Supporting Information for

Carbenoid Chain Reactions: Substitutions by Organolithium Compounds at Unactivated 1-Chloro-1-alkenes

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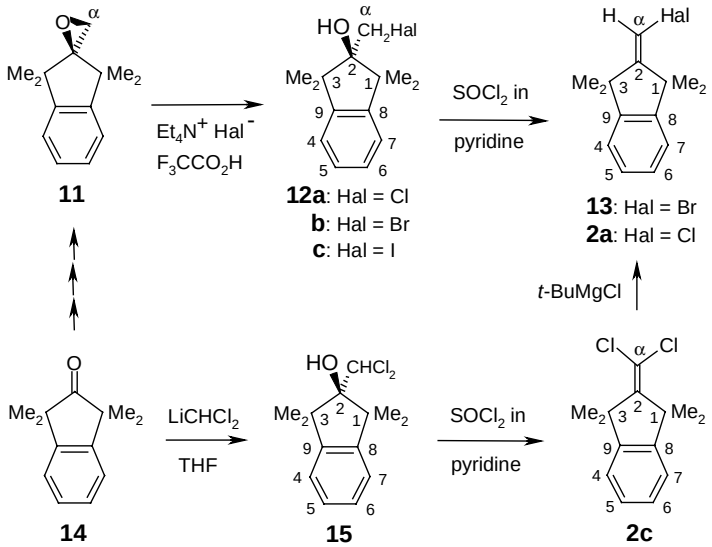
Note: Formulae, Schemes, and literature references taken over from the Main Text are utilized with their unchanged numbers, whereas those cited here for the first time are denominated beginning with S.

1. General Experimental Procedures. Organolithium compounds were handled under a stream of dry argon cover gas. Experiments in NMR tubes (5 mm) were performed with nondeuterated solvents (≈ 0.7 mL, containing ≈ 0.035 mL of C_6D_6 or C_6D_{12} if required as "lock substances"); this allowed product analyses to be carried out *in situ* before workup. Concentrations were estimated by comparison with the ^{1}H NMR integral of a sealed capillary filled with pure $ClCH_2C{\equiv}N$ ($\delta_H \approx 3.9$) or of the low-field ^{13}C satellites of the solvents. Hydrogen versus deuterium distributions were determined by pairwise integrations of the baseline separated NMR absorptions having sufficiently large isotope-induced shift differences, with the machine parameters set for maximum resolution [for example, number of points *np* = 160000 (^{1}H at 400 MHz) or 524288 (^{13}C), and acquisition times *at* ≈ 13 sec]. Commercially available solutions of methyllithium ($\delta_H \approx -2$) in Et_2O containing LiBr, of *n*-butyllithium in hexanes ($\delta_H \approx -0.75$ in benzene), and of *tert*-butyllithium (*t*-BuLi) in pentane were used. The Br/Li interchange reaction with ensuing β-elimination of HBr (*t*-BuLi + ArBr → *t*-BuBr + ArLi, *t*-BuLi + *t*-BuBr → *t*-BuH + LiBr + $Me_2C{=}CH_2$) was employed in ethereal solvents to prepare solutions of phenyllithium ($\delta_H \approx 8.0$ for two *o*-H), **21m**, and **21n**. However, **21p** could be prepared best with *n*-BuLi in place of *t*-BuLi because it precipitated from its solution in THF/hexanes (1:4)[S1] immediately.

2. Preparatory Synthetic Studies: 12a, **12c**, **15**, 4-$(Me_3Si)C_6H_4$,Br, and 2,4,6-$(t\text{-}Bu)_3C_6H_2Cl$ (ClMes*).

Scheme 2



Nucleophilic iodination of the oxirane **11** to afford **12c** (Scheme 2) was easily achieved, but all attempts to eliminate water from **12c** were unsuccessful.

2-Chloromethyl-1,1,3,3-tetramethyl-2-indanol (12a). Tetraethylammonium chloride (1.15 g, 6.92 mmol) in chloroform (5 mL) was dried overnight with a few small pieces of $CaCl_2$. The dry solution was quickly decanted under dry argon cover gas into a dry Schlenk flask (25 mL) equipped with a reflux condenser and a drying tube. After addition of the oxirane[9] **11** (300 mg, 1.48 mmol) and trifluoroacetic acid (0.21 mL, 2.74 mmol), the mixture was heated to reflux for four hours and then cooled, washed with water (no NaOH!) until neutral, and dried over Na_2SO_4. Removal of the solvent furnished 230 mg (65%) of the almost uncontaminated, solid alcohol **12a**. After two recrystallizations from pentane, the mp was 87–88 °C. It is important to avoid the contact of **12a** with strong alkali because this would cause recyclization to the oxirane **11**. – ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 1-/3-CH_3 *cis* to CH_2Cl), 1.45 (s, 1-/3-CH_3 *trans* to CH_2Cl), 2.43 (s, OH), 3.95 (s, CH_2Cl), 7.14 (m, 4-,7-H), 7.23 (m, 5-/6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.73 (qq, ^1J = 126.9 Hz, ^3J = 4.9 Hz, 1-/3-CH_3 *trans* to CH_2Cl), 28.84 (qq, ^1J = 126.9 Hz, ^3J = 4.9 Hz, 1-/3-CH_3 *cis* to CH_2Cl), 49.82 (t, ^1J = 150.0 Hz, CH_2Cl), 50.53 (m, $C^{1,3}$), 84.21 (m, C^2), 122.41 (dm, ^1J = 157.1 Hz, $C^{4,7}$), 127.46 (ddd, ^1J = 159.1 Hz, ^3J = 7.4 Hz, $C^{5,6}$), 148.52 (m, $C^{8,9}$); IR (KBr) 3581 and 3567 (2 sharp O–H), 2962, 2879, 1482, 1450, 1366, 1074, and 760 cm^{-1}. Anal. Calcd for $C_{14}H_{19}ClO$ (238.8): C, 70.43; H, 8.02; Cl, 14.85. Found: C, 70.67; H, 7.76; Cl, 14.27.

NMR Assignments: Molecular mechanics calculations (PC-Model) indicated that the CH_2Cl group prefers a quasi-equatorial position at the five-membered ring, with dihedral angles Cl–CH_2–C^2–O = 53° and H–O–C^2–CH_2 = 51°. Consequently, CH_2Cl showed crosspeaks in the NOESY (^{1}H,^{1}H) spectrum with both the *cis*-1-/3-CH_3 (stronger, quasi-axial, upfield) and the *trans*-1-/3-CH_3 protons (weaker, quasi-equatorial, downfield). This geometry was also in accord with the NOESY correlations OH ↔ *trans*-1-/3-CH_3 ↔ 4-/7-H. On this basis, the signals of the *cis* (downfield) and *trans* (upfield) methyl carbon nuclei were assigned by selective decoupling of the methyl protons. The resonances of $C^{4,7}$ are known[58] to be always upfield from those of $C^{5,6}$.

2-Iodomethyl-1,1,3,3-tetramethyl-2-indanol (12c). A chloroform solution (7.20 mL) of the oxirane[9] **11** (400 mg, 1.98 mmol) and well-dried tetraethylammonium iodide (2.08 g, 8.10 mmol) was heated to reflux for 3.5 h with trifluoroacetic acid (0.30 mL, 3.92 mmol) under argon. The mixture was washed with distd. water until neutral, dried over Na_2SO_4, and concentrated to give 590 mg of crude **12c**, contaminated with olefin **4a** (7%) and, as usual,[9] with 1,2,3,3-tetramethylindene (19%). These side-products were removed by dissolving the mixture in pentane, transfering the soluble portion to a silica column, elution with petroleum ether, and distillation at 100–115 °C (bath temp.)/0.2 mbar to furnish 153 mg (23%) of pure **12c**. Colorless plates, mp 66–67 °C (cooled pentane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (s, 1-/3-CH_3 *cis* to CH_2I), 1.47 (s, 1-/3-CH_3 *trans* to CH_2I), 2.03 (s, OH), 3.65 (s, CH_2I), 7.14 (m, 4-/7-H), 7.23 (m, 5-/6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.37 (CH_2I), 23.71 (1-

/3-CH_3 *trans* to CH_2I), 29.06 (1-/3-CH_3 *cis* to CH_2I), 50.92 (m, $C^{1,3}$), 82.67 (C^2), 122.41 ($C^{4,7}$), 127.49 ($C^{5,6}$), 148.69 ($C^{8,9}$), assigned by comparison with the very similar spectra of chloride **12a**; IR (KBr) 3571 (sharp O–H), 2984, 2960, 2870, 1482, 1450, and 754 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{19}IO$ (330.2): C, 50.92; H, 5.80; I, 38.43. Found: C, 51.03; H, 5.58; I, 38.69.

Although **12c** was stable in pyridine solution, it was reduced quickly to olefin **4a** upon the addition of thionyl chloride (1.8 or 6 equiv) to this solution. The desired dehydration was also not achieved on treatment of **12c** with oxalyl chloride in CCl_4 with or without DMF/NEt_3 up to +65 °C, or with acetyl chloride in CCl_4 up to +80 °C, **12c** being reisolated in every case. Unidentified product mixtures resulted from the slow reaction of **12c** with acetic anhydride at up to +140 °C, or with acetyl chloride and 4-dimethylaminopyridine in refluxing CCl_4, or from treatment of the olefin **4a** with elemental iodine.

