# Supporting Information

# Visible-Light Mediated Oxidative Fragmentation of Ethers and Acetals by Means of Fe(III) Catalysis

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# **General information**

All chemicals were purchased from Sigma-Aldrich and VWR. All chemicals were used as received (exception being 2-(3-bromophenyl)-1,3-dioxolane which was purified by precipitating the aldehyde impurity as its bisulfite adduct). All reactions were performed under an atmosphere of argon using Schlenck techniques. TLC plates (Silica gel 60  $F_{254}$  coated on aluminum plates purchased from Sigma-Aldrich and VWR) were visualized by either UV light (254 nm), Seebach's stain (superior for THF-derivatives) or KMnO<sub>4</sub> solution. Flash column chromatography was performed both manually (using Silica gel 40-63 µm from VWR) and with Büchi Pure C-810 Flash (using Büchi FlashPure EcoFlex cartridges of either 50 µm or 20 µm).

GC-MS(EI) was performed on Agilent 19091S-433 gas chromatograph with an Agilent 5977E MSD detector. Separations were performed on HP-5MS Phenyl Methyl Silox of 30 m x 250  $\mu$ m x 0.25  $\mu$ m column.

LC-(HR)MS was performed on a Waters Acquity<sup>TM</sup> UPLC coupled with a SYNAPT G2-Si Mass Spectrometer using a LockSpray (Zspray<sup>TM</sup>) ESI ionization source.

IR-spectra were recorded on a Bruker FT-IR Spectrometer INVENIO<sup>®</sup>.

A Büchi<sup>®</sup> Melting Point B-545 was used to determine the melting points.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Varian NMR 400 or Bruker Avance III HD 800 MHz spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm relative to the residual solvent peak. Splitting patterns are indicated as (s) singlet, (d) doublet, (dd) doublet of doublets, (ddd) doublet of doublet of doublet of doublet of doublet of triplets, (dt) doublet of triplets, (q) quartet, (dq) doublet of quartets, (qt) quartet of triplet, (dq) doublet of quartet of doublets, (quint) quintet, (sext) sextet, (hept) heptet, (m) multiplet. Coupling constants (*J*) are reported in Hertz (Hz).

Photoreactions were conducted in Biotage<sup>®</sup> Microwave Reaction Vials placed in EvoluChem<sup>TM</sup> PhotoRedOx Box By HepatoChem equipped with an EvoluChem LED 18 W (P201-18-2, 450-455 nm) as irradiation source and was used without any filter. Emission spectrum can be found at https://www.hepatochem.com/photoreactors-leds-accessories/led-evoluchem.

# **Deviation from standard conditions**

The reactions were prepared according to the procedure described in the section *Experimental* procedure for photoreaction.

	O Oxida	catalyst, ant, Solvent	o ↓ ∧ ,Br	
	CI 1aa Blue LE	r.t. (27 °C) EDs (455 nm) CI	1a V	
Entry	Catalyst	BrCCl <sub>3</sub>	Solvent	Yield (%) <sup>[a]</sup>
1 <sup>[b]</sup>	Ru(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub> (1-5 mol%)	2-10 eq.	Solvents	0-quant
2	$Ru(bpy)_3(PF_6)_2$ (1 mol%)	3 eq.	DCE	$31(full conv.^{[c]})^{[g]}$
3	$Fe(acac)_3$ (1 mol%)	5 eq.	DCE	76
4	Fe(acac) <sub>3</sub> (1 mol%)	3 eq.	DCE	<b>89 (90</b> <sup>[d]</sup> )
5	Fe(acac) <sub>3</sub> (1 mol%)	1.2 eq.	DCE	59
6	$Fe(acac)_3$ (1 mol%)	0 eq.	DCE	No reaction
7	Fe(acac) <sub>3</sub> (1 mol%)	3 eq.	Toluene	52
8	Fe(acac) <sub>3</sub> (1 mol%)	3 eq.	MeCN	41
9	Fe(acac) <sub>3</sub> (1 mol%)	3 eq.	EtOAc	66
10	$Fe(acac)_3$ (1 mol%)	3 eq.	DMF	Trace
11	Fe(acac) <sub>3</sub> (1 mol%)	CBr <sub>4</sub> , 3 eq.	DCE	64
12	$Fe(acac)_3$ (0.1 mol%)	3 eq.	DCE	64
13	FeBr <sub>3</sub> (1 mol%)	3 eq.	DCE	55
14 <sup>[e]</sup>	$Fe(acac)_3$ (1 mol%)	3 eq.	DCE	Trace
15 <sup>[f]</sup>	Fe(acac) <sub>3</sub> (1 mol%)	3 eq.	DCE	No reaction
16 <sup>[g]</sup>	No catalyst	3 eq.	DCE	Trace

**Table 1**. [a] Isolated yields conducted at 0.1 mmol scale. [b] Note, irreproducible yields were consistently obtained also when keeping all parameters constant. Yields were determined by <sup>1</sup>H-NMR using dimethyl sulfone or ethylene carbonate as internal standard. [c] Reaction run for 18 h. [d] Average isolated yield of two runs at 0.2 mmol scale. [e] Heat control (80 °C). [f] Control experiment in the dark. [g] Reaction conducted either in a brand new vial or a vial cleaned with aqua regia.

# Screening of metal additives

The reactions were prepared according to the procedure described in the section *Experimental procedure for photoreaction*. The reactions were analyzed by taking 0.1 ml of crude reaction mixture and diluted with 0.6 ml CDCl<sub>3</sub> followed by recording <sup>1</sup>H-NMR, no prior work-up. Results are summarized below.

No.	Metal additive	Conversion (%)
1	$Ce(SO_4)_2$	0
2	$Co(ClO_4)_2$	100
3	Sc(OTf) <sub>3</sub>	0
4	Pd(CF <sub>3</sub> COO) <sub>2</sub>	0
5	Gd(OTf) <sub>3</sub>	0
6	La(OTf) <sub>3</sub>	0
7	Bi(OTf) <sub>3</sub>	0
8	AgBF <sub>4</sub>	0
9	Rh <sub>2</sub> (CH <sub>3</sub> COO) <sub>4</sub>	0
10	MnCl <sub>2</sub>	0
11	RuCl <sub>3</sub>	0
12	Ni(acac) <sub>2</sub>	29
13	CuCl	17
14	CuCl <sub>2</sub>	0
15	Fe(acac) <sub>3</sub>	100

**Table 2.** 1 mol% of the metal additive and 2-(4-chlorophenyl)tetrahydrofuran (**1aa**) were used in each reaction and run for 6 hours. All vials and stir bars were carefully cleaned with aqua regia before reaction.

To double-check that  $Fe(acac)_3$  and  $Co(ClO_4)_2$  are active catalysts for the reaction experiments were conducted again for these two metal complexes in brand new vials. In case of  $Fe(acac)_3$  the results were always reproducible while for  $Co(ClO_4)_2$  slightly diminished yields were sometimes obtained. Hence, we concluded that  $Fe(acac)_3$  was the most efficient catalyst and continued exploring it in our system.

# Synthesis of starting materials

Two general methods have been used to prepare a large portion of the starting materials. The specific syntheses of starting materials beyond these two methods are described in the following section together with the characterization data for that compound.

