JOC The Journal of Organic Chemistry

Article

Organocatalytic chlorination of alcohols by P(III)/P(V) redox cycling

Lars Longwitz, Stefan Jopp, and Thomas Werner

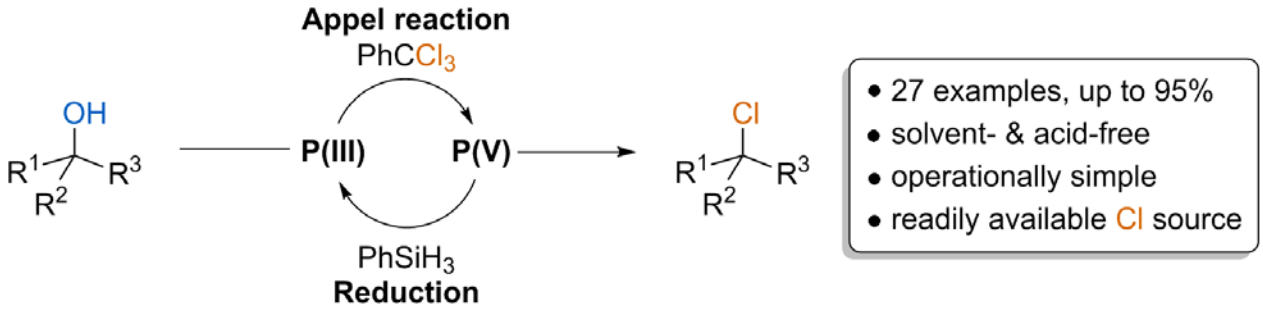
J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b00741 • Publication Date (Web): 28 May 2019

Organocatalytic chlorination of alcohols by P(III)/P(V) redox cycling

Lars Longwitz, Stefan Jopp, Thomas Werner*

Leibniz Institute for Catalysis at the University of Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany

Supporting Information Placeholder

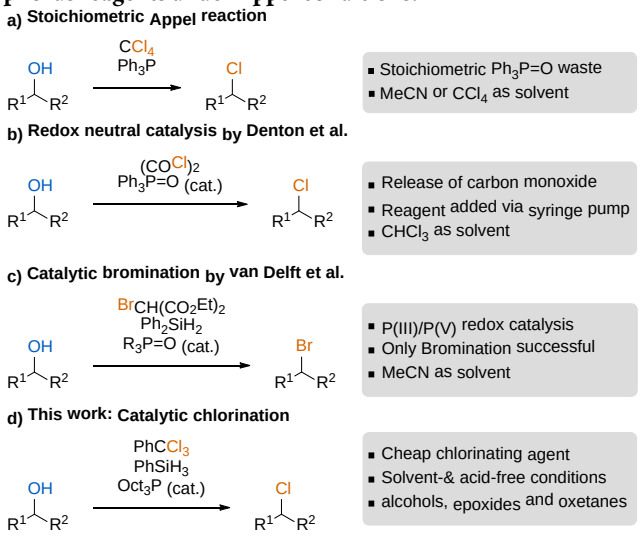


ABSTRACT: A catalytic system for the chlorination of alcohols under Appel conditions was developed. Benzotrichloride is used as a cheap and readily available chlorinating agent in combination with trioctylphosphane as the catalyst and phenylsilane as the terminal reductant. The reaction has several advantages over other variants of the Appel reaction, e.g. no additional solvent is required and the phosphane reagent is used only in catalytic amounts. In total, 27 different primary, secondary and tertiary alkyl chlorides were synthesized in yields up to 95%. Under optimized conditions, it was also possible to convert epoxides and an oxetane to the dichlorinated products.

INTRODUCTION

Chlorinated hydrocarbons are amongst the most utilized starting materials in organic synthesis due to the great value of nucleophilic substitution reactions for the stepwise construction of complex molecules.[1] Their direct synthesis from alcohols can be achieved in various ways and is performed even on industrial scale.[2-7] The Appel reaction uses phosphanes and organic chlorinating agents like carbon tetrachloride to convert alcohols stereoselectively to the corresponding alkyl chlorides (Scheme 1a).[8] Although this methodology is excellent for the conversion of complex structures under mild conditions, a definite drawback is the generation of stoichiometric phosphane oxide by-product, which complicates product purification.[9] Recently, there has been a growing interest in the development of catalytic variants of common organic transformations like the Wittig[10-15], Cadogan[16], Mitsonobu[17, 18] or Staudinger[19, 20] reaction.[21, 22] In these reactions, the phosphane oxide is reduced in situ back to the phosphane by a suitable terminal reductant which eliminates problems concerning the separation of the product from the phosphane oxide waste. The terminal reductant needs to chemoselectively react with the phosphane oxide and organosilanes have been found to be especially fitting for this task.[23] In recent years, variations of the Appel reaction largely focused on the use of alternative chlorinating agents like dichloroselenurane (Ph_2SeCl_2)[24], ammonium salts in combination with DDQ[25] or 1,2-dihaloethanes[26], trichloroisocyanuric acid[27] or other small compounds bearing a CCl_3 group.[28] These procedures improved reaction times, stereoselectivity and allowed for the conversion of more

Scheme 1. Synthesis of alkyl halides from alcohols using phosphorus reagents under Appel conditions.

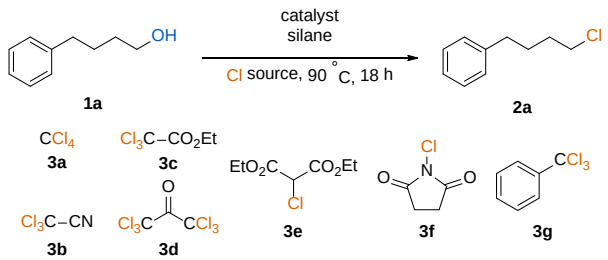


demanding substrates, but all required the use of stoichiometric amounts of phosphane reagent. In 2010 Denton et al. presented a catalytic chlorination employing a phosphane oxide catalyst under redox neutral conditions (Scheme 1b).[29-32] The active chlorophosphonium salt is generated from the oxalylchloride, releasing CO_2 and toxic CO in the process. Concerning the development of a catalytic Appel reaction, van Delft et al. presented dibenzophosphole oxides as catalysts for the bromination of alcohols using diphenylsilane as the terminal reductant (Scheme 1c).[33, 34] While alkyl bromides could be obtained in moderate to good yields under catalytic conditions, the protocol could not be transferred to the chlorination of alcohols. The authors pointed out that the balance of electrophilicity of the chlorinating agent and nucleophilicity of the phosphane catalyst would be crucial for a successful catalytic Appel reaction. Huijbregts et al. reported a life cycle assessment of the catalytic Appel reaction compared to a classic variant using stoichiometric amounts of phosphane.[35] The highest share of the cumulative energy demand and greenhouse gas emissions for the catalytic reaction was attributed the solvent (MeCN) and chlorine source (diethyl chloromalonate). Thus, a catalytic Appel reaction would require improvements in these areas to be competitive with the classic reaction. Herein, we present a protocol using benzotrichloride ($PhCCl_3$) as the chlorine source in combination with trioctylphosphane (Oct_3P) as the catalyst to convert alcohols under solvent-free conditions to the respective chlorides.

RESULTS AND DISCUSSION

We started our investigation by staying close to the classic Appel conditions in the model reaction of 4-phenyl 1-butanol (**1a**) to the corresponding chloride **2a**.[36] When alcohol **1a** was converted with an excess of CCl_4 in the presence of 10 mol % triphenylphosphane and a stoichiometric amount of phenylsilane at 90 °C for 18 h, only 9% of the product was obtained, indicating no successful turnover under these conditions (Table 1, entry 1). Alkyl phosphanes are not commonly used in the classic Appel reaction due to their high nucleophilicity and violent reaction with CCl_4.[8, 37, 38] However, since the slow reduction of the phosphane oxide limits the amount of free phosphane present in the reaction mixture, we envisioned a controlled reaction when using a more nucleophilic trialkyl phosphane in catalytic amounts. Indeed, a significant higher yield of 39% was observed using 10 mol % of tributyl phosphane (Bu_3P) as the catalyst (entry 2). Increasing the steric demand on the phosphane generally leads to lower yields and the best catalyst was found to be trioctylphosphane giving the product in a yield of 45% (entry 3 and 4). Phenylsilane proved to be most suitable terminal reductant compared to other more substituted organosilanes like diphenylsilane or trimethoxysilane (entry 5 and 6). Subsequently, we turned our attention to the chlorination reagent **3**, which were used in a large excess (entries 7–12). Enhancing the electrophilic character by introduction of cyano or ester groups reduced the yield slightly to 34% and 27%, respectively, but the selectivity of the reaction greatly decreased (entry 7 and 8). Triphosgene (**3d**) could be used as chlorine source with a moderate yield of 51%, albeit a poor selectivity was observed (entry 9). Van Delft et al. used diethyl chloromalonate (**3e**) in their catalytic Appel reaction, but only with limited success.[34] We also investigated this chlorinating agent with trioctylphosphane as the catalyst, but only a poor yield of 6% was observed (entry 10).

