

Photocatalytic dehalogenation of benzyl chloride employing samarium(II)–Buⁱ₂AlH system

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General Methods

The following commercial reagents were used in the work: samarium trichloride hexahydrate $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ of chemically pure grade, a solution of Bu^i_2AlH (DIBAL) in toluene (73%, Acros Organics), extra pure and stabilized benzyl chloride (Acros Organics) and THF of chemically pure grade. To remove adsorbed water from $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, it was first kept under vacuum (~ 1 Torr) for 1 hour at room temperature. DIBAL and benzyl chloride were used without further purification. THF was distilled as described [R. G. Bulgakov, S. M. Eliseeva and D. I. Galimov, *J. Lumin.*, 2016, **172**, 71; <https://doi.org/10.1016/j.jlumin.2015.11.029>]. Argon (99.99%) was further purified by passing through a gas absorber. The standard procedure for the photocatalytic reaction involved three stages. First, $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ (0.02 mmol, 7.30 mg) and 1.8 ml of freshly distilled THF were placed in a 10 ml Pyrex Schlenk flask mounted on a magnetic stirrer. Next, Bu^i_2AlH (0.2 ml, 0.8 mmol) was added under stirring in an argon atmosphere. As a result of the first stage (duration ~ 30 seconds), a homogeneous solution was formed. In the second stage, this homogeneous solution was irradiated with UV light (15 minutes) to activate the reduction process. The third stage involved the addition of benzyl chloride (0.2 mmol, 23 μl) into the system and irradiation of the resulting reaction solution (the distance from the light source to the reactor was ~ 6 cm). All reactions were conducted at constant temperature (295 K), monitored using a thermocouple with an accuracy of ± 0.5 K. Temperature fluctuations during photochemical experiments did not exceed 1 K. After completion of the photochemical reaction, the resulting reaction mixture was decomposed with 10% HCl at 0 $^\circ\text{C}$. The products were extracted with diethyl ether, and the organic layer was dried over CaCl_2 . Conversion of benzyl chloride, product yields, and identification of reaction products were determined by HPLC, GC-MS, and NMR spectroscopy. Each experimental data point was obtained by averaging the results of three independent measurements.

The HPLC analysis was performed on a Shimadzu LC-20 chromatograph using a C18 column (4.5 × 250 mm) with a mobile phase consisting of acetonitrile (80%) and water (20%) at a flow rate of 1 ml·min⁻¹, with detection at 254 nm. The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (400.13 MHz (¹H), 100.62 MHz (¹³C)) (Bruker, Rheinstetten, Germany). CDCl₃ was employed as the solvent and the internal standard. The products were analyzed using a gas chromatograph-mass spectrometer GCMS-QP2010 Ultra (Shimadzu, Tokyo, Japan) equipped with the GC-2010 Plus chromatograph (Shimadzu, Tokyo, Japan), TD-20 thermal desorber (Shimadzu, Tokyo, Japan), and an ultrafast quadrupole mass-selective detector (Shimadzu, Tokyo, Japan).

The light source used was a Hamamatsu LC8 irradiator (150 W xenon lamp) equipped with a standard IR-blocking filter A10062-01 (51.00 mW cm⁻², transmission 300-850 nm). The following cut-off-filters were employed to filter the light of the xenon lamp: UFS-6 (0.76 mW cm⁻², transmission 375-390 nm with λ_{max} = 385 nm), KS-10 (35.30 mW cm⁻², transmission ≥ 590 nm with λ_{max} = 635 nm), as well as a combination of filters ZhS-11/SS-8 (1.78 mW cm⁻², transmission 430-485 nm with λ_{max} = 465 nm), SZS-21/ZhS-17 (2.80 mW cm⁻², transmission 490-570 nm with λ_{max} = 515 nm). Absorption spectra of the reaction solutions were recorded using a Shimadzu UV-1800 spectrophotometer. Photoluminescence (PL) spectra, including excited-state lifetimes of samarium ions, and output spectra of the light source without and with the used cut-off-filters were measured on a Horiba Jobin Yvon FluoroLog-3 spectrofluorimeter. The radiation intensity of lamp without and with various light filters was measured using an Asahi SSP-TS5-TP100 laser power meter.

