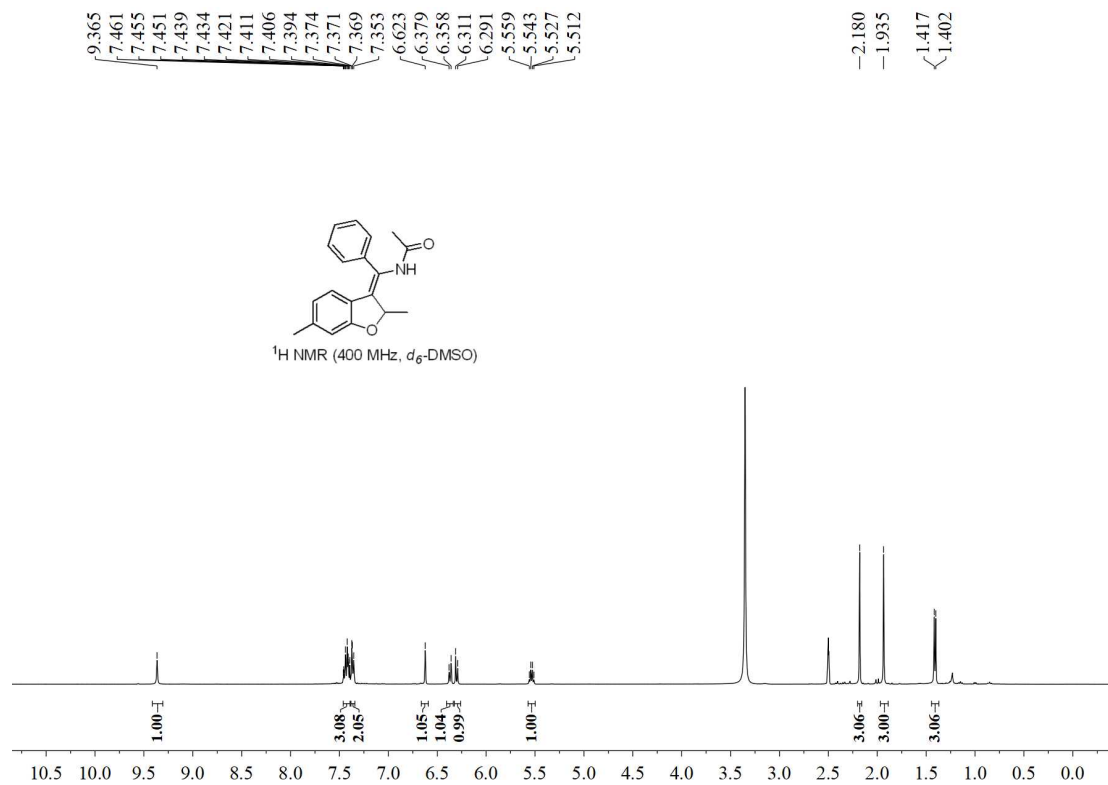
**(Z)-N-((2-Methyl-5-(trifluoromethyl)benzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-3za)**



