Supporting Information

A General Rhodium-Catalyzed Regioselective C-H Functionalization: Accessing Heteroarylated and Alkenylated Arenes

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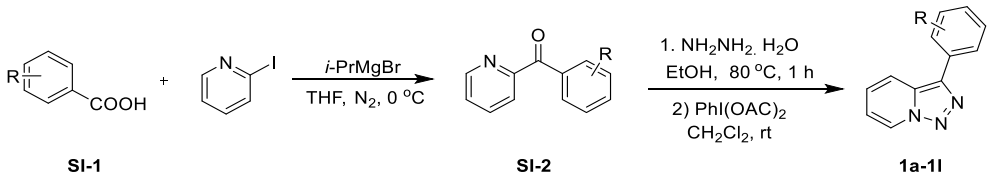
General Information

The chemical reagents were purchased from commercial sources and used directly without purification. Analytical thin-layer chromatography (TLC): HSGF 254 (0.15~0.2 mm thickness). Detection was conducted under UV light at 254 nm. Preparative thin layer chromatography was HSFG 254 (0.4~0.5 mm thickness). Yields refer to isolated compounds. ^{1}H, ^{13}C, and ^{19}F NMR spectra were collected on a Brucker 500 and 600 MHz instrument in chloroform-*d* or DMSO-d_6. Chemical shifts (δ) are expressed as parts per million (ppm). Proton coupling patterns were recorded as singlet (s), broad (br), doublet (d), triplet (t), quartet (q), and multiplet (m). HRMS (high-resolution mass spectrometry) were obtained by using a quadrupole mass analyzer with electrospray ionization (ESI) source. Crystal of compound **3zd** were grown by slow diffusion of MeOH/hexane (1/9, v/v, 10 mL) in a sample bottle at room temperature. X-ray diffractions of single crystal was carried out on a Bruker D8 VENTURE diffractometer using MoKα radiation (λ = 0.71073 Å).

Preparation of Starting Materials

General procedure A for the preparation of 1a-1l [1,2]

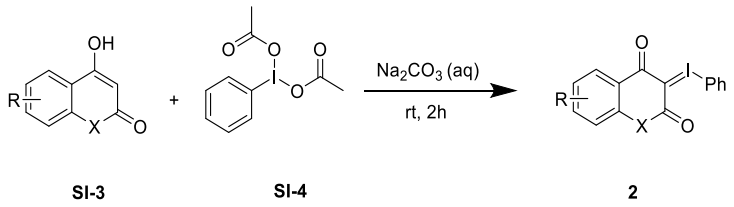


SI-1 **SI-2** **1a-1l**

Step 1: SI-1 (500 mg, 1.0 eq) and anhydrous tetrahydrofuran (10.0 mL) were added to a reaction vessel at room temperature under nitrogen atmosphere. The reaction mixture was cooled in an ice bath. Isopropyl magnesium bromide (2.75 eq) was added at 0 °C and stirred for 15 minutes. Then 2-iodopyridine (1.4 eq) was added to the reaction mixture at 0 °C. Subsequently, the reaction mixture was stirred at room temperature for 4 h. The reaction was quenched with H_2O and saturated aqueous NH_4Cl, extracted with EA and H_2O, and purified by column chromatography to provide the corresponding product.

Step 2: SI-2 (1.0 eq) in ethanol (10 mL) was added to hydrazine monohydrate (3.0 eq) in a 100 mL flask. The reaction mixture was refluxed for 1 h. Then it was allowed to cool to room temperature, and the mixture solvent was removed under reduced pressure. The reaction mixture was diluted with EtOAc, and the residue was extracted with aqueous NH_4Cl. The organic layer was dried over Mg_2SO_4. After removal of the solvent, the crude product was dissolved in CH_2Cl_2 (20 mL), and then $PhI(OAc)_2$ (1.0 eq) was added at room temperature for 30 min. Subsequently, the reaction mixture was diluted with CH_2Cl_2, and the residue was extracted with aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography to provide the corresponding product.

General procedure C for the preparation of 2 [3,4]

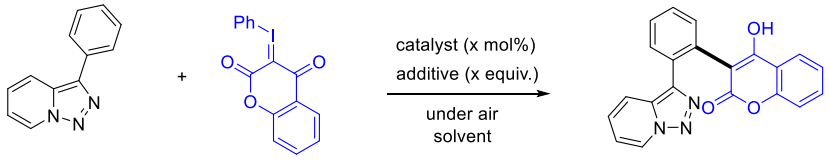


SI-3 **SI-4** **2**

$PhI(OAc)_2$ (6.2 mmol) was added to 60.0 mL of a saturated sodium carbonate aqueous solution and stirred at room temperature for 30 mins. Subsequently, a saturated sodium carbonate aqueous solution containing 4-hydroxycoumarin compounds (6.2 mmol) was added to the mixture. The reaction was stirred for 2 hours at room temperature, then cooled using an ice bath. The resulting mixture was filtered, and the residue was washed with water. The white precipitate obtained was the desired product.

General Procedure for the Synthesis of 3

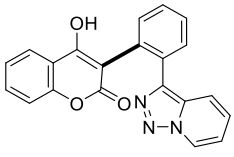
Representative Procedure for the Synthesis of **3a**



1a **2a** **3a**

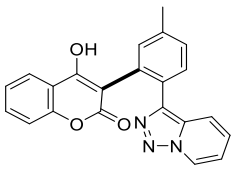
In a 10 mL reaction tube, the mixture of **1a** (39.3 mg, 0.20 mmol, 1.0 eq), **2a** (87.4 mg, 0.24 mmol, 1.2 eq), $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol%), and $Zn(OAc)_2$ (36.7 mg, 0.2 mmol, 1.0 eq) was dissolved in HFIP (2.0 mL). Then the resulting mixture was stirred at room temperature. When the reaction was finished, the products are purified by preparative thin layer chromatography (DCM/MeOH = 20/1). The product **3a** was obtained as a pale-white solid (64 mg, 89% yield). Other products were prepared by a similar procedure.

Characterization Data of Products 3

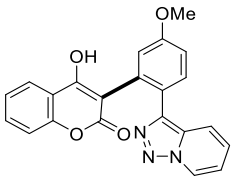


3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-2H-chromen-2-one (3a): column solvent: DCM/MeOH = 20:1, white solid (64 mg, 89% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.93 (d, J = 7.0 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.68 (d, J = 7.3 Hz, 1H), 7.58 – 7.40 (m, 4H), 7.31 – 7.21 (m, 3H), 7.07 (t, J = 6.8 Hz, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.8, 152.6, 137.5, 133.1, 131.8, 131.6, 130.4, 129.6, 127.8, 125.7, 125.6, 123.8, 123.4, 118.0,

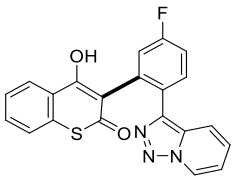
115.9, 115.7. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{21}H_{13}N_3O_3$ 356.1030; Found: 356.1029.



3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-methylphenyl)-4-hydroxy-2H-chromen-2-one (3b): column solvent: DCM/MeOH = 30/1, white solid (71mg, yield 96%). **^{1}H NMR (600 MHz, DMSO-*d*$_6$)** δ 8.93 (d, J = 7.0 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 8.9 Hz, 1H), 7.63 – 7.51 (m, 2H), 7.35 (d, J = 7.9 Hz, 1H), 7.28 (d, J = 8.4 Hz, 4H), 7.16 – 7.00 (m, 1H), 2.40 (s, 3H). **^{13}C NMR (151 MHz, DMSO-*d*$_6$)** δ 161.6, 161.0,152.4, 137.3, 137.2, 133.3, 131.8, 131.6, 130.4, 129.5, 128.9, 128.9, 125.7, 125.6, 123.6, 117.9, 116.8, 116.0, 115.7, 105.9, 20.8. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{16}N_3O_3$ 370.1186; found: 370.1187.

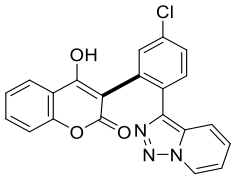


3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-methoxyphenyl)-4-hydroxy-2H-chromen-2-one (3c): column solvent: DCM/MeOH = 30/1, yellow solid (73mg, yield 95%). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.90 (d, J = 6.9 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.58 (s, 1H), 7.54 (s, 1H), 7.26 (d, J = 8.1 Hz, 3H), 7.13 – 7.00 (m, 3H), 3.83 (s, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.5, 158.9, 152.5, 137.3, 133.6, 131.7, 130.8, 130.4, 125.5, 125.4, 124.3, 123.8, 123.5, 118.2, 117.9, 117.2, 115.9, 115.6, 113.7, 105.3, 55.3. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{16}N_3O_4$ 386.1135; found: 386.1137.

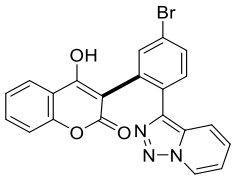


3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-fluorophenyl)-4-hydroxy-2H-chromen-2-one (3d): column solvent: DCM/MeOH = 20:1, yellow solid (58 mg, 78% yield). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.91 (d, J = 7.0 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.68 (t, J = 6.9 Hz, 2H), 7.54 – 7.44 (m, 1H), 7.34 – 7.24 (m, 2H), 7.24 – 7.14 (m, 3H), 7.05 (t, J = 6.8 Hz, 1H). **^{13}C NMR (151 MHz, DMSO-*d*$_6$)** δ 162.4, 161.6, 160.8, 152.9, 136.1, 131.5, 131.4, 131.4, 128.6, 125.6, 125.4, 124.1, 123.0, 119.70 (d, J = 19.9 Hz), 118.0, 115.72 (d, J = 35.8 Hz), 114.15 (d, J = 21.0 Hz), 102.89. **^{19}F**

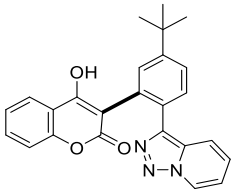
NMR (471 MHz, DMSO-d_6) δ -115.55. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{21}H_{12}FN_3O_3$ 374.0935; Found: 374.0935.



3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-chlorophenyl)-4-hydroxy-2H-chromen-2-one (3e): column solvent: DCM/MeOH = 20:1, yellow solid (60 mg, 77% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.91 (d, J = 6.9 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.67 – 7.59 (m, 2H), 7.48 – 7.39 (m, 3H), 7.19 – 7.07 (m, 3H), 7.04 – 6.98 (m, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.9, 153.0, 137.1, 132.9, 131.8, 131.3, 131.1, 131.0, 130.3, 128.3, 128.0, 126.6, 125.5, 125.3, 124.3, 122.7, 118.0, 115.7, 115.6. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{21}H_{12}ClN_3O_3$ 390.0640; Found: 390.0640.

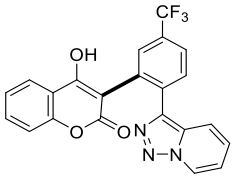


3-(2-([1,2,3] triazolo[1,5-a]pyridin-3-yl)-5-bromophenyl)-4-hydroxy-2H-chromen-2-one (3f): column solvent: DCM/MeOH = 30/1, yellow solid (86 mg, yield 99%). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.96 (d, J = 7.0 Hz, 1H), 7.85 (dd, J = 8.1, 1.5 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.71 (dd, J = 8.3, 2.1 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.57 (s, 1H), 7.37 – 7.25 (m, 3H), 7.11 (t, J = 6.8 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 161.8, 161.4, 152.5, 136.2, 135.4, 134.3, 132.0, 131.4, 131.1, 130.9, 130.5, 126.2, 125.7, 123.8, 123.6, 120.8, 117.7, 116.9, 116.0, 115.8, 104.4. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{21}H_{13}BrN_3O_3$ 434.0135; found: 434.0141.

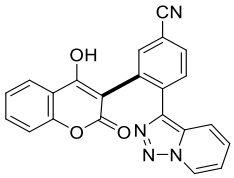


3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-(tert-butyl)phenyl)-4-hydroxy-2H-chromen-2-one (3g): column solvent: DCM/MeOH = 30/1, yellow solid (78 mg, yield 95%). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.93 (d, J = 7.0 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.86 (dd, J = 7.9, 1.6 Hz,1H), 7.78 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.45 (d, J = 2.1 Hz,1H), 7.31 – 7.24 (m, 3H), 7.08 (t, J = 6.8 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 161.68,

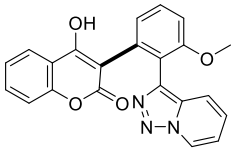
152.5, 150.0, 137.4, 131.6, 130.4, 129.6, 129.2, 129.0, 125.6, 125.0, 124.8, 123.7, 123.5, 118.0, 115.9, 115.7, 34.4, 31.1. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{25}H_{22}N_3O_3$ 412.1656, found: 412.1658.



3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-4-(trifluoromethyl)phenyl)-4-hydroxy-2H-chromen-2-one (3h): column solvent: DCM/MeOH = 30/1, yellow solid (77 mg, yield 91%). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.00 (d, J = 7.0 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.93 – 7.82 (m, 4H), 7.60 (t, J = 7.8 Hz, 1H), 7.39 (dd, J = 9.0, 6.6 Hz, 1H), 7.32 (d, J = 8.6 Hz, 2H), 7.15 (t, J = 6.9 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 161.47, 152.51, 135.86, 132.73, 132.19, 130.75, 130.27, 129.79, 129.76, 128.33, 128.07, 126.75, 125.88, 125.36, 124.96, 123.78, 123.73, 123.20, 117.62, 116.60, 116.14, 116.03, 104.77. **^{19}F NMR (471 MHz, DMSO-d_6)** δ -60.88. HRMS (ESI-MS) m/z: $[M+H]^+$ calculated for $C_{22}H_{13}F_3N_3O_3$ 424.0903; found: 424.0907.

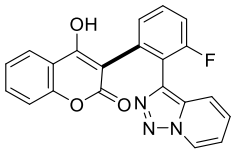


4-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-3-(4-hydroxy-2-oxo-2H-chromen-3-yl)benzonitrile (3i): column solvent: DCM/MeOH = 30/1, yellow solid (51 mg, yield 67%). **^{1}H NMR (600 MHz, DMSO-d_6)** δ 8.95 (d, J = 6.9 Hz, 1H), 7.86 (s, 1H), 7.80 (t, J = 8.5 Hz, 3H), 7.64 (d, J = 8.9 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.16 (d, J = 7.0 Hz, 2H), 7.10 (d, J = 8.2 Hz, 1H), 7.04 (t, J = 6.9 Hz, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.9, 153.2, 137.4, 137. 5, 136.9, 136.5, 130.9, 130.5, 130.2, 129.7, 129.5, 125.6, 124.5, 122.5, 119.2, 118.0, 116.2, 115.7, 115.6, 109.7. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{13}N_4O_3$ 381.0982; found: 381.0982.

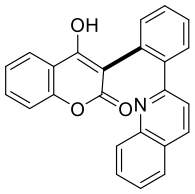


3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-3-methoxyphenyl)-4-hydroxy-2H-chromen-2-one (3j): column solvent: DCM/MeOH = 30/1, white solid (45 mg, yield 58%). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.88 (d, J = 7.0 Hz, 1H), 7.79 (dd, J = 7.9, 1.6 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.48 (s, 2H), 7.31 (dd, J = 8.9, 6.6 Hz, 1H), 7.24 – 7.07 (m, 4H), 7.00 (d, J = 7.6 Hz, 1H), 3.74 (s, 3H). **^{13}C NMR (151**

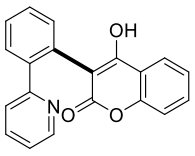
MHz, DMSO-*d*$_6$) δ 161.5, 157.5, 152.5, 133.6, 131.8, 131.4, 129.6, 125.3, 125.0, 124.7, 123.9, 123.2, 120.3, 119.3, 115.8, 110.5, 104.6, 55.6. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{16}N_3O_4$ 386.1135; found: 386.1135.



3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-3-fluorophenyl)-4-hydroxy-2H-chromen-2-one (3k): column solvent: DCM/MeOH = 30/1, yellow solid (64 mg, yield 86%). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.96 (d, *J* = 6.9 Hz, 1H), 7.82 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.61 – 7.52 (m, 2H), 7.44 – 7.35 (m, 2H), 7.32 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.26 (dd, *J* = 8.1, 3.4 Hz, 2H), 7.17 – 7.11 (m, 1H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 161.9, 161.3, 160.0 (d, *J* = 244.9 Hz), 152.4, 135.5, 131.9, 131.6, 130.8, 129.9 (d, *J* = 9.3 Hz), 128.8, 126.0, 125.6, 123.7 (d, *J* = 22.1 Hz), 119.7, 119.6, 118.2 (d, *J* = 4.4 Hz), 116.9, 115.9 (d, *J* = 24.7 Hz), 115.1, 114.9, 104.1. **^{19}F NMR (471 MHz, DMSO-*d*$_6$)** δ -114.40. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{21}H_{13}FN_3O_3$ 374.0935; found: 374,0937.

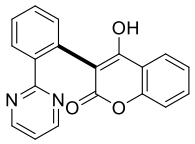


4-hydroxy-3-(2-(quinolin-2-yl)phenyl)-2H-chromen-2-one (3l): column solvent: DCM/MeOH = 30/1, yellow solid (68 mg, yield 93%). **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.27 (d, J = 8.6 Hz, 1H), 7.87 (m, 4H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.54 (t, *J* = 8.1 Hz, 4H), 7.42 (d, *J* = 6.5 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 162.11, 158.73, 152.67, 146.52, 140.51, 136.54, 132.96, 132.26, 131.78, 129.99, 128.84, 128.11, 127.87, 126.57, 123.93, 123.58, 121.40, 117.72, 116.02. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{24}H_{16}NO_3$ 366.1130; found: 366.1129.

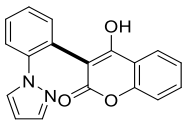


4-hydroxy-3-(2-(pyridin-2-yl)phenyl)-2H-chromen-2-one (3m): column solvent: DCM/MeOH = 20:1, yellow solid (60 mg, 95% yield). **1H NMR (500 MHz, Chloroform-d)** δ 8.26 – 8.17 (m, 1H), 7.94 – 7.89 (m, 1H), 7.89 – 7.81 (m, 1H), 7.53 – 7.44 (m, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 7.23 – 7.17 (m, 2H), 7.00 – 6.90 (m, 2H). **^{13}C NMR (151 MHz, Chloroform-*d*)** δ 172.8, 164.0,

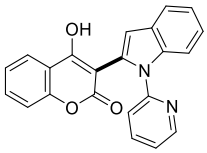
159.1, 153.5, 147.5, 140.7, 139.4, 134.5, 133.6, 131.2, 130.8, 129.0, 126.9, 124.7, 124.5, 123.3, 123.1, 120.8, 116.1, 103.9. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{20}H_{13}NO_3$ 316.0968; Found: 316.0964.



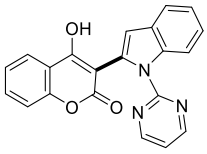
4-hydroxy-3-(2-(pyrimidin-2-yl)phenyl)-2H-chromen-2-one (3n): column solvent: DCM/MeOH = 20:1, yellow solid (46 mg, 72% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.68 (d, J = 4.9 Hz, 2H), 7.99 (d, J = 7.4 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.61 – 7.38 (m, 4H), 7.33 – 7.19 (m, 3H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 166.1, 161.9, 156.8, 152.5, 138.9, 132.8, 131.1, 130.0, 129.0, 127.1, 123.8, 123.2, 118.9, 115.8. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{19}H_{12}N_2O_3$ 317.0921; Found: 317.0919.



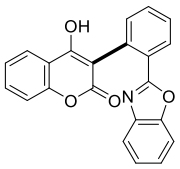
3-(2-(1H-pyrazol-1-yl)phenyl)-4-hydroxy-2H-chromen-2-one (3o): column solvent: DCM/MeOH = 20:1, yellow solid (61 mg, 95% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 7.93 (d, J = 2.4 Hz, 1H), 7.86 – 7.80 (m, 1H), 7.53 – 7.42 (m, 3H), 7.42 – 7.34 (m, 2H), 7.32 – 7.26 (m, 1H), 7.20 – 7.11 (m, 2H), 6.26 (t, J = 2.2 Hz, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 162.5, 153.3, 140.3, 139.5, 134.3, 130.8, 130.6, 127.4, 127.2, 125.1, 124.5, 122.3, 115.6, 106.0. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{18}H_{12}N_2O_3$ 305.0921; Found: 305.0918.



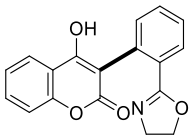
4-hydroxy-3-(1-(pyridin-2-yl)-1H-indol-2-yl)-2H-chromen-2-one (3p): column solvent: DCM/MeOH = 30/1, yellow solid (66 mg, yield 93%). **^{1}H NMR (600 MHz, Chloroform-d)** δ 8.50 (d, J = 4.8 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 7.67 (d, J = 6.2 Hz, 1H), 7.58 (d, J = 6.3 Hz, 1H), 7.50 (s, 1H), 7.37 (s, 1H), 7.29 – 7.17 (m, 3H), 7.15 – 7.07 (m, 2H), 6.58 (s, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 162.0, 153.3, 151.5, 148.3, 138.2, 136.3, 131.3, 128.4, 124.5, 122.8, 121.4, 121.3, 120.2, 119.7, 119.3, 115.8, 111.4, 106.6. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{15}N_2O_3$ 355.1077; found: 355.1070.



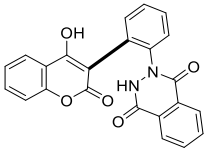
4-hydroxy-3-(1-(pyrimidin-2-yl)-1H-indol-2-yl)-2H-chromen-2-one (3q): column solvent: DCM/MeOH = 30/1, yellow solid (36 mg, yield 51%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 8.62 (d, J = 4.8 Hz, 2H), 8.20 (dd, J = 8.3, 1.1 Hz, 1H), 7.78 (dd, J = 7.9, 1.6 Hz, 1H), 7.58 (m, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.26 (s, 3H), 7.24 – 7.16 (m, 1H), 7.09 (t, J = 4.8 Hz, 1H), 6.77 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 161.5, 161.1, 158.1, 157.2, 153.2, 137.4, 132.5, 128.4, 127.8, 124.7, 124.3, 124.1, 122.4, 120.6, 117.6, 116.6, 115.6, 114.9, 111.0, 101.1. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{21}H_{14}N_3O_3$ 356.1030; found: 356.1024.



3-(2-(benzo[d]oxazol-2-yl)phenyl)-4-hydroxy-2H-chromen-2-one (3r): column solvent: DCM/MeOH = 30/1, white solid (47 mg, yield 66%). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.23 – 8.16 (m, 1H), 8.02 – 7.93 (m, 1H), 7.66 – 7.60 (m, 3H), 7.60 – 7.51 (m, 3H), 7.45 – 7.25 (m, 4H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 162.8, 161.9, 152.6, 149.8, 141.4, 133.3, 131.8, 130.9, 129.5, 127.8, 127.4, 125.1, 124.4, 123.9, 123.5, 119.7, 116.1, 110.5. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{14}NO_4$ 356.0923; found: 356.0923.

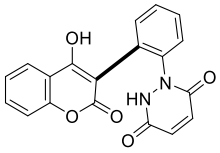


4-hydroxy-3-(2-(oxazol-2-yl)phenyl)-2H-chromen-2-one (3s): column solvent: DCM/MeOH = 30/1, yellow solid (37 mg, yield 60%). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.61 (d, J = 8.3 Hz, 1H), 8.29 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 7.9 Hz, 1H), 7.90 – 7.71 (m, 3H), 7.61 – 7.47 (m, 2H), 5.05 (t, J = 6.1 Hz, 1H), 4.47 (t, J = 6.1 Hz, 2H), 3.76 (q, J = 6.1 Hz, 2H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 174.8, 160.8, 155.8, 151.8, 134.0, 133.8, 132.9, 127.4, 126.8, 125.8, 125.4, 125.2, 122.3, 122.2, 117.7, 97.4, 58.2, 44.3. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{14}NO_4$ 308.0923; found: 308.0915.

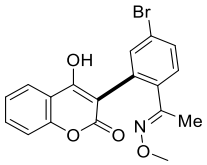


2-(2-(4-hydroxy-2-oxo-2H-chromen-3-yl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3t): column solvent: DCM/MeOH = 30/1, yellow solid (25 mg, yield 31%); ^{1}H NMR (600 MHz,

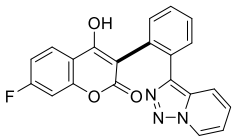
DMSO-d_6) δ 11.50 (br, 2H), 8.09 (d, J = 7.9 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.80 – 7.74 (m, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.50 – 7.42 (m, 2H), 7.27 – 7.22 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.0, 157.0, 152.4, 150.2, 141.4, 133.4, 132.8, 132.2, 132.0, 130.0, 129.7, 128.9, 128.5, 128.2, 128.1, 127.6, 126.7, 124.2, 123.7, 123.6, 116.6, 116.0, 103.6. HRMS (ESI-MS) m/z*:* $[M+H]^+$ Calcd for $C_{23}H_{15}N_2O_5$: 399.0976; Found: 399.0965.



1-(2-(4-hydroxy-2-oxo-2H-chromen-3-yl)phenyl)-1,2-dihydropyridazine-3,6-dione (3u): column solvent: DCM/MeOH = 30/1, yellow solid (18 mg, yield 26%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.26 (br, 1H), 11.10 (s, 1H), 7.93 – 7.87 (m, 1H), 7.64 – 7.58 (m, 1H), 7.52 – 7.43 (m, 3H), 7.43 – 7.39 (m, 1H), 7.36 – 7.30 (m, 2H), 6.99 (d, J = 9.7 Hz, 1H), 6.79 (d, J = 9.8 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.8, 160.5, 157.5, 152.4, 152.3, 141.3, 133.1, 132.6, 132.2, 129.3, 128.4, 127.8, 127.5, 125.5, 123.8, 123.7, 116.3, 116.1, 103.7. HRMS (ESI-MS) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}N_2O_5$: 349.0819; Found: 349.0811.

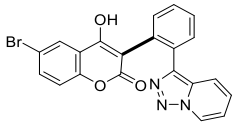


(E)-3-(5-bromo-2-(1-(methoxyimino)ethyl)phenyl)-4-hydroxy-2H-chromen-2-one (3v): column solvent: DCM/MeOH=20:1, pale yellow (72 mg, yield 94%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, J = 7.9 Hz, 1H), 7.62 – 7.47 (m, 3H), 7.38 (d, J = 8.3 Hz, 1H), 7.34 – 7.26 (m, 2H), 3.58 (s, 3H), 1.94 (s, 3H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.82, 152.78, 137.35, 135.14, 131.60, 130.04, 129.78, 124.08, 123.29, 121.03, 115.98, 61.07, 14.56. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{18}H_{16}BrNO_4$ 388.0184, found: 388.0179.

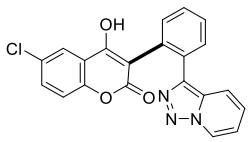


3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-7-fluoro-4-hydroxy-2H-chromen-2-one (3w): column solvent: DCM/MeOH = 30/1, yellow solid (44 mg, yield 59%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.60 (s, 1H), 7.76 (d, J = 8.9 Hz, 1H), 7.47 – 7.27 (m, 3H), 7.12 (d, J = 58.1 Hz, 4H), 6.91 (d, J = 9.7 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 163.64 (d, J = 248.4 Hz), 161.6, 153.7 (d, J = 13.3 Hz), 137.4, 133.0, 132.1, 131.8, 131.1, 130.4, 129.5, 127.9, 127.8, 125.9 (d, J =

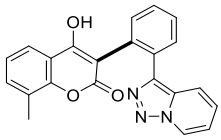
10.5 Hz), 125.8, 125.6, 117.9, 115.7, 114.4, 111.2 (d, J = 22.4 Hz), 103.3 (d, J = 25.3 Hz). **^{19}F NMR (471 MHz, DMSO-d_6)** δ -74.58. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{21}H_{13}FN_3O_3$ 374.0935; found: 374.0936.



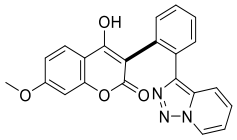
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-6-bromo-4-hydroxy-2H-chromen-2-one (3x): column solvent: DCM/MeOH = 30/1, white solid (62 mg, yield 71%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.94 (d, J = 7.0 Hz, 1H), 7.94 (d, J = 2.4 Hz, 1H), 7.78 (d, J = 8.9 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.58 – 7.40 (m, 3H), 7.31 (dd, J = 9.0, 6.6 Hz, 1H), 7.26 (d, J = 8.7 Hz, 1H), 7.10 (t, J = 6.8 Hz, 1H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 161.3, 151.5, 137.3, 134.2, 132.9, 131.6, 130.5, 129.5, 128.1, 127.9, 125.9, 125.6, 118.4, 117.9, 115.8, 115.4. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{21}H_{13}BrN_3O_3$ 434.0134; found: 434.0139.



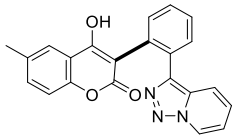
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-6-chloro-4-hydroxy-2H-chromen-2-one (3y): column solvent: DCM/MeOH = 30/1, yellow solid (70 mg, yield 90%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 8.60 (d, J = 7.0 Hz,1 H), 7.75 (d, J = 8.9 Hz, 1H), 7.63 (s, 1H), 7.50 – 7.37 (m, 2H), 7.34 – 7.24 (m, 2H), 7.22 – 7.04 (m, 4H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 161.4, 151.2, 137.4, 133.0, 132.5, 131.7, 131.1, 130.4, 129.5, 127.8, 127.4, 125.7, 125.5, 123.5, 123.1, 121.2, 119.6, 118.0, 117.9, 115.7. **HRMS (ESI-MS)** m/z: $[M+H]^+$ m/z calculated for $C_{21}H_{13}ClN_3O_3$ 390.0639; found: 390.0641.



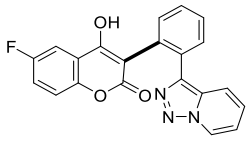
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-8-methyl-2H-chromen-2-one (3z): column solvent: DCM/MeOH = 30/1, yellow solid (70 mg, yield 95%). **^{1}H NMR (600 MHz, DMSO-d_6)** δ 8.95 (d, J = 7.0 Hz, 1H), 7.81 (d, J = 8.9 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.60 – 7.47 (m, 2H), 7.48 – 7.39 (m, 2H), 7.32 (dd, J = 9.0, 6.5 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.10 (t, J = 6.8 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.5, 150.7, 137.3, 132.9, 132.8, 131.9, 131.7, 130.4, 129.5, 128.1, 127.9, 125.8, 125.6, 124.7, 123.0, 121.3, 117.9, 116.5, 115.7, 105.4, 15.1. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{16}N_3O_3$ 370.1186; found: 370.1187



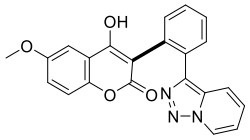
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-7-methoxy-2H-chromen-2-one (3za): column solvent: DCM/MeOH = 30/1, yellow solid (76 mg, yield 98%). **^{1}H NMR (600 MHz, DMSO-d_6)** δ 8.95 (d, J = 7.0 Hz, 1H), 7.74 (dd, J = 8.9, 4.4 Hz, 2H), 7.67 (d, J = 9.0 Hz, 1H), 7.60 – 7.42 (m, 4H), 7.36 – 7.25 (m, 1H), 7.09 (t, J = 6.8 Hz, 1H), 6.95 – 6.76 (m, 2H), 3.82 (s, 3H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 162.2, 161.8, 154.1, 137.3, 133.0, 132.1, 131.8, 130.4, 129.6, 127.9, 127.8, 125.7, 125.6, 124.7, 117.8, 115.6, 111.5, 109.8, 103.3, 100.2, 55.8. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{16}N_3O_4$ 386.1135; found: 386.1135.



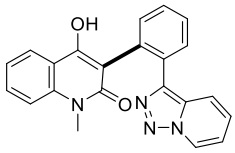
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-6-methyl-2H-chromen-2-one (3zb): column solvent: DCM/MeOH = 30/1, yellow solid (70 mg, yield 95%). **^{1}H NMR (600 MHz, DMSO-d_6)** δ 8.95 (d, J = 7.0 Hz, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.63 (s, 1H), 7.57 – 7.47 (m, 2H), 7.45 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.17 (d, J = 8.4 Hz, 1H), 7.09 (t, J = 6.8 Hz, 1H), 2.33 (s, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.8, 150.6, 137.3, 132.9, 132.7, 132.6, 132.0, 131.8, 130.4, 129.6, 128.0, 127.9, 125.8, 125.6, 123.3, 117.8, 116.5, 115.7, 115.7, 105.6, 20.4. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{16}N_3O_3$ 370.1186; found: 370.1188.



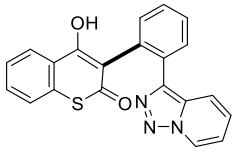
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-6-fluoro-4-hydroxy-2H-chromen-2-one (3zc): column solvent: DCM/MeOH = 20:1, yellow solid (70 mg, 94% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.95 (d, J = 6.9 Hz, 1H), 7.78 (d, J = 9.0 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.61 – 7.40 (m, 5H), 7.36 – 7.28 (m, 2H), 7.10 (t, J = 6.8 Hz, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.5, 158.5, 156.9, 148.7, 137.3, 132.8, 131.9, 131.6, 130.4, 129.4, 128.0, 127.7, 125.8, 125.6, 118.92 (d, J = 24.6 Hz), 118.02 (d, J = 8.2 Hz), 117.9, 115.7, 109.19 (d, J = 25.6 Hz), 105.9. **^{19}F NMR (565 MHz, DMSO-d_6)** δ -118.45. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{21}H_{12}FN_3O_3$ 374.0935; Found: 374.0936.



