

Formation of Benzyne from 2,6-Dihaloarylithiums:
Mechanistic Basis of the Regioselectivity

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Supporting Information

NMR Spectroscopy

- I** ¹³C NMR spectrum of 2-chloro-6-fluorophenyllithium (**6**) in neat THF.
- II** ⁶Li NMR spectrum of 2-chloro-6-fluorophenyllithium (**6**) in THF (10.3 M).
- III** ⁶Li NMR spectra of 2-chloro-6-fluorophenyllithium (**6**) in THF (5.0 and 0.3 M).

Kinetics of Benzyne Formation

- IV** Plot of $k_{\text{obsd}(\mathbf{6})}$ versus [**6**] in THF (0.3 M) and toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzyne.
- V** Plot of $k_{\text{obsd}(\mathbf{6})}$ versus [**6**] in THF (6.8 M) and toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzyne.

VI Plot of $k_{\text{obsd}(6)}$ versus [THF] in toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzene from **6** (0.2 M).

VII Plot of $k_{\text{obsd}(2)}$ versus [THF] in toluene cosolvent for the formation of 3-chlorobenzene from **6** (0.2 M).

VIII Plot of $k_{\text{obsd}(3)}$ versus [THF] in toluene cosolvent for the formation of 3-fluorobenzene from **6** (0.2 M).

IX Plot of $k_{\text{obsd}(6)}$ versus [spiro[2.4]hepta-4,6-diene] in THF (0.3 M) and toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzene from **6** (0.2 M).

X Plot of $k_{\text{obsd}(6)}$ versus [**6**] in THF (0.3 M) and toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzene from **6** (0.2 M).

XI Table of data for plot in Section IV.

XII Table of data for plot in Section V.

XIII Table of data for plot in Section VI.

XIV Table of data for plot in Section VII.

XV Table of data for plot in Section VIII.

XVI Table of data for plot in Section IX.

XVII Table of data for plot in Section X.

XVIII Table of data for observed ratio of [4]:[5].

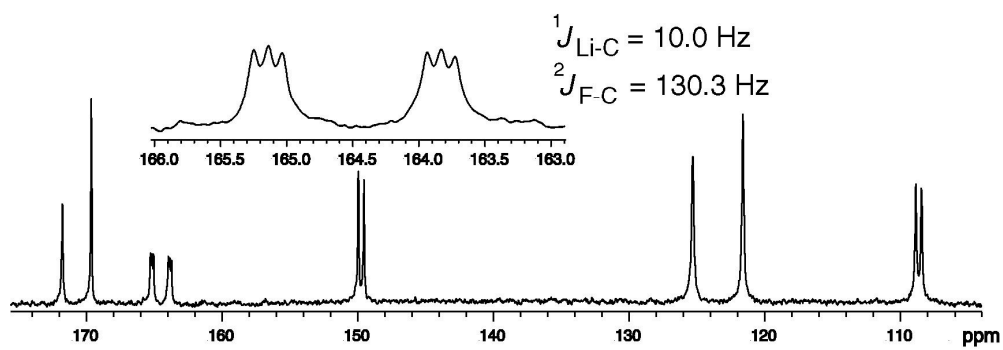
DFT Calculations

XIX Optimized structures for the serial solvation of 2-chloro-6-fluorophenyllithium.

Experimental Section.

