

## Supporting Information

### Facile synthesis of 1,4-diketones via three-component reactions of $\alpha$ -ketoaldehyde, 1,3-dicarbonyl compound, and a nucleophile in water

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#### Table of Contents

1. General remarks.....	S2
2. Synthesis of 1,4-diketones (4a–4ag, 4ah, 5a–5k).....	S2
3. Synthesis of 6a, 6b and 6c.....	S2
4. Synthesis of 7a.....	S3
5. Synthesis of 7b.....	S3
6. Synthesis of 8a.....	S3
7. Synthesis of 9a.....	S3
8. Synthesis of 10a.....	S3
9. Synthesis of 11a and 11b.....	S3
10. Spectroscopic data of products.....	S4
11. Copy of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra.....	S14

## 1. General remarks

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Indole, 2-methylindole, 5-bromoindole, methyl 3-oxovalerate, *N,N*-dimethylaniline, and benzoylformic acid were purchased from Energy Chemical Company. 2-Methoxyethyl acetoacetate, ethyl 4-chloroacetoacetate, 1,2,3,4-tetrahydroquinoline, 1-methylpyrrole, benzyl mercaptan, and glyoxal dimethyl acetal were purchased from Alfa Aesar Chemical Company. 6-Methylindole, 5-methoxyindole, 4-nitroindole, and ethyl-3-(2-furyl)-3-oxopranone were purchased from Accela ChemBio Co., Ltd. 2-Methylfuran was purchased from Aladdin Industrial Corporation. Methyl acetoacetate, ethyl acetoacetate, and 2,4-pentanedione were purchased from Sinopharm Chemical Reagent Co., Ltd. Pyruvic aldehyde, 5-methoxy-7-methylindole, 5-fluoro-2-methylindole, 7-ethyl-1*H*-indole, 4-chloroindole, and 6-bromoindole were purchased from Adamas Reagent Co., Ltd. 6-Nitroindole, 5-methylindole, 7-azaindole, 5-methyl-1*H*-pyrrolo[2,3-*b*]pyridine, 3,4-(methylenedioxy) phenylglyoxal hydrate, 5-bromo-2-thiopheneglyoxal hydrate, and 4-bromophenylglyoxal hydrate were purchased from BePharm Co., Ltd. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV-400. Chemical shifts are expressed in ppm relative to Me<sub>4</sub>Si in CDCl<sub>3</sub> or DMSO-d<sub>6</sub>. IR spectra were recorded on a FT-IR Bruker (EQUINOX 55). Unless otherwise noted, all reactions were conducted in a 10 mL of V-type flask equipped with triangle magnetic stirring.

## 2. Synthesis of 1,4-diketones (**4a–4ag**, **4ah**, **5a–5k**)

In a typical reaction, an aqueous solution of pyruvic aldehyde **1a** (90.0 mg, 0.5 mmol, 40 wt%) was mixed with 2,4-pentanedione **2a** (50.0 mg, 0.5 mmol) and indole **3a** (58.5 mg, 0.5 mmol) in water (1.0 mL) under air. The mixture was then stirred at 80 °C for 5 h. After reaction completion, the mixture was cooled to room temperature and then extracted with ethyl acetate (1.5 ml × 3). The organic phases were combined, and subjected to isolation with preparative TLC [eluting solution: petroleum ether/ethyl acetate = 3/1 (v/v)]. Tests for substrate scope were all performed with an analogous procedure. Large scale synthesis of **4a** was performed also in the similar procedure. The product **4a** was isolated by silica column chromatography.

## 3. Synthesis of **6a**, **6b** and **6c**

In a 10 mL of V-type flask equipped with triangle magnetic stirring, **1c** (53.5 mg, 0.5 mmol), **2a** (50.0 mg, 0.5 mmol) and **3b** (80.5 mg, 0.5 mmol) was mixed in EtOH (1.0 mL, 50 wt%). The mixture was then stirred 4 hours under 80 °C. After reaction, the mixture was cooled to room temperature, and the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether / ethyl acetate = 3 / 1 (v/v)). The desired product **6a** was obtained in 67 % yield, 105.6 mg.

In a 10 mL of V-type flask equipped with triangle magnetic stirring, **1d** (53.5 mg, 0.5 mmol), **2a** (50.0 mg, 0.5 mmol) and **3b** (80.5 mg, 0.5 mmol) was mixed in EtOH (1.0 mL, 50 wt%), The mixture was then stirred 4 hours under 80 °C. After reaction, the mixture was cooled to room temperature, and the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether / ethyl acetate = 3 / 1 (v/v)). The desired product **6b** was obtained below 5 % yield.

In a 10 mL of V-type flask equipped with triangle magnetic stirring, **1e** (87.0 mg, 0.5 mmol, 60 wt%), **2a** (50.0 mg, 0.5 mmol) and **3a** (58.5 mg, 0.5 mmol) was mixed in EtOH (1.0 mL, 50 wt%). The mixture was then stirred 4 hours under 80 °C. After reaction, the mixture was cooled to room temperature, and the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether / ethyl acetate = 3/1 (v/v)). The desired product **6c** was obtained in 86 % yield, 130.6 mg.

#### 4. Synthesis of **7a**

Compound **4a** (135.5 mg, 0.5 mmol) mixed with EtOH (1.0 mL) and PTSA (17.2 mg, 20 mol %) in a 10 mL of V-type flask equipped with triangle magnetic stirring. The mixture was then stirred at 60 °C for 3 hours. After reaction, the mixture was cooled to room temperature, and the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether / ethyl acetate = 5/1 (v/v)). The desired product **7a** was obtained in 89 % yield, 112.6 mg.

#### 5. Synthesis of **7b**

Compound **4a** (135.5 mg, 0.5 mmol) mixed with EtOH (1.0 mL) and Sc(OTf) (12.2 mg, 5 mol %) in a 10 mL of V-type flask equipped with triangle magnetic stirring. The mixture was then stirred at 80 °C for 5 hours. After reaction, the mixture was cooled to room temperature, and the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether / ethyl acetate = 5/1 (v/v)). The desired product **7b** was obtained in 55 % yield, 58.0 mg.

#### 6. Synthesis of **8a**

In a 10 mL of V-type flask equipped with triangle magnetic stirring, **4a** (135.5 mg, 0.5 mmol) and **12a** (80.3 mg, 0.75 mmol) was mixed in water (1.0 mL). The mixture was then stirred 6 hours under 100 °C. After reaction, the mixture was cooled to room temperature and then extracted with ethyl acetate (1.5 ml × 3). The organic phase was combined together, and then subjected to isolation with preparative TLC (eluting solution: petroleum ether / ethyl acetate = 3/1 (v/v)). The desired product **8a** was obtained in 74 % yield, 126.5 mg.

#### 7. Synthesis of **9a**

Compound **4a** (135.5 mg, 0.5 mmol) mixed with EtOH (1.0 mL) and K<sub>2</sub>CO<sub>3</sub> (69.0 mg, 0.5 mmol) in a 10 mL of V-type flask equipped with triangle magnetic stirring. The mixture was then stirred at 80 °C for 1h. After reaction, the mixture was cooled to room temperature, and the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether / ethyl acetate = 3/1 (v/v)). The desired product **9a** was obtained in 62 % yield, 71.0 mg.

#### 8. Synthesis of **10a**

Compound **4a** (135.5 mg, 0.5 mmol) mixed with EtOH (1.0 mL) and K<sub>2</sub>CO<sub>3</sub> (138.0 mg, 1.0 mmol) in a 10 mL of V-type flask equipped with triangle magnetic stirring. The mixture was then stirred at 80 °C for 10 h. After reaction, the mixture was cooled to room temperature, and the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether / ethyl acetate = 3/1 (v/v)). The desired product **10a** was obtained in 40 % yield, 44.2 mg.

#### 9. Synthesis of **11a** and **11b**

Compound **4a** (135.5 mg, 0.5 mmol) mixed with CH<sub>3</sub>CN (1.0 mL) and K<sub>2</sub>CO<sub>3</sub> (69.0 mg, 0.5 mmol) in a 10 mL of V-type flask equipped with triangle magnetic stirring. The mixture was then stirred at 80 °C for 10 hours. After reaction, the mixture was cooled to room temperature, and the product was obtained by isolation with preparative TLC (eluting solution: petroleum ether / ethyl acetate = 3/1 (v/v)). The desired product **11a** was obtained in 48 % yield, 60.7 mg and product **11b** was obtained in 42 % yield, 53.2 mg.

## 10. Spectroscopic data of products

**3-Acetyl-4-(1*H*-indol-3-yl)hexane-2,5-dione (**4a**):** Brown solid, mp: 100 – 102 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.80 (s, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 7.03 (d, J = 2.4 Hz, 1H), 4.84 (s, 2H), 2.33 (s, 3H), 2.07 (s, 3H), 1.85 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.5, 203.5, 202.5, 136.5, 126.0, 124.2, 122.8, 120.5, 118.6, 111.8, 108.5, 69.4, 50.4, 30.4, 30.3, 28.3 ppm. IR (film): 3399, 2926, 1701, 1422, 1356, 1250, 746, 426 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>17</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 294.1106, found 294.1102.

**3-Acetyl-4-(4-hydroxy-1*H*-indol-3-yl)hexane-2,5-dione (**4b**):** Brown viscous liquid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 25 °C) δ = 10.99 (s, 1H), 9.69 (s, 1H), 7.07 (s, 1H), 6.87 (t, J = 8.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 7.6 Hz, 1H), 5.23 (s, 1H), 4.68 (d, J = 11.6 Hz, 1H), 2.23 (s, 3H), 1.98 (s, 3H), 1.90 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C) δ = 206.6, 203.4, 202.9, 151.6, 138.8, 123.6, 122.9, 116.2, 108.5, 104.0, 103.8, 70.6, 30.6, 29.6, 28.2 ppm. IR (film): 3391, 2924, 1696, 1457, 1355, 1271, 1041, 740, 567 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>17</sub>NNaO<sub>4</sub>, [M + Na]<sup>+</sup> 310.1055, found 310.1047.

**3-Acetyl-4-(4-chloro-1*H*-indol-3-yl)hexane-2,5-dione (**4c**):** Yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 9.10 (s, 1H), 7.34 – 7.30 (m, 1H), 7.18 – 7.15 (m, 2H), 7.03 (d, J = 2.4 Hz, 1H), 5.89 (d, J = 11.2 Hz, 1H), 4.57 (d, J = 11.6 Hz, 1H), 2.34 (s, 3H), 2.18 (s, 3H), 2.00 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.6, 203.6, 203.1, 137.6, 125.4, 125.2, 123.3, 122.7, 121.9, 110.8, 109.2, 72.4, 48.0, 30.2, 28.7, 28.0 ppm. IR (film): 3371, 2924, 1699, 1422, 1357, 1192, 937, 738, 568, 502 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>16</sub>ClNNaO<sub>3</sub>, [M + Na]<sup>+</sup> 328.0716, found 328.0715.

**3-Acetyl-4-(5-bromo-1*H*-indol-3-yl)hexane-2,5-dione (**4d**):** Yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.59 (s, 1H), 7.76 (s, 1H), 7.31 (d, J = 8.8 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 7.07 (d, J = 1.6 Hz, 1H), 4.78 (s, 2H), 2.33 (s, 3H), 2.09 (s, 3H), 1.87 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.0, 203.0, 202.1, 135.0, 127.7, 125.9, 125.3, 121.2, 113.9, 113.2, 108.4, 69.3, 50.1, 30.4, 30.3, 28.4 ppm. IR (film): 3413, 2937, 1701, 1456, 1356, 1194, 802, 607, 423 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>16</sub>BrNNaO<sub>3</sub>, [M + Na]<sup>+</sup> 372.0211, found 372.0209.

**3-Acetyl-4-(5-methyl-1*H*-indol-3-yl)hexane-2,5-dione (**4e**):** Brownish solid, mp: 148–150 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.56 (s, 1H), 7.38 (s, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 6.98 (d, J = 2.4 Hz, 1H), 4.81 (s, 2H), 2.46 (s, 3H), 2.33 (s, 3H), 2.07 (s, 3H), 1.85 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.6, 203.4, 202.5, 134.8, 129.8, 126.3, 124.4, 124.2, 118.1, 111.4, 108.0, 69.4, 50.4, 30.4, 30.2, 28.2, 21.6 ppm. IR (film): 3384, 2918, 1724, 1697, 1355, 1263, 1157, 1100, 790, 618, 559 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>17</sub>H<sub>19</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 308.1263, found 308.1262.

**3-Acetyl-4-(5-methoxy-1*H*-indol-3-yl)hexane-2,5-dione (**4f**):** Brownish viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.68 (s, 1H), 7.26 (d, J = 8.8 Hz, 1H), 7.05 (s, 1H), 7.00 (s, 1H),

6.88 (d,  $J$  = 8.4 Hz, 1H), 4.80 (s, 2H), 3.87 (s, 3H), 2.32 (s, 3H), 2.09 (s, 3H), 1.86 ppm (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 206.4, 203.5, 202.5, 154.7, 131.6, 126.6, 124.7, 112.9, 112.5, 108.1, 100.4, 69.2, 55.9, 50.3, 30.4, 30.3, 28.3 ppm. IR (film): 3397, 2941, 1701, 1582, 1486, 1356, 1254, 1216, 1030, 801, 637, 562  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{17}\text{H}_{19}\text{NNaO}_4$ , [M + Na]<sup>+</sup> 324.1212, found 324.1208.

**3-(4-Acetyl-2,5-dioxohexan-3-yl)-1*H*-indole-5-carboxylic acid (4g):** Brown solid, mp: 225–227 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , 25 °C)  $\delta$  = 12.49 (s, 1H), 11.53 (s, 1H), 8.23 (s, 1H), 7.74 (dd,  $J$  = 8.4, 1.2 Hz, 1H), 7.48 (d,  $J$  = 2.4 Hz, 1H), 7.44 (d,  $J$  = 8.8 Hz, 1H), 4.85 (d,  $J$  = 11.2 Hz, 1H), 4.80 (d,  $J$  = 11.6 Hz, 1H), 2.25 (s, 3H), 2.00 (s, 3H), 1.86 ppm (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ , 25 °C)  $\delta$  = 206.2, 203.5, 202.6, 168.7, 139.4, 127.6, 125.9, 123.2, 122.4, 121.7, 112.2, 109.2, 68.8, 50.0, 30.9, 30.5, 28.3 ppm. IR (film): 3317, 3005, 1703, 1358, 1243, 998, 757, 428  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{17}\text{H}_{17}\text{NNaO}_5$ , [M + Na]<sup>+</sup> 338.1004, found 338.1001.

**3-Acetyl-4-(6-fluoro-1*H*-indol-3-yl)hexane-2,5-dione (4h):** Yellow viscous liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C)  $\delta$  = 8.86 (s, 1H), 7.54 – 7.51 (m, 1H), 7.08 – 7.05 (m, 2H), 6.92 (t,  $J$  = 9.2 Hz, 1H), 4.81 (s, 2H), 2.33 (s, 3H), 2.09 (s, 3H), 1.87 ppm (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 206.4, 203.3, 202.4, 160.1. ( $J$  = 237.7 Hz), 136.5. ( $J$  = 12.5 Hz), 124.5, 122.6, 119.5. ( $J$  = 10.1 Hz), 109.4. ( $J$  = 20.6 Hz), 108.6. ( $J$  = 2.3 Hz), 98.1. ( $J$  = 25.9 Hz), 69.26, 50.35, 30.43, 30.36, 28.24 ppm.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = -119.93, -119.94, -119.95, -119.97 ppm. IR (film): 3375, 2936, 1700, 1627, 1354, 1255, 1093, 949, 804, 567, 431  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{16}\text{H}_{16}\text{FNNaO}_3$ , [M + Na]<sup>+</sup> 312.1012, found 312.1010.

**Methyl 3-(4-acetyl-2,5-dioxohexan-3-yl)-1*H*-indole-6-carboxylate (4i):** Yellow viscous liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C)  $\delta$  = 9.48 (s, 1H), 8.18 (s, 1H), 7.85 (d,  $J$  = 8.4 Hz, 1H), 7.66 (d,  $J$  = 8.4 Hz, 1H), 7.28 (d,  $J$  = 2.0 Hz, 1H), 4.88 (d,  $J$  = 11.2 Hz, 1H), 4.83 (d,  $J$  = 11.2 Hz, 1H), 3.95 (s, 3H), 2.35 (s, 3H), 2.10 (s, 3H), 1.87 ppm (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 206.2, 203.2, 202.2, 168.0, 135.9, 129.5, 127.6, 124.4, 121.4, 118.3, 114.3, 108.9, 69.4, 52.1, 50.2, 30.4, 30.3, 28.3 ppm. IR (film): 3367, 2951, 1707, 1435, 1357, 1285, 1220, 983, 775, 567  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{18}\text{H}_{19}\text{NNaO}_5$ , [M + Na]<sup>+</sup> 352.1161, found 352.1157.

**3-Acetyl-4-(6-methyl-1*H*-indol-3-yl)hexane-2,5-dione (4j):** Brown viscous liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C)  $\delta$  = 8.51 (s, 1H), 7.50 (d,  $J$  = 8.4 Hz, 1H), 7.17 (s, 1H), 7.00 (d,  $J$  = 8.0 Hz, 1H), 6.96 (s, 1H), 4.81 (s, 2H), 2.45 (s, 3H), 2.32 (s, 3H), 2.07 (s, 3H), 1.84 ppm (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 206.5, 203.4, 202.5, 136.9, 132.7, 123.9, 123.5, 122.3, 118.3, 111.6, 108.4, 69.5, 50.4, 30.3, 30.2, 28.2, 21.6 ppm. IR (film): 3397, 2923, 1703, 1356, 1252, 1155, 803, 266, 429  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{17}\text{H}_{19}\text{NNaO}_3$ , [M + Na]<sup>+</sup> 308.1263, 308.1269.

**3-Acetyl-4-(6-nitro-1*H*-indol-3-yl)hexane-2,5-dione (4k):** Yellow viscous liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C)  $\delta$  = 11.43 (s, 1H), 8.39 (d,  $J$  = 2.0 Hz, 1H), 8.00 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 7.67 (d,  $J$  = 8.8 Hz, 1H), 7.43 (d,  $J$  = 2.4 Hz, 1H), 4.83 (q,  $J$  = 11.6 Hz, 2H), 2.33 (s, 3H), 2.09 (s, 3H), 1.87 ppm (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 205.7, 202.4, 201.7, 143.1, 135.3, 130.5, 118.4, 115.1, 109.1, 108.7, 69.2, 49.8, 30.4, 30.2, 28.2 ppm. IR (film): 3380, 2924, 1704, 1511, 1340, 1063, 736, 567, 425  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{NaO}_5$ , [M + Na]<sup>+</sup> 339.0957, found 339.0950.

**3-Acetyl-4-(7-bromo-1*H*-indol-3-yl)hexane-2,5-dione (4l):** Brown viscous liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C)  $\delta$  = 8.80 (s, 1H), 7.54 (d,  $J$  = 1.2 Hz, 1H), 7.48 (d,  $J$  = 8.8 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.04 (d,  $J$  = 2.4 Hz, 1H), 4.80 (s, 2H), 2.33 (s, 3H), 2.08 (s, 3H), 1.86 ppm (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 206.2, 203.2, 202.2, 137.3, 124.9, 124.8, 124.7, 123.9, 123.8, 120.0, 116.4, 114.8, 114.7, 108.8, 69.3, 50.2, 30.5, 30.4, 28.3 ppm. IR (film): 3382, 2923, 1702,

1418, 1357, 1252, 1155, 895, 805, 732, 568, 425 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>16</sub>BrNNaO<sub>3</sub>, [M + Na]<sup>+</sup> 372.0211, found 372.0214.

**3-Acetyl-4-(7-ethyl-1*H*-indol-3-yl)hexane-2,5-dione (4m):** Brown solid, mp: 129 – 131 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.58 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 4.85 (d, J = 11.2 Hz, 1H), 4.80 (d, J = 11.2 Hz, 1H), 2.84 (q, J = 7.6 Hz, 2H), 2.33 (s, 3H), 2.09 (s, 3H), 1.86 (s, 3H), 1.34 ppm (t, J = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.5, 203.4, 202.5, 135.3, 127.1, 125.9, 123.7, 121.2, 120.8, 116.3, 109.1, 69.6, 50.4, 30.3, 30.0, 28.3, 23.8, 13.7 ppm. IR (film): 3380, 2963, 1726, 1697, 1432, 1357, 1263, 1151, 796, 752, 628, 562, 463 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>18</sub>H<sub>21</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 322.1419, found 322.1411.

**3-Acetyl-4-(5-methoxy-7-methyl-1*H*-indol-3-yl)hexane-2,5-dione (4n):** Brown solid, mp: 167 – 169 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.52 (s, 1H), 7.00 (d, J = 2.4 Hz, 1H), 6.89 (d, J = 1.2 Hz, 1H), 6.71 (s, 1H), 4.81 – 4.75 (m, 2H), 3.86 (s, 3H), 2.43 (s, 3H), 2.32 (s, 3H), 2.10 (s, 3H), 1.87 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.4, 203.4, 202.6, 154.8, 131.3, 126.1, 124.2, 122.1, 113.6, 108.7, 97.8, 69.4, 55.9, 50.3, 30.3, 30.2, 28.3, 16.6 ppm. IR (film): 3386, 2941, 1723, 1699, 1488, 1357, 1261, 1208, 1051, 828, 572 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>18</sub>H<sub>21</sub>NNaO<sub>4</sub>, [M + Na]<sup>+</sup> 338.1368, found 338.1363.

**3-Acetyl-4-(2-methyl-1*H*-indol-3-yl)hexane-2,5-dione (4o):** Yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.35 (s, 1H), 7.47 (s, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.15 – 7.09 (m, 2H), 5.00 (s, 1H), 4.76 (s, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 2.00 (s, 3H), 1.79 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.70, 203.2, 202.1, 135.5, 134.0, 126.9, 121.7, 120.2, 118.1, 110.9, 103.8, 66.6, 50.8, 31.6, 30.5, 27.9, 11.6 ppm. IR (film): 3391, 2926, 1703, 1460, 1427, 1356, 1252, 746, 435 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>17</sub>H<sub>19</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 308.1263, found 308.1267.

**3-Acetyl-4-(5-fluoro-2-methyl-1*H*-indol-3-yl)hexane-2,5-dione (4p):** White solid, mp: 167 – 169 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.50 (s, 1H), 7.21 – 7.15 (m, 2H), 6.89 – 6.85 (m, 1H), 4.96 (s, 1H), 4.73 (s, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 2.02 (s, 3H), 1.83 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.4, 203.0, 202.0, 159.2, 156.9, 136.0, 131.9, 111.5 (J = 9.7 Hz), 109.8 (J = 26.0 Hz), 104.0, 103.2, 66.4, 50.5, 31.7, 30.5, 28.0, 11.7 ppm. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ = -123.21, -123.21, -123.23, -123.24 ppm. IR (film): 3373, 2924, 1703, 1584, 1484, 1453, 1357, 1253, 1186, 966, 732, 608 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>17</sub>H<sub>18</sub>FNNaO<sub>3</sub>, [M + Na]<sup>+</sup> 326.1168, found 326.1163.

**3-Acetyl-4-(1-ethyl-2-methyl-1*H*-indol-3-yl)hexane-2,5-dione (4q):** Brownish solid, mp: 116 – 118 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 7.45 (s, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.17 (t, J = 6.8 Hz, 1H), 7.09 (s, 1H), 5.00 (s, 1H), 4.75 (s, 1H), 4.13 (dd, J = 10.6 Hz, 6.4 Hz, 2H), 2.44 (s, 3H), 2.33 (s, 3H), 2.00 (s, 3H), 1.74 (s, 3H), 1.30 ppm (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.7, 203.1, 201.7, 135.9, 134.7, 126.1, 121.2, 119.7, 118.5, 109.1, 103.5, 66.5, 51.2, 38.0, 31.6, 30.5, 27.9, 15.2, 9.9 ppm. IR (film): 3401, 2974, 1693, 1468, 1419, 1348, 1192, 745, 484 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>19</sub>H<sub>23</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 336.1576, found 336.1578.

**3-Acetyl-4-(1-methyl-1*H*-indol-3-yl)hexane-2,5-dione (4r):** Yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 7.62 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.16 (t, J = 7.6 Hz, 1H), 6.93 (s, 1H), 4.80 (q, J = 11.6 Hz, 2H), 3.75 (s, 3H), 2.32 (s, 3H), 2.09 (s, 3H), 1.85 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.2, 203.0, 202.4, 137.2, 128.4, 126.7, 122.3, 120.1, 118.8, 109.7, 107.1, 69.7, 50.1, 32.9, 30.3, 29.9, 28.3 ppm. IR (film): 3402, 2936, 1704, 1473, 1424, 1356, 1259, 1155, 745, 429 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>17</sub>H<sub>19</sub>NNaO<sub>3</sub>, [M +

$\text{Na}^+$  308.1263, found 308.1262.

**Ethyl 3-acetyl-2-(1*H*-indol-3-yl)-4-oxopentanoate (4s):** Brown viscous liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C)  $\delta$  = 8.34 (s, 1H), 7.77 (d,  $J$  = 7.6 Hz, 1H), 7.34 (d,  $J$  = 8.0 Hz, 1H), 7.27 – 7.16 (m, 2H), 7.04 (d,  $J$  = 2.4 Hz, 1H), 4.82 (d,  $J$  = 11.6 Hz, 1H), 4.74 (d,  $J$  = 12.0 Hz, 1H), 4.17 – 4.09 (m, 1H), 4.03 – 3.95 (m, 1H), 2.33 (s, 3H), 1.87 (s, 3H), 1.13 ppm (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 202.6, 202.3, 172.5, 136.2, 126.1, 123.3, 122.6, 120.2, 119.3, 111.5, 109.6, 70.4, 61.5, 42.5, 30.0, 29.4, 14.0 ppm. IR (film): 3403, 2983, 1725, 1423, 1358, 1253, 1189, 1160, 1099, 1019, 746, 505  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{17}\text{H}_{19}\text{NNaO}_4$ ,  $[\text{M} + \text{Na}]^+$  324.1212, found 324.1216.

**3-Acetyl-1-cyclopropyl-2-(5-methoxy-1*H*-indol-3-yl)pentane-1,4-dione (4t):** Yellow solid, mp: 162 – 164 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ , 25 °C)  $\delta$  = 11.01 (s, 1H), 7.28 – 7.24 (m, 2H), 7.01 (d,  $J$  = 2.0 Hz, 1H), 6.75 (dd,  $J$  = 8.8, 2.4 Hz, 1H), 4.90 (d,  $J$  = 11.2 Hz, 1H), 4.79 (d,  $J$  = 11.2 Hz, 1H), 3.75 (s, 3H), 2.22 (s, 3H), 2.00 – 1.96 (m, 1H), 1.85 (s, 3H), 0.86 – 0.79 (m, 1H), 0.74 – 0.54 ppm (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ , 25 °C)  $\delta$  = 208.0, 203.6, 202.6, 154.0, 132.0, 127.1, 126.3, 112.9, 111.8, 107.5, 100.9, 68.7, 55.9, 50.3, 30.7, 30.7, 19.6, 11.4, 10.8 ppm. IR (film): 3377, 2939, 1727, 1694, 1485, 1357, 1218, 1063, 1026, 804, 629, 560  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{19}\text{H}_{21}\text{NNaO}_4$ ,  $[\text{M} + \text{Na}]^+$  350.1368, found 350.1361.

**3-Acetyl-1-(benzofuran-2-yl)-2-(1*H*-indol-3-yl)pentane-1,4-dione (4u):** Brown viscous liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C)  $\delta$  = 8.59 (s, 1H), 7.86 (d,  $J$  = 7.2 Hz, 1H), 7.52 (d,  $J$  = 8.0 Hz, 1H), 7.47 (s, 1H), 7.43 (d,  $J$  = 8.4 Hz, 1H), 7.35 (t,  $J$  = 8.0 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.19 – 7.14 (m, 4H), 5.63 (d,  $J$  = 11.4 Hz, 1H), 5.09 (d,  $J$  = 11.4 Hz, 1H), 2.32 (s, 3H), 1.92 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 203.3, 202.1, 188.2, 155.5, 151.3, 136.4, 128.3, 127.0, 125.9, 124.3, 123.8, 123.3, 122.67, 120.5, 119.1, 114.2, 112.3, 111.7, 108.7, 69.7, 45.5, 31.1, 30.3. IR (film): 3400, 3060, 1726, 1699, 1553, 1356, 1244, 1139, 910, 746, 612, 428  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{23}\text{H}_{19}\text{NNaO}_4$ ,  $[\text{M} + \text{Na}]^+$  396.1212, found 396.1211.

**3-Acetyl-1-(benzo[d][1,3]dioxol-5-yl)-2-(1*H*-indol-3-yl)pentane-1,4-dione (4v):** Yellow viscous liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C)  $\delta$  = 8.43 (s, 1H), 7.72 – 7.69 (m, 1H), 7.61 (dd,  $J$  = 8.4, 1.6 Hz, 1H), 7.40 (d,  $J$  = 1.6 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.16 – 7.13 (m, 2H), 7.03 (d,  $J$  = 2.0 Hz, 1H), 6.66 (d,  $J$  = 8.4 Hz, 1H), 5.90 (s, 2H), 5.58 (d,  $J$  = 10.8 Hz, 1H), 5.03 (d,  $J$  = 10.8 Hz, 1H), 2.29 (s, 3H), 1.87 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 203.9, 202.2, 195.9, 151.7, 147.9, 136.4, 130.4, 125.7, 125.2, 123.9, 122.6, 120.5, 119.0, 111.6, 109.8, 108.6, 107.9, 101.7, 70.3, 45.3, 31.5, 30.3 ppm. IR (film): 3401, 2908, 1726, 1689, 1669, 1606, 1501, 1441, 1357, 1258, 1038, 744, 501, 430  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{22}\text{H}_{19}\text{NNaO}_5$ ,  $[\text{M} + \text{Na}]^+$  400.1161, found 400.1164.

**3-Acetyl-2-(1*H*-indol-3-yl)-1-phenylpentane-1,4-dione (4w):** Brown viscous liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C)  $\delta$  = 8.55 (s, 1H), 7.93 (d,  $J$  = 7.4 Hz, 2H), 7.72 – 7.70 (m, 1H), 7.35 (t,  $J$  = 7.6 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.15 – 7.12 (m, 2H), 6.98 (d,  $J$  = 2.4 Hz, 1H), 5.67 (d,  $J$  = 11.2 Hz, 1H), 5.05 (d,  $J$  = 11.2 Hz, 1H), 2.27 (s, 3H), 1.85 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  = 204.1, 202.4, 197.9, 136.4, 135.8, 133.1, 128.7, 128.5, 125.7, 124.2, 122.6, 120.4, 118.9, 111.7, 109.0, 70.2, 45.5, 31.6, 30.3. IR (film): 3398, 2934, 1725, 2696, 1597, 1355, 1264, 744, 691, 560, 504, 427  $\text{cm}^{-1}$ . HRMS-ESI (m/z) calcd for  $\text{C}_{21}\text{H}_{19}\text{NNaO}_3$ ,  $[\text{M} + \text{Na}]^+$  356.1263, found 356.1266.

**3-Acetyl-1-(4-bromophenyl)-2-(1*H*-indol-3-yl)pentane-1,4-dione (4x):** Brown viscous liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, 25 °C)  $\delta$  = 8.51 (s, 1H), 7.78 (d,  $J$  = 8.4 Hz, 2H), 7.69 – 7.67 (m, 1H), 7.39 (d,  $J$  = 8.4 Hz, 2H), 7.29 – 7.27 (m, 1H), 7.16 – 7.14 (m, 2H), 7.00 (d,  $J$  = 2.0 Hz, 1H), 5.59 (d,  $J$  = 11.2 Hz, 1H), 5.03 (d,  $J$  = 11.2 Hz, 1H), 2.29 (s, 3H), 1.87 ppm (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,

25 °C) δ = 203.7, 202.1, 196.8, 136.4, 134.6, 131.7, 130.2, 128.1, 125.6, 124.1, 122.8, 120.6, 118.8, 111.7, 108.8, 70.1, 45.4, 31.6, 30.3 ppm. IR (film): 3398, 3059, 1725, 1677, 1584, 1421, 1355, 1262, 1173, 1071, 909, 789, 742, 509, 426 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>21</sub>H<sub>18</sub>BrNNaO<sub>3</sub>, [M + Na]<sup>+</sup> 434.0368, found 434.0362.

**Methyl 2-acetyl-3-(1*H*-indol-3-yl)-4-oxopentanoate (4y):** A mixture of diastereomers, yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.75 (s, 0.5H), 8.68 (s, 0.5H), 7.61 (t, J = 6.8 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.21 – 7.18 (m, 1H), 7.15 – 7.11 (m, 1H) 7.05 (dd, J = 6.4, 2.4 Hz, 1H), 4.86 (d, J = 11.6 Hz, 0.5H), 4.76 (d, J = 11.6 Hz, 0.5H), 4.65 (d, J = 11.6 Hz, 0.5H), 4.55 (d, J = 11.2 Hz, 0.5H), 3.74 (s, 1.4H), 3.39 (s, 1.6H), 2.37 (s, 1.6H), 2.11 (s, 1.3H), 2.09 (s, 1.5H), 1.85 ppm (s, 1.4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.7, 206.5, 203.3, 202.0, 169.2, 168.2, 136.5, 136.4, 126.3, 126.0, 124.5, 124.0, 122.7, 122.5, 120.4, 120.1, 118.9, 118.8, 111.7, 111.6, 108.7, 108.1, 62.0, 60.0, 52.7, 52.5, 49.7, 49.6, 31.4, 29.9, 28.5, 28.4 ppm. IR (film): 3402, 2953, 1743, 1710, 1429, 2355, 1266, 1159, 747, 427 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>17</sub>NNaO<sub>4</sub>, [M + Na]<sup>+</sup> 310.1055, found 310.1051.

**Ethyl 2-acetyl-3-(1*H*-indol-3-yl)-4-oxopentanoate (4z):** A mixture of diastereomers, yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.77 – 8.72 (m, 1H), 7.64 – 7.61, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 6.8, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.06 – 7.04 (m, 1H), 4.85 (d, J = 11.2 Hz, 0.6H), 4.77 (d, J = 11.6 Hz, 0.4H), 4.65 (d, J = 11.6 Hz, 0.4H), 4.56 (d, J = 11.2 Hz, 0.6H), 4.20 (q, J = 7.2 Hz, 0.8H), 3.83 (q, J = 7.2 Hz, 1.1H), 2.37 (s, 1.7H), 2.12 (s, 1.2H), 2.10 (s, 1.5H), 1.87 (s, 1.2H), 1.27 (t, J = 7.2 Hz, 1.5H), 0.84 ppm (t, J = 7.2 Hz, 1.7H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.7, 206.4, 203.3, 202.1, 168.7, 167.9, 136.5, 136.4, 126.4, 126.0, 124.4, 124.0, 122.6, 122.5, 120.4, 120.1, 118.9, 118.9, 111.70, 111.5, 108.8, 108.2, 62.1, 61.8, 61.4, 60.2, 49.6, 49.4, 31.4, 29.7, 28.5, 28.4, 14.0, 13.6 ppm. IR (film): 3401, 2983, 1739, 1710, 1357, 1266, 1159, 746, 426 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>17</sub>H<sub>19</sub>NNaO<sub>4</sub>, [M + Na]<sup>+</sup> 324.1212, found 324.1209.

**Ethyl 2-benzoyl-3-(1*H*-indol-3-yl)-4-oxopentanoate (4aa):** A mixture of diastereomers, yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.73 (d, J = 11.2 Hz, 0.6H), 8.45 (d, J = 10.8 Hz, 0.4H), 8.12 (d, J = 7.6 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.57 (t, J = 7.2 Hz, 0.6H), 7.46 (t, J = 7.6 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.22 – 7.08 (m, 4H), 6.94 (d, J = 2.0 Hz, 0.4H), 5.49 (d, J = 11.2 Hz, 0.4H), 5.30 (d, J = 11.2 Hz, 0.6H), 5.13 (d, J = 11.2 Hz, 0.6H), 5.03 (d, J = 11.2 Hz, 0.4H), 4.16 (q, J = 3.6 Hz, 0.7H), 3.72 (q, J = 7.2 Hz, 1H), 2.15 (s, 3H), 1.18 (t, J = 7.2 Hz, 1.3H), 0.70 ppm (t, J = 7.2 Hz, 1.7H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 207.1, 206.4, 195.5, 193.9, 168.9, 168.4, 136.6, 136.5, 136.3, 136.0, 133.7, 133.2, 128.9, 128.7, 128.6, 128.2, 126.6, 126.1, 124.4, 124.2, 122.5, 122.3, 120.2, 120.1, 119.0, 118.9, 111.6, 111.4, 108.7, 108.3, 61.8, 61.4, 57.4, 54.9, 50.4, 50.0, 28.6, 28.6, 14.0, 13.4 ppm. IR (film): 3398, 2936, 1735, 1711, 1453, 1349, 1278, 1160, 745, 690, 427 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>22</sub>H<sub>21</sub>NNaO<sub>4</sub>, [M + Na]<sup>+</sup> 386.1368, found 386.1364.

**2-Methoxyethyl 2-acetyl-3-(1*H*-indol-3-yl)-4-oxopentanoate (4ab):** A mixture of diastereomers, brown viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.74 – 8.65 (m, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.05 (dd, J = 12.4, 2.4 Hz, 1H), 4.86 (d, J = 11.2 Hz, 0.6H), 4.77 (d, J = 11.2 Hz, 0.4H), 4.66 (d, J = 11.6 Hz, 0.6H), 4.60 (d, J = 11.2 Hz, 0.4H), 4.33 – 4.28 (m, 0.7H), 4.00 – 3.88 (m, 1.3H), 3.62 – 3.58 (m, 0.8H), 3.37 (s, 1.1H), 3.25 – 3.20 (m, 0.7H), 3.163 – 3.08 (m, 2.5H), 2.38 (s, 1.9H), 2.11 (s, 1.2H), 2.10 (s, 1.7H), 1.86 ppm (s, 1.1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.6, 206.3, 203.0, 201.8, 168.6, 167.8, 136.5, 136.4, 126.4, 126.0, 124.5, 124.2, 122.6, 122.5, 120.4, 120.1, 118.9, 118.9, 111.7, 111.5, 108.7, 108.2, 70.2, 69.8, 64.5, 64.1, 61.9, 60.2, 58.9, 58.6, 49.7, 49.5, 31.2, 29.7, 28.5, 28.3 ppm.

IR (film): 3401, 2930, 1742, 1711, 1457, 1424, 1356, 1267, 1030, 746, 554, 427 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>18</sub>H<sub>21</sub>NNaO<sub>5</sub>, [M + Na]<sup>+</sup> 354.1317, found 354.1321.

