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Supporting Information

Carbonylation of Anthranilic Acid with Aryl and Heteroaryl Bromides to Synthesize Benzoxazinone Derivatives

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ajoc_201600253_sm_miscellaneous_information.pdf

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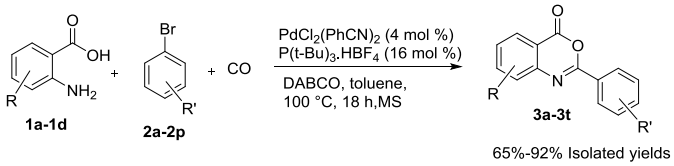
1. General information:–

All reactions were performed in 100 mL stainless steel high pressure reactor. Reactions were monitored on Perkin Elmer Clarus 400 GC equipped with flame ionization detector (FID) with a capillary column (30 m × 0.25 mm × 0.25 μm) and TLC on Merck silica gel 60 F254 plates visualized by UV lump at 254 nm. Products were purified by column chromatography on silica gel (120–200) mesh. All yields reported in Table 2 and Scheme 2 referred to isolated yields. While yields reported in Table 1 are GC yields. ^{1}H and ^{13}C NMR spectra were obtained on 400 and 500 MHz spectrometers using tetramethylsilane as internal standard in $CDCl_3$. Chemical shifts of ^{1}H NMR and ^{13}C NMR are reported as δ values relative to TMS and $CDCl^3$ respectively. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Single-crystal diffraction analysis were obtained on BRUKER KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) at 100K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). More information on crystal structures can also be obtained from the Cambridge Crystallographic Data Centre, CCDC 1443655 for 3s. Mass spectra were obtained on GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (df) = 0.25 μm) (column flow 2 mLmin-1, 80 °C to 240 °C at 10 °C/min rise). Reagents and anhydrous solvents were used as obtained from commercial vendors.

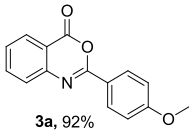
2. General procedure for the synthesis of benzoxazinones (3a-3t) from anthranilic acid:



To a 100 mL stainless steel high pressure reactor, anthranilic acid (1 mmol), aryl bromide (1.15 mmol), DABCO (2 mmol), $PdCl_2PhCN_2$ (3 mol %) and P(*t*-Bu)$_3$·HBF_4 (12 mol %) were added in 10 mL anhydrous toluene. The 400 mg activated 3 Å MS were added in the reaction mixture and the autoclave was closed. The autoclave was purged three times with carbon monoxide, pressurized with CO 200 psi at ambient temperature. The reaction mixture was stirred with a mechanical stirrer (500 rpm) at the 100 °C temperature for 24 h. After completion of reaction, the reactor was cooled to room temperature and the remaining CO was carefully vented. The reactor vessel was washed with ethyl acetate (3 × 10 mL) to remove traces of product, if present. The ethyl acetate layer was washed with water (2 × 10 mL), dried over Na_2SO_4, and the solvent was evaporated under vacuum. The crude residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether as eluents to give corresponding benzoxazinones.

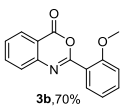
Representative analytical data of benzoxazinones:

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



Isolated as a white solid 233 mg (92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.8 Hz, 2H), 8.20 (d, J = 7.9 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.23, 159.81, 157.09, 147.27, 136.50, 130.25, 128.53, 127.70, 126.88, 122.54, 116.66, 114.12, 55.50.

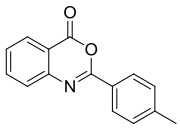
2-(2-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3b) [1]



Isolated as a white solid 177 mg (70%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (dd, J = 7.8, 1.5 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.72 (d, J = 7.6 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.09 – 7.03 (m,

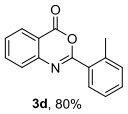
2H), 3.94 (s, 3H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 158.5, 157.7, 147.0, 136.4, 133.2, 131.3, 128.4, 128.3, 127.2, 120.5, 120.5, 116.9, 112.1, 56.0.

2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3c) [2]



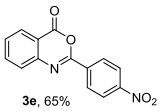
Isolated as a white solid 216 mg (91%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23-8.18 (m, 3H), 7.80 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.7, 157.2, 147.1, 143.3, 136.4, 129.4, 128.5, 128.2, 127.9, 127.4, 127.0, 116.9, 21.6.

2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3d) [3]



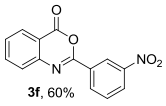
Isolated as a white solid 190 mg (80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 – 8.25 (m, 1H), 8.04 (d, J = 7.9 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.72 – 7.68 (m, 1H), 7.57 – 7.52 (m, 1H), 7.46 – 7.41 (m, 1H), 7.36 – 7.31 (m, 2H), 2.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 158.3, 146.8, 139.1, 136.4, 131.9, 131.5, 130.1, 129.8, 128.4, 128.4, 127.2, 126.0, 116.7, 22.2.

2-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3e) [4]



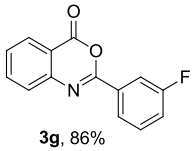
Isolated as a white solid 174 mg (65%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 – 8.48 (m, 2H), 8.39 – 8.34 (m, 2H), 8.30 – 8.26 (m, 1H), 7.92 – 7.87 (m, 1H), 7.77 – 7.74 (m, 1H), 7.63 – 7.58 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 154.9, 150.1, 146.2, 136.9, 135.8, 129.3, 129.2, 129.2, 128.8, 127.6, 123.8, 123.8, 117.1.

2-(3-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3f) [4]



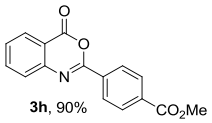
Isolated as a white solid 161 mg (60%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.51 (d, J = 7.8 Hz, 1H), 8.31 (d, J = 8.3 Hz, 1H), 8.15 (d, J = 7.9 Hz, 1H), 7.77 (t, J = 7.4 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.48 (t, J = 7.5 Hz, 1H).

2-(3-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3g) [4]



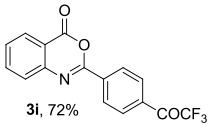
Isolated as a white solid 207 mg (86%);[1]H NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, J = 7.8 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.81 (t, J = 7.7 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.56 – 7.41 (m, 2H), 7.29 – 7.20 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.0, 161.5, 159.1, 155.8, 155.8, 146.5, 136.6, 132.4, 132.3, 130.3, 130.3, 128.6, 128.5, 127.3, 123.9, 123.9, 119.7, 119.5, 116.9, 115.2, 115.0.

methyl 4-(4-oxo-4*H*-benzo[*d*][1,3]oxazin-2-yl)benzoate (3h)



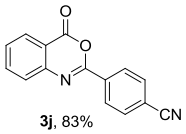
Isolated as a white solid 253 mg (90%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.38 (d, J = 8.0 Hz, 2H), 8.25 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 8.0 Hz, 2H), 7.85 (t, J = 7.6 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.2, 159.1, 156.5, 146.6, 136.8, 133.4, 129.8, 128.7, 128.6, 128.2, 127.4, 117.0, 114.5, 52.4.
HRMS (ESI): calc. for $[(C_{16}H_{11}NO_4)H]^+$ 282.0766, measured 282.0763.

2-(4-(2,2,2-trifluoroacetyl)phenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3i)



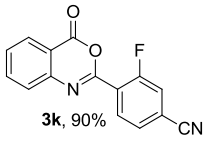
Isolated as a white solid 230 mg (72%);[1]H NMR ($CDCl_3$, 400 MHz): δ 8.46 (d, J = 8.8 Hz, 2H), 8.25 (d, J = 8.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 2H), 7.86 (t, J = 7.6 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.5, 180.1, 179.7, 179.4, 158.8, 155.2, 146.3, 136.8, 136.3, 132.4, 130.2, 130.2, 129.2, 128.7, 128.6, 127.6, 117.8, 117.1, 115.
HRMS (ESI): calc. for $[(C_{16}H_8F_3NO_3)H]^+$ 320.0535, measured 320.0529.

4-(4-oxo-4*H*-benzo[*d*][1,3]oxazin-2-yl)benzonitrile (3j)



Isolated as a white solid 206 mg (83%);[1]H NMR ($CDCl_3$, 400 MHz): δ 8.39 (d, J = 8.2 Hz, 2H), 8.24 (d, J = 7.7 Hz, 1H), 7.85 (t, J = 7.5 Hz, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H)

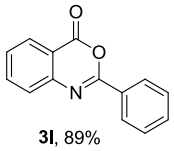
3-fluoro-4-(4-oxo-4*H*-benzo[*d*][1,3]oxazin-2-yl)benzonitrile (3k)



3k, 90%

Isolated as a white solid 240 mg (90%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.28 – 8.24 (m, 2H), 7.89 – 7.85 (m, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.62 – 7.51 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.0, 159.3, 158.4, 146.0, 136.8, 132.1, 129.5, 128.7, 127.9, 127.90, 127.7, 121.2, 120.9, 117.0, 116.8, 116.6.
HRMS (ESI): calc. for $[(C_{15}H_7FN_2O_2)H]$+ 267.0570, measured 267.0562.

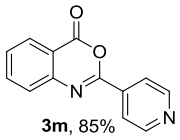
2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (3l) [3]



3l, 89%

Isolated as a white solid 199 mg (89%);^{1}H NMR ($CDCl_3$, 400 MHz): δ δ 8.32 – 8.28 (m, 2H), 8.23 (d, J = 7.9 Hz, 1H), 7.85 – 7.79 (m, 1H), 7.69 (d, J = 8.1 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.54 – 7.47 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 157, 146.9, 136.5, 132.5, 130.1, 128.7, 128.5, 128.2, 128.2, 127.1, 116.9.

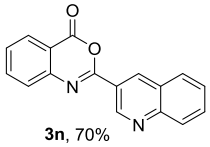
2-(pyridin-4-yl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3m) [5]



3m, 85%

Isolated as a white solid 190 mg (85%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.49 (s, 1H), 8.77 (d, *J* = 3.6 Hz, 1H), 8.56 – 8.49 (m, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 7.84 (t, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.47 – 7.40 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.9, 155.3, 152.9, 149.6, 146.4, 136.7, 135.4, 128.8, 128.7, 127.3, 126.3, 123.4, 117.1.

2-(quinolin-3-yl)-4*H*-benzo[*d*][1,3]oxazin-4-one(3n)

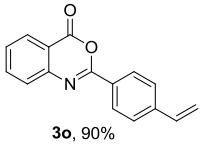


3n, 70%

Isolated as a white solid 192 mg (70%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.40 (s, 1H), 9.35 (s, 1H), 9.21 (d, *J* = 8.7 Hz, 1H), 8.35 – 8.29 (m, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.95 – 7.87 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.63 – 7.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.1, 156.5, 156.3, 146.5, 146.1, 136.7, 133.0, 132.3, 128.9, 128.6, 128.5, 128.4, 127.8, 127.4, 125.1, 120.9, 117.1.

HRMS (ESI): calc. for $[(C_{17}H_{10}N_2O_2)H]^+$ 275.0821, measured 275.0.816

2-(4-vinylphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3o)

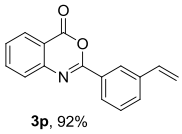


3o, 90%

Isolated as a white solid 224 mg (90%);^{1}H NMR ($CDCl_3$, 400 MHz):δ 8.28 – 8.19 (m, 3H), 7.80 (t, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.44 (m, 3H), 6.76 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.39 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 156.8, 147, 141.6, 136.5, 135.9, 129.2, 128.5, 128.1, 127.1, 126.4, 116.9, 116.5.

HRMS (ESI): calc. for $[(C_{15}H_{11}NO_2)H]^+$ 238.0868, measured 238.0862.

2-(3-vinylphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3q)

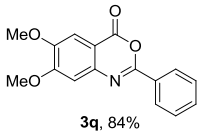


3p, 92%

Isolated as a white solid 229 mg (92%);^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (s, 1H), 8.22 (d, *J* = 7.9 Hz, 1H), 8.17 (d, *J* = 7.7 Hz, 1H), 7.80 (t, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.40 (m, 2H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.87 (d, *J* = 17.6 Hz, 1H), 5.34 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 156.9, 146.8, 138.1, 136.5, 135.8, 130.4, 130.1, 128.9, 128.5, 128.2, 127.5, 127.1, 126.0, 116.9, 115.3.

HRMS (ESI): calc. for $[(C_{16}H_{11}NO_2)H]^+$ 250.0868, measured 250.0872.

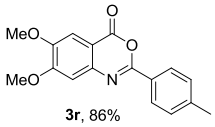
6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (3q) [6]



3q, 84%

Isolated as a white solid 238 mg (84%);^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (d, *J* = 7.8 Hz, 2H), 7.57 – 7.46 (m, 4H), 7.11 (s, 1H), 4.03 (s, 3H), 3.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.6, 156.7, 156.6, 149.8, 143.4, 132.4, 130.5, 128.8, 128.1, 109.7, 108.2, 107.7, 56.68, 56.61.

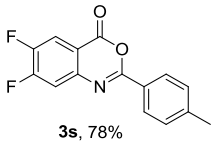
6,7-dimethoxy-2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3r) [7]



3r, 86%

Isolated as a white solid 256 mg (86%);[1]H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.48 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.03 (s, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 156.7, 156.3, 149.4, 143.4, 142.9, 129.4, 127.9, 127.5, 109.38, 107.8, 107.4, 56.4, 56.3, 21.6.

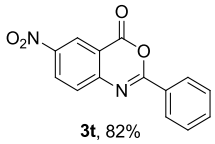
6,7-difluoro-2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3s)



3s, 78%

Isolated as a white solid 213 mg (78%);[1]H NMR ($CDCl_3$, 400 MHz) δ 8.14 (d, J = 8.2 Hz, 2H), 7.97 (t, J = 8.8 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.30 (d, J = 8.1 Hz, 2H), 2.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.7, 152.4, 145.8, 143.9, 129.5, 128.3, 126.7, 116.3, 116.2, 115.5, 115.3, 21.7.
HRMS (ESI): calc. for $[(C_{15}H_9F_2NO_2)H]^+$ 274.0680, measured 274.0675.

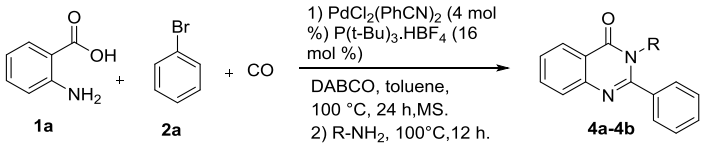
6-nitro-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (3t) [8]



3t, 82%

Isolated as a yellow solid 220 mg (82%);[1]H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 9.0 Hz, 2H), 8.34 (d, J = 9.0 Hz, 2H), 8.26 (d, J = 7.9 Hz, 1H), 7.87 (t, J = 7.7 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.73, 154.90, 150.08, 146.22, 136.91, 135.83, 129.33, , 128.80, 127.63, 123.87, 117.06.

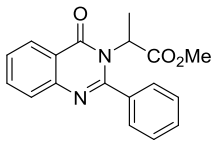
3. General procedure for the synthesis of quinazolinones (4a-4b) from anthranilic acid:



To a 100 mL stainless steel high pressure reactor, anthranilic acid (1 mmol), aryl bromide (1.15 mmol), DABCO (2 mmol), $PdCl_2PhCN_2$ (4 mol %) and P(*t*-Bu)$_3$·HBF_4 (16 mol %) were added in 10 mL anhydrous toluene. The 400 mg activated 3 Å MS were added in the reaction mixture and the autoclave was closed. The autoclave was purged three times with

carbon monoxide, pressurized with CO 200 psi at ambient temperature. The reaction mixture was stirred with a mechanical stirrer (500 rpm) at the 100 °C temperature for 24 h. After completion of reaction, the reactor was cooled to room temperature and the remaining CO was carefully vented. The corresponding amine were added in reaction mixture and further stirred for 12 h at 100 °C temperature. After completion of reaction, the reactor was cooled to room temperature. The reactor vessel was washed with ethyl acetate (3 × 5 mL) to remove traces of product, if present. The ethyl acetate layer was washed with water (2 × 5 mL), dried over Na_2SO_4, and the solvent was evaporated under vacuum. The crude residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether as eluents to give corresponding quinazolinones.

methyl 2-(4-oxo-2-phenylquinazolin-3(4*H*)-yl)propanoate (4b)

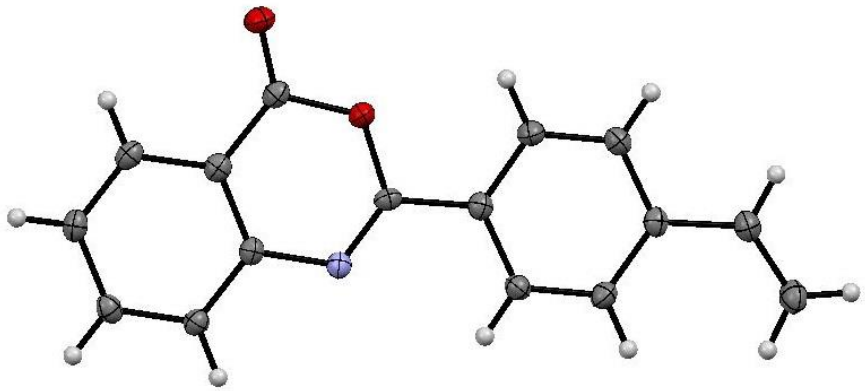


4b 80%

Isolated as a yellow solid 246 mg (80%); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.63 (d, J = 8.3 Hz, 1H), 7.93 – 7.85 (m, 3H), 7.66 – 7.53 (m, 4H), 7.22 (t, J = 7.6 Hz, 1H), 4.64 – 4.48 (m, 1H), 3.36 (s, 3H), 1.42 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.1, 161.4, 147.3, 145.4, 134.9, 132.9, 132.5, 129.4, 129.0, 127.3, 123.3, 120.8, 120.5, 52.4, 48.8, 16.9.