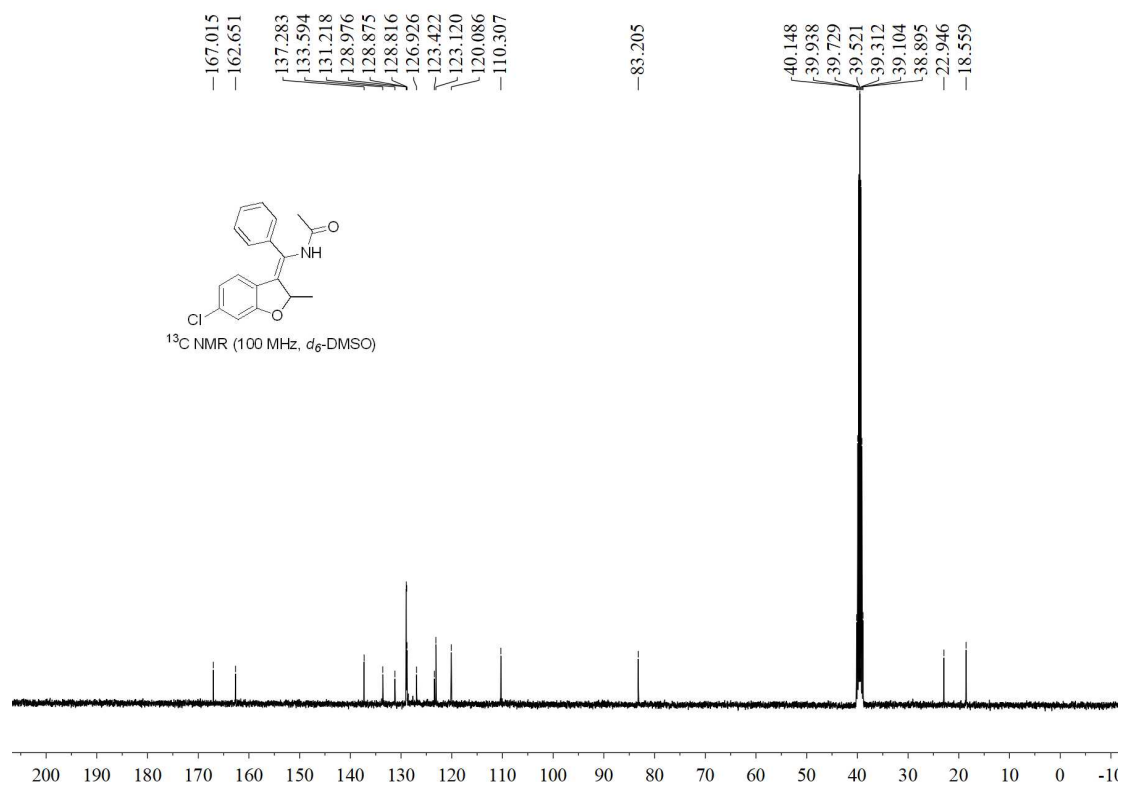
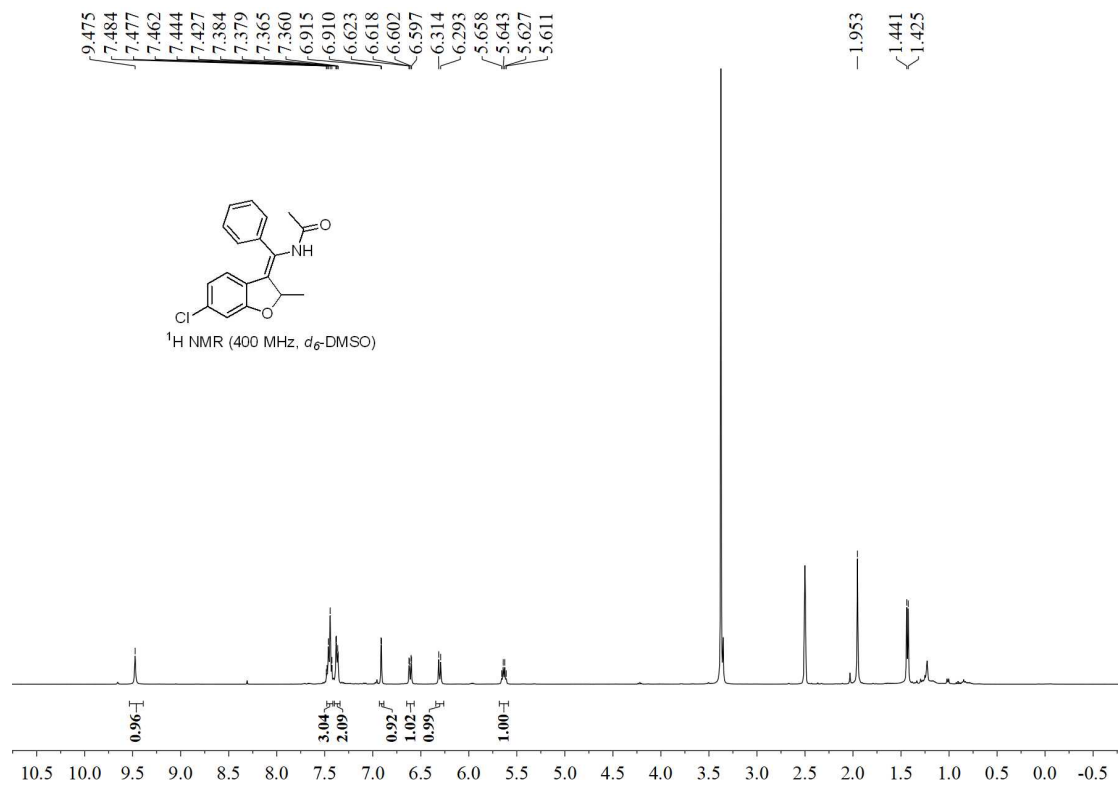




