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# A Highly Efficient Method for the Bromination of Alkenes, Alkynes and Ketones Using Dimethyl Sulfoxide and Oxalyl Bromide

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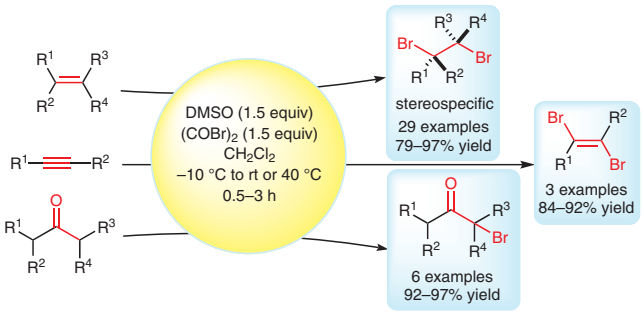


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**Abstract** The pairing of DMSO and oxalyl bromide is reported as a highly efficient brominating reagent for various alkenes, alkynes and ketones. This bromination approach demonstrates remarkable advantages, such as mild conditions, low cost, short reaction times, provides excellent yields in most cases and represents a very attractive alternative for the preparation of dibromides and α-bromoketones.

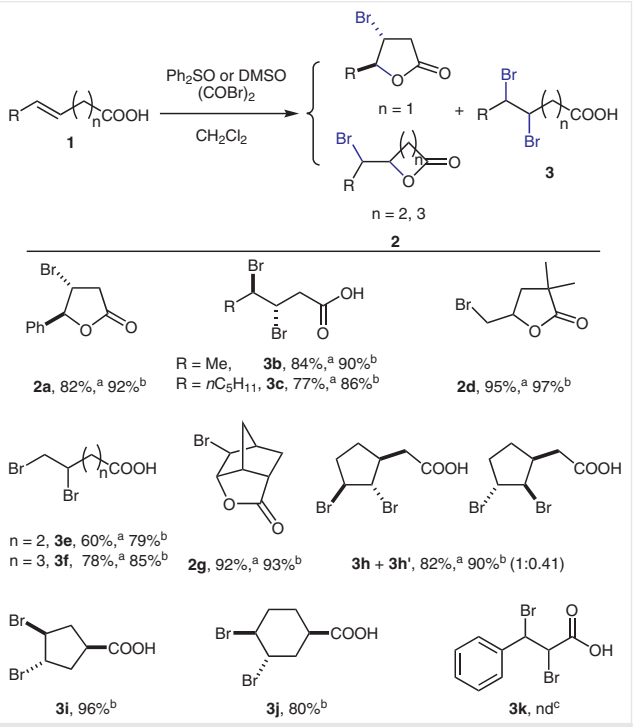
**Key words** bromination, dimethyl sulfoxide, oxalyl bromide, alkenes, alkynes, ketones, bromodimethylsulfonium salt

Alkene and alkyne bromination are very important reactions in organic synthesis since the bromides can be transformed into various other functional groups.[1] Previously, the preparation of vicinal dibromides was performed by using molecular bromine as the reagent.[2] In view of the disadvantages of toxicity, hazards and corrosion related to bromine, many alternative approaches have been developed. These alternatives can be subdivided into two groups: one using bromine carrying agents[3] and the other with bromine generated in situ from bromides and oxidants.[4] Although these methods circumvent the use of molecular bromine, the newly developed reagents are also problematic, especially from the perspective of atom economy. As Eissen and Lenoir pointed out in their comparative review of 24 bromination methods, most of the new alternatives do not present significant advantages compared with molecular bromine owing to their higher resource demands and waste production.[5] Therefore, the development of efficient and practical bromination methods is still needed.

The bromodimethylsulfonium salt is a very versatile reagent for various transformations, such as the preparation of vinylsulfonium salts by addition of bromodimethylsulfonium bromide to olefins and subsequent dehydrobromination,[6] the formation of alkyl bromides from alcohols,[7] dethioacetalization,[8] the reductive bromination of aromatic aldehydes in combination with polymethylhydrosiloxane,[9] oxidative dehydrogenation,[10] acetalization,[11] and bromolactonization.[12] In addition, commercially available bromodimethylsulfonium bromide was reported for the efficient bromination of alkenes and alkynes.[13] Recently, a new bromination method with HBr and DMSO was independently developed by two groups,[14] in which bromodimethylsulfonium bromide, generated by the reaction of HBr and DMSO, was proposed to be the real species for the bromination reactions. These two bromination approaches differed only in the solvent employed for the reaction: one in chloroform[14a] and the other in ethyl acetate.[14b] The latter involved a broader substrate scope including alkynes and ketones in addition to alkenes.[14b] All the examples gave the brominated products in good to excellent yields. This method offers a very useful alternative to the use of bromine due to advantages such as safety, simplicity, and the easy accessibility of the reagents. Herein, we also report a bromination method utilizing bromodimethylsulfonium bromide, but which is generated by the reaction of DMSO with oxalyl bromide. Our approach demonstrates obvious advantages compared to the method using HBr and DMSO, such as milder conditions, shorter reaction times and higher yields.

Our initial work was not aimed toward the preparation of vicinal dibromides. We had developed a new chlorolactonization method for alkenoic acids by using diphenyl sulfoxide and oxalyl chloride in our earlier work.[15] The formation of the dibromides interfered severely with these reactions when the corresponding bromolactonization was attempted by using diphenyl sulfoxide and oxalyl bromide (Scheme 1). Among the eight substrates under investigation, only three, including (*E*)-4-phenyl-3-butenoic acid (**1a**), 2,2-dimethyl-4-pentenoic acid (**1d**), and 5-norbornene-2-carboxylic acid (**1g**) gave the corresponding bro-

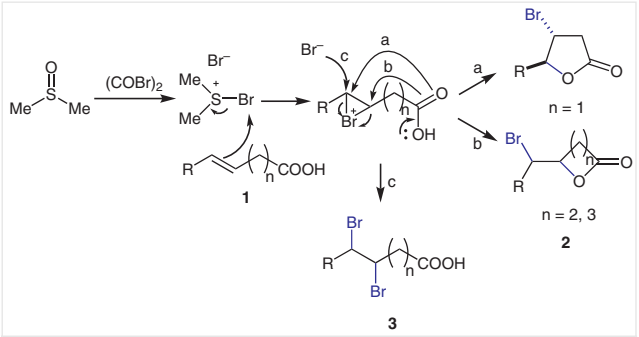
molactones **2a**, **2d** and **2g** in good yields without the formation of dibromides. In contrast, the other five substrates, including 3-pentenoic acid (**1b**), 3-nonenoic acid (**1c**), 4-pentenoic acid (**1e**), 5-hexenoic acid (**1f**) and 2-cyclopentene-1-acetic acid (**1h**), produced the corresponding dibromides as the major products in moderate to good yields.




**Scheme 1** Bromination of alkenoic acids with $Ph_2SO$ or DMSO and oxalyl bromide. [a] $Ph_2SO$ (1.5 equiv)/$(COBr)_2$ (1.5 equiv), –78 to 0 °C, 0.5 h. [b] DMSO (1.5 equiv)/$(COBr)_2$ (1.5 equiv), –10 °C to rt, 0.5 h. [c] No reaction occurred.

These results indicated to us that this process might be an efficient way to undertake bromination of alkenes. In continuation of our studies, diphenyl sulfoxide was replaced with DMSO in view of waste production and removal of the by-product diphenyl sulfide. Thus, the bromination of various substrates was investigated in detail by using DMSO and oxalyl bromide. First, the bromination of alkenoic acids was explored using DMSO and oxalyl bromide (Scheme 1).

