Palladium-Catalyzed Suzuki Couplings of 2,3-Dibromonorbornadiene: Synthesis of Symmetrical and Unsymmetrical Aryl-Substituted Norbornadienes

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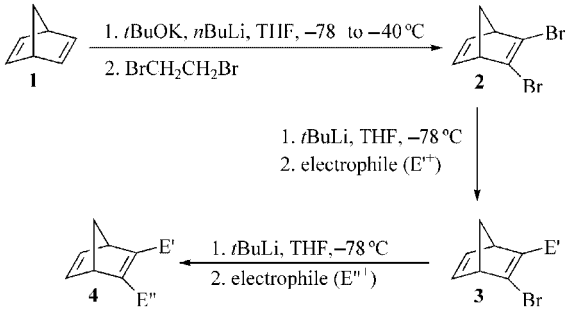
Palladium-catalyzed Suzuki coupling reactions between 2,3-dibromonorbornadiene and arylboronic acids were investigated. These reactions provide an efficient method for the synthesis of symmetrical 2,3-diarylnorbornadienes which are not accessible using the traditional Diels–Alder cycloaddition reactions. The optimized reaction conditions of the Suzuki coupling reactions were found using [$Pd_2(dba)_3$] (0.5 mol%), tBu$_3$P (1.4 mol%) and CsF in THF. High yields of the Suzuki coupling products were obtained when electron-rich arylboronic acids were used. On the other hand, Suzuki coupling reactions with electronic-deficient or sterically hindered arylboronic acids gave lower yields of the corresponding 2,3-diarylnorbornadienes. Unsymmetrical mono- and diaryl-substituted norbornadienes were also prepared in good yields using this method.

Introduction

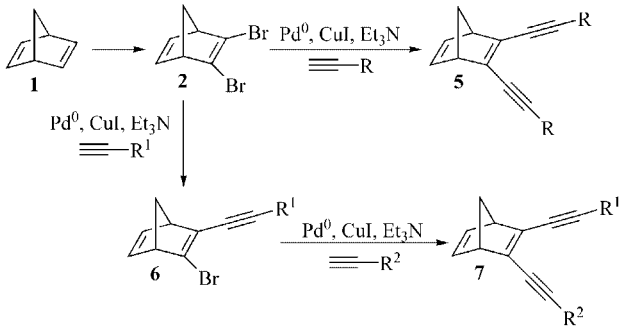
2,3-Disubstituted norbornadienes are important compounds which have found a place as key intermediates in the synthesis of many natural products such as the prostaglandin endoperoxides PGH_2 and PGG_2,[1] *cis*-Trikentrin B[2] and β-santalol.[3] Photochemical valence isomerization between norbornadiene and quadricyclane is of interest as a solar energy conversion and storage system.[4,5] Extensive investigations of 2,3-disubstituted norbornadienes/quadricyclanes for solar energy storage have demonstrated the efficiency and switching potential of these reversible systems.[6] This photochemical isomerization reaction has recently been investigated as an optical waveguide utilising photoinduced refractive index changes,[7] as a photochromic system potentially applicable to data storage[8] or as light-driven, carrier-mediated, active transport across a membrane against a concentration gradient.[9]

Syntheses of the 2,3-disubstituted norbornadienes used in the above studies rely mainly on the Diels–Alder reaction between cyclopentadiene and the corresponding alkyne. Since nonctivated alkynes are poor dienophiles in Diels–Alder cycloadditions,[10] the variety of 2,3-disubstituted norbornadienes which could be synthesized using the Diels–Alder method is rather limited (they usually contain at least one electronic withdrawing group such as an ester, an amide or a cyano group etc). We have recently reported the synthesis of a variety of 2,3-disubstituted norbornadienes by a double lithium-halide exchange of 2,3-dibromonorbornadiene (Scheme 1)[11] and the synthesis of symmetrical and unsymmetrical norbornadiene-2,3-diynes by Pd-catalyzed Sonogashira couplings (Scheme 2).[12] These studies significantly broadened the variety of 2,3-disubstituted norborna-



E', E" = alkyl groups, silyl groups, Bn, Cl, Br, I, R_3Sn, COOR, $R^1R^2C(OH)$

Scheme 1. Synthesis of 2,3-disubstituted norbornadienes by double lithium-halide exchange



Scheme 2. Synthesis of symmetrical and unsymmetrical norbornadiene-2,3-diynes **5** and **7** by palladium-catalyzed Sonogashira coupling

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dienes which cannot be prepared by the Diels–Alder methodology. However, one limitation of these synthetic methods is that substitutents with an sp^2-hybridized carbon (aryl and vinyl groups) cannot be prepared. To the best of our knowledge, there is no general method for the synthesis of 2,3-diarylsubstituted norbornadienes. In this paper, we report our studies on palladium-catalyzed Suzuki couplings of 2,3-dibromonorbornadiene with arylboronic acids for the synthesis of symmetrical and unsymmetrical 2,3-diarylsubstituted norbornadienes.

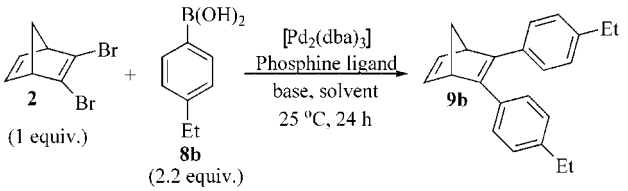
Results and Discussion

Synthesis of Symmetrical 2,3-Diarylsubstituted Norbornadienes

Removal of a vinylic proton from the norbornadiene **1** with the Schlosser's base (*t*BuOK and *n*BuLi) followed by trapping the metallated norbornadiene with 1,2-dibromoethane provided the 2,3-dibromonorbornadiene **2** in 65% yield (Scheme 1).[11] Optimization of the Pd-catalyzed Suzuki coupling reaction between 2,3-dibromonorbornadiene **2** and 4-ethylphenylboronic acid **8b** under various conditions (different phosphane ligands, different bases and different solvents) is shown in Table 1. Depending on the structures of the coupling partners, the use of different phosphane ligands, different bases and different solvents can alter the yields of Suzuki coupling reactions significantly.[13] In our case, we found that among various phosphane ligands tested, only tBu$_3$P provided good yields in the coupling reactions between 2,3-dibromonorbornadiene **2** and 4-ethylphenylboronic acid **8b** (entries 1–8). In the presence of [Pd$_2$(dba)$_3$] (0.5 mol%), a monodentate phosphane (1.4 mol%; Ph$_3$P, Cy$_3$P, nBu$_3$P, (2-furyl)$_3$P or TTMPP, entries 1–4, 6) or phosphite (1.4 mol%, entry 5) or a bidentate phosphane (entry 7) and CsF (6.6 equiv.) in THF at room temperature, Suzuki coupling between 2,3-dibromonorbornadiene **2** and 4-ethylphenylboronic acid **8b** only provides the coupling product **9b** in <5% yield (entries 1–7). On the other hand, when a bulky monodentate phosphane tBu$_3$P (1.4 mol%) was used under the same reaction conditions, the coupling product **9b** was formed in 95% yield (entry 8). The use of different bases also significantly changed the yields of the coupling reaction and CsF was found to be the most useful base in this case (entries 8–11). Both THF and DMF were found to give high yields in the coupling reactions while the use of other solvents lowered the yields significantly (entries 8, 12–15). Thus, the optimized Suzuki coupling conditions were found with tBu$_3$P and CsF in THF (entry 8).

