Supporting Information

for

Photocatalyzed synthesis of isochromanones and isobenzofuranones under batch and flow conditions

Manuel Anselmo, Lisa Moni, Hossny Ismail, Davide Comoretto, Renata Riva and Andrea Basso*

Address: Università degli Studi di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, Genova, Italy

Email: Prof. Andrea Basso - andrea.basso@unige.it

*Corresponding author

Experimental details and detailed spectroscopic data

Table of contents

General experimental methods S2
General procedures S3
Emission spectrum of blue LEDs S4
Analytical data S5
Copies of NMR spectra S15
General experimental methods.

NMR spectra were recorded at 300 MHz (\(^1\text{H}\)) and 75 MHz (\(^{13}\text{C}\)) and the chemical shifts (\(\delta\)) are expressed in parts per million relative to tetramethylsilane (TMS) as internal standard (0.00 ppm). Coupling constants are reported in hertz. NMR acquisitions were performed at 295 K and CDCl\(_3\) was used as solvent.

GC–MS analyses were carried out on a Hewlett Packard 5890 Series II, using a HP-1 column, coupled with a HP-5971A spectrometer (electron impact). Analysis conditions are as follows: flow (He) 0.9 mL/min; initial temperature 100 °C; initial time 2 min; gradient temperature 20 °C/min; final temperature 280 °C; final time 5 min.

HPLC–MS analyses were carried out on a Hewlett Packard 1100, using a Gemini C6-Phenyl (150x3mm) column, coupled with a Microsaic 4000 MiD Mass Spectrometer (electrospray). Analysis conditions are as follows: flow 0.34 mL/min; temperature 26 °C; solvent A: water + 0.1% formic acid; solvent B: acetonitrile + 0.1% formic acid; gradient: from 10% B to 100% B in 20 min; VWD 220 nm; MASS: FullScan 100-800 m/z ES\(^+\), Tic voltage 750 V.

Photoinduced reactions were performed with blue LEDs (LED stripe GBC SMD 3528 INDOOR BLU 12Vcc) or LASER (CNI diode laser MDL-442, 40 mW power driven by power supply unit model PSU-III-LED. The output of laser is coupled to an optical fiber).

Reactions were monitored by TLC. TLC analyses were carried out on silica gel plates (thickness = 0.25 mm), viewed at UV (\(\lambda = 254\) nm) and developed with Hanessian stain (dipping into a solution of (NH\(_4\))\(_4\)MoO\(_4\)·4H\(_2\)O (21 g) and Ce(SO\(_4\))\(_2\)·4H\(_2\)O (1 g) in H\(_2\)SO\(_4\) (31 mL) and H\(_2\)O (469 mL) and warming).

Column chromatography was performed with the “flash” methodology using 220–400 mesh silica. Solvents employed as eluents and for all other routinary operations, as well as anhydrous solvents and all reagents used were purchased from commercial suppliers and employed without any further purification.

Benzenediazonium salts were prepared from the corresponding anilines according to literature procedures (i.e., Schuster G. B. et al. *J. Am. Chem. Soc.*, 1995, 117, 5206-5211).
General procedures

Synthesis of isochromanones 4 under batch conditions

A solution of benzendiazonium tetrafluoroborate 2 (1 mmol, 1 equiv) and Ru(bpy)$_3$Cl$_2$ (0.005 equiv) in CH$_3$CN (4 mL, 0.25 M with respect to the diazonium salt) was added with alkene 3 (2 mmol, 2 equiv) in a glass vial (Ø = 1.2 cm). The vial was exposed to the light generated by 440 nm LED bulbs for 6–8 hours. The solution was transferred into a round-bottomed flask, evaporated, and the crude was subsequently purified by column chromatography (PE/EA mixtures) to afford the final products as white solids/foams.

