Supporting Information

for

Microsolvation and sp²-stereoinversion of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium as measured by NMR

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Preparation, properties, and derivatives of α-(2,4,6-tri-*tert*-butylphenyl)vinyllithium (10); Table

S1 of diastereotopomerization rate constants; Tables S2–S17 of primary NMR data.

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1. α-(2,4,6-Tri-*tert*-butylphenyl)vinyllithium (10).

Preparation and properties. In spite of the two-sided shielding [S1] of the bromoalkene S1, its Br/Li interchange reaction with *n*-BuLi (Scheme S1) occurred rapidly in THF, Et₂O, or *t*-BuOMe at low temperatures with formation of 10 and 1-bromobutane (*n*-BuBr). These high rates created a mixing problem during the addition of *n*-BuLi to S1 in NMR tubes: After the local consumption of *n*-BuLi by a portion of the locally present S1, up to two equivalents of the just generated 10 were consumed in eliminating HBr from residual S1 and in the subsequent deprotonation of the emerging arylalkyne, forming the arylacetylide S3 along with up to two equivalents of the known [S1] olefin S6. This was recognized through carboxylation with solid CO₂, which furnished the arylpropiolic acid [S1] S4 (from S3) and the α -arylacrylic acid S7 (from residual 10). Before or without such a carboxylation, 10 reacted with its coproduct *n*-BuBr immediately in THF solution but slowly in Et₂O or in *t*-BuOMe. Therefore, this butylation of 10 was avoided in Et₂O (though not in THF) by the addition of *n*-BuLi (1.3 equiv) to S1 at or below $-50 \,^{\circ}$ C and quick mixing, followed by rapid warm-up and careful evaporation of all volatile compounds (including *n*-BuBr) under a falling pressure of dry argon gas down to 0.01 mbar. The pot residue contained nonvolatile (because coordinated) Et₂O but did not crystallize; it was dissolved in THF, Et₂O, or *t*-BuOMe.



Scheme S1: Preparation and derivatives of α -(2,4,6-tri-*tert*-butylphenyl)vinyllithium (10).

10 is a trisolvated monomer in THF solution, as established by the triplet (1:1:1) splitting of its ¹³C- α NMR resonance by one ⁶Li nuclear spin; the magnitude 10.9 Hz of its scalar one-bond coupling constant ¹J_{CLi} at -82 °C revealed microsolvation by d = 3 THF ligands at lithium according to the empirical equation 1 in the Main Text. This monomer was the only species of 10 in THF between -82

and +3 °C since its ¹H and ¹³C NMR chemical shifts δ (Tables S4 and S12) did not depend on the temperature. The cis/trans stereoinversion of **10** was obviously retarded by the 4-*tert*-butyl group, but reliable rate constants could not be determined: **10** was rapidly destroyed at and above 3 °C through proton transfer from THF that generated the olefin **S6**. Moreover, **10** was soluble even in cyclopentane and could not be purified, so that the NMR signals of the coproducts overlapped those of **10** in samples that were prepared with *n*-BuLi both from the trimethylstannyl precursor **S2** (without evaporation) or directly from bromoalkene **S1** with evaporation. At lower temperatures, the H₂C= group exhibited the expected AB-type ¹H NMR doublets with ²J_{HH} = 8.6 Hz that characterizes trisolvation according to the Main Text.

In *t*-BuOMe as the solvent, ${}^{2}J_{\text{HH}} = 7.4 \text{ Hz}$ indicated that **10** is a disolvated monomer like those listed in entries 5–8 of Table 1 in the Main Text. In Et₂O, **10** appeared to be a disolvated monomer with ${}^{2}J_{\text{HH}} = 7.0 \text{ Hz}$ at 25 °C and possibly a certain trend toward trisolvation at -50 °C where ${}^{2}J_{\text{HH}} = 8.0 \text{ Hz}$.

Procedure. A dried NMR tube (5 mm) was charged with the bromoalkene [S1] **S1** (70 mg, 0.20 mmol) and anhydrous Et₂O (0.50 mL), then cooled at -50 °C under a stream of dry argon gas, and treated with *n*-BuLi (0.30 mmol) in hexanes (0.011 mL). After 10 min and subsequent warm-up, the solution contained the α -arylvinyllithium **10** and the lithium β -arylacetylide **S3** in a 4:1 ratio along with *n*-BuLi but very little olefin **S6** and no starting material **S1**. In futile attempts to obtain crystals of **10**, the opened NMR tube was placed in a big Schlenk tube that was fixed in an inclined position and evacuated cautiously under dry argon gas down to dryness (0.01 mbar). The foamy, yellow pot residue was dissolved under argon gas cover in one of the anhydrous solvents that were used for NMR measurements at variable temperatures.