To test the generality of the Suzuki coupling reactions of 2,3-dibromonorbornadiene **2** for the synthesis of a variety of symmetrical diaryl-substituted norbornadienes, several arylboronic acids were employed (**8a-8j**) and the results of these coupling reactions are shown in Table 2. In the presence of [Pd$_2$(dba)$_3$] (0.5 mol%), tBu$_3$P (1.4 mol%) and CsF (6.6 equiv.) in THF at room temperature, Suzuki coupling between 2,3-dibromonorbornadiene **2** and the parent phenylboronic acid **8a** occurred smoothly to afford the 2,3-diphenylnorbornadiene **9a** in 88% yield (entry 1). Under the same reaction conditions, good yields (88–92%) were obtained with the electron-rich, unhindered arylboronic acids **8b** (*p*-Et), **8d** (*p*-OMe) and **8e** (*m*-OMe) (entries 2, 4, 5) with the exception of [4-(dimethylamino)phenyl]boronic acid **8c** which gave a poorer yield of 48% (*p*-NMe$_2$, entry 3). On the other hand, the Suzuki coupling of an electron-deficient arylboronic acid **8g** gave a much lower yield (21%) and a slight improvement in the yield was observed when the reaction temperature was increased to 65 °C (entry 7). An increase in the steric hindrance of the arylboronic acid led to a decrease in the yield of the coupling reaction (compare entries 4 and 5 with entry 6). Suzuki couplings of chloroarylboronic acids with 2,3-dibromonorbornadiene **2** also provided the corresponding 2,3-diarylnorbornadienes in good yields (84–88%, entries 8–10).

Table 1. Optimization of the Pd-catalyzed Suzuki coupling reaction between 2,3-dibromonorbornadiene **2** and (4-ethylphenyl)boronic acid **8b**



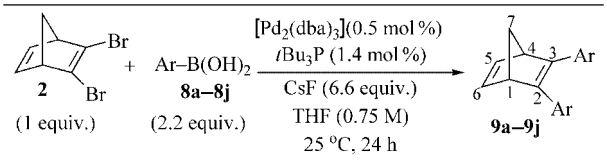
Entry	Ligand	Base	Solvent	Yield [%][a]
1	Ph$_3$P	CsF	THF	< 5
2	Cy$_3$P	CsF	THF	< 5
3	nBu$_3$P	CsF	THF	< 5
4	(2-furyl)$_3$P	CsF	THF	< 5
5	(MeO)$_3$P	CsF	THF	5
6	TTMPP[b]	CsF	THF	< 5
7	BINAP	CsF	THF	< 5
8	tBu$_3$P	CsF	THF	95 (92)
9	tBu$_3$P	KF	THF	41
10	tBu$_3$P	K$_2$CO$_3$	THF	43
11	tBu$_3$P	tBuOK	THF	< 5
12	tBu$_3$P	CsF	pentane	< 5
13	tBu$_3$P	CsF	toluene	17
14	tBu$_3$P	CsF	CH_2Cl_2	24
15	tBu$_3$P	CsF	DMF	95

[a] GC yields using naphthalene as internal standard. Isolated yields after column chromatography (silica gel, hexanes) are shown in parentheses. [b] TTMPP: tris(2,4,6-trimethoxyphenyl)phosphane.

Synthesis of Unsymmetrical Mono- and Diaryl-Substituted Norbornadienes

Synthesis of monoaryl-substituted norbornadienes **11a**–**11d** was achieved by the Pd-catalyzed Suzuki coupling reac-

Table 2. Pd-catalyzed Suzuki coupling reaction between 2,3-dibromonorbornadiene **2** and arylboronic acids **8a**–**8j**

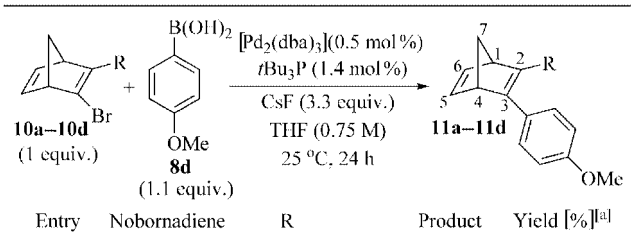


Entry	Aryl boronic acid	Ar	Product	Yield [%][a]
1	**8a**	C_6H_5	**9a**	88
2	**8b**	*p*-Et–C_6H_4	**9b**	92
3	**8c**	*p*-NMe_2–C_6H_4	**9c**	48[b]
4	**8d**	*p*-OMe–C_6H_4	**9d**	92
5	**8e**	*m*-OMe–C_6H_4	**9e**	92
6	**8f**	*o*-OMe–C_6H_4	**9f**	61
7	**8g**	*p*-Ac–C_6H_4	**9g**	21[c]
8	**8h**	*p*-Cl–C_6H_4	**9h**	88
9	**8i**	*m*-Cl–C_6H_4	**9i**	88
10	**8j**	*o*-Cl–C_6H_4	**9j**	84

[a] Isolated yields after column chromatography (silica gel, hexanes or ethyl acetate/hexanes). [b] When the coupling was carried out at 65 °C, decomposition was observed and no coupling product was isolated. [c] When the coupling was carried out at 65 °C, isolated yields of the coupling product **8g** were improved to 37%.

tions between 2-bromo-3-R-norbornadienes **10a**–**10d**[14] and *p*-methoxyphenylboronic acid **8d** (Table 3). Pd-catalyzed Suzuki coupling between 2-bromo-3-methylnorbornadiene **10a** and *p*-methoxyphenylboronic acid **8d** occurred smoothly to provide the monoaryl-substituted norbornadiene **11a** in 81% yield (entry 1). Upon replacing the Me group on the bromonorbornadiene with a bulky silyl group (Si*t*BuMe$_2$) or with an electron-withdrawing group such as Cl and COOEt, Suzuki coupling also occurred smoothly giving the corresponding monoaryl-substituted norbornadienes in excellent yields (86–93%, entries 2–4). Thus, both steric and electronic effects on the bromonorbornadiene do not affect the effectiveness of the Suzuki coupling reactions.

Table 3. Synthesis of mono-aryl-substituted norbornadienes

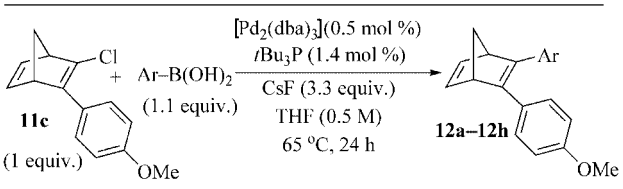


Entry	Nobornadiene	R	Product	Yield [%][a]
1	**10a**	Me	**11a**	81
2	**10b**	Si*t*BuMe$_2$	**11b**	86
3	**10c**	Cl	**11c**	86
4	**10d**	COOEt	**11d**	93

[a] Isolated yields after column chromatography.

It is noteworthy to mention that in the case of 2-chloro-3-bromonorbornadiene **10c**, Suzuki coupling only occurred selectively with the more reactive vinyl bromide leaving the vinyl chloride unreacted and giving the monoaryl-substituted norbornadiene **11c** in a good yield. The synthesis of several unsymmetrical diaryl-substituted norbornadienes are shown in Table 4. Pd-catalyzed Suzuki coupling between 2-chloro-3-(*p*-methoxyphenyl)norbornadiene **11c** with various arylboronic acids occurred smoothly at 65 °C to provide the corresponding unsymmetrical 2,3-diarylnorbornadienes **12a**–**12h** in good yields (75–90%).

