

Note

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## Bromination of Olefins with HBr and DMSO

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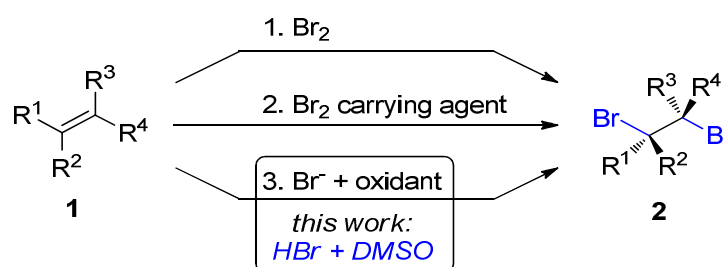
We dedicate this manuscript to the memory of the late Dr. Aaron D. Mills.

**Abstract:** A simple and inexpensive methodology is reported for the conversion of alkenes to 1,2-dibromo alkanes via oxidative bromination using HBr paired with dimethylsulfoxide which serves as the oxidant as well as co-solvent. The substrate scope includes 21 olefins brominated in good to excellent yields. Three of six styrene derivatives yielded bromohydrins under the reaction conditions.

**Keywords:** Bromination, dimethylsulfoxide, HBr, alkene, 1,2-dibromoalkane, bromohydrin

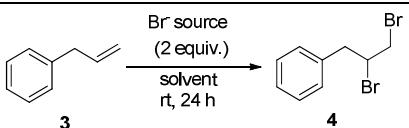
Vicinal dibromoalkanes (**2**) are useful synthetic precursors to cyclopropanes,<sup>1</sup> alkynes,<sup>2</sup> and vinylbromides of value in cross-coupling chemistry.<sup>2-3</sup> Their various preparations from alkenes (**1**) can be classified into three general approaches: 1) treatment with molecular bromine in halogenated solvent<sup>4</sup> or alternative media,<sup>5</sup> 2) treatment with a bromine carrying agent such as a tribromide salt<sup>6</sup> or analogous reagent,<sup>7</sup> and 3) treatment with bromide in the presence of a stoichiometric oxidant such as Oxone,<sup>8</sup> H<sub>2</sub>O<sub>2</sub>,<sup>9</sup> O<sub>2</sub>,<sup>10</sup> Selectfluor,<sup>11</sup> and others<sup>12</sup> (Scheme 1). The third of these strategies, oxidative bromination, is analogous to the biological solution to electrophilic halogenation which employs haloperoxidase (H<sub>2</sub>O<sub>2</sub>) or flavin dependent halogenase (O<sub>2</sub>) enzymes to produce 'X<sup>+</sup>' from X<sup>-</sup>.<sup>13</sup> In their 2008 comparative review of 24 methods,

Eissen and Lenoir concluded that many modern bromination methods that circumvent the use of molecular bromine suffer from significantly higher resource demands and waste production compared to the traditional choice of Br<sub>2</sub> in CHCl<sub>3</sub>.<sup>14</sup> The authors emphasize the need for continued development in this field and highlight oxidative bromination in general, and the use of H<sub>2</sub>O<sub>2</sub>/HBr specifically,<sup>9c</sup> as the most favorable of current methods based on a number of environmental, health, and safety factors.



**Scheme 1.** General approaches to bromination of olefins.

Herein we present our discovery of a simple oxidative bromination of olefins using HBr and dimethylsulfoxide (DMSO). DMSO is a polar aprotic solvent widely used for synthetic applications at all scales.<sup>15</sup> In the presence of various activating reagents, DMSO is a mild oxidant that has been employed primarily for the oxidation of alcohols.<sup>16</sup> DMSO-based oxidations are metal-free, mild, and inexpensive. For these reasons, we are interested in expanding the use of this oxidant. In the present case we sought to test the potential applicability of DMSO in the context of oxidative bromination. We began by treating allylbenzene (**3**) with four bromide reagents in DMSO (Table 1).

**Table 1.** Reaction discovery.<sup>a</sup>


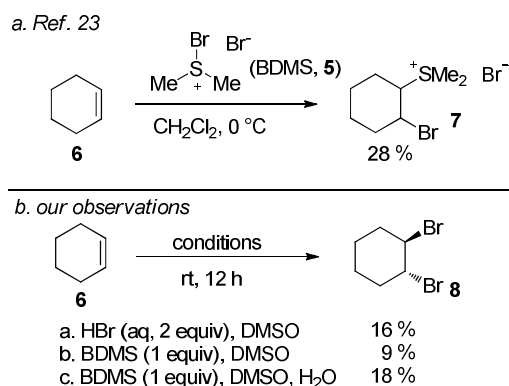
Entry	Br <sup>-</sup> source	solvent	yield <sup>b</sup>
1	Bu <sub>4</sub> NBr	DMSO	0
2	KBr	DMSO	0
3	NaBr	DMSO	0
4	HBr (48% aq.)	DMSO	13
5	HBr (48% aq.)	CHCl <sub>3</sub>	0

<sup>a</sup> Reaction conditions: Substrate (0.5 mmol), solvent (0.5 mL), 'Br<sup>-</sup> source' (2 equiv); reaction workup with Et<sub>2</sub>O/H<sub>2</sub>O. <sup>b</sup> NMR yield with CH<sub>2</sub>Br<sub>2</sub> as internal standard.

Although no reaction occurred with Bu<sub>4</sub>NBr, KBr, or NaBr in DMSO, we were pleased to observe that HBr yielded some of the desired 2,3-dibromopropylbenzene (**4**, entry 4). The reaction did not proceed when DMSO was replaced with chloroform (entry 5) in which case trace hydrobromination was observed but most of the substrate remained unreacted.

