Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

# Supporting Information



69451 Weinheim, Germany

**Relative Rates of Bromine-Magnesium Exchange Reactions in Substituted Bromobenzenes**

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**General information:**

All reactions involving the use of Grignard reagents were carried out under nitrogen atmosphere in dried glassware using Schlenk techniques. The materials were purchased from commercial sources and used without further purification. The solvent THF was dried and freshly distilled over sodium/benzophenone before use. Isopropylmagnesium chloride/lithium chloride 1:1 (*i*-PrMgCl·LiCl) in THF was from Chemetall GmbH.

**Gas chromatographic equipment:**

GC analyses were performed on a GC-8130 gas chromatograph (Fisons) equipped with a standard injector, a FI detector, and an Optima-1710 capillary column (0.25 μm × 25m × 0.25mm, Macherey-Nagel). The carrier gas was nitrogen; peak areas were obtained with the integration tool of the Chrom-Card software.

**Determination of relative response factors for the gas chromatographic analysis:**

The relative response factors ($f$)[S1] are now calculated as

$$\frac{A_{R1}}{A_{IS}} = f_{R1}\frac{[R1]}{[IS]} \Rightarrow f_{R1} = \frac{A_{R1}[IS]}{A_{IS}[R1]}$$

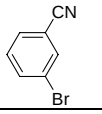
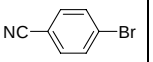
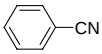
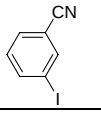
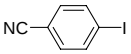
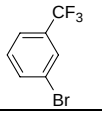
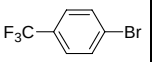
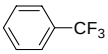
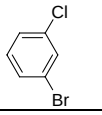
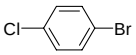
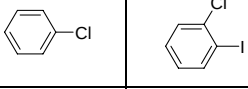
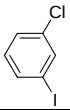
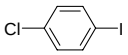
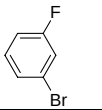
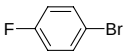
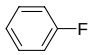
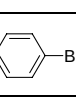
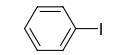
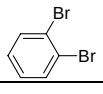
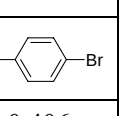
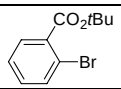
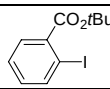
$$\frac{A_{P1}}{A_{IS}} = f_{P1}\frac{[P1]}{[IS]} \Rightarrow f_{P1} = \frac{A_{P1}[IS]}{A_{IS}[P2]}$$

$A_{R1}$, $A_{P1}$, $A_{IS}$ are areas of R1 (reactant 1), P1 (product 1) and internal standard ($n$-$C_{14}H_{30}$).
[R1], [P1], [IS] are the corresponding concentrations.

**Typical procedure**: A mixture of R1, R2, P1, P2, and internal standard ($n$-$C_{14}H_{30}$) was analyzed by GC to give area ratios. Each mixture was run at least three times. For each compound in one run we can get appropriate relative response factor, and the reported values of relative response factors (see **Table 1**) are an average obtained from all runs.

[S1] D. J. David, *Gas Chromatographic Detectors*, Wiley, New York, **1974**; Chapter 3.

***Table 1.*** Relative response factor of reactants and products *versus* internal standard ($n$-$C_{14}H_{30}$)

| *f* |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| Average value | 0.443 | 0.431 | 0.447 | 0.469 | 0.408 | 0.424 | 0.403 |
| | | | | | | | |
| *f* |  |  |  |  |  |  |  |
| Average value | 0.488 | 0.465 | 0.476 | 0.518 | 0.480 | 0.428 | 0.411 |
| | | | | | | | |
| *f* |  |  |  |  |  |  |  |
| Average value | 0.418 | 0.439 | 0.413 | 0.401 | 0.423 | 0.441 | 0.443 |
| | | | | | | | |
| *f* |  |  |  |  |  |  |  |
| Average value | 0.402 | 0.487 | 0.373 | 0.367 | 0.376 | 0.402 | 0.406 |
| | | | | | | | |
| *f* |  |  |  | | | | |
| Average value | 0.482 | 0.654 | 0.630 | | | | |

**Determination of the concentration of *i*-PrMgCl·LiCl solution**

**Method 1**) A 10 mL round-bottom flask equipped with a magnetic stirring bar and a septum was heated with a heat gun under reduced pressure and cooled to room temperature under a nitrogen atmosphere. The dry flask was charged with accurately weighed $I_2$ (*ca.* 1 mmol), fitted with a rubber septum, and flushed with nitrogen. After the iodine was completely dissolved in THF (5 mL), the resulting brown solution was cooled to 0 $^{o}$C in an ice bath and stirred. The *i*-PrMgCl·LiCl was added dropwise *via* a 1.00 mL syringe until the brown color disappeared.

***Table 2***. Determination of the concentration of *i*-PrMgCl·LiCl with $I_2$

| $m_{iodine}$ (mg) | 256.7 | 259.4 | 248.6 | 262.7 |
|---|---|---|---|---|
| $M_{iodine}$ (g/mol) | 253.81 | | | |
| $n_{iodine}$ (mmol) | 1.0114 | 1.0220 | 0.9795 | 1.0350 |
| $V_{i\text{-PrMgCl·LiCl}}$ (mL) | 0.852 | 0.878 | 0.834 | 0.885 |
| $c_{i\text{-PrMgCl·LiCl}}$ (mol/L) | 1.1871 | 1.1640 | 1.1744 | 1.1695 |
| Av $c_{i\text{-PrMgCl·LiCl}}$ (mol/L) | 1.17 | | | |

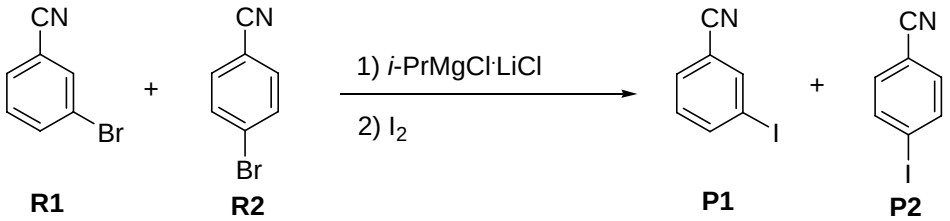
**Method 2**) A 25mL flame-dried, round-bottom flask with a magnetic stirring bar was rapidly charged with a sample of accurately weighed menthol and 1,10-phenanthroline (4 mg) before being capped with a rubber septum and flushed with dry nitrogen via a syringe needle. Freshly distilled (from Na, benzophenone) dry THF (8 mL) was introduced and the resulting solution was stirred at room temperature under nitrogen atmosphere. Dropwise addition of Grignard solution to be assayed was carried out by syringe technique until a distinct violet or burgundy color persisted longer than one minute.

*Table 3*. Determination of the concentration of *i*-PrMgCl·LiCl with menthol

| $m_{menthol}$ (mg) | 177.4 | 142.4 | 184.1 |
|---|---|---|---|
| $M_{menthol}$ (g/mol) | 156.27 | | |
| $n_{menthol}$ (mmol) | 1.1352 | 0.9112 | 1.1781 |
| $V_{i\text{-PrMgCl·LiCl}}$ (mL) | 0.980 | 0.778 | 1.005 |
| $c_{i\text{-PrMgCl·LiCl}}$ (mol/L) | 1.1584 | 1.1713 | 1.1722 |
| Av $c_{i\text{-PrMgCl·LiCl}}$ (mol/L) | 1.17 | | |

**Determination of the Relative Exchange Rates κ**

For a reaction, where reactant R1 gives product P1 and reactant R2 gives product P2, e.g.




