Supporting Information

Rhodium(III)-Catalyzed Cascade Reactions of Benzoic Acids with Dioxazolones: Discovery of 2,5-Substitued Benzoxazinones as AIE Molecules

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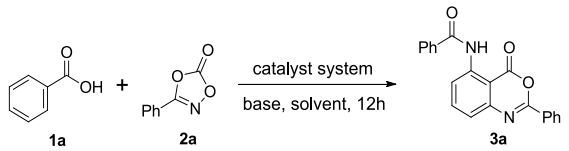
1. General Information

Catalytic reactions were carried out in Schlenk tubes using pre-dried glassware. 1,4,2-Dioxazol-5-ones **2a-l** were prepared according to previously described procedures (Xiong, H. *et. al.* Org. Chem. Front. **2018**, *5*, 2880–2284). Other chemicals were obtained from commercial sources and used without further purification. Column chromatography purifications were performed using 200–300 mesh silica gel. Melting points were determined with a SGW X-4 digital melting point apparatus, and the thermometer was uncorrected. NMR spectra were mostly recorded for ^{1}H NMR at 500 MHz, for ^{13}C NMR at 125 MHz and for ^{19}F NMR at 471 MHz. $CDCl_3$ and d_6-DMSO was used as solvent. Chemical shifts were referenced relative to residual solvent signal ($CDCl_3$, ^{1}H NMR: δ 7.26 ppm, ^{13}C NMR: δ 77.16 ppm; d_6-DMSO, ^{1}H NMR: δ 2.50 ppm, ^{13}C NMR: δ 39.99 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Bruker Vector 22 infrared spectrometer and reported in cm^{-1}. HRMS were performed on Agilent Technologies 6224 TOF LC/MS apparatus (ESI). UV-Visible absorption spectra were measured using Shimadzu UV-1800 spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5301PC spectrometer with a slit width 3 nm for emission. The water/THF mixtures with different water fractions were prepared by slowly adding distilled water into the THF solution of samples under ultrasound at room temperature. Fluorescence quantum yields of compounds in solution and in powders were measured on Absolutely Photoluminescence Quantum Yield Measurement System (HAMAMARSU, C11347-11Quantaurus-QY).

2. Optimization of Reaction Conditions

We embarked on our study with the optimization of reaction conditions first, using benzoic acid **1a** and 1,4,2-dioxazolone **2a** as the model substrates (Table S1). The reaction afforded no product with $[Cp^*RhCl_2]_2$ as the catalyst and NaOAc as the base in THF at 120 °C (entry 1). However, an addition of 15% $AgSbF_6$ altered the result and led to the formation of desired product **3a** in 40% isolated yield (entry 2), indicating the crucial role $AgSbF_6$ played as a halogen scavenger additive in this reaction. Next, we screened various solvents and found that THF was the most favorable among all to give desired product in good yield (entries 2–5). Several base candidates were then surveyed for the reaction and the uniformly decreased amount of products (entries 6–8) indicated NaOAc is the base of choice. Lowering temperature from 120 °C to 50 °C led to a continuous reduction of the product turnover (entries 9–10). Meanwhile, significant improvement in reaction yield (48%, entry 11) was observed when the concentration of $AgSbF_6$ was increased from 15% to 30%, although further densifying $AgSbF_6$ only resulted in a slight additional increase of the yield (50%, entry 12). In the presence of 30% $AgSbF_6$, we examined the base ratio and found that increasing the molarity of NaOAc from 0.1 to 0.2 mmol accelerated the reaction to afford more products (entries 13 and 14). However, further addition of NaOAc (0.4 mmol, entry 15) completely depleted the product. On the other hand, decreasing the amount of 1,4,2-dioxazolone **2a** by half afforded less product **3a** (42%, entry 16). Based on these results, we were able to determine the optimal reaction conditions as shown by entry 14.

Table S1. Optimization of Reaction Conditions[a]



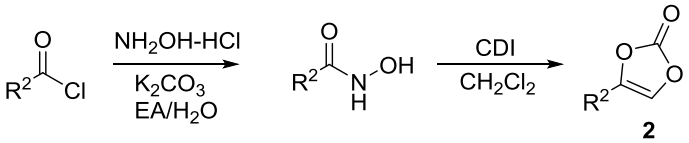
entry	catalyst system	base	solvent	yield[b]
1	$[RhCp^*Cl_2]_2$	NaOAc	THF	0%
2	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	THF	40%
3	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	MeOH	0%
4	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	DCE	18%
5	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	DMF	27%
6	$[RhCp^*Cl_2]_2/AgSbF_6$	$Cu(OAc)_2$	THF	16%
7	$[RhCp^*Cl_2]_2/AgSbF_6$	K_2CO_3	THF	22%
8	$[RhCp^*Cl_2]_2/AgSbF_6$	Et_3N	THF	0%
9[c]	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	THF	38%
10[d]	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	THF	25%
11[e]	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	THF	48%
12[f]	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	THF	50%
13[g]	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	THF	53%
14[h]	**$[RhCp^*Cl_2]_2/AgSbF_6$**	**NaOAc**	**THF**	**60%**
15[i]	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	THF	0%
16[j]	$[RhCp^*Cl_2]_2/AgSbF_6$	NaOAc	THF	42%

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), cat (5 mol%), $AgSbF_6$ (15 mol%), base (0.04 mmol), solvent (2 mL), 120 °C, 12 h. [b]Isolated yields calculated by dioxazolones **2**. [c]80 °C. [d]50 °C. [e]$AgSbF_6$ (30 mol%). [f]$AgSbF_6$ (45 mol%). [g]$AgSbF_6$ (30 mol%), NaOAc (0.1 mmol). [h]$AgSbF_6$ (30 mol%), NaOAc (0.2 mmol). [i]$AgSbF_6$ (30 mol%), NaOAc (0.4 mmol). [j]**2a** (0.1 mmol).

3. General Procedure for the Synthesis and Characterization

3.1 General procedure for the synthesis of 3-substituted-1,4,2-dioxazol-5-ones (2)

3-Substituted-1,4,2-dioxazol-5-ones **2** were prepared according to the methods given in the cited references (Xiong, H. *et. al.* Org. Chem. Front. **2018**, *5*, 2880–2284).



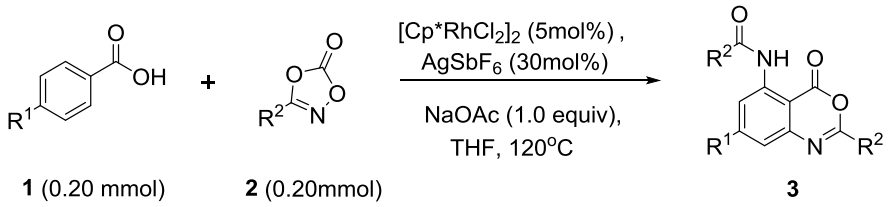
2

A flask was charged with hydroxylamine hydrochloride (1 equivalent), potassium carbonate (1 equivalent) and solvent (EA/H_2O, 7:1). The reaction was cooled to 0 °C with vigorous stirring and

substituted acyl chloride (1 equivalent) was added dropwise. The reaction was stirred overnight, diluted with water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The crude hydroxamic acid product was purified by recrystallization from EtOAc/Pentane.

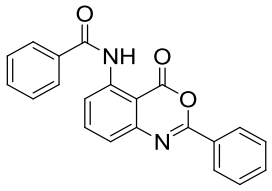
To a slurry of hydroxamic acid (1 equivalent) in dichloromethane was added carbonyl diimidazole (CDI, 1.5 equivalents). The reaction was stirred for 30 minutes, diluted with 1M aqueous HCl and extracted with dichloromethane. The combined organic layers were dried over sodium sulfate, and concentrated *in vacuo* to give dioxazolone **2**. Purification by dissolving in toluene and filtration was performed in necessary.

3.2 General procedure for the synthesis of desired product 3



Benzoic acid **1** (0.20 mmol), 1,4,2-dioxazol-5-one **2** (0.20 mmol), NaOAc (17 mg, 0.20 mmol), $AgSbF_6$ (20 mg, 0.06 mmol) and $[Cp^*RhCl_2]_2$ (6 mg, 0.010 mmol) were placed into a 10 mL sealing tube. THF (2.0 mL) was then introduced and the reaction mixture was stirred at 120 °C for 12 h. After cooling to ambient temperature, a saturated $NaHCO_3$ solution was added to the reaction and the mixture was extracted three times with $CHCl_3$ followed by washing with water and saturated brine. Then it was concentrated under vacuum and the residue was loaded onto silica gel and purified by flash column chromatography (petroleum ether/chloroform/EtOAc) to afford the desired product **3**.

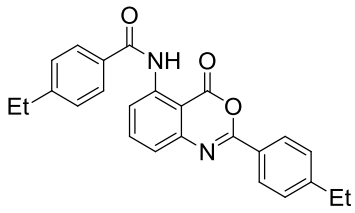
3.3 Characterization data of 3



***N*-(4-Oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3a)**

Compound **3a** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 60% yield (20.5 mg). Mp: 200.5−201.4 °C.

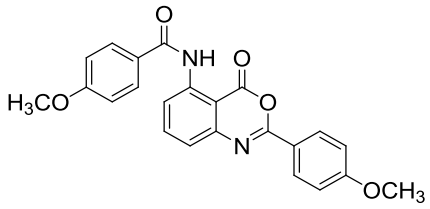
^{1}H NMR (500 MHz, $CDCl_3$): δ 12.00 (1H, s), 8.97 (1H, dd, J = 8.0, 1.0 Hz), 8.27 (2H, m), 8.07 (2H, m), 7.82 (1H, t, J = 8.0 Hz), 7.57 (2H, m), 7.52 (4H, m), 7.37 (1H, dd, J = 8.0, 1.0 Hz); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 165.9, 162.1, 156.2, 147.5, 141.5, 138.2, 134.2, 132.9, 132.4, 129.6, 128.9, 128.8, 128.3, 127.5, 121.4, 118.5, 104.1; **IR (KBr)**: 3303.0, 1726.1, 1678.2, 1645.6, 1625.0, 1572.0, 1542.0, 1294.0, 1261.3, 1181.6, 1127.5 cm^{-1}; **HRMS (ESI)** *m/z* calcd for $C_{21}H_{14}N_2O_3$ $[M+H]^+$ 343.1083, found 343.1082.



4-Ethyl-*N*-(2-(4-ethylphenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3b)

Compound **3b** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 68% yield (27.3 mg). Mp: 185.5−186.7 °C.

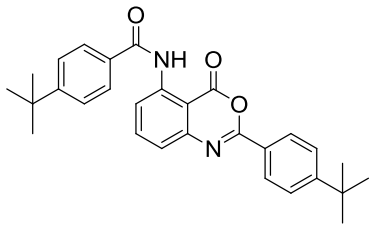
^{1}H NMR (500 MHz, $CDCl_3$): δ 11.94 (1H, s), 8.89 (1H, dd, J = 8.5, 1.0 Hz), 8.13 (2H, d, J = 8.5 Hz), 7.94 (2H, d, J = 8.5 Hz), 7.56 (1H, t, J = 7.5 Hz), 7.29 (5H, m), 2.67 (4H, q, J = 7.5 Hz), 1.22 (6H, t, J = 8.0 Hz); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 165.2, 161.5, 155.6, 149.2, 148.4, 144.9, 142.0, 141.1, 137.4, 130.9, 127.7, 126.9, 126.2, 120.4, 117.4, 103.2, 28.2, 28.1, 12.5, 14.4; **IR (KBr)**: 3295.2, 2964.4, 1705.5, 1684.0, 1607.0, 1578.2, 1542.1, 1508.9, 1297.3, 1262.0, 1181.6, 1122.3; **HRMS (ESI)** *m/z* calcd for $C_{25}H_{22}N_2O_5$ $[M+H]^+$ 399.1709, found 399.1704.



4-Methoxy-*N*-(2-(4-methoxyphenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3c)

Compound **3c** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 72% yield (29.0 mg). Mp: 182.8−183.6 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.96 (1H, s), 8.93 (1H, d, J = 8.5 Hz), 8.24 (2H, d, J = 9.0 Hz), 8.06 (2H, d, J = 9.0 Hz), 7.81 (1H, t, J = 8.0 Hz), 7.34 (1H, d, J = 8.0 Hz), 7.02 (4H, m); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 165.5, 163.5, 163.9, 162.4, 156.2, 147.9, 142.0, 138.2, 130.3, 129.5, 126.6, 121.9, 120.8, 117.9, 114.3, 114.2, 103.7, 55.6, 55.5; **IR (KBr)**: 3307.6, 2923.6, 2850.9, 1716.1, 1680.8, 1602.4, 1569.7, 1541.4, 1507.7, 1293.4, 1268.9, 1110.4, 1180.6 cm^{-1}; **HRMS (ESI)** *m/z* calcd for $C_{23}H_{18}N_2O_5$ $[M+H]^+$ 403.1294, found 403.1290.

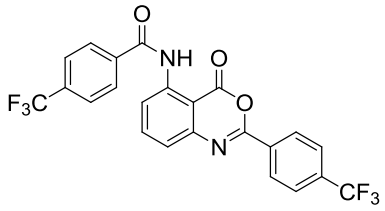


4-(tert-Butyl)-*N*-(2-(4-(tert-butyl)phenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3d)

Compound **3d** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 63% yield (28.6mg). Mp: 219.7−220.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 12.02 (1H, s), 8.97 (1H, dd, J = 8.0, 1.0 Hz), 8.22(2H, d, J = 7.5, 2.0 Hz), 8.03 (2H, d, J = 8.5, 2.0 Hz), 7.83 (1H, t, J = 8.5 Hz), 7.56 (2H, d, J = 5.5 Hz), 7.545 (2H, d, J = 5.5 Hz); 7.39 (1H, dd, J = 8.0, 0.5 Hz)**^{13}C NMR (125 MHz, $CDCl_3$):**166.0, 162.3, 156.8,

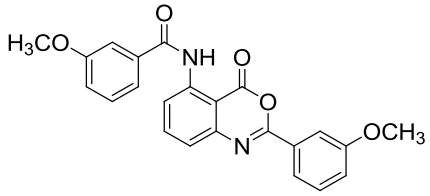
156.4, 156.0, 147.7, 141.9, 138.1, 131.4, 128.2, 127.4, 126.8, 125.9, 125.9, 121.2, 118.2, 104.0, 35.2, 35.1, 31.2, 31.1. **IR (KBr)**: 3305.3, 2918.3, 2854.8, 1714.6, 1672.4, 1611.1, 1568.1, 1509.6, 1292.3, 1266.0, 1180.5, 1121.7 cm^{-1}; **HRMS (ESI)** m/z calcd for $C_{29}H_{30}N_2O_3$ $[M+H]^+$ 455.2335, found 455.2331.



***N*-(4-Oxo-2-(4-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]oxazin-5-yl)-4-(trifluoromethyl)benzamide (3e)**

Compound **3e** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 47% yield (22.5 mg). Mp: 197.4−198.2 °C.

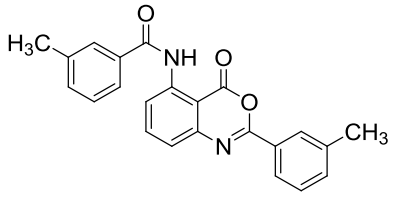
^{1}H NMR (500 MHz, $CDCl_3$): δ 12.04 (1H, s), 9.00 (1H, dd, J = 8.5, 1.0 Hz), 8.42 (2H, d, J = 8.5 Hz), 8.19 (2H, d, J = 8.5 Hz), 7.90 (1H, t, J = 8.0 Hz), 7.81 (4H, t, J = 8.0 Hz), 7.47 (1H, dd, J = 8.0, 1.0 Hz), **^{13}C NMR (125 MHz, $CDCl_3$):** δ 164.5, 161.8, 154.9, 147.1, 141.4, 138.5, 137.3, 134.3(q, $^2J_{C\text{-}F}$ = 38.8HZ), 134.1(q, $^2J_{C\text{-}F}$ = 38.8HZ), 132.8, 128.6, 127.9, 126.0(q, $^3J_{C\text{-}F}$ = 3.6HZ), 125.9(q, $^3J_{C\text{-}F}$ = 3.7HZ), 124.7(q, $^1J_{C\text{-}F}$ = 270.9HZ), 122.5(q, $^1J_{C\text{-}F}$ = 271.1HZ), 121.1, 118.2, 103.2; **^{19}F NMR (471 MHz, $CDCl_3$):** δ −63.02 (3F, s), −63.10 (3F, s); **IR (KBr)**: 3297.6, 2961.8, 2924.1, 1720.7, 1694.1, 1606.3, 1574.8, 1541.4, 1294.7, 1261.9, 1170.8, 1113.8; **HRMS (ESI)** m/z calcd for $C_{23}H_{13}F_6N_2O_3$ $[M+H]+$ 479.0830, found 479.0835.



3-Methoxy-*N*-(2-(4-methoxyphenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3f)

Compound **3f** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 62% yield (24.9 mg). Mp: 190.3−191.1 °C.

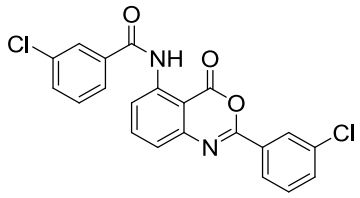
^{1}H NMR (500 MHz, $CDCl_3$): δ 12.01 (1H, s), 8.97 (1H, dd, J = 8.5, 1.0 Hz), 7.89 (1H, m), 7.85 (1H, t, J = 8.0 Hz), 7.80 (1H, m), 7.65 (1H, m), 7.63 (1H, m), 7.42 (3H, m), 7.12 (2H, m),3.92 (3H, s), 3.91 (3H, s,) ; **^{13}C NMR (125 MHz, $CDCl_3$):** δ 165.8, 162.1, 160.1, 160.1, 156.1, 157.5, 141.8, 141.7, 138.2, 135.7, 130.9, 130.0, 129.9, 121.5, 120.9, 119.6, 119.4, 119.0, 118.5, 112.6, 112.4, 104.1, 55.6, 55.5; **IR (KBr)**: 3302.4, 2923.9, 2850.7, 1716.2, 1682.2, 1603.1, 1573.1, 1541.3, 1294.8, 1261.8; **HRMS (ESI)** m/z calcd for $C_{23}H_{18}N_2O_5$ $[M+H]^+$ 403.1294, found 403.1297.



3-Methyl-*N*-(4-oxo-2-(p-tolyl)-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3g)

Compound **3g** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 64% yield (23.7mg). Mp: 194.4−195.6 °C.

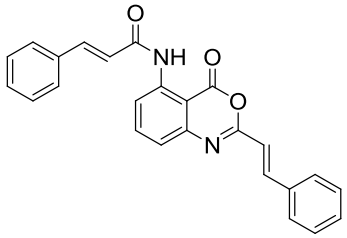
^{1}H NMR (500 MHz, $CDCl_3$): δ 11.99 (1H, s), 8.97 (1H, dd, J = 8.5, 1.0 Hz), 8.11 (1H, s), 8.09(1H, m), 7.89 (2H, m), 7.84 (1H, t, J = 8.5 Hz), 7.41 (5H, m), 2.47 (3H, s), 2.46 (3H, s); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 166.2, 162.3, 156.5, 147.6, 141.8, 138.9, 138.8, 138.3, 134.3, 133.8, 133.3, 129.6, 128.9, 128.9, 128.8, 128.3, 125.6, 124.6, 121.4, 118.6, 104.2, 21.6, 21.5; **IR (KBr)**: 3304.2, 2954.8, 2853.9, 1703.5, 1683.3, 1606.9, 1573.6, 1539.9, 1297.9, 1271.3, 1171.3, 1119.0; **HRMS (ESI)** m/z calcd for $C_{23}H_{18}N_2O_3$ $[M+H]^+$ 371.1396, found 371.1382.



3-Chloro-*N*-(2-(4-chlorophenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3h)

Compound **3h** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 47% yield (19.3 mg). Mp: 202.3−203.1 °C.

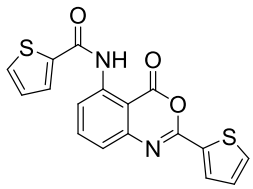
^{1}H NMR (500 MHz, $CDCl_3$): δ 11.91 (1H, s), 8.92 (1H, dd, J = 8.5, 0.5 Hz), 8.25 (1H, t, J = 1.5 Hz), 8.18 (1H, m), 8.04 (1H, t, J = 1.5 Hz), 7.92 (1H,m), 7.83 (1H, t, J = 8.0 Hz), 7.53 (2H, m), 7.45 (2H, m), 7.39 (1H, dd, J = 8.0, 1.0 Hz) ; **^{13}C NMR (125 MHz, $CDCl_3$):** δ 163.4, 160.8, 154.0., 146.2, 140.5, 137.4, 134.9, 134.4, 134.2, 131.9, 131.5, 130.3, 129.2, 129.1, 127.4, 127.1, 125.3, 124.2, 120.8, 117.9, 103.1; **IR (KBr)**: 3275.3, 1715.0, 1676.9, 1625.4, 1609.2, 1576.5, 1540.7,1298.2,1260.0,1176.3,1103.3,1075.6 **HRMS (ESI)** m/z calcd for $C_{21}H_{12}Cl_2N_2O_3$ $[M+H]^+$ 411.0303, found 411.0306.



***N*-(4-Oxo-2-((E)-styryl)-4H-benzo[d][1,3]oxazin-5-yl)cinnamamide (3i)**

Compound **3i** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 60% yield (28.3 mg). Mp: 210.5−211.2 °C.

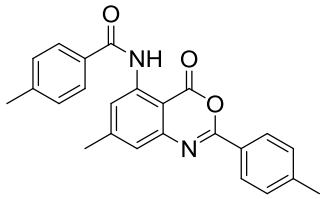
^{1}H NMR (500 MHz, $CDCl_3$): δ 11.26 (1H, s), 8.87 (1H, dd, J = 8.5, 0.5 Hz), 7.82 (1H, d, J = 16.5 Hz), 7.77 (2H, m), 7.57 (4H,m), 7.40 (6H,m), 7.28 (1H, d, J = 1.0 Hz), 4.76 (1H, d, J = 16Hz), 6.63 (1H, d, J = 15.5Hz); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 164.7, 161.5, 156.5, 147.5, 143.1, 142.5, 141.8, 138.0, 134.5, 134.4, 128.4, 130.5, 130.2, 129.1, 128.9, 128.2, 128.1, 121.4, 121.0, 118.6, 118.2,103.6; **IR (KBr)**: 3283.7, 1721.0, 1686.4, 1628.9, 1601.3, 1569.1, 1530.6, 1278.1, 1199.5, 1158.6, 760.3, 722.8; **HRMS (ESI)** m/z calcd for $C_{25}H_{19}N_2O_3$ $[M+H]^+$ 395.1396, found 395.1392.



***N*-(4-Oxo-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazin-5-yl)thiophene-2-carboxamide (3j)**

Compound **3j** was prepared according to the **2.2** and was purified on silica gel to give a yellow solid in 64% yield (16.3mg). Mp: 189.4−190.2 °C.

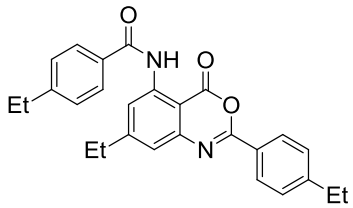
^{1}H NMR (500 MHz, $CDCl_3$): δ 11.87 (1H, s), 8.81 (1H, dd, J = 8.5, 1.0 Hz), 7.93 (1H, dd, J = 4.0, 1.5 Hz), 7.81 (1H, dd, J = 4.0, 1.0 Hz),7.77 (1H, t, J = 8.0 Hz s), 7.62 (1H, dd, J = 5.0, 1.5 Hz), 7.61 (1H, dd, J = 5.0, 1.5 Hz), 7.29 (1H, dd, J = 8.0, 1.0 Hz), 7.16 (2H, m); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 161.6, 160.5, 152.8, 147.6, 141.6, 139.7, 138.3, 133.5, 132.9, 132.0, 132.0, 129.0, 128.4, 128.1, 121.0, 118.1, 103.5; **IR (KBr)**: 3350.5, 1720.5, 1673.2, 1625.7, 1604.6, 1578.3, 1543.5, 1269.1, 1219.2, 1117.1, 1079.2; **HRMS (ESI)** m/z calcd for $C_{17}H_{10}N_2O_3S_2$ $[M+H]^+$ 355.0221, found 355.0225.



4-Methyl-*N*-(4-oxo-2-(p-tolyl)-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3k)

Compound **3k** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 58% yield (22.2 mg). Mp: 196.2−196.8 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.95 (1H, s), 8.81 (1H, d, J = 0.5 Hz), 8.15 (2H, d, J = 8.5 Hz), 7.97 (2H, d, J = 8.0 Hz), 7.32 (4H, m), 7.18 (1H, d, J = 1.0 Hz), 2.52 (3H, s), 2.44 (6H, s); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 165.9, 162.1, 156.5, 150.2, 147.5, 143.6, 143.0, 141.5, 131.5, 129.6, 129.6, 128.3, 127.5, 127.0, 121.6, 119.1, 101.7, 22.8, 21.8, 21.6; **IR (KBr)**: 2956.2, 2869.6, 1714.1, 1688.8, 1673.0, 1610.8, 1569.1, 1292.6, 1265.3, 1181.5, 1149.6; **HRMS (ESI)** *m/z* calcd for $C_{24}H_{20}N_2O_3$ $[M+H]^+$ 385.1552, found 385.1557.

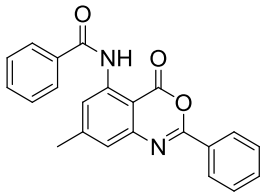


4-Ethyl-*N*-(7-ethyl-2-(4-ethylphenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3l)

Compound **3l** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 49% yield (20.8 mg). Mp: 194.4−195.3 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.99 (1H, s), 8.87 (1H, d, J = 1.0 Hz), 8.21 (2H, d, J = 8.0 Hz), 7.36 (4H, m), 7.25 (1H,s), 2.83 (2H, q, J = 2.5 Hz), 2.75 (4H, q, J = 2.5 Hz), 1.36 (3H, t, J = 2.5 Hz), 1.29 (6H, t, J = 2.5 Hz); **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.0, 162.2, 156.5, 156.2, 149.8, 149.1, 147.7, 141.7, 131.8, 128.4, 128.4, 128.4, 127.6, 127.2, 120.4, 118.2, 101.8, 29.9, 29.0, 28.9,

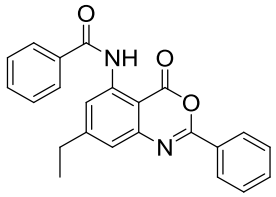
15.3, 15.2, 14.8; **IR (KBr)**: 3306.9, 2958.3, 2869.8, 1733.4, 1702.7, 1688.7, 1611.3, 1567.3, 1540.5, 1508.2, 1283.7, 1262.6, 1183.8, 1138.6; **HRMS (ESI)** m/z calcd for $C_{27}H_{27}N_2O_3$ $[M+H]^+$ 427.2022, found 427.2021.