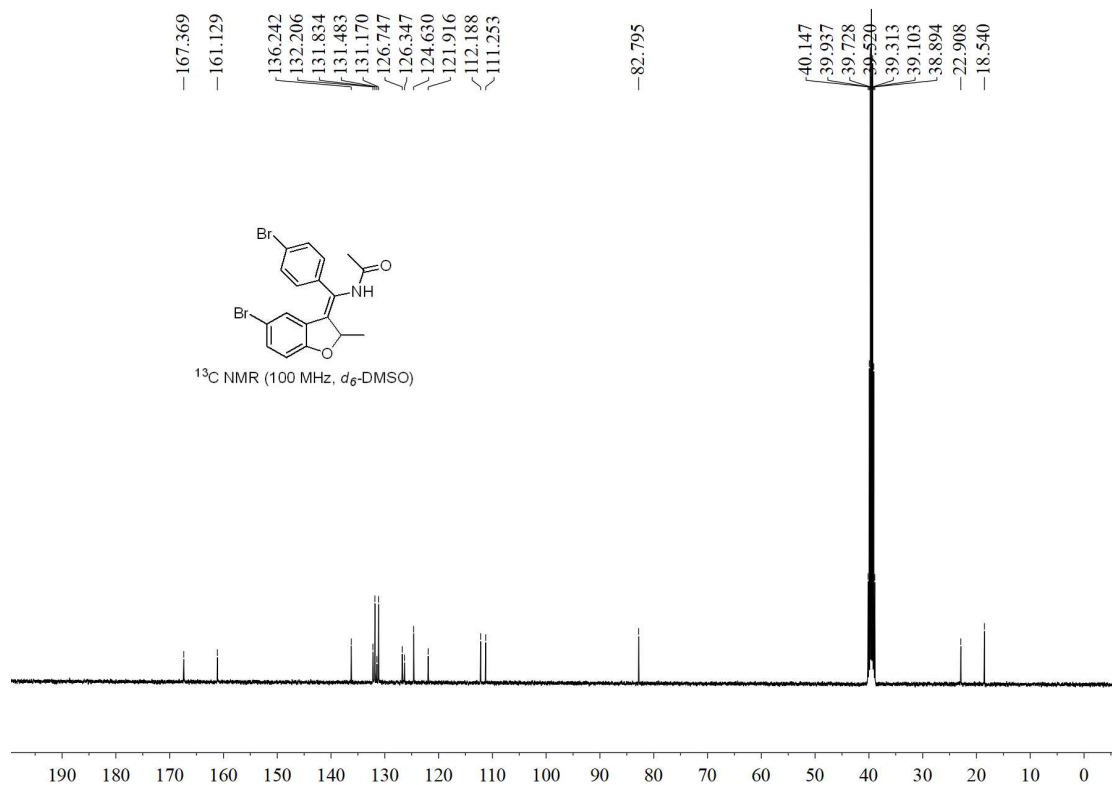
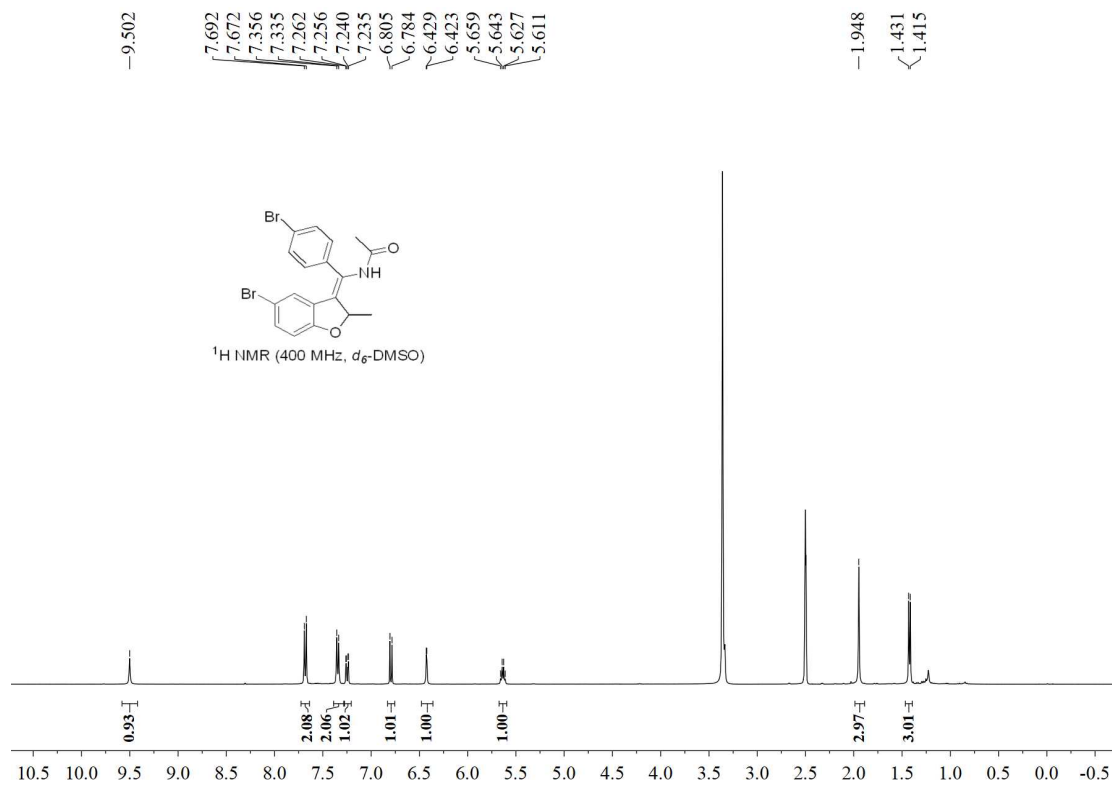
**(Z)-N-((2,6-Dimethylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-3aaa)**