A clear solution in cyclopentane displayed **10**, olefin **S6** (0.3 equiv), and Et₂O (1.2 equiv) that had remained coordinated at Li during the evaporation. Because this yellow solution deposited only a fine white powder (LiBr) in the course of four hours in a refrigerator, it was poured onto solid CO₂, warmed up, and dissolved in Et₂O (10 mL) and aqueous NaOH (2 M, 3 mL). The Et₂O layer was shaken with two further portions of NaOH (3 mL), then discarded. The combined aqueous phases were acidified and shaken with Et₂O (2 × 10 mL). The latter two Et₂O extracts were washed with dist. water until neutral, dried over Na₂SO₄, and evaporated to leave the acids **S4** [S1] and **S7** (64:36) as a white solid (48 mg, 76%).

¹H NMR of **10** (*t*-BuOMe, 80 MHz) δ 5.42 (d, ${}^{2}J = 7.4$ Hz, 1H, β-H trans to aryl), 5.68 (d, ${}^{2}J = 7.4$ Hz, 1H, β-H cis), 7.08 (s, 2H, 3-/5-H) ppm. ¹H NMR of **10** (Et₂O, 400 MHz, 25 °C) δ 1.302 (s, 9H, 4-CMe₃), 1.504 (s, 18H, 2-/6-CMe₃), 5.43 (d, ${}^{2}J = 7.0$ Hz, $\Delta\delta = +0.06$ ppm, 1H, β-H trans to aryl), 5.72 (d, ${}^{2}J = 7.0$ Hz, $\Delta\delta = +0.79$ ppm, 1H, β-H cis), 7.17 (s, 2 H, 3-/5-H) ppm. ¹H NMR of **10** (Et₂O, 400 MHz, 25 °C) δ 1.302 (s, 9H, 4-CMe₃), 1.504 (s, 18H, 2-/6-CMe₃), 5.43 (d, ${}^{2}J = 7.0$ Hz, $\Delta\delta = +0.06$ ppm, 1H, β-H trans to aryl), 5.72 (d, ${}^{2}J = 7.0$ Hz, $\Delta\delta = +0.79$ ppm, 1H, β-H cis), 7.17 (s, 2 H, 3-/5-H) ppm. ¹H NMR of **10** (Et₂O, 400 S4

MHz, -50 °C) δ 1.295, 1.517, 5.44 (d, ${}^{2}J = 8.0 \text{ Hz}$, 1H, β -H trans), 5.73 (d, ${}^{2}J = 8.0 \text{ Hz}$, 1H, β -H cis), 7.11 ppm.

2-(2',4',6'-Tri-*tert*-butylphenyl)hex-1-ene (S5).

This was obtained as a mixture with the olefin [S1] S6. ¹H NMR of S5 (CDCl₃, 400 MHz) δ 0.94 (t, ³*J* = 7.3 Hz, 3H, CH₃-6), 1.31 (s, 9H, 4′-CMe₃), 1.38 (m, ³*J* = 7 Hz, 2H, CH₂-5), 1.41 (s, 18H, 2′-/6′-CMe₃), 1.57 (qi, ³*J* = 7.5 Hz, 2H, CH₂-4), 2.26 (tdd, ³*J* = 8 Hz, 2H, CH₂-3), 5.18 (dt, ²*J* = 1.8 Hz, ⁴*J* = 1.7 Hz, 1H, 1-H cis to aryl), 5.33 (dt, ²*J* = 1.8 Hz, ⁴*J* = 2.0 Hz, 1H, 1-H trans), 7.42 (s, 2H, 3′-/5′-H) ppm, assigned through comparison with 7 in the Main Text. ¹³C NMR (CDCl₃, 100.6 MHz) δ 14.11 (CH₃-6), 22.60 (CH₂-5), 28.30 (CH₂-4), 31.44 (4′-CMe₃), 33.52 (2′-/6′-CMe₃), 34.78 (quart. 4′-C), 38.29 (quart. 2′-/6′-C), 40.95 (CH₂-3), 115.89 (C-1), 123.07 (C-3′/-5′), 139.98 (C-1′), 146.39 (C-2′/-6′), 147.18 (C-4′), 150.55 (C-2) ppm, assigned as above.