Table 4. Synthesis of unsymmetric 2,3-diarylnorbornadienes



Entry	Aryl boronic acid	Ar	Product	Yield [%][a]
1	**8a**	C_6H_5	**12a**	85
2	**8b**	*p*-Et–C_6H_4	**12b**	80
3	**8c**	*p*-NMe_2–C_6H_4	**12c**	75
4	**8e**	*m*-OMe–C_6H_4	**12d**	88
5	**8f**	*o*-OMe–C_6H_4	**12e**	79
6	**8h**	*p*-Cl–C_6H_4	**12f**	90
7	**8i**	*m*-Cl–C_6H_4	**12g**	84
8	**8j**	*o*-Cl–C_6H_4	**12h**	85

[a] Isolated yields after column chromatography.

Conclusions

In summary, we have investigated the Pd-catalyzed Suzuki coupling reactions between 2,3-dibromonorbornadienes and arylboronic acids. The optimum reaction conditions of the Suzuki coupling reactions were [$Pd_2(dba)_3$] (0.5 mol%), *t*Bu_3P (1.4 mol%) and CsF in THF. High yields of the Suzuki coupling products were obtained when electron-rich arylboronic acids were used. On the other hand, Suzuki coupling reactions with electronic-deficient or sterically hindered arylboronic acids gave lower yields of the 2,3-diarylnorbornadienes. Unsymmetrical mono and diaryl-substituted norbornadienes were also prepared in good yields using this method. This study provides an efficient method and high yielding syntheses of several new symmetrical and unsymmetrical aryl-substituted norbornadienes which are not accessible using the traditional Diels–Alder cycloaddition method or using double lithium-halide exchange reactions.

Experimental Section

General Remarks: All reactions were carried out in an inert atmosphere glovebox system at ambient temperature unless otherwise

stated. Standard column chromatography was performed on 230–400 mesh silica gel (obtained from Silicycle) by use of flash column chromatographic techniques. Analytical thin-layer chromatography (TLC) was conducted on Merck precoated silica gel 60 F_{254} plates. All glassware was flame dried under dry nitrogen. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ = 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ = 77.0 ppm). High resolution mass spectra were recorded at the McMaster Regional Centre for Mass Spectrometry at McMaster University, Hamilton, Ontario. Elemental analyses were performed by the Canadian Microanalytical Service Ltd., British Columbia or by Quantitative Technologies Inc., New Jersey. Unless stated otherwise, commercial reagents were used without purification. Solvents were purified by distillation (dichloromethane, pentane and DMF from CaH_2, toluene from sodium and THF from potassium/benzophenone) under dry nitrogen then degassed using freeze–pump–thaw cycles. 2,3-Dibromonorbornadiene **2** and the bromonorbornadienes **10a**–**10d** were prepared according to literature procedures.[11]

General Procedure (A) for Suzuki Coupling between 2,3-Dibromonorbornadiene 2 and Arylboronic Acids 8a-8j

Synthesis of Symmetrical 2,3-Diarylnorbornadienes: In an inert atmosphere (Ar) glovebox, 2,3-dibromonorbornadiene **2** (0.3 mmol) was added to an oven-dried vial along with [$Pd_2(dba)_3$] (0.5 mol%, 0.0016 mmol), arylboronic acid (0.66 mmol) and caesium fluoride (2.1 mmol). The mixture was dissolved in THF (0.4 mL) and stirred for 1 min. The phosphane tBu$_3$P (1.4 mol%, 0.0043 mmol) was then added and the reaction was stirred at room temperature inside the glovebox for 24 h. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography.

2,3-Diphenylbicyclo[2.2.1]hepta-2,5-diene (9a): This was prepared following the above general procedure (A) with 2,3-dibromonorbornadiene **2** (77.5 mg, 0.310 mmol) and phenylboronic acid **8a** (83.3 mg, 0.683 mmol). The crude product was purified by column chromatography (hexanes) to provide **9a** (66.6 mg, 0.273 mmol, 88%) as a white solid. M.p. 52–53 °C. R_f 0.18 (hexanes). IR (film): $\tilde{\nu}$ = 3058, 2983, 2868, 1723, 1681, 1598, 1498, 1447, 1390, 1259, 1077, 1003, 918, 744 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.11 (dt, J = 1.5 and 6.1 Hz, 1 H, H-7), 2.39 (dt, J = 1.5 and 6.1 Hz, 1 H, H-7′), 3.92 (t, J = 1.7 Hz, 2 H, H-1 and H-4), 7.01 (t, J = 1.8 Hz, 2 H, H-5 and H-6), 7.20 (m, 2 H, Ar), 7.26 ppm (m, 8 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 56.8 (C-1 and C-4), 70.3 (C-7), 126.6 (ArCH), 127.0 (ArCH), 128.2 (ArCH), 137.7 (Ar-C), 142.6 (C-5 and C-6), 148.6 ppm (C-2 and C-3). HRMS for $C_{19}H_{16}$: calcd. 244.1252; found 244.1258 [M]$^+$. $C_{19}H_{16}$ (244.34): calcd. C 93.40, H 6.60; found C 93.62, H, 6.51.

2,3-Bis(4-ethylphenyl)bicyclo[2.2.1]hepta-2,5-diene (9b): This was prepared following the above general procedure (A) with 2,3-dibromonorbornadiene **2** (75.4 mg, 0.302 mmol) and 4-ethylphenylboronic acid **8b** (108.9 mg, 0.726 mmol). The crude product was purified by column chromatography (hexanes) to provide **9b** (83.2 mg, 0.277 mmol, 92%) as a clear yellow oil. R_f 0.19 (hexanes). IR (film): $\tilde{\nu}$ = 3121, 3021, 2964, 2932, 2867, 1557, 1515, 1455, 1411, 1297, 1183, 1015, 831, 714, 608 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.26 (t, J = 7.6 Hz, 6 H, 2 × CH_3), 2.08 (dt, J = 6.1 and 1.4 Hz, 1 H, H-7), 2.35 (dt, J = 6.1 and 1.4 Hz, 1 H, H-7′), 2.65 (q, J = 7.6 Hz, 4 H, 2 × CH_2), 3.89 (tm, J = 1.8 Hz, 2 H, H-1 and H-4), 6.99 (t, J = 1.8 Hz, 2 H, H-5 and H-6), 7.11 (d, J = 8.1 Hz, 4 H, Ar), 7.21 ppm (d, J = 8.2 Hz, 4 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 15.4 (CH_3), 28.5 (CH_2), 56.7 (C-1 and C-4), 70.1 (C-7), 126.9 (ArCH), 127.6 (ArCH), 135.2 (ArC), 142.47 (C-5 and C-6), 142.51 (ArC attached to Et), 147.7 ppm (C-2 and C-3). $C_{23}H_{24}$ (300.44): calcd. C 91.95, H 8.05; found C 91.70, H 8.19.

