Synthesis of 2,3-disubstituted norbornadienes

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Abstract: Various 2,3-disubstituted norbornadienes that can hardly be made by the traditional Diels–Alder method were synthesized by double lithium halide exchange of 2,3-dibromonorbornadiene in moderate to good yields.

Key words: 2,3-disubstituted norbornadienes, Diels-Alder reaction, lithium halide exchange.

Résumé: Faisant appel à un double échange de lithium/halogénure sur le 2,3-dibromonorbornadiène, on a réalisé la synthèse, avec des rendements allant de modérés à bons, de divers norbornadiènes 2,3-disubstitués qui peuvent à peine être fabriqués par la méthode traditionnelle de Diels–Alder.

Mots clés: norbornadiènes 2,3-disubstitués, réaction de Diels-Alder, échange lithium halogénure.

Introduction

During our study of the effect of a C-3 substituent on regio- and stereoselectivity in the intramolecular 1,3-dipolar cycloaddition of norbornadiene-tethered nitrile oxides (Scheme 1) (1), we came across a problem for the synthesis of the 2,3-disubstituted norbornadienes (1). Most of the literature syntheses of 2,3-disubstituted norbornadienes rely on Diels–Alder reactions between cyclopentadiene and highly activated acetylenes (2–6). Less activated or unactivated acetylenes are poor dienophiles in Diels–Alder reactions, thus limiting the substituents on the norbornadiene ring system to electron-withdrawing groups. In this paper, we report a more general and simple procedure for the synthesis of 2,3-disubstituted norbornadienes 8 and 9 with a variety of substituents (E₁ and E₂) (Scheme 2).

2,3-Disubstituted norbornadienes are important compounds, which have found a place as key intermediates in the synthesis of many natural products, such as prostaglandin endoperoxides PGH₂ and PGG₂ (7), *cis*-trikentrin B (8), and β -santalol (9, 10). 2,3-Disubstituted norbornadienes also serve in the reversible photoinduced isomerization of norbornadiene derivatives into the corresponding quadricyclanes (11–14). Extensive investigation of 2,3-disubstituted norbornadienes–quadricyclanes interconversion for solar energy storage has demonstrated the efficiency and switching potential of these reversible systems (15–17).

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Results and discussion

Schlosser and co-workers (18) and Brandsma and co-worker (19) have shown independently that deprotonation of a vinyl hydrogen of norbornadiene 6 can be achieved by the use of Schlosser's base, a mixture of *n*-butyllithium (^{*n*}BuLi) and potassium or sodium *tert*-butoxide (^tBuOK or ^tBuONa). Trapping of the metalated norbornadiene 10 with electrophiles leads to the formation of 2-substituted norbornadienes (11) (Scheme 3). This method has been used in the synthesis of 2.3-dibromonorbornadiene (7) (20). We have modified the procedure to achieve a more reliable large-scale (10–20g scale) synthesis of 2,3-dibromonorbornadiene (7) (Scheme 4). After deprotonation of norbornadiene with Schlosser's base, 1,2-dibromoethane (0.5 equiv) was added to the norbornadienyl potassium (10) at -78° C, and the reaction mixture was stirred at -40°C for 1.5 h. At this point, 0.5 equiv. of 2bromonorbornadiene (12) would have been formed together with the remaining 0.5 equiv. of norbornadienyl potassium (10). We found that the temperature control is very important at this stage. If the temperature was too low or too high, the yield of the reaction was very poor. The Br in 12 enhances the acidity of its adjacent vinyl hydrogen, and the leftover norbornadienyl potassium (10) is basic enough to remove that proton to generate 13. Trapping of 13 with excess 1,2-dibromoethane leads to the formation of 2,3dibromonorbornadiene (7).

Monolithium-halide exchange of the 2,3-dibromonorbornadiene (7) with 'BuLi (2 equiv) produces 2-bromo-3-lithionorbornadiene (14). Trapping of this organolithium with water (Table 1, entry 1) gave 8a, and trapping with alkyl halides (entries 2–5) and benzyl bromide (entry 6) afforded the corresponding 2,3-disubstituted norbornadienes (8b–8f) in moderate to good yields. The disubstituted analogs 8d and 8e have been used in the synthesis of C-2, C-3-disubstituted norbornadiene-tethered nitrile oxides 1 (Scheme 1) in our studies of intramolecular 1,3-dipolar cycloadditions (1). We prepared 2,3-disubstituted norbornadienes with heteroatoms (Si, Cl, I, and Sn) by trapping the 2-bromo-3-lithionorbornadiene (14) with silyl chlorides (entries 7 and 8), tosyl chloride (entry 9), iodine (entry 10), and tributyltin chloride Scheme 1.



(entry 11). In reacting with the intermediate 2-bromo-3lithionorbornadiene (14), ethyl chloroformate (entry 12) provided the corresponding ester 81, aldehydes (entries 13 and 14) afforded secondary alcohols 8m and 8n, and ketones (entries 15 and 16) gave tertiary alcohols 80 and 8p. In all these cases, we saw no evidence for the intermediacy of norbornenyne (15) (21) (Scheme 5).

A second lithium halide exchange of bromide **8b** followed by trapping with 1-bromohexane (Table 2, entry 1), 1,4dibromobutane (entry 2), trimethylsilyl chloride (entry 3), tosyl chloride (entry 4), iodine (entry 5), ethyl chloroformate (entry 6), and acetone (entry 7) provided in moderate to good yields a broad range of 2,3-disubstituted norbornadienes (**9a–9g**) with various functional groups. Trapping of bromides **8c** and **8d** with 1,4-dibromobutane (entry 8) and methyl chloroformate (entry 9), respectively, led to the formation of 2,3-disubstituted norbornadienes **9h** and **9i**, which are precursors of the norbornadiene-tethered nitrile oxides in our studies of 1,3-dipolar cycloadditions (1).

In conclusion, we have developed a simple and convenient access to a variety of 2,3-disubstituted norbornadienes that can hardly be prepared by traditional Diels-Alder methodology. Analogs 8a-8p are very useful precursors for the synthesis of many other 2,3-disubstituted norbornadienes. Obviously, instead of the second lithium halide exchange as discussed above to provide 2,3-disubstituted norbornadienes such as 9a-9i, one could presumably couple the bromides 8 with organotin compounds (for the Stille coupling see refs. (22) and (23)), with organoboron compounds (for the Suzuki coupling see ref. (24)), with alkenes (for the Heck reaction see ref. (25)), and with 1-alkynes (for the Castro-Stephens-Sonogashira coupling see ref. (26)) to generate broad classes of vinyl, aryl, and alkynyl norbornadienes. We are currently investigating these coupling reactions in the synthesis of novel conjugated norbornadiene-based polymers. Studies on asymmetric lithium halide exchange of 2,3dibromonornadiene (7) by precomplexation of t BuLi with a chiral base are also underway in our laboratory and will be reported in due course.

Experimental

General Information

All reactions were carried out in an atmosphere of dry nitrogen at ambient temperature unless otherwise stated. Standard column chromatography was performed on 230–400 Scheme 2.