## **Method I - THF-derivatives**

The corresponding 4-oxo-4-phenylbutyric acid (5 mmol) was added portion wise to a suspension of LiAlH<sub>4</sub> (4 eq.) in Et<sub>2</sub>O (50 ml) at 0 °C. Reaction was then stirred at r.t until completed as judged by TLC. Work-up procedure according to the Fieser protocol. Almost quantitative yields of the diols were obtained, and the diols were used in the next step without further purification.

The cyclization of the diols to tetrahydrofurans was conducted as described in<sup>[1]</sup>. No purification on silica was necessary.

## Method II – THF, THP and dioxane-derivatives

Cyclic ethers were synthesized according to procedure  $in^{[2]}$ . Oven dried Biotage MW vial (20 ml) was charged with the boronic acid (2 mmol), Ni(acac)<sub>2</sub> (10 mol%, 51 mg), PPh<sub>3</sub> (10 mol%, 52 mg), K<sub>3</sub>PO<sub>4</sub> (1 eq., 425 mg) and THF (anhydrous, 12 ml). The vial was capped and reaction mixture sparged with argon for 10 min. Then DTBP (1.2 eq., 0.44 ml) was added in one portion and the reaction mixture heated to 100 ° C overnight. After cooled to r.t the reaction was diluted with 20 ml HCl<sub>(aq)</sub> (2M)<sup>1</sup> and extracted 3 times with 20 ml Et<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Products were then purified on silica. Seebach's stain turned out to be superior in visualizing the product on TLC plates.

Care must be taken regarding reduced pressure since the compounds are, in some cases, volatile. 20 mbar and 40 °C water bath worked fine in most cases, exception being the 2,4-difluoro (compound X).

<sup>1</sup>In cases where acid sensitive compounds were used only water was used and turned out to work OK.

# Characterization data and preparation of starting materials





(1aa) 2-(4-chlorophenyl)tetrahydrofuran: Prepared according to *Method I*. Slight yellowish oil (595 mg, **66**% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.18 (m, 4H), 4.86 (t, J = 7.2 Hz, 1H), 4.08 (dt, J = 8.3, 6.8 Hz, 1H), 3.93 (dt, J = 8.3, 6.9 Hz, 1H), 2.37 – 2.26 (m, 1H), 2.05 – 1.96 (m, 2H), 1.80 – 1.69 (m, 1H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  142.2, 132.9, 128.5, 127.1, 80.1, 68.9, 34.8, 26.1. MS-EI(m/z): calculated for C<sub>10</sub>H<sub>11</sub>ClO<sup>+</sup>, 182,0498; found 182.1. Spectroscopic data is in agreement with<sup>[2]</sup>.

(2aa) 2-phenyltetrahydrofuran: Prepared according to *Method I* (2.28 mmol scale). Slight yellowish oil (219 mg, **53** % yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 – 7.31 (m, 4H), 7.28 – 7.22 (m, 2H), 4.89 (t, *J* = 7.2 Hz, 1H), 4.10 (ddd, *J* = 8.3, 7.1, 6.5 Hz, 1H), 3.94 (ddd, *J* = 8.2, 7.5, 6.4 Hz, 1H), 2.37 – 2.27 (m, 1H), 2.07 – 1.95 (m, 2H), 1.81 (ddt, *J* = 12.2, 8.6, 7.5 Hz, 1H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  143.6, 128.4, 127.2, 125.8, 80.8, 68.8, 34.7, 26.2. MS-EI(m/z): calculated for C<sub>10</sub>H<sub>12</sub>O<sup>+</sup>, 148,0888; found 148.1. Spectroscopic data is in agreement with<sup>[2]</sup>.

(2bb) 2-([1,1'-biphenyl]-4-yl)tetrahydrofuran: Prepared according *Method II*. Colorless oil (135 mg, **30**% yield), R<sub>f</sub> (2% EtOAc in hexane) = 0.10. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 – 7.54 (m, 4H), 7.46 – 7.39 (m, 4H), 7.36 – 7.31 (m, 1H), 4.94 (t, *J* = 7.2 Hz, 1H), 4.13 (ddd, *J* = 8.3, 7.1, 6.4 Hz, 1H), 3.96 (ddd, *J* = 8.2, 7.6, 6.3 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.12 – 1.96 (m, 2H), 1.86 (ddt, *J* = 12.2, 8.8, 7.6 Hz, 1H). <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.6, 141.0, 140.1, 128.8, 127.2, 127.1, 127.1, 126.1, 80.5, 68.7, 34.6, 26.1. MS-EI(m/z): calculated for C<sub>16</sub>H<sub>16</sub>O<sup>+</sup>, 224.1201; found 224.2. Spectroscopic data is in agreement with<sup>[3]</sup>



(2cc) 4-(tetrahydrofuran-2-yl)benzonitrile: Prepared according to *Method II*. Colorless oil (130 mg, **38**% yield), R<sub>f</sub> (5% EtOAc in petroleum ether) = 0.08. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.41 (m, 2H), 4.94 (t, *J* = 7.2 Hz, 1H), 4.10 (dtd, *J* = 8.3, 6.7, 0.5 Hz, 1H), 3.97 (ddd, *J* = 8.4, 7.3, 6.5 Hz, 1H), 2.43 – 2.33 (m, 1H), 2.08 – 1.95 (m, 2H), 1.74 (ddt, *J* = 12.2, 8.0, 7.6 Hz, 1H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  149.4, 132.3, 126.3, 119.1, 110.9, 80.0, 69.1, 34.8, 26.1. MS-EI(m/z): calculated for C<sub>11</sub>H<sub>11</sub>NO<sup>+</sup>, 173.0841; found 173.1. Spectroscopic data is in agreement with<sup>[4]</sup>.



(2dd) 2-(4-methoxyphenyl)tetrahydrofuran: Prepared according to *Method I*. Slight yellowish oil (523 mg, **58** % yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 – 7.23 (m, 2H), 6.89 – 6.84 (m, 2H), 4.83 (t, J = 7.2 Hz, 1H), 4.11 – 4.03 (m, 1H), 3.94 – 3.87 (m, 1H), 3.80 (s, 3H), 2.32 – 2.22 (m, 1H), 2.08 – 1.92 (m, 2H), 1.84 – 1.73 (m, 1H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  158.9, 135.5, 127.1, 113.8, 80.6, 68.6, 55.4, 34.6, 26.2. MS-EI(m/z): calculated for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub><sup>+</sup>, 178.0994; found 178.1. Spectroscopic data is in agreement with<sup>[2]</sup>.

(2ee) methyl 4-(tetrahydrofuran-2-yl)benzoate: Prepared according to *Method II*. White solid (161 mg, **39**% yield), R<sub>f</sub> (2% EtOAc in hexane) = 0.05. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 4.95 (t, J = 7.2 Hz, 1H), 4.15 – 4.07 (m, 1H), 4.00 – 3.93 (m, 1H), 3.91 (s, 3H), 2.41 – 2.31 (m, 1H), 2.06 – 1.96 (m, 2H), 1.83 – 1.72 (m, 1H). <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.2, 151.3, 131.9, 131.2, 127.7, 82.4, 71.1, 54.3, 37.0, 28.2. MS-EI(m/z): calculated for C<sub>12</sub>H<sub>14</sub>O<sub>3</sub><sup>+</sup>, 206.0943; found 206.1. Spectroscopic data is in agreement with<sup>[4]</sup>.

