Small organic radicals are ubiquitous intermediates in photocatalysis and are used in organic synthesis to install functional groups and to tune electronic properties and pharmacokinetic parameters of the final molecule. Development of new methods to generate small organic radicals with added functionality can further extend the utility of photocatalysis for synthetic needs. Herein, we present a method to generate dichloromethyl radicals from chloroform using a heterogeneous potassium poly(heptazine imide) (K-PHI) photocatalyst under visible light irradiation for C1-extension of the enone backbone. The method is applied on 15 enones, with γ,γ'-dichloroketones yields of 18–89%. Due to negative zeta-potential (−40 mV) and small particle size (100 nm) K-PHI suspension is used in quasi-homogeneous flow-photoreactor increasing the productivity by 19 times compared to the batch approach. The resulting γ,γ'-dichloroketones, are used as bifunctional building blocks to access value-added organic compounds such as substituted furans and pyrroles.
Carbon nitrides (CNs) are “all-in-one” photocatalysts that mediate dozens of different photocatalytic reactions and enable bifunctionalization of (hetero)arenes in one pot. The organic semiconductors have also been efficiently employed in a continuous flow system for chemical synthesis eliminating the last obstacle (poor light penetration in heterogeneous solid-liquid mixture) on the way to widespread applications in organic synthesis. Because of their low cost, ease of synthesis and stability against reactive intermediates and photobleaching, CNs already play an important role as heterogeneous photocatalysts for organic transformations. CNs are also very versatile, and can be tailored depending on the application by bandgap engineering at the atomic and molecular level.

Most photocatalytic reactions are based on single electron transfer between the reagents and the photocatalyst. Therefore, reactive open shell species are ubiquitous intermediates in photocatalytic processes. Small organic radicals, such as CH₃, CF₃, CHF₂, and perfluoroalkyl, CH₃O, etc. are used for the functionalization of the organic molecules in order to tune steric and electronic properties. Furthermore, the lipophilicity and metabolic stability of pharmaceuticals may be adjusted in this way. Despite their importance for medicinal chemistry, CF₃, alkyl, and CH₃O groups are chemically stable. Therefore, further diversification of the molecule at these newly formed sites is problematic. For example, cleavage of C–F bond in CF₃ group is extremely demanding. The same applies to C–O bond in the CH₃O-group.

Conversely CHCl₂ radical from the pool of small organic radicals is synthetically more useful. It enables the installation of an electrophilic carbon, and the C–Cl bonds can be conveniently cleaved using weak nucleophiles. In other words, the CHCl₂ radical allows for C₁-extension of the substrate framework, while simultaneously adding a chemically active functionality. From this point of view, the CHCl₂ radical can be regarded as a “small functional radical”.

Despite the obvious synthetic utility of the dichloromethyl radical, literature is still lacking reactions using dichloromethyl moieties in conjugate additions—the kind of reaction resembling a traditional polar Michael addition. The latter was well studied in photoredox catalysis. An example shown in Fig. 1 employs methyl groups in tertiary amines and C=C double bond as coupling partners. The chemistry of dichloromethyl radicals is restricted to a few examples, while such radicals are generated predominantly by catalyst containing rare precious metals or expensive partners. The chemistry of dichloromethyl radicals is restricted to a few examples, while such radicals are generated predominantly by catalyst containing rare precious metals or expensive partners. Our alternative approach uses cheap heterogenous carbon nitride (CN) photocatalysts (1–10 Euro per gram on a gram-scale synthesis) and have a low toxicity.

We hypothesized that chloroform can be used as atom efficient source of CHCl₂ radicals. Although chloroform readily gives dichlorocarbene in the presence of strong bases, we concede that photocatalyst will alter the path of chloroform decomposition. Formation of the dichloromethyl radical thereby may be achieved by one-electron reduction of chloroform followed by elimination of a chloride anion.

In order to trigger this process, we chose potassium poly (heptazine imide) (K-PHI), a member of the CN family. Upon irradiation with visible light, metastable long-lived radicals are generated that have been used as a pool of electrons to reduce different substrates. Earlier, we developed photocatalytic methods to synthesize thioamides, dibenzyl sulfanes, N-fused pyroles, cyclopentanes, and halogenated aromatic hydrocarbons using K-PHI. In related works, the long-lived carbon nitride radicals were applied in the delayed evolution of hydrogen.

Due to the advantages of flow reactors, several types of such photoreactors employing carbon nitrides have been reported—packed bed photoreactor, serial micro batch photoreactors, and triphasic flow photoreactor. Due to relatively small particle size (average diameter 100 nm) and highly negative zeta-potential (~40 mV), K-PHI gives stable colloidal solution and has been used in quasi-homogeneous catalysis. Due to these features colloidal solution of K-PHI can be used in simple plug-flow photoreactors that are designed for homogeneous reaction mixtures.

