

---

## Supporting Information for:

# The Rearrangement of Peroxides for the Construction of Fluorophoric 1,4-benzoxazin-3-one Derivatives

Moreshwar B. Chaudhari, Atul Chaudhary, Vishnupriya Kumar, and Boopathy Gnanaprakasam\*

---

Department of Chemistry, Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pashan, Pune -  
411008, India. \*Email- gnanaprakasam@iiserpune.ac.in

### TABLE OF CONTENTS

1. General Information and data collection	2
2. Experimental section	2-3
3. Detection of isobutylene gas using GC-MS:	3-4
4. Reaction monitoring using NMR	4-5
5. Deuteration experiments	5-9
6. Analytical data for the products	9-16
7. Copies of NMR spectra	17-30
8. References	31

---

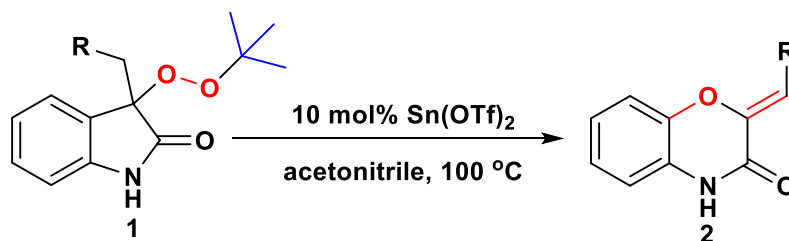
## 1. General information and data collection :

Column chromatographic separations were performed over 100-200 mesh size silica-gel. Visualization was accomplished with UV light and PMA, CAM stain followed by heating. The Amberlyst-15 (Dry form), Sn(OTf)<sub>2</sub> and other metal triflates were purchased from Sigma-Aldrich. The solvent used as received without drying in all the experiments. The <sup>1</sup>H and <sup>13</sup>C NMR spectra was recorded on 400 and 100 MHz respectively, using a Bruker or JEOL spectrometers. Abbreviations used in the NMR follow-up experiments: b, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectra were recorded with Waters- synapt G2 using electrospray ionization (ESI).

## 2. Experimental section :

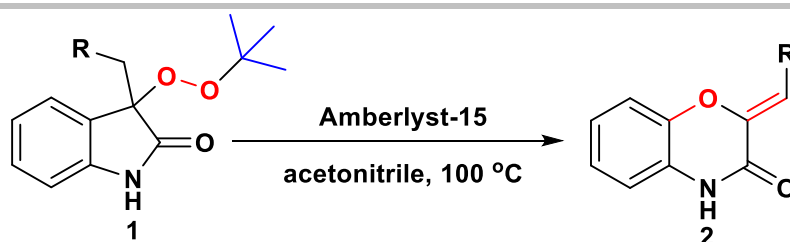
### A) General experimental procedure for the rearrangement reaction (with Sn(OTf)<sub>2</sub>):

In a 20 mL re-sealable vial (equipped with rubber septum and N<sub>2</sub> balloon) was added Sn(OTf)<sub>2</sub> (10 mol%), acetonitrile 2 mL, and finally, peroxy compound (0.25 mmol, 1 equivalent). The tube was purged with N<sub>2</sub> and sealed with a cap using crimper. The reaction mixture was heated at 100 °C in an oil bath for 16 hrs. After 16 hrs (conversion checked by TLC, if reaction is not completed then added 10 mol % Sn(OTf)<sub>2</sub> and continued until better conversion) added methanol and a volatile component was evaporated using a vacuum and residue was directly purified by silica gel chromatography (EtOAc : hexane= 15:85 to 30:70).



### B) General experimental procedure for the rearrangement reaction (with Amberlyst-15):

In a 20 mL re-sealable vial (equipped with rubber septum and N<sub>2</sub> balloon) was added Amberlyst-15 (substrate to Amberlyst-15 weight ratio of 1:2), acetonitrile 2 mL, and finally, peroxy compound (0.25 mmol). The tube was purged with N<sub>2</sub> and sealed with a cap using crimper. The reaction mixture was heated at 100 °C in an oil bath for 16 hrs. (conversion checked by TLC, if reaction is not completed then added 1 equivalent wt/wt Amberlyst-15 and continued until better conversion). After reaction completion methanol was added in the reaction mixture and filtered to remove Amberlyst-15 and volatile component was evaporated using a vacuum. The residue was directly purified by silica gel chromatography (EtOAc : hexane= 15:85 to 30:70).



### C) Experimental procedure for 1 mmol scale:

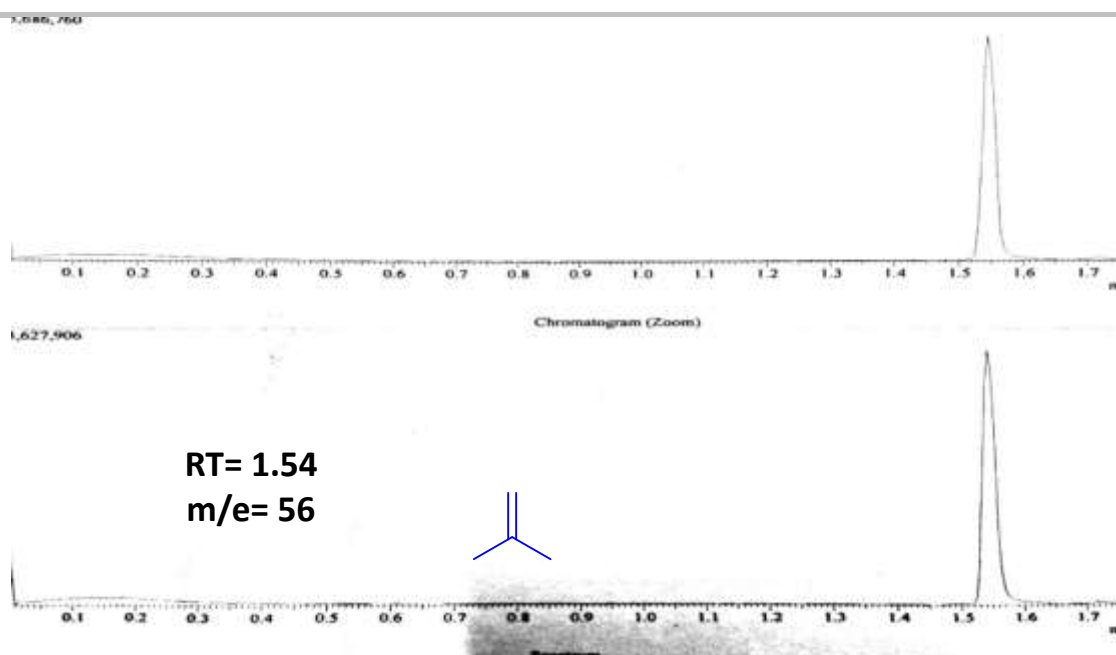
In a 20 mL re-sealable vial (equipped with rubber septum and N<sub>2</sub> balloon) was added Amberlyst-15 (622 mg) (substrate to Amberlyst-15 weight ratio of 1:2), acetonitrile 8 mL, and finally, peroxy compound (1 mmol, 311 mg). The tube was purged with N<sub>2</sub> and sealed with a cap using crimper. The reaction mixture was heated at 100 °C in an oil bath until the reaction completion. After reaction completion methanol was added in the reaction mixture and filtered to remove Amberlyst-15 and volatile component was evaporated using a vacuum. The residue was directly purified by silica gel chromatography to afford (*Z*)-2-benzylidene-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one **2a** (190 mg, 80%) using Amberlyst-15 as a faint yellow solid (EtOAc : hexane= 15:85).

### D) General experimental procedure for the Hock-rearrangement/cleavage (with Amberlyst-15):

In a 20 mL re-sealable vial was added FeCl<sub>3</sub>·6H<sub>2</sub>O (10 mol %), acetonitrile 2 mL, and finally, peroxy compound (0.25 mmol). The tube was sealed with a cap using crimper. The reaction mixture was heated at 100 °C in an oil bath for 10 hrs. After reaction completion volatile component was evaporated using a vacuum and the residue was directly purified by silica gel chromatography to afford isatin and aldehyde.

### 3. Detection of *iso*-butylene gas liberation using GCMS:

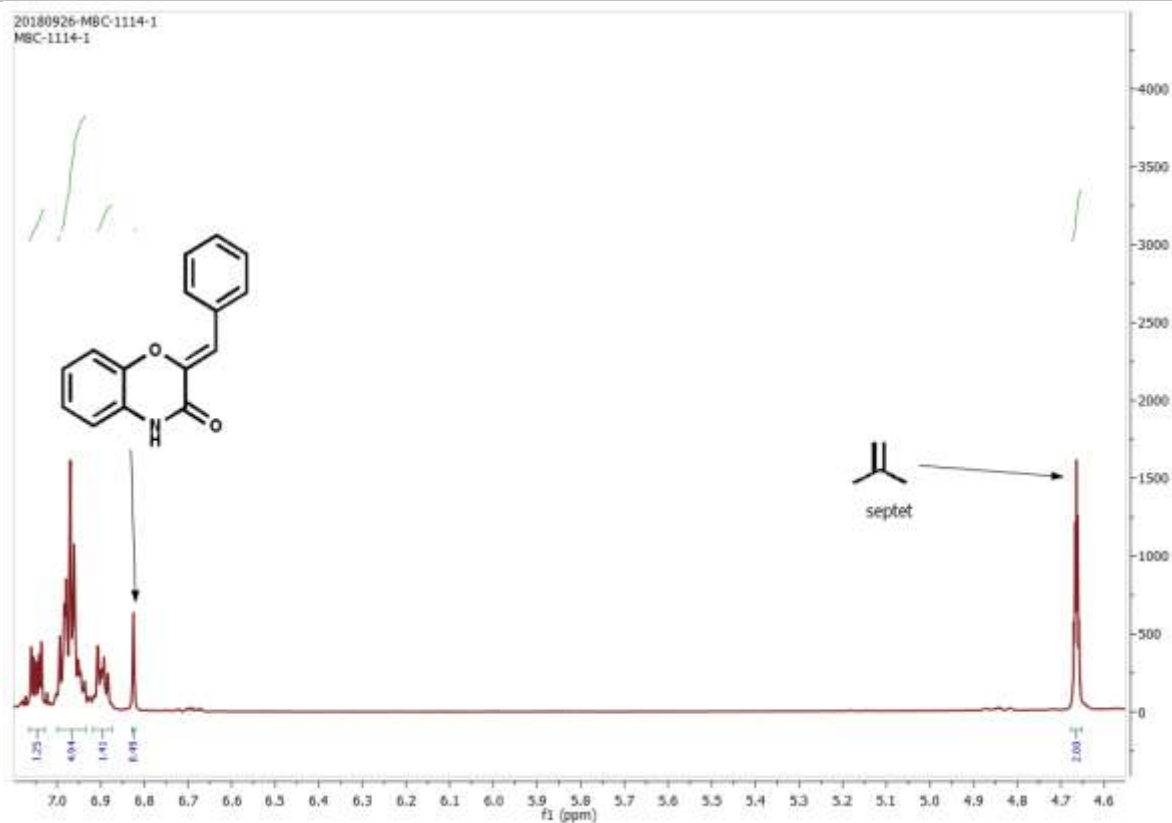
In a 20 mL re-sealable vial (equipped with rubber septum and N<sub>2</sub> balloon) was added Sn(OTf)<sub>2</sub> (10 mol %), acetonitrile 2 mL, and finally, peroxy compound (0.25 mmol, 1 equivalent). The tube was purged with N<sub>2</sub> and sealed with a cap using crimper. The reaction mixture was heated at 100 °C in an oil bath for 16 hrs. After reaction completion, the gaseous component was taken using Gas tight syringe and injected to a GCMS instrument. The presence of *m/e*= 56 corresponds to *iso*-butylene gas (Figure S1).