In previous literature the pairing of HBr and DMSO has been used for the alpha oxidation of ketones,<sup>17</sup> bromination of arenes,<sup>18</sup> and benzylic oxidation.<sup>19</sup> In most cases, it was believed that HBr reacts with DMSO to yield bromodimethylsulfonium bromide (BDMS, **5**), a well-established electrophilic bromination reagent that is more commonly prepared from dimethylsulfide and bromine.<sup>20</sup> BDMS is an orange solid that precipitates from dichloromethane solution upon addition of DMS and Br<sub>2</sub>.<sup>21</sup> Most commonly this reagent has been used to brominate various arenes and carbonyl derivatives.<sup>20</sup> In 2008 Das and co-workers reported bromination of olefins with BDMS in acetonitrile.<sup>22</sup> Earlier, similar reaction conditions were employed by Chow and Bakker to form 1-bromo-2-sulfonium bromides, such as **7**, which

precipitated in low yields upon treatment of olefins with BDMS in  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_3\text{CN}$  at  $0^\circ\text{C}$  (Scheme 2a).<sup>23</sup>

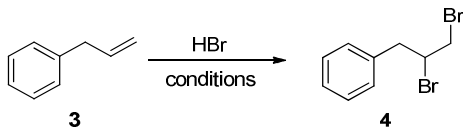


**Scheme 2.** Work of Chow and Bakker<sup>23</sup> and our comparison of HBr with BDMS.

We compared directly the reactivity of HBr in DMSO to BDMS in DMSO using cyclohexene as the substrate (Scheme 2b). In neither case was precipitation of sulfonium salts observed but rather exclusive conversion to *trans*-1,2-dibromocyclohexane in low yields after 12 hours at room temperature. Upon addition of water to the BDMS/DMSO reaction (intended to mimic the water present in our HBr/DMSO system) the rates of the two processes were similar with 18% and 16% yields respectively after 12 hours at room temperature. These observations lend support to the notion that the active brominating species in the HBr/DMSO process is BDMS.

We conducted a brief optimization of this reaction (Table 2). The yield of (2,3-dibromopropyl)benzene (**4**) from allylbenzene was improved to 57% and 96% by increasing the amount of HBr to 5 and 10 equivalents respectively and extending reaction time to 24 hours (entries 2 and 3). When the reaction temperature was warmed to  $65^\circ\text{C}$ , a yield of 86% was observed in just 12 hours with 5 equiv. of HBr (entry 4). A screen of co-solvents identified the two solvent mixture of DMSO and  $\text{CHCl}_3$  (1:1) as optimal giving nearly quantitative conversion, and 80% isolated yield, of the desired product after 12 hours at  $65^\circ\text{C}$ .

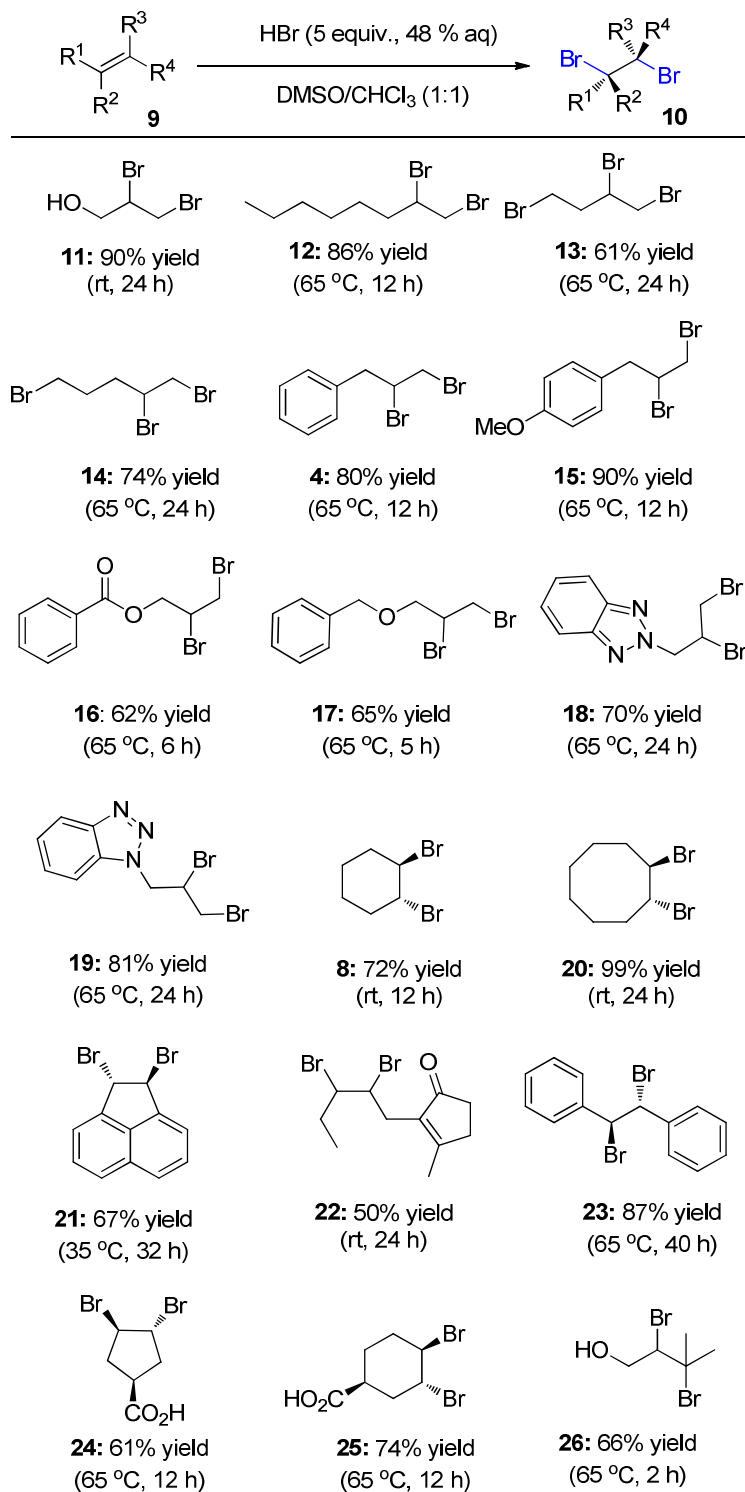
**Table 2.** Reaction Optimization.<sup>a</sup>



