Supporting Information

An Approach to Comparing the Functional Group Tolerance of Reactions

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1. General information

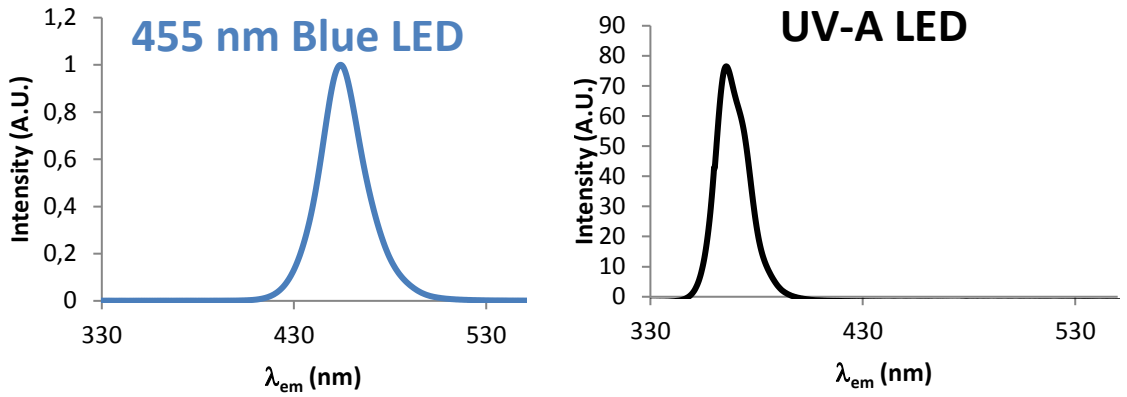


Figure S1. Emission spectra of the light sources used. Recorded using a Jasco FP-8300 spectrofluorometer.

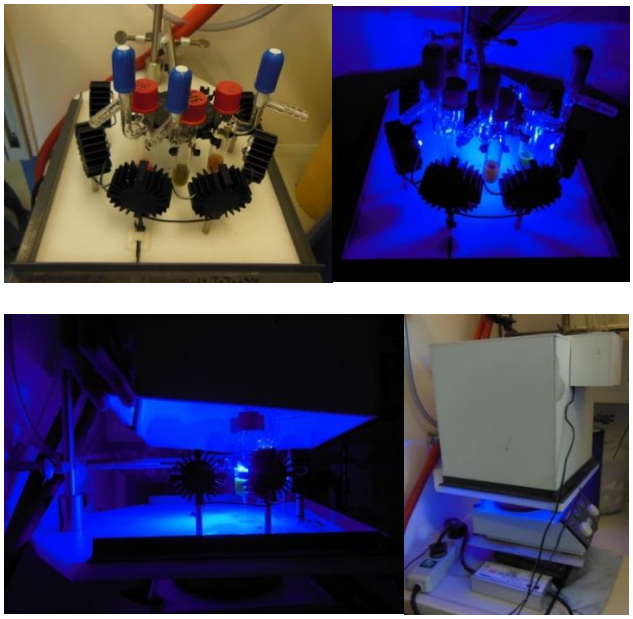
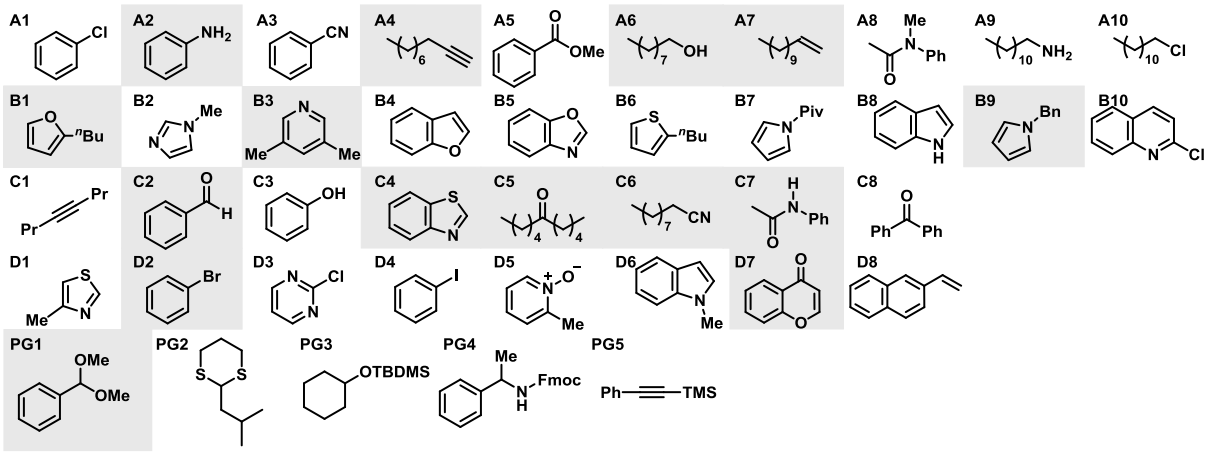


Figure S2. Photographs of the custom-made "light box" used for reactions conducted under blue LED and UV-A irradiation.

2. General procedure for the additive-based screening

In order to evaluate the robustness and the functional group preservation of the investigated reactions, we decided to apply an intermolecular additive-based screen to these transformations.[1] This screening technique, previously reported by our group, evaluates the tolerance of a given reaction to a series of additives (robustness), as well as the stability of these additives to the reaction conditions (functional group preservation).

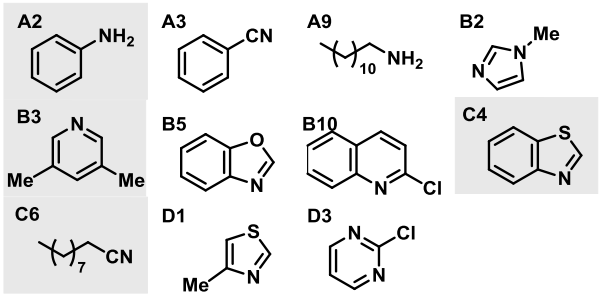
Scheme S1. Additive sets used in this study.



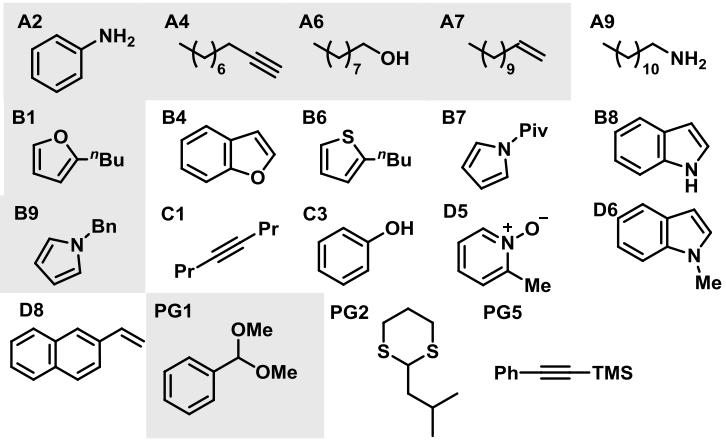
Case studies 1 and 2 were carried out with all 41 additives. In case studies 3 and 4 we used a truncated set consisting of the 15 additives highlighted in grey in Scheme S1.

For a systematic and intuitive analysis of the later obtained results, the 41 additives were categorized into their dominating reactivity properties such as basic, nucleophilic or electrophilic. Some additives are in more than one category, where appropriate. While the allocation to these categories might be ambiguous in some cases, it serves to observe general reactivity trends. The respective additives combined in these categories can be found in Schemes S2-S4. The analysis according to these groups of additives was carried out with all 41 additives in case studies 1 and 2, and with the reduced set of 15 additives in case studies 3 and 4.

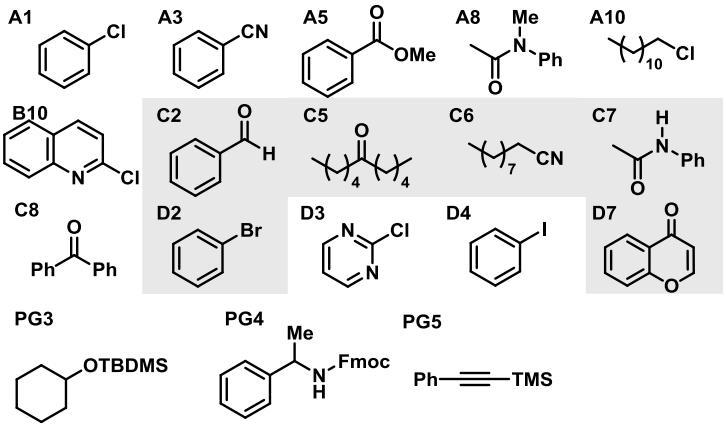
Scheme S2. Basic additives.



Scheme S3. Nucleophilic additives.



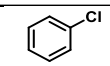
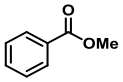
Scheme S4. Electrophilic additives.

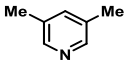
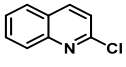


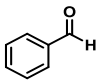
Color-coding should help the ready assessment of the yields: green (> 66%), yellow (34…66%), red (< 34%). The color-coding for facilitated assessment of the reactions yield is scaled using these percentages relative to the yield of the standard reaction in the absence of any additive.

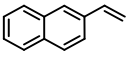
3. Results of the additive-based screening applied to the photocatalytic decarboxylative trifluoromethylthiolation

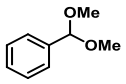
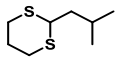
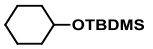
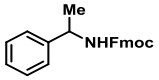
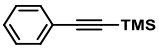
Table S1. Results of the decarboxylative trifluoromethylthiolation of carboxylic acids.

		Condition A (365 nm)		Condition B (455 nm)	
Group A		Yield Product	Additive remaining	Yield Product	Additive remaining
A1		75	37	85	105
A2		24	28	8	90
A3		66	46	77	105
A4		49	15	58	67
A5		79	105	67	101
A6		68	0	67	70
A7		75	22	83	72
A8		77	78	86	103
A9		11	0	8	19
A10		78	37	85	74

		Yield Product	Additive remaining	Yield Product	Additive remaining
Group B					
B1		74	15	72	54
B2		69	2	73	103
B3		63	44	56	69
B4		83	88	74	103
B5		35	88	36	105
B6		64	17	76	13
B7		57	20	48	86
B8		3	4	6	47
B9		86	51	78	60
B10		56	52	10	101

Group C		Yield Product	Additive remaining	Yield Product	Additive remaining
C1		14	32	15	80
C2		45	0	76	8
C3		0	0	0	78
C4		73	58	78	103
C5		49	0	81	68
C6		80	51	80	50
C7		27	2	20	42
C8		56	103	72	103

Group D		Yield Product	Additive remaining	Yield Product	Additive remaining
D1		77	34	80	56
D2		84	93	75	97
D3		70	82	77	98
D4		83	90	81	91
D5		9	0	2	0
D6		77	28	82	30
D7		84	0	75	87
D8		22	0	5	32

Group PG		Yield Product	Additive remaining	Yield Product	Additive remaining
PG1		66	17	64	14
PG2		54	35	46	54
PG3		57	47	50	84
PG4		77	58	73	97
PG5		70	84	87	87
Average Yield		58	38	58	71

1 **2** **3**

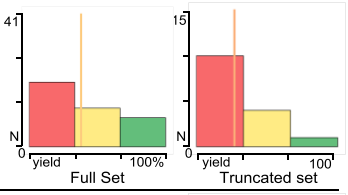
Conditions A

[Ir-F] (2.0 mol%), CsOBz (0.2 equiv.), 3-Me toluate (2.0 equiv.), C_6H_5F, **UV-A LED: 365 nm**

Standard yield 89%

Average yield 63%

Additive recovery:

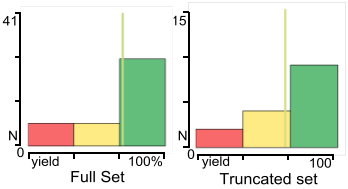


Conditions B

[Ir-F] (2.0 mol%), CsOBz (0.2 equiv.), 3-Me toluate, (2.0 equiv.), C_6H_5F, **blue LED: 455 nm**

Standard yield 90%

Average yield 65%



Basic additives		
	Product	Additives
Conditions A (365 nm)	57	44
Conditions B (455 nm)	53	82

Nucleophilic additives		
	Product	Additives
Conditions A (365 nm)	48	24
Conditions B (455 nm)	46	56

Electrophilic additives		
	Product	Additives
Conditions A (365 nm)	67	54
Conditions B (455 nm)	70	83

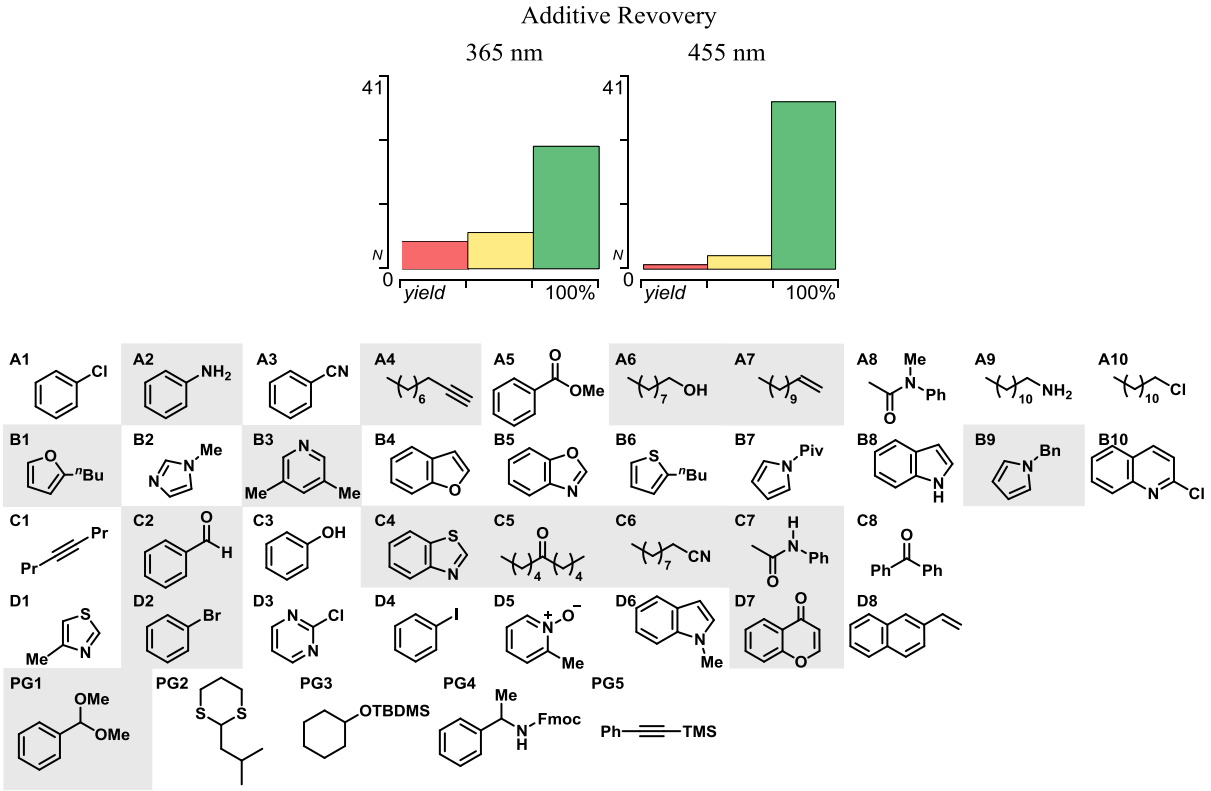
The color-coding for facilitated assessment of the results is scaled relative to the yield of the standard reaction in the absence of any additive, representing > 54% in green, 27…54% in yellow and < 27% in red for the product yields and > 66% in green, 34…66% in yellow and < 34% in red for the additive recovery in both protocols.

To facilate operation and uptake of the method, we further selected a truncated set of 15 additives out of 41. As shown above, the truncated set reproduces the trends of the full set for the photocatalytic decarboxylative trifluoromethylthiolation.

3.1. Results of the additive-stability investigation under 365 nm/455 nm irradiation

In the cases where decomposition of the additive was observed under the reaction conditions (recovery < 67%), a separate isolated assessment was made in which a solution of the additive was irradiated with visible or UV-A light in the absence of the photocatalyst and any other reagents or additives.

Table S2. Results of the additive-stability investigation under 455 nm/365 nm irradiation.

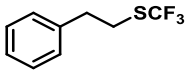


Wavelength	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
365 nm	54	71	53	92	-	93	84	-	0	76
455 nm	-	-	-	-	-	-	-	-	88	-
Wavelength	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B8**	**B9**	**B10**
365 nm	100	0	28	-	-	71	86	106	90	105
455 nm	94	-	-	-	-	68	-	105	90	-
Wavelength	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**		
365 nm	84	13	91	57	31	43	80	-		
455 nm	-	43	-	-	88	90	90	-		
Wavelength	**D1**	**D2**	**D3**	**D4**	**D5**	**D6**	**D7**	**D8**		
365 nm	35	-	-	-	0	56	83	51		
455 nm	42	-	-	-	0	92	-	47		
Wavelength	**PG1**	**PG2**	**PG3**	**PG4**	**PG5**					
365 nm	70	80	76	52	-					
455 nm	91	86	-	-	-					

3.2. Preparation of multifunctional substrates to validate the additive-based screen

Table S3. Results of the preparation of multifunctional substrates to validate the additive-based screening.

Reference Product

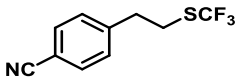


14

	365 nm	455 nm
Yield of **14**	55%	60%
Recovered SM	/	/

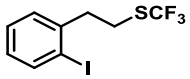
Additives

A3 D4 A9



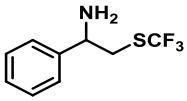
15

	365 nm	455 nm
Yield of **15**	21%	33%
Recovered SM	/	/
Yield of **3** in presence of **A3**	66	77
Recovered **A3**	46	105
Match Quality	MEDIUM	GOOD



16

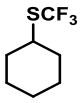
	365 nm	455 nm
Yield of **16**	54%	57%
Recovered SM	/	/
Yield of **3** in presence of **D4**	83	81
Recovered **D4**	90	91
Match Quality	GOOD	GOOD



17

	365 nm	455 nm
Yield of **17**	Trace	Trace
Recovered SM	/	/
Yield of **3** in presence of **A9**	11	8
Recovered **A9**	0	19
Match Quality	GOOD	GOOD

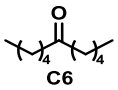
Reference Product



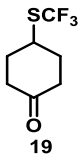
18

	455 nm	365 nm
Yield 18	79%	83%
Recovered SM	n. d.	n. d.

Additive



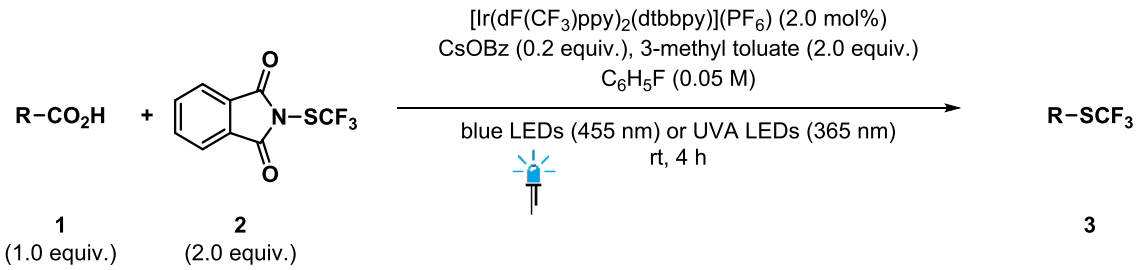
C6



19

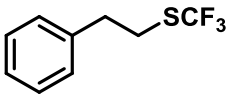
	365 nm	455 nm
Yield of **19**	83%	79%
Recovered SM	/	/
Yield of **3** in presence of **C6**	49	81
Recovered **C6**	51	50
Match Quality	BAD	GOOD

General procedure for the decarboxylative trifluoromethylthiolation (GP2):[2]



To a 10 ml Schlenk tube was added cesium benzoate (15.2 mg, 0.06 mmol, 0.2 equiv.) and trifluoromethylthiolation reagent **2** (148 mg, 0.6 mmol, 2.0 equiv.) in a glove-box. The vial was removed from the glovebox and carboxylic acid **1** (1.0 equiv), $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ (9.9 mg, 0.009 mmol, 2 mol%), fluorobenzene (6 mL, 0.05 M), and 3-methyl toluate (86 µL, 0.6 mmol, 2.0 equiv.) were added. The solution was degassed using three freeze-pump-thaw cycles. The mixture was stirred under irradiation from UV-A LEDs (λ_{max} = 365 nm) or blue LEDs (λ_{max} = 455 nm). After 4 hours, the reaction outcome was analyzed using GC-MS. The yield was determined by ^{19}F-NMR-Spectroscopy using trifluoromethoxybenzene as internal standard.

Phenylethyltrifluoromethylsulfane 14[3]



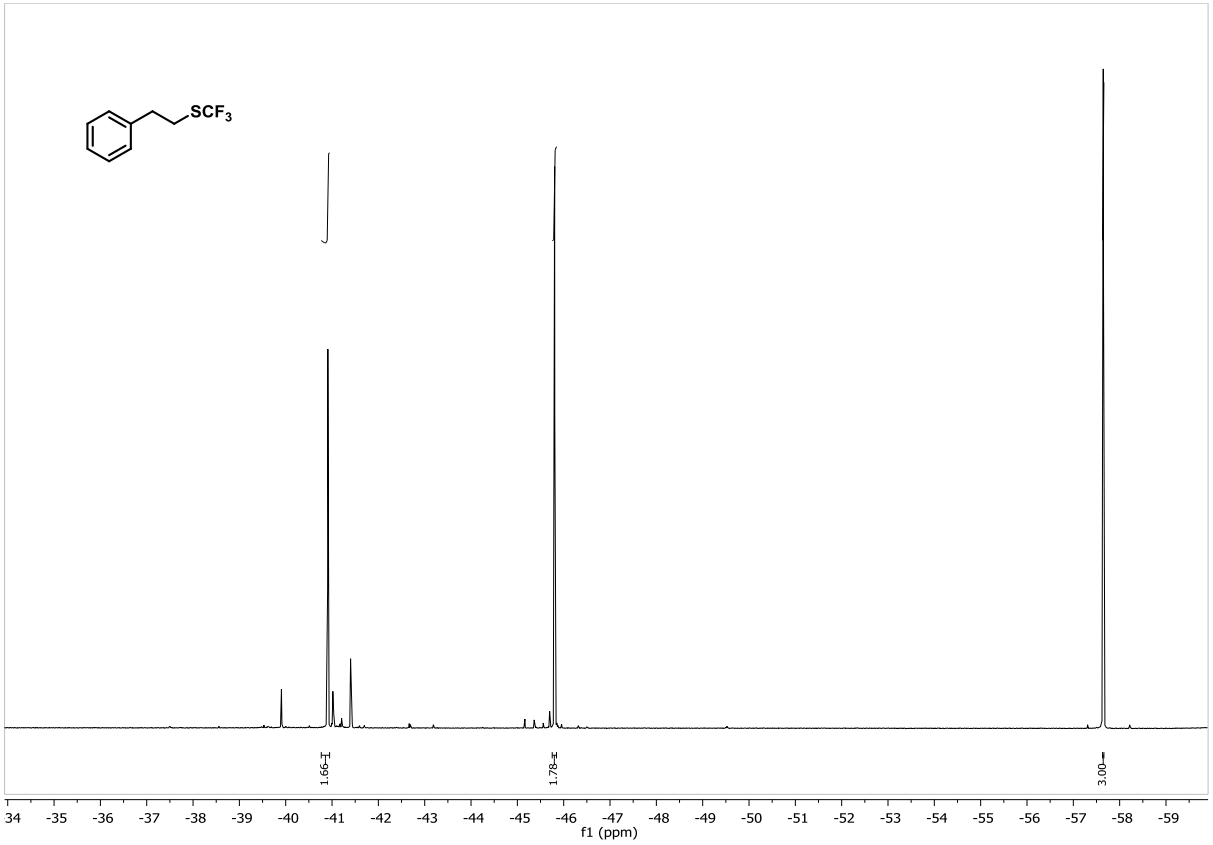
Prepared according to **GP2** using 1-phenylpropionic acid (45.5 mg, 0.3 mmol, 1.0 equiv) as starting material.