XX Physical and Spectral Data

NMR Spectroscopy

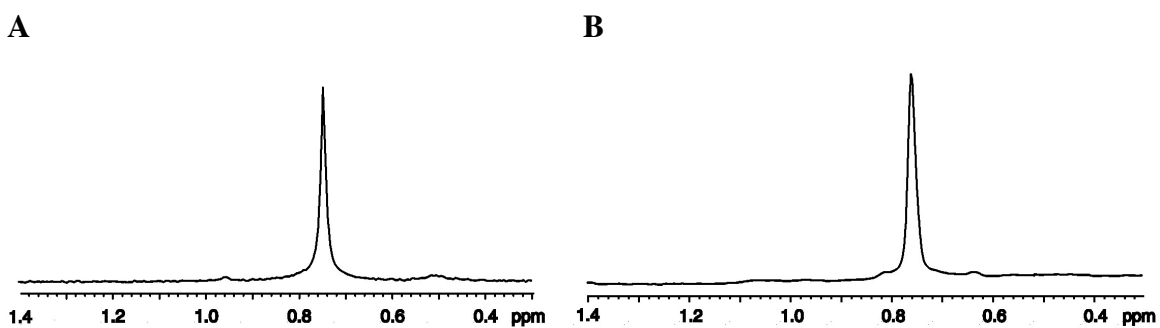


I. ^{13}C NMR spectrum in neat THF at -100°C of 0.4 M $[^6\text{Li}]2\text{-chloro-6-fluorophenyllithium}$ (**6**).

$^3J_{\text{F-Li}} = 1.2 \text{ Hz}$

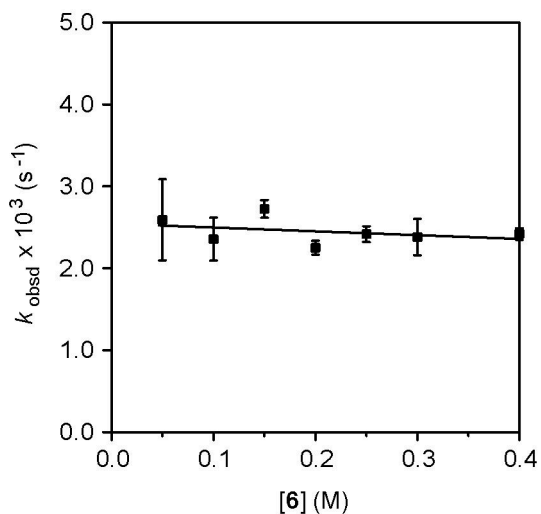


II. ^6Li NMR spectrum in THF (10.3 M) with toluene cosolvent at -100°C of 0.2 M $[\text{}^6\text{Li}]2\text{-chloro-6-fluorophenyllithium}$ (**6**).

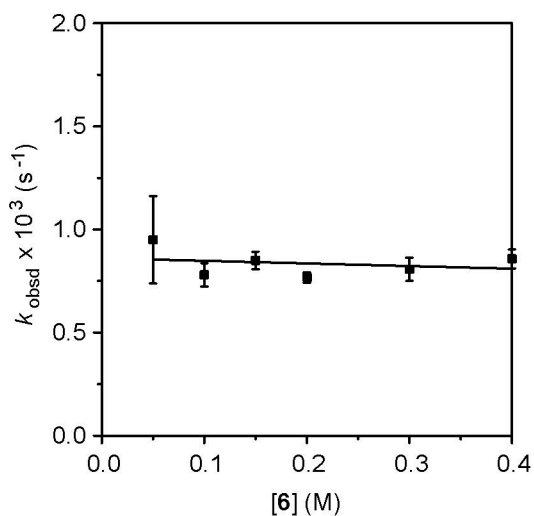


III. ^6Li NMR spectra in THF and toluene/pentane cosolvent at -85°C : (**A**) 0.10 M $[\text{}^6\text{Li}]2\text{-chloro-6-fluorophenyllithium}$ (**6**) in $[\text{THF}] = 5.0\text{ M}$; (**B**) 0.10 M $[\text{}^6\text{Li}]2\text{-chloro-6-fluorophenyllithium}$ (**6**) in $[\text{THF}] = 0.30\text{ M}$.

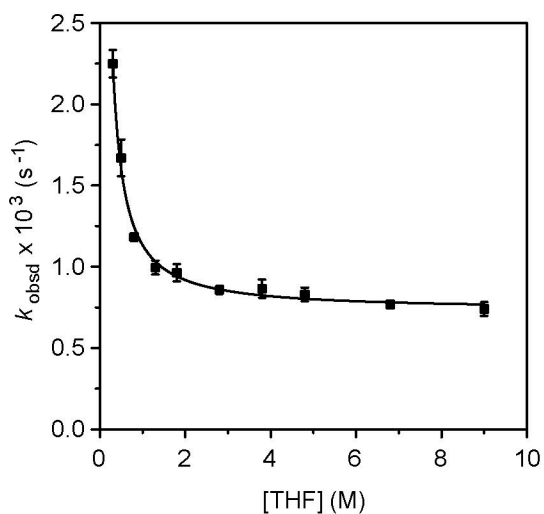
Kinetics of Benzyne Formation



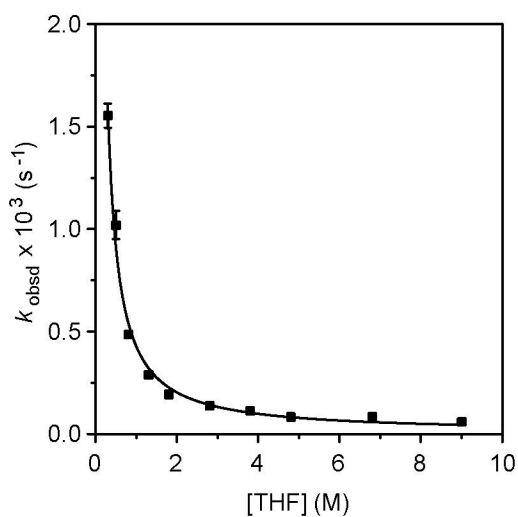
IV. Plot of $k_{\text{obsd}(6)}$ versus $[6]$ in THF (0.3 M) and toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzynes at $-25\text{ }^{\circ}\text{C}$. The curve depicts the result of an unweighted least-squares fit to $k_{\text{obsd}(6)} = k[6] + k'$ ($k = 5 \pm 5 \times 10^{-4}$, $k' = 2.5 \pm 0.1 \times 10^{-3}$).