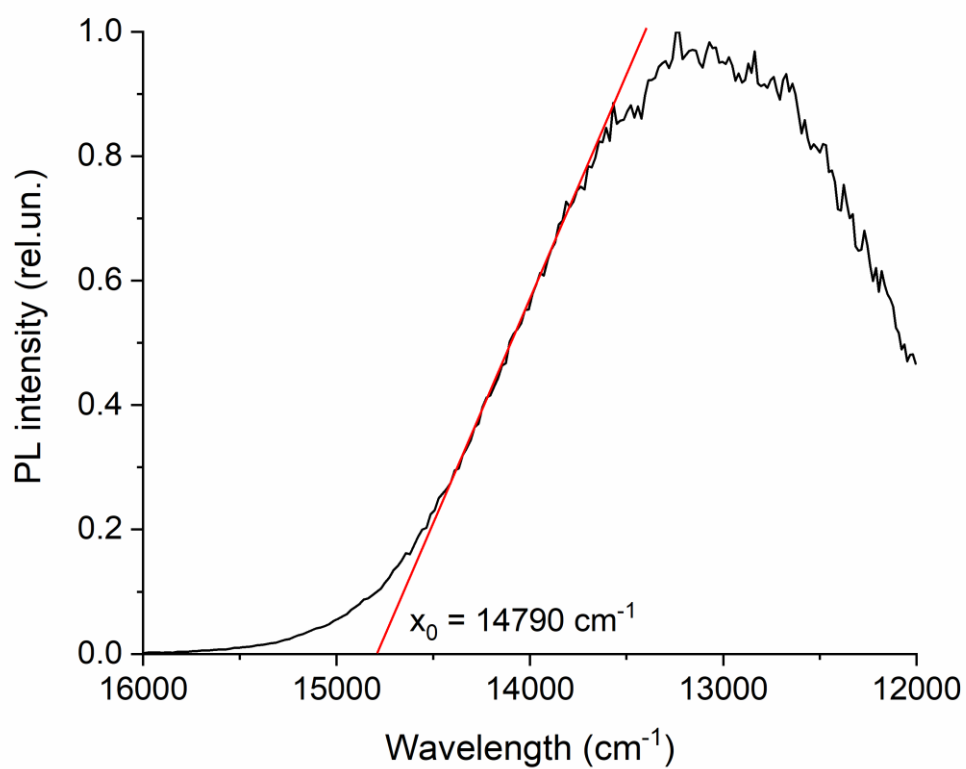


Figure S1. PL spectrum of the solution obtained in the Sm^{II}-DIBAL-THF system, used for estimating the energy of the excited state of *Sm²⁺ in complex **2**.

