# Vicinal Dichlorination of Olefins Using $NH_4Cl$ and Oxone®

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**Abstract:** A mild and efficient protocol for the preparation of 1,2-dichloroalkane derivatives from olefins using $NH_4Cl$ and Oxone® at room temperature is described. A variety of terminal, internal, and cyclic alkenes reacted smoothly to give the corresponding dichlorinated products in good to excellent yields. Moreover, 1,2-disubstituted symmetrical and unsymmetrical olefins dichlorinated with moderate to excellent diastereoselectivity. This method precludes the use of acidic additives and transition metals in the synthesis of vicinal dichlorides.

**Key words:** vicinal dichlorination, olefins, $NH_4Cl$, Oxone®, diastereoselectivity

Halogenated organic compounds are essential building blocks for chemical synthesis[1] and play an important role in industrial, agricultural, and pharmaceutical applications.[2] More than 2000 chlorine-containing natural products are currently known,[3] and many of which display interesting biological activity of various kinds.[4] In many cases, the natural and non-natural compounds of biological importance possess halogens within their structures for enhancing either the biological activity or chemical stability and intrinsic potency.[5] For instance, the naturally occurring bioactive polychlorides, such as chlorosulfolipids, have chlorine-substituted multiple stereogenic centers as their structural feature (Figure 1).[6] These chlorosulfolipids, which constitute an intriguing subclass of naturally occurring organochlorines, have recently gained interest as targets of synthesis and inspired methods for stereoselective chlorination.[7]

Stereoselective vicinal dichlorination of olefins is both relevant and valuable, which enables the construction of key motifs common to chlorosulfolipids.[8] The most straightforward approach for olefin dichlorination is the direct addition of molecular chlorine across the double bond. The potential safety problems, toxic nature, and hazardous HCl by-products circumvented its routine synthetic utility as chlorinating agent. Alternatively, a few reagent combinations have been developed for the dichlorination of alkenes.[9] Among them, the Markó–Maguire reagent ($BnEt_3NCl/KMnO_4/TMSCl$)[10] and the Mioskowski reagent ($Et_4NCl_3$)[11] have found successful applications in stereoselective vicinal dichlorination of alkenes. More recently, Yoshimitsu and co-workers[12a] and Tong and Ren[12b] developed the methods by employing NCS/$Ph_3P$ and NaCl/Oxone®, respectively, for the dichlorination of olefins. However, most of the existing methods usually have the disadvantages of using expensive reagents, stoichiometric amounts of transition metals, acidic additives, excess amount of molecular chlorine for reagent preparation prior to use, strong acids as chlorinating agents, and limited applicability to olefinic substrates. In view of the shortcomings of the above-mentioned methods and widespread interest in chlorine-containing compounds, research in viable synthetic strategy development

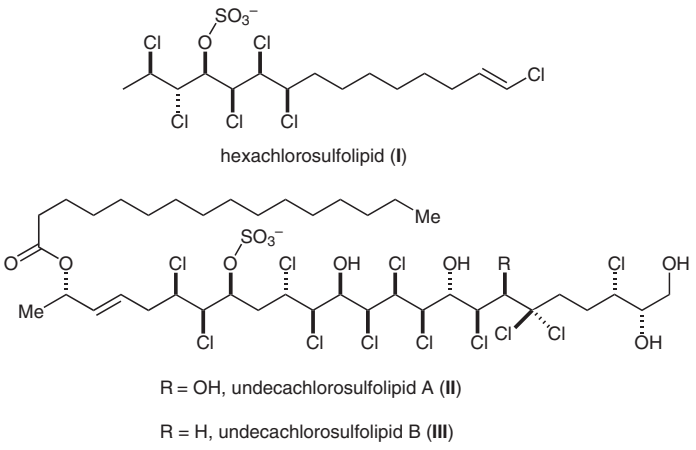


**Figure 1** Natural bioactive chlorosulfolipids **I–III**

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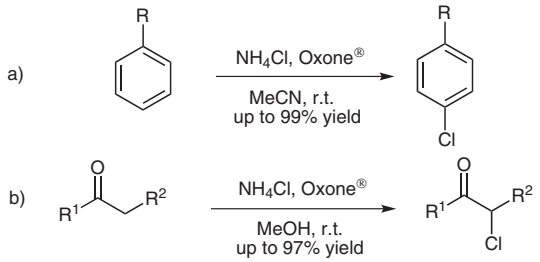
for installation of $sp^3C$–Cl ($sp^3$ carbon–chlorine) bond remains an important topic.