**R1** **R2** **P1** **P2**

the relative reactivity of R1 and R2 is expressed by the competition constant κ which is defined by eq. (1)

$$\kappa 1 = \frac{\log([R1]_0/[R1]_t)}{\log([R2]_0/[R2]_t)} \qquad (1)$$

Three different methods have been employed to determine κ

**Method 1**: κ1

Substitution of $[R1]_0$ and $[R2]_0$ in eq.(1) by the expressions in eq.(2) and (3) (mass balance) yields eq.(4)

$$[R1]_0 = [R1]_t + [P1]_t \qquad (2)$$

$$[R2]_0 = [R2]_t + [P2]_t \qquad (3)$$

$$\kappa = \frac{\log(1 + [P1]_t/[R1]_t)}{\log(1 + [P2]_t/[R2]_t)} \qquad (4)$$

Competition constants calculated according to eq. (4) from the chromatographically determined ratios $[P1]_t/[R1]_t$ and $[P2]_t/[R2]_t$ are represented as κ1 in the following Tables.

**Method 2**: κ2

In some cases, the products obtained from R1 and R2 are identical, e.g. in the case of trapping regioisomeric Grignard reagents with methanol. The competition constant (represented as κ2) is then calculated by determining $[R1]_t$ and $[R2]_t$ gas chromatographically (comparison of the areas with that of the internal standard *n*-$C_{14}H_{30}$) and substituting directly into eq. (1). Particularly in the case of a low conversion, the κ2 values are not very reliable and will only be used, if method 1 (κ1) is not applicable.

**Method 3**: κ3

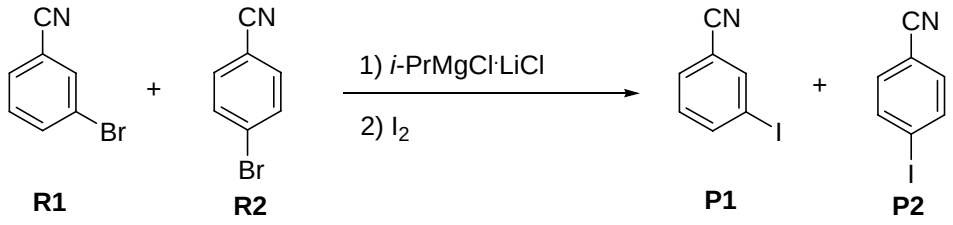
With $[R1]_t = [R1]_0 - [P1]_t$ and $[R2]_t = [R2]_0 - [P2]_t$ eq.(1) is converted into eq.(5)

$$\kappa 3 = \log\left(\frac{[R1]_0}{[R1]_0 - [P1]_t}\right) / \log\left(\frac{[R2]_0}{[R2]_0 - [P2]_t}\right) \qquad (5)$$

$[P1]_t$ and $[P2]_t$ are obtained gas chromatographically by comparison with the internal standard *n*-$C_{14}H_{30}$.

**Typical Procedure (Iodine Quench):** (0.25M : 0.25M)

A dry and nitrogen flushed 25-mL flask, equipped with a magnetic stirrer, was charged with 3-bromobenzonitrile R1 (1.17 mmol, 214 mg), 4-bromobenzonitrile R2 (1.17 mmol, 214 mg) and internal standard (*n*-$C_{14}H_{30}$) in THF (3.70 mL). The reaction mixture was cooled to 0 $^{o}$C. *i*-PrMgCl·LiCl (1.17 mmol, 1.00 mL solution in THF) was added in one portion. After certain times (for example 20 min), about 0.2 mL of the mixture was taken out with a syringe and sprayed on some crystals of iodine under nitrogen protection. The reaction mixture was washed with aqueous $Na_2S_2O_3$ solution (50 mL, 0.15 M). The aqueous phase was extracted with diethylether (about 25 ~ 30 mL). The etheral solutions were dried over $Na_2SO_4$ and analyzed by GC.



Combination of 0.25M 3-bromobenzonitrile (R1), 0.25M 4-bromobenzonitrile (R2), 0.25M internal standard (*n*-$C_{14}H_{30}$), and 0.25M *i*-PrMgCl·LiCl, quenched by iodine, gave the following results:

| | R1 | R2 | IS |
|---|---|---|---|
| m (mg) | 211.7 | 210.9 | 235.6 |
| M (g/mol) | 182.02 | 182.02 | 198.39 |
| c (mol/L) | 0.2475 | 0.2465 | 0.2527 |

| t (h) | $A_{R1}$ | $A_{R2}$ | $A_{P1}$ | $A_{P2}$ | $A_{IS}$ | κ1 | κ2 | κ3 |
|---|---|---|---|---|---|---|---|---|
| 1/3 | 15.0499 | 19.5453 | 6.7717 | 3.4923 | 55.1408 | 2.08 | 2.10 | 2.00 |
| | 15.0143 | 19.5673 | 6.8893 | 3.5328 | 54.9962 | 2.10 | 2.14 | 2.01 |
| | 15.3857 | 19.9790 | 7.0619 | 3.6436 | 53.9298 | 2.08 | (2.40) | 2.01 |
| | Average value | | | | | 2.09 | | 2.01 |
| 2/3 | 12.9983 | 18.5669 | 9.2092 | 4.8034 | 54.4222 | 2.15 | 2.32 | 2.06 |
| | 12.8613 | 18.4479 | 9.0977 | 4.8311 | 54.7621 | 2.13 | 2.27 | 2.01 |
| | 12.8072 | 18.3216 | 9.2977 | 4.7862 | 54.8050 | 2.17 | 2.22 | 2.09 |
| | Average value | | | | | 2.15 | 2.27 | 2.05 |
| 1 | 11.7117 | 17.6839 | 10.2137 | 5.4700 | 54.9206 | 2.15 | 2.25 | 2.03 |
| | 11.8182 | 17.8220 | 10.1801 | 5.4371 | 54.7426 | 2.16 | 2.29 | 2.04 |
| | 11.7127 | 17.7140 | 10.2782 | 5.2270 | 55.0680 | 2.25 | 2.25 | 2.16 |
| | Average value | | | | | 2.19 | 2.26 | 2.08 |
| 2 | 10.9379 | 17.1585 | 11.5968 | 5.9128 | 54.3940 | 2.26 | 2.29 | 2.23 |
| | 10.2767 | 16.6634 | 10.9819 | 6.0799 | 55.9982 | 2.16 | 2.18 | 1.98 |
| | 10.5143 | 16.9494 | 11.1536 | 6.0747 | 55.3081 | 2.19 | 2.26 | 2.03 |
| | Average value | | | | | 2.20 | 2.24 | 2.08 |
| 3 | 10.3427 | 16.5974 | 11.2096 | 6.2144 | 55.6359 | 2.14 | 2.16 | 1.99 |
| | 10.3809 | 16.8515 | 11.2091 | 6.1304 | 55.4282 | 2.19 | 2.25 | 2.02 |
| | 10.2362 | 16.6213 | 11.0693 | 6.2496 | 55.8236 | 2.13 | 2.18 | 1.94 |
| | Average value | | | | | 2.15 | 2.20 | 1.98 |
| 5 | 10.4780 | 17.0178 | 10.2839 | 5.5460 | 56.6743 | 2.24 | 2.21 | 2.01 |
| | 10.3312 | 16.8924 | 10.3730 | 5.6222 | 56.7812 | 2.24 | 2.20 | 2.00 |
| | 10.3504 | 17.0060 | 10.2820 | 5.7380 | 56.6236 | 2.20 | 2.24 | 1.93 |
| | Average value | | | | | 2.23 | 2.22 | 1.98 |