2-(Dichloromethyl)-1,1,3,3-tetramethyl-2-indanol (15). 1,1,3,3-Tetramethyl-2-indanone[8] (**14**, 12.00 g, 63.74 mmol), anhydrous THF (100 mL), and anhydrous dichloromethane (12.3 mL, 191.2 mmol) were placed in a dry three-necked flask (500 mL) fitted with a thermometer, dropping funnel (250 mL), magnetic stirring bar, and an inlet connected to a slow stream of dry argon cover gas. The flask was cooled to –50 °C and its contents stirred during the dropwise addition (45 min) of lithium diisopropylamide in THF solution, which had been prepared from diisopropylamine (29.6 mL, 210 mmol), anhydrous THF (50 mL), and *n*-butyllithium in hexane (79.6 mL, 191 mmol) at below +9° C. Stirring was continued for 90 min during warm-up to an internal temperature of –20 °C and a subsequent re-cooling to –40 °C. The temperature rose to –20 °C during the dropwise addition of acetic acid (20 mL dissolved in 75 mL of THF), and there was the formation of a voluminous white precipitate. The flask was warmed up until its contents could be poured onto 2 M HCl (500 mL, dissolving the precipitate), and the solution was then extracted with Et_2O (400 mL, then 2 × 200 mL). The combined ethereal extracts were washed with distd. water (no alkali!) until neutral, dried over $MgSO_4$, and concentrated to give 15.67 g (90%) of the only marginally contaminated alcohol **15** as a brown powder. Recrystallization form low-boiling petroleum ether (150 mL) furnished 11.81 g (68%) of spectroscopically pure, brown crystals with mp 138–141 °C. The analytically pure, colorless crystals were obtained through repeated crystallization and had mp 146–147.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 1-/3-CH_3 *cis* to $CHCl_2$), 1.57 (s, 1-/3-CH_3 *trans* to $CHCl_2$), 2.46 (sharp s, exchangeable with D_2O, OH), 6.26 (s, $CHCl_2$), 7.11 (m, 4-/7-H), 7.22 (m, 5-/6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.7 (qq, ^1J = 127.0 Hz, ^3J = 4.7 Hz, 1-/3-CH_3 *trans* to $CHCl_2$), 28.2 (qq, ^1J = 127.0 Hz, ^3J = 4.7 Hz, 1-/3-CH_3 *cis* to $CHCl_2$), 52.1 (unresolved m, $C^{1,3}$), 79.0 (sharp d, ^1J = 174.1 Hz, $CHCl_2$), 87.9 (unresolved m, C^2), 122.3 (dm, ^1J = 158 Hz, $C^{4,7}$), 127.7 (ddd, ^1J = 160 Hz, ^3J = 7.3 Hz, $C^{5,6}$), 148.0 (m, $C^{8,9}$), assigned by comparison with the monochloride **12a**; IR (KBr) 3533 and 3487 (2 sharp O–H), 3010,

2985, 2963, 2873, 1482, 1386, 1371, 1088, 1077, 784, 768, 760, 744, and 734 cm^{-1}. Anal. Calcd for $C_{14}H_{18}Cl_2O$ (273.2): C, 61.55; H, 6.64; Cl, 25.95. Found: C, 61.59; H, 6.72; Cl, 26.63.

1-Bromo-4-(trimethylsilyl)benzene. The published[S2–S4] preparation via 4-bromophenyllithium was modified by the employment of *n*-BuLi[S4,S5] at –30 °C. A dried Schlenk flask (250 mL) was charged with 1,4-dibromobenzene (10.62 g, 45.02 mmol) in anhydrous Et_2O (80 mL) and then cooled at –30 °C with stirring under argon cover gas. After the dropwise addition (30 min) of *n*-BuLi (49.4 mmol) in hexane (20.60 mL), the mixture was cooled in an ice bath and treated with chlorotrimethylsilane (6.25 mL, 49.5 mmol). After further stirring for 30 min, the contents were poured into distd. water (100 mL). The separated aqueous layer was extracted with Et_2O (3×50 mL), and the combined Et_2O phases were washed until neutral, dried over $MgSO_4$, and concentrated to furnish 9.918 g (96%) of the almost pure product (^{1}H NMR as in ref S4). The alternative preparation via 4-bromophenylmagnesium bromide[S2,S6,S7] was reported[S2] to produce a significant admixture of 1,4-bis(trimethylsilyl)benzene.

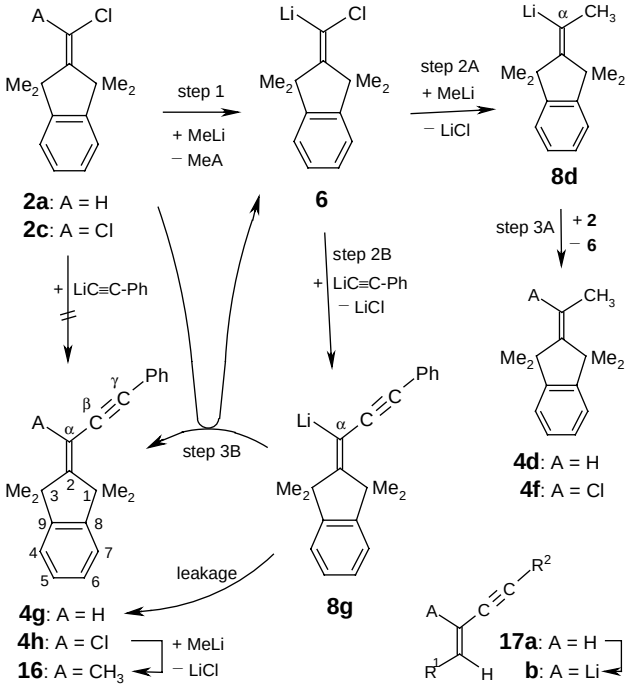
Independent Preparation of Chloro-2,4,6-tri-*tert*-butylbenzene (ClMes*). An independently prepared sample of this byproduct of **4p** was required for the identification of its NMR signals in the crude product mixtures. It was obtained by the addition of isopentyl nitrite to a mixture of 2,4,6-tri-*tert*-butylaniline (H_2NMes*) and $BrCCl_3$ in 1,2-dimethoxyethane at 60–75 °C.[S8] The glistening platelets, recrystallized from ethanol in 14% yield, had mp 153–155 °C (ref S9: 156–158 °C; ref S10: 156.5–160 °C; ref S11: 162 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 4-*t*-Bu), 1.53 (s, 2-/6-*t*-Bu), 7.38 (s, 3-/5-H) as in ref S12 (compare ref S11); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 30.5 (2-/6-C*Me*$_3$), 31.4 (4-C*Me*$_3$), 34.9 (4-*C*Me$_3$), 37.2 (2-/6-*C*Me$_3$), 123.2 ($C^{3,5}$), 131.3 (C^4), 147.0 ($C^{2,6}$), 147.8 (C^1), compare ref S12; IR (KBr) 2963, 2872, 1594, 1476, 1411, 1365 (s), 1221, 1038, and 879 cm^{-1}. Anal. Calcd for $C_{18}H_{29}Cl$ (280.9): C, 76.97; H, 10.40; Cl, 12.62. Found: C, 77.21; H, 10.24; Cl, 12.15.

3. Substitution Products (4, 10i, 16, and 20), ^{13}C NMR spectra, and NMR Assignments.

2-Ethylidene-1,1,3,3-tetramethylindan (4d). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.09 (C^β), 29.35 (2 1-CH_3), 32.52 (2 3-CH_3), 46.37 (C^1), 47.10 (C^3), 116.24 (C^α), 122.37 and 122.58 ($C^{4,7}$), 126.80 and 126.91 ($C^{5,6}$), 149.42 (C^9), 150.92 (C^8), 158.86 (C^2), assigned by selective {^{1}H} decoupling in THF solution: {3-CH_3} → C^3 (d, ^3J = 5.0 Hz) and C^α (dq, ^1J = 148.0 Hz, ^2J = 6.8 Hz) and C^β (dd, ^1J = 123 Hz, ^2J = 2.6 Hz) and C^9 (pseudo-t), {1-CH_3} → C^1 (d, ^3J = 9.4 Hz) and C^α (dq) and C^β (dd) and C^8 (dd).

2-(1-Chloroethylidene)-1,1,3,3-tetramethylindan (4f). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 25.69 (C^{β}), 28.03 (2 1-CH_3), 29.52 (2 3-CH_3), 48.38 and 49.40 ($C^{1,3}$), 122.26 (C^4), 122.48 (C^7), 125.86 (C^{α}), 127.13 (C^5), 127.24 (C^6), 149.45 and 149.92 ($C^{8,9}$), 152.09 (C^2), assigned by ^{1}H/^{13}C heterocorrelation.

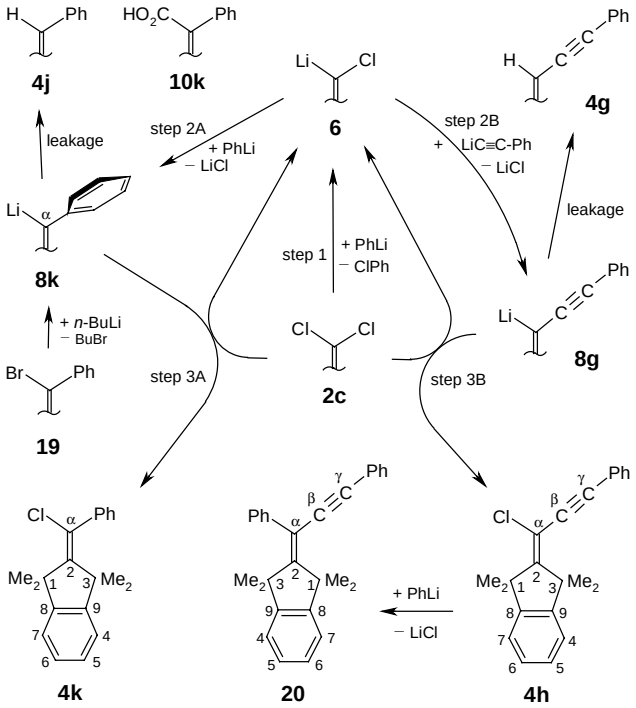
Scheme 5



2-(3-Phenyl-2-propyn-1-ylidene)-1,1,3,3-tetramethylindan (4g). A dry NMR tube (5 mm) was charged under argon cover gas with MeLi (0.57 mmol) in Et_2O (0.46 mL), anhydrous THF (0.5 mL), and [D_{12}]-cyclohexane (NMR lock, 0.080 mL), then cooled at –78 °C. After injection of phenylacetylene (0.054 mL, 0.50 mmol), the solution contained phenylethynyllithium (0.50 mmol) and residual MeLi (0.027 mmol), checked by ^{1}H NMR. Solid monochloride **2a** (60 mg, 0.27 mmol) was added at –30 °C and dissolved by vigorous shaking at room temperature, whereupon all MeLi was consumed within 10 min. The next day, MeLi (0.020 mL, 0.025 mmol) was injected, and the reaction was observed by ^{1}H NMR which revealed that MeLi disappeared again within 10 min while the product **4g** *continued to increase* over the next 140 min. After another night at room temperature and the subsequent injection of more MeLi (0.020 mL, 0.025 mmol), **2a** and MeLi approached the detection limit in the course of five hours and vanished over the third night. The tube was emptied onto solid CO_2, and the product mixture was dissolved in Et_2O plus 2 M NaOH. The acidified NaOH layer furnished phenylpropiolic acid only (30 mg, 89%), mp 136–138 °C (CCl_4; ref S13: 136–137 °C). The Et_2O layer was washed until neutral and dried over $MgSO_4$ to provide almost pure **4g** (52 mg, 67%), which was distilled at 180–210 °C (bath temp.)/1 mbar and then crystallized from ethanol: colorless thin needles (34 mg), mp 82–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$, numbering of Scheme 5) δ 1.41 (s,

