# One-pot aromatic bromination–rearrangement catalyzed by $GaCl_3$

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**This paper is dedicated to Prof. Keiichiro Fukumoto in recognition of his outstanding contributions to organic chemistry**

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**Abstract**

Reaction of monoalkylbenzenes with bromine in the presence of a catalytic amount of $GaCl_3$ (5 mol %) initially gives *o/p*-bromination products, which are converted into mixtures containing considerable amounts of the *m*-brominated products. Notably, the bromination of dimethyl-, trimethyl-, and tetramethylbenzenes gives dibromo- and/or tribromoarenes, which are converted into monobromoarenes.

**Keywords:** Gallium trichloride, aromatic bromination, isomerization

## Introduction

The bromination of aromatic compounds has been conducted using halogenating reagents such as $Br_2$ and HOBr in the presence or absence of catalysts.[1] These methods convert monoalkylbenzenes into *o*/*p*-brominated products. Since the *m*-derivatives are formed in small amounts, their preparations in general employ multistep processes.[2] A previous report that $Al_2Cl_6$–water catalyst promotes the isomerization of bromoarenes[3] led us to study one-pot catalytic procedures for the *o*/*p*- bromination of monoalkylbenzenes followed by isomerization to give mixtures containing the *m*- derivatives.[4] We now show that $GaCl_3$[5,6,7] catalyzes such bromination of alkylbenzenes. Also, it was found that the bromination of dimethyl-, trimethyl-, and tetramethylbenzenes initially gives dibromo- and/or tribromoarenes, which are converted into monobromoarenes.

## Results and Discussion

 

To a solution of hexylbenzene and $GaCl_3$ (5 mol %) in methylcyclohexane was added an equimolar amount of bromine, and the mixture was stirred at room temperature for 12 h giving the bromohexylbenzenes *o*-**1**, *m*-**1**, and *p*-**1** in 18%, 38%, and 15% yields, respectively (Table 1, entry 3). The structures were determined by comparison with the authentic samples prepared separately (see Experimental Section). Benzyl bromination proceeded in the absence of the catalyst, and **1** was not detected. The use of $FeCl_3$ (3.6 mol %) exhibited normal orientations, giving *o*-**1** (20%) and *p*-**1** (78%). Such aromatic bromination isomerization could also be carried out with $AlCl_3$ (5 mol %), although the reaction was sometimes not reproducible, probably because of the insolubility of $AlCl_3$ in this solvent. The bromination using $GaCl_3$ is rapid, and *o*-**1** and *p*-**1** are obtained in 5 min in 23% and 42% yields, respectively, with a very small amount of *m*-**1** (entry 4). When the mixture is stirred for 12 h at room temperature, *p*-**1** decreases and *m*-**1** increases. Bromination of several alkylbenzenes catalyzed by $GaCl_3$ is shown in Table 1. In the case of neopentylbenzene and isobutylbenzene, larger amounts of the *m*-derivatives are obtained, which may be a result of steric reasons (entries 6 and 7). The different *o*/*p* ratio of toluene and ethylbenzene may also be explained analogously (entries 1 and 2): a methyl group behaves as a considerably smaller group than an ethyl group in this reaction.

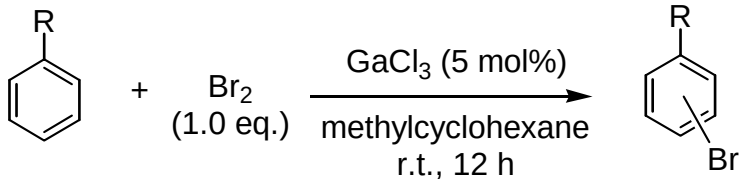


**Table 1.** Bromination of alkylbenzenes catalyzed by $GaCl_3$

| Entry | R | Yield[a] (%) | | |
|---|---|---|---|---|
| | | *o*- | *m*- | *p*- |
| 1 | $CH_3$ | 32 | 32 | 11 |
| 2 | $CH_3CH_2$ | 16 | 32 | 14 |
| 3 | $CH_3(CH_2)_4CH_2$ | 18 | 38 | 15 |
| 4[a] | $CH_3(CH_2)_4CH_2$ | 23 | 3 | 42 |
| 5 | $CH_3(CH_2)_6CH_2$ | 23 | 34 | 20 |
| 6 | $(CH_3)_2CHCH_2$ | 21 | 49 | 19 |
| 7 | $(CH_3)_3CCH_2$ | 8 | 62 | 22 |

[a]Determined by $^1$H-NMR. [b]The reaction was conducted for 5 min.

Polymethylbenzenes exhibit interesting behaviors: polybrominated products are initially formed, which are converted into monobromides. Reaction of *m*-xylene for 1 min gives the 4,6-dibrominated 4,6-**3** as the major product, and the monobromide **2** predominates after 12 h (Table

2). Such a phenomenon has not been reported before. Bromination of *m*-xylene with $AlCl_3$ under the same conditions for 1 min gives 4-**2** predominantly, which is the usual orientation.

