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Reactions of vinylidenecyclopropanes with xanthydrol and xanthene

Wei Yuan, Min Shi *

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032 China

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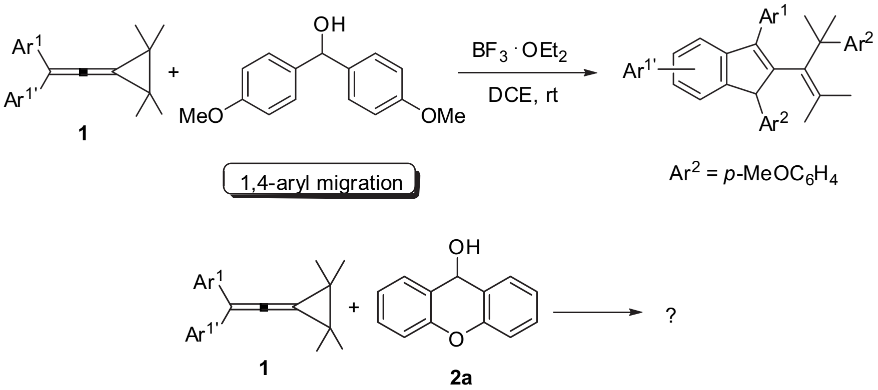
ABSTRACT

Vinylidenecyclopropanes undergo ring-opening reactions with xanthydrol in the presence of $BF_3\cdot OEt_2$ or with xanthene in the presence of DDQ at 0 °C in 1,2-dichloroethane to give the corresponding conjugate triene derivatives in moderate to good yields. Plausible reaction mechanisms have been discussed on the basis of previous literature and the control experiments. The further transformation of these trienes has been disclosed in DCE in the presence of $BF_3\cdot OEt_2$ along with a plausible reaction mechanism.

1. Introduction

Vinylidenecyclopropanes (VDCPs) **1**, which have strained cyclopropyl group connected with an allene moiety and yet are thermally stable and reactive substances in organic chemistry, are versatile intermediates in organic synthesis.[1] Thus far, many novel transformations of these interesting highly strained small molecules have been disclosed by many organic chemists. For example, we and others have recently been investigating the Lewis acid/transition metal-mediated/catalyzed ring-opening reactions of VDCPs **1** with a variety of nucleophiles, such as alcohols and aromatic amines as well as other reactants under mild conditions to produce a variety of interesting compounds.[2,3] More recently, we have found a novel cationic 1,4-aryl migration process in the $BF_3\cdot Et_2O$-catalyzed intermolecular reactions of vinylidenecyclopropanes **1** with bis(*p*-alkoxyphenyl)methanols, such as bis(*p*-methoxyphenyl)methanol in 1,2-dichloroethane (DCE) to give the corresponding indene derivatives in good yields under mild conditions (Scheme 1).[4] It is conceivable that if using similarly electron-rich xanthydrol **2a** as the electrophile in this reaction, 1,4-aryl migration will not be able to take place. Therefore, it is quite interesting to examine what happens in this type of $BF_3\cdot Et_2O$-catalyzed reaction. In this paper, we wish to report the full details of ring-opening reactions of vinylidenecyclopropanes with



Scheme 1. $BF_3\cdot Et_2O$-catalyzed Intermolecular Reactions of Vinylidenecyclopropanes **1** with Bis(*p*-methoxyphenyl)methanol.

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* Corresponding author. E-mail address: mshi@mail.sioc.ac.cn (M. Shi).

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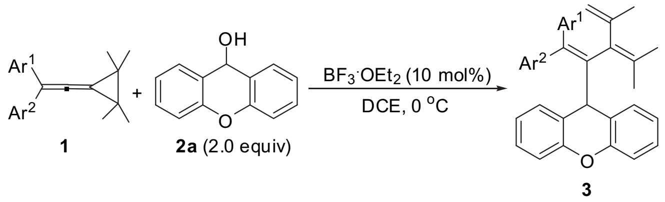
xanthydrol **2a** in the presence of $BF_3\cdot OEt_2$ and its derivative xanthene **2b** in the presence of 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) as well as the further transformation of the obtained ring-opening products.

