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Article

Photo-on-Demand In Situ Synthesis of N-Substituted Trichloroacetamides with Tetrachloroethylene and Their Conversions to Ureas, Carbamates, and Polyurethanes

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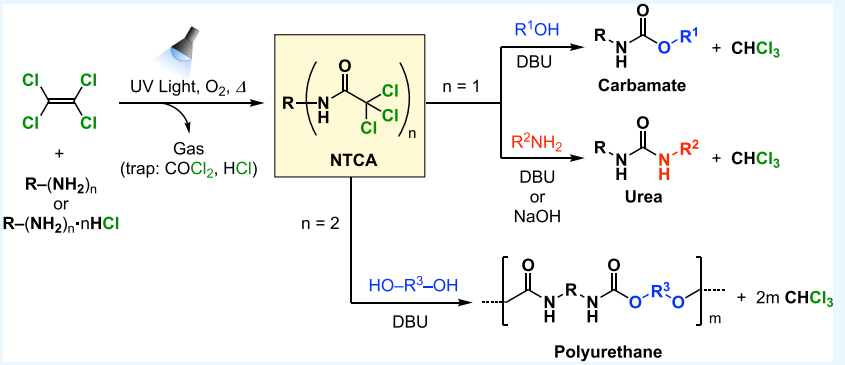

ABSTRACT: N-substituted trichloroacetamides (NTCAs), which serve as blocked isocyanates, were synthesized in ∼97% yields by in situ photo-on-demand trichloroacetylation of amines with tetrachloroethylene (TCE). The reactions were performed by photoirradiation of TCE solutions containing an amine under O_2 bubbling over 70 °C with a low-pressure mercury lamp. TCE underwent photochemical oxidation to afford trichloroacetyl chloride having high toxicity and corrosivity, which then reacts in situ with the amine to afford NTCA. Compared with conventional NTCA synthesis with hexachloroacetone, the present reaction has the advantage of being widely applicable to a variety of amines, even those with low nucleophilicity such as amides, fluorinated amines, and amine HCl salts. NTCAs could be converted to the corresponding N-substituted ureas and carbamates through base-catalyzed condensation with amines and alcohols, respectively, with the elimination of $CHCl_3$. The reaction may proceed by the initial formation of isocyanate and its subsequent addition reaction with the amine or alcohol. This photochemical reaction also enables the synthesis of fluorinated NTCAs, which accelerate the reactions, and realizes the synthesis of novel fluorinated chemicals including polyurethanes.

INTRODUCTION

Tetrachloroethylene (TCE) is an organic solvent used in dry cleaning, textile processing, vapor degreasing, and organic synthesis.[1] It has high chemical stability but undergoes photochemical oxidation upon irradiation with UV-C light to afford complex products such as trichloroacetyl chloride (TCAC), phosgene ($COCl_2$), CO, and Cl_2.[2−6] These compounds are highly toxic and corrosive and have high environmental impacts but nevertheless are very important chemicals in organic synthesis.[7] However, less attention has been paid to their practical uses in organic synthesis. With the recent global environmental issues, a method of chemical recycling of TCE is required. To develop a sustainable chemical synthesis, we have studied photo-on-demand chemical reactions with TCE.

We previously reported that the products generated upon photochemical oxidation of TCE were practically available in organic synthesis (Scheme 1, reaction III).[8] $COCl_2$ and Cl_2, the gaseous minor products, were utilized for synthesizing N-substituted ureas, chloroformates, carbonate esters, and organochlorides, while TCAC, the main liquid product, enabled the synthesis of N-substituted trichloroacetamides (NTCAs). Since TCAC is a phosgene analogue, the as-prepared photo-oxidized TCE solution was thus carefully used to prepare the NTCAs by sequential mixing with an amine reactant and an organic base, which served as a catalyst and/or a HCl scavenger. The photo-oxidized TCE solution contains

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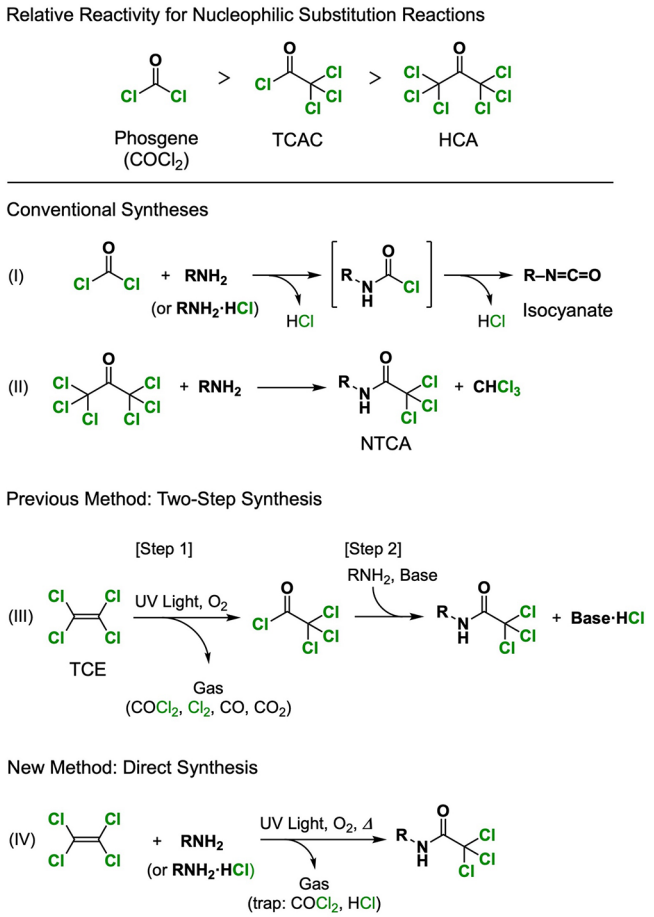
Scheme 1. General Reactivity of Chlorinated Carbonyl Compounds and Syntheses of Isocyanates (I) and NTCAs (Blocked Isocyanate) Reported in Previous Studies (II and III) and in This Study (IV)



not only TCAC but also $COCl_2$, which is difficult to remove completely from the solution. Clearly, there are safety problems and complications with this method. This background motivated us to develop direct in situ photo-on-demand synthesis of NTCAs from TCE solutions containing primary amines (Scheme 1, reaction IV). We have intensively studied photo-on-demand phosgenation reactions with chloroform ($CHCl_3$), which allows in situ photochemical conversion of $CHCl_3$ to $COCl_2$ even in the presence of reaction substrates and organic bases capable of absorbing UV light.[9−14] We thus expected that photochemical conversion of TCE to TCAC would occur similarly in the presence of amine substrates, and the generated TCAC would then immediately react in situ with the amine without an organic base to afford NTCA.

NTCAs, which serve as blocked isocyanates, are building blocks for synthesizing lactams,[15] isocyanates,[16] carbamates,[17] and N-substituted ureas,[18] which are important chemicals especially in the industry. Isocyanates are generally synthesized from primary amines and $COCl_2$ (Scheme 1, reaction I).[19−21] However, due to the potential safety risk of $COCl_2$, it should be replaced in part by NTCAs, which are typically synthesized by the reactions of hexachloroacetone (HCA) (Scheme 1, reaction II).[22] However, the reactivity of HCA for nucleophilic substitution reactions is lower than that of $COCl_2$ and TCAC, and it is also more expensive than $COCl_2$ (Scheme 1, top). For these reasons, there is a need to develop an innovative synthetic method for NTCAs capable of being performed under safe conditions with inexpensive raw materials.

In this study, we found that NTCAs were directly obtained by photo-irradiation of a mixed solution of TCE, a more common and accessible organic solvent, and an amine or a HCl salt of an amine without base. This direct synthetic method is simpler and safer than the two-step method reported previously and enables convenient syntheses of various NCTAs with fewer reagents, solvents, and waste in the reaction. We then successfully converted the obtained NTCAs to N-substituted ureas and carbamates through base-catalyzed substitution reactions with amines or alcohols. Additionally, we found that a novel fluoroalkylene-bridged bisNTCA allowed the formation of a polyurethane (PU) through its base-catalyzed condensation reaction with a diol. To the best of our knowledge, the synthesis of a PU with NTCA has never been reported.

RESULTS AND DISCUSSION

Photochemical Oxidation of TCE by a Low-Pressure Mercury Lamp. A low-pressure mercury lamp (LPML), which mainly generates 184.9 and 253.7 nm light, has low electric power consumption. This light covers the electronic absorption bands of chlorinated alkanes, originating from $\sigma-\sigma^*$ and/or $n-\sigma^*$ transitions.[23] A 20 W LPML (ø24 mm × 120 mm, illuminance at 5 mm distance: 40 μW cm^{-2} at 185 nm) was inserted into the reaction solution via a quartz glass jacket (ø28 × 150 mm) fixed in the center of a cylindrical flask (ø42 × 170 mm). The quartz glass jacket allows for transmission of UV-C light while protecting the lamp from corrosive products generated by the reactions. The photochemical syntheses were carried out in this reaction system with 20 mL (196 mmol) of TCE containing 10−40 mmol of an amine under O_2 bubbling (0.1 L/min). The gaseous side products and byproducts such as $COCl_2$ and HCl (g) having high toxicity and corrosivity were removed by dual traps containing an alcohol and aqueous $NaHCO_3$, respectively.

We estimated in advance the amounts of TCAC and $COCl_2$ generated from TCE with this photoreaction system [corresponding to step 1 of reaction (III) in Scheme 1]. When 20 mL (196 mmol) of TCE was subjected to the photoreaction at 80 °C for 1 h, TCAC and $COCl_2$ were produced in 33 and 8% yields, respectively (65 and 32 mmol, respectively), with respect to the carbon content of TCE (Figure 1). Their yields were increased to 46/17, 62/19, and

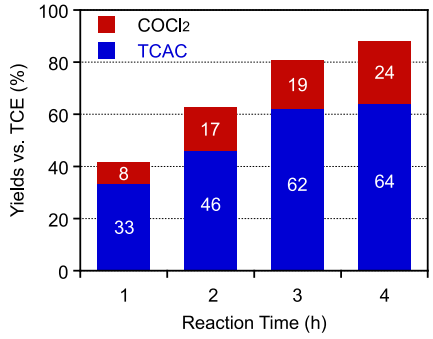


Figure 1. Yields of TCAC and $COCl_2$ generated upon photo-irradiation of 20 mL of TCE under O_2 bubbling (0.1 L/min) at 80 °C with a 20 W LPML. The yields were estimated from the products formed through the reactions with 1-butanol.