entry	Solvent	HBr (equiv.)	Temp. (°C)	Time (h)	yield <sup>b</sup>
1	DMSO	2	rt	24	13
2	DMSO	5	rt	24	57
3	DMSO	10	rt	24	96
4	DMSO	5	65	12	86
5	DMSO/CHCl <sub>3</sub> <sup>c</sup>	5	65	12	98 (80) <sup>d</sup>

<sup>a</sup> Reaction conditions: Substrate (0.5 mmol), solvent (0.5 mL). <sup>b</sup> NMR yield with CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>c</sup> DMSO (0.5 mL) and CHCl<sub>3</sub> (0.5 mL). <sup>d</sup> Isolated yield.

The substrate scope of this bromination was evaluated with 10 terminal olefins and 8 polysubstituted olefins (Table 3).

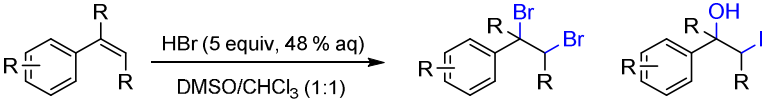
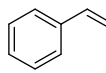
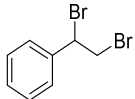
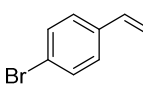
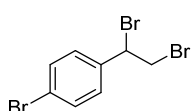
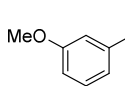
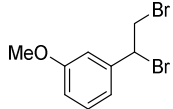
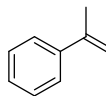
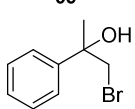
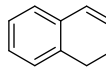
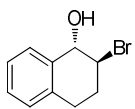
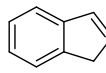
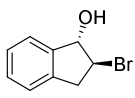
**Table 3:** Substrate Scope <sup>a</sup>

<sup>a</sup>. Reaction Conditions: Alkene substrate (0.5 - 1.0 mmol), HBr (48% aq., 5 equiv.), DMSO (1 mL per mmol of substrate), CHCl<sub>3</sub> (1 mL per mmol of substrate); Reported yields are for isolated products after chromatography.

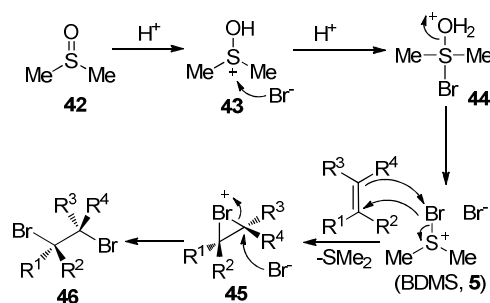
Allyl alcohol was converted to 2,3-dibromopropan-1-ol (**11**) in 90% yield in 24 hours at room temperature. 1-octene was brominated in 12 hours at 65 °C to yield the corresponding dibromooctane **12** in 86% isolated yield. Allyl benzene and *p*-methoxy allylbenezene were readily brominated to give bromoalkanes **4** and **15** in 80% and 90% respectively. Reaction of allyl benzoate gave dibromide **16** in 6 hours with 62% isolated yield. Longer reaction times resulted in considerable hydrolysis of the ester. *N*-allyl benzotriazoles gave compounds **18** and **19** in good yields. For cyclohexene, the reaction temperature was lowered to room temperature to avoid loss of the volatile substrate. The reaction was completed in 12 hours giving *trans*-1,2-dibromocyclohexane (**8**) in 72% isolated yield. Conversion of cyclooctene was also complete at room temperature in 24 hours to give **20** in 99% yield. The temperature was also lowered for two other substrates, acenaphthylene and *cis*-jasmone, to minimize the formation of unidentified side products. In these cases the desired dibromoalkanes **21** and **22** were obtained in 67% and 50% after 32 and 24 hours respectively. A reaction time of 40 hours at 65 °C was required for complete conversion of *trans*-stilbene to the corresponding product (**23**) which was obtained in 87% yield. Carboxylic acids are well tolerated under these reaction conditions with compounds **24** and **25** obtained in good yields. Compound **25** was isolated as a single diastereomer in 74% yield. Finally, 3-methylbut-2-en-1-ol reacted rapidly giving the dibromoalcohol **26** in 66% yield. We next applied this reaction to a series of styrene derivatives (Table 4). Styrene (**30**), *p*-bromostyrene (**32**), and *m*-methoxystyrene (**34**) behaved as expected giving the corresponding dibromides in good yields. However, in the case of  $\alpha$ -methylstyrene (**36**), we observed nearly exclusive formation of the *trans*-bromohydrin **37** which was isolated in 93% yield. Similarly 1,2-dihydronaphthalene (**38**) and indene (**40**) afforded *trans*-bromohydrins **39** and **41**