Synthesis of isochromanones 4 under flow conditions

Reactions in flow conditions were performed by means of a handmade mesoflow reactor consisting of a FEP tubing (internal Ø = 0.8 mm) wrapped up a glass cylinder (Ø = 2.5 cm) for a length corresponding exactly of 1 mL. The tube was equipped at one end with a connection for a gastight syringe (10 mL), fitting in a syringe pump. The wrapped cylinder was fitted inside a plastic cylinder (Ø = 4.5 cm) covered inside with LED bulbs (440 nm, model of the stripe).

A solution of benzendiazonium tetrafluoroborate 2 (1 equiv) and Ru(bpy)$_3$Cl$_2$ (0.005 eq) in CH$_3$CN (0.13 M with respect to the diazonium salt) was added with alkene 3 (2 equiv). The resulting clear solution was collected inside a 10 mL gastight syringe and pumped inside the flow reactor by means of a syringe pump at 0.1 mL/h. A fixed volume of the reacted solution was collected in a shielded round-bottomed flask, evaporated, and purified by column chromatography (PE/EA mixtures) to afford the final products as white solids/foams.

Synthesis of isobenzofuranones 13 and benzoxazepinones 14 under batch conditions

A solution of benzendiazonium tetrafluoroborate 11 (1 mmol, 1 equiv) and Ru(bpy)$_3$Cl$_2$ (0.005 equiv) in CH$_3$CN (4 mL, 0.25 M with respect to the diazonium salt) was added with alkene 12 (1.2 mmol, 1.2 equiv) in a glass vial (Ø = 1.2 cm). The vial was exposed to the light generated by 440 nm LED bulbs for 6–8 hours. The solution was transferred into a round-bottomed flask, evaporated, and the crude was subsequently purified by column chromatography (PE/EA mixtures) to afford the final products as white solids/foams.

Synthesis of isobenzofuranones 13 and benzoxazepinones 14 under flow conditions

The same conditions applied for the synthesis of isochromanones 4 were applied.
$\lambda_{\text{max}} = 455 \text{ nm}$
Analytical data

*Methyl 7-chloro-3-methyl-1-oxoisochroman-3-carboxylate (4a)*

![Chemical structure](image)

White solid, m.p. = 82.9–84.2°C

$R_f = 0.22$ (PE:EtOAc=4:1)

$^1$H NMR: 8.01 (d, $J = 2.2$, 1H Ar), 7.46 (dd, $J = 8.2, 2.2$, 1H Ar), 7.16 (d, $J = 8.2$, 1H Ar), 3.60 (s, 3H), 3.35 (d, $J = 16.5, 1H$), 3.16 (d, $J = 16.5$, 1H), 1.73 (s, 3H).

$^{13}$C NMR: 171.94, 163.12, 134.59, 134.14, 134.09, 129.87, 129.10, 126.09, 82.12, 53.24, 36.53, 24.96.

HPLC-MS: 13.0 min, 257 (255) [M+H]$^+$. 

GC-MS: 7.2 min, 256 (2, M, $^{37}$Cl), 254 (6, M, $^{35}$Cl), 197 (30, $^{37}$Cl), 195 (30, $^{35}$Cl), 169 (12, $^{37}$Cl), 167 (40, $^{35}$Cl), 124 (11), 89 (25), 63 (13), 43 (73).

*7-Chloro-3-phenylisochroman-1-one (4b)*

![Chemical structure](image)

White solid, m.p. = 139.2–141.5

$R_f = 0.44$ (PE:EtOAc=4:1)

$^1$H NMR: 8.12 (d, $J = 2.1$, 1H), 7.53 (dd, $J = 8.1, 2.1$, 1H), 7.49 – 7.35 (m, 5H), 7.24 (d, $J = 8.3$, 1H), 5.53 (dd, X part of ABX system, $J = 12.3, 3.1$, 1H), 3.30 (dd, A part of ABX system, $J = 16.5, 12.3$, 1H), 3.13 (dd, B part of ABX system, $J = 16.5, 3.1$, 1H).

$^{13}$C NMR: 164.23, 138.24, 137.28, 134.07, 134.02, 130.31, 128.99, 128.94, 128.88, 126.72, 126.21, 80.12, 35.09.

