

## Supporting Information

### Efficient one-pot catalyst-free synthesis of novel coumarin-spiro [indoline-3,4'-pyran] conjugates via three-component domino reaction in aqueous medium

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#### Table of Contents

1. General Methods .....	S2
2. General procedure for the synthesis of dicarbonyl compounds <b>3aa–ca</b> .....	S2
3. General procedure for the synthesis of compounds <b>6aaa–dbc</b> .....	S2-6
4. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and IR spectra.....	S7-44

## Experimental

### General Methods

Reagents and solvents were from Aladdin, Acros or Energy Chemical. Melting points were determined in capillary tubes using Buchi B-540 digital melting point apparatus; they are uncorrected. The progress of the reaction was monitored by TLC using analytical-grade silica gel plates (GF254). All target compounds were characterized from their <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, and MS spectra. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) were run on a Bruker Inova-400 instrument using DMSO-d<sub>6</sub> as solvent. Chemical shifts are given in ppm relative to TMS as an internal standard, and J values are given in Hz. IR spectra were recorded on a Bruker Vertex70 spectrophotometer using samples as KBr pellets. ESI-MS spectra and HRMS data were obtained using Thermo Scientific LTQ Orbitrap XL spectrometer.

### General procedure for the synthesis of β-dicarbonyl compounds 3aa–ca

To a stirred solution of the appropriate beta-ketoester **2** (10 mmol) and the corresponding salicylaldehyde **1** (10 mmol) in ethanol (25 mL) was added piperidine (2.5 mmol) dropwise. The mixture was stirred at room temperature for 1–24 h and after completion (followed by TLC), the precipitate was filtered and washed with cold ethanol to afford the desired compound.

### General procedure for the synthesis of compounds 6aaa–dbc

A mixture of beta-ketoester coumarin compound **3** (0.4 mmol), the corresponding isatin **4** (0.4 mmol) and malononitrile **5** (0.4 mmol) in EtOH-H<sub>2</sub>O (1:1, 5mL) was taken in a round-bottomed flask connected to a reflux condenser, and the mixture was stirred in an oil-bath (75 °C). The progress of the reaction was monitored by TLC using acetone–chloroform(1 : 5) as the eluent. After completion of the reaction, the reaction mixture was cooled to room temperature. Then the precipitate product was filtered and washed with ethanol and pure product was obtained after further recrystallization from ethanol.

#### *Methyl 2'-amino-3'-cyano-6'-(7-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6aaa)*

Yield: 65%; mp 275–277 °C; IR (KBr, cm<sup>-1</sup>) 3432, 3286, 3168, 3068, 2955, 2194, 1724, 1698, 1612, 1567, 1503, 1468, 1410, 1375, 1327; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.93 (s, 1H), 10.51 (s, 1H), 8.28 (s, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.30 (s, 2H), 7.21 (td, J = 7.7, 1.3 Hz, 1H), 7.11 (d, J = 6.8 Hz, 1H), 6.98 (td, J = 7.5, 1.0 Hz, 1H), 6.88 – 6.78 (m, 3H), 3.21 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 177.96, 164.47, 163.00, 159.79, 158.09, 155.78, 151.03, 144.19, 142.06, 134.22, 131.05, 129.03, 123.78, 122.22, 117.52, 116.52, 114.21, 110.67, 109.66, 108.70, 102.31, 56.77, 51.67, 49.72; HRMS (ESI) m/z calcd for C<sub>24</sub>H<sub>16</sub>N<sub>3</sub>O<sub>7</sub><sup>+</sup> (M+H)<sup>+</sup> 458.09828, found 458.09836.

#### *Methyl 2'-amino-5-chloro-3'-cyano-6'-(7-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6aad)*

Yield: 80%; mp 282–284 °C; IR (KBr, cm<sup>-1</sup>) 3358, 3150, 2963, 2197, 1733, 1678, 1514, 1474, 1436, 1370, 1323; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.94 (s, 1H), 10.67 (s, 1H), 8.30 (d, J = 0.7 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.39 (s, 2H), 7.30 – 7.19 (m, 2H), 6.91 – 6.81 (m, 2H), 6.79 (d, J = 2.2 Hz, 1H), 3.26 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 177.74, 164.39, 163.02, 159.75, 158.08, 155.79, 151.70, 144.34, 140.98, 136.42, 131.04, 128.98, 126.05, 123.86, 117.36, 116.53, 114.24, 111.16, 110.63, 107.80, 102.35, 56.19, 51.83, 50.05; HRMS (ESI) m/z calcd for C<sub>24</sub>H<sub>15</sub>ClN<sub>3</sub>O<sub>7</sub><sup>+</sup> (M+H)<sup>+</sup> 492.05930, found 492.05930.

#### *Methyl 2'-amino-5-bromo-3'-cyano-6'-(7-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6aae)*

Yield: 55%; mp 291–293 °C; IR (KBr, cm<sup>-1</sup>) 3342, 3195, 3050, 2975, 2890, 2200, 1708, 1676, 1642, 1612, 1473, 1451, 1411, 1379, 1330; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.93 (s, 1H), 10.67 (s, 1H), 8.30 (d, J = 0.7 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.40 – 7.38 (m, 3H), 7.32 (d, J = 2.1 Hz, 1H), 6.87 (dd, J = 8.6, 2.3 Hz, 1H), 6.76 (s, 2H), 3.26 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 177.62, 164.41, 163.04, 159.74, 158.10, 155.80, 151.73, 144.36, 141.40, 136.83, 131.85, 131.05, 126.56, 117.39, 116.55, 114.25, 113.73, 111.71, 110.64, 107.77, 102.36, 51.84, 49.99; HRMS (ESI) m/z calcd for C<sub>24</sub>H<sub>15</sub>BrN<sub>3</sub>O<sub>7</sub><sup>+</sup> (M+H)<sup>+</sup> 536.00879, found 536.00897.

*Methyl 2'-amino-3'-cyano-6'-(7-hydroxy-2-oxo-2H-chromen-3-yl)-5-nitro-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6aa)*

Yield: 59%; mp >300 °C; IR (KBr, cm<sup>-1</sup>) 3645, 3541, 3451, 3370, 3320, 3199, 2200, 1711, 1659, 1619, 1563, 1564, 1523, 1504, 1481, 1453, 1420, 1368, 1344, 1327; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.29 (s, 1H), 10.96 (s, 1H), 8.35 (s, 1H), 8.21 (dd, *J* = 8.6, 2.4 Hz, 1H), 8.07 (d, *J* = 2.4 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.52 (s, 2H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.88 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.80 (d, *J* = 2.2 Hz, 1H), 3.26 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 178.50, 164.38, 163.10, 159.86, 158.10, 155.83, 152.24, 148.60, 144.57, 142.71, 135.47, 131.10, 126.58, 119.43, 117.21, 116.43, 114.29, 110.61, 110.01, 107.10, 102.38, 55.43, 51.99, 49.93, 40.61; HRMS (ESI) m/z calcd for C<sub>24</sub>H<sub>15</sub>N<sub>4</sub>O<sub>9</sub><sup>+</sup> (M+H)<sup>+</sup> 503.08335, found 503.08331.

*Ethyl 2'-amino-3'-cyano-6'-(7-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6aba)*

Yield: 62%; mp 281–283 °C; IR (KBr, cm<sup>-1</sup>) 3472, 3416, 3311, 3141, 2999, 2201, 1707, 1664, 1619, 1569, 1503, 1470, 1409, 1369, 1323; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.91 (s, 1H), 10.50 (s, 1H), 8.25 (s, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.29 (s, 2H), 7.21 (td, *J* = 7.7, 1.3 Hz, 1H), 7.12 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.97 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 – 6.76 (m, 3H), 3.67 (qd, *J* = 7.1, 5.2 Hz, 2H), 0.68 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 177.97, 163.73, 162.84, 159.71, 158.07, 155.70, 151.43, 143.97, 142.18, 134.30, 130.91, 128.92, 123.74, 122.12, 117.45, 116.83, 114.12, 110.64, 109.59, 108.71, 102.23, 60.51, 56.16, 49.62, 13.05; HRMS (ESI) m/z calcd for C<sub>25</sub>H<sub>18</sub>N<sub>3</sub>O<sub>7</sub><sup>+</sup> (M+H)<sup>+</sup> 472.11393, found 472.11407.

*Ethyl 2'-amino-5-chloro-3'-cyano-6'-(7-hydroxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6abd)*

Yield: 60%; mp 286–288 °C; IR (KBr, cm<sup>-1</sup>) 3375, 3308, 3189, 2980, 2930, 2202, 1719, 1661, 1618, 1570, 1505, 1476, 1417, 1370; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.92 (s, 1H), 10.66 (s, 1H), 8.28 (s, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.38 (s, 2H), 7.31 – 7.20 (m, 2H), 6.91 – 6.81 (m, 2H), 6.79 (d, *J* = 2.2 Hz, 1H), 3.71 (qd, *J* = 7.1, 2.3 Hz, 2H), 0.71 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 177.79, 163.67, 162.90, 159.70, 158.12, 155.73, 152.09, 144.19, 141.11, 136.52, 130.95, 128.92, 126.02, 123.87, 117.38, 116.82, 114.20, 111.13, 110.62, 107.79, 102.29, 60.76, 56.20, 56.18, 49.95, 18.74, 13.12; HRMS (ESI) m/z calcd for C<sub>25</sub>H<sub>17</sub>ClN<sub>3</sub>O<sub>7</sub><sup>+</sup> (M+H)<sup>+</sup> 506.07495, found 506.07516.

*Ethyl 2'-amino-3'-cyano-6'-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-5-fluoro-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6bac)*

Yield: 70%; mp 283–285 °C; IR (KBr, cm<sup>-1</sup>) 3327, 3271, 3179, 2976, 2934, 2903, 2712, 2637, 2202, 1739, 1711, 1660, 1614, 1584, 1512, 1488, 1459, 1413, 1352, 1319; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.48 (s, 1H), 8.10 (s, 1H), 7.52 (d, *J* = 8.9 Hz, 1H), 7.28 (s, 2H), 7.03 (ddt, *J* = 10.7, 7.7, 2.8 Hz, 2H), 6.79 (ddd, *J* = 16.9, 8.7, 3.4 Hz, 2H), 6.59 (d, *J* = 2.3 Hz, 1H), 3.76 – 3.64 (m, 2H), 3.46 (q, *J* = 7.1 Hz, 4H), 1.14 (t, *J* = 7.0 Hz, 6H), 0.74 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 178.15, 163.97, 159.88, 159.50, 157.61 (d, <sup>1</sup>J<sub>CF</sub> = 192.1 Hz), 157.14, 156.63, 152.06, 151.84, 143.96, 138.39, 136.16 (d, <sup>3</sup>J<sub>CF</sub> = 7.6 Hz), 130.52, 117.47, 115.28, 115.05, 112.80, 111.60, 111.36, 110.40, 110.5 (d, <sup>2</sup>J<sub>CF</sub> = 24 Hz), 107.32, 106.99, 96.39, 60.48, 56.30, 50.27, 44.35, 39.15, 13.21, 12.48; HRMS (ESI) m/z calcd for C<sub>29</sub>H<sub>26</sub>FN<sub>4</sub>O<sub>6</sub><sup>+</sup> (M+H)<sup>+</sup> 545.18309, found 545.18335.

*Methyl 2'-amino-5-bromo-3'-cyano-6'-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6bae)*

Yield: 57%; mp 260–262 °C; IR (KBr, cm<sup>-1</sup>) 3347, 3295, 3177, 3040, 2973, 2898, 2204, 1717, 1665, 1611, 1582, 1510, 1472, 1453, 1415, 1346, 1329; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.63 (s, 1H), 8.14 (s, 1H), 7.53 (d, *J* = 8.9 Hz, 1H), 7.38 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.33 (s, 2H), 7.28 (d, *J* = 2.1 Hz, 1H), 6.83 – 6.74 (m, 2H), 6.60 (d, *J* = 2.4 Hz, 1H), 3.45 (dq, *J* = 11.0, 7.1 Hz, 4H), 3.26 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 177.73, 164.72,

159.88, 158.56, 156.69, 151.94, 151.89, 144.12, 141.38, 136.93, 131.72, 130.62, 126.48, 117.47, 113.65, 112.48, 111.64, 109.83, 107.03, 106.99, 96.45, 56.19, 51.66, 50.12, 44.39, 12.50; HRMS (ESI) m/z calcd for C<sub>28</sub>H<sub>24</sub>BrN<sub>4</sub>O<sub>6</sub><sup>+</sup> (M+H)<sup>+</sup> 591.08737, found 591.08826.

*Methyl 2'-amino-3'-cyano-6'-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-5-nitro-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6ba<sup>f</sup>)*

Yield: 64%; mp >300 °C; IR (KBr, cm<sup>-1</sup>) 3338, 3260, 3184, 3083, 2976, 2716, 2634, 2199, 1720, 1660, 1614, 1581, 1511, 1459, 1412, 1342; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 11.25 (s, 1H), 8.25 – 8.14 (m, 2H), 8.02 (d, J = 2.4 Hz, 1H), 7.53 (d, J = 9.0 Hz, 1H), 7.46 (s, 2H), 7.06 (d, J = 8.6 Hz, 1H), 6.78 (dd, J = 9.0, 2.5 Hz, 1H), 6.60 (d, J = 2.3 Hz, 1H), 3.46 (dt, J = 12.8, 6.9 Hz, 4H), 3.26(s, 3H), 1.14 (t, J = 7.0 Hz, 6H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 178.62, 164.74, 160.00, 158.57, 156.74, 152.43, 152.01, 148.61, 144.33, 142.64, 135.59, 130.67, 126.47, 119.30, 117.29, 112.31, 109.95, 109.88, 107.01, 106.30, 96.47, 56.19, 55.40, 51.80, 50.05, 44.40, 39.59, 18.73, 12.51; HRMS (ESI) m/z calcd for C<sub>28</sub>H<sub>24</sub>N<sub>5</sub>O<sub>8</sub><sup>+</sup> (M+H)<sup>+</sup> 558.16194, found 558.16229.

*Ethyl 2'-amino-5-bromo-3'-cyano-6'-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6bbe)*

Yield: 66%; mp 286–288 °C; IR (KBr, cm<sup>-1</sup>) 3340, 3283, 3186, 3072, 2973, 2930, 2900, 2715, 2639, 2200, 1892, 1739, 1659, 1614, 1584, 1512, 1474, 1413, 1351, 1320; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.62 (s, 1H), 8.11 (s, 1H), 7.53 (d, J = 8.9 Hz, 1H), 7.39 (dd, J = 8.2, 2.1 Hz, 1H), 7.33 (s, 2H), 7.29 (d, J = 2.0 Hz, 1H), 6.78 (dd, J = 12.2, 8.8 Hz, 2H), 6.59 (d, J = 2.4 Hz, 1H), 3.72 (q, J = 7.1 Hz, 2H), 3.46 (p, J = 6.3, 5.4 Hz, 4H), 1.10 (dt, J = 33.2, 7.0 Hz, 6H), 0.75 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 177.77, 163.99, 159.86, 158.59, 156.65, 152.24, 151.85, 144.02, 141.52, 136.99, 131.68, 130.54, 126.50, 117.49, 113.62, 112.82, 111.62, 109.77, 107.09, 106.99, 96.39, 60.57, 56.18, 50.03, 44.37, 39.35, 13.22, 12.49; HRMS (ESI) m/z calcd for C<sub>29</sub>H<sub>26</sub>B<sub>1</sub>N<sub>4</sub>O<sub>6</sub><sup>+</sup> (M+H)<sup>+</sup> 605.10302, found 605.10315.

*Methyl 2'-amino-3'-cyano-6'-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6caa)*

Yield: 72%; mp 233–235 °C; IR (KBr, cm<sup>-1</sup>) 3417, 3335, 3158, 3022, 2999, 2950, 2845, 2623, 2196, 1711, 1670, 1617, 1599, 1506, 1469, 1443, 1412, 1376, 1312; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.48 (s, 1H), 8.34 (s, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.27 (s, 2H), 7.21 (td, J = 7.7, 1.3 Hz, 1H), 7.15 – 7.07 (m, 2H), 7.07 – 6.93 (m, 2H), 6.83 (d, J = 7.7 Hz, 1H), 3.89 (s, 3H), 3.22 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 177.93, 164.41, 163.93, 159.76, 158.00, 155.70, 150.94, 143.96, 142.06, 134.19, 130.68, 129.06, 123.78, 122.22, 117.65, 117.49, 113.57, 111.70, 109.68, 108.89, 100.87, 56.79, 56.36, 51.71, 49.71; HRMS (ESI) m/z calcd for C<sub>25</sub>H<sub>18</sub>N<sub>3</sub>O<sub>7</sub><sup>+</sup> (M+H)<sup>+</sup> 472.11393, found 472.11398.

*Methyl 2'-amino-4-bromo-3'-cyano-6'-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6cab)*

Yield: 86%; mp 260–262 °C; IR (KBr, cm<sup>-1</sup>) 3277, 3180, 3011, 2962, 2195, 1710, 1608, 1504, 1443, 1406, 1377, 1355, 1318; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.76 (s, 1H), 8.30 (s, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.39 (s, 2H), 7.24 – 7.07 (m, 3H), 7.03 (dd, J = 8.7, 2.4 Hz, 1H), 6.85 (dd, J = 7.4, 1.2 Hz, 1H), 3.89 (s, 3H), 3.27 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 177.21, 164.34, 163.91, 160.40, 157.69, 155.70, 152.03, 144.24, 143.61, 130.93, 130.71, 125.62, 119.01, 117.86, 117.27, 113.50, 111.68, 109.16, 106.64, 100.82, 56.34, 54.06, 51.82, 51.56, 39.38; HRMS (ESI) m/z calcd for C<sub>25</sub>H<sub>17</sub>BrN<sub>3</sub>O<sub>7</sub><sup>+</sup> (M+H)<sup>+</sup> 550.02444, found 550.02509.

*Methyl 2'-amino-3'-cyano-5-fluoro-6'-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-oxospiro[indoline-3,4'-pyran]-5'-carboxylate (6cac)*

Yield: 81%; mp 241–243 °C; IR (KBr, cm<sup>-1</sup>) 3413, 3348, 3295, 3167, 3007, 2952, 2844, 2628, 2556, 2196, 1714, 1674, 1602, 1564, 1507, 1483, 1454, 1414, 1378, 1354, 1319; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.56 (s, 1H), 8.35 (s, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.39 (s, 2H), 7.11 (d, J = 2.4 Hz, 1H), 7.10 – 7.00 (m, 3H), 6.87 – 6.79 (m, 1H), 3.89 (s, 3H), 3.25 (s, 3H); <sup>13</sup>C NMR

(101 MHz, DMSO-*d*<sub>6</sub>) δ 177.94, 164.31, 163.94, 159.53, 159.25 (d, <sup>1</sup>J<sub>CF</sub> = 256 Hz), 157.17, 155.69, 151.39, 144.06, 138.26, 138.25, 135.96, 135.89, 130.65, 117.60, 117.34, 115.38 (d, <sup>2</sup>J<sub>CF</sub> = 23.5 Hz), 113.58, 111.65, 111.40, 110.49 (d, <sup>3</sup>J<sub>CF</sub> = 8.3 Hz),, 108.19, 100.88, 56.35, 56.29, 51.80, 50.22, 39.36; HRMS (ESI) m/z calcd for C<sub>25</sub>H<sub>17</sub>FN<sub>3</sub>O<sub>7</sub><sup>+</sup> (M+H)<sup>+</sup> 490.10450, found 490.10483.

*Methyl 2'-amino-5-chloro-3'-cyano-6'-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-oxospiro [indoline-3,4'-pyran]-5'-carboxylate (6cad)*

Yield: 69%; mp 254–256 °C; IR (KBr, cm<sup>-1</sup>) 3375, 3341, 3303, 3176, 2950, 2846, 2203, 1717, 1660, 1614, 1560, 1507, 1475, 1435, 1412, 1374, 1310; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.67 (s, 1H), 8.36 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.40 (s, 2H), 7.31 – 7.20 (m, 2H), 7.14 – 7.09 (m, 1H), 7.04 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.85 (dd, *J* = 8.2, 0.5 Hz, 1H), 3.89 (s, 3H), 3.26 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 177.66, 164.28, 163.93, 159.68, 157.95, 155.68, 151.57, 144.07, 140.97, 136.36, 130.63, 128.97, 126.03, 123.84, 117.62, 117.29, 113.56, 111.64, 111.14, 107.96, 100.88, 56.34, 56.19, 51.83, 50.01, 39.38, 39.16, 18.72; HRMS (ESI) m/z calcd for C<sub>25</sub>H<sub>17</sub>ClN<sub>3</sub>O<sub>7</sub><sup>+</sup> (M+H)<sup>+</sup> 506.07495, found 506.07544.

*Methyl 2'-amino-5-bromo-3'-cyano-6'-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-oxospiro [indoline-3,4'-pyran]-5'-carboxylate (6cae)*

Yield: 72%; mp 263–265 °C; IR (KBr, cm<sup>-1</sup>) 3403, 3338, 3230, 3089, 3040, 2959, 2933, 2837, 2191, 1726, 1676, 1642, 1610, 1556, 1504, 1472, 1441, 1408, 1378, 1325; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.69 (s, 1H), 8.36 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.44 – 7.31 (m, 4H), 7.11 (d, *J* = 2.4 Hz, 1H), 7.04 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 3.89 (s, 3H), 3.27 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 177.52, 164.28, 163.93, 159.68, 157.95, 155.68, 151.60, 144.06, 141.37, 136.75, 131.81, 130.62, 126.51, 117.64, 117.27, 113.68, 113.53, 111.67, 111.63, 107.96, 100.88, 56.32, 56.26, 51.81, 49.96; HRMS (ESI) m/z calcd for C<sub>25</sub>H<sub>17</sub>BrN<sub>3</sub>O<sub>7</sub><sup>+</sup> (M+H)<sup>+</sup> 550.02444, found 550.02441.