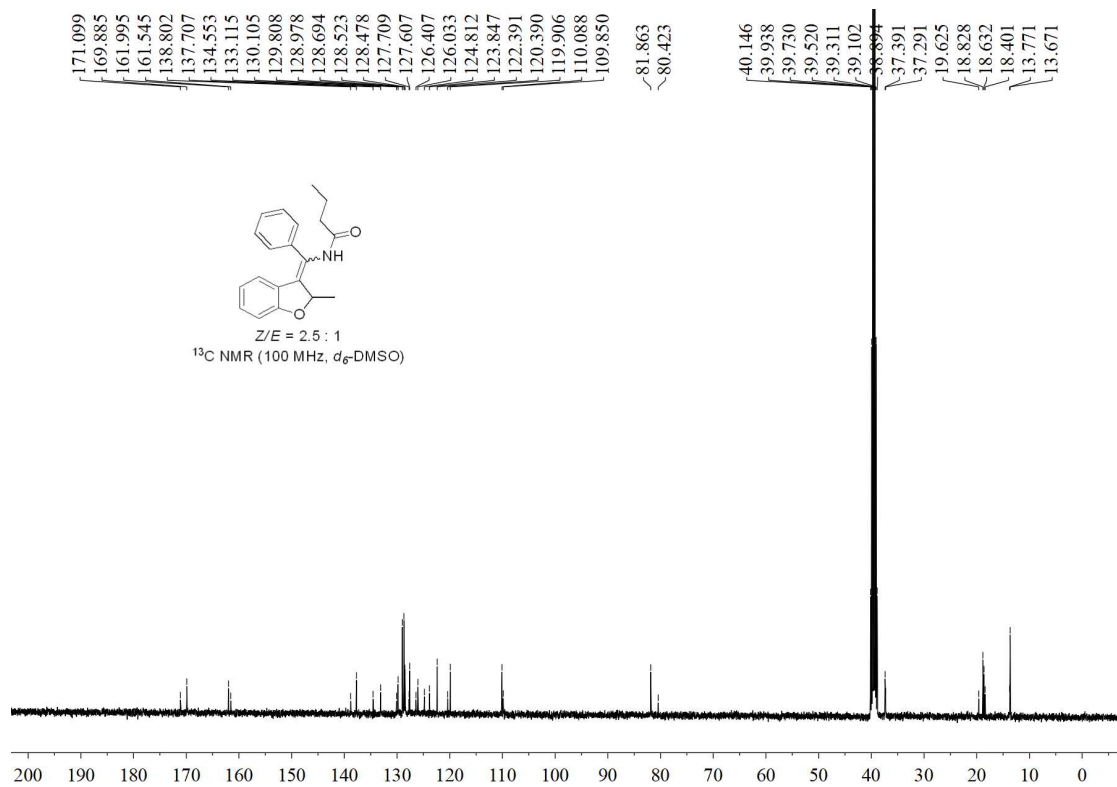
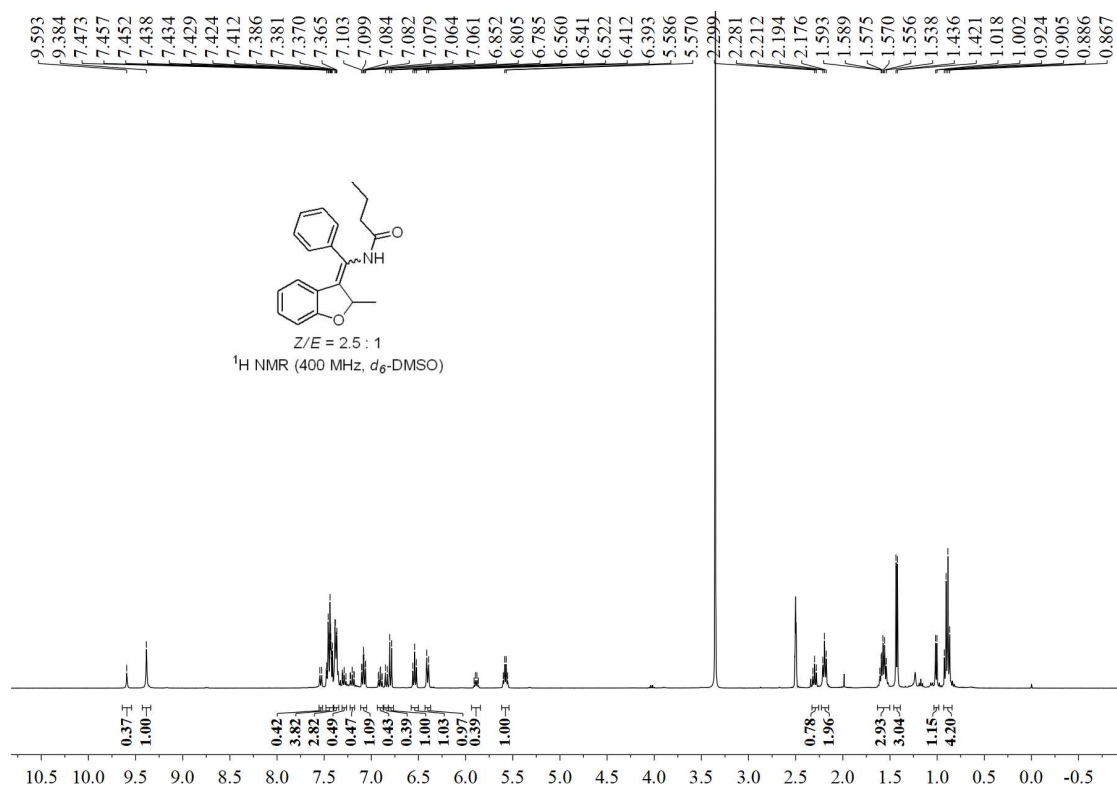
**(Z)-N-((6-Chloro-2-methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acetamide (Z-3aba)**



