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Cobalt(II)-Catalyzed Intermolecular Benzylic C−H Amination with 2,2,2-Trichloroethoxycarbonyl Azide (TrocN$_3$)

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2,2,2-Trichloroethoxycarbonyl azide (TrocN$_3$) is an effective nitrene source for cobalt(II)-catalyzed intermolecular nitrene insertion of C−H bonds. Among different metalloporphyrins studied, Co(II)(TPP) was shown to be a competent catalyst for the selective amination of various benzylic C−H bonds under mild conditions without the need of other reagents or additives, forming the desired Troc-protected amines in moderate to high yields with nitrogen gas as the only byproduct.

Introduction

The biological and medicinal importance of the prevalent amine functionalities in natural and synthetic products has prompted vast efforts to develop effective and selective amination methodologies.[1] Metal-catalyzed nitrene insertion into ubiquitous C−H bonds with suitable nitrene sources has emerged as one of the most promising approaches for general synthesis of amine derivatives in a direct and controlled manner.[2] While enormous progress has been achieved for intermolecular C−H amination with the widely used reagent PhI=NTs and related iminoiodane derivatives as nitrene sources,[3−5] significant challenges have remained in the field that validate the need to identify more effective nitrene sources in conjunction with the development of more selective metal catalysts. To this end, recent efforts have been made to employ alternative nitrene sources for catalytic C−H amination processes, including haloamine-T,[4g,6] tosyloxycarbamates,[7] and azides.[8]

Employing porphyrins as supporting ligands, we have recently developed several Co(II)-catalyzed nitrene transfer processes, including olefin aziridination and C−H amination, with the use of bromamine-T[9] and azides[10] as alternative nitrene sources. We demonstrated previously the capability of cobalt(II) porphyrins ([Co(Por)]) in catalyzing intermolecular nitrene insertion of C−H bonds with bromamine-T.[9a] While the desired amination products could be formed under milder conditions with NaBr as the byproduct, the catalytic system suffered from low yields and narrow substrate scope. Encouraged by our recent work on intramolecular C−H amination with azides,[10a] we hoped to improve the Co(II)-catalyzed intermolecular nitrene C−H

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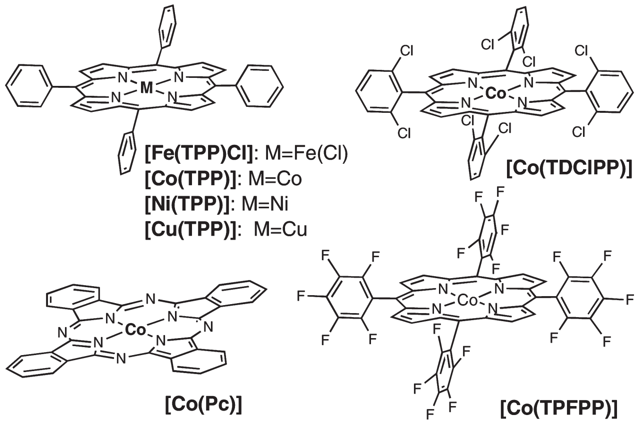
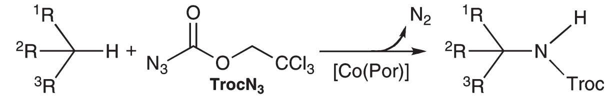


Figure 1. Structures of metalloporphyrin catalysts.

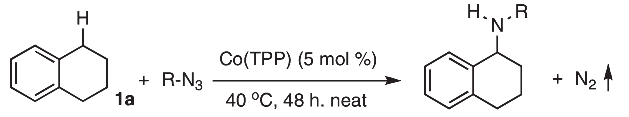
Scheme 1. Cobalt(II)-Catalyzed C−H Amination with $TrocN_3$

