

Supporting Information

Decarbonylation of benzaldehydes by dual photoorgano-cobalt catalysis

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1. General Information

Chemicals and solvents: all commercially available chemicals were purchased in high quality and used without further purification. Solvents for column chromatography were distilled prior to use. Moisture and oxygen-sensitive reactions were carried out using dry solvents in oven-dried glassware under inert atmosphere of pre-dried nitrogen. The evaporation of solvents was carried out in a rotary evaporator at temperatures below 40 °C, under reduced pressure. The water content of acetonitrile (215 ± 6 ppm water) used for photocatalyzed reactions was determined by Karl Fischer titration.

Flash Column Chromatography (FCC): flash silica gel (Merck, 40-63 μm) was used as the stationary phase. Binary eluent mixtures are reported as v/v solutions normalized to 100 volume units. Purification by automated flash column chromatography was performed on a Biotage® Isolera™ Spektra One device using either pre-packed Biotage® columns or silica gel 60 M (particle size 40–63 μm , 230–440 mesh, Merck) self-packed columns.

Analytical TLC: performed on silica gel pre-coated aluminium sheets (Machery-Nagel, silica gel 60 G/UV254, 0.2 mm). Visualization was accomplished by exposure to UV-light (254 nm). Eluent mixtures for TLC are reported as v/v solutions normalized to 100 volume units.

Nuclear magnetic resonance (NMR): spectra were recorded at room temperature using a Bruker Avance 400 (400 MHz for ^1H , 101 MHz for ^{13}C) NMR spectrometer. Chemical shifts are reported in δ -scale as parts per million [ppm] relative to the solvent residual peaks as internal standard. Coupling constants J are given in Hertz [Hz] and the multiplicity of the signals is abbreviated as: singlet (s), broad singlet (bs), doublet (d), doublet of doublets (dd), triplet (t), doublet of triplets (dt), triplet of doublets (td), quadruplet (q), or multiplet (m). Signals are reported as follows: (multiplicity, coupling constant J , number of protons). Spectra were analyzed using MestReNova 6.0.2.

High Resolution Mass Spectrometry (HRMS): spectra were obtained from the central analytical mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, University of Regensburg. All mass spectra were recorded on a Finnigan MAT 95, Thermo Quest Finnigan TSQ 7000, Finnigan MATSSQ 710 A or an Agilent Q-TOF 6540 UHD instrument.

GC-FID and GC-MS: GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent Chem Station Rev.C.01.04. GC-MS measurements were performed on a 7890A GC system from Agilent Technologies with an Agilent 5975 MSD Detector. Data acquisition and evaluation was done

with MSD Chem Station E.02.02.1431. A capillary column HP-5MS/30 mx 0.25 mm/0.25 μ M film and helium as carrier gas (flow rate of 1 mL/min) were used. The injector temperature (split injection: 40:1 split) was 280 °C, detection temperature 300 °C (FID). GC measurements were made and investigated via integration of the signal obtained. The GC oven temperature program was adjusted as follows: initial temperature 40 °C was kept for 3 minutes, the temperature was increased at a rate of 15 °C/min over a period of 16 minutes until 280 °C was reached and kept for 5 minutes, the temperature was again increased at a rate of 25 °C/min over a period of 48 seconds until the final temperature (300 °C) was reached and kept for 5 minutes.

Gas analyzer: evolved carbon monoxide analysis was performed on a micro-GC 3000 series (Inficon) provided with a 5A Molsieve column (10 m x 320 μ m x 30 μ m) and a TCD detector. Argon was used as carrier gas at 60 °C for 3 min. Data acquisition and evaluation was done with EZ IQ from Inficon.

UV-Vis Spectroscopy: UV-Vis measurements were recorded with an Agilent 8453 spectrophotometer in acetonitrile as solvent.

Photoreactor setup: photoreactions were irradiated with LEDs (Engine LZ4-40UB00-00U5, λ = 385 nm (\pm 25), average radiant flux 3610 \pm 45 mW, 89 V, 700 mA). Reaction mixtures were exposed to light under stirring (350 rpm, magnetic stirrer) from the bottom side of the vial. The temperature of the system was controlled by a water-cooling circuit consisting of an aluminium cooling block connected to a thermostat (Figure S1).

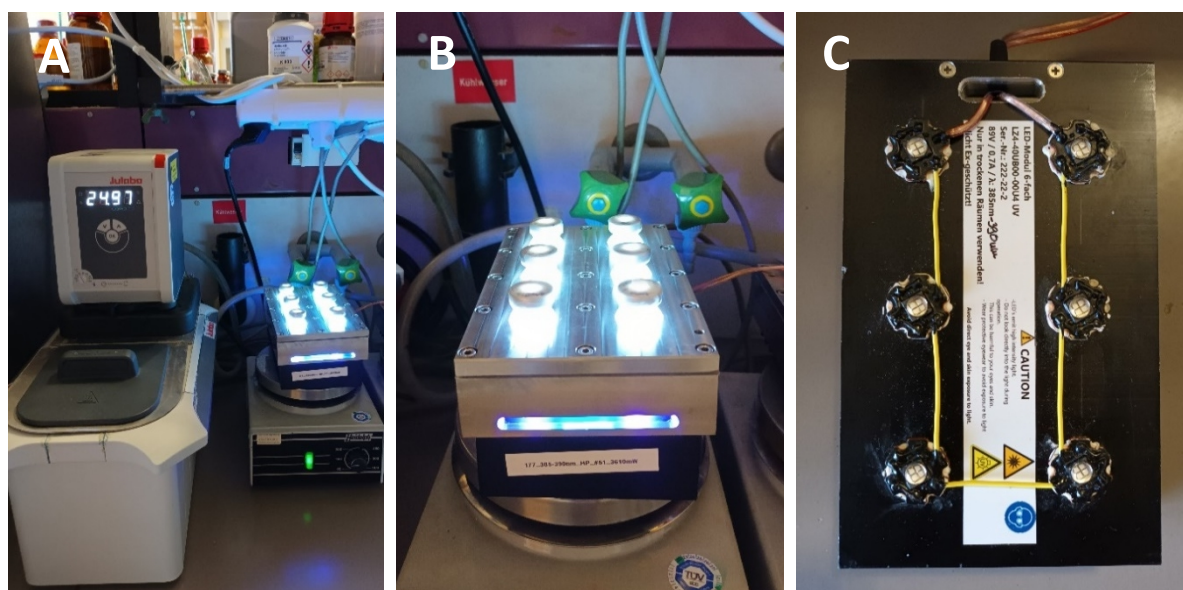


Figure S1 Photoreactor setup. A: Thermostat connected to the aluminium cooling block. B: Cooling block and LED on top of stirrer. C: LED module.

The optical power of the LEDs was determined using a FieldMaxII-TOTM laser power meter equipped with a PM3 sensor. The emission spectrum of the LEDs (Figure S2) was recorded using an Ocean Optics HR4000CG-UV-NIR Glass fibre and diffusor.

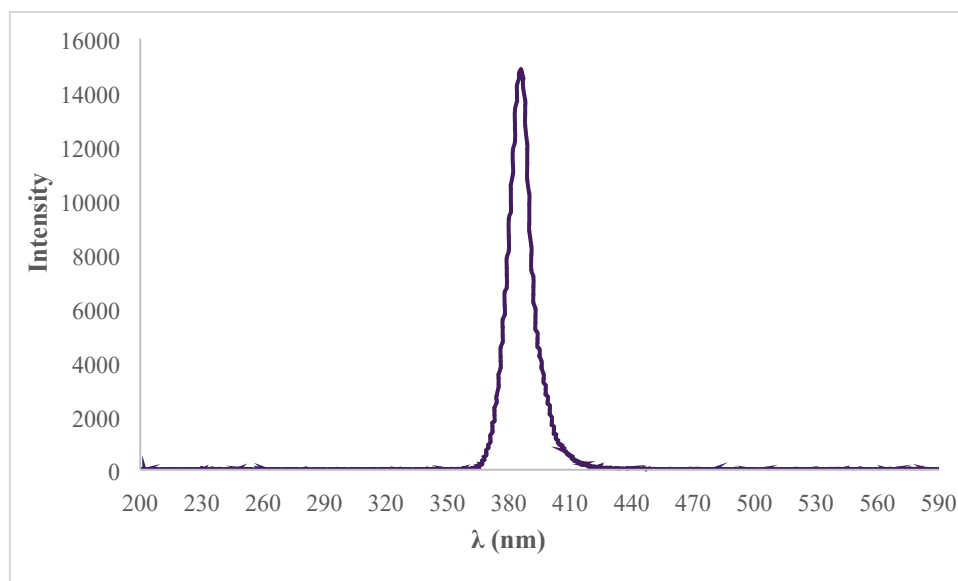


Figure S2 Emission spectrum of the LEDs used for the photoreactions.

Glassware absorption: photoreactions were carried out in WICOM[®] 20 mm crimp-cap vials (5 mL, 38.5 x 22.0 mm) made of borosilicate glass. The vials transmit 100% of incident light above 350 nm (Figure S3).

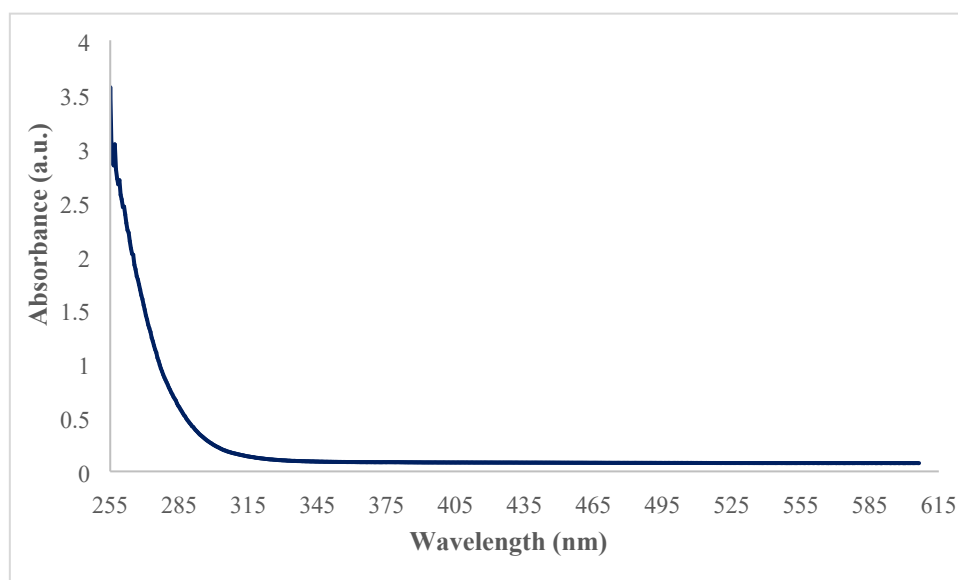
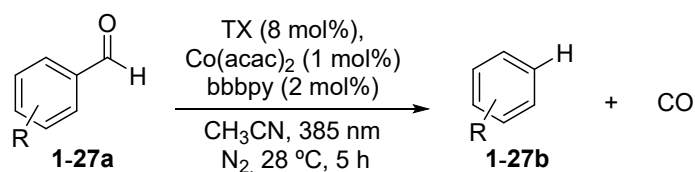


Figure S3 Absorption spectrum of vials used for photoreactions.

2. General procedure for the photocatalytic decarbonylation of benzaldehydes (GP1)



A 5 mL crimp-cap vial equipped with a stirring bar, was loaded with the corresponding benzaldehyde (50 μ mol, 1.00 equiv.), thioxanthone (0.9 mg, 4 μ mol, 8 mol%), cobalt (II) acetylacetonate (0.13 mg, 0.5 μ mol, 1 mol%) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (0.27 mg, 1 μ mol, 2 mol%). The vial was sealed, non-dried CH₃CN (0.5 mL) was added, and the mixture was sonicated for 1 min. After degassing via freeze-pump-thaw cycling (3 x), the reaction mixture was stirred under irradiation using a 3.6 W 385 nm (\pm 25 nm) LED set-up for 5 h at 28 °C (temperature controlled by a thermostat). Reaction progress was monitored by TLC or GC-FID analysis. Afterwards, for compounds with relatively high vapor pressure, the reaction yield was determined via GC-FID analysis using mesitylene as internal standard. For products **16b** and **25b** the solvent was evaporated under reduced pressure and the crude product was purified via FCC.

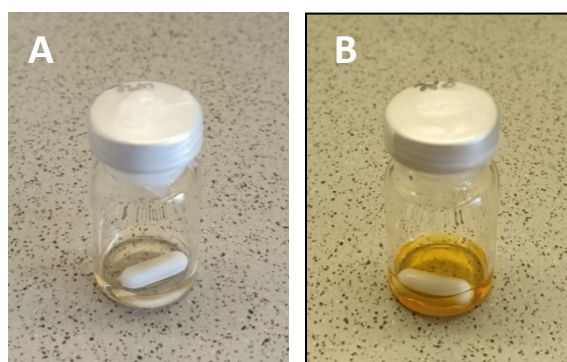
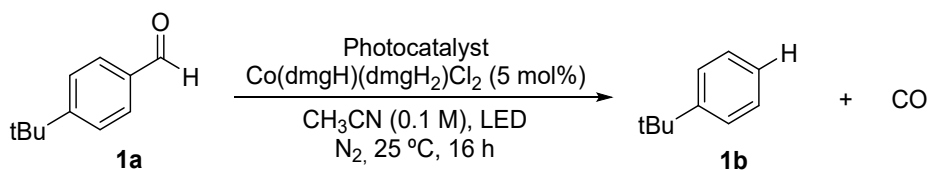


Figure S4 Vial containing reaction mixture of **1a**. A: before irradiation. B: after 5 h irradiation.

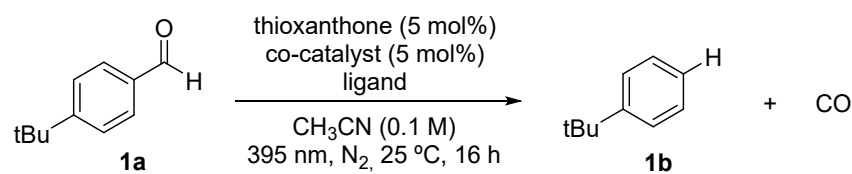
3. Reaction conditions optimization

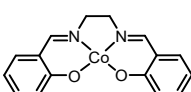
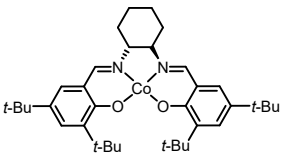
Table S1 Screening of photocatalyst.



Entry	photocatalyst (mol%)	Irradiation	Yield of 1b (%) ^a
1	Eosin Y (5 mol%)	450 nm (1.3 W)	3
2	Rhodamine 6G (5 mol%)	450 nm (1.3 W)	7
3	TBADT (5 mol%)	395 nm (2.2 W)	52
4	Anthraquinone (5 mol%)	395 nm (2.2 W)	11
5	2-Chloroanthraquinone (5 mol%)	395 nm (2.2 W)	11
6	Xanthone (5 mol%)	395 nm (2.2 W)	19
7	Thioxanthone (5 mol%)	395 nm (2.2 W)	62
8	2-chlorothioxanthone (5 mol%)	395 nm (2.2 W)	38
9	4-Methoxy-4'-trifluoromethylbenzophenone (5 mol%)	365 (3.1 W)	32
10	Anthrone (5 mol%)	365 (3.1 W)	19

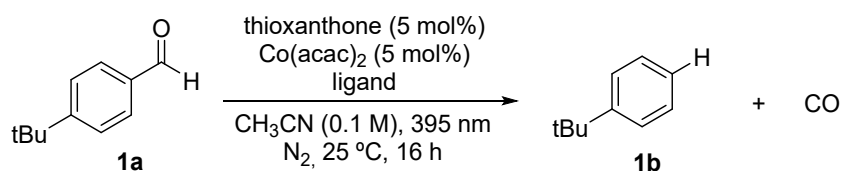
1a (0.05 mmol), photocatalyst, $\text{Co}(\text{dmgh})(\text{dmgh}_2)\text{Cl}_2$ (5 mol%), CH_3CN (0.5 mL), LED, 25 °C, 16 h, N_2 . ^aYields were determined by GC-FID analysis against mesitylene as internal standard.