*Methyl 2'-amino-3'-cyano-6'-(7-methoxy-2-oxo-2H-chromen-3-yl)-5-nitro-2-oxospiro [indoline-3,4'-pyran]-5'-carboxylate (6caf)*

Yield: 91%; mp 280–282 °C; IR (KBr, cm<sup>-1</sup>) 3339, 3258, 3183, 2952, 2843, 2200, 1723, 1660, 1615, 1554, 1524, 1482, 1449, 1416, 1344, 1314; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.28 (s, 1H), 8.41 (s, 1H), 8.22 (dd, *J* = 8.8, 2.3 Hz, 1H), 8.08 (d, *J* = 2.2 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.51 (s, 2H), 7.14 – 7.01 (m, 3H), 3.90 (s, 3H), 3.26 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 178.46, 164.30, 164.00, 159.82, 158.00, 155.74, 152.13, 148.59, 144.32, 142.72, 135.43, 130.70, 126.57, 119.44, 117.55, 117.17, 113.62, 111.63, 110.00, 107.28, 100.91, 56.36, 56.20, 55.44, 52.01, 49.91, 30.86, 18.73; HRMS (ESI) m/z calcd for C<sub>25</sub>H<sub>17</sub>N<sub>4</sub>O<sub>9</sub><sup>+</sup> (M+H)<sup>+</sup> 517.09900, found 517.09961.

*Ethyl 2'-amino-3'-cyano-2-oxo-6'-(3-oxo-3H-benzof[f]chromen-2-yl)spiro[indoline-3,4'-pyran]-5'-carboxylate (6dba)*

Yield: 90%; mp 262–264 °C; IR (KBr, cm<sup>-1</sup>) 3379, 3159, 2977, 2200, 1720, 1666, 1617, 1567, 1517, 1471, 1408, 1392, 1365; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.50 (s, 1H), 9.24 (s, 1H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 9.1 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.81 (ddd, *J* = 8.5, 7.0, 1.3 Hz, 1H), 7.74 – 7.62 (m, 2H), 7.33 (s, 2H), 7.27 – 7.18 (m, 2H), 7.00 (td, *J* = 7.5, 1.1 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.48 – 3.41 (m, 2H), 0.68 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 177.95, 163.67, 159.77, 157.77, 153.66, 151.04, 142.14, 139.75, 135.04, 134.49, 130.22, 129.21, 129.05, 128.98, 128.89, 126.68, 123.87, 122.69, 122.17, 120.93, 117.52, 116.70, 112.50, 109.63, 109.08, 60.65, 56.19, 13.06; HRMS (ESI) m/z calcd for C<sub>29</sub>H<sub>20</sub>N<sub>3</sub>O<sub>6</sub><sup>+</sup> (M+H)<sup>+</sup> 506.13466, found 506.13486.

*Ethyl 2'-amino-4-bromo-3'-cyano-2-oxo-6'-(3-oxo-3H-benzof[f]chromen-2-yl)spiro[indoline-3,4'-pyran]-5'-carboxylate (6bb)*

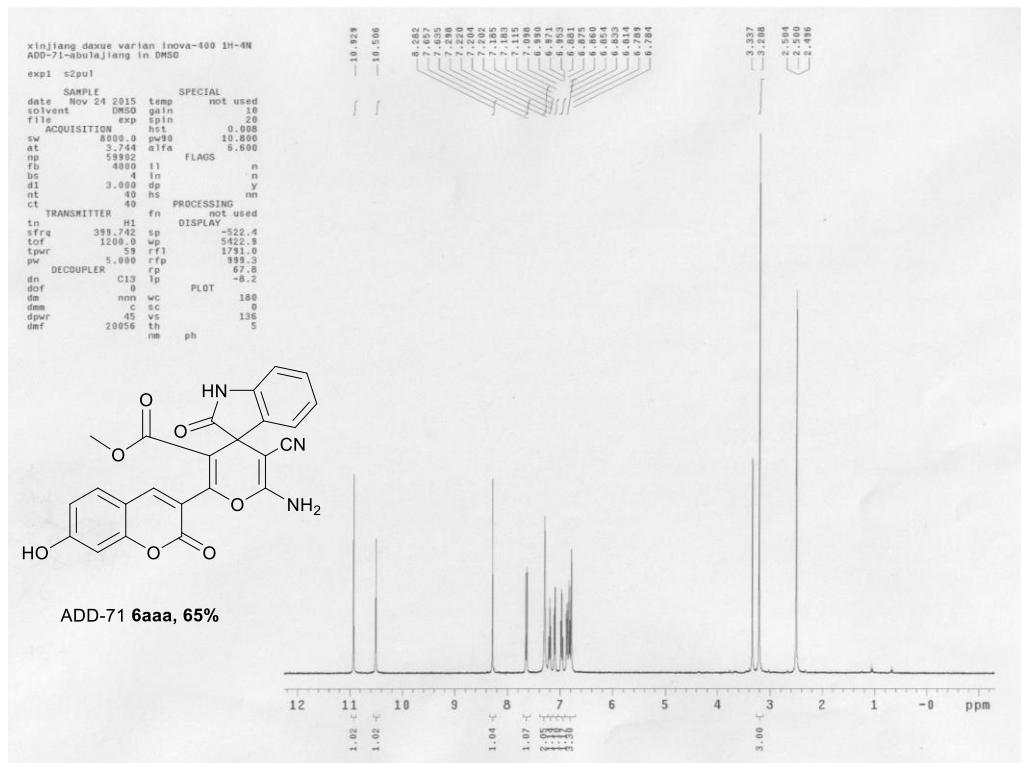
Yield: 93%; mp 278–280 °C; IR (KBr, cm<sup>-1</sup>) 3584, 3501, 3358, 3281, 3162, 2979, 2198, 1911, 1865, 1726, 1661, 1611, 1585, 1564, 1515, 1467, 1446, 1414, 1392, 1365; <sup>1</sup>H NMR (400

MHz, DMSO-*d*<sub>6</sub>) δ 10.77 (s, 1H), 9.10 (s, 1H), 8.74 – 8.66 (m, 1H), 8.31 (d, *J* = 9.0 Hz, 1H), 8.15 – 8.07 (m, 1H), 7.80 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.73 – 7.62 (m, 2H), 7.43 (s, 2H), 7.23 – 7.10 (m, 2H), 6.86 (dd, *J* = 7.4, 1.2 Hz, 1H), , 3.44 (q, *J* = 7.0 Hz, 2H), 0.73 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 177.20, 163.65, 160.51, 157.38, 153.67, 151.76, 144.27, 139.19, 135.10, 130.88, 130.80, 130.17, 129.15, 128.95, 128.83, 126.64, 125.59, 122.72, 121.00, 119.19, 117.28, 116.63, 112.35, 109.04, 107.03, 60.72, 54.29, 51.53, 13.09; HRMS (ESI) m/z calcd for C<sub>29</sub>H<sub>19</sub>BrN<sub>3</sub>O<sub>6</sub><sup>+</sup> (M+H)<sup>+</sup> 584.04517, found 584.04596.

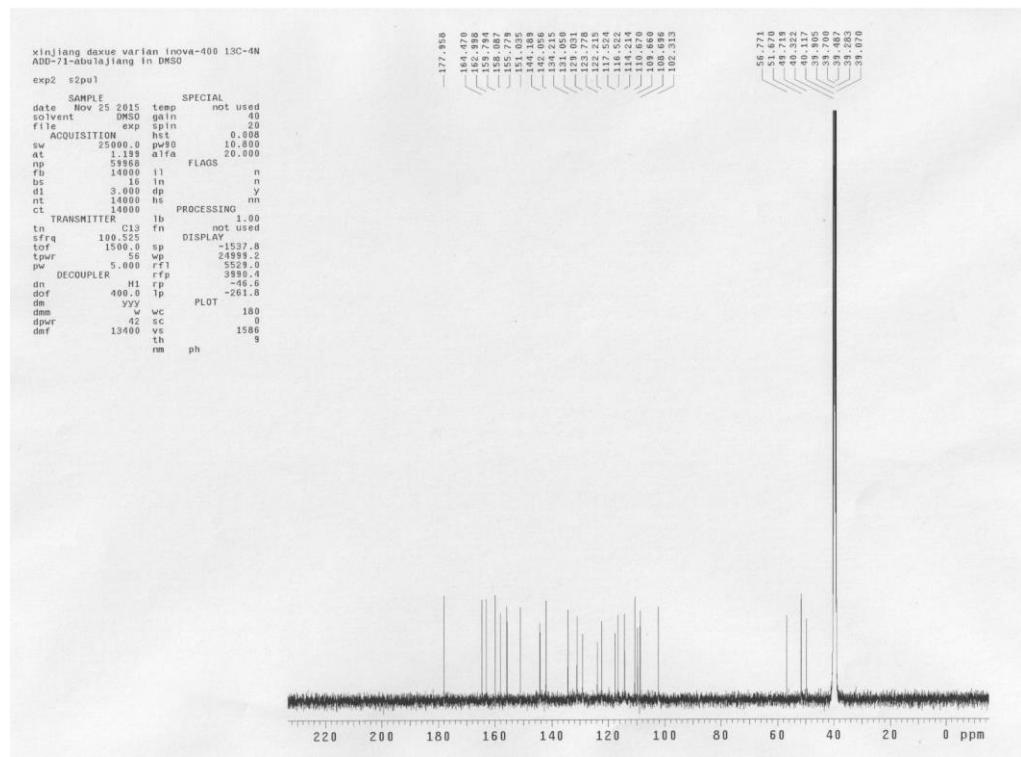
*Ethyl 2'-amino-3'-cyano-5-fluoro-2-oxo-6'-(3-oxo-3H-benzo[f]chromen-2-yl)spiro[indoline-3,4'-pyran]-5'-carboxylate (6dbc)*

Yield: 70%; mp 270–272 °C; IR (KBr, cm<sup>-1</sup>) 3421, 3278, 3081, 2989, 2198, 1720, 1665, 1626, 1598, 1564, 1515, 1488, 1393, 1366, 1348, 1302; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.56 (s, 1H), 9.26 (s, 1H), 8.65 (d, *J* = 8.5 Hz, 1H), 8.31 (d, *J* = 9.0 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.82 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.42 (s, 2H), 7.15 – 7.02 (m, 2H), 6.89 – 6.80 (m, 1H), 3.72 (tdd, *J* = 7.2, 5.6, 1.7 Hz, 2H), 0.70 (td, *J* = 7.1, 1.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 178.02, 163.58, 159.59, 158.69 (d, <sup>1</sup>J<sub>CF</sub> = 2175 Hz), 157.23, 153.71, 151.64, 139.93, 138.36, 136.30, 136.28 (d, <sup>3</sup>J<sub>CF</sub> = 7.5 Hz), 135.11, 130.25, 129.17 (d, <sup>2</sup>J<sub>CF</sub> = 22.8 Hz), 128.97, 126.73, 122.58, 120.92, 117.39, 116.74, 115.46, 115.23, 112.48, 111.74, 111.49, 110.54, 110.46, 108.39, 60.83, 56.52, 50.18, 13.10; HRMS (ESI) m/z calcd for C<sub>29</sub>H<sub>19</sub>FN<sub>3</sub>O<sub>6</sub><sup>+</sup> (M+H)<sup>+</sup> 524.12524, found 524.12512.

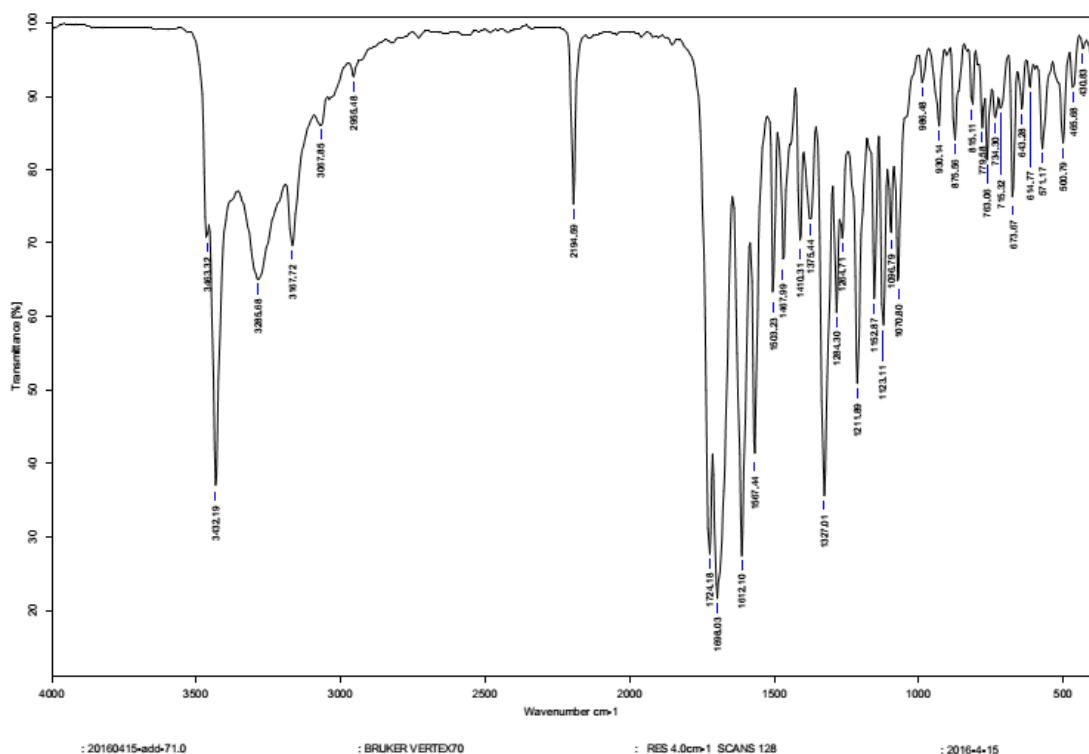
**<sup>1</sup>H NMR of compound 6aaa (400 MHz, DMSO-*d*<sub>6</sub>)**



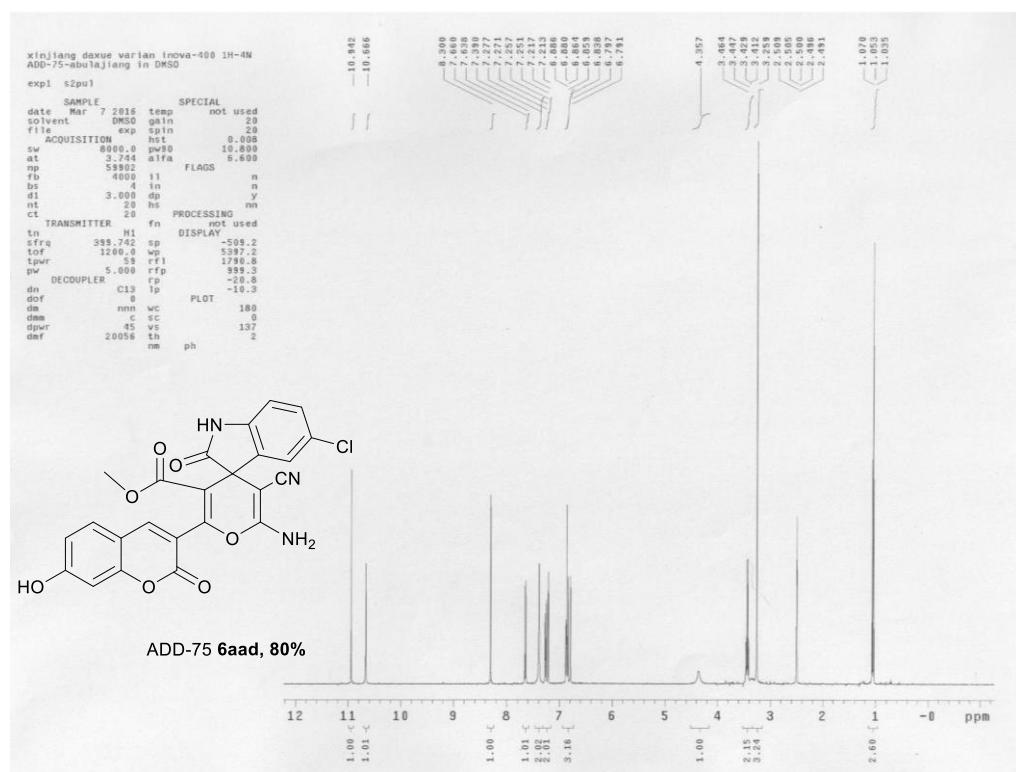
**<sup>13</sup>C NMR of compound 6aaa (400 MHz, DMSO-*d*<sub>6</sub>)**



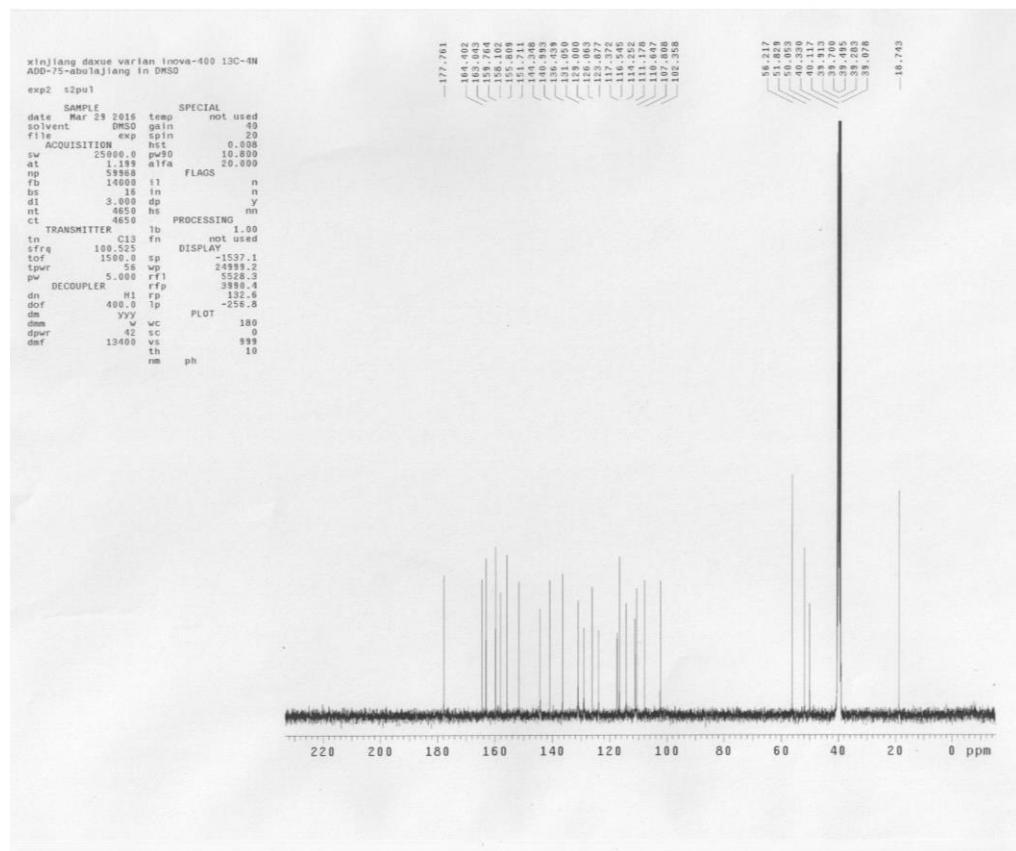
**IR spectrum of compound 6aaa**



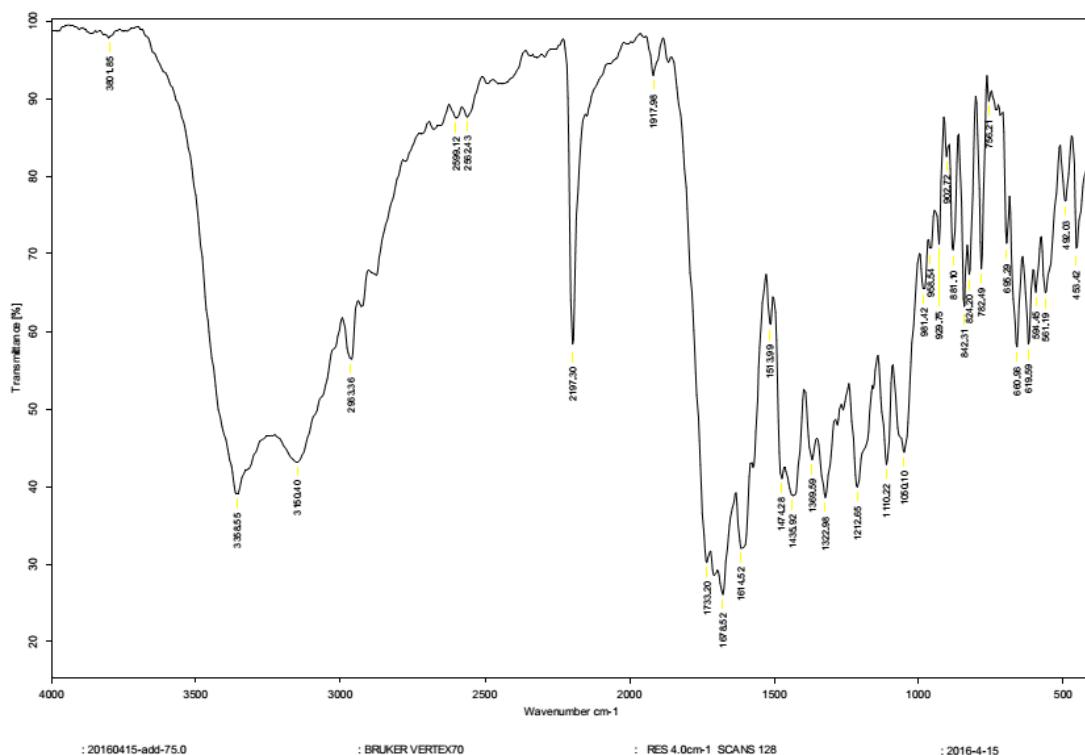
**<sup>1</sup>H NMR of compound 6aad (400 MHz, DMSO-d<sub>6</sub>)**