Table 1. Screening of potential catalysts, various silanes as reducing agents, chlorine sources and optimization of the reaction conditions.[36]



entry	catalyst (10 mol %)	silane (equiv)	Cl source	yield **2a** /%[a]
1	Ph_3P	$PhSiH_3$ (1.00)	**3a**	9 (14)
2	Bu_3P	$PhSiH_3$ (1.00)	**3a**	39 (46)
3	tBu_3P	$PhSiH_3$ (1.00)	**3a**	2 (13)
4	Oct_3P	$PhSiH_3$ (1.00)	**3a**	45 (50)
5	Oct_3P	Ph_2SiH_2 (1.50)	**3a**	7 (18)
6	Oct_3P	$(MeO)_3SiH$ (3.00)	**3a**	3 (96)
7	Oct_3P	$PhSiH_3$ (1.00)	**3b**	34 (84)
8	Oct_3P	$PhSiH_3$ (1.00)	**3c**	27 (52)
9	Oct_3P	$PhSiH_3$ (1.00)	**3d**	51 (94)
10	Oct_3P	$PhSiH_3$ (1.00)	**3e**	6 (68)
11[b]	Oct_3P	$PhSiH_3$ (1.00)	**3f**	8 (84)
12	Oct_3P	$PhSiH_3$ (1.00)	**3g**	55 (65)
13[c]	Oct_3P	$PhSiH_3$ (1.00)	**3g**	82 (96)
14[d]	Oct_3P	$PhSiH_3$ (1.00)	**3g**	93 (>99)

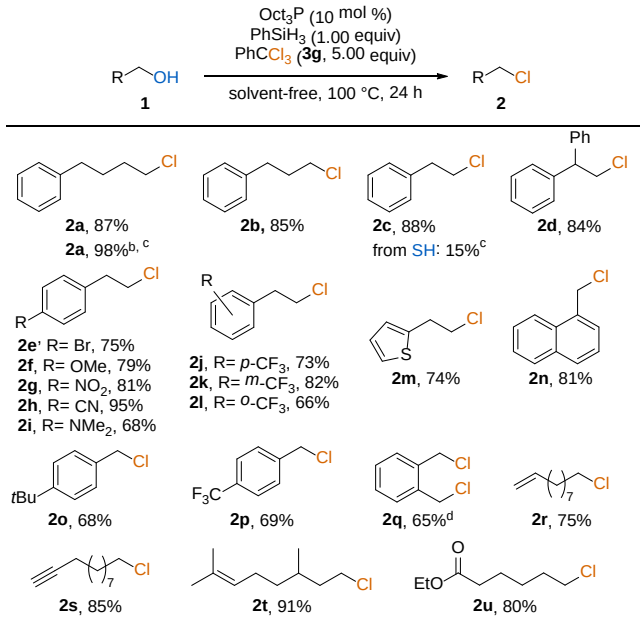
Standard reaction conditions: **1** (1.00 mmol, 1.00 equiv), catalyst (10 mol %), silane (1.00 equiv), chlorine source **3** (2 mL); 90 °C for 18 h. [a] Conversion given in parenthesis. Yield and conversion were determined by GC-FID using hexadecane as internal standard. [b] Solvent-free, 1.00 equiv of **3f**. [c] Solvent-free, 5.00 equiv of **3g**. [d] Solvent-free, 5.00 equiv of **3g**, 100 °C, 24 h.

The chloronium source *N*-chlorosuccinimide (**3f**) leads to a complex reaction mixture under these conditions, even when only a stoichiometric amount of **3f** was added (entry 11). Additionally, benzotrichloride (**3g**) was employed as a halogen source and a yield of 55% with good selectivity was observed (entry 12). Notably, benzotrichloride(**3g**) is readily available in large amounts at low prices and has to the best of our knowledge not been used successfully as a chlorination reagent up until now. Subsequently, the reaction conditions were adjusted by reducing the amount of the chlorinating agent (entry 13) and changing reaction temperature and time to give the desired product in a yield of 93%(entry 14).[36]

With a suitable protocol for the catalytic chlorination of alcohols in hand, we examined the substrate scope of our catalytic system under optimized conditions (Scheme 2). The product **2a** of the model reaction was isolated in a yield of 87%. The scalability of the progress was tested by converting the model substrate **1a** in a multigram scale and a yield of 98% of the corresponding chloride **2a** was obtained. Alkyl chlorides **2b** and **2c** bearing shorter alkyl chains were isolated in excellent yields of 85% and 88%, respective-

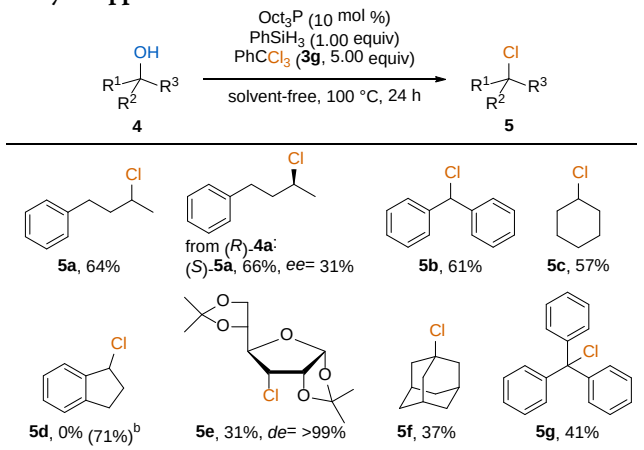
ly. We were also interested in the possible conversion of mercaptans, but a yield of only 15% of 1-chloro-2-phenyl ethane (**2c**) was obtained starting from the respective thiol. The diphenyl substituted ethanol **1d** gave the respective chloride **2d** in a yield of 84%. Furthermore, different *para* substituted 2-phenyl 1-ethanol derivates **1e**–**i** were converted with good to excellent yields and functional groups like nitro (**2g**), cyano (**2h**) or amino (**2i**) were compatible with the protocol.

Scheme 2. Scope of primary alcohols in the catalytic Appel reaction.[a]



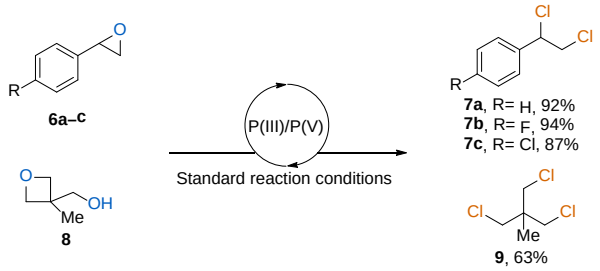
[a]Standard reaction conditions: **1** (1.00 mmol, 1.00 equiv), Oct_3P (10 mol %), phenylsilane (1.00 equiv), $PhCCl_3$ (**3g**, 5.00 equiv), solvent-free; 100 °C for 24 h. Isolated yields are given. [b] The reaction was performed on a 5.00 g (33.3 mmol) scale. [c] Yield was determined with GC-FID using hexadecane as internal standard. [d] 1,2-Benzenedimethanol (**1q**, 1.00 mmol, 1.00 equiv), Oct_3P (20 mol %), phenylsilane (2.00 equiv), $PhCCl_3$ (**3g**, 10.00 equiv).

Scheme 3. Scope of secondary and tertiary alcohols in the catalytic Appel reaction.[a]



[a] For standard reaction conditions, see Scheme 2. Enantiomeric excess (*ee*) was determined by chiral GC-FID. Diastereomeric excess (*de*) was determined by GC-FID. [b] Isolated yield of corresponding alkene derivate in parenthesis.

Scheme 4. Conversion of strained oxocycles under catalytic Appel conditions.[a]



[a]Standard reaction conditions: **6** or **8** (1.00 mmol, 1.00 equiv), Oct_3P (10 mol %), phenylsilane (1.00 equiv), $PhCCl_3$ (**3g**, 5.00 equiv), solvent-free; 100 °C for 24 h. Isolated yields are given.