Similar tendencies are observed in the bromination of *p*-xylene with $GaCl_3$ (Table 3). The reaction for 5 min gives 2,5-dibrominated **5** predominantly, which is converted into 2-brominated **4** after 12 h. In this case, $AlCl_3$ also shows somewhat related isomerization behaviors, although less prominently than with $GaCl_3$.

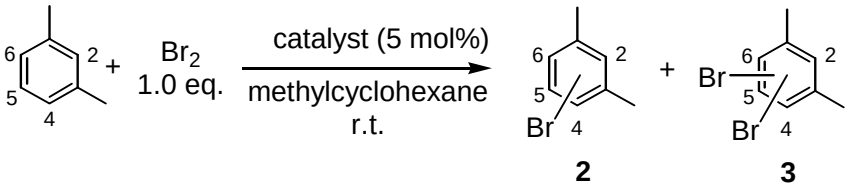


**Table 2.** Bromination of *m*-Xylene

| Catalyst | Time | Yield[a] (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | **2** | | | **3** | | |
| | Position[b] | 2- | 4- | 5- | 2,4- | 2,5- | 4,6- |
| $GaCl_3$ | 1 min | 5 | 15 | trace | 24 | trace | 40 |
| | 12 h | 11 | 30 | 19 | 2 | 11 | 18 |
| $AlCl_3$ | 1 min | 9 | 83 | trace | nd[c] | nd[c] | trace |

[a]Based on bromine, as determined by $^1$H-NMR. [b]Bromide positions. Numbering based on the starting *m*-xylene. [c]Not detected by GC–MS.

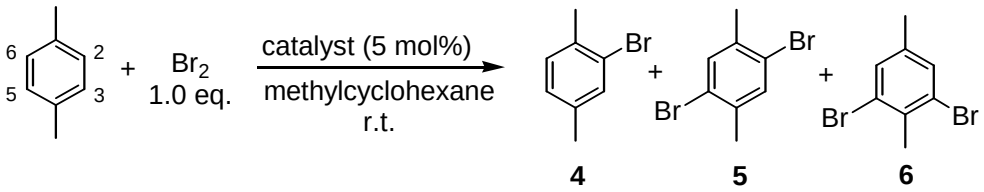


**Table 3.** Bromination of *p*-Xylene

| Catalyst | Time | Yield[a] (%) | | |
|---|---|---|---|---|
| | | **4** | **5** | **6** |
| $GaCl_3$ | 5 min | 20 | 64 | 8 |
| | 12 h | 64 | 28 | 6 |
| $AlCl_3$ | 5 min | 47 | 46 | 6 |
| | 12 h | 67 | 29 | 3 |

[a]Based on bromine, as determined by $^1$H-NMR.

Bromination of 1,2,3- and 1,3,5-trimethylbenzene with $GaCl_3$ initially gives considerable amounts of dibromo- and tribromoarenes, which are converted into monobromoarenes (Table 4). It should be noted that 5-bromo-1,2,3-trimethylbenzene can be prepared in one step from the corresponding hydrocarbon. The previous preparation of this compound employed a multistep process.[8] Reactions of both 1,2,3,4-tetramethyl- and 1,2,4,5-tetramethylbenzene with $GaCl_3$ give initially equal amounts of monobromides and dibromides, which are converted into the monobromides after 12 h (Table 4). Thus, the second and/or the third brominations are faster than the first bromination in the reactions catalyzed by $GaCl_3$. It seems that the bromide group behaves as an activating group in the electrophilic substitution. We propose that the interaction of $GaCl_3$ with Br, as well as the C-H bonds of neighboring methyl groups, promote such polybromination. Previously, we reported aromatic substitution reactions which involve interactions between $GaCl_3$ and C-H bonds.[5] The monobrominated arenes obtained here are the thermodynamically controlled products, because of the lower numbers of *o*- interactions between the bromide and the methyl group.