Table S2 Screening of co-catalyst.

Entry	co-catalyst (5 mol%)	Ligand (mol%)	Yield of 1b (%) ^a
1	Co(dmgh)(dmgh ₂)Cl ₂	-	62
2	COPC	-	58
3	Co(acac) ₂	-	28
4	Co(acac) ₂	4,4'-di- <i>tert</i> -butyl-2,2'-dipyridyl (bbbpy) (10 mol%)	72
5	Co(NO ₃) ₂ ·6H ₂ O	bbbpy (10 mol%)	48
6	Co(OAc) ₂	bbbpy (10 mol%)	67
7	CoCl ₂	-	37
8	CoCl ₂	bbbpy (10 mol%)	62
9		-	54
10		-	20
11	CuCl ₂	bbbpy (10 mol%)	Not detected (n.d.)
12	NiCl ₂	bbbpy (10 mol%)	n.d.
13	FeCl ₂	bbbpy (10 mol%)	n.d.

1a (0.05 mmol), thioxanthone (5 mol%), co-catalyst (5 mol%), CH₃CN (0.5 mL), 395 nm LED (2.2 W), 25 °C, 16 h, N₂. ^aYields were determined by GC-FID analysis against mesitylene as internal standard.

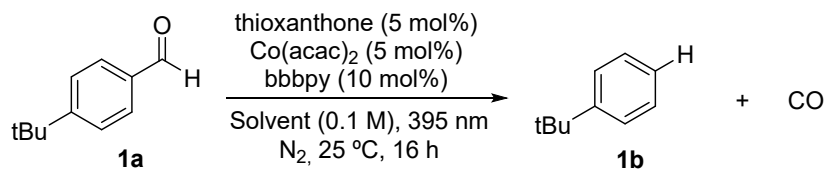
Table S3 Screening of ligand.



Entry	Ligand (mol%)	Yield of 1b (%) ^a
1	bbppy (10 mol%)	72
2	2,2'-bipyridine (10 mol%)	40
3	6,6'-Dimethyl-2,2'-bipyridyl (10 mol%)	34
4	neocuproin (10 mol%)	25
5	Pyridine (10 mol%)	21

1a (0.05 mmol), thioxanthone (5 mol%), Co(acac)₂ (5 mol%), ligand, CH₃CN (0.5 mL), 395 nm LED (2.2 W), 25 °C, 16 h, N₂. ^aYields were determined by GC-FID analysis against mesitylene as internal standard.

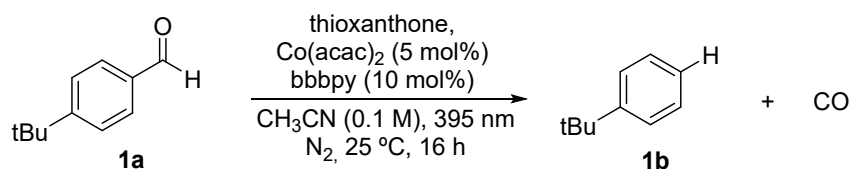
Table S4 Screening of solvent.



Entry	Solvent	Yield of 1b (%) ^a
1 ^b	Non-dry CH ₃ CN (215 ± 6 ppm water)	72
2	Dry CH ₃ CN	66
3	CH ₃ CN/H ₂ O (9/1 in vol.)	6
4	EtOAc	70
5	Dry CH ₂ Cl ₂	10
6	Dry acetone	51
7	Dry MeOH	9

1a (0.05 mmol), thioxanthone (5 mol%), Co(acac)₂ (5 mol%), bbbpy (10 mol%) solvent (0.5 mL), 395 nm LED (2.2 W), 25 °C, 16 h, N₂. ^aYields were determined by GC-FID analysis against mesitylene as internal standard. ^bwater content determined by Karl-Fischer titration.

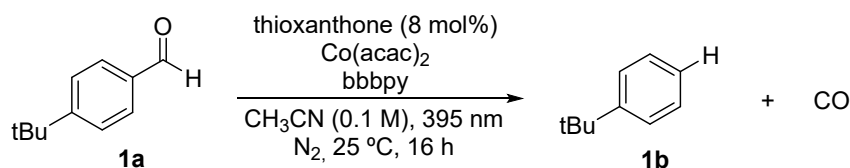
Table S5 Screening of photocatalyst loading.



Entry	Photocatalyst (mol%)	Yield of 1b (%) ^a
1	thioxanthone (2 mol%)	55
2	thioxanthone (5 mol%)	72
3	thioxanthone (8 mol%)	73
4	thioxanthone (11 mol%)	60

1a (0.05 mmol), thioxanthone, Co(acac)₂ (5 mol%), bbbpy (10 mol%), CH₃CN (0.5 mL), 395 nm LED (2.2 W), 25 °C, 16 h, N₂. ^aYields were determined by GC-FID analysis against mesitylene as internal standard.

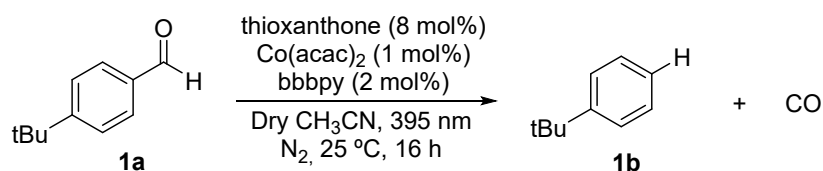
Table S6 Screening of co-catalyst and ligand loading.



Entry	Co-catalyst (mol%)	Ligand (mol%)	Yield of 1b (%) ^a
1	Co(acac) ₂ (1 mol%)	-	17
2	Co(acac) ₂ (1 mol%)	bbbpy (2 mol%)	77
3	Co(acac) ₂ (2 mol%)	dtbbpy (4 mol%)	72
4	Co(acac) ₂ (2 mol%)	dtbbpy (6 mol%)	69
5	Co(acac) ₂ (5 mol%)	dtbbpy (5 mol%)	70
6	Co(acac) ₂ (5 mol%)	dtbbpy (10 mol%)	73

1a (0.05 mmol), thioxanthone (8 mol%), Co(acac)₂, bbbpy, CH₃CN (0.5 mL), 395 nm LED (2.2 W), 25 °C, 16 h, N₂. ^aYields were determined by GC-FID analysis against mesitylene as internal standard.

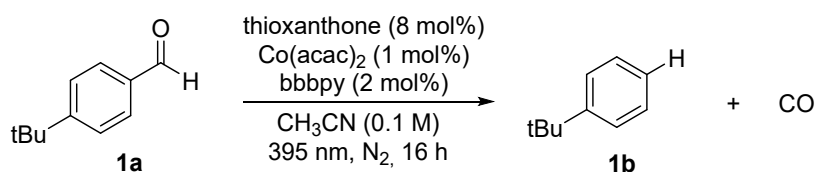
Table S7 Screening of concentration.



Entry	Concentration (M)	Yield of 1b (%) ^a
1	0.05	65
2	0.1	77
3	0.15	64

1a, thioxanthone (8 mol%), Co(acac)₂ (1 mol%), bbbpy (2 mol%), CH₃CN (0.5 mL), 395 nm LED (2.2 W), 25 °C, 16 h, N₂. ^aYields were determined by GC-FID analysis against mesitylene as internal standard.

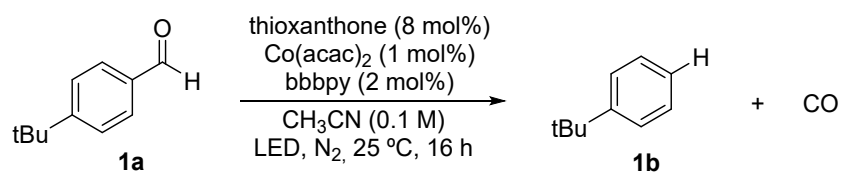
Table S8 Screening of temperature.



Entry	Temperature (°C)	Yield of 1b (%) ^a
1	10	44
2	25	77
3	40	81
4	60	86

1a (0.05 mmol), thioxanthone (8 mol%), Co(acac)₂ (1 mol%), bbbpy (2 mol%), CH₃CN (0.5 mL), 395 nm LED (2.2 W), 16 h, N₂. ^aYields were determined by GC-FID analysis against mesitylene as internal standard.

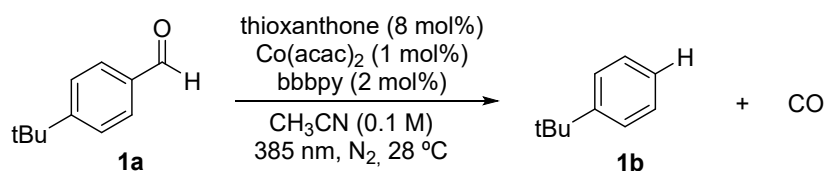
Table S9 Screening of light source.



Entry	Light source	Yield of 1b (%) ^a
1	420 nm (0.5 W)	9
2	395 nm (0.6 W)	22
3	395 nm (2.2 W)	77
4	385 nm (3.6 W)	91
5	365 nm (2.6 W)	69

1a (0.05 mmol), thioxanthone (8 mol%), Co(acac)₂ (1 mol%), bbbpy (2 mol%), CH₃CN (0.5 mL), LED, 25 °C, 16 h, N₂. ^aYields were determined by GC-FID analysis against mesitylene as internal standard.

Table S10 Screening of reaction time.



Entry	Reaction time	Yield of 1b (%) ^a
1	5 min	22
2	15 min	48
3	30 min	59
4	1 h	71
5	2 h	82
6	4 h	88
7	5 h	94
8	6 h	92
9	8 h	92
10	16 h	91

1a (0.05 mmol), thioxanthone (8 mol%), Co(acac)₂ (1 mol%), bbbpy (2 mol%), CH₃CN (0.5 mL), 385 nm LED (3.6 W), 28 °C, N₂. ^aYields were determined by GC-FID analysis against mesitylene as internal standard.

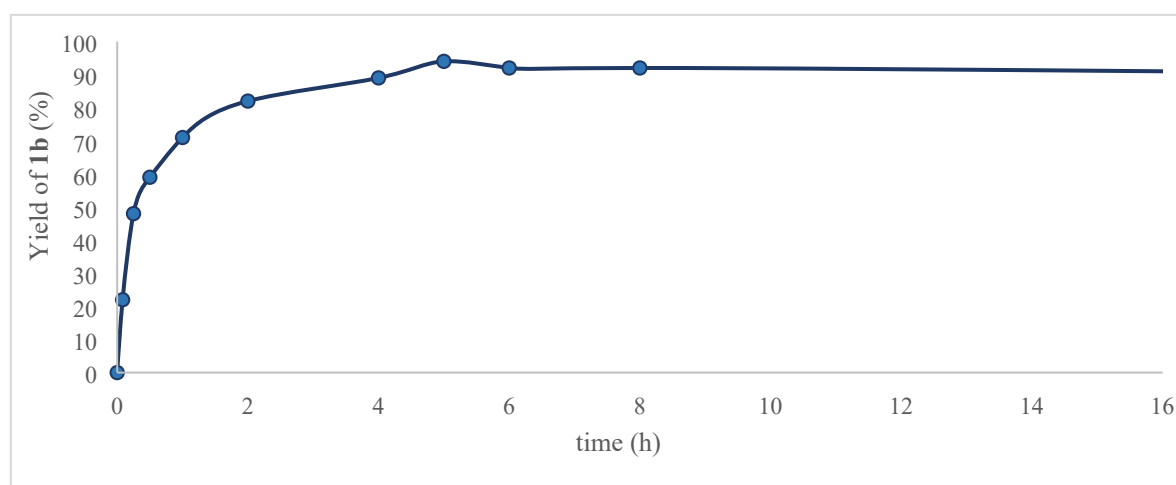
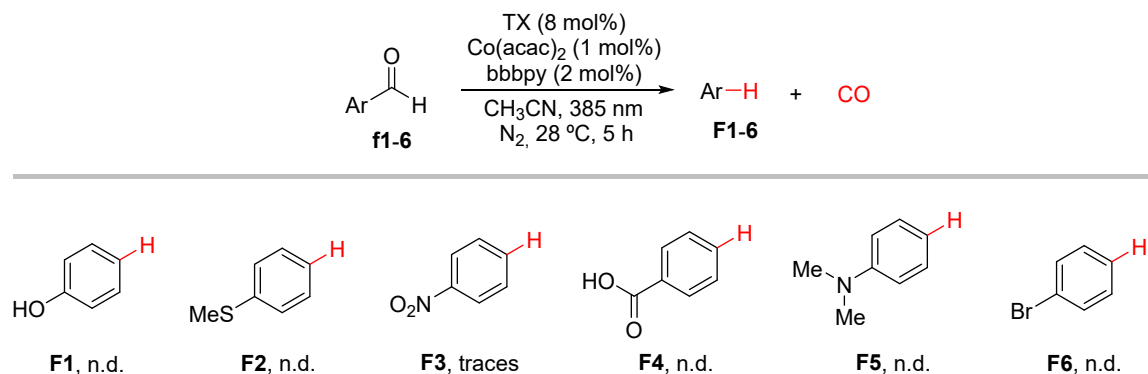


Figure S5 Kinetic profile with optimized reaction conditions for the decarbonylation of **1a**.

4. Failed substrates

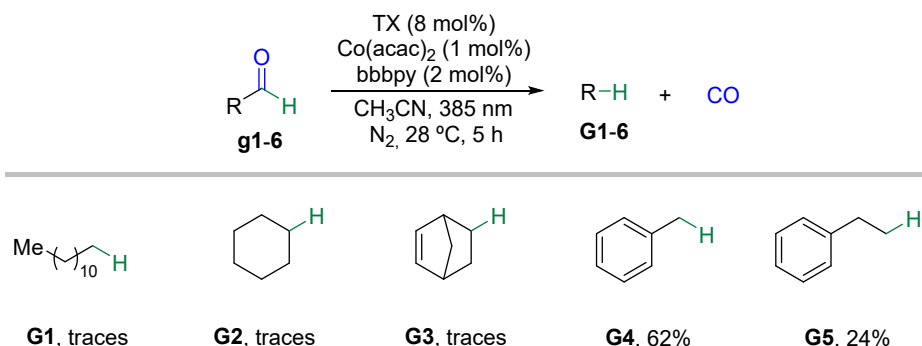
The presence of certain moieties such as phenol-, amine-, nitro-, bromo-, thioether-, or acid substituents hampered reaction progress. (Scheme S1).



Scheme S1 Failed substrates for the photocatalytic decarbonylation. Reaction conditions: **f** (0.05 mmol), thioxanthone (8 mol%), Co(acac)₂ (1 mol%), bbbpy (2 mol%), CH₃CN (0.5 mL), 385 nm LED (3.6 W), 28 °C, 5 h, N₂. Reaction mixtures analyzed via GC-MS analysis.

5. Tested aliphatic aldehydes

Similarly to benzaldehydes, the C–H bond of aliphatic aldehydes exhibits relatively low bond dissociation energies. Encouraged by the excellent results achieved with aromatic substrates, a few aliphatic aldehydes were additionally tested. Unfortunately, only acceptable results were obtained with phenylacetaldehyde (**g4**) and 3-phenylpropionaldehyde (**g5**) (Scheme S2). While starting materials **g1** and **g2** remained mostly unreacted, subjecting **g3** to the reaction conditions led to degradation.



Scheme S2 Tested aliphatic aldehydes. Reaction conditions: **g** (0.05 mmol), thioxanthone (8 mol%), Co(acac)₂ (1 mol%), bbbpy (2 mol%), CH₃CN (0.5 mL), 385 nm LED (3.6 W), 28 °C, 5 h, N₂. Yields determined by GC-FID analysis against mesitylene as internal standard.