Combination of 0.25M 3-bromobenzonitrile (R1), 0.25M 4-bromobenzonitrile (R2) and 0.25M *i*-PrMgCl·LiCl (evaluation without internal standard), quenched by iodine, gave the following results:

| | R1 | R2 |
|---|---|---|
| m (mg) | 215.7 | 215.7 |
| M (g/mol) | 182.02 | 182.02 |
| c (mol/L) | 0.2521 | 0.2521 |

| t (h) | $A_{R1}$ | $A_{R2}$ | $A_{P1}$ | $A_{P2}$ | κ1 |
|---|---|---|---|---|---|
| 1/3 | 33.0606 | 43.4491 | 15.5554 | 7.9259 | 2.12 |
| | 33.1733 | 43.6104 | 15.5182 | 7.6981 | 2.18 |
| | 33.0770 | 43.5244 | 15.4916 | 7.9070 | 2.12 |
| | Average value | | | | 2.14 |
| 2/3 | 27.7730 | 40.4694 | 20.6560 | 11.1015 | 2.12 |
| | 27.7775 | 40.3213 | 20.8327 | 11.0685 | 2.13 |
| | 27.7483 | 40.3756 | 20.7637 | 11.1125 | 2.12 |
| | Average value | | | | 2.13 |
| 1 | 25.8154 | 38.8883 | 22.9086 | 12.3876 | 2.13 |
| | 25.8185 | 38.8620 | 23.0081 | 12.3114 | 2.14 |
| | 25.6521 | 38.7670 | 23.1014 | 12.4794 | 2.13 |
| | Average value | | | | 2.13 |
| 2 | 23.9543 | 38.1413 | 24.4855 | 13.4190 | 2.16 |
| | 24.0403 | 38.1583 | 24.5550 | 13.2463 | 2.19 |
| | 23.9785 | 38.0808 | 24.5577 | 13.3830 | 2.17 |
| | Average value | | | | 2.17 |
| 3 | 23.9347 | 38.2331 | 24.4719 | 13.3603 | 2.18 |
| | 24.0544 | 38.5069 | 24.4424 | 12.9962 | 2.23 |
| | 24.0774 | 38.5497 | 24.2494 | 13.1235 | 2.20 |
| | Average value | | | | 2.20 |
| 5 | 25.1026 | 39.8214 | 22.6096 | 12.4664 | 2.18 |
| | 24.8764 | 39.6718 | 23.0093 | 12.4425 | 2.22 |
| | 24.9051 | 39.6895 | 23.0831 | 12.3224 | 2.24 |
| | Average value | | | | 2.22 |
| 6 | 26.0706 | 41.5961 | 21.0968 | 11.2366 | 2.29 |
| | 26.1772 | 41.7117 | 21.0196 | 11.0915 | 2.31 |
| | 26.0454 | 41.5641 | 21.2195 | 11.1709 | 2.31 |
| | Average value | | | | 2.30 |

Combination of 0.5M 3-bromobenzonitrile (R1), 0.5M 4-bromobenzonitrile (R2), 0.5M internal standard (*n*-$C_{14}H_{30}$), and 0.5M *i*-PrMgCl·LiCl, quenched by iodine, gave the following results:

| | R1 | R2 | IS |
|---|---|---|---|
| m (mg) | 217.6 | 221.4 | 232.3 |
| M (g/mol) | 182.02 | 182.02 | 198.39 |
| c (mol/L) | 0.5087 | 0.5176 | 0.4983 |

| t (h) | $A_{R1}$ | $A_{R2}$ | $A_{P1}$ | $A_{P2}$ | $A_{IS}$ | κ1 | κ2 | κ3 |
|---|---|---|---|---|---|---|---|---|
| 1/3 | 12.7072 | 19.6216 | 9.694 | 5.0685 | 52.9087 | 2.28 | (2.69) | 2.12 |
| | 12.5848 | 19.0246 | 9.5247 | 4.6538 | 54.211 | 2.38 | 2.28 | 2.27 |
| | 12.4496 | 19.0421 | 9.8044 | 4.986 | 53.718 | 2.31 | 2.37 | 2.18 |
| | Average value | | | | | 2.32 | | 2.19 |
| 2/3 | 10.8027 | 18.0186 | 11.4816 | 6.1555 | 53.5416 | 2.28 | 2.42 | 2.13 |
| | 10.8712 | 18.1586 | 11.4923 | 6.0495 | 53.4302 | 2.32 | 2.47 | 2.18 |
| | 10.774 | 18.0142 | 11.5037 | 6.2149 | 53.4932 | 2.27 | 2.43 | 2.11 |
| | Average value | | | | | 2.29 | 2.44 | 2.14 |
| 1 | 10.1614 | 17.5698 | 12.3319 | 6.3635 | 53.5734 | 2.38 | 2.42 | 2.27 |
| | 10.3132 | 17.8859 | 12.299 | 6.1599 | 53.3419 | 2.45 | 2.52 | 2.36 |
| | 9.9353 | 17.2725 | 12.6884 | 6.5651 | 53.5387 | 2.37 | 2.37 | 2.29 |
| | Average value | | | | | 2.40 | 2.44 | 2.31 |
| 2 | 9.4324 | 16.9795 | 12.4221 | 6.7239 | 54.4422 | 2.33 | 2.34 | 2.14 |
| | 9.4945 | 16.9765 | 12.1855 | 6.5304 | 54.8131 | 2.35 | 2.30 | 2.15 |
| | 9.7155 | 17.4122 | 12.2226 | 6.6992 | 53.9505 | 2.32 | 2.45 | 2.11 |
| | Average value | | | | | 2.33 | 2.37 | 2.13 |
| 3 | 9.7079 | 17.3976 | 11.7542 | 6.3612 | 54.7787 | 2.36 | 2.39 | 2.11 |
| | 9.504 | 17.0587 | 11.8489 | 6.435 | 55.1535 | 2.34 | 2.31 | 2.10 |
| | 9.5755 | 17.1947 | 11.8389 | 6.3281 | 55.0628 | 2.38 | 2.34 | 2.14 |
| | Average value | | | | | 2.36 | 2.35 | 2.12 |
| 5 | 9.6787 | 17.348 | 11.0215 | 5.9149 | 56.0368 | 2.40 | 2.31 | 2.09 |
| | 9.6723 | 17.329 | 11.1292 | 5.9121 | 55.9574 | 2.41 | 2.31 | 2.12 |
| | 9.6804 | 17.2693 | 11.1313 | 5.9498 | 55.9693 | 2.39 | 2.28 | 2.10 |
| | Average value | | | | | 2.40 | 2.30 | 2.10 |
| 6 | 9.6238 | 17.4446 | 10.781 | 5.7658 | 56.3848 | 2.43 | 2.33 | 2.08 |
| | 10.1009 | 18.2554 | 11.1745 | 5.8137 | 54.6555 | 2.49 | 2.63 | 2.18 |
| | 9.5068 | 17.1999 | 10.8816 | 5.6451 | 56.7666 | 2.49 | 2.26 | 2.16 |
| | Average value | | | | | 2.47 | 2.41 | 2.14 |