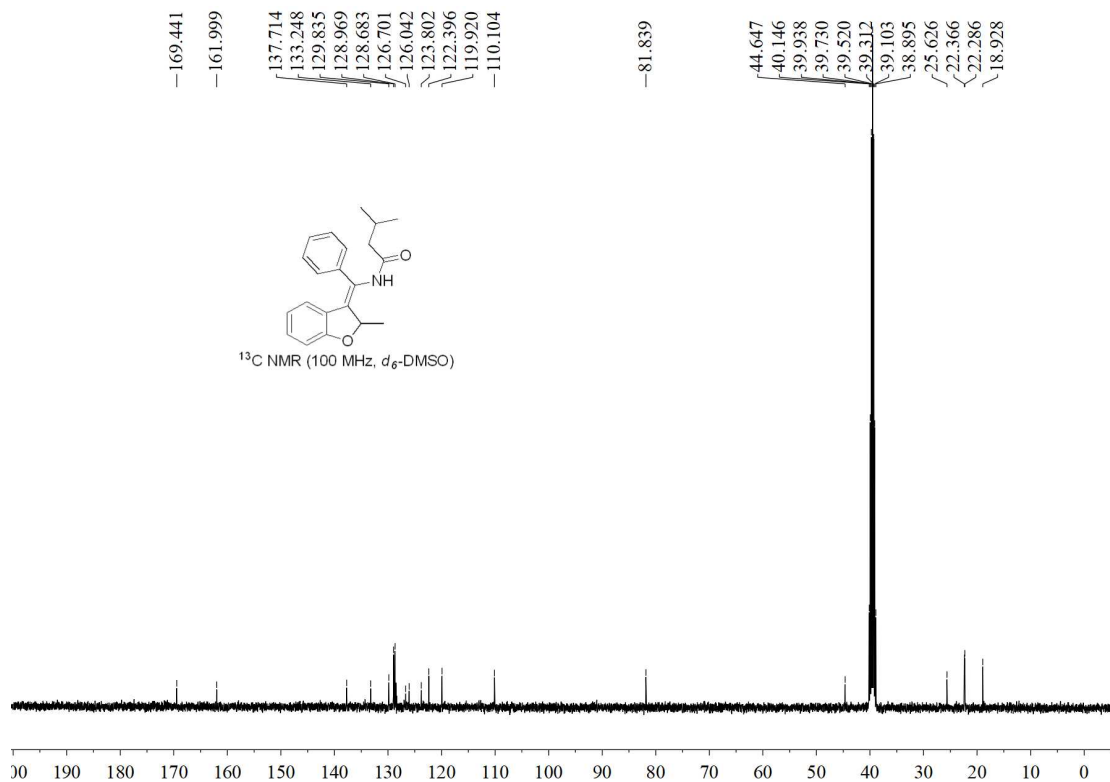
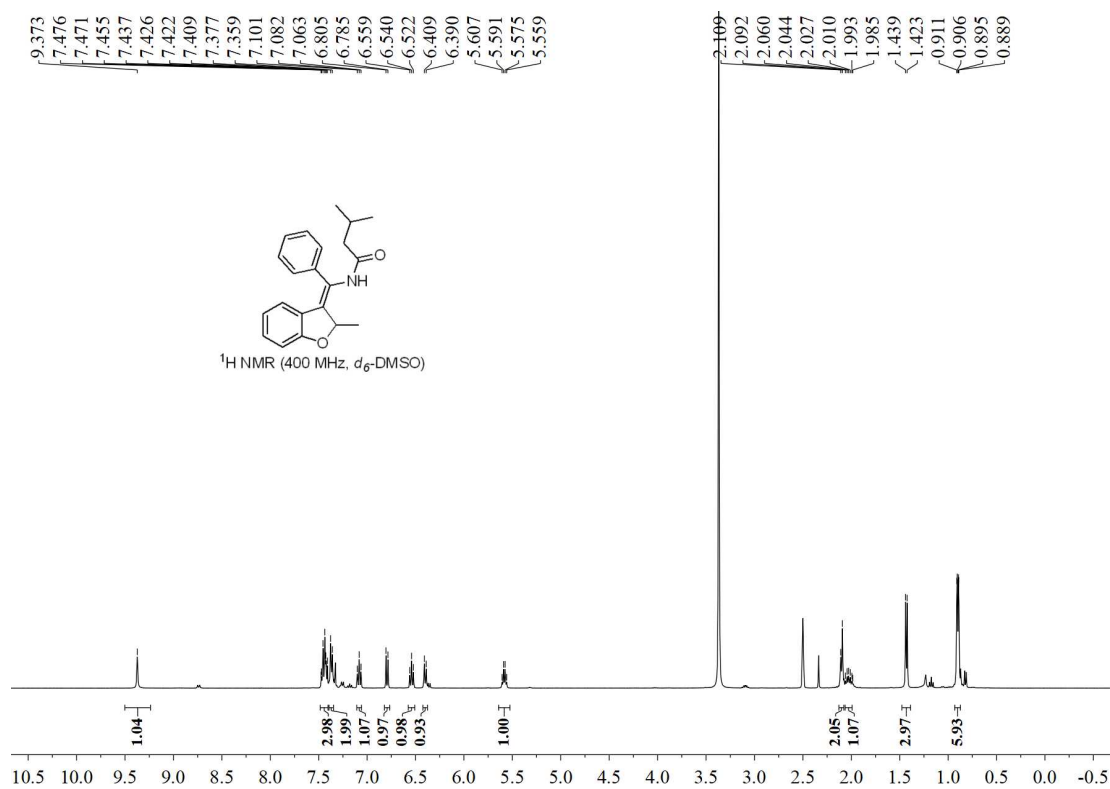
**(Z)-N-((5-Bromo-2-methylbenzofuran-3(2H)-ylidene)(4-bromophenyl)methyl)acetamide (Z-3aca)**