NMR-yield using 365 nm irradiation: 55%.
NMR-yield using 455 nm irradiation: 60%.

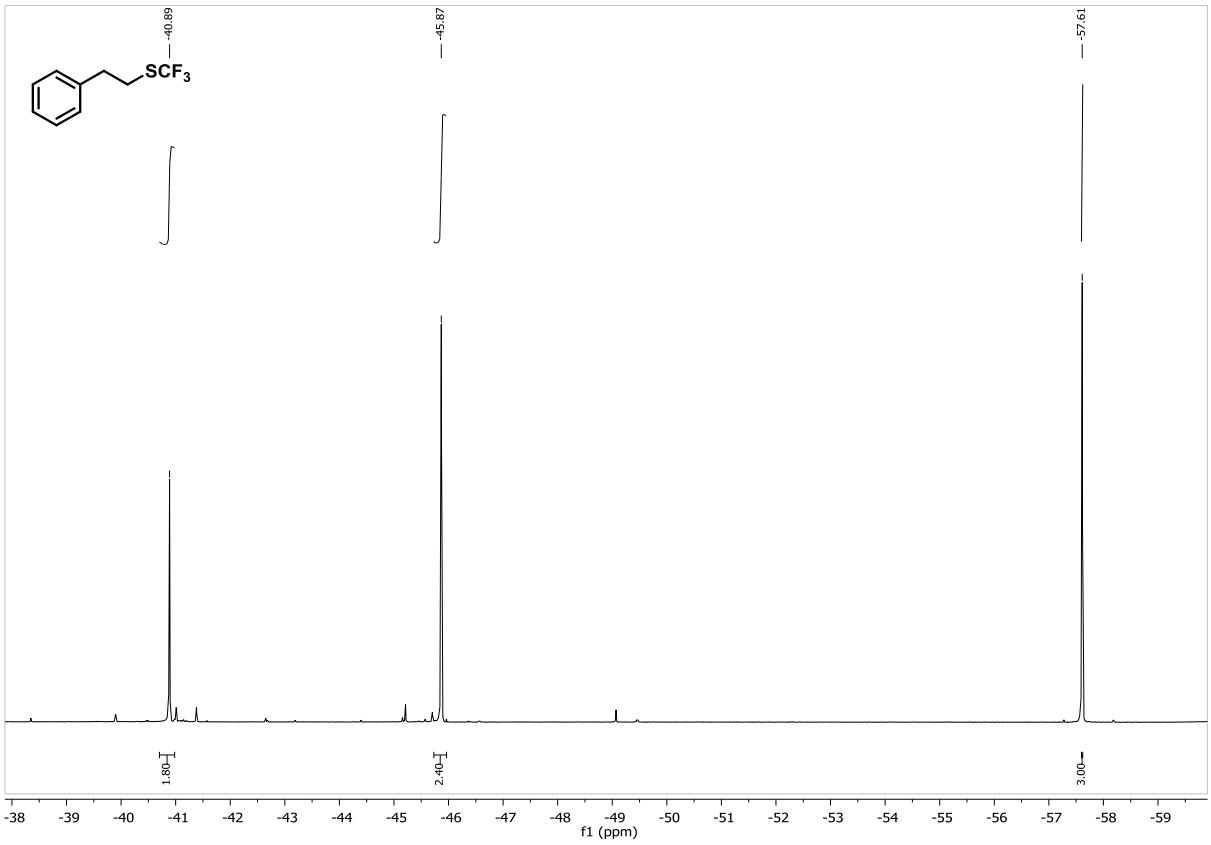
^{19}F NMR (282 MHz, Chloroform-*d*): δ –40.89.

GC-MS: t_R (50_40): 5.97 min; **EI-MS:** *m/z* (%): 206 (36), 105 (11), 91 (100), 77 (11), 69 (24).

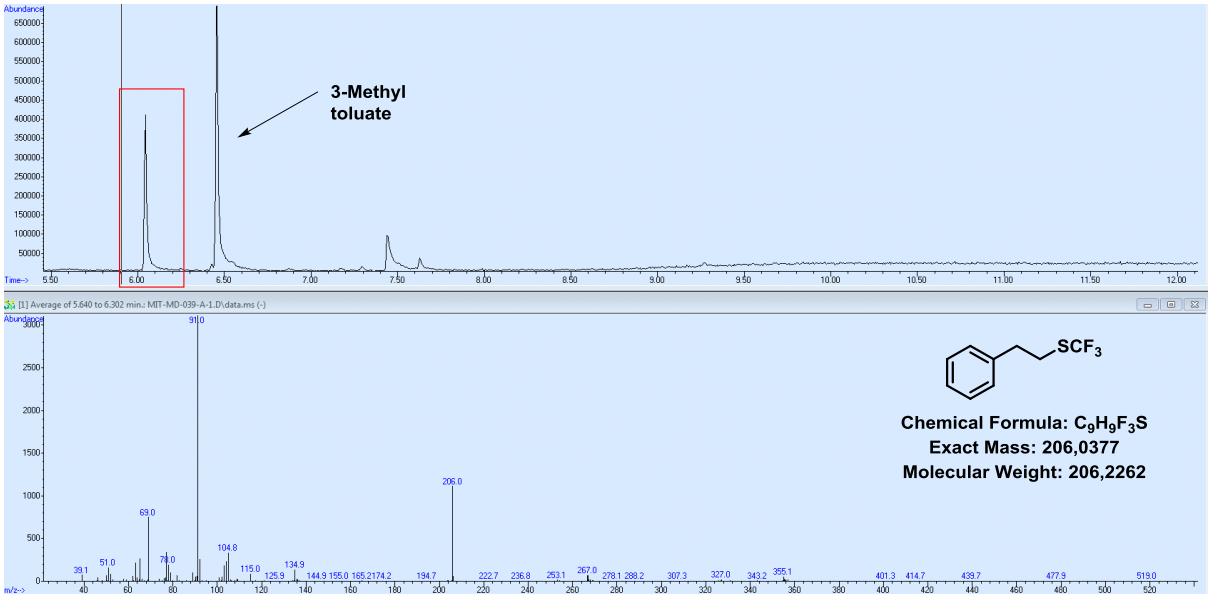
^{19}F NMR of crude reaction using 365 nm LEDs:



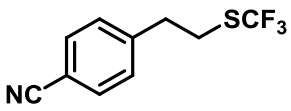
^{19}F NMR of crude reaction using 455 nm LEDs:



GC-MS of crude reaction mixture:[4]



4-(2-((trifluoromethyl)thio)ethyl)benzonitrile 15[5]



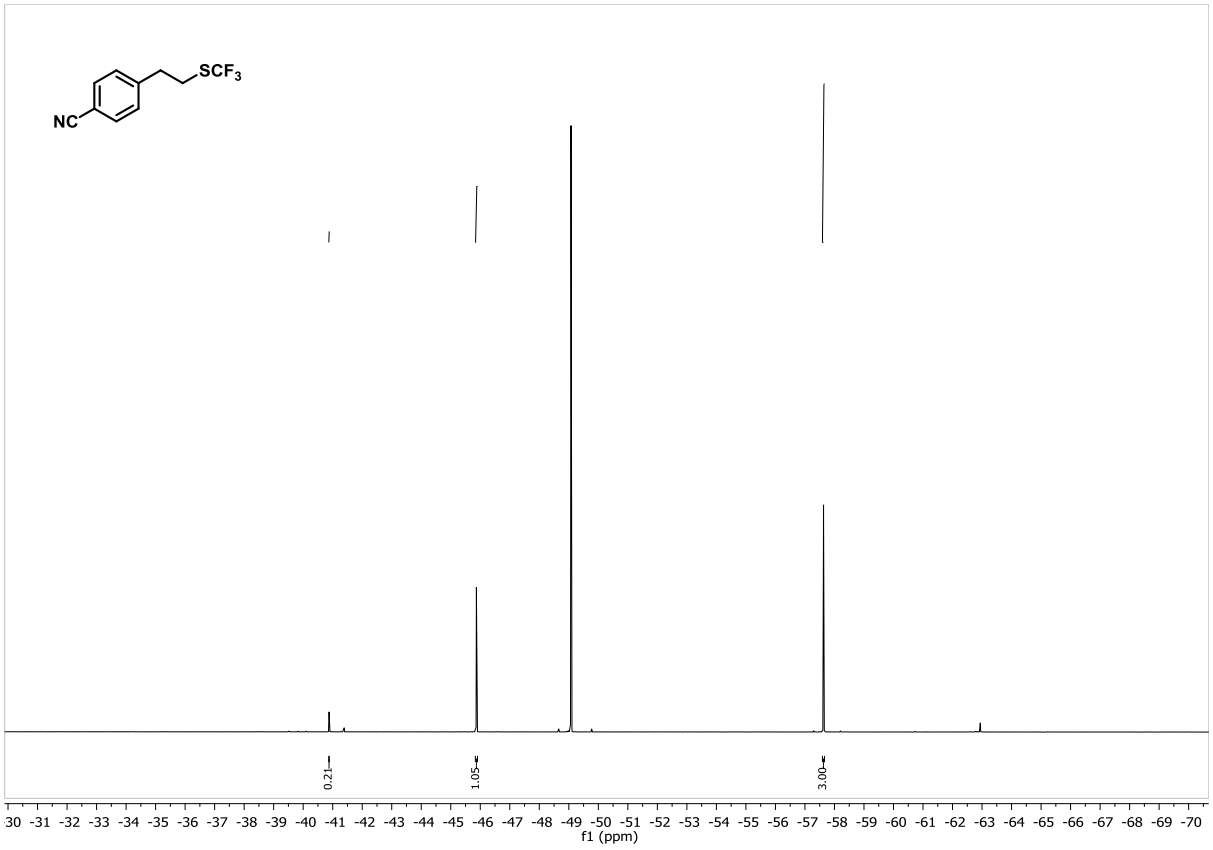
Prepared according to **GP2** using 3-(2-cyanophenyl)propionic acid (52.5 mg, 0.3 mmol, 1.0 equiv) as starting material.

NMR-yield using 365 nm irradiation: 21%.
NMR-yield using 455 nm irradiation: 33%.

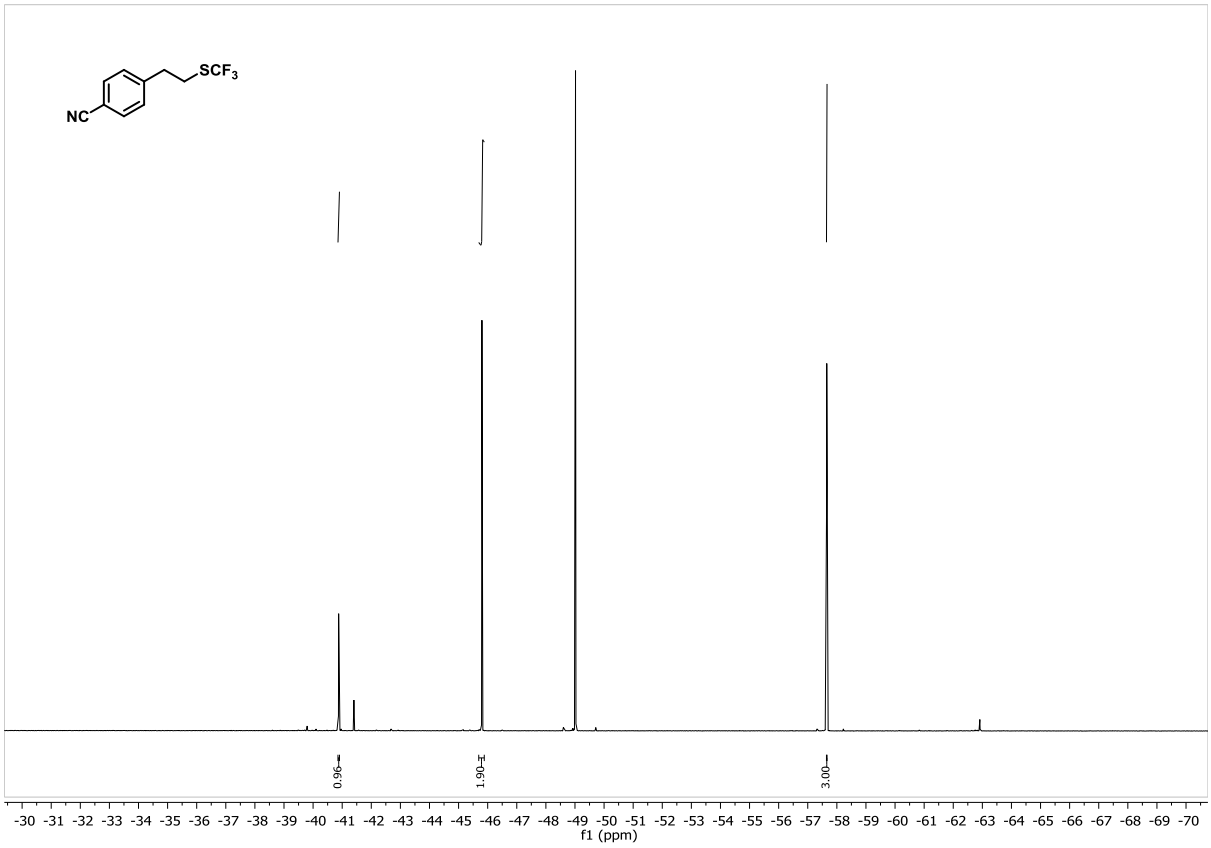
^{19}F NMR (282 MHz, Chloroform-*d*): δ –40.88.

GC-MS: t_R (50_40): 7.44 min; **EI-MS:** *m/z* (%):231 (38), 147 (60), 129 (14), 116 (100), 115 (20), 104 (42), 103 (48), 89 (21), 76 (62), 74 (26).

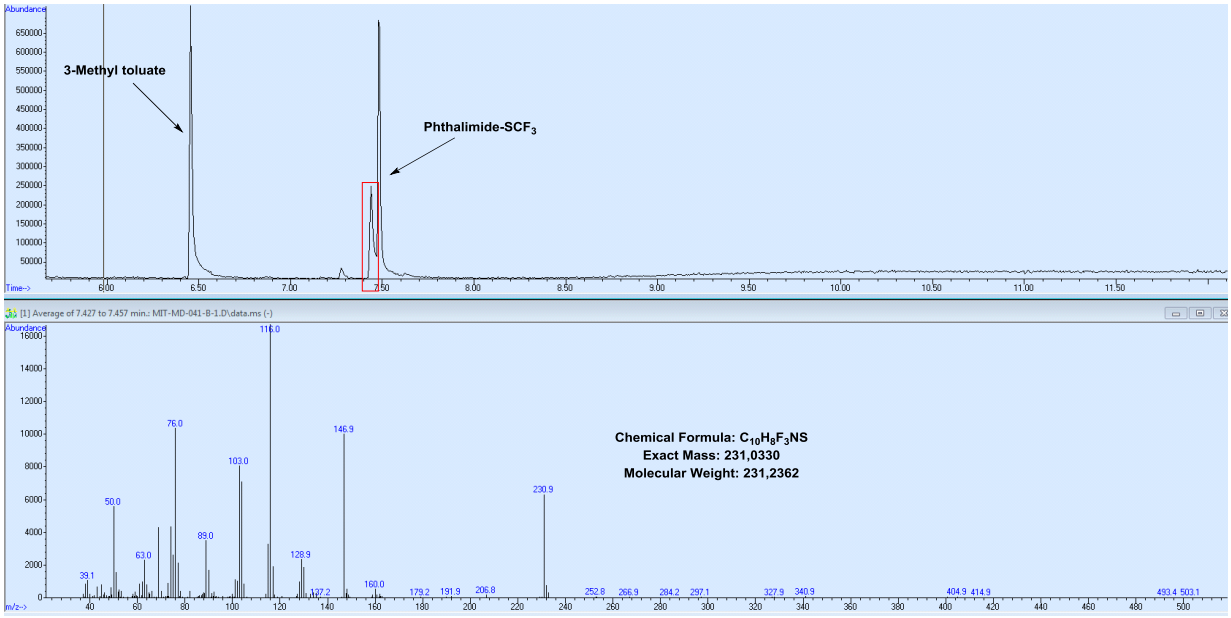
^{19}F NMR of crude reaction using 365 nm LEDs:



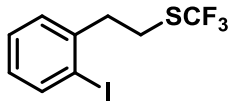
^{19}F NMR of crude reaction using 455 nm LEDs:



GC-MS of crude reaction mixture:



(2-iodophenethyl)(trifluoromethyl)sulfane 16



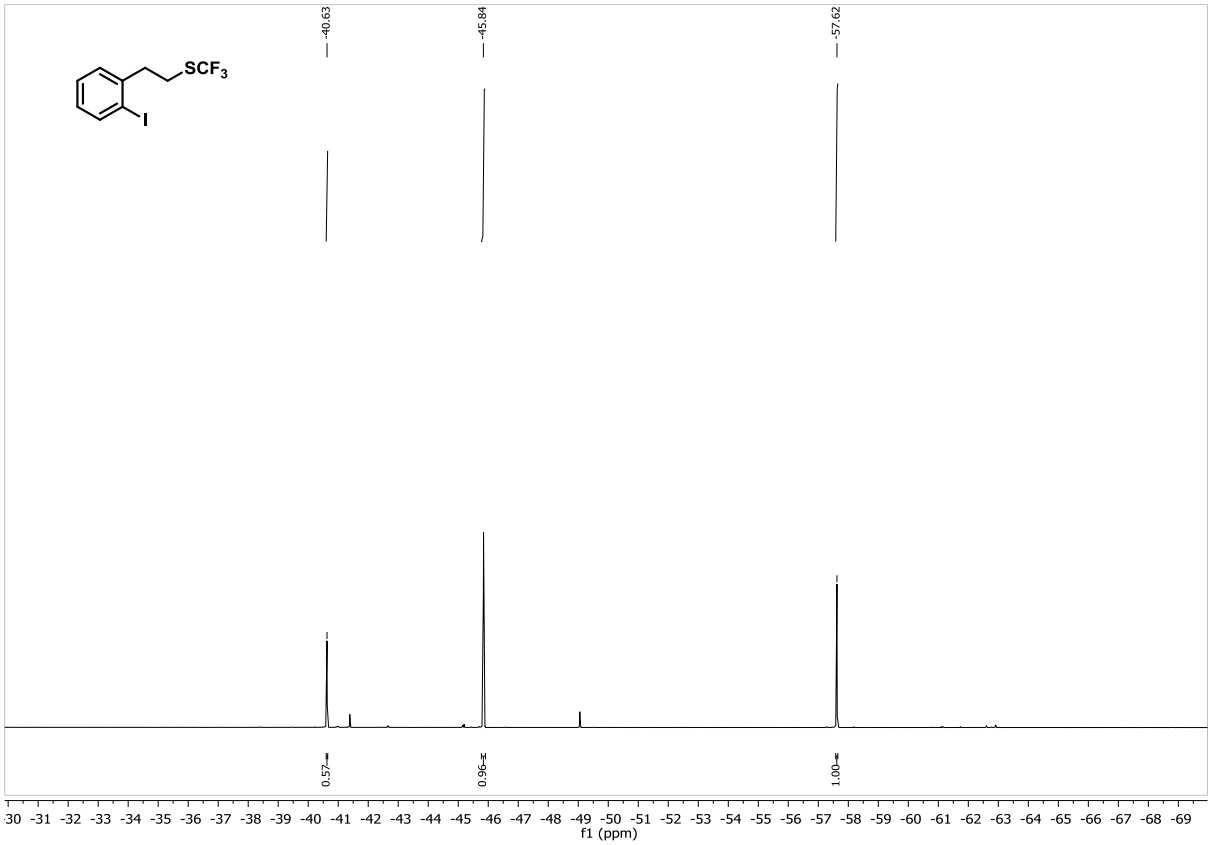
Prepared according to **GP2** using 3-(2-iodophenyl)propionic acid (82.8 mg, 0.3 mmol, 1.0 equiv) as starting material.

NMR-yield using 365 nm irradiation: 54%.
NMR-yield using 455 nm irradiation: 57%.

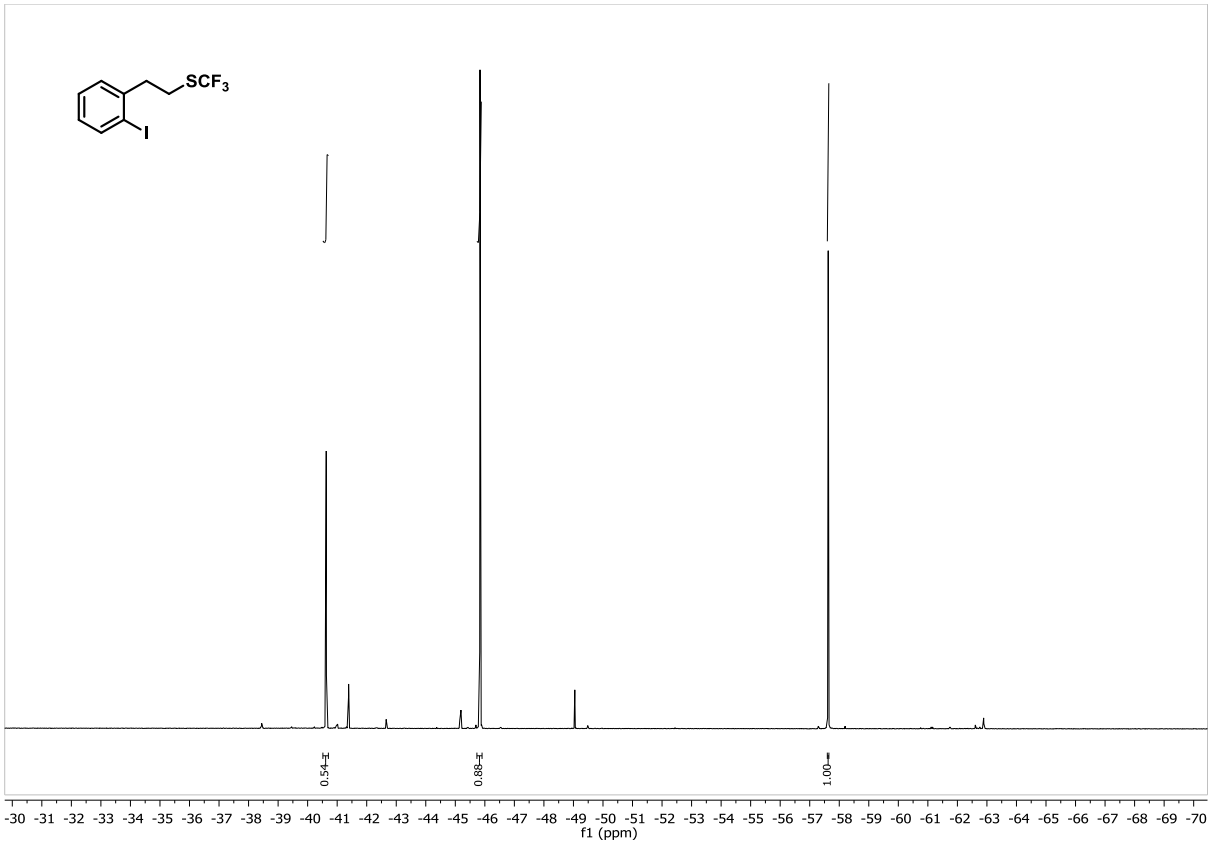
^{19}F NMR (282 MHz, Chloroform-*d*): δ –40.62.

GC-MS: t_R (50_40): 5.97 min; **EI-MS:** *m/z* (%): 231 (5), 217 (47), 205 (98), 137 (12), 136 (100), 135 (55), 134 (14), 91 (36), 90 (27), 89 (17), 77 (15).

