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Auto de-bromine-coupling reactions of 1-aryl-7-bromocycloheptenes

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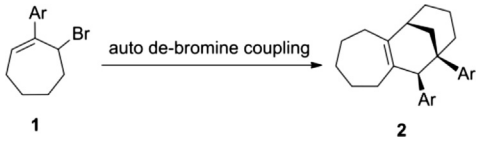
ABSTRACT

Auto de-bromine-coupling reactions of 1-aryl-7-bromocycloheptenes to a new series of [7-6-6] tricyclic system were described. A variety of substituents at the *para*-position of the phenyl were amenable to this transformation, including electron-donating groups and halides. The presence of electron-donating groups resulted in a more efficient reaction, with higher yields than the case of halides.

1. Introduction

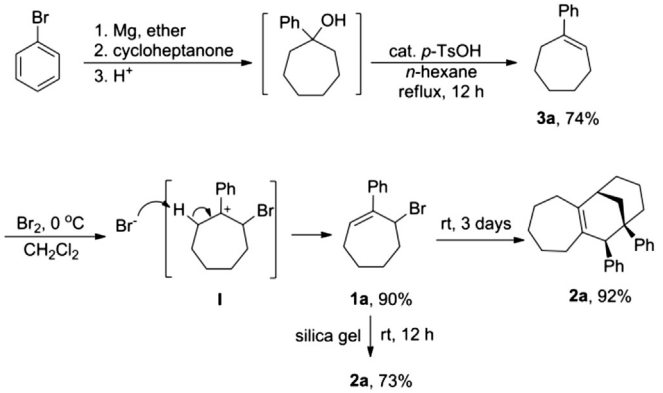
De-halogen-coupling reactions of various organic halides have been a useful method to construct a new carbon–carbon bond through a simple operation. Metal mediated coupling reactions are common ways for this transformation, such as Wurtz,[1] Ullmann,[1g,2] Grignard,[3] and nickel complexes[4] reactions. The coupling reactions could also be achieved without any metal or metal complex reagents, such as electrochemical[5] and photochemical[6] reactions. In this paper, we reported that auto de-bromine-coupling reactions of 1-aryl-7-bromocycloheptenes to give a new series of [7-6-6] tricyclic diaryl adducts (Scheme 1). This tricyclic system was not found in either nature compounds or synthetic products.



Scheme 1. Auto de-bromine-coupling reactions of 1-aryl-7-bromocycloheptenes.

2. Results and discussion

The synthesis of the starting material 7-bromo-1-phenylcycloheptene (**1a**) is illustrated in Scheme 2. 1-Phenylcycloheptene (**3a**), the immediate precursor via bromination to compound **1a**, was generated from bromobenzene. Bromobenzene proceeded via Grignard reaction followed by dehydration to give cycloheptene **3a**. Cycloheptene **3a** reacted with bromine via intermediate **I** to give a 90% isolated yield of **1a**. After compound **1a** was purified, it was kept at room temperature in neat conditions for 3 days. A red liquid



Scheme 2. Synthesis of 1,2-diphenyltricyclo[8.3.1.$0^{3,9}$]tetradec-3(9)-ene (**2a**).

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was produced during this period, compound **2a**, could be isolated in 92% yield by using flash chromatography. This reaction was accelerated to complete in 12 h upon addition of silica gel, leading to a yield of 73% (Scheme 2).

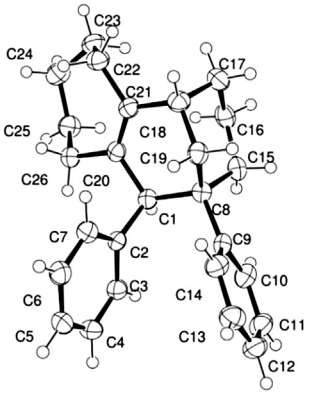
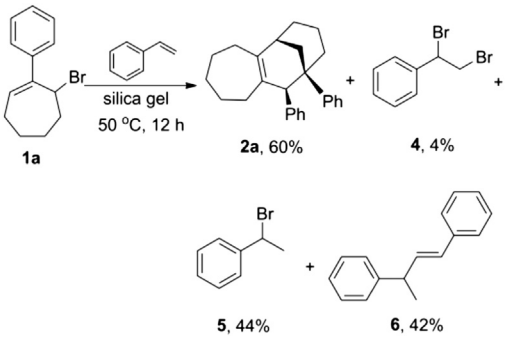


Fig. 1. X-ray crystal structure of **2a**.

The structure of compound **2a** was confirmed by X-ray crystallography (Fig. 1). The structure clearly shows that compound **2a** was produced from two molecules of compound **1a** and released one molecule of bromine.

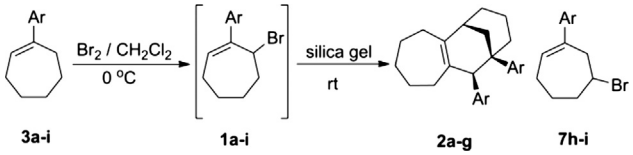
To prove that the red liquid is bromine, styrene was subjected to the reaction. As anticipated, (1,2-dibromoethyl)benzene (**4**) was produced along with (1-bromoethyl)benzene (**5**), and the dimerized derivative of styrene, compound **6** (Scheme 3). The isolation of these products revealed that both bromine and hydrogen bromide were released during the reaction. Compound **1a** does not react under vacuum condition without silica gel, indicating that an acid source was required for this transformation.



