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Improved preparative route toward 3-arylcyclopropenes

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ABSTRACT

A convenient preparative protocol for the synthesis of various 3-arylcyclopropenes in a multigram scale is disclosed. Optimization of the reaction conditions and isolation procedures allowed for significant improvement of the chemical yields of these strained products. The described protocol was used for efficient preparation of a series of 3-methyl-3-arylcyclopropenes possessing different substituents in the aromatic ring. The effect of substitution in the aryl group on the stability of 3-arylcyclopropenes, as well as the corresponding precursors, is discussed.

1. Introduction

The chemistry of cyclopropenes has increasingly become a focus of research in the past decade, as these unique synthons often provide an inimitable opportunity for the preparation of stereodefined cyclopropyl scaffolds with otherwise inaccessible substitution patterns.[1] Development of powerful methods for catalytic enantioselective cyclopropenation of alkynes,[2,3] as well as novel efficient protocols for chiral separation[4] and chiral kinetic resolution[5] of racemic cyclopropenes opened new opportunities for the use of optically active cyclopropenes in asymmetric synthesis.[1a,6] On the other hand, several efficient diastereo- and enantioselective transformations involving prochiral C_S-symmetric 3,3-disubsituted cyclopropenes have been recently reported, which highlight the remarkable versatility of these compounds (Scheme 1). They include: the Alder–ene reaction with homochiral alkenes (a);[7] asymmetric carbomagnesation in the presence of chiral amino alcohols (b);[8] iron-catalyzed asymmetric alkylzincation (c);[9] and ROM–CM reaction (d).[10] Furthermore, this type of substrates was also used in the preparation of optically active cyclopropyltins and cyclopropylboronates via the Rh(I)-catalyzed asymmetric hydrometalations (e,f),[11] as well as in catalytic hydroformylation of cyclopropenes (g).[12]

With the growing number of impressive novel methodologies utilizing 3,3-disubstituted cyclopropenes, the question is repeatedly raised as to whether these strained and very reactive synthons can be efficiently prepared in a multigram scale. Herein we disclose a detailed improved synthetic procedure applicable for medium and large scale preparation of a series of 3-arylcyclopropenes. We also comment on the stability and reactivity of 3-arylcyclopropenes, as well as the corresponding precursors, possessing various substituents in the aryl group at C3.

2. Results and discussion

Two general approaches to cyclopropenes unsubstituted at the double bond are depicted in Scheme 2. The first approach involves the Rh-catalyzed [2+1] cycloaddition of carbenoid species to acetylene gas. This method provides rapid access to monosubstituted cyclopropenes possessing an ester function at C3.[13] Alternatively, 3,3-disubstituted ester-containing cyclopropenes can be prepared via the Cu- or Rh-catalyzed reaction between a diazocarbonyl compound and bis-trimethylsilylacetylene or trimethylsilylacetylene, followed by in situ protiodesilylation of the resulting trisubstituted cyclopropene **2** (Scheme 2, Method A).[14] The latter route provides high yields with phenyl diazoacetate and electron poor aryl diazoacetates, however, our experience suggests that it is poorly applicable to the synthesis of analogs possessing electron-donating substituents in the aryl ring. The main problem lies in the poor chemoselectivity of the reaction, which produces significant amounts of fumarates **4** or diazines via the concurrent Rh-catalyzed dimerization of diazoacetate **1**.[15] Furthermore, cyclopropenes **2** possessing electron-rich aryl groups are more prone to partial decomposition in the presence of Rh(II) via the ring expansion into furans **3**.[16]

An alternative synthetic approach toward 3,3-disubstituted cyclopropenes involves a three-step sequence, including initial [2+1] cycloaddition of a dihalocarbene to 1,1-disubstituted olefin **6**,[17] followed by partial reduction of the resulting dibromocyclopropane **7** to afford bromocyclopropane **8**, and 1,2-elimination of HBr with an appropriate base (Scheme 1, Method B). Method B was successfully utilized to assemble cyclopropenes possessing aryl,[18] alkenyl,[19] alkynyl,[20] and ferrocenyl[21] substituents at C3. Furthermore, this protocol was demonstrated to be compatible with

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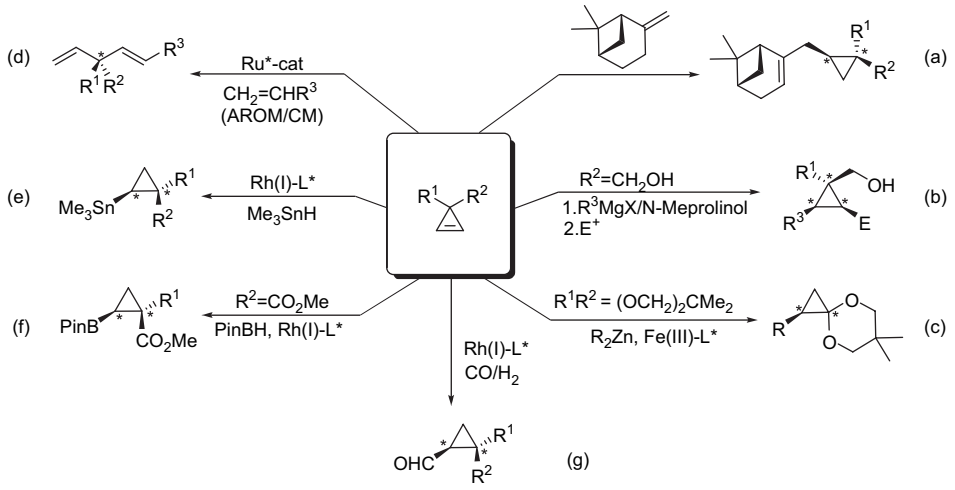
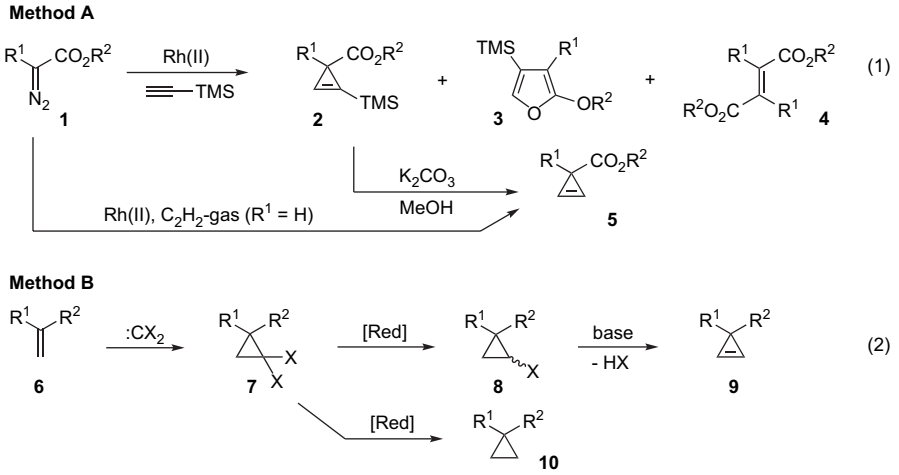


Scheme 1. Asymmetric reactions of prochiral 3,3-disubstituted cyclopropenes.