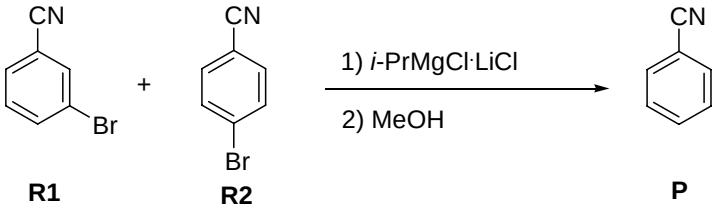
Combination of 0.5M 3-bromobenzonitrile (R1), 0.5M 4-bromobenzonitrile (R2) and 0.5M *i*-PrMgCl·LiCl (evaluation without internal standard), quenched by iodine, gave the following results:

| | R1 | R2 |
|---|---|---|
| m (mg) | 211.3 | 213.2 |
| M (g/mol) | 182.02 | 182.02 |
| c (mol/L) | 0.4940 | 0.4984 |

| t (h) | $A_{R1}$ | $A_{R2}$ | $A_{P1}$ | $A_{P2}$ | κ1 |
|---|---|---|---|---|---|
| 1/3 | 24.7991 | 38.7878 | 24.0129 | 12.4003 | 2.26 |
| | 24.6494 | 38.6380 | 24.1125 | 12.6002 | 2.24 |
| | 24.6191 | 38.6194 | 24.0657 | 12.6959 | 2.22 |
| | Average value | | | | 2.24 |
| 2/3 | 21.7712 | 36.8402 | 26.8215 | 14.5671 | 2.23 |
| | 21.7726 | 36.8342 | 26.7287 | 14.6646 | 2.22 |
| | 21.8168 | 36.8310 | 26.7986 | 14.5536 | 2.23 |
| | Average value | | | | 2.23 |
| 1 | 21.0487 | 36.5367 | 27.2280 | 15.1866 | 2.21 |
| | 20.9870 | 36.4980 | 27.3229 | 15.1921 | 2.22 |
| | 20.8254 | 36.1798 | 27.4724 | 15.5224 | 2.19 |
| | Average value | | | | 2.21 |
| 2 | 20.0592 | 35.4990 | 28.7395 | 15.7023 | 2.25 |
| | 19.8939 | 35.4310 | 29.0278 | 15.6473 | 2.28 |
| | 19.8137 | 35.1210 | 29.2237 | 15.8416 | 2.26 |
| | Average value | | | | 2.26 |
| 3 | 20.6299 | 36.5294 | 27.7164 | 15.1243 | 2.28 |
| | 20.2842 | 36.1873 | 28.0150 | 15.5135 | 2.26 |
| | 20.4817 | 36.3626 | 27.9860 | 15.1698 | 2.29 |
| | Average value | | | | 2.27 |
| 5 | 21.0938 | 37.4609 | 26.7860 | 14.6594 | 2.30 |
| | 21.1396 | 37.5619 | 26.7702 | 14.5283 | 2.32 |
| | 21.1307 | 37.4301 | 26.7581 | 14.6811 | 2.29 |
| | Average value | | | | 2.30 |
| 6 | 21.5601 | 38.7269 | 25.7889 | 13.9240 | 2.37 |
| | 21.5770 | 38.8135 | 25.8400 | 13.7695 | 2.40 |
| | 21.5307 | 38.8538 | 25.7207 | 13.8948 | 2.38 |
| | Average value | | | | 2.38 |

**Typical Procedure (Methanol Quench):** (0.25M : 0.25M)

A dry and nitrogen flushed 25-mL flask, equipped with a magnetic stirrer, was charged with 3-bromobenzonitrile R1 (1.17 mmol, 214 mg), 4-bromobenzonitrile R2 (1.17 mmol, 214 mg) and internal standard (*n*-$C_{14}H_{30}$) in THF (3.70 mL). The reaction mixture was cooled to 0 $^{o}$C. *i*-PrMgCl·LiCl (1.17 mmol, 1.00 mL solution in THF) was added in one portion. After certain times (for example 20 min), about 0.2 mL of mixture was taken out and injected in methanol. The reaction mixture was washed with saturated aqueous NaCl solution (30 mL). The aqueous phase was extracted with diethylether (about 25 ~ 30 mL). The etheral solutions were dried over $Na_2SO_4$ and analyzed by GC.




**R1** **R2** **P**

Combination of 0.25M 3-bromobenzonitrile (R1), 0.25M 4-bromobenzonitrile (R2), 0.25M internal standard (*n*-$C_{14}H_{30}$), and 0.25M *i*-PrMgCl·LiCl, quenched by methanol, gave the following results:

| | R1 | R2 | IS |
|---|---|---|---|
| m (mg) | 209.4 | 213.2 | 219.8 |
| M (g/mol) | 182.02 | 182.02 | 198.39 |
| c (mol/L) | 0.2448 | 0.2492 | 0.2357 |

| t (h) | $A_{R1}$ | $A_{R2}$ | $A_{IS}$ | κ2 |
|---|---|---|---|---|
| 1/3 | 17.3723 | 23.4499 | 59.1778 | 2.39 |
| | 17.4305 | 23.5647 | 59.0047 | 2.46 |
| | 17.1356 | 23.1655 | 59.6988 | 2.25 |
| | Average value | | | 2.37 |
| 2/3 | 15.0018 | 22.4505 | 62.5477 | 2.27 |
| | 14.9115 | 22.4665 | 62.6220 | 2.29 |
| | 14.9179 | 22.4491 | 62.6330 | 2.28 |
| | Average value | | | 2.28 |
| 1 | 13.6989 | 21.9526 | 64.3485 | 2.28 |
| | 13.8256 | 22.0255 | 64.1489 | 2.29 |
| | 13.8049 | 22.0752 | 64.1199 | 2.31 |
| | Average value | | | 2.29 |
| 2 | 12.1159 | 20.8786 | 67.0055 | 2.17 |
| | 12.1875 | 20.9720 | 66.8405 | 2.19 |
| | 12.6577 | 21.5647 | 65.7776 | 2.31 |
| | Average value | | | 2.22 |
| 3 | 11.7920 | 20.3080 | 67.9000 | 2.07 |
| | 12.5068 | 21.4990 | 65.9943 | 2.31 |
| | 12.9765 | 22.4533 | 64.5702 | 2.61 |
| | Average value | | | 2.33 |
| 5 | 11.9593 | 20.8163 | 67.2243 | 2.18 |
| | 11.9088 | 20.6552 | 67.4360 | 2.14 |
| | 12.1327 | 20.9162 | 66.9511 | 2.18 |
| | Average value | | | 2.17 |
| 6 | 11.4366 | 19.7257 | 68.8377 | 1.98 |
| | 11.3859 | 19.6748 | 68.9393 | 1.98 |
| | 11.6449 | 20.0801 | 68.2750 | 2.03 |
| | Average value | | | 2.00 |

Combination of 0.5M 3-bromobenzonitrile (R1), 0.5M 4-bromobenzonitrile (R2), 0.5M internal standard (*n*-$C_{14}H_{30}$), and 0.5M *i*-PrMgCl·LiCl, quenched by methanol, gave the following results:

| | R1 | R2 | IS |
|---|---|---|---|
| m (mg) | 210.2 | 208.5 | 223.7 |
| M (g/mol) | 182.02 | 182.02 | 198.39 |
| c (mol/L) | 0.4914 | 0.4874 | 0.4798 |

| t (h) | $A_{R1}$ | $A_{R2}$ | $A_{IS}$ | κ2 |
|---|---|---|---|---|
| 1/3 | 14.1996 | 21.5952 | 64.2051 | 2.30 |
| | 14.4116 | 21.9502 | 63.6382 | 2.42 |
| | 14.3856 | 22.0438 | 63.6198 | 2.47 |
| | Average value | | | 2.40 |
| 2/3 | 12.1417 | 20.3773 | 67.5509 | 2.20 |
| | 12.6378 | 21.4068 | 65.9554 | 2.48 |
| | 12.6245 | 21.1224 | 66.2532 | 2.37 |
| | Average value | | | 2.35 |
| 1 | 11.5950 | 20.5793 | 67.8257 | 2.35 |
| | 11.6007 | 20.6243 | 67.7751 | 2.37 |
| | 11.7404 | 20.8692 | 67.3904 | 2.43 |
| | Average value | | | 2.38 |
| 2 | 11.1001 | 20.4270 | 68.4729 | 2.38 |
| | 11.3648 | 20.7221 | 67.9130 | 2.44 |
| | 11.3000 | 20.6750 | 68.0251 | 2.43 |
| | Average value | | | 2.42 |
| 3 | 11.2939 | 20.6915 | 68.0145 | 2.44 |
| | 11.0759 | 20.3329 | 68.5911 | 2.36 |
| | 11.0165 | 20.3398 | 68.6437 | 2.37 |
| | Average value | | | 2.39 |
| 5 | 11.0072 | 20.1865 | 68.8063 | 2.32 |
| | 11.0777 | 20.2714 | 68.6509 | 2.34 |
| | 11.0169 | 20.1523 | 68.8308 | 2.31 |
| | Average value | | | 2.32 |
| 6 | 11.3459 | 20.8204 | 67.8337 | 2.48 |
| | 11.3754 | 20.8725 | 67.7521 | 2.49 |
| | 11.6085 | 21.3514 | 67.0401 | 2.64 |
| | Average value | | | 2.53 |