Scheme 3. Acid-catalyzed de-bromine-coupling reaction with styrene.

The scope of the acid-catalyzed reaction was then examined by testing a variety of substituents on the phenyl at the *para* position (Table 1, entries 2–8). Higher yields (61–67% over two steps) of tricyclic products were obtained for compounds with electron-donating groups such as methyl, methoxy, and thiomethyl groups (Table 1, entries 2–4). In addition, halides (Table 1, entries 5–7) could be used in this transformation, but the product yields were dropped to 32–58%. The structures of all tricyclic compounds (**2a**–**g**) were confirmed by X-ray crystallography. An isomerization product 1-(4-acetylphenyl)-6-bromocycloheptene (**7h**) was produced when the electron-donating group was replaced with an electron-withdrawing group, namely, an acetyl group (Table 1, entry 8). To further explore the importance of using an aryl group, an *ortho*-substituted system (Table 1, entry 9) was employed, and an isomerization adduct 6-bromo-1-(*o*-tolyl)cycloheptene (**7i**) was

Table 1
De-bromine-coupling reactions with various of aryl groups

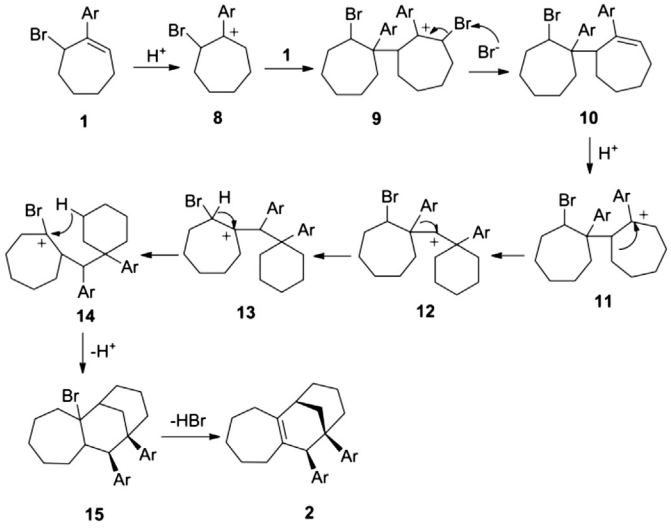


Entry	**3a**–**3i**, Ar–	Time (h)	Product	Yield[a] (%)
1	**3a**, Ph–	12	**2a**	60
2	**3b**, *p*-MePh–	12	**2b**	64
3	**3c**, *p*-MeOPh–	12	**2c**	67
4	**3d**, *p*-MeSPh–	12	**2d**	61
5	**3e**, *p*-BrPh–	12	**2e**	58
6	**3f**, *p*-ClPh–	12	**2f**	41
7	**3g**, *p*-FPh–	12	**2g**	32
8	**3h**, *p*-MeCOPh–	72	**7h**	75
9	**3i**, *o*-MePh–	72	**7i**	82

[a] Isolated yield.

afforded. The structures of **7h** and **7i** were readily deduced on the basis of ^{1}H, ^{13}C, and ^{1}H–^{1}H COSY NMR spectra.

A mechanism that accounts for these observations is shown in Schemes 4 and 5. Under acidic conditions, the cation **8** is initially generated, which then reacts with compound **1** to yield cation **9**. Abstraction of a brominium cation to generate compound **10**, which is protonated to give a benzylic carbocation. To release the ring strain energy, cation **11** is transformed into **12**. Cation **12** converted into a more stable bromo-stabilized tertiary cation **14** through aryl group migration and a hydrogen shift. The aryl group migrates from the same site of another aryl group because of the π–π interaction between two aryl group. However, an intramolecular alkylation is

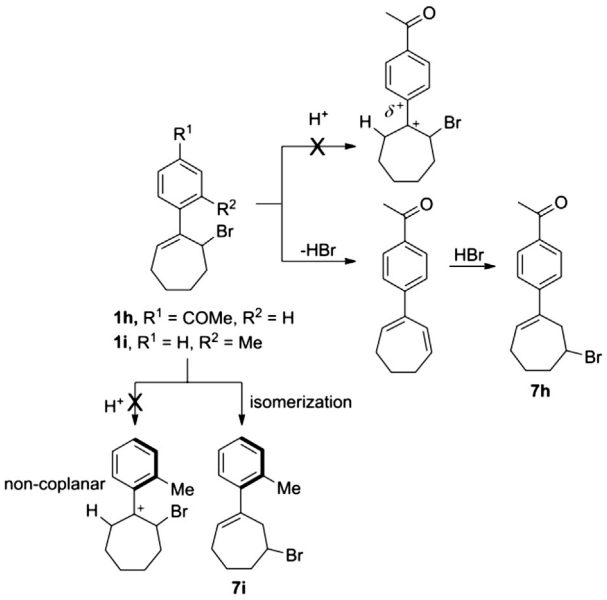


Scheme 4. Plausible mechanism for de-bromine-coupling reaction.

possible when the C–H bond is in close proximity to the positively charged carbon.[7] Therefore, cation **14** would undergo an intramolecular alkylation followed by dehydrobromination to yield the tricyclic compound **2** (Scheme 4).

On the basis of this mechanism, we proposed that the stability of the cation **8**, which could affect the yields in the reactions, is resonance stabilized from the electron-donating groups (entries 2–4) and therefore gives higher yields than the halides (entries 5–7).