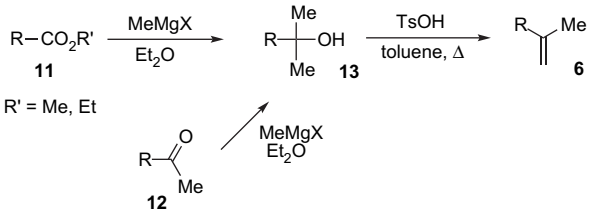
Scheme 2.

several functional groups, such as ethers,[22] silyl ethers,[10] acetals,[11a,23] carboxylates,[11b,24] and nitriles.[25] A few rather exotic compounds containing a spiro-bicyclic scaffold[26] and tethered bis-cyclopropenes[27] were also obtained via this method. Until recently, one substantial limitation of the described approach was the lack of highly selective and general methods for preparative partial reduction of dibromocyclopropanes **7** into monobromides **8**. Although a plethora of various reduction protocols have been developed, most of them provide an insufficient degree of chemoselectivity, as judged by our own experience and the data in the literature.[28] Thus, to avoid product loss associated with purification, the chemoselectivity of the reduction method should exceed 98%. Specifically, the method should allow for complete control over eventual overreduction, which results in inevitable contamination of the target cyclopropene with a cyclopropane side product. A few known highly chemoselective reducing agents, such as $(EtO)_2POH$[29] and Bu_3SnH,[30] are extremely toxic, which becomes a major liability for synthesis scale-up. A viable, more environmentally benign alternative to the latter methods was suggested by Baird and Bolesov who demonstrated the possibility of selective partial reduction of geminal dihalocyclopropanes **7** into monohalocyclopropanes **8** by use of ethylmagnesium bromide in the presence of catalytic amounts of titanium(IV).[31] This reduction protocol was successfully incorporated into Method B and used in the synthesis of a few 3,3-disubstituted cyclopropenes.[10,11,14]

Our studies of novel synthetic transformations involving cyclopropenes[12,32] stimulated us to develop a general and practical approach to a series of 3-arylcyclopropenes possessing differently substituted aromatic ring. It should be mentioned that, although the parent 3-methyl-3-phenylcyclopropene was previously synthesized from the commercially available α-methylstyrene on a multigram scale;[14] no preparative syntheses of analogs functionalized at the aryl group have been reported to date.[33]

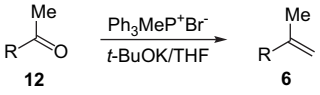
*Synthesis of α-methyl styrenes (**6**).* Multigram scale preparation of diverse 3,3-disubstituted cyclopropenes via the 1,2-elimination protocol (Method B) greatly relies on the availability of the corresponding 1,1-disubstituted olefins. While α-methylstyrene (**3a**) is a monomer industrially produced in a multi-ton scale, the corresponding substituted analogs are not available from commercial sources. Most of styrenes **6** described in this report were prepared from the readily available alkyl benzoates (**11**) or acetophenones (**12**) via a two-step sequence including addition of Grignard reagent followed by the acid-catalyzed dehydration of the resulting tertiary alcohols (**13**) (Scheme 3). Maintaining the temperature around 80 °C during the dehydration step allowed for minimizing the concurrent acid-catalyzed cationic polymerization. The reaction times varied significantly depending on the electronic properties of the substituents at the aromatic ring of styrenes **6**. Thus, substrates possessing electron-rich groups (**13b–e**,**i**) reacted within 1 h, the chlorosubstituted analogs **13f**,**g** required 2–3 h for complete

conversion, while dehydration of the electron poor alcohol **13h** took almost 9 days (Scheme 3). Preparation of olefins highly susceptible to acid-catalyzed cationic polymerization (**6k**,**l**) was carried out via the Wittig olefination (Scheme 4). Although this route is somewhat more expensive, it avoids exposing olefins **6** to strong acid. We found it convenient to carry out steps **11**→**6** without purification, which dramatically expedited the synthesis, and helped to significantly improve the overall yields, mainly by avoiding partial polymerization of olefin **6** upon purification.



6b: R = *p*-MeC_6H_4
6c: R = *m*-MeC_6H_4
6d: R = *o*-MeC_6H_4
6e: R = *p*-(*t*-Bu)C_6H_4
6f: R = *p*-ClC_6H_4
6g: R = *o*-ClC_6H_4
6h: R = *p*-$CF_3C_6H_4$
6i: R = 1-Naphthyl

Scheme 3.

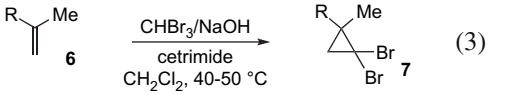


6j: R = *p*-FC_6H_4
6k: R = *p*-$MeOC_6H_4$
6l: R = *o*-$MeOC_6H_4$

Scheme 4.

*Synthesis of dibromocyclopropanes (**7**).* Dibromocyclopropanes **7** were prepared by cyclopropanation of crude olefins **6** with dibromocarbene generated under modified Makosza's PTC conditions[34] (Eq. 3, Table 1). It was found that employment of the addition mode opposite to that originally described by Makosza (i.e., the dropwise addition of concentrated aqueous base solution to a vigorously stirred mixture of the organic components) was also beneficial for the reaction yields. This modification allowed for significantly suppressing the formation of resins and, accordingly, for more efficient isolation of the product. To control the intensive heat release at the initial stages of the reaction, it was found convenient to carry out the reaction in a 1:1 (v/v) mixture of bromoform and dichloromethane, refluxing of which prevented overheating of the reaction mixtures above 40–45 °C. At the later stages of the process, after the intense exothermic effects have ceased, the remaining dichloromethane was boiled off by heating the reaction mixture at 50 °C.

It is well documented that kinetic rates of cyclopropanation under the phase transfer conditions greatly depend on the structure of the phase transfer catalyst. Thus, the highest rates and best conversions are normally obtained with benzyltriethylammonium (TEBA) salts. We found, however, that employment of tetrabutylammonium (TBA) and TEBA salts brings about additional problems with excessive foaming and formation of steady emulsions during aqueous workup, when the reaction is performed in a large scale. In contrast, much better separation of the biphasic solutions was observed when hexadecyl- or tetradecyltrimethylammonium salts were employed as catalysts. As a result, extraction could be done faster and more efficiently, which ultimately provided better overall yields. Isolation of the final product in a large scale was done using short-path vacuum distillation at temperatures below 100 °C. In smaller scale (up to 10 g) a simple filtration through a short pad of silica gel was used instead. Albeit this isolation method does not allow for removal of all the residual bromoform, it was found that small amounts of this impurity do not compromise the next step.[35] Therefore, simple removal of bromoform in vacuum followed by filtration afforded material sufficiently pure to use in the following transformations.