2 3-CH_3), 1.70 (s, 2 1-CH_3), 5.83 (s, α-H), 7.18 (m, 4-H), 7.21 (m, 7-H), 7.25 (m, 5-/6-H), 7.32 (tm, 2 *m*-H), 7.34 (m, *p*-H), and 7.47 (dm, 2 *o*-H), assigned by the NOESY correlations α-H ↔ 3-CH_3 ↔ 4-H, 1-CH_3 ↔ 7-H, and *o*-H ↔ *m*-H; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.55 (qq, ^1J = 127 Hz, ^3J = 4.6 Hz, 2 1-CH_3), 31.93 (qq, ^1J = 127 Hz, ^3J = 4.6 Hz, 2 3-CH_3), 48.00 (ddm, ^3J = 8.0 Hz, ^3J = 2.0 Hz, C^1), 48.09 (ddm, ^3J = 4.4 Hz, ^3J = 2 Hz, C^3), 87.11 (narrow m, C^β), 96.16 (td, ^3J = 5 Hz, ^3J = 4.7 Hz, C^γ), 101.22 (sharp d, ^1J = 160 Hz, C^α), 122.53 (dm, ^1J = 156.8 Hz, $C^{4,7}$), 124.07 (t, ^3J = 7.5 Hz, C^i), 127.17 (ddd, ^1J = 159 Hz, ^3J = 7 Hz, C^5), 127.34 (ddd, ^1J = 159 Hz, ^3J = 7 Hz, C^6), 127.90 (dt, ^1J = 161 Hz, ^3J = 7.5 Hz, C^p), 128.37 (dd, ^1J = 160.5 Hz, ^3J = 7 Hz, C^m), 130.91 (dt, ^1J = 162.4 Hz, ^3J = 6.3 Hz, C^o), 148.14 (tm, ^3J = 6.3 Hz, C^9), 149.73 (tm, ^3J = 6.3 Hz, C^8), 174.92 (m, $^3J \approx 3.5$ Hz, C^2), assigned by ^{1}H/^{13}C heterocorrelation and by selective {^{1}H} decoupling: {3-CH_3} → C^3 (dd) and C^9 (t), {1-CH_3} → C^1 (dd) and C^8 (t), {α-H} → C^γ (t), {ortho-H} → C^γ (d); IR (KBr) 2961, 2200 (w), 1490, 1444, 754 (s), and 690 cm^{-1}. Anal. Calcd for $C_{22}H_{22}$ (286.4): C, 92.26; H, 7.74. Found: C, 91.74; H, 7.80.

Scheme 7



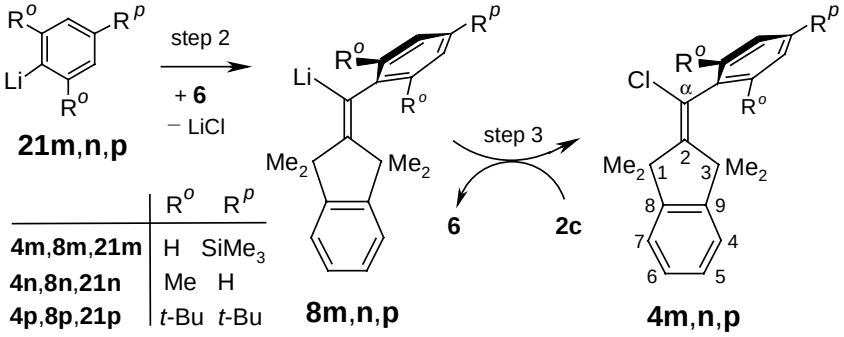
2-(1-Chloro-3-phenyl-2-propyn-1-ylidene)-1,1,3,3-tetramethylindan (4h). A solution of LiMes* (**21p**, 0.2 equiv) in Et_2O (0.25 mL) was added under argon cover gas to PhC≡CLi (0.58 mmol, 1.5 equiv) in THF (0.4 mL) in a dried NMR tube kept at –78 °C. After the introduction of dichloride **2c** (100 mg, 0.39 mmol), the tube was sealed and warmed up with shaking at room temperature. The next day, another batch of LiMes* (0.1 equiv) in Et_2O (0.2 mL) was added. After two further nights, the

mixture was poured onto solid CO_2, warmed up, and dissolved in 2 M NaOH and Et_2O. The washed (Et_2O) and acidified NaOH phase furnished 23 mg (0.16 mmol) of PhC≡CCO_2H, indicating that 0.41 equiv of PhC≡CLi had survived. The combined and washed Et_2O layers afforded a mixture (169 mg) of **2c**, **4g**, **4h**, ClMes*, and HMes* in the molar ratio 18:8:35:21:18. Elution of the contaminations by chromatography on silica (4.0 g) with petroleum ether (low-boiling) provided **4h** as a yellow oil that crystallized from methanol: mp 109–110.5 °C (CH_3OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 and 1.70 (2 s, 2 + 2 1-/3-CH_3), 7.17 and 7.26 (2 m, 2 + 2 indan-H), 7.37 (m, 2 *m*-H and 1 *p*-H), 7.52 (m, 2 *o*-H); ^{13}C NMR (100.6 MHz, $CDCl_3$, numbering of Scheme 7) δ 27.43 and 28.44 (2 + 2 1-/3-CH_3), 49.68 and 50.24 ($C^{1,3}$), 86.90 (C^{β}), 94.74 (C^{γ}), 108.98 (C^{α}), 122.38 ($C^{4,7}$), 122.57 (C^{i}), 127.46 and 127.48 ($C^{5,6}$), 128.49 (2 C^{m}), 128.89 (C^{p}), 131.22 (2 C^{o}), 148.72 and 149.01 ($C^{8,9}$), 165.12 (C^{2}), assigned by comparison with **4g**; IR (KBr) 2964, 2927, 2202 (w), 1486, 848 (C–Cl), 756, 688 cm^{-1}. Anal. Calcd for $C_{22}H_{21}Cl$ (320.9): C, 82.35; H, 6.60; Cl, 11.05. Found: C, 82.28; H, 6.56; Cl, 11.26.

2-(α-Chlorobenzylidene)-1,1,3,3-tetramethylindan (4k). Crystalline **8k** (Scheme 7) was prepared[46] from the bromoalkene **19** with *n*-BuLi, washed with pentane (4 ×) to remove the self-coupled allenic side-product,[47] dissolved in dry Et_2O, and cooled at –78 °C. The solution became colorless instantly upon the addition of hexachloroethane (173 mg, 0.73 mmol). After 1 h at room temperature and addition of water, the mixture was extracted with Et_2O (3 ×), and the combined Et_2O layers were washed until neutral and dried over $MgSO_4$. The filtered and concentrated material crystallized from methanol (2 ×) as colorless needles of pure **4k** (141 mg, 65%): mp 108–110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 2 3-CH_3), 1.76 (s, 2 1-CH_3), 7.03 (m, 4-H), 7.20 (m, 7-H), 7.21 (m, 5-H), 7.25 (m, 6-H), 7.34 (m, *p*-H), 7.36 (m, 2 *o*-H), and 7.38 (m, 2 *m*-H), assigned by the NOESY correlations *ortho*-H ↔ 3-CH_3 ↔ 4-H ↔ 5-H and 1-CH_3 ↔ 7-H ↔ 6-H; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.97 (qq, ^1J = 127 Hz, ^3J = 4.7 Hz, 2 1-CH_3), 31.16 (qq, ^1J = 127 Hz, ^3J = 4.7 Hz, 2 3-CH_3), 49.04 (dm, ^3J = 1.8 Hz, C^3), 49.92 (dm, ^3J = 1.5 Hz, C^1), 122.17 (ddd, ^1J = 157 Hz, ^3J = 7.8 Hz, C^4), 122.44 (ddm, ^1J = 157 Hz, ^3J = 7.8 Hz, C^7), 127.16 (ddm, ^1J = 159 Hz, C^5), 127.25 (ddd, ^1J = 159 Hz, C^6), 127.61 (br t, $^3J \approx 3$ Hz, C^{α}), 127.95 (ddm, ^1J = 160 Hz, 2 C^{m}), 128.06 (dtt, ^1J = 160 Hz, ^3J = 6.7 Hz, C^{p}), 130.01 (dtm, ^1J = 160 Hz, 2 C^{o}), 140.56 (t, ^3J = 6.8 Hz, C^{i}), 149.07 (tm, ^3J = 6.7 Hz, C^9), 149.65 (tm, ^3J = 6.7 Hz, C^8), 155.13 (m, $^3J \approx 3.5$ Hz, C^2), assigned by ^{1}H/^{13}C heterocorrelation and by selective {^{1}H} decoupling: {3-CH_3} → C^3 (d) and C^9 (pseudo-t), {1-CH_3} → C^1 (d) and C^8 (t); IR (KBr) 2990, 2962, 1648 (w), 1484, 839, 759 (vs), 716, and 701 cm^{-1}. Anal. Calcd for $C_{20}H_{21}Cl$ (296.8): C, 80.93; H, 7.13; Cl, 11.94. Found: C, 81.06; H, 7.26; Cl, 11.21.