(2ff) 2-(2-isopropylphenyl)tetrahydrofuran: Prepared according to *Method II*. Colorless oil (139 mg, **37**% yield),  $R_f$  (2% EtOAc in pentane) = 0.12. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 – 7.43 (m, 1H), 7.29 – 7.16 (m, 3H), 5.18 (t, J = 7.2 Hz, 1H), 4.16 (ddd, J = 8.3, 7.0, 6.1 Hz, 1H), 3.94 (dt, J = 8.2, 7.1 Hz, 1H), 3.16 (hept, J = 6.9 Hz, 1H), 2.42 – 2.28 (m, 1H), 2.10 – 1.93 (m, 2H), 1.72 (ddt, J = 12.2, 8.5, 7.4 Hz, 1H), 1.25 (d, J = 6.8 Hz, 6H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  145.4, 140.3, 127.3, 126.0, 125.2, 125.0, 77.5, 68.8, 34.7, 28.5, 26.3, 24.3, 24.0. HRMS-ESI(m/z): calculated for C<sub>13</sub>H<sub>19</sub>O<sup>+</sup> [(M+H)<sup>+</sup>] 191.1430; found 191.1429. IR (cm<sup>-1</sup>): 1054 (C-O).

(2gg) 2-(3,4,5-trimethoxyphenyl)tetrahydrofuran: Prepared according to *Method II*. Colorless oil (179 mg, **38**% yield), R<sub>f</sub> (15% EtOAc in hexane) = 0.23. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.56 (d, J = 0.6 Hz, 2H), 4.82 (t, J = 7.2 Hz, 1H), 4.10 (ddd, J = 8.3, 7.2, 6.4 Hz, 1H), 3.96 – 3.89 (m, 1H), 3.87 (s, 6H), 3.83 (s, 3H), 2.36 – 2.25 (m, 1H), 2.10 – 1.93 (m, 2H), 1.80 (ddt, J = 12.1, 8.7, 7.7 Hz, 1H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  153.3, 139.2, 137.1, 102.6, 80.9, 68.8, 61.0, 56.2, 34.7, 26.1. MS-EI(m/z): calculated for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub><sup>+</sup>, 238.1205; found 238.2. Spectroscopic data is in agreement with<sup>[5]</sup>.

(2hh) 2-(4-bromophenyl)tetrahydrofuran: Prepared according to *Method II*. Colorless oil (118 mg, 26% yield),  $R_f$  (2% EtOAc in petroleum ether) = 0.11. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 4.84 (t, J = 7.2 Hz, 1H), 4.11 – 4.04 (m, 1H), 3.96 – 3.88 (m, 1H), 2.36 – 2.25 (m, 1H), 2.04 – 1.94 (m, 2H), 1.80 – 1.68 (m, 1H). <sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.6, 131.3, 127.3, 120.8, 80.0, 68.7, 34.6, 25.9. MS-EI(m/z): calculated for  $C_{10}H_{11}BrO^+$ , 225.9993; found 226.1. Spectroscopic data is in agreement with<sup>[6]</sup>.









(2ii) 2-(*p*-tolyl)tetrahydrofuran: Prepared according to *Method II*. Colorless oil (102 mg, **31**% yield), R<sub>f</sub> (2% EtOAc in pentane) = 0.09. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz 2H), 4.86 (t, J = 7.2 Hz, 1H), 4.09 (dt, J = 8.1, 6.9 Hz, 1H), 3.96 – 3.88 (m, 1H), 2.34 (s, 3H), 2.33 – 2.25 (m, 1H), 2.08 – 1.93 (m, 2H), 1.80 (ddt, J = 12.1, 8.6, 7.6 Hz, 1H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  140.5, 136.8, 129.1, 125.8, 80.7, 68.7, 34.7, 26.2, 21.2. MS-EI(m/z): calculated for C<sub>11</sub>H<sub>14</sub>O<sup>+</sup>, 162.1045; found 162.1. Spectroscopic data is in agreement with<sup>[5]</sup>.

(2jj) 2-(2,4-difluorophenyl)tetrahydrofuran: Prepared according to *Method II*. Colorless liquid (26 mg, **10**% yield), R<sub>f</sub> (2% Et<sub>2</sub>O in petroleum ether) = 0.14. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 (tdd, J = 8.5, 6.6, 0.8 Hz, 1H), 6.88 - 6.81 (m, 1H), 6.76 (ddd, J = 10.6, 8.9, 2.5 Hz, 1H), 5.08 (t, J = 7.1 Hz, 1H), 4.08 (dt, J = 8.3, 6.7 Hz, 1H), 3.92 (dt, J = 8.3, 6.9 Hz, 1H), 2.38 (dqd, J = 12.2, 6.9, 1.2 Hz, 1H), 2.05 – 1.94 (m, 2H), 1.75 (dqd, J = 247.1, 11.9 Hz), 159.9 (dd, J = 248.4, 11.8 Hz), 127.8 (dd, J = 9.6, 6.2 Hz), 126.8 (d, J = 13.7 Hz), 111.1 (dd, J = 21.1, 3.6 Hz), 103.7 (t, J = 25.5 Hz), 74.9, 68.8, 33.7, 26.1. <sup>19</sup>F-NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -112.75 (quint, J = 7.6 Hz, 1F), -114.87 (q, J = 8.5 Hz, 1F). HRMS-ESI(m/z): calculated for C<sub>10</sub>H<sub>11</sub>F<sub>2</sub>O<sup>+</sup> [(M+H)<sup>+</sup>] 185.0772; found 185.0755. IR (cm<sup>-1</sup>): 1271 (C-F), 1062 (C-O).

(2kk) 2-(3-methoxyphenyl)tetrahydrofuran: Prepared according to *Method II*. Colorless oil (131 mg, **37**% yield), R<sub>f</sub> (5% EtOAc in petroleum ether) = 0.16. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 (t, *J* = 8.1 Hz, 1H), 6.92 - 6.89 (m, 2H), 6.79 (dddd, *J* = 8.2, 2.5, 1.1, 0.4 Hz, 1H), 4.88 (t, *J* = 7.1 Hz, 1H), 4.13 - 4.06 (m, 1H), 4.00 - 3.89 (m, 1H), 3.81 (s, 3H), 2.37 - 2.26 (m, 1H), 2.07 - 1.92 (m, 2H), 1.86 - 1.75 (m, 1H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  159.8, 145.4, 129.4, 118.1, 112.7, 111.2, 80.6, 68.8, 55.3, 34.7, 26.1. **MS-EI**(m/z): calculated for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub><sup>+</sup>, 178.0994; found 178.1. Spectroscopic data is in agreement with<sup>[4]</sup>.

(21) 2-(tetrahydrofuran-2-yl)benzo[*d*]thiazole: Prepared according to previously reported procedure<sup>[7]</sup>. Slight yellowish oil (59 mg, 14% yield),  $R_f$  (5% EtOAc in petroleum ether) = 0.07. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.89 (ddd, *J* = 8.0, 1.3, 0.6 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.37 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 5.35 (dd, *J* = 7.8, 5.4 Hz, 1H), 4.16 (dt, *J* = 8.4, 6.6 Hz, 1H), 4.01 (dt, *J* = 8.3, 7.0 Hz, 1H), 2.53 (dq, *J* = 12.6, 7.6 Hz, 1H), 2.34 – 2.23 (m, 1H), 2.10 – 1.99 (m, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  176.6, 153.7, 134.8, 126.1, 125.0, 122.9, 121.9, 78.9, 69.6, 33.5, 25.9. MS-EI(m/z): calculated for C<sub>11</sub>H<sub>11</sub>NOS<sup>+</sup>, 205.0561; found 205.1. Spectroscopic data is in agreement with<sup>[7]</sup>.