All in all, we present an unusual photocatalyzed radical addition of dichloromethyl radicals to enones to form a new C–C bond (Fig. 1d). In this approach chloroform is used as a source of dichloromethyl radicals. The reaction is catalyzed by K-PHI using blue light irradiation. Using the discovered reaction, we show that light scattering by semiconductor particular strongly affects their performance in batch reactors limiting the scalability of such transformations. A nineteen times higher productivity is achieved using a dedicated flow photoreactor employing quasi-homogeneous K-PHI nanoparticles. Finally, dichloromethyl adducts, i.e., γ,γ-dichloroketones, are used to access bifunctional building blocks and several classes of heterocyclic compounds.

**Results**

**Optimization of reaction conditions.** Along these arguments, we studied the designed reaction between chalcone 1a, chloroform, tetrahydroisoquinoline (THIQ) as an electron donor and K-PHI as the photocatalyst (see SI for preparation and characterization of K-PHI, Supplementary Fig. 1). Dichloroketone 2a was synthesized with 17% yield when 1 equivalent of THIQ was used (Table 1, entry 1). By increasing the amount of THIQ gradually to four equivalents, the yield of 2a was increased to 51% (entry 3). However, even higher yield (62%) of 2a was achieved by...
using 3 equivalents of triethanolamine (TEOA) as electron donor (entry 4). The optimum conditions include ten equivalents of TEOA, under which we achieved 97% yield (entry 5). The reaction does not proceed without catalyst, light or a sacrificial electron donor (entry 6–8). CDC13 is a suitable source of CDCl2 radicals offering a route for d-labeled dichloroketones 2a–d1 with 99% yield (entry 9). We also evaluated the robustness of the reaction using different alcohols as hole scavengers, observing the formation of the desired product in all cases, albeit in lower yield (Table S1, entry 11–14). These results illustrate the better ability of amines to donate electrons compared to alcohols, due to lower oxidation potentials (e.g., +0.5 V for TEOA, +1.5 V for benzyl alcohol and +1.9 V for MeOH, EtOH, 1H-PROH (Supplementary Note 1). It is also supported by higher H2 production rate over carbon nitride materials using TEOA as electron donor compared to MeOH and EtOH40,41 and comparative tests of benzyl alcohol oxidation versus benzylamine37,42. Moderate heating (50 °C) facilitates the reaction, as the yield of 2a was 64% when reaction was performed at 20 °C (Supplementary Table 1, entry 21). We also compared the catalytic activity of other materials and photoredox complexes. Na-PHI gave 2a with 49% yield (entry 10)43. Similar behavior was already observed during the photocatalytic synthesis of thioamides28. Mesoporous graphite carbon nitride (mpg-CN) gave 2a with comparable yield 85% (entry 11). The inorganic semiconductors CdS and TiO2 gave 2a in 70 and 94% yield, respectively (entries 12,13). Homogeneous Ir(ppy)3 gave 2a with 97% yield (entry 14), while [Ru(bpy)3]Cl2 only resulted in 8% of 2a (entry 15). Furthermore, it was also shown that recycled K-PHI remains photocatalytically active for at least two further cycles (Supplementary Table 2).

**Reaction scope.** Using the optimized conditions fifteen dichloroketones have been isolated with 18–89% yield (Figs. 2a–o). The characterization of products was conducted by NMR analysis. Dichloroketones 2 do not give stable molecular ions in the mass spectra (electron ionization). For example, the expected m/z value for 2a is 292. However, a signal with m/z 221 was detected (Supplementary Fig. 2). The latter corresponds to 2,4-diphenylfuran. In general 2,4-diallylsulfurated furans are products of oxygen nucleophilic attack at CHCl2-group followed by elimination of two molecules HCl under the conditions of GC-MS data acquisition. Below we employ the reactivity of CHCl2 group in synthesis of pyrroles and furans. Nonetheless, elemental analysis of 2a revealed chlorine content in excellent agreement with the calculated content confirming the proposed structure. We further proved the product structure, using deuterated chloroform as dichloromethyl source, observing the rise of the triplet in the 13C NMR spectrum in the d-labeled compound (2a-d1).