2-(4-Trimethylsilylbenzylidene)-1,1,3,3-tetramethylindan (4l). *n*-BuLi (2.4 mmol) in hexane (1.0 mL) was added with stirring to the chloroalkene **4m** (339 mg, 0.92 mmol, Scheme 8) in *t*-BuOMe (5.0 mL) and stirred for one day at room temperature. The mixture was worked up with water and Et_2O (3 × 3 mL). The combined Et_2O phases were washed until neutral, dried over $MgSO_4$, evaporated to dryness, and distilled at 113–133 °C (bath temperature)/10^{-3} mbar to give 133 mg (43%) of almost pure **4l**: mp 63.5–65 °C (methanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, $SiMe_3$), 1.31 (s, 2 1-CH_3), 1.48 (s, 2 3-CH_3), 6.63 (s, α-H), 7.11 (dm, 7-H), 7.18–7.23 (m, 4-/5-/6-H), 7.25 (dm, ^3J = 8 Hz, 2 *o*-H), and 7.47 (dt, ^3J = 8 Hz, 2 *m*-H), assigned by the NOE difference correlations *ortho*-H ← {1-CH_3} → 7-H and α-H ← {3-CH_3} → 4-H; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ –1.0 (qm, ^1J = 119 Hz, ^3J = 2 Hz, $^1J(^{13}C^{29}Si)$ = 52 Hz, $SiMe_3$), 31.00 (qq, ^1J = 127 Hz, ^3J = 4.6 Hz, 2 1-CH_3), 32.4 (qq, ^1J = 127 Hz, ^3J = 4.6 Hz, 2 3-CH_3), 47.2 (ddm, ^3J = 9.0 Hz, ^3J = 2 Hz, C^1), 47.8 (ddm, ^3J = 4.8 Hz, ^3J = 2 Hz, C^3), 122.3 (dm, ^1J = 156 Hz, C^7), 122.5 (dm, ^1J = 156 Hz, C^4), 122.7 (dt, ^1J = 150.0 Hz, ^3J = 4.2 Hz, C^α), 126.9 (ddm, ^1J = 159 Hz, C^5), 127.1 (ddm, ^1J = 159 Hz, C^6), 128.7 (dm, ^1J = 156 Hz, 2 C^o), 132.7 (ddm, ^1J = 155 Hz, 2 C^m), 137.9 (unresolved, C^p), 139.4 (t, ^3J = 7.4 Hz, C^i), 148.7 (tm, C^9), 150.6 (tm, C^8), 161.9 (m, $^3J \approx 3.5$ Hz, C^2), assigned by ^{1}H/^{13}C heterocorrelation and by selective {^{1}H} decoupling: {1-CH_3} → C^1 (dd) and C^8 (pseudo-t), {3-CH_3} → C^3 (dd) and C^9 (dd), {7-H} → C^7 (s), {*m*-H} → C^m (s) and C^i (s). IR (KBr) 2957, 1596 (vw), 1483 (w), 1250 (w), 1108, 840 (s), and 758 cm^{-1}. Anal. Calcd for $C_{23}H_{30}Si$ (334.6): C, 82.57; H, 9.04. Found: C, 82.29; H, 9.17.

Scheme 8



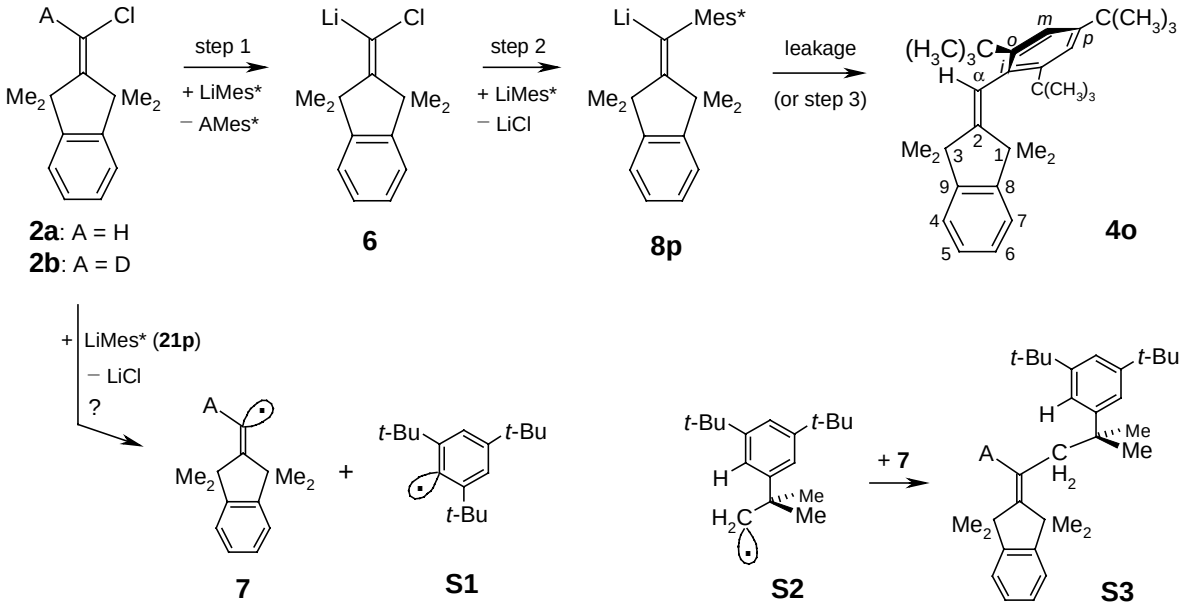
	R^o	R^p
4m,**8m**,**21m**	H	$SiMe_3$
4n,**8n**,**21n**	Me	H
4p,**8p**,**21p**	*t*-Bu	*t*-Bu

2-(α-Chloro-4-trimethylsilylbenzylidene)-1,1,3,3-tetramethylindan (4m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ –1.1 (qm, ^1J = 119.5 Hz, ^3J = 2 Hz, $^1J(^{13}C^{29}Si)$ = 52.3 Hz, $SiMe_3$), 28.0 (qq, ^1J = 127.5 Hz, ^3J = 4.5 Hz, 2 1-CH_3), 31.2 (qq, ^1J = 127.5 Hz, ^3J = 4.5 Hz, 2 3-CH_3), 49.1 (m, C^3), 49.9 (m, C^1), 122.2 (ddm, ^1J = 157 Hz, C^4), 122.4 (ddm, ^1J = 157 Hz, C^7), 127.1 (ddm, ^1J = 160 Hz, C^5), 127.2 (ddm, ^1J = 160 Hz, C^6), 127.6 (t, $^3J \approx 5$ Hz, C^α), 129.1 (dm, $^1J \approx 158$ Hz, 2 C^o), 132.9 (dm, $^1J \approx 158$ Hz, 2 C^m),

140.5 (m, C^p), 140.8 (t, ^3J = 7.6 Hz, C^i), 149.1 (m, C^9), 149.7 (m, C^8), 155.1 (m, C^2), assigned by comparison with **4k**.

2-(α-Chloro-2,6-dimethylbenzylidene)-1,1,3,3-tetramethylindan (4n). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.1 (qd, ^1J = 127 Hz, ^3J = 5 Hz, 2 *o*-CH_3), 27.9 (qq, ^1J = 127.7 Hz, ^3J = 4.5 Hz, 2 1-CH_3), 28.8 (qq, ^1J = 127.7 Hz, ^3J = 4.5 Hz, 2 3-CH_3), 49.4 (m, C^1), 50.1 (m, C^3), 122.1 (dd, ^1J = 158 Hz, ^3J = 7.5 Hz, C^4), 122.4 (dd, ^1J = 157 Hz, ^3J = 7.5 Hz, C^7), 126.0 (sharp s, C^α), 127.1 (ddm, $^1J \approx 160$ Hz, ^3J = 7 Hz, C^6), 127.3 (ddm, $^1J \approx 159$ Hz, ^3J = 7 Hz, C^5), 127.4 (ddq, ^1J = 159 Hz, 2 C^m), 128.3 (sharp d, ^1J = 159.5 Hz, C^p), 136.8 (dq, $^2J \approx {}^3J \approx 6.5$ Hz, 2 C^o), 138.9 (br m, C^i), 149.0 (m, C^8), 149.7 (m, C^9), 153.3 (m, C^2), assigned by comparisons with **19**[S14] and **4o**.

Scheme S1



2-(2,4,6-Tri-*tert*-butylbenzylidene)-1,1,3,3-tetramethylindan (4o). The deprotonation of reagent **2a** (0.10 mmol, 0.19 M in THF, Scheme S1) with an excess of LiMes* (see **4p** below) took place with a first $t_{1/2} \approx 20$ min,[16] furnishing **4o**[52] (merely 0.021 mmol), HMes*, and unknown side-products. The intermediacy of carbenoid **6** was established under the same conditions with reagent **2b** which reacted much more slowly (at least tenfold)[16] to afford plenty of ethylene (from THF with LiMes*) and, through a carboxylative workup 28 hours later, HO_2C–Mes* (0.13 mmol) and the totally unlabeled leakage product **4o** (again merely 0.021 mmol). Such a loss of deuterium revealed that chain propagation (step 3) was no longer achieved here (non-chain carbenoid mechanism due to the faster leakage reaction) and excluded the possibility that this strongly retarded conversion of **2b** might have proceeded by electron transfer from LiMes* to **2c**, which would have generated the aryl radical **S1**

which can rearrange[S15] by internal hydrogen transfer with formation of **S2**. Indeed, products such as **S3** bearing the CH_2 group of **S2** were not detected by ^{13}C NMR in the present studies.

^1H NMR (400 MHz, $CDCl_3$, numbering of Scheme S1) δ 0.93 (s, 2 1-CH_3), 1.33 (s, *p*-*t*-Bu), 1.36 (s, 2 *o*-*t*-Bu), 1.55 (s, 2 3-CH_3), 6.98 (dm, $^3J \approx 8$ Hz, 7-H), 7.11 (s, α-H), 7.16 (m, 5-H), 7.18 (m, 4-H and 6-H), 7.26 (s, 2 *m*-H), as in ref 52; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 30.62 (qq, $^1J = 126$ Hz, $^3J = 4.8$ Hz, 2 1-CH_3), 31.29 (qq, $^1J = 126$ Hz, $^3J = 4.8$ Hz, 2 3-CH_3), 31.52 (qsept, $^1J = 125$ Hz, $^3J = 4.8$ Hz, *p*-C*Me*$_3$), 33.85 (qsept, $^1J = 125.5$ Hz, $^3J = 4.9$ Hz, 2 *o*-C*Me*$_3$), 34.58 (partially hidden m, *p*-*C*Me$_3$), 38.18 (m, 2 *o*-*C*Me$_3$), 46.73 (m, C^1), 48.02 (narrower m, C^3), 121.17 (dd, $^1J = 152$ Hz, $^3J = 7$ Hz, 2 C^m), 121.92 (ddm, $^1J = 157$ Hz, $^3J \approx 7$ Hz, C^7), 122.37 (ddm, $^1J = 155$ Hz, C^4), 125.58 (sharp d, $^1J = 150.3$ Hz, C^α), 126.62 (ddm, $^1J = 159$ Hz, $^3J = 7.6$ Hz, C^5), 126.92 (ddm, $^1J = 160$ Hz, C^6), 131.48 (t, $^3J = 6.9$ Hz, C^i), 147.51 (m, $^3J \approx 3.5$ Hz, C^p), 148.56 (m, $^3J = 3.5$ Hz, 2 C^o), 148.78 (m, C^9), 150.82 (br m, C^8), 152.69 (narrower m, C^2).