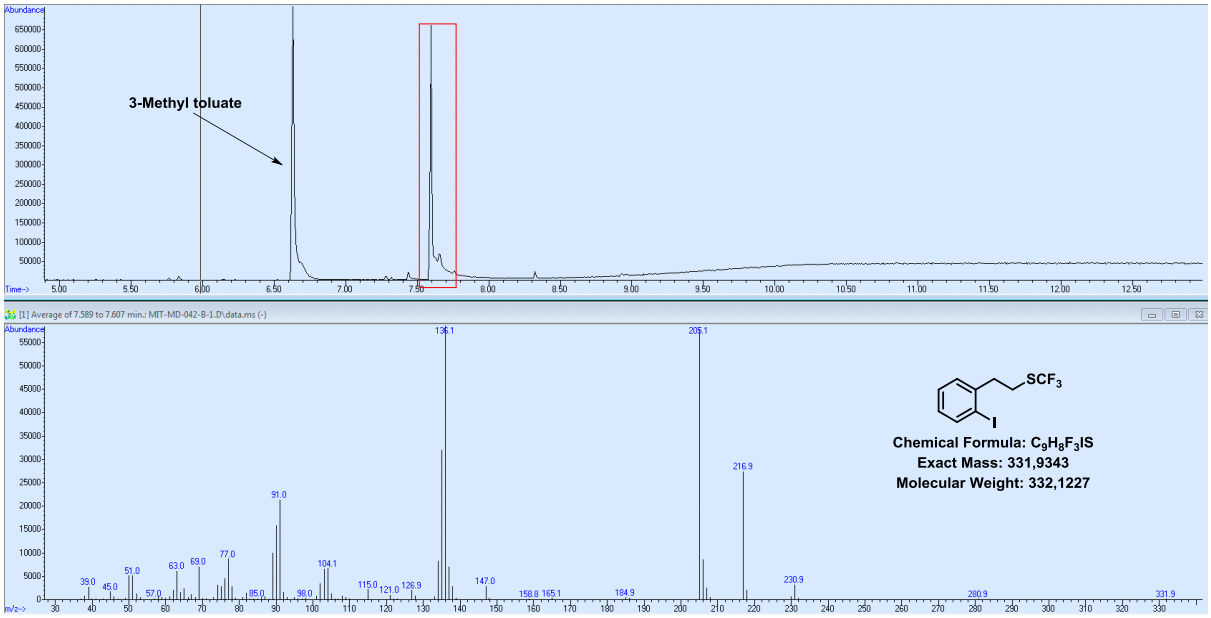
^{19}F NMR of crude reaction using 365 nm LEDs:



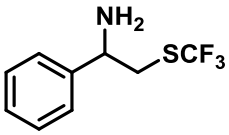
^{19}F NMR of crude reaction using 455 nm LEDs:



GC-MS of crude reaction mixture:



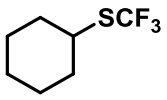
1-phenyl-2-((trifluoromethyl)thio)ethan-1-amine 17



Prepared according to **GP2** using 3-amino-3-phenylpropionic acid (82.8 mg, 0.3 mmol, 1.0 equiv) as starting material.

NMR-yield using 365 nm irradiation: /.
NMR-yield using 455 nm irradiation: /.

Cyclohexyl(trifluoromethyl)sulfane 18[3]



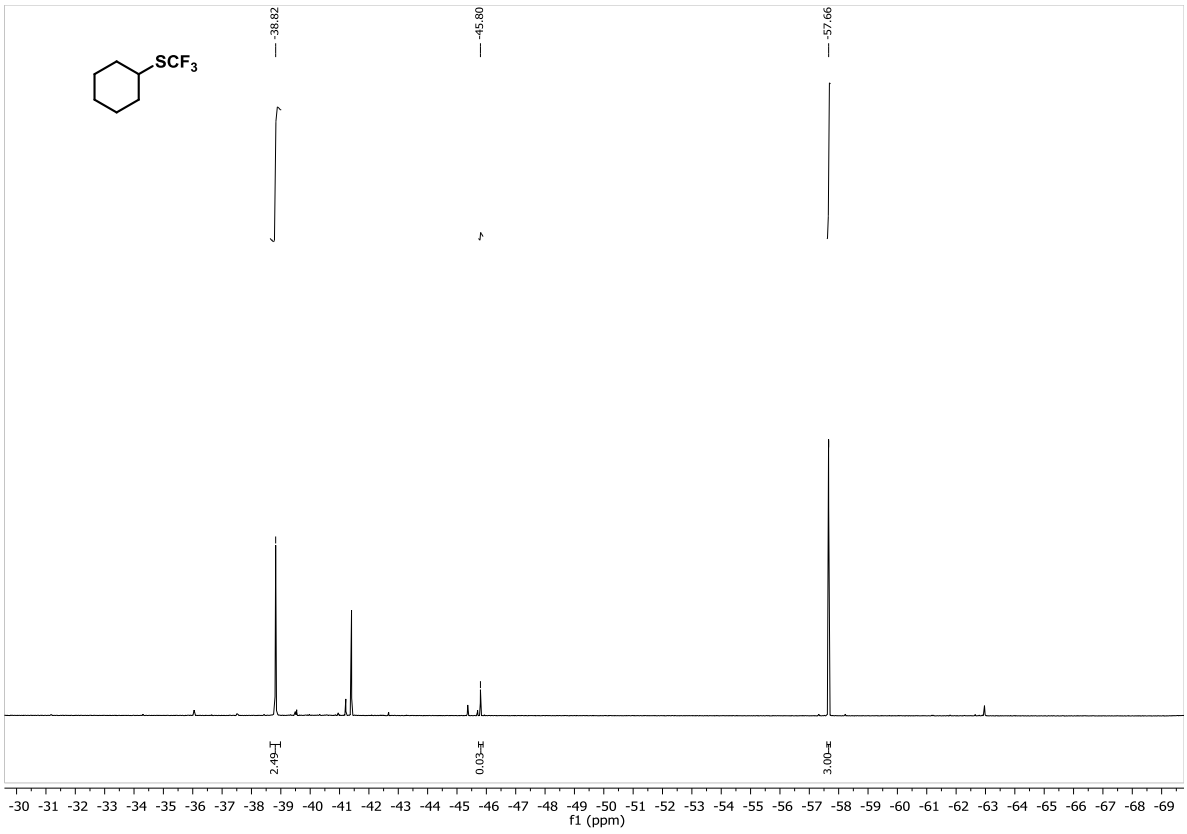
Prepared according to **GP2** using cyclohexylcarboxylic acid (38.4 mg, 0.3 mmol, 1.0 equiv) as starting material.

NMR-yield using 365 nm irradiation: 83%.
NMR-yield using 455 nm irradiation: 79%.

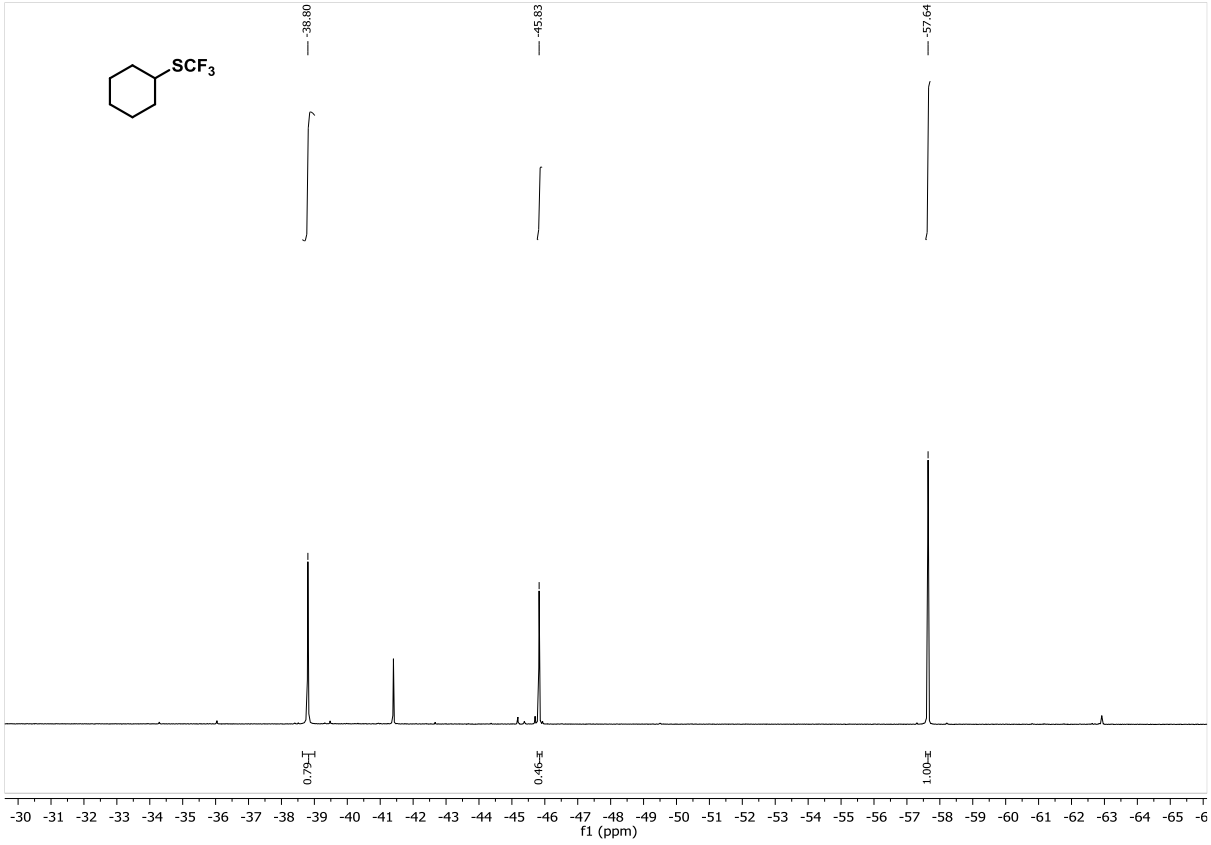
^{19}F NMR (282 MHz, Chloroform-*d*): δ –38.80.

GC-MS: t_R (50_40): 4.90 min; **EI-MS:** *m/z* (%): 184 (17), 115 (9), 83 (100), 82 (19), 67 (21). 55 (60), 41 (23).

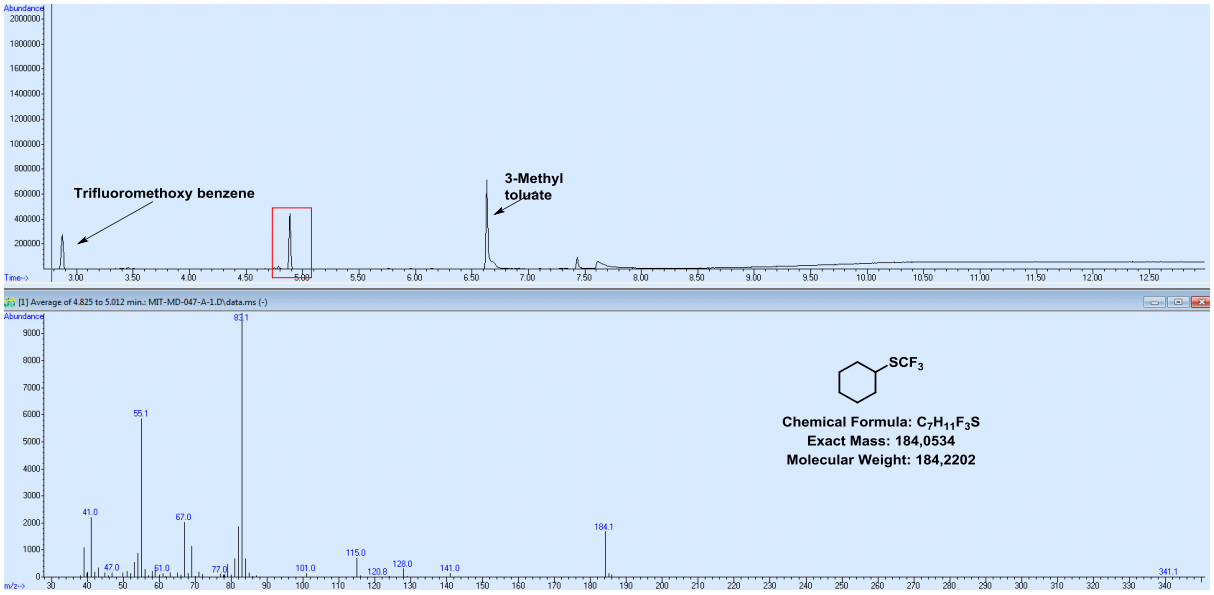
^{19}F NMR of crude reaction using 365 nm LEDs:



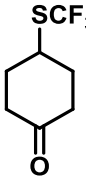
^{19}F NMR of crude reaction using 455 nm LEDs:



GC-MS of crude reaction mixture



4-((trifluoromethyl)thio)cyclohexan-1-one 19[6]



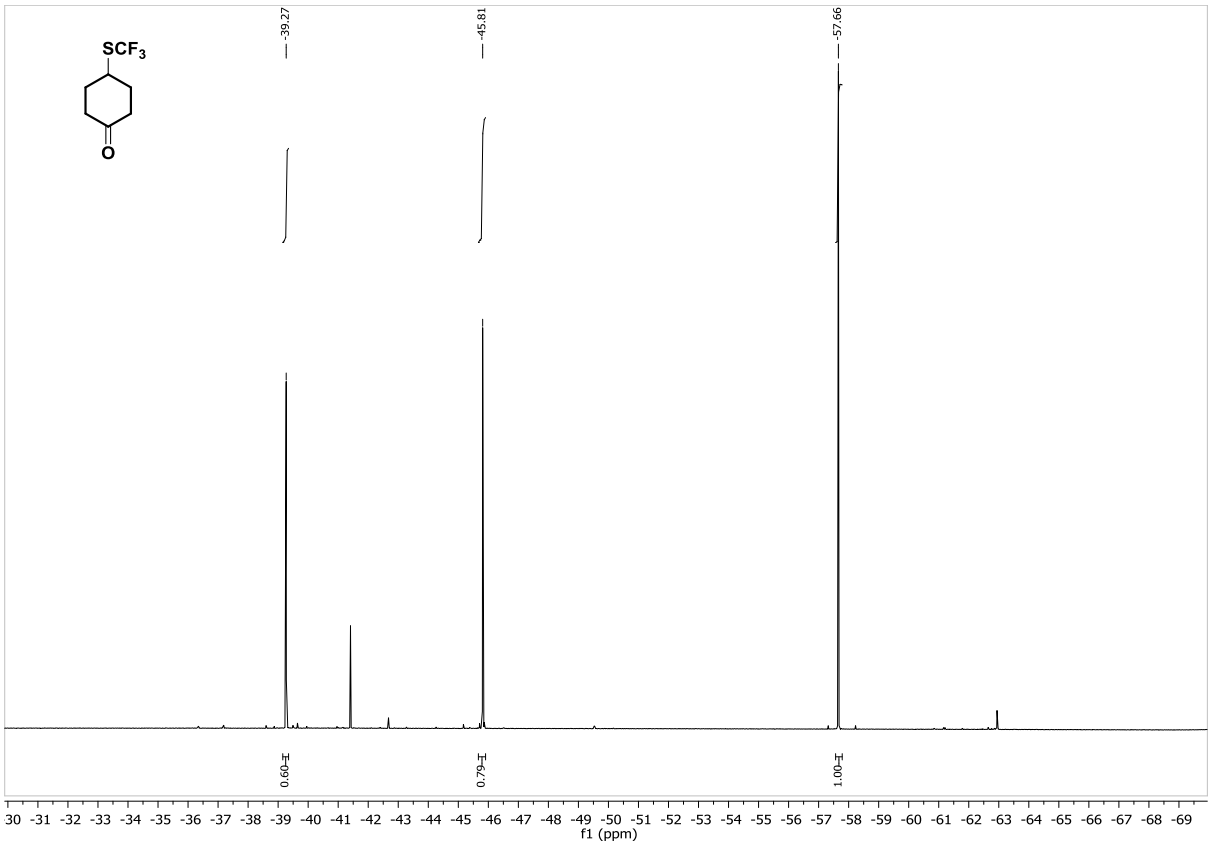
Prepared according to **GP2** using 4-oxocyclohexylcarboxylic acid (42.6 mg, 0.3 mmol, 1.0 equiv) as starting material.

NMR-yield using 365 nm irradiation: 60%.
NMR-yield using 455 nm irradiation: 62%.

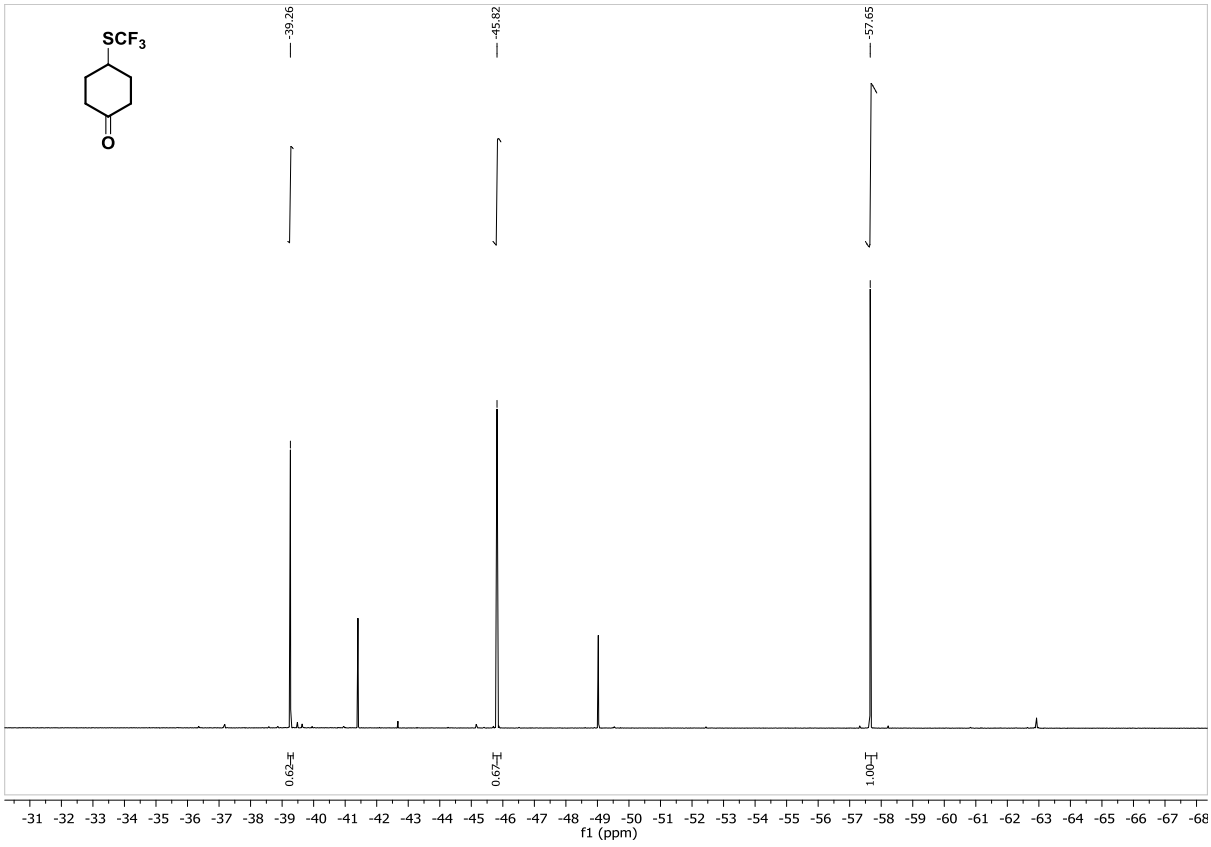
^{19}F NMR (282 MHz, Chloroform-*d*): δ –39.26.

GC-MS: t_R (50_40): 5.94 min; **EI-MS:** *m/z* (%): 198 (82), 128 (35), 101 (16), 97 (15), 71 (11), 69 (100), 67 (13), 59 (19), 55 (100).

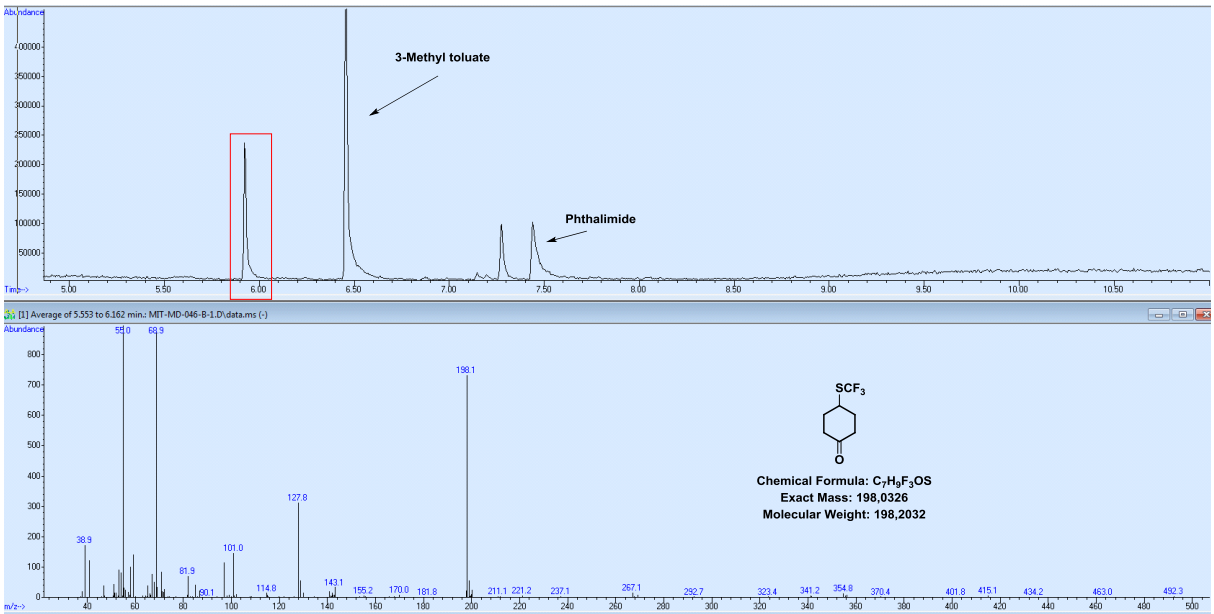
^{19}F NMR of crude reaction using 365 nm LEDs:



^{19}F NMR of crude reaction using 455 nm LEDs:

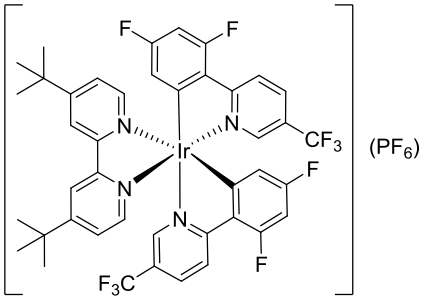


GC-MS of crude reaction mixture



3.3. Luminescence quenching studies

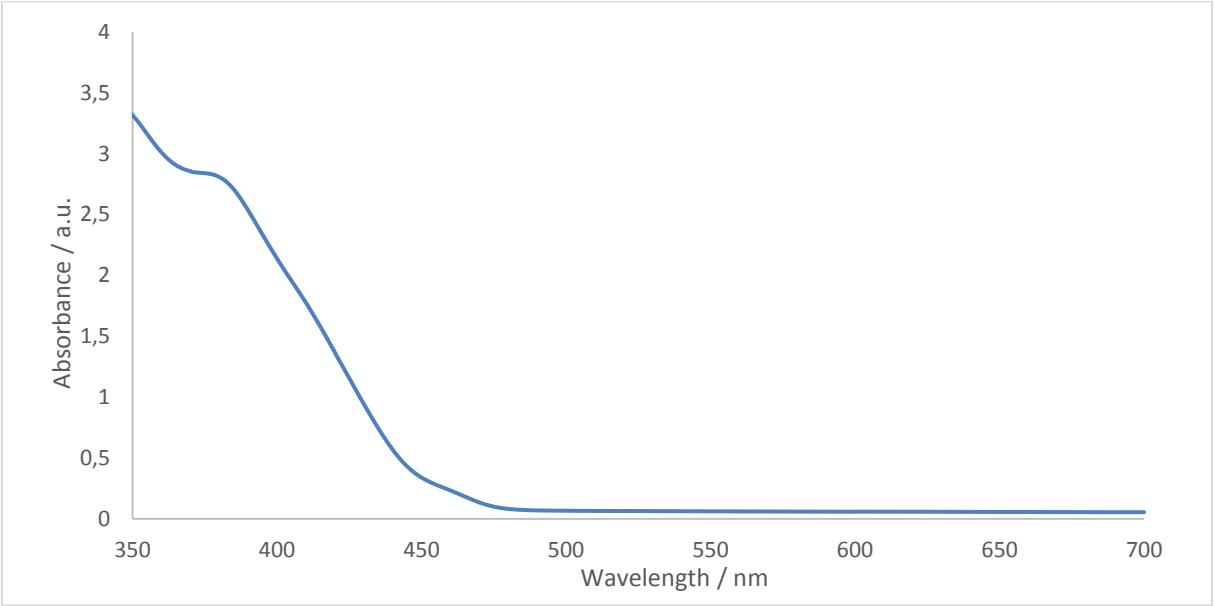
The structure of the photocatalyst **[Ir-F]** employed in this study and the emission wavelength used to calculate the quenching percentage (F) is shown in Figure S3. UV/vis absorption spectra and extinction coefficients at 455 nm and 365 nm for the selected photocatalyst can be found in Figure S4.