***N*-(7-Methyl-4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3m)**

Compound **3m** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 80% yield (28.5 mg). Mp: 196.7−197.6 °C.

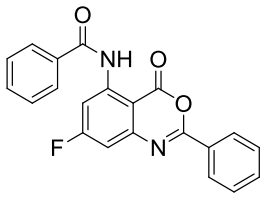
^{1}H NMR (500 MHz, $CDCl_3$): δ 11.98 (1H, s), 8.83 (1H, s), 8.26 (2H, m), 8.07 (2H, m), 7.57 (2H, m), 7.52 (4H, m), 7.22 (1H, s), 2.53 (3H, s); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 166.0, 162.1, 156.4, 150.3, 147.4, 141.5, 134.3, 132.9, 132.4, 129.8, 128.9, 128.4, 127.5, 122.0, 119.4, 101.8, 22.9; **IR (KBr)**: 3304.7, 2923.3, 2853.3, 1715.6, 1673.9, 1612.8, 1571.4, 1542.1, 1294.7, 1264.8, 1178.8, 1145.8; **HRMS (ESI)** m/z calcd for $C_{22}H_{16}N_2O_3$ $[M+H]^+$ 357.1239, found 357.1234.



***N*-(7-Ethyl-4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3n)**

Compound **3n** was prepared according to the **2.2** and was purified on silica gel to give a yellow solid in 74% yield (27.4mg). Mp: 192.4−193.2 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.95 (1H, s), 8.83 (1H, d, J = 1.5 Hz), 8.23 (2H, dd, J = 7.5, 1.0 Hz), 8.07 (2H, dd, J = 7.5, 1.0 Hz), 7.53 (6H, m), 2.79 (2H, q, J = 7.5 Hz), 1.36 (3H, t, J = 7.5 Hz); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 165.8, 162.0, 156.2, 147.4, 141.5, 134.2, 132.8, 132.3, 129.7, 128.9, 128.8, 128.2, 127.5, 120.6, 118.4, 101.9, 29.9, 14.7; **IR (KBr)**: 3308.4, 2957.2, 2870.0, 1792.5, 1718.3, 1676.7, 1614.7, 1567.7, 1287.7, 1265.5, 1189.4; **HRMS (ESI)** m/z calcd for $C_{22}H_{19}N_2O_3$ $[M+H]^+$ 371.1396, found 371.1392.

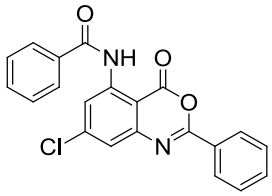


***N*-(7-Fluoro-4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3o)**

Compound **3o** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 55% yield (19.9 mg). Mp: 205.7−206.4 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 12.087 (1H, s), 8.77 (1H, dd, J = 12, 2.5 Hz), 8.27 (2H, d, J = 7.5 Hz), 8.06 (2H, d, J = 7.5 Hz), 7.60 (2H, m), 7.53 (4H, m), 7.06 (1H, dd, J = 8.5, 2.5 Hz); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 169.6 (d, $^1J_{C\text{-}F}$ = 279.8 Hz), 166.0, 161.4, 157.1, 149.8 (d, $^3J_{C\text{-}F}$ =15.4 Hz),

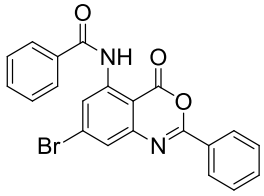
143.9 (d, $^{3}J_{C\text{-}F}$ = 15.4 Hz), 133.7, 133.3, 132.7, 129.2, 129.0, 128.9, 128.5, 127.5, 108.0 (d, $^{2}J_{C\text{-}F}$ = 23.5 Hz), 106.7 (d, $^{2}J_{C\text{-}F}$ = 23.5 Hz), 100.8 (d, $^{4}J_{C\text{-}F}$ = 7.0 Hz); **^{19}F NMR (471 MHz, CDCl$_3$):** δ −93.91 (1F, t, J = 10.8 Hz); **IR (KBr)**: 3296.7, 1718.7, 1694.2, 1594.9, 1561.4, 1260.9, 1184.4; **HRMS (ESI)** m/z calcd for $C_{21}H_{13}FN_2O_3$ $[M+H]^+$ 361.0988, found 361.0983.



***N*-(7-Chloro-4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3p)**

Compound **3p** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 64% yield (24.1 mg). Mp: 209.4−209.9 °C.

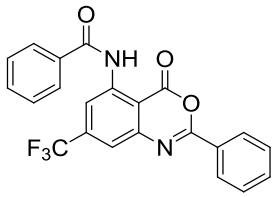
^{1}H NMR (500 MHz, CDCl$_3$): δ 11.99 (1H, s), 9.03 (1H, d, J = 2.0 Hz), 8.26 (2H, dd, J = 8.0, 3.0 Hz), 8.07 (2H, dd, J = 8.0, 3.0 Hz), 7.62 (2H, td, J = 7.5, 1.5 Hz), 7.54 (4H, m), 7.38 (1H, d, J = 3.0 Hz); **^{13}C NMR (125 MHz, CDCl$_3$):** δ 165.8, 161.5, 157.2, 148.2, 144.8, 142.3, 133.7, 133.3, 132.7, 129.2, 129.0, 128.9, 128.5, 127.5, 121.3, 118.5, 102,4; **IR (KBr)**: 3299.7, 1723.8, 1685.0, 1625.9, 1604.6, 1561.1, 1288.9, 1261.8, 1182.5; **HRMS (ESI)** m/z calcd for $C_{21}H_{13}ClN_2O_3$ $[M+H]^+$ 377.0693, found 377.0697.



***N*-(7-Bromo-4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3q)**

Compound **3q** was prepared according to the **2.2** and was purified on silica gel to give a white solid in 55% yield (23.1 mg). Mp: 210.5−211.7 °C.

^{1}H NMR (500 MHz, CDCl$_3$): δ 11.96 (1H, s), 9.19 (1H, d, J = 1.5 Hz), 8.25 (2H, m), 8.06 (2H, m), 7.60 (2H, ,m), 7.53 (5H, m); **^{13}C NMR (125 MHz, CDCl$_3$):** δ 165.8, 161.6, 157.1, 148.0, 142.1, 133.7, 133.5, 133.3, 132.6, 129.2, 129.0, 128.9, 128.4, 127.5, 121.4, 102.7; **IR (KBr)**: 3298.2, 1721.1, 1706.2, 1693.9, 1606.6, 1574.8, 1541.5, 1295.0, 1171.2, 1116.3; **HRMS (ESI)** m/z calcd for $C_{21}H_{13}ClN_2O_3$ $[M+H]^+$ 421.0188, found 421.0186.



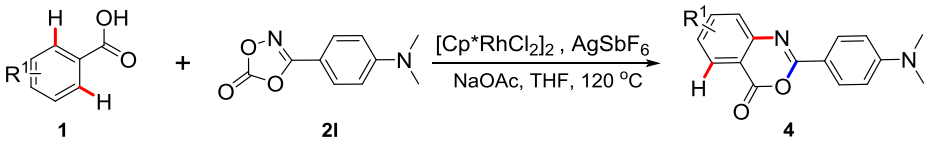
***N*-(4-Oxo-2-phenyl-7-(trifluoromethyl)-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3r)**

Compound **3r** was prepared according to the **2.2** and was purified on silica gel to give a yellow solid in 51% yield (20.9mg). Mp: 200.4−201.7 °C.

^{1}H NMR (500 MHz, CDCl$_3$): δ 12.05(1H, s), 9.31 (1H, d, J = 0.5 Hz), 8.31 (2H, m), 8.31 (2H, m), 7.66 (1H, d, J = 1.5 Hz), 7.63(2H, m),7.56 (4H, m); **^{13}C NMR (125 MHz, CDCl$_3$):** δ 167.0, 161.4,

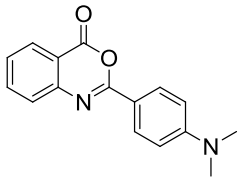
157.3, 148.0, 139.3(q, $^{2}J_{C-F}$=33.1HZ), 133.6, 133.5, 132.8, 129.1, 129.0, 128.3, 128.5, 122.9(q, $^{1}J_{C-F}$=272.3HZ), 118.0(q, $^{2}J_{C-F}$=3.8HZ), 114.7(q, $^{2}J_{C-F}$=3.8HZ), 105.9; **^{19}F NMR (471 MHz, CDCl$_3$):** δ −64.00 (3F, s); **IR (KBr)**: 3309.7, 1719.9, 1687.8, 1618.2, 1574.5, 1289.9, 1250.3, 1180.6, 1128.2; **HRMS (ESI)** m/z calcd for $C_{22}H_{14}F_3N_2O_3$ $[M+H]^+$ 411.0957, found 411.0959.

3.4 General procedure for the synthesis of 4



Benzoic acid **1** (0.20 mmol), 3-(4-(dimethylamino)phenyl)-1,4,2-dioxazol-5-one **2l** (0.20 mmol), NaOAc (17 mg, 0.20 mmol), $AgSbF_6$ (20 mg, 0.06 mmol), $[Cp^*RhCl_2]_2$ (6 mg, 0.010 mmol) and THF (2.0 mL) were placed into a 10 mL sealing tube. The reaction mixture was stirred at 120 °C for 12 h. After cooling to ambient temperature, a saturated $NaHCO_3$ solution was added to the reaction solution, and the mixture was extracted three times with $CHCl_3$. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The mixture was purified by flash column chromatography on silica gel with Petroleum ether-chloroform-EA as the eluent to give the desired products **4**.

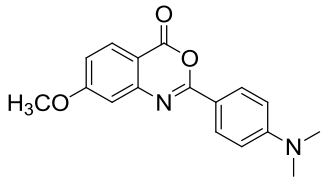
3.5 Characterization data of 4



2-(4-(Dimethylamino)phenyl)-4H-benzo[d][1,3]oxazin-4-one (4a) (CAS Registry Number 95654-38-9)

Compound **4a** was prepared according to the **2.4** and was purified on silica gel to give a yellow solid in 70% yield (37.2mg). Mp: 176.4−177.6 °C.

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.19 (3H, m), 7.76 (1H, td, J = 8.5, 1.5 Hz), 7.62 (1H, d, J = 8.0, 1.5 Hz), 7.42 (1H, t, J = 8.0 Hz),7.77 (2H, d, J = 9.0 Hz s), 3.09 (6H, s); **^{13}C NMR (125 MHz, CDCl$_3$):** δ 159.1, 157.0, 151.9, 146.8, 135.4, 129.1, 127.5, 125.9, 125.5, 116.1, 116.1, 115.4, 110.6, 39.3; **IR (KBr)**: 2911.7, 2856.7, 1738.5, 1593.8, 1557.9, 1528.4, 1270.1, 1185.1; **HRMS (ESI)** m/z calcd for $C_{16}H_{14}N_2O_2$ $[M+H]^+$ 267.1134, found 267.1138.

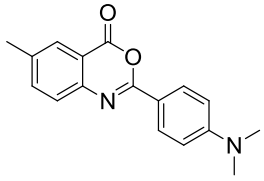


2-(4-(Dimethylamino)phenyl)-7-methoxy-4H-benzo[d][1,3]oxazin-4-one (4b)

Compound **4b** was prepared according to the **2.4** and was purified on silica gel to give a yellow

solid in 82% yield (48.5mg). Mp: 181.9−182.4 °C.

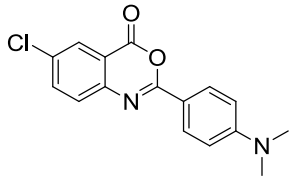
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (2H, d, J = 9.0 Hz), 8.05 (1H, d, J = 9.0), 7.00 (1H, d, J = 2.5 Hz, 6.94 (1H, dd, J = 9.0, 2.0 Hz), 6.70 (2H, d, J = 9.0 Hz), 3.92 (3H, s), 3.06 (6H, s); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 166.2, 159.9, 158.9, 153.1, 150.3, 130.1, 130.08, 116.8, 116.2, 111.3, 109.3, 108.0, 55.8, 40.1; **IR (KBr)**: 2908.7, 2819.3, 1737.6, 1595.4, 1557.6, 1530.6, 1270.7, 1186.7; **HRMS (ESI)** m/z calcd for $C_{17}H_{16}N_2O_3$ $[M+H]^+$ 297.1239, found 297.1235.



2-(4-(Dimethylamino)phenyl)-6-methyl-4H-benzo[d][1,3]oxazin-4-one (4c)

Compound **4c** was prepared according to the **2.4** and was purified on silica gel to give a yellow solid in 72% yield (40.3mg). Mp: 184.5−185.8 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (2H, d, J = 9.0 Hz), 7.92 (1H, d, J = 1.0 Hz), 7.57 (1H, dd, J = 8.0, 1.5 Hz),), 7.50 (1H, d, J = 8.5 Hz), 6.73 (2H, d, J = 8.0 Hz), 3.07 (6H, s), 2.45 (3H, s); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 159.4, 156.3, 151.9, 144.7, 136.6, 136.1, 128.8, 127.0, 125.3, 116.0, 115.1, 110.3, 39.1, 20.2; **IR (KBr)**: 2956.3, 2923.7, 2869.8, 2850.6, 1733.1, 1596.0, 1570.3, 1521.1, 1261.6, 1188.8, 1159.9; **HRMS (ESI)** m/z calcd for $C_{17}H_{16}N_2O_2$ $[M+H]^+$ 281.1290, found 281.1288.

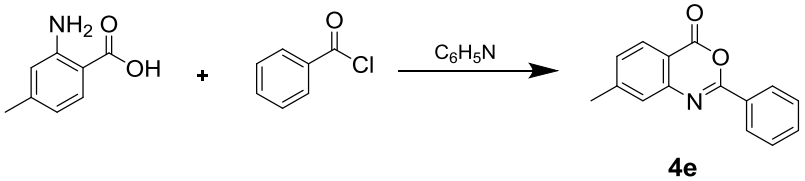


6-Chloro-2-(4-(dimethylamino)phenyl)-4H-benzo[d][1,3]oxazin-4-one (4d)

Compound **4d** was prepared according to the **2.4** and was purified on silica gel to give a yellow solid in 43% yield (25.8mg). Mp: 192.2−193.5 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (3H, m), 7.65 (1H, dd, J = 8.5, 2.5 Hz), 7.50 (1H, d, J = 8.5 Hz), 6.82 (2H, d, J = 8.5 Hz), 3.06 (6H, s); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 159.2, 158.2, 153.1, 146.5, 136.5, 132.1, 130.1, 128.1, 127.7, 117.4, 116.4, 111.3, 40.1; **IR (KBr)**: 2955.6, 2869.4, 1737.8, 1595.9, 1557.8, 1530.8, 1270.6, 1187.1; **HRMS (ESI)** m/z calcd for $C_{16}H_{13}ClN_2O_2$ $[M+H]^+$ 301.0744, found 301.0748.

3.6 Procedure for the synthesis of 4e

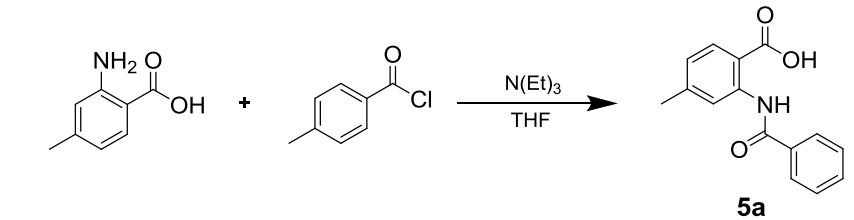


4e

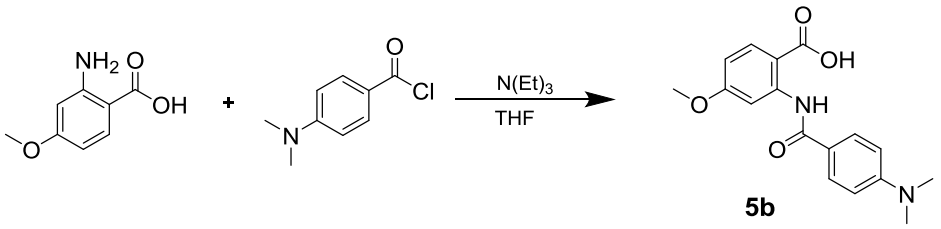
Under argon atmosphere, 2-amino-4-methylbenzoic acid (302.0mg, 2.0 mmol) was dissolved in 10 ml of dry pyridine at room temperature and the solution was cooled to 0°C. Subsequently, benzoyl chloride (560.0 mg, 4.0 mmol) in pyridine (2.0 ml) was added slowly to this solution. The

reaction mixture was stirred at 0°C for 1 h and then at room temperature for 2 h. After completion, the mixture was neutralized with $NaHCO_3$ solution and poured into ice water. The precipitate was collected by filtration and dried to yield the desired compounds. The crude product was purified by recrystallization from EtOAc/Pentane to give a yellow solid **4e** in 82% yield (388.7 mg). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 8.29 (2H, m), 8.10 (1H, d, J = 8.0 Hz), 7.56 (1H, td, J = 8.5, 1.5 Hz), 7.50 (3H, m), 7.31 (1H, dd, J = 8.0, 1.0 Hz), 2.51 (3H, s); **^{13}C NMR (125 MHz, $CDCl_3$):** δ 158.6, 156.2, 147.1, 146.0, 131.5, 128.6, 127..7, 127.4, 127.2, 126.2, 113.4, 21.1; **HRMS (ESI)** *m/z* calcd for $C_{15}H_{12}NO_2$ $[M+H]^+$ 238.0863, found 238.0862.

3.7 Procedure for the synthesis of 5a and 5b



5a



5b

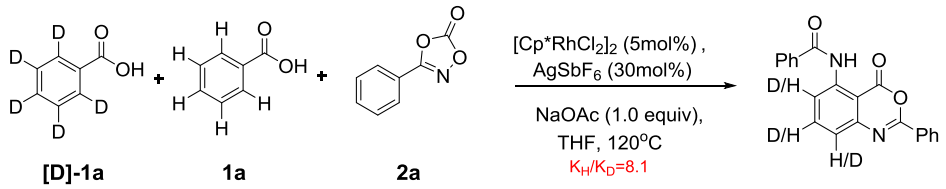
To a solution of anthranilic acid (1.1 mmol) in anhydrous THF (4 mL) was added 1.0 mmol of the appropriate benzoyl chloride at room temperature. After cooling the solution using ice-water bath, 1.5 mmol of triethylamine was added dropwise and reaction was stirred at room temperature for additional 4–12 h. The mixture was poured into a 20–30 mL cold solution of 1.0 M HCl, and the precipitate was collected by filtration. Recrystallization from THF-hexane solution afforded the desired compound in quantitative yield of compound **5a** (90%) and **5b** (78%).

Compound **5a** (459.1 mg)**: ^{1}H NMR (500 MHz, d_6-DMSO):** δ 13.68 (1H, s), 12.25 (1H, s), 8.61 (1H, s), 7.96 (3H, m), 7.66 (1H, m), 7.60 (2H, m), 7.03 (1H, dd, J = 8.0, 1.0 Hz), 2.40 (3H, s); **^{13}C NMR (125 MHz, d_6-DMSO):** δ 170.6, 165.1, 145.4, 141.7, 135.03, 131.7, 129.5, 127.4, 124.2, 120.5, 114.1, 22.2; **HRMS (ESI)** *m/z* calcd for $C_{15}H_{14}NO_3$ $[M+H]^+$ 256.0968, found 256.0964.

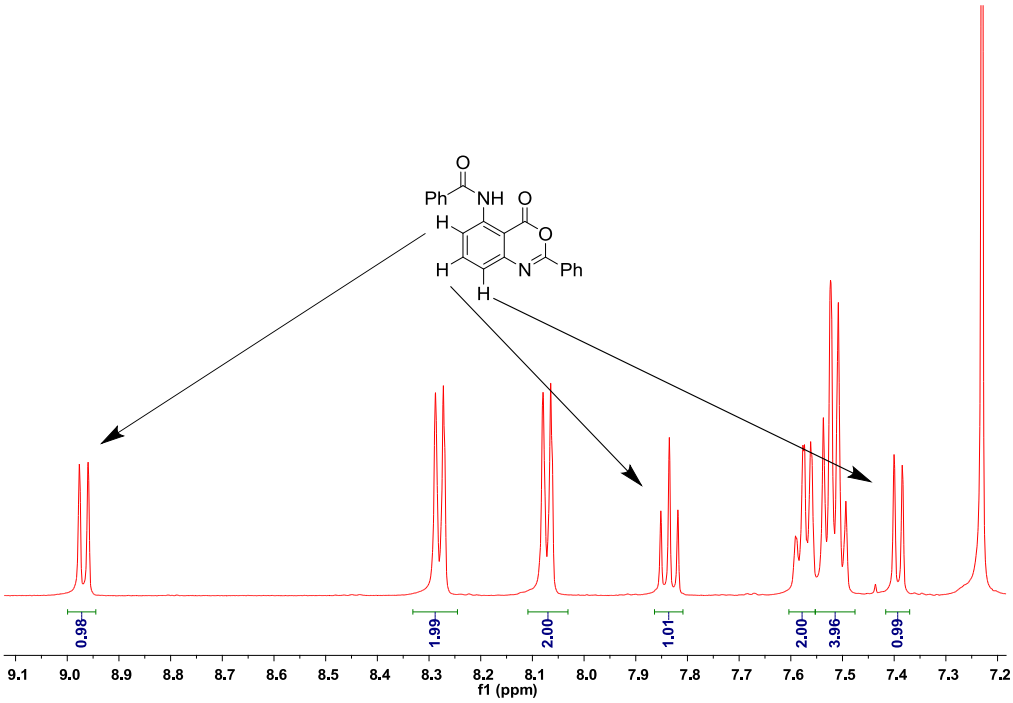
Compound **5b** (496.1 mg): **^{1}H NMR (500 MHz, d_6-DMSO):** δ 13.39 (1H, s),12.29 (1H, s), 8.48 (1H, d, J = 2.5 Hz), 8.00 (1H, d, J = 9.0 Hz), 7.82 (2H, d, J = 9.0 Hz), 6.81 (2H, d, J = 9.0 Hz), 6.71 (1H, d, J = 9.0, 2.5 Hz), 3.86 (3H, s), 3.02 (6H, s); **^{13}C NMR (125 MHz, d_6-DMSO):** δ 165.2, 153.1, 144.2, 133.5, 129.0, 121.1, 111.7, 108.3, 104.3, 55.8; **HRMS (ESI)** *m/z* calcd for $C_{17}H_{19}N_2O_4$ $[M+H]^+$ 315.1339, found 315.1338.

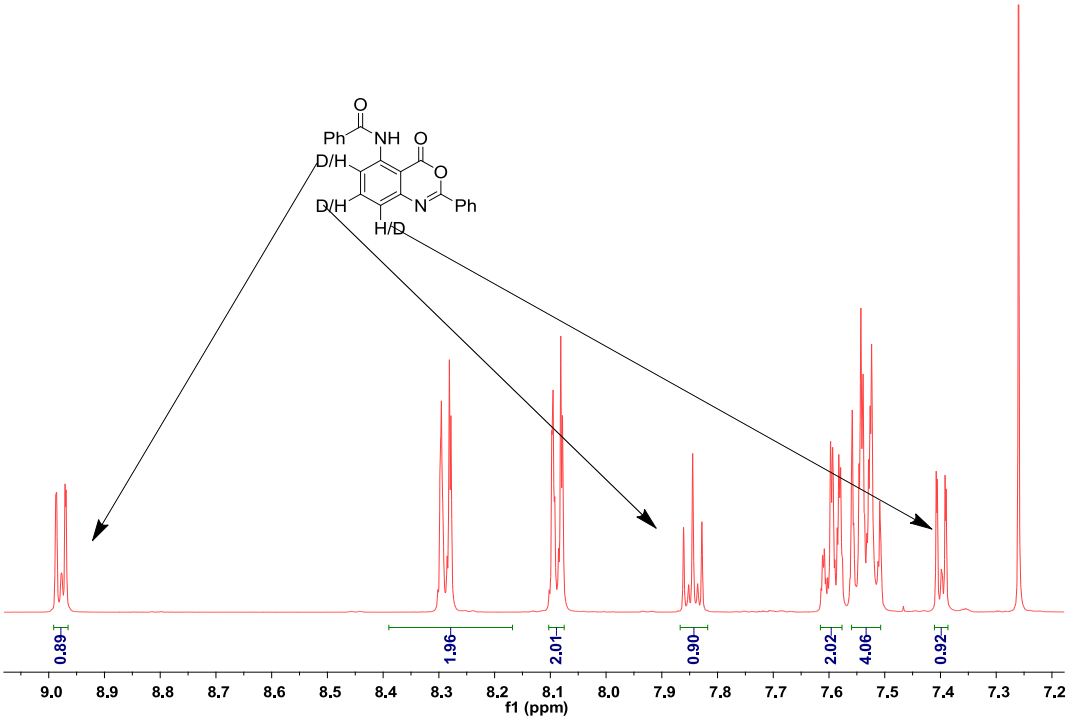
4. Kinetic Isotope Effect (KIE) Experiment

4.1 Competition KIE experiment

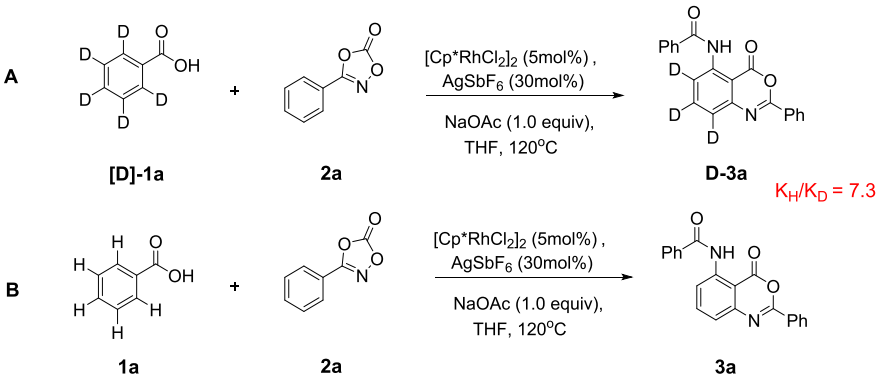


Benzoic acid **1** (0.20 mmol), **[D]-1a** (0.20 mmol), 3-phenyl-1,4,2-dioxazol-5-one **2a** (0.40 mmol), NaOAc (34 mg, 0.40 mmol), $AgSbF_6$ (40 mg, 0.12 mmol) and $[Cp^*RhCl_2]_2$ (12 mg, 0.020 mmol) were placed into a 10 ml sealing tube. THF (4.0 mL) was introduced and the reaction mixture was stirred at 120 °C for 2.5 h. After cooling to ambient temperature, a saturated $NaHCO_3$ solution was added to the reaction solution, and the mixture was extracted three times with $CHCl_3$ followed by washing with water and saturated brine. Then it was concentrated and loaded onto silica gel for purification by flash column chromatography (Petroleum ether/ chloroform/ EtOAc) to afford the desired product.





