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Reactions of diarylvinylidenecyclopropanes with bromine at −100 °C in dichloromethane and ether. A drastic solvent effect

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Abstract—For diarylvinylidenecyclopropanes **1** having two aromatic groups at C-1 position and one methyl group at the C-2 position of cyclopropyl ring, the reaction with bromine at low temperature (−100 °C) produces the brominated indene derivatives **2** and conjugated triene derivatives **3** in high yields in dichloromethane and ether within 10 min, respectively. This drastic solvent effect has been discussed on the basis of previous investigation.
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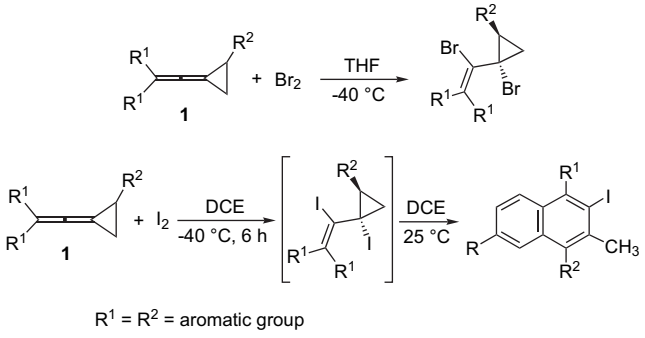
1. Introduction

Vinylidenecyclopropanes **1**, are a class of interesting organic compounds known. They have an allene moiety connected by a cyclopropyl ring and yet they are thermally stable and reactive substances. Thus far, thermal and photochemical skeletal conversions of vinylidenecyclopropanes **1** have attracted much attention from mechanistic, theoretical, spectroscopic, and synthetic viewpoints.[1,2] Recently, we have been investigating the Lewis acid- or Brønsted acid-catalyzed/mediated ring-opening reactions of **1**, and have found some novel reaction patterns of these substrates.[3,4] For example, we previously reported that the addition reactions of arylvinylidenecyclopropanes **1** with equimolar amount of bromine and iodine produce either the corresponding addition products at low temperature (−40 °C) in tetrahydrofuran (THF) or the corresponding iodinated naphthalene derivatives at room temperature (20 °C) in 1,2-dichloroethane (DCE) in moderate to good yields under mild conditions (Scheme 1).[5] In this paper, we wish to report that for arylvinylidenecyclopropanes **1** having two aromatic groups at C-1 position and one methyl group at the C-2 position of cyclopropyl ring, the reaction with bromine at low temperature (−100 °C) produces the brominated indene derivatives **2** and conjugated triene derivatives **3** in moderate to good yields depending on the employed solvents.



Scheme 1. Addition reaction of arylvinylidenecyclopropanes **1** with halogen at −40 °C in THF or at 20 °C in DCE.

2. Results and discussion

Initial examination was performed using diphenylvinylidenecyclopropane **1a** as substrate in dichloromethane at different temperatures (from room temperature to −100 °C) in the reaction with bromine in order to find out the optimal conditions. The results are summarized in Table 1. We found that the corresponding brominated indene derivative **2a** was produced in moderate yields under mild conditions along with some unidentified polymerized by-products at room temperature (20 °C) to 0 °C within 10 min (Table 1, entries 1 and 2). At lower temperatures such as −60 °C and −100 °C, **2a** was produced in 86% and 97% yields, respectively (Table 1, entries 3 and 4). These results suggest that low reaction temperature (−100 °C) facilitates the formation of the brominated indene derivative **2a** by suppressing polymerization of

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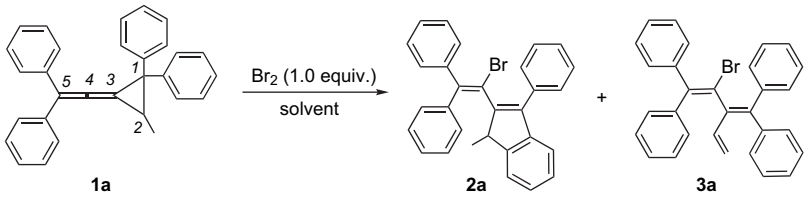
Table 1. Optimization of the reaction conditions of **1a** with Br_2 in different solvents at different temperatures



1a **2a** **3a**

Entry	Solvent	Temp/°C	Time/min	Yield[a]/%	
				2a	**3a**
1	CH_2Cl_2	rt	10	25	0
2	CH_2Cl_2	0	10	39	0
3	CH_2Cl_2	−60	10	86	0
4	CH_2Cl_2	−100	10	97	0
5	*n*-Pentane	−100	10	78	0
6	Et_2O	−100	10	Trace	89

[a] Isolated yields.