2. Results and discussion

Initial examination in the $BF_3\cdot Et_2O$ (10 mol %)-catalyzed reaction of diphenylvinylidenecyclopropane **1a** (1.0 equiv) with **2a** (2.0 equiv) revealed that the ring-opening reaction took place efficiently to give a conjugate triene product **3a** in good yield within 20 min rather than the 1,4-aryl migration product. The results of these experiments on the examination of the substrate scope are summarized in Table 1. As can be seen from Table 1, all of the reactions proceeded smoothly to give the corresponding trienes **3** in moderate to good yields. As for electron-neutral phenyl groups substituted VDCPs **1a** and **1c** as well as electron-rich aromatic groups substituted VDCPs **1g**, **1h**, and **1i**, the corresponding trienes **3a**, **3c**, **3g**, **3h**, and **3i** were obtained in 65–94% yields (Table 1, entries 1, 3, and 7–9). Only in the case of VDCP **1f** bearing one *ortho*-methyl group on the benzene ring, the corresponding triene **3f** was obtained in 44% yield, presumably due to the steric hindrance (Table 1, entry 6). In the cases of VDCPs **1d** and **1e** in which the aromatic rings bearing electron-withdrawing groups, the corresponding trienes **3d** and **3e** were formed in moderate yields (Table 1, entries 4 and 5). For unsymmetrical diaryl-substituted VDCPs **1c**, **1f**, and **1g**, the corresponding trienes **3c**, **3f**, and **3g** were attained as *E*- and *Z*-isomeric mixtures with different ratios (Table 1, entries 3, 6, and 7).

Table 1
$BF_3\cdot OEt_2$-catalyzed Ring-opening Reactions of Vinylidenecyclopropanes with Xanthydrol **2a** in DCE

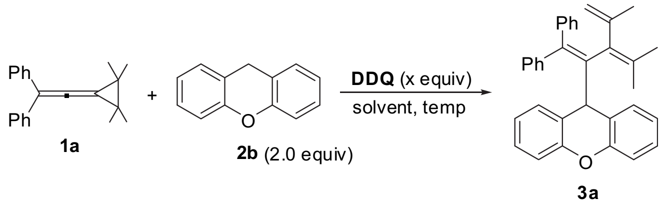


Entry[a]	Ar^1/Ar^2	Yield[b] (%)
		3
1	C_6H_5/C_6H_5, **1a**	**3a**, 83
2	*p*-FC_6H_4/*p*-FC_6H_4, **1b**	**3b**, 76
3	*p*-ClC_6H_4/C_6H_5, **1c**	**3c**, 65[c]
4	*p*-ClC_6H_4/*p*-ClC_6H_4, **1d**	**3d**, 42
5	*p*-BrC_6H_4/*p*-BrC_6H_4, **1e**	**3e**, 41
6	C_6H_5/*o*-$CH_3C_6H_4$, **1f**	**3f**, 44[d]
7	*p*-$CH_3C_6H_4/C_6H_5$, **1g**	**3g**, 88[e]
8	*p*-$CH_3C_6H_4$/*p*-$CH_3C_6H_4$, **1h**	**3h**, 94
9	*p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$, **1i**	**3i**, 86

[a] All reactions were carried out using **1** (0.20 mmol), **2a** (0.4 mmol, 2.0 equiv), and $BF_3\cdot Et_2O$ (10 mol %) in DCE at rt within 20 min unless otherwise specified.
[b] Isolated yields.
[c] *E*- or *Z*-isomeric mixture (ratio=1.2:1).
[d] *E*-or *Z*-isomeric mixture (ratio=4:1).
[e] *E*- or *Z*-isomeric mixture (ratio=1.2:1).

This result also stimulated us to investigate the reaction of VDCPs **1** with xanthene **2b** because it has been reported that the similar cationic intermediate as that in the reaction of **2a** with $BF_3\cdot OEt_2$ could be generated if using **2b** in the presence of 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) under mild conditions.[5] The initial examination was carried out in DCE using **1a** (1.0 equiv) and **2b** (2.0 equiv) as the substrates in the presence of DDQ (1.5 equiv) to verify the reaction outcome. It was found that the corresponding triene **3a** was indeed formed in 44% yield at room temperature (20 °C) within 5 min and in 48% yield after 20 min (Table 2, entries 1 and 2). Next, we attempted to optimize the reaction conditions and the results of these experiments are summarized in Table 2. We found that increasing the employed amount of DDQ to 2.0 equiv or 2.5 equiv could improve the yields of **3a** to 70% or 75% at room temperature and raising the reaction temperature to 30 °C or 40 °C did not significantly affect the yields of **3a** (Table 2, entries 3–5 and 6–7). Performing the reaction at 0 °C afforded **3a** in 85% yield in DCE in the presence of 2.0 equiv of **2a**