In continuation of our research program to develop environmentally friendly and viable protocols for halogenation,[13] earlier we have explored the aromatic chlorination[13b] and α-chlorination of carbonyl compounds[13c] using $NH_4Cl$ as chlorine source and Oxone® as an oxidant. We disclose herein the vicinal dichlorination of olefins using $NH_4Cl$ and Oxone® under mild conditions.

Oxone® ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$), a potassium triple salt containing potassium peroxy monosulfate, is an inexpensive and effective oxidant. As a result of its stability, nontoxic 'green' nature, affordability and safety profile, Oxone® is becoming an increasingly popular reagent for several oxidative transformations.[14]

We envisioned the synthesis of vicinal dichloro derivatives from olefins following our experience with previously developed methods for the chlorination (Scheme 1).[13b,c] In this context, our preliminary investigations commenced with the model reaction of styrene (**1a**) with $NH_4Cl$ and Oxone® in a single or mixture of solvents in order to evaluate the effect of solvent on the vicinal dichlorination (Table 1). The results summarized in Table 1 revealed that the sole solvent system could not provide good results (Table 1, entries 1–10) and the two-phase solvent system consisting of $H_2O$ and a chlorinated solvent is crucial to achieve high yields of the desired products (Table 1, entries 23–32). In particular, the best results were obtained when a 1:4 mixture of dichloromethane and water was used as the solvent system (Table 1, entry 26).




**Scheme 1** Our previous work on chlorination using $NH_4Cl$ and Oxone®

With the optimized conditions in hand, the generality of the reaction was investigated with a variety of olefins (Table 2 and Table 3). All the substrates were treated with 2.2 equivalents of $NH_4Cl$ and 1.1 equivalent of Oxone® in a 1:4 mixture of dichloromethane and water at room temperature (Scheme 2). As shown in Table 2, all the terminal aromatic, heteroaromatic, and aliphatic alkenes resulted in the formation of the corresponding vicinal dichlorination products **2a**–**i** in good to excellent yields. Aromatic terminal alkenes with activated phenyl ring including 4-methylstyrene (**1b**) and 2,4-dimethylstyrene (**1c**) reacted smoothly to afford the dichlorinated products **2b** and **2c** in 83% and 84% yield, respectively (Table 2, entries 2 and

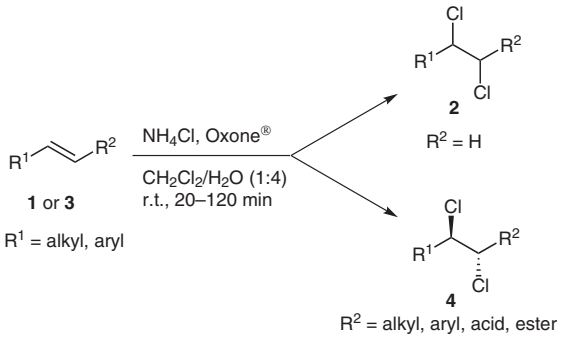
**Table 1** Effect of Solvent on the Vicinal Dichlorination of Styrene[a]