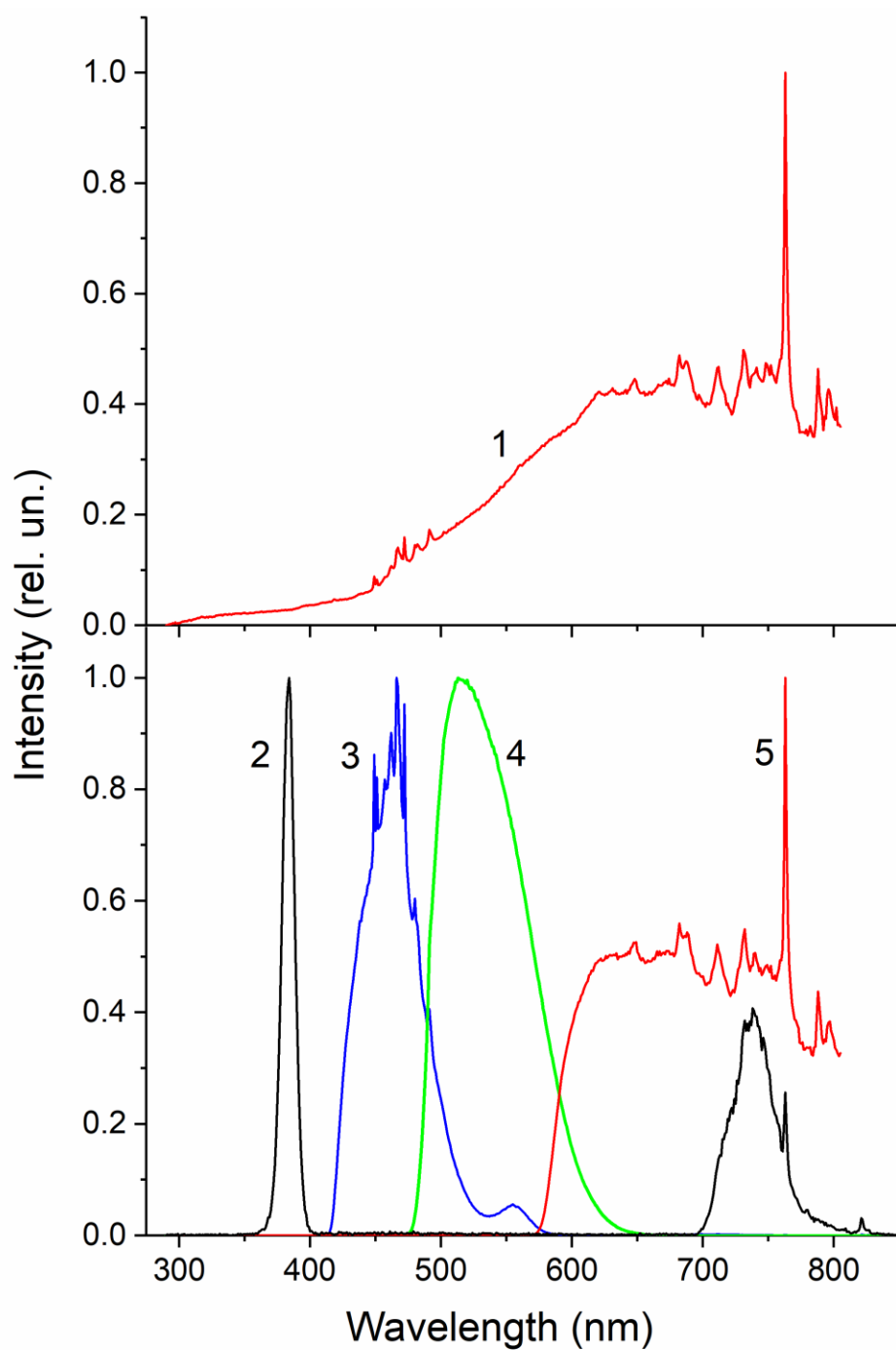


Figure S2. The emission spectra of the Hamamatsu LC8 xenon lamp irradiator without a filter (1) and with the optical filters used in this study: UFS-6 (2), ZhS-11/SS-8 (3), SZS-21/ZhS-17 (4), and KS-10 (5).

