–Supporting Information–

Kinetics of Bromine-Magnesium Exchange Reactions in Heteroaryl Bromides

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General information:
All reactions were carried out under nitrogen atmosphere in dried glassware using Schlenk techniques. The 2- and 3-bromo-substituted N-methylpyrroles,[S1] 2-bromofuran,[S2] 2-iodofuran,[S3] 3-iodofuran,[S4] 3,4-dibromofuran,[S5] and 4-bromopyridine[S6] were prepared according to literature procedures. The other 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*) are now calculated as

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

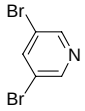
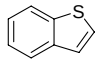
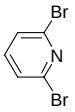
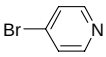
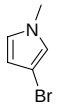
$$\frac{A_{P1}}{A_{IS}} = f_{P1}\frac{[P1]}{[IS]} \Rightarrow f_{P1} = \frac{A_{P1}[IS]}{A_{IS}[P2]}$$

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

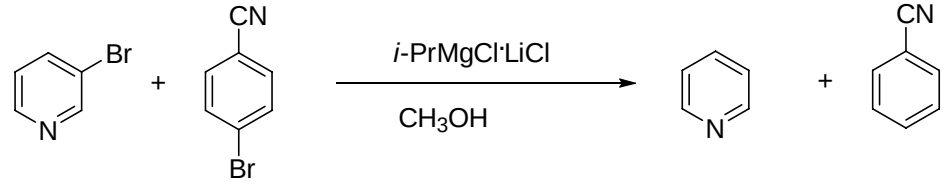
Typical procedure: A mixture of **R1**, **R2**, **P1**, **P2**, and internal standard (*n*-$C_{14}H_{30}$) was analyzed by GC. Each mixture was analyzed at least three times, and the relative response factors in Table S1 are the average of all runs. The relative response factors of benzene derivatives were reported in the previous articles.[S7]

[S1] Dvornikova, E.; Kamieńska-Trela, K. *Synlett.* **2002**, 1152–1154.
[S2] Keegstra, M. A.; Klomp, A. J. A.; Brandsma, L. *Syn. Commun.* **1990**, *20*, 3371–3374.
[S3] (a) Kim, G.; Shim, J. H.; Kim, J. H. *Bull. Korean Chem. Soc.* **2003**, *24*, 1832–1834. (b) Fuji, K.; Morimoto, T.; Tsutsumi, K.; Kakiuchi, K. *Chem. Commun.* **2005**, 3295–3297.
[S4] Deng, H.; Yang, X.; Tong, Z.; Li, Z.; Zhai, H. *Org. Lett.* **2008**, *10*, 1791–1793.
[S5] Mee, S. P. H.; Lee, V.; Baldwin, J. E.; Cowley, A. *Tetrahedron* **2004**, *60*, 3695–3712.
[S6] Feast, W. J.; Tsibouklis, J. *Polymer International* **1994**, *35*, 67–74.
[S7] (a) Shi, L.; Chu, Y.; Knochel, P.; Mayr, H. *Angew. Chem.* **2008**, *120*, 208–210; *Angew. Chem., Int. Ed.* **2008**, *47*, 202–204. (b) Shi, L.; Chu, Y.; Knochel, P.; Mayr, H. *J. Org. Chem.* **2009**, *74*, 2760–2764.

Table S1. Relative response factor of reactants and products *versus* internal standard (n-$C_{14}H_{30}$)

f					
Average value	0.309	0.158	0.281	0.280	0.535
f					
Average value	0.319	0.172	0.303	0.304	0.560
f					
Average value	0.297	0.303	0.285	0.298	0.295
f					
Average value	0.225	0.305	0.217	0.328	0.157
f					
Average value	0.211	0.200			

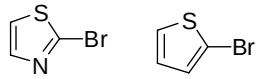
Determination of the Relative Exchange Rates κ
Typical Procedure (Methanol Quench)



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

A dry and nitrogen flushed 25-mL flask, equipped with a magnetic stirrer, was charged with 3-bromopyridine **R1** (1.30 mmol, 205 mg), 4-bromobenzonitrile **R2** (1.30 mmol, 237 mg) and internal standard (n-$C_{14}H_{30}$) in THF (4.20 mL). The reaction mixture was cooled to 0 °C. *i*-PrMgCl·LiCl (1.3 mmol, 1.00 mL solution in THF) was added in one portion. After certain times (for example 60 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 diethyl ether (about 25 ~ 30 mL). The etheral solutions were dried over Na_2SO_4 and analyzed by GC.