In contrast, an electron-withdrawing group on the phenyl group was intended to decrease the activity of the alkene. Additionally, the protonated intermediate was unstable due to the partial positive and positive charge on the neighboring carbon position.



Scheme 5. Plausible mechanism for isomerization.

Therefore, compound **1h** would undergo dehydrobromination followed by hydrobromination to give compound **7h**. For compound **1i**, a non-coplanar conformation arose from the stereo effect at the *ortho*-position. Thus, the carbocation could not be resonance stabilized by the electron-donating group, a methyl group, and would undergo isomerization to give compound **7i** (Scheme 5). Futhermore, theoretical calculations shows that the heat of formation of compound **7h** is 2.66 kcal/mol lower than that of compound **1h**, and that of compound **7i** is 6.94 kcal/mol lower than that of compound **1i**.

3. Conclusion

In conclusion, acid-catalyzed de-bromine-coupling of 1-aryl-7-bromocycloheptenes to produce a series of 1,2-diaryltricyclo-[8.3.1.0^{3,9}]tetradec-3(9)-enes are reported. The versatility of this transformation is dependent on the presence of the acid source and the stability of the cation intermediates.

4. Experimental section

4.1. General information

Melting points were measured with a Barloworld SMP3 melting point apparatus and were uncorrected. NMR spectra were measured in $CDCl_3$ solution with a Bruker AC-300 MHz NMR spectrometer, with $CHCl_3$ (7.26 ppm) as the internal standard. Carbon-13 NMR was measured in $CDCl_3$ solution on a 75 MHz NMR spectrometer and referenced to $CDCl_3$ (77.1 ppm). Chemical shifts (δ) are expressed in parts per million (ppm) downfield from tetramethylsilane. Coupling constants (J) are expressed in hertz (Hz). Mass spectra were measured with a Finnigan/Thermo Quest MAT 95XL mass spectrometer. The elemental analyses were recorded on a Elementar vario EL III elemental analyzer. Infrared spectra were recorded on KBr pellets. Flash chromatography was performed on silica gel (230 mesh). Column chromatography was performed on silica gel (70–230 mesh). Solvents are of reagent grade. The theoretical calculations reported here were performed via DFT/MP2 level with LanL2DZ basis set, using the Gaussian 03 series of packages.

4.2. General procedure for preparation of 1-arylcycloheptenes (3a–i)

To a stirred solution of magnesium turnings (5.1 g, 0.21 mol) and 0.5 g of iodine in 200 mL of anhydrous diethyl ether. To initiate the Grignard reaction, add 1 mL of aryl bromide from the dropping funnel and heat the mixture. When the Grignard reagent begins to form, the ether solution will become cloudy and then begin to boil. After the reaction has been initiated, another amount of aryl bromide (0.2 mol) was added dropwise from a dropping funnel at a rate that maintains a gentle reflux. The arylmagnesium bromide was allowed to cool to room temperature, and cycloheptanone (22.4 g, 0.2 mol) was added slowly to the vigorously stirred arylmagnesium bromide solution. When the addition of cycloheptanone is completed, allow the mixture to stir for 2 h. The mixture was poured slowly into a 1 L beaker with 100 g of crushed ice, and 3 N HCl solution was added slowly to the mechanically stirred mixture until the liquid is clear. The organic layer was separated and washed with water and brine, and then dried over anhydrous $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator. To a stirred solution of crude alcohol in 100 mL of *n*-hexane was added catalytic amount of *p*-TsOH and the mixture was refluxed for 12 h. The *n*-hexane solution was dried over anhydrous K_2CO_3. After filtration, the solvent was removed and the crude product was distilled under vacuum to give the corresponding 1-arylcycloheptenes (**3a**–**i**).

*4.2.1. 1-Phenylcycloheptene (**3a**).* Colorless liquid. Yield: 25.5 g, 74%. The NMR data are consistent with those reported in the literature.[8] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.17 (m, 5H), 6.09 (t, 1H, J=6.7 Hz), 2.63–2.60 (m, 2H), 2.29 (m, 2H), 1.86–1.80 (m, 2H), 1.69–1.54 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.11 (C), 145.05 (C), 130.4 (CH), 128.2 (CH), 126.3 (CH), 125.7 (CH), 32.9 (CH_2), 32.8 (CH_2), 29.0 (CH_2), 27.0 (CH_2), 26.9 (CH_2).

*4.2.2. 1-(p-Tolyl)cycloheptene (**3b**).* Colorless liquid. Yield: 26.1 g, 70%. The NMR data are consistent with those reported in the literature.[9] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, 2H, J=8.0 Hz), 7.11 (d, 2H, J=8.0 Hz), 6.07 (t, 1H, J=6.8 Hz), 2.62–2.58 (m, 2H), 2.34 (s, 3H), 2.31–2.26 (m, 2H), 1.88–1.80 (m, 2H), 1.68–1.52 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8 (C), 142.2 (C), 135.9 (C), 129.6 (CH), 128.9 (CH), 125.6 (CH), 32.87 (CH_2), 32.86 (CH_2), 28.9 (CH_2), 27.0 (CH_2), 26.9 (CH_2), 21.1 (CH_3). MS m/z (%) 186 (M^+, 89), 171 (70), 158 (55), 143 (73), 132 (51), 129 (73), 128 (55), 119 (100), 115 (56), 105 (75), 91 (70). HRMS (EI) calcd for $C_{14}H_{18}$ m/z 186.1409 (M^+), found 186.1405.