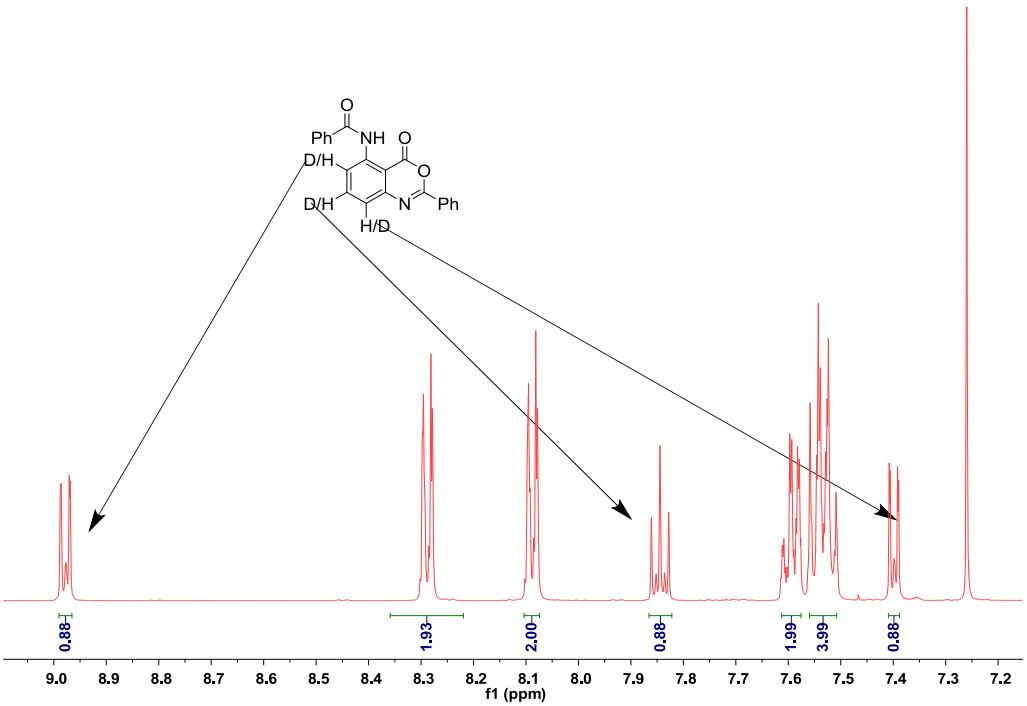
4.2 Parallel KIE experiment



Reaction A: Benzoic acid **[D]-1a** (0.20 mmol), 3-phenyl-1,4,2-dioxazol-5-one **2a** (0.20 mmol), NaOAc (17 mg, 0.20 mmol), $AgSbF_6$ (20 mg, 0.06 mmol) and $[Cp^*RhCl_2]_2$ (6 mg, 0.01 mmol) were placed into a 10 ml sealing tube. THF (2.0 mL) was introduced and the reaction mixture was stirred at 120 °C for 2.5 h.

Reaction B: Benzoic acid **1a** (0.20 mmol), 3-phenyl-1,4,2-dioxazol-5-one **2a** (0.20 mmol), NaOAc (17 mg, 0.20 mmol), $AgSbF_6$ (20 mg, 0.06 mmol) and $[Cp^*RhCl_2]_2$ (6 mg, 0.01 mmol) were placed into a 10 ml tube sealing. THF (2.0 mL) was introduced and the reaction mixture was stirred at 120 °C for 2.5 h.

After cooling to ambient temperature, reaction A and B were mixed and a saturated $NaHCO_3$ solution was added to the mixture. The mixture was extracted three times with $CHCl_3$, washed with water and saturated brine. Then it was concentrated in vacuum and loaded onto silica gel for purification by flash column chromatography (Petroleum ether/chloroform/EtOAc) to afford the mixed desired product **D-3a** and **3a**.


O
Ph
NH
O
D/H
O
N
Ph
D/H
H/D
0.88
1.93
2.00
0.88
1.99
3.99
0.88
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)

5. Optical properties of compound 3

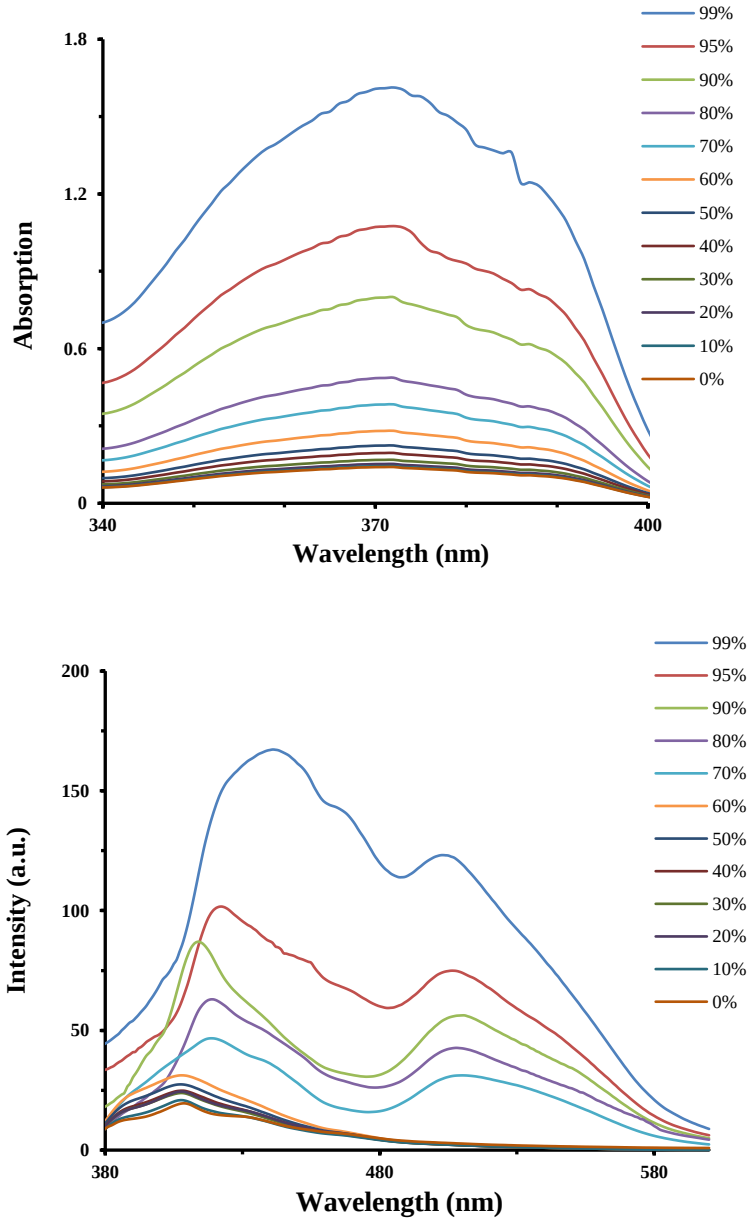


Figure S1. UV absorption (up) and emission (down) spectra of **3a** (concentration: 10 μM) in THF/water mixtures with different water fractions.

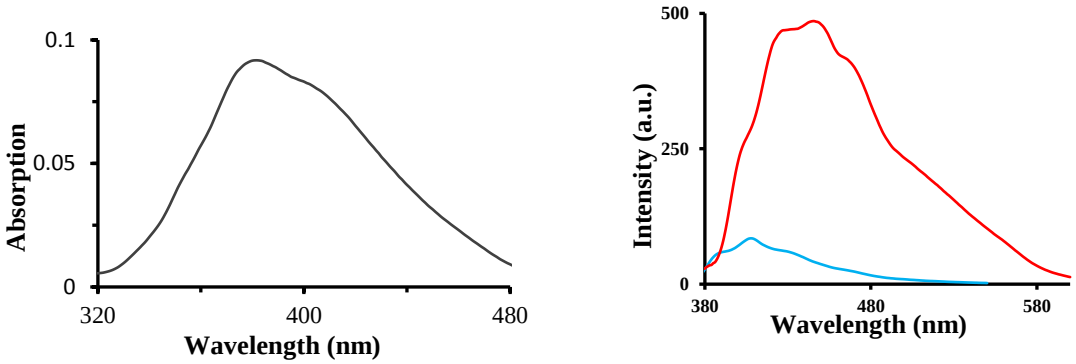


Figure S2. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3b** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

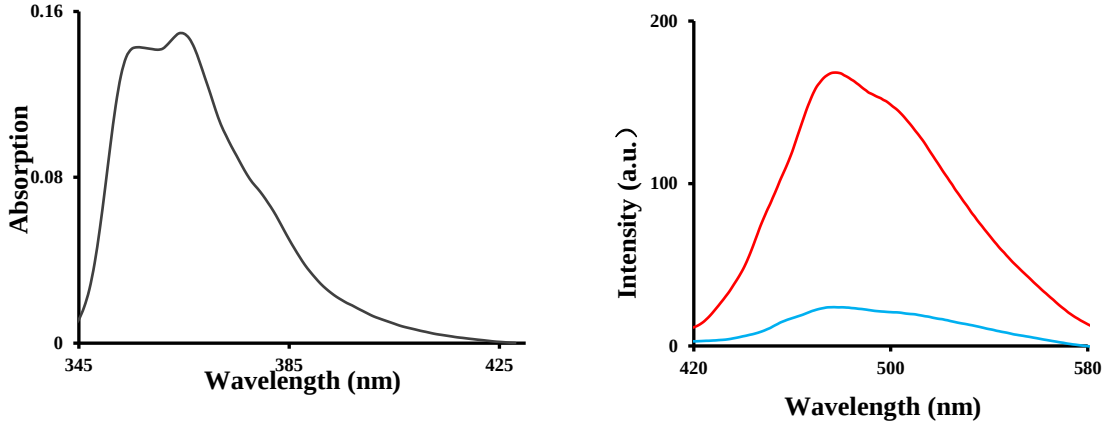


Figure S3. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3c** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

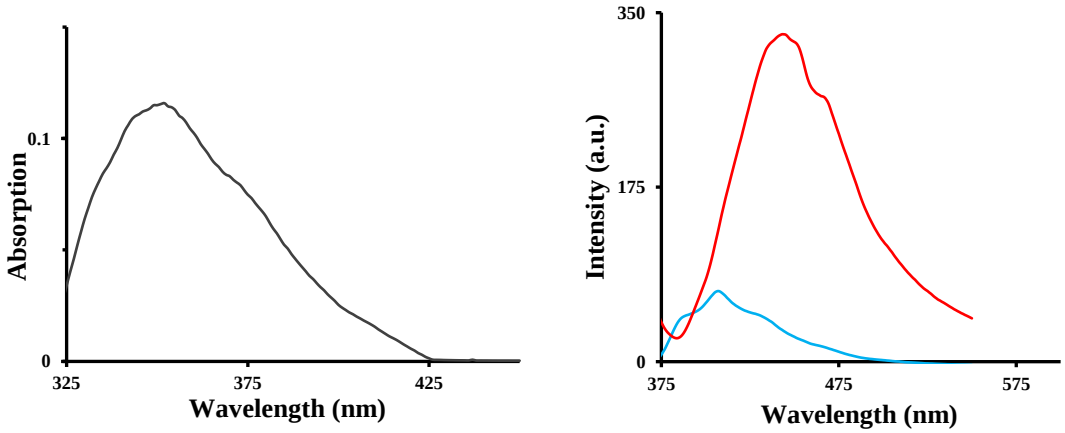


Figure S5. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3d** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

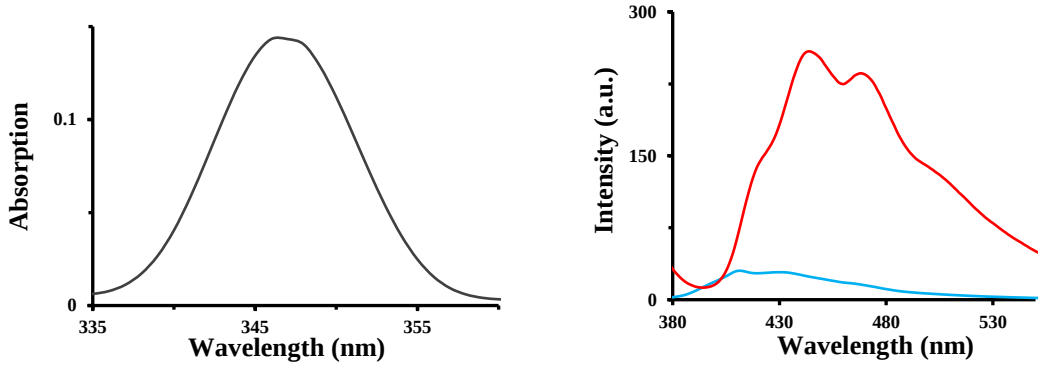


Figure S6. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3e** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

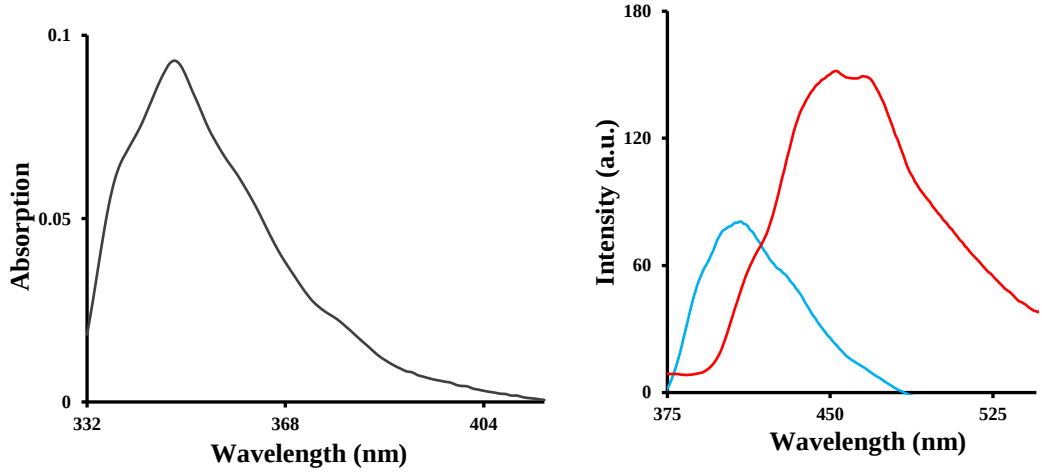


Figure S7. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3f** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

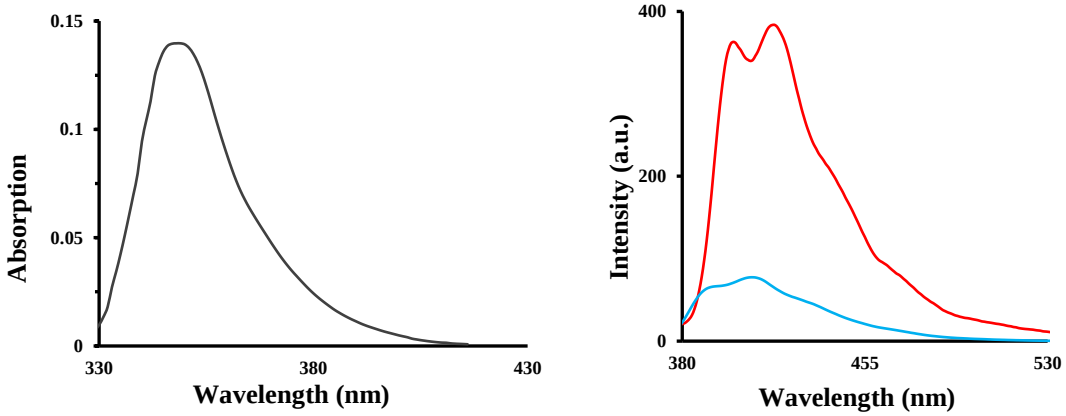


Figure S8. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3g** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

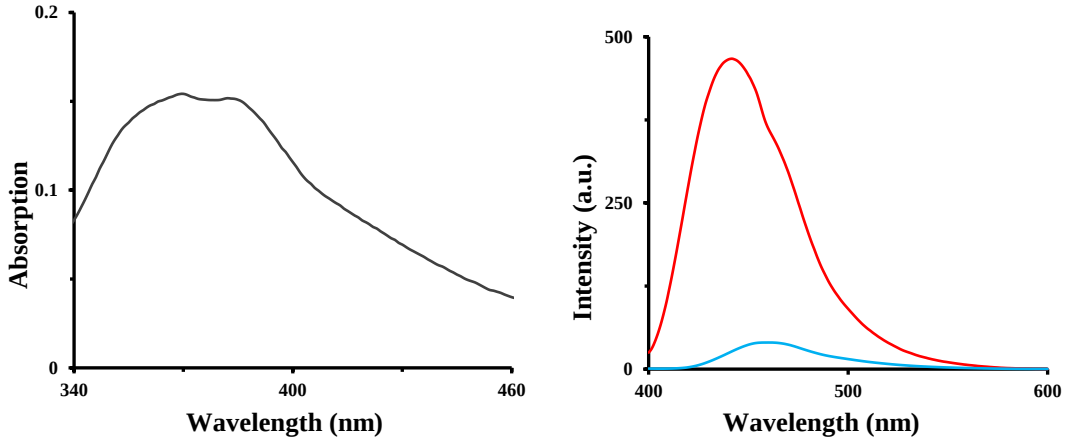


Figure S9. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3h** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

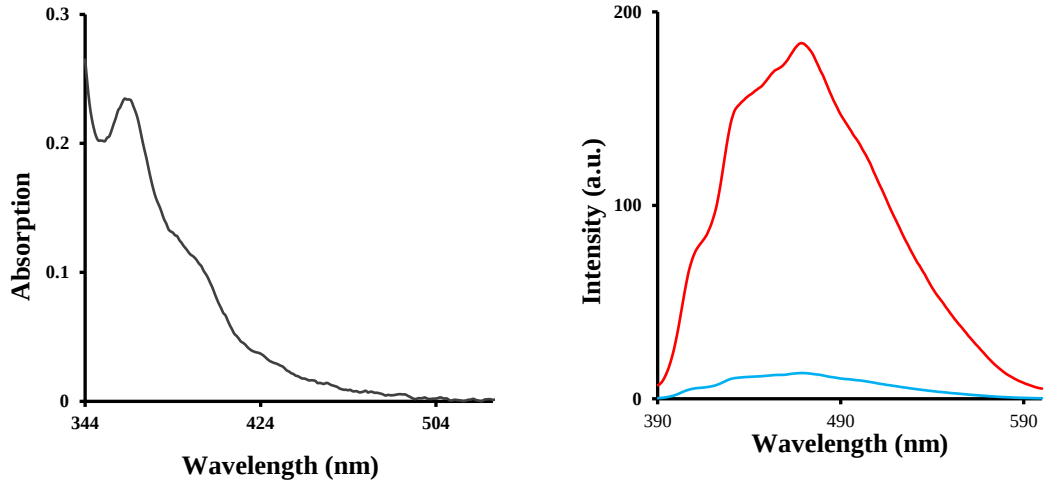


Figure S10. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3i** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

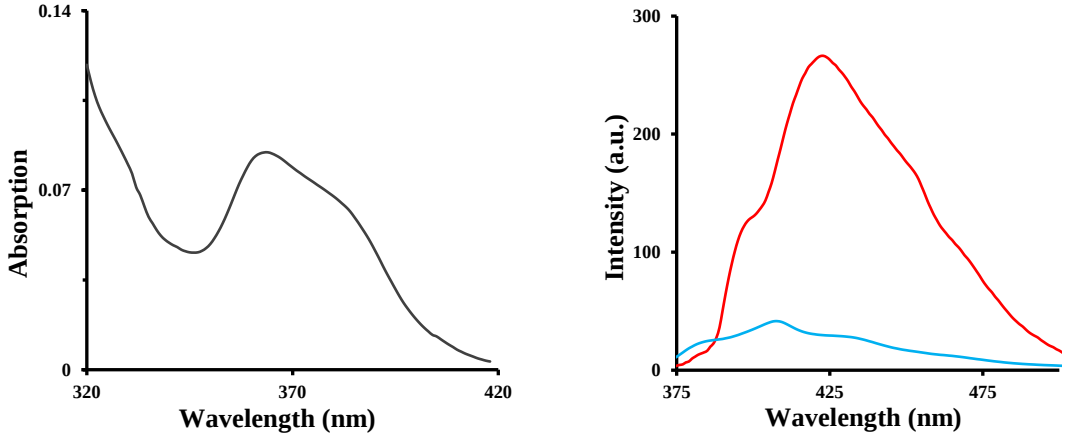


Figure S11. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3j** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

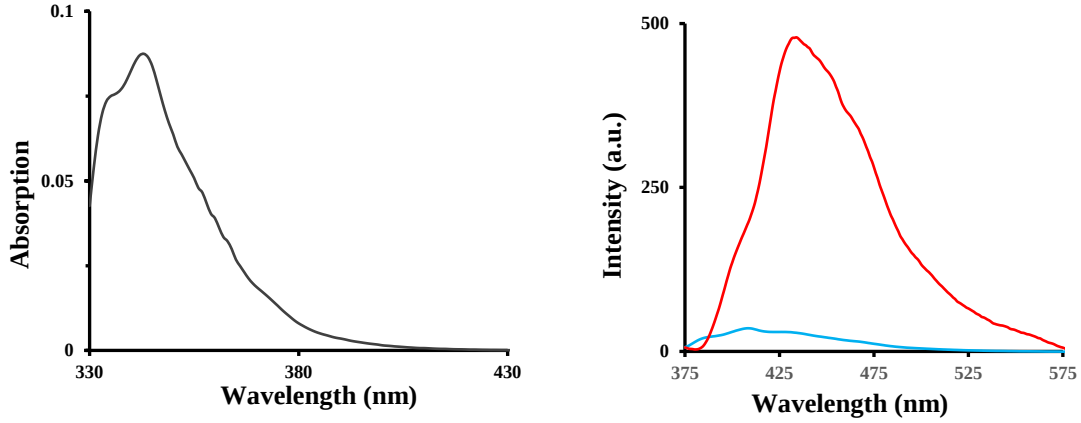


Figure S12. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3l** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

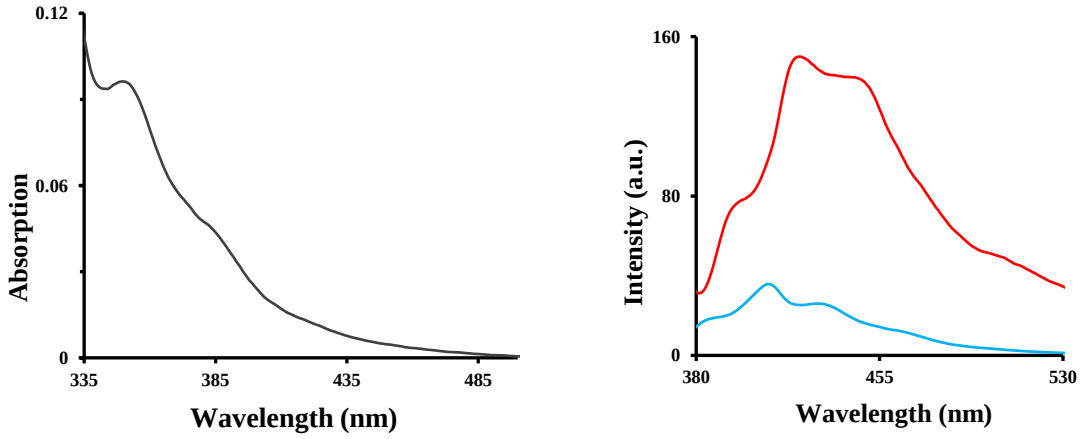


Figure S13. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3n** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

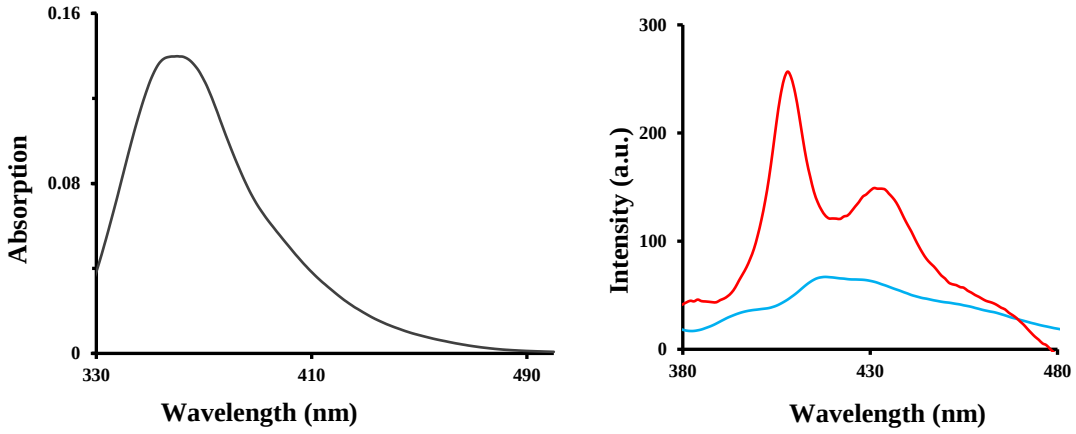


Figure S14. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3o** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

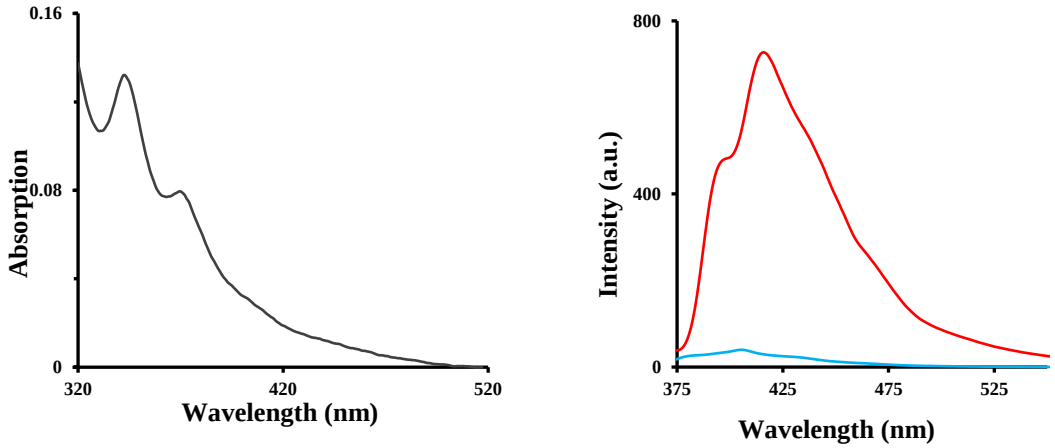


Figure S15. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3p** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