| Entry | Solvent | Time (h) | Yield (%)[b] |
|---|---|---|---|
| 1 | acetone | 24 | 0 |
| 2 | MeCN | 24 | 0 |
| 3 | $CHCl_3$ | 24 | 5 |
| 4 | $CH_2Cl_2$ | 24 | 7 |
| 5 | DCE | 24 | 16 |
| 6 | $CCl_4$ | 24 | 7 |
| 7 | DME | 24 | 37 |
| 8 | 1,4-dioxane | 24 | 47 |
| 9 | THF | 24 | 13 |
| 10 | $H_2O$ | 0.08 | 46 |
| 11 | DCE–MeCN (4:1) | 24 | 33 |
| 12 | DCE–DME (4:1) | 24 | 56 |
| 13 | DCE–THF (4:1) | 24 | 27 |
| 14 | DCE–acetone (4:1) | 24 | 58 |
| 15 | $CH_2Cl_2$–MeCN (4:1) | 24 | 37 |
| 16 | $CH_2Cl_2$–DME (4:1) | 24 | 49 |
| 17 | $CH_2Cl_2$–THF (4:1) | 24 | 30 |
| 18 | $CH_2Cl_2$–acetone (4:1) | 24 | 39 |
| 19 | $CHCl_3$–acetone (4:1) | 24 | 56 |
| 20 | $CHCl_3$–DME (4:1) | 24 | 53 |
| 21 | $H_2O$–1,4-dioxane (4:1) | 0.58 | 66 |
| 22 | $H_2O$–DME (4:1) | 0.58 | 45 |
| 23 | $H_2O/CHCl_3$ (4:1) | 0.58 | 70 |
| 24 | $H_2O/CCl_4$ (4:1) | 0.58 | 63 |
| 25 | $H_2O$/DCE (4:1) | 0.58 | 62 |
| 26 | $H_2O/CH_2Cl_2$ (4:1) | 0.58 | 76 |
| 27 | $H_2O/CH_2Cl_2$ (1:1) | 0.58 | 74 |
| 28 | $H_2O/CH_2Cl_2$ (2:1) | 0.58 | 75 |
| 29 | $H_2O/CH_2Cl_2$ (3:1) | 0.58 | 75 |
| 30 | $H_2O/CH_2Cl_2$ (1:2) | 0.58 | 74 |
| 31 | $H_2O/CH_2Cl_2$ (1:3) | 0.58 | 74 |
| 32 | $H_2O/CH_2Cl_2$ (1:4) | 0.58 | 72 |

[a] Reaction conditions: substrate **1a** (2 mmol), $NH_4Cl$ (4.4 mmol), Oxone® (2.2 mmol), solvent (10 mL), r.t.
[b] The product was characterized by NMR spectroscopy and the yield was based on GC.

3), while those with deactivated phenyl ring comprising 4-chlorostyrene (**1d**), 4-bromostyrene (**1e**), and 4-vinylbenzoic acid (**1f**) generated the corresponding products **2d**, **2e**, and **2f** in relatively lower yields (Table 2, entries 4–6). Polyaromatic alkene, 2-vinylnaphthalene (**1g**), and heteroaromatic alkene **1h** were observed to be excellent substrates for the reaction and the corresponding products **2g** and **2h** were obtained in 77% and 86% yield, respectively (Table 2, entries 7 and 8). Aliphatic terminal alkene **1i** also gave the corresponding vicinal dichloro product **2i** smoothly in 85% yield (Table 2, entry 9).




**Scheme 2** Vicinal dichlorination of olefins using $NH_4Cl$ and Oxone®

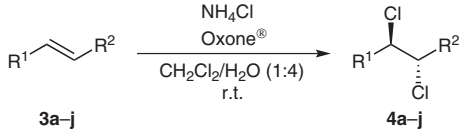
**Table 2** Vicinal Dichlorination of Terminal Olefins Using $NH_4Cl$ and Oxone®[a]

| Entry | Substrate | Time (min) | Product | Yield (%)[b] |
|---|---|---|---|---|
| 1 | **1a** | 35 | **2a** | 76 |
| 2 | **1b** | 35 | **2b** | 83 |
| 3 | **1c** | 40 | **2c** | 84 |
| 4 | **1d** | 45 | **2d** | 76 |
| 5 | **1e** | 45 | **2e** | 77 |
| 6 | **1f** | 120 | **2f** | 69 |
| 7 | **1g** | 50 | **2g** | 77 |
| 8 | **1h** | 30 | **2h** | 86 |
| 9 | **1i** | 35 | **2i** | 85 |