$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$
(**[Ir-F]**)
λ_{em} = 472 nm

Figure S3. Structure of photocatalyst **[Ir-F]** and wavelength used to calculate quenching fraction (F).

$[Ir(dF(CF_3)ppy)_2(dtbbpy))(PF_6)$ ([Ir-F])



Extinction coefficient:

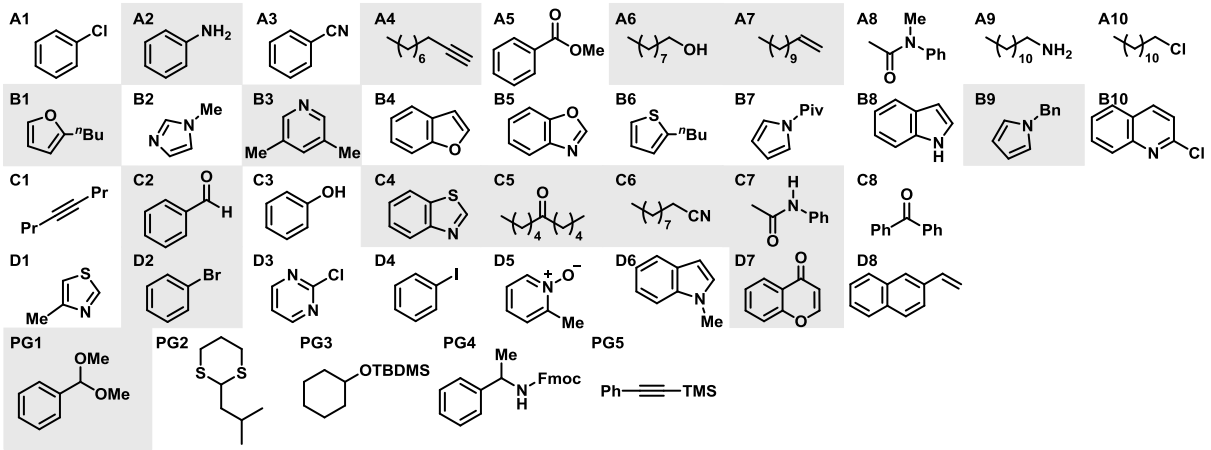
Irradiation wavelength / nm	Extinction coefficient ϵ / L mol^{-1} cm^{-1}
455	376
365	5519

Figure S4. UV/vis absorption spectra and extinction coefficients at 365 nm and 455 nm for $[Ir(dF(CF_3)ppy)_2(dtbbpy))(PF_6)$ (**[Ir-F]**). The concentration of the photocatalyst was 0.5 mM. Extinction coefficients were determined using three data points.

Results of the Luminescence Quenching Screening and Spectra

The quenching fractions F obtained at the wavelengths defined in Figure S3 with the different additives are shown in Table 1 below using $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$ (**[Ir-F]**). An F value of 70% or greater is displayed in a green circle, values between 26% and 69% in an amber circle, and F values of 25% or lower in a red circle. The respective luminescence spectra for each combination are shown below.

Table S4. Quenching fractions F in % of different additives in the presence of $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$ (**[Ir-F]**).



	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
F	5	96	21	7	9	4	11	10	10	5

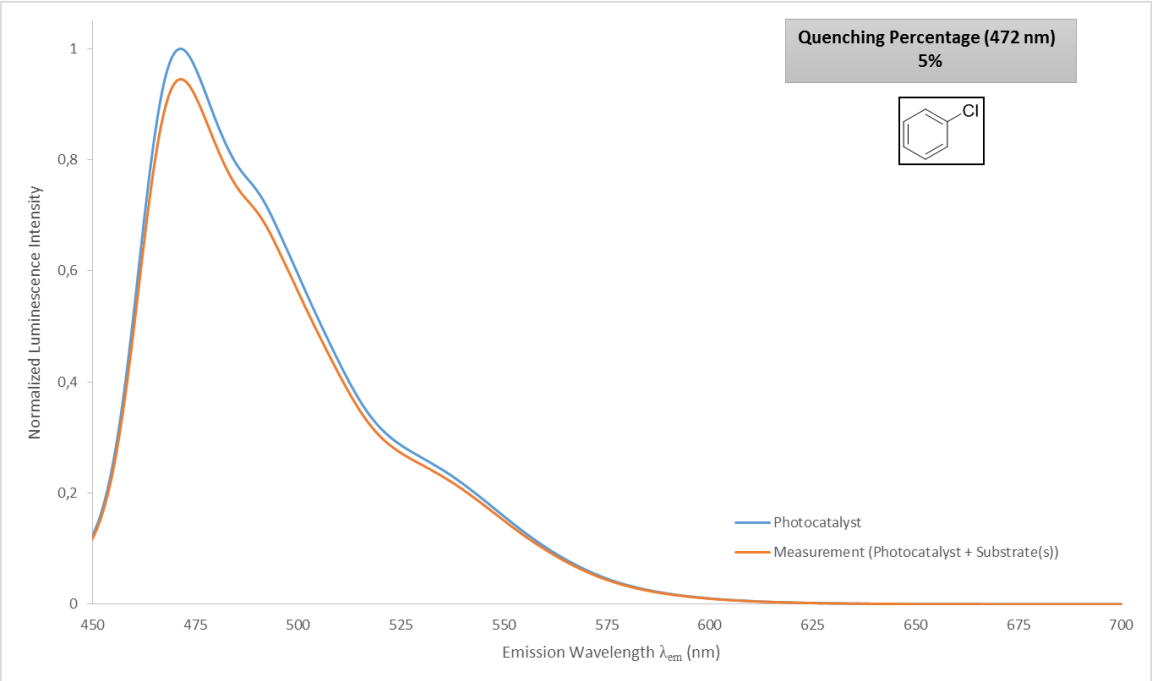
	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10
F	25	31	18	41	14	15	88	95	13	91

	C1	C2	C3	C4	C5	C6	C7	C8
F	7	2	9	48	9	9	13	6

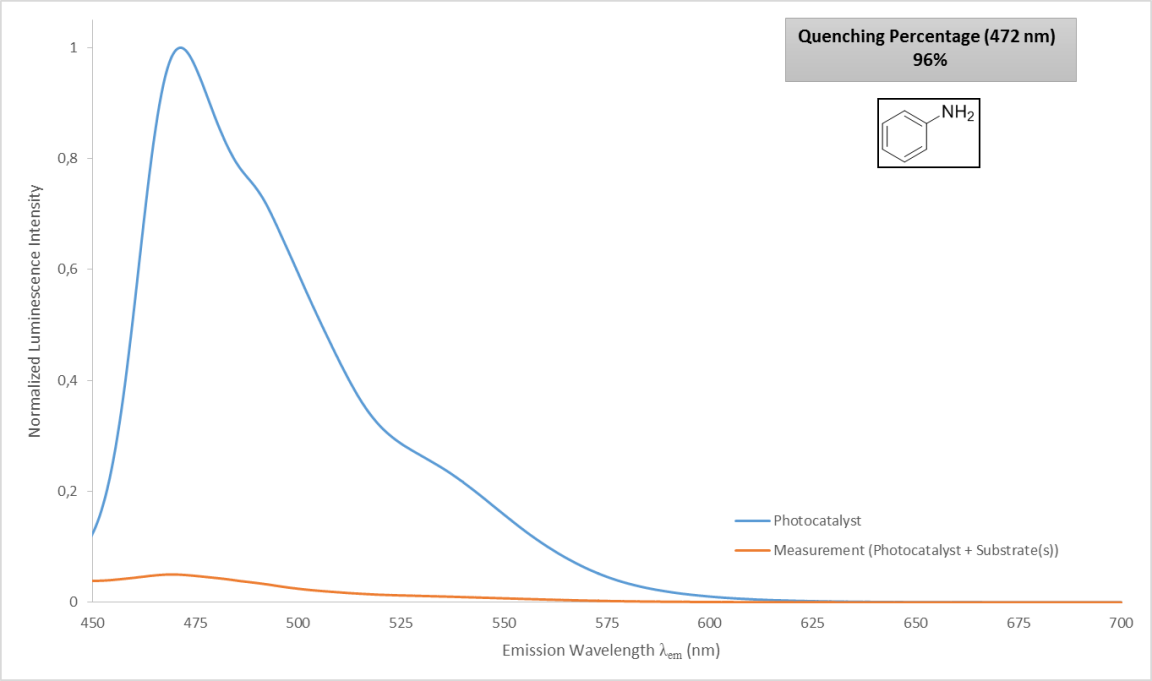
	D1	D2	D3	D4	D5	D6	D7	D8
F	0	0	3	4	97	97	37	90

	PG1	PG2	PG3	PG4	PG5
F	0	27	5	0	0

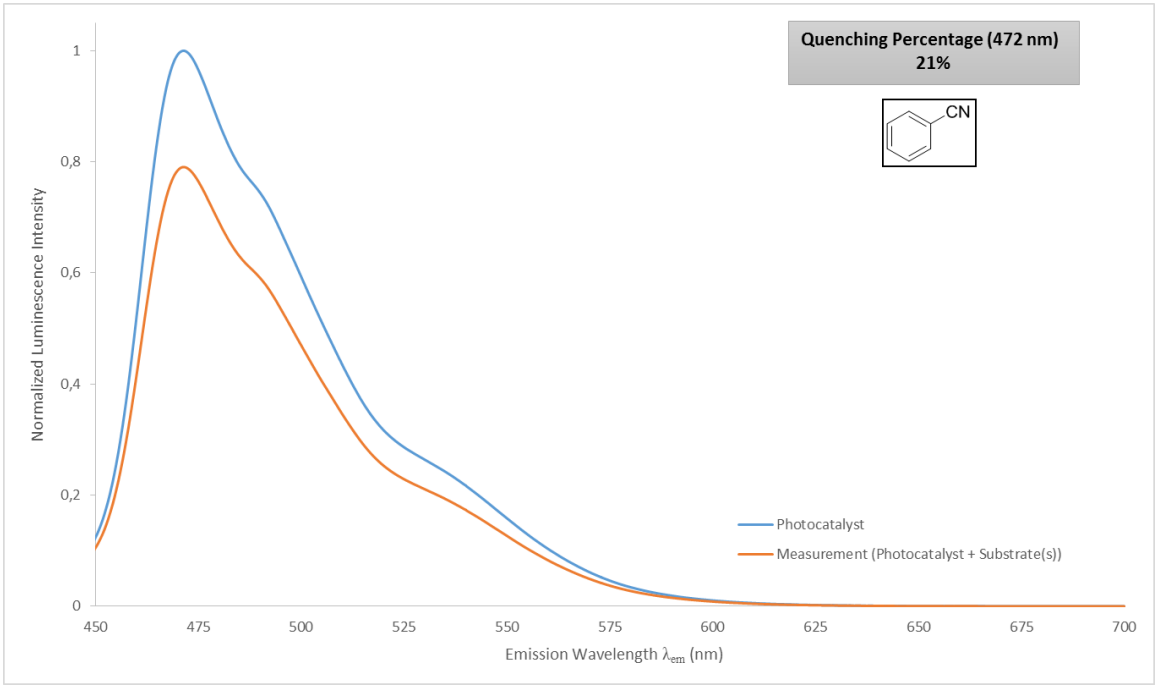
A1 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



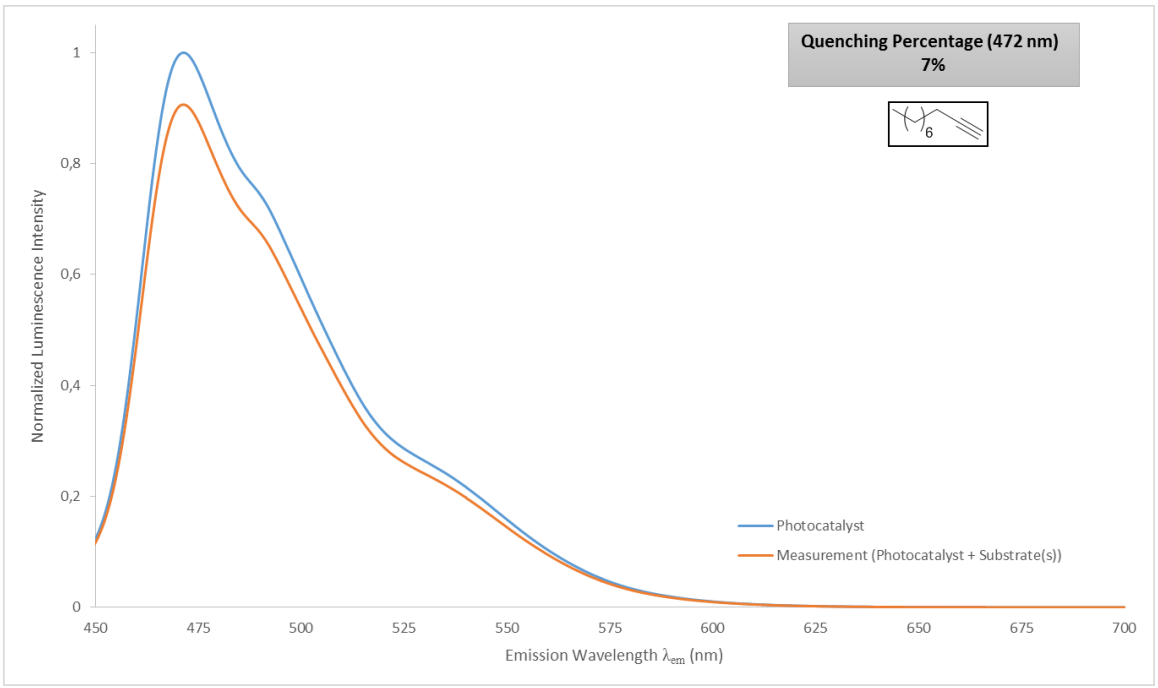
A2 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



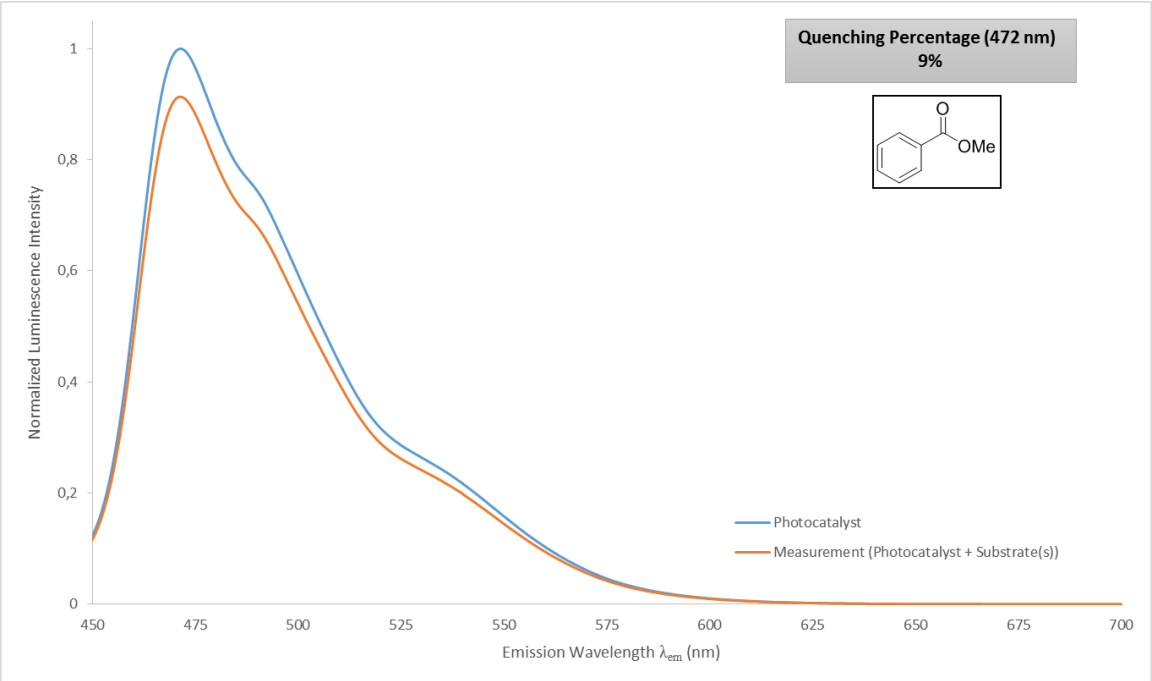
A3 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



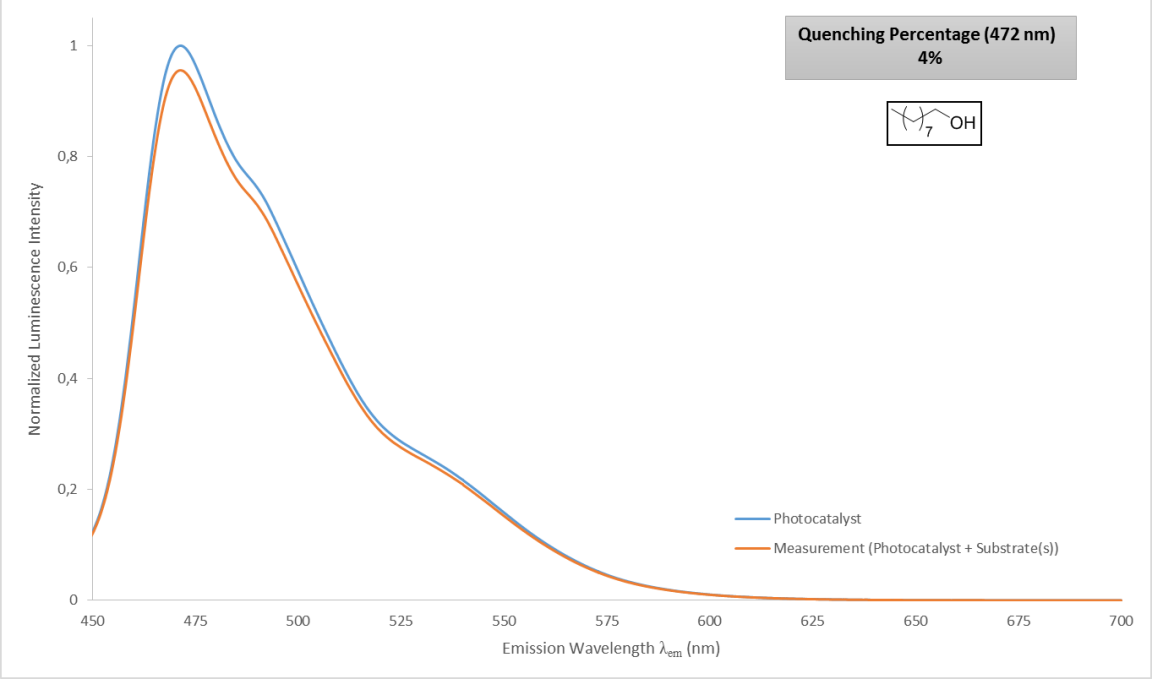
A4 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



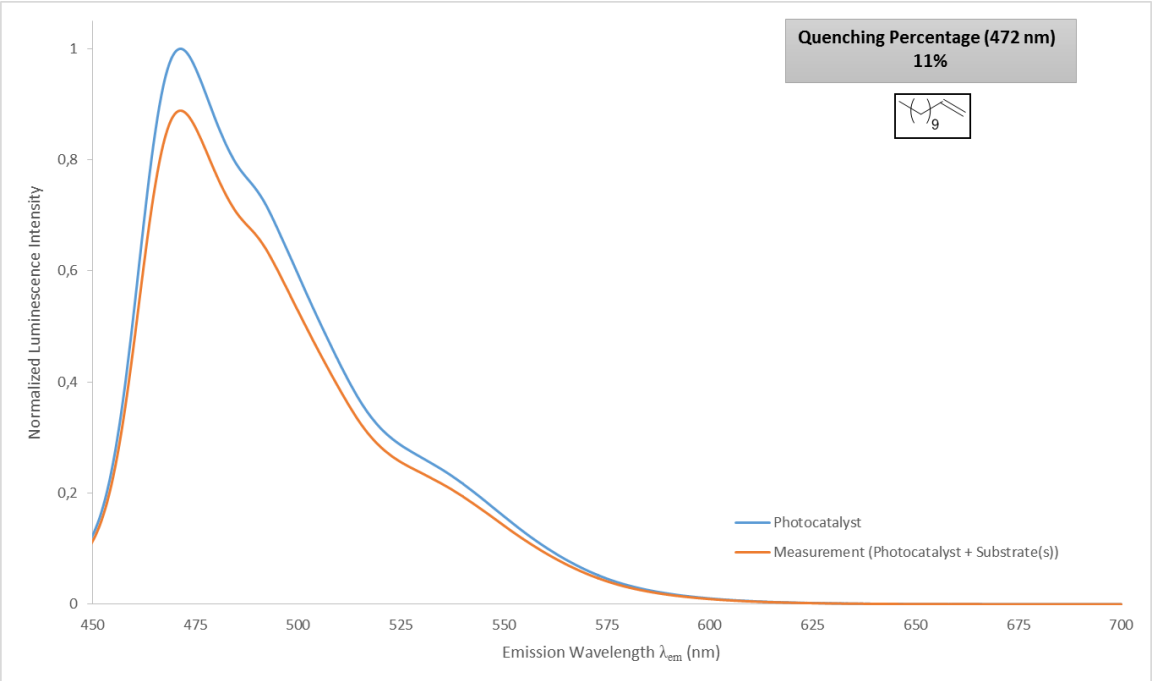
A5 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