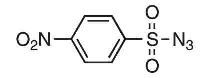
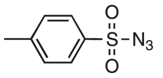
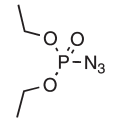
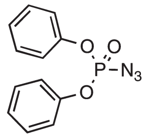
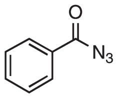
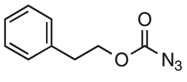
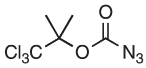
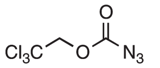


insertion process by further utilizing azides as nitrene sources. Herein, we report that 2,2,2-trichloroethoxycarbonyl azide ($TrocN_3$) is an effective nitrene source for Co(II)-catalyzed intermolecular nitrene insertion of C−H bonds (Scheme 1).[11] Among different metalloporphyrins studied (Figure 1), Co(TPP) was shown to be a competent catalyst for the selective amination of various benzylic C−H bonds, forming the desired Troc-protected amines in moderate to high yields. The Co(II)-based catalytic system can be operated under mild conditions without the need for other reagents or additives while generating nitrogen gas as the only byproduct.

Results and Discussion

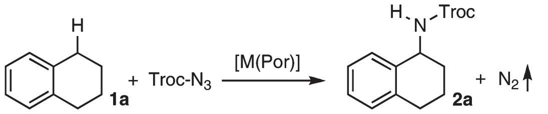
Table 1. Intermolecular C−H Amination of Tetralin with Different Azides[a]



entry	R-N3	yield[b]	entry	R-N3	yield[b]
1		<5%	2		32%
3		0%	4		0%
5		0%	6		0%
7		0%	8		85%

[a] Performed under N_2 in the presence of 5 Å molecular sieves: [**1a**] = 2.0 mmol/2 mL; **1a**:$TrocN_3$ = 10:1. [b] Isolated yields.

Table 2. Intermolecular C−H Amination of Tetralin with $TrocN_3$ by Metalloporphyrins[a]



entry	[M(Por)][b]	mol (%)	solvent	temp (°C)	time (h)	yield (%)[c]
1	Co(TPP)	5	ClC_6H_5	60	24	50
2	Co(TPP)	10	ClC_6H_5	60	24	52
3	Co(TPP)	10	ClC_6H_5	60	42	58
4[d]	Co(TPP)	5	ClC_6H_5	60	48	69
5[d]	Co(TPP)	5	$CF_3C_6H_5$	60	48	71
6[d]	Co(TPP)	5	$CH_3C_6H_5$	60	48	50
7[d]	Co(TPP)	5	C_6H_{14}	60	48	73
8[d]	Co(TPP)	5	CH_3CN	60	48	0
9[d]	Co(TPP)	5	ClC_6H_5	40	32	70
10[d]	Co(TPP)	5	ClC_6H_5	80	48	68
11[d,e]	Co(TPP)	5	ClC_6H_5	60	48	34
12	Co(TPP)	5	–[f]	60	48	79
13	Co(TPP)	5	–[f]	40	48	85
14	Co(TPP)	2	–[f]	40	48	79
15	Co(TPP)	5	–[f]	RT	48	66
16	Co(TPFPP)	5	–[f]	40	48	26
17	Co(TDClPP)	5	–[f]	40	48	10
18	Co(*Pc*)	5	–[f]	40	48	< 5
19	Fe(TPP)Cl	5	–[f]	40	48	0
20	Ni(TPP)	5	–[f]	40	48	0
21	Cu(TPP)	5	–[f]	40	48	0

[a] Performed under N_2 in the presence of 5 Å molecular sieves: [**1a**] = 2.0 mmol/2 mL; **1a**:$TrocN_3$ = 10:1. [b] See Figure 1 for structures. [c] Isolated yields. [d] [**1a**] = 2.0 mmol/0.5 mL. [e] **1a**:$TrocN_3$ = 3:1. [f] Neat reaction.

