

Toward C2-nitrogenated chromones by copper-catalyzed β - C(sp²)-H *N*-heteroarylation of enaminones

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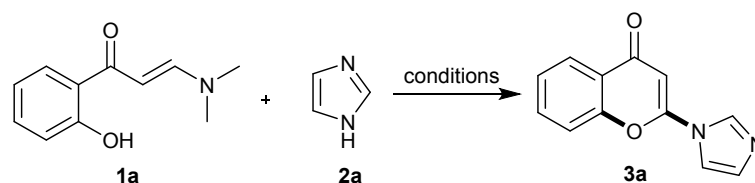
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General experimental information

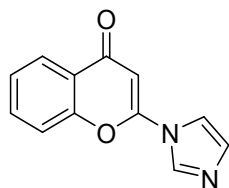
All experiments were carried out under air atmosphere. All enaminones **1** were synthesized following literature method,¹ and other chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. The ¹H NMR and ¹³C NMR were recorded in 400 MHz apparatus using CDCl₃ or DMSO-*d*₆ as solvent, the frequency for ¹H NMR and ¹³C NMR test are 400 MHz and 100MHz, respectively. The chemical shifts were reported in ppm using TMS as internal standard. HRMS results were tested under ESI model in a spectrometer equipped with TOF analyzer. The melting points for solid samples were recorded in an X-4A apparatus.

Table 1 Optimization on the reaction conditions for 2-imidazolyl chromone^a

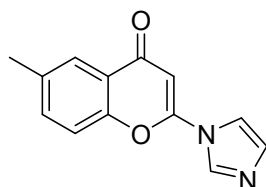
entry	catalyst	oxidant	base	solvent	Yield(%) ^b
1 ^c	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	trace
2	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	40
3	-	PhI(OAc) ₂	Na ₂ CO ₃	DMF	0
4	CuI	-	Na ₂ CO ₃	DMF	trace
5 ^d	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	26
6 ^e	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	38
7	CuI	KIO ₃	Na ₂ CO ₃	DMF	0
8	CuI	K ₂ S ₂ O ₈	Na ₂ CO ₃	DMF	0
9	CuI	TBHP (70% aq.)	Na ₂ CO ₃	DMF	0
10	CuI	BPO	Na ₂ CO ₃	DMF	<10
11 ^f	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	51
12 ^g	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	30
13 ^f	Cu ₂ O	PhI(OAc) ₂	Na ₂ CO ₃	DMF	12
14 ^f	CuSO ₄	PhI(OAc) ₂	Na ₂ CO ₃	DMF	26
15 ^f	Cu(OAc) ₂	PhI(OAc) ₂	Na ₂ CO ₃	DMF	30
16 ^f	CuBr ₂	PhI(OAc) ₂	Na ₂ CO ₃	DMF	34
17 ^{f,h}	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	46
18 ^f	CuI	PhI(OAc) ₂	Et ₃ N	DMF	48
19 ^f	CuI	PhI(OAc) ₂	DBU	DMF	21
20 ^f	CuI	PhI(OAc) ₂	NaHCO ₃	DMF	30
21 ^f	CuI	PhI(OAc) ₂	NaOBu ^t	DMF	29
22 ^f	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMSO	45
23 ^f	CuI	PhI(OAc) ₂	Na ₂ CO ₃	dioxane	trace
24 ^f	CuI	PhI(OAc) ₂	Na ₂ CO ₃	PhH	0
25 ^f	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DCE	0
26 ^{f,i}	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	45
27 ^{f,j}	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	38
28 ^{f,k}	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	63
29 ^{f,l}	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	73
30 ^{f,m}	CuI	PhI(OAc) ₂	Na ₂ CO ₃	DMF	70

^aGeneral conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), catalyst (20 mol%), oxidant (2 equiv), base (2 equiv), I₂ (20 mol%) in 2 mL solvent, heated at 120 °C for 12 h. ^bYield of isolated product based on **1a**. ^cWithout I₂. ^dWith 10 mol% I₂. ^eWith 40 mol% I₂. ^fWith 4 equiv PhI(OAc)₂. ^gWith 5 equiv PhI(OAc)₂. ^hWith 10 mol% CuI. ⁱReaction at 110 °C. ^jReaction at 130 °C. ^kWith 0.3 mmol **2a**. ^lWith 0.4 mmol **2a**. ^mWith 0.5 mmol **2a**.

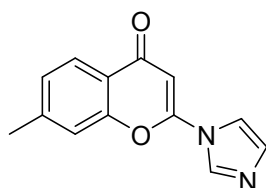
Characterization data for products 3



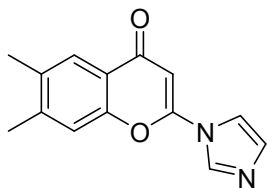
2-(1*H*-Imidazol-1-yl)-4*H*-chromen-4-one (3a).² White solid; mp: 191-192 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 10.8 Hz, 2 H), 7.77–7.72 (m, 1 H), 7.55 (d, *J* = 8.4 Hz, 1 H), 7.48 (d, *J* = 6.2 Hz, 2 H), 7.27 (s, 1 H), 6.41 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.7, 154.2, 153.4, 134.8, 134.3, 131.8, 126.2, 126.0, 123.4, 117.6, 115.9, 97.1.



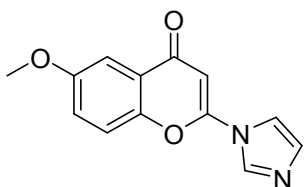
2-(1*H*-Imidazol-1-yl)-6-methyl-4*H*-chromen-4-one (3b). White solid; mp: 125 -126 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.22 (s, 1 H), 7.99 (s, 1 H), 7.55 (d, *J* = 8.4 Hz, 1 H), 7.45 (d, *J* = 10.6 Hz, 2 H), 7.26 (s, 1 H), 6.38 (s, 1 H), 2.48 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.9, 153.3, 152.5, 136.4, 135.4, 134.8, 131.7, 125.4, 123.0, 117.3, 115.9, 97.0, 20.92; HRMS (ESI) *m/z* calcd for C₁₃H₁₀N₂NaO₂⁺ (*M*+Na)⁺ 249.0634, found 249.0640.



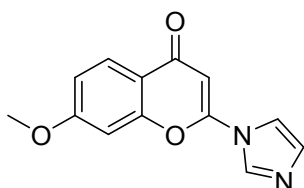
2-(1*H*-Imidazol-1-yl)-7-methyl-4*H*-chromen-4-one (3c). White solid; mp: 218-219 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.21 (s, 1 H), 8.10 (d, *J* = 8.1 Hz, 1 H), 7.46 (s, 1 H), 7.35 (s, 1 H), 7.31–7.26 (m, 2 H), 6.35 (s, 1 H), 2.53 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.7, 154.4, 153.2, 145.9, 134.8, 131.8, 127.6, 125.8, 121.1, 117.4, 115.9, 97.1, 21.8; HRMS (ESI) *m/z* calcd for C₁₃H₁₀N₂NaO₂⁺ (*M*+Na)⁺ 249.0634, found 249.0638.



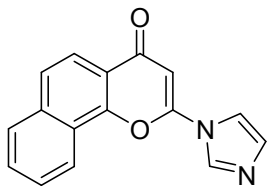
2-(1*H*-Imidazol-1-yl)-6,7-dimethyl-4*H*-chromen-4-one (3d). White solid; mp: 212-213 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.19 (s, 1 H), 7.94 (s, 1 H), 7.45 (s, 1 H), 7.32 (s, 1 H), 7.26 (s, 1 H), 6.33 (s, 1 H), 2.42 (s, 3 H), 2.38 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.9, 153.1, 152.8, 144.9, 135.6, 134.8, 131.7, 125.7, 121.2, 117.8, 115.9, 97.0, 20.5, 19.3; HRMS (ESI) *m/z* calcd for C₁₄H₁₂N₂NaO₂⁺ (M+Na)⁺ 263.0791 found 263.0795.



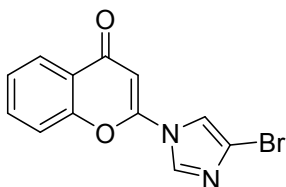
2-(1*H*-Imidazol-1-yl)-6-methoxy-4*H*-chromen-4-one (3e). White solid; mp: 184-185 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.21 (s, 1 H), 7.58 (d, *J* = 3.0 Hz, 1 H), 7.47 (t, *J* = 4.4 Hz, 2 H), 7.34–7.29 (m, 1 H), 7.26 (s, 1 H), 6.38 (s, 1 H), 3.91 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.6, 157.7, 153.2, 148.8, 134.8, 131.8, 124.1, 123.9, 118.9, 115.9, 105.6, 96.5, 56.0; HRMS (ESI) *m/z* calcd for C₁₃H₁₀N₂NaO₃⁺ (M+Na)⁺ 265.0584, found 265.0587.



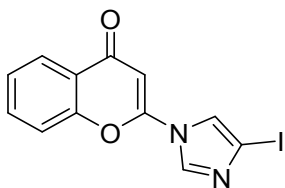
2-(1*H*-Imidazol-1-yl)-7-methoxy-4*H*-chromen-4-one (3f). White solid; mp: 129-130 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.21 (s, 1 H), 8.10 (d, *J* = 8.9 Hz, 1 H), 7.47 (s, 1 H), 7.26 (s, 1 H), 7.05–6.99 (m, 1 H), 6.94 (d, *J* = 2.1 Hz, 1 H), 6.33 (s, 1 H), 3.94 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.2, 164.6, 155.9, 153.1, 134.8, 131.7, 127.3, 117.0, 115.9, 114.9, 100.5, 97.0, 56.0; HRMS (ESI) *m/z* calcd for C₁₃H₁₀N₂NaO₃⁺ (M+Na)⁺ 265.0584, found 265.0593.



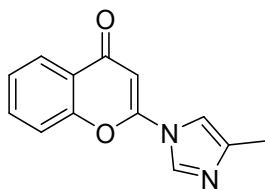
2-(1H-Imidazol-1-yl)-4H-benzo[h]chromen-4-one (3g). Yellow solid; mp: 250-251 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.45–8.39 (m, 1 H), 8.33 (s, 1 H), 8.15 (d, *J* = 8.7 Hz, 1 H), 8.00–7.95 (m, 1 H), 7.85 (d, *J* = 8.7 Hz, 1 H), 7.75 (t, *J* = 3.8 Hz, 2 H), 7.57 (s, 1 H), 7.34 (s, 1 H), 6.52 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.6, 153.0, 151.6, 136.2, 134.8, 132.0, 129.7, 128.4, 127.7, 126.3, 123.2, 121.6, 120.6, 119.9, 116.1, 98.5; HRMS (ESI) *m/z* calcd for C₁₆H₁₀N₂NaO₂⁺ (M+Na)⁺ 285.0634, found 285.0646.



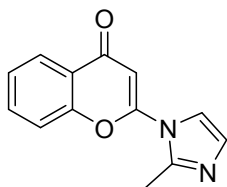
2-(4-Bromo-1H-imidazol-1-yl)-4H-chromen-4-one (3h). Yellow solid; mp: 179-180 °C; ¹H NMR (400 MHz, DMSO): δ 8.63 (s, 1 H), 8.23 (s, 1 H), 8.04 (d, *J* = 7.8 Hz, 1 H), 7.86 (t, *J* = 7.7 Hz, 1 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 6.86 (s, 1 H); ¹³C NMR (100 MHz, DMSO) δ 177.6, 154.3, 152.8, 136.5, 135.1, 126.7, 125.4, 123.3, 118.7, 117.8, 116.6, 97.1; HRMS (ESI) *m/z* calcd for C₁₂H₈BrN₂O₂⁺ (M+H)⁺ 290.9764, found 290.9775.



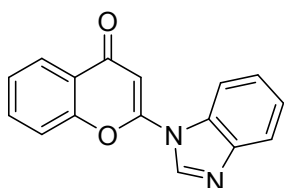
2-(4-Iodo-1H-imidazol-1-yl)-4H-chromen-4-one (3i). Yellow solid; mp: 193-194 °C; ¹H NMR (400 MHz, DMSO): δ 8.58 (d, *J* = 1.3 Hz, 1 H), 8.25 (d, *J* = 1.4 Hz, 1 H), 8.05–8.00 (m, 1 H), 7.88–7.82 (m, 1 H), 7.75 (d, *J* = 7.9 Hz, 1 H), 7.55–7.50 (m, 1 H), 6.85 (s, 1 H); ¹³C NMR (100 MHz, DMSO) δ 177.6, 154.3, 152.7, 138.0, 135.0, 126.6, 125.3, 123.3, 122.3, 118.7, 96.9, 87.0; HRMS (ESI) *m/z* calcd for C₁₂H₈IN₂O₂⁺ (M+H)⁺ 338.9625, found 338.9639.



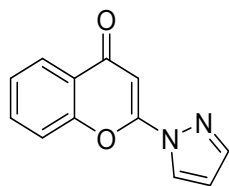
2-(4-Methyl-1H-imidazol-1-yl)-4H-chromen-4-one (3j). Yellow solid; mp: 150-151 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.22 (d, *J* = 7.9 Hz, 1 H), 8.14 (s, 1 H), 7.76–7.71 (m, 1 H), 7.53 (d, *J* = 8.4 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.16 (s, 1 H), 6.32 (s, 1 H), 2.31 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.8, 154.2, 153.3, 141.4, 134.1, 126.1, 126.0, 123.4, 117.5, 111.9, 96.4, 13.7; HRMS (ESI) *m/z* calcd for C₁₃H₁₀N₂NaO₂⁺ (*M*+*Na*)⁺ 249.0634, found 249.0642.



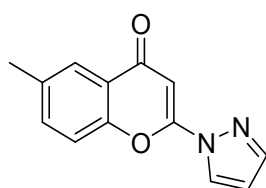
2-(2-Methyl-1H-imidazol-1-yl)-4H-chromen-4-one (3k). Yellow solid; mp: 128-129 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.25 (d, *J* = 7.4 Hz, 1 H), 7.76 (t, *J* = 6.7 Hz, 1 H), 7.51 (t, *J* = 7.7 Hz, 2 H), 7.28 (s, 1 H), 7.08 (s, 1 H), 6.33 (s, 1 H), 2.67 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 178.0, 167.8, 154.7, 154.3, 134.4, 129.3, 126.2, 126.1, 123.3, 118.4, 117.6, 102.3, 15.6; HRMS (ESI) *m/z* calcd for C₁₃H₁₁N₂O₂⁺ (*M*+*H*)⁺ 227.0815, found 227.0825.



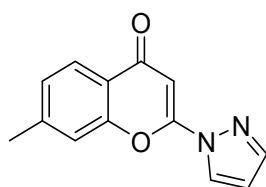
2-(1H-Benzo[d]imidazol-1-yl)-4H-chromen-4-one (3l).² Yellow solid; mp: 224-225 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.49 (s, 1 H), 8.27 (d, *J* = 7.7 Hz, 1 H), 7.90 (s, 2 H), 7.77 (t, *J* = 7.3 Hz, 1 H), 7.61 (d, *J* = 8.0 Hz, 1 H), 7.53–7.44 (m, 3 H), 6.59 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.8, 154.5, 153.9, 144.4, 139.9, 134.3, 131.0, 126.3, 126.1, 125.5, 124.7, 123.5, 121.4, 117.6, 112.5, 98.9.



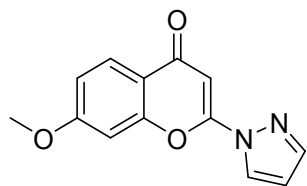
2-(1H-Pyrazol-1-yl)-4H-chromen-4-one (3m).² White solid; mp: 131-132 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.24 (d, *J* = 7.9 Hz, 2 H), 7.84 (s, 1 H), 7.71 (t, *J* = 7.7 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 1 H), 6.90 (s, 1 H), 6.58 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 178.0, 155.3, 154.10, 144.3, 133.8, 127.7, 126.1, 125.9, 123.8, 117.4, 109.6, 96.4.



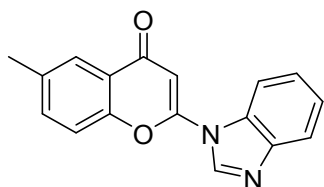
6-Methyl-2-(1H-pyrazol-1-yl)-4H-chromen-4-one (3n). White solid; mp: 153-154 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.20 (d, *J* = 2.5 Hz, 1 H), 7.99 (s, 1 H), 7.82 (s, 1 H), 7.49 (d, *J* = 8.5 Hz, 1 H), 7.40 (d, *J* = 8.5 Hz, 1 H), 6.85 (s, 1 H), 6.57 (s, 1 H), 2.45 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 178.1, 155.2, 152.3, 144.2, 135.9, 134.9, 127.7, 125.5, 123.4, 117.2, 109.5, 96.2, 20.9; HRMS (ESI) *m/z* calcd for C₁₃H₁₀N₂NaO₂⁺ (*M*+Na)⁺ 249.0634, found 249.0640.



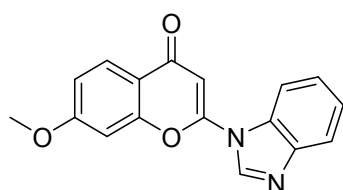
7-Methyl-2-(1H-pyrazol-1-yl)-4H-chromen-4-one (3o). White solid; mp: 154-155 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.19 (s, 1 H), 8.09 (d, *J* = 8.0 Hz, 1 H), 7.82 (s, 1 H), 7.31 (s, 1 H), 7.24 (d, *J* = 7.9 Hz, 1 H), 6.84 (s, 1 H), 6.56 (s, 1 H), 2.50 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.9, 155.1, 154.2, 145.3, 144.2, 127.7, 127.3, 125.8, 121.5, 117.3, 109.5, 96.2, 21.8; HRMS (ESI) *m/z* calcd for C₁₃H₁₀N₂NaO₂⁺ (*M*+Na)⁺ 249.0634, found 249.0647.



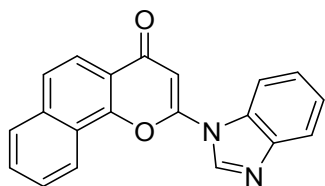
7-Methoxy-2-(1H-pyrazol-1-yl)-4H-chromen-4-one (3p). White solid; mp: 155-156 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.18 (d, *J* = 2.7 Hz, 1 H), 8.11 (d, *J* = 8.8 Hz, 1 H), 7.82 (s, 1 H), 7.00–6.97 (m, 1 H), 6.92 (d, *J* = 2.3 Hz, 1 H), 6.78 (s, 1 H), 6.59–6.53 (m, 1 H), 3.92 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.4, 164.2, 155.7, 155.1, 144.1, 127.6, 127.3, 117.4, 114.5, 109.4, 100.5, 96.1, 55.9; HRMS (ESI) *m/z* calcd for C₁₃H₁₀N₂NaO₃⁺ (*M*+Na)⁺ 265.0584, found 265.0591.



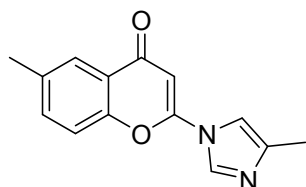
2-(1H-Benzo[d]imidazol-1-yl)-6-methyl-4H-chromen-4-one (3q). White solid; mp: 236-237 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.47 (s, 1 H), 8.04 (s, 1 H), 7.88 (d, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 8.0 Hz, 1 H), 7.51–7.42 (m, 3 H), 6.55 (s, 1 H), 2.49 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.9, 153.8, 152.8, 144.5, 139.9, 136.4, 135.4, 125.5, 125.5, 124.7, 123.1, 121.4, 117.3, 112.5, 98.8, 21.0; HRMS (ESI) *m/z* calcd for C₁₇H₁₂N₂NaO₂⁺ (*M*+Na)⁺ 299.0791, found 299.0796.