2,3-Bis[4-(dimethylamino)phenyl]bicyclo[2.2.1]hepta-2,5-diene (9c): This was prepared following the above general procedure (A) with 2,3-dibromonorbornadiene **2** (73.2 mg, 0.293 mmol) and [4-(dimethylamino)phenyl]boronic acid **8c** (100.5 mg, 0.661 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 7.5:92.5, 3:17) to provide **9c** (46.6 mg, 0.141 mmol, 48%) as a clear yellow oil. R_f 0.36 (EtOAc:hexanes = 3:17). IR (film): $\tilde{\nu}$ = 3039, 2979, 2861, 2800, 1884, 1608, 1522, 1444, 1352, 1298, 1224, 1195, 1061 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.02 (dm, J = 5.5 Hz, 1 H, H-7), 2.29 (dm, J = 5.8 Hz, 1 H, H-7′), 2.99 (s, 12 H, 4 × CH_3), 3.84 (m, 2 H, H-1 and H-4), 6.66 (dm, J = 8.8 Hz, 4 H, Ar), 7.23 (m, 2 H, H-5 and H-6), 7.25 ppm (dm, J = 8.8 Hz, 4 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 40.6 (CH_3), 56.3 (C-1 and C-4), 69.4 (C-7), 112.2 (ArCH), 126.7(ArC attached to N), 127.8 (ArCH), 142.4 (C-5 and C-6), 145.1 (Ar-C), 149.0 ppm (C-2 and C-3). $C_{23}H_{26}N_2$ (330.47): calcd. C 83.59, H 7.93; found C 83.70, H 7.88.

2,3-Bis(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (9d): This was prepared following the above general procedure (A) with 2,3-dibromonorbornadiene **2** (75.9 mg, 0.304 mmol) and 4-methoxyphenylboronic acid **8d** (102.5 mg, 0.675 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 5:95, 1:9) to provide **9d** (85.5 mg, 0.281 mmol, 92%) as a clear yellow oil. R_f 0.32 (EtOAc:hexanes = 1:9). IR (film): $\tilde{\nu}$ = 3063, 2976, 2933, 2835, 1705, 1603, 1513, 1463, 1248, 1174, 1037, 831, 731, 714, 610 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.07 (d, J = 6.0 Hz, 1 H, H-7), 2.33 (d, J = 6.0 Hz, 1 H, H-7′), 3.81 (s, 6 H, 2 × CH_3), 3.85 (m, 2 H, H-1 and H-4), 6.81 (dt, J = 2.8 and 8.8 Hz, 4 H, Ar), 6.98 (t, J = 1.7 Hz, 2 H, H-5 and H-6), 7.21 ppm (dt, J = 2.8 and 8.8 Hz, 4 H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 55.1(CH_3), 56.6 (C-1 and C-4), 69.9 (C-7), 113.6 (ArCH), 128.1 (ArCH), 130.5 (ArC), 142.4 (C-5 and C-6), 146.4 (C-2 and C-3), 158.2 ppm (ArC attached to OMe). HRMS for $C_{21}H_{20}O_2$: calcd. 304.1463; found 304.1451 [M]$^+$.

2,3-Bis(3-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (9e): This was prepared following the above general procedure (A) with 2,3-dibromonorbornadiene **2** (75.9 mg, 0.304 mmol) and 3-methoxyphenylboronic acid **8e** (102.5 mg, 0.675 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 5:95, 1:9) to provide **9e** (85.5 mg, 0.281 mmol, 92%) as a clear yellow oil. R_f 0.39 (EtOAc:hexanes = 1:9). IR (film): $\tilde{\nu}$ = 3064, 2980, 2936, 2865, 2833, 1732, 1682, 1598, 1464, 1263, 1213, 1049, 876, 785, 695 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.10 (d, J = 6.1 Hz, 1 H, H-7), 2.38 (d, J = 6.1 Hz, 1 H, H-7′), 3.70 (s, 6 H, 2 × CH_3), 3.91 (m, 2 H, H-1 and H-4), 6.75 (dd, J = 7.8 and 2.0 Hz, 2 H, Ar), 6.77 (m, 2 H, Ar), 6.82 (d, J = 7.7 Hz, 2 H, Ar), 7.01 (m, 2 H, C-5 and C-6), 7.19 ppm (t, J = 7.9 Hz, 2 H). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 55.0 (CH_3), 56.7 (C-1 and C-4), 70.3 (C-7), 112.2 (ArCH), 112.5 (ArCH), 119.5 (ArCH), 129.1 (ArCH), 139.0 (ArC), 142.5 (C-5 and C-6), 148.8 (C-2 and C-3), 159.3 ppm (ArC attached to OMe). HRMS for $C_{21}H_{20}O_2$: calcd. 304.1463; found 304.1671 [M]$^+$.

2,3-Bis(2-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (9f): This was prepared following the above general procedure (A) with 2,3-dibromonorbornadiene **2** (73.0 mg, 0.292 mmol) and 2-methoxyphenylboronic acid **8f** (98.3 mg, 0.647 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 5:95, 1:9) to provide **9f** (54.2 mg, 0.178 mmol, 61%) as a white solid.

M.p. 74–76 °C. R_f 0.36 (EtOAc:hexanes = 1:9). IR (film): $\tilde{\nu}$ = 3066, 2995, 2958, 2933, 2863, 2834, 1594, 1558, 1494, 1434, 1297, 1242, 1160, 1033 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.06 (d, J = 5.9 Hz, 1 H, H-7), 2.40 (d, J = 5.9 Hz, 1 H, H-7′), 3.71 (s, 6 H, 2 × CH_3), 3.90 (s, 2 H, H-1 and H-4), 6.72 (m, 2 H, H-5 and H-6), 6.82 (m, 4 H, Ar), 6.95 (s, 2 H, Ar), 7.12 ppm (m, 2 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 55.3 (CH_3), 55.9 (C-1 and C-4), 70.2 (C-7), 110.9 (ArCH), 120.2 (ArCH), 127.5 (ArCH), 127.7 (ArC), 129.0 (ArCH), 143.0 (C-5 and C-6), 148.2 (C-2 and C-3), 156.9 ppm (ArC attached to OMe). $C_{21}H_{20}O_2$ (304.39): calcd. C 82.86, H 6.62; found C 82.59, H 6.80.

2,3-Bis(4-acetylphenyl)bicyclo[2.2.1]hepta-2,5-diene (9g): This was prepared following the above general procedure (A) with 2,3-dibromonorbornadiene **2** (75.8 mg, 0.303 mmol) and 4-acetylphenylboronic acid **8** (117.4 mg, 0.716 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 1:9, 2:8) to provide **9g** (21.2 mg, 0.0646 mmol, 21%) as a yellow solid. M.p. 83–85 °C. R_f 0.23 (EtOAc:hexanes = 2:8). IR (film): $\tilde{\nu}$ = 3062, 2977, 2869, 1682, 1600, 1557, 1405, 1359, 1266, 1180, 1014, 958, 738, 612 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.14 (d, J = 6.3 Hz, 1 H, H-7), 2.40 (d, J = 6.4 Hz, 1 H, H-7′), 2.57 (s, 6 H, 2 × CH_3), 3.94 (m, 2 H, H-1 and H-4), 6.99 (m, 2 H, H-5 and H-6), 7.27 (d, J = 8.5 Hz, 4 H, Ar), 7.83 ppm (d, J = 8.4 Hz, 4 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 26.5 (CH_3), 56.9 (C-1 and C-4), 70.6 (C-7), 127.1 (ArCH), 128.5 (ArCH), 135.5 (ArC), 142.1 (ArC attached to C=O), 142.5 (C-5 and C-6), 150.6 (C-2 and C-3), 197.5 ppm (C=O). $C_{23}H_{20}O_2$ (328.41): calcd. C 84.12, H 6.14; found C 84.50, H 6.02.