At the outset of the project, tetralin was selected as a model substrate to identify a suitable azide for the catalytic amination reaction. Different kinds of azides, including sulfonyl, phosphoryl, and carbonyl azides, were evaluated as potential nitrene sources. While most of the azides were found to be ineffective for the process (Table 1), the use of $TrocN_3$, a carbonyl azide that is relatively small in size and contains an electron-withdrawing group, allowed for the amination of tetralin (**1a**) by [Co(Por)] under proper conditions (Table 2). For example, the amination of **1a** with $TrocN_3$ (**1a**:$TrocN_3$ = 10:1) could be successfully catalyzed using 5 mol % Co(TPP) at 60 °C in chlorobenzene, forming the corresponding Troc-protected amine **2a** in 50% yield via selective nitrene insertion into one of the benzylic C−H bonds (Table 2, entry 1). While no noticeable improvement was realized using higher catalyst loading, a longer reaction time gave a better result (Table 2, entries 2 and 3). More significant increase in yield was attained when the reaction was conducted at a higher concentration (Table 2, entry 4). Other solvents such as trifluorotoluene, toluene, and *n*-hexane could also be effectively utilized for the reaction, producing **2a** in 71%, 50%, and 73% yields, respectively (Table 2, entries 5−7). However, no desired product was observed when the reaction was performed in acetonitrile (Table 2, entry 8). When using chlorobenzene as solvent, it was noticed that temperature had no obvious effect on the amination, as the reactions at 40, 60, and 80 °C gave

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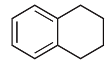
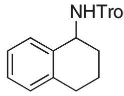
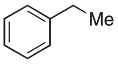
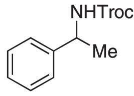
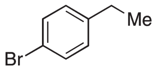
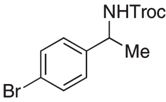
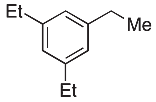
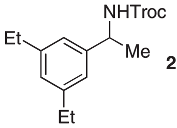
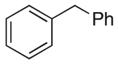
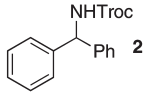
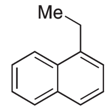
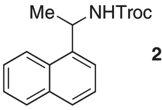
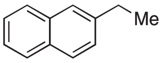
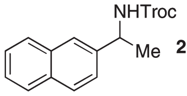
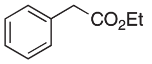
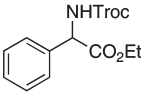
[11] $TrocN_3$ was readily synthesized from the commercially available $CCl_3CH_2OC(O)Cl$ in high yield and on a multiple-gram scale; DSC showed it decomposed at 157 °C (see Supporting Information). $TrocN_3$ was previously used for a Ru-catalyzed sulfimidation process; see: Tamura, Y.; Uchida, T.; Katsuki, T. *Tetrahedron Lett.* **2003**, *44*, 3301.

practically the same isolated yield of **2a** (Table 2, entries 4, 9, and 10). While a decrease in the ratio of **1a** to $TrocN_3$ reduced the yield (only a trace amount of product was observed when **1a** was used as a limiting reagent), a significantly higher yield was achieved for a reaction carried out in neat form (Table 2, entries 11 and 12). It is worthy of note that the yield was raised further to 85% when the reaction temperature was changed from 60 to 40 °C, due to decreased formation of the corresponding $TrocNH_2$ (Table 2, entry 13). Further experiments showed that the neat reaction could be productively carried out with 2 mol % catalyst loading or at room temperature (Table 2, entries 14 and 15).

Changing Co(TPP) to sterically hindered and/or electronically deficient catalysts such as Co(TDClPP) and Co(TPFPP) (Figure 1), which were shown to be more effective for C−H amination with bromamine-T,[9a] produced the desired **2a** in greatly reduced yields (Table 2, entries 16 and 17). This result reveals the difference in reactivity between $TrocN_3$ and bromamine-T as nitrene sources. Only a trace amount of the desired amination product could be detected when the cobalt complex of phthalocyanine [Co(Pc)] (Figure 1) was used as the catalyst (Table 2, entry 18). As observed previously in other azide-based nitrene transfer reactions by metalloporphyrins,[10] the cobalt ion seems crucial to the successful C−H amination with $TrocN_3$. While Co(TPP) could effectively catalyze the amination of **1a** (Table 2, entries 1−15), the employment of other metalloporphyrins, including Fe(TPP)Cl, Ni(TPP), and Cu(TPP) (Figure 1), led to no formation of the desired product **2a** (Table 2, entries 19−21).[12]