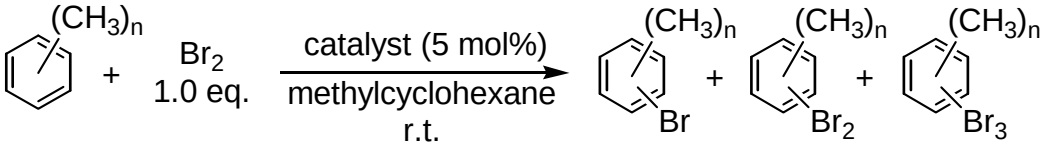


**Table 4.** Bromination of tri- and tetramethylbenzenes

| Substrate | Catalyst | Time | Yield[a] (%) | | |
|---|---|---|---|---|---|
| | | | Monobromide | Dibromide | Tribromide |
| 1,2,3-Trimethylbenzene | $GaCl_3$ | 1 min | 18 (4), 15 (5) | 25 (4,6) | 42 |
| | | 12 h | 22 (4), 50 (5) | 10 (4,6) | nd[b] |
| 1,3,5-Trimethylbenzene | $GaCl_3$ | 1 min | 16 | 54 | 27 |
| | | 12 h | 40 | 34 | 22 |
| | $AlCl_3$ | 1 min | 84 | 14 | Trace |
| 1,2,3,4-Tetramethylbenzene | $GaCl_3$ | 1 min | 52 | 41 | - |
| | | 12 h | 90 | 4 | - |
| 1,2,4,5-Tetramethylbenzene | $GaCl_3$ | 1 min | 50 | 41 | - |
| | | 12 h | 71 | 26 | - |
| | $AlCl_3$ | 1 min | 76 | 22 | - |

[a]Based on bromine, as determined by $^1$H-NMR. In parentheses is the brominated position. Numbering based on starting trialkylbenzene. [b]Not detected by GC–MS.

## Experimental Section

**Typical procedures for bromination.** Under an argon atmosphere, a 1.0 *M* solution of $GaCl_3$ in methylcyclohexane (0.25 mL, 5 mol %) was added to a methylcyclohexane (7.5 mL) solution of hexylbenzene (0.90 mL, 5.0 mmol) at room temperature. After 5 min, bromine (0.25 mL, 5.0 mmol) was added, and the mixture was stirred for 12 h. Then saturated aqueous $Na_2SO_3$ was added, and the organic materials were extracted three times with hexane, the extracts dried over $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography (*n*-hexane) to give a mixture (852 mg) of *o*-**1**, *m*-**1**, and *p*-**1** in 18%, 38%, and 15% yield, respectively. $^1$H-NMR (400 MHz, $CDCl_3$): δ 0.88–0.91 (9H, m, *o, m, p*), 1.29–1.39 (18H, m, *o, m, p*), 1.55–1.62 (6H, m, *o, m, p*), 2.52–2.58 (4H, m, *m, p*), 2.71 (2H, t, *J* = 8.0 Hz, *o*), 7.00–7.05 (m, 1H, *o*, 2H, *p*), 7.06 (1H, d, *J* = 8.8 Hz, *m*), 7.13 (1H, t, *J* = 8.0 Hz, *m*), 7.19–7.21 (2H, m, *o*), 7.29 (1H, d, *J* = 7.2 Hz, *m*), 7.34 (1H, s, *m*), 7.37 (2H, d, *J* = 8.8 Hz, *p*), 7.51 (1H, d, *J* = 8.0 Hz, *o*). $^{13}$C-NMR (100 MHz, $CDCl_3$): δ14.2 (*o, m, p*), 22.7 (*m, p*), 22.7 (*o*), 29.0 (*p*), 29.0 (*m*), 29.2 (*o*), 30.0 (*o*), 31.3 (*m*), 31.4 (*p*), 31.8 (*o, m, p*), 35.4 (*p*), 35.7 (*m*), 36.3 (*o*), 119.1 (*p*), 122.2 (*m*), 124.3 (*o*), 126.9 (*m*), 127.1 (*o*), 127.2 (*o*), 128.5 (*m*), 129.6 (*m*), 130.0 (*o*), 130.1 (*o*), 131.1 (*p*), 131.3 (*m*), 132.6 (*o*), 141.7 (*p*), 142.0 (*o*), 145.1 (*m*). IR (neat) 2955, 2927, 2856, 1595, 1568, 1488, 1469, 1378, 1072, 1024, 1011, 774, 749, 692 cm$^{-1}$. MS (EI) *m/z* 242 ($M^+$+2, 37), 240 ($M^+$, 38), 172 ($M^+$-68, 54), 171 ($M^+$-69, 71), 169 ($M^+$-71, 68), 91 ($M^+$-149, 100), 43 ($M^+$-197, 63). HRMS. Calcd for $C_{12}H_{17}Br$: 240.0513. Found: 240.0523. Anal. Calcd for $C_{12}H_{17}Br$: C; 59.76, H; 7.10, Br; 33.13%. Found: C; 59.60, H; 7.09, Br; 33.28%.

