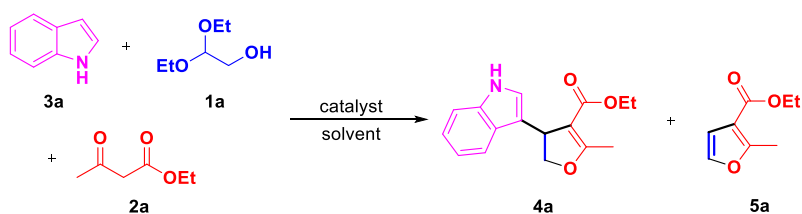


Utilization of bio-based glycolaldehyde aqueous solution in organic synthesis: application to the synthesis of 2,3-dihydrofurans

Jing Xu,^a Wenbo Huang,^a Rongxian Bai,^a Yves Queneau,^d Francois Jerome^{*c} and Yanlong Gu^{*a,b}

1. Optimization of the reaction parameters

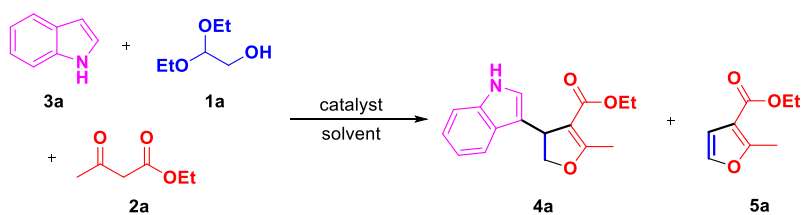
Table S1. Three-component reaction of **1a**, **2a** and **3a**.^a



Entry	Catalyst and specified conditions	Yield (%) ^b	
		4a	5a ^c
1	Sc(OTf) ₃ (5 mol%), CH ₃ NO ₂ , r.t., 1 h	81	0
2	Sc(OTf) ₃ (5 mol%), CH ₃ NO ₂ , r.t., 3 h	81	15
3	Sc(OTf) ₃ (5 mol%), CH ₃ NO ₂ , r.t., 5 h	81	21
4	Sc(OTf) ₃ (5 mol%), CH ₃ NO ₂ , 60 °C, 1 h	0	13
5	Ni(ClO ₄) ₂ ·6H ₂ O (20 mol%), CH ₃ CN, r.t., 6 h	0	0
6	Ni(ClO ₄) ₂ ·6H ₂ O (20 mol%), CH ₃ CN, 60 °C, 6 h	68	10
7	Ni(ClO ₄) ₂ ·6H ₂ O (20 mol%), CH ₃ CN, 80 °C, 1 h	23	0
8	Ni(ClO ₄) ₂ ·6H ₂ O (20 mol%), CH ₃ CN, 80 °C, 4 h	71	10
9	Ni(ClO ₄) ₂ ·6H ₂ O (20 mol%), CH ₃ CN, 80 °C, 6 h	79	12
10	Ni(ClO ₄) ₂ ·6H ₂ O (20 mol%), CH ₃ CN, 80 °C, 8 h	79	18

^a: **1a** (0.4 mmol), **2a** (0.4 mmol), **3a** (0.2 mmol), solvent (1.0 mL). ^b: Isolated yield, and calculated with respect to **3a**. ^c: Isolated yield, and calculated with respect to **1a**.

Table S2. Three-component reaction of **1a**, **2a** and **3a**.^a



Entry	Catalyst and specified conditions	Yield (%) ^b	
		4a	5a ^c
1	Sc(OTf) ₃ (0.5 mol%), CH ₃ NO ₂ , r.t., 3 h	21	0
2	Sc(OTf) ₃ (0.5 mol%), CH ₃ NO ₂ , r.t., 6 h	45	0
3	Sc(OTf) ₃ (0.5 mol%), CH ₃ NO ₂ , r.t., 9 h	69	0

4	Sc(OTf) ₃ (0.5 mol%), CH ₃ NO ₂ , r.t., 12 h	72	0
5	Ni(ClO ₄) ₂ ·6H ₂ O (5 mol%), CH ₃ CN, 80 °C, 6 h	61	8
6	Ni(ClO ₄) ₂ ·6H ₂ O (5 mol%), CH ₃ CN, 80 °C, 8 h	62	14
7	Ni(ClO ₄) ₂ ·6H ₂ O (5 mol%), CH ₃ CN, 80 °C, 10 h	62	21

^a: **1a** (0.4 mmol), **2a** (0.4 mmol), **3a** (0.2 mmol), solvent (1.0 mL). ^b: Isolated yield, and calculated with respect to **3a**. ^c: Isolated yield, and calculated with respect to **1a**.

2. FTIR spectra

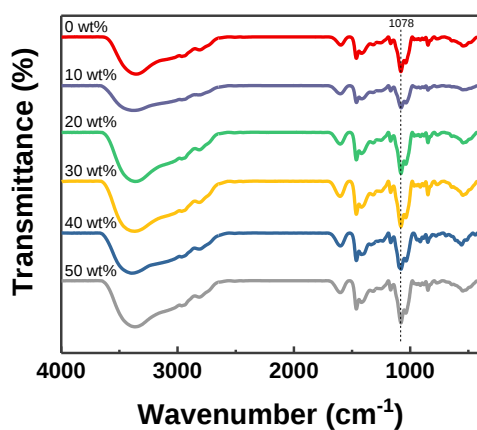


Figure S1. FTIR spectroscopy of FeCl₃·6H₂O/meglumine DES-H₂O at a loading below 50 wt%.

3. Effect of water amount

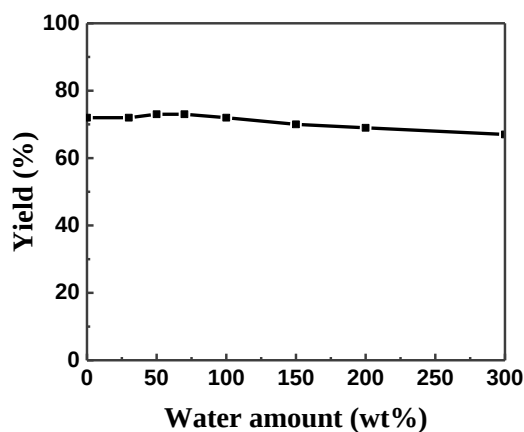


Figure S2. Effect of water amount in FeCl₃·6H₂O/meglumine DES on the model reaction. Reaction conditions: **1a** (0.4 mmol), **2a** (0.4 mmol), **3a** (0.2 mmol), method C: FeCl₃·6H₂O/meglumine-H₂O (15 mol%), 80 °C, 10 h.

4. DSC curve

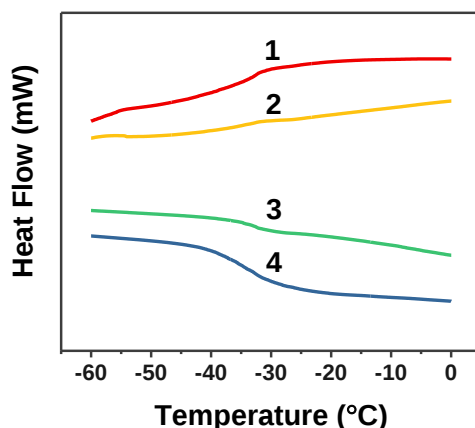
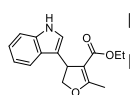
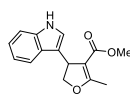


Figure S3. DSC of fresh (line 1: the first scan, line 4: the second scan) and recovered (line 2: the first scan, line 3: the second scan) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /meglumine DES

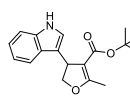
5. All spectroscopic data of obtained compounds



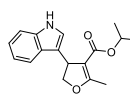
Ethyl 4-(1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4a): yellow liquid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 10.86 (s, 1H), 7.46 (d, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 1H), 7.12–7.03 (m, 2H), 6.98 (t, $J = 7.4$ Hz, 1H), 4.74 (t, $J = 9.6$ Hz, 1H), 4.56 (dd, $J_a = 9.8$ Hz, $J_b = 3.9$ Hz, 1H), 4.34 (dd, $J_a = 8.9$ Hz, $J_b = 4.6$ Hz, 1H), 3.94 (q, $J = 7.0$ Hz, 2H), 2.29 (s, 3H), 1.04 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 168.0, 165.4, 137.0, 126.0, 122.8, 121.3, 118.8, 118.7, 117.1, 112.0, 106.5, 77.6, 59.1, 39.5, 14.5, 14.4. IR (cm^{-1}) 3409, 3353, 3056, 2979, 2927, 1677, 1639, 1382, 1204, 987, 743. HRMS (ESI) $m/z = 294.1120$, calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3$ [$\text{M} + \text{Na}$] $^+$ 294.1101.



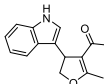
Methyl 4-(1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4b): yellow liquid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 10.85 (s, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 7.10–7.02 (m, 2H), 6.96 (t, $J = 7.4$ Hz, 1H), 4.72 (t, $J = 9.6$ Hz, 1H), 4.54 (dd, $J_a = 9.9$ Hz, $J_b = 3.7$ Hz, 1H), 4.29 (dd, $J_a = 8.9$ Hz, $J_b = 4.5$ Hz, 1H), 3.47 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 168.5, 165.8, 137.0, 126.0, 122.7, 121.3, 118.8, 118.7, 117.0, 112.0, 106.1, 77.7, 50.9, 39.4, 14.5. IR (cm^{-1}) 3358, 3056, 2950, 2926, 2852, 1962, 1640, 1437, 1384, 1342, 1323, 1198, 1087, 993, 744. HRMS (ESI) $m/z = 280.0936$, calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3$ [$\text{M} + \text{Na}$] $^+$ 280.0944.

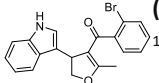


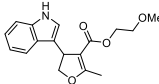
tert-Butyl 4-(1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4c): brown liquid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 10.83 (s, 1H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 7.11–7.03 (m, 2H), 6.94 (d, $J = 7.1$ Hz, 1H), 4.70 (t, $J = 9.6$ Hz, 1H), 4.49 (dd, $J_a = 9.8$ Hz, $J_b = 4.8$ Hz, 1H), 4.27 (dd, $J_a = 8.8$ Hz, $J_b = 5.2$ Hz, 1H), 2.24 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 167.1, 164.9, 137.0, 126.1, 122.8, 121.2, 118.8, 118.7, 117.1, 111.9, 107.6, 78.8, 77.2, 39.8, 28.3, 14.4. IR (cm^{-1}) 3358, 2975, 2929, 1690, 1455, 1385, 1367, 1333, 1251, 1209, 1172, 1136, 1084, 989, 743. HRMS (ESI) $m/z = 300.1572$, calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$ 300.1594.

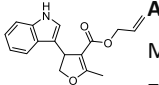


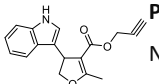
iso-Propyl 4-(1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4d): yellow liquid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 10.84 (s, 1H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 7.09–7.02 (m, 2H), 6.95 (t, $J = 7.3$ Hz, 1H), 4.80–4.68 (m, 2H), 4.53 (dd, $J_a = 9.9$ Hz, $J_b = 4.4$ Hz, 1H), 4.32 (dd, $J_a = 8.9$ Hz, $J_b = 4.9$ Hz, 1H), 2.26 (s, 3H), 1.10 (d, $J = 6.2$ Hz, 3H), 0.88 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 167.7, 164.9, 136.9, 126.1, 122.9, 121.2, 118.8, 118.7, 117.0, 112.0, 106.8, 77.4, 66.1, 39.5, 22.2, 21.9, 14.4. IR (cm^{-1}) 3411, 3354, 3056, 2979, 2932, 1677, 1641, 1458, 1383, 1313, 1204, 1109, 1083, 989, 743. HRMS (ESI) $m/z = 308.1249$, calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_3$ [$\text{M} + \text{Na}$] $^+$ 308.1257.

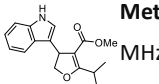
 **1-(4-(1H-Indol-3-yl)-2-methyl-4,5-dihydrofuran-3-yl) ethan-1-one (4e):** yellow liquid. ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm) 8.29 (s, 1H), 7.54 (d, $J = 7.9$ Hz, 1H), 7.37 (s, 1H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.11 (t, $J = 7.4$ Hz, 1H), 6.97 (d, $J = 2.0$ Hz, 1H), 4.79–4.71 (m, 1H), 4.66 (dd, $J_a = 10.0$ Hz, $J_b = 4.0$ Hz, 1H), 4.39 (dd, $J_a = 8.5$ Hz, $J_b = 4.5$ Hz, 1H), 2.38 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ (ppm) 195.8, 169.4, 136.8, 125.8, 122.3, 121.8, 119.6, 118.6, 118.1, 115.0, 111.4, 77.9, 40.1, 29.3, 15.1. IR (cm^{-1}) 3408, 3329, 3114, 2958, 2925, 1658, 1586, 1423, 1382, 1231, 1070, 804, 743. HRMS (ESI) $m/z = 264.1014$, calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2$ $[\text{M} + \text{Na}]^+$ 264.0995.

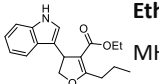
 **(4-(1H-Indol-3-yl)-2-methyl-4,5-dihydrofuran-3-yl)(2-bromophenyl)methanone (4f):** yellow liquid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 10.80 (s, 1H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 7.8$ Hz, 1H), 7.38 – 7.26 (m, 3H), 7.06 (t, $J = 7.5$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 4.83 (t, $J = 9.6$ Hz, 1H), 4.70 (dd, $J_a = 9.8$, $J_b = 4.6$ Hz, 1H), 4.33 (dd, $J_a = 8.8$, $J_b = 5.0$ Hz, 1H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 190.2, 171.4, 143.0, 137.0, 133.0, 131.1, 128.2, 126.1, 123.0, 121.4, 118.8, 118.7, 118.2, 116.7, 116.5, 112.0, 100.0, 78.3, 39.6, 14.9. IR (cm^{-1}) 3411, 3354, 3056, 2979, 2932, 1677, 1641, 1458, 1383, 1313, 1204, 1109, 1083, 989, 743. HRMS (ESI) $m/z = 404.0234$, calcd for $\text{C}_{20}\text{H}_{16}\text{BrNO}_2$ $[\text{M} + \text{Na}]^+$ 404.0257.

 **1-(4-(1H-Indol-3-yl)-2-methyl-4,5-dihydrofuran-3-yl)-3-methoxypropan-1-one (4g):** brown liquid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 10.87 (s, 1H), 7.45 (d, $J = 7.9$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 1H), 7.10 – 7.04 (m, 1H), 6.97 (t, $J = 7.4$ Hz, 1H), 4.75 (t, $J = 9.6$ Hz, 1H), 4.56 (dd, $J_a = 9.9$ Hz, $J_b = 4.0$ Hz, 1H), 4.34 (dd, $J_a = 8.9$ Hz, $J_b = 4.6$ Hz, 1H), 4.07 – 3.97 (m, 1H), 3.15 (s, 2H), 2.29 (s, 2H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 168.4, 165.3, 137.0, 126.0, 122.9, 121.3, 118.8, 118.7, 116.9, 112.0, 106.3, 77.6, 70.3, 62.4, 58.4, 39.5, 14.5. IR (cm^{-1}) 3360, 3056, 2928, 2895, 1695, 1639, 1455, 1385, 1202, 1124, 1083, 987, 744. HRMS (ESI) $m/z = 324.1209$, calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_4$ $[\text{M} + \text{Na}]^+$ 324.1206.

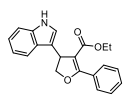
 **Allyl 4-(1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4h):** yellow liquid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 10.86 (s, 1H), 7.45 (d, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 1H), 7.12 – 7.03 (m, 2H), 6.97 (t, $J = 7.3$ Hz, 1H), 5.85 – 5.72 (m, 1H), 5.07 – 4.98 (m, 2H), 4.75 (t, $J = 9.6$ Hz, 1H), 4.59 (dd, $J_a = 9.9$ Hz, $J_b = 3.7$ Hz, 1H), 4.53 – 4.38 (m, 2H), 4.32 (dd, $J_a = 8.9$ Hz, $J_b = 4.6$ Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 168.8, 165.0, 137.1, 133.5, 126.0, 122.9, 121.3, 118.8, 118.7, 117.0, 116.9, 112.0, 106.1, 77.8, 63.6, 39.4, 14.5. IR (cm^{-1}) 3410, 3057, 2927, 1687, 1386, 1319, 1203, 1124, 1079, 990, 922, 743. HRMS (ESI) $m/z = 306.1088$, calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$ $[\text{M} + \text{Na}]^+$ 306.1101.

 **Prop-2-yn-1-yl 4-(1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4i):** yellow liquid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 10.88 (s, 1H), 7.45 (d, $J = 7.8$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 7.07 (d, $J = 7.4$ Hz, 2H), 6.97 (t, $J = 7.4$ Hz, 1H), 4.76 (t, $J = 9.6$ Hz, 1H), 4.63 (dd, $J_a = 15.8$ Hz, $J_b = 2.2$ Hz, 1H), 4.57 (dd, $J_a = 8.5$ Hz, $J_b = 3.3$ Hz, 2H), 4.34 (dd, $J_a = 8.9$ Hz, $J_b = 4.4$ Hz, 1H), 3.43 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 169.5, 164.5, 137.1, 125.9, 122.8, 121.4, 118.9, 118.7, 116.8, 112.0, 105.6, 79.4, 77.9, 77.4, 51.0, 39.3, 14.6. IR (cm^{-1}) 3410, 3287, 3056, 2927, 2126, 1697, 1636, 1387, 1319, 1203, 1120, 1076, 922, 744. HRMS (ESI) $m/z = 304.0899$, calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 304.0944.

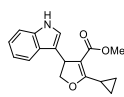
 **Methyl 4-(1H-indol-3-yl)-2-isopropyl-4,5-dihydrofuran-3-carboxylate (4j):** yellow liquid. ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm) 8.07 (s, 1H), 7.57 (d, $J = 7.9$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.09 (t, $J = 7.4$ Hz, 1H), 6.98 (s, 1H), 4.71 – 4.64 (m, 1H), 4.58 (dd, $J_a = 10.0$ Hz, $J_b = 3.9$ Hz, 1H), 4.50 (dd, $J_a = 8.5$ Hz, $J_b = 4.0$ Hz, 1H), 3.73 (m, 1H), 3.55 (s, 3H), 1.26 (d, $J = 6.9$ Hz, 2H), 1.20 (d, $J = 6.9$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ (ppm) 176.4, 166.3, 136.7, 125.8, 121.9, 121.6, 119.3, 118.9, 118.4, 111.3, 103.7, 77.2, 50.6, 39.6, 27.1, 19.7, 19.6. IR (cm^{-1}) 3411, 3055, 2968, 2931, 2874, 1678, 1628, 1460, 1436, 1343, 1195, 1117, 1067, 1034, 934, 742. HRMS (ESI) $m/z = 308.1237$, calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_3$ $[\text{M} + \text{Na}]^+$ 308.1257.

 **Ethyl 2-butyl-4-(1H-indol-3-yl)-4,5-dihydrofuran-3-carboxylate (4k):** brown liquid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 10.85 (s, 1H), 7.47 (d, $J = 7.8$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.06 (d,

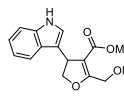
$J = 8.4$ Hz, 2H), 6.96 (t, $J = 7.4$ Hz, 1H), 4.72 (t, $J = 9.6$ Hz, 1H), 4.55 (dd, $J_a = 10.0$ Hz, $J_b = 4.2$ Hz, 1H), 4.35 (dd, $J_a = 8.8$ Hz, $J_b = 4.5$ Hz, 1H), 3.94 (m, 2H), 2.68 (dq, $J_a = 13.7$ Hz, $J_b = 7.3$ Hz, 2H), 1.64 (h, $J = 7.0$ Hz, 2H), 1.04 (t, $J = 7.1$ Hz, 3H), 0.97 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ (ppm) 171.2, 137.0, 126.0, 122.8, 121.3, 118.7, 118.7, 117.1, 112.0, 106.4, 77.4, 59.1, 39.5, 39.5, 29.7, 20.4, 14.5, 14.18. IR (cm^{-1}) 3410, 2964, 2933, 1678, 1633, 1458, 1374, 1324, 1193, 1101, 1036, 1008, 743. HRMS (ESI) $m/z = 300.1556$, calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$ 300.1594.



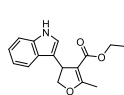
Ethyl 4-(1H-indol-3-yl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (4l): yellow liquid. ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm) 8.07 (s, 1H), 7.85 (d, $J = 6.5$ Hz, 2H), 7.66 (d, $J = 7.9$ Hz, 1H), 7.43 (t, $J = 7.4$ Hz, 3H), 7.36 (d, $J = 8.1$ Hz, 1H), 7.19 (t, $J = 7.3$ Hz, 1H), 7.12 – 7.07 (m, 2H), 4.91 – 4.80 (m, 2H), 4.63 (dd, $J_a = 7.4$ Hz, $J_b = 3.1$ Hz, 1H), 4.03 – 3.94 (m, 2H), 1.01 (t, $J = 7.1$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ (ppm) 165.4, 165.1, 136.6, 130.4, 130.2, 129.5, 127.7, 125.9, 121.9, 121.9, 119.5, 119.0, 118.2, 111.3, 106.8, 76.8, 59.5, 41.4, 13.9. IR (cm^{-1}) 3408, 3366, 3058, 2927, 2855, 1682, 1623, 1454, 1330, 1197, 1092, 743. HRMS (ESI) $m/z = 356.1276$, calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_3$ [$\text{M} + \text{Na}$] $^+$ 356.1257.



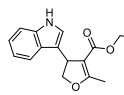
Methyl 2-cyclopropyl-4-(1H-indol-3-yl)-4,5-dihydrofuran-3-carboxylate (4m): white solid, mp 80–81 °C. ^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ (ppm) 10.85 (s, 1H), 7.42 (d, $J = 7.9$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 7.06 (d, $J = 7.5$ Hz, 2H), 6.97 (t, $J = 7.4$ Hz, 1H), 4.64 (t, $J = 9.3$ Hz, 1H), 4.54 (dd, $J_a = 9.9$ Hz, $J_b = 3.8$ Hz, 1H), 4.26 (dd, $J_a = 8.6$ Hz, $J_b = 3.9$ Hz, 1H), 3.50 (s, 3H), 2.81 – 2.72 (m, 1H), 1.12 – 0.91 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ (ppm) 172.5, 167.1, 136.7, 125.9, 121.8, 121.8, 119.3, 118.9, 118.2, 111.4, 105.2, 77.2, 50.7, 39.9, 9.4, 8.0, 7.33. IR (cm^{-1}) 3049, 2949, 2928, 2854, 1690, 1622, 1437, 1384, 1197, 1119, 1060, 1041, 743. HRMS (ESI) $m/z = 284.1252$, calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$ 284.1281.



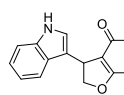
Methyl 4-(1H-indol-3-yl)-2-(methoxymethyl)-4,5-dihydrofuran-3-carboxylate (4n): yellow liquid. ^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ (ppm) 10.89 (s, 1H), 7.49 (d, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.11 – 7.05 (m, 2H), 6.97 (t, $J = 7.4$ Hz, 1H), 4.79 (t, $J = 9.6$ Hz, 1H), 4.62 (dd, $J_a = 10.1$ Hz, $J_b = 4.2$ Hz, 1H), 4.55 (d, $J = 13.2$ Hz, 1H), 4.47 (d, $J = 13.2$ Hz, 1H), 4.38 (dd, $J_a = 8.7$ Hz, $J_b = 4.4$ Hz, 1H), 3.50 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ (ppm) 166.3, 165.2, 137.0, 125.9, 122.9, 121.4, 118.9, 118.7, 116.4, 112.1, 108.9, 78.0, 65.4, 58.6, 51.2, 39.4. HRMS (ESI) $m/z = 310.1046$, calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_4$ [$\text{M} + \text{Na}$] $^+$ 310.1050.



2-(Thiophen-3-yl) ethyl 4-(1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4o): brown liquid. ^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ (ppm) 10.84 (s, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 7.28 (d, $J = 5.1$ Hz, 1H), 7.06 (t, $J = 7.5$ Hz, 1H), 7.01 (s, 1H), 6.96 (t, $J = 7.2$ Hz, 1H), 6.88 – 6.83 (m, 1H), 6.72 (s, 1H), 4.73 (t, $J = 9.6$ Hz, 1H), 4.55 (dd, $J_a = 9.8$ Hz, $J_b = 3.8$ Hz, 1H), 4.31 (dd, $J_a = 8.9$ Hz, $J_b = 4.6$ Hz, 1H), 4.10 (tp, $J_a = 11.1$ Hz, $J_b = 6.5$ Hz, $J_c = 5.5$ Hz, 2H), 3.02 – 2.90 (m, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ (ppm) 168.6, 165.2, 140.5, 137.1, 127.3, 126.0, 124.6, 122.9, 121.3, 118.8, 118.7, 117.0, 112.0, 106.2, 77.7, 63.8, 39.4, 29.1, 14.5. IR (cm^{-1}) 3411, 3057, 2954, 2925, 1682, 1638, 1390, 1334, 1320, 1204, 1122, 1086, 991, 744, 700. HRMS (ESI) $m/z = 376.0968$, calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_3\text{S}$ [$\text{M} + \text{Na}$] $^+$ 376.0978.

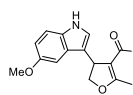


Furan-2-ylmethyl 4-(1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4p): yellow liquid. ^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ (ppm) 10.84 (s, 1H), 7.61 (s, 1H), 7.41 (d, $J = 7.9$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 7.06 (t, $J = 7.4$ Hz, 1H), 6.99 (s, 1H), 6.94 (t, $J = 7.4$ Hz, 1H), 6.39 (s, 1H), 6.33 (s, 1H), 5.02 – 4.88 (m, 2H), 4.73 (t, $J = 9.6$ Hz, 1H), 4.53 (dd, $J_a = 9.8$ Hz, $J_b = 3.8$ Hz, 1H), 4.32 (dd, $J_a = 8.9$ Hz, $J_b = 4.5$ Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ (ppm) 168.9, 164.8, 150.2, 143.7, 137.0, 125.9, 122.8, 121.3, 118.8, 118.7, 116.8, 112.0, 111.0, 110.3, 106.0, 77.7, 57.1, 39.4, 14.6. IR (cm^{-1}) 3411, 3121, 3056, 2927, 1691, 1638, 1456, 1386, 1327, 1206, 1075, 990, 743. HRMS (ESI) $m/z = 346.1034$, calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_4$ [$\text{M} + \text{Na}$] $^+$ 346.1050.



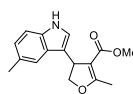
2-(Methacryloyloxy)ethyl 4-(1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4q): yellow liquid. ^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ (ppm) 10.83 (s, 1H), 7.42 (d, $J = 7.9$ Hz,

1H), 7.33 (d, $J = 8.1$ Hz, 1H), 7.09 – 6.99 (m, 2H), 6.94 (t, $J = 7.5$ Hz, 1H), 5.89 (s, 1H), 5.66 – 5.54 (m, 1H), 4.74 (t, $J = 9.6$ Hz, 1H), 4.54 (dd, $J_a = 10.7$, $J_b = 4.5$ Hz, 1H), 4.32 (dd, $J_a = 9.0$, $J_b = 4.7$ Hz, 1H), 4.16 (s, 4H), 2.26 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ (ppm) 168.7, 166.8, 165.1, 137.1, 135.9, 126.4, 126.0, 122.8, 121.3, 118.8, 118.7, 116.9, 112.0, 106.1, 77.8, 62.9, 61.2, 39.5, 18.3, 14.5. IR (cm^{-1}) 3411, 3354, 3056, 2979, 2932, 1677, 1641, 1458, 1383, 1313, 1204, 1109, 1083, 989, 743. HRMS (ESI) $m/z = 378.1296$, calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_3$ $[\text{M} + \text{Na}]^+$ 378.1312.