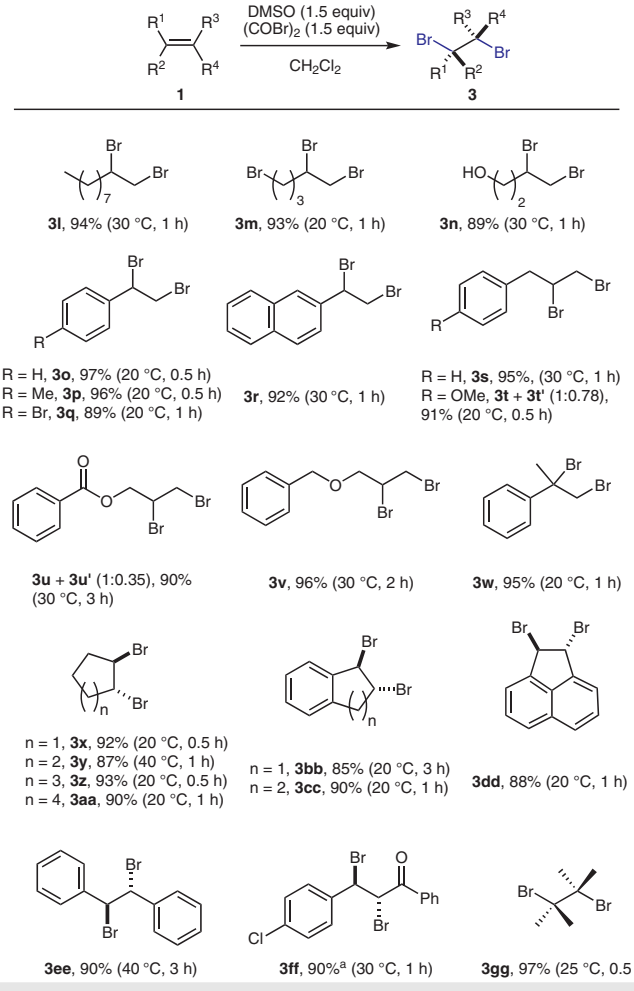
The amounts of both DMSO and oxalyl bromide were set as 1.5 equivalents since small amounts of alkenoic acids were found to remain when 1.2 equivalents of the reagents were used. Most of the substrates gave the corresponding dibromides in good to excellent yields. Three substrates (**1a**, **1d** and **1g**) produced the bromolactones in excellent yields, similar to those obtained with $Ph_2SO$ and $(COBr)_2$. In our previous work on chlorolactonization, these three substrates also demonstrated good reactivity for the production of chlorolactones.[15] Compared with the preliminary results obtained by using $Ph_2SO$ and $(COBr)_2$, the replacement of $Ph_2SO$ by DMSO increased the yields of the bromination to some extent. This is interesting since we found that the reaction failed when $Ph_2SO$ was replaced by DMSO in our previous work on the chlorolactonization of alkenoic acids using $Ph_2SO/(COCl)_2$.[15] In addition, the optimum reaction temperature was different when DMSO/$(COBr)_2$ was used as the brominating reagent. For the reactions with $Ph_2SO$ and $(COBr)_2$, the addition needed to be carried out at –78 °C and the reactions were complete in 0.5 hours at 0 °C. In comparison, the addition could be carried out at –10 °C and the reactions were again complete in 0.5 hours, but at a higher temperature (ca. 20–30 °C) with DMSO/$(COBr)_2$. For only one α,β-unsaturated carboxylic acid, cinnamic acid (**1k**), no dibromide was obtained, and the substrate was recovered even after the reaction mixture had been refluxed for 5 hours. This failure to react might be due to the weak nucleophilicity of the double bond conjugated to a carboxylic acid. The actual species for the formation of the bromolactones or dibromides was thought to be bromodimethylsulfonium bromide similar to that we had proposed for the chlorolactonization in our previous work (Scheme 2).[15] Most of the brominated products involving stereoselectivity, including **2a**, **3b**,**c**, **2g** and **3i**,**j**, were obtained stereospecifically. Only the substrate **1h**, 2-cyclopentene-1-acetic acid, was converted into a mixture of **3h** and **3h′** in 90% yield and the two vicinal bromines in both isomers (**3h** and **3h′**) were also *trans*. These results implied the intervention of a cyclic bromonium ion in the above bromination of alkenoic acids.



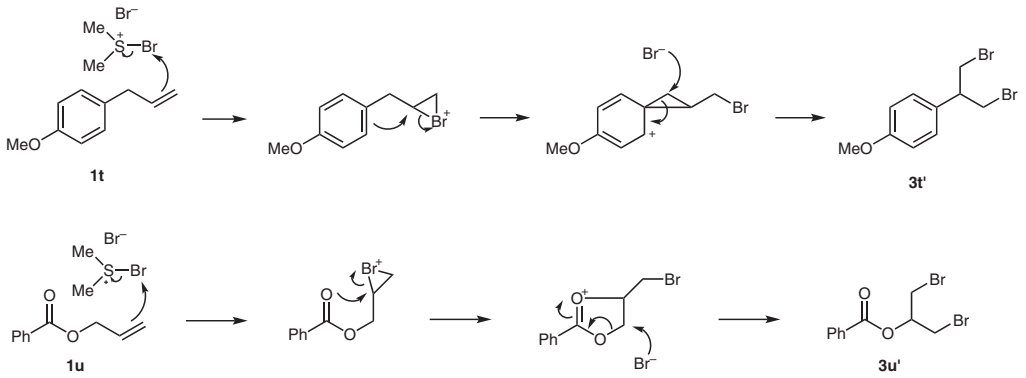

**Scheme 2** Proposed mechanism for the formation of the bromolactones and dibromides

In the earlier literature method describing the bromination with HBr and DMSO,[14] alkenoic acids were paid less attention compared with other alkene substrates. Magolan reported the bromination of substrates **1i** and **1j** producing the corresponding dibromides **3i** and **3j** in 61% and 74% yields at 65 °C.[14a] In comparison, these two dibromides were obtained in much higher yields of 96% and 80% at room temperature in our work. In addition, the reactions were complete in about 30 minutes compared to the much longer reaction time of 12 hours in Magolan's work.[14a]

The results obtained from the bromination of alkenoic acids indicated that the pairing of DMSO and $(COBr)_2$ was more suitable for the synthesis of vicinal dibromides from alkenes than for bromolactonization. Therefore, the substrate scope of this bromination was investigated further with various terminal and internal alkenes (Scheme 3). All twelve terminal alkenes **1l–w**, connecting with alkyl or aryl groups, were converted into the corresponding dibromides **3l–w** in 89–97% yields. 3-Buten-1-ol (**1n**) was brominated to produce 3,4-dibromo-1-butanol (**3n**) in 89% yield with the hydroxy group remaining intact. All the cyclic alkenes **1x–dd** were brominated to give the *trans* products **3x–dd** in 85–93% yields. The bromination of *trans*-stilbene (**1ee**) afforded *anti*-1,2-dibromo-1,2-diphenylethane (**3ee**) in 90% yield. The tetrasubstituted alkene, 2,3-dimethyl-2-butene (**1gg**) was converted into 2,3-dibromo-2,3-dimethylbutane (**3gg**) in an almost quantitative 97% yield. For most of the alkenes under investigation, the brominated products could be obtained with high purity without additional purification. Moreover, those dibromides involving stereoselectivity, including **3x–ee**, were also produced stereospecifically. The only exception was **3ff**, which was a mixture of *anti*- and *syn*-isomers in a ratio of 10:1. Substrate **1ff** was the only alkene conjugated to a carbonyl group under investigation, which was also brominated smoothly to produce the dibromide **3ff** in 90% yield. In Das's work, this substrate underwent bromination with bromodimethylsulfonium bromide to give the dibromide in 96% yield, but without mentioning the relative configuration of the product.[13] In contrast, the bromination method with HBr and DMSO was reported to be unsuitable for α,β-unsaturated carbonyl derivatives in Magolan's work.[14a]




**Scheme 3** Investigation of the substrate scope of alkenes. All the reactions were started at –10 °C with the temperature rising to 20–40 °C after the addition. The formation of **3t'** and **3u'** are discussed below (see Scheme 4). [a] Determined by $^1$H NMR spectroscopy; the product was obtained as a mixture of *anti*- and *syn*-isomers in a ratio of 10:1

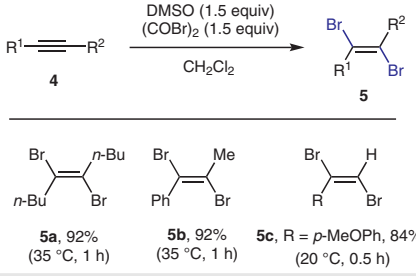



**Scheme 4** Proposed mechanisms for the rearrangements

Many of these substrates were reported to be brominated with HBr and DMSO.[14] In comparison, the yields in our work were much higher. In addition, the substrates **1w**, **1bb** and **1cc** were converted into the corresponding bromohydrins in Magolan's work.[14a] The relatively vigorous conditions in the literature method with HBr and DMSO, such as an excess of HBr and a high temperature of about 60 °C, might be the reason for the lower yields and the formation of bromohydrins. In contrast, the conditions in our method were much milder such that most of the brominated products could be obtained in almost quantitative yields.