**Figure S1.** GC-MS spectra of gaseous phase of reaction mixture

#### **4. Reaction monitoring using NMR:**

In a NMR tube was added  $\text{Sn}(\text{OTf})_2$  (10 mol %), acetonitrile- $d_3$  0.6 mL, and finally, peroxy compound (20 mg, 0.06 mmol, 1 equivalent). The tube was purged with  $\text{N}_2$  and closed using cap. The reaction mixture was heated at 100 °C. After 2 hrs NMR tube was cooled and subjected for  $^1\text{H}$ -NMR. The notable peaks was observed at 6.82, singlet which belongs to alkene C-H of arylidene product **2a**. Moreover, at 4.66 ppm (septet) and 1.71 (triplet) was also observed which arises due to the presence of isobutylene (Figure S2).

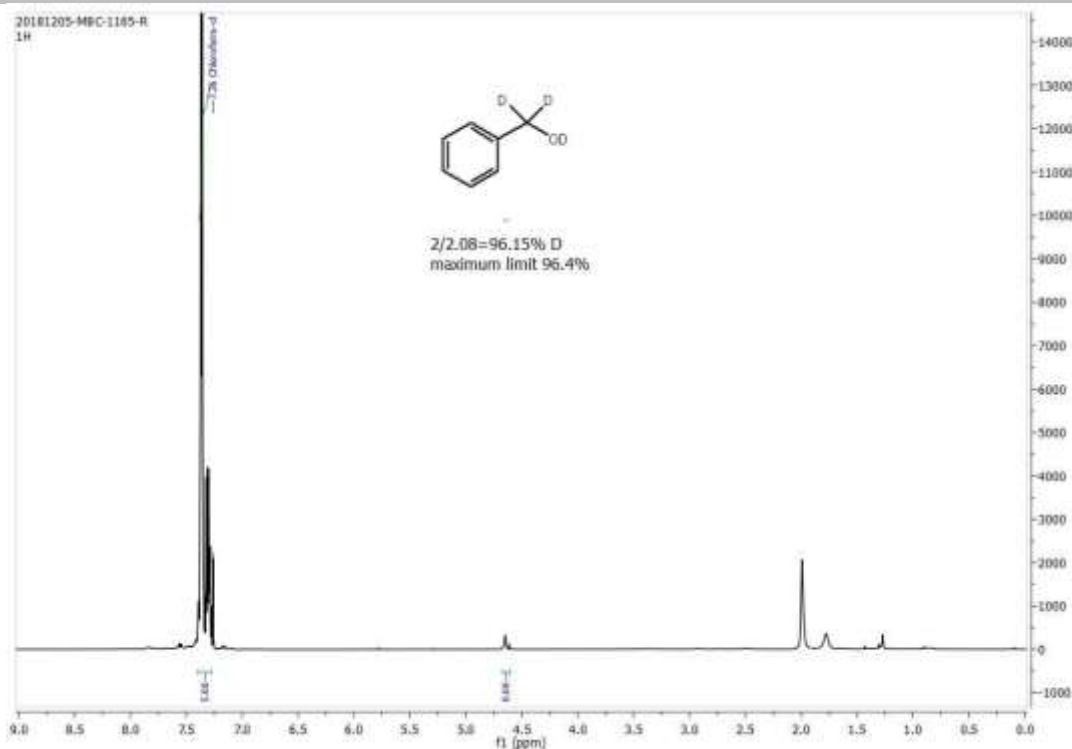


**Figure S2.**  $^1\text{H}$ -NMR spectra of crude reaction mixture

## 5. Deuteration experiments:

### Procedure for synthesis of benzyl alcohol-d<sub>3</sub>:

The deuterated benzyl alcohol was prepared by using reported procedure with few modifications by Gunanathan *et al.*<sup>1</sup> In a typical procedure, benzyl alcohol (2 mmol), Ru-MACHO (0.004 mmol), K<sub>2</sub>OtBu (0.001 mmol) were charged in a 20 mL resealable vial which was equipped rubber septum and N<sub>2</sub> balloon. The D<sub>2</sub>O (1.6 mL) was added using syringe and reaction mixture purged with N<sub>2</sub> and tube is sealed with cap using crimper and heated at 60 °C in a oil bath. The reaction was stopped after 6 hrs and reaction mixture is extracted with dichloromethane and the combined organic layer is washed with brine solution. The removal of solvent under reduced pressure provided pure products for further reaction. The  $^1\text{H}$ -NMR data resembles with previous report and showed 96 % deuterium incorporation.

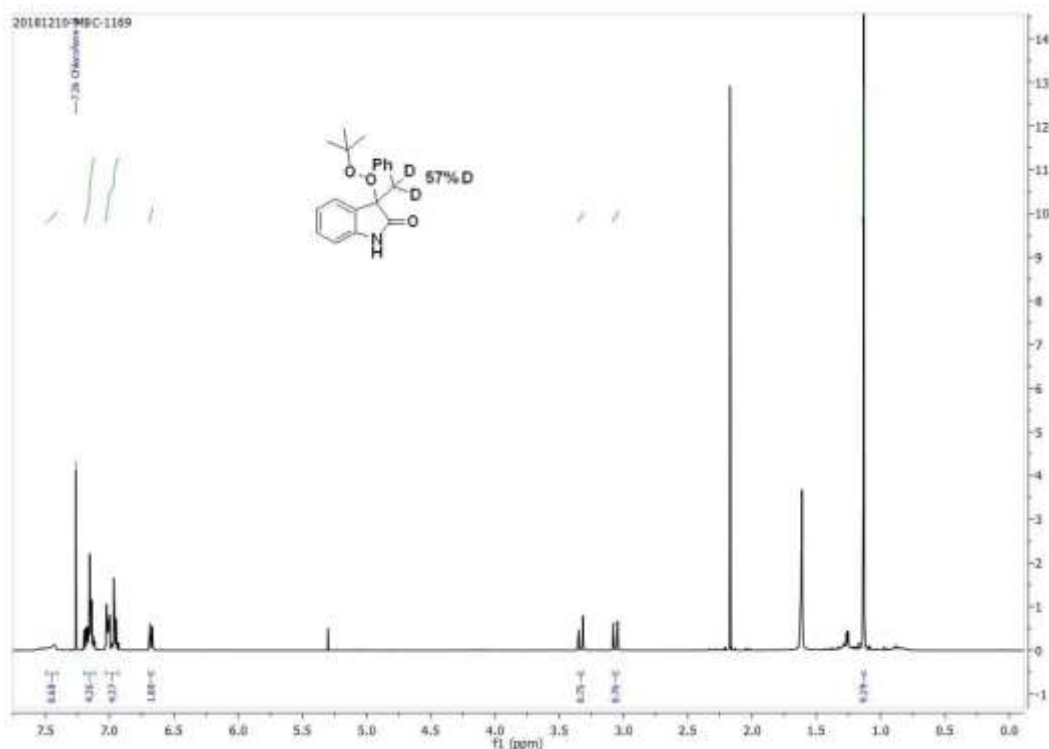
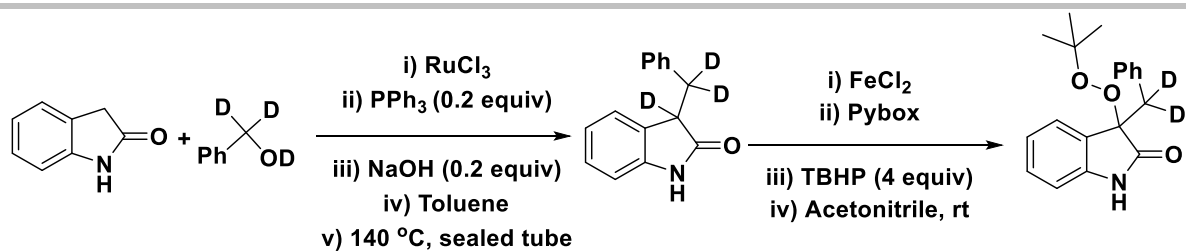


**Figure S3.**  $^1\text{H}$ -NMR spectrum of benzyl alcohol- $\text{d}_3$  (400 MHz,  $\text{CDCl}_3$ ):

**Procedure for the synthesis of 3-(phenylmethyl- $\text{d}_2$ )indolin-2-one:**

a) In a 20 mL resealable tube added  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  (0.162 mmol),  $\text{PPh}_3$  (0.324 mmol),  $\text{NaOH}$  (0.324 mmol), 2-oxindole (1.297 mmol) and benzyl alcohol- $\text{d}_3$  (1.62 mmol, 1 equivalent) after addition the vial was purged with  $\text{N}_2$  and sealed with cap using crimper and heated at  $140^\circ\text{C}$  for 24 hrs. The reaction mixture was cooled and volatile component was evaporated using vacuum and directly purified column chromatography. (Ethyl acetate: Pet ether= 18: 82).

b) For C3-peroxidation, In a 5 mL round-bottom flask mixture of iron(II) chloride (0.031 mmol, 5 mol%) and (2,6-Bis[(4S)-(-)-isopropyl-2-oxazolin-2-yl]pyridine) (pybox) ligand (0.031 mmol, 5 mol%) in acetonitrile 3 mL was stirred at room temperature for 20–30 min. To the obtained deep-red solution was added 5.0–6.0 M tert-butyl hydroperoxide (TBHP) in decane solution (2.48 mmol, 0.45 mL) and finally, 3-(phenylmethyl- $\text{d}_2$ )indolin-2-one- $\text{d}_3$  (0.62 mmol, 1 equiv) was added, and septum placed over it. The resulting solution was stirred at room temperature for 16 h without maintaining any special conditions such as the inert atmosphere. After completion of the reaction, a volatile component was evaporated using a vacuum. The residue was directly purified by silica gel chromatography (EtOAc:hexane= 15:85). The deuterium incorporation was measured by  $^1\text{H}$ -NMR analysis which showed 57% deuterium incorporation.