Scheme 3.

$$\begin{array}{c|c}
 & t \\
\hline & F \\
\hline & -78^{\circ} \text{ to } -40^{\circ} \text{C} \\
\end{array}
\left[\begin{array}{c}
 & \downarrow \\
\hline & 10 \\
\hline & K \\
\hline & H \\
\hline & (E^{+}) \\
\hline & 11 \\
\hline & E \\
\hline & H \\
\hline$$

mesh silica gel (obtained from Silicycle) by use of flash column chromatography techniques (27). Analytical thin-layer chromatography (TLC) was conducted on Merck precoated silica gel 60 F254 plates. All glassware was flame dried under an inert atmosphere of dry nitrogen. Infrared spectra were taken on a Bomem MB-100 FTIR spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini-200 or a Bruker-400 spectrometer. Chemical shifts for ¹H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.26). Chemical shifts for ¹³C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ 77.0). High resolution mass spectra were done by Mass Spectrometry Laboratory Services Division at the University of Guelph. Elemental analyses were performed by Canadian Microanalytical Service Ltd., British Columbia or by Quantitative Technologies Inc., New Jersey.

Reagents

Unless stated otherwise, commercial reagents were used without purification. THF was purified by distillation from potassium/benzophenone under dry nitrogen. 1,2-Dibromoethane, 1-iodohexane, 1,4-dibromobutane, chlorotrimethyl-silane, acetone, acetaldehyde, and methyl chloroformate were purified by distillation from 4 Å molecular sieves under dry nitrogen.

2,3-Dibromonorbornadiene (7)

Norbornadiene **6** (35.0 mL, 324 mmol) was added to a flame-dried 3-neck flask containing potassium *tert*-butoxide (18.7 g, 167 mmol) and THF (240 mL), which was cooled at -78° C (cryobath). *n*-Butyllithium (66.0 mL, 2.5M, 165 mmol) was added dropwise through a dropping funnel over 2 h, which the temperature was maintained below -70° C. The mixture was stirred at -65° C for 30 min. then at -40° C for 30 min. After the mixture was cooled to -78° C, 1,2-dibromoethane (7.20 mL, 83.5 mmol) was added, and



the mixture was stirred at -40°C for 1.5 h. Excess 1,2dibromoethane (21.6 mL, 250 mmol) was then added at -70°C. The brown mixture was stirred at -40°C for 2 h then at room temperature for 4 h. After quenching the mixture with saturated ammonium chloride (150 mL) and water (300 mL), the aqueous layer was extracted with diethyl ether $(4 \times 300 \text{ mL})$, and the combined organic layers were washed sequentially with water (500 mL) and brine (500 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the crude product was purified by vacuum distillation to give three fractions. The first fraction $(20-30 \text{ torr } (1 \text{ torr} = 133.322 \text{ Pa}) \text{ at } 40-60^{\circ}\text{C}) \text{ contained}$ mainly the excess 1,2-dibromoethane and norbornadiene. The second fraction (10-15 torr (1 torr = 133.322 Pa) at 50-60°C) contained 2-bromonorbornadiene and 2,3-dibromonorbornadiene in a ratio of 2:1 as determined by ¹H NMR. The third fraction (6-9 torr (1 torr = 133.322 Pa) at 80-100°C) contained pure 2,3-dibromonorbornadiene 7 (13.6 g, 54.4 mmol, 65%) as colorless oil. R_f : 0.67 (hexanes). ¹H NMR (CDCl₃, 400 MHz) δ: 6.88 (s, 2H), 3.61 (m, 2H), 2.45 (dd, 1H, J = 6.3, 1.1 Hz), 2.18 (dt, 1H, J = 6.3, 1.4 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 141.2, 133.0, 72.0, 58.6. Spectral data were identical to those reported in the literature (20).

2-Bromonorbornadiene (8a)

tert-Butyllithium (1.04 mL, 1.7M, 1.77 mmol) was added to a flame-dried flask containing dibromide **7** (222 mg, 0.887 mmol) in THF (4 mL) at -78° C. After the yellow mixture was stirred for 15 min, distilled water (0.50 mL, 28.0 mmol) was added at -78° C. The mixture was stirred at -78° C for 30 min. then at room temperature for 1 h. After quenching the mixture with water (5 mL), the aqueous layer was extracted with diethyl ether (3 × 10 mL), and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give **8a** (93.2 mg, 0.545 mmol, 61%) as colorless oil. Note: **8a** is not very stable and it turned to blackened oil upon standing at room temperature for a few days. Scheme 5.



 R_f : 0.69 (hexanes). ¹H NMR (CDCl₃, 400 MHz) δ: 6.89 (dd, 1H, J = 5.2, 3.2 Hz), 6.78 (dd, 1H, J = 5.2, 3.2 Hz), 6.65 (d, 1H, J = 3.2 Hz), 3.61 (br. s, 1H), 3.48 (br. s, 1H), 2.67 (dt, 1H, J = 6.0, 1.6 Hz), 2.07 (dt, 1H, J = 6.0, 1.6 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 142.9, 141.8, 139.6, 136.6, 73.9, 58.2, 51.6. Spectral data were identical to those reported in the literature (20).

2-Bromo-3-methylnorbornadiene (8b)

tert-Butyllithium (17.3 mL, 1.7M, 29.4 mmol) was added to a flame-dried flask containing dibromide 7 (3.67 g, 14.7 mmol) in THF (40 mL) at -78°C. After the yellow mixture was stirred for 1 h, methyl iodide (2.30 mL, 36.8 mmol) was added at -78°C. The mixture was stirred at -78 °C for 30 min then at room temperature for 2 h. After quenching the mixture with water (40 mL), the aqueous layer was extracted with diethyl ether $(3 \times 50 \text{ mL})$, and the combined organic layers were washed sequentially with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by bulb-to-bulb distillation (15-20 torr (1 torr = 133.322 Pa) at 70–80°C) to give **8b** (2.39 g, 12.9 mmol, 88%) as colorless oil. R_f : 0.74 (hexanes). IR (neat, NaCl) cm⁻¹: 2973 (s), 2939 (s), 2905 (w), 2869 (w), 1639 (w), 1557 (w), 1439 (m), 1376 (w), 1262 (w). ¹H NMR $(CDCl_3, 400 \text{ MHz}) \delta$: 6.87 (dd, 1H, J = 5.0, 2.9 Hz), 6.78(m, 1H), 3.47 (m, 1H), 3.36 (br. s, 1H), 2.21 (dt, 1H, J = 6.0, 1.5 Hz), 2.02 (dt, 1H, J = 6.0, 1.7 Hz), 1.76 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 147.6, 142.1, 141.5, 128.7, 71.4, 57.9, 55.2, 15.4. Anal. calcd. for C₈H₉Br: C 51.92, H 4.90; found C 51.90, H 4.84.

2-Bromo-3-hexylnorbornadiene (8c)

tert-Butyllithium (9.70 mL, 1.7M, 16.5 mmol) was added to a flame-dried flask containing dibromide **7** (1.87 g, 7.48 mmol) in THF (25 mL) at -78° C. After the yellow mixture was

Table 1.