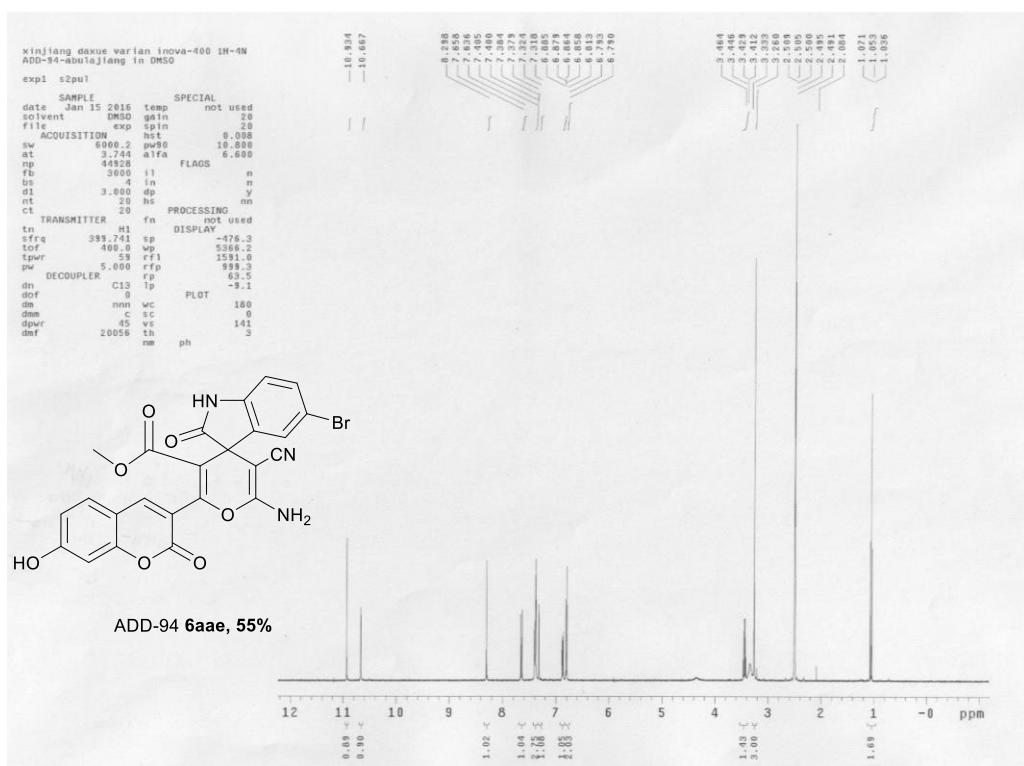
**<sup>13</sup>C NMR of compound 6aad (400 MHz, DMSO-*d*<sub>6</sub>)**



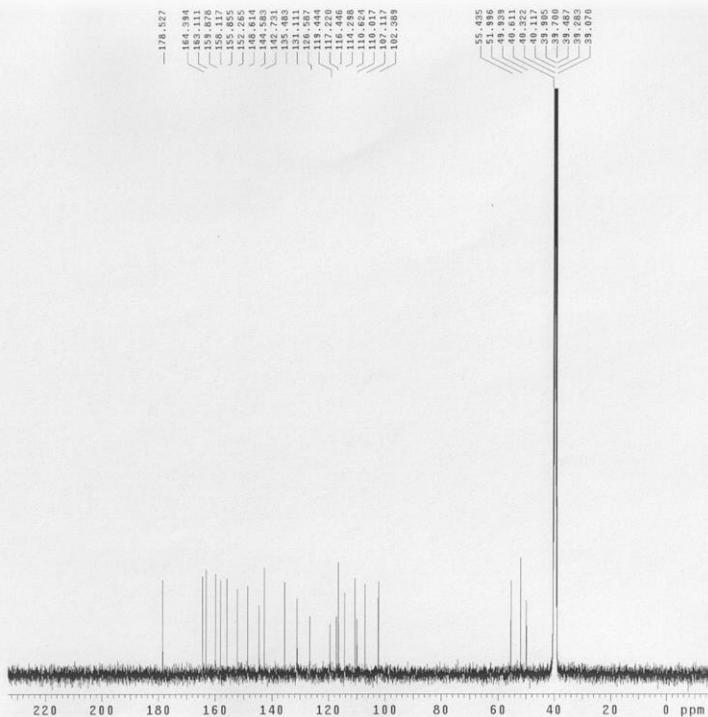
**IR spectrum of compound 6aad**



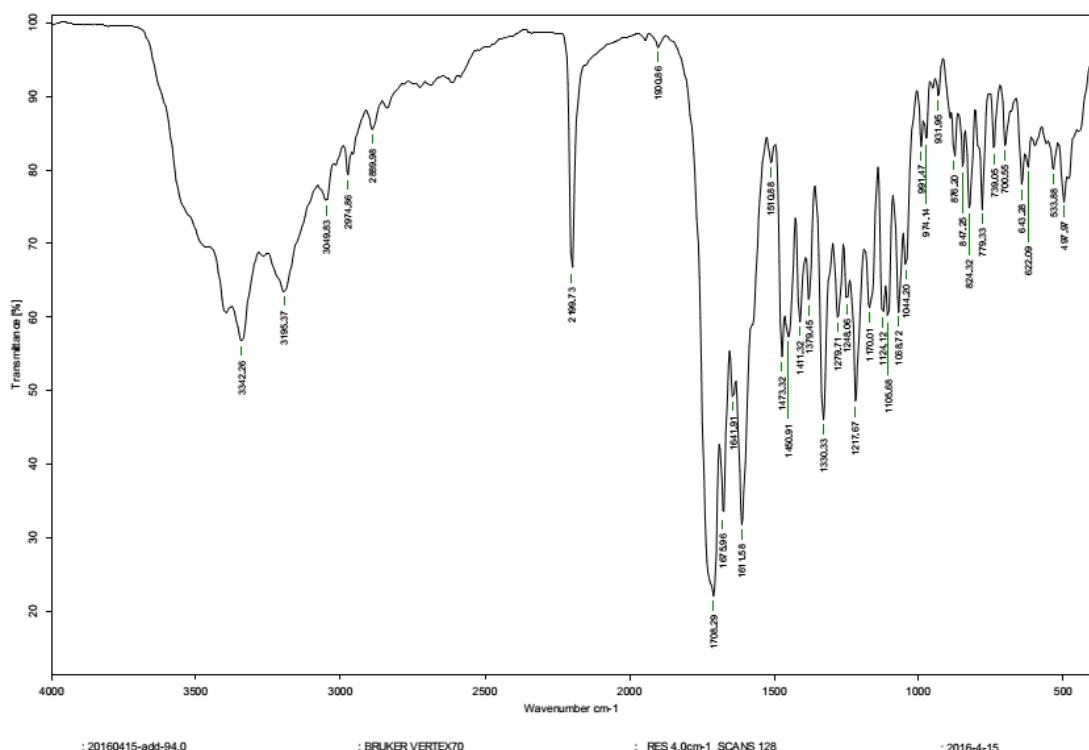
**<sup>1</sup>H NMR of compound 6aae (400 MHz, DMSO-d<sub>6</sub>)**



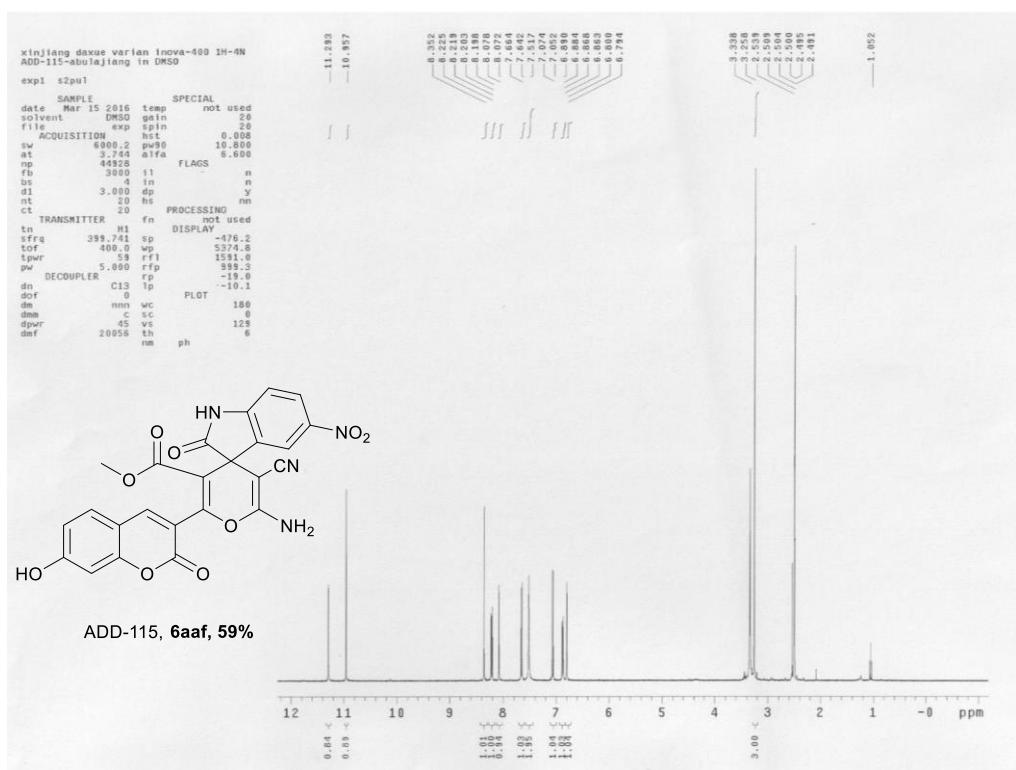
**<sup>13</sup>C NMR of compound 6aae (400 MHz, DMSO-d<sub>6</sub>)**



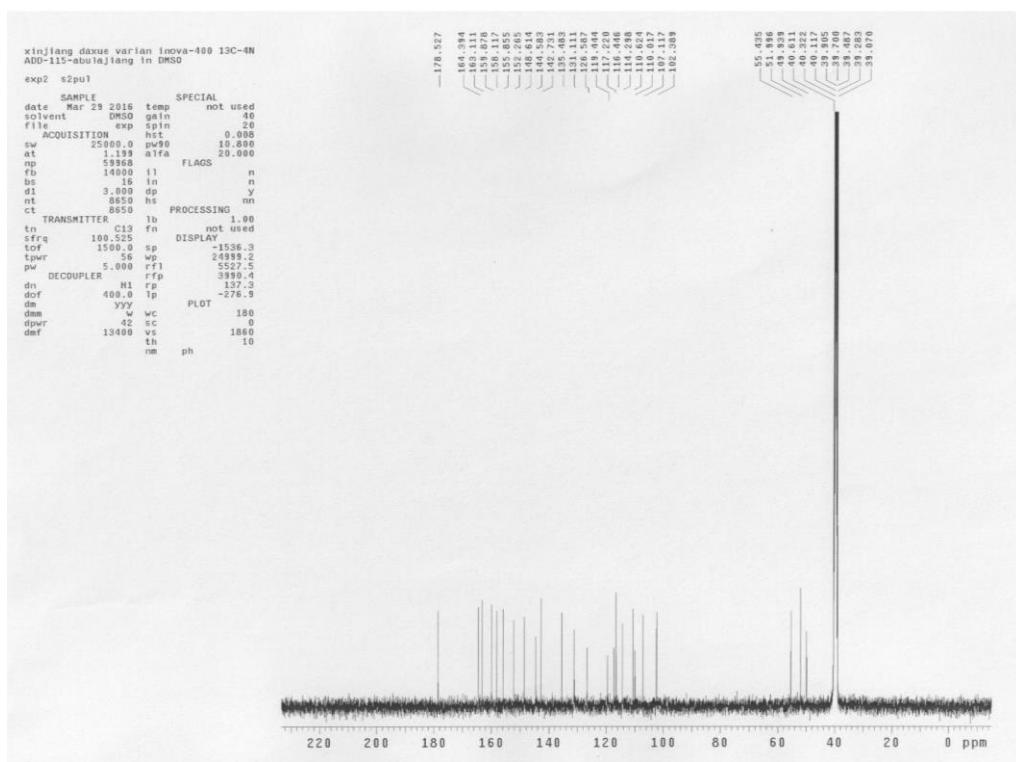
**IR spectrum of compound 6aae**



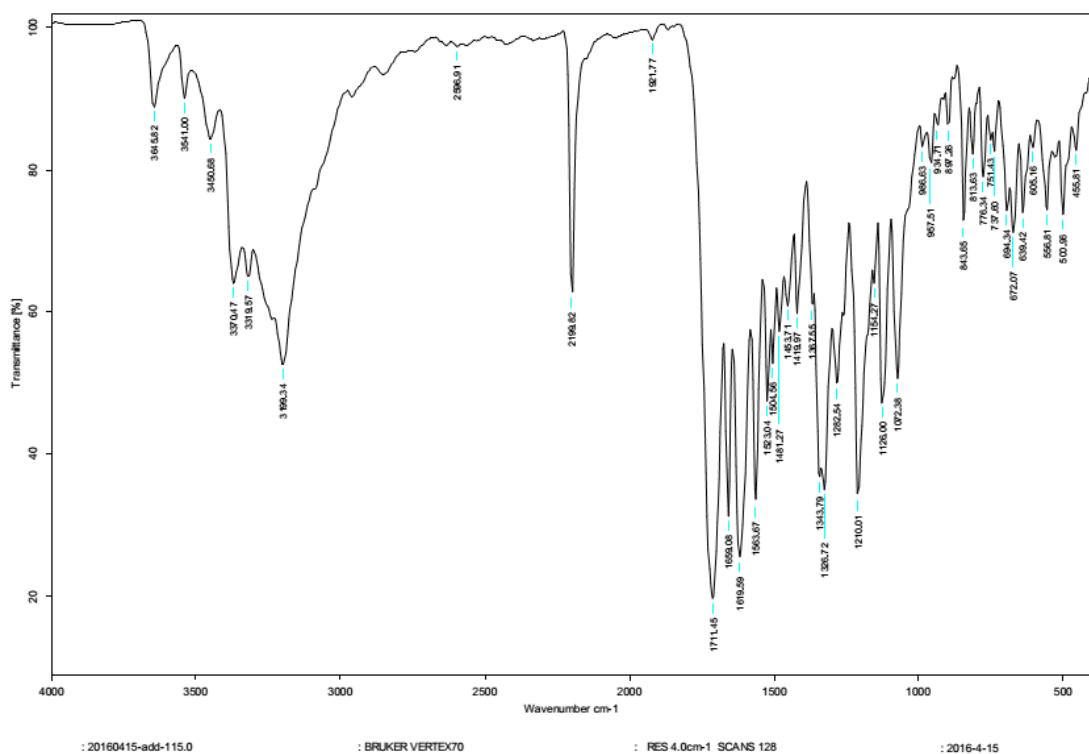
**<sup>1</sup>H NMR of compound 6aaf (400 MHz, DMSO-d<sub>6</sub>)**



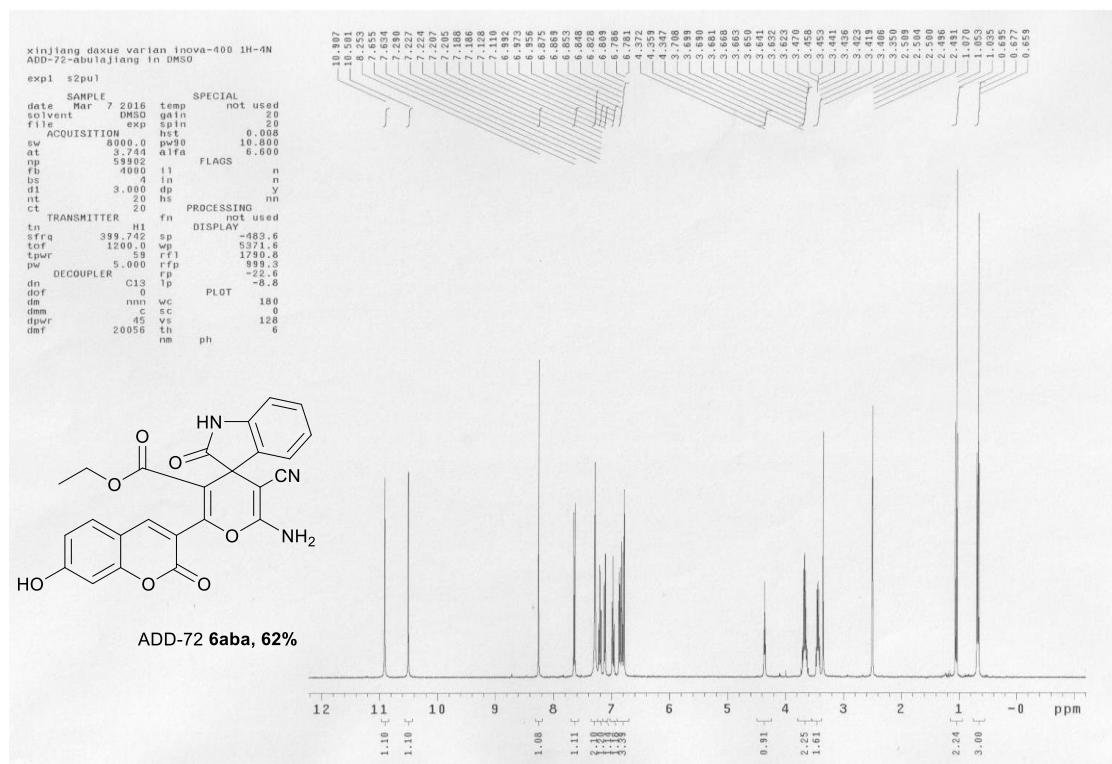
**<sup>13</sup>C NMR of compound 6aaf (400 MHz, DMSO-d<sub>6</sub>)**



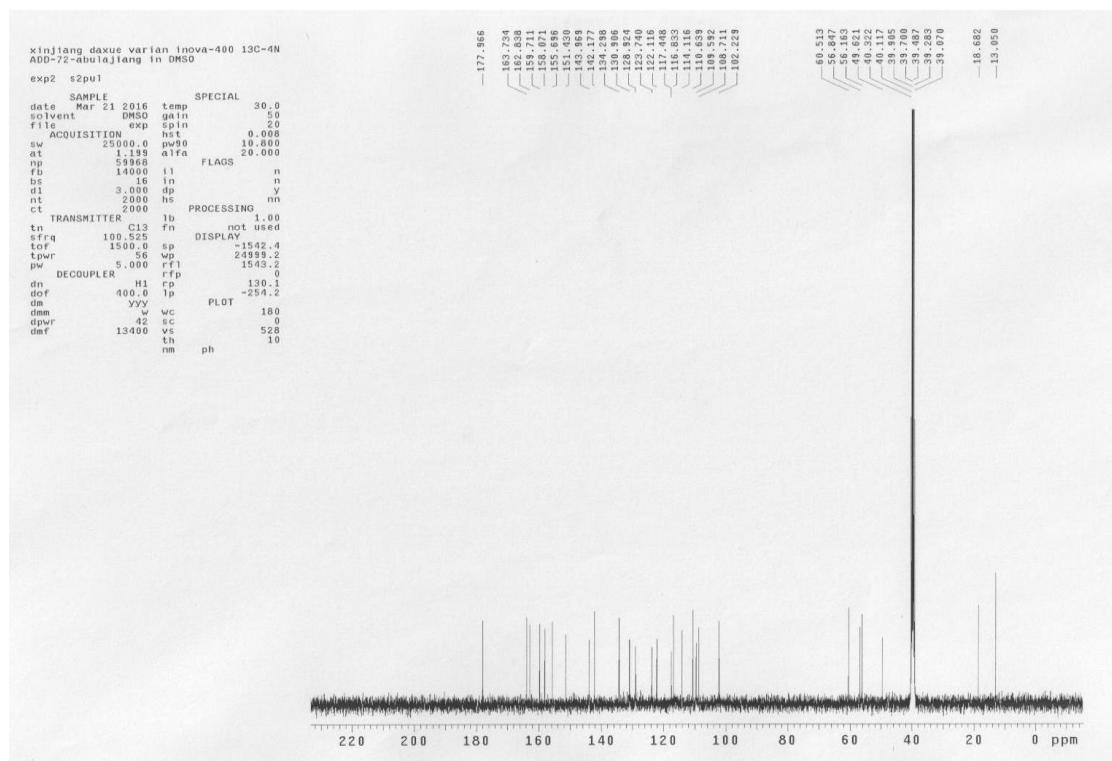
**IR spectrum of compound 6aaf**



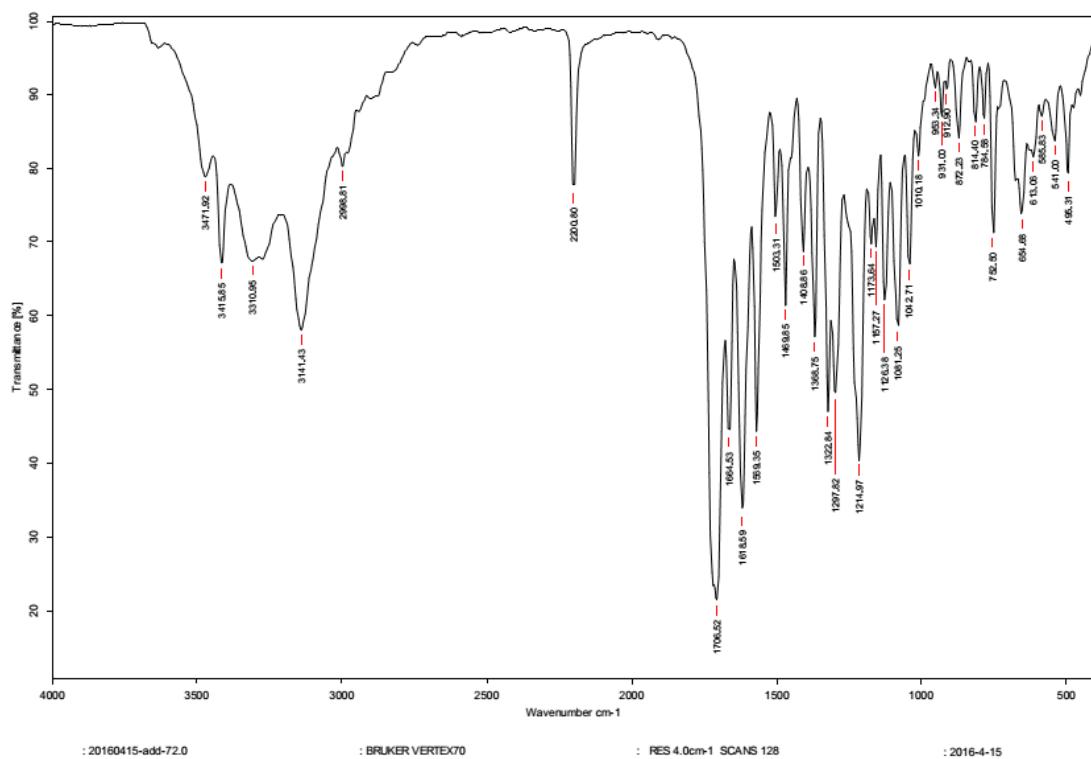
**<sup>1</sup>H NMR of compound 6aba (400 MHz, DMSO-d<sub>6</sub>)**