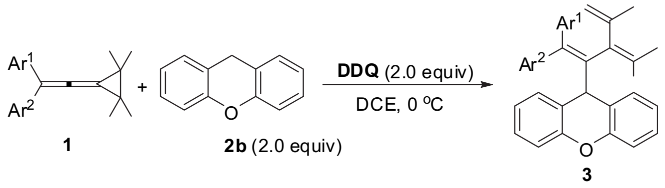
Table 2
Reactions of VDCP **1a** with xanthene **2b** in the presence of DDQ



Entry[a]	Solvent	*x*	Time (min)	Temp (°C)	Yield[b] (%)
					3a
1	DCE	1.5	5	rt	44
2	DCE	1.5	30	rt	48
3	DCE	2.0	30	rt	70
4	DCE	2.5	30	rt	70
5[c]	DCE	2.0	30	rt	75
6	DCE	2.0	30	30	59
7	DCE	2.0	30	40	68
8	***DCE***	***2.0***	**30**	***0***	***85***
9	DCM	2.0	30	0	81
10	THF	2.0	30	0	31
11	CH_3CN	2.0	30	0	80
12	Et_2O	2.0	30	0	57
13	Toluene	2.0	30	0	11
14	DMF	2.0	30	0	Trace

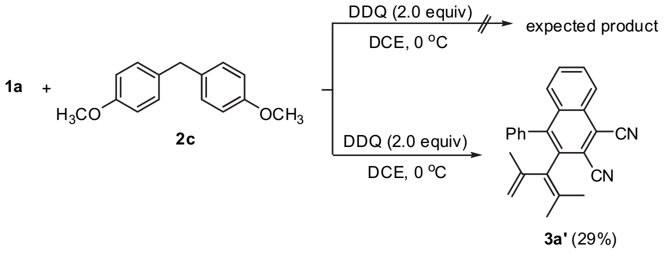
Bold values signify the best reaction conditions.
[a] VDCP **1a** (0.20 mmol), **2a** (2.0 equiv) and DDQ were dissolved in 2 mL of solvent under argon atmosphere, and the reaction mixtures were stirred for several minutes at certain temperatures.
[b] Isolated yields.
[c] Compound **2a** and DDQ were dissolved in solvent at rt under argon atmosphere. After 2.0 min, VDCP **1a** was added into the flask.

Table 3
Reactions of various VDCPs **1** with xanthene **2b** in the presence of DDQ



Entry[a]	Ar^1/Ar^2	Yield[b] (%)
		3
1	C_6H_5/C_6H_5, **1a**	**3a**, 85
2	*p*-FC_6H_4/*p*-FC_6H_4, **1b**	**3b**, 74
3	*p*-ClC_6H_4/C_6H_5, **1c**	**3c**, 71[c]
4	*p*-ClC_6H_4/*p*-ClC_6H_4, **1d**	**3d**, 80
5	*p*-BrC_6H_4/*p*-BrC_6H_4, **1e**	**3e**, 85
6	C_6H_5/*o*-$CH_3C_6H_4$, **1f**	**3f**, 31[d]
7	*p*-$CH_3C_6H_4/C_6H_5$, **1g**	**3g**, 65[e]
8	*p*-$CH_3C_6H_4$/*p*-$CH_3C_6H_4$, **1h**	**3h**, 82
9	*p*-$MeOC_6H_4$/*p*-$MeOC_6H_4$, **1i**	**3i**, 58
10	*p*-FC_6H_4/C_6H_5, **1j**	**3j**, 92[f]

[a] All reactions were carried out using **1** (0.20 mmol), **2a** (0.40 mmol, 2.0 equiv), and $BF_3\cdot Et_2O$ (10 mol %) in DCE at room temperature within 20 min unless otherwise specified.
[b] Isolated yields.
[c] *E*- or *Z*-isomeric mixture (ratio=1.2:1).
[d] *E*- or *Z*-isomeric mixture (ratio=4:1).
[e] *E*- or *Z*-isomeric mixture (ratio=1.2:1).
[f] *E*- or *Z*-isomeric mixture (ratio=1:1).



Scheme 2. The reaction of **1a** with **2c** in the Presence of DDQ.

within 30 min, which served as the best reaction conditions for this transformation (Table 2, entry 8). The examination of solvent effects revealed that dichloromethane (DCM) and acetonitrile (CH_3CN) are the suitable solvents for this reaction, giving **3a** in 81% and 80% yield, respectively (Table 2, entries 9–14).