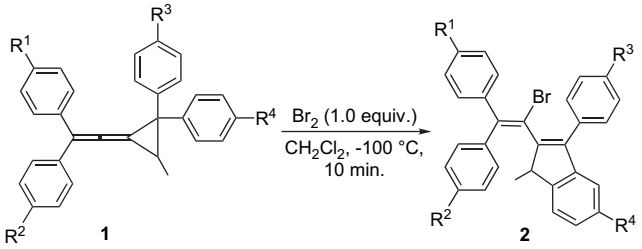
starting material **1a**. Since only a few solvents can be used at −100 °C, we utilized pentane as a nonpolar solvent and diethyl ether as an oxygen atom-containing solvent to examine this reaction under otherwise identical conditions. In pentane at −100 °C, we found that **2a** was obtained in 78% yield (Table 1, entry 5). However, in diethyl ether at −100 °C, we interestingly found that a brominated conjugated triene derivative **3a** was formed in 89% yield along with trace of **2a** (Table 1, entry 6).

Under these optimized conditions, we next examined the generality of this transformation using a variety of diarylvinylidenecyclopropanes **1**. The results are summarized in Table 2. We found that the corresponding brominated indene derivatives **2** were obtained in moderate to high yields within 10 min in spite of R^1 group in **1** bearing electron-rich, electron-neutral, and electron-poor substituents on the benzene ring (Table 2). Only when R^3 and R^4 groups in **1** bear a chloro substituent at 4-position of benzene ring, the corresponding brominated indene derivative **2d** was obtained in 66% yield along with 30% of starting materials (Table 2, entry 3). In other cases, the corresponding brominated indene derivatives **2** were obtained in pure form.

Using these optimized reaction conditions, we next also examined the reaction of a variety of diarylvinylidenecyclopropanes **1** with bromine in diethyl ether. The results are shown in Table 3. For **1** having electron-rich, electron-neutral, and electron-poor substituents on the benzene ring, the corresponding brominated conjugated triene derivatives **3** were obtained in good to high yields within 10 min (Table 3, entries 1–6). In all cases shown in Table 3, the corresponding brominated conjugated triene derivatives **3** were isolated in pure form.

Their structures were determined by spectroscopic and analytical data. In order to unambiguously confirm this drastic solvent difference on the reaction product, X-ray crystal diffraction of **2a** was carried out. The ORTEP drawing of **2a** is shown in Figure 1.[6] As can be seen from Figure 1, a π–π stacking interaction between two benzene rings can be identified.

Table 2. Reaction of **1** with Br_2 in CH_2Cl_2 at −100 °C

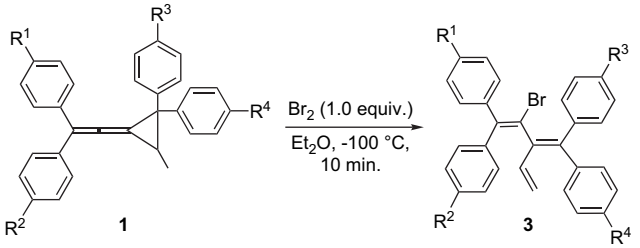


1 **2**

Entry	Substrate	$R^1/R^2/R^3/R^4$	Yield[a]/%
			2
1	**1b**	H/H/CH_3/CH_3	**2b**, 90
2	**1c**	CH_3/CH_3/H/H	**2c**, 92
3	**1d**	H/H/Cl/Cl	**2d**, 66[b]
4	**1e**	Cl/Cl/H/H	**2e**, 77
5	**1f**	H/H/F/F	**2f**, 70
6	**1g**	F/F/H/H	**2g**, 72

[a] Isolated yields.
[b] Containing 30% of starting materials.

Table 3. Reaction of **1** with Br_2 in Et_2O at −100 °C



1 **3**

Entry	Substrate	$R^1/R^2/R^3/R^4$	Yield[a]/%
			3
1	**1b**	H/H/CH_3/CH_3	**3b**, 99
2	**1c**	CH_3/CH_3/H/H	**3c**, 84
3	**1d**	H/H/Cl/Cl	**3d**, 76
4	**1e**	Cl/Cl/H/H	**3e**, 65
5	**1f**	H/H/F/F	**3f**, 78
6	**1g**	F/F/H/H	**3g**, 80

[a] Isolated yields.

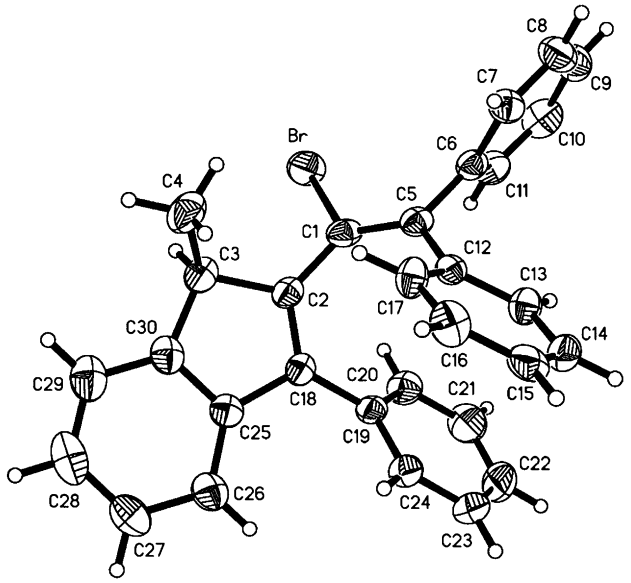


Figure 1. ORTEP drawing of **2a**.