**Methyl 2-(cyclopropanecarbonyl)-3-(1*H*-indol-3-yl)-4-oxopentanoate (4ac):** A mixture of diastereomers, yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.56 (s, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.35 (dd, J = 8.0, 2.0 Hz, 1H), 7.19 (t, J = 7.2 Hz, 1H), 7.13 (dd, J = 15.6, 7.6 Hz, 1H), 7.06 (dd, J = 12.4, 2.4 Hz, 1H), 4.86 (d, J = 11.6 Hz, 0.5H), 4.80 (d, J = 11.6 Hz, 0.5H), 4.74 (d, J = 4.4 Hz, 0.6H), 4.71 (d, J = 4.0 Hz, 0.4H), 3.75 (s, 1.6H), 3.40 (s, 1.5H), 2.21 – 2.17 (m, 0.6H), 2.13 (d, J = 4.4 Hz, 3H), 1.71 – 1.65 (m, 0.5H), 1.19 – 1.08 (m, 1H), 1.06 – 0.92 (m, 1H), 0.79 – 0.73 (m, 0.6H), 0.68 – 0.61 (m, 0.6H), 0.50 – 0.44 (m, 0.6H), 0.36 – 0.29 ppm (m, 0.5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.5, 206.3, 205.2, 204.1, 169.5, 168.5, 136.4, 136.4, 126.4, 126.3, 124.4, 123.9, 122.5, 122.4, 120.3, 120.1, 119.0, 118.9, 111.5, 108.8, 108.5, 62.4, 60.2, 52.7, 52.4, 49.9, 48.7, 28.7, 28.4, 21.9, 20.6, 12.0, 11.8, 11.6, 11.5 ppm. IR (film): 3394, 2953, 1740, 1706, 1432, 1384, 1245, 1158, 1066, 746, 594, 427 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>18</sub>H<sub>19</sub>NNaO<sub>4</sub>, [M + Na]<sup>+</sup> 336.1212, found 336.1218.

**Methyl 3-(1*H*-indol-3-yl)-4-oxo-2-propionylpentanoate (4ad):** A mixture of diastereomers, yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.53 (d, J = 12.4 Hz, 1H), 7.60 (dd, J = 7.6, 4.8 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.2 Hz, 1H), 7.16 – 7.11 (m, 1H), 7.08 (d, J = 2.4 Hz, 0.5H), 7.05 (d, J = 2.4 Hz, 0.5H), 4.91 (d, J = 11.2 Hz, 0.5H), 4.77 (d, J = 11.6 Hz, 0.5H), 4.63 (d, J = 11.6 Hz, 0.5H), 4.53 (d, J = 11.2 Hz, 0.5H), 3.73 (s, 1.6H), 3.38 (s, 1.5H), 2.82 – 2.65 (m, 1H), 2.44- 1.34 (m, 0.6H), 2.12 (d, J = 10.8 Hz, 3H), 1.83 – 1.79 (m, 0.6H), 1.11 (t, J = 7.2 Hz, 1.5H), 0.65 (t, J = 7.2 Hz, 1.6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.7, 206.6, 205.9, 204.8, 169.2, 168.4, 136.4, 136.4, 126.3, 125.9, 124.3, 124.0, 122.7, 122.5, 120.4, 120.2, 119.1, 118.9, 111.6, 111.52, 109.0, 108.3, 61.1, 59.1, 52.7, 52.4, 49.9, 49.7, 38.0, 36.0, 28.5, 28.4, 7.6, 7.0. IR (film): 3401, 2951, 1743, 1710, 1353, 1268, 1160, 746, 597, 426 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>17</sub>H<sub>19</sub>NNaO<sub>4</sub>, [M + Na]<sup>+</sup> 324.1212, found 324.1210.

**3-Benzoyl-4-(1*H*-indol-3-yl)hexane-2,5-dione (4ae):** A mixture of diastereomers, brown viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.70 (s, 0.5H), 8.32 (s, 0.5H), 8.09 (d, J = 7.2 Hz, 1H), 7.01 – 7.64 (m, 1.6H), 7.62 – 7.57 (m, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.37 (dd, J = 16.0, 8.0 Hz, 1H), 7.23 – 7.16 (m, 2.5H), 7.13 (d, J = 2.4, 0.6H), 7.11 – 7.07 (m, 1H), 6.94 (d, J = 2.4 Hz, 0.5H), 5.73 (d, J = 10.8 Hz, 0.5H), 5.59 (d, J = 11.2 Hz, 0.5H), 5.14 (d, J = 11.2 Hz, 0.5H), 5.04 (d, J = 11.2 Hz, 0.5H), 2.22 (s, 1.5H), 2.14 (s, 1.6H), 2.11 (s, 1.5H), 1.83 ppm (s, 1.6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 207.3, 206.1, 203.3, 201.8, 195.8, 194.9, 136.8, 136.5, 136.3, 133.7, 133.4, 128.9, 128.4, 126.2, 126.1, 124.4, 124.3, 122.8, 122.4, 120.5, 120.2, 119.0, 118.7, 111.8, 111.4, 108.5, 108.5, 64.7, 63.1, 51.1, 50.8, 30.3, 29.4, 28.5, 28.4 ppm. IR (film): 3395, 3060, 1709, 1673, 1354, 1272, 1181, 977, 743, 694, 488 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>21</sub>H<sub>19</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 356.1263, found 356.1258.

**Allyl 2-acetyl-3-(1*H*-indol-3-yl)-4-oxopentanoate (4af):** A mixture of diastereomers, yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.68 (s, 0.4H), 8.60 (s, 0.6H), 7.61 (t, J = 7.6 Hz, 1H), 7.35 (dd, J = 8.4, 2.4 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.13 (t, J = 7.2 Hz, 1H), 7.05 (t, J = 2.8 Hz, 1H), 5.93 – 5.86 (m, 0.4H), 5.50 – 5.42 (m, 0.6H), 5.35 – 5.31 (m, 0.4H), 5.27 – 5.24 (m, 0.4H), 5.01 – 4.92 (m, 1.2H), 4.86 (d, J = 11.6 Hz, 0.6H), 4.77 (d, J = 11.6 Hz, 0.4H), 4.68 (d, J = 11.6 Hz, 0.5H), 4.64 (d, J = 6.0 Hz, 1H), 4.58 (d, J = 11.2 Hz, 0.6H), 4.27 – 4.25 (m, 1.2H), 2.37 (s, 1.8H), 2.11 (s, 1.2H), 2.10 (s, 1.8H), 1.86 ppm (s, 1.2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.6, 206.4, 203.2, 201.9, 168.3, 167.5, 136.5, 136.4, 131.46, 131.0, 126.4, 126.0, 124.4, 124.1, 122.7, 122.5,

120.4, 120.1, 118.9, 118.8, 118.7, 111.7, 111.5, 108.8, 108.1, 66.3, 66.0, 62.0, 60.1, 49.7, 49.5, 31.5, 29.8, 28.5, 28.4 ppm. IR (film): 3404, 2948, 1741, 1710, 1357, 1270, 1158, 936, 746, 426 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>18</sub>H<sub>19</sub>NNaO<sub>4</sub>, [M + Na]<sup>+</sup> 336.1212, found 336.1207.

**Ethyl 2-(furan-2-carbonyl)-3-(1*H*-indol-3-yl)-4-oxopentanoate (4ag):** A mixture of diastereomers, brownish viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.47 (s, 0.6H), 8.31 (s, 0.5H), 7.68 – 7.62 (m, 1.6H), 7.41 – 7.37 (m, 1.6H), 7.24 – 7.09 (m, 3H), 7.03 (d, J = 2.0 Hz, 0.4H), 7.00 (d, J = 3.6 Hz, 0.4H), 6.57 – 6.56 (m, 0.6H), 6.29 – 6.28 (m, 0.4H), 5.19 (d, J = 11.6 Hz, 0.5H), 5.09 – 5.03 (m, 1H), 4.99 (d, J = 11.2 Hz, 0.5H), 4.20 – 4.16 (m, 1H), 3.77 (q, J = 7.2 Hz, 1H), 2.17 (d, J = 6.4 Hz, 3H), 1.22 (t, J = 7.2 Hz, 1.4H), 0.76 (t, J = 7.2 Hz, 1.7H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.6, 206.1, 182.8, 182.0, 168.6, 168.1, 151.8, 151.6, 147.3, 136.3, 136.3, 126.6, 126.1, 124.5, 124.1, 122.5, 122.4, 120.2, 119.5, 119.3, 119.1, 119.0, 112.6, 112.4, 111.4, 111.3, 108.7, 108.2, 61.8, 61.4, 57.3, 55.5, 49.9, 49.1, 28.6, 14.0, 13.5. IR (film): 3398, 2982, 1734, 1711, 1672, 1463, 1354, 1300, 1159, 1098, 1019, 744, 593, 427 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>20</sub>H<sub>19</sub>NNaO<sub>5</sub>, [M + Na]<sup>+</sup> 376.1161, found 376.1155.

**Diethyl 2-(1-(1*H*-indol-3-yl)-2-oxopropyl)malonate (4ah):** Brown viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.67 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.04 (d, J = 2.4 Hz, 1H), 4.79 (d, J = 11.6 Hz, 1H), 4.37 (d, J = 11.6 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 3.81 – 3.78 (m, 2H), 2.16 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H), 0.78 ppm (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.1, 168.7, 168.3, 136.3, 126.4, 124.1, 122.5, 120.1, 118.9, 111.5, 108.2, 61.9, 61.3, 54.4, 49.2, 28.6, 14.0, 13.5. IR (film): 3397, 2982, 1742, 1714, 1459, 1275, 1158, 1099, 1032, 746 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>18</sub>H<sub>21</sub>NNaO<sub>5</sub>, [M + Na]<sup>+</sup> 354.1317, found 354.1321.

**3-Acetyl-4-(1-methyl-1*H*-pyrrol-2-yl)hexane-2,5-dione (5a):** Brown viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 6.57 (s, 1H), 6.06 (t, J = 3.2 Hz, 1H), 5.95 – 5.94 (m, 1H), 4.61 (dd, J = 16.8, J = 11.2 Hz, 2H), 3.62 (s, 3H), 2.29 (s, 3H), 2.04 (s, 3H), 1.96 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 203.8, 202.9, 201.2, 125.1, 123.6, 108.7, 108.0, 68.8, 49.9, 31.5, 30.9, 30.3, 28.1 ppm. IR (film): 3404, 2949, 1707, 1357, 1256, 1154, 720, 565, 489 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>13</sub>H<sub>17</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 258.1106, found 258.1102.

**3-Acetyl-4-(1,2,5-trimethyl-1*H*-pyrrol-3-yl)hexane-2,5-dione (5b):** Brown viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 5.55 (s, 1H), 4.52 (d, J = 11.2 Hz, 1H), 4.37 (d, J = 11.6 Hz, 1H), 3.34 (s, 3H), 2.25 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 2.04 (s, 3H), 1.94 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.8, 203.4, 202.7, 128.3, 125.4, 110.6, 104.4, 69.5, 50.7, 30.3, 30.3, 30.2, 28.0, 12.3, 10.0. IR (film): 3406, 2930, 1702, 1613, 1514, 1356, 1152, 820, 453 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>15</sub>H<sub>21</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 286.1419, found 286.1414.

**3-Acetyl-4-(5-methylfuran-2-yl)hexane-2,5-dione (5c):** Yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 6.11 (d, J = 2.8 Hz, 1H), 5.92 – 5.91 (m, 1H), 4.61 (s, 2H), 2.28 (s, 3H), 2.25 (s, 3H), 2.14 (s, 3H), 2.02 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 203.3, 202.3, 201.4, 153.1, 146.0, 110.42, 107.0, 67.9, 52.3, 30.1, 29.6, 28.2, 13.5 ppm. IR (film): 3389, 2925, 1717, 1358, 1191, 1023, 956, 792, 490 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>13</sub>H<sub>16</sub>NNaO<sub>4</sub>, [M + Na]<sup>+</sup> 259.0946, found 259.0944.

**3-Acetyl-4-(1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)hexane-2,5-dione (5d):** Brown solid, mp: 165–167 °C . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 11.21 (m, 1H), 8.35 (d, J = 4.8 Hz, 1H), 8.00 (dd, J = 7.6, 0.8 Hz, 1H), 7.29 (s, 1H), 7.16 (dd, J = 8.0, 4.8 Hz, 1H), 4.81 (dd, J = 14.0, 11.6 Hz, 2H), 2.32 (s, 3H), 2.12 (s, 3H), 1.89 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.0, 202.7, 201.9, 148.7, 143.2,

128.0, 125.0, 118.9, 116.5, 107.2, 69.4, 50.4, 30.5, 30.3, 28.4. IR (film): 3400, 3140, 3038, 2894, 1704, 1420, 1357, 1270, 1156, 775, 639, 563, 457 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>NaO<sub>3</sub>, [M + Na]<sup>+</sup> 295.1059, found 295.1060.

**3-Acetyl-4-(5-methyl-1*H*-pyrrolo[2,3-*b*]pyridin-3-yl)hexane-2,5-dione (5e):** Yellow solid, mp: 171 – 173 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 12.02 (s, 1H), 8.21 (s, 1H), 7.79 (s, 1H), 7.30 (s, 1H), 4.82 (s, 2H), 2.48 (s, 3H), 2.33 (s, 3H), 2.12 (s, 3H), 1.90 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.2, 202.9, 202.0, 147.6, 144.0, 127.7, 125.5, 125.3, 118.8, 106.2, 69.3, 50.6, 30.5, 30.3, 28.3, 18.6 ppm. IR (film): 3134, 3009, 2874, 1704, 1408, 1357, 1261, 1194, 1155, 913, 801, 733, 645 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>3</sub>, [M + Na]<sup>+</sup> 309.1215, found 309.1213.

**3-Acetyl-4-(5-methoxy-1*H*-pyrrolo[3,2-*b*]pyridin-3-yl)hexane-2,5-dione (5f):** Brown viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.98 (s, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.09 (d, J = 2.8 Hz, 1H), 6.62 (d, J = 8.8 Hz, 1H), 5.10 (d, J = 11.2 Hz, 1H), 4.81 (d, J = 11.4 Hz, 1H), 4.00 (s, 3H), 2.35 (s, 3H), 2.12 (s, 3H), 2.00 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.7, 203.9, 203.3, 160.2, 140.5, 125.5, 124.6, 122.3, 108.9, 106.4, 70.3, 53.3, 48.8, 30.4, 28.8, 28.2. IR (film): 3377, 2945, 1701, 1578, 1491, 1409, 1357, 1257, 1026, 810, 565 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>4</sub>, [M + Na]<sup>+</sup> 325.1164, found 325.1162.

**3-Acetyl-4-(4-(dimethylamino)phenyl)hexane-2,5-dione (5g):** Yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 7.03 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 8.8 Hz, 2H), 4.58 (d, J = 11.6 Hz, 1H), 4.40 (d, J = 11.6 Hz, 1H), 2.94 (s, 6H), 2.27 (s, 3H), 2.07 (s, 3H), 1.90 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.4, 203.1, 202.2, 150.2, 129.5, 121.1, 112.9, 70.5, 57.9, 40.3, 30.6, 30.2, 28.4 ppm. IR (film): 3392, 2924, 1695, 1606, 1523, 1357, 1185, 813, 533, 460. cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>21</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 298.1419, found 297.1418.

**3-Acetyl-4-(4-(methylamino)phenyl)hexane-2,5-dione (5h):** Yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 6.98 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 4.57 (d, J = 11.6 Hz, 1H), 4.38 (d, J = 11.6 Hz, 1H), 3.85 (br, 1H), 2.81 (s, 3H), 2.26 (s, 3H), 2.07 (s, 3H), 1.90 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.4, 203.1, 202.2, 149.2, 129.6, 122.0, 113.0, 70.4, 58.0, 30.6, 30.5, 30.2, 28.4 ppm. IR (film): 3412, 2925, 1703, 1613, 1524, 1357, 1259, 1187, 1154, 828, 542, 495 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>15</sub>H<sub>19</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 284.1263, found 284.1259.

**3-Acetyl-4-(1,2,3,4-tetrahydroquinolin-6-yl)hexane-2,5-dione (5i):** Brown viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 6.75 – 6.72 (m, 2H), 6.39 (d, J = 8.0 Hz, 1H), 4.55 (d, J = 11.6 Hz, 1H), 4.32 (d, J = 11.2 Hz, 1H), 3.90 (s, 1H), 3.28 (t, J = 5.2 Hz, 2H), 2.70 (t, J = 6.4 Hz, 2H), 2.26 (s, 3H), 2.07 (s, 3H), 1.92 – 1.89 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 206.6, 203.2, 202.4, 144.7, 129.7, 127.2, 122.1, 121.7, 114.6, 70.5, 58.1, 41.8, 30.6, 30.2, 28.5, 26.9, 21.8. IR (film): 3402, 2919, 1704, 1418, 1354, 1152, 965, 774, 489 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>17</sub>H<sub>21</sub>NNaO<sub>3</sub>, [M + Na]<sup>+</sup> 310.1419, found 31.1421.

**3-Acetyl-4-(phenylthio)hexane-2,5-dione (5j):** Yellow viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 7.40 – 7.37 (m, 5H), 4.35 (d, J = 11.6 Hz, 1H), 4.23 (d, J = 11.6 Hz, 1H), 2.35 (s, 6H), 2.19 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 202.0, 201.5, 200.9, 134.5, 130.0, 129.4, 129.4, 68.6, 55.1, 30.2, 29.7, 28.2 ppm. IR (film): 3402, 2924, 1704, 1357, 1254, 1150, 748, 465 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>14</sub>H<sub>16</sub>NaO<sub>3</sub>S, [M + Na]<sup>+</sup> 287.0718, found 287.0716

**3-Acetyl-4-(benzylthio)hexane-2,5-dione (5k):** Yellowish viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 7.32 – 7.26 (m, 5H), 4.42 (d, J = 11.2 Hz, 1H), 4.07 (d, J = 11.2 Hz, 1H), 3.65 (d, J = 12.8 Hz, 1H), 3.55 (d, J = 12.4 Hz, 1H), 2.19 (d, J = 2.8 Hz, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 202.2, 201.3, 200.9, 136.8, 129.3, 128.7, 127.6, 68.1, 50.9, 34.7, 30.1, 27.4 ppm. IR (film): 3402,

2925, 1729, 1703, 1596, 1357, 1258, 1193, 1153, 957, 704, 567, 471 cm<sup>-1</sup>. HRMS-ESI (m/z) calcd for C<sub>15</sub>H<sub>18</sub>NaO<sub>3</sub>S, [M + Na]<sup>+</sup> 301.1874, found 301.1877.

**3-((5-Methoxy-2-methyl-1H-indol-3-yl)(pyridin-2-yl)methyl)pentane-2,4-dione (6a):** Brown viscous liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.43 (dd, J = 5.6, 1.6 Hz, 1H), 8.00 (d, J = 5.2 Hz, 1H), 7.41 (td, J = 7.6, 1.6 Hz, 1H), 7.07 (d, J = 8.6 Hz, 1H), 7.02–7.00 (m, 2H), 6.89 (s, 1H), 6.69 (dd, J = 8.8, 2.4 Hz, 1H), 5.38 (d, J = 11.6 Hz, 1H), 5.26 (d, J = 11.6 Hz, 1H), 3.75 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H), 1.86 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 204.4, 202.8, 161.1, 153.8, 147.5, 136.3, 133.4, 130.5, 127.9, 123.7, 121.3, 111.4, 110.4, 109.9, 101.4, 69.2, 55.9, 43.9, 30.6, 12.1 ppm. IR (cm<sup>-1</sup>): 3388, 2937, 1727, 1695, 1588, 1483, 1431, 1355, 1251, 1216, 1033, 910, 731, 625. HRMS-ESI (m/z) calcd for C<sub>21</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>, [M+H]<sup>+</sup> 351.1709, found 351.1707.

**3-((5-Methoxy-2-methyl-1H-indol-3-yl)(pyridin-4-yl)methyl)pentane-2,4-dione (6b):** Brown viscous liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.88 (s, 1H), 8.45 (d, J = 5.6 Hz, 2H), 7.23 (d, J = 6.0 Hz, 2H), 7.09 (d, J = 8.8 Hz, 1H), 6.99 (d, J = 2.0 Hz, 1H), 6.74 – 6.72 (m, 1H), 5.07 (dd, J = 15.2 Hz, J = 11.6 Hz, 2H), 3.82 (s, 3H), 2.42 (s, 3H), 2.19 (s, 3H), 1.87 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 202.6, 202.3, 153.9, 150.5, 149.8, 133.5, 130.7, 127.2, 123.1, 122.8, 111.4, 110.0, 101.5, 70.6, 56.0, 41.3, 29.6, 12.3 ppm. IR (cm<sup>-1</sup>): 3392, 2938, 1728, 1699, 1595, 1484, 1357, 1250, 1216, 732. HRMS-ESI (m/z) calcd for C<sub>21</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>, [M+H]<sup>+</sup> 351.1709, found 351.1704.

**3-(1-(1H-indol-3-yl)-2,2-dimethoxyethyl)pentane-2,4-dione (6c):** Brown viscous liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.52 (s, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.17–7.13 (m, 2H), 6.97 (s, 1H), 4.51 (d, J = 11.2 Hz, 1H), 4.40 (d, J = 4.8 Hz, 1H), 4.28–4.24 (m, 1H), 3.31 (s, 3H), 3.26 (s, 3H), 2.30 (s, 3H), 1.83 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 204.2, 203.4, 135.9, 126.9, 123.9, 122.1, 119.7, 118.8, 111.4, 107.5, 69.7, 56.5, 54.6, 40.8, 30.8, 28.5 ppm. IR (cm<sup>-1</sup>): 3389, 2935, 1727, 1694, 1457, 1355, 1122, 1074, 978, 744, 426. HRMS-ESI (m/z) calcd for C<sub>17</sub>H<sub>21</sub>NNaO<sub>4</sub>, [M + Na]<sup>+</sup> 326.1318, found 326.1315.

**1-(4-(1H-indol-3-yl)-2,5-dimethylfuran-3-yl)ethanone (7a):** Brown viscous liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.47 (s, 1H), 7.43 – 7.38 (m, 2H), 7.25 – 7.21 (m, 1H), 7.14 – 7.10 (m, 2H), 2.59 (s, 3H), 2.15 (s, 3H), 1.91 (s, 3H).. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 197.0, 156.6, 148.2, 136.0, 128.0, 123.5, 122.4, 120.2, 119.6, 112.6, 111.3, 108.6, 29.9, 14.5, 11.8 ppm. IR (cm<sup>-1</sup>): 3406, 3355, 2922, 1662, 1563, 1421, 1184, 1097, 1014, 944, 744, 427. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>15</sub>NNaO<sub>2</sub>, [M + Na]<sup>+</sup> 276.1000, found 276.1001.

**3-(2,5-Dimethylfuran-3-yl)-1H-indole (7b):** Brown viscous liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.14 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.19 – 7.12 (m, 2H), 6.21 (s, 1H), 2.36 (s, 3H), 2.33 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 149.7, 145.6, 136.1, 126.9, 122.2, 121.6, 120.0, 119.8, 114.3, 111.2, 110.3, 108.0, 13.6, 12.7 ppm. IR (cm<sup>-1</sup>): 3411, 2921, 1697, 1548, 1423, 1094, 743. HRMS-ESI (m/z) calcd for C<sub>14</sub>H<sub>13</sub>NNaO, [M + Na]<sup>+</sup> 234.0895, found 234.0899.

**1-(4-(1H-indol-3-yl)-2,5-dimethyl-1-(p-tolyl)-1H-pyrrol-3-yl)ethanone (8a):** Brown viscous liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.39 (s, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 7.6 Hz, 1H), 7.17 – 7.10 (m, 4H), 2.44 (s, 3H), 2.35 (s, 3H), 1.94 (s, 3H), 1.84 ppm (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 197.8, 138.5, 136.1, 135.4, 135.2, 130.0, 128.6, 128.2, 127.9, 123.4, 122.3, 122.1, 120.1, 119.9, 113.2, 112.0, 111.1, 30.0, 21.2, 13.3, 11.4. ppm. IR (cm<sup>-1</sup>): 3331, 2924, 1706, 1634, 1511, 1408, 1192, 818, 741, 513. HRMS-ESI (m/z) calcd for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>NaO, [M + Na]<sup>+</sup> 365.1630, found 365.1633.

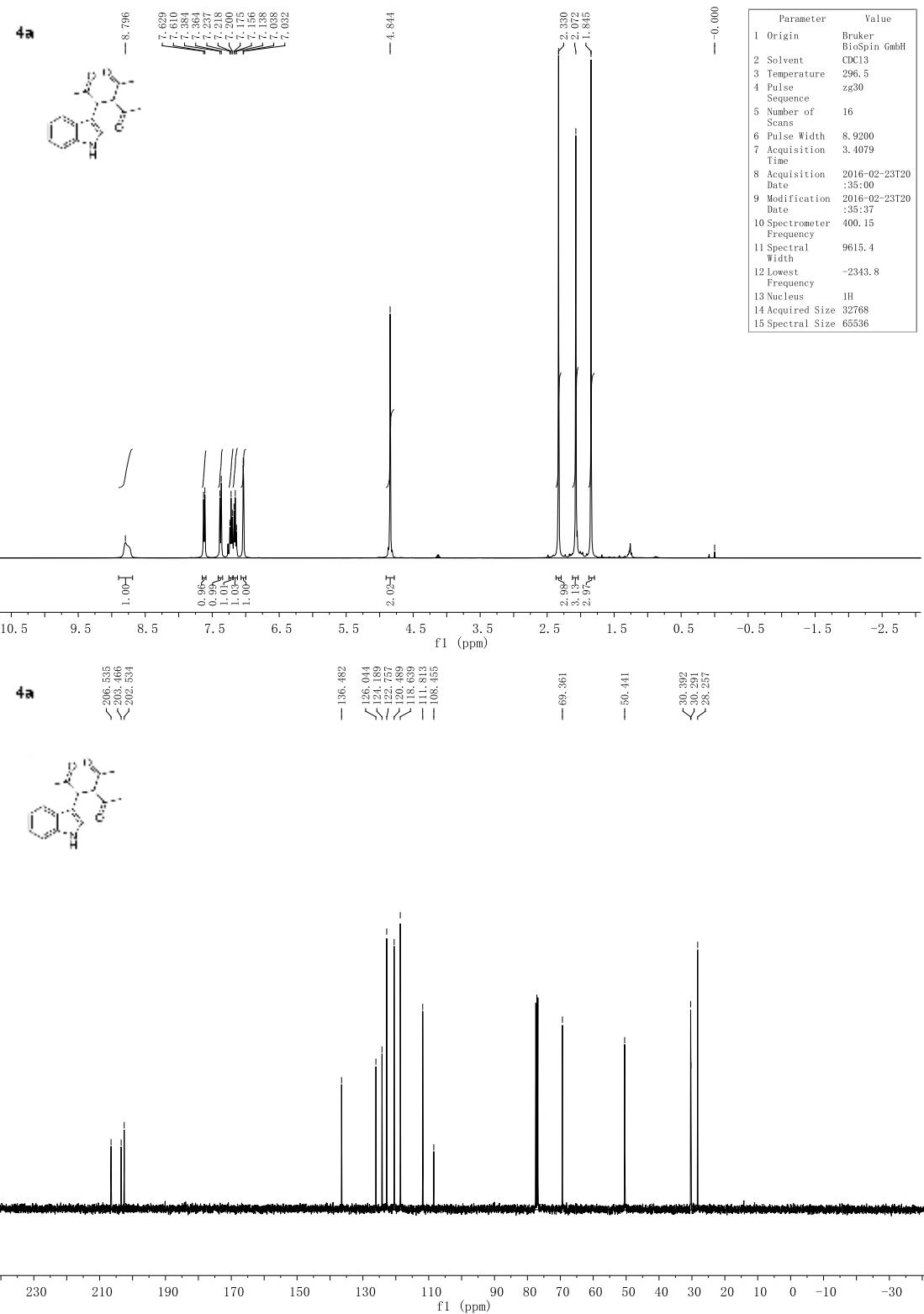
**3-(1H-indol-3-yl)hexane-2,5-dione (9a):** Brown viscous liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25

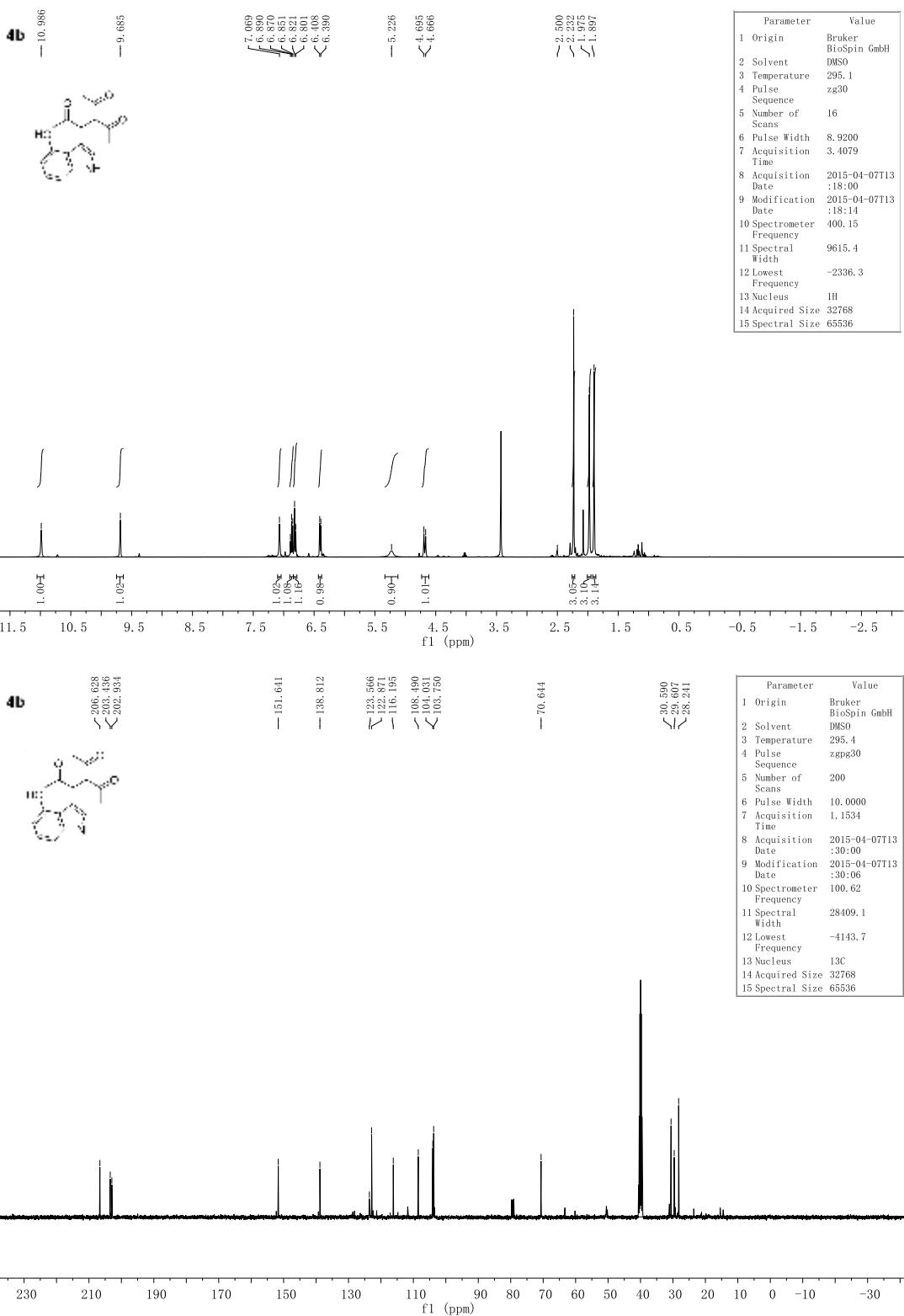
<sup>°C</sup>) δ = 8.28 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8. Hz, 1H), 7.23 (t, *J* = 6.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 4.52 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.55 (dd, *J* = 18.0, 10.0 Hz, 1H), 2.67 (dd, *J* = 18.0, 4.0 Hz, 1H), 2.17 (d, *J* = 6.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 208.0, 207.7, 136.4, 126.2, 122.8, 122.5, 120.0, 118.8, 112.3, 112.3, 111.5, 45.6, 45.1, 30.1, 28.7. IR (cm<sup>-1</sup>): 3404, 2919, 1708, 1423, 1356, 1248, 1161, 746. HRMS-ESI (m/z) calcd for C<sub>14</sub>H<sub>15</sub>NNaO<sub>2</sub>, [M + Na]<sup>+</sup> 252.1000, found 252.1001.

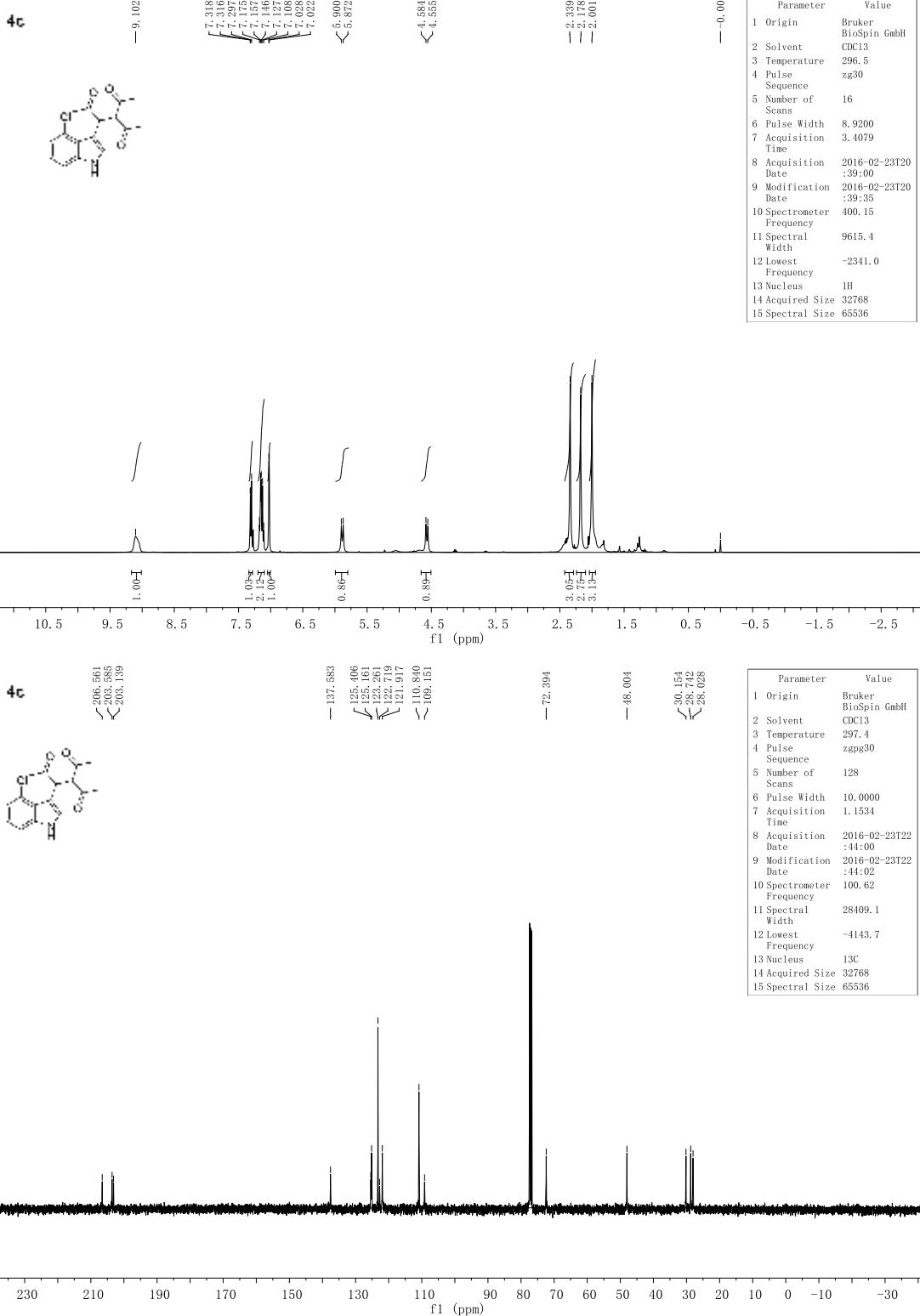
**4-hydroxy-3-(1H-indol-3-yl)-4-methylcyclopent-2-enone (10a):** Brown viscous liquid, <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 25 °C) δ = 9.17 (s, 1H), 8.10 (d, *J* = 2.8 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.21 (m, 3H), 6.45 (s, 1H), 2.65 (dd, *J* = 26.0, 18.0 Hz, 2H), 1.66 (s, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, 25 °C) δ = 204.7, 136.5, 130.3, 126.0, 123.4, 123.2, 122.1, 120.7, 112.0, 109.3, 79.1, 53.0, 28.9. IR (cm<sup>-1</sup>): 3288, 2926, 1667, 1566, 1427, 1230, 1130, 740. HRMS-ESI (m/z) calcd for C<sub>14</sub>H<sub>13</sub>NNaO<sub>2</sub>, [M + Na]<sup>+</sup> 250.0844, found 250.0842.

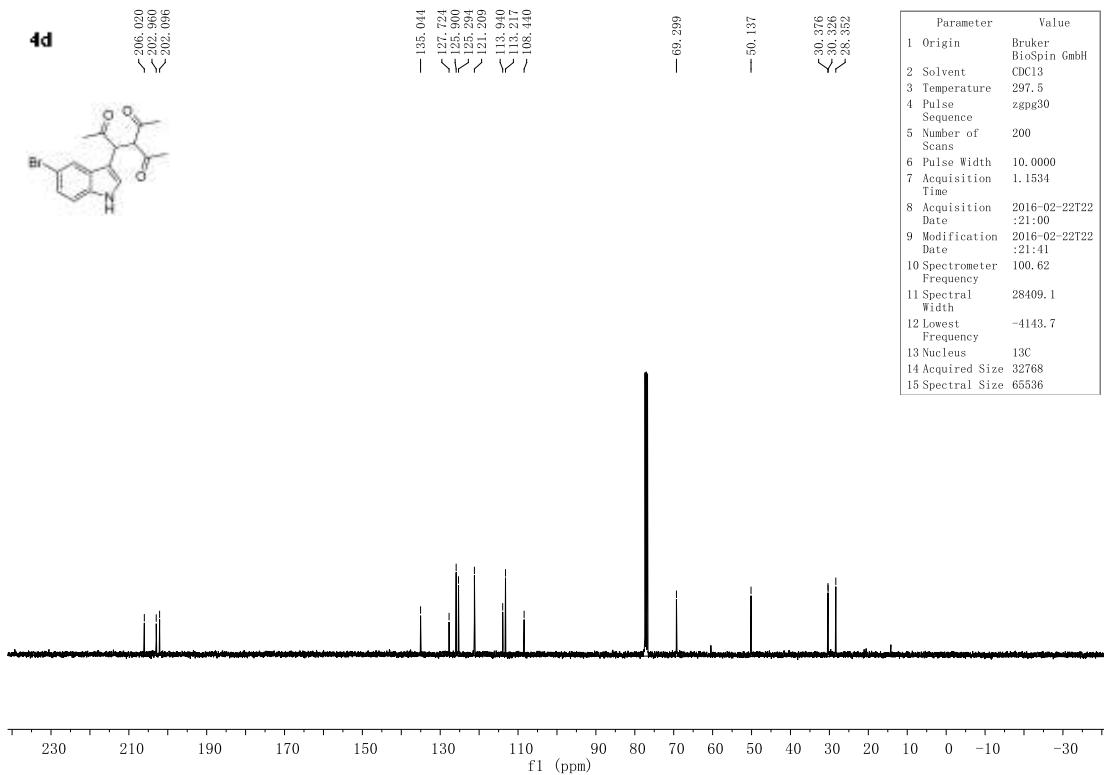
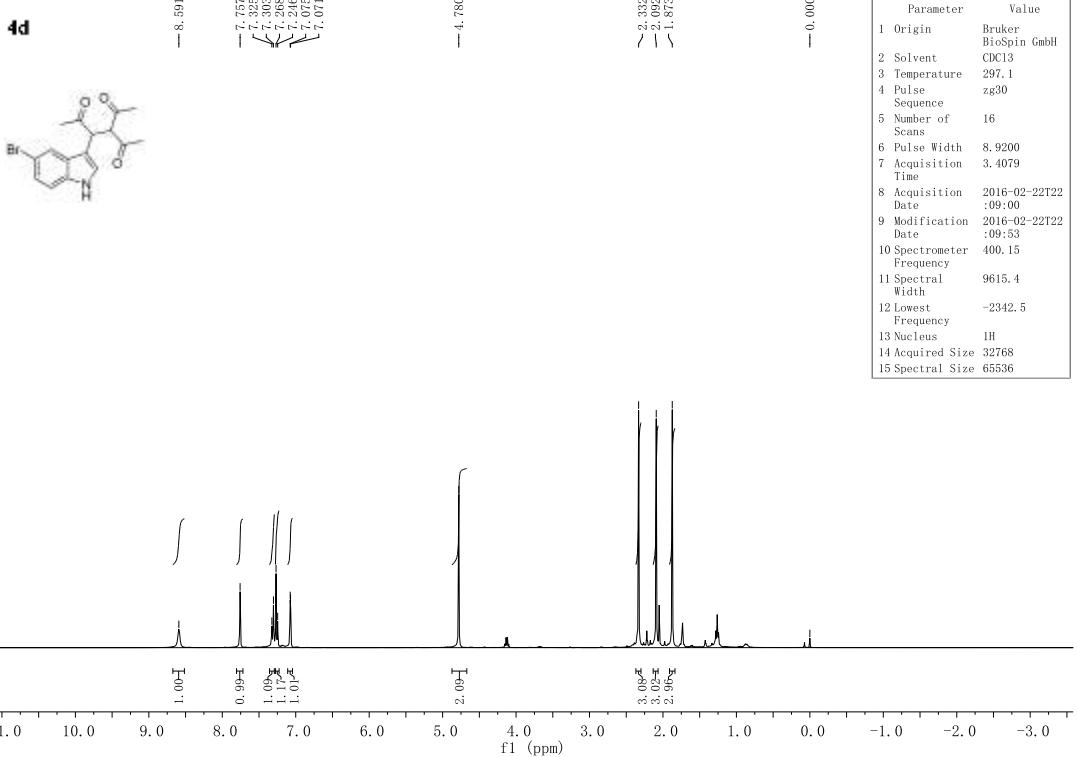
**5-Acetyl-4-(1H-indol-3-yl)-3-methylcyclopent-2-enone (11a):** Brown viscous liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.86 (s, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.19 – 7.15 (m, , 1H), 3.71 (s, 1H), 2.93 (d, *J* = 18.8 Hz, 1H), 2.76 (d, *J* = 18.4 Hz, 1H), 2.14 (s, 3H), 1.71 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 205.5, 205.4, 159.7, 137.2, 136.0, 127.2, 126.3, 123.1, 121.3, 119.4, 111.8, 105.0, 77.4, 77.0, 76.7, 76.1, 51.1, 30.7, 27.9 ppm. IR (cm<sup>-1</sup>): 3404, 2920, 1708, 1356, 1247, 1161, 1099, 746. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>15</sub>NNaO<sub>2</sub>, [M + Na]<sup>+</sup> 276.1000, found 276.1002.