4. Experimental procedure for X-ray crystallographic analysis of compound 3o (CCDC 1478766):

The crystal of compound **3o** (CCDC 1478766) was obtained by slow evaporation of the samples in dichloromethane and hexane. A suitable single crystal was mounted in a glass fibre, and diffraction measurements were taken with a diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using the programme SHELXS-1997 (Sheldrick, 2008). The refinement and all further calculations were carried out using SHELXL-1997(Sheldrick, 2008).



Identification code	3o
Bond precision: C-C	0.0020 Å
Chemical Formula	$C_{16}H_{11}NO_2$
Formula Weight	249.26
Temperature	100 K
Wavelength	0.71073
Crystal System	monoclinic
Crystal description	Needle
Crystal colour	Colourless
Space group	P 21/n
Unit cell dimensions	
a Å	12.255(9)
b Å	3.849(3)
c Å	25.380(16)
α (°)	90
β (°)	94, 92(2)
γ (°)	90
cell_volume	1192.8(15)
Z	4
Calculated density (mg/m3)	1.388
Absorption coefficient (mm^{-1})	0.092
F(000)	520
Theta range for data collection ( )°	1.61 to 29.60
Limiting indices	-17<= h<=17, -5<=k<=5,- 35<=l<=35

Reflection collected	3317
Independent reflections	3367 [R_{int} =0.0574]
Absorption correction	Multi scan
Refinement method	SHELXL-97 (Sheldrick, 2008)
Data / restraints / parameters	3317/0/172
Goodness-of-fit on F 2	1.012
Final R indices [I>2sigma(I)]	0.0780
R indices (all data)	0.0501

5. References

1) S. P. Chavan, B. M. Bhanage, *Eur. J. Org. Chem.* **2015**, 2405–2410.

2) L. Xue, L. Shi, Y. Han, C. Xia, H. V. Huynh, F. Li, *Dalt. Trans.* **2011**, *40*, 7632.

3) X. Wu, J. Schranck, H. Neumann, M. Beller, *Chem. Eur. J.* **2011**, *17*, 12246–12249.

4) Z.A. Khan, S.A.R. Naqvi, S.A. Shahzad, N. Mahmood, M. Yar, A.F. Zahoor, *Asian J. Chem.* **2013**, *25*, 152–156.

5) S. Munusamy, S. Venkatesan, K. I. Sathiyanarayanan, *Tetrahedron Lett*. **2015**, *56*, 203-205.

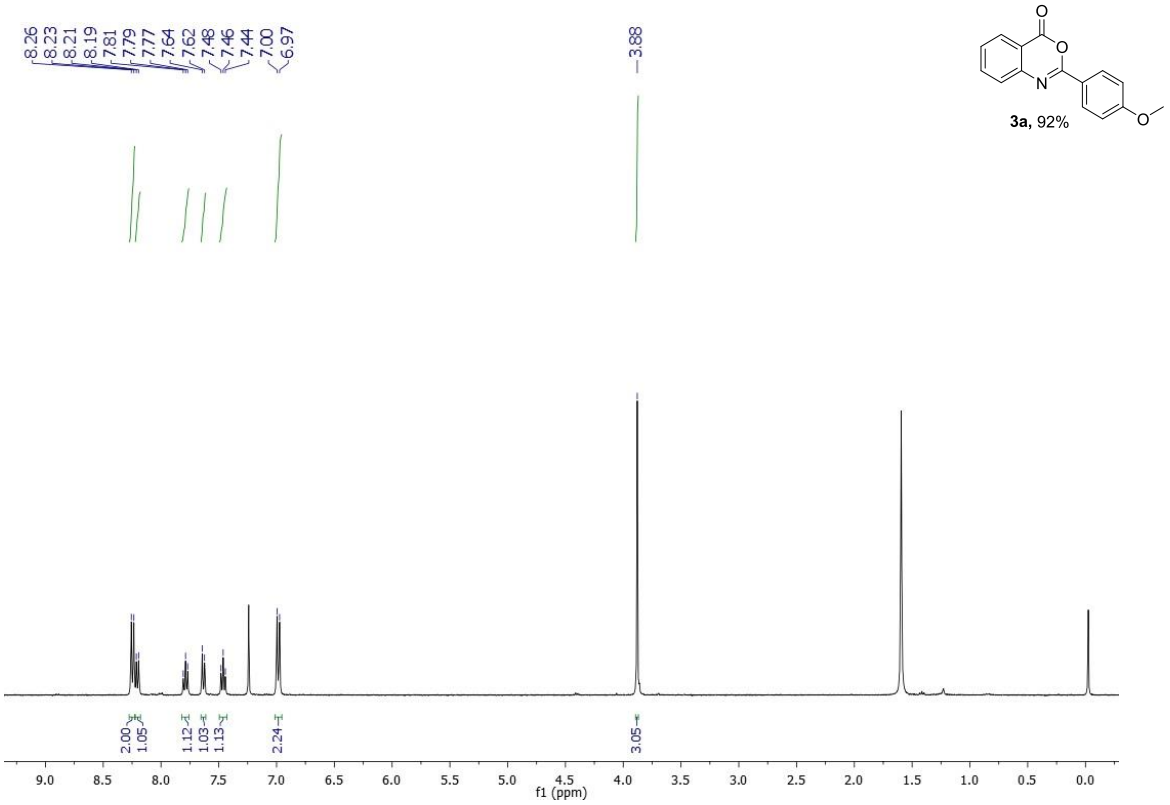
6) Z-Y. Ge, Q-M. Xu, X-D. Fei, T. Tang, Y-M. Zhu, S-J Ji, *J. Org. Chem.* **2013**, *78*, 4524−4529

7) J. K. Laha, K. S. S. Tummalapalli, A. Nair, N. Patel *J. Org. Chem.* **2015**, *80*, 11351−11359.

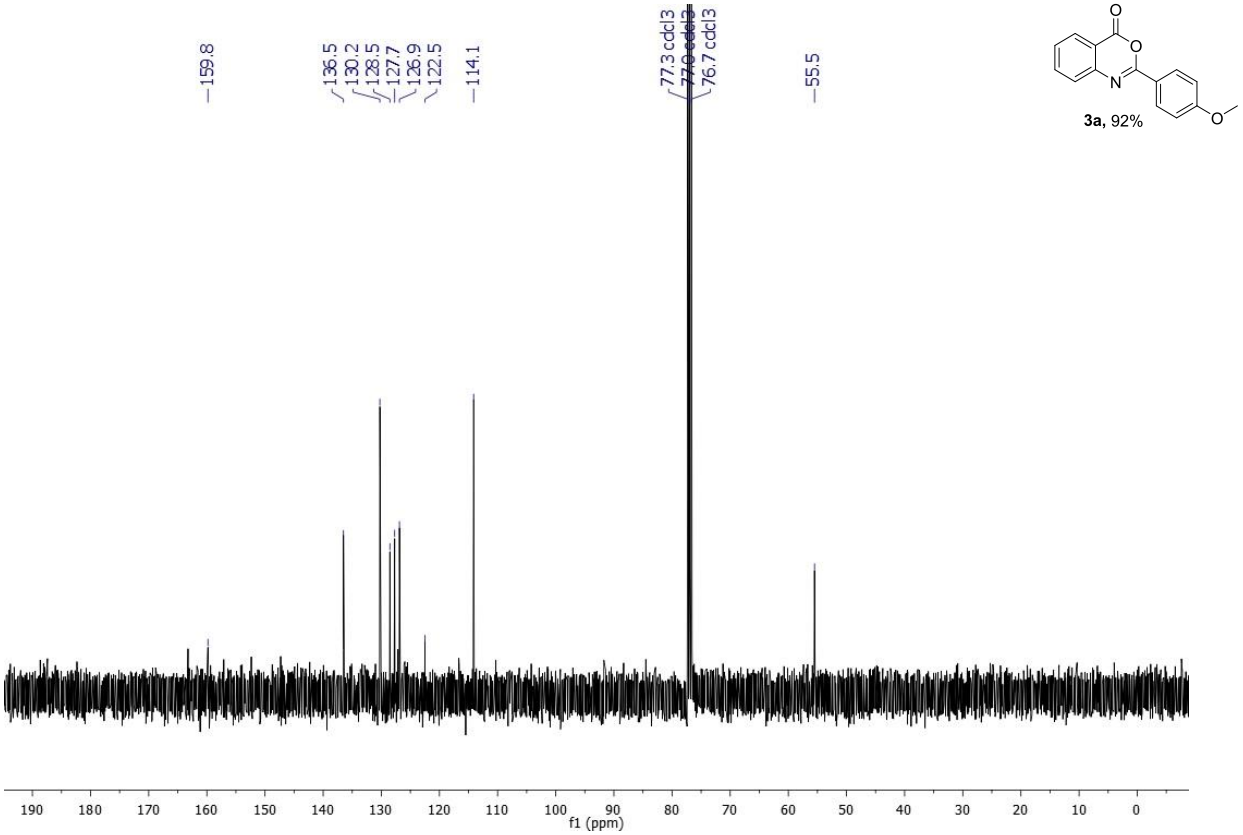
8) A. M. Rana, K. R. Desai, S. Jauhari, *Med Chem Res* **2013**, *22*, 225–233

6. ^{1}H and ^{13}C NMR spectra of products

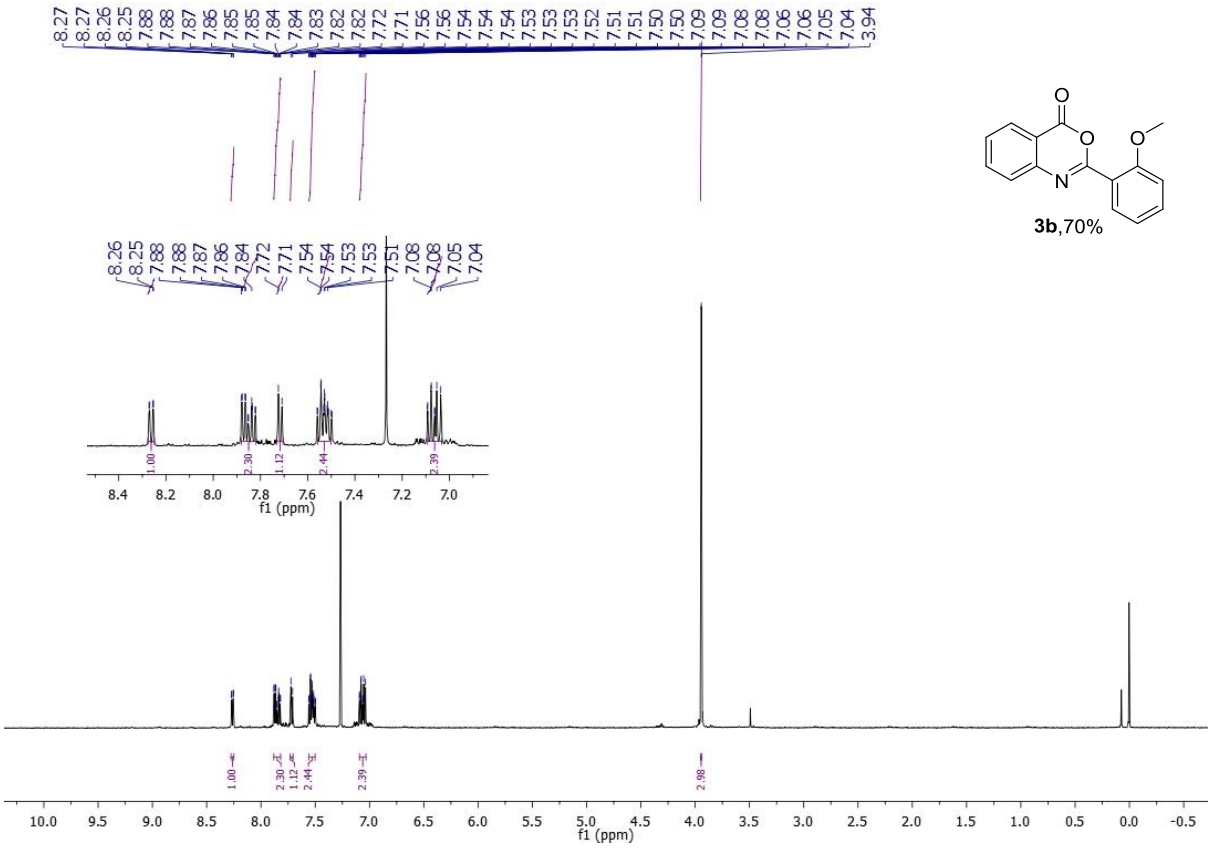
2-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3a)



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

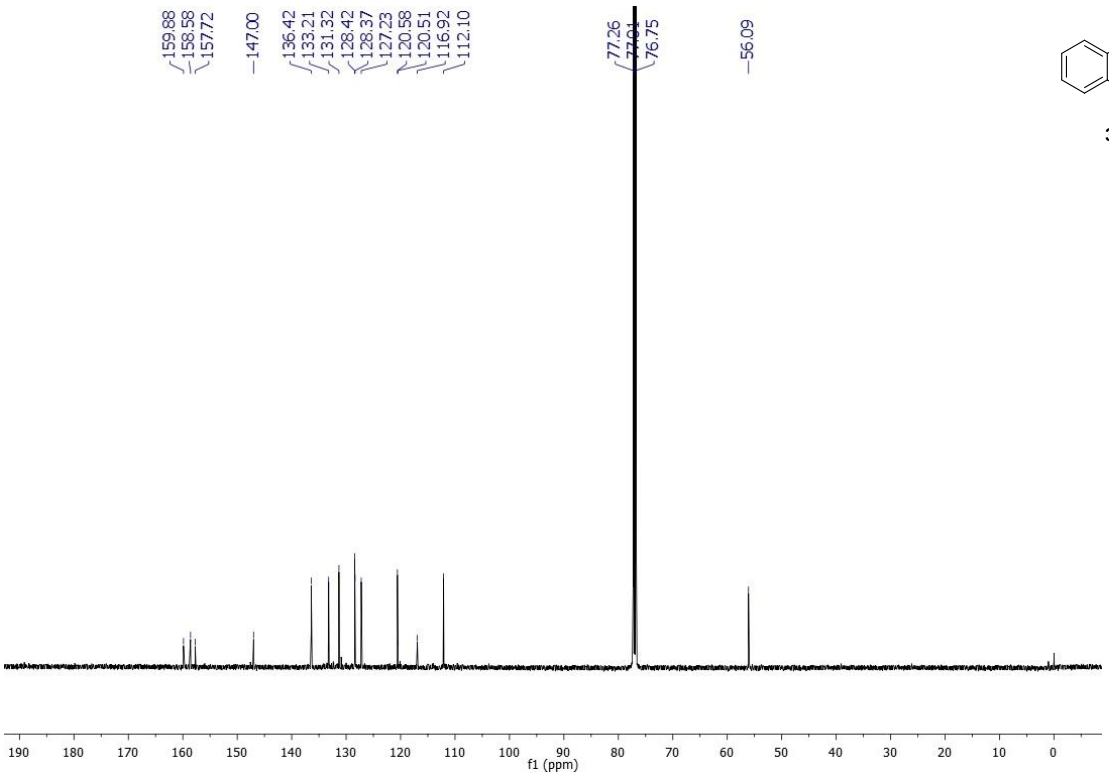


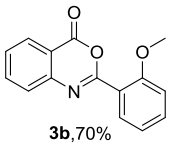
2-(2-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3b)



3b,70%

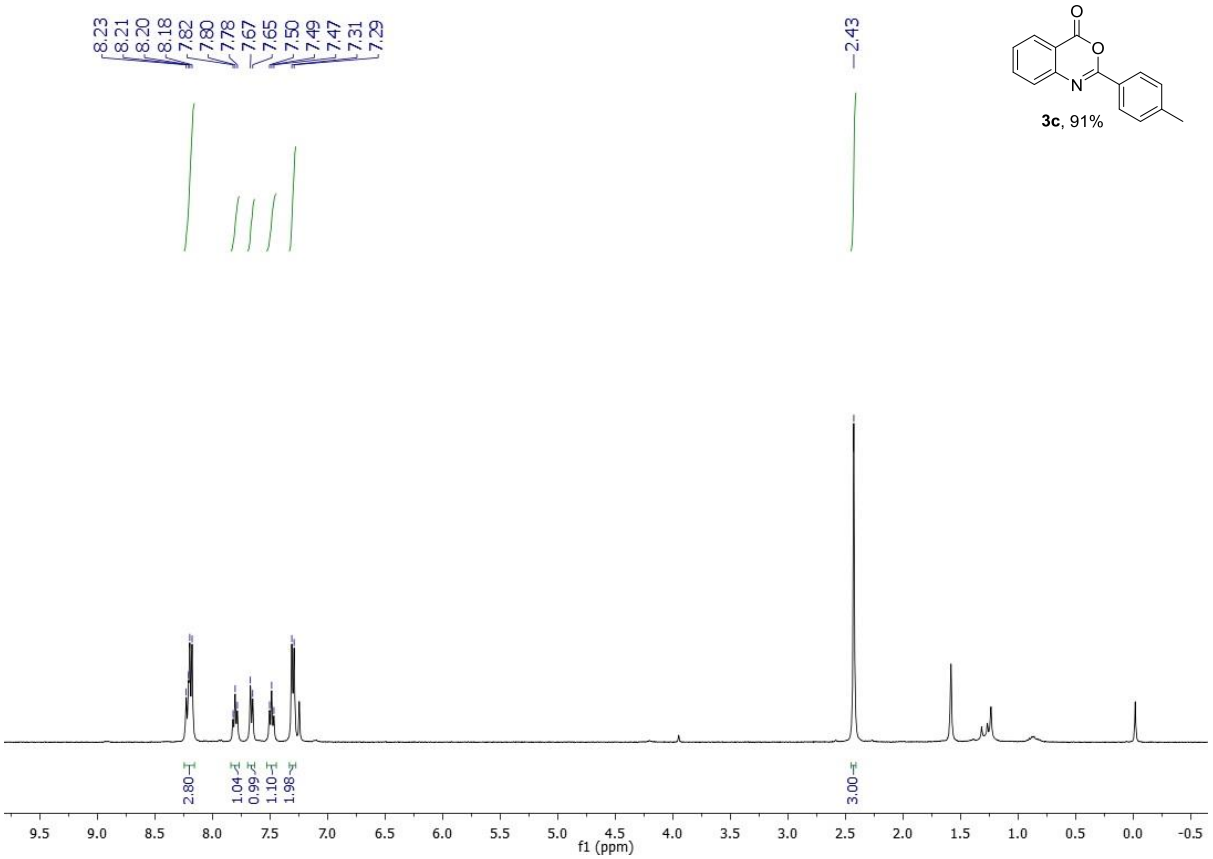
2-(2-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3b)