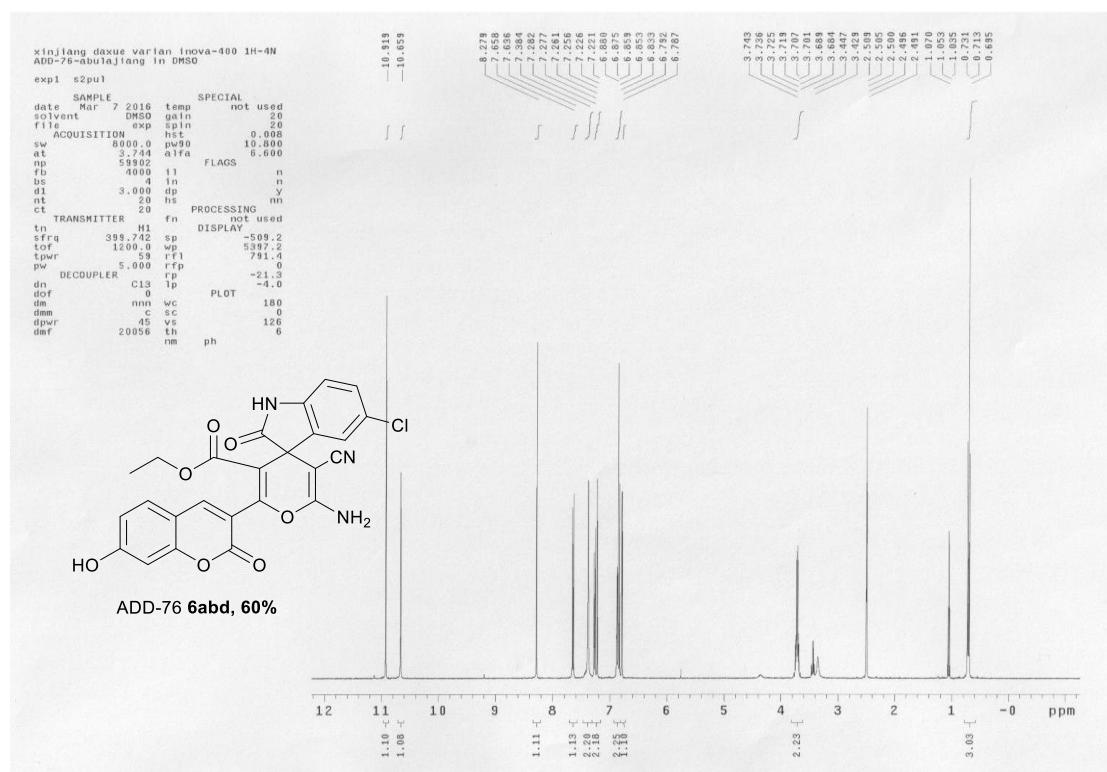
**<sup>13</sup>C NMR of compound 6aba (400 MHz, DMSO-d<sub>6</sub>)**



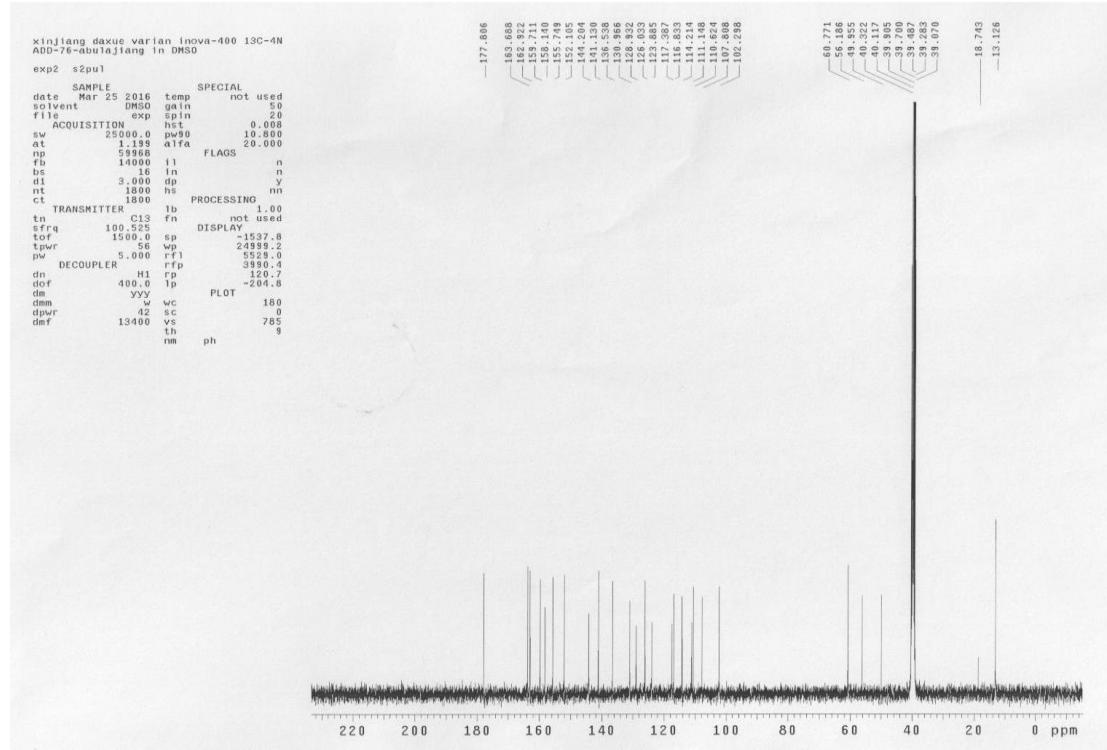
**IR spectrum of compound 6aba**



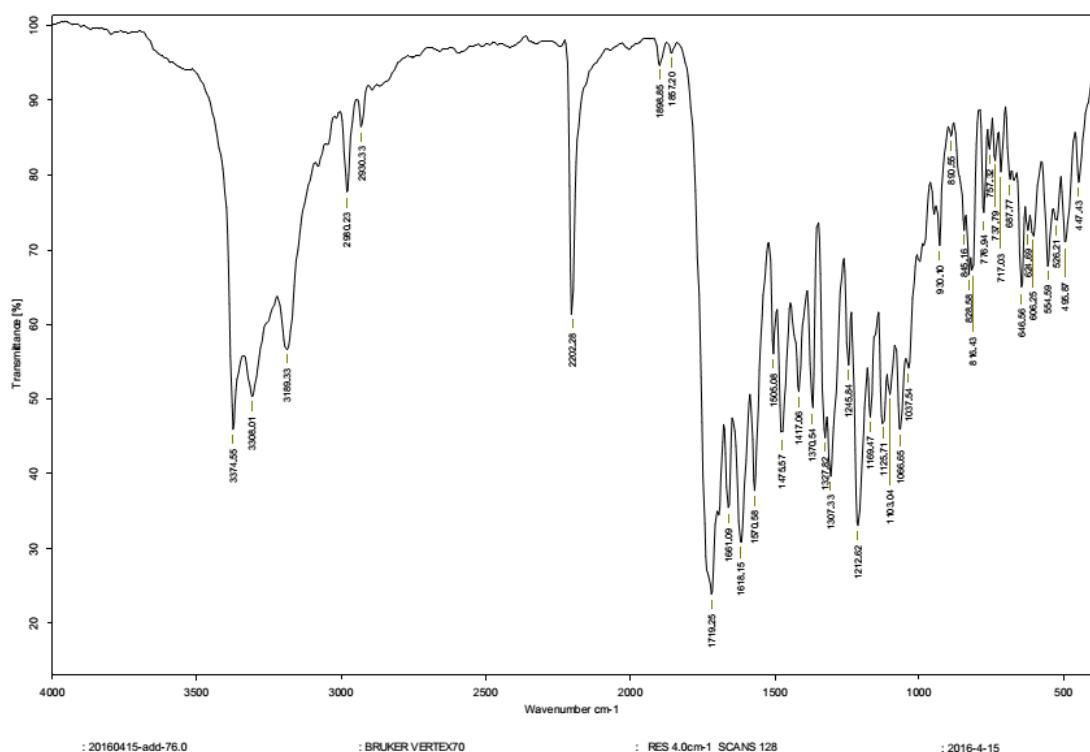
**<sup>1</sup>H NMR of compound 6abd (400 MHz, DMSO-d<sub>6</sub>)**



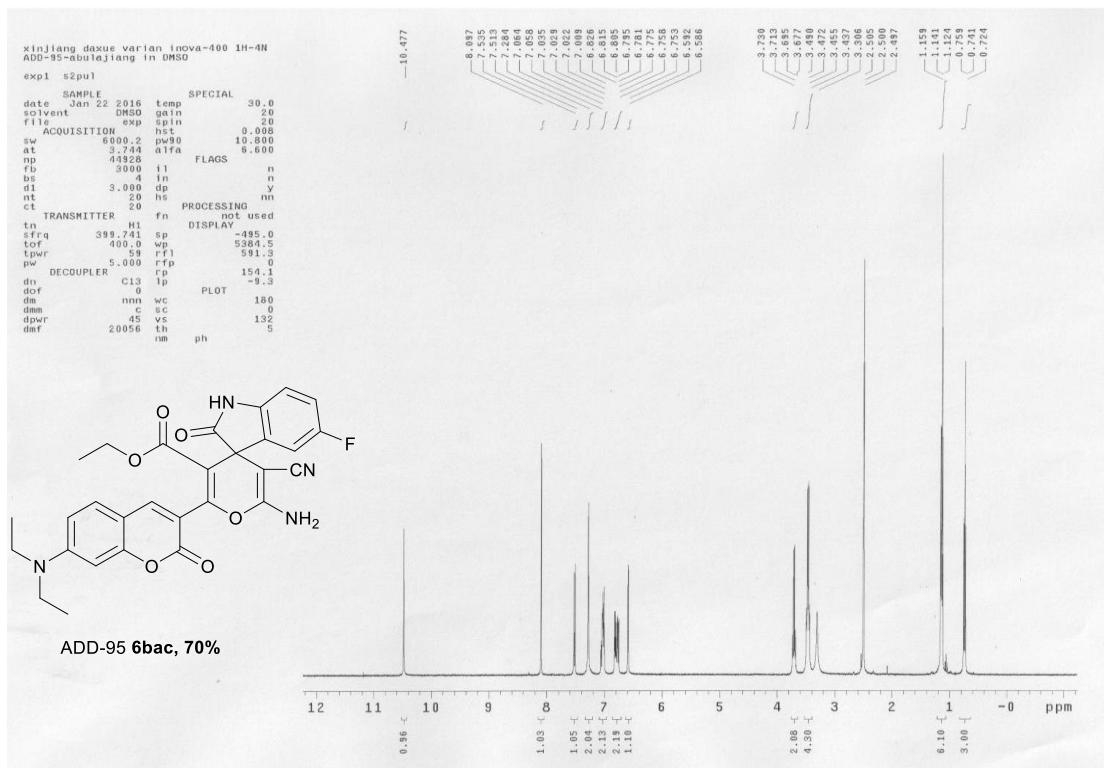
**<sup>13</sup>C NMR of compound 6abd (400 MHz, DMSO-d<sub>6</sub>)**



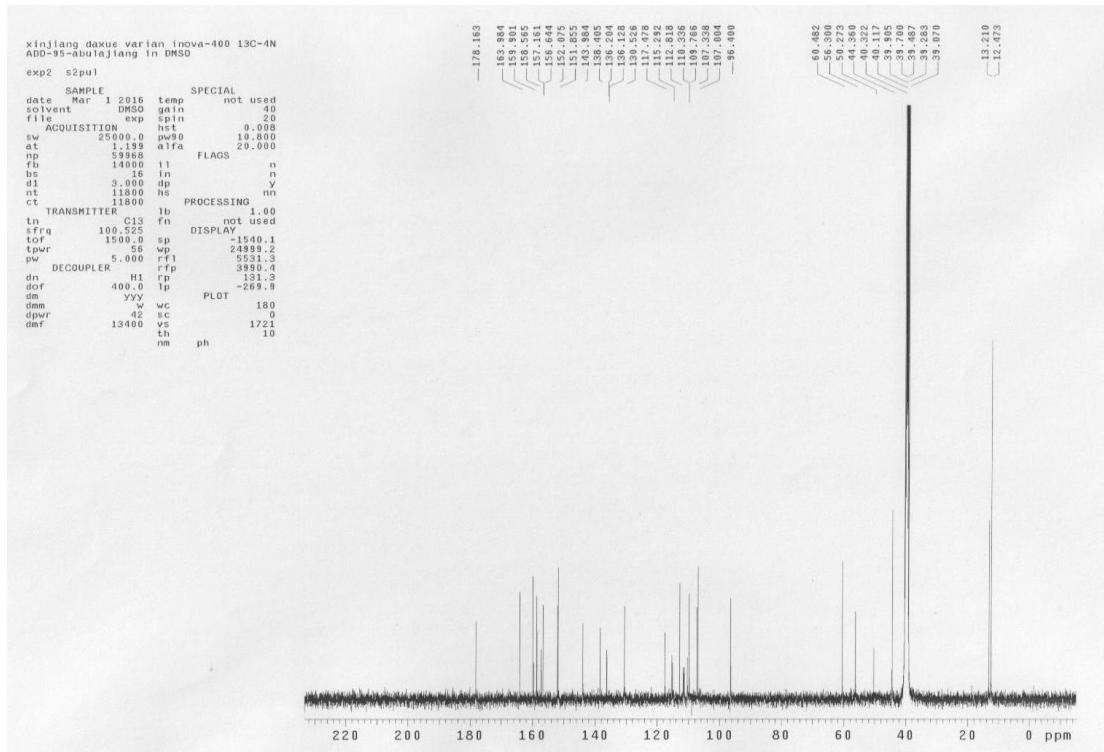
**IR spectrum of compound 6abd**



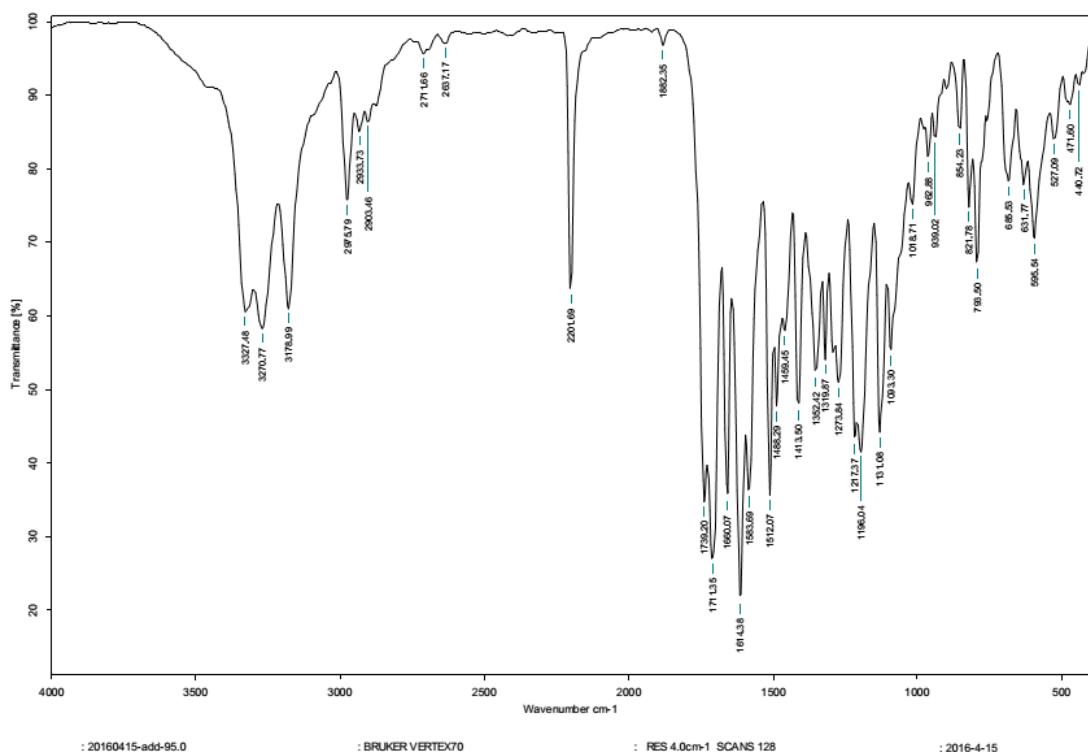
**<sup>1</sup>H NMR of compound 6bac (400 MHz, DMSO-d<sub>6</sub>)**



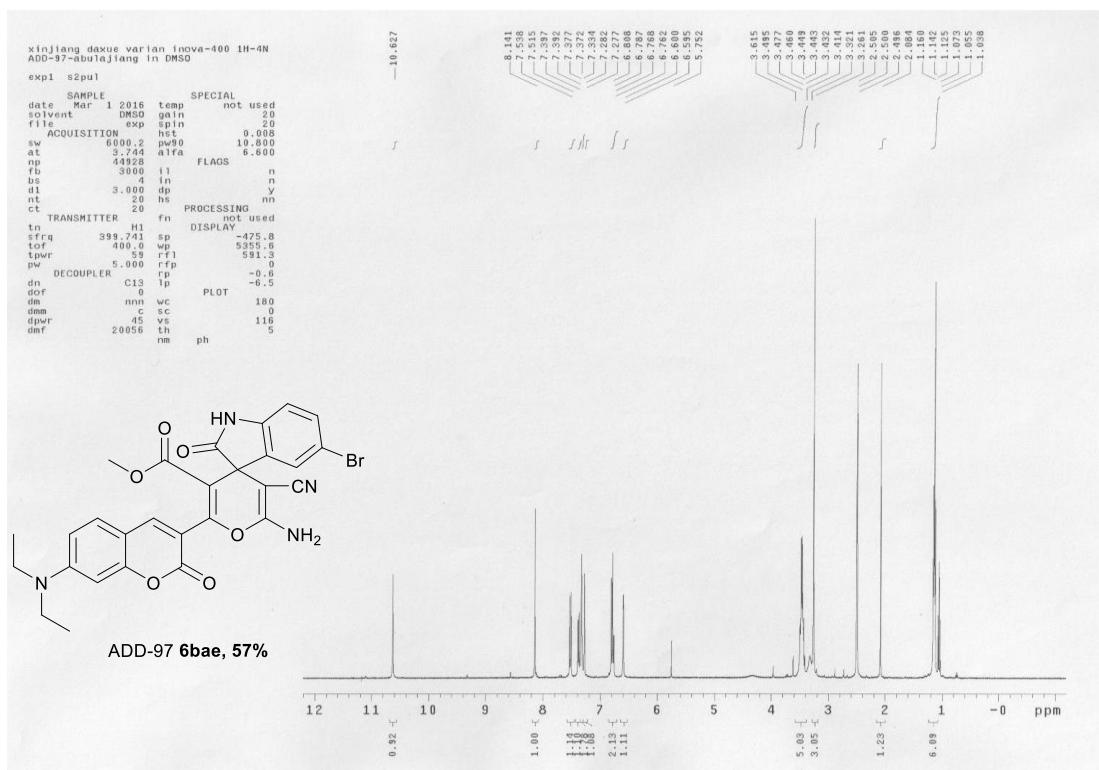
**<sup>13</sup>C NMR of compound 6bac (400 MHz, DMSO-d<sub>6</sub>)**



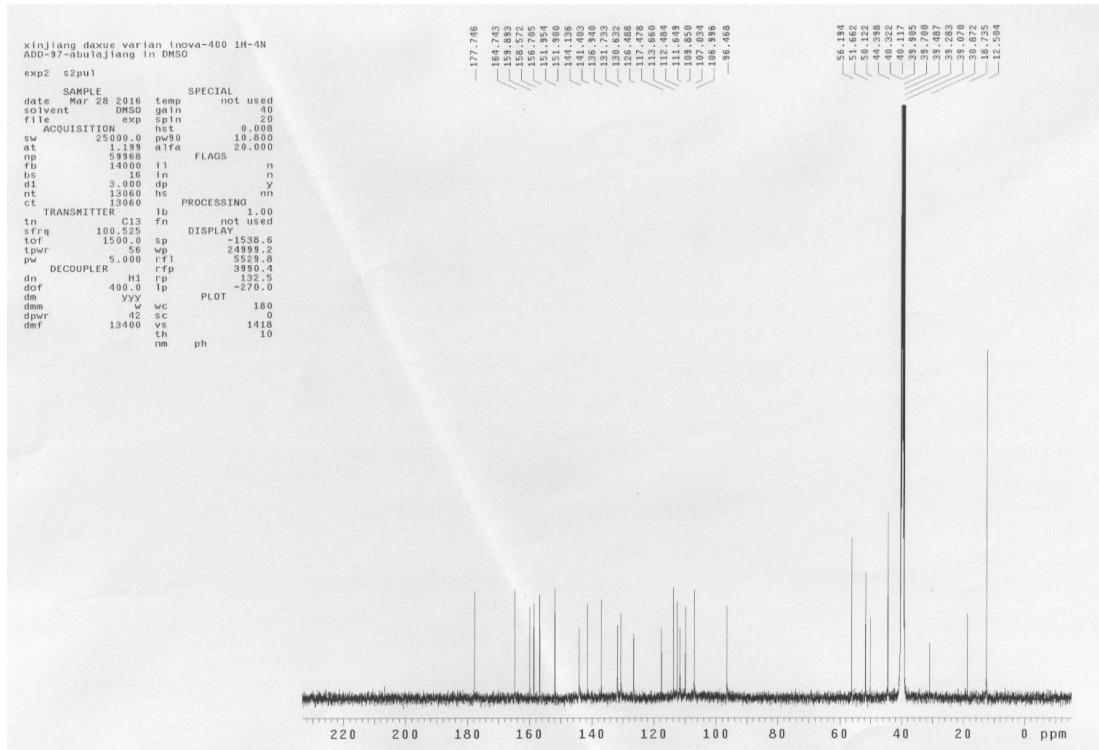
**IR spectrum of compound 6bac**



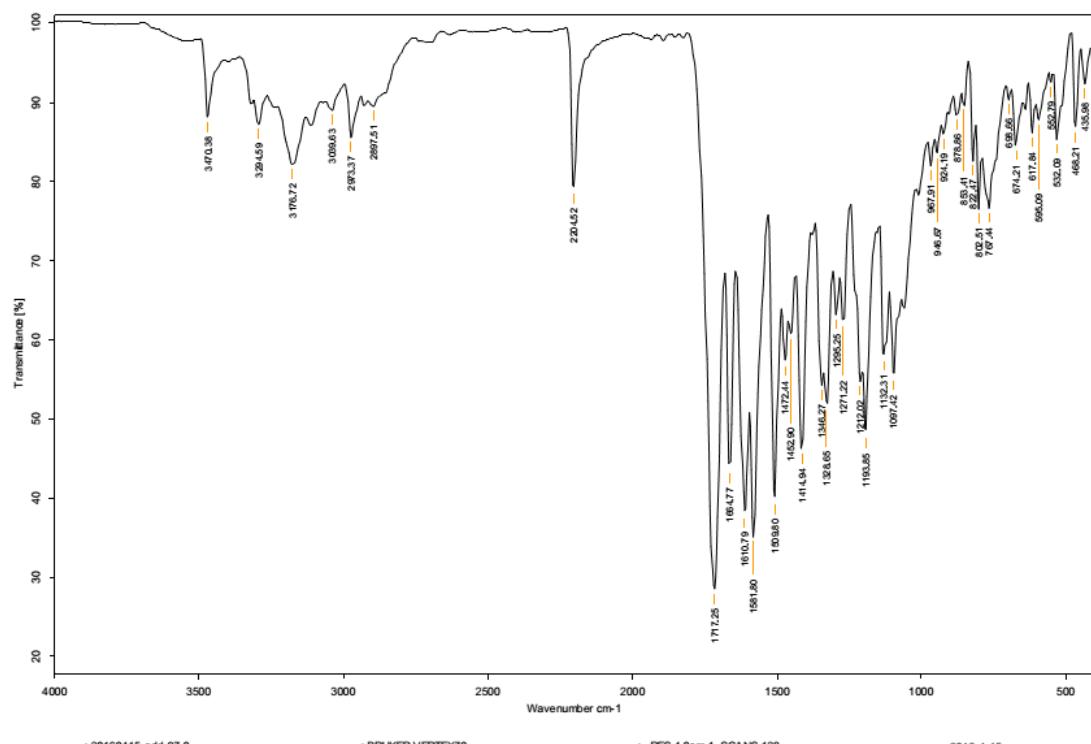
**<sup>1</sup>H NMR of compound 6bae (400 MHz, DMSO-d<sub>6</sub>)**