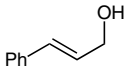
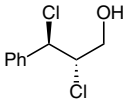
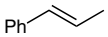
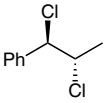
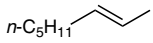
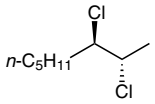
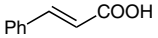
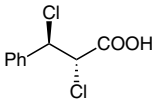
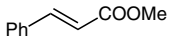
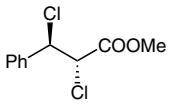
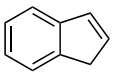
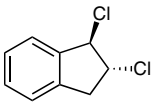
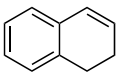
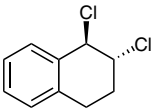
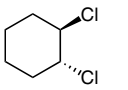
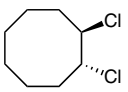
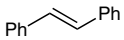
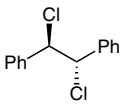
[a] Reaction conditions: substrate (2 mmol), $NH_4Cl$ (4.4 mmol), Oxone® (2.2 mmol), $CH_2Cl_2/H_2O$ (1:4) (10 mL), r.t.
[b] The products were characterized by NMR spectroscopy and yields were based on GC.

Subsequently, 1,2-disubstituted unsymmetrical and symmetrical olefins were submitted to the vicinal dichlorination and the products **4a–j** were obtained in good to excellent yields (Table 3). Unsymmetrical acyclic olefins with aryl/alkyl and alkyl substituents **3a**, **3b**, and **3c** afforded the respective dichlorinated products **4a**, **4b**, and **4c** in 71% (dr 3.4:1), 87% (dr 5.2:1), and 86% (dr 4.3:1) yield, respectively (Table 3, entries 1–3). The deactivated olefins containing acid and ester functionalities with aryl substituents **3d** and **3e** reacted incompletely even after 120 minutes and gave the desired products **4d** and **4e** in 58% (dr 4.9:1) and 63% (dr 5:1) yield, respectively (Table

**Table 3** Vicinal Dichlorination of 1,2-Disubstituted Alkenes Using $NH_4Cl$ and Oxone®[a]




$R^1$ = aryl, alkyl
$R^2$ = aryl, alkyl, acid, ester

| Entry | Substrate **3** | | Time (min) | Product **4** | | Yield (%)[b] | dr[c] |
|---|---|---|---|---|---|---|---|
| 1 | **3a** |  | 20 | **4a** |  | 71 | 3.4:1 |
| 2 | **3b** |  | 35 | **4b** |  | 87 | 5.2:1 |
| 3 | **3c** |  | 20 | **4c** |  | 86 | 4.3:1 |
| 4 | **3d** |  | 120 | **4d** |  | 58 | 4.9:1 |
| 5 | **3e** |  | 120 | **4e** |  | 63 | 5:1 |
| 6 | **3f** |  | 20 | **4f** |  | 94 | >33:1 |
| 7 | **3g** |  | 20 | **4g** |  | 80 | 10:1 |
| 8 | **3h** |  | 20 | **4h** |  | 63 | 20:1 |
| 9 | **3i** |  | 20 | **4i** |  | 90 | >6.4:1 |
| 10 | **3j** |  | 35 | **4j** |  | 84 (92)[d] | 2.1:1 (>2.8:1)[d] |

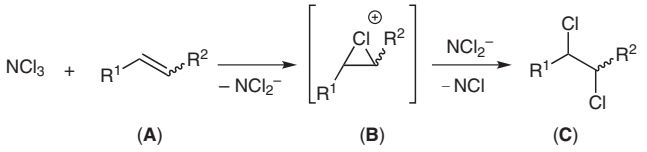
[a] Reaction conditions: substrate **3** (2 mmol), $NH_4Cl$ (4.4 mmol), Oxone® (2.2 mmol), $CH_2Cl_2/H_2O$ (1:4) (10 mL), r.t.
[b] The products were characterized by NMR spectroscopy and yields were based on GC.
[c] Determined on the crude by $^1H$ NMR spectroscopy.
[d] The values shown in parentheses were obtained when *cis*-stilbene was used as the substrate.