(3aa) 3-methyl-2-phenyltetrahydrofuran: Under dry and inert conditions, LDA (1.1 eq. 3.3 ml (2M)) and 30 ml anhydrous THF was cooled to -78 °C. Propiophenone (1 eq., 6 mmol, 0.8 ml) dissolved in 3 ml anhydrous THF was added slowly to the LDA solution and stirred for 1h at -78 °C. Methyl-2-bromoacetate (1.2 eq., 0.68 ml) dissolved in 3 ml anhydrous THF was slowly added to the reaction solution and then warmed to r.t and stirred overnight. Reaction was quenched with sat. NH<sub>4</sub>Cl and extracted with EtOAc three times, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Crude mixture was purified on silica (4% EtOAc in petroleum ether) to give methyl 3-methyl-4-oxo-4-phenylbutanoate (690 mg, 56% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 – 7.96 (m, 2H), 7.60 – 7.54 (m, 1H), 7.51 – 7.44 (m, 2H), 3.95 (dqd, J = 8.4, 7.2, 5.8 Hz, 1H), 3.65 (s, 3H), 2.97 (dd, J = 16.8, 8.4 Hz)1H), 2.47 (dd, *J* = 16.8, 5.8 Hz, 1H), 1.23 (d, *J* = 7.2 Hz, 3H). Methyl 3-methyl-4-oxo-4-phenylbutanoate was then transformed to methyl-2phenyltetrahydrofuran by following Method I, yielding an inseparable mixture of two diastereoisomers. Colorless oil (132 mg, 25% overall yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.29 (m, 2H), 7.26 - 7.20 (m, 3H), 4.96 (d, J = 6.5 Hz, 1H), 4.19 (dddd, J = 8.2, 7.6,5.6, 0.5 Hz, 1H), 3.93 (td, *J* = 8.1, 6.8 Hz, 1H), 2.59 – 2.46 (m, 1H), 2.23 - 2.13 (m, 1H), 1.80 - 1.64 (m, 1H), 0.61 (d, J = 7.0 Hz, 3H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>) δ 140.9, 128.0, 126.9, 126.4, 83.8, 67.4, 37.8, 33.9, 15.5. **MS-EI**(m/z): calculated for  $C_{11}H_{14}O^+$ , 162.1045; found 162.1. Spectroscopic data is in agreement with<sup>[8]</sup>.

(3bb) 2-phenyltetrahydro-2*H*-pyran: Prepared according to *Method II*. Colorless oil (83 mg, 26% yield),  $R_f$  (2% EtOAc in petroleum ether) = 0.17. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 4.32 (dd, *J* = 10.8, 2.3 Hz, 1H), 4.19 – 4.10 (m, 1H), 3.62 (td, *J* = 11.6, 2.5 Hz, 1H), 1.99 – 1.91 (m, 1H), 1.87 – 1.80 (m, 1H), 1.74 – 1.56 (m, 4H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  143.5, 128.4, 127.4, 126.0, 80.3, 69.2, 34.2, 26.0, 24.2. MS-EI(m/z): calculated for C<sub>11</sub>H<sub>14</sub>O<sup>+</sup>, 162.1045; found 162.2. Spectroscopic data is in agreement with<sup>[9]</sup>.



(3cc) 2-phenyl-1,4-dioxane: Prepared according to *Method II*. Colorless oil (171 mg, 52% yield), R<sub>f</sub> (2% EtOAc in petroleum ether) = 0.12. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 4.63 (dd, J = 10.2, 2.8 Hz, 1H), 3.99 – 3.70 (m, 5H), 3.48 (dd, J = 11.7, 10.2 Hz, 1H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  138.4, 128.6, 128.2, 126.4, 78.1, 72.6, 67.2, 66.5. MS-EI(m/z): calculated for C<sub>10</sub>H<sub>12</sub>O<sub>2</sub><sup>+</sup>, 164.0837; found 164.1. Spectroscopic data is in agreement with<sup>[2]</sup>.





(3gg) 2-(3-bromobenzo[*b*]thiophen-2-yl)-1,3-dioxolane: 3bromobenzo[*b*]thiophene-2-carbaldehyde (1.5 mmol, 362 mg), ethylene glycol (2 eq., 0.17 ml), *para*-toluenesulfonic acid (0.1 eq., 29 mg) and toluene (10 ml) were refluxed with a Dean-Stark trap overnight. Reaction was cooled to r.t and diluted with sat. NaHCO<sub>3</sub>, extracted three times with EtOAc, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Crude mixture was purified on silica R<sub>f</sub> (5% EtOAc in petroleum ether) = 0.15. Colorless oil (240 mg, **56**% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 – 7.79 (m, 2H), 7.49 – 7.37 (m, 2H), 6.35 (s, 1H), 4.26 – 4.04 (m, 4H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$ 138.3, 137.8, 137.2, 126.1, 125.2, 123.4, 122.9, 107.9, 100.0, 65.8. MS-EI(m/z): calculated for C<sub>11</sub>H<sub>9</sub>BrO<sub>2</sub>S<sup>+</sup>, 283.9507; found 284.0. Spectroscopic data is in agreement with<sup>[10]</sup>.

(3hh) 2-(1,3-dioxolan-2-yl)benzofuran: benzofuran-2-carbaldehyde (2 mmol, 293 mg), ethylene glycol (2 eq. 0.23 ml), *para*-toluenesulfonic acid (0.1 eq., 38 mg) and toluene (15 ml) were refluxed with a Dean-Stark trap overnight. Reaction was cooled to r.t and diluted with sat. NaHCO<sub>3</sub>, extracted three times with EtOAc, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Crude mixture was purified on silica R<sub>f</sub> (3% EtOAc in petroleum ether) = 0.09. Yellow oil (185 mg, **49**% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (ddd, *J* = 7.6, 1.4, 0.7 Hz, 1H), 7.50 (dq, *J* = 8.2, 0.9 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.2, 1.4 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.83 – 6.79 (m, 1H), 6.10 (s, 1H), 4.24 – 4.04 (m, 4H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  155.4, 153.6, 127.6, 125.0, 123.1, 121.6, 111.8, 105.4, 98.2, 65.5. MS-EI(m/z): calculated for C<sub>11</sub>H<sub>10</sub>O<sub>3</sub><sup>+</sup>, 190.0630; found 190.1. Spectroscopic data is in agreement with<sup>[11]</sup>.

(3ii) 2-octyltetrahydrofuran: Prepared at 2x1 mmol scale according to the procedure in *Adv. Synth. Catal.* **2020**, 362, 2367-2372. Purified on silica R<sub>f</sub> (1% EtOAc in hexane) = 0.19, colorless oil (215 mg, **58**% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.91 – 3.82 (m, 1H), 3.81-3.74 (m, 1H), 3.74-3.67 (m, 1H), 2.02 – 1.77 (m, 3H), 1.47 – 1.35 (m, 3H), 1.35 – 1.22 (m, 12H), 0.92 – 0.85 (m, 3H). <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  79.4, 67.6, 35.8, 31.9, 31.4, 29.8, 29.6, 29.3, 26.4, 25.7, 22.6, 14.1. **MS-EI**(m/z): calculated for C<sub>12</sub>H<sub>24</sub>O<sup>+</sup>, 184.1822; found 184.2 (only weekly ionizing).