**Preparation of 1-bromo-3-hexylbenzene.** Under an argon atmosphere, a 1.6 *M* hexane solution of *n*-BuLi (44 mL, 70 mmol) was added to a THF solution (100 mL) of 1-pentyltriphenylphosphonium bromide (24.8 g, 60 mmol) at –78 ºC. After stirring for 1 h at room temperature, *m*-bromobenzaldehyde (5.83 mL, 50 mmol) was added at –78 ºC, and the mixture was stirred for 2 h at room temperature, then saturated aq. $NH_4Cl$ was added. The organic materials were extracted three times with *n*-hexane, dried over $MgSO_4$ and concentrated. Flash chromatography over silica gel (*n*-hexane) gave 1-bromo-3-(2-hexenyl)benzene (9.24 g, 78%, *E*:*Z* = 2:5). Under a hydrogen atmosphere, a mixture of methanol (35 mL), 1-bromo-3-(2-hexenyl)benzene (9.24 g, 38.8 mmol) and $PtO_2$ (158.5 mg, 1.8 mol %) was stirred for 5 h at room temperature. Then $PtO_2$ was removed by filtration, and the solution concentrated. Flash chromatography over silica gel (*n*-hexane) gave 1-bromo-3-hexylbenzene (6.25 g, 95%). $^1$H-NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 7.2 Hz), 1.25–1.35 (6H, m), 1.58 (2H, quintet, *J* = 7.2 Hz), 2.56 (2H, t, *J* = 8.0 Hz), 7.08 (1H, d, *J* = 7.2 Hz), 7.12 (1H, t, *J* = 8.0 Hz), 7.29 (1H, d, *J* = 7.6 Hz), 7.32 (1H, s). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 29.0, 31.3, 31.7, 35.7, 122.1, 126.9, 128.5, 129.6, 131.2, 145.1. IR (neat) 2955, 2928, 2856, 1594, 1567, 1470, 1424, 1071, 776, 691 cm$^{-1}$. MS (EI) *m/z* 242 ($M^+$+2, 27), 240 ($M^+$, 27), 172 ($M^+$-68, 68), 171 ($M^+$-69, 41), 170 ($M^+$-70, 69), 169 ($M^+$-71, 37), 91 ($M^+$-149, 100), 43 ($M^+$-197, 54). HRMS. Calcd for $C_{12}H_{17}Br$: 240.0513. Found: 240.0541.

1-Bromo-2-hexylbenzene and 1-bromo-4-hexylbenzene were also synthesized by this method.

**1-Bromo-2-hexylbenzene.** $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, *J* = 7.2 Hz), 1.29–1.41 (6H, m), 1.60 (2H, quintet, *J* = 7.6 Hz), 2.71 (2H, t, *J* = 8.0 Hz), 7.00–7.04 (1H, m), 7.18–7.23 (2H, m), 7.51 (1H, d, *J* = 8.0 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 29.1, 30.0, 31.7, 36.3, 124.3, 127.1, 127.1, 130.1, 132.5, 141.9. IR (neat) 2955, 2927, 2857, 1566, 1469, 1438, 1377, 1024, 748, 658 cm$^{-1}$. MS (EI) *m*/*z* 242 ($M^+$+2, 22), 240 ($M^+$, 23), 172 ($M^+$-68, 24), 171 ($M^+$-69, 38), 170 ($M^+$-70, 25), 169 ($M^+$-71, 36), 91 ($M^+$-149, 100), 43 ($M^+$-197, 57). HRMS. Calcd for $C_{12}H_{17}Br$: 240.0513. Found: 240.0512.

**1-Bromo-4-hexylbenzene.**[9] $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* = 6.4 Hz), 1.24–1.32 (6H, m), 1.57 (2H, quintet, *J* = 7.2 Hz), 2.54 (2H, t, *J* = 10.8 Hz), 7.40 (2H, d, *J* = 8.0 Hz), 7.37 (2H, d, *J* = 8.0 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 28.9, 31.3, 31.7, 35.4, 119.1, 130.0, 131.0, 141.6. IR (neat) 2955, 2927, 2856, 1487, 1465, 1072, 1011, 801 cm$^{-1}$. MS (EI) *m*/*z* 242 ($M^+$+2, 46), 240 ($M^+$, 47), 171 ($M^+$-69, 98), 169 ($M^+$-71, 100), 91 ($M^+$-149, 46), 43 ($M^+$-197, 27). HRMS. Calcd for $C_{12}H_{17}Br$: 240.0513. Found: 240.0525.