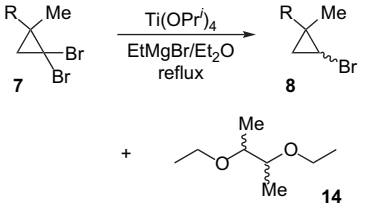
(3)

Table 1
Synthesis of dibromocyclopropanes **7** via [2+1] cycloaddition of dibromocarbene to styrenes

Entry	R		Time, h	Scale, mmol	Isolated yield of **7**, %	
					Based on **6**	Overall
1	Ph	**6a**, **7a**	30	700	92	N/A
2	*p*-MeC_6H_4	**6b**, **7b**	120	55.8	66	56
3	*m*-MeC_6H_4	**6c**, **7c**	36	66.5	73	65
4	*o*-MeC_6H_4	**6d**, **7d**	48	42.7	93	53
5	*p*-(*t*-Bu)C_6H_4	**6e**, **7e**	24	45.0	ND	72
6	*p*-ClC_6H_4	**6f**, **7f**	24	19.0	ND	91
7	*o*-ClC_6H_4	**6g**, **7g**	48	20.0	ND	74
8	*p*-$CF_3C_6H_4$	**6h**, **7h**	216	29.2	75	58
9	1-Naphthyl	**6i**, **7i**	72	28.4	66	61
10	*p*-FC_6H_4	**6j**, **7j**	48	56.4	86	71
11	*p*-$MeOC_6H_4$	**6k**, **7k**	48	61.3	86	79
12	*o*-$MeOC_6H_4$	**6l**, **7l**	48	49.3	70	55

2.1. Partial reduction of dibromocyclopropanes

Reduction of dibromocyclopropanes (Eq. 4, Table 2) was performed according to the previously reported protocol,[31] with a few practical modifications that become essential during scale up. First, since the reaction is accompanied by evolution of gaseous flammable byproducts, including ethylene and ethane, it should be set up in a well-ventilated fume hood. The reaction flask should not be more than one third full and must be equipped with an efficient reflux condenser. This extra space is used as a damper against uneven boiling and sudden splashes, and also proves indispensable during the quench, when a lot of heat and a large volume of gases are evolved. Second, the reaction has a certain initiation period, during which the first 20 mol % of the Grignard reagent, added dropwise, is



(4)

Table 2
Ti-catalyzed partial reduction of dibromocyclopropanes **5** en route to bromocyclopropanes **6**

Entry	R		Scale, mmol	trans/cis ratio[a]	Yield **8**,[b] %
1	Ph	**7a**, **8a**	644	1.2:1	85
2	*p*-MeC_6H_4	**7b**, **8b**	30.8	2.0:1	68
3	*m*-MeC_6H_4	**7c**, **8c**	28.9	2.4:1	64
4	*o*-MeC_6H_4	**7d**, **8d**	39.5	trans only	71
5	*p*-(*t*-Bu)C_6H_4	**7e**, **8e**	34.3	2.6:1	82
6	*p*-ClC_6H_4	**7f**, **8f**	17.4	1.8:1	72
7	*o*-ClC_6H_4	**7g**, **8g**	14.7	5.9:1	84
8	*p*-$CF_3C_6H_4$	**7h**, **8h**	21.5	1.7:1	76
9	1-Naphthyl	**7i**, **8i**	17.3	trans only	80
10	*p*-FC_6H_4	**7j**, **8j**	47.8	1.9:1	75
11	*p*-$MeOC_6H_4$	**7k**, **8k**	52.8	2.3:1	60
12	*o*-$MeOC_6H_4$	**7l**, **8l**	34.3	2.5:1	84

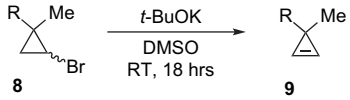
[a] Determined by ^1H NMR.
[b] Isolated yields of mixtures of *trans*-**8** and *cis*-**8**.

being used to reduce the Ti(IV) complex into the Ti(II) species. Complete formation of the catalytically active complex can be judged by the color change from pale-yellow to very dark-brown. This, however, does not always indicate the completion of the activation period, which may take longer, in case the initial addition of the Grignard reagent was carried out too quickly (i.e., much faster than the rate of the Ti(IV)→Ti(II) reduction). In the latter case the risk of violent boiling off and splashing of the reaction mixture dramatically increases. Accordingly, at the initial stages of the reaction it is crucial to maintain a reasonably slow dropwise addition of the Grignard reagent, such as to allow relatively slow boiling of the solvent and evolution of the gaseous byproducts. Finally, the reaction should be carefully monitored by GC analysis to avoid overreduction of the target monobromide **8** into cyclopropane **10** (Eq. 2). The possibility of this side process to occur increases when the exact concentration of the employed Grignard reagent batch is unknown (i.e., it was not titrated prior to use or eventual moisture was present in the reaction mixture). We found it convenient to add ca. 1.1 equiv of EtMgBr using a graduated addition funnel, then allowed the reaction mixture to stir for 15 min, and analyzed it by GC. Additional amount of Grignard reagent, if needed, could be accurately estimated based on GC conversion. In a typical reaction run, the crude reaction mixture would consist of 98–99% of bromocyclopropane **8**, and no more than 1% of the starting material **7** and cyclopropane **10** (Eq. 2). In the perspective of the next step, it is better to leave behind some dibromide **7** rather than to allow overreduction into **10**, since **7** will eventually be destroyed upon treatment with *t*-BuOK during the 1,2-elimination step, while separation of cyclopropene **9** and cyclopropane **10** is essentially impossible. Therefore, if notable amounts of the over reduced product **10** were obtained, monobromide **8** must be purified by vacuum distillation, which also allows for removal of the byproduct **14**, resulting from radical dimerization of diethyl ether (Eq. 4). Purification by column chromatography can be an option, if the reaction is performed in a relatively small scale and side product **10** is present in insignificant amounts. In the latter case it is essential to completely remove any remaining ethereal solvent from the crude product by evaporation in vacuum, as even a small amount of diethyl ether in the mixture affects the polarity of the system and complicates separation. The yields of monobromides **8** were generally high, while the diastereoselectivity depended on the nature of aromatic substituent at C3. Generally, substrates possessing bulky aryl groups, such as *ortho*-substituted phenyls (Table 2, entries 4 and 7) or 1-naphthyl (entry 9) provided higher diastereoselectivities, than those bearing less bulky *para*- or *meta*-substituted arenes. In contrast, both *para*-(**8k**) and *ortho*-(**8l**) anisyl cyclopropanes were obtained as mixtures of trans- and cis-isomers with almost the same ratios (entries 11, 12). In the context of cyclopropene synthesis, however, the diastereoselectivity is not an issue since both diastereomers of **8** are reactive toward dehydrohalogenation.

2.2. Dehydrohalogenation of monobromocyclopropanes

Synthesis of cyclopropenes **9** from monobromocyclopropanes **8** was carried out in anhydrous DMSO in the presence of slight excess of *t*-BuOK (Table 3).[18] It should be mentioned that the reaction is very sensitive to both traces of moisture and oxygen, and must be set-up with appropriate precautions. In all our experiments potassium *tert*-butoxide was stored and handled in the nitrogen-filled glovebox, while Schlenk techniques were used for operations with all other reagents and solvents. The level of oxygen and moisture in the system could be visually monitored by the color of the reaction mixture, which, depending on the substitution pattern, ranged from a baltic blue to dark spruce. The correctly set up reaction develops color very quickly and retains it until completion; however, in the presence of even small amounts of moisture and oxygen the mixture rapidly turns dark brown. The product should be extracted and purified as quickly as possible after completion of the reaction to avoid decomposition. We found that extraction can be carried out under ambient atmosphere, as the product is reasonably stable in solution toward aqueous workup. Removal of solvents after extraction can be carried out using a rotovap; however, upon completion, the rotovap should be filled with inert gas in order to avoid exposure of the concentrated crude product to air. Final purification by distillation should be carried out in vacuum at the highest possible rate, at temperatures below 65 °C. The purified product should be stored in a freezer and handled under inert atmosphere, if prolonged storage is planned. We noticed that accidental brief exposure of arylcyclopropenes to air causes their slow decomposition, potentially, via a free radical-catalyzed polymerization. Thus, when a sample of cyclopropene **9a** was exposed to air for 1 h at room temperature, and then sealed under nitrogen, it completely decomposed within two weeks. Generally, cyclopropenes possessing electron-donating groups (**9b**–**d**, **k**,**l**) were more susceptible to decomposition, while more electron-deficient compounds **9f**–**h**,**j** were significantly more stable.[36] However, with all the above-mentioned precautions the shelf-life of arylcyclopropenes can be extended to more than a year.