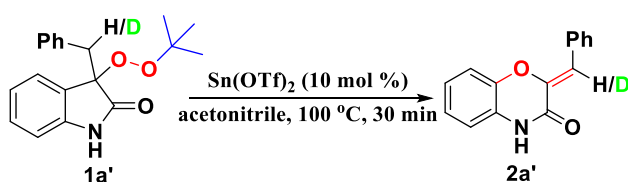


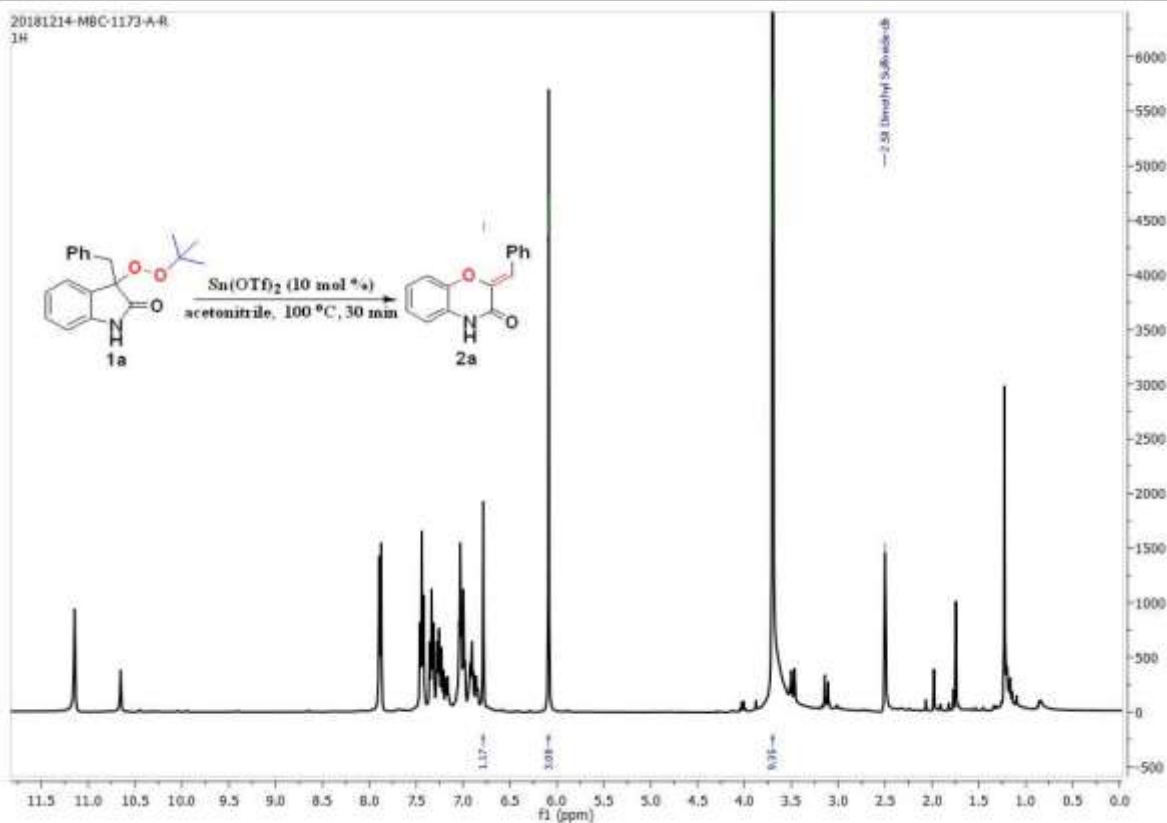
**Figure S4.**  $^1\text{H-NMR}$  spectrum of 3-(tert-butylperoxy)-3-(phenylmethyl- $\text{d}_2$ )indolin-2-one (400 MHz,  $\text{CDCl}_3$ ):

**Procedure for the catalytic H/D exchange reaction (Parallel reaction):**

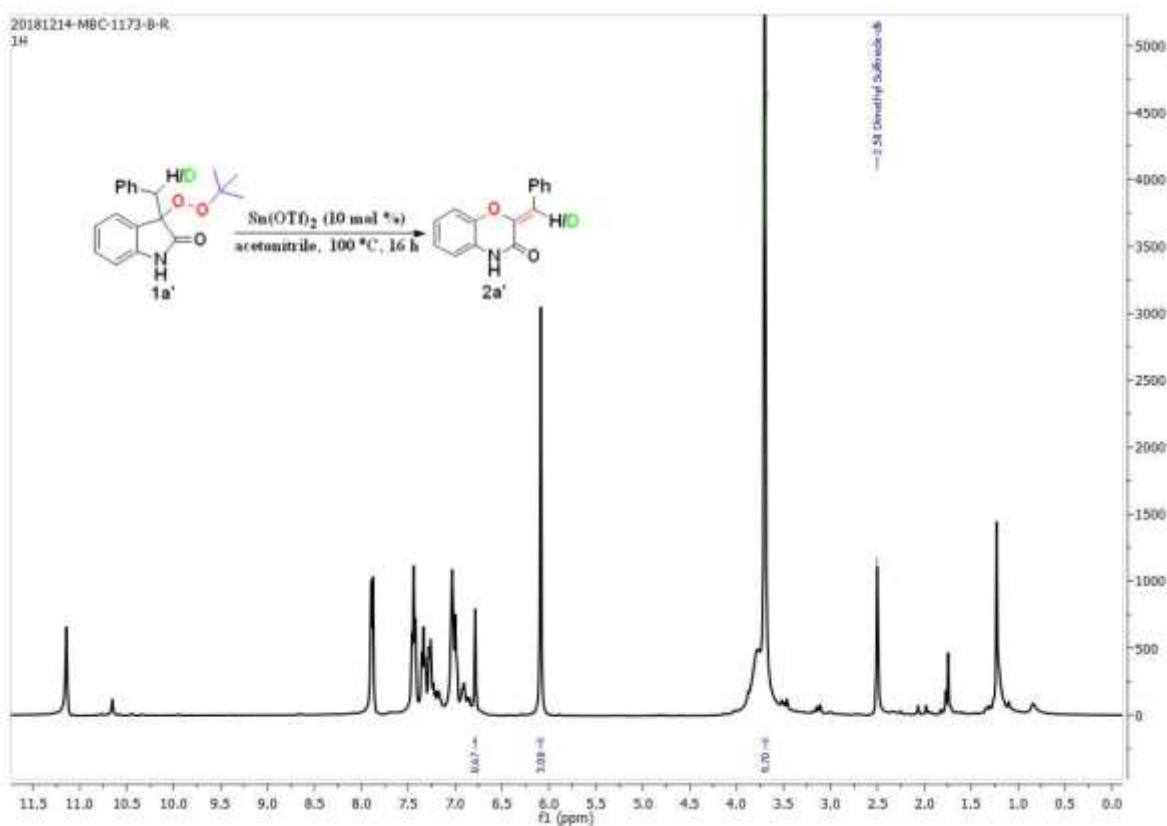
**Reaction with isotope labeled peroxide:**

In a 20 mL re-sealable vial (equipped with rubber septum and  $\text{N}_2$  balloon) was added  $\text{Sn}(\text{OTf})_2$  (5.32 mg, 10 mol %), acetonitrile 2 mL, and finally, deuterated peroxy compound (40 mg, 0.1277 mmol, 1 equivalent). The tube was purged with  $\text{N}_2$  and sealed with a cap using crimper. The reaction mixture was heated at  $100\text{ }^\circ\text{C}$  in an oil bath for 30 min. After reaction completion a volatile component was evaporated using a vacuum and analyzed by crude  $^1\text{H-NMR}$  using 1,3,5-trimethoxybenzene as an internal standard.





**Figure S5.**  $^1\text{H}$ -NMR for crude reaction mixture of unlabelled peroxide.



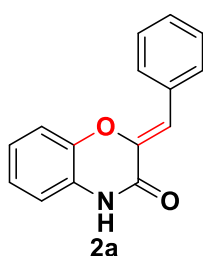
**Figure S6.**  $^1\text{H}$ -NMR for crude reaction mixture of labelled peroxide.

### Reaction with unlabeled peroxide:

In a 20 mL re-sealable vial (equipped with rubber septum and N<sub>2</sub> balloon) was added Sn(OTf)<sub>2</sub> (5.32 mg, 10 mol %), acetonitrile 2 mL, and finally, peroxy compound (40 mg, 0.1277 mmol, 1 equivalent). The tube was purged with N<sub>2</sub> and sealed with a cap using crimper. The reaction mixture was heated at 100 °C in an oil bath for 30 min. After reaction completion a volatile component was evaporated using a vacuum and analyzed by crude <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as an internal standard.

The K<sub>H</sub>/K<sub>D</sub> ratio was calculated by <sup>1</sup>H-NMR analysis and found k<sub>H</sub>/k<sub>D</sub>= 1.17/0.67= 1.75.

### 6. Analytical data for the product:



#### (Z)-2-benzylidene-2H-benzo[b][1,4]oxazin-3(4H)-one (2a):

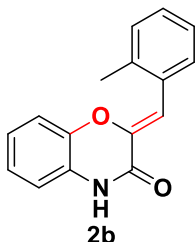
Prepared according to general procedure (A) and (B), using 3-benzyl-3-(*tert*-butylperoxy)indolin-2-one (77.7 mg, 0.25 mmol) to afford (*Z*)-2-benzylidene-2H-benzo[b][1,4]oxazin-3(4H)-one **2a** (53.8 mg, 90%) using Sn(OTf)<sub>2</sub> and (51.6 mg, 87%) using Amberlyst-15 as a faint yellow solid.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 11.15 (bs, 1H), 7.90-7.88 (m, 2H), 7.46-7.42 (m, 2H), 7.37-7.32 (m, 1H), 7.30-7.27 (m, 1H), 7.06-7.02 (m, 2H), 7.01-6.97 (m, 1H), 6.78 (s, 1H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 156.26, 141.78, 140.44, 133.24, 129.74, 128.68, 128.18, 125.37, 123.49, 123.20, 115.57, 110.50.