**Preparation of 1-bromo-3-isobutylbenzene.** Under an argon atmosphere, a 1.6 *M* hexane solution of *n*-BuLi (14.5 mL, 23.3 mmol) was added to a THF solution (40 mL) of 2-propyltriphenylphosphonium bromide (5.70 g, 20 mmol) at –78 ºC. After stirring for 1 h at room temperature, *m*-bromobenzaldehyde (1.94 mL, 16.6 mmol) was added at –78 ºC, and the mixture was stirred for 1 h at room temperature. Then saturated $NH_4Cl$ aq. was added. The organic materials were extracted three times with *n*-hexane, dried over $MgSO_4$ and concentrated. Flash chromatography over silica gel (*n*-hexane) gave 1-bromo-3-(2-methyl-1-propenyl)benzene (1.80 g, 51%). To a methanol solution (5.0 mL) of 1-bromo-3-(2-methyl-1-propenyl)benzene (210.0 mg, 1.0 mmol) was added $PtO_2$ (92 mg, 1.8 mol %), and the mixture was stirred for 5 h under a hydrogen atmosphere at room temperature. $Pt/PtO_2$ were removed by filtration, and the solution concentrated. Flash chromatography over silica gel (*n*-hexane) gave 1-bromo-3-isobutylbenzene (72.6 mg, 34%). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 0.89 (6H, d, *J* = 6.8 Hz), 1.84 (1H, septet, *J* = 6.8 Hz), 2.43 (2H, d, *J* = 6.4 Hz), 7.05 (1H, d, *J* = 7.2 Hz), 7.13 (1H, t, *J* = 8.0 Hz), 7.29 (1H, s), 7.30 (1H, d, *J* = 8.4 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 22.4, 30.2, 45.0, 122.0, 127.6, 128.6, 129.4, 131.9, 143.8. IR (neat) 2955, 2924, 2868, 1591, 1566, 1471, 1425, 1073, 770, 693, 669 cm$^{-1}$. MS (EI) *m*/*z* 214 ($M^+$+2, 50), 212 ($M^+$, 51), 172 ($M^+$-40, 86), 171 ($M^+$-41, 62), 170 ($M^+$-42, 87), 169 ($M^+$-43, 58), 91 ($M^+$-121, 58), 43 ($M^+$-169, 100). HRMS. Calcd for $C_{10}H_{13}Br$: 212.0200 Found: 212.0241.

1-Bromo-2-isobutylbenzene and 1-bromo-4-isobutylbenzene were also synthesized by this method.

**1-Bromo-2-isobutylbenzene.** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 0.93 (6H, d, *J* = 6.4 Hz), 0.98 (1H, septet, *J* = 7.2 Hz), 2.60 (2H, d, *J* = 7.2 Hz), 7.04 (1H, t, *J* = 7.2 Hz), 7.16 (1H, d, *J* = 7.2 Hz), 7.21 (1H, t, *J* = 7.2 Hz), 7.52 (1H, d, *J* = 8.0 Hz). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 22.4, 28.8, 45.2, 124.7, 126.8, 127.2, 131.1, 132.6, 140.8. IR (neat) 2956, 2927, 2867, 1566, 1468, 1438, 1383, 1366, 1166, 1076, 1021, 746, 659 cm$^{-1}$. MS (EI) *m*/*z* 214 ($M^+$+2, 46), 212 ($M^+$, 47), 172 ($M^+$-40, 90), 171 ($M^+$-41, 100), 170 ($M^+$-42, 91), 169 ($M^+$-43, 97), 133 ($M^+$-79, 32), 91 ($M^+$-121,

95), 90 ($M^+$-122, 48), 89 ($M^+$-123, 38), 43 ($M^+$-169, 85). HRMS. Calcd for $C_{10}H_{13}Br$: 212.0200 Found: 212.0211.

**1-Bromo-4-isobutylbenzene.** $^1$H NMR (400 MHz, $CDCl_3$) δ 0.88 (6H, d, *J* = 6.8 Hz), 1.82 (1H, septet, *J* = 6.8 Hz), 2.42 (2H, d, *J* = 7.2 Hz), 7.01 (2H, d, *J* = 8.0 Hz), 7.37 (2H, d, *J* = 8.0 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 22.3, 30.2, 44.8, 119.2, 130.6, 130.9, 140.4. IR (neat) 2955, 2923, 2868, 1591, 1488, 1466, 1073, 1012, 839, 785 $cm^{-1}$. MS (EI) *m*/*z* 214 ($M^+$+2, 32), 212 ($M^+$, 32), 172 ($M^+$-40, 34), 171 ($M^+$-41, 98), 170 ($M^+$-42, 35), 169 ($M^+$-43, 100), 91 ($M^+$-121, 27), 90 ($M^+$-122, 28), 43 ($M^+$-169, 38). HRMS. Calcd for $C_{10}H_{13}Br$: 212.0200 Found: 212.0200.

**Bromotoluene (mixture of isomers).** The structures of the products were determined by comparison with authentic commercial samples.

**Bromoethylbenzenes (mixture of isomers).** The structures of 1-bromo-2-ethylbenzene and 1-bromo-4-ethylbenzene were determined by comparison with authentic commercial samples. For 1-bromo-3-ethylbenzene, see ref. 10.