6. Mechanistic studies

6.1 UV-Vis spectra of reaction components

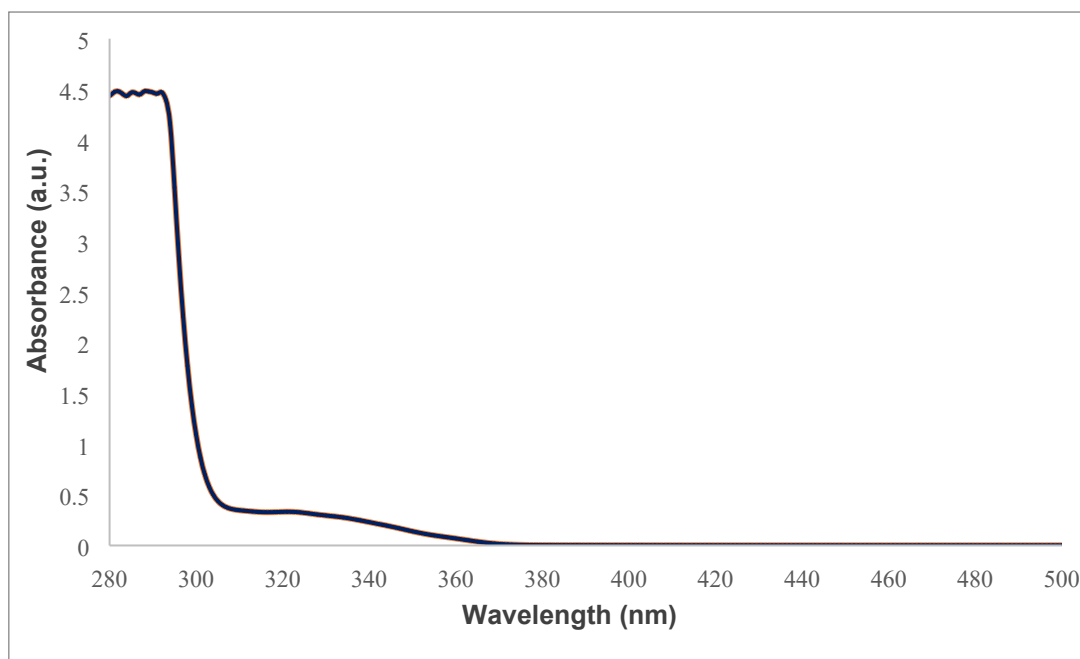


Figure S6 UV-Vis absorption spectrum of **1a** in CH_3CN (1.4 mM).

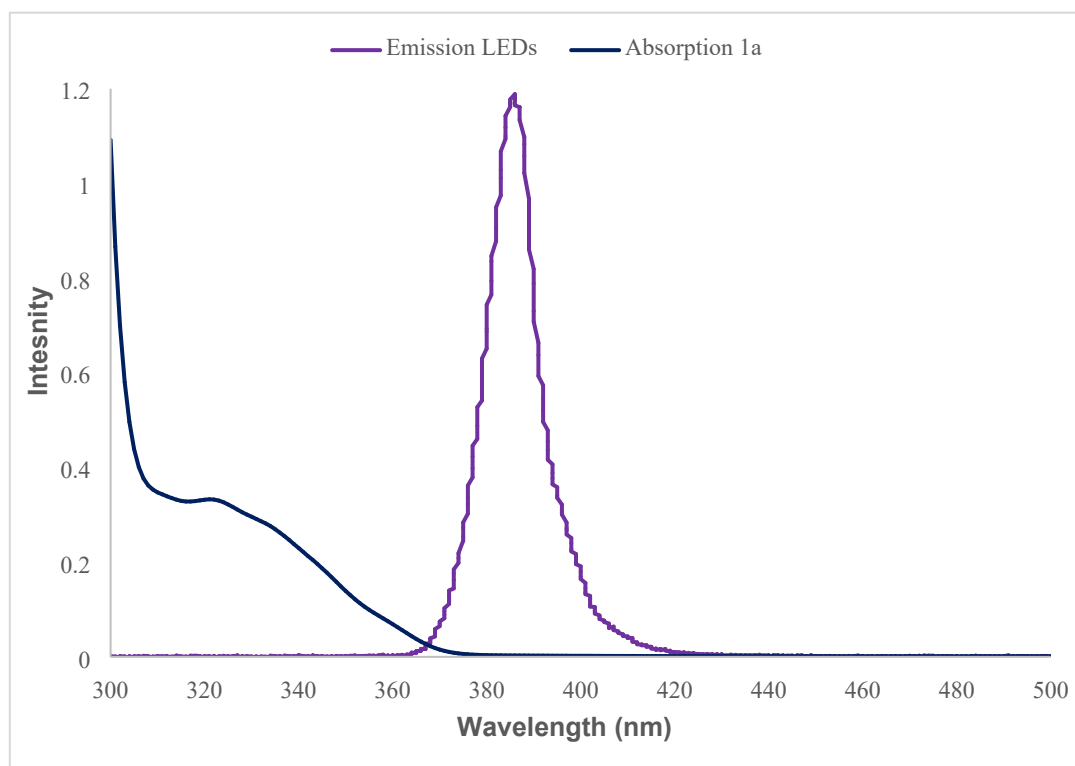


Figure S7 Combined UV-Vis absorption spectrum of **1a** in CH_3CN (1.4 mM) and emission spectrum of the LEDs.

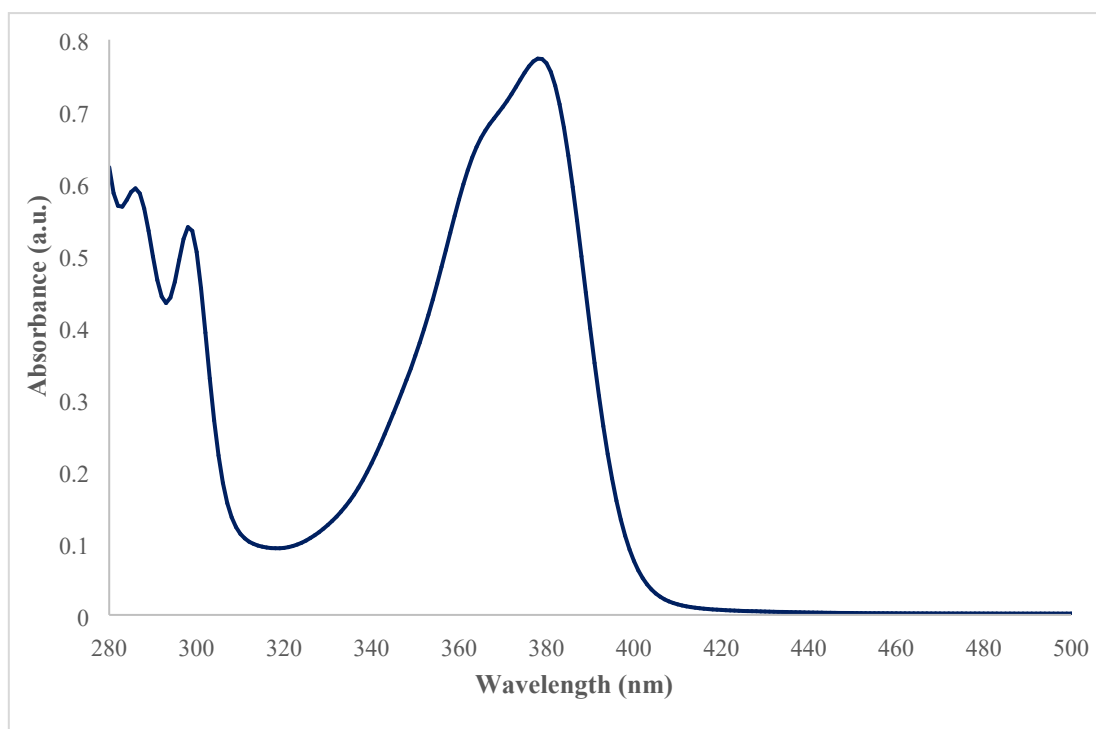


Figure S8 UV-Vis absorption spectrum of TX in CH₃CN (0.5 mM).

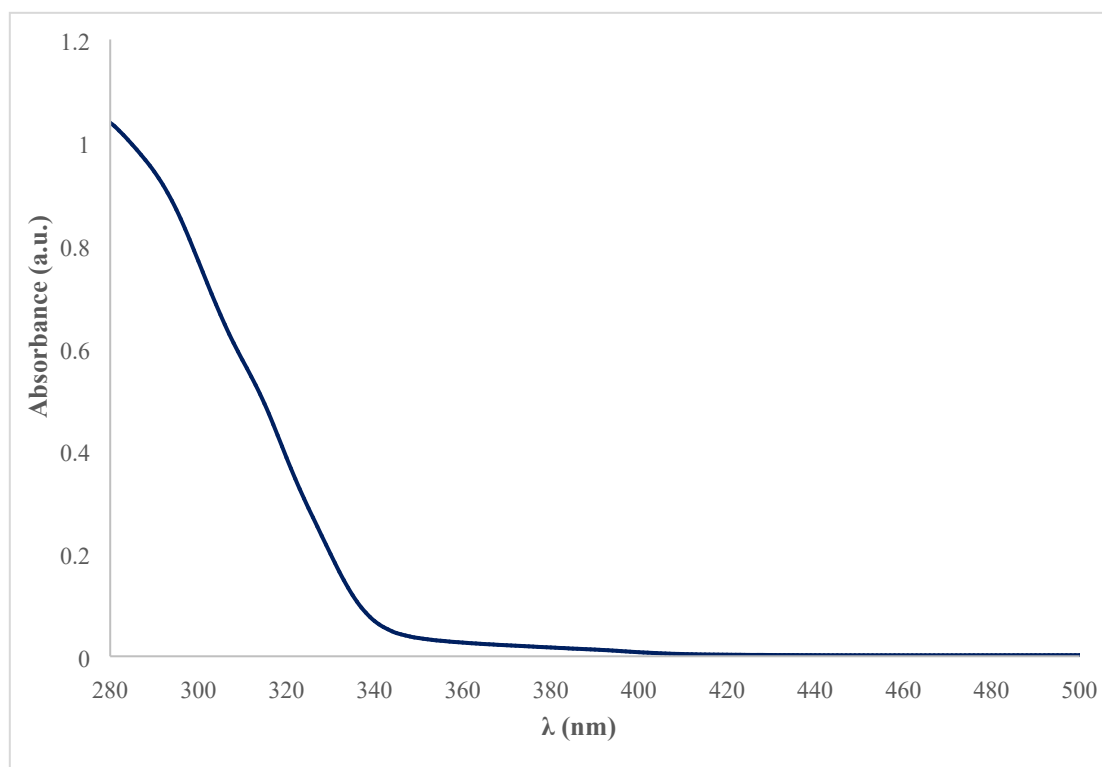


Figure S9 UV-Vis absorption spectrum of Co(acac)₂ in CH₃CN (0.1 mM).

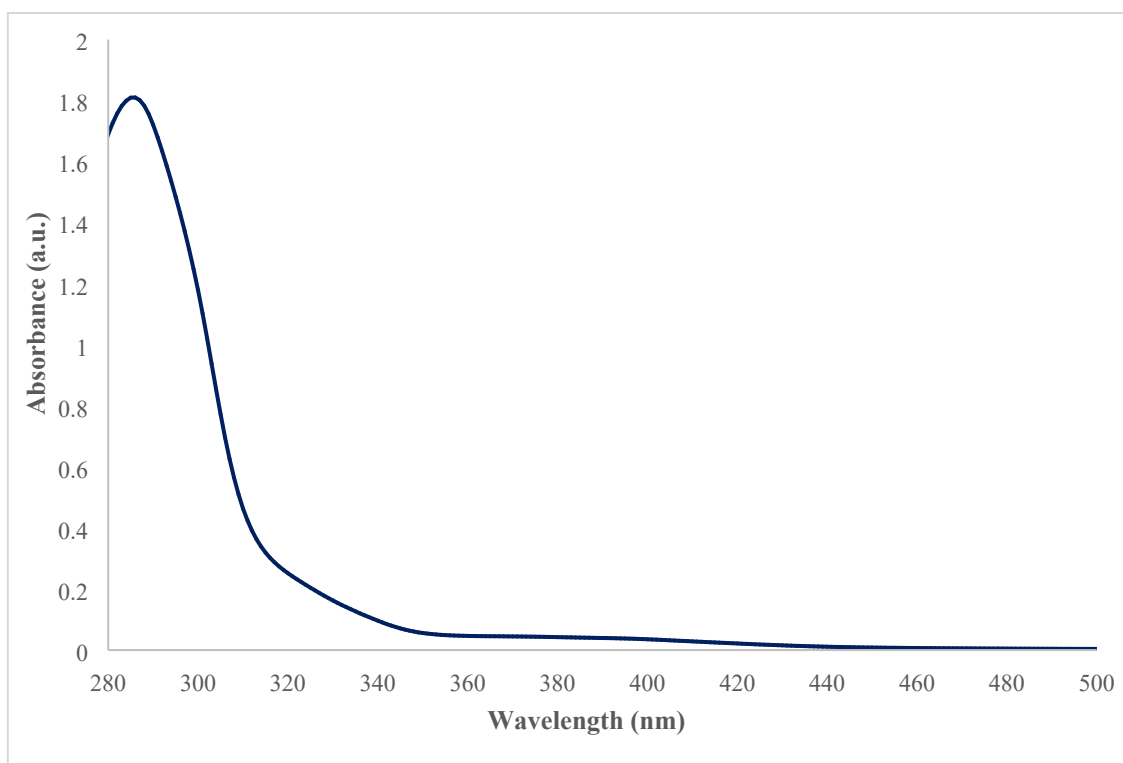


Figure S10 UV-Vis absorption spectrum of $\text{Co}(\text{acac})_2$ (0.2 mM) + bbbpy (0.4 mM) in CH_3CN .

6.2 GC-MS study of the reaction mixture of 1a

In the case of the reaction mixture of the decarbonylation of **1a**, the mass corresponding to the molecular ion of the benzophenone by-product **1c** can be clearly seen (Figure S11).

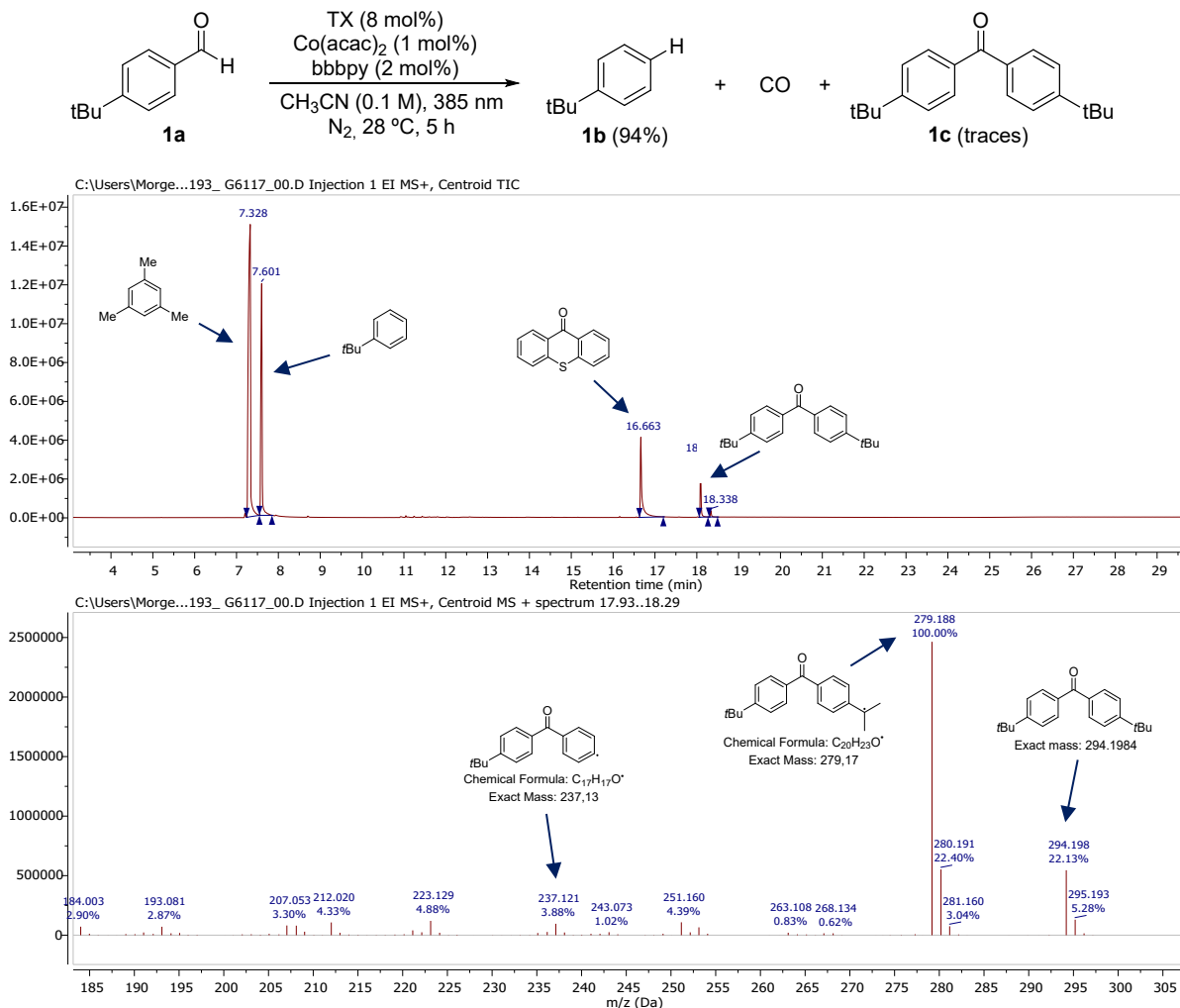
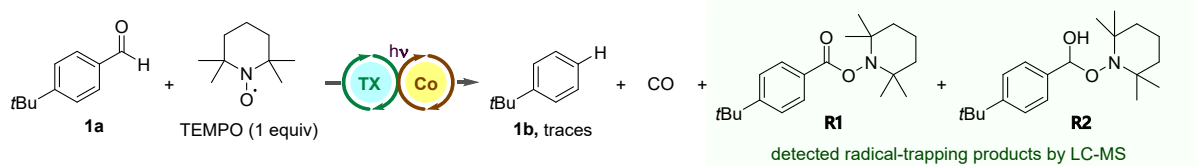


Figure S11 GC-MS chromatogram for the photocatalyzed decarbonylation of **1a** displaying benzophenone **1c** as by-product.