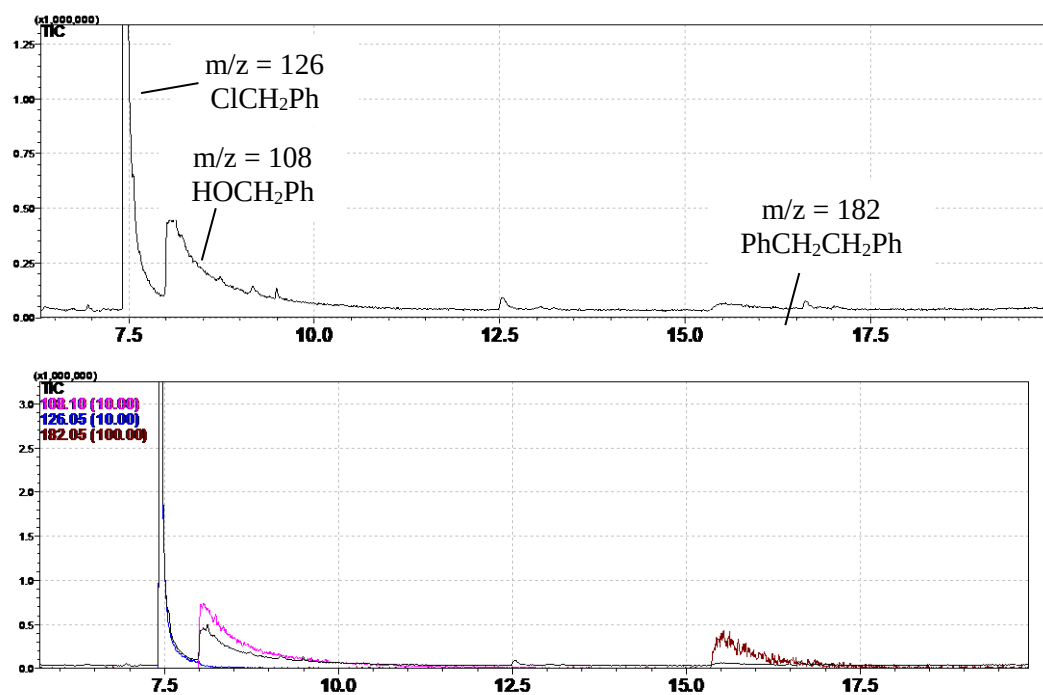


Figure S3. MS-chromatogram of solution after oxidation and hydrolysis of the reaction mixture, obtained after 3 hours of photo-irradiation of the Sm^{II} -DIBAL-THF-BnCl system. HOCH_2Ph , m/z (%) [M]= 108 (81), 107 (46), 91 (35), 79 (100), 77 (52).

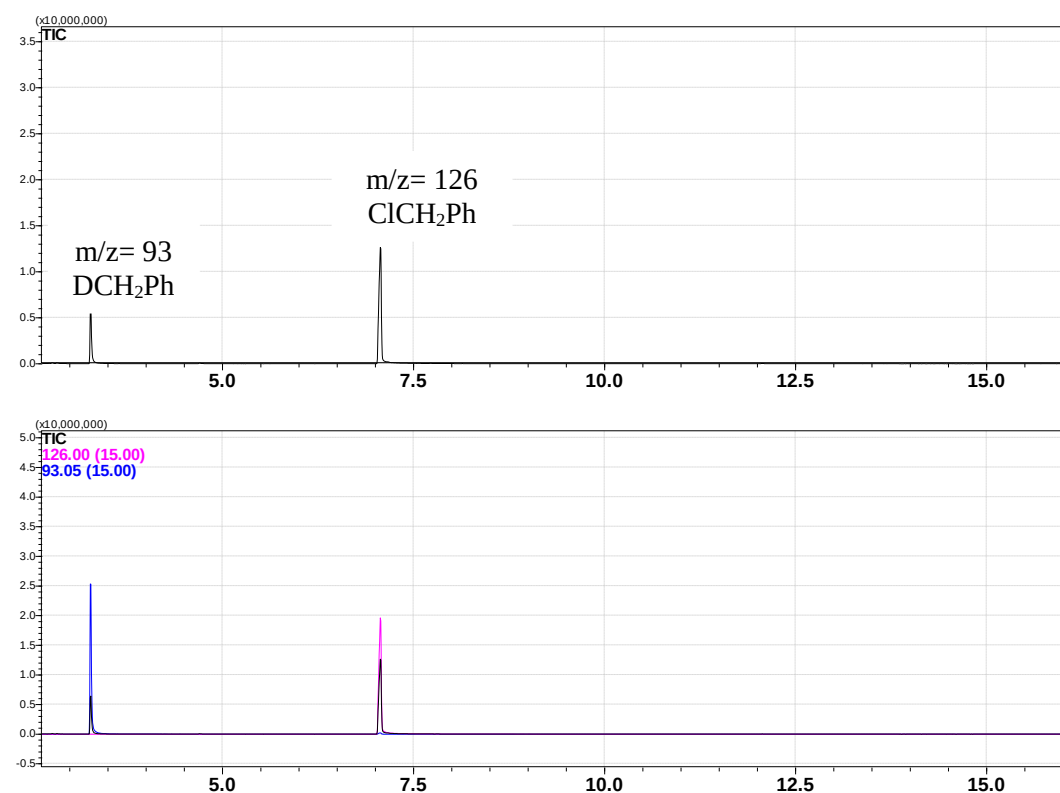


Figure S4. MS-chromatogram of solution after deuterolysis of the reaction mixture, obtained after 3 hours of photo-irradiation of the Sm^{II} -DIBAL-THF-BnCl system. DCH_2Ph , m/z (%) [M]= 93 (71), 92 (100).