**Bromooctylbenzenes (mixture of isomers).** The structures were determined by analogy with bromohexylbenzenes. For 1-bromo-4-octylbenzene, see ref. 11. $^1$H NMR (400 MHz, $CDCl_3$) δ 0.88 (9H, t, *J* = 7.2 Hz, *o*, *m*, *p*), 1.26–1.29 (30H, m, *o*, *m*, *p*), 1.53-1.62 (6H, m, *o*, *m*, *p*), 2.52–2.58 (4H, m, *m*, *p*), 2.71 (2H, t, *J* = 8.0 Hz, *o*), 7.00–7.05 (m, 1H, *o*, 2H, *p*), 7.08 (1H, d, *J* = 7.4 Hz, *m*), 7.13 (1H, t, *J* = 7.2 Hz, *m*), 7.19–7.21 (2H, m, *o*), 7.30 (1H, d, *J* = 8.0 Hz, *m*), 7.32 (1H, s, *m*), 7.37 (2H, d, *J* = 8.0 Hz, *p*), 7.51 (1H, d, *J* = 8.0 Hz, *o*). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 14.3 (*o*, *m*, *p*), 22.8 (*m*, *p*), 22.8 (*o*), 29.3 (*o*, *m*, *p*), 29.3 (*o*, *m*, *p*), 29.4 (*m*, *p*), 29.5 (*o*), 30.1 (*o*), 31.4 (*m*), 31.4 (*p*), 32.0 (*m*, *p*), 32.0 (*o*), 35.5 (*p*), 35.7 (*m*), 36.3 (*o*), 119.1 (*p*), 122.2 (*m*), 124.3 (*o*), 126.9 (*m*), 127.1 (*o*), 127.2 (*o*), 128.5 (*m*), 129.6 (*m*), 130.0 (*o*), 130.1 (*o*), 131.1 (*p*), 131.3 (*m*), 132.6 (*o*), 141.7 (*p*), 142.0 (*o*), 145.1 (*m*). IR (neat) 2954, 2925, 2855, 1595, 1568, 1488, 1469, 1072, 1023, 1011, 777, 748, 692 $cm^{-1}$. MS (EI) *m*/*z* 270 ($M^+$+2, 17), 268 ($M^+$, 17), 172 ($M^+$-96, 28), 171 ($M^+$-97, 37), 170 ($M^+$-98, 29), 169 ($M^+$-99, 37), 91 ($M^+$-177, 100), 57 ($M^+$-211, 78), 43 ($M^+$-225, 60). HRMS. Calcd for $C_{14}H_{21}Br$: 268.0826. Found: 268.0799. Anal. Calcd for $C_{14}H_{21}Br$: C; 62.46, H; 7.86, Br; 29.68%. Found: C; 61.98, H; 8.03, Br; 29.76%.

**Bromoisobutylbenzenes (mixture of isomers).** $^1$H NMR (400 MHz, $CDCl_3$) δ 0.89 (6H, d, *J* = 6.8 Hz, *p*), 0.89 (6H, d, *J* = 6.8 Hz, *m*), 0.93 (6H, d, *J* = 6.4 Hz, *o*), 1.79–1.90 (2H, m, *m*, *p*), 1.99 (1H, septet, *J* = 7.2 Hz, *o*), 2.41–2.44 (4H, m, *m*, *p*), 2.60 (2H, d, *J* = 7.2 Hz, *o*), 7.00 (2H, d, *J* = 8.0 Hz, *p*), 7.01–7.06 (2H, m, *o*, *m*), 7.13 (1H, t, *J* = 8.0 Hz, *m*), 7.16 (1H, d, *J* = 8.0 Hz, *o*), 7.21 (1H, t, *J* = 7.6 Hz, *o*), 7.29 (1H, s, *m*), 7.30 (1H, d, *J* = 8.4 Hz, *m*), 7.37 (2H, d, *J* = 8.0 Hz, *p*), 7.52 (1H, d, *J* = 8.4 Hz, *o*). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 22.4 (*o*), 22.4 (*m*), 22.4 (*p*), 28.9 (*o*), 30.2 (*m*, *p*), 44.8 (*p*), 45.1 (*m*), 45.2 (*o*), 119.2 (*p*), 122.1 (*m*), 124.7 (*o*), 126.8 (*o*), 127.2 (*o*), 127.6 (*m*), 128.6 (*m*), 129.5 (*m*), 130.7 (*p*), 131.0 (*p*), 131.2 (*o*), 131.9 (*m*), 132.6 (*o*), 140.4 (*p*), 140.8 (*o*), 143.9 (*m*). IR (neat) 2955, 2925, 2868, 1592, 1567, 1488, 1469, 1384, 1366, 1167, 1074, 1021, 841, 771, 747, 693, 669 $cm^{-1}$. MS (EI) *m*/*z* 214 ($M^+$+2, 62), 212 ($M^+$, 63), 172 ($M^+$-40, 90), 171 ($M^+$-41, 100), 170 ($M^+$-42, 93), 169 ($M^+$-43, 95), 91 ($M^+$-121, 48), 43

($M^+$-169, 90). HRMS. Calcd for $C_{10}H_{13}Br$: 212.0200. Found: 212.0187. Anal. Calcd for $C_{10}H_{13}Br$: C; 56.36, H; 6.15, Br; 37.49%. Found: C; 56.12, H; 6.08, Br; 37.52%.