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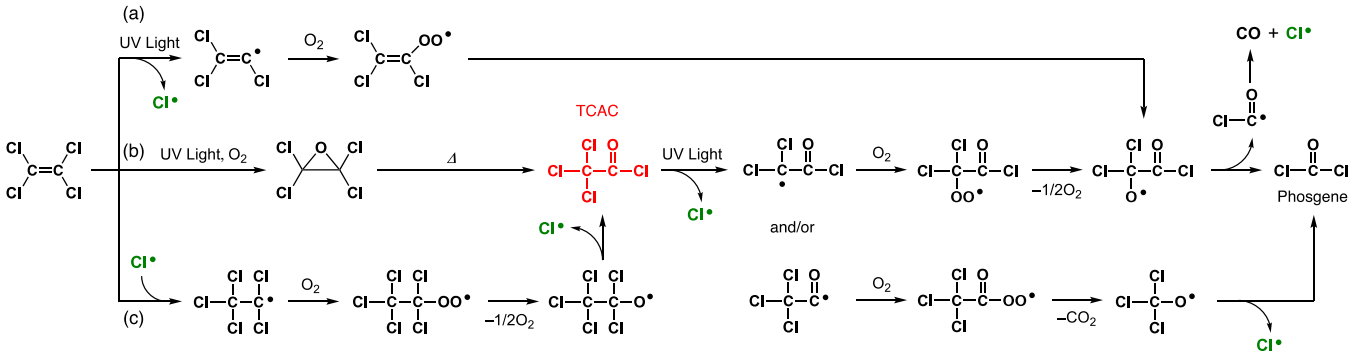
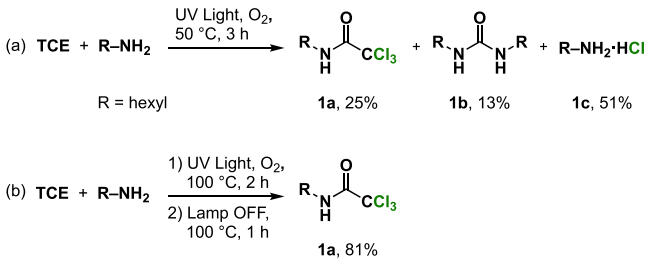
Scheme 2. Proposed Mechanism for Multi-reaction Pathways (a–c) in Photochemical Oxidation of TCE



64/24% by increasing the reaction times to 2, 3, and 4 h, respectively. In contrast, the yields were decreased to 52/13 and 47/10% with decreasing temperatures of 50 and 30 °C, respectively, for 3 h. The ratio of TCAC/$COCl_2$ increased with decreasing temperature. With respect to the reaction mechanism, these oxidized products may form through multiple reaction pathways including radical chain reactions initiated by the photolysis of the C–Cl bond and direct photooxidation of the C=C bond as shown in Scheme 2.[8]

Direct In Situ Photochemical Synthesis of NTCAs from TCE Solutions Containing Amines. With the expectation that TCAC and/or $COCl_2$ generated by the photochemical oxidation of TCE would react with amines, we then examined the in situ synthesis of NTCA with hexylamine in TCE. A 20 mL TCE solution containing hexylamine (20 mmol) was exposed to UV light under O_2 bubbling with stirring at 50 °C for 3 h [Scheme 3, reaction (a)]. ^{1}H NMR

Scheme 3. Photochemical Synthesis of NTCA with TCE and Hexylamine at (a) 50 and (b) 100 °C[a]



[a]Reaction procedures and conditions: irradiation by UV light of 20 mL (196 mmol) of TCE containing 20 mmol of amine under O_2 bubbling (0.1 L/min) with a 20 W LPML.

analysis of the sample solution showed that the reaction occurred to afford the corresponding NTCA **1a**, urea **1b**, and HCl salt of hexylamine **1c** in 25, 13, and 51% yields, respectively. The products **1a** and **1b** may originate from the reactions of amine with TCAC and $COCl_2$, respectively, generated by the photochemical oxidation of TCE. Here, HCl generated by the condensation reactions resulted in the formation of the amine HCl salt **1c**, which most likely decelerated the formation of **1a** and **1b**. However, it is known that amine HCl salts bring about condensation reactions with $COCl_2$ at high temperature, and these reactions have been used for the industrial production of isocyanates (Scheme 1, reaction 1).[20] With an expectation that TCAC, having an analogous structure with phosgene, undergoes similar reactions with amine HCl salts, the photochemical reaction was performed at a higher temperature of 100 °C with incubation for 1 h after turning off the light. Interestingly, only **1a** was obtained in 81% yield without **1b** and **1c** [Scheme 3, reaction (b)]. Judging from the total amount of chloroformate and carbonate ester (0.5 equiv for **1a**) in the attached methanol trap, $COCl_2$ generated by the photochemical reactions may vaporize immediately from the sample solution before reacting with the amine.

Based on these optimized reaction conditions, a series of NTCAs were synthesized (Scheme 4). Butylamine, benzylamine, and cyclohexylamine, having aliphatic alkyl groups, provided NTCAs **2**, **3**, and **4** in 97, 60, and 88% yields, respectively. Piperidine, a secondary aliphatic amine, provided the corresponding NTCA **5** in 86% yield. However, aniline, an aromatic amine, provided **6** in only 11% yield due to the formation of aniline black by the oxidation.[24] Fluorine-substituted anilines, capable of suppressing oxidation, participated in the reactions to afford **7**, **8**, and **9** in 51, 51, and 85% yields, respectively. Even pentafluoroaniline, which should exhibit the weakest nucleophilicity in the series of aliphatic and aromatic amines, reacted to afford **10** in 65% yield. As a reference experiment, HCA showed no notable reaction when mixed with pentafluoroaniline at 100 °C. Benzamide, whose basicity is weaker than that of aniline, underwent the reaction to afford **11** in 23% yield. Fluorine-substituted benzamide, which has lower nucleophilicity but higher oxidation resistance, afforded fluorine-substituted **12** in higher 77% yield. These results suggest a clear advantage of the present photochemical reaction for substrates having weak nucleophilicity. This reaction was also available for the synthesis of bistrichloroacetamides from diamines. Alkyl diamines such as 1,6-diaminohexane and 1,2-bis(2-aminoethoxy)ethane provided the corresponding bisNTCAs **13** and **14** in 68 and 56% yields, respectively. Aromatic diamines such as 2,4-diaminotoluene and 4,4′-diaminodiphenyl methane afforded the corresponding bisNTCAs **15** and **16** in 70 and 85% yields, respectively.

Generally, amines that are unstable under air and light, and/or have high volatility, can be stored in their HCl salt forms. Based on the reaction mechanism for NTCA generation described above, we demonstrated the synthesis of NTCAs with amine HCl salts (Scheme 5). Aniline, which provided aniline black in the photochemical reaction (vide ante), caused a dramatic increase in the yield of **6** to 59% when using its HCl salt. As a reference, the HCl salt of aniline showed no notable reaction with HCA upon heating at 100 °C for 12 h. Although there are technical difficulties with using methylamine, whose boiling point is −6 °C, in the present photochemical synthesis, its HCl salt with a melting point of 231–233 °C allowed the

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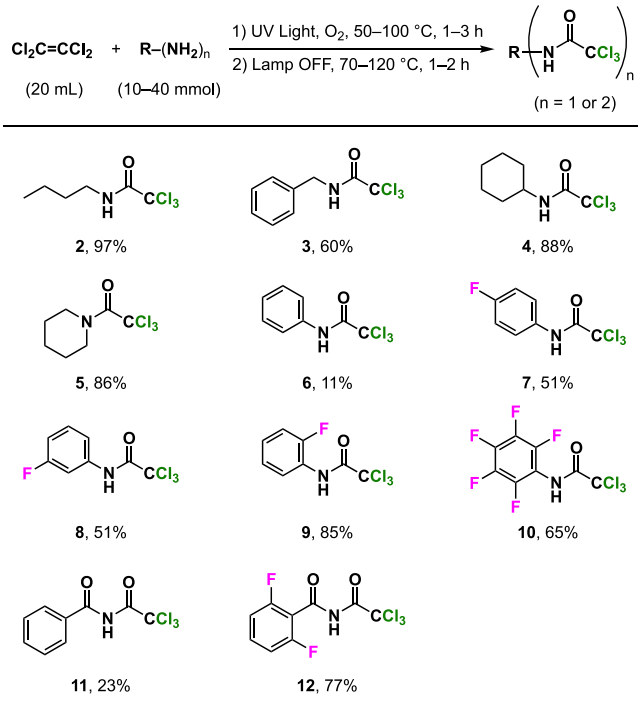
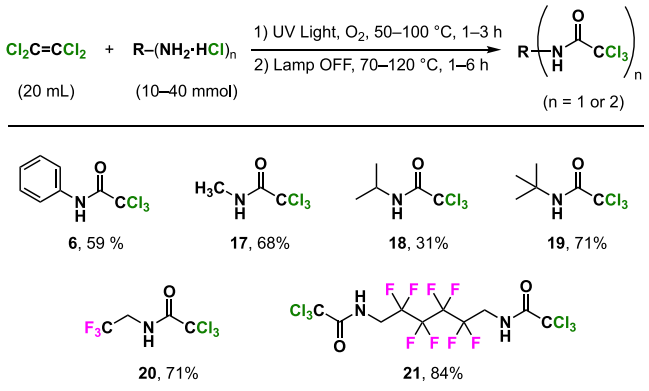
Scheme 4. Photochemical Synthesis of NTCAs with TCE and a Series of Amines[a]



[a]Reaction procedures and conditions: irradiation by UV light of 20 mL (196 mmol) of TCE containing 10−40 mmol of amine under O_2 bubbling (0.1 L/min) with a 20 W LPML.

Scheme 5. Photochemical Synthesis of NTCAs with TCE and Amine HCl Salts[a]

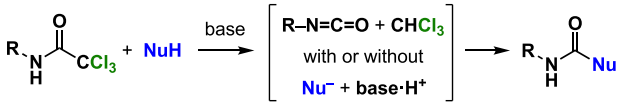


[a]Reaction procedures and conditions: irradiation by UV light of 20 mL (196 mmol) of TCE containing 3−40 mmol of the amine HCl salt under O_2 bubbling (0.1 L/min) with a 20 W LPML.

reaction to afford **17** in 68% yield. Likewise, HCl salts of isopropylamine and *tert*-butylamine, with sterically crowded structures, provided the corresponding NTCAs **18** and **19** in 31 and 71% yields, respectively. The synthetic method developed herein was then applied to the synthesis of novel fluoroalkyl-substituted NTCAs. The photochemical reaction of TCE with the HCl salt of 2,2,2-trifluoroethylamine, having an electron-withdrawing alkyl group, was found to afford NTCA **20** in 71% yield. The HCl salt of 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diamine underwent the photochemical reaction to afford bisNTCA **21** in 84% yield.

Synthesis of N-Substituted Ureas through Base-Catalyzed Condensation of NTCAs with Amines. NTCAs are known to serve as blocked isocyanates, which react with strong organic bases such as 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and inorganic bases such as NaOH to afford the corresponding isocyanates.[17] There have been some reports on the reactions of NTCAs with amines and alcohols that afforded the N-substituted ureas and carbamates, respectively, via in situ formation of the isocyanates in solution (Scheme 6). To increase the utility and versatility of the

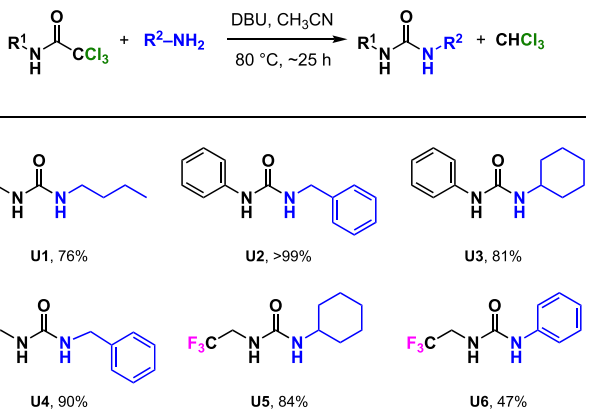
Scheme 6. Mechanism for Base-Catalyzed Condensation of NTCA with a Nucleophile



present photochemical reaction to allow safe and convenient synthesis of NTCAs, we next demonstrated the synthesis of both known and unknown N-substituted ureas and carbamates with some of the obtained NTCAs.