7	Br ^t BuLi (2 e THF, -78	equiv) B°C 14 Br	Li electrophile 8a	E Br
Entry	Electrophile	Norbornadiene	E ₁	Yield (%)
1	H ₂ O	8a	н	61
2	Mel	8b	Me	88
3		8c	ⁿ Hexyl	87
4	тнро	[,] 8d	(CH ₂) ₄ OTHP	90
5	Br	8e	(CH ₂) ₄ Br	53
6	BnBr	8f	CH ₂ Ph	63
7	Me ₃ SiCI	8g	SiMe ₃	88
8	^t BuMe ₂ SiCl	8h	SiMe2 ^t Bu	77
9	TsCl	8i	CI	75
10	I ₂	8j	I	82
11	Bu ₃ SnCl	8k	SnBu ₃	73
12	EtOC(O)Cl	81	COOEt	61
13	CH₃CHO	8m	CH(OH)CH ₃	83
14	PhCHO	8n	CH(OH)Ph	70
15	CH ₃ COCH ₃	80	C(OH)(CH ₃) ₂	73
16	PhCOPh	8p	C(OH)Ph ₂	66

stirred for 1 h, 1-iodohexane (2.00 mL, 13.6 mmol) was added at -78°C. The mixture was stirred at -78 °C for 90 min then at room temperature for 2 h. After quenching the mixture with water (50 mL), the aqueous layer was extracted with diethyl ether (4×50 mL), and the combined organic layers were washed sequentially with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by bulb-to-bulb distillation (1-2 torr (1 torr = 133.322 Pa) at 60°C for 1 h) to remove excess 1iodohexane, then 0.3 torr (1 torr = 133.322 Pa) at 100° C) to give **8c** (1.66 g, 6.50 mmol, 87%) as colorless oil. R_f : 0.85 (hexanes). IR (neat, NaCl) cm⁻¹: 3068 (w), 2958 (s), 2929 (s), 2857 (s), 1633 (w), 1557 (w), 1466 (m), 1378 (w), 1297 (m), 1263 (w), 1224 (w); ¹H NMR (CDCl₃, 400 MHz) δ: 6.86 (m, 1H), 6.75 (m, 1H), 3.47 (m, 1H), 3.43 (m, 1H), 2.24–2.08 (m, 3H), 2.03 (dt, 1H, J = 5.9, 1.7 Hz), 1.44–1.24 (m, 8H), 0.89 (t, 3H, J = 6.8 Hz). ¹³C NMR (CDCl₃, Table 2.

8b,0	E ₁ .	1. ^t BuLi (2 equiv) ⁻ 2. electrophile	ΓΗF, -78	3°C 9a-9i	E ₂
Entry	' E ₁	Electrophile No	rbornad	iene E ₂ Yie	ld (%)
1	Me	∕~~~ _{Br}	9a	ⁿ Hexyl	80
2	Me	Br	9b	(CH ₂) ₄ Br	41
3	Me	Me ₃ SiCl	9c	SiMe ₃	71
4	Ме	TsCl	9d	CI	73
5	Me	l ₂	9e	1	60
6	Me	EtOC(O)CI	9f	COOEt	77
7	Me	MeCOMe	9g	C(OH)Me ₂	80
8	ⁿ Hexyl	Br Br	9h	(CH ₂) ₄ Br	54
9	(CH ₂) ₄ OT	HP MeOC(O)CI	9i	COOMe	74

100 MHz) δ : 151.3, 141.90, 141.87, 129.0, 71.5, 57.9, 53.5, 31.6, 29.2, 28.8, 26.4, 22.6, 14.1. HRMS *m*/*z* for C₁₃H₁₉Br: calcd. 254.0671; found 254.0677.

2-Bromo-3-(4-tetrahydropyranyloxybutyl)norbornadiene (8d)

tert-Butyllithium (24.0 mL, 1.7M, 40.8 mmol) was added to a flame-dried flask containing dibromide 7 (5.10 g, 20.4 mmol) in THF (41 mL) at -78°C. After the yellow mixture was stirred for 30 min, 1-iodo-4-tetrahydropyranyloxybutane (4.43 g, 15.6 mmol) was added at -78°C. The mixture was stirred at -78°C for 1 h then at room temperature for 20 h. After quenching the mixture with water (80 mL), the aqueous layer was extracted with diethyl ether (3 \times 80 mL), and the combined organic layers were washed sequentially with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:hexanes = 1:19) to give **8d** (6.01 g, 18.4 mmol, 90%) as colorless oil. R_f : 0.35 (EtOAc:hexanes = 1:19). IR (neat, NaCl) cm^{-1} : 3067 (w), 2939 (s), 2867 (s), 1633 (w), 1558 (m), 1440 (m), 1352 (m), 1323 (w), 1297 (m), 1260 (m), 1224 (w), 1201 (m), 1137 (m), 1120 (m), 1077 (m), 1033 (m). H NMR (CDCl₃, 400 MHz) δ: 6.84 (dd, 1H, *J* = 4.9, 2.9 Hz), 6.73 (dd, 1H, J = 4.9, 2.9 Hz), 4.55 (m, 1H), 3.85 (m, 1H), 3.71 (m, 1H), 3.51-3.42 (m, 3H), 3.37 (m, 1H), 2.27-2.10 (m, 3H), 2.01 (dm, 1H, J = 5.9 Hz), 1.80 (m, 1H), 1.70 (m, 1H), 1.59–1.42 (m, 8H). ¹³C NMR (CDCl₃, 100 MHz) δ: 150.9, 141.8 (2), 129.3, 98.8, 98.7, 71.5, 67.2, 62.24, 62.22, 57.9, 53.3, 30.7, 29.1, 28.9, 25.4, 23.13, 23.11, 19.61, 19.59. HRMS m/z for C₁₆H₂₃BrO₂: calcd. 326.0882; found 326.0886.

2-Bromo-3-(4-bromobutyl)norbornadiene (8e)

tert-Butyllithium (8.20 mL, 1.7M, 13.9 mmol) was added to a flame-dried flask containing dibromide 7 (1.60 g, 6.40 mmol) in THF (30 mL) at -78°C. After stirring the reaction mixture for 1 h, the resulting vellow reaction mixture was added to a flame-dried flask containing 1,4-dibromobutane (5.50 mL, 46.1 mmol) in THF (30 mL) at -78°C. The mixture was stirred at -78°C for 1 h then at room temperature for 12 h. After quenching the mixture with water (100 mL), the aqueous layer was extracted with diethyl ether $(4 \times 50 \text{ mL})$, and the combined organic layers were washed sequentially with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the excess 1,4-dibromobutane was removed by bulb-to-bulb distillation (4 torr (1 torr = 133.322) Pa) at 70°C for 4 h) and the crude product was purified by column chromatography (hexanes) to give 8e (1.04 g. 3.40 mmol, 53%) as colorless oil. R_f : 0.50 (EtOAc:hexanes = 1:9). IR (neat, NaCl) cm⁻¹: 3066 (w), 2973 (m), 2937 (s), 2866 (w), 1632 (w), 1557 (w), 1451 (w), 1296 (s), 1249 (w). ¹H NMR (CDCl₃, 400 MHz) δ : 6.85 (dd, 1H, J = 5.1, 2.9 Hz), 6.76 (dd, 1H, J = 4.6, 3.0 Hz), 3.47 (m, 1H), 3.44 (m, 1H), 3.40 (t, 2H, J = 6.6 Hz), 2.28–2.12 (m, 3H), 2.04 (dt, 1H, J = 6.0, 1.7 Hz), 1.78 (m, 2H), 1.57 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ: 150.3, 141.9, 141.8, 129.9, 71.6, 57.9, 53.3, 33.7, 31.8, 28.1, 24.8. HRMS m/z for C₁₁H₁₄Br₂: calcd. 303.9463; found 303.9460.