**Bromoneopentylbenzenes (mixture of isomers).** The structures of all the isomers were determined by analogy with bromo-isobutylbenzenes. For 1-bromo-2-neopentylbenzene and 1-bromo-4-neopentyl-benzene, see ref. 12. $^1$H-NMR (400 MHz, $CDCl_3$) δ 0.89 (9H, s, *p*), 0.90 (9H, s, *m*), 0.97 (9H, s, *o*), 2.44 (2H, s, *p*), 2.45 (2H, s, *m*), 2.74 (2H, s, *o*), 6.99 (2H, d, *J* = 8.8 Hz, *p*), 7.00–7.03 (1H, m, *o*) 7.04 (1H, d, *J* = 7.6 Hz, *m*), 7.13 (1H, t, *J* = 7.2 Hz, *m*), 7.20–7.21 (2H, m, *o*), 7.27 (1H, s, *m*), 7.33 (1H, d, *J* = 8.0 Hz, *m*), 7.38 (2H, d, *J* = 8.0 Hz, *p*), 7.54 (1H, d, *J* = 8.0 Hz, *o*). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 29.4, 29.4, 29.7, 31.8, 31.9, 33.3, 48.0, 49.6, 49.9, 119.6, 121.6, 125.9, 126.4, 127.3, 128.7, 128.9, 129.0, 130.5, 132.0, 132.2, 132.8, 133.1, 138.5, 139.2, 141.9 cm$^{-1}$. IR (neat) 2953, 2865, 1592, 1567, 1488, 1474, 1423, 1393, 1364, 1236, 1205, 1073, 997, 890, 841, 804, 785, 741, 696. MS (EI) *m*/*z* 228 ($M^+$+2, 10), 226 ($M^+$, 11), 172 ($M^+$-54, 19), 170 ($M^+$-56, 20), 57 ($M^+$-169, 100). HRMS. Calcd for $C_{11}H_{15}Br$: 226.0357. Found: 226.0346. Anal. Calcd for $C_{11}H_{15}Br$: C; 58.17, H; 6.66, Br; 35.18%. Found: C; 57.93, H; 6.71, Br; 35.01%.

**2-Bromo-1,3-dimethylbenzene, 1-bromo-2,4-dimethylbenzene and 1-bromo-3,5 dimethylbenzene.** Structures determined by comparison with commercial authentic samples.

**1-Bromo-2,5-dimethylbenzene and 1,4-dibromo-2,5-dimethylbenzene.** Structures determined by comparison with commercial authentic samples.

**Dibromo-1,3-dimethylbenzene (mixture of isomers).** For 2,5-dibromo-1,3-dimethylbenzene and 4,6-dibromo-1,3-dimethylbenzene, see ref. 13. $^1$H NMR (400 MHz, $CDCl_3$) δ 2.30 (6H, s, *4,6*), 2.37 (3H, s, *2,4*), 2.38 (6H, s, *2,5*), 2.60 (6H, s, *2,4*), 6.93 (1H, d, *J* = 8.0 Hz, *2,4*), 7.09 (1H, s, *4,6*), 7.21 (1H, s, *2,5*), 7.38 (1H, d, *J* = 8.0 Hz, *2,4*), 7.67 (1H, s, *4,6*). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 22.3, 23.7, 24.2, 24.4, 120.1, 121.8, 126.1, 127.9, 128.7, 130.6, 130.7, 132.4, 134.7, 136.6, 137.1, 137.6, 140.0. FT-IR (neat) 2978, 2952, 2920, 1560, 1456, 1378, 1261, 1122, 1051, 1029, 997, 854. MS (EI) *m*/*z* 266 ($M^+$+4, 51), 264 ($M^+$+2, 100), 262 ($M^+$, 55), 185 ($M^+$-77, 68), 183 ($M^+$-79, 72), 104 ($M^+$-158, 53), 103 ($M^+$-159, 59), 51 ($M^+$-211, 48). HRMS. Calcd for $C_8H_8Br_2$: 261.8992. Found: 261.8980.

**1-Bromo-2,4,6-trimethylbenzene and 1,3-dibromo-2,4,6-trimethylbenzene.** The structures of the products were determined by comparison with commercial authentic samples.

**1,3,5-Tribromo-2,4,6-trimethylbenzene.**[14] $^1$H NMR (400 MHz, $CDCl_3$) δ 2.65 (9H, s). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 26.4, 124.8, 136.8. IR (KBr) 2919, 1538, 1434, 1375, 1349, 1017, 954, 647 cm$^{-1}$. MS (EI) *m*/*z* 358 ($M^+$+4, 97), 356 ($M^+$+2, 100), 354 ($M^+$, 279 ($M^+$-75, 50), 277 ($M^+$-77, 95), 275 ($M^+$-79, 50), 117 ($M^+$-237, 56), 116 ($M^+$-238, 66), 115 ($M^+$-239, 72). HRMS. Calcd for $C_9H_9Br_3$: 353.8255. Found: 353.8283.