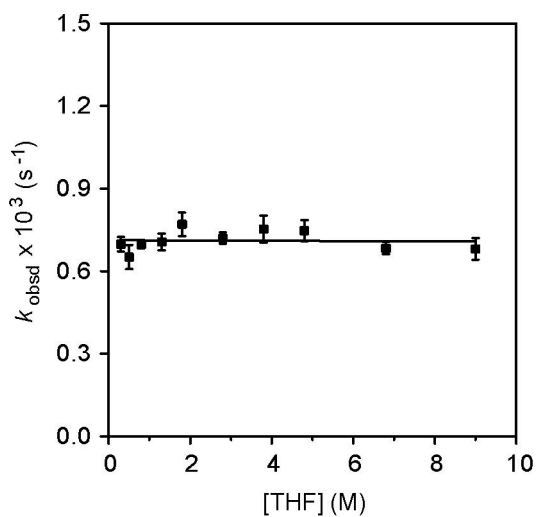
V. Plot of $k_{\text{obsd}(6)}$ versus $[6]$ in THF (6.8 M) and toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzynes at $-25\text{ }^{\circ}\text{C}$. The curve depicts the result of an unweighted least-squares fit to $k_{\text{obsd}(6)} = k[6] + k'$ ($k = 1 \pm 2 \times 10^{-4}$, $k' = 8.6 \pm 0.6 \times 10^{-4}$).



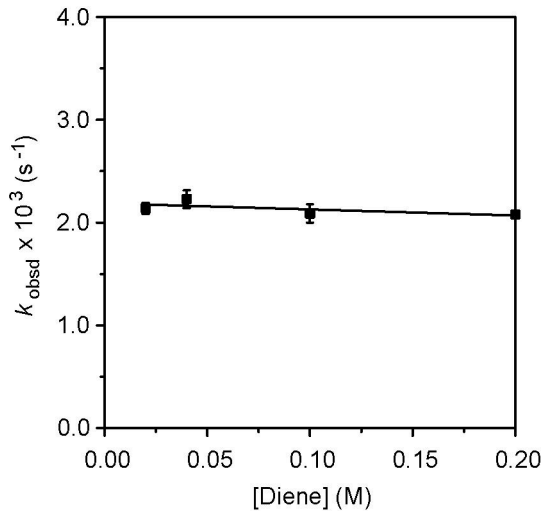
VI. Plot of $k_{\text{obsd}(6)}$ versus [THF] in toluene cosolvent for the formation of 3-chloro- and 3-fluorobenzynes from **6** (0.2 M) at $-25\text{ }^{\circ}\text{C}$. The curve depicts the result of an unweighted least-squares fit to $k_{\text{obsd}(6)} = k[\text{THF}]^n + k'$ ($k = 4.0 \pm 0.4 \times 10^{-5}$, $n = -1.12 \pm 0.09$, $k' = 7.3 \pm 0.3 \times 10^{-4}$).



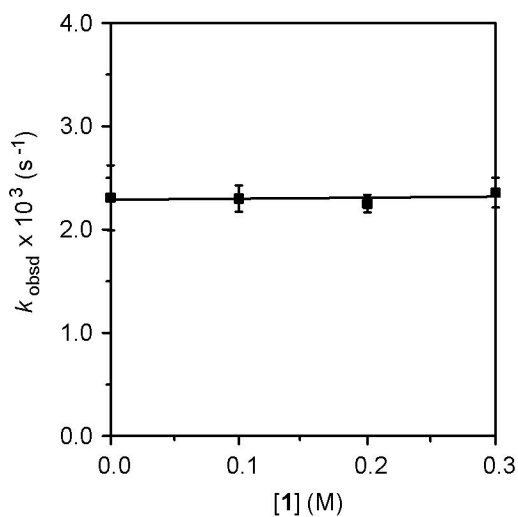
VII. Plot of $k_{\text{obsd}(2)}$ versus [THF] in toluene cosolvent for the formation of 3-chlorobenzynes from **6** (0.2 M) at $-25\text{ }^{\circ}\text{C}$. The curve depicts the result of an unweighted least-squares fit to $k_{\text{obsd}(2)} = k[\text{THF}]^n + k'$ ($k = 4.2 \pm 0.6 \times 10^{-4}$, $n = -1.1 \pm 0.1$, $k' = 1 \pm 4 \times 10^{-5}$).



VIII. Plot of $k_{\text{obsd}(3)}$ versus [THF] in toluene cosolvent for the formation of 3-fluorobenzynes from **6** (0.2 M) at -25°C . The curve depicts the result of an unweighted least-squares fit to $k_{\text{obsd}(3)} = k[\text{THF}] + k'$ ($k = -1 \pm 4 \times 10^{-6}$, $k' = 7.1 \pm 0.2 \times 10^{-4}$).



IX. Plot of $k_{\text{obsd}(6)}$ versus [spiro[2.4]hepta-4,6-diene] in THF (0.3 M) and toluene cosolvent for the formation of 3-chloro and 3-fluorobenzynes from **6** (0.2 M) at -25°C . The curve depicts the result of an unweighted least-squares fit to $k_{\text{obsd}(6)} = k[\text{diene}] + k'$ ($k = -1 \pm 4 \times 10^{-4}$, $k' = 2.2 \pm 0.1 \times 10^{-3}$).