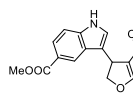
Methyl 4-(5-methoxy-1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4r): brown liquid.

^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm) 8.10 (s, 1H), 7.19 (d, $J = 8.8$ Hz, 1H), 6.99 (s, 1H), 6.92 (s, 1H), 6.83 (dd, $J_a = 8.8$ Hz, $J_b = 2.1$ Hz, 1H), 4.70 (t, $J = 9.4$ Hz, 1H), 4.55 (dd, $J_a = 10.0$ Hz, $J_b = 3.4$ Hz, 1H), 4.46 (dd, $J_a = 8.7$ Hz, $J_b = 4.2$ Hz, 1H), 3.84 (s, 2H), 3.57 (s, 2H), 2.33 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ (ppm) 168.7, 166.5, 153.8, 131.9, 126.2, 122.6, 117.8, 112.0, 111.9, 106.0, 100.9, 77.4, 55.8, 50.8, 39.6, 14.3. IR (cm^{-1}) 3407, 2991, 2949, 2900, 2831, 1682, 1639, 1485, 1439, 1384, 1345, 1323, 1210, 1127, 1085, 993, 801, 433. HRMS (ESI) $m/z = 310.1042$, calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_4$ $[\text{M} + \text{Na}]^+$ 310.1050.



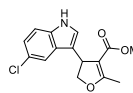
Methyl 2-methyl-4-(5-methyl-1H-indol-3-yl)-4,5-dihydrofuran-3-carboxylate (4s): yellow liquid.

^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ (ppm) 10.71 (s, 1H), 7.27 – 7.17 (m, 2H), 6.97 (s, 1H), 6.89 (d, $J = 8.2$ Hz, 1H), 4.71 (t, $J = 9.5$ Hz, 1H), 4.50 (dd, $J_a = 9.8$ Hz, $J_b = 3.6$ Hz, 1H), 4.27 (dd, $J_a = 8.9$ Hz, $J_b = 4.4$ Hz, 1H), 3.47 (s, 3H), 2.36 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ (ppm) 168.5, 165.9, 135.5, 127.2, 126.3, 122.9, 122.7, 118.3, 116.7, 111.8, 106.1, 77.8, 50.9, 39.4, 21.8, 14.5. IR (cm^{-1}) 3407, 2949, 1682, 1640, 1437, 1384, 1344, 1324, 1198, 1127, 1087, 993, 794. HRMS (ESI) $m/z = 294.1096$, calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3$ $[\text{M} + \text{K}]^+$ 294.1101.



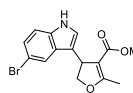
Ethyl 3-(4-(methoxycarbonyl)-5-methyl-2,3-dihydrofuran-3-yl)-1H-indole-5-carboxylate (4t): yellow liquid.

^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm) 8.39 (s, 1H), 8.33 (s, 1H), 7.88 (d, $J = 8.5$ Hz, 1H), 7.33 (d, $J = 8.6$ Hz, 1H), 7.02 (s, 1H), 4.75 (t, $J = 9.5$ Hz, 1H), 4.66 – 4.60 (m, 1H), 4.42 (dd, $J_a = 8.8$ Hz, $J_b = 4.1$ Hz, 1H), 3.93 (s, 3H), 3.58 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ (ppm) 169.4, 168.2, 166.4, 139.2, 125.7, 123.4, 122.8, 121.9, 121.5, 120.0, 111.0, 105.8, 77.6, 51.9, 50.8, 39.3, 14.4. IR (cm^{-1}) 3340, 2952, 2925, 2851, 1701, 1640, 1620, 1438, 1384, 1321, 1247, 1196, 1109, 1086, 993, 771, 752. HRMS (ESI) $m/z = 338.1007$, calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_5$ $[\text{M} + \text{Na}]^+$ 338.0999.



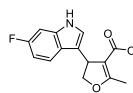
Methyl 4-(5-chloro-1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4u): yellow liquid.

^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ (ppm) 11.09 (s, 1H), 7.48 – 7.45 (m, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.15 (d, $J = 2.1$ Hz, 1H), 7.07 (dd, $J_a = 8.6$ Hz, $J_b = 1.8$ Hz, 1H), 4.72 (t, $J = 9.6$ Hz, 1H), 4.54 (dd, $J_a = 9.8$ Hz, $J_b = 3.5$ Hz, 1H), 4.28 (dd, $J_a = 9.0$ Hz, $J_b = 4.4$ Hz, 1H), 3.49 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ (ppm) 168.6, 165.8, 135.8, 127.2, 124.7, 123.6, 121.3, 118.0, 117.2, 113.6, 106.1, 77.8, 50.9, 39.1, 14.5. IR (cm^{-1}) 3344, 2950, 2926, 2854, 1679, 1639, 1461, 1439, 1384, 1346, 1200, 1128, 1091, 993, 799. HRMS (ESI) $m/z = 314.0574$, calcd for $\text{C}_{15}\text{H}_{14}\text{ClNO}_3$ $[\text{M} + \text{Na}]^+$ 314.0554.



Methyl 4-(5-bromo-1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4v): yellow liquid.

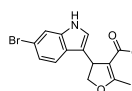
^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ (ppm) 11.10 (s, 1H), 7.61 (s, 1H), 7.32 (d, $J = 8.6$ Hz, 1H), 7.18 (dd, $J = 8.6$, 1.6 Hz, 1H), 7.12 (s, 1H), 4.72 (t, $J = 9.6$ Hz, 1H), 4.53 (dd, $J_a = 9.9$ Hz, $J_b = 3.5$ Hz, 1H), 4.27 (dd, $J_a = 9.0$ Hz, $J_b = 4.3$ Hz, 1H), 3.48 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO- d_6 , 25 °C) δ (ppm) 168.6, 165.7, 135.6, 127.9, 124.4, 123.8, 121.1, 117.2, 114.1, 111.6, 106.1, 77.8, 50.9, 39.0, 14.5. IR (cm^{-1}) 3340, 2950, 2898, 1680, 1640, 1457, 1439, 1384, 1346, 1324, 1199, 1128, 1089, 994, 884, 796. HRMS (ESI) $m/z = 358.0048$, calcd for $\text{C}_{15}\text{H}_{14}\text{BrNO}_3$ $[\text{M} + \text{Na}]^+$ 358.0049.



Methyl 4-(6-fluoro-1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4w): brown liquid.

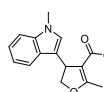
^1H NMR (400 MHz, DMSO- d_6 , 25 °C) δ (ppm) 10.93 (s, 1H), 7.41 (dd, $J_a = 8.6$ Hz, $J_b = 5.5$ Hz, 1H), 7.11 (dd, $J_a = 10.1$ Hz, $J_b = 2.0$ Hz, 1H), 7.06 (d, $J = 1.9$ Hz, 1H), 6.88 – 6.79 (m, 1H), 4.72 (t, $J = 9.6$

Hz, 1H), 4.53 (dd, $J_a = 9.8$ Hz, $J_b = 3.7$ Hz, 1H), 4.27 (dd, $J_a = 8.0$ Hz, $J_b = 4.5$ Hz, 1H), 3.47 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 -d, 25 °C) δ (ppm) 169.0, 166.5, 161.1, 158.7, 136.7 (d, $J_{C,F} = 22.6$ Hz), 122.4, 122.1 (d, $J_{C,F} = 7.5$ Hz), 119.5 (d, $J_{C,F} = 18.9$ Hz), 118.1 (d, $J_{C,F} = 47.1$ Hz), 108.0, 106.0, 97.6 (d, $J_{C,F} = 37.7$ Hz), 77.4, 50.9, 39.7, 14.5. ^{19}F NMR (377 MHz, CDCl_3 , 25 °C) δ (ppm) -121.4. IR (cm^{-1}) 3353, 2952, 2925, 2851, 1680, 1631, 1553, 1499, 1456, 1439, 1384, 1344, 1324, 1202, 1138, 1088, 993, 955, 802. HRMS (ESI) $m/z = 298.0854$, calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_5$ $[\text{M} + \text{Na}]^+$ 298.0850.



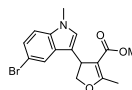
Methyl 4-(6-bromo-1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4x): yellow liquid.

^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 11.02 (s, 1H), 7.53 (s, 1H), 7.39 (d, $J = 8.5$ Hz, 1H), 7.14 – 7.07 (m, 2H), 4.72 (t, $J = 9.6$ Hz, 1H), 4.53 (dd, $J_a = 9.8$ Hz, $J_b = 3.7$ Hz, 1H), 4.27 (dd, $J_a = 9.0$ Hz, $J_b = 4.5$ Hz, 1H), 3.47 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 168.6, 165.8, 137.9, 125.1, 123.9, 121.8, 120.5, 117.5, 114.6, 114.2, 106.1, 77.7, 50.9, 39.2, 14.5. IR (cm^{-1}) 3341, 2950, 2926, 2852, 1689, 1640, 1439, 1384, 1326, 1199, 1088, 994, 802. HRMS (ESI) $m/z = 358.0038$, calcd for $\text{C}_{15}\text{H}_{14}\text{BrNO}_3$ $[\text{M} + \text{Na}]^+$ 358.0049.



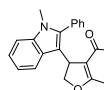
Methyl 2-methyl-4-(1-methyl-1H-indol-3-yl)-4,5-dihydrofuran-3-carboxylate (4y): yellow liquid.

^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 7.46 (d, $J = 7.9$ Hz, 1H), 7.37 (d, $J = 8.2$ Hz, 1H), 7.13 (t, $J = 7.3$ Hz, 1H), 7.05 (s, 1H), 7.00 (t, $J = 7.3$ Hz, 1H), 4.72 (t, $J = 9.5$ Hz, 1H), 4.53 (dd, $J_a = 9.9$ Hz, $J_b = 3.5$ Hz, 1H), 4.26 (dd, $J_a = 8.9$ Hz, $J_b = 4.3$ Hz, 1H), 3.71 (s, 3H), 3.48 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 168.6, 165.8, 137.4, 127.1, 126.4, 121.5, 118.9, 118.9, 116.5, 110.3, 106.1, 77.9, 50.9, 39.2, 32.7, 14.5. IR (cm^{-1}) 3053, 2949, 1697, 1643, 1471, 1436, 1381, 1325, 1196, 1117, 1084, 992, 741. HRMS (ESI) $m/z = 294.1094$, calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3$ $[\text{M} + \text{Na}]^+$ 294.1101.



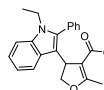
Methyl 4-(5-bromo-1-methyl-1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4z): yellow liquid.

^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm) 7.64 (s, 1H), 7.30 – 7.24 (m, 1H), 7.13 (d, $J = 8.7$ Hz, 1H), 6.85 (s, 1H), 4.69 (t, $J = 9.5$ Hz, 1H), 4.52 (dd, $J_a = 9.9$ Hz, $J_b = 3.6$ Hz, 1H), 4.39 (dd, $J_a = 8.9$ Hz, $J_b = 4.2$ Hz, 1H), 3.70 (s, 3H), 3.58 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ (ppm) 168.9, 166.3, 136.0, 128.0, 127.5, 124.4, 121.6, 116.7, 112.4, 110.9, 105.9, 77.6, 50.8, 39.3, 32.8, 14.4. IR (cm^{-1}) 2925, 2854, 1697, 1624, 1475, 1436, 1383, 1321, 1196, 1118, 1083, 992, 793. HRMS (ESI) $m/z = 372.0199$, calcd for $\text{C}_{16}\text{H}_{16}\text{BrNO}_3$ $[\text{M} + \text{Na}]^+$ 372.0206.



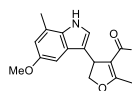
Methyl 2-methyl-4-(1-methyl-2-phenyl-1H-indol-3-yl)-4,5-dihydrofuran-3-carboxylate (4aa): yellow liquid.

^1H NMR (400 MHz, CDCl_3 , 25 °C) δ (ppm) 7.55 – 7.50 (m, 2H), 7.48 (d, $J = 6.9$ Hz, 2H), 7.44 (d, $J = 7.5$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 1H), 7.23 (t, $J = 7.5$ Hz, 1H), 7.10 (t, $J = 7.4$ Hz, 1H), 4.62 – 4.52 (m, 2H), 4.46 (dd, $J_a = 7.0$ Hz, $J_b = 4.4$ Hz, 1H), 3.53 (s, 3H), 3.50 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 168.4, 165.7, 138.1, 137.4, 131.6, 131.2, 128.8, 128.6, 125.7, 121.8, 119.6, 118.9, 113.5, 110.6, 105.7, 77.1, 50.9, 30.9, 14.5. IR (cm^{-1}) 3055, 2947, 2852, 1697, 1643, 1467, 1436, 1210, 1086, 993, 742. HRMS (ESI) $m/z = 370.1439$, calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_3$ $[\text{M} + \text{Na}]^+$ 370.1414.



Methyl 4-(1-ethyl-2-phenyl-1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4ab): yellow liquid.

^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm) 7.74 – 7.39 (m, 5H), 7.40 – 7.18 (m, 3H), 7.09 (t, $J = 7.5$ Hz, 1H), 4.57 (d, $J = 10.7$ Hz, 1H), 4.48 (t, $J = 5.2$ Hz, 2H), 3.98 (q, $J = 7.1$ Hz, 2H), 3.50 (s, 3H), 2.25 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 168.4, 165.7, 137.7, 136.3, 131.9, 131.1, 128.8, 128.7, 126.1, 121.7, 119.6, 119.1, 113.8, 110.6, 105.7, 77.0, 50.8, 39.3, 38.4, 15.5, 14.5. IR (cm^{-1}) 3053, 2929, 1698, 1643, 1462, 1382, 1343, 1207, 1116, 1085, 993, 742. HRMS (ESI) $m/z = 384.1589$, calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_3$ $[\text{M} + \text{Na}]^+$ 384.1570.



Methyl 4-(5-methoxy-7-methyl-1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4ac): yellow liquid.

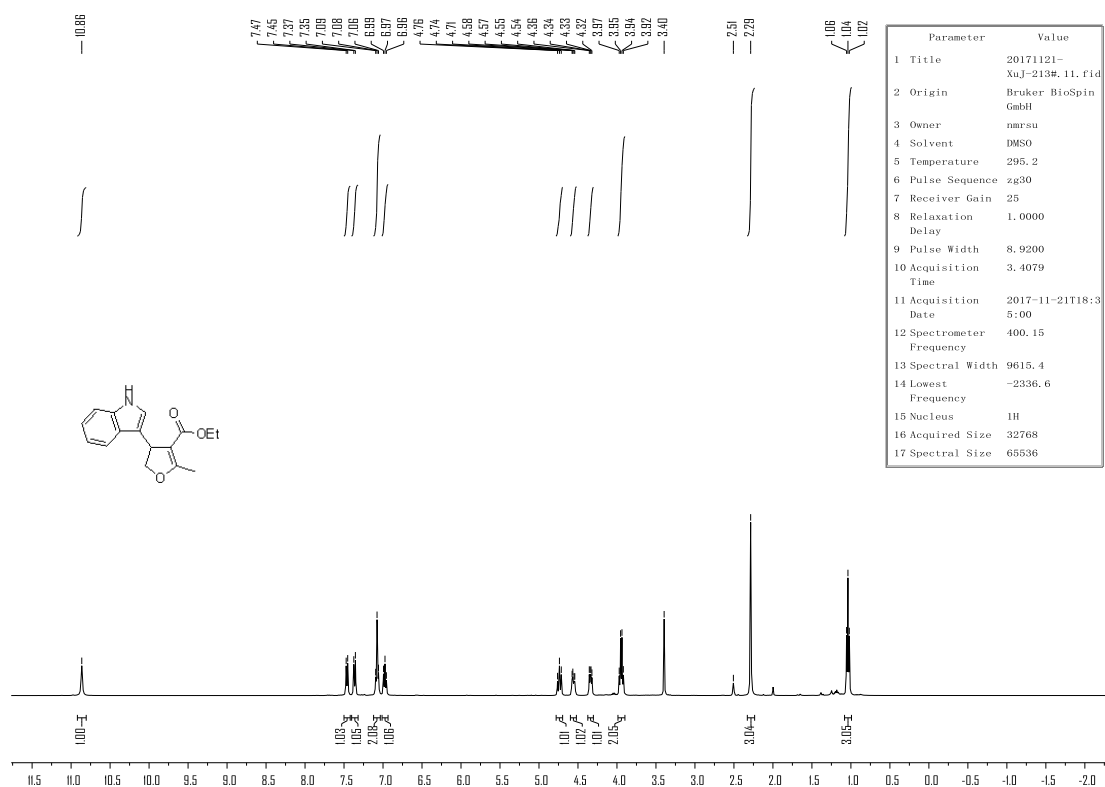
^1H NMR (400 MHz, CDCl_3 , 25 °C) δ (ppm) 7.91 (s, 1H), 6.95 (s, 1H), 6.85 (s, 1H), 6.67 (s, 1H), 4.71 (t, $J = 9.4$ Hz, 1H), 4.59 – 4.51 (m, 1H), 4.46 (dd, $J_a = 8.7$ Hz, $J_b = 4.3$ Hz, 1H), 3.83 (s,

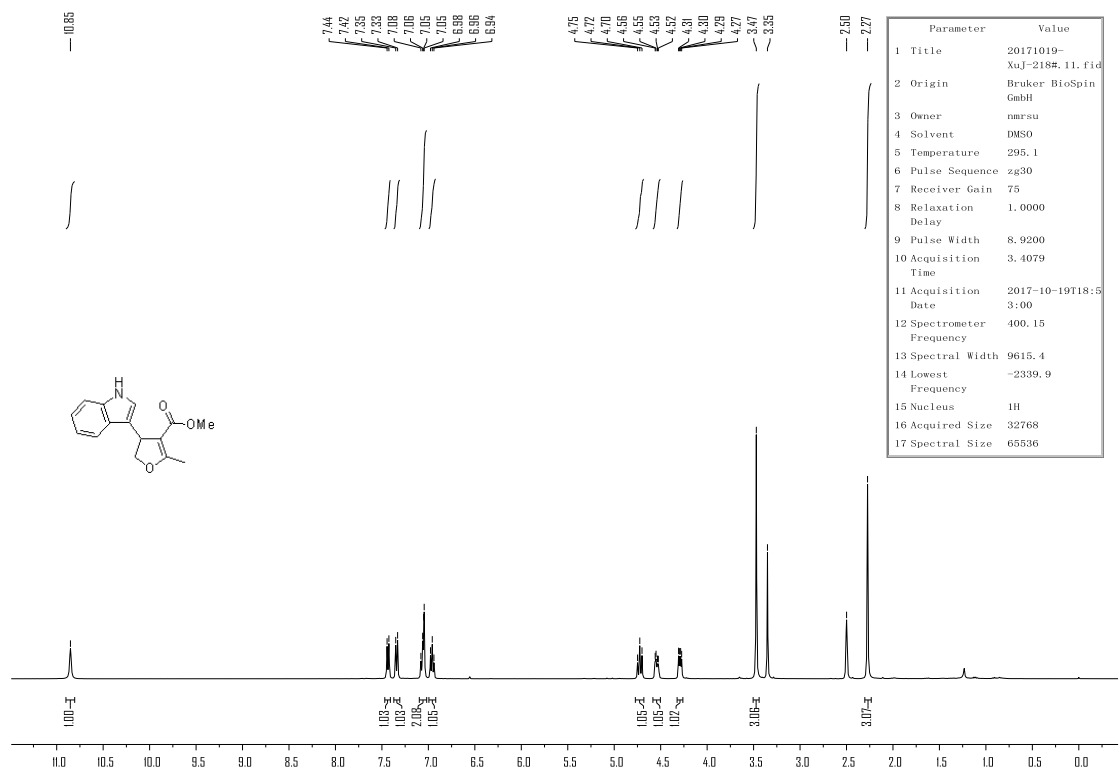
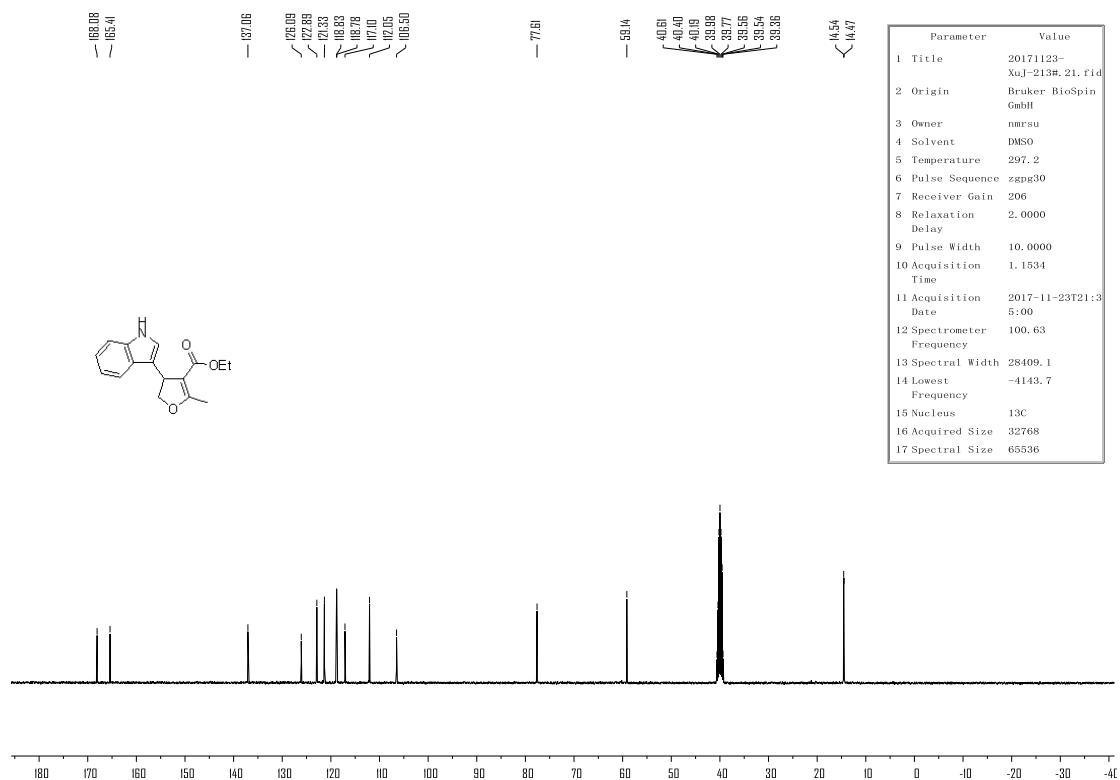
3H), 3.58 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ (ppm) 168.7, 166.5, 154.1, 131.5, 125.6, 122.1, 121.5, 118.4, 112.7, 105.9, 98.4, 77.4, 55.8, 50.8, 39.7, 16.6, 14.4. IR (cm^{-1}) 3415, 3362, 2927, 2856, 1683, 1641, 1438, 1383, 1320, 1204, 1130, 1086, 1053, 993, 810, 784. HRMS (ESI) m/z = 324.1198, calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_4$ $[\text{M} + \text{Na}]^+$ 324.1206.

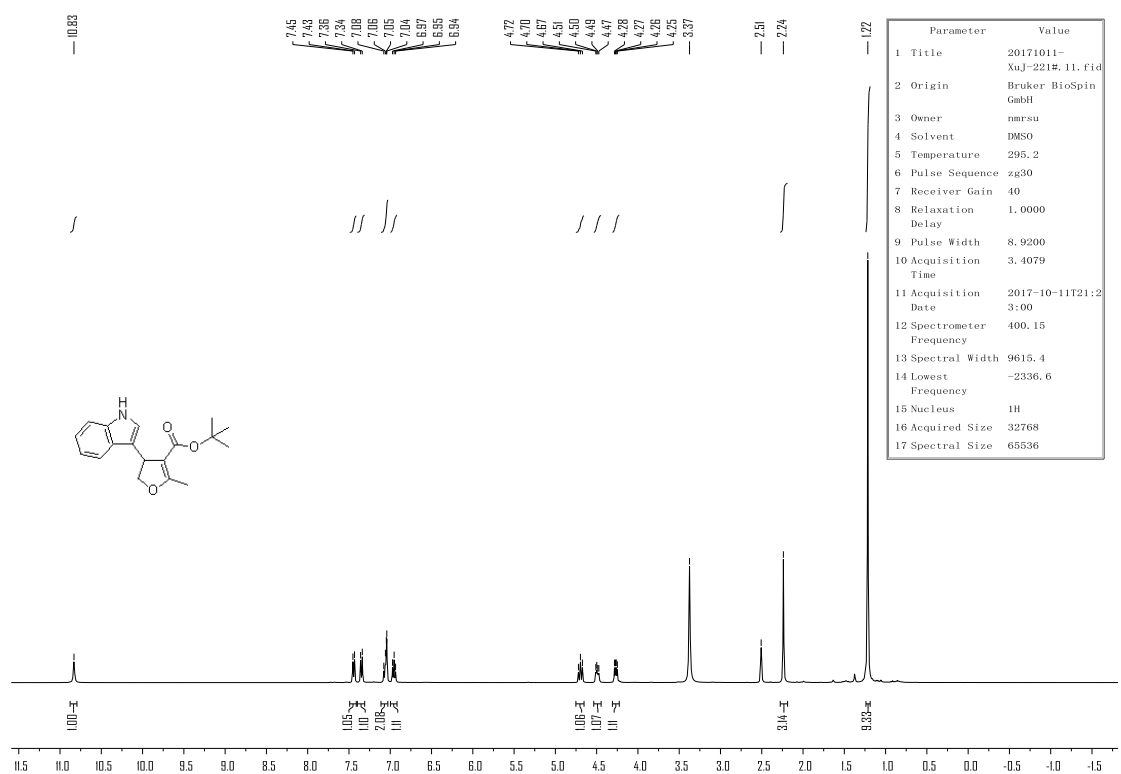
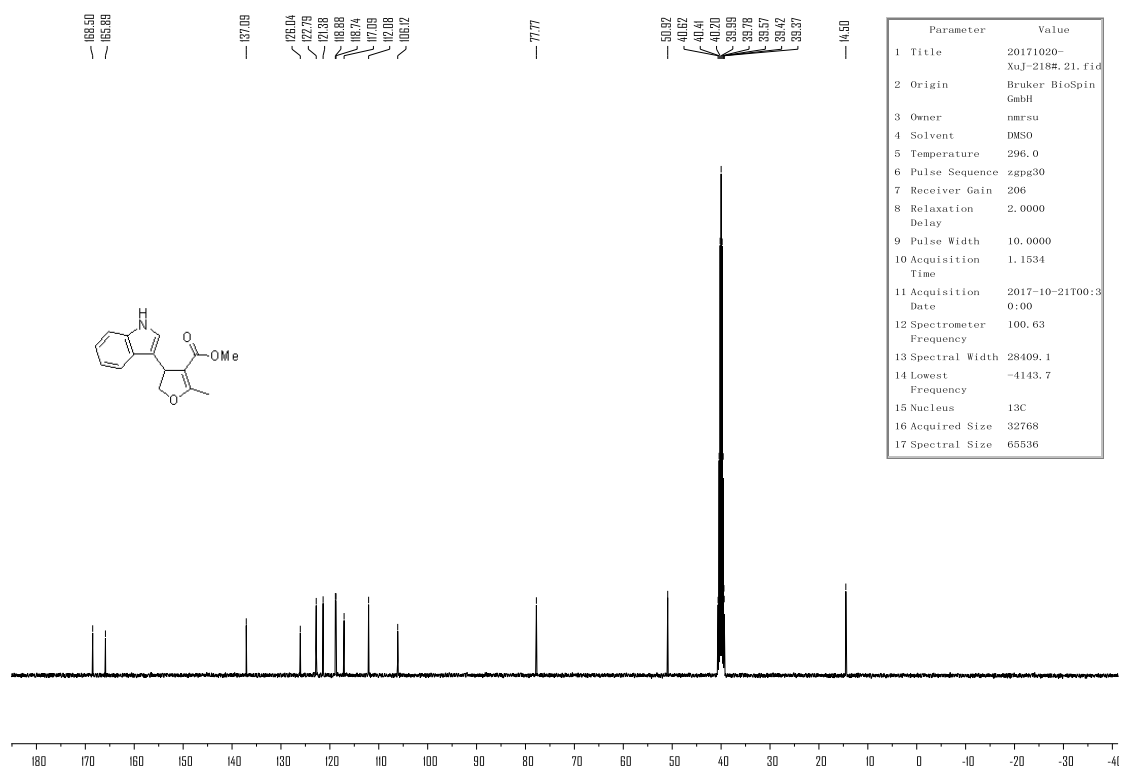
Ethyl 2-methylfuran-3-carboxylate (5a): colorless. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 7.59 (d, J = 1.7 Hz, 1H), 6.66 (d, J = 1.6 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.54 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 163.5, 158.9, 141.9, 110.8, 60.2, 14.6, 13.8. IR (cm^{-1}) 2927, 2856, 1712, 1650, 1416, 1384, 1224, 1090, 1023, 805