A plausible mechanism for this interesting reaction of diarylvinylidenecyclopropanes **1** with bromine is shown in Scheme 2 using diphenylvinylidenecyclopropane **1a** as a model. The addition of bromine (Br_2) to a double bond of **1a** produces the corresponding cationic intermediate **A**,[5,7] which successively gives the corresponding ring-opened cationic intermediate **B**. Then, elimination of a proton takes place to give the corresponding brominated conjugated triene derivative **3a**. Intramolecular Friedel–Crafts reaction of intermediate **B** produces intermediate **C**, which gives the corresponding brominated indene derivative **2a** via deprotonation (Scheme 2). The π–π stacking interaction between two benzene rings presumably causes the intramolecular Friedel–Crafts reaction to take place exclusively to furnish intermediate **C**. In diethyl ether, an oxygen atom-containing solvent, the key intermediate **A** might be coordinated by oxygen atom to give an oxonium ion **A′**, which blocks out the intramolecular Friedel–Crafts reaction (Fig. 2).[8] Therefore, the proton elimination exclusively takes place to give the corresponding brominated conjugated triene derivative **3a** in ether solution. In addition, it should be emphasized here that the two aromatic groups at C-1 position and one methyl group at the C-2 position of cyclopropyl ring of **1** are essential for these reactions with bromine to proceed smoothly at low temperature, affording the corresponding brominated indene derivatives **2** and conjugated triene derivatives **3** in good yields. When **1** has only two aromatic groups at C-1 position of cyclopropyl ring, a disordered reaction was observed, presumably due to the fact that the corresponding key intermediate **B** is not as stable as that bearing a methyl group. Moreover, it should be noted that only at −100 °C, the key intermediate **B** can undergo intramolecular rearrangement and Friedel–Crafts reaction to produce **2a** and **3a** in high yields. At higher reaction temperature, a cationic polymerization can take place from key intermediate **B** and therefore, the desired products **2** or **3** are produced in low yields.[9]

The further transformation of **2a** is presented in Scheme 3. Using $Pd(PPh_3)_4$ as a catalyst in mixed solvent of toluene (2.0 mL), H_2O (0.1 mL), and EtOH (0.1 mL), the Suzuki

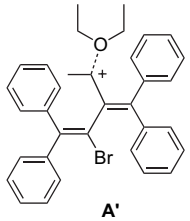
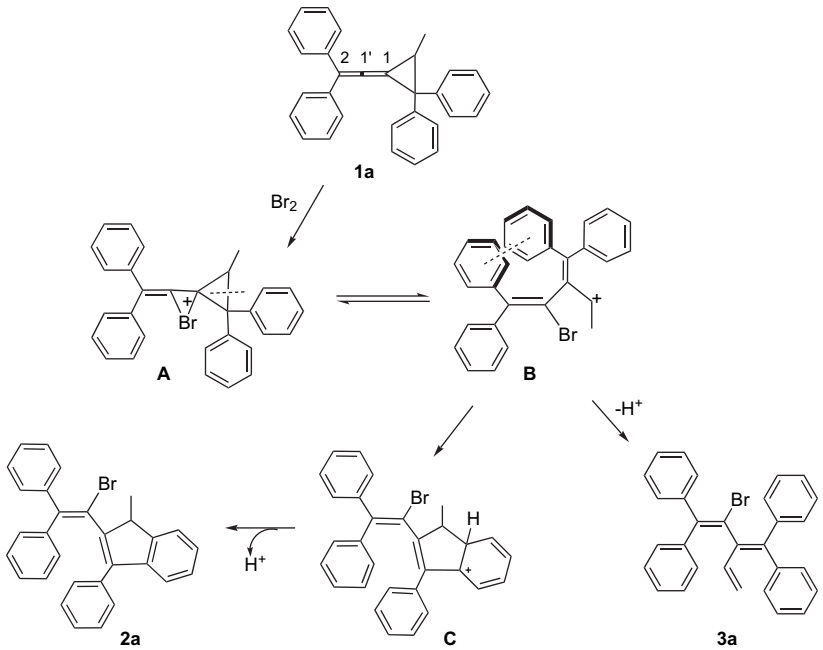
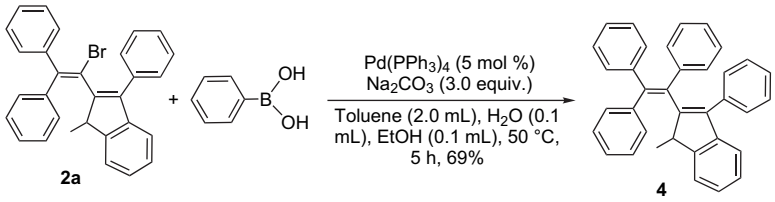


Figure 2. An oxygen atom coordinated oxonium ion.



Scheme 2. A possible reaction mechanism.



Scheme 3. Suzuki coupling reaction of **2a**.

coupling reaction of **2a** with phenylboronic acid was carried out at 50 °C in the presence of sodium carbonate to give the desired product **4** in 69% yield (Scheme 3).