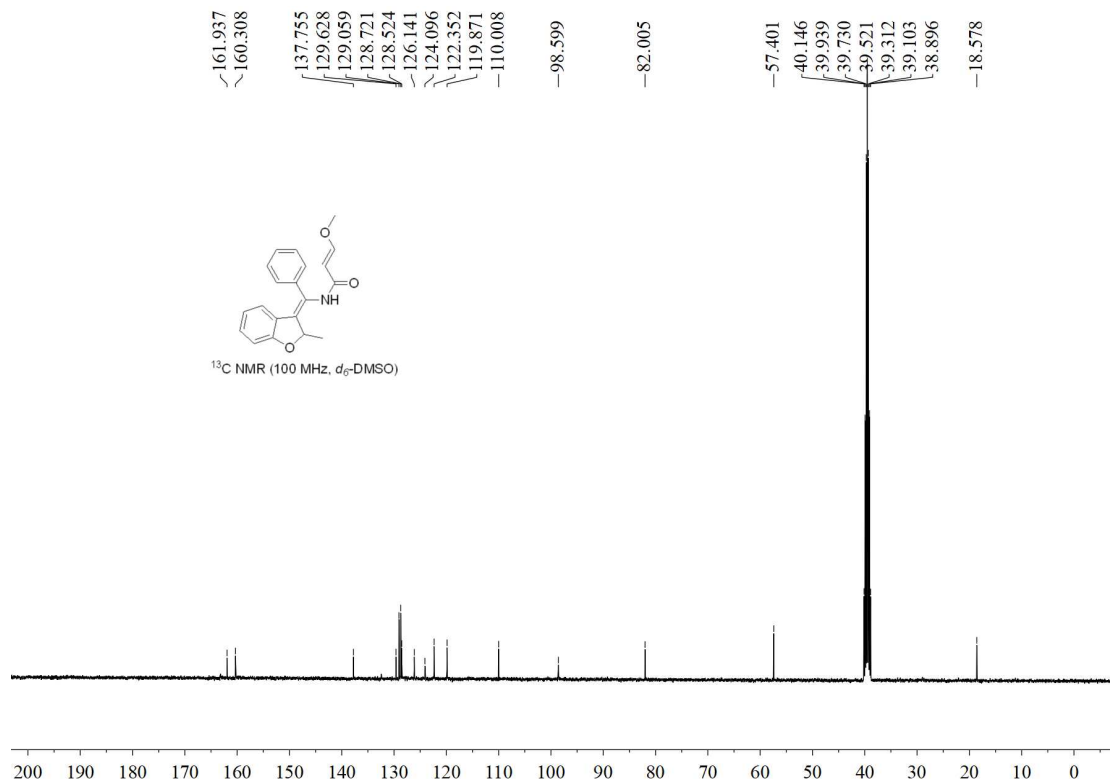
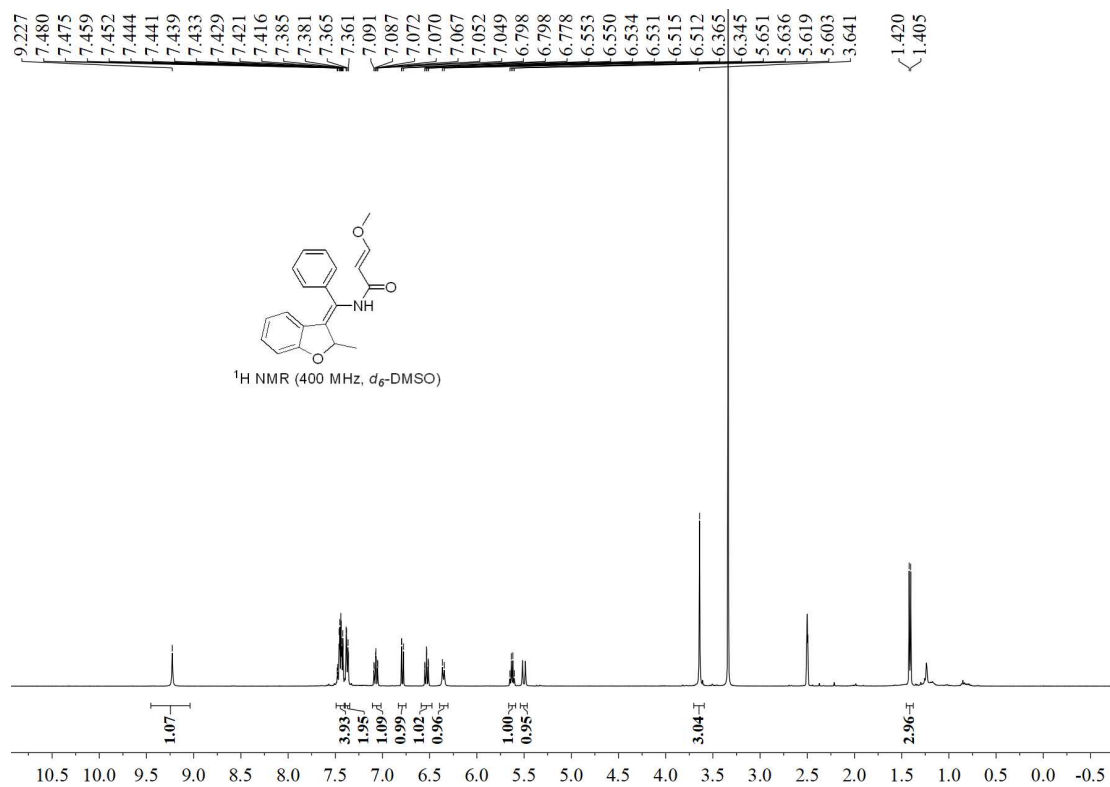
**N-((2-Methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)butyramide (3ab)**



