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

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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.

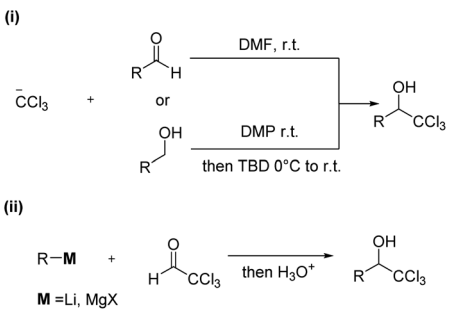
Introduction

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 α-substituted 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 Rh-catalyzed 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 N-heterocyclic 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.

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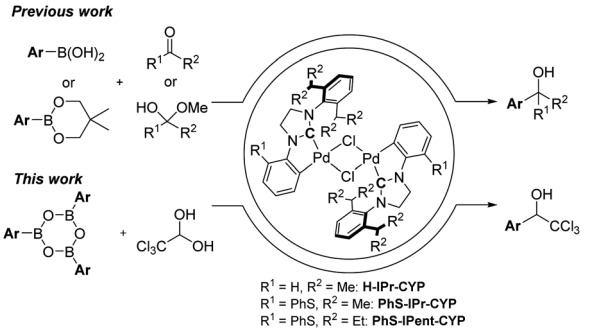


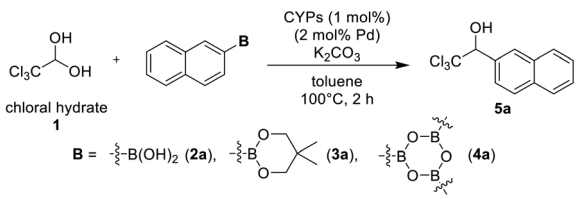
Scheme 2 NHC-CYPs-catalyzed 1,2-addition of arylboron compounds and carbonyl compounds.

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 4-bromophenylboroxines 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 cross-coupling 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

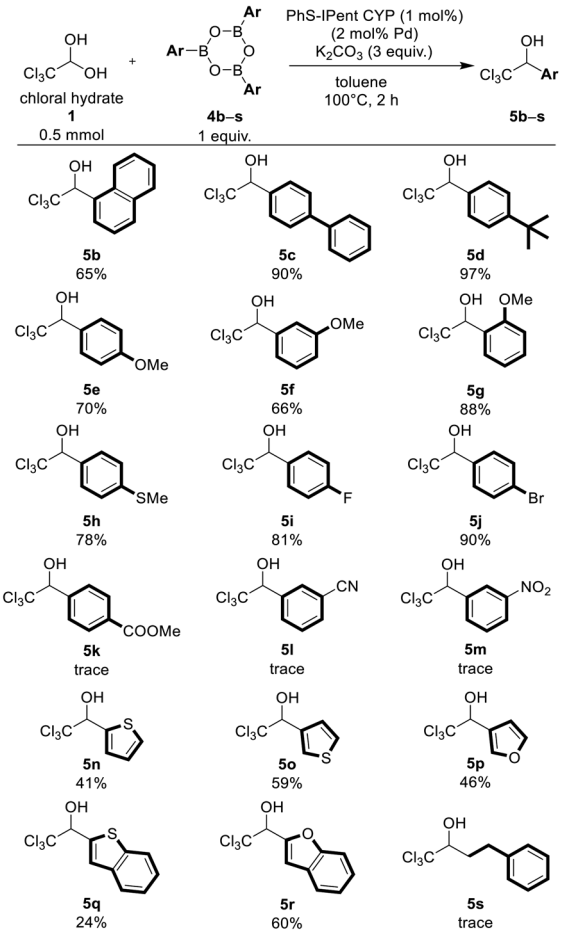
Table 1 Optimization of reaction conditions of CYPs-catalyzed 1,2-addition of chloral hydrate **1** and 2-naphtalenelboron compounds



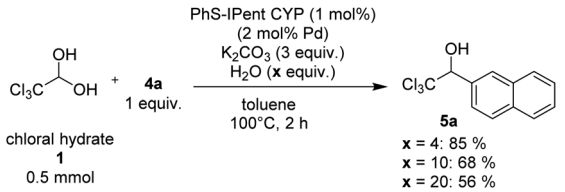
Entry	1 (mmol)	B (mmol)	K_2CO_3 (mmol)	CYPs	Yield[a] (%)
1	2.0	0.5	0.5	PhS-IPr-CYP	39
2	0.5	1.5	1.5	PhS-IPr-CYP	66
3[b]	0.5	1.5	1.5	PhS-IPr-CYP	70
4[c]	0.5	0.5	1.5	PhS-IPr-CYP	82
5[c,d]	0.5	0.5	1.5	PhS-IPr-CYP	81
6[c]	0.5	0.5	1.5	H-IPr-CYP	73
7[c]	0.5	0.5	1.5	PhS-IPent-CYP	95 (95)[e]

[a] Yields were determined by ^{1}H-NMR using triphenylmethane as an internal standard. [b] **3a** was used instead of **2a**. [c] **4a** was used instead of **2a**. [d] Dehydrated chloral was used instead of chloral hydrate. [e] Isolated yield.