3. Conclusion

We disclosed here a previously unknown transformation involving diarylvinylidenecyclopropanes **1** and bromine at −100 °C. In this transformation, the brominated indene derivatives **2** were obtained in good to high yields in dichloromethane. In addition, the brominated conjugated triene derivatives **3** could be formed in good to high yields in ether. A wide range of diarylvinylidenecyclopropanes **1** have been examined in this reaction. The plausible reaction mechanism of this drastic solvent effect has been discussed on the basis of previous investigations. This process provides a novel and efficient route to the synthesis of useful brominated indene and conjugated triene derivatives under mild conditions because those substances are remarkably useful compounds serving as building blocks for many functional materials.[10] Efforts are in progress to further elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

4. Experimental section

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by EI and MALDI methods, and HRMS was measured on Kratos Analytical Concept mass spectrometer (EI), Bruker FT mass spectrometer (ESI), and IonSpec 4.7 Tesla FTMS (MALDI). Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Yinlong GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure.

4.1.1. General procedure for the reactions of diarylvinylidenecyclopropane with bromine in CH_2Cl_2. In a dry 20 mL Schlenk tube, which was sealed and purged with argon through the septum inlet, diarylvinylidenecyclopropane **1** (0.1 mmol) was added, and then 2 mL of dried CH_2Cl_2 was added by a syringe. The mixture was cooled to −100 °C by a CO_2–Et_2O bath, and then added 1.0 mL of Br_2–CH_2Cl_2 (0.1 N) within 2 min by a syringe. The resulting mixture was stirred for another 10 min at this temperature and quenched by addition of 100 mg Na_2SO_3 solid. After filtration, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether as eluent to give the corresponding product.

4.1.1.1. 2-(1-Bromo-2,2-diphenylvinyl)-1-methyl-3-phenyl-1*H*-indene 2a. Following the general procedure described above, from **1a** (39 mg, 0.1 mmol), compound **2a** (46 mg, 97%) was obtained as a yellow solid. Mp: 146–148 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.69 (d, 3H, J=6.9 Hz, CH_3), 4.27 (q, 1H, J=6.9 Hz, CH), 6.44–7.47 (m, 20H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.1, 46.3, 120.8, 122.8, 125.9, 126.5, 126.6, 127.2, 127.4, 127.5, 128.0, 128.2, 128.5, 128.6, 129.1, 134.3, 140.7, 143.0, 143.8, 145.1, 145.9, 148.1. IR (CH_2Cl_2) ν 3057, 3026, 2962, 2868, 1598, 1492, 1443, 1349, 1074, 1030, 965, 774, 745, 697, 671, 628, 610, 592, 553 cm^{-1}. MS (%) *m/e* 466 (M^+, 22), 382 (87), 366 (35), 304 (92), 290 (100), 275 (15), 167 (64), 144 (23), 91 (64), 77 (73), 51 (74), 44 (35). Anal. Calcd for $C_{30}H_{23}Br$, requires C, 77.75; H, 5.00%. Found: C, 77.63; H, 5.03%.

4.1.1.2. 2-(1-Bromo-2,2-diphenylvinyl)-1,6-dimethyl-3-*p*-tolyl-1*H*-indene 2b. Following the general procedure described above, from **1b** (50 mg, 0.12 mmol), compound **2b** (53 mg, 90%) was obtained as a yellow solid. Mp: 142–144 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.66 (d, 3H, J=6.9 Hz, CH_3), 2.35 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 4.21 (q, 1H, J=6.9 Hz, CH), 6.44–6.46 (m, 2H, Ar), 6.81–7.35 (m, 15H, Ar), 6.98–7.48 (m, 13H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.2, 21.4, 21.6, 46.0, 119.4, 120.6, 123.7, 126.3, 127.3, 127.8, 128.0, 128.4, 128.8, 129.1, 129.2, 130.3, 131.5, 135.8, 136.7, 140.6, 140.9, 144.0, 144.6, 148.5. IR (CH_2Cl_2) ν 3056, 3023, 2962, 2924, 1597, 1560, 1505, 1491, 1442, 1344, 1265, 1134, 1031, 966, 891, 822, 739, 691 cm^{-1}. MS (%) *m/e* 490 (M^+, 15), 411 (100), 396 (17), 381 (22), 333 (22), 319 (62), 303 (18), 167 (9). HRMS (EI) for $C_{32}H_{27}Br$: 492.1276. Found: 492.1325.

4.1.1.3. 2-(1-Bromo-2,2-di-*p*-tolylvinyl)-1-methyl-3-phenyl-1*H*-indene 2c. Following the general procedure described above, from **1c** (42 mg, 0.1 mmol), compound **2c** (45 mg, 92%) was obtained as a yellow solid. Mp: 184–186 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.68 (d, 3H, J=7.8 Hz, CH_3), 2.15 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 4.27 (q, 1H, J=7.8 Hz, CH), 6.30–6.33 (m, 2H, Ar), 6.61–6.64 (m, 2H, Ar), 7.06–7.48 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.1, 21.0, 21.3, 46.3, 120.8, 122.8, 125.8, 126.6, 127.1, 128.1, 128.4, 128.7, 129.1, 137.1, 138.1, 143.2, 145.2. IR (CH_2Cl_2) ν 3050, 3023, 2963, 2923, 2868, 1510, 1505, 1455, 1178, 1021, 964, 816, 775, 740, 698 cm^{-1}. MS (%) *m/e* 492 (M^+, 39), 411 (100), 396 (22), 333 (31), 319 (72), 305 (39), 289 (26). HRMS (EI) for $C_{32}H_{27}Br$: 492.1276. Found: 492.1319.