FTIR (KBr): 3175, 2974, 2897, 1692, 1638, 1498, 1387, 1109 cm<sup>-1</sup>

HRMS (ESI) m/z calculated for C<sub>15</sub>H<sub>11</sub>NO<sub>2</sub> (M+H)<sup>+</sup>: 238.0868, found: 238.0869.



(*Z*)-2-(2-methylbenzylidene)-2H-benzo[b][1,4]oxazin-3(4H)-one (**2b**): Prepared according to general procedure (A) and (B), using 3-(*tert*-butylperoxy)-3-(2-methylbenzyl)indolin-2-one (81.2 mg, 0.25

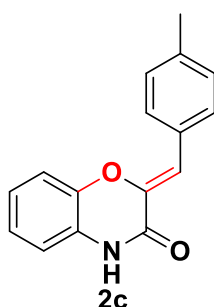
mmol) to afford (*Z*)-2-(2-methylbenzylidene)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one **2b** (55 mg, 88%) using Sn(OTf)<sub>2</sub> and (59 mg, 94%) using Amberlyst-15 as a cream colored solid.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 11.19 (bs, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.32-7.21 (m, 3H), 7.18-7.16 (m, 1H), 7.06-6.97 (m, 3H), 6.91 (s, 1H), 2.36 (s, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 156.39, 141.68, 140.39, 136.71, 131.65, 130.24, 129.00, 128.02, 126.06, 125.39, 123.42, 123.21, 115.54, 115.47, 107.49, 19.90.

FTIR (KBr): 3180, 2962, 2920, 1688, 1634, 1503, 1387, 1112 cm<sup>-1</sup>

HRMS (ESI) *m/z* calculated for C<sub>16</sub>H<sub>13</sub>NO<sub>2</sub> (M+H)<sup>+</sup>: 252.1025, found: 252.1024.



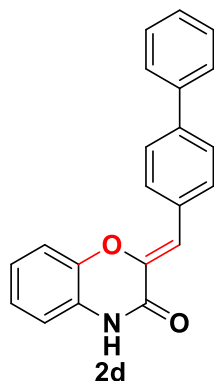
(*Z*)-2-(4-methylbenzylidene)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (**2c**): Prepared according to general procedure (A) and (B), using 3-(*tert*-butylperoxy)-3-(4-methylbenzyl)indolin-2-one (81.2 mg, 0.25 mmol) to afford (*Z*)-2-(4-methylbenzylidene)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one **2c** (31.7 mg, 50%) using Sn(OTf)<sub>2</sub> and (32.6 mg, 52%) using Amberlyst-15 as a cream colored solid.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): 11.09 (bs, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.26-7.24 (3H), 7.06 – 6.94 (m, 3H), 6.75 (s, 1H), 2.34 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.39, 141.16, 140.50, 137.81, 130.44, 129.72, 129.29, 125.42, 123.39, 123.13, 115.52, 115.49, 110.67, 21.00.

FTIR (KBr): 3150, 2919, 1687, 1635, 1504, 1387, 1112 cm<sup>-1</sup>

HRMS (ESI) *m/z* calculated for C<sub>16</sub>H<sub>13</sub>NO<sub>2</sub> (M+H)<sup>+</sup>: 252.1025, found: 252.1027.



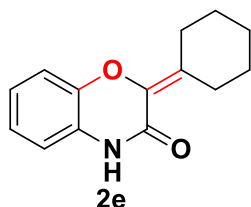
**(Z)-2-([1,1'-biphenyl]-4-ylmethylene)-2H-benzo[*b*][1,4]oxazin-3(4*H*)-one (2d):** Prepared according to general procedure (A) and (B), using 3-([1,1'-biphenyl]-4-ylmethyl)-3-(*tert*-butylperoxy)indolin-2-one (96.7 mg, 0.25 mmol) to afford (Z)-2-([1,1'-biphenyl]-4-ylmethylene)-2H-benzo[*b*][1,4]oxazin-3(4*H*)-one **2d** (45.9 mg, 58%) using Sn(OTf)<sub>2</sub> and (41.5 mg, 53%) using Amberlyst-15 as a cream colored solid.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.16 (bs, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.77-7.72 (m, 4H), 7.51-7.47 (m, 2H), 7.41-7.37 (m, 1H), 7.32-7.29 (m, 1H), 7.07 – 7.03 (m, 2H), 7.01 – 6.98 (m, 1H), 6.84 (s, 1H).

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 156.24, 141.92, 140.46, 139.55, 139.46, 132.45, 130.33, 129.03, 127.69, 126.82, 126.57, 125.41, 123.52, 123.21, 115.59, 115.53, 110.10.

FTIR (KBr): 3150, 2959, 2920, 1679, 1635, 1500, 1387, 1106 cm<sup>-1</sup>

HRMS (ESI) *m/z* calculated for C<sub>21</sub>H<sub>15</sub>NO<sub>2</sub> (M+H)<sup>+</sup>: 314.1181, found: 314.1183.



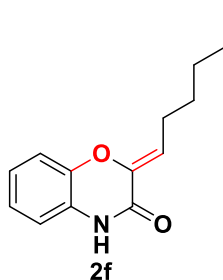
**2-cyclohexylidene-2H-benzo[*b*][1,4]oxazin-3(4*H*)-one (2e):** Prepared according to general procedure (A) and (B), using 3-(*tert*-butylperoxy)-3-cyclohexylindolin-2-one (75.8 mg, 0.25 mmol) to afford 2-cyclohexylidene-2H-benzo[*b*][1,4]oxazin-3(4*H*)-one **2e** (45 mg, 78%) using Sn(OTf)<sub>2</sub> and (47 mg, 82%) using Amberlyst-15 as a white solid.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.65 (bs, 1H), 7.03 – 6.99 (m, 1H), 6.96 – 6.90 (m, 2H), 6.89 – 6.85 (m, 1H), 2.88-2.84 (m, 2H), 2.46 – 2.43 (m, 2H), 1.58-1.52 (m, 6H).

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 158.72, 142.67, 134.09, 133.72, 126.47, 122.75, 122.62, 115.00, 114.87, 28.32, 27.52, 27.22, 27.11, 25.77.

FTIR (KBr): 3181, 2985, 2920, 1677, 1628, 1451, 1387, 1117 cm<sup>-1</sup>

HRMS (ESI) *m/z* calculated for C<sub>14</sub>H<sub>15</sub>NO<sub>2</sub> (M+H)<sup>+</sup>: 230.1181, found: 230.1187.



**(Z)-2-hexylidene-2H-benzo[*b*][1,4]oxazin-3(4*H*)-one (2f):** Prepared according to general procedure (A) and (B), using 3-(*tert*-butylperoxy)-3-hexylindolin-2-one (76 mg, 0.25 mmol) to afford (Z)-2-

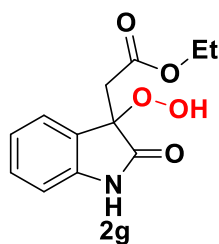
hexylidene-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one **2f** (43 mg, 75%) using Sn(OTf)<sub>2</sub> and (50.5 mg, 87%) using Amberlyst-15 as a white solid.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.88 (bs, 1H), 7.04 – 7.00 (m, 1H), 6.97 – 6.90 (m, 3H), 5.87 (t, *J* = 7.7 Hz, 1H), 2.24 (q, *J* = 7.5 Hz, 2H), 1.47 – 1.39 (m, 2H), 1.34 – 1.26 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 156.26, 141.98, 140.99, 125.37, 123.03, 122.82, 115.44, 115.15, 114.69, 30.92, 27.85, 23.92, 21.89, 13.90.

FTIR (KBr): 3168, 2948, 2919, 1692, 1653, 1504, 1394, 1288 cm<sup>-1</sup>

HRMS (ESI) *m/z* calculated for C<sub>14</sub>H<sub>17</sub>NO<sub>2</sub> (M+H)<sup>+</sup>: 232.1338, found: 232.1339.



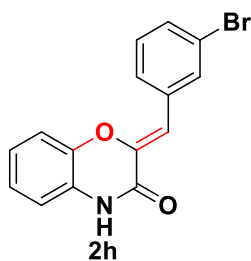
ethyl 2-(3-hydroperoxy-2-oxoindolin-3-yl)acetate (**2g**): Prepared according to general procedure (A) and (B), using ethyl 2-(3-(*tert*-butylperoxy)-2-oxoindolin-3-yl)acetate (76.7 mg, 0.25 mmol) to afford ethyl 2-(3-hydroperoxy-2-oxoindolin-3-yl)acetate **2g** (46 mg, 73%) using Sn(OTf)<sub>2</sub> and (44.5 mg, 71%) using Amberlyst-15 as a white solid.

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.74 (bs, 1H), 7.68 (bs, 1H), 6.96 – 6.88 (m, 4H), 4.01 (q, *J* = 7.1 Hz, 2H), 3.31 (d, *J* = 16.4 Hz, 1H), 2.90 (d, *J* = 16.4 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 168.28, 162.96, 140.84, 126.85, 122.81, 122.19, 116.95, 115.25, 95.16, 59.98, 41.34, 13.98.

FTIR (KBr): 3416, 2923, 1691, 1630, 1580, 1384 cm<sup>-1</sup>

HRMS (ESI) *m/z* calculated for C<sub>12</sub>H<sub>13</sub>NO<sub>5</sub> (M+Na)<sup>+</sup>: 274.0691, found: 274.0698.



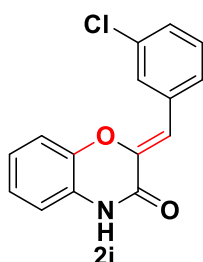
(*Z*)-2-(3-bromobenzylidene)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (**2h**): Prepared according to general procedure (A) and (B), using 3-(3-bromobenzyl)-3-(*tert*-butylperoxy)indolin-2-one (97.2 mg, 0.25 mmol) to afford (*Z*)-2-(3-bromobenzylidene)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one **2h** (42 mg, 53%) using Sn(OTf)<sub>2</sub> and (48 mg, 61%) using Amberlyst-15 as a white solid.

**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>): δ 11.22 (bs, 1H), 8.04 (t, *J* = 1.6 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.08 – 7.03 (m, 2H), 7.01 – 6.98 (m, 1H), 6.77 (s, 1H).

**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 176.84, 161.32 (d, *J* = 247.1 Hz), 141.04, 132.82 (d, *J* = 3.6 Hz), 129.58, 129.01 (d, *J* = 8.2 Hz), 127.44, 125.69, 123.67 (d, *J* = 3.6 Hz), 122.10, 121.12 (d, *J* = 15.2 Hz), 115.16 (d, *J* = 22.5 Hz), 109.90, 85.12, 80.79, 32.63, 26.60.