6.3 Radical trapping experiment with TEMPO



A 5 mL crimp-cap vial equipped with a stirring bar, was loaded with the 4-*tert*-butyl benzaldehyde (9 μ L, 50 μ mol, 1.00 equiv.), thioxanthone (0.9 mg, 4 μ mol, 8 mol%), cobalt (II) acetylacetonate (0.13 mg, 0.5 μ mol, 1 mol%), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (0.27 mg,

1 μmol , 2 mol%), and TEMPO (8 mg, 50 μmol , 1.00 equiv.). The vial was sealed, non-dried CH_3CN (0.5 mL) was added, and the mixture was sonicated for 1 min. After degassing via freeze-pump-thaw cycling (3 x), the reaction mixture was stirred under irradiation using a 3.6 W 385 nm LED set-up for 5 h at 28 $^\circ\text{C}$. The resulting reaction mixture was analyzed via LC-MS and GC-FID. Product **1b** was observed in trace amounts, thereby indicating a radical pathway. The formation of **R1** and **R2** indicated the in-situ formation of acyl and benzyl radicals.

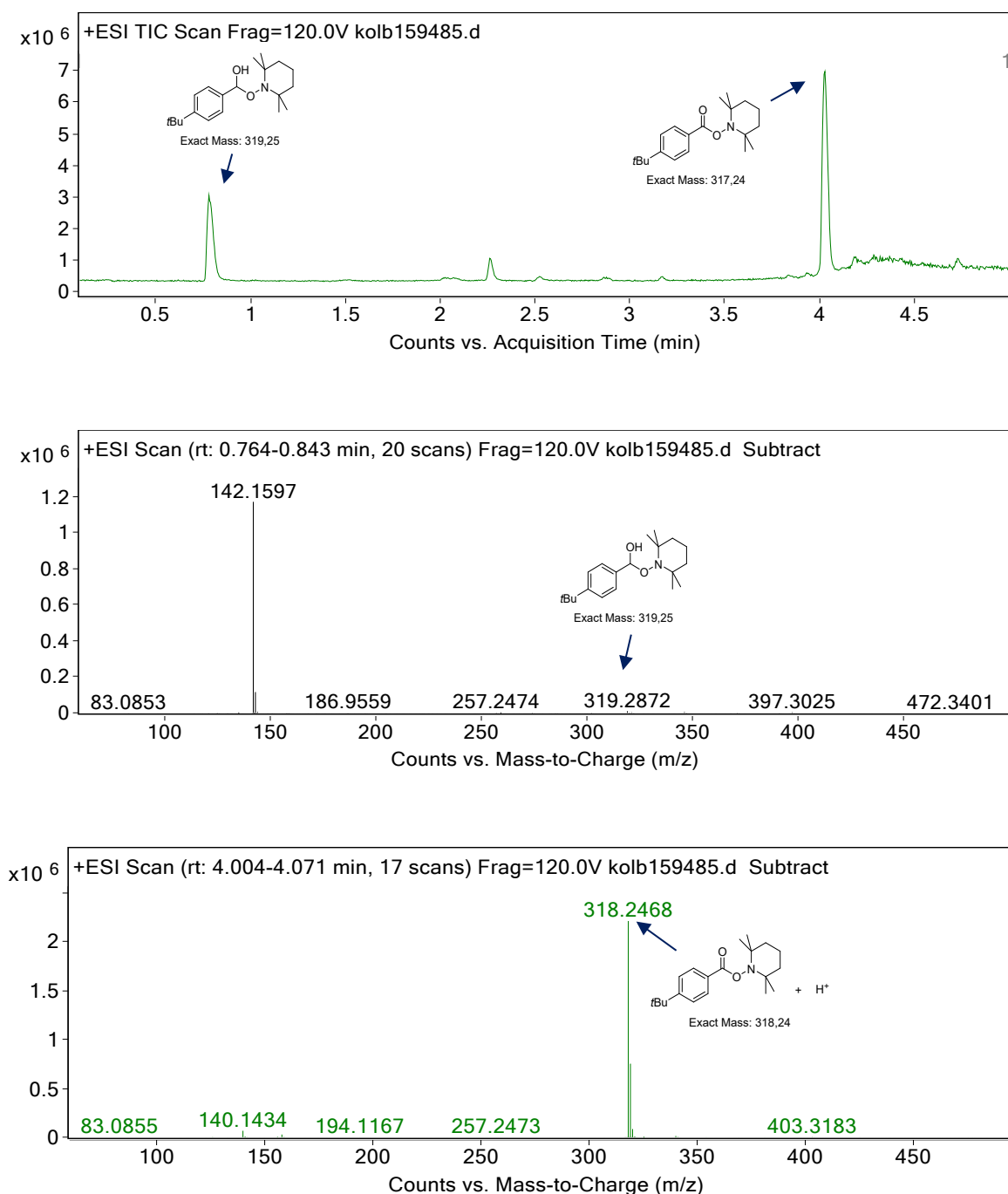
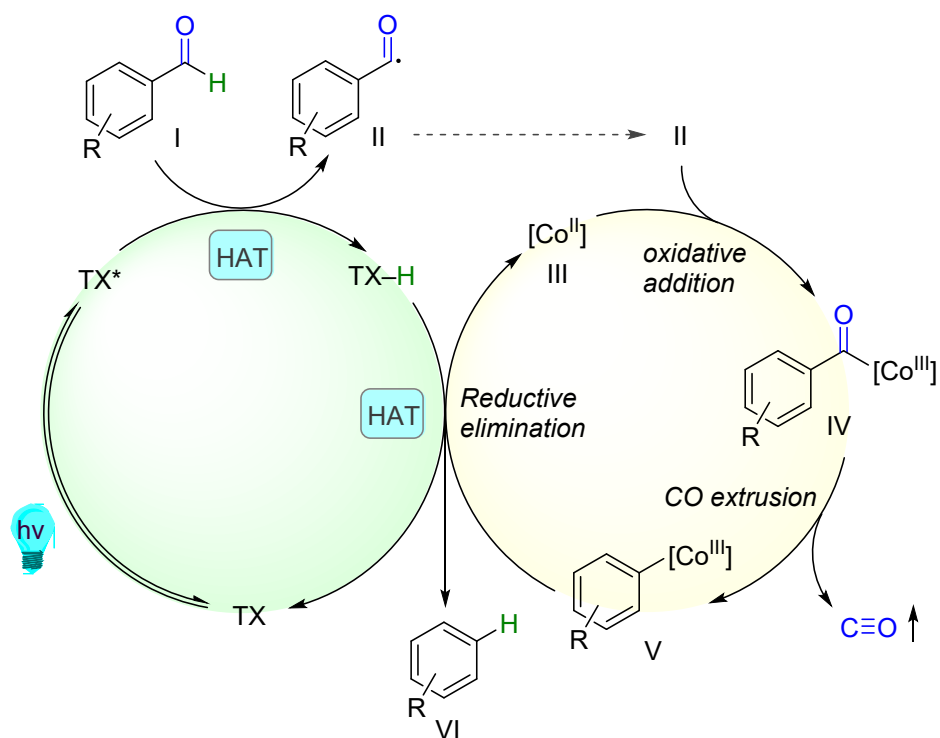
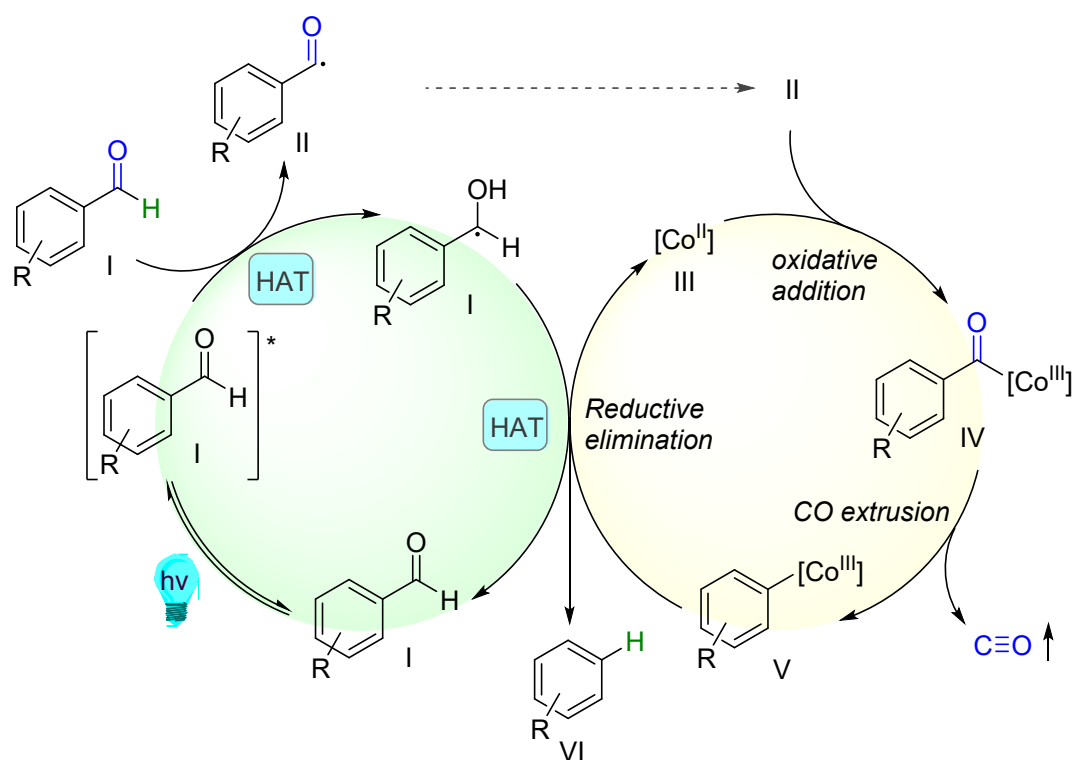


Figure S12 LC-MS chromatogram for the photocatalyzed decarbonylation of **1a** in presence of TEMPO (1 equiv.).

6.4 Detailed mechanistic pathways



Scheme S3 TX-mediated photocatalyzed decarbonylation pathway.



Scheme S4 self-photocatalyzed decarbonylation pathway.

6.5 Photocatalytic decarbonylation of **1a** in CD₃CN

The reaction mixture was prepared according to general procedure **GP1** from 4-*tert*butyl benzaldehyde (9 μ L, 50 μ mol, 1.00 equiv.), thioxanthone (0.9 mg, 4 μ mol, 8 mol%), cobalt (II) acetylacetonate (0.13 mg, 0.5 μ mol, 1 mol%) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (0.27 mg, 1 μ mol, 2 mol%), using CD₃CN (0.5 mL) as a solvent.

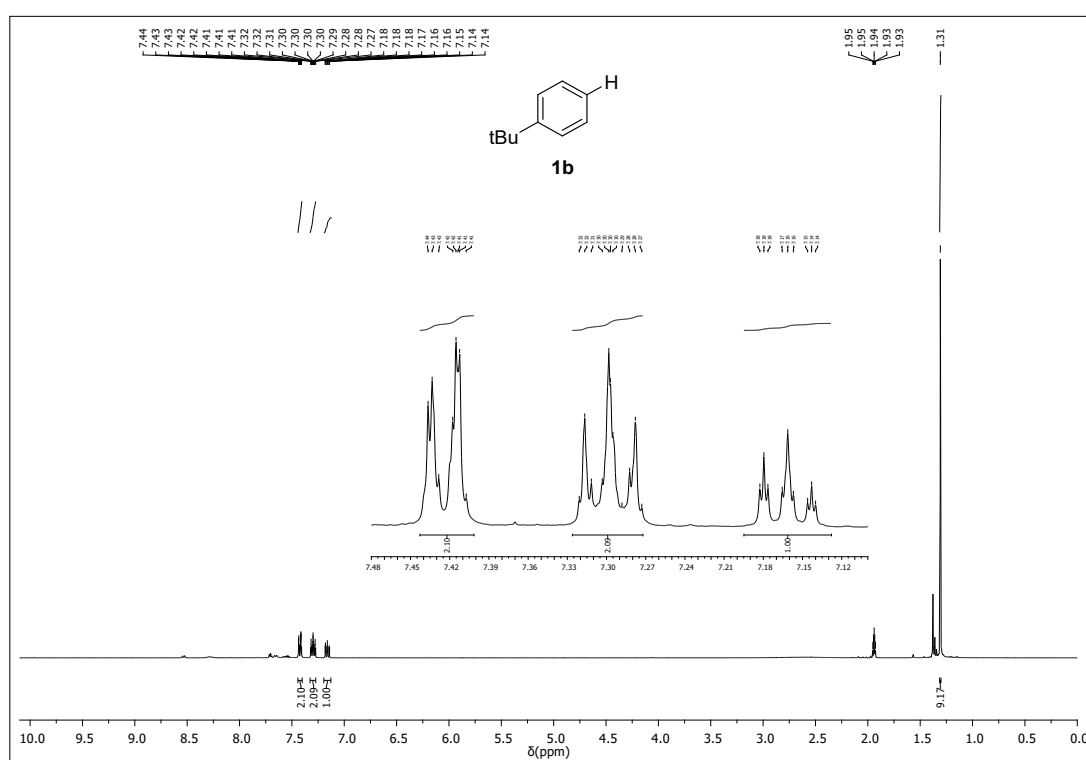
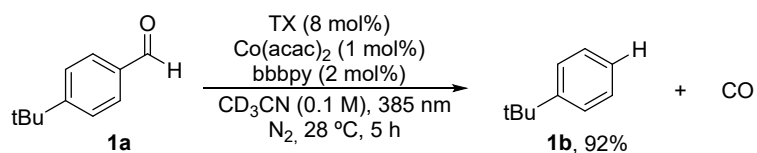


Figure S13 ¹H-NMR crude spectrum for the decarbonylation of **1a** in CD₃CN.