Introduction of a trifluoromethyl group in *para*, *meta* or *ortho* position gave the corresponding alkyl halides **2j**–**2l** in moderate to good yields. The thiophene substituted alcohol **1m** and naphthyl derivate **1n** were converted in yields of 74% and 81%. The *para* substituted benzylchlorides **2o** and **2p** were obtained in yields of 68% and 69%. Doubling the amount of phosphane, silane and chlorinating agent enabled the isolation of the dichloride **2q** in a moderate yield of 65%. Four aliphatic alcohols **1r**–**u** were converted to the respective alkyl chlorides in yields between 75% and 91% and the alkene groups (**2r** and **2t**) as well as an alkyne group (**2s**) were well tolerated.

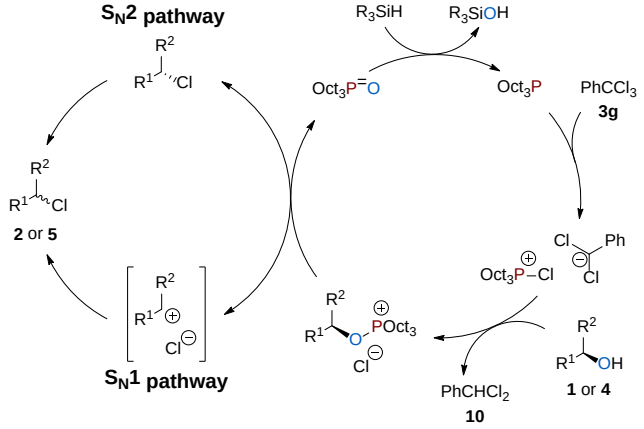
With overall good to excellent yields for the primary substrates, we then applied our reaction conditions onto secondary and tertiary alcohols **4a**–**h** (Scheme 3). The secondary alkyl chloride **5a** was obtained in a good yield of 64% without changing reaction conditions. Biaryl-substituted alcohol **4b** was converted to the respective chloromethylene dibenzene (**5b**) in a yield of 61%. The conversion of cyclohexanol (**4c**) gave chlorocyclohexane (**5c**) in an isolated yield of 57%. The chloride **5d** could not be obtained under these conditions and only the elimination product was isolated. Furthermore, the protected glucose substrate **4e** was chlorinated to **5e** in a yield of 31%. Tertiary alcohols bearing an adamantyl or trityl group gave the corresponding chlorides in rather low yields of 37% and 41%.

It is also possible to synthesize 1,2-dichloro substituted alkanes by converting epoxides under Appel reaction conditions, which was among other things utilized for the stereoselective synthesis of chlorosulfolipids.[39-42] In fact, our catalytic methodology converted styrene oxide derivates **6a**–**c** to the respective dichloroalkanes **7a**–**c** in excellent yields up to 94% (Scheme 4). When oxetane derivate **8** was converted, three chlorination reactions took place and the trichloride **9** was isolated.

A major advantage over other chlorination methods is the stereoselectivity of the Appel reaction. Our next goal was to verify the stereoselectivity of the catalytic Appel reaction by converting the enantiopure alcohol (*R*)-**4a** to the respective alkyl halide (*S*)-**5a** (Scheme 3). While the product was isolated in a yield similar to the racemic substrate **5a**, significant racemization was observed and only an enantiomeric excess of 31% was found in the alkyl halide. We further investigated the poor stereoselectivity by converting an enatiopure alkyl chloride (*S*)-5a under the standard reaction conditions. Interestingly, stereodegradation was observed and the alkyl

chloride was isolated quantitatively with an enantiomeric excess of only 35%. We also investigated the carbohydrate derivate **5e**, which was isolated as a single diastereomer, indicating no epimerization occurred during the reaction. We suspect that the carbohydrate **5e** is protected from this epimerization due to the bulky isopropylidene groups.[36]

Scheme 5. Proposed mechanism for the catalytic Appel reaction with benzotrichloride and trioctylphosphane.



We propose a mechanism very similar to the classic Appel reaction (Scheme 5).[36] The nucleophilic phosphane reacts with the electrophilic chlorinating agent to a chlorophosphonium salt. This salt can further react with an alcohol to form an alkoxyphosphonium salt and dichlorotoluene (**10**) as a side product. The alkoxyphosphonium salt undergoes a Michaelis-Arbusov-rearrangement under the reaction conditions to liberate the product. The product may undergo a nucleophilic substitution reaction which leads overall to the loss of stereoinformation in the case of chiral alcohols. Another possible pathway is a S_N1 type mechanism, in which the phosphane oxide is eliminated and a carbocation is formed. This leads to the formation of elimination side products for secondary alcohols like **4d** and could also be the reason for the poor stereoselectivity of substrate (*R*)-**4a**. Subsequently, the phosphane oxide is then reduced by the organosilane to close the catalytic cycle. It is also possible to start the reaction with the corresponding oxide without significant loss of activity, which is especially useful since most phosphanes are oxygen-sensitive. Furthermore, we investigated the resting state of the catalyst by in situ ^{31}P NMR spectroscopy and found a mixture of phosphane oxide and phosphane during the reaction. Thus it appears that both the reduction and nucleophilic attack on the benzotrichloride (**3g**) influence the rate of the reaction.

CONCLUSION

In conclusion, we have developed a highly effective new methodology for the chlorination of alcohols. The key to the high activity and selectivity of the system is the balance of the nucleophilicity of the alkyl phosphane catalyst and electrophilic character of the chlorinating agent in the presence of an organosilane as the terminal reductant. In total, 21 primary alcohols were converted into the alkyl chlorides with good functional group tolerance and good to excellent yields. Secondary and tertiary alcohols were also compatible with the procedure, although lower yields were obtained. The conversion of chiral alcohols indicates partial racemization under the reaction conditions. Moreover, the protocol can be used for the direct conversion of epoxides or oxetanes to the chlorinated derivates via a ring opening reaction.

EXPERIMENTAL SECTION

General considerations. All reagents and solvents were purchased from commercial sources and used as received without further purification. All reactions were performed in 6 mL 12x100 DURAN® culture tubes with GL 14 screw caps and heated in an aluminum block. It is also possible to perform the reaction in standard pressure tubes. Thin layer chromatography was performed on *Merck* TLC-plates with fluorescence indication (silica type 60, F254), visualization was accomplished using UV-light, iodine stains or 10% ethanolic sulphuric acid solution. Flash chromatography was performed using silica with a grain size of 40–63 µm from *Macherey-Nagel*. Deuterated chloroform was purchased from *Deutero*. NMR spectra were recorded on *Bruker* AV 300 and *Bruker* AV 400 spectrometers. The chemical shifts (δ) for ^{1}H and ^{13}C in $CDCl_3$ are given in parts per million (ppm) and referenced to 7.27 and 77.0 ppm, respectively. Coupling constants are given in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quadruplet, p = pentet, sext = sextet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets. IR spectra were recorded on a Nicolet iS10 MIR FT-IR-spectrometer from *Thermo Fisher Scientific*. Gas chromatography was performed on *Agilent* 7890A GC System, mass spectra were measured on downstream 5975C inert XL MSD mass detector from *Agilent*. The reported GC-FID yields are based on a calibrated area of hexadecane as internal standard. High resolution mass spectra were obtained either from a MAT 95 XP from *Thermo* (EI) or from an HPLC system 1200 and downstream ESI-TOF-MS 6210 from *Agilent* (ESI).

General procedure (GP1) for catalyst screening and optimization: A solution of 4-phenylbutan-1-ol (**1a**, 150 mg, 1.00 mmol, 1.00 equiv), chlorinating agent **3** (2 mL or 5.00 equiv), phenylsilane (108 mg, 1.00 mmol, 1.00 equiv) and the catalyst (0.10 mmol, 0.10 equiv) was stirred in a culture tube at 100 °C for 24 h. The reaction mixture was cooled to room temperature, diluted with EtOAc (5 mL) and hexadecane (113 mg, 0.50 mmol, 0.50 equiv) was added. The conversion and yield were determined by GC-FID analysis using hexadecane as internal standard.

General procedure (GP2) for the synthesis of alkyl chlorides: Alcohol **1** or **4** (1.00 mmol), **3g** (977 mg, 5.00 mmol), and tri-*n*-octylphosphane (37 mg, 0.01 mmol) were added to a 5 mL culture tube. The vial is purged with argon and after adding phenylsilane (108 mg, 1.00 mmol) the vial was capped and stirredfor 24 h at 100 °C. After cooling to room temperature the reaction mixture is diluted with EtOAc (5 mL) and the product is isolated by column chromatography (SiO_2) or Kugelrohr distillation. All volatiles were removed carefully in vacuum to afford the desired alkyl chloride **2** or **5**.