(3jj(a)) Benzylmethyl ether: To a solution of benzaldehyde (2 mmol, 212 mg) in 20 ml MeOH was added NaBH<sub>4</sub> (1.2 eq. 91 mg). Reaction was stirred until completed as judged by TLC. Reaction mixture was concentrated under reduced pressure and redissolved in Et<sub>2</sub>O and washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Without further purification, the benzyl alcohol was dissolved in 20 ml anhydrous THF and NaH (1.5 eq. 60% dispersion in paraffin liquid, 120 mg) was added portionwise and stirred for 10 minutes. Then methyl iodide (5 eq., 0.62 ml) was added in one portion and stirred overnight. The reaction mixture was adsorbed onto Celite and purified on silica R<sub>f</sub>(5% EtOAc in hexane) = 0.28, colorless oil (110 mg, **45**% yield over two steps). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 – 7.26 (m, 5H), 4.46 (s, 2H), 3.39 (s, 3H). MS-EI(m/z): calculated for C<sub>8</sub>H<sub>10</sub>O<sup>+</sup>, 122.0726; found 122.1.

(**3jj(b**)) (**3-(benzyloxy)propyl)benzene**: To a solution of 3-phenyl-1propanol (2 mmol, 272 mg) in 20 ml anhydrous THF and NaH (1.5 eq. 60% dispersion in paraffin liquid, 120 mg) was added portionwise and stirred for 10 minutes. Then benzyl bromide (2 eq. 0.50 ml) was added in one portion and stirred overnight. Reaction mixture was adsorbed onto Celite and purified on silica R<sub>f</sub>(2% EtOAc in hexane) = 0.25, colorless oil (334 mg, 74% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 – 7.26 (m, 7H), 7.22 – 7.15 (m, 3H), 4.52 (s, 2H), 3.50 (t, *J* = 6.4 Hz, 2H), 2.77 – 2.68 (t, *J* = 7.5 Hz, 2H), 2.02 – 1.89 (m, 2H). <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  142.1, 138.7, 128.6, 128.4, 128.4, 127.7, 127.6, 125.8, 73.0, 69.6, 32.5, 31.4. MS-EI(m/z): calculated for C<sub>16</sub>H<sub>18</sub>O<sup>+</sup>, 226.1352; found 226.2.



(3kk) 1-(1-methoxyethyl)-4-(trifluoromethyl)benzene: To a solution of 4'-(trifluoromethyl)acetophenone (2 mmol, 376 mg) in 20 ml MeOH was added NaBH<sub>4</sub> (1.2 eq. 91 mg). Reaction was stirred until completed as judged by TLC. Reaction mixture was concentrated under reduced pressure and redissolved in Et<sub>2</sub>O and washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Without further 2-(4-(trifluoromethyl)phenyl)-2-propanol purification, the was dissolved in 20 ml anhydrous THF and NaH (1.5 eq. 60% dispersion in paraffin liquid, 120 mg) was added portionwise and stirred for 10 minutes. Then methyl iodide (5 eq., 0.62 ml) was added in one portion and stirred overnight. The reaction mixture was adsorbed onto Celite and purified on silica  $R_{f}(10\% \text{ EtOAc in hexane}) = 0.40$ , colorless oil (145 mg, 36% yield over two steps). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.61 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 4.35 (q, J = 6.5 Hz, 1H), 3.24 (s, 3H), 1.43 (d, J = 6.5, 3H). <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ 147.8, 147.8, 147.8, 147.8, 130.1, 129.8, 129.6, 129.3, 126.4, 125.5, 125.4, 125.4, 125.4, 123.1, 121.0, 79.1, 56.6, 23.8. MS-EI(m/z): calculated for  $C_{10}H_{11}F_{3}O^{+}$ , 204.0757; found 204.1.



(4aa) 2-methyl-2-(4-(tetrahydrofuran-2-yl)phenyl)propane nitrile: Prepared at 0.4 mmol scale according to the procedure in *J. Org. Chem.* 2011, 76, 7, 2187–2194. Purified on silica R<sub>f</sub> (10% EtOAc in petroleum ether) = 0.11, colorless oil (59 mg, **68**% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 – 7.41 (m, 2H), 7.37 – 7.33 (m, 2H), 4.89 (t, *J* = 7.2 Hz, 1H), 4.09 (ddd, *J* = 8.3, 7.1, 6.5 Hz, 1H), 3.98 – 3.90 (m, 1H), 2.38 – 2.27 (m, 1H), 2.06 – 1.96 (m, 2H), 1.84 – 1.74 (m, 1H), 1.71 (s, 6H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  143.3, 140.4, 126.3, 125.2, 124.7, 80.3, 68.8, 37.1, 34.7, 29.3, 29.3, 26.2. HRMS-ESI(m/z): calculated for C<sub>14</sub>H<sub>18</sub>NO<sup>+</sup> [(M+H)<sup>+</sup>] and C<sub>13</sub>H<sub>17</sub>O<sup>+</sup> [(M-HCN+H)<sup>+</sup>] 189.1279; found 189.1282. IR (cm<sup>-1</sup>): 2235 (Nitrile), 1060 (C-O).

# **Experimental procedure for photoreaction**

All reactions were run in duplicate unless otherwise stated. Dichloroethane (DCE, anhydrous) and BrCCl<sub>3</sub> were deoxygenated by sparging with argon for 20 min. Cyclic ether or acetal (0.2 mmol), Fe(acac)<sub>3</sub> (1 mol%) and a stir bar was added to a Biotage MW vial (10 ml) and capped. Reaction atmosphere was exchanged to argon by "sparging" head space for 10 min. Then BrCCl<sub>3</sub> (3 eq. 60  $\mu$ L) followed by DCE (0.1 M, 2 ml) was added. The capped end of the vial was wrapped with parafilm and then placed in a photoreactor and irradiated with 455 nm light for 18 h at 27 °C (with fan). The two duplicated reactions were combined and adsorbed onto Celite and purified on silica. Isolated yields were thereby obtained as an average.

Compounds on TLC-plates were visualized with UV (254 nm), Seebach's stain or KMnO<sub>4</sub>.

## Characterization data for photoproducts



(1a) 4-bromo-1-(4-chlorophenyl)butan-1-one: Colorless oil (93 mg, 90% isolated yield),  $R_f(2\%$  EtOAc in hexane) = 0.12. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 3.54 (t, J = 6.3 Hz, 2H), 3.15 (t, J = 6.9 Hz, 2H), 2.30 (appar. quint, J = 6.5 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  197.7, 139.9, 135.2, 129.6, 129.1, 36.7, 33.6, 26.9. MS-ESI(m/z): calculated for C<sub>10</sub>H<sub>11</sub>BrClO<sup>+</sup> [(M+H)<sup>+</sup>] 260.9682; found 260.1. Spectroscopic data is in agreement with<sup>[12]</sup>.



(2a) 4-bromo-1-phenylbutan-1-one: Yellow/greenish oil (71 mg, 78% isolated yield),  $R_f$  (2% EtOAc in petroleum ether) = 0.14. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 – 7.96 (m, 2H), 7.61 – 7.55 (m, 1H), 7.51 – 7.45 (m, 2H), 3.56 (t, J = 6.3 Hz, 2H), 3.19 (t, J = 6.9 Hz, 2H), 2.32 (tt, J = 6.9, 6.3 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  199.0, 136.9, 133.4, 128.8, 128.2, 36.7, 33.8, 27.0. MS-ESI(m/z): calculated for  $C_{10}H_{12}BrO^+$  [(M+H)<sup>+</sup>] 227.0072; found 227.1. Spectroscopic data is in agreement with<sup>[12]</sup>.