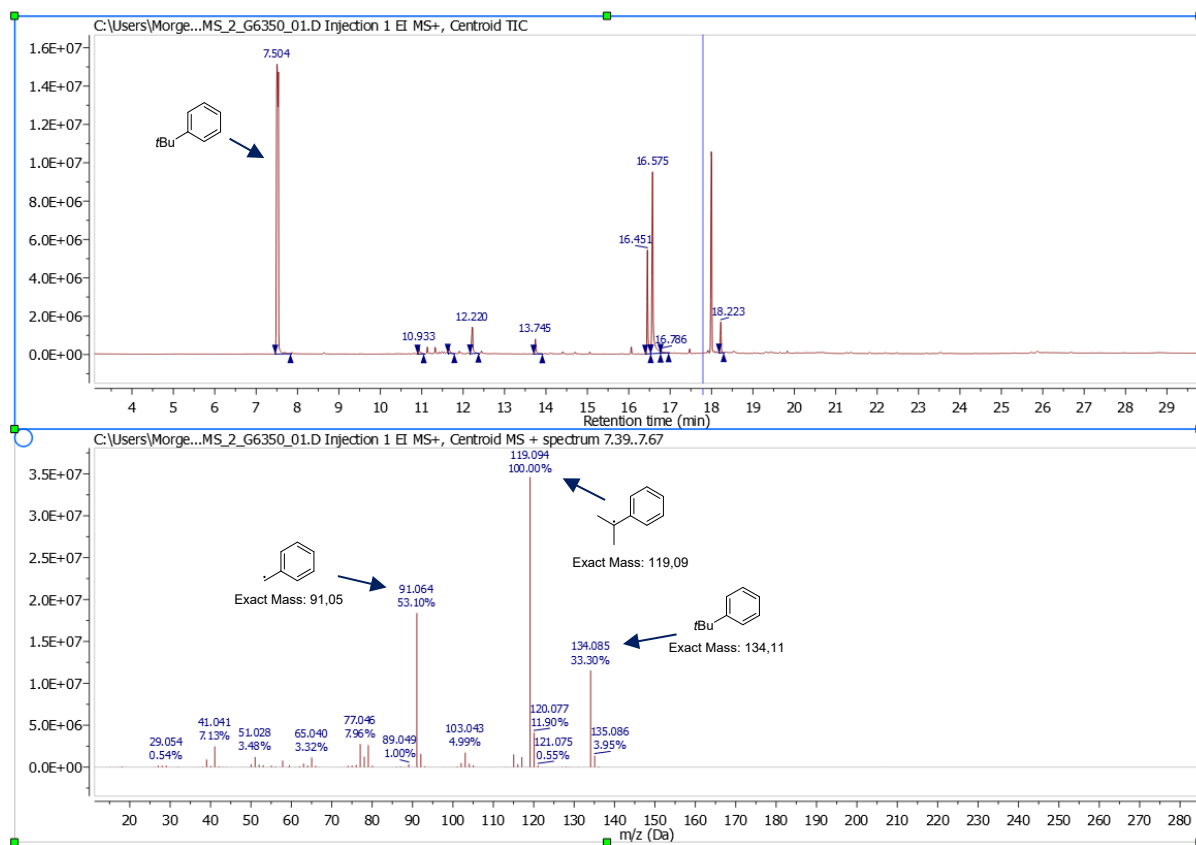


Figure S14 GC-MS chromatogram for the photocatalytic decarbonylation of **1a** in CD₃CN.

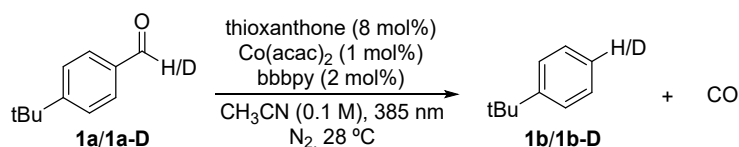
6.6 Independent KIE experiments between 1a and 1a-D

For the KIE studies two different sets of reaction mixtures were prepared. The yield of **1b** or **1b-D** was measured at different time intervals via GC-FID.

Decarbonylation of **1a**: according to **GPI**, six vials were set in parallel for the decarbonylation of **1a**. In total, 4-*tert*-butylbenzaldehyde (52 μ L, 300 μ mol, 1.00 equiv.), thioxanthone (5.4 mg, 24 μ mol, 8 mol%), cobalt (II) acetylacetonate (0.8 mg, 3 μ mol, 1 mol%) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (1.7 mg, 6 μ mol, 2 mol%) in non-dried CH₃CN (3 mL) were used and distributed equally in six different 5 mL crimp-cap vials.

Decarbonylation of **1a-D**: according to **GPI**, six vials were set in parallel for the decarbonylation of **1a-D**. In total, **1a-D** (52 μ L, 300 μ mol, 1.00 equiv.), thioxanthone (5.4 mg, 24 μ mol, 8 mol%), cobalt (II) acetylacetonate (0.8 mg, 3 μ mol, 1 mol%) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (1.7 mg, 6 μ mol, 2 mol%) in non-dried CH₃CN (3 mL) were used and distributed equally in six different 5 mL crimp-cap vials.

Table S11 Competition KIE experiments between 1a and 1a-D.



Entry	Time (h)	Yield of 1b (%) ^a	Yield of 1b-D (%) ^a
1	0,083	22	5
2	0,5	59	17
3	1	71	24
4	2	82	39
5	4	89	60
6	5,5	94	71

a (0.05 mmol), thioxanthone (8 mol%), Co(acac)₂ (1 mol%), bbbpy (2 mol%), CH₃CN (0.5 mL), 385 nm LED (3.6 W), 28 °C, N₂. ^aYields were determined by GC-FID analysis against mesitylene as internal standard.

6.7 Qualitative analysis of evolved carbon monoxide via gas chromatography

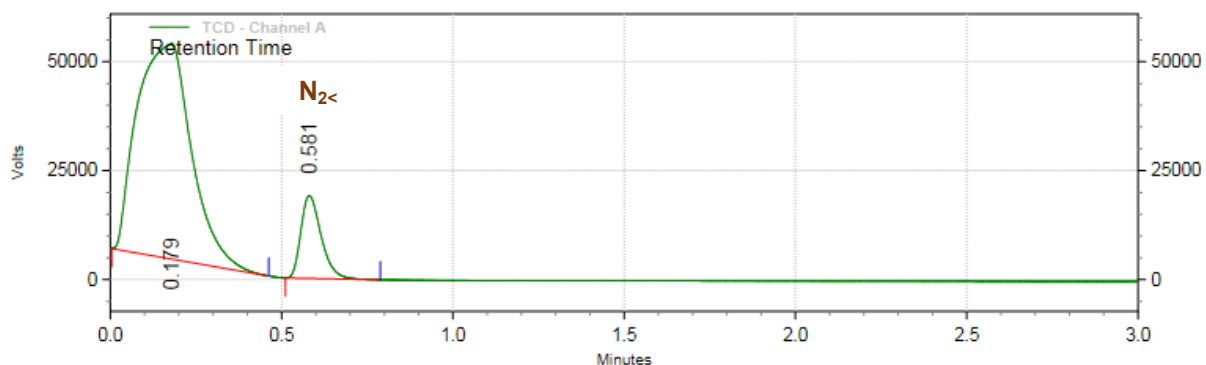


Figure S15 gas chromatogram of vial filled with pre-dried nitrogen.

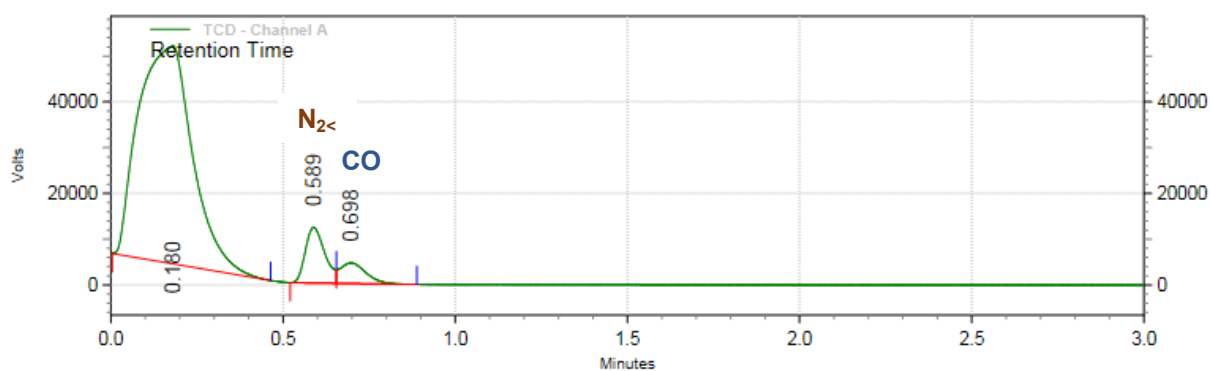


Figure S16 gas chromatogram of vial filled with a mixture of pre-dried nitrogen and carbon monoxide.

The carbon monoxide used as reference (Figure S16) was generated following a procedure reported by Borggraeve et al.¹

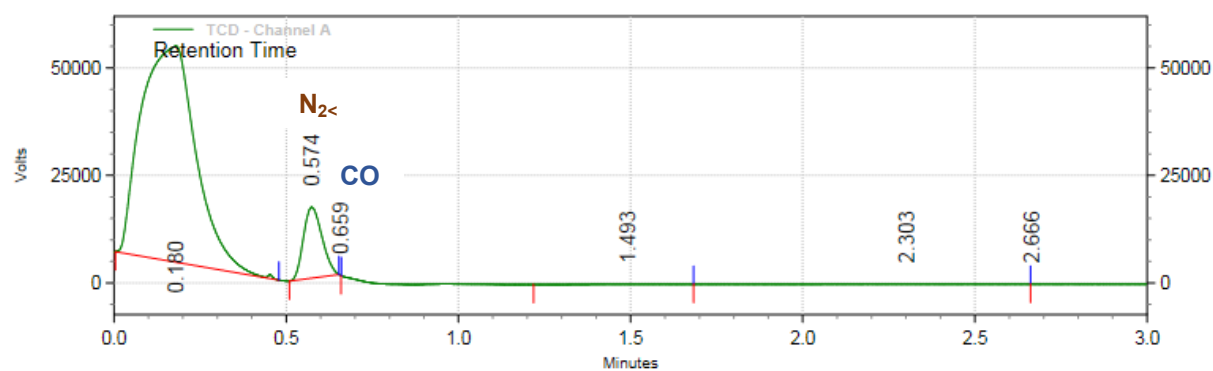
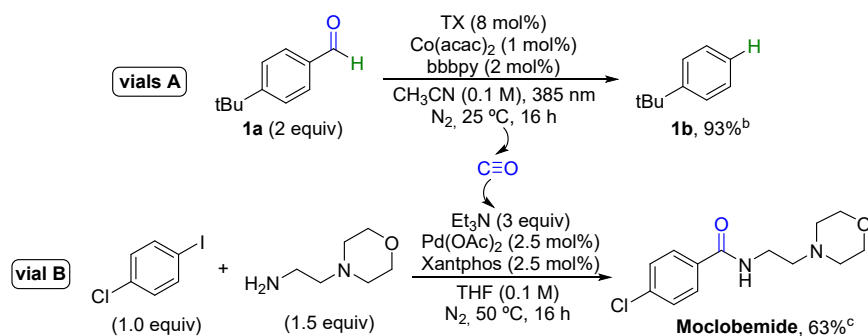


Figure S17 measurement of evolved carbon monoxide after irradiating 5 h a reaction mixture containing **1a**.

6.8 Test reaction for the qualitative determination of evolved carbon monoxide



Carbon monoxide generating reaction (**vials A**): According to **GP1**, four vials were set in parallel for the decarbonylation of **1a**. In total, 4-*tert*-butylbenzaldehyde (35 μ L, 200 μ mol, 1.00 equiv.), thioxanthone (3.6 mg, 16 μ mol, 8 mol%), cobalt (II) acetylacetonate (0.52 mg, 2 μ mol, 1 mol%) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (1.1 mg, 4 μ mol, 2 mol%) in non-dried CH₃CN (2 mL) were used and distributed equally in four different 5 mL crimp-cap vials. Upon reaction completion, the gas phases of the four vials were transferred via syringe to a separate vial containing the test reaction mixture (**vial B**).

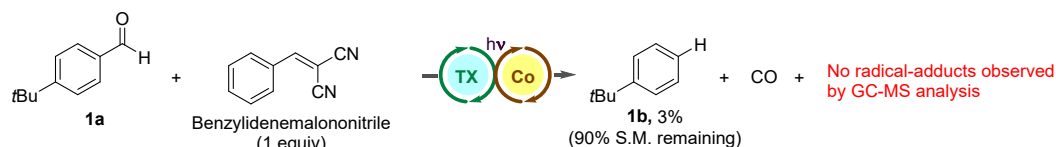
Carbon monoxide consuming test reaction (**vial B**): the procedure was inspired by a protocol reported by Uzunlu et al.² A 10 mL crimp-cap vial was charged with a cross-shaped stirring bar, Pd(OAc)₂ (0.7 mg, 2.5 μ mol, 2.5 mol%), xantphos (3.6 mg, 2.5 μ mol, 2.5 mol%) and 1-chloro-4-iodobenzene (23.9 mg, 100 μ mol, 1.00 equiv.). The vial was sealed, evacuated, and backfilled with N₂. Then, dry THF (1 mL), 4-(2-aminoethyl)morpholine (20 μ L, 150 μ mol, 1.50 equiv.) and Et₃N (42 μ L, 300 μ mol, 3.00 equiv.) were added. The resulting mixture was purged with N₂ for 10 min, and the evolved carbon monoxide in **vials A** after 5 h irradiation was transferred via syringe to the sealed **vial B**. The resulting mixture was stirred at 50 °C for 16 h. Afterwards water was added (5 mL) and the product was extracted with EtOAc (3 x 8 mL). The combined organic layers were dried over Na₂SO₄, and the solvent was removed under reduced pressure. The crude product was purified via FCC (PE/EtOAc = 40/60), obtaining **moclobemide** as a white solid (17 mg, 63%).

Analytical data for **moclobemide**:

¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 7.71 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 6.74 (s, 1H), 3.76 – 3.69 (m, 4H), 3.54 (dd, J = 11.2, 5.6 Hz, 2H), 2.60 (t, J = 6.0 Hz, 2H), 2.55 – 2.46 (m, 4H). ¹³C-NMR (101 MHz, CDCl₃): δ (ppm) = 166.3, 137.7, 133.0, 128.9, 128.4, 67.0, 56.8, 53.3, 36.1. Spectroscopic data is consistent with literature values.¹ R_f = 0.22

(PE/EtOAc = 40/60). **mp** = 135–137 °C. **HRMS** (EI-MS): $[C_{13}H_{17}N_2O_2Cl]^+ [M]^+$ calcd: 268.09731; found: 268.09707.

6.9 Radical trapping experiment with benzylidenemalononitrile



In an attempt to expand the scope of our methodology to the acylation of activated alkenes, an the decarbonylation of **1a** was performed in presence of benzylidenemalononitrile.

A 5 mL crimp-cap vial equipped with a stirring bar, was loaded with 4-*tert*-butylbenzaldehyde (9 μ L, 50 μ mol, 1.00 equiv.), thioxanthone (0.9 mg, 4 μ mol, 8 mol%), cobalt (II) acetylacetonate (0.13 mg, 0.5 μ mol, 1 mol%), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (0.27 mg, 1 μ mol, 2 mol%), and benzylidenemalononitrile (7.9 mg, 50 μ mol, 1.00 equiv.). The vial was sealed, non-dried CH_3CN (0.5 mL) was added, and the mixture was sonicated for 1 min. After degassing via freeze-pump-thaw cycling (3 x), the reaction mixture was stirred under irradiation using a 3.6 W 385 nm LED set-up for 5 h at 28 °C. Analysis via GC-MS and GC-FID analysis revealed the presence of unconsumed benzylidenemalononitrile, while the decarbonylation process was significantly inhibited, obtaining **1b** in poor yield (..%).