1-Chloro-4-phenylbutane (2a)[43]: According to **GP2**, 4-phenylbutan-1-ol (**1a**, 150 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2a** (146 mg, 0.866 mmol, 87%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.46; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ= 1.71–1.75 (m, 4H), 2.59 (t, *J*= 6.9 Hz, 2H), 3.48 (t, *J*= 6.0 Hz, 2H), 7.12–7.16 (m, 3H), 7.21–7.26 (m, 2H) ppm; ^{13}C{^{1}H}-NMR

(75 MHz, $CDCl_3$, 25 °C): δ= 28.5 (CH_2), 32.0 (CH_2), 35.0 (CH_2), 44.8 (CH_2), 125.8 (CH), 128.3 (CH), 141.8 (C) ppm.

1-Chloro-3-phenylpropane (2b)[31]: According to **GP2**, 3-phenylpropan-1-ol (**1b**, 136 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2b** (131 mg, 0.847 mmol, 85%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.54; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ= 2.15 (p, *J*= 6.9 Hz, 2H), 2.85 (t, *J*= 7.4 Hz, 2H), 3.59 (t, *J*= 6.5 Hz, 2H), 7.26–7.30 (m, 3H), 7.35–7.40 (m, 2H) ppm; ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 25 °C): δ= 32.7 (CH_2), 34.0 (CH_2), 44.1 (CH_2), 126.0 (CH), 128.4 (CH), 128.5 (CH), 140.6 (C) ppm.

1-Chloro-2-phenylethane (2c)[24]: According to **GP2**, 2-phenylethanol (**1c**, 122 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2c** (123 mg, 0.875 mmol, 88%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.51; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ= 3.14 (t, *J*= 7.5 Hz, 2H), 3.79 (t, *J*= 7.5 Hz, 2H), 7.29–7.44 (m, 5H) ppm; ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 25 °C): δ= 39.1 (CH_2), 44.9 (CH_2), 126.8 (CH), 128.4 (CH), 128.7 (CH), 138.0 (C) ppm.

1-Chloro-2,2-diphenylethane (2d)[44]: According to **GP2**, 2,2-diphenylethanol (**1d**, 198 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2d** (182 mg, 0.840 mmol, 84%) was obtained as yellow oil. R_f (SiO_2, cyclohexane)= 0.34; ^{1}H-NMR (300 MHz, $CDCl_3$, 20 °C): δ= 4.00 (d, *J*= 7.8 Hz, 2H), 4.27 (t, *J*= 7.8 Hz, 2H), 7.14–7.19 (m, 6H), 7.22–7.28 (m, 4H) ppm; ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 25 °C): δ= 41.2 (CH_2), 53.6 (CH), 127.0 (CH), 128.0 (CH), 128.7 (CH), 141.2 (C) ppm.

1-Chloro-2-(4-bromophenyl)ethane (2e)[45]: According to **GP2**, 2-(4-bromophenyl)ethanol (**1e**, 201 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2e** (165 mg, 0.752 mmol, 75%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.44; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ= 3.02 (t, *J*= 7.2 Hz, 2H), 3.69 (t, *J*= 7.2 Hz, 2H), 7.10 (d, *J*= 8.6 Hz, 2H), 7.45 (d, *J*= 8.44 Hz, 2H) ppm; ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 25 °C): δ= 38.40 (CH_2), 44.6 (CH_2), 120.8 (C), 130.5 (CH), 131.6 (CH), 137.0 (C) ppm.

1-Chloro-2-(4-methoxyphenyl)ethane (2f)[46]: According to **GP2**, 2-(4-methoxyphenyl)ethanol (**1f**, 152 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2f** (134 mg, 0.785 mmol, 79%) was obtained as yellow liquid. R_f (SiO_2, cyclohexane)= 0.14; ^{1}H-NMR (300 MHz, $CDCl_3$, 23 °C): δ= 3.03 (t, *J*= 7.5 Hz, 2H), 3.70 (t, *J*= 7.5 Hz, 2H), 3.82 (s, 3H), 6.86–6.91 (m, 2H), 7.14–7.19 (m, 2H) ppm; ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 23 °C): δ= 38.3 (CH_3), 45.3 (CH_2), 55.2 (CH_2), 113.9 (CH), 129.8 (CH), 130.2 (C), 158.5 (C) ppm.

1-Chloro-2-(4-nitrophenyl)ethane (2g)[47]: According to **GP2**, 2-(4-nitrophenyl)ethanol (**1g** 167 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane/EtOAc, 15:1) **2g** (151 mg, 0.814 mmol, 81%) was obtained as yellow solid. R_f (SiO_2, cyclohexane/EtOAc 15:1)= 0.33; ^{1}H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 3.19 (t, *J*= 6.9 Hz, 2H), 3.78 (t, *J*= 6.9 Hz, 2H), 7.41 (d, *J*= 8.9 Hz, 2H), 8.19 (d, *J*= 8.7 Hz, 2H) ppm; ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 38.48 (CH_2), 43.96 (CH_2), 123.73 (CH), 129.73 (CH), 145.54 (C), 147.01 (C) ppm.

1-Chloro-2-(4-cyanophenyl)ethane (2h): According to **GP2**, 2-(4-cyanophenyl)ethanol (**1h**, 147 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane/EtOAc, 15:1) **2h** (157 mg, 0.948 mmol, 95%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane/EtOAc 15:1)= 0.21; ^{1}H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 3.13 (t, *J*= 6.9 Hz, 2H), 3.74 (t, *J*= 6.9 Hz, 2H), 7.35 (d, *J*= 8.1 Hz, 2H), 7.61 (d, *J*= 8.2 Hz, 2H) ppm; ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 38.7 (CH_2), 44.00 (CH_2), 110.7 (C), 118.7 (C), 129.6 (CH), 132.2 (CH), 143.4 (C) ppm; IR (ATR): 2960 (vw), 2228 (m), 1924 (vw), 1608 (w), 1505 (w), 1435 (vw), 1415 (vw), 1299 (vw), 1285 (w), 1250 (vw), 1178 (w), 1107 (vw), 1021 (w), 943 (vw), 906 (w), 851 (vw), 821 (m), 760 (w), 706 (w), 688 (w), 652 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 165 (20) [M^+ (^{35}Cl)], 116 (100), 89 (12); HRMS (ESI-TOF) *m/z*: [M (^{37}Cl)]$^+$ calcd for C_9H_8ClN 167.0310; Found: 167.0310.

1-Chloro-2-(4-dimethylaminophenyl)ethane (2i): According to **GP2**, 2-(4-dimethylaminophenyl)ethanol (**1i**, 165 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane/EtOAc, 15:1) **2i** (125 mg, 0.681 mmol, 68%) was obtained as yellow liquid. R_f (SiO_2, cyclohexane/EtOAc 15:1)= 0.38; ^{1}H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 2.94 (s, 6H), 2.99 (t, *J*= 7.7 Hz, 2H), 3.67 (t, *J*= 7.7 Hz, 2H), 6.71 (d, *J*= 8.7 Hz, 2H), 7.11 (d, *J*= 8.9 Hz, 2H) ppm; ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 38.4 (CH_2), 40.7 (CH_3), 45.5 (CH_2), 112.8 (CH), 129. 5 (CH), 129.6 (C), 149.6 (C) ppm; IR (ATR): 2954 (vw), 2925 (vw), 2804 (vw), 1676 (w), 1612 (w), 1519 (w), 1430 (vw), 1346 (vw), 1132 (m), 1115 (w), 945 (vw), 810 (vw), 745 (vw), 700 (vw) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 183 (18) [M^+ (^{35}Cl)], 135 (11), 134 (100), 118 (11); HRMS (ESI-TOF) *m/z*: [M (^{35}Cl)]$^+$ calcd for $C_{10}H_{14}ClN$ 183.0809; Found: 183.0810.

1-Chloro-2-(4-trifluoromethylphenyl)ethane (2j): According to **GP2**, 2-(4-trifluoromethylphenyl)ethanol (**1j**, 190 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2j** (152 mg, 0.729 mmol, 73%) was obtained as yellow liquid. R_f (SiO_2, cyclohexane)= 0.38; ^{1}H-NMR (300 MHz, $CDCl_3$, 22 °C): δ= 3.14 (t, *J*= 7.1 Hz, 2H), 3.75 (t, *J*=

7.1 Hz, 2H), 7.36 (d, *J*= 8.1 Hz, 2H), 7.60 (d, *J*= 8.1 Hz, 2H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 22 °C): δ= 38.7 (CH_2), 44.4 (CH_2), 124.2 (q, *J*= 271.9 Hz, CF_3), 125.5 (q, *J*= 3.8 Hz, CH), 129.2 (CH), 129.2 (q, *J*= 32.4 Hz, C), 142.1 (q, *J*= 1.3 Hz, C) ppm; ^{19}F-NMR (282 MHz, $CDCl_3$, 22 °C): δ= 62.06 ppm; IR (ATR): 1620 (vw), 1438 (vw), 1419 (vw), 1322 (vs), 1249 (vw), 1162 (m), 1118 (s), 1105 (s), 1067 (vs), 1019 (s), 944 (vw), 907 (w), 851 (w), 823 (m), 772 (vw), 738 (w), 715 (w), 660 (w) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 208 (19) [M^+ (^{35}Cl)], 160 (9), 159 (100), 109 (14); HRMS (ESI-TOF) *m/z*: [M (^{35}Cl)]$^+$ calcd for $C_9H_8ClF_3$ 208.0261; Found: 208.0263.