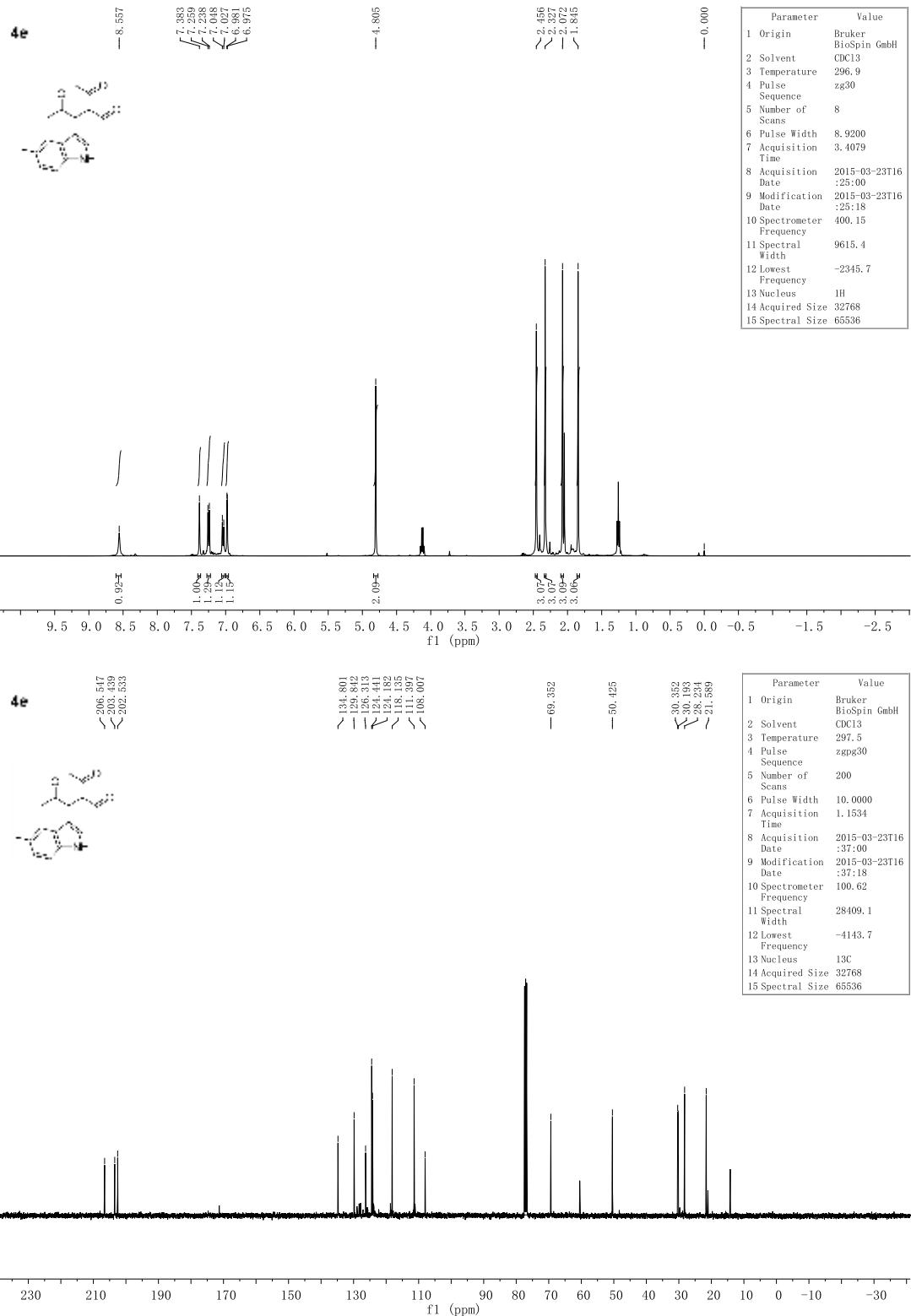
**1-(2-Hydroxy-5-(1H-indol-3-yl)-4-methylcyclopenta-1,4-dien-1-yl)ethanone (11b):** Brown viscous liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS, 25 °C) δ = 8.94 (s, 1H), 7.55 (d, *J* = 2.8 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 3.74 (s, 1H), 2.93 (d, *J* = 18.4 Hz, 1H), 2.76 (d, *J* = 18.8 Hz, 1H), 2.14 (s, 3H), 1.71 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 25 °C) δ = 205.6(*J* = 26.9 Hz), 159.8, 137.238, 136.018, 127.3, 126.258, 123.1, 121.2, 119.4, 111.9, 104.9, 76.1, 51.1, 30.7, 27.9. IR (cm<sup>-1</sup>): 3391, 1713, 1427, 1355, 1238, 1201, 1128, 748. HRMS-ESI (m/z) calcd for C<sub>16</sub>H<sub>15</sub>NNaO<sub>2</sub>, [M + Na]<sup>+</sup> 276.1000, found 276.1005.

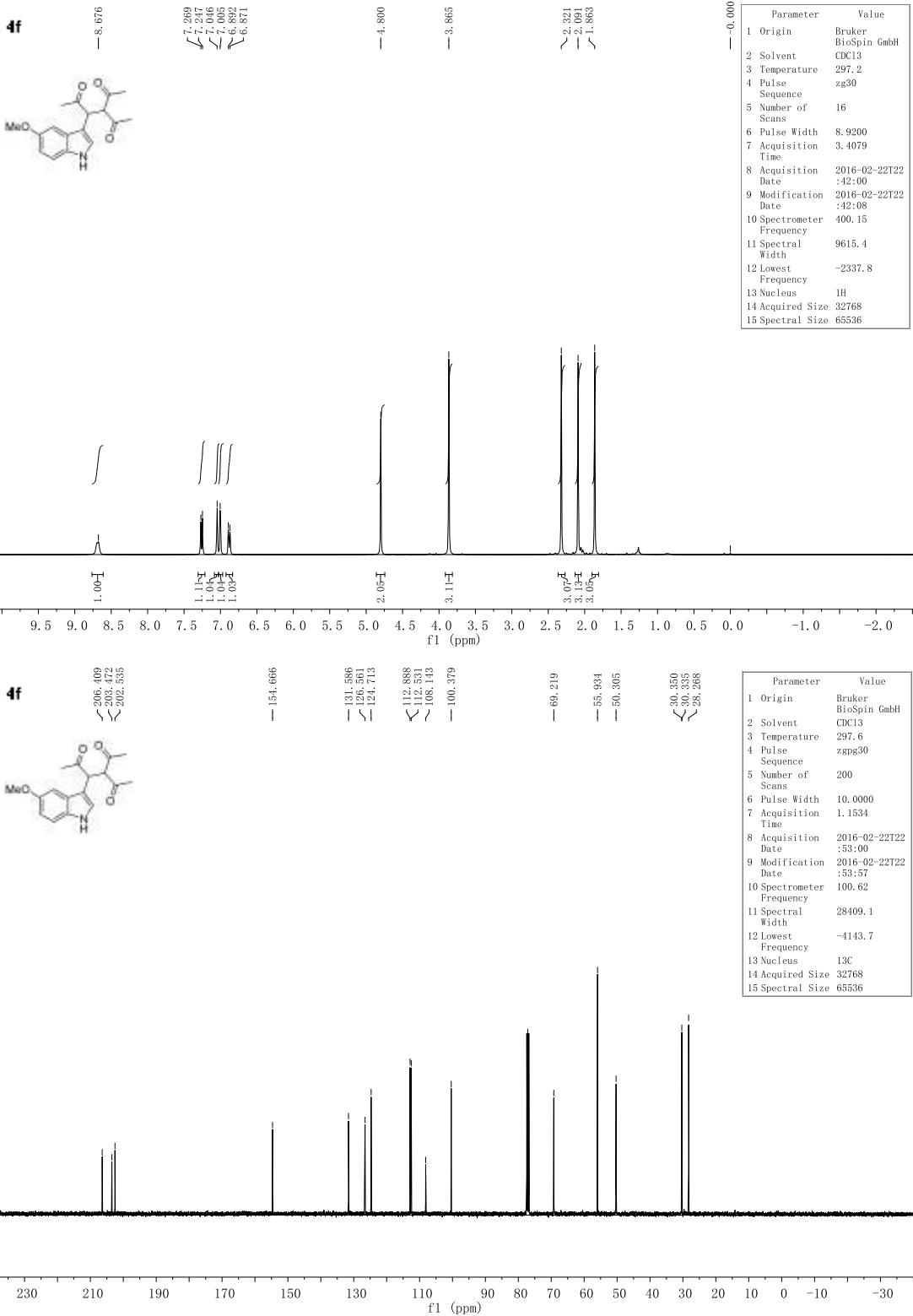








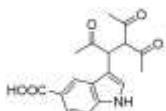




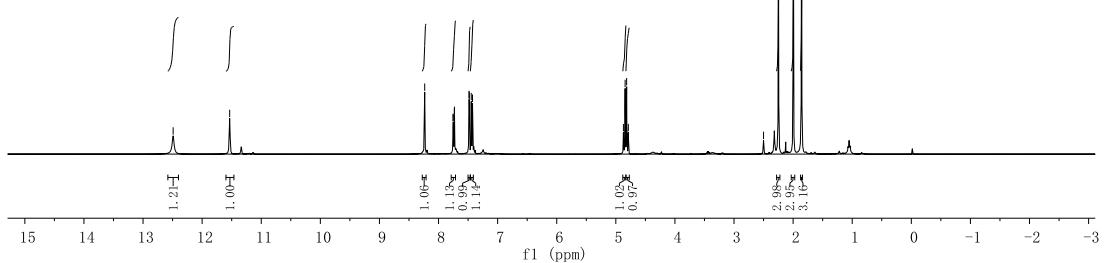
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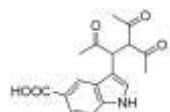
**4g**

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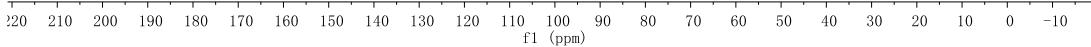
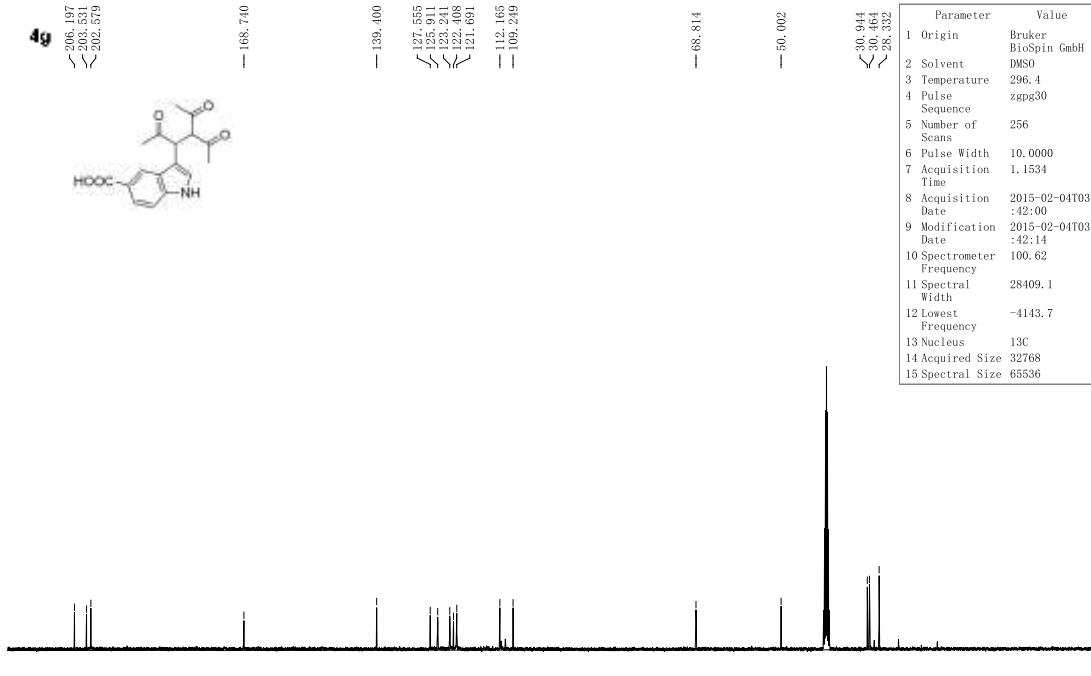
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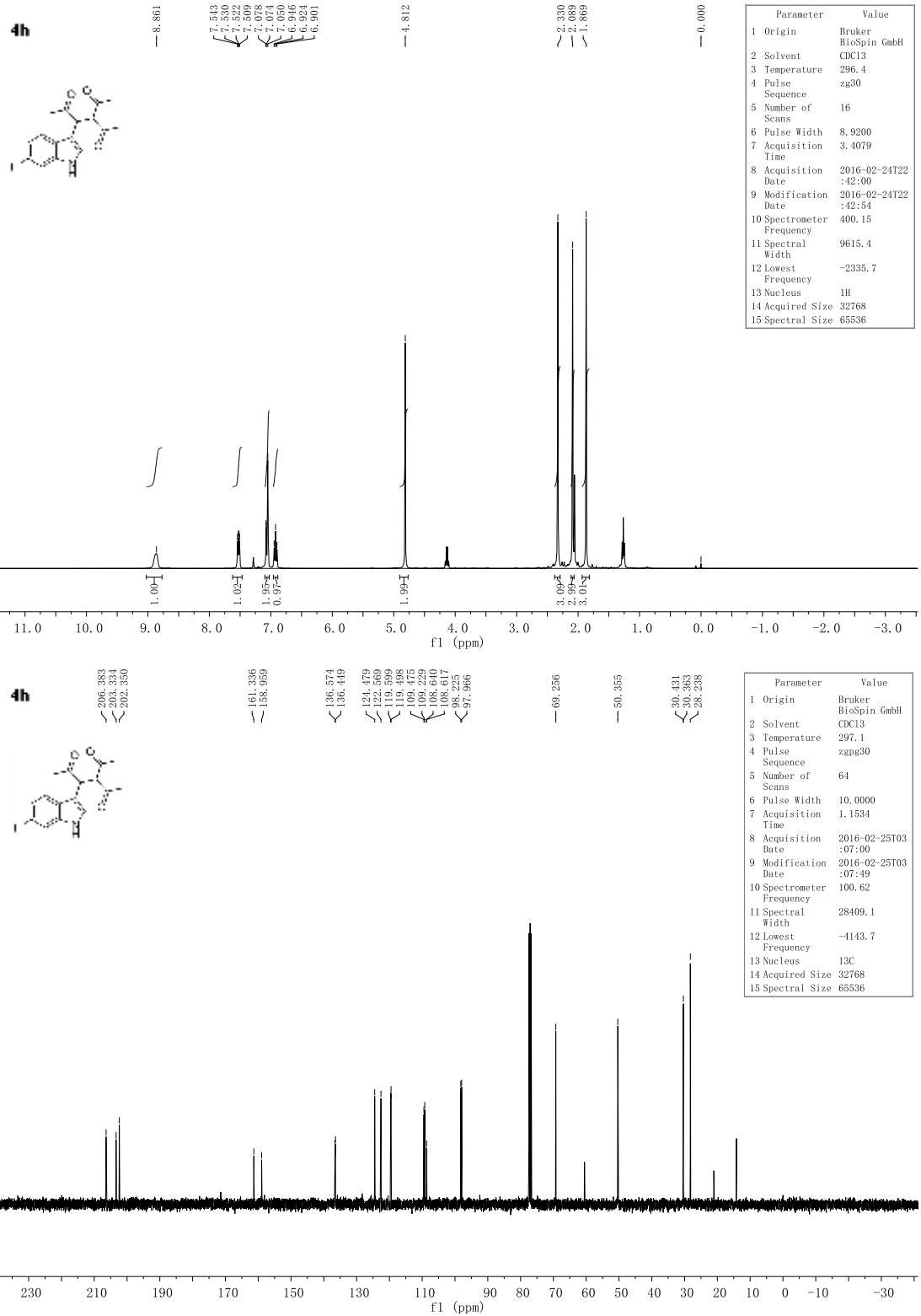
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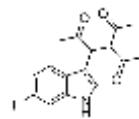
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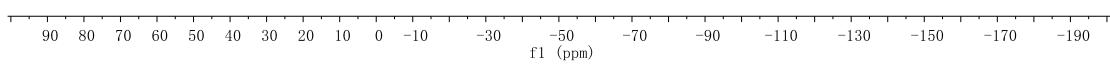
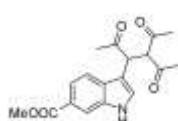




**4h**

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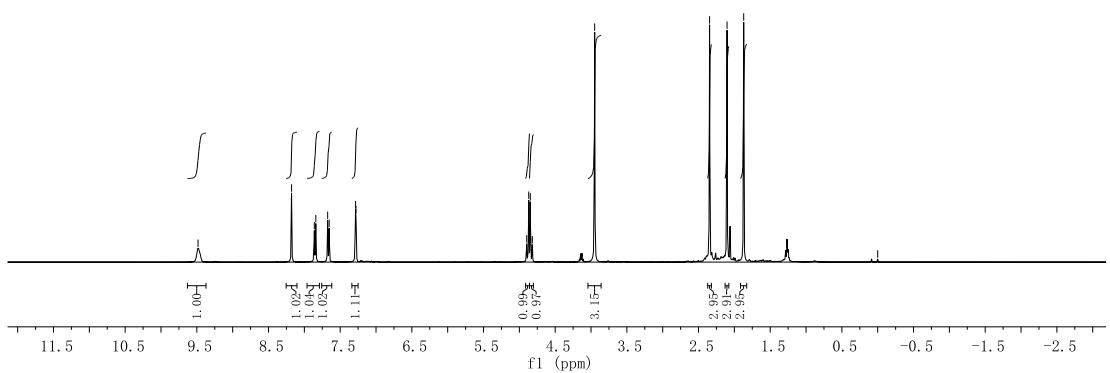
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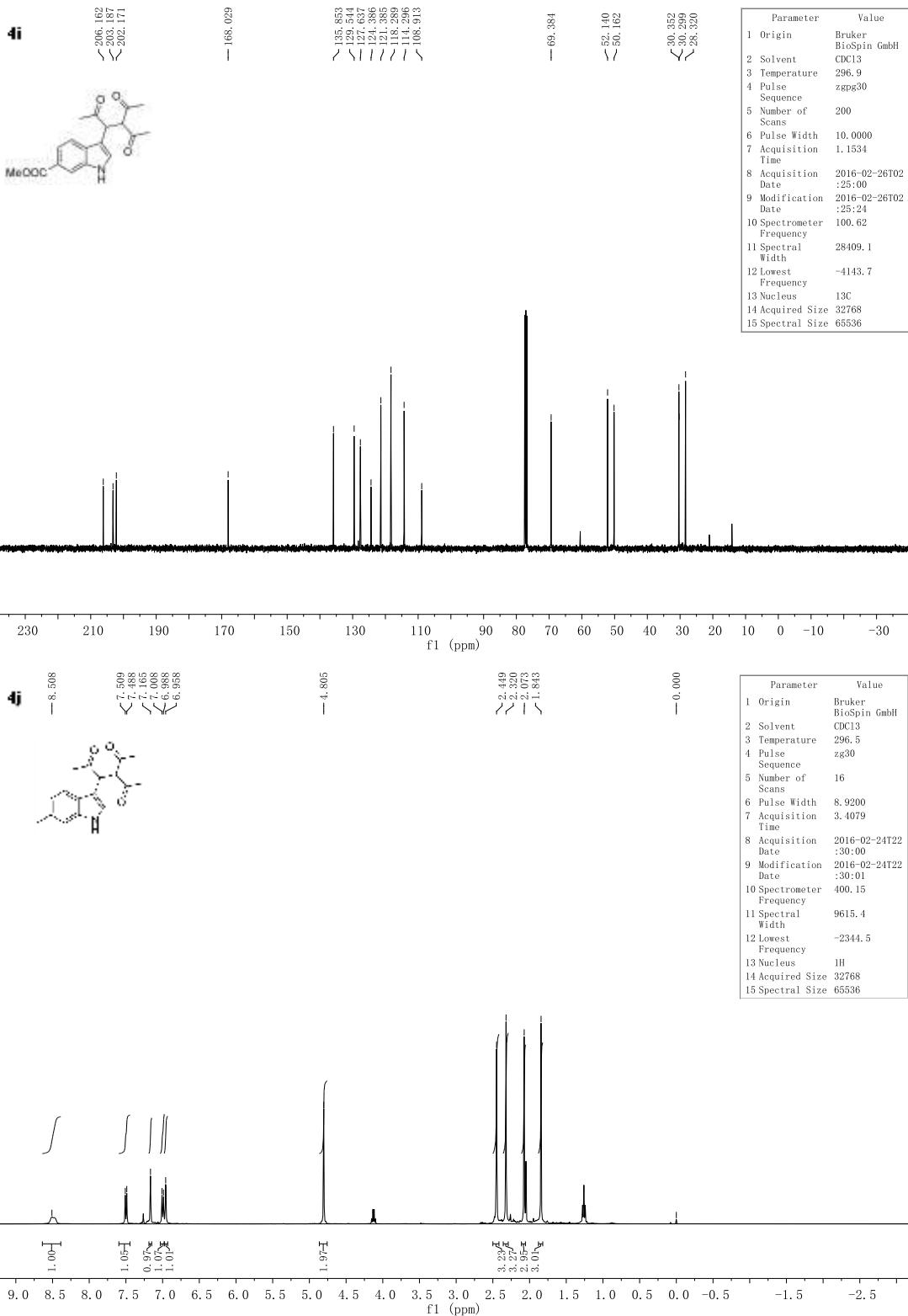
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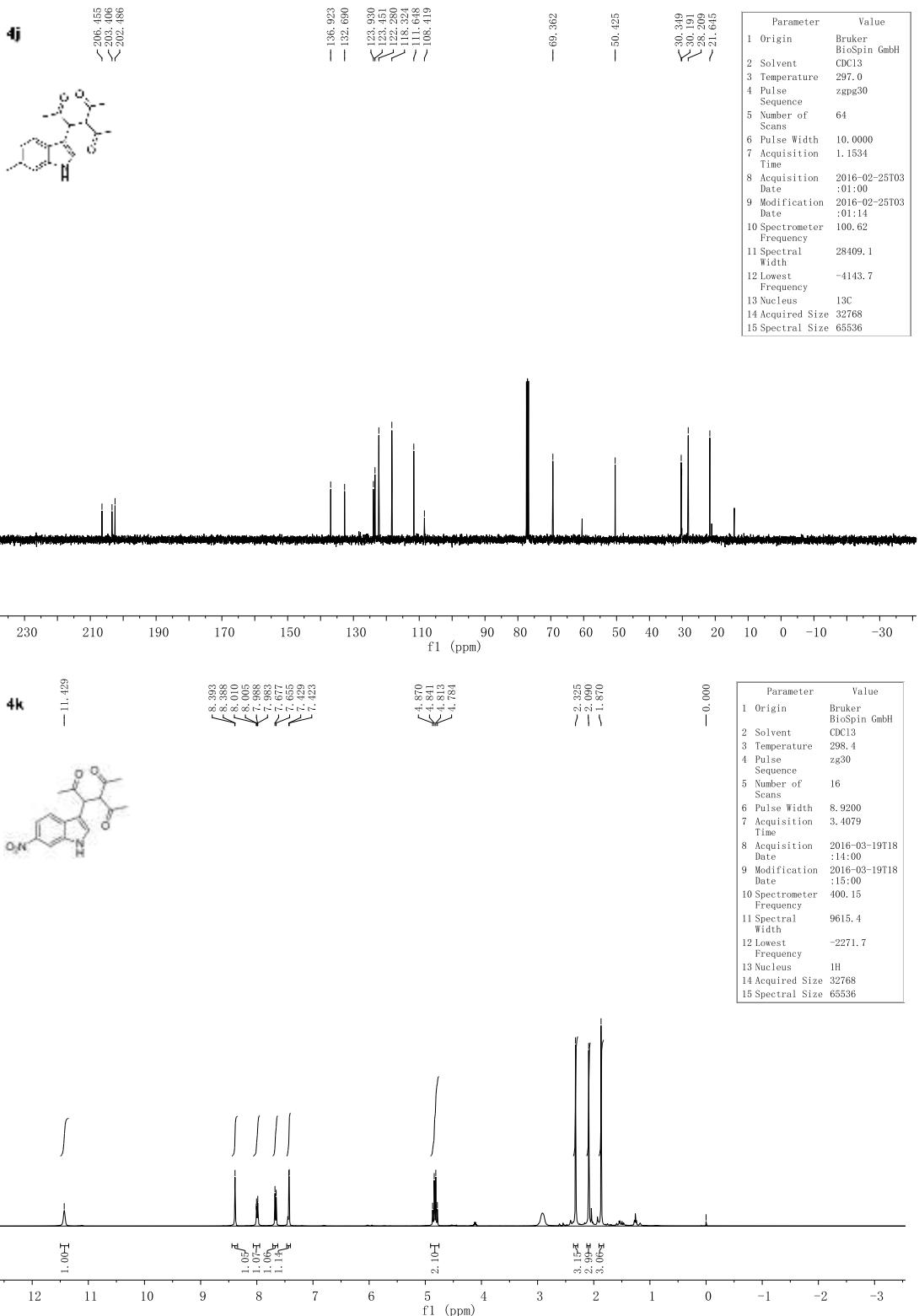
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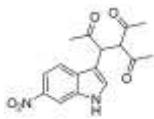






**4k**

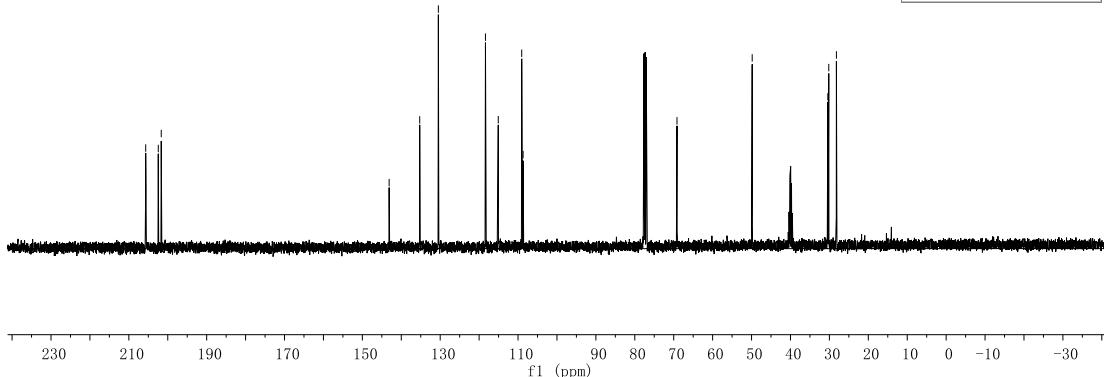
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— 69.157  
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Parameter	Value
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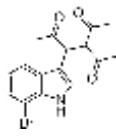


**4l**

— 8.796

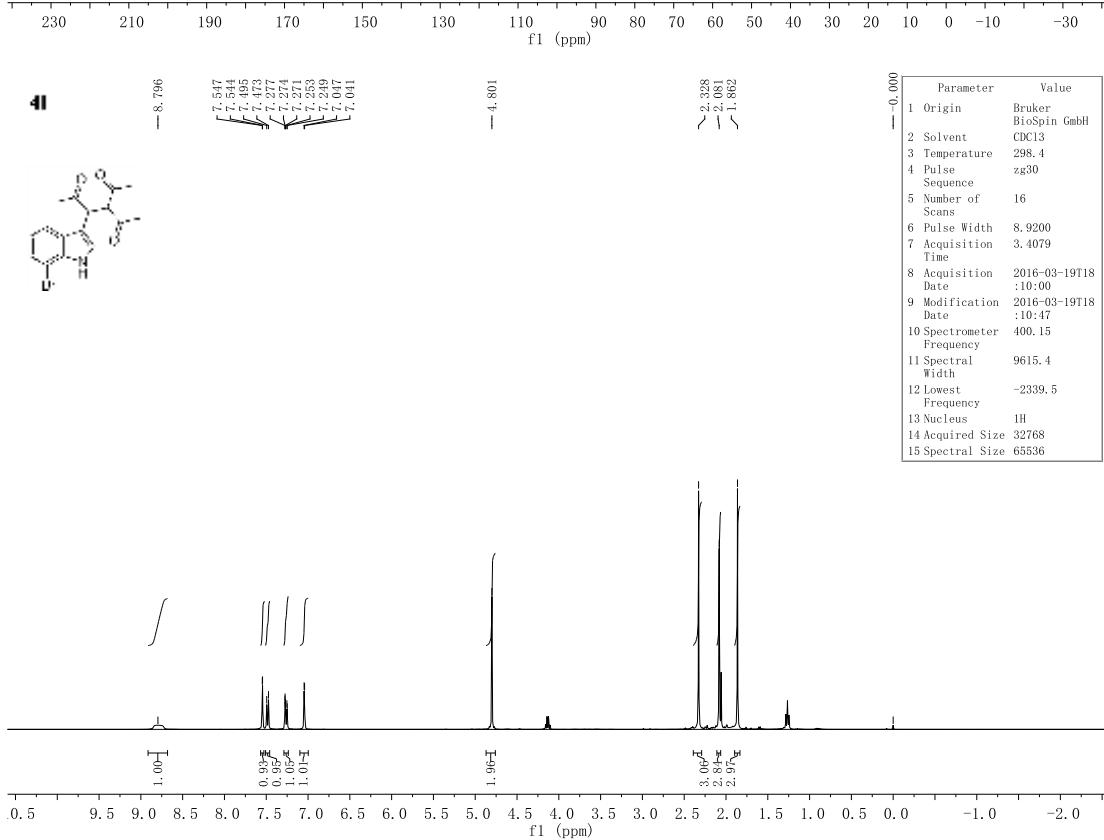
— 7.547  
— 7.644  
— 7.495  
— 7.413  
— 7.277  
— 7.274  
— 7.273  
— 7.353  
— 7.249  
— 7.097  
— 7.041

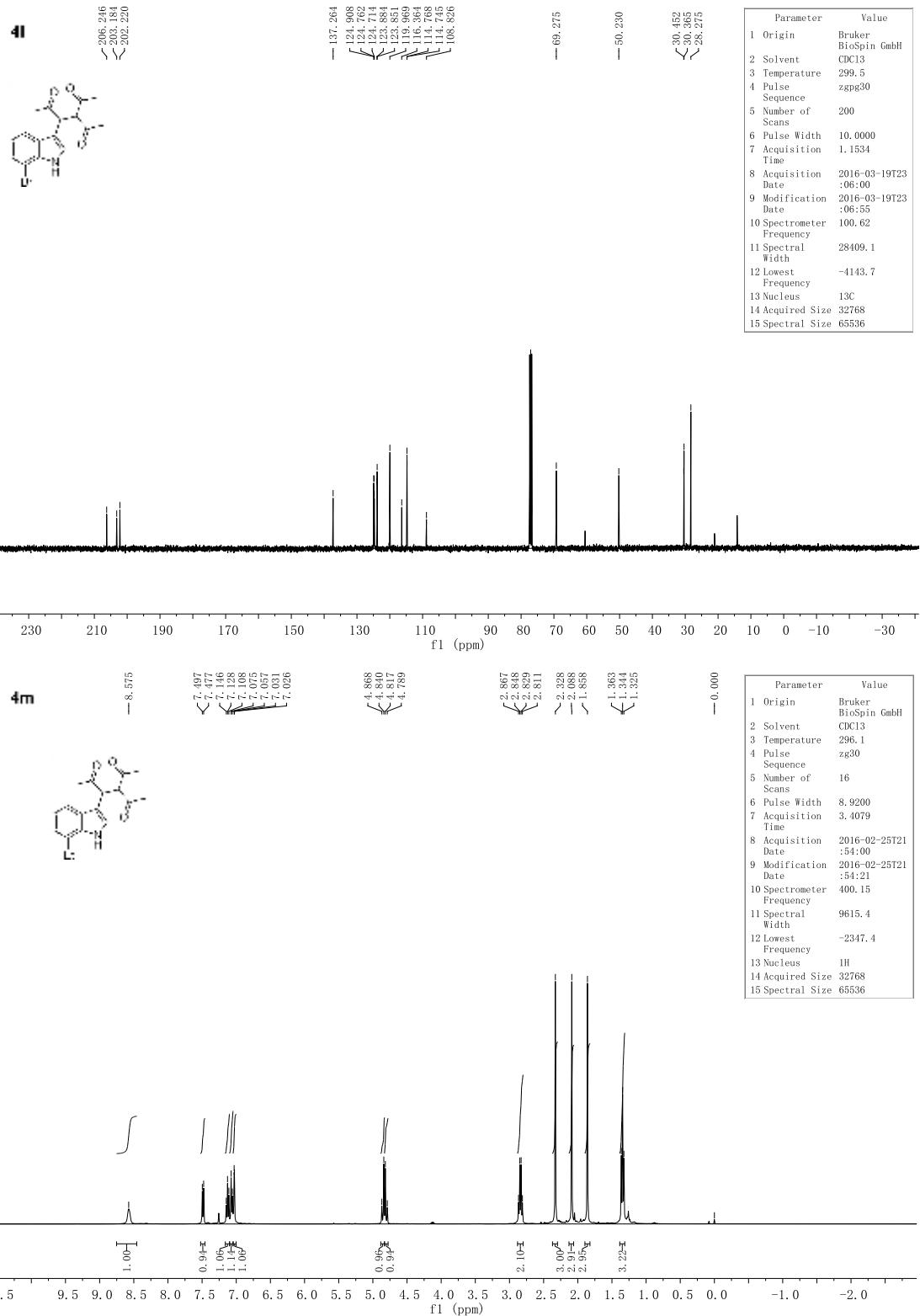
— 4.801

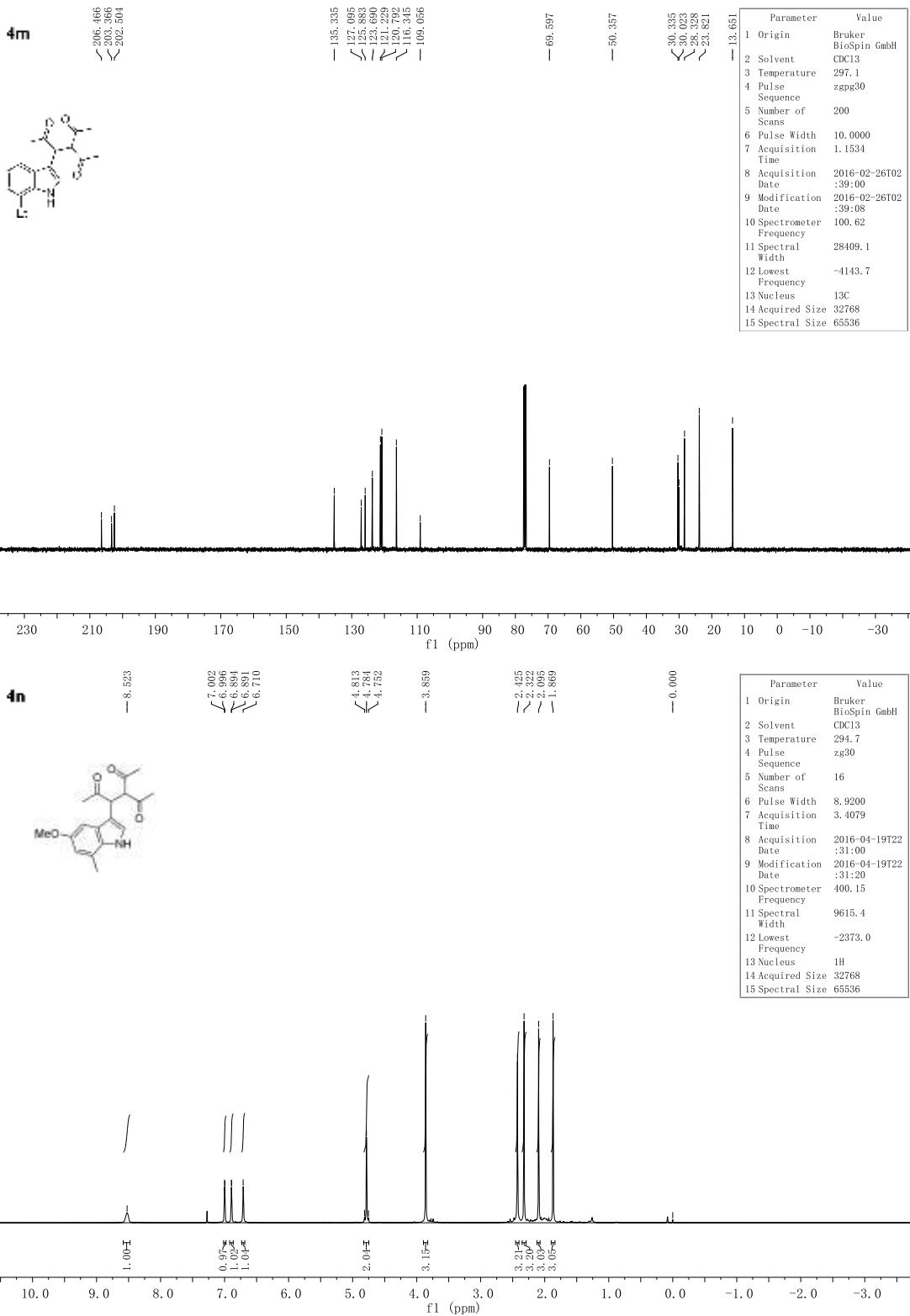


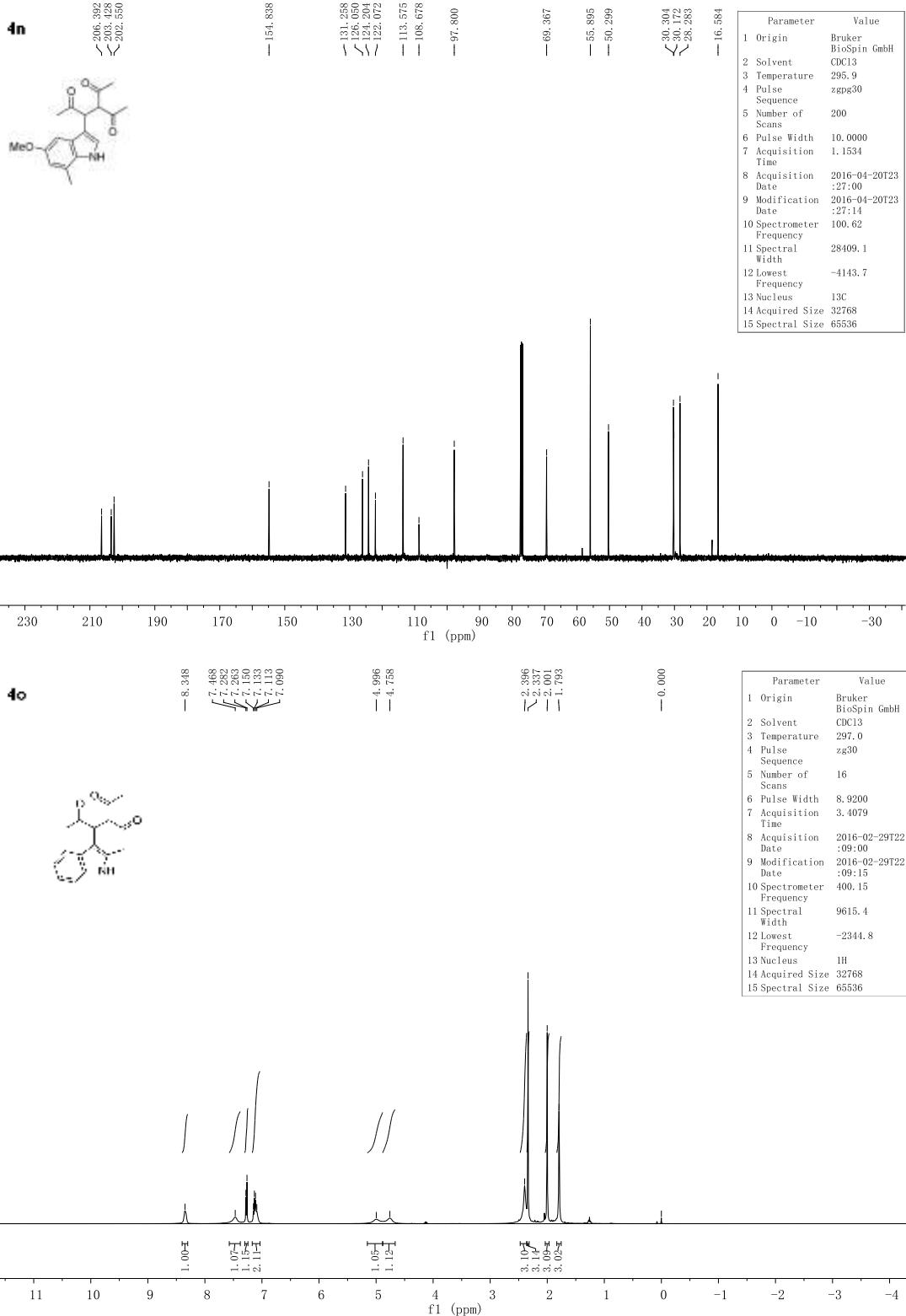
— 2.328  
— 2.081  
— 1.862

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	298.4
4 Pulse Sequence	zg30
5 Number of Scans	16
6 Pulse Width	8.9200
7 Acquisition Time	3.4079
8 Acquisition Date	2016-03-19T18:10:00
9 Modification Date	2016-03-19T18:10:47
10 Spectrometer Frequency	400.15
11 Spectral Width	9615.4
12 Lowest Frequency	-2339.5
13 Nucleus	<sup>1</sup> H
14 Acquired Size	32768
15 Spectral Size	65536