Table 2 PhS-IPent-CYP-catalyzed 1,2-addition of arylboroxines **4** to chloral 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.

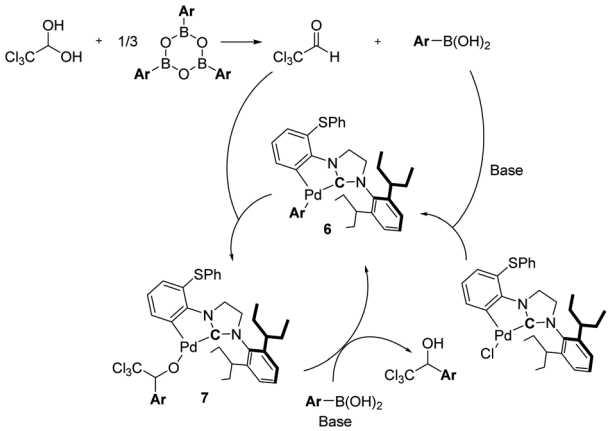


Scheme 3 The effect of the used amount of H_2O on the catalytic addition reaction.

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



Scheme 4 Proposed reaction mechanism.

Experimental

General

All reactions were carried out under an argon atmosphere. ^{1}H, ^{13}C, and ^{19}F 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 **4**[13] 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). ^{1}H NMR (400 MHz, $CDCl_3$, 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)CCl_3), 3.39 (d, $J = 3.4$ Hz, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 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 (CCl_3), 84.7 (*C*H(OH)CCl_3); HRMS (EI) *m*/*z*: $[M + Cl]^-$ calcd for $C_{12}H_9OCl_4$: 308.9413. Found: 308.9424.

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%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.28 (d, J = 8.5 Hz, 1H, Ar*H*), 8.09 (d, J = 8.5 Hz, 1H, Ar*H*), 7.91–7.97 (m, 2H, Ar*H*), 7.51–7.62 (m, 3H, Ar*H*), 6.23 (d, J = 4.2 Hz, 1H, C*H*(OH)CCl_3), 3.45 (d, J = 4.2 Hz, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 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 (*C*Cl_3), 79.0 (*C*H(OH)CCl_3); HRMS (EI) m/z: $[M + Cl]^-$ calcd for $C_{12}H_9OCl_4$: 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. ^{1}H NMR (400 MHz, $CDCl_3$, 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, C*H*(OH)CCl_3), 3.32 (s, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 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 (*C*Cl_3), 84.4 (*C*H(OH)CCl_3); HRMS (EI) m/z: $[M + Cl]^-$ calcd for $C_{14}H_{11}OCl_4$: 334.9569. Found: 334.9583.

1-(4-(*tert*-Buthyl)phenyl)-2,2,2-trichloroethan-1-ol[7a] 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. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.52 (d, J = 8.4 Hz, 2H, Ar*H*), 7.39 (d, J = 8.4 Hz, 2H, Ar*H*), 5.16 (d, J = 4.1 Hz, 1H, C*H*(OH)CCl_3), 3.33 (d, J = 4.1 Hz, 1H, O*H*) 1.32 (s, 9H, C(CH_3)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.6 (Ar), 132.0 (Ar), 128.9 (Ar), 124.8 (Ar), 103.3 (*C*Cl_3), 84.4 (*C*H(OH)CCl_3), 34.7 (*C*(CH_3)$_3$), 31.3 (C(*C*H_3)$_3$); HRMS (EI) m/z: $[M + Cl]^-$ calcd for $C_{12}H_{15}OCl_4$: 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 4-methoxyphenyl boroxine (201 mg, 0.500 mmol) and was isolated as a pale yellow liquid (90 mg, 0.35 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.52 (d, J = 8.7 Hz, 2H, Ar*H*), 6.90 (d, J = 8.7 Hz, 2H, Ar*H*), 5.15 (d, J = 2.3 Hz, 1H, C*H*(OH)CCl_3), 3.81 (s, 3H, OCH_3), 3.35 (d, J = 2.3 Hz, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.4 (Ar), 130.4 (Ar), 127.0 (Ar), 113.2 (Ar), 103.5 (*C*Cl_3), 84.2 (*C*H(OH)CCl_3), 55.3 (O*C*H_3); HRMS (EI) m/z: $[M + Cl]^-$ calcd for $C_9H_9O_2Cl_4$: 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%). ^{1}H NMR (400 MHz, $CDCl_3$, 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)CCl_3), 3.80 (s, 3H, OCH_3), 3.43 (d, J = 12 Hz, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.0 (Ar), 136.4 (Ar), 128.8 (Ar), 121.8 (Ar), 115.0 (Ar), 114.9 (Ar), 103.0 (*C*Cl_3), 84.4 (*C*H(OH)CCl_3), 55.3 (O*C*H_3); HRMS (EI) m/z: $[M + Cl]^-$ calcd for $C_9H_9O_2Cl_4$: 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%). ^{1}H NMR (400 MHz, $CDCl_3$, 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, C*H*(OH)CCl_3), 4.25 (d, J = 6.9 Hz, 1H, O*H*), 3.84 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 157.7 (Ar), 130.6 (Ar), 130.4 (Ar), 123.5 (Ar), 120.5 (Ar), 111.2 (Ar), 103.5 (*C*Cl_3), 80.3 (*C*H(OH)CCl_3), 55.6 (O*C*H_3); HRMS (EI) m/z: $[M + Cl]^-$ calcd for $C_9H_9O_2Cl_4$: 288.9362. Found: 288.9371.