Combination of 0.25M 3-bromobenzonitrile (R1), 0.5M 4-bromobenzonitrile (R2), internal standard (*n*-$C_{14}H_{30}$), and 0.25M *i*-PrMgCl·LiCl, quenched by methanol, gave the following results:

| | R1 | R2 | IS |
|---|---|---|---|
| m (mg) | 214.5 | 421.3 | 59.2 |
| M (g/mol) | 182.02 | 182.02 | 198.39 |
| c (mol/L) | 0.2507 | 0.4925 | 0.0635 |

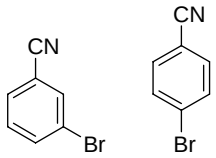
| t (h) | $A_{R1}$ | $A_{R2}$ | $A_{IS}$ | κ2 |
|---|---|---|---|---|
| 2/3 | 21.5370 | 58.3131 | 20.1499 | 2.57 |
| | 21.5327 | 58.3775 | 20.0897 | 2.61 |
| | 21.5468 | 58.1604 | 20.2929 | 2.47 |
| | Average value | | | 2.55 |

Combination of 0.5M 3-bromobenzonitrile (R1), 1.0M 4-bromobenzonitrile (R2), internal standard (*n*-$C_{14}H_{30}$), and 0.5M *i*-PrMgCl·LiCl, quenched by methanol, gave the following results:

| | R1 | R2 | IS |
|---|---|---|---|
| m (mg) | 212.8 | 423.3 | 57.9 |
| M (g/mol) | 182.02 | 182.02 | 198.39 |
| c (mol/L) | 0.4975 | 0.9896 | 0.1242 |

| t (h) | $A_{R1}$ | $A_{R2}$ | $A_{IS}$ | κ2 |
|---|---|---|---|---|
| 2/3 | 20.4561 | 58.7930 | 20.7510 | 2.45 |
| | 20.4799 | 58.7651 | 20.7550 | 2.43 |
| | 20.4412 | 58.7376 | 20.8212 | 2.42 |
| | Average value | | | 2.43 |

In an analogous way, all other relative reactivities have been determined, and the results are summarized in the following Tables.




Quenching with $I_2$ **κ1=2.25** κ2=2.31 κ3=2.10

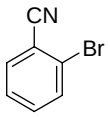
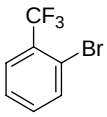
| t (h) | κ1 | | | | κ2 | | κ3 | |
|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *(0.25[a]:0.25[b])[c]* | *0.5[a]:0.5[b]* | *(0.5[a]:0.5[b])[c]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* |
| 1/3 | 2.09 | 2.14 | 2.32 | 2.24 | | | 2.01 | 2.19 |
| 2/3 | 2.15 | 2.13 | 2.29 | 2.23 | 2.27 | 2.44 | 2.05 | 2.14 |
| 1 | 2.19 | 2.13 | 2.40 | 2.21 | 2.26 | 2.44 | 2.08 | 2.31 |
| 2 | 2.20 | 2.17 | 2.33 | 2.26 | 2.24 | 2.37 | 2.08 | 2.13 |
| 3 | 2.15 | 2.20 | 2.36 | 2.27 | 2.20 | 2.35 | 1.98 | 2.12 |
| 5 | 2.23 | 2.22 | 2.40 | 2.30 | 2.22 | 2.30 | 1.98 | 2.10 |
| 6 | | 2.30 | 2.47 | 2.38 | | 2.41 | | 2.14 |
| Av | 2.17 | 2.18 | 2.37 | 2.27 | 2.24 | 2.38 | 2.03 | 2.16 |

a) Concentration of 3-bromobenzonitrile and of *i*-PrMgCl·LiCl (mol·$L^{-1}$)
b) Concentration of 4-bromobenzonitrile (mol·$L^{-1}$)
c) Evaluation without internal standard

Quenching with $CH_3OH$ κ2=2.41

| t (h) | κ2 | | | |
|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1/3 | 2.37 | 2.40 | | |
| 2/3 | 2.28 | 2.35 | 2.55 | 2.43 |
| 1 | 2.29 | 2.38 | | |
| 2 | 2.22 | 2.42 | | |
| 3 | 2.33 | 2.39 | | |
| 5 | 2.17 | 2.32 | | |
| 6 | 2.00 | 2.53 | | |
| Av | 2.24 | 2.40 | 2.55 | 2.43 |

a) Concentration of 3-bromobenzonitrile and of *i*-PrMgCl·LiCl (mol·$L^{-1}$)
b) Concentration of 4-bromobenzonitrile (mol·$L^{-1}$)

Average from quenching with $I_2$ and $CH_3OH$: **κ1=1.59**

Quenching with $I_2$ **κ1=1.68** κ2=1.57 κ2=1.68

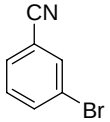
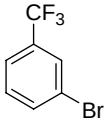
| t (h) | κ1 | | κ2 | | κ3 | |
|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* |
| 1/3 | 1.61 | 1.73 | | | 1.73 | 1.88 |
| 2/3 | 1.59 | 1.76 | 1.55 | 1.52 | 1.60 | 1.83 |
| 1 | 1.62 | 1.78 | | | 1.72 | 1.84 |
| 2 | 1.60 | 1.80 | | 1.71 | 1.62 | 1.75 |
| 3 | 1.61 | 1.77 | | | 1.50 | 1.83 |
| 5 | 1.58 | 1.78 | 1.43 | 1.61 | 1.53 | 1.70 |
| 6 | 1.56 | 1.78 | 1.57 | | 1.39 | 1.56 |
| Av | 1.60 | 1.77 | 1.52 | 1.62 | 1.58 | 1.77 |

a) Concentration of 2-bromobenzonitrile and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-2-(trifluoromethyl)benzene (mol·L$^{-1}$)

Quenching with $CH_3OH$ **κ1=1.50** κ2=1.42 κ3=1.51

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1/3 | 1.54 | 1.62 | | | | | | | 1.64 | 1.63 | | |
| 2/3 | 1.51 | 1.67 | 1.41 | 1.47 | | | 1.42 | | 1.51 | 1.63 | 1.43 | 1.52 |
| 1 | 1.48 | 1.62 | | | | | | | 1.48 | 1.59 | | |
| 2 | 1.49 | 1.57 | | | | | | | 1.52 | 1.51 | | |
| 3 | 1.48 | 1.60 | | | | | | | 1.53 | 1.55 | | |
| 5 | 1.54 | 1.62 | | | | | | | 1.57 | 1.57 | | |
| 6 | 1.46 | | | | 1.42 | | | | 1.32 | | | |
| Av | 1.50 | 1.62 | 1.41 | 1.47 | 1.42 | | 1.42 | | 1.51 | 1.58 | 1.43 | 1.52 |

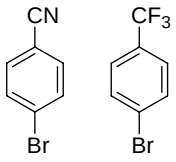
a) Concentration of 2-bromobenzonitrile and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-2-(trifluoromethyl)benzene (mol·L$^{-1}$)