α-(2,4,6-Tri-*tert*-butylphenyl)acrylic acid (S7).

An acidic product mixture (56 mg) of **S4** and **S7**, obtained as described above from a cyclopentane solution of **10**, was recrystallized from hexane (15 mL) that deposited a felt of white needles (24 mg) which began to sublime at 230 °C and had a mp of 245–247 °C in a closed tubule.

¹H NMR (CDCl₃, 400 MHz) δ 1.32 (s, 9H, 4-CMe₃), 1.35 (s, 18H, 2-/6-CMe₃), 5.91 (d, ²*J* = 1.71 Hz, 1H, β-H cis to aryl), 6.85 (d, ²*J* = 1.71 Hz, 1H, β-H trans), 7.45 (s, 2H, 3-/5-H) ppm, assigned through selective {¹H} decoupling (see below). ¹³C (CDCl₃, 100.6 MHz) δ 31.40 (q ¹*J* = 125.5 Hz, sept ³*J* = 4.9 Hz, 4-C*Me*₃), 32.99 (q ¹*J* = 125.5 Hz, sept ³*J* = 4.9 Hz, 2-/6-C*Me*₃), 34.96 (m, quart. 4-C), 37.72 (m, quart. 2-/6-C), 122.70 (dd, ¹*J* = 153.0 Hz, ³*J* = 6.7 Hz, C-3/-5), 131.31 (m, C-1), 133.24 (sharp t, ¹*J* = 161.9 Hz, C-β), 142.40 [broadened d, ²*J* = (-)3.6 Hz to trans-H only [S2], C-α], 147.99 (m, C-2/-6), 149.14 (m, C-4), 172.53 (dd, ³*J* = 12.4 and 6.6 Hz, CO₂H) ppm, assigned through selective {¹H} decoupling as follows: {all C*H*₃} \rightarrow C-2/-6 and C-4 as two s; {cis-H} \rightarrow C-β as a d, C-1 simplified, CO₂H as a narrowed d; {trans-H} \rightarrow C-β as a d, C-1 simplified, CO₂H as a narrowed d; {3-/5-H} \rightarrow C-1 as a dd. IR (KBr) v 3500–2500 (broad H–O), 2963, 1696 (s), 1684 (s), 1613, 1362, 1196 cm⁻¹. Anal. Calcd for C₂₁H₃₂O₂ (316.48): C, 79.69; H, 10.19. Found: C, 79.54; H, 10.05.

2. References

S1. Knorr, R.; Rossmann, E. C.; Knittl, M.; Böhrer, P. Tetrahedron 2014, 70, 5332–5338.

S2. For negative and zero values of olefinic ${}^{2}J_{CH}$, see: Vögeli, U.; Herz, D.; von Philipsborn, W. *Org. Magn. Reson.* **1980**, *13*, 200–209, Table 1 therein.

3. Cis/trans diastereotopomerization rate constants

Table S1. Temperature-dependent pseudo-first-order rate constants k_{ψ} (s⁻¹) of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (4) in THF (47% by volume) and hydrocarbons at 400 MHz.

°C ^a	1000/T	conc. ^b	k_{ψ}	Δk_{ψ}	ln kψ	$\Delta \ln k \psi$
-20	3.950	0.16	15.5	±0.5	2.74	±0.03
-12	3.829	0.10	24.0	±1.0	3.18	±0.04
-5	3.729	0.17	34.0	±2.0	3.53	±0.06
+1	3.648	0.09	46.0	±6.0	3.83	±0.13
+6	3.582	0.09	61.0	±9.0	4.11	±0.15
+10	3.532	0.16	78.0	± 8.0	4.36	±0.10
+14	3.482	0.09	90.0	±10.0	4.50	±0.11
+25	3.354	0.13	150.0	±10.0	5.01	±0.07

^a Uncertainty ±0.5 °C. ^b Concentrations of carbanion units in mol/L.