(2b) 1-([1,1'-biphenyl]-4-yl)-4-bromobutan-1-one: Off-white solids (94 mg, 78% isolated yield),  $R_f(2\%$  EtOAc in hexane) = 0.14. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 – 8.03 (m, 2H), 7.72 – 7.67 (m, 2H), 7.66 – 7.60 (m, 2H), 7.51 – 7.45 (m, 2H), 7.44 – 7.38 (m, 1H), 3.58 (t, *J* = 6.3 Hz, 2H), 3.23 (t, *J* = 6.9 Hz, 2H), 2.34 (appar. quint, *J* = 6.6 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  198.6, 146.1, 140.0, 135.6, 129.1, 128.8, 128.4, 127.5, 127.4, 36.8, 33.8, 27.1. MS-ESI(m/z): calculated for C<sub>16</sub>H<sub>16</sub>BrO<sup>+</sup> [(M+H)<sup>+</sup>] 303.0385; found 303.0. Spectroscopic data is in agreement with<sup>[12]</sup>.



(2c) 4-(4-bromobutanoyl)benzonitrile: Off-white solids (82 mg, 81% isolated yield),  $R_f$  (5% EtOAc in petroleum ether) = 0.07. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d, J = 8.7 Hz, 2H), 7.79 (d, J = 8.7 Hz 2H), 3.56 (t, J = 6.2 Hz, 2H), 3.21 (t, J = 6.9 Hz, 2H), 2.33 (appar. quint, J = 6.6 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  197.6, 139.7, 132.7, 128.6, 118.0, 116.7, 37.0, 33.4, 26.6. HRMS-ESI(m/z): calculated for  $C_{11}H_{11}BrNO^+$  [(M+H)<sup>+</sup>] 252.0019; found 252.0000. IR (cm<sup>-1</sup>): 2228 (Nitrile), 1691(C=O). mp: 76.0-77.1 °C.



(2d) 4-bromo-1-(4-methoxyphenyl)butan-1-one: Pinkish oil (82 mg, 79% isolated yield),  $R_f$  (3% EtOAc in petroleum ether) = 0.09. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (d, J = 9.0 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 3.88 (s, 3H), 3.55 (t, J = 6.3 Hz, 2H), 3.13 (t, J = 6.9 Hz, 2H), 2.31 (appar. quint, J = 6.7 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  197.5, 163.7, 130.4, 130.0, 113.9, 55.6, 36.3, 33.9, 27.2. MS-ESI(m/z): calculated for  $C_{11}H_{14}BrO_2^+$  [(M+H)<sup>+</sup>] 257.0177; found 257.0. Spectroscopic data is in agreement with<sup>[12]</sup>.



Br

(2e) methyl 4-(4-bromobutanoyl)benzoate: White solids (94 mg, 82% isolated yield),  $R_f$  (5% EtOAc in hexane) = 0.07. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.13 (d, J = 8.5 Hz, 2H), 8.03 (d, J = 8.5 Hz, 2H), 3.96 (s, 3H), 3.56 (t, J = 6.3 Hz, 2H), 3.22 (t, J = 6.9 Hz, 2H), 2.33 (appar. quint, J = 6.6 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  198.5, 166.3, 140.0, 134.2, 130.1, 128.1, 52.6, 37.1, 33.6, 26.8. HRMS (m/z): calculated for C<sub>12</sub>H<sub>14</sub>BrO<sub>3</sub><sup>+</sup> [(M+H)<sup>+</sup>] 285.0126; not detected using either EI, ESI or APCI. IR (cm<sup>-1</sup>): 1715 (C=O), 1687 (C=O ester). mp: 66.7-77.9 °C.

(2f) 4-bromo-1-(2-isopropylphenyl)butan-1-one: Yellow oil (99 mg, 92% isolated yield),  $R_f(2\%$  EtOAc in pentane) = 0.10. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 – 7.39 (m, 3H), 7.25 – 7.21 (m, 1H), 3.55 (t, J = 6.4 Hz, 2H), 3.31 (hept, J = 6.8 Hz, 1H), 3.07 (t, J = 6.9 Hz, 2H), 2.29 (appar. quint, J = 6.5 Hz, 2H), 1.24 (d, J = 6.8, 6H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  205.1, 147.5, 139.0, 131.1, 127.1, 126.7, 125.6, 40.9, 33.5, 29.7, 27.0, 24.3. HRMS-ESI(m/z): calculated for C<sub>13</sub>H<sub>18</sub>BrO<sup>+</sup> [(M+H)<sup>+</sup>] 269.0536; found 269.0513. IR (cm<sup>-1</sup>): 1686 (C=O).

(2g) 4-bromo-1-(3,4,5-trimethoxyphenyl)butan-1-one: Off-white solids (109 mg, 86% isolated yield),  $R_f(10\%$  EtOAc in petroleum ether) = 0.10. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (s, 2H), 3.93 (s, 6H), 3.92 (s, 3H), 3.56 (t, J = 6.2 Hz, 2H), 3.15 (t, J = 6.9 Hz, 2H), 2.32 (appar. quint, J = 6.5 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  197.8, 153.2, 142.9, 132.1, 105.7, 61.1, 56.5, 36.4, 33.8, 27.3. HRMS-ESI(m/z): calculated for  $C_{13}H_{18}BrO_4^+$  [(M+H)<sup>+</sup>] 317.0388; found 317.0393. IR (cm<sup>-1</sup>): 1671 (C=O), 1231 (C-O). mp: 87.3-88.5 °C.

(2h) 4-bromo-1-(4-bromophenyl)butan-1-one: Colorless oil (101 mg, 83% isolated yield),  $R_f(2\%$  EtOAc in petroleum ether) = 0.10. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 3.54 (t, J = 6.3 Hz, 2H), 3.15 (t, J = 6.9 Hz, 2H), 2.30 (appar. quint, J = 6.6 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  197.9, 135.6, 132.1, 129.7, 128.6, 36.7, 33.6, 26.8. MS-ESI(m/z): calculated for  $C_{10}H_{11}Br_2O^+$  [(M+H)<sup>+</sup>] 304.9177; found 305.0. Spectroscopic data is in agreement with<sup>[12]</sup>.

(2i) 4-bromo-1-(*p*-tolyl)butan-1-one: Colorless oil (75 mg, 78% isolated yield),  $R_f(2\%$  EtOAc in pentane) = 0.10. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, J = 8.2 Hz, 2H), 7.28 – 7.23 (m, 2H), 3.54 (t, J = 6.4 Hz, 2H), 3.15 (t, J = 7.0 Hz, 2H), 2.41 (s, 3H), 2.30 (tt, J = 6.9, 6.3 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  198.6, 144.2, 134.4, 129.5, 128.3, 36.6, 33.8, 27.1, 21.8. MS-ESI(m/z): calculated for C<sub>11</sub>H<sub>14</sub>BrO<sup>+</sup> [(M+H)<sup>+</sup>] 241.0228; found 241.0. Spectroscopic data is in agreement with<sup>[12]</sup>.