Dichloromethylated chalcones bearing strong electron withdrawing groups, i.e., CN−, MeO2C−, and pyridin-2-yl, 1p-r, gave the corresponding products 2p-r in low yields as analyzed by 1H-NMR spectrometry of the crude reaction mixture (Supplementary Note 2). Nevertheless, we envision toolbox of synthetic organic chemistry to be useful for further diversification of the products structures employing, for example, methyl-group in 2b, F-atoms in 2de.h and intrinsically reactive sites in 2i,j. Common reactive Michael acceptors, such as methyl vinyl ketone and acrylonitrile, gave only trace amounts of CHCl2 addition to the double bond as evidenced by GC-MS (Supplementary Note 3). Even more reactive Michael acceptors, i.e., methacrolein, methyl acrylate, and 2-furanone, gave a complex mixture and the desired products could not be identified (Supplementary Note 4).

Analysis of the substrates scope suggests that dialysubstituted enones in general are more suitable substrates for photocatalytic dichloromethylation than terminal alkenes. Nevertheless, the advantages of the developed method are a simpler protocol and safer conditions. For example, the synthesis of 2a and 2l was

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**Table 1 Screening of reaction conditions.**

| Entry | Amine      | Photocatalyst | Yield (%) |
|-------|------------|---------------|-----------|
| 1     | THIQ (1 eq., 0.05 mmol) | K-PHI (5 mg) | 17        |
| 2     | THIQ (2 eq., 0.1 mmol) | K-PHI (5 mg) | 33        |
| 3     | THIQ (4 eq., 0.2 mmol) | K-PHI (5 mg) | 51        |
| 4     | TEOA (3 eq., 0.15 mmol) | K-PHI (5 mg) | 62        |
| 5     | TEOA (10 eq., 0.5 mmol) | K-PHI (5 mg) | 97        |
| 6     | TEOA (10 eq., 0.5 mmol) | –           | –         |
| 7b    | TEOA (10 eq., 0.5 mmol) | K-PHI (5 mg) | –         |
| 8     | –          | K-PHI (5 mg) | –         |
| 9c    | TEOA (10 eq., 0.5 mmol) | K-PHI (5 mg) | 99        |
| 10    | TEOA (10 eq., 0.5 mmol) | Na-PHI (5 mg) | 49        |
| 11    | TEOA (10 eq., 0.5 mmol) | mpg-CN (5 mg) | 85        |
| 12    | TEOA (10 eq., 0.5 mmol) | CdS (20% mol) | 70        |
| 13d   | TEOA (10 eq., 0.5 mmol) | TiO2 (20% mol) | 94        |
| 14    | TEOA (10 eq., 0.5 mmol) | Ir(ppy)3 (2.5% mol) | 97        |
| 15    | TEOA (10 eq., 0.5 mmol) | [Ru(bpy)3]Cl2 (2.5% mol) | 8         |

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1Reaction conditions: 1 eq., 0.05 mmol, 10.4 mg of 1a, under light irradiation (λ = 461 nm, 51 ± 0.03 mW cm−2), blue LED.

2Reaction performed under UV light (λ = 365 nm, 17.5 ± 0.03 mW cm−2).

3Yields estimated by GC-MS.

4No light.

5Reaction performed in CDCl3.

6Reaction performed under UV light (λ = 365 nm, 17.5 ± 0.03 mW cm−2).
described earlier using exotic reagents such as dichloromethyl-lithium. A comparison of K-PHI, mpg-CN, and Ir(ppy) 3 photocatalysts using selected enones, 11–I, n, p, revealed that K-PHI in general gives the products in higher yields.

In the course of studying suitable reagents to install CxHalyHz-groups, CHI2-groups, and C2HCl4-groups to enone 1a backbone extension. Careful analysis of the reaction mixture revealed that addition of chloroethane and tetrachloromethane (Supplementary Table 1). Including dichloromethane, bromoform, iodoform, 1,1,2,2-tetrachloroethane) (Supplementary Note 5). Compared to bromoform and iodoform) or dichlorodihydropyranes (in case of photolysis to 2,4-diphenylfuran (in case of undergo further chemical transformations, such as HX elimination and subsequent cyclizations to 2,4-diphenylfuran (in case of tetrachloroethane) (Supplementary Table 1). Compared to bromoform and iodoform, chloroform is beneficial due to higher selectivity in the reaction of enones Cl backbone extension.

Scaling the dichloromethylation reaction of 1a in batch led to gradual decrease of the dichloroketone yield, from 88% (on 0.05 mmol scale) to 23% (on 5 mmol scale) (Supplementary Table 3). After careful investigation, we concluded that the origin for such drastic drop of the product 2a yield is poor light penetration in the depth of the batch reactor due to light scattering by suspended semiconductor particles (Supplementary Note 6).