4.1.1.4. 2-(1-Bromo-2,2-diphenylvinyl)-6-chloro-3-(4-chlorophenyl)-1-methyl-1*H*-indene 2d. Following the general procedure described above, from **1d** (50 mg, 0.11 mmol), compound **2d** (39 mg, 67%) was obtained as a yellow solid. Mp: 182–184 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.68 (d, 3H, J=7.2 Hz, CH_3), 4.26 (q, 1H, J=7.2 Hz, CH), 6.47–6.49 (m, 2H, Ar), 6.84–7.53 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.8, 46.4, 121.4, 123.5, 126.8, 127.0, 128.1, 128.5, 128.6, 129.0, 129.2, 129.7, 132.2, 132.3, 133.2, 140.6, 141.1, 143.5, 145.7, 146.7, 149.7. IR (CH_2Cl_2) ν 3080, 3057, 2928, 2853, 1599, 1489, 1443, 1415, 1398, 1090, 1015, 828, 751, 697 cm^{-1}. MS (%) *m/e* 534 (M^+, 3), 454 (7), 273 (34), 271 (36), 193 (11), 191 (100), 165 (42). HRMS (EI) for $C_{30}H_{21}BrCl_2$: 534.0154. Found: 534.0184.

4.1.1.5. 2-(1-Bromo-2,2-bis(4-chlorophenyl)vinyl)-1-methyl-3-phenyl-1*H*-indene 2e. Following the general procedure described above, from **1e** (91 mg, 0.2 mmol), compound **2e** (82 mg, 77%) was obtained as a yellow solid. Mp: 196–198 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.67 (d, 3H, J=7.2 Hz, CH_3), 4.27 (q, 1H, J=7.2 Hz, CH), 6.34 (d, 2H, J=8.1 Hz, Ar), 6.80 (d, 2H, J=8.1 Hz, Ar), 7.02–7.48 (m, 13H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.1, 21.0, 46.3, 120.0, 121.0, 122.9, 126.3, 126.8, 127.4, 127.8, 128.4, 129.7, 130.7, 132.7, 133.5, 134.1, 138.9, 141.6, 142.0, 142.7, 145.3, 148.1. IR (CH_2Cl_2) ν 3062, 2966, 1888, 1589, 1488, 1397, 1264, 1090, 1016, 838, 826, 772, 741, 699 cm^{-1}. MS (%) *m/e* 532 (M^+, 48), 453 (57), 451 (100), 416 (35), 401 (54), 339 (37), 325 (39), 289 (46), 277 (48), 235 (25), 165 (16). Anal. Calcd for $C_{30}H_{21}BrCl_2$, requires C, 67.69; H, 3.98%. Found: C, 67.74; H, 3.91%.

4.1.1.6. 2-(1-Bromo-2,2-diphenylvinyl)-6-fluoro-3-(4-fluorophenyl)-1-methyl-1*H*-indene 2f. Following the general procedure described above, from **1f** (42 mg, 0.1 mmol), compound **2f** (35 mg, 70%) was obtained as a yellow solid. Mp: 168–170 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.70 (d, 3H, J=7.2 Hz, CH_3), 4.26 (q, 1H, J=7.2 Hz, CH), 6.50–6.52 (m, 2H, Ar), 6.89–7.37 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.0, 46.3, 110.7 (d, J_{C-F}=22.9 Hz), 113.6 (d, J_{C-F}=22.3 Hz), 115.2 (d, J_{C-F}=21.5 Hz), 115.3 (d, J_{C-F}=21.2 Hz), 121.4 (d, J_{C-F}=8.6 Hz), 126.7, 127.5, 127.6, 127.9, 128.0, 128.1, 128.3, 128.5, 129.0, 129.2, 130.2, 138.7, 140.7, 145.4, 145.7 (d, J_{C-F}=4.0 Hz), 162.2 (d, J_{C-F}=243.9 Hz). IR (CH_2Cl_2) ν 3055, 2967, 2921, 2868, 1607, 1504, 1472, 1442, 1346, 1266, 1232, 1157, 897, 866, 834, 751, 697, 638, 573 cm^{-1}. MS (%) *m/e* 498 (M^+, 29), 419 (100), 403 (34), 325 (55.88), 341 (55), 327 (73), 91 (10), 77 (5), 51 (16). Anal. Calcd for $C_{30}H_{21}F_2Br$, requires C, 72.15; H, 4.24%. Found: C, 72.13; H, 4.09%.