2,3-Bis(4-chlorophenyl)bicyclo[2.2.1]hepta-2,5-diene (9h): This was prepared following the above general procedure (A) with 2,3-dibromonorbornadiene **2** (78.9 mg, 0.316 mmol) and 4-chlorophenylboronic acid **8h** (115.9 mg, 0.741 mmol). The crude product was purified by column chromatography (hexanes) to provide **9h** (87.1 mg, 0.278 mmol, 88%) as a clear yellow oil. R_f 0.33 (hexanes). IR (film): $\tilde{\nu}$ = 3067, 2982, 2938, 2867, 1493, 1484, 1295, 1093, 1012, 886, 828, 788, 737 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.08 (dt, J = 1.5 and 6.2 Hz, 1 H, H-7), 2.33 (dt, J = 1.4 and 6.2 Hz, 1 H, H-7′), 3.84 (t, J = 1.8 Hz, 2 H, H-1 and H-4), 6.96 (t, J = 1.8 Hz, 2 H, H-5 and H-6), 7.12 (dm, J = 8.7 Hz, 4 H, Ar), 7.21 ppm (dm, J = 8.7 Hz, 4 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 56.7 (C-1 and C-4), 70.4 (C-7), 128.2 (ArCH), 128.5 (ArCH), 132.5 (ArC attached to Cl), 135.8 (ArC), 142.4 (C-5 and C-6), 148.3 ppm (C-2 and C-3). HRMS for $C_{19}H_{14}Cl_2$: calcd. 312.0473; found 312.0479 [M]$^+$.

2,3-Bis(3-chlorophenyl)bicyclo[2.2.1]hepta-2,5-diene (9i): This was prepared following the above general procedure (A) with 2,3-dibromonorbornadiene **2** (75.9 mg, 0.304 mmol) and 3-chlorophenylboronic acid **8i** (102.6 mg, 0.656 mmol). The crude product was purified by column chromatography (hexanes) to provide **9i** (83.9 mg, 0.268 mmol, 88%) as a clear colorless oil. R_f 0.32 (hexanes). IR (film): $\tilde{\nu}$ = 3066, 2981, 2937, 2867, 1687, 1592, 2561, 1478, 1421, 1297, 1264, 1079, 934, 783, 713 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.09 (dt, J = 1.5 and 6.3 Hz, 1 H, H-7), 2.39 (dt, J = 1.6 and 6.3 Hz, 1 H, H-7′), 3.86 (t, J = 1.9 Hz, 2 H, H-1 and H-4), 6.97 (t, J = 1.9 Hz, 2 H, H-5 and H-6), 7.04 (m, 2 H, Ar), 7.17 ppm (m, 6 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 56.8 (C-1 and C-4), 70.6 (C-7), 125.2 (ArCH), 126.8 (ArCH), 126.9 (ArCH), 129.6 (ArCH), 134.2 (ArC attached to Cl), 139.0 (ArC), 142.5 (C-5 and C-6), 148.9 ppm (C-2 and C-3). HRMS for $C_{19}H_{14}Cl_2$: calcd. 312.0473; found 312.0484 [M]$^+$.

2,3-Bis(2-chlorophenyl)bicyclo[2.2.1]hepta-2,5-diene (9j): This was prepared following the above general procedure (A) with 2,3-dibromonorbornadiene **2** (78.2 mg, 0.313 mmol) and 2-chlorophenylboronic acid **8j** (112.3 mg, 0.718 mmol). The crude product was purified by column chromatography (hexanes) to provide **9j** (82.4 mg, 0.263 mmol, 84%) as a white solid. M.p. 79–80 °C. R_f 0.27 (hexanes). IR (film): $\tilde{\nu}$ = 3124, 2973, 2867, 1951, 1802, 1631, 1461, 1435, 1296, 1231, 1038, 942, 813, 735, 649 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.18 (d, J = 6.0 Hz, 1 H, H-7), 2.60 (d, J = 6.0 Hz, 1 H, H-7′), 3.95 (m, 2 H, H-1 and H-4), 6.79 (dd, J = 1.4 and 7.6 Hz, 2 H, H-5 and H-6), 7.01 (m, 4 H, Ar), 7.10 (td, J = 1.6 and 7.6 Hz, 2 H, Ar), 7.34 ppm (d, J = 8.0 Hz, 2 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 56.1 (C-1 and C-4), 71.7 (C-7), 126.4 (ArCH), 128.0 (ArCH), 129.6 (ArCH), 130.0 (ArCH), 133.2 (ArC attached to Cl), 136.9 (ArC), 142.8 (C-5 and C-6), 151.4 ppm (C-2 and C-3). HRMS for $C_{19}H_{14}Cl_2$: 312.0473; found 312.0467 [M]$^+$.

General Procedure (B) for Suzuki Couplings Between 3-Substituted 2-Bromonorbornadienes 10a–10d and 4-Methoxyphenylboronic Acid 8d

Synthesis of Monoaryl-Substituted Norbornadienes: In an inert atmosphere (Ar) glovebox, the 3-substituted 2-bromonorbornadiene **10a**–**10d** (0.20–0.54 mmol) was added to an oven-dried vial along with [Pd_2(dba)$_3$] (0.5 mol%, 0.001–0.003 mmol), (4-methoxyphenyl) boronic acid **8d** (0.22–0.59 mmol) and caesium fluoride (0.66–1.78 mmol). The mixture was dissolved in THF (0.2–0.4 mL) and stirred for 1 min. The phosphane tBu$_3$P (1.4 mol% 0.0028–0.0076 mmol) was then added and the reaction stirred at room temperature inside the glovebox for 24 h. The solvent was removed by rotary evaporation and the crude product purified by column chromatography.

2-(4-Methoxyphenyl)-3-methylbicyclo[2.2.1]hepta-2,5-diene (11a): This was prepared following the above general procedure (B) with 2-bromo-3-methylbicyclo[2.2.1]hepta-2,5-diene **10a** (100.1 mg, 0.541 mmol) and (4-methoxyphenyl)boronic acid **8d** (90.4 mg, 0.595 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 5:95) to provide **11a** (92.5 mg, 0.436 mmol, 81%) as a clear yellow oil. R_f 0.43 (EtOAc:hexanes = 5:95). IR (film): $\tilde{\nu}$ = 3061, 2967, 2906, 2836, 1886, 1704, 1606, 1511, 1463, 1370, 1247, 1174, 1108, 1037 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.99 (dt, J = 1.4 and 5.9 Hz, 1 H, H-7), 2.03 (s, 3 H, CH_3 attached to C-3), 2.13 (dt, J = 1.4 and 5.9 Hz, 1 H, H-7′), 3.43 (m, 1 H, H-4), 3.76 (m, 1 H, H-1), 3.83 (s, 3 H, CH_3 attached to O), 6.88 (m, 1 H, H-6), 6.93 (dm, J = 8.8 Hz, 2 H, Ar), 6.97 (m, 1 H, H-5), 7.25 ppm (dm, J = 8.7 Hz, 2 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 16.1 (CH_3 attached to C-3), 54.8 (CH_3 attached to O), 55.2 (C-4), 57.1 (C-1), 70.1 (C-7), 113.6 (ArCH), 127.1 (ArCH), 130.4 (ArC), 141.9 (C-5), 142.5 (C-6), 144.6 (C-3), 145.2 (C-2), 157.7 ppm (ArC attached to OMe). HRMS for $C_{15}H_{16}O$: calcd. 212.1201; found 212.1212 [M]$^+$.