4o is identical with a known[52] substance whose NMR spectra were incompletely reported (2 *ortho*-C missing) and not assigned. Our NMR assignments were achieved as follows: NOESY (^1H,^1H) showed the correlations *o*-*t*-Bu ↔ *m*-H ↔ *p*-*t*-Bu, *o*-*t*-Bu ↔ 1-CH_3 ↔ 7-H ↔ 6-H, *o*-*t*-Bu ↔ 3-CH_3 ↔ 4-H, *o*-*t*-Bu ↔ α-H ↔ 3-CH_3. ^{13}C NMR resonances of all CH and CH_3 groups were assigned by ^1H/^{13}C heterocorrelation and confirmed by COLOCS (^{13}C,^1H with window 5.7 Hz), which identified also the signals of carbon atoms carrying no hydrogen by the $^2J_{CH}$ correlations C^1 ↔ 1-C*H*$_3$, C^3 ↔ 3-C*H*$_3$, *o*-*C*Me$_3$ ↔ *o*-C*Me*$_3$, and *p*-*C*Me$_3$ ↔ *p*-C*Me*$_3$, in addition to the $^3J_{CH}$ correlations C^5 ↔ 7-H, C^6 ↔ 4-H, C^7 ↔ 5-H, C^9 ↔ 3-C*H*$_3$ ↔ C^2 ↔ 1-C*H*$_3$ ↔ C^8 ↔ 6-H, C^1 ↔ α-H ↔ C^3, α-H ↔ C^o ↔ *o*-C*Me*$_3$, C^p ↔ *p*-C*Me*$_3$, C^i ↔ *m*-H ↔ C^m, and *o*-*C*Me$_3$ ↔ *m*-H ↔ *p*-*C*Me$_3$.

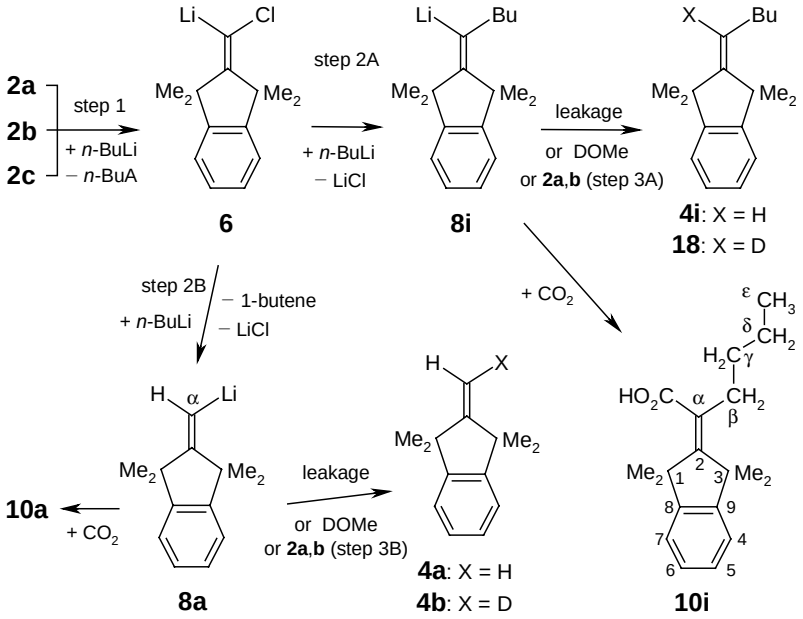
2-(α-Chloro-2,4,6-tri-*tert*-butylbenzylidene)-1,1,3,3-tetramethylindan (4p). The solution of bromo-2,4,6-tri-*tert*-butylbenzene (BrMes*, 1.20 g, 3.68 mmol) in THF (1.5 mL) and pentane (6 mL)[S1] was placed in an oven–dried Schlenk flask (25 mL, with magnetic stirring bar) under dry argon and cooled to –70 °C. A hexane solution (2.40 mL) of *n*-BuLi (5.02 mmol) was added dropwise with gentle swirling, which caused the immediate precipitation of 2,4,6-tri-*tert*-butylphenyllithium (LiMes*, **21p** in Scheme 8).[43] The cooling bath was removed and the Schlenk flask left at ambient temperature for 20 min, whereupon the supernatant liquid was withdrawn from the precipitate with a pipet under argon and discarded (although it contained some LiMes*). The colorless precipitate (LiMes*) was covered with pentane (4 mL), whirled up and left for deposition. The pentane phase was withdrawn, and this washing procedure was repeated twice with two further batches of pentane. The washed precipitate dissolved completely during the dropwise addition of a solution of dichloride **2c** (470 mg, 1.84 mmol) in THF (5.0 mL) with stirring at room temperature. After 2 h, the contents of the Schlenk flask were

poured onto solid CO_2 and, after warming to room temperature, dissolved in 2 M NaOH (20 mL) plus Et_2O (40 mL). The NaOH layer was extracted with more Et_2O (20 mL) and then acidified, delivering no organic acid. The combined Et_2O layers were washed with pure water until neutral, dried over Na_2SO_4, and concentrated to give 810 mg of a mixture (mp 129–134 °C) of the crude product **4p** (78% yield by NMR) along with chloro-2,4,6-tri-*tert*-butylbenzene (ClMes*, 8%), HMes* (9% with respect to **4p**), an unidentified tetramethylindan derivative, and a tiny amount of reagent **2c**. The mixture was extracted with boiling ethanol (22 mL), leaving 85 mg (10%) of almost pure **4p** with mp 173.5–175.5 °C. The cooled ethanol extract deposited 506 mg (59%) of a second modification of **4p** with mp 145–146.5 °C. Analytically pure **4r**, recrystallized twice from hexane, melted first at 148–149.5 °C but had a second mp 177–178 °C after resolidification; the NMR spectra of both modifications were identical. ^{1}H NMR (400 MHz, $CDCl_3$, numbering of Scheme 8) δ 1.14 (s, 2 3-CH_3), 1.33 (s, *p*-C*Me*$_3$), 1.52 (s, 2 *o*-C*Me*$_3$), 1.72 (s, 2 1-CH_3), 6.98 (dm, ^3J = 7 Hz, 4-H), 7.16 (m, 7-H), 7.18 (m, 5-H), 7.22 (td, $^3J \approx 7$ Hz, $^4J \approx 1.4$ Hz, 6-H), 7.42 (s, 2 *m*-H), assigned by the NOESY correlations *o*-*t*-Bu ↔ *m*-H ↔ *p*-*t*-Bu, *o*-*t*-Bu ↔ 1-CH_3 ↔ 7-H ↔ 6-H, *o*-*t*-Bu ↔ 3-CH_3 ↔ 4-H ↔ 5-H; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 26.64 (qq, ^1J = 127.4 Hz, ^3J = 4.6 Hz, 2 1-CH_3), 30.73 (qq, ^1J = 127.4 Hz, ^3J = 4.6 Hz, 2 3-CH_3), 31.32 (qsept, ^1J = 125.5 Hz, ^3J = 4.9 Hz, *p*-C*Me*$_3$), 34.24 (qsept, ^1J = 125.8 Hz, ^3J = 4.8 Hz, 2 *o*-C*Me*$_3$), 34.64 (partially hidden m, *p*-*C*Me$_3$), 39.60 (m, 2 *o*-*C*Me$_3$), 49.40 (m, C^3), 50.52 (m, C^1), 121.88 (dm, ^1J = 156 Hz, C^4), 122.41 (dm, ^1J = 156 Hz, C^7), 124.06 (dd, ^1J = 152.3 Hz, ^3J = 6.8 Hz, 2 C^m), 126.99 (dm, ^1J = 159 Hz, C^5), 127.04 (dm, ^1J = 159 Hz, C^6), 129.00 (sharp s, C$^\alpha$), 130.74 (t, ^3J = 7.2 Hz, C^i), 148.15 (m, ^3J = 3.3 Hz, 2 C^o), 149.00 (m, C^2), 149.24 (m, C^9), 149.58 (m, $^3J \approx 3.7$ Hz, C^p), 149.61 (m, C^8); CH and CH_3 resonances were assigned by ^{1}H/^{13}C heterocorrelation and confirmed by COLOCS (^{13}C,^{1}H with window 6 Hz) which identified also the signals of carbon atoms carrying no hydrogen by the $^2J_{CH}$ correlations C^1 ↔ 1-C*H*$_3$, C^3 ↔ 3-C*H*$_3$, *o*-*C*Me$_3$ ↔ *o*-C*Me*$_3$, and *p*-*C*Me$_3$ ↔ *p*-C*Me*$_3$, in addition to the $^3J_{CH}$ correlations C^5 ↔ 7-H ↔ C^9 ↔ 3-C*H*$_3$ ↔ C^2 ↔ 1-C*H*$_3$ ↔ C^8 ↔ 4-H ↔ C^6, C^o ↔ *o*-C*Me*$_3$, C^p ↔ *p*-C*Me*$_3$, C^i ↔ *m*-H ↔ C^m, C^4 ↔ 6-H, C^7 ↔ 5-H, and *o*-*C*Me$_3$ ↔ *m*-H ↔ *p*-*C*Me$_3$.; IR (KBr) 2966 (s), 2869, 1486, 1366, and 754 cm^{-1}. Anal. Calcd for $C_{32}H_{45}Cl$ (465.16): C, 82.63; H, 9.75; Cl, 7.62. Found: C, 83.06; H, 9.79; Cl, 7.52. – This substitution reaction is much slower in Et_2O at room temperature ($t_{1/2} \approx 0.5$ h).[16]

2-(1,1,3,3-Tetramethyl-2-indanylidene)hexanoic Acid (10i). The combined acid fractions from several experiments were distilled at 0.025 mbar to afford a forerun of **10a** (90–100 °C bath temperature) and then the main component **10i** (132–140 °C bath) which was recrystallized from CCl_4: Colorless platelets, mp 168–169 °C; ^{1}H NMR (400 MHz, $CDCl_3$, numbering of Scheme 6) δ 0.96 (t, ^3J = 7.1 Hz, 3 ε-H), 1.44 and 1.50 (2 m, 2 + 2 δ-/γ-H), 1.54 and 1.56 (2 s, 2 + 2 1-/3-CH_3), 2.62

(pseudo-t, $^3J \approx 7.9$ Hz, 2 β-H), 7.13 and 7.15 (2 m, 4-/7-H), 7.24 (m, 5-/6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.04 (C^{ε}), 22.75 (C^{δ}), 30.15 and 30.44 (2 + 2 1-/3-CH_3), 30.64 (C^{γ}), 31.40 (C^{β}), 47.69 and 48.26 ($C^{1,3}$), 122.15 and 122.18 ($C^{4,7}$), 127.11 and 127.23 ($C^{5,6}$), 128.75 (C^{α}), 149.20 and 149.69 ($C^{8,9}$), 158.12 (C^2), 175.75 (CO_2H); IR (KBr) 3600–2500 (br, O–H), 2962, 2928, 2870, 1690 (s, C=O), 1283, and 756 cm^{-1}. Anal. Calcd for $C_{19}H_{26}O_2$ (286.4): C, 79.68; H, 9.15. Found: C, 79.39; H, 9.23.