X. Plot of $k_{\text{obsd}(6)}$ versus $[1]$ in THF (0.3 M) and toluene cosolvent for the formation of 3-chloro and 3-fluorobenzynes from **6** (0.2 M) at $-25\text{ }^{\circ}\text{C}$. The curve depicts the result of an unweighted least-squares fit to $k_{\text{obsd}(6)} = k[1] + k'$ ($k = 1 \pm 2 \times 10^{-4}$, $k' = 2.3 \pm 0.1 \times 10^{-3}$).

XI. Table of data for plot in Section IV

$[6]$ (M)	$k_{\text{obsd}(6)} 1$ (s^{-1})	$k_{\text{obsd}(6)} 2$ (s^{-1})	$k_{\text{obsd}(6)}$ (avg) (s^{-1})
0.050	$0.0029 \pm 3\text{E-}4$	$0.0022 \pm 2\text{E-}4$	$0.0026 \pm 5\text{E-}4$
0.100	$0.0022 \pm 1\text{E-}4$	$0.0025 \pm 2\text{E-}4$	$0.0023 \pm 3\text{E-}4$
0.150	$0.0026 \pm 1\text{E-}4$	$0.0028 \pm 3\text{E-}4$	$0.0027 \pm 1\text{E-}4$
0.200	$0.0022 \pm 2\text{E-}4$	$0.0023 \pm 2\text{E-}4$	$0.0022 \pm 1\text{E-}4$
0.250	$0.0025 \pm 3\text{E-}4$	$0.0023 \pm 2\text{E-}4$	$0.0024 \pm 1\text{E-}4$
0.300	$0.0025 \pm 2\text{E-}4$	$0.0022 \pm 2\text{E-}4$	$0.0024 \pm 2\text{E-}4$
0.400	$0.0024 \pm 2\text{E-}4$	$0.0025 \pm 3\text{E-}4$	$0.0024 \pm 1\text{E-}4$

XII. Table of data for plot in Section V

[6] (M)	$k_{\text{obsd}(6)} 1$ (s^{-1})	$k_{\text{obsd}(6)} 2$ (s^{-1})	$k_{\text{obsd}(6)} (\text{avg})$ (s^{-1})
0.050	$0.0008 \pm 1\text{E-}4$	$0.0011 \pm 1\text{E-}4$	$0.0009 \pm 2\text{E-}4$
0.100	$0.00082 \pm 5\text{E-}5$	$0.00074 \pm 3\text{E-}5$	$0.00078 \pm 6\text{E-}5$
0.150	$0.00088 \pm 4\text{E-}5$	$0.00082 \pm 5\text{E-}5$	$0.00085 \pm 4\text{E-}5$
0.200	$0.00075 \pm 8\text{E-}5$	$0.00078 \pm 5\text{E-}5$	$0.00077 \pm 2\text{E-}5$
0.300	$0.0008 \pm 1\text{E-}4$	$0.00077 \pm 4\text{E-}5$	$0.00081 \pm 5\text{E-}5$
0.400	$0.0008 \pm 1\text{E-}4$	$0.00089 \pm 1\text{E-}5$	$0.00086 \pm 5\text{E-}5$

XIII. Table of data for plot in Section VI

[THF] (M)	$k_{\text{obsd}(6)}$ (s^{-1})	$k_{\text{obsd}(6)} 2$ (s^{-1})	$k_{\text{obsd}(6)} (\text{avg})$ (s^{-1})
0.30	$0.0022 \pm 2\text{E-}4$	$0.0023 \pm 2\text{E-}4$	$0.0022 \pm 1\text{E-}4$
0.50	$0.0017 \pm 1\text{E-}4$	$0.0016 \pm 2\text{E-}4$	$0.0017 \pm 1\text{E-}4$
0.80	$0.0012 \pm 1\text{E-}5$	$0.0012 \pm 1\text{E-}4$	$0.0012 \pm 1\text{E-}4$
1.30	$0.0010 \pm 1\text{E-}5$	$0.00096 \pm 8\text{E-}5$	$0.00099 \pm 4\text{E-}5$
1.80	$0.00092 \pm 5\text{E-}5$	$0.0010 \pm 1\text{E-}4$	$0.00096 \pm 5\text{E-}5$
2.80	$0.00087 \pm 4\text{E-}5$	$0.00084 \pm 5\text{E-}5$	$0.00086 \pm 2\text{E-}5$

3.80	$0.00082 \pm 4E-6$	$0.00090 \pm 3E-5$	$0.00086 \pm 6E-5$
4.80	$0.0009 \pm 1E-4$	$0.00080 \pm 5E-5$	$0.00083 \pm 4E-5$
6.80	$0.00075 \pm 8E-5$	$0.00078 \pm 5E-5$	$0.00077 \pm 2E-5$
9.00	$0.00071 \pm 6E-5$	$0.00077 \pm 8E-5$	$0.00074 \pm 4E-5$