When a CH_3CN solution containing *N*-phenyl-substituted **6** (2.0 mmol), which forms a relatively stable aromatic isocyanate, butylamine (2.0 mmol), and DBU (1.0 mmol), was stirred at 80 °C for 28 h, unsymmetric N-substituted urea **U1** was obtained in 76% yield after work-up (Scheme 7). NTCA **6** also reacted with other alkyl amines such as benzylamine and cyclohexylamine to afford the corresponding ureas **U2** and **U3** in >99 and 81% yields, respectively. In contrast, no notable reactions were observed for combinations of NTCA **3** and aliphatic amines such as butylamine under the same reaction conditions. However, NTCA **20**, bearing an

Scheme 7. DBU-Catalyzed Synthesis of N-Substituted Ureas from NTCAs and Primary Amines[a]



[a]Reaction procedures and conditions: stirring a CH_3CN (10 mL) solution containing NTCA (2 mmol), amine (1.0−1.1 equiv), and DBU (0.25−0.5 equiv) at 80 °C for 19−186 h.

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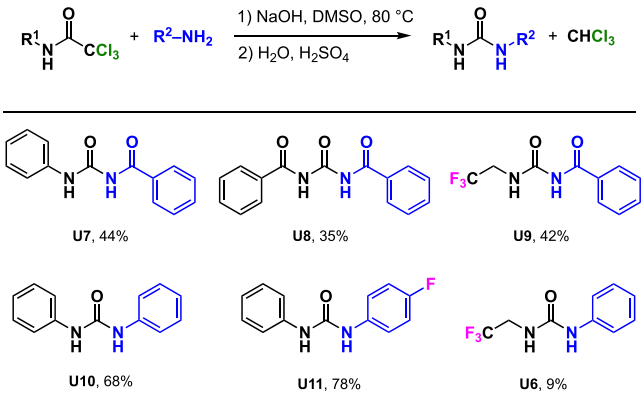
electron-withdrawing fluoroalkyl group, allowed the reaction with benzylamine and cyclohexylamine to produce **U4** and **U5** in 90 and 84% yields, respectively. NTCA **20** also reacted with aniline, having lower nucleophilicity than the alkyl amines, to afford **U6** in 47% yield.

It is reported that carboxamides and sulfonamides, having relatively higher acidities than ordinary alkyl and aromatic amines, reacted with NTCAs in DMSO at 80 °C in the presence of an excess amount of NaOH.[18] Their sodium salts with increased nucleophilicity underwent addition reactions with the isocyanates generated in solution. With this as a reference, we further demonstrated the synthesis of N-substituted ureas with NTCA and benzamide (Scheme 8).

Scheme 8. NaOH-Catalyzed Synthesis of N-Substituted Ureas from NTCAs and Benzamide or Aniline[a]

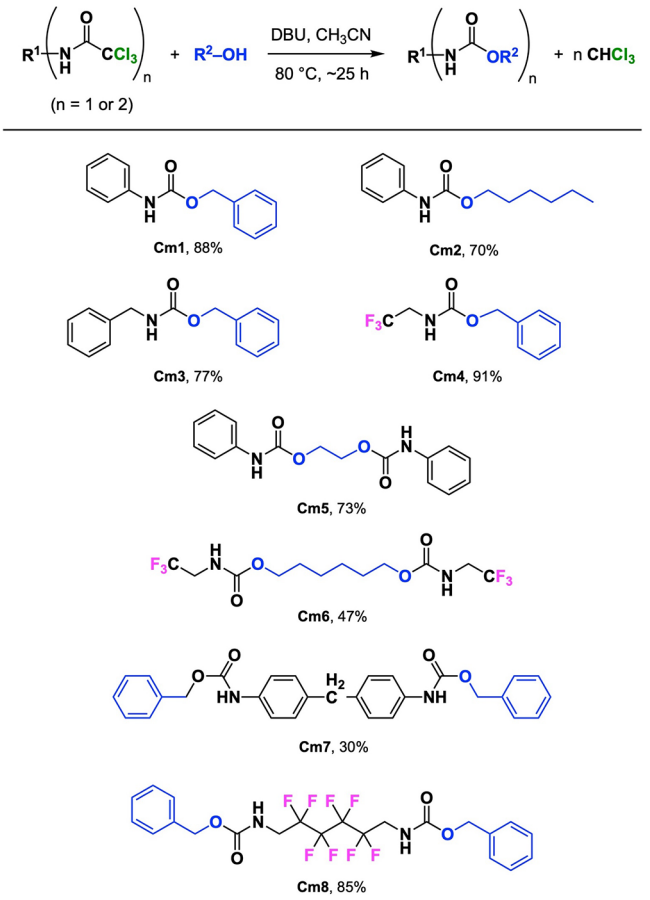


[a]Reaction procedures and conditions: [1] stirring a DMSO (2.5−5.0 mL) solution containing an amide or amine (1.25−5.0 mmol), 2.5 equiv NaOH, and 0.5−1.0 equiv NTCA at 80 °C for 0.5−23 h. [2] Acidifying the sample solution to pH = 2 with concd H_2SO_4.

The phenyl- and benzoyl-substituted NTCAs **6** and **11** reacted with benzamide to afford **U7** and **U8** in 44 and 35% yields, respectively. Although benzyl-substituted **3** showed no reaction with benzamide, the fluoroalkyl-substituted **20** afforded **U9** in 42% yield. We then examined the reactions of the phenyl and fluoroalkyl NTCAs with aniline, having lower acidity than benzamide. NTCA **11** underwent a NaOH-catalyzed substitution reaction with aniline to afford 1,3-diphenyl urea **U10** in 68% yield. Expectedly, the yield of the product **U11** was increased to 78% with fluoroaniline, having higher acidity. Fluoroalkyl-substituted **20** also reacted with aniline to afford the corresponding unsymmetric urea **U6** in 9% yield.

Synthesis of Carbamates and a PU through Base-Catalyzed Condensation of NTCAs with Alcohols. As a further extension of the base-catalyzed condensation reaction of NTCAs, carbamates were synthesized through reactions with alcohols. When a CH_3CN solution containing *N*-phenyl-substituted **6** (2.0 mmol), benzyl alcohol (BnOH) (2.2 mmol), and DBU (1.0 mmol) was stirred at 80 °C for 67 h, the corresponding carbamate **Cm1** was obtained in 88% yield after work-up (Scheme 9). NTCA **6** provided **Cm2** in 70% yield through the reaction with 1-hexanol. These reactions, however, were accompanied by the formation of 1,3-diphenylurea as a minor side product, which likely originated from the reaction of phenyl isocyanate and aniline formed from decomposition of the isocyanate.[25] When examining the reaction of NTCA **6** with phenol, having lower nucleophilicity, in the presence of DBU or NaOH, only diphenylurea was obtained without the

Scheme 9. DBU-Catalyzed Synthesis of Carbamates from NTCAs and Primary Aliphatic Alcohols[a]



[a]Reaction procedures and conditions: stirring a CH_3CN (1−10 mL) solution containing NTCA (0.18−3 mmol), alcohol (0.5−2.5 equiv), and DBU (0.5−1.0 equiv) at 80 °C for 16−67 h.

formation of the carbamates. It was also obtained as the sole product with isopropyl and *tert*-butyl alcohols, having sterically crowded OH groups. In contrast to the case of N-substituted ureas, aliphatic NTCA **3**, which most likely formed a less stable isocyanate than **6**, caused the base-catalyzed condensation with BnOH to afford the corresponding carbamate **Cm3** in 77% yield. This result can be explained by the different acidities of −OH and $-NH_2$ groups. The hydroxy group, generally possessing higher acidity than the amino group, can form an alkoxide ion upon interaction with DBU to enhance its nucleophilicity, while the amino group with lower acidity hardly forms the anion. As expected, the fluoroalkyl-substituted NTCA **20** accelerated the reaction to afford **Cm4** in a higher, 91%, yield. *N*-Phenyl- and *N*-fluoroalkyl-substituted biscarbamates **Cm5** and **Cm6** could be synthesized in 73 and 47% yields, respectively, from the combinations of **6**/ethylene glycol (EG) and **20**/1,6-hexanediol (HD), respectively. N−N bridged biscarbamates **Cm7** and **Cm8** could also be synthesized in 30 and 85% yields from the combinations of **17**/BnOH and **21**/BnOH, respectively. On the other hand, neither *N*-benzoyl- nor *N*-2,6-difluorobenzoyl-substituted NTCAs **11** and **12** provided the corresponding carbamates, instead of producing benzamide and 2,6-difluorobenzamide, respectively, upon mixing with BnOH and DBU in CH_3CN.

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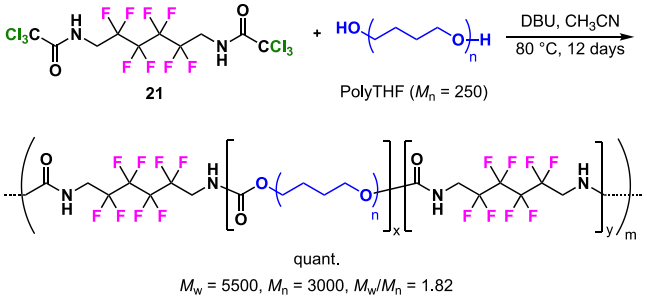
These products might form through the decomposition of the corresponding isocyanates.

Finally, we demonstrated the synthesis of a PU by the DBU-catalyzed condensation of N−N-bridged biscarbamates and polyTHF with a number-average molecular weight (M_n) of 250. When the reactions were performed with aromatic biscarbamates **15** and **16**, corresponding to blocked TDI and MDI, respectively, no notable reactions were observed owing to their low solubilities in the organic solvents. Although alkylene-bridged **13** and **14** reacted with diols in CH_3CN, the observed polymerization degrees were below M_n = 1000. However, interestingly, the N−N fluoroalkylene-bridged biscarbamate **21** accelerated the reaction to afford the fluorinated PU quantitatively with M_w/M_n = 5500/3000 (Scheme 10). Judging from the NMR and IR spectral data, the polymer likely contains urea components formed to some extent upon decomposition of the isocyanate (vide ante).

Scheme 10. DBU-Catalyzed Synthesis of Fluoroalkyl PU from NTCAs and PolyTHF[a]



[a]Reaction procedures and conditions: stirring a CH_3CN (0.5 mL) solution containing **21** (0.2 mmol), polyTHF (1 equiv), and DBU (0.1 equiv) at 80 °C for 12 days.