**FTIR** (KBr): 3180, 2979, 2920, 1685, 1642, 1501, 1393, 1110 cm<sup>-1</sup>

**HRMS** (ESI) *m/z* calculated for C<sub>15</sub>H<sub>10</sub>BrNO<sub>2</sub> (M+H)<sup>+</sup>: 315.9973, found: 315.9969.



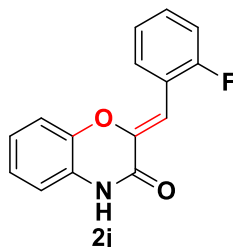
**(Z)-2-(3-chlorobenzylidene)-2H-benzo[*b*][1,4]oxazin-3(4H)-one (2i)**: Prepared according to general procedure (A) and (B), 3-using (*tert*-butylperoxy)-3-(3-chlorobenzyl)indolin-2-one (86.4 mg, 0.25 mmol) to afford (*Z*)-2-(3-chlorobenzylidene)-2H-benzo[*b*][1,4]oxazin-3(4H)-one **2i** (48 mg, 71%) using Sn(OTf)<sub>2</sub> and (49 mg, 72%) using Amberlyst-15 as a white solid.

**<sup>1</sup>H NMR** (400 MHz, DMSO-*D*<sub>6</sub>) δ 11.23 (bs, 1H), 7.91 – 7.87 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.40 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.26 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.08-7.04 (m, 2H), 7.01 – 6.97 (m, 1H), 6.78 (s, 1H).

**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 155.88, 142.81, 140.25, 135.42, 133.28, 130.50, 129.01, 128.17, 127.81, 125.29, 123.69, 123.29, 115.66, 115.53, 108.80.

**FTIR** (KBr): 3147, 3083, 2921, 1694, 1641, 1502, 1390, 1111 cm<sup>-1</sup>

**HRMS** (ESI) *m/z* calculated for C<sub>15</sub>H<sub>10</sub>ClNO<sub>2</sub> (M+H)<sup>+</sup>: 272.0478, found: 272.0481.



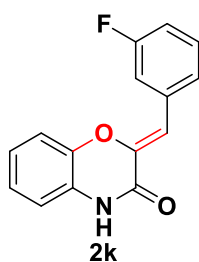
**(Z)-2-(2-fluorobenzylidene)-2H-benzo[*b*][1,4]oxazin-3(4H)-one (2j)**: Prepared according to general procedure (A) and (B), using 3-(*tert*-butylperoxy)-3-(2-fluorobenzyl)indolin-2-one (82.3 mg, 0.25 mmol) to afford (*Z*)-2-(2-fluorobenzylidene)-2H-benzo[*b*][1,4]oxazin-3(4H)-one **2j** (43 mg, 67%) using Sn(OTf)<sub>2</sub> and (41 mg, 64%) using Amberlyst-15 as a white solid.

**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.27 (bs, 1H), 8.31 (td, *J* = 7.8, 1.7 Hz, 1H), 7.41 (tdd, *J* = 7.3, 5.5, 1.8 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.09 – 7.03 (m, 2H), 7.03 – 6.98 (m, 1H), 6.91 (s, 1H).

**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 159.64 (d, *J* = 249.1 Hz), 155.81, 143.19 (d, *J* = 1.9 Hz), 140.23, 130.09, 130.01, 129.96, 125.26, 124.80 (d, *J* = 3.5 Hz), 123.67, 123.26, 120.69 (d, *J* = 11.1 Hz), 115.64 (d, *J* = 1.8 Hz), 115.31 (d, *J* = 22.0 Hz), 100.53 (d, *J* = 8.2 Hz).

**FTIR** (KBr): 3150, 2920, 1687, 1635, 1500, 1391, 1127 cm<sup>-1</sup>

**HRMS** (ESI) *m/z* calculated for C<sub>15</sub>H<sub>10</sub>FNO<sub>2</sub> (M+H)<sup>+</sup> : 256.0774, found: 256.0776.



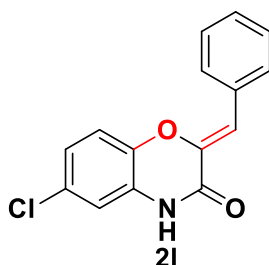
**(Z)-2-(3-fluorobenzylidene)-2H-benzo[*b*][1,4]oxazin-3(4H)-one (2k)**: Prepared according to general procedure (A) and (B), using 3-(*tert*-butylperoxy)-3-(3-fluorobenzyl)indolin-2-one (82.3 mg, 0.25 mmol) to afford (Z)-2-(3-fluorobenzylidene)-2H-benzo[*b*][1,4]oxazin-3(4H)-one **2k** (45 mg, 70%) using Sn(OTf)<sub>2</sub> and (41 mg, 64%) using Amberlyst-15 as a white solid.

**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.22 (bs, 1H), 7.74 – 7.68 (m, 2H), 7.48 (td, *J* = 8.1, 6.4 Hz, 1H), 7.30 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.21 – 7.15 (m, 1H), 7.09 – 7.03 (m, 2H), 7.02 – 6.98 (m, 1H), 6.80 (s, 1H).

**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 162.15 (d, *J* = 242.7 Hz), 155.91, 142.68, 140.27, 135.55 (d, *J* = 8.5 Hz), 130.53 (d, *J* = 8.6 Hz), 125.95 (d, *J* = 2.6 Hz), 125.27, 123.66, 123.27, 115.83, 115.63, 115.62, 114.88 (d, *J* = 21.3 Hz), 109.09 (d, *J* = 2.7 Hz).

**FTIR** (KBr): 3183, 2920, 1694, 1641, 1501, 1390, 1110 cm<sup>-1</sup>

**HRMS** (ESI) *m/z* calculated for C<sub>15</sub>H<sub>10</sub>FNO<sub>2</sub> (M+H)<sup>+</sup> : 256.0774, found: 256.0775.



**(Z)-2-benzylidene-6-chloro-2H-benzo[*b*][1,4]oxazin-3(4H)-one (2l)**: Prepared according to general procedure (A) and (B), using 3-benzyl-3-(*tert*-butylperoxy)-6-chloroindolin-2-one (86.5 mg, 0.25 mmol) to afford (Z)-2-benzylidene-6-chloro-2H-benzo[*b*][1,4]oxazin-3(4H)-one **2l** (35 mg, 51%) using

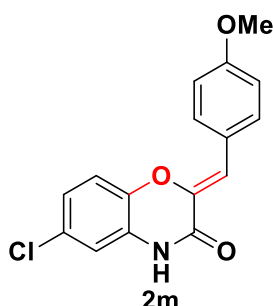
Sn(OTf)<sub>2</sub> and (24 mg, 35%) using Amberlyst-15 as a white solid. (Low yield due to formation of 30% and 38% deprotected hydroperoxy compound respectively).

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 11.22 (s, 1H), 7.89 – 7.86 (m, 2H), 7.44 (m, 2H), 7.38 – 7.31 (m, 2H), 7.06 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.79 (s, 1H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 156.08, 141.22, 139.41, 132.99, 129.86, 128.68, 128.34, 126.96, 126.76, 122.55, 117.13, 114.82, 111.08.

FTIR (KBr): 3175, 2924, 1683, 1635, 1494, 1380, 1240 cm<sup>-1</sup>

HRMS (ESI) *m/z* calculated for C<sub>15</sub>H<sub>10</sub>ClNO<sub>2</sub> (M+H)<sup>+</sup> : 272.0478, found: 272.0493.



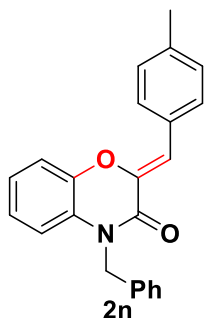
**(Z)-6-chloro-2-(4-methoxybenzylidene)-2H-benzo[*b*][1,4]oxazin-3(4H)-one (2m):** Prepared according to general procedure (A) and (B), using 3-(*tert*-butylperoxy)-6-chloro-3-(4-methoxybenzyl)indolin-2-one (94 mg, 0.25 mmol) to afford (Z)-6-chloro-2-(4-methoxybenzylidene)-2H-benzo[*b*][1,4]oxazin-3(4H)-one **2m** (40 mg, 53%) using Sn(OTf)<sub>2</sub> and (45 mg, 60%) using Amberlyst-15 as a white solid. (Low yield due to formation of 24% and 20% deprotected peroxy compound respectively).

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 11.10 (bs, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.04 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.01 – 6.98 (m, 2H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.75 (s, 1H), 3.80 (s, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 159.30, 156.39, 139.58, 139.56, 131.56, 127.09, 126.60, 125.62, 122.47, 117.02, 114.75, 114.17, 111.29, 55.18..

FTIR (KBr): 3149, 2925, 1686, 1637, 1509, 1396, 1119 cm<sup>-1</sup>

HRMS (ESI) *m/z* calculated for C<sub>16</sub>H<sub>12</sub>ClNO<sub>3</sub> (M+H)<sup>+</sup> : 302.0584, found: 302.0586.



**(Z)-4-benzyl-2-(4-methylbenzylidene)-2H-benzo[*b*][1,4]oxazin-3(4H)-one (2n):** Prepared according to general procedure (A) and (B), using 1-benzyl-3-(*tert*-butylperoxy)-3-(4-methylbenzyl)indolin-2-one

---

(94 mg, 0.25 mmol) to afford (*Z*)-4-benzyl-2-(4-methylbenzylidene)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one **2n** (71 mg, 83%) using Sn(OTf)<sub>2</sub> and (75 mg, 88%) using Amberlyst-15 as a white solid.

**<sup>1</sup>H NMR** (400 MHz, DMSO-*d*<sub>6</sub>) 7.82 (d, *J* = 8.2 Hz, 2H), 7.34-7.32 (m, 5H), 7.29-7.26 (m, 3H), 7.10 – 6.99 (m, 3H), 6.90 (s, 1H), 5.28 (s, 2H), 2.35 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>) δ 156.54, 141.18, 140.28, 138.03, 136.03, 130.44, 129.82, 129.35, 128.71, 127.23, 126.61, 126.02, 123.80, 123.38, 115.88, 115.59, 112.11, 44.34, 21.02.

**FTIR** (KBr): 3059, 2922, 1671, 1628, 1503, 1394, 1112 cm<sup>-1</sup>

**HRMS** (ESI) *m/z* calculated for C<sub>23</sub>H<sub>19</sub>NO<sub>2</sub> (M+H)<sup>+</sup> : 342.1494, found: 342.1486.