It is noteworthy that two substrates, *p*-allylanisole (**1t**) and allyl benzoate (**1u**), gave a mixture of two isomers, one of which was thought to be generated by rearrangement. The pathway for the formation of the two rearrangement products is shown in Scheme 4. The rearrangement product **3t′** would be generated by a 1,2-shift of the *p*-methoxyphenyl group on the intermediate bromonium ion, the ratio of which with the normal vicinal dibromide was 0.78:1. This rearrangement product was also observed in the literature describing the bromination of **1t** with molecular bromine.[16] Likewise, for the substrate allyl benzoate (**1u**), the rearrangement product **3u′** might be generated by a 1,2-shift of the benzoyloxy group via a five-membered ring, the ratio of which with the normal vicinal dibromide was 0.35:1. The bromination of these two substrates was also investigated in Magolan's work;[14a] it is odd that these rearrangement products were not reported.

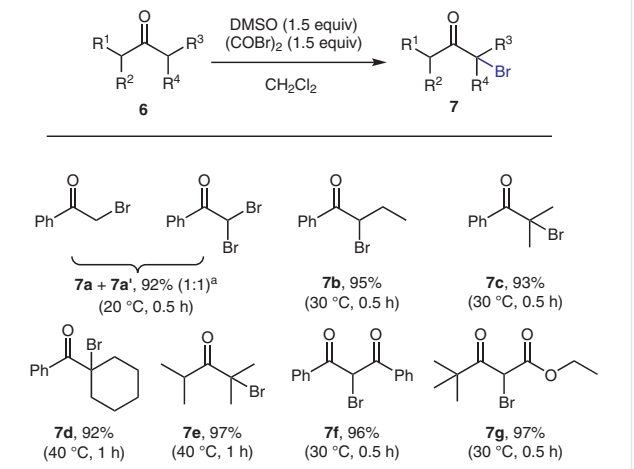
The bromination of alkynes with DMSO and $(COBr)_2$ was also explored (Scheme 5). Two internal alkynes, **4a** and **4b**, were converted into the dibromoalkenes **5a** and **5b**, both in 92% yield. It was observed that heating the reaction mixture gently to 35 °C after addition could promote the reaction to completion in 1 hour. The terminal alkyne **4c** was brominated at room temperature to produce a mixture of a *trans*-dibromoalkene **5c** and a tetrabromoalkane with a ratio of about 1:1. The amount of the reagents was reduced from 1.5 equivalents to 1.2 equivalents in order to avoid the formation of the tetrabromoalkane. The *trans*-dibromoalkene **5c** was then obtained as the major product, and the ratio of *trans*-**5c** and the tetrabromoalkane decreased to 1:0.14. In Jiao's work, these three alkynes were converted into the corresponding dibromoalkenes in 83%, 86% and 81% yields, respectively, by treatment with HBr and DMSO at 60 °C for 5–8 h.[14b] For the two internal alkynes, the dibromoalkenes were obtained in higher yields in our work. For the substrate **4c**, Jiao did not report the formation of the tetrabromoalkane.




**Scheme 5** Investigation of the substrate scope of alkynes. All the reactions were started at –10 °C with the temperature rising to 20–35 °C after the addition. [a] Determined by $^1$H NMR spectroscopy; 1.2 equivalents of the reagents were used

This bromination method was also applied to ketones (Scheme 6). Four phenyl alkyl ketones **6a–d** with α hydrogens on only one side of carbonyl groups were examined. The bromination of acetophenone **6a** afforded a mixture of monobrominated and dibrominated ketones (1:1) in 92% yield. With lower amounts of the reagents (1.2 equiv each), a mixture of **7a** and **7a′** (1:0.6) was obtained in 88% yield with about 10% of the substrate being recovered. In contrast, the other three ketones **6b–d** with α-substituted groups were converted into the α-bromoketones **7b–d** in excellent yields within 1 hour. In Jiao's work, the ketones **6a–c** were converted into the corresponding α-monobromoketones in 73%, 94%, and 90% yields, respectively, by treatment with HBr and DMSO at 60 °C for 2–6 hours.[14b] For acetophenone **6a**, no dibrominated ketone was reported.[14b] A symmetric ketone, 2,4-dimethyl-3-pentanone (**6e**) was converted into the α-monobromoketone **7e** in 97% yield.

Two further 1,3-dicarbonyl compounds, **6f** and **6g**, were also brominated smoothly to produce the monobromoketones **7f** and **7g** in almost quantitative yields.




**Scheme 6** Investigation of the substrate scope of ketones. All the reactions were started at –10 °C with the temperature rising to 20–40 °C after the addition. [a] The product obtained was a mixture of monobrominated and dibrominated ketones with a ratio of 1:1.

In summary, we have developed a highly efficient bromination method for alkenes, alkynes and ketones with DMSO and $(COBr)_2$, which overcomes the common drawbacks of resource demands and waste production suffered from most existing brominating reagents replacing bromine. Compared with the newly developed method utilizing HBr and DMSO, it also possesses advantages of higher yields, milder conditions, shorter reaction times, and offers a very competitive approach for bromination. However, the application of this bromination method to alkynes, ketones, and alkenes conjugated to a carbonyl group require further detailed studies and more examples need to be examined in order to demonstrate the generality of this methodology.

Reagents and solvents are commercial grade and were used as supplied. Substrates are commercially available and were purchased from Sigma-Aldrich. TLC was performed using precoated Synthware TLC plates (silica gel 60F-254, layer thickness: 0.25 mm). Flash chromatography was performed on Synthware silica gel (200–400 mesh). NMR spectra were obtained on a Bruker AV 300 spectrometer ($^1$H NMR at 300 MHz, $^{13}$C NMR at 75 MHz) in $CDCl_3$ using TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. HRMS data were obtained on a SolariX mass spectrometer.

### Bromination of Alkenoic Acids Using $Ph_2SO$ and $(COBr)_2$; General Procedure

To a solution of $(COBr)_2$ (1.07 mL, 7.5 mmol, 1.5 equiv) in $CH_2Cl_2$ (10 mL) at –78 °C was added dropwise a solution of $Ph_2SO$ (1.52 g, 7.5 mmol, 1.5 equiv) in $CH_2Cl_2$ (10 mL) under an atmosphere of nitrogen. After 10 min, a solution of alkenoic acid **1** (5 mmol, 1.0 equiv) in $CH_2Cl_2$ (10 mL) was added. The mixture was then allowed to warm to 0 °C and stirred for 1 h. Distilled $H_2O$ (30 mL) was added dropwise at 0 °C. After stirring for 10 min, the organic layer was separated and washed with brine (2 × 30 mL), dried ($Na_2SO_4$), filtered and concentrated under vacuum. Purification by flash chromatography (silica gel, PE/EtOAc, 10:1) afforded the corresponding bromolactones **2a**,**d**,**g**.

The vicinal dibromo acids **3** can be obtained in high purity through simple pH adjustment. When the reaction was complete, the mixture was carefully made basic with saturated aqueous $NaHCO_3$ solution at 0 °C. The aqueous layer was separated and extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic extracts consisted of a mixture of the corresponding bromolactone and the by-product diphenyl sulfide. The aqueous layer was acidified with 2 M HCl solution and extracted with $CH_2Cl_2$ (3 × 20 mL). The combined extracts were washed with brine (2 × 30 mL), dried ($Na_2SO_4$), filtered and concentrated under vacuum to afford the corresponding dibromides **3b**,**c**,**e**,**f**,**h**.

### Bromination of Alkenoic Acids Using DMSO and $(COBr)_2$; General Procedure

To a solution of $(COBr)_2$ (1.07 mL, 7.5 mmol, 1.5 equiv) in $CH_2Cl_2$ (10 mL) at –10 °C was added dropwise a solution of DMSO (0.53 mL, 7.5 mmol, 1.5 equiv) in $CH_2Cl_2$ (10 mL) under an atmosphere of nitrogen. After 10 min, a solution of alkenoic acid **1** (5 mmol, 1.0 equiv) in $CH_2Cl_2$ (10 mL) was added. The mixture was then allowed to warm to room temperature and stirred for 1 h. Distilled $H_2O$ (30 mL) was added dropwise at 0 °C. After stirring for 10 min, the organic layer was separated and washed with brine (2 × 30 mL), dried ($Na_2SO_4$), filtered, and concentrated under vacuum. Purification by flash chromatography (silica gel, PE/EtOAc, 10:1) afforded the corresponding bromolactones **2a**,**d**,**g**.