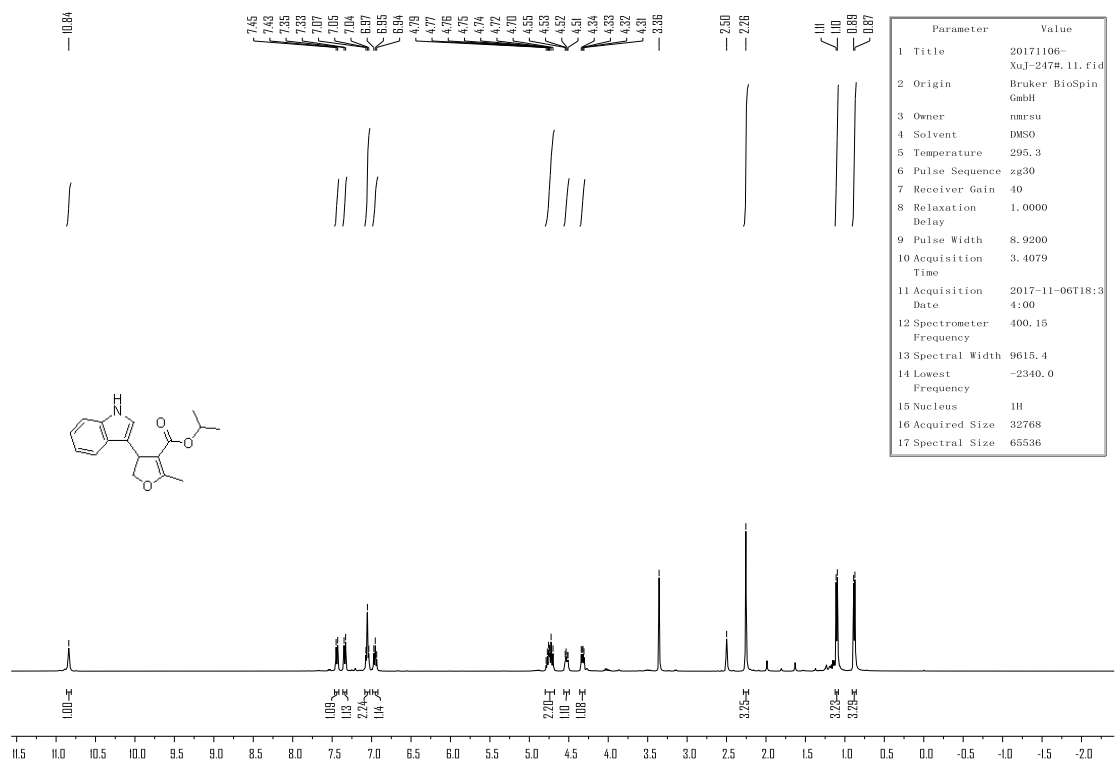
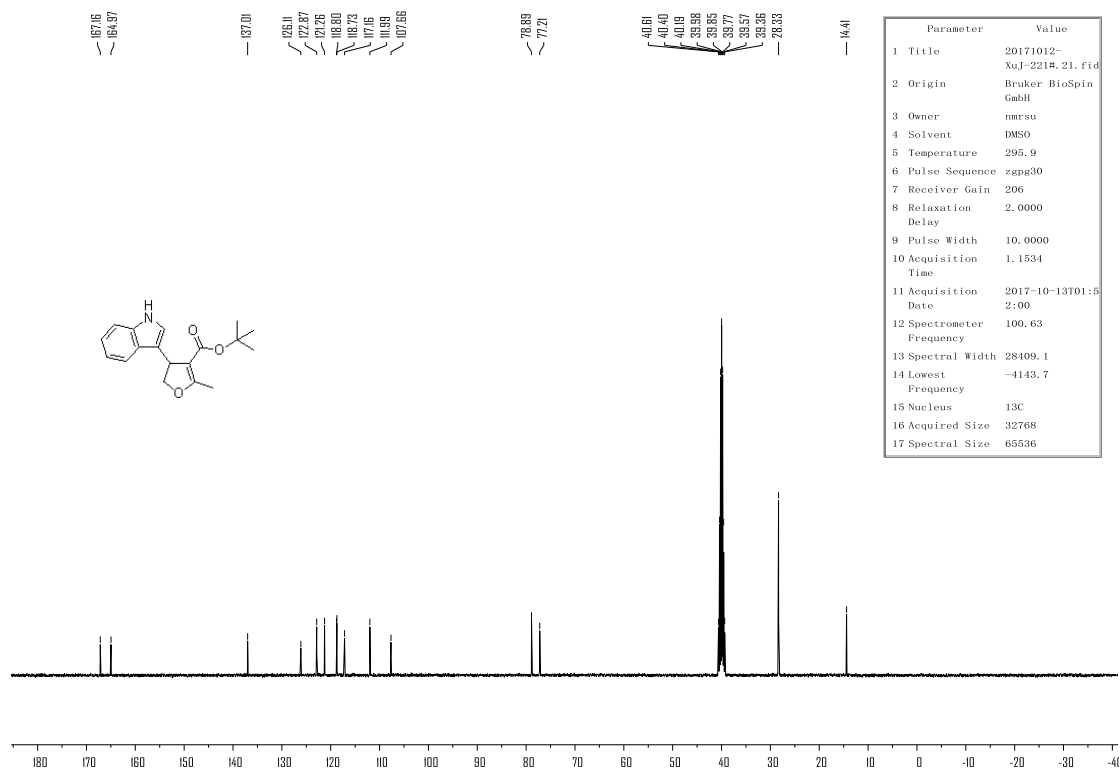
Methyl 4-(1H-indol-3-yl)-2-methyl-4,5-dihydrothiophene-3-carboxylate (4ad): light yellow liquid. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 10.91 (s, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 7.10 – 7.00 (m, 2H), 4.94 (d, J = 9.2 Hz, 1H), 3.84 (dd, J_a = 11.3 Hz, J_b = 9.4 Hz, 1H), 3.54 (s, 3H), 3.08 (dd, J_a = 11.3 Hz, J_b = 2.8 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$, 25 °C) δ (ppm) 164.2, 156.6, 137.1, 126.3, 123.5, 122.4, 121.5, 119.0, 118.9, 115.9, 112.0, 51.3, 45.5, 38.9, 16.9. IR (cm^{-1}) 3409, 3056, 2949, 2924, 2851, 2248, 1695, 1596, 1457, 1434, 1325, 1304, 1255, 1098, 1057, 743. HRMS (ESI) m/z = 274.0895, calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_4$ $[\text{M} + \text{H}]^+$ 274.0896.

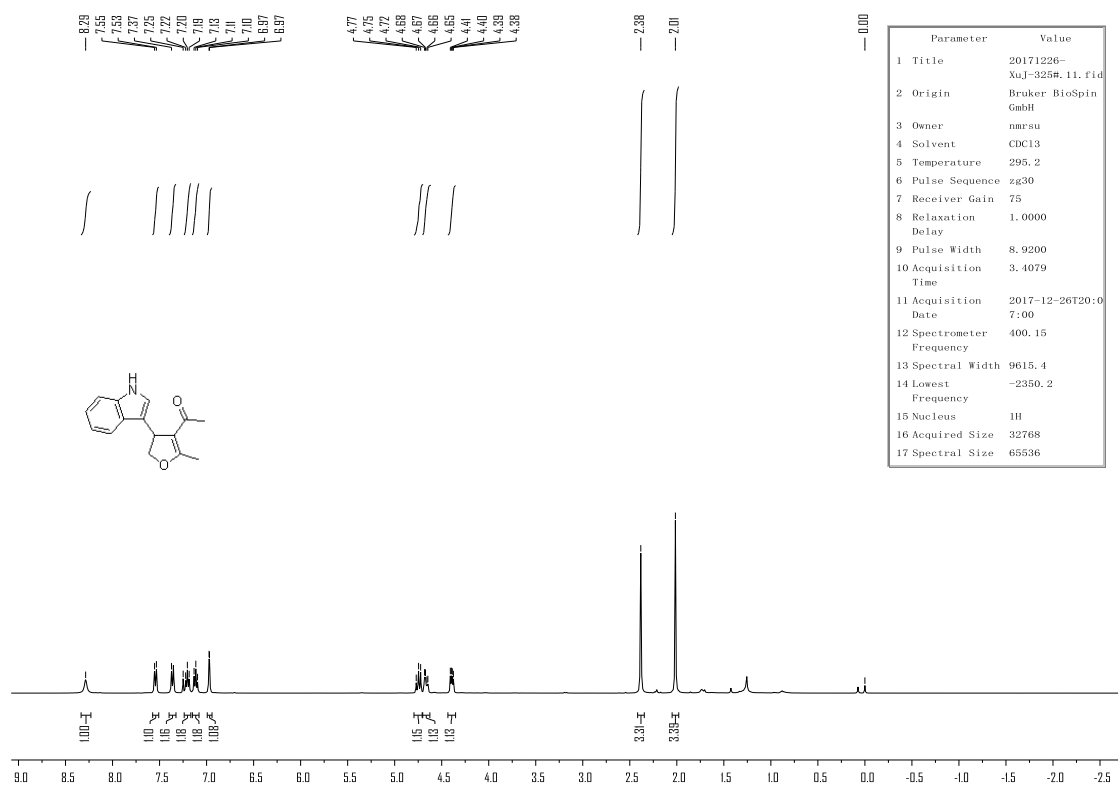
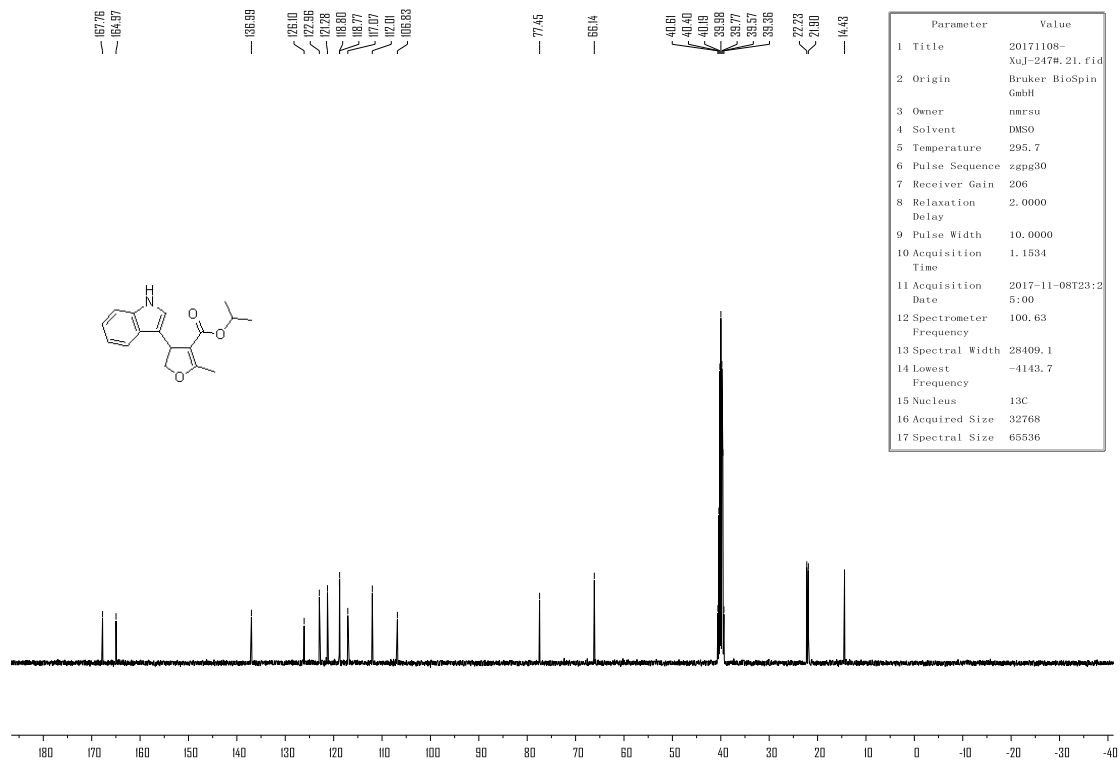
Methyl 5-(hydroxymethyl)-4-(1H-indol-3-yl)-2-methyl-4,5-dihydrofuran-3-carboxylate (4ae): light yellow liquid. ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS) δ (ppm) 8.24 (s, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.81 – 6.70 (m, 1H), 4.56 (q, J = 5.3 Hz, 1H), 4.24 (d, J = 5.5 Hz, 1H), 3.63 (d, J = 5.1 Hz, 2H), 3.41 (s, 3H), 2.64 (s, 1H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ (ppm) 168.0, 166.7, 136.8, 125.9, 122.2, 121.9, 119.3, 118.9, 117.0, 111.6, 105.8, 89.5, 64.1, 50.9, 41.7, 14.6. IR (cm^{-1}) 3410, 3057, 2951, 2926, 2249, 1680, 1640, 1439, 1383, 1334, 1207, 1127, 1097, 1016, 976, 910, 740. HRMS (ESI) m/z = 288.1228, calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_4$ $[\text{M} + \text{H}]^+$ 288.1230.

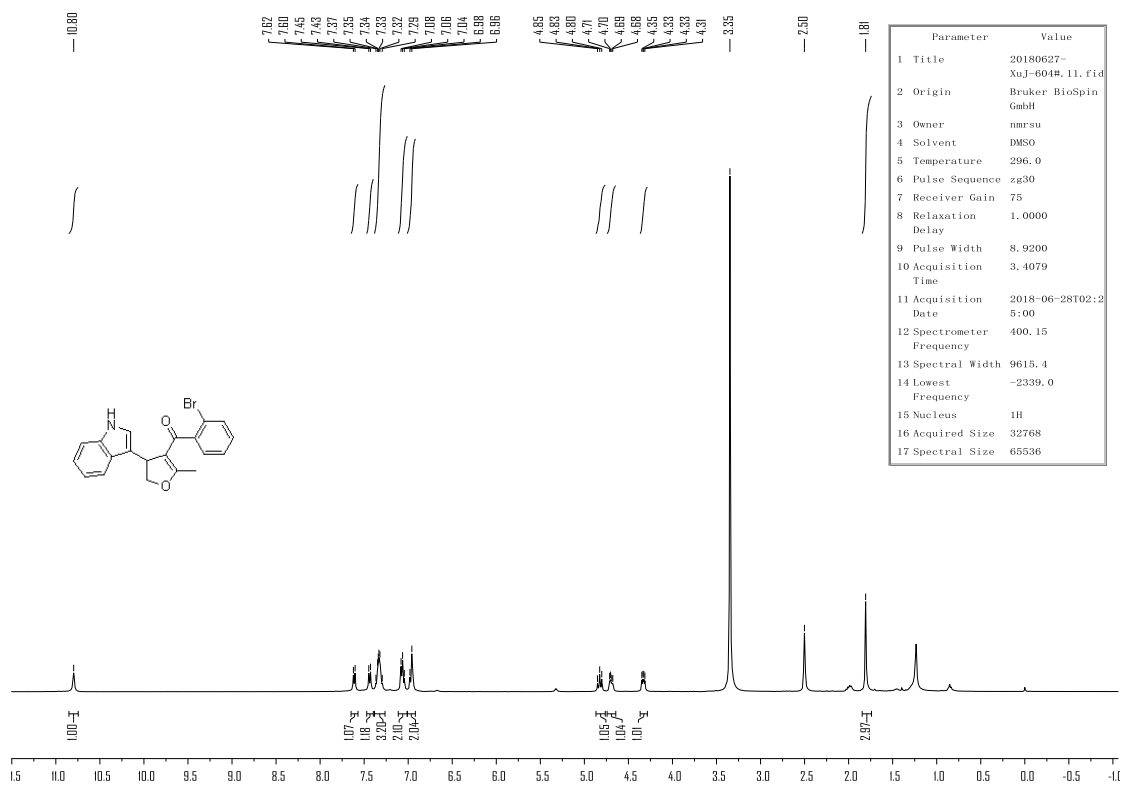
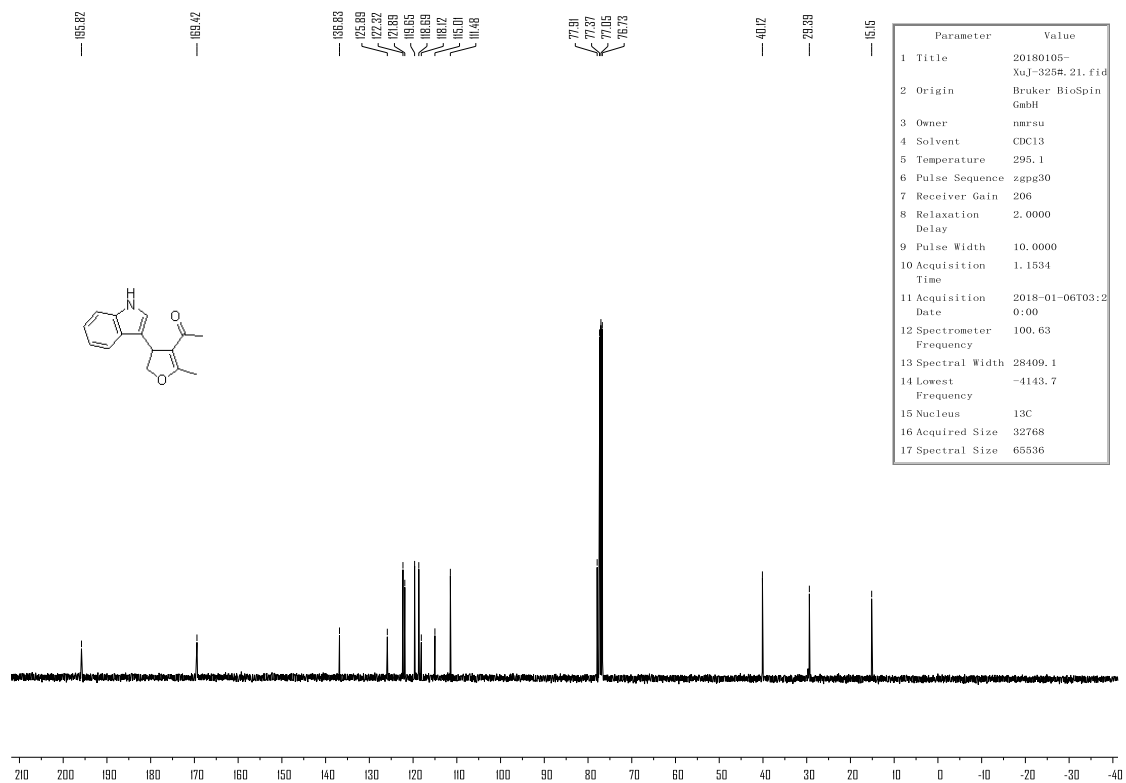


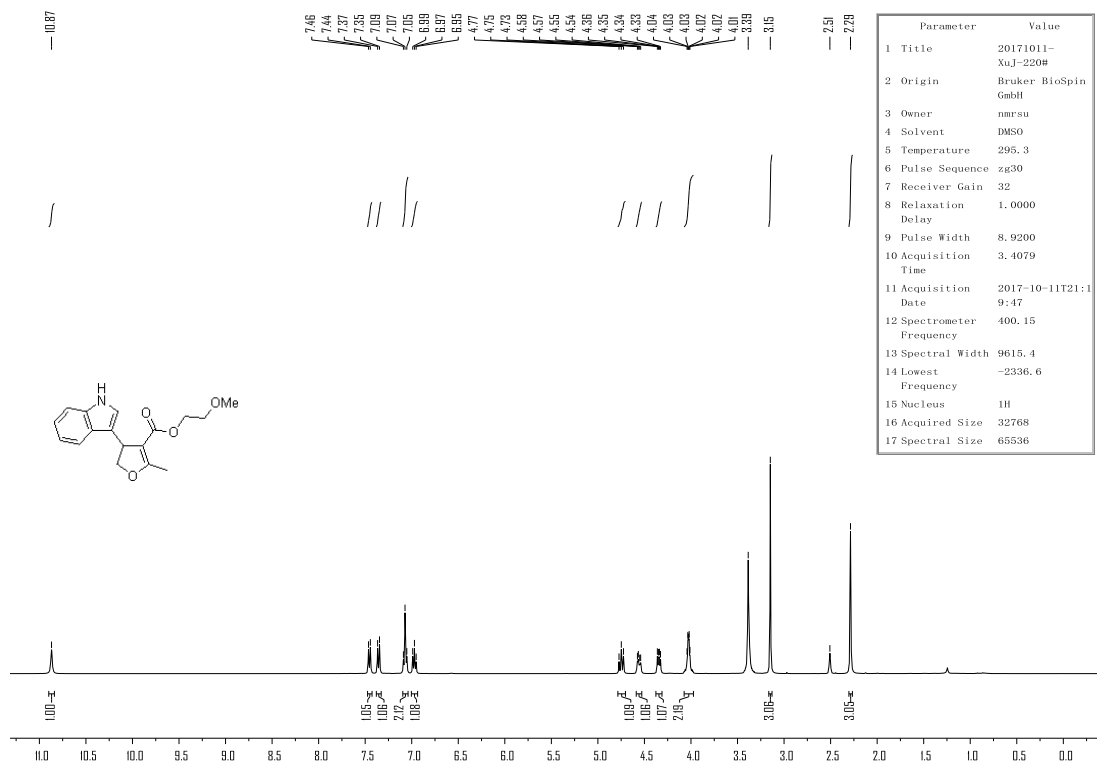
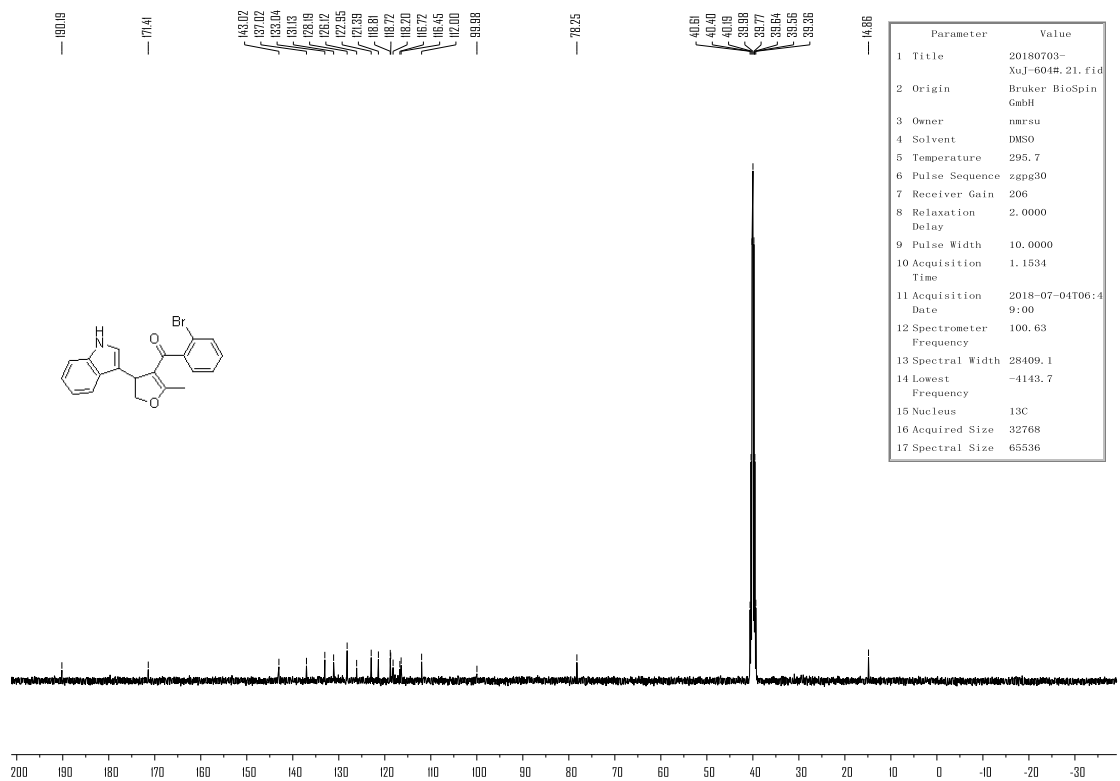