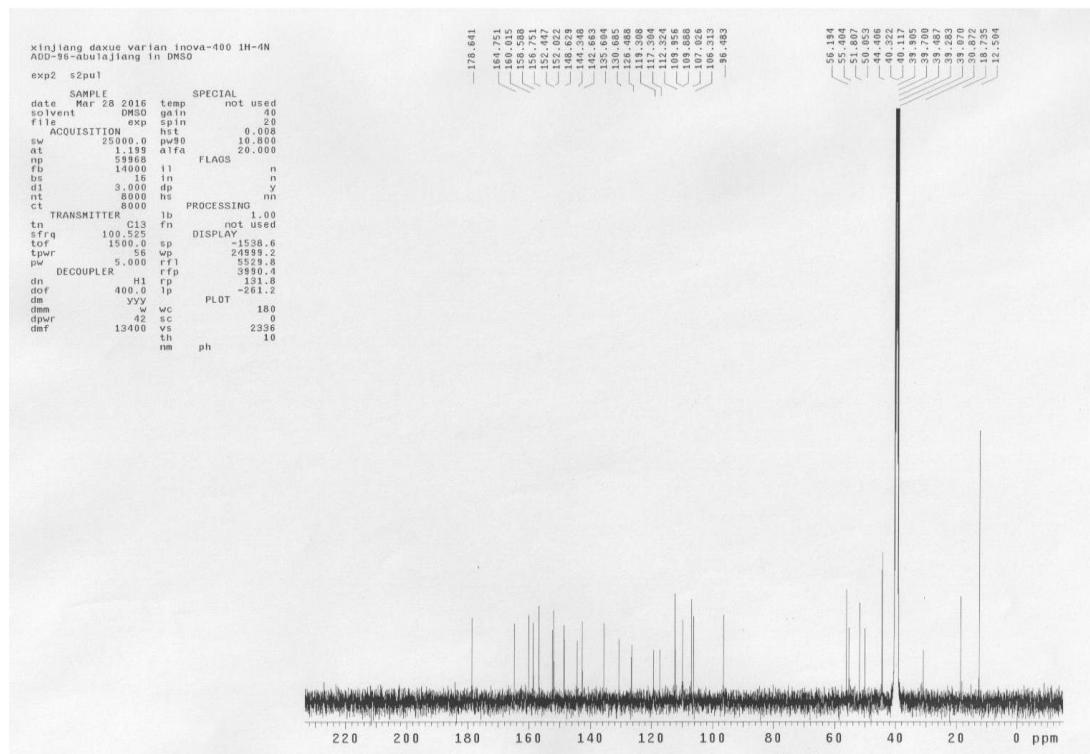
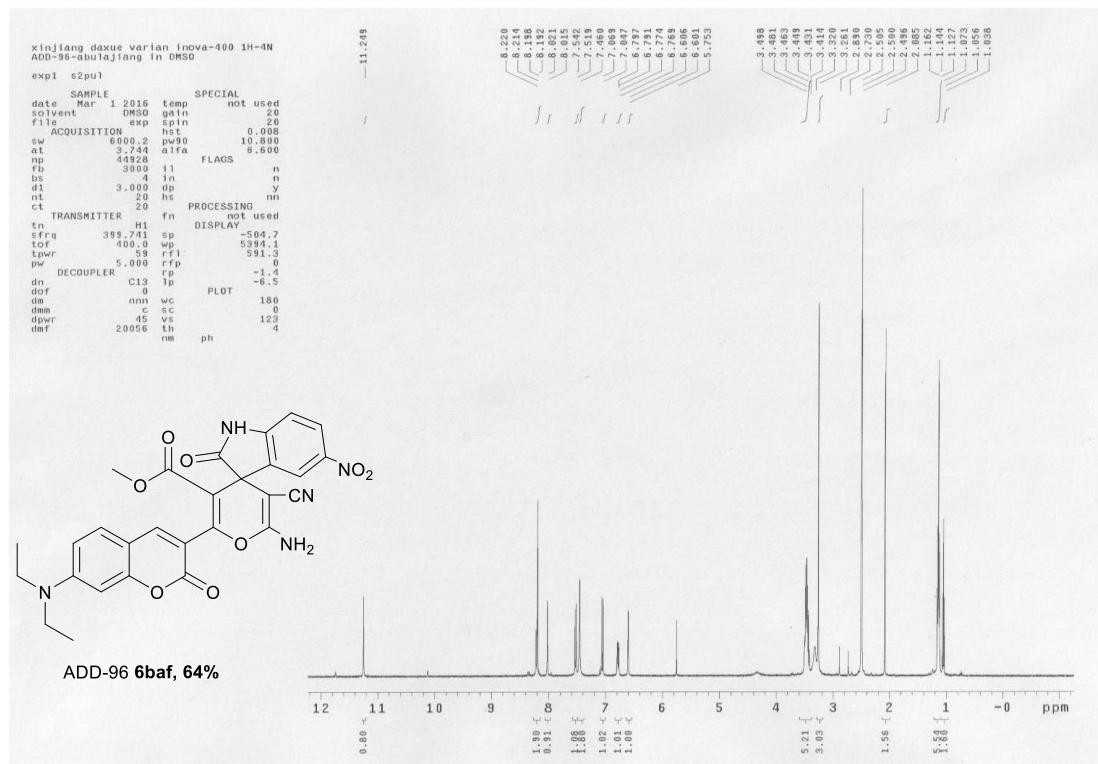
**<sup>13</sup>C NMR of compound 6bae (400 MHz, DMSO-d<sub>6</sub>)**



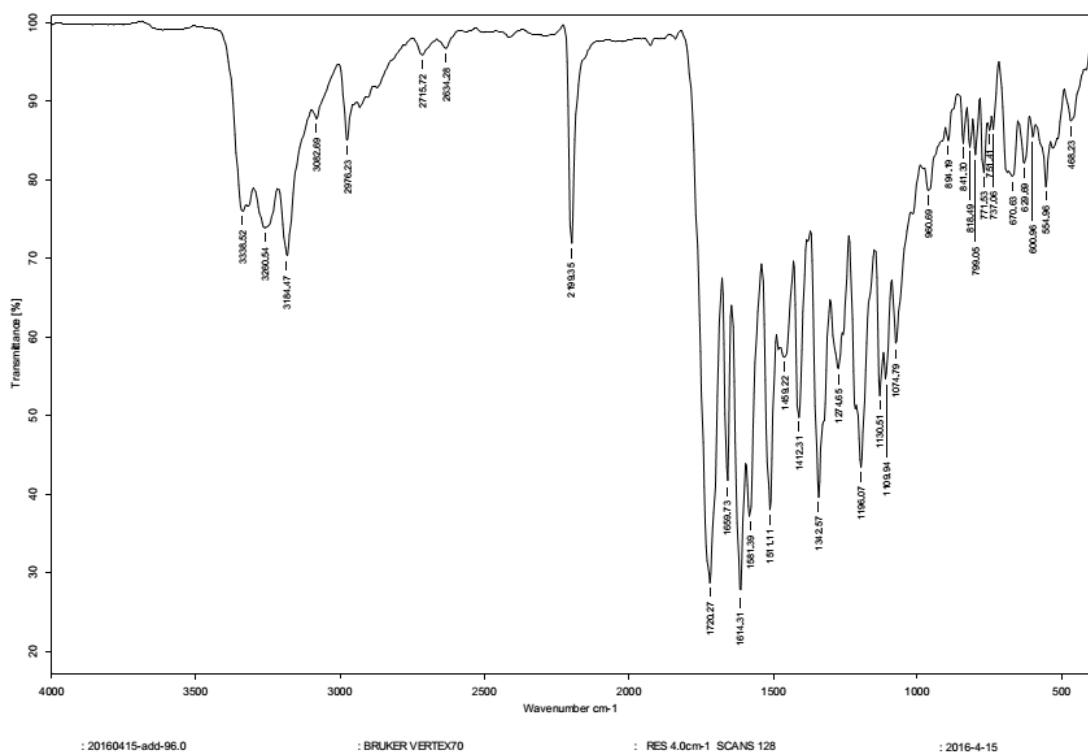
### IR spectrum of compound 6bae



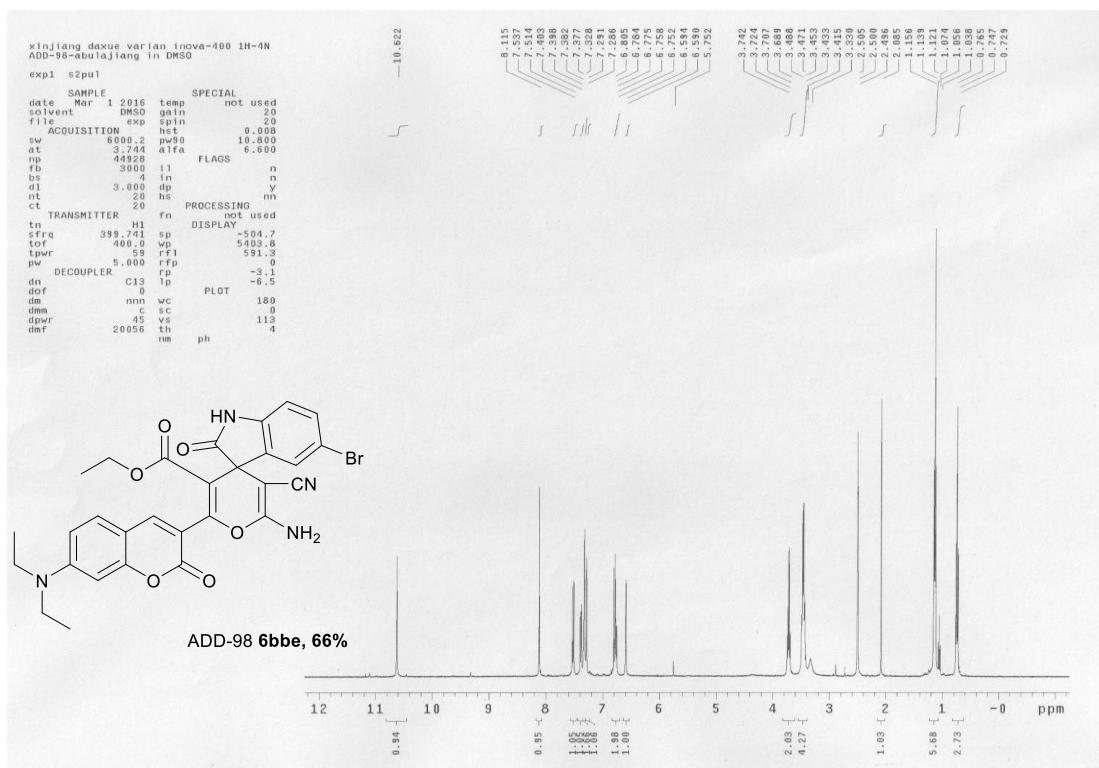
**<sup>1</sup>H NMR of compound 6baf (400 MHz, DMSO-d<sub>6</sub>)**



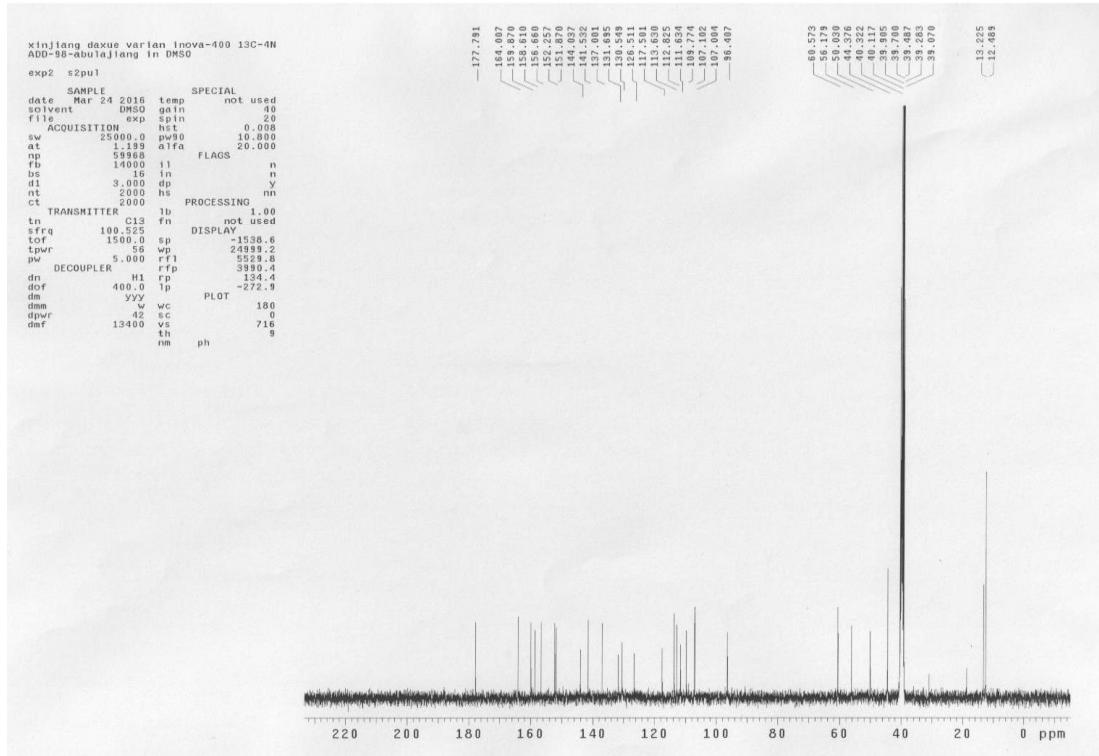
**IR spectrum of compound 6baf**



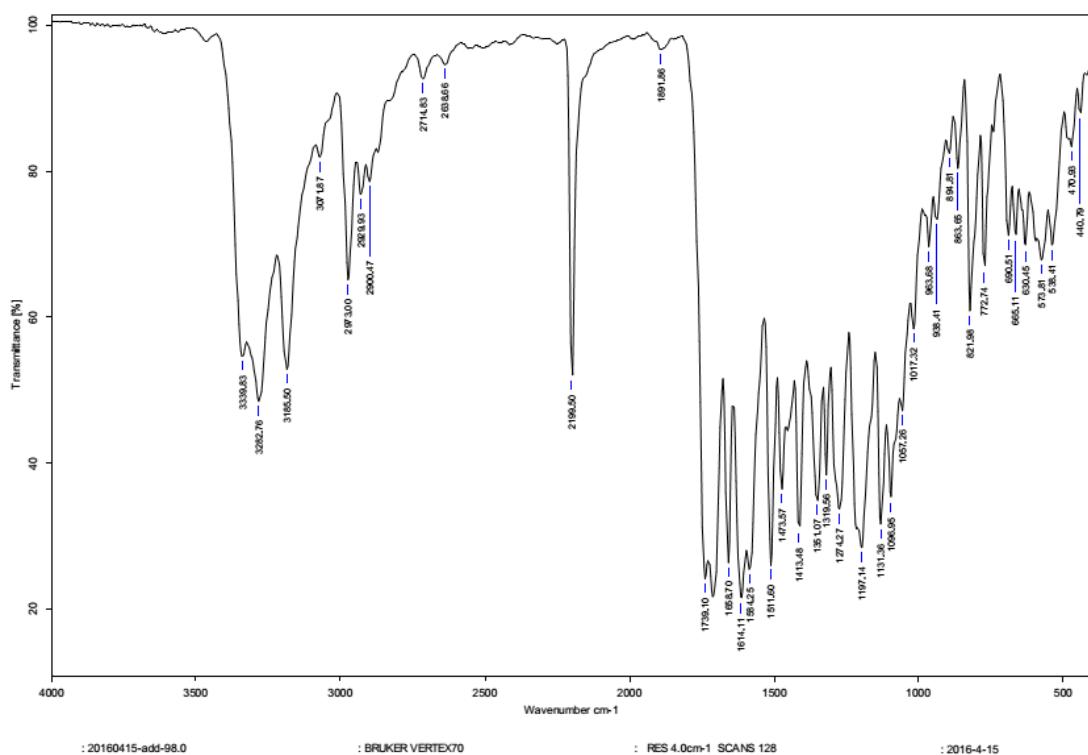
**<sup>1</sup>H NMR of compound 6bbe (400 MHz, DMSO-d<sub>6</sub>)**



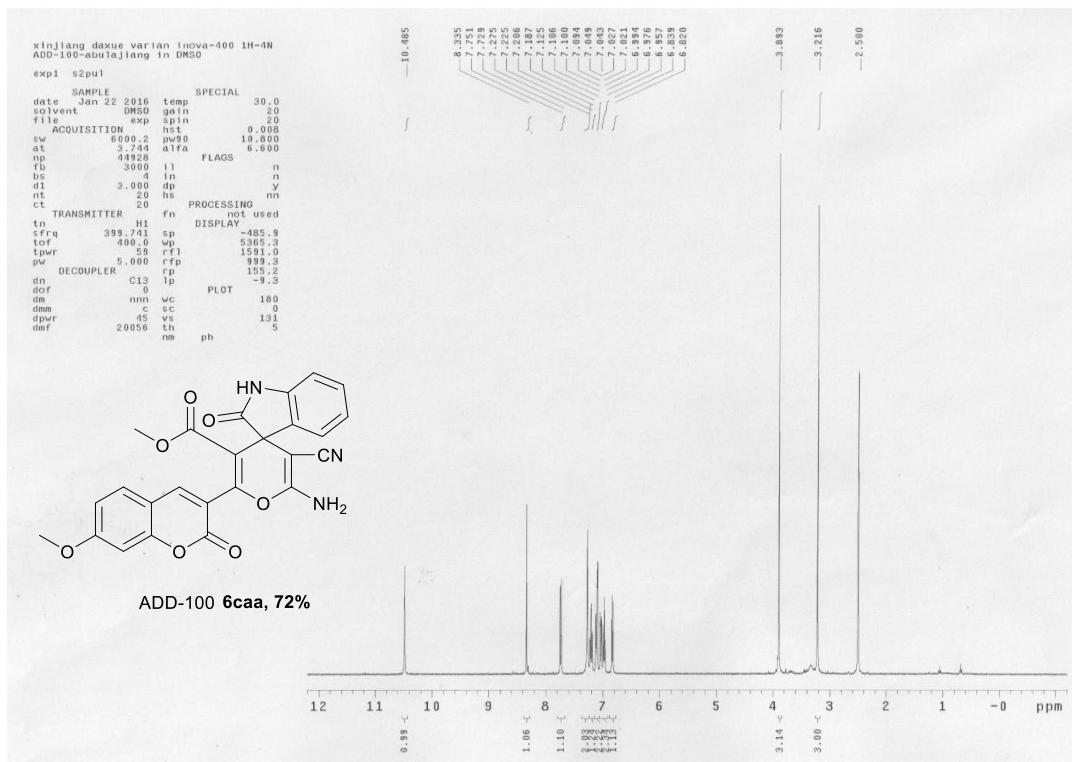
**<sup>13</sup>C NMR of compound 6bbe (400 MHz, DMSO-d<sub>6</sub>)**