3, entries 4 and 5). Unsymmetrical cyclic olefins including indene (**3f**) and 1,2-dihydronaphthalene (**3g**) reacted smoothly and furnished the corresponding dichlorinated products **4f** and **4g** in excellent yields and diastereoselectivities within 20 minutes (Table 3, entries 6 and 7). Similarly, symmetrical cyclic olefins, such as cyclohexene (**3h**) and *cis*-cyclooctene (**3i**), were used in this reaction and the respective vicinal dichlorinated products **4h** and **4i** were obtained in 63% (dr 20:1) and 90% (dr >6.4:1) yield, respectively (Table 3, entries 8 and 9). Both the *trans*- and *cis*-stilbenes provided the corresponding product **4j** in 84% (dr 2.1:1) and 92% (dr >2.8:1) yield, respectively.

As can be seen from Table 3, it is evident that the dichlorination of 1,2-disubstituted olefins provided the corresponding dichlorinated products with predominant *anti*-stereoselectivity. The stereochemistry of the isolated vicinal dichloro products was established based on $^1H$ NMR spectroscopy by comparing chemical shift (δ) and coupling constant (*J*) values of protons attached to the carbons bearing Cl atoms with the previously reported data (see Supporting Information).

A plausible reaction mechanism for the vicinal dichlorination of olefins is depicted in Scheme 3. The reaction of Oxone® with $NH_4Cl$ in a $CH_2Cl_2/H_2O$ solvent system generates trichloramine[12b] ($NCl_3$) in situ, which further reacts[15] with olefin **A** to form a three-membered cyclic chloronium ion intermediate **B**. The cyclic intermediate **B** undergoes ring opening by the nucleophile $Cl^-$ ($NCl_2^-$) via an $S_N2$ pathway to yield the corresponding dichlorinated product **C**.




**Scheme 3** Plausible reaction mechanism

In conclusion, we have developed an efficient, mild, and economically acceptable method for the vicinal dichlorination of olefins. Simple reaction conditions, short reaction times, and use of nonhazardous, easy to handle, and commercially available reagents render this dichlorination method as an extremely practical and safe for the synthesis of 1,2-dichloroalkane derivatives. A broad substrate scope was demonstrated; thus both 1,2-disubstituted unsymmetrical (cyclic and acyclic) and symmetrical (cyclic and acyclic), and terminal aromatic and aliphatic alkenes are good substrates for the vicinal dichlorination reaction in the presence of $NH_4Cl$/Oxone®. Internal olefins were dichlorinated with moderate to high diastereoselectivities.

All chemicals used were reagent grade and used as received without further purification. $^1H$ NMR spectra were recorded at 300 and 500 MHz and $^{13}C$ NMR spectra at 75 and 125 MHz in $CDCl_3$. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for $^1H$ NMR and $CDCl_3$ for $^{13}C$ NMR spectra. Coupling constants (*J*) are reported in hertz (Hz) and standard abbreviations were used to denote signal multiplicities. Column chromatography was carried out using silica gel (100–200 mesh).

**Vicinal Dichlorination of Olefins 1 and 3; General Procedure**

Oxone® (1.35 g, 2.2 mmol) was slowly added to a well stirred solution of $NH_4Cl$ (4.4 mmol) and olefin **1** or **3** (2 mmol) in $CH_2Cl_2/H_2O$ (1:4; 10 mL) and the reaction mixture was allowed to stir at r.t., until the olefin had completely disappeared (monitored by TLC, eluent: *n*-hexane or *n*-hexane–EtOAc). The organic layer was separated, and the aqueous phase was extracted with $CH_2Cl_2$ (2 × 15 mL). The combined organic layers were dried ($Na_2SO_4$), filtered, and concentrated. The residue was purified by column chromatography on silica gel (100–200 mesh) using *n*-hexane or *n*-hexane–EtOAc as eluent to give the desired products.