CONCLUSIONS

Chemical conversion of TCE into valuable chemicals and polymers with low energy and emissions is an important issue in terms of sustainable organic synthesis. In the present study, we have developed in situ photo-on-demand synthesis of N-substituted NTCAs, which serve as blocked isocyanates, from TCE and amines. A variety of NTCAs could be directly synthesized upon photo-irradiation of a TCE solution containing an amine or its HCl salt under O_2 bubbling at over 70 °C with a LPML. TCE underwent photochemical oxidation to afford TCAC, which then reacts in situ with the amine to afford the corresponding NTCA. Note that exhaust gas contains toxic $COCl_2$ and HCl, which must be trapped with alcohol and aqueous alkaline solutions, respectively. Compared with the convenient NTCA synthesis with HCA, the present reaction has the clear advantage of being applicable to a wide variety of amines, even those having lower nucleophilicity such as fluorinated amines, amides, and amine HCl salts. The produced NTCAs could be converted to N-substituted ureas and carbamates through base-catalyzed condensation reactions with amines and alcohols, respectively, with the elimination of $CHCl_3$. The newly synthesized fluorine-substituted NTCAs also underwent the reactions and enabled new transformations with a variety of nucleophiles to afford fluorine-containing chemicals and PUs. These reactions extended the utility of NTCAs as blocked isocyanates. The present chemical reaction is a simpler, safer, and convenient method of converting TCE to valuable chemicals and PUs with less energy and chemical consumption and is expected to be applied to sustainable organic synthesis and chemical recycling of TCE.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. 2,2,3,3,4,4,5,5-Octafluoro-1,6-diaminohexane hydrochloride was synthesized according to the literature method.[26] For column chromatography, Wakogel (60 N, particle size 38−100 μm, silica gel, irregular) was used. For vacuum distillation, a glass tube oven (SIBATA SCIENTIFIC TECHNOLOGY, Model GTO-1000) was used with an oil rotary vacuum pump. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer or a Bruker AVANCE 500 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane as an internal standard. ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 spectrometer, where chemical shifts (δ in ppm) were determined with respect to hexafluorobenzene as an external standard. Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR 4700 equipped with an ATR PR0450-S, and samples were loaded neat. FAB mass spectrometry was performed on a JEOL JMS-BU30 LC Mate spectrometer with 3-nitrobenzyl alcohol as a matrix. High-resolution mass spectrometry (HRMS) was performed (in ESI) by the Kobe University mass spectral facility (Research Facility Center for Science and Technology) with a Thermo Scientific Orbitrap Exploris mass spectrometer. Size exclusion chromatography measurements were performed at 40 °C on TOHSOH TSKgel G5000H_{HR} and TSKgel G4000H_{HR} columns using a JASCO Type PU-2089 quaternary gradient pump, equipped with a JASCO Type RI-4030 refractive index detector with THF as an eluent. Melting points were recorded on a J-SCIENCE LAB RFS-10A melting point apparatus.

General Procedure for the Photochemical Synthesis of NTCAs from TCE and Amines or HCl Salts of Amines. A cylindrical flask (ø42 × 120 mm), equipped with a LPML (Sen Light Co., UVL20PH-6, 20 W, ø24 × 120 mm) and a magnetic stirring bar, was charged with 20 mL of TCE containing an amine or a HCl salt of an amine (3−40 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 1−3 h at 50−80 °C. The lamp was turned off, and the sample solution was stirred at 70−120 °C for 1−22 h. The resulting gas passed through the photoreactor must be washed with an aqueous alkaline solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate, which was filtered by suction filtration, and dried under vacuum to afford the product. Otherwise, the sample solution was washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure to leave the product. The product was purified by recrystallization if necessary.

*N-Hexyl-2,2,2-trichloroacetamide (**1**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 1-hexylamine (2.7 mL, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/

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min) under exposure to UV light for 2 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. The sample solution was then washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure to afford *N*-hexyl-2,2,2-trichloroacetamide as a colorless liquid in 81% yield (3.99 g, 16.2 mmol). ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ/ppm 6.77 (br s, 1H, NH), 3.39 (q, J = 8.3 Hz, 2H, methylene), 1.62 (quin, J = 8.0 Hz, 2H, methylene), 1.40−1.30 (m, 6H, methylene), 0.90 (t, J = 8.0 Hz, 3H, methyl); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ/ppm 163.3, 92.5, 41.7, 31.3, 28.8, 26.3, 22.5, 14.0; IR (ATR) ν: 3331, 2930, 2859, 1760, 1694, 1523, 1466, 1247, 821, 675 cm^{-1}; FAB-MS m/z: $[M + H]^+$ calcd for $C_8H_{15}Cl_3NO$, 246.02; found, 246.23; Anal. Calcd for $C_8H_{14}Cl_3NO$: C, 38.97; H, 5.72; N, 5.68. Found: C, 39.02; H, 5.60; N, 5.77.

N-Butyl-2,2,2-trichloroacetamide (**2**). A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 1-butylamine (1.0 mL, 10 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 70 °C. The lamp was turned off, and the sample solution was stirred at 70 °C for 1 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. The sample solution was then washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure to leave *N*-butyl-2,2,2-trichloroacetamide as a colorless liquid in 97% yield (2.12 g, 9.7 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[27] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 6.71 (br s, 1H, NH), 3.39 (q, J = 6.7 Hz, 2H, methylene), 1.60 (quin, J = 3.2 Hz, 2H, methylene), 1.40 (sext, J = 7.6 Hz, 2H, methylene), 0.96 (t, J = 7.4 Hz, 3H, methyl); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 161.9, 92.8, 41.2, 31.0, 19.9, 13.7. IR (ATR) ν: 3334, 2960, 2873, 1692, 1519, 818, 645 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_6H_{10}Cl_3NONa$, 239.9720; found, 239.9717.

N-Benzyl-2,2,2-trichloroacetamide (**3**). A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing benzylamine (2.2 mL, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 50 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 1 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. The sample solution was then washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure to afford *N*-benzyl-2,2,2-trichloroacetamide as a white solid in 60% yield (3.01 g, 12.0 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[28] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.43−7.34 (m, 5H, phenyl), 6.96 (br s, 1H, NH), 4.59 (d, J = 5.6 Hz, 2H, methylene); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 161.9, 136.3, 129.0, 128.2, 127.7, 92.5, 45.3. IR (ATR) ν: 3264, 1684, 1528, 1357, 1237, 819, 756, 701, 648, 624, 592, 570 cm^{-1}; FAB-MS m/z: $[M + H]^+$ calcd for $C_9H_9Cl_3NO$, 251.97; found, 252.26.

N-Cyclohexyl-2,2,2-trichloroacetamide (**4**). A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing cyclohexylamine (2.3 mL, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 70 °C. The lamp was turned off, and the sample solution was stirred at 70 °C for 2.5 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. The sample solution was then washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure to afford *N*-cyclohexyl-2,2,2-trichloroacetamide as a white solid in 85% yield (4.16 g, 17.0 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[8b] White solid, mp 98.0−100.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 6.51 (br s, 1H, NH), 3.81−3.72 (m, 1H), 2.02−1.98 (m, 2H), 1.78−1.73 (m, 2H), 1.68−1.63 (m, 1H), 1.47−1.36 (m, 2H), 1.32−1.17 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 160.9, 92.9, 50.5, 32.3, 25.3, 24.5. IR (ATR) ν: 3347, 2933, 2855, 1684, 1518, 1224, 1084, 816, 731, 687, 614 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_8H_{12}Cl_3NONa$, 265.9877; found, 265.9871.

2,2,2-Trichloro-1-(piperidin-1-yl)ethan-1-one (**5**). A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing piperidine (1.98 mL, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. The sample solution was then washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure to afford 2,2,2-trichloro-1-(piperidin-1-yl)ethan-1-one as a colorless liquid in 86% yield (3.96 g, 17.2 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[29] White solid, mp 41.0−44.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 3.75 (br, 4H), 1.69 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 159.0, 93.4, 49.4, 47.9, 47.0, 25.6, 24.1. IR (ATR) ν: 3334, 2960, 2873, 1692, 1519, 1465, 1252, 819, 645 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + H]^+$ calcd for $C_7H_{11}Cl_3NO$, 229.9901; found, 229.9894.

N-Phenyl-2,2,2-trichloroacetamide (**6**). A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing anilinium chloride (5.2 g, 40 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 3 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 80 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a

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precipitate. It was filtered by suction filtration and dried under vacuum to afford *N*-phenyl-2,2,2-trichloroacetamide as a white solid in 59% yield (5.60 g, 23.5 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[8b] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 8.33 (br s, 1H, NH), 7.58 (dd, J = 6.8, 0.8 Hz, 2H, phenyl), 7.41 (t, J = 6.4 Hz, 2H, phenyl), 7.24 (t, J = 5.8 Hz, 1H, phenyl); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 159.2, 135.9, 129.3, 126.1, 120.3, 92.8; IR (ATR) ν: 3306, 1693, 1600, 1528, 1498, 1444, 1245, 877, 823, 813, 742, 686, 639 cm^{-1}; FAB-MS m/z: $[M + H]^+$ calcd for $C_8H_7Cl_3NO$, 237.96; found, 237.81.

N-4-Fluorophenyl-2,2,2-trichloroacetamide (**7**). A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 4-fluoroaniline (1.9 mL, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 1 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate. It was filtered by suction filtration and dried under vacuum to afford *N*-4-fluorophenyl-2,2,2-trichloroacetamide as a white solid in 51% yield (2.60 g, 10.2 mmol). White solid, mp 87.3−88.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ/ppm 8.36 (br s, 1H, NH), 7.56−7.53 (m, 2H, phenyl), 7.11−7.08 (m, 2H, phenyl); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ/ppm 160.4 (d, $^{1}J_{C-F}$ = 239.5 Hz), 159.4, 131.9 (d, $^{4}J_{C-F}$ = 2.8 Hz), 122.4 (d, $^{3}J_{C-F}$ = 8.3 Hz), 116.1 (d, $^{2}J_{C-F}$ = 22.8 Hz), 92.7; ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −115.2; IR (ATR) ν: 3303, 1692, 1524, 1507, 1410, 1223, 828, 816, 799, 638 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_8H_5Cl_3FNONa$, 277.9313; found, 277.9312.

N-3-Fluorophenyl-2,2,2-trichloroacetamide (**8**). A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 3-fluoroaniline (3.8 mL, 40 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2.5 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate. It was filtered by suction filtration and dried under vacuum to afford *N*-3-fluorophenyl-2,2,2-trichloroacetamide as a white solid in 51% yield (5.20 g, 20.3 mmol). White solid, mp 78.3−79.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ/ppm 8.35 (br s, 1H, NH), 7.52 (dt, J = 10.5, 2.3 Hz, 1H, phenyl), 7.38−7.34 (m, 1H, phenyl), 7.25 (dd, J = 7.8, 1.8 Hz, 1H, phenyl), 6.95 (tdd, J = 8.2, 2.5, 0.8 Hz, 1H, phenyl); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ/ppm 163.0 (d, $^{1}J_{C-F}$ = 245.0 Hz), 159.2, 137.4 (d, $^{3}J_{C-F}$ = 10.9 Hz), 130.5 (d, $^{3}J_{C-F}$ = 9.1 Hz), 115.7, 112.9 (d, $^{2}J_{C-F}$ = 21.0 Hz), 107.4 (d, $^{2}J_{C-F}$ = 26.5 Hz), 92.6; ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −110.3; IR (ATR) ν: 3312, 1697, 1607, 1531, 1489, 1444, 1433, 1221, 841, 813, 773, 672, 640 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_8H_5Cl_3FNONa$, 277.9313; found, 277.9312.