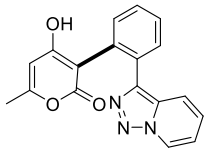
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-6-methoxy-2H-chromen-2-one (3zd): column solvent: DCM/MeOH = 20:1, yellow solid (70 mg, 91% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.94 (d, J = 7.0 Hz, 1H), 7.81 – 7.63 (m, 2H), 7.55 – 7.40 (m, 3H), 7.36 – 7.24 (m, 2H), 7.20 (d, J = 9.0 Hz, 1H), 7.15 – 7.04 (m, 2H), 3.76 (s, 3H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.9, 155.0, 146.8, 137.5, 132.9, 132.6, 131.7, 130.4, 129.5, 127.7, 125.6, 125.5, 119.2, 117.9, 117.1, 115.6, 105.8, 105.3, 55.6. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{15}N_3O_4$ 386.1135; Found: 386.1134.



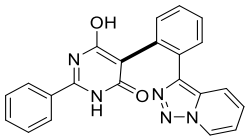
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-1-methylquinolin-2(1H)-one (3ze): column solvent: DCM/MeOH = 20:1, grey solid (60 mg, 81% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.90 (s, 1H), 8.08 (s, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.77 – 7.62 (m, 2H), 7.61 – 7.31 (m, 5H), 7.29 – 7.11 (m, 2H), 7.08 – 6.94 (m, 1H), 3.47 (s, 3H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.9, 156.3, 138.9, 137.5, 133.3, 132.8, 131.8, 130.7, 130.4, 129.7, 127.8, 127.7, 125.5, 123.4, 121.1, 117.8, 116.1, 115.5, 114.2, 112.2, 29.0. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{16}N_4O_2$ 369.1346; Found: 369.1345.



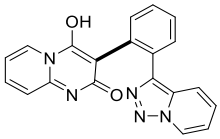
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-2H-thiochromen-2-one (3zf): column solvent: DCM/MeOH = 20:1, yellow solid (63 mg, 85% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.92 (d, J = 7.0 Hz, 1H), 8.31 (s, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 7.3 Hz, 1H), 7.57 – 7.43 (m, 4H), 7.44 – 7.32 (m, 2H), 7.27 (t, J = 7.9 Hz, 1H), 7.07 (t, J = 6.8 Hz, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 137.3, 135.2, 132.9, 132.0, 130.4, 130.2, 129.7, 128.1, 128.0, 126.7, 126.0, 125.6, 125.5, 125.1, 118.0, 117.4, 115.6. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{21}H_{13}N_3O_2S$ 372.0801; Found: 372.0798.



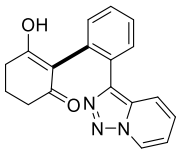
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-6-methyl-2H-pyran-2-one (3zg): column solvent: DCM/MeOH = 20:1, yellow solid (60 mg, 94% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.99 (s, 1H), 7.75 – 7.54 (m, 2H), 7.48 – 7.23 (m, 5H), 7.17 – 7.01 (m, 1H), 5.81 (s, 1H), 2.07 (s, 3H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 163.5, 160.7, 137.8, 132.6, 131.5, 130.2, 129.6, 127.5, 127.2, 125.5, 125.4, 117.7, 115.6, 101.7, 100.7, 19.2. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{18}H_{13}N_3O_3$ 320.1030; Found: 320.1028.



5-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-6-hydroxy-2-phenylpyrimidin-4(3H)-one (3zh): column solvent: DCM/MeOH = 20:1, white solid (10 mg, 13% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.94 (d, J = 7.0 Hz, 1H), 8.01 (d, J = 7.7 Hz, 2H), 7.71 – 7.59 (m, 2H), 7.56 – 7.51 (m, 1H), 7.50 – 7.41 (m, 5H), 7.21 (t, J = 7.8 Hz, 1H), 7.05 (t, J = 6.8 Hz, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 138.2, 132.6, 131.5, 130.2, 129.6, 128.5, 127.4, 127.3, 126.9, 125.0, 125.1, 117.8, 115.4. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{22}H_{15}N_5O_2$ 382.1299; Found: 382.1296.

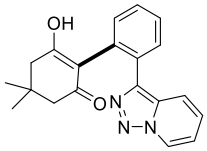


3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-2H-pyrido[1,2-a]pyrimidin-2-one (3zi): column solvent: DCM/MeOH = 20:1, yellow solid (18 mg, 25% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.90 (d, J = 7.0 Hz, 1H), 8.81 (d, J = 6.9 Hz, 1H), 8.00 (t, J = 7.8 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.52 – 7.47 (m, 1H), 7.46 – 7.39 (m, 2H), 7.31 (d, J = 8.7 Hz, 1H), 7.23 (t, J = 6.9 Hz, 1H), 7.18 – 7.11 (m, 1H), 7.01 (t, J = 6.8 Hz, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 172.1, 161.5, 154.6, 146.7, 140.8, 138.3, 134.0, 133.2, 131.8, 130.1, 129.6, 128.8, 127.3, 126.7, 125.4, 125.0, 117.7, 115.3, 115.3, 95.9. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{20}H_{13}N_5O_2$ 356.1142; Found: 356.1140.



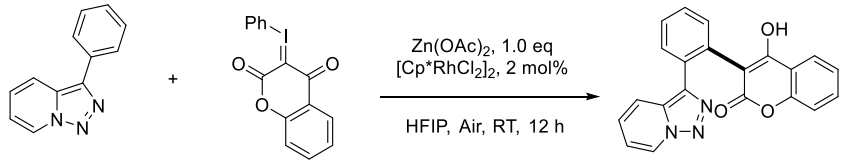
2'-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (3zj): column solvent: DCM/MeOH = 30/1, yellow solid (50 mg, yield 82%). **^{1}H NMR (600 MHz, DMSO-d_6)** δ 10.41 (s, 1H), 9.00 (d, J = 7.0 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.50 (d, J = 8.9 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.36 – 7.31 (m, 1H), 7.19 – 7.15 (m, 1H), 7.15 – 7.11 (m, 1H), 2.48 – 1.93 (m,

4H), 1.84 – 1.73 (m, 1H), 1.62 – 1.51 (m, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 196.1, 172.1, 138.1, 134.0, 132.5, 131.4, 130.1, 129.6, 127.4, 126.7, 125.6, 125.3, 117.9, 116.5, 115.5, 36.6, 29.3, 20.2. **HRMS (ESI-MS)** *m/z*: $[M+H]^+$ calculated for $C_{18}H_{16}N_3O_2$ 306.1243, found: 306.1237.



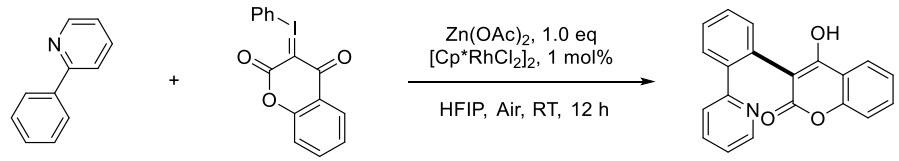
2'-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-6-hydroxy-4,4-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (3zk): column solvent: DCM/MeOH = 20:1, grey solid (58 mg, 87% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 9.00 (d, J = 7.0 Hz, 1H), 7.59 (d, J = 8.9 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.42 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 7.18 – 7.08 (m, 2H), 2.20 (d, J = 16.5 Hz, 2H), 1.95 (d, J = 16.5 Hz, 2H), 0.96 (s, 3H), 0.74 (s, 3H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 138.0, 134.4, 132.5, 131.5, 130.4, 129.5, 127.4, 126.7, 125.4, 125.3, 118.0, 115.5, 115.3, 31.2, 28.2, 27.6. **HRMS (ESI-MS)** m/z: $[M+H]^+$ calculated for $C_{20}H_{19}N_3O_2$ 334.1550; Found: 334.1548.

Scale-up Synthesis



1a **2a** **3a**

In a 100 mL reaction tube, the mixture of **1a** (392.5 mg, 2.00 mmol, 1.0 eq), **2a** (873.9 mg, 2.40 mmol, 1.2 eq), $[Cp^*RhCl_2]_2$ (12.5 mg, 0.01 mmol, 2 mol%) and $Zn(OAc)_2$ (367 mg, 2.00 mmol, 1.0 eq) was dissolved in HFIP (10.0 mL). Then the resulting mixture was stirred at room temperature for 12.0 h. When the reaction was finished, the product was purified by preparative thin layer chromatography (DCM/MeOH = 20/1). **3a**, a pale-white solid (639 mg, 85% yield).

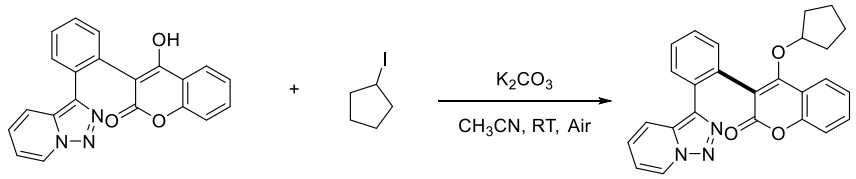


1m **2a** **3m**

In a 100 mL reaction tube, the mixture of **1m** (310.4 mg, 2.00 mmol, 1.0 eq), **2a** (873.9 mg, 2.40 mmol, 1.2 eq), $[Cp^*RhCl_2]_2$ (12.4 mg, 0.01 mmol, 1 mol%) and $Zn(OAc)_2$ (366.9 mg, 2.00 mmol, 1.0 eq) was dissolved in HFIP (10.0 mL). Then the resulting mixture was stirred at room temperature

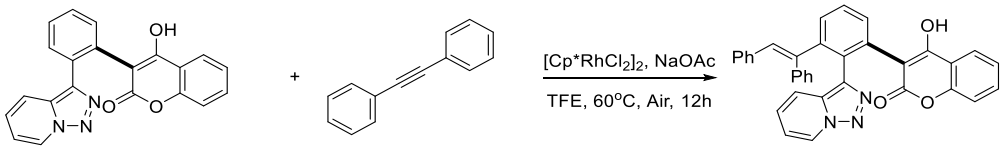
for 12.0 h. When the reaction was finished, the product was purified by preparative thin layer chromatography (DCM/MeOH = 20/1). The product **3m** was obtained as a pale-yellow solid (500 mg, 79% yield).

Transformation assays



3a **4a**

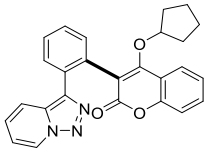
In a 25 mL reaction tube, compound **3a** (35.5 mg, 0.1 mmol, 1.0 eq) iodocyclopentane (23.5 mg, 0.15 mol, 1.5 eq), and K_2CO_3 (13.8 mg, 0.10 mol, 1.0 eq) were dissolved in CH_3CN (4 mL). Then the resulting mixture was stirred and refluxed at 60 °C for 12.0 h. When the reaction was finished, the product was separated by thin layer chromatography plates (DCM/MeOH = 20/1), the product **4a** was obtained as a white solid (26 mg, 62% yield).



3a **4b**

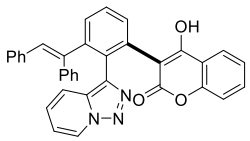
In a 25 mL reaction tube, compound **3a** (35.5 mg, 0.1 mmol, 1.0 eq.) 1,2-diphenylethyne (21.4 mg, 0.12 mol, 1.2 eq), and NaOAc (8.2 mg, 0.10 mol, 1.0 eq) were dissolved in TFE (4 mL). Then the resulting mixture was stirred and refluxed at 60 °C for 12.0 h. When the reaction was finished, the product was separated by thin layer chromatography plates (DCM/MeOH = 20/1), the product **4b** was obtained as a white solid (30 mg, 57% yield).

Characterization Data of 4a and 4b.



3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-(cyclopentyloxy)-2H-chromen-2-one (4a): yellow solid (61 mg, yield 89%). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.98 (d, J = 7.0 Hz, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.66 – 7.51 (m, 5H), 7.47 – 7.39 (m, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.20 – 7.13 (m, 1H), 4.59 – 4.53 (m, 1H), 1.67 – 1.43 (m, 4H),

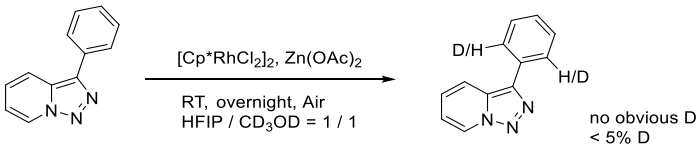
1.43 – 1.31 (m, 3H), 1.33 – 1.26 (m, 1H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.7, 160.2, 151.9, 136.7, 132.5, 132.0, 131.8, 131.0, 130.5, 129.0, 128.9, 127.8, 126.5, 125.8, 124.3, 123.7, 117.9, 117.6, 116.0, 116.0, 112.9, 84.6, 32.7, 32.4, 22.9, 22.8. **HRMS (ESI-MS)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}N_3O_3$ 424.1656; Found: 424.1652.



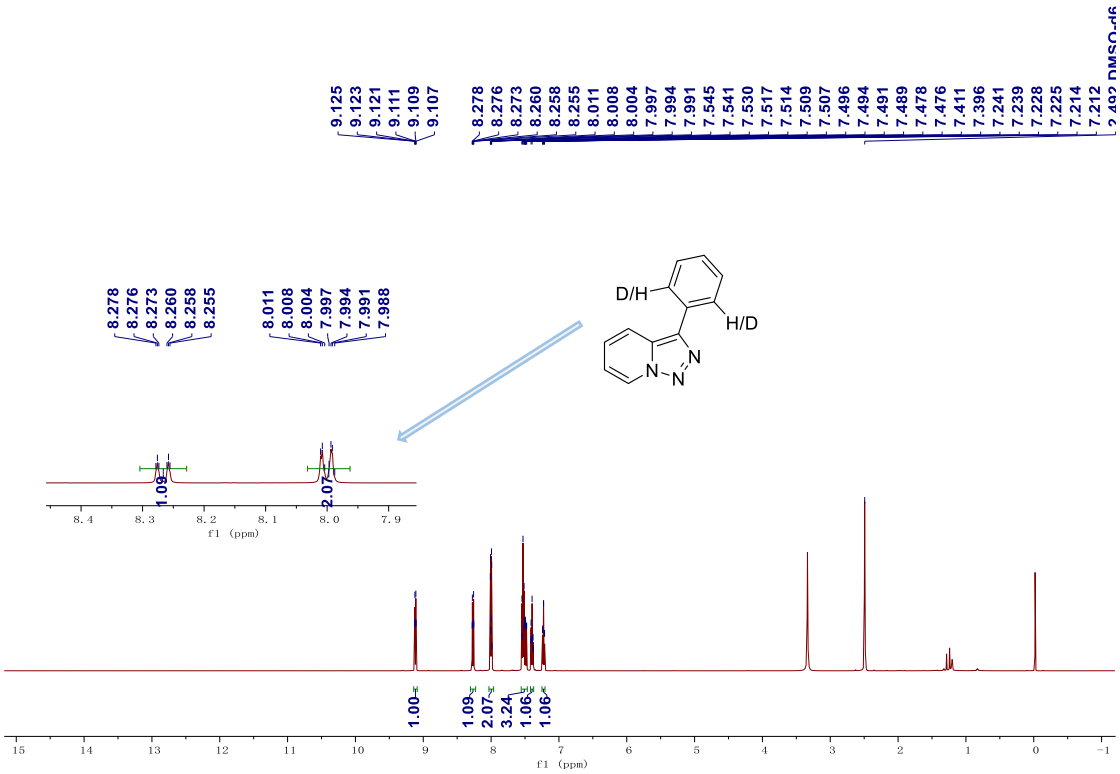
(E)-3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-3-(1,2-diphenylvinyl)phenyl)-4-hydroxy-2H-chromen-2-one (4b): yellow solid (30 mg, 57% yield). **^{1}H NMR (500 MHz, DMSO-d_6)** δ 8.63 (d, J = 7.0 Hz, 1H), 7.86 – 7.66 (m, 1H), 7.65 – 7.53 (m, 2H), 7.52 – 7.35 (m, 3H), 7.35 – 7.13 (m, 3H), 7.13 – 6.96 (m, 4H), 6.94 – 6.62 (m, 6H), 6.46 (d, 2H). **^{13}C NMR (151 MHz, DMSO-d_6)** δ 161.5, 152.2, 145.8, 142.4, 139.3, 136.8, 131.6, 131.2, 130.3, 130.0, 128.7, 128.3, 127.8, 127.3, 126.7, 126.4, 124.8, 123.5, 118.1, 115.8, 114.9. **HRMS (ESI-MS)** m/z: $[M+H]^+$ Calcd for $C_{35}H_{23}N_3O_3$ 534.1812; Found: 534.1808.

Mechanistic Experiments

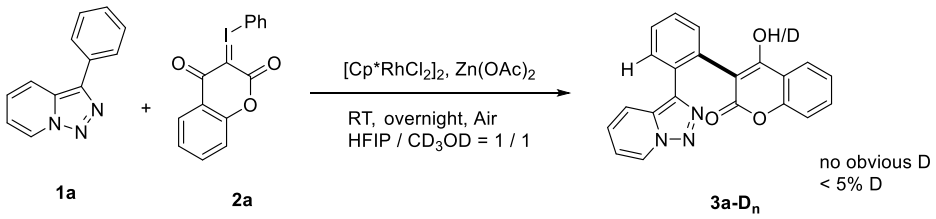
Deuterium Incorporation Experiment A



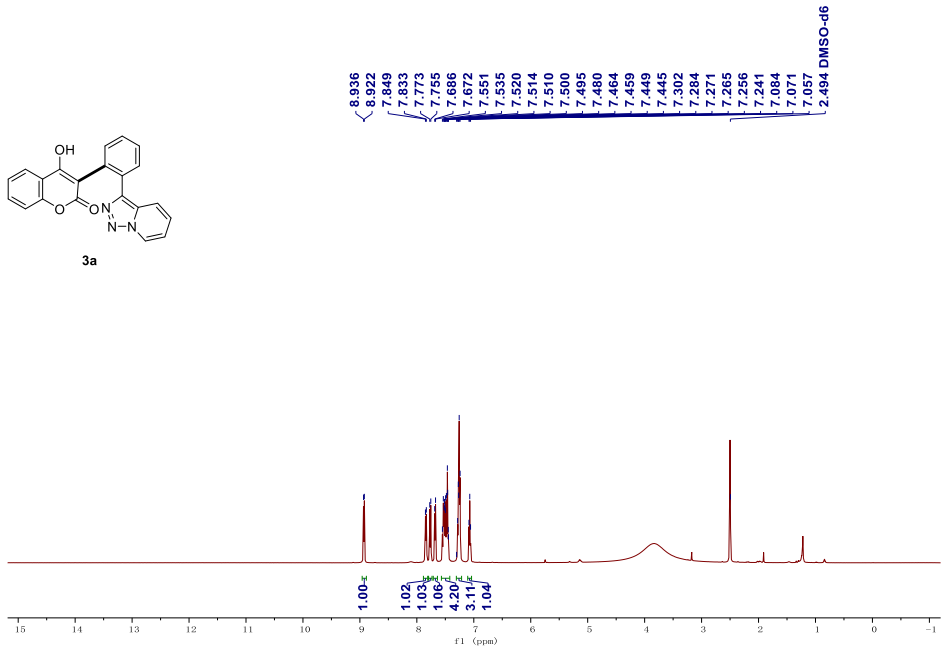
A mixture of **1a** (19.6 mg, 0.1 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 5 mol%), and $Zn(OAc)_2$ (18.3 mg, 0.1 mmol, 1.0 equiv) was placed in a 5 mL reaction tube. To this, a solvent mixture of HFIP and CD_3OD (0.5 mL each) was added. Then the resulting mixture was stirred at room temperature for overnight. When the reaction was finished, the product was separated by thin layer chromatography plates (DCM/MeOH = 20/1), the product **1a-D_n** was used for ^{1}H-NMR analysis. Found no obvious H/D exchange occurred at the phenyl group of **1a-D_n** (< 5% D).

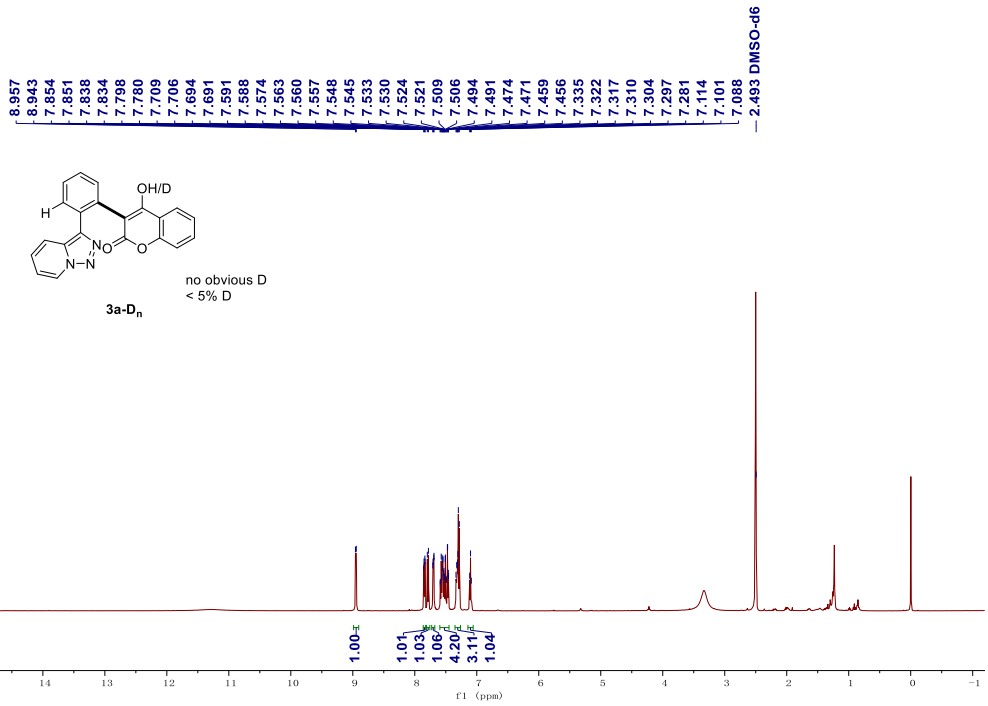


Deuterium Incorporation Experiment B



To a mixture of **1a** (19.6 mg, 0.1 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 5 mol%), and $Zn(OAc)_2$ (18.3 mg, 0.1 mmol, 1.0 equiv.) in a 5 mL reaction tube, a solvent mixture of HFIP/CD_3OD (0.5 mL/0.5 mL) was added. Then the resulting mixture was stirred at room temperature for overnight. When the reaction was finished, the product was separated by thin layer chromatography plates (DCM/MeOH = 20/1). The reaction of **1a** (19.6 mg, 0.1 mmol, 1.0 eq) with **2a** (54.6 mg, 0.15 mmol, 1.5 eq.) provided the product **3a-*D*.** Found no obvious H/D exchange occurred on the **3a-*D*** (< 5% D).


8.936
8.922
7.849
7.833
7.773
7.755
7.686
7.672
7.551
7.535
7.520
7.514
7.510
7.500
7.495
7.480
7.464
7.459
7.449
7.445
7.302
7.284
7.271
7.265
7.256
7.241
7.084
7.071
7.057
2.494 DMSO-d6
OH
O
O
N
N
N
3a
1.00
1.02
1.03
1.06
4.20
3.11
1.04
f1 (ppm)


8.957
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7.706
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7.588
7.574
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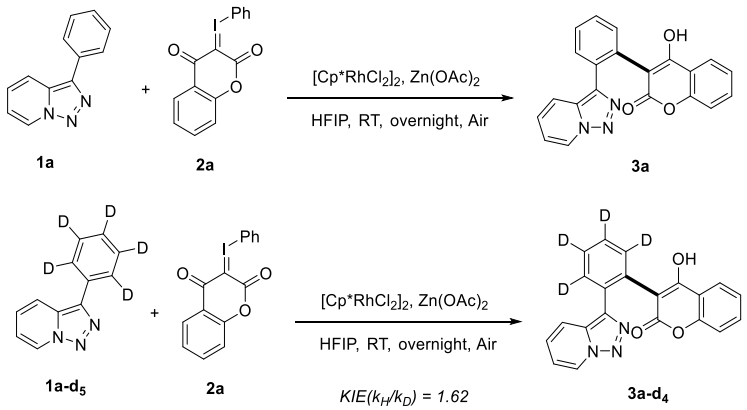
7.560
7.557
7.548
7.545
7.533
7.530
7.524
7.521
7.509
7.506
7.494
7.491
7.474
7.471
7.459
7.456
7.335
7.322
7.317
7.310
7.304
7.297
7.281
7.114
7.101
7.088
2.493 DMSO-d6
OH/D
H
O
O
N
N
N
no obvious D
< 5% D
3a-Dn
1.00
1.01
1.03
1.06
4.20
3.11
1.04
f1 (ppm)

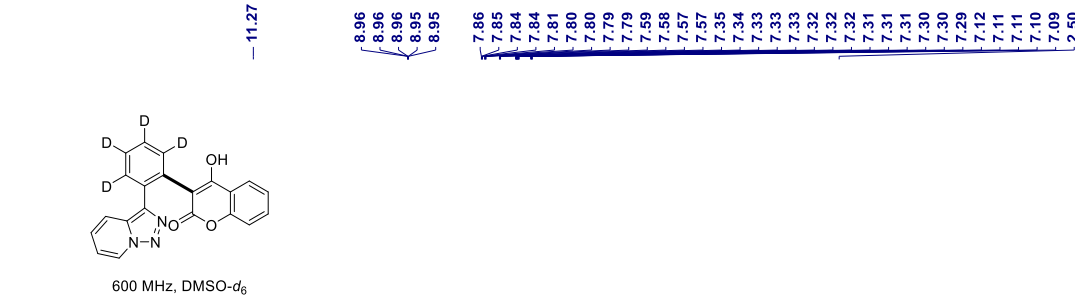
Determination of the KIE

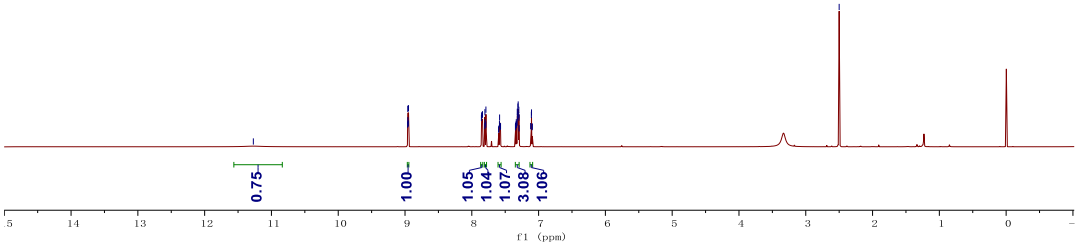
Two parallel reactions for KIE value measurement



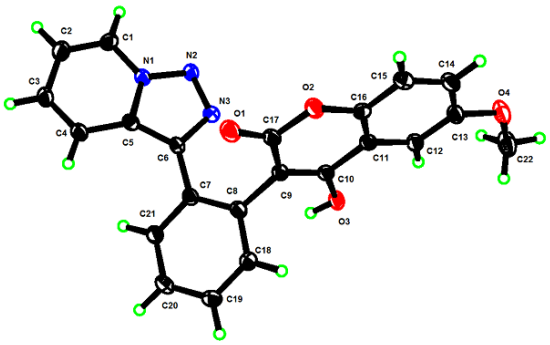
Following general procedure for the synthesis of **3a**. **1a** (0.1 mmol) or **1a-d$_5$** (0.1 mmol), **2a** (0.15 mmol), ZnOAc (0.1 mmol), [Cp*RhCl$_2$]$_2$ (5 mol%), HFIP (1 mL) were submitted to the typical reaction condition. These reactions were stopped at 0.5 h, 1 h, 2 h, and 4 h and the resulting mixture was separately extracted with diethyl ether. The yields of product were shown below. After plotting the product yield (%) vs time (min), the k_H/k_D ratio of 1.62 was obtained.

Time (h)	0.5	1	2	4
3a (%)	19	28	40	56
3a-d$_4$ (%)	8	14	22	31





X-ray data of compound 3zd (Deposition Data: CCDC 2412343)



Crystal structure of compound **3zd**, showing an ellipsoid contour probability level of 50%.

Table S1. Crystal data and structure refinement for compound 3zd.

Identification code	**3zd**
Identification code	mo_20241834_0m
Empirical formula	$C_{22}H_{15}N_3O_4$
Formula weight	385.37
Temperature/K	170
Crystal system	monoclinic
Space group	C2/c
a/Å	17.7123(9)
b/Å	13.5331(5)
c/Å	15.9381(7)
α/°	90
β/°	106.648(2)
γ/°	90
Volume/Å^3	3660.3(3)
Z	8
ρcalcg/cm^3	1.399
μ/mm^{-1}	0.099
F(000)	1600.0
Crystal size/mm^3	0.15 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.85 to 52.766
Index ranges	-22 ≤ h ≤ 17, -16 ≤ k ≤ 16, -17 ≤ l ≤ 19

Reflections collected	11560
Independent reflections	3692 [Rint = 0.0752, Rsigma = 0.0797]
Data/restraints/parameters	3692/0/264
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1151
Final R indexes [all data]	R_1 = 0.0953, wR_2 = 0.1382

References

[1] Demkiw K, Araki H, Elliott E L, et al. A Nitrogen-Assisted One-Pot Heteroaryl Ketone Synthesis from Carboxylic Acids and Heteroaryl Halides. *J. Org. Chem.* **2016**, 81, 3447-3456.

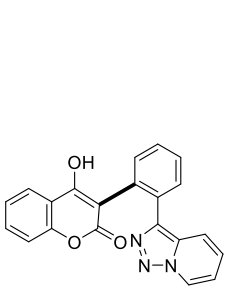
[2] Lv G, Zhang Q, Zhang C, et al. The Pyridotriazole Works as a Traceless Directing Group: A C‐H Activation/Annulation Cascade Reaction with Iodonium Ylides. *Org. Lett.* **2023**, 25, 4022-4027.

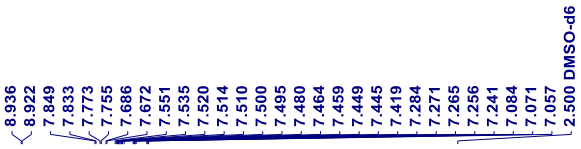
[3] Ren J, Pi C, Cui X, Wu Y. Transition Metal-Controlled Divergent Annulations of Azomethine Imines with Iodonium Ylides via C-Centered [1,2]-Rearrangement. *Org. Lett.* **2023**, 25, 2582-2587.

[4] Jiang Y, Li P, Zhao J, Liu B, Li X. Iodonium Ylides as Carbene Precursors in Rh(III)-Catalyzed C-H Activation. *Org. Lett.* **2020**, 22, 7475-7479.