**1-(1,2-Dichloroethyl)benzene (2a)**[9g]

Yield: 266 mg (1.52 mmol, 76%); yellow oil.

$^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.46–7.34 (m, 5 H), 5.04–4.96 (m, 1 H), 4.05–3.88 (m, 2 H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 137.89, 129.07, 128.73, 127.31, 61.69, 48.27.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_8H_8Cl_2$: 174.00031; found: 174.00008.

**1-(1,2-Dichloroethyl)-4-methylbenzene (2b)**

Yield: 313 mg (1.66 mmol, 83%); colorless oil.

$^1H$ NMR (500 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.24 Hz, 2 H), 7.20 (d, *J* = 7.93 Hz, 2 H), 4.99–4.95 (m, 1 H), 4.01–3.89 (m, 2 H), 2.36 (s, 3 H).

$^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 139.05, 134.98, 129.41, 127.20, 61.66, 48.26, 21.16.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_9H_{10}Cl_2$: 188.01596; found: 188.01544.

**1-(1,2-Dichloroethyl)-2,4-dimethylbenzene (2c)**

Yield: 341 mg (1.68 mmol, 84%); colorless oil.

$^1H$ NMR (500 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 7.93 Hz, 1 H), 7.08 (d, *J* = 7.93 Hz, 1 H), 7.01 (s, 1 H), 5.30–5.25 (m, 1 H), 4.06–3.96 (m, 2 H), 2.38 (s, 3 H), 2.31 (s, 3 H).

$^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 138.82, 136.01, 133.07, 131.50, 127.43, 126.21, 57.71, 47.48, 21.07, 19.11.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_{10}H_{13}Cl_2$: 203.03943; found: 203.03943.

**1-Chloro-4-(1,2-dichloroethyl)benzene (2d)**

Yield: 318 mg (1.52 mmol, 76%); yellow oil.

$^1H$ NMR (300 MHz, $CDCl_3$): δ = 7.42–7.30 (m, 4 H), 5.00–4.92 (m, 1 H), 4.02–3.82 (m, 2 H).

$^{13}C$ NMR (125 MHz, $CDCl_3$): δ = 136.43, 135.00, 128.99, 128.79, 60.63, 48.00.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_8H_9Cl_3$: 209.97698; found: 209.97686.

**1-Bromo-4-(1,2-dichloroethyl)benzene (2e)**

Yield: 391 mg (1.54 mmol, 77%); colorless oil.

$^1H$ NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.39 Hz, 2 H), 7.29 (d, *J* = 8.39 Hz, 2 H), 4.98–4.92 (m, 1 H), 4.01–3.95 (m, 1 H), 3.91–3.85 (m, 1 H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 136.89, 131.91, 129.06, 123.14, 60.63, 47.91.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_8H_9BrCl_2$: 253.92647; found: 253.92631.

**4-(1,2-Dichloroethyl)benzoic Acid (2f)**
Yield: 302 mg (1.38 mmol, 69%); white solid.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.24 Hz, 2 H), 7.54 (d, *J* = 8.24 Hz, 2 H), 5.07–5.03 (m, 1 H), 4.05–4.00 (m, 1 H), 3.96–3.91 (m, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 171.61, 143.62, 130.68, 130.29, 128.84, 60.51, 47.82.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_9H_8Cl_2O_2$: 218.99796; found: 218.99714.

**2-(1,2-Dichloroethyl)naphthalene (2g)**
Yield: 346 mg (1.54 mmol, 77%); white solid.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 7.77–7.68 (m, 4 H), 7.42–7.35 (m, 3 H), 5.07–5.00 (m, 1 H), 3.98–3.86 (m, 2 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 135.08, 133.45, 132.87, 128.92, 128.12, 127.72, 127.22, 126.80, 126.63, 124.09, 61.99, 48.11.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_{12}H_{11}Cl_2$: 225.02378; found: 225.02370.