Table 3
Synthesis of cyclopropenes **7** via 1,2-dehydrobromination of bromocyclopropanes **6**



8 **9** (5)

Entry	R		Scale, mmol	Bp, °C (Torr)	Yield **9**,[a] %
1	Ph[14]	**8a**, **9a**	540	61–62 (10)	79
2	*p*-MeC_6H_4	**8b**, **9b**	17.8	30–35 (0.4)	77
3	*m*-MeC_6H_4	**8c**, **9c**	18.4	60–61 (5)	76
4	*o*-MeC_6H_4	**8d**, **9d**	27.9	25–29 (0.4)	68
5	*p*-(*t*-Bu)C_6H_4	**8e**, **9e**	34.3	ND[b]	86
6	*p*-ClC_6H_4	**8f**, **9f**	12.5	ND[b]	79
7	*o*-ClC_6H_4	**8g**, **9g**	12.3	ND[b]	86
8	*p*-$CF_3C_6H_4$	**8h**, **9h**	16.3	49–52 (5)	69
9	1-Naphthyl	**8i**, **9i**	17.3	ND[b]	66
10	*p*-FC_6H_4	**8j**, **9j**	47.8	58–61 (10)	76
11	*p*-$MeOC_6H_4$	**8k**, **9k**	25.2	64–65 (5)	82
12	*o*-$MeOC_6H_4$	**8l**, **9l**	28.9	64–65 (5)	92

[a] Isolated yields.
[b] Boiling points were not determined; compounds were isolated by flash column chromatography.

In conclusion, an efficient preparative protocol for synthesis of various 3-arylcyclopropenes in a multigram scale was designed. Optimization of the reaction conditions and isolation procedures allowed for significant improvement of the chemical yields of these strained products. The described protocol was used for efficient preparation of a series of 3-methyl-3-arylcyclopropenes possessing different substituents in the aromatic ring. Further work to expand the scope of this method to 3-alkyl-3-aryl- and 3-alkyl-3-hetaryl-cyclopropenes is currently underway in our laboratories.

3. Experimental section

3.1. Preparation of dibromocyclopropanes 7, typical procedure A

3.1.1. Compound **7f**

Magnesium turnings (1.44 g, 60 mmol) were stirred in anhydrous ether (60 mL) and methyl iodide (3.7 mL) was added dropwise maintaining moderate reflux of the reaction mixture. Then the mixture was stirred for 30 min and ethyl *p*-chlorobenzoate (3.50 g, 19 mmol) in ether (10 mL) was added dropwise. The resulting mixture was stirred for 2 h, then quenched with saturated aqueous

NH_4Cl and extracted with ether. Combined ethereal layers were washed consecutively with 5% aqueous HCl, 10% $NaHCO_3$, and brine, dried with $MgSO_4$, filtered, and concentrated. The residue was dissolved in toluene (50 mL), *p*-toluenesulfonic acid (100 mg) was added, and the mixture was stirred at reflux for 2 h. When GC analysis showed the reaction complete, the mixture was cooled to room temperature, and quenched with aqueous $NaHCO_3$. The organic phase was separated, aqueous layer was extracted with ethyl acetate (2×30 mL). The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated. To the vigorously stirred solution of the resulting residue, bromoform (61 mmol, 4.9 mL), and cetrimide (100 mg) in dichloromethane (20 mL), 50% aqueous solution of NaOH (5 mL) was added dropwise. The stirring at room temperature was continued for 24 h, when GC analysis showed the reaction complete. Then the mixture was quenched with water (100 mL) and extracted with dichloromethane (3×50 mL). Combined organic phases were washed consecutively with dilute aqueous HCl, water, and brine, then dried with $MgSO_4$, filtered, and concentrated in vacuum. Flash column chromatography of the residual oil on silica gel (eluent–hexane) gave dibromocyclopropane **7f** as colorless oil. Overall yield 5.63 g (17.4 mmol, 91%). ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.36 (d, J=8.0 Hz, 2H), 7.26 (d, J=8.0 Hz, 2H), 2.15 (d, J=7.6 Hz, 1H), 1.81 (d, J=7.6 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 140.8, 133.0, 129.9 (+, 2C), 128.6 (+, 2C), 36.0, 35.2, 33.8 (−), 27.5 (+). GC/MS (EI 70 eV) 12.01 min, m/z 324 (M^+, <1%), 309 (M−Me, 1%)$^+$, 245 (34%), 163 (55%), 129 (100%); HRMS (TOF-ES) found 242.9578, calcd for $C_{10}H_9BrCl$ (M−Br) 242.9576 (0.1 ppm).

3.1.2. Compound **7b**[37]

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.25 (d, J=8.3 Hz, 2H), 7.22 (d, J=8.3 Hz, 2H), 2.40 (s, 3H), 2.19 (d, J=7.6 Hz, 1H), 1.81 (d, J=7.6 Hz, 1H), 1.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.67 MHz) δ 139.3, 136.9, 129.1 (+, 2C), 128.3 (+, 2C), 37.1, 35.4, 33.7 (+), 27.7 (−), 21.2 (+); HRMS (TOF-ES) found 223.0122, calcd for $C_{11}H_{12}Br$ (M−Br) 223.0122 (0.0 ppm).

3.1.3. Compound **7c**

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.28 (t, J=7.8 Hz, 1H), 7.15 (s, 1H), 7.14 (d, J=7.8 Hz, 2H), 2.41 (s, 3H), 2.19 (d, J=7.6 Hz, 1H), 1.80 (d, J=7.6 Hz, 1H), 1.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.67 MHz) δ 142.2, 138.0, 129.2 (+), 128.2 (+), 128.0 (+), 125.5 (+), 36.9, 35.7, 33.7 (−), 27.8 (+), 21.5 (+); HRMS (TOF-ES) found 223.0114, calcd for $C_{11}H_{12}Br$ (M−Br) 223.0122 (3.6 ppm).

3.1.4. Compound **7d**[38]

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.29 (d, J=7.6 Hz, 1H), 7.25 (ps.-t, J=7.6, 7.1 Hz, 1H), 7.19 (ps.-t, J=7.3, 7.1 Hz, 1H), 7.13 (d, J=7.3 Hz, 1H), 2.58 (s, 3H), 2.14 (d, J=7.3 Hz, 1H), 1.84 (d, J=7.3 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.67 MHz) δ 140.9, 137.6, 130.8 (+), 128.4 (+), 127.3 (+), 126.0 (+), 37.7, 35.8, 34.4 (−), 25.7 (+), 20.0 (+).