**(Z)-3-Methyl-N-((2-methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)butanamide (Z-3ac)**

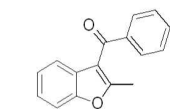


**(E)-3-Methoxy-N-((Z)-(2-methylbenzofuran-3(2H)-ylidene)(phenyl)methyl)acrylamide (Z-3ae)**

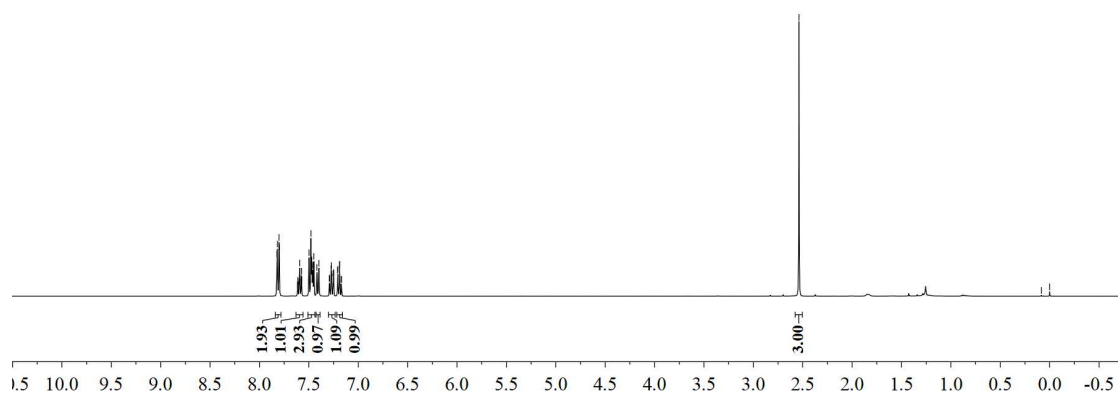


(2-Methylbenzofuran-3-yl)(phenyl)methanone (4)

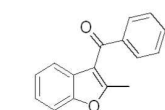
7.822  
7.819  
7.802  
7.798  
7.615  
7.612  
7.608  
7.598  
7.593  
7.588  
7.578  
7.574  
7.571  
7.498  
7.478  
7.471  
7.470  
7.460  
7.452  
7.449  
7.447  
7.418  
7.398  
7.292  
7.289  
7.274  
7.271  
7.268  
7.253  
7.250  
7.248  
7.209  
7.206  
7.190  
7.187  
7.171  
7.168  
2.538  
-0.083  
-0.000