XIV. Table of data for plot in Section VII

[THF] (M)	$k_{\text{obsd}(2)} 1 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}(2)} 2 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}(2)} \text{ (avg) (s}^{-1}\text{)}$
0.30	$0.0015 \pm 1E-4$	$0.0016 \pm 1E-4$	$0.0015 \pm 1E-4$
0.50	$0.0011 \pm 1E-4$	$0.00097 \pm 6E-5$	$0.0010 \pm 1E-4$
0.80	$0.00048 \pm 5E-5$	$0.00049 \pm 5E-5$	$0.00048 \pm 1E-5$
1.30	$0.00030 \pm 4E-5$	$0.00028 \pm 3E-5$	$0.00029 \pm 1E-5$
1.80	$0.00018 \pm 2E-5$	$0.00020 \pm 2E-5$	$0.00019 \pm 1E-5$
2.80	$0.00014 \pm 2E-5$	$0.00013 \pm 1E-5$	$0.00014 \pm 1E-5$
3.80	$0.00011 \pm 1E-5$	$0.00012 \pm 1E-5$	$0.00011 \pm 1E-5$
4.80	$0.000086 \pm 8E-6$	$0.00008 \pm 1E-5$	$0.000083 \pm 4E-6$
6.80	$0.000082 \pm 9E-6$	$0.000086 \pm 8E-6$	$0.000084 \pm 3E-6$
9.00	$0.000057 \pm 8E-6$	$0.000062 \pm 7E-6$	$0.000059 \pm 3E-6$

XV. Table of data for plot in Section VIII

[THF] (M)	$k_{\text{obsd}(3)} 1 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}(3)} 2 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}(3)} \text{ (avg) (s}^{-1}\text{)}$
0.30	$0.00068 \pm 6E-5$	$0.00072 \pm 5E-5$	$0.00070 \pm 3E-5$
0.50	$0.00068 \pm 6E-5$	$0.00062 \pm 5E-5$	$0.00065 \pm 4E-5$

0.80	$0.00069 \pm 7\text{E-}5$	$0.00071 \pm 7\text{E-}5$	$0.00070 \pm 1\text{E-}5$
1.30	$0.00073 \pm 8\text{E-}5$	$0.00068 \pm 7\text{E-}5$	$0.00070 \pm 3\text{E-}5$
1.80	$0.00074 \pm 8\text{E-}5$	$0.00080 \pm 8\text{E-}5$	$0.00077 \pm 4\text{E-}5$
2.80	$0.00073 \pm 8\text{E-}5$	$0.00071 \pm 6\text{E-}5$	$0.00072 \pm 2\text{E-}5$
3.80	$0.00072 \pm 7\text{E-}5$	$0.00079 \pm 7\text{E-}5$	$0.00075 \pm 5\text{E-}5$
4.80	$0.00077 \pm 8\text{E-}5$	$0.00072 \pm 7\text{E-}4$	$0.00075 \pm 4\text{E-}5$
6.80	$0.00067 \pm 7\text{E-}5$	$0.00070 \pm 5\text{E-}5$	$0.00068 \pm 2\text{E-}5$
9.00	$0.00065 \pm 8\text{E-}5$	$0.00071 \pm 8\text{E-}5$	$0.00068 \pm 4\text{E-}5$

XVI. Table of data for plot in Section IX

[Diene] (M)	$k_{\text{obsd}(\text{6})} 1 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}(\text{6})} 2 \text{ (s}^{-1}\text{)}$	$k_{\text{obsd}(\text{6})} \text{ (avg) (s}^{-1}\text{)}$
0.02	$0.0022 \pm 2\text{E-}4$	$0.00212 \pm 4\text{E-}5$	$0.00216 \pm 5\text{E-}5$
0.04	$0.0022 \pm 2\text{E-}4$	$0.0023 \pm 2\text{E-}4$	$0.00225 \pm 8\text{E-}5$
0.10	$0.0020 \pm 1\text{E-}4$	$0.00217 \pm 4\text{E-}5$	$0.00211 \pm 9\text{E-}5$
0.20	$0.00207 \pm 3\text{E-}5$	$0.0021 \pm 2\text{E-}4$	$0.00210 \pm 4\text{E-}5$

XVII. Table of data for plot in Section X

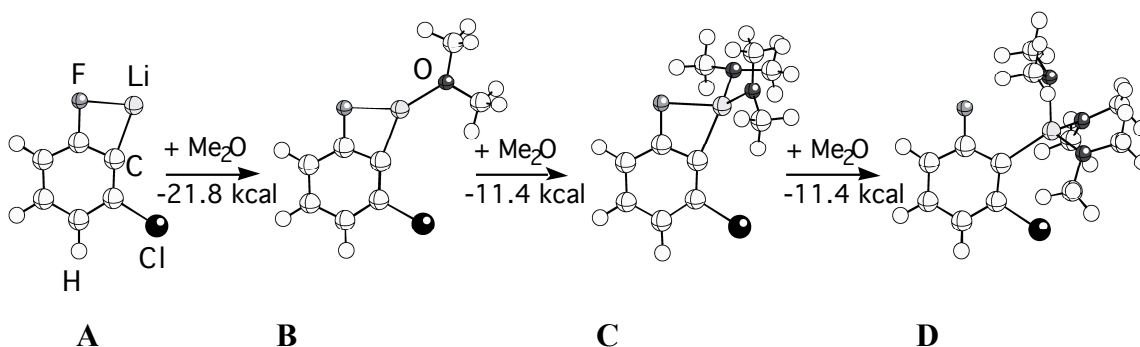
[1] (M)	$k_{\text{obsd}(\mathbf{6})} 1$ (s ⁻¹)	$k_{\text{obsd}(\mathbf{6})} 2$ (s ⁻¹)	$k_{\text{obsd}(\mathbf{6})}$ (avg) (s ⁻¹)
0.00	0.0025 ± 3E-4	0.0021 ± 2E-4	0.0023 ± 3E-4
0.10	0.0022 ± 2E-4	0.0024 ± 3E-4	0.0023 ± 1E-4
0.20	0.0022 ± 2E-4	0.0023 ± 2E-4	0.00225 ± 8E-5
0.30	0.00225 ± 3E-5	0.0025 ± 2E-4	0.0024 ± 1E-4