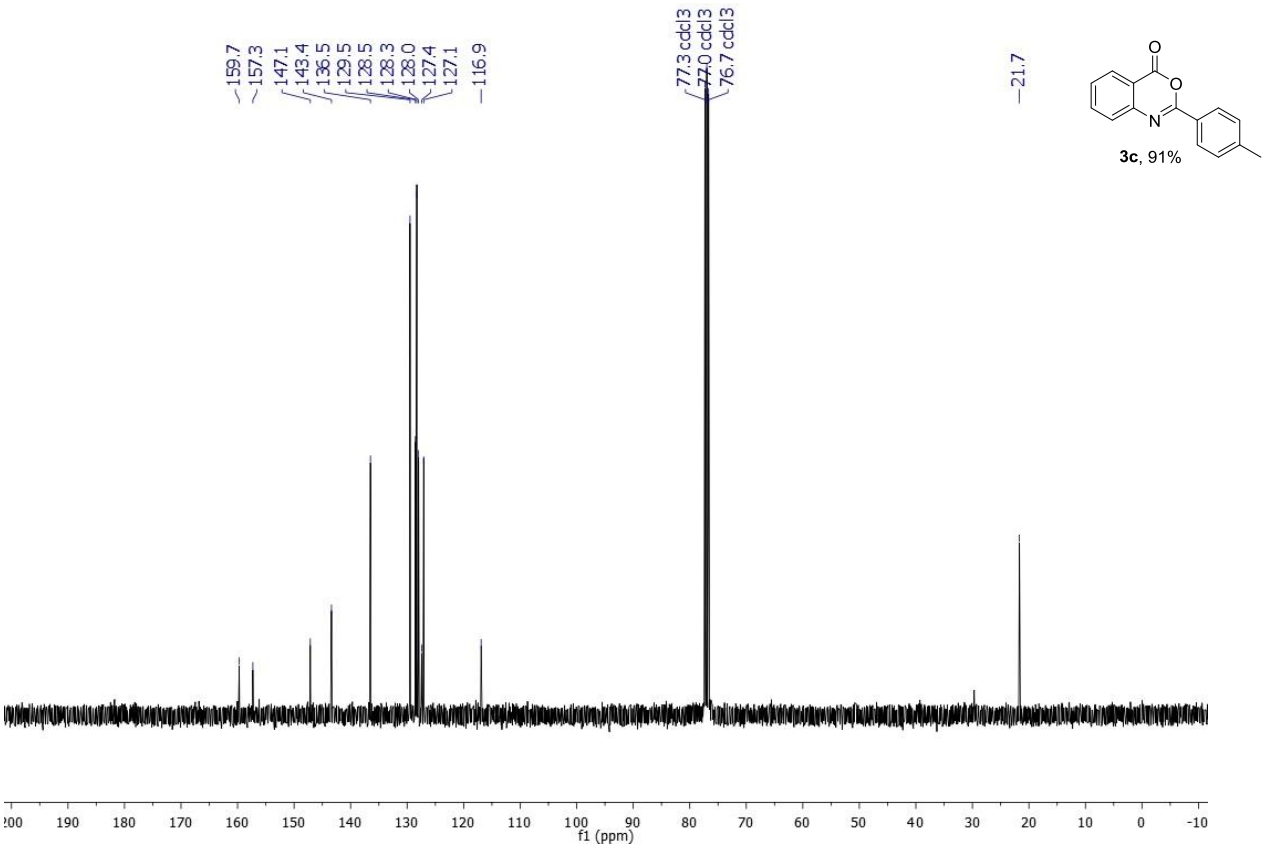


3b,70%

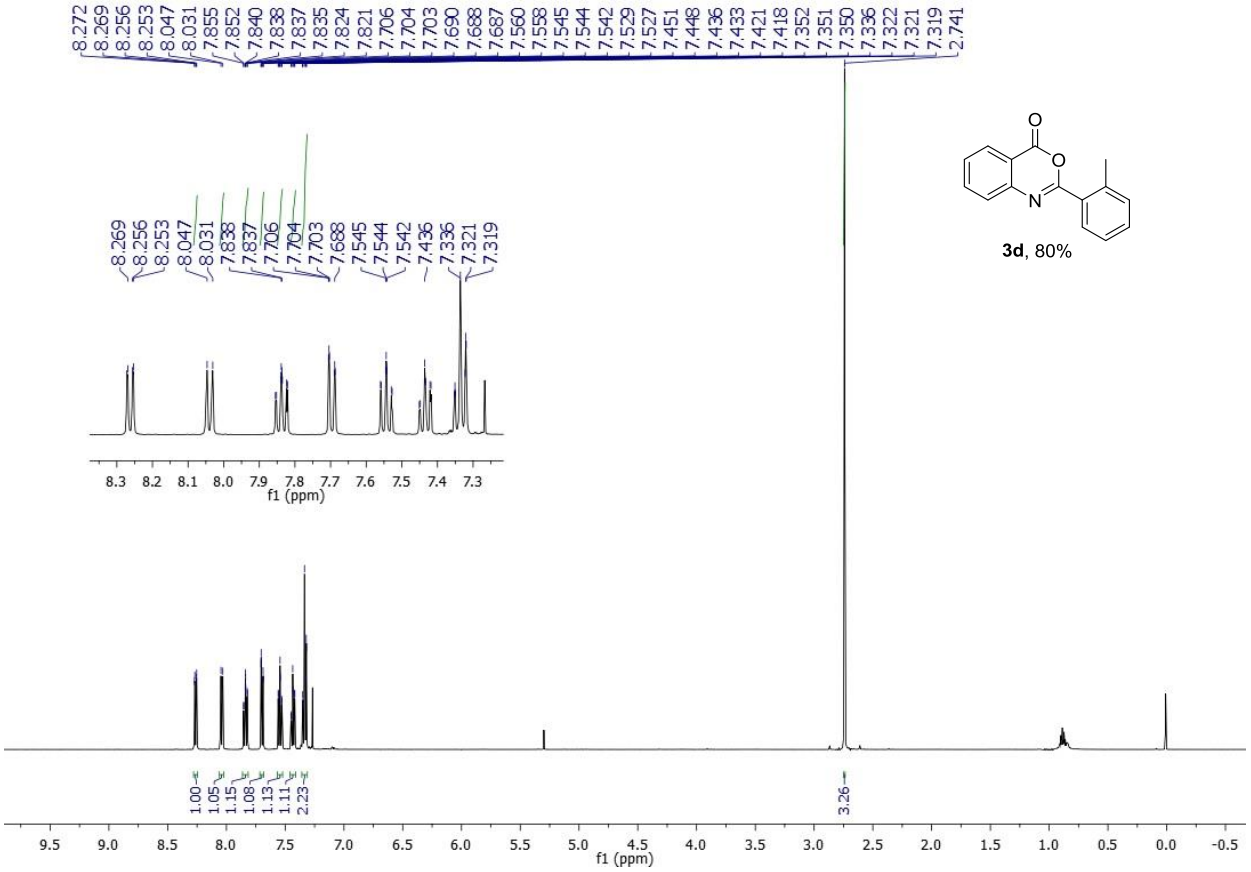
2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3c)



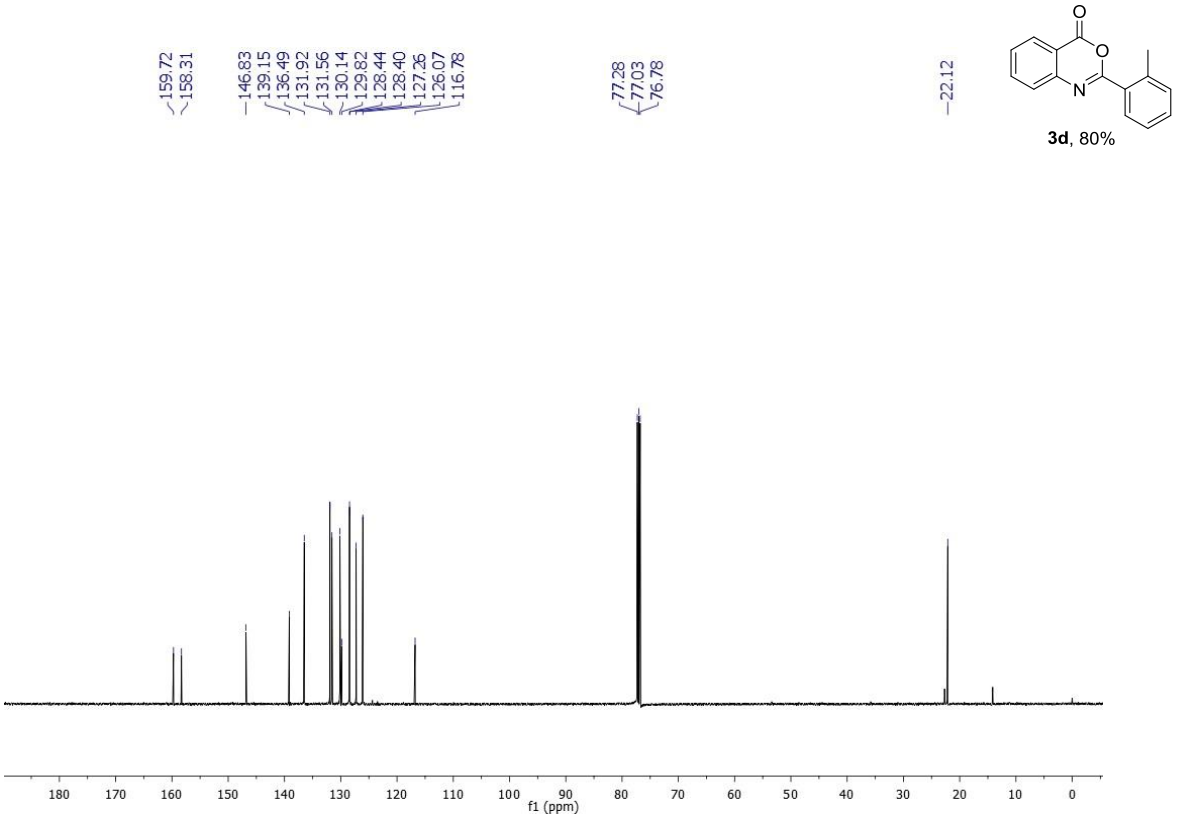
2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3c)



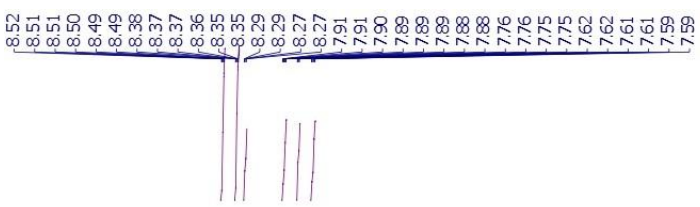
2-(*o*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3d)

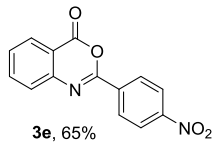


2-(*o*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3d)

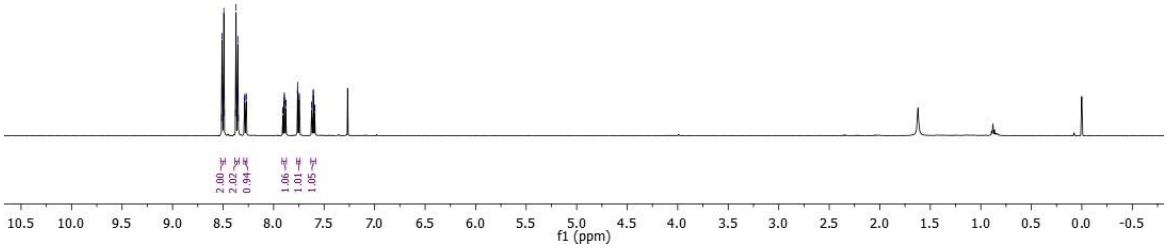


2-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3e)





3e, 65%



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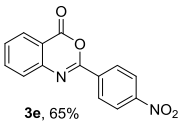
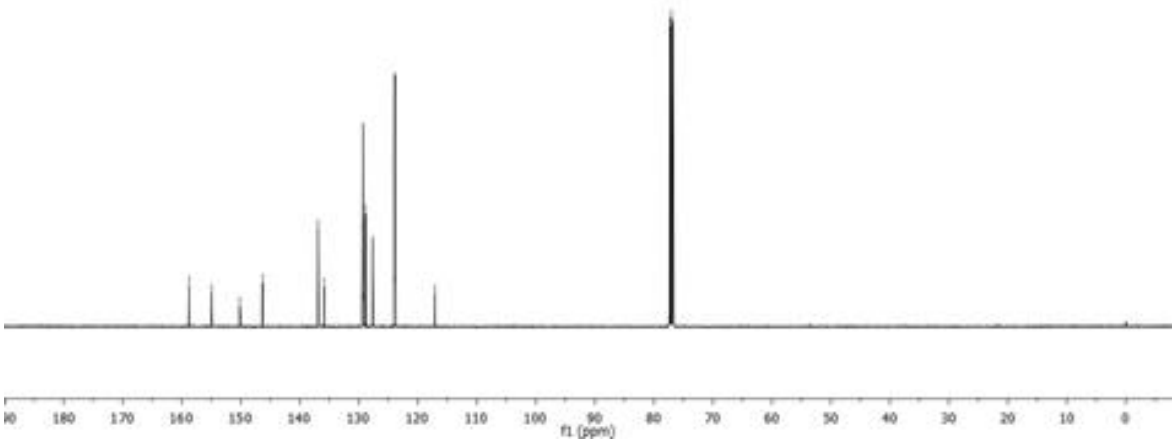
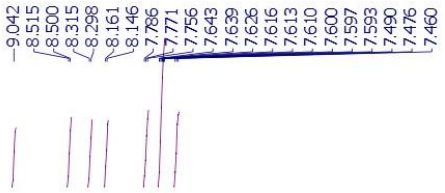
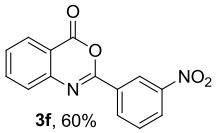


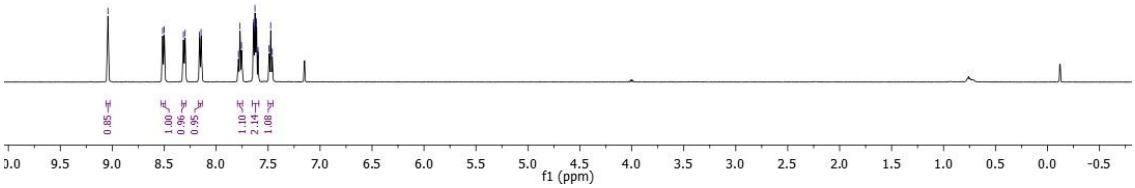
3e, 65%



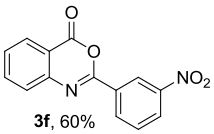
2-(3-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3f)