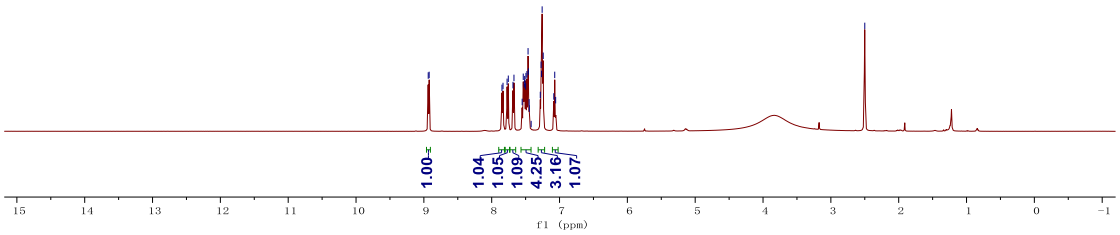
Copies of ^{1}H, ^{13}C NMR and ^{19}F NMR spectra

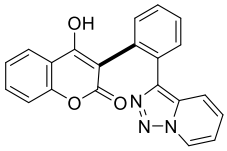
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-2H-chromen-2-one (3a)

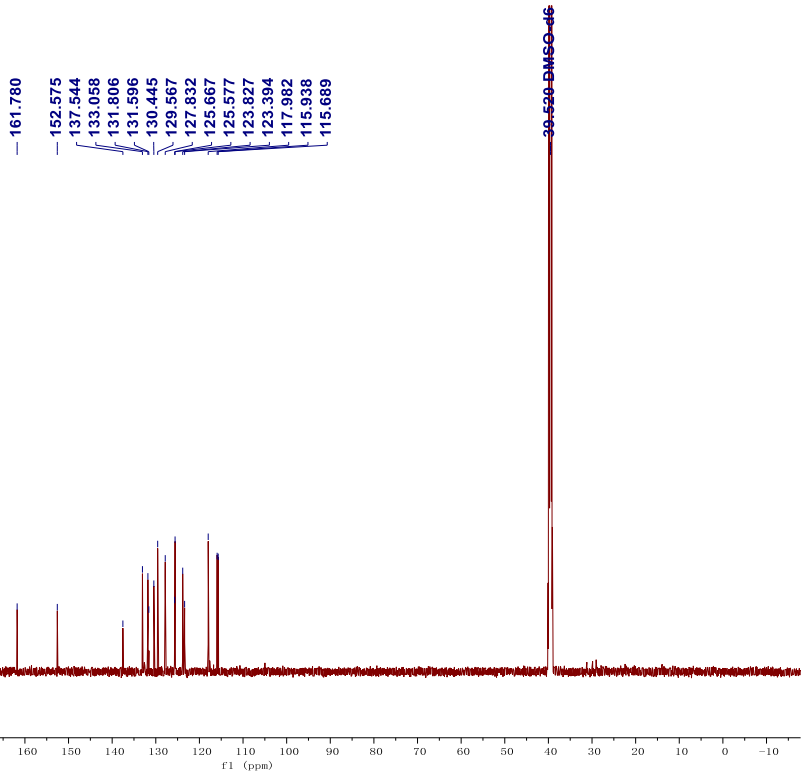




3a, 500 MHz, DMSO-d_6

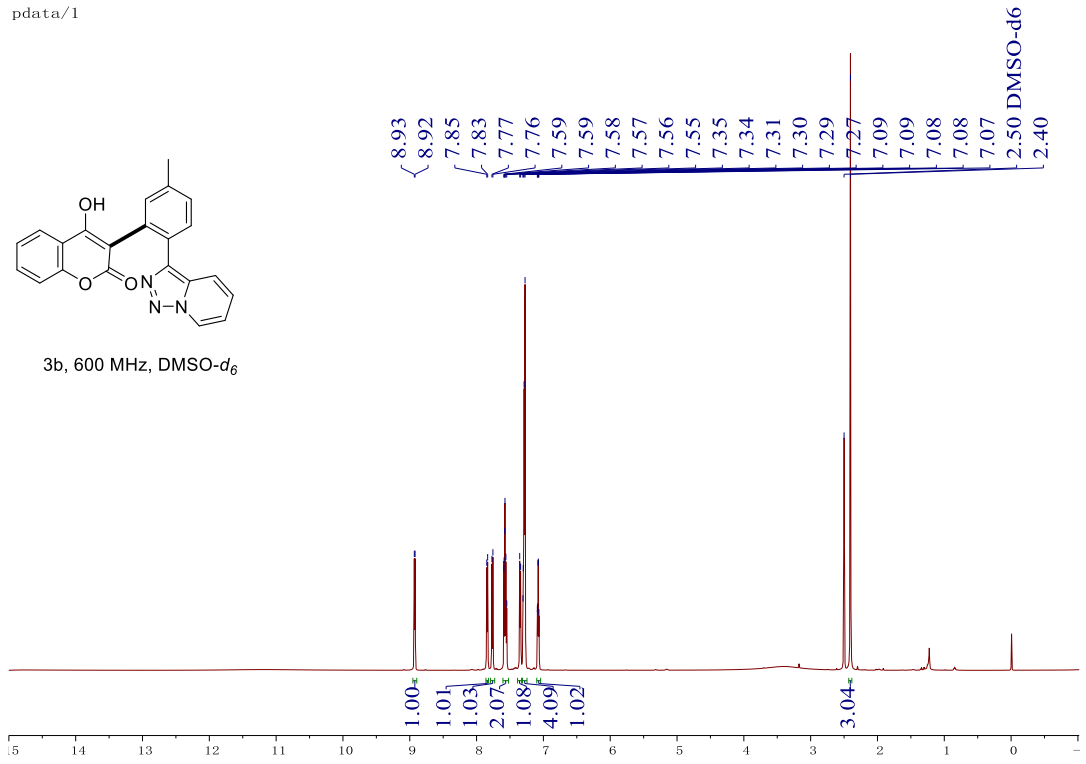


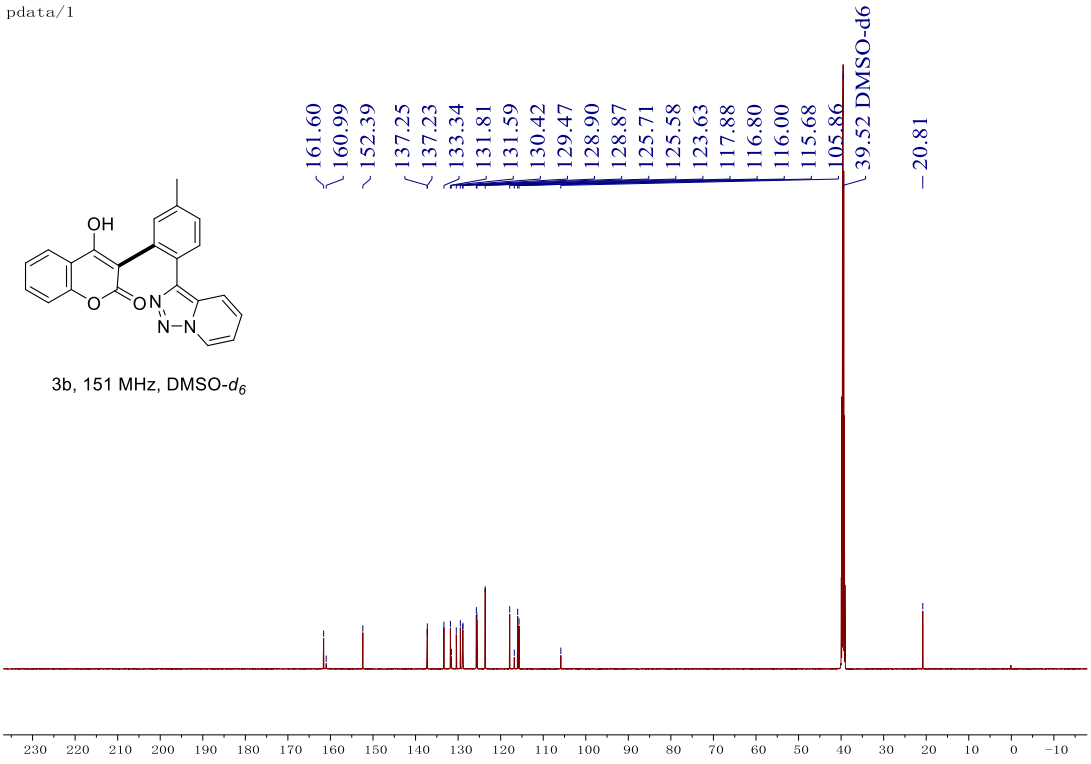




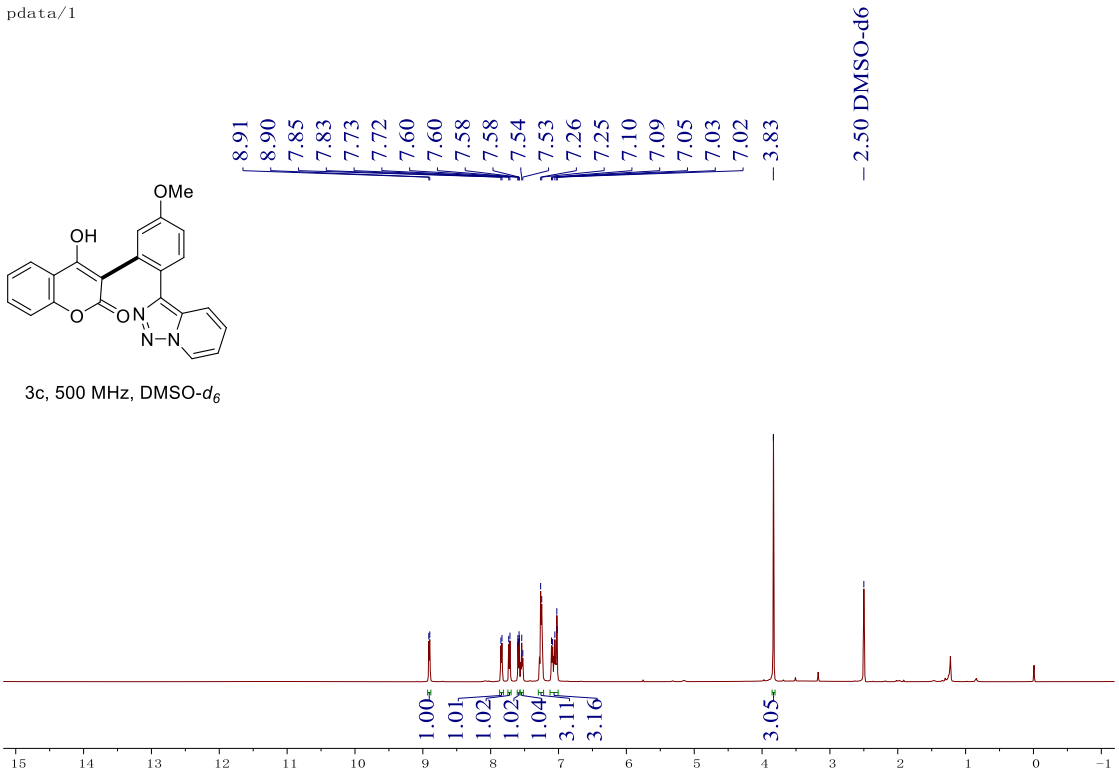
3a, 126 MHz, DMSO-d_6

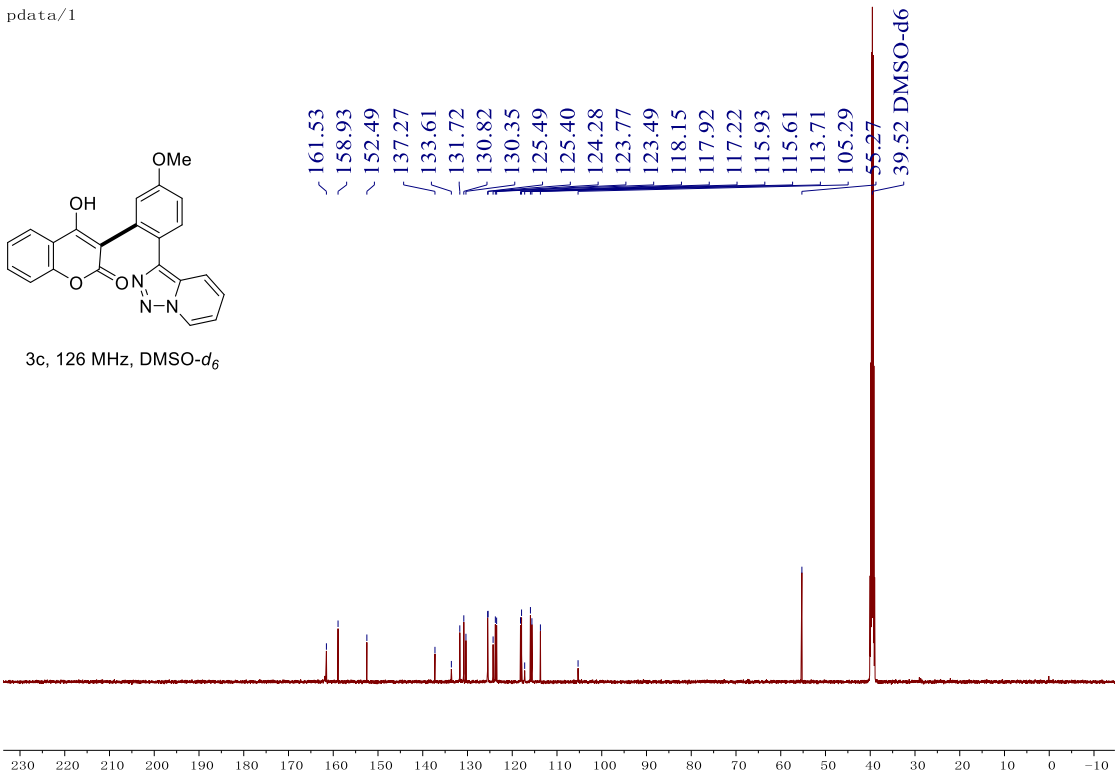
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-methylphenyl)-4-hydroxy-2H-chromen-2-one (3b)



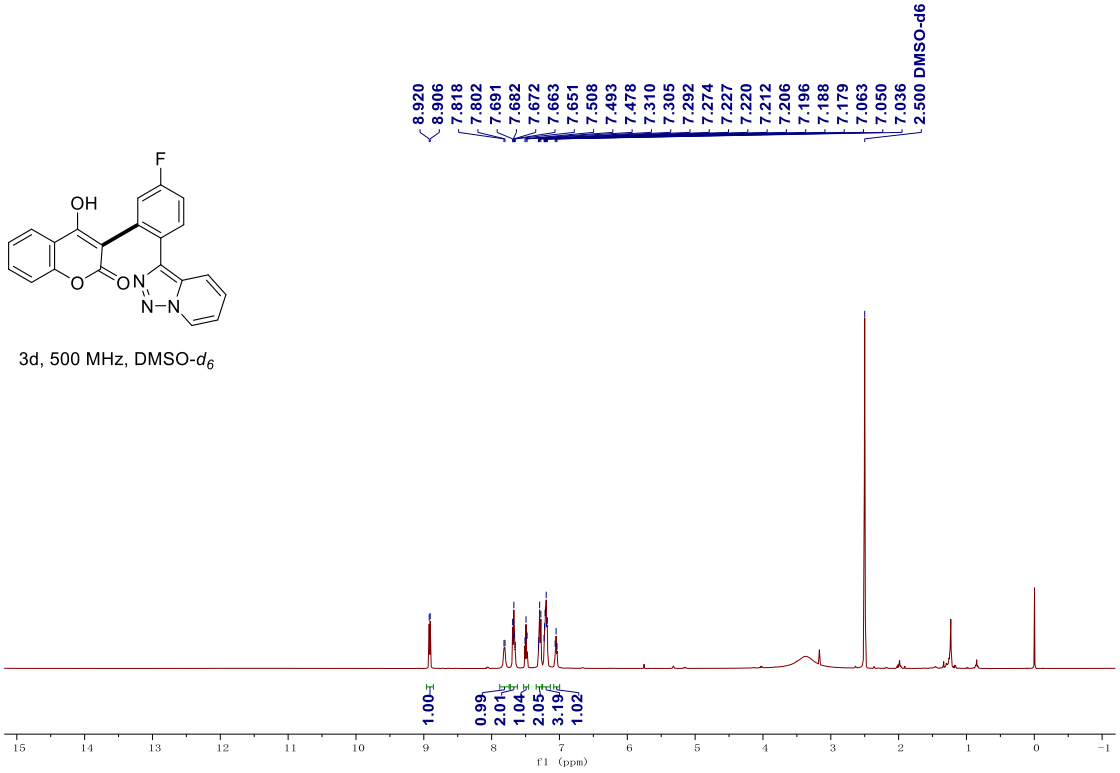


3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-methoxyphenyl)-4-hydroxy-2H-chromen-2-one (3c)

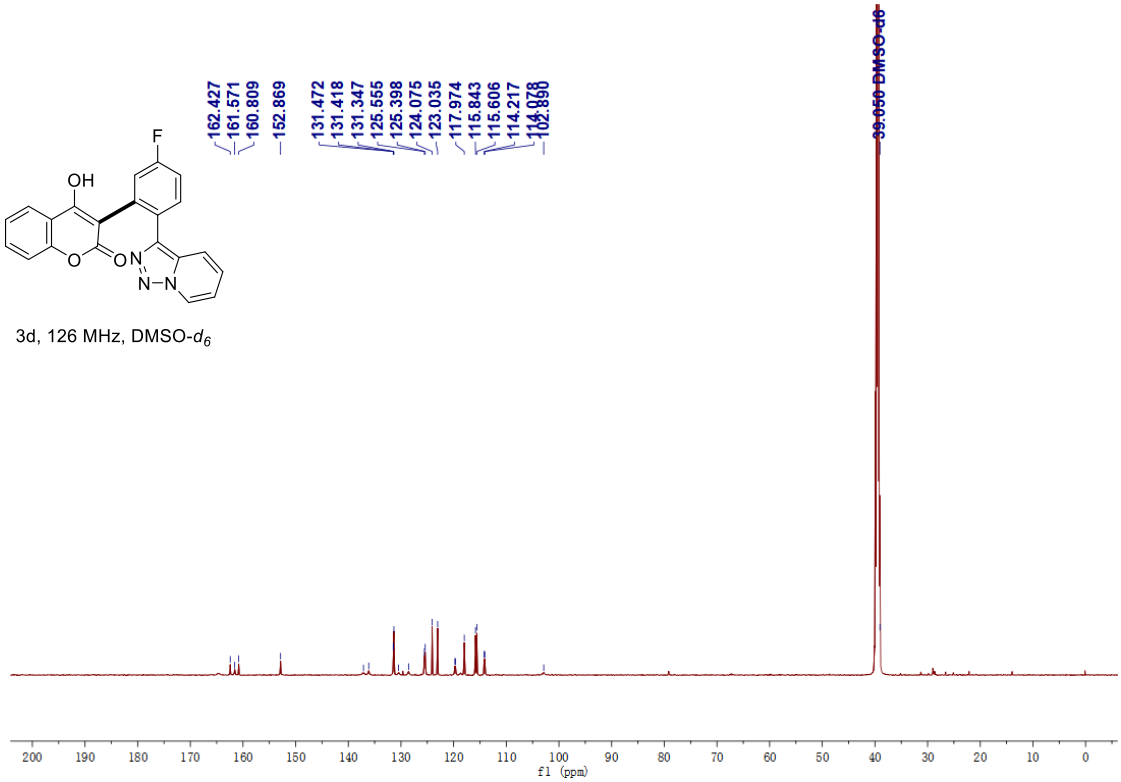




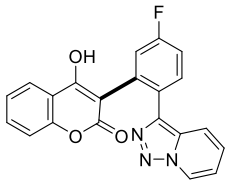
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-fluorophenyl)-4-hydroxy-2H-chromen-2-one (3d)



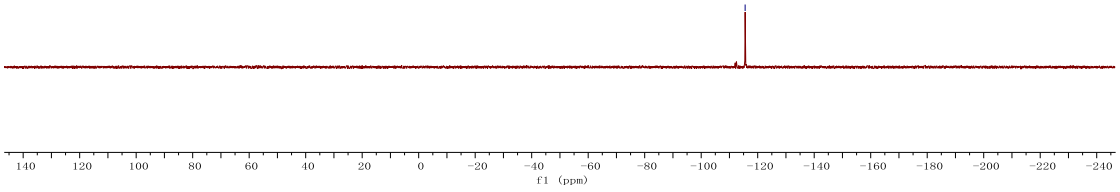
3d, 500 MHz, DMSO-d_6



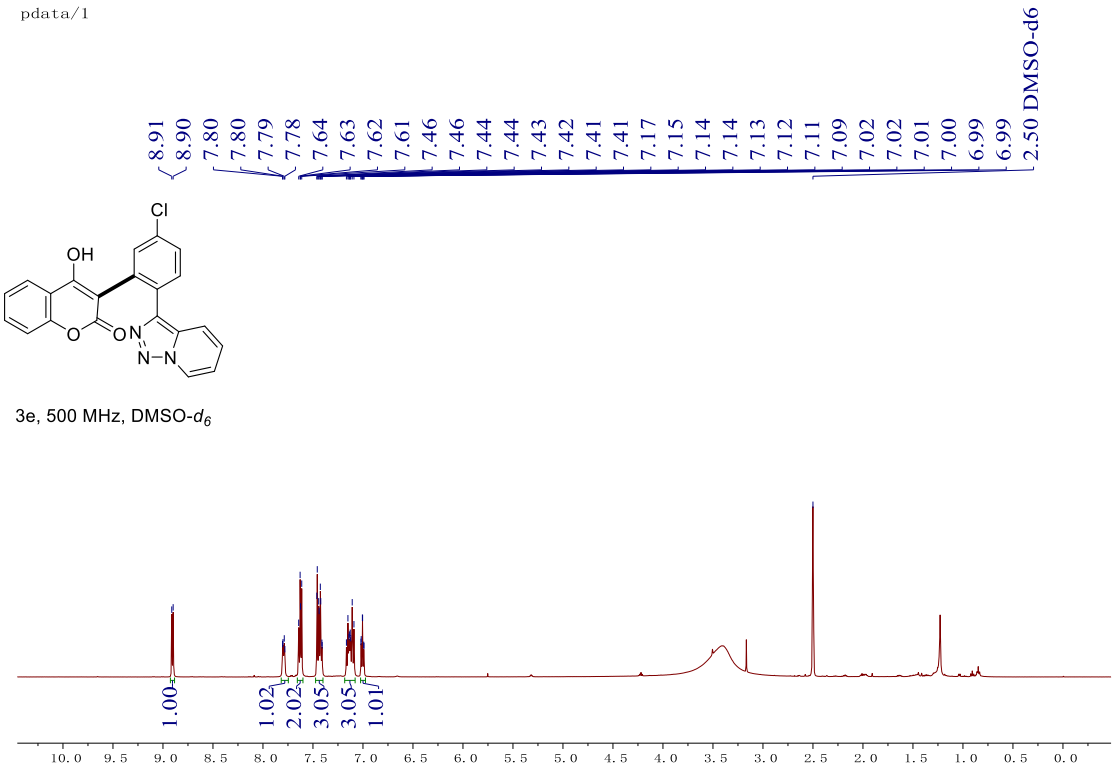
3d, 126 MHz, DMSO-d_6



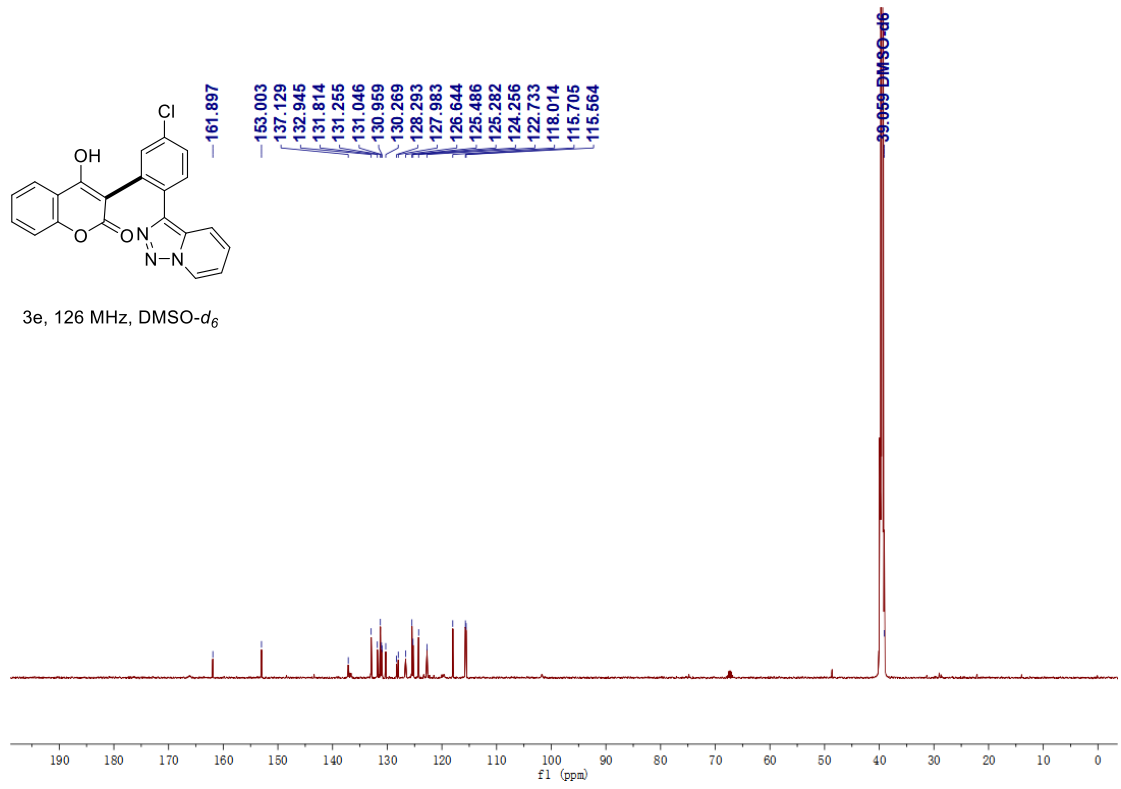
3d, 471 MHz, DMSO-d_6



3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-chlorophenyl)-4-hydroxy-2H-chromen-2-one (3e)

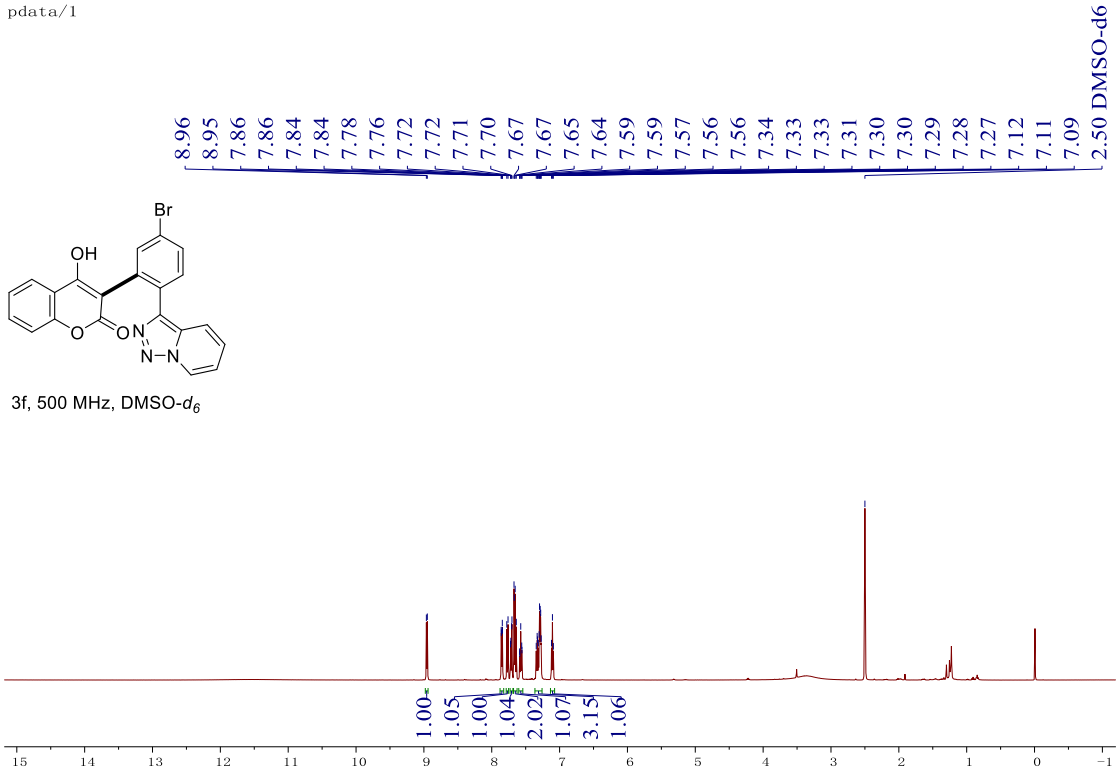


3e, 500 MHz, DMSO-d_6

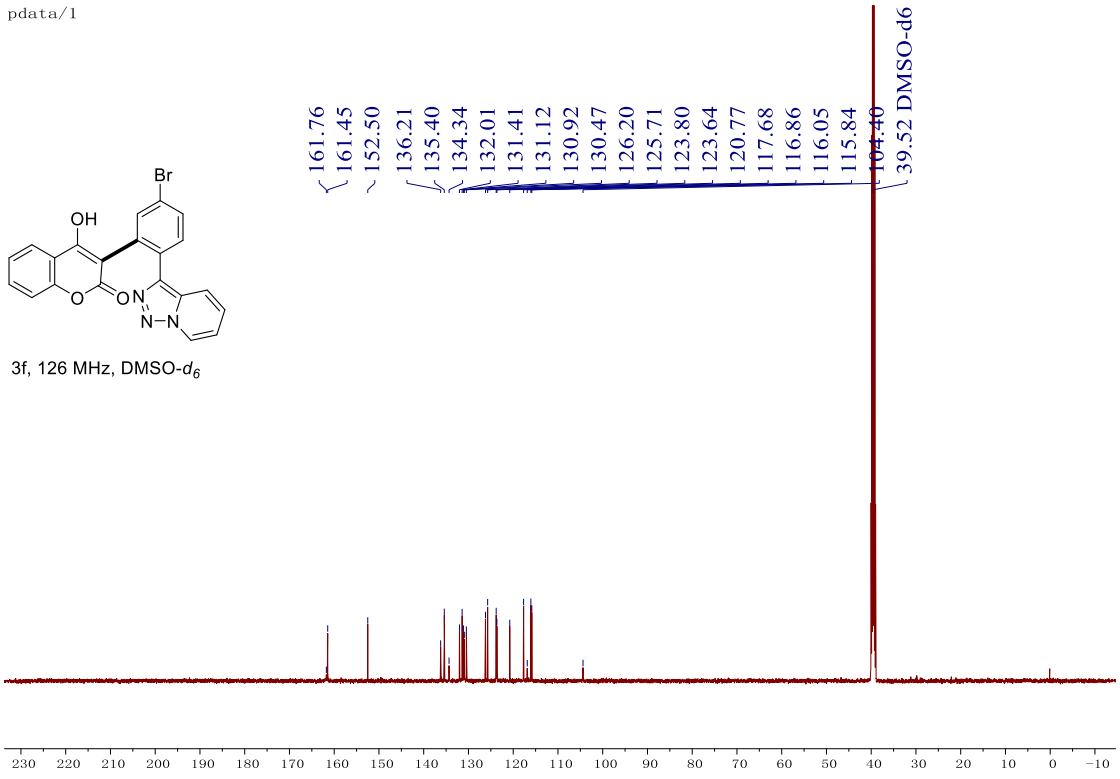


3e, 126 MHz, DMSO-d_6

3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-bromophenyl)-4-hydroxy-2H-chromen-2-one (3f)

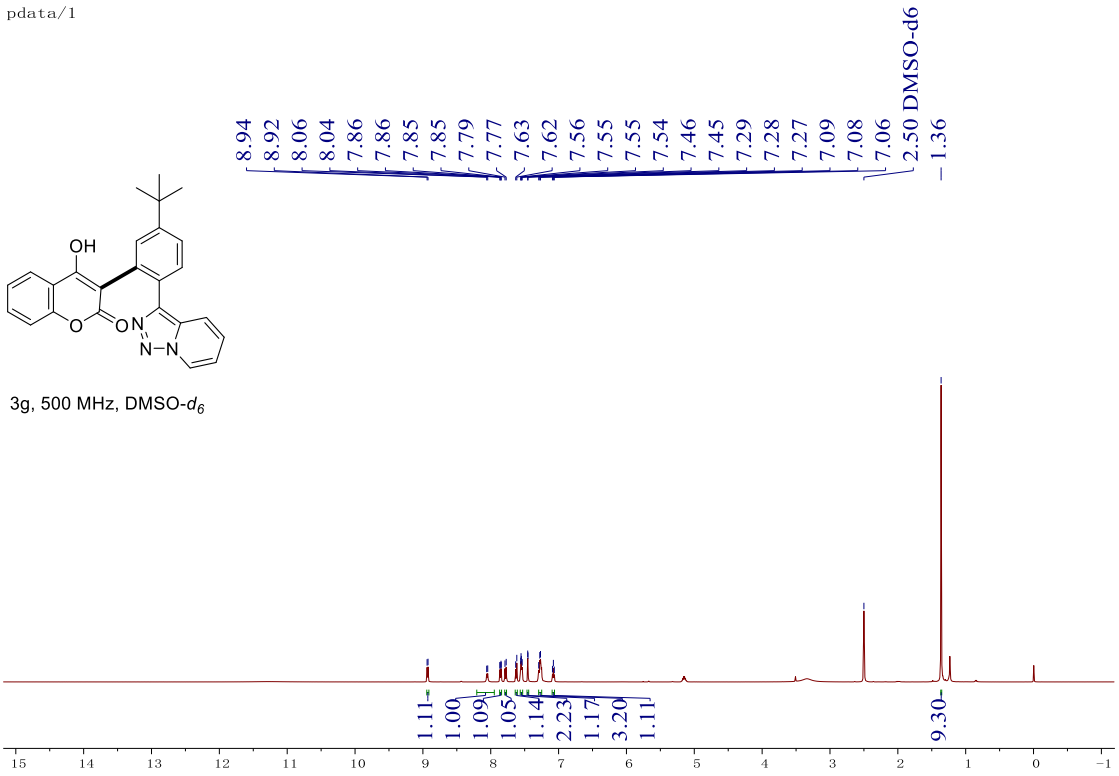


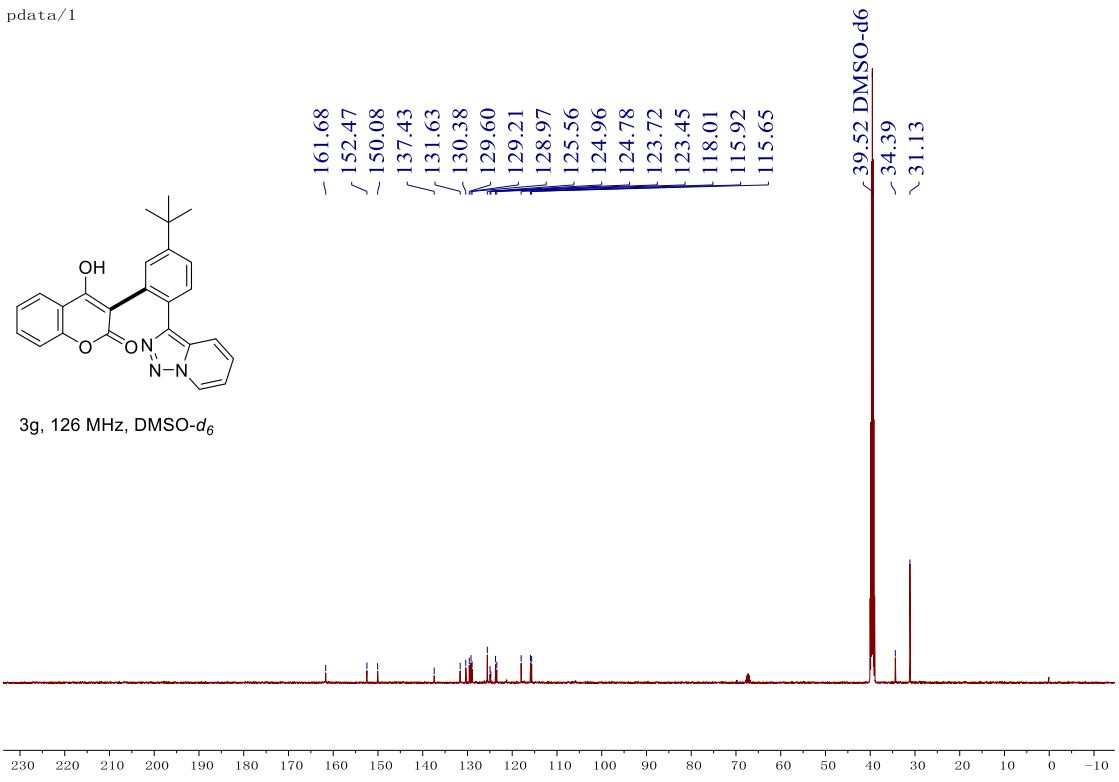
3f, 500 MHz, DMSO-d_6



3f, 126 MHz, DMSO-d_6

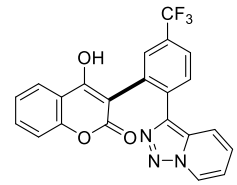
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-5-(tert-butyl)phenyl)-4-hydroxy-2H-chromen-2-one (3g)