Scheme 6



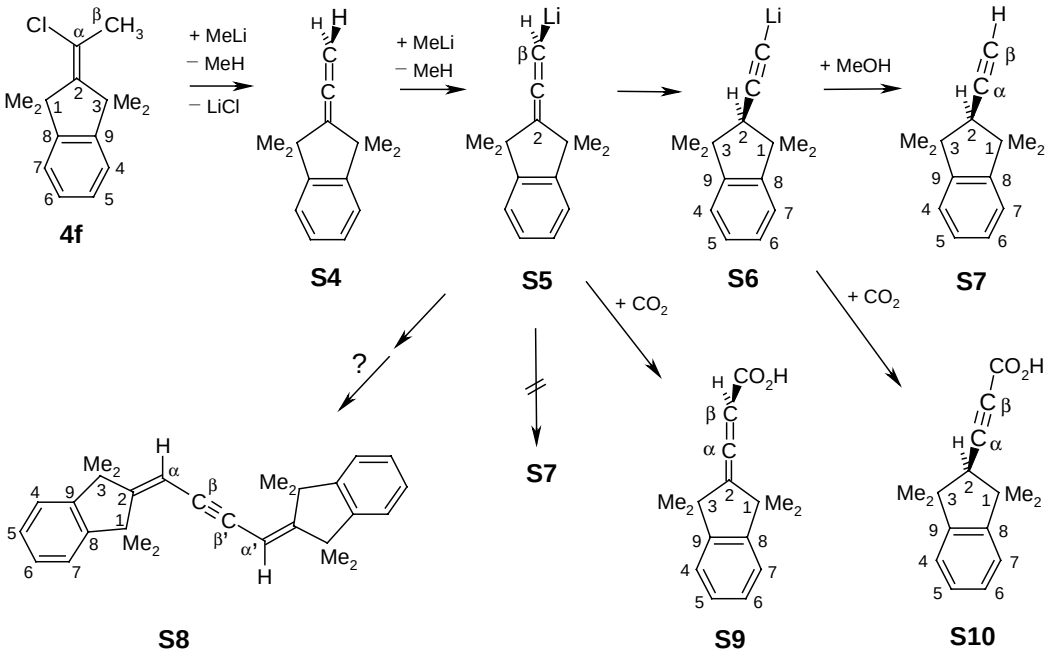
2-(1-Methyl-3-phenyl-2-propyn-1-ylidene)-1,1,3,3-tetramethylindan (16). Phenylethynyllithium (0.20 mmol, 1.0 equiv), prepared in a dry NMR tube (5 mm) at –78 °C under argon cover gas from phenylacetylene (0.022 mL, 0.20 mmol) in THF (0.5 mL) with *n*-BuLi (1 equiv) in hexane (0.10 mL), did not react with dichloride **2c** (50 mg, 0.196 mmol) at ambient temperature over three days. After addition at –78 °C of one portion of MeLi (0.22 mmol, 1.1 equiv) in Et_2O (0.17 mL), the ^{1}H NMR singlet of MeLi was observed for 125 min at room temperature and had dropped to zero overnight. The solution was poured onto solid CO_2, warmed up, and dissolved in Et_2O plus 2 M NaOH. The acidified NaOH phase afforded PhC≡CCO_2H (75%). The Et_2O phase was washed until neutral, dried over $MgSO_4$, and concentrated to yield a solidifying 2:1 mixture (38 mg) of **16** and **4f**. Pale yellow, pure **16** was obtained through recrystallizations from methanol: mp 115–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$, numbering of Scheme 6) δ 1.55 (s, 2 3-CH_3), 1.71 (s, 2 1-CH_3), 2.20 (s, α-CH_3), 7.17 (m, 4-/7-H), 7.24 (m, 5-/6-H), 7.33 (m, 2 *m*-H and 1 *p*-H), and 7.47 (dm, ^3J = 8 Hz, 2 *o*-H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.19 (α-CH_3), 28.86 (2 1-CH_3), 29.13 (2 3-CH_3), 48.16 (C^3), 48.62 (C^1), 92.27 (C^{β}), 93.80 (C^{γ}), 111.76 (C^{α}), 122.23 and 122.47 ($C^{4,7}$), 124.21 (C^{i}), 127.02 and 127.11 ($C^{5,6}$), 127.78 (C^{p}), 128.35

(C^m), 130.86 (C^o), 149.82 (C^9), 149.93 (C^8), 165.15 (C^2), assigned by comparison with **4g**; IR (KBr) 2962, 1486, 1021, 770, 756 (s), and 689 cm^{-1}. Anal. Calcd for $C_{23}H_{24}$ (300.4): C, 91.95; H, 8.05. Found: C, 91.35; H, 8.08.

2-(1,3-Diphenyl-2-propyn-1-ylidene)-1,1,3,3-tetramethylindan (20). The constitution was verified by treatment of the chloroalkene **4h** at room temperature in THF with PhLi. The *in situ* ^{1}H NMR spectra revealed that no product was formed within 50 min but that PhLi vanished overnight. The non-acidic portion isolated after carboxylation contained **20** with the characteristic ^{1}H NMR resonances: δ (400 MHz, $CDCl_3$) 1.54 and 1.94 (2 s, 2 + 2 1-/3-CH_3), 7.58 (m, 4 aromat. H).

4. Side-products S7 – S10 Formed from 2-(1-Chloroethylidene)-1,1,3,3-tetramethylindan (4f).

Scheme S2



The product **4f** of chlorine transfer from **2c** to **8d** can undergo the following slow changes in the presence of an excess of MeLi in THF. The elimination of HCl to produce an allene (**S4**) is not unusual[S16] and was followed here by the faster deprotonation of **S4** to give **S5**, as shown by carboxylation which furnished the allenecarboxylic acid **S9** (10% yield) already after one night, accompanied only by residual **4f** but no allene **S4**. The deprotonation of other allenes was reported to occur rapidly with *n*-butyllithium in THF at –50 °C,[S17] but slowly with MeLi in Et_2O[S18] at room temperature. The ensuing formal β,2-hydrogen shift in **S5** to give **S6** has precedence in slowly[S18–S20] or

rapidly[S21] occurring similar isomerizations and is probably[S19,S21] catalyzed by the 2,β-dilithio intermediate. Bimolecular mechanisms such as these would predict the formation of **S6** to be retarded by steric shielding, in keeping with the isolation of **S7** (quantitative) or of **S10** (69%) after at least one week at room temperature.

2-Ethynyl-1,1,3,3-tetramethylindan (S7). MeLi (6.27 mmol) in Et_2O (5.06 mL) was added at –78 °C under argon cover gas to the dichloride **2c** (400 mg, 1.57 mmol) in anhydrous THF (5.0 mL). After one week at room temperature, the black solution was cooled, protonated with methanol, and diluted with water and Et_2O (75 mL). The washed and dried ($MgSO_4$) Et_2O layer was concentrated to yield the almost pure alkyne **S7** (310 mg, 100%). Its solution in ethanol precipitated a colorless powder (20 mg) with the structure **S8** of a rearranged "dehydro-dimer" of **S5** or **S6**. The remaining material was distilled at 120–140 °C (bath temp.)/12 Torr to afford **S7** as a colorless oil (131 mg, 28%), which crystallized from methanol at –78 °C: mp 35–36 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 and 1.39 (2 s, 2 + 2 1-/3-CH_3), 2.29 (d, ^4J = 2.7 Hz, 2-H), 2.79 (d, ^4J = 2.7 Hz, ≡C–H), 7.15 and 7.22 (2 m, C_6H_4); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.51 (qqi, ^1J = 126.8 Hz, ^3J = 4.7 Hz, 1-/3-CH_3 *trans* or *cis* to C≡C), 29.35 (qqi, ^1J = 126.0 Hz, ^3J = 4.9 Hz, 1-/3-CH_3 *cis* or *trans* to C≡C), 45.40 (unresolved, $C^{1,3}$), 54.79 (dm, ^1J = 129.2 Hz, C^2), 73.34 (dd, ^1J = 246.8 Hz, ^3J = 4.1 Hz, C^β), 82.38 (dd, ^2J = 49.0 Hz, ^2J = 10.5 Hz, C^α), 122.71 (dm, ^1J = 156 Hz, $C^{4,7}$), 127.05 (dd, ^1J = 159 Hz, ^3J = 7.2 Hz, $C^{5,6}$), 149.25 (m, ^3J ≈ 3.7 Hz, $C^{8,9}$); IR (KBr) 3308 (≡C–H), 2962, 2866, 2113 (w, C≡C), 1481, and 756 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{18}$ (198.3): C, 90.85; H, 9.15. Found: C, 91.01; H, 9.11.