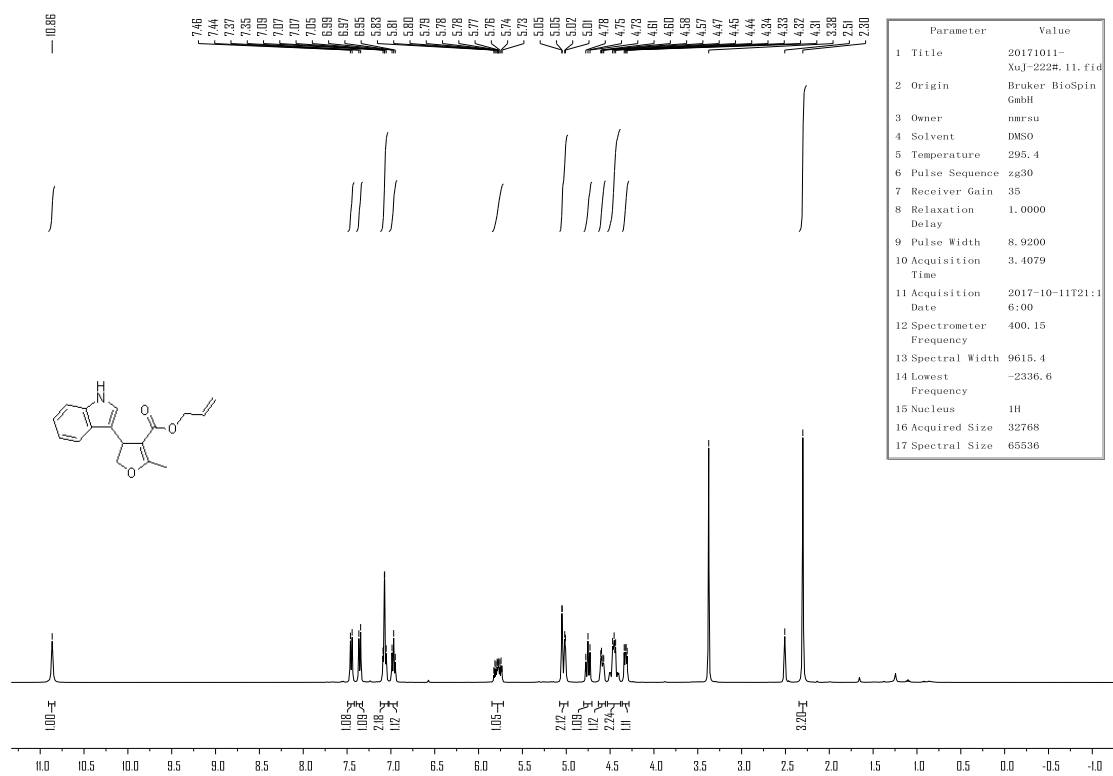
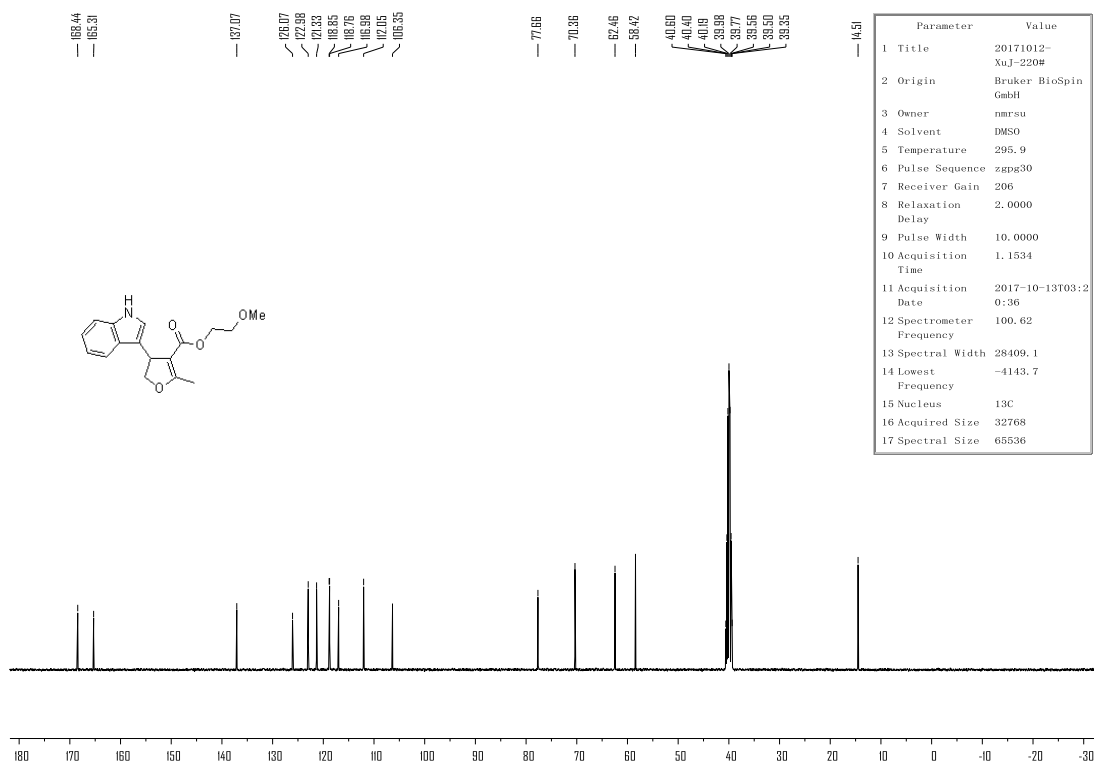


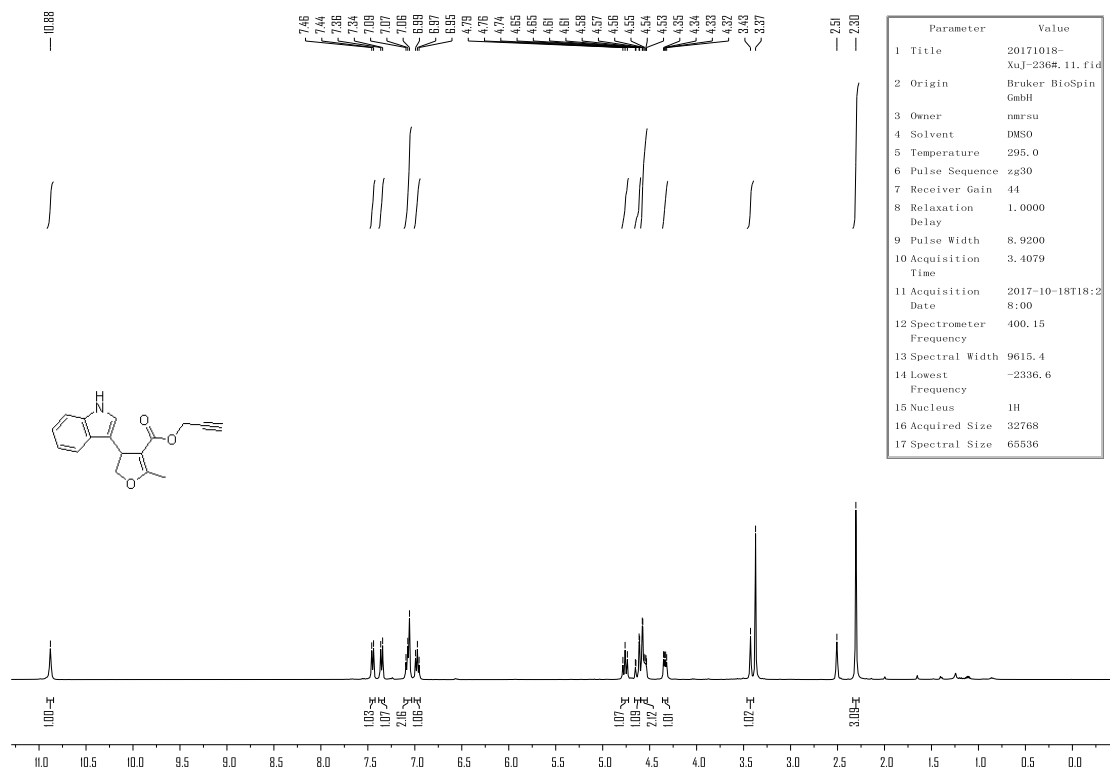
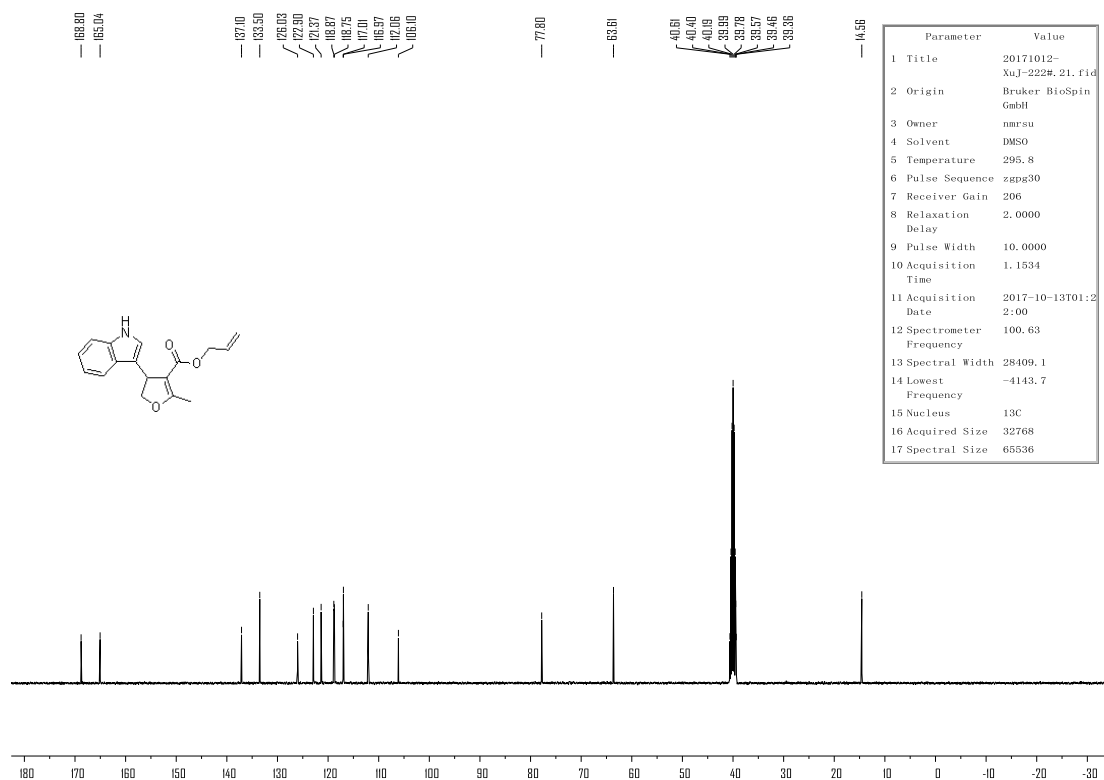


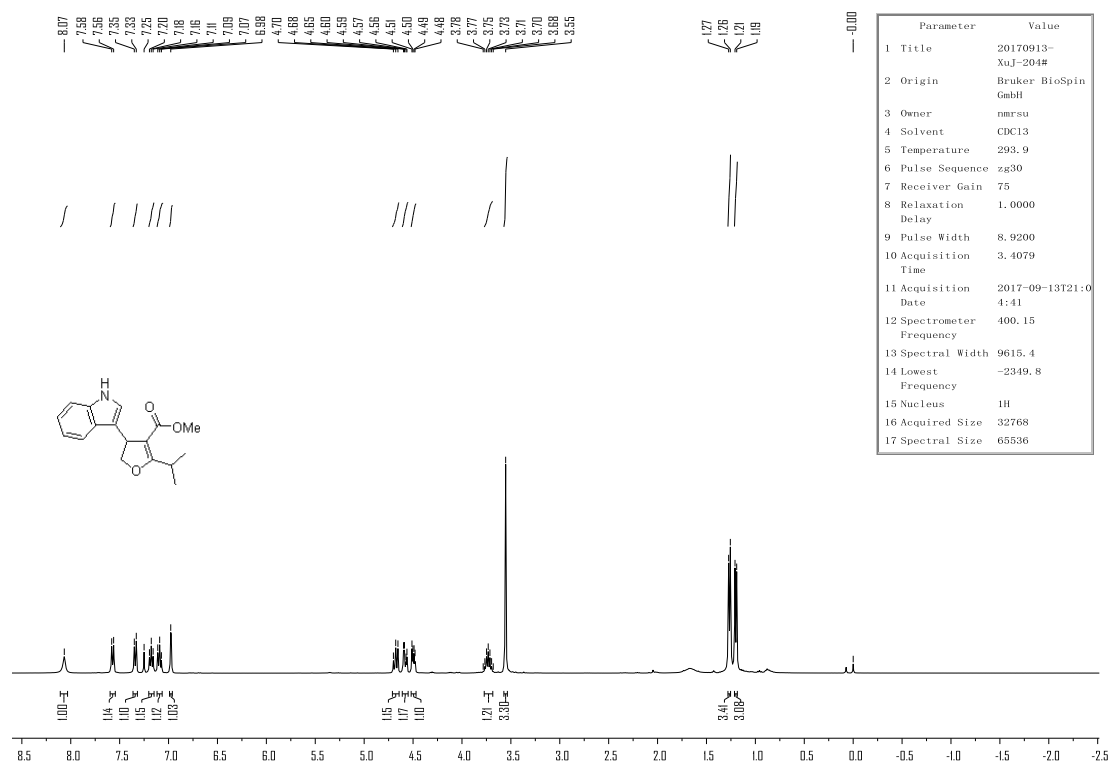
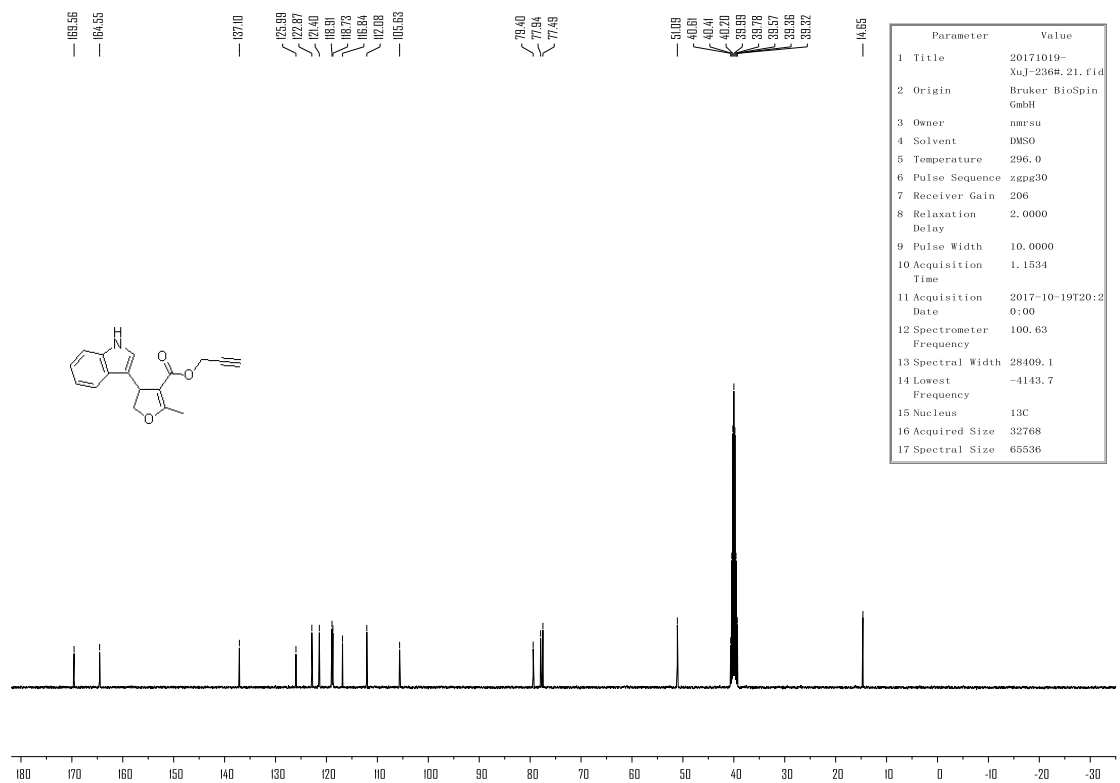


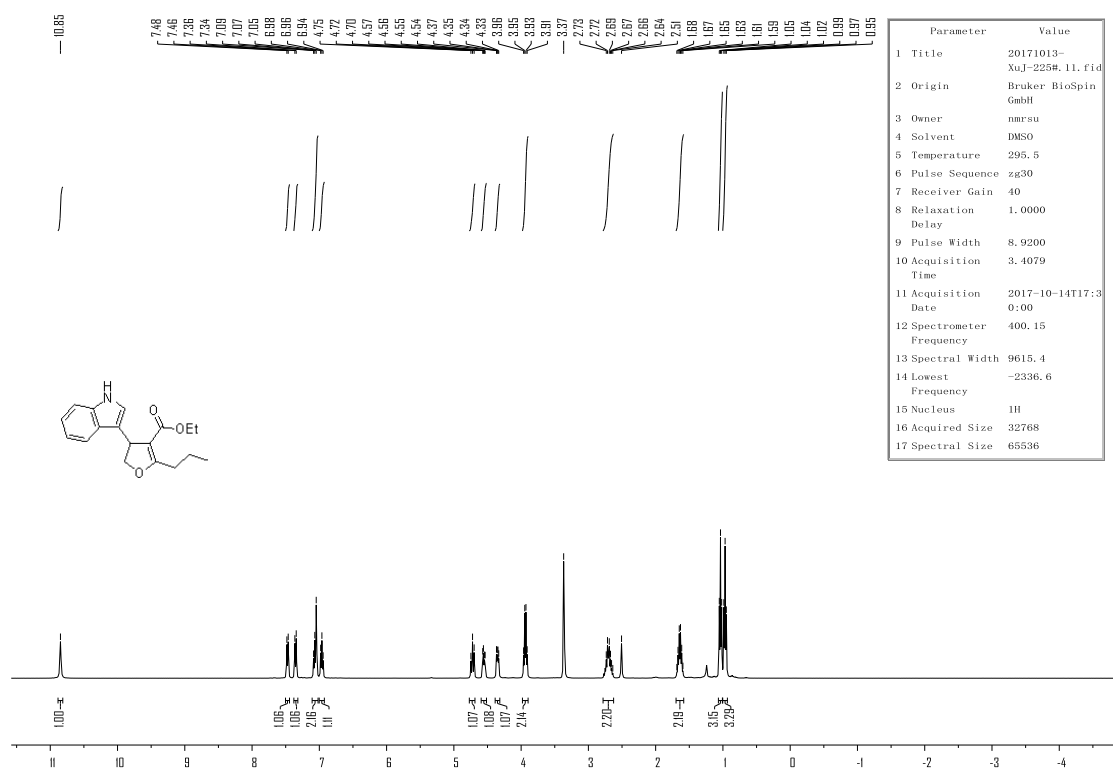
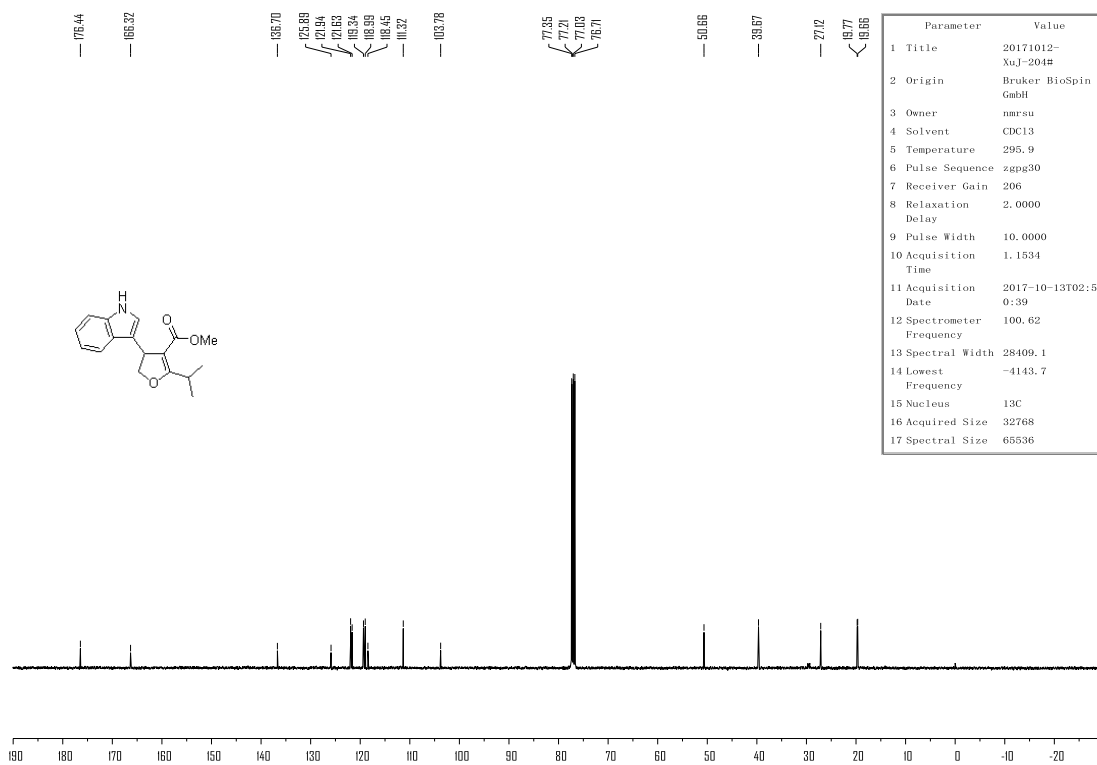


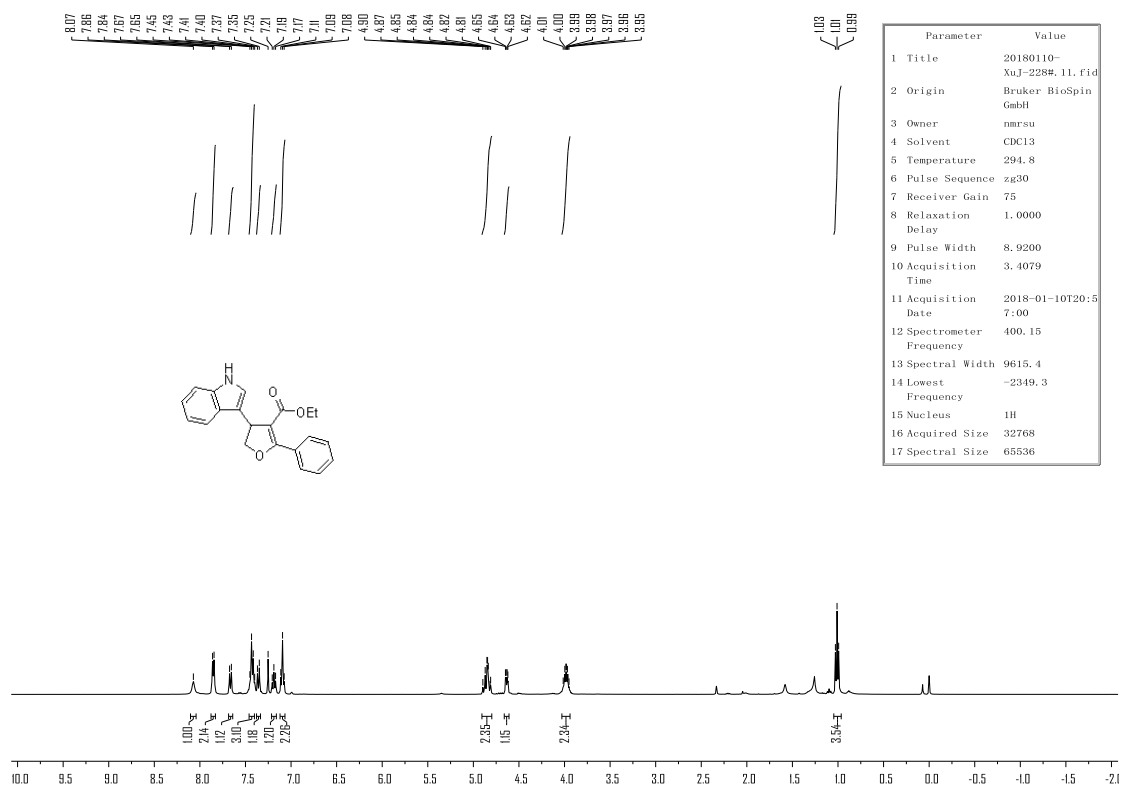
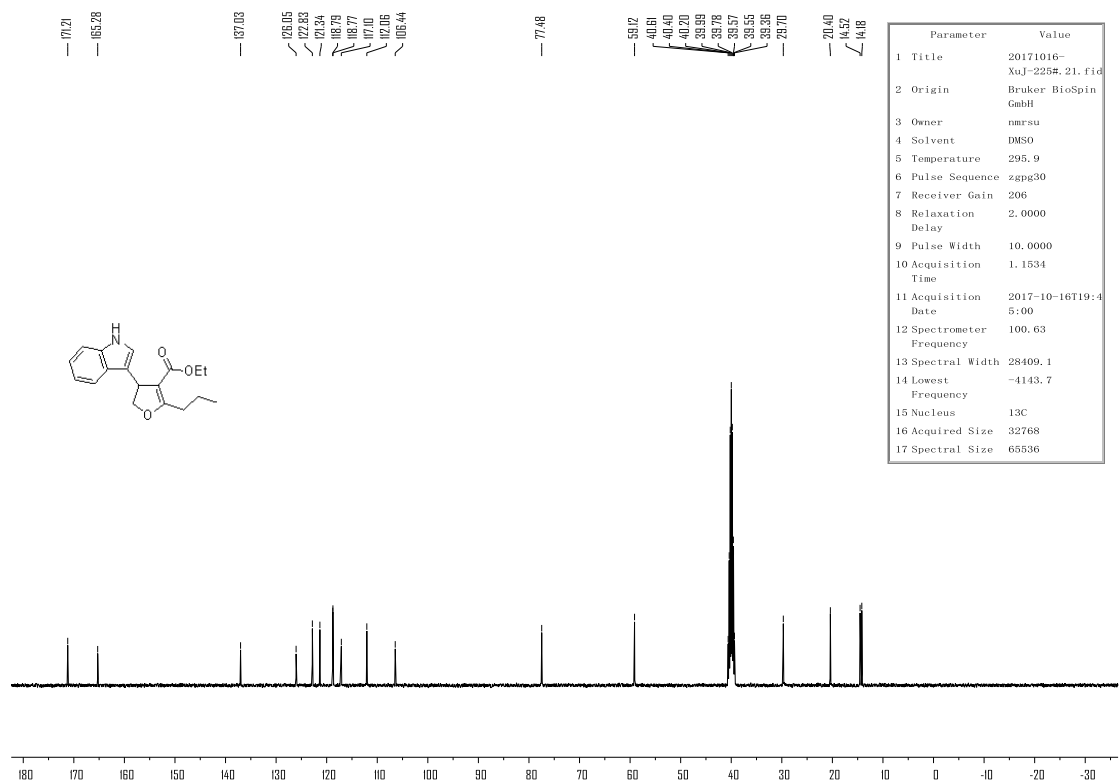