4.1.1.7. 2-(1-Bromo-2,2-bis(4-fluorophenyl)vinyl)-1-methyl-3-phenyl-1*H*-indene 2g. Following the general procedure described above, from **1g** (42 mg, 0.1 mmol), compound **2g** (41 mg, 72%) was obtained as a yellow solid. Mp: 202–203 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.68 (d, 3H, J=7.2 Hz, CH_3), 4.29 (q, 1H, J=7.2 Hz, CH), 6.37–6.39 (m, 2H, Ar), 6.51–6.54 (m, 2H, Ar), 6.98–7.48 (m, 13H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.1, 46.3, 114.5 (d, J_{C-F}=21.8 Hz), 115.1 (d, J_{C-F}=21.8 Hz), 120.9, 122.9, 126.2, 126.8, 127.4, 127.8, 128.3, 128.5, 130.2 (d, J_{C-F}=9.2 Hz), 131.1 (d, J_{C-F}=8.0 Hz), 134.3, 136.7, 142.9 (d, J_{C-F}=14.9 Hz), 146.8 (d, J_{C-F}=186.1 Hz) 162.0 (d, J_{C-F}=246.2 Hz). IR (CH_2Cl_2) ν 3060, 2966, 2925, 2864, 1600, 1506, 1229, 1156, 1019, 964, 834, 777, 747, 699, 594 cm^{-1}. MS (%) *m/e* 498 (M^+, 39), 419 (100), 404 (43), 323 (51), 309 (95), 203 (42), 154 (41), 109 (11). Anal. Calcd for $C_{30}H_{21}F_2Br$, requires C, 72.15; H, 4.24%. Found: C, 72.14; H, 4.19%.

4.1.2. General procedure for the reactions of diarylvinylidenecyclopropane with bromine in Et_2O. In a dry 20 mL Schlenk tube, which was sealed and purged with argon through the septum inlet, diarylvinylidenecyclopropane **1** (0.1 mmol) was added, and then 2.0 mL of dried Et_2O was added by a syringe. The mixture was cooled to −100 °C by a CO_2–Et_2O bath, and then added 1.0 mL of Br_2–CH_2Cl_2 (0.1 N) within 2 min by a syringe. The resulting mixture was stirred for another 10 min at this temperature and quenched by addition of 100 mg of Na_2SO_3 solid. After filtration, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether as eluent to give the desired product.

4.1.2.1. 2-Bromo-3-(diphenylmethylene)-1,1-diphenylpenta-1,4-diene 3a. Following the general procedure described above, from **1a** (39 mg, 0.1 mmol), compound **3a** (36 mg, 89%) was obtained as a yellow solid. Mp: 96–98 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 5.46 (dd, 1H, J=1.2 Hz, J=11.1 Hz, CH), 5.75 (dd, 1H, J=1.5 Hz, J=17.4 Hz, CH), 6.43 (dd, 1H, J=11.1 Hz, J=17.4 Hz, CH), 6.78–7.30 (m, 20H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 118.6, 121.6, 127.27, 127.29, 127.4, 127.6, 127.7, 127.8, 128.5, 129.1, 129.7, 130.3, 134.9, 136.8, 140.4, 140.9, 142.0, 142.7, 144.0, 145.2. IR (CH_2Cl_2) ν 3071, 3055, 2920, 1720, 1599, 1491, 1443, 1263, 1182, 1154, 1075, 1001, 912, 821, 752, 697, 535 cm^{-1}. MS (%) *m/e* 462 (M^+, 11), 383 (100), 367 (12), 305 (84), 291 (47), 289 (28), 215 (9), 167 (12), 91 (10), 77 (4). HRMS (EI) for $C_{30}H_{23}Br$: 462.0983. Found: 462.0998.

4.1.2.2. 2-Bromo-3-(di-*p*-tolylmethylene)-1,1-diphenylpenta-1,4-diene 3b. Following the general procedure described above, from **1b** (42 mg, 0.1 mmol), compound **3b** (49 mg, 99%) was obtained as a yellow solid. Mp: 160–162 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.30 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 5.42 (dd, 1H, J=1.2 Hz, J=10.8 Hz, CH), 5.72 (dd, 1H, J=1.2 Hz, J=17.7 Hz, CH), 6.42 (dd, 1H, J=10.8 Hz, J=17.7 Hz, CH), 6.77–6.83 (m, 6H, Ar), 7.05–7.12 (m, 9H, Ar), 7.23–7.29 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.2, 21.3, 117.9, 122.1, 127.2, 127.3, 127.8, 127.9, 128.3, 128.4, 129.2, 129.8, 130.3, 135.2, 136.1, 137.0, 137.4, 138.2, 139.4, 140.6, 142.7, 144.3, 144.9. IR (CH_2Cl_2) ν 3060, 3022, 2921, 2864, 1605, 1508, 1487, 1443, 1408, 1265, 1183, 1109, 1074, 1036, 909, 820, 758, 740, 698, 637, 602 cm^{-1}. MS (%) *m/e* 490 (M^+, 15), 411 (100), 365 (8), 303 (20), 243 (4), 167 (9), 165 (6), 77 (4). HRMS (EI) for $C_{32}H_{27}Br$: 490.1296. Found: 490.1334.