3.1.5. Compound **7e**

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.40 (d, J=8.3 Hz, 2H), 7.26 (d, J=8.3 Hz, 2H), 2.19 (d, J=7.6 Hz, 1H), 1.80 (d, J=7.6 Hz, 1H), 1.74 (s, 3H), 1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 100.67 MHz) δ 150.0, 139.2, 128.0 (+, 2C), 125.2 (+, 2C), 37.1, 35.3, 34.5, 33.7 (+), 31.4 (+, 3C), 27.7 (−); HRMS (TOF-ES) found 265.0588, calcd for $C_{14}H_{18}Br$ (M−Br) 265.0592 (1.5 ppm).

3.1.6. Compound **7g**

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ major atropomer: 7.47 (m, 1H), 7.28–7.24 (m, 2H), 7.20 (m, 1H), 2.11 (d, J=7.6 Hz, 1H), 1.84 (d, J=7.6 Hz, 1H), 1.75 (s, 3H); minor atropomer: 7.59 (dd, J=7.6, 1.8 Hz, 1H), 7.38 (dd, J=7.7, 1.3 Hz, 1H), 7.33 (td, J=7.6, 1.3 Hz, 1H), 7.28 (m, 1H), 2.21 (d, J=8.1 Hz, 1H), 2.05 (d, J=8.1 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ major atropomer: 140.4, 135.2, 130.2 (+), 130.0 (+), 128.7 (+), 127.0 (+), 36.2, 35.6, 34.3 (−), 24.5 (+); minor atropomer: 138.8, 134.1, 132.7 (+), 130.1 (+), 128.5 (+), 126.4 (+), 37.5 (−), 36.2, 34.1, 27.1 (+); GC/MS (EI 70 eV) 11.75 min, m/z 324 (M^+, <1%), 309 (M−Me, 3%)$^+$, 245 (35%), 163 (58%), 129 (100%); HRMS (TOF-ES) found 242.9576, calcd for $C_{10}H_9BrCl$ (M−Br) 242.9576 (0.0 ppm).

3.1.7. Compound **7h**

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.65 (d, J=8.3 Hz, 2H), 7.46 (d, J=8.3 Hz, 2H), 2.21 (d, J=7.6 Hz, 1H), 1.87 (d, J=7.6 Hz, 1H), 1.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.67 MHz) δ 146.2, 129.5 (q, $^2J_{CF}$=32.9 Hz), 129.0 (+, 2C), 125.4 (q, $^3J_{CF}$=3.7 Hz, +, 2C), 124.1 (q, $^1J_{CF}$=272.3 Hz), 35.5, 35.2, 33.8 (−), 27.5 (+); ^{19}F NMR ($CDCl_3$, 376.50 MHz) δ −62.4; HRMS (TOF-ES) found 276.9843, calcd for $C_{11}H_9BrF_3$ (M−Br) 276.9840 (1.1 ppm).

3.1.8. Compound **7i**

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 8.23 (d, J=8.6 Hz, 1H), 7.96 (d, J=8.1 Hz, 1H), 7.85 (d, J=8.1 Hz, 1H), 7.71 (ps.-t, J=7.3, 7.1 Hz, 1H), 7.59 (t, J=7.3 Hz, 1H), 7.46 (ps.-t, J=7.8, 7.3 Hz, 1H), 7.36 (d, J=7.1 Hz, 1H), 2.31 (d, J=7.6 Hz, 1H), 2.01 (d, J=7.6 Hz, 1H), 1.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.67 MHz) δ 139.7, 134.0, 131.4, 128.6 (+), 128.0 (+), 126.2 (+), 126.0 (+), 125.9 (+, 2C), 125.4 (+), 37.3, 35.4, 34.4 (−), 27.0 (+); HRMS (TOF-ES) found 259.0130, calcd for $C_{14}H_{12}Br$ (M−Br) 259.0122 (3.1 ppm).

3.2. Preparation of dibromocyclopropanes 7 from acid-sensitive styrenes, alternative procedure B

3.2.1. Compound **7j**

To a stirred at 0 °C suspension of methyltriphenylphosphonium bromide (41.37 g, 115.8 mmol, 1.6 equiv) in anhydrous THF (175 mL) was added dropwise solution of potassium *tert*-butoxide (7.76 g, 69.13 mmol, 0.955 equiv) The resulting yellow suspension was stirred for 1 h at 0 °C, then *p*-fluoroacetophenone (10.0 g, 8.7 mL, 72.39 mmol) was added dropwise. The mixture was stirred overnight, then quenched with aqueous NH_4Cl, and partitioned between water and diethyl ether. The ethereal extract was dried with Na_2SO_4, filtered, and concentrated. The residue was purified by short column chromatography (eluent–hexane) to afford *p*-fluoro-α-methylstyrene (**10e**) as a colorless oil. Yield 7.68 g (56.4 mmol, 82%). This material without further purification was mixed with bromoform (25.22 g, 8.7 mL, 99.8 mmol, 1.66 equiv), benzyltriethylammonium chloride (TEBAC) (117 mg, 0.51 mmol, 0.85 mol %), and dichloromethane (20 mL). The mixture was vigorously stirred and 50% aqueous solution of sodium hydroxide was added dropwise. The mixture was stirred (900–1100 rpm) overnight at 30–35 °C, when GC/MS analysis indicated full conversion of the olefin. Then, the mixture was quenched with water (100 mL) and extracted with dichloromethane (3×50 mL). Combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel, eluting with hexane. Yield 14.63 g (50.97 mmol, 86%). ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.31 (dd, J=8.3 Hz, $^4J_{HF}$=5.3 Hz, 2H), 7.07 (ps.-t, J=$^3J_{HF}$=8.3 Hz, 2H), 2.16 (d, J=7.6 Hz, 1H), 1.82 (d, J=7.6 Hz, 1H), 1.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 161.8 (d, $^1J_{CF}$=245.9 Hz), 138.1 (d, $^4J_{CF}$=3.7 Hz), 130.1 (d, $^3J_{CF}$=8.1 Hz, +, 2C), 115.3 (d, $^2J_{CF}$=21.2 Hz, +, 2C), 36.4, 35.1, 33.8 (−), 27.7 (+); HRMS (TOF-ES) found 226.9872, calcd for $C_{10}H_9BrF$ (M−Br) 226.9872 (1.3 ppm).

3.2.2. Compound **7k**[18]

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.25 (d, J=8.6 Hz, 2H), 6.92 (d, J=8.6 Hz, 2H), 3.84 (s, 3H), 2.15 (d, J=7.6 Hz, 1H), 1.78 (d, J=7.6 Hz, 1H), 1.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 158.6, 134.5, 129.5 (+, 2C), 113.7 (+, 2C), 55.2 (+), 37.4, 35.1, 33.7 (−), 27.7 (+).

3.2.3. Compound ***7l***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.32 (td, J=7.8, 1.8 Hz, 1H), 7.09 (dd, J=7.6, 1.8 Hz, 1H), 6.97 (d, J=8.3 Hz, 1H), 6.95 (ps.-t, J=8.3, 7.6 Hz, 1H), 3.99 (s, 3H), 2.05 (d, J=7.6 Hz, 1H), 1.77 (d, J=7.6 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 158.1, 131.2, 128.9 (+), 128.6 (+), 120.4 (+), 110.8 (+), 55.6 (+), 37.5, 34.1 (−), 34.0, 24.6 (+); HRMS (TOF-ES) found 239.0072, calcd for $C_{11}H_{12}BrO$ (M−Br) 239.0072 (0.0 ppm).

