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Pd-catalyzed synthesis of 1-(hetero)aryl-2,2,2trichloroethanols using chloral hydrate and (hetero)arylboroxines†

Minori Shimizu,^a Yuta Okuda,^b Koki Toyoda,^c Ryo Akiyama,^b Hiraku Shinozaki^c and Tetsuya Yamamoto ^b*^{abc}

1-(Hetero)aryl-2,2,2-trichloroethanols are useful key intermediates for the synthesis of various bioactive compounds. Herein, we describe N-heterocyclic carbene (NHC)-coordinated cyclometallated palladium

complex (CYP)-catalyzed (hetero)aryl addition of chloral hydrate using (hetero)arylboroxines, providing

a new approach to 1-(hetero)aryl-2,2,2-trichloroethanols. Notably, PhS-IPent-CYP which coordinated

the bulky yet flexible 2,6-di(pentan-3-yl)aniline (IPent)-based NHC showed good catalytic activities and

promoted the transformation in 24-97% yields.

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Introduction

1-(Hetero)aryl-2,2,2-trichloroethanols are one of the most useful building blocks for the synthesis of bioactive compounds,¹ because the carbinol moiety is easily transformed to various αsubstituted carboxylic acid derivatives.²⁻⁶ So far, 1-(hetero)aryl-2,2,2-trichloroethanols have two kinds of possible synthetic routes as depicted in Scheme 1. One is an addition of the trichloromethyl anion to carbonyl compounds such as aldehydes or ketones (i).⁷ This way has generally needed the use of toxic trichloromethyl anion sources such as chloroform and trichloroacetic acid. The other is an addition of moisture-sensitive organometallic reagents such as organomagnesium compounds to dehydrated chloral (ii).8

The transition metal-catalyzed 1,2-addition of organoboronic acids and their derivatives to carbonyl compounds is a convenient method compared to the Grignard reaction, because this could be conducted in the presence of water.⁹ Although several research groups have reported the Rhcatalyzed 1,2-addition of arylboronic acids to trifluoromethyl ketones,¹⁰ the transition metal-catalyzed addition of arylboron compounds to trichloromethyl carbonyl compounds such as chloral have not been examined yet. It is well known that Nheterocyclic carbenes (NHC) coordinated palladium complexes are useful for various applications such as anticancer drugs, OLEDs and catalysts.¹¹ Recently, we have developed the NHC coordinated cyclometallated palladium complexes (CYPs) that catalyzed the 1,2-addition of organoboron compounds to a wide range of carbonyl compounds including hemiacetals such as aqueous formaldehyde and glyoxylate hemiacetals (Scheme 2).¹² Therefore, we envisaged that the NHC-CYPs exhibit a good catalytic activity of the addition of arylboron compounds to chloral hydrate without a dehydration process. Here, we report the direct aryl addition to chloral hydrate with triarylboroxines using NHC-CYPs as a catalyst.

Results and discussion

At first, we examined CYPs-catalyzed 1,2-addition of chloral hydrate 1 and 2-naphthylboron compounds (Table 1). PhS-IPr-CYP have catalyzed the addition of arylboronic acids to an excess amount of aqueous formaldehyde to provide the corresponding benzylic alcohols in satisfactory yields,^{12a,d} although PhS-IPr-CYP catalyzed reaction of 2-



Scheme 1 Previous synthesis of trichloromethylcarbinols.

[&]quot;Department of Materials and Life Sciences, Tokyo Denki University, 5 Senju-Asahicho, Adachi Tokyo 120-8551, Japan. E-mail: t-yamamoto@mail.dendai.ac.jp

^bDepartment of Materials Science and Engineering, Tokyo Denki University, 5 Senju-Asahicho, Adachi-ku, Tokyo 120-8551, Japan

^cDepartment of Applied Chemistry, Tokyo Denki University, 5 Senju-Asahicho, Adachiku, Tokyo 120-8551, Japan

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Scheme 2 NHC-CYPs-catalyzed 1,2-addition of arylboron compounds and carbonyl compounds.