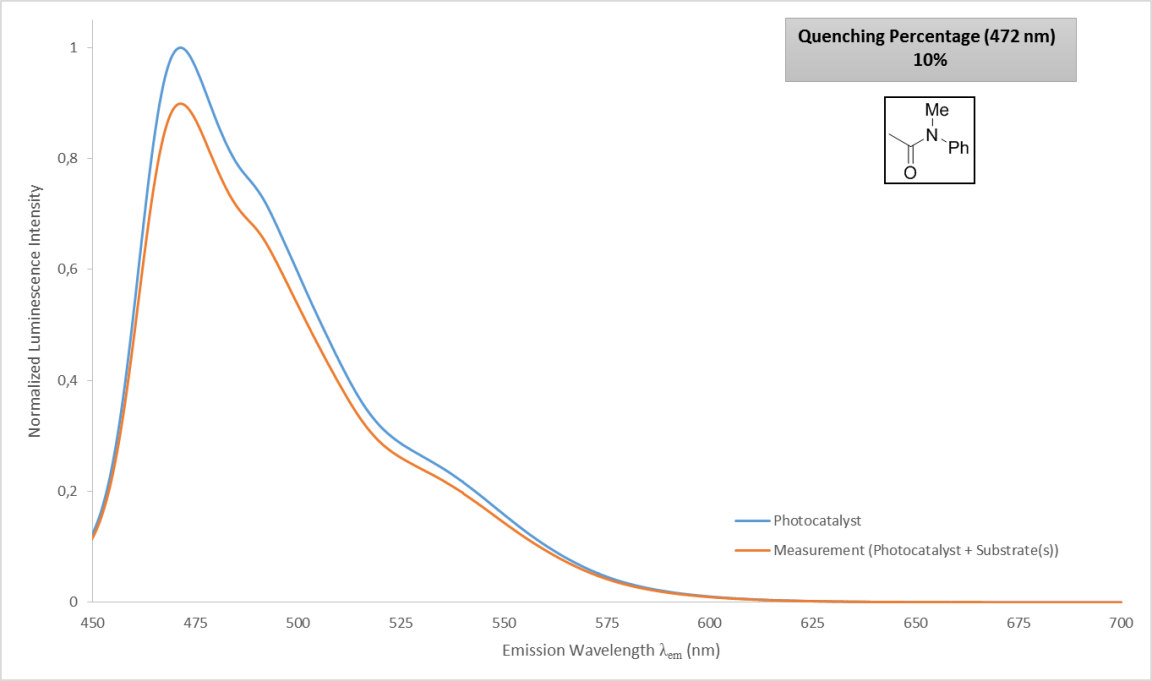
A6 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



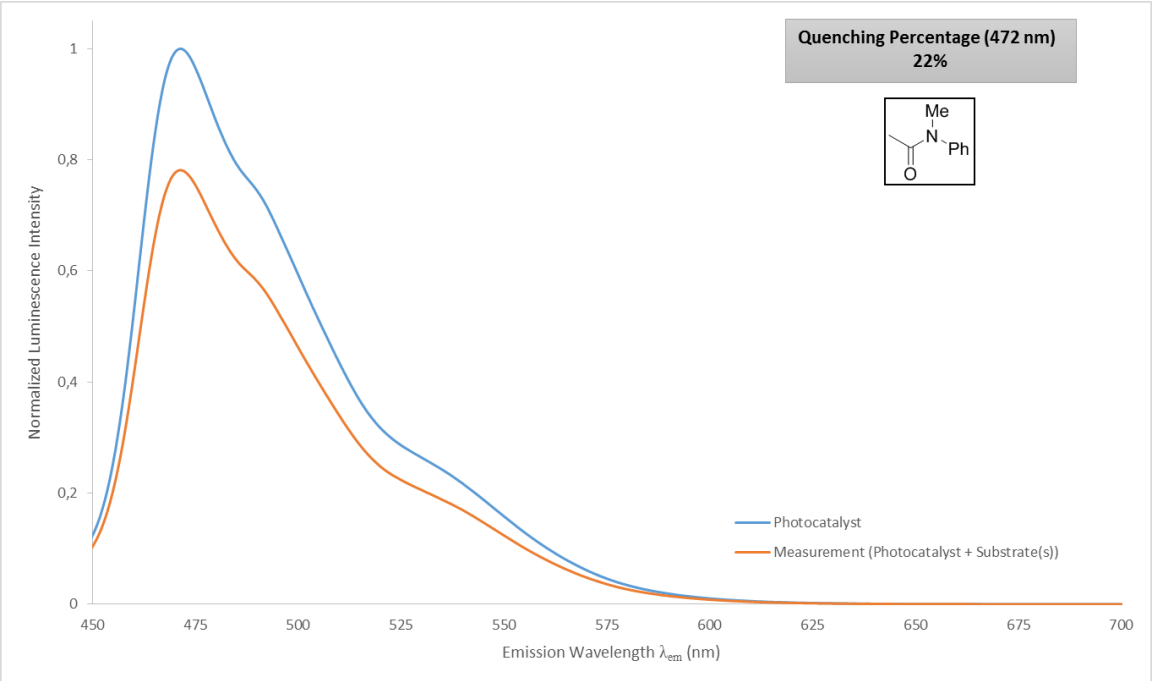
A7 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



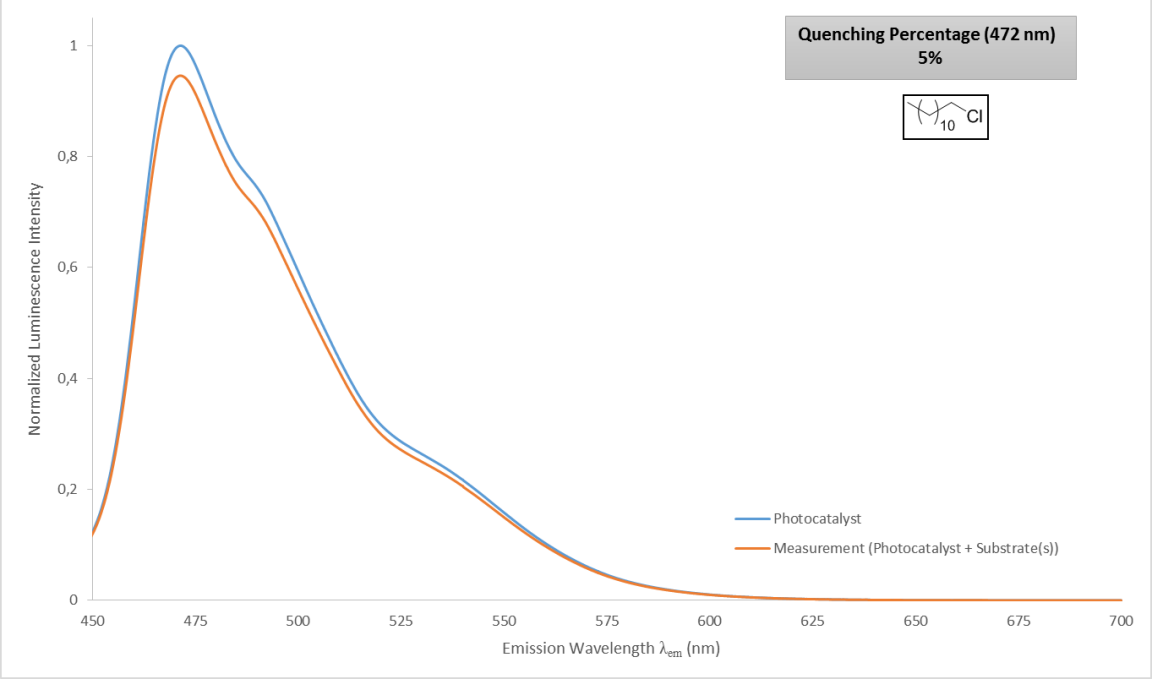
A8 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



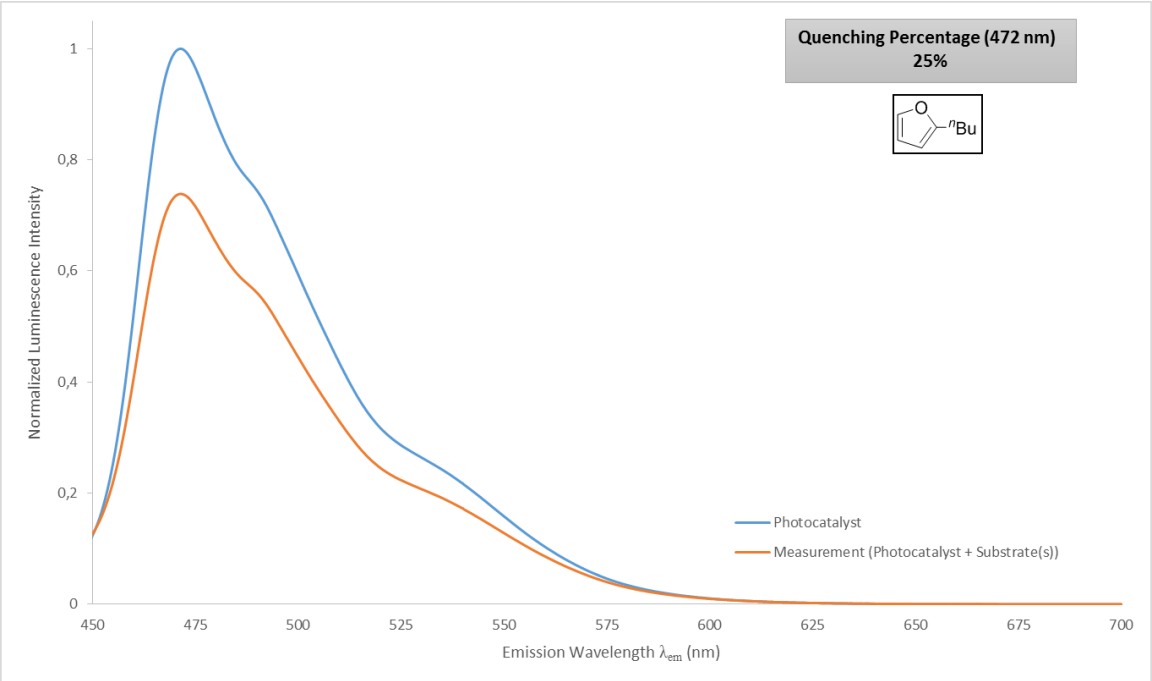
A9 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



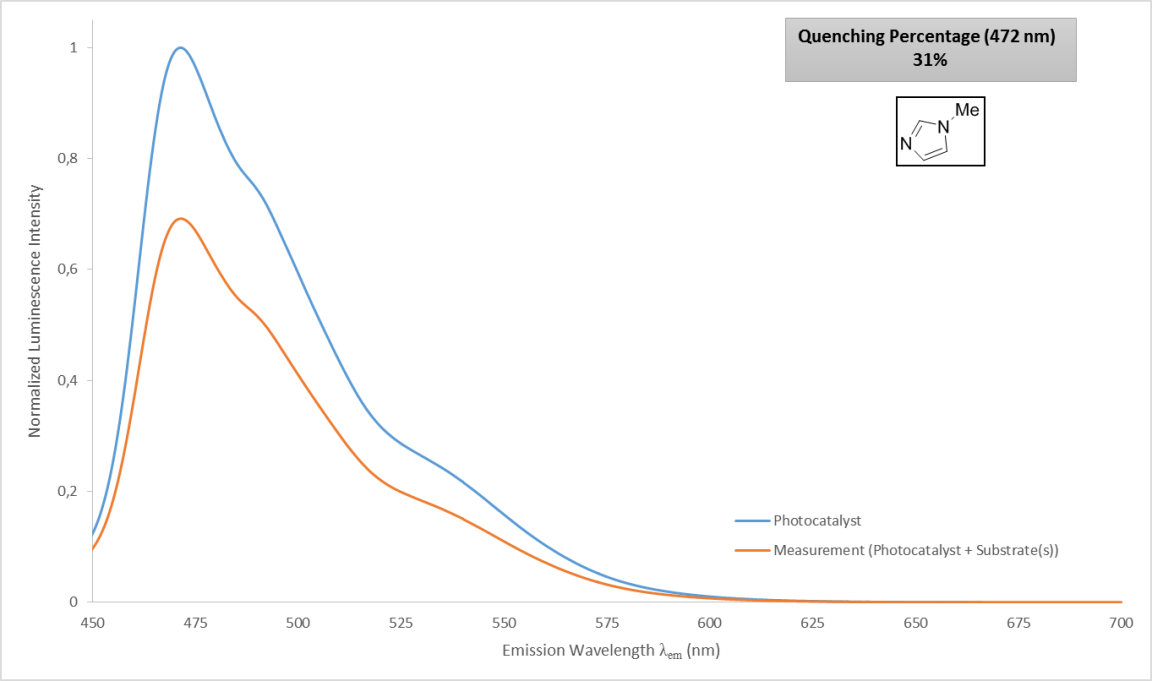
A10 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



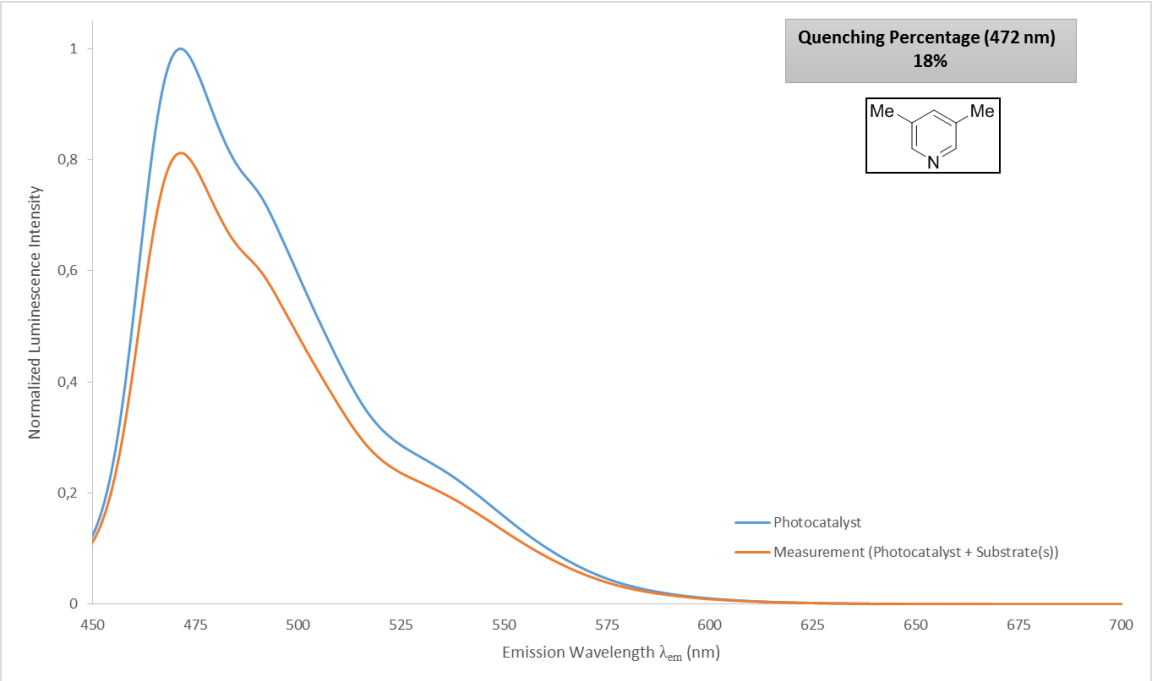
B1 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



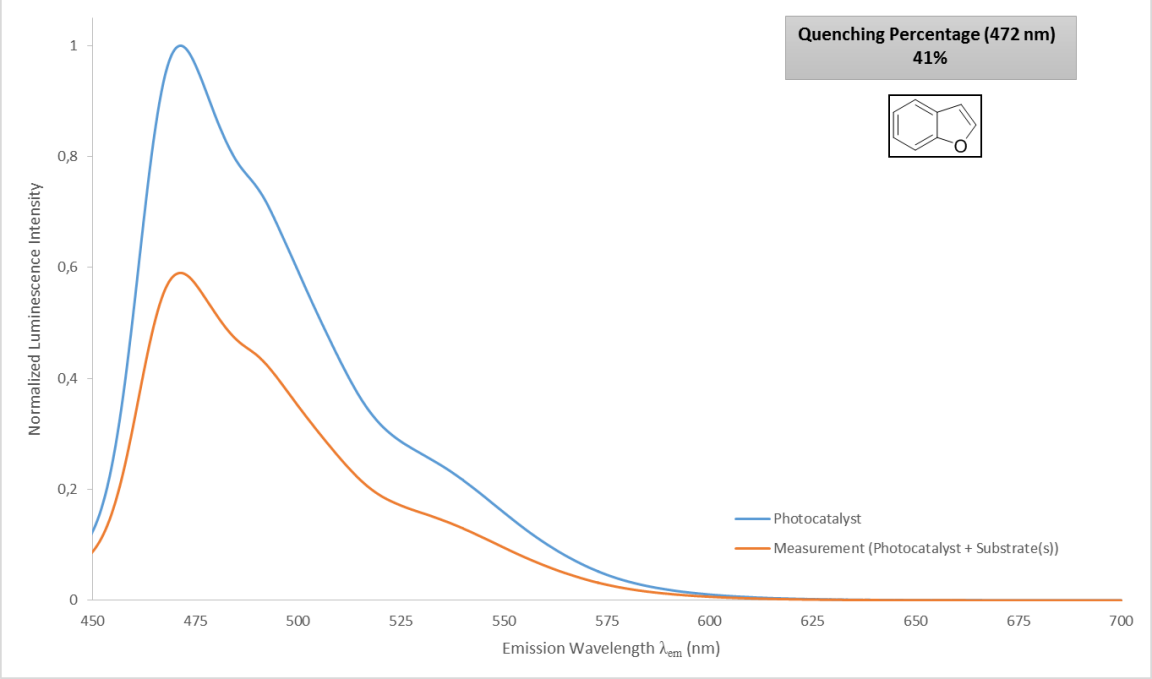
B2 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



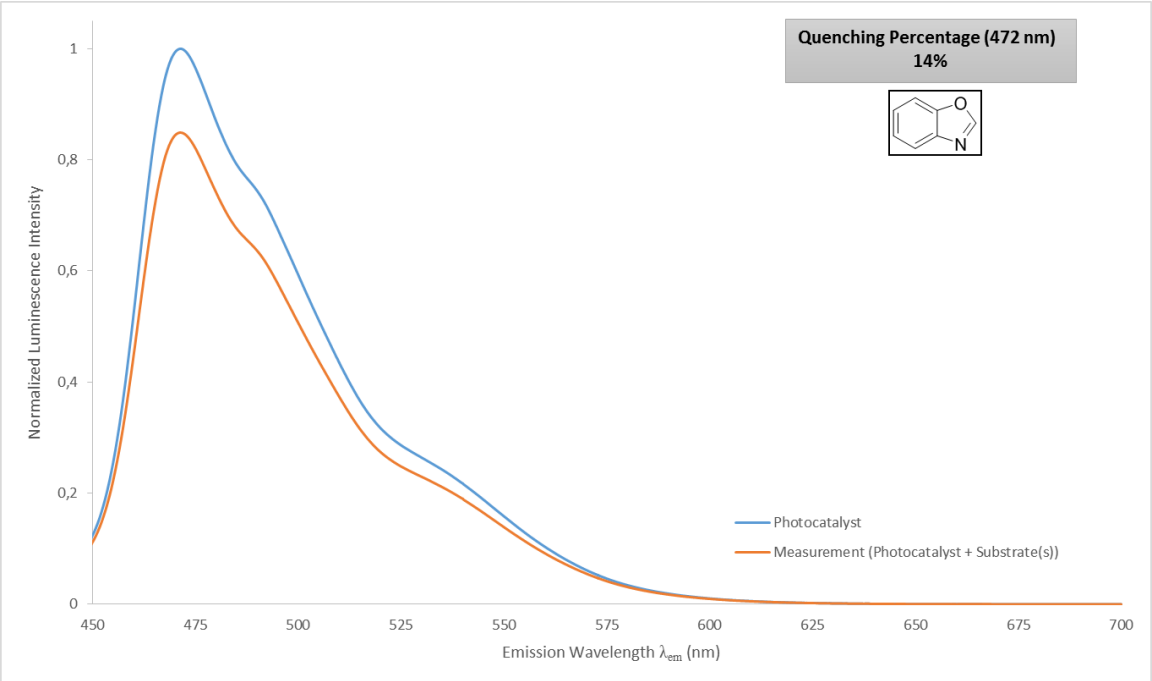
B3 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



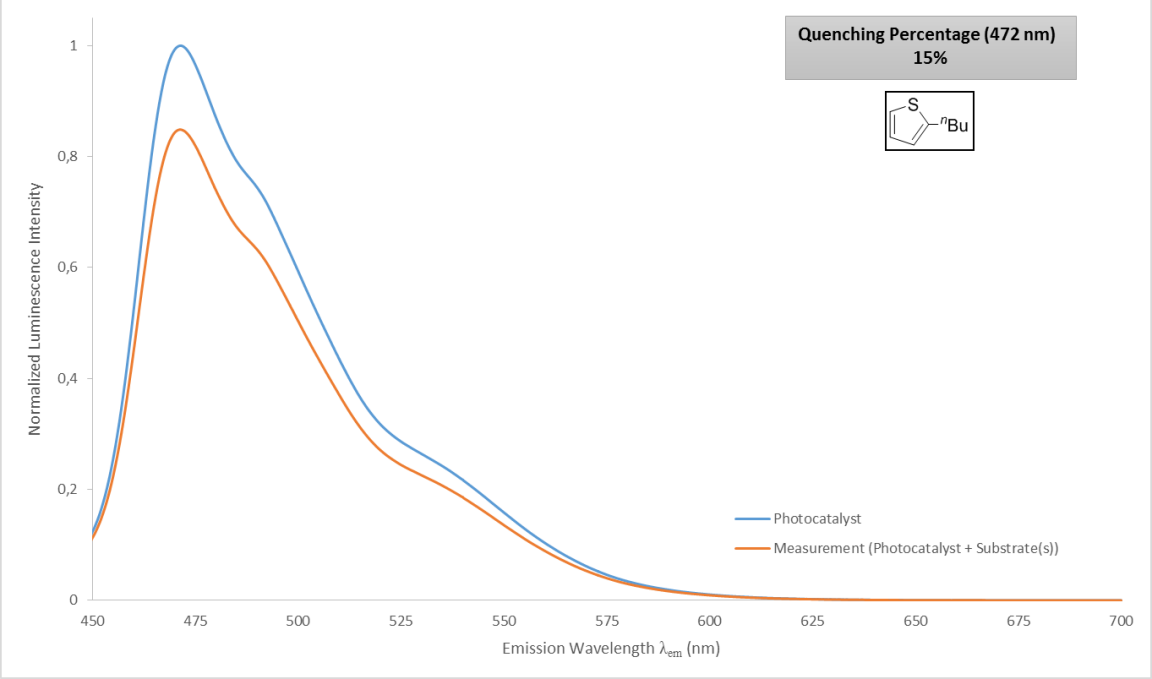
B4 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



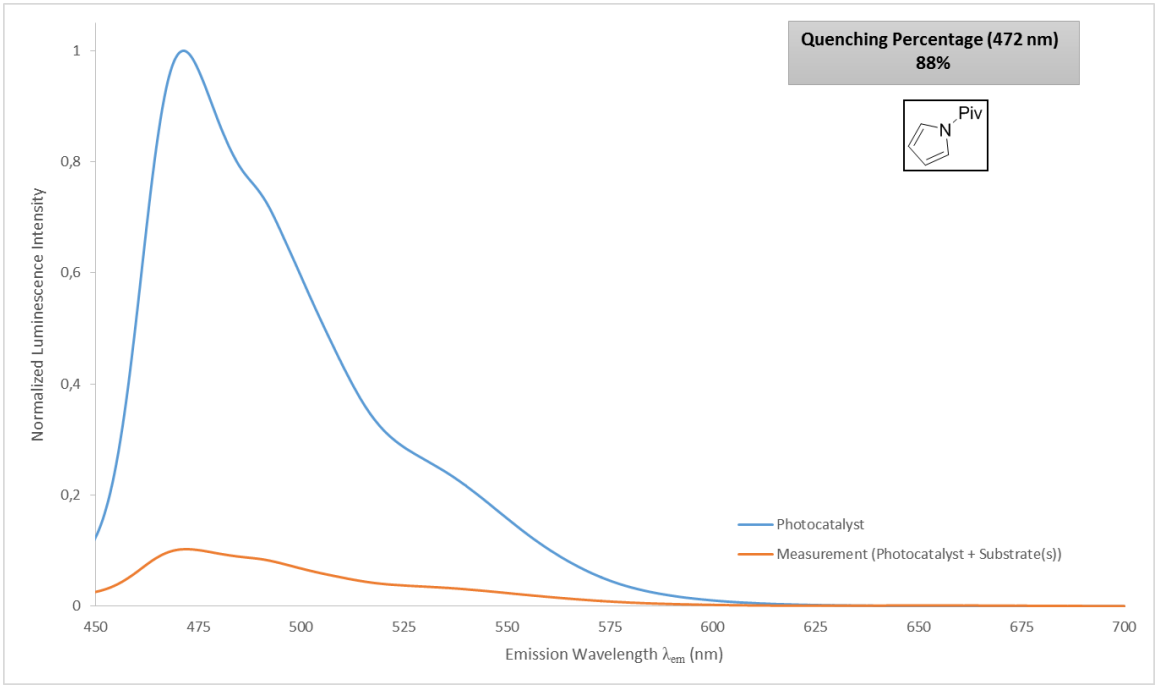
B5 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