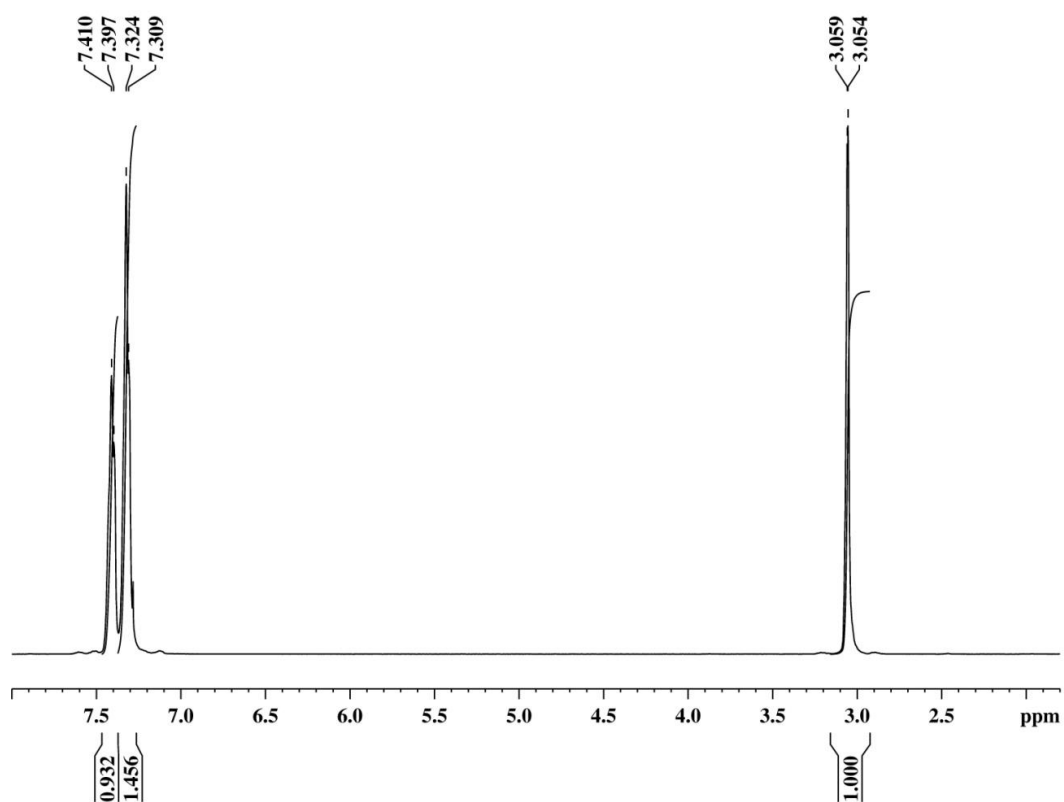


Figure S5. ¹H NMR of 1,2-diphenylethane obtained in the photocatalytic system Sm^{II}-DIBAL-THF-BnCl (Sm:DIBAL:BnCl = 1:40:10).

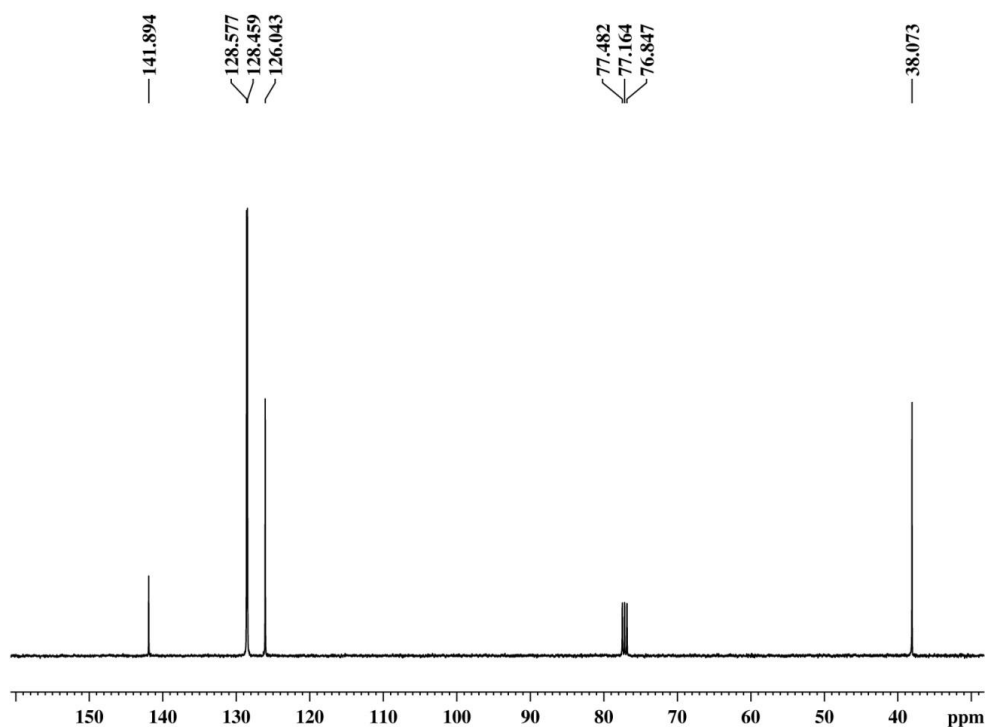


Figure S6. ¹³C NMR of 1,2-diphenylethane obtained in the photocatalytic system Sm^{II}-DIBAL-THF-BnCl (Sm:DIBAL:BnCl = 1:40:10).