3.3. Partial reduction of dibromocyclopropanes, typical procedure

3.3.1. Compound ***8f***

To a stirred solution of dibromocyclopropane **7f** (5.63 g, 17.4 mmol) and titanium (IV) isopropoxide (10 mol %, 1.7 mmol, 490 μL) in anhydrous diethyl ether (50 mL) was added dropwise 3 M solution of ethylmagnesium bromide (21 mmol, 7.0 mL). When intensive gas evolution had ceased, the mixture was stirred at room temperature for 2 h, then cooled in an ice bath and quenched by consecutive addition of water (10 mL) and 10% aqueous sulfuric acid (20 mL). Organic phase was separated and aqueous layer was extracted with ether (3×25 mL). Combined ethereal phases were washed consecutively with 10% aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, filtered, and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (eluent–hexane) to afford bromocyclopropane **8f** as colorless oil (mixture of two diastereomers 1.8:1).[39] Yield 3.08 g (12.5 mmol, 72%). ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ major: 7.29 (d, J=8.3 Hz, 2H), 7.21 (d, J=8.3 Hz, 2H), 3.20 (dd, J=8.0, 4.8 Hz, 1H), 1.64 (ps.-t, J=8.0, 7.2 Hz, 1H), 1.62 (s, 3H), 3.20 (dd, J=7.2, 4.8 Hz, 1H); minor: 7.35 (d, J=8.3 Hz, 2H), 7.28 (d, J=8.3 Hz, 2H), 3.11 (dd, J=7.4, 4.5 Hz, 1H), 1.46 (s, 3H), 1.41 (ps.-t, J=7.4, 6.8 Hz, 1H), 1.37 (dd, J=6.8, 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ major: 142.9, 132.2, 128.6 (+, 2C), 128.4 (+, 2C), 30.1 (+), 25.3, 23.8 (+), 23.3 (−); minor: 140.7, 132.5, 130.7 (+, 2C), 128.3 (+, 2C), 27.9 (+), 27.0, 26.8 (+), 22.2; GC/MS (EI 70 eV) major: 10.80 min, m/z 246 (M^+, <1%), 165 (M−Br, 100%); minor: 10.65 min, m/z 246 (M^+, <1%), 165 (M−Br, 100%), HRMS (TOF-ES) found 165.0047, calcd for $C_{10}H_{10}Cl$ (M−Br) 165.0470 (0.6 ppm).

3.3.2. Compound ***8b***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ major: 7.17 (d, J=8.3 Hz, 2H), 7.14 (d, J=8.3 Hz, 2H), 3.23 (dd, J=7.8, 4.3 Hz, 1H), 2.35 (s, 3H), 1.65 (ps.-t, J=7.8, 6.5 Hz, 1H), 1.62 (s, 3H), 1.07 (dd, J=6.5, 4.6 Hz, 1H); minor: 7.25 (d, J=8.1 Hz, 2H), 7.20 (d, J=8.1 Hz, 2H), 3.11 (dd, J=7.2, 4.6 Hz, 1H), 2.38 (s, 3H), 1.47 (s, 3H), 1.40–1.37 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ major 141.5, 136.1, 129.2 (+, 2C), 126.9 (+, 2C), 30.6 (+), 25.4, 24.0 (+), 23.2 (−), 21.0 (+); minor 139.2, 136.3, 129.2 (+, 2C), 128.9 (+, 2C), 28.4 (+), 27.2, 27.0 (+), 22.1 (−), 21.1 (+); HRMS (TOF-ES) found 223.0121, calcd for $C_{11}H_{12}Br$ (M−H) 223.0122 (0.4 ppm).

3.3.3. Compound ***8c***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ major: 7.36–7.11 (m, 4H), 3.31 (dd, J=8.1, 4.8 Hz, 1H), 2.43 (s, 3H), 1.72 (ps.-t, J=8.1, 6.3 Hz, 1H), 1.70 (s, 3H), 1.14 (dd, J=6.3, 4.8 Hz, 1H); minor: 7.36–7.11 (m, 4H), 3.15 (dd, J=7.6, 4.3 Hz, 1H), 2.47 (s, 3H), 1.53 (s, 3H), 1.48–1.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ major: 144.4, 138.1, 128.4 (+), 127.8 (+), 127.2 (+), 124.0 (+), 30.6 (+), 27.0 (+), 25.7, 24.0 (+), 23.2 (−); minor: 142.0, 137.6, 130.1 (+), 128.0 (+), 127.6 (+), 126.4 (+), 28.3 (+), 27.5 (+), 22.0 (−), 21.5, 21.4 (+); HRMS (TOF-ES) found 223.0123, calcd for $C_{11}H_{12}Br$ (M−H) 223.0122 (0.4 ppm).

3.3.4. Compound ***8d***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.24–7.21 (m, 1H), 7.18–7.14 (m, 3H), 3.22 (dd, J=8.1, 4.6 Hz, 1H), 2.43 (s, 3H), 1.57 (ps.-t, J=8.1, 6.3 Hz, 1H), 1.52 (s, 3H), 1.09 (dd, J=6.3, 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 142.7, 137.2, 130.6 (+), 128.9 (+), 126.9 (+), 126.0 (+), 30.8 (+), 26.1, 23.3 (+), 23.2 (−), 19.3 (+); HRMS (TOF-ES) found 208.9958, calcd for $C_{10}H_{10}Br$ (M−Me) 208.9966 (3.8 ppm).

3.3.5. Compound ***8e***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ major: 7.41 (d, J=8.3 Hz, 2H), 7.26 (d, J=8.3 Hz, 2H), 3.30 (dd, J=7.8, 4.8 Hz, 1H), 1.73 (dd, J=7.8, 6.3 Hz, 1H), 1.42 (s, 3H), 1.40 (s, 9H), 1.14 (dd, J=6.3, 4.8 Hz, 1H); minor 7.45 (d, J=8.3 Hz, 2H), 7.34 (d, J=8.3 Hz, 2H), 3.16 (dd, J=7.3, 4.3 Hz, 1H), 1.70 (s, 3H), 1.47–1.43 (m, 2H), 1.42 (s, 9H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ major: 149.3, 141.3, 126.5 (+, 2C), 125.4 (+, 2C), 34.4, 31.3 (+, 3C), 30.7 (+), 25.1, 23.8 (+), 23.4 (−); minor: 149.4, 139.0, 128.9 (+, 2C), 125.0 (+, 2C), 34.4, 31.4 (+, 3C), 28.5 (+), 27.1, 27.0 (+), 22.1 (−); HRMS (TOF-ES) found 187.1491, calcd for $C_{14}H_{19}$ (M−Br) 187.1487 (2.1 ppm).

3.3.6. Compound ***8g***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ major: 7.40–7.37 (m, 1H), 7.34–7.31 (m, 1H), 7.26–7.18 (m, 2H), 3.28 (dd, J=8.3, 4.9 Hz, 1H), 1.61 (dd, J=8.3, 6.2 Hz, 1H), 1.59 (s, 3H), 1.16 (dd, J=6.2, 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ major: 141.9, 135.0, 130.5 (+), 129.9 (+), 128.2 (+), 126.9 (+), 30.3 (+), 26.1, 23.4 (−), 22.6 (+); HRMS (TOF-ES) found 165.0478, calcd for $C_{10}H_{10}Cl$ (M−Br) 165.0471 (4.2 ppm).