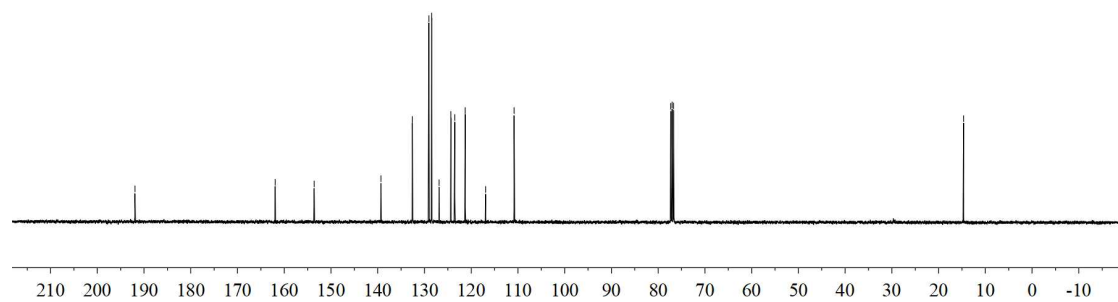
<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>Cl)



-191.944  
-161.929  
-153.601  
139.307  
132.586  
129.065  
128.461  
126.879  
124.347  
123.530  
121.286  
116.924  
110.818  
77.318  
77.001  
76.683  
-14.672



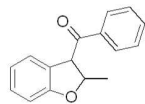
<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>Cl)



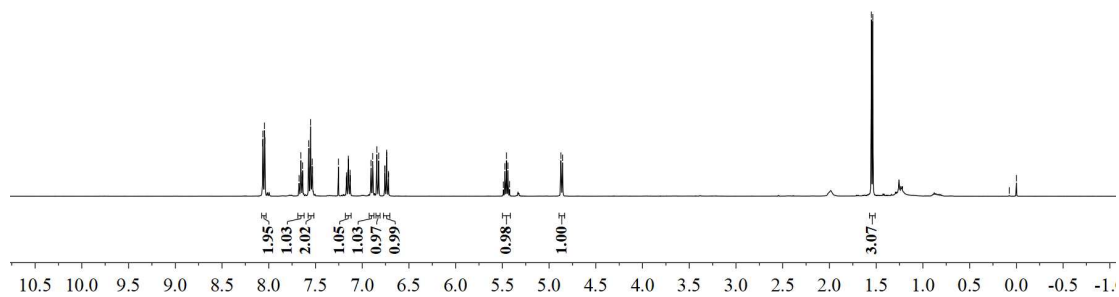


(2-Methyl-2,3-dihydrobenzofuran-3-yl)(phenyl)methanone (5)

8.065  
8.062  
8.045  
8.041  
7.675  
7.657  
7.652  
7.642  
7.638  
7.635  
7.573  
7.569  
7.556  
7.553  
7.535  
7.533  
7.255  
7.171  
7.168  
7.165  
7.152  
7.150  
7.148  
7.146  
7.145  
7.132  
7.129  
7.126  
6.906  
6.887  
6.844  
6.823  
6.758  
6.755  
6.739  
6.737  
6.720  
6.718  
6.718  
5.473  
5.457  
5.440  
4.874  
4.857  
1.552  
1.536  
0.075  
0.000



<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>Cl)



-196.476

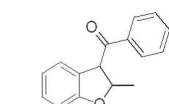
-159.389

136.450  
133.703  
129.302  
129.093  
128.931  
125.393  
124.842  
120.293  
110.136

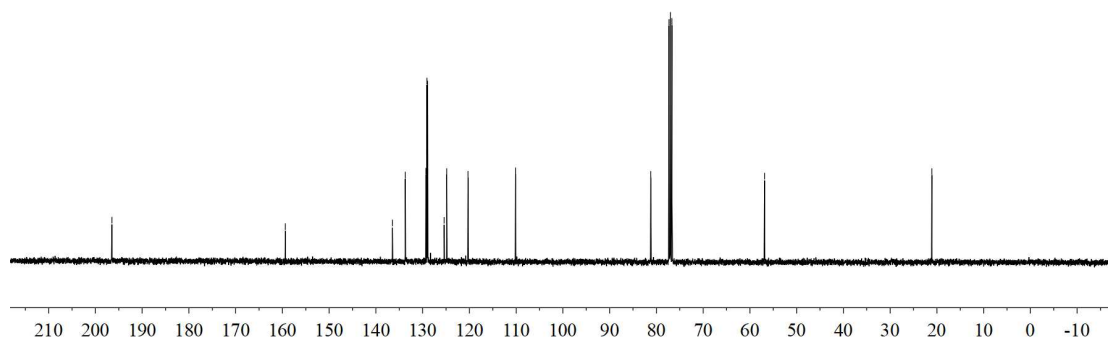
81.200  
77.318  
77.000  
76.682

-56.874

-21.077



<sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>Cl)



**(Z)-N-((2-Methyl-5-(phenylethynyl)benzofuran-3(H)-ylidene)(phenyl)methyl)acetamide (6)**