4.1.2.3. 2-Bromo-3-(diphenylmethylene)-1,1-di-*p*-tolylpenta-1,4-diene 3c. Following the general procedure

described above, from **1c** (42 mg, 0.1 mmol), compound **3c** (41 mg, 84%) was obtained as a yellow solid. Mp: 136–138 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.25 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 5.46 (dd, 1H, J=0.9 Hz, J=11.1 Hz, CH), 5.75 (dd, 1H, J=1.5 Hz, J=17.4 Hz, CH), 6.43 (dd, 1H, J=11.1 Hz, J=17.4 Hz, CH), 6.69 (d, 2H, J=7.8 Hz, Ar), 6.90–6.97 (m, 8H, Ar), 7.07 (d, 2H, J=7.8 Hz, Ar), 7.20–7.26 (m, 6H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.2, 21.3, 118.5, 120.6, 127.1, 127.5, 127.7, 127.9, 128.5, 129.0, 129.7, 130.3, 134.8, 136.9, 137.0, 137.1, 137.9, 140.0, 142.2, 143.8, 145.2. IR (CH_2Cl_2) ν 3022, 2921, 2848, 2363, 1898, 1609, 1509, 1490, 1443, 1265, 1032, 912, 817, 755, 734, 699, 585 cm^{-1}. MS (%) *m/e* 490 (M^+, 10), 411 (100), 319 (62), 305 (26), 303 (23), 289 (18), 215 (10), 105 (15), 91 (10), 77 (5). Anal. Calcd for $C_{32}H_{27}Br$, requires C, 78.20; H, 5.54%. Found: C, 77.94; H, 5.49%.

4.1.2.4. 3-Bis(4-chlorophenyl)methylene-2-bromo-1,1-diphenylpenta-1,4-diene 3d. Following the general procedure described above, from **1d** (46 mg, 0.1 mmol), compound **3d** (41 mg, 76%) was obtained as a yellow solid. Mp: 120–122 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 5.52 (d, 1H, J=10.8 Hz, CH), 5.79 (d, 1H, J=17.4 Hz, CH), 6.37 (dd, 1H, J=10.8 Hz, J=17.4 Hz, CH), 6.79–7.31 (m, 18H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 119.7, 120.7, 127.4, 127.55, 127.62, 128.0, 128.1, 128.3, 129.0, 131.2, 131.6, 133.4, 133.9, 134.4, 137.8, 138.9, 140.1, 140.4, 141.2, 142.2, 145.7. IR (CH_2Cl_2) ν 3084, 3055, 2924, 2852, 2367, 1898, 1589, 1490, 1443, 1398, 1264, 1091, 1037, 1015, 917, 829, 767, 698, 599 cm^{-1}. MS (%) *m/e* 532 (M^+, 21), 451 (100), 416 (36), 380 (28), 338 (50), 302 (88), 289 (53), 202 (37), 165 (37), 91 (21), 77 (21). HRMS (EI) for $C_{30}H_{21}BrCl_2$: 532.0183. Found: 532.0216.

4.1.2.5. 2-Bromo-1,1-bis(4-chlorophenyl)-3-(diphenylmethylene)penta-1,4-diene 3e. Following the general procedure described above, from **1e** (45 mg, 0.1 mmol), compound **3e** (35 mg, 65%) was obtained as a yellow solid. Mp: 124–126 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 5.47 (d, 1H, J=10.5 Hz, CH), 5.70 (d, 1H, J=17.1 Hz, CH), 6.44 (dd, 1H, J=10.5 Hz, J=17.1 Hz, CH), 6.68–7.26 (m, 18H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 118.8, 122.8, 127.4, 127.6, 127.9, 128.2, 129.6, 129.9, 130.2, 130.6, 133.4, 133.5, 134.7, 136.4, 138.6, 140.4, 140.5, 141.9, 142.9, 144.3. IR (CH_2Cl_2) ν 3080, 3055, 3027, 2926, 1899, 1826, 1608, 1590, 1489, 1442, 1397, 1264, 1090, 1031, 1016, 913, 827, 794, 765, 744, 699, 640, 527, 500 cm^{-1}. MS (%) *m/e* 532 (M^+, 19), 451 (55), 303 (100), 302 (99), 289 (55), 215 (64), 182 (54), 151 (83), 91 (29). HRMS (EI) for $C_{30}H_{21}Cl_2Br$: 530.0204. Found: 530.0203.

