Electronic Supplementary Information (ESI) for:

Aromatic substitution in ball mills: Formation of aryl chlorides and bromides using potassium peroxomonosulfate and NaX

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Spectral data of halogenated products listed in Tables 4 and 5 as well as Scheme 2

In case of **5a,b** and **9a,b-12,a,b** spectral data for the mixture of *o*- and *p*-isomers are presented. Comparison with original compounds and the ratio of the GC-MS signals was used for identification and determination of the isomeric ratio, respectively. Side products of the reactions have not been isolated.

Products **15a,b** were not isolated due to low selectivity. For spectral data of the main products see literature.[1]

Bromomesitylene (**2a**):[2] EIMS, m/z (rel. Int.):198 (70, M^+), 119 (100), 91 (35); ^{1}H NMR ($CDCl_3$) δ (ppm) = 6.89 (s, 2H), 2.39 (s, 6H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 137.85, 136.23, 128.99, 124.17, 23.66, 20.62.

Chloromesitylene (**3a**):[2] EIMS, m/z (rel. Int.):154 (60, M^+), 139 (10), 119 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 6.92 (s, 1H), 2.37 (s, 6H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 135.78, 135.49, 131.55, 129.15, 20.61, 20.50

4-Bromotoluene (**5a**):[2] EIMS, m/z (rel. Int.): 170 (45, M+), 91(100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.378 (d, *J* = 8.30 Hz, 2H), 7,050 (d, *J* = 8.05 Hz, 2H), 2,311 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 136.73, 131.22, 130.79, 119.05, 20.88.

4-Chlorotoluene (**5b**):[2] EIMS, m/z (rel. Int.): 126 (45, M+), 91 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.21 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 136.19, 131.06, 130.33, 128.24, 20.78.

1-Bromo-3,4-dimethylbenzene (**6a**):[3] EIMS, m/z (rel. Int.): 184 (55, M+), 105 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.4 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 2.27 (s, 3H), 2.22 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 138.9, 135.4, 132.29, 131.16, 238.70, 119.20, 19.60, 16.25.

1-Chloro-3,4-dimethylbenzene (**6b**):[2] EIMS, m/z (rel. Int.):140 (45, M^+), 125 (25), 105 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.2-7.0 (m, 3H), 2.30 (s, 3H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 138.2, 134.88, 131.11, 130.75, 129.60, 125.80, 19.64, 19.14.

1-Bromo-2,4-dimethylbenzene (**7a**):[2] EIMS, m/z (rel. Int.):184 (55, M^+), 105 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.41 (d, *J* = 8.1 Hz, 1H), 7.06 (s, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 2.38 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 137.42, 137.02, 132.01, 131.65, 128.15, 121.49, 22.74, 20.78.

1-Chloro-2,4-dimethylbenzene (**7b**):[2] EIMS, m/z (rel. Int.):140 (45, M^+), 125 (25), 105 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.19 (d, *J* = 8.06 Hz, 1H), 7.05 (s, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 1.18 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 136.28, 135.57, 131.68, 128.72, 128.36, 127.75, 20.73, 19.89.

1-Bromo-2,5-dimethylbenzene (**8a**):[2] EIMS, m/z (rel. Int.): 184 (55, M^+), 105 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.37 (s, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 2.37 (s, 3H, 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 137.0, 134.64, 132.74, 130.48, 128.0, 134.63, 22.32, 20.51.

1-Chloro-2,5-dimethylbenzene (**8b**):[2] EIMS, m/z (rel. Int.):140 (45, M^+), 125 (25), 105 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.17 (s, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 2.32 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 136.96, 133.98, 132.71, 130.63, 129.5, 127.3, 20.64, 19.48.

1-Bromo-4-ethylbenzene (**9a**):[2] EIMS, m/z (rel. Int.):184 (55, M^+), 169 (100), 105 (60); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.41 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.60 (m, 2H), 1.22 (3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 143.14, 131.33, 129.64, 119.27, 28.32, 15.61.