All relative reactivities have been determined, and the results are summarized in the following Tables.

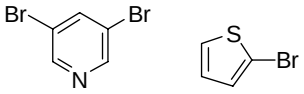


Quenching with CH_3OH **κ ≈ 10²**

T(min)	κ			
	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	151.12	174.31	110.06	74.88
5	126.77	143.47		
Av	138.94	158.89	110.06	74.88

a) Concentration of 2-bromothiazole and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 2-bromothiophene (mol·L^{-1})

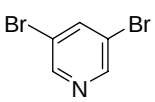


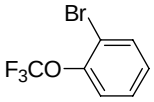
Quenching with CH_3OH **κ = 1.20**

T(min)	κ			
	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	1.30	1.21	1.12	1.15
5	1.33	1.22		
Av	1.32	1.22	1.12	1.15

a) Concentration of 3,5-dibromopyridine and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 2-bromothiophene (mol·L^{-1})



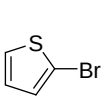


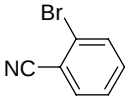
Quenching with CH_3OH **κ = 19.1**

T(min)	κ			
	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	17.42	21.55	16.78	19.63
5	17.88	22.91		
Av	17.65	22.23	16.78	19.63

a) Concentration of 3,5-dibromopyridine and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 1-bromo-2-(trifluoromethoxy)benzene (mol·L^{-1})



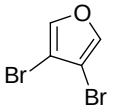


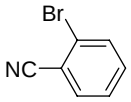
Quenching with CH_3OH **κ = 14.2**

T(min)	κ			
	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	14.25	14.56	14.04	13.88
5	14.41	14.82		
Av	14.33	14.69	14.04	13.88

a) Concentration of 2-bromothiophene and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 2-bromobenzonitrile (mol·L^{-1})



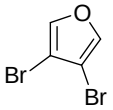
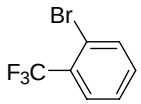


Quenching with CH_3OH **κ = 5.02**

T(min)	κ			
	0.25[a]:0.25[b]	*0.5[a]:0.5[b]*	*0.25[a]:0.5[b]*	*0.5[a]:1.0[b]*
5	5.00	5.10	4.86	4.97
20	5.23	5.17		
Av	5.12	5.13	4.86	4.97

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

b) Concentration of 2-bromobenzonitrile (mol·L^{-1})

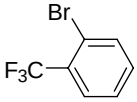
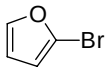



Quenching with CH_3OH **κ = 7.47**

T(min)	κ			
	0.25[a]:0.25[b]	*0.5[a]:0.5[b]*	*0.25[a]:0.5[b]*	*0.5[a]:1.0[b]*
5	7.47	7.77	7.18	7.40
20	7.69	7.63		
Av	7.58	7.70	7.18	7.40

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

b) Concentration of 1-bromo-2-(trifluoromethyl)benzene (mol·L^{-1})

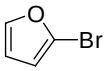
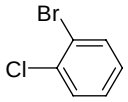



Quenching with I_2 **κ =1.32**

T(min)	κ			
	0.25[a]:0.25[b]	*0.5[a]:0.5[b]*	*0.25[a]:0.5[b]*	*0.5[a]:1.0[b]*
5	1.46	1.31	1.28	1.33
20	1.31	1.30		
Av	1.39	1.30	1.28	1.33

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

b) Concentration of 2-bromofuran (mol·L^{-1})

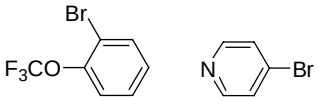



Quenching with I_2 **κ = 2.49**

T(min)	κ			
	0.25[a]:0.25[b]	*0.5[a]:0.5[b]*	*0.25[a]:0.5[b]*	*0.5[a]:1.0[b]*
5	2.51	2.22	2.44	2.79
20	2.48	2.29		
Av	2.50	2.25	2.44	2.79

a) Concentration of 2-bromofuran and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 1-bromo-2-chlorobenzene (mol·L^{-1})