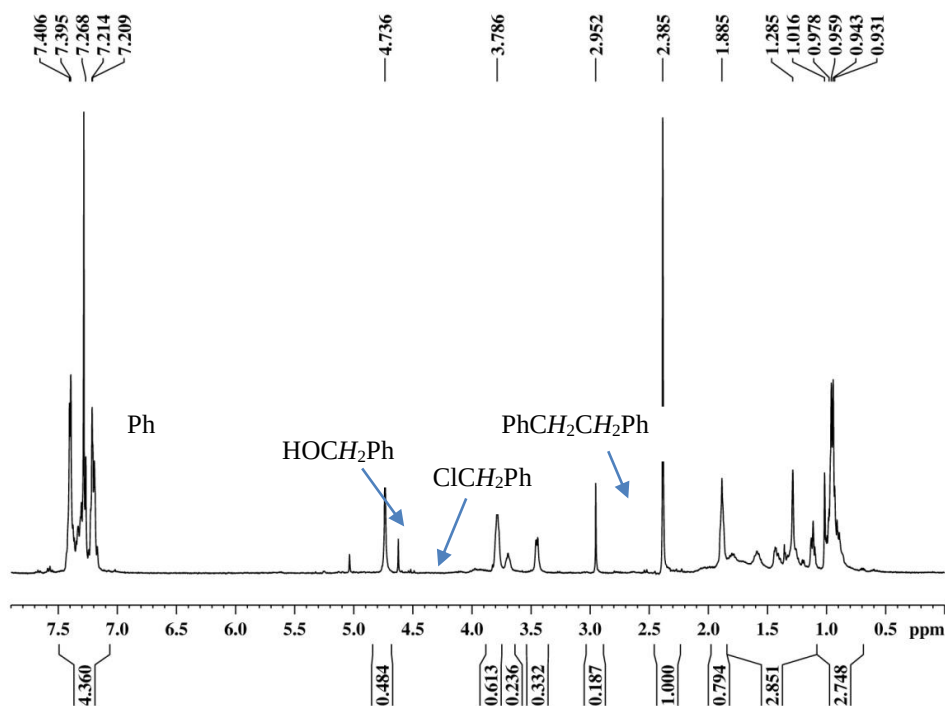


Figure S7. ^1H NMR of reaction products after oxidation and hydrolysis of the system Sm^{II} -DIBAL-THF-BnCl ($\text{Sm}:\text{DIBAL}:\text{BnCl} = 1:40:10$).