HPLC-MS: 13.5 min, 261 (259) [M+H]$^+$. 

GC-MS: 9.2 min, 260 (2, M, $^{37}$Cl), 258 (5, M, $^{35}$Cl), 154 (29, $^{37}$Cl), 152 (100, $^{35}$Cl), 126 (9, $^{37}$Cl), 124 (29, $^{35}$Cl), 89 (23).
Methyl 3-methyl-1-oxoisochroman-3-carboxylate (4c)

![Chemical structure of Methyl 3-methyl-1-oxoisochroman-3-carboxylate (4c)](image)

White solid, m.p. = 99.5-101.3

$R_f = 0.29$ (PE:EtOAc=4:1)

$^1$H NMR: 8.04 (d, $J = 7.6$, 1H Ar), 7.50 (td, $J = 7.6$, 1.2, 1H Ar), 7.35 (t, $J = 7.6$, 1H Ar), 7.19 (d, $J = 7.6$, 1H Ar), 3.58 (s, 3H), 3.38 (d, $J = 16.4$, 1H), 3.20 (d, $J = 16.4$, 1H), 1.73 (s, 3H).

$^{13}$C NMR: 172.28, 164.31, 136.33, 134.13, 130.16, 128.20, 127.57, 124.57, 82.02, 53.12, 37.07, 25.09.

HPLC-MS: 11.7 min, 221 [M+H]$^+$. GC-MS: 6.5 min, 220 (2, M), 162 (11), 161 (100), 133 (64), 105 (14), 91 (11), 90 (24), 89 (22), 63 (11), 43 (45).

Analytical data are in accordance with those reported in the literature (ref. 5 of the manuscript)

3-Phenylisochroman-1-one (4d)

![Chemical structure of 3-Phenylisochroman-1-one (4d)](image)

White solid, m.p. = 83.8-85.7

$R_f = 0.55$ (PE:EtOAc=4:1)

$^1$H NMR: 8.16 (d, $J = 7.8$, 1H Ar), 7.57 (td, $J = 7.5$, 1.0, 1H Ar), 7.49-7.35 (m, 6 H Ar), 7.29 (d, $J = 7.6$, 1H Ar), 5.56 (dd, X part of ABX system, $J = 11.9$, 4.6, 1 H), 3.35 (dd, A part of ABX system, $J = 15.8$, 11.9, 1 H), 3.13 (dd, B part of ABX system, $J = 15.8$, 4.6, 1H).

$^{13}$C NMR: 165.46, 139.05, 138.66, 134.05, 130.55, 128.81, 128.78, 128.01, 127.48, 126.24, 125.24, 80.09, 35.74.

HPLC-MS: 12.8 min, 225 [M+H]$^+$. GC-MS: 8.4 min, 224 (9, M), 178 (6), 119 (18), 118 (100), 90 (68), 89 (26), 77 (13), 63 (10), 51 (12).

Analytical data are in accordance with those reported in the literature (ref. 5 of the manuscript)
**Methyl 3,5-dimethyl-1-oxoisochroman-3-carboxylate (4e)**

![Structural formula of Methyl 3,5-dimethyl-1-oxoisochroman-3-carboxylate (4e)](image)

White solid, m.p.= 69.8-72.4

\[ R_f = 0.30 \ (\text{PE}:\text{EtOAc}=4:1) \]

\[^1\text{H} \text{NMR:} \ 7.95 (d, J = 7.7, 1H \text{ Ar}), 7.38 (d, J = 7.7, 1H \text{ Ar}), 7.27 (t, J = 7.7, 1H \text{ Ar}), 3.61 (s, 3H), 3.47 (d, J = 16.6, 1H), 2.99 (d, J = 16.6, 1H), 2.31 (s, 3H), 1.77 (s, 3H). \]

\[^{13}\text{C} \text{NMR:} \ 172.63, 164.75, 135.50, 135.49, 135.11, 128.08, 127.60, 124.62, 81.56, 53.20, 34.23, 25.37, 19.00. \]

HPLC-MS (ESI+): 13.6 min, 235 [M+H]^+.