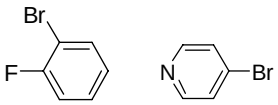


Quenching with CH_3OH **κ = 3.04**

T(min)	κ			
	0.25[a]:0.25[b]	*0.5[a]:0.5[b]*	*0.25[a]:0.5[b]*	*0.5[a]:1.0[b]*
5	3.04	3.10		
20	2.73	2.53	3.38	3.06
Av	2.88	2.82	3.38	3.06

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

b) Concentration of 4-bromopyridine (mol·L^{-1})

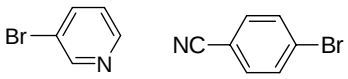


Quenching with CH_3OH **κ = 1.36**

T(min)	κ			
	0.25[a]:0.25[b]	*0.5[a]:0.5[b]*	*0.25[a]:0.5[b]*	*0.5[a]:1.0[b]*
5	1.21	1.24	1.59	1.30
20	1.44	1.22		
Av	1.32	1.23	1.59	1.30

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

b) Concentration of 4-bromopyridine (mol·L^{-1})

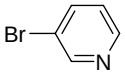


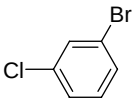
Quenching with CH_3OH **κ = 2.03**

T(h)	κ			
	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	1.67	2.13	1.83	2.37
4	1.70	2.32		
Av	1.69	2.22	1.83	2.37

a) Concentration of 3-bromopyridine and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 4-bromobenzonitrile (mol·L^{-1})



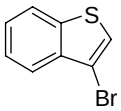


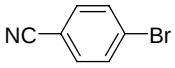
Quenching with CH_3OH **κ = 8.51**

T(h)	κ			
	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	6.94	10.13	7.51	9.14
4	7.04	10.64		
Av	6.99	10.39	7.51	9.14

a) Concentration of 3-bromopyridine and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 1-bromo-3-chlorobenzene (mol·L^{-1})



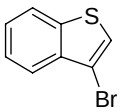


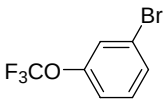
Quenching with CH_3OH **κ = 1.11**

T(h)	κ			
	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	1.02	1.11	1.14	1.17
4	0.98	1.16		
Av	1.00	1.14	1.14	1.17

a) Concentration of 3-bromobenzo[b]thiophene and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 4-bromobenzonitrile (mol·L^{-1})



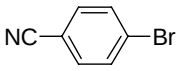


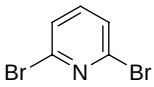
Quenching with CH_3OH **κ = 2.22**

T(h)	κ			
	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	2.16	2.33	2.14	2.19
4	2.30	2.29		
Av	2.23	2.31	2.14	2.19

a) Concentration of 3-bromobenzo[b]thiophene and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 1-bromo-3-(trifluoromethoxy)benzene (mol·L^{-1})



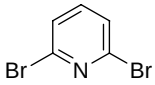


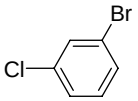
Quenching with CH_3OH **κ = 1.45**

T(min)	κ			
	0.25[a]:0.25[b]	*0.5[a]:0.5[b]*	*0.25[a]:0.5[b]*	*0.5[a]:1.0[b]*
20	1.37	1.35		
60	1.40	1.50	1.49	1.50
Av	1.38	1.42	1.49	1.50

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

b) Concentration of 2,6-dibromopyridine (mol·L^{-1})



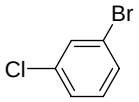


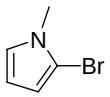
Quenching with CH_3OH **κ = 3.16**

T(min)	κ			
	0.25[a]:0.25[b]	*0.5[a]:0.5[b]*	*0.25[a]:0.5[b]*	*0.5[a]:1.0[b]*
20	3.14	3.14		
60	3.02	3.08	3.23	3.23
Av	3.08	3.11	3.23	3.23

a) Concentration of 2,6-dibromopyridine and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 1-bromo-3-chlorobenzene (mol·L^{-1})



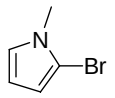
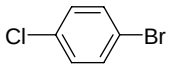


Quenching with CH_3OH **κ = 1.34**

T(min)	κ			
	0.25[a]:0.25[b]	*0.5[a]:0.5[b]*	*0.25[a]:0.5[b]*	*0.5[a]:1.0[b]*
20	1.06	1.46		1.24
30	1.38	1.90	1.20	
Av	1.22	1.68	1.20	1.24