1-Chloro-2-(3-trifluoromethylphenyl)ethane (2k): According to **GP2**, 2-(3-trifluoromethylphenyl)ethanol (**1k**, 190 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2k** (170 mg, 0.815 mmol, 82%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.38; ^1H-NMR (300 MHz, $CDCl_3$, 23 °C): δ= 3.14 (t, *J*= 7.1 Hz, 2H), 3.75 (t, *J*= 7.1 Hz, 2H), 7.14–7.55 (m, 4H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 23 °C): δ= 38.7 (CH_2), 44.4 (CH_2), 123.8 (q, *J*= 3.9 Hz, CH), 124.1 (q, *J*= 272.3 Hz, CF_3), 125.6 (q, *J*= 3.8 Hz, CH), 129.0 (CH), 130.9 (q, *J*= 32.2 Hz, C), 132.3 (CH), 138.9 (C) ppm; ^{19}F-NMR (282 MHz, $CDCl_3$, 23 °C): δ= 62.23 ppm; IR (ATR): 1492 (vw), 1455 (w), 1324 (s), 1248 (w), 1197 (w), 1162 (m), 1118 (vs), 1071 (s), 1002 (vw), 955 (vw), 913 (w), 878 (w), 838 (vw), 797 (m), 759 (w), 735 (w), 700 (s), 658 (s) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 208 (26) [M^+ (^{35}Cl)], 189 (9), 160 (12), 159 (100), 109 (14); HRMS (ESI-TOF) *m/z*: [M (^{35}Cl)]$^+$ calcd for $C_9H_8ClF_3$ 208.0261; Found: 208.0265.

1-Chloro-2-(2-trifluoromethylphenyl)ethane (2l): According to **GP2**, 2-(2-trifluoromethylphenyl)ethanol (**1l**, 190 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2l** (137 mg, 0.657 mmol, 66%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.44; ^1H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 3.29 (t, *J*= 7.5 Hz, 2H), 3.74 (t, *J*= 7.5 Hz, 2H), 7.36–7.44 (m, 2H), 7.51–7.56 (m, 1H), 7.67–7.70 (m, 1H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 35.9 (q, *J*= 1.4 Hz, CH_2), 44.0 (q, *J*= 1.5 Hz, CH_2), 124.4 (q, *J*= 273.4 Hz, CF_3), 126.1 (CH), 126.2 (q, *J*= 5.7 Hz, CH), 127.09 (CH), 129.7 (q, *J*= 32.8 Hz, C), 131.9 (CH), 136.4 (q, *J*= 1.5 Hz, C) ppm; ^{19}F-NMR (282 MHz, $CDCl_3$, 23 °C): δ= 59.17 ppm; IR (ATR): 1608 (vw), 1584 (vw), 1493 (vw), 1453 (w), 1311 (s), 1251 (vw), 1174 (m), 1143 (m), 1114 (s), 1101 (s), 1060 (m), 1039 (s), 956 (vw), 908 (vw), 870 (vw), 837 (vw), 765 (s), 745 (w), 715 (m), 652 (m) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 208 (21) [M^+ (^{35}Cl)], 160 (8), 159 (100), 109 (14); HRMS (ESI-TOF) *m/z*: [M (^{35}Cl)]$^+$ calcd for $C_9H_8ClF_3$ 208.0261; Found: 208.0267.

2-(2-Chloroethyl)thiophene (2m)[25]: According to **GP2**, 2-thiopheneethanol (**1m**, 128 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2m** (108 mg, 0.737 mmol, 74%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.47; ^1H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 3.30 (t, *J*= 7.3 Hz, 2H), 3.74 (t, *J*= 7.3 Hz, 2H), 6.91 (dd, *J*= 3.4 Hz, *J*= 0.9 Hz, 1H), 6.97 (dd, *J*= 5.1 Hz, *J*= 3.4 Hz, 1H), 7.20 (dd, *J*= 5.1 Hz, *J*= 1.2 Hz, 1H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 33.2 (CH_2), 44.7 (CH_2), 124.2 (CH), 125.8 (CH), 126.9 (CH), 140.1 (C) ppm.

1-(Chloromethyl)napthalene (2n)[48]: According to **GP2**, 1-naphthalenemethanol (**1n**, 158 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2n** (143 mg, 0.810 mmol, 81%) was obtained as colorless solid. R_f (SiO_2, cyclohexane)= 0.40; ^1H-NMR (300 MHz, $CDCl_3$, 20 °C): δ= 5.08 (s, 2H), 7.43–7.48 (m, 1H), 7.53–7.66 (m, 3H), 7.87–7.93 (m, 2H), 8.18 (d, *J*= 8.2 Hz, 1H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 20 °C): δ= 44.5 (CH_2), 123.6 (CH), 125.2 (CH), 126.1 (CH), 126.7 (CH), 127.6 (CH), 128.8 (CH), 129.7 (CH), 131.1 (C), 132.9 (C), 133.9 (C) ppm.

4-*tert*-Butylbenzyl chloride (2o)[49]: According to **GP2**, 4-*tert*-butylbenzyl alcohol (**1o**, 164 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2o** (124 mg, 0.679 mmol, 68%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.46; ^1H-NMR (300 MHz, $CDCl_3$, 23 °C): δ= 1.42 (s, 9H), 4.65 (s, 2H), 7.40–7.50 (m, 4H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 23 °C): δ= 31.2 (CH_3), 34.6 (C), 46.1 (CH_2), 125.6 (CH), 128.3 (CH) 134.5(C), 151.4 (C) ppm.

4-Trifluoromethylbenzyl chloride (2p)[50]: According to **GP2**, 4-trifluoromethylbenzyl alcohol (**1p**, 176 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2p** (134 mg, 0.689 mmol, 69%) was obtained as yellow liquid. R_f (SiO_2, cyclohexane)= 0.41; ^1H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 4.63 (s, 2H), 7.53 (d, *J*= 8.2 Hz, 2H), 7.64 (d, *J*= 8.2 Hz, 2H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 45.1 (CH_2), 124.0 (q, *J*= 277.0 Hz, CF_3), 125.7 (q, *J*= 3.7 Hz, CH), 128.8 (CH), 130.6 (q, *J*= 32.50 Hz, C), 141.3 (q, *J*= 1.49 Hz, C) ppm; ^{19}F-NMR (282 MHz, $CDCl_3$, 22 °C): δ= 62.30 ppm.

1,2-Bis(chloromethyl)benzene (2q)[51]: According to **GP2**, 1,2-phenylenedimethanol (**1q**, 138 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2q** (113 mg, 0.646 mmol, 65%) was obtained as colorless solid. R_f (SiO_2, cyclohexane)= 0.33; ^1H-NMR (300 MHz, $CDCl_3$, 26 °C): δ= 4.77 (s, 4H), 7.34–7.43 (m, 4H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 26 °C): δ= 43.2 (CH_2), 129.4 (CH), 130.7 (CH), 136.2 (C) ppm.

1-Chlorodec-9-ene (2r)[52]: According to **GP2**, dec-9-en-1-ol (**1r**, 156 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2r** (131 mg, 0.750 mmol, 75%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.60; ^1H-NMR (300 MHz, $CDCl_3$, 25 °C): δ= 1.30–1.42 (m, 10H), 1.72–1.81 (m, 2H), 2.01–2.07 (m, 2H), 3.53 (t, *J*= 6.8 Hz, 2H),

4.91–5.03 (m, 2H), 5.74–5.88 (m, 1H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 25 °C): δ= 26.8 (CH_2), 28.8 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 29.3 (CH_2), 32.6 (CH_2), 33.8 (CH_2), 45.1 (CH_2), 114.2 (CH_2), 139.1 (CH), ppm.