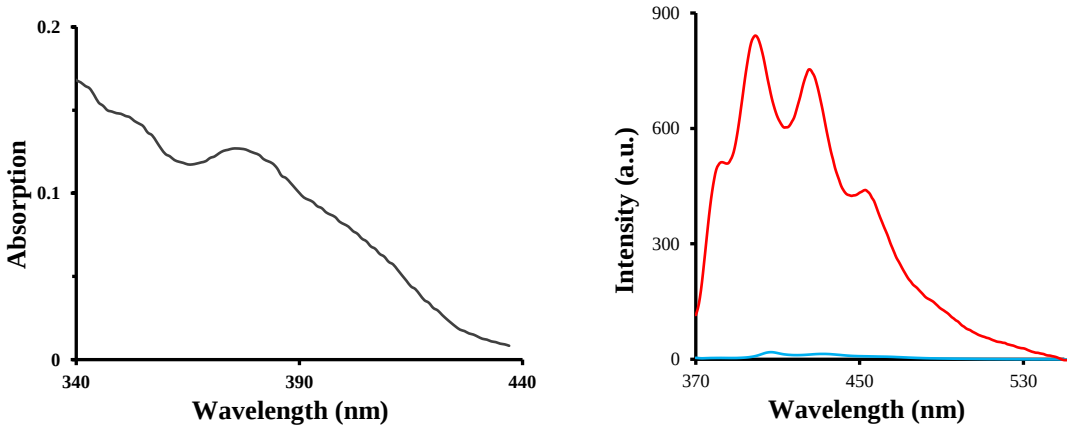


Figure S16. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3q** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

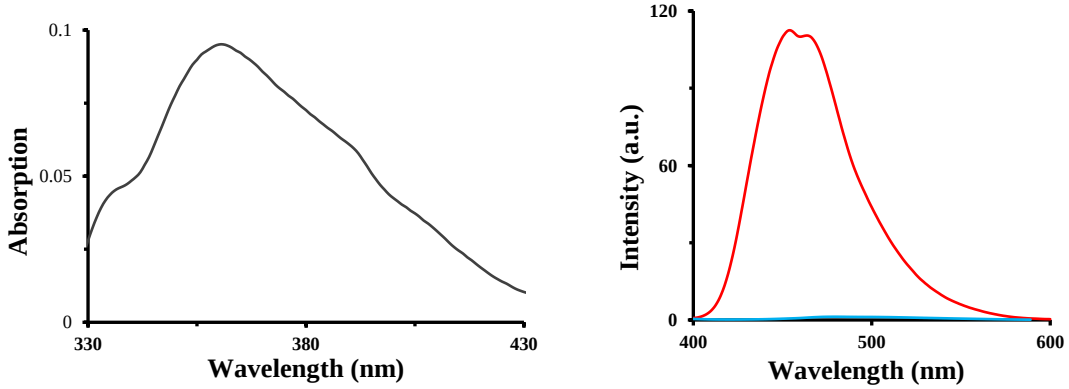
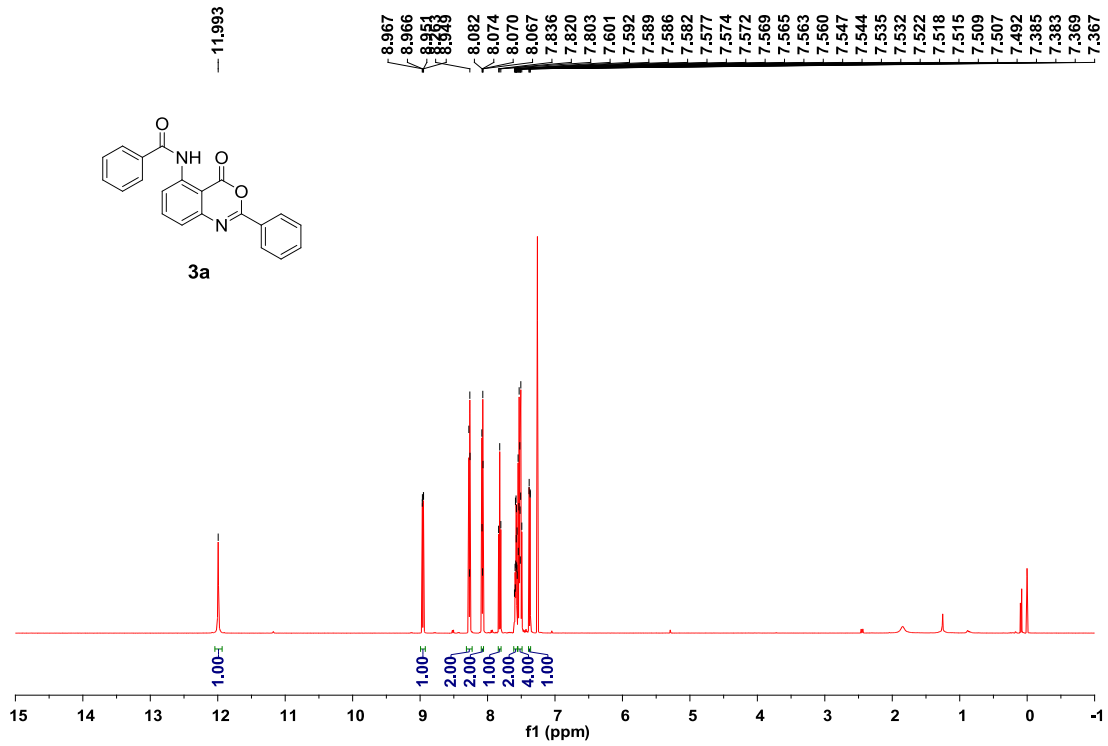
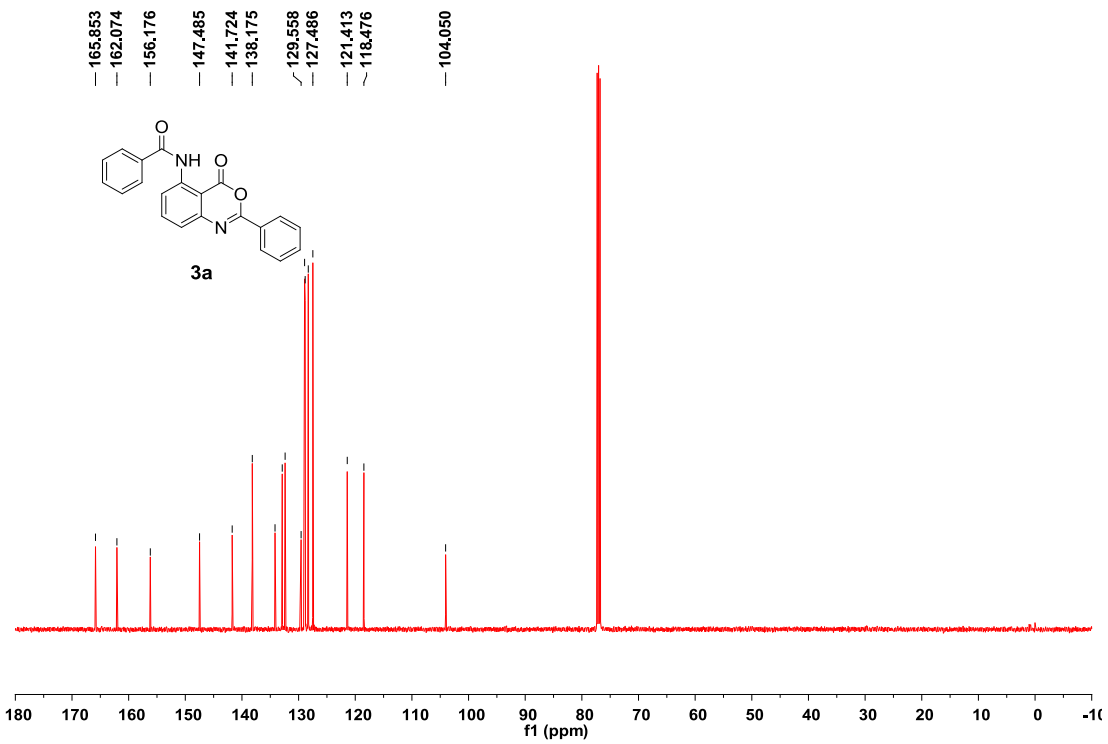


Figure S17. UV absorption (left, THF, 10 μM) and emission spectra (right) of **3r** in THF (blue line, 10 μM) and in 95% water/THF mixture (red line, 10 μM).

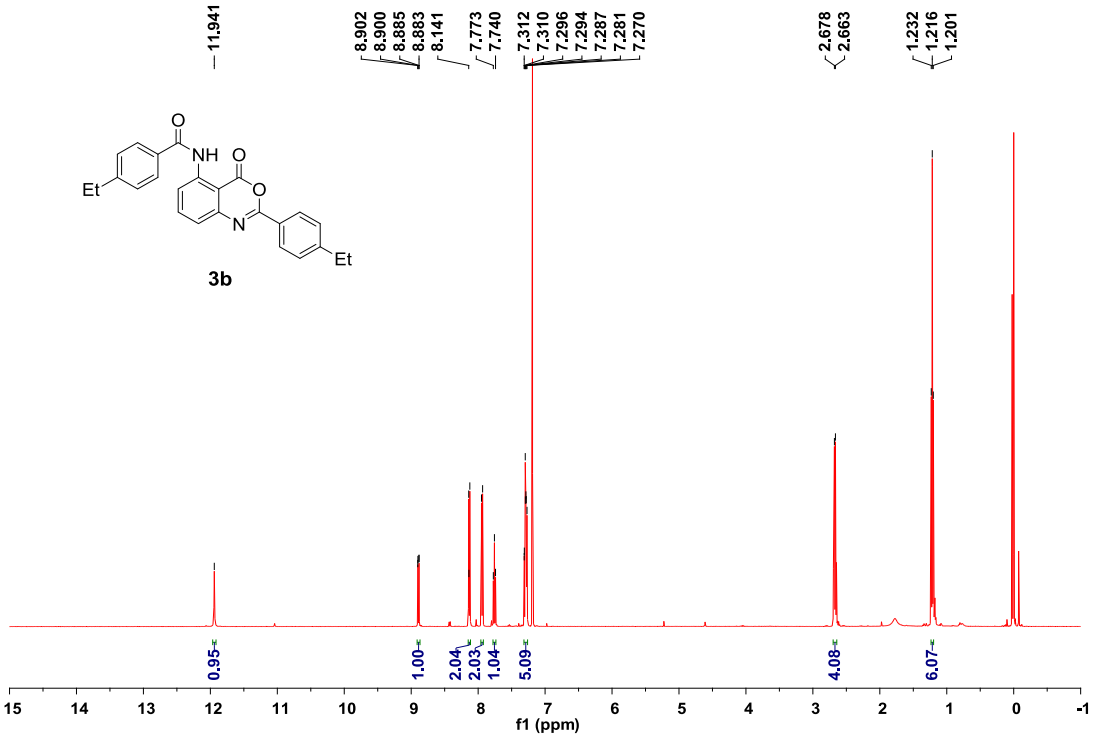
6. NMR spectroscopic data

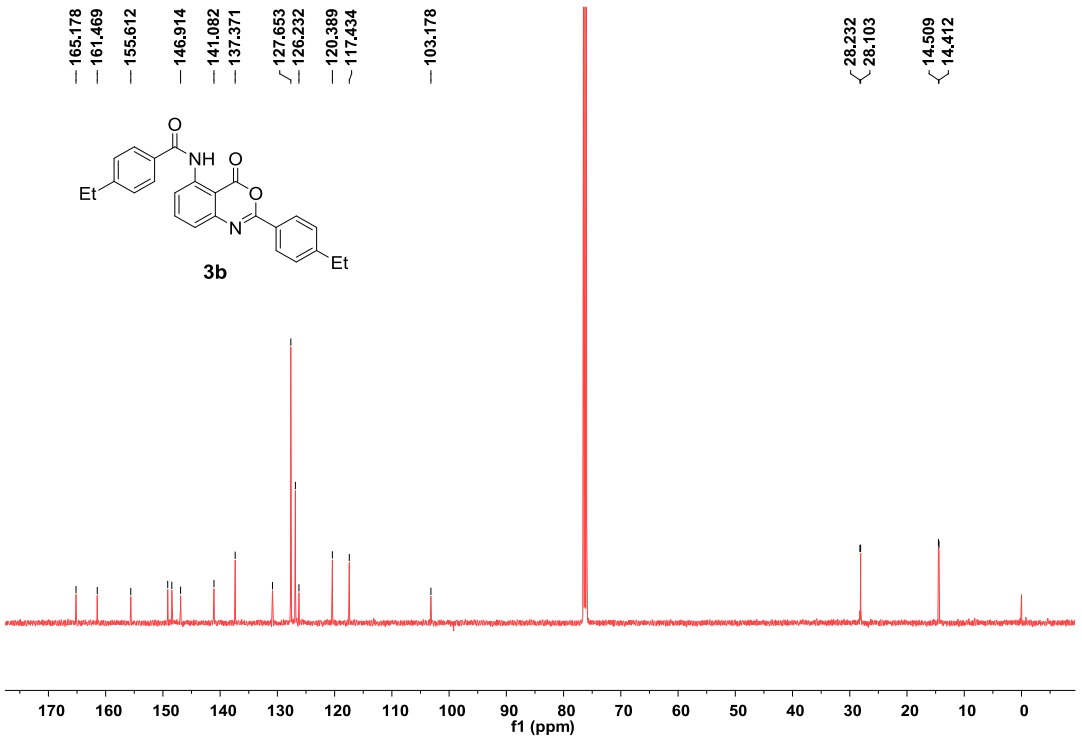
N-(4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3a)



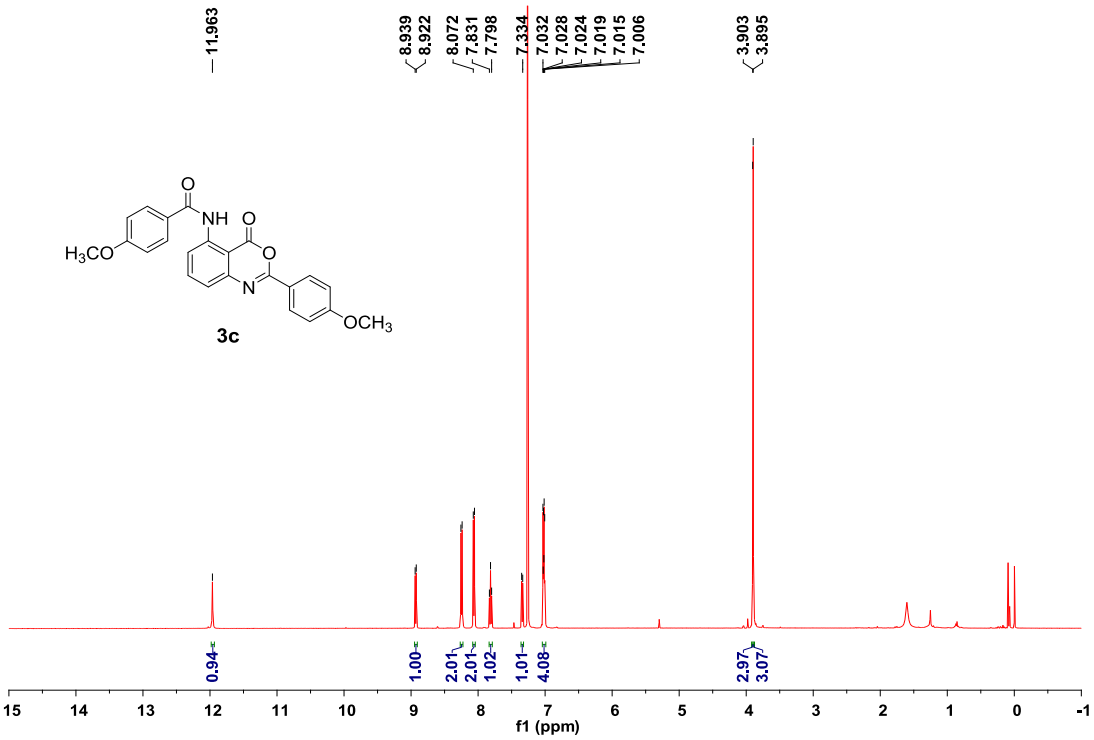


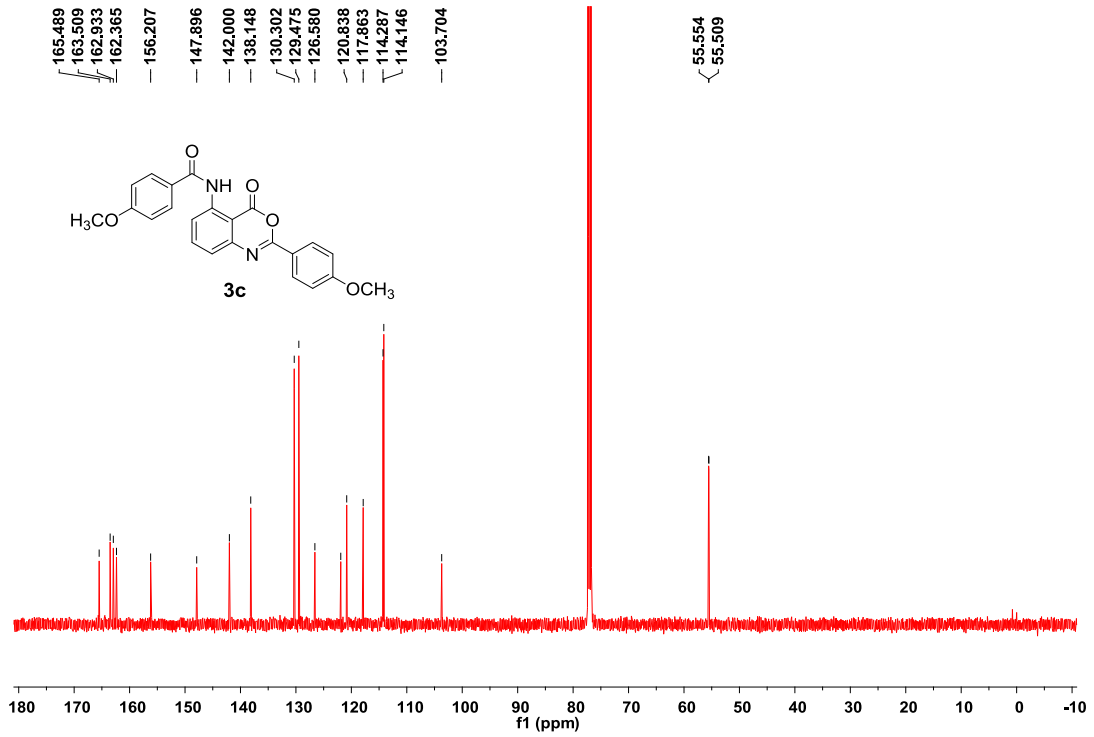
4-ethyl-N-(2-(4-ethylphenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3b)



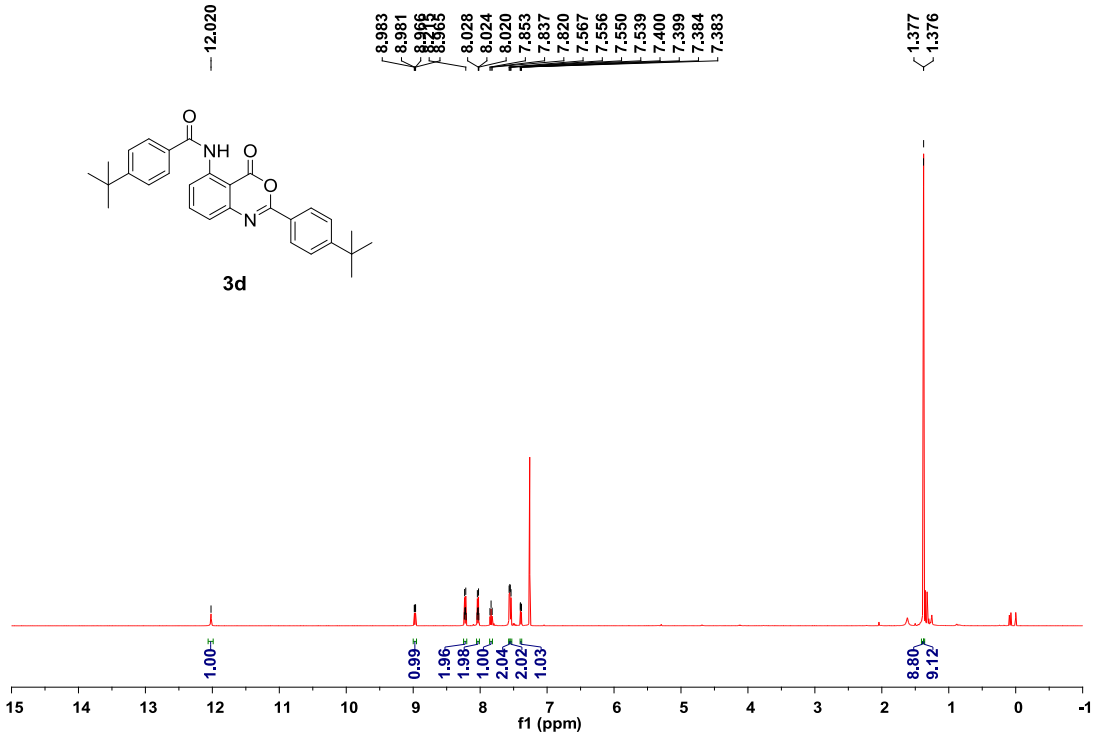


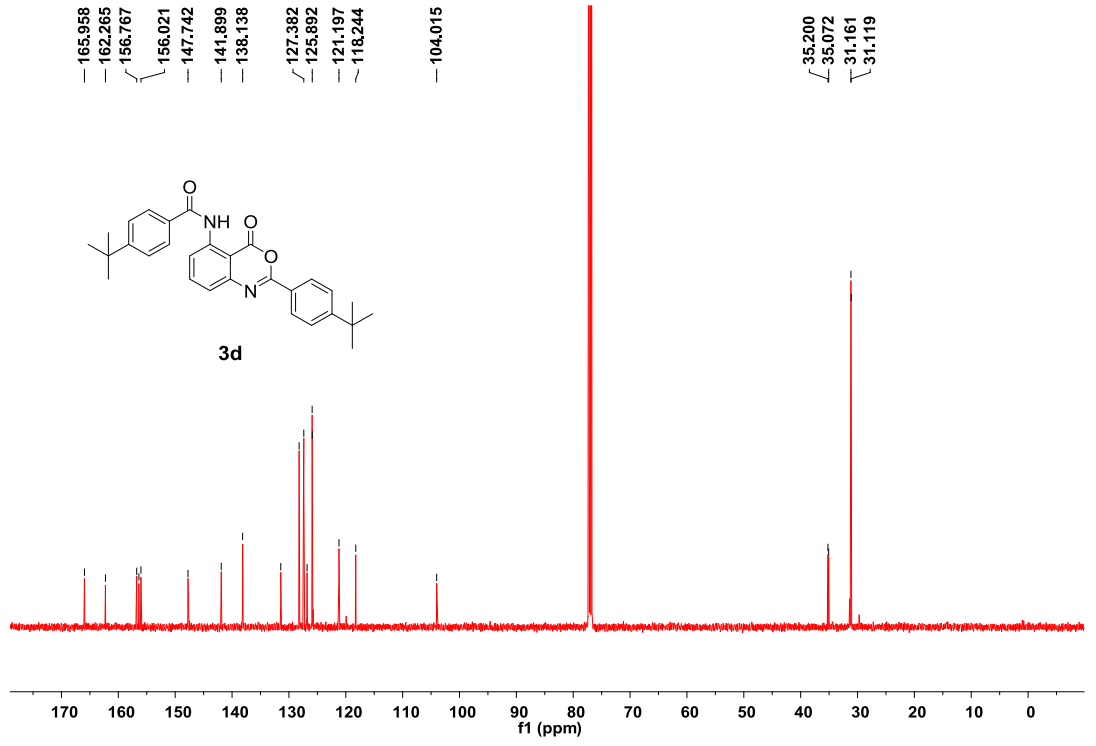
4-methoxy-N-(2-(4-methoxyphenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3c)



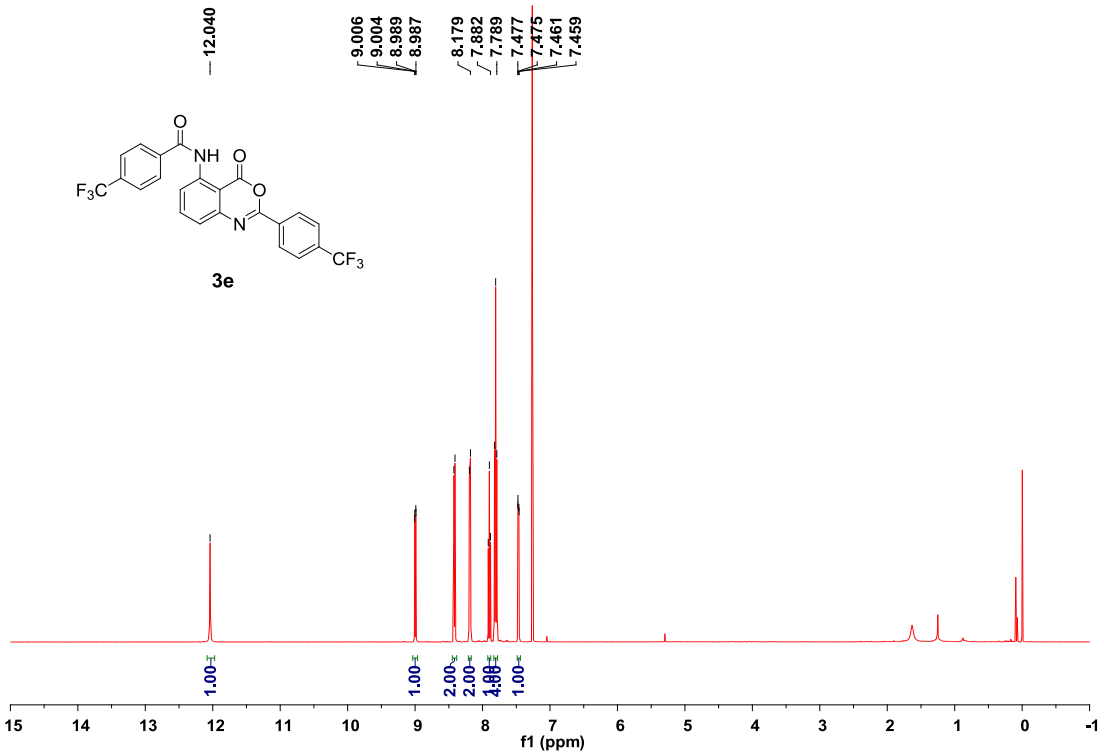


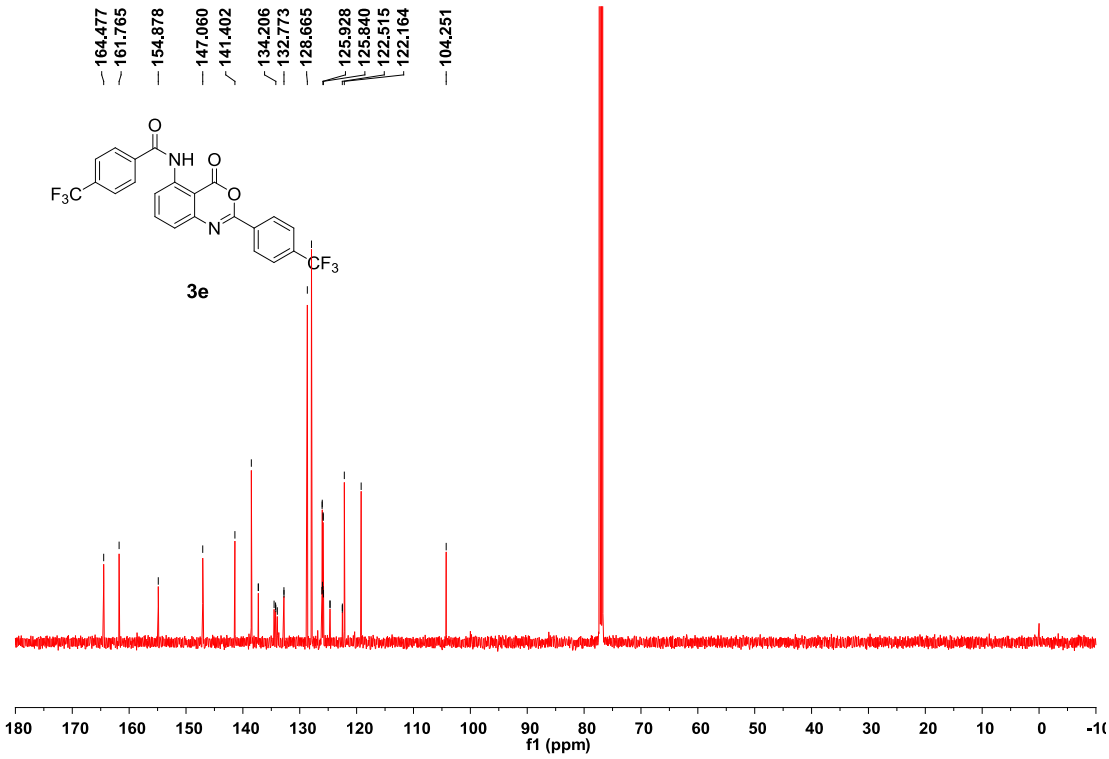
4-(tert-butyl)-N-(2-(4-(tert-butyl)phenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3d)