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

b) Concentration of 2-bromo-*N*-methyl-pyrrole (mol·L^{-1})

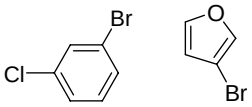



Quenching with CH_3OH **κ = 3.40**

T(min)	κ			
	0.25[a]:0.25[b]	*0.5[a]:0.5[b]*	*0.25[a]:0.5[b]*	*0.5[a]:1.0[b]*
20	3.52	3.52	3.58	3.54
30	3.08	2.87		
Av	3.30	3.20	3.58	3.54

a) Concentration of 2-bromo-*N*-methyl-pyrrole and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 1-bromo-4-chlorobenzene (mol·L^{-1})

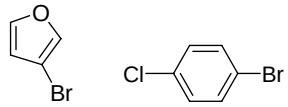


Quenching with I_2 **κ = 1.81**

T(h)	κ			
	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	1.81	1.77	1.75	1.77
4	1.88	1.98		
Av	1.84	1.88	1.75	1.77

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

b) Concentration of 3-bromofuran (mol·L^{-1})

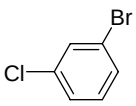
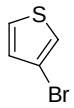


Quenching with I_2 **κ = 3.26**

T(h)	κ			
	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	3.07	3.19	3.19	3.60
4	2.93	3.29		
Av	3.00	3.24	3.19	3.60

a) Concentration of 3-bromofuran and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 1-bromo-4-chlorobenzene (mol·L^{-1})

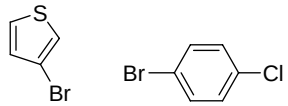



Quenching with CH_3OH **κ = 2.02**

T(h)	κ			
	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	2.14	2.13	1.91	1.95
3	2.10	2.04		
Av	2.12	2.09	1.91	1.95

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

b) Concentration of 3-bromothiophene (mol·L^{-1})

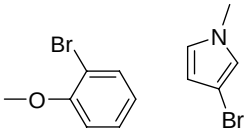


Quenching with CH_3OH **κ = 2.32**

T(h)	κ			
	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	2.61		
3	2.15	2.56	2.13	2.42
Av	2.14	2.59	2.13	2.42

a) Concentration of 3-bromothiophene and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 1-bromo-4-chlorobenzene (mol·L^{-1})

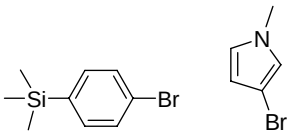


Quenching with CH_3OH **κ = 4.84**

T(h)	κ			
	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	4.49	4.33	4.60	4.55
4	5.91	5.68		
Av	5.20	5.01	4.60	4.55

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

b) Concentration of 3-bromo-*N*-methyl-pyrrole (mol·L^{-1})

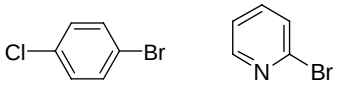


Quenching with CH_3OH **κ = 1.92**

T(h)	κ			
	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	1.95	1.78	1.91	1.75
4	2.22	2.06		
Av	2.08	1.92	1.91	1.75

a) Concentration of (4-bromophenyl)trimethylsilane and of *i*-PrMgCl·LiCl (mol·L^{-1})

b) Concentration of 3-bromo-*N*-methyl-pyrrole (mol·L^{-1})



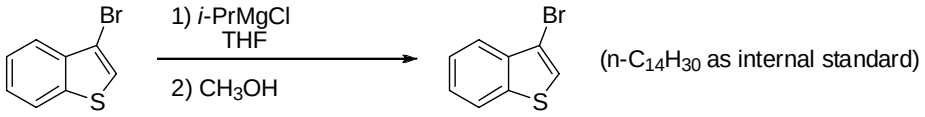
Quenching with CH_3OH

T(h)	κ	
	0.25[a]:0.25[a]	*0.5[a]:0.5[a]*
1		1.50
2	1.39	0.70
3		0.48
4	0.73	0.38
5		0.37
6	0.58	0.34
7		0.31
8	0.56	0.32
31		0.31

a) Concentration of 1-bromo-4-chlorobenzene, 2-bromopyridine and of *i*-PrMgCl·LiCl (mol·L^{-1})

Because of the large scatter of κ from different experiments, the data from these competition experiments (i.e., 1-bromo-4-chloro-benzene/2-bromo-pyridine) were not used for the calculation of relative reactivities.