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2  
3 respectively in good isolated yields. In these two cases a small amount of dibromination was  
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5 also observed via crude  $^1\text{H}$  NMR. A control experiment was conducted to determine the  
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7 potential that bromohydrins **37**, **39**, and **41** are formed via initial bromination and subsequent  
8  
9 substitution of  $-\text{Br}$  with  $-\text{OH}$ . We subjected 1,2-dibromoindane (prepared via standard  $\text{Br}_2$ -  
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11 based bromination of indene) to our  $\text{HBr}/\text{DMSO}$  reaction conditions. We observed complete  
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13 conversion of 1,2-dibromoindane to bromohydrin **41** in 12 hours. Thus it is possible that  
14  
15 substrates **36**, **38**, and **40** undergo initial dibromination before conversion to bromohydrins. The  
16  
17 isolated bromohydrins have a *trans* relationship between hydroxyl and bromide groups.  
18  
19 Therefore, if a substitution of  $-\text{Br}$  to  $-\text{OH}$  occurs, the observed stereochemistry indicates an  $\text{S}_{\text{N}}1$   
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21 process whereby a carbocation intermediate reacts with water at its less sterically hindered face.  
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Table 1. Reaction of Styrene derivatives					
					
Entry	Substrate	Product	Time (h)	Temp (° C)	Isolated Yield (%)
1			12	65	61
2			24	65	65
3			12	65	61
4			3	65	93
5			12	65	72
6			12	65	65

Scheme 3 offers a proposed mechanism for the conversion of DMSO to BDMS followed by subsequent olefin bromination.



**Scheme 3.** Proposed reaction mechanism.

This methodology was not suitable for the bromination of  $\alpha,\beta$ -unsaturated carbonyl derivatives. We also attempted to replace HBr with HCl for an analogous chlorination reaction without success. We must report that our work directly contradicts Yusobov et al. who have reported the oxidation of olefins to 1,2-diketones under identical conditions.<sup>24</sup>

In summary, we have described a unique process for dibromination of olefins with HBr and DMSO. This methodology offers a simple, inexpensive, and mild alternative to the use of Br<sub>2</sub> or other more resource-intensive strategies.

## Experimental Section

**General Considerations:** Unless otherwise noted, commercially available reagents and solvents were used without further purification. Infrared spectra were obtained on a Thermo Scientific Nicolet 380 FT-IR spectrometer as thin films on ZnSe disks and peaks are reported in cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR experiments were performed on a Bruker AVANCE 500 MHz instrument and samples were obtained in CDCl<sub>3</sub> (referenced to 7.26 ppm for <sup>1</sup>H and 77.0 ppm for <sup>13</sup>C). Coupling constants (J) are in Hz. The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. MALDI-HRMS of compounds were recorded on a Q-TOF mass spectrometer using 2,5-dihydroxybenzoic acid as a matrix and mixture of polyethylene glycol (PEG 600) and (PEG 1000) as internal

calibration standards. Elemental analyses were obtained on a CE0440 elemental analyzer (EAI Exeter Analytical). Reaction progress was monitored by thin-layer chromatography (TLC, EMD Chemicals Inc, Silica Gel 60 F254), visualized under UV light, and plates were developed using *p*-anisaldehyde or potassium permanganate stains. Flash chromatography was performed using silica gel (Sorbent Technologies, particle size 40-63  $\mu\text{m}$ ). Melting points were determined using a Mel-Temp II apparatus and are uncorrected.

**General Procedure for Dibromination Reaction:** A solution of HBr (48% aq., 5 equiv.) in DMSO (1 mL per mmol of substrate) is added to a reaction vial containing a magnetic stir bar and the alkene substrate (0.5 - 1.0 mmol) in  $\text{CHCl}_3$  (1 mL per mmol of substrate). The reaction vial is capped and stirred at the specified temperature (rt or 65  $^\circ\text{C}$ ) until complete disappearance of starting material is observed by TLC or  $^1\text{H}$  NMR (TLC plates visualized using *p*-anisaldehyde or potassium permanganate stains). The reaction is transferred to a separatory funnel containing water and extracted with ether (3 x 30 mL). The combined organic extracts are dried over  $\text{MgSO}_4$ , and solvent removed *in vacuo*. The residue is purified by flash column chromatography on silica gel (gradient elution with EtOAc and hexanes). *Note: Flash chromatography effectively removes all trace DMSO that may remain after workup.*

**(2,3-Dibromopropyl) benzene (4):** The standard procedure was used with allylbenzene (132.5  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 12 hours of stirring at 65  $^\circ\text{C}$ , the reaction was worked up and purified as described above to yield compound 4 as oil (0.223 g, 80% yield).  $R_f = 0.87$  (Hexanes/EtOAc 70:30 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.37 – 7.27 (m, 5H), 4.41 – 4.33 (m, 1H), 3.83 (dd,  $J = 10.5, 4.2$  Hz, 1H), 3.64 (dd,  $J = 10.4, 8.9$  Hz, 1H), 3.51 (dd,  $J = 14.5, 4.8$  Hz, 1H), 3.14 (dd,  $J = 14.5, 7.8$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125

MHz)  $\delta$  136.9, 129.5, 128.5, 127.2, 52.4, 42.0, 36.0.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>25</sup>

***trans*-1,2-Dibromocyclohexane (8):** The standard procedure was used with cyclohexene (101  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 12 hours of stirring at room temperature, the reaction was worked up and purified as described above to yield compound 8 as a colorless liquid product (175 mg, 72% yield).  $R_f$  = NA;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  4.45 (s, 2H), 2.57 – 2.31 (m, 2H), 1.96 – 1.74 (m, 4H), 1.57 – 1.46 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  55.2, 32.1, 22.4.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>5d</sup>