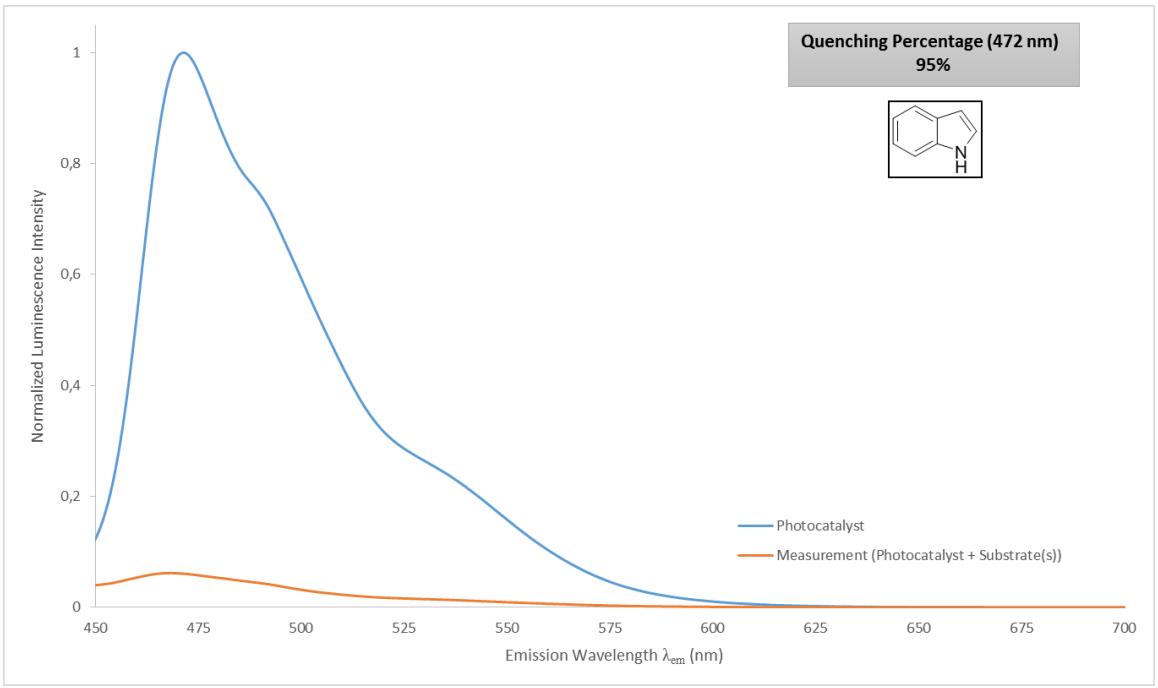
B6 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



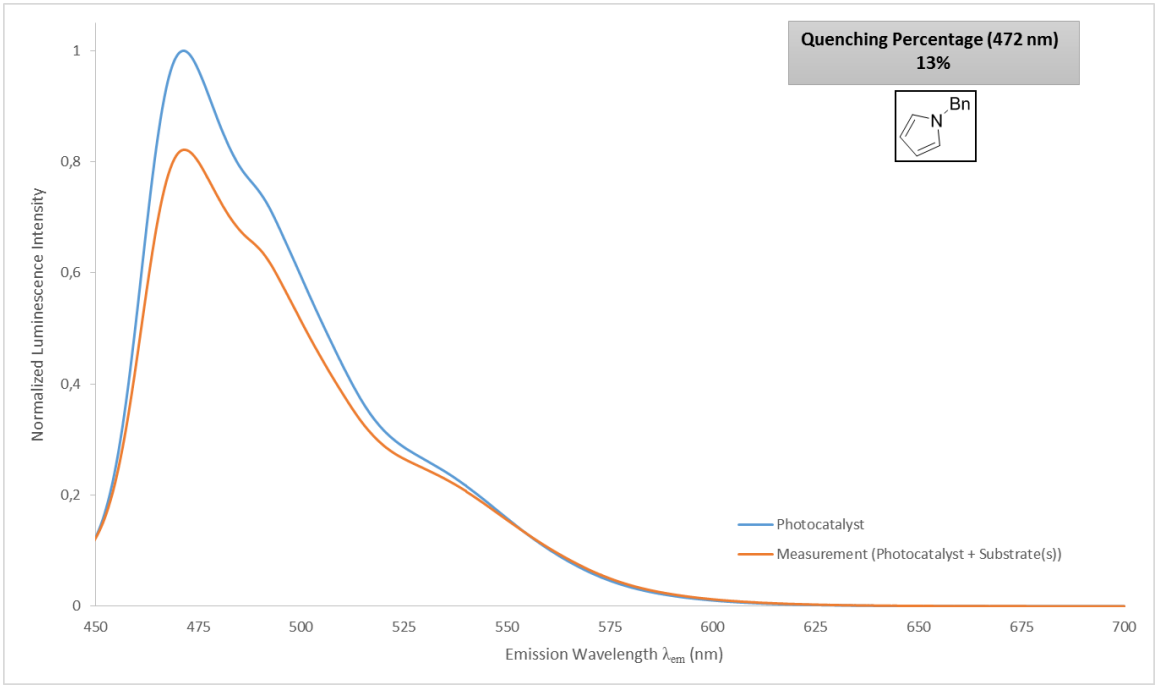
B7 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



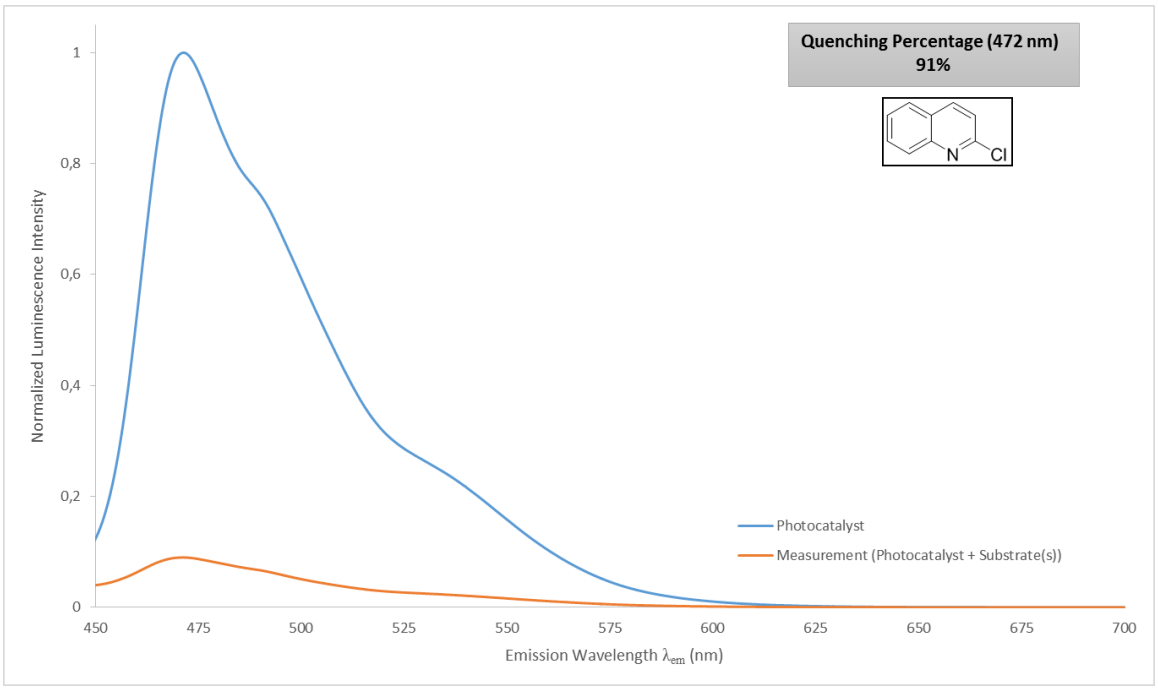
B8 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



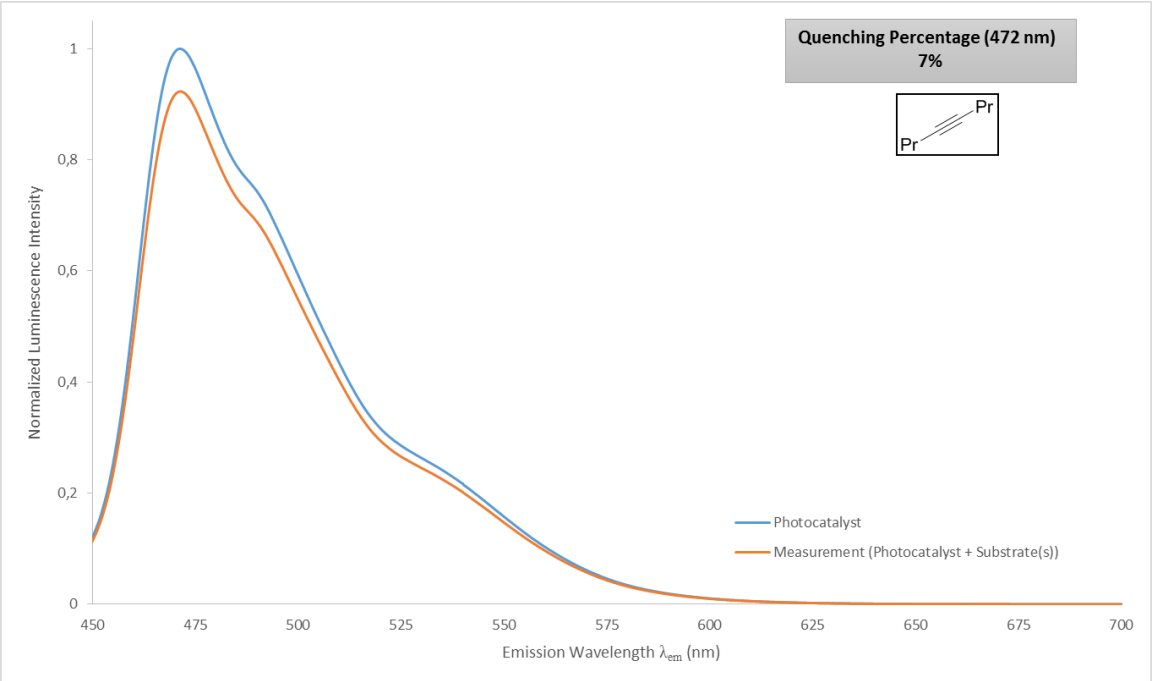
B9 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



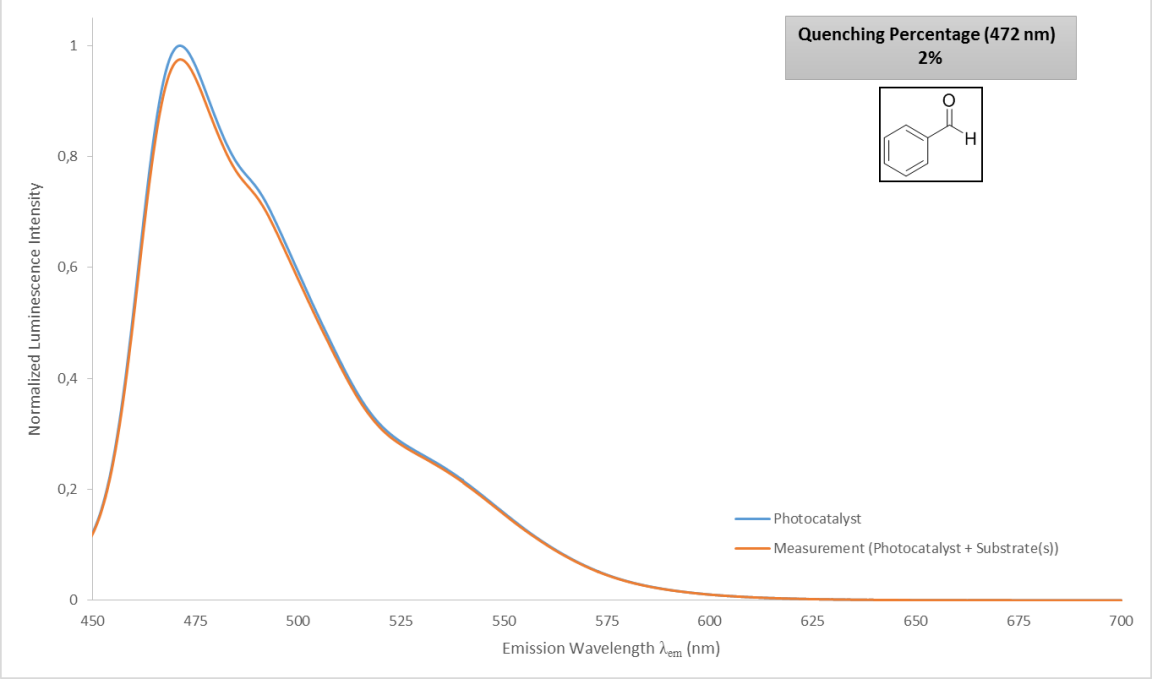
B10 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



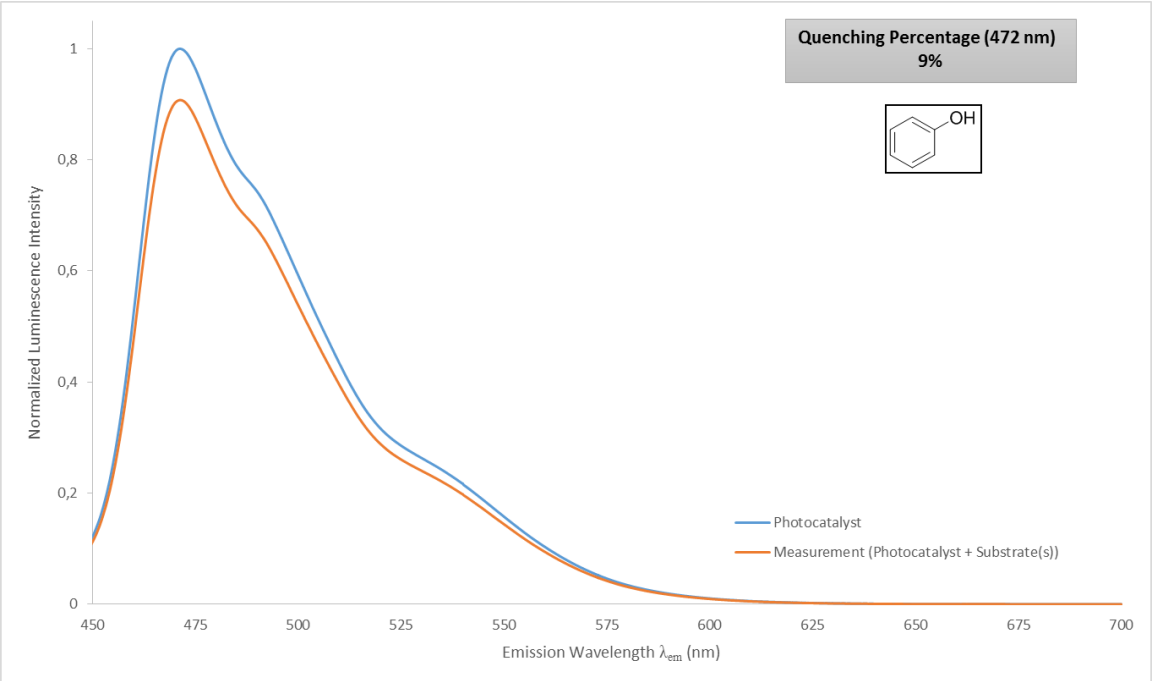
C1 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



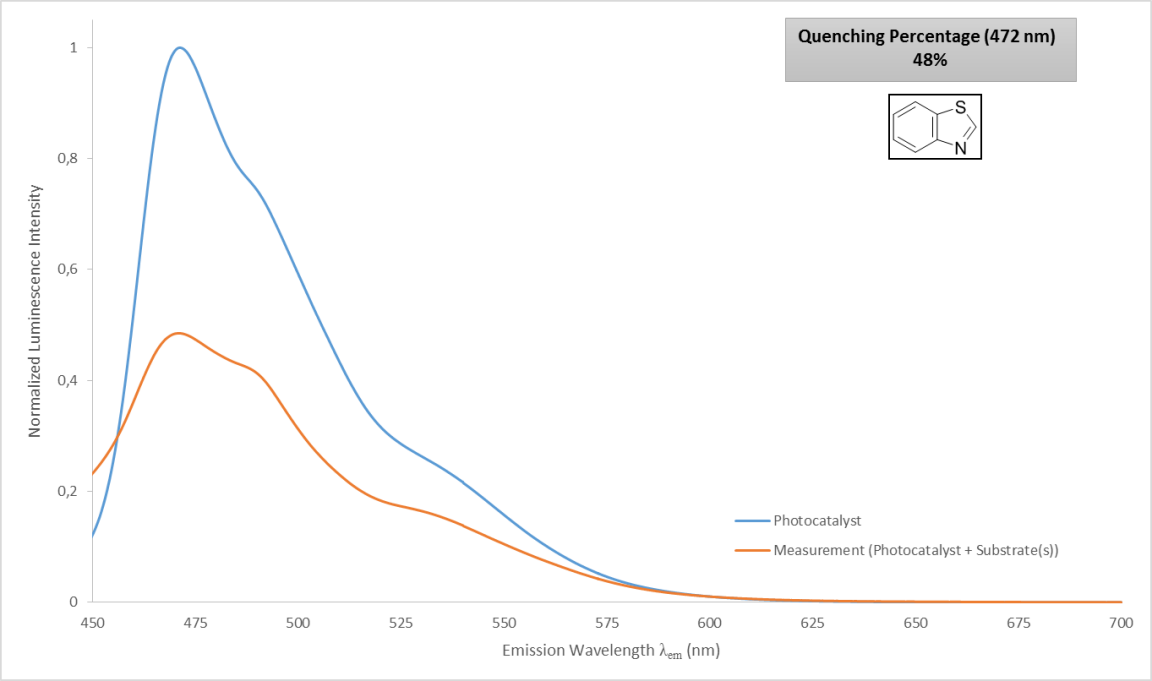
C2 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



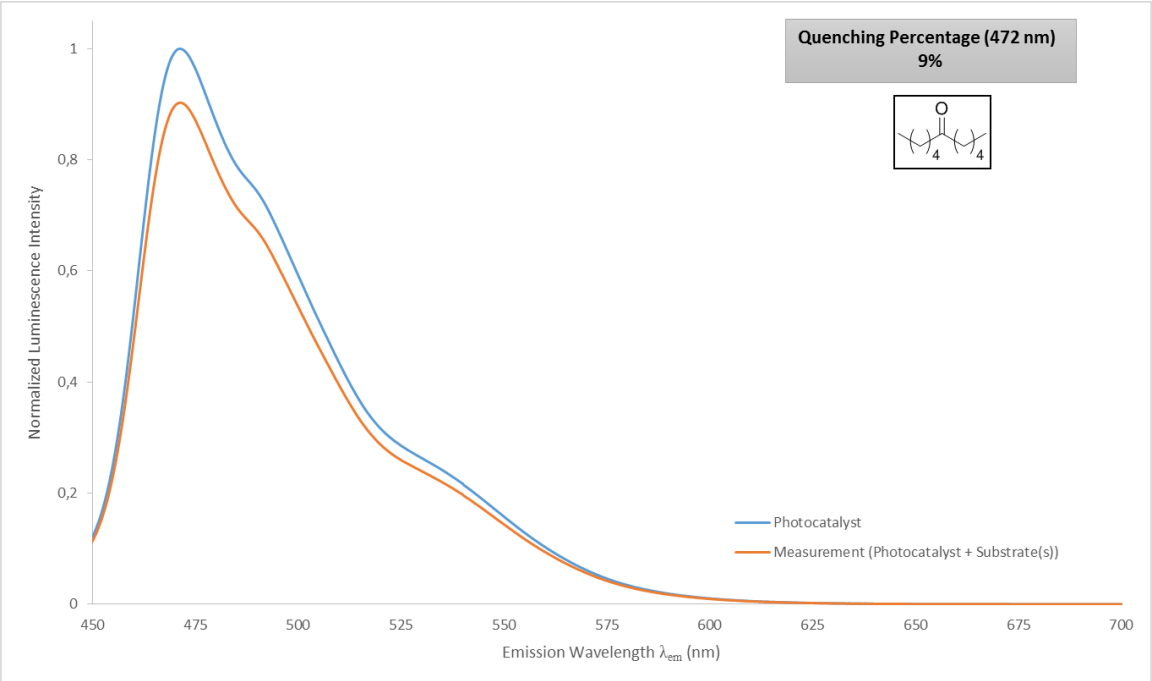
C3 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



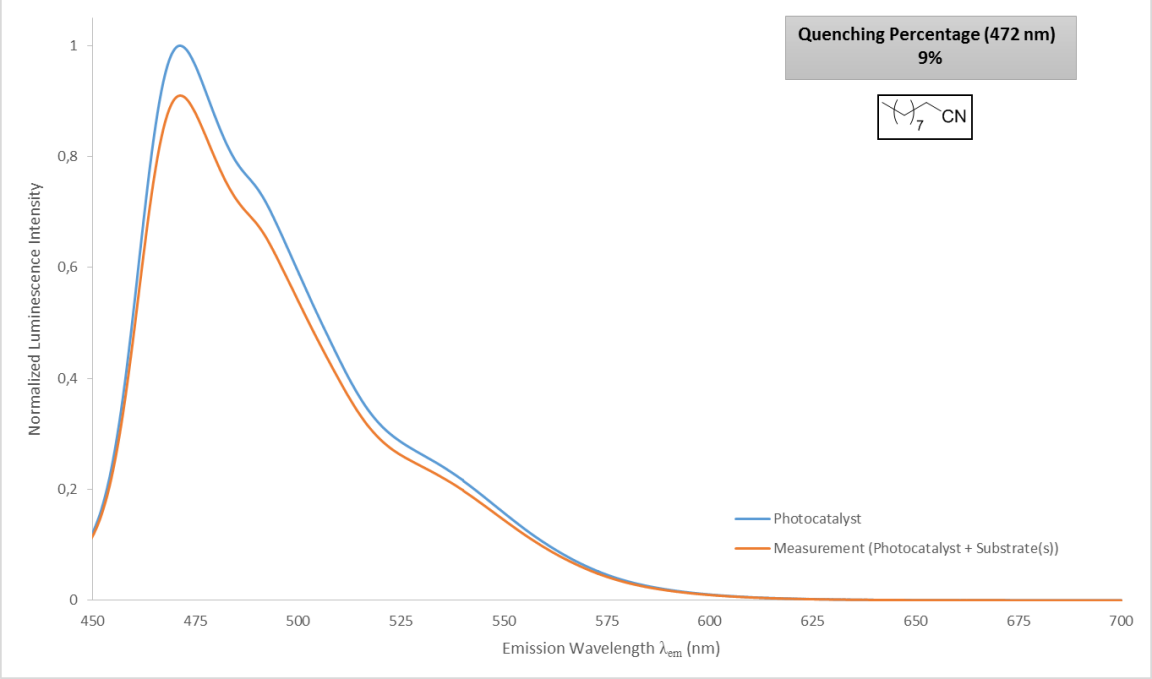
C4 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