**2-(1,2-Dichloroethyl)pyridine (2h)**
Yield: 302 mg (1.72 mmol, 86%); yellow oil.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.67–8.60 (m, 1 H), 7.74 (dt, *J* = 7.7, 1.1 Hz, 1 H), 7.45 (d, *J* = 7.7 Hz, 1 H), 7.33–7.25 (m, 1 H), 5.15–5.07 (m, 1 H), 4.33–4.22 (m, 1 H), 4.10–4.01 (m, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 156.14, 149.67, 136.97, 123.67, 123.00, 61.08, 46.71.

HRMS-ESI: *m*/*z* $[M]^+$ calcd for $C_7H_7Cl_2N$: 176.0028; found: 176.0028.

**1,2-Dichlorododecane (2i)**[16]
Yield: 406 mg (1.70 mmol, 85%); colorless oil.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.09–4.00 (m, 1 H), 3.76 (dd, *J* = 11.2, 5.1 Hz, 1 H), 3.65 (dd, *J* = 11.2, 7.4 Hz, 1 H), 2.07–1.91 (m, 1 H), 1.77–1.65 (m, 1 H), 1.60–1.50 (m, 1 H), 1.44–1.20 (m, 15 H), 0.88 (t, *J* = 6.7 Hz, 3 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 61.20, 48.21, 35.02, 31.88, 29.55, 29.52, 29.39, 29.30, 28.97, 25.79, 22.66, 14.09.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_{12}H_{24}Cl_2$: 238.12551; found: 238.12560.

***erythro*-2,3-Dichloro-3-phenylpropan-1-ol (4a)**[17]
Yield: 291 mg (1.42 mmol, 71%); a 3.4:1 diastereomeric mixture; white solid (major isomer).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.23 (m, 5 H), 5.02 (d, *J* = 9.0 Hz, 1 H), 4.38–4.29 (m, 1 H), 4.14–3.94 (m, 2 H), 2.30 (br s, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 138.07, 128.92, 128.57, 127.79, 65.93, 64.10, 61.29.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_9H_{10}Cl_2O$: 205.01870; found: 205.01810.

***erythro*-1,2-Dichloro-1-phenylpropane (4b)**[18]
Yield: 328 mg (1.74 mmol, 87%); a 5.2:1 diastereomeric mixture; yellow oil (major isomer).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.30 (m, 5 H), 4.91 (d, *J* = 7.9 Hz, 1 H), 4.44–4.33 (m, 1 H), 1.71 (d, *J* = 6.4 Hz, 3 H).

$^{13}$C NMR (125 MHz, $CDCl_3$): δ = 138.60, 128.73, 128.47, 127.71, 67.38, 60.16, 22.12.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_9H_{10}Cl_2$: 189.02378; found: 189.02370.

***erythro*-2,3-Dichlorooctane (4c)**
Yield: 314 mg (1.72 mmol, 86%); a 4.3:1 diastereomeric mixture; colorless oil (major isomer).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.16–4.05 (m, 1 H), 3.99–3.89 (m, 1 H), 2.03–1.88 (m, 1 H), 1.82–1.67 (m, 1 H), 1.62 (d, *J* = 6.61 Hz, 3 H), 1.43–1.21 (m, 6 H), 0.90 (t, *J* = 6.61 Hz, 3 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 67.40, 60.19, 34.98, 31.15, 25.78, 22.45, 21.83, 13.96.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_8H_{16}Cl_2$: 182.06291; found: 182.06279.

***erythro*-2,3-Dichloro-3-phenylpropanoic Acid (4d)**
Yield: 254 mg (1.16 mmol, 58%); white solid.

$^1$H NMR (500 MHz, $CDCl_3$): δ = 7.48–7.36 (m, 5 H), 6.63 (br s, 1 H), 5.19 (d, *J* = 10.68 Hz, 1 H), 4.65 (d, *J* = 10.52 Hz, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 172.07, 135.98, 129.57, 128.84, 128.08, 60.62, 58.70.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_9H_8Cl_2O_2$: 218.99796; found: 218.99715.