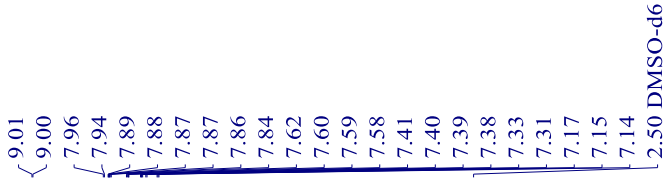


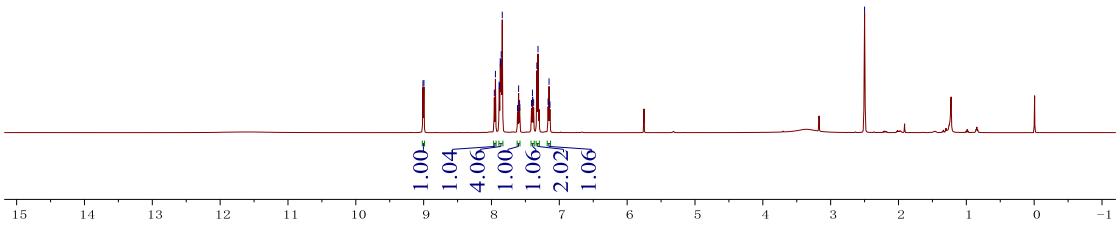
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-4-(trifluoromethyl)phenyl)-4-hydroxy-2H-chromen-2-one (3h)

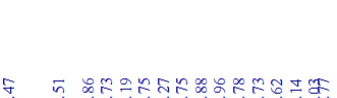
pdata/1

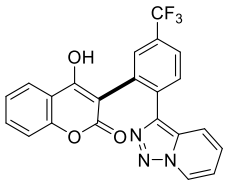


3h, 500 MHz, DMSO-d_6

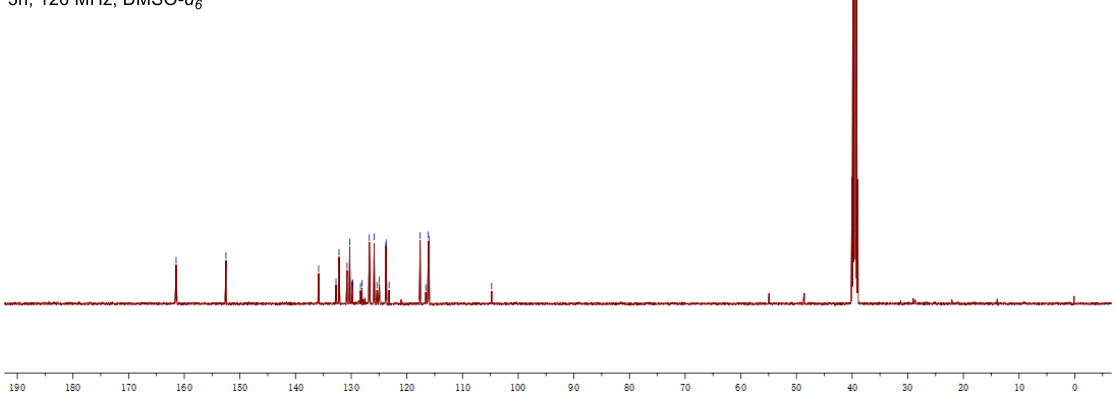








3h, 126 MHz, DMSO-d_6



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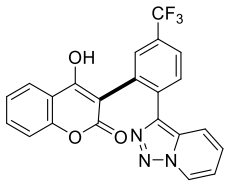
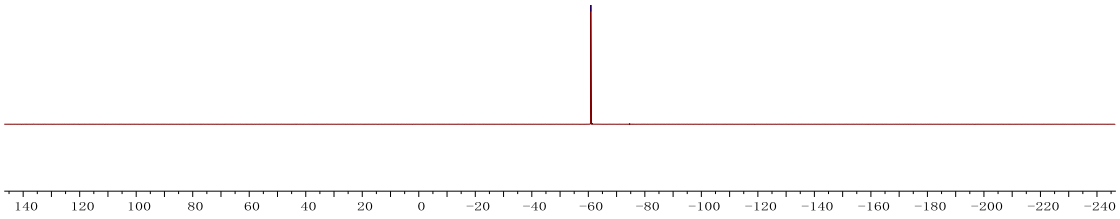
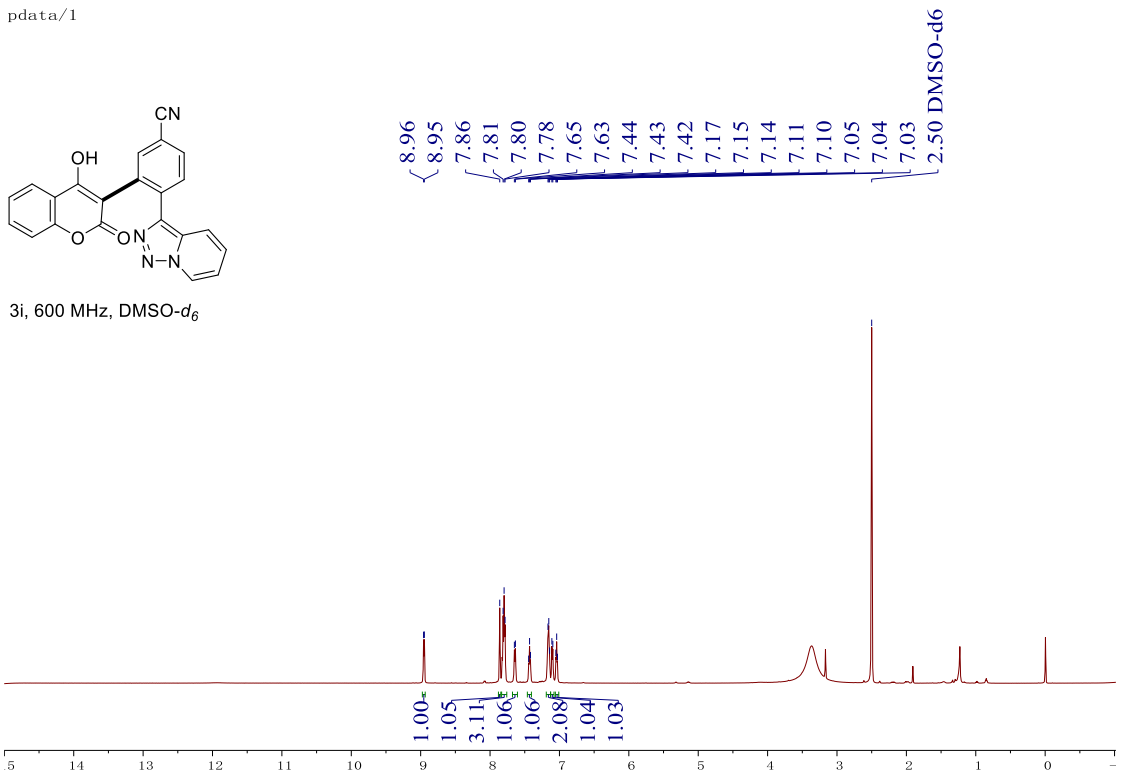


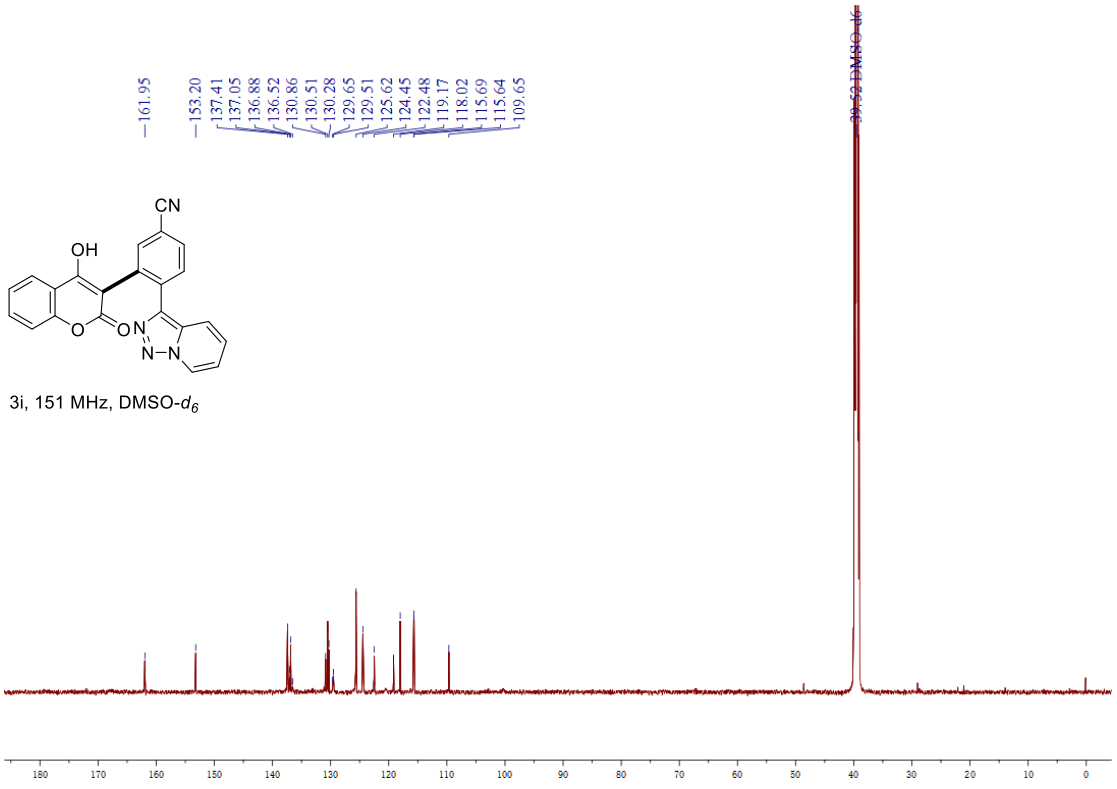
3h, 471 MHz, DMSO-d_6



4-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-3-(4-hydroxy-2-oxo-2H-chromen-3-yl)benzonitrile (3i)

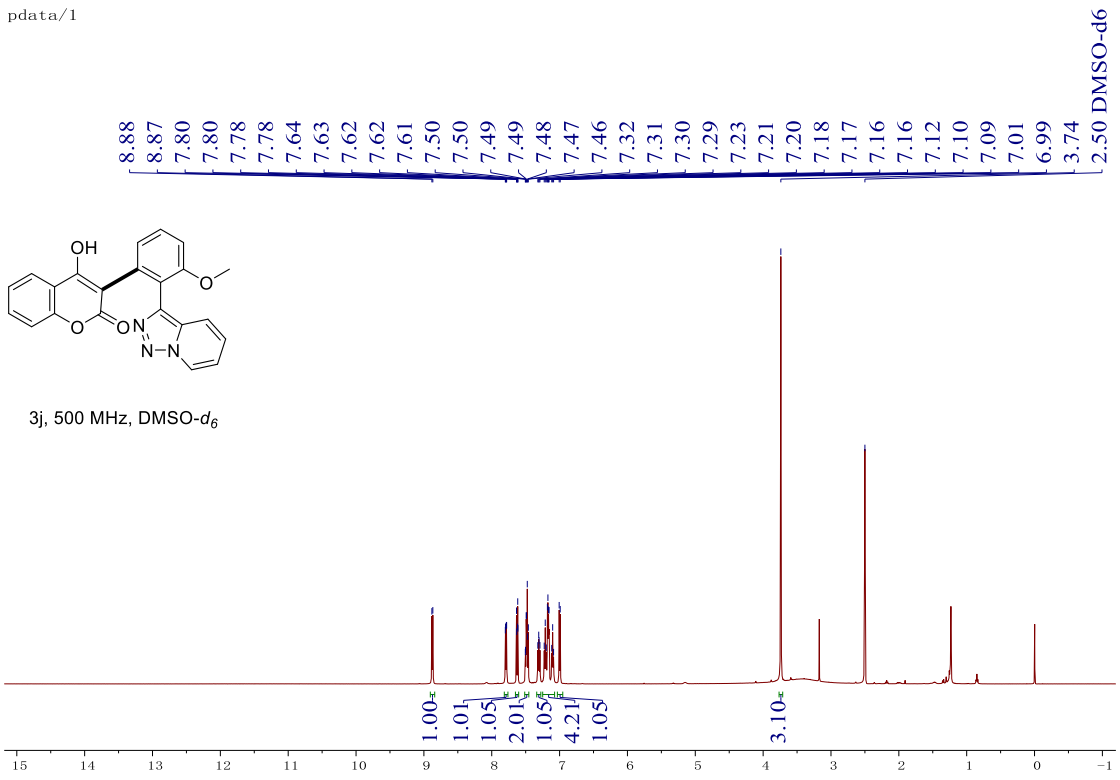


3i, 600 MHz, DMSO-d_6

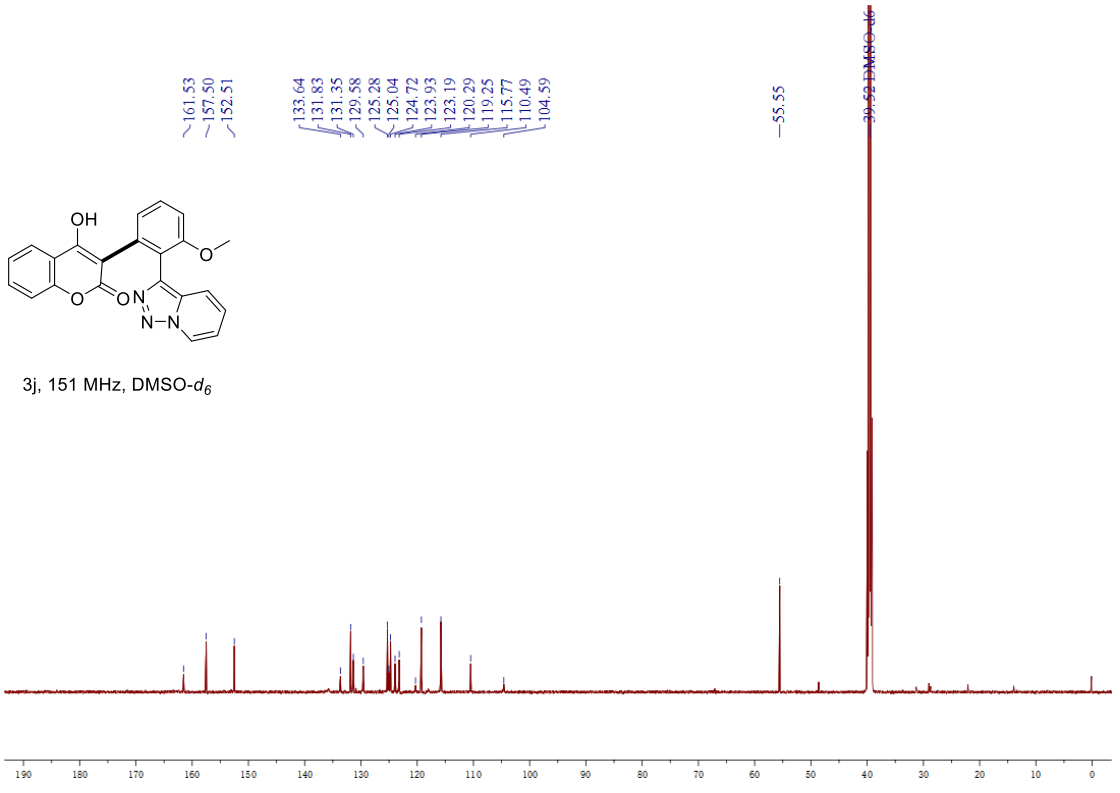


3i, 151 MHz, DMSO-d_6

3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-3-methoxyphenyl)-4-hydroxy-2H-chromen-2-one (3j)

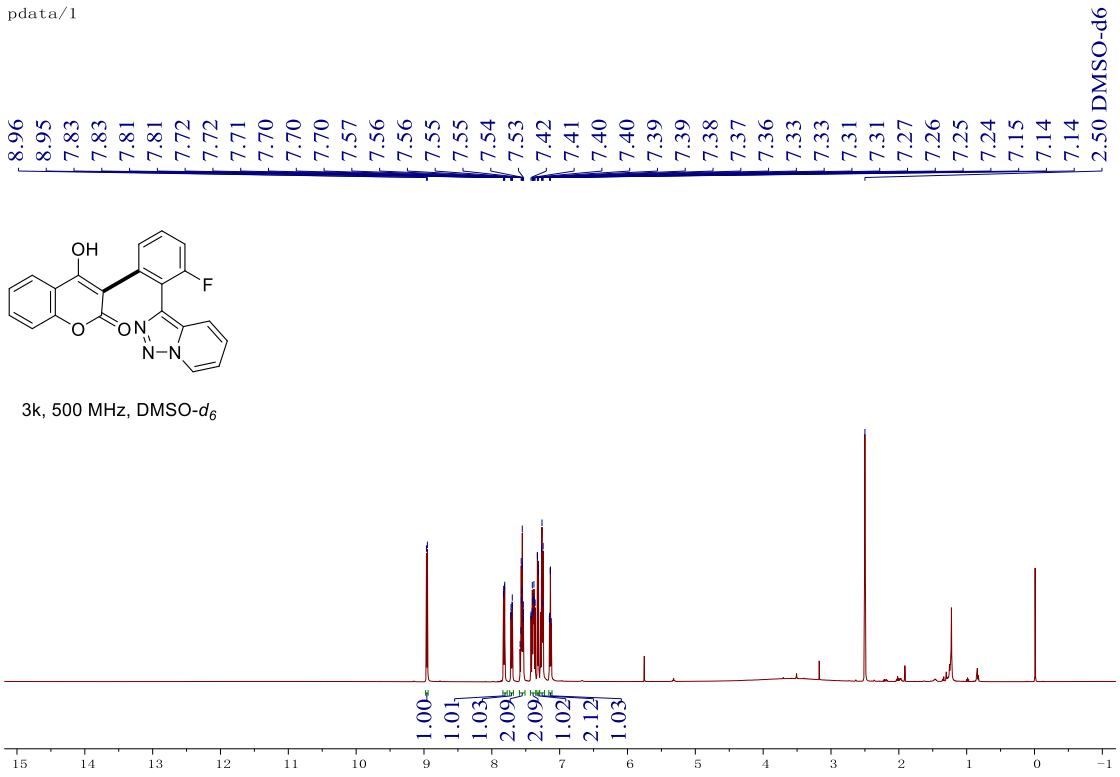


3j, 500 MHz, DMSO-d_6

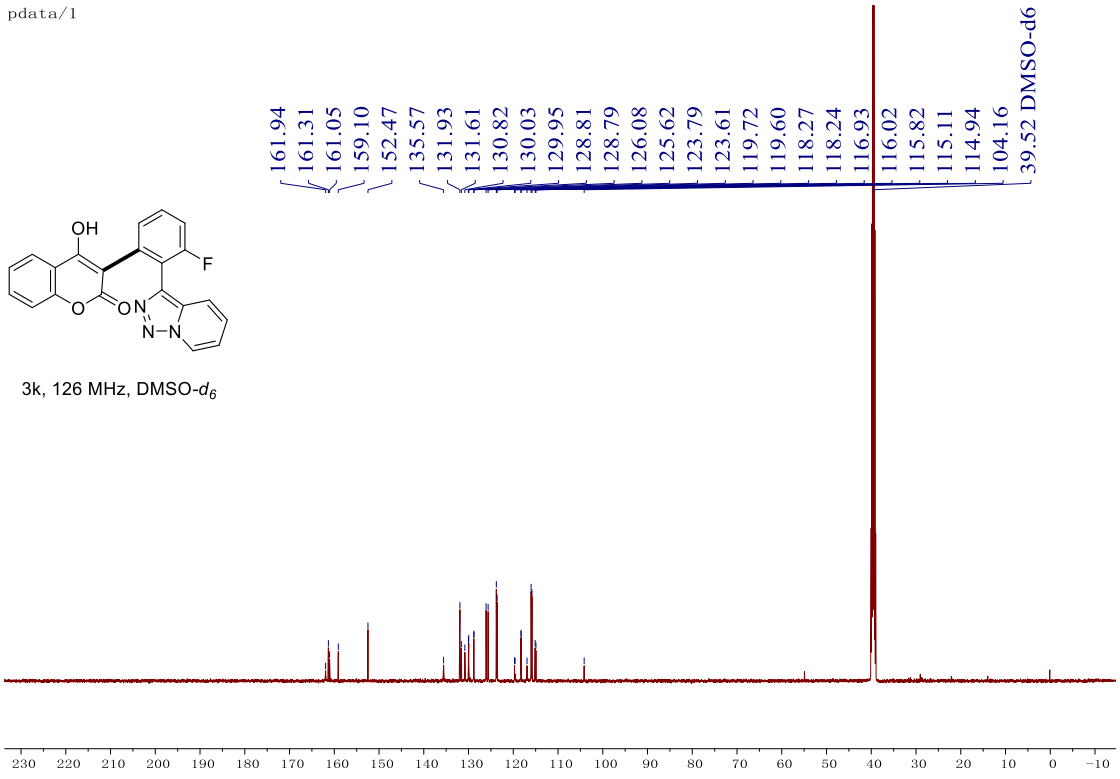


3j, 151 MHz, DMSO-d_6

3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-3-fluorophenyl)-4-hydroxy-2H-chromen-2-one (3k)

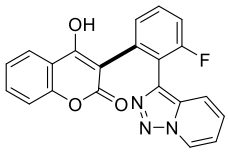


3k, 500 MHz, DMSO-d_6

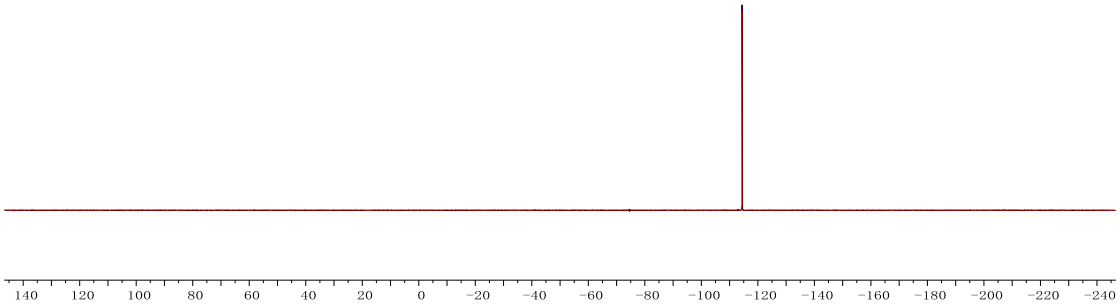


3k, 126 MHz, DMSO-d_6

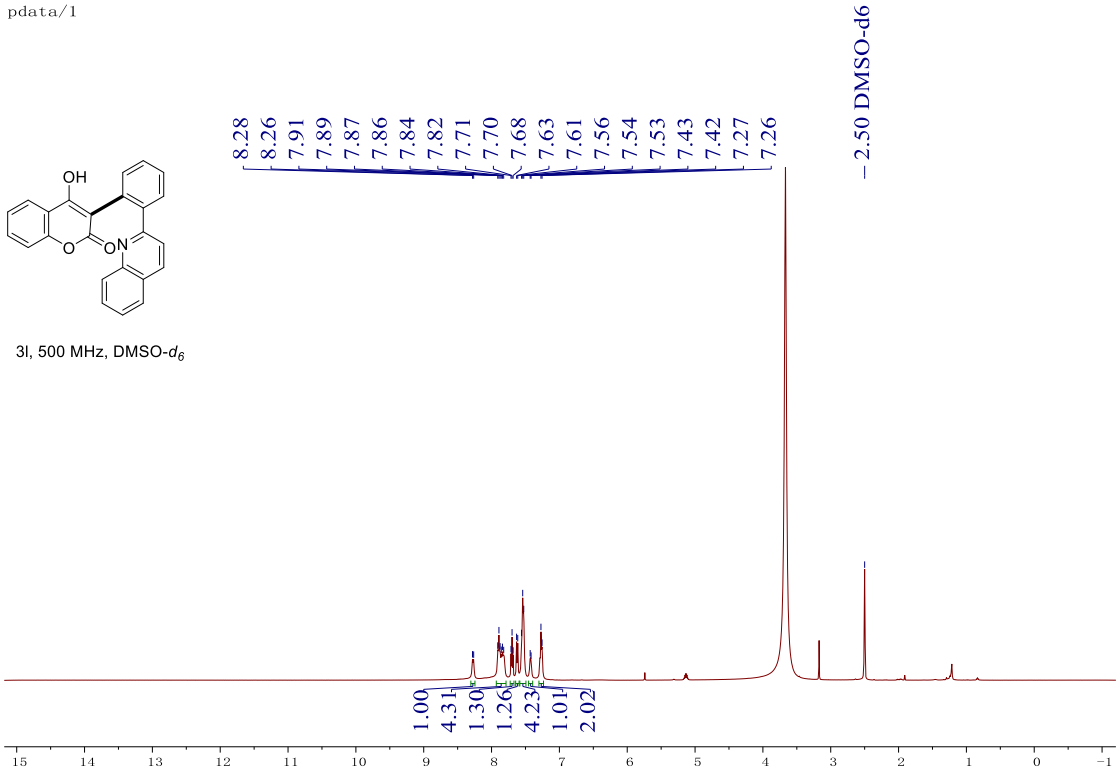
pdata/1



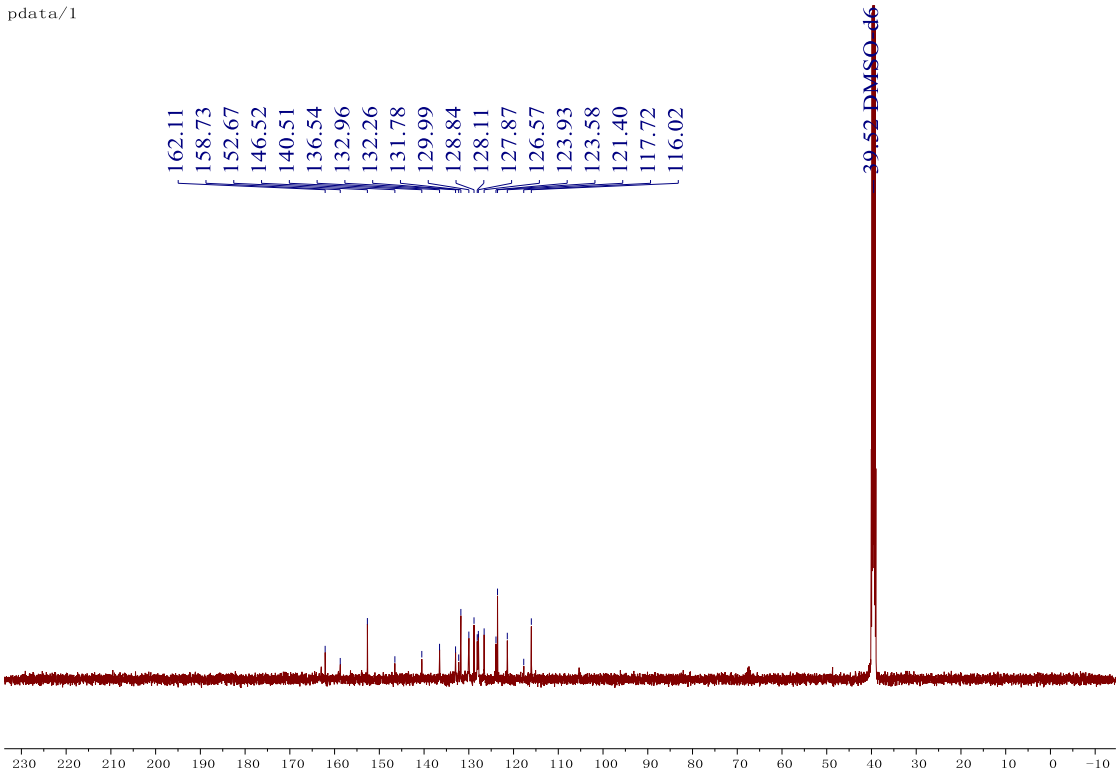
3k, 471 MHz, DMSO-d_6



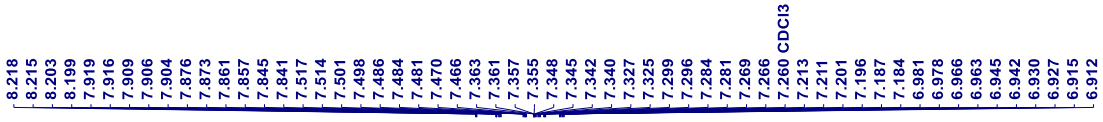
4-hydroxy-3-(2-(quinolin-2-yl)phenyl)-2H-chromen-2-one (3l)

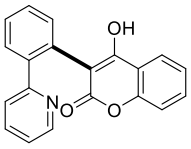


3l, 500 MHz, DMSO-d_6

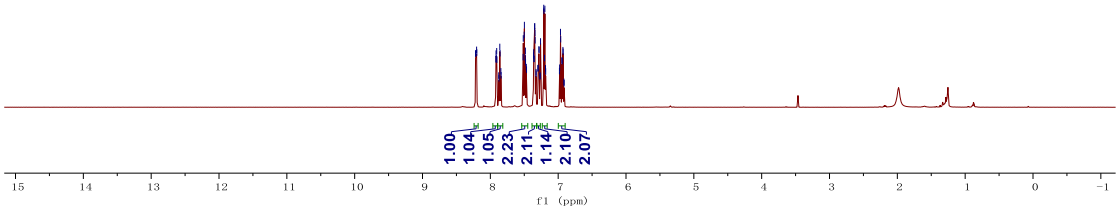


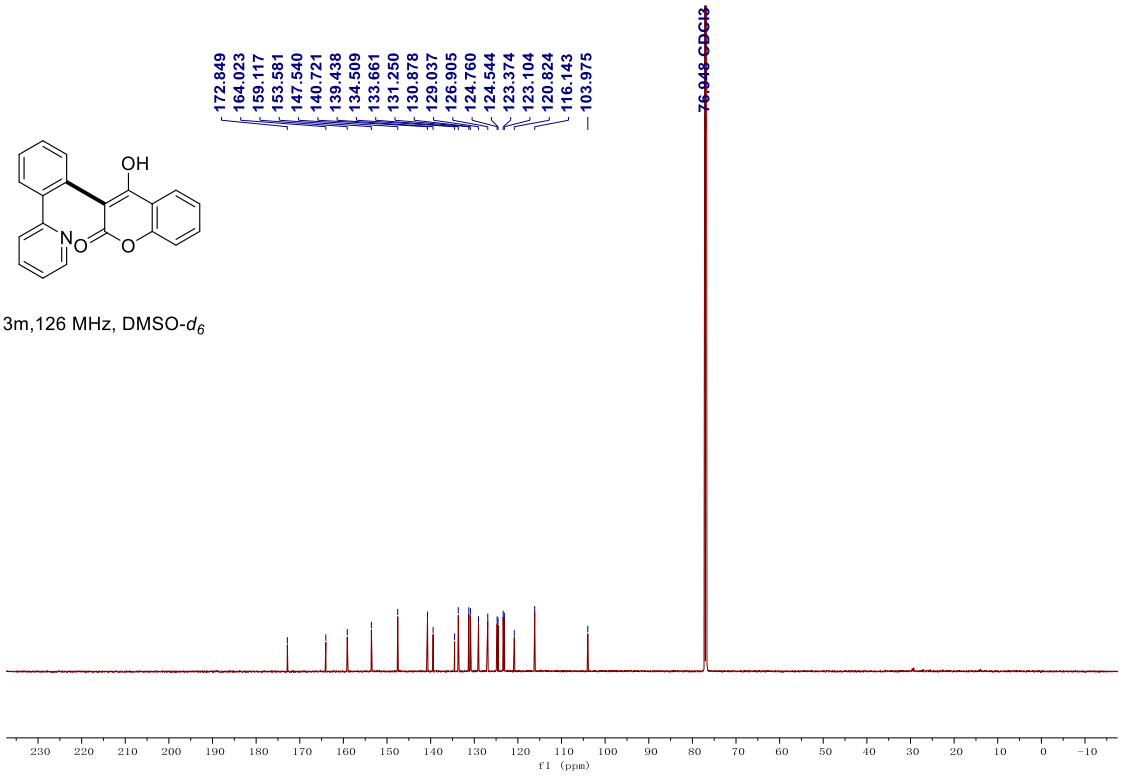
4-hydroxy-3-(2-(pyridin-2-yl)phenyl)-2H-chromen-2-one (3m)