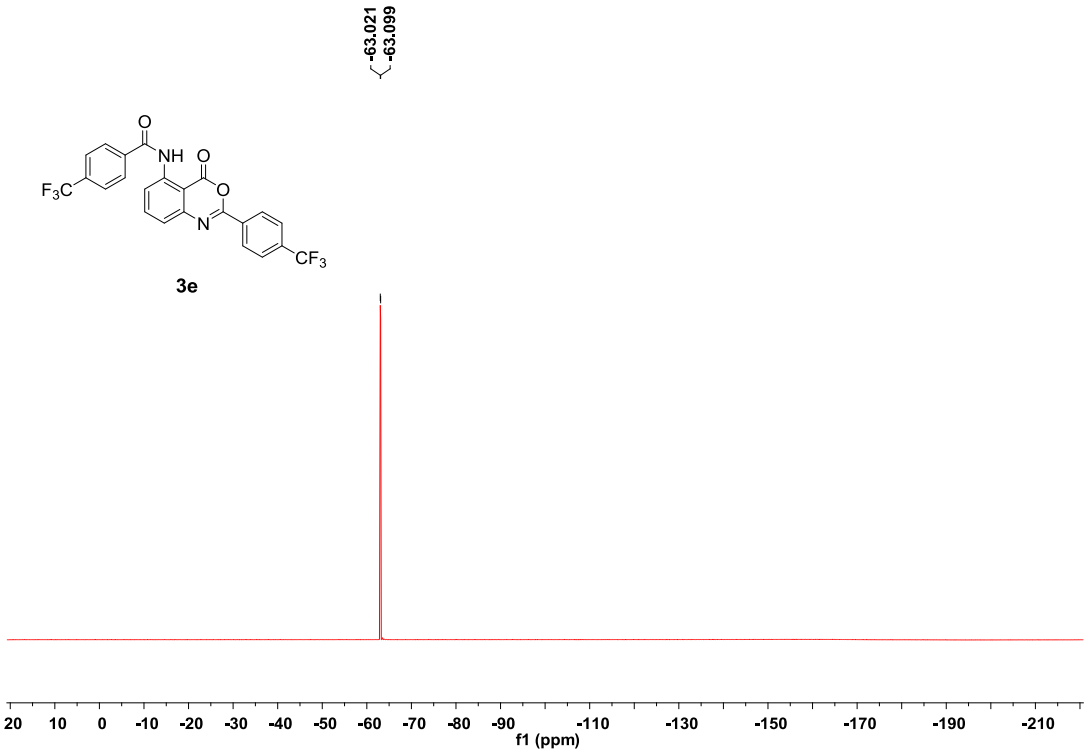




N-(4-oxo-2-(4-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]oxazin-5-yl)-4-(trifluoromethyl)benzamide (3e)



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F3C
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N
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3e
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0
-10
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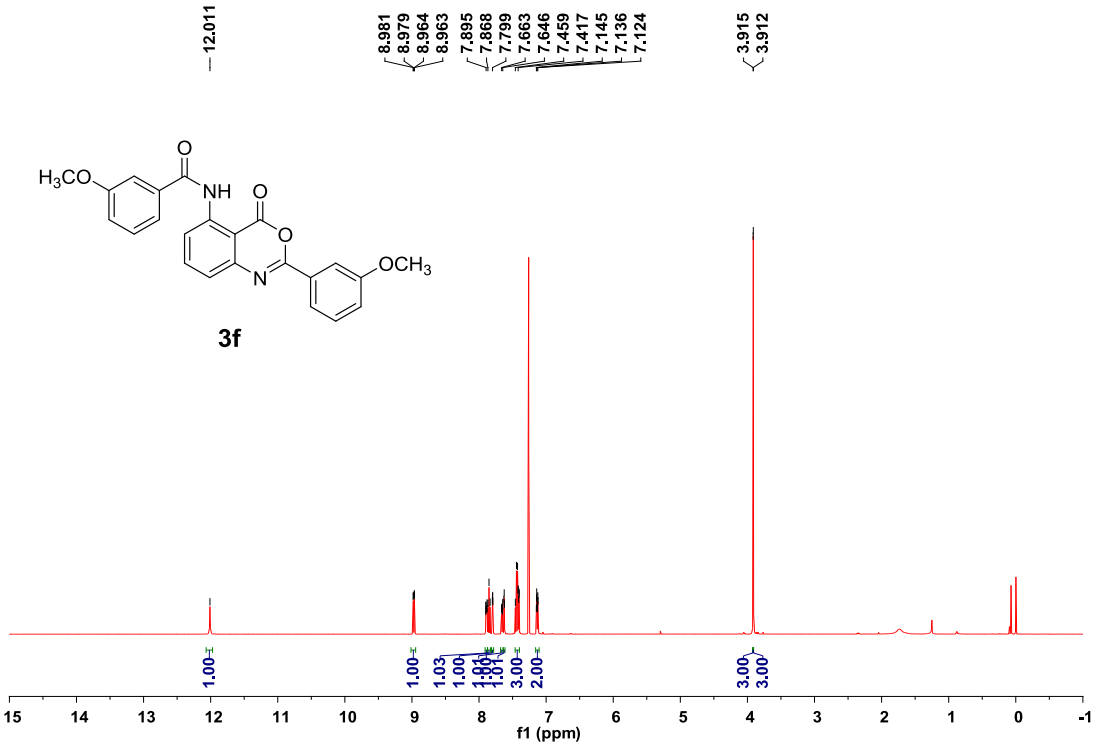
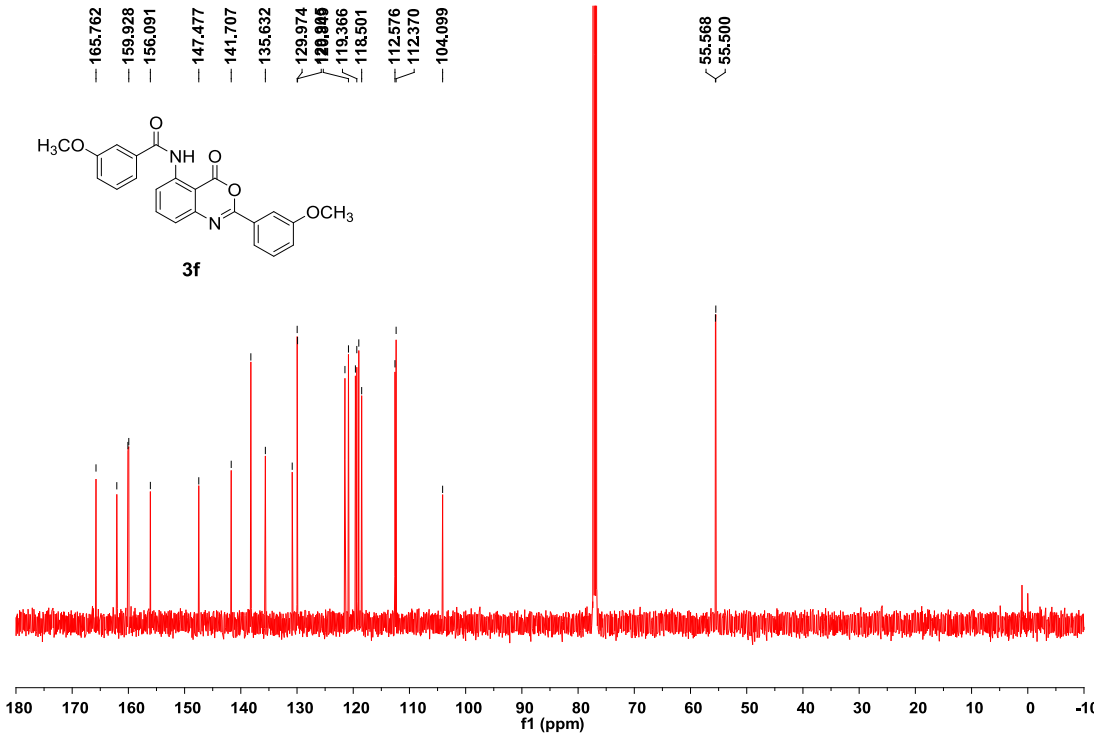
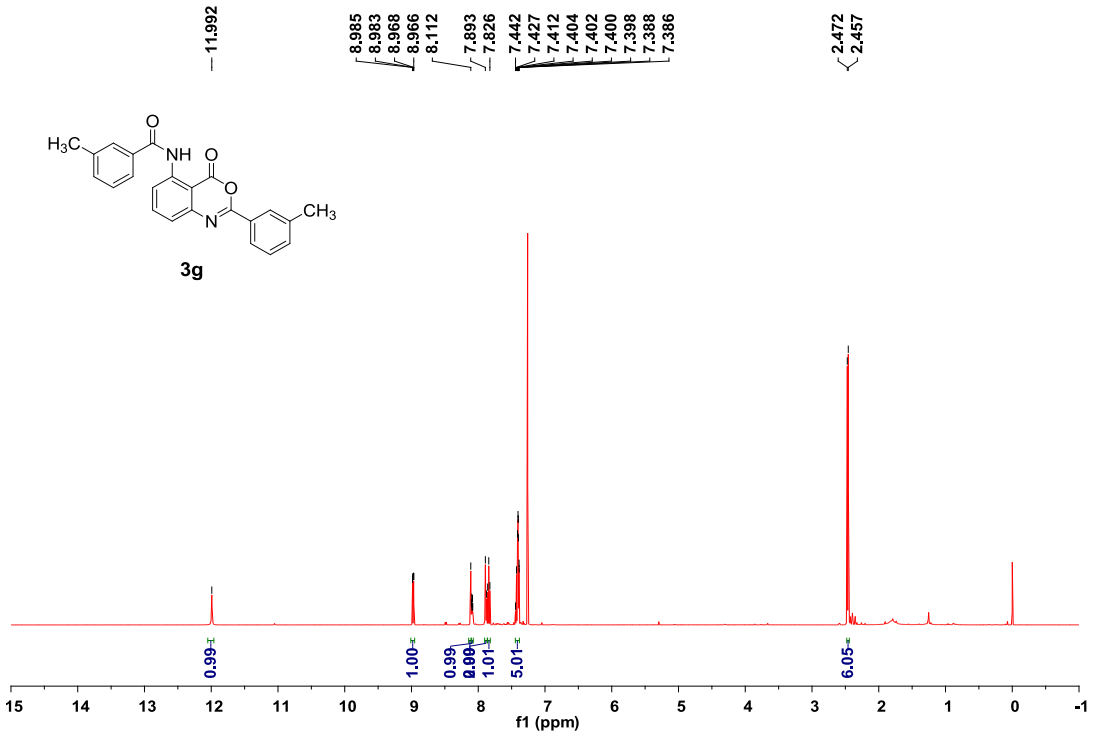
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

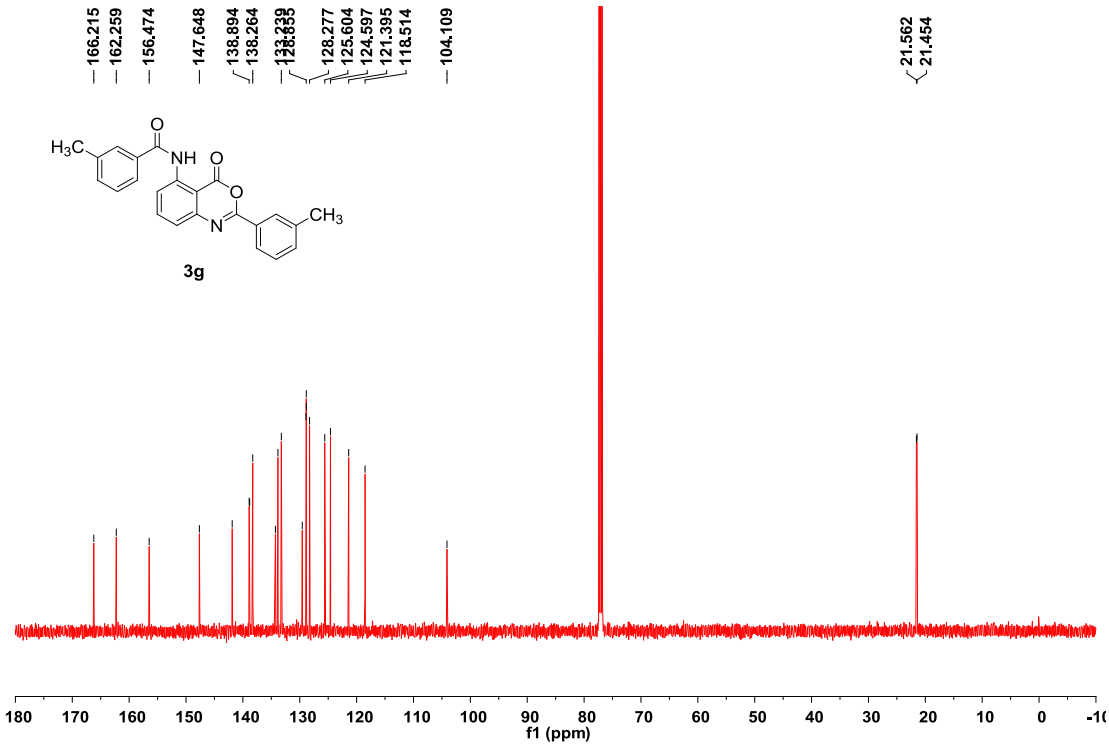
3-methoxy-N-(2-(4-methoxyphenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide(3f)



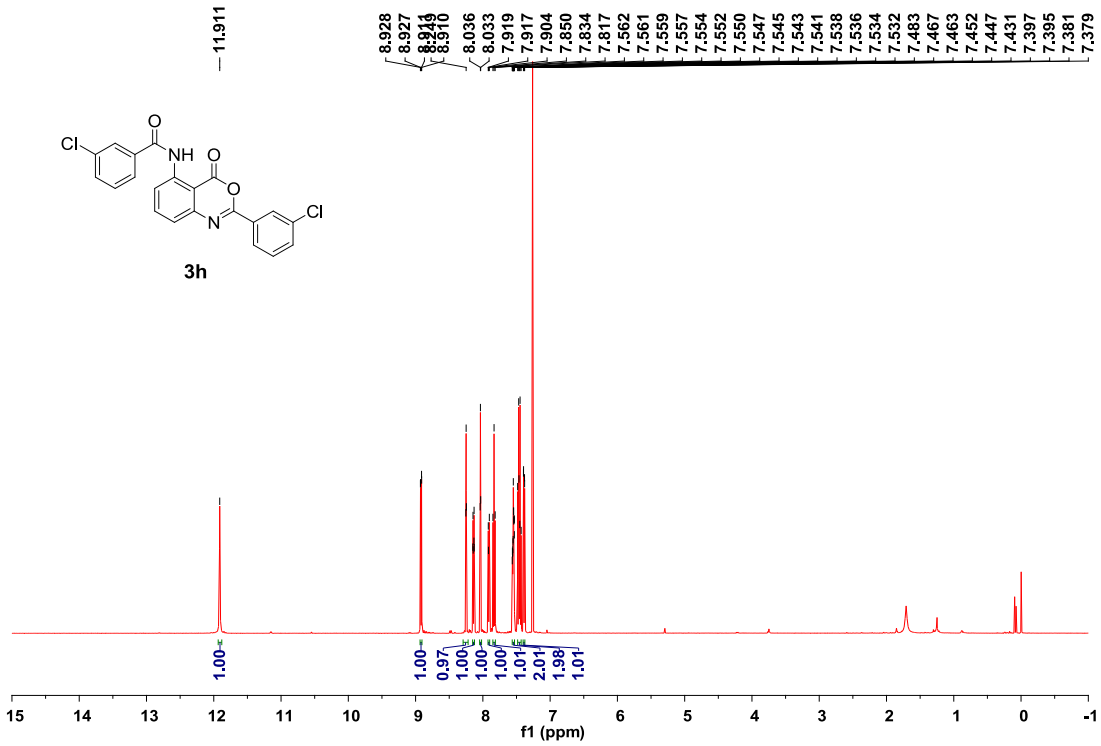


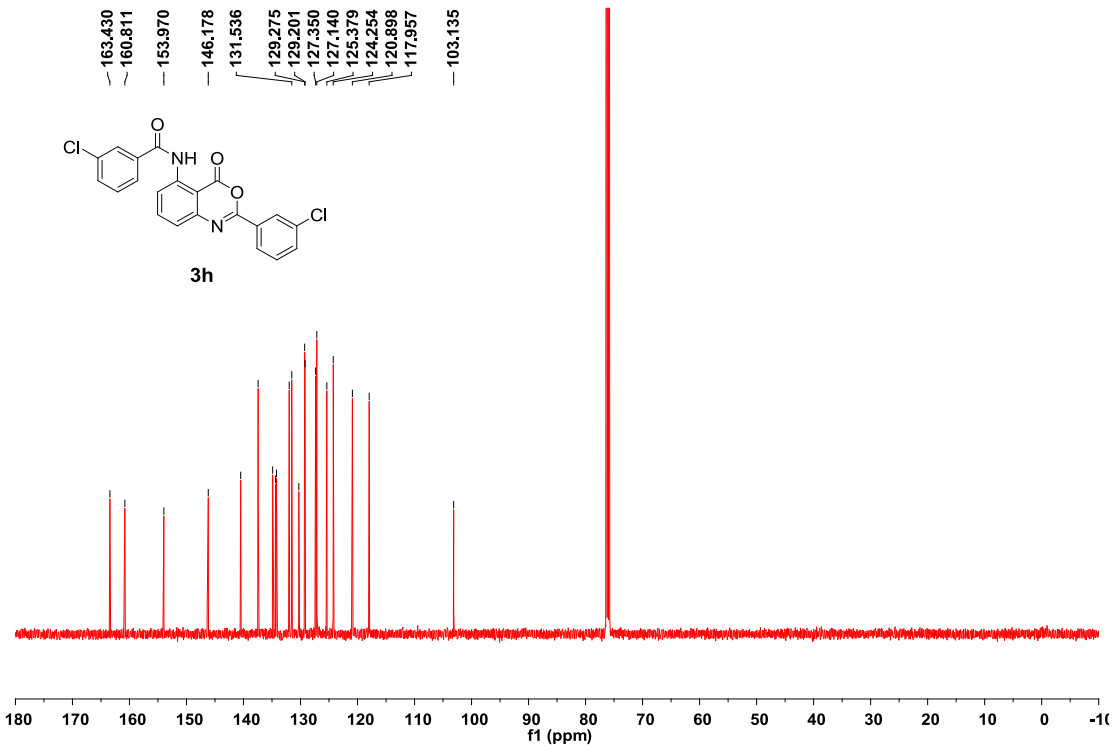
3-methyl-N-(4-oxo-2-(p-tolyl)-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3g)



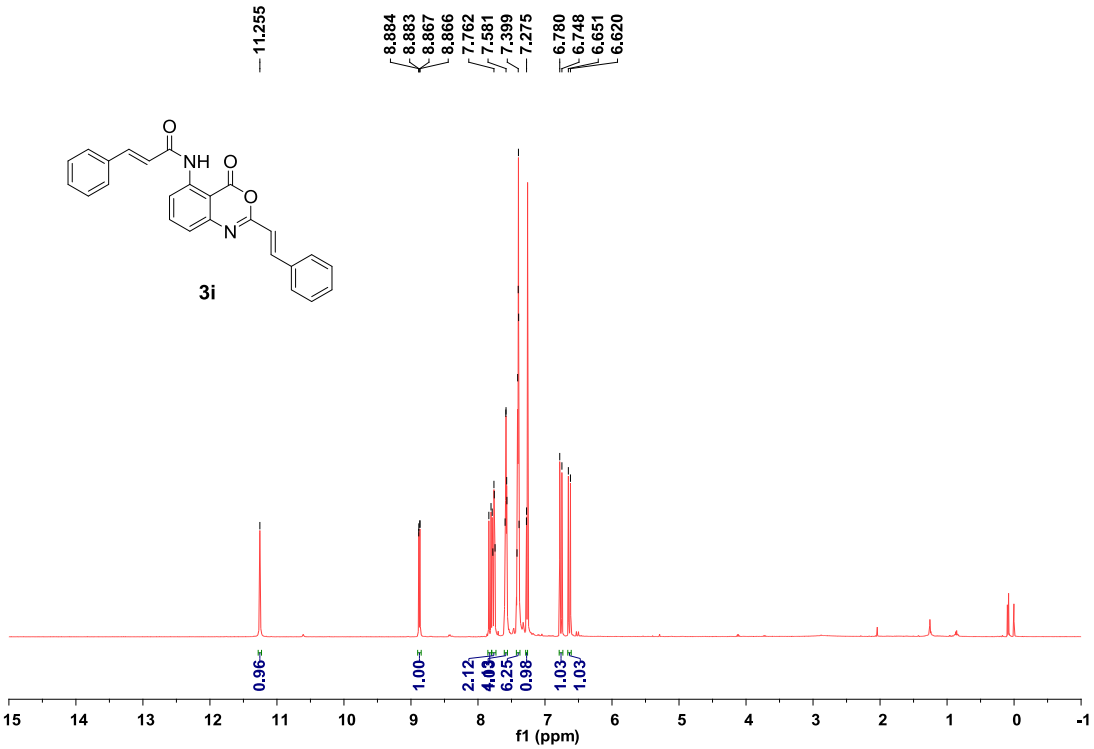


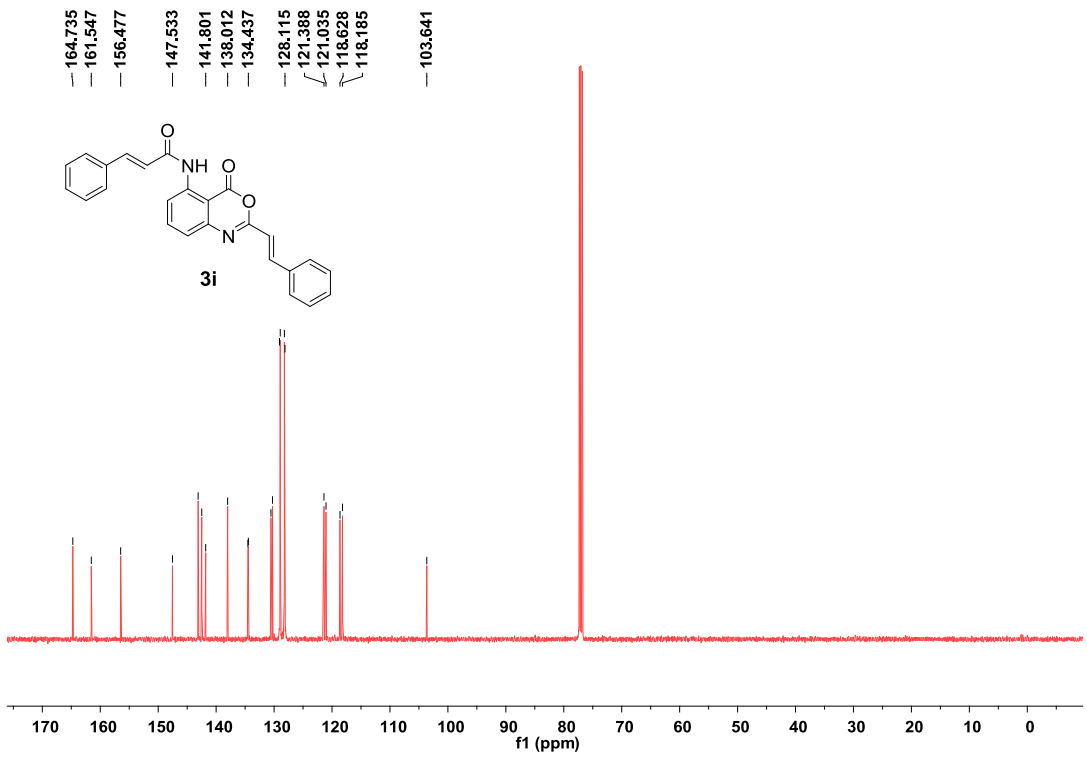
3-chloro-N-(2-(4-chlorophenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3h)