On the basis of the catalytic conditions optimized for the amination of **1a**, the scope of the Co(TPP)/$TrocN_3$-based catalytic system toward nitrene insertion of other benzylic C−H bonds was then investigated using different substrates (Table 3).[13] Like the cyclic **1a** (Table 3, entry 1), the benzylic C−H bonds of ethyl benzene (**1b**) and its *para*-brominated derivative (**1c**) could also be selectively aminated to provide the corresponding amine products **2b** and **2c** in 69% and 79% yields, respectively (Table 3, entries 2 and 3). Ethyl benzene derivatives substituted with alkyl groups such as **1d** could be properly aminated with $TrocN_3$, producing the C−H insertion product **2d** in 74% yield (Table 3, entry 4). While diphenylmethane **1e** is a good substrate for the catalytic amination (Table 3, entry 5), the best results were achieved for the reactions of 1-ethyl- and 2-ethylnaphthalene **1f** and **1g**, forming the desired amines **2f** and **2g** in 87% and 92% yields, respectively (Table 3, entries 6 and 7). It is noteworthy that the Co(TPP)/$TrocN_3$-based catalytic system was also capable of aminating challenging substrates such as ethyl phenylacetate **1p** to produce the α-amino acid derivative **2h** albeit in a low yield (Table 3, entry 8). This notable reaction presents an encouraging prospect for catalytic synthesis of α-amino acids via selective C−H amination directly from the corresponding carboxylic acids. It was noted that the corresponding $TrocNH_2$ of $TrocN_3$ was the common side product of the Co(II)-catalyzed amination process. In most cases, $TrocN_3$ was completely consumed; the formation of $TrocNH_2$ was primarily responsible for the lower yielding reactions (Table 3). Control experiments showed that addition of a small amount of water resulted in a significant decrease in the yield of desired amination product with a concomitant increase of $TrocNH_2$.

Table 3. Co(TPP)-Catalyzed Intermolecular C−H Amination Reactions with $TrocN_3$[a]

entry	substrate		product		yield (%)[b]
1		**1a**		**2a**	85
2		**1b**		**2b**	69
3		**1c**		**2c**	79
4		**1d**		**2d**	74
5		**1e**		**2e**	71
6		**1f**		**2f**	87
7		**1g**		**2g**	92
8		**1h**		**2h**	18

[a] Performed in neat at 40 °C for 48 h under N_2 with 5 mol % Co(TPP) in the presence of 5 Å MS: substrate:$TrocN_3$ = 10:1. [b] Isolated yields.

On the basis of the previously proposed mechanism for Co(II)-catalyzed aziridination with DPPA,[10b] one possible mechanism for the Co(TPP)/$TrocN_3$-based amination is outlined in Scheme 2 to provide a means to better understand the catalytic process. As a 15*e* metalloradical, the initial Co(II) catalyst **A** reacts with $TrocN_3$ to generate the cobalt-nitrene intermediate **B** with simultaneous release of nitrogen. The intermediate **B**, which is assumed to be a Co(III) 16*e* complex having a Co−N single bond with nitrogen-based radical character, reacts with substrate R−H via hydrogen abstraction to form intermediate **C** with a caged $R^\bullet$ radical nearby. Formation of the C−N bond produces the amine product and regenerates the catalyst **A** to turn over the catalytic cycle. Due to its weak Co−N bond, homolysis of intermediate **C** may generate an aminyl free radical that results in the formation of the observed side product $TrocNH_2$. While the proposed mechanism may allow comprehension of the results summarized in Tables 2 and 3, it should be emphasized that no experimental evidence have been obtained to support the intermediates presented in Scheme 2.

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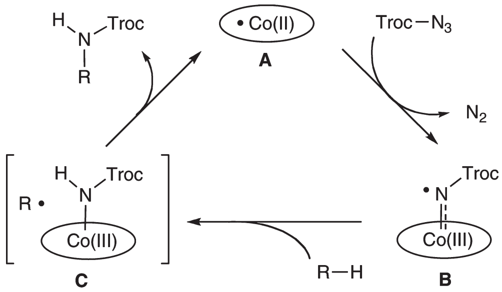
(12) Under similar conditions, use of a porphyrin complex of the second-row transition metal ruthenium, Ru(TPP)(CO), could produce **2a** in 79% yield.

(13) The current catalytic system appeared to be ineffective for primary benzylic C−H bonds (such as toluene) and non-benzylic C−H bonds (such as cyclohexane). Reactions with tertiary benzylic C−H bonds gave the desired products in much lower yields.