*4.2.3. 1-(4-Methoxyphenyl)cycloheptene (**3c**).* Colorless liquid. Yield: 32.8 g, 81%. The NMR data are consistent with those reported in the literature.[10] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, 2H, J=8.7 Hz), 6.84 (d, 2H, J=8.7 Hz), 6.02 (t, 1H, J=6.8 Hz), 3.80 (s, 3H), 2.60–2.56 (m, 2H), 2.30–2.24 (m, 2H), 1.87–1.79 (m, 2H), 1.67–1.50 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3 (C), 144.4 (C), 137.7 (C), 128.9 (CH), 126.8 (CH), 113.6 (CH), 55.4 (CH_3), 32.92 (CH_2), 32.86 (CH_2), 28.9 (CH_2), 27.0 (CH_2). MS m/z (%) 202 (M^+, 100), 174 (71), 159 (56), 148 (52), 121 (55). HRMS (EI) calcd for $C_{14}H_{18}O$ m/z 202.1358 (M^+), found 202.1362.

*4.2.4. 1-(4-Thiomethylphenyl)cycloheptene (**3d**).* Colorless liquid. Yield: 35.8 g, 82%. IR (KBr, cm^{-1}) 3077, 3020, 2985, 2923, 2851, 2830, 1593, 1491, 1447, 1437, 825. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, 2H, J=8.5 Hz), 7.19 (d, 2H, J=8.5 Hz), 6.08 (t, 1H, J=6.8 Hz), 2.60–2.56 (m, 2H), 2.48 (s, 3H), 2.31–2.25 (m, 2H), 1.87–1.80 (m, 2H), 1.67–1.51 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3 (C), 142.0 (C), 136.0 (C), 130.1 (CH), 126.8 (CH), 126.1 (CH), 32.7 (CH_2), 32.6 (CH_2), 28.9 (CH_2), 26.9 (CH_2), 26.8 (CH_2), 16.3 (CH_3). MS m/z (%) 220, (M^++2, 5), 218 (M^+, 100), 129 (39). HRMS (EI) calcd for $C_{14}H_{18}S$ m/z

218.1129 (M^+), found 218.1134. Anal. Calcd for $C_{14}H_{18}S$: C 77.01, H 8.31. Found: C 77.09, H 7.92.

*4.2.5. 1-(4-Bromophenyl)cycloheptene (**3e**).* Colorless liquid. Yield: 37.2 g, 74%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, 2H, J=8.5 Hz), 7.18 (d, 2H, J=8.5 Hz), 6.08 (t, 1H, J=6.8 Hz), 2.58–2.55 (m, 2H), 2.31–2.25 (m, 2H), 1.88–1.80 (m, 2H), 1.66–1.51 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.02 (C), 144.0 (C), 131.2 (CH), 131.1 (CH), 127.4 (CH), 120.1 (C), 32.74 (CH_2), 32.71 (CH_2), 28.9 (CH_2), 26.9 (CH_2), 26.7 (CH_2). MS m/z (%) 252 (M^++2, 60), 250 (M^+, 61), 171 (66), 128 (80), 129 (100), 115 (63). HRMS (EI) calcd for $C_{13}H_{15}Br$ m/z 250.0357 (M^+), found 250.0353.

*4.2.6. 1-(4-Chlorophenyl)cycloheptene (**3f**).* Colorless liquid. Yield: 29.4 g, 71%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 4H), 6.08 (t, 1H, J=6.8 Hz), 2.59–2.55 (m, 2H), 2.31–2.25 (m, 2H), 1.88–1.80 (m, 2H), 1.67–1.51 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0 (C), 143.5 (C), 132.0 (C), 131.0 (CH), 128.2 (CH), 127.1 (CH), 32.8 (CH_2), 32.7 (CH_2), 28.9 (CH_2), 26.9 (CH_2), 26.8 (CH_2). MS m/z (%) 208 (M^++2, 30), 206 (M^+, 87), 178 (59), 171 (55), 154 (57), 152 (57), 139 (76), 138 (54), 129 (100), 128 (62), 125 (56), 115 (76). HRMS (EI) calcd for $C_{13}H_{15}Cl$ m/z 206.0862 (M^+), found 206.0860.

*4.2.7. 1-(4-Fluorophenyl)cycloheptene (**3g**).* Colorless liquid. Yield: 25.5 g, 67%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.07–7.00 (m, 2H), 6.12 (t, 1H, J=6.7 Hz), 2.67–2.64 (m, 2H), 2.38–2.33 (m, 2H), 1.96–1.88 (m, 2H), 1.75–1.62 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7 (d, C, J=243.3 Hz), 144.1 (C), 141.1 (C), 130.3 (CH), 127.2 (d, CH, J=7.6 Hz), 114.8 (d, CH, J=21 Hz), 33.0 (CH_2), 32.8 (CH_2), 28.9 (CH_2), 26.9 (CH_2), 26.8 (CH_2).

*4.2.8. 1-(4-Acetylphenyl)cycloheptene (**3h**).* Colorless liquid. Yield: 29.1 g, 68%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 2H, J=8.4 Hz), 7.38 (d, 2H, J=8.4 Hz), 6.20 (t, 1H, J=6.8 Hz), 2.62–2.57 (m, 2H), 2.57 (s, 3H), 2.34–2.28 (m, 2H), 1.88–1.81 (m, 2H), 1.68–1.52 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.7 (C), 149.8 (C), 144.3 (C), 135.1 (C), 132.9 (CH), 128.5 (CH), 125.7 (CH), 32.7 (CH_2), 32.5 (CH_2), 29.0 (CH_2), 26.8 (CH_2), 26.63 (CH_2), 26.60 (CH_3). MS m/z (%) 214 (M^+, 100), 213 (69), 199 (69), 178 (67), 145 (52). HRMS (EI) calcd for $C_{15}H_{18}O$ m/z 214.1358 (M^+), found 214.1361.