1-Chloro-4-ethylbenzene (**9b**):[4] EIMS, m/z (rel. Int.):140 (40, M^+), 125 (100), 105 (50); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.3-7.1 (m), 2.64 (s, 2H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 142.53, 131.22, 129.43, 128.29, 28.81, 15.51.

4-Bromoanisole (**10a**):[2] EIMS, m/z (rel. Int.):186 (100, M^+), 171 (40), 143 (40); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.352 (d, *J* = 8.92 Hz, 2H), 6.756 (d, *J* = 8.92 , 2H), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 158.66, 132.17, 115.68, 112.75, 55.35.

4-Chloroanisole (**10b**):[2] EIMS, m/z (rel. Int.):142 (100, M^+), 127 (60), 99 (50); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.21 (d, *J* = 8.93 Hz, 2H), 6.80 (d, *J* = 8.96 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 158.17, 129.24, 125.49, 115.14, 55.42.

4–Bromophenol (**11a**):[2] EIMS, m/z (rel. Int.):172 (100), 93, (10), 65 (30); ^{1}H NMR ($CDCl_3$) δ (ppm) = 6.95 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 8.8 Hz, 2H), 5,7 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 155.68, 132.29, 117.29, 111.95.

4-Chlorophenol (**11b**):[2] EIMS, m/z (rel. Int.):128 (100), 64 (30); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.28 (d, *J* = 7.95 Hz, 2H), 6.97 (d, *J* = 8.15 Hz, 2H), 5.2 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 154.99, 129.29, 124.76, 116.72.

4-Chloro-2,3,5-trimethylphenol (**12b**): EIMS, m/z (rel. Int.): 170 (80, M^+), 155 (25), 135 (100), 91 (30); ^{1}H NMR ($CDCl_3$) δ (ppm) = 6.6 (2, 1H), 5.6 (2, 1H), 2.44 (s, 3H), 2.31 (s, 3H), 2.28 (2, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 149.1, 135.8, 132.4, 126.4, 121.1, 117.6, 19.6, 13.3.

4-Bromo-2,3,6-trimethylphenol (**13a**):[2] EIMS, m/z (rel. Int.):214 (100, M^+), 135 (80), 91 (40); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.19 (s, 1H), 4.61 (s, 1H), 2,35 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 151.13, 134.55, 131.00, 123.73, 122.06, 115.65, 19.71, 15.58, 13.04.

4-Chloro-2,3,6-trimethylphenol (**13b**):[5] EIMS, m/z (rel. Int.):170 (90, M^+), 155 (15), 135 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 6.94 (s, 1H), 4.5 (s, 1H), 2,30 (s, 3H), 2.20 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 150.59, 132.71, 127.77, 125.36, 121.68, 16.53, 15.69, 12.74.

3-Bromo-4-hydroxybenzaldehyde (**14a**):[6] EIMS, m/z (rel. Int.):200(100, M^+), 171 (20), 143 (20); ^{1}H NMR ($CDCl_3$) δ (ppm) = 9.80 (s, 1H), 7.98 (s, 1H), 7.83-7.74 (m, 1H), 7.14 (d, J=8.3, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 190.19, 158.18, 134.50, 131.44, 116.17, 111.15.

3-Chloro-4-hydroxybenzaldehyde (**14b**):[2] EIMS, m/z (rel. Int.):156 (75, M^+), 155 (100), 127 (25), 99 (25); ^{1}H NMR ($CDCl_3$) δ (ppm) = 9.82 (s, 1H), 8,07-7,02 (m, 4H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 190.22, 157.05, 132.69, 131.02, 130.37, 121.26, 117.8.

1-Bromonaphthalene (**19a**):[2] EIMS, m/z (rel. Int.): 206 (100, M^+), 127 (95); ^{1}H NMR ($CDCl_3$) δ (ppm) = 8.28 (d, *J* = 7.8 Hz, 1H), 7.82-7.7 (m, 3H), 7.68-7.5 (m, 2H), 7.37-7.23 (m, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 134.5, 132.1, 129.9, 128.3, 127.9, 127.3, 127.1, 126.7, 126.2, 122.9.