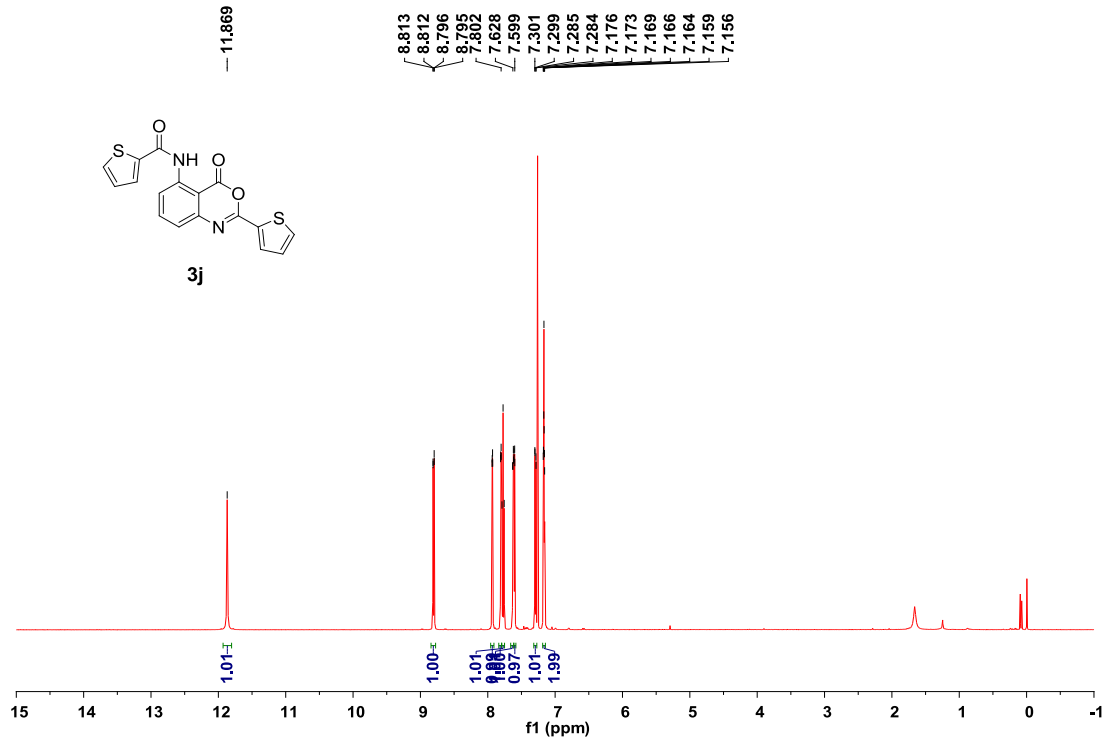


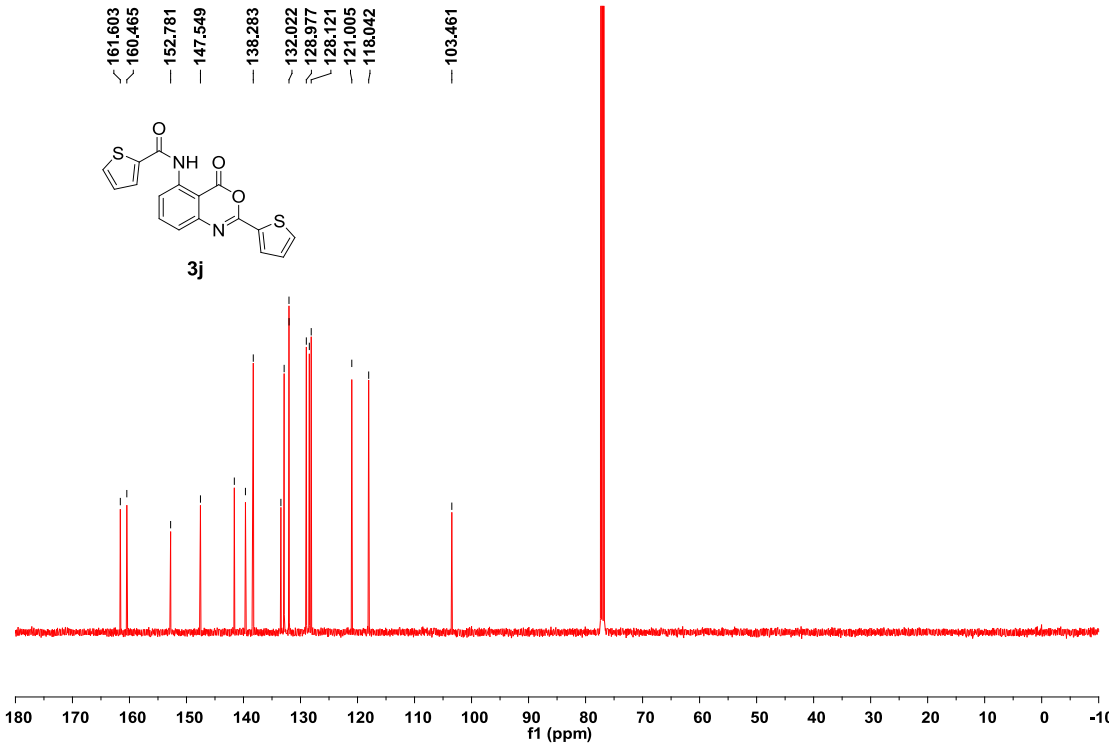
N-(4-oxo-2-((E)-styryl)-4H-benzo[d][1,3]oxazin-5-yl)cinnamamide (3i)



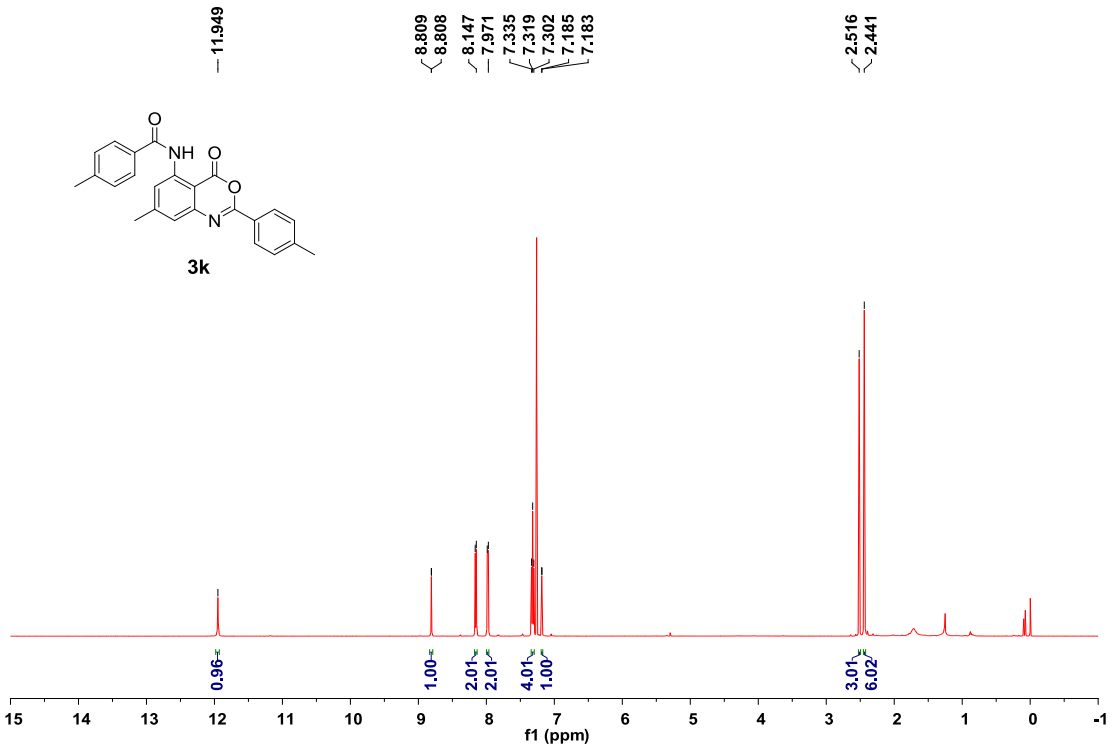


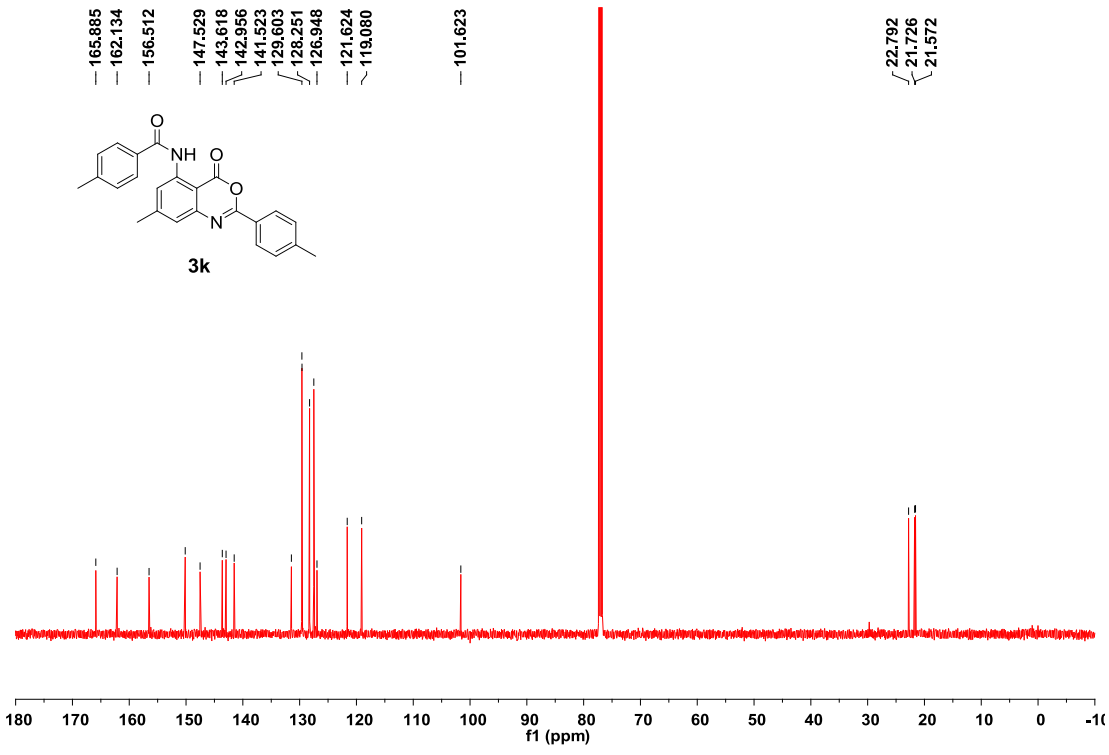
N-(4-oxo-2-(thiophen-2-yl)-4H-benzo[d][1,3]oxazin-5-yl)thiophene-2-carboxamide (3j)



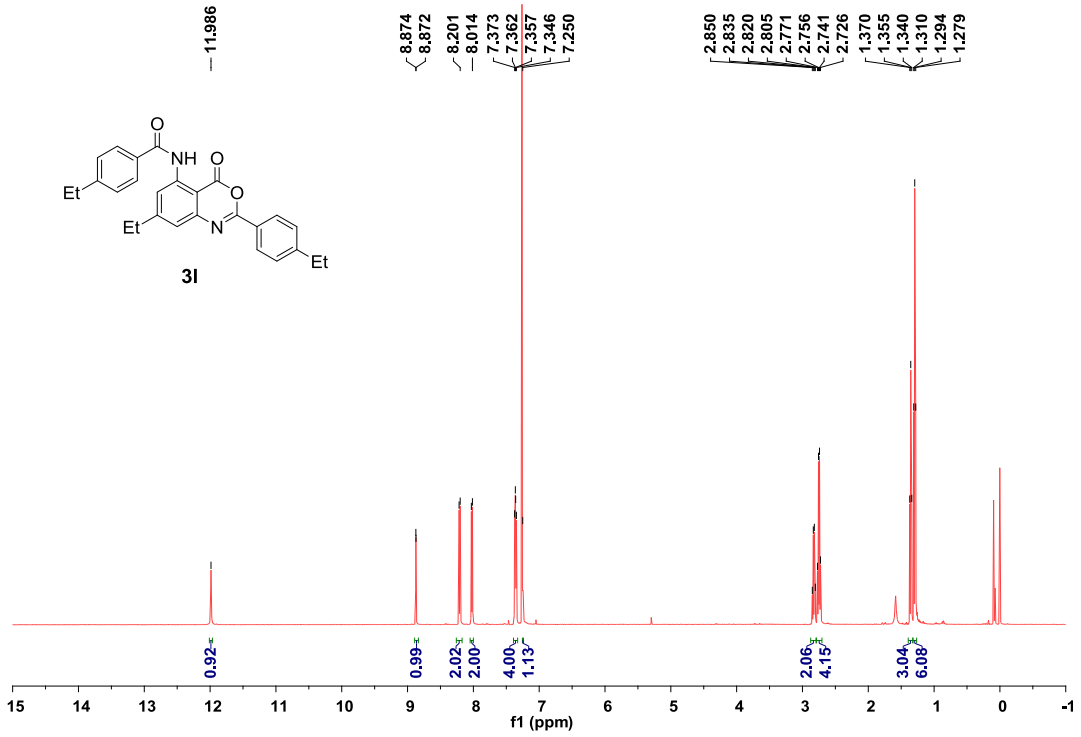


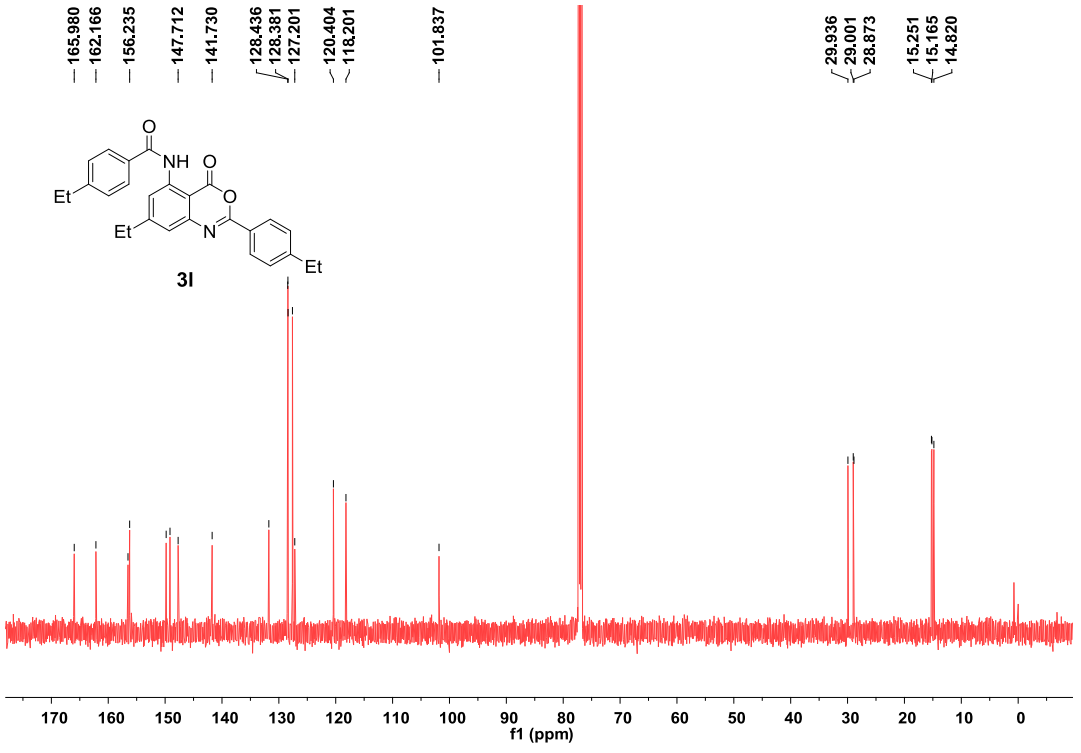
4-methyl-N-(4-oxo-2-(p-tolyl)-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3k)



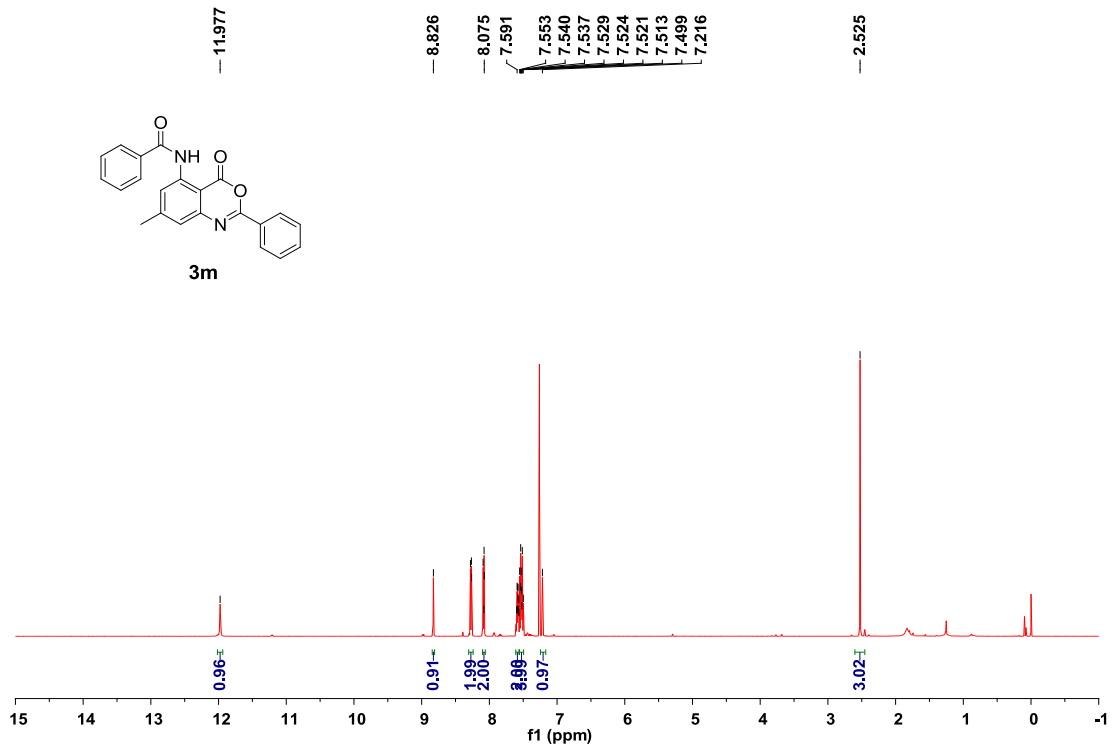


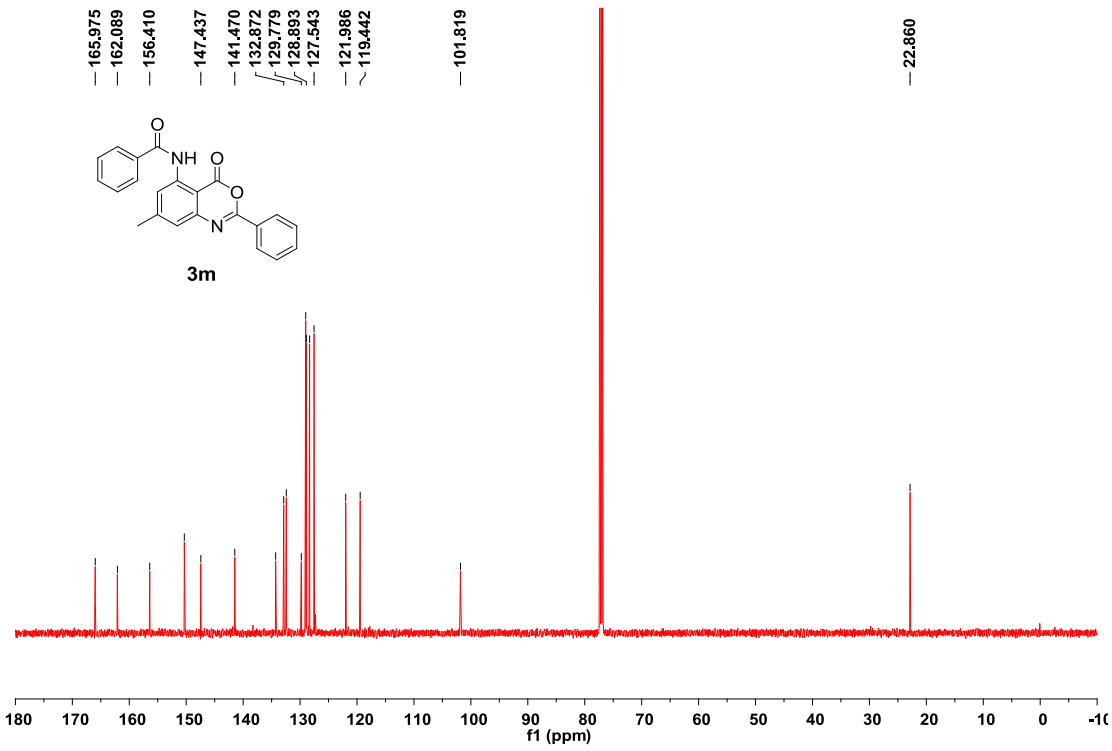
4-ethyl-N-(7-ethyl-2-(4-ethylphenyl)-4-oxo-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3l)



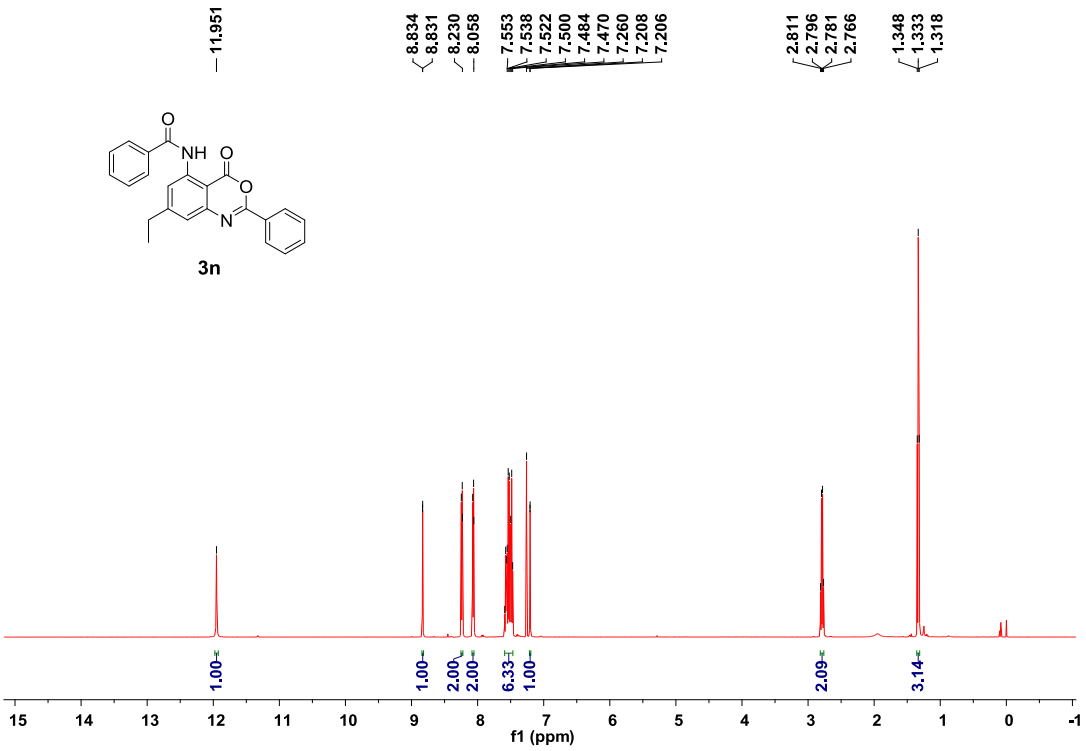


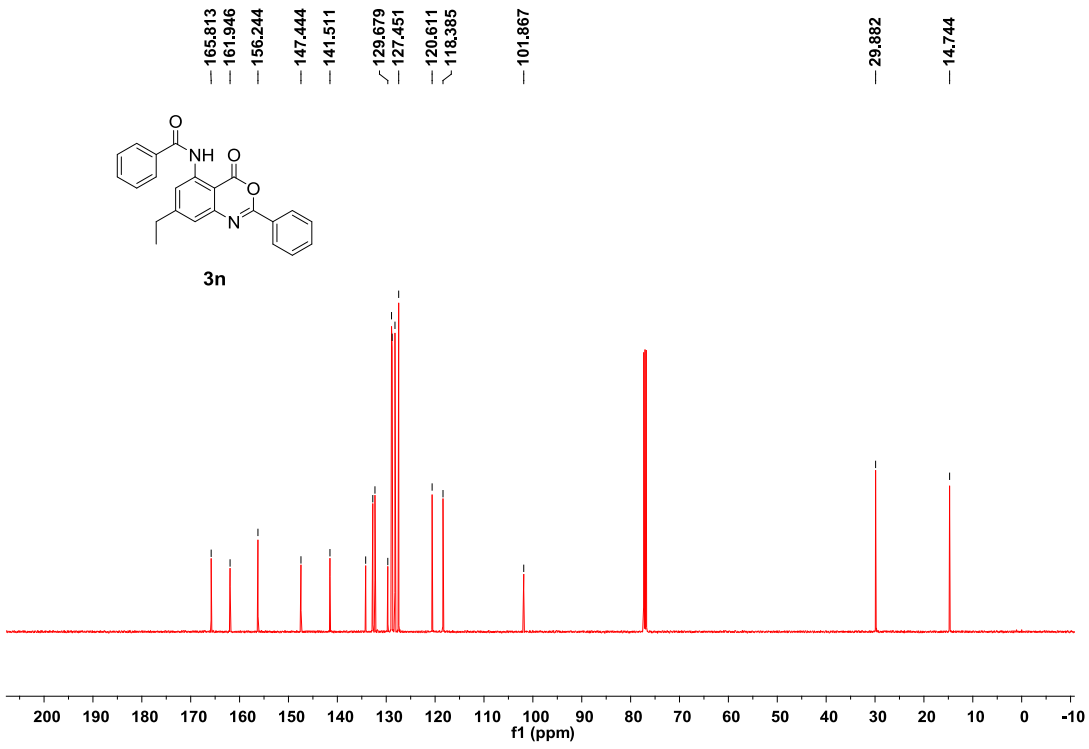
N-(7-methyl-4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3m)