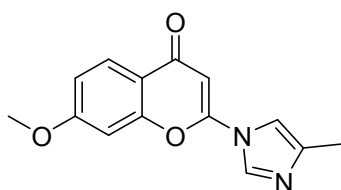
2-(1H-Benzo[d]imidazol-1-yl)-7-methoxy-4H-chromen-4-one (3r). White solid; mp: 184-185 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.45 (s, 1 H), 8.17 (d, *J* = 8.9 Hz, 1 H), 7.90 (d, *J* = 7.6 Hz, 1 H), 7.85 (d, *J* = 7.9 Hz, 1 H), 7.50–7.42 (m, 2 H), 7.06 (d, *J* = 11.0 Hz, 1 H), 6.99 (s, 1 H), 6.52 (s, 1 H), 3.97 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 201.9, 177.3, 164.6, 156.3, 153.5, 139.9, 127.5, 125.4, 124.6, 121.4, 117.2, 114.9, 112.3, 100.5, 99.1, 56.1; HRMS (ESI) *m/z* calcd for C₁₇H₁₂N₂NaO₃⁺ (*M*+Na)⁺ 315.0740, found 315.0751.



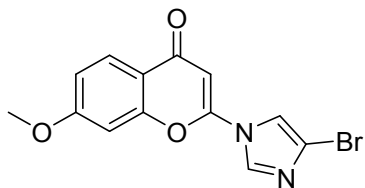
2-(1H-Benzo[d]imidazol-1-yl)-4H-benzo[h]chromen-4-one (3s). Brown solid; mp: 182-183 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.56 (d, *J* = 7.2 Hz, 1 H), 8.53 (s, 1 H), 8.48 (d, *J* = 8.0 Hz, 1 H), 8.19 (d, *J* = 8.0 Hz, 1 H), 7.99-7.93 (m, 3 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.76–7.74 (m, 2 H), 7.55-7.45 (m, 2 H), 6.70 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.6, 153.2, 152.1, 144.5, 140.2, 136.3, 131.2, 129.6, 128.5, 128.0, 126.2, 125.6, 124.8, 123.3, 121.5, 120.8, 119.9, 111.8, 100.9; HRMS (ESI) *m/z* calcd for C₂₀H₁₂N₂NaO₂⁺ (M+Na)⁺ 335.0791, found 335.804.



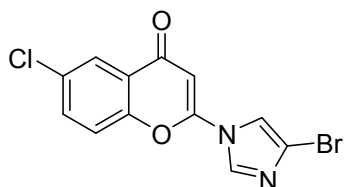
6-Methyl-2-(4-methyl-1H-imidazol-1-yl)-4H-chromen-4-one (3t). Yellow solid; mp: 193-194 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.12 (s, 1 H), 7.99 (s, 1 H), 7.53 (d, *J* = 8.5 Hz, 1 H), 7.41 (d, *J* = 8.5 Hz, 1 H), 7.15 (s, 1 H), 6.28 (s, 1 H), 2.47 (s, 3 H), 2.31 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.9, 153.2, 152.5, 141.3, 136.2, 135.3, 134.1, 125.4, 123.1, 117.3, 111.9, 96.3, 20.9, 13.7; HRMS (ESI) *m/z* calcd for C₁₄H₁₂N₂NaO₂⁺ (M+Na)⁺ 263.0791, found 263.0802.



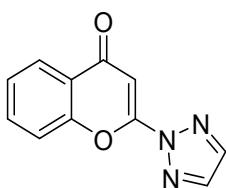
7-Methoxy-2-(4-methyl-1H-imidazol-1-yl)-4H-chromen-4-one (3u). Yellow solid; mp: 184-185 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 8.0 Hz, 2 H), 7.14 (s, 1 H), 7.01 (d, *J* = 8.8 Hz, 1 H), 6.93 (s, 1 H), 6.25 (s, 1 H), 3.94 (s, 3 H), 2.31 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 177.2, 164.5, 155.9, 153.0, 141.2, 134.0, 127.2, 117.0, 114.8, 111.9, 100.4, 96.3, 56.0, 13.6; HRMS (ESI) *m/z* calcd for C₁₄H₁₂N₂NaO₃⁺ (M+Na)⁺ 279.0740, found 279.0752.



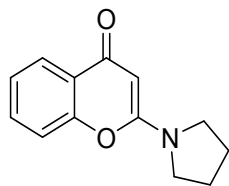
2-(4-Bromo-1H-imidazol-1-yl)-7-methoxy-4H-chromen-4-one (3v). Yellow solid; mp: 135-136 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 8.56 (s, 1 H), 8.17 (s, 1 H), 7.89 (d, $J = 8.8$ Hz, 1 H), 7.26 (s, 1 H), 7.06 (d, $J = 8.5$ Hz, 1 H), 6.74 (s, 1 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 176.8, 164.4, 156.0, 152.5, 136.3, 126.7, 117.7, 116.9, 116.5, 115.3, 101.5, 96.7, 56.6; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{BrN}_2\text{NaO}_3^+$ ($\text{M}+\text{H}$) $^+$ 320.9883, found 320.9869.



2-(4-Bromo-1H-imidazol-1-yl)-6-chloro-4H-chromen-4-one (3w). White solid; mp: 188-189 °C; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 8.64 (d, $J = 1.3$ Hz, 2 H), 8.24 (d, $J = 1.3$ Hz, 2 H), 7.95 (d, $J = 2.5$ Hz, 1 H), 7.93–7.89 (m, 1 H), 7.82 (d, $J = 8.9$ Hz, 1 H), 6.91 (s, 1 H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 176.5, 153.0, 152.9, 136.6, 134.9, 131.1, 124.5, 124.4, 121.1, 118.0, 116.6, 97.0; HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_6\text{BrClN}_2\text{NaO}_2^+$ ($\text{M}+\text{Na}$) $^+$ 346.9193, found 346.9212.



2-(2H-1,2,3-Triazol-2-yl)-4H-chromen-4-one (3x). White solid; mp: 131-132 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.26 (d, $J = 9.2$ Hz, 1 H), 8.01 (s, 2 H), 7.76 (t, $J = 8.4$ Hz, 1 H), 7.68 (d, $J = 8.3$ Hz, 1 H), 7.50 (t, $J = 7.5$ Hz, 1 H), 7.05 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 178.0, 154.5, 154.3, 138.3, 134.3, 126.2, 126.0, 123.8, 118.1, 98.6; HRMS (ESI) m/z calcd for $\text{C}_{11}\text{H}_7\text{N}_3\text{NaO}_2^+$ ($\text{M}+\text{Na}$) $^+$ 236.0430, found 236.0437.



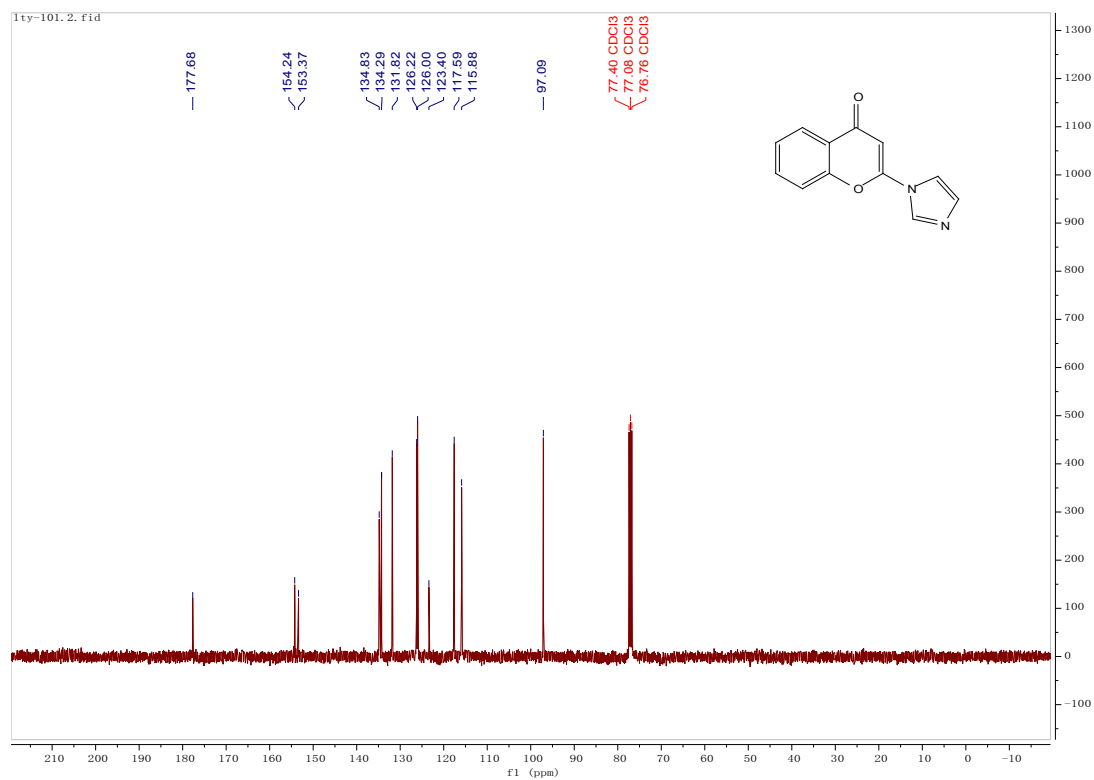
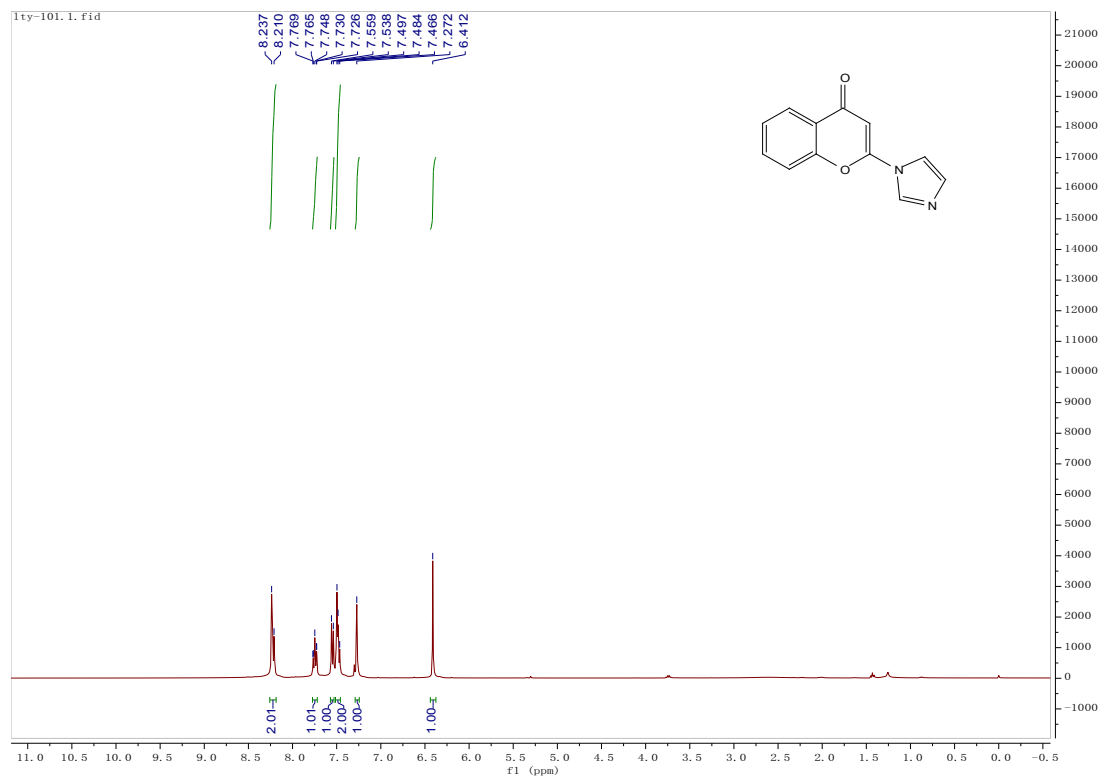
2-(Pyrrolidin-1-yl)-4H-chromen-4-one (3y). White solid; mp: 198-199 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.18–8.13 (m, 1 H), 7.54–7.49 (m, 1 H), 7.34–7.26 (m, 2 H), 5.32 (s, 1 H), 3.50 (s, 4 H), 2.07–2.01 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.0, 161.3, 153.8, 131.8, 125.6, 124.5, 123.1, 116.2, 86.3, 46.7, 25.1; HRMS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{NNaO}_2^+$ ($\text{M}+\text{Na}$) $^+$ 238.0838, found 238.0849.

References

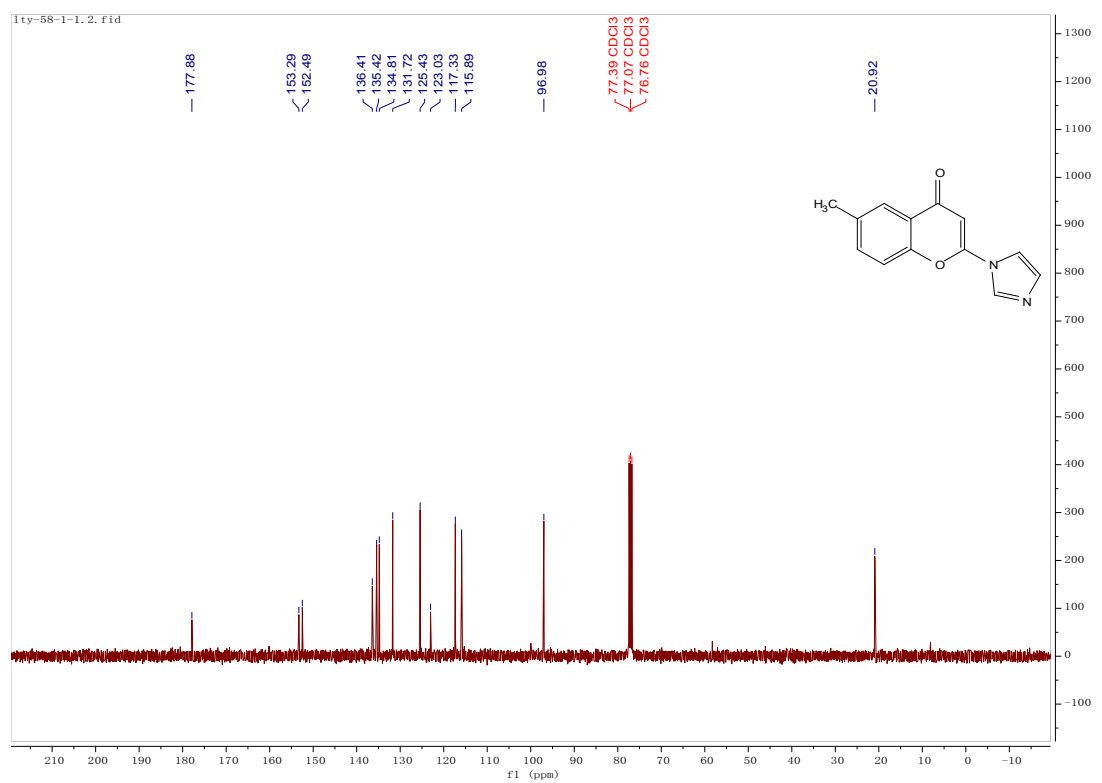
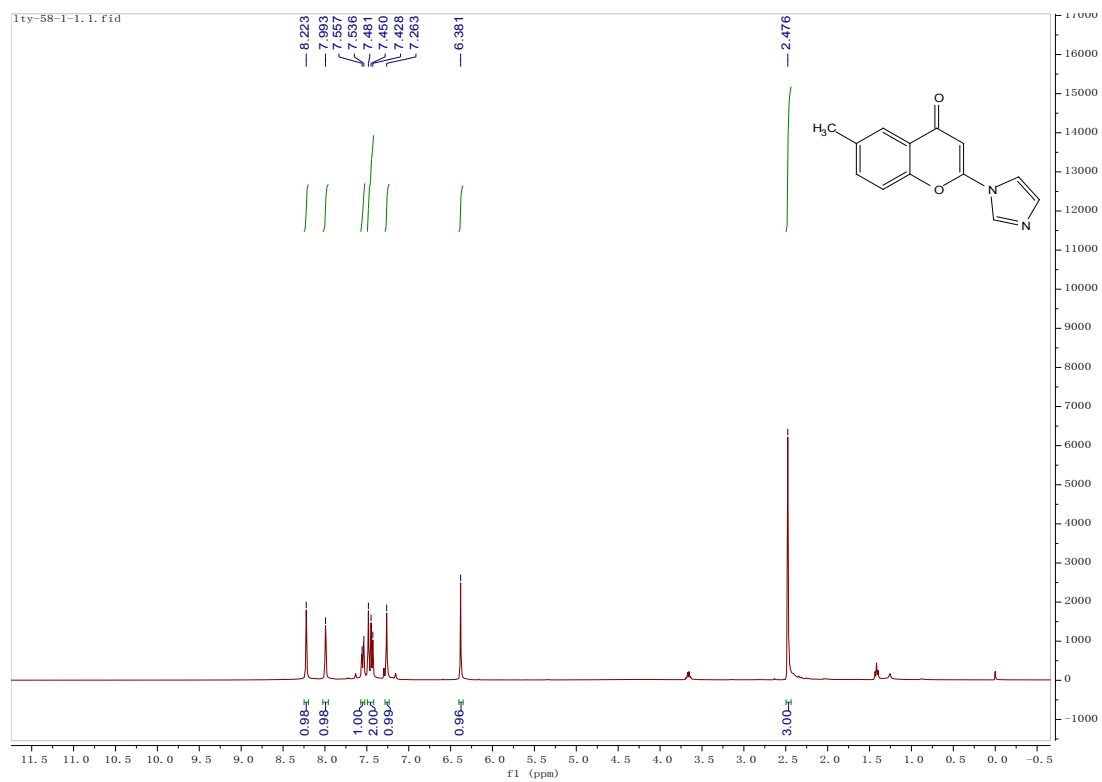
1. Y. Gao, Y. Liu and J.-P. Wan, *J. Org. Chem.*, 2019, **84**, 2243-2251.
- R. Samanta, R. Narayan, J. O. Bauer, C. Strohmman, S. Sievers and A. P. Antonchick, *Chem. Commun.*, 2015, **51**, 925-928.