Kinetics of the Reaction of 3-Bromobenzo[b]thiophene with *i*-PrMgCl in THF[S8]



Typical procedure (0.01 M 3-bromobenzo[b]thiophene with 0.5 M *i*-PrMgCl, 0 °C, THF):
A solution of 3-bromobenzo[b]thiophene (41.4 mg, 0.194 mmol) and n-$C_{14}H_{30}$ (internal standard, 8.2 mg, 0.041 mmol) in 14.12 mL of dry THF was combined with a 1.70 M solution of *i*-PrMgCl in THF (5.88 mL) at 0 °C to give 20 mL of a solution with the concentration listed in Table S2. The mixture was stirred under a nitrogen atmosphere at 0 °C, and after variable times (typically every 4 min) 1.5 mL of this mixture was taken with a gas-tight syringe and injected into 3 mL of methanol. The mixture was extracted with diethyl ether, then analyzed by GC.

[S8] GC was performed with nitrogen as mobile phase and FID detector on a Thermo Electron Focus apparatus equipped with an Optima-1710 capillary column (0.25 μm × 25m × 0.25mm, Macherey-Nagel) and an automatic injection unit. Here $f_{\text{3-bromobenzo[b]thiophene}} = 0.514$, $f_{\text{benzo[b]thiophene}} = 0.624$.

Table S2. Reaction of 0.01M 3-bromobenzo[b]thiophene with 0.5 M *i*-PrMgCl (0 ^{o}C, THF)

T(min)	A_{R1}	A_{P1}	A_{IS}	[R]	[P]
0				0.00972	0.00000
4	69.5945	3.1334	27.2720	0.00938	0.00035
	69.4247	3.3568	27.2185	0.00935	0.00037
	70.0364	3.2630	26.7006	0.00936	0.00036
	Average value			0.00936	0.00036
8	66.7595	4.7573	28.4832	0.00918	0.00054
	66.8870	4.7131	28.3999	0.00919	0.00053
	66.2497	4.8608	28.8896	0.00917	0.00055
	Average value			0.00918	0.00054
12	65.8306	6.2901	27.8793	0.00901	0.00071
	66.4644	6.1888	27.3468	0.00903	0.00069
	66.1351	6.2534	27.6116	0.00902	0.00070
	Average value			0.00902	0.00070
16	65.5497	7.6412	26.8091	0.00887	0.00085
	65.5244	7.6739	26.8017	0.00887	0.00086
	65.9393	7.6432	26.4175	0.00888	0.00085
	Average value			0.00887	0.00085
20	64.1479	9.0401	26.8120	0.00871	0.00101
	64.1329	9.1529	26.7142	0.00870	0.00102
	64.0116	8.9706	27.0178	0.00872	0.00101
	Average value			0.00871	0.00101
24	62.7008	10.2375	27.0617	0.00857	0.00115
	63.1564	10.1189	26.7247	0.00859	0.00113
	64.3506	9.7553	25.8940	0.00864	0.00108
	Average value			0.00860	0.00112
28	61.9999	11.5496	26.4505	0.00843	0.00129
	62.3996	11.3793	26.2211	0.00845	0.00127
	62.0993	11.5891	26.3116	0.00843	0.00130
	Average value			0.00844	0.00129
32	60.4049	12.5753	27.0198	0.00830	0.00142
	60.1671	12.5916	27.2413	0.00829	0.00143
	60.7903	12.3996	26.8102	0.00832	0.00140
	Average value			0.00831	0.00142

Table S3. Reaction of 0.01 M 3-bromobenzo[b]thiophene with 0.4 M *i*-PrMgCl (0 ^{o}C, THF)