## 7. Copies of NMR Spectra:

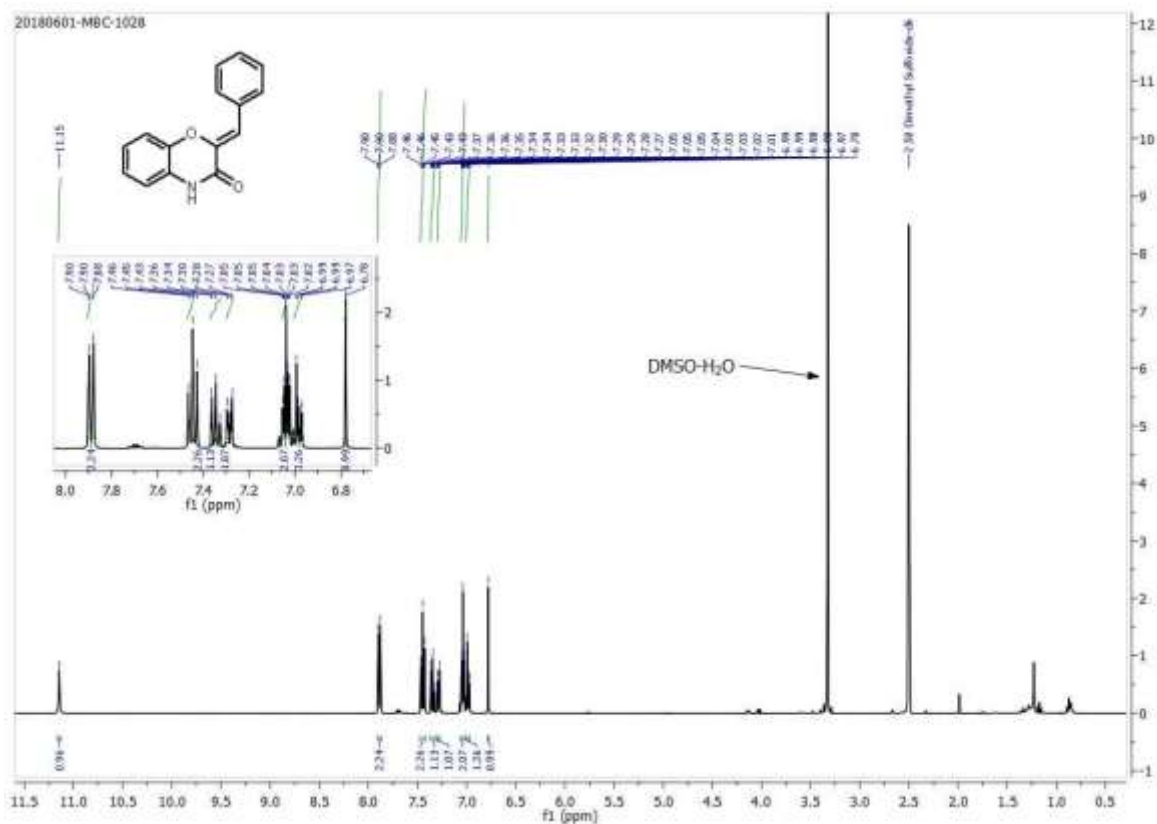


Figure S7. <sup>1</sup>H NMR of Compound 2a

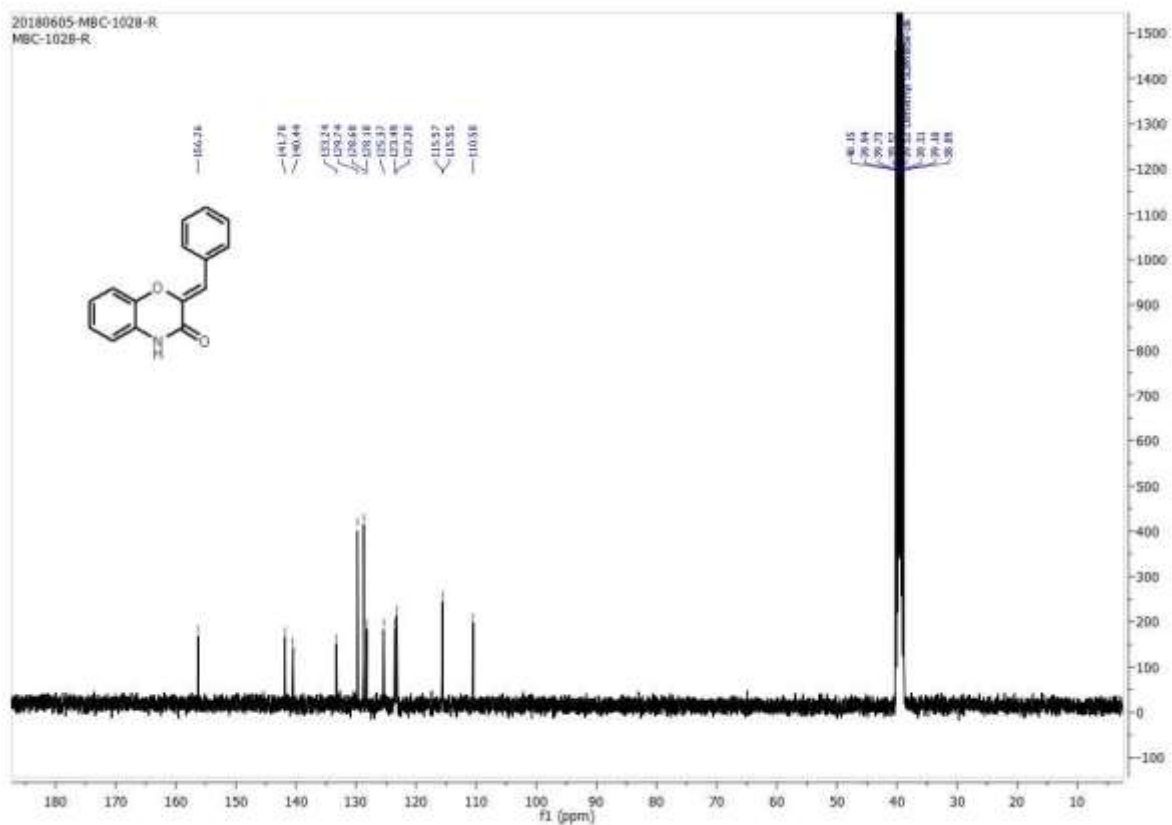


Figure S8. <sup>13</sup>C NMR of Compound 2a







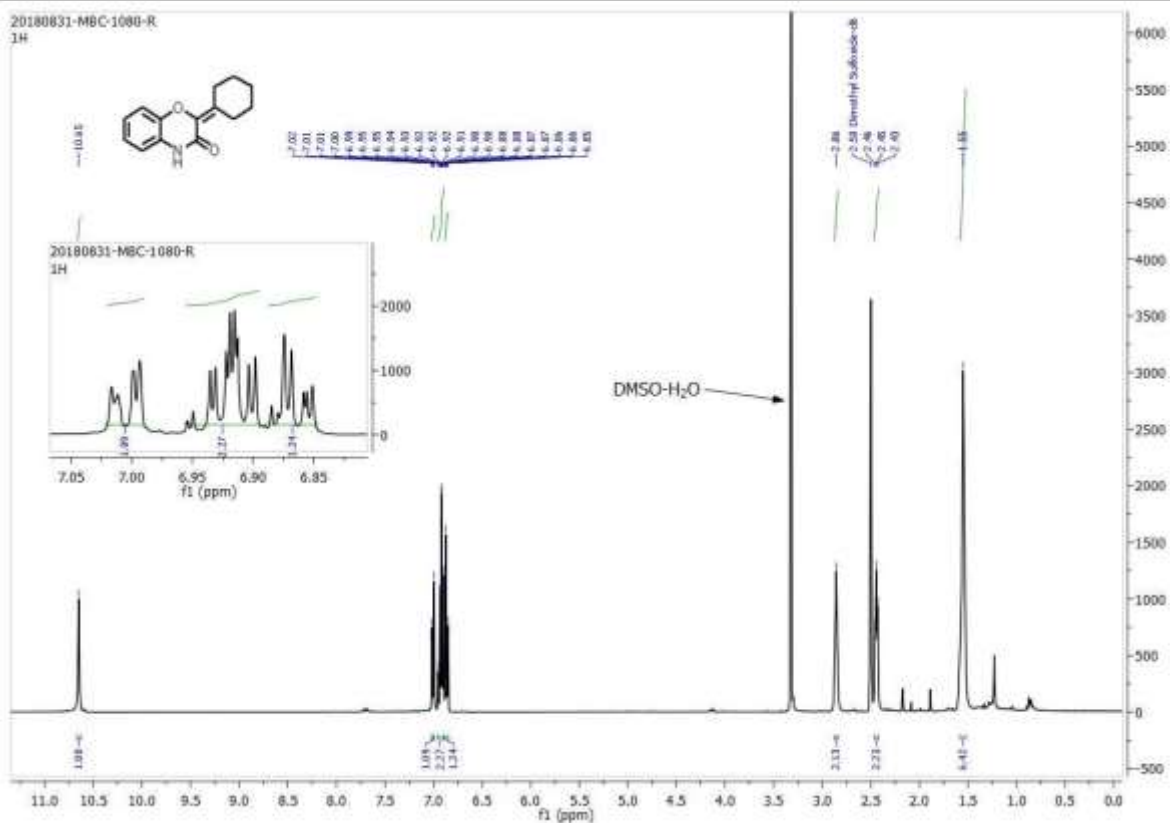


Figure S15. <sup>1</sup>H NMR of Compound 2e

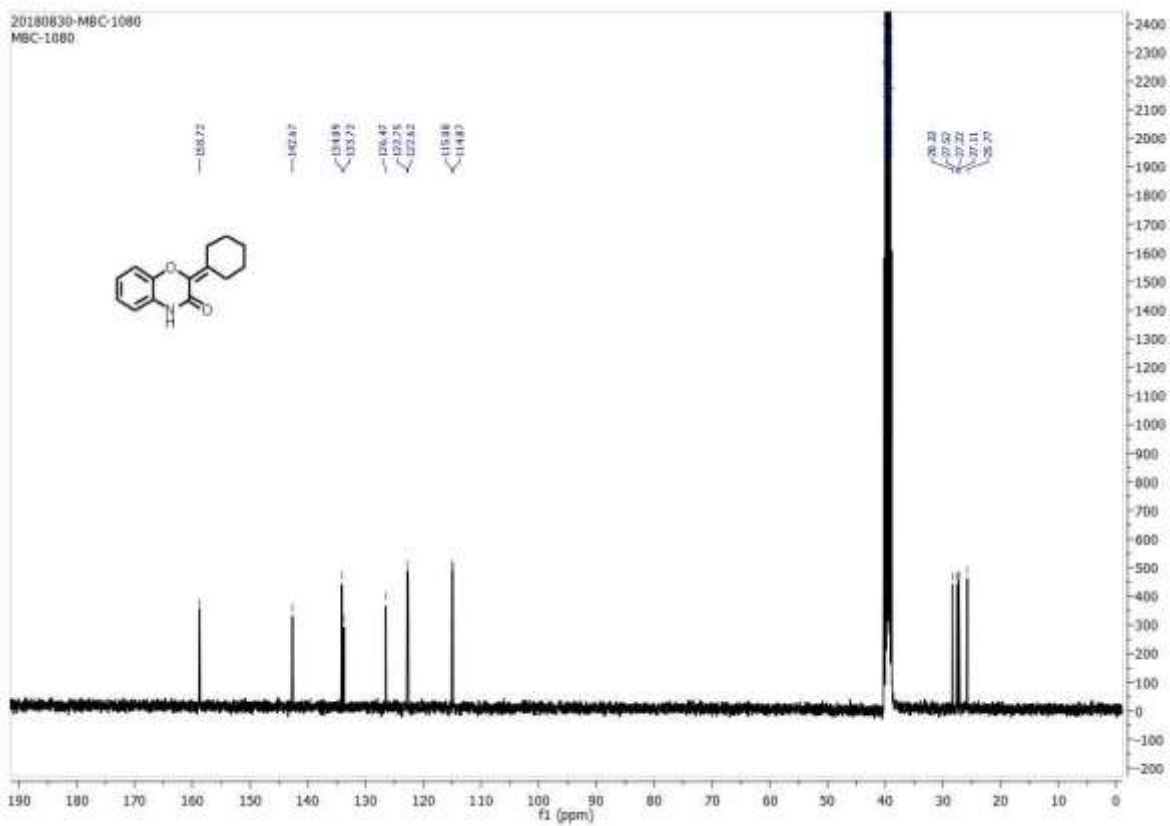