Quenching with $CH_3OH$ **κ1=6.02** κ3=5.25

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 2/3 | 5.62 | 6.02 | 5.87 | 6.32 | | | | | 5.20 | 5.28 | 5.06 | 5.77 |
| 3 | 5.95 | 6.20 | | | | | | | 5.31 | 5.38 | | |
| Av | 5.78 | 6.11 | 5.87 | 6.32 | | | | | 5.26 | 5.33 | 5.06 | 5.77 |

a) Concentration of 3-bromobenzonitrile and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-3-(trifluoromethyl)benzene (mol·L$^{-1}$)

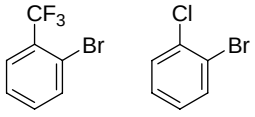



Quenching with $CH_3OH$ **κ1=5.29** κ2=5.09 κ3=4.98

| t (h) | κ1 | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *(0.25[a]:0.25[b])[d]* | *(0.25[a]:0.25[b])[e]* | *(0.25[a]:0.25[b])[c]* | *(0.5[a]:0.5[b])[d]* | *(0.5[a]:0.5[b])[e]* | *(0.5[a]:0.5[b])[c]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1/3 | 4.89 | 4.76 | | 5.57 | 4.87 | 5.18 | | |
| 2/3 | 5.04 | 5.05 | 5.06 | 5.44 | 5.12 | 5.19 | 5.12 | 5.46 |
| 1 | 5.09 | 5.10 | | 5.42 | 5.38 | 5.29 | | |
| 2 | 5.41 | 5.22 | | 5.32 | 5.32 | 5.28 | | |
| 3 | 5.44 | 5.16 | 5.32 | 5.64 | 5.47 | 5.30 | | |
| 5 | 5.26 | 5.42 | | 5.77 | 5.41 | 5.41 | | |
| 6 | 5.46 | 5.41 | | 5.68 | 5.45 | 5.61 | | |
| Av | 5.23 | 5.16 | 5.19 | 5.55 | 5.29 | 5.32 | 5.12 | 5.46 |

| t (h) | κ2 | | | κ3 | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *(0.25[a]:0.25[b])[e]* | *(0.5[a]:0.5[b])[d]* | *(0.5[a]:0.5[b])[e]* | *(0.25[a]:0.25[b])[d]* | *(0.25[a]:0.25[b])[e]* | *(0.5[a]:0.5[b])[d]* | *(0.5[a]:0.5[b])[e]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1/3 | | | | 4.80 | 4.56 | 5.39 | 4.68 | | |
| 2/3 | | | | 4.79 | 4.93 | 5.10 | 4.92 | 5.03 | 5.13 |
| 1 | | | | 4.53 | 4.89 | 5.04 | 5.10 | | |
| 2 | | | | 5.02 | 4.99 | 4.77 | 5.06 | | |
| 3 | 5.11 | | | 4.92 | 4.74 | 4.91 | 4.91 | | |
| 5 | | 5.05 | 5.14 | 4.64 | 5.03 | 4.94 | 4.85 | | |
| 6 | | | 5.08 | 5.14 | 5.04 | 5.50 | 4.84 | | |
| Av | 5.11 | 5.05 | 5.11 | 4.83 | 4.88 | 5.09 | 4.91 | 5.03 | 5.13 |

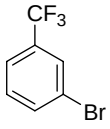
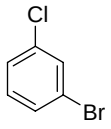
a) Concentration of 4-bromobenzonitrile and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-4-(trifluoromethyl)benzene (mol·L$^{-1}$)
c) Evaluation without internal standard
d) Concentration of internal standard ≈ concentration of 4-bromobenzonitrile (mol·L$^{-1}$)
e) Concentration of internal standard ≈ 1/4 of concentration of 4-bromobenzonitrile (mol·L$^{-1}$)




Quenching with $CH_3OH$ **κ1= 3.51** κ2= 3.44 κ3=3.35

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 2/3 | 3.51 | 3.38 | 3.57 | 3.47 | 3.48 | | | 3.34 | 3.39 | 3.22 | 3.34 | 3.30 |
| 3 | 3.60 | 3.52 | | | 3.62 | | | | 3.49 | 3.37 | | |
| Av | 3.56 | 3.45 | 3.57 | 3.47 | 3.55 | | | 3.34 | 3.44 | 3.30 | 3.34 | 3.30 |

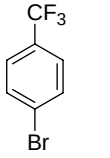
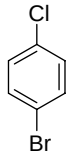
a) Concentration of 1-bromo-2-(trifluoromethyl)benzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-2-chlorobenzene (mol·L$^{-1}$)

Quenching with $CH_3OH$ **κ1=1.56** κ2= 1.63 κ3=1.50

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1 | 1.58 | 1.56 | 1.58 | 1.53 | | 1.64 | | | 1.52 | 1.53 | 1.49 | 1.46 |
| 4 | 1.58 | 1.54 | | | 1.66 | 1.57 | | | 1.51 | 1.51 | | |
| Av | 1.58 | 1.55 | 1.58 | 1.53 | 1.66 | 1.60 | | | 1.51 | 1.52 | 1.49 | 1.46 |

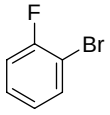
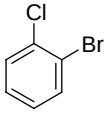
a) Concentration of 1-bromo-3-(trifluoromethyl)benzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-3-chlorobenzene (mol·L$^{-1}$)

Quenching with $CH_3OH$ **κ1=4.25** κ3=3.85

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1 | 4.11 | 4.23 | 4.22 | 4.34 | | | | | 3.80 | 3.88 | 3.80 | 3.89 |
| 4 | 4.16 | 4.41 | | | | | | | 3.70 | 4.02 | | |
| Av | 4.13 | 4.32 | 4.22 | 4.34 | | | | | 3.75 | 3.95 | 3.80 | 3.89 |

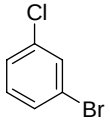
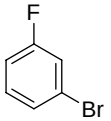
a) Concentration of 1-bromo-4-(trifluoromethyl)benzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-4-chlorobenzene (mol·L$^{-1}$)

Quenching with $CH_3OH$ **κ1=1.47** κ2= 1.54 κ3=1.41

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.5[a]:0.25[b]* | *1.0[a]:0.5[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.5[a]:0.25[b]* | *1.0[a]:0.5[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.5[a]:0.25[b]* | *1.0[a]:0.5[b]* |
| 2/3 | 1.51 | 1.50 | 1.43 | 1.46 | 1.56 | 1.54 | 1.54 | 1.54 | 1.49 | 1.44 | 1.39 | 1.39 |
| 3 | 1.51 | 1.50 | | | 1.54 | 1.54 | | | 1.43 | 1.40 | | |
| Av | 1.51 | 1.50 | 1.43 | 1.46 | 1.55 | 1.54 | 1.54 | 1.54 | 1.46 | 1.42 | 1.39 | 1.39 |

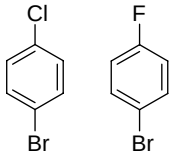
a) Concentration of 1-bromo-2-fluorobenzene (mol·L$^{-1}$)
b) Concentration of 1-bromo-2-chlorobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)

Quenching with $CH_3OH$ **κ1=2.73** κ3=2.84

| t (h) | K1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1 | 2.64 | 2.66 | 2.79 | 2.72 | | | | | 2.81 | 2.75 | 2.88 | 2.79 |
| 4 | 2.63 | 2.92 | | | | | | | 2.75 | 3.05 | | |
| Av | 2.64 | 2.79 | 2.79 | 2.72 | | | | | 2.78 | 2.90 | 2.88 | 2.79 |

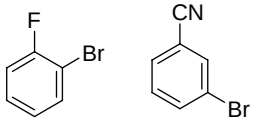
a) Concentration of 1-bromo-3-chlorobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-3-fluorobenzene (mol·L$^{-1}$)