1,4-Bis(1,1,3,3-tetramethyl-2-indanylidene)-2-butyne (S8). This high-melting "dehydro-dimer" (> 240 °C) was isolated in a very low yield (20 mg) from the crude material containing the alkyne **S7**. It may have been formed by an oxydative dimerization of the alkenyllithium (**S5**) or the alkynyllithium (**S6**) intermediate and subsequent tautomerizations. It reminds of earlier observations by Ludvig and Lagow who reported[S22] that Ph_2C=CHLi furnished Ph_2C=CH–CH=CPh_2 as the main product through pyrolysis at +125 °C (or "in smaller amounts when kept in THF solution"). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (s, 3-CH_3), 1.66 (s, 1-CH_3), 5.86 (s, α-H), 7.18 (m, 4-H), 7.21 (m, 7-H), 7.25 (m, 5-/6-H), assigned by the NOESY correlations α-H ↔ 3-CH_3 ↔ 4-H and 1-CH_3 ↔ 7-H; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.7 (qq, ^1J = 127.4 Hz, ^3J = 4.6 Hz, 1-CH_3), 32.0 (qq, ^1J = 127.4 Hz, ^3J = 4.6 Hz, 3-CH_3), 47.85 (ddm, ^3J = 8.5 Hz, ^3J = 1.5 Hz, C^1), 47.97 (m, C^3), 93.8 (X part of AA´X with $^2J_{AX}$ = –1.07 Hz, $^3J_{A'X}$ = 4.78 Hz, and $^5J_{AA'}$ = +2.81 Hz, C^β coupled to both A = α-H and A´ = α´-H as analysed through spectrum simulation), 101.7 (dd, ^1J = 158.9 Hz, ^4J = 1.9 Hz, C^α), 122.51 and 122.52 (2 dm, both with ^1J = 155.6 Hz, $C^{4,7}$), 127.1 and 127.3 (2 ddd, both with ^1J = 158.8 Hz, ^3J = 7 Hz, $C^{5,6}$), 148.3 (tm, ^3J = 6.1 Hz, C^9), 149.9 (tm, ^3J = 6.2 Hz, C^8), 172.8 (m, C^2); IR (KBr) 2960, 2929, 2860, 1480,

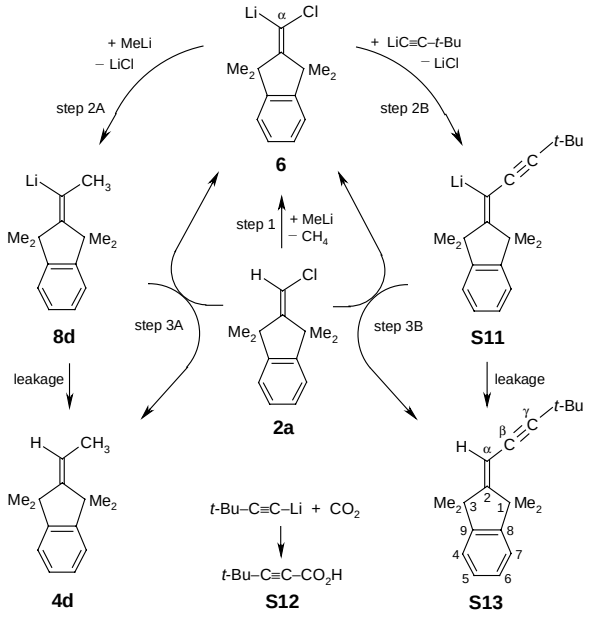
1450, 1110, and 760 cm^{-1}. The constitution of **S8** followed from its spectral C_{2h} symmetry, combined with the unusual CH coupling pattern of $^{13}C^{\beta}$ as caused by *two* isochronous protons (α-H and α´-H) which was confirmed through spectrum simulation and selective decoupling of α-H (→ C^{β} became a singlet).

3-(1,1,3,3-Tetramethyl-2-indanylidene)propenoic Acid (S9). MeLi (3.13 mmol) in Et_2O (2.53 mL) was added at –78 °C under argon cover gas to a stirred solution of dichloride **2c** (400 mg, 1.57 mmol) in anhydrous THF (4.0 mL). After one night at room temperature, the solution was poured onto solid CO_2, warmed up, and diluted with Et_2O plus 2M NaOH. The Et_2O phase was washed until neutral, dried over $MgSO_4$, filtered, and concentrated to afford the almost pure chloroalkene **4f** (280 mg, 76%). The acidified NaOH layer was extracted with Et_2O to give the hardly contaminated allenecarboxylic acid **S9** (38 mg, 10%): Colorless powder, mp 204–205 °C (CCl_4); ^1H NMR (400 MHz, $CDCl_3$) δ 1.45 and 1.49 (2 s, 2 + 2 1-/3-CH_3), 5.82 (s, β-H), 7.16 and 7.26 (2 m, C_6H_4); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 30.86 and 31.01 (2 + 2 1-/3-CH_3), 48.21 ($C^{1,3}$), 92.61 (C^{β}), 122.45 ($C^{4,7}$), 127.58 ($C^{5,6}$), 128.70 (C^{2}), 148.04 ($C^{8,9}$), 171.43 (CO_2H), 208.44 (C^{α}); IR (KBr) 3600–2400 (O–H), 2965, 1958 (s, C=C=C), 1666 (vs, C=O), 1294, and 761 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_2$ (242.3): C, 79.31; H, 7.49. Found: C, 79.23; H, 7.45.

3-(1,1,3,3-Tetramethyl-2-indanyl)propiolic Acid (S10). MeLi (6.20 mmol) in Et_2O (5.0 mL) was added at –78 °C under argon cover gas to a stirred solution of dichloride **2c** (100 mg, 0.39 mmol) in anhydrous THF (5.0 mL). After two weeks at room temperature, the solution was poured onto solid CO_2, warmed up, and diluted with Et_2O plus 2M NaOH. The washed and dried Et_2O layer furnished a mixture (< 20 mg) of the ethylidene compound **4d** and very little alkyne **S7**. The Et_2O extract of the acidified NaOH phase was washed until neutral, dried over $MgSO_4$, concentrated, and crystallized from low-boiling petroleum ether: 44 mg (47%), mp 176–177 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 and 1.43 (2 s, 2 + 2 1-/3-CH_3), 2.95 (s, 2-H), 7.15 and 7.24 (2 m, C_6H_4); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.79 and 29.57 (2 + 2 1-/3-CH_3), 46.33 ($C^{1,3}$), 54.78 (C^{2}), 77.66 (C^{β}), 90 .71 (C^{α}), 122.66 ($C^{4,7}$), 127.39 ($C^{5,6}$), 148.55 ($C^{8,9}$), 157.22 (CO_2H); IR (KBr) 3500–2500 (O–H), 2964, 2231 (s, C≡C), 1682 (vs, C=O), 1410, 1279, 753 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_2$ (242.3): C, 79.31; H, 7.49. Found: C, 78.95; H, 7.65.

5. Substitutions with *t*-BuC≡CLi: S11 – S15.

Scheme S3



Methyllithium (MeLi) can react via the carbenoid chain route with both the α-chloroalkene **2a** and the α,α-dichloroalkene **2c**, as established in the Main Text and depicted here in the left-hand sides of Schemes S3 and S4, respectively. *t*-BuC≡CLi alone is not sufficiently basic to react with reagents **2a** or **2c**, but it can compete (step 2B of Scheme S3) successfully with MeLi (step 2A) for substitution at C^{α} of the carbenoid **6** that was generated by MeLi in the initiating step 1. The experiments were performed in analogy with those employing PhC≡CLi and gave analogous results; but *t*-BuC≡CLi reacted slower than PhC≡CLi by a factor of 2.1 (± 0.2) according to competition experiments.

5.1. Using Reagent 2a.

The intermediate substitution products **S11** and **8d** are both suffiently basic to deprotonate reagent **2a**, so that carbenoid **6** is regenerated in the chain propagating steps 3B and 3A. The product **S13** is formed from the chain carrier **S11** not only via step 3B but also through protonation by adventitious sources other than **2a** ("leakage" to **S13**); this interrupts the chain and halts the conversion until another batch of the initiator MeLi restarts the chain. Final carboxylation was intended to furnish *t*-BuC≡CCO_2H (**S12**), in order to provide evidence that a sufficient amount of *t*-BuC≡CLi had remained in the solution.

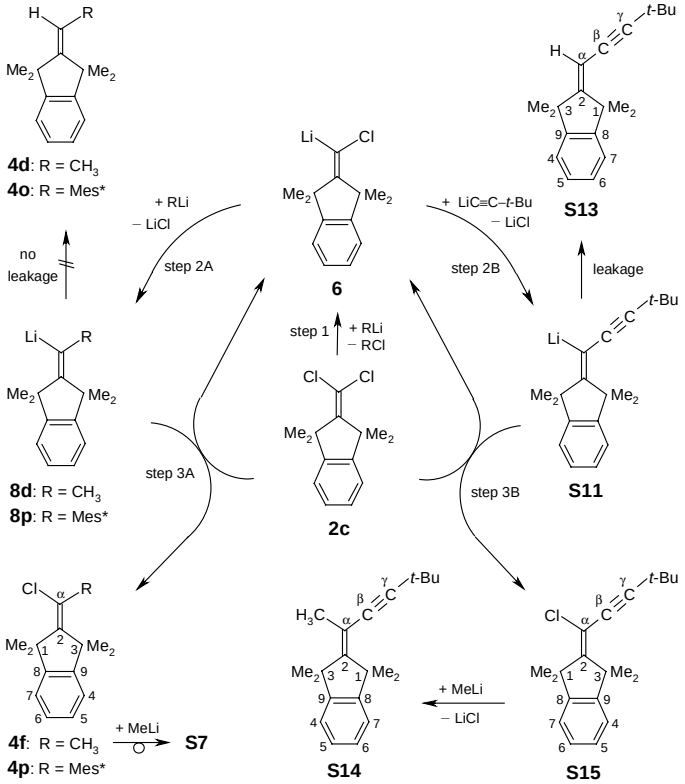
2-(4,4-Dimethyl-2-pentyn-1-ylidene)-1,1,3,3-tetramethylindan (S13). Reagent **2a** (110 mg, 0.50 mmol, 0.23 M) in Et_2O plus THF (74:26 by volume) did not react with *t*-BuC≡CLi (0.46 M) at room

temperature during one night. After the addition of MeLi (finally 0.30 M), **2a** vanished in the course of 6 h. After one further night, the mixture was poured onto solid CO_2, warmed up to ambient temperature, and dissolved in Et_2O plus 2 M NaOH. The acidified NaOH phase furnished 42 mg (0.33 mmol) of pure *t*-BuC≡CCO_2H (**S12**). The non-acidic fraction (67 mg) consisted of **S13** (36% yield) and **4d** (19%). The colorless oil **S13** could not be purified completely through distillation at 120–130 °C (bath temperature)/1 mbar and subsequent chromatography on SiO_2 with petroleum ether plus Et_2O (10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, C*Me*$_3$), 1.35 (s, 2 3-CH_3), 1.62 (s, 2 1-CH_3), 5.59 (s, α-H), 7.15, 7.18, and 7.23 (3 m, 1 + 1 + 2 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.10 (2 1-CH_3), 28.36 (*C*Me$_3$), 30.87 (C*Me*$_3$), 31.99 (2 3-CH_3), 47.64 (C^1), 47.73 (C^3), 101.60 (C^α), 105.13 (C^β), 122.50 ($C^{4,7}$), 125.62 (C^γ), 127.02 (C^5), 127.21 (C^6), 148.38 (C^9), 150.03 (C^8), 172.36 (C^2), assigned by comparison with **4g**. Anal. Calcd for $C_{20}H_{26}$ (266.4): C, 90.16; H, 9.84. Found: C, 88.74; H, 10.18.