*4.2.9. 1-(o-Tolyl)cycloheptene (**3i**).* Colorless liquid. Yield: 27.6 g, 74%. The NMR data are consistent with those reported in the literature.[9] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15–7.05 (m, 4H), 5.74 (t, 1H, J=6.5 Hz), 2.44–2.41 (m, 2H), 2.30–2.24 (m, 2H), 2.28 (s, 3H), 1.88–1.80 (m, 2H), 1.68–1.54 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7 (C), 145.9 (C), 134.7 (C), 131.1 (CH), 130.0 (CH), 128.4 (CH), 126.3 (CH), 125.5 (CH), 34.9 (CH_2), 32.7 (CH_2), 29.0 (CH_2), 27.3 (CH_2), 27.1 (CH_2), 20.3 (CH_3). MS m/z (%) 186 (M^+, 100), 171 (47), 143 (62), 129 (62), 128 (51), 115 (48), 105 (47). HRMS (EI) calcd for $C_{14}H_{18}$ m/z 186.1409 (M^+), found 186.1419.

4.3. Bromination of 1-phenylcycloheptene (3a)

To a stirred solution of compound **3a** (8.0 g, 46.4 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added bromine (2.4 mL, 46.4 mmol in 10 mL CH_2Cl_2) dropwise from a dropping funnel. After the addition was completed, the mixture was stirred for 1 h at 0 °C and then warmed to room temperature and stirred for 1 h. The reaction mixture was washed with 5% aqueous sodium bisulphate solution (20 mL). The organic layer was separated, washed with water and brine, and then dried over anhydrous $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator and the residue was purified by flash chromatography (1% Et_3N in hexane) to give colorless oil **1a** (10.5 g, 90%). IR (KBr, cm^{-1}) 3060, 3023, 2925, 2852, 1597, 1491, 758, 698, 576; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.26 (m, 5H), 6.17 (t, 1H, J=6.6 Hz), 5.29 (d, 1H, J=5.7 Hz), 2.46–2.43 (m, 2H), 2.29–2.25 (m, 2H), 2.03–1.97 (m, 2H), 1.58–1.50 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.0 (C), 143.4 (C), 136.3 (CH), 128.4 (CH), 127.2 (CH), 126.2 (CH), 57.4 (CH), 35.6 (CH_2), 28.6 (CH_2), 27.2 (CH_2), 26.8 (CH_2). MS m/z (%): 252 (M^++2, 2), 250 (M^+, 2), 172 (57), 170 (48), 155 (56), 142 (55), 129 (100), 115 (57), 91 (57), 77 (25). HRMS (EI) calcd for $C_{13}H_{15}Br$ m/z 250.0357 (M^+), found 250.0363.

4.4. Acid-catalyzed reaction of 7-bromo-1-phenylcycloheptene (1a)

Compound **1a** (5 g, 20 mmol) and 0.1 g of silica gel were stirred at room temperature for 12 h. The crude material was purified by flash column chromatography (hexane) to afford white solid **2a** (2.5 g, 73%). Mp 146–147 °C; IR (KBr, cm^{-1}) 3092, 3054, 2937, 2840, 1598, 1493, 775, 727, 694; ^{1}H NMR (300 MHz, $CDCl_3$, 318 K) 7.03–6.8 (m, 10H), 3.27 (s, 1H), 2.59–2.34 (m, 4H), 2.19 (dd, 1H, J=8.0, 14.4), 2.01–1.33 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$, 318 K) 149.9 (C), 142.8 (C), 137.9 (C), 136.3 (C), 130.4 (CH), 127.3 (CH), 126.9 (CH), 125.9 (CH), 125.2 (CH), 125.0 (CH), 59.8 (CH), 41.5 (CH_2), 41.2 (C), 39.3 (CH), 35.5 (CH_2), 35.2 (CH_2), 33.0 (CH_2), 32.5 (CH_2), 27.3 (CH_2), 27.23 (CH_2), 27.15 (CH_2), 19.8 (CH_2). MS m/z (%) 342 (M^+, 70), 251 (100), 167 (24), 141 (31), 91 (56), 77 (8). HRMS (EI) calcd for $C_{26}H_{30}$ m/z 342.2348 (M^+), found 342.2343. Anal. Calcd for $C_{26}H_{30}$: C 91.17, H 8.83. Found: C 91.18, H 8.75. X-ray: CCDC 966895.

4.5. Acid-catalyzed reaction of 7-bromo-1-phenylcycloheptene (1a) with styrene

Compound **1a** (4g, 15.9 mmol), styrene (1.66g, 15.9 mmol), and 0.1 g silica gel were stirred at 50 °C for 12 h. The crude material was purified by column chromatography (hexane) to give **2a** (1.63 g, 60%), **4** (0.17 g, 4%), **5** (1.3 g, 44%), **6** (0.7 g, 42%). The spectral data for compounds **4**, **5**, and **6** are consistent with those reported in the literature.[11–13] Compound **4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–7.36 (m, 5H), 5.15 (dd, 1H, J=5.6, 10.4 Hz), 4.11–3.99 (m, 2H). Compound **5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.27 (m, 5H), 5.24 (q, 1H, J=6.9 Hz), 2.07 (d, 3H, J=6.9 Hz). Compound **6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.18 (m, 10H), 6.47–6.35 (m, 2H), 3.70–3.61 (m, 1H), 1.48 (d, 3H, J=7.0 Hz).