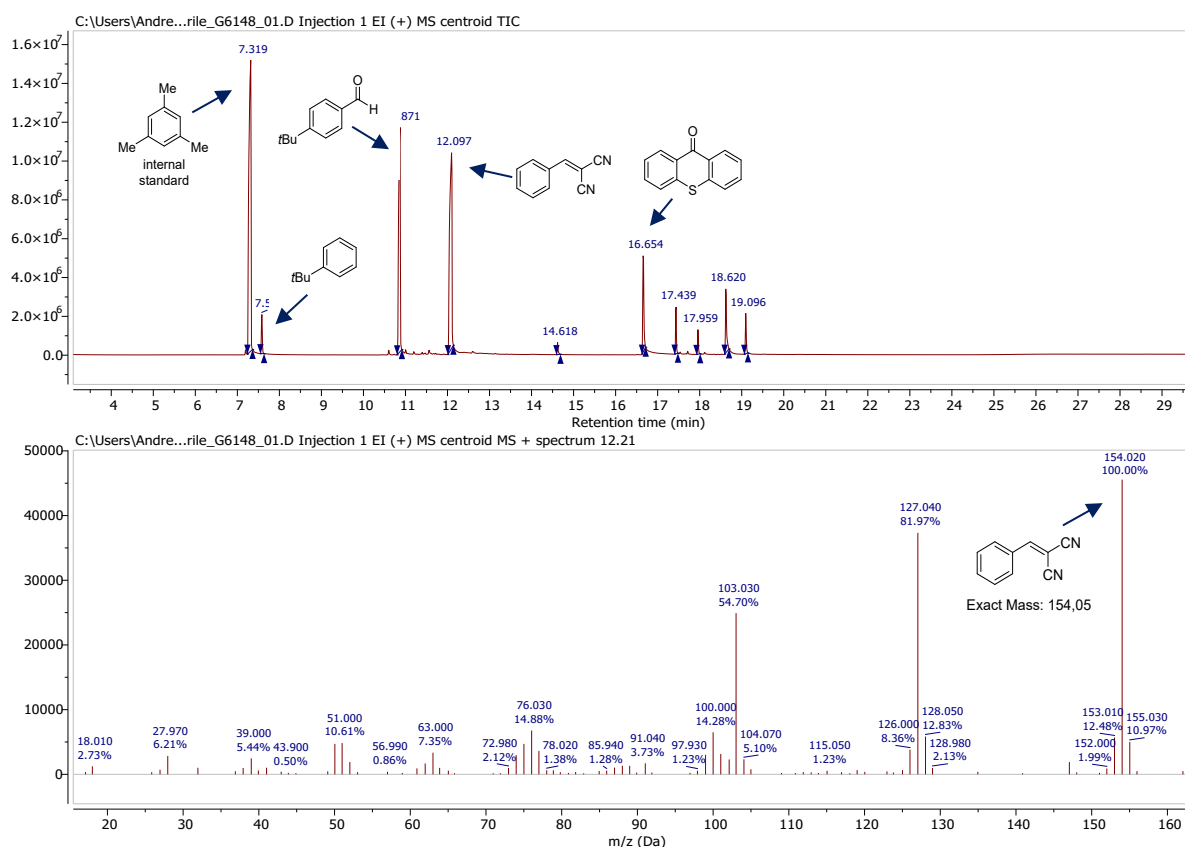
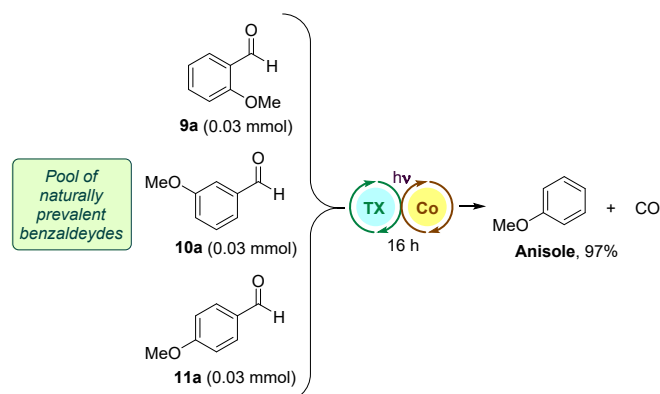


Figure S18 GC-MS chromatogram for the photocatalyzed decarbonylation of **1a** in presence of benzylidenemalononitrile (1 equiv.).

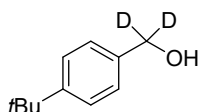
7. Procedure for the convergent defunctionalization of methoxybenzaldehydes



A 5 mL crimp-cap vial equipped with a stirring bar, was loaded with 2-methoxybenzaldehyde (4.2 mg, 30 μmol , 1.00 equiv.), 3-methoxybenzaldehyde (4.2 mg, 30 μmol , 1.00 equiv.), 4-methoxybenzaldehyde (4.2 mg, 30 μmol , 1.00 equiv.), thioxanthone (1.6 mg, 7.2 μmol , 8 mol%), cobalt (II) acetylacetonate (0.23 mg, 0.9 μmol , 1 mol%) and 4,4'-di-*tert*-butyl-2,2'-dipyridyl (0.49 mg, 1.8 μmol , 2 mol%). The vial was sealed, non-dried CH_3CN (0.9 mL) was added, and the mixture was sonicated for 1 min. After degassing via freeze-pump-thaw cycling (3 x), the reaction mixture was stirred under irradiation using a 3.6 W 385 nm LED set-up for 16 h at 28 $^\circ\text{C}$. Reaction progress was determined via GC-FID analysis against mesitylene as internal standard (97%, GC-FID yield).

8. Analytical data of isolated compounds

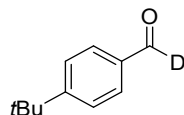
Synthesis of SM-A



Prepared according to a procedure reported by Nisal et al.³ In an oven-dried schlenk flask, LiAlD₄ (212 mg, 5.05 mmol, 1.50 equiv.) was dissolved in dry THF (30 mL) at 0 °C under N₂ atmosphere. Next, 4-*tert*butyl benzoic acid (600 mg, 3.37 mmol, 1.00 equiv.) was added and the mixture was stirred at 20 °C for 18 h. Afterwards, another portion of LiAlD₄ (106 mg, 2.52 mmol, 0.75 equiv.) was added and the mixture was stirred for additional 24 h at 20 °C. Upon reaction completion, the reaction crude was quenched with aqueous 0.05 M NaOH solution (20 mL) and the product was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was evaporated. The crude product was purified via FCC (PE/EtOAc = 75/25), to obtain **SM-A** as a clear oil (360 mg, 64% yield).

¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 7.43 – 7.37 (m, 2H), 7.36 – 7.28 (m, 2H), 1.68 (bs, 1H), 1.33 (s, 9H). **¹³C-NMR** (101 MHz, CDCl₃): δ (ppm) = 150.8, 137.9, 127.0, 125.6, 60.5, 34.6, 31.4. Spectroscopic data is consistent with literature values. **R_f** = 0.32 (PE/EtOAc = 75/25). **HRMS** (EI-MS): [C₁₁H₁₄OD₂]⁺ [M]⁺ calcd: 166.13212; found: 166.13207.

Synthesis of 1a-D

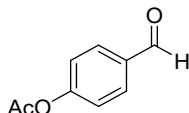


Prepared according to a procedure reported by Luo et al.⁴ In an oven-dried schlenk flask, **SM-A** (310 mg, 1.86 mmol, 1.00 equiv.) was dissolved in CH₂Cl₂ (15 mL). Next, NaHCO₃ (312 mg, 3.72 mmol, 2.00 equiv.) and Dess-Martin Periodinane (1.10 g, 2.60 mmol, 1.40 equiv.) were subsequently added at 0 °C under N₂ atmosphere. The resulting mixture was stirred at 20 °C for 20 h. Afterwards, water (10 mL) and saturated aqueous NaHCO₃ solution (10 mL) were added, and the product was extracted with CH₂Cl₂ (4 x 8 mL). The combined organic layers were dried over Na₂SO₄, and the solvent was evaporated under reduced pressure. The crude product was purified via FCC (PE/EtOAc = 95/5), to obtain **1a-D** as a clear oil (252 mg, 83% yield).

¹H-NMR (400 MHz, CD₃CN): δ (ppm) = 7.85 – 7.81 (m, 2H), 7.64 – 7.61 (m, 2H), 1.34 (s, 9H). **¹³C-NMR** (101 MHz, CD₃CN): δ (ppm) = 193.2, 159.3, 135.3, 130.4, 127.1, 36.0, 31.3.

Spectroscopic data is consistent with literature values. $R_f = 0.25$ (PE/EtOAc = 95/5). **HRMS** (EI-MS): $[C_{11}H_{13}OD]^+ [M]^+$ calcd: 163.11019; found: 163.11038.

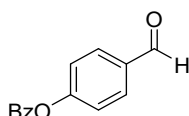
Synthesis of 4-acetoxybenzaldehyde (**13a**)



In an oven-dried schlenk flask, to a solution of 4-hydroxybenzaldehyde (1.00 g, 8.19 mmol, 1.00 equiv.) in EtOAc (15 mL) at 0 °C were added Et_3N (2.85 mL, 20.5 mmol, 2.50 equiv.) and acetylchloride (1.17 mL, 16.4 mmol, 2.00 equiv.). The resulting mixture was stirred at 20 °C for 2 h. Afterwards, water (10 mL) and saturated aq. $NaHCO_3$ solution (20 mL) were added, and the product was extracted with EtOAc (3 x 10 mL). The combined organic layers were successively washed with saturated aq. $NaHCO_3$ solution (20 mL), saturated aq. NH_4Cl solution (20 mL) and brine (20 mL), dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified via FCC (PE/EtOAc = 90/10), to obtain **13a** as a clear colourless oil (1.13 g, 84% yield).

1H -NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.96 (s, 1H), 7.91 – 7.86 (m, 2H), 7.28 – 7.21 (m, 2H), 2.31 (s, 3H). **^{13}C -NMR** (101 MHz, $CDCl_3$): δ (ppm) = 190.9, 168.7, 155.4, 134.0, 131.2, 122.4, 21.2. Spectroscopic data is consistent with literature values.⁵ $R_f = 0.29$ (PE/EtOAc = 90/10). **HRMS** (EI-MS): $[C_9H_8O_3]^+ [M]^+$ calcd: 164.04680; found: 164.04682.

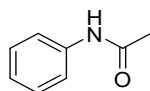
Synthesis of 4-benzoyloxybenzaldehyde (**14a**)



In an oven-dried schlenk flask, to a solution of 4-hydroxybenzaldehyde (1.00 g, 8.19 mmol, 1.00 equiv.) in DCM (15 mL) at 0 °C were added Et_3N (2.85 mL, 20.5 mmol, 2.50 equiv.) and benzoylchloride (1.90 mL, 16.4 mmol, 2.00 equiv.). The resulting mixture was stirred at 20 °C for 2 h. Afterwards, water (10 mL) and saturated aq. $NaHCO_3$ solution (20 mL) were added, and the product was extracted with DCM (3 x 10 mL). The combined organic layers were successively washed with saturated aq. $NaHCO_3$ solution (20 mL), saturated aq. NH_4Cl solution (20 mL) and brine (20 mL), dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified via FCC (PE/EtOAc = 90/10), to obtain **14a** as a white solid (1.25 g, 67% yield).

¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 10.03 (s, 1H), 8.24 – 8.19 (m, 2H), 8.02 – 7.95 (m, 2H), 7.71 – 7.64 (m, 1H), 7.57 – 7.51 (m, 2H), 7.45 – 7.39 (m, 2H). **¹³C-NMR** (101 MHz, CDCl₃): δ (ppm) = 191.0, 155.7, 134.0, 131.3, 130.3, 128.9, 128.7, 122.6. Spectroscopic data is consistent with literature values.⁶ **R_f** = 0.33 (PE/EtOAc = 90/10). **HRMS** (EI-MS): [C₁₄H₁₀O₃]⁺ [M]⁺ calcd: 226.06245; found: 226.06229.

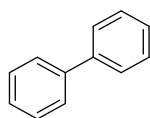
Synthesis of acetanilide (16b)



Prepared according to general procedure **GP1** from 4-acetamidobenzaldehyde (8.2 mg, 50 μmol). The crude product was purified via FCC (PE/EtOAc = 60/40), to obtain **16b** as a white solid (5.6 mg, 83% yield).

¹H-NMR (400 MHz, CD₂Cl₂): δ (ppm) = 7.50 (d, *J* = 7.9 Hz, 3H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.13 (s, 3H). **¹³C-NMR** (101 MHz, CD₂Cl₂): δ (ppm) = 168.3, 138.3, 128.9, 124.1, 119.8, 24.4. Spectroscopic data is consistent with literature values.⁷ **R_f** = 0.20 (PE/EtOAc = 60/40). **mp** = 114–116 °C. **HRMS** (APCI-MS): [C₈H₉NO]⁺ [M + H]⁺ calcd: 136.0757; found: 136.0758.

Synthesis of biphenyl (25b)



Prepared according to general procedure **GP1** from biphenyl-4-carboxaldehyde (9.4 mg, 50 μmol). The crude product was purified via FCC (*n*-hexane), to obtain **25b** as a white solid (4.8 mg, 62% yield).

¹H-NMR (400 MHz, CD₂Cl₂): δ (ppm) = 7.61 (dt, *J* = 8.2, 1.7 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.39 – 7.32 (m, 1H). **¹³C-NMR** (101 MHz, CD₂Cl₂): δ (ppm) = 141.2, 128.8, 127.4, 127.1. Spectroscopic data is consistent with literature values.⁸ **R_f** = 0.53 (*n*-hexane). **mp** = 67–69 °C. **HRMS** (EI-MS): [C₁₂H₁₀]⁺ [M]⁺ calcd: 154.0777; found: 154.07733.

9. References

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- 4 S. Luo, C. Weng, Y. Ding, C. Ling, M. Szostak, X. Ma and J. An, *Synlett*, 2020, **32**, 51.
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10. NMR spectra of isolated compounds

Figure S19 $^1\text{H-NMR}$ (400 MHz, CDCl_3) compound moclobemide

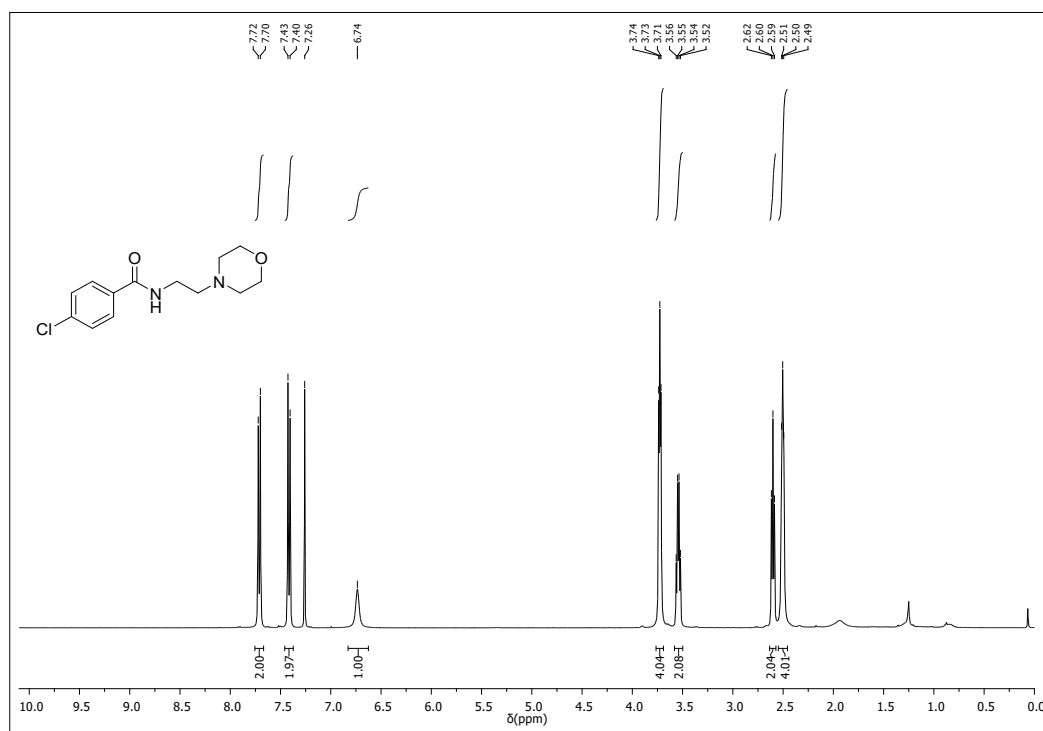


Figure S20 $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) compound moclobemide