2-*tert*-Butyldimethylsilyl-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (11b): This was prepared following the above general procedure (B) with (3-bromobicyclo[2.2.1]hepta-2,5-dien-2-yl)-*tert*-butyl-dimethylsilane **10b** (56.2 mg, 0.197 mmol) and 4-methoxyphenylboronic acid **8d** (32.9 mg, 0.217 mmol). The crude product was purified by column chromatography (hexanes) to provide **11b** (52.7 mg, 0.169 mmol, 86%) as a clear colorless oil. R_f 0.13 (hexanes). IR (film): $\tilde{\nu}$ = 3064, 2954, 2929, 2855, 1609, 1504, 1463, 1301, 1247, 1174, 1040, 832, 770, 674 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = –0.16 (s, 3 H, CH_3 attached to Si), –0.11 (s, 3 H, CH_3 attached to Si), 0.95 (s, 9 H, tBu attached to Si), 1.88 (dm, J = 6.1 Hz, 1 H, H-7), 2.06 (dm, J = 6.0 Hz, 1 H, H-7′), 3.65 (m, 1 H, H-1), 3.81 (s, 3 H, CH_3 attached to O), 3.88 (m, 1 H, H-4), 6.77 (m, 1 H, H-6), 6.83 (dm, J = 8.6 Hz, 2 H, Ar), 6.87 (m, 1 H, H-5), 7.14 ppm (dm, J = 8.5 Hz, 2 H, Ar). ^{13}C NMR (APT, $CDCl_3$,

100 MHz): δ = –5.5 (CH_3 attached to Si), –4.8 (CH_3 attached to Si), 18.3 (C of *t*Bu attached to Si), 27.3 (CH_3 of *t*Bu), 55.2 (CH_3 attached to O), 57.0 (C-4), 59.1 (C-1), 71.4 (C-7), 113.0 (ArCH), 127.8 (ArCH), 132.7 (ArC), 141.4 (C-2), 143.5 (C-3), 143.7 (C-5), 158.6 (ArC attached to OMe), 168.3 ppm (C-6). $C_{20}H_{28}OSi$ (312.53): calcd. C 76.86, H 9.03; found C 76.62, H 9.10.

2-Chloro-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (11c): This was prepared following the above general procedure (B) with 2-bromo-3-chlorobicyclo[2.2.1]hepta-2,5-diene **10c** (105.2 mg, 0.512 mmol) and 4-methoxyphenylboronic acid **8d** (72.2 mg, 0.475 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 1:49) to provide **11c** (102.6 mg, 0.441 mmol, 86%) as a white solid. M.p. 56–58 °C. R_f 0.41 (EtOAc:hexanes = 5:95). IR (film): $\tilde{\nu}$ = 3122, 3067, 2938, 2907, 2836, 2360, 1602, 1557, 1508, 1291, 1249, 1180, 1095, 1036 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.12 (dm, J = 6.2 Hz, 1 H, H-7), 2.33 (dm, J = 6.2 Hz, 1 H, H-7′), 3.55 (m, 1 H, H-1), 3.83 (s, 3 H, CH_3), 3.93 (m, 1 H, H-4), 6.93 (m, 4 H, H-5, H-6, and Ar), 7.59 ppm (m, 2 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 53.9 (C-1), 55.3 (CH_3), 58.3 (C-4), 69.6 (C-7), 113.7 (ArCH), 127.2 (ArC), 127.3 (ArCH), 138.8 (C-2), 141.5 (C-6), 141.8 (C-5), 143.7 (C-3), 158.6 ppm (ArC attached to OMe). HRMS for $C_{14}H_{13}ClO$: calcd. 232.0655; found 232.0660 [M^+].

Ethyl 3-(4-Methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (11d): This was prepared following the above general procedure (B) with 3-bromobicyclo[2.2.1]hepta-2,5-diene-2-carboxylic acid ethyl ester **10d** (100.5 mg, 0.413 mmol) and 4-methoxyphenylboronic acid **8d** (69.7 mg, 0.459 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 5:95) to provide **11d** (104.4 mg, 0.3862 mmol, 93%) as a clear yellow oil. R_f 0.45 (EtOAc:hexanes = 1:4). IR (film): $\tilde{\nu}$ = 3058, 2982, 2939, 2906, 2838, 1697, 1604, 1509, 1444, 1370, 1295, 1253, 1175, 1035 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.28 (t, J = 7.1 Hz, 3 H, CH_3 of COOEt), 2.06 (dt, J = 1.5 and 6.6 Hz, 1 H, H-7), 2.24 (dt, J = 1.5 and 6.6 Hz, 1 H, H-7′), 3.85 (s, 3 H, CH_3 of OMe), 3.87 (m, 1 H, H-1), 4.07 (m, 1 H, H-4), 4.18 (m, 2 H, CH_2 of COOEt), 6.91 (dm, J = 8.9 Hz, 3 H, H-6), 7.13 (m, 1 H, H-5), 7.60 ppm (dm, J = 8.9 Hz, 2 H,). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 14.2 (CH_3 of COOEt), 52.9 (C-4), 55.3 (CH_3 of OMe), 58.3 (C-1), 60.0 (CH_2 of COOEt), 70.0 (C-7), 113.0 (ArCH), 128.0 (ArC), 129.7 (ArCH), 137.1 (C-2), 140.4 (C-5), 143.7 (C-6), 159.9 (ArC attached to OMe), 165.7 (C-3), 166.3 ppm (C=O). $C_{17}H_{18}O_3$ (270.33): calcd. C 75.53, H 6.71; found C 75.77, H 6.60.

General Procedure (C) for Suzuki Couplings Between 2-Chloro-3-(4-methoxy-phenyl)norboronadiene 11c and the Arylboronic Acids 8a–8j

Synthesis of Unsymmetrical 2,3-Diarylnorbornadienes: In an inert atmosphere (Ar) glovebox, 2-chloro-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene **11c** (0.21 mmol) was added to an oven-dried vial along with [$Pd_2(dba)_3$] (0.5 mol%, 0.001 mmol), arylboronic acid (0.23 mmol) and caesium fluoride (0.69 mmol). The mixture was dissolved in THF (0.4 mL) and stirred for 1 min. The phosphane *t*Bu_3P (1.4 mol% 0.003 mmol) was then added and the reaction was stirred at 65 °C under argon for 24 h. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography.