naphthaleneboronic acid 2a and 4 equivalent of chloral hydrate afforded the desired product 5a in 39% yield (entry 1). In this case, the yield of 5a was improved by the use of an excess of 2a relative to chloral hydrate (entry 2). Then, using 2-naphthaleneboronate 3a instead of 2a increased slightly the yield of 3a to 70% (entry 3). We have confirmed the efficacy of arylboroxines in the arylation of trifluoroacetaldehyde hemiacetal from a preliminary investigation.^{12c} When this reaction was performed using tri(naphthalene-2-yl)boroxine 4a, the yield of 5a was improved considerably to 82% (entry 4). Dehydrated chloral was usable as well as chloral hydrate for this addition reaction (entry 5). H-IPr-CYP has shown more catalytic activity than PhS-IPr-CYP in the CYPs-catalyzed arylation of glyoxylate hemiacetals,12b but it was not suitable for this reaction (entry 6). PhS-IPent-CYP having sterically bulky alkyl group had more active towards the addition than PhS-IPr-CYP (entry 7).

Under the optimized conditions, we synthesized various functionalized trichloromethyl carbinols using PhS-IPent-CYP catalyzed reaction (Table 2). Substrates bearing sterically hindered 1-naphthyl group was also converted to the

corresponding alcohol 5b in moderate yield of 65%. Arylboroxines bearing electron-donating groups like tert-butyl, phenyl, methoxy and methylthio groups furnished the corresponding products 5c-5h in satisfactory yields of 66-97%. Interestingly, sterically bulky 2-methoxyphenylboroxine reacted more smoothly than 3-methoxyphenyl and 4-methoxyphenylboroxines. 4-Fluorophenyl and 4bromophenylboroxines provided the corresponding products 5i and 5j in excellent yields, but the reaction using arylboroxines having strong electron-withdrawing groups such as nitrile, nitro or methoxycarbonyl group have not afforded the products 5k-5m. Remarkably, the bromo group on the aromatic ring remained intact, and the Suzuki-Miyaura crosscoupling product did not observe under this reaction condition. This catalytic reaction was also applicable to heteroarylboroxines containing oxygen or sulfur atom and provided the products 5n-5r in low to moderate yields, but was not applicable to an aliphatic boroxine such as 2-phenylethylboroxine 4s.

Since arylboroxines are more suitable for this reaction than arylboronic acids, we examined an experiment under the reaction conditions with H_2O (Scheme 3). Because arylboroxines is known to rapidly absorb H_2O and transform to boronic acids, and adding water is expected to reduce the dehydration performance of boroxine. Practically, the yield declined as the amount of H_2O added increased, indicating that arylboroxines may be involved in the dehydration step of chloral hydrate. So, we proposed a plausible catalytic cycle which is described in Scheme 4. Initially, dehydrated chloral and arylboronic acids are generated from the hydrolysis of arylboroxines by chloral hydrate. Then arylpalladium intermediate **6** is formed from a base-promoted transmetallation between an arylboronic acid and PhS-IPent-CYP, alkoxypalladium 7 is generated from an insertion of the aryl group on **6** to chloral. Finally, a transmetallation of complex 7 between an arylboronic acid

Table 1 Optimization of reaction conditions of CYPs-catalyzed 1,2-addition of chloral hydrate 1 and 2-naphtalenelboron compounds

| OH the the the the the the the the the the | CYPs (1 mol%) (2 mol% Pd) K ₂ CO ₃ | OH Cl ₃ C |
|--|--|-----------------------------|
| cl ₃ C OH hloral hydrate 1 | toluene 100°C, 2 h | ت برنہ میرنہ |
| B = -ξ-B(OH) ₂ (2a), -ξ-Β΄ C | (3a), -ξ-B | −B O (4a) −B |