4.1.2.6. 3-(Bis(4-fluorophenyl)methylene)-2-bromo-1,1-diphenylpenta-1,4-diene 3f. Following the general procedure described above, from **1f** (42 mg, 0.1 mmol), compound **3f** (39 mg, 78%) was obtained as a light yellow solid. Mp: 104–106 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 5.50 (d, 1H, J=10.8 Hz, CH), 5.77 (d, 1H, J=17.7 Hz, CH), 6.38 (dd, 1H, J=10.8 Hz, J=17.7 Hz, CH), 6.73–7.30 (m, 18H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 114.3 (d, J_{C-F}=21.2 Hz), 114.9 (d, J_{C-F}=21.2 Hz), 119.2, 121.2, 127.4, 127.5 (2C), 127.7, 127.8, 127.9, 128.1, 128.3, 129.0 (2C), 129.2, 131.6 (d, J_{C-F}=8.0 Hz), 132.0 (d, J_{C-F}=8.0 Hz), 134.5, 136.6 (d, J_{C-F}=3.5 Hz), 137.2, 137.9 (d, J_{C-F}=3.5 Hz), 140.4, 141.5, 142.3, 145.4, 162.0 (d, J_{C-F}=246.2 Hz), 162.3 (d, J_{C-F}=246.8 Hz). IR (CH_2Cl_2) ν 3052, 2917, 2359, 1601, 1506, 1443, 1261, 1230, 1157, 1092, 1035, 1011, 837, 699, 586 cm^{-1}. MS (%) *m/e* 498 (M^+, 17), 419 (100), 341 (54), 327 (52), 309 (37), 201 (22), 160 (32), 109 (18), 91 (25), 77 (8). HRMS (EI) for $C_{30}H_{21}F_2Br$: 498.0795. Found: 498.0781.

4.1.2.7. 2-Bromo-3-(diphenylmethylene)-1,1-bis(4-fluorophenyl)penta-1,4-diene 3g. Following the general procedure described above, from **1g** (42 mg, 0.1 mmol), compound **3g** (40 mg, 80%) was obtained as a white solid. Mp: 98–100 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 5.47 (dd, 1H, J=0.9 Hz, J=12.0 Hz, CH), 5.71 (dd, 1H, J=1.2 Hz, J=21.0 Hz, CH), 6.45 (dd, 1H, J=12.0 Hz, J=21.0 Hz, CH), 6.74–6.82 (m, 4H, Ar), 6.92–7.00 (m, 8H, Ar), 7.22–7.26 (m, 6H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 114.3 (d, J_{C-F}=21.0 Hz), 114.9 (d, J_{C-F}=21.8 Hz), 118.6, 122.1, 127.4, 127.5, 127.8, 129.6, 130.2, 130.3, 130.9, 131.0, 134.8, 136.4, 137.5 (d, J_{C-F}=130.5 Hz), 138.29, 143.2, 141.3 (d, J_{C-F}=108.5 Hz), 143.7 (d, J_{C-F}=72.5 Hz), 162.0 (d, J_{C-F}=246.2 Hz), 162.1 (d, J_{C-F}=246.2 Hz). IR (CH_2Cl_2) ν 3057, 2925, 2367, 1601, 1507, 1443, 1267, 1230, 1157, 1032, 1013, 917, 836, 760, 740, 700, 583 cm^{-1}. MS (%) *m/e* 498 (M^+, 18), 419 (100), 341 (28), 323 (43), 309 (35), 205 (5), 165 (15), 109 (16), 91 (14), 77 (7). HRMS (EI) for $C_{30}H_{21}F_2Br$: 498.0795. Found: 498.0831.

4.1.3. Reaction procedure for the Suzuki coupling reaction of 2a with phenylboronic acid catalyzed by $Pd(PPh_3)_4$. In a dry 20 mL Schlenk tube, which was sealed and purged with argon through the septum inlet, **2a** (46 mg, 0.1 mmol), phenylboronic acid (16 mg, 1.2 equiv), $Pd(PPh_3)_4$ (6 mg, 5 mol %), and Na_2CO_3 (26 mg, 3.0 equiv) were added, and then 2 mL of degassed toluene, 0.1 mL of degassed EtOH, and 0.1 mL of distilled water were added by a syringe. The mixture was stirred at 50 °C for 5 h and quenched by adding 10 mL of water. The resulting mixture was extracted three times with 20 mL of Et_2O. The combined organic layers were washed three times with 20 mL of brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure, and the residue was purified by silica gel column chromatography using petroleum ether as eluent to give the desired product.

4.1.3.1. 1-Methyl-3-phenyl-2-(1,2,2-triphenylvinyl)-1*H*-indene 4. A light yellow solid. Mp: 178–180 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.49 (d, 3H, J=6.6 Hz, CH_3), 3.51 (q, 1H, J=6.6 Hz, CH), 6.50–7.23 (m, 24H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.5, 45.4, 109.7, 120.2, 122.6, 125.0, 125.9, 126.2, 126.3, 126.6, 127.4, 127.9, 128.1, 129.4, 130.4, 130.9, 131.3, 134.5, 135.1, 140.9, 143.2, 143.4, 143.7, 143.9, 148.7, 148.9. IR (CH_2Cl_2) ν 3055, 3021, 2962, 2926, 1597, 1491, 1443, 1265, 1074, 1029, 777, 760, 723, 697, 632, 560 cm^{-1}. MS (%) *m/e* 460 (M^+, 100), 369 (30), 367 (35), 291 (23), 289 (23), 255 (24), 239 (17), 191 (15), 175 (11), 91 (4). HRMS (EI) for $C_{36}H_{28}$: 460.2191. Found: 460.2197.

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Supplementary data

^{1}H and ^{13}C NMR spectra for the brominated products **2** and **3**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.04.082.

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