2-Benzyl-3-bromonorbornadiene (8f)

tert-Butyllithium (19.0 mL, 1.7M, 32.3 mmol) was added to a flame-dried flask containing dibromide 7 (4.0 g, 16 mmol) in THF (48 mL) at -78°C. After the yellow mixture was stirred for 1.2 h, benzyl bromide (2.85 mL, 24.0 mmol) was added at -78°C. The mixture was stirred at -78 °C for 2 h then at room temperature for 22 h. After quenching the mixture with water (25 mL), the aqueous layer was extracted with diethyl ether (4 \times 25 mL), and the combined organic layers were washed sequentially with water (25 mL) and brine (25 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the excess benzyl bromide was by vacuum bulb-to-bulb distillation (5 torr (1 torr = 133.322 Pa) at 120°C for 3 h). The crude product was purified by column chromatography (hexanes) to give **8f** (2.62 g, 10.0 mmol, 63%) as yellow oil. R_f : 0.85 (EtOAc:hexanes = 1:9). IR (neat, NaCl) cm^{-1} : 3064 (m), 3027 (s), 2976 (s), 2938 (s), 2867 (s), 1630 (m), 1601 (m), 1557 (m), 1494 (s), 1453 (s), 1428 (w), 1297 (s), 1264 (m), 1224 (m), 1168 (w), 1087 (w), 1074 (m), 1029 (s), 1010 (m). ¹H NMR (CDCl₃, 400 MHz) δ : 7.31–7.20 (m, 3H), 7.12 (dm, 2H, J = 7.2 Hz), 6.81 (dd, 1H, J = 4.9, 3.0 Hz), 6.55 (dd, 1H, J = 4.9, 2.9 Hz), 3.57 (d_{AB}, 1H, J = 14.9 Hz), 3.55 (br. s, 1H), 3.48 (d_{AB} , 1H, J = 14.9 Hz), 3.30 (m, 1H), 2.21 (dt, 1H, *J* = 6.0, 1.5 Hz), 2.00 (dt, 1H, *J* = 6.0, 1.6 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 149.7, 142.0, 140.9, 137.5, 129.9, 128.8, 128.3, 126.2, 71.4, 57.9, 53.4, 35.7. HRMS *m*/*z* for C₁₄H₁₃Br: calcd. 260.0201; found 260.0189.

2-Bromo-3-trimethylsilylnorbornadiene (8g)

tert-Butyllithium (1.01 mL, 1.7M, 1.72 mmol) was added to a flame-dried flask containing dibromide 7 (215 mg, 0.862 mmol) in THF (4 mL) at -78° C. After the yellow mix-

ture was stirred for 30 min, chlorotrimethylsilane (0.27 mL, 2.10 mmol) was added at -78°C. The mixture was stirred at -78°C for 1 h then at room temperature for 1 h. After quenching the mixture with water (5 mL), the aqueous layer was extracted with diethyl ether $(3 \times 10 \text{ mL})$, and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give 8g (185 mg, 0.762 mmol, 88%) as colorless oil. R_f : 0.88 (EtOAc:hexanes = 1:19). IR (neat, NaCl) cm⁻¹: 2957 (s), 2938 (s), 1571 (s), 1549 (s), 1296 (s), 1248 (s), 1022 (m), 836 (s). ¹H NMR (CDCl₃, 400 MHz) δ: 6.83 (dd, 1H, J = 5.0, 3.2 Hz), 6.70 (dd, 1H, J = 5.0, 3.2 Hz), 3.73 (br. s, 1H), 3.54 (br. s, 1H), 2.14 (dt, 1H, J = 6.1, 1.5 Hz), 1.94 (dt, 1H, J = 6.1, 1.5 Hz), 0.15 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ: 147.6, 147.2, 142.7, 141.0, 72.3, 61.4, 55.7, -1.7. HRMS m/z for C₁₀H₁₅SiBr: calcd. 242.0127; found 242.0124.

2-Bromo-3-tert-Butyldimethylsilylnorbornadiene (8h)

tert-Butyllithium (1.00 mL, 1.7M, 1.70 mmol) was added to a flame-dried flask containing dibromide 7 (212 mg, 0.847 mmol) in THF (4 mL) at -78°C. After the yellow mixture was stirred for 30 min, tert-butyldimethylsilyl chloride (338 mg, 2.24 mmol) was added at -78°C. The mixture was stirred at -78°C for 1 h then at room temperature for 1 h. After quenching the mixture with water (5 mL), the aqueous layer was extracted with diethyl ether (3 \times 10 mL), and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give 8h (187 mg, 0.655 mmol, 77%) as colorless oil. R_f : 0.88 (EtOAc:hexanes = 1:19). IR (neat, NaCl) cm⁻¹: 2953 (s), 2928 (s), 2855 (s), 1570 (s), 1548 (s), 1470 (m), 1296 (s), 1249 (s), 1019 (s), 835 (s). ¹H NMR $(CDCl_3, 400 \text{ MHz}) \delta$: 6.85 (dd, 1H, J = 4.9, 3.1 Hz), 6.72(dd, 1H, J = 4.9, 2.9 Hz), 3.77 (br. s, 1H), 3.55 (br. s, 1H), 2.18 (d, 1H, J = 6.1 Hz), 1.94 (dm, 1H, J = 6.1 Hz), 0.88 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 148.8, 146.1, 142.9, 140.9, 72.4, 61.7, 56.7, 26.7, 18.4, -5.4, -5.8. HRMS m/z for C₁₃H₂₁SiBr: calcd. 284.0596; found 284.0597.

2-Bromo-3-chloronorbornadiene (8i)

tert-Butyllithium (1.00 mL, 1.7M, 1.70 mmol) was added to a flame-dried flask containing dibromide **7** (213 mg, 0.852 mmol) in THF (4 mL) at -78° C. After the yellow mixture was stirred for 30 min, *p*-toluenesulfonyl chloride (345 mg, 1.81 mmol) was added at -78° C. The mixture was stirred at -78° C for 45 min then at room temperature for 1 h. After quenching the mixture with water (5 mL), the aqueous layer was extracted with diethyl ether (3 × 10 mL), and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give **8i** (130 mg, 0.635 mmol, 75%) as colorless oil. R_f : 0.76 (hexanes). ¹H NMR (CDCl₃, 400 MHz) δ : 6.89 (m, 2H), 3.60 (m, 1H), 3.52 (m, 1H), 2.43 (dtd, 1H, J = 6.3, 1.6, 0.3 Hz), 2.19 (dt, 1H, J = 6.3, 1.9 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ : 144.0, 141.6, 141.1, 128.3, 71.5, 57.8, 56.8. Spectral data were identical to those reported in the literature (20).

2-Bromo-3-iodonorbornadiene (8j)

tert-Butyllithium (1.00 mL, 1.7M, 1.70 mmol) was added to a flame-dried flask containing dibromide 7 (213 mg, 0.854 mmol) in THF (3 mL) at -78°C. After the yellow mixture was stirred for 30 min, iodine (456 mg, 1.80 mmol), in a separate flame-dried flask containing 4Å molecular sieves (550 mg) and THF (1 mL), was added via a cannula at -78°C. The mixture was stirred at -78°C for 45 min then at room temperature for 1 h. After quenching the mixture with saturated sodium thiosulfate (5 mL), the aqueous layer was extracted with diethyl ether $(3 \times 10 \text{ mL})$, and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give 8j (207 mg, 0.699 mmol, 82%) as pale-yellow oil. $R_f: 0.77$ (hexanes). IR (neat, NaCl) cm⁻¹: 2993 (s), 2940 (s), 2867 (w), 1573 (s), 1551 (w), 1291 (s), 1220 (w), 711 (s). ¹H NMR (CDCl₃, 400 MHz) δ: 6.87 (m, 2H), 3.71 (m, 1H), 3.62 (m, 1H), 2.44 (dm, 1H, J = 6.4 Hz), 2.14 (dm, 1H, J =6.4 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 141.9, 141.4, 140.8, 105.0, 72.5, 61.9, 59.0. HRMS *m*/*z* for C₇H₆BrI: calcd. 295.8700; found 295.8697.