1-Chloroundec-10-yne (2s)[15]: According to **GP2**, undec-10-yn-1-ol (**1s**, 168 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2s** (158 mg, 0.846 mmol, 85%) was obtained as yellow liquid. R_f (SiO_2, cyclohexane)= 0.29; ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ= 1.29–1.56 (m, 12H), 1.75 (p, *J*= 7.1 Hz, 2H), 1.92 (t, *J*= 2.6 Hz, 1H), 2.16 (dt, *J*= 6.8 Hz, *J*= 2.6 Hz, 2H), 3.51 (t, *J*= 6.7 Hz, 2H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 25 °C): δ= 18.3 (CH_2), 25.8 (CH_2), 28.4 (CH_2), 28.6 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 32.6 (CH_2), 45.1 (CH_2), 68.0 (CH), 84.6 (C) ppm.

***(R)*-Citronellyl chloride (2t):** According to **GP2**, *(R)*-citronellol (**1t**, 156 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2t** (159 mg, 0.910 mmol, 91%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.58; ^{1}H-NMR (300 MHz, $CDCl_3$, 26 °C): δ= 0.92 (d, *J*= 6.4 Hz, 3H), 1.13–1.41 (m, 2H), 1.83–1.86 (m, 9H), 1.95–2.05 (m, 2H), 3.50–3.64 (m, 2H), 5.10 (tt, *J*= 7.1 Hz, *J*= 1.4 Hz, 1H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 26 °C): δ= 17.6 (CH_3), 19.0 (CH_3), 25.3 (CH_2), 25.7 (CH_3), 30.1 (CH), 36.7 (CH_2), 39.7 (CH_2), 43.3 (CH_2), 124.5 (CH), 131.5 (C) ppm; IR (ATR): 2964 (vw), 2915 (w), 2872 (vw), 2854 (vw), 1448 (vw), 1378 (vw), 1286 (vw), 1110 (vw), 984 (vw), 881 (vw), 830 (vw), 805 (vw), 725 (w), 658 (w) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 174 (26) [M^+ (^{35}Cl)], 83 (13), 70 (22), 69 (100), 67 (16), 56 (30), 55 (45), 53 (12), 41 (57), 39 (17); HRMS (ESI-TOF) *m/z*: [M (^{35}Cl)]$^+$ calcd for $C_{10}H_{19}Cl$ 174.1170; Found: 174.1172.

Ethyl 6-chlorohexanoate (2u): According to **GP2**, ethyl 6-hydroxyhexanoate (**1u**, 160 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **2u** (142 mg, 0.795 mmol, 80%) was obtained as yellow liquid. ^{1}H-NMR (300 MHz, $CDCl_3$, 23 °C): δ= 1.24 (t, *J*= 7.1 Hz, 3H), 1.43–1.51 (m, 2H), 1.59–1.69 (m, 2H), 1.73–1.82 (m, 2H), 2.30 (t, *J*= 7.4 Hz, 2H), 3.52 (t, *J*= 6.7 Hz, 2H), 4.11 (q, *J*= 7.1 Hz, 2H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 23 °C): δ= 14.2 (CH_3), 24.1 (CH_2), 26.3 (CH_2), 32.2 (CH_2), 34.0 (CH_2), 44.7 (CH_2), 60.2 (CH_2), 173.4 (C=O) ppm; IR (ATR): 2982 (vw), 2938 (vw), 2868 (vw), 1731 (s), 1446 (vw), 1372 (w), 1300 (vw), 1260 (w), 1178 (m), 1096 (w), 1096 (vw), 1027 (w), 910 (w), 858 (w), 749 (w) cm^{-1}; MS (EI, 70 eV): *m/z* (%): 179 (1) [M^++H (^{35}Cl)], 143 (6), 135 (17) , 133 (52), 115 (13), 101 (15), 88 (100), 73 (14), 70 (18), 69 (51), 61 (11), 60 (20), 55 (17), 43 (10), 42 (12), 41 (29), 39 (12). HRMS (ESI-TOF) *m/z*: [M (^{35}Cl) + Na]$^+$ calcd for $C_8H_{15}ClO_2Na$ 201.0653; Found: 201.0652.

2-Chloro-4-phenylbutane (5a)[53]: According to **GP2**, 4-phenylbutan-2-ol (**4a**, 150 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **5a** (108 mg, 0.640 mmol, 64%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.41; ^{1}H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 1.57 (d, *J*= 6.5 Hz, 3H), 2.01–2.09 (m, 2H), 2.73–2.94 (m, 2H), 4.03 (sext, *J*= 6.6 Hz, 1H), 7.21–7.26 (m, 3H), 7.31–7.36 (m, 2H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 26.0 (CH_3), 32.9 (CH_2), 41.9 (CH_2), 57.9 (CH), 126.0 (CH), 128.4 (CH), 128.5 (CH), 141.1 (C) ppm.

Chlorodiphenylmethane (5b)[31]: According to **GP2**, diphenylmethanol (**4b**, 184 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by Kugelrohr distillation **5b** (124 mg, 0.612 mmol, 61%) was obtained as colourless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 6.15 (s, 1H), 7.29–7.38 (m, 6H), 7.42–7.46 (m, 4H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 64.2 (CH), 127.7 (CH), 128.0 (CH), 128.5 (CH), 141.0 (C) ppm.

Cyclohexyl chloride (5c)[31]: According to **GP2**, cyclohexanol (**4c**, 100 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by Kugelrohr distillation **5c** (68 mg, 0.573 mmol, 57%) was obtained as colourless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 1.28–1.42 (m, 3H), 1.49–1.56 (m, 1H), 1.60–1.72 (m, 2H), 1.75–1.85 (m, 2H), 2.02–2.09 (m, 2H), 3.95–4.04 (m, 1H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 24.8 (CH_2), 25.1 (CH_2), 35.6 (CH_2), 60.1 (CH) ppm.

***(3R)*-3-Chloro-3-deoxy-1,2:5,6-di-O-isopropylidene-α-D-allofuranose (5e)[54]**: According to **GP2**, 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (**4e**, 260 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.1 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane/EtOAc, 15:1) **5e** (87 mg, 0.312 mmol, 31%) was obtained as a viscous, yellow liquid. R_f (SiO_2, cyclohexane/EtOAc, 15:1)= 0.24; ^{1}H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 1.34 (s, 3H), 1.38 (s, 3H), 1.39 (s, 3H), 1.50 (s, 3H), 3.61 (dd, *J*= 12.3 Hz, *J*= 7.7 Hz, 1H), 3.73–3.78 (m, 2H), 4.24 (d, *J*= 3.9 Hz, 1H), 4.36 (dd, *J*= 7.0 Hz, *J*= 3.9 Hz, 1H), 4.59 (d, *J*= 3.7 Hz, 1H), 6.00 (d, *J*= 3.7 Hz, 1H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 23.8 (CH_3), 23.9 (CH_3), 26.5 (CH_3), 27.2 (CH_3), 45.0 (CH_2), 72.2 (CH), 75.1 (CH), 80.5 (CH), 83.9 (CH), 101.3 (C), 106.4 (CH), 112.3 (C) ppm.

1-Chloroadamantane (5f)[46]: According to **GP2**, 1-adamantol (**4f**, 152 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **5f** (63 mg, 0.369 mmol, 37%) was obtained as colorless crystals. ^{1}H-NMR (300 MHz, $CDCl_3$, 28 °C): δ= 1.68 (s, 6H), 2.15 (s, 9H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 28 °C): δ= 31.7 (CH), 35.6 (CH_2), 47.7 (CH_2), 68.9 (C) ppm.

Trityl chloride (5g)[55]: According to **GP2**, triphenylmethanol (**4g**, 260 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column

chromatography (SiO_2, cyclohexane/EtOAc, 15:1) **5g** (113 mg, 0.405 mmol, 41%) was obtained as colorless crystals. R_f (SiO_2, cyclohexane/EtOAc, 15:1)= 0.21; ^{1}H-NMR (300 MHz, $CDCl_3$, 22 °C): δ= 7.28–7.37 (m, 15H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 22 °C): δ= 81.3 (C), 127.7 (CH), 127.8 (CH), 129.7 (CH), 145.2 (C) ppm.

(1,2-Dichloroethyl)benzene (7a)[56]: According to **GP2**, styrene oxide (**6a**, 120 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **7a** (161 mg, 0.920 mmol, 92%) was obtained as yellow liquid. R_f (SiO_2, cyclohexane)= 0.42; ^{1}H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 3.91–4.05 (m, 2H), 5.00–5.05 (m, 1H), 7.38–7.45 (m, 5H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 48.3 (CH_2), 61.7 (CH), 127.4 (CH), 128.8 (CH), 129.1 (CH), 138.0 (C) ppm.