^1H and ^{13}C NMR spectra of all products

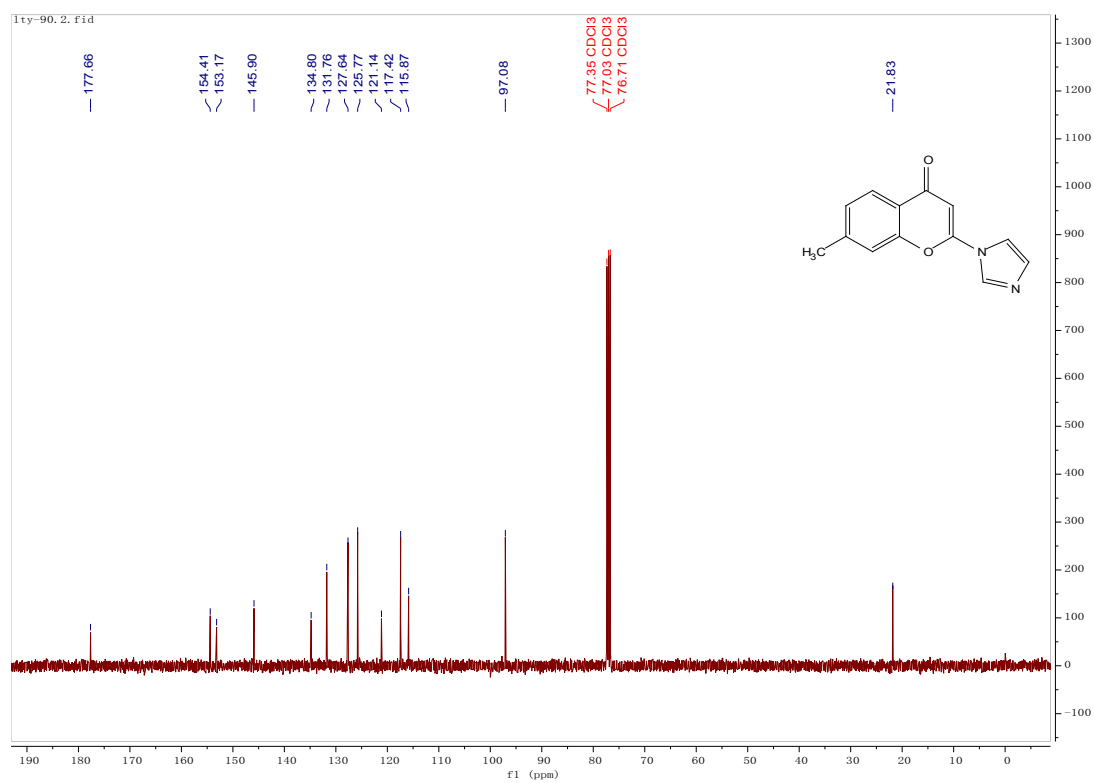
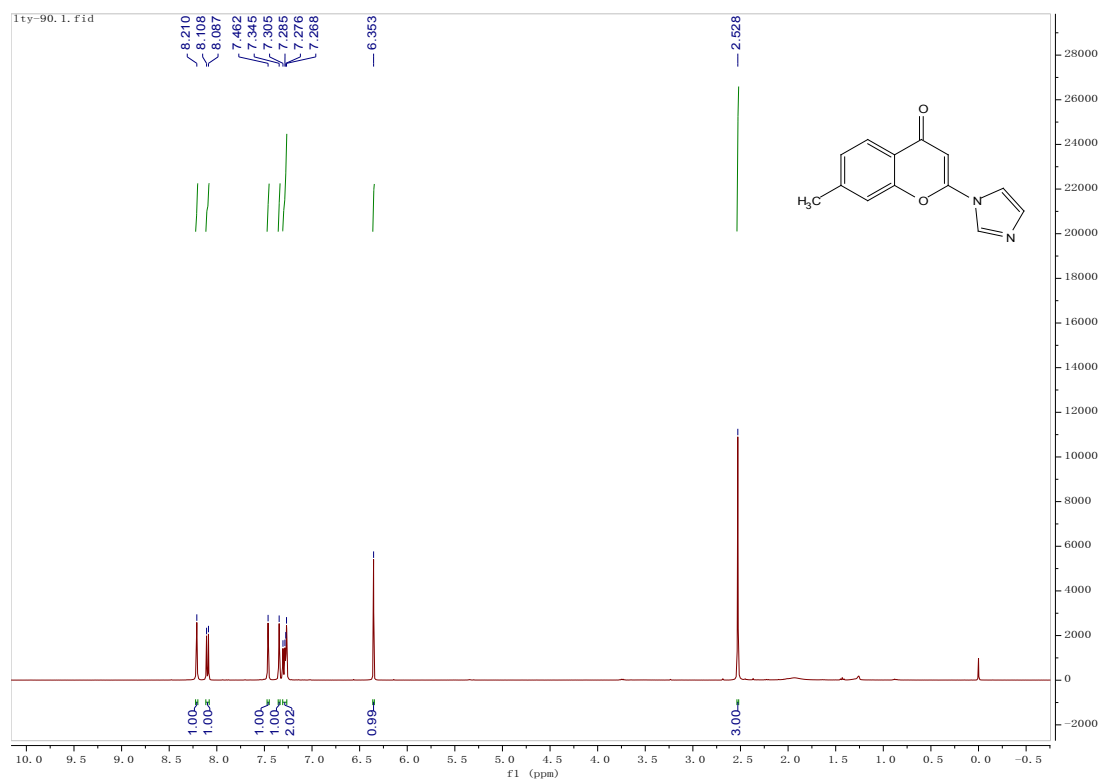
^1H and ^{13}C NMR spectra of 3a



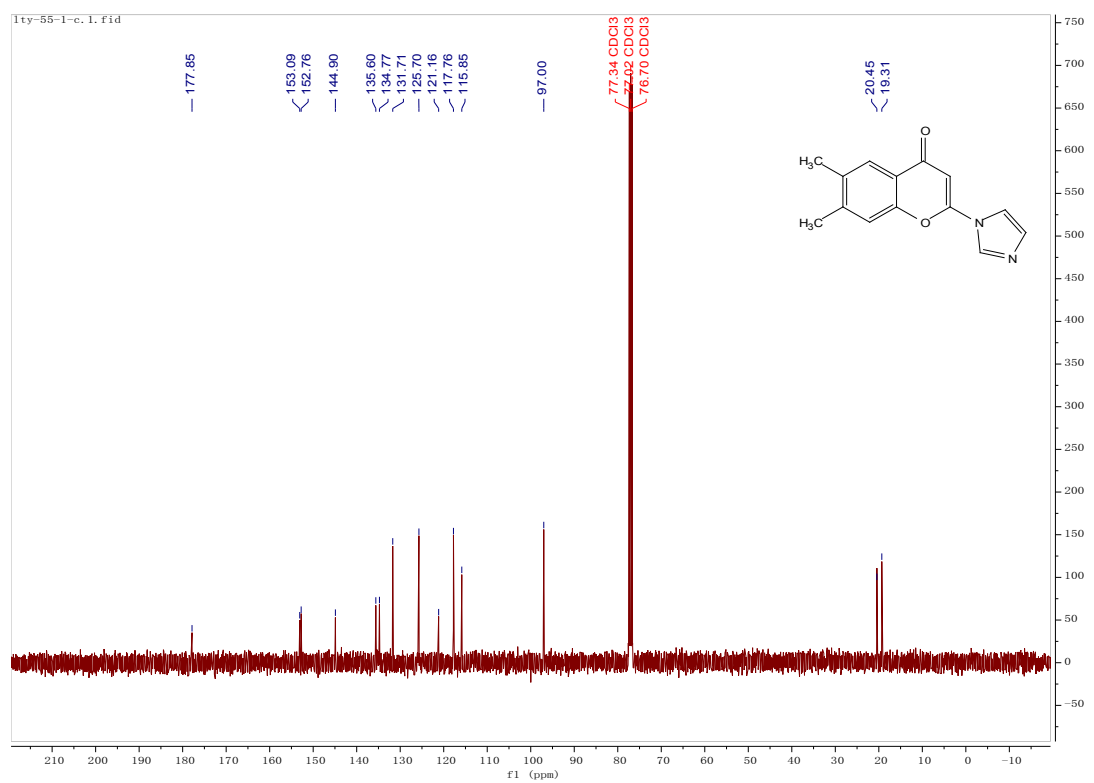
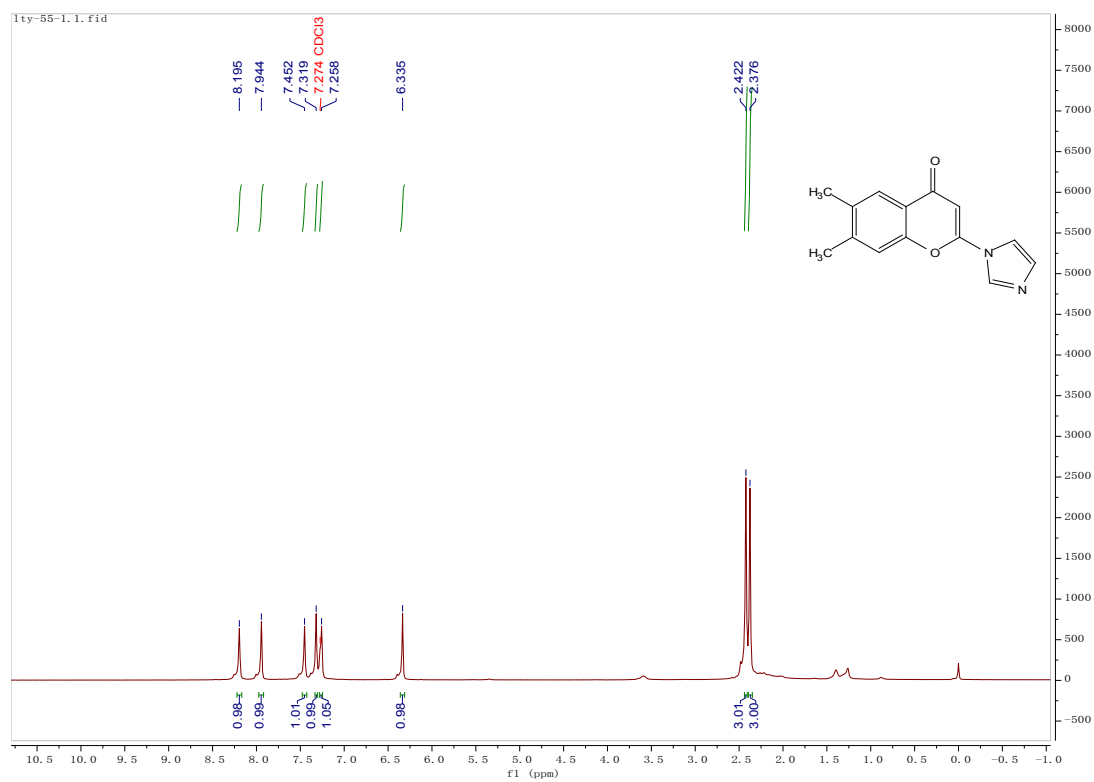
¹H and ¹³C NMR spectra of **3b**



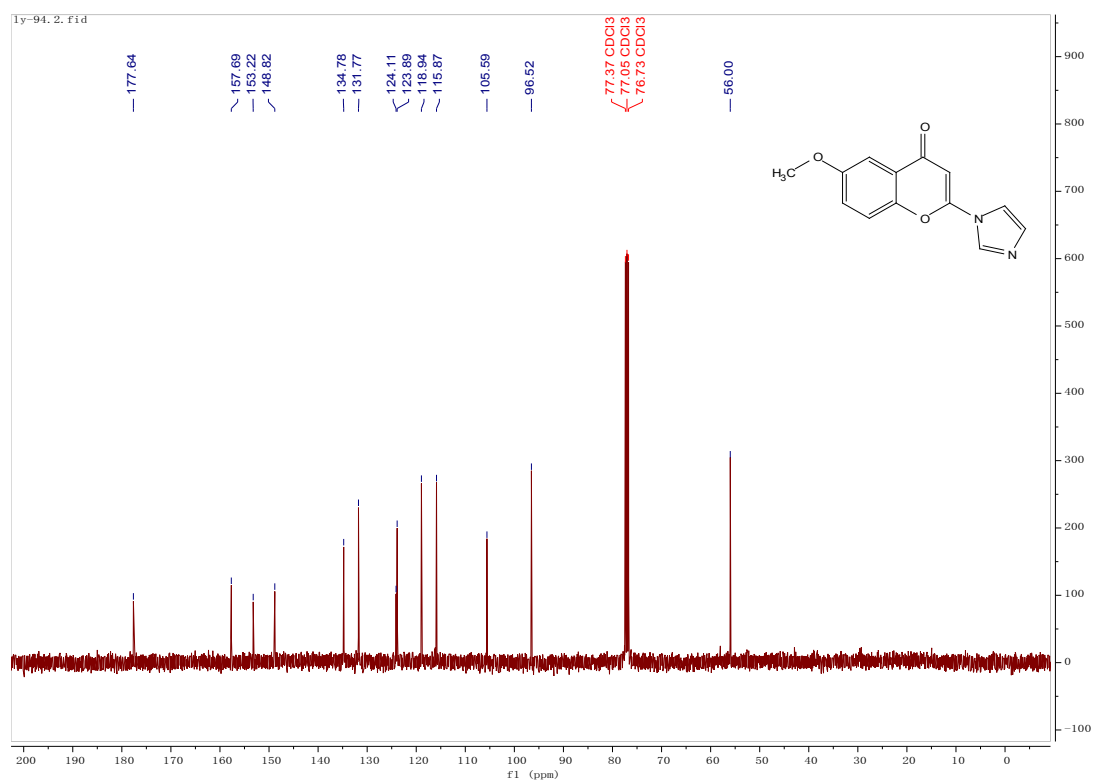
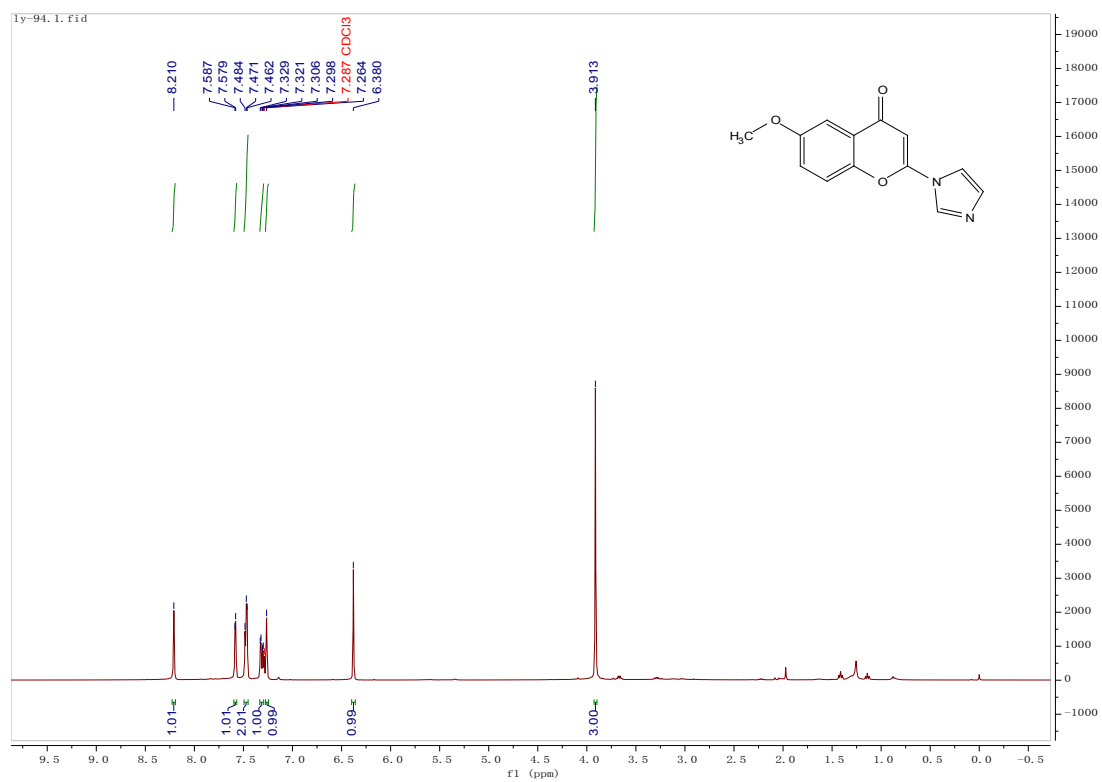
¹H and ¹³C NMR spectra of 3c



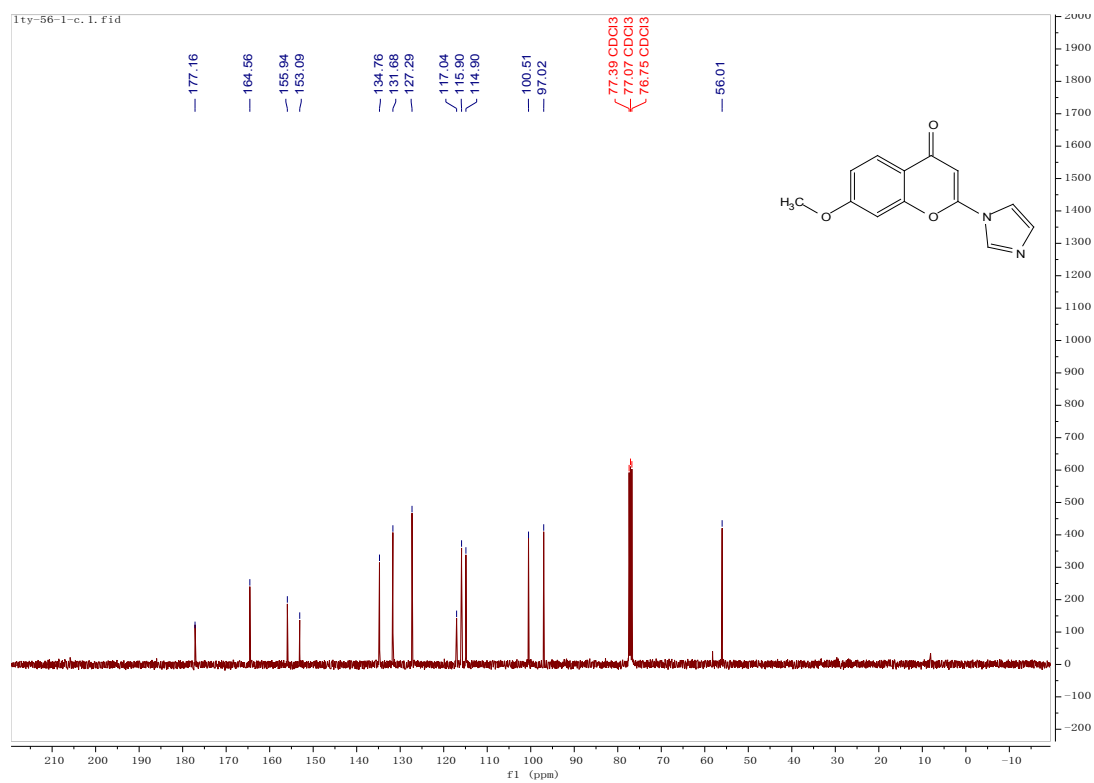
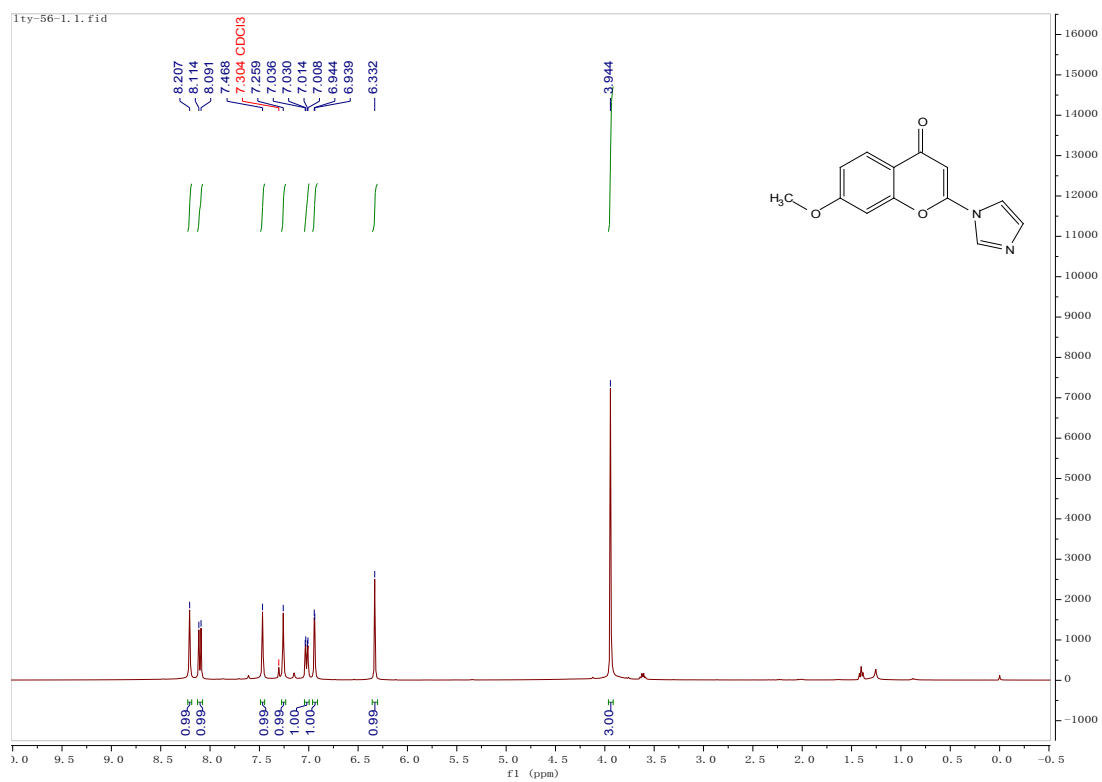
^1H and ^{13}C NMR spectra of **3d**