**Quasi-homogeneous flow photoreactor.** In order to overcome limitations of the batch approach, we performed the reaction in a continuous flow reactor made out of thin (inner diameter 1.6 mm) fluorinated ethylene propylene (FEP) tubing (Fig. 3). The use of carbon nitrides has been reported in serial micro-batch reactors, that use gas-liquid segments to avoid clogging. A simplified system is applicable for K-PHI due to relatively small particle diameter (100 nm) and negative zeta-potential (ζ) (Fig. 3a). Electrostatic stabilization allows pumping colloidal solution (Fig. 3b and Supplementary Note 7) without using a gas-liquid system (Fig. 3c). Using flow approach, 2a was obtained with 57% yield. Considering convenience of K-PHI suspension pumping through thin FEP tubing along with easiness of the photocatalyst recovery, the entire system enables quasi-homogeneous photocatalysis in flow.

As seen from the light intensity measurements (Fig. 3d–f), the FEP tubing filled with the reaction mixture absorbs 74% \([I_0 - I_{12}]/I_0\) of light. These results suggest that by performing the reaction in flow, more homogeneous irradiation of K-PHI particulate is achieved compared to the reaction in batch (Supplementary Note 6). Furthermore, we solved the problem of poor light permeability through a semiconductor suspension and increased the productivity of γ,γ-dichloroketone 2a synthesis by a factor of 19.

**Fig. 2 Scope of enone substrates.** Reaction conditions: enone 1 (1 eq., 0.05 mmol); TEOA (10 eq., 0.5 mmol, 67°C); CHCl3 (2 mL); Argon atmosphere; under light irradiation (λ = 461 nm, 51 ± 0.03 mW cm−2, blue LED), isolated yields. Superscript “a” indicates the yields determined by 1H NMR using 1,2,3-trimethoxybenzene as internal standard.
Application of γ,γ-dichloroketones in organic synthesis

Finally, the γ,γ-dichloroketones obtained by the photocatalytic generation and addition of dichloromethyl radicals to enones were used to install other reactive functional groups. As a practical example, dichloroketone 2a was converted to β-formyl ketone 3a by simple hydrolysis with 60% yield (Fig. 4). The ketoaldehyde 3a was then transformed into multi-substituted heterocycles (4a–6a) using microwave assisted condensations with a series of nucleophiles. For instance, furan and pyrrole scaffolds have been used in synthesis of bioactive substances.46,47

Mechanism. To support the role of chloroform as electron acceptor, we developed a method for oxidative coupling of...
benzylamines (Fig. 5)\(^{48}\). As example, we synthesized four imines with 83–100% yield. These results offer an alternative route for such transformations using chloroform as a solvent and electron acceptor (Supplementary Fig. 3 for detailed mechanism of amines coupling).

The proposed mechanism of the reported photocatalytic reaction is shown in Fig. 6. In the first step, K-PHI is excited by blue photons giving excited state of the photocatalyst (K-PHI\(^+\)). Removal of an electron from TEOA by K-PHI\(^+\) (reductive quenching of the photocatalyst), leads to the formation of the long-lived radical anion K-PHI\(^{++}\), that has the typical deep green color\(^{27,29}\). Chloroform is subsequently oxidized by a single electron transfer event, forming the chloroform radical anion that eliminates a chloride anion resulting in a dichloromethyl radical. Addition of the dichloromethyl radical to the β-carbon atom of the enone gives intermediate \(i-1\). Abstraction of hydrogen from TEOA leads to the desired product 2. While TEOA acts as hole scavenger, chloroform simultaneously acts as solvent and electron acceptor to complete the photocatalytic cycle, as it was already proposed by Chen et al.\(^{49}\) It is also possible to detect traces of different chlorinated compounds, that result from side radical reactions of the dichloromethyl radical, via GC-MS. By running experiments in the absence of the enone, we observed the formation of halogenated compounds including tetrachloroethane that is likely formed via a homocoupling of dichloromethyl radicals (Supplementary Table 4; Supplementary Figs. 4, 5, 6).