1-(1,2-Dichloroethyl)-4-fluorobenzene (7b)[42]: According to **GP2**, 4-fluorostyrene oxide (**6b**, 138 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **7b** (181 mg, 0.938 mmol, 94%) was obtained as colourless liquid. R_f (SiO_2, cyclohexane)= 0.33; ^{1}H-NMR (400 MHz, $CDCl_3$, 27 °C): δ= 3.87–4.03 (m, 2H), 4.98–5.02 (m, 1H), 7.07–7.12 (m, 2H), 7.39–7.43 (m, 2H) ppm; $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$, 27 °C): δ= 48.2 (CH_2), 60.8 (CH), 115.8 (d, *J*= 21.8 Hz, CH), 129.3 (d, *J*= 8.3 Hz, CH), 133.9 (d, *J*= 3.7 Hz, C), 162.9 (d, *J*= 248.5 Hz, CF) ppm; ^{19}F-NMR (282 MHz, $CDCl_3$, 23 °C): δ= 111.63 ppm.

1-(1,2-Dichloroethyl)-4-chlorobenzene (7c)[57]: According to **GP2**, 4-chlorostyrene oxide (**6c**, 157 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by Kugelrohr distillation **7c** (12 mg, 0.87 mmol, 87%) was obtained as colourless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 3.77–3.94 (m, 2H), 4.86–4.91 (m, 1H), 7.11–7.32 (m, 4H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 48.0 (CH2), 60.7 (CH), 128.8 (CH), 129.0 (CH), 135.1 (C), 136.5 (C) ppm.

1,3-Dichloro-2-(chloromethyl)-2-methylpropane (9)[58]: According to **GP2**, 3-methyl-3-hydroxymethyloxetane (**8**, 102 mg, 1.00 mmol), benzotrichloride (977 mg, 5.00 mmol), phenylsilane (108 mg, 1.00 mmol) and tri-*n*-octylphosphane (37 mg, 0.10 mmol) were reacted and after purification by column chromatography (SiO_2, cyclohexane) **9** (110 mg, 0.627 mmol, 63%) was obtained as colourless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$, 27 °C): δ= 1.20 (s, 3H), 3.58 (s, 6H) ppm; $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$, 27 °C): δ= 19.3 (CH_3), 41.9 (C), 48.3 (CH_2) ppm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information includes spectral data and also additional information on the optimization experiments and mechanistic investigations. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

thomas.werner@catalysis.de

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

This research was performed within the scope of the Leibniz-ScienceCampus Phosphorus Research Rostock.

REFERENCES

(1) Rossberg, M.; Lendle, W.; Pfleiderer, G.; Tögel, A.; Dreher, E.; Langer, E.; Rassaerts, H.; Kleinschmidt, P.; Strack, H.; Cook, R.; Beck, U.; Lipper, K.; Torkelson, T. R.; Löser, E.; Beutel, K. K.; Mann, T., Chlorinated Hydrocarbons. In *Ullmann's Encyclopedia of Industrial Chemistry*, Elvers, B., Ed. Wiley-VCH: Weinheim, 2006.

(2) Carey, J. S.; Laffan, D.; Thomson, C.; Williams, M. T. Analysis of the reactions used for the preparation of drug candidate molecules. *Org. Biomol. Chem.* **2006,** *4*, 2337–2347.

(3) Huy, P. H.; Hauch, T.; Filbrich, I. Lewis Base Catalyzed Nucleophilic Substitutions of Alcohols. *Synlett* **2016,** *27*, 2631–2636.

(4) Huy, P. H.; Motsch, S.; Kappler, S. M. Formamides as Lewis Base Catalysts in SN Reactions—Efficient Transformation of Alcohols into Chlorides, Amines, and Ethers. *Angew. Chem. Int. Ed.* **2016,** *55*, 10145–10149.

(5) Larock, R. C.; Zhang, L., Halogenation of Alcohols. In *Comprehensive Organic Transformations*, Larock, R. C., Ed. Wiley-VCH: Weinheim, 2018.

(6) Stach, T.; Dräger, J.; Huy, P. H. Nucleophilic Substitutions of Alcohols in High Levels of Catalytic Efficiency. *Org. Lett.* **2018,** *20*, 2980–2983.

(7) Huy, P. H.; Filbrich, I. A General Catalytic Method for Highly Cost- and Atom-Efficient Nucleophilic Substitutions. *Chem. Eur. J.* **2018,** *24*, 7410–7416.

(8) Appel, R. Tertiary Phosphane/Tetrachloromethane, a Versatile Reagent for Chlorination, Dehydration, and P-N Linkage. *Angew. Chem. Int. Ed.* **1975,** *14*, 801–811.

(9) Batesky, D. C.; Goldfogel, M. J.; Weix, D. J. Removal of Triphenylphosphine Oxide by Precipitation with Zinc Chloride in Polar Solvents. *J. Org. Chem.* **2017,** *82*, 9931–9936.

(10) O'Brien, C. J.; Tellez, J. L.; Nixon, Z. S.; Kang, L. J.; Carter, A. L.; Kunkel, S. R.; Przeworski, K. C.; Chass, G. A. Recycling the Waste: The Development of a Catalytic Wittig Reaction. *Angew. Chem. Int. Ed.* **2009,** *48*, 6836–6839.

(11) Hoffmann, M.; Deshmukh, S.; Werner, T. Scope and Limitation of the Microwave-Assisted Catalytic Wittig Reaction. *Eur. J. Org. Chem.* **2015,** *2015*, 4532–4543.

(12) Schirmer, M.-L.; Adomeit, S.; Werner, T. First Base-Free Catalytic Wittig Reaction. *Org. Lett.* **2015,** *17*, 3078–3081.

(13) Lao, Z.; Toy, P. H. Catalytic Wittig and aza-Wittig reactions. *Beilstein J. Org. Chem.* **2016,** *12*, 2577–2587.

(14) Longwitz, L.; Werner, T. Recent advances in catalytic Wittig-type reactions based on P(III)/P(V) redox cycling. *Pure Appl. Chem.* **2019,** *91*, 95–102.

(15) Grandane, A.; Longwitz, L.; Roolf, C.; Spannenberg, A.; Murua Escobar, H.; Junghanss, C.; Suna, E.; Werner, T. Intramolecular Base-Free Catalytic Wittig Reaction: Synthesis of Benzoxepinones. *J. Org. Chem.* **2019,** *84*, 1320–1329.

(16) Nykaza, T. V.; Ramirez, A.; Harrison, T. S.; Luzung, M. R.; Radosevich, A. T. Biphilic Organophosphorus-Catalyzed Intramolecular Csp2–H Amination: Evidence for a Nitrenoid in