Figure S16. <sup>13</sup>C NMR of Compound 2e

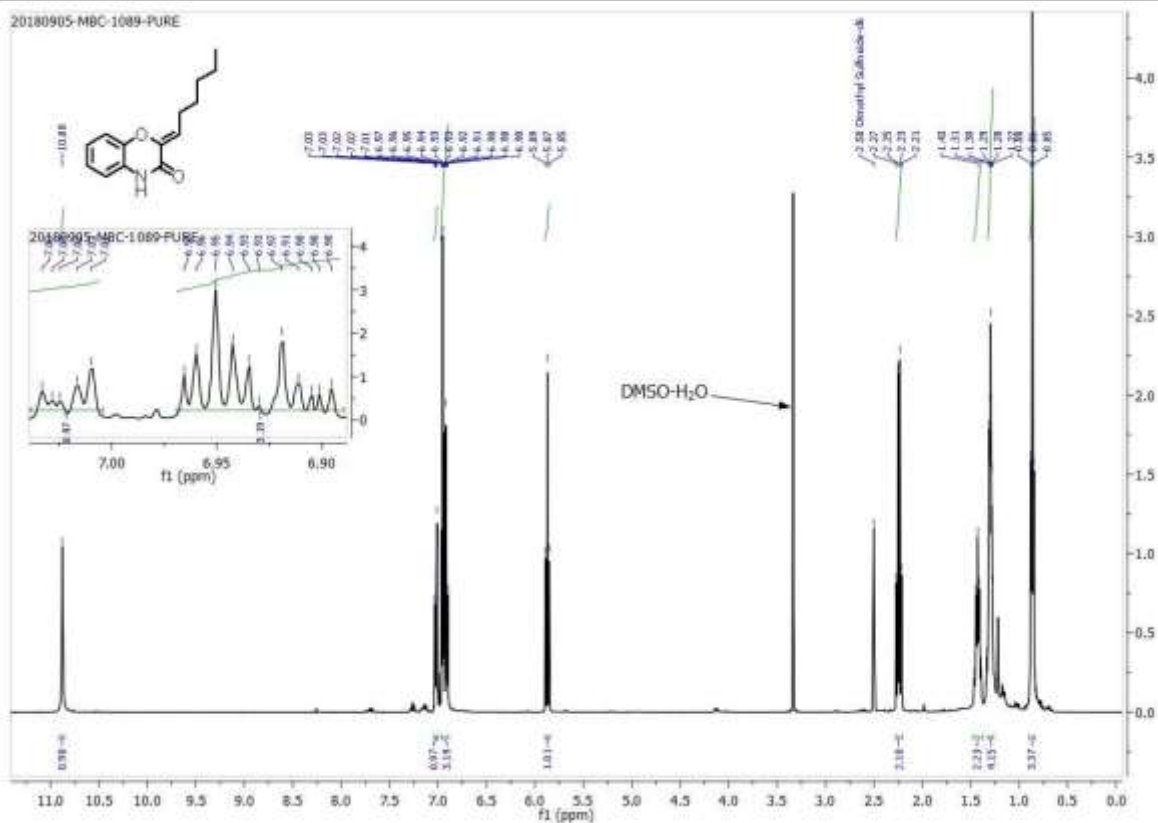


Figure S17. <sup>1</sup>H NMR of Compound 2f

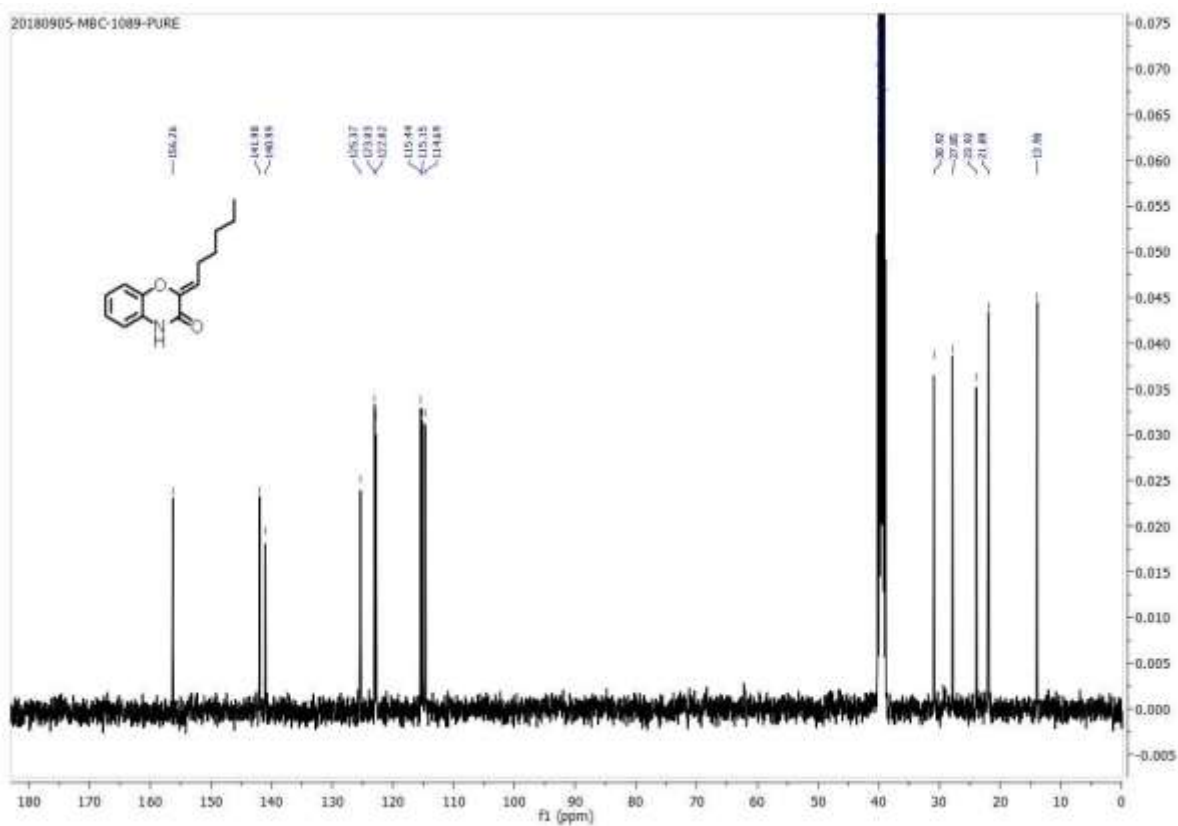


Figure S18. <sup>13</sup>C NMR of Compound 2f

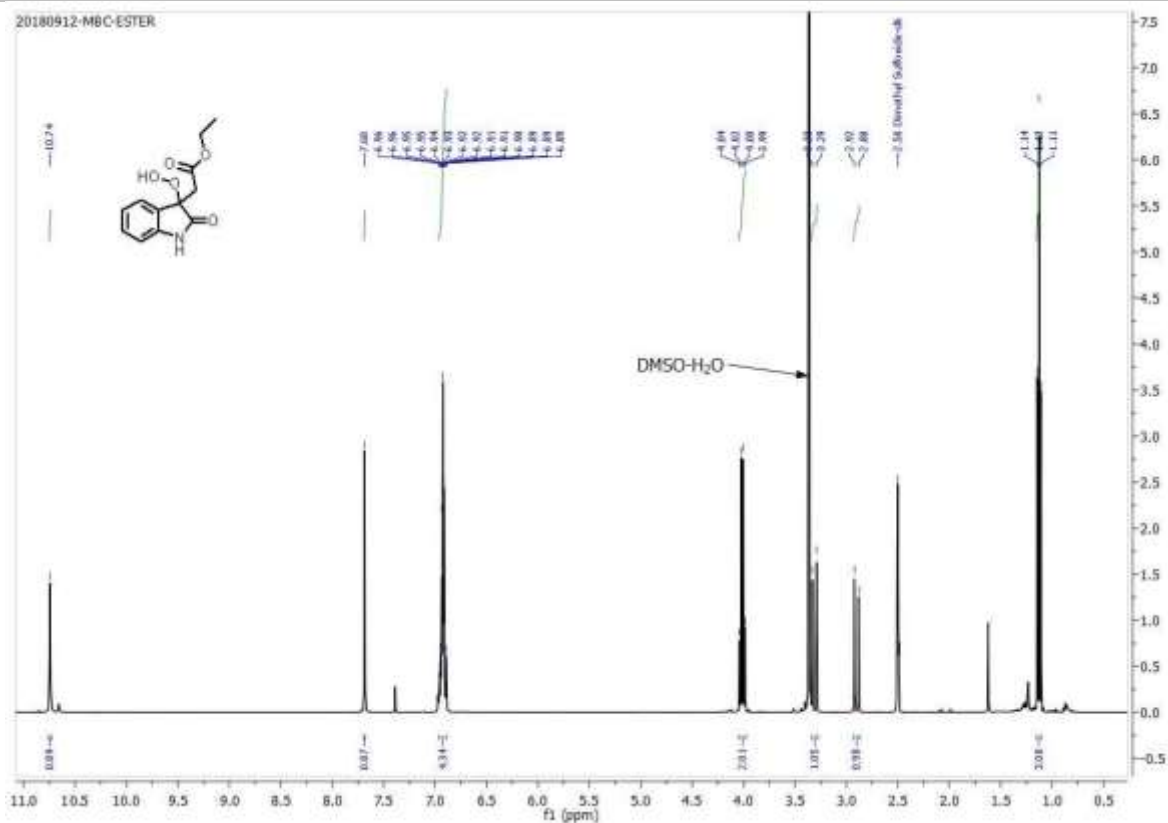


Figure S19. <sup>1</sup>H NMR of Compound 2g

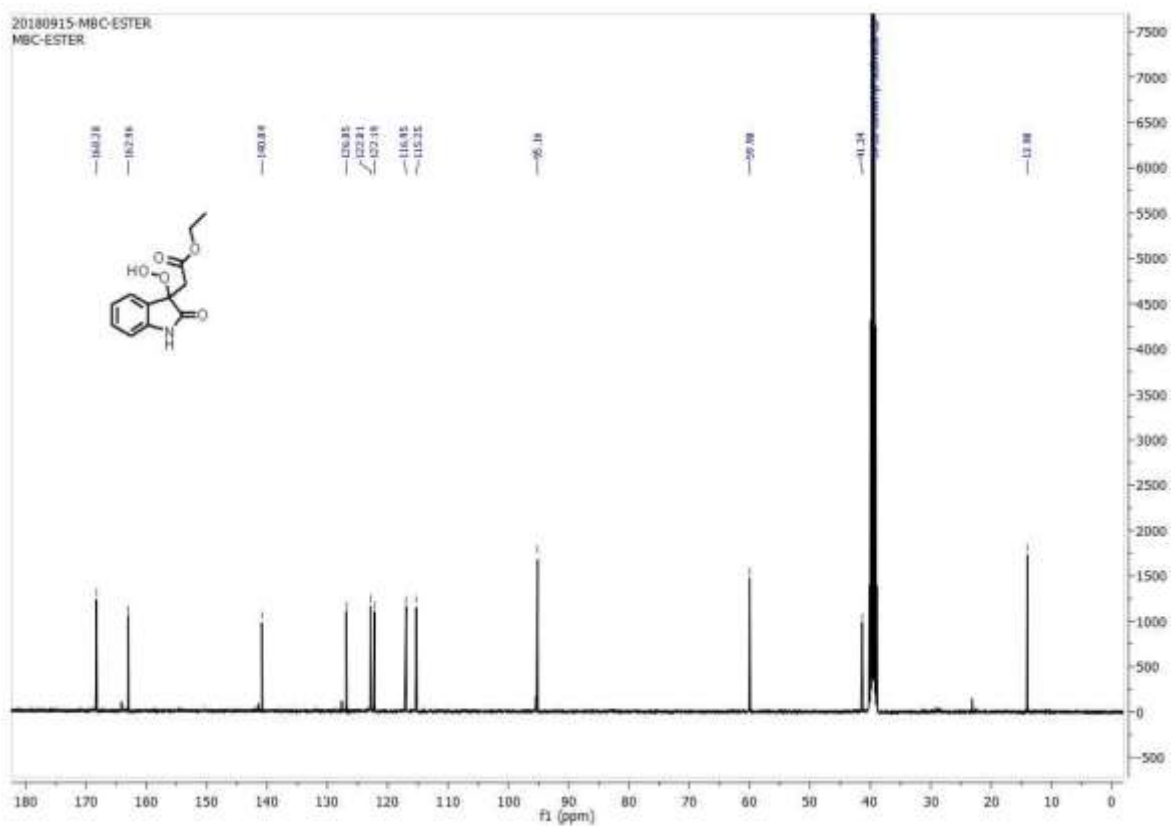


Figure S20. <sup>13</sup>C NMR of Compound 2g