4. Tabulated primary NMR data

Table S2. Temperature dependence of the ¹H NMR chemical shifts δ of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (4&TMEDA) in THF (83% by volume) and hydrocarbons at 400 MHz.^a

temp.	conc.	chemical shifts δ (ppm) ²								
°C	[4] ^b	3,5-H ^c	4-H ^d	cis-H ^e	trans-H ^e	<i>t</i> -Bu	CH ₂ N	NMe ₂	Hz	
+30	0.016	6.92	6.30	coal		1.43	2.31	2.15	_	
+17	0.035	6.92	6.30	coal		1.42	2.30	2.15	—	
-8	0.047	6.91	6.30	vbr	vbr	1.42	2.30	2.15	_	
-50	0.048	6.90	6.29	5.59	5.29	1.42	2.29	2.14	8.5	
-60	0.053	6.90	6.29	5.59	5.29	1.42	2.29	2.15	8.5	
-75	0.057	6.89	6.29	5.58	5.29	1.42	2.29	2.15	8.5	

^a coal = in coalescence; vbr = very broad. ^b Concentrations of carbanion units in mol/L. ^c Doublet ${}^{3}J = 7.8$ Hz. ^d Triplet ${}^{3}J = 7.8$ Hz ^e In relation to α -aryl.

temp.	conc.		chem	ical shifts δ	(ppm)		$^{2}J_{\mathrm{HH}}$
°C	[4] ^b 3,5-H ^c 4-H ^d		4-H ^d	cis-H ^e	trans-H ^e	<i>t</i> -Bu	Hz
+34	0.04	6.94	6.32	xbr	xbr	1.43	_
+25	0.13	6.93	6.31	(5.59) vbr	(5.34) vbr	1.42	_
$+23 \ ^{\rm f}$	0.10	6.93	6.31	co	al	_	_
+20	0.08	6.93	6.32	(5.61) br	(5.32) br	1.43	_
+14	0.09	6.93	6.32	(5.62) br	(5.32) br	1.43	_
+10	0.16	6.92	6.31	(5.61) br	(5.31) br	1.43	_
+6	0.09	6.92	6.31	5.62 br	5.31 br	1.43	_
+1	0.09	6.92	6.31	5.62 br	5.31 br	1.43	_
-5	0.17	6.92	6.31	5.62	5.31	1.43	brd
-12	0.10	6.92	6.31	5.62	5.31	1.43	brd
-20	0.16	6.91	6.30	5.61	5.30	1.43	brd
-45	0.16	6.91	6.30	5.60	5.29	1.43	8.5
-85	0.17	6.90	6.30	5.59	5.28	1.43	8.5
-100	0.18	6.90	6.30	5.58	5.28	1.43	brd

Table S3. Temperature dependence of the ¹H NMR chemical shifts δ of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (**4**) in THF (47% by volume), with *n*-BuSnMe₃, hydrocarbons, and MeLi at 400 MHz. ^a

^a coal = in coalescence; br = broad; brd = broadened; vbr = very broad; xbr = extremely broad. ^b Concentrations of carbanion units in mol/L. ^c Doublet ³J = 7.8 Hz. ^d Triplet ³J = 7.8 Hz. ^e In relation to α -aryl. ^f At 200 MHz.

Table S4. Temperature dependence of the ¹H NMR chemical shifts δ of monomeric α -(2,4,6-tri-*tert*-

butylphenyl)vinyllithium (10) in THF at 400 MH
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temp.	chemical shifts δ (ppm)									
°C	3,5-H ^a	cis-H	trans-H	2,6- <i>t</i> -Bu ₂	2,6- <i>t</i> -Bu ₂ 4- <i>t</i> -Bu					
-60	7.19	5.65	5.31	1.50	1.26	8.6				
-82	7.18	5.64	5.30	1.50	1.26	8.6				

^a Singlet.

(,										
temp.	conc.		chemical shifts δ (ppm)								
°C	[4] ^b	3,5-Н ^с	4-H ^d	cis-H ^e	trans-H ^e	<i>t</i> -Bu	CH_2N	NMe ₂	TMEDA	Hz	
+25	0.055	6.94	6.34	5.63	5.29	1.44	2.35	2.18	0.072	7.4	
-24	0.058	6.93	6.34	5.62	5.29	1.44	2.36	2.18	0.082	7.4	
-68	0.057	6.93	6.34	5.61	5.28	1.44	2.38 vbr	2.18 brd	0.070	7.4	
-88	0.057	6.93	6.35	5.59	5.27	1.44	ca. 2.3 ^f 2.41 vbr ^g	2.14 ^f 2.20 ^g	$0.015^{ m f}$ $0.060^{ m g}$	7.4 7.4	

Table S5. Temperature dependence of the ¹H NMR chemical shifts δ of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (**4**&TMEDA) in *t*-BuOMe (77% by volume) and cyclopentane (22%) at 400 MHz. ^a

^a brd = broadened; vbr = very broad. ^b Concentrations of carbanion units in mol/L. ^c Doublet ${}^{3}J = 7.8$ Hz.