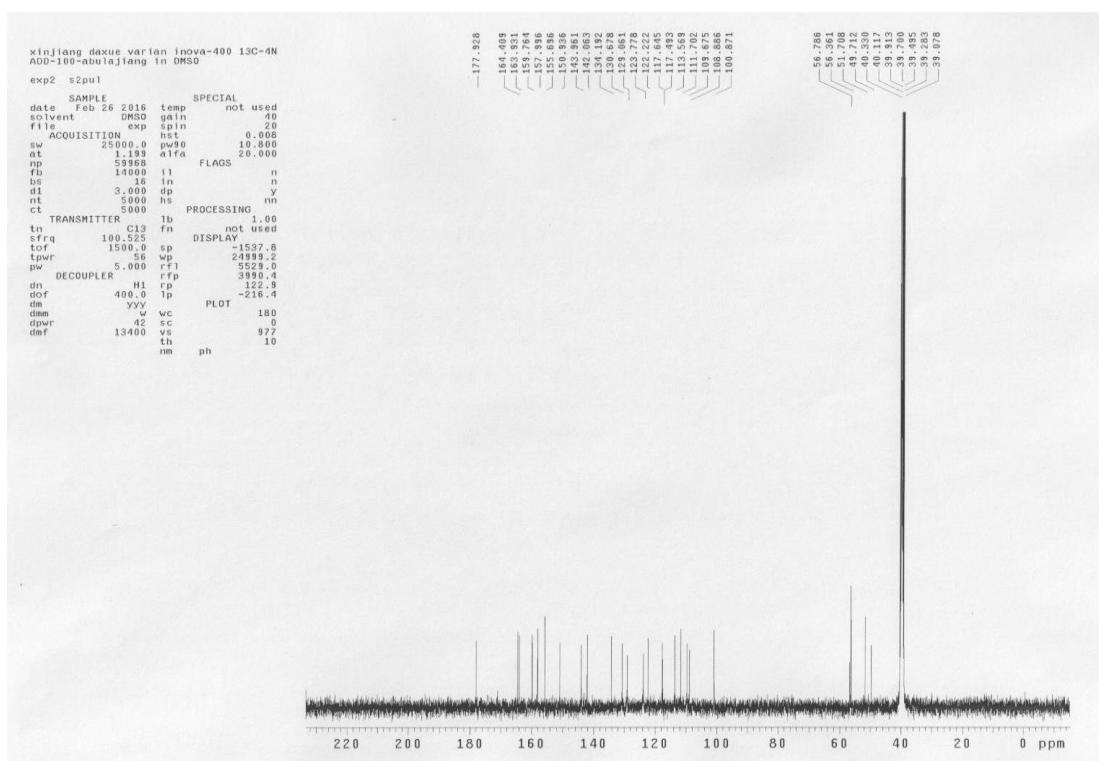
**IR spectrum of compound 6bbe**



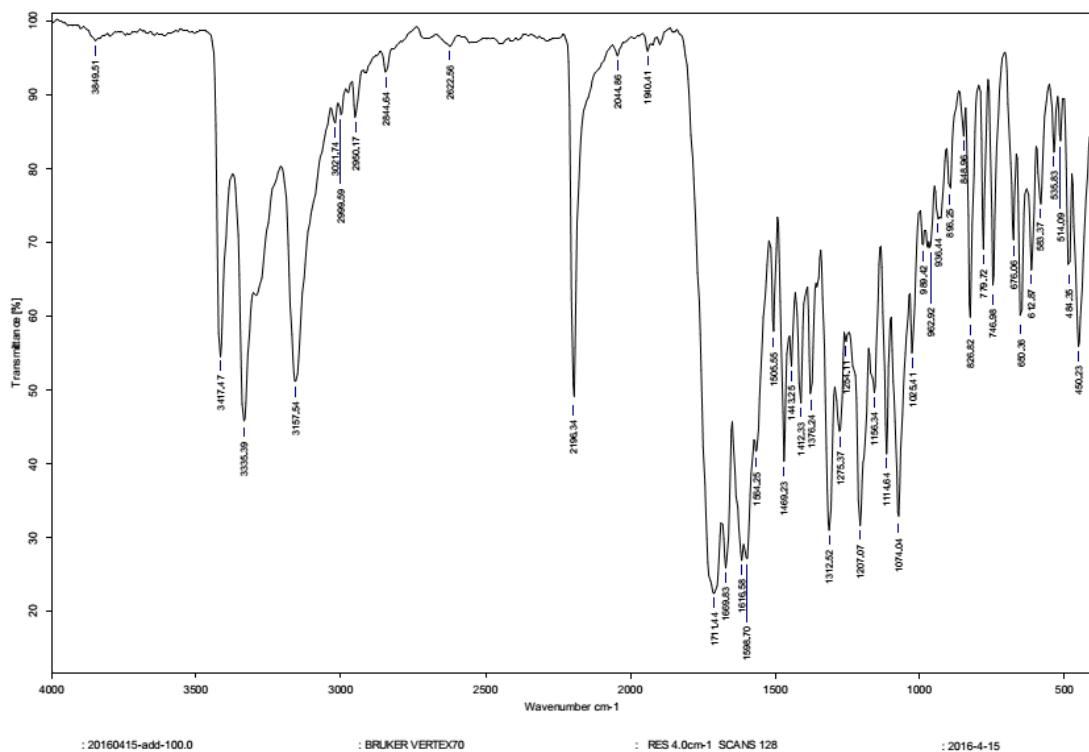
**<sup>1</sup>H NMR of compound 6caa (400 MHz, DMSO-d<sub>6</sub>)**



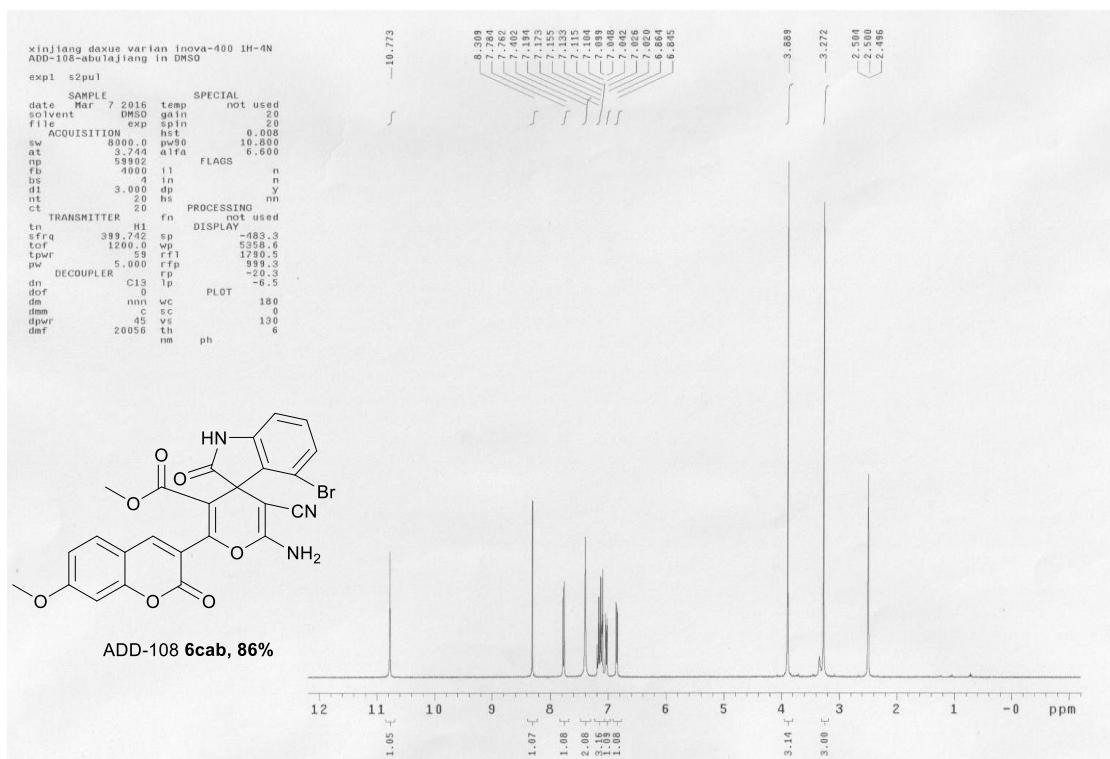
**<sup>13</sup>C NMR of compound 6caa (400 MHz, DMSO-d<sub>6</sub>)**



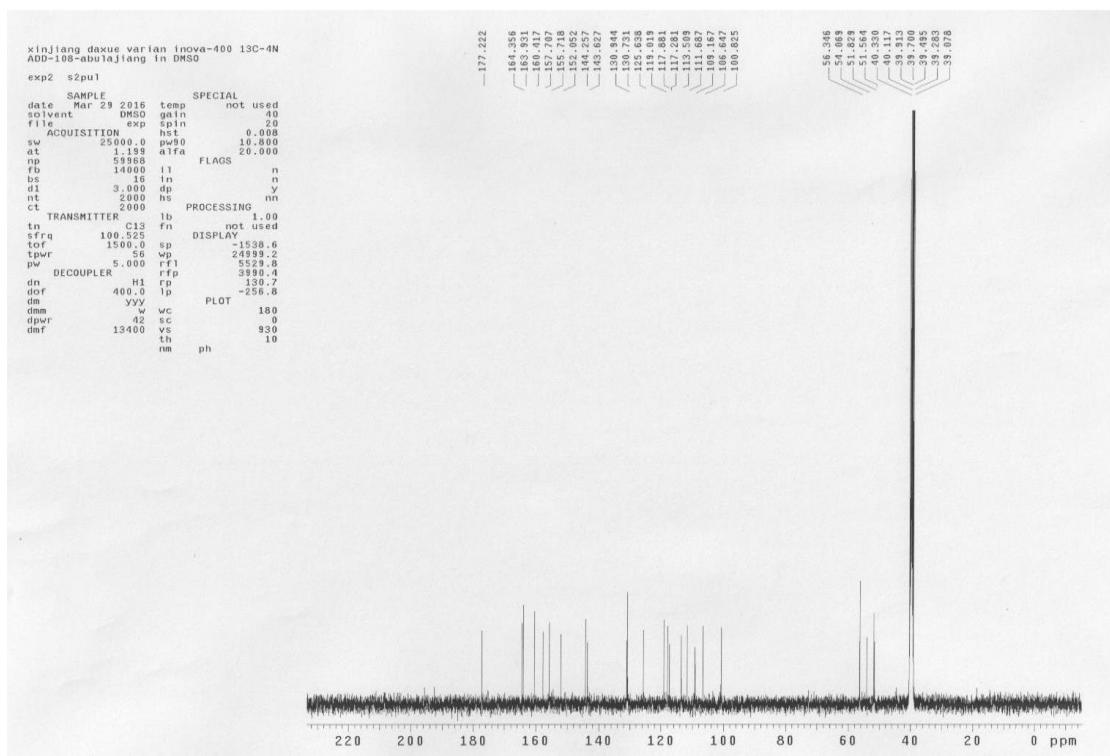
**IR spectrum of compound 6caa**



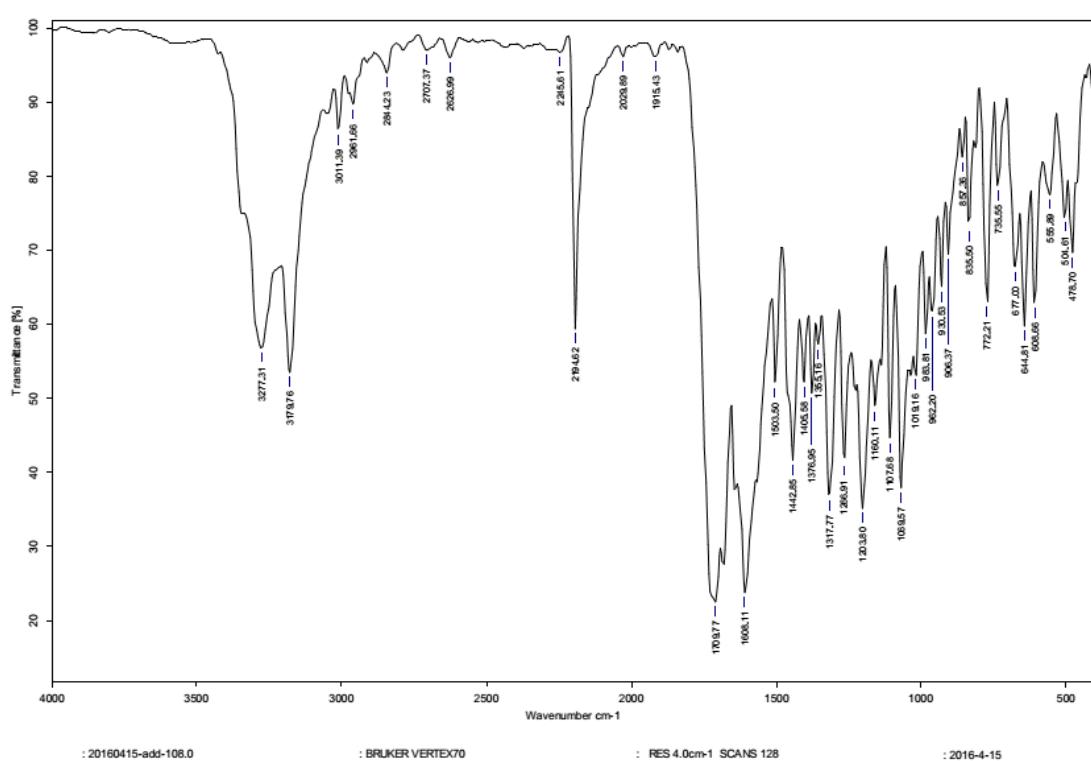
**<sup>1</sup>H NMR of compound 6cab (400 MHz, DMSO-d<sub>6</sub>)**



**<sup>13</sup>C NMR of compound 6cab (400 MHz, DMSO-d<sub>6</sub>)**



**IR spectrum of compound 6cab**



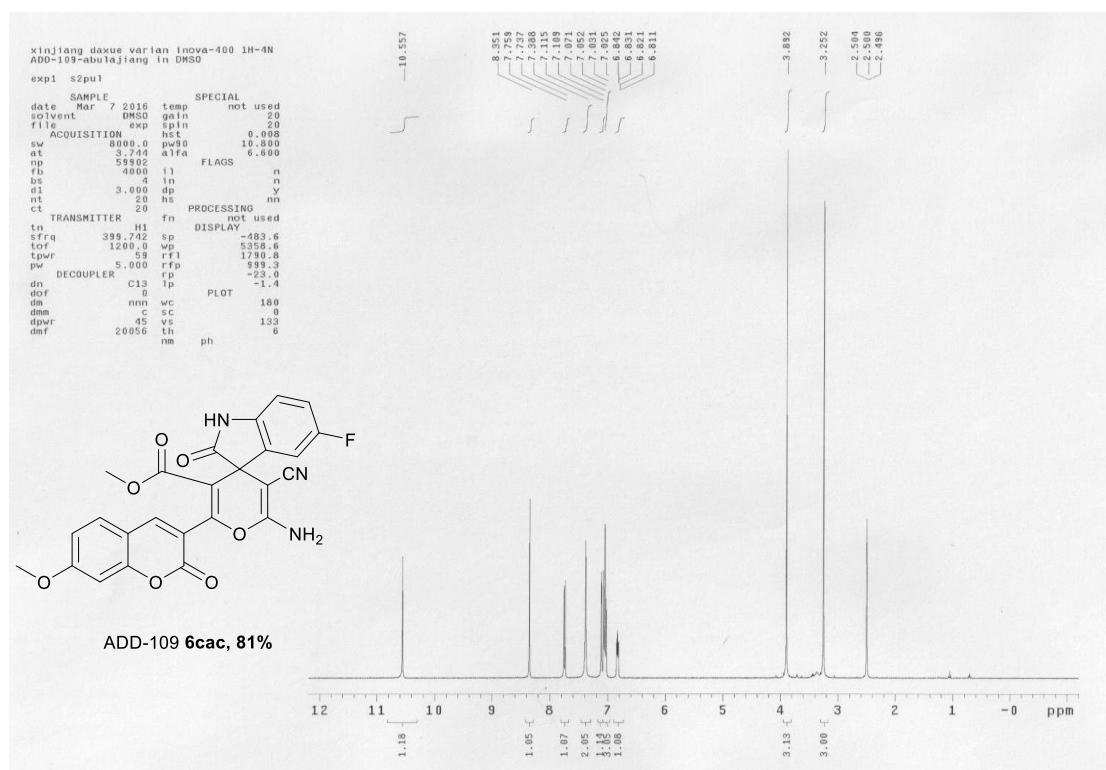
: 20160415-add-106.0

: BRUKER VERTEX70

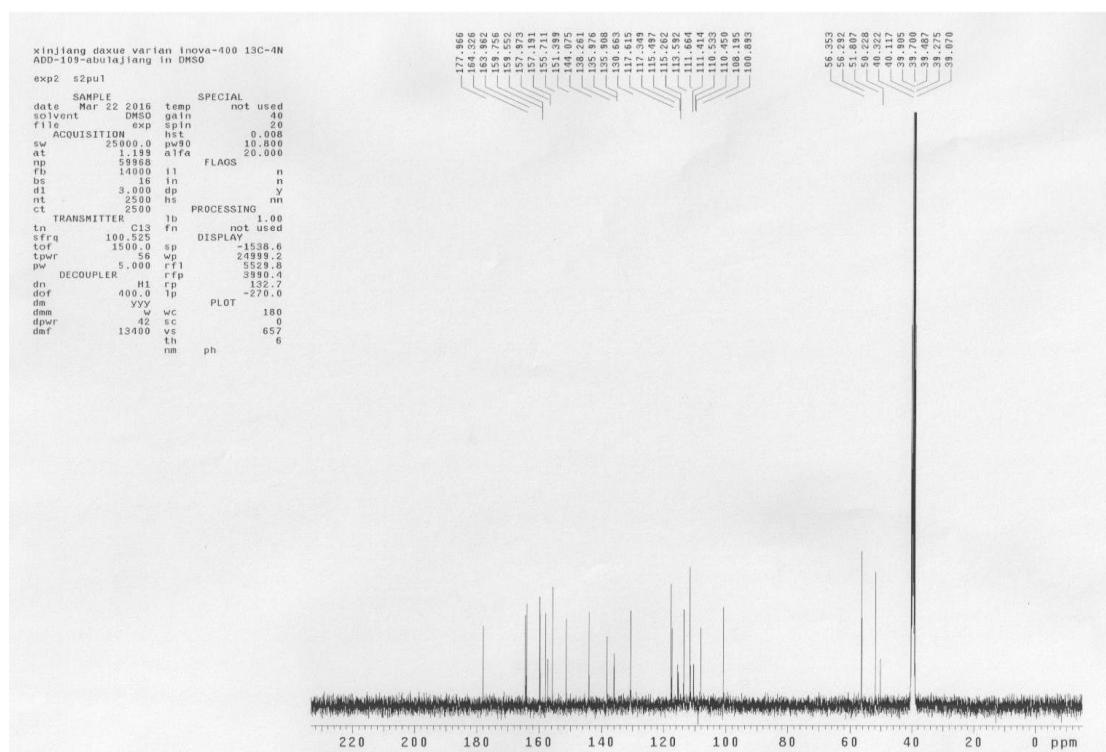
: RES 4.0cm<sup>-1</sup> SCANS 128

: 2016-4-15

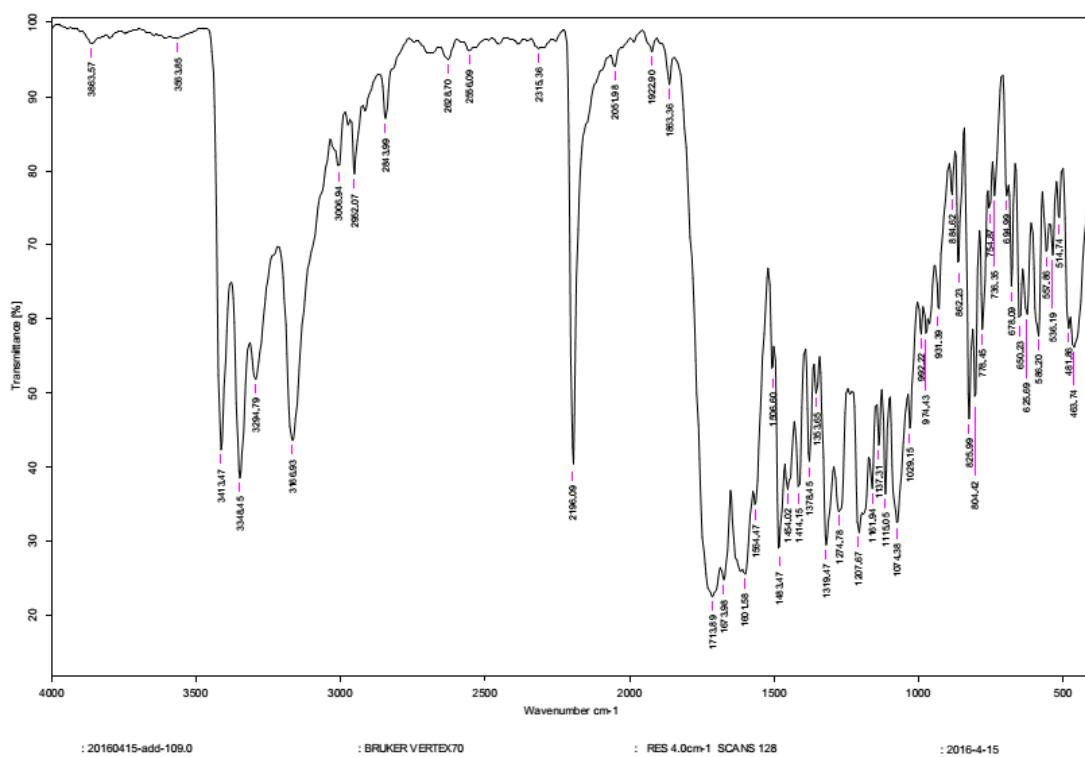
**<sup>1</sup>H NMR of compound 6cac (400 MHz, DMSO-d<sub>6</sub>)**



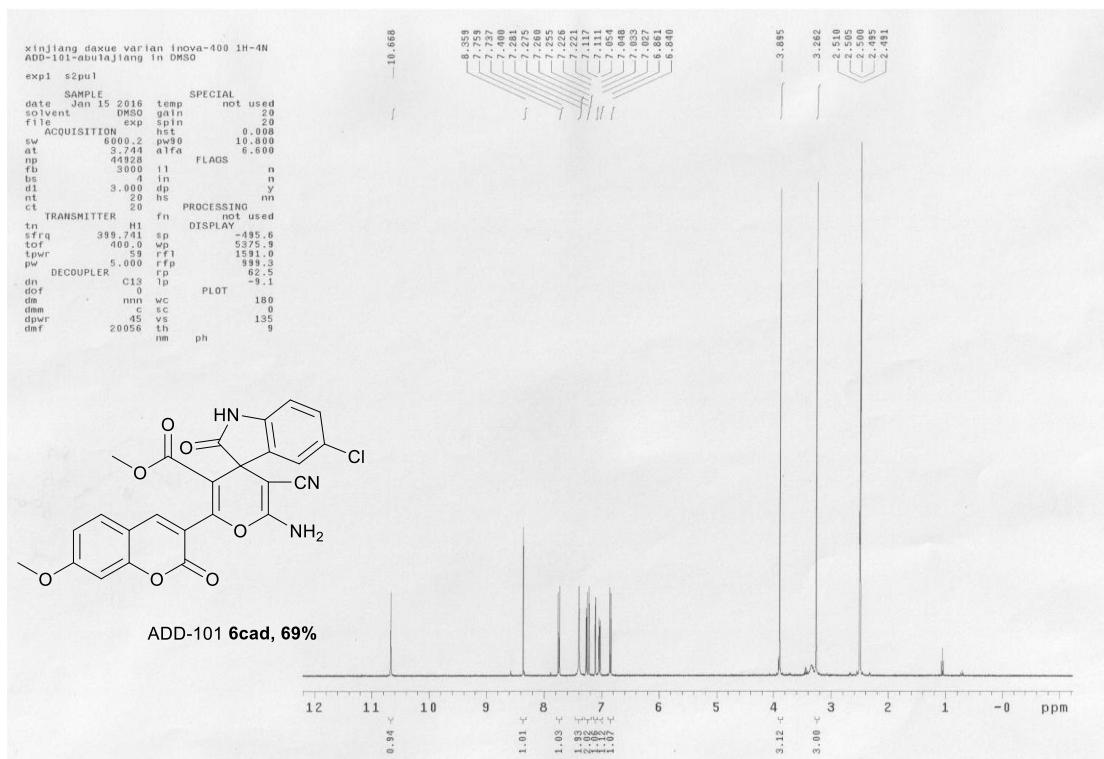
**<sup>13</sup>C NMR of compound 6cac (400 MHz, DMSO-d<sub>6</sub>)**