4.6. General procedure for the synthesis of 1,2-diaryl tricyclo[8.3.1.0^{3,9}]tetradec-3(9)-enes (2a–g)

To a stirred solution of 1-arylcycloheptene (20 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added bromine (20 mmol in 10 mL CH_2Cl_2) dropwise from a dropping funnel. After the addition was completed, the mixture was stirred for 1 h at 0 °C and then warmed to room temperature and stirred for 1 h. The solvent was removed on a rotary evaporator and added 0.1 g silica gel. The mixture stirred at room temperature for 12 h and the crude material was purified by flash chromatography (hexane) afforded the corresponding products **2a**–**g**.

*4.6.1. 1,2-Di(p-tolyl)tricyclo[8.3.1.0^{3,9}]tetradec-3(9)-ene (**2b**).* White solid. Yield: 2.37 g, 64%. Mp 161.5–162.5 °C. IR (KBr, cm^{-1}) 3093, 3060, 3026, 2943, 2915, 2882, 2841, 1508, 1447, 814. ^{1}H NMR (300 MHz, $CDCl_3$, 318 K) 6.87 (d, 2H, J=8.4 Hz), 6.83 (d, 2H, J=8.4 Hz), 6.72 (d, 2H, J=8.1 Hz), 6.68 (d, 2H, J=8.1 Hz), 3.23 (s, 1H), 2.61–2.32 (m, 4H), 2.24–2.11 (m, 1H), 2.19 (s, 3H), 2.15 (s, 3H), 2.0–1.34 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$, 318 K) δ 147.1 (C), 139.8 (C), 138.1 (C), 135.9 (C), 134.3 (C), 134.1 (C), 130.3 (CH), 128.0 (CH), 127.6 (CH), 125.7 (CH), 59.4 (CH), 41.7 (CH_2), 40.8 (C), 39.3 (CH), 35.5 (CH_2), 35.2 (CH_2), 33.0 (CH_2), 32.5 (CH_2), 27.4 (CH_2),

27.23 (CH_2), 27.15 (CH_2), 20.9 (CH_3), 20.8 (CH_3), 19.8 (CH_2). MS *m*/*z* (%) 370 (M^+, 92), 170 (100). HRMS (EI) calcd for $C_{28}H_{34}$ *m*/*z* 370.2661 (M^+), found 370.2652. Anal. Calcd for $C_{28}H_{34}$: C 90.75, H 9.25. Found: C 90.68, H 9.21. X-ray: CCDC 966896.

*4.6.2. 1,2-Di(4-methoxyphenyl)tricyclo[8.3.1.0^{3,9}]tetradec-3(9)-ene (**2c**).* White solid. Yield: 2.7 g, 67%. Mp 147–148 °C. IR (KBr, cm^{-1}) 3005, 2924, 2914, 2887, 2843, 1612, 1512, 1468, 1444, 1254, 1032, 821. ^{1}H NMR (300 MHz, $CDCl_3$, 318 K) δ 6.86 (d, 2H, *J*=8.7 Hz), 6.67 (d, 2H, *J*=8.2 Hz), 6.57 (d, 2H, *J*=8.7 Hz), 6.46 (d, 2H, *J*=8.2 Hz), 3.68 (s, 3H), 3.65 (s, 3H), 3.16 (s, 1H), 2.58–2.49 (m, 1H), 2.48–2.29 (m, 3H), 2.16 (dd, 1H, *J*=8.2, 14.5 Hz), 1.96–1.33 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$, 318 K) δ 157.4 (C), 157.1 (C), 142.6 (C), 138.1 (C), 135.9 (C), 135.2 (C), 131.1 (CH), 126.6 (CH), 112.9 (CH), 112.5 (CH), 59.1 (CH), 55.2 (CH_3), 55.1 (CH_3), 41.4 (CH_2), 40.5 (C), 39.3 (CH), 35.5 (CH_2), 35.2 (CH_2), 33.0 (CH_2), 32.6 (CH_2), 27.3 (CH_2), 27.23 (CH_2), 27.15 (CH_2), 19.7 (CH_2). MS *m*/*z* (%) 402 (M^+, 75), 294 (100), 281 (78), 148 (50), 121 (86). HRMS (EI) calcd for $C_{28}H_{34}O_2$, *m*/*z* 402.2559 (M^+), found 402.2550. Anal. Calcd for $C_{28}H_{34}O_2$: C 83.54, H 8.51. Found: C 83.48, H 8.47. X-ray: CCDC 966897.