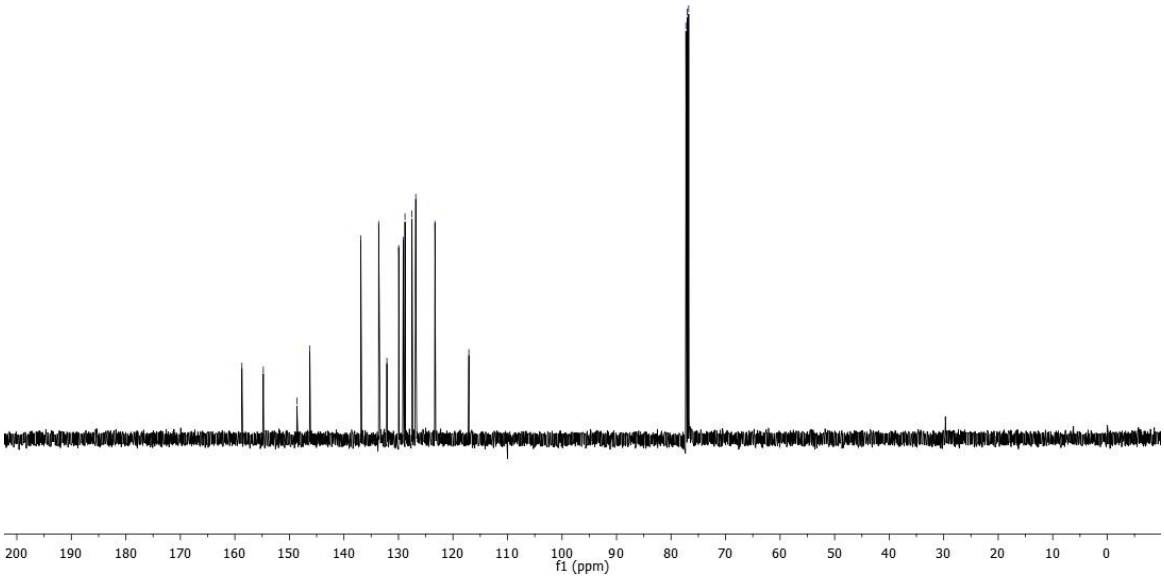




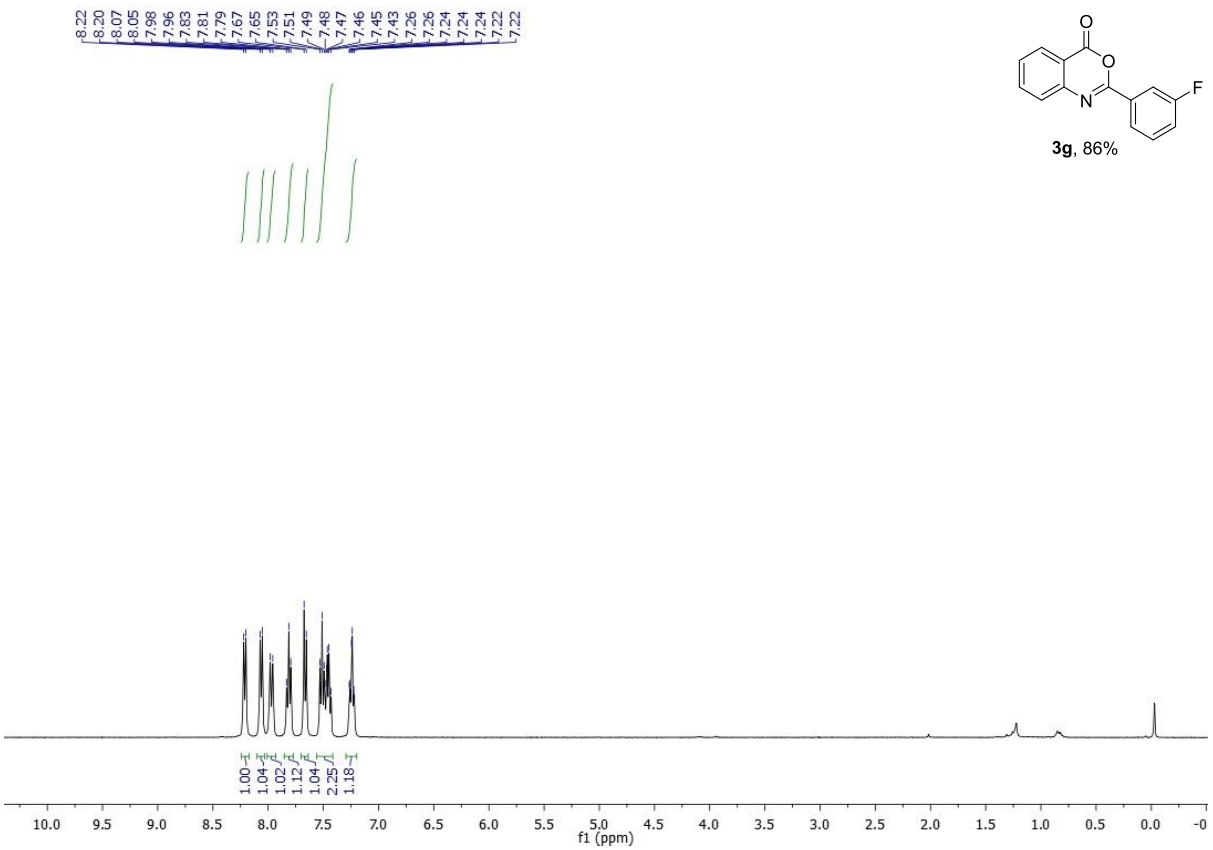


2-(3-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3f)

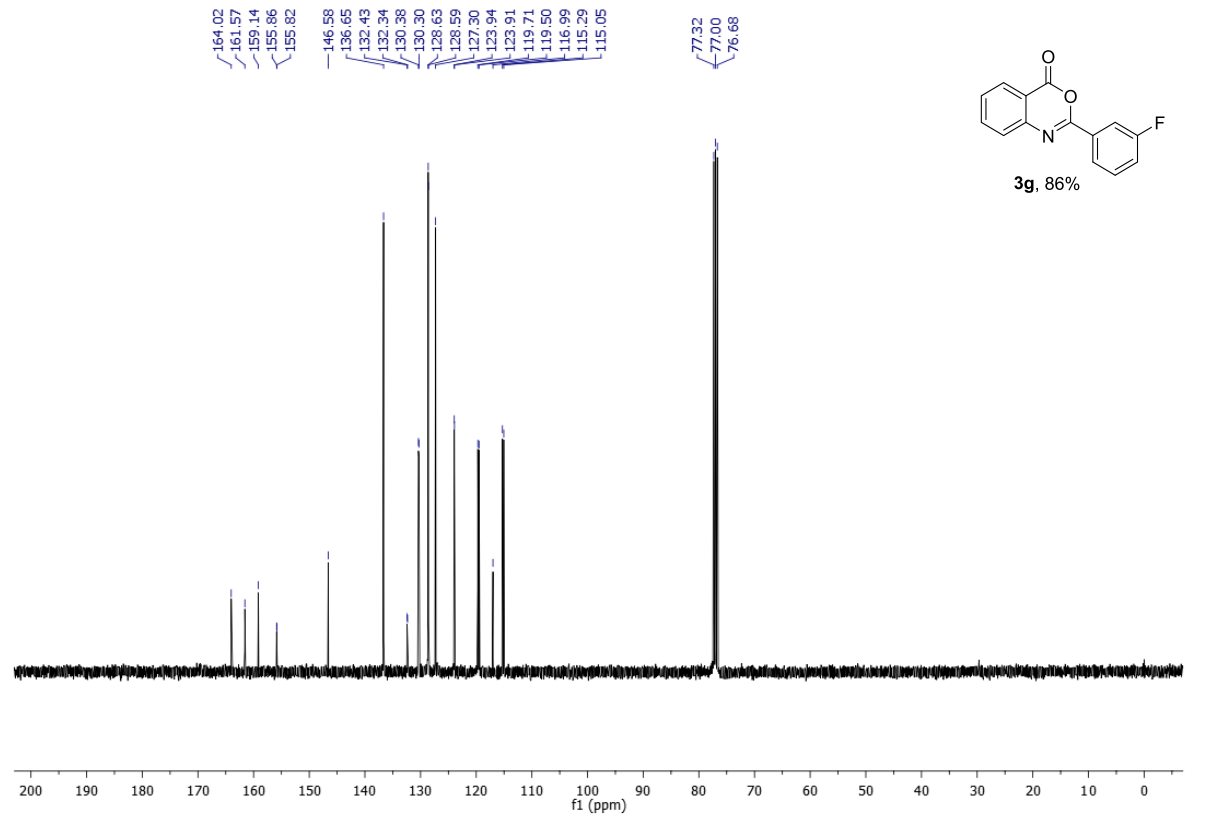




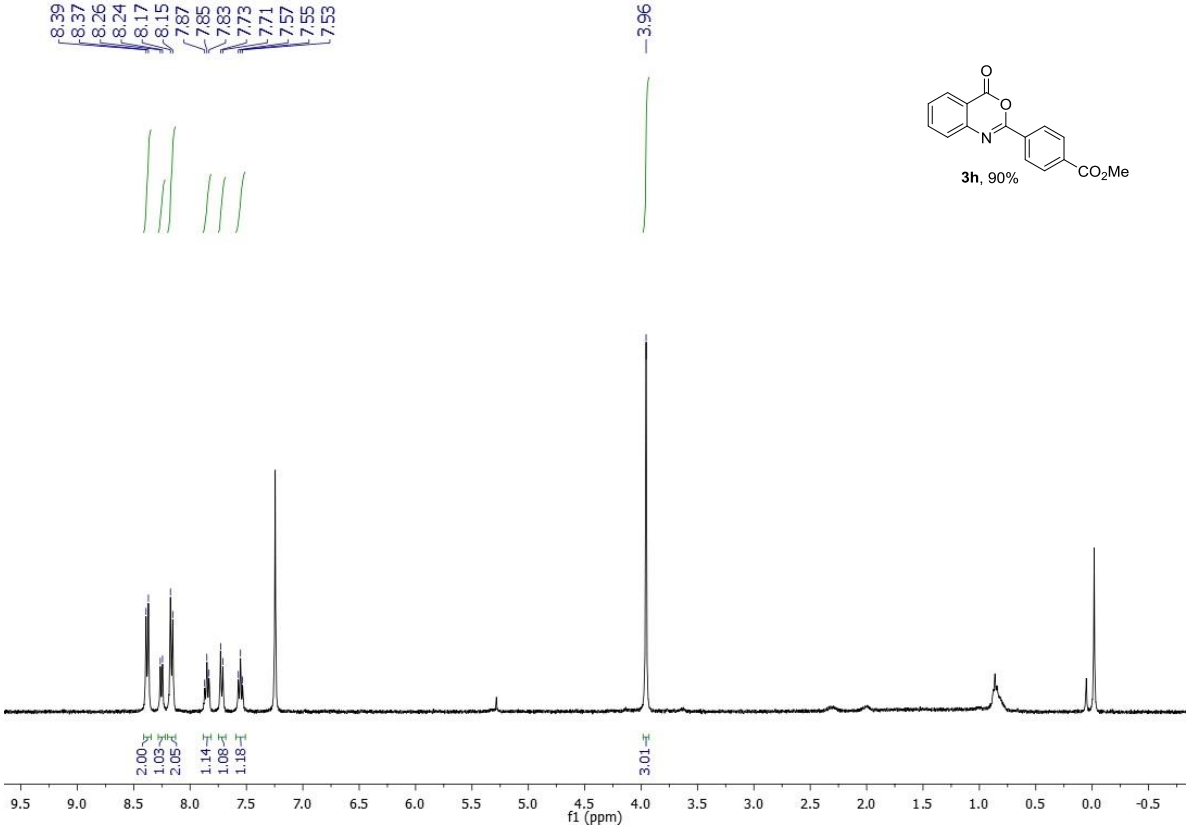
2-(3-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3g)



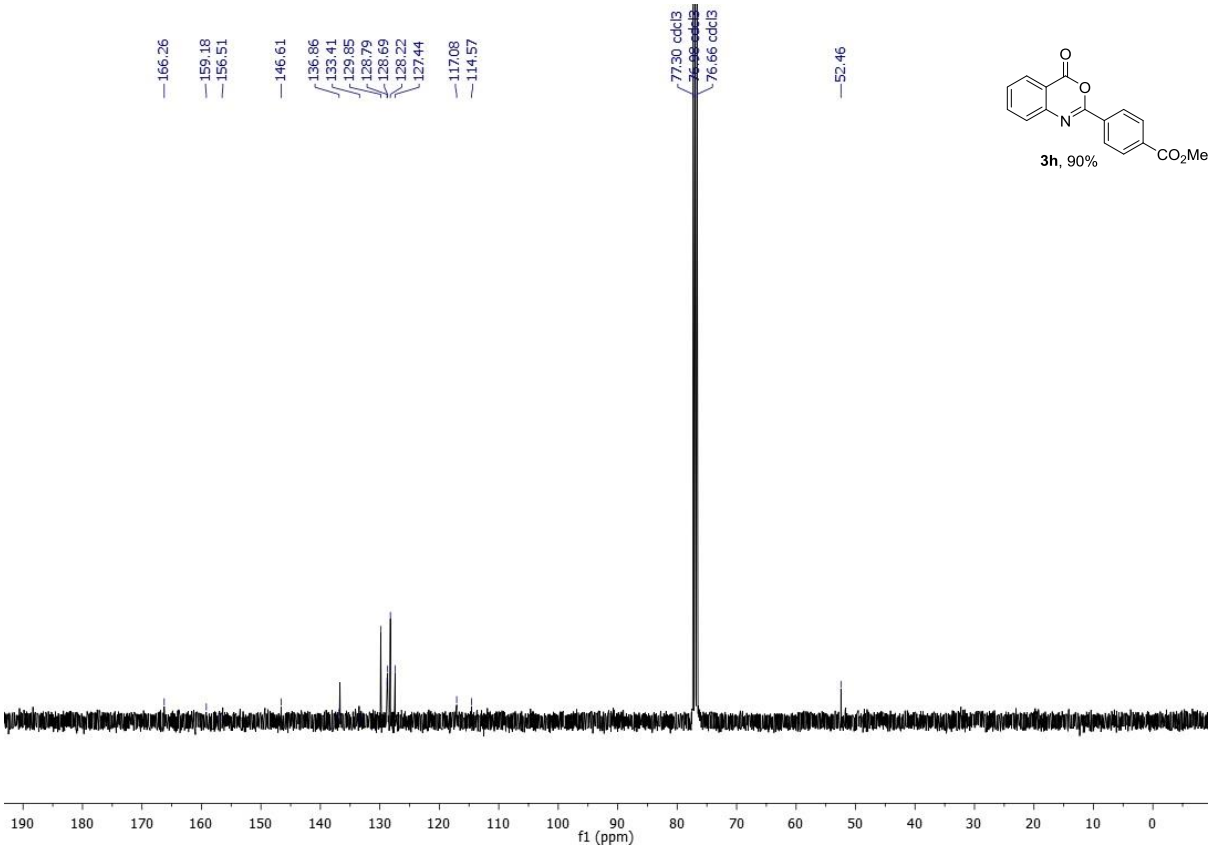
2-(3-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3g)



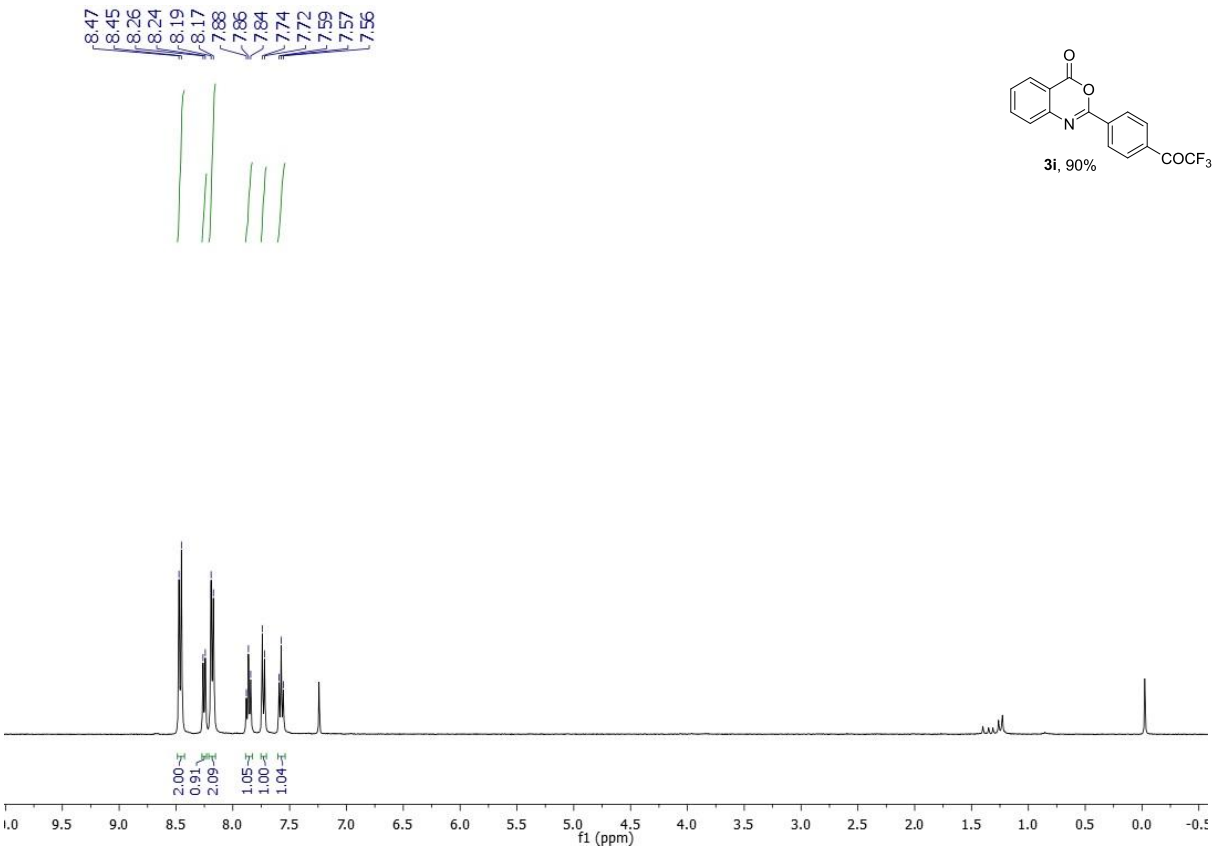
methyl 4-(4-oxo-4*H*-benzo[*d*][1,3]oxazin-2-yl)benzoate (3h)



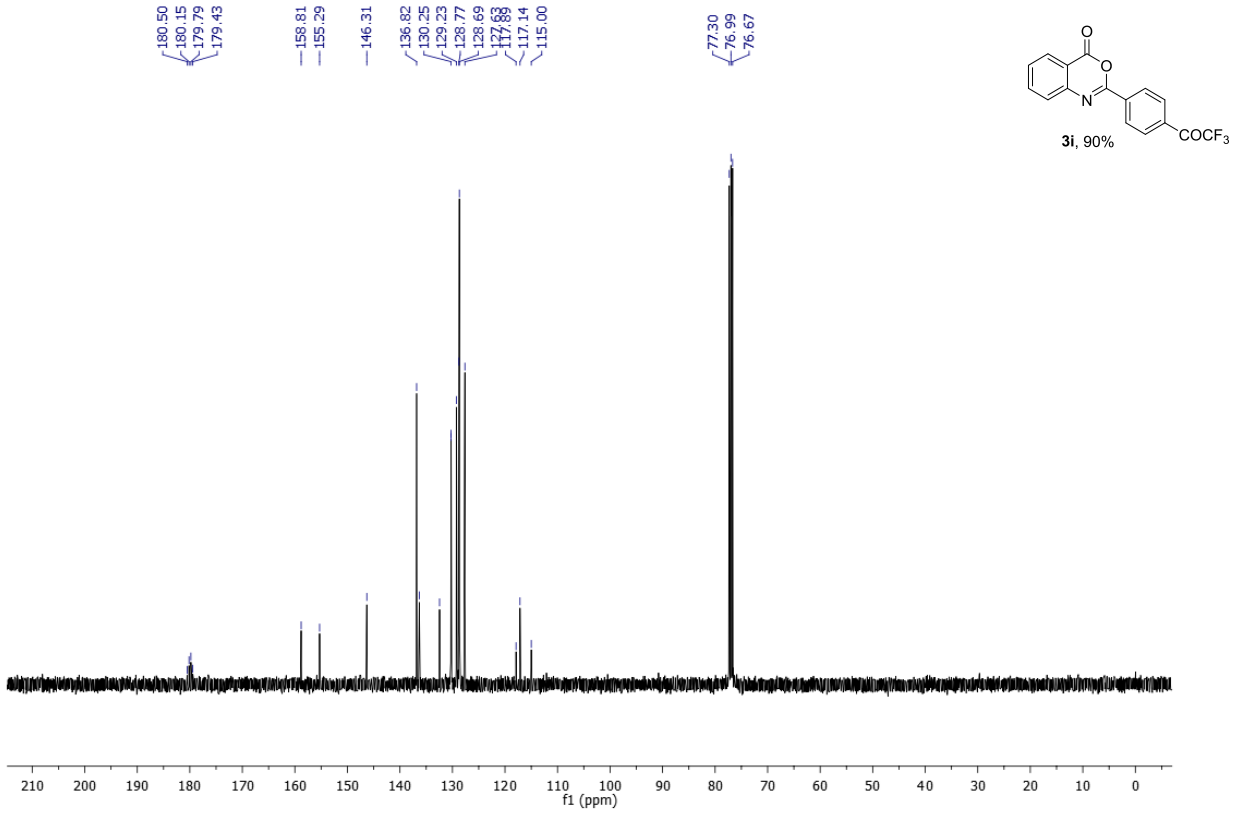
methyl 4-(4-oxo-4*H*-benzo[*d*][1,3]oxazin-2-yl)benzoate (3h)