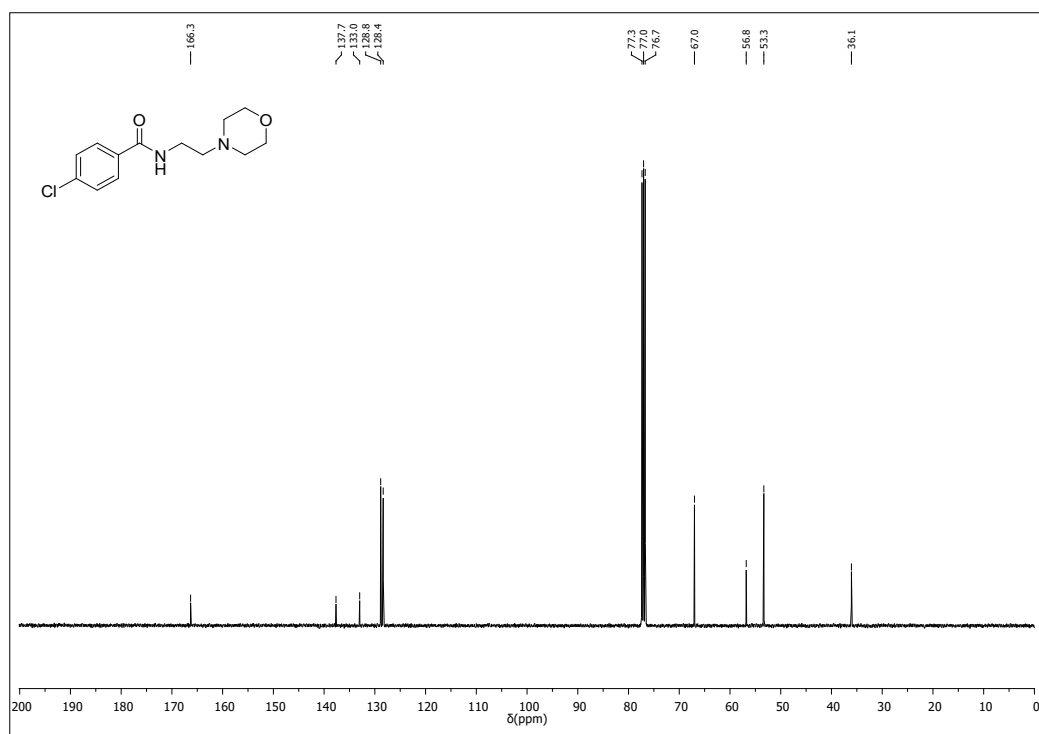


Figure S21 $^1\text{H-NMR}$ (400 MHz, CDCl_3) compound SM-A

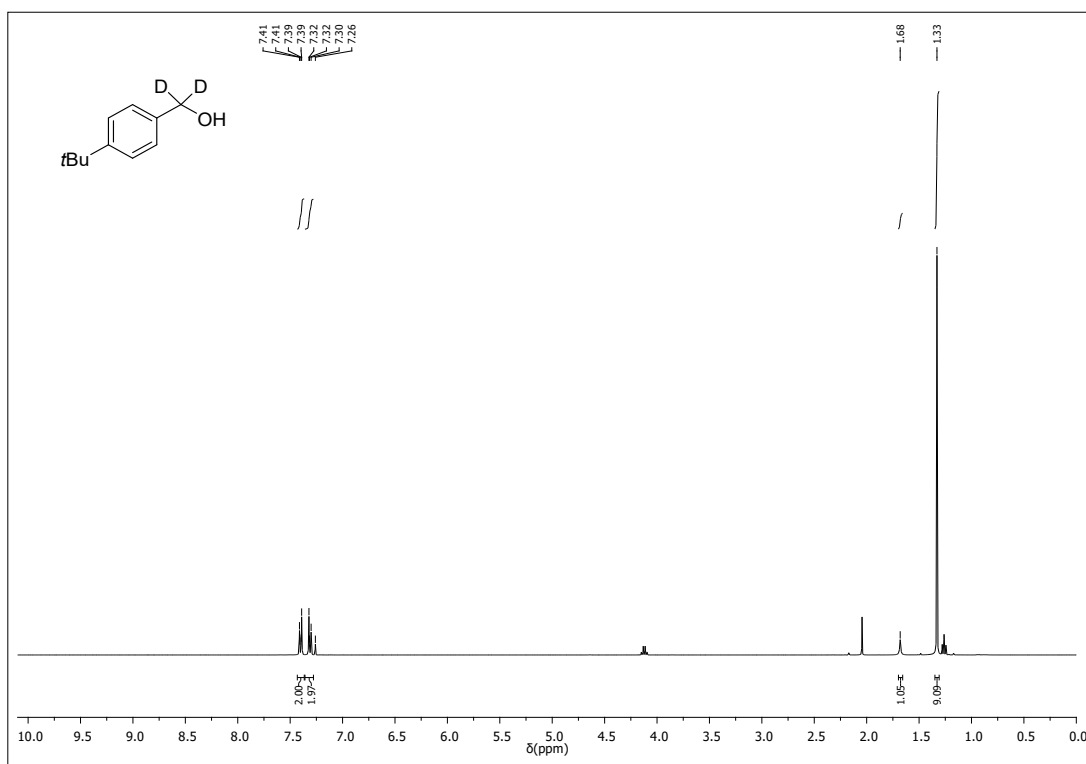


Figure S22 $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) compound SM-A

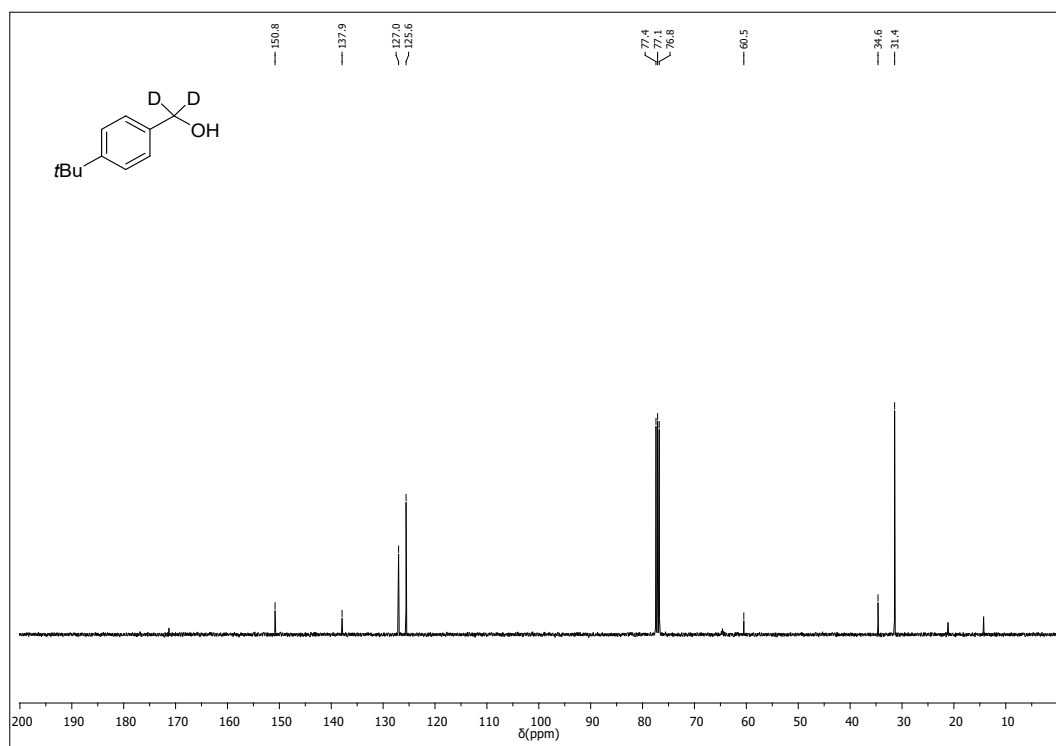


Figure S23 $^1\text{H-NMR}$ (400 MHz, CD_3CN) compound **1a-D**

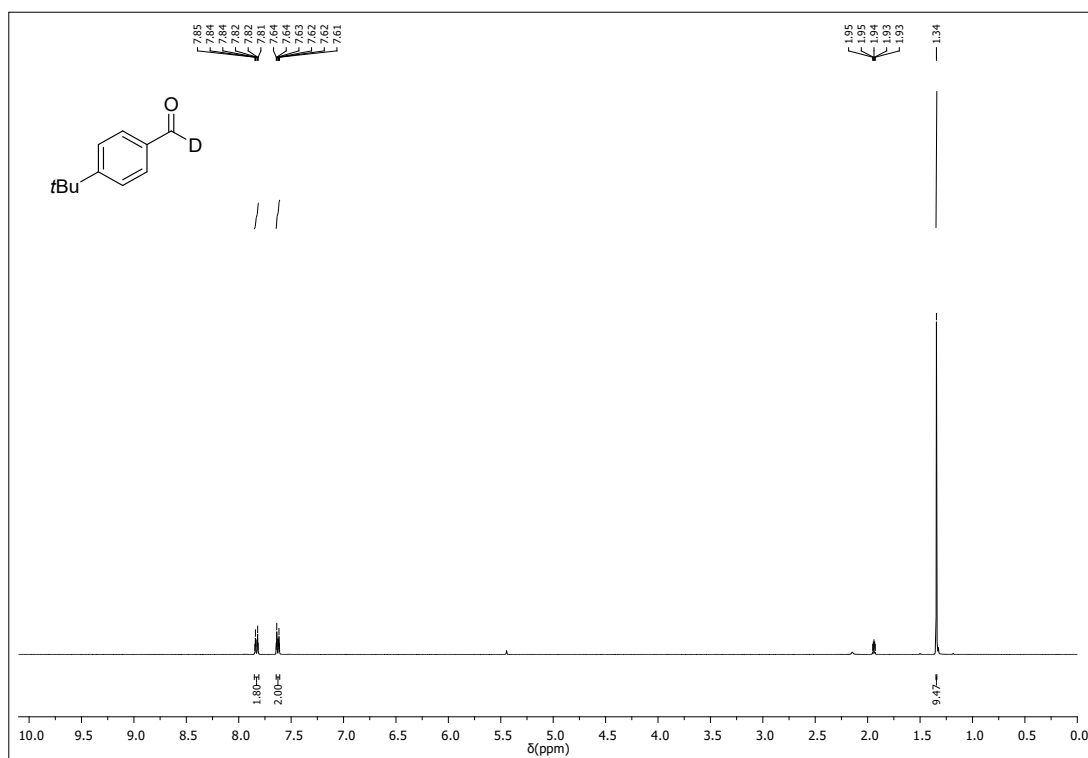


Figure S24 $^{13}\text{C-NMR}$ (101 MHz, CD_3CN) compound **1a-D**

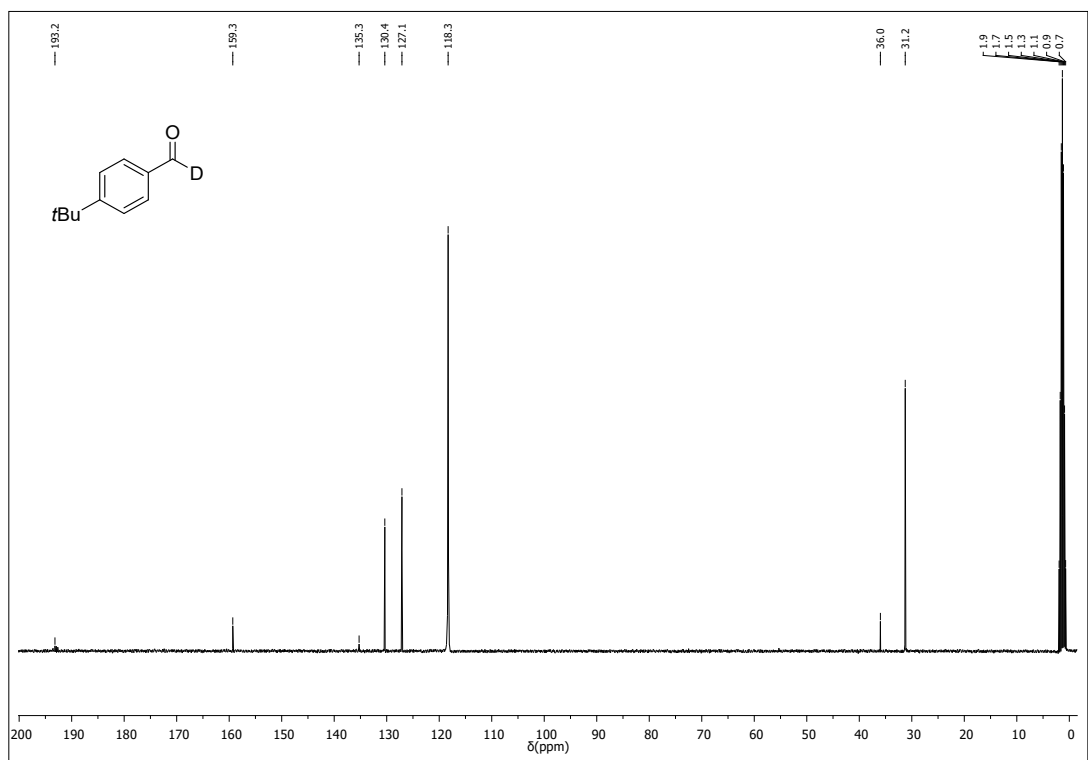


Figure S25 $^1\text{H-NMR}$ (400 MHz, CDCl_3) compound **13a**

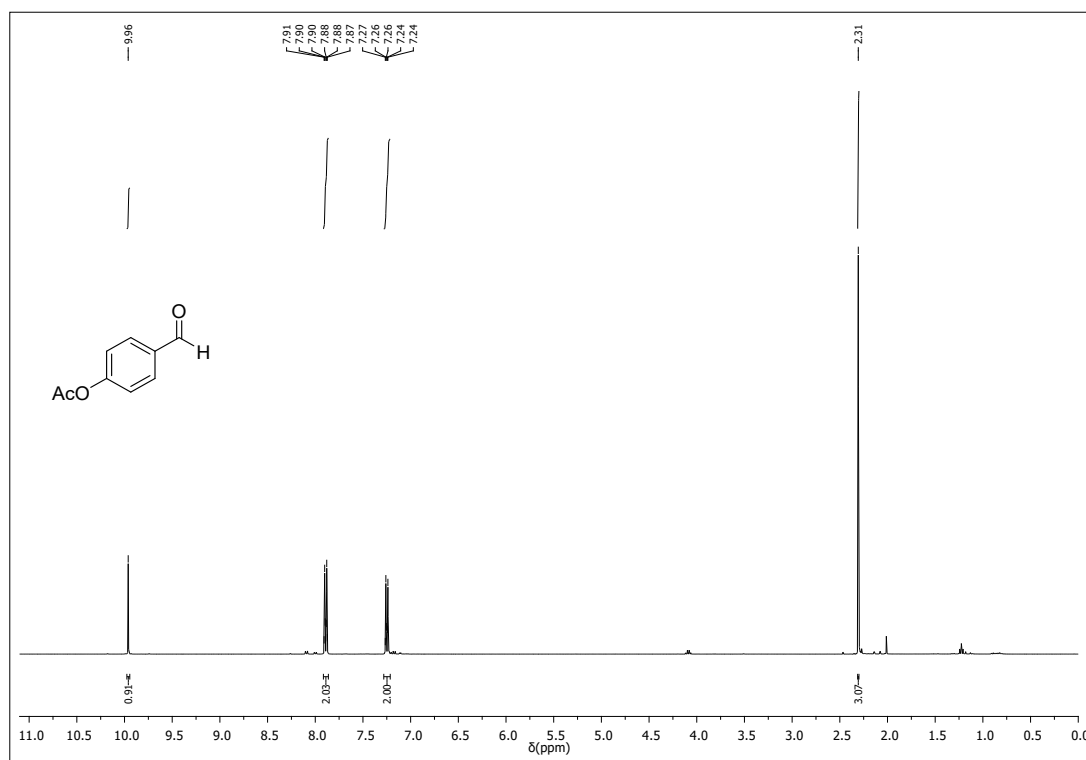


Figure S26 $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) compound **13a**