1-Chloronaphthalene (**19b**):[2] EIMS, m/z (rel. Int.):162 (100, M^+), 127 (50); ^{1}H NMR ($CDCl_3$) δ (ppm) = 8.32 (d, *J* = 8,2 Hz, 1H), 7.89-7.2 (m, 7H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 134.58, 131.95, 130.84, 128.20, 127.14, 127.01, 126.66, 126.14, 125.69, 124.42.

9-Bromoanthracene (**20a**):[2] EIMS, m/z (rel. Int.):256 (100, M^+), 176 (40); ^{1}H NMR ($CDCl_3$) δ (ppm) = 8.5-8.3 (m), 7.7-7.46 (m); ^{13}C NMR ($CDCl_3$) δ (ppm) = 132.16, 130.59, 128.58, 127.62, 127.18, 127.09, 125.63, 122.34.

9,10-Dichloroanthracene:[2] EIMS, m/z (rel. Int.):246 (100, M^+), 176 (40); ^{1}H NMR ($CDCl_3$) δ (ppm) = 8.58-8.5 (m, 2H), 7.7-7.6 (m, 2H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 129.11, 128.54, 127.15, 125.16.

1,2-Dibromo-1-phenylethane (**24a**):[7] EIMS, m/z (rel. Int.):264 (5, M^+), 183 (100), 104 (90), 77 (25); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.4-7.3 (m, 5H), 5.1 (dd, *J* = 5.8 Hz, 1H), 4.08-4.02 (m, 2H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 138.6, 129.08, 127.60, 50.79, 34.91.

1,2-Dichloro-1-phenylethane (**24b**):[8] EIMS, m/z (rel. Int.):174 (20, M^+), 139 (20), 125 (100), 103 (35), 77 (30); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.6-7.3 (m), 5.02 (dd, *J* = 6.6 Hz, 1H), 4.05-3.9 (m); ^{13}C NMR ($CDCl_3$) δ (ppm) = 138.0, 129, 128.64, 127.40, 61.77, 48.35.

1,2-Dibromo-1-phenylethene (**26a**):[9] EIMS, m/z (rel. Int.):260 (35, M^+), 181 (60), 102 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.43-7.31 (m, 5H), 6.68 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 136.9, 132.0, 129.34, 129.14, 128.52, 102.92.

1,2-Dichloro-1-phenylethene (**26b**): EIMS, m/z (rel. Int.):75 (50), 102 (90), 137 (100), 172 (70, M^+); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.5-7.3 (m, 5H), 6.5 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 133.9, 131.5, 129.4, 128.6, 128.5, 114.2.

2,2-Dibromo-1-phenylethanone (**27a**):[10] EIMS, m/z (rel. Int.):171 (5), 169 (5), 105 (100), 77 (40); ^{1}H NMR ($CDCl_3$) δ (ppm) = 8.12-7.9 (m, 2H), 7.29-7.61 (m, 3H), 6.64 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 185.93, 134.42, 130.86, 129.69, 128.92, 39.65, 30.85.

2,2-Dichloro-1-phenylethanone (**27b**):[11] EIMS, m/z (rel. Int.): 125 (10), 105 (100), 77 (50); ^{1}H NMR ($CDCl_3$) δ (ppm) = 8.08 (m, 2H), 7.6-7.2 (m, 3H), 6.77 (s, 1H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 185.88, 134.54, 131.35, 129.74, 128.91, 67.8.

1,2-Dibrom-1,2-diphenylethene (**28a**):[12] ^{1}H NMR (CDCl3) δ (ppm) = 7.74-7.12 (m, 10H); ^{13}C NMR (CDCl3) δ (ppm) = 130.21, 129.97, 129.89, 129.65, 128.89, 128.54, 128.33, 128.03.

1,2-Dichloro-1,2-diphenylethene (**28b**):[13] EIMS, m/z (rel. Int.):248 (45, M^+), 213, (25), 178 (100); ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.5-6.9 (m, 10H); ^{13}C NMR ($CDCl_3$) δ (ppm) = 139.56, 130.63, 129.82, 128.84, 128.08

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