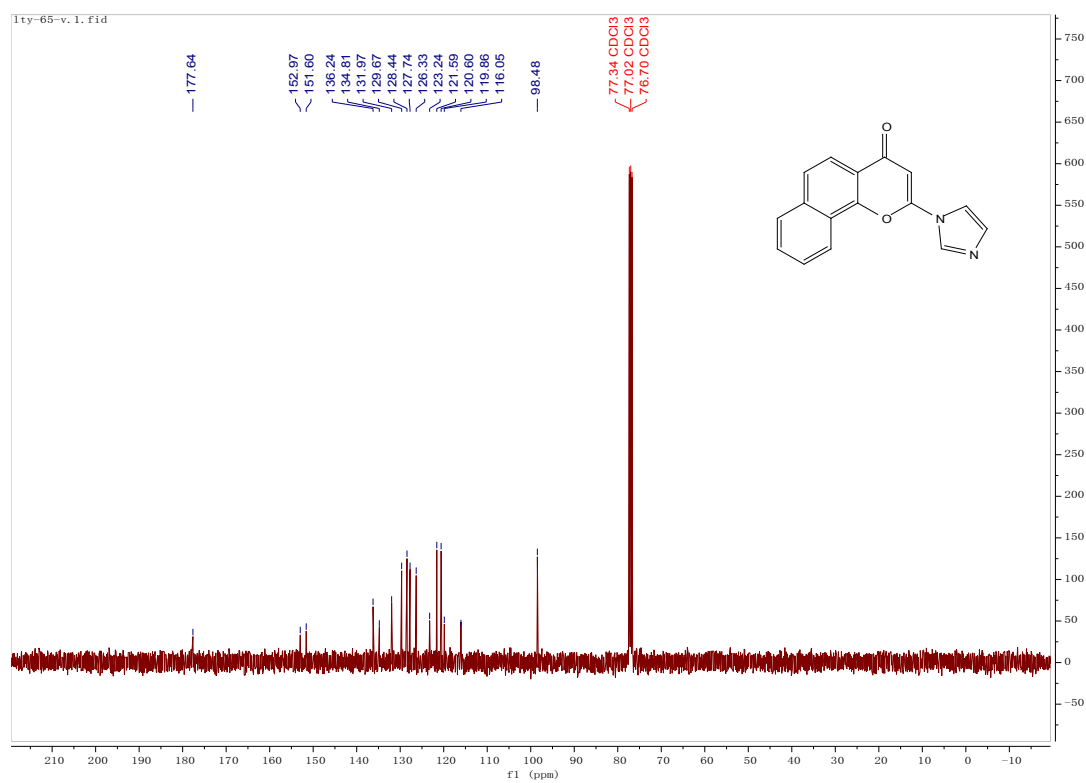
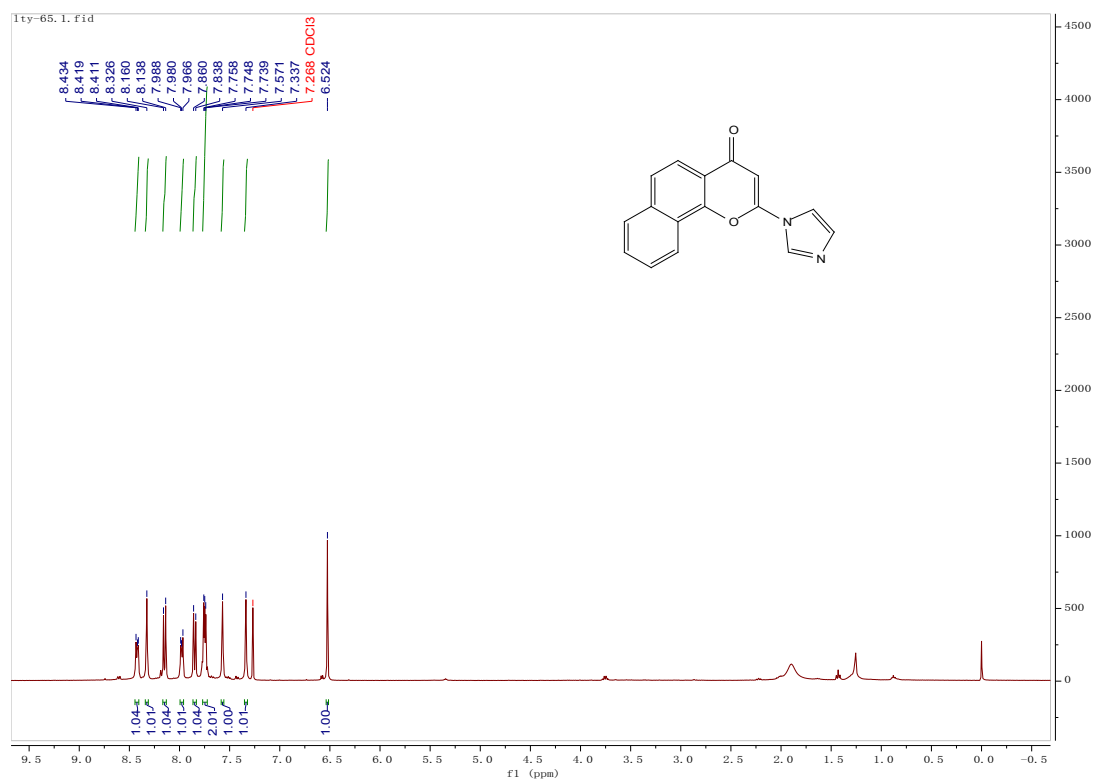
¹H and ¹³C NMR spectra of 3e



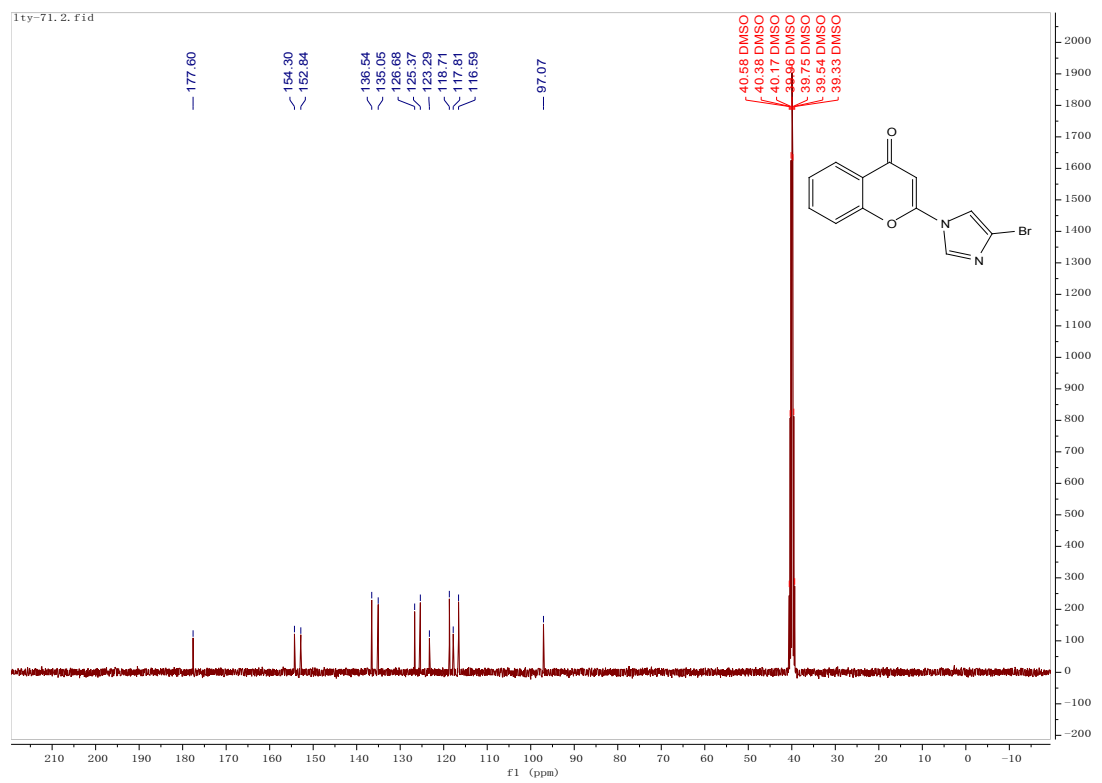
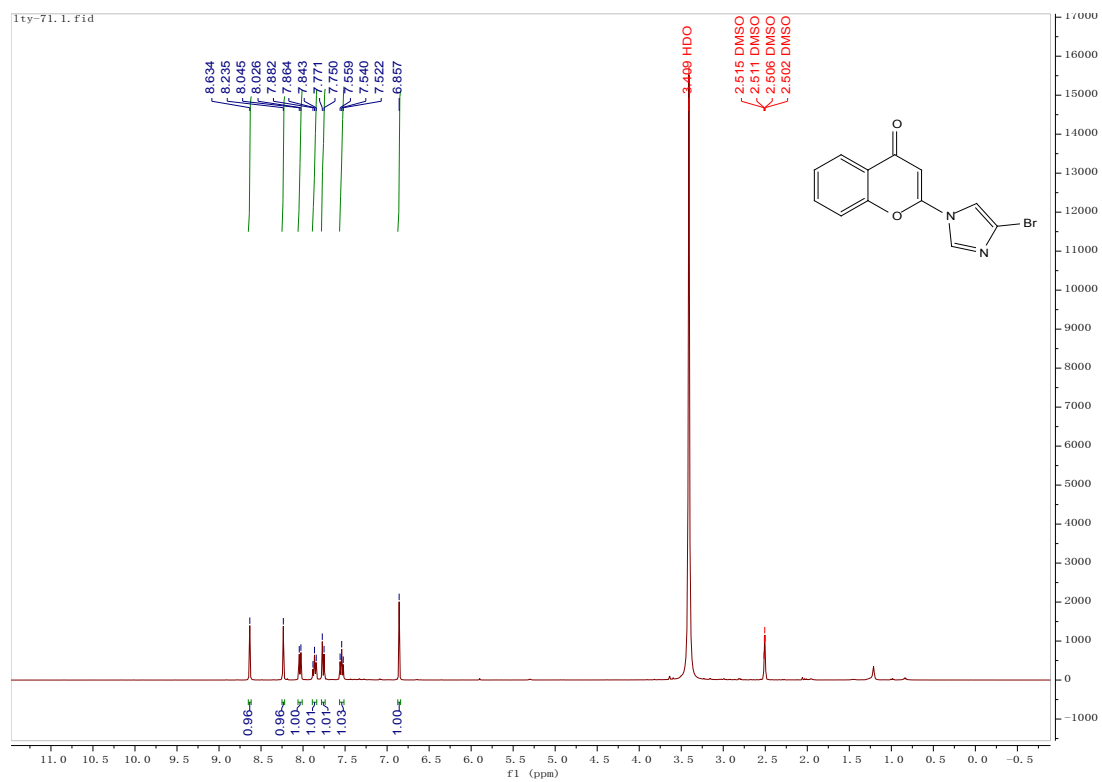
^1H and ^{13}C NMR spectra of **3f**



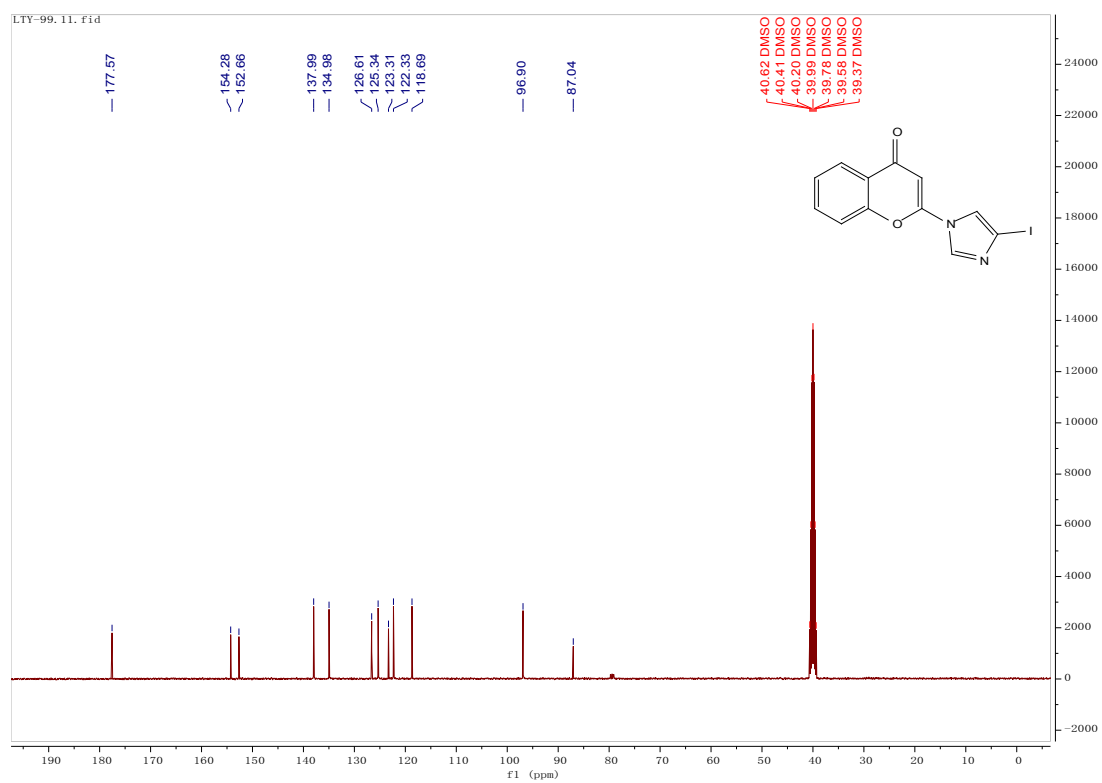
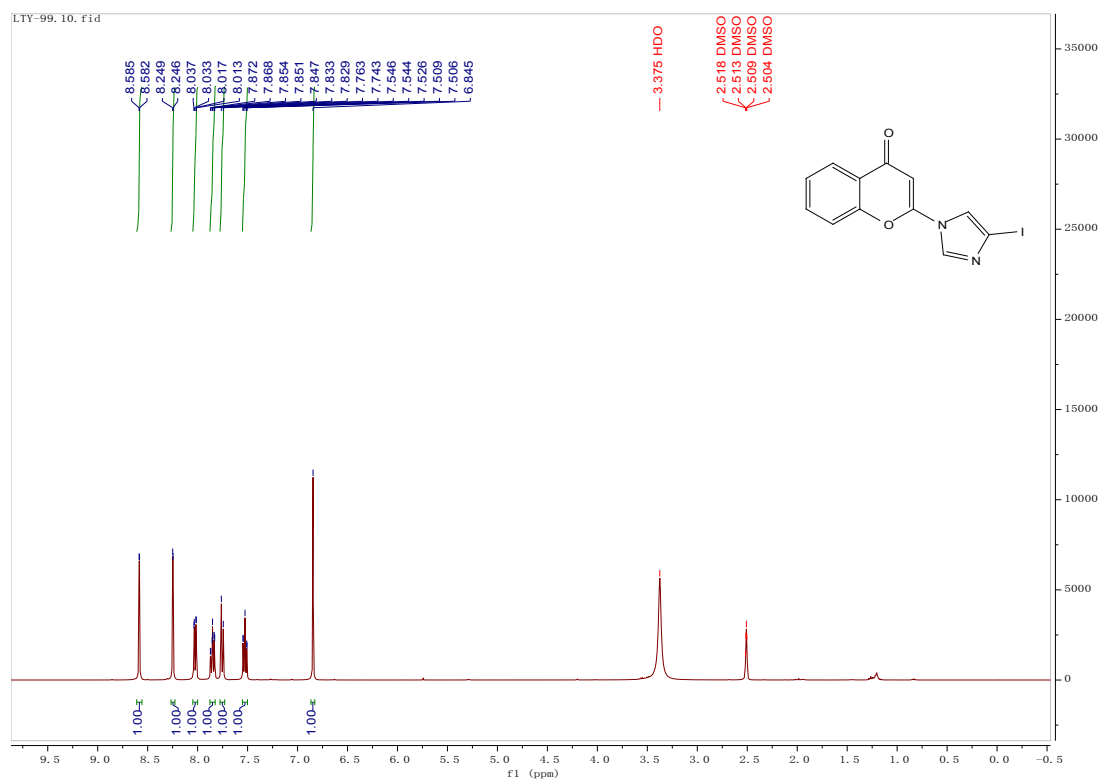
^1H and ^{13}C NMR spectra of **3g**



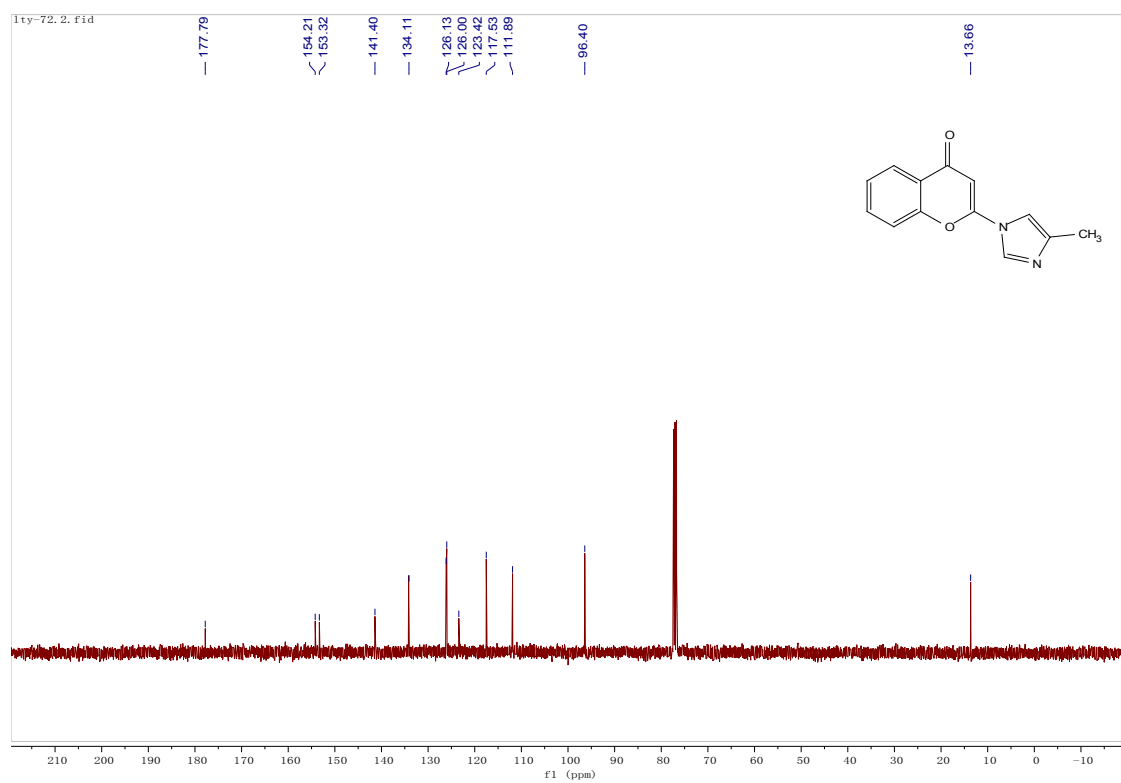
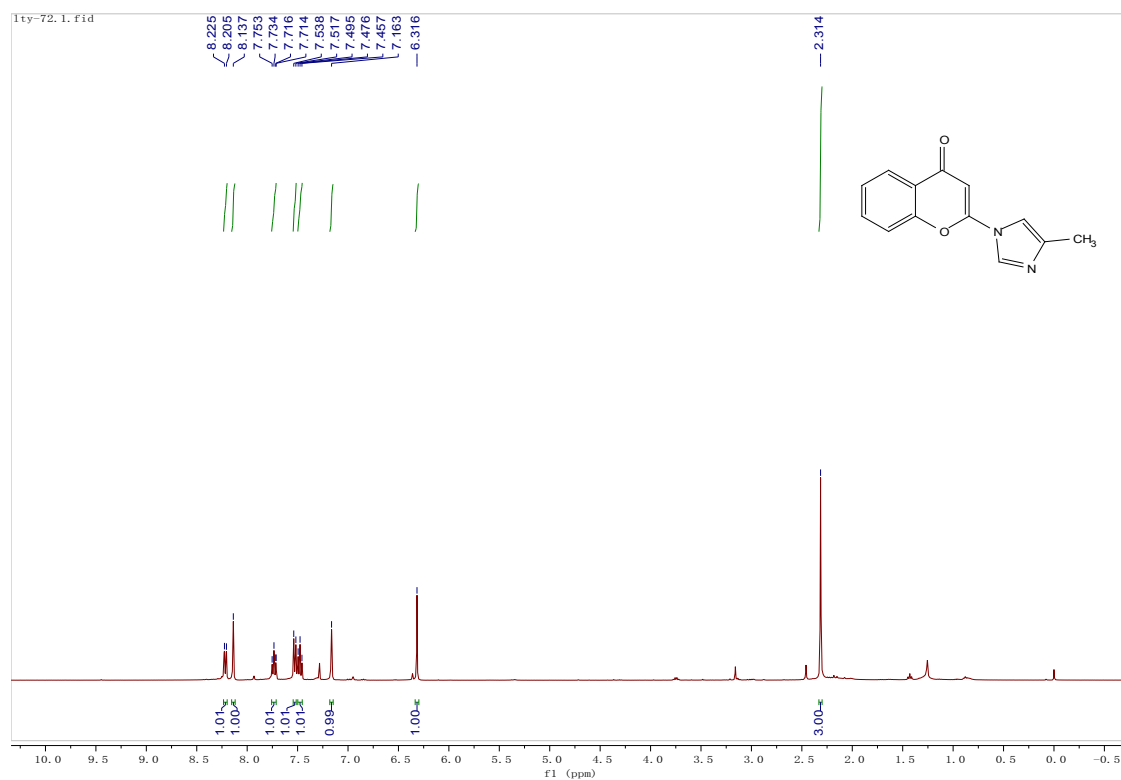
^1H and ^{13}C NMR spectra of **3h**