^d Triplet ³J = 7.8 Hz. ^e In relation to α -aryl. ^f Free. ^g Coordinated.

temp.	conc.			chemical	l shifts δ	(ppm)			conc. (M)	$^{2}J_{\mathrm{HH}}$
°C	[4] ^b	3,5-Н ^с	4-H ^d	cis ^e	trans ^e	<i>t</i> -Bu	CH ₂ N	NMe ₂	TMEDA	Hz
+60	0.025	7.28	6.70	6.06 br	5.49 br	1.65	1.88	1.93	0.130	br
+45	0.079	7.30	6.72	6.09	5.51	1.67	1.84	1.90	0.170	brd
+25	0.126	7.32	6.74	6.12	5.52	1.69	1.77 br	1.84	0.176	7.3
-20	0.089	7.36	6.80	6.20	5.58	1.71	xbr	xbr	(0.136)	7.3
-44	0.083	7.40	6.84	6.26	5.62	1.73	xbr ^f	xbr ^f (1.58) ^g	$0.055^{\rm f}$ $0.097^{\rm g}$	7.3 br
-56	0.127	7.41	6.85	6.26	5.63	1.74	xbr ^f	vbr ^f (1.57) ^g	0.039 ^f	7.4 shp
-68	0.125	7.43	6.87	6.29	5.65	1.75	(2.3) ^f	(2.1) ^f (1.53) ^g	0.037 ^f	7.4 shp
-82	0.022	7.47	ca. 6.9	6.38	5.70	1.78	2.30 ^f	2.07 ^f	0.039 ^f -	7.4 brd

Table S6. Temperature dependence of the ¹H NMR chemical shifts δ of monomeric α -(2,6-di*tert*-butylphenyl)vinyllithium (**4**&TMEDA) in [D₈]toluene (85% by volume) at 400 MHz.^a

^a br = broad; brd = broadened; vbr = very broad; xbr = extremely broad; shp = sharp. ^b Concentrations of carbanion units in mol/L. ^c Doublet ${}^{3}J = 7.8$ Hz. ^d Triplet ${}^{3}J = 7.8$ Hz. ^e In relation to α -aryl. ^f Free. ^g Coordinated.

Table S7. Temperature dependence of the ¹H NMR chemical shifts δ of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (**4**) in TMEDA (64% by volume) with hydrocarbons and MeLi at 400 MHz.^a

temp.	conc.		chemic	chemical shifts δ (ppm)						
°C	[4] ^b	3,5-Н ^с	4-H ^d	cis-H ^e	trans-H ^e	<i>t</i> -Bu	Hz			
+23 ^f	0.077	6.93	6.34	5.64 br	5.28 br	1.44	br			
+25	0.030	6.95	6.35	5.66	5.28	1.44	ca. 7.4			
+25	0.018	6.94	6.35	5.65	5.28	1.44	ca. 7.4			
+25	0.010	6.95	6.36	5.66	5.29	1.44	ca. 7.4			
+10	0.020	6.93	6.35	5.65	5.28	1.44	7.4			
-22	0.012	6.92	6.33	5.63	5.28	(1.44)	7.4			
+25 +25 +10 -22	0.018 0.010 0.020 0.012	6.946.956.936.92	6.356.366.356.33	5.65 5.63	5.28 5.29 5.28 5.28	1.44 1.44 1.44 (1.44)	ca. 7.4 ca. 7.4 7.4 7.4			

^a br = broad. ^b Concentrations of carbanion units in mol/L. ^c Doublet ${}^{3}J = 7.8$ Hz. ^d Triplet ${}^{3}J = 7.8$ Hz. ^e In relation to α -aryl. ^f At 200 MHz.