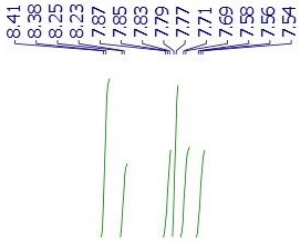
2-(4-(2,2,2-trifluoroacetyl)phenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3i)

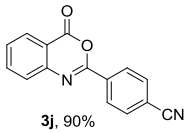


2-(4-(2,2,2-trifluoroacetyl)phenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3i)

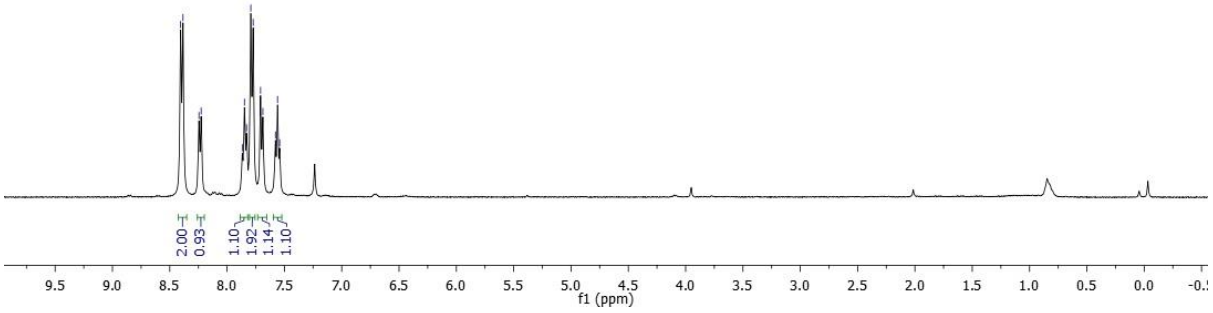


4-(4-oxo-4*H*-benzo[*d*][1,3]oxazin-2-yl)benzonitrile (3j)

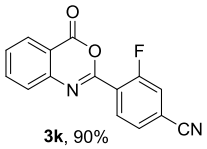




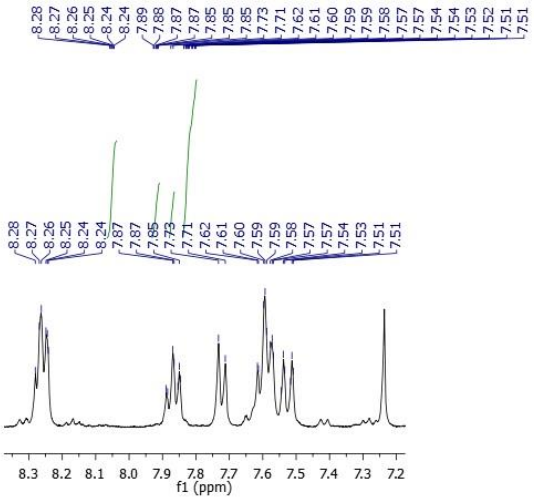
3j, 90%

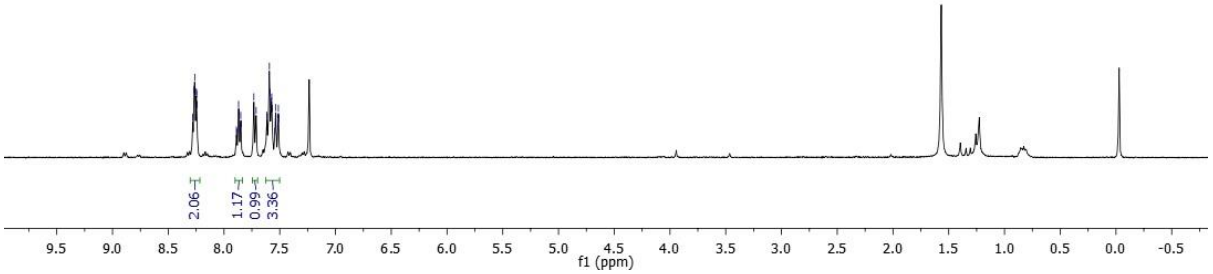


3-fluoro-4-(4-oxo-4*H*-benzo[*d*][1,3]oxazin-2-yl)benzonitrile (3k)

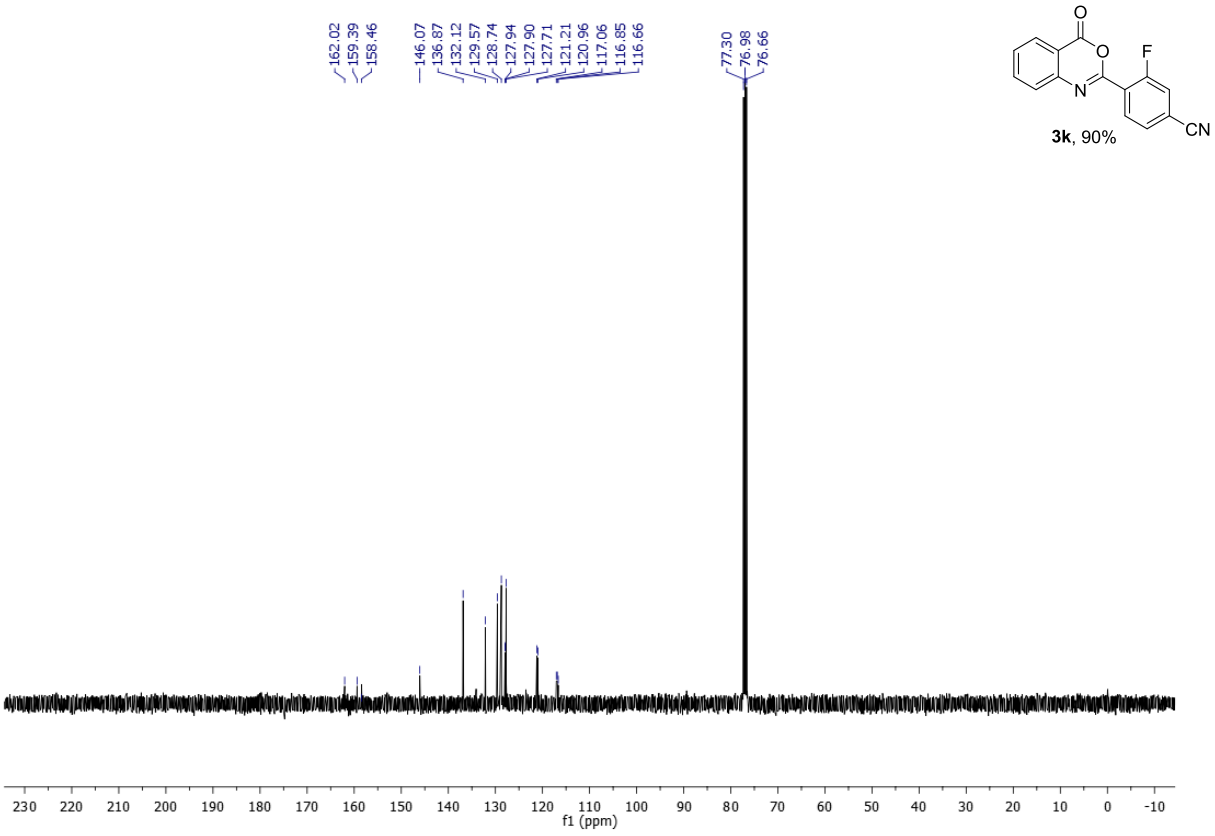


3k, 90%

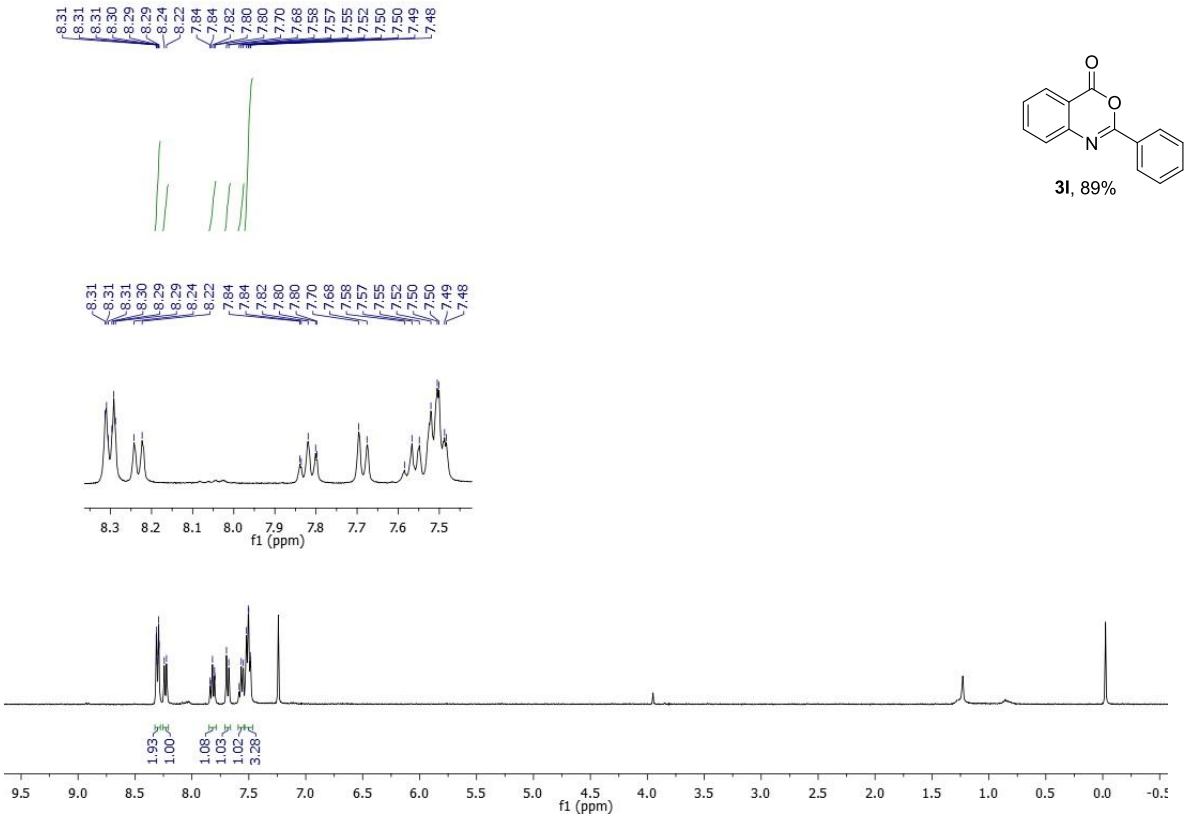




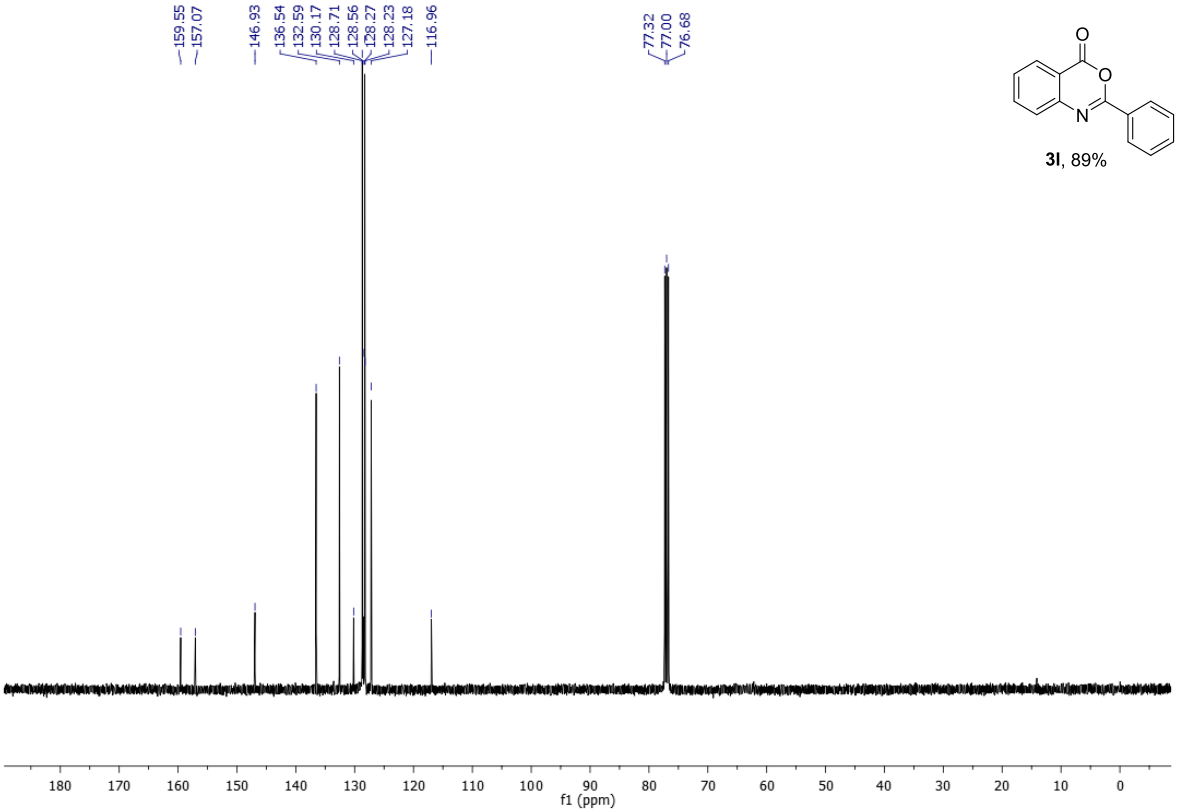
3-fluoro-4-(4-oxo-4*H*-benzo[*d*][1,3]oxazin-2-yl)benzonitrile (3k)



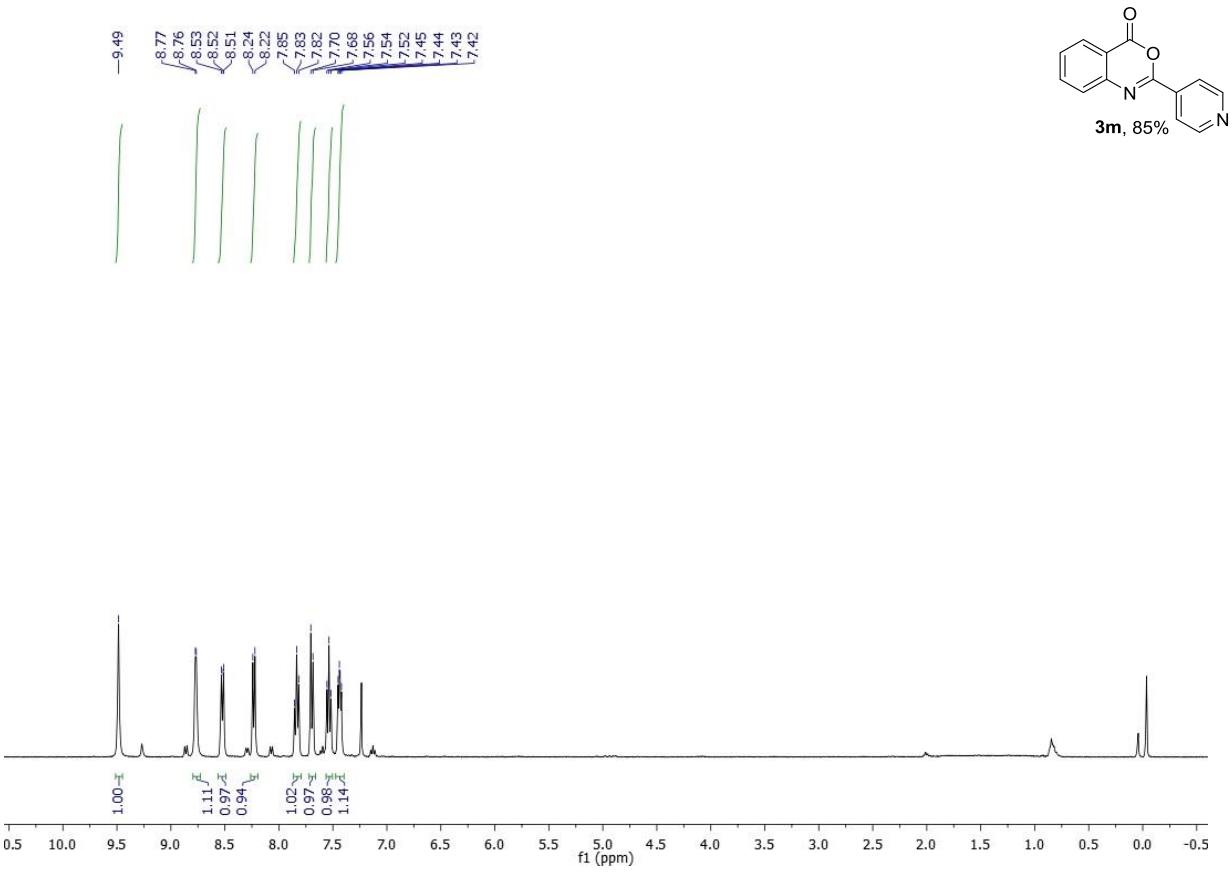
2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (3l)