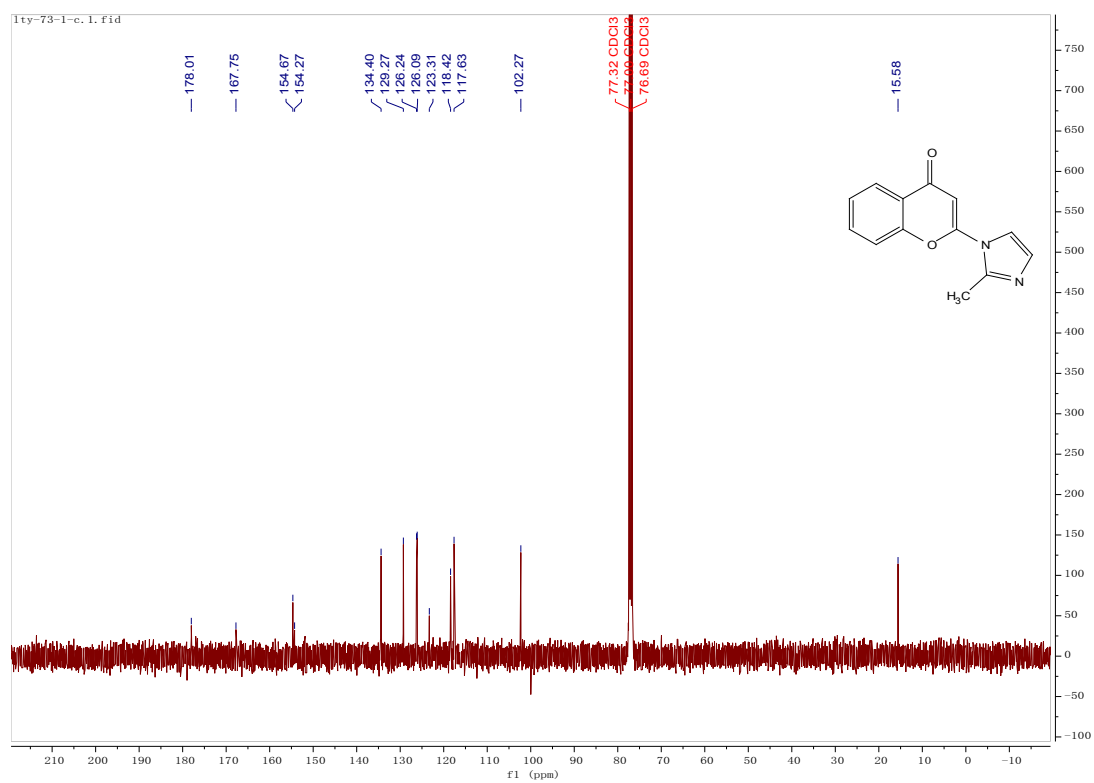
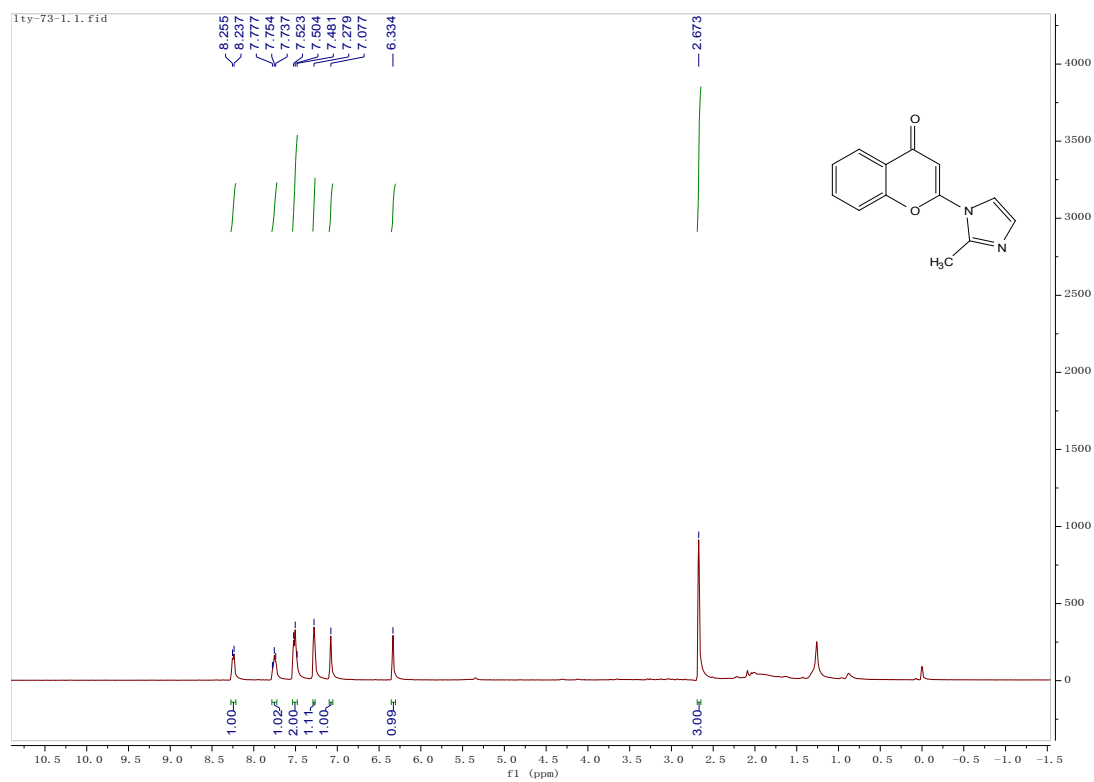
^1H and ^{13}C NMR spectra of **3i**



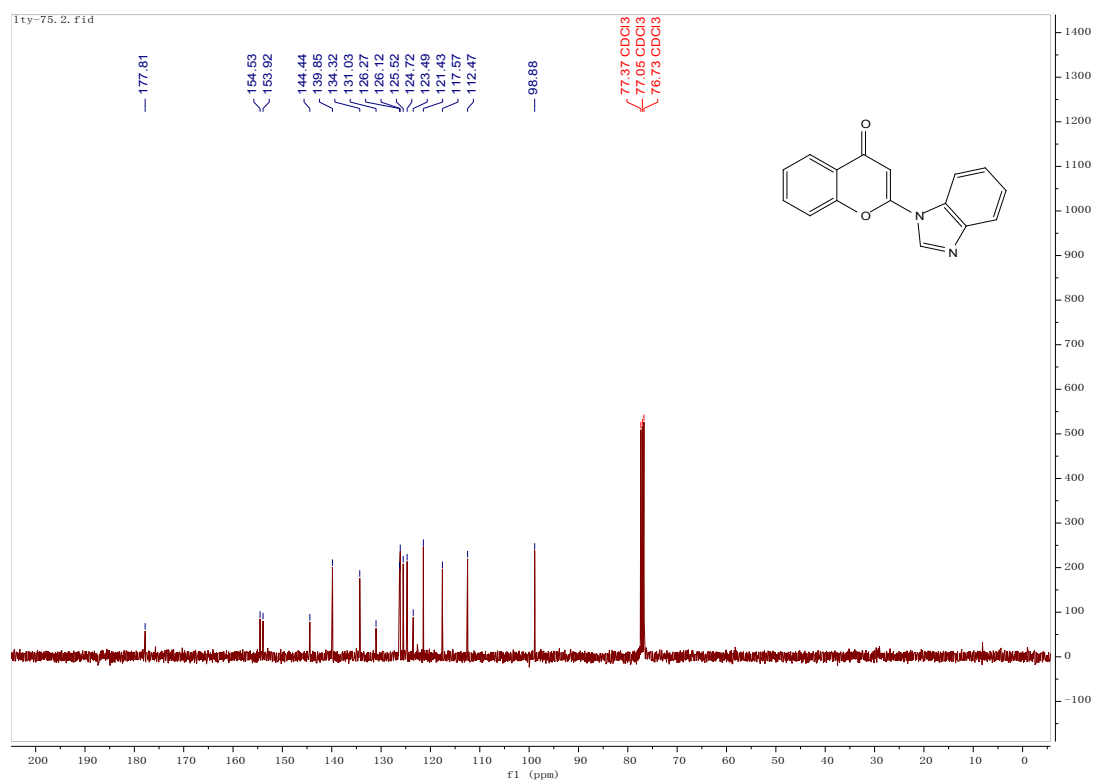
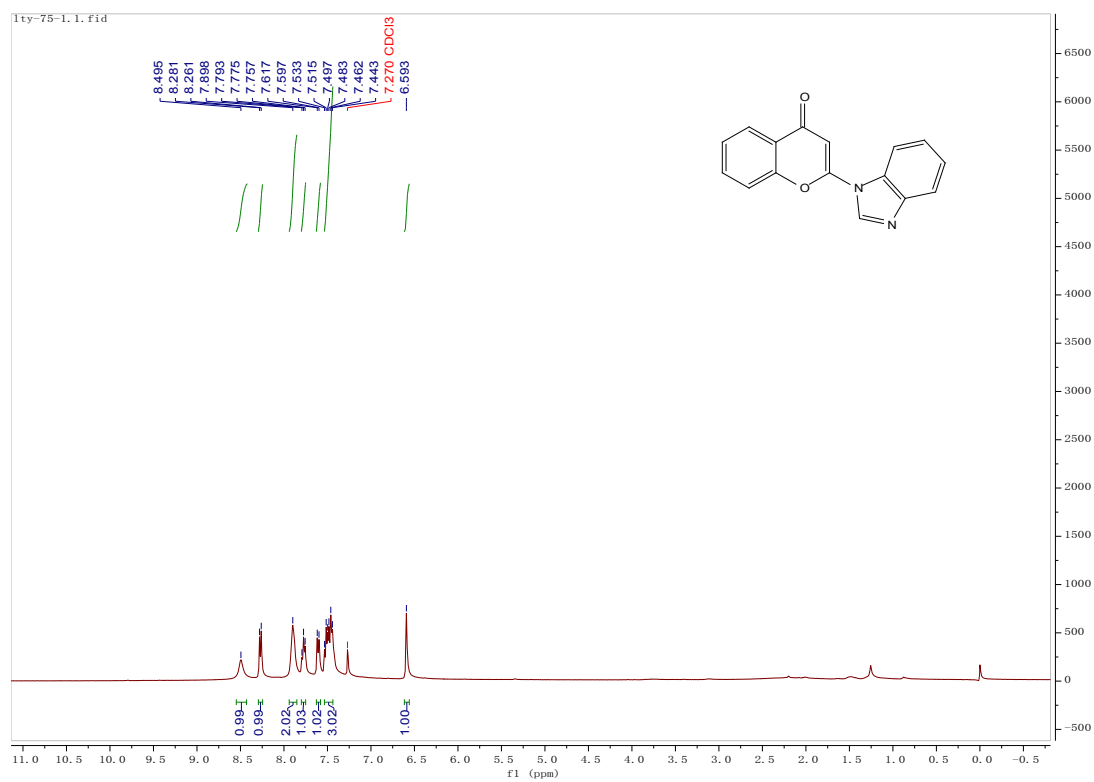
^1H and ^{13}C NMR spectra of **3j**



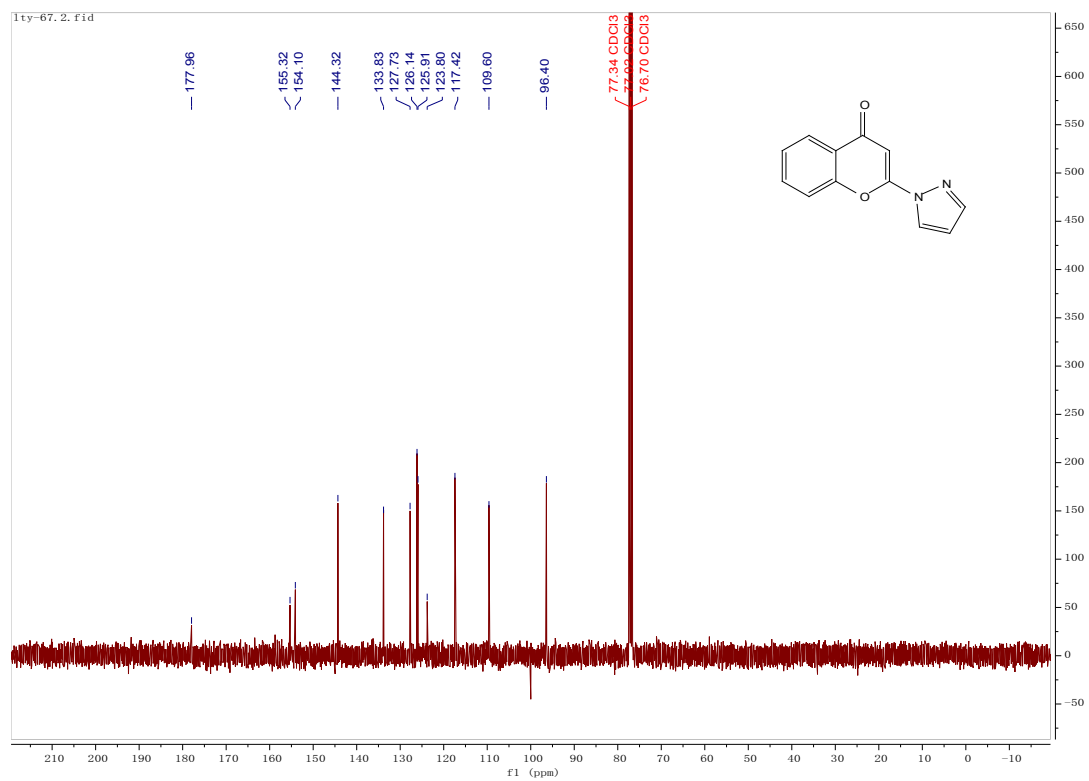
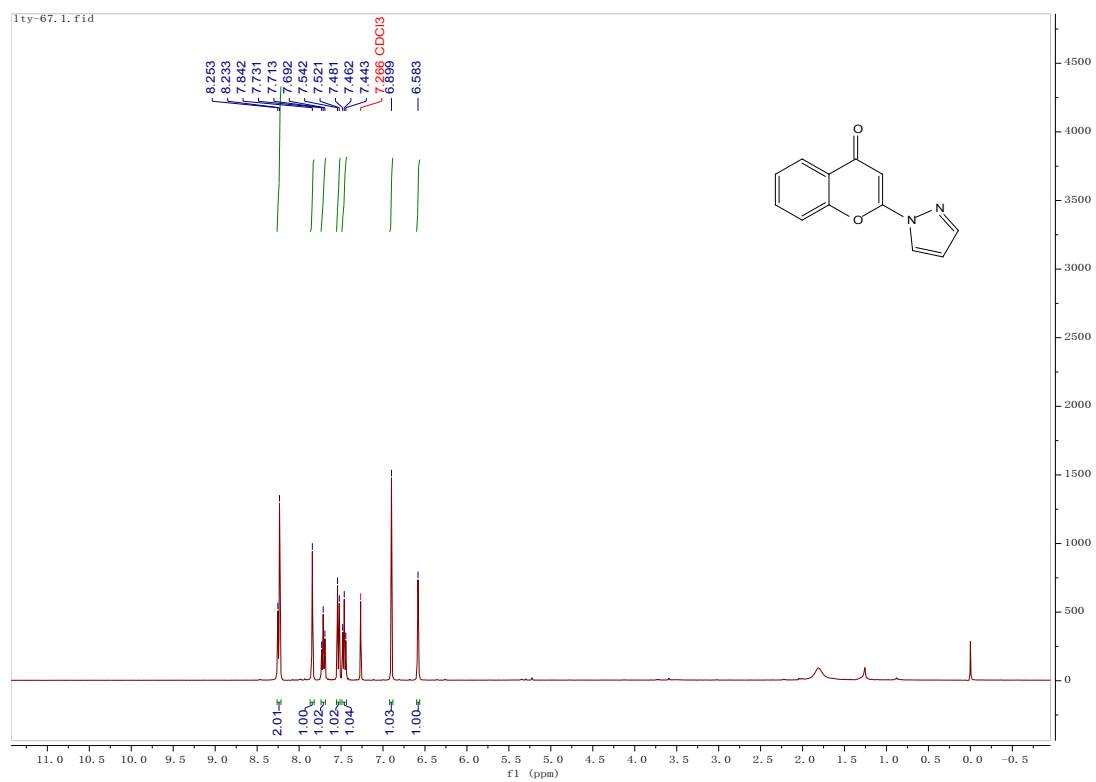
¹H and ¹³C NMR spectra of **3k**