Table S8. Temperature dependence of the ¹H NMR chemical shifts δ of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (**4**) in Et₂O (54% by volume) with cyclopentane, *n*-BuLi and MeLi at 400 MHz.^a

temp.	conc.	chemical shifts δ (ppm)								
°C	[4] ^b	3,5-H ^c	4-H ^d	cis-H ^e	trans-H ^e	<i>t</i> -Bu	Hz			
+36	0.14	7.00	6.41	5.64 brd	5.34 brd	1.44	brd			
$+23^{ m f}$	0.15	7.00	6.40	5.63	5.34	1.44	7.4			
+25	0.10	7.01	6.42	5.64	5.34	1.44	7.4			
+25	0.11	7.00	6.41	5.64	5.34	1.44	7.4			
+25	0.15	7.00	6.40	5.63	5.34	1.44	7.4			
+25 ^g	0.018	6.95	6.34	5.64	5.31	1.44	7.4 shp			
+11 ^g	0.017	6.95	6.34	5.64	5.30	1.44	7.4			
-30	0.09	6.96 br	6.37 br	5.62	5.35	1.44	7.4			
-66	0.12	6.96	6.35	5.61	5.35	1.44	7.4			
-83	0.09	6.96	6.35	5.61 brd	5.35 brd	1.44 br	7.4			
-85	0.14	6.95	6.35	5.60 brd	5.35 brd	1.44 brd	(7.5)			

^a br = broad; brd = broadened; shp = sharp. ^b Concentrations of carbanion units in mol/L. ^c Doublet ${}^{3}J = 7.8$ Hz. ^d Triplet ${}^{3}J = 7.8$ Hz. ^e In relation to α -aryl. ^f At 200 MHz. ^g In Et₂O (80%) with *free* TMEDA.

temp.	conc.	chemical shifts δ (ppm)								$^{2}J_{\mathrm{HH}}$
°C	[4] ^b	3,5-Н ^с	4-H ^d	cis-H ^e	trans-H ^e	<i>t</i> -Bu	Et ₂ O	Et ₂ O	(M)	Hz
+75	0.03	7.22	6.66	X	br	1.49	3.24	1.02	0.26	_
+55	0.09	7.27	6.78	(5.56	(5.56) xbr		3.23	1.00	0.25	—
+25	0.12	7.32	6.83	5.91 vbr	5.24 br	1.53	3.19 brd	0.97	0.25	_
$+23^{\rm f}$	_	7.30	6.81	5.86 vbr	5.25 vbr	1.51	3.30 brd	0.94	_	_
-55	0.07	7.41	6.94	5.97	5.30	1.64	2.99 br	0.95	0.25	3.7 brd
-72	0.08	7.42	obsc	6.00	5.32	1.66	2.97 br	0.96	0.23	brd
-84	0.08	7.44	6.98	6.03	5.33	1.67	(3.04) ^g	0.98 ^g 0.61 br ^h	0.23	brd

Table S9. Temperature dependence of the ¹H NMR chemical shifts δ of aggregated α -(2,6-di*tert*-butylphenyl)vinyllithium in [D₈]toluene with Et₂O (ca. 2 equiv) and *n*-BuLi at 400 MHz.^a

^a br = broad; brd = broadened; vbr = very broad; xbr = extremely broad; obsc = obscured. ^b Concentrations of carbanion units in mol/L. ^c Doublet ³J = 7.8 Hz. ^d Triplet ³J = 7.8 Hz. ^e In relation to α-aryl. ^f At 200 MHz. ^g Free. ^h Coordinated.

Table S10. Temperature dependence of the ¹³C NMR chemical shifts δ of monomeric α -(2,6-di*tert*-butylphenyl)vinyllithium (**4**&TMEDA) in THF (83% by volume) and hydrocarbons at 100.6 MHz.^a

temp.	conc.	chemical shifts δ (ppm)									
°C	[4] ^b	C-α	C-1	C-2,6	C-3,5	C-4	С-β	2,6-C	CMe ₃	CH ₂ N	NCH ₃
-8	0.047	214.9 shp	163.7	138.3	123.4	116.5	112.2	37.6	32.2	58.8	46.2
-50	0.048	214.8 (t)	163.7	138.1	123.3	116.4	112.1	37.5	32.0	58.7	46.3
-60	0.053	214.8 t ^c	163.7	136.1	123.3	116.4	112.1	37.5	31.9	58.7	46.3
-75	0.057	214.8 t ^c	163.7	138.0	123.3	116.3	112.1	37.6	31.9	58.7	46.3

^a shp = sharp; t = triplet. ^b Concentrations of carbanion units in mol/L. ^{c 1} $J_{C,Li} = 10.8$ Hz.