Quenching with $CH_3OH$ **κ1=2.43** κ3=2.36

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1 | 2.20 | 2.38 | 2.15 | 2.63 | | | | | 2.19 | 2.30 | 2.06 | 2.55 |
| 4 | 2.62 | 2.66 | | | | | | | 2.63 | 2.56 | | |
| Av | 2.41 | 2.52 | 2.15 | 2.63 | | | | | 2.41 | 2.43 | 2.06 | 2.55 |

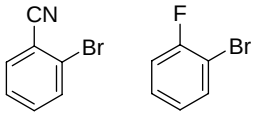
a) Concentration of 1-bromo-4-chlorobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-4-fluorobenzene (mol·L$^{-1}$)




Quenching with $CH_3OH$ **κ1=2.38** κ2= 2.34 κ3=2.30

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 2/3 | 2.30 | 2.22 | 2.45 | 2.53 | | 2.33 | | 2.58 | 2.31 | 2.01 | 2.53 | 2.41 |
| 3 | 2.21 | 2.33 | | | 2.14 | 2.27 | | | 2.12 | 2.15 | | |
| Av | 2.26 | 2.28 | 2.45 | 2.53 | 2.14 | 2.30 | | 2.58 | 2.21 | 2.08 | 2.53 | 2.41 |

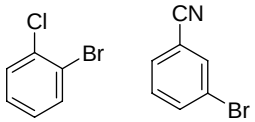
a) Concentration of 1-bromo-2-fluorobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 3-bromobenzonitrile (mol·L$^{-1}$)




Quenching with $CH_3OH$ **κ1=3.37** κ2= 3.17 κ3=3.31

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 2/3 | 3.39 | 3.47 | 3.32 | 3.31 | | | 3.17 | | 3.38 | 3.52 | 3.26 | 3.16 |
| 2 | 3.36 | 3.36 | | | | | | | 3.34 | 3.38 | | |
| Av | 3.38 | 3.42 | 3.32 | 3.31 | | | 3.17 | | 3.36 | 3.45 | 3.26 | 3.16 |

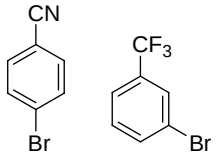
a) Concentration of 2-bromobenzonitrile and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-2-fluorobenzene (mol·L$^{-1}$)




Quenching with $CH_3OH$ **κ1=1.57** κ2= 1.50 κ3=1.60

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 2/3 | 1.49 | 1.54 | 1.58 | 1.65 | 1.39 | 1.43 | 1.70 | 1.46 | 1.55 | 1.61 | 1.56 | 1.69 |
| 3 | 1.51 | 1.54 | | | 1.43 | 1.42 | | | 1.53 | 1.63 | | |
| Av | 1.50 | 1.54 | 1.58 | 1.65 | 1.41 | 1.42 | 1.70 | 1.46 | 1.54 | 1.62 | 1.56 | 1.69 |

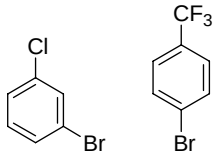
a) Concentration of 1-bromo-2-chlorobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 3-bromobenzonitrile (mol·L$^{-1}$)




Quenching with $CH_3OH$ **κ1=2.49** κ2= 2.65 κ3=2.26

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1 | 2.55 | 2.39 | 2.49 | 2.56 | | | | | 2.46 | 2.10 | 2.30 | 2.35 |
| 4 | 2.45 | 2.40 | | | 2.65 | | | | 2.24 | 2.01 | | |
| Av | 2.50 | 2.39 | 2.49 | 2.56 | 2.65 | | | | 2.35 | 2.05 | 2.30 | 2.35 |

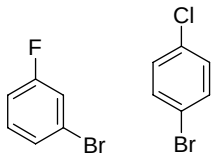
a) Concentration of 4-bromobenzonitrile and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-3-(trifluoromethyl)benzene (mol·L$^{-1}$)




Quenching with $CH_3OH$ **κ1=1.30** κ2= 1.31 κ3=1.29

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1 | 1.26 | 1.32 | 1.35 | 1.26 | | 1.32 | | | 1.27 | 1.33 | 1.32 | 1.25 |
| 4 | 1.27 | 1.31 | | | 1.25 | 1.43 | | | 1.28 | 1.28 | | |
| Av | 1.26 | 1.32 | 1.35 | 1.26 | 1.25 | 1.37 | | | 1.28 | 1.31 | 1.32 | 1.25 |

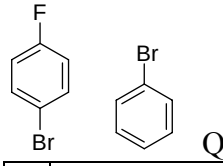
a) Concentration of 1-bromo-3-chlorobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-4-(trifluoromethyl)benzene (mol·L$^{-1}$)




Quenching with $CH_3OH$ **κ1=2.15** κ3=2.01

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1 | 2.13 | 2.12 | 2.26 | 2.02 | | | | | 2.08 | 1.98 | 2.07 | 1.84 |
| 4 | 2.15 | 2.23 | | | | | | | 2.13 | 2.09 | | |
| Av | 2.14 | 2.18 | 2.26 | 2.02 | | | | | 2.10 | 2.03 | 2.07 | 1.84 |

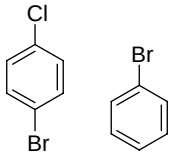
a) Concentration of 1-bromo-3-fluorobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-4-chlorobenzene (mol·L$^{-1}$)




Quenching with $I_2$ **κ1=9.69** κ3=8.33

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 7 | 9.07 | 10.52 | 9.12 | 10.13 | | | | | 7.59 | 8.83 | 7.60 | 9.59 |
| 24 | 9.10 | 10.36 | | | | | | | 7.29 | 8.58 | | |
| Av | 9.08 | 10.44 | 9.12 | 10.13 | | | | | 7.44 | 8.71 | 7.60 | 9.59 |

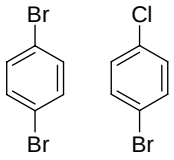
a) Concentration of 1-bromo-4-fluorobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromobenzene (mol·L$^{-1}$)



Quenching with $I_2$ **κ1=24.10** κ3=17.79

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 4 | | 27.60 | | | | | | | | 20.47 | | |
| 7 | 21.54 | 26.88 | 20.52 | 27.65 | | | | | 16.51 | 19.46 | 15.17 | 20.68 |
| 24 | 21.01 | 26.38 | | | | | | | 15.00 | 18.73 | | |
| Av | 21.27 | 26.95 | 20.52 | 27.65 | | | | | 15.75 | 19.55 | 15.17 | 20.68 |

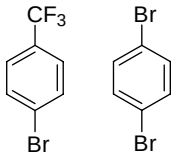
a) Concentration of 1-bromo-4-chlorobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromobenzene (mol·L$^{-1}$)



Quenching with $CH_3OH$ **κ1=2.74** κ2= 2.59 κ3=2.87

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1 | 2.73 | 2.83 | | | | | | | 2.84 | 2.97 | | |
| 4 | 2.68 | 2.76 | 2.74 | 2.70 | | 2.59 | | | 2.82 | 3.01 | 2.82 | 2.84 |
| Av | 2.70 | 2.80 | 2.74 | 2.70 | | 2.59 | | | 2.83 | 2.99 | 2.82 | 2.84 |

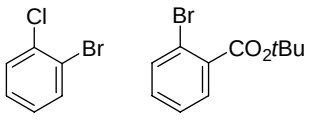
a) Concentration of 1,4-dibromobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1-bromo-4-chlorobenzene (mol·L$^{-1}$)



Quenching with $CH_3OH$ **κ1=1.53** κ3=1.41

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1 | 1.42 | 1.56 | 1.49 | 1.61 | | | | | 1.31 | 1.43 | 1.40 | 1.45 |
| 4 | 1.54 | 1.56 | | | | | | | 1.44 | 1.38 | | |
| Av | 1.48 | 1.56 | 1.49 | 1.61 | | | | | 1.37 | 1.41 | 1.40 | 1.45 |