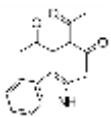






4o

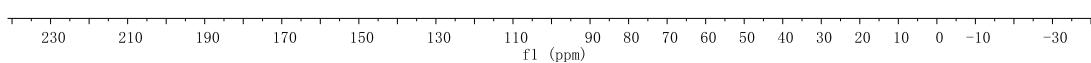
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< 203.169  
< 202.145



> 185.482  
> 184.036  
> 126.870  
> 121.664  
> 120.206  
> 118.075  
— 110.851  
— 103.774

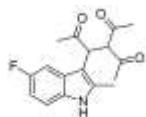
— 66.562  
— 50.817  
— 11.641

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	298.6
4 Pulse Sequence	zpg30
5 Number of Scans	1024
6 Pulse Width	10.0000
7 Acquisition Time	1.1534
8 Acquisition Date	2016-03-29T23:07:00
9 Modification Date	2016-03-29T23:07:03
10 Spectrometer Frequency	100.62
11 Spectral Width	28409.1
12 Lowest Frequency	-4143.7
13 Nucleus	<sup>13</sup> C
14 Acquired Size	32768
15 Spectral Size	65536



4p

— 8.502



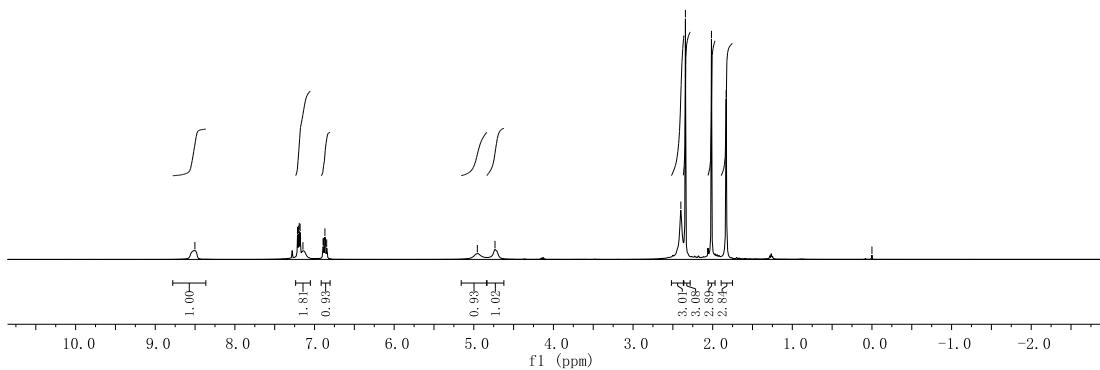
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7.203  
7.192  
7.181  
7.165  
6.882  
6.888  
6.899  
6.897

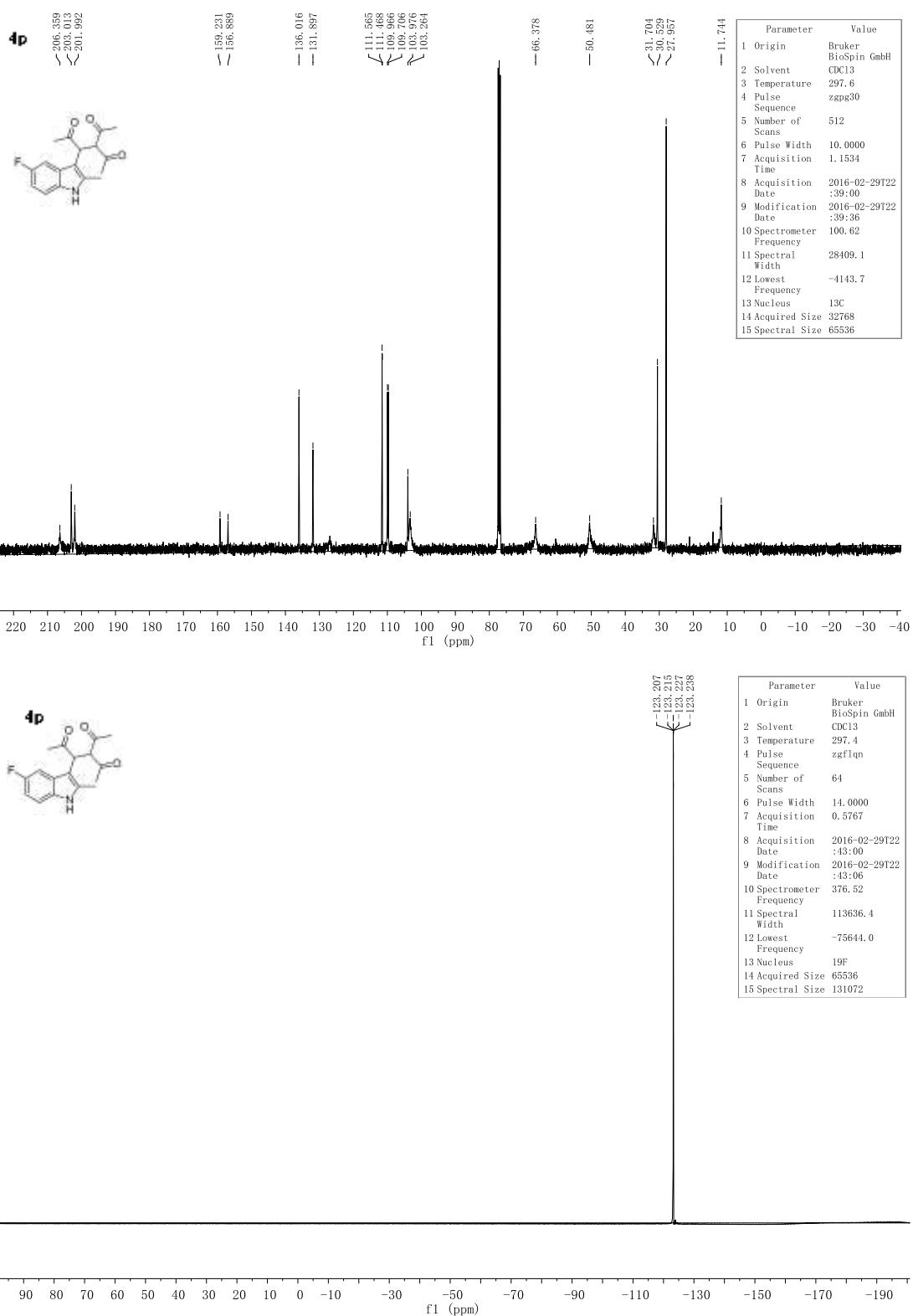
— 4.995  
— 4.734

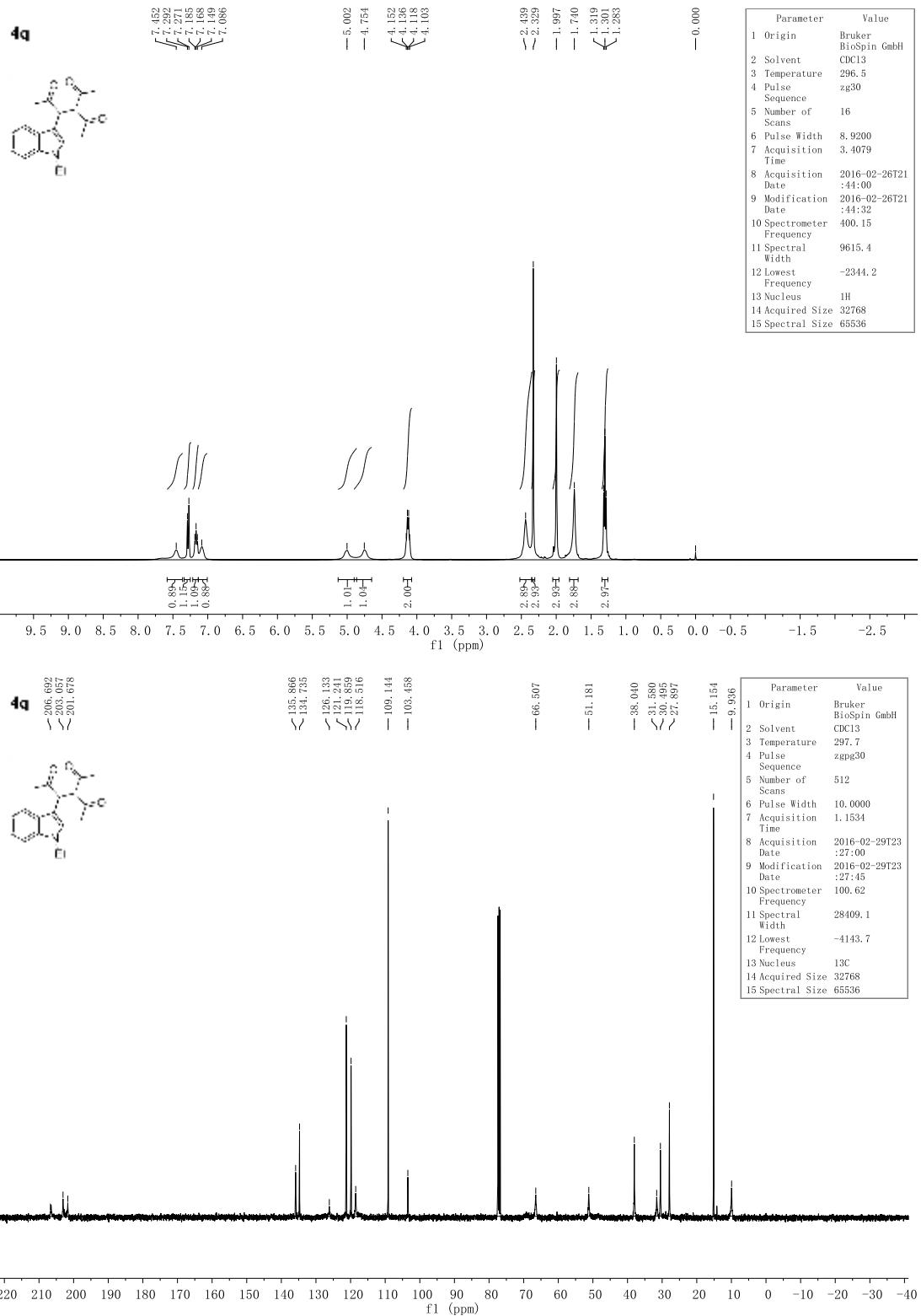
— 2.490  
— 2.342  
— 2.05  
— 1.830

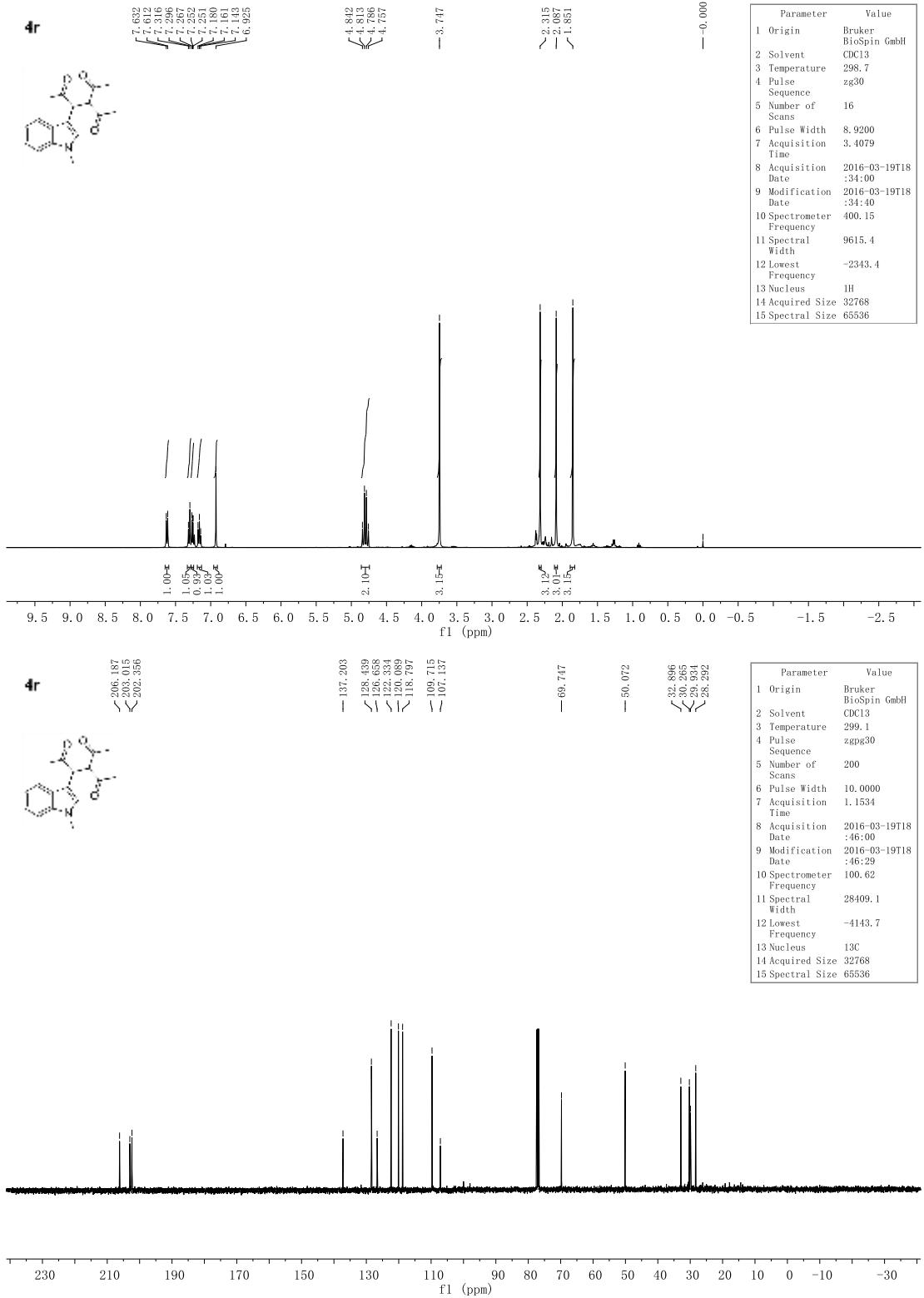
— 0.000

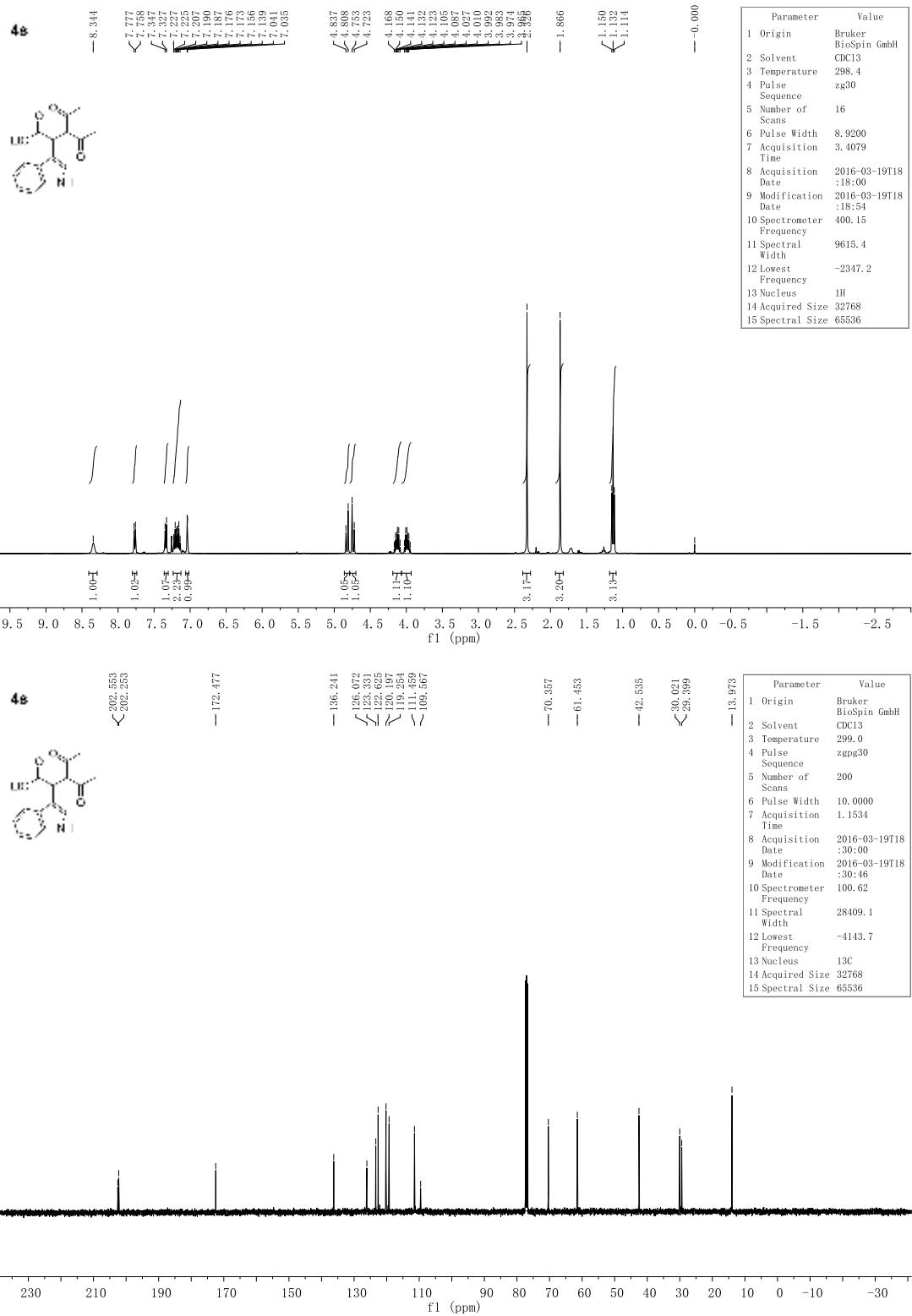
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	296.5
4 Pulse Sequence	zg30
5 Number of Scans	16
6 Pulse Width	8.9200
7 Acquisition Time	3.4079
8 Acquisition Date	2016-02-26T21:49:00
9 Modification Date	2016-02-26T21:49:04
10 Spectrometer Frequency	400.15
11 Spectral Width	9615.4
12 Lowest Frequency	-2337.9
13 Nucleus	<sup>1</sup> H
14 Acquired Size	32768
15 Spectral Size	65536

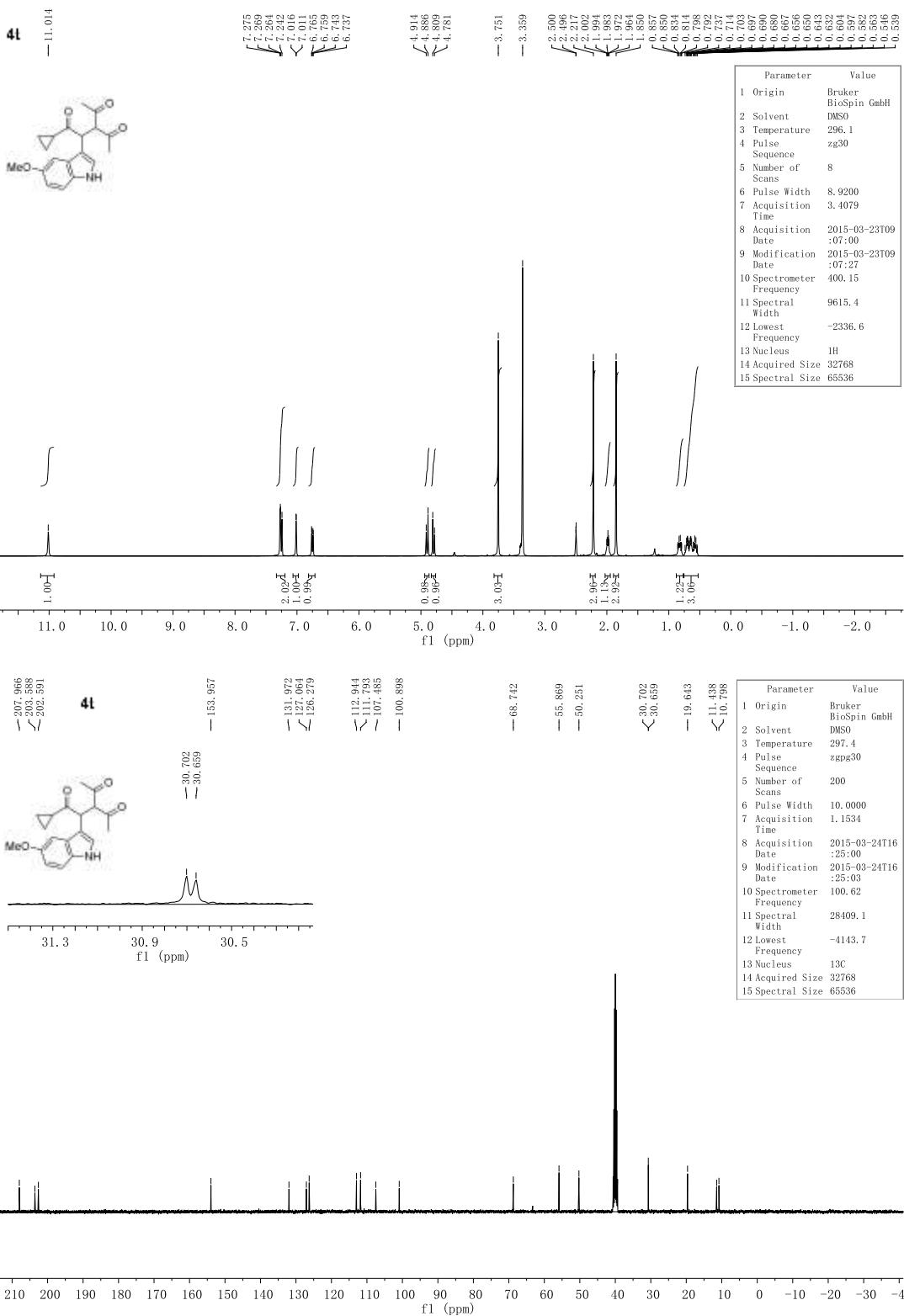






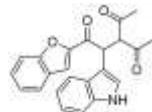




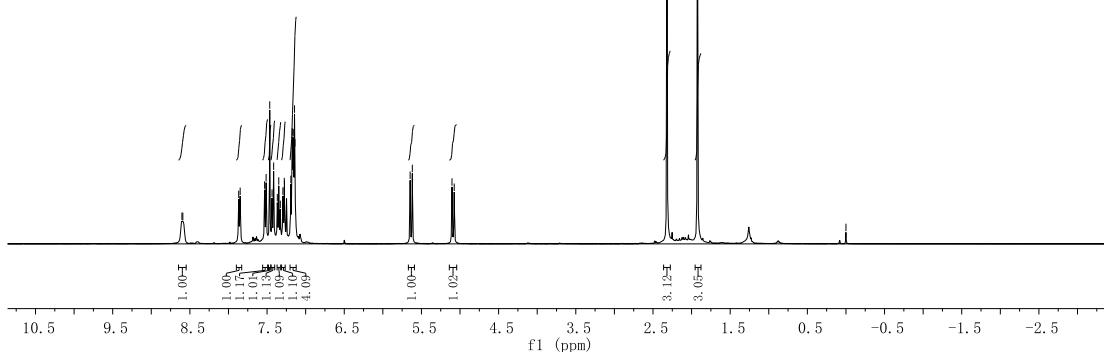


**4u**

<8.603  
<8.591  
7.899  
7.532  
7.512  
7.463  
7.415  
7.348  
7.295  
7.277  
7.274  
7.192  
7.174  
7.161  
7.155  
7.144  
7.038  
5.618



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	294.7
4 Pulse Sequence	zg30
5 Number of Scans	16
6 Pulse Width	8.9200
7 Acquisition Time	3.4079
8 Acquisition Date	2016-04-19T22:35:00
9 Modification Date	2016-04-19T22:35:16
10 Spectrometer Frequency	400.15
11 Spectral Width	9615.4
12 Lowest Frequency	-2351.3
13 Nucleus	1H
14 Acquired Size	32768
15 Spectral Size	65536

**4u**

&lt;203.321

— 188.221

— 155.546

— 151.330

— 136.361

— 128.288

— 126.956

— 125.950

— 124.331

— 123.786

— 123.233

— 122.668

— 120.501

— 119.062

— 114.338

— 114.154

— 111.704

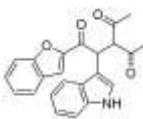
— 108.717

— 69.657

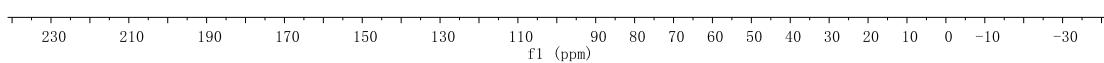
— 45.457

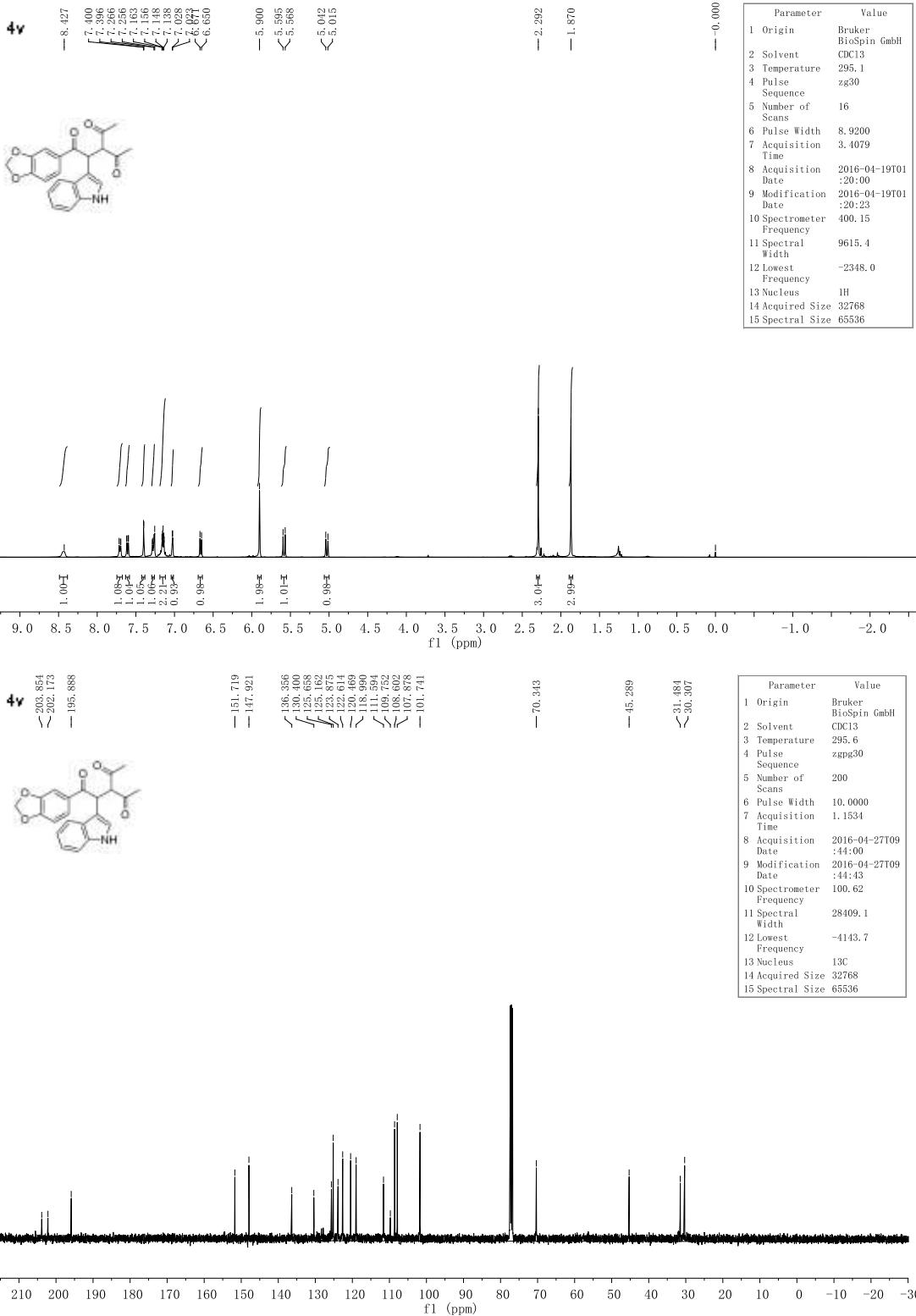
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&lt;30.262

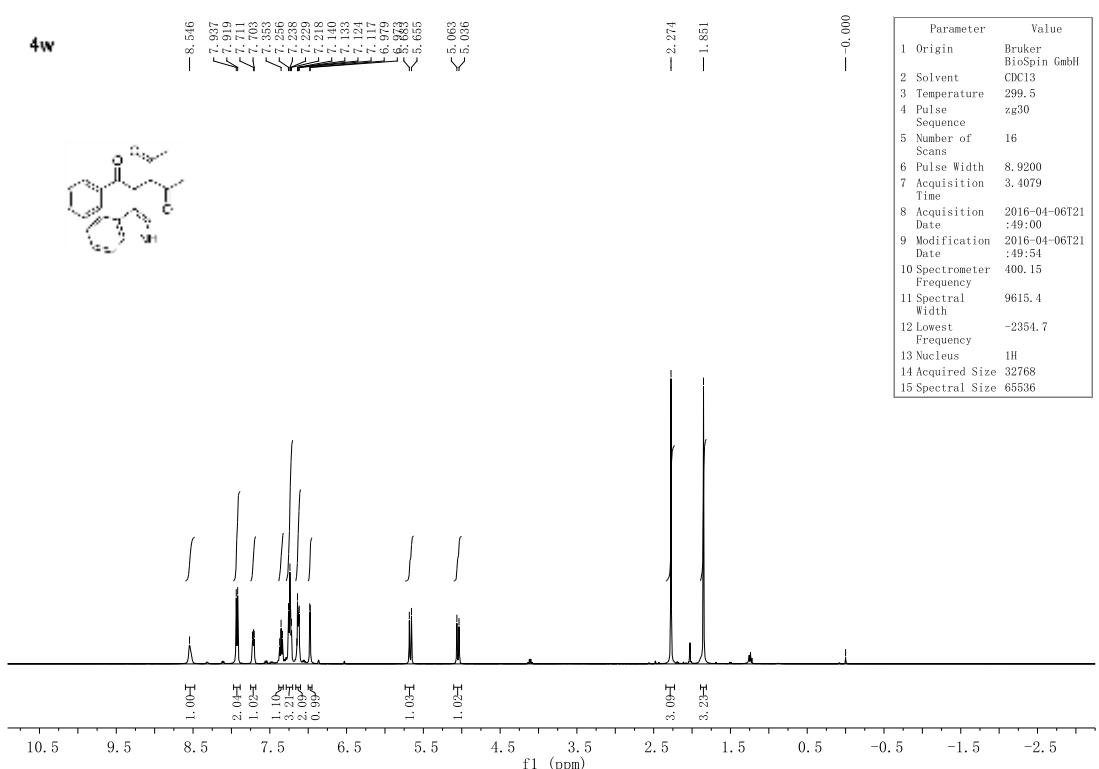


Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	295.9
4 Pulse Sequence	zgpg30
5 Number of Scans	200
6 Pulse Width	10.0000
7 Acquisition Time	1.1534
8 Acquisition Date	2016-04-20T23:41:00
9 Modification Date	2016-04-20T23:41:12
10 Spectrometer Frequency	100.62
11 Spectral Width	28409.1
12 Lowest Frequency	-4143.7
13 Nucleus	<sup>13</sup> C
14 Acquired Size	32768
15 Spectral Size	65536