Table S11. Temperature dependence of the ¹³C NMR chemical shifts δ of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (4) in THF (47% by volume), with *n*-BuSnMe₃, hydrocarbons, and MeLi at 100.6 MHz.^a

temp.	conc.		chemical shifts δ (ppm)								
°C	[4] ^b	C-α	C-1	C-2,6	C-3,5	C-4	C-β	2,6-C	CMe ₃		
+25	0.13	214.7	163.5	138.2	123.4	116.5	112.2	37.5	32.1		
-20	0.16	214.5	163.5	138.2	123.4	116.5	112.2	37.5	32.1		
-45	0.16	214.6 br	163.6	138.1	123.3	116.5	112.2	37.5	32.0		
-85	0.17	214.6 t ^c	163.6	138.0	123.3	116.4	112.1	37.5	31.8		
-100	0.18	214.6 t ^c	163.6	137.9	123.3	116.3	112.0	37.5	31.7		

^a t = triplet. ^b Concentrations of carbanion units in mol/L. ^{c 1} $J_{C,Li} = 10.8$ Hz.

Table S12. Temperature dependence of the ¹³C NMR chemical shifts δ of monomeric α -(2,4,6-tri-*tert*-butylphenyl)vinyllithium (**10**) in THF at 100.6 MHz.

temp.	chemical shifts δ (ppm)									
°C	C-α	C-1	C-2,6	C-3,5	C-4	C-β	2,6-C	4-C	2,6-C <i>Me</i> ₃	4-C <i>Me</i> ₃
+3	_	160.6	137.8	120.2	136.8	112.5	38.0	37.3	32.4	30.2
-60	(215.3)	161.0	137.8	120.2	136.4	112.5	37.9	37.3	32.1	30.5
-82	215.3 t ^a	161.0	137.7	120.1	136.3	112.5	37.9	37.3	32.0	30.4

^a t = triplet, ${}^{1}J_{C,Li} = 10.9$ Hz.

Table S13. Temperature dependence of the ¹³C NMR chemical shifts δ of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (**4**&TMEDA) in *t*-BuOMe (77% by volume) and cyclopentane (22%) at 100.6 MHz.^a

temp.	conc.		chemical shifts δ (ppm)									
°C	[4] ^b	C-a	C-1	C-2,6	C-3,5	C-4	C-β	2,6-C	CMe ₃	CH ₂ N	NCH ₃	
+25	0.055	212.1	161.2	137.6	123.8	117.1	111.9	37.7	32.4	57.8	45.9	
-24	0.058	211.9 (t)	161.2	137.2	123.8	117.0	111.7	37.6	32.1	57.5 brd	45.9	
-68	0.057	211.9 t ^c	161.1	137.1	123.8	116.9	111.6	37.6	31.9	58.7 brd ^d 56.8 ^e	46.3 brd ^d 45.7 ^e	
-88	0.057	211.8 t ^c	161.2	137.0	123.8	116.8	111.5	37.7	31.8	58.7 ^d 56.7 ^e	46.4 ^d 45.7 ^e	

^a brd = broadened; t = triplet. ^b Concentrations of carbanion units in mol/L. ^{c 1} $J_{C,Li} = 13.9$ Hz. ^d Free. ^e TMEDA (1 equiv) coordinated.

Table S14. Temperature dependence of the ¹³C NMR chemical shifts δ of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (**4**&TMEDA) in [D₈]toluene (85% by volume) at 100.6 MHz.^a

temp.	conc.	chemical shifts δ (ppm)									
°C	[4] ^b	C-α	C-1	C-2,6	C-3,5	C-4	C-β	2,6-C	CMe_3	CH ₂ N	NCH ₃
+25	0.126	212.4	161.1	137.7	124.1	117.3	111.8	37.7	32.4	56.9	45.4
-20	0.089	212.2 vbr	160.9	137.2	124.1	117.2	111.6	37.7	32.1	56.6 vbr	45.3 vbr
-44	0.083	212.1 (t)	160.8	137.0	124.1	117.1	111.5	37.7	31.9	57.7 xbr ^d 55.8 br ^e	46.1 br ^d 44.8 br ^e
-56	0.127	212.0 t ^c	160.9	137.0	124.1	117.1	111.4	37.7	31.9	(57) ^d 55.6 ^e	46.0 br ^d 44.8 brd ^e
-68	0.125	212.0 t ^c	160.9	137.0	124.1	117.0	111.3	37.7	31.8	_ 55.5 ^e	46.2 br ^d 44.6 br ^e
-82	0.022 ^g	_	160.8	136.8	124.2	117.0	111.3	37.7	31.7	58.3 ^d 55.3 ^f	$46.2 \text{ shp}^{\text{ d}}$ xbr ^f

^a br = broad; brd = broadened; vbr = very broad; xbr = extremely broad; shp = sharp; t = triplet. ^b Concentrations of carbanion units in mol/L. ^c ${}^{1}J_{C,Li} = 13.8$ Hz. ^d Free. ^e TMEDA (1 equiv) coordinated. ^f Coordinated. ^g Weakly soluble.