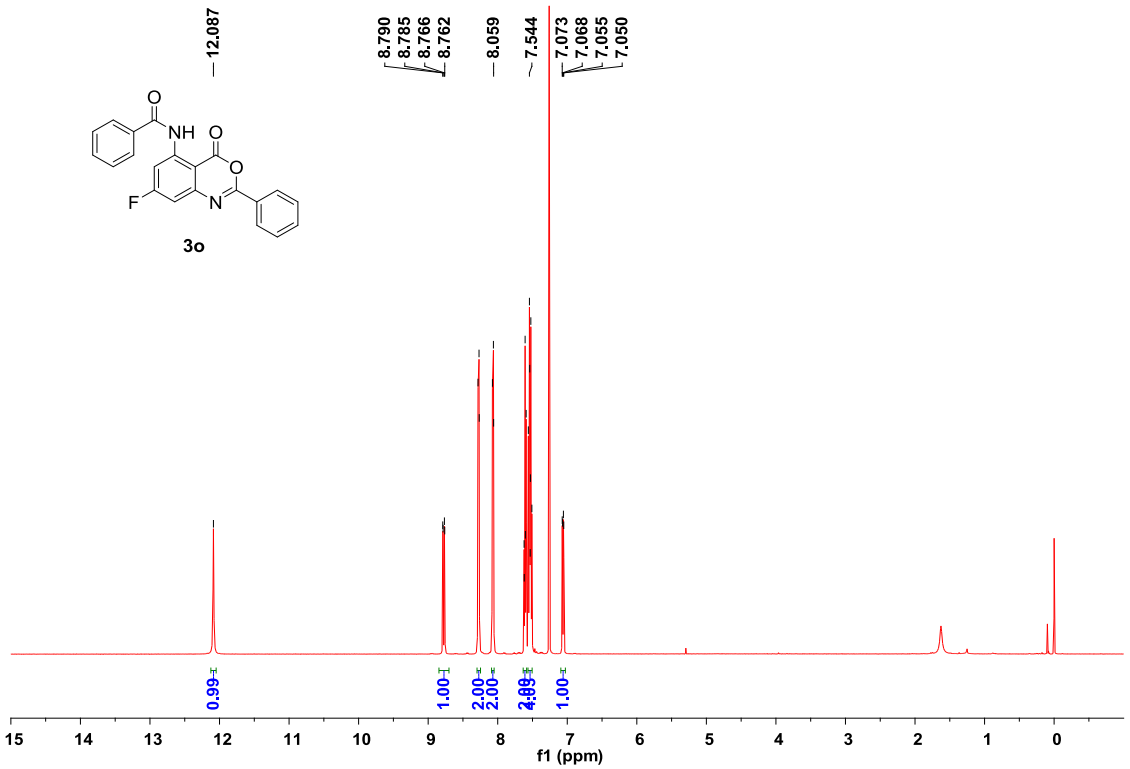


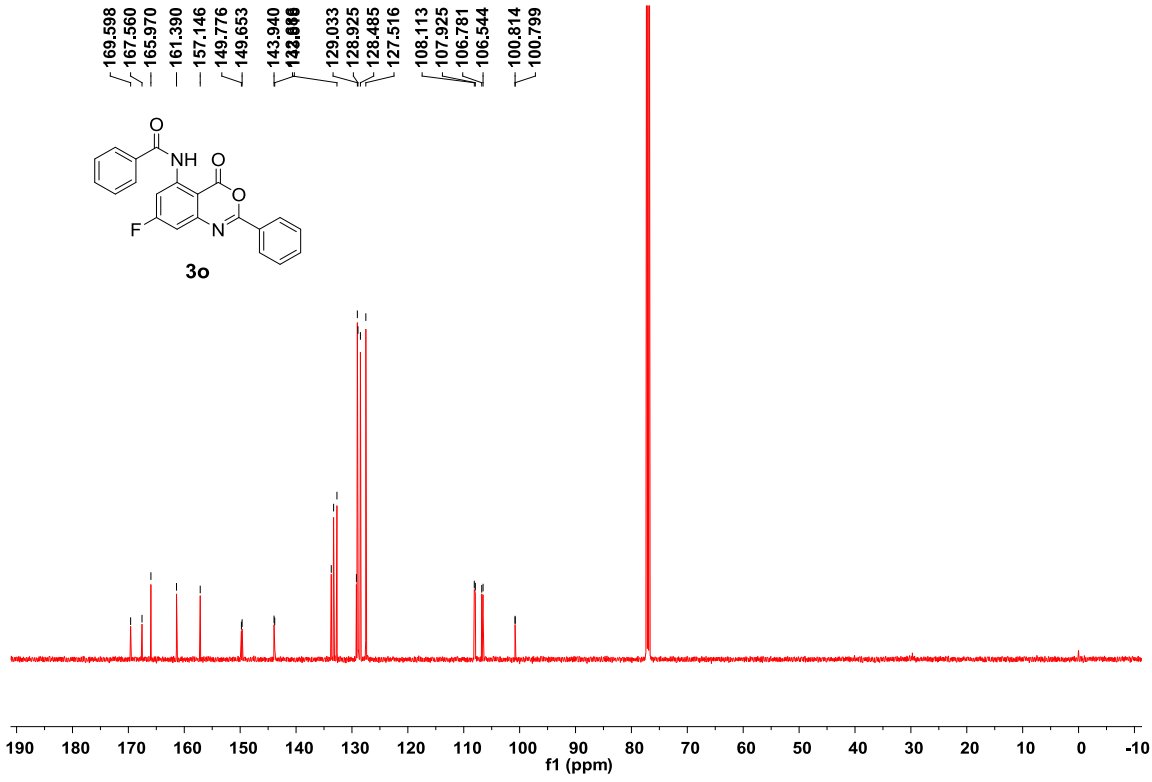
N-(7-ethyl-4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3n)

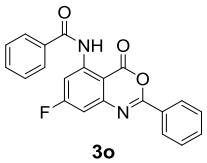




N-(7-fluoro-4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3o)



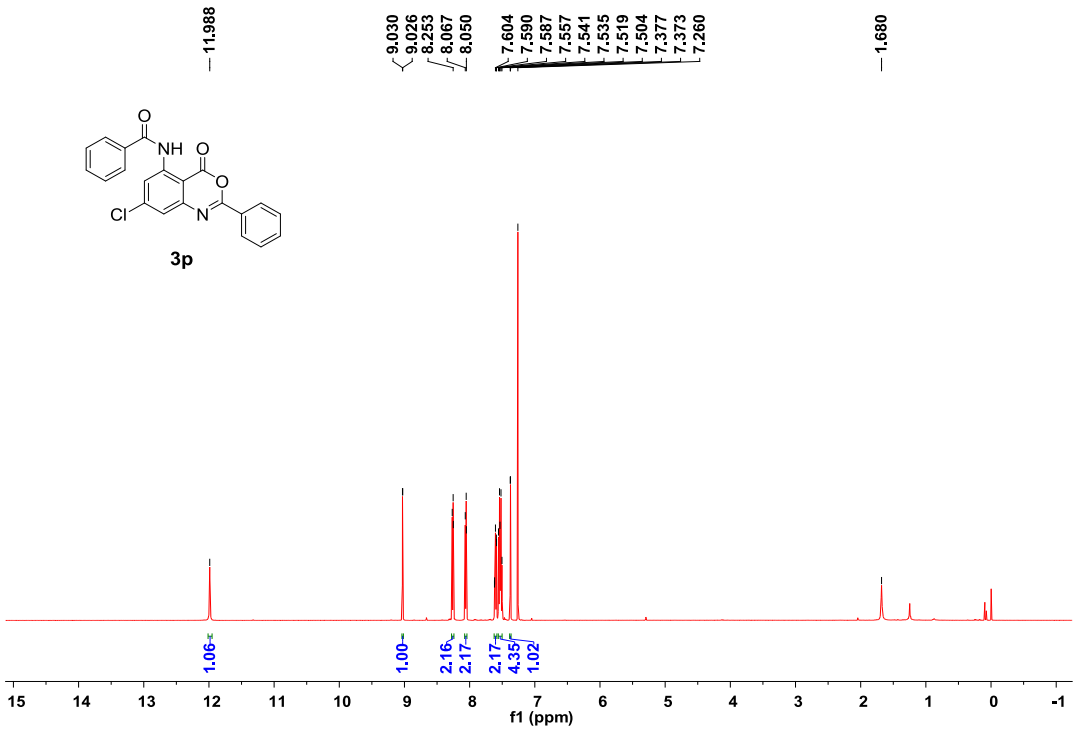


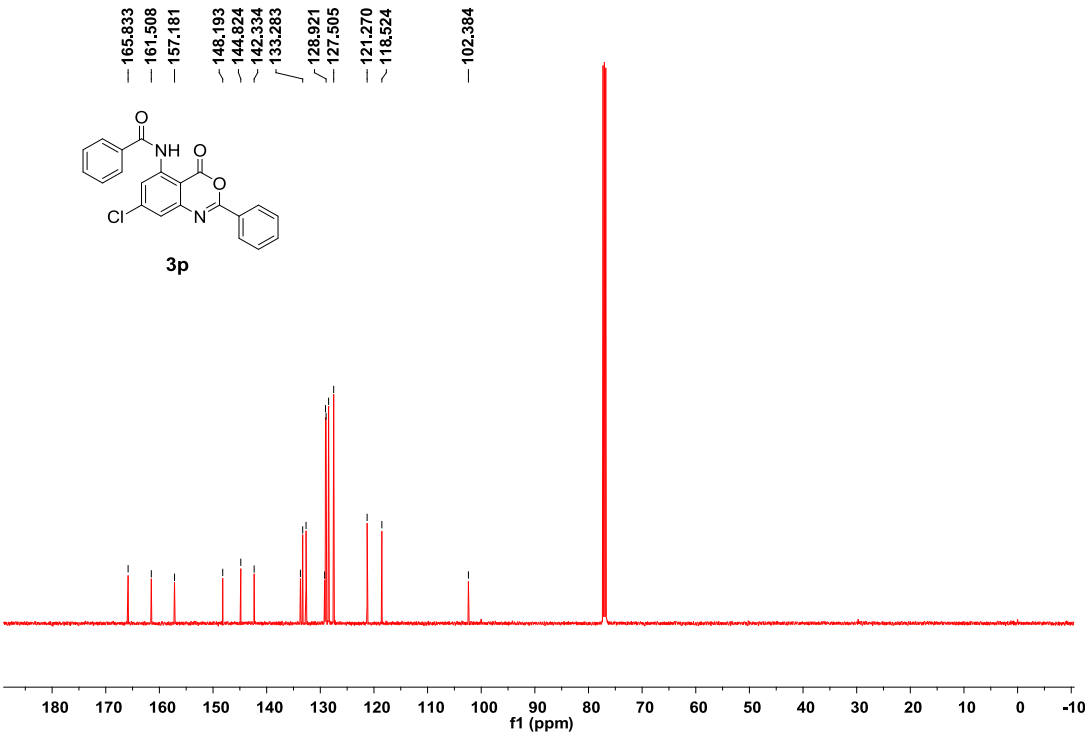

O
NH
O
O
F
N

3o

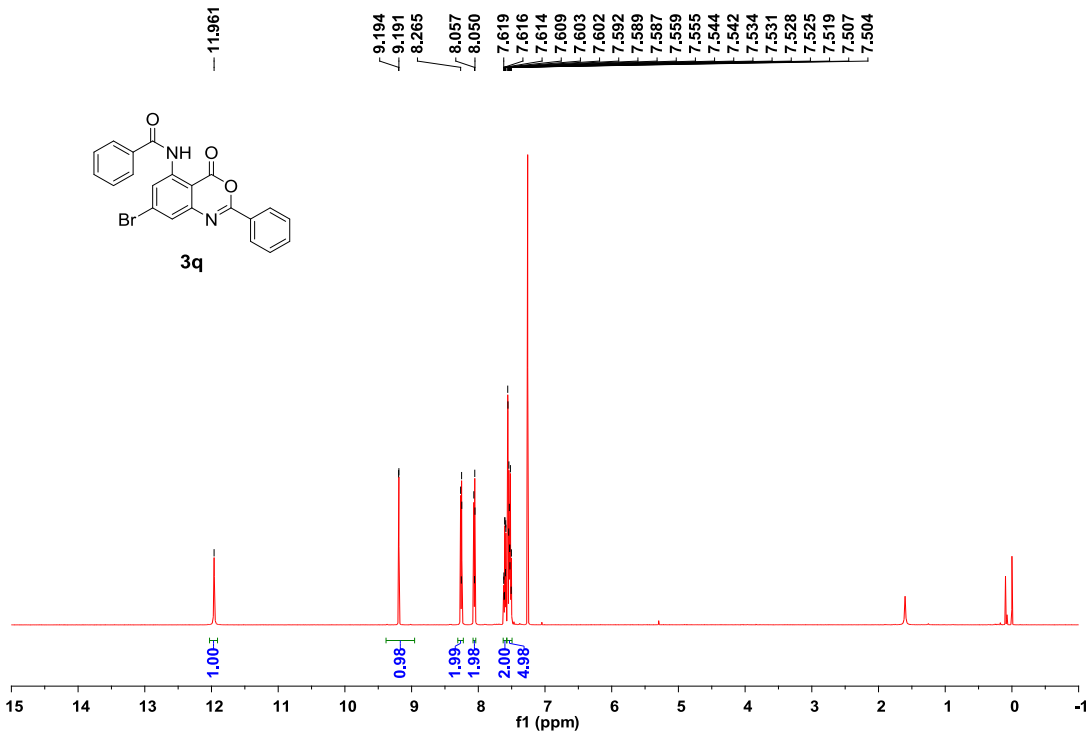
-93.883
-93.906
-93.927
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

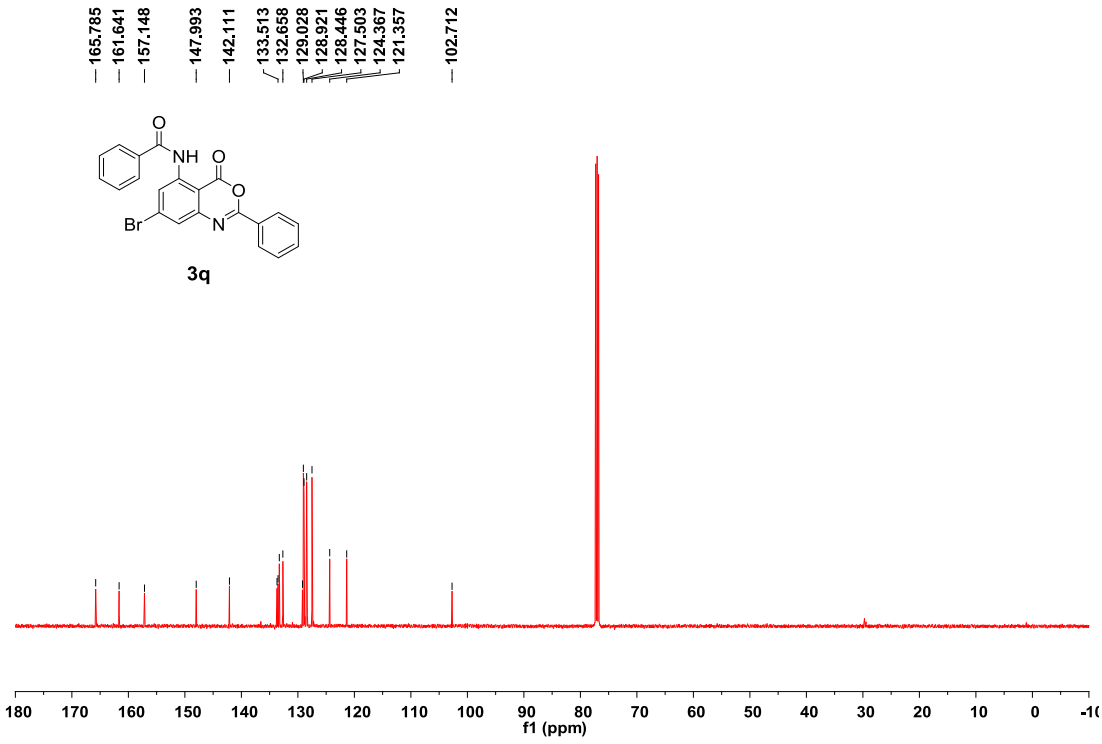
N-(7-chloro-4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3p)



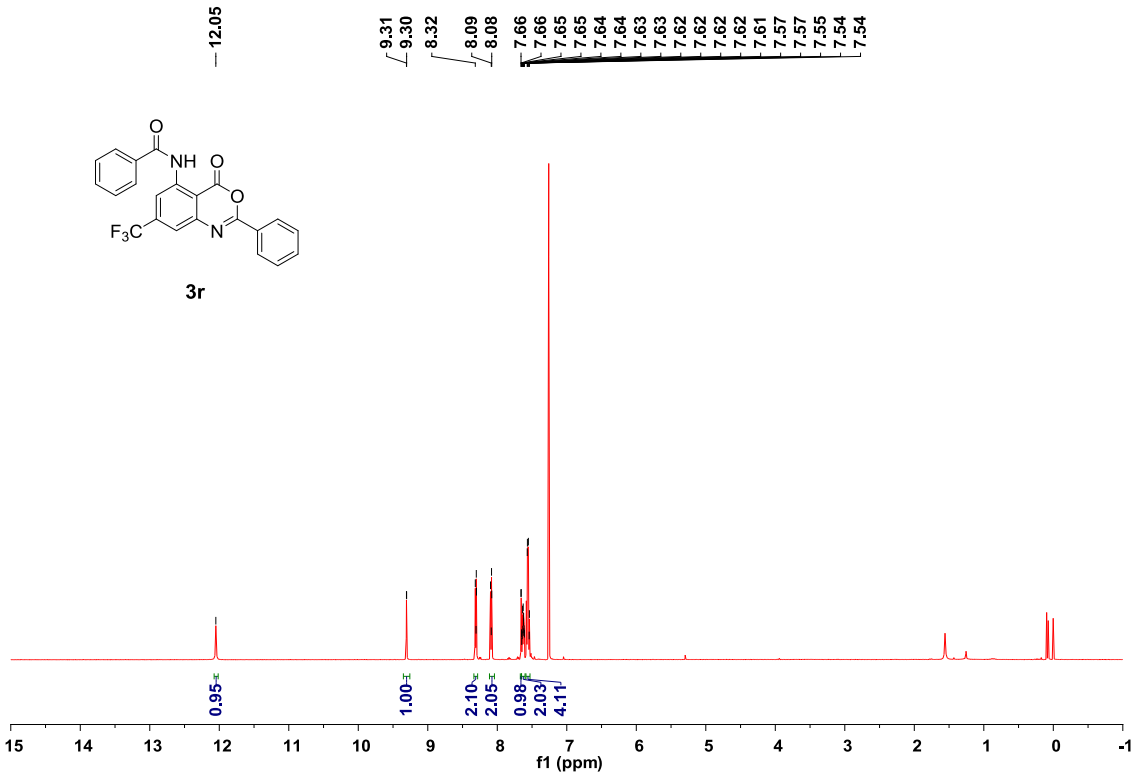


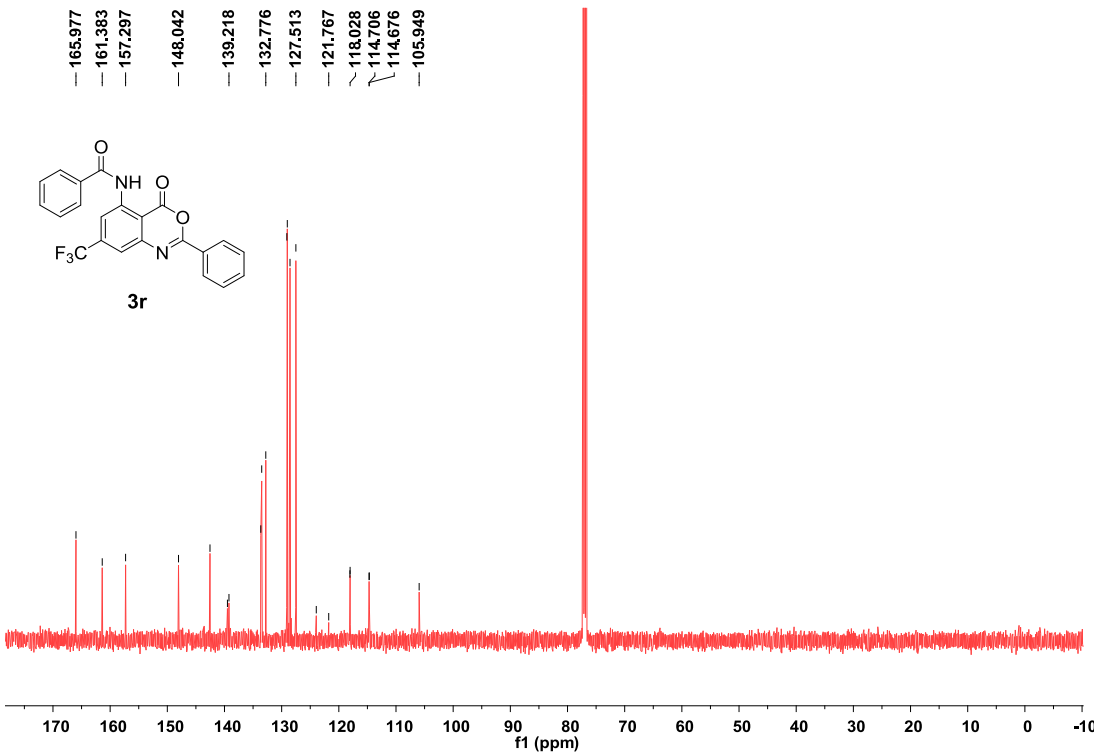
N-(7-bromo-4-oxo-2-phenyl-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3q)

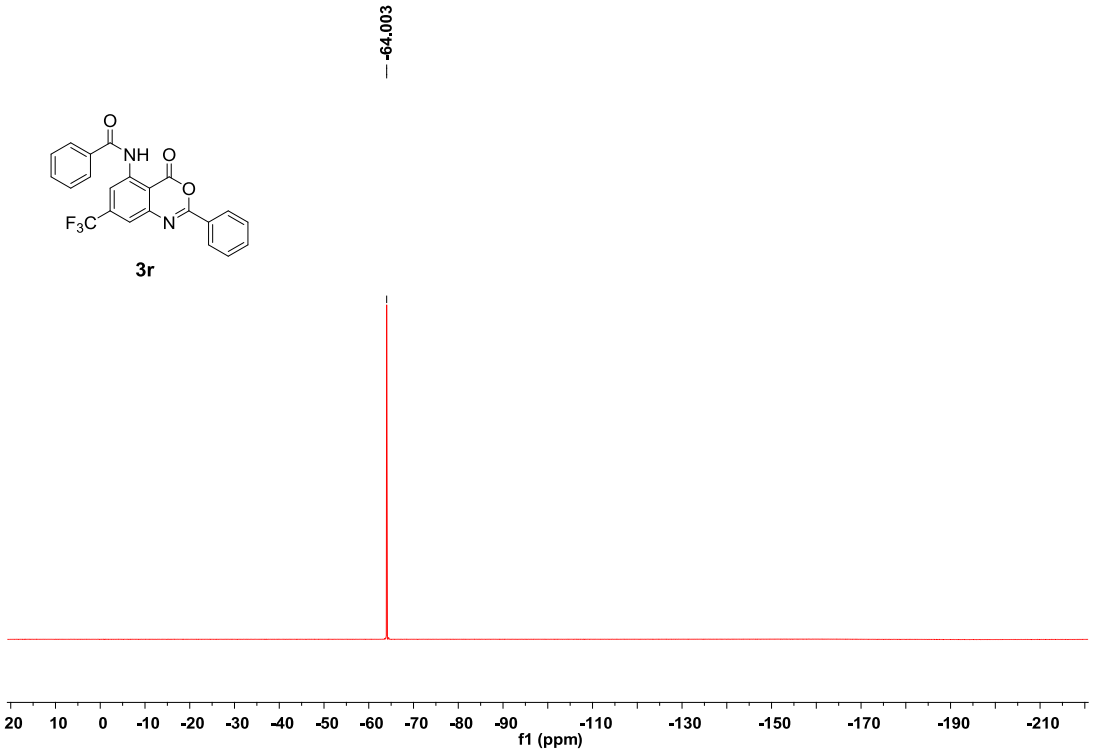




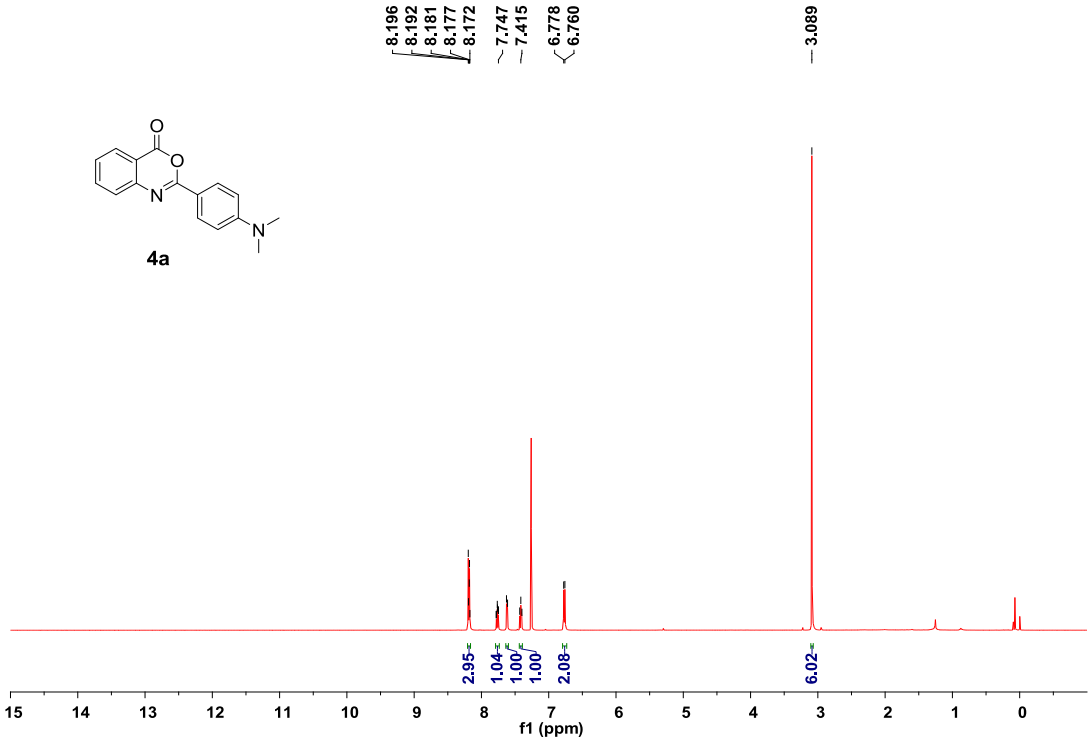
N-(4-oxo-2-phenyl-7-(trifluoromethyl)-4H-benzo[d][1,3]oxazin-5-yl)benzamide (3r)