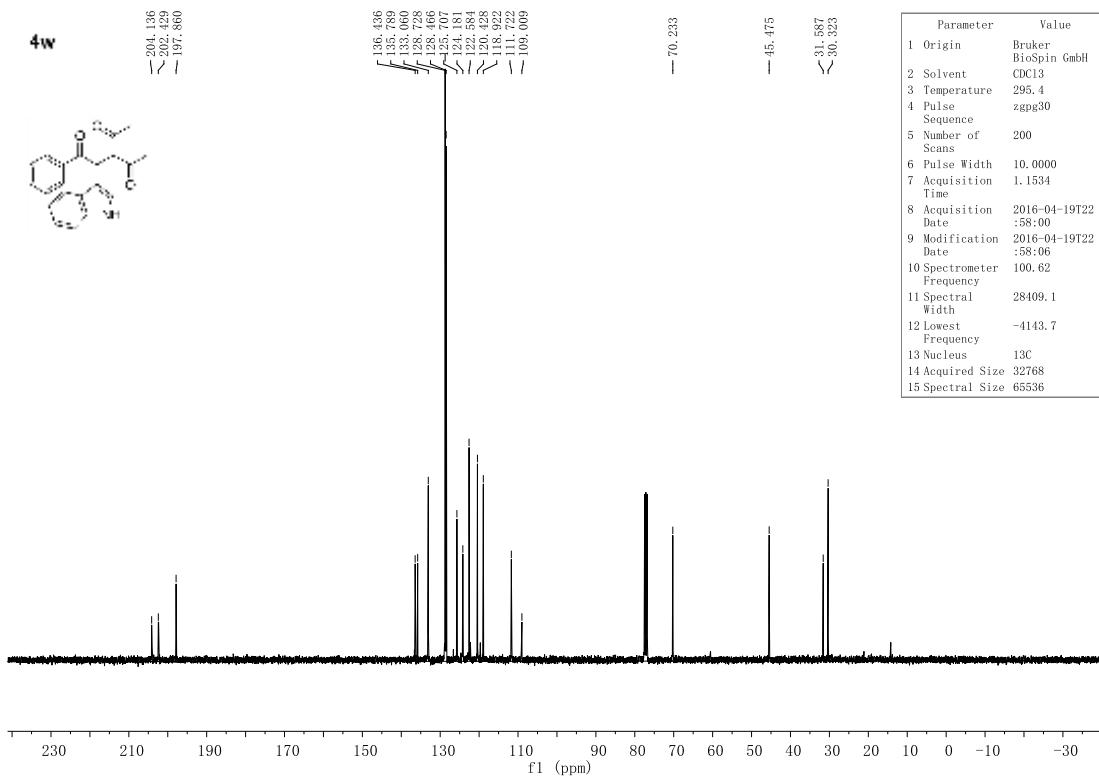




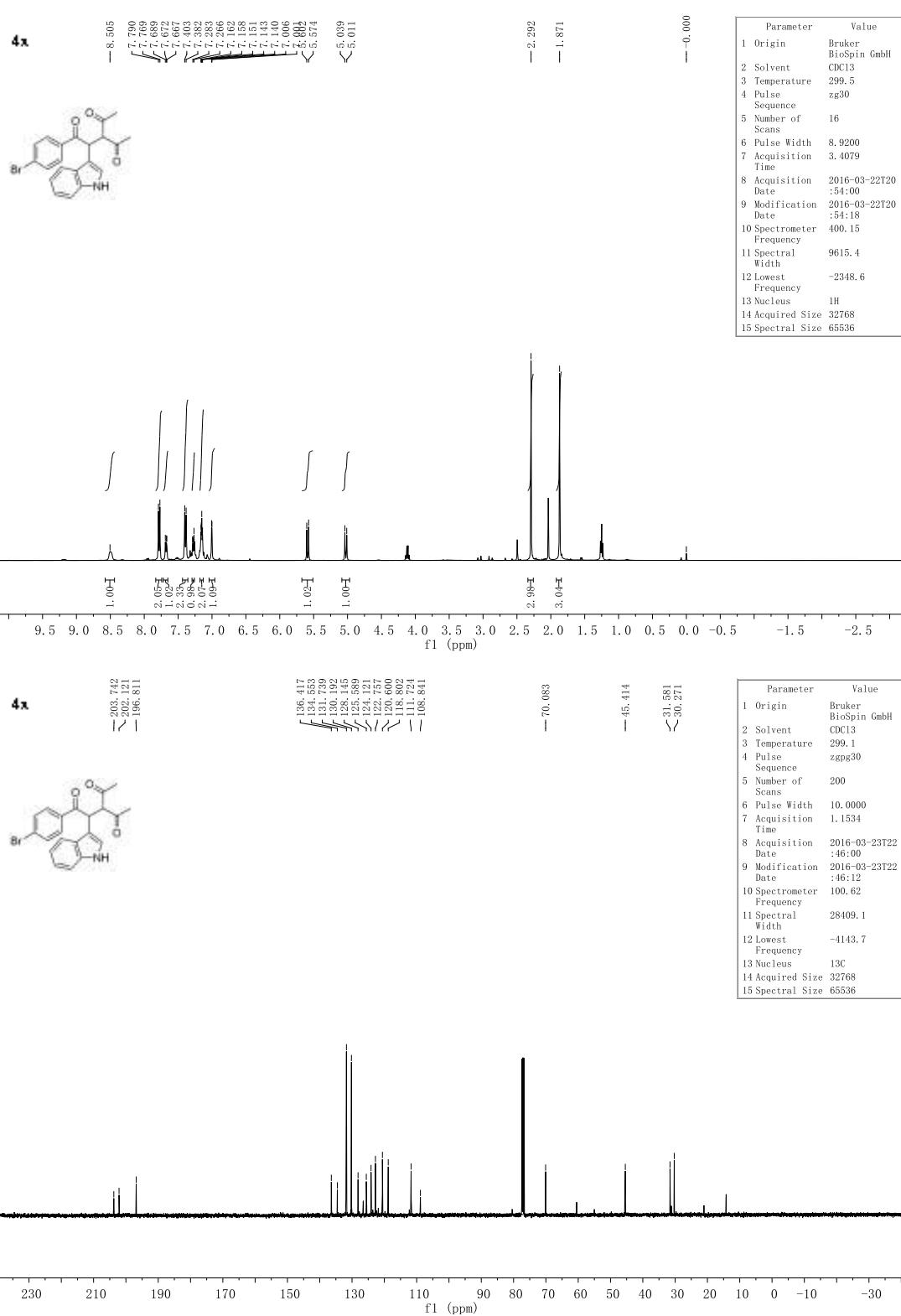
**4w**

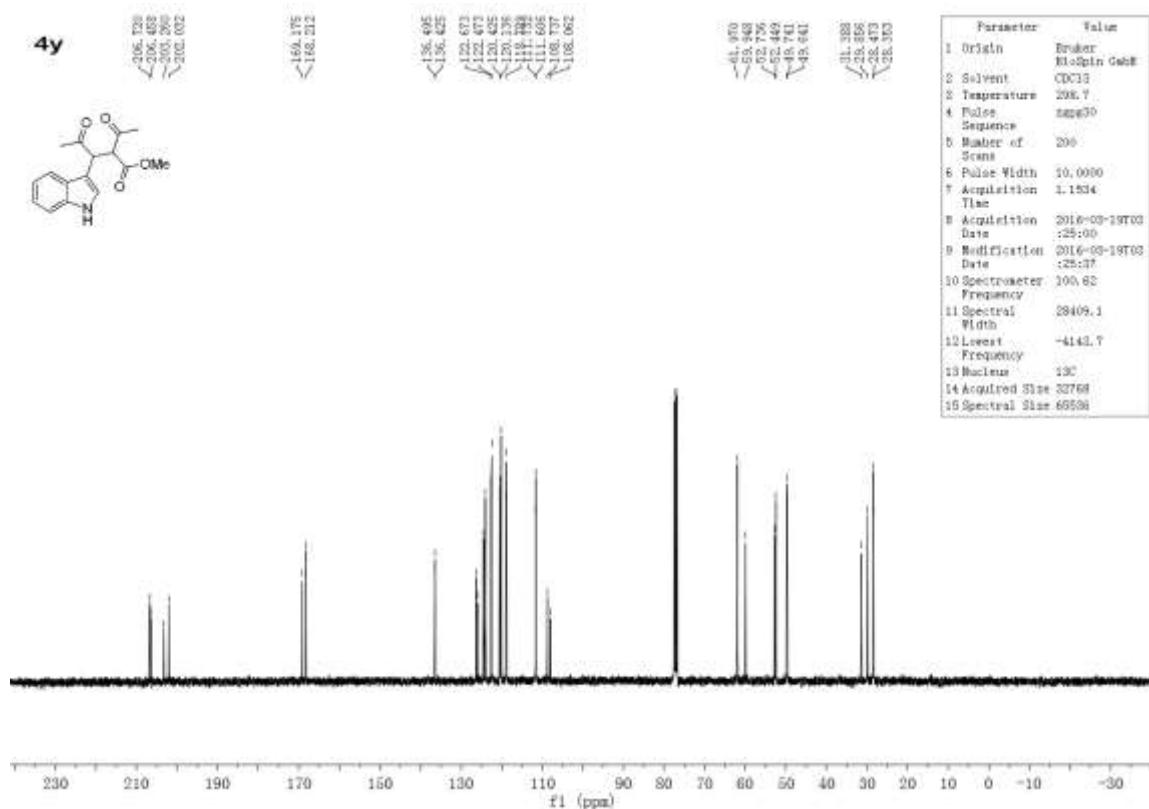
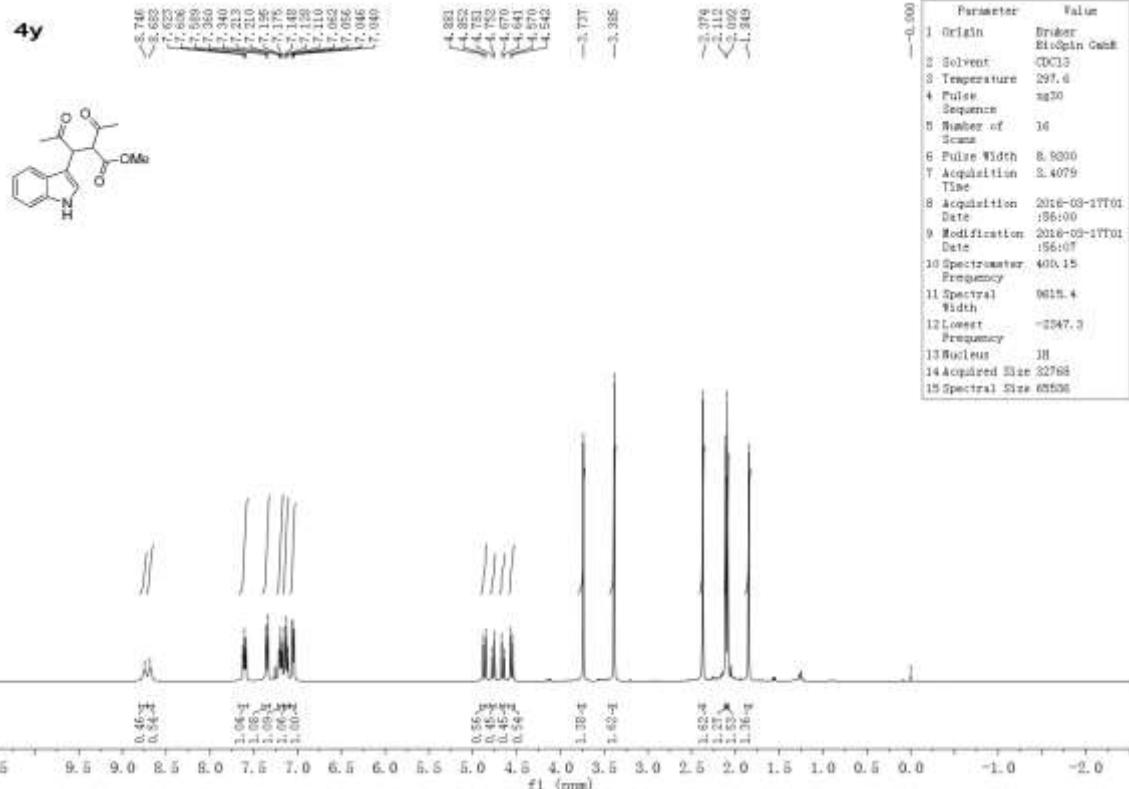


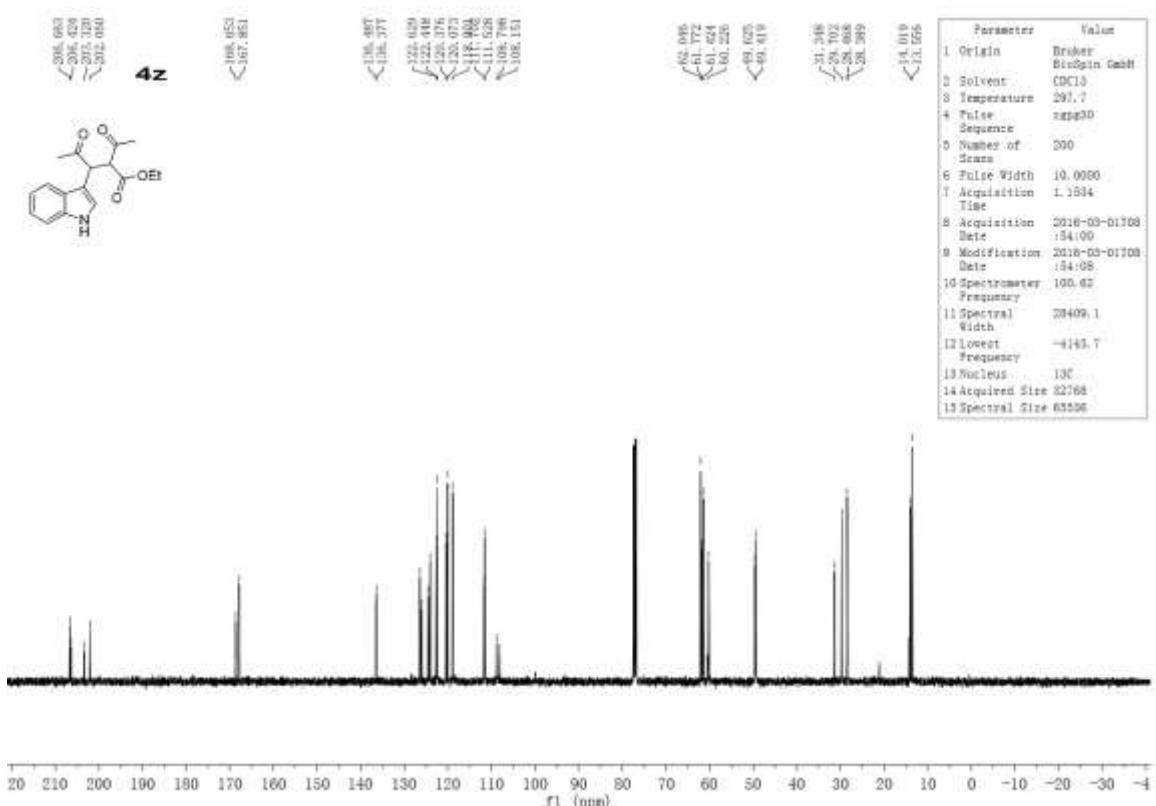
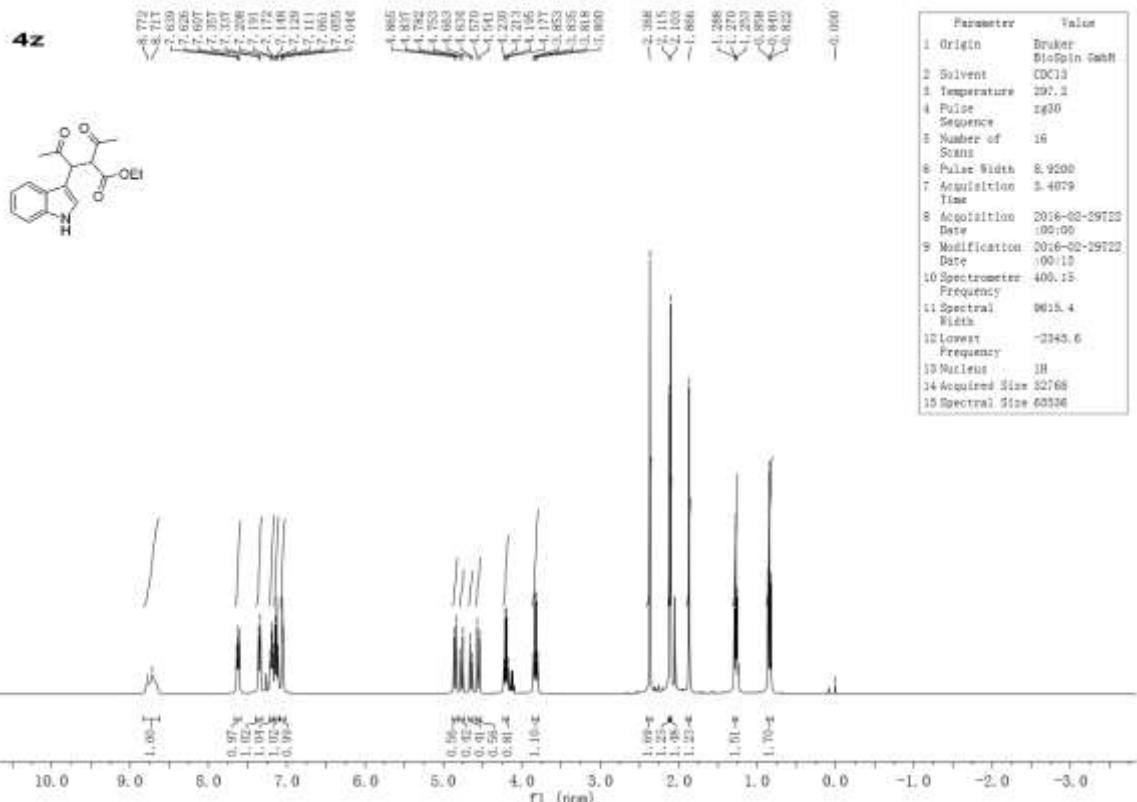
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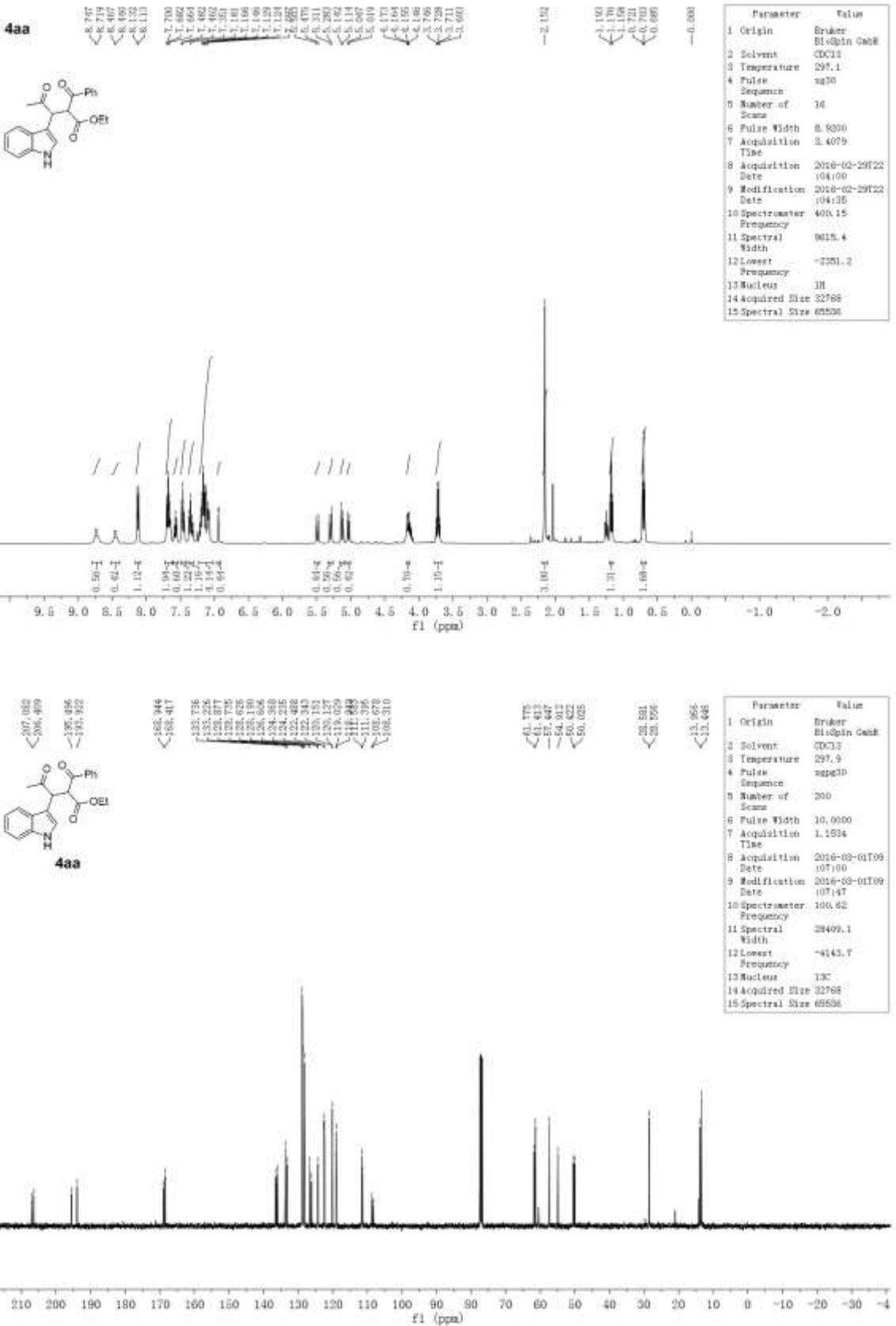


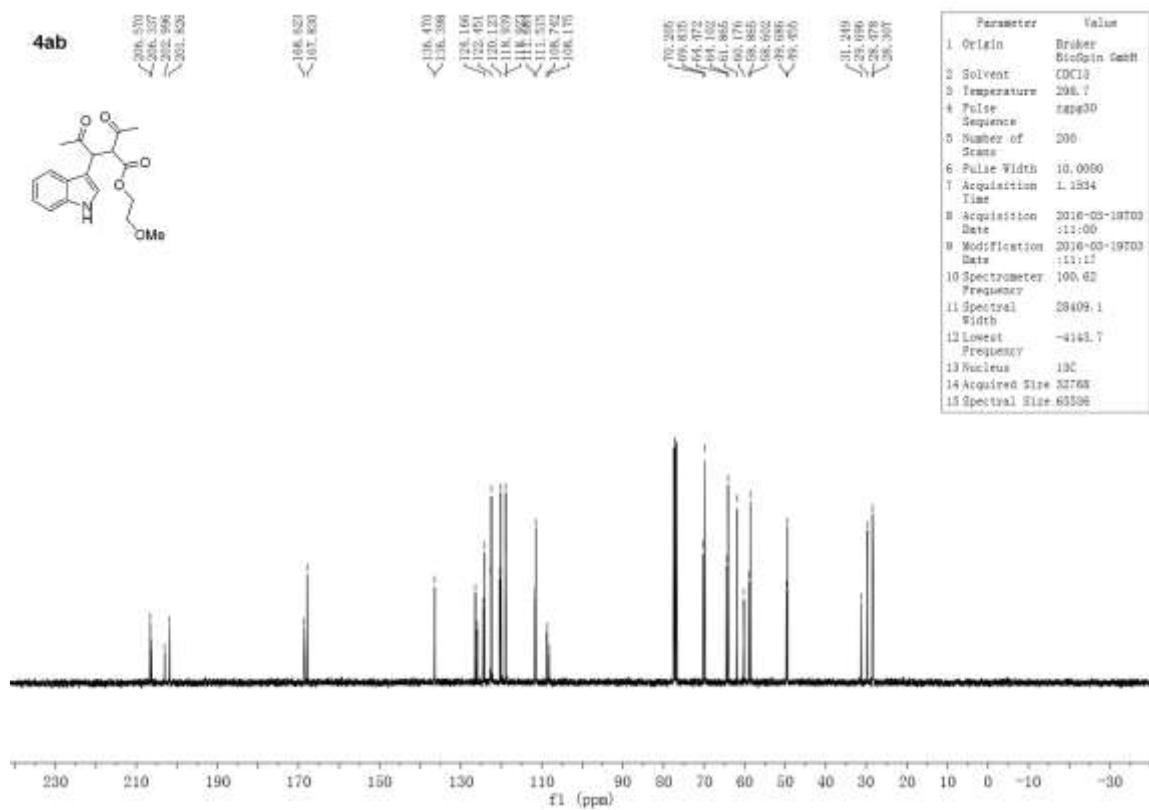
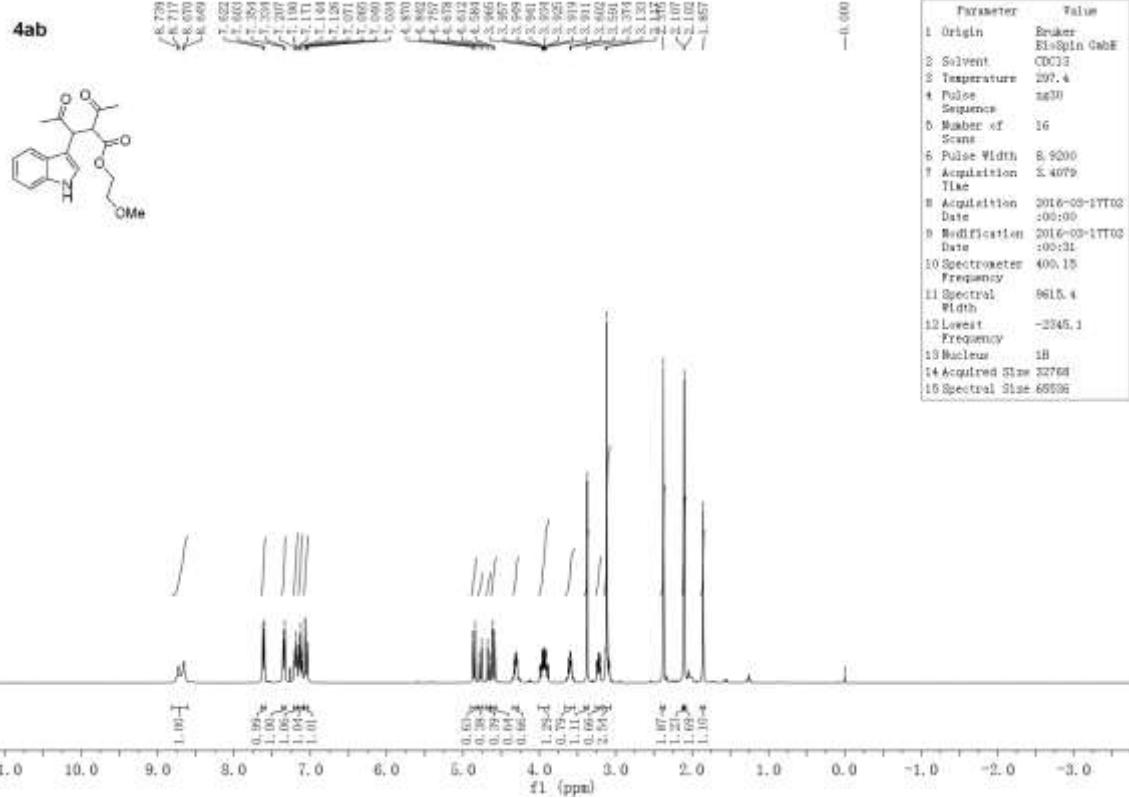
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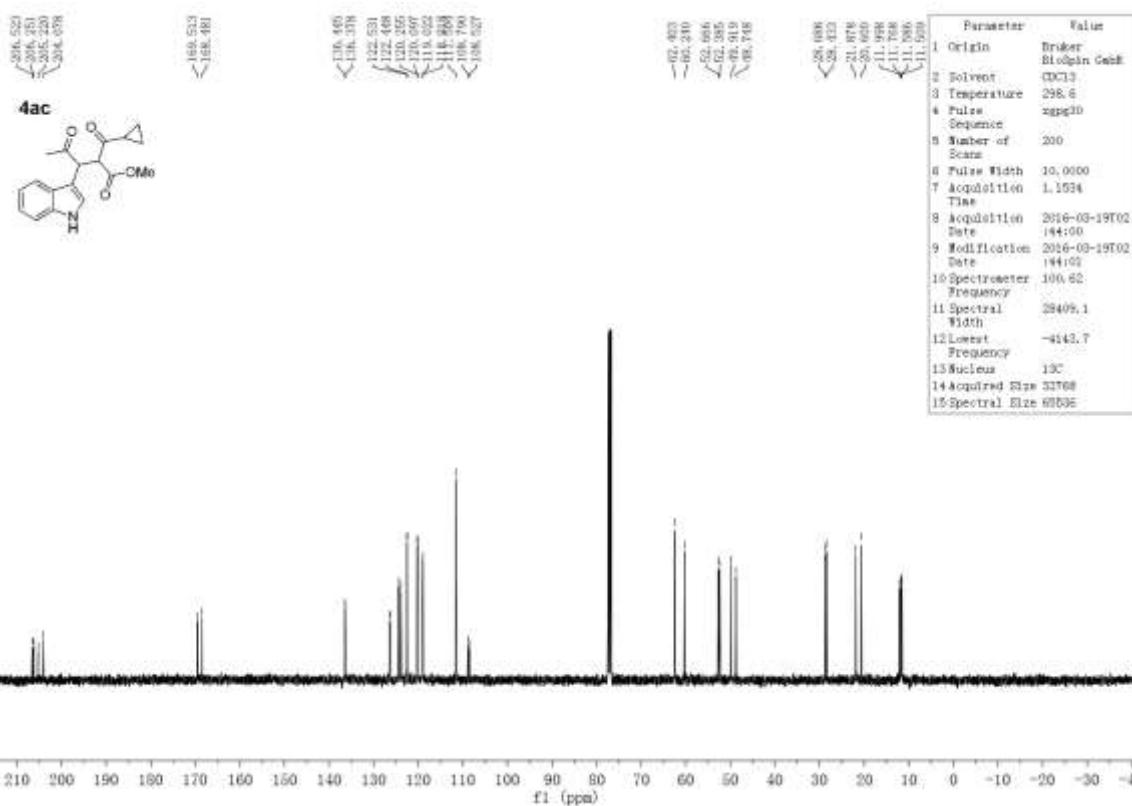
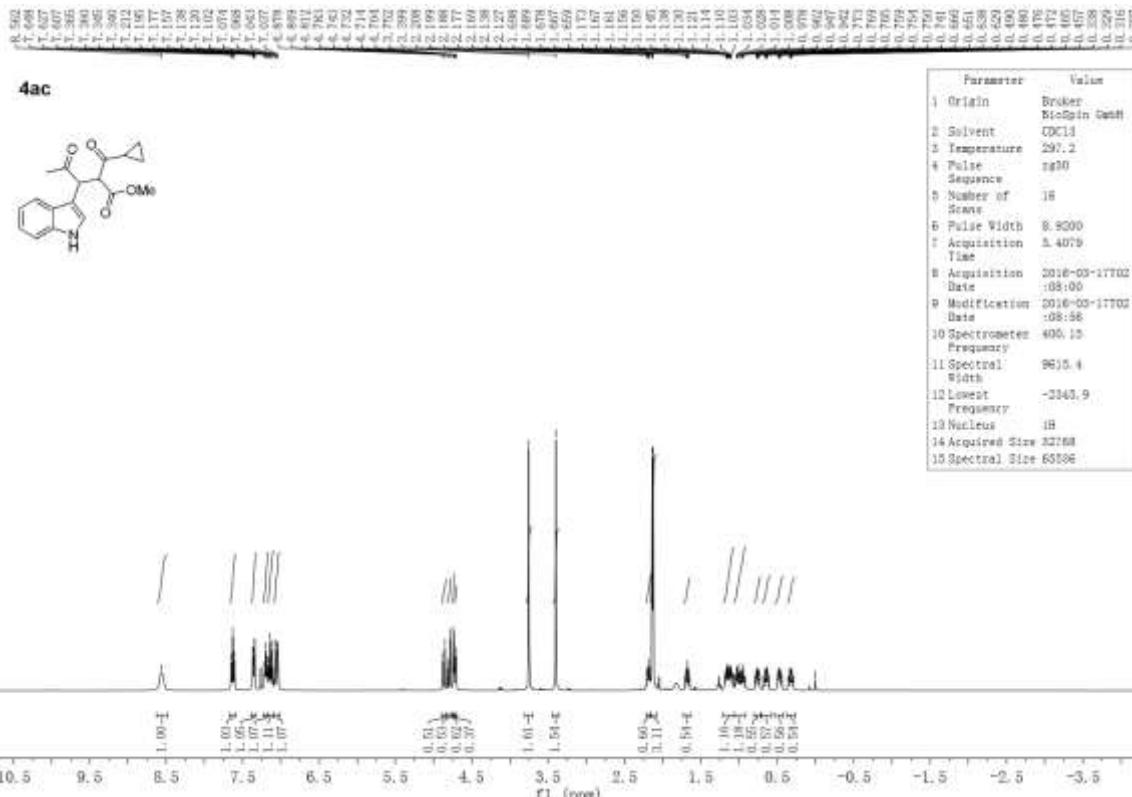




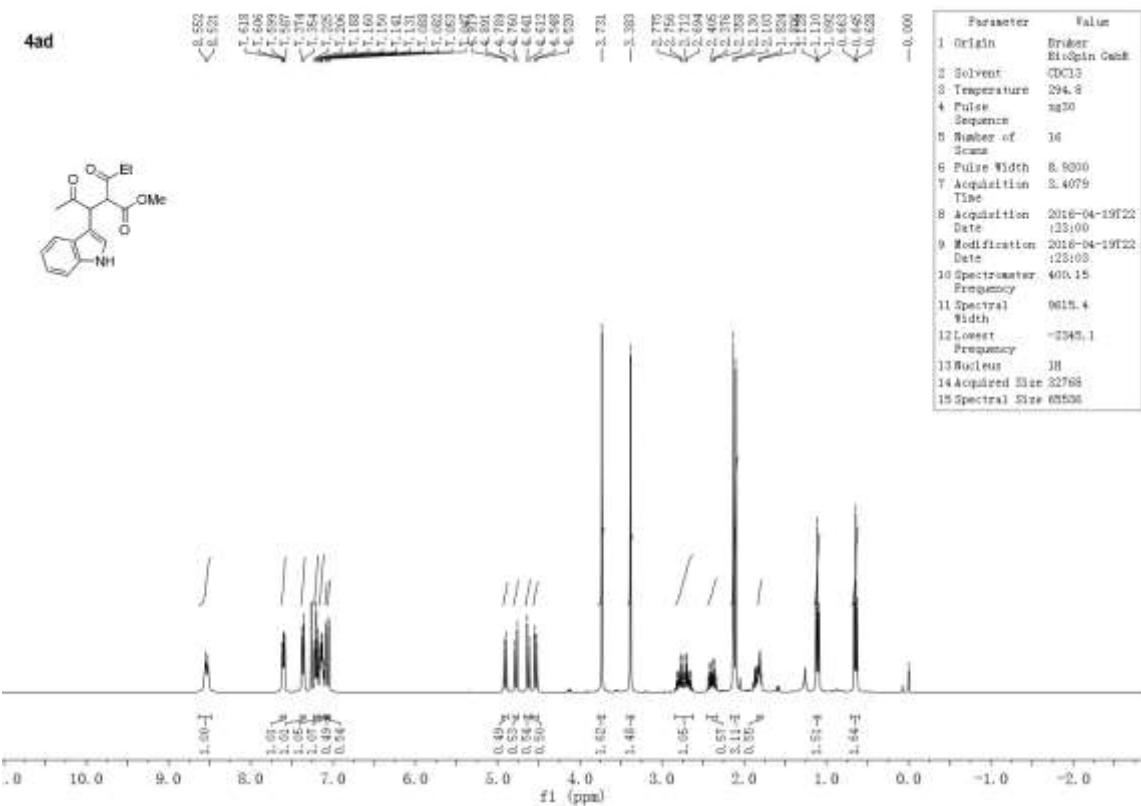
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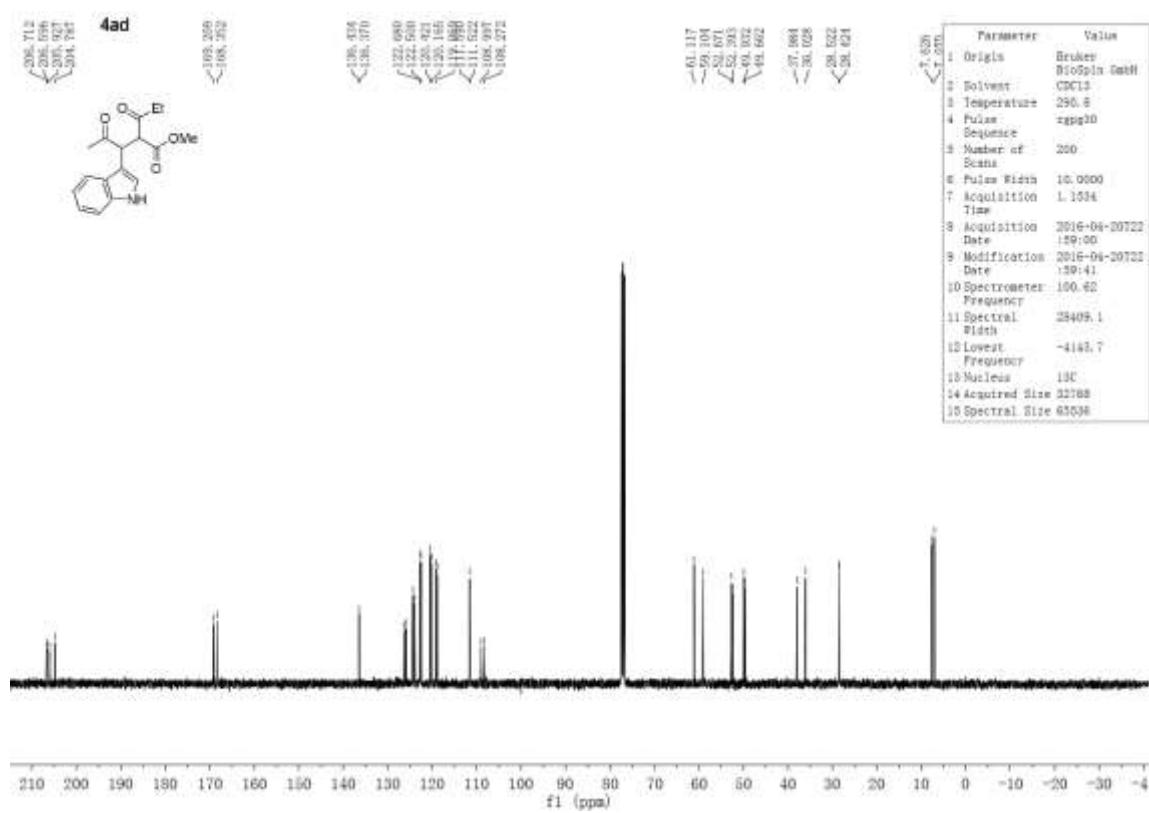


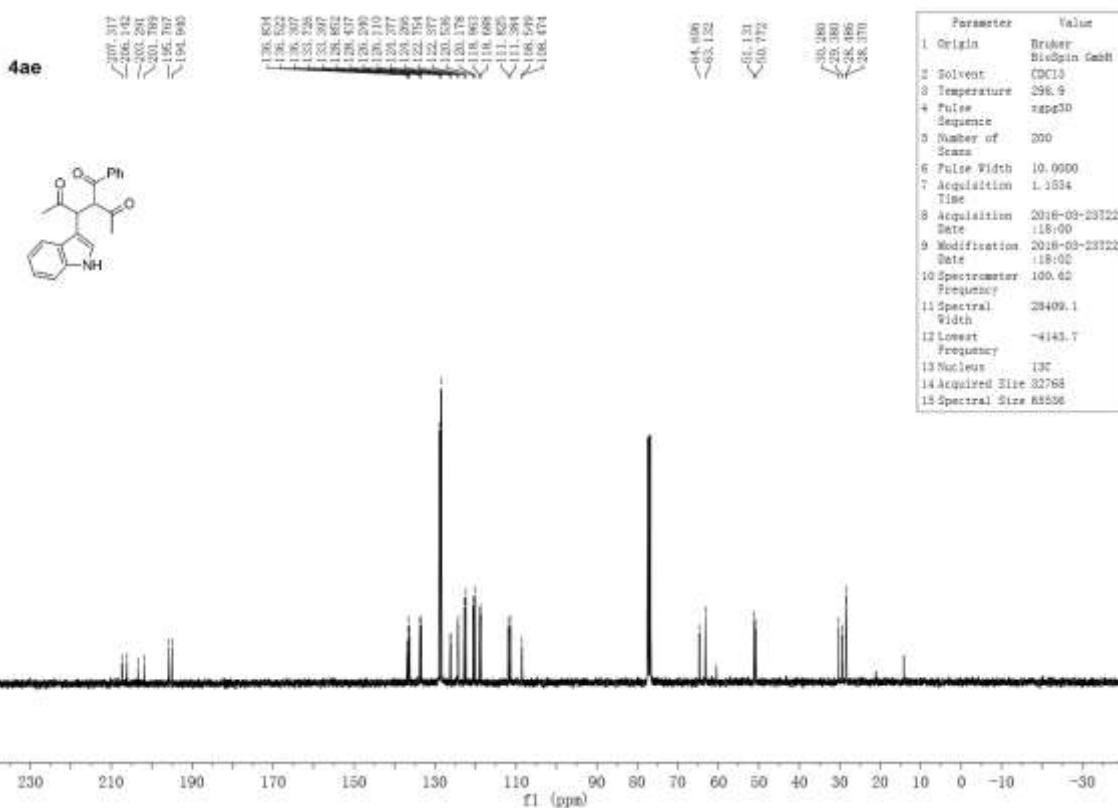
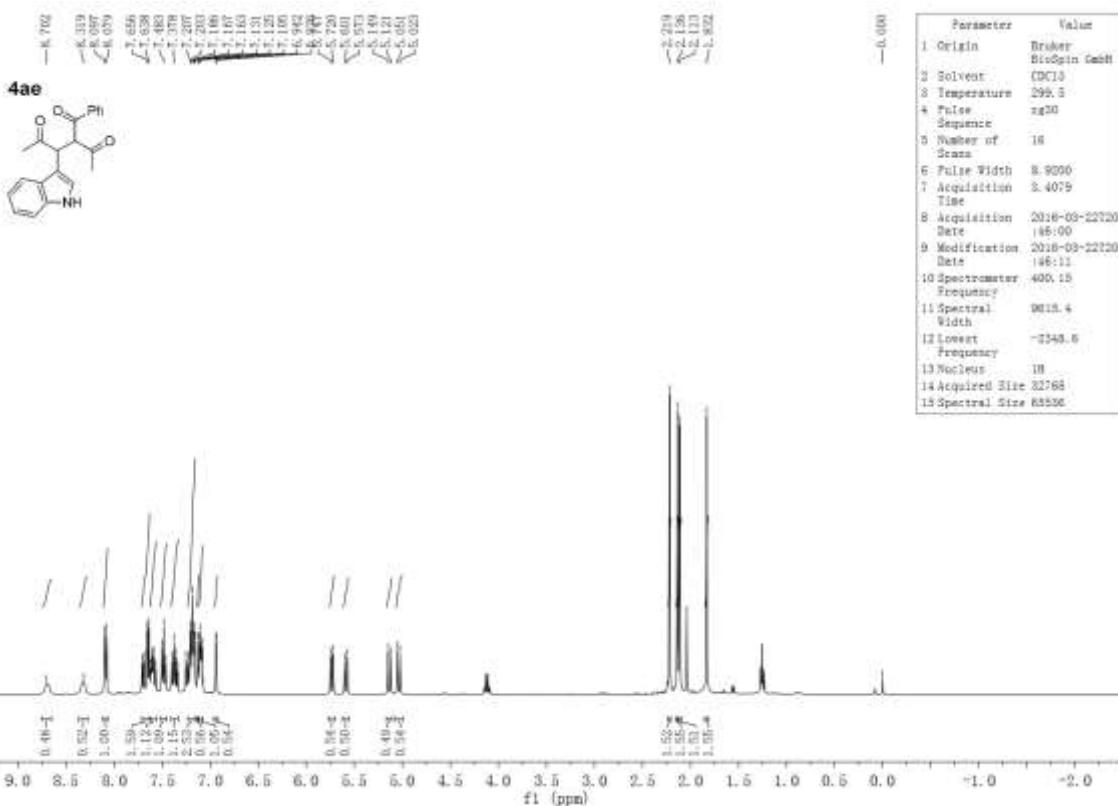