N-2-Fluorophenyl-2,2,2-trichloroacetamide (**9**). A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 2-fluoroaniline (3.9 mL, 40 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2.5 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate. It was filtered by suction filtration and dried under vacuum to afford *N*-2-fluorophenyl-2,2,2-trichloroacetamide as a white solid in 85% yield (8.70 g, 34.0 mmol). ^{1}H NMR (400 MHz, DMSO-d_6, 293 K): δ/ppm 11.03 (br s, 1H, NH), 7.60−7.53 (m, 2H, phenyl), 7.48−7.44 (m, 1H, phenyl), 7.06 (tdd, J = 8.4, 6.0, 0.9 Hz, 1H, phenyl); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ/ppm 161.8 (d, $^{1}J_{C-F}$ = 240.5 Hz), 159.7, 138.8 (d, $^{3}J_{C-F}$ = 11 Hz), 130.5 (d, $^{3}J_{C-F}$ = 9.5 Hz), 117.0 (d, $^{4}J_{C-F}$ = 2.9 Hz), 111.8 (d, $^{2}J_{C-F}$ = 21.1 Hz), 108.0 (d, $^{2}J_{C-F}$ = 26.3 Hz), 92.7; ^{19}F NMR (376 MHz, DMSO-d_6, 293 K): δ/ppm −130.2; IR (ATR) ν: 3411, 1766, 1721, 1621, 1599, 1536, 1486, 1458, 1319, 1260, 1216, 1191, 1103, 882, 815, 750, 670, 579 cm^{-1}; FAB-MS m/z: $[M + H]^+$ calcd for $C_8H_6Cl_3FNO$, 255.95; found, 255.69. Anal. Calcd for $C_8H_5Cl_3FNO$: C, 34.46; H, 1.97; N, 5.46. Found: C, 34.22; H, 2.09; N, 5.44.

N-Pentafluorophenyl-2,2,2-trichloroacetamide (**10**). A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing pentafluoroaniline (3.7 g, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate. It was filtered by suction filtration and dried under vacuum to afford *N*-pentafluorophenyl-2,2,2-trichloroacetamide as a white solid in 65% yield (4.20 g, 12.9 mmol). White solid, mp 115.3−117.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ/ppm 7.94 (br s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ/ppm 160.4, 144.6, 142.4, 142.0, 139.9, 139.2, 136.6, 110.2, 91.3; ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −144.2, −153.4, −160.9; IR (ATR) ν: 3264, 1718, 1523, 1496, 1458, 1235, 1151, 1001, 965, 837, 818, 679, 617 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_8HCl_3F_5NONa$, 349.8936; found, 349.8933.

N-(2,2,2-Trichloroacetyl)benzamide (**11**). A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing benzamide (2.4 g, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 1.5 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a

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precipitate. It was filtered by suction filtration and dried under vacuum to afford *N*-(2,2,2-trichloroacetyl)benzamide as a white solid in 23% yield (1.20 g, 4.5 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[18] White solid, mp 77.2−77.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ/ppm 9.39 (br s, 1H, NH), 7.85 (dd, J = 8.5, 1.0 Hz, 2H, phenyl), 7.68 (tt, J = 7.5, 1.5 Hz, 1H, phenyl), 7.56 (t, J = 8.5 Hz, 2H, phenyl); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ/ppm 164.3, 157.6, 134.0, 132.1, 129.3, 127.9, 92.3; IR (ATR) ν: 3280, 1765, 1699, 1505, 1488, 1252, 1177, 1157, 1068, 824, 723, 710, 661, 605 cm^{-1}; FAB-MS m/z: $[M + H]^+$ calcd for $C_9H_7Cl_3NO_2$, 265.95; found, 265.74.

*2,6-Difluoro-N-(2,2,2-trichloroacetyl)benzamide (**12**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 2,6-difluorobenzamide (3.1 g, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 1 h at 50 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 1 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate. It was filtered by suction filtration and dried under vacuum to afford 2,6-difluoro-*N*-(2,2,2-trichloroacetyl)benzamide as a white solid in 77% yield (4.60 g, 15.3 mmol). White solid, mp 37.8−39.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K): δ/ppm 9.26 (br s, 1H, NH), 7.55−7.49 (m, 1H, phenyl), 7.03 (t, J = 8.3 Hz, 2H, phenyl); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 165.1, 164.9, 161.4 (d, $^{1}J_{C-F}$ = 254.4 Hz), 160.4 (d, $^{1}J_{C-F}$ = 253.7 Hz), 133.2 (t, $^{3}J_{C-F}$ = 10.9 Hz), 112.5 (dd, $^{2}J_{C-F}$ = 22.6, 2.9 Hz), 111.7 (t, $^{2}J_{C-F}$ = 17.5 Hz), 90.3; ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −111.6; IR (ATR) ν: 3287, 3207, 1771, 1708, 1624, 1591, 1506, 1468, 1281, 1252, 1233, 1173, 1150, 1087, 1011, 839, 822, 794, 655, 582 cm^{-1}; FAB-MS m/z: $[M + H]^+$ calcd for $C_9H_5Cl_3F_2NO_2$, 301.94; found, 301.71. Anal. Calcd for $C_9H_4Cl_3F_2NO_2$: C, 35.74; H, 1.33; N, 4.63. Found: C, 35.68; H, 1.35; N, 4.70.

*N,N′-(Hexane-1,6-diyl)bis(2,2,2-trichloroacetamide) (**13**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 1,6-diaminohexane (1.2 g, 10 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2.5 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate. It was filtered by suction filtration and dried under vacuum to afford *N,N′*-(hexane-1,6-diyl)bis(2,2,2-trichloroacetamide) as a white solid in 68% yield (2.80 g, 6.8 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[30] White solid, mp 153.4−153.6 °C. ^{1}H NMR (500 MHz, DMSO-d_6, 293 K): δ/ppm 9.00 (t, J = 5.5 Hz, 2H, NH), 3.44 (br s, 2H, methylene), 2.50 (quin, J = 1.8 Hz, 2H, methylene), 1.49 (t, J = 6.5 Hz, 4H, methylene), 1.33−1.25 (m, 4H, methylene); ^{13}C NMR (125 MHz, DMSO-d_6, 293 K): δ/ppm 161.3, 92.9, 40.5, 28.1, 25.6; IR (ATR) ν: 3318, 2953, 2926, 2858, 1696, 1528, 1439, 1293, 1263, 1219, 818, 739, 642 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_{10}H_{14}Cl_6N_2O_2Na$, 426.9079; found, 426.9075.

*N,N′-((Ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis-(2,2,2-trichloroacetamide) (**14**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 1,2-bis(2-aminoethoxy)ethane (2.96 g, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. The sample solution was then washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure to afford *N,N′*-((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(2,2,2-trichloroacetamide) as a white solid in 56% yield (4.91 g, 11.2 mmol). White solid, mp 77.5−80.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.14 (br s, 2H, NH), 3.67−3.64 (m, 8H, methylene), 3.60−3.56 (m, 4H, methylene); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 162.0, 92.5, 70.2, 68.6, 41.0; IR (ATR) ν: 3361, 2952, 2871, 1686, 1513, 1434, 1244, 1091, 820, 734, 624 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + H]^+$ calcd for $C_{10}H_{15}Cl_6N_2O_4$, 436.9157; found, 436.9144.

*N,N′-(4-Methyl-1,3-phenylene)bis(2,2,2-trichloroacetamide) (**15**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 2,4-diaminotoluene (1.2 g, 10 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2.5 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate. It was filtered by suction filtration and dried under vacuum to afford *N,N′*-(4-methyl-1,3-phenylene)bis(2,2,2-trichloroacetamide) as a white solid in 70% yield (2.90 g, 7.0 mmol). White solid, mp 208.9−209.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 293 K): δ/ppm 10.89 (s, 1H, NH), 10.65 (s, 1H, NH), 7.58−7.56 (m, 2H, phenyl), 7.34 (d, J = 8.0 Hz, 1H, phenyl), 2.19 (s, 3H, methyl); ^{13}C NMR (125 MHz, DMSO-d_6, 293 K): δ/ppm 160.5, 159.6, 135.3, 134.7, 131.5, 130.7, 120.2, 119.7, 92.9, 92.8, 16.7; IR (ATR) ν: 3273, 1697, 1613, 1497, 1274, 1230, 838, 812, 793, 753, 653, 597 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_{11}H_8Cl_6N_2O_2Na$, 432.8609; found, 432.8600.

*N,N′-(Methylenebis(4,1-phenylene))bis(2,2,2-trichloroacetamide) (**16**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 4,4′-diaminodiphenylmethane (4.0 g, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After

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cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate. It was filtered by suction filtration and dried under vacuum to afford *N*,*N*′-(methylenebis(4,1-phenylene))bis(2,2,2-trichloroacetamide) as a white solid in 85% yield (8.30 g, 16.9 mmol). White solid, mp 194.3−194.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 293 K): δ/ppm 10.78 (s, 2H, NH), 7.56 (d, J = 8.4 Hz, 4H, phenyl), 7.25 (d, J = 8.4 Hz, 4H, phenyl), 3.93 (s, 2H, methylene); ^{13}C NMR (125 MHz, DMSO-d_6, 293 K): δ/ppm 159.5, 138.2, 135.1, 129.2, 128.9, 121.5, 93.0; IR (ATR) ν: 3378, 3329, 1712, 1699, 1597, 1527, 1509, 1408, 1311, 1242, 883, 813, 730, 674, 591 cm^{-1}; HRMS (ESI orbitrap) m/z: [M + Na]$^+$ calcd for $C_{17}H_{12}Cl_6N_2O_2Na$, 508.8922; found, 508.8919.

*2,2,2-Trichloro-N-methylacetamide (**17**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing methylamine hydrochloride (1.35 g, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 21.5 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. The sample solution was then washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure to afford 2,2,2-trichloro-*N*-methylacetamide as a white solid in 68% yield (2.38 g, 13.5 mmol). White solid, mp 78.5−79.2 °C. ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[27] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 6.77 (br s, 1H, NH), 3.00 (d, J = 4.8 Hz, 3H, methyl); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 162.7, 92.4, 28.1; IR (ATR) ν: 3367, 2944, 1758, 1688, 1513, 1408, 1253, 815, 611 cm^{-1}.

*2,2,2-Trichloro-N-isopropylacetamide (**18**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing isopropylamine hydrochloride (1.91 g, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 3 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. The sample solution was then washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure, and the residue was recrystallized with CH_2Cl_2 and *n*-hexane to afford 2,2,2-trichloro-*N*-isopropylacetamide as a white solid in 31% yield (1.24 g, 6.1 mmol). White solid, mp 81.5−82.5 °C. ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[29] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 6.45 (br s, 1H, NH), 4.11−4.03 (m, 1H), 1.27 (d, J = 6.8 Hz, 6H, methyl); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 160.9, 92.8, 44.0, 22.1; IR (ATR) ν: 3309, 2979, 1683, 1525, 1252, 1148, 868, 819, 637 cm^{-1}; HRMS (ESI orbitrap) m/z: [M + Na]$^+$ calcd for $C_5H_8Cl_3NONa$, 225.9564; found, 225.9563.

*N-(tert-Butyl)-2,2,2-trichloroacetamide (**19**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing *tert*-butylamine hydrochloride (2.19 g, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 3 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. The sample solution was then washed with water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure, and the residue was washed with *n*-hexane to afford *N*-(*tert*-butyl)-2,2,2-trichloroacetamide as a white solid in 71% yield (3.10 g, 14.3 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[16] White solid, mp 111.8−112.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 6.48 (br s, 1H, NH), 1.43 (s, 9H, methyl); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 160.4, 93.3, 53.0, 28.0; IR (ATR) ν: 3353, 2979, 1697, 1519, 1364, 1270, 1214, 919, 820, 680, 568 cm^{-1}; HRMS (ESI orbitrap) m/z: [M + Na]$^+$ calcd for $C_6H_{10}Cl_3NONa$, 239.9720; found, 239.9719.