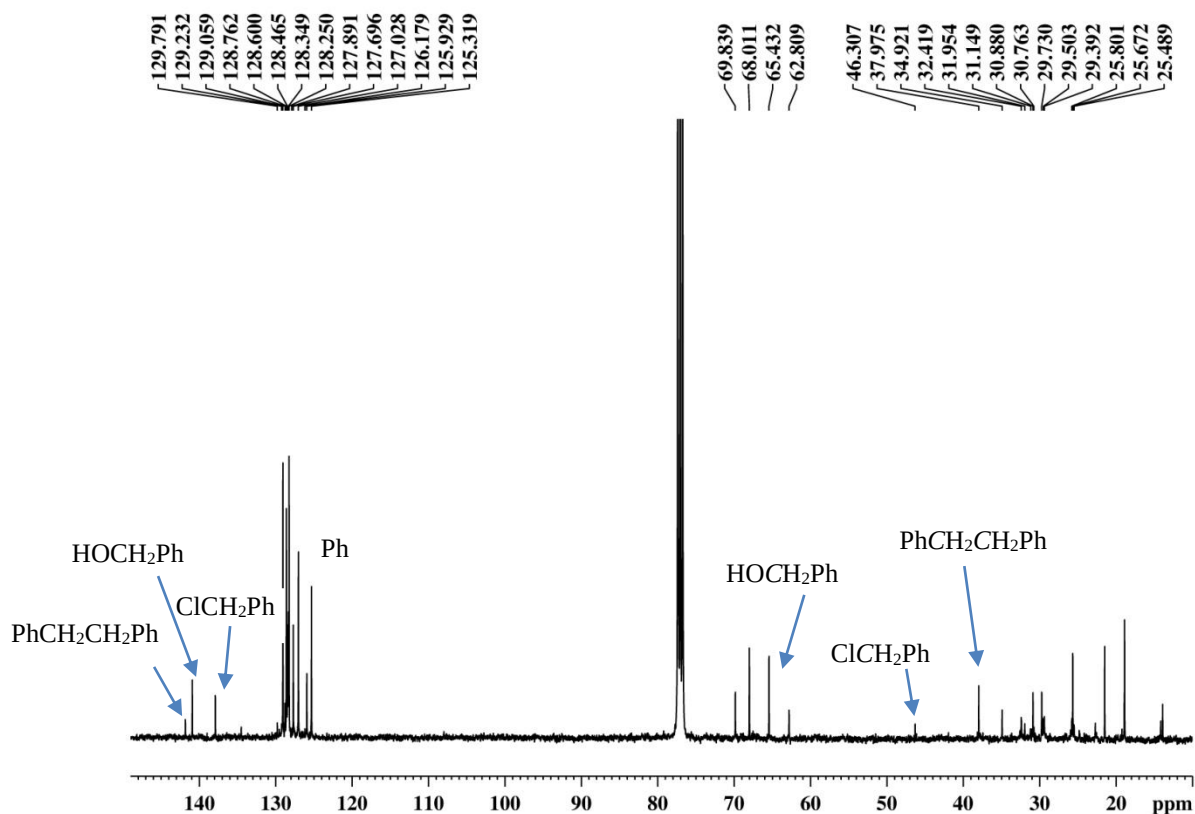


Figure S8. ^{13}C NMR of reaction products after oxidation and hydrolysis of the system Sm^{II} -DIBAL-THF-BnCl ($\text{Sm}:\text{DIBAL}:\text{BnCl} = 1:40:10$).

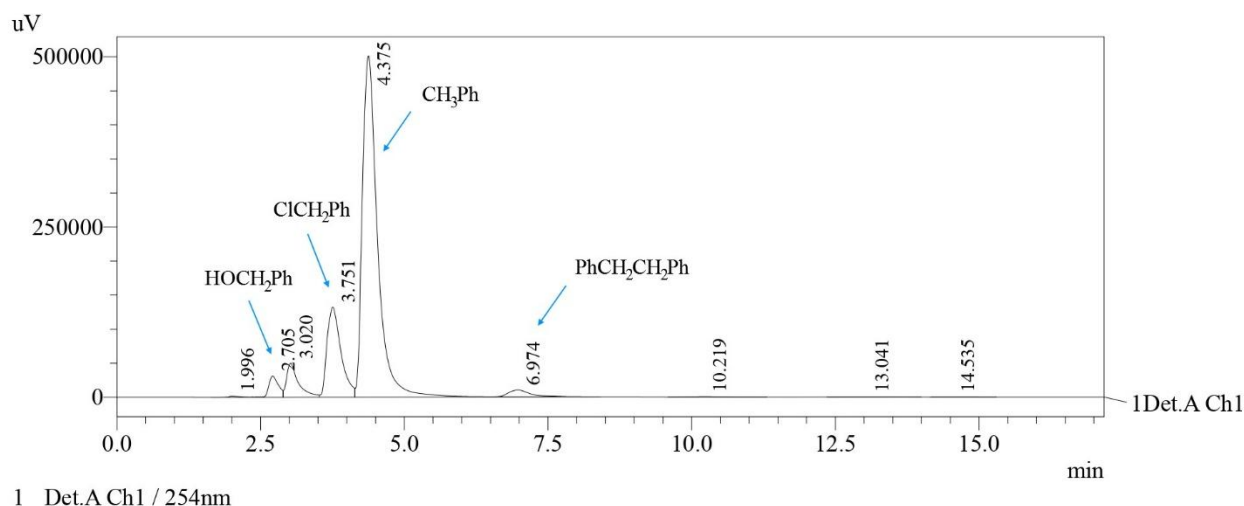


Figure S9. HPLC analysis of the organic phase – the decomposition product of the reaction solution obtained after three-hour irradiation with unfiltered light of the homogeneous system Sm^{II} -DIBAL-THF-BnCl ($\text{Sm}:\text{DIBAL}:\text{BnCl} = 1:40:10$).