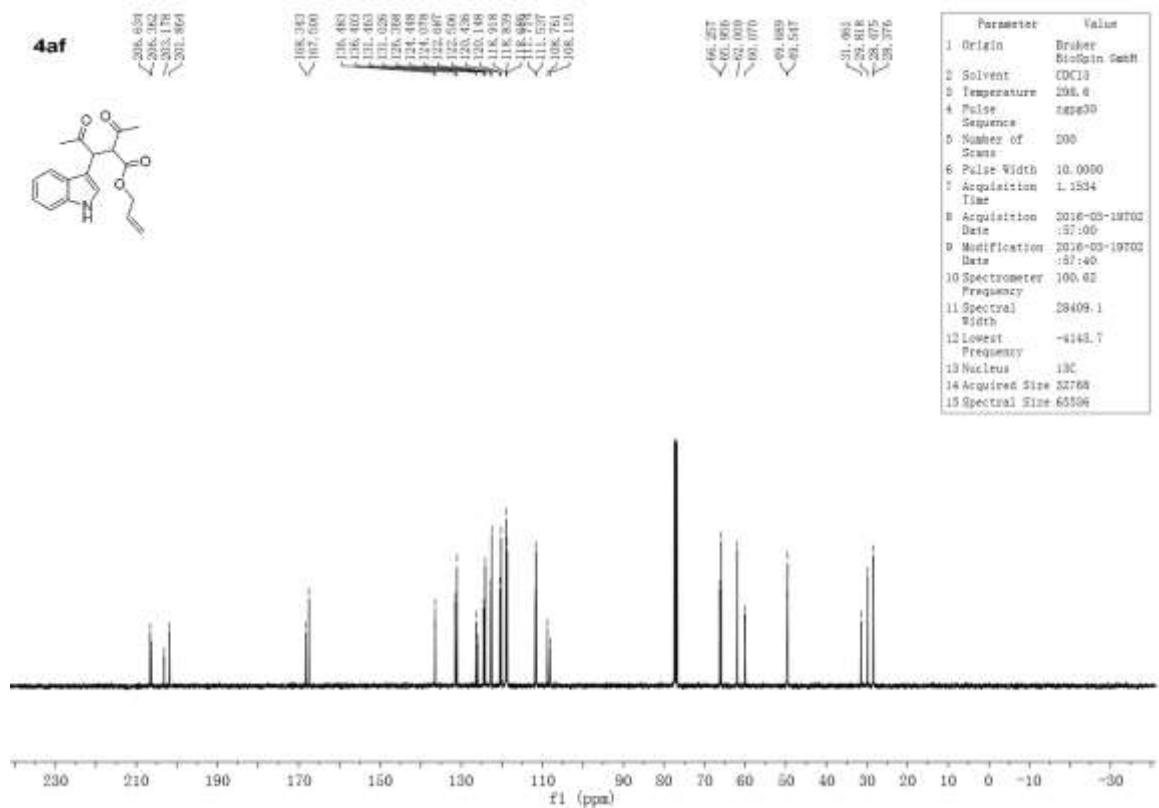
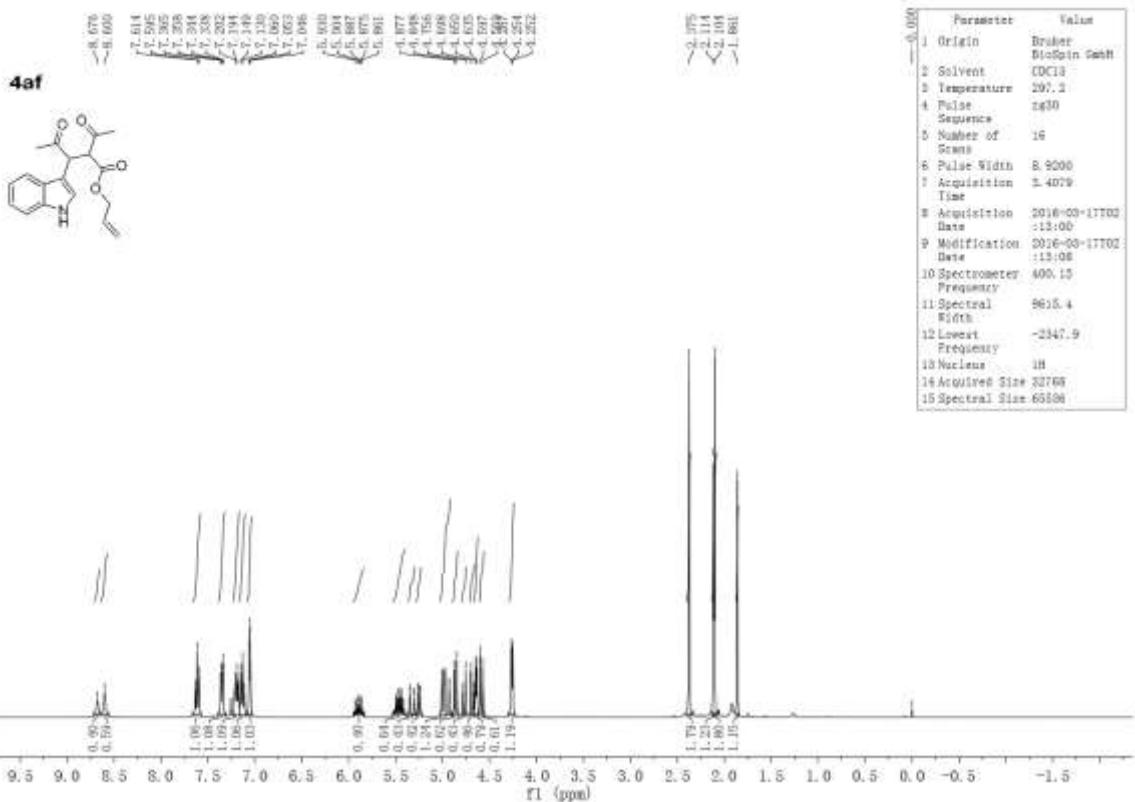
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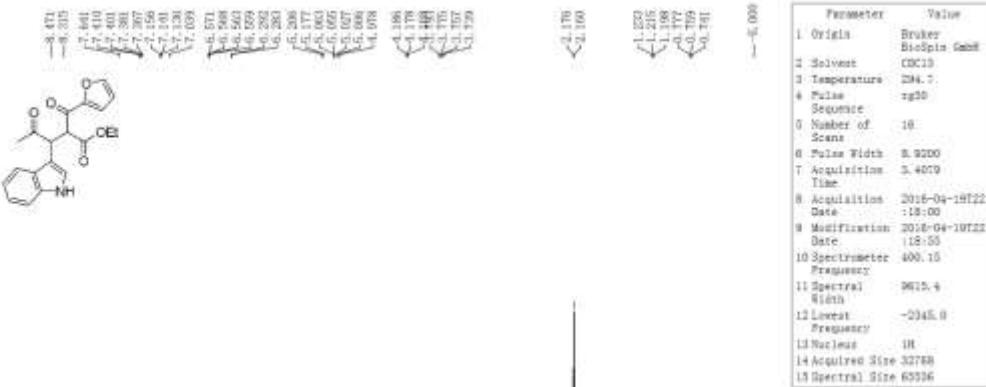
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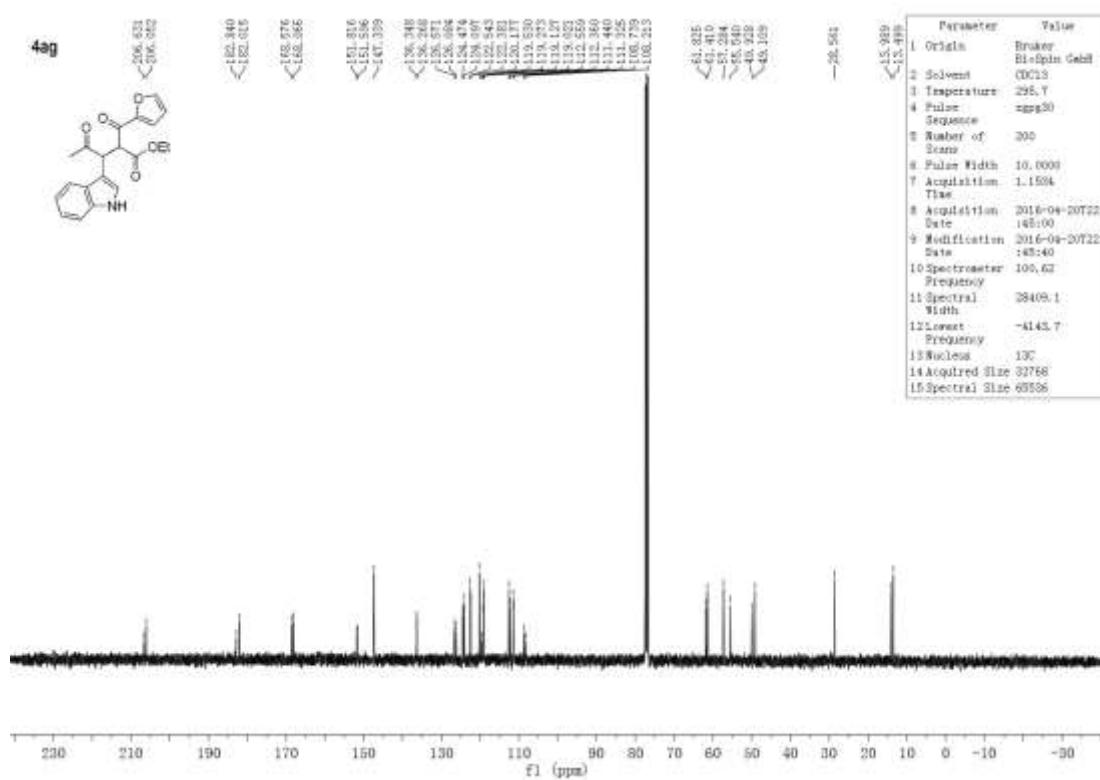


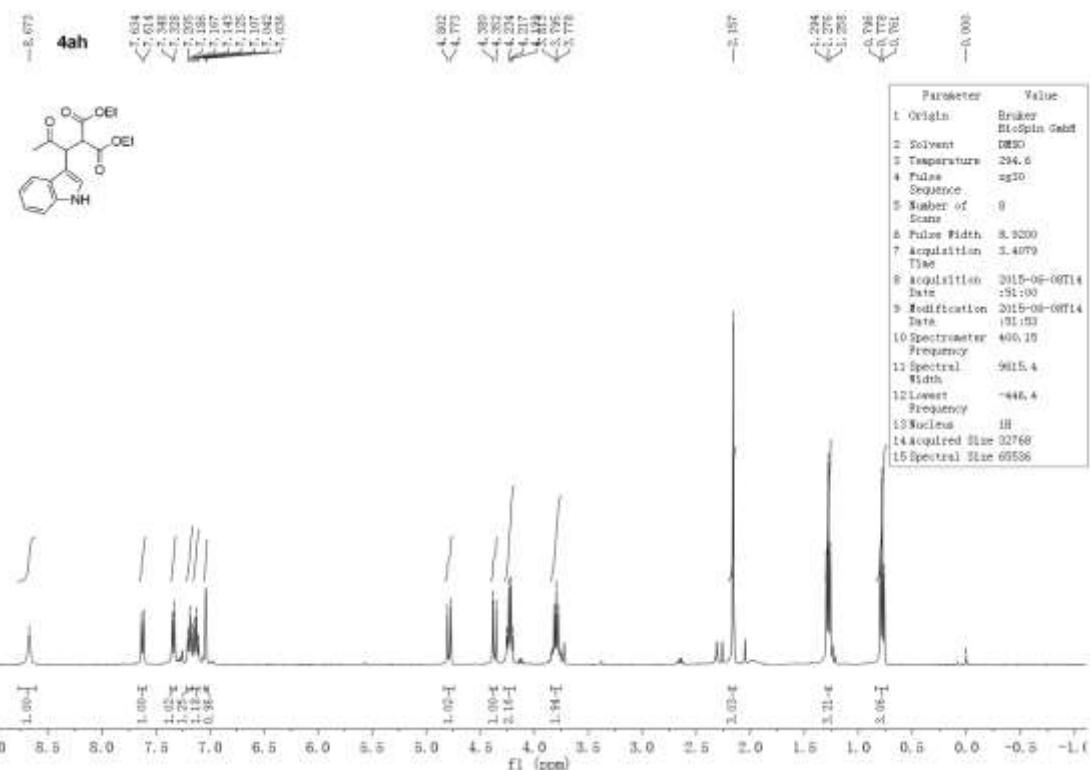


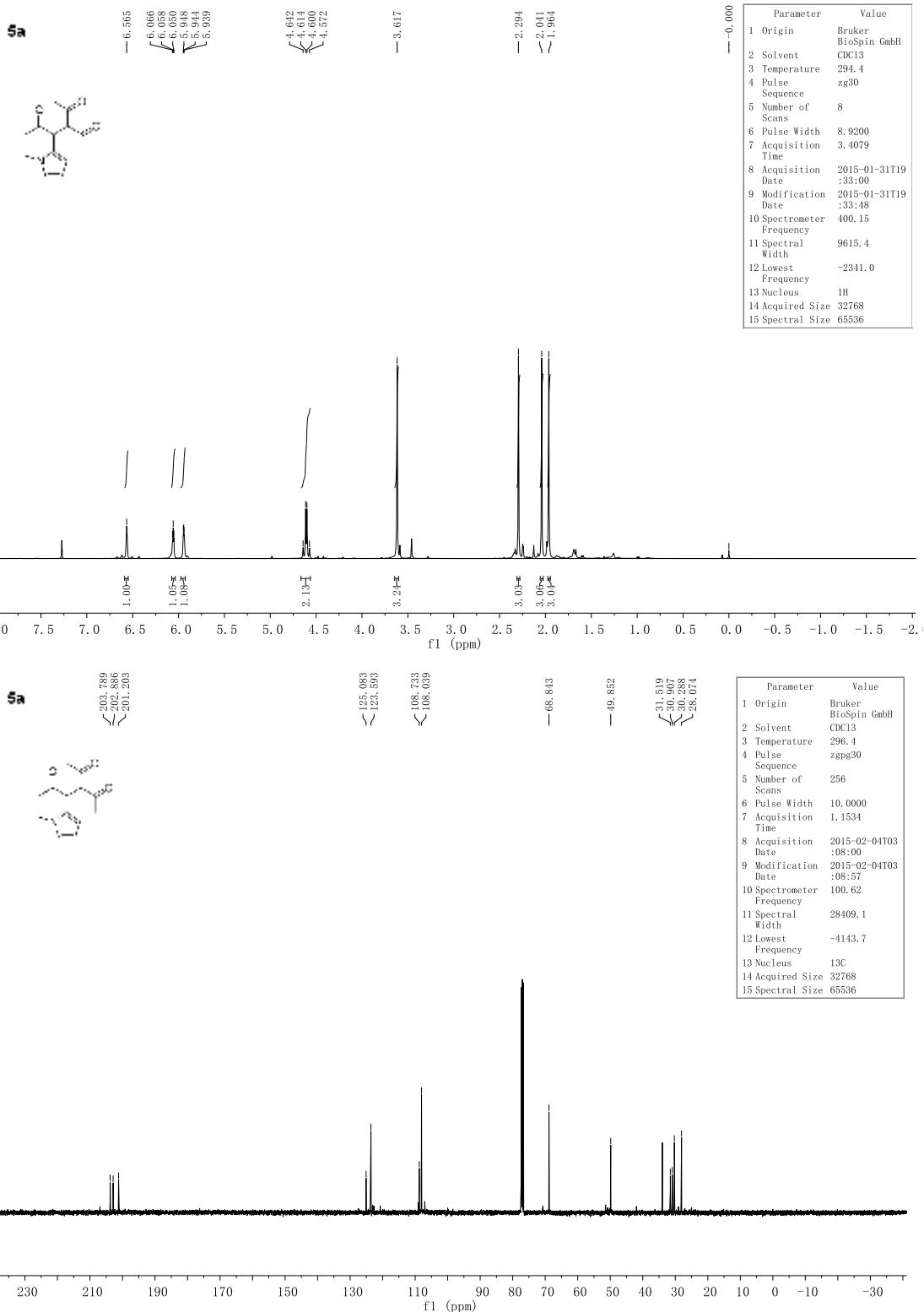
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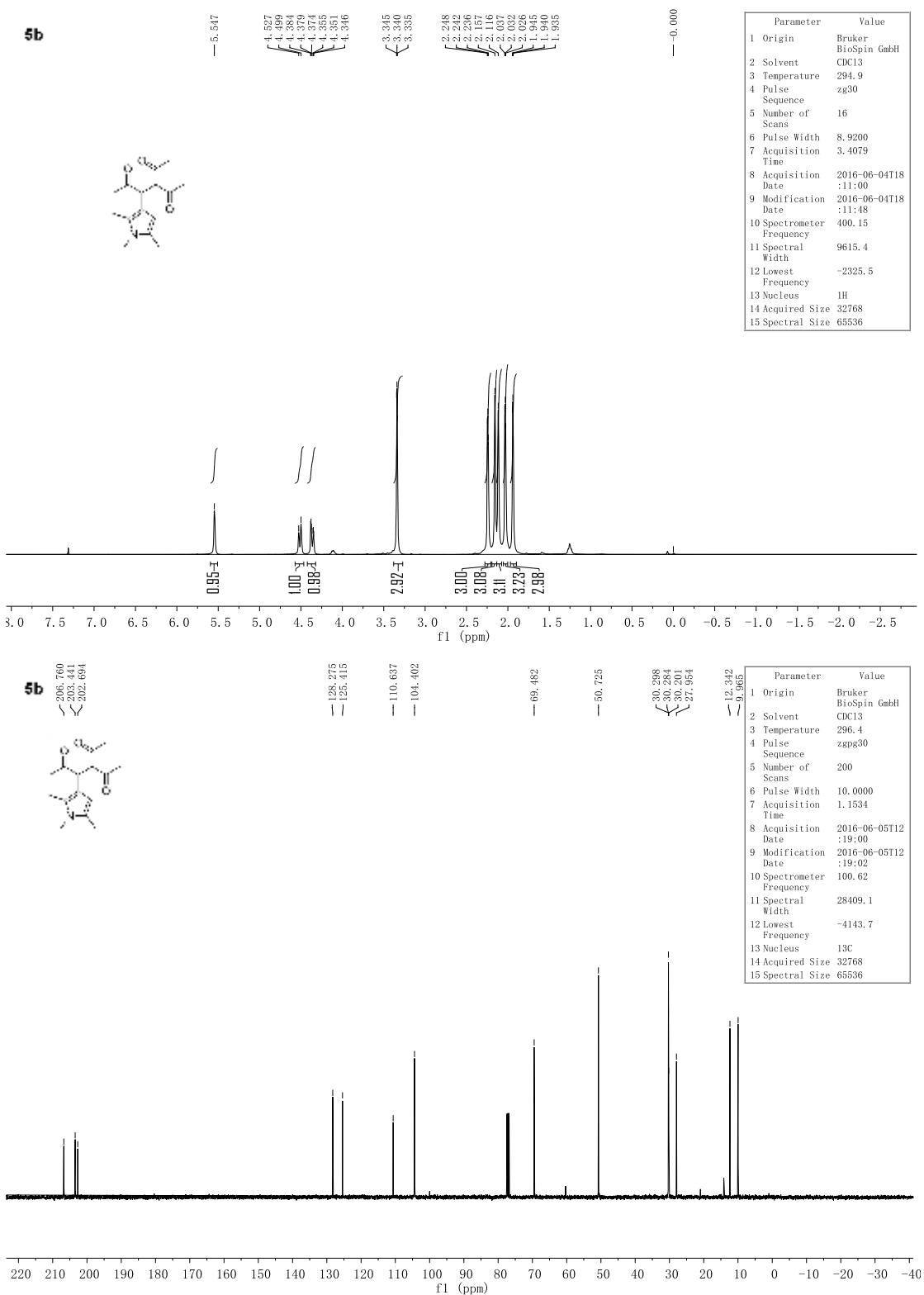


**4ag**

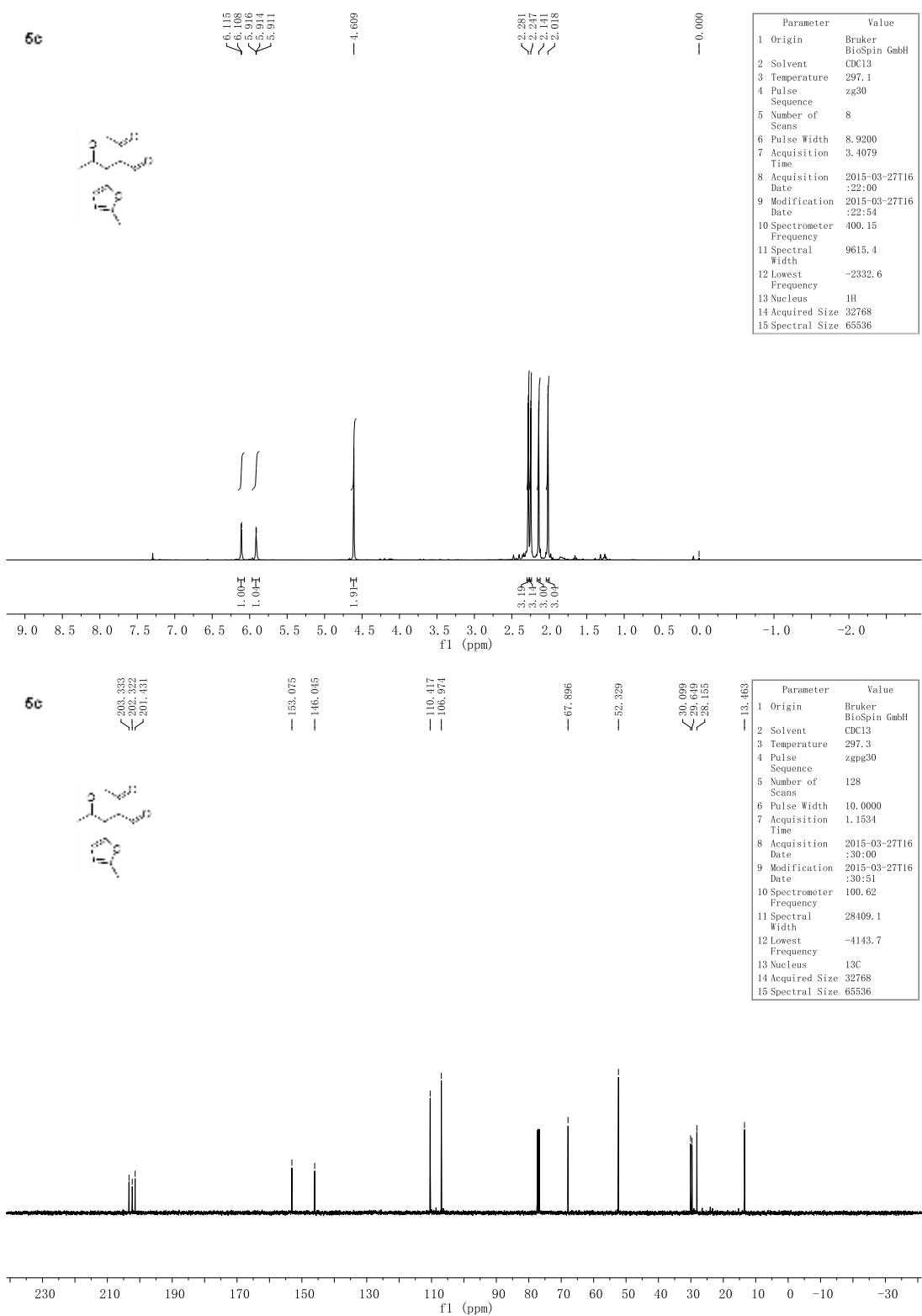


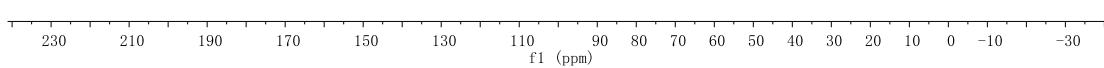
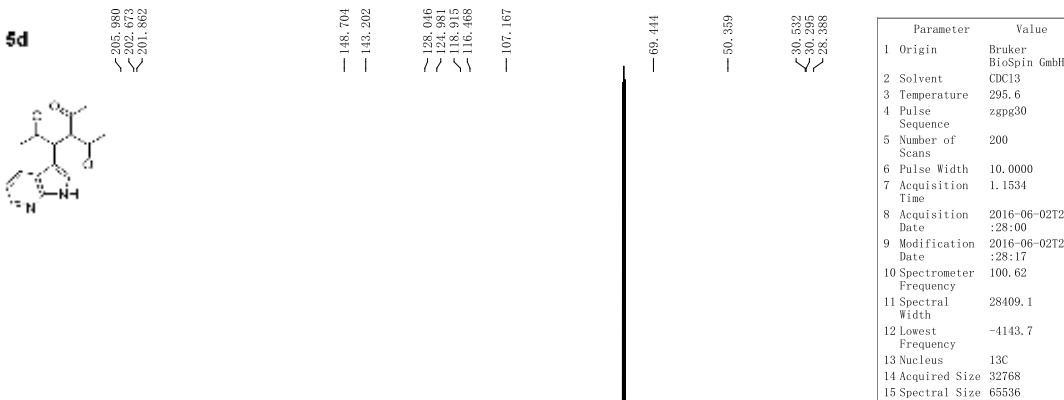
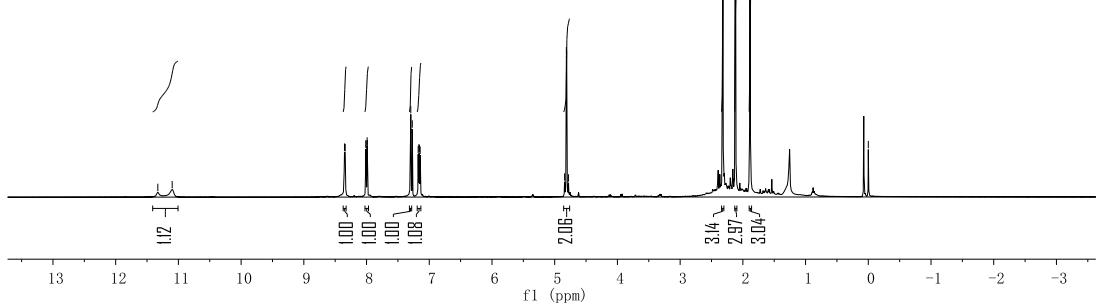
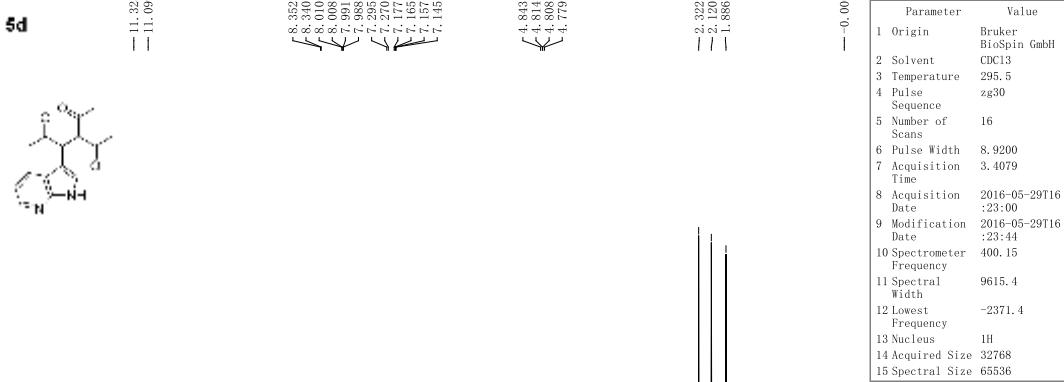


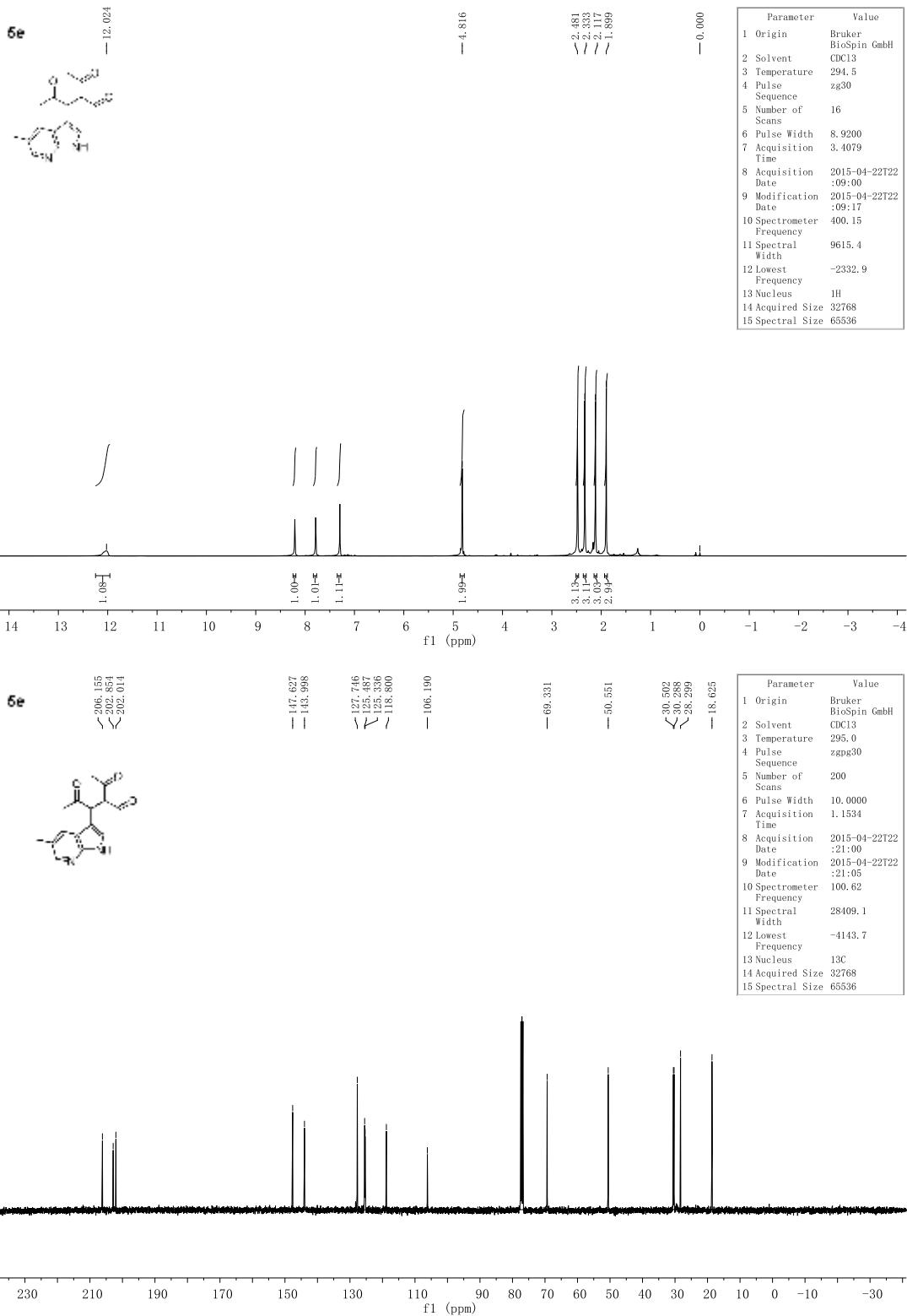


**5b**

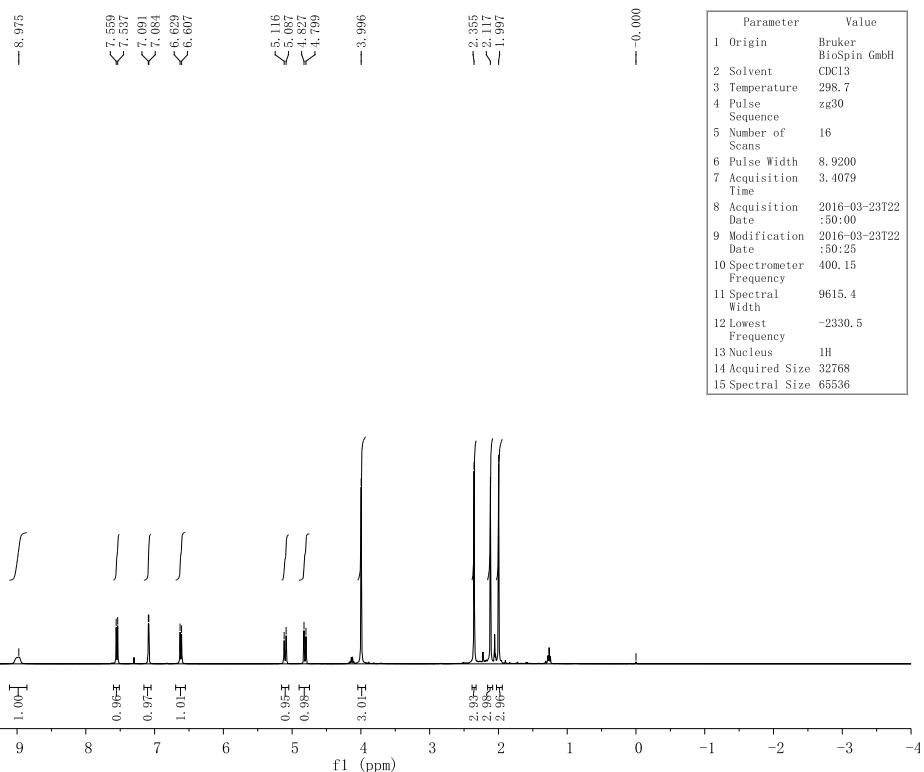
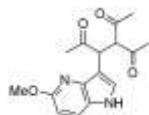
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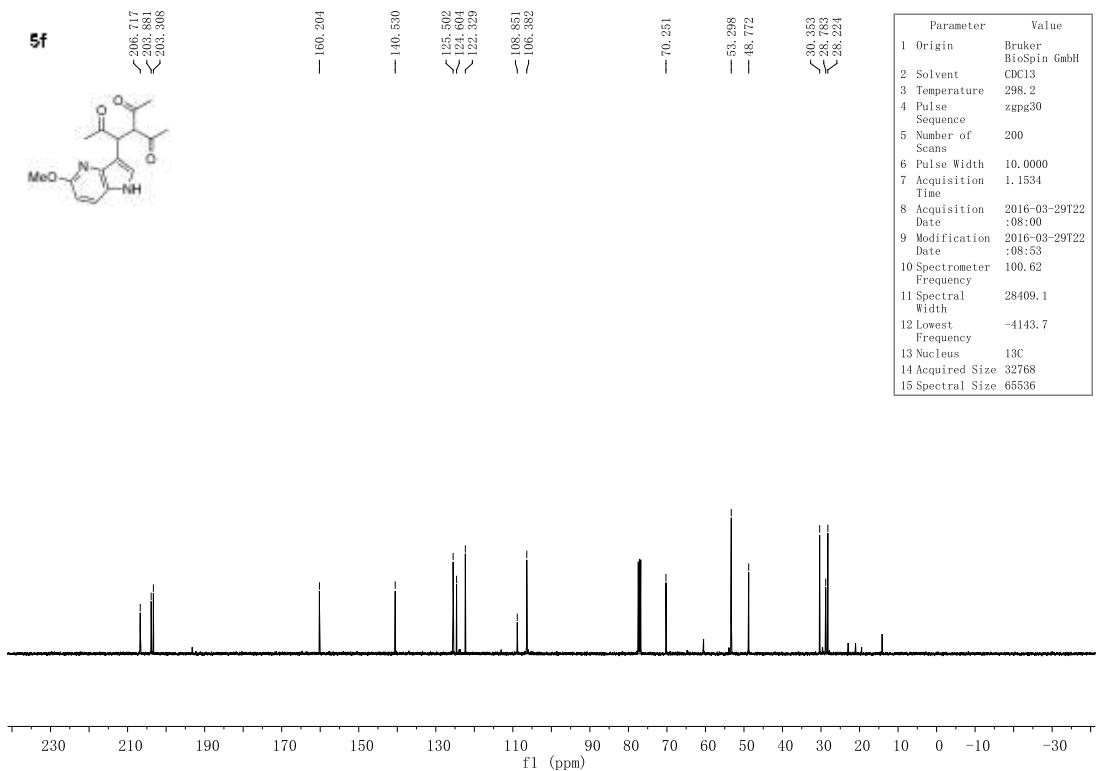
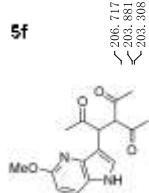