**Methyl *erythro*-2,3-Dichloro-3-phenylpropanoate (4e)**[9e]
Yield: 293 mg (1.26 mmol, 63%); a 5:1 diastereomeric mixture; white solid (major isomer).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.38 (m, 5 H), 5.15 (d, *J* = 10.68 Hz, 1 H), 4.61 (d, *J* = 10.68 Hz, 1 H), 3.89 (s, 3 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 167.95, 136.26, 130.26, 129.43, 128.02, 60.97, 58.74, 53.36.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_{10}H_{10}Cl_2O_2$: 233.01361; found: 233.01361.

***trans*-1,2-Dichloro-2,3-dihydro-1*H*-indene (4f)**[9g]
Yield: 351 mg 1.88 mmol (94%); a >33:1 diastereomeric mixture; yellow oil (major isomer).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.40 (m, 1 H), 7.37–7.25 (m, 3 H), 5.34 (d, *J* = 3.0 Hz, 1 H), 4.68–4.61 (m, 1 H), 3.69 (dd, *J* = 16.8, 6.0 Hz, 1 H), 3.17 (dd, *J* = 16.8, 3.3 Hz, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 139.75, 129.63, 127.86, 125.42, 125.03, 67.54, 64.43, 40.67.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_9H_8Cl_2$: 187.00813; found: 187.00850.

***trans*-1,2-Dichloro-1,2,3,4-tetrahydronaphthalene (4g)**[19]
Yield: 321 mg (1.6 mmol, 80%); a 10:1 diastereomeric mixture; colorless oil (major isomer).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 7.37–7.32 (m, 1 H), 7.28–7.19 (m, 2 H), 7.14 (d, *J* = 7.3 Hz, 1 H), 5.23 (d, *J* = 2.7 Hz, 1 H), 4.67–4.63 (m, 1 H), 3.19–3.10 (m, 1 H), 2.89–2.83 (m, 1 H), 2.70–2.62 (m, 1 H), 2.17–2.10 (m, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 134.76, 132.23, 130.95, 128.97, 128.71, 126.59, 59.63, 59.35, 24.86, 23.74.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_{10}H_{10}Cl_2$: 200.01596; found: 200.01645.

***trans*-1,2-Dichlorocyclohexane (4h)**[20]
Yield: 192 mg (1.26 mmol, 63%); a 20:1 diastereomeric mixture; yellow oil (major isomer).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.14–3.88 (m, 2 H), 2.41–2.24 (m, 2 H), 1.85–1.63 (m, 4 H), 1.51–1.33 (m, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 63.13, 33.36, 23.04.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_6H_{10}Cl_2$: 152.01596; found: 152.01550.

***trans*-1,2-Dichlorocyclooctane (4i)**[12]
Yield: 325 mg (1.8 mmol, 90%); a >6.4:1 diastereomeric mixture; colorless oil (major isomer).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.33–4.24 (m, 2 H), 2.35–2.21 (m, 2 H), 2.13–1.96 (m, 2 H), 1.93–1.78 (m, 2 H), 1.77–1.65 (m, 2 H), 1.64–1.49 (m, 2 H), 1.48–1.32 (m, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 68.08, 33.23, 25.37, 25.00.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_8H_{14}Cl_2$: 181.05508; found: 181.05501.

***erythro*-1,2-Dichloro-1,2-diphenylethane (4j)**[21]
Yield: 421 mg (1.68 mmol, 84%; a 2.1:1 diastereomeric mixture) from *cis*-stilbene and 462 mg (1.84 mmol, 92%; a >2.8:1 diastereomeric mixture) from *trans*-stilbene; white crystals (major isomer).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.7–7.13 (m, 10 H), 5.21 (s, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 138.28, 128.95, 128.50, 127.99, 65.68.

HRMS-EI: *m*/*z* $[M]^+$ calcd for $C_{14}H_{12}Cl_2$: 250.03161; found: 250.03199.

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