T(min)	A_{R1}	A_{P1}	A_{IS}	[R]	[P]
0				0.00972	0.00000
4	71.6376	2.2087	26.1537	0.00948	0.00024
	71.3465	2.7204	25.9331	0.00943	0.00030
	70.6194	2.8569	26.5238	0.00941	0.00031
	Average value			0.00944	0.00028
8	70.3579	2.5861	27.0561	0.00944	0.00029
	68.7414	4.0104	27.2482	0.00928	0.00045
	68.7951	3.5197	27.6852	0.00933	0.00039
	Average value			0.00935	0.00037
12	67.9036	5.2821	26.8144	0.00914	0.00059
	67.7321	5.3523	26.9156	0.00913	0.00059
	67.8624	5.1824	26.9552	0.00915	0.00058
	Average value			0.00914	0.00059
16	65.5322	6.4010	28.0668	0.00900	0.00072
	65.3044	6.6932	28.0024	0.00897	0.00076
	65.0770	6.6833	28.2397	0.00896	0.00076
	Average value			0.00898	0.00075
20	66.0416	7.7403	26.2180	0.00887	0.00086
	66.8524	7.7934	25.3542	0.00887	0.00085
	66.9563	7.4269	25.6168	0.00891	0.00081
	Average value			0.00888	0.00084
24	65.1036	8.6402	26.2562	0.00876	0.00096
	65.1453	8.4942	26.3605	0.00878	0.00094
	64.5683	8.7835	26.6482	0.00874	0.00098
	Average value			0.00876	0.00096
28	63.8986	9.2440	26.8574	0.00869	0.00104
	63.0376	9.7512	27.2113	0.00862	0.00110
	62.8232	9.4784	27.6984	0.00865	0.00107
	Average value			0.00865	0.00107
32	61.8352	10.9478	27.2171	0.00849	0.00124
	61.7892	10.9308	27.2800	0.00849	0.00124
	62.7767	10.5788	26.6445	0.00854	0.00119
	Average value			0.00850	0.00122

Table S4. Reaction of 0.01 M 3-bromobenzo[b]thiophene with 0.3 M *i*-PrMgCl (0 ^{o}C, THF)

T(min)	A_{R1}	A_{P1}	A_{IS}	[R]	[P]
0				0.00972	0.00000
12	68.3637	3.0106	28.6257	0.00938	0.00034
	67.6877	3.7960	28.5164	0.00929	0.00043
	67.6583	3.9569	28.3847	0.00928	0.00045
	Average value			0.00932	0.00041
24	64.5612	6.2382	29.2006	0.00901	0.00072
	64.9121	6.1616	28.9263	0.00902	0.00071
	64.9260	6.1931	28.8809	0.00901	0.00071
	Average value			0.00901	0.00071
36	64.8251	7.9592	27.2157	0.00883	0.00089
	64.5784	8.1393	27.2803	0.00881	0.00091
	64.1339	8.3288	27.5373	0.00878	0.00094
	Average value			0.00881	0.00092
48	60.9452	10.2929	28.7620	0.00854	0.00119
	61.0682	10.3325	28.5993	0.00853	0.00119
	60.9960	9.9763	29.0278	0.00857	0.00115
	Average value			0.00855	0.00118
60	58.8399	12.4185	28.7416	0.00828	0.00144
	58.9014	12.2666	28.8320	0.00830	0.00142
	58.9718	12.2774	28.7508	0.00830	0.00142
	Average value			0.00829	0.00143
72	57.7627	14.2763	27.9610	0.00808	0.00164
	57.6428	14.3628	27.9945	0.00807	0.00166
	57.4424	14.7845	27.7731	0.00802	0.00170
	Average value			0.00806	0.00167
84	54.5639	16.1072	29.3289	0.00782	0.00190
	54.8479	16.0792	29.0730	0.00783	0.00189
	54.4003	16.1200	29.4797	0.00782	0.00191
	Average value			0.00782	0.00190
96	53.1191	17.8874	28.9935	0.00761	0.00211
	53.0747	17.5026	29.4228	0.00765	0.00208
	52.7800	18.0956	29.1244	0.00758	0.00214
	Average value			0.00761	0.00211

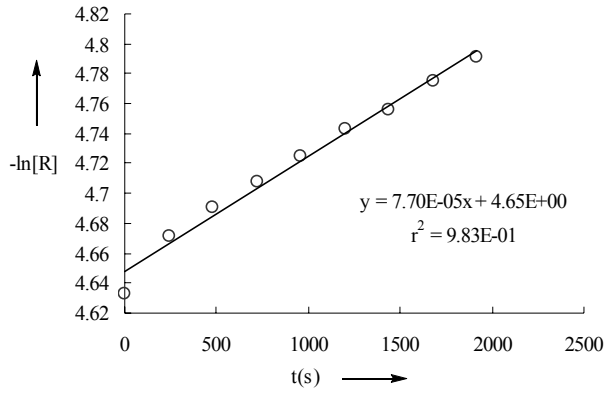


Figure S1. (Pseudo-)first-order for the reaction of 0.01 M 3-bromobenzo[b]thiophene with 0.5 M *i*-PrMgCl (0°C, THF, data from Table S2).