Under these optimal reaction conditions, we next carried out this interesting ring-opening reaction of a variety of VDCPs **1** with **2b** to probe the substrate scope and the results of these experiments are outlined in Table 3. As can be seen from Table 3, the reactions proceeded smoothly to give the corresponding trienes **3** in moderate to good yields. As for VDCP **1f**, the corresponding product **3f** was attained

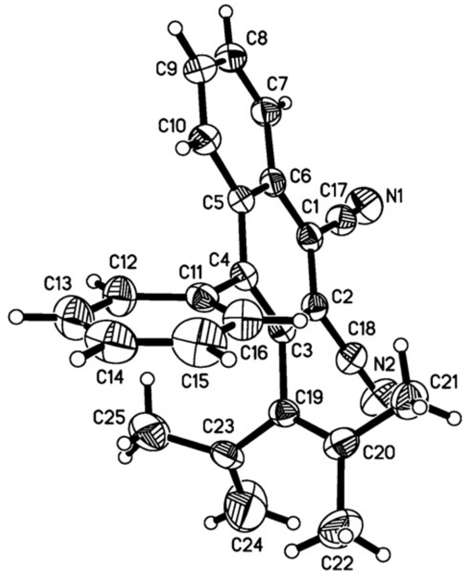
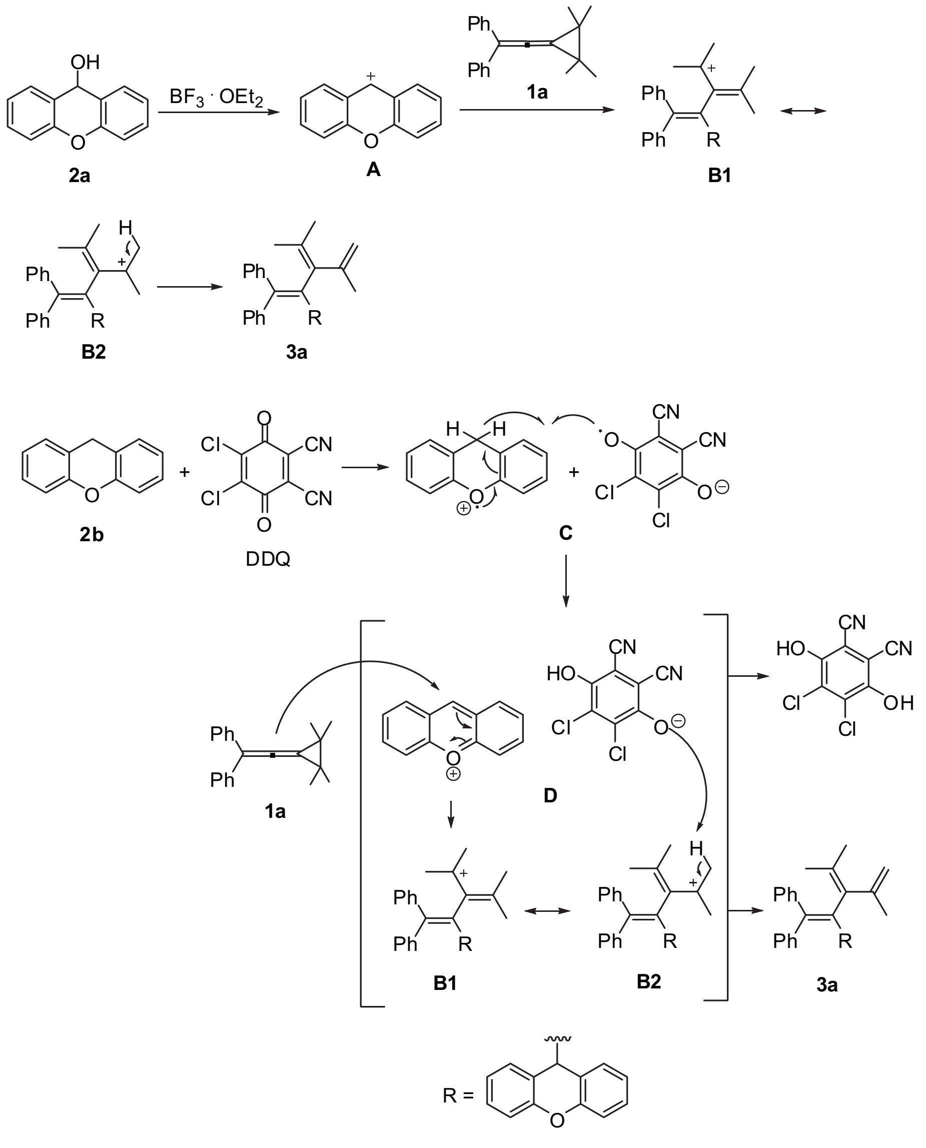


Figure 1. ORTEP drawing of **3a′**.



Scheme 3. Plausible reaction mechanisms.

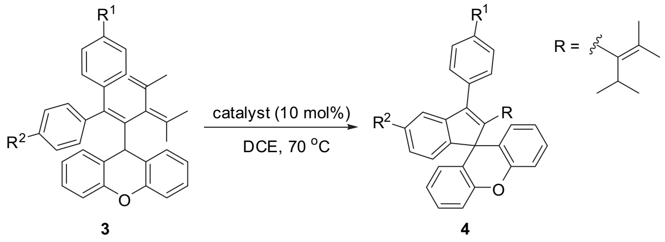
in 31% yield similarly due to the steric effect (Table 3, entry 6). For these unsymmetrical diaryl-substituted VDCPs **1d**, **1f**, **1g**, and **1j**, the corresponding trienes **1d**, **1f**, **1g**, and **1j** were obtained similarly as *E*- and *Z*-isomeric mixtures with different ratios (Table 3, entries 3, 6, and 7).

The control experiment indicated that using bis(4-methoxyphenyl)methane **2c** to replace **2b** in this reaction, none of the expected product was produced under the standard conditions, instead, another cycloaddition product **3a**′ of **1a** with DDQ was formed in 29% yield, suggesting that the structure and electronic property of xanthene **2b** played an important role in this reaction (Scheme 2). The structure of **3a**′ was unambiguously determined by X-ray diffraction. Its ORTEP drawing is shown in Figure 1 and its CIF data are presented in the Supplementary data.[6] A plausible reaction mechanism has been shown in the reference section[7] on the basis of the previous literature.[8]

The reaction mechanisms of VDCP **1** with **2a** catalyzed by $BF_3 \cdot OEt_2$ and **1** with **2b** in the presence of DDQ are outlined in Scheme 3 using VDCP **1a** as a model. Initially, the cationic intermediate **A** is formed by the treatment of **2a** with $BF_3 \cdot OEt_2$,[2,4] which reacts with **1a** to give the corresponding resonance-stabilized cationic intermediates **B1** and **B2** (allylic cation) (Scheme 3). Deprotonation of **B2** affords triene **3a**. On the other hand, if using **2b** as the substrate, the charge-transfer complex **C** (radical ionic pair) is firstly formed with DDQ via a single electron-transfer,[5] which undergoes H transfer to give intermediate **D** (ionic pair). The reaction of cationic xanthene intermediate with **1a** produces the similar resonance-stabilized cationic intermediates **B1** and **B21**, which gives product **3a** via deprotonation (Scheme 3).

The further transformation of **3** has been examined in the presence of several catalysts, such as $AlCl_3$, Brønsted acid trifluoromethanesulfonic acid CF_3SO_3H (TfOH), and $BF_3 \cdot OEt_2$ (10 mol %) in DCE. We found that $AlCl_3$ (10 mol %) did not promote the further transformation of **3**, but using TfOH or $BF_3 \cdot OEt_2$ (10 mol %) as the catalyst gave a novel spiro-alkane **4a** in 97% yield at 70 °C if using **3a** as substrate (Table 4, entries 1–3). The generality of this transformation is good for a variety of compounds **3** under the standard conditions using $BF_3 \cdot OEt_2$ (10 mol %) as the catalyst to give the products **4** in moderate to good yields (Table 4). As for substrates **3b**, **3d**, and **3e** having electron-withdrawing groups on their benzene rings, the corresponding products **4b**, **4d**, and **4e** were obtained in moderate yields (Table 4, entries 4, 6, and 7) and others were obtained in good yields (Table 4, entries 5 and 8–10). In the cases of unsymmetrical substrates **3c** and **3g** (R^1 and R^2 are not identical), the products **4c** and **4g** were formed as isomeric mixtures in good yields (Table 4, entries 5 and 8, see the Supplementary data for the detail). The structure of **4i** has been ambiguously determined by X-ray diffraction (Fig. 2) and its CIF data are presented in the Supplementary data.[9]

Table 4
Further transformation of **3** and the formation of spiro-alkanes **4**



Entry[a]	Catalyst	R1/R2	Yield[b] (%)
			3
1	$AlCl_3$	H/H, **3a**	nr
2	HOTf	H/H, **3a**	**4a**, 97
3	$BF_3 \cdot OEt_2$	H/H, **3a**	**4a**, 97
4	$BF_3 \cdot OEt_2$	F/F, **3b**	**4b**, 56
5	$BF_3 \cdot OEt_2$	Cl/H, **3c**	**4c**, 97[c]
6	$BF_3 \cdot OEt_2$	Cl/Cl, **3d**	**4d**, 62
7	$BF_3 \cdot OEt_2$	Br/Br, **3e**	**4 e**, 50
8	$BF_3 \cdot OEt_2$	CH_3/H, **3g**	**4g**, 89[d]
9	$BF_3 \cdot OEt_2$	CH_3/CH_3, **3h**	**4h**, 92
10	$BF_3 \cdot OEt_2$	CH_3O/CH_3O, **3i**	**4i**, 88

[a] Compound **1** (0.20 mmol) was dissolved in DCE (2.0 mL) in a flask under argon, then, *x* (10 mol %) was added into the flask. The reaction was carried out at 70 °C within 3 h.

[b] Isolated yields.

[c] The *E*/*Z* isomeric mixtures were used in this reaction and the ratio of the product mixtures is 1.2:1.

[d] The *E*/*Z* isomeric mixtures were used in this reaction and the ratio of the product mixtures is 1.2:1.

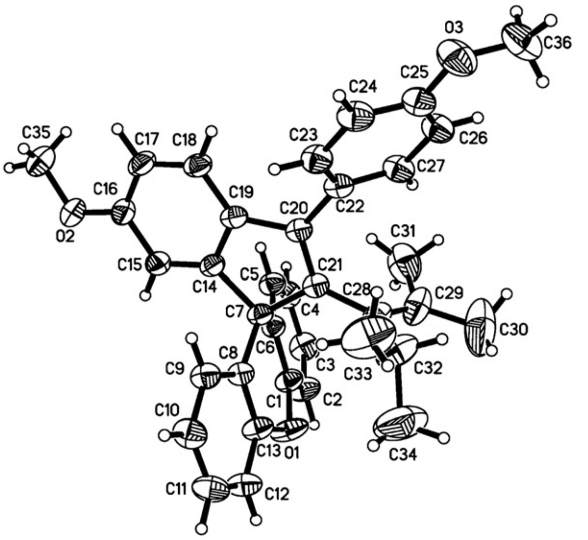
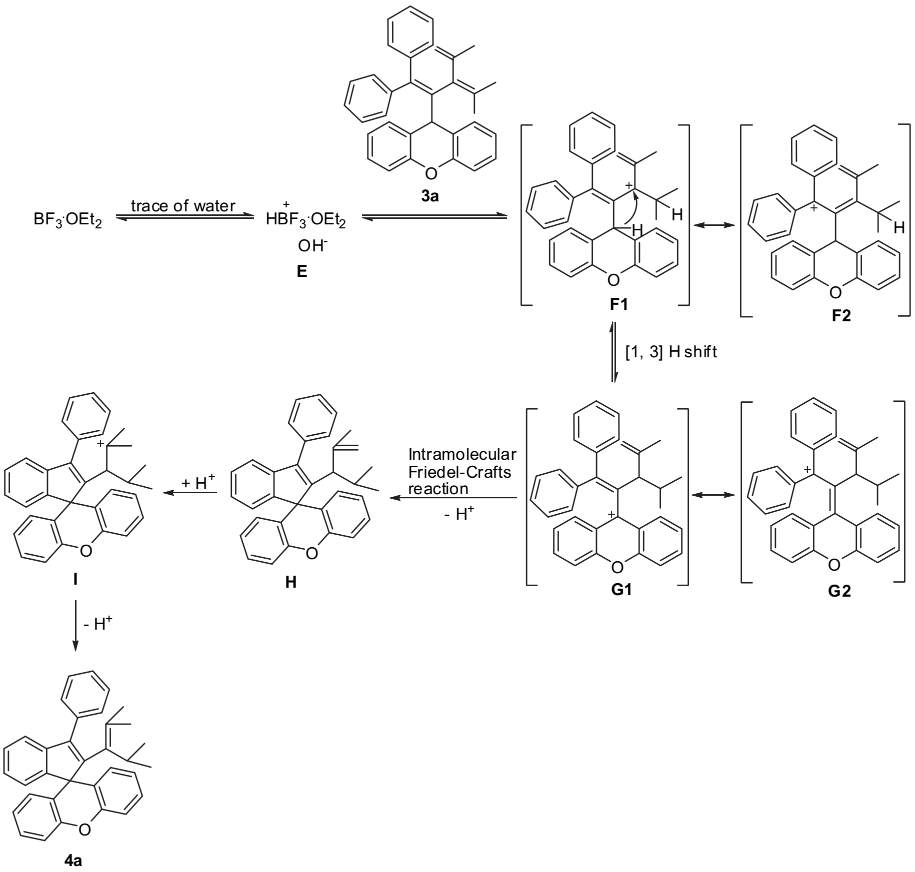


Figure 2. ORTEP drawing of **4i**.

A plausible reaction mechanism for the formation of spiro-alkane **4** is outlined in Scheme 4 using **3a** as a model. $BF_3 \cdot OEt_2$ may play as a Brønsted acid type catalyst **E** in the presence of trace of water,[10] which reacts with **3a** gives the corresponding resonance-stabilized cationic intermediates **F1** and **F2** (allylic cation). Intermediate **F1** affords the corresponding resonance-stabilized cationic intermediates **G1** and **G2** (allylic cation) through 1,3-σ hydrogen shift and then, intermediate **G1** undergoes intramolecular Friedel–Crafts reaction to afford spiro-alkyl intermediate **H**, which gives spiro-alkane **4a** via a protonation and a deprotonation through intermediate **I** (Scheme 4).

3. Conclusion

In summary, we have disclosed the reactions of vinylidenecyclopropanes (VDCPs) **1** with xanthydrol **2a** in the presence of $BF_3 \cdot OEt_2$ (10 mol %) or **1** with xanthene in the presence of DDQ (2.0 equiv) at 0 °C in 1,2-dichloroethane to give the corresponding conjugate triene derivatives **3** in moderate to good yields. Plausible reaction mechanisms have been discussed on the basis of previous literature and the control experiments. An interesting transformation of these conjugate trienes has been disclosed in the presence of $BF_3 \cdot OEt_2$ (10 mol %) at 70 °C, affording a series of novel spiro-alkanes **4** in moderate to good yields. Efforts are in progress to further elucidate the mechanistic details of this reaction and to determine its scope and limitations.



Scheme 4. A Plausible Reaction mechanism for the formation of **4a**.

4. Experimental procedures

4.1. General methods

^{1}H and ^{13}C NMR spectra were recorded at the 300 and 75 MHz or the 400 and 100 MHz, respectively. Mass and HRMS spectra were recorded by EI or ESI method. Organic solvents used were dried by standard methods when necessary. Satisfactory CHN microanalyses were obtained with an analyzer. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

4.2. General procedure for the reactions of VDCPs 1 with xanthydrol 2a in the presence of $BF_3 \cdot OEt_2$ (10 mol %)

Under argon atmosphere, vinylidenecyclopropanes (VDCPs) **1** (0.20 mmol), and xanthydrol **2a** (0.40 mmol) were dissolved in DCE (2.0 mL) in a Schlenk tube at 0 °C, then, $BF_3 \cdot OEt_2$ (10 mol %) was inserted into the tube. The reaction mixture was stirred at 0 °C until the reaction completed. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **3** in moderate to good yields.

4.3. General procedure for the reactions of VDCPs 1 with xanthene 2b in the presence of DDQ

Under argon atmosphere, vinylidenecyclopropanes **1** (0.20 mmol) and xanthene **2b** (0.40 mmol) were added into a Schlenk tube, and then the solvent of DCE (2.0 mL) was added. The reaction mixture was stirred at 0 °C for a while until the solid substrates dissolved, then DDQ (0.40 mmol) was added. The reaction was stirred at 0 °C for 20 min. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **3** in moderate to good yields.

4.3.1. Compound ***3a****.* A white solid, mp: 154–155 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.23 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 4.19 (s, 1H), 4.70 (s, 1H), 5.57 (s, 1H), 6.81–6.96 (m, 4H, Ar), 7.08–7.23 (m, 7H, Ar), 7.27–7.38 (m, 7H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.9, 22.9, 23.3, 40.2, 115.9, 116.0, 118.8, 121.9, 122.0, 122.2, 123.2, 126.2, 126.7, 127.2, 127.6, 127.7, 128.6, 129.0, 129.4, 129.5, 130.2, 132.7, 135.1, 140.5, 143.1, 143.4, 143.72, 143.75, 150.9, 151.4. IR (CH_2Cl_2) ν 3075, 2925, 2853, 1738, 1600, 1574, 1481, 1450, 1367, 1322, 1258, 1216, 1096, 905, 751 cm^{-1}. MS (ESI) *m*/*e* 455.2 ($M^{+}+1$). HRMS (MALDI) calcd for $C_{34}H_{31}O$: 455.2377, found: 455.2369.

4.3.2. Compound ***3b****.* A white solid, mp: 160–162 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.22 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 4.32 (s, 1H), 4.82 (s, 1H), 5.50 (s, 1H), 6.80–7.02 (m, 8H, Ar), 7.07–7.28 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.9, 23.21, 23.23, 39.9, 114.2 (d, $J_{C-F}=21.2$ Hz), 115.5 (d, $J_{C-F}=21.2$ Hz), 115.9, 116.2, 119.1, 122.0, 122.09, 122.11, 123.1, 127.7, 127.8, 128.6, 129.1, 130.9 (d, $J_{C-F}=8.0$ Hz), 131.5 (d, $J_{C-F}=7.4$ Hz), 132.8, 135.4, 139.2 (d, $J_{C-F}=3.7$ Hz), 139.6 (d, $J_{C-F}=3.5$ Hz), 141.4, 141.7, 143.0, 150.6, 151.2, 161.3 (d, $J_{C-F}=244.8$ Hz), 161.6 (d, $J_{C-F}=245.1$ Hz). IR (CH_2Cl_2) ν 3075, 3040, 2923, 2854, 1715, 1601, 1577, 1504, 1481, 1451, 1367, 1323, 1258, 1223, 1096, 905, 752 cm^{-1}. MS (ESI) *m*/*e* 491.2 ($M^{+}+1$). HRMS (MALDI) calcd for $C_{34}H_{29}OF_2$: 491.2196, found: 491.2181.

4.3.3. Compound ***3c****.* (A *E*/*Z* mixture, ratio=1.2:1.0). A white solid, mp: 162–164 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.21 (s, 1.65H, CH$_3$), 1.24 (s, 1.35H, CH$_3$), 1.31 (s, 3H, CH$_3$), 1.43 (s, 1.65H, CH$_3$), 1.53 (s, 1.35H, CH$_3$), 4.21 (s, 0.55H), 4.31 (s, 0.45H), 4.72 (s, 0.55H), 4.80 (s, 0.45H), 5.49 (s, 0.45H), 5.55 (s, 0.55H), 6.81–6.96 (m, 4H, Ar), 7.10–7.35 (m, 13H, Ar). ^{13}C NMR (CDCl$_3$, 100 MHz, TMS) δ 21.91, 21.94, 22.9, 23.3, 40.0, 40.2, 115.90, 115.92, 116.1, 116.2, 118.9, 119.1, 121.96, 122.00, 122.02, 122.06, 122.09, 122.2, 123.0, 123.1, 126.4, 127.0, 127.3, 127.5, 127.67, 127.75, 127.8, 128.63, 128.64, 128.7, 128.9, 129.2, 129.3, 129.4, 130.7, 131.4, 132.0, 132.6, 132.9, 133.0, 135.0, 135.4, 141.3, 141.5, 142.0, 142.1, 142.2, 142.3, 142.7, 143.2, 143.4, 150.6, 150.8, 151.3, 151.4. IR (CH$_2$Cl$_2$) ν 3077, 2969, 2906, 2852, 1715, 1601, 1574, 1481, 1450, 1367, 1322, 1257, 1217, 1092, 904, 749 cm^{-1}. MS (%) *m/e* 488 (M$^+$, 4.94), 445 (0.65), 393 (0.51), 335 (0.53), 215 (1.57), 181 (100.00), 165 (1.91), 152 (4.13). HRMS (EI) calcd for C$_{34}$H$_{29}$OCl: 488.1907, found: 488.1908.

4.3.4. Compound ***3d***. A white solid, mp: 174–176 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 1.22 (s, 3H, CH