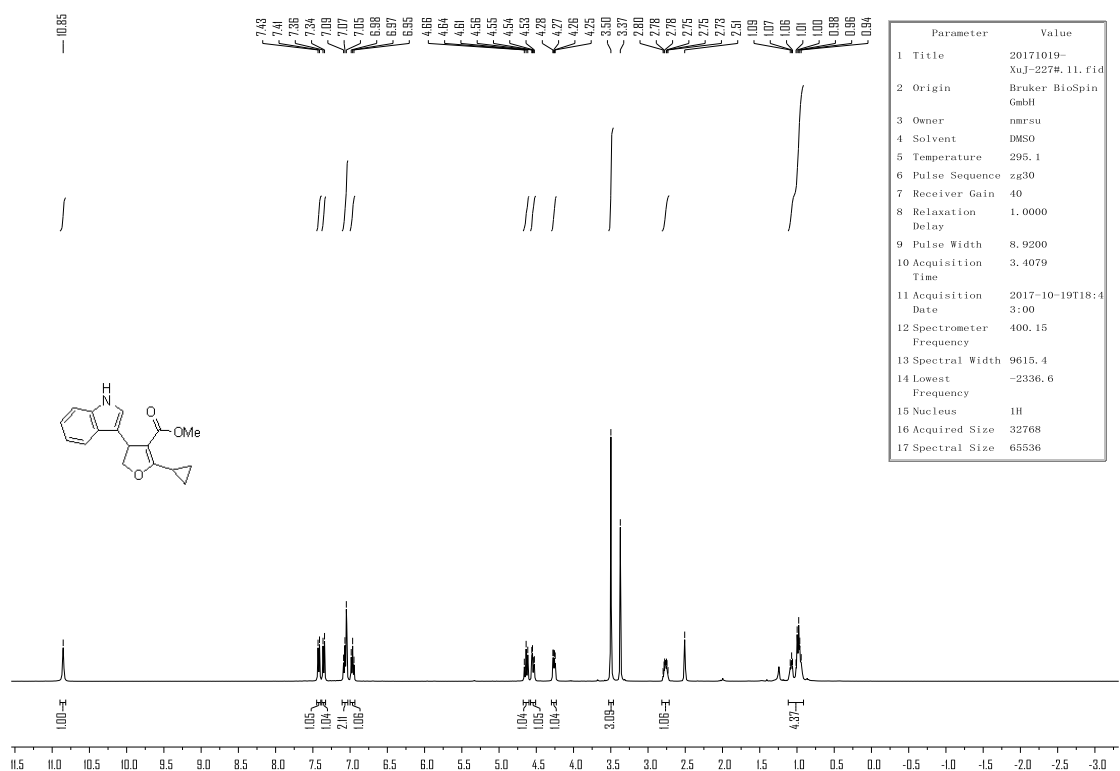
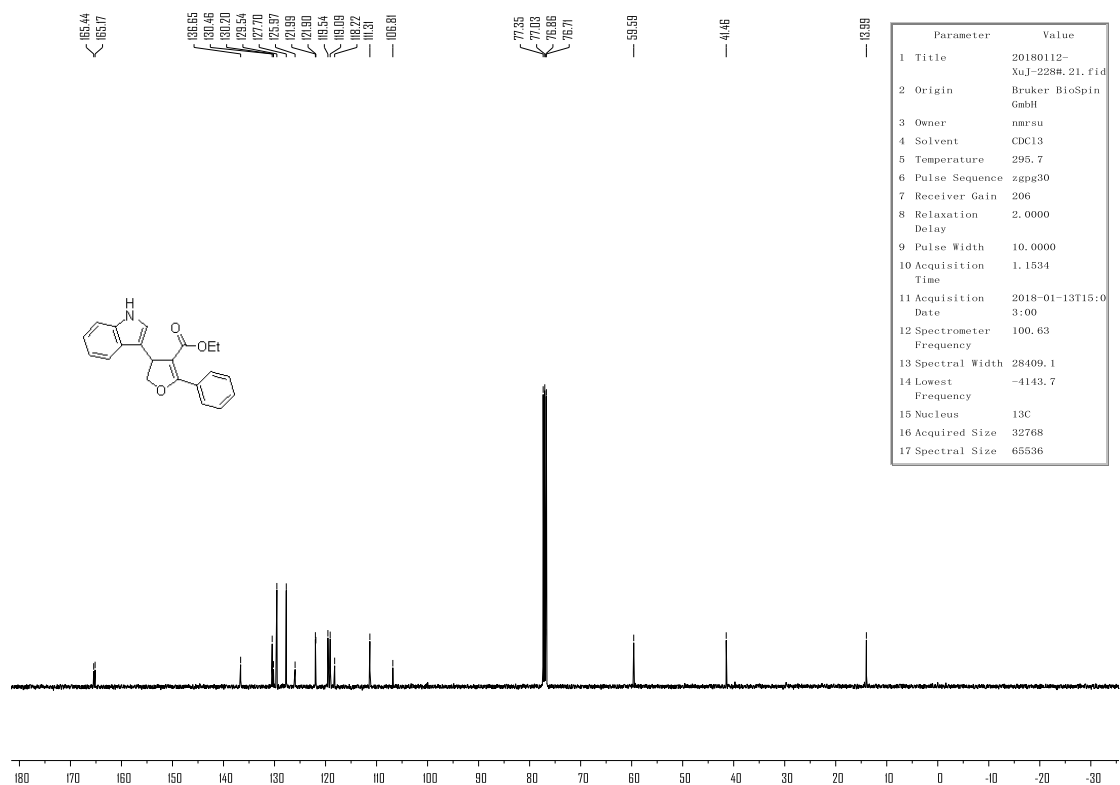


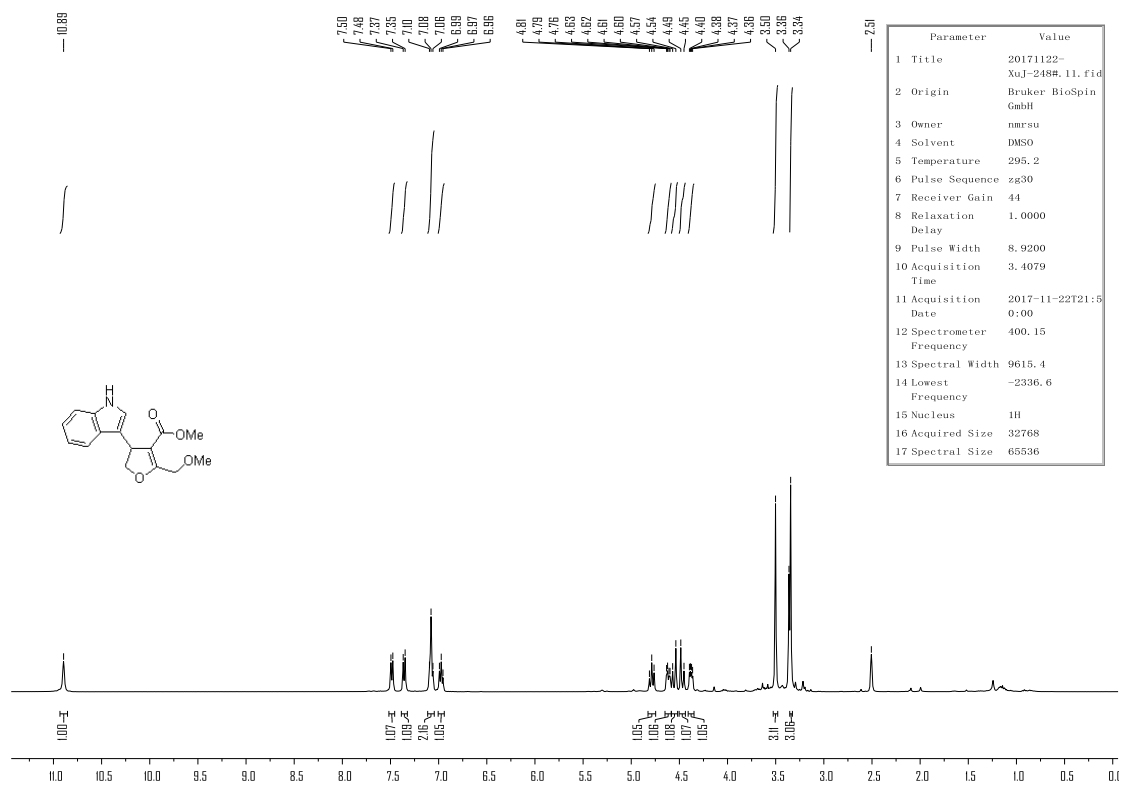
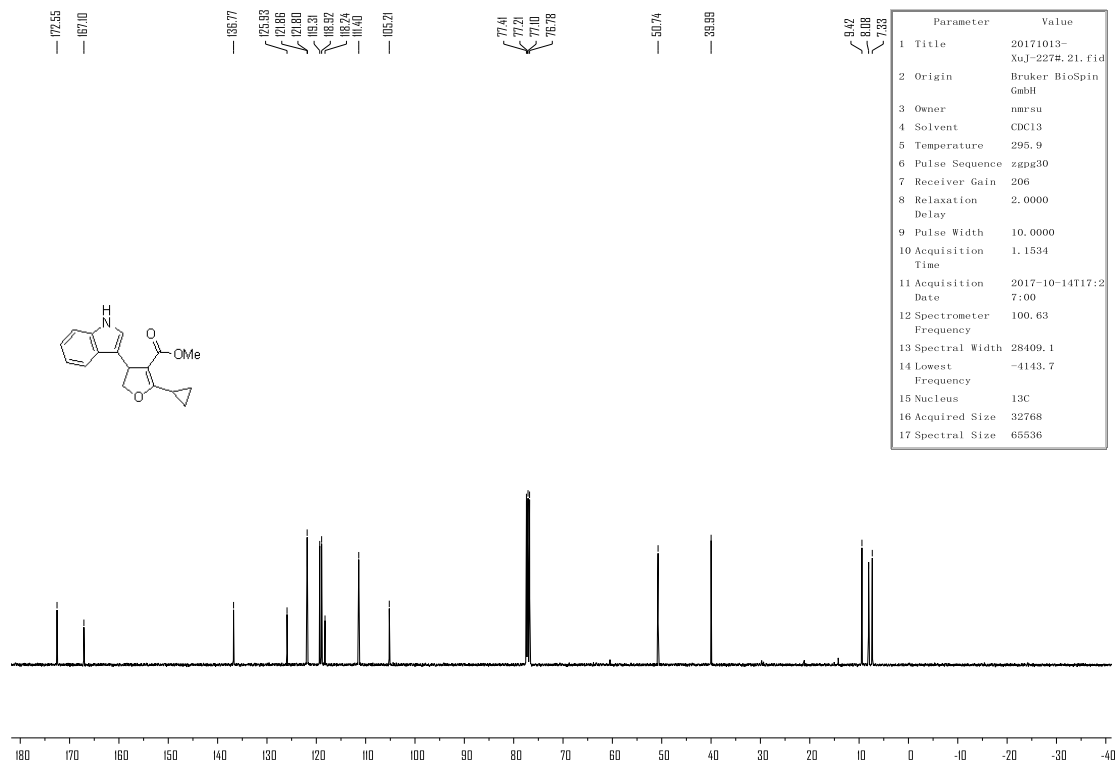


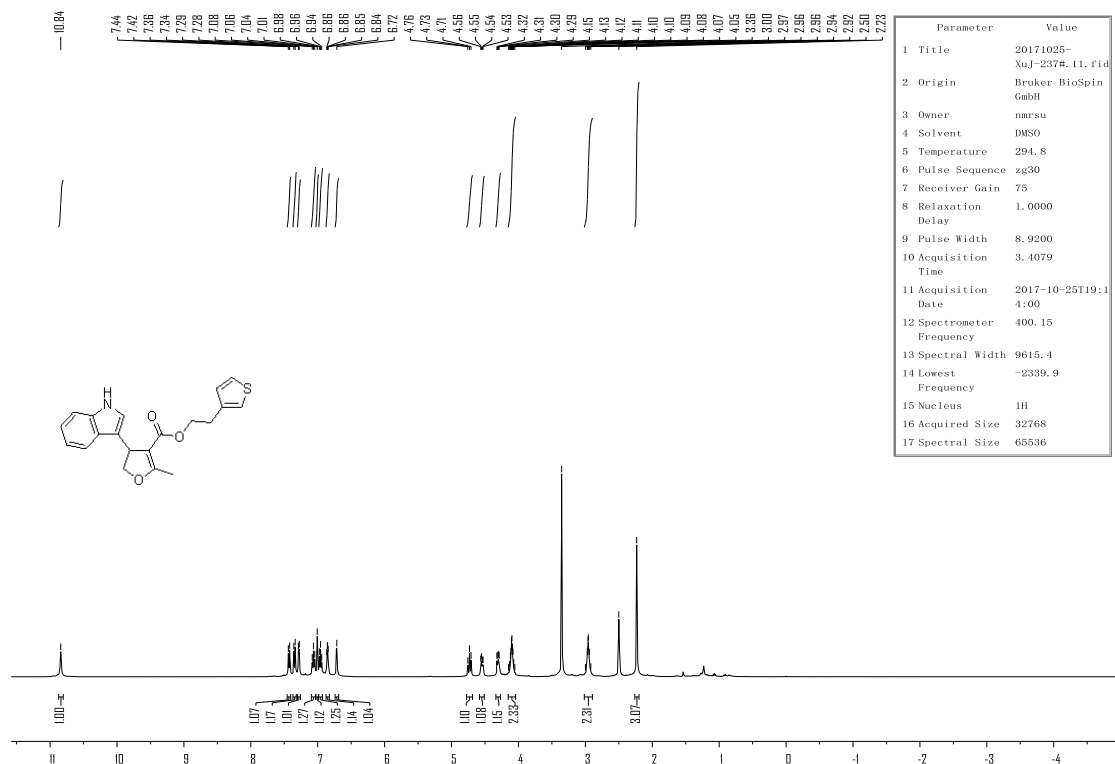
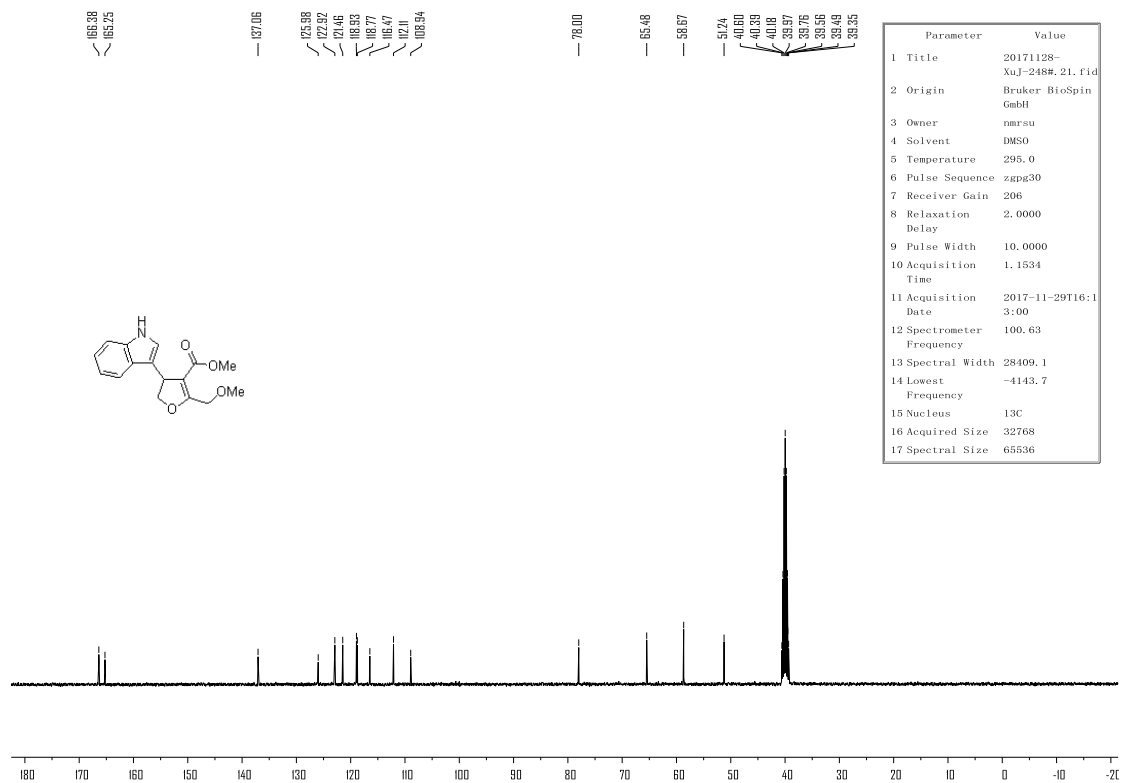


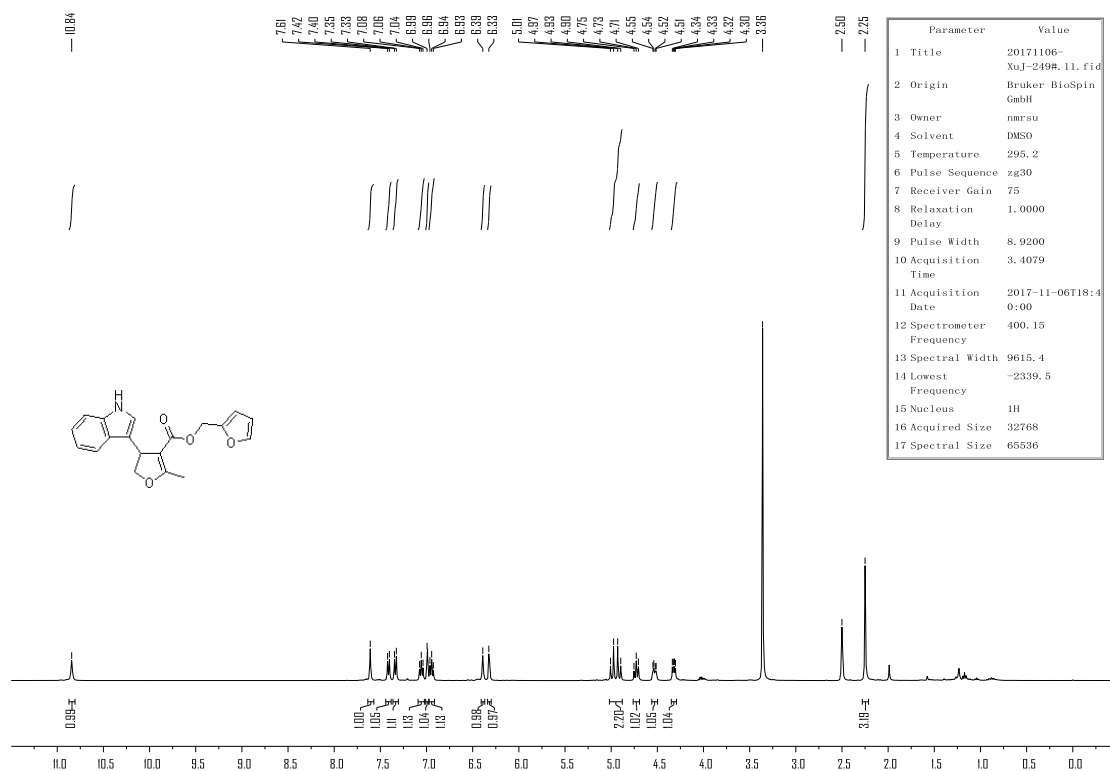
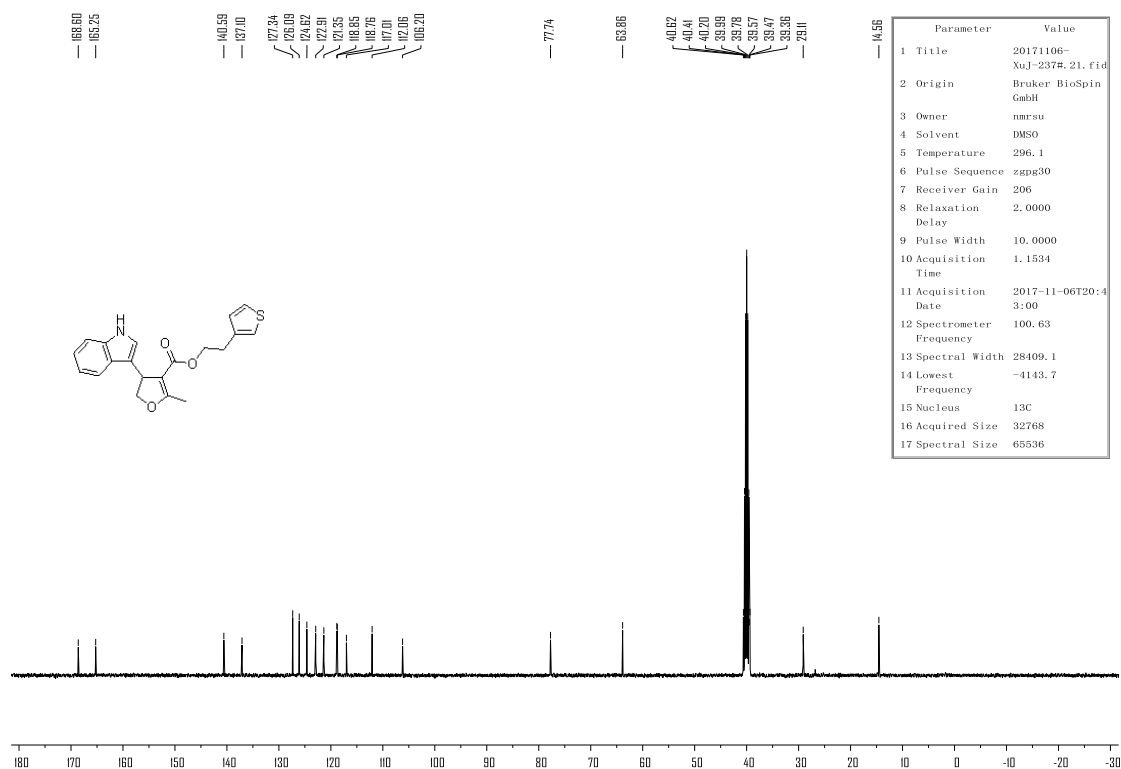


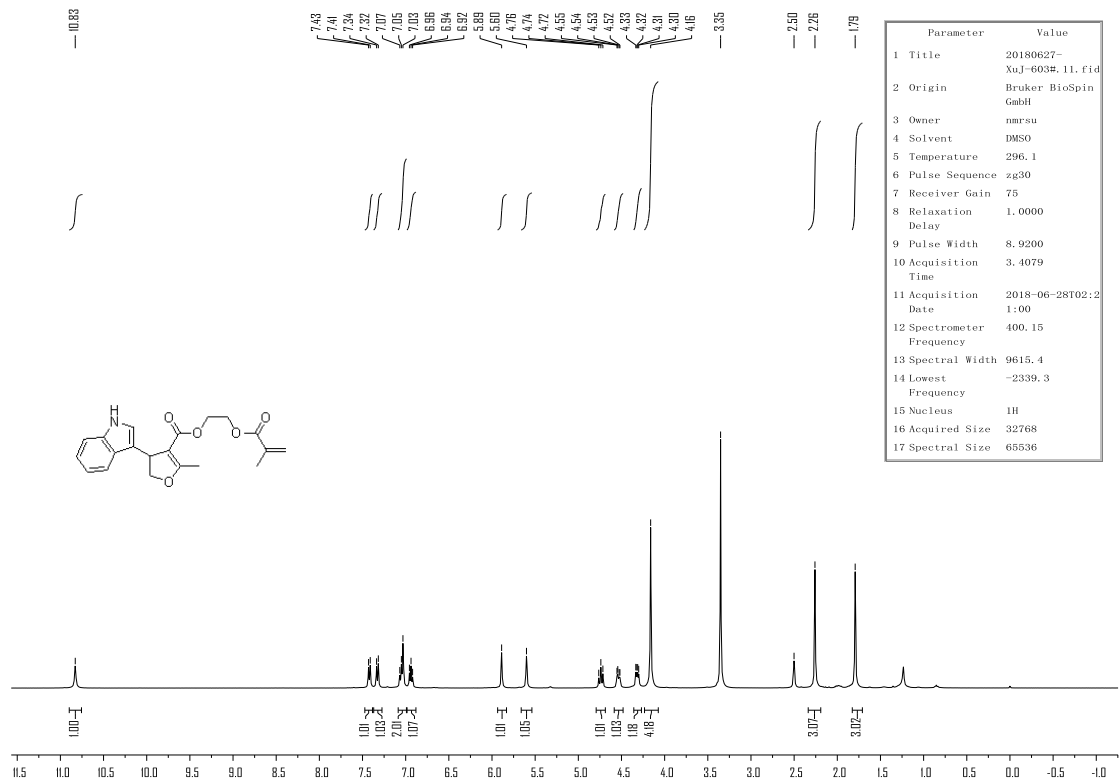
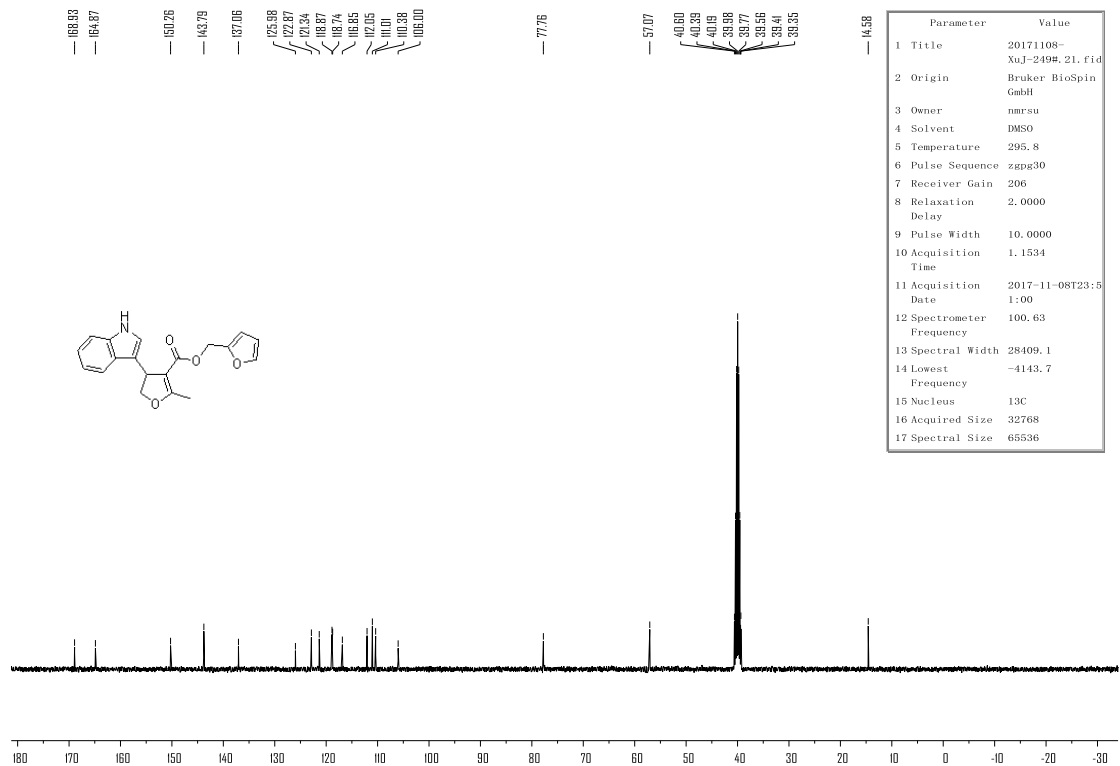