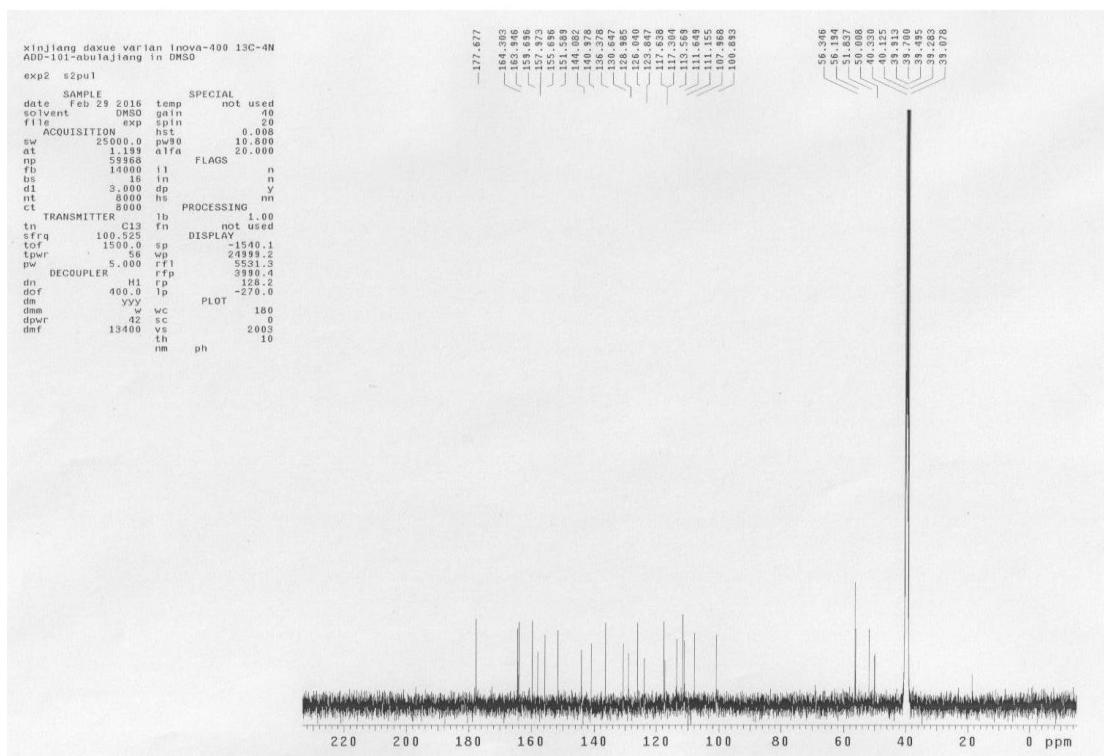
**IR spectrum of compound 6cac**



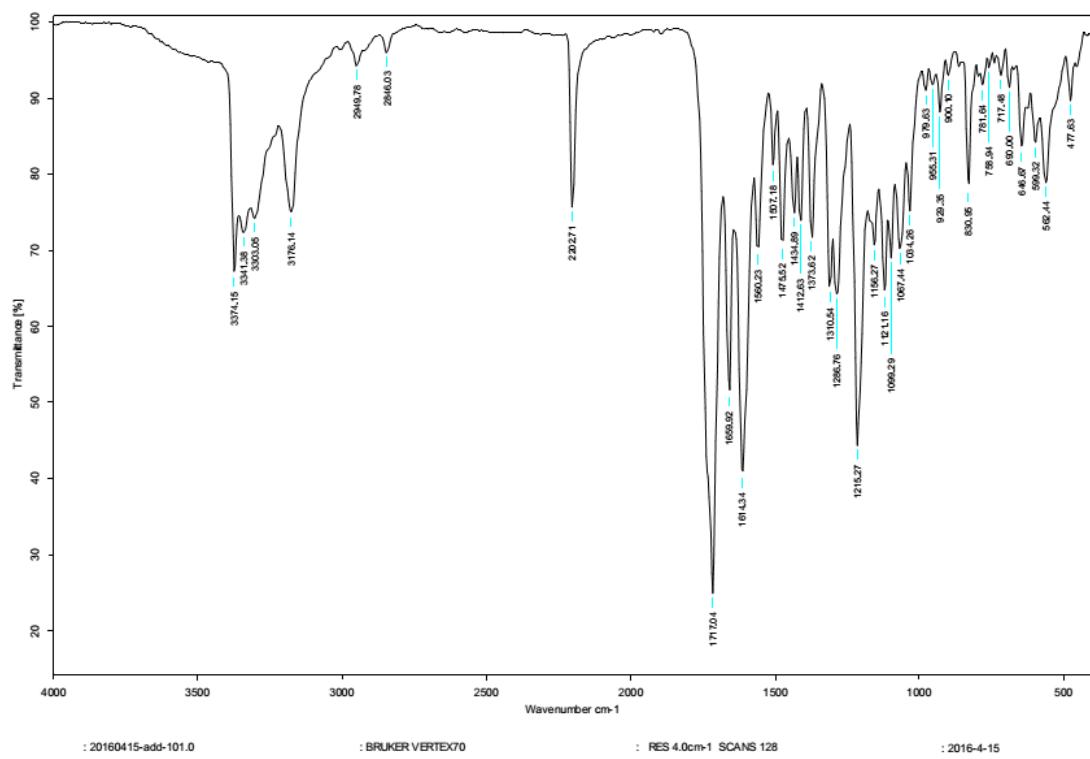
**<sup>1</sup>H NMR of compound 6cad (400 MHz, DMSO-d<sub>6</sub>)**



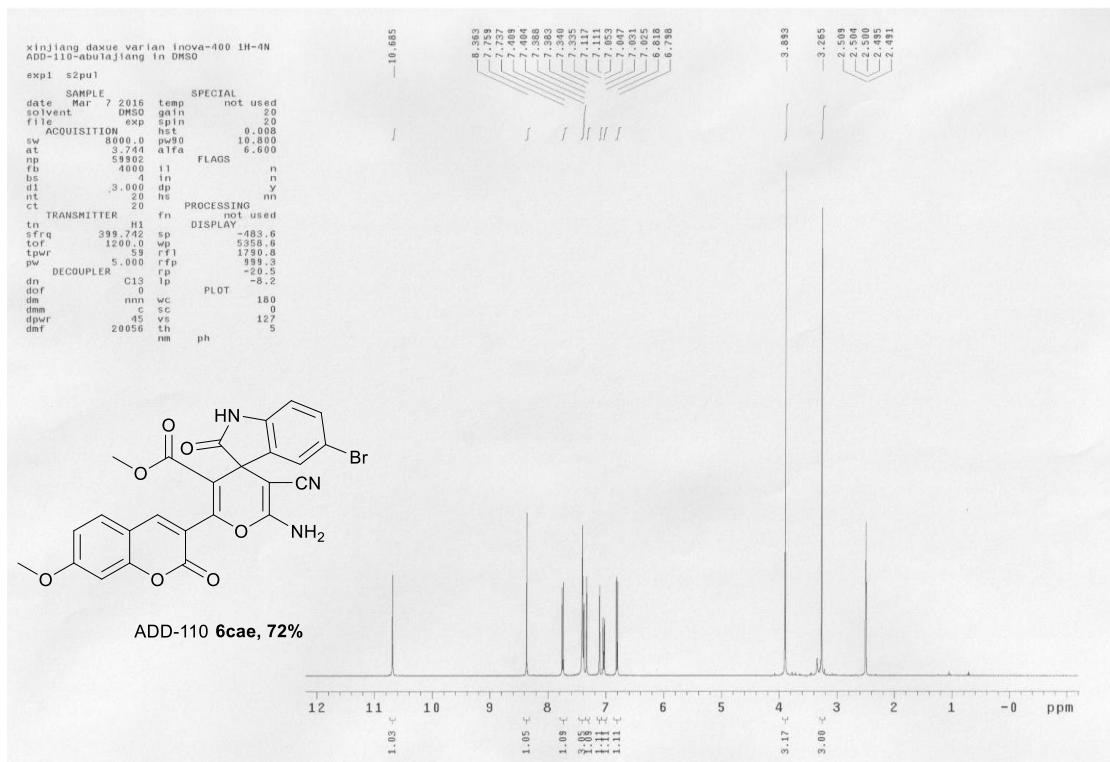
**<sup>13</sup>C NMR of compound 6cad (400 MHz, DMSO-d<sub>6</sub>)**



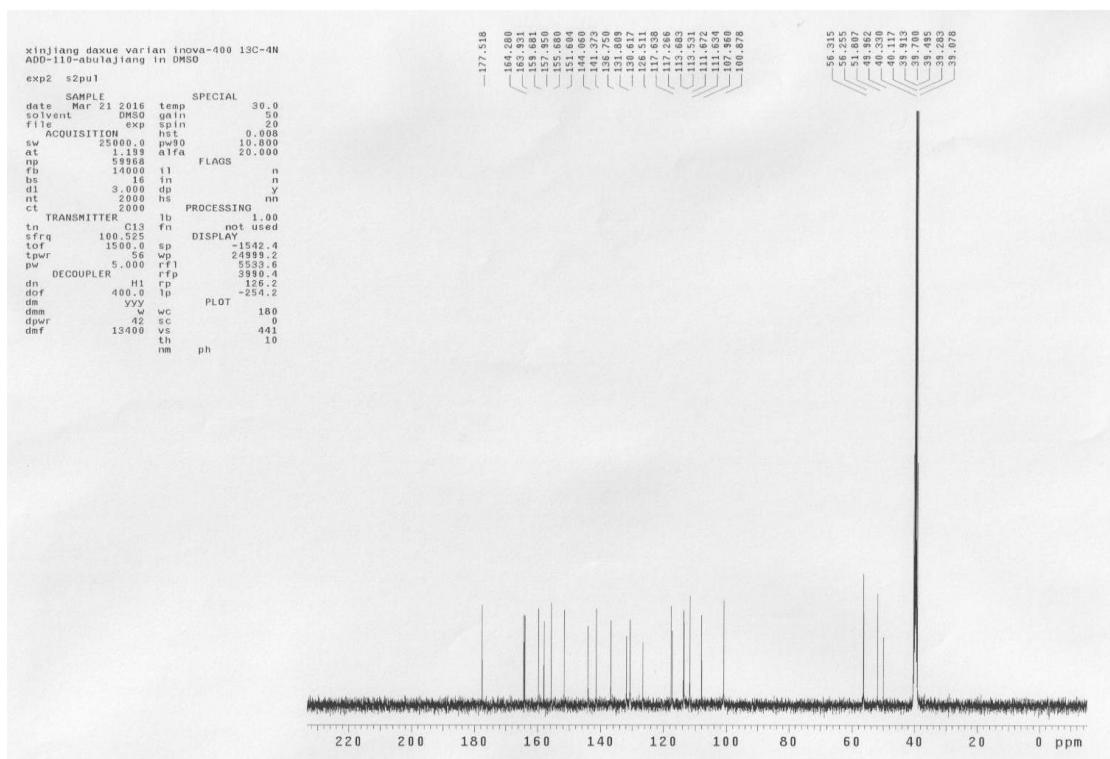
**IR spectrum of compound 6cad**



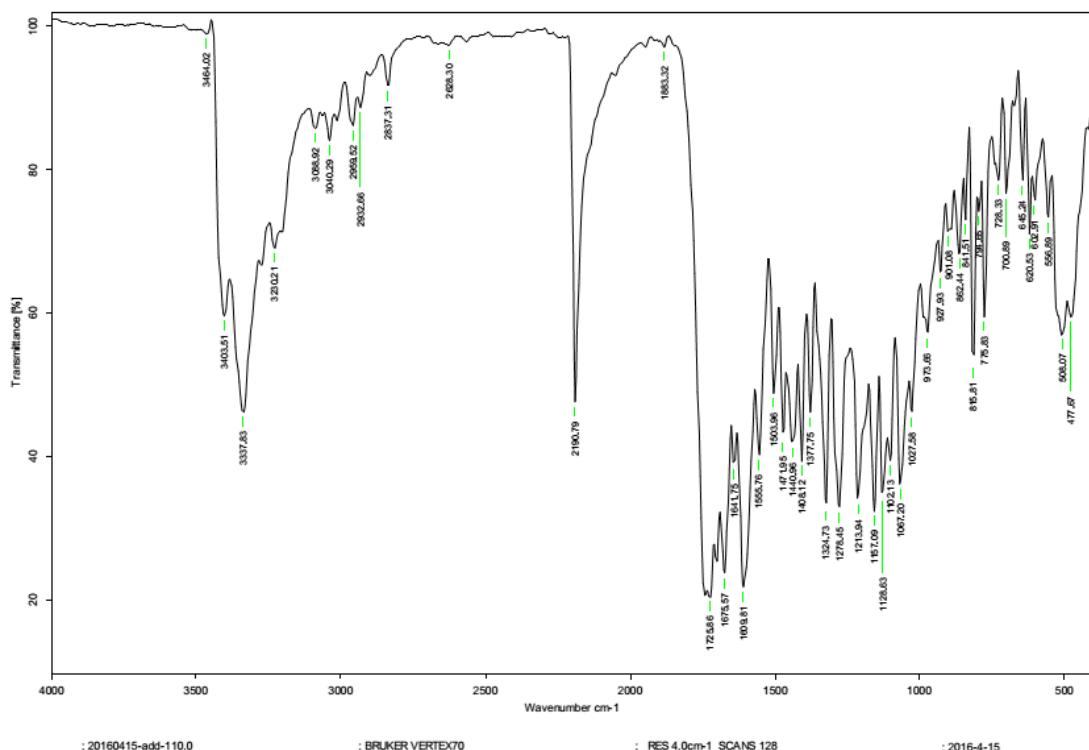
**<sup>1</sup>H NMR of compound 6cae (400 MHz, DMSO-d<sub>6</sub>)**



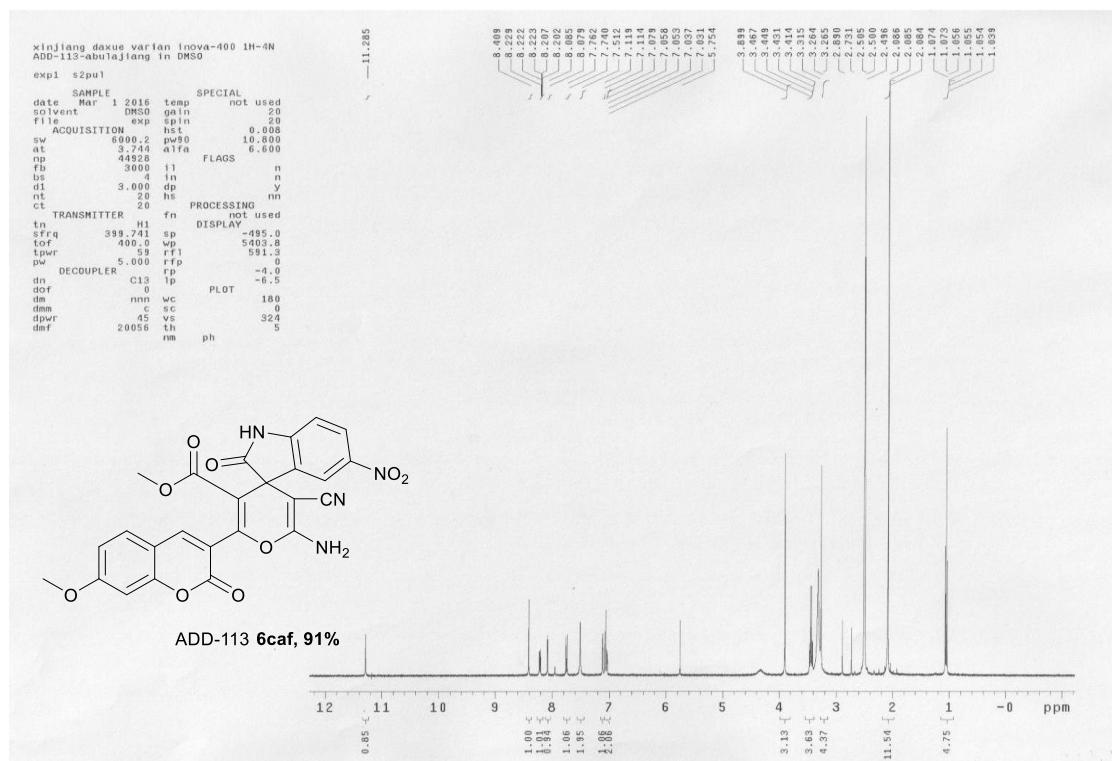
**<sup>13</sup>C NMR of compound 6cae (400 MHz, DMSO-d<sub>6</sub>)**



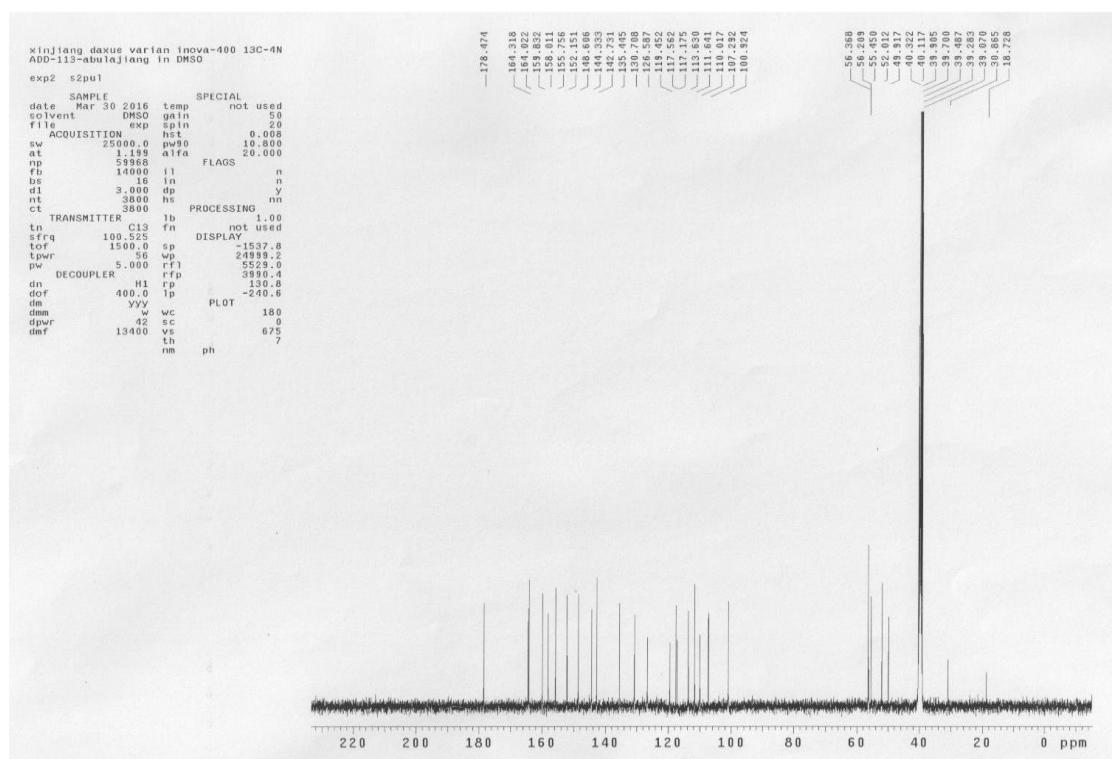
**IR spectrum of compound 6cae**



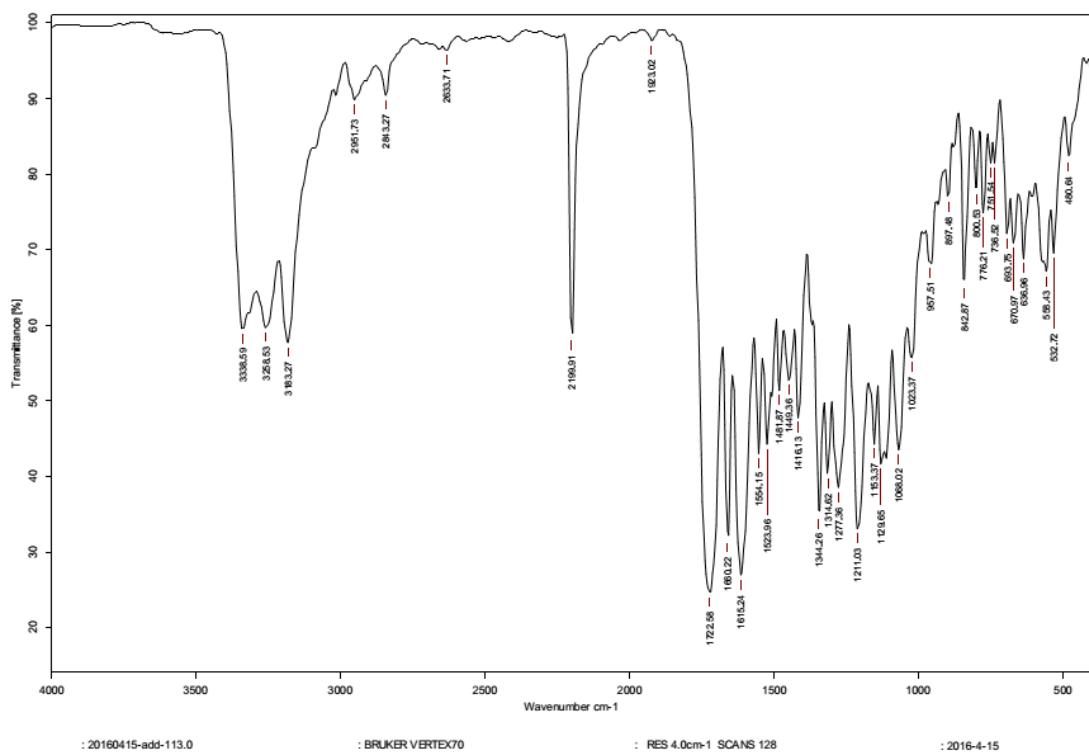
**<sup>1</sup>H NMR of compound 6caf (400 MHz, DMSO-d<sub>6</sub>)**