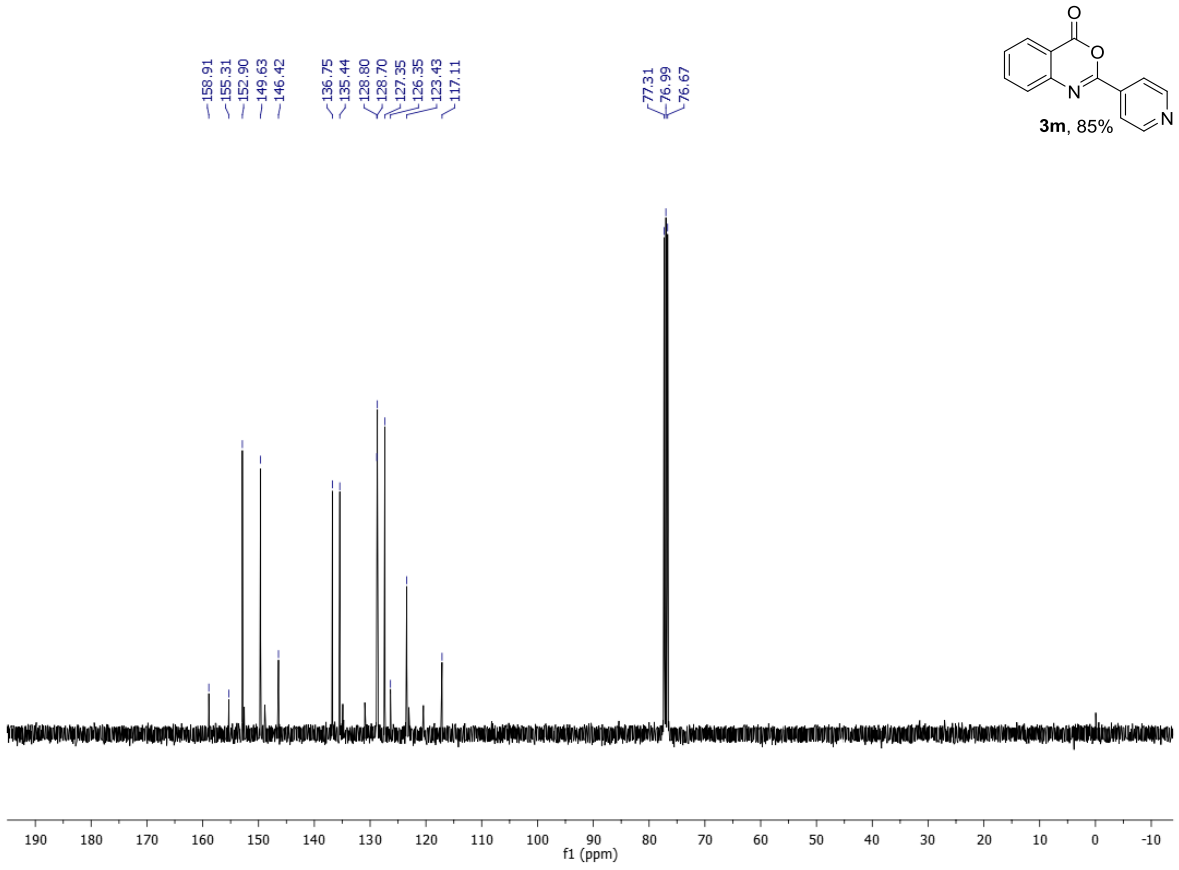
2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (3l)



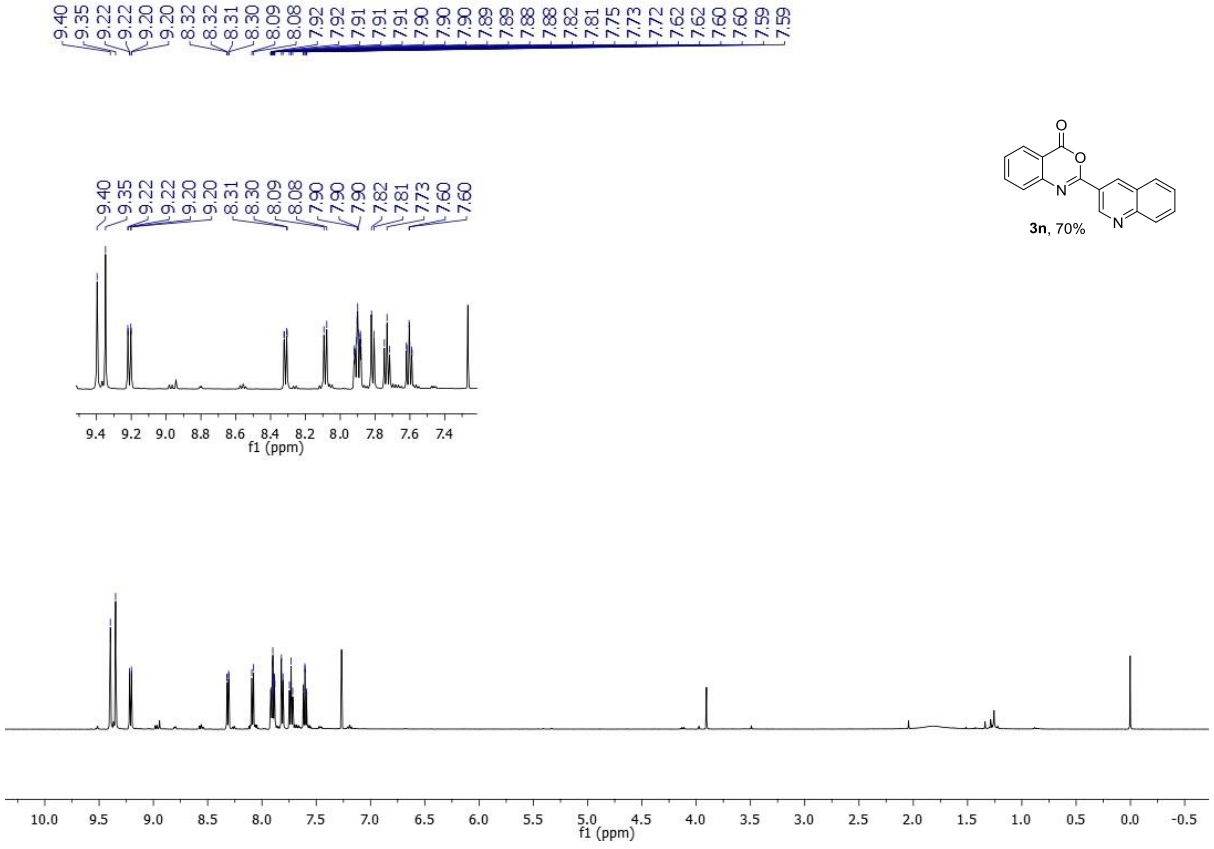
2-(pyridin-4-yl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3m)



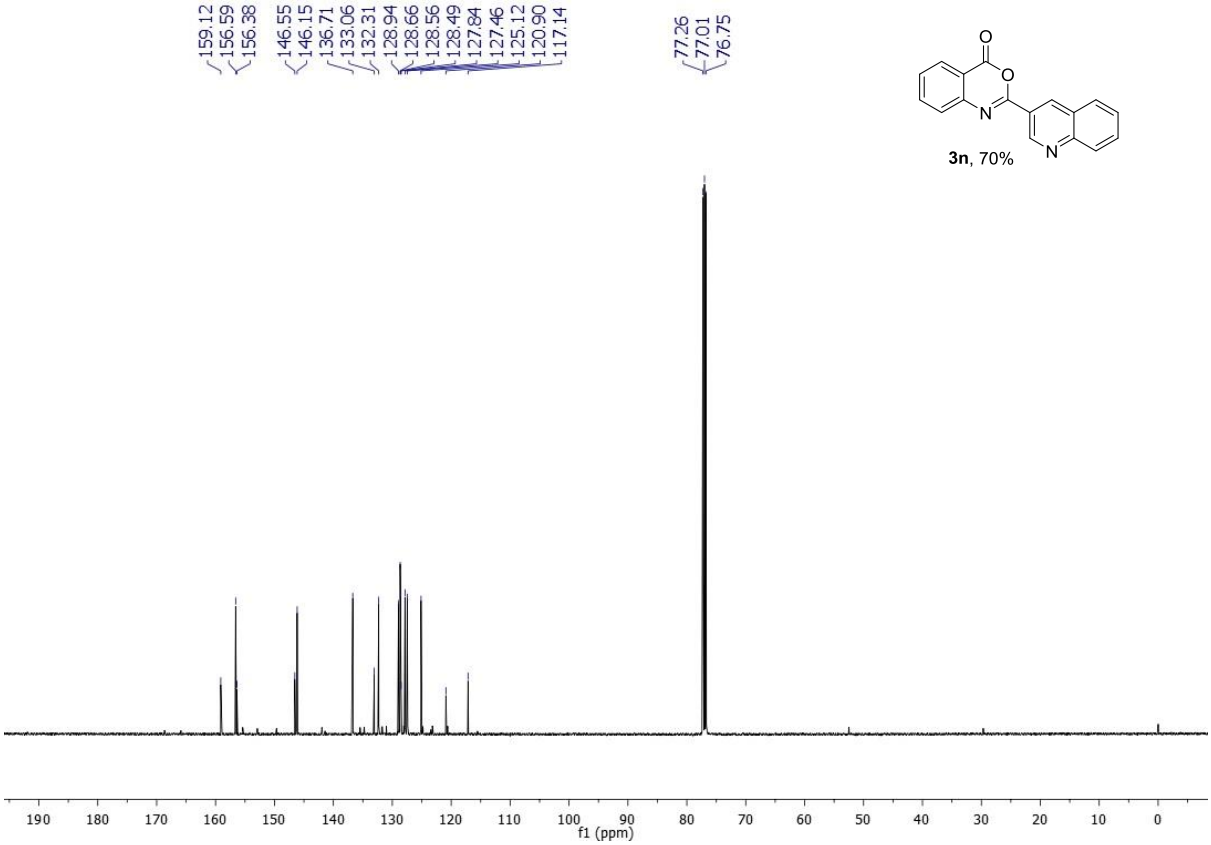
2-(pyridin-4-yl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3m)



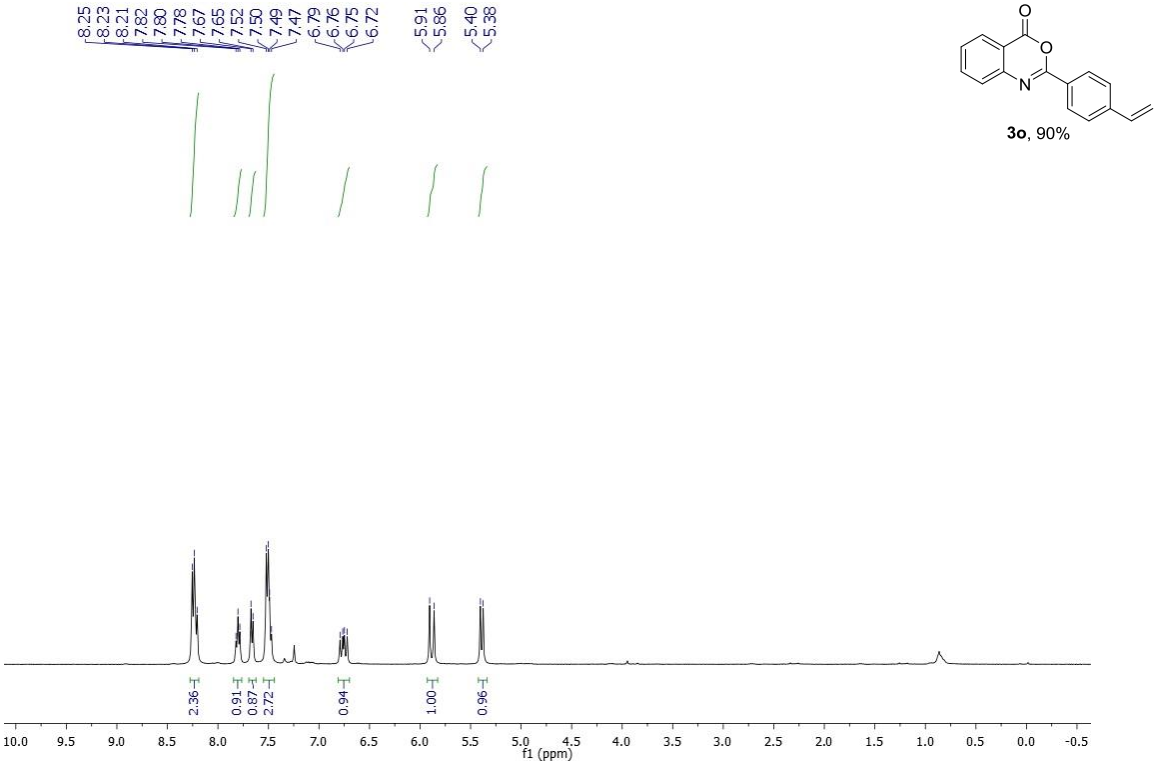
2-(quinolin-3-yl)-4*H*-benzo[*d*][1,3]oxazin-4-one(3n)



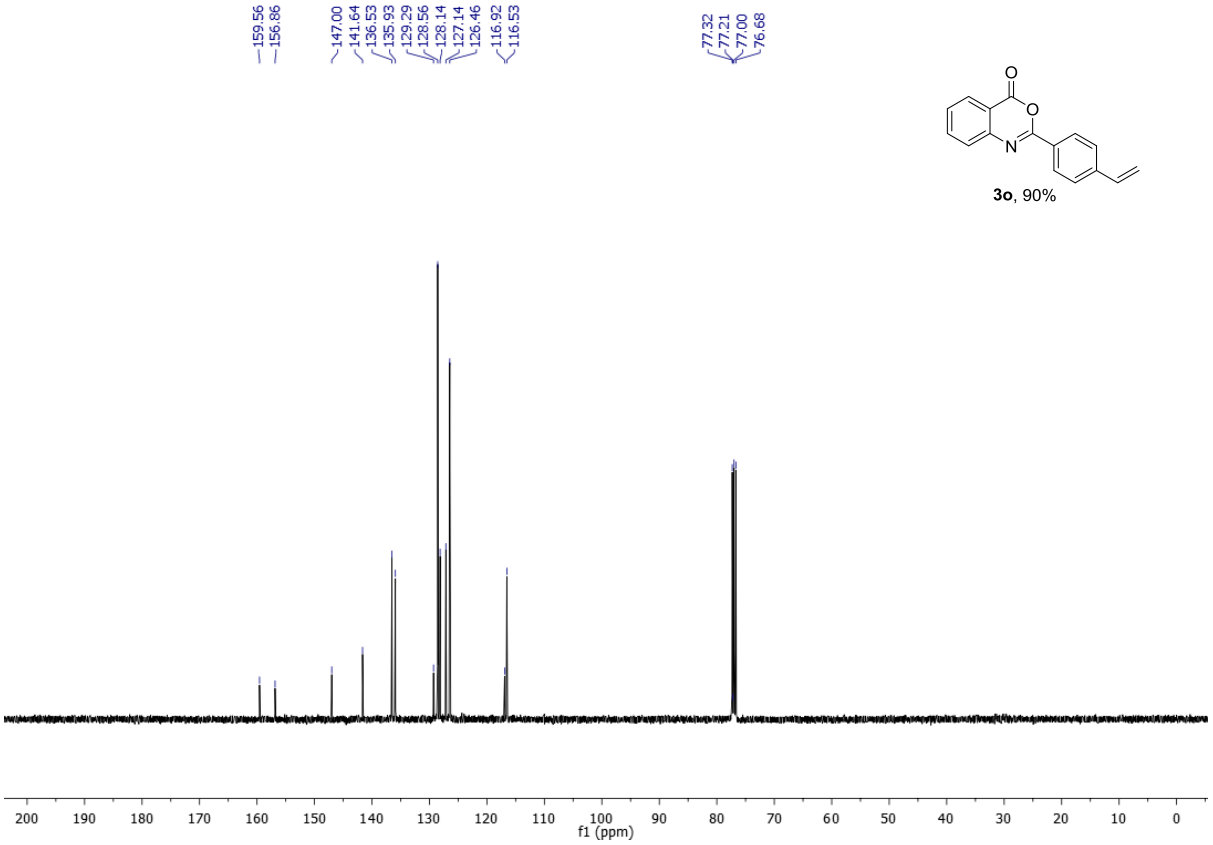
2-(quinolin-3-yl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3n)