Table S1 Dependence of BnCl conversion on UV irradiation time ($\lambda_{\text{max}} = 365 \text{ nm}$) in the photocatalytic system Sm^{II} -DIBAL-THF ($\text{Sm}:\text{DIBAL}:\text{BnCl} = 1:40:10$).

t/h	Conversion of BnCl, %	Product yield, %		
		1,2-Diphenylethane	Toluene	Benzyl alcohol
1	19.5	0.7	15.5	1.0
2	23.5	1.6	19.2	0.6
3	38.7	1.3	25.2	1.1
4	40.7	1.7	33.9	1.1
5	53.4	1.7	44.7	1.7
6	66.7	1.8	54.0	2.0

Table S2 Dependence of BnCl conversion in the Sm(II)-DIBAL-THF-BnCl system on the ratio of Sm²⁺ and DIBAL after three-hour UV irradiation ($\lambda_{\text{max}} = 365 \text{ nm}$).

Sm ^{II} :DIBAL:BnCl	Conversion of BnCl, %	Product yield, %		
		1,2-Diphenylethane	Toluene	Benzyl alcohol
Effect of Sm ²⁺				
0.2:40:10	17.5	4.5	9.9	0.9
0.5:40:10	28.4	3.0	20.4	1.5
1:40:10	38.7	1.3	25.2	1.1
2:40:10				
3:40:10	36	0.8	28.8	1.8
5:40:10	32.1	0.7	26.0	1.4
10:40:10	36.0	0.3	19.7	1.3
	13.4	0.3	0	1.9
Effect of DIBAL				
1:20:10	31.3	1.2	23.2	1.4
1:40:10	38.7	1.3	25.2	1.1
1:60:10	29.6	1.0	25.4	0.7
1:80:10	36.1	2.9	28.6	1.6

Control experiments

System 1. SmCl₃·6H₂O-DIBAL-THF-BnCl without irradiation

SmCl₃·6H₂O (0.02 mmol, 7.30 mg) and 1.8 ml of freshly distilled THF were placed in a glass Schlenk flask. The resulting reaction solution was irradiated with UV light for 15 min to activate the Sm^{III} → Sm^{II} reduction process. Then BnCl (23 μ l, 0.2 mmol) was added to the solution and left in the dark with stirring for 3 h. After this time, the reaction mixture was decomposed with 10% HCl at 0 °C, extracted with diethyl ether, and the organic layer was dried over CaCl₂. According

to the analysis of the organic phase by HPLC and GC-MS, no conversion of BnCl and formation of reaction products were observed.

System 2. DIBAL-THF-BnCl with photoirradiation.

Freshly distilled THF (1.8 ml), DIBAL (0.2 ml, 0.8 mmol), and BnCl (23 μ l, 0.2 mmol) were placed in a glass Schlenk vessel. The resulting reaction solution was irradiated with UV light (365 nm) for 3 h with constant stirring. After 3 h, the reaction mixture was decomposed with 10% HCl at 0 °C, extracted with diethyl ether, and the organic layer was dried over CaCl₂. According to HPLC and GC-MS analysis of the organic phase, no conversion of BnCl or formation of reaction products were observed.

System 3. SmCl₃·6H₂O-THF-BnCl with photoirradiation.

SmCl₃·6H₂O (0.02 mmol, 7.30 mg), 2.0 ml of freshly distilled THF and BnCl (23 μ l, 0.2 mmol) were placed in a glass Schlenk vessel. The resulting heterogeneous solution was irradiated with UV light (365 nm) for 3 h with constant stirring. After 3 h, the mixture was decomposed with 10% HCl at 0 °C, extracted with diethyl ether, and the organic layer was dried over CaCl₂. According to the analysis of the organic phase by HPLC and GC-MS, the conversion of BnCl and the formation of reaction products were not observed.

Thus, control experiments confirmed that the key condition for the efficiency of the photocatalytic reaction of benzyl chloride dehalogenation is the presence of the divalent Sm²⁺ ion and DIBAL in the reaction solution.