2-Bromo-3-tributylstannylnorbornadiene (8k)

tert-Butyllithium (1.05 mL, 1.7M, 1.79 mmol) was added to a flame-dried flask containing dibromide 7 (233 mg, 0.894 mmol) in THF (4 mL) at -78°C. After the yellow mixture was stirred for 30 min, tributyltin chloride (0.61 mL, 2.25 mmol) was added at -78°C. The mixture was stirred at -78°C for 45 min then at room temperature for 1 h. After quenching the mixture with water (5 mL), the aqueous layer was extracted with diethyl ether $(3 \times 10 \text{ mL})$, and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give 8k (299 mg, 0.649 mmol, 73%) a\$s colorless oil. R_f : 0.89 (hexanes). IR (neat, NaCl) cm⁻¹: 2956 (s), 2930 (s), 2870 (m), 2853 (m), 1566 (m), 1541 (s), 1463 (m), 1294 (s), 1009 (s), 874 (w). ¹H NMR (CDCl₃, 400 MHz) δ: 6.85 (dd, 1H, J = 5.1, 3.0 Hz), 6.65 (dd, 1H, J = 5.1, 2.9 Hz), 3.74 (br. s, 1H), 3.51 (br. s, 1H), 2.19 (dm, 1H, J = 6.0 Hz), 1.98 (dm, 1H J = 6.0 Hz), 1.49 (m, 6H), 1.29 (m, 6H), 1.00 (t, 6H, J = 8.0 Hz), 0.88 (t, 9H, J = 7.2 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 151.2, 148.9, 142.6, 141.3, 73.1, 60.3, 57.5, 29.1, 27.2, 13.7, 9.7. HRMS *m*/*z* for C₁₉H₃₃SnBr: calcd. 460.0788; found 460.0792.

2-Bromo-3-ethoxycarbonylnorbornadiene (81)

tert-Butyllithium (1.20 mL, 1.7M, 2.04 mmol) was added to a flame-dried flask containing dibromide **7** (219 mg, 0.876 mmol) in THF (2.4 mL) at -78° C. After stirring the mixture for 1 h, the resulting yellow mixture was added to a flame-dried flask containing ethyl chloroformate (0.40 mL, 4.18 mmol) in THF (2 mL) at -78° C. The mixture was stirred at -78°C for 3 h. After quenching the mixture with water (15 mL), the aqueous layer was extracted with diethyl ether (4 \times 15 mL), and the combined organic layers were washed sequentially with water (20 mL) and brine (20 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:hexanes = 1:19) to give 81 (130 mg, 0.535 mmol, 61%) as colorless oil. R_f : 0.70 (EtOAc:hexanes = 1:4). IR (neat, NaCl) cm⁻¹: 2980 (m), 2943 (m), 2872 (w), 1718 (s), 1717 (s), 1704 (s), 1699 (s), 1695 (s), 1559 (m), 1368 (m), 1310 (s), 1290 (s), 1277 (s), 1249 (s), 1235 (s), 1203 (w), 1150 (m), 1101 (s), 1086 (s), 1024 (w). ¹H NMR (CDCl₃, 400 MHz) δ : 6.90 (dd, 1H, J = 4.9, 3.0 Hz), 6.84 (m, 1H), 4.21 (m, 2H), 3.99 (m, 1H), 3.67 (m, 1H), 2.30 (dt, 1H, J = 6.6, 1.5 Hz), 2.11 (dt, 1H, J = 6.7, 1.6 Hz), 1.30 (t, 3H, J = 7.1 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 163.7, 148.4, 143.0, 142.0, 140.4, 71.7, 61.6, 60.4, 52.0, 14.2. Anal. calcd. for C₁₀H₁₁BrO₂: C 49.41, H 4.56; found C 49.23, H 4.58.

2-Bromo-3-(1-hydroxyethyl)norbornadiene (8m)

tert-Butyllithium (0.50 mL, 1.7M, 0.850 mmol) was added to a flame-dried flask containing dibromide 7 (106 mg, 0.424 mmol) in THF (2 mL) at -78°C. After the yellow mixture was stirred for 45 min, acetaldehyde (0.10 mL, 2.88 mmol) was added at -78°C. The mixture was stirred at -78°C for 1 h. After quenching the mixture with water (5 mL), the aqueous layer was extracted with diethyl ether $(3 \times 10 \text{ mL})$, and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:hexanes = 1:4) to give **8m** (75.9 mg, 0.353 mmol, 83%, 1:1 inseparable mixture of diastereomers) as colorless oil. R_f : 0.33 (EtOAc:hexanes = 1:4); IR (neat, NaCl) cm⁻¹: 3354 (br. s), 3069 (w), 2973 (s), 2939 (s), 2869 (s), 1628 (m), 1558 (m), 1449 (m), 1368 (m), 1327 (m), 1296 (s), 1268 (m), 1224 (m), 1209 (m), 1091 (s), 1062 (s), 1030 (m), 1009 (m). ¹H NMR (CDCl₃, 400 MHz) δ: 6.86–6.76 (m, 2H), 4.70 (q, 0.5H, J = 6.2 Hz), 4.69 (q, 0.5H, J = 6.2 Hz), 3.72 (br. s, 0.5H), 3.68 (br. s, 0.5H), 3.50 (br. s, 1H), 2.16 (m, 1H), 2.04 (m, 1H), 1.87 (br. s, 1H), 1.62 (br. s, 1H), 1.33 (d, 1.5H, J = 6.4 Hz), 1.11 (d, 1.5H, J =6.5 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 152.6, 152.4, 142.9, 142.5, 141.4, 141.2, 130.4, 130.2, 71.8, 71.3, 64.6, 64.5, 58.2, 58.1, 50.0, 49.5, 20.8, 18.9. Anal. calcd. for C₉H₁₁BrO: C 50.26, H 5.15; found C 50.09, H 5.16.