XVIII. Table of data for observed ratio of [4]:[5] versus [THF] in toluene cosolvent for the formation of 3-chloro and 3-fluorobenzynes from **6** (0.2 M).

[THF] (M)	ratio [4]:[5] (avg)
0.30	0.69 ± 0.08
0.50	0.61 ± 0.07
0.80	0.41 ± 0.05
1.30	0.29 ± 0.02
1.80	0.20 ± 0.02
2.80	0.16 ± 0.02
3.80	0.13 ± 0.01
4.80	0.10 ± 0.01
6.80	0.11 ± 0.01
9.00	0.08 ± 0.01

DFT Calculations

XIX Optimized structures for the serial solvation of 2-chloro-6-fluorophenyllithium using Gaussian 98W at the B3LYP level of DFT theory with the 6-31G* basis set. Only the most stable isomers are shown. THF is modeled by Me₂O. Vibrational frequencies calculated at the same level characterize these stationary points as minima (NIMAG = 0). Enthalpies (ΔH , kcal/mol) include thermal corrections at 248 °C.



	<u>H (Hartrees)</u>
Me ₂ O	-154.94063
A	-797.92399
B	-952.89941
C	-1107.85826
D	-1262.81714

Geometries of stationary points are given below:

Me₂O

SCF Done: E(RB+HF-LYP) = -155.025044227 A.U. after 1 cycles
 Zero-point correction= 0.08030 (Hartree/Particle)
 Thermal correction to Energy= 0.083627
 Thermal correction to Enthalpy= 0.084413

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	0.000000	-0.589888	-0.000009
2	6	0	-1.171072	0.195261	0.000015
3	6	0	1.171072	0.195261	-0.000009
4	1	0	1.232500	0.839668	0.892951
5	1	0	2.021947	-0.491384	-0.000033
6	1	0	1.232477	0.839704	-0.892944
7	1	0	-1.232496	0.839702	-0.892920
8	1	0	-2.021947	-0.491385	0.000010
9	1	0	-1.232480	0.839670	0.892975

	1	2	3
	A	A	A
Frequencies --	224.0277	250.1852	415.2505

A

SCF Done: E(RB+HF-LYP) = -798.002004980 A.U. after 14 cycles
 Zero-point correction= 0.071769 (Hartree/Particle)
 Thermal correction to Energy= 0.077227
 Thermal correction to Enthalpy= 0.078012

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.193425	-0.864690	-0.000013
2	6	0	-1.416565	-0.239413	0.000003
3	9	0	-2.538598	-1.169689	-0.000019
4	6	0	-1.728034	1.108292	0.000023
5	6	0	-0.621208	1.963405	0.000034
6	6	0	0.676630	1.441627	0.000023
7	6	0	0.852017	0.053561	-0.000004
8	17	0	2.536845	-0.542211	-0.000014
9	3	0	-1.237038	-2.549999	-0.000035
10	1	0	-2.749682	1.473450	0.000029
11	1	0	-0.770017	3.039494	0.000052
12	1	0	1.535346	2.105143	0.000033

	1	2	3
	A	A	A
Frequencies --	134.6060	180.2365	218.7280

B

SCF Done: E(RB+HF-LYP) = -953.064378177 A.U. after 14 cycles
Zero-point correction= 0.154053 (Hartree/Particle)
Thermal correction to Energy= 0.164183
Thermal correction to Enthalpy= 0.164969

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.517707	-0.097437	-0.000476
2	6	0	1.657750	0.695168	-0.000110
3	6	0	2.967961	0.205485	0.000482
4	6	0	3.168674	-1.178510	0.000714
5	6	0	2.074672	-2.050366	0.000360
6	6	0	0.834489	-1.435254	-0.000214
7	9	0	-0.320455	-2.305072	-0.000618
8	17	0	1.476361	2.484006	-0.000386
9	3	0	-1.409738	-0.682707	-0.001178
10	8	0	-3.164529	-0.001791	0.000023
11	6	0	-3.253293	1.429716	0.000814
12	6	0	-4.433844	-0.649305	0.000061
13	1	0	2.190355	-3.129549	0.000518
14	1	0	4.179222	-1.577679	0.001170
15	1	0	3.814451	0.884673	0.000751
16	1	0	-5.006245	-0.375859	0.895737
17	1	0	-4.250755	-1.726097	-0.000339
18	1	0	-2.230337	1.811378	0.000551
19	1	0	-3.781265	1.775216	0.898331
20	1	0	-3.782093	1.776163	-0.895851
21	1	0	-5.006626	-0.375238	-0.895182