*2,2,2-Trichloro-N-(2,2,2-trifluoroethyl)acetamide (**20**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 2,2,2-trifluoroethylamine hydrochloride (2.7 g, 20 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 1 h at 80 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate. It was filtered by suction filtration and dried under vacuum to afford 2,2,2-trichloro-*N*-(2,2,2-trifluoroethyl)acetamide as a white solid in 71% yield (3.50 g, 14.2 mmol). White solid, mp 64.1−66.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 6.98 (br s, 1H, NH), 4.04 (quin, J = 6.8 Hz, 2H, methylene); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 162.4, 123.5 (q, $^1J_{C-F}$ = 221.5 Hz), 91.7, 42.5 (q, $^2J_{C-F}$ = 28.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −72.2; IR (ATR) ν: 3331, 1703, 1672, 1532, 1424, 1397, 1274, 1236, 1158, 842, 823, 665, 601 cm^{-1}; HRMS (ESI orbitrap) m/z: [M + Na]$^+$ calcd for $C_4H_3Cl_3F_3NONa$, 265.9125; found, 265.9120.

*N,N′-(Octafluorohexane-1,6-diyl)bis(2,2,2-trichloroacetamide) (**21**).* A cylindrical flask (ø42 × 170 mm), equipped with a LPML and a magnetic stirring bar, was charged with 20 mL (196 mmol) of TCE containing 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diamine hydrochloride (1.0 g, 3.0 mmol). An aluminum block bath was used to heat the sample solution. The sample solution was vigorously stirred upon bubbling with O_2 (0.1 L/min) under exposure to UV light for 2.5 h at 50 °C. The lamp was turned off, and the sample solution was stirred at 120 °C for 2 h. The resulting gas passed through the photoreactor was washed with aqueous $NaHCO_3$ solution at the trap system attached. After cooling the sample solution to room temperature, *n*-hexane was added to the sample solution to afford a precipitate. It was filtered by suction filtration and dried under vacuum to afford *N*,*N*′-(octafluorohexane-1,6-diyl)bis(2,2,2-trichloroacetamide) as a white solid in 84% yield (1.40 g, 2.5 mmol). White solid, mp 197.4−197.6 °C. ^{1}H

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NMR (500 MHz, DMSO-d_6, 293 K): δ/ppm 9.65 (br s, 2H, NH), 4.05 (q, J = 8.3 Hz, 4H, methylene); ^{13}C NMR (125 MHz, DMSO-d_6, 293 K): δ/ppm 162.5, 115.5, 110.8, 91.9, 40.4 (t, $^2J_{C-F}$ = 23.6 Hz); ^{19}F NMR (376 MHz, DMSO-d_6, 293 K): δ/ppm −118.0, −123.3; IR (ATR) ν: 3315, 1706,1530, 1155, 1122, 832, 821, 632 cm^{-1}; HRMS (ESI orbitrap) m/z: [M + H]$^+$ calcd for $C_{10}H_7Cl_6F_8N_2O_2$, 548.8505; found, 548.8503.

Synthesis of N-Substituted Ureas with NTCAs and Amines. *1-Butyl-3-phenylurea (**U1**).* To 10 mL of CH_3CN solution containing *N*-phenyl-2,2,2-trichloroacetamide (**6**) (0.48 g, 2.0 mmol) and butylamine (0.15 g, 2.0 mmol) was added DBU (0.15 mL, 1.0 mmol). The sample solution was stirred at 80 °C for 28 h. The solvent was removed by evaporation under reduced pressure. The residue was subjected to short alumina column chromatography with CH_2Cl_2 containing ∼50% acetone as an eluent and then recrystallized with acetone and *n*-hexane to afford 1-butyl-3-phenylurea as a white solid in 76% yield (0.29 g, 1.5 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[31] White solid, mp 123.8−127.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.34−7.28 (m, 4H, phenyl), 7.10 (tt, J = 7.2, 1.6 Hz, 1H, phenyl), 6.37 (br s, 1H, NH), 4.79 (br s, 1H, NH), 3.25 (q, J = 6.7 Hz, 2H, methylene), 1.50 (quin, J = 7.3 Hz, 2H, methylene), 1.35 (sext, J = 7.4 Hz, 2H, methylene), 0.92 (t, J = 7.4 Hz, 3H, methyl); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 155.9, 138.6, 129.3, 123.9, 121.3, 40.1, 32.2, 20.0, 13.8; IR (ATR) ν: 3381, 3191, 2958, 2870, 1552, 1316, 1230, 1035, 749 cm^{-1}; HRMS (ESI orbitrap) m/z: [M + Na]$^+$ calcd for $C_{11}H_{16}N_2ONa$, 215.1155; found, 215.1150.

*1-Benzyl-3-phenylurea (**U2**).* To 10 mL of CH_3CN solution containing *N*-phenyl-2,2,2-trichloroacetamide (**6**) (0.48 g, 2.0 mmol) and phenylmethanol (0.23 mL, 2.2 mmol) was added DBU (0.15 mL, 1.0 mmol). The sample solution was stirred at 80 °C for 19 h. The solvent was removed by evaporation under reduced pressure. The residue was subjected to short alumina column chromatography with CH_2Cl_2 as an eluent and then recrystallized with CH_2Cl_2 and *n*-hexane to afford 1-benzyl-3-phenylurea as a white solid in 99% yield (0.48 g, 2.0 mmol).^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[31] White solid, mp 170.5−172.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 293 K): δ/ppm 8.55 (s, 1H, NH), 7.39 (dd, J = 8.6, 1.0 Hz, 2H, phenyl), 7.34−7.29 (m, 4H, phenyl), 7.26−7.19 (m, 3H, phenyl), 6.89 (tt, J = 7.6, 1.2 Hz, 1H, phenyl), 6.60 (t, J = 5.8 Hz, 1H, NH), 4.29 (d, J = 6.0 Hz, 2H, methylene); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ/ppm 155.7, 140.9, 140.8, 129.1, 128.8, 127.6, 127.2, 121.6, 118.2, 43.2; IR (ATR) ν: 3303, 1544, 695 cm^{-1}; HRMS (ESI orbitrap) m/z: [M + Na]$^+$ calcd for $C_{14}H_{14}N_2ONa$, 249.0998; found, 249.0992.

*1-Cyclohexyl-3-phenylurea (**U3**).* To 10 mL of CH_3CN solution containing *N*-phenyl-2,2,2-trichloroacetamide (**6**) (0.48 g, 2.0 mmol) and cyclohexanamine (0.23 mL, 2.0 mmol) was added DBU (0.15 mL, 1.0 mmol). The sample solution was stirred at 80 °C for 28 h. The solvent was removed by evaporation under reduced pressure. The residue was subjected to short alumina column chromatography with CH_2Cl_2 containing ∼50% acetone as an eluent and then recrystallized with acetone and *n*-hexane to afford 1-cyclohexyl-3-phenylurea as a white solid in 81% yield (0.36 g, 1.7 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[31] White solid, mp 188.0−189.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.34−7.27 (m, 4H, phenyl), 7.09 (tt, J = 7.2, 1.2 Hz, 1H, phenyl), 6.17 (br s, 1H, NH), 4.58 (br s, 1H, NH), 3.70−3.62 (m, 1H), 1.99−1.95 (m, 2H), 1.72−1.59 (m, 3H), 1.43−1.32 (m, 2H), 1.20−1.07 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 155.2, 138.8, 129.2, 123.5, 120.8, 48.9, 33.7, 25.5, 24.9; IR (ATR) ν: 3320, 2931, 2851, 1625, 1567, 1246, 893, 691 cm^{-1}; HRMS (ESI orbitrap) m/z: [M + Na]$^+$ calcd for $C_{13}H_{18}N_2ONa$, 241.1311; found, 241.1308.

*1-Benzyl-3-(2,2,2-trifluoroethyl)urea (**U4**).* To 10 mL of CH_3CN solution containing 2,2,2-trichloro-*N*-(2,2,2-trifluoroethyl)acetamide (**20**) (0.59 g, 2.0 mmol) and phenylmethanamine (0.22 g, 2.0 mmol) was added DBU (0.07 mL, 0.5 mmol). The sample solution was stirred at 80 °C for 186 h. The solvent was removed by evaporation under reduced pressure. The residue was subjected to short alumina column chromatography with CH_2Cl_2 containing ∼50% acetone as an eluent and then recrystallized with CH_2Cl_2 and *n*-hexane to afford 1-benzyl-3-(2,2,2-trifluoroethyl)urea as a white solid in 90% yield (0.42 g, 1.8 mmol). White solid, mp 141.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 293 K): δ/ppm 7.33−7.30 (m, 2H, phenyl), 7.25−7.21 (m, 3H, phenyl), 6.65 (t, J = 6.0 Hz, 1H, NH); 6.59 (t, J = 6.4 Hz, 1H, NH), 4.23 (d, J = 6.0 Hz, 2H, methylene), 3.88−3.79 (m, 2H, methylene); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ/ppm 157.3, 140.3, 128.1, 126.9, 126.6, 125.1 (q, $^1J_{C-F}$ = 277.7 Hz), 42.9, 40.5 (q, $^2J_{C-F}$ = 32.8 Hz); ^{19}F NMR (376 MHz, DMSO-d_6, 293 K): δ/ppm −71.7; IR (ATR) ν: 3336, 1637, 1583, 1295, 1241, 1152, 755, 697 cm^{-1}; HRMS (ESI orbitrap) m/z: [M + Na]$^+$ calcd for $C_{10}H_{11}F_3N_2ONa$, 255.0716; found, 255.0706.

*1-Cyclohexyl-3-(2,2,2-trifluoroethyl)urea (**U5**).* To 10 mL of CH_3CN solution containing 2,2,2-trichloro-*N*-(2,2,2-trifluoroethyl)acetamide (**20**) (0.49 g, 2.0 mmol) and cyclohexanamine (0.23 mL, 2 mmol) was added DBU (0.15 mL, 1.0 mmol). The sample solution was stirred at 80 °C for 25 h. The solvent was removed by evaporation under reduced pressure. The residue was subjected to short alumina column chromatography with CH_2Cl_2 containing ∼50% acetone as an eluent and then recrystallized with acetone to afford 1-cyclohexyl-3-(2,2,2-trifluoroethyl)urea as a white solid in 84% yield (0.38 g, 1.7 mmol). White solid, mp 144.0−148.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 4.74 (t, J = 6.0 Hz, 1H, NH), 4.51 (br, 1H, NH), 3.90−3.81 (m, 2H, methylene), 3.59−3.49 (m, 1H), 1.96−1.92 (m, 2H), 1.73−1.68 (m, 2H), 1.60−1.58 (m, 1H), 1.40−1.30 (m, 2H), 1.20−1.06 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 157.0, 124.6 (q, $^1J_{C-F}$ = 277.1 Hz), 49.2, 41.5 (q, $^2J_{C-F}$ = 34.3 Hz), 33.7, 25.5, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −73.3; IR (ATR) ν: 3338, 2944, 2863, 1631, 1297, 1155, 661 cm^{-1}; HRMS (ESI orbitrap) m/z: [M + H]$^+$ calcd for $C_9H_{15}F_3N_2ONa$, 247.1029; found, 247.1023.