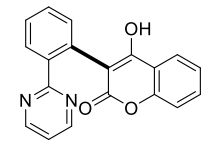
3m, 500 MHz, DMSO-d_6

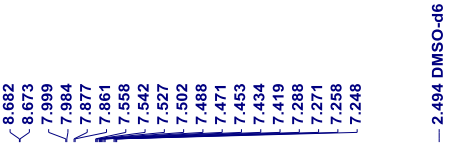




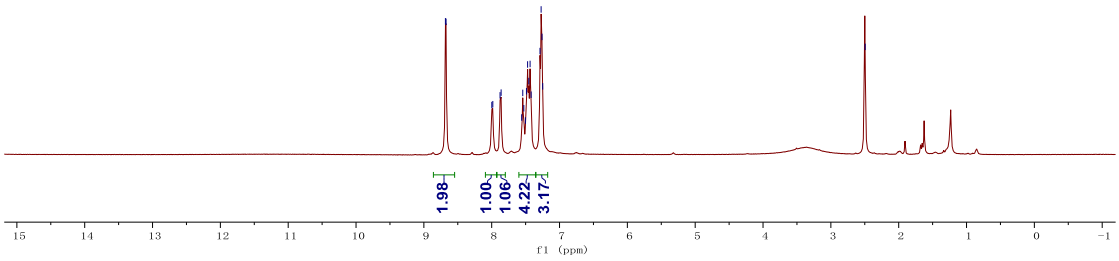
3m,126 MHz, DMSO-d_6

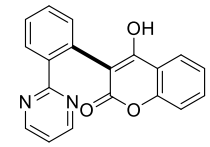
4-hydroxy-3-(2-(pyrimidin-2-yl)phenyl)-2H-chromen-2-one (3n)



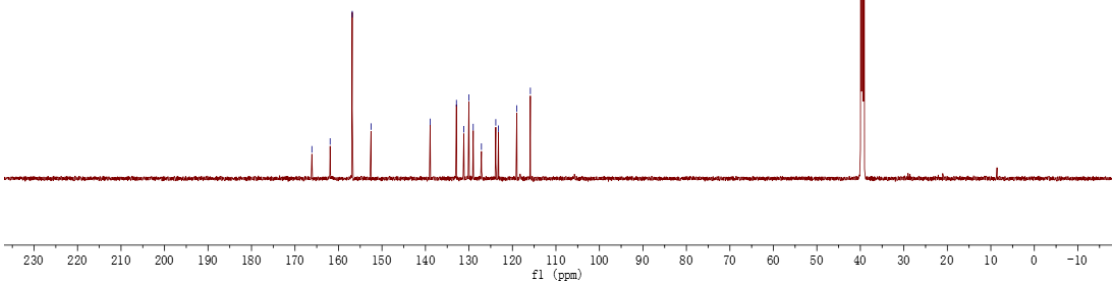


3n, 500 MHz, DMSO-d_6

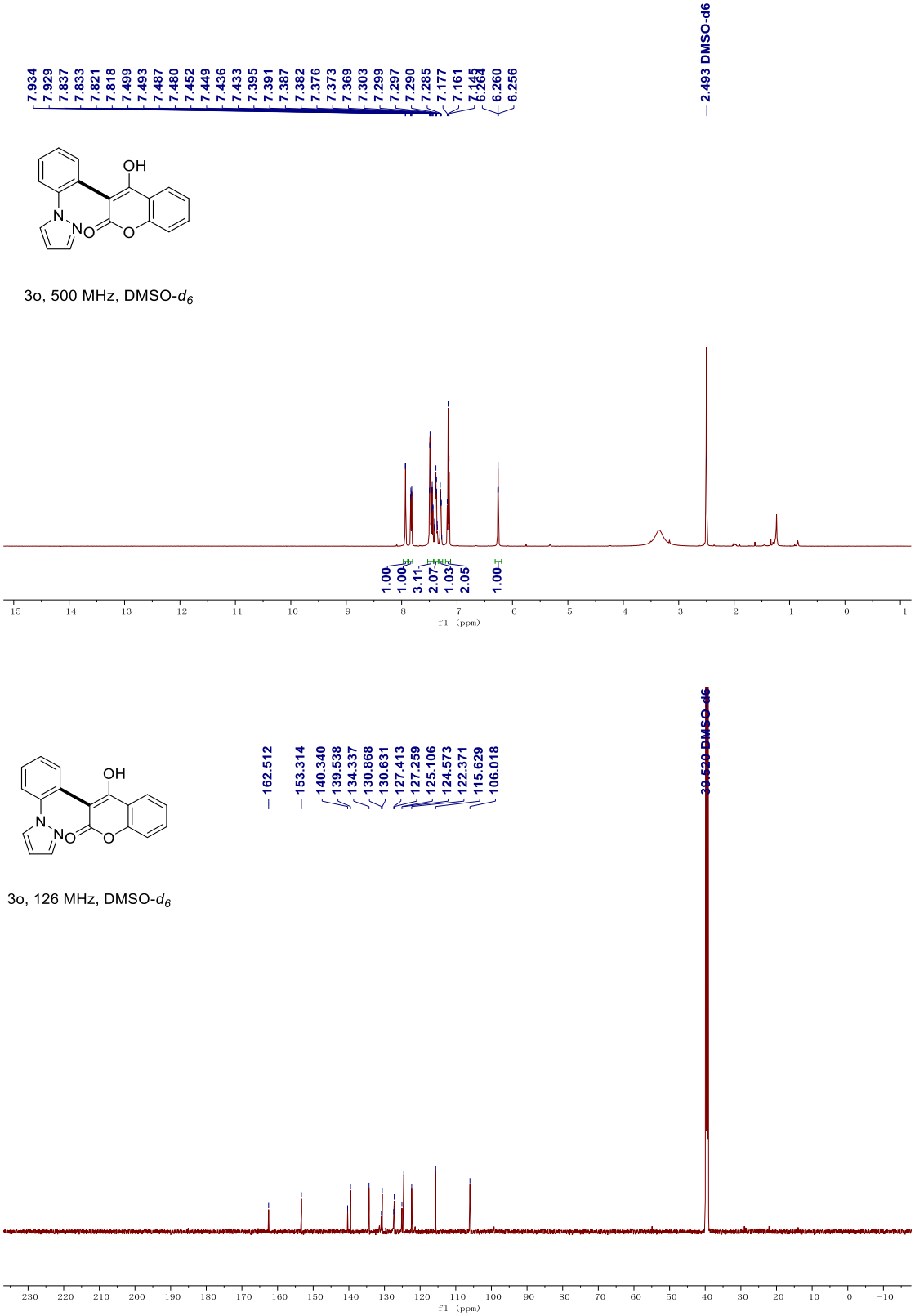




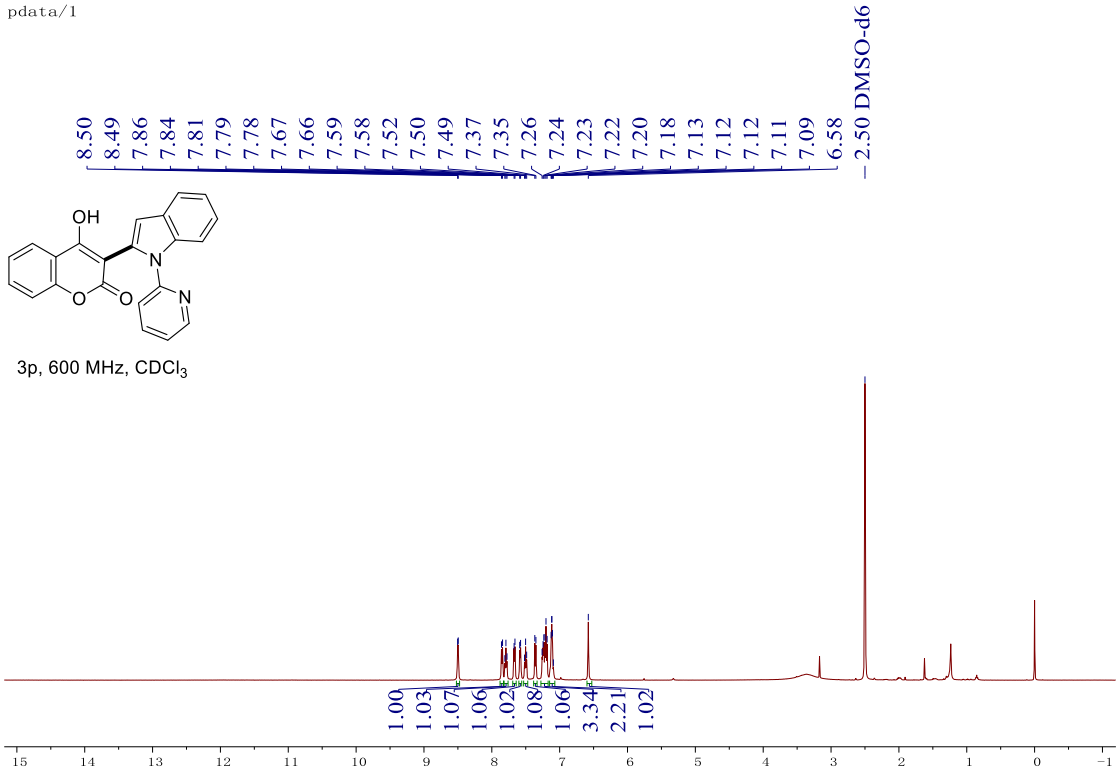
3n, 126 MHz, DMSO-d_6



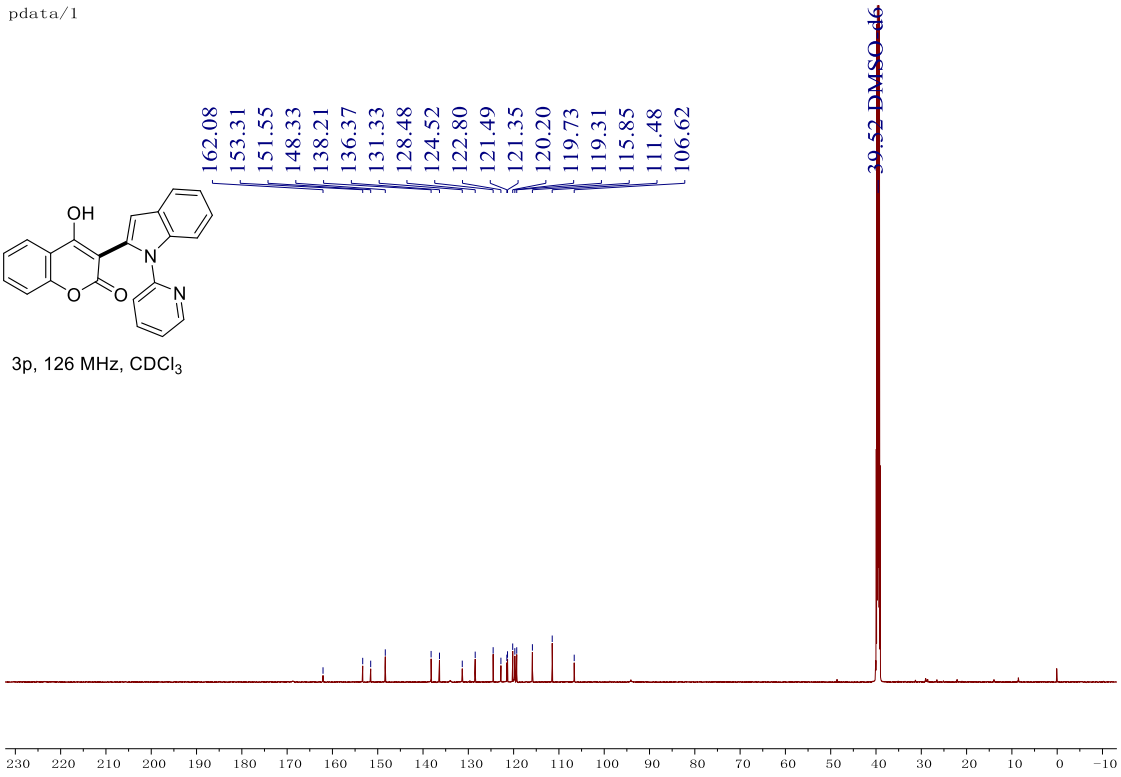
3-(2-(1H-pyrazol-1-yl)phenyl)-4-hydroxy-2H-chromen-2-one (3o)



4-hydroxy-3-(1-(pyridin-2-yl)-1H-indol-2-yl)-2H-chromen-2-one (3p)

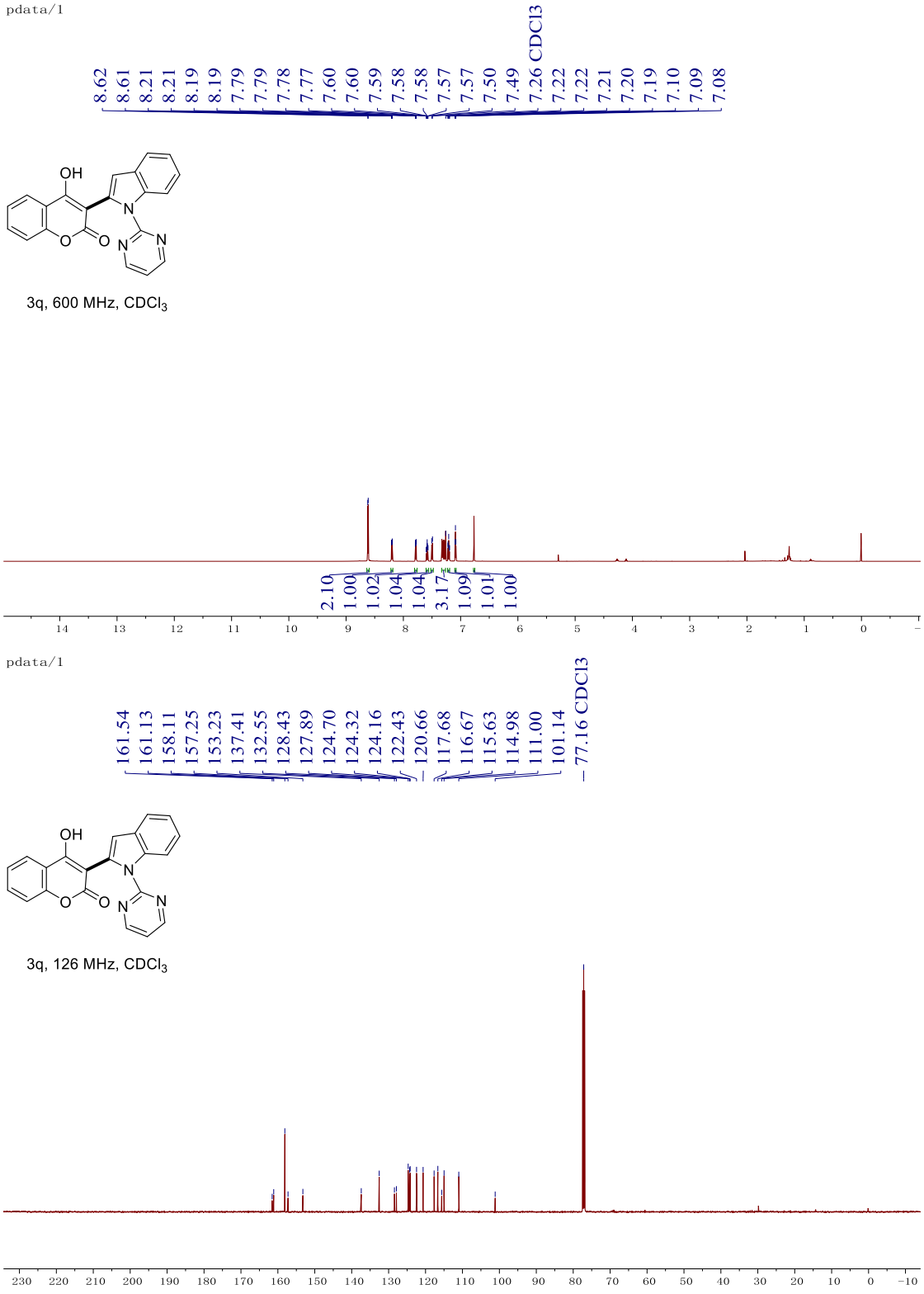


3p, 600 MHz, $CDCl_3$



3p, 126 MHz, $CDCl_3$

4-hydroxy-3-(1-(pyrimidin-2-yl)-1H-indol-2-yl)-2H-chromen-2-one (3q)

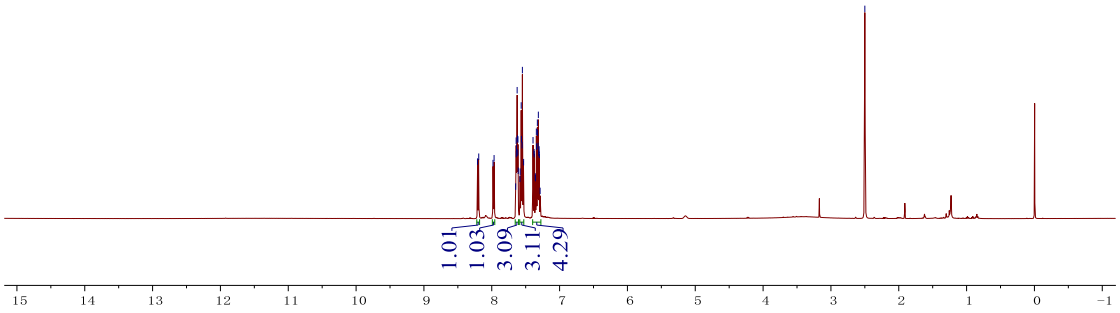


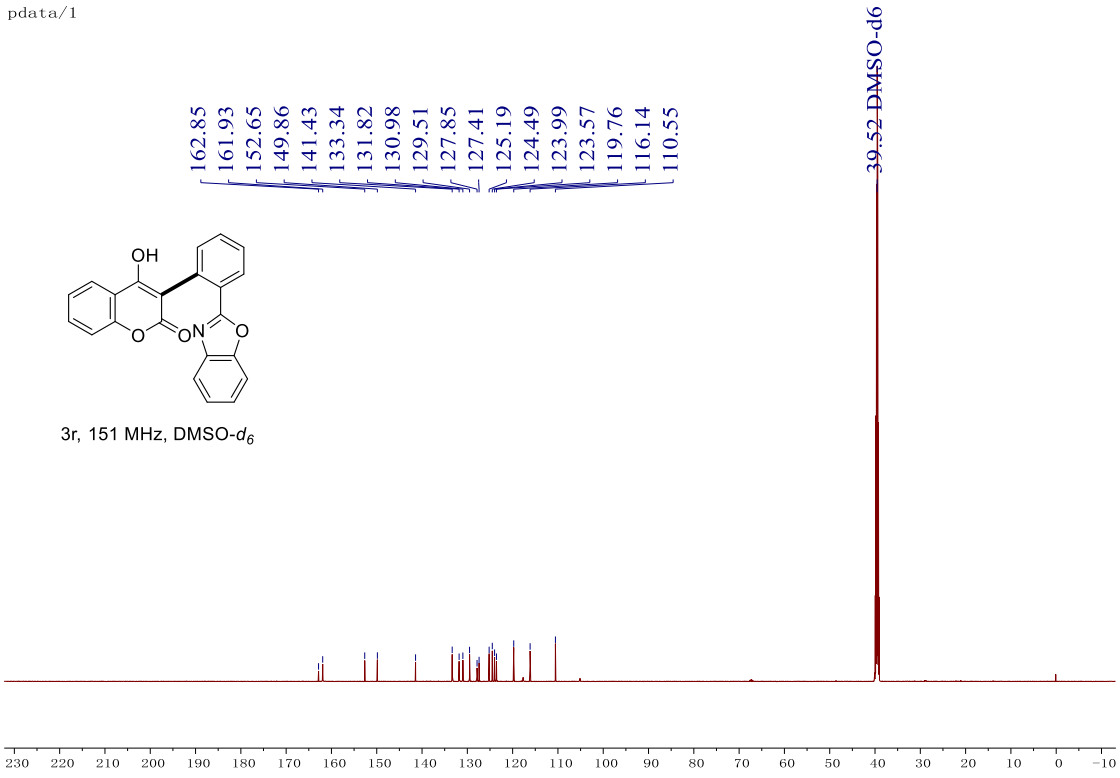
3q, 600 MHz, $CDCl_3$

3q, 126 MHz, $CDCl_3$

3-(2-(benzo[d]oxazol-2-yl)phenyl)-4-(l3-oxidanyl)-2H-chromen-2-one (3r)

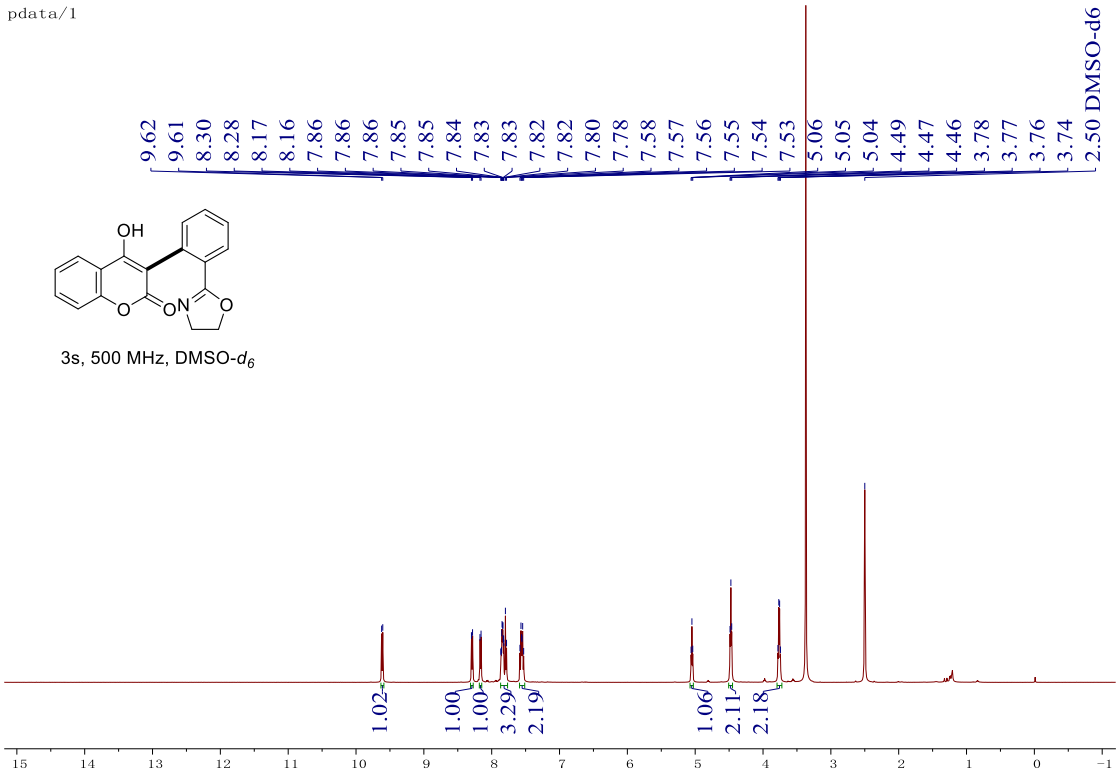
3r, 500 MHz, DMSO-d_6



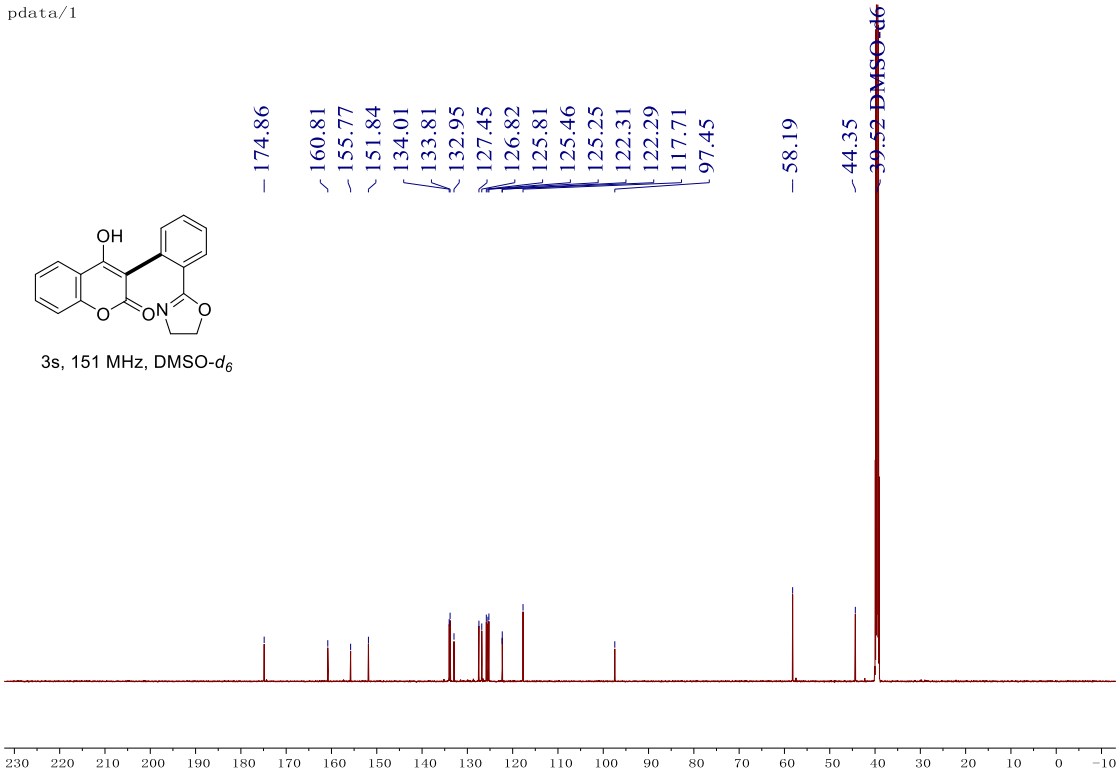


3r, 151 MHz, DMSO-d_6

4-hydroxy-3-(2-(oxazol-2-yl)phenyl)-2H-chromen-2-one (3s)

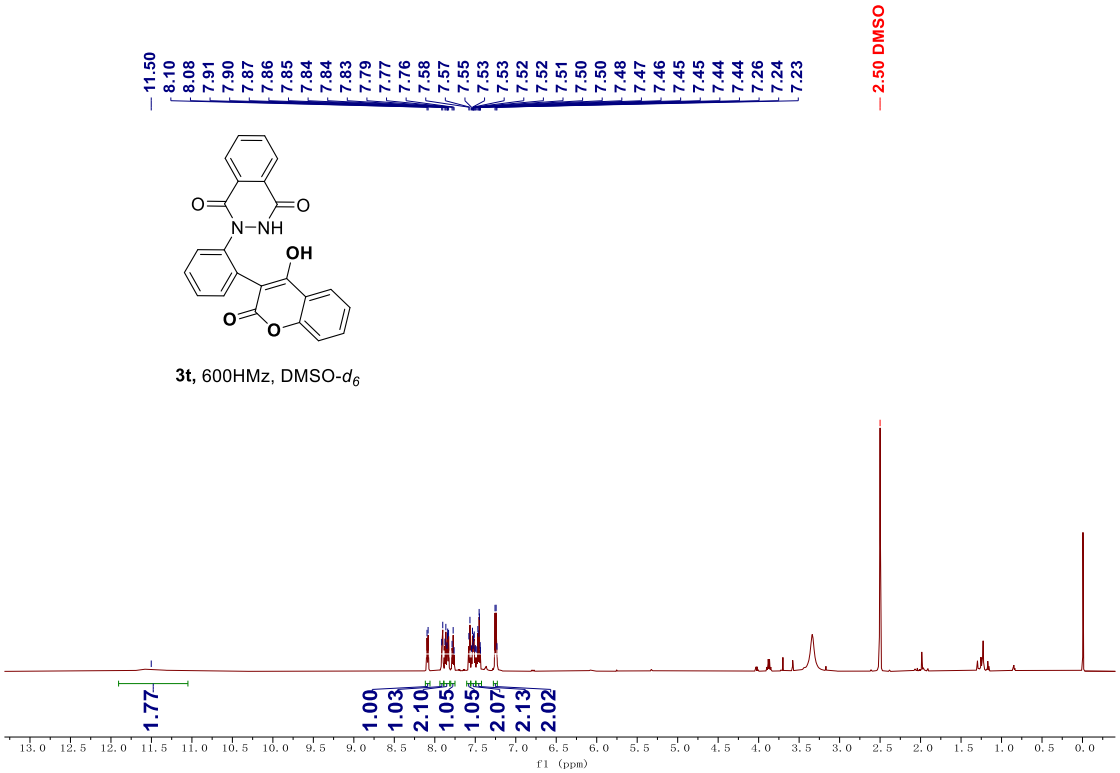


3s, 500 MHz, DMSO-d_6

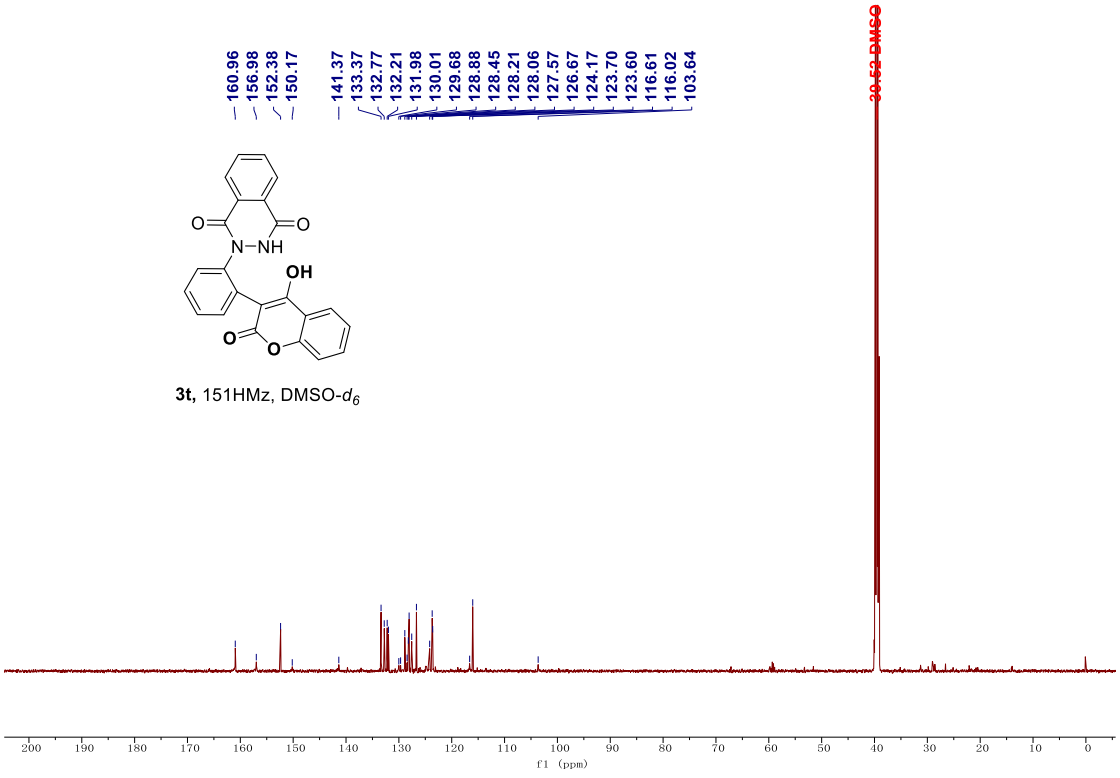


3s, 151 MHz, DMSO-d_6

2-(2-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)phenyl)-2,3-dihydrophthalazine-1,4-dione (3t)