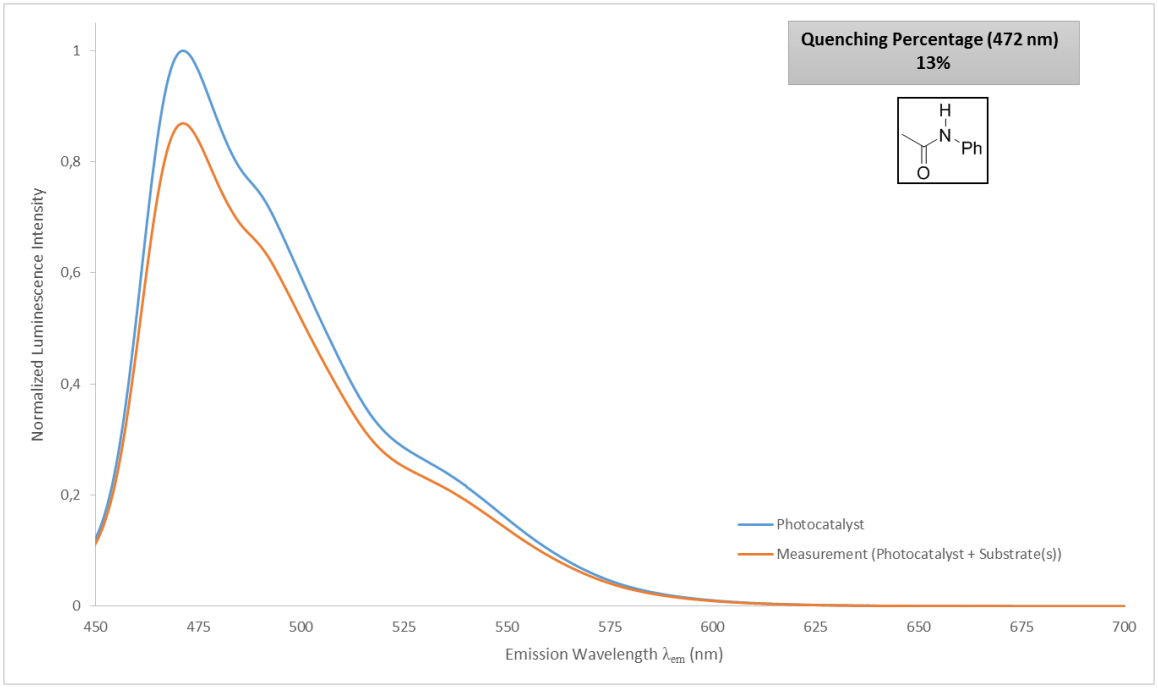
C5 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



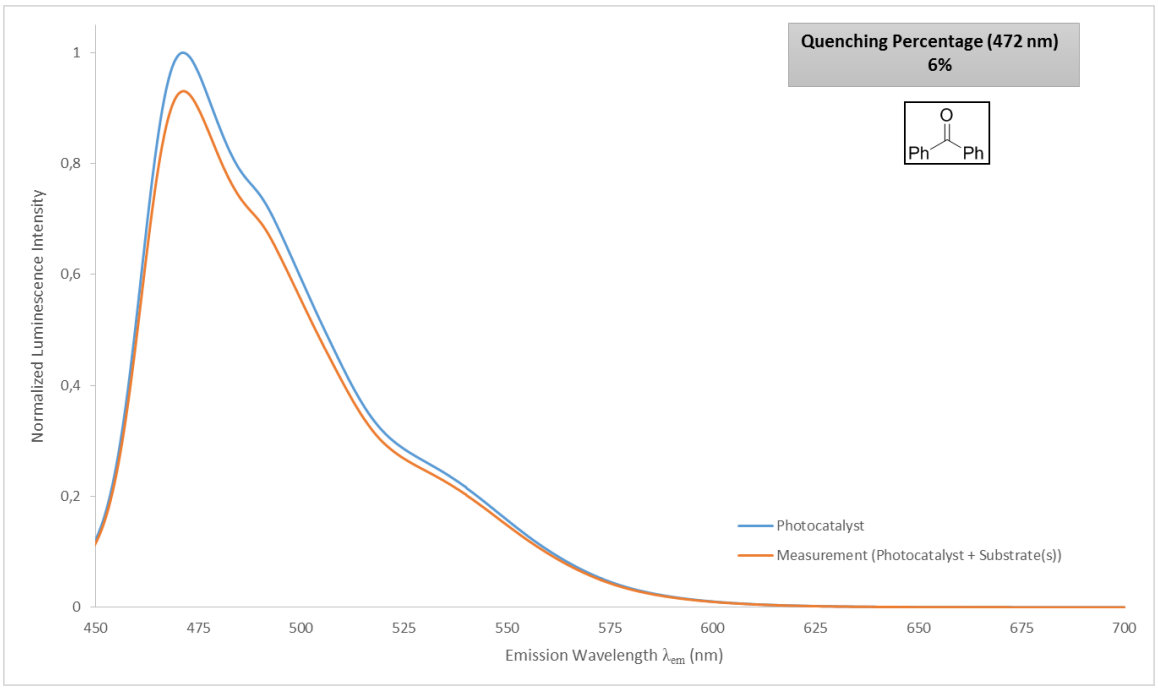
C6 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



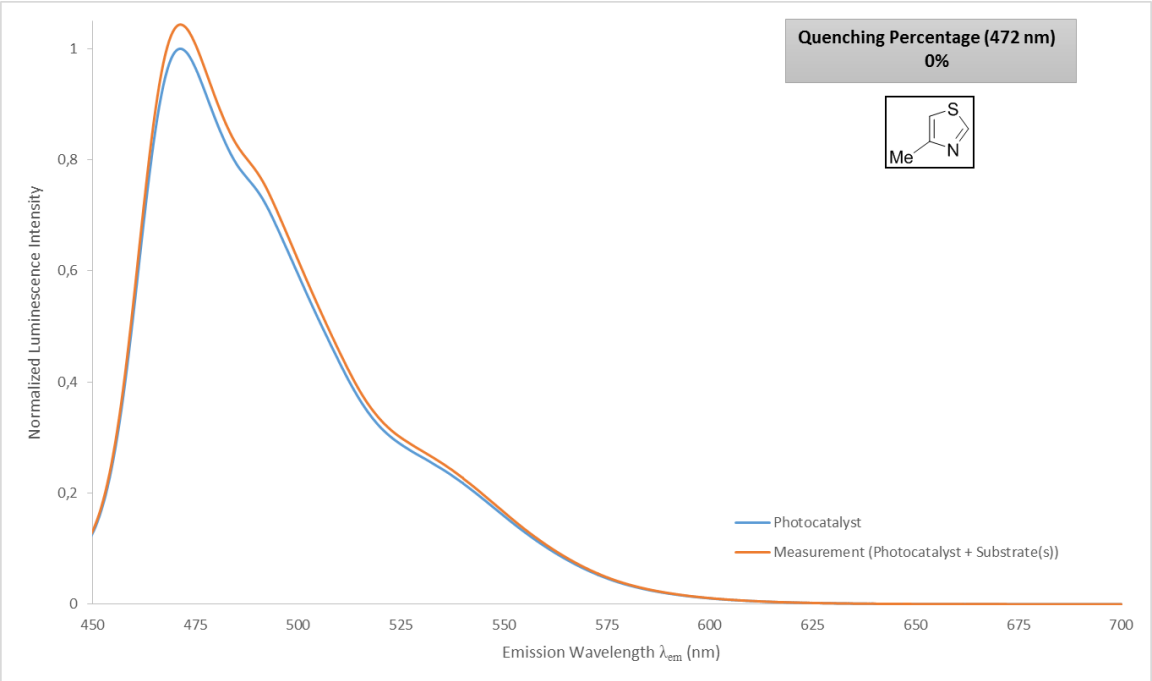
C7 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



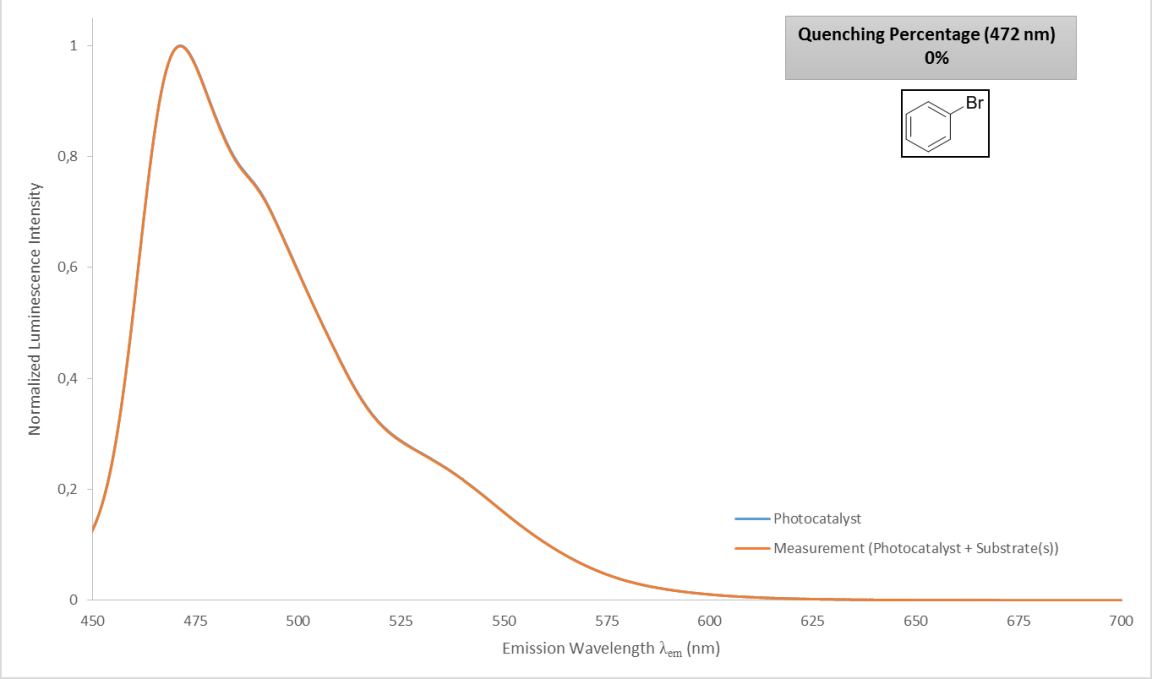
C8 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



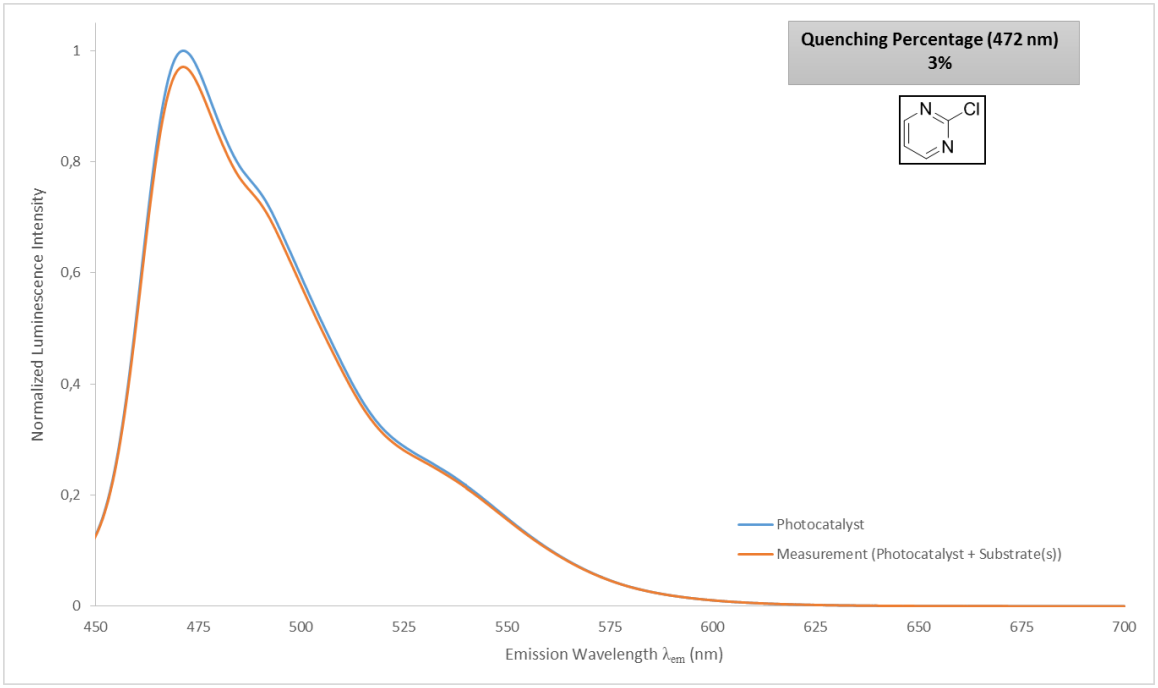
D1 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



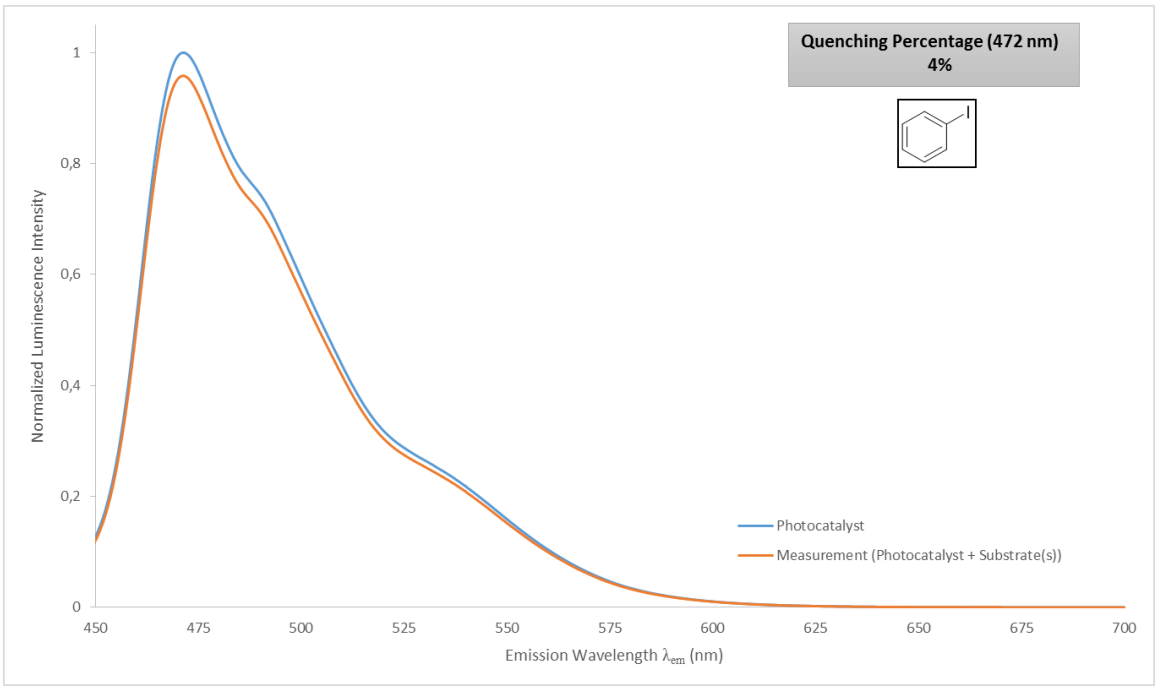
D2 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



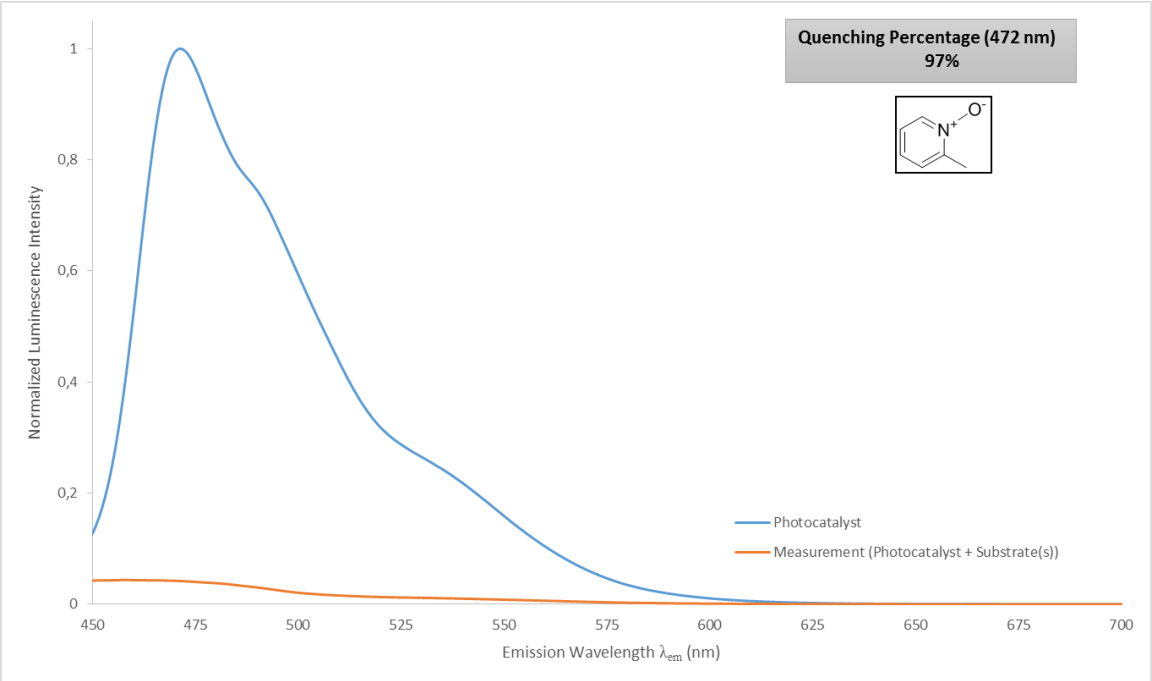
D3 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



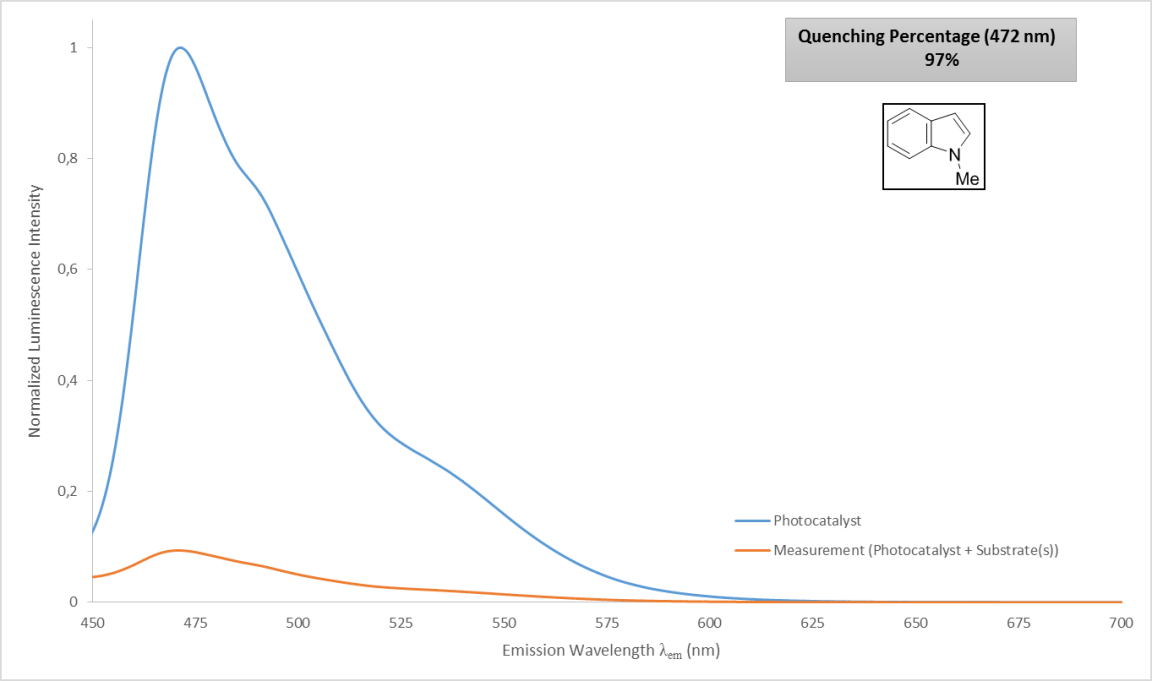
D4 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



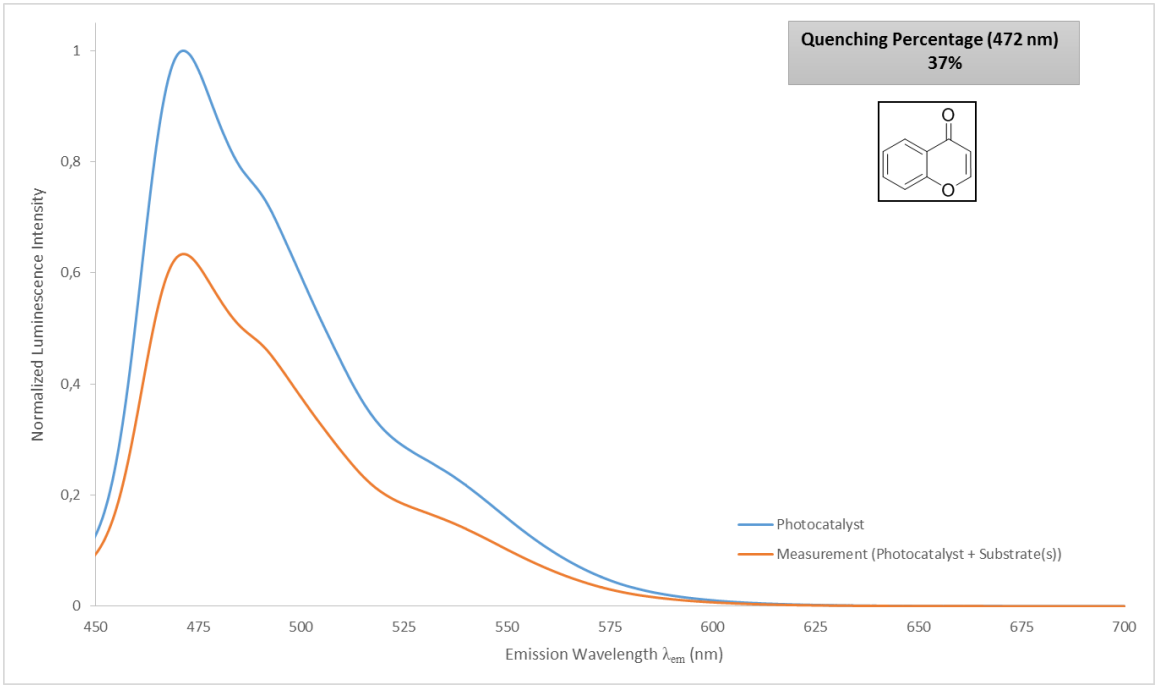
D5 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



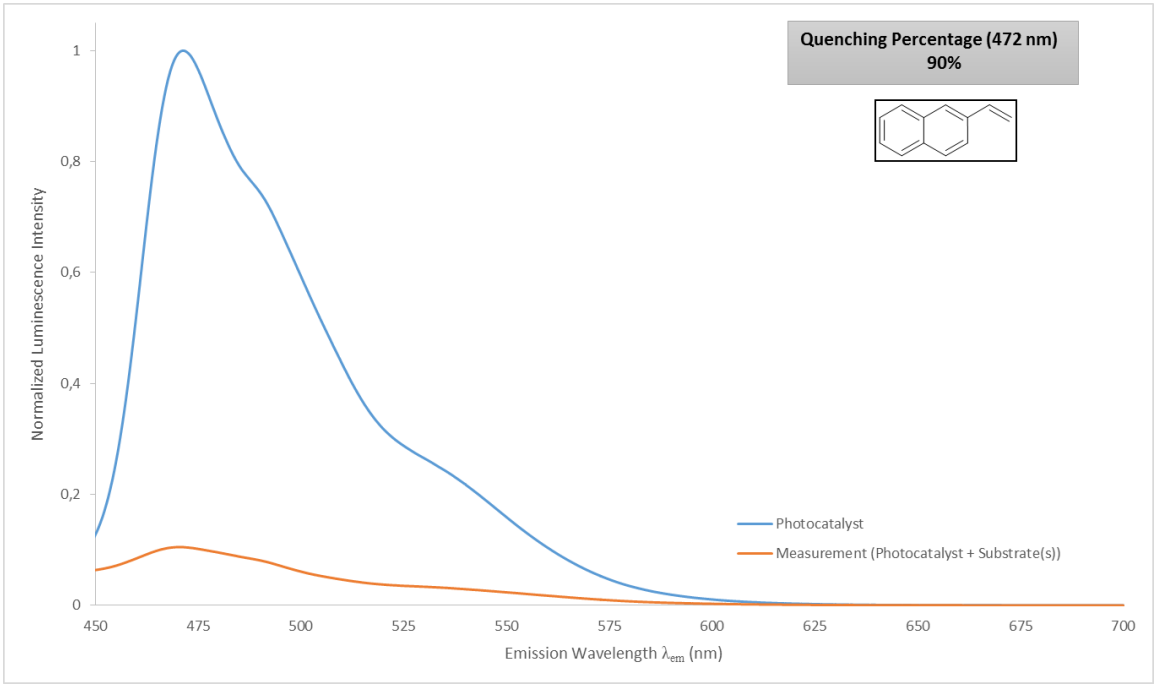
D6 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