3.3.7. Compound ***8h***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ major: 7.59 (d, J=8.2 Hz, 2H), 7.39 (d, J=8.2 Hz, 2H), 3.24 (dd, J=8.1, 4.8 Hz, 1H), 1.71 (dd, J=8.1, 6.6 Hz, 1H), 1.66 (s, 3H), 1.17 (dd, J=6.6, 4.8 Hz, 1H); minor: 7.64 (d, J=8.0 Hz, 2H), 7.47 (d, J=8.0 Hz, 2H), 3.14 (dd, J=7.5, 4.4 Hz, 1H), 1.50 (s, 3H), 1.47 (dd, J=7.5, 6.6 Hz, 1H), 1.43 (dd, J=6.6, 4.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.67 MHz) δ major: 148.4, 128.8 (q, $^2J_{CF}$=32.9 Hz), 127.4 (+, 2C), 125.5 (q, $^3J_{CF}$=3.7 Hz, +, 2C), 124.1 (q, $^1J_{CF}$=272.3 Hz), 30.0 (+), 25.6, 23.54 (+), 23.49 (−); minor: 146.2, 129.8 (+, 2C), 129.0 (q, $^2J_{CF}$=32.9 Hz), 125.2 (q, $^3J_{CF}$=3.7 Hz, +, 2C), 124.1 (q, $^1J_{CF}$=271.5 Hz), 27.5 (+), 26.6 (+), 25.6, 22.3 (−); ^{19}F NMR ($CDCl_3$, 376.50 MHz) δ major: −62.44; minor: −62.37; GC/MS: major (t_R=9.40 min) 278 (M^+, <1%), 259 (M^+−F, 1%), 209 (M^+−CF_3, 1%), 199 (M^+−Br, 100%); minor (t_R=9.22 min) 278 (M^+, <1%), 259 (M^+−F, 1%), 209 (M^+−CF_3, 1%), 199 (M^+−Br, 100%). HRMS (TOF-ES) found 199.0734, calcd for $C_{11}H_{10}F_3$ (M−Br) 199.0735 (0.5 ppm).

3.3.8. Compound ***8i***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 8.24 (d, J=8.3 Hz, 1H), 7.91 (d, J=8.1 Hz, 1H), 7.79 (dd, J=6.3, 3.3 Hz, 1H), 7.63 (td, J=8.3, 1.7 Hz, 1H), 7.55 (td, J=8.1, 1.0 Hz, 1H), 7.46–7.43 (m, 2H), 3.39 (d, J=8.1, 4.5 Hz, 1H), 1.75 (s, 3H), 1.76 (m, 1H), 1.28 (dd, J=6.3, 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 141.1, 134.0, 131.6, 128.8 (+), 127.6 (+), 126.3 (+), 126.0 (+), 125.7 (+), 125.5 (+), 124.8 (+), 30.8 (+), 25.6, 24.2 (+), 23.1 (−); HRMS (TOF-ES) found 181.1014, calcd for $C_{14}H_{13}$ (M−Br) 181.1017 (1.7 ppm).

3.3.9. Compound ***8j***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ major: 7.25 (dd, J=8.6 Hz, $^4J_{HF}$=5.3 Hz, 2H), 7.02 (ps.-t, J=$^3J_{HF}$=8.6 Hz, 2H), 3.22 (dd, J=7.8, 4.8 Hz, 1H), 1.64 (dd, J=7.8, 6.3 Hz, 1H), 1.62 (s, 3H), 1.10 (dd, J=6.3, 4.8 Hz, 1H); minor: 7.31 (dd, J=8.8 Hz, $^4J_{HF}$=5.6 Hz, 2H), 7.07 (ps.-t, J=$^3J_{HF}$=8.8 Hz, 2H), 3.11 (dd, J=7.3, 4.3 Hz, 1H), 1.47 (s, 3H), 1.41 (dd, J=7.3, 6.8 Hz, 1H), 1.37 (dd, J=6.8, 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ major: 161.4 (d, $^1J_{CF}$=245.2 Hz), 140.2 (d, $^4J_{CF}$=2.9 Hz), 128.7 (d, $^3J_{CF}$=8.1 Hz, +, 2C), 115.3 (d, $^2J_{CF}$=21.2 Hz, +, 2C), 30.1 (+), 25.3, 24.1 (+), 23.2 (−); minor: 161.6 (d, $^1J_{CF}$=245.2 Hz), 138.0 (d, $^4J_{CF}$=3.7 Hz), 130.9 (d, $^3J_{CF}$=8.1 Hz, +, 2C), 115.0 (d, $^2J_{CF}$=21.2 Hz, +, 2C), 28.1 (+), 26.97 (+), 26.94, 22.3 (−); HRMS (TOF-ES) found 149.0767, calcd for $C_{10}H_{10}F$ (M−Br) 149.0767 (0.7 ppm).

3.3.10. Compound ***8k***[18]

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ major: 7.20 (d, J=8.7 Hz, 2H), 6.87 (d, J=8.7 Hz, 2H), 3.82 (s, 3H), 3.22 (dd, J=8.3, 4.8 Hz, 1H), 1.63 (dd, J=8.7, 4.1 Hz, 1H), 1.62 (s, 3H), 1.07 (dd, J=6.1, 4.8 Hz, 1H); minor: 7.28 (d, J=8.7 Hz, 2H), 6.93 (d, J=8.7 Hz, 2H), 3.84 (s, 3H), 3.11 (ps.-t), 1.46 (s, 3H), 1.37 (d, J=5.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ major: 158.2, 136.6, 128.1 (+, 2C), 113.9 (+, 2C), 55.3 (+), 30.5 (+), 25.2, 24.2 (+), 23.2 (−); minor: 158.3, 134.4, 130.4 (+, 2C), 113.5 (+, 2C), 55.1 (+), 28.7 (+), 27.1 (+), 26.9, 22.2 (−).

3.3.11. Compound ***8l***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ major: 7.29–7.23 (m, 2H), 6.96 (t, J=7.5 Hz, 1H), 6.91 (d, J=8.1 Hz, 1H), 3.92 (s, 3H), 3.25 (dd, J=7.8, 4.8 Hz, 1H), 1.57 (s, 3H), 1.54 (ps.-t, J=7.8, 6.1 Hz, 1H), 1.07 (dd, J=6.1, 4.8 Hz, 1H); minor: 7.35–7.26 (m, 2H), 7.01–6.96 (m, 2H), 3.93 (s, 3H), 3.17 (dd, J=7.6, 4.3 Hz, 1H), 1.46 (s, 3H), 1.39 (dd, J=7.6, 6.3 Hz, 1H), 1.31 (dd, J=6.3, 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ major: 158.3, 132.6, 129.4 (+), 128.0 (+), 120.3 (+), 110.6 (+), 55.29 (+), 30.6 (+), 23.6, 22.84 (+), 22.78 (−); minor: 158.6, 130.7 (+), 130.5, 128.2 (+), 120.2 (+), 110.7 (+), 55.32 (+), 28.4 (+), 25.4, 24.3 (+), 22.6 (−); HRMS (TOF-ES) found 161.0968, calcd for $C_{11}H_{13}O$ (M−Br) 161.0966 (1.2 ppm).