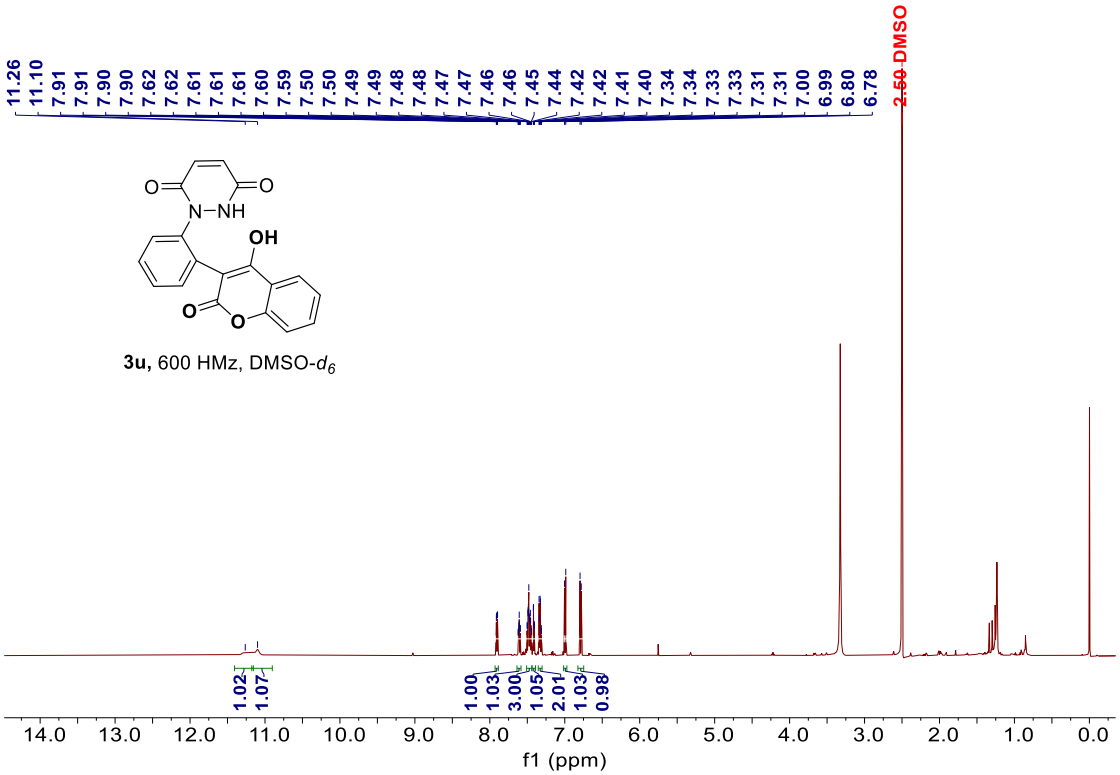


3t, 600HMz, DMSO-d_6

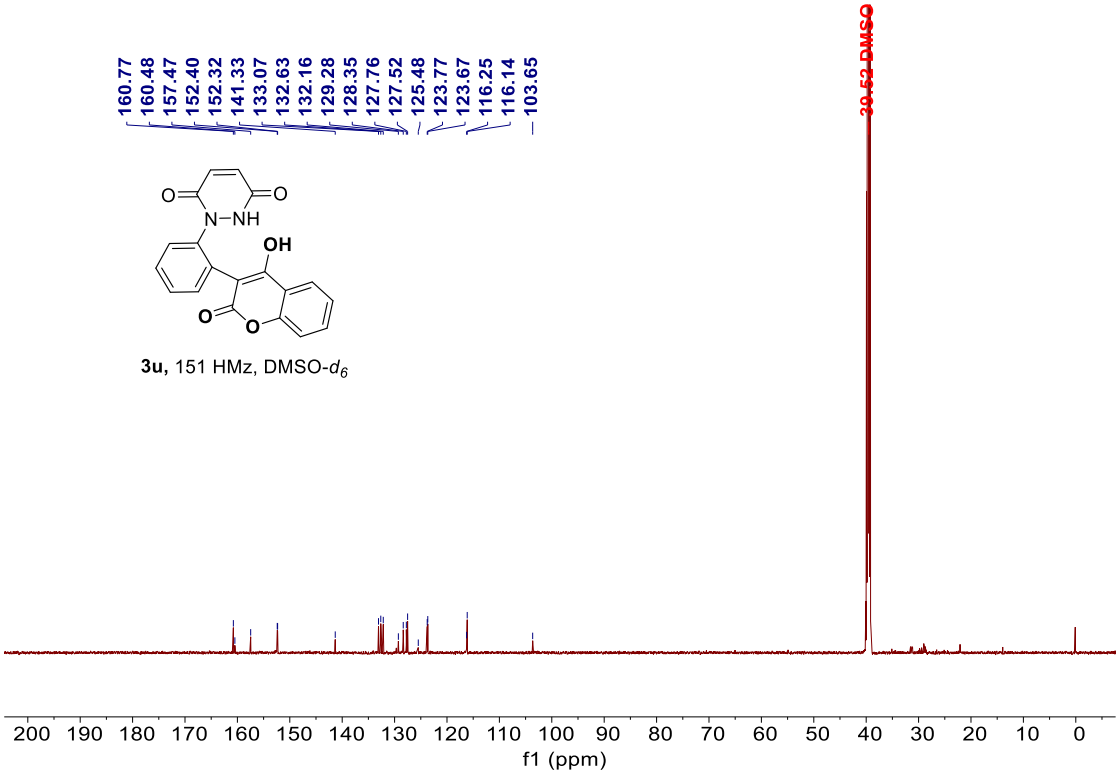


3t, 151HMz, DMSO-d_6

1-(2-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)phenyl)-1,2-dihydropyridazine-3,6-dione (3u)

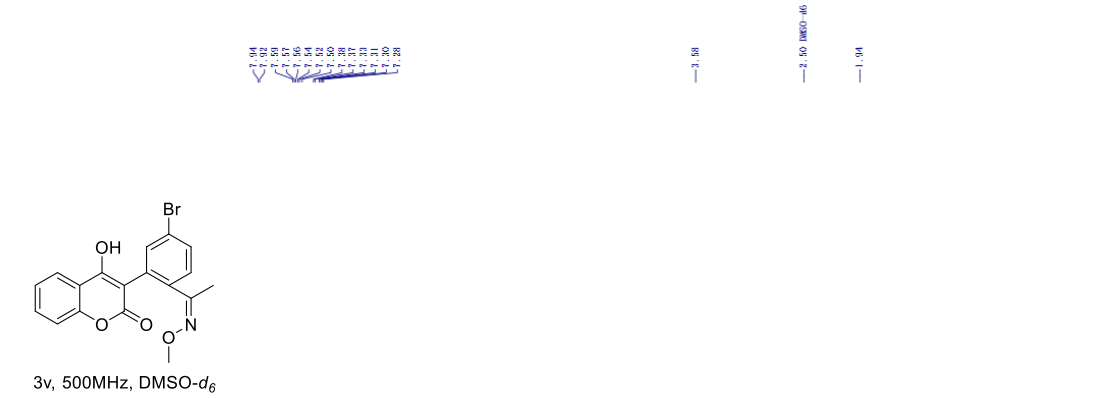


3u, 600 HMz, DMSO-d_6

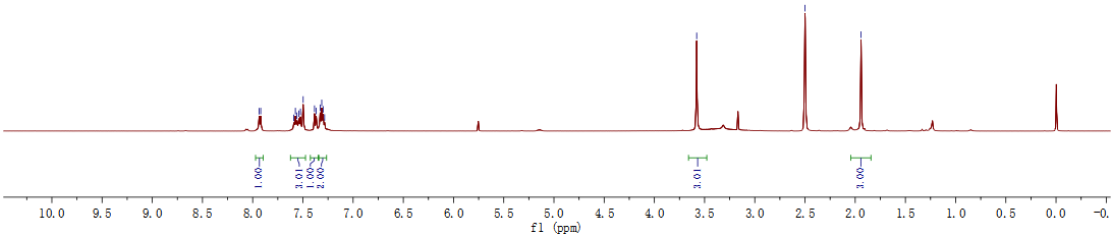


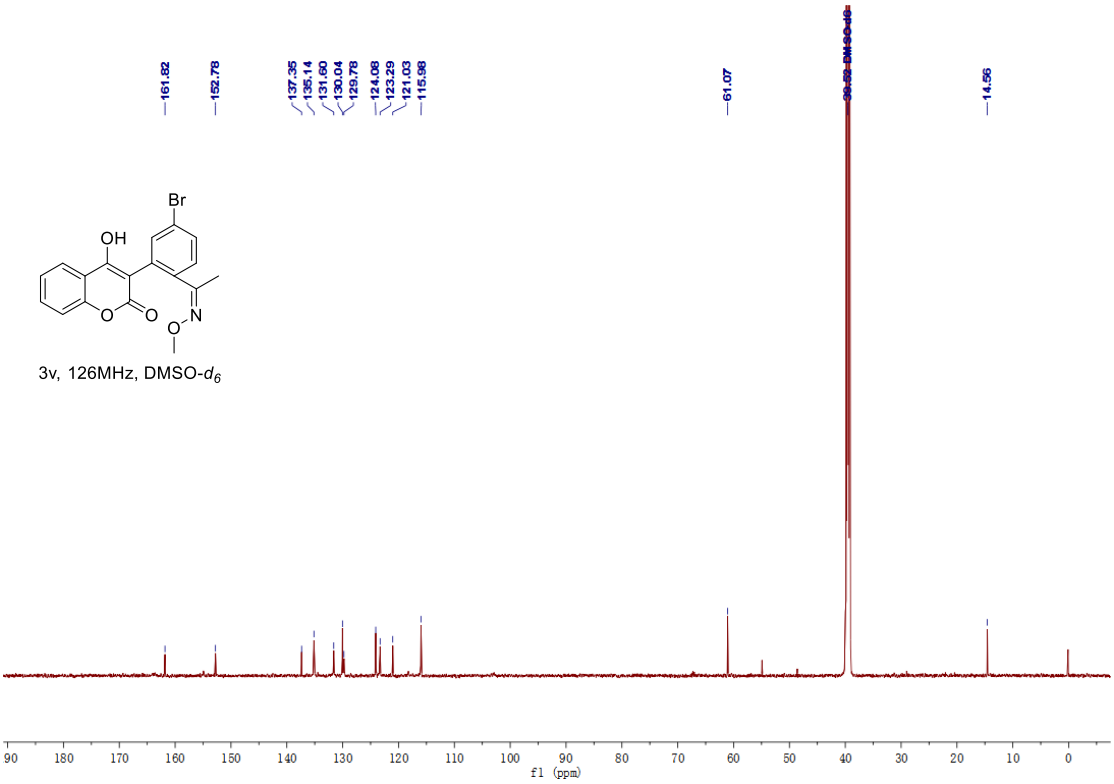
3u, 151 HMz, DMSO-d_6

(Z)-3-(5-bromo-2-(1-(methoxyimino)ethyl)phenyl)-4-hydroxy-2*H*-chromen-2-one (3v)



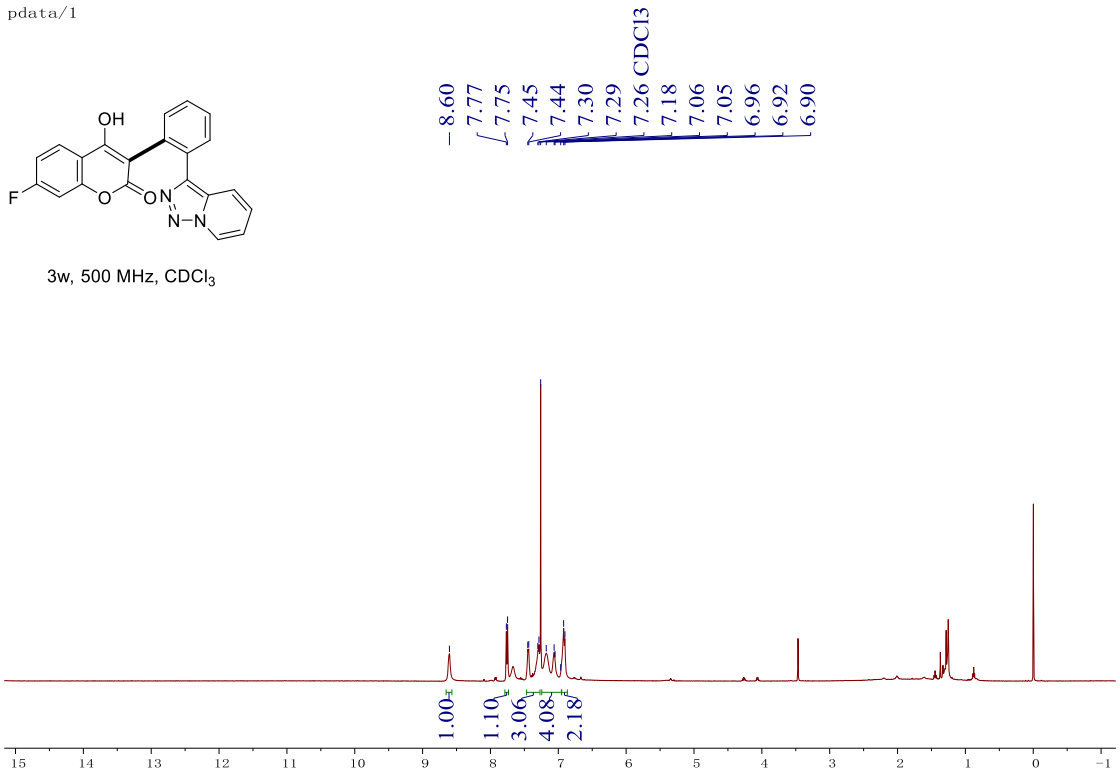
3v, 500MHz, DMSO-d_6



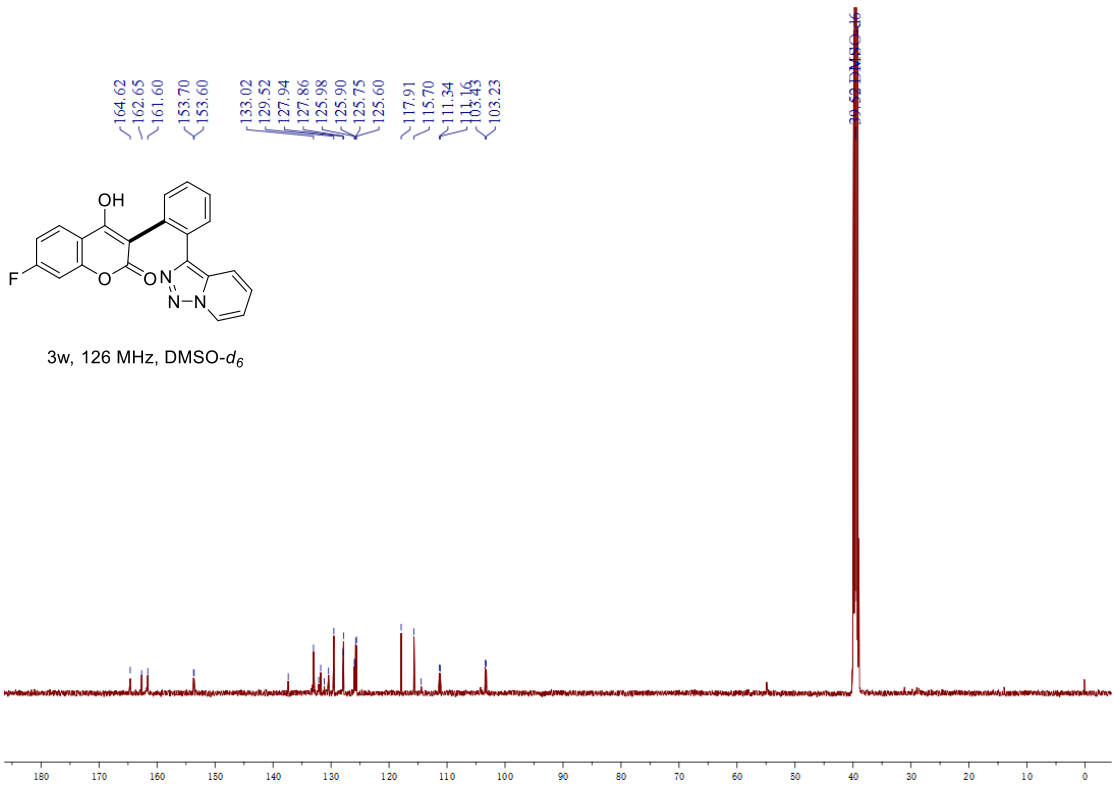


3v, 126MHz, DMSO-d_6

3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-7-fluoro-4-hydroxy-2H-chromen-2-one (3w)

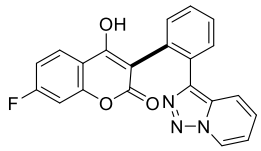


3w, 500 MHz, $CDCl_3$



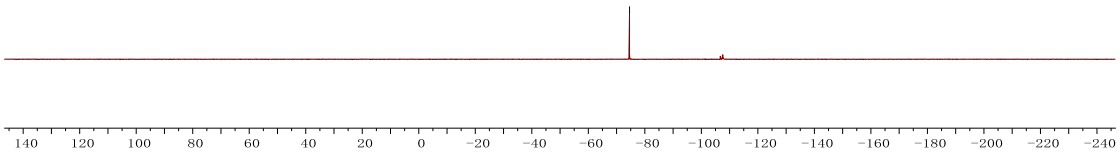
3w, 126 MHz, DMSO-d_6

pdata/1

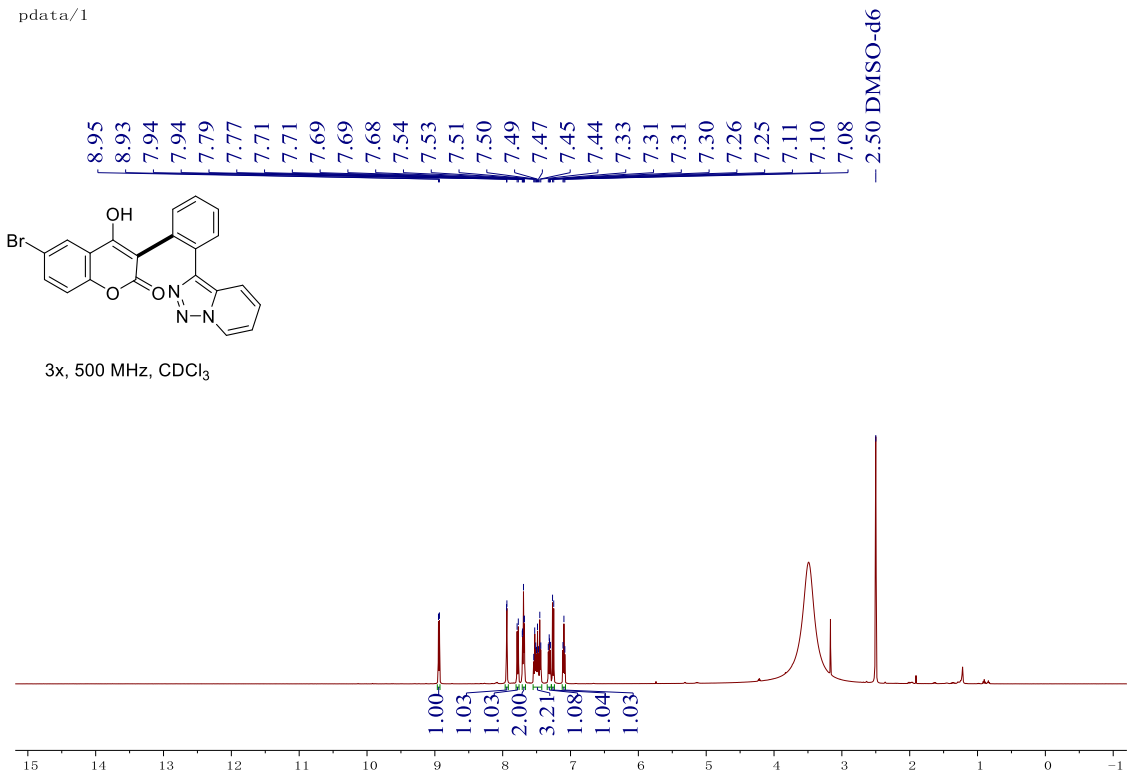


3w, 471 MHz, DMSO-d_6

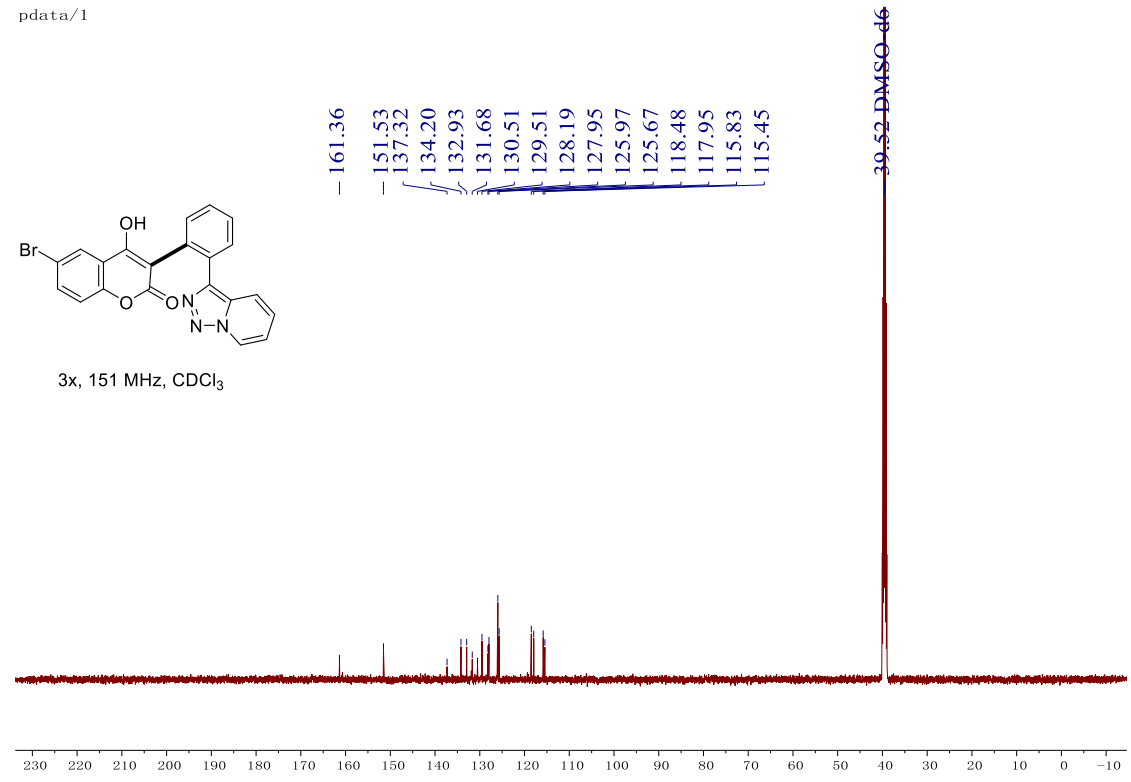
-74.58



3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-6-bromo-4-hydroxy-2H-chromen-2-one (3x)



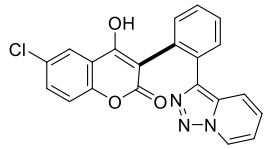
3x, 500 MHz, $CDCl_3$



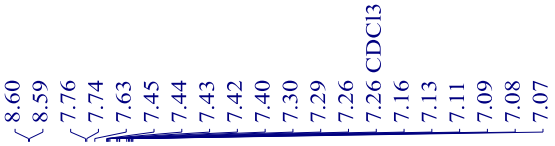
3x, 151 MHz, $CDCl_3$

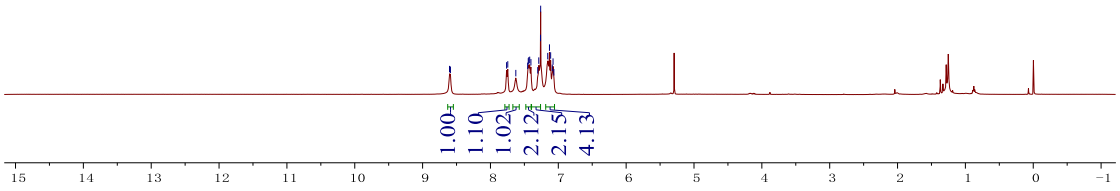
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-6-chloro-4-hydroxy-2H-chromen-2-one (3y)

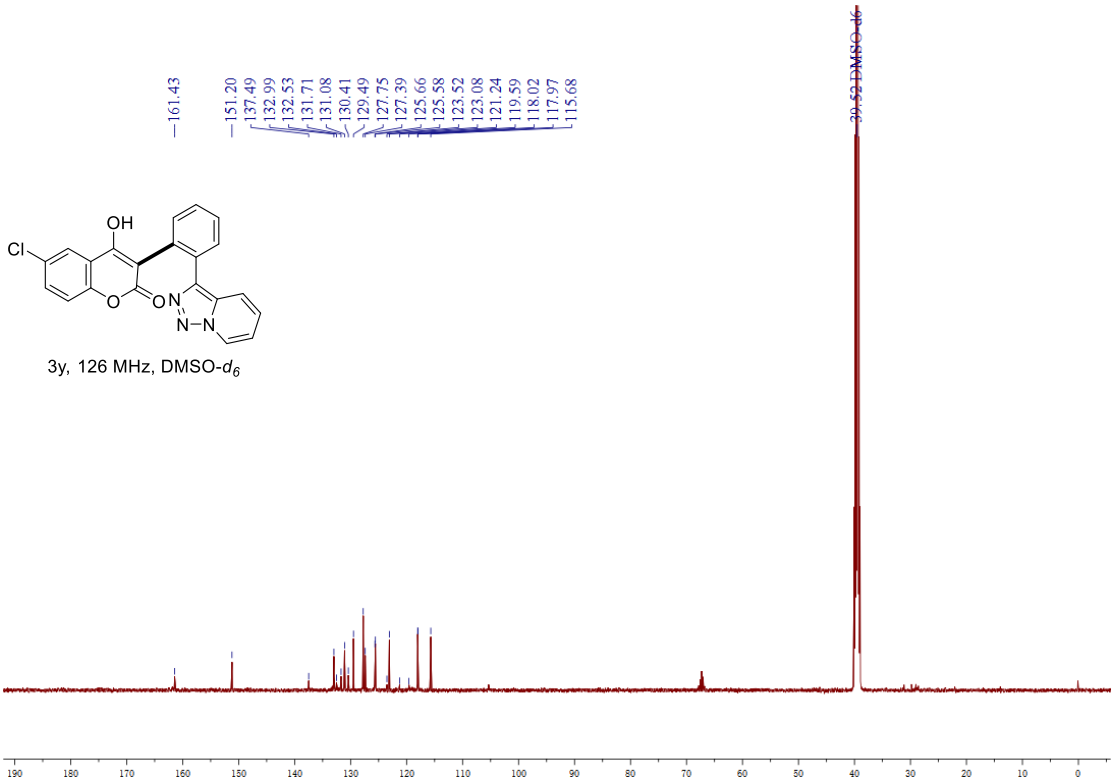
pdata/1



3y, 500 MHz, $CDCl_3$

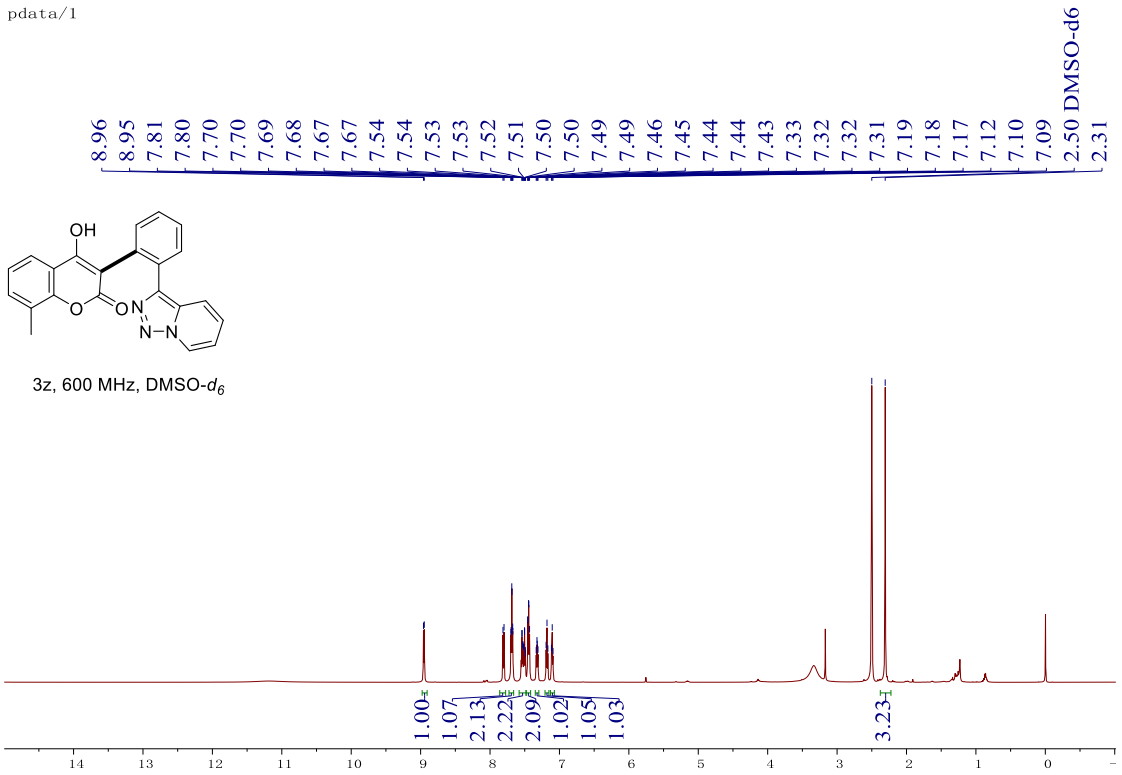




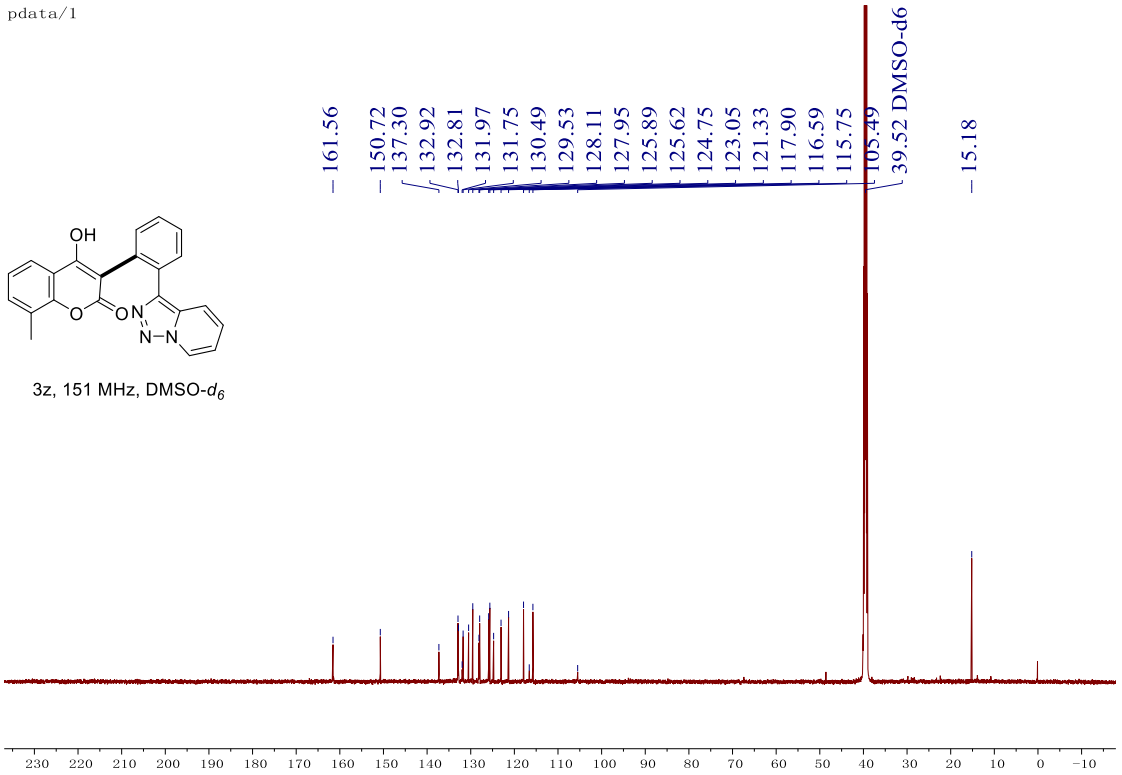


3y, 126 MHz, DMSO-d_6

3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-8-methyl-2H-chromen-2-one (3z)