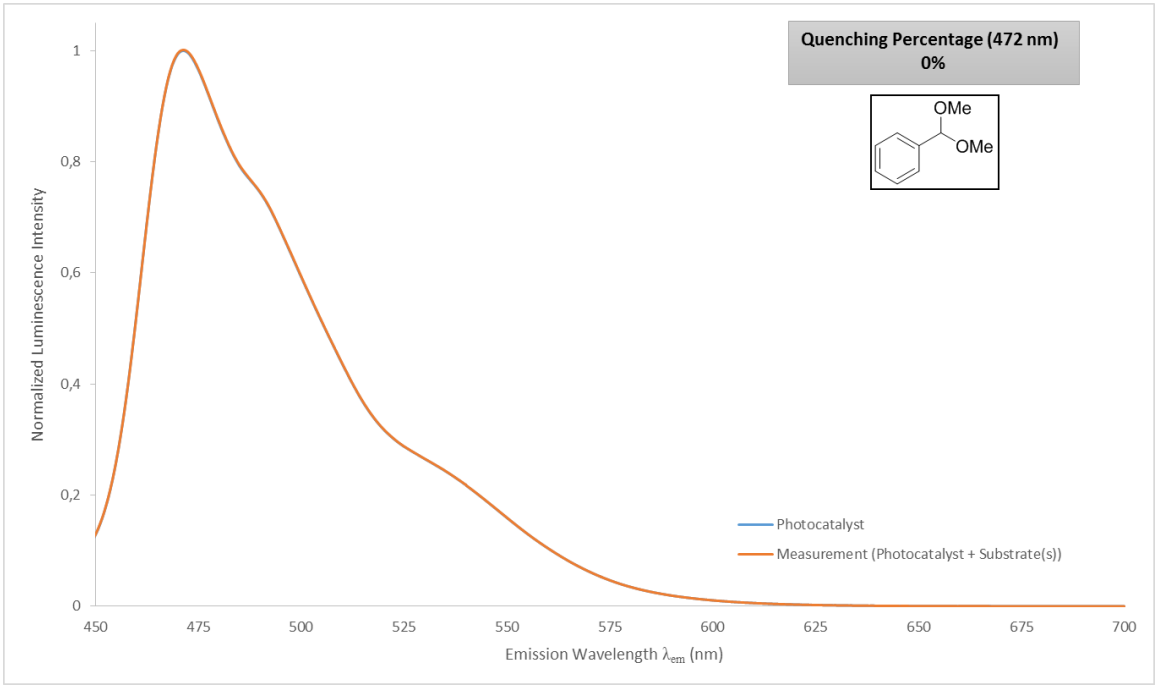
D7 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



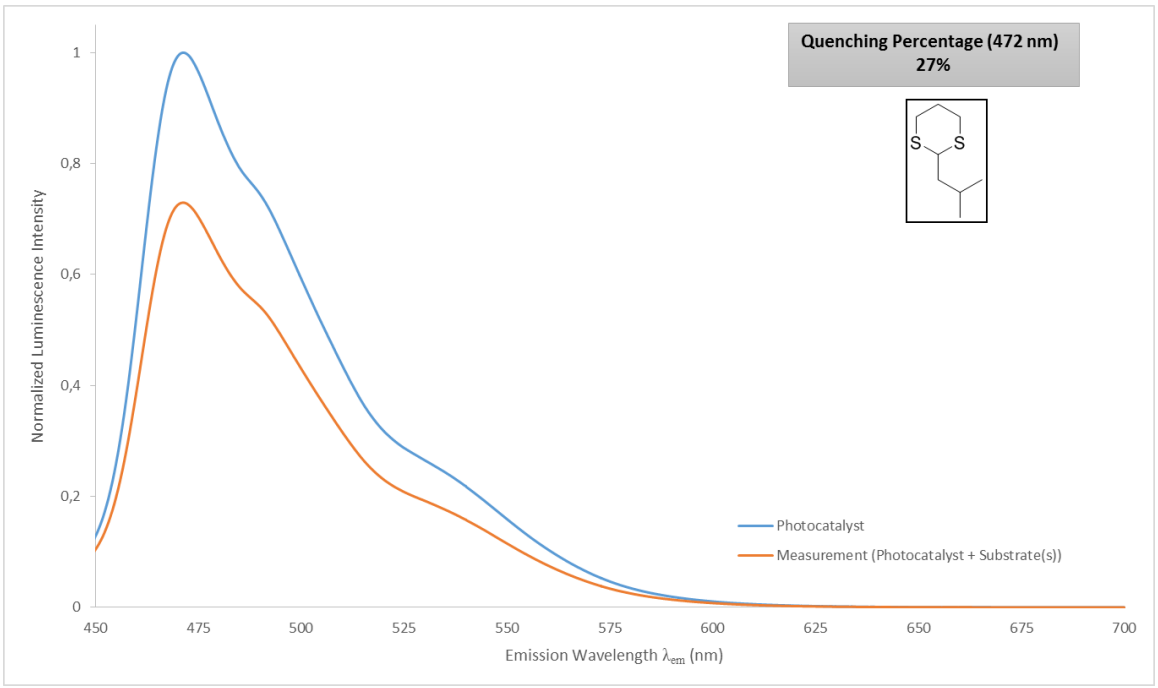
D8 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



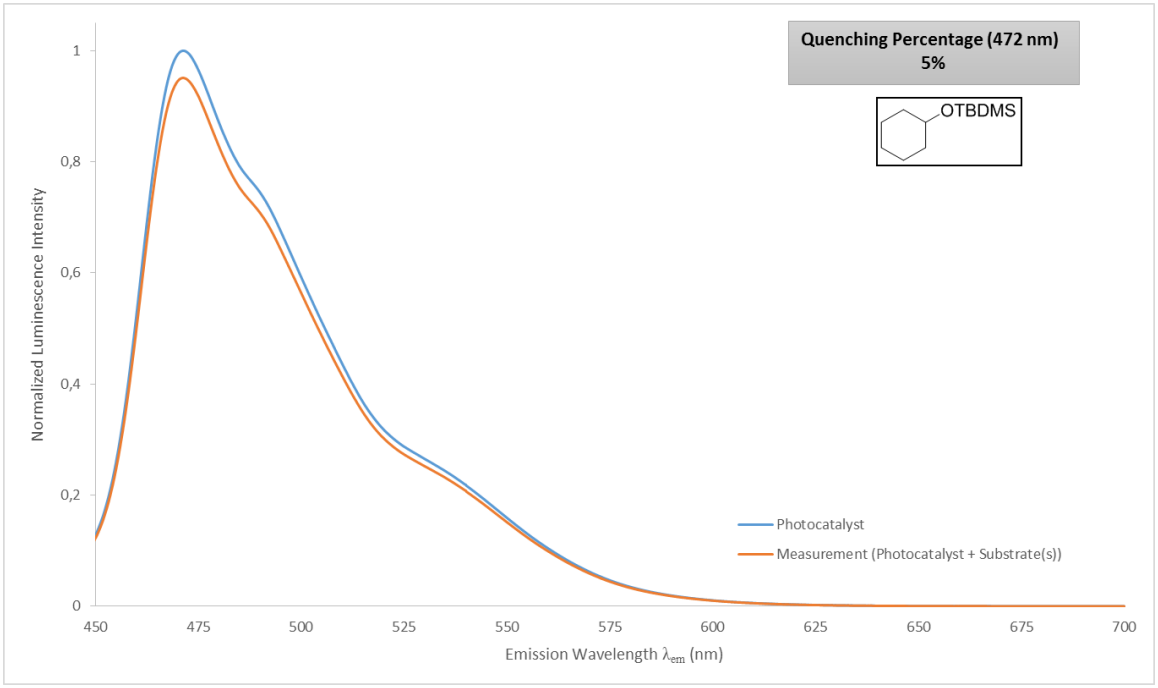
PG1 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



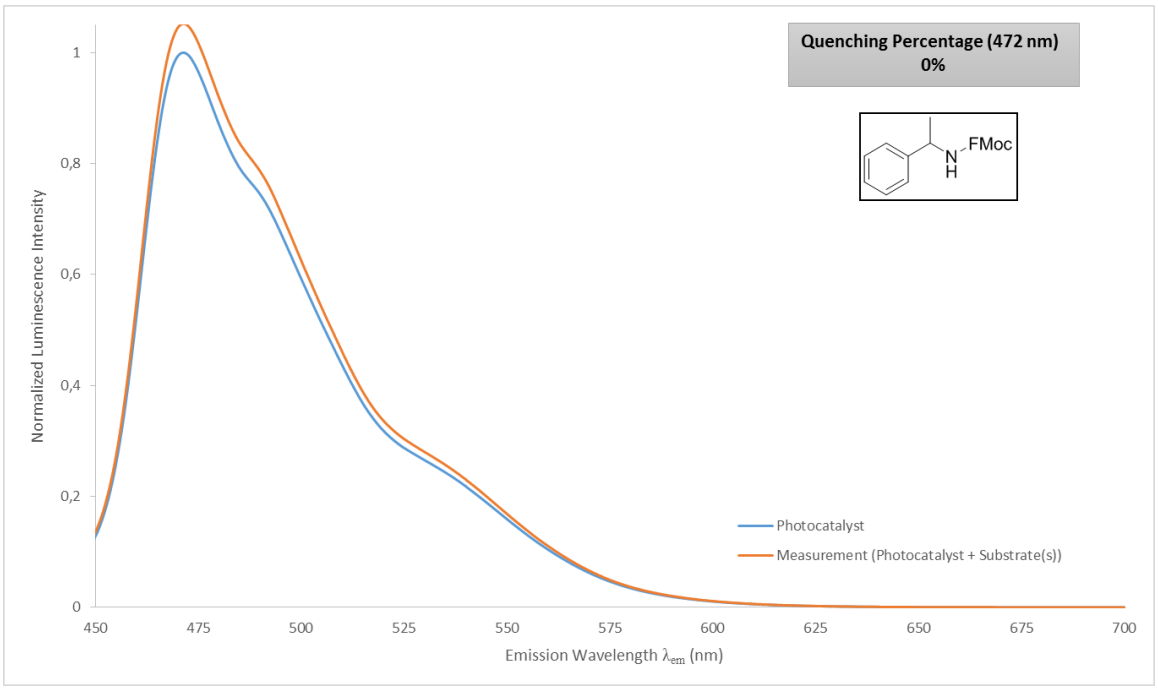
PG2 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



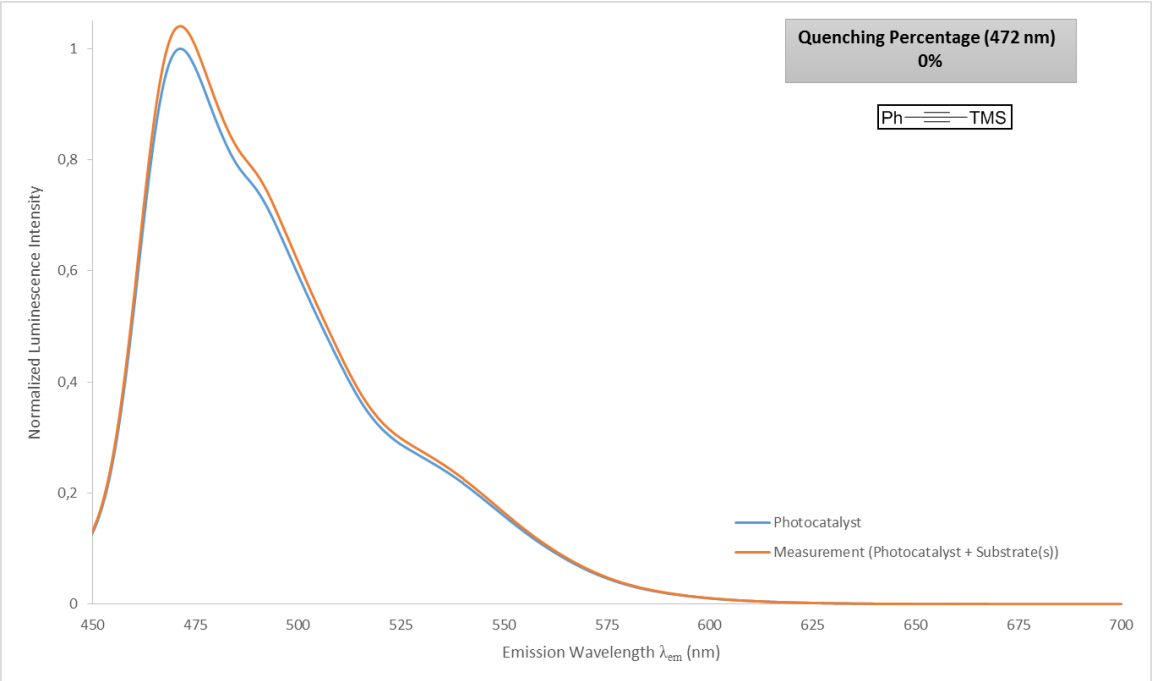
PG3 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$



PG4 + $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF)_6$

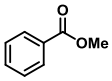


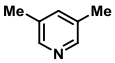
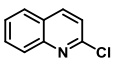
PG5 + [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)](PF)$_6$



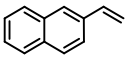
4. Results of the additive-based Rh^{III}-catalyzed oxidative olefination

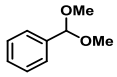
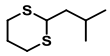
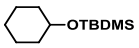
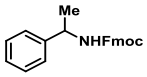
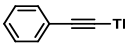
Table S5: Results for the additive-based $Cp^{E}Rh$/Cp*Rh-catalyzed oxidative olefination.

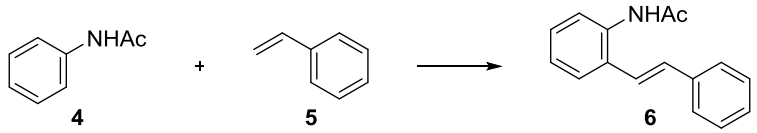
		Conditions A				Conditions B			
Group A		Yield Product	Additive remaining	Remaining SM Anilide %	Remaining SM Styrene %	Yield Product	Additive remaining	Remaining SM Anilide %	Remaining SM Styrene %
A1		89	105	7	27	83	67	102	8
A2		0	43	83	129	1	47	190	99
A3		73	64	19	38	81	81	106	9
A4		1	0	96	140	1	48	189	93
A5		80	99	7	20	90	85	1	5
A6		23	0	76	87	85	0	109	11
A7		31	0	57	89	25	0	112	67
A8		84	95	7	19	79	100	119	16
A9		0	84	69	120	1	35	188	99
A10		51	93	39	61	84	90	92	9

Group B		Yield Product	Additive remaining	Remaining SM Anilide %	Remaining SM Styrene %	Yield Product	Additive remaining	Remaining SM Anilide %	Remaining SM Styrene %
B1		68	-	0	-	64	-	75	-
B2		1	0	92	138	3	0	170	74
B3		0	0	100	146	0	8	173	75
B4		64	100	0	28	62	74	74	0
B5		4	12	98	147	1	54	175	73
B6		62	86	0	36	49	67	97	16
B7		2	84	97	144	1	65	169	69
B8		12	60	88	109	9	66	158	63
B9		59	83	0	41	61	68	90	2
B10		36	84	48	97	66	101	85	0

Group C		Yield Product	Additive remaining	Remaining SM Anilide %	Remaining SM Styrene %	Yield Product	Additive remaining	Remaining SM Anilide %	Remaining SM Styrene %
C1		7	33	26	120	2	69	156	95
C2		57	58	0	29	51	53	96	11
C3		41	57	0	89	40	52	135	39
C4		1	0	100	137	0	80	193	93
C5		66	51	0	30	63	75	98	5
C6		63	46	0	54	44	92	120	29
C7		-	-	-	-	-	-	-	-
C8		51	56	35	6	62	94	106	10

Group D		Yield Product	Additive remaining	Remaining SM Anilide %	Remaining SM Styrene %	Yield Product	Additive remaining	Remaining SM Anilide %	Remaining SM Styrene %
D1		3	7	82	116	1	29	207	98
D2		61	94	0	31	64	96	107	11
D3		2	0	56	92	48	81	129	32
D4		58	79	0	31	69	89	91	0
D5		5	0	97	117	2	0	217	95
D6		60	51	0	40	8	51	190	84
D7		65	84	0	15	49	108	66	10
D8		-	-	-	-	-	-	-	-

Group PG		Yield Product	Additive remaining	Remaining SM Anilide %	Remaining SM Styrene %	Yield Product	Additive remaining	Remaining SM Anilide %	Remaining SM Styrene %
PG1		33	0	0	56	46	0	72	4
PG2		0	51	42	101	2	63	173	74
PG3		38	54	0	55	56	15	79	1
PG4		62	107	9	30	53	94	87	6
PG5		1	0	61	154	10	39	120	59
Average		36	51			39	59		



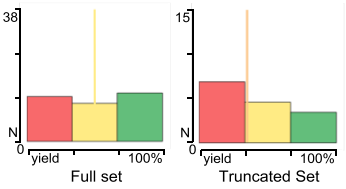
4 5 6

Conditions A

$(Cp^*RhCl_2)_2$ (0.5 mol%), $AgSbF_6$ (2 mol%), $Cu(OAc)_2$ (2.1 equiv.), ^{t}AmOH, 120 °C

Standard yield 73%

Average yield 38%

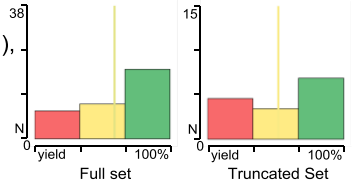


Conditions B

$(Cp^ERhCl_2)_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2 \cdot H_2O$ (20 mol%), air, acetone, rt

Standard yield 87%

Average yield 40%



Basic additives		
	Product	Additives
Conditions A (Rh-Cp*)	17	31
Conditions B (Rh-Cp^E)	22	55

Nucleophilic additives		
	Product	Additives
Conditions A (Rh-Cp*)	26	43
Conditions B (Rh-Cp^E)	26	44

Electrophilic additives		
	Product	Additives
Conditions A (Rh-Cp*)	55	69
Conditions B (Rh-Cp^E)	62	80

The color-coding for facilitated assessment of the results is scaled relative to the yield of the standard reaction in the absence of any additive, representing

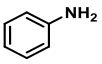
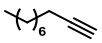
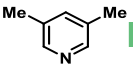
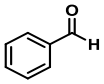
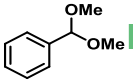
- >48% in green, >24…48% in yellow and ≤ 24% in red for the product yields of the Cp*Rh-catalyzed oxidative olefination,
- >57% in green, >29…57% in yellow and ≤ 29% in red for the product yields of the Cp^ERh-catalyzed oxidative olefination,
- and > 66% in green, 34…66% in yellow and < 34% in red for the additive recovery in both protocols.

In the reaction with additive **B1**, styrene (**5**) and **B1** could not be quantitated because of completely overlapping peaks. Additives **C7** and **D8** were excluded because of being (near) identical to the starting materials.

As for the photocatalytic decarboxylative trifluoromethylthiolation, the truncated set reproduces the trends of the full set in reasonable agreement in case of the oxidative olefination.

5. Results of the additive-based screen applied to the amidation of phenyl acetic acid

Table S6: Results for the amidation of phenyl acetic acid.

			Conditions A		Conditions B	
Entry	Additive		Yield Product	Additive remaining	Yield Product	Additive remaining
1	A2		49	74	66	77
2	A4		59	68	56	89
3	A6		46	0	62	0
4	A7		54	61	57	61
5	B1		54	86	58	96
6	B3		57	20	56	59
7	B9		49	106	56	101
8	C2		46	0	0	4
9	C4		46	77	54	93
10	C5		54	29	51	73
11	C6		57	86	57	91
12	C7		33	78	61	103
13	D2		56	85	60	102
14	D7		33	18	43	63
15	PG1		46	51	58	72
16	none		61	-	62	-
	Average Yield		49	56	53	72

Basic additives		
	Product	Additives
Conditions A (Thermal)	**52**	**64**
Conditions B (Silane)	**58**	**80**

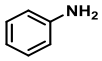
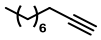
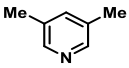
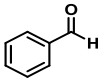
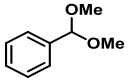
Nucleophilic additives		
	Product	Additives
Conditions A (Thermal)	**51**	**64**
Conditions B (Silane)	**59**	**71**

Electrophilic additives		
	Product	Additives
Conditions A (Thermal)	**47**	**49**
Conditions B (Silane)	**45**	**73**

The color-coding for facilitated assessment of the results is scaled relative to the yield of the standard reaction in the absence of any additive, representing > 41% in green, 21…41% in yellow and < 21% in red for the product yields and > 66% in green, 34…66% in yellow and < 34% in red for the additive recovery in both protocols.

6. Results of the additive-based screening applied to the Appel reaction

Table S7. Results of the additive-based screening applied to the Appel reaction.

		Conditions A		Conditions B	
		Yield Product	Additive remaining	Yield Product	Additive remaining
A2		95	5	29	7
A4		68	85	66	100
A6		88	0	3	0
A7		88	67	43	43
B1		83	35	70	91
B3		88	91	96	10
B9		86	31	76	69
C2		92	28	43	80
C4		94	49	68	84
C5		96	27	73	95
C6		97	70	75	65
C7		86	56	71	98
D2		71	95	78	90
D7		98	43	93	53
PG1		52	0	3	0
	none	94	-	89	-
Average Yield		85	45	59	59

Basic additives		
	Product	Additives
Conditions A (Photoredox)	**94**	**54**
Conditions B (PPh_3)	**67**	**42**

Nucleophilic additives		
	Product	Additives
Conditions A (Photoredox)	**80**	**32**
Conditions B (PPh_3)	**41**	**44**

Electrophilic additives		
	Product	Additives
Conditions A (Photoredox)	**90**	**53**
Conditions B (PPh_3)	**72**	**80**

The color-coding for facilitated assessment of the results is scaled relative to the yield of the standard reaction in the absence of any additive, representing > 59% in green, 30…59% in yellow and < 30% in red for the product yields and > 66% in green, 34…66% in yellow and < 34% in red for the additive recovery in both protocols.

7. References

1 Collins, K. D.; Rühling, A.; Glorius, F. *Nat. Protoc.* **2014**, *9*, 1348.

2 Candish, L.; Pitzer, L.; Gómez-Suárez, A.; Glorius, F. *Chem. Eur. J.* **2016**, *22*, 4753.

3 Zhong, W.; Liu, X. *Tetrahedron Lett.* **2014**, *55*, 4909.

4 GC-MS of crude reaction mixture for one condition is shown (455 nm, Conditions B) due to the identical spectra observed under both reaction conditions.

5 Shao, X.; Liu, T.; Lu, L.; Shen, Q. *Org. Lett.* **2014**, *16*, 4738.

6 Wu, H.; Xiao, Z.; Wu, J.; Guo, Y.; Xiao, J.-C.; Liu, C.; Chen, Q.-Y. *Angew. Chem. Int. Ed.* **2015**, *54*, 4070.