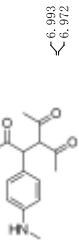
**5f**



**5f**



**5g**



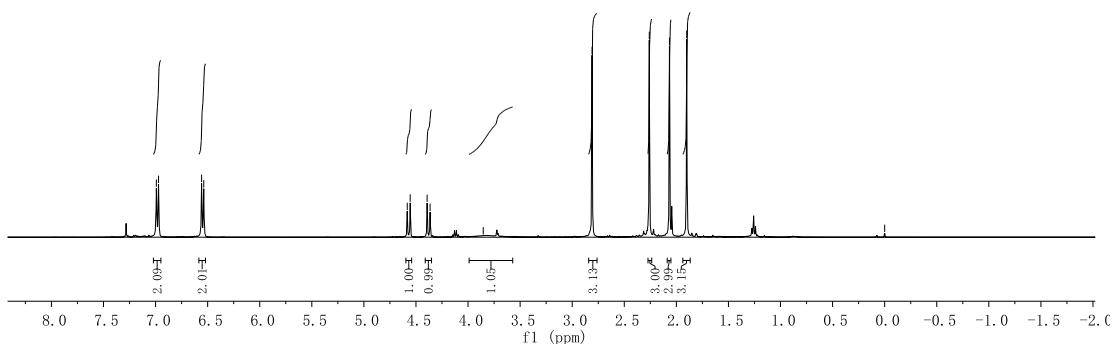
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< 6.972  
< 6.558  
< 6.537

< 4.584  
< 4.555  
< 4.395  
< 4.364

— 3.854

— 2.809  
~ 2.266  
— 2.066  
— 1.901

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	295.5
4 Pulse Sequence	zg30
5 Number of Scans	8
6 Pulse Width	8.9200
7 Acquisition Time	3.4079
8 Acquisition Date	2015-03-10T11:21:00
9 Modification Date	2015-03-10T11:22:00
10 Spectrometer Frequency	400.15
11 Spectral Width	9615.4
12 Lowest Frequency	-2337.3
13 Nucleus	1H
14 Acquired Size	32768
15 Spectral Size	65536



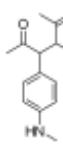
**5g**

< 206.448  
< 203.129  
< 202.201

— 149.196  
— 129.625  
— 122.014  
— 112.978

— 70.436  
— 58.020

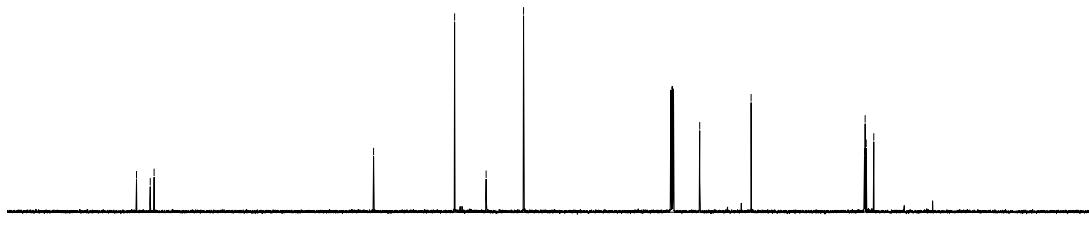
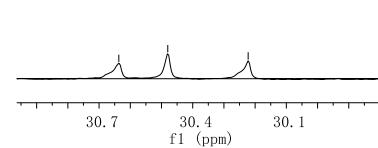
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl <sub>3</sub>
3 Temperature	295.8
4 Pulse Sequence	zgpg30
5 Number of Scans	200
6 Pulse Width	10.0000
7 Acquisition Time	1.1534
8 Acquisition Date	2015-03-12T11:45:00
9 Modification Date	2015-03-12T11:45:48
10 Spectrometer Frequency	100.62
11 Spectral Width	28409.1
12 Lowest Frequency	-4143.7
13 Nucleus	13C
14 Acquired Size	32768
15 Spectral Size	65536

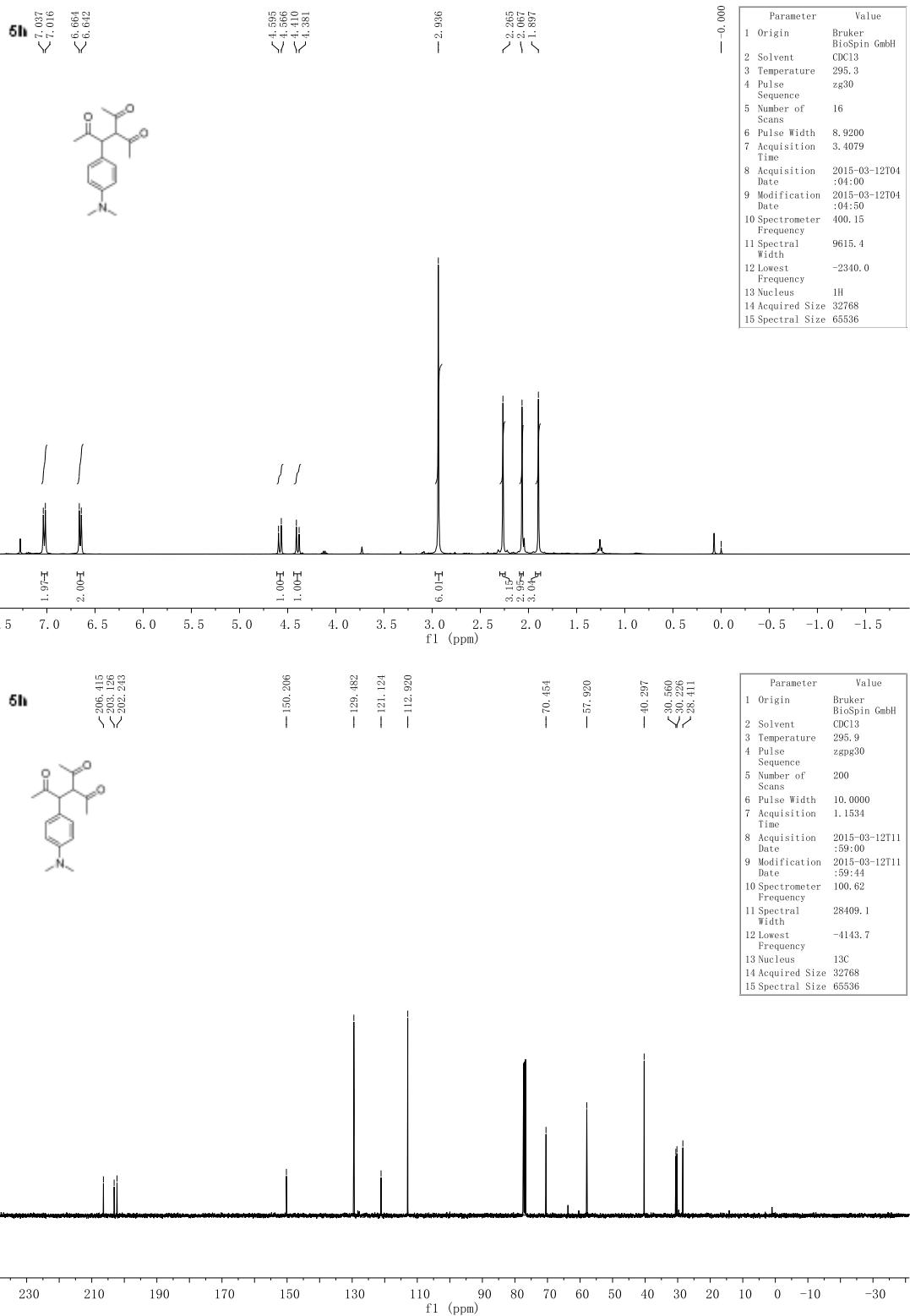


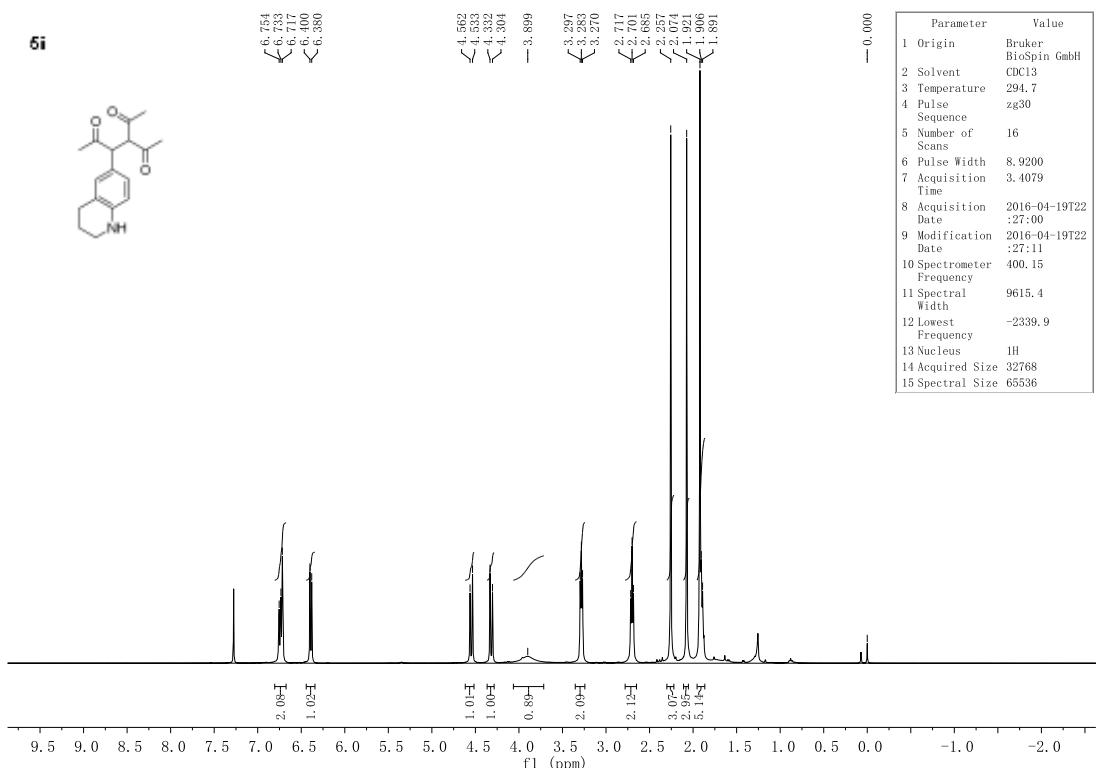
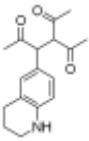
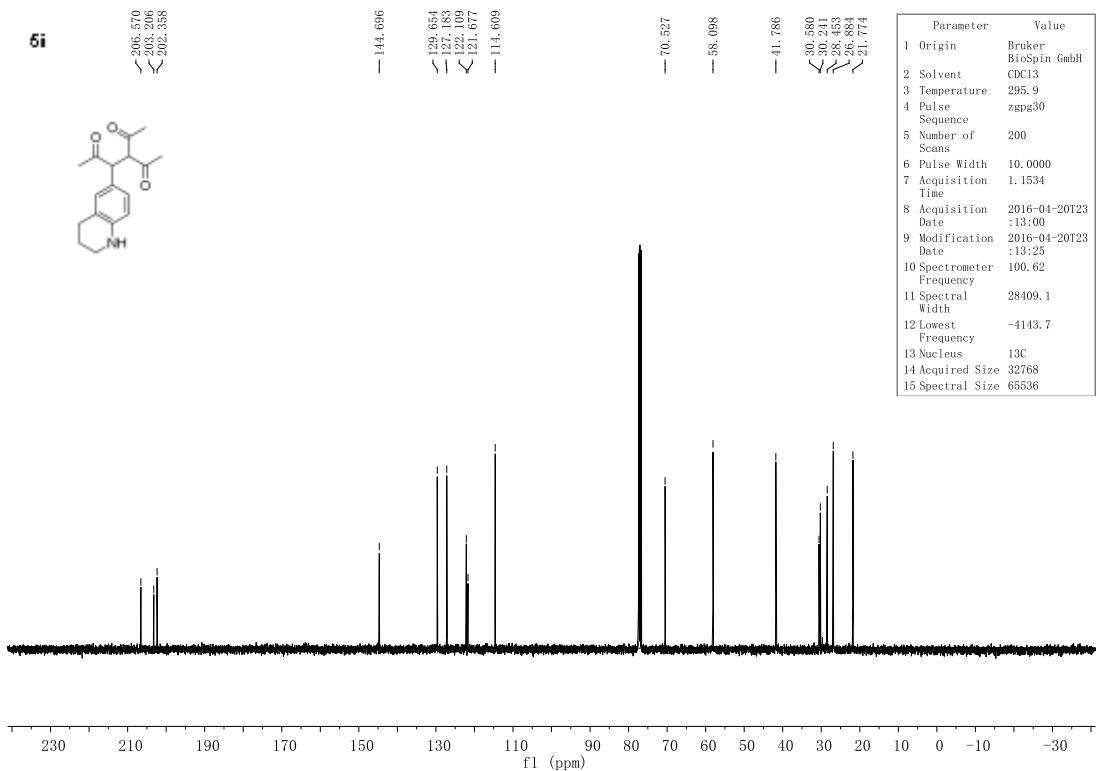
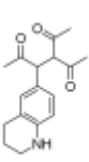
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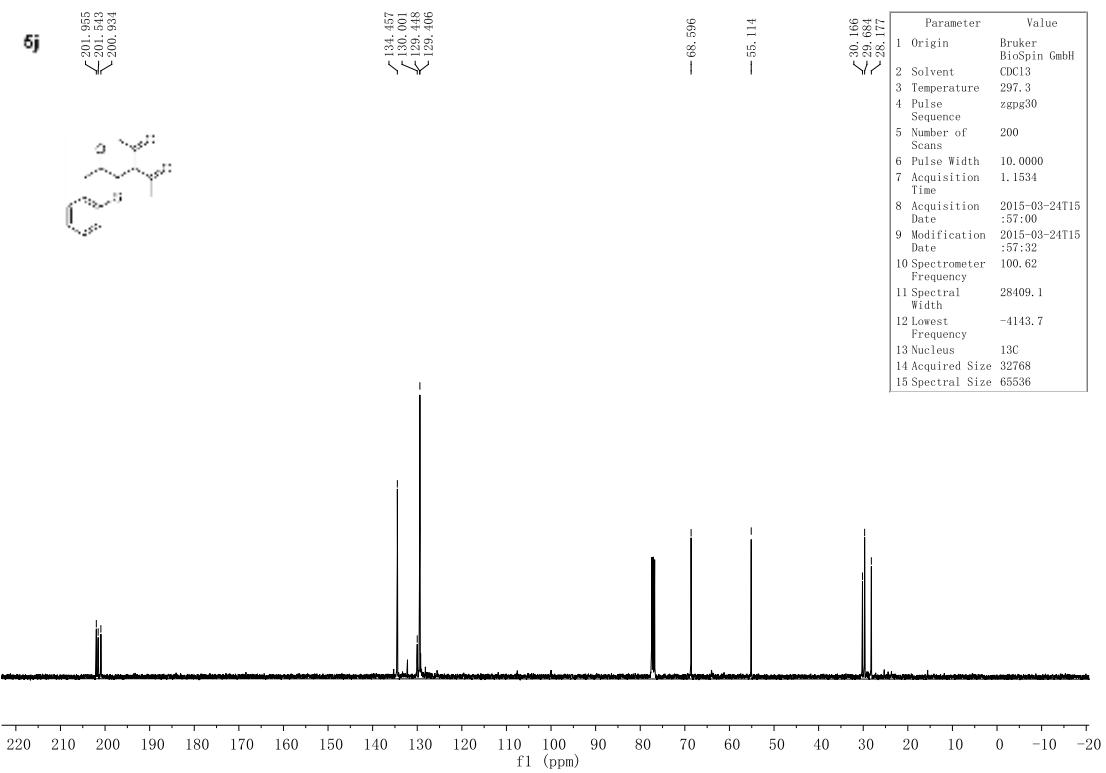
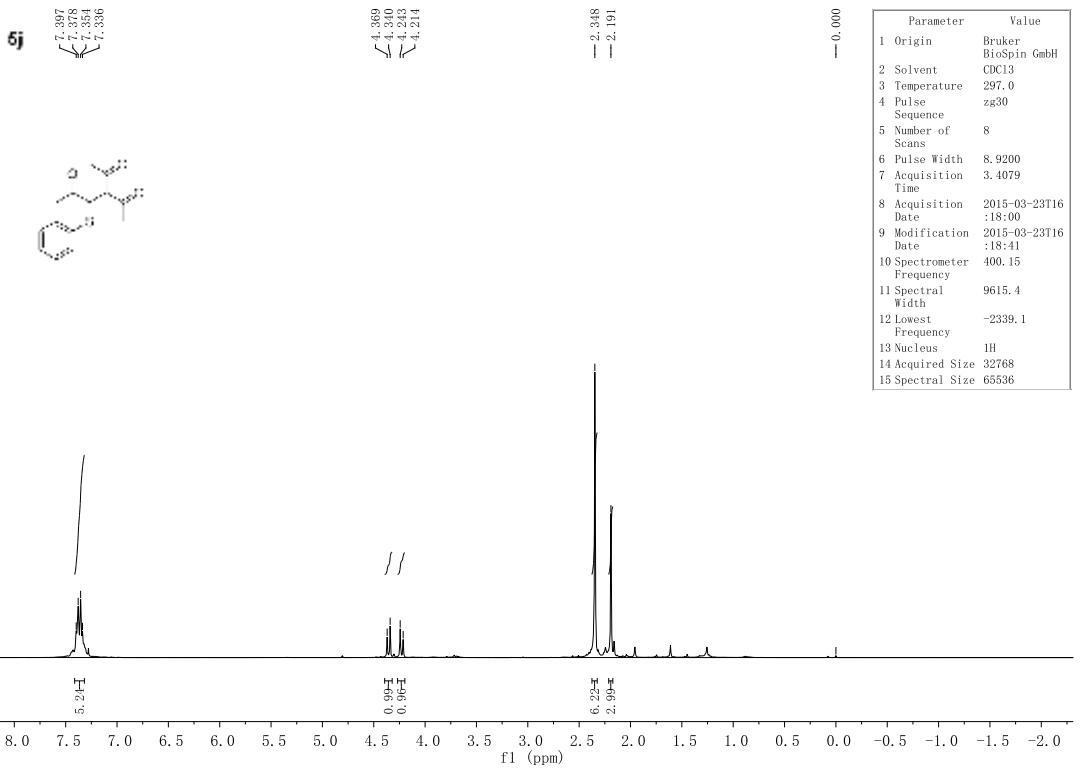
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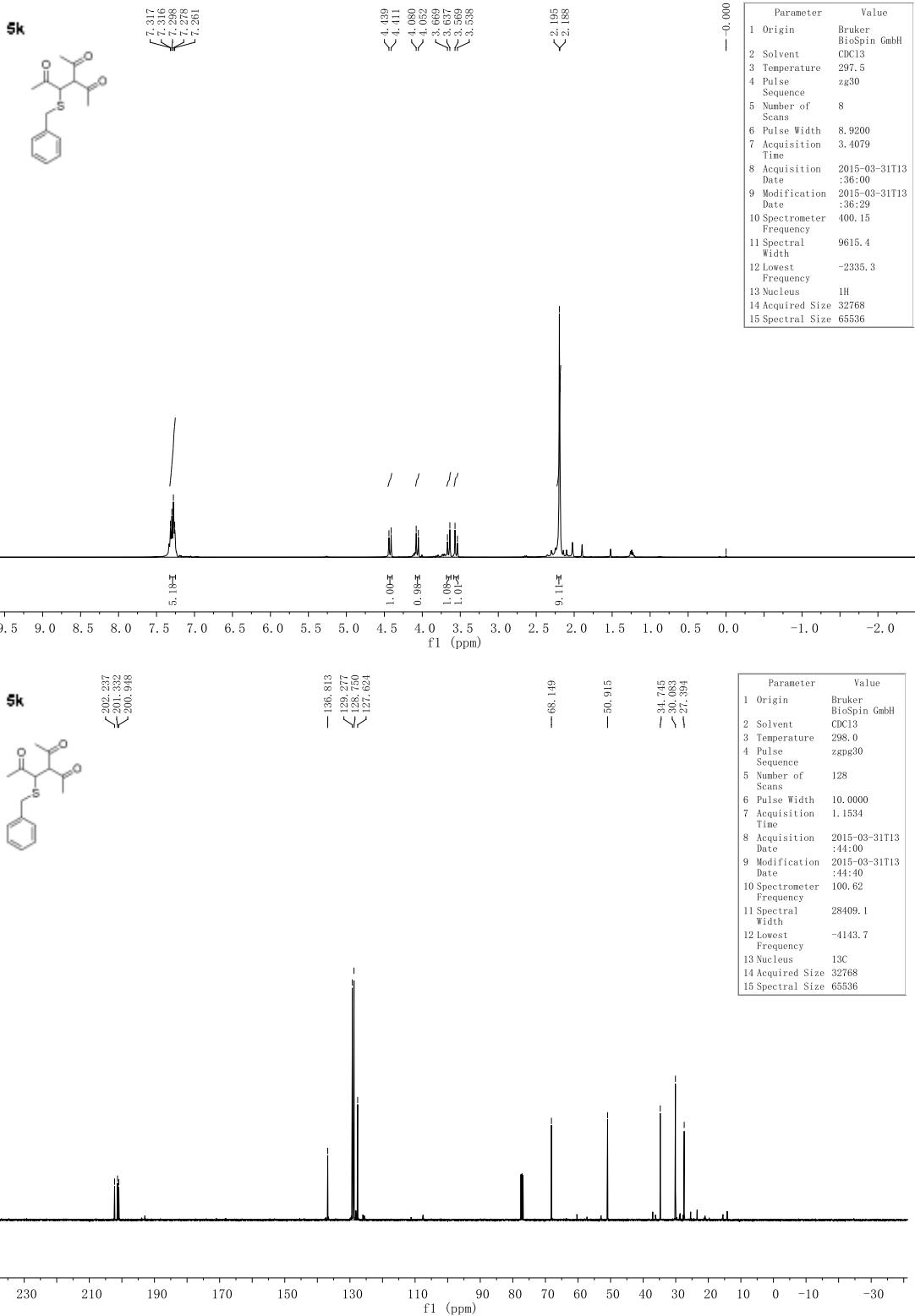
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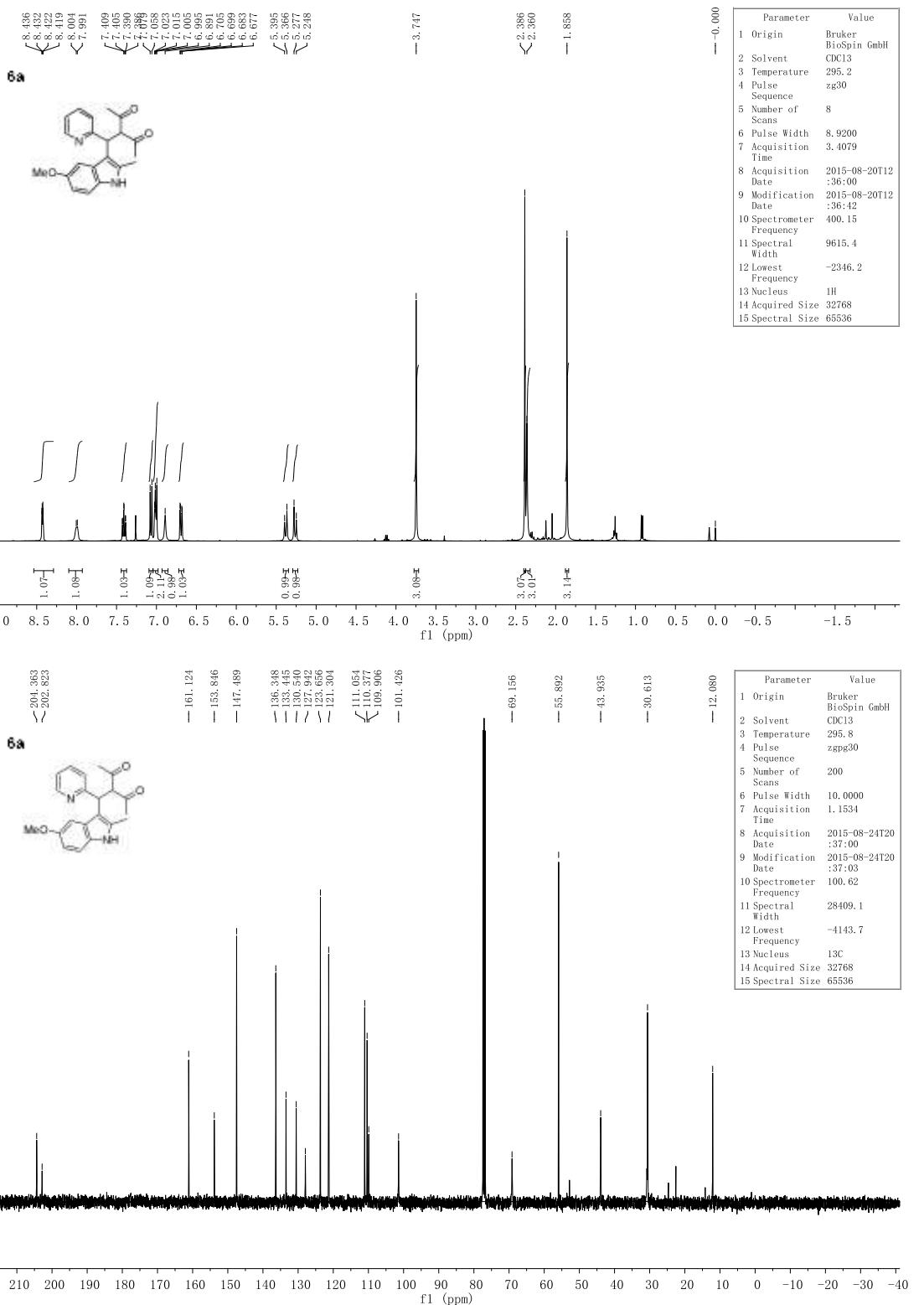


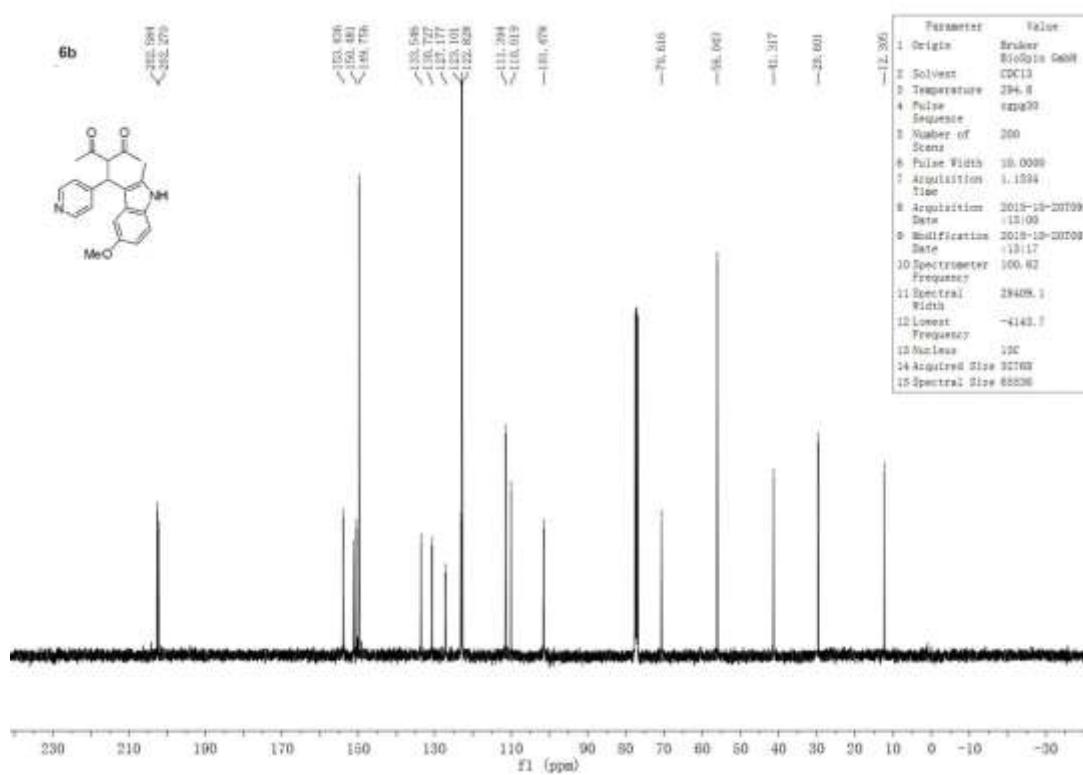
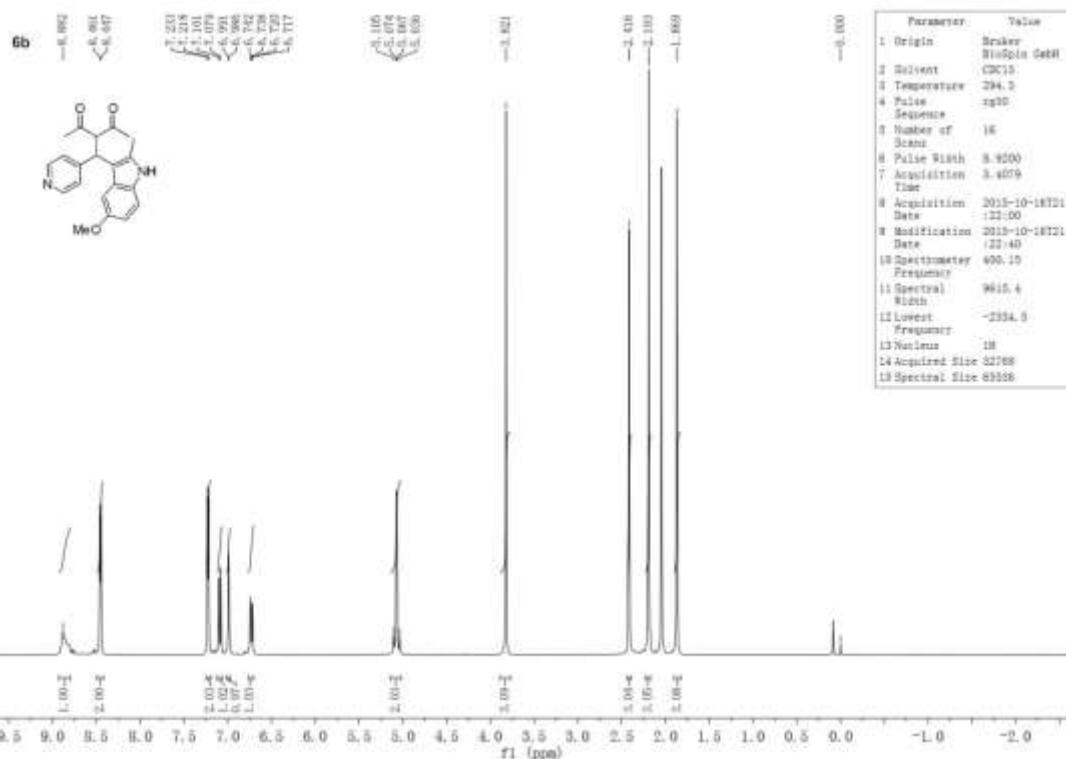


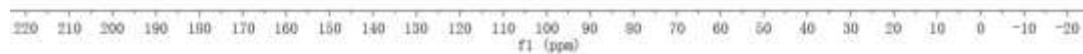
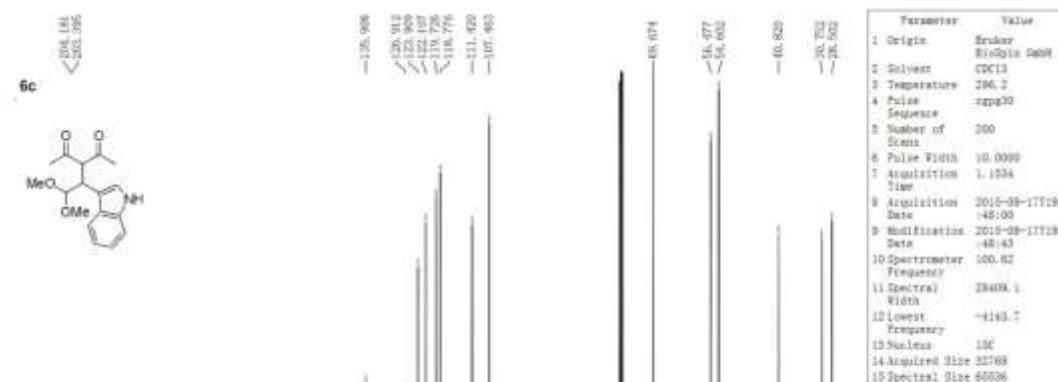
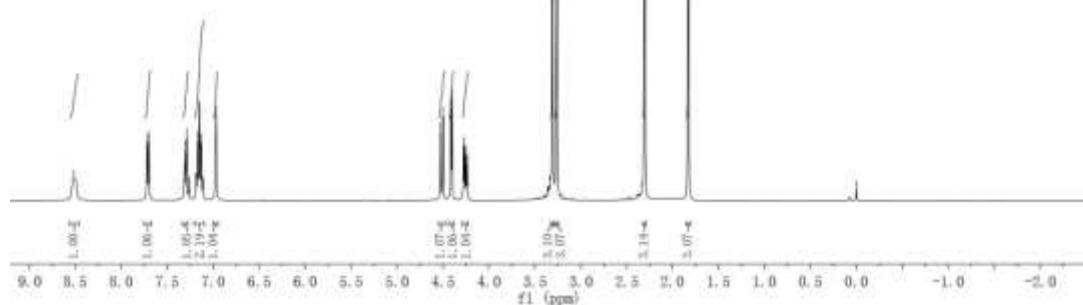
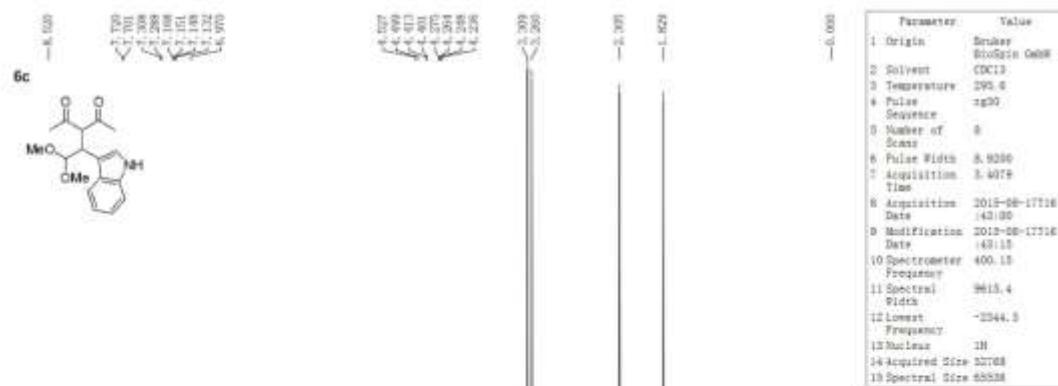
**5i****5i**