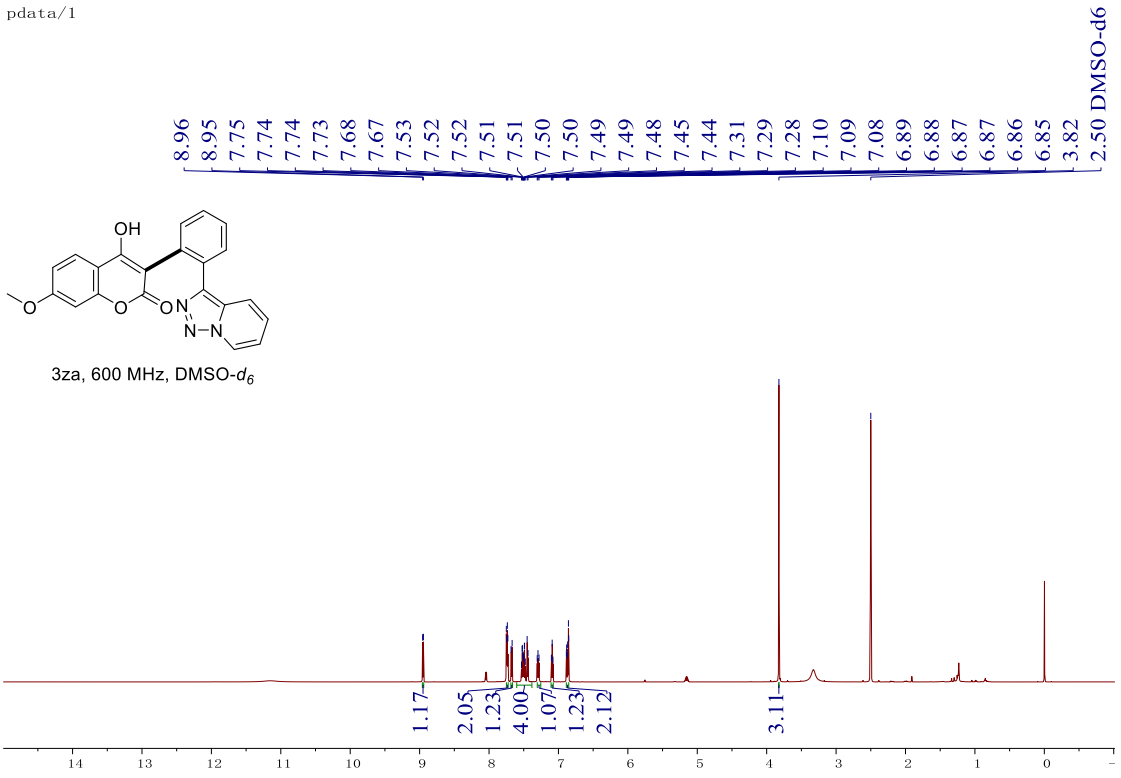


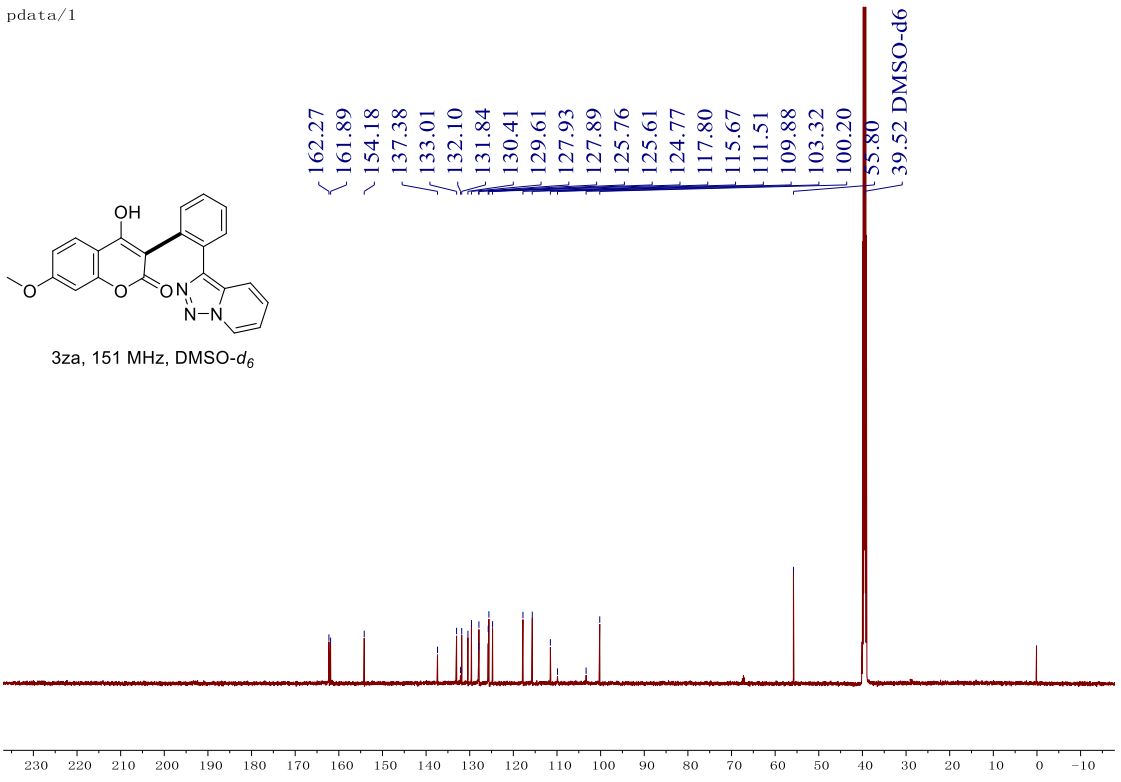
3z, 600 MHz, DMSO-d_6



3z, 151 MHz, DMSO-d_6

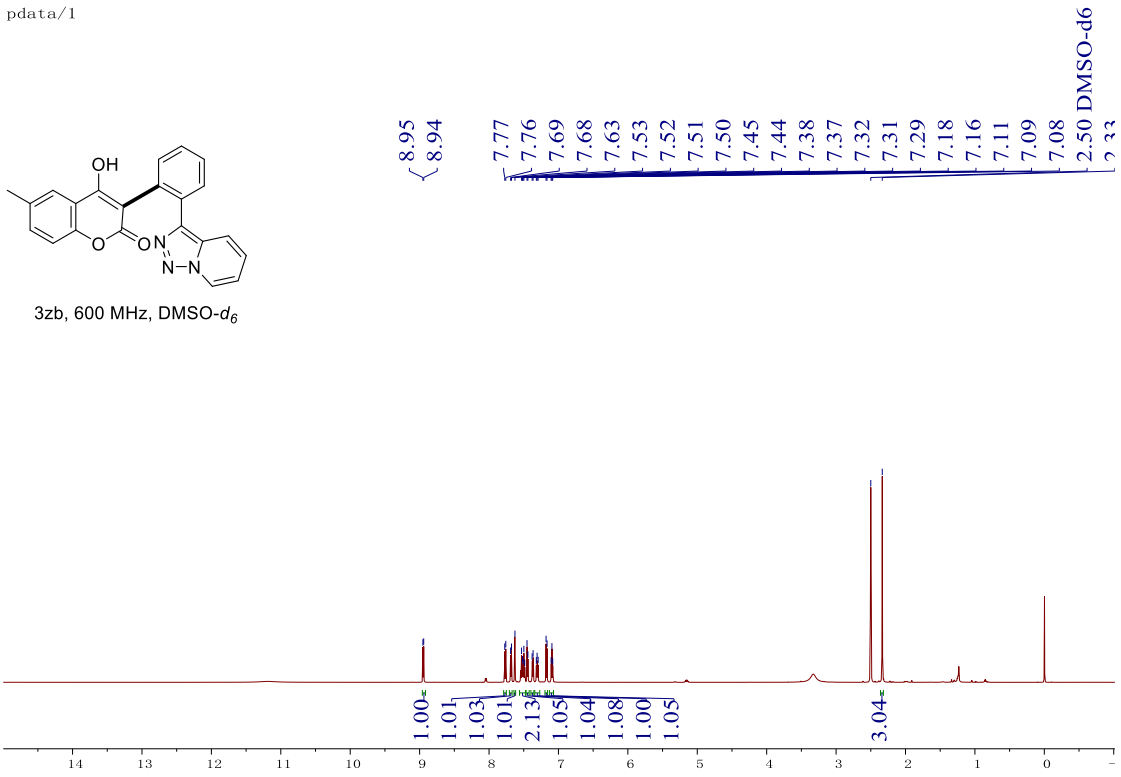
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-7-methoxy-2H-chromen-2-one (3za)



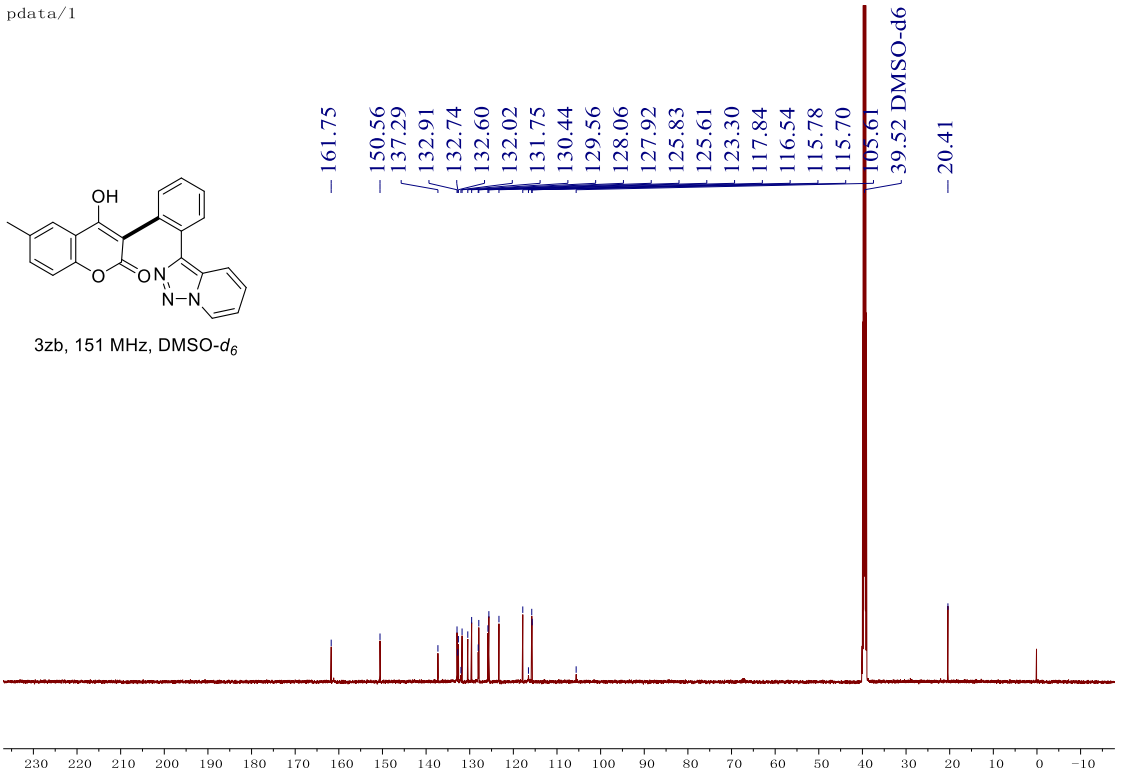


3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-6-methyl-2H-chromen-2-one (3zb)

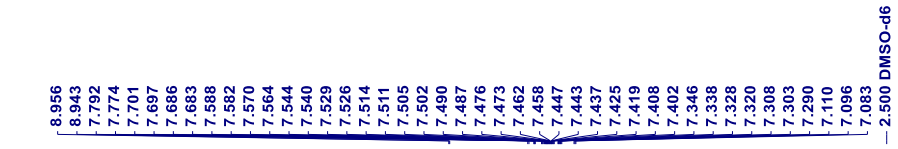
3zb, 600 MHz, DMSO-d_6

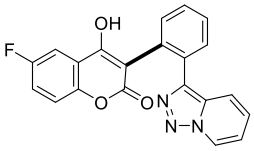


3zb, 151 MHz, DMSO-d_6

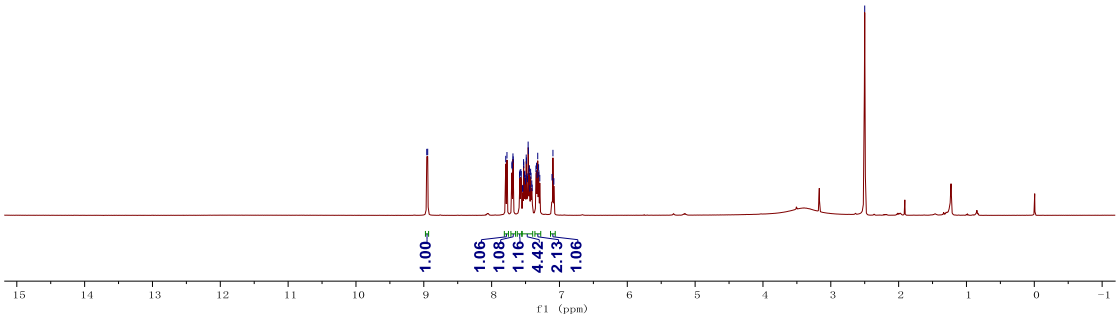


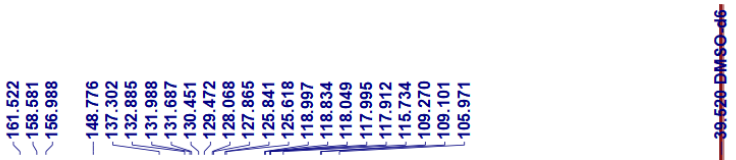
3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-6-fluoro-4-hydroxy-2H-chromen-2-one (3zc)

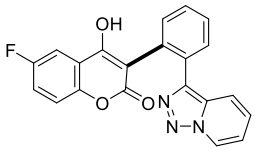




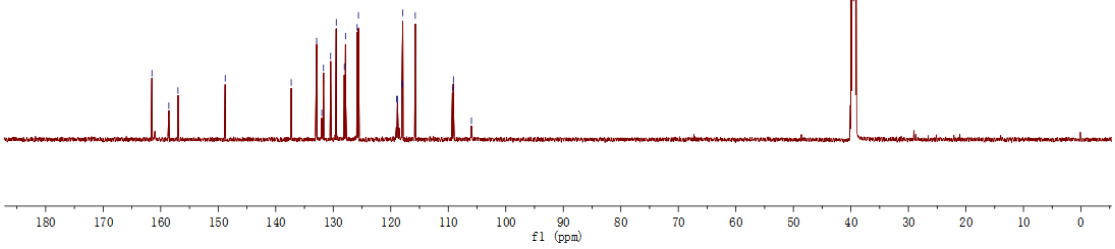
3zc, 500 MHz, DMSO-d_6

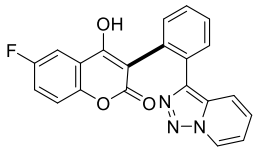




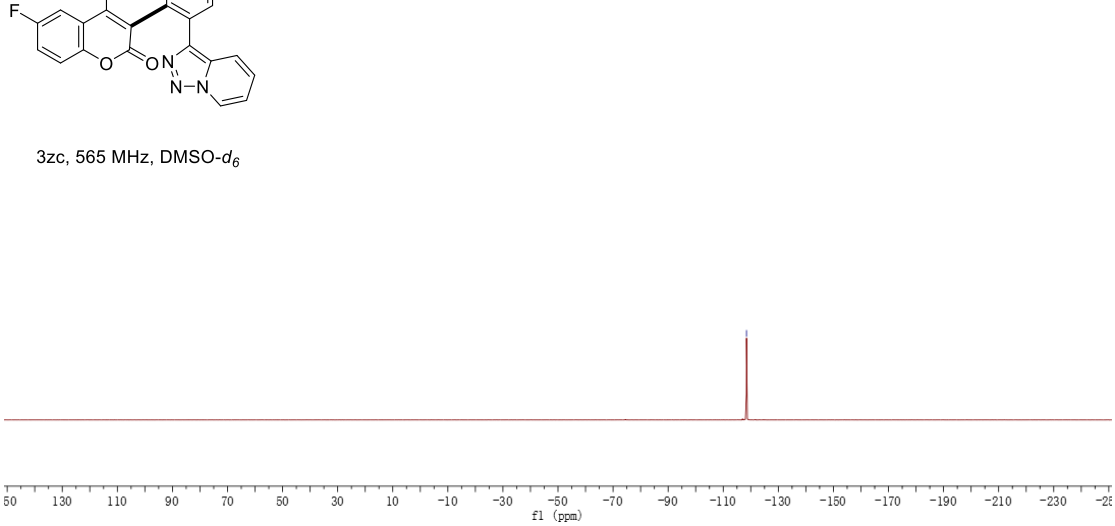


3zc, 126 MHz, DMSO-d_6

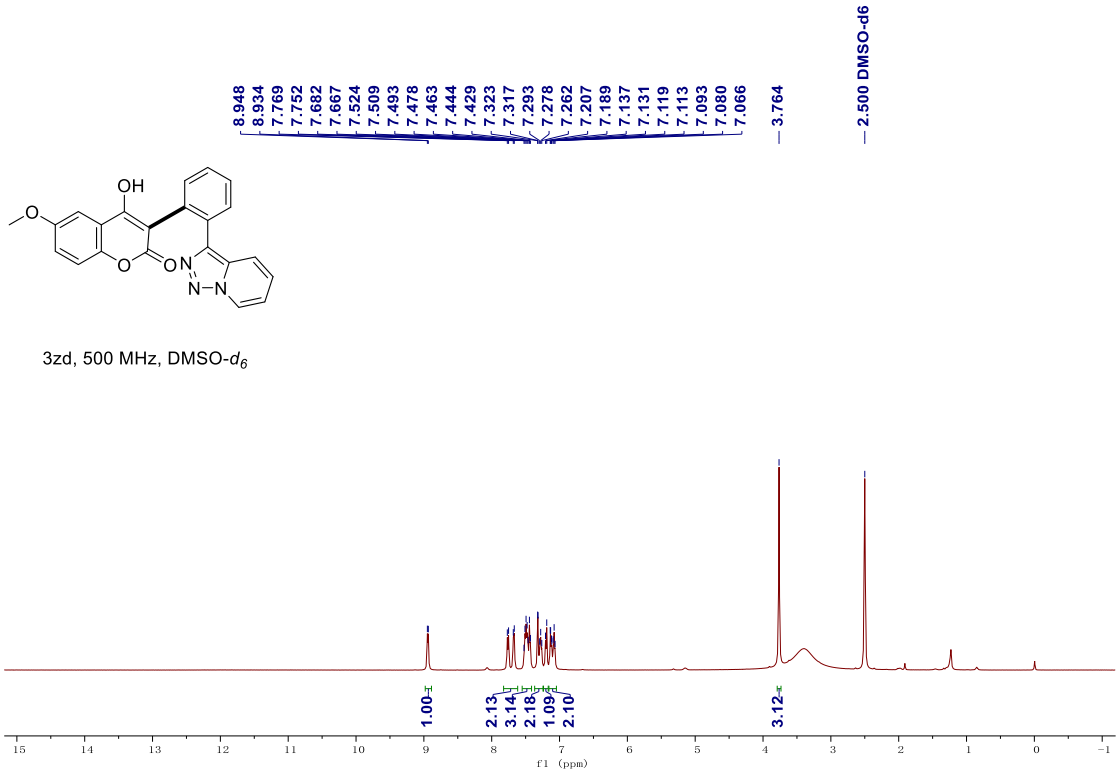




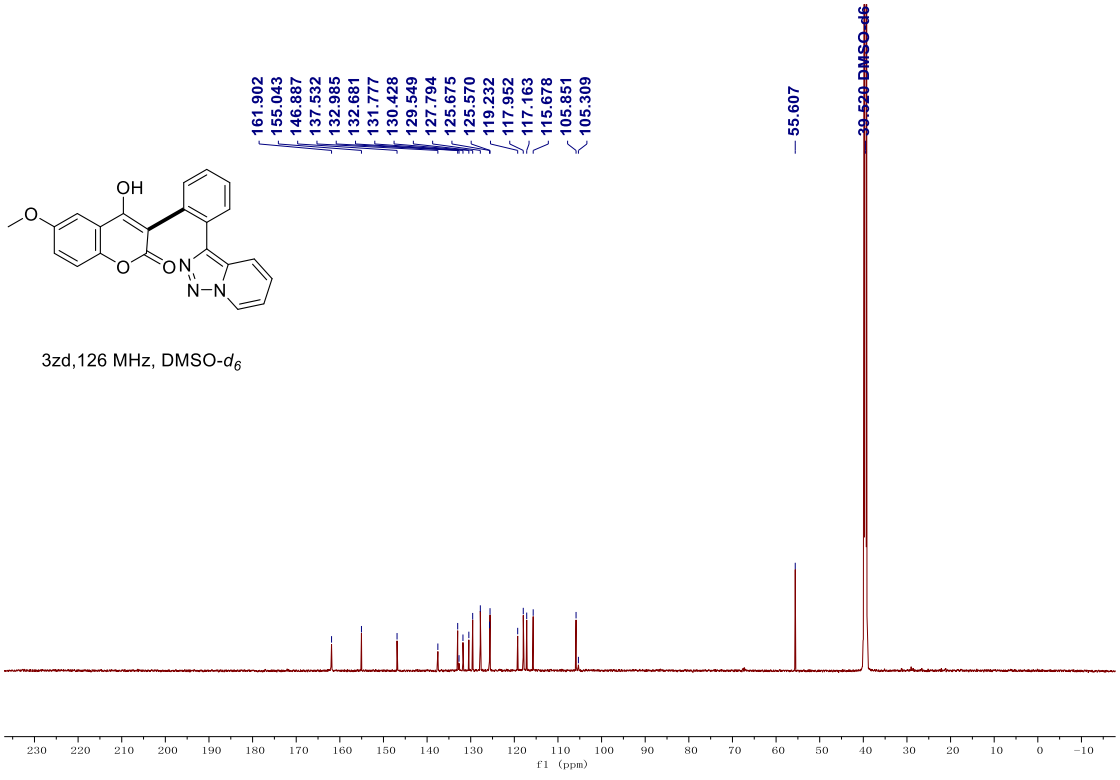
3zc, 565 MHz, DMSO-d_6



3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-6-methoxy-2H-chromen-2-one (3zd)

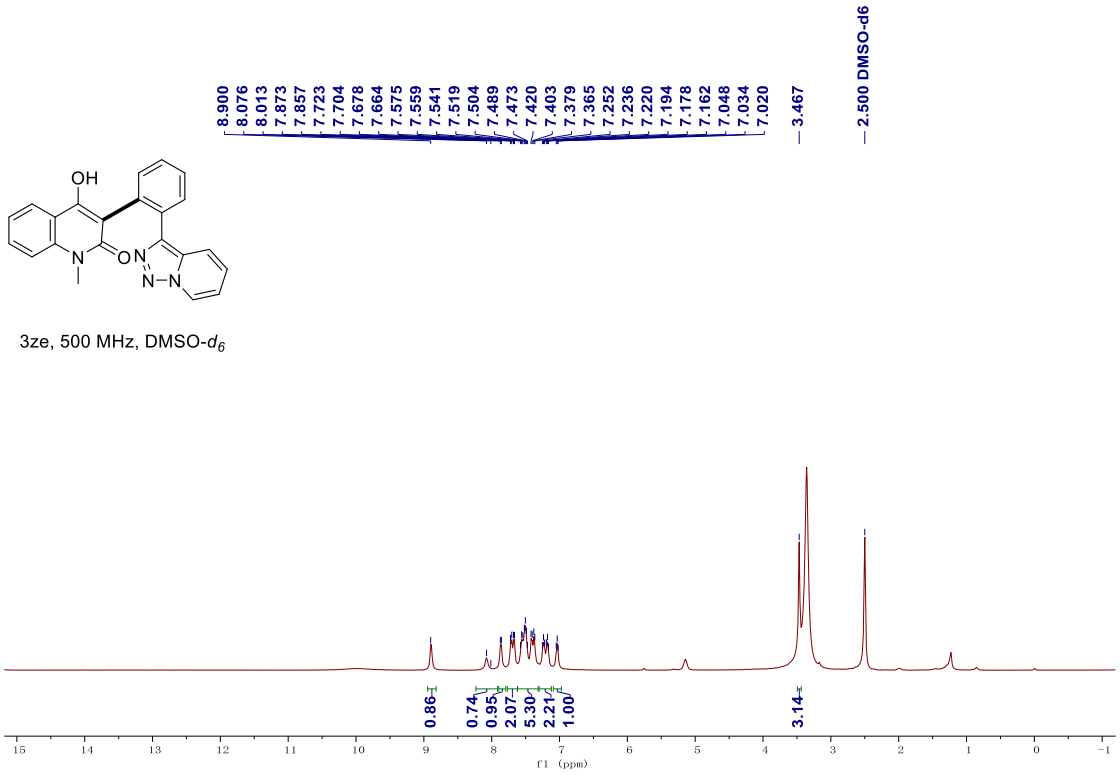


3zd, 500 MHz, DMSO-d_6

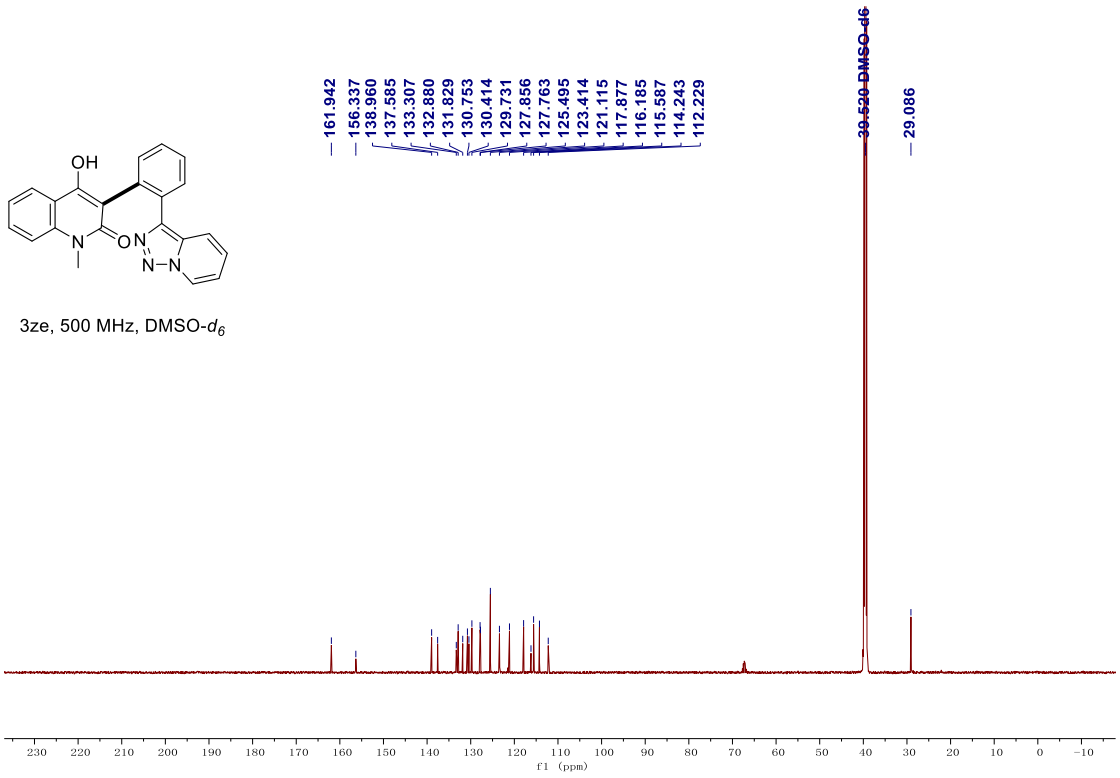


3zd,126 MHz, DMSO-d_6

3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-1-methylquinolin-2(1H)-one (3ze)

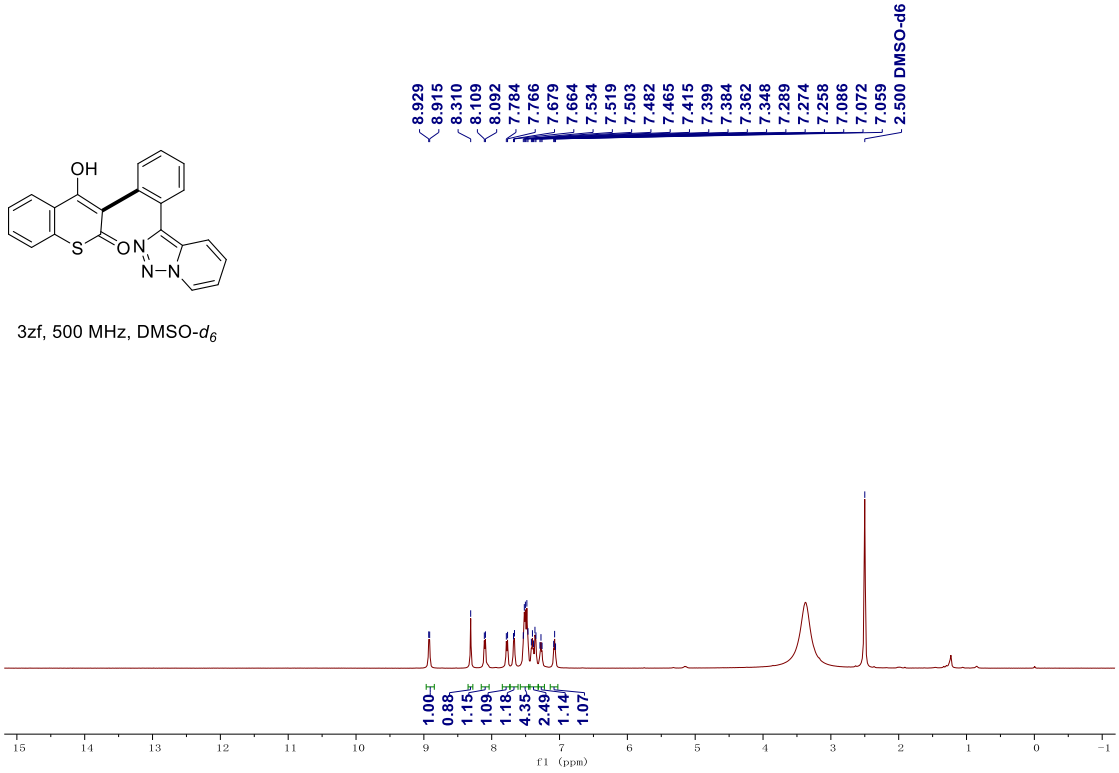


3ze, 500 MHz, DMSO-d_6

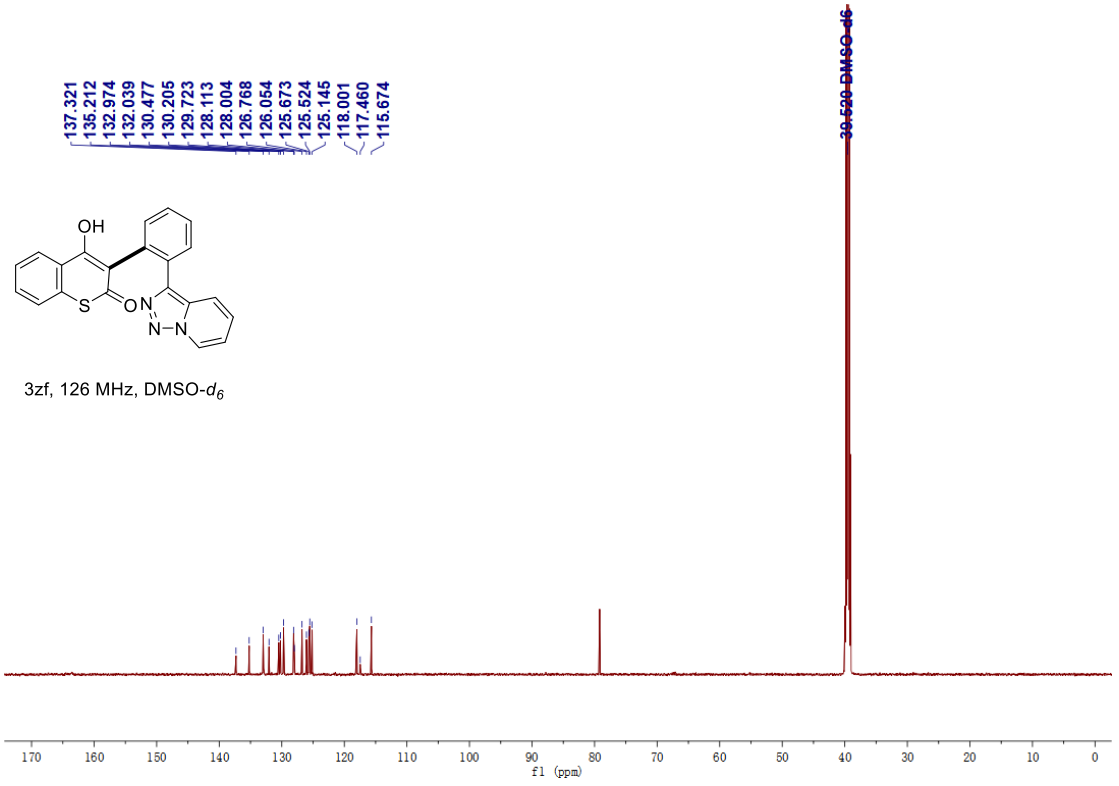


3ze, 500 MHz, DMSO-d_6

3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-2H-thiochromen-2-one (3zf)



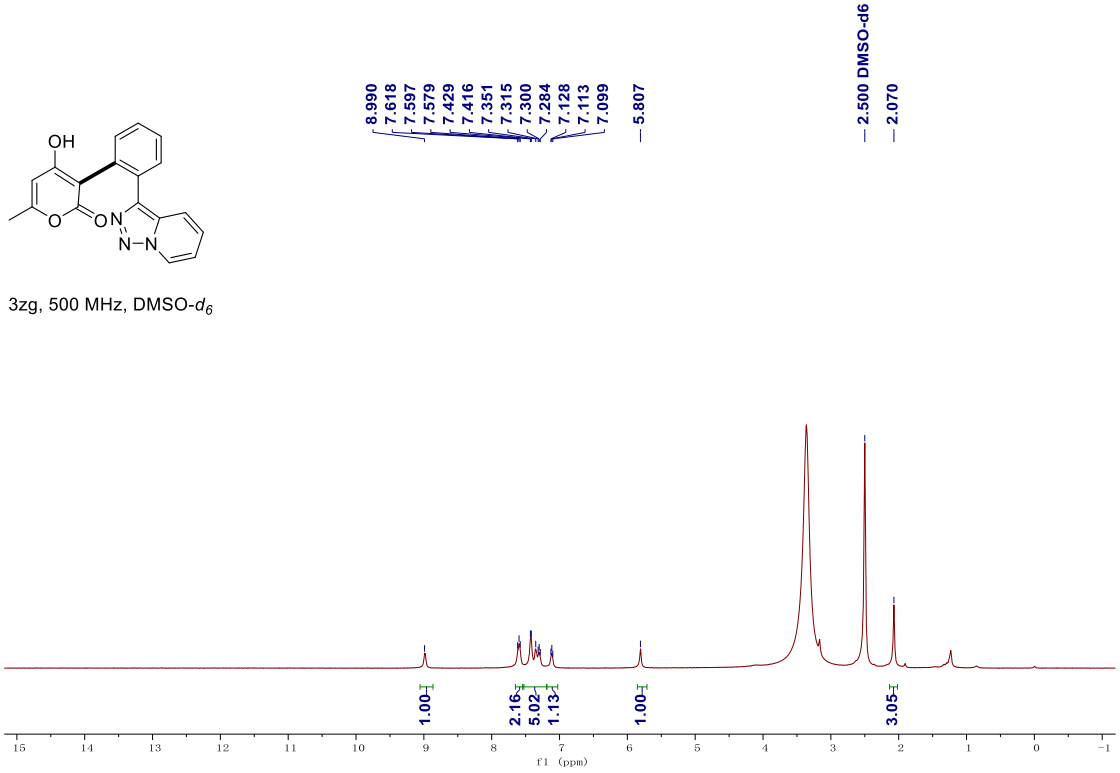
3zf, 500 MHz, DMSO-d_6



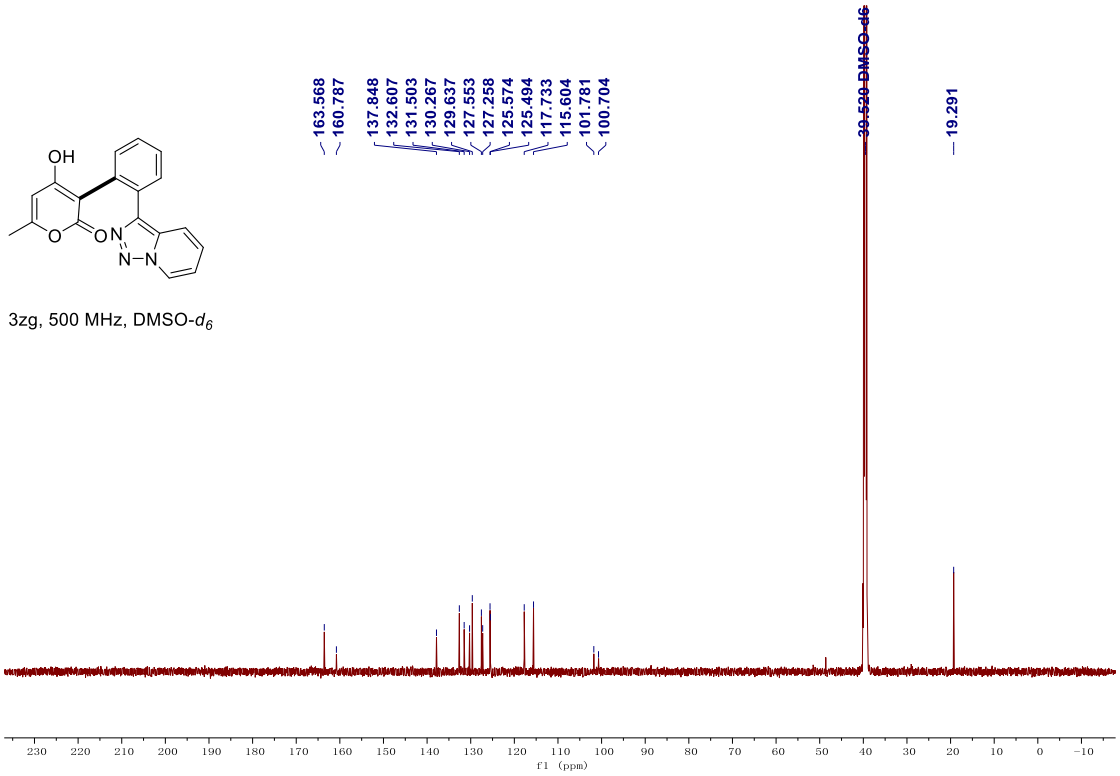
3zf, 126 MHz, DMSO-d_6

3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-6-methyl-2H-pyran-2-one (3zg)

