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

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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)arylborexines, 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

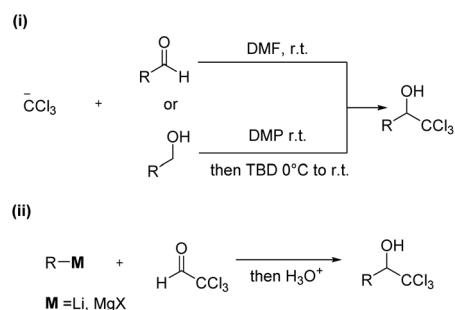
1-(Hetero)aryl-2,2,2-trichloroethanols are one of the most useful building blocks for the synthesis of bioactive compounds,¹ because the carbinol moiety is easily transformed to various α -substituted carboxylic acid derivatives.^{2–6} So far, 1-(hetero)aryl-2,2,2-trichloroethanols have two kinds of 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 triarylborexines 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.

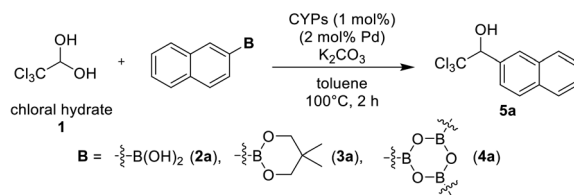
naphthaleneboronic acid **2a** and 4 equivalent of chloral hydrate afforded the desired product **5a** in 39% yield (entry 1). In this case, the yield of **5a** was improved by the use of an excess of **2a** relative to chloral hydrate (entry 2). Then, using 2-naphthaleneboronate **3a** instead of **2a** 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 H₂O (Scheme 3). Because arylboroxines is known to rapidly absorb H₂O 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 H₂O 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 transmetalation 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 transmetalation 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-naphthalenelboron compounds



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 ^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 ¹H-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), K₂CO₃ (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.

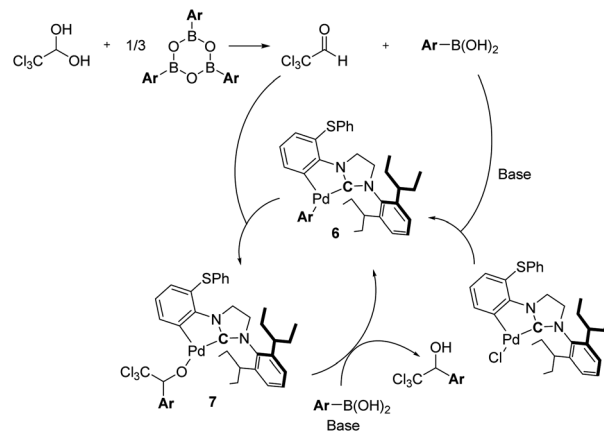


Scheme 3 The effect of the used amount of H₂O on the catalytic addition reaction.

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-naphthyl 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 through 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, ArH), 7.85–7.90 (m, 3H, ArH), 7.88 (dd, *J*₁ = 7.3 Hz, *J*₂ = 9.8 Hz, 1H, ArH), 7.52 (t, *J* = 4.1 Hz, 2H, ArH), 5.40 (d, *J* = 3.4 Hz, 1H, CH(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.