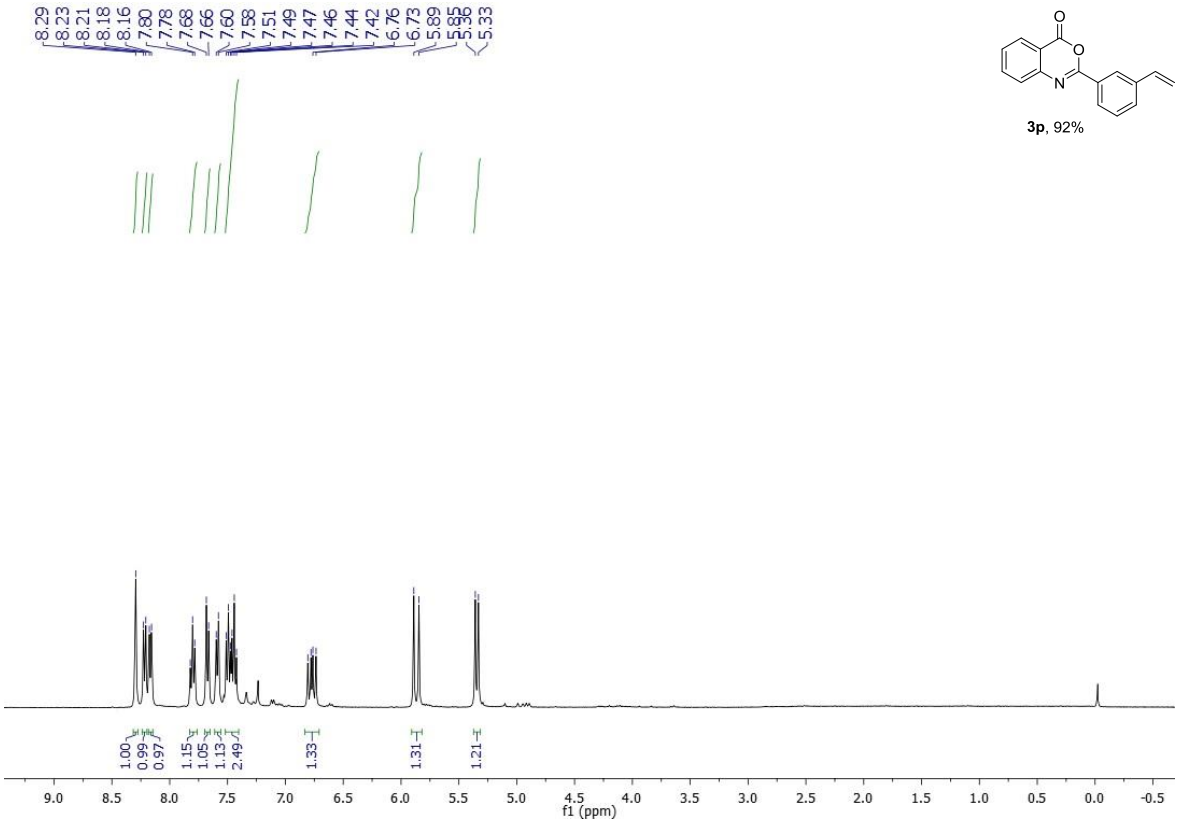
2-(4-vinylphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3o)



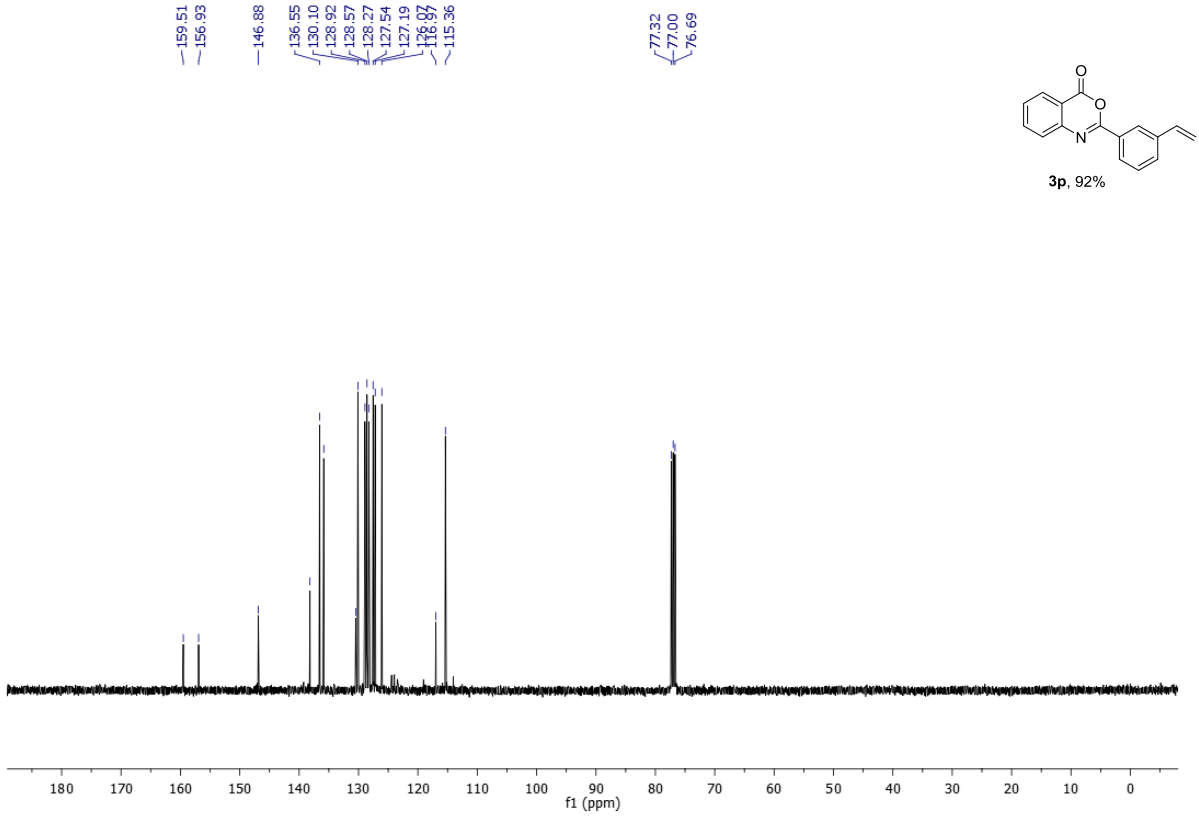
2-(4-vinylphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3o)



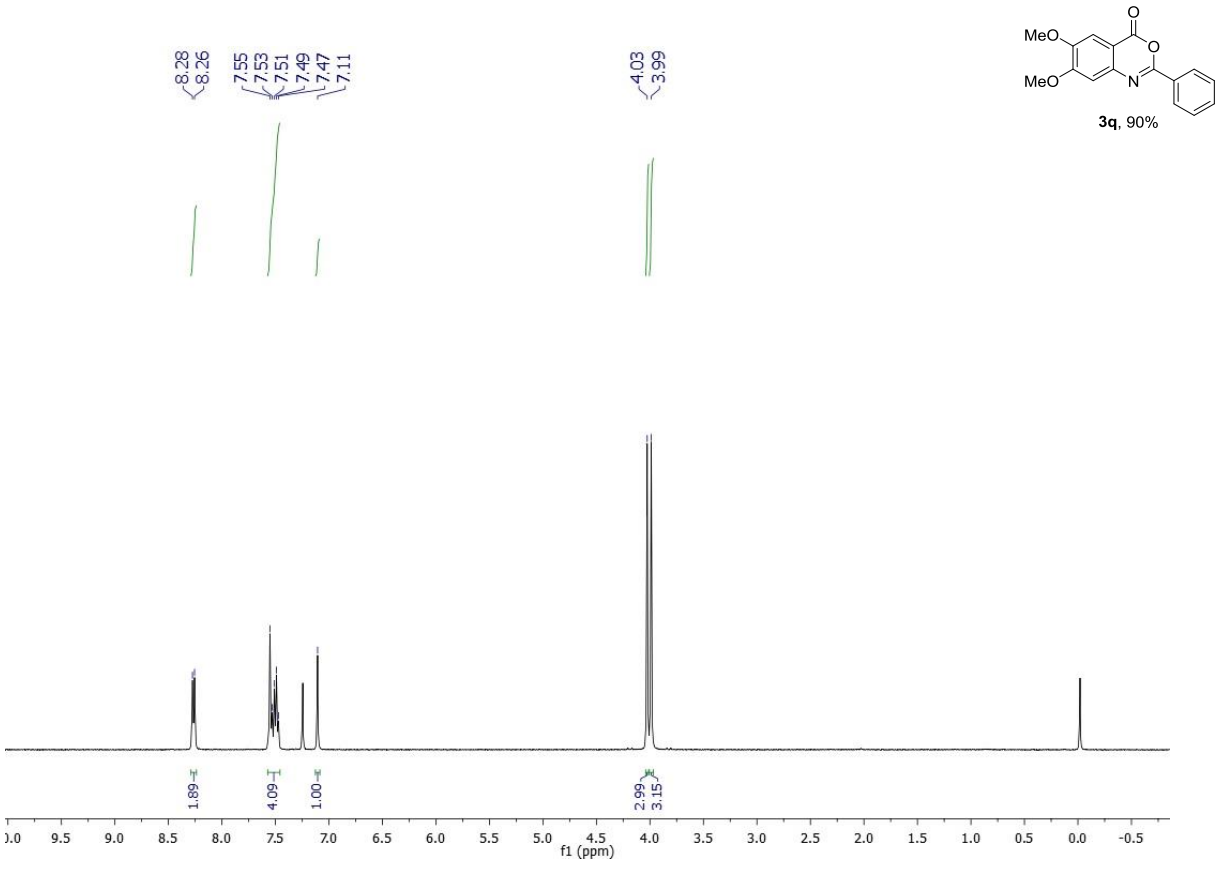
2-(3-vinylphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3q)



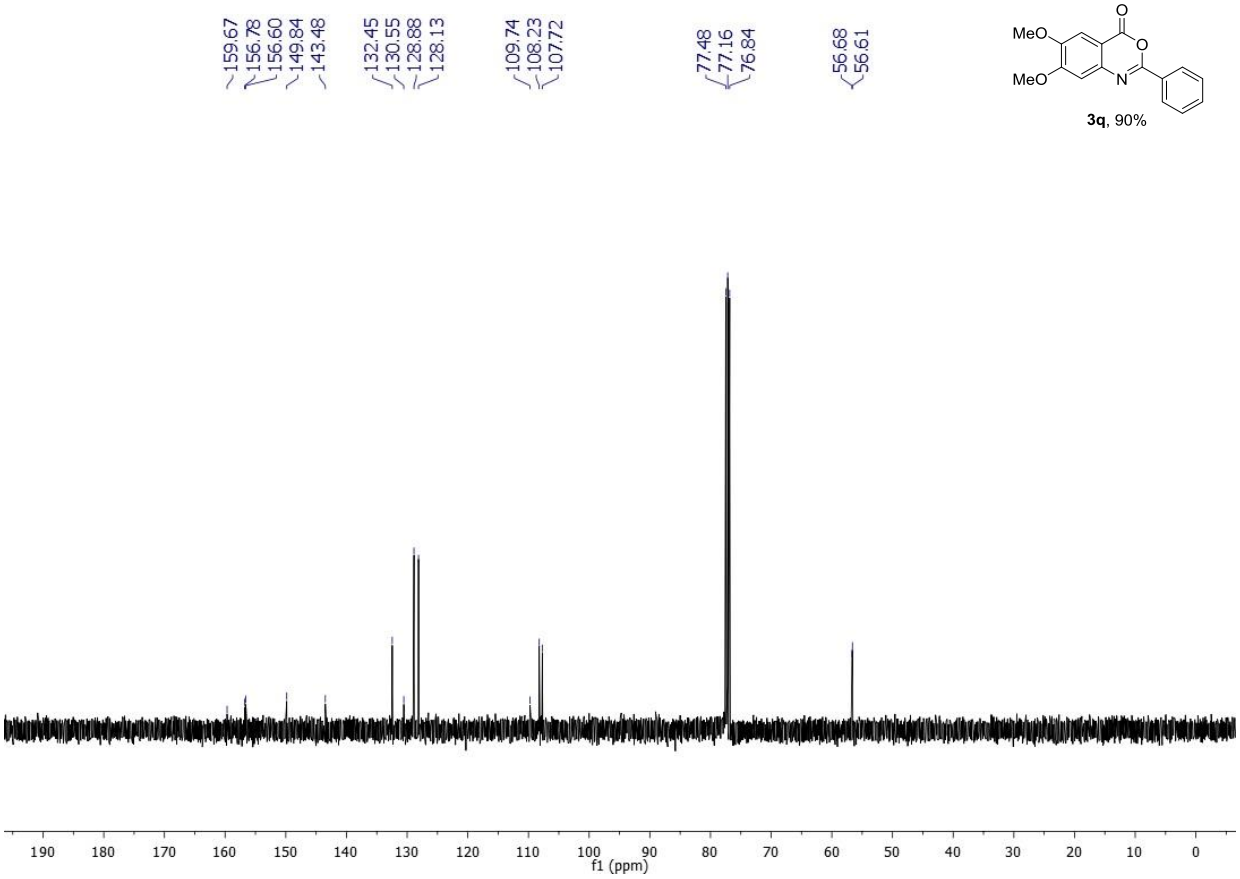
2-(3-vinylphenyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3q)



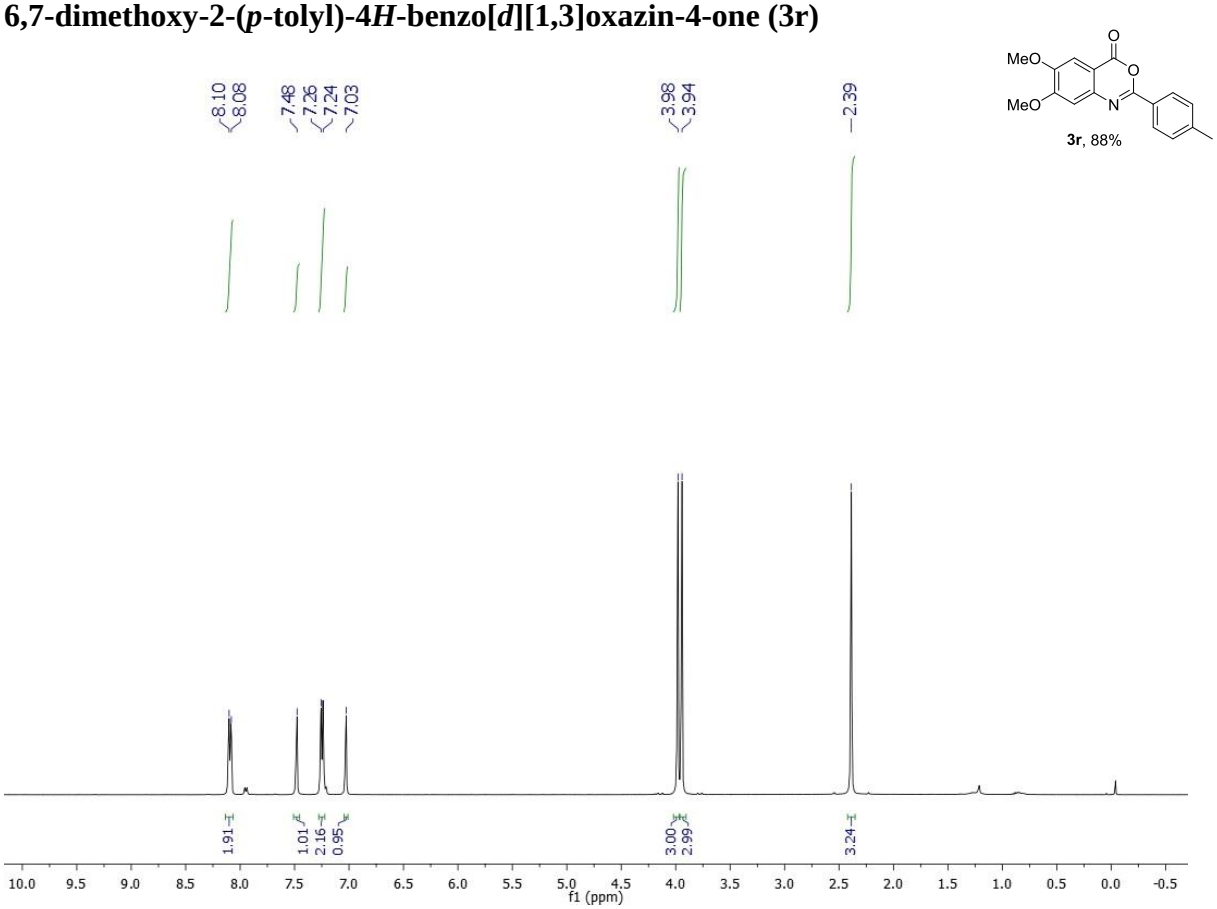
6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (3q)



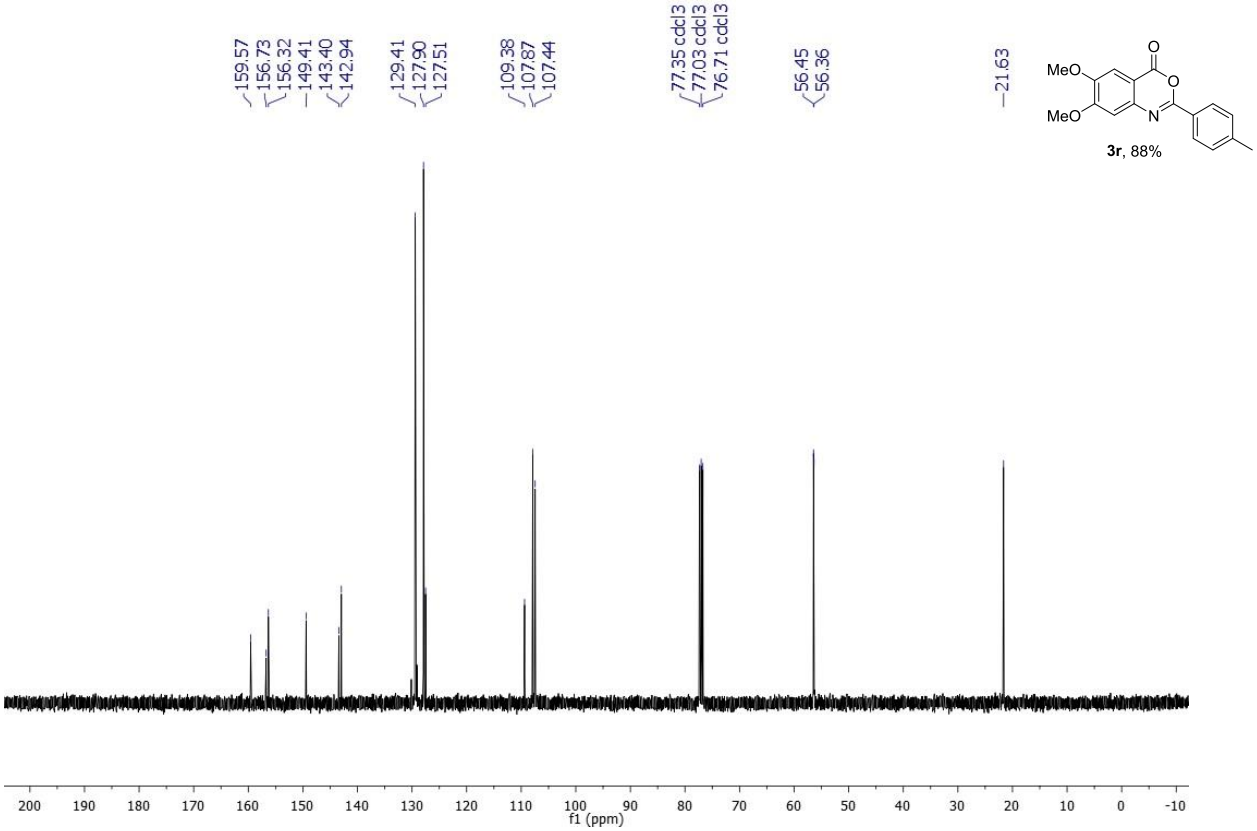
6,7-dimethoxy-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (3q)