**Discussion**

In this work, we extended the library of small organic radicals available for photocatalytic synthesis to dichloromethyl radicals than can be conveniently generated from chloroform. The method was validated in a 1,4 addition of dichloromethyl radicals to enones. The process is photocatalyzed by the heterogeneous, metal free carbon nitride photocatalyst K-PHI. Fifteen γγ-dichloroketones were isolated in moderate to excellent yield. The possibility to use other polyhalogenated compounds such as bromoform, iodoform and 1,1,2,2-tetrachloroethane has been demonstrated. Light scattering by carbon nitride particles has been identified as limiting factor for scaling these transformations. The results suggest that, in a typical photocatalytic experiment using 2.5 mg mL\(^{-1}\) of semiconductor particles, the penetration depth of light is only 3 mm. In polar solvent, such as DMSO, nanoparticles of K-PHI give stable suspension that was pumped through a thin (1.6 mm internal diameter) tubing γγ-dichloroketone 2a has been also synthesized using quasi-homogeneous photoreactor. The γγ-dichloroketones obtained in this work were proved to be useful building blocks with applications in the synthesis of bifunctional compounds that can be used for the preparation of heterocyclic bioactive molecules. The use of chloroform as solvent and electron acceptor was also demonstrated in the oxidative coupling of benzylamines.

**Methods**

**Microwave reactions.** Experiments were carried out in a CEM Discover\(^*\) SP System microwave reactor.

**Compounds characterization.** \(^1\)H and \(^13\)C NMR spectra were recorded on Agilent 400 MHz (at 400 MHz for Protons and 101 MHz for Carbon-13). Chemical shifts are reported in ppm versus solvent residual peak: chloroform-\(d_2\) 7.26 ppm (\(^1\)H NMR), 77.1 ppm (\(^13\)C NMR); acetonitrile-\(d_3\) 1.94 ppm (\(^1\)H NMR), 118.3 ppm (\(^13\)C NMR).

Mass spectral data were obtained using Agilent GC 6890 gas chromatograph, equipped with HP-5MS column (inner diameter = 0.25 mm, length = 30 m, and film = 0.25 μm), coupled with Agilent MSD 5975 mass spectrometer (electron ionization).

**Electrochemistry.** Cyclic voltammetry (CV) measurements were performed in a glass single-compartment electrochemical cell. Glassy carbon (diameter 3 mm) was used as a working electrode (WE), Ag wire in AgNO\(_3\) (0.01 M) with tetra-n-butylammonium perchlorate (0.1 M) in MeCN as a reference electrode (RE), Pt wire as a counter electrode. Each compound was studied in a 50 mM concentration in a 0.1 M tetrabutylammonium perchlorate (TBAP)/chloroform electrolyte solution (10 mL). Before voltammograms were recorded, the solution was purged with Ar, and an Ar flow was kept in the headspace volume of the electrochemical cell during CV measurements. A potential scan rate of 0.050 V s\(^{-1}\) was chosen, and the potential window ranging from \(\sim-2.5\) V to \(\sim-2.5\) V (and backwards) was investigated. Cyclic voltammetry was performed under room-temperature conditions (\(\sim20\)–22 °C).

**Fig. 5** Oxidative coupling of benzylamines. GC-MS yields are shown. **Fig. 6** Proposed mechanism of the generation of dichloromethyl radicals and their addition to enones. Inset shows images of the reaction mixture before and after light irradiation and structures of TEOA oxidation products.
Photocatalysts characterization. Zeta-potentials were measured in aqueous colloidal solution of K-PH1 using a Malvern Zetasizer instrument. Hydrodynamic diameter of K-PH1 particles in water was measured using Malvern Zetasizer instrument.

General method for dichloro-ketone preparation (2a-I). A glass tube with rubber-lined cap was evacuated and filled with argon three times. To this tube triethanolamine (74.6 mg, 66 μL, 0.5 mmol), corresponding chalcone (50 μmol), K-PH1 (5 mg) and chloroform (2 mL) were added. Resulting mixture was stirred at 50 °C under irradiation of Blue LED (λ = 461 nm) for 20 h. Then reaction mixture was cooled to room temperature and centrifuged, clear solution was separated and organic phase was washed with chloroform (2 mL) and centrifuged again. Organic solution was combined and evaporated to dryness. Residue after evaporation was solid residue was washed with chloroform (2 mL) and centrifuged. Organic layer was cooled to room temperature and centrifuged, clear solution was separated and organic layer was dried with anhydrous 

Data availability
The data that support the findings of this study are available from the corresponding author upon reasonable request. The source data underlying Fig. 2a and Supplementary Fig. 1a–j are provided as a Source Data file.

Code availability
This study does not use custom computer code or algorithm to generate results that are reported in the paper and central to its main claims.

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**Author contributions**

S.M. synthesis of precursors, photocatalytic tests, chemical properties of γ,γ-dichloroketones, flow photoreactor, preparation of manuscript and ESI; B.K. synthesis of precursors, photocatalytic tests; B.P. flow photoreactor; M.A. planning of research work; A.S. planning of research work, preparation of manuscript and ESI.

**Competing interests**

The authors declare no competing interests.

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**Correspondence** and requests for materials should be addressed to A.S.

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