*4.6.3. 1,2-Di(4-thiomethylphenyl)tricyclo[8.3.1.0^{3,9}]tetradec-3(9)-ene (**2d**).* White solid. Yield: 2.65 g, 61%. Mp 119–120 °C. IR (KBr, cm^{-1}) 3088, 3067, 3032, 3011, 2988, 1594, 1489, 1443, 815. ^{1}H NMR (300 MHz, $CDCl_3$, 318 K) δ 6.96 (d, 2H, *J*=8.4 Hz), 6.86 (d, 2H, *J*=8.4 Hz), 6.84 (d, 2H, *J*=7.9 Hz), 6.68 (d, 2H, *J*=7.9 Hz), 3.18 (s, 1H), 2.58–2.51 (m, 1H), 2.48–2.30 (m, 3H), 2.36 (s, 3H), 2.33 (s, 3H), 2.15 (dd, 1H, *J*=8.5, 15.2 Hz), 1.96–1.84 (3H, m), 1.82–1.29 (11H, m). ^{13}C NMR (75 MHz, $CDCl_3$, 318 K) δ 147.3 (C), 140.2 (C), 137.6 (C), 136.5 (C), 134.8 (C), 134.5 (C), 130.8 (CH), 126.9 (CH), 126.4 (CH), 126.2 (CH), 59.3 (CH), 41.2 (CH_2), 40.9 (C), 39.2 (CH), 35.5 (CH_2), 35.2 (CH_2), 33.0 (CH_2), 32.4 (CH_2), 27.22 (CH_2), 27.18 (CH_2), 27.1 (CH_2), 19.7 (CH_2), 16.8 (CH_3), 16.6 (CH_3). MS *m*/*z* (%) 438, (M^++4, 0.4), 436 (M^++2, 13), 434 (M^+, 100), 310 (55), 297 (62), 137 (43). HRMS (EI) calcd for $C_{28}H_{34}S_2$ *m*/*z* 434.2102 (M^+), found 434.2099. Anal. Calcd for $C_{28}H_{34}S_2$: C 77.36, H 7.88. Found: C 77.39, H 7.87. X-ray: CCDC 966898.

*4.6.4. 1,2-Di(4-bromophenyl)tricyclo[8.3.1.0^{3,9}]- tetradec-3(9)-ene (**2e**).* White solid. Yield: 2.9 g, 58%. Mp 144–145 °C. IR (KBr, cm^{-1}) 3082, 3023, 2925, 2847, 1586, 1484, 1450, 1010, 818. ^{1}H NMR (300 MHz, $CDCl_3$, 318 K) δ 7.16 (d, 2H, *J*=8.6 Hz), 7.06 (d, 2H, *J*=8.1 Hz), 6.82 (d, 2H, *J*=8.6 Hz), 6.65 (d, 2H, *J*=8.1 Hz), 3.19 (s, 1H), 2.59–2.52 (m, 1H), 2.44–2.26 (m, 3H), 2.17 (dd, 1H, *J*=8.5, 14.4 Hz), 1.99–1.26 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$, 318 K) δ 148.6 (C), 141.6 (C), 137.2 (C), 136.8 (C), 132.0 (CH), 130.6 (CH), 130.2 (CH), 127.6 (CH), 119.6 (C), 119.2 (C), 58.9 (CH), 41.3 (CH_2), 40.9 (C), 39.1 (CH), 35.4 (CH_2), 35.1 (CH_2), 32.9 (CH_2), 32.2 (CH_2), 27.09 (CH_2), 27.07, (CH_2), 19.6 (CH_2). MS *m*/*z* (%) 502 (M^++4, 34), 500 (M^++2, 67), 498 (M^+, 35), 331 (99), 329 (100). HRMS (EI) calcd for $C_{26}H_{28}Br_2$ *m*/*z* 498.0558 (M^+), found 498.0549. Anal. Calcd for $C_{26}H_{28}Br_2$: C 62.42, H 5.64. Found: C 62.25, H 5.75. X-ray: CCDC 966899.

*4.6.5. 1,2-Di(4-chlorophenyl)tricyclo[8.3.1.0^{3,9}]tetradec-3(9)-ene (**2f**).* White solid. Yield: 1.7 g, 41%. Mp 125–126 °C. IR (KBr, cm^{-1}) 3091, 3020, 2921, 2893, 2849, 1594, 1487, 1450, 1441, 817. ^{1}H NMR (300 MHz, $CDCl_3$, 318 K) δ 7.0 (d, 2H, *J*=8.7 Hz), 6.90 (d, 2H, *J*=8.0 Hz), 6.86 (d, 2H, *J*=8.7 Hz), 6.71 (d, 2H, *J*=8.0 Hz), 3.20 (s, 1H), 2.60–2.52 (m, 1H), 2.45–2.27 (m, 3H), 2.17 (dd, 1H, *J*=8.4, 14.4 Hz), 2.0–1.27 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$, 318 K) δ 148.2 (C), 141.2 (C), 137.3 (C), 136.8 (C), 131.5 (CH), 131.4 (C), 131.0 (C), 127.6 (CH), 127.3 (CH), 127.2 (CH), 59.0 (CH), 41.3 (CH_2), 40.9 (C), 39.1 (CH), 35.4 (CH_2), 35.1 (CH_2), 32.9 (CH_2), 32.3 (CH_2), 27.1 (CH_2), 19.6 (CH_2). MS *m*/*z* (%) 414 (M^++4, 3), 412 (M^++2, 16), 410 (M^+, 25), 152 (69), 125 (100). HRMS (EI) calcd for $C_{26}H_{28}Cl_2$ *m*/*z* 410.1568 (M^+), found 410.1570. Anal. Calcd for $C_{26}H_{28}Cl_2$: C 75.91, H 6.86. Found: C 75.85, H 6.53. X-ray: CCDC 966900.