2,2,2-Trichloro-1-(4-(methylthio)phenyl)ethan-1-ol 5h. Product **5h** 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. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.50 (d, J = 8.4 Hz, 2H, ArH), 7.23 (d, J = 8.4 Hz, 2H, Ar*H*), 5.14 (d, J = 3.0 Hz, 1H, C*H*(OH)CCl_3), 3.46 (d, J = 3.0 Hz, 1H, O*H*), 2.48 (s, 3H, SCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 140.4 (Ar), 131.4 (Ar), 129.6 (Ar), 125.3 (Ar), 103.1 (*C*Cl_3), 84.2 (*C*H(OH)CCl_3), 15.2 (S*C*H_3); HRMS (EI) m/z: $[M + Cl]^-$ calcd for $C_9H_9OCl_4S$: 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%). ^{1}H NMR (400 MHz, $CDCl_3$, 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)CCl_3), 3.40 (d, J = 3.1 Hz, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 163.4 (d, $^1J_{C-F}$ = 247 Hz, Ar), 131.1 (d, $^2J_{C-F}$ = 8.6 Hz, Ar), 130.6 (d, $^3J_{C-F}$ = 3.0 Hz, Ar), 114.9 (d, $^4J_{C-F}$ = 21.4 Hz, Ar), 103.1 (d, $^5J_{C-F}$ = 2.4 Hz, *C*Cl_3), 83.8 (*C*H(OH)CCl_3); ^{19}F (377 MHz, $CDCl_3$, ppm): δ −117.8(s, 1F, Ar*F*); HRMS (EI) m/z: $[M + Cl]^-$ calcd for $C_8H_6OCl_4F$: 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%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.49–7.56 (m, 4H, Ar*H*), 5.18 (s, 1H, C*H*(OH)CCl_3), 3.59 (s, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 133.8 (Ar), 131.1 (Ar), 130.9 (Ar), 123.9 (Ar), 102.7 (*C*Cl_3), 83.9 (*C*H(OH)CCl_3); HRMS (EI) m/z: $[M + Cl]^-$ calcd for $C_8H_6OBrCl_4$: 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%). ^{1}H NMR (400 MHz, $CDCl_3$, 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)CCl_3), 3.40 (d, J = 4.4 Hz, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 137.3 (Ar), 129.2 (Ar), 127.1 (Ar), 126.3 (Ar), 102.5 (*C*Cl_3), 81.6 (*C*H(OH)CCl_3); HRMS (EI) m/z: $[M + Cl]^-$ calcd for $C_6H_5OCl_4S$: 264.8821. Found: 264.8833.

2,2,2-Trichloro-1-(thiophen-3-yl)ethan-1-ol[14] 5o. Product **5o** 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%). ^{1}H NMR (400 MHz, $CDCl_3$, 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, C*H*(OH)CCl_3), 3.29 (d, $J = 4.4$ Hz, 1H, CCl_3); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 136.0 (Ar), 127.6 (Ar), 126.2 (Ar), 125.2 (Ar), 102.8 (*C*Cl_3), 81.3 (*C*H(OH)CCl_3); HRMS (EI) *m*/*z*: $[M + Cl]^-$ calcd for $C_6H_5OCl_4S$: 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%). ^{1}H NMR (400 MHz, $CDCl_3$, 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)CCl_3), 3.28 (d, $J = 4.7$ Hz, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 142.8 (Ar), 142.6 (Ar), 120.8 (Ar), 110.0 (Ar), 102.8 (*C*Cl_3), 79.0 (*C*H(OH)CCl_3); HRMS (EI) *m*/*z*: $[M + Cl]^-$ calcd for $C_6H_5O_2Cl_4$: 248.9049. Found: 248.9056.

1-(Benzo[*b*]thiophene-2-yl)-2,2,2-trichloroethan-1-ol[8a] 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.[8a] 109–110 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 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)CCl_3), 3.48 (d, $J = 4.4$ Hz, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 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 (*C*Cl_3), 82.0 (*C*H(OH)CCl_3); HRMS (EI) *m*/*z*: $[M + Cl]^-$ calcd for $C_{10}H_7OCl_4S$: 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 2-benzofuran boroxine (207 mg, 0.500 mmol) and was isolated as a pale yellow solid (80 mg, 0.30 mmol, 60%), mp 71–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 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)CCl_3), 3.59 (d, $J = 7.2$ Hz, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 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 (*C*Cl_3), 79.7 (*C*H(OH)CCl_3); HRMS (EI) *m*/*z*: $[M + Cl]^-$ calcd. for $C_{10}H_7O_2Cl_4$: 298.9206. Found: 298.9216.

Conflicts of interest

There are no conflicts to declare.

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