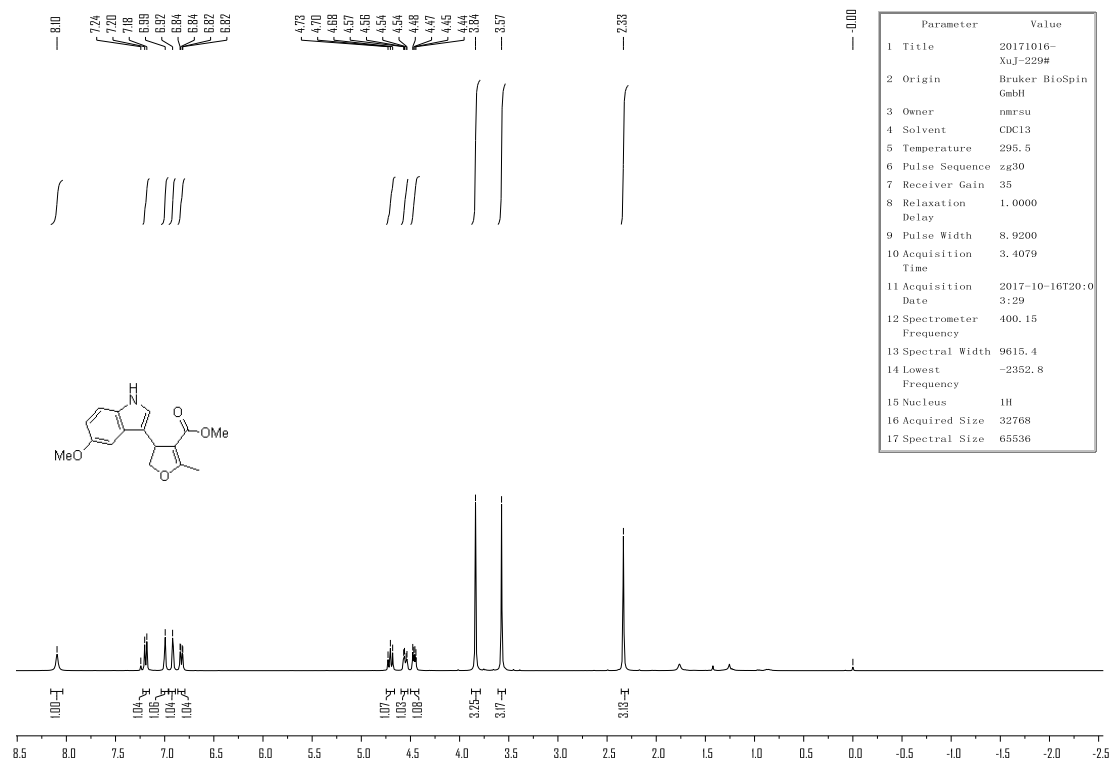
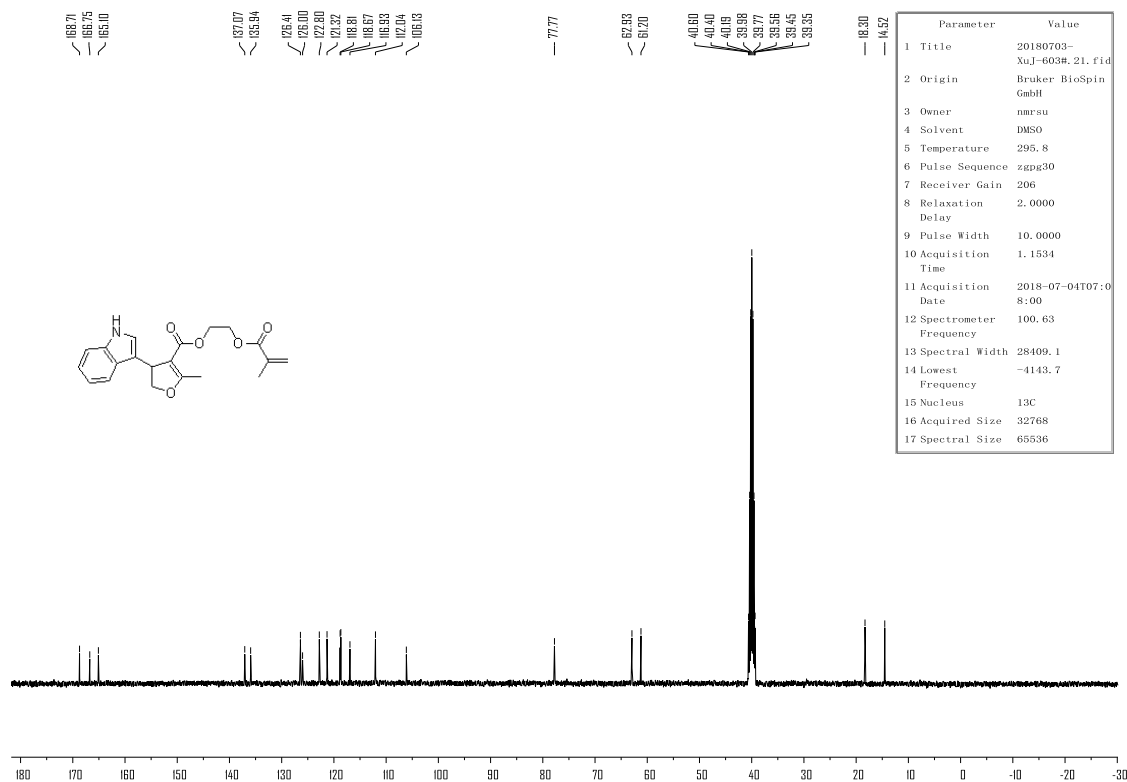


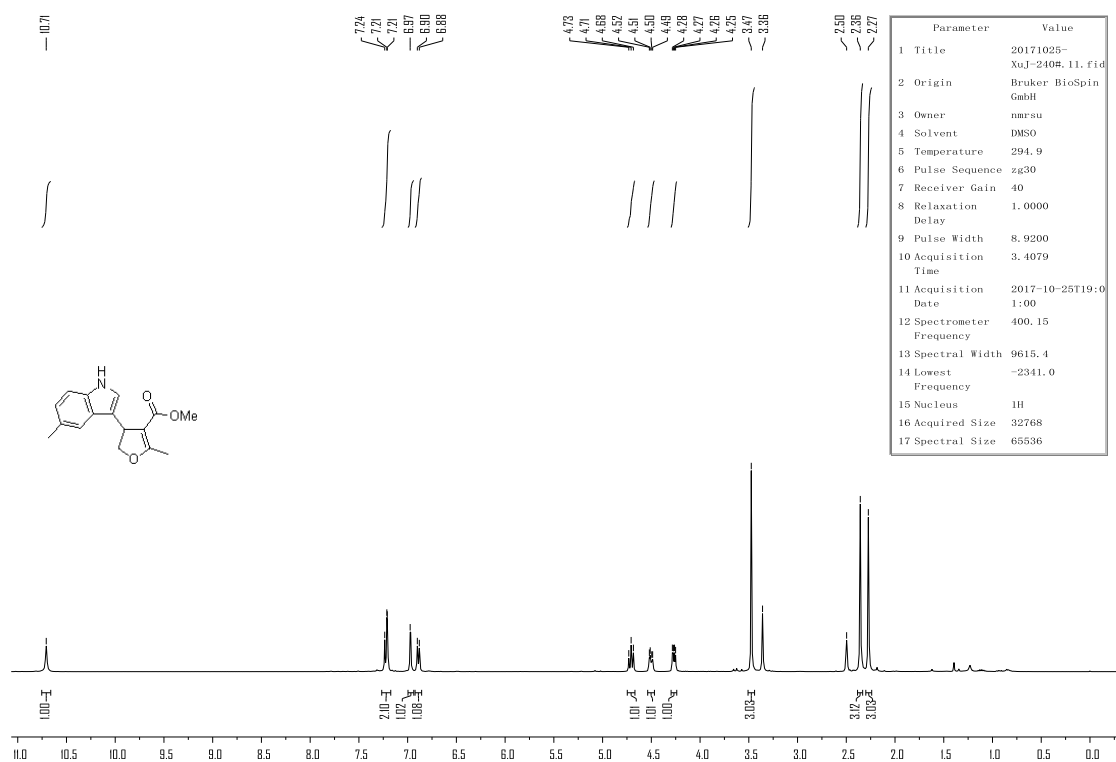
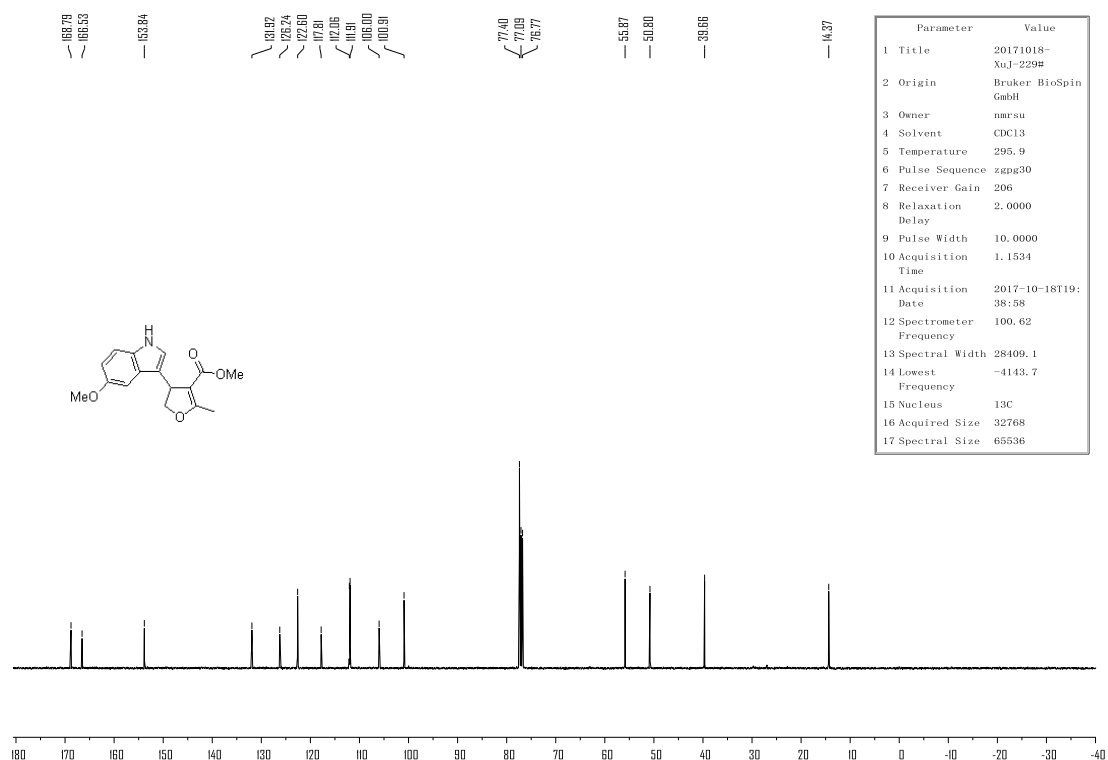


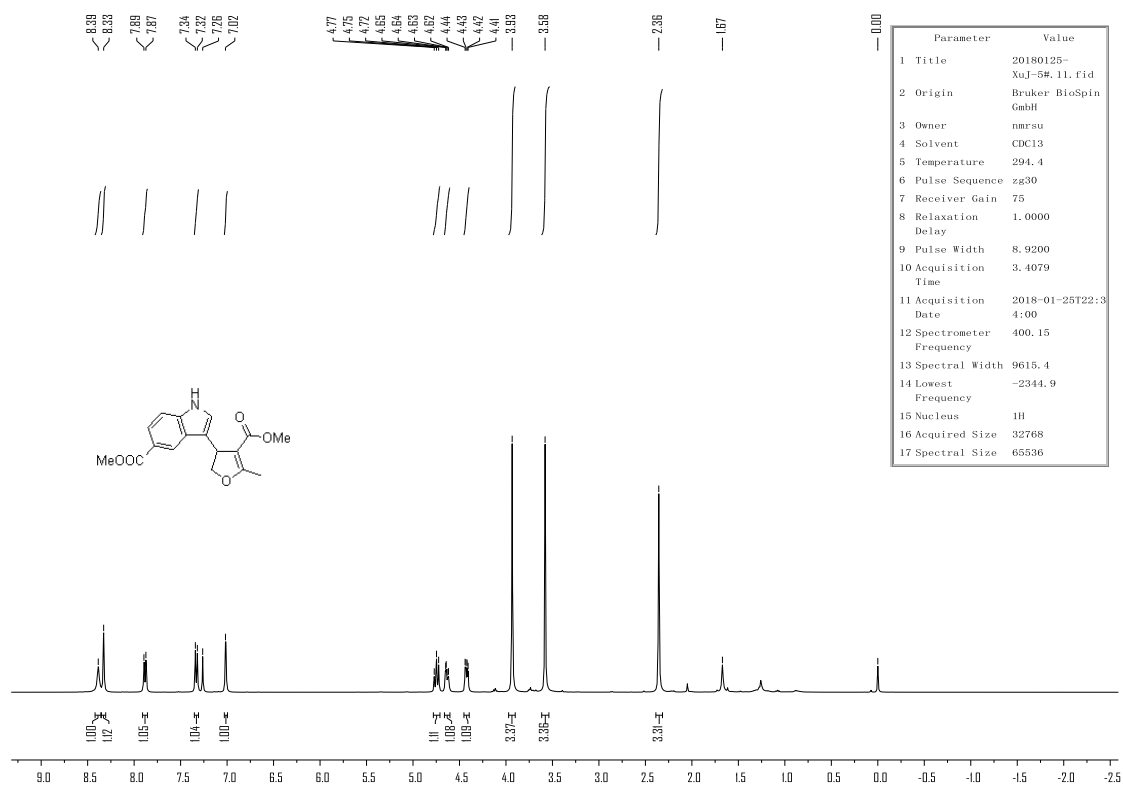
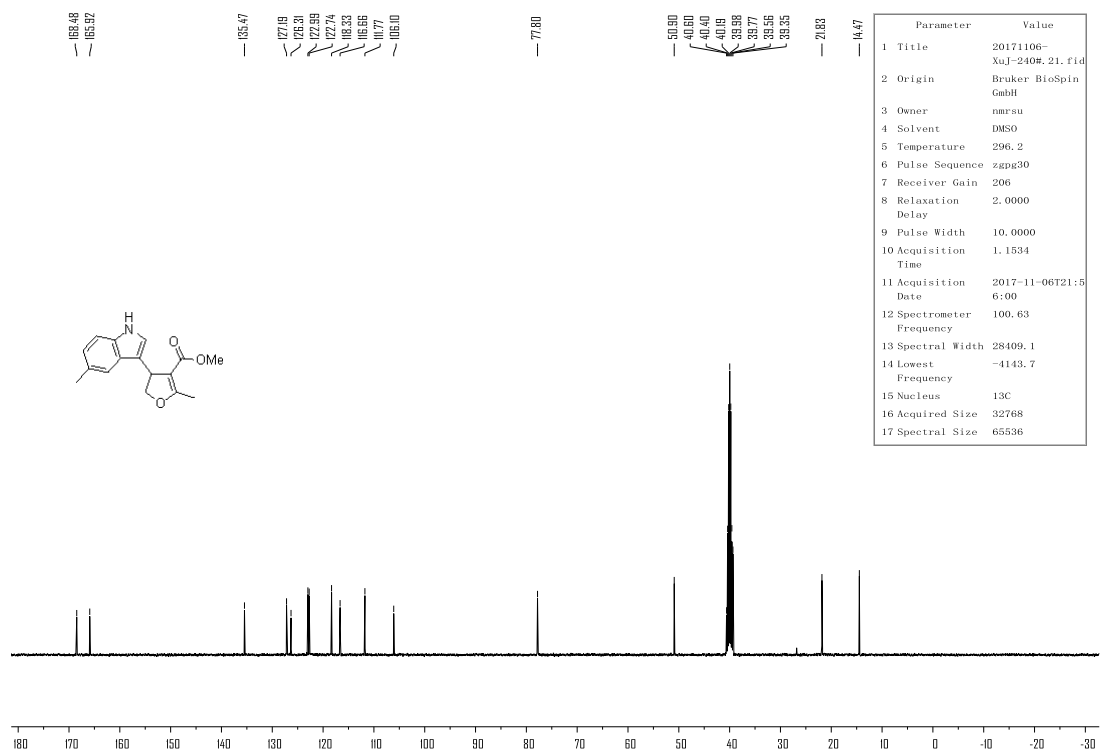


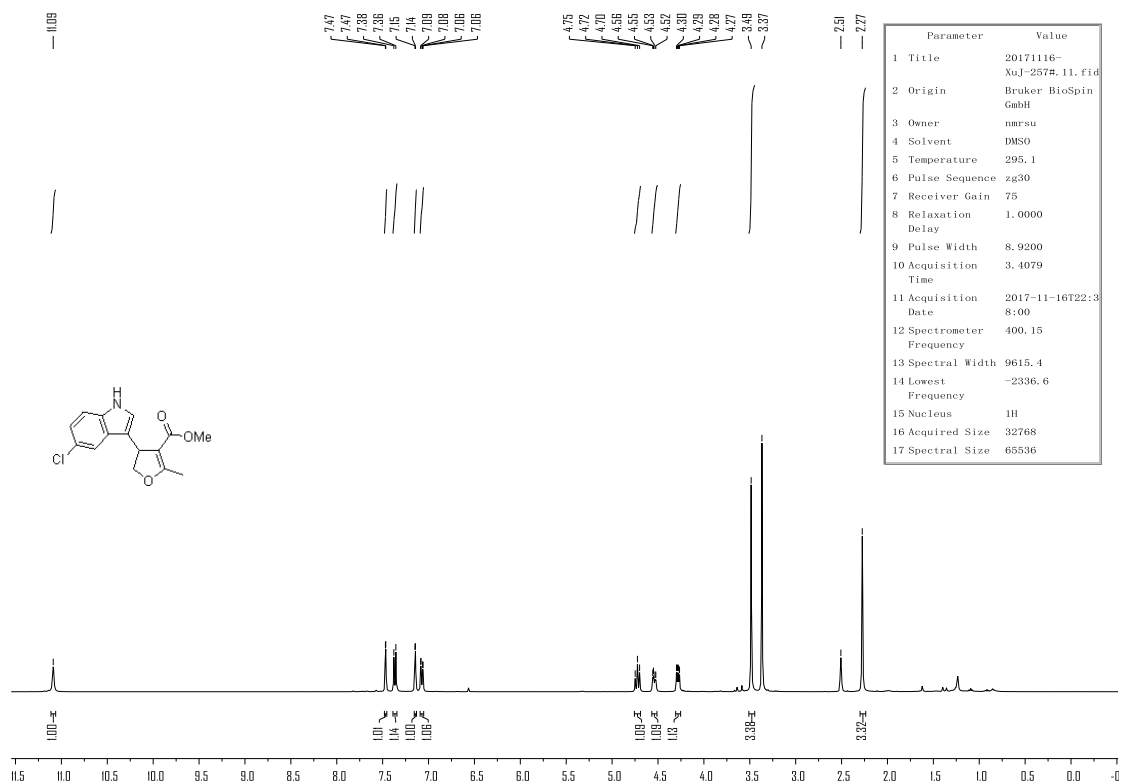
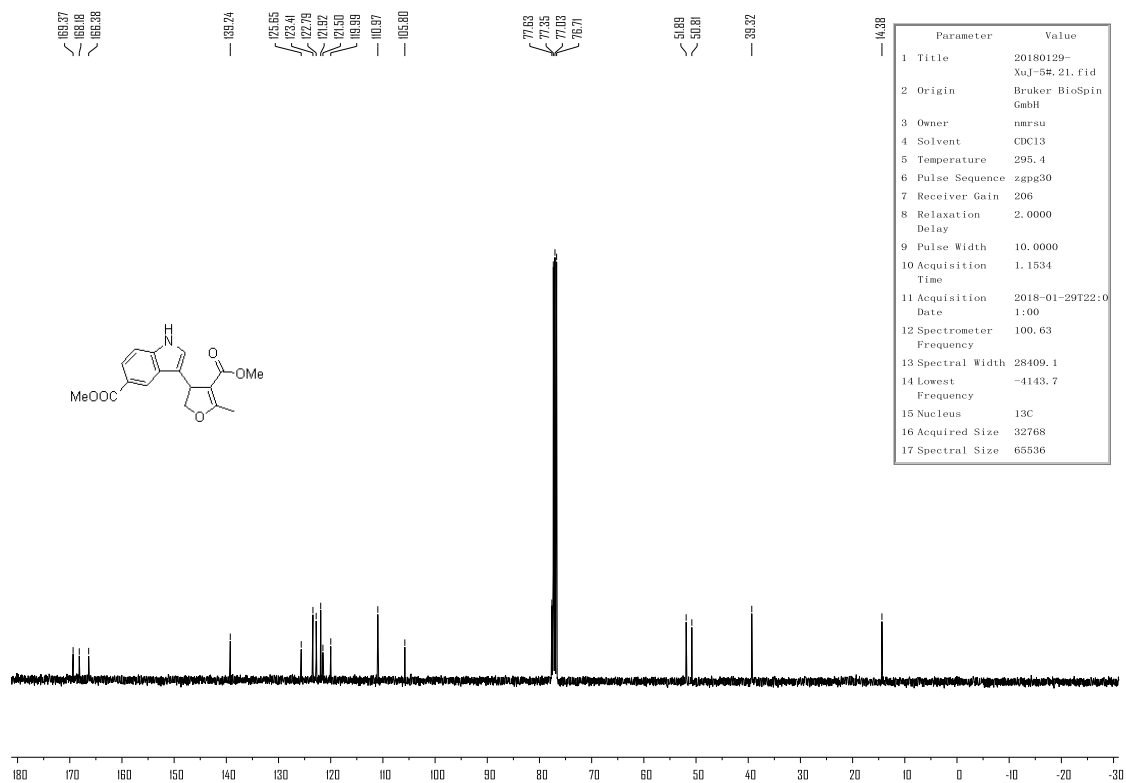


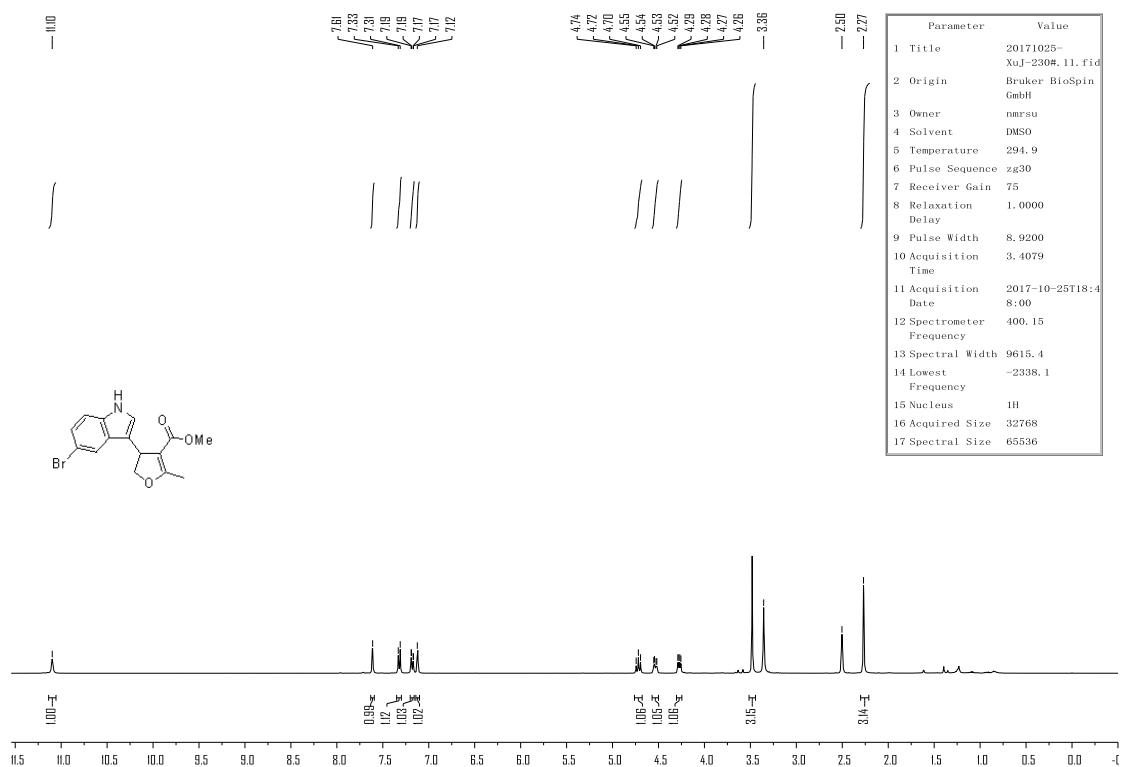
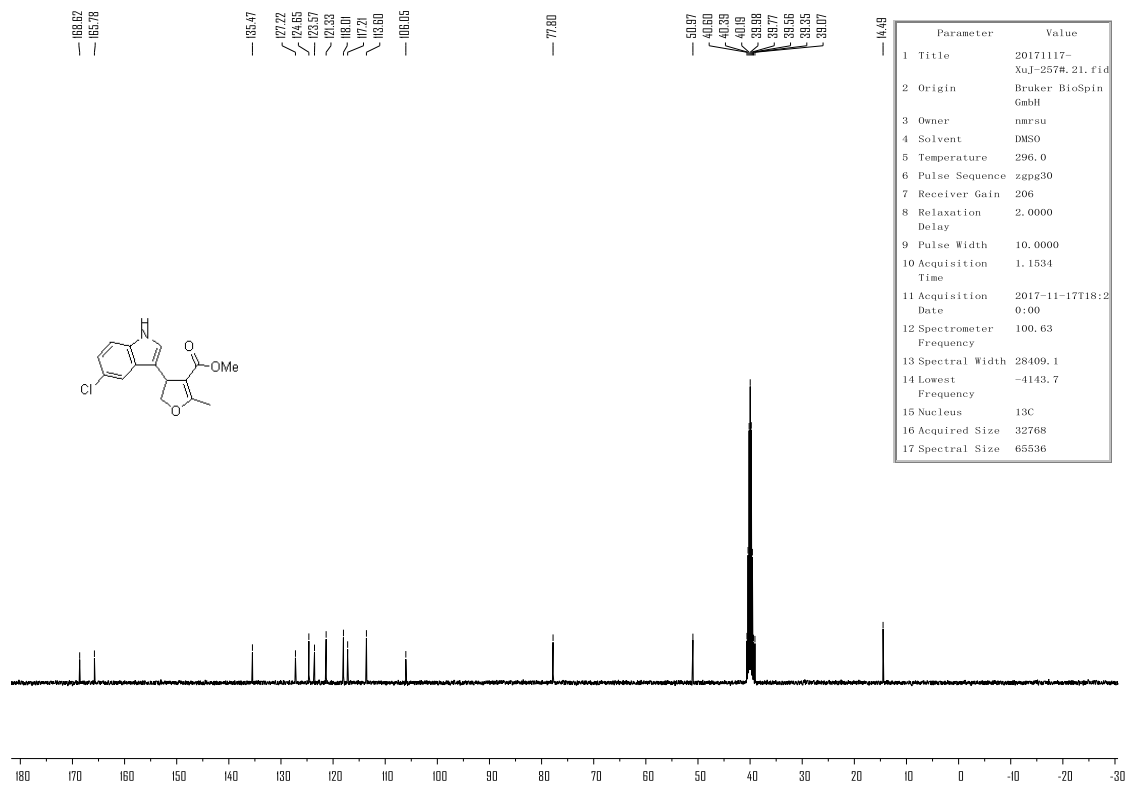