The vicinal dibromo acids **3b**,**c**,**e**,**f**,**h–j** can be obtained in high purity through simple pH adjustment as described above.

### Bromination of Alkenes, Alkynes and Ketones; General Procedure

To a solution of $(COBr)_2$ (0.43 mL, 3.0 mmol, 1.5 equiv) in $CH_2Cl_2$ (10 mL) at –10 °C was added dropwise a solution of DMSO (0.21 mL, 3.0 mmol, 1.5 equiv) in $CH_2Cl_2$ (10 mL) under an atmosphere of nitrogen. After 10 min, a solution of alkene, alkyne or ketone (2 mmol, 1.0 equiv) in $CH_2Cl_2$ (5 mL) was added. The mixture was then allowed to warm to 20–40 °C and stirred for 0.5–3 h. Distilled $H_2O$ (20 mL) was added dropwise at 0 °C. After stirring for 10 min, the organic layer was separated and washed with brine (2 × 20 mL), dried ($Na_2SO_4$), filtered and concentrated under vacuum to afford the brominated product. Most products can be obtained in high purity without further purification, except **3n**, **7d**, and **7f**. The three products need purification by flash chromatography (silica gel, PE/EtOAc = 10:1 for **3n**, PE/EtOAc = 60:1 for **7d**, PE/EtOAc = 20:1 for **7f**).

### *trans*-4-Bromo-5-phenyldihydrofuran-2(3*H*)-one (2a)[17]

[CAS Reg. No. 76837-88-2]

White solid; yield: 985 mg (82%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.36 (m, 5 H, H-phenyl), 5.66 (d, *J* = 5.1 Hz, 1 H, H-C-5), 4.37 (ddd, *J* = 7.2, 6.3, 5.1 Hz, 1 H, H-C-4), 3.24 (dd, *J* = 18.3, 7.5 Hz, 1 H, H-C-3), 2.97 (dd, *J* = 18.3, 6.6 Hz, 1 H, H′-C-3).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 173.08 (C-2), 135.98 (C1-phenyl), 129.48 (C4-phenyl), 129.18 (C3- and C5-phenyl), 125.52 (C2- and C6-phenyl), 87.99 (C-5), 45.70 (C-4), 38.94 (C-3).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_9BrNaO_2$: 262.96836; found: 262.96792.

**5-(Bromomethyl)-3,3-dimethyldihydrofuran-2(4*H*)-one (2d)**[18]

[CAS Reg. No. 174362-60-8]

Colorless oil; yield: 980 mg (95%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.66–4.57 (m, 1 H, H-C-5), 3.54 (dd, *J* = 10.8, 5.1 Hz, 1 H, H-$CH_2$Br, A part of ABX), 3.47 (dd, *J* = 10.8, 6.0 Hz, 1 H, H′-$CH_2$Br, B part of ABX), 2.25 (dd, *J* = 12.9, 6.3 Hz, 1 H, H-C-4), 1.91 (dd, *J* = 12.9, 9.3 Hz, 1 H, H′-C-4), 1.28 (s, 3 H, $CH_3$), 1.26 (s, 3 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 180.97 (C-2), 74.74 (C-5), 41.87 (C-4), 40.61 (C-3), 33.74 ($CH_2$Br), 24.96 ($CH_3$), 24.91 ($CH_3$).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_7H_{11}BrNaO_2$: 228.98401; found: 228.98355.

**6-Bromohexahydro-2*H*-3,5-methanocyclopenta[*b*]furan-2-one (2g)**[19]

[CAS Reg. No. 16512-03-1]

Light yellow oil; yield: 995 mg (92%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.90 (d, *J* = 5.1 Hz, 1 H, H-CH-O-), 3.82 (d, *J* = 2.1 Hz, 1 H, H-CH-Br), 3.21 (tq, *J* = 4.8, 1.5 Hz, 1 H, H-C*H*CH-Br), 2.66–2.64 (m, 1 H, H-CH-CO), 2.57–2.51 (m, 1 H, H-C*H*CH-O), 2.30 (dq, *J* = 11.4, 1.5 Hz, 1 H, H-C*H*$_2$CH-CO), 2.12 (ddd, *J* = 13.8, 11.4, 4.2 Hz, 1 H, H-C*H*$_2$CHCH-Br), 1.80–1.69 (m, 2 H, H′-C*H*$_2$CHCH-Br and H′-C*H*$_2$CH-CO).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 179.29 (C=O), 87.69 (CH-O), 53.58 (CH-Br), 45.93 (*C*HCH-Br), 45.55 (*C*H-CO), 37.56 (*C*HCH-O), 35.78 (*C*H$_2$CH-CO), 33.99 (*C*H$_2$CHCH-Br).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_8H_9BrNaO_2$: 238.96836; found: 238.96767.

***trans*-3,4-Dibromopentanoic Acid (3b)**

Colorless oil; yield: 1.16 g (90%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 11.21 (s, 1 H, COOH), 4.41 (dt, *J* = 8.7, 3.0 Hz, 1 H, H-C-3), 4.33 (dq, *J* = 8.7, 6.3 Hz, 1 H, H-C-4), 3.50 (dd, *J* = 17.1, 3.0 Hz, 1 H, H-C-2), 3.03 (dd, *J* = 17.1, 9.0 Hz, 1 H, H′-C-2), 1.90 (d, *J* = 6.3 Hz, 3 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 176.07 (COOH), 52.31 (C-3), 51.17 (C-4), 43.08 (C-2), 25.37 ($CH_3$).

***trans*-3,4-Dibromononanoic Acid (3c)**

Colorless oil; yield: 1.35 g (86%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.50–4.41 (m, 1 H, H-C-3), 4.25 (td, *J* = 8.7, 3.0 Hz, 1 H, H-C-4), 3.50 (dd, *J* = 17.1, 3.0 Hz, 1 H, H-C-2), 3.03 (dd, *J* = 17.1, 9.6 Hz, 1 H, H′-C-2), 2.21–2.10 (m, 1 H, H-C-5), 1.99–1.85 (m, 1 H, H′-C-5), 1.70–1.55 (m, 1 H, H-C-6), 1.54–1.41 (m, 1 H, H′-C-6), 1.40–1.27 (m, 4 H, H-C-7 and H-C-8), 0.91 (t, *J* = 6.9 Hz, 3 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 176.33 (C-1), 58.68 (C-4), 50.64 (C-3), 42.97 (C-2), 36.95 (C-5), 31.12 (C-7), 26.56 (C-6), 22.56 (C-8), 14.11 ($CH_3$).

**4,5-Dibromopentanoic Acid (3e)**[20]

[CAS Reg. No. 78181-02-9]

Colorless oil; yield: 1.02 g (79%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.23 (tdd, *J* = 9.6, 4.2, 2.7 Hz, 1 H, H-C-4), 3.86 (dd, *J* = 10.5, 4.5 Hz, 1 H, H-C-5), 3.61 (t, *J* = 10.2 Hz, 1 H, H′-C-5), 2.74–2.47 (m, 3 H, H-C-2 and H-C-3), 2.09–1.94 (m, 1 H, H′-C-3).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 179.10 (C-1), 51.29 (C-4), 35.89 (C-5), 31.69 (C-2), 31.13 (C-3).

**5,6-Dibromohexanoic Acid (3f)**[21]

[CAS Reg. No. 279214-91-4]

Colorless oil; yield: 1.16 g (85%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.21–4.11 (m, 1 H, H-C-5), 3.86 (dd, *J* = 10.2, 4.5 Hz, 1 H, H-C-6), 3.62 (t, *J* = 10.2 Hz, 1 H, H′-C-6), 2.47–2.40 (m, 2 H, H-C-2), 2.27–2.18 (m, 1 H, H-C-4), 2.01–1.92 (m, 1 H, H-C-3), 1.89–1.71 (m, 2 H, H′-C-3 and H′-C-4).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 179.64 (C-1), 52.06 (C-5), 36.05 (C-6), 35.35 (C-4), 33.26 (C-2), 22.16 (C-3).

**2-(2,3-Dibromocyclopentyl)acetic Acid (3h/3h′)**

White solid; yield: 1.28 g (90%); obtained as a mixture of isomers **3h** and **3h′** in a ratio of 1:0.41.