Another run *in pure Et_2O* with **2a** (0.26 M), *t*-BuC≡CLi (0.52 M), and MeLi (0.08 M plus 0.065 M in two batches) furnished a similar product mixture within eight days at room temperature: 22% of **S13**, 17% of **4d**, 6% of residual **2a**, and 0.08 mmol of the pure acid **S12**.

5.2. Using Reagent 2c.

Scheme S4



The carbenoid chain process of reagent **2c** with *t*-BuC≡CLi (right-hand side of Scheme S4) did not occur without an initiator. It proceeded most cleanly when started (step 1) with 2,4,6-tri-*tert*-butylphenyllithium (RLi = LiMes*),[43] furnishing **S15** as the main product together with **4p** but practically no leakage products **S13** and **4o**. The initiator RLi = MeLi behaved less nicely because it tended to modify the products **S15** and **4f** of both chains B and A: **S15** (but not **4f**) was substituted slowly at reaction time to give **S14**; this necessitated to employ a larger than catalytic amount of MeLi, with the consequence of a significant contribution of the MeLi chain process (A). The much slower conversion of **4f** led to the alkyne **S7**, as detailed in Scheme S2.

2-(1,4,4-Trimethyl-2-pentyn-1-ylidene)-1,1,3,3-tetramethylindan (S14). The sluggish conversion of *t*-BuC≡CLi (0.75 mmol, 0.60 M) and reagent **2c** (0.40 mmol) in Et_2O plus THF (72:30 by volume) at room temperature had to be started and restarted with three portions (3×0.08 mmol) of MeLi in Et_2O and a final batch of MeLi (0.62 mmol) in the course of six days until **2c** was consumed. The mixture was poured onto solid CO_2, warmed up, and dissolved in Et_2O plus 2 M NaOH. The Et_2O extracts of the acidified NaOH layer were washed until neutral, dried over Na_2SO_4, and concentrated to furnish pure *t*-BuC≡CCO_2H (**S12**, 64 mg, 0.51 mmol) which crystallized after several days with mp 44–46 °C (ref S23: 47–48 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30 (s, C*Me*$_3$), 8.0 (OH). The ethereal layer with the non-acidic fraction was washed until neutral, dried over $MgSO_4$, and concentrated to give 111 mg of a yellow oil containing **4f**, **S14**, and **S15** in the molar ratio 25:47:28. Prolonged treatment with MeLi in Et_2O/THF (1:1) destroyed **4f** (section 4) and converted **S15** to **S14**. After carboxylation and removal of the acids (**S9**, **S10**), this non-acidic fraction was distilled at 135–145 °C (bath temperature)/2 mbar to afford **S14** as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, C*Me*$_3$), 1.50 (s, 2 3-CH_3), 1.64 (s, 2 1-CH_3), 2.07 (s, α-CH_3), 7.13 (m, 4-H), 7.15 (m, 7-H), and 7.22 (m, 5-/6-H), assigned by the NOESY correlations α-CH_3 ↔ 3-CH_3 ↔ 4-H and 1-CH_3 ↔ 7-H; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.69 (sharp q, ^1J = 127.8 Hz, α-CH_3), 28.18 (m, ^2J = 4 Hz, *C*Me$_3$), 28.43 (^1J = 126.7 Hz, ^3J = 4.4 Hz, 2 1-CH_3), 29.18 (^1J = 126.7 Hz, ^3J = 4.4 Hz, 2 3-CH_3), 30.84 (qm, ^1J = 127.0 Hz, ^3J = 4.6 Hz, C*Me*$_3$), 47.82 (m, C^3), 48.24 (m, C^1), 81.78 (q, ^3J = 5.3 Hz, C^β), 102.48 (m, ^3J = 5.1 Hz, C^γ), 112.15 (q, ^2J = 6.3 Hz, C^α), 122.21 and 122.42 (2 dm, both ^1J = 156 Hz, $C^{4,7}$), 126.87 and 126.96 (2 dm, both ^1J = 159 Hz, $C^{5,6}$), 150.06 (m, C^9), 150.25 (m, C^8), 162.41 (m, C^2), assigned by selective {^{1}H} decoupling as follows: {C*Me*$_3$} → *C*Me$_3$ (s) and C^γ (s), {3-CH_3} → C^3 (s) and C^9 (t, ^3J = 6.2 Hz), {1-CH_3} → C^1 (s) and C^8 (t, ^3J = 6 Hz), {α-CH_3} → C^α (s) and C^β (s); IR (KBr) 2965, 2926, 2864, 1590 (w), 1485, 1458, 1362, 1022, and 755 cm^{-1}. Anal. Calcd for $C_{21}H_{28}$ (280.5): C, 89.94; H, 10.06. Found: C, 88.19; H, 9.98.

2-(1-Chloro-4,4-dimethyl-2-pentyn-1-ylidene)-1,1,3,3-tetramethylindan (S15). The reaction of *t*-BuC≡CLi (0.48 M) with reagent **2c** (100 mg, 0.39 mmol, 0.32 M) in Et_2O plus THF (8:2 by volume) was started with LiMes* (**21p**, 0.067 M) whose concentration dropped to 66% in the course of 115 min at room temperature. After two restarts with LiMes* over the next days, the mixture was poured onto solid CO_2, warmed up to room temperature, and dissolved in Et_2O plus 2 M NaOH. The acidified NaOH phase afforded pure *t*-BuC≡CCO_2H[S23] (**S12**, 11 mg, 0.09 mmol). The non-acidic fraction (148 mg) was a mixture of **S15** (0.20 mmol, 71% yield), **4p** (0.033 mmol, 12% yield), ClMes* (0.064 mmol), HMes* (0.110 mmol), residual **2c** (0.109 mmol), and not more than traces of the leakage products **S13** and **4o**. Pure **S15** was obtained through chromatography on SiO_2 (petroleum ether, then Et_2O) and subsequent distillation at 140–160 °C (bath temperature)/2 mbar, followed by crystallization from methanol: mp 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, C*Me*$_3$), 1.61 and 1.63 (2 s, 2 + 2 1-/3-CH_3), 7.15 (m, 4-/7-H), and 7.24 (m, 5-/6-H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.42 and 27.99 (2 + 2 1-/3-CH_3), 28.27 (*C*Me$_3$), 30.37 (C*Me*$_3$), 49.27 and 49.90 ($C^{1,3}$), 103.96 (C^{γ}), 109.42 (C^{β}), 120.31 (C^{α}), 122.34 and 122.35 ($C^{4,7}$), 127.31 and 127.33 ($C^{5,6}$), 148.94 and 149.17 ($C^{8,9}$), 162.61 (C^2), assigned by comparison with **4h**; IR (KBr) 2960, 2924, 2863, 2214 (w, C≡C), 1485, 1460, 1360, 1266, 850, and 750 cm^{-1}; MS (70 eV) m/z (%) 302.2 (1.5, M^+), 300.2 (5.2, M^+), 287.1 (13), 285.1 (41), 265.2 (100, M^+ – Cl). Anal. Calcd for $C_{20}H_{25}Cl$ (300.9): C, 79.84; H, 8.38; Cl, 11.79. Found: C, 80.25; H, 8.50.

6. Kinetic H/D Isotope Effect in the Competition of Reagents 2a and 2b for MeLi.

A solution of the deuterated (**2b**) and the unlabeled monochloride (**2a**) in anhydrous THF (0.400 mL) and [D_{12}]-cyclohexane ("lock" signal, 0.080 mL) was prepared in an NMR tube (5 mm) and analyzed by ^{13}C NMR at maximum resolution: The initial concentrations $[\mathbf{2a}]_o$ = 0.061 M and $[\mathbf{2b}]_o$ = 0.056 M were found through integration of isotope-shifted, baseline-separated signals of C^1 and C^3 of **2a** and **2b**. MeLi (1.24 M in Et_2O) was added under argon cover gas in an amount (0.040 mL) that would have made up the concentration to $[MeLi]_o \leq 0.08$ M. After the rapid consumption of MeLi, the mixture was analyzed again to provide the new concentrations $[\mathbf{2a}]_\infty$ = 0.030 M, $[\mathbf{2b}]_\infty$ = 0.053 M, $[\mathbf{4d}]_\infty$ = 0.0162 M, and $[\mathbf{4e}]_\infty$ = 0.0018 M, the latter two by integration of their isotope-shifted C^1 and C^{β} resonances. The rate ratio $k_H/k_D = 11 \pm 4$ was obtained as the average of $k_H/k_D = \{\ln[\mathbf{2a}]_o - \ln[\mathbf{2a}]_\infty\}/\{\ln[\mathbf{2b}]_o - \ln[\mathbf{2b}]_\infty\}$ and $k_H/k_D = \{\ln[\mathbf{2a}]_o - \ln([\mathbf{2a}]_o - \ln[\mathbf{4d}]_\infty)\}/\{\ln[\mathbf{2b}]_o - \ln([\mathbf{2b}]_o - \ln[\mathbf{4e}]_\infty)\}$ without corrections for the slight dilution and the leakage protonation. After a second

addition corresponding to [MeLi] = 0.060 M, a third *in situ* analysis revealed that **2a** had disappeared completely, leaving an excess of **2b**. Upon carboxylative workup (no organic acids found), a high resolution ^{13}C NMR analysis showed the final distribution of **2a**, **2b**, **4d**, and **4e** to be 0:39:43:18, confirming a high isotope effect through the total consumption of **2a**.

7. References

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(16) All $t_{1/2}$ values in this work are meant to convey semiquantitative rate information only and to point at primary kinetic isotope effects in reactions of **2b**. They cannot be used directly to quantitate k_H/k_D ratios because $t_{1/2}$ increases with decreasing initial concentrations [RLi] which varied by factors up to three here.

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