**1-Bromo-2,3,4-trimethylbenzene.**[14,15] $^1$H NMR (400 MHz, $CDCl_3$) δ 2.23 (6H, s), 2.39 (3H, s), 6.84 (1H, d, *J* = 8.0 Hz), 7.28 (1H, d, *J* = 8.0 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 16.9, 20.1, 20.7, 122.7, 128.4, 129.2, 135.4, 135.4, 136.8. IR (neat) 2942, 1582, 1455, 1405, 1378, 1250, 1181, 1134, 1077, 1000, 893, 851, 826, 801 cm$^{-1}$. MS (EI) *m*/*z* 200 ($M^+$+2, 69), 198 ($M^+$, 72), 119 ($M^+$-79, 100). HRMS. Calcd for $C_9H_{11}Br$: 198.0044 Found: 198.0028.

**5-Bromo-1,2,3-trimethylbenzene.**[16] $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 2.10 (3H, s), 2.24 (6H, s), 7.14 (2H, s). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 15.1, 20.5, 20.7, 118.1, 129.9, 133.8, 138.3. IR (neat) 2920, 1579, 1470, 1455, 1377, 1185, 1000, 851, 801 cm$^{-1}$. MS (EI) *m*/*z* 200 ($M^+$+2, 59), 198 ($M^+$, 60), 119 ($M^+$-79, 100). HRMS. Calcd for $C_9H_{11}Br$: 198.0044 Found: 198.0046.

**1,5-Dibromo-2,3,4-trimethylbenzene.**[17] $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 2.30 (3H, s), 2.35 (6H, s), 7.64 (1H, s). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 18.4, 20.2, 122.5, 132.6, 134.8, 138.1. IR (KBr) 2920, 1557, 1440, 1415, 1378, 1160, 1008, 904, 856, 655 cm$^{-1}$. MS (EI) m/z 280 ($M^+$+4, 50), 278 ($M^+$+2, 100), 276 ($M^+$, 53), 199 ($M^+$-77, 57), 197 ($M^+$-79, 58). HRMS. Calcd for $C_9H_{10}Br_2$: 275.9149. Found: 375.9164.

**1,2,3-Tribromo-4,5,6-trimethylbenzene.**[14] $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 2.30 (3H, s), 2.49 (9H, s). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 19.0, 23.0, 125.5, 125.7, 136.2, 137.2. IR (KBr) 2919, 1430, 1371, 1354, 1232, 1004, 930, 657 cm$^{-1}$. MS (EI) *m*/*z* 358 ($M^+$+4, 96), 356 ($M^+$+2, 100), 354 ($M^+$, 36), 277 ($M^+$-77, 62), 115 ($M^+$-239, 40). HRMS. Calcd for $C_9H_9Br_3$: 353.8254. Found: 353.8244.

**3-Bromo-1,2,4,5-tetramethylbenzene.** The structure of the product was determined by comparison with commercial authentic sample.

**1,4-Dibromo-2,3,5,6-tetramethylbenzene.**[14] $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 2.48 (12H, s). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 22.4, 127.9, 134.8. IR (KBr) 2922, 1414, 1381, 1173, 987, 690 cm$^{-1}$. MS (EI) *m*/*z* 294 ($M^+$+4, 50), 292 ($M^+$+2, 100), 290 ($M^+$, 53), 213 ($M^+$-77, 69), 211 ($M^+$-79, 74). HRMS. Calcd for $C_{10}H_{12}Br_2$: 289.9305. Found: 289.9333.

**1-Bromo-2,3,4,5-tetramethylbenzene.**[14,15] $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 2.14 (3H, s), 2.22 (3H, s), 2.24 (3H, s), 2.37 (3H, s), 7.23 (1H, s). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 16.1, 17.4, 20.1, 20.5, 122.0, 130.6, 132.8, 134.0, 135.2, 136.6. IR (neat) 2922, 1460, 1379, 1199, 941, 859, 752 cm$^{-1}$. MS (EI) *m*/*z* 214 ($M^+$+2, 60), 212 ($M^+$, 62), 133 ($M^+$-79, 100). HRMS. Calcd for $C_{10}H_{13}Br$: 212.0200. Found: 212.0191.

**1,2-Dibromo-3,4,5,6-tetramethylbenzene.**[14] $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 2.24 (6H, s), 2.49 (6H, s). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 17.9, 22.8, 125.3, 135.2, 135.4. IR (KBr) 2918, 1374, 1255, 1193, 992, 951, 889, 770 cm$^{-1}$. MS (EI) *m*/*z* 294 ($M^+$+4, 51), 292 ($M^+$+2, 100), 290 ($M^+$, 53), 213 ($M^+$-77, 55), 211 ($M^+$-79, 56). HRMS. Calcd for $C_{10}H_{12}Br_2$: 289.9305. Found: 289.9316.

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