2-(4-Methoxyphenyl)-3-phenylbicyclo[2.2.1]hepta-2,5-diene (12a): This was prepared following the above general procedure (C) with 2-chloro-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene **11c** (47.1 mg, 0.202 mmol) and phenylboronic acid **8a** (29.4 mg, 0.241 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 1:49) to provide **12a** (47.0 mg, 0.171 mmol, 85%) as a clear colorless oil. R_f 0.34 (EtOAc:hexanes = 5:95). IR (film): $\tilde{\nu}$ = 3119, 3062, 2979, 2835, 1950, 1606, 1509, 1442, 1248, 1039, 833, 697, 610, 439 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.10 (dm, J = 6.1 Hz, 1 H, H-7), 2.37 (dm, J = 6.1 Hz, 1 H, H-7′), 3.82 (s, 3 H, CH_3 attached to O), 3.90 (s, 2 H, H-1 and H-9), 6.82 (m, 2 H, Ar), 7.01 (m, 2 H, H-5 and H-6), 7.21 (m, 3 H, Ar), 7.28 ppm (m, 4 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 55.2 (CH_3 attached to O), 56.7 (C-1 and C-4), 70.1 (C-7), 113.6 (ArCH), 126.4 (ArCH), 126.9 (ArCH), 128.1 (ArCH), 128.2 (ArCH), 130.2 (ArC), 138.0 (ArC), 142.4 (C-6), 142.6 (C-5), 146.8 (C-2), 148.2 (C-3), 158.3 ppm (ArC attached to OMe). HRMS for $C_{20}H_{18}O$: calcd. 274.1358; found 274.1366 [M^+].

2-(4-Ethylphenyl)-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (12b): This was prepared following the above general procedure (C) with 2-chloro-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene **11c** (49.3 mg, 0.212 mmol) and (4-ethylphenyl)boronic acid **8b** (45.4 mg, 0.3027 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 1:49) to provide **12b** (51.4 mg, 0.170 mmol, 80%) as a clear yellow oil. R_f 0.37 (EtOAc:hexanes = 5:95). IR (film): $\tilde{\nu}$ = 3120, 3064, 2964, 2868, 1604, 1557, 1514, 1452, 1413, 1374, 1248, 1175, 1108, 1039 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.25 (t, J = 7.6 Hz, 3 H, CH_3 of Et), 2.07 (dt, J = 1.6 and 6.1 Hz, 1 H, H-7), 2.34 (dt, J = 1.6 and 6.1 Hz, 1 H, H-7′), 2.64 (q, J = 7.6 Hz, 2 H, CH_2 of Et), 3.81 (s, 3 H, CH_3 of OMe), 3.87 (m, 2 H, H-1 and H-4), 6.81 (m, 2 H, Ar), 6.98 (m, 2 H, H-5 and H-6), 7.10 (m, 2 H, Ar), 7.21 ppm (m, 4 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 15.4 (CH_3 of Et), 28.5 (CH_2 of Et), 55.2 (CH_3 of OMe), 56.6 (C-1), 56.7 (C-4), 70.0 (C-7), 113.6 (ArCH), 126.8 (ArCH), 127.7 (ArCH), 128.1 (ArCH), 130.4 (ArC), 135.2 (ArC), 142.3 (C-6), 142.4 (ArC attached to Et), 142.5 (C-5), 146.8 (C-2), 147.3 (C-3), 158.2 ppm (ArC attached to OMe). HRMS for $C_{22}H_{22}O$: calcd. 302.1671; found 302.1680 [M^+].

2-[4-(Dimethylamino)phenyl]-3-(4-methoxyphenyl)bicyclo[2.2.1]-hepta-2,5-diene (12c): This was prepared following the above general procedure (C) with 2-chloro-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene **11c** (47.1 mg, 0.202 mmol) and [4-(dimethylamino)phenyl]boronic acid **8c** (46.7 mg, 0.283 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 1:24) to provide **12c** (48.0 mg, 0.151 mmol, 75%) as a clear yellow oil. R_f 0.33 (EtOAc:hexanes = 1:9). IR (film): $\tilde{\nu}$ = 3062, 2932, 2801, 1886, 1727, 1607, 1505, 1353, 1039, 947, 822, 713, 610, 578 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.05 (dm, J = 6.0 Hz, 1 H, H-7), 2.32 (dm, J = 6.0 Hz, 1 H, H-7′), 2.97 (s, 6 H, 2 × CH_3 attached to N), 3.83 (m, 4 H, H-4 and CH_3 attached to O), 3.88 (m, 1 H, H-1), 6.66 (dm, J = 8.9 Hz, 2 H, Ar), 6.82 (dm, J = 8.8 Hz, 2 H, Ar), 6.97 (m, 2 H, H-5 and H-6), 7.20 (dm, J = 8.8 Hz, 2 H, Ar), 7.25 ppm (dm, J = 8.8 Hz, 2 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 40.5 (CH_3 attached to N), 55.2 (CH_3 attached to O), 56.3 (C-4), 56.5 (C-1), 69.6 (C-7), 112.1 (ArCH), 113.5 (ArCH), 126.1 (ArC attached to NMe_2), 127.8 (ArCH), 128.1 (ArCH), 131.0 (ArC), 142.4 (C-6), 144.6 (ArC), 146.8 (C-2), 148.4 (C-5), 149.1 (C-3), 158.0 ppm (ArC attached to OMe). HRMS for $C_{22}H_{23}NO$: calcd. 317.1780; found 317.1786 [M^+].

2-(3-Methoxyphenyl)-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (12d): This was prepared following the above general procedure (C) with 2-chloro-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene **11c** (54.8 mg, 0.236 mmol) and 3-methoxyphenylboronic acid **8e** (53.9 mg, 0.355 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 1:24) to provide **12d** (63.0 mg, 0.207 mmol, 88%) as a clear yellow oil. R_f 0.32 (EtOAc:hexanes = 1:9). IR (film): $\tilde{\nu}$ = 3118, 3064, 2935, 2834, 1602,

1575, 1509, 1464, 1428, 1277, 1038, 719, 682 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.10 (dm, J = 6.1 Hz, 1 H, H-7), 2.37 (dm, J = 6.1 Hz, 1 H, H-7′), 3.72 (s, 3 H, CH_3 of *m*-OMe), 3.82 (s, 3 H, CH_3 of *p*-OMe), 3.90 (m, 2 H, H-1 and H-2), 6.76 (m, 1 H, Ar), 6.83 (m, 3 H, Ar), 6.88 (m, 1 H, Ar), 6.99 (m, 2 H, H-5 and H-6), 7.29 ppm (m, 3 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 55.0 (CH_3 attached to *m*-OMe), 55.2 (CH_3 attached to *p*-OMe), 56.6 (C-4), 56.7 (C-1), 70.1 (C-7), 112.1 (ArCH), 112.2 (ArCH), 113.6 (ArCH), 119.4 (ArCH), 128.2 (ArCH), 129.2 (ArCH), 130.1 (ArC), 139.3 (ArC), 142.3 (C-5), 142.6 (C-6), 146.7 (C-3), 148.5 (C-2), 158.4 (ArC attached to *p*-OMe), 159.4 ppm (ArC attached to *m*-OMe). HRMS for $C_{21}H_{20}O_2$: calcd. 304.1463; found 304.1470 $[M]^+$.