Catalytic Cadogan Cyclizations. *J. Am. Chem. Soc.* **2018,** *140*, 3103–3113.
(17) Buonomo, J. A.; Aldrich, C. C. Mitsunobu Reactions Catalytic in Phosphine and a Fully Catalytic System. *Angew. Chem. Int. Ed.* **2015,** *54*, 13041–13044.
(18) Hirose, D.; Gazvoda, M.; Košmrlj, J.; Taniguchi, T. The "Fully Catalytic System" in Mitsunobu Reaction Has Not Been Realized Yet. *Org. Lett.* **2016,** *18*, 4036–4039.
(19) Kosal, A. D.; Wilson, E. E.; Ashfeld, B. L. Phosphine-Based Redox Catalysis in the Direct Traceless Staudinger Ligation of Carboxylic Acids and Azides. *Angew. Chem. Int. Ed.* **2012,** *51*, 12036–12040.
(20) Lenstra, D. C.; Lenting, P. E.; Mecinović, J. Sustainable organophosphorus-catalysed Staudinger reduction. *Green Chem.* **2018,** *20*, 4418–4422.
(21) Lenstra, D. C.; Rutjes, F. P. J. T.; Mecinović, J. Triphenylphosphine-catalysed amide bond formation between carboxylic acids and amines. *Chem. Commun.* **2014,** *50*, 5763–5766.
(22) Voituriez, A.; Saleh, N. From phosphine-promoted to phosphine-catalyzed reactions by in situ phosphine oxide reduction. *Tetrahedron Lett.* **2016,** *57*, 4443–4451.
(23) Tamara, K.; Gyorgy, K. The Reduction of Tertiary Phosphine Oxides by Silanes. *Curr. Org. Chem.* **2017,** *21*, 569–585.
(24) Drabowicz, J.; Luczak, J.; Mikolajczyk, M. Triphenylphosphine/Dichloroselenurane: A New Reagent for a Selective Conversion of Alcohols into Alkyl Chlorides. *J. Org. Chem.* **1998,** *63*, 9565–9568.
(25) Iranpoor, N.; Firouzabadi, H.; Aghapour, G.; Vaez zadeh, A. R. Triphenylphosphine/2,3-dichloro-5,6-dicyanobenzoquinone as a new, selective and neutral system for the facile conversion of alcohols, thiols and selenols to alkyl halides in the presence of halide ions. *Tetrahedron* **2002,** *58*, 8689–8693.
(26) Chen, J.; Lin, J.-H.; Xiao, J.-C. Halogenation through Deoxygenation of Alcohols and Aldehydes. *Org. Lett.* **2018,** *20*, 3061–3064.
(27) Hiegel, G. A.; Ramirez, J.; Barr, R. K. Chlorine Substitution Reactions using Trichloroisocyanuric Acid with Triphenylphosphine. *Synth. Commun.* **1999,** *29*, 1415–1419.
(28) Pluempanupat, W.; Chantarasriwong, O.; Taboonpong, P.; Jang, D. O.; Chavasiri, W. Reactivity of chlorinating agents/PPh3 for the chlorination of alcohols and carboxylic acids: a comparative study. *Tetrahedron Lett.* **2007,** *48*, 223–226.
(29) Denton, R. M.; An, J.; Adeniran, B. Phosphine oxide-catalysed chlorination reactions of alcohols under Appel conditions. *Chem. Commun.* **2010,** *46*, 3025–3027.
(30) Denton, R. M.; Tang, X.; Przeslak, A. Catalysis of Phosphorus(V)-Mediated Transformations: Dichlorination Reactions of Epoxides Under Appel Conditions. *Org. Lett.* **2010,** *12*, 4678–4681.
(31) Denton, R. M.; An, J.; Adeniran, B.; Blake, A. J.; Lewis, W.; Poulton, A. M. Catalytic Phosphorus(V)-Mediated Nucleophilic Substitution Reactions: Development of a Catalytic Appel Reaction. *J. Org. Chem.* **2011,** *76*, 6749–6767.
(32) Tang, X.; An, J.; Denton, R. M. A procedure for Appel halogenations and dehydrations using a polystyrene supported phosphine oxide. *Tetrahedron Lett.* **2014,** *55*, 799–802.
(33) van Kalkeren, H. A.; Leenders, S. H. A. M.; Hommersom, C. R. A.; Rutjes, F. P. J. T.; van Delft, F. L. In Situ Phosphine Oxide Reduction: A Catalytic Appel Reaction. *Chem. Eur. J.* **2011,** *17*, 11290–11295.
(34) van Kalkeren, H. A.; van Delft Floris, L.; Rutjes Floris, P. J. T. Catalytic Appel reactions. *Pure Appl. Chem.* **2012,** *85*, 817–828.
(35) van Kalkeren, H. A.; Blom, A. L.; Rutjes, F. P. J. T.; Huijbregts, M. A. J. On the usefulness of life cycle assessment in early chemical methodology development: the case of organophosphorus-catalyzed Appel and Wittig reactions. *Green Chem.* **2013,** *15*, 1255–1263.
(36) For additional details see Supporting Information.
(37) Hofmann, A. W. V. Researches on the phosphorus-bases.—No. VII. Triphosphonium-compounds. *Proc. R. Soc. London* **1860,** *10*, 189–192.
(38) Kolodiazhnyi, O. I. P-halogène-alcoylidène-phosphoranes. *Tetrahedron Lett.* **1980,** *21*, 3983–3986.
(39) Thakore, A. N.; Pope, P.; Oehlschlager, A. C. Studies in organophosphorus chemistry: Reaction of epoxides with tertiary phosphine dihalides. *Tetrahedron* **1971,** *27*, 2617–2626.
(40) Yoshimitsu, T.; Fukumoto, N.; Nakatani, R.; Kojima, N.; Tanaka, T. Asymmetric Total Synthesis of (+)-Hexachlorosulfolipid, a Cytotoxin Isolated from Adriatic Mussels. *J. Org. Chem.* **2010,** *75*, 5425–5437.
(41) Chung, W.-j.; Vanderwal, C. D. Stereoselective Halogenation in Natural Product Synthesis. *Angew. Chem. Int. Ed.* **2016,** *55*, 4396–4434.
(42) Long, J.; Chen, J.; Li, R.; Liu, Z.; Xiao, X.; Lin, J.-H.; Zheng, X.; Xiao, J.-C. Ph3P/I--Promoted Dichlorination or Dibromination of Epoxides with XCH2CH2X (X = Cl or Br). *Synlett* **2018,** *30*, 181–184.
(43) Yang, C.-T.; Zhang, Z.-Q.; Liu, Y.-C.; Liu, L. Copper-Catalyzed Cross-Coupling Reaction of Organoboron Compounds with Primary Alkyl Halides and Pseudohalides. *Angew. Chem. Int. Ed.* **2011,** *50*, 3904–3907.
(44) Villalpando, A.; Ayala, C. E.; Watson, C. B.; Kartika, R. Triphosgene–Amine Base Promoted Chlorination of Unactivated Aliphatic Alcohols. *J. Org. Chem* **2013,** *78*, 3989–3996.
(45) Schüpbach, B.; Terfort, A. A divergent synthesis of oligoarylalkanethiols with Lewis-basic N-donor termini. *Org. Biomol. Chem.* **2010,** *8*, 3552–3562.
(46) Guziec, F. S.; Wei, D. Convenient halodeamination and hydrodeamination of primary amines. *J. Org. Chem.* **1992,** *57*, 3772–3776.
(47) Baraldi, P. G.; Cacciari, B.; Romagnoli, R.; Spalluto, G.; Monopoli, A.; Ongini, E.; Varani, K.; Borea, P. A. 7-Substituted 5-Amino-2-(2-furyl)pyrazolo[4,3-e]-1,2,4-triazolo[1,5-c]pyrimidines as A2A Adenosine Receptor Antagonists: A Study on the Importance of Modifications at the Side Chain on the Activity and Solubility. *J. Med. Chem.* **2002,** *45*, 115–126.
(48) McGeary, R. P.; Vella, P.; Mak, J. Y. W.; Guddat, L. W.; Schenk, G. Inhibition of purple acid phosphatase with α-alkoxynaphthylmethylphosphonic acids. *Bioorganic Med. Chem. Lett.* **2009,** *19*, 163–166.
(49) Savela, R.; Wärnå, J.; Murzin, D. Y.; Leino, R. Iron catalyzed halogenation of benzylic aldehydes and ketones. *Catal. Sci. Technol.* **2015,** *5*, 2406–2417.
(50) Sun, Y.-Y.; Yi, J.; Lu, X.; Zhang, Z.-Q.; Xiao, B.; Fu, Y. Cu-Catalyzed Suzuki–Miyaura reactions of primary and secondary benzyl halides with arylboronates. *Chem. Commun.* **2014,** *50*, 11060–11062.
(51) Froborg, J.; Magnusson, G.; Thoren, S. Synthesis of the bicyclo[4.3.1]decan-10-one system by cycloalkylation of specific cyclohexanone enolates with reactive 1,4-dichlorides. *J. Org. Chem* **1974,** *39*, 848–849.
(52) Bissember, A. C.; Levina, A.; Fu, G. C. A Mild, Palladium-Catalyzed Method for the Dehydrohalogenation of Alkyl Bromides: Synthetic and Mechanistic Studies. *J. Am. Chem. Soc.* **2012,** *134*, 14232–14237.
(53) Vanos, C. M.; Lambert, T. H. Development of a Catalytic Platform for Nucleophilic Substitution: Cyclopropenone-Catalyzed Chlorodehydration of Alcohols. *Angew. Chem. Int. Ed.* **2011,** *50*, 12222–12226.
(54) Azad, C. S.; Saxena, A. K. One pot conversion of carbohydrates alcohol into chloride via benzotriazole sulfonate. *Tetrahedron* **2013,** *69*, 2608–2612.

(55) Tandiary, M. A.; Masui, Y.; Onaka, M. Chlorination of Benzylic and Allylic Alcohols with Trimethylsilyl Chloride Enhanced by Natural Sodium Montmorillonite. *Synlett* **2014,** *25*, 2639–2643.

(56) Xia, X.; Toy, P. H. Rasta resin–triphenylphosphine oxides and their use as recyclable heterogeneous reagent precursors in halogenation reactions. *Beilstein J. Org. Chem.* **2014,** *10*, 1397–1405.

(57) Swamy, P.; Reddy, M. M.; Kumar, M. A.; Naresh, M.; Narender, N. Vicinal Dichlorination of Olefins Using NH4Cl and Oxone®. *Synthesis* **2014,** *46*, 251–257.

(58) Bushweller, C. H.; Whalon, M. R.; Laurenzi, B. J. 1,3-Interactions among three polar bonds. 2-chloromethyl-2-methyl-1,3-dichloropropane. *Tetrahedron Lett.* **1981,** *22*, 2945–2948.