3.4. Synthesis of cyclopropenes, typical procedure

3.4.1. Compound ***9f***

Bromocyclopropane **8f** (3.08 g, 12.5 mmol) was added dropwise to a stirred solution of *t*-BuOK (1.68 g, 15 mmol) in anhydrous DMSO (20 mL). The resulting mixture was stirred at room temperature overnight, quenched with water (150 mL), and then extracted with ether (3×50 mL). Combined organic phases were washed consecutively with water (3×50 mL) and brine (50 mL), dried with $MgSO_4$, filtered, and concentrated. Flash column chromatography of a residue[40] (eluent–hexane) afforded cyclopropene **9f** as colorless oil. Yield 1.62 g (9.8 mmol, 79%). ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.28 (d, J=8.6 Hz, 2H), 7.28 (s, 2H), 7.17 (d, J=8.6 Hz, 2H), 1.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 148.5, 130.7, 127.7 (+, 2C), 127.4 (+, 2C), 115.3 (+, 2C), 25.2 (+), 21.4; HRMS (TOF-ES) found 165.0480, calcd for $C_{10}H_{10}^{35}Cl$ (M+H) 165.0471 (5.5 ppm).

3.4.2. Compound ***9b***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.37 (s, 2H), 7.23 (s, 4H), 2.45 (s, 3H), 1.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 146.9, 134.4, 128.5 (+, 2C), 125.9 (+, 2C), 115.7 (+, 2C), 25.5 (+), 21.5, 20.8 (+); HRMS (TOF-ES) found 145.1023, calcd for $C_{11}H_{13}$ (M+H) 145.1017 (4.1 ppm).

3.4.3. Compound ***9c***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.31 (s, 2H), 7.26 (t, J=7.6 Hz, 1H), 7.11–7.09 (m, 2H), 7.05 (d, J=7.6 Hz, 1H), 2.41 (s, 3H), 1.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 149.9, 137.3, 127.7 (+), 126.8 (+), 125.8 (+), 123.1 (+), 115.5 (+, 2C), 25.5 (+), 21.7, 21.5 (+); HRMS (TOF-ES) found 143.0866, calcd for $C_{11}H_{11}$ (M−H) 143.0861 (3.5 ppm).

3.4.4. Compound ***9d***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.77 (s, 2H), 7.30–7.19 (m, 4H), 2.56 (s, 3H), 1.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 147.6, 135.6, 130.3 (+), 127.5 (+), 126.2 (+), 125.9 (+), 121.4 (+, 2C), 28.2 (+), 23.5, 19.1 (+); HRMS (TOF-ES) found 145.1019, calcd for $C_{11}H_{13}$ (M+H) 145.1017 (1.4 ppm).

3.4.5. Compound ***9e***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.46 (d, J=8.6 Hz, 2H), 7.36 (s, 2H), 7.30 (d, J=8.6 Hz, 2H), 1.76 (s, 3H), 1.45 (s, 9H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 147.7, 146.9, 125.7 (+, 2C), 124.7 (+, 2C), 115.5 (+, 2C), 34.3, 31.4 (+, 3C), 25.4 (+), 21.4; HRMS (TOF-ES) found 159.1179, calcd for $C_{12}H_{15}$ (M−Me) 159.1174 (3.1 ppm).

3.4.6. Compound ***9g***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.70 (s, 2H), 7.34 (dd, J=7.8, 1.3 Hz, 1H), 7.30 (dd, J=7.5, 1.8 Hz, 1H), 7.22 (td, J=7.4, 1.3 Hz, 1H), 7.15 (td, J=7.8, 1.8 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 146.6, 133.6, 129.6 (+), 129.3 (+), 127.2 (+), 127.1 (+), 120.6 (+, 2C), 27.3 (+), 23.7; HRMS (TOF-ES) found 165.0476, calcd for $C_{10}H_{10}^{35}Cl$ (M+H) 165.0471 (3.0 ppm).

3.4.7. Compound ***9h***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.56 (d, J=8.3 Hz, 2H), 7.34 (d, J=8.3 Hz, 2H), 7.28 (s, 2H), 1.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 154.1, 127.2 (q, $^2J_{CF}$=32.2 Hz), 126.3 (+, 2C), 124.7 (q, $^3J_{CF}$=3.7 Hz, +, 2C), 124.5 (q, $^1J_{CF}$=271.5 Hz), 114.9 (+, 2C), 25.01 (+), 21.9; ^{19}F NMR ($CDCl_3$, 376.50 MHz) δ major: −62.1; HRMS (TOF-ES) found 179.0677, calcd for $C_{11}H_9F_2$ (M−F) 179.0672 (2.8 ppm).

3.4.8. Compound ***9i***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 8.47 (d, J=8.6 Hz, 1H), 7.94 (d, J=8.1 Hz, 1H), 7.91 (s, 2H), 7.77 (d, J=7.6 Hz, 1H), 7.63 (ps.-t, J=7.8, 7.1 Hz, 1H), 7.56 (ps.-t, J=7.6, 7.3 Hz, 1H), 7.50–7.44 (m, 2H), 1.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 146.3, 134.0, 130.1, 128.8 (+), 126.4 (+), 126.0 (+), 125.5 (+), 125.4 (+), 124.8 (+), 124.0 (+), 121.2 (+, 2C), 29.1 (+), 23.0; HRMS (TOF-ES) found 147.0609, calcd for $C_{10}H_8F$ (M−H) 147.0610 (0.7 ppm).

3.4.9. Compound ***9j***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.31 (s, 2H), 7.22 (dd, J=8.8 Hz, $^4J_{HF}$=5.3 Hz, 2H), 7.02 (ps.-t, J=$^3J_{HF}$=8.8 Hz, 2H), 1.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 160.8 (d, $^1J_{CF}$=243.0 Hz), 145.6 (d, $^4J_{CF}$=2.9 Hz), 127.4 (d, $^3J_{CF}$=8.1 Hz, +, 2C), 115.7 (+, 2C), 114.4 (d, $^2J_{CF}$=21.2 Hz, +, 2C), 25.5 (+), 21.4; ^{19}F NMR ($CDCl_3$, 376.50 MHz) δ −119.0; HRMS (TOF-ES) found 180.0931, calcd for $C_{14}H_{12}$ (M^+) 180.0939 (4.4 ppm).

3.4.10. Compound ***9k***[18]

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.33 (s, 2H), 7.20 (d, J=8.8 Hz, 2H), 6.91 (d, J=8.8 Hz, 2H), 3.85 (s, 3H), 1.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 157.2, 142.1, 126.9 (+, 2C), 116.0 (+, 2C), 113.2 (+, 2C), 55.2 (+), 25.6 (+), 21.2; HRMS (TOF-ES) found 161.0968, calcd for $C_{11}H_{13}O$ (M+H) 161.0966 (1.2 ppm).

3.4.11. Compound ***9l***

^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.70 (s, 2H), 7.22 (td, J=8.1, 2.0 Hz, 1H), 7.19 (dd, J=7.1, 1.8 Hz, 1H), 6.94 (td, J=7.3, 1.0 Hz, 1H), 6.90 (d, J=8.1 Hz, 1H), 3.93 (s, 3H), 1.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.61 MHz) δ 157.8, 137.6, 128.3 (+), 126.9 (+), 121.0 (+, 2C), 120.6 (+), 110.8 (+), 55.2 (+), 27.7 (+), 21.3; HRMS (TOF-ES) found 161.0970, calcd for $C_{11}H_{13}O$ (M+H) 161.0966 (2.5 ppm).

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Supplementary data

Experimental details are provided. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2008.06.087.

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