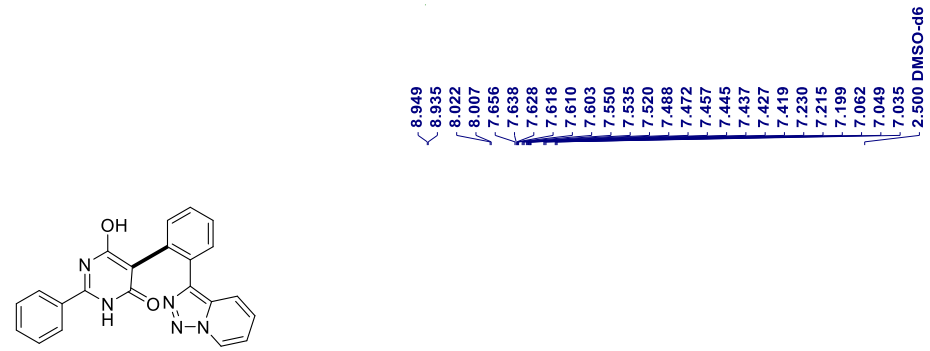
3zg, 500 MHz, DMSO-d_6



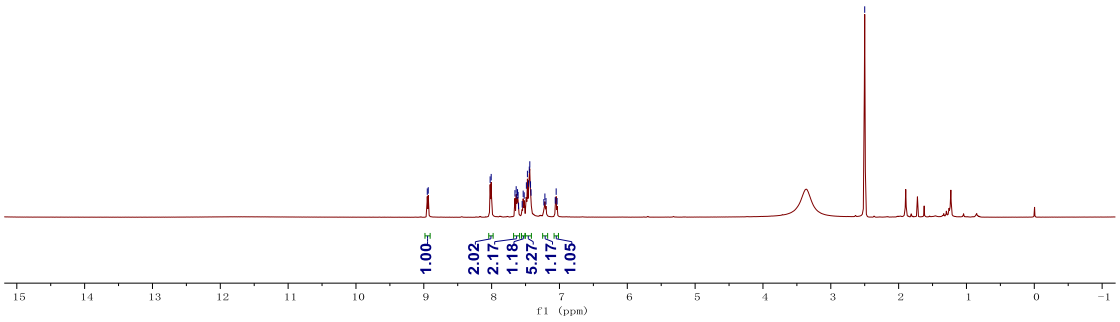
3zg, 500 MHz, DMSO-d_6



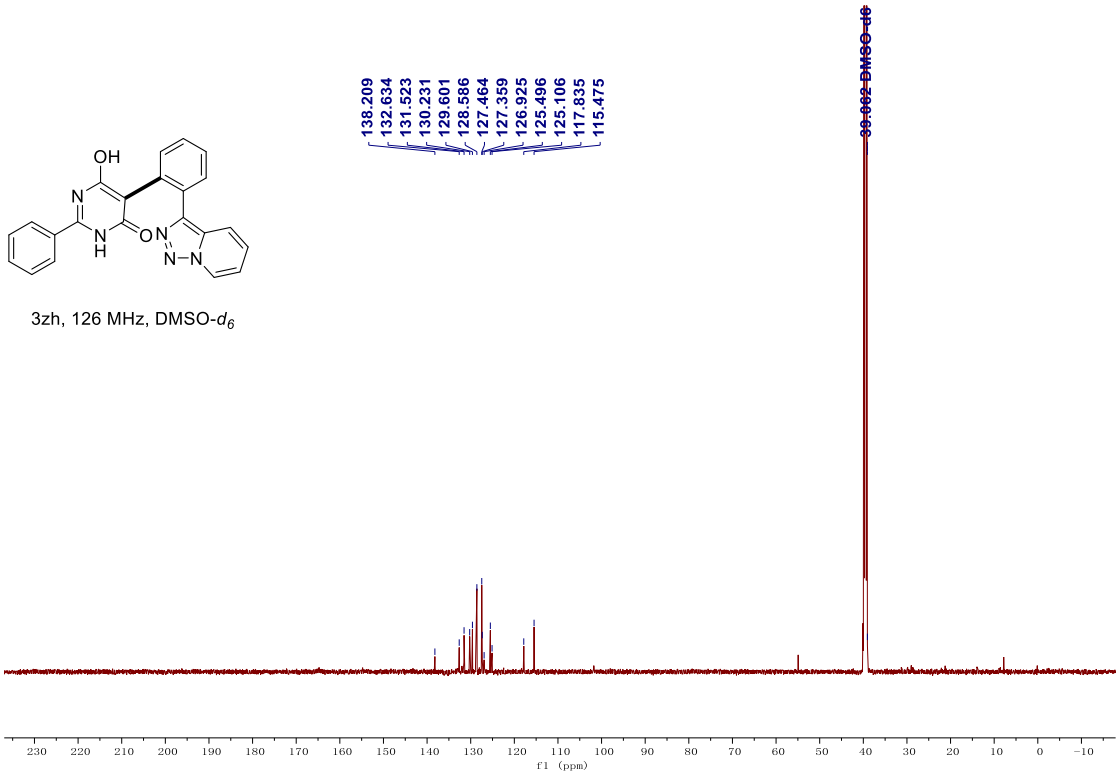
5-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-6-hydroxy-2-phenylpyrimidin-4(3H)-one (3zh)



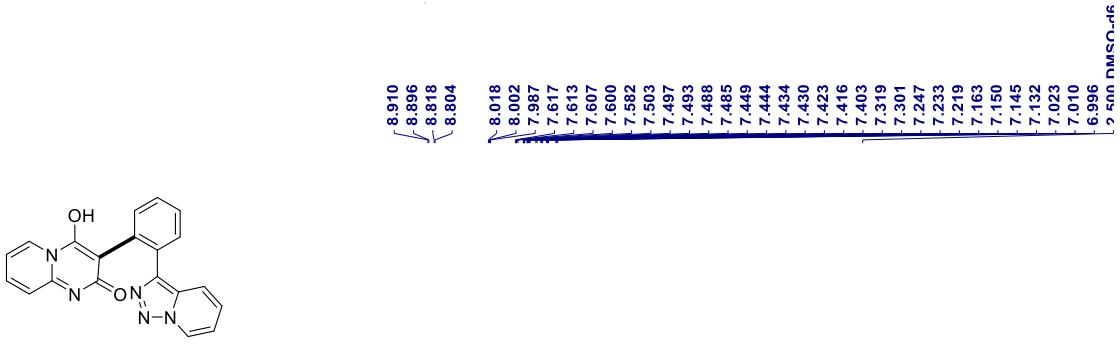
3zh, 500 MHz, DMSO-d_6



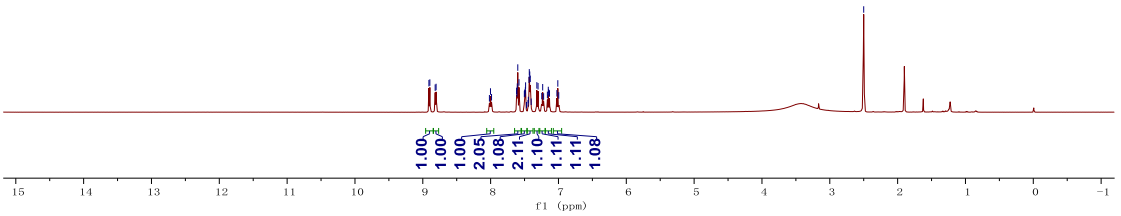
3zh, 126 MHz, DMSO-d_6

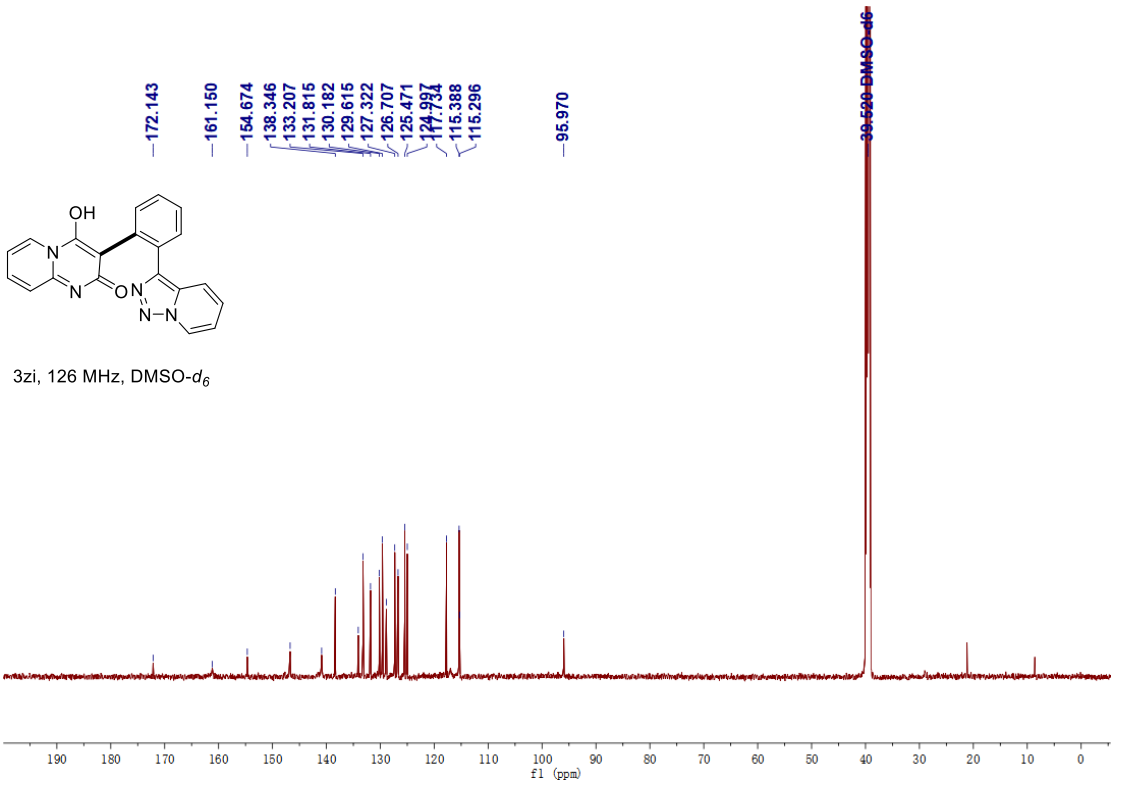


3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-hydroxy-2H-pyrido[1,2-a]pyrimidin-2-one (3zi)



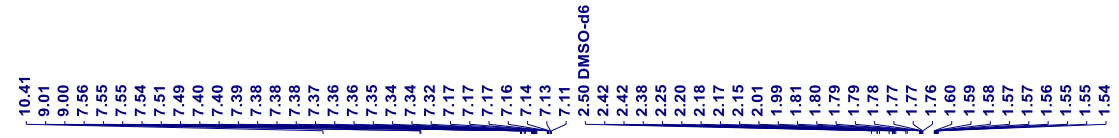
3zi, 500 MHz, DMSO-d_6

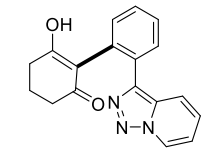




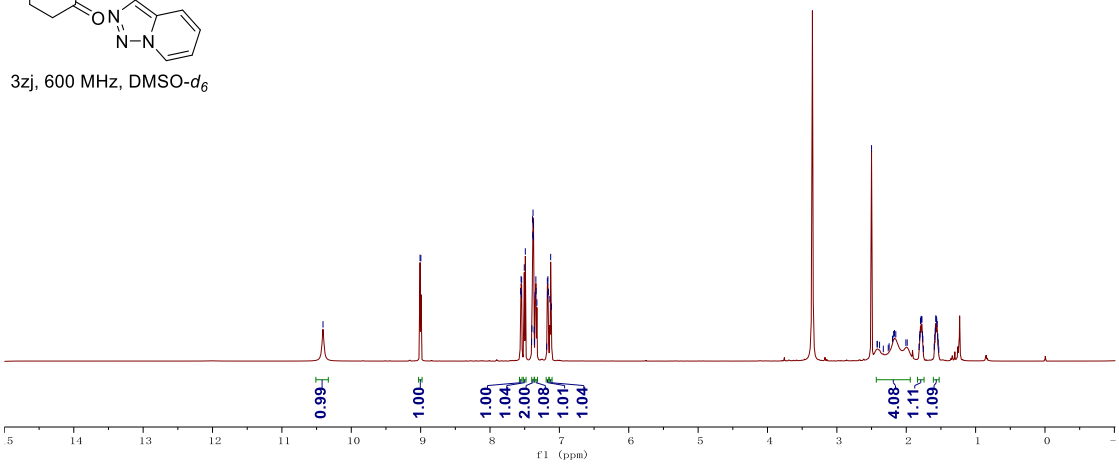
3zi, 126 MHz, DMSO-d_6

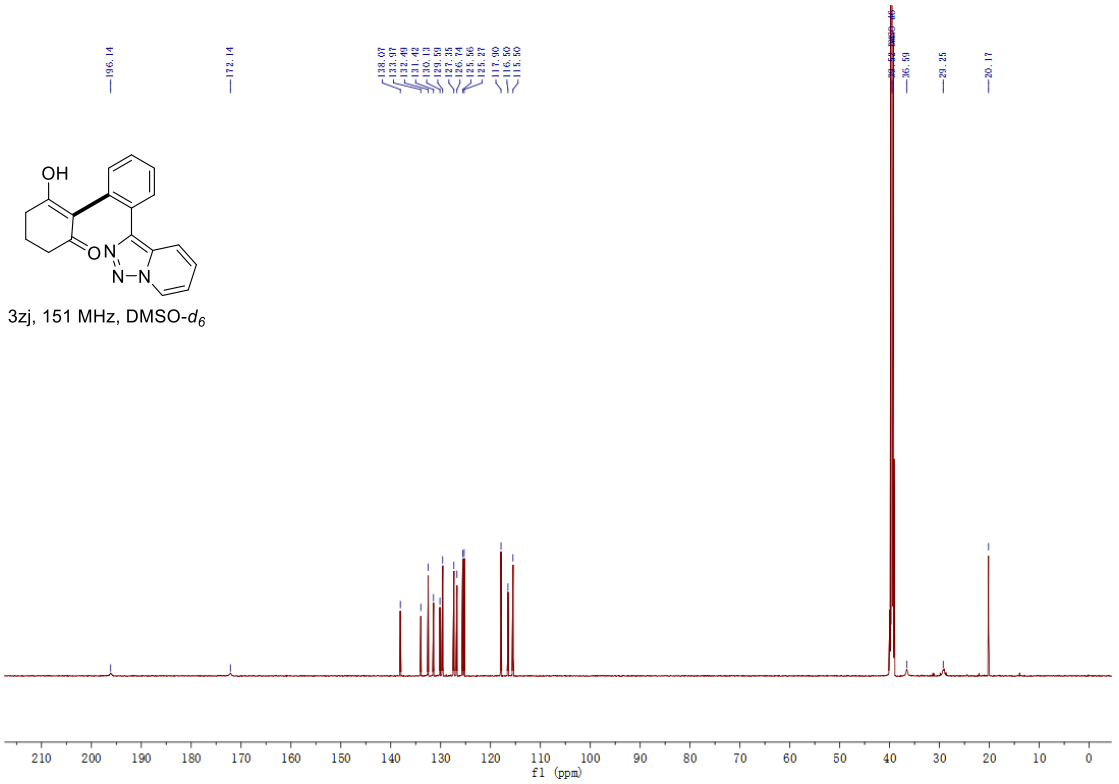
2'-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-6-hydroxy-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (3zj)





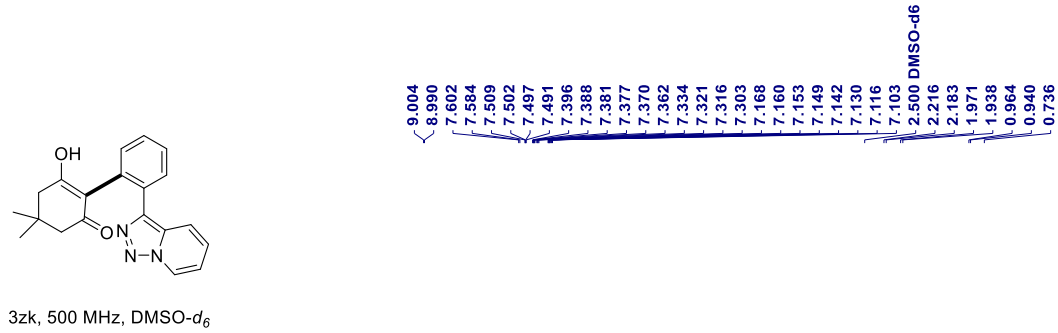
3zj, 600 MHz, DMSO-d_6



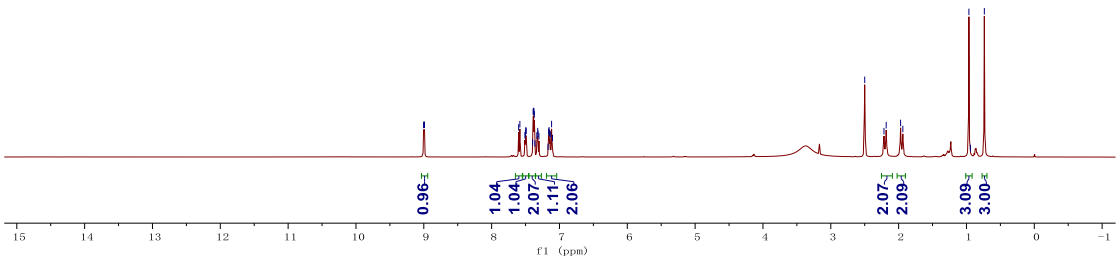


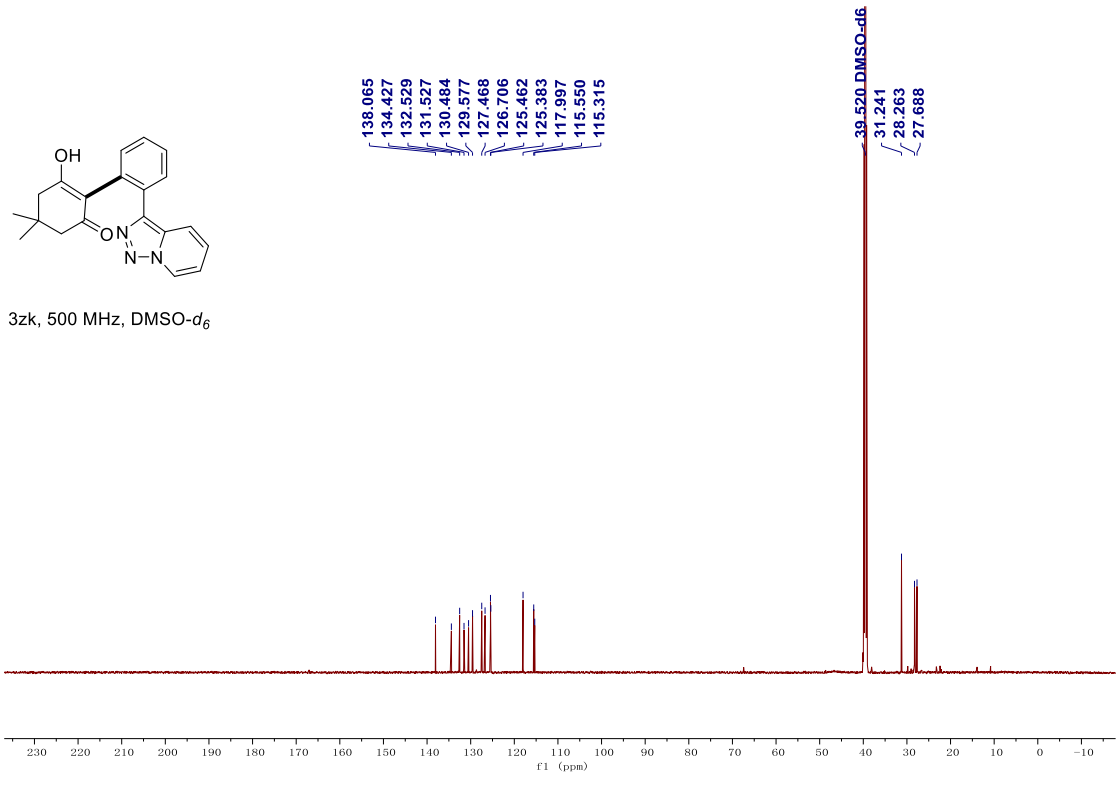
3zj, 151 MHz, DMSO-d_6

2'-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-6-hydroxy-4,4-dimethyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (3zk)



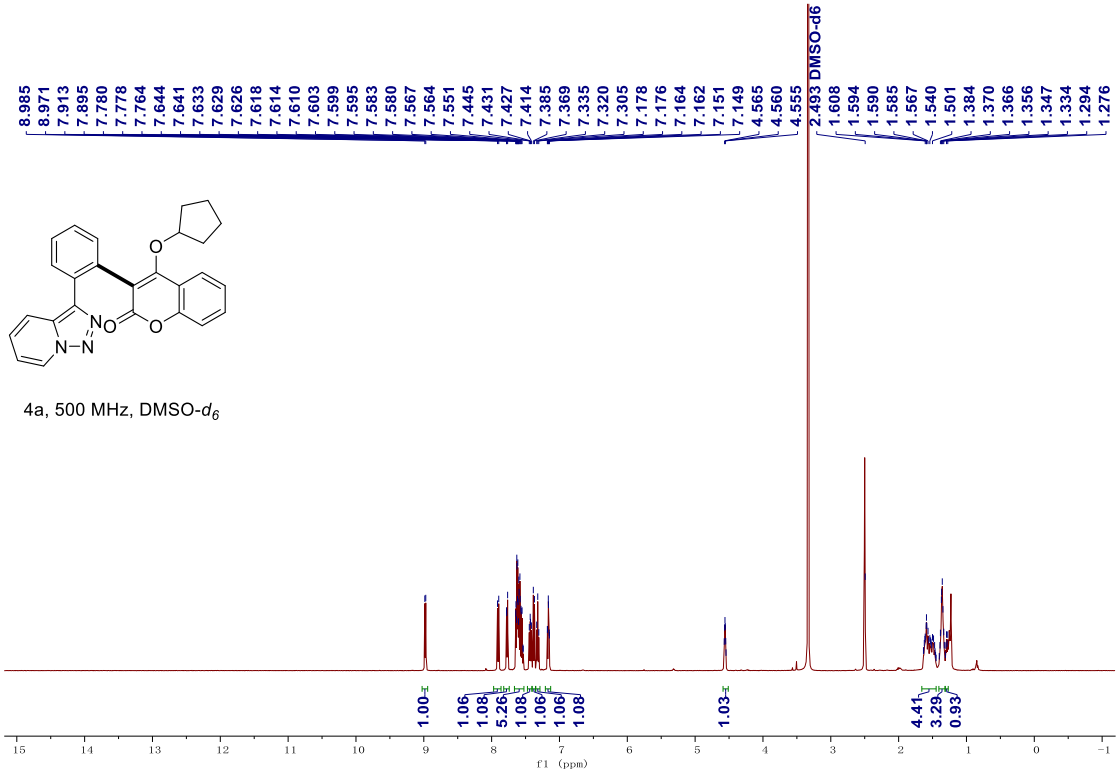
3zk, 500 MHz, DMSO-d_6



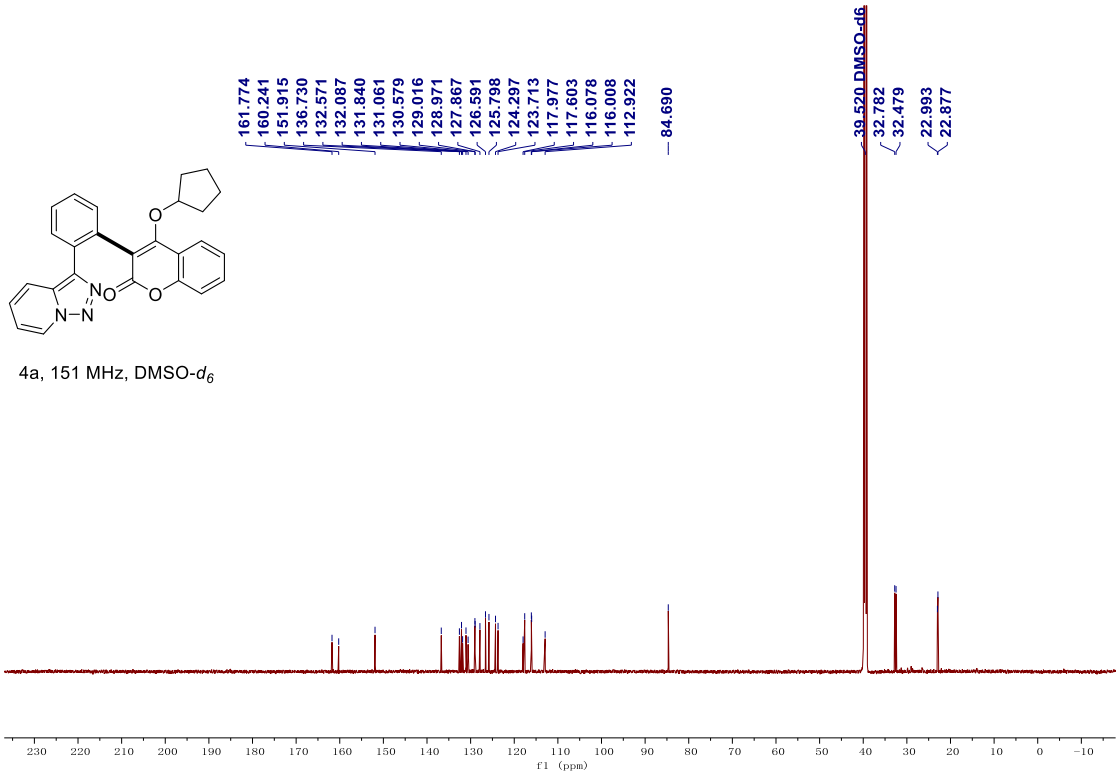


3zk, 500 MHz, DMSO-d_6

3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)phenyl)-4-(cyclopentyloxy)-2H-chromen-2-one (4a)

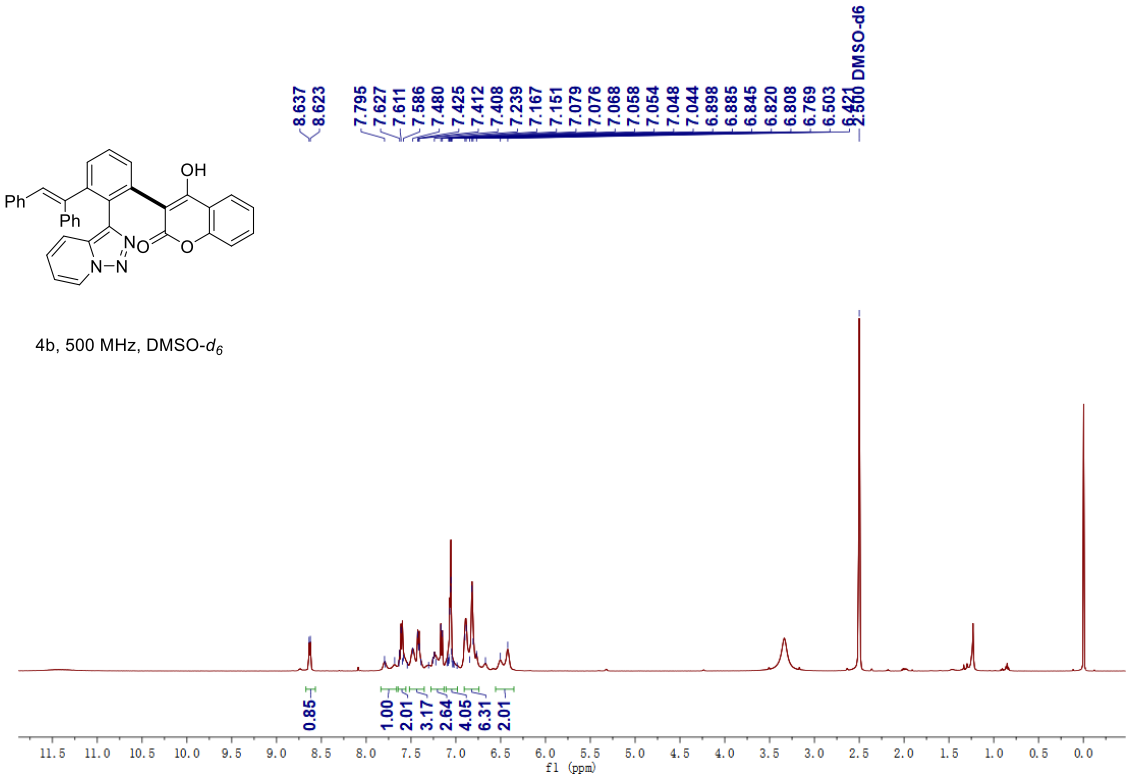


4a, 500 MHz, DMSO-d_6

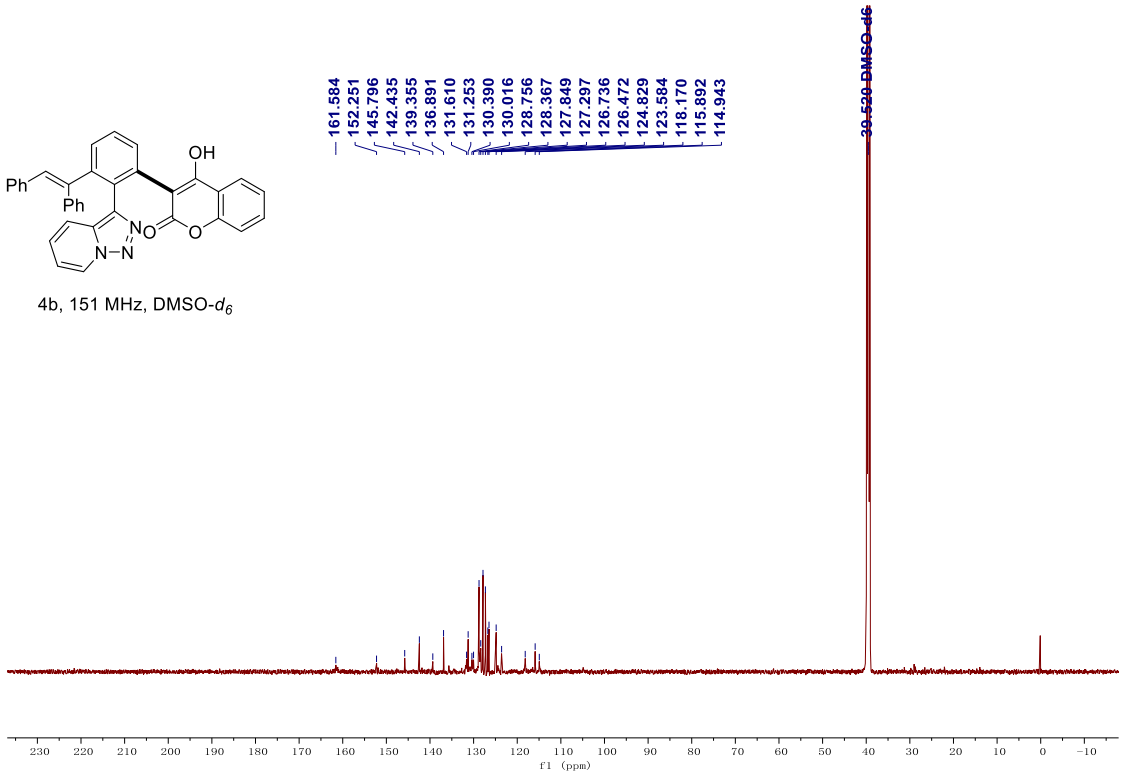


4a, 151 MHz, DMSO-d_6

(E)-3-(2-([1,2,3]triazolo[1,5-a]pyridin-3-yl)-3-(1,2-diphenylvinyl)phenyl)-4-hydroxy-2H-chromen-2-one (4b)



4b, 500 MHz, DMSO-d_6



4b, 151 MHz, DMSO-d_6