| Entry | 1 (mmol) | B (mmol) | K ₂ CO ₃ (mmol) | CYPs | Yield ^a (%) |
|-----------------------|----------|----------|---------------------------------------|---------------|------------------------|
| 1 | 2.0 | 0.5 | 0.5 | PhS-IPr-CYP | 39 |
| 2 | 0.5 | 1.5 | 1.5 | PhS-IPr-CYP | 66 |
| 3^b | 0.5 | 1.5 | 1.5 | PhS-IPr-CYP | 70 |
| 4^c | 0.5 | 0.5 | 1.5 | PhS-IPr-CYP | 82 |
| $5^{c,d}$ | 0.5 | 0.5 | 1.5 | PhS-IPr-CYP | 81 |
| 6 ^{<i>c</i>} | 0.5 | 0.5 | 1.5 | H-IPr-CYP | 73 |
| 7 ^c | 0.5 | 0.5 | 1.5 | PhS-IPent-CYP | 95 $(95)^e$ |

^{*a*} Yields were determined by ¹H-NMR using triphenylmethane as an internal standard. ^{*b*} **3a** was used instead of **2a**. ^{*c*} **4a** was used instead of **2a**. ^{*c*} **4a** was used instead of **2a**. ^{*c*} **4a** was used instead of **2a**.

Table 2PhS-IPent-CYP-catalyzed 1,2-addition of arylboroxines 4 tochloral hydrate 1^{a}



^{*a*} Reaction conditions: **1** (1 equiv., 0.5 mmol), **4** (1.0 equiv., 0.5 mmol), K_2CO_3 (3.0 equiv., 1.5 mmol), PhS-Ipent-CYP (0.005 mmol, 1 mol%) and toluene (1 mL) at 100 °C for 2 h in a sealed tube. Isolated yield.



Scheme 3 The effect of the used amount of ${\rm H}_2{\rm O}$ on the catalytic addition reaction.

results in the formation of 1-(hetero)aryl-2,2,2-trichloroethanol and the regeneration of complex **6**.

Conclusions

We have achieved a nucleophilic arylation to chloral hydrate using PhS-IPent-CYP as a catalyst. The use of arylboroxine is critical for this reaction, and arylboroxines have acted not only



Scheme 4 Proposed reaction mechanism

as an arylcarbanion source but also as a dehydrating agent for chloral hydrate.

Experimental

General

All reactions were carried out under an argon atmosphere. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on an AVANCE III 400 spectrometer (400.15 MHz) at ambient temperature. Melting points were recorded on Yanako MP-S3. HRMS were recorded on a Thermo Fisher Scientific Exactive (Orbitrap) using ESI or APCI. Commercially available organic and inorganic compounds were used without purification. PhS-IPr-CYP,^{12a} H-IPr-CYP,^{12a} PhS-IPent-CYP^{12d} and arylboroxines 4¹³ were prepared according to the literature procedures.

Preparation and characterizations of compounds

2,2,2-Trichloro-1-(naphthalen-2-yl)ethan-1-ol^{7b} 5a. Chloral hydrate (83 mg, 0.50 mmol), 2-naphtyl boroxine (231 mg, 0.500 mmol), PhS-IPent-CYP (6.1 mg, 0.0050 mmol) and potassium carbonate (207 mg, 1.50 mmol) were charged in 10 mL test tube sealed with a rubber septum. The test tube was evacuated and backfilled with argon. This sequence was repeated three times. Then dehydrated toluene (1 mL) was added via the rubber septum with syringe. In an argon flow, the rubber septum was replaced with a Teflon liner screw cap. The sealed test tube was placed into an oil bath preheated 100 °C. After the reaction was stirred for 2 h and cooled to room temperature, the obtained crude was purified by passing it though a silica gel column with a hexane/ethyl acetate to give 131 mg (0.475 mmol, 95%) of product 5a as a pale yellow solid, mp 93–94 °C (lit.^{7b} 93–94 °C). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.09 (s, 1H, Ar*H*), 7.85–7.90 (m, 3H, Ar*H*), 7.88 (dd, $J_1 = 7.3$ Hz, $J_2 = 9.8$ Hz, 1H, Ar*H*), 7.52 (t, *J* = 4.1 Hz, 2H, Ar*H*), 5.40 (d, *J* = 3.4 Hz, 1H, C*H*(OH)CCl₃), 3.39 (d, J = 3.4 Hz, 1H, OH); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 133.8 (Ar), 132.5 (Ar), 132.3 (Ar), 129.3 (Ar), 128.4 (Ar), 127.7 (Ar), 127.4 (Ar), 126.9 (Ar), 126.4 (Ar), 126.2 (Ar), 103.3 (CCl₃), 84.7 (CH(OH)CCl₃); HRMS (EI) m/z: [M + Cl]⁻ calcd for C12H9OCl4: 308.9413. Found: 308.9424.