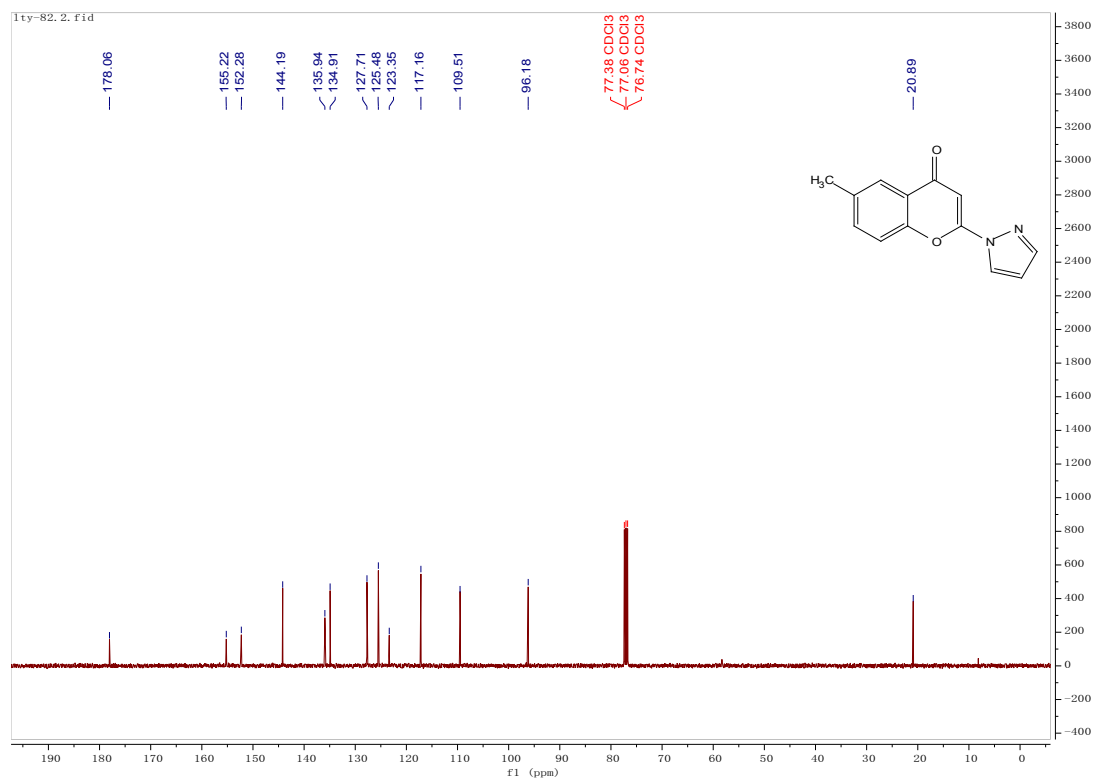
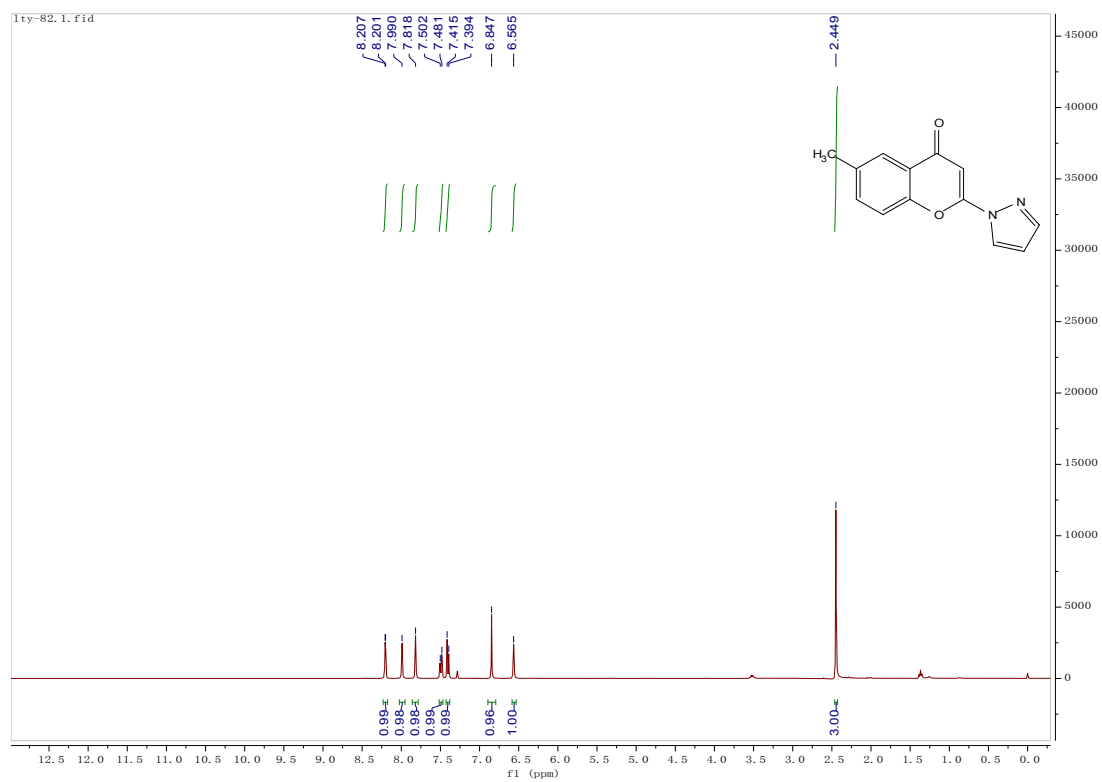
¹H and ¹³C NMR spectra of **31**



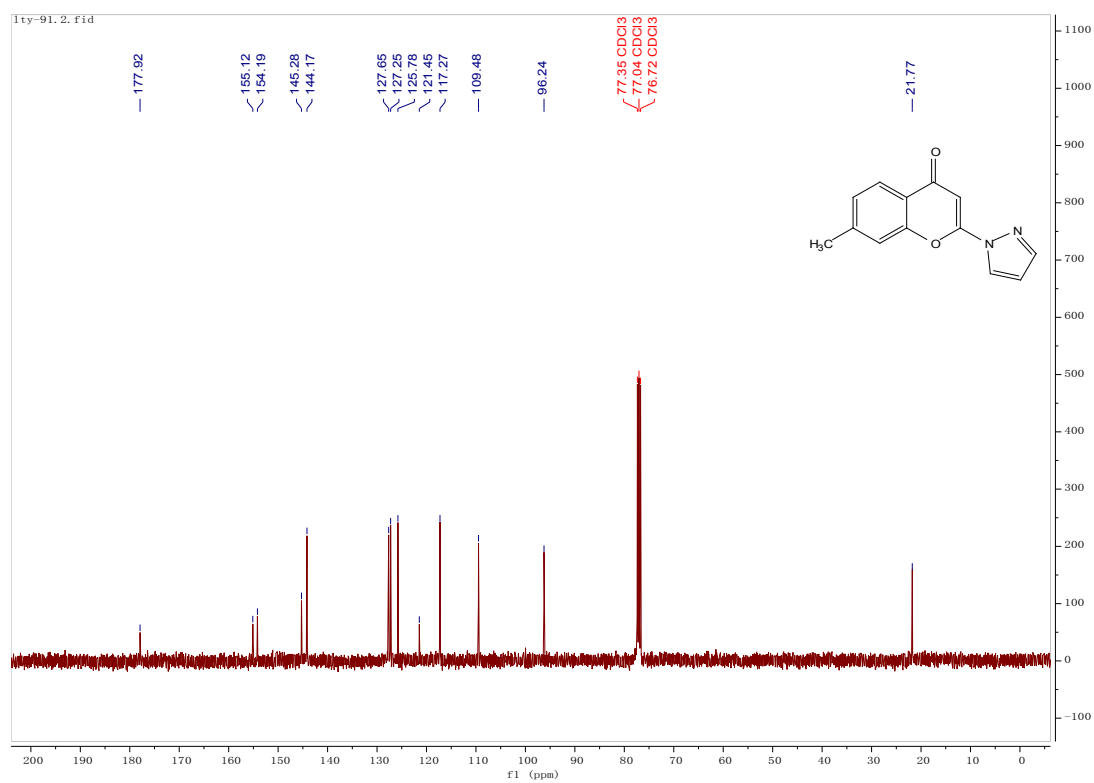
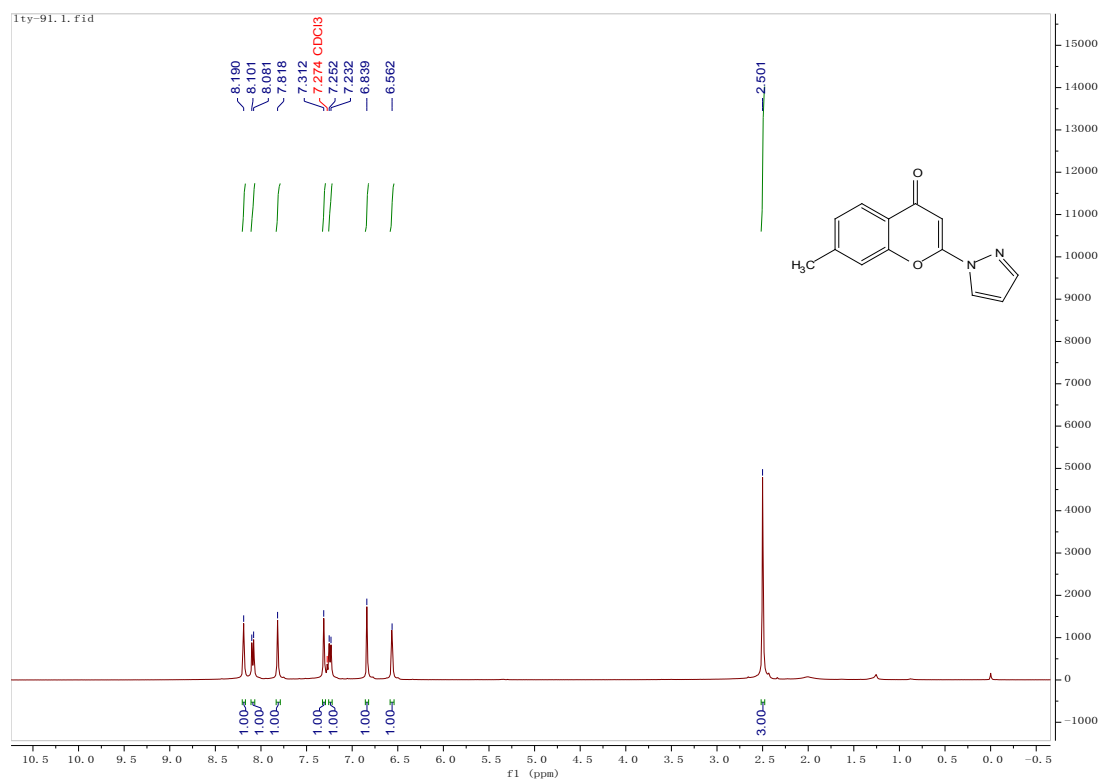
¹H and ¹³C NMR spectra of **3m**



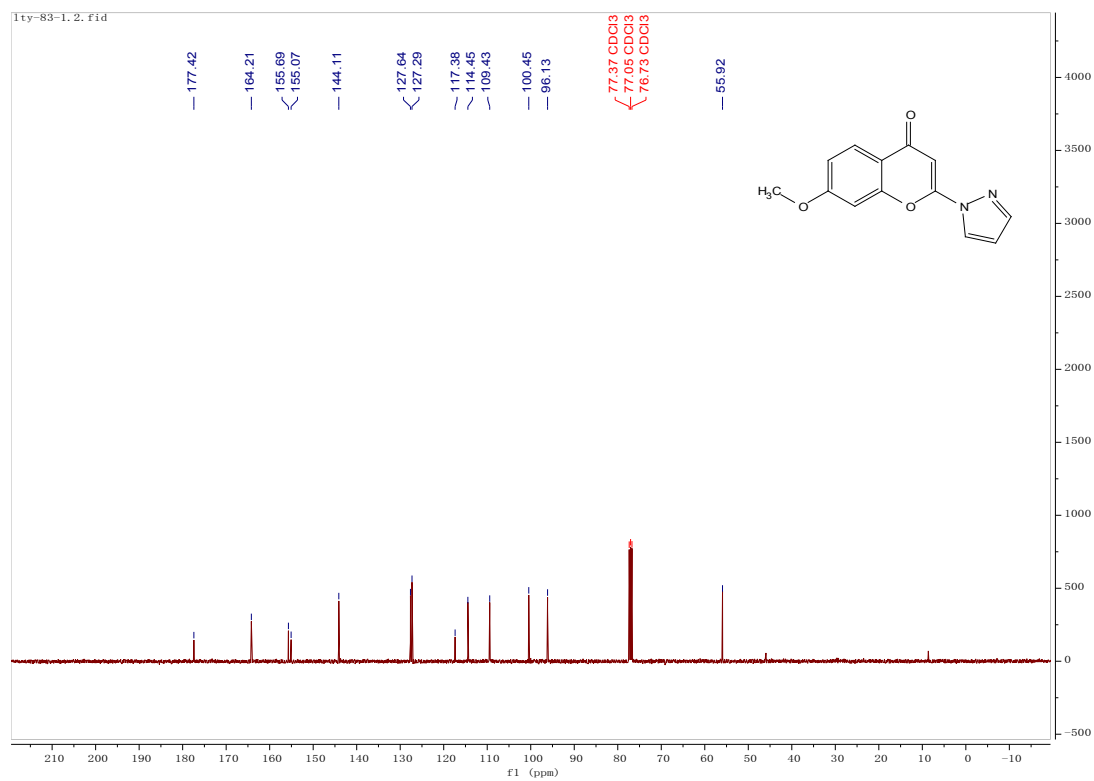
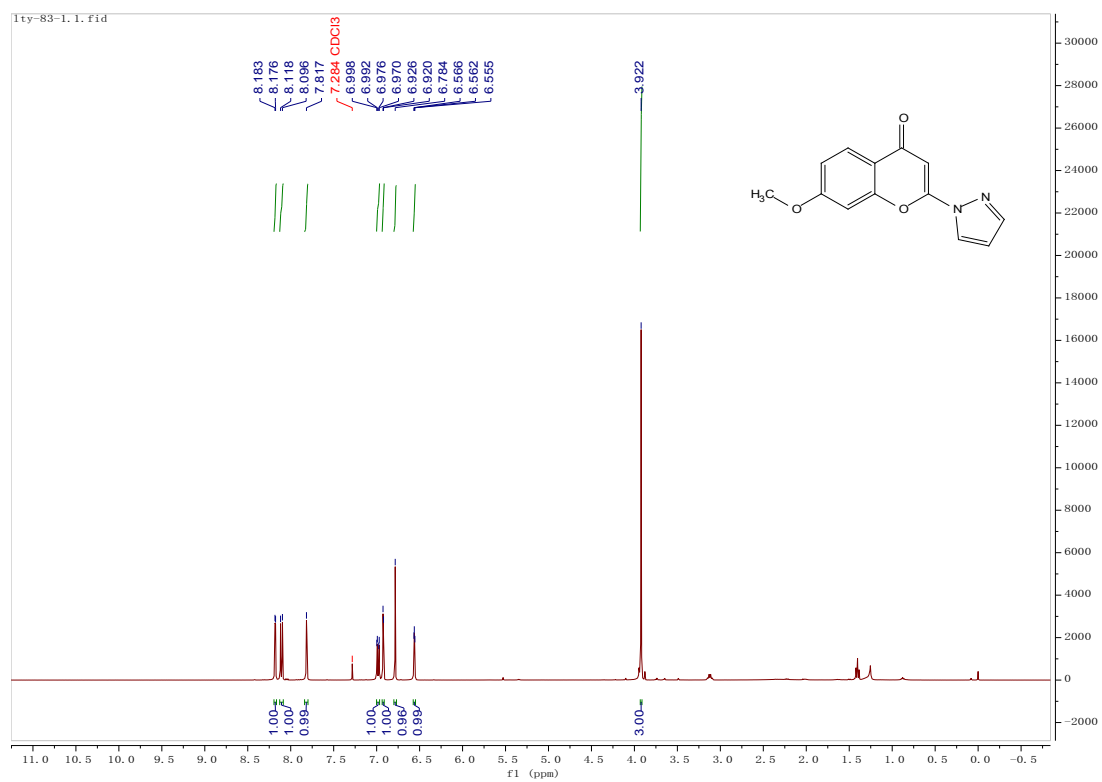
^1H and ^{13}C NMR spectra of **3n**



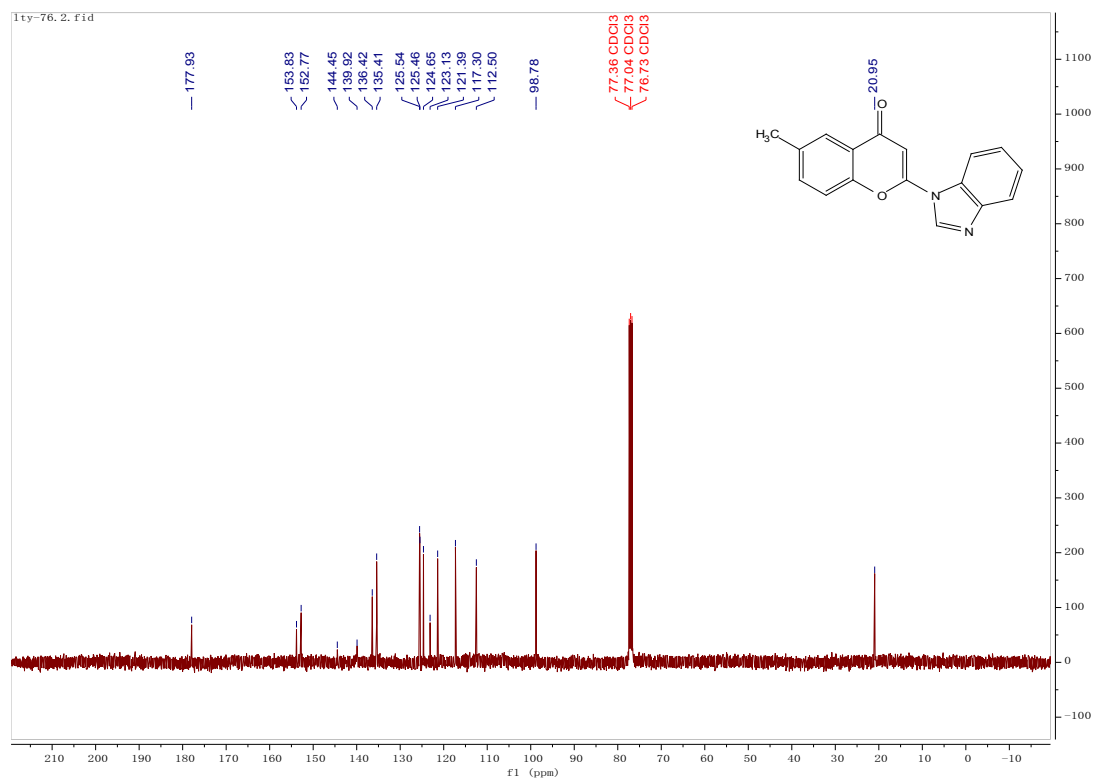
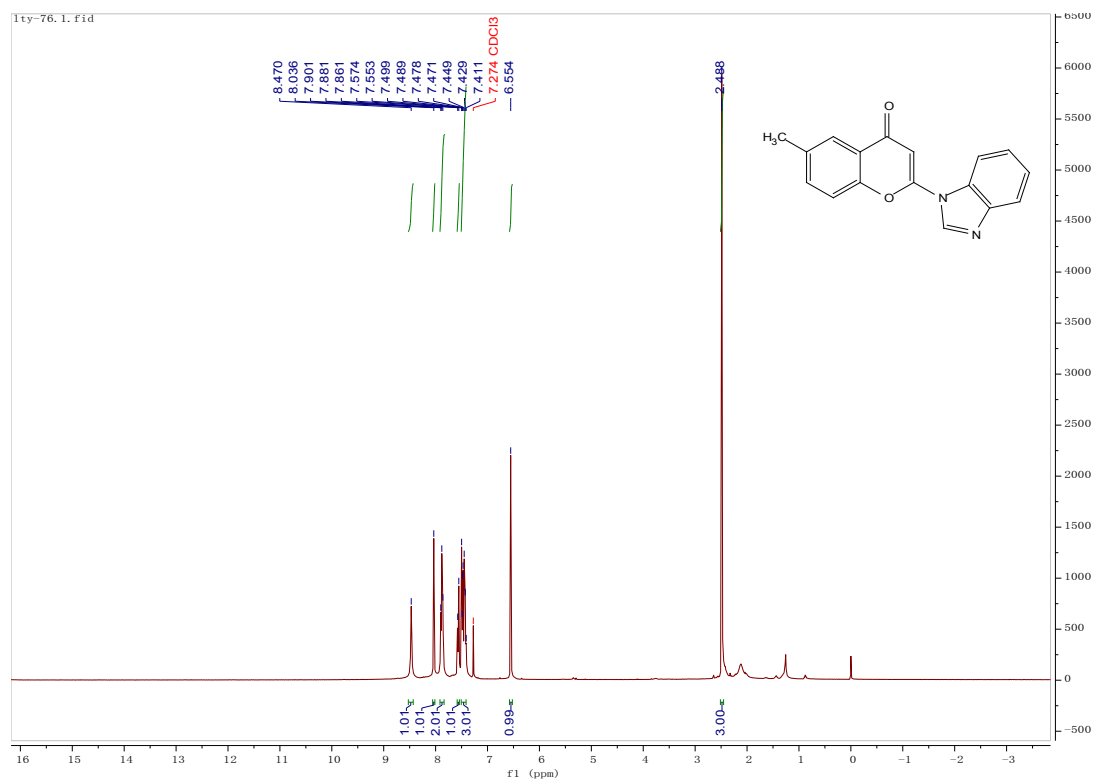
¹H and ¹³C NMR spectra of **3o**