**2,3-Dibromopropan-1-ol (11):** The standard procedure was used with allyl alcohol (68  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). The reaction was stirred for 24 hours at room temperature. After workup and purification above compound 11 was obtained as a colorless liquid (196 mg, 90 % yield).  $R_f$  = 0.62 (Hexanes/EtOAc 70:30 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  4.39 – 4.23 (m, 1H), 4.02 (d,  $J$  = 3.9 Hz, 2H), 3.88 – 3.74 (m, 2H), 1.94 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  64.2, 53.6, 31.5.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>26</sup>

**1,2-Dibromooctane (12):** The standard procedure was used with 1-octene (78.5  $\mu\text{L}$ , 0.5 mmol), HBr (48% aq., 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 12 hours of stirring at 65  $^\circ\text{C}$ , the reaction was worked up and purified as described above to yield compound 12 as a colorless liquid product (116.2 mg, 86% yield);  $R_f$  = 0.65 (Hexanes/EtOAc 70:30 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  4.25 – 4.08 (m, 1H), 3.85 (dd,  $J$  = 10.2, 4.5 Hz, 1H), 3.63 (t,  $J$  = 9.9 Hz, 1H), 2.20 – 2.07 (m, 1H), 1.79 (dddd,  $J$  = 14.6, 10.0, 9.0, 4.6 Hz, 1H), 1.64 – 1.48 (m, 1H), 1.48 – 1.24 (m,

6H), 0.94 – 0.86 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  53.2, 36.4, 36.1, 31.6, 28.5, 26.7, 22.5, 14.0.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>5b</sup>

**1,2,4-Tribromobutane (13):** The standard procedure was used with 4-bromobut-1-ene (102  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 hours of stirring at 65  $^\circ\text{C}$ , the reaction was worked up and purified as described above to yield compound 13 as clear colorless oil (179 mg, 61 % yield);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  4.38 (tdd,  $J$  = 9.8, 4.3, 2.8 Hz, 1H), 3.90 (dd,  $J$  = 10.5, 4.2 Hz, 1H), 3.72 – 3.51 (m, 3H), 2.68 (dddd,  $J$  = 15.5, 9.3, 6.4, 2.8 Hz, 1H), 2.26 (dddd,  $J$  = 15.5, 10.0, 5.5, 4.3 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  50.3, 39.2, 35.9, 30.4; IR ( $\text{cm}^{-1}$ ): 2923.3, 1462.9, 736.8, 475.43; Elemental analysis: ( $\text{C}_4\text{H}_7\text{Br}_3$ , 294.81) Calcd: C, 16.3%; H, 2.39%. Found: C, 16.73%; H, 2.07%.

**1,2,5-Tribromopentane (14):** The standard procedure was used with 5-bromopent-1-ene (118.5  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 hours of stirring at 65 $^\circ\text{C}$ , the reaction was worked up and purified as described above to yield compound 14 as oil (227 mg, 74 % yield);  $R_f$  = 0.66 (Hexanes/EtOAc 90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  4.18 (tdd,  $J$  = 9.8, 4.4, 3.0 Hz, 1H), 3.87 (dd,  $J$  = 10.3, 4.4 Hz, 1H), 3.63 (t,  $J$  = 10.1 Hz, 1H), 3.51 – 3.40 (m, 2H), 2.43 – 2.33 (m, 1H), 2.24 – 2.13 (m, 1H), 2.07 – 1.88 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  51.43, 35.82, 34.71, 32.27, 30.02; IR ( $\text{cm}^{-1}$ ): 2959.7, 1257.0, 1141.0, 563.8; Elemental analysis: ( $\text{C}_5\text{H}_9\text{Br}_3$ , 308.84) Calcd: C, 19.45%; H, 2.94%. Found: C, 19.71%; H, 2.84%.

**1-(2,3-Dibromopropyl)-4-methoxybenzene (15):** The standard procedure was used with 1-allyl-4-methoxybenzene (153.4  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 12 hours of stirring at 65  $^\circ\text{C}$ , the reaction was worked up and purified as described above to yield compound 15 as colorless oil (276.6 mg, 90% yield);  $R_f$  = 0.65 (Hexanes/EtOAc

90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.25 – 7.15 (m, 2H), 6.92 – 6.83 (m, 2H), 4.33 (dddd,  $J = 9.0, 7.4, 4.9, 4.2$  Hz, 1H), 3.84 – 3.78 (m, 3H), 3.81 (s, 3H), 3.61 (dd,  $J = 10.5, 8.9$  Hz, 1H), 3.42 (dd,  $J = 14.6, 4.9$  Hz, 1H), 3.10 (dd,  $J = 14.7, 7.5$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  158.8, 130.6, 128.8, 113.9, 55.2, 52.9, 41.1, 35.9; IR( $\text{cm}^{-1}$ ): 2929.8, 2833.6, 1610.4, 1509.9, 1463.1, 1430.4, 1242.7, 1176.3, 1031.6, 806.2, 594.5; Elemental analysis: ( $\text{C}_{10}\text{H}_{12}\text{Br}_2\text{O}$ , 308.01) Calcd: C, 38.99%; H, 3.93%. Found: C, 39.21%; H, 3.84%.

**2,3-Dibromopropyl benzoate (16):** The standard procedure was used with allyl benzoate (154  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 6 hours of stirring at 65  $^\circ\text{C}$ , the reaction was worked up and purified as described above to yield compound 16 as clear colorless oil (182 mg, 62% yield);  $R_f = 0.35$  (Hexanes/EtOAc 90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.11 – 8.04 (m, 2H), 7.63 – 7.56 (m, 1H), 7.51 – 7.45 (m, 2H), 4.77 (dd,  $J = 12.2, 4.5$  Hz, 1H), 4.72 (dd,  $J = 12.2, 5.3$  Hz, 1H), 4.47 (ddt,  $J = 9.2, 5.3, 4.6$  Hz, 1H), 3.88 (dd,  $J = 10.7, 4.8$  Hz, 1H), 3.83 (dd,  $J = 10.7, 9.1$  Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  165.8, 133.4, 129.8, 129.5, 128.5, 65.60, 47.0, 32.1; IR ( $\text{cm}^{-1}$ ) 2950, 1720.6, 1602.1, 1451.92, 1377.2, 1267.7, 725.9, 707.04; APCI-HRMS Calcd for  $\text{C}_{10}\text{H}_{11}\text{Br}_2\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 320.9126. Found: 320.9115.