**2-[(1*S**,2*S**,3*S**)-2,3-Dibromocyclopentyl]acetic Acid (3h)**

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.77 (d, *J* = 3.9 Hz, 1 H, H-C2-cyclopentyl), 4.70 (d, *J* = 6.3 Hz, 1 H, H-C3-cyclopentyl), 3.13–2.98 (m, 1 H, H-C1-cyclopentyl), 2.83–2.71 (m, 1 H, H-C4-cyclopentyl), 2.71 (dd, *J* = 17.1, 7.8 Hz, 1 H, H-C-2), 2.62 (dd, *J* = 17.1, 6.9 Hz, 1 H, H′-C-2), 2.26–2.10 (m, 2 H, H-C5- and H′-C4-cyclopentyl), 1.70–1.52 (m, 1 H, H′-C5-cyclopentyl).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.83 (C-1), 64.07 (C2-cyclopentyl), 55.71 (C3-cyclopentyl), 38.05 (C1-cyclopentyl), 37.68 (C-2), 33.45 (C4-cyclopentyl), 27.27 (C5-cyclopentyl).

**2-[(1*S**,2*R**,3*R**)-2,3-Dibromocyclopentyl]acetic Acid (3h′)**

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.41–4.34 (m, 1 H, H-C3-cyclopentyl), 4.11 (dd, *J* = 7.2, 5.7 Hz, 1 H, H-C2-cyclopentyl), 2.87 (dd, *J* = 16.2, 5.1 Hz, 1 H, H-C-2), 2.72–2.62 (m, 1 H, H-C1-cyclopentyl), 2.54–2.45 (m, 2 H, H-C4-cyclopentyl and H′-C-2), 2.27–2.08 (m, 2 H, H-C5- and H′-C4-cyclopentyl), 1.78–1.69 (m, 1 H, H′-C5-cyclopentyl).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.04 (C-1), 59.95 (C2-cyclopentyl), 55.72 (C3-cyclopentyl), 45.33 (C1-cyclopentyl), 38.68 (C-2), 34.43 (C4-cyclopentyl), 29.21 (C5-cyclopentyl).

**(3*S**,4*S**)-3,4-Dibromocyclopentanecarboxylic Acid (3i)**[14a]

[CAS Reg. No. 140451-75-8]

White solid; yield: 1.30 g (96%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.64–4.62 (m, 1 H, H-C-3), 4.57–4.54 (m, 1 H, H-C-4), 3.45–3.34 (m, 1 H, H-C-1), 3.07–2.99 (m, 2 H, H-C-2 and H-C-5), 2.65–2.57 (m, 1 H, H′-C-2 or H′-C-5), 2.48 (ddt, *J* = 15.0, 8.7, 1.5 Hz, 1 H, H′-C-2 or H′-C-5).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 180.68 (COOH), 56.34 (C-3), 54.45 (C-4), 40.83 (C-1), 37.27, 37.08 (C-2 and C-5).

**(1*R**,3*S**,4*S**)-3,4-Dibromocyclohexanecarboxylic Acid (3j)**[14a]

[CAS Reg. No. 38361-06-7]

White solid; yield: 1.14 g (80%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.71–4.68 (m, 1 H, H-C-3), 4.62–4.59 (m, 1 H, H-C-4), 3.02–2.90 (m, 1 H, H-C-1), 2.62 (ddd, *J* = 14.7, 11.7, 3.3 Hz, 1 H, H-C-2), 2.56–2.44 (m, 1 H, H-C-5), 2.28–2.17 (m, 1 H, H′-C-2), 2.08–2.03 (m, 1 H, H′-C-5), 2.01–1.94 (m, 2 H, H-C-6).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 180.78 (COOH), 52.01, 51.96 (C-3 and C-4), 37.50 (C-1), 30.75 (C-2), 28.28 (C-5), 23.13 (C-6).

**1,2-Dibromodecane (3l)**[22]

[CAS Reg. No. 28467-71-2]

Colorless oil; yield: 560 mg (94%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.22–4.12 (m, 1 H, H-C-2), 3.85 (dd, *J* = 10.2, 4.5 Hz, 1 H, H-C-1), 3.63 (t, *J* = 9.9 Hz, 1 H, H′-C-1), 2.19–2.08 (m, 1 H, H-C-3), 1.84–1.72 (m, 1 H, H′-C-3), 1.62–1.50 (m, 1 H, H-C-4), 1.47–1.38 (m, 1 H, H′-C-4), 1.36–1.24 (m, 10 H, C-5 to C-9), 0.88 (t, *J* = 6.6 Hz, 3 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 53.32 (C-2), 36.51 (C-1), 36.17 (C-3), 31.97 (C-8), 29.50, 29.34, 28.96 (C-5 to 7), 26.90 (C-4), 22.80 (C-9), 14.26 ($CH_3$).

**1,2,5-Tribromopentane (3m)**[14a]

[CAS Reg. No. 28885-22-5]

Colorless oil; yield: 569 mg (93%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.23–4.12 (m, 1 H, H-C-2), 3.87 (dd, *J* = 10.2, 4.5 Hz, 1 H, H-C-1), 3.62 (t, *J* = 10.2 Hz, 1 H, H′-C-1), 3.52–3.38 (m, 2 H, H-C-5), 2.43–2.31 (m, 1 H, H-C-3), 2.25–2.09 (m, 1 H, H-C-4), 2.08–1.85 (m, 2 H, H′-C-3 and H′-C-4).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 51.59 (C-2), 36.00 (C-1), 34.77 (C-3), 32.50 (C-5), 30.11 (C-4).

**3,4-Dibromobutan-1-ol (3n)**

[CAS Reg. No. 87018-30-2]

Light yellow oil; yield: 375 mg (89%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.39 (tdd, *J* = 9.6, 4.5, 3.0 Hz, 1 H, H-CHBr), 3.92–3.80 (m, 2 H, H-$CH_2$OH), 3.90 (dd, *J* = 10.2, 4.2 Hz, 1 H, H-$CH_2$Br), 3.69 (dd, *J* = 10.2, 9.3 Hz, 1 H, H′-$CH_2$Br), 2.45 (dddd, *J* = 14.7, 8.4, 6.0, 3.3 Hz, 1 H, H-C-2), 1.95 (ddt, *J* = 14.7, 9.9, 4.5 Hz, 1 H, H′-C-2), 1.71 (s, 1 H, H-OH).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 60.41 (C-$CH_2$OH), 49.52 (C-CHBr), 38.79 (C-2), 36.79 (C-$CH_2$Br).

**(1,2-Dibromoethyl)benzene (3o)**[14a]

[CAS Reg. No. 93-52-7]

White solid; yield: 508 mg (97%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.32 (m, 5 H, H-phenyl), 5.15 (dd, *J* = 10.5, 5.7 Hz, 1 H, H-CHBr), 4.09 (dd, *J* = 10.2, 5.7 Hz, 1 H, H-$CH_2$Br), 4.03 (t, *J* = 10.2 Hz, 1 H, H′-$CH_2$Br).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 138.75 (C1-phenyl), 129.32 (C4-phenyl), 129.00 (C3- and C5-phenyl), 127.79 (C2- and C6-phenyl), 51.01 (C-CHBr), 35.16 (C-$CH_2$Br).

**1-(1,2-Dibromoethyl)-4-methylbenzene (3p)**[23]

[CAS Reg. No. 33458-08-1]

White solid; yield: 530 mg (96%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.1 Hz, 2 H, H-C2- and H-C6-phenyl), 7.17 (d, *J* = 7.8 Hz, 2 H, H-C3- and H-C5-phenyl), 5.13 (dd, *J* = 10.5, 5.7 Hz, 1 H, H-CHBr), 4.06 (dd, *J* = 10.2, 5.7 Hz, 1 H, H-$CH_2$Br), 4.00 (t, *J* = 10.5 Hz, 1 H, H′-$CH_2$Br), 2.34 (s, 3 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 139.33 (C4-phenyl), 135.76 (C1-phenyl), 129.69 (C3- and C5-phenyl), 127.63 (C2- and C6-phenyl), 51.18 (C-CHBr), 35.19 (C-$CH_2$Br), 21.41 ($CH_3$).