*1-Phenyl-3-(2,2,2-trifluoroethyl)urea (**U6**).* To 10 mL of CH_3CN solution containing 2,2,2-trichloro-*N*-(2,2,2-trifluoroethyl)acetamide (**20**) (0.49 g, 2.0 mmol) and aniline (0.18 mL, 2.0 mmol) was added DBU (0.15 mL, 1 mmol). The sample solution was stirred at 80 °C for 23 h. It was then washed with 1 M HCl aq and extracted with CH_2Cl_2 and water. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was recrystallized with toluene and *n*-hexane to afford 1-phenyl-3-(2,2,2-trifluoroethyl)urea as a white solid in

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47% yield (0.21 g, 0.9 mmol). White solid, mp 168.0−169.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.36 (td, J = 8.0, 2.0 Hz, 2H, phenyl), 7.29 (dd, J = 8.8, 1.4 Hz, 2H, phenyl), 7.17 (tt, J = 7.6, 1.2 Hz, 1H, phenyl), 6.41 (br s, 1H, NH), 5.00 (br s, 1H, NH), 3.97−3.89 (m, 2H, methylene); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ/ppm 155.2, 140.3, 129.2, 125.6 (q, $^1J_{C-F}$ = 277.7 Hz), 122.2, 118.5, 40.7 (q, $^2J_{C-F}$ = 32.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −71.5; IR (ATR) ν: 3323, 2958, 1643, 1597, 1440, 1240, 1151, 1021, 829, 762, 665 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + H]^+$ calcd for $C_9H_9F_3N_2ONa$, 241.0559; found, 241.0551.

Synthesis of N-Substituted Ureas with NTCAs and Amides. *N-(Phenylcarbamoyl)benzamide (**U7**).* *N*-Phenyl-2,2,2-trichloroacetamide (**6**) (1.19 g, 5.0 mmol) was added to a stirred suspension of benzamide (0.61 g, 5.0 mmol) and powdered NaOH (0.5 g, 12.5 mmol) in 5 mL of DMSO. The sample solution was stirred at 80 °C for 0.5 h. After cooling the sample solution to room temperature, it was poured into 10 mL of water. The resulting sample solution was acidified to pH ∼ 2 with concd H_2SO_4. The precipitated product was filtered by suction filtration and dried under vacuum to afford the product. The crude product was recrystallized from acetone and *n*-hexane to afford *N*-(phenylcarbamoyl)benzamide in 44% yield (0.53 g, 2.2 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 10.94 (br s, 1H, NH), 9.59 (br s, 1H, NH), 8.04 (dd, J = 6.0, 1.2 Hz, 2H, phenyl), 7.65 (t, J = 7.2 Hz, 1H, phenyl), 7.60 (d, J = 8.0 Hz, 2H, phenyl), 7.53 (t, J = 8.0 Hz, 2H, phenyl), 7.37 (t, J = 8.0 Hz, 2H, phenyl), 7.16 (t, J = 7.2 Hz, 1H, phenyl); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 168.6, 151.9, 137.2, 133.4, 132.1, 129.0, 128.9, 128.0, 124.5, 120.5; IR (ATR) ν: 3236, 1693, 1597, 1560, 1445, 1273, 1228, 919, 701 cm^{-1}.

*N,N′-Carbonyldibenzamide (**U8**).* *N*-(2,2,2-Trichloroacetyl)benzamide (**11**) (0.33 g, 1.25 mmol) was added to a stirred suspension of benzamide (0.15 g, 1.25 mmol) and powdered NaOH (0.13 g, 3.13 mmol) in 2.5 mL of DMSO. The sample solution was stirred at 80 °C for 0.5 h. After cooling the sample solution to room temperature, it was poured into 10 mL of water. The resulting sample solution was acidified to pH ∼ 2 with concd H_2SO_4. The precipitated product was filtered by suction filtration and dried under vacuum to afford the product. The crude product was recrystallized from THF and *n*-hexane to afford *N*,*N*′-carbonyldibenzamide in 35% yield (0.12 g, 0.5 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[18] White solid, mp 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.98 (d, J = 7.2 Hz, 4H, phenyl), 7.67 (tt, J = 7.6, 1.2 Hz, 2H, phenyl), 7.57 (td, J = 7.2, 1.6 Hz, 4H, phenyl); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ/ppm 166.7, 148.9, 133.2, 132.4, 128.8, 127.9; IR (ATR) ν: 3281, 1765, 1699, 1505, 1262, 1180, 1069, 834, 710, 607 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}N_2O_3$, 269.0921; found, 269.0917.

*N-((2,2,2-Trifluoroethyl)carbamoyl)benzamide (**U9**).* 2,2,2-Trichloro-*N*-(2,2,2-trifluoroethyl)acetamide (**20**) (0.61 g, 2.5 mmol) was added to a stirred suspension of benzamide (0.30 g, 2.5 mmol) and powdered NaOH (0.25 g, 6.25 mmol) in 2.5 mL of DMSO. The sample solution was stirred at 80 °C for 0.5 h. After cooling the sample solution to room temperature, it was poured into 10 mL of water. The resulting sample solution was acidified to pH ∼ 2 with concd H_2SO_4. The precipitated product was filtered by suction filtration and dried under vacuum to afford the product. The crude product was recrystallized from THF and *n*-hexane to afford *N*-((2,2,2-trifluoroethyl)carbamoyl)benzamide in 42% yield (0.26 g, 1.11 mmol). White solid, mp 197.0−201.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 9.30 (br s, 1H, NH), 9.21 (br, 1H, NH), 7.94 (dt, J = 8.4, 1.6 Hz, 2H, phenyl), 7.63 (tt, J = 7.6, 1.4 Hz, 1H, phenyl), 7.51 (tt, J = 8.4, 1.6 Hz, 2H, phenyl), 4.07−3.98 (m, 2H, methylene); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ/ppm 168.4, 153.9, 132.9, 132.2, 128.5, 128.2, 124.8 (q, $^1J_{C-F}$ = 277.1 Hz), 40.7 (q, $^2J_{C-F}$ = 33.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −72.6; IR (ATR) ν: 3294, 1709, 1667, 1537, 1470, 1275, 1222, 1147, 695 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_{10}H_9F_3N_2O_2Na$, 269.0508; found, 269.0502.

*1,3-Diphenylurea (**U10**).* *N*-Phenyl-2,2,2-trichloroacetamide (**6**) (0.60 g, 2.5 mmol) was added to a stirred suspension of aniline (0.24 g, 2.5 mmol) and powdered NaOH (0.25 g, 6.25 mmol) in 2.5 mL of DMSO. The sample solution was stirred at 80 °C for 7.5 h. After cooling the sample solution to room temperature, it was poured into 10 mL of water. The resulting sample solution was acidified to pH ∼ 2 with concd H_2SO_4. The precipitated product was filtered by suction filtration and dried under vacuum to afford the product. The crude product was recrystallized from THF and *n*-hexane to afford 1,3-diphenylurea in 68% yield (0.36 g, 1.7 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[8b] ^{1}H NMR (400 MHz, DMSO-d_6, 293 K): δ/ppm 8.64 (s, 2H, NH), 7.45 (dd, J = 8.8, 1.2 Hz, 4H, phenyl), 7.28 (tt, J = 8.0, 2.0 Hz, 4H, phenyl), 6.97 (tt, J = 6.8, 1.2 Hz, 2H, phenyl); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ/ppm 153.0, 140.2, 129.3, 122.3, 118.7; IR (ATR) ν: 3291, 1626, 1406, 1207, 735 cm^{-1}.

*1-Phenyl-3-(4-fluorophenyl)urea (**U11**).* *N*-Phenyl-2,2,2-trichloroacetamide (**6**) (0.60 g, 2.5 mmol) was added to a stirred suspension of 4-fluoro-benzenamine (0.28 g, 2.5 mmol) and powdered NaOH (0.25 g, 6.25 mmol) in 2.5 mL of DMSO. The sample solution was stirred at 80 °C for 19 h. After cooling the sample solution to room temperature, it was poured into 10 mL of water. The resulting sample solution was acidified to pH ∼ 2 with concd H_2SO_4. The precipitated product was filtered by suction filtration and dried under vacuum to afford the product. The crude product was recrystallized from THF and *n*-hexane to afford 1-phenyl-3-(4-fluorophenyl)urea in 78% yield (0.45 g, 2.0 mmol). White solid, mp 248.4−250.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 293 K): δ/ppm 8.69 (s, 1H, NH), 8.65 (s, 1H, NH), 7.48−7.44 (m, 4H, phenyl), 7.28 (t, J = 7.2 Hz, 2H, phenyl), 7.12 (t, J = 5.2 Hz, 2H, phenyl), 6.97 (t, J = 7.6 Hz, 1H, phenyl); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ/ppm 157.2 (d, $^1J_{C-F}$ = 236.9 Hz), 152.5, 139.6, 135.9, 128.7, 121.7, 119.9, 118.1 (d, $^3J_{C-F}$ = 5.8 Hz), 115.2, (d, $^2J_{C-F}$ = 21.9 Hz); ^{19}F NMR (376 MHz, DMSO-d_6, 293 K): δ/ppm −121.6; IR (ATR) ν: 3291, 1626, 1556, 1506, 1443, 1293, 1207, 831, 735, 634 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + K]^+$ calcd for $C_{13}H_{12}FN_2OK$, 269.0487; found, 271.0646.

*1-Phenyl-3-(2,2,2-trifluoroethyl)urea (**U6**).* 2,2,2-Trichloro-*N*-(2,2,2-trifluoroethyl)acetamide (**20**) (0.31 g, 1.25 mmol) was added to a stirred suspension of bezenamine (0.23 mL, 2.5 mmol) and powdered NaOH (0.25 g, 6.25 mmol) in 2.5 mL of DMSO. The sample solution was stirred at 80 °C for 23 h. After cooling the sample solution to room temperature, it was poured into 10 mL of water. The resulting sample solution was

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acidified to pH ∼ 2 with concd H_2SO_4. The precipitated product was filtered by suction filtration and dried under vacuum to afford the product. The crude product was recrystallized from toluene to afford 1-phenyl-3-(2,2,2-trifluoroethyl)urea in 9% yield (0.02 g, 0.1 mmol).

Synthesis of Carbamates with NTCAs and Alcohols. *Benzyl Phenylcarbamate (**Cm1**).* To 10 mL of CH_3CN solution containing *N*-phenyl-2,2,2-trichloroacetamide (**6**) (0.48 g, 2.0 mmol) and benzyl alcohol (0.23 mL, 2.2 mmol) was added DBU (0.15 mL, 1.0 mmol). The sample solution was stirred at 80 °C for 67 h. It was then washed with 1 M HCl aq and extracted with $CHCl_3$ and water. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was recrystallized with $CHCl_3$ and *n*-hexane to afford benzyl phenylcarbamate as a white solid in 88% yield (0.40 g, 1.75 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[32] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.40−7.29 (m, 9H, phenyl), 7.07 (tt, J = 7.2, 1.2 Hz, 1H, phenyl), 6.65 (br s, 1H, NH), 5.21 (s, 2H, methylene); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 153.3, 137.7, 136.0, 129.0, 128.6, 128.3, 128.3, 123.5, 118.7, 67.0; FAB-MS m/z: $[M + H]^+$ calcd for $C_{14}H_{14}NO_2$, 228.10; found, 227.60.

*Hexyl Phenylcarbamate (**Cm2**).* To 10 mL of CH_3CN solution containing *N*-phenyl-2,2,2-trichloroacetamide (**6**) (0.72 g, 3.0 mmol) and 1-hexanol (0.45 mL, 3.6 mmol) was added DBU (0.23 mL, 1.5 mmol). The sample solution was stirred at 80 °C for 16 h. It was then washed with 1 M HCl aq and extracted with $CHCl_3$ and water. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was recrystallized with $CHCl_3$ and *n*-hexane to afford hexyl phenylcarbamate as a white solid in 70% yield (0.46 g, 2.1 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[33] ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.38 (d, J = 8.4 Hz, 2H, phenyl), 7.29 (t, J = 7.6 Hz, 2H, phenyl), 7.05 (tt, J = 7.2, 1.2 Hz, 1H, phenyl), 6.69 (br s, 1H, NH), 4.15 (t, J = 6.8 Hz, 2H, methylene), 1.65 (quin, J = 7.2 Hz, 2H, methylene), 1.38−1.29 (m, 6H, methylene), 0.90 (t, J = 6.8 Hz, 3H, methyl); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 153.8, 138.0, 129.0, 123.3, 118.6, 65.4, 31.5, 28.9, 25.5, 22.6, 14.0; IR (ATR) ν: 3305, 2955, 2930, 2858, 1704, 1599, 1541, 1500, 1443, 1313, 1220, 1084, 1066, 751, 691 cm^{-1}; FAB-MS m/z: $[M + H]^+$ calcd for $C_{13}H_{20}NO_2$, 222.15; found, 221.59.