Scheme 2. Possible Mechanism for Cobalt(II)-Catalyzed Nitrene Insertion of Benzylic C−H Bonds with TrocN$_3$



Conclusions

In summary, we have demonstrated a Co(II)-catalyzed intermolecular C−H amination process with TrocN$_3$ as a nitrene source. This represents the first example of a carbonyl azide being utilized for the metal-catalyzed nitrene insertion of sp^3 C−H bonds. The Co(TPP)/TrocN$_3$-based catalytic system can selectively aminate benzylic C−H bonds in a range of substrates to form the desired Troc-protected amines in moderate to high yields while generating nitrogen gas as the byproduct. Efforts are underway in our laboratory to develop new porphyrins as supporting ligands for the Co-based catalytic amination system with a goal to improve its reactivity and selectivity.

Experimental Section

General Considerations. All reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Diphenylphosphoryl azide was purchased from Sigma-Aldrich Company. Chlorobenzene was distilled under nitrogen from calcium hydride. Thin-layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230−400 mesh, 32−63 μm). Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker 250-MHz instrument and referenced with respect to internal TMS standard. Infrared spectra were measured with a Nicolet Avatar 320 spectrometer with a Smart Miracle accessory. HRMS data were obtained on an Agilent 1100 LC/MS ESI/TOF mass spectrometer with electrospray ionization.

General Procedure for Synthesis of Azides. To a well-stirred suspension of NaN$_3$ (1.95 g, 30 mmol) in acetone (40 mL) protected from light by aluminum foil was added acyl chloride (20 mmol) at room temperature. The reaction was monitored by TLC. After the reaction finished, the mixture was then poured into a flash chromatography column filled with Celite (dry) and was washed with methylene chloride until all the product was washed out. The filtrate was collected and concentrated by rotary evaporation at room temperature to give the product, which was further purified by flash chromatography column (silica gel).

4-Nitrobenzenesulfonyl azide[10c,14] (Table 1, entry 1) was prepared using the general procedure as a solid in 75% yield. ^{1}H NMR (250 MHz, CDCl$_3$): δ 8.46 (d, J = 9.0 Hz, 2H), 8.17 (d, J = 9.0 Hz, 2H). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 151.2, 143.6, 128.9, 124.9. IR (neat, cm^{-1}): 2141, 1529, 1375, 1349, 1176, 1157, 1085, 854, 769.

4-Methylbenzenesulfonyl azide[10c,14] (Table 1, entry 2) was prepared using the general procedure as a colorless liquid in 75% yield. ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.82 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 146.2, 135.3, 130.2, 127.4, 21.6. IR (neat, cm^{-1}): 2123, 1368, 1163, 1085, 813, 745, 657.

Diethylphosphoroazidate[15] (Table 1, entry 3) was prepared by following the literature procedure.[2] ^{1}H NMR (250 MHz, CDCl$_3$): δ 4.24−4.12 (m, 4H), 1.36 (t, J = 7.0 Hz, 6H). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 64.9, 64.8, 16.0, 15.9. IR (neat, cm^{-1}): 2158, 1275, 1014, 983, 780. IR (neat, cm^{-1}): 2161, 1266, 1016, 983, 782.

Benzoyl azide[16] (Table 1, entry 5) was prepared by following the literature procedure.[3] ^{1}H NMR (250 MHz, CDCl$_3$): δ 8.04−8.00 (m, 2H), 7.65−7.57 (m, 1H), 7.48−7.41 (m, 2H). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 172.4, 134.3, 130.5, 129.4, 128.6. IR (neat, cm^{-1}): 2132, 1692, 1234, 1175, 985, 694, 684.

2-Phenylethyl azidocarbonate[17] (Table 1, entry 6) was prepared by following the literature procedure.[4] ^{1}H NMR (CDCl$_3$, 250 MHz): δ 7.26−7.13 (m, 5H), 4.34 (t, J = 7.0 Hz, 2H), 2.93 (t, J = 7.0 Hz, 2H). ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 157.3, 136.7, 128.8, 128.6, 126.8, 68.8, 34.8.