Table S15. Temperature dependence of the ¹³C NMR chemical shifts δ of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (4) in TMEDA (64% by volume) with hydrocarbons and MeLi at 100.6 MHz.^a

temp.	conc.		chemical shifts δ (ppm)								
°C	[4] ^b	C-α	C-1	C-2,6	C-3,5	C-4	C-β	2,6-C	CMe ₃		
+25	0.030	211.8 brd	160.7	137.3	123.8	117.2	111.9	37.7	32.4		
+25	0.010	_	160.8	137.3	123.8	117.2	111.9	37.7	32.4		
+10	0.020	_	160.9	137.2	123.8	117.1	111.9	37.7	32.4		
-22	0.012	_	161.2	137.1	123.7	116.9	111.8	37.6	32.3		

^a brd = broadened. ^b Concentrations of carbanion units in mol/L.

Table S16. Temperature dependence of the ¹³C NMR chemical shifts δ of monomeric α -(2,6-di-*tert*-butylphenyl)vinyllithium (4) in Et₂O (54% by volume) with cyclopentane, *n*-BuLi and MeLi at 100.6 MHz.^a

temp.	conc.	chemical shifts δ (ppm)								
°C	[4] ^b	C-α	C-1	C-2,6	C-3,5	C-4	C-β	2,6-C	CMe ₃	
+25	0.10	209.3	161.6	138.8	124.2	118.1	113.3	37.7	32.3	
+25	0.15	209.6	161.8	138.7	124.1	118.0	113.2	37.7	32.3	
+11 ^c	0.017	_ ^d	_ ^d	137.6	123.9	117.1	112.0	37.7	32.2	
-10 °	_	_ ^d	_ ^d	137.4	123.9	117.0	112.0	37.7	32.1	
-30	0.09	210.3	162.0	137.8	124.0	117.3	112.6	37.7	32.0	
-66	0.12	210.3 br	162.0	137.5	123.9	117.1	112.4	37.7	31.8	
-83	0.09	210.2 t ^e	162.0	137.4	123.9	117.1	112.2	37.7	31.7	
-85	0.14	210.3 t ^e	162.0	137.3	123.9	117.0	112.2	37.7	31.7	

^a br = broad; t = triplet. ^b Concentrations of carbanion units in mol/L. ^c In Et₂O (80%) with *free* TMEDA. ^d Weakly soluble. ^{e 1} $J_{C,Li} = 13.7$ Hz.

Table S17. Temperature dependence of the ¹³C NMR chemical shifts δ of aggregated α -(2,6-di-*tert*-butylphenyl)vinyllithium in [D₈]toluene with Et₂O (ca. 2 equiv) and *n*-BuLi at 100.6 MHz.^a

temp.	conc.	chemical shifts δ (ppm)									
°C	[4] ^b	C-α	C-1	C-2,6	C-3,5	C-4	C-β	2,6-C	CMe ₃	Et ₂ O	Et ₂ O
+55	0.09	_	_	140.9 vbr	125.3	120.8 br	115.4 br	37.1	32.5	65.6	15.2
+25	0.12	_	_	141.0 br	125.1	120.9 br	115.5 br	37.4	32.3	65.0	14.9
-55	0.07	199.1	159.7	141.4 shp	125.0	120.8	115.4	37.4	31.9	63.6 vbr	14.6 xbr
-72 -84	$\begin{array}{c} 0.08 \\ 0.08 \end{array}$	198.7 br 198.6 br	159.6 159.6	141.2 shp 141.3 shp	125.0 125.0	120.7 120.7	115.3 115.4	37.4 37.4	31.8 31.8	(64.1) xbr 65.1 xbr	14.6 xbr 14.6 xbr

^a br = broad; vbr = very broad; xbr = extremely broad; shp = sharp. ^b Concentrations of carbanion units in mol/L.