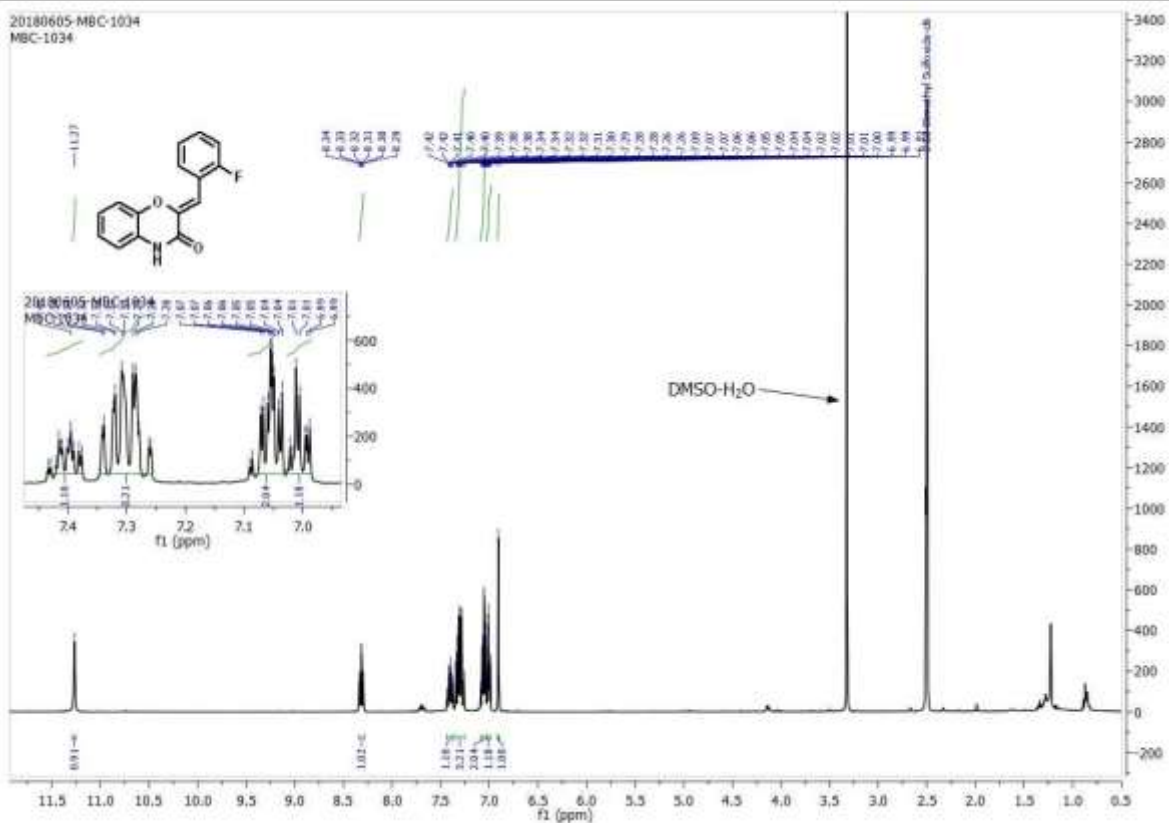


Figure S25. <sup>1</sup>H NMR of Compound 2j

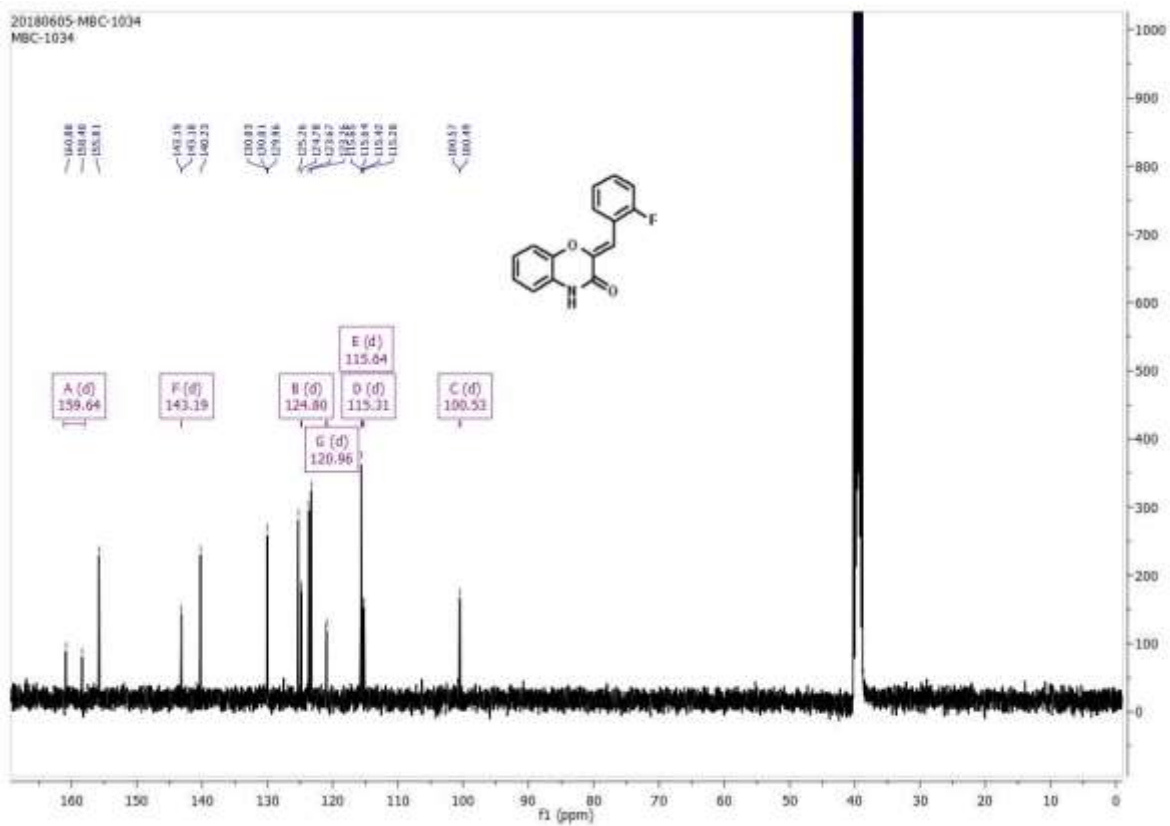


Figure S26. <sup>13</sup>C NMR of Compound 2j









---

## 8. References:

1) Chatterjee, B.; Gunanathan, C. *Org. Lett.* **2015**, *17*, 4794–4797.

2) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176–2179.