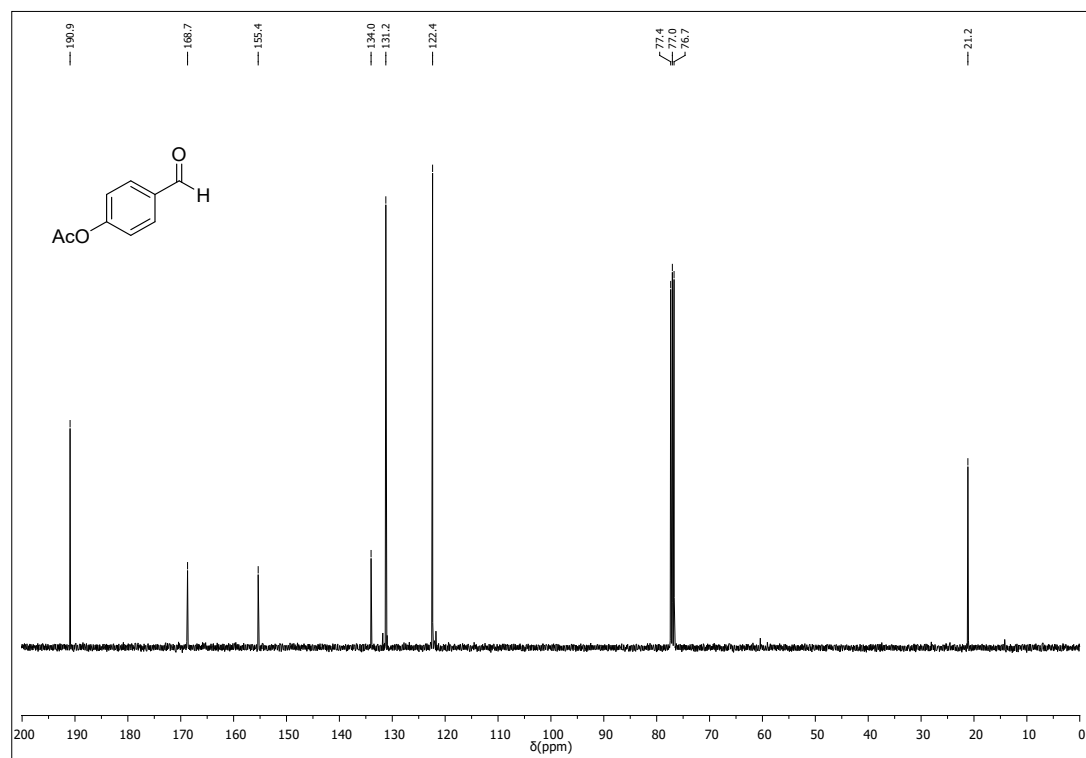


Figure S27 $^1\text{H-NMR}$ (400 MHz, CDCl_3) compound 14a

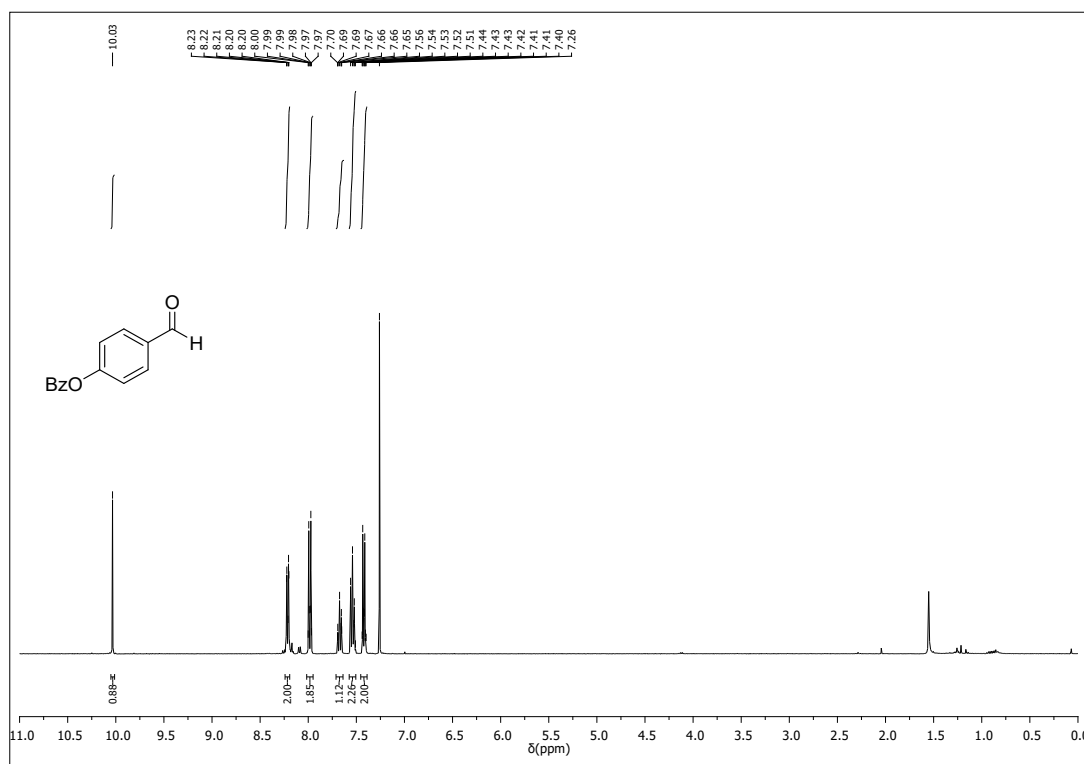


Figure S28 $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) compound 14a

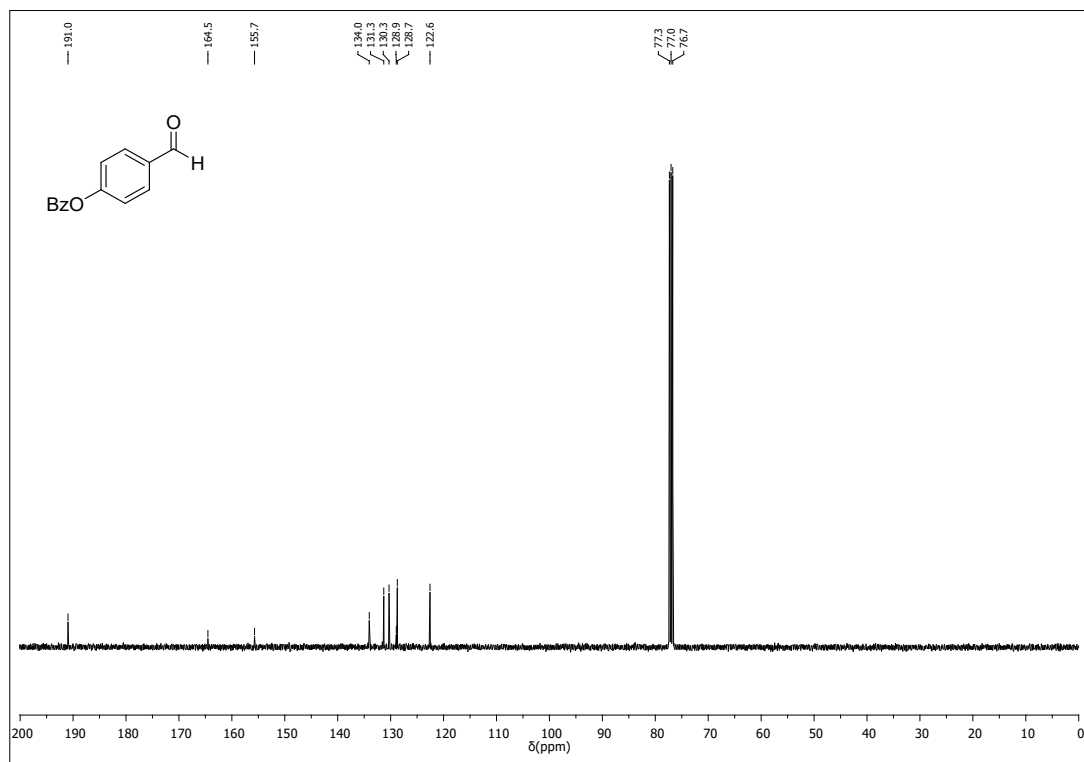


Figure S29 $^1\text{H-NMR}$ (400 MHz, CD_2Cl_2) compound **16b**

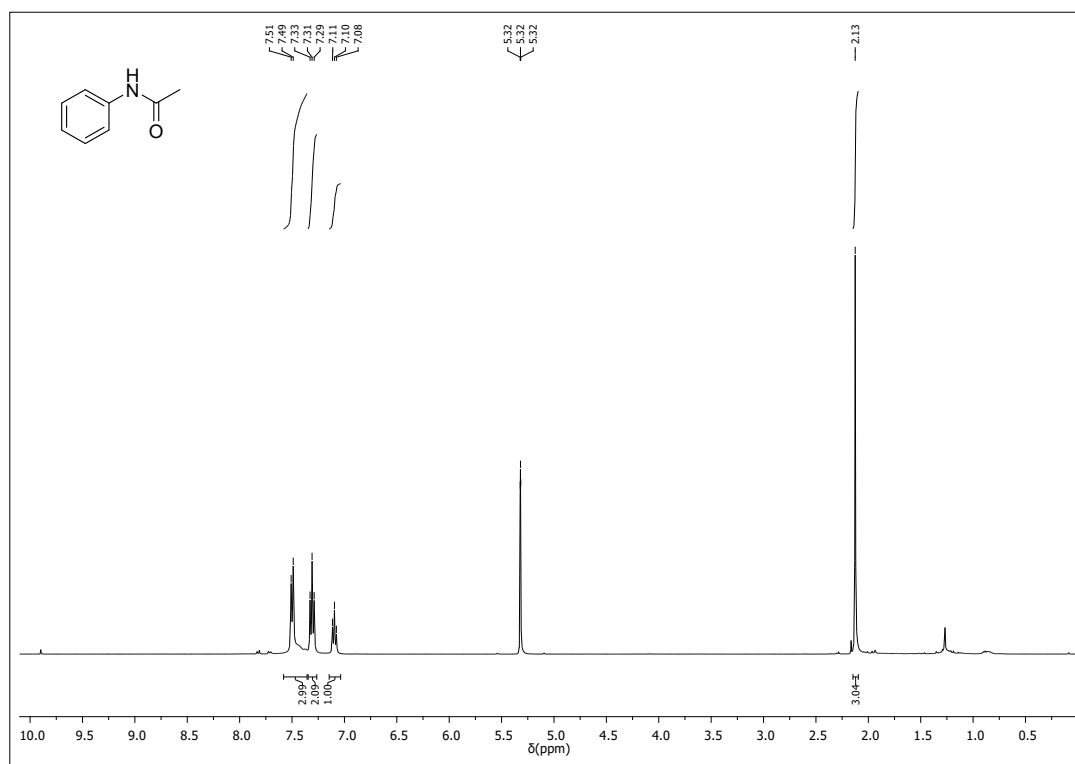


Figure S30 $^{13}\text{C-NMR}$ (101 MHz, CD_2Cl_2) compound **16b**

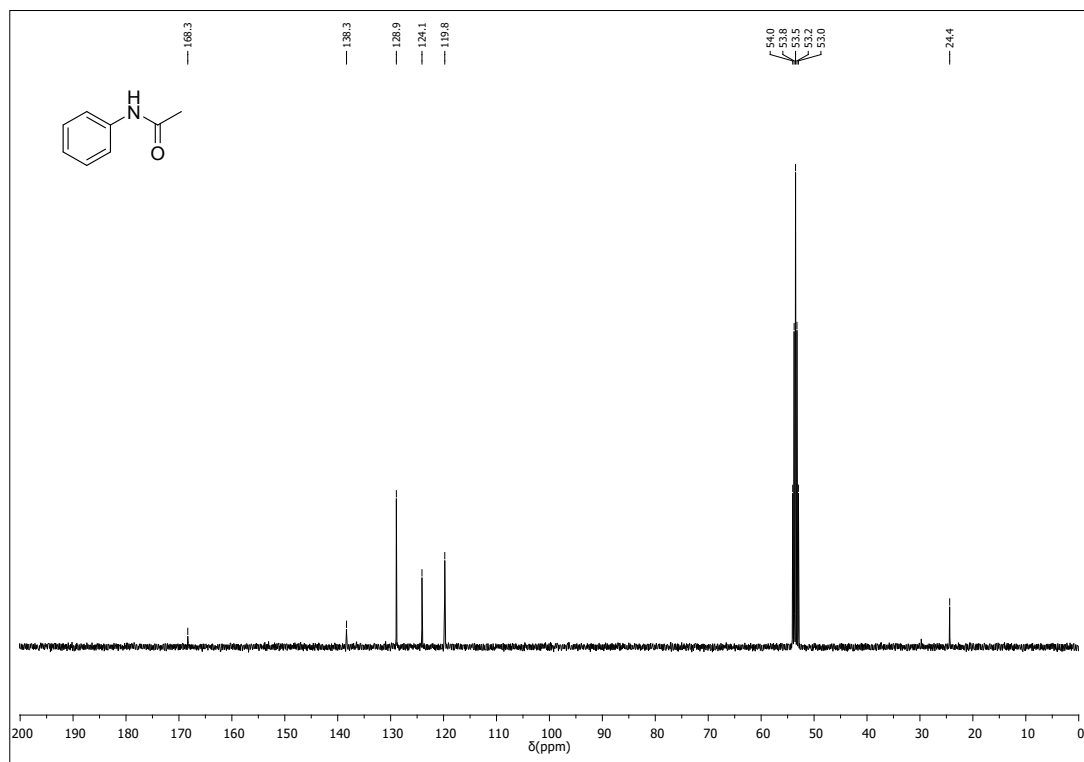


Figure S31 $^1\text{H-NMR}$ (400 MHz, CD_2Cl_2) compound **25b**

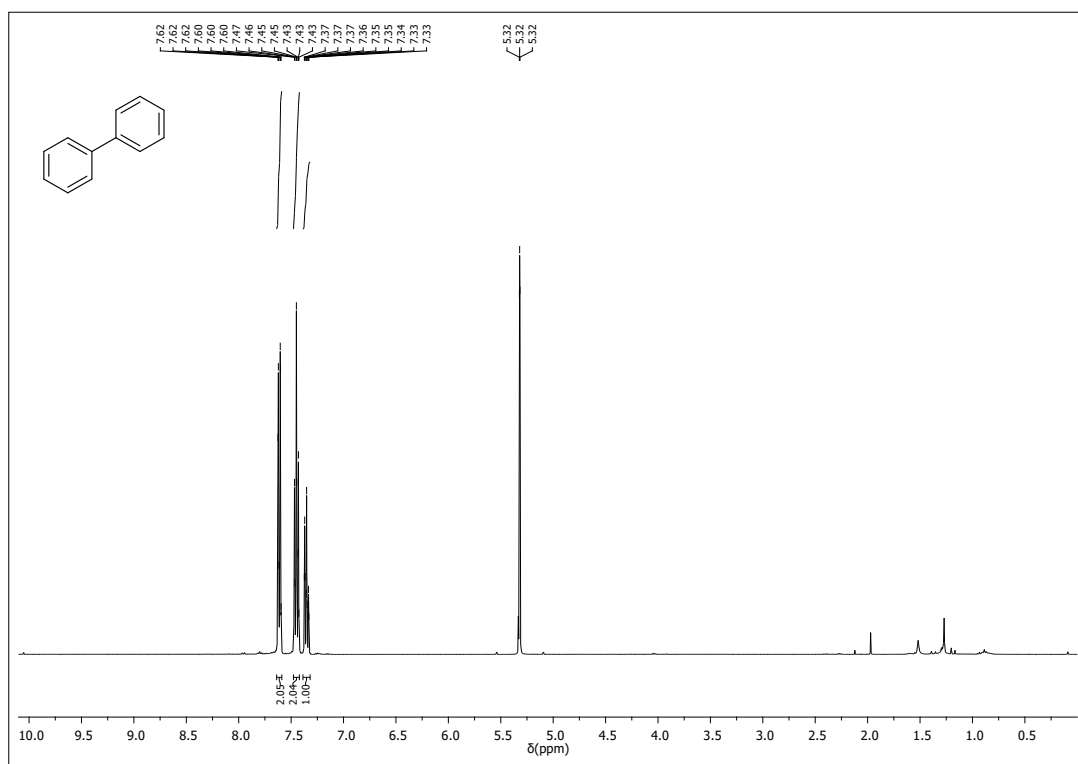


Figure S32 $^{13}\text{C-NMR}$ (101 MHz, CD_2Cl_2) compound **25b**