**1-Bromo-4-(1,2-dibromoethyl)benzene (3q)**[14a]

[CAS Reg. No. 33458-10-5]

Light yellow solid; yield: 605 mg (89%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.49 (m, 2 H, H-C2- and H-C6-phenyl), 7.31–7.25 (m, 2 H, H-C3- and H-C5-phenyl), 5.09 (dd, *J* = 11.1, 5.1 Hz, 1 H, H-CHBr), 4.06 (dd, *J* = 10.5, 5.1 Hz, 1 H, H-$CH_2$Br), 3.96 (t, *J* = 10.8 Hz, 1 H, H′-$CH_2$Br).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 137.79 (C4-phenyl), 132.20 (C2- and C6-phenyl), 129.45 (C3- and C5-phenyl), 123.31 (C1-phenyl), 49.67 (C-CHBr), 34.71 (C-$CH_2$Br).

**2-(1,2-Dibromoethyl)naphthalene (3r)**[23]

[CAS Reg. No. 156635-83-5]

White solid; yield: 575 mg (92%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.83 (m, 4 H, H-C1-, H-C4-, H-C5- and H-C8-naphthalene), 7.54–7.51 (m, 3 H, H-C3-, H-C6- and H-C7-naphthalene), 5.34 (dd, *J* = 9.0, 6.9 Hz, 1 H, H-C-1), 4.19–4.10 (m, 2 H, H-C-2).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 135.83 (C2-naphthalene), 133.64, 133.03 (C4a- and C8a-naphthalene), 129.25, 128.34, 127.93, 127.58, 127.06, 126.84, 124.48 (C1-, C3-, C4-, C5 to C8-naphthalene), 51.47 (C-1), 34.93 (C-2).

**1-(2,3-dibromopropyl)benzene (3s)**[14a]

[CAS Reg. No. 1586-98-7]

Light yellow oil; yield: 524 mg (95%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 5 H, H-phenyl), 4.32–4.33 (m, 1 H, H-CHBr), 3.84 (dd, *J* = 10.5, 4.2 Hz, 1 H, H-$CH_2$Br), 3.64 (dd, *J* = 10.5, 9.0 Hz, 1 H, H′-$CH_2$Br), 3.52 (dd, *J* = 14.5, 4.8 Hz, 1 H, H-$CH_2$), 3.15 (dd, *J* = 14.5, 7.8 Hz, 1 H, H′-$CH_2$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 136.96 (C1-phenyl), 129.63 (C3- and C5-phenyl), 128.63 (C2- and C6-phenyl), 127.32 (C4-phenyl), 52.55 (CHBr), 42.10 ($CH_2$), 36.18 ($CH_2$Br).

**1-(2,3-Dibromopropyl)-4-methoxybenzene (3t)**[14a] **and 1-(1,3-Dibromopropan-2-yl)-4-methoxybenzene (3t′)**

The bromination of *p*-allylanisole (**1t**) gave a mixture of two isomers, **3t** and **3t′**, in a ratio of 1:0.78.

Light yellow oil; yield: 557 mg (91%).

**1-(2,3-Dibromopropyl)-4-methoxybenzene (3t)**[14a]

[CAS Reg. No. 83333-66-8]

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.19 (m, 2 H, H-C2- and H-C6-phenyl), 6.90–6.85 (m, 2 H, H-C3- and H-C5-phenyl), 4.38–4.29 (m, 1 H, H-CHBr), 3.85–3.79 (m, 1 H, H-$CH_2$Br), 3.81 (s, 3 H, H-$OCH_3$), 3.62 (dd, *J* = 10.5, 9.0 Hz, 1 H, H′-$CH_2$Br), 3.42 (dd, *J* = 14.7, 4.8 Hz, 1 H, H-$CH_2$), 3.11 (dd, *J* = 14.4, 7.5 Hz, 1 H, H′-$CH_2$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 158.83 (C4-phenyl), 130.69 (C2- and C6-phenyl), 128.84 (C1-phenyl), 113.96 (C3- and C5-phenyl), 55.35 (C-$OCH_3$), 53.02 (C-CHBr), 41.09 (C-$CH_2$), 35.98 (C-$CH_2$Br).

**1-(1,3-Dibromopropan-2-yl)-4-methoxybenzene (3t′)**

[CAS Reg. No. 37983-33-8]

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.18–7.13 (m, 2 H, H-C2- and H-C6-phenyl), 6.93–6.89 (m, 2 H, H-C3- and H-C5-phenyl), 3.81 (s, 3 H, H-$OCH_3$), 3.77 (dd, *J* = 10.5, 6.9 Hz, 2 H, H-$CH_2$Br), 3.69 (dd, *J* = 10.2, 6.3 Hz, 2 H, H′-$CH_2$Br), 3.34 (quin, *J* = 6.6 Hz, 1 H, H-CHPh).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 159.25 (C4-phenyl), 131.63 (C1-phenyl), 128.69 (C2- and C6-phenyl), 114.21 (C3- and C5-phenyl), 55.35 (C-$OCH_3$), 48.29 (C-CHPh), 36.07 [C-$(CH_2Br)_2$].

**2,3-Dibromopropyl Benzoate (3u) and 1,3-Dibromopropan-2-yl Benzoate (3u′)**

The bromination of allyl benzoate (**1u**) gave a mixture of two isomers, **3u** and **3u′**, in a ratio of 1:0.35.

Light yellow oil; yield: 576 mg (90%).

**2,3-Dibromopropyl Benzoate (3u)**[14a]

[CAS Reg. No. 6186-90-9]

$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.5 Hz, 2 H, H-C2- and H-C6-phenyl), 7.60 (t, *J* = 7.5 Hz, 1 H, H-C4-phenyl), 7.47 (t, *J* = 7.5 Hz, 2 H, H-C3- and H-C5-phenyl), 4.77 (dd, *J* = 12.3, 4.8 Hz, 1 H, H-$OCH_2$), 4.71 (dd, *J* = 12.3, 5.1 Hz, 1 H, H′-$OCH_2$), 4.46 (dq, *J* = 9.6, 4.8 Hz, 1 H, H-CHBr), 3.88 (dd, *J* = 10.5, 5.1 Hz, 1 H, H-$CH_2Br$), 3.82 (dd, *J* = 10.8, 9.0 Hz, 1 H, H′-$CH_2Br$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 165.84 (C=O), 133.52 (C4-phenyl), 129.86 (C2- and C6-phenyl), 129.47 (C1-phenyl), 128.62 (C3- and C5-phenyl), 65.64 (C-$OCH_2$), 47.09 (C-CHBr), 32.26 (C-$CH_2Br$).

**1,3-Dibromopropan-2-yl Benzoate (3u′)**

[CAS Reg. No. 103273-71-8]

$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 7.5 Hz, 2 H, H-C2- and H-C6-phenyl), 7.60 (t, *J* = 7.5 Hz, 1 H, H-C4-phenyl), 7.47 (t, *J* = 7.5 Hz, 2 H, H-C3- and H-C5-phenyl), 5.38 (quin, *J* = 5.1 Hz, 1 H, H-OCH), 3.78 (dd, *J* = 11.1, 4.8 Hz, 2 H, H-$CH_2Br$), 3.73 (dd, *J* = 11.1, 5.4 Hz, 2 H, H′-$CH_2Br$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 165.32 (C=O), 133.71 (C4-phenyl), 130.01 (C2- and C6-phenyl), 129.23 (C1-phenyl), 128.62 (C3- and C5-phenyl), 71.38 (C-OCH), 31.59 [C-$(CH_2Br)_2$].

**1-[(2,3-Dibromopropoxy)methyl]benzene (3v)**[14a]

[CAS Reg. No. 60276-38-2]

Colorless oil; yield: 588 mg (96%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 5 H, H-phenyl), 4.69–4.57 (m, 2 H, H-Ph$CH_2$), 4.33–4.23 (m, 1 H, H-CHBr), 3.94–3.78 (m, 4 H, H-$CH_2Br$ and H-O$CH_2$CHBr).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 137.64 (C1-phenyl), 128.59 (C3- and C5-phenyl), 128.02 (C4-phenyl), 127.83 (C2- and C6-phenyl), 73.53 (C-Ph$CH_2$), 71.14 (C-O$CH_2$CHBr), 49.22 (C-CHBr), 33.23 (C-$CH_2Br$).