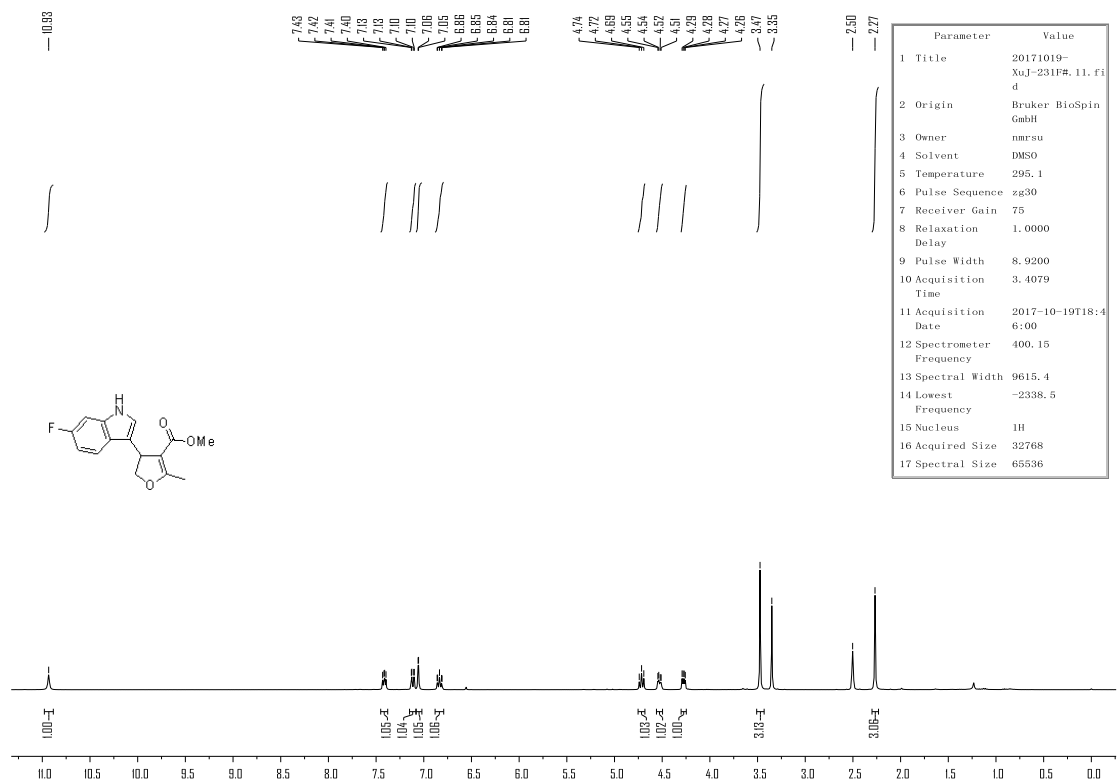
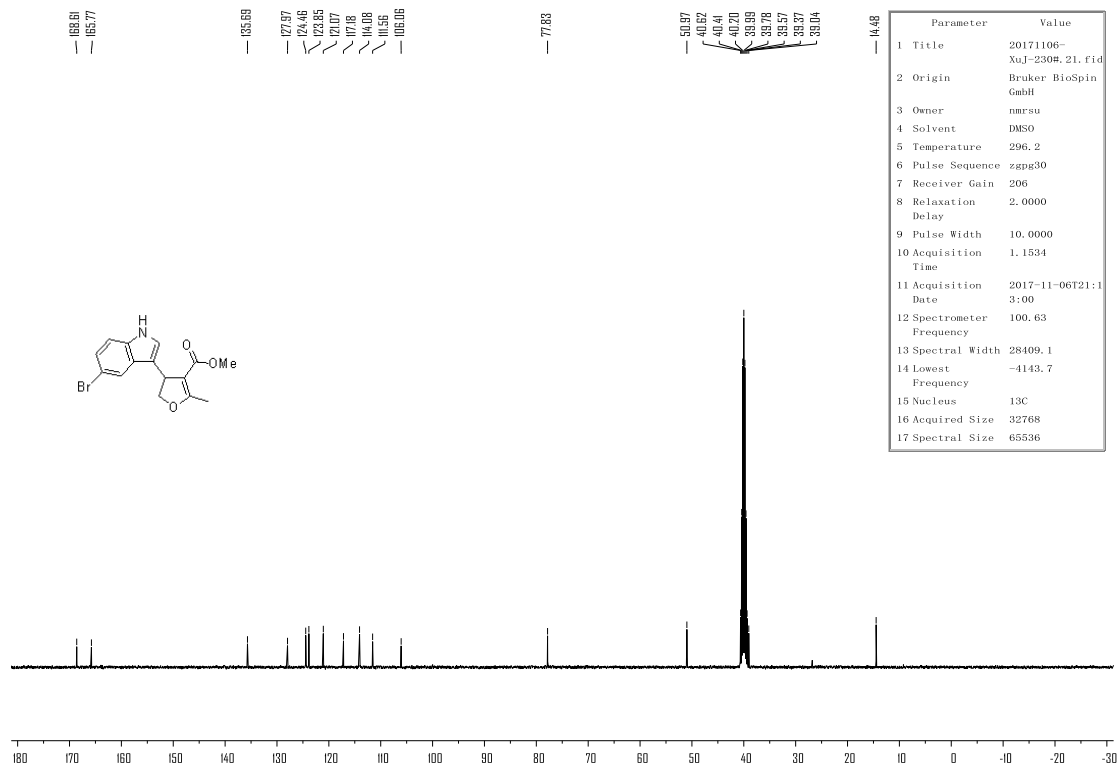


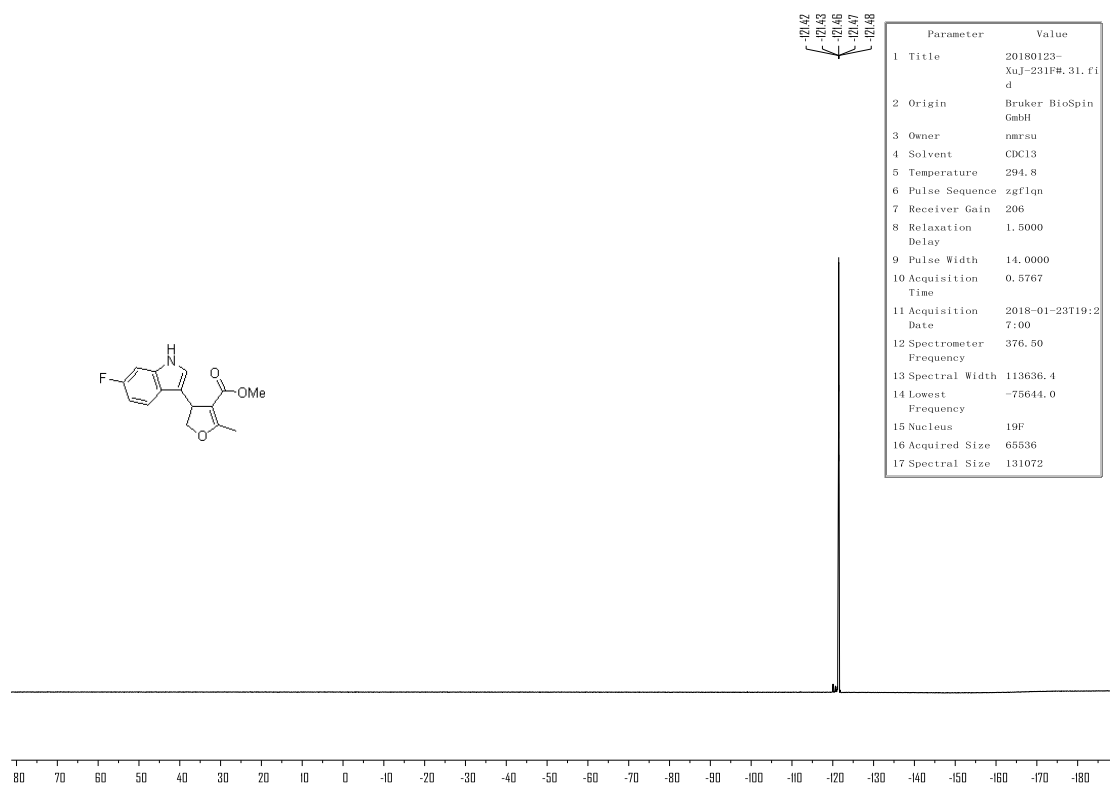
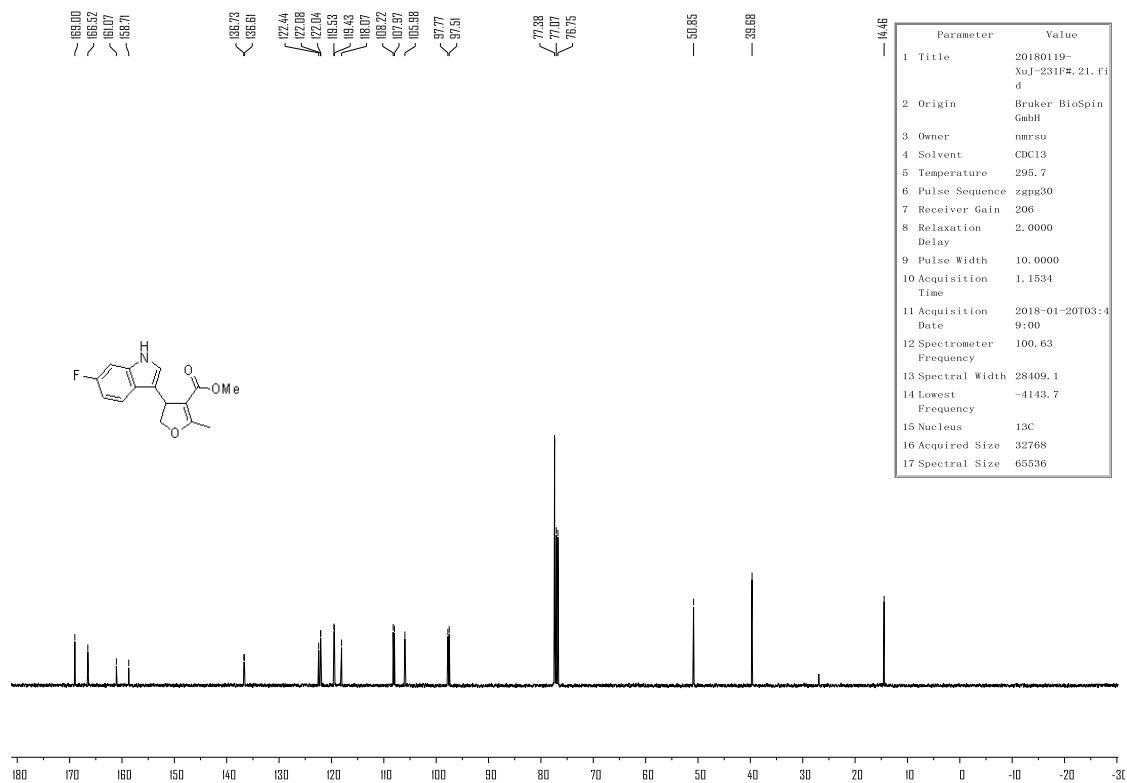


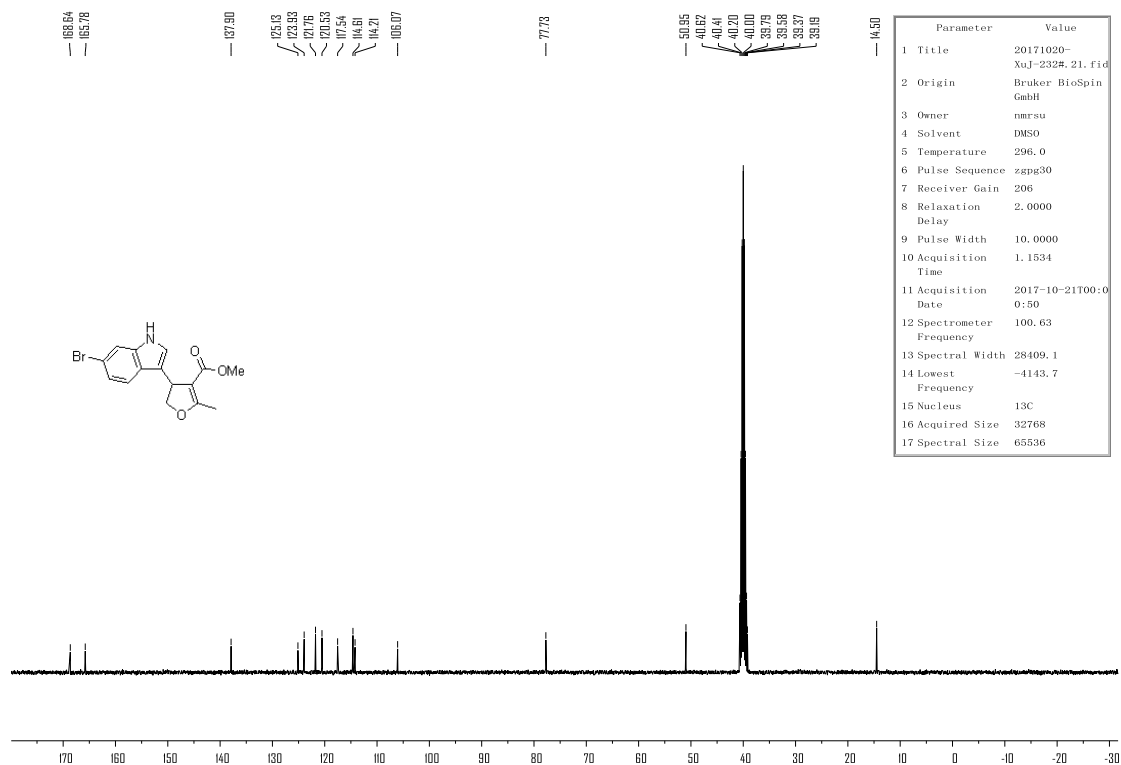
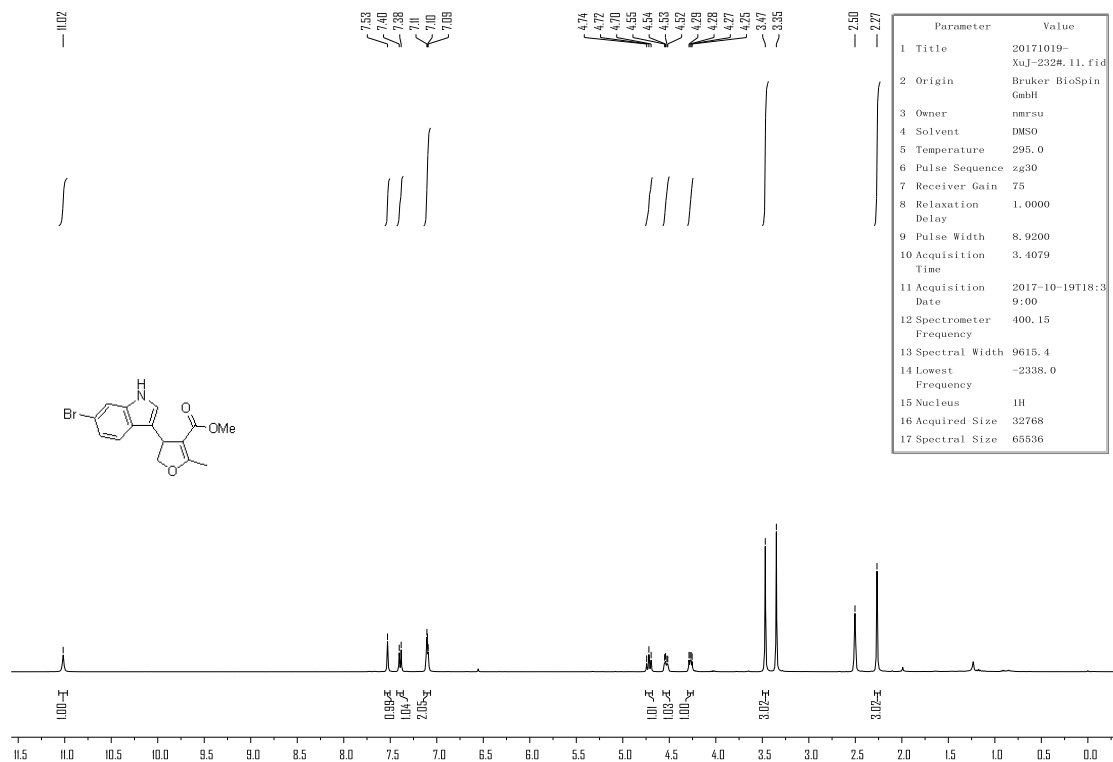


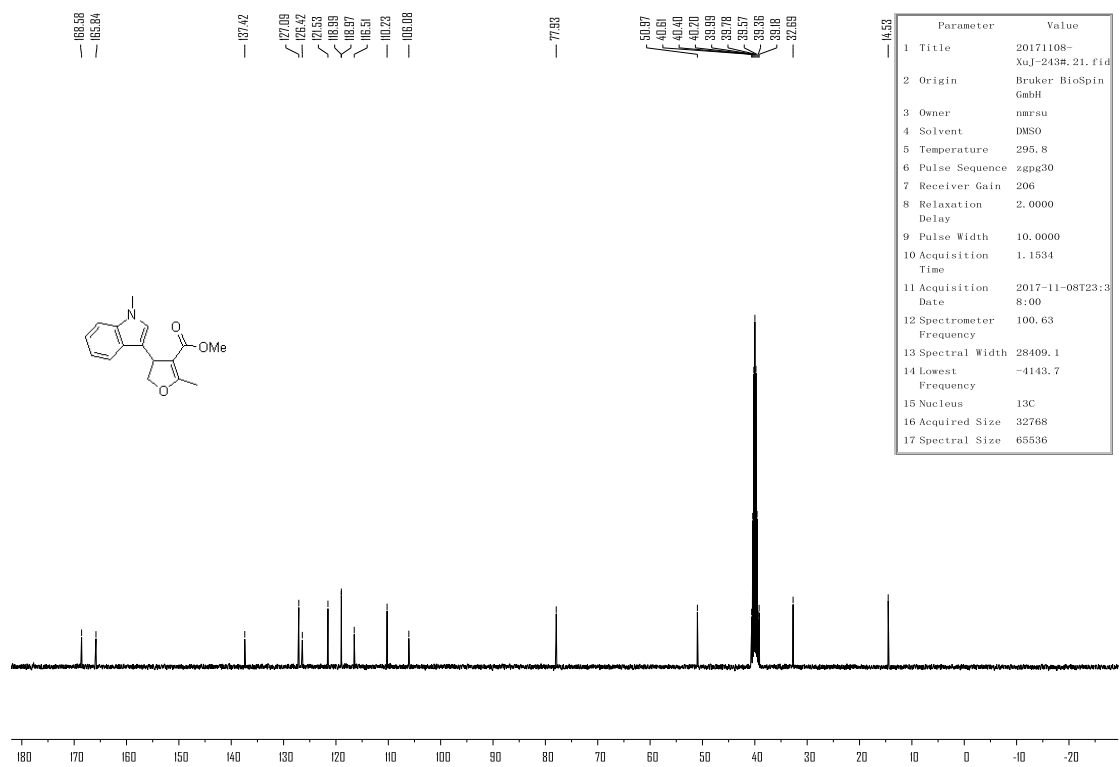
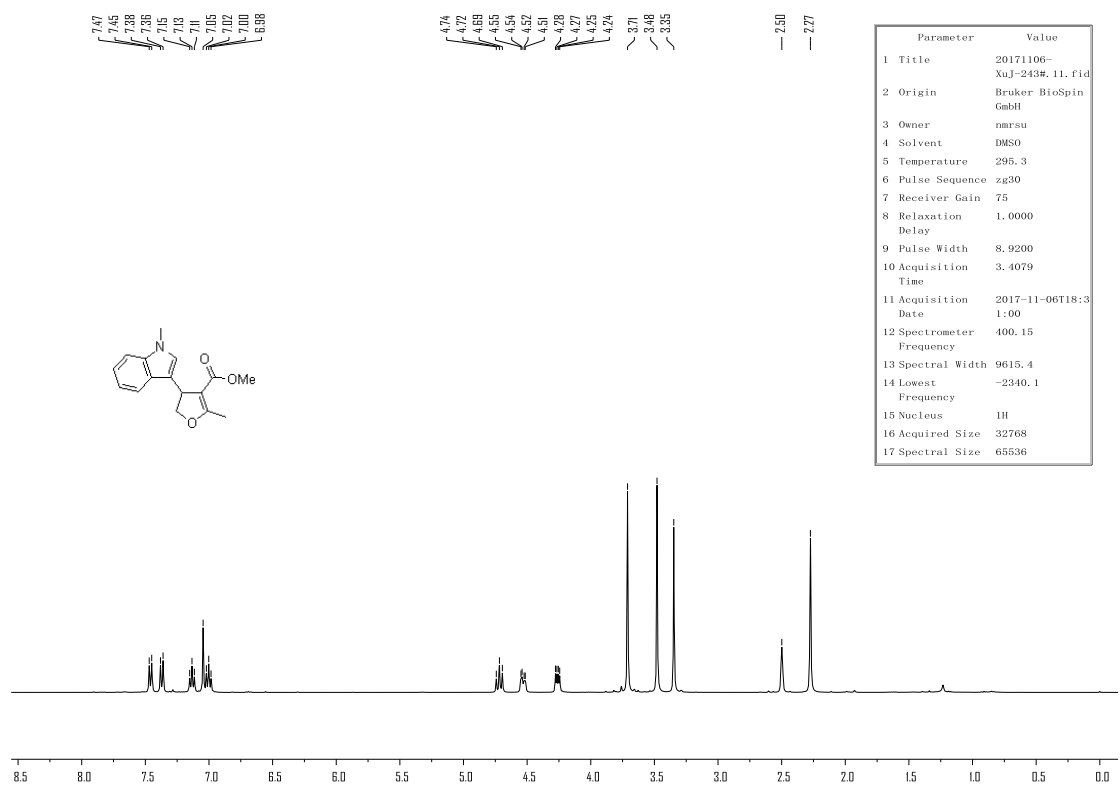


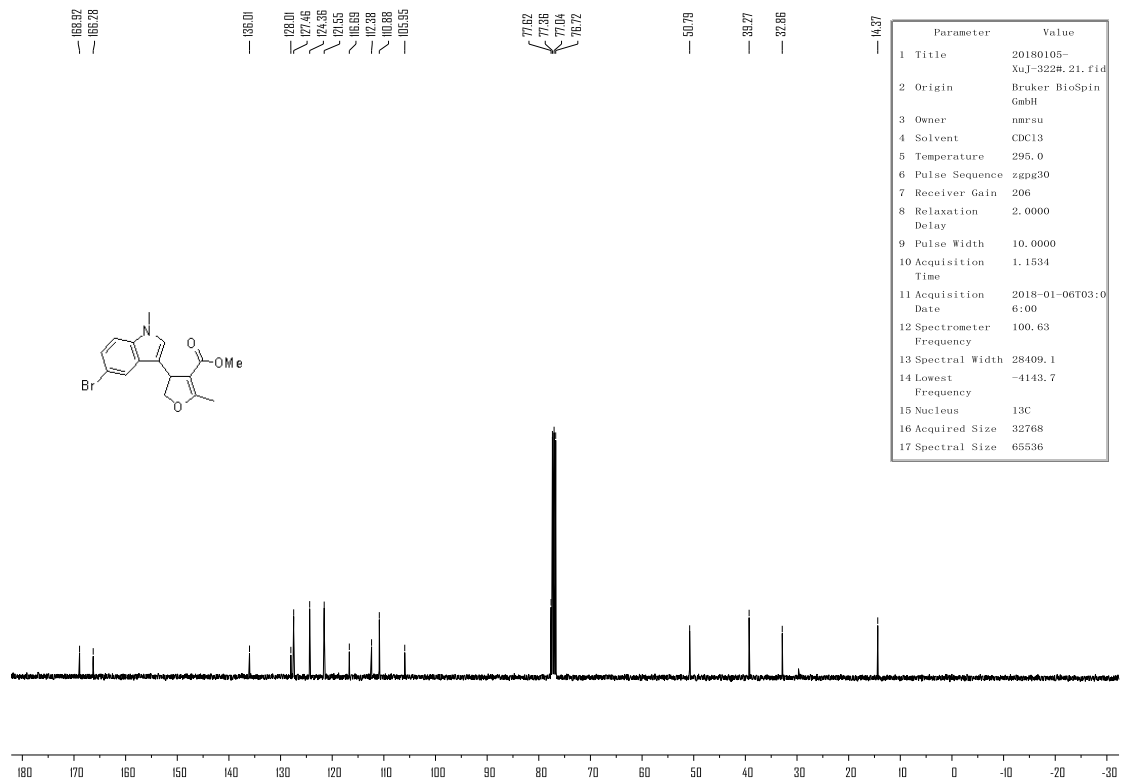
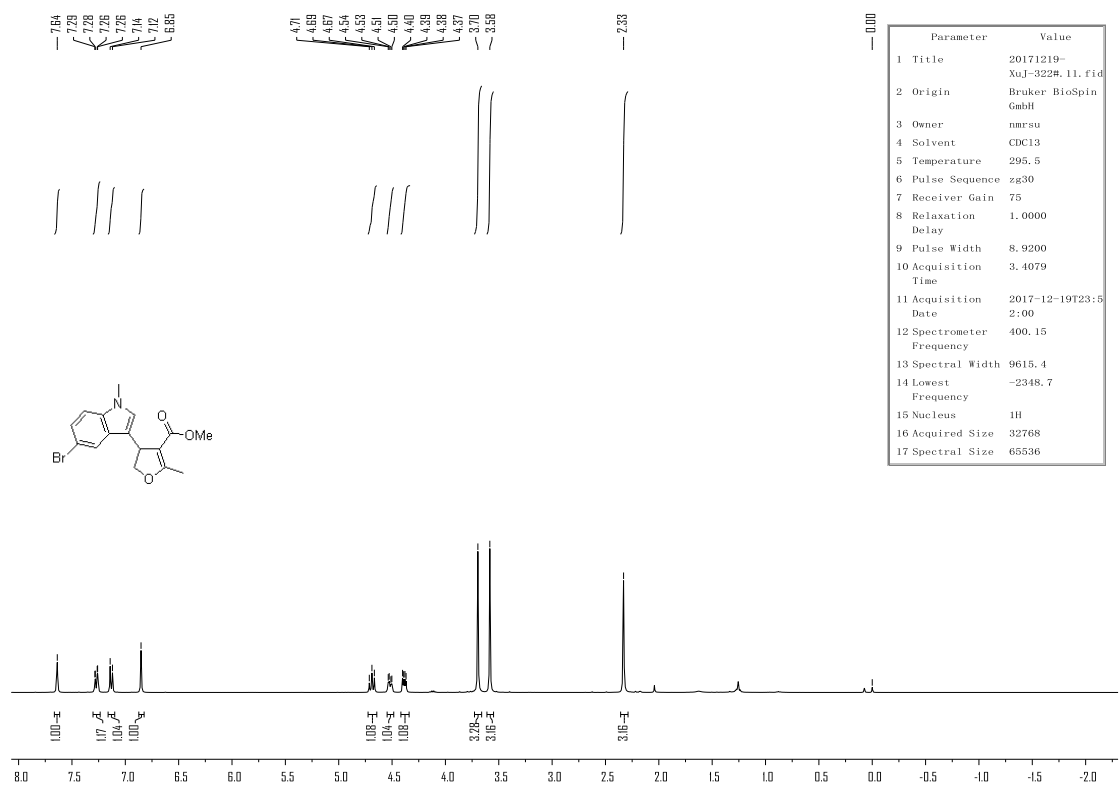