2-Bromo-3-(1-hydroxybenzyl)norbornadiene (8n)

tert-Butyllithium (1.10 mL, 1.7M, 1.87 mmol) was added to a flame-dried flask containing dibromide **7** (212 mg, 0.849 mmol) in THF (4.2 mL) at -78° C. After the yellow mixture was stirred for 1 h, benzaldehyde (0.10 mL, 0.98 mmol) was added at -78° C. The mixture was stirred at -78° C for 2 h. After quenching the mixture with water (15 mL), the aqueous layer was extracted with diethyl ether (4 × 15 mL), and the combined organic layers were washed sequentially with water (15 mL) and brine (15 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:hexanes = 1:9) to give **8n**

(164 mg, 0.592 mmol, 70%, 1:1 inseparable mixture of diastereomers) as colorless oil. R_f : 0.55 (EtOAc:hexanes = 1:4). IR (neat, NaCl) cm⁻¹: 3395 (s), 3064 (m), 3028 (m), 2992 (s), 2939 (s), 2869 (m), 1626 (m), 1602 (w), 1557 (w), 1494 (m), 1449 (s), 1299 (s), 1266 (m), 1224 (m), 1127 (w), 1037 (s), 1021 (s), 1002 (s). ¹H NMR (CDCl₃, 400 MHz) δ : 7.42–7.22 (m, 5H), 6.88 (dd, 0.5H, J = 5.0, 3.0 Hz), 6.82 (dd, 0.5H, J = 5.0, 3.0 Hz), 6.58 (dd, 0.5H, J = 4.9, 3.0 Hz), 6.22 (dd, 0.5H, J = 4.9, 2.9 Hz), 5.70 (br. s, 0.5H), 5.68 (d, 0.5H, J = 2.7 Hz, 3.58 (br. s, 0.5H), 3.55 (br. s, 1H), 3.47 (br. s, 0.5H), 2.26 (dm, 0.5H, J = 2.0 Hz), 2.19 (dm, 0.5H, J= 6.2 Hz), 2.09 (dm, 0.5H, J = 6.2 Hz), 2.03 (d, 0.5H, J =3.4 Hz), 1.98 (dd, 1H, J = 6.2, 1.3 Hz). ¹³C NMR (CDCl₃, 100 MHz) $\delta:$ 151.3, 151.1, 142.7, 142.5, 141.5, 141.1, 139.2, 139.0, 132.0, 130.9, 128.4, 128.2, 127.4, 127.3, 125.6, 125.5, 72.1, 70.4, 70.3, 70.0, 58.2, 58.1, 50.8, 49.6. Anal. calcd. for C₁₄H₁₃BrO: C 60.67, H 4.73; found C 60.83, H 4.71.

2-Bromo-3-(2-hydroxypropyl)norbornadiene (80)

tert-Butyllithium (1.05 mL, 1.7M, 1.79 mmol) was added to a flame-dried flask containing dibromide 7 (199 mg, 0.797 mmol) in THF (4.0 mL) at -78°C. After the yellow mixture was stirred for 1 h, acetone (0.40 mL, 5.4 mmol) was added at -78°C. The mixture was stirred at -78 °C for 2 h. After quenching the mixture with water (15 mL), the aqueous layer was extracted with diethyl ether $(4 \times 15 \text{ mL})$, and the combined organic layers were washed sequentially with water (15 mL) and brine (15 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:hexanes = 1:9) to give **80** (0.133 mg, 0.580 mmol, 73%) as colorless oil. R_f : 0.45 (EtOAc:hexanes = 1:4). IR (neat, NaCl) cm^{-1} : 3400 (s), 3122 (w), 3069 (w), 2975 (s), 2937 (s), 2869 (m), 1614 (m), 1557 (m), 1463 (m), 1363 (s), 1296 (s), 1269 (m), 1249 (m), 1232 (m), 1170 (s), 1141 (s), 1058 (m). ¹H NMR (CDCl₃, 400 MHz) δ : 6.87(dd, 1H, J = 5,0, 3.3 Hz), 6.80 (dd, 1H, J= 5.0, 2.9 Hz), 3.67 (m, 1H), 3.47 (m, 1H), 2.17 (dt, 1H, J =6.1, 1.5 Hz), 2.13 (br. s, 1H), 1.94 (dt, 1H, J = 6.1, 1.7 Hz), 1.38 (s, 3H), 1.37 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ : 154.1, 142.2, 141.6, 126.0, 71.9, 70.7, 60.2, 53.0, 28.1, 28.0. Anal. calcd. for $C_{10}H_{13}BrO$: C 52.42, H 5.72; found C 52.61, H 5.70.

2-Bromo-3-(1,1-diphenyl-1-hydroxymethyl)norbornadiene (8p)

tert-Butyllithium (1.20 mL, 1.7M, 2.04 mmol) was added to a flame-dried flask containing dibromide **7** (225 mg, 0.902 mmol) in THF (4.5 mL) at -78° C. After the yellow mixture was stirred for 1 h, benzophenone (204 mg, 1.12 mmol) was added at -78° C. The mixture was stirred at -78° C for 3 h. After quenching the mixture with water (15 mL), the aqueous layer was extracted with diethyl ether (4 × 15 mL), and the combined organic layers were washed sequentially with water (20 mL) and brine (20 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:hexanes = 1:19) to give **8p** (210 mg, 0.594 mmol, 66%) as colorless oil. R_f : 0.40 (EtOAc:hexanes = 1:9). IR (neat, NaCl) cm⁻¹: 3560 (m), 3061 (m), 2938 (m), 2868 (m), 1557 (w), 1492 (s), 1448 (s), 1329 (m), 1295 (s), 1259 (w), 1210 (w), 1163 (m), 1032 (s), 1017 (s). ¹H NMR (CDCl₃, 400 MHz) δ : 7.34–7.25 (m, 10H), 6.79 (dd, 1H, *J* = 4.7, 3.0 Hz), 6.48 (dd, 1H, *J* = 4.8, 2.9 Hz), 3.58 (m, 1H), 3.41 (m, 1H), 2.98 (s, 1H), 2.36 (dt, 1H, *J* = 6.2, 1.5 Hz), 1.95 (dt, 1H, *J* = 6.3, 1.7 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ : 153.0, 143.81, 143.77, 142.5, 140.2, 129.7, 128.1, 128.0, 127.6, 127.5, 80.7, 70.3, 60.7, 54.5. HRMS *m*/*z* for C₂₀H₁₇BrO: calcd. 352.0463; found 352.0461.

2-Hexyl-3-methylnorbornadiene (9a)

tert-Butyllithium (0.96 mL, 1.7M, 1.63 mmol) was added to a flame-dried flask containing bromide 8b (151 mg, 0.817 mmol) in THF (4 mL) at -78°C. After the yellow mixture was stirred for 20 min, 1-bromohexane (0.25 mL, 1.78 mmol) was added at -78°C. The mixture was stirred at -78°C for 45 min then at room temperature for 1 h. After quenching the mixture with water (5 mL), the aqueous layer was extracted with diethyl ether $(3 \times 10 \text{ mL})$, and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give 9a (124 mg, 0.652 mmol, 80%) as colorless oil. R_f : 0.83 (hexanes). IR (neat, NaCl) cm⁻¹: 2970 (s), 2938 (s), 2870 (s), 1558 (w), 1440 (m), 1378 (w), 1295 (m), 715 (s). ¹H NMR (CDCl₃, 400 MHz) δ : 6.74 (m, 2H), 3.29 (br. s, 1H), 3.20 (br. s, 1H), 2.13 (m, 1H), 2.02 (m, 1H), 1.88 (dt, 1H, J = 5.6, 1.5 Hz), 1.82 (dm, 1H, J = 5.6 Hz), 1.69 (s, 3H), 1.40–1.17 (m, 8H), 0.87 (t, 3H, J = 6.8 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 146.3, 142.8, 142.6, 142.1, 70.9, 55.2, 53.2, 31.8, 28.9, 28.0, 27.4, 22.6, 14.2, 14.1. Anal. calcd. for C₁₄H₂₂: C 88.35, H 11.65; found C 88.04, H 11.69.