C







(2j) 4-bromo-1-(2,4-difluorophenyl)butan-1-one: Colorless liquid (34 mg, 71% isolated yield),  $R_f(2\%$  EtOAc in hexane) = 0.12. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (td, J = 8.6, 6.6 Hz, 1H), 7.01 – 6.93 (m, 1H), 6.89 (ddd, J = 11.1, 8.6, 2.4 Hz, 1H), 3.53 (t, J = 6.4 Hz, 2H), 3.16 (td, J = 6.9, 3.3 Hz, 2H), 2.30 (appar. quint, J = 6.6 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  195.6 (d, J = 4.8 Hz), 166.0 (dd, J = 257.4, 12.3 Hz), 163.0 (dd, J = 257.7, 12.5 Hz), 132.8 (dd, J = 10.6, 4.3 Hz), 122.0 (d, J = 13.7 Hz), 112.4 (d, J = 21.4 Hz), 105.0 (t, J = 26.6 Hz), 41.6 (d, J = 7.8 Hz), 33.4, 26.8. <sup>19</sup>F-NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -101.52 – -101.73 (m, 1F), -104.09 (tdd, J = 11.7, 7.2, 3.3 Hz, 1F). HRMS-ESI(m/z): calculated for C<sub>10</sub>H<sub>10</sub>BrF<sub>2</sub>O<sup>+</sup> [(M+H)<sup>+</sup>] 262.9883; found 262.9881. IR (cm<sup>-1</sup>): 1685 (C=O).



(2k) 4-bromo-1-(3-methoxyphenyl)butan-1-one: Colorless oil (83 mg, 82% isolated yield),  $R_f(2\%$  EtOAc in petroleum ether) = 0.10. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 (ddd, J = 7.7, 1.6, 0.9 Hz, 1H), 7.49 (dd, J = 2.7, 1.6 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 7.11 (ddd, J = 8.2, 2.7, 1.0 Hz, 1H), 3.86 (s, 3H), 3.54 (t, J = 6.4 Hz, 2H), 3.17 (t, J = 6.9 Hz, 2H), 2.30 (appar. quint, J = 6.7 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  198.8, 160.0, 138.2, 129.8, 120.8, 119.8, 112.4, 55.6, 36.8, 33.7, 27.1. MS-ESI(m/z): calculated for C<sub>11</sub>H<sub>14</sub>BrO<sub>2</sub><sup>+</sup> [(M+H)<sup>+</sup>] 257.0177; found 257.0. Spectroscopic data is in agreement with<sup>[13]</sup>.

(21) 2-(3-(trichloromethyl)tetrahydrofuran-2-yl)benzo[*d*]thiazole: Colorless oil (27 mg, 21% isolated yield),  $R_f$  (5% EtOAc in petroleum ether ) = 0.33. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.49 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.40 (ddd, *J* = 8.2, 7.2, 1.0 Hz, 1H), 5.54 (d, *J* = 3.6 Hz, 1H), 4.40 (ddd, *J* = 9.3, 5.9, 3.6 Hz, 1H), 4.29 (td, *J* = 8.4, 4.5 Hz, 1H), 4.07 (appar. q, *J* = 8.2 Hz, 1H), 2.55 – 2.34 (m, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  172.0, 153.3, 135.8, 126.3, 125.6, 123.6, 122.0, 101.5, 81.1, 69.2, 66.0, 31.3. HRMS-ESI(m/z): calculated for C<sub>12</sub>H<sub>11</sub>Cl<sub>3</sub>NOS<sup>+</sup> [(M+H)<sup>+</sup>] 321.9621; found 321.9627. IR (cm<sup>-1</sup>): 1129 (C-O), 762 (C-Cl).



Cl<sub>3</sub>C

(3a) 4-bromo-2-methyl-1-phenylbutan-1-one: Greenish oil (81 mg, 95% isolated yield), R<sub>f</sub> (2% EtOAc in petroleum ether) = 0.11. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 – 7.98 (m, 2H), 7.61 – 7.56 (m, 1H), 7.52 – 7.46 (m, 2H), 3.81 (appar. sext, J = 6.4 Hz, 1H), 3.51 (ddd, J = 10.2, 7.0, 5.8 Hz, 1H), 3.43 (ddd, J = 10.2, 7.5, 5.7 Hz, 1H), 2.44 (dtd, J = 14.3, 7.1, 5.7 Hz, 1H), 1.96 (ddt, J = 14.5, 7.5, 6.0 Hz, 1H), 1.23 (d, J = 7.0 Hz, 3H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  203.3, 136.3, 133.4, 128.9, 128.6, 39.0, 35.8, 32.2, 17.4. IR (cm<sup>-1</sup>): 1678 (C=O). HRMS-ESI(m/z): calculated for C<sub>11</sub>H<sub>14</sub>BrO<sup>+</sup> [(M+H)<sup>+</sup>] 241.0228; found 241.0225.







O O O Br



(3b) 5-bromo-1-phenylpentan-1-one: Off-white solids (80 mg, 84% isolated yield),  $R_f$  (2% EtOAc in petroleum ether) = 0.12. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 – 7.93 (m, 2H), 7.60 – 7.54 (m, 1H), 7.50 – 7.44 (m, 2H), 3.46 (t, J = 6.4 Hz, 2H), 3.02 (t, J = 6.9 Hz, 2H), 2.02 – 1.85 (m, 4H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  199.7, 137.0, 133.2, 128.8, 128.1, 37.5, 33.5, 32.3, 22.9. MS-ESI(m/z): calculated for  $C_{11}H_{14}BrO^+$  [(M+H)<sup>+</sup>] 241.0228; found 241.0. Spectroscopic data is in agreement with<sup>[12]</sup>.

(3d) methyl benzoate: Slight yellow liquid (39 mg, 71% isolated yield),  $R_f(2\% \text{ EtOAc in pentane}) = 0.19$ . <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 – 8.01 (m, 2H), 7.58 – 7.53 (m, 1H), 7.47 – 7.41 (m, 2H), 3.92 (s, 3H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  167.3, 133.0, 130.3, 129.7, 128.5, 52.2. MS-EI(m/z): calculated for  $C_8H_8O_2^+$ , 136.0524; found 136.1. Spectroscopic data is in agreement with<sup>[14]</sup>.

(3e) 2-bromoethyl 3-bromobenzoate: (purified prior to reaction). Colorless oil (107 mg, 86% isolated yield and 252 mg, 82% isolated yield for the 1 mmol scale reaction),  $R_f(3\%$  EtOAc in petroleum ether) = 0.16. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (ddd, J = 2.0, 1.6, 0.4 Hz, 1H), 8.00 (ddd, J = 7.8, 1.6, 1.1 Hz, 1H), 7.71 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.34 (td, J = 7.9, 0.4 Hz, 1H), 4.64 (t, J = 6.1 Hz, 2H), 3.64 (t, J = 6.1 Hz, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  164.9, 136.4, 132.9, 131.7, 130.2, 128.5, 122.7, 64.7, 28.7. HRMS (m/z): calculated for C<sub>9</sub>H<sub>9</sub>Br<sub>2</sub>O<sup>+</sup> [(M+H)<sup>+</sup>] 306.8969; not detected using either EI, ESI or APCI. IR (cm<sup>-1</sup>): 1721 (C=O).