	1	2	3
	A	A	A
Frequencies --	16.4185	24.5809	36.7070

C

SCF Done: E(RB+HF-LYP) = -1108.11491248 A.U. after 2 cycles
 Zero-point correction= 0.236176 (Hartree/Particle)
 Thermal correction to Energy= 0.255708
 Thermal correction to Enthalpy= 0.256652

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.941928	-0.004917	0.006531
2	6	0	-2.203597	0.394607	0.424847
3	6	0	-3.412979	-0.126936	-0.047072
4	6	0	-3.372515	-1.131278	-1.018607
5	6	0	-2.143289	-1.593294	-1.500385
6	6	0	-1.021205	-0.992964	-0.950024
7	9	0	0.247461	-1.448197	-1.435408
8	17	0	-2.339067	1.694548	1.669751
9	3	0	1.111564	-0.061364	-0.092483
10	8	0	2.349638	-1.171238	0.950354
11	8	0	2.139234	1.421288	-0.804696
12	6	0	1.424015	2.620173	-1.115815
13	6	0	3.352912	1.283858	-1.533547
14	6	0	1.982743	-2.545182	1.097865
15	6	0	2.914665	-0.620222	2.137273
16	1	0	-2.072095	-2.369119	-2.256733
17	1	0	-4.298707	-1.552209	-1.400715
18	1	0	-4.362701	0.239047	0.330154
19	1	0	3.159723	1.261759	-2.614802
20	1	0	3.807402	0.340082	-1.224188
21	1	0	0.493060	2.585753	-0.548322
22	1	0	1.199163	2.665216	-2.189590
23	1	0	1.500054	-2.842287	0.166558
24	1	0	1.278555	-2.669456	1.930662
25	1	0	2.200985	-0.673205	2.970091
26	1	0	3.150597	0.424845	1.925489
27	1	0	2.874965	-3.160040	1.275794
28	1	0	3.833969	-1.155470	2.410559
29	1	0	2.015391	3.499768	-0.828612
30	1	0	4.038038	2.112392	-1.307662

	1	2	3
	A	A	A
Frequencies --	15.6234	27.2839	31.2522

D

SCF Done: E(RB+HF-LYP) = -1263.15555432 A.U. after 1 cycles
 Zero-point correction= 0.318964 (Hartree/Particle)
 Thermal correction to Energy= 0.337628
 Thermal correction to Enthalpy= 0.338413

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.237202	-0.183550	-0.101580
2	6	0	2.379766	0.606120	-0.113680
3	6	0	3.700645	0.158558	-0.216079
4	6	0	3.919881	-1.216726	-0.313210
5	6	0	2.832849	-2.094241	-0.300318
6	6	0	1.568395	-1.526871	-0.192752
7	9	0	0.503343	-2.438785	-0.163327
8	17	0	2.206331	2.413110	0.029336
9	3	0	-0.865117	0.029217	0.034984
10	8	0	-1.667152	1.900208	0.046561
11	8	0	-1.571027	-0.702604	1.813882
12	8	0	-2.113353	-0.718243	-1.416262
13	6	0	-1.681818	-1.717046	-2.339968
14	6	0	-3.399541	-0.205562	-1.730425
15	6	0	-0.587545	-1.280256	2.675543
16	6	0	-2.812640	-1.388955	1.880201
17	6	0	-1.367372	2.703681	-1.095365
18	6	0	-1.520667	2.625809	1.267254
19	1	0	2.962245	-3.170738	-0.367208
20	1	0	4.933122	-1.601323	-0.395573
21	1	0	4.531412	0.856854	-0.217218
22	1	0	-0.726277	-2.090196	-1.976835
23	1	0	-1.569304	-1.289142	-3.345869
24	1	0	-3.415516	0.225650	-2.742051
25	1	0	-3.620298	0.575531	-1.001204
26	1	0	-2.707589	-2.429305	1.542061
27	1	0	-3.511773	-0.864021	1.226563
28	1	0	0.329057	-0.707728	2.534081
29	1	0	-0.402336	-2.326084	2.402321
30	1	0	-1.486140	2.066267	-1.973809
31	1	0	-0.336034	3.069820	-1.051284
32	1	0	-0.495897	3.001635	1.372752
33	1	0	-1.741727	1.926638	2.075260
34	1	0	-2.065314	3.550702	-1.159531
35	1	0	-2.228120	3.466711	1.299378
36	1	0	-0.919848	-1.221232	3.721395
37	1	0	-3.204603	-1.384351	2.907314
38	1	0	-4.160687	-0.997522	-1.675024
39	1	0	-2.409418	-2.540273	-2.380415