2,2,2-Trichloro-1-(naphthalen-1-yl)ethan-1-ol^{3d} 5b. Product **5b** was prepared by utilizing the general procedure using 1-naphthyl 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-ol^{7a} 5d. Product **5d** was prepared by utilizing the general procedure using 4-*tert*-buthylphenyl 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 4-methoxyphenyl 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, ArH), 7.16–7.17 (m, 2H, ArH), 6.94 (d, *J* = 8.0 Hz, 1H, ArH), 5.16 (d, *J* = 4 Hz, 1H, CH(OH)CCl₃), 3.80 (s, 3H, OCH₃), 3.43 (d, *J* = 12 Hz, 1H, OH); 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, ArH), 7.35 (m, 1H, ArH), 6.91–7.01 (m, 1H, ArH), 5.59 (d, *J* = 6.9 Hz, 1H, CH(OH)CCl₃), 4.25 (d, *J* = 6.9 Hz, 1H, OH), 3.84 (s, 3H, OCH₃); 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 (CCl₃), 80.3 (CH(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 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. 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, ArH), 7.07 (t, *J* = 8.7 Hz, 2H, ArH), 5.20 (d, *J* = 3.1 Hz, 1H, CH(OH)CCl₃), 3.40 (d, *J* = 3.1 Hz, 1H, OH); 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 (CH(OH)CCl₃); ¹⁹F (377 MHz, CDCl₃, ppm): δ −117.8 (s, 1F, ArF); 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, ArH), 5.18 (s, 1H, CH(OH)CCl₃), 3.59 (s, 1H, OH); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 133.8 (Ar), 131.1 (Ar), 130.9 (Ar), 123.9 (Ar), 102.7 (CCl₃), 83.9 (CH(OH)CCl₃); HRMS (EI) *m/z*: [M + Cl][−] calcd for C₈H₆OBrCl₄: 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, ArH), 7.31 (m, 1H, ArH), 7.04 (dd, *J*₁ = 3.6 Hz, *J*₂ = 5.1 Hz, 1H, ArH), 5.48 (d, *J* = 4.4 Hz, 1H, CH(OH)CCl₃), 3.40 (d, *J* = 4.4 Hz, 1H, OH); 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 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%). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.55 (t, $J = 2.4$ Hz, 1H, ArH), 7.32 (m, 2H, ArH), 5.32 (d, $J = 4.4$ Hz, 1H, CH(OH)CCl₃), 3.29 (d, $J = 4.4$ Hz, 1H, CCl₃); ^{13}C NMR (100 MHz, CDCl_3 , 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 : $[\text{M} + \text{Cl}]^-$ calcd for $\text{C}_6\text{H}_5\text{OCl}_4\text{S}$: 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, CDCl_3 , ppm): δ 7.66 (t, $J = 0.7$ Hz, 1H, ArH), 7.45 (t, $J = 1.7$ Hz, 1H, ArH), 6.66 (dd, $J_1 = 0.7$ Hz, $J_2 = 1.7$ Hz, 1H, ArH), 5.21 (d, $J = 4.7$ Hz, 1H, CH(OH)CCl₃), 3.28 (d, $J = 4.7$ Hz, 1H, OH); ^{13}C NMR (100 MHz, CDCl_3 , 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 : $[\text{M} + \text{Cl}]^-$ calcd for $\text{C}_6\text{H}_5\text{O}_2\text{Cl}_4$: 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). ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.82–7.89 (m, 2H, ArH), 7.59 (s, 1H, ArH), 7.39–7.41 (m, 2H, ArH), 5.57 (d, $J = 4.4$ Hz, 1H, CH(OH)CCl₃), 3.48 (d, $J = 4.4$ Hz, 1H, OH); ^{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 (CCl₃), 82.0 (CH(OH)CCl₃); HRMS (EI) m/z : $[\text{M} + \text{Cl}]^-$ calcd for $\text{C}_{10}\text{H}_7\text{OCl}_4\text{S}$: 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. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.60 (m, 1H, ArH), 7.51 (m, 1H, ArH), 7.24–7.36 (m, 2H, ArH), 6.98 (s, 1H, ArH), 5.35 (d, $J = 7.2$ Hz, 1H, CH(OH)CCl₃), 3.59 (d, $J = 7.2$ Hz, 1H, OH); ^{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 (CCl₃), 79.7 (CH(OH)CCl₃); HRMS (EI) m/z : $[\text{M} + \text{Cl}]^-$ calcd. for $\text{C}_{10}\text{H}_7\text{O}_2\text{Cl}_4$: 298.9206. Found: 298.9216.

Conflicts of interest

There are no conflicts to declare.

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