2,2,2-Trichloro-1,1-dimethylethyloxycarbonyl azide[11,18] (Table 1, entry 7) was prepared using the general procedure as a colorless solid in 90% yield. ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.97 (s, 6H). ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ 154.4, 104.9, 91.4, 21.1. IR (neat, cm^{-1}): 2201, 2144, 1717, 1261, 1240, 1209, 1139, 831, 789, 759.

2,2,2,-Trichloroethoxycarbonyl azide[11] (Table 1, entry 8) was prepared using the general procedure as a colorless liquid in 92% yield. ^{1}H NMR (250 MHz, CDCl$_3$): δ 4.83 (s, 2H). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 156.5, 93.8, 76.5. IR (neat, cm^{-1}): 2179, 2143, 1769, 1734, 1223, 712.

General Procedure for Amination. Molecular sieves (5 Å, 100 mg) were placed in a resealable Schlenk tube and dried in an oven for 24 h. Catalyst (5 mol %) was added to the tube, which was then capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum, and TrocN$_3$ (0.4 mmol) was added via syringe, followed by 10 equiv of substrate. After the Schlenk tube was purged with nitrogen for 1 min, the rubber septum was replaced with the screwcap. The reaction content was stirred at a specified temperature for a certain period of time. After completion of the reaction, the resulting mixture was purified directly by flash chromatography (silica gel) to afford the pure product.

2,2,2-Trichloroethyl-1,2,3,4-tetrahydronaphthalen-1-ylcarbamate (**2a**, Table 3, entry 1). ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.35−7.31 (m, 1H), 7.21−7.08 (m, 3H), 5.22 (br, 1H), 4.98−4.72 (m, 3H), 2.83−2.75 (m, 2H), 2.10−2.05 (m, 1H), 1.93−1.82 (m, 3H). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 154.0, 137.4, 136.0, 129.2, 128.6, 127.5, 126.3, 95.7, 74.4, 49.6, 30.2, 29.1, 20.0. IR (neat, cm^{-1}): 3320, 2930, 2359, 1704, 1527, 1235, 1082, 1034, 711. HRMS (ESI) ([M + H]$^+$): calcd for $C_{13}H_{15}Cl_3NO_2$ 322.0163, found 322.0161.

2,2,2-Trichloroethyl-1-phenylethylcarbamate[7c] (**2b**, Table 3, entry 2). ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.37−7.25 (m, 5H), 5.30 (br, 1H), 4.92−4.85 (m, 1H), 4.79−4.65 (m, 2H), 1.53 (d, J = 7.0 Hz, 3H). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ 153.7, 142.7, 128.7, 127.5, 125.9, 95.5, 74.4, 51.0, 22.2. IR (neat, cm^{-1}): 3327, 2361, 1716, 1522, 1234, 1117, 1088. HRMS (ESI) ([M + H]$^+$): calcd for $C_{11}H_{13}Cl_3NO_2$ 296.0006, found 296.0005.

2,2,2-Trichloroethyl-1-(4-bromophenyl)ethylcarbamate (**2c**, Table 3, entry 3). ^{1}H NMR (250 MHz, CDCl$_3$): δ 7.47 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 5.25 (br, 1H), 4.86−4.64

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(m, 3H), 1.50 (d, J = 6.8 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 153.6, 141.9, 131.7, 127.6, 121.2, 95.4, 74.4, 50.5, 22.1. IR (neat, cm^{-1}): 3397, 2982, 2929, 1712, 1513, 1232, 1058, 1008, 824, 710. HRMS (ESI) ([M + H]$^+$): calcd for $C_{11}H_{12}BrCl_3NO_2$ 375.9079, found 375.9017.

2,2,2-Trichloroethyl-1-(3,5-diethylphenyl)ethylcarbamate (2d, Table 3, entry 4). ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.98 (s, 3H), 5.27 (br, 1H), 4.91−4.67 (m, 3H), 2.63 (q, J = 7.5 Hz, 4H), 1.53 (d, J = 6.8 Hz, 3H), 1.24 (t, J = 7.5 Hz, 6H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 153.7, 144.7, 142.7, 126.7, 122.8, 95.6, 74.4, 51.1, 28.8, 22.3, 15.6. IR (neat, cm^{-1}): 3333, 2965, 2929, 2360, 1719, 1523, 1234, 1116, 1087. HRMS (ESI) ([M + H]$^+$): calcd for $C_{15}H_{21}Cl_3NO_2$ 352.0632, found 352.0623.