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2,2,2-Trichloro-1-(naphthalen-1-yl)ethan-1-ol^{3d} **5b**. Product **5b** was prepared by utilizing the general procedure using 1-naphtyl boroxine (231 mg, 0.500 mmol) and was isolated as a pale yellow liquid (91 mg, 0.33 mmol, 66%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.28 (d, J = 8.5 Hz, 1H, ArH), 8.09 (d, J = 8.5 Hz, 1H, ArH), 7.91–7.97 (m, 2H, ArH), 7.51–7.62 (m, 3H, ArH), 6.23 (d, J = 4.2 Hz, 1H, CH(OH)CCl₃), 3.45 (d, J = 4.2 Hz, 1H, OH); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 133.5 (Ar), 132.0 (Ar), 131.4 (Ar), 130.3 (Ar), 129.0 (Ar), 127.2 (Ar), 126.4 (Ar), 125.6 (Ar), 124.9 (Ar), 123.7 (Ar), 103.5 (CCl₃), 79.0 (CH(OH)CCl₃); HRMS (EI) *m/z*: [M + Cl]⁻ calcd for C₁₂H₉OCl₄: 308.9413. Found: 308.9422.

1-([1,1'-Biphenyl]-4-yl)-2,2,2-trichloroethan-ol 5c. Product **5c** was prepared by utilizing the general procedure using 4-biphenyl boroxine (270 mg, 0.500 mmol) and was isolated as a pale yellow solid (136 mg, 0.451 mmol, 90%), mp 119–120 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.70 (s, 1H, Ar), 7.67 (s, 1H, Ar), 7.59–7.62 (m, 4H, Ar), 7.45 (t, *J* = 7.5 Hz, 2H, Ar), 7.36 (t, *J* = 7.5 Hz, 1H, Ar), 5.26 (s, 1H, CH(OH)CCl₃), 3.32 (s, 1H, OH); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 142.4 (Ar), 140.4 (Ar), 133.8 (Ar), 129.7 (Ar), 128.9 (Ar), 127.7 (Ar), 127.2 (Ar), 126.6 (Ar), 103.2 (CCl₃), 84.4 (CH(OH)CCl₃); HRMS (EI) *m/z*: [M + Cl]⁻ calcd for C₁₄H₁₁OCl₄: 334.9569. Found: 334.9583.

1-(4-(*tert***-Buthyl)phenyl)-2,2,2-trichloroethan-1-ol^{7α} 5d.** Product 5d was prepared by utilizing the general procedure using 4-*tert*-buthylpheny boroxine (240 mg, 0.500 mmol) and was isolated as a pale yellow solid (95 mg, 0.34 mmol, 67%), mp 77–78 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.52 (d, J = 8.4 Hz, 2H, ArH), 7.39 (d, J = 8.4 Hz, 2H, ArH), 5.16 (d, J = 4.1 Hz, 1H, CH(OH)CCl₃), 3.33 (d, J = 4.1 Hz, 1H, OH) 1.32 (s, 9H, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 152.6 (Ar), 132.0 (Ar), 128.9 (Ar), 124.8 (Ar), 103.3 (CCl₃), 84.4 (CH(OH)CCl₃), 34.7 (C(CH₃)₃), 31.3 (C(CH₃)₃); HRMS (EI) *m/z*: [M + Cl]⁻ calcd for C₁₂H₁₅OCl₄: 314.9882. Found: 314.9894.