**((2,3-Dibromopropoxy)methyl)benzene (17):** The standard procedure was used with ((allyloxy)methyl)benzene (77.6  $\mu\text{L}$ , 0.5 mmol), HBr (48% aq., 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 5 hours of stirring at 65  $^\circ\text{C}$ , the reaction was worked up and purified as described above to yield compound 17 as clear colorless oil (100 mg, 65% yield);  $R_f = 0.69$  (Hexanes/EtOAc 90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.36 (d,  $J = 4.8$  Hz, 5H), 4.66 – 4.58 (m, 2H), 4.27 (dd,  $J = 8.3, 4.9$  Hz, 1H), 3.92 – 3.79 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  137.5, 128.5, 127.9, 127.7, 73.5, 71.1, 49.1, 33.1; IR ( $\text{cm}^{-1}$ ) 3028.9, 2859.7, 1495.3, 1452.4,

1360.0, 1072.6, 695.4, 573.9.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>27</sup>

**2-(2,3-Dibromopropyl)-2*H*-benzotriazole (18):** The standard procedure was used with 2-allyl-2*H*-benzotriazole (125 mg, 0.79 mmol), HBr (48% aq., 0.44 mL, 3.95 mmol), and DMSO (1 mL). After 24 hours of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound 18 as white solid (175 mg, 70% yield); mp = 81-83 °C;  $R_f$  = 0.79 (Hexanes/EtOAc 70:30 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.98 – 7.79 (m, 2H), 7.41 (dd,  $J$  = 6.6, 3.1 Hz, 2H), 5.34 (dd,  $J$  = 14.1, 5.4 Hz, 1H), 5.13 (dd,  $J$  = 14.1, 7.1 Hz, 1H), 4.87 (tt,  $J$  = 7.3, 5.4 Hz, 1H), 3.99 – 3.77 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  144.6, 126.9, 118.2, 59.9, 47.0, 33.4; IR ( $\text{cm}^{-1}$ ): 3041.2, 2922.59, 1561.2, 1425.4, 1345.9, 1168.2, 751.2; ESI-HRMS Calcd for  $\text{C}_9\text{H}_9\text{Br}_2\text{N}_3$  ( $\text{M}+\text{H}$ )<sup>+</sup>: 317.9243. Found: 317.9243.

**1-(2,3-Dibromopropyl)-1*H*-benzotriazole (19):** The standard procedure was used with 1-allyl-1*H*-benzotriazole (159 mg, 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 hours of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound 19 as white solid. (130 mg, 81% yield);  $R_f$  = 0.85 (Hexanes/EtOAc 90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.12 – 8.07 (m, 1H), 7.64 (dt,  $J$  = 8.4, 0.9 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.41 (ddd,  $J$  = 8.4, 6.9, 1.0 Hz, 1H), 5.25 (dd,  $J$  = 14.9, 5.0 Hz, 1H), 5.05 (dd,  $J$  = 14.9, 6.9 Hz, 1H), 4.76 (dddd,  $J$  = 8.2, 6.9, 5.1, 4.5 Hz, 1H), 3.89 – 3.76 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  145.8, 133.6, 127.9, 124.2, 120.3, 109.4, 51.9, 47.8, 33.5, 29.7; IR ( $\text{cm}^{-1}$ ): 2977.3, 1590.5, 1488.0, 1407.2, 1102.47, 728.77; ESI-HRMS Calcd for  $\text{C}_9\text{H}_9\text{Br}_2\text{N}_3$  ( $\text{M}+\text{H}$ )<sup>+</sup>: 317.9241. Found 317.9244.

**1,2-Dibromocyclooctane (20):** The standard procedure was used with cyclooctene (130  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 hours of stirring at room



temperature, the reaction was worked up and purified as described above to yield compound 20 as a colorless liquid product (268 mg, 99% yield);  $R_f = 0.81$  (Hexanes/EtOAc 90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  4.64 – 4.51 (m, 1H), 2.41 (dddd,  $J = 15.8, 8.9, 3.6, 1.3$  Hz, 1H), 2.09 (dddd,  $J = 15.7, 7.8, 5.0, 2.7$  Hz, 1H), 1.90 – 1.79 (m, 1H), 1.72 – 1.54 (m, 2H), 1.53 – 1.42 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  61.5, 33.2, 25.9, 25.4.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>28</sup>

***trans*-1,2-Dibromoacenaphthene (21):** The standard procedure was used with acenaphthylene (100 mg, 0.66 mmol), HBr (48% aq., 0.37 mL, 5 mmol), and DMSO (0.5 mL). After 32 hours of stirring at 35 °C, the reaction was worked up and purified as described above to yield compound 21 as light brown solid (138 mg, 67% yield); mp = 111-114 °C;  $R_f = 0.83$  (Hexanes/EtOAc 90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.82 (dd,  $J = 7.5, 1.4$  Hz, 2H), 7.70 – 7.56 (m, 4H), 6.01 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  140.5, 134.8, 131.0, 128.8, 125.9, 122.5, 54.9;  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>29</sup>