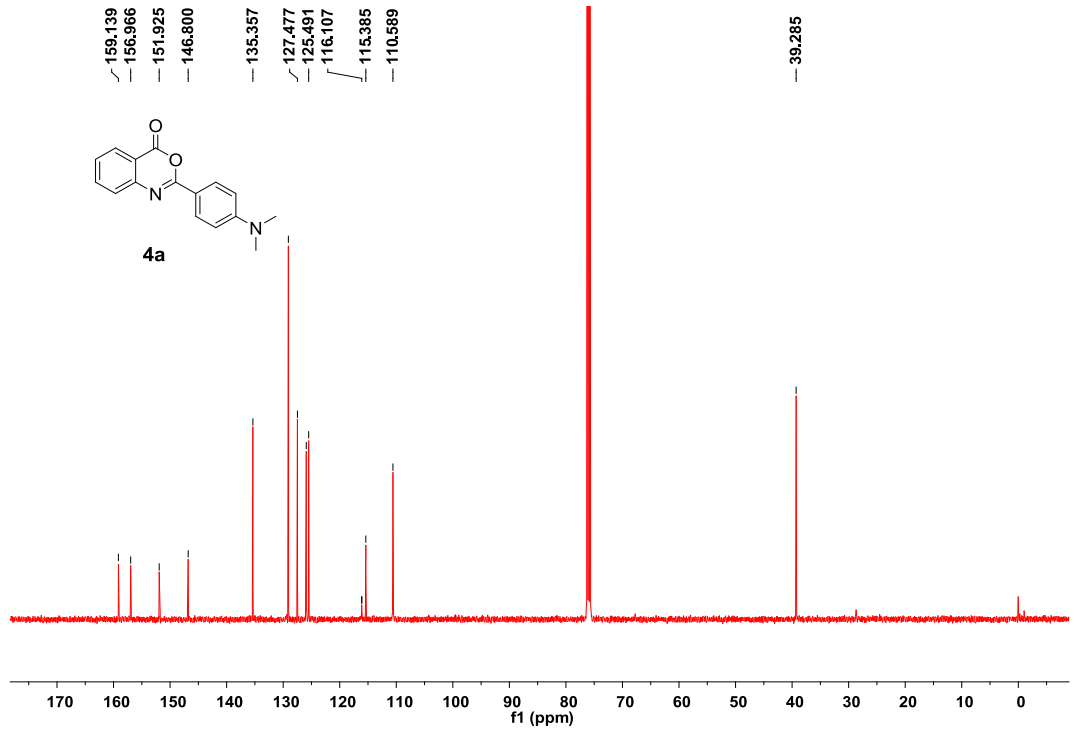




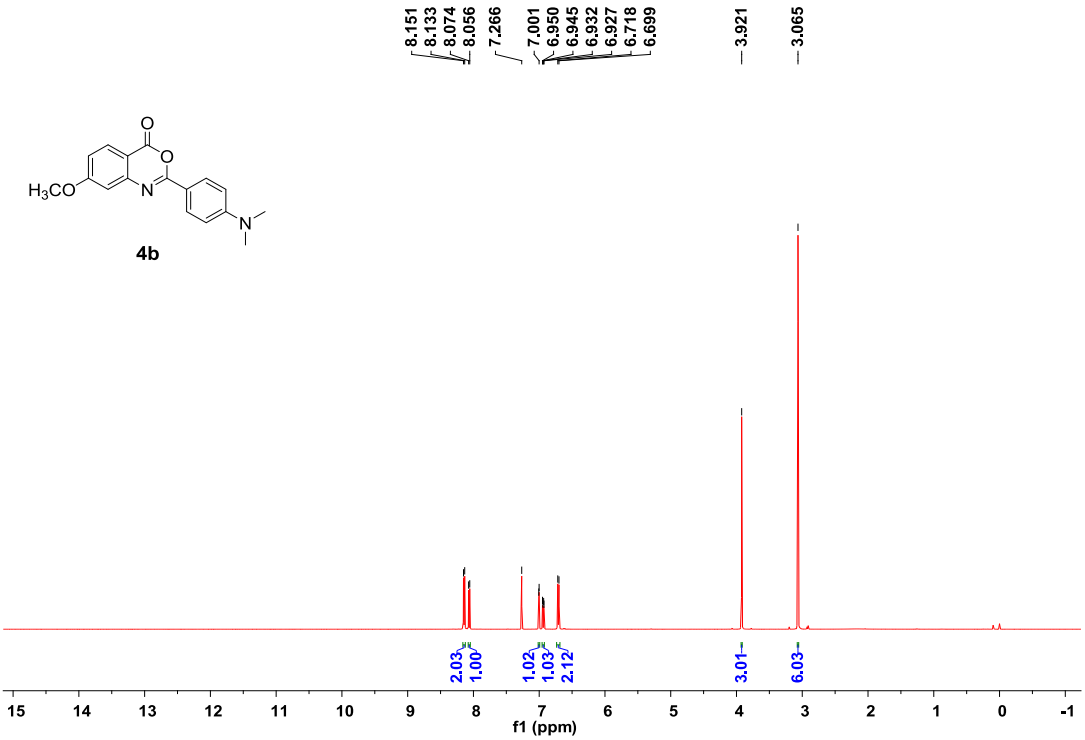

-64.003
O
NH
O
O
F3C
N
3r
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

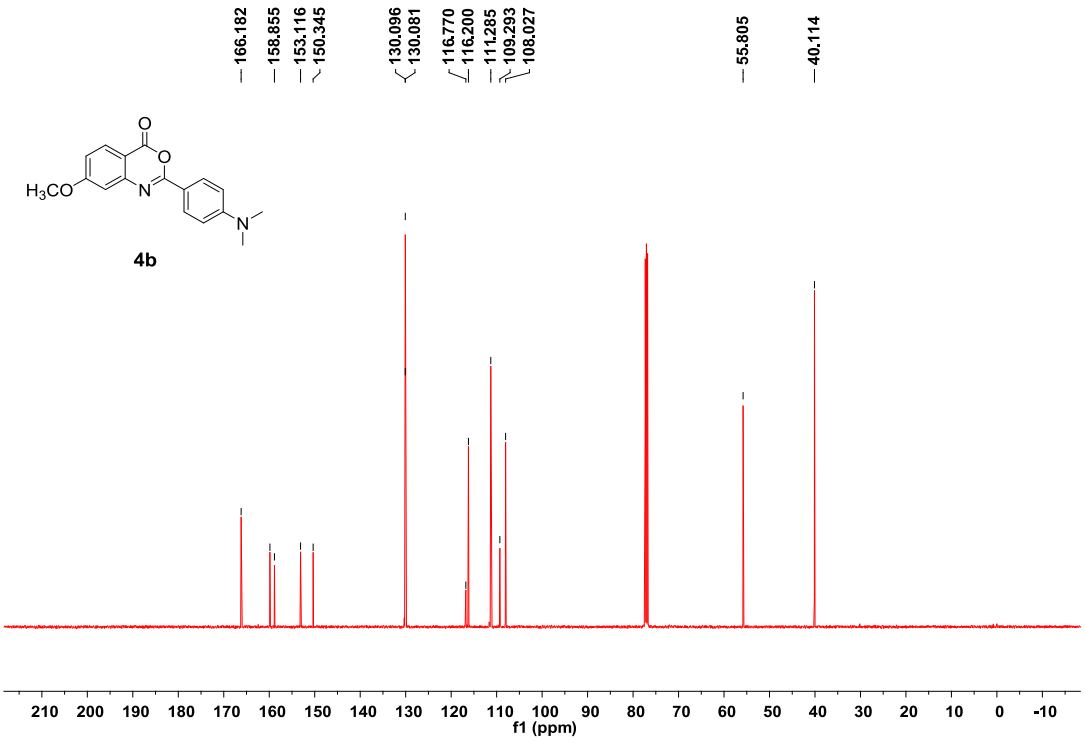
2-(4-(dimethylamino)phenyl)-4H-benzo[d][1,3]oxazin-4-one (4a)



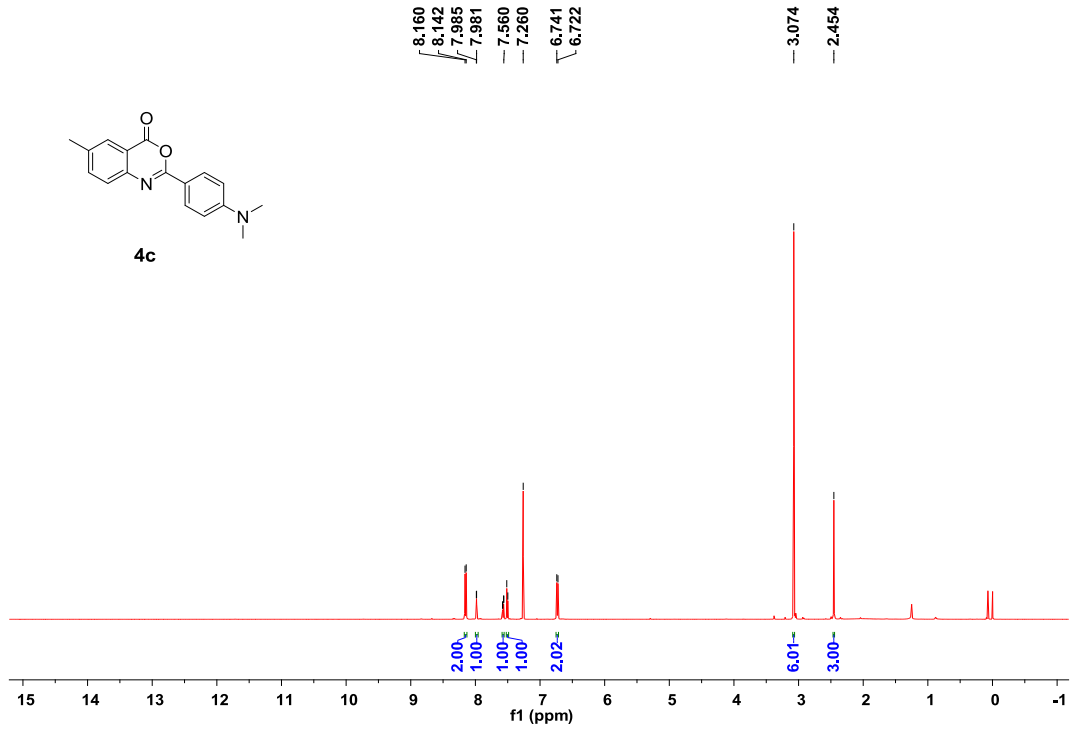


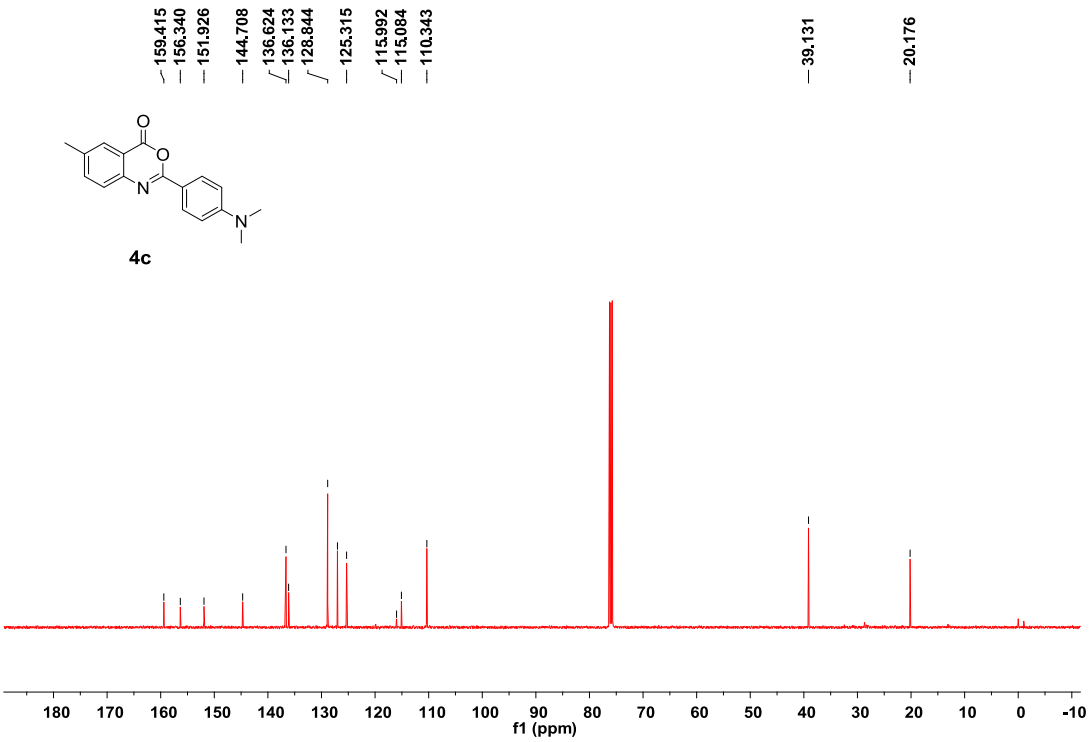
2-(4-(dimethylamino)phenyl)-7-methoxy-4H-benzo[d][1,3]oxazin-4-one (4b)



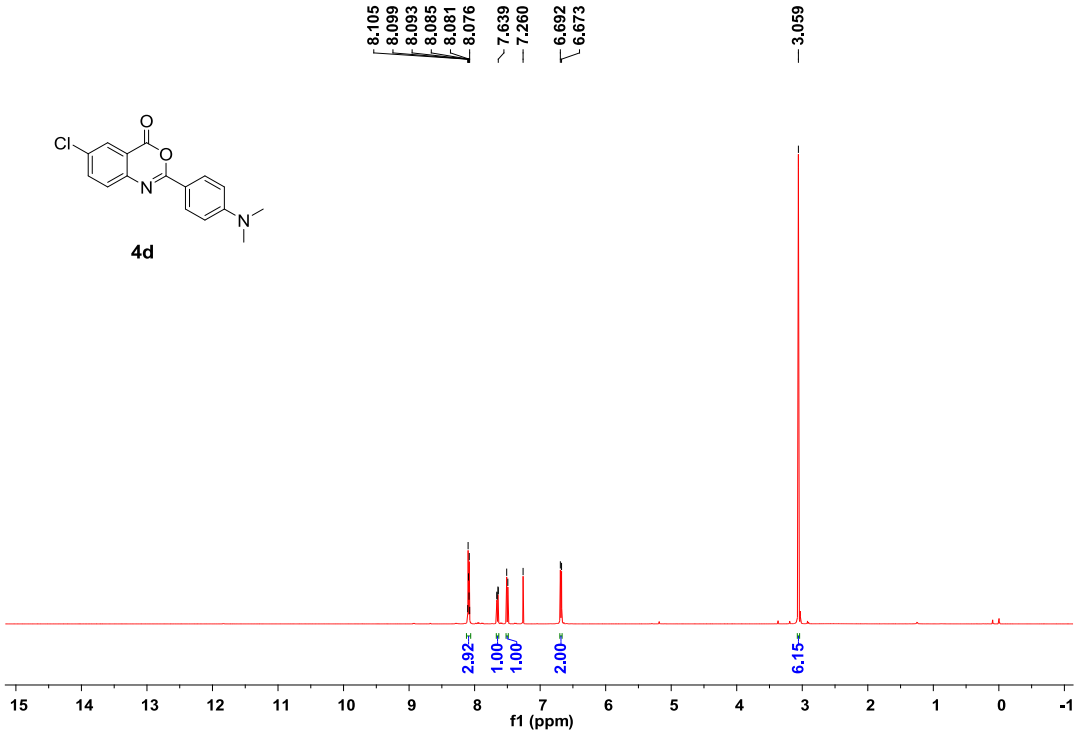


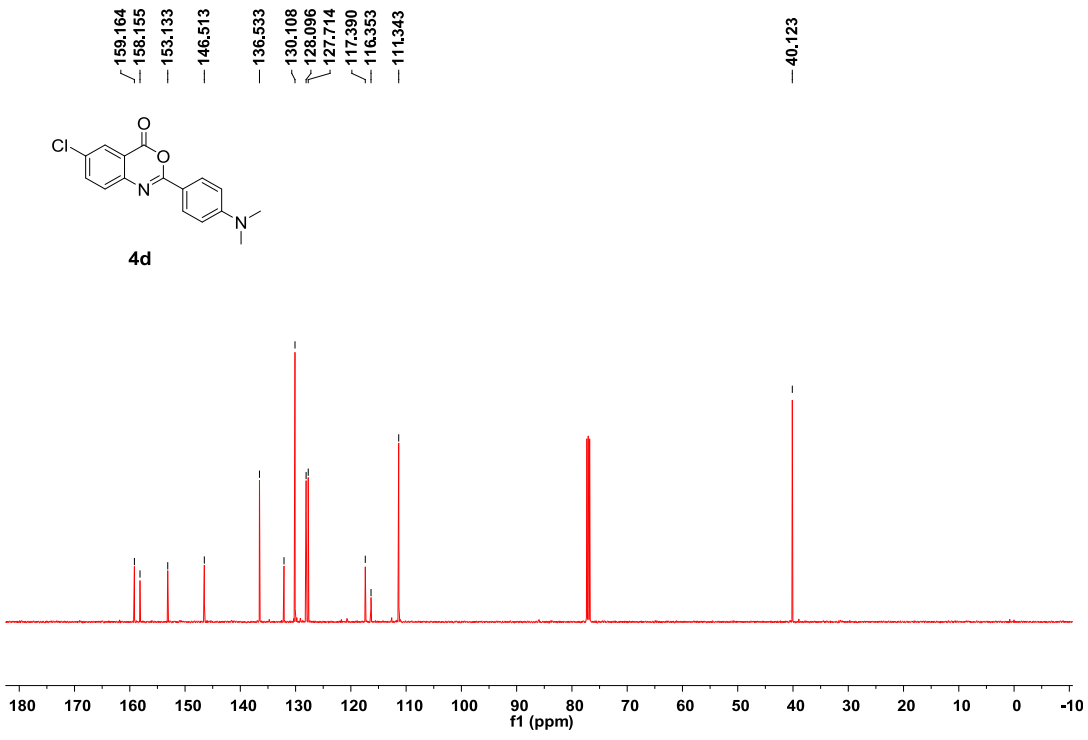
2-(4-(dimethylamino)phenyl)-6-methyl-4H-benzo[d][1,3]oxazin-4-one (4c)



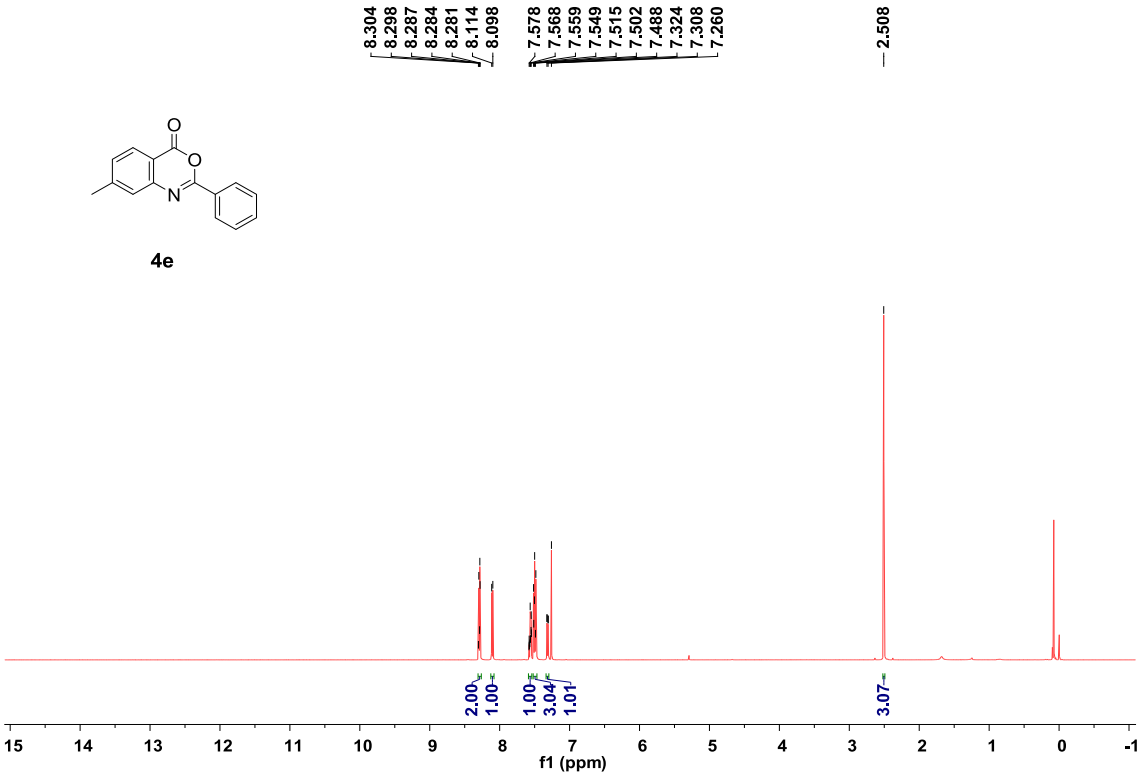


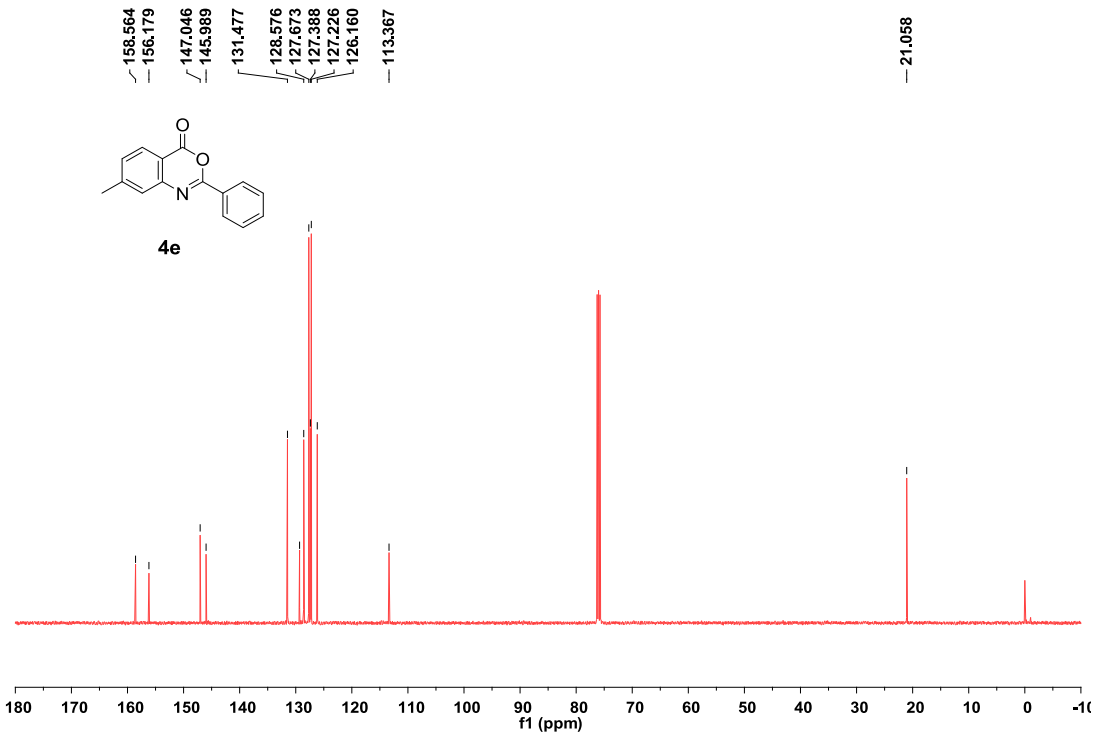
6-chloro-2-(4-(dimethylamino)phenyl)-4H-benzo[d][1,3]oxazin-4-one (4d)



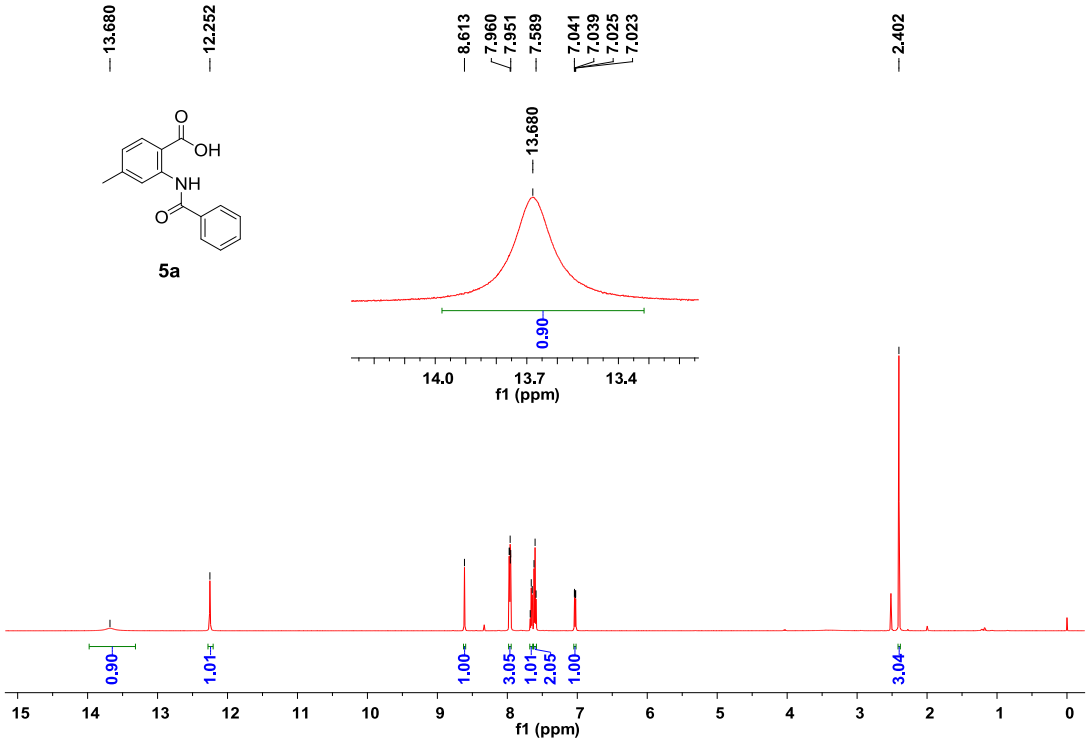


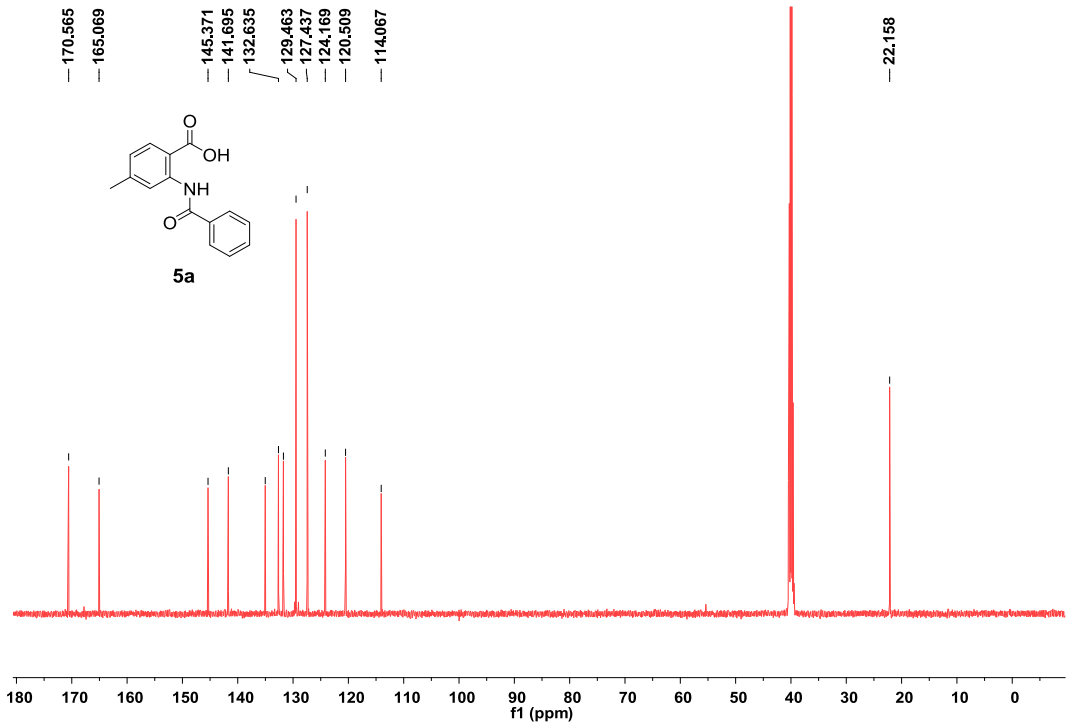
7-methyl-2-phenyl-4H-benzo[d][1,3]oxazin-4-one (4e)





2-benzamido-4-methylbenzoic acid (5a)





2-(4-(dimethylamino)benzamido)-4-methoxybenzoic acid (5b)