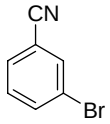
a) Concentration of 1-bromo-4-(trifluoromethyl)benzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of 1,4-dibromobenzene (mol·L$^{-1}$)

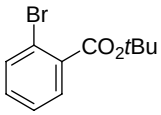


Quenching with $I_2$ **κ1=8.50** κ3=8.53

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.25[a]:0.5[b]* | *0.5[a]:1.0[b]* |
| 1/3 | 8.68 | 8.79 | 8.97 | 8.54 | | | | | 7.91 | 9.06 | 8.36 | 9.82 |
| 2 | 7.91 | 7.59 | | | | | | | 7.20 | 7.72 | | |
| Av | 8.30 | 8.19 | 8.97 | 8.54 | | | | | 7.55 | 8.39 | 8.36 | 9.82 |

a) Concentration of 1-bromo-2-chlorobenzene and of *i*-PrMgCl·LiCl (mol·L$^{-1}$)
b) Concentration of *tert*-butyl 2-bromobenzoate (mol·L$^{-1}$)






Quenching with $I_2$ **κ1=4.96** κ3=4.51

| t (h) | κ1 | | | | κ2 | | | | κ3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.5[a]:0.25[b]* | *1.0[a]:0.5[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.5[a]:0.25[b]* | *1.0[a]:0.5[b]* | *0.25[a]:0.25[b]* | *0.5[a]:0.5[b]* | *0.5[a]:0.25[b]* | *1.0[a]:0.5[b]* |
| 2/3 | 5.56 | 5.55 | 5.02 | 4.32 | | | | | 4.91 | 4.97 | 4.65 | 4.08 |
| 2 | 4.92 | 4.94 | | | | | | | 4.36 | 4.42 | | |
| Av | 5.24 | 5.25 | 5.02 | 4.32 | | | | | 4.63 | 4.69 | 4.65 | 4.08 |

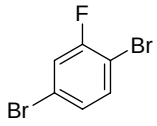
a) Concentration of 3-bromobenzonitrile (mol·$L^{-1}$)

b) Concentration of *tert*-butyl 2-bromobenzoate and of *i*-PrMgCl·LiCl (mol·$L^{-1}$)

**Intramolecular exchange**

**Typical Procedure:** (0.5M)

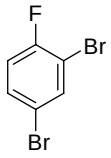
A dry and nitrogen flushed 25-mL flask, equipped with a magnetic stirrer, was charged with 1,4-dibromo-2-fluorobenzene (2.35 mmol, 597 mg) and internal standard (*n*-$C_{14}H_{30}$) in THF (3.70 mL). The reaction mixture was cooled to 0 $^{o}$C. 0.5 equiv. *i*-PrMgCl·LiCl (1.17 mmol, 1.00 mL) was added in one portion. After certain times (for example 15 min), about 0.2 mL of mixture was taken out and injected in methanol. The reaction mixture was washed with saturated aqueous NaCl solution (30 mL). The aqueous phase was extracted with diethylether (about 25 ~ 30 mL). The etheral solutions were dried over $Na_2SO_4$ and analyzed by GC.




Quenching with $CH_3OH$ κ=79.79

| t (h) | κ | |
|---|---|---|
| | *0.5*[a] | *1.0*[a] |
| 1/4 | 71.93 | 71.46 |
| 4 | 87.22 | 88.53 |
| Av | 79.58 | 79.99 |

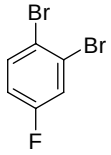
a) Concentration of 1,4-dibromo-2-fluorobenzene (mol·$L^{-1}$)




Quenching with $CH_3OH$ κ=94.19

| t (h) | κ | |
|---|---|---|
| | *0.5*[a] | *1.0*[a] |
| 1/4 | 92.72 | 88.26 |
| 4 | 97.82 | 97.94 |
| Av | 95.27 | 93.1 |

a) Concentration of 2,4-dibromo-1-fluorobenzene (mol·$L^{-1}$)

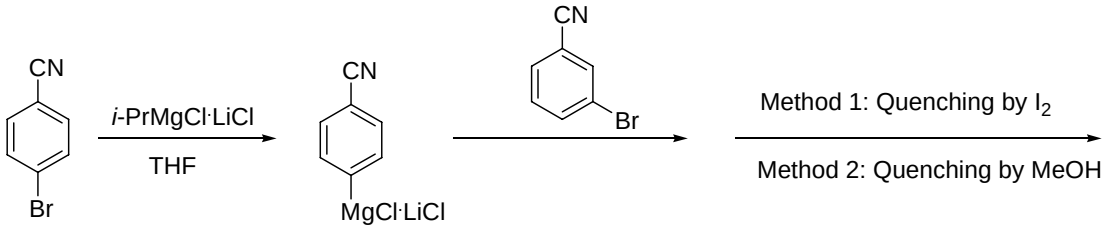



Quenching with $CH_3OH$ κ=4.76

| t (h) | κ | |
|---|---|---|
| | *0.5*[a] | *1.0*[a] |
| 1/4 | 4.74 | 4.66 |
| 4 | 4.84 | 4.78 |
| Av | 4.79 | 4.72 |

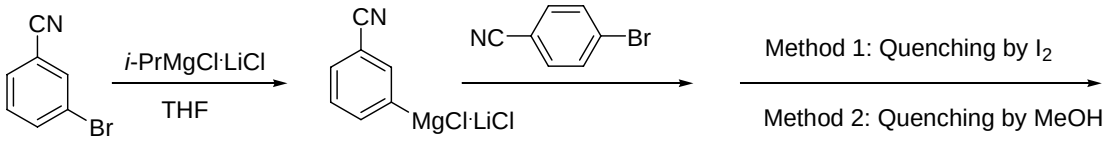
a) Concentration of 1,2-dibromo-4-fluorobenzene (mol·$L^{-1}$)

Exclusion of Bromine-Magnesium Exchange between Bromoarenes and Arenemagnesium Halides


Method 1: To *i*-PrMgCl·LiCl (1.17 M, 1 mL) in 1 mL of THF was added 1.2 mmol of 4-bromobenzonitrile at 0 °C. The reaction mixture was stirred for 3 h before 1.1 mmol of 3-bromobenzonitrile was added. After certain times, about 0.2 mL of the mixture was taken out with a syringe and quenched by $I_2$. Even after 5 h we cannot detect the peak of 3-iodobenzonitrile by GC-MS.

Method 2: To *i*-PrMgCl·LiCl (1.17 M, 1 mL) in 1 mL of THF was added 1.17 mmol of 4-bromobenzonitrile at 0 °C. The reaction mixture was stirred for 3 h before 1.1 mmol of 3-bromobenzonitrile was added. After certain times, about 0.2 mL of the mixture was taken out with a syringe and quenched by MeOH. After 3 days we cannot detect the peak of 4-bromobenzonitrile by GC-MS.




Method 1: To *i*-PrMgCl·LiCl (1.17 M, 1 mL) in 1 mL of THF was added 1.2 mmol of 3-bromobenzonitrile at 0 °C. The reaction mixture was stirred for 3 h before 1.1 mmol of 4-bromobenzonitrile was added. After certain times, about 0.2 mL of the mixture was taken out with a syringe and quenched by $I_2$. After 5 h we cannot detect the peak of 4-iodobenzonitrile by GC-MS.

Method 2: To *i*-PrMgCl·LiCl (1.17 M, 1 mL) in 1 mL of THF was added 1.17 mmol of 3-bromobenzonitrile at 0 °C. The reaction mixture was stirred for 3 h before 1.1 mmol of 4-bromobenzonitrile was added. After certain times, about 0.2 mL of the mixture was taken out with a syringe and quenched by MeOH. After 3 days we cannot detect the peak of 3-bromobenzonitrile by GC-MS.