2,2,2-Trichloro-1-(4-methoxyphenyl)ethan-1-ol^{7b} 5e. Product 5e was prepared by utilizing the general procedure using 4methoxyphenyl boroxine (201 mg, 0.500 mmol) and was isolated as a pale yellow liquid (90 mg, 0.35 mmol, 70%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.52 (d, J = 8.7 Hz, 2H, ArH), 6.90 (d, J= 8.7 Hz, 2H, ArH), 5.15 (d, J = 2.3 Hz, 1H, CH(OH)CCl₃), 3.81 (s, 3H, OCH₃), 3.35 (d, J = 2.3 Hz, 1H, OH); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 160.4 (Ar), 130.4 (Ar), 127.0 (Ar), 113.2 (Ar), 103.5 (CCl₃), 84.2 (CH(OH)CCl₃), 55.3 (OCH₃); HRMS (EI) m/z: [M + Cl]⁻ calcd for C₉H₉O₂Cl₄: 288.9362. Found: 288.9374.

2,2,2-Trichloro-1-(3-methoxyphenyl)ethan-1-ol 5f. Product **5f** was prepared by utilizing the general procedure using 3-methoxyphenyl boroxine (201 mg, 0.500 mmol) and was isolated as a colourless liquid (85 mg, 0.33 mmol, 66%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.28 (dd, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 1H, Ar*H*), 7.16–7.17 (m, 2H, Ar*H*), 6.94 (d, J = 8.0 Hz, 1H, Ar*H*), 5.16 (d, J = 4 Hz, 1H, C*H*(OH)CCl₃), 3.80 (s, 3H, OC*H*₃), 3.43 (d, J = 12 Hz, 1H, O*H*); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 159.0 (Ar), 136.4 (Ar), 128.8 (Ar), 121.8 (Ar), 115.0 (Ar), 114.9 (Ar), 103.0 (CCl₃), 84.4 (CH(OH)CCl₃), 55.3 (OCH₃); HRMS (EI) *m/z*: [M + Cl]⁻ calcd for C₉H₉O₂Cl₄: 288.9362. Found: 288.9372.

2,2,2-Trichloro-1-(2-methoxyphenyl)ethan-1-ol 5g. Product **5g** was prepared by utilizing the general procedure using 2-methoxyphenyl boroxine (201 mg, 0.500 mmol) and was isolated as a colourless liquid (113 mg, 0.44 mmol, 88%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.60 (dd, $J_1 = 1.7$ Hz, $J_2 = 7.7$ Hz, 1H, Ar*H*), 7.35 (m, 1H, Ar*H*), 6.91–7.01 (m, 1H, Ar*H*), 5.59 (d, J = 6.9 Hz, 1H, *CH*(OH)CCl₃), 4.25 (d, J = 6.9 Hz, 1H, O*H*), 3.84 (s, 3H, OC*H*₃); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 157.7 (Ar), 130.6 (Ar), 130.4 (Ar), 123.5 (Ar), 120.5 (Ar), 111.2 (Ar), 103.5 (*C*Cl₃), 80.3 (*C*H(OH)CCl₃), 55.6 (OCH₃); HRMS (EI) *m*/*z*: [M + Cl]⁻ calcd for C₉H₉O₂Cl₄: 288.9362. Found: 288.9371.

2,2,2-Trichloro-1-(4-(methylthio)phenyl)ethan-1-ol 5**h**. Product 5**h** was prepared by utilizing the general procedure using 4-(methylthio)phenyl boroxine (225 mg, 0.500 mmol) and was isolated as a pale yellow solid (107 mg, 0.394 mmol, 78%), mp 89.5–90.0 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.50 (d, *J* = 8.4 Hz, 2H, ArH), 7.23 (d, *J* = 8.4 Hz, 2H, ArH), 5.14 (d, *J* = 3.0 Hz, 1H, CH(OH)CCl₃), 3.46 (d, *J* = 3.0 Hz, 1H, OH), 2.48 (s, 3H, SCH₃); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 140.4 (Ar), 131.4 (Ar), 129.6 (Ar), 125.3 (Ar), 103.1 (CCl₃), 84.2 (CH(OH)CCl₃), 15.2 (SCH₃); HRMS (EI) *m/z*: [M + Cl][−] calcd for C₉H₉OCl₄S: 304.9134. Found: 304.9146.