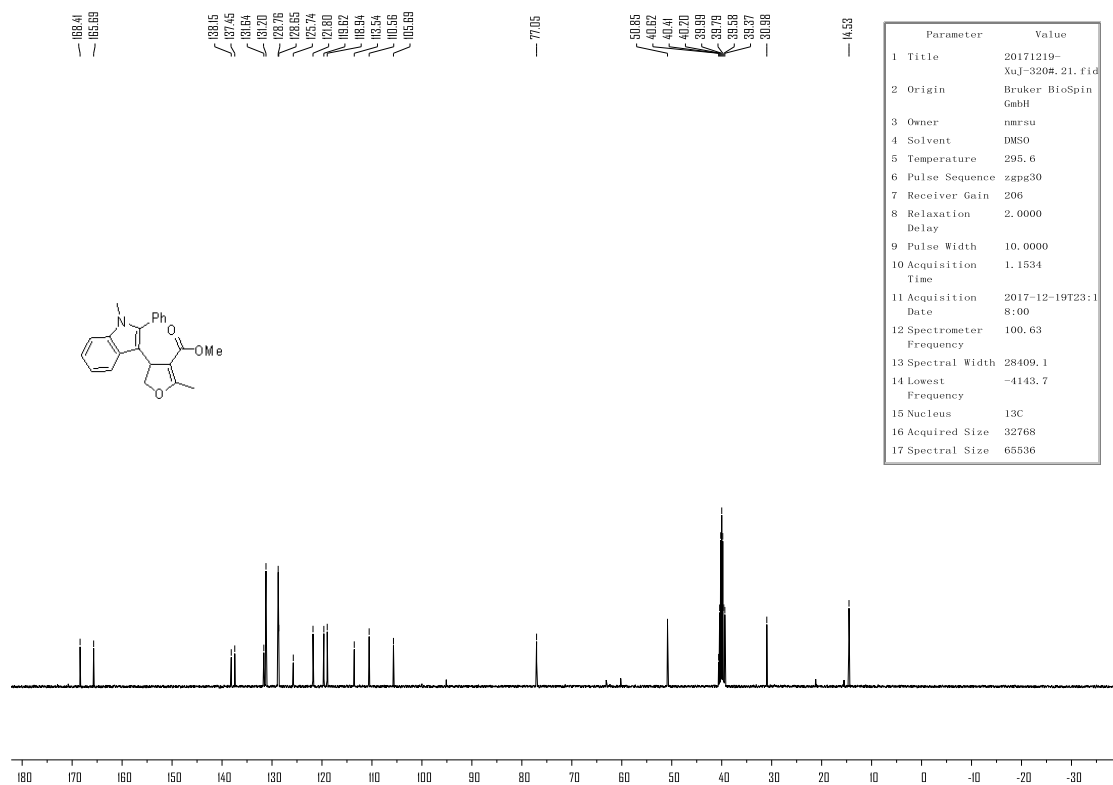
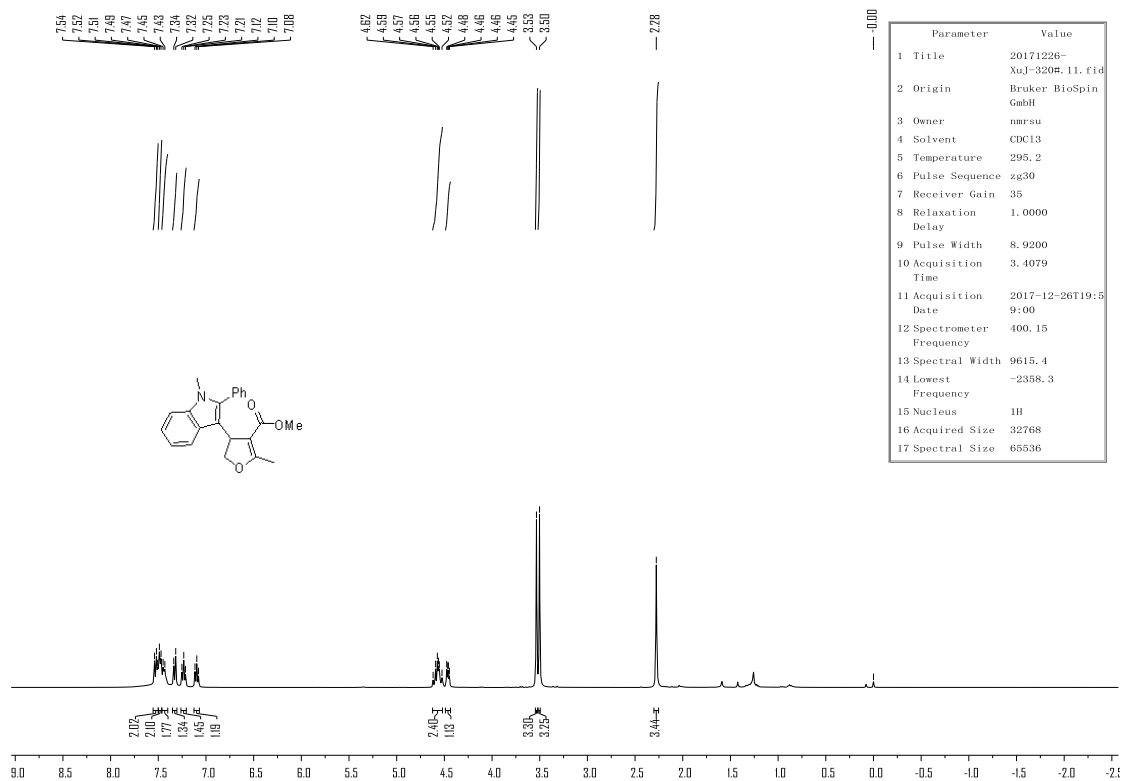


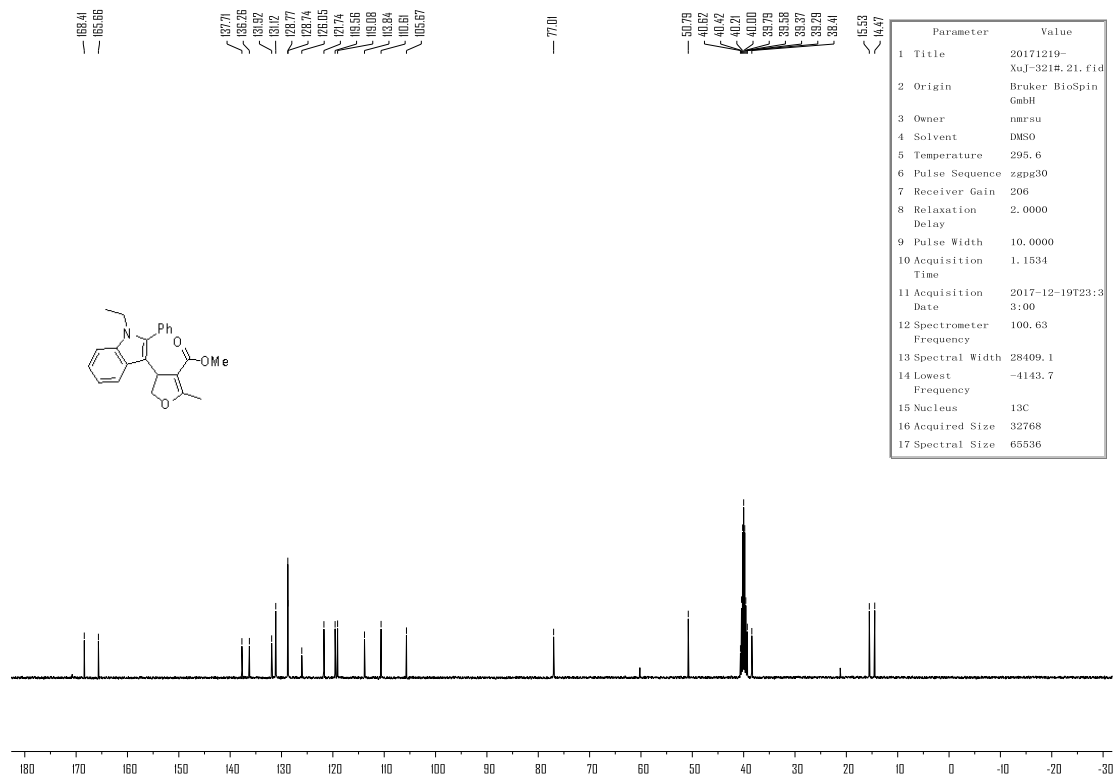
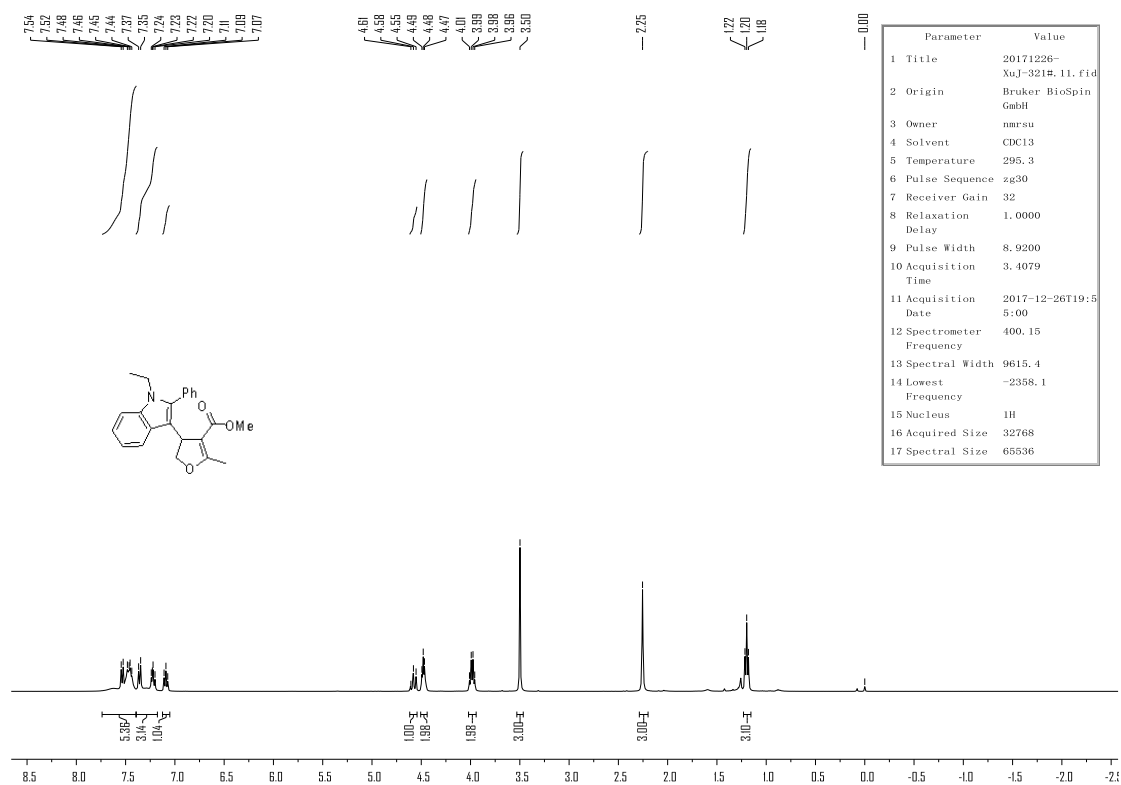


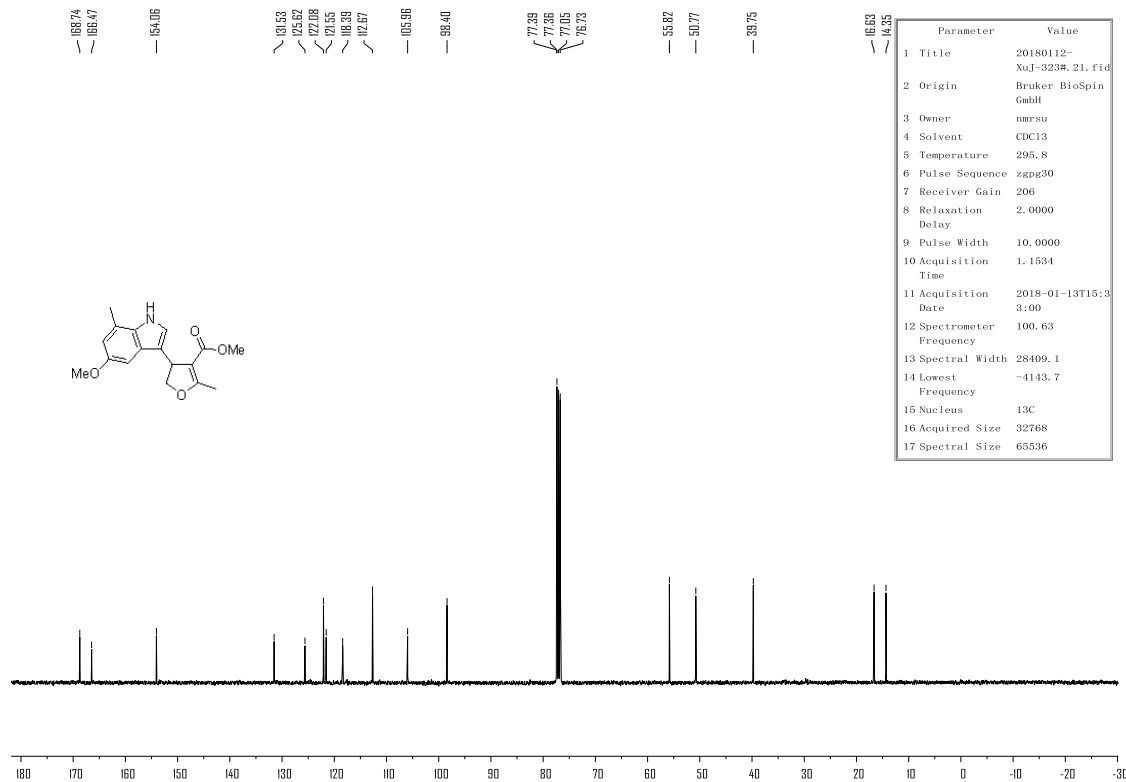
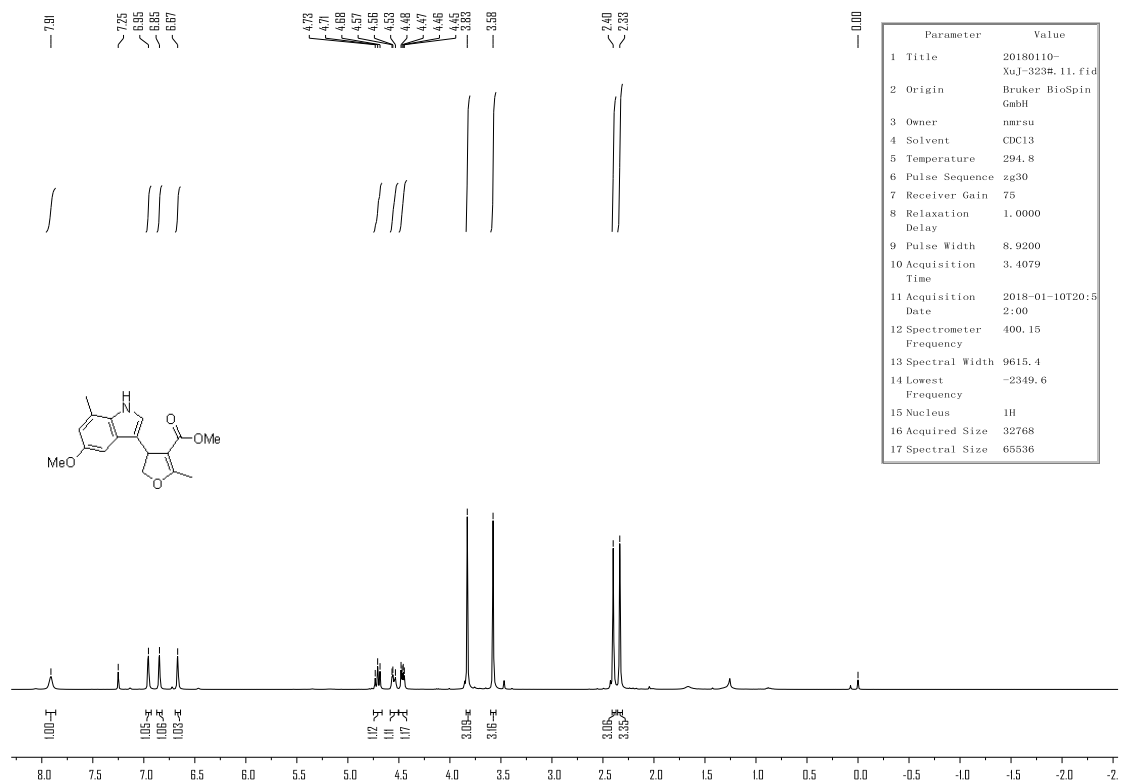


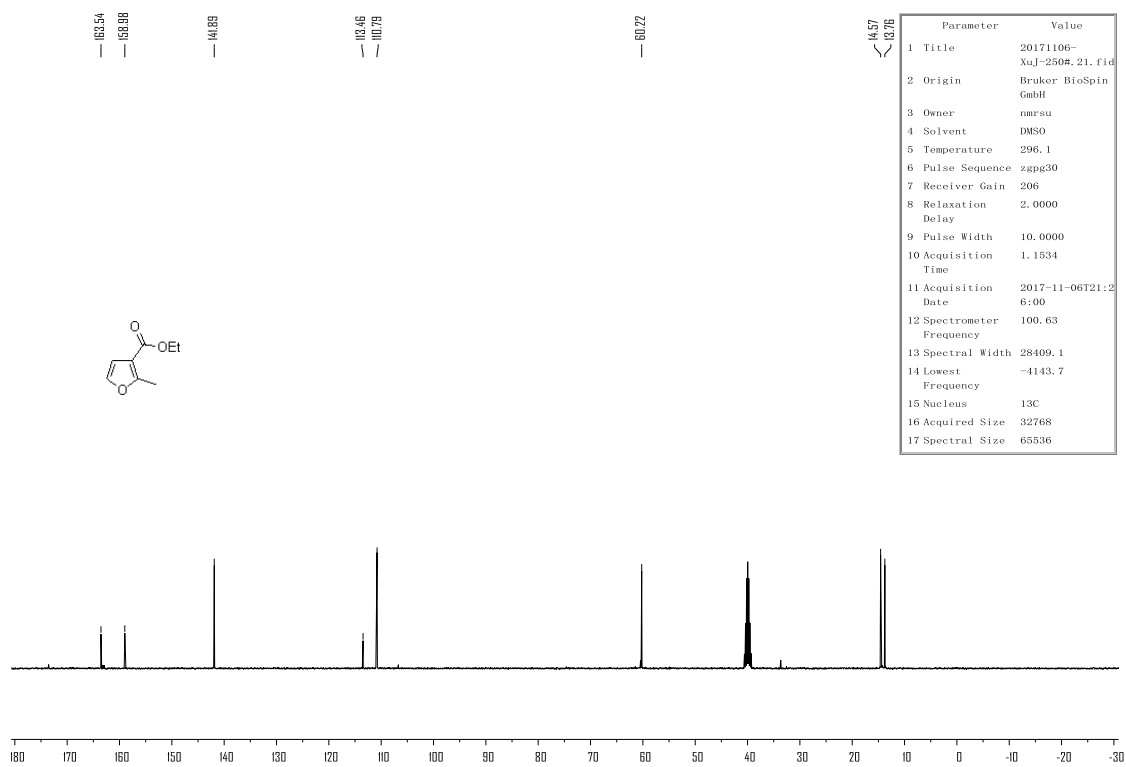
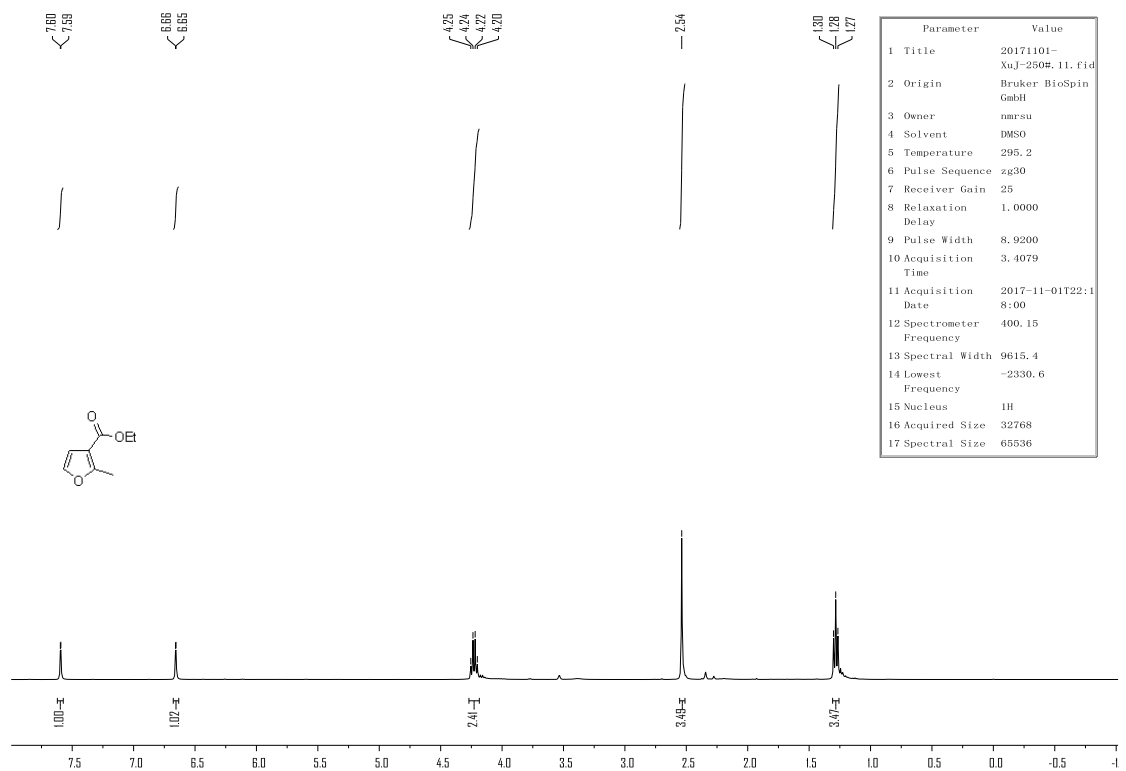


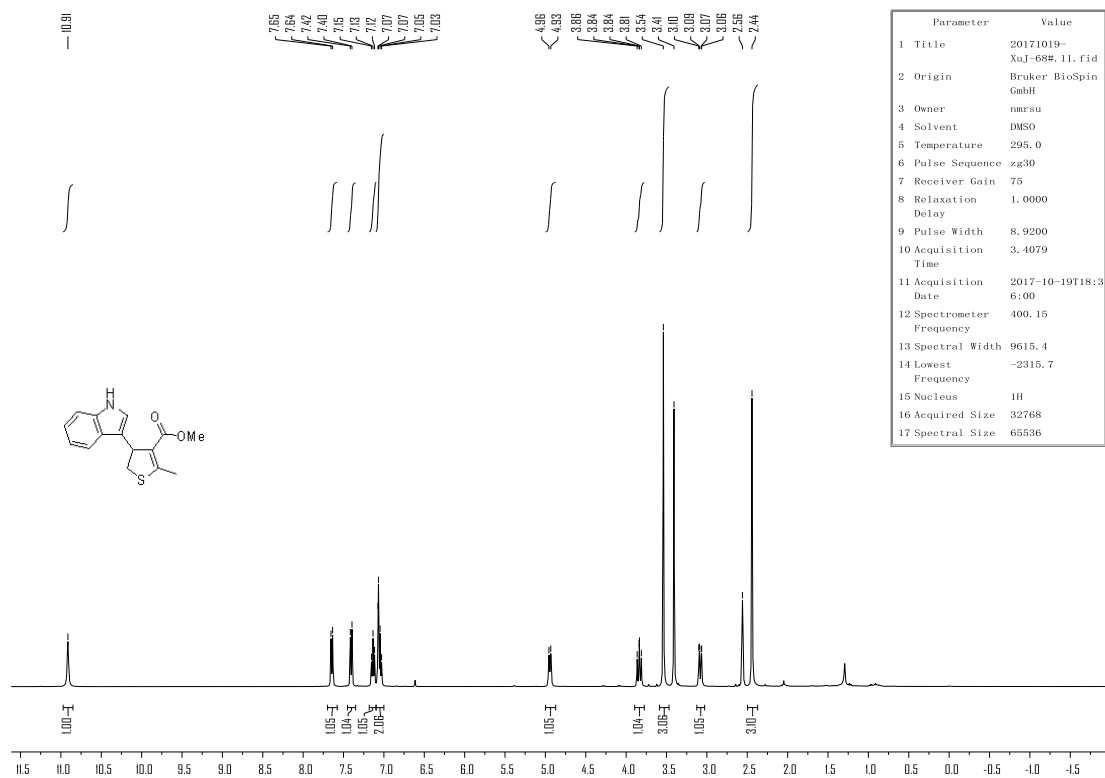




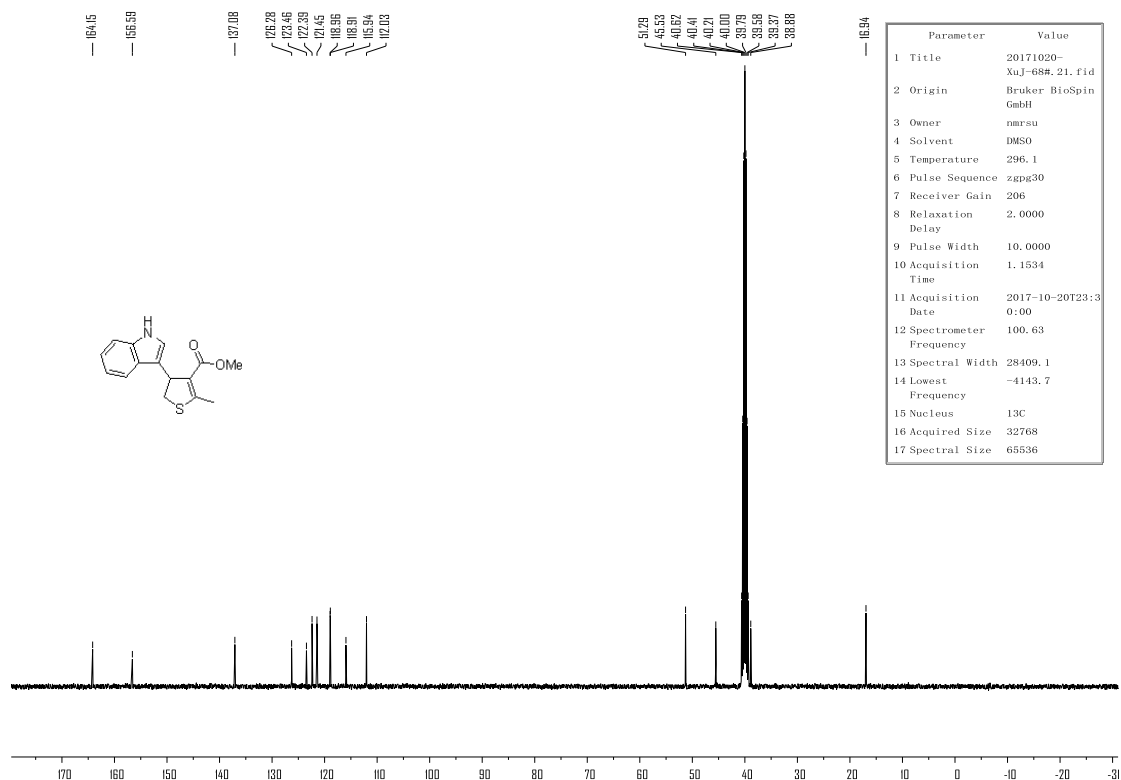








Parameter	Value
1 Title	20171019-XuJ-68#.11.fid
2 Origin	Bruker BioSpin GmbH
3 Owner	nmsu
4 Solvent	DMSO
5 Temperature	295.0
6 Pulse Sequence	zg30
7 Receiver Gain	75
8 Relaxation Delay	1.0000
9 Pulse Width	8.9200
10 Acquisition Time	3.4079
11 Acquisition Date	2017-10-19T18:36:00
12 Spectrometer Frequency	400.15
13 Spectral Width	9615.4
14 Lowest Frequency	-2315.7
15 Nucleus	1H
16 Acquired Size	32768
17 Spectral Size	65536



Parameter	Value
1 Title	20171020-XuJ-68#.21.fid
2 Origin	Bruker BioSpin GmbH
3 Owner	nmsu
4 Solvent	DMSO
5 Temperature	296.1
6 Pulse Sequence	zgpg30
7 Receiver Gain	206
8 Relaxation Delay	2.0000
9 Pulse Width	10.0000
10 Acquisition Time	1.1534
11 Acquisition Date	2017-10-20T23:30:00
12 Spectrometer Frequency	100.63
13 Spectral Width	28409.1
14 Lowest Frequency	-4143.7
15 Nucleus	13C
16 Acquired Size	32768
17 Spectral Size	65536