**2-(2,3-Dibromobutyl)-3-methylcyclopent-2-enone (22):** The standard procedure was used with *cis*-jasmane (170  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 hours of stirring at room temperature, the reaction was worked up and purified as described above to yield compound 22 as clear oil (151 mg, 50% yield);  $R_f = 0.72$  (Hexanes/EtOAc 70:30 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  4.57 (td,  $J = 7.0, 2.3$  Hz, 1H), 4.02 (ddd,  $J = 8.0, 5.5, 2.3$  Hz, 1H), 2.88 (d,  $J = 7.0$  Hz, 2H), 2.61 – 2.51 (m, 2H), 2.44 – 2.36 (m, 2H), 2.15 (s, 3H), 2.05 – 1.94 (m, 2H), 1.06 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  209.2, 173.7, 136.5, 62.0, 56.9, 34.2, 32.0, 32.0, 30.6, 17.8, 12.4; IR ( $\text{cm}^{-1}$ ): 2967.6, 2912.6, 1690.9, 1644.6, 1432.9, 1382.5, 545.91.512.9; Elemental analysis: ( $\text{C}_{11}\text{H}_{16}\text{Br}_2\text{O}$ , 324.06) Calcd: C, 40.77%; H, 4.98 %. Found: C, 40.95 %; H, 4.91 %.

**meso-1,2-Dibromo-1,2-diphenylethane (23):** The standard procedure was used with *trans*-stilbene (180 mg, 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 40 hours of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound 23 as white solid (295 mg, 87% yield); mp = 236-238 °C;  $R_f$  = 0.78 (Hexanes/EtOAc 90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.55 – 7.49 (m, 4H), 7.45 – 7.34 (m, 6H), 5.48 (s, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  140.0, 129.0, 128.8, 127.9, 56.1; Elemental analysis: ( $\text{C}_{14}\text{H}_{12}\text{Br}_2$ , 340.06) Calcd: C, 49.45%; H, 3.56%. Found: C, 49.7%; H, 3.37%.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>11</sup>

**3,4-Dibromocyclopentanecarboxylic acid (24):** The standard procedure was used with cyclopent-3-enecarboxylic acid (103  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 12 hours of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound 24 as white powder (167 mg, 61% yield); mp = 111-113 °C;  $R_f$  = 0.51 (Hexanes/EtOAc 70:30 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  4.63 (ddd,  $J$  = 4.8, 2.1, 1.2 Hz, 1H), 4.55 (dt,  $J$  = 6.2, 1.8 Hz, 1H), 3.45 – 3.33 (m, 1H), 3.11 – 2.97 (m, 2H), 2.68 – 2.57 (m, 1H), 2.49 (ddt,  $J$  = 15.0, 8.6, 1.5 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  179.0, 56.2, 54.3, 40.5, 37.2, 37.1; IR ( $\text{cm}^{-1}$ ) 2920.93, 1686.83, 1315.21, 914.17, 535.45; Elemental Analysis: ( $\text{C}_6\text{H}_8\text{Br}_2\text{O}_2$ , 271.94); Calcd: C, 26.50%; H, 2.97%; Found: C, 26.31%; H, 2.88%.

**(1S,3R,4R)-3,4-dibromocyclohexanecarboxylic acid (25):** The standard procedure was used with cyclohex-3-enecarboxylic acid (117  $\mu\text{L}$ , 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 12 hours of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound 25 as pale yellow solid (211.7 mg, 74% yield); mp = 80-82 °C;  $R_f$  = 0.59 (Hexanes/EtOAc 70:30 v/v);  $\delta$  4.70 (dd, 1H), 4.60 (dd,  $J$  = 3.3 Hz, 1H), 3.01 – 2.92 (m, 1H), 2.67 – 2.59 (m, 1H), 2.57 – 2.47 (m, 1H), 2.28 – 2.20 (m, 1H), 2.08 – 1.93 (m, 4H).  $^{13}\text{C}$

NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  180.2, 51.9, 51.8, 37.4, 30.7, 28.2, 23.0; IR (cm<sup>-1</sup>) 2929.89, 2605.09, 1701.33, 1451.40, 1283.43, 1026.09, 928.75, 889.46, 686.92, 541.99. <sup>1</sup>H and <sup>13</sup>C NMR spectral data is consistent with previously reported values.<sup>30</sup>

**2,3-Dibromo-3-methylbutan-1-ol (26):** The standard procedure was used with 3-methylbut-2-en-1-ol, (102  $\mu$ L, 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 2 hours of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound 26 as white crystals (162 mg, 66% yield); mp = 38-39 °C; R<sub>f</sub> = 0.59 (Hexanes/EtOAc 70:30 v/v); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  4.42 (dd, *J* = 8.2, 2.9 Hz, 1 H), 4.33 (d, *J* = 12.6, 2.9 Hz, 1 H), 3.98 (dd, *J* = 8.2, 12.5 Hz, 1 H), 1.98 (s, 3 H), 1.84 (s, 3 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  69.0, 66.1, 64.8, 35.5, 29.7; IR (cm<sup>-1</sup>) 3243.76, 2972.09, 2953.23, 1376.92, 1093.64, 1067.70, 975.03, 548.19; Elemental analysis: (C<sub>5</sub>H<sub>10</sub>Br<sub>2</sub>O, 245.94) Calcd: C, 24.42%; H, 4.1%. Found: C, 24.81%; H, 4.01%.