2,2,2-Trichloro-1-(4-fluorophenyl)ethan-1-ol^{1c} **5i.** Product **5i** was prepared by utilizing the general procedure using 4-fluorophenyl boroxine (183 mg, 0.500 mmol) and was isolated as a pale yellow liquid (99 mg, 0.41 mmol, 81%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.58–7.61 (m, 2H, Ar*H*), 7.07 (t, *J* = 8.7 Hz, 2H, Ar*H*), 5.20 (d, *J* = 3.1 Hz, 1H, C*H*(OH)CCl₃), 3.40 (d, *J* = 3.1 Hz, 1H, O*H*); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 163.4 (d, ¹*J*_{C-F} = 247 Hz, Ar), 131.1 (d, ²*J*_{C-F} = 8.6 Hz, Ar), 130.6 (d, ³*J*_{C-F} = 3.0 Hz, Ar), 114.9 (d, ⁴*J*_{C-F} = 21.4 Hz, Ar), 103.1 (d, ⁵*J*_{C-F} = 2.4 Hz, CCl₃), 83.8 (*C*H(OH)CCl₃); ¹⁹F (377 MHz, CDCl₃, ppm): δ -117.8(s, 1F, Ar*F*); HRMS (EI) *m*/*z*: [M + Cl]⁻ calcd for C₈H₆OCl₄F: 276.9162. Found: 276.9170.

1-(4-Bromophenyl)-2,2,2-trichloroethan-1-ol^{7c} 5j. Product 5j was prepared by utilizing the general procedure using 4-bromophenyl boroxine (274 mg, 0.500 mmol) and was isolated as a pale yellow liquid (138 mg, 0.45 mmol, 90%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.49–7.56 (m, 4H, Ar*H*), 5.18 (s, 1H, C*H*(OH)CCl₃), 3.59 (s, 1H, O*H*); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 133.8 (Ar), 131.1 (Ar), 130.9 (Ar), 123.9 (Ar), 102.7 (CCl₃), 83.9 (*C*H(OH)CCl₃); HRMS (EI) *m/z*: [M + Cl]⁻ calcd for C₈H₆-OBrCl₄: 336.8362. Found: 336.8374.

2,2,2-Trichloro-1-(thiophen-2-yl)ethan-1-ol^{7b} **5n.** Product **5n** was prepared by utilizing the general procedure using 2-thiophene boroxine (165 mg, 0.500 mmol) and was isolated as a pale yellow liquid (47 mg, 0.20 mmol, 41%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.40 (dd, $J_1 = 1.2$ Hz, $J_2 = 5.1$ Hz, 1H, Ar*H*), 7.31 (m, 1H, Ar*H*), 7.04 (dd, $J_1 = 3.6$ Hz, $J_2 = 5.1$ Hz, 1H, Ar*H*), 5.48 (d, J = 4.4 Hz, 1H, C*H*(OH)CCl₃), 3.40 (d, J = 4.4 Hz, 1H, O*H*); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 137.3 (Ar), 129.2 (Ar), 127.1 (Ar), 126.3 (Ar), 102.5 (CCl₃), 81.6 (CH(OH)CCl₃); HRMS (EI) *m/z*: [M + Cl]⁻ calcd for C₆H₅OCl₄S: 264.8821. Found: 264.8833.