2-(2-Methoxyphenyl)-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (12e): This was prepared following the above general procedure (C) using 2-chloro-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene **11c** (48.1 mg, 0.207 mmol) and 2-methoxyphenylboronic acid **8f** (34.6 mg, 0.228 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 1:24) to provide **12e** (49.9 mg, 0.1639 mmol, 79%) as a clear colorless oil. R_f 0.41 (EtOAc:hexanes = 1:9). IR (film): $\tilde{\nu}$ = 3119, 3064, 2934, 2055, 1890, 1594, 1557, 1510, 1435, 1245, 1174, 1087, 1037, 822 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.09 (dm, J = 6.0 Hz, 1 H, H-7), 2.38 (dm, J = 6.0 Hz, 1 H, H-7′), 3.79 (s, 3 H, CH_3 of *o*-OMe), 3.82 (s, 3 H, CH_3 of *p*-OMe), 3.85 (m, 1 H, H-4), 3.97 (m, 1 H, H-1), 6.77 (dm, J = 8.9 Hz, 2 H, Ar), 6.85 (td, J = 1.0 and 7.4 Hz, 1 H, Ar), 6.97 (m, 4 H, H-5, H-6 and Ar), 7.17 (dm, J = 8.9 Hz, 2 H, Ar), 7.25 ppm (m, 1 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 54.6 (C-1), 55.1 (CH_3 of *p*-OMe), 55.5 (CH_3 of *o*-OMe), 57.2 (C-4), 69.8 (C-7), 111.1 (ArCH), 113.3 (ArCH), 120.6 (ArCH), 127.7 (ArCH), 127.9 (ArCH), 128.1 (ArC), 129.3 (ArCH), 129.8 (ArC), 141.7 (C-5), 143.4 (C-6), 145.4 (C-3), 148.3 (C-2), 157.4 (ArC attached to *o*-OMe), 158.0 ppm (ArC attached to *p*-OMe). HRMS for $C_{21}H_{20}O_2$: calcd. 304.1463; found 304.1473 $[M]^+$. $C_{21}H_{20}O_2$ (304.15): calcd. C 82.86, H 6.62; found C 80.60, H 6.88.

2-(4-Chlorophenyl)-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (12f): This was prepared following the above general procedure (C) with 2-chloro-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene **11c** (49.1 mg, 0.211 mmol) and 4-chlorophenylboronic acid **8h** (49.3 mg, 0.315 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 1:24) to provide **12f** (58.4 mg, 0.189 mmol, 90%) as a clear yellow oil. R_f 0.27 (EtOAc:hexanes = 1:9). IR (film): $\tilde{\nu}$ = 3119, 3.64, 2979, 2835, 1604, 1509, 1487, 1335, 1248, 1039, 1012, 830, 610 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.09 (m, 1 H, H-7), 2.35 (m, 1 H, H-7′), 3.84 (m, 4 H, H-4 and CH_3), 3.88 (m, 1 H, H-1), 6.83 (m, 2 H, Ar), 7.00 (m, 2 H, H-5 and H-6), 7.21 ppm (m, 6 H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 55.2 (CH_3), 56.5 (C-4), 56.8 (C-1), 70.1 (C-7), 113.7 (ArCH), 128.1 (ArCH), 128.2 (ArCH), 128.4 (ArCH), 129.8 (ArC), 131.9 (ArC attached to Cl), 136.4 (ArC), 142.4 (C-5 and C-6), 145.7 (C-3), 149.1 (C-2), 158.5 ppm (ArC attached to OMe). HRMS for $C_{20}H_{17}ClO$: calcd. 308.0968; found 308.0960 $[M]^+$.

2-(3-Chlorophenyl)-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (12g): This was prepared following the above general procedure (C) with 2-chloro-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene **11c** (46.0 mg, 0.198 mmol) and 3-chlorophenylboronic acid **8i** (46.3 mg, 0.296 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 1:24) to provide **12g** (51.4 mg, 0.166 mmol, 84%) as a clear yellow oil. R_f 0.33 (EtOAc:hexanes = 1:9). IR (film): $\tilde{\nu}$ = 3120, 3063, 2979, 2934, 2835, 1605, 1558, 1509, 1248, 1175, 1037, 834, 806, 697 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.07 (dm, J = 6.1 Hz, 1 H, H-7), 2,32 (dm, J = 6.1 Hz, 1 H, H-7′), 3.80 (s, 3 H, CH_3), 3.83 (m, 1 H, H-4), 3.86 (m, 1 H, H-1), 6.80 (dm, J = 8.8 Hz, 2 H, Ar), 6.97 (m, 2 H, H-5 and H-6), 7.12 (m, 5 H, Ar), 7.22 ppm (m, 1 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 55.2 (CH_3), 56.5 (C-4), 56.9 (C-1), 70.2 (C-7), 113.8 (ArCH), 125.2 (ArCH), 126.4 (ArCH), 126.8 (ArCH), 128.2 (ArCH), 129.4 (ArCH), 129.6 (ArC), 134.1 (Ar attached to Cl), 139.9 (ArC), 142.4 (C-6), 142.5 (C-5), 145.5 (C-2), 149.9 (C-3), 158.6 ppm (ArC attached to OMe). HRMS for $C_{20}H_{17}ClO$: calcd. 308.0968; found 308.0959 $[M]^+$.

2-(2-Chlorophenyl)-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene (12h): This was prepared following the above general procedure (C) with 2-chloro-3-(4-methoxyphenyl)bicyclo[2.2.1]hepta-2,5-diene **11c** (44.8 mg, 0.193 mmol) and 2-chlorophenylboronic acid **8j** (44.1 mg, 0.282 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0:1, 1:24) to provide **12h** (50.6 mg, 0.164 mmol, 85%) as a clear colorless oil. R_f 0.37 (EtOAc:hexanes = 1:9). IR (film): $\tilde{\nu}$ = 3120, 3063, 2981, 2935, 2835, 1606, 1510, 1465, 1291, 1249, 1177, 1036, 832, 647 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.11 (dm, J = 6.1 Hz, 1 H, H-7), 2.46 (dm, J = 6.0 Hz, 1 H, H-7′), 3.76 (s, 3 H, CH_3), 3.82 (m, 1 H, H-4), 3.96 (m, 1 H, H-1), 6.73 (dm, J = 8.8 Hz, 2 H, Ar), 6.88 (m, 1 H, Ar), 6.97 (m, 2 H, H-5 and Ar), 7.06 (dm, J = 8.8 Hz, 2 H, H-6 and Ar), 7.11 (tm, J = 7.5 Hz, 1 H, Ar), 7.18 (tm, J = 7.8 Hz, 1 H, Ar), 7.44 ppm (m, 1 H, Ar). ^{13}C NMR (APT, $CDCl_3$, 100 MHz): δ = 54.7 (CH_3), 55.2 (C-4), 57.2 (C-1), 70.5 (C-7), 113.5 (ArCH), 126.8 (ArCH), 127.7 (ArCH), 128.0 (2 × ArCH), 129.0 (ArC), 129.7 (ArCH), 133.7 (ArC attached to Cl), 138.7 (ArC), 141.9 (C-5), 143.0 (C-6), 145.6 (C-3), 150.0 (C-2), 158.3 ppm (ArC attached to OMe). HRMS for $C_{20}H_{17}ClO$: calcd. 308.0968; found 308.975 $[M]^+$.

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[14] Norbornadienes **10a**–**10d** were synthesized by mono lithium-halide exchange of 2,3-dibromonorbornadiene **2** followed by trapping with the corresponding electrophiles (R = Me: MeI, R = TBS: TBSCl, R = COOEt: ethyl chloroformate, R = Cl: TsCl). See ref.[11] for details.

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