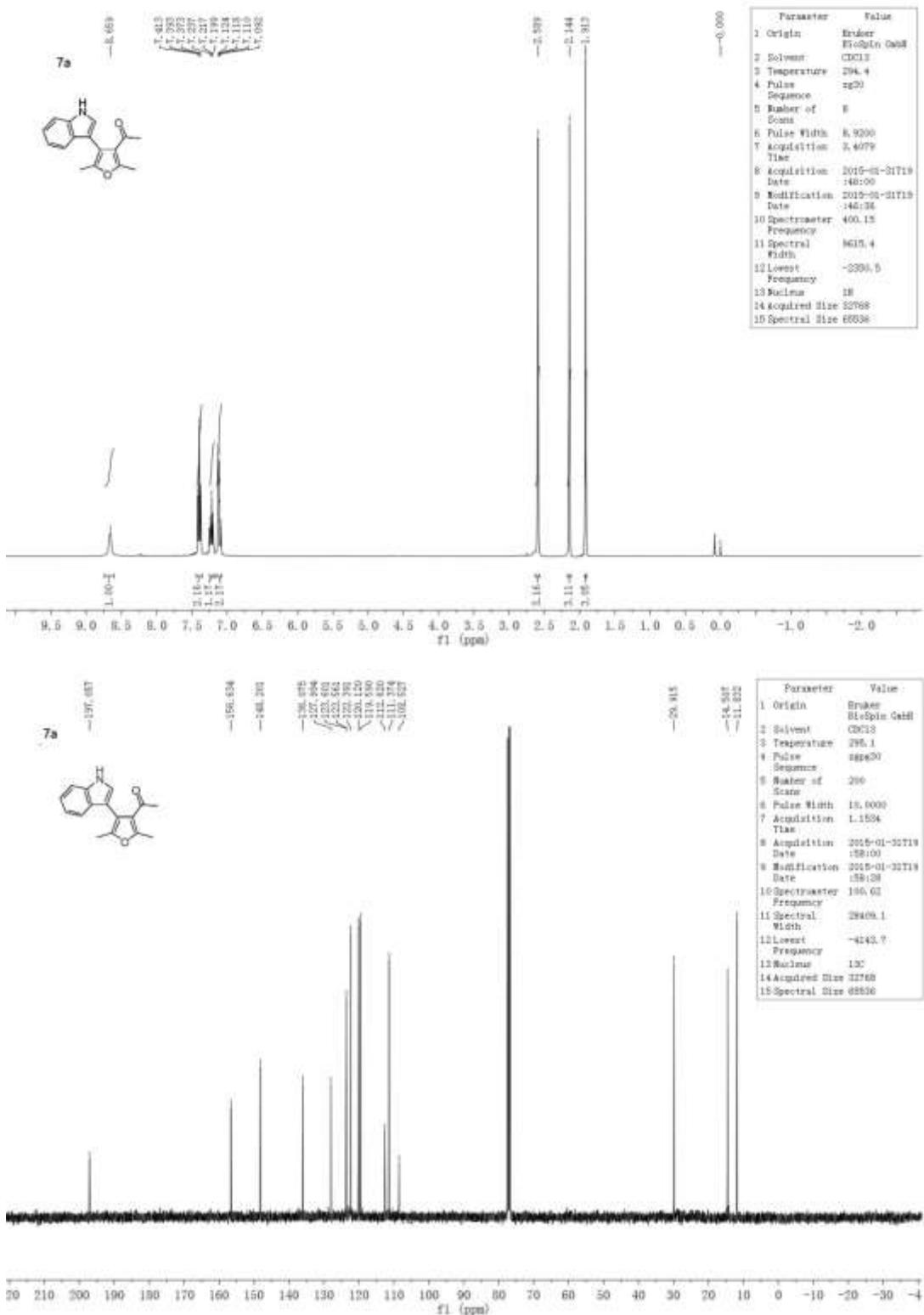




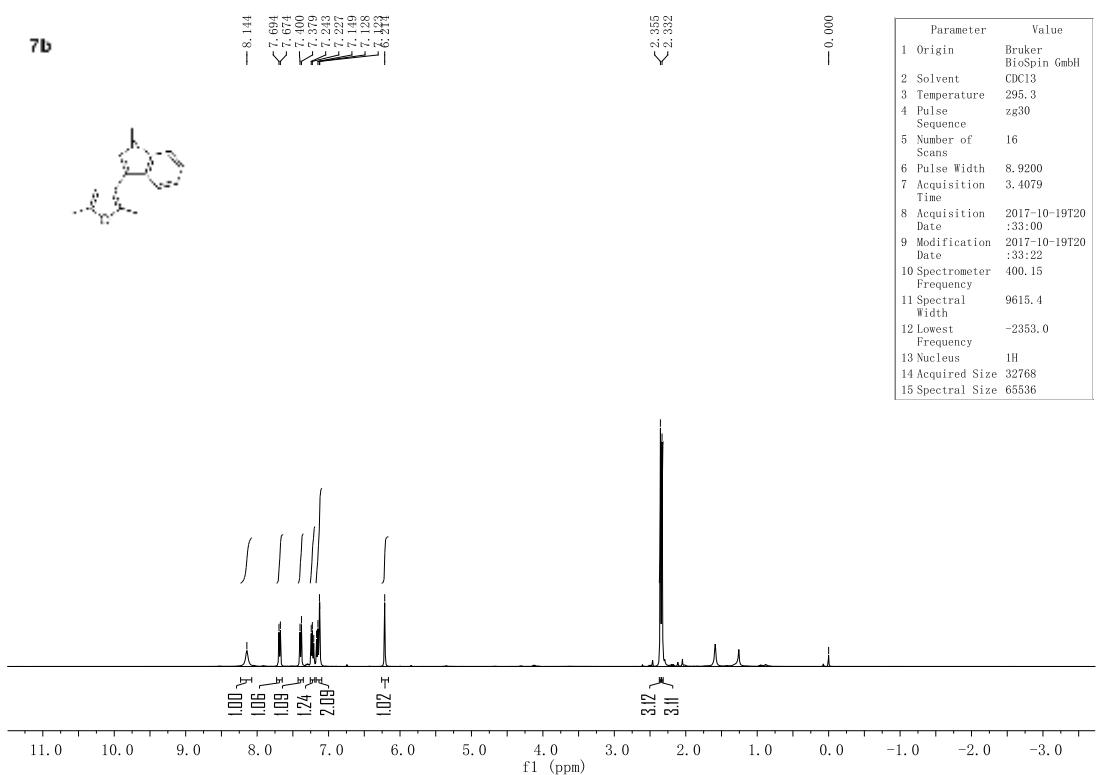




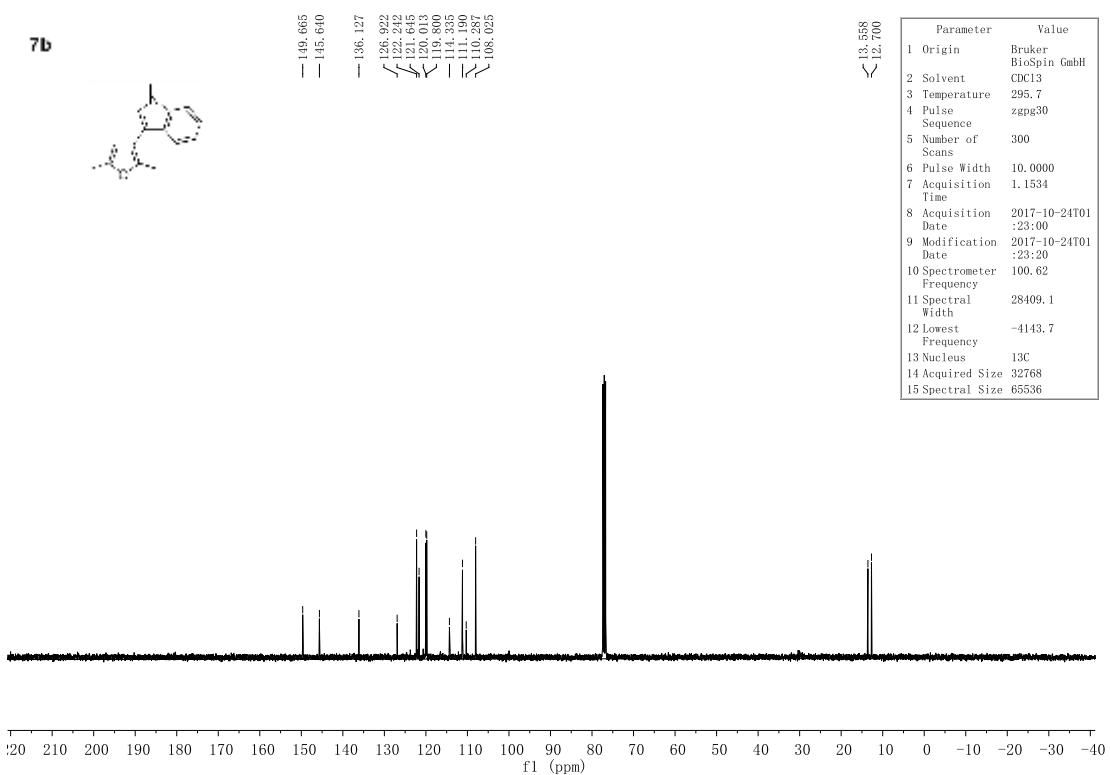


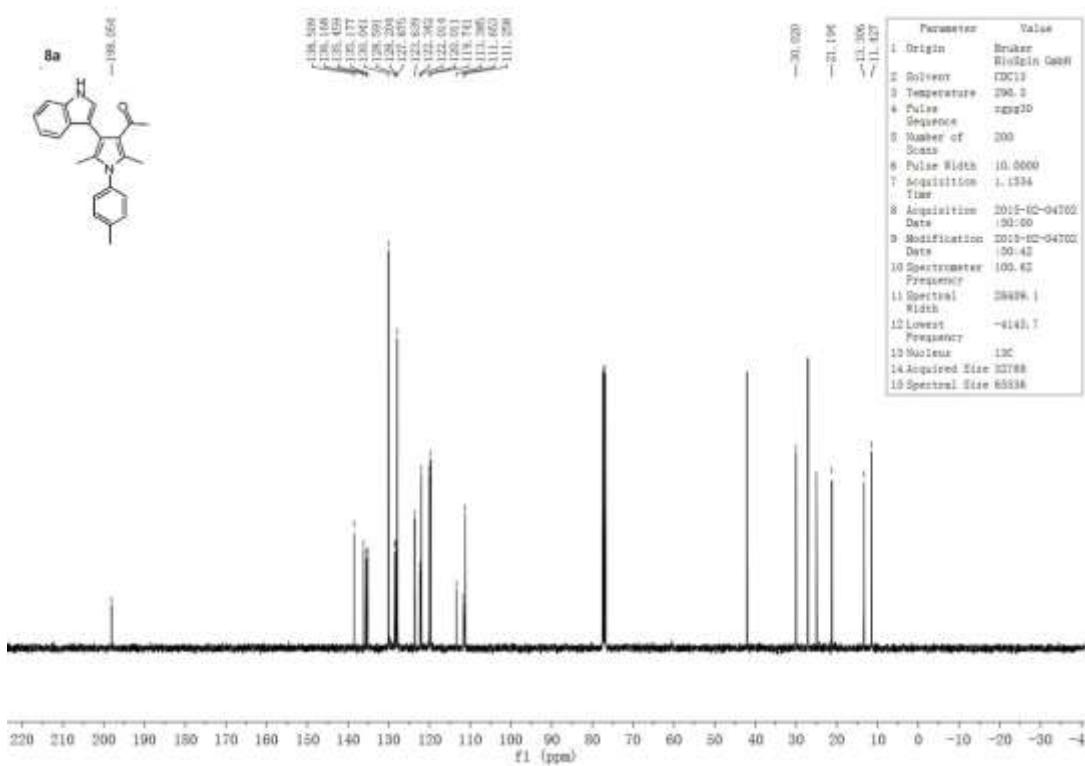
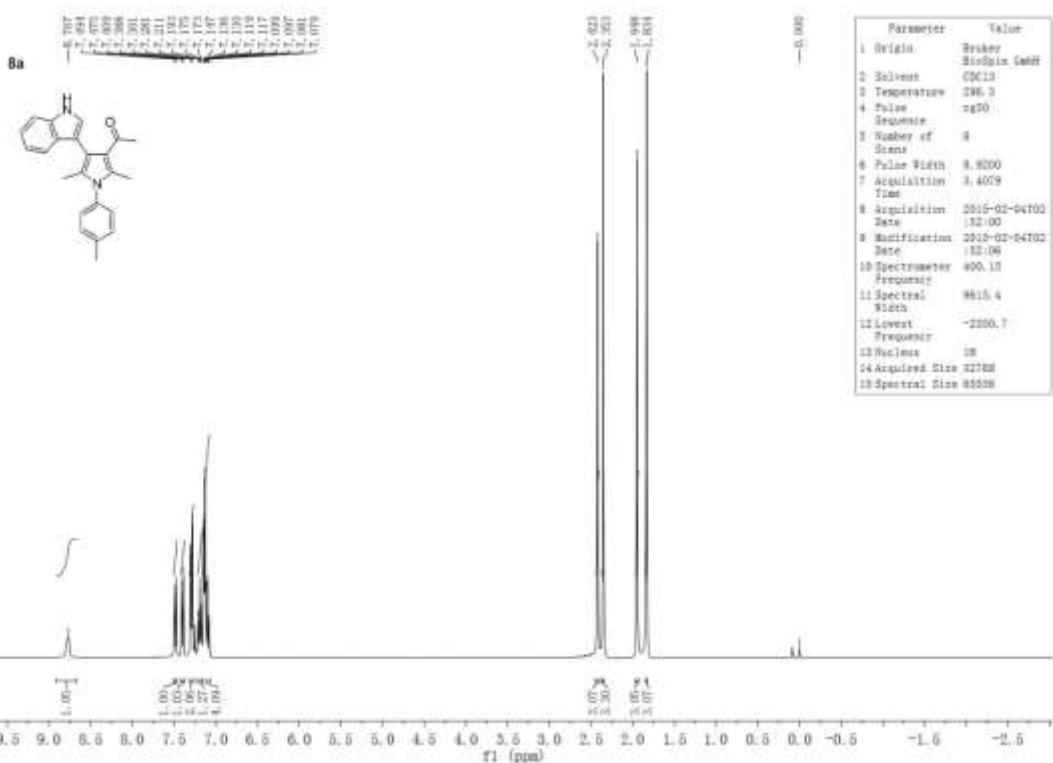


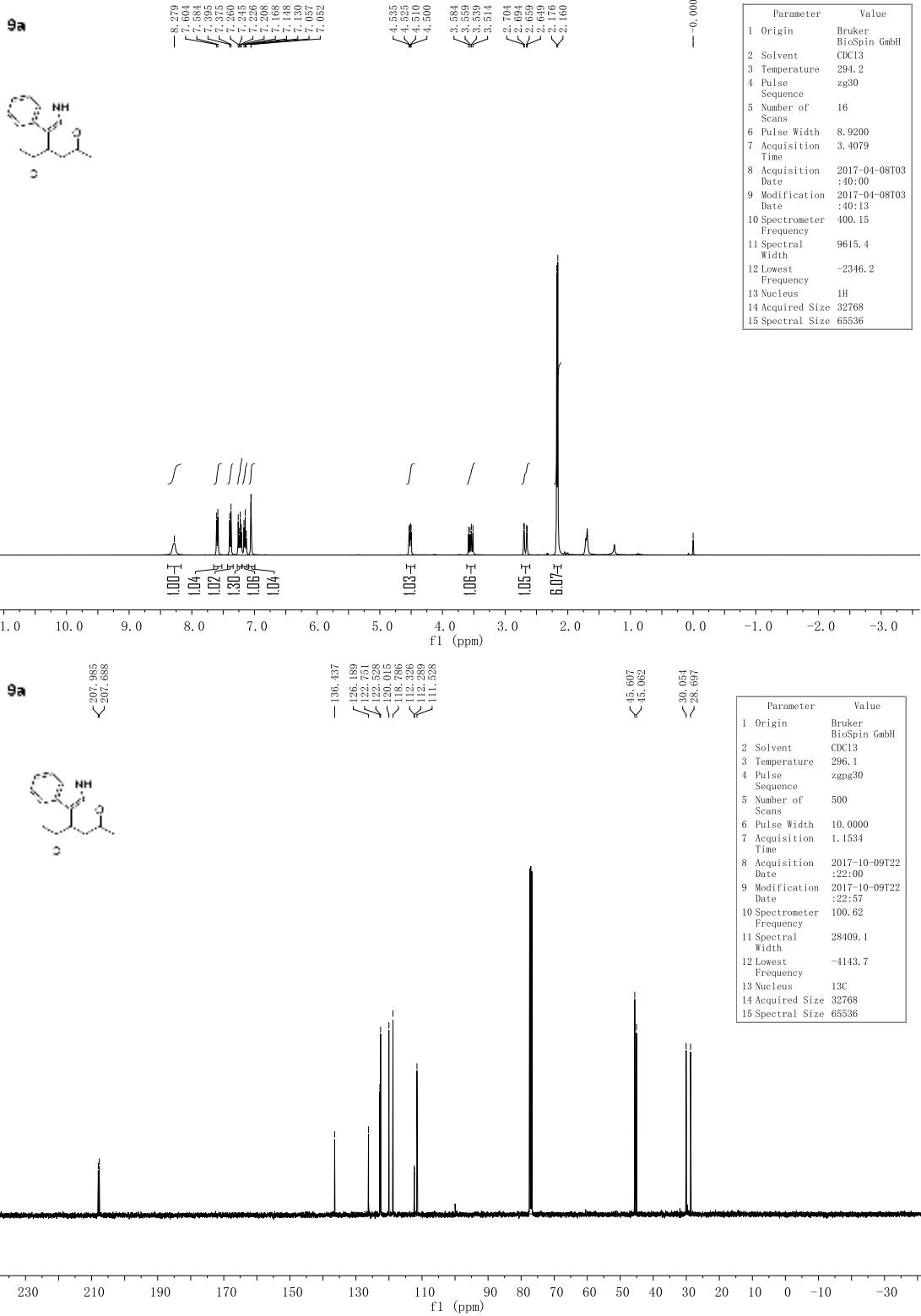
**7b**



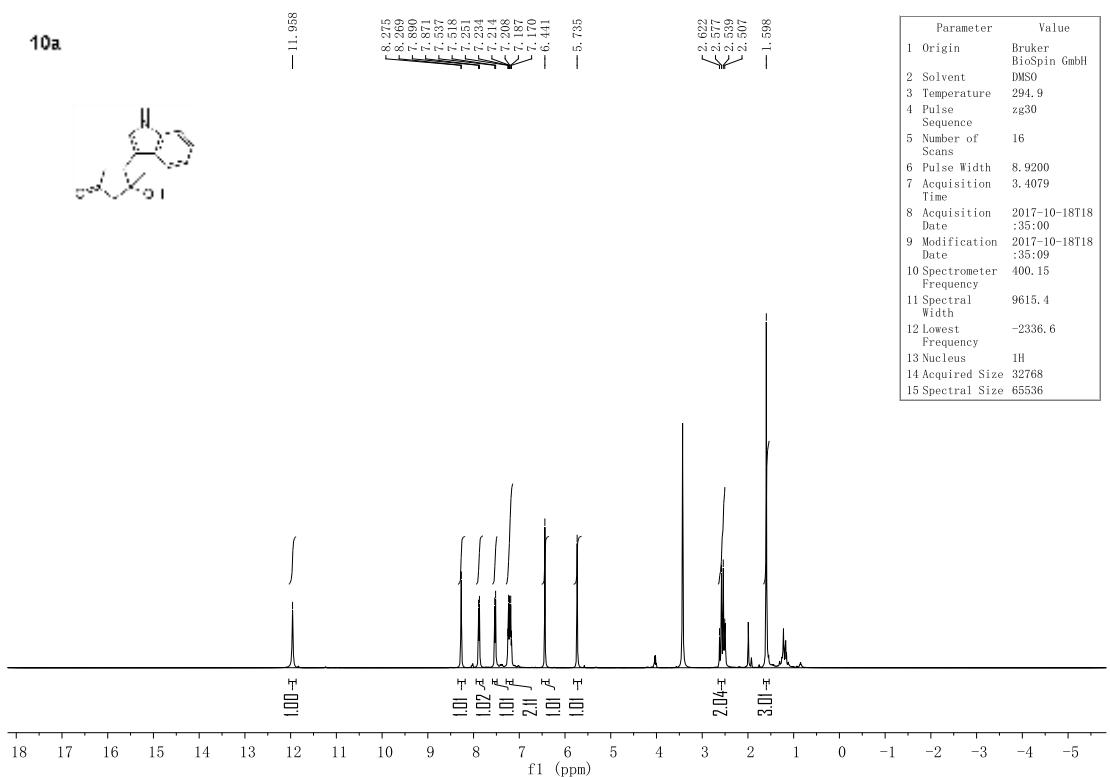
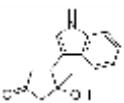
**7b**







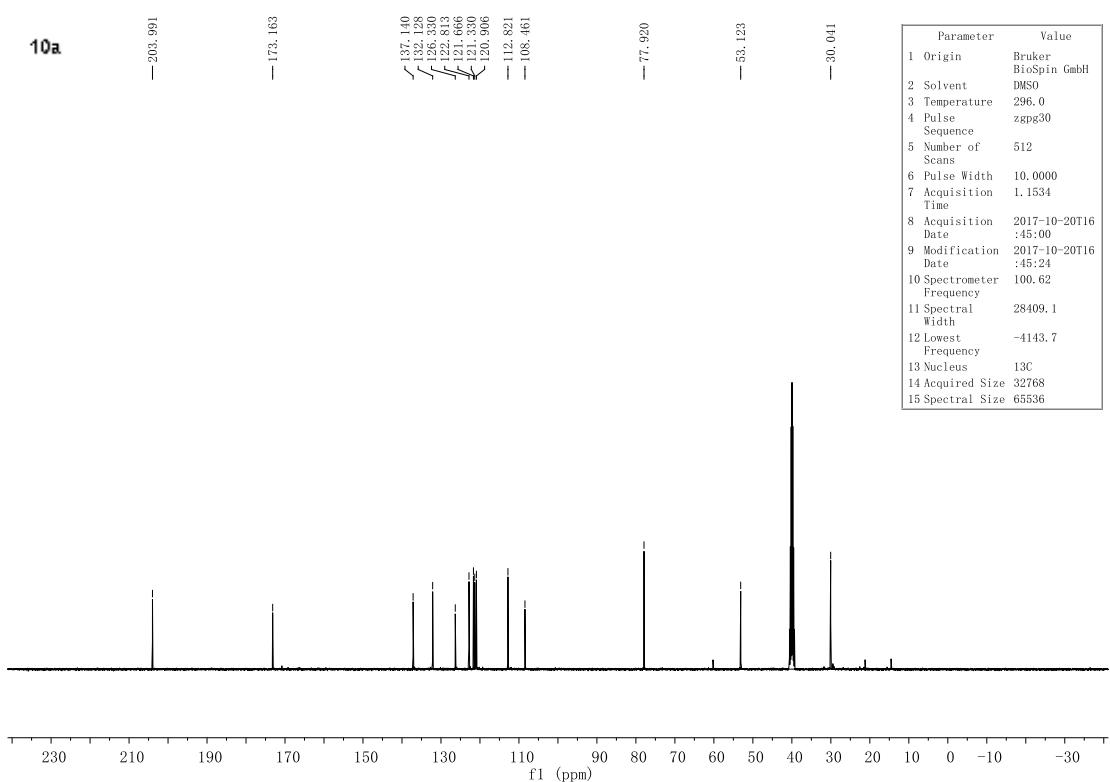
**10a**



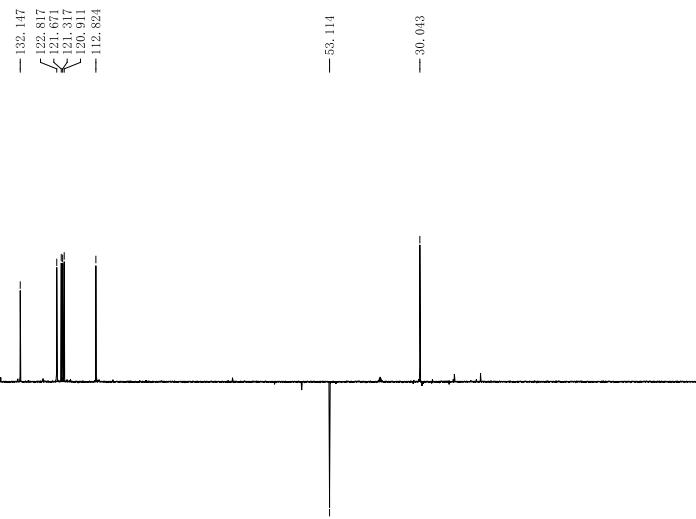
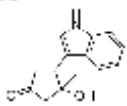
**10a**

— 203.991

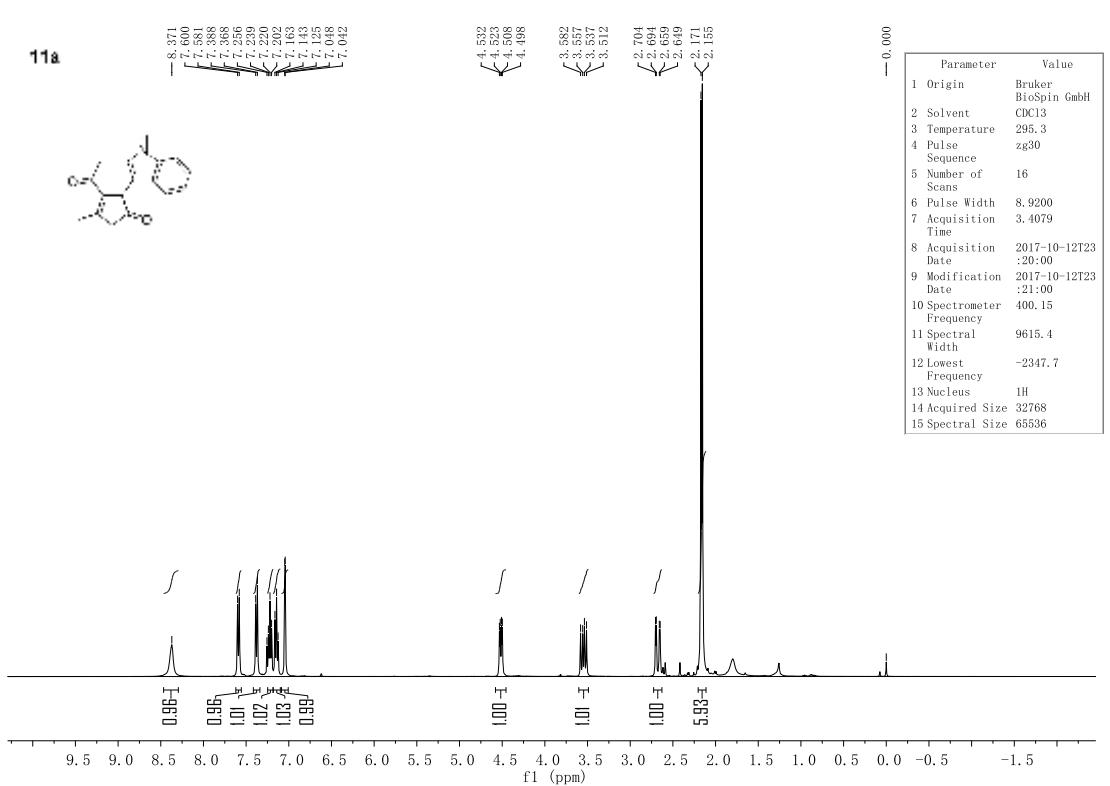
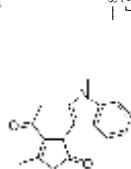
— 173.163

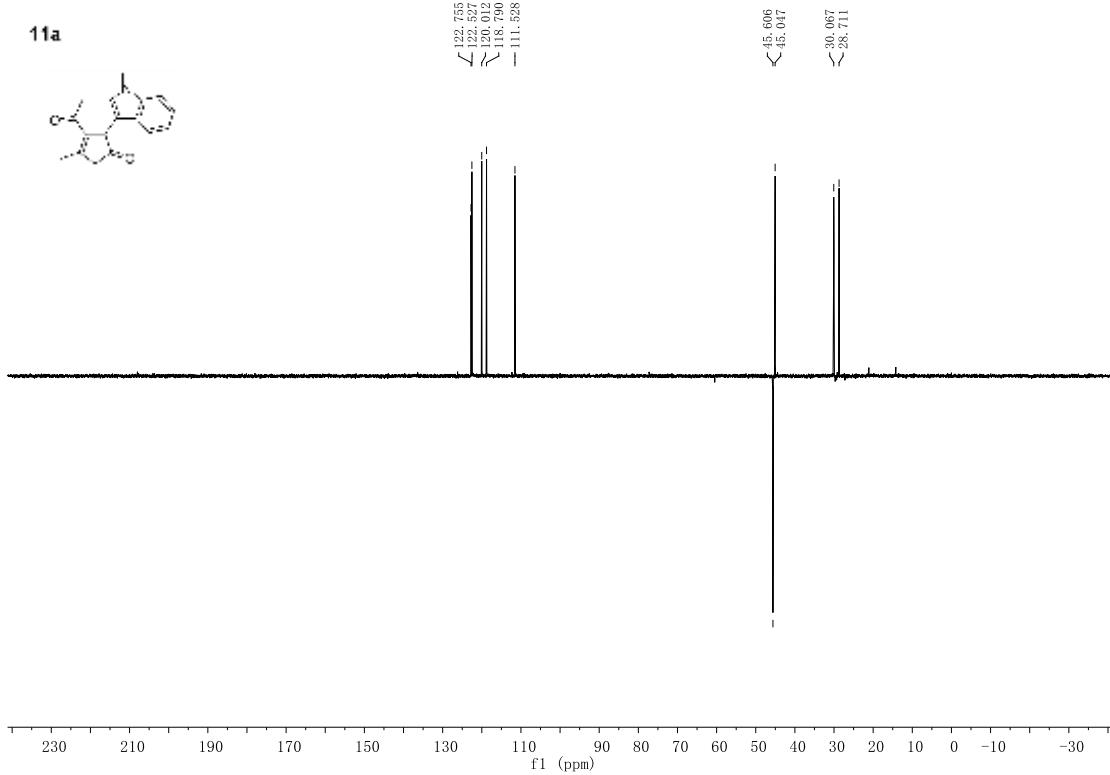
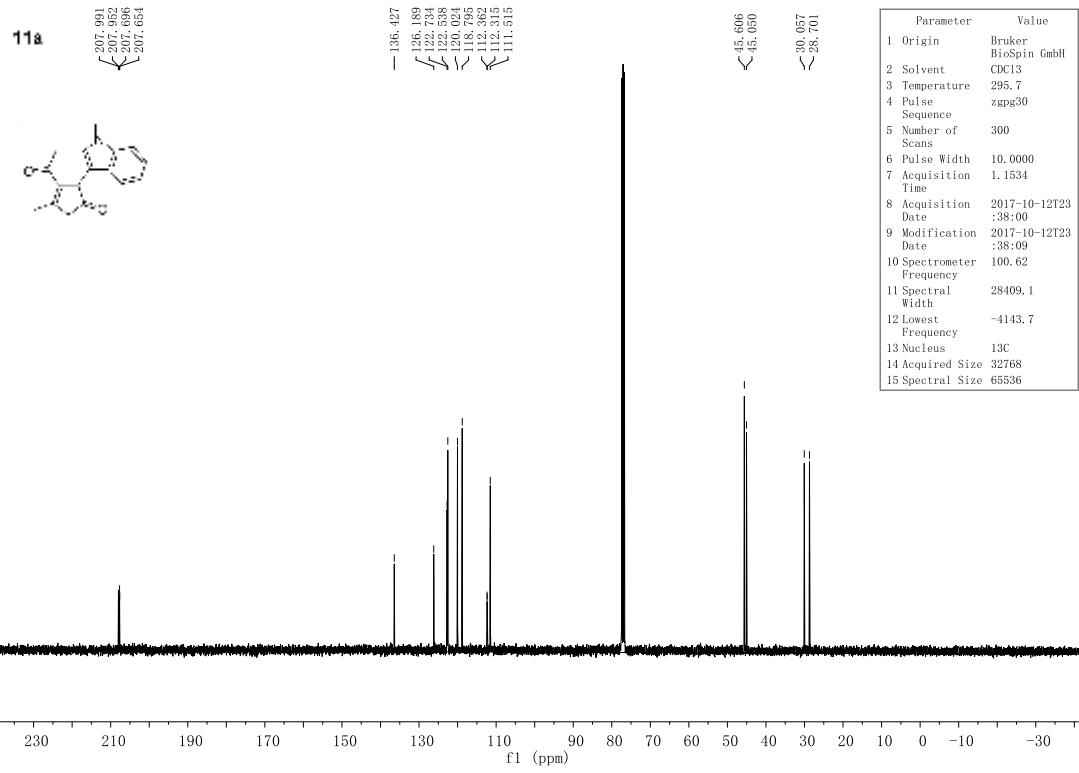


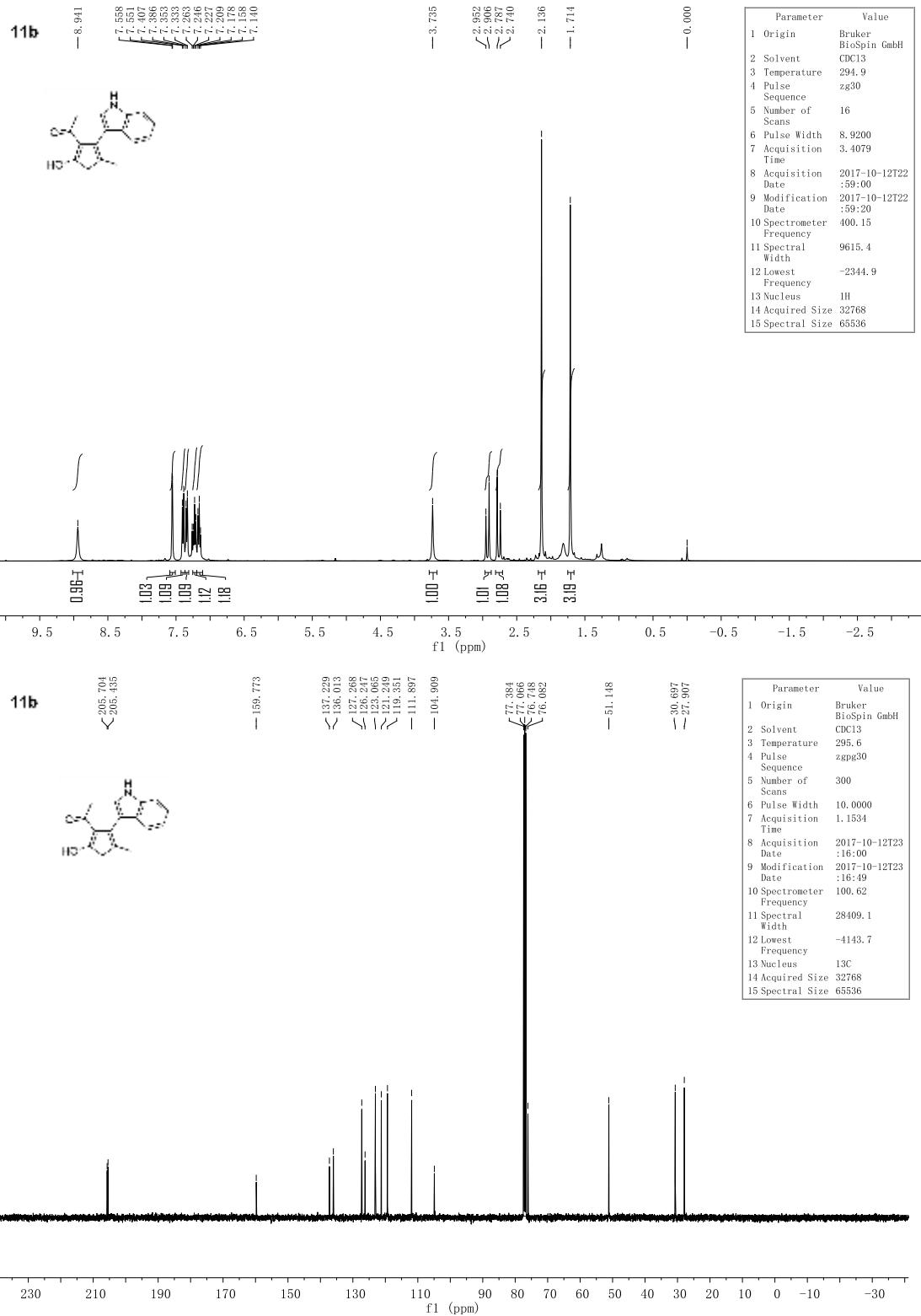
**10a**



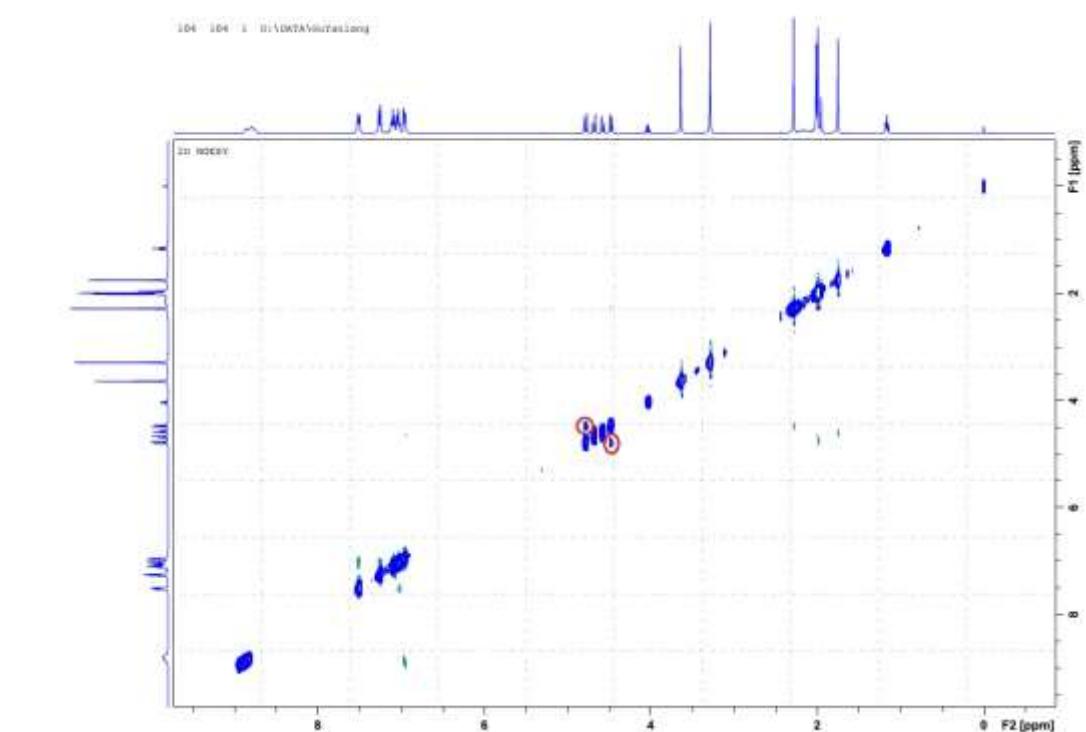
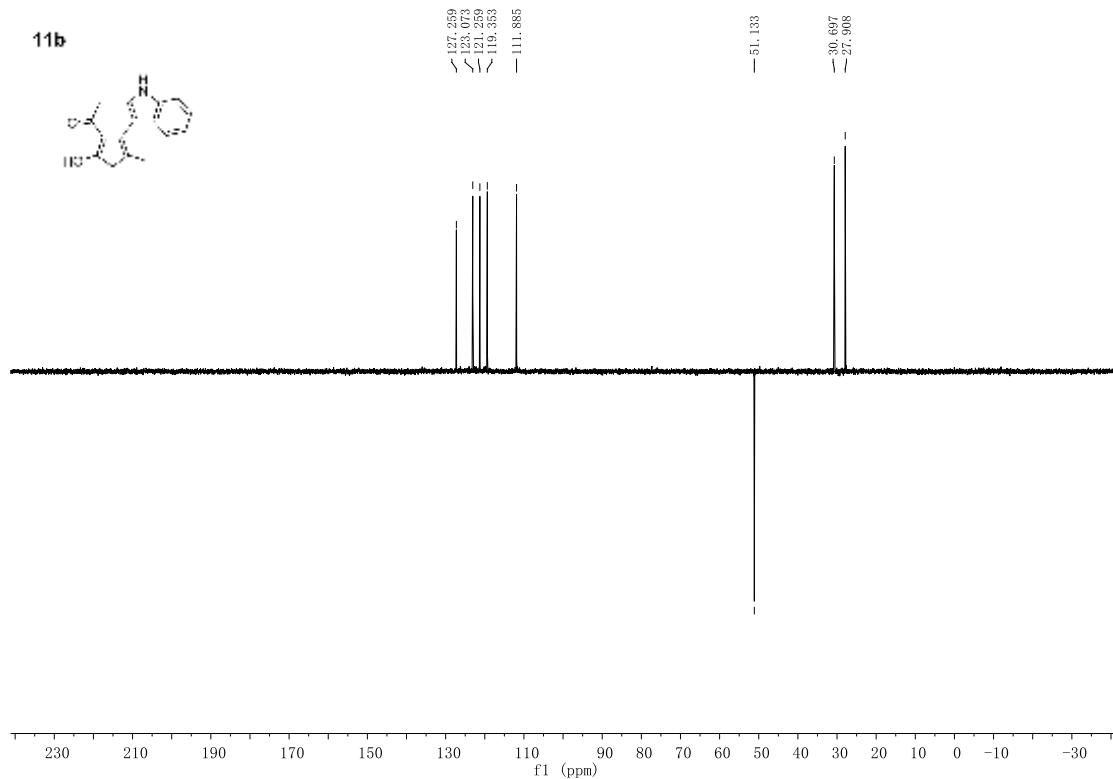
**11a**



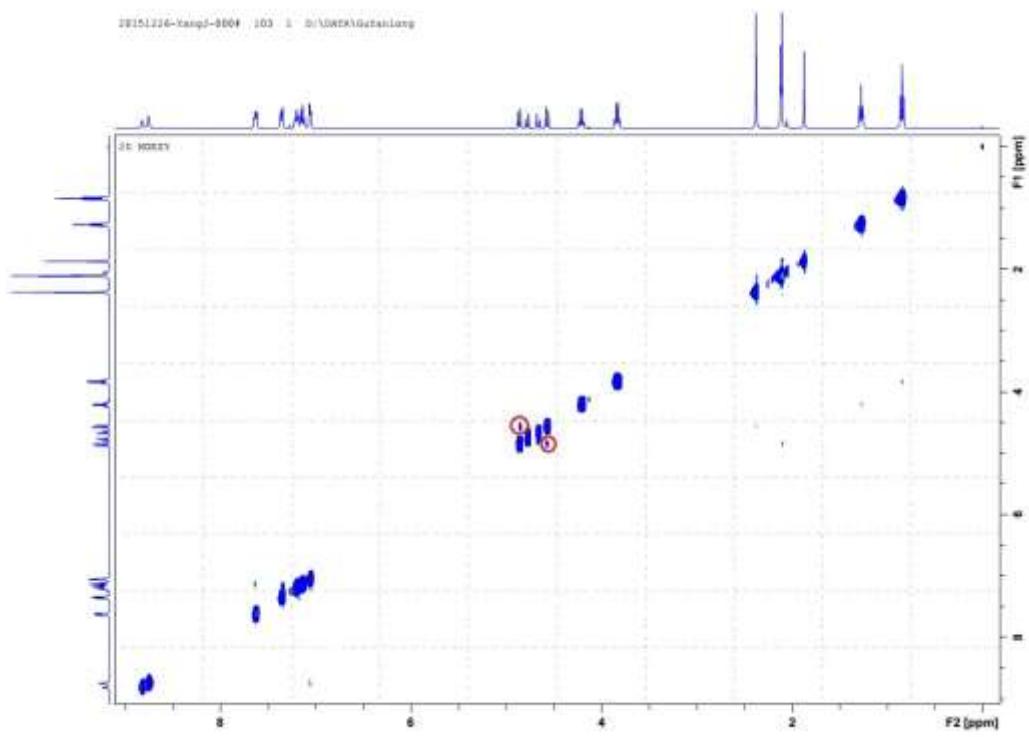




**11b**



<sup>1</sup>H-<sup>1</sup>H NOESY of **4y**



$^1\text{H}$ - $^1\text{H}$  NOESY of **4z**