GC-MS: 6.8 min, 234 (M), 175 (100), 147 (39), 105 (10), 104 (11), 103 (12) 78 (11), 77 (13), 43 (28).

**5-Methyl-3-phenylisochroman-1-one (4f)**

![Structural formula of 5-Methyl-3-phenylisochroman-1-one (4f)](image)

White solid, m.p.= 137.1-139.4

\[ R_f = 0.60 \ (\text{PE}:\text{EtOAc}=4:1) \]

\[^1\text{H} \text{NMR:} \ 8.03 (dd, J = 7.7, 0.6, 1H \text{ Ar}), 7.52-7.26 (m, 7H \text{ Ar}), 5.52 (dd, J = 9.8, 5.6, 1H), 3.14 (m, 2H), 2.33 (s, 3H). \]

\[^{13}\text{C} \text{NMR:} \ 165.87, 138.95, 137.66, 135.42, 135.25, 128.83, 128.80, 128.41, 127.40, 126.31, 125.22, 79.53, 33.00, 19.04. \]

HPLC-MS: 14.4 min, 239 [M+H]^+.

GC-MS: 9.0 min, 238 (M), 132 (100), 104 (33), 103 (13), 78 (15), 77 (16).

Analytical data are in accordance with those reported in the literature (ref. 5 of the manuscript)
Methyl 3,7-dimethyl-1-oxoisochroman-3-carboxylate (4g)

Foam

$R_f = 0.19$ (PE:EtOAc=5:1)

$^1$H NMR: 7.86 (s, 1H Ar), 7.30 (dd, $J = 7.7, 1.4, 1$H Ar), 7.08 (d, $J = 7.7, 1$H Ar), 3.58 (s, 3H), 3.33 (d, $J = 16.3, 1$H), 3.15 (d, $J = 16.3, 1$H), 2.34 (s, 3H), 1.72 (s, 3H).

$^{13}$C NMR: 172.40, 164.58, 138.08, 134.96, 133.35, 130.39, 127.44, 124.33, 82.09, 53.08, 36.76, 25.07, 21.08.

HPLC-MS: 12.2 min, 235 [M+H]$^+$.  
GC-MS: 6.9 min, 234 (7, M), 175 (100), 147 (51), 104 (15), 103 (12), 78 (11), 77 (13) 43 (28).

7-Methyl-3-phenylisochroman-1-one (4h)

White solid, m.p.= 129.5-131.4°C

$R_f = 0.35$ (PE:EtOAc=6:1)

$^1$H NMR: 7.97 (s, 1H Ar), 7.50-7.36 (m, 6H Ar), 7.18 (d, $J = 7.7, 1$H Ar), 5.53 (dd, X part of ABX system, $J = 12.2, 2.8, 1$H), 3.29 (dd, A part of ABX system, $J = 18.0, 12.2, 1$H), 3.10 (dd, B part of ABX system, $J = 18.0, 2.8, 1$H), 2.41 (s, 3H).

$^{13}$C NMR: 165.72, 138.81, 137.90, 136.12, 134.92, 130.78, 128.78, 128.72, 127.36, 126.25, 125.01, 80.20, 35.39, 21.18.

HPLC-MS: 13.4 min, 239 [M+H]$^+$.  
GC-MS: 8.9 min, 238 (28, m), 178 (19), 132 (100), 104 (100), 78 (23), 77 (34).
Methyl 7-bromo-3-methyl-1-oxoisochroman-3-carboxylate (4i)

![Chemical Structure]

White solid, m.p. = 87.0-88.9°C

$R_f = 0.34$ (PE:EtOAc=4:1)

$^1$H NMR: 8.20 (d, $J = 2.1$, 1H Ar), 7.63 (dd, $J = 8.1$, 2.1, 1H Ar), 7.10 (d, $J = 8.1$, 1H Ar), 3.62 (s, 3H), 3.35 (d, $J = 16.7$, 1H), 3.15 (d, $J = 16.7$, 1H), 1.75 (s, 3H).