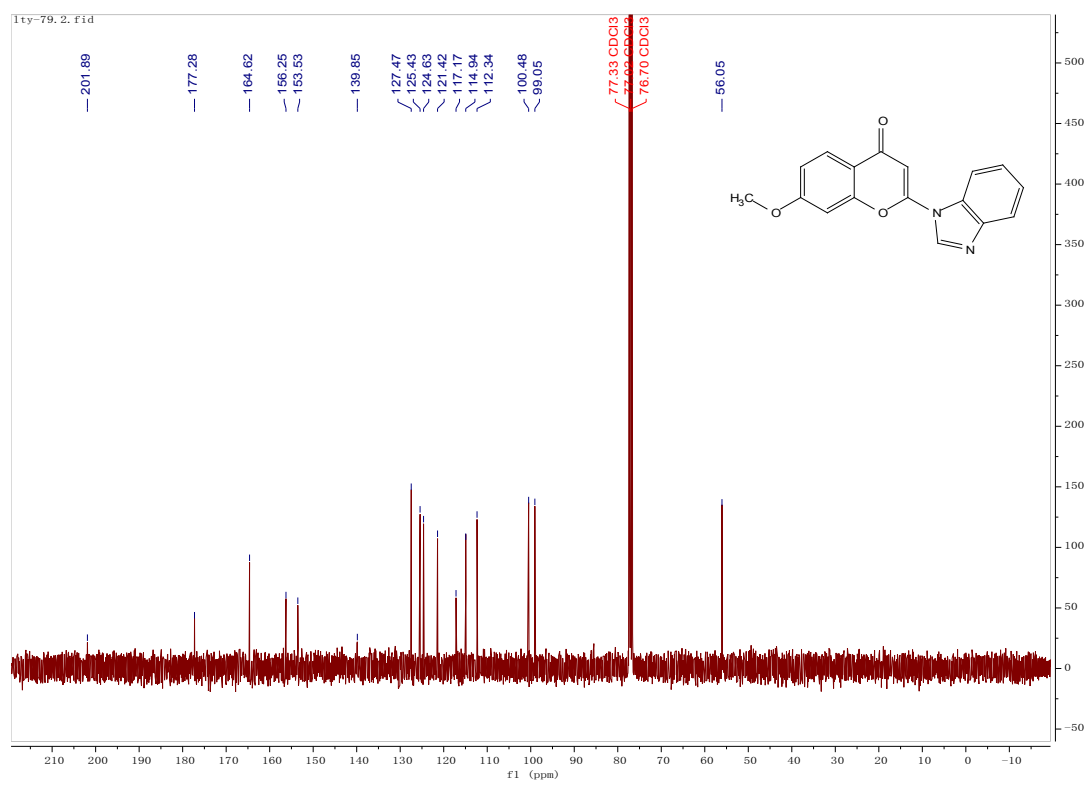
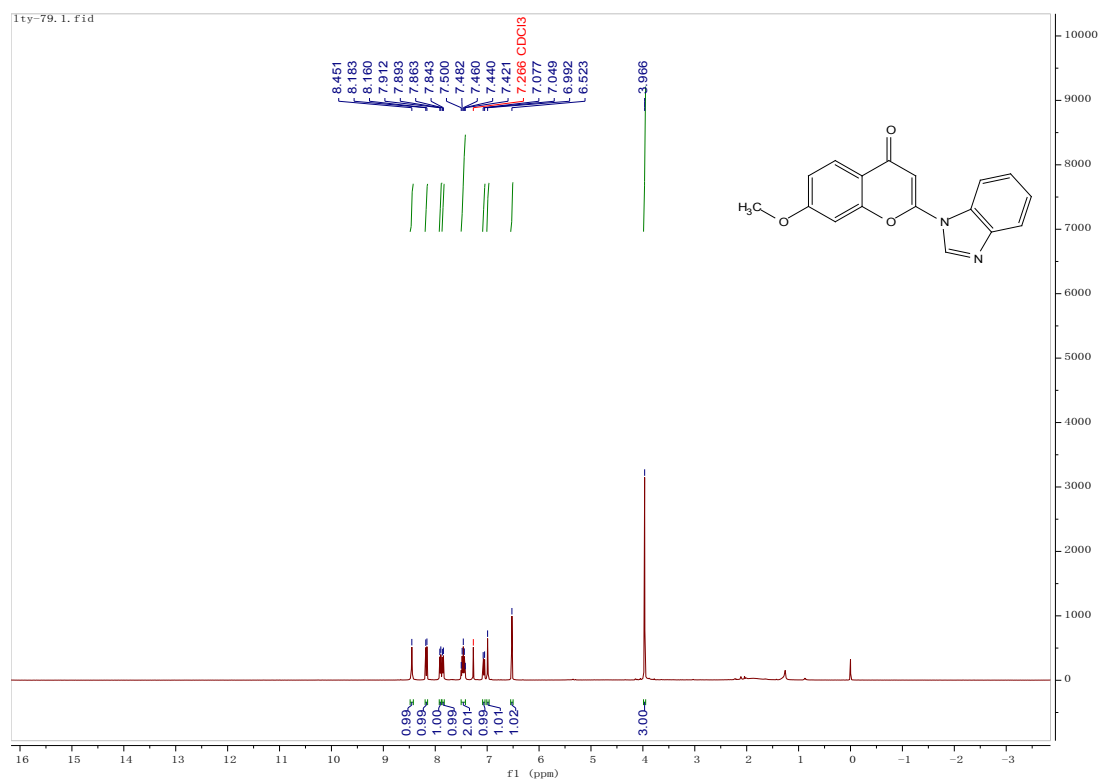
¹H and ¹³C NMR spectra of **3p**



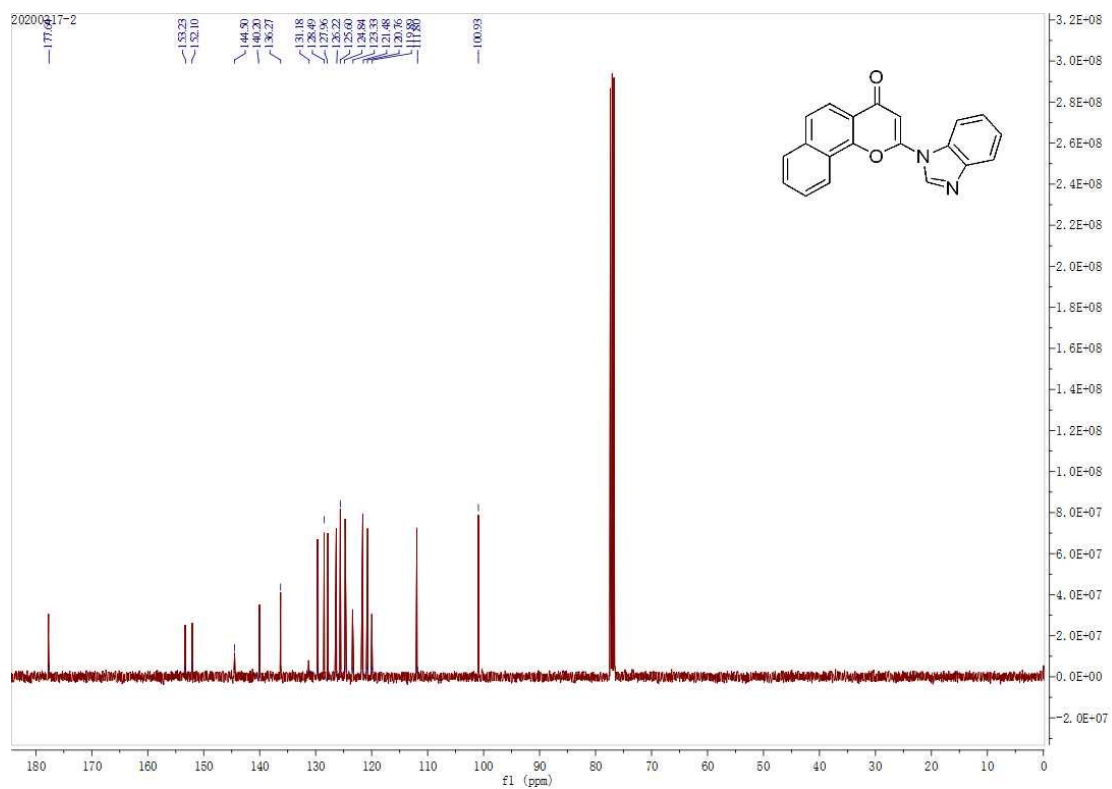
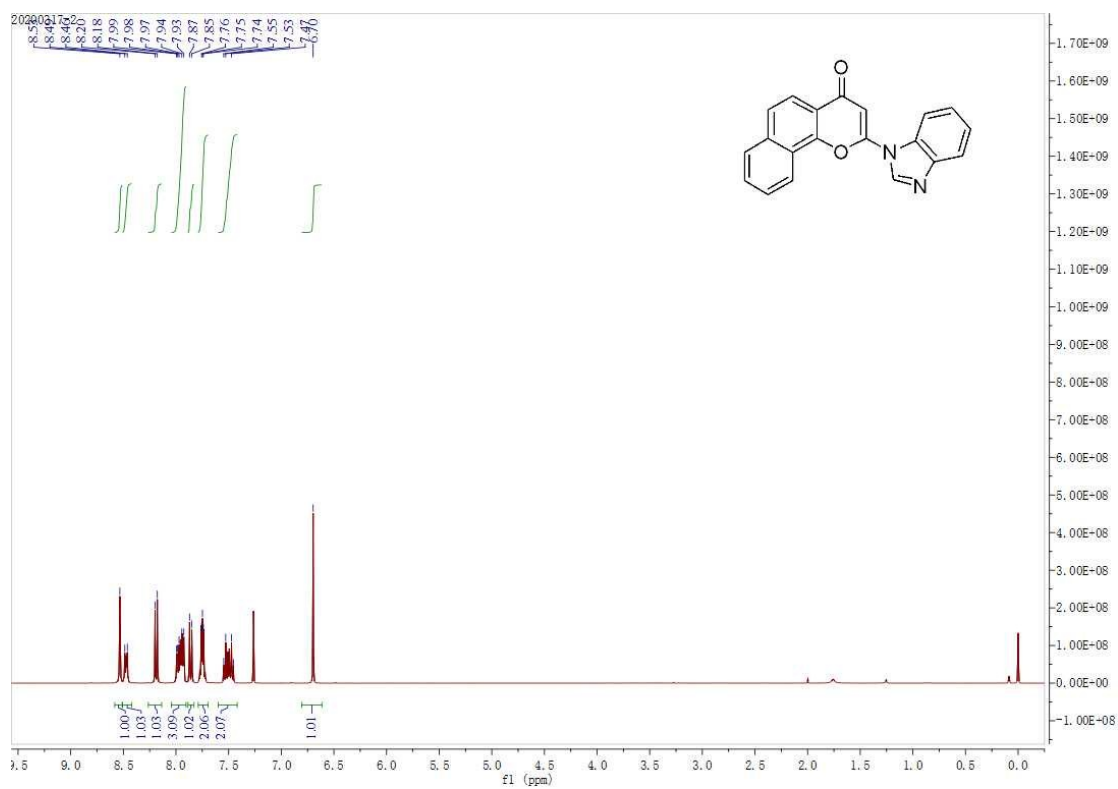
¹H and ¹³C NMR spectra of **3q**



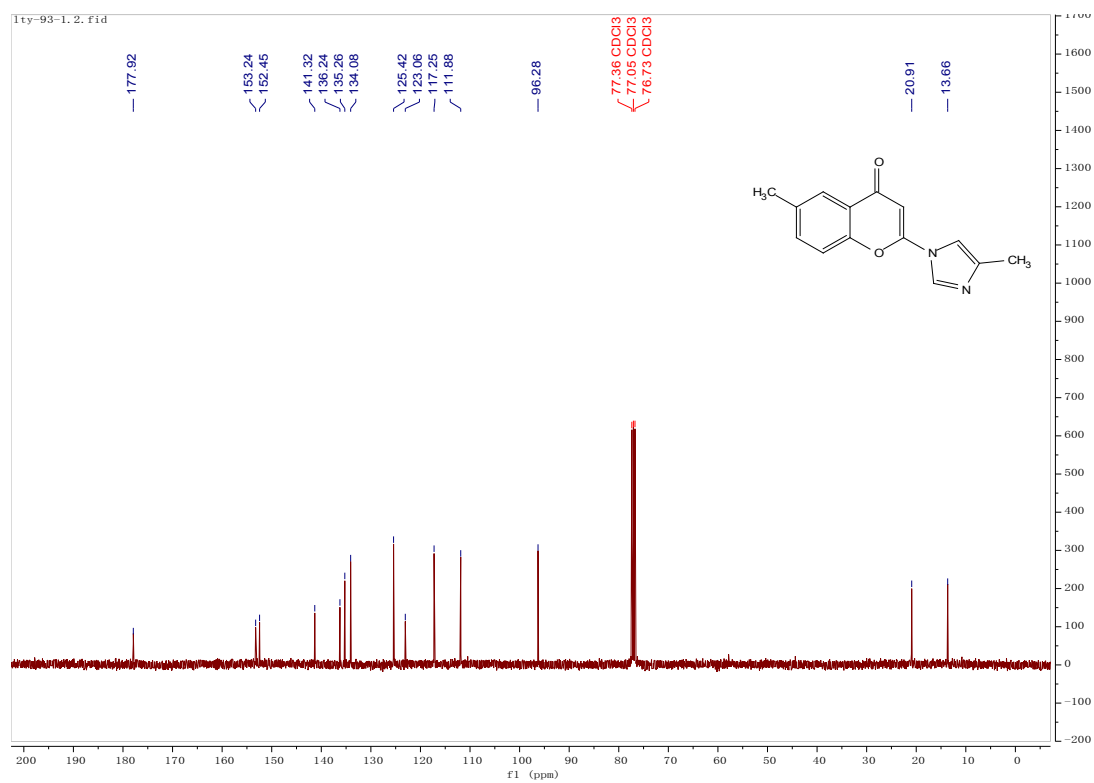
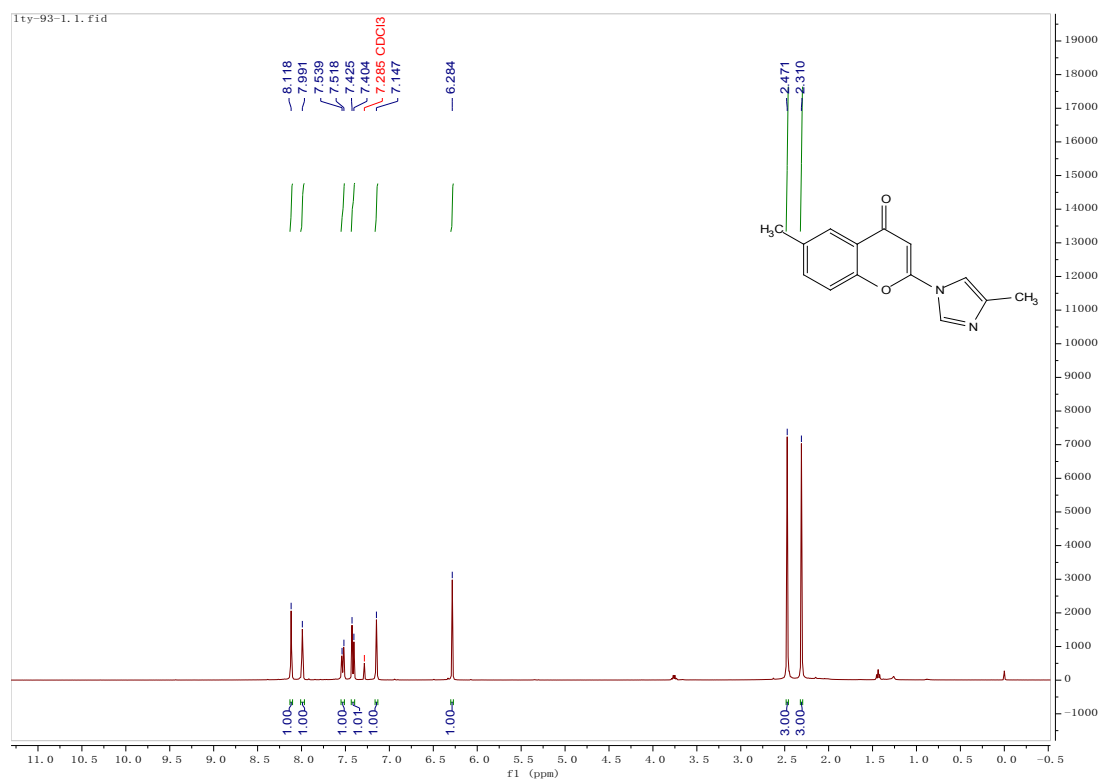
¹H and ¹³C NMR spectra of 3r