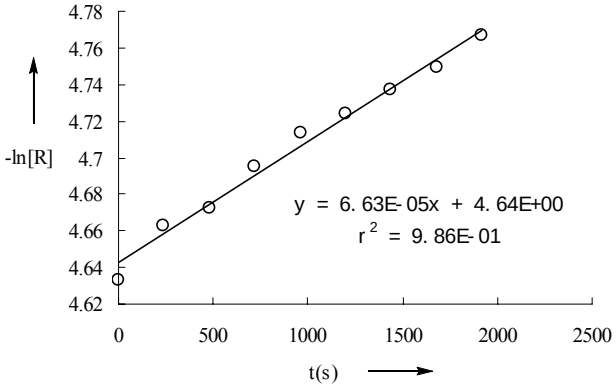


Figure S2. (Pseudo-)first-order for the reaction of 0.01 M 3-bromobenzo[b]thiophene with 0.4 M *i*-PrMgCl (0°C, THF, data from Table S3).

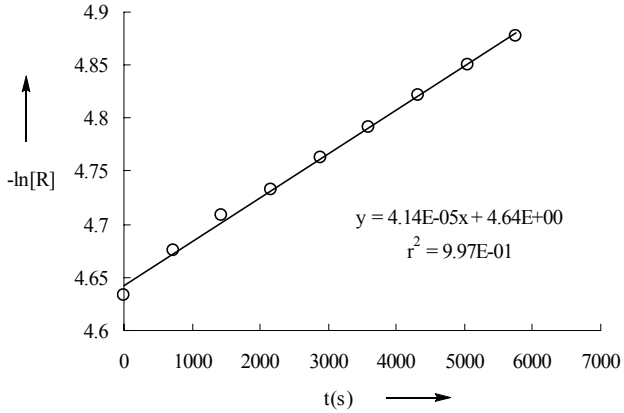


Figure S3. (Pseudo-)first-order for the reaction of 0.01 M 3-bromobenzo[b]thiophene with 0.3 M *i*-PrMgCl (0°C, THF, data from Table S4).

Table S5. Summary of observed (pseudo-)first-order rate constants of 3-bromobenzo[b]thiophene (0 ^{o}C, THF).

[*i*-PrMgCl·LiCl]/mol·L^{-1}	k_{obs}/s^{-1}
0.3	4.14E-05
0.4	6.63E-05
0.5	7.70E-05

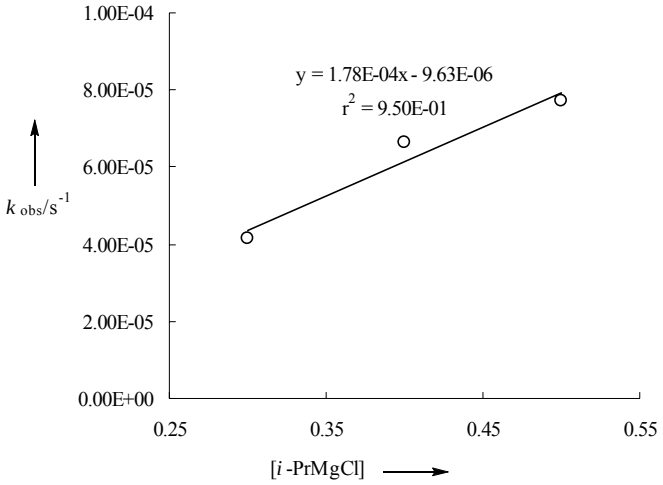


Figure S4. Plot of observed rate constant vs. the concentration of *i*-PrMgCl (0 ^{o}C, THF).

$k_{(3\text{-bromobenzo[b]thiophene})}$ **= 1.78 × 10^{-4} M^{-1} s^{-1} (0 ^{o}C, THF)**