$^{13}$C NMR: 172.02, 163.05, 137.04, 135.08, 132.98, 129.31, 126.34, 121.95, 82.12, 53.35, 36.67, 25.08.

HPLC-MS: 15.3 min, 301 (299) [M+H]$^+$. GC-MS: 7.8 min, 300 (9, M, $^{81}$Br), 298 (9, M, $^{79}$Br), 241 (88), 239 (90), 213 (31), 211 (33), 170 (11), 168 (11), 132 (24), 89 (43), 43 (100).

7-Bromo-3-phenylisochroman-1-one (4j)

![Chemical Structure]

White solid, m.p. = 141.5-143.3°C

$R_f = 0.16$ (PE:EtOAc=10:1)

$^1$H NMR: 8.28 (d, $J = 2.0$, 1H Ar), 7.68 (dd, $J = 8.2$, 2.2, 1H Ar), 7.48-7.37 (m, 5H Ar), 7.18 (d, $J = 8.2$, 1H Ar), 5.55 (dd, X part of ABX system, $J = 12.3$, 2.7, 1H), 3.28 (dd, A part of ABX system, $J = 16.5$, 12.3, 1H), 3.12 (dd, B part of ABX system, $J = 16.5$, 2.7, 1H).

$^{13}$C NMR: 164.11, 138.20, 137.76, 136.95, 133.28, 129.21, 128.95, 128.88, 126.94, 126.20, 121.67, 80.06, 35.16.

HPLC-MS: 16.2 min, 305 (303) [M+H]$^+$. GC-MS: 9.7 min, 304 (7, M, $^{81}$Br), 302 (7, M, $^{79}$Br), 198 (94, $^{81}$Br), 196 (100, $^{79}$Br), 170 (26, $^{81}$Br), 168 (27, $^{79}$Br), 89 (41), 77 (14), 63 (18).
trans 3,4-Diphenylisochroman-1-one (4k)

White solid, m.p. = 135.1-137.2

$R_f = 0.43$ (PE:EtOAc=6:1)

$^1$H NMR: 8.24 (dd, $J = 7.4$, 1.7, 1H Ar), 7.50 (td, $J = 7.4$, 1.7, 1H Ar), 7.47-7.41 (m, 1H Ar), 7.27-7.14 (m, 8H Ar), 7.03-7.00 (m, 2H Ar), 6.92 (d, $J = 7.4$, 1H Ar), 5.64 (d, $J = 10.0$, 1H), 4.51 (d, $J = 10.0$, 1H).

$^{13}$C NMR: 165.06, 142.67, 137.93, 137.42, 134.20, 130.44, 129.71, 128.94, 128.58, 128.30, 128.15, 127.98, 127.80, 127.20, 125.17, 85.40, 51.11.

HPLC-MS: 18.1 min, 301 [M+H]$^+$. Decomposes during GC-MS analysis

N-(4-methoxybenzyl)acetamide (5)

$R_f = 0.13$ (PE:EtOAc=1:1)

$^1$H NMR: 7.21 (d, $J = 8.7$, 2H Ar), 6.87 (d, $J = 8.7$, 2H Ar), 5.67 (broad s, 1H NH), 4.36 (d, $J = 5.6$, 2H), 3.80 (s, 3H), 2.01 (s, 3H).

Analytical data are in accordance with those reported in the literature (i.e. Chem. Commun. 2012, 48, 11626-11628)
3-Phenylisochroman-1-imine (9)

The crude mixture was concentrated under vacuum, no work-up was performed at this stage. A quick column chromatography was performed using EA/PE 1:4 with 5% Et$_3$N, affording the target compound as an oil.

Rf = 0.30 (PE:EtOAc=1:1)

$^1$H NMR: 8.23 (d, $J$ = 7.5, 1H Ar), 7.55–7.33 (m, 8H, Ar + NH), 7.23 (d, $J$ = 7.5 Hz, 1H Ar), 5.28 (dd, X part of ABX system $J$ = 11.6, 2.9, 1H), 3.27 (dd, A part of ABX system $J$ = 16.1, 11.6, 1H), 3.06 (dd, B part of ABX system $J$ = 16.2, 2.9 Hz, 1H).