*4.6.6. 1,2-Di(4-fluorophenyl)tricyclo[8.3.1.0^{3,9}]tetradec-3(9)-ene (**2g**).* White solid. Yield: 1.21 g, 32%. Mp 154–155 °C. IR (KBr, cm^{-1}) 2918, 2903, 2837, 1599, 1509, 1502, 1447, 1237, 1219, 825, 808. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89–6.61 (m, 8H), 3.20 (s, 1H), 2.60–2.50 (m, 1H), 2.41–2.32 (m, 3H), 2.18–2.10 (m, 1H), 2.0–1.52 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.9 (d, C, *J*=242.1 Hz), 160.6 (d, C, *J*=242.1 Hz), 145.5 (d, C, *J*=2.8 Hz), 138.4 (d, C, *J*=2.7 Hz), 137.6 (C), 136.5 (C), 131.8 (CH), 127.1 (d, CH, *J*=7.3 Hz), 114.0 (d, CH, *J*=20.8 Hz), 113.7 (d, CH, *J*=21.2 Hz), 58.8 (CH), 41.2 (CH_2), 40.6 (C), 39.0 (CH), 35.4 (CH_2), 35.1 (CH_2), 33.0 (CH_2), 32.3 (CH_2), 27.10 (CH_2), 27.06 (CH_2), 27.0 (CH_2), 19.5 (CH_2). MS *m*/*z* (%) 378 (M^+, 48), 269 (100), 109 (53). HRMS (EI) calcd for $C_{26}H_{28}F_2$ *m*/*z* 378.2159 (M^+), found 378.2155. Anal. Calcd for $C_{26}H_{28}F_2$: C 82.50, H 7.46. Found: C 82.31, H 7.40. X-ray: CCDC 985976.

4.7. Synthesis of 1-(4-acetylphenyl)-6-bromocycloheptene (7h)

To a stirred solution of compound **3h** (4.0 g, 18.7 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added bromine (1 mL, 18.7 mmol in 10 mL CH_2Cl_2) dropwise from a dropping funnel. The mixture was stirred at 0 °C for 1 h and then warmed to room temperature and stirred for 1 h. The solvent was removed on a rotary evaporator and added 0.1 g silica gel. The mixture was stirred at room temperature for 72 h and the crude material was purified by flash chromatography (hexane) to give white solid **7g** (4.1g, 75%). Mp 62–62.5 °C. IR (KBr, cm^{-1}) 3039, 3003, 2951, 2929, 2906, 2848, 1671, 1600, 1407, 1357, 822. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, 2H, *J*=8.5), 7.41 (d, 2H, *J*=8.5), 6.35 (t, 1H, *J*=7.0), 4.40–4.32 (m, 1H), 3.33–3.21 (m, 2H), 2.59 (s, 3H), 2.57–2.48 (m, 1H), 2.38–2.26 (m, 3H), 1.89–1.77 (m, 1H), 1.61–1.48 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.6 (C), 148.3 (C), 140.3 (C), 135.5 (C), 134.4 (CH), 128.6 (CH), 126.0 (CH), 51.5 (CH), 43.8 (CH_2), 42.5 (CH_2), 28.2 (CH_2), 26.6 (CH_3), 25.6 (CH_2). MS *m*/*z* (%) 294 (M^++2, 60), 292 (M^+, 60), 213 (100), 169 (55). HRMS (EI) calcd for $C_{15}H_{17}BrO$, *m*/*z* 292.0463 (M^+), found 292.0471. Anal. Calcd for $C_{15}H_{17}BrO$: C 61.45, H 5.84. Found: C 61.64, H 6.16.

4.8. Synthesis of 6-bromo-1-(*o*-tolyl)cycloheptene (7i)

To a stirred solution of compound **3i** (4.0 g, 21.5 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added bromine (1.1 mL, 21.5 mmol in 10 mL CH_2Cl_2) dropwise from a dropping funnel. The mixture was stirred at 0 °C for 1 h and then warmed to room temperature and stirred for 1 h. The solvent was removed on a rotary evaporator and added 0.1 g silica gel. The mixture was stirred at room temperature for 72 h and the crude material was purified by flash column chromatography (hexane) to give colorless oil **7h** (4.7g, 82%). IR (KBr, cm^{-1}) 3059, 3016, 2928, 2853, 1484, 1443, 1378, 752. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–7.07 (m, 4H), 5.90 (td, 1H, *J*=6.7, 1.5 Hz), 4.33 (tdd, 1H, *J*=10.5, 3.3, 2.1 Hz), 3.22 (dd, 1H, *J*=14.4, 11.0 Hz), 2.98 (td, 1H, *J*=14.4, 2.1 Hz), 2.67–2.57 (m, 1H), 2.34–2.21 (m, 3H), 2.28 (s, 3H), 1.91–1.80 (m, 1H), 1.63–1.49 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1 (C), 141.8 (C), 134.6 (C), 133.4 (CH), 130.2 (CH), 128.6 (CH), 126.9 (CH), 125.8 (CH), 52.0 (CH), 45.2 (CH_2), 44.4 (CH_2), 28.0 (CH_2), 27.0 (CH_2), 20.3 (CH_3). MS *m*/*z* (%) 266 (M^++2, 77), 264 (M^+, 80), 185 (100), 105 (91). HRMS (EI) calcd for $C_{14}H_{17}Br$, *m*/*z* 264.0514 (M^+), found 264.0511. Anal. Calcd for $C_{14}H_{17}Br$: C 63.41, H 6.46. Found: C 63.54, H 6.50.

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Supplementary data

X-ray crystallographic data for the structure **2a**–**2g** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 966895–966900 and 985976. Full spectroscopic data for all new compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.03.023.

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