1-Bromo-4-(3-methyl-2-norbornadienyl)butane (9b)

tert-Butyllithium (30.0 mL, 1.7M, 51.0 mmol) was added to a flame-dried flask containing bromide 8b (4.40 g, 23.8 mmol) in THF (120 mL) at -78°C. After stirring the mixture for 1 h, the resulting yellow mixture was added to a flame-dried flask containing 1,4-dibromobutane (18.0 mL, 151 mmol) in THF (120 mL) at -78°C. The mixture was stirred at -78°C for 30 min then at room temperature for 12 h. After quenching the mixture with water (300 mL), the aqueous layer was extracted with diethyl ether (4×150 mL), and the combined organic layers were washed sequentially with water (150 mL) and brine (150 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by vacuum distillation to give two fractions. The first fraction (4-6 torr (1 torr = 133.322 Pa) at 70–80°C) contained mainly the excess 1,4-dibromobutane. The second fraction (0.4-1 torr (1 torr = 133.322 Pa) at 60-80°C) contained **9b** (2.35 g, 9.74 mmol, 41%) as colorless oil. R_f : 0.54 (hexanes). IR (neat, NaCl) cm^{-1} : 3066 (w), 2963 (s), 2932 (s), 2862 (m), 1557 (w), 1438 (m), 1376 (w), 1301 (m), 1249 (w), 1230 (w), 1202 (w). ¹H NMR (CDCl₃, 400 MHz) δ: 6.74 (m, 2H), 3.38 (t, 2H, J = 7.0 Hz), 3.29 (br. s, 1H), 3.22 (m, 1H), 2.17 (m, 1H), 2.06 (m, 1H), 1.89 (dt, 1H, J = 5.7, 1.5 Hz), 1.84 (m, 1H), 1.74 (m, 2H), 1.69 (br. s, 3H), 1.52 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ: 145.3, 143.5, 142.7, 142.1,

70.9, 55.3, 53.1, 33.9, 32.1, 27.0, 25.9, 14.2. HRMS *m*/*z* for C₁₂H₁₇Br: calcd. 240.0514; found 240.0516.

2-Methyl-3-trimethylsilylnorbornadiene (9c)

tert-Butyllithium (0.99 mL, 1.7M, 1.68 mmol) was added to a flame-dried flask containing bromide 8b (156 mg, 0.845 mmol) in THF (4 mL) at -78°C. After the yellow mixture was stirred for 20 min, chlorotrimethylsilane (0.27 mL, 2.13 mmol) was added at -78°C. The mixture was stirred at -78°C for 45 min then at room temperature for 1 h. After quenching the mixture with water (5 mL), the aqueous layer was extracted with diethyl ether $(3 \times 10 \text{ mL})$, and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give 9c (106 mg, 596 mmol, 71%) as colorless oil. R_f : 0.79 (hexanes). IR (neat, NaCl) cm⁻¹: 2965 (s), 2933 (s), 2864 (s), 1608 (m), 1556 (m), 1439 (w), 1299 (s), 1247 (s), 835 (s), 709 (s). ¹H NMR (CDCl₃, 400 MHz) δ: 6.72 (dd, 1H, J = 5.2, 3.1 Hz), 6.67 (dd, 1H, J = 5.2, 2.9 Hz), 3.63 (br. s, 1H), 3.27 (br. s, 1H), 1.93 (s, 3H), 1.83 (dm, 1H, J =6.0 Hz), 1.77 (dm, 1H, J = 6.0 Hz), 0.08 (m, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ: 164.4, 143.6, 141.5, 140.9, 71.6, 57.9, 54.5, 18.1, -0.9. Anal. calcd. for C11H18Si: C 74.08, H 10.17; found C 74.38, H 10.13.

2-Chloro-3-methylnorbornadiene (9d)

tert-Butyllithium (1.00 mL, 1.7M, 1.70 mmol) was added to a flame-dried flask containing bromide 8b (159 mg, 0.860 mmol) in THF (4 mL) at -78°C. After the yellow mixture was stirred for 20 min, p-toluenesulfonyl chloride (259 mg, 1.36 mmol) was added at -78°C. The mixture was stirred at -78°C for 45 min then at room temperature for 1 h. After quenching the mixture with water (5 mL), the aqueous layer was extracted with diethyl ether $(3 \times 10 \text{ mL})$, and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give 9d (88.3 mg, 0.628 mmol, 73%) as colorless oil. R_f : 0.78 (hexanes). IR (neat, NaCl) cm⁻¹: 2970 (s), 2938 (s), 2870 (m), 1670 (w), 1646 (m), 1440 (m), 1295 (s), 1015 (s). ¹H NMR (CDCl₃, 400 MHz) δ : 6.87 (dd, 1H, J = 4.9, 2.9 Hz), 6.79 (dd, 1H, J = 4.9, 2.9 Hz), 3.37 (br. s, 1H), 3.35 (br. s, 1H), 2.19 (dt, 1H, J = 6.0, 1.6 Hz), 2.01 (dt, 1H, J = 5.6, 2.0 Hz), 1.75 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 143.6, 142.0(2), 139.6, 71.0, 56.3, 54.8, 13.7.

2-Iodo-3-methylnorbornadiene (9e)

tert-Butyllithium (0.97 mL, 1.7M, 1.65 mmol) was added to a flame-dried flask containing bromide **8b** (152 mg, 0.822 mmol) in THF (4 mL) at -78° C. After the yellow mixture was stirred for 20 min, iodine (437 mg, 1.72 mmol) was added at -78° C. The mixture was stirred at -78° C for 30 min then at room temperature for 1 h. After quenching the mixture with saturated sodium thiosulfate (5 mL), the aqueous layer was extracted with diethyl ether (3 × 10 mL), and the combined organic layers were washed sequentially with water (10 mL) and brine (10 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give **9e** (115 mg, 0.496 mmol, 60%) as colorless oil. R_f : 0.79 (hexanes). IR (neat, NaCl) cm⁻¹: 2970 (s), 2938 (s), 2870 (m), 1646 (w), 1558 (w), 1440 (m), 1295 (s), 1163 (m), 715 (s). ¹H NMR (CDCl₃, 400 MHz) δ : 6.86 (dd, 1H, J = 4.9, 2.9 Hz), 6.75 (dd, 1H, J = 4.9, 3.0 Hz), 3.58 (br. s, 1H), 3.37 (br. s, 1H), 2.19 (dt, 1H, J = 6.0, 1.6 Hz), 1.99 (dt, 1H, J = 6.0, 1.6 Hz), 1.80 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ : 155.4, 142.3, 141.1, 100.2, 72.0, 61.0, 55.2, 18.5. HRMS m/z for C₈H₉I: calcd. 231.9751; found 231.9760.