**1,2-(Dibromoethyl)-benzene (31):** The standard procedure was used with styrene (**30**, 57.5  $\mu$ L, 0.5 mmol), HBr (48% aq., 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 12 hours of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound 30 as white solid (80 mg, 61% yield); mp = 71-73 °C; R<sub>f</sub> = 0.79 (Hexanes/EtOAc 90:10 v/v); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$  7.44 – 7.32 (m, 3H), 5.15 (dd, *J* = 10.6, 5.4 Hz, 1H), 4.11 – 3.99 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)  $\delta$  138.7, 129.2, 128.9, 127.7, 50.9, 35.0. <sup>1</sup>H and <sup>13</sup>C NMR spectral data is consistent with previously reported values.<sup>12f</sup>

**1-Bromo-4-(1, 2-bromoethyl)benzene (33):** The standard procedure was used with 4-bromostyrene (**32**, 131  $\mu$ L, 1.0 mmol), HBr (48% aq., 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 hours of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound 33 as white solid (222 mg, 65% yield); mp = 56-58 °C; R<sub>f</sub> = 0.82

(Hexanes/EtOAc 90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.54 – 7.50 (m, 2H), 7.30 – 7.26 (m, 2H), 5.09 (dd,  $J$  = 11.0, 5.1 Hz, 1H), 4.06 (dd,  $J$  = 10.3, 5.1 Hz, 1H), 3.96 (dd,  $J$  = 11.0, 10.3 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  137.7, 132.1, 129.3, 123.2, 49.6, 34.6.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>31</sup>

**1-(1,3-Dibromoethyl)-3-methoxybenzene (35):** The standard procedure was used with 3-methoxystyrene (**34**, 69.4  $\mu\text{L}$ , 0.5 mmol), HBr (48% aq., 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 12 hours of stirring at 65  $^\circ\text{C}$ , the reaction was worked up and purified as described above to yield compound **35** as white solid (90 mg, 61% yield); mp = 64-66  $^\circ\text{C}$ ;  $R_f$  = 0.61 (Hexanes/EtOAc 90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.30 (t,  $J$  = 7.9 Hz, 1H), 6.99 (ddd,  $J$  = 7.8, 1.6, 0.8 Hz, 1H), 6.94 (t,  $J$  = 2.1 Hz, 1H), 6.88 (ddd,  $J$  = 8.3, 2.6, 0.9 Hz, 1H), 5.11 (dd,  $J$  = 10.5, 5.4 Hz, 1H), 4.11 – 3.93 (m, 2H), 3.83 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  159.8, 140.1, 129.9, 119.9, 114.6, 113.5, 55.3, 50.8, 35.0; IR ( $\text{cm}^{-1}$ ): 2917.1, 2833.9, 1600.22, 1490.4, 1462.29, 1434.1, 1047.0, 698.3; Elemental analysis: ( $\text{C}_9\text{H}_{10}\text{Br}_2\text{O}$ , 293.99) Calcd: C, 36.77%; H, 3.43%. Found: C, 36.44%; H, 3.45%.

**1-Bromo-2-phenylpropan-2-ol (37):** The standard procedure was used with  $\alpha$ -methylstyrene (**36**, 65  $\mu\text{L}$ , 0.5 mmol), HBr (48% aq., 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 3 hours of stirring at 65  $^\circ\text{C}$ , the reaction was worked up and purified as described above to yield compound **37** as colorless oil (100 mg, 93% yield);  $R_f$  = 0.76 (Hexanes/EtOAc 70:30 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.49 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 1H), 3.82 – 3.67 (m, 1H), 2.53 (s, 1H), 1.69 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  144.2, 128.4, 127.5, 124.9, 73.1, 46.3, 28.1; IR ( $\text{cm}^{-1}$ ) 3437.57, 2975.72, 1492.64, 1445.88, 1373.48, 1064.98, 696.85.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>32</sup>

***trans*-2-Bromo-1,2,3,4-tetrahydronaphthalen-1-ol (39):** The standard procedure was used with 1,2-dihydronaphthalene (**38**, 65.3  $\mu$ L, 0.5 mmol), HBr (48% aq., 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 12 hours of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound 39 as white powder (82 mg, 72% yield); mp = 108-110 °C;  $R_f$  = 0.5 (Hexanes/EtOAc 90:10 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.57 – 7.48 (m, 1H), 7.26 – 7.23 (m, 2H), 7.14 – 7.07 (m, 1H), 4.91 (d,  $J$  = 7.0 Hz, 1H), 4.37 (ddd,  $J$  = 10.0, 7.0, 3.2 Hz, 1H), 3.09 – 2.85 (m, 2H), 2.51 (td,  $J$  = 5.7, 3.1 Hz, 1H), 2.29 (dddd,  $J$  = 13.7, 9.7, 8.4, 6.0 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  135.4, 135.0, 128.5, 128.03, 126.7, 74.2, 56.2, 29.8, 28.1.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>33</sup>

***trans*-2-Bromo-1-indanol (41):** The standard procedure was used with indene (**40**, 57.8  $\mu$ L, 0.5 mmol), HBr (48% aq., 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 12 hours of heating at 65 °C, the reaction was worked up and purified as described above to yield compound 41 as white powder (69.3 mg, 65% yield); mp = 120-122 °C;  $R_f$  = 0.68 (Hexanes/EtOAc 70:30 v/v);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.44 – 7.40 (m, 1H), 7.31 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 5.32 (d,  $J$  = 5.8 Hz, 1H), 4.29 (td,  $J$  = 7.3, 5.8 Hz, 1H), 3.59 (dd,  $J$  = 16.2, 7.3 Hz, 1H), 3.28 – 3.19 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  141.7, 139.7, 129.0, 127.6, 124.6, 124.1, 83.5, 54.5, 40.5; IR ( $\text{cm}^{-1}$ ) 3211.77, 2908.20, 2849.39, 1477.19, 1461.02, 1438.36, 1343.48, 1289.79, 1183.46, 1063.85, 750.17, 729.86.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data is consistent with previously reported values.<sup>8b</sup>

## Associated Content

**Supporting Information:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are provided. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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## Graphical Abstract