The compound degraded during $^{13}$C NMR analysis

GC-MS: 8.1 min, 223 (7, M), 178 (7), 146 (13), 118 (17), 117 (80), 107 (100), 90 (19), 89 (18), 79 (15), 77 (18), 51 (11).

3-(4-Methoxybenzyl)isobenzofuran-1(3H)-one (13a)

Foam

Rf = 0.40 (PE:EtOAc=4:1)

$^1$H NMR: 7.84 (d, $J$ = 7.5, 1H Ar), 7.60 (td, $J$ = 7.5, 1.1, 1H Ar), 7.48 (t, $J$ = 7.5, 1H Ar), 7.17 (dd, $J$ = 7.5 Hz, 0.8, 1H Ar), 7.13–7.09 (m, 2H Ar), 6.84–6.79 (m, 2H Ar), 5.65 (t, X part of ABX system, $J$ = 6.3, 1H), 3.78 (s, 3H), 3.23 (dd, A part of ABX system, $J$ = 14.1, 6.3, 1H), 3.10 (dd, B part of ABX system, $J$ = 14.1, 6.3, 1H)

$^{13}$C NMR: 170.41, 158.81, 149.28, 133.78, 130.87, 129.24, 126.97, 126.42, 125.78, 122.4, 114.03, 81.50, 55.34, 40.03.

HPLC-MS: 13.0 min, 239 [M+H]$^+$.  

GC-MS: 9.1 min, 254 (22, M), 133 (19), 121 (100), 78 (12) 77 (25).

Analytical data are in accordance with the literature (J. Chem. Soc., Perkin Trans. 1 1982, 2819-2826)
3-(4-Methylbenzyl)isobenzofuran-1(3H)-one (13b)

![Chemical structure of 3-(4-Methylbenzyl)isobenzofuran-1(3H)-one](image)

White solid, m.p.= 87.7-89.4 (lit. 83-84)

$R_f = 0.47$ (PE:EtOAc=4:1)

$^1$H NMR: 7.85 (d, $J = 7.6$, 1H Ar), 7.60 (td, $J = 7.6$, 1.2, 1H Ar), 7.49 (t, 7.6, 1H Ar), 7.16 (dd, $J = 7.6$, 0.8, 1H Ar), 7.10 (s, 4H Ar), 5.67 (t, X part of ABX system, $J = 6.4$, 1H), 3.26 (dd, A part of ABX system, $J = 14.1$, 6.5, 1H), 3.10 (dd, B part of ABX system, $J = 14.1$, 6.5, 1H), 2.32 (s, 3H).

$^{13}$C NMR: 170.47, 149.35, 136.91, 133.80, 131.97, 129.72, 129.38, 129.28, 126.42, 125.82, 122.48, 81.51, 40.58, 21.23.

HPLC-MS: 14.5 min, 239 [M+H]$^+$.  
GC-MS: 8.4 min, 238 (5, M), 133 (34), 106 (12), 105 (100), 77 (15).

Analytical data are in accordance with the literature (Org. Lett. 2009, 11, 4712-4715)

Methyl 2-((3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl)benzoate (13c)

![Chemical structure of Methyl 2-((3-oxo-1,3-dihydroisobenzofuran-1-yl)methyl)benzoate](image)

White solid, m.p.= 107.8-109.5 (lit. 111-112)

$R_f = 0.36$ (PE:EtOAc=4:1)

$^1$H NMR: 8.03 (dd, $J = 8.1$, 1.4, 1H Ar), 7.96-7.84 (m, 1H Ar), 7.66 (td, $J = 7.5$, 1.1, 1H Ar), 7.59-7.44 (m, 3H Ar), 7.40-7.34 (m, 2H Ar), 5.77 (dd, X part of ABX system, $J = 9.0$, 3.5, 1H), 3.95 (dd A part of ABX system, $J = 13.7$, 3.5, 1H), 3.94 (s, 3H), 3.12 (dd B part of ABX system, $J = 13.7$, 9.0, 1H).