2,2,2-Trichloroethylbenzhydrylcarbamate (2e, Table 3, entry 5). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.24−7.13 (m, 10H), 5.90 (d, J = 8.0 Hz, 1H), 5.61 (d, J = 7.3 Hz, 1H), 4.64 (s, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 153.8, 140.9, 128.7, 127.7, 127.2, 95.4, 74.6, 59.0. IR (neat, cm^{-1}): 3301, 2921, 2360, 1709, 1528, 1134, 1024, 761. HRMS (ESI) ([M + H]$^+$): calcd for $C_{16}H_{14}Cl_3NO_2$ 358.0163, found 358.0156.

2,2,2-Trichloroethyl-1-(naphthalen-1-yl)ethylcarbamate (2f, Table 3, entry 6). ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.13 (d, J = 7.5 Hz, 1H), 7.92−7.87 (m, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.60−7.43 (m, 4H), 5.71 (dt, $J_1 = J_2$ = 7.0 Hz, 1H), 5.44 (d, J = 7.3 Hz, 1H), 4.77 (s, 2H), 1.70 (t, J = 6.8 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 153.6, 137.9, 133.9, 130.7, 128.8, 128.4, 126.5, 125.8, 125.2, 123.1, 122.2, 95.6, 74.4, 46.9, 21.3. IR (neat, cm^{-1}): 3321, 2924, 2360, 1716, 1509, 1232, 1113, 1050, 799, 775, 715. HRMS (ESI) ([M + H]$^+$): calcd for $C_{15}H_{15}Cl_3NO_2$ 346.0163, found 346.0167.

2,2,2-Trichloroethyl-1-(naphthalen-2-yl)ethylcarbamate (2g, Table 3, entry 7). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.86−7.77 (m, 4H), 7.53−7.42 (m, 3H), 5.39 (d, J = 7.3 Hz, 1H), 5.05 (dt, $J_1 = J_2$ = 7.0 Hz, 1H), 4.74 (q, J = 7.0 Hz, 2H), 1.62 (t, J = 6.8 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 153.7, 140.1, 133.3, 132.8, 128.6, 127.9, 127.6, 126.3, 126.0, 124.4, 124.2, 95.5, 74.5, 51.1, 22.2. IR (neat, cm^{-1}): 3312, 2359, 1708, 1522, 1239, 1086, 803, 746. HRMS (ESI) ([M + H]$^+$): calcd for $C_{15}H_{15}Cl_3NO_2$ 346.0163, found 346.0156.

Ethyl 2-phenyl-2-((2,2,2-trichloroethoxy)carbonylamino)acetate (2h, Table 3, entry 8). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.45−7.29 (m, 5H), 6.01 (d, J = 8.0 Hz, 1H), 5.36 (d, J = 7.3 Hz, 1H), 4.77−4.65 (m, 2H), 4.30−4.12 (m, 2H), 1.22 (t, J = 7.3 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 170.3, 153.5, 136.2, 129.0, 128.8, 127.1, 95.2, 74.7, 62.1, 58.1, 14.0. IR (neat, cm^{-1}): 3355, 2979, 2360, 1724, 1498, 1208, 1092, 1043, 698. HRMS (ESI) ([M + H]$^+$): calcd for $C_{13}H_{15}Cl_3NO_4$ 354.0061, found 354.0057.

1-*p*-Tolylsulfonylaminotetralin[6a] (Table 1, entry 2). ^{1}H NMR (250 MHz, $CDCl_3$): 7.84 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.18−6.91 (m, 4H), 4.61(d, J = 7.8 Hz, 1H), 4.47−4.43 (m, 1H), 2.81−2.62 (m, 2H), 2.47 (s, 3H), 1.87−1.71 (m, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 143.5, 138.1, 137.6, 135.6, 129.8, 129.3, 128.8, 127.7, 127.2, 126.3, 51.9, 30.8, 28.9, 21.6, 19.1.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for all products and DSC for $TrocN_3$. This material is available free of charge via the Internet at http://pubs.acs.org.