**1-(1,2-Dibromopropan-2-yl)benzene (3w)**[14b]

[CAS Reg. No. 36043-44-4]

Colorless oil; yield: 524 mg (95%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.55 (dt, *J* = 8.7, 2.1 Hz, 2 H, H-C3- and H-C5-phenyl), 7.43–7.32 (m, 3 H, H-C2-, H-C4- and H-C6-phenyl), 4.39 (d, *J* = 10.2 Hz, 1 H, H-$CH_2Br$), 4.16 (d, *J* = 10.2 Hz, 1 H, H′-$CH_2Br$), 2.34 (s, 3 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 141.99 (C1-phenyl), 128.64 (C4-phenyl), 128.58 (C2- and C6-phenyl), 126.67 (C3- and C5-phenyl), 63.85 (C-CBr), 43.64 (C-$CH_2Br$), 30.02 ($CH_3$).

***trans*-1,2-Dibromocyclopentane (3x)**[24]

[CAS Reg. No. 10230-26-9]

Colorless oil; yield: 416 mg (92%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.60–4.57 (m, 2 H, H-C-1 and H-C-2), 2.66 (ddt, *J* = 14.1, 5.1, 8.7 Hz, 2 H, H-C-3 and H-C-5), 2.20–2.11 (m, 2 H, H′-C-3 and H′-C-5), 2.05–1.95 (m, 2 H, H-C-4).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 57.44 (C-1 and C-2), 34.01 (C-3 and C-5), 21.24 (C-4).

***trans*-1,2-Dibromocyclohexane (3y)**[14a]

[CAS Reg. No. 7429-37-0]

Colorless oil; yield: 418 mg (87%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.53–4.37 (m, 2 H, H-C-1 and H-C-2), 2.50–2.40 (m, 2 H, H-C-3 and H-C-6), 1.93–1.76 (m, 4 H, H′-C-3 and H′-C-6, H-C-4 and H-C-5), 1.55–1.45 (m, 2 H, H′-C-4 and H′-C-5).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 55.32 (C-1 and C-2), 32.06 (C-3 and C-6), 22.50 (C-4 and C-5).

***trans*-1,2-Dibromocycloheptane (3z)**[24]

[CAS Reg. No. 52021-35-9]

Colorless oil; yield: 472 mg (93%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.70–4.62 (m, 2 H, H-C-1 and H-C-2), 2.39–2.29 (m, 2 H, H-C-3 and H-C-7), 2.13–1.98 (m, 2 H, H′-C-3 and H′-C-7), 1.90–1.78 (m, 2 H, H-C-4 and H-C-6), 1.72–1.57 (m, 4 H, H′-C-4 and H′-C-6, H-C-5).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 60.27 (C-1 and C-2), 33.29 (C-3 and C-7), 26.55 (C-5), 23.27 (C-4 and C-6).

***trans*-1,2-Dibromocyclooctane (3aa)**[14a]

[CAS Reg. No. 34969-65-8]

Colorless oil; yield: 482 mg (90%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 4.62–4.52 (m, 2 H, H-C-1 and H-C-2), 2.40 (ddd, *J* = 15.6, 9.0, 3.3 Hz, 2 H, H-C-3 and H-C-8), 2.15–2.02 (m, 2 H, H′-C-3 and H′-C-8), 1.90–1.77 (m, 2 H, H-C-5 and H-C-6), 1.73–1.62 (m, 2 H, H-C-4 and H-C-7), 1.61–1.52 (m, 2 H, H′-C-5 and H′-C-6), 1.51–1.42 (m, 2 H, H′-C-4 and H′-C-7).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 61.72 (C-1 and C-2), 33.39 (C-3 and C-8), 26.09 (C-5 and C-6), 25.50 (C-4 and C-7).

***trans*-1,2-Dibromo-2,3-dihydro-1*H*-indene (3bb)**[14b]

[CAS Reg. No. 19598-15-3]

Colorless oil; yield: 466 mg (85%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.46 (m, 1 H, H-phenyl), 7.37–7.29 (m, 3 H, H-phenyl), 5.64 (s, 1 H, H-C-1), 4.89 (dt, *J* = 5.1, 1.2 Hz, 1 H, H-C-2), 3.82 (dd, *J* = 17.5, 5.1 Hz, 1 H, H-C-3), 3.28 (d, *J* = 17.5 Hz, 1 H, H′-C-3).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 140.69 (C-3a and C-7a), 129.85, 128.10, 125.85, 125.56 (C-4 to 7), 57.86 (C-1), 54.58 (C-2), 41.57 (C-3).

***trans*-1,2-Dibromo-1,2,3,4-tetrahydronaphthalene (3cc)**[14b]

[CAS Reg. No. 31357-86-5]

Light brown solid; yield: 518 mg (90%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 7.2 Hz, 1 H, H-phenyl), 7.19–7.08 (m, 2 H, H-phenyl), 7.04 (d, *J* = 7.5 Hz, 1 H, H-phenyl), 5.56 (m, 1 H, H-C-1), 4.85–4.84 (m, 1 H, H-C-2), 3.18 (ddd, *J* = 17.7, 11.7, 6.0 Hz, 1 H, H-C-4), 2.85 (dd, *J* = 17.4, 6.0 Hz, 1 H, H′-C-4), 2.79–2.67 (m, 1 H, H-C-3), 2.15–2.05 (m, 1 H, H′-C-3).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 134.56 (C-8a), 132.93 (C-4a), 131.35, 129.33, 129.03, 126.78 (C-5 to 8), 51.67 (C-1 and C-2), 25.25 (C-3), 24.59 (C-4).

***trans*-1,2-Dibromo-1,2-dihydroacenaphthylene (3dd)**[14a]

[CAS Reg. No. 25226-58-8]

Light brown solid; yield: 546 mg (88%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.83 (dd, *J* = 6.6, 2.1 Hz, 2 H, H-C-5 and H-C-6), 7.66–7.59 (m, 4 H, H-C-3, H-C-4, H-C-7 and H-C-8), 6.01 (s, 2 H, H-CHBr).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 140.62 (C-2a and C-8a), 134.95 (C-2b), 131.11 (C-5a), 128.98 (C-4 and C-7), 126.01 (C-5 and C-6), 122.69 (C-3 and C-8), 55.03 [C-$(CHBr)_2$].

***trans*-1,2-Dibromo-1,2-diphenylethane (3ee)**[14a]

[CAS Reg. No. 13440-24-9]

White solid; yield: 608 mg (90%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.49 (m, 4 H, H-C3- and H-C5-phenyl), 7.46–7.34 (m, 6 H, H-C2-phenyl, H-C4- and H-C6-phenyl), 5.48 (s, 2 H, H-CHBr).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 140.18 (C1-phenyl), 129.17 (C4-phenyl), 128.93 (C2- and C6-phenyl), 128.07 (C3- and C5-phenyl), 56.23 (C-CHBr).

**2,3-Dibromo-3-(4-chlorophenyl)-1-phenylpropan-1-one (3ff)**

The product was obtained as a mixture of *anti*- and *syn*-isomers in a ratio of 10:1.

White solid; yield: 760 mg (90%).

***trans*-2,3-Dibromo-3-(4-chlorophenyl)-1-phenylpropan-1-one (3ff)**

[CAS Reg. No. 24213-15-8]

$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.12–8.08 (m, 2 H, H-C2- and H-C6-phenyl), 7.70–7.65 (m, 1 H, H-C4-phenyl), 7.59–7.53 (m, 2 H, H-C3- and H-C5-phenyl), 7.47 (dt, *J* = 8.7, 2.1 Hz, 2 H, H-C3- and H-C5-chlorophenyl), 7.41 (dt, *J* = 8.7, 2.1 Hz, 2 H, H-C2- and H-C6-chlorophenyl), 5.77 (d, *J* = 11.3 Hz, 1 H, H-C-2), 5.62 (d, *J* = 11.3 Hz, 1 H, H-C-3).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 191.06 (C=O), 136.99 (C1-chlorophenyl), 135.27 (C4-chlorophenyl), 134.44 (C1- and C4-phenyl), 129.85 (C3- and C5-chlorophenyl), 129.28 (C2- and C6-chlorophenyl), 129.19 (C3- and C5-phenyl), 129.05 (C2- and C6-phenyl), 48.82 (C-3), 46.75 (C-2).

**2,3-Dibromo-2,3-dimethylbutane (3gg)**

[CAS Reg. No. 594-81-0]

White solid; yield: 469 mg (97%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 12 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 74.04 (C-CBr), 32.04 ($CH_3$).