$^{13}$C NMR: 170.62, 167.86, 149.99, 138.77, 134.03, 133.06, 132.64, 131.30, 129.31, 129.16, 127.52, 126.23, 125.73, 122.67, 82.12, 52.28, 40.65.

HPLC-MS: 13.4 min, 283 [M+H]$^+$.  
GC-MS: 9.5 min, 282 (1, M), 250 (6), 149 (11), 133 (100), 105 (13), 77 (21), 51 (11).

Analytical data are in accordance with the literature (Chem. Heterocycl. Compd. 2012, 47, 1212-1224)
3-Methyl-5-(4-methoxybenzyl)benzo[e][1,3]oxazepin-1(5H)-one (14a)

![Chemical Structure]

**Foam**

$R_f = 0.45$ (PE:EtOAc=4:1)

$^1$H NMR: 7.77 (d, $J = 7.6$, 1H Ar), 7.59 (td, $J = 7.6$, 1H Ar), 7.45 (t, $J = 7.6$, 1H Ar), 7.19 (dd, $J = 7.6$, 0.6, 1H Ar), 6.75-6.72 (m, 2H Ar), 6.69-6.66 (m, 2H Ar), 5.42 (dd, X part of ABX system, $J = 7.4$, 3.1, 1H), 3.74 (s, 3H), 3.47 (dd, A part of ABX system, $J = 12.8$, 7.4, 1H), 3.19 (dd, B part of ABX system, $J = 12.8$, 3.1, 1H), 2.66 (s, 3H).

$^{13}$C NMR: 171.47, 167.94, 158.64, 145.55, 133.83, 130.81, 130.76, 128.82, 127.17, 125.16, 123.53, 113.73, 60.13, 55.27, 37.65, 25.73.

HPLC-MS: 10.3 min, 296 [M+H]$^+$.

GC-MS: 9.6 min, 295 (3, M), 132 (17), 121 (100), 77 (13), 43 (13).

3-Methyl-5-(4-methylbenzyl)benzo[e][1,3]oxazepin-1(5H)-one (14b)

![Chemical Structure]

White solid, m.p.= 109.1-110.7°C

$R_f = 0.52$ (PE:EtOAc=4:1)

$^1$H NMR: 7.77 (d, $J = 7.6$, 1H Ar), 7.59 (td, $J = 7.6$, 1.1 Hz, 1H Ar), 7.45 (t, $J = 7.6$, 1H Ar), 7.18 (d, $J = 7.6$, 1H Ar), 6.95 (d, $J = 8.0$, 2H Ar), 6.72 (d, $J = 8.0$, 2H Ar), 5.44 (d, X part of ABX system, $J = 7.6$, 2.9, 1H), 3.50 (dd, A part of ABX system, $J = 12.8$, 7.6, 1H), 3.18 (dd, B part of ABX system, $J = 12.8$, 2.9, 1H), 2.66 (s, 3H), 2.26 (s, 3H).

$^{13}$C NMR: 171.46, 167.95, 145.57, 136.62, 133.80, 132.09, 130.79, 129.65, 129.03, 128.80, 125.12, 123.56, 60.06, 38.11, 25.74, 21.19.
HPLC-MS: 11.8 min, 280 [M+H]$^+$.  
GC-MS: 8.9 min, 279 (9, M), 132 (100), 105 (48), 77 (13), 43 (14).
Compound 4b
Compound 4c
Compound 4d
Compound 4e
Compound 4f
Compound 4g
Compound 4h
Compound 4k
Compound 5

[Chemical Structure Image]

S26
Compound 9

red: compound 9
blue: spectrum after addition of 5 μL of H2O (conversion into compound 8d)
Compound 13a
Compound 13b
Compound 13c
Compound 14a