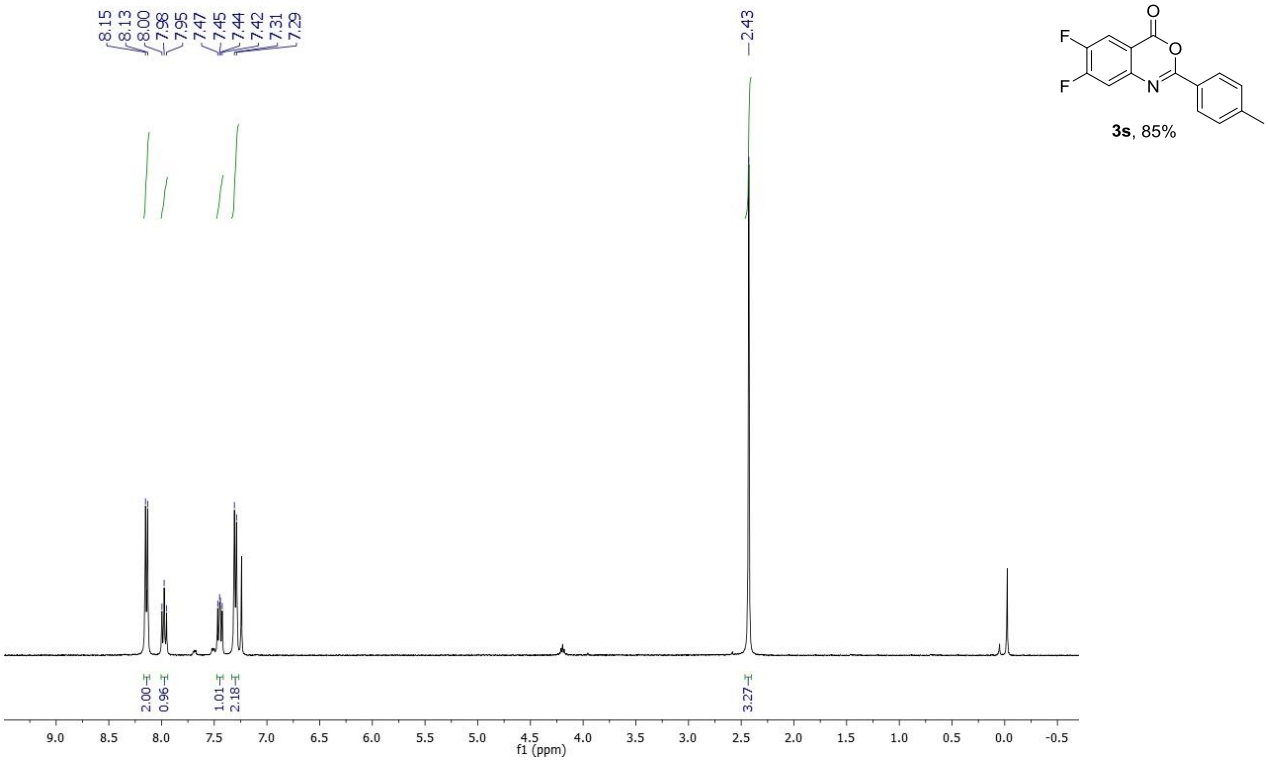
6,7-dimethoxy-2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3r)



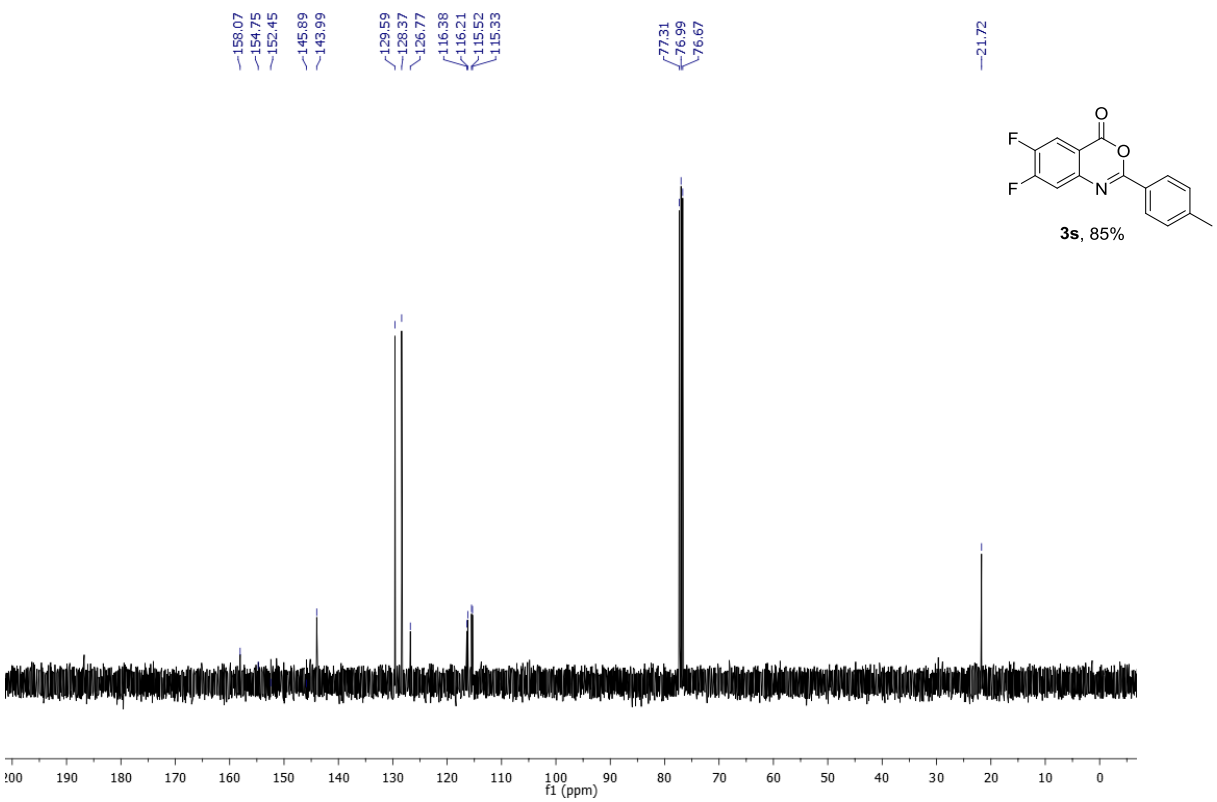
6,7-dimethoxy-2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3r)



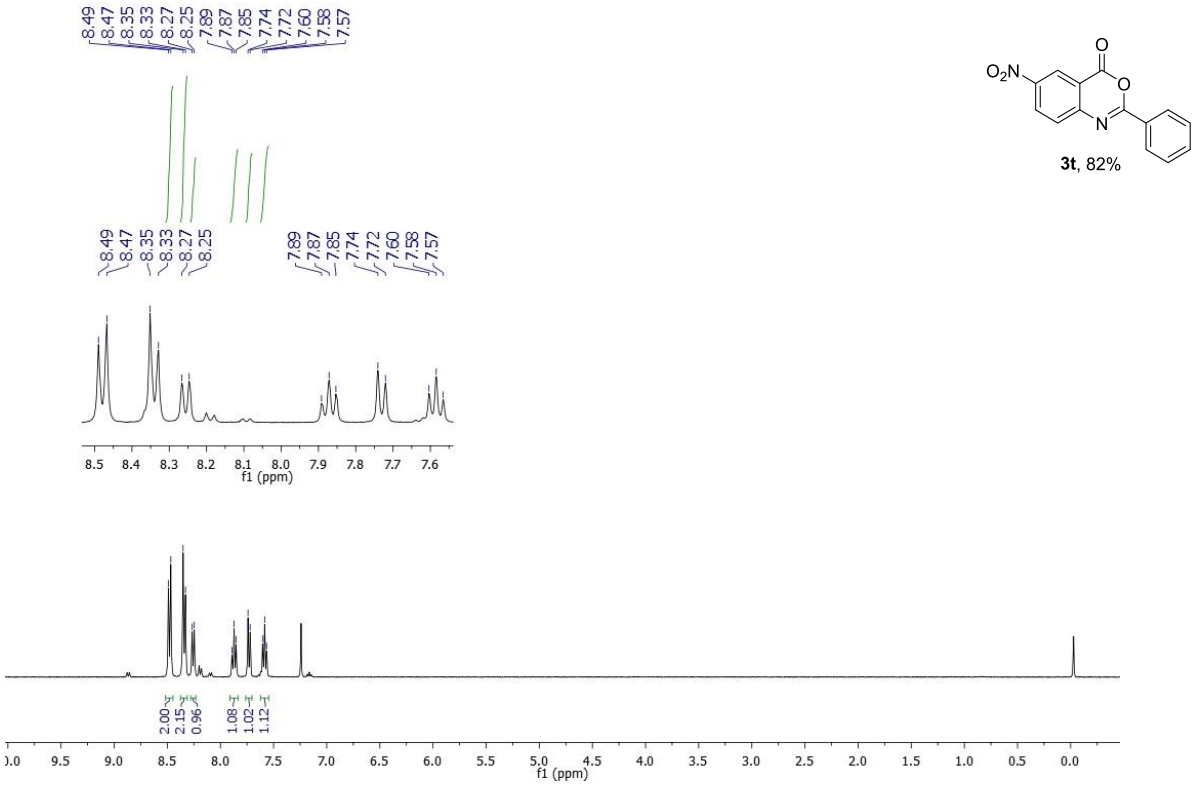
6,7-difluoro-2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3s)



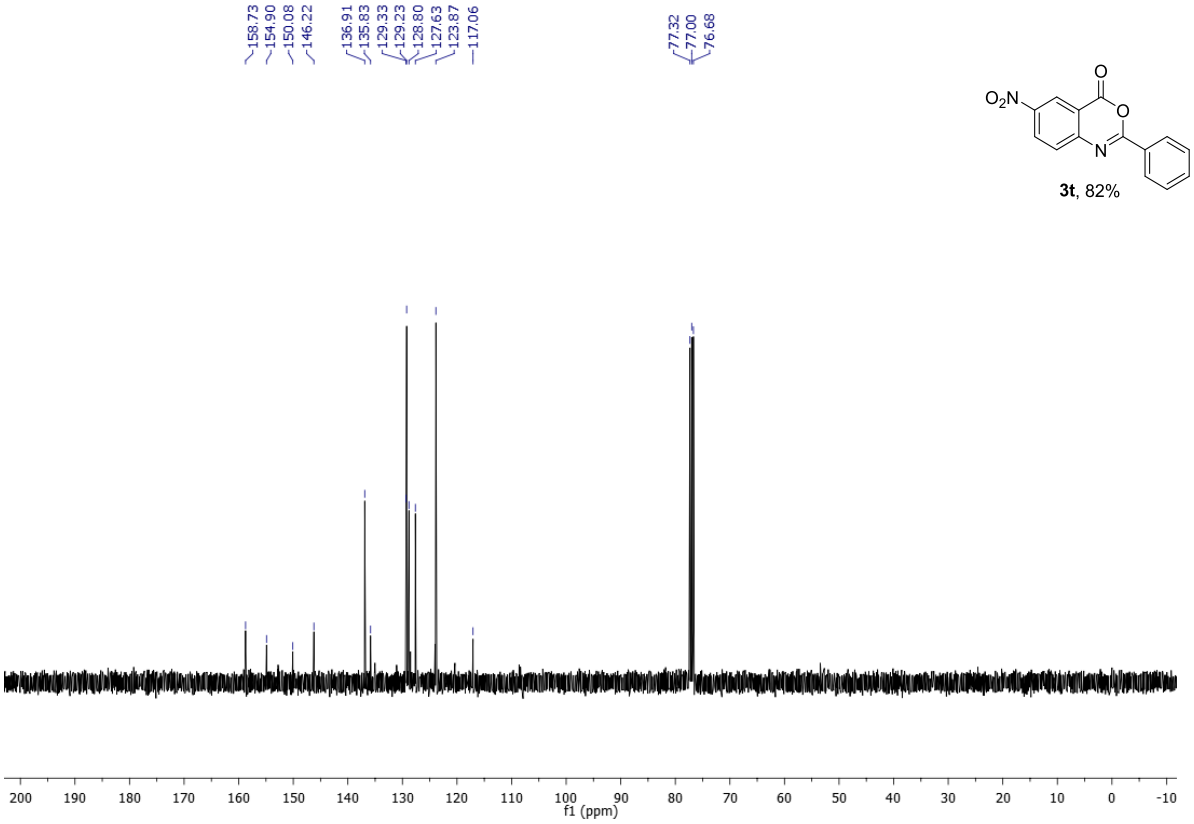
6,7-difluoro-2-(*p*-tolyl)-4*H*-benzo[*d*][1,3]oxazin-4-one (3s)



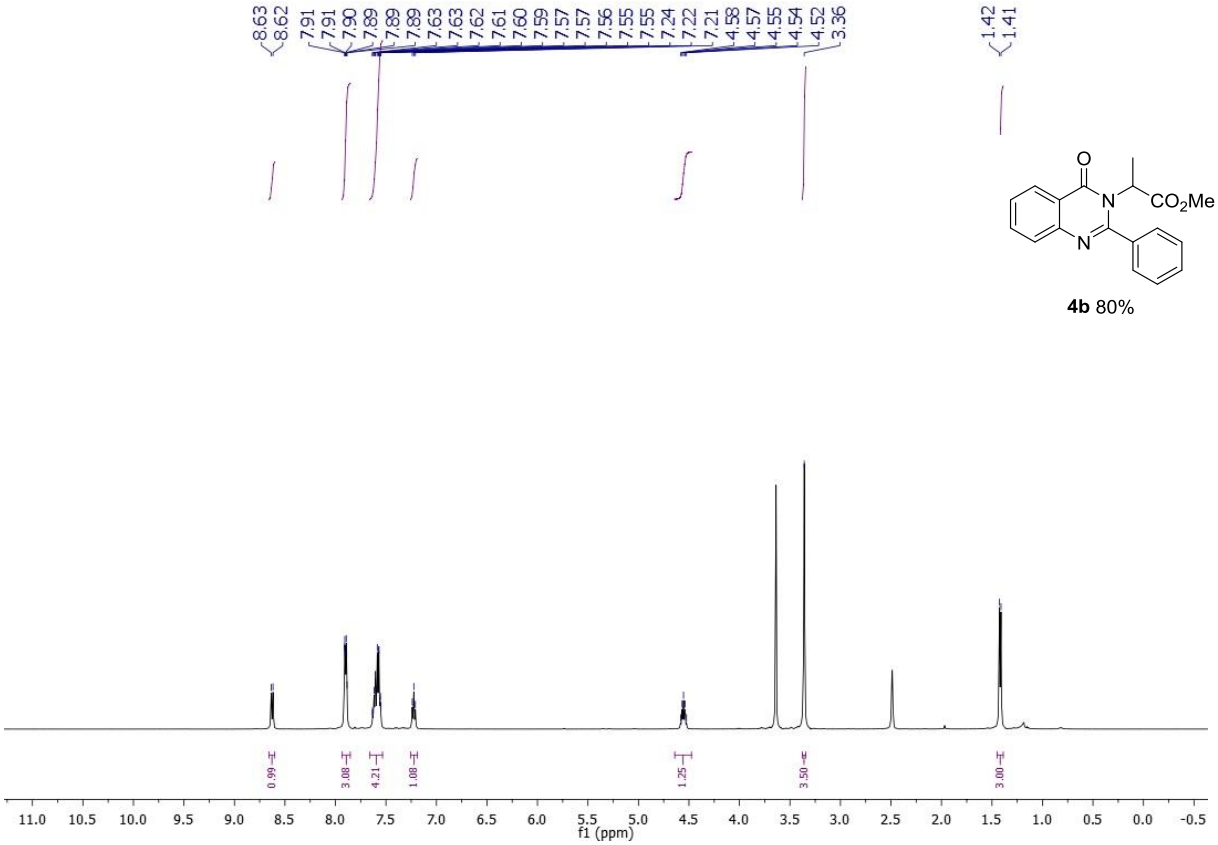
6-nitro-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (3t)



6-nitro-2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (3t)



methyl 2-(4-oxo-2-phenylquinazolin-3(4*H*)-yl)propanoate (4b)



methyl 2-(4-oxo-2-phenylquinazolin-3(4*H*)-yl)propanoate (4b)