*Benzyl Benzylcarbamate (**Cm3**).* To 10 mL of CH_3CN solution containing *N*-benzyl-2,2,2-trichloroacetamide (**3**) (0.51 g, 2.0 mmol) and benzyl alcohol (0.23 mL, 2.2 mmol) was added DBU (0.15 mL, 1.0 mmol). The sample solution was stirred at 80 °C for 16 h. It was then washed with 1 M HCl aq and extracted with $CHCl_3$ and water. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was recrystallized with $CHCl_3$ and *n*-hexane to afford benzyl benzylcarbamate as a white solid in 77% yield (0.36 g, 1.5 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[34] White solid, mp 170.5−172.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.37−7.28 (m, 10H, phenyl), 5.14 (s, 2H, methylene), 5.05 (br s, 1H, NH), 4.40 (d, J = 6.0 Hz, 2H, methylene); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 162.0, 138.4, 136.4, 129.0, 128.7, 128.6, 128.2, 127.8, 127.5, 66.9, 45.3; IR (ATR) ν: 3319, 1684, 1541, 1494, 1453, 1255, 1145, 1051, 1003, 692 cm^{-1}; FAB-MS m/z: $[M + H]^+$ calcd for $C_{15}H_{16}NO_2$, 242.12; found, 242.54.

*Benzyl (2,2,2-Trifluoroethyl)carbamate (**Cm4**).* To 10 mL of CH_3CN solution containing 2,2,2-trichloro-*N*-(2,2,2-trifluoroethyl)acetamide (**20**) (0.59 g, 2.0 mmol) and benzyl alcohol (0.23 mL, 2.2 mmol) was added DBU (0.15 mL, 1.0 mmol). The sample solution was stirred at 80 °C for 67 h. It was then washed with 1 M HCl aq and extracted with $CHCl_3$ and water. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was recrystallized with $CHCl_3$ and *n*-hexane to afford benzyl(2,2,2-trifluoroethyl)carbamate as a white solid in 91% yield (0.42 g, 1.82 mmol). White solid, mp 141.5−141.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.40−7.32 (m, 5H, phenyl), 5.15 (s, 2H, methylene), 5.05 (br s, 1H, NH), 3.84 (quin, J = 9.6 Hz, 2H, methylene); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 156.0, 135.8, 128.6, 128.4, 128.3, 124.1 (q, $^1J_{C-F}$ = 277.0 Hz), 67.6, 42.7 (q, $^2J_{C-F}$ = 44.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −73.3; IR (ATR) ν: 3335, 3034, 2949, 1637, 1582, 1524, 1295, 1151, 835, 756, 666 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + H]^+$ calcd for $C_{10}H_{11}F_3NO_2$, 234.0736; found, 233.1544.

*Ethane-1,2-diyl Bis(phenylcarbamate) (**Cm5**).* To 5 mL of CH_3CN solution containing *N*-phenyl-2,2,2-trichloroacetamide (**6**) (0.48 g, 2.0 mmol) and EG (0.06 mL, 1.0 mmol) was added DBU (0.15 mL, 1.0 mmol). The sample solution was stirred at 80 °C for 65 h. The solvent was removed by evaporation under reduced pressure. The residue was subjected to short alumina column chromatography with CH_2Cl_2 containing ∼50% acetone as an eluent and then recrystallized with CH_2Cl_2 and *n*-hexane to afford ethane-1,2-diyl bis(phenylcarbamate) as a white solid in 73% yield (0.44 g, 1.5 mmol). White solid, mp 145.9−148.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.39−7.29 (m, 8H, phenyl); 7.08 (tt, J = 7.2, 1.2 Hz, 2H, phenyl), 6.69 (br s, 2H, NH), 4.43 (s, 4H, methylene); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 153.1, 137.6, 129.1, 123.7, 118.8, 63.3; IR (ATR) ν: 3343, 2972, 1708, 1596, 1528, 1445, 1299, 1216, 1073, 903, 739, 689, 617 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_{16}H_{16}N_2O_4Na$, 323.1002; found, 323.0996.

*Hexane-1,6-diyl Bis((2,2,2-trifluoroethyl)carbamate) (**Cm6**).* To 5 mL of CH_3CN solution containing 2,2,2-trichloro-*N*-(2,2,2-trifluoroethyl)acetamide (**20**) (0.24 g, 1 mmol) and HD (0.06 g, 0.5 mmol) was added DBU (0.07 mL, 0.5 mmol). The sample solution was stirred at 80 °C for 44 h. It was then washed with 1 M HCl aq and extracted with CH_2Cl_2 and water. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was recrystallized with CH_2Cl_2 and *n*-hexane to afford hexane-1,6-diyl bis((2,2,2-trifluoroethyl)-carbamate) as a white solid in 48% yield (0.18 g, 0.49 mmol). ^{1}H and ^{13}C NMR spectra are in agreement with those reported in the literature.[35] White solid, mp 105.7−108.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 5.01 (br s, 2H, NH), 4.11 (t, J = 6.4 Hz, 4H, methylene), 3.82 (quin, J = 8.8 Hz, 4H, methylene), 1.64 (quin, J = 6.4 Hz, 4H, methylene), 1.39 (quin, J = 3.6 Hz, 4H, methylene); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ/ppm 157.0, 125.3 (q, $^1J_{C-F}$ = 277.8 Hz), 64.9, 42.1 (q, $^2J_{C-F}$ = 33.6 Hz), 28.9, 25.4; ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −73.4; IR (ATR) ν: 3297, 3079, 2937, 2863, 1696, 1546, 1251, 1146, 1021, 975, 668 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_{12}H_{18}F_6N_2O_4Na$, 391.1063; found, 391.1052.

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*Dibenzyl (Methylenebis(4,1-phenylene))dicarbamate (**Cm7**).* To 10 mL of CH_3CN solution containing *N*,*N*′-(methylenebis(4,1-phenylene))bis(2,2,2-trichloroacetamide) (**17**) (0.49 g, 1.0 mmol) and benzyl alcohol (0.26 mL, 2.5 mmol) was added DBU (0.15 mL, 1.0 mmol). The sample solution was stirred at 80 °C for 65 h. The solvent was removed by evaporation under reduced pressure. The residue was subjected to short alumina column chromatography with CH_2Cl_2 containing ∼50% acetone as an eluent and then recrystallized with THF and *n*-hexane to afford dibenzyl-(methylenebis(4,1-phenylene))dicarbamate as a white solid in 30% yield (0.16 g, 0.34 mmol). White solid, mp 183.0−184.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.49 (d, J = 6.8 Hz, 2H, phenyl), 7.41−7.30 (m, 10H, phenyl), 7.20 (d, J = 8.8 Hz, 2H, phenyl), 7.10 (dd, J = 8.4, 2.8 Hz, 4H, phenyl), 6.61 (br s, 2H, NH), 5.20 (s, 4H, methylene), 3.94 (s, 2H, methylene); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 159.1, 139.2, 136.0, 134.0, 129.7, 129.5, 128.6, 128.3, 120.5, 67.0, 40.6; IR (ATR) ν: 3341, 2897, 1803, 1695, 1632, 1591, 1535, 1413, 1308, 1220, 1156, 1061, 891, 818, 736, 695 cm^{-1}. HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_{29}H_{26}N_2O_4Na$, 489.1785; found, 489.1775.

*Dibenzyl(2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyl)-dicarbamate (**Cm8**).* To 1 mL of CH_3CN solution containing *N*,*N*′-(2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyl)bis(2,2,2-trichloroacetamide) (**22**) (0.1 g, 0.18 mmol) and benzyl alcohol (0.02 mL, 0.2 mmol) was added DBU (0.01 mL, 0.09 mmol). The sample solution was stirred at 80 °C for 23 h. The solvent was removed by evaporation under reduced pressure. The residue was subjected to short alumina column chromatography with CH_2Cl_2 containing ∼50% acetone as an eluent and then recrystallized with CH_2Cl_2 and *n*-hexane to afford dibenzyl(2,2,3,3,4,4,5,5-octafluorohexane-1,6-diyl)dicarbamate as a white solid in 85% yield (0.09 g, 0.17 mmol). White solid, mp 155.0−156.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 7.39−7.32 (m, 10H, phenyl), 5.15 (s, 4H, methylene), 5.05 (t, J = 5.6 Hz, 2H, NH), 3.96−3.87 (m, 4H, methylene); ^{13}C NMR (100 MHz, DMSO-d_6, 293 K): δ/ppm 156.4, 136.5, 128.3, 127.9, 127.8, 65.9, 40.4 (t, $^2J_{C-F}$ = 20.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −119.0, −123.6; IR (ATR) ν: 3331, 3071, 2959, 1697, 1547, 1427, 1264, 1127, 1026, 811, 734 cm^{-1}; HRMS (ESI orbitrap) m/z: $[M + Na]^+$ calcd for $C_{22}H_{20}F_8N_2O_4Na$, 551.1188; found, 551.1172.

PU from N,N′-(Octafluorohexane-1,6-diyl)bis(2,2,2-trichloroacetamide) and PolyTHF. A screw cap test tube (ø13 × 100 mm) containing a magnetic stirring bar was charged with 0.5 mL of CH_3CN containing *N*,*N*′-(octafluorohexane-1,6-diyl)bis(2,2,2-trichloroacetamide) (**22**) (110 mg, 0.2 mmol) and 1.0 equiv of polyTHF (M_n = 250) (50 mg). DBU (3 mg, 0.02 mmol) was added to the sample solution and stirred for 12 days at 80 °C in an aluminum block bath. The sample solution was evaporated under reduced pressure. The residue was reprecipitated with CH_2Cl_2 and *n*-hexane and then dried under reduced pressure at 100 °C for 2 h to afford the PU quantitatively as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ/ppm 10.41, 7.03, 5.64 (br s, 2H), 4.12 (br s, 4H), 3.88 (br s, 4H), 3.64 (br s, 1H), 3.50−3.42 (m, 14H), 3.24, 2.86 (br s, 1H), 2.36 (br s, 1H), 2.01 (br s, 1H), 1.73−1.62 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K): δ/ppm 166.3, 156.6, 70.8, 70.6, 70.1, 65.6, 54.4, 48.7, 41.2, 38.1, 29.0, 26.9, 26.7, 26.4, 26.0, 25.8, 23.9, 19.4; ^{19}F NMR (376 MHz, $CDCl_3$, 293 K): δ/ppm −118.1, −119.1, −123.7, −129.1, 152.6; IR (ATR) ν: 3316, 2942, 2863, 2252, 1723, 1650, 1539, 1254, 1164, 1107 cm^{-1}; M_w = 5500, M_n = 3000, M_w/M_n = 1.83.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c07233.

Experimental procedures and copies of ^{1}H and ^{13}C NMR spectra (PDF)

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