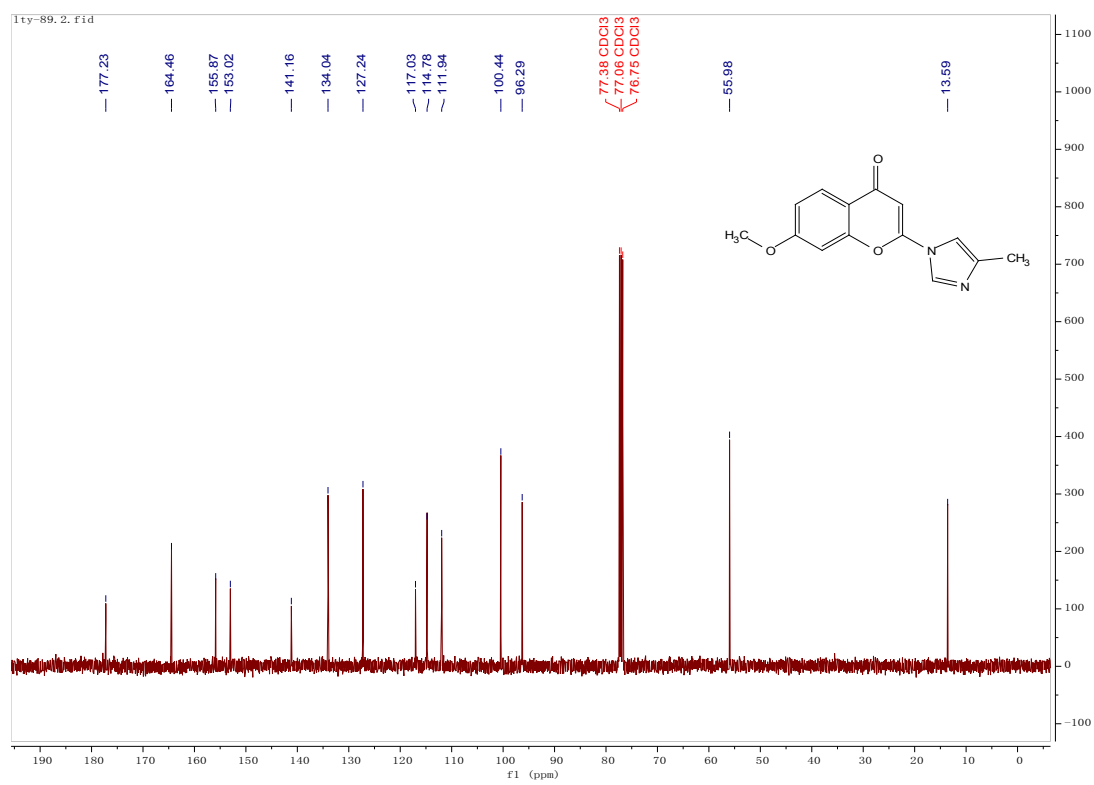
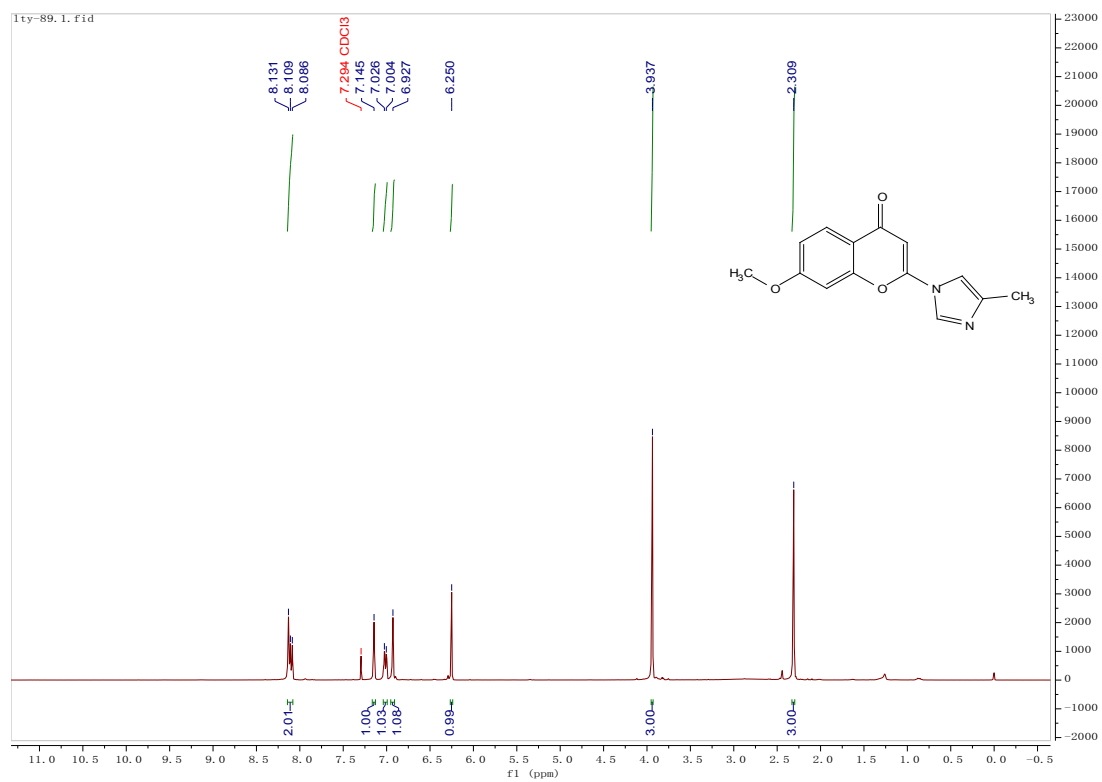
^1H and ^{13}C NMR spectra of **3s**



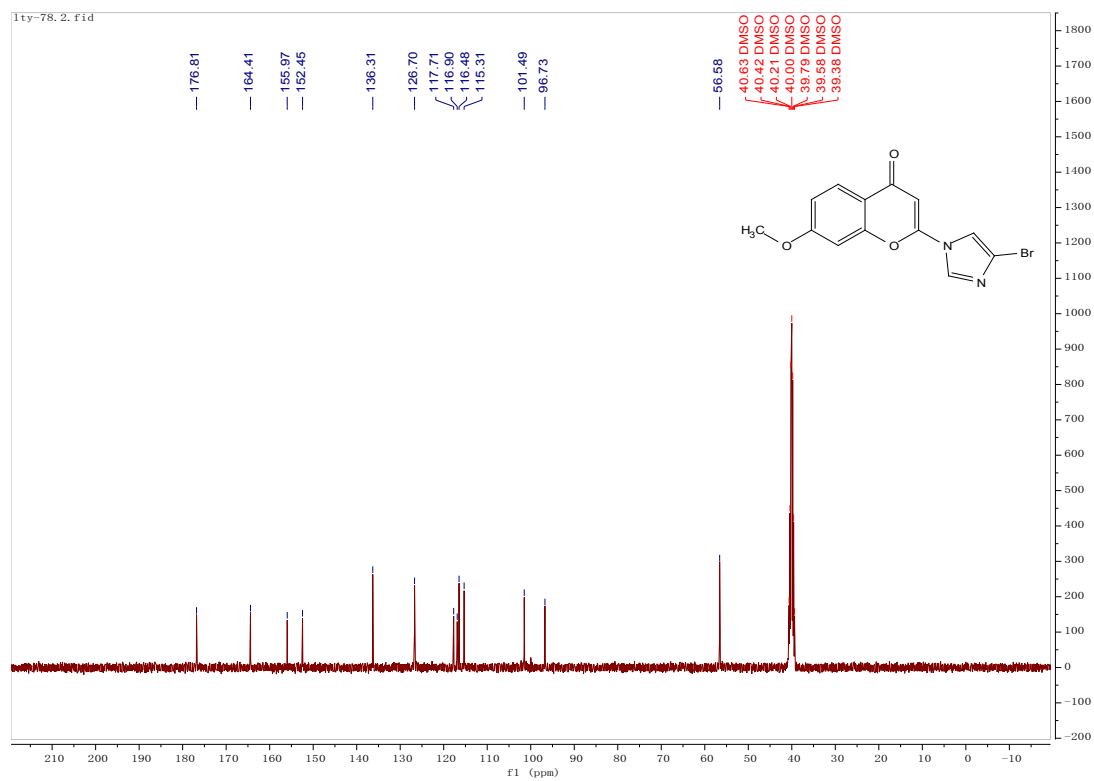
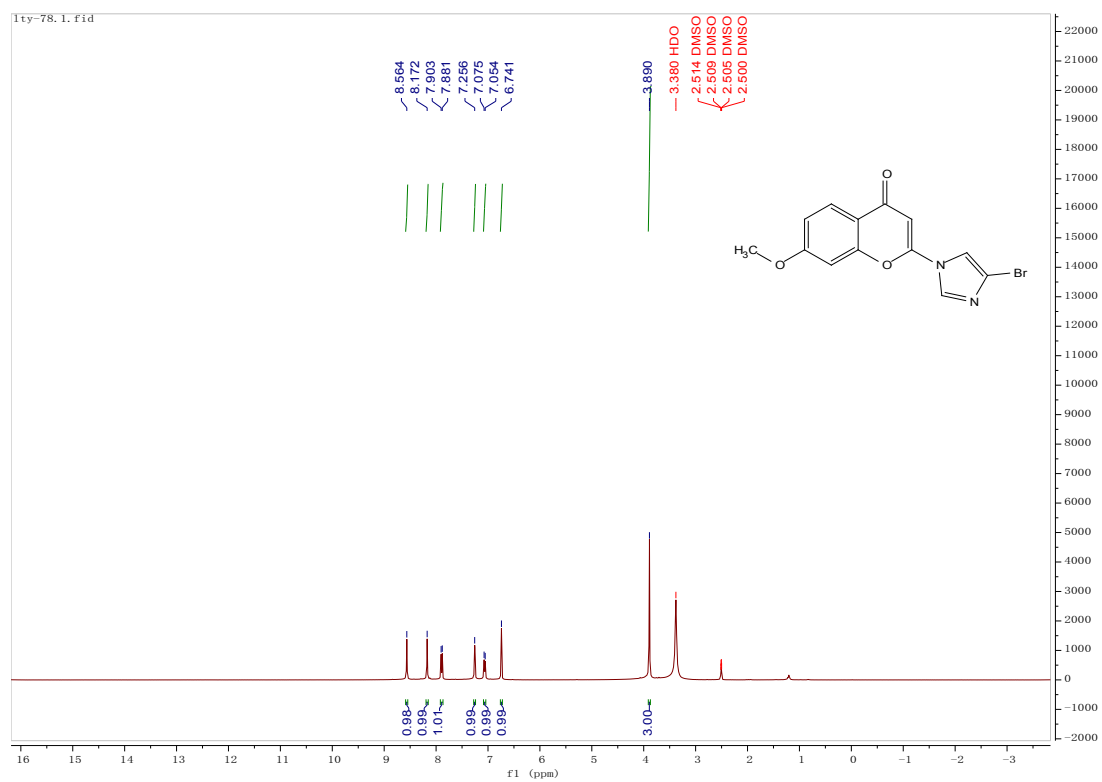
¹H and ¹³C NMR spectra of **3t**



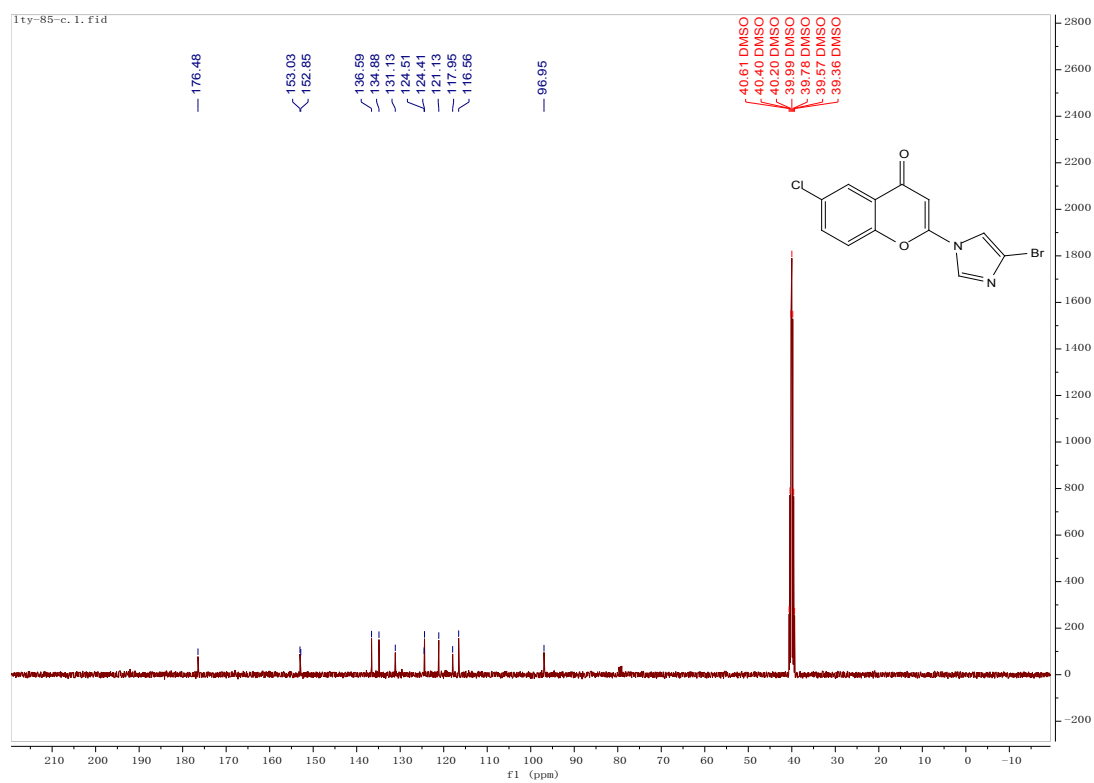
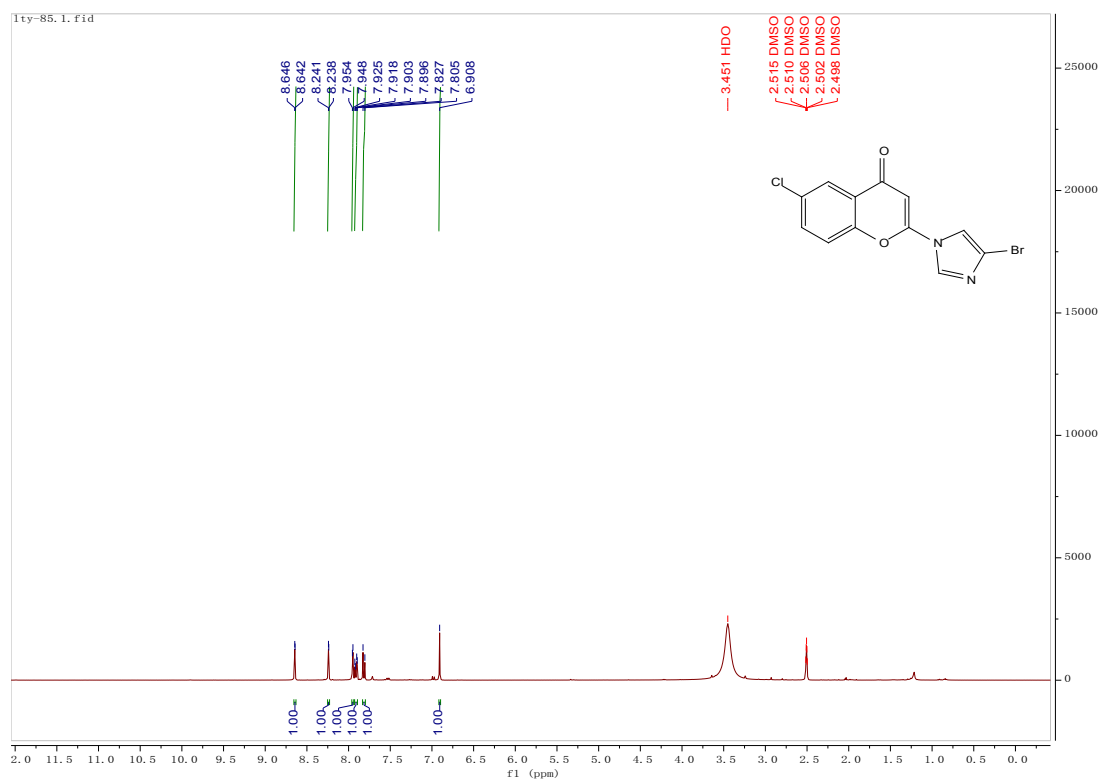
¹H and ¹³C NMR spectra of **3u**



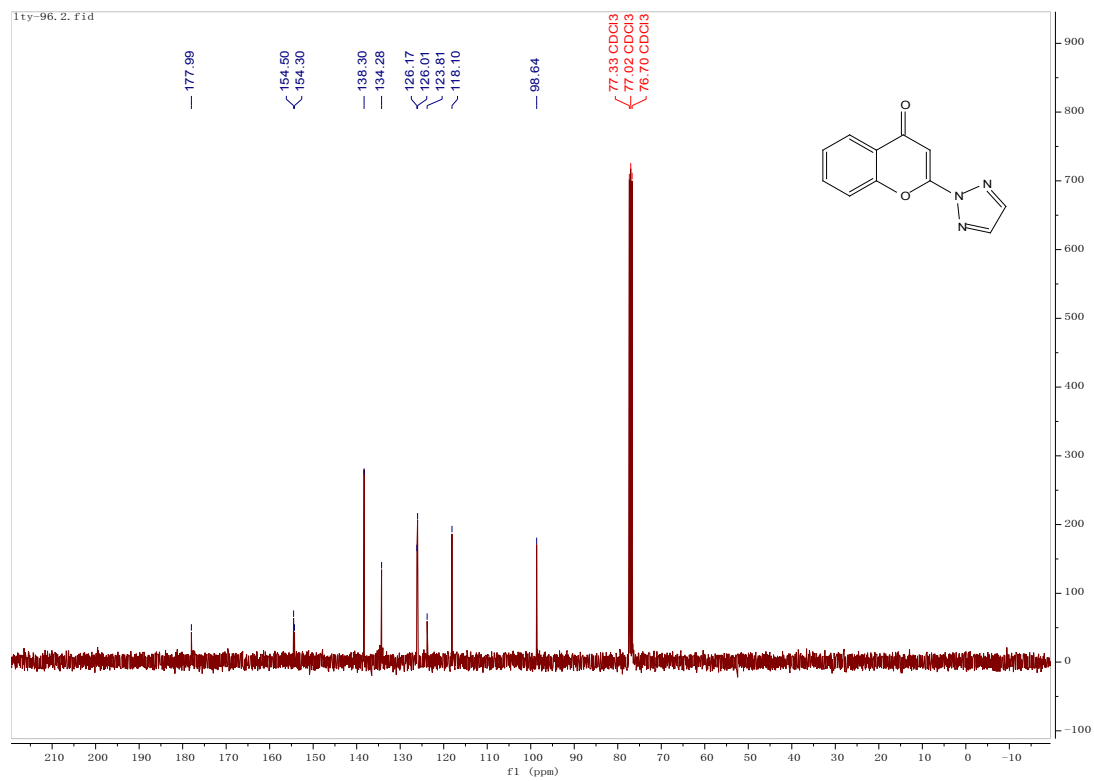
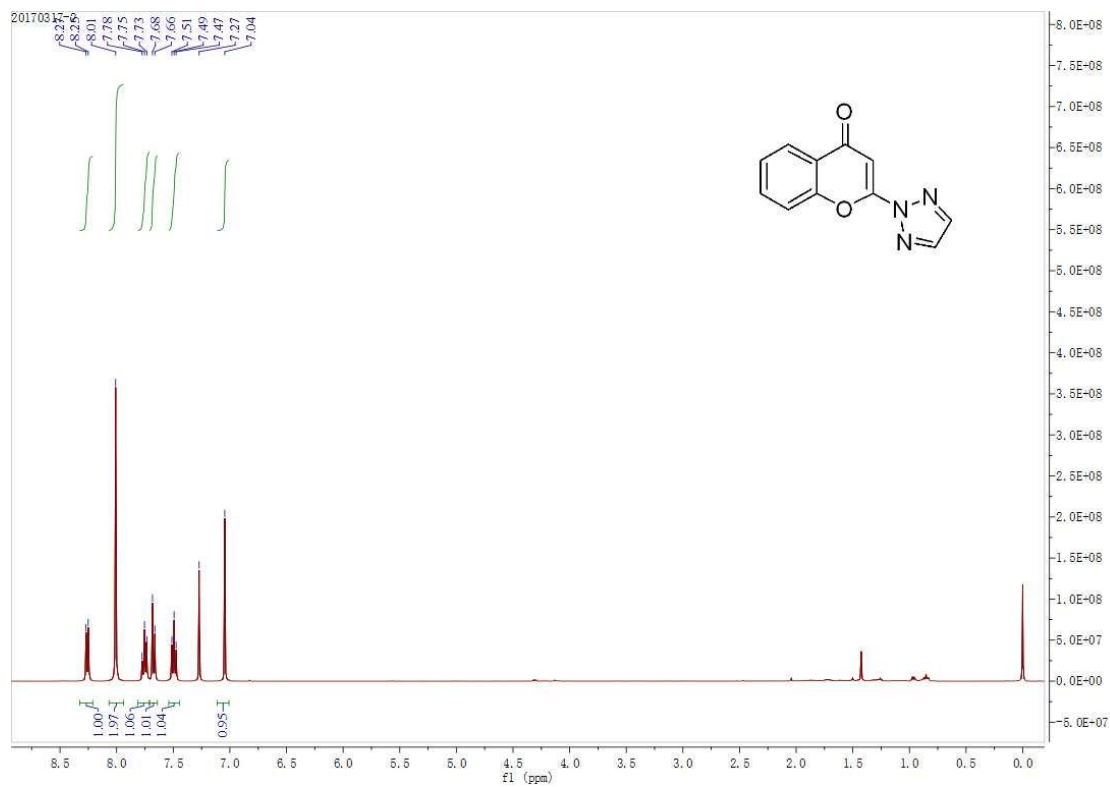
^1H and ^{13}C NMR spectra of **3v**



^1H and ^{13}C NMR spectra of **3w**



¹H and ¹³C NMR spectra of 3x



^1H and ^{13}C NMR spectra of **3y**