**(*E*)-5,6-Dibromodec-5-ene (5a)**[14b]

[CAS Reg. No. 1027523-53-0]

Yellow oil; yield: 545 mg (92%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.67 (t, *J* = 7.5 Hz, 4 H, H-C-4 and H-C-7), 1.62–1.50 (m, 4 H, H-C-3 and H-C-8), 1.41–1.29 (m, 4 H, H-C-2 and H-C-9), 0.94 (t, *J* = 7.2 Hz, 6 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 121.80 (C-5 and C-6), 40.70 (C-4 and C-7), 29.74 (C-3 and C-8), 21.83 (C-2 and C-9), 14.09 (C-1 and C-10).

**(*E*)-1-(1,2-Dibromoprop-1-enyl)benzene (5b)**[14b]

[CAS Reg. No. 67824-63-9]

Light yellow oil; yield: 505 mg (92%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.30 (m, 5 H, H-phenyl), 2.63 (s, 3 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 140.91 (C1-phenyl), 129.23 (C3- and C5-phenyl), 128.73 (C4-phenyl), 128.36 (C2- and C6-phenyl), 117.36 (C2-propenyl), 116.96 (C1-propenyl), 29.47 ($CH_3$).

**(*E*)-1-(1,2-Dibromovinyl)-4-methoxybenzene (5c)**[14b]

*p*-Methoxyphenyl ethyne (**4c**) gave a mixture of *trans*-dibromoalkene **5c** and tetrabromoalkane in a ratio of 1:0.14.

[CAS Reg. No. 1334219-22-5]

Purple oil; yield: 580 mg (84%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.47 (m, 2 H, H-C2- and H-C6-phenyl), 6.93–6.89 (m, 2 H, H-C3- and H-C5-phenyl), 6.74 (s, 1 H, H-CHBr), 3.84 (s, 3 H, $OCH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 160.32 (C4-phenyl), 130.94 (C2- and C6-phenyl), 129.30 (C1-phenyl), 121.63 (C-CBr), 113.70 (C3- and C5-phenyl), 102.09 (C-CHBr), 55.48 ($OCH_3$).

**2-Bromo-1-phenylethanone (7a)**[14b] **and 2,2-Dibromo-1-phenylethanone (7a')**[25]

Acetophenone (**6a**) gave a mixture of monobrominated and dibrominated ketones in a ratio of 1:1.

Light yellow oil; yield: 436 mg (92%).

**2-Bromo-1-phenylethanone (7a)**[14b]

[CAS Reg. No. 70-11-1]

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.87 (m, 2 H, H-C2- and H-C6-phenyl), 7.57–7.47 (m, 1 H, H-C4-phenyl), 7.44–7.35 (m, 2 H, H-C3- and H-C5-phenyl), 4.36 (s, 2 H, H-$CH_2$Br).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 191.35 (C=O), 134.54 (C1-phenyl), 134.05 (C4-phenyl), 128.99, 128.95 (C2-, C3-, C5- and C6-phenyl), 31.13 (C-$CH_2$Br).

**2,2-Dibromo-1-phenylethanone (7a')**[25]

[CAS Reg. No. 13665-04-8]

$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.96 (m, 2 H, H-C2- and H-C6-phenyl), 7.57–7.47 (m, 1 H, H-C4-phenyl), 7.44–7.35 (m, 2 H, H-C3- and H-C5-phenyl), 6.64 (s, 1 H, H-$CHBr_2$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 186.03 (C=O), 134.54 (C1-phenyl), 130.90 (C4-phenyl), 129.76, 129.03 (C2-, C3-, C5- and C6-phenyl), 39.90 (H-$CHBr_2$).

**2-Bromo-1-phenylbutan-1-one (7b)**[14b]

[CAS Reg. No. 877-35-0]

Light yellow oil; yield: 430 mg (95%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.05–7.99 (m, 2 H, H-C2- and H-C6-phenyl), 7.60 (tt, *J* = 7.5, 1.5 Hz, 1 H, H-C4-phenyl), 7.52–7.46 (m, 2 H, H-C3- and H-C5-phenyl), 5.08 (dd, *J* = 7.8, 6.3 Hz, 1 H, H-CHBr), 2.31–2.09 (m, 2 H, H-$CH_2$), 1.09 (t, *J* = 7.2 Hz, 3 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 193.37 (C=O), 134.66 (C1-phenyl), 133.78 (C4-phenyl), 128.96 (C2- and C6-phenyl), 128.89 (C3- and C5-phenyl), 49.20 (C-CHBr), 27.04 (C-$CH_2$), 12.30 ($CH_3$).

**2-Bromo-2-methyl-1-phenylpropan-1-one (7c)**[14b]

[CAS Reg. No. 10409-54-8]

Colorless oil; yield: 420 mg (93%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.17–8.10 (m, 2 H, H-C2- and H-C6-phenyl), 7.56–7.50 (m, 1 H, H-C4-phenyl), 7.47–7.40 (m, 2 H, H-C3- and H-C5-phenyl), 2.04 (s, 6 H, $CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 197.03 (C=O), 134.98 (C1-phenyl), 132.49 (C4-phenyl), 130.19 (C2- and C6-phenyl), 128.27 (C3- and C5-phenyl), 60.46 (C-CBr), 31.65 [C(Br)($CH_3$)$_2$].

**(1-Bromocyclohexyl)(phenyl)methanone (7d)**[14b]

[CAS Reg. No. 7500-66-5]

Colorless oil; yield: 491 mg (92%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.09–8.05 (m, 2 H, H-C2- and H-C6-phenyl), 7.55–7.47 (m, 1 H, H-C4-phenyl), 7.46–7.37 (m, 2 H, H-C3- and H-C5-phenyl), 2.39–2.26 (m, 2 H, H-C2- and H-C6-cyclohexyl), 2.25–2.11 (m, 2 H, H′-C2- and H′-C6-cyclohexyl), 1.88–1.72 (m, 2 H, H-C3- and H-C5-cyclohexyl), 1.61–1.45 (m, 3 H, H′-C3-, H′-C5- and H-C4-cyclohexyl), 1.45–1.32 (m, 1 H, H′-C4-cyclohexyl).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 197.58 (C=O), 135.96 (C1-phenyl), 132.12 (C4-phenyl), 129.88 (C2- and C6-phenyl), 128.22 (C3- and C5-phenyl), 68.06 (C1-cyclohexyl), 38.36 (C2- and C6-cyclohexyl), 25.07 (C4-cyclohexyl), 23.66 (C3- and C5-cyclohexyl).

**2-Bromo-2,4-dimethylpentan-3-one (7e)**[26]

[CAS Reg. No. 3212-63-3]

Colorless oil; yield: 375 mg (97%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.43 [sept, *J* = 6.6 Hz, 1 H, H-C*H*($CH_3$)$_2$], 1.85 [s, 6 H, H-C($CH_3$)$_2$Br], 1.15 [d, *J* = 6.6 Hz, 6 H, H-CH(C*H*$_3$)$_2$].

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 210.06 (C=O), 64.70 (C-CBr), 34.66 [*C*H($CH_3$)$_2$], 29.40 [C($CH_3$)$_2$Br], 21.03 [CH(*C*H$_3$)$_2$].

**2-Bromo-1,3-diphenylpropane-1,3-dione (7f)**[27]

[CAS Reg. No. 728-84-7]

White solid; yield: 580 mg (96%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 8.01–7.98 (m, 4 H, H-C2- and H-C6-phenyl), 7.63–7.58 (m, 2 H, H-C4-phenyl), 7.50–7.44 (m, 4 H, H-C3- and H-C5-phenyl), 6.56 (s, 1 H, H-CHBr).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 189.10 (C=O), 134.39 (C4-phenyl), 133.93 (C1-phenyl), 129.39 (C2- and C6-phenyl), 129.16 (C3- and C5-phenyl), 52.82 (C-CHBr).

**Ethyl 2-Bromo-4,4-dimethyl-3-oxopentanoate (7g)**

[CAS Reg. No. 81569-29-1]

Colorless oil; yield: 487 mg (97%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 5.23 (s, 1 H, H-CHBr), 4.23 (q, *J* = 7.2 Hz, 2 H, H-$OCH_2$), 1.26 (t, *J* = 7.2 Hz, 3 H, H-$OCH_2CH_3$), 1.24 (s, 9 H, H-3$CH_3$).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 203.67 (C=O), 165.20 (C-*C*OOEt), 63.25 (C-$OCH_2$), 45.34 [*C*($CH_3$)$_3$], 43.56 (C-CHBr), 26.71 (C-3$CH_3$), 13.99 ($OCH_2CH_3$).

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## Supporting Information

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