	1	2	3
	A	A	A
Frequencies --	27.4884	29.5158	40.0022

Experimental Section

Reagents and Solvents. 1-Chloro-3-fluorobenzene (**1**) is commercially available. *n*-BuLi used in the kinetics was recrystallized [see ref 10 in text]. Spiro[2.4]hepta-4,6-diene was prepared and purified according to literature procedures [see ref 8 in text]. [⁶Li]*n*-BuLi was prepared and recrystallized as described previously [Chadwick, S. T.; Rennels, R. A.; Rutherford, J. L.; Collum, D. B. *J. Am. Chem. Soc.* **2000**, *122*, 8640]. THF, *n*-pentane and toluene were distilled from sodium/benzophenone. The pentane still contained 1% tetraglyme to dissolve the ketyl. The diphenylacetic acid used to check solution titers [Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879] was recrystallized from methanol and sublimed at 120 °C under full vacuum. Air- and moisture sensitive materials were manipulated under argon or nitrogen using standard glove box, vacuum line, and syringe techniques.

NMR Spectroscopic Analyses. Samples for spectroscopic analyses were prepared by using a protocol described elsewhere [Romesberg, F. E.; Bernstein, M. P.; Fuller, D. J.; Harrison, A. T.; Collum, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 3475]. ⁶Li and ¹³C NMR spectra were recorded on a Varian XL-400 spectrometer operating at 58.84 and 100.58 MHz, respectively. The ⁶Li and ¹³C resonances are referenced to 0.30 M [⁶Li]LiCl/MeOH (0.0 ppm, -100 °C), and the THF β-methylene resonance (25.37 ppm, -100 °C), respectively.

Kinetics. For a kinetic run corresponding to a single rate constant, a relatively concentrated (2.2 M) solution of *n*-BuLi in toluene at -78 °C was prepared and titrated to determine the precise concentration. The solution was diluted to a concentration appropriate for the particular series and titrated a second time. A series of oven-dried, argon-flushed 5 mL serum vials (10 per rate constant) fitted with stir bars were charged with a stock solution containing 1-chloro-3-fluorobenzene (**1**), spiro[2.4]hepta-4,6-diene, THF, and *n*-octane as a GC standard. The reaction vials were held under argon at -25.0 ± 0.2 °C. The reactions were initiated by adding aliquots of a stock solution of *n*-BuLi in

toluene, also refrigerated at $-25\text{ }^{\circ}\text{C}$, to achieve a concentration 0.2 M below the actual 1-chloro-3-fluorobenzene (**1**) concentration. The metalations were monitored by following the decrease of **1** relative to the internal standard at early percent conversion. The vessels were periodically quenched with 1:1 H_2O -THF at intervals chosen to ensure an adequate sampling of early conversion at 10% consumption of the starting material. The quenched aliquots were extracted into Et_2O and the extracts analyzed using an auto injecting GC fitted with a 60 meter DB-5 column. The initial rates were determined by linear least-squares analyses, and were shown to be reproducible within $\pm 10\%$. Following the formation of cycloadducts **4** and **5** afforded equivalent rate constants within $\pm 10\%$. Beyond 20% consumption of the starting material, GC analyses showed detectable amounts ($< 5\%$) of butyl adducts resulting from nucleophilic addition of *n*-BuLi to the intermediate 3-halobenzynes [Coe, J. W.; Wirtz, M. C.; Bashore, C. G.; Candler, J. *Org. Lett.* **2004**, *6*, 1589]. The observed rate constants (k_{obsd}) were calculated by dividing the initial rates (linear slopes) by the corresponding concentrations of 2-chloro-6-fluorophenyllithium (**6**). The reported errors correspond to one standard deviation.

XX. Physical and Spectral Data.

5-Chloro-9,9-spirocyclopropyl-1,4-dihydro-1,4-methano-naphthalene (4).

Clear colorless oil. TLC: $R_f = 0.60$ (100% hexanes); MS m/z 202 (M^+). ^1H NMR (400 MHz, CDCl_3) δ 7.04 (d, $J = 6.6$ Hz, 1H), 6.89 (dd, $J = 7.9, 1.2$ Hz, 1H), 6.87 - 6.82 (m, 3H), 3.56 (d, $J = 2.1$ Hz, 1H), 3.32 (br s, 1H), 0.67 - 0.52 (m, 2H), 0.50 - 0.43 (m, 2H). Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{Cl}$: C, 77.04; H, 5.47. Found: C, 75.78; H, 5.57. Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{Cl}\cdot 1/4\text{H}_2\text{O}$: C, 75.36; H, 5.59.

5-Fluoro-9,9-spirocyclopropyl-1,4-dihydro-1,4-methano-naphthalene (5).

Clear colorless oil. TLC: $R_f = 0.60$ (100% hexanes); MS m/z 186, 184 (M^+). ^1H NMR (400 MHz, CDCl_3) δ 6.97 (d, $J = 7.0$ Hz, 1H), 6.87 (m, 1H), 6.83 (br s, 2H), 6.63 (ddd, $J = 8.7, 8.3, 0.9$ Hz, 1H), 3.58 (d, $J = 1.6$ Hz, 1H), 3.32 (m, 1H), 0.66 - 0.61 (m, 2H), 0.60 - 0.45 (m, 2H). Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{F}$: C, 83.84; H, 5.95. Found: C, 83.40; H, 6.12.