(3f) 1-bromopropan-2-yl benzoate: Colorless oil (92 mg, 95% isolated yield),  $R_f$  (3% EtOAc in petroleum ether) = 0.16. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 – 8.04 (m, 2H), 7.60 – 7.54 (m, 1H), 7.49 – 7.42 (m, 2H), 5.33 (qt, J = 6.4, 5.1 Hz, 1H), 3.59 (dd, J = 5.1, 1.9 Hz, 2H), 1.49 (d, J = 6.4 Hz, 3H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  165.9, 133.3, 130.2, 129.9, 128.5, 69.9, 35.6, 18.9. HRMS (m/z): calculated for C<sub>10</sub>H<sub>12</sub>BrO<sub>2</sub><sup>+</sup> [(M+H)<sup>+</sup>] 243.0021; not detected using either EI, ESI or APCI. IR (cm<sup>-1</sup>): 1715 (C=O). Spectroscopic data is in agreement with.<sup>[15]</sup>

(3g) 2-bromoethyl 3-bromobenzo[*b*]thiophene-2-carboxylate: White solids (115 mg, 78 % isolated yield),  $R_f$  (2% EtOAc in petroleum ether) = 0.09. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 – 7.98 (m, 1H), 7.86 – 7.82 (m, 1H), 7.58 – 7.49 (m, 2H), 4.68 (t, *J* = 6.2, 2H), 3.67 (t, *J* = 6.2, 2H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  161.0, 139.7, 138.8, 128.5, 126.8, 125.9, 125.6, 122.8, 116.0, 64.9, 28.3. HRMS-ESI(m/z): calculated for C<sub>11</sub>H<sub>9</sub>Br<sub>2</sub>O<sub>2</sub>S<sup>+</sup> [(M+H)<sup>+</sup>] 362.8685; found 362.8690. IR (cm<sup>-1</sup>): 1716 (C=O). mp: 93.0-94.2 °C.











(3i) 1-bromododecan-4-one: Colorless oil isolated as an inseparable mixture of product and starting material with a conversion of 48% as determined from <sup>1</sup>H-NMR (See Appendix).  $R_f(0.5\% \text{ EtOAc} \text{ in hexane}) = 0.07$ . MS-EI(m/z): calculated for  $C_{12}H_{23}BrO^+$ , 262.0927; found 262.1 (only weekly ionizing).

(3j) Benzaldehyde: Slight yellow oil (36 mg, 85% yield (from 3jj(a)) and 32 mg, 81% yield (from 3jj(b)),  $R_f(2\%$  EtOAc in hexane) = 0.18. Care needs to be taken when evaporating the solvents as benzaldehyde seems abnormally volatile in these cases. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  10.05 (s, 1H), 7.89 (d, J = 7.3 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.5 Hz, 2H).

(3k) 4'-(trifluoromethyl)acetophenone: Colorless oil (60 mg, 80% yield),  $R_f(2\%$  EtOAc in hexane) = 0.17. Care needs to be taken when evaporating the solvents in this case to as the product seems somewhat volatile. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 2.65 (s, 3H).



(4a) 2-(4-(4-bromobutanoyl)phenyl)-2-methylpropanenitrile: Conducted once at 0.1 mmol scale. White solids (24 mg, **82** % isolated yield),  $R_f(10\%$  EtOAc in petroleum ether) = 0.09. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H), 3.55 (t, J = 6.3 Hz, 2H), 3.18 (t, J = 6.9 Hz, 2H), 2.31 (appar. quint, J = 6.6 Hz, 2H), 1.75 (s, 6H). <sup>13</sup>C-NMR (201 MHz, CDCl<sub>3</sub>)  $\delta$  198.2, 146.7, 136.4, 128.9, 125.7, 124.0, 37.5, 36.8, 33.6, 29.1, 26.9. MS-ESI(m/z): calculated for C<sub>14</sub>H<sub>17</sub>BrNO<sup>+</sup> [(M+H)<sup>+</sup>] 294.0493; found 294.0. Spectroscopic data is in agreement with<sup>[16]</sup>.

## **Mechanism – Experiments and Calculations**

#### **UV-Vis**

To test whether  $Fe(acac)_3$  and  $BrCCl_3$  could form an electron-donor-acceptor complex (EDA complex) UV-Vis were recorded for the two pure substances in DCE as well as their mixtures. A solution of  $Fe(acac)_3$  and  $BrCCl_3$  in DCE (0.2 mM and 60 mM respectively) was initially measured.  $BrCCl_3$  (300 eq. 17.7 µL) was then added to the cuvette and UV-Vis was once more measured (Mixture 1). A second equal portion of  $BrCCl_3$  was added to the same cuvette and UV-Vis recorded once more (Mixture 2). In the plot below the concentration has been corrected for the added volume of  $BrCCl_3$ . As can be seen in Figure S1 below, no shift of the bands has occurred upon mixing  $Fe(acac)_3$  and  $BrCCl_3$  and no new charge-transfer bands can be seen. The only difference is a slight decrease in absorbance for Mixture 1 and Mixture 2, which correlates with the slightly diluted solution by the added volume of  $BrCCl_3$ .



Figure S1. UV-vis absorbance spectroscopy experiments on mixture. No shifts of bands was observed indicating there is no formation of an EDA-complex.

#### Reactions

Reactions in this section refers to those in Scheme 5 and Scheme 6. All reaction were prepared as described in *Experimental procedure for photoreaction* and conducted at 0.1 mmol scale with respect to **1aa**.

*Experiment i):* **1aa**, 1 eq.  $Fe(acac)_3$  and no BrCCl<sub>3</sub> in DCE, irradiated for 6 h. These conditions did not provide any product.



*Experiment ii*): **1aa**, 3 eq. methyl acrylate, 1 eq.  $Fe(acac)_3$  and no BrCCl<sub>3</sub> in DCE, irradiated for 6 h. These conditions did not provide any product.



*Experiment iii):* **1aa**, 1 eq. NBu<sub>4</sub>Br, 1 eq. Fe(acac)<sub>3</sub> and no BrCCl<sub>3</sub> irradiated for 6h. These conditions did not provide any product.



*Experiment iv*): 0.1 mmol Fe(acac)<sub>3</sub> and 1 eq. BrCCl<sub>3</sub> was dissolved in 0.5 ml DCE and irradiated for 6 h. These conditions afforded hexachloroethane as detected my GC-MS(EI).

 $Fe(acac)_3 + BrCCl_3 \xrightarrow{Blue LEDs} Cl_3C-CCl_3$ 

*Experiment v):* **1aa**, 1 eq. TEMPO, 1 eq. Fe(acac)<sub>3</sub>, 3 eq. BrCCl<sub>3</sub> in DCE, irradiated for 6h. These conditions did not provide any product.



## Calculations on BrCCl<sub>3</sub>

Geometry optimization was performed with the method CCSD+PCM/cc-pVTZ, solvent: dichloroethane.

#### **Optimized geometry (Å):**

С	0.00000	0.00000	-0.40878
Br	0.00000	0.00000	1.52862
Cl	0.00000	1.66949	-1.00096
Cl	1.44582	-0.83474	-1.00096
Cl	-1.44582	-0.83474	-1.00096

Energy: -3989.827393 Hartree

#### **Single-point calculations:**

Performed with the method (R/U)CCSD(T)+PCM/aug-cc-pVQZ, solvent: dichloroethane.

Energy <sup>1</sup>A<sub>1</sub>: -3990.085935 Hartree Energy <sup>3</sup>A<sub>1</sub>: -3989.868337 Hartree

#### Jablonski diagram



Figure S2. Schematic Jablonski diagram of the some excited states of Fe(acac)<sub>3</sub>.

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# **Appendix – Experimental NMR-Spectra**





























































