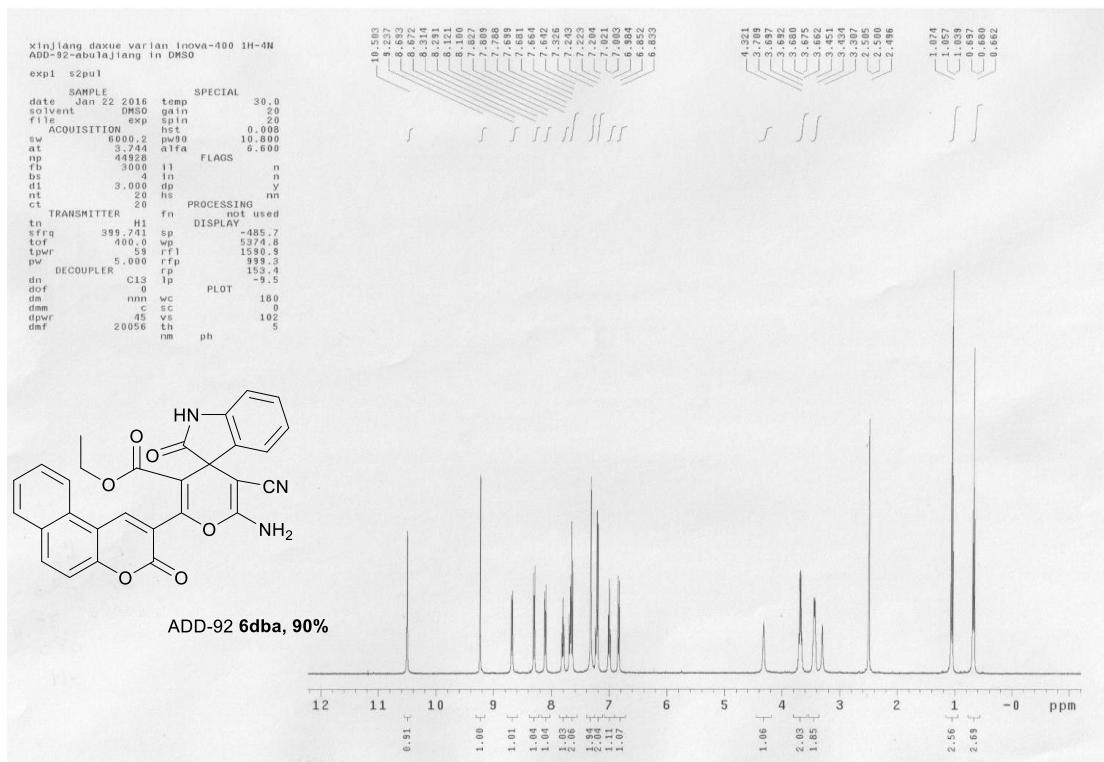
**<sup>13</sup>C NMR of compound 6caf (400 MHz, DMSO-*d*<sub>6</sub>)**



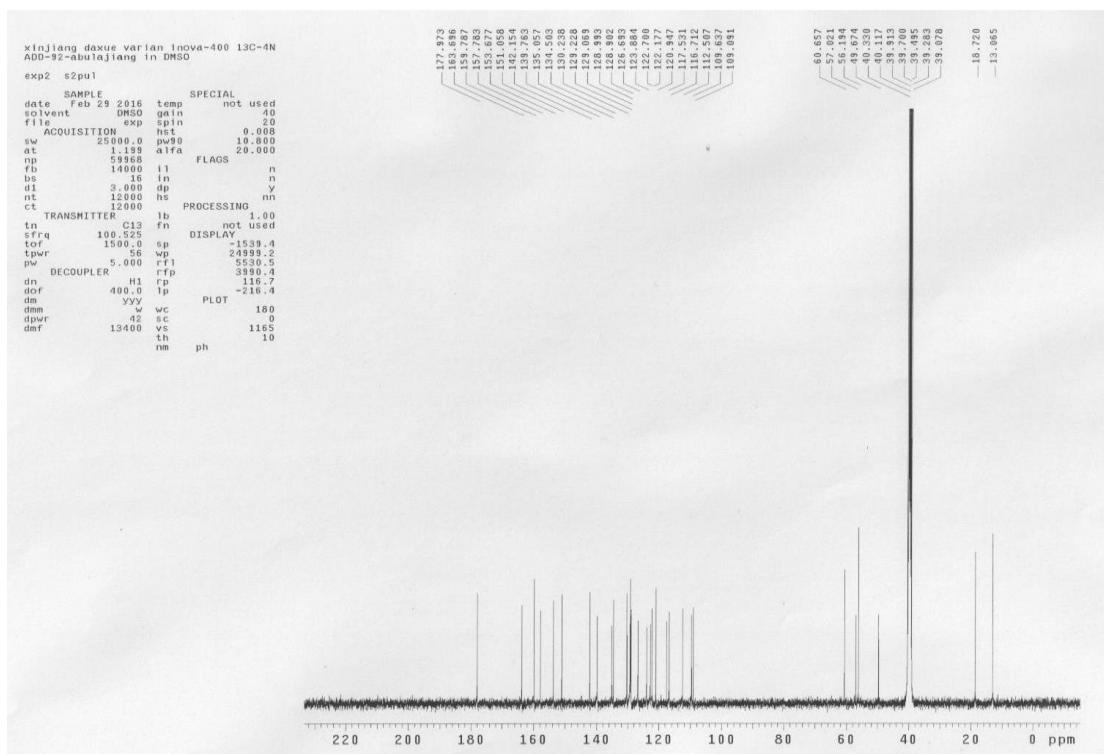
**IR spectrum of compound 6caf**



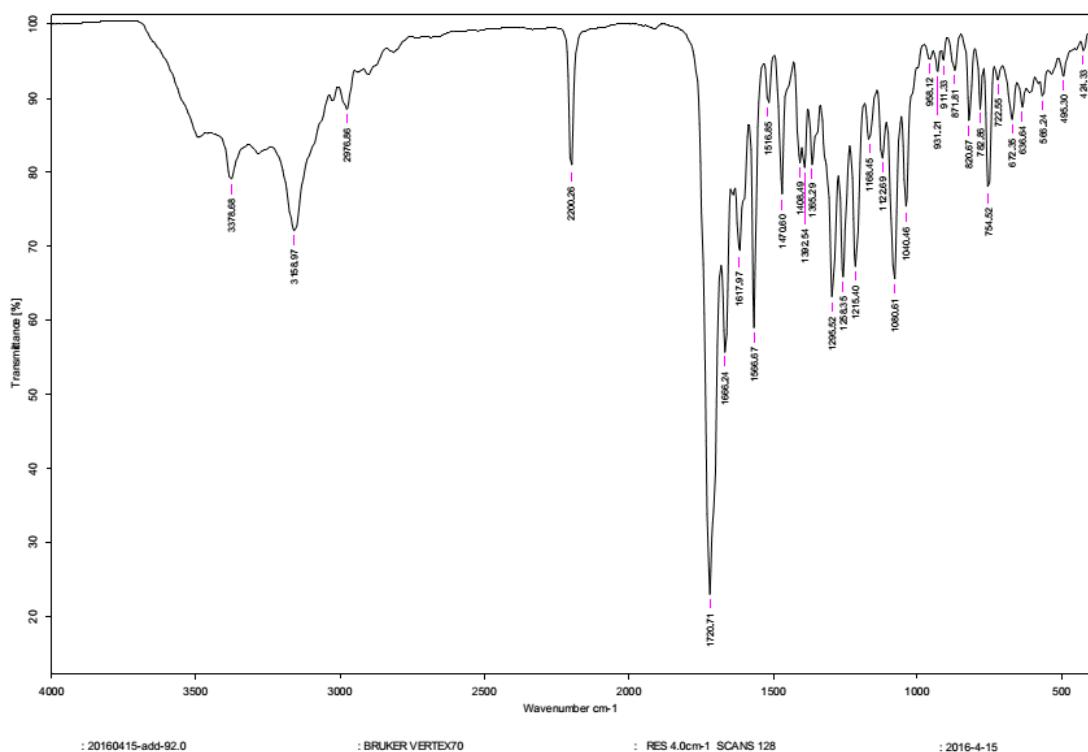
**<sup>1</sup>H NMR of compound 6dba (400 MHz, DMSO-d<sub>6</sub>)**



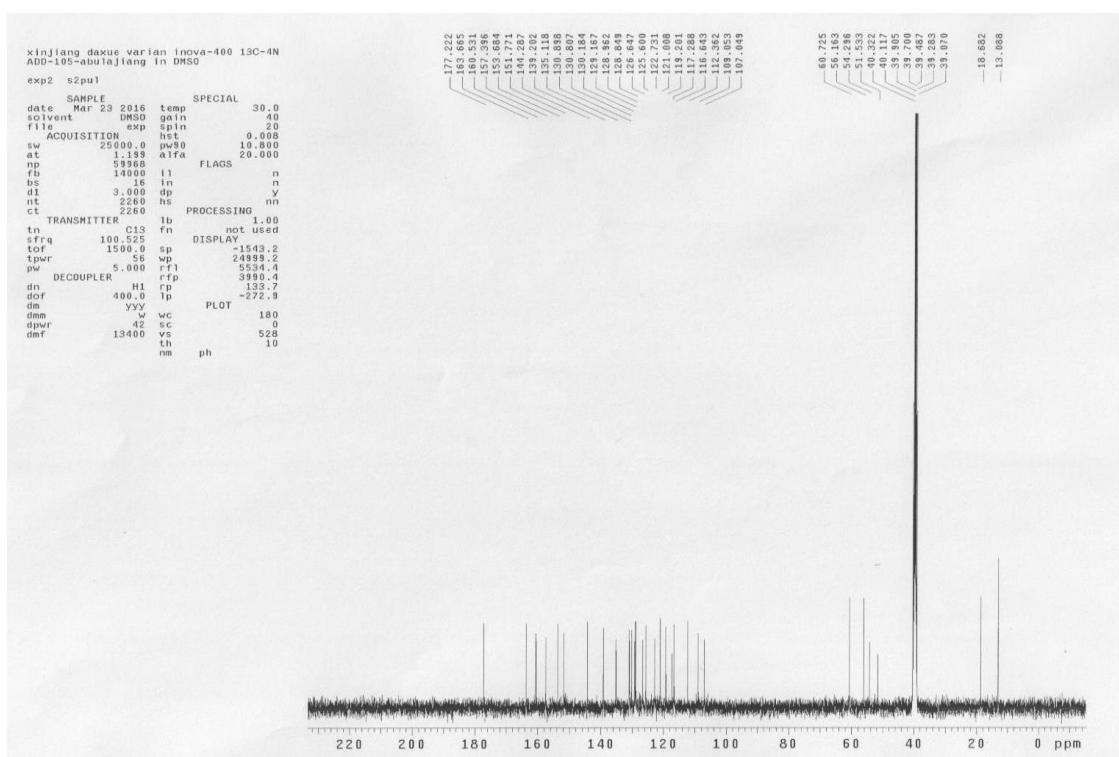
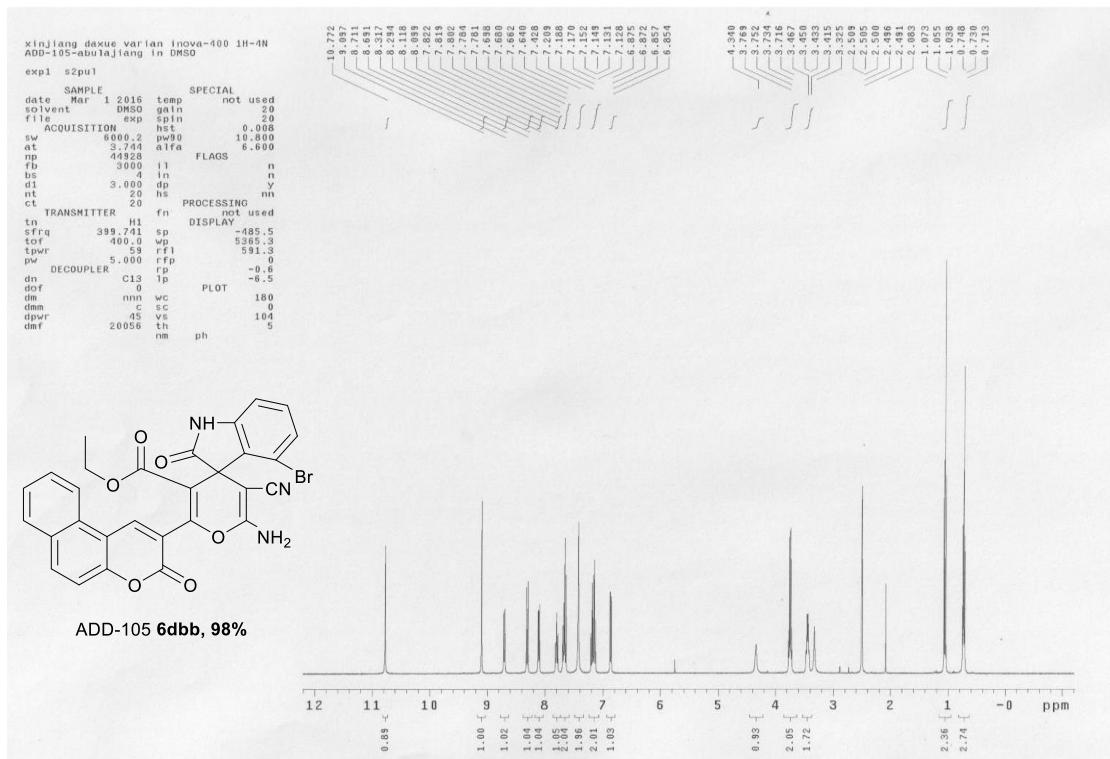
**<sup>13</sup>C NMR of compound 6dba(400 MHz, DMSO-d<sub>6</sub>)**



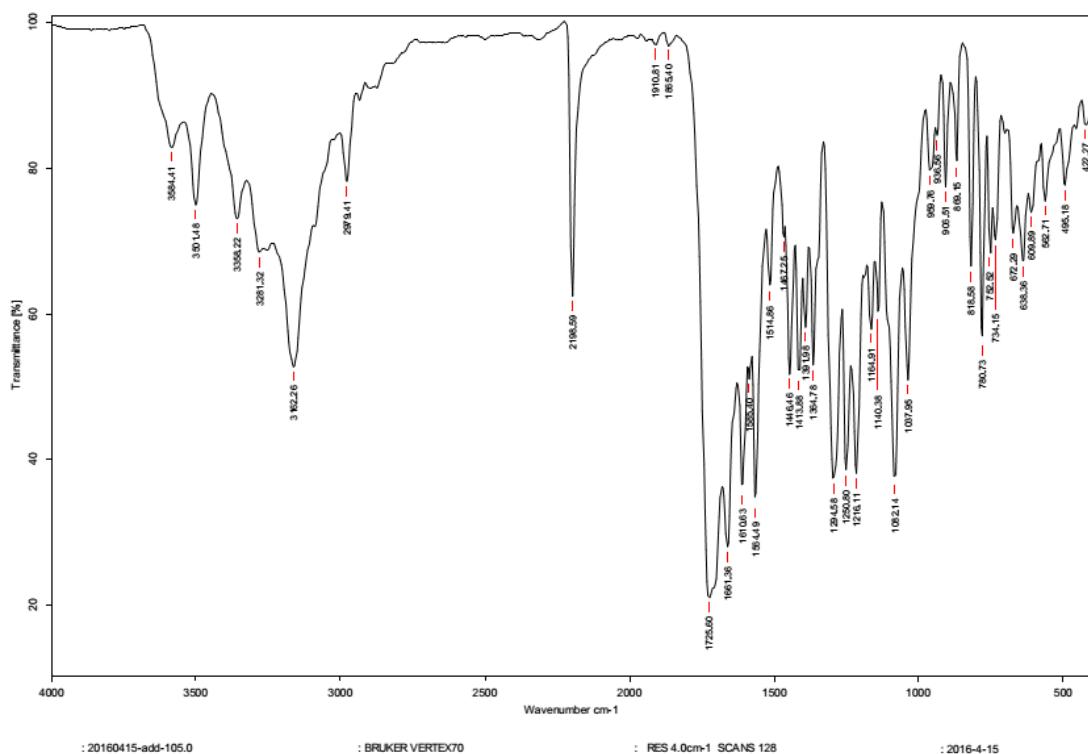
**IR spectrum of compound 6dba**



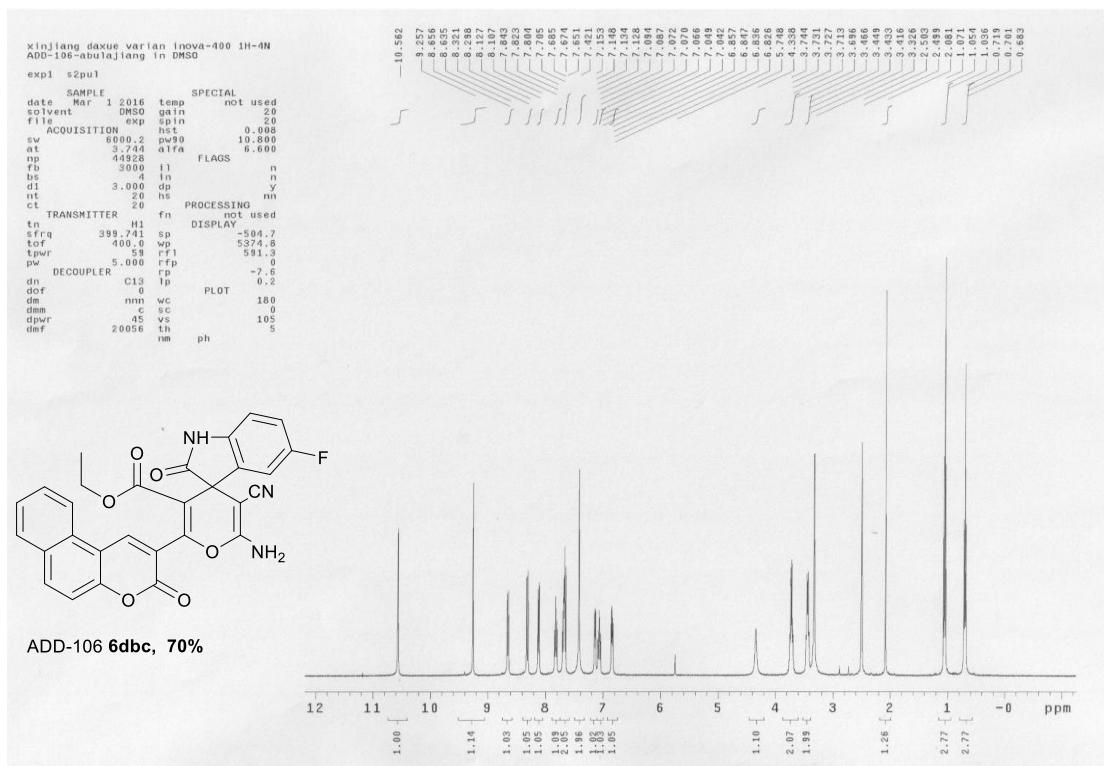
**<sup>1</sup>H NMR of compound 6dbb (400 MHz, DMSO-d<sub>6</sub>)**



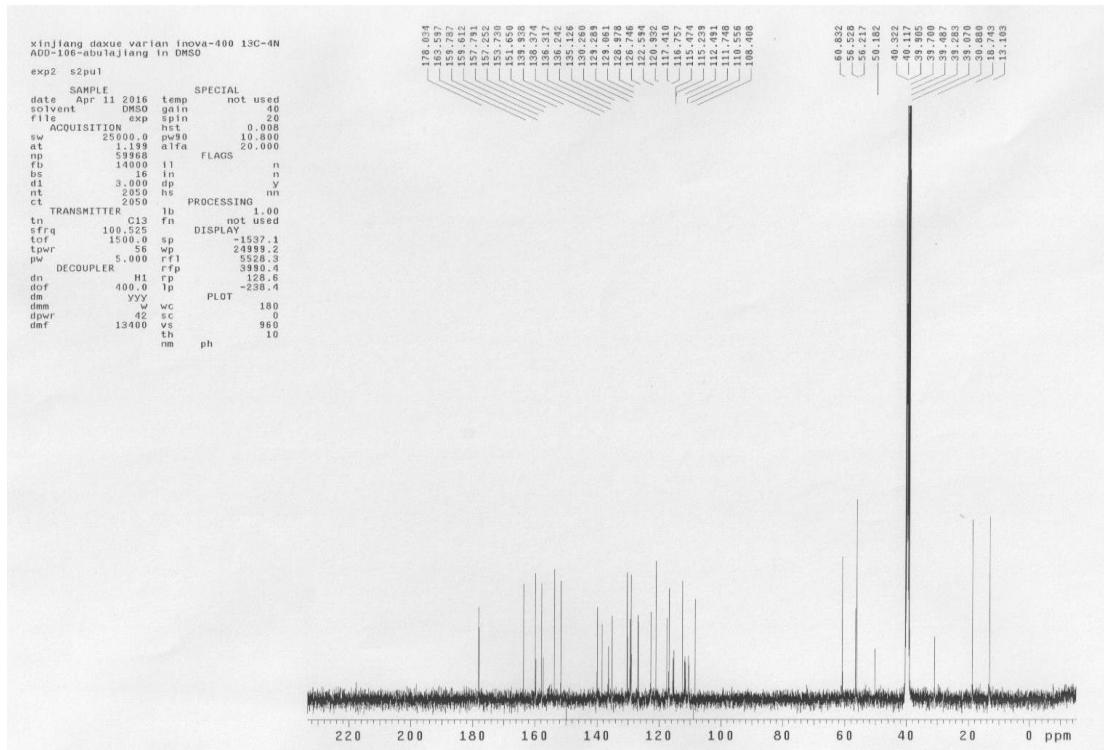
**IR spectrum of compound 6dbb**



**<sup>1</sup>H NMR of compound 6dbc (400 MHz, DMSO-*d*<sub>6</sub>)**



**<sup>13</sup>C NMR of compound 6dbc(400 MHz, DMSO-*d*<sub>6</sub>)**



**IR spectrum of compound 6dbc**