2,2,2-Trichloro-1-(thiophen-3-yl)ethan-1-ol¹⁴ **50.** Product **50** was prepared by utilizing the general procedure using 3-thiophene boroxine (165 mg, 0.500 mmol) and was isolated as a pale yellow

liquid (68 mg, 0.29 mmol, 59%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.55 (t, *J* = 2.4 Hz, 1H, Ar*H*), 7.32 (m, 2H, Ar*H*), 5.32 (d, *J* = 4.4 Hz, 1H, CH(OH)CCl₃), 3.29 (d, *J* = 4.4 Hz, 1H, CCl₃); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 136.0 (Ar), 127.6 (Ar), 126.2 (Ar), 125.2 (Ar), 102.8 (CCl₃), 81.3 (CH(OH)CCl₃); HRMS (EI) *m*/*z*: [M + Cl]⁻ calcd for C₆H₅OCl₄S: 264.8821. Found: 264.8831.

2,2,2-Trichloro-1-(furan-3-yl)ethan-1-ol 5p. Product **5p** was prepared by utilizing the general procedure using 3-furan boroxine (141 mg, 0.500 mmol) and was isolated as a pale yellow liquid (50 mg, 0.23 mmol, 46%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.66 (t, J = 0.7 Hz, 1H, Ar*H*), 7.45 (t, J = 1.7 Hz, 1H, Ar*H*), 6.66 (dd, $J_1 = 0.7$ Hz, $J_2 = 1.7$ Hz, 1H, Ar*H*), 5.21 (d, J = 4.7 Hz, 1H, C*H*(OH)CCl₃), 3.28 (d, J = 4.7 Hz, 1H, O*H*); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 142.8 (Ar), 142.6 (Ar), 120.8 (Ar), 110.0 (Ar), 102.8 (CCl₃), 79.0 (CH(OH)CCl₃); HRMS (EI) m/z: [M + Cl]⁻ calcd for C₆H₅O₂Cl₄: 248.9049. Found: 248.9056.

1-(Benzo[b]thiophene-2-yl)-2,2,2-trichloroethan-1-ol^{sα} **5q.** Product **5q** was prepared by utilizing the general procedure using 2-benzo[*b*]thiophene boroxine (240 mg, 0.500 mmol) and was isolated as a pale yellow solid (34 mg, 0.12 mmol, 24%), mp 109–110 °C(lit.^{sα} 109–110 °C). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.82–7.89 (m, 2H, Ar*H*), 7.59 (s, 1H, Ar*H*), 7.39–7.41 (m, 2H, Ar*H*), 5.57 (d, *J* = 4.4 Hz, 1H, C*H*(OH)CCl₃), 3.48 (d, *J* = 4.4 Hz, 1H, O*H*); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 140.1 (Ar), 138.4 (Ar), 138.0 (Ar), 126.2 (Ar), 125.2 (Ar), 124.5 (Ar), 124.1 (Ar), 122.3 (Ar), 102.1 (CCl₃), 82.0 (CH(OH)CCl₃); HRMS (EI) *m/z*: [M + Cl]⁻ calcd for C₁₀H₇OCl₄S: 314.8977. Found: 314.8992.

1-(Benzofuran-2-yl)-2,2,2-trichloroethan-1-ol 5r. Product **5r** was prepared by utilizing the general procedure using 2benzofuran boroxine (207 mg, 0.500 mmol) and was isolated as a pale yellow solid (80 mg, 0.30 mmol, 60%), mp 71–72 °C. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.60 (m, 1H, Ar*H*), 7.51 (m, 1H, Ar*H*), 7.24–7.36 (m, 2H, Ar*H*), 6.98 (s, 1H, Ar*H*), 5.35 (d, *J* = 7.2 Hz, 1H, C*H*(OH)CCl₃), 3.59 (d, *J* = 7.2 Hz, 1H, O*H*); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 154.7 (Ar), 150.7 (Ar), 127.4 (Ar), 125.3 (Ar), 123.3 (Ar), 121.6 (Ar), 111.6 (Ar), 107.9 (Ar), 100.9 (CCl₃), 79.7 (CH(OH)CCl₃); HRMS (EI) *m/z*: [M + Cl]⁻ calcd. for C₁₀H₇O₂Cl₄: 298.9206. Found: 298.9216.

Conflicts of interest

There are no conflicts to declare.

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