2-ethoxycarbonyl-3-methylnorbornadiene (9f)

tert-Butyllithium (1.10 mL, 1.7M, 1.87 mmol) was added to a flame-dried flask containing bromide 8b (158 mg, 0.852 mmol) in THF (2.0 mL) at -78°C. After stirring the mixture for 1 h, the resulting yellow mixture was added to a flame-dried flask containing ethyl chloroformate (0.38 mL, 4.0 mmol) in THF (2.5 mL) at -78°C. The mixture was stirred at -78°C for 3 h. After quenching the mixture with water (15 mL), the aqueous layer was extracted with diethyl ether (4 \times 15 mL), and the combined organic layers were washed sequentially with water (20 mL) and brine (20 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:hexanes = 1:9) to give **9f** (109 mg, 0.655 mmol, 77%) as colorless oil. R_{f} : 0.50 (EtOAc:hexanes = 1:4). IR (neat, NaCl) cm⁻¹: 2978 (m), 2939 (m), 2870 (w), 1702 (s), 1632 (m), 1558 (w), 1370 (m), 1331 (m), 1314 (m), 1295 (s), 1249 (m), 1237 (s), 1189 (m), 1146 (m), 1101 (m), 1066 (m), 1047 (m), 1019 (w). ¹H NMR (CDCl₃, 400 MHz) δ : 6.86 (dd, 1H, J = 5.0, 3.0 Hz), 6.70 (dd, 1H, J = 4.9, 3.2 Hz), 4.14 (m, 2H), 3.86 (br. s, 1H), 3.37 (br. s, 1H), 2.19 (s, 3H), 2.02 (dm, 1H, J = 6.4 Hz), 1.92 (dm, 1H, J = 6.4 Hz), 1.26 (t, 3H, J = 7.1 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 169.4, 165.9, 144.0, 140.3, 138.3, 70.8, 59.6, 58.0, 50.9, 17.1, 14.3. Anal. calcd. for C₁₁H₁₄O₂: C 74.13, H 7.92; found C 73.99, H 7.95.

2-(2-Methyl-3-norbornadienyl)-2-propanol (9g)

tert-Butyllithium (0.80 mL, 1.7M, 1.4 mmol) was added to a flame-dried flask containing bromide 8b (116 mg, 0.627 mmol) in THF (3.0 mL) at -78°C. After the yellow mixture was stirred for 1 h, acetone (0.35 mL, 4.8 mmol) was added at -78°C. The mixture was stirred at -78 °C for 3 h. After quenching the mixture with water (15 mL), the aqueous layer was extracted with diethyl ether $(4 \times 15 \text{ mL})$, and the combined organic layers were washed sequentially with water (20 mL) and brine (20 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:hexanes = 1:4) to give 9g (82 mg, 0.50 mmol, 80%) as colorless oil. R_f : 0.45 (EtOAc:hexanes = 1:4). IR (neat, NaCl) cm⁻¹: 3384 (s), 3063 (m), 2971 (s), 2932 (s), 2864 (s), 1557 (w), 1448 (m), 1372 (m), 1299 (s), 1250 (m), 1236 (m), 1174 (m), 1132 (m), 1112 (m), 1023 (w). ¹H NMR (CDCl₃, 400 MHz) δ: 6.76 (m, 2H), 3.48 (m, 1H), 3.16 (m, 1H), 1.92 (s, 3H), 1.89 (dm, 1H, J = 5.7 Hz), 1.75 (dm, 1H, J = 5.7 Hz), 1.53 (br. s, 1H), 1.34 (s, 3H), 1.32 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ: 150.3, 143.0, 142.9,

141.9, 72.4, 70.0, 57.6, 52.5, 29.2, 28.8, 15.9. HRMS *m*/*z* for C₁₁H₁₆O: calcd. 164.1201; found 164.1206.

2-(4-bromobutyl)-3-hexylnorbornadiene (9h)

tert-Butyllithium (7.50 mL, 1.7M, 12.8 mmol) was added to a flame-dried flask containing bromide 8c (1.48 g, 5.80 mmol) in THF (30 mL) at -78°C. After stirring the mixture for 1 h, the resulting yellow mixture was added to a flame-dried flask containing 1,4-dibromobutane (4.50 mL, 37.7 mmol) in THF (30 mL) at -78°C. The mixture was stirred at -78°C for 1 h then at room temperature for 12 h. After quenching the mixture with water (100 mL), the aqueous layer was extracted with diethyl ether (4 \times 50 mL), and the combined organic layers were washed sequentially with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the excess 1,4-dibromobutane was removed by bulb-tobulb distillation (2.5 torr (1 torr = 133.322 Pa) at 65° C for 2 h) and the crude product was purified by column chromatography (hexanes) to give 9h (980 mg, 3.15 mmol, 54%) as colorless oil. R_f : 0.50 (EtOAc:hexanes = 1:9). IR (neat, NaCl) cm⁻¹: 3063 (w), 2960 (s), 2928 (s), 2857 (s), 1557 (w), 1456 (m), 1378 (w), 1303 (m), 1249 (w). ¹H NMR $(\text{CDCl}_3, 400 \text{ MHz}) \delta$: 7.26 (m, 2H), 3.39 (t, 2H, J = 6.9 Hz), 3.29 (m, 2H), 2.21-1.95 (m, 4H), 1.87 (dt, 1H, J = 5.6)1.6 Hz), 1.84 (dm, 1H, J = 5.6 Hz), 1.76 (m, 2H), 1.56–1.22 (m, 10H), 0.88 (t, 3H, J = 6.8 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 147.6, 145.6, 142.5, 142.3, 71.0, 53.3, 53.0, 33.9, 32.3, 31.7, 29.0, 28.1, 27.5, 27.1, 26.1, 22.6, 14.1. HRMS m/z for C₁₇H₂₇Br: calcd. 310.1297; found 310.1303.

2-methoxycarbonyl-3-(4-

tetrahydropyranyloxybutyl)norbornadiene (9i)

tert-Butyllithium (14.0 mL, 1.7M, 23.8 mmol) was added to a flame-dried flask containing bromide 8d (3.00 g, 9.17 mmol) in THF (17.0 mL) at -78°C. After stirring the mixture for 1 h, the resulting yellow mixture was added to a flame-dried flask containing methyl chloroformate (3.0 mL, 39 mmol) in THF (7.0 mL) at -78°C. The mixture was stirred at -78° C for 3 h. After quenching the mixture with water (20 mL), the aqueous layer was extracted with diethyl ether (4 \times 20 mL), and the combined organic layers were washed sequentially with water (25 mL) and brine (25 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:hexanes = 1:9) to give **9i** (2.07 g, 6.76 mmol, 74%) as colorless oil. R_f : 0.55 (EtOAc:hexanes = 1:4). IR (neat, NaCl) cm⁻¹: 2941 (s), 2868 (m), 1700 (s), 1695 (s), 1558 (w), 1435 (m), 1342 (m), 1295 (s), 1238 (s), 1200 (m), 1163 (m), 1138 (m), 1119 (m), 1103 (m), 1074 (s), 1034 (s), 1022 (m). ¹H NMR (CDCl₃, 400 MHz) δ : 6.85 (dd, 1H, J = 5.0, 3.0 Hz), 6.67 (dd, 1H, J = 4.7, 3.3 Hz), 4.55 (m, 1H), 3.86–3.84 (m, 2H), 3.72 (m, 1H), 3.69 (s, 3H), 3.50–3.48 (m, 2H), 3.37 (m, 1H), 2.76– 2.64 (m, 2H), 2.01 (dm, 1H, J = 6.4 Hz), 1.94 (dm, 1H, J =6.4 Hz), 1.80 (m, 1H), 1.69 (m, 1H), 1.61–1.44 (m, 8H). ¹³C NMR (CDCl₃, 100 MHz) δ: 173.3, 166.2, 143.8, 140.7, 138.5, 98.81, 98.78, 71.0, 67.2, 62.30, 62.27, 55.9, 51.0, 50.9, 30.7, 29.9, 29.3, 25.4, 23.5, 19.64, 19.62. Anal. calcd. for C₁₈H₂₆O₄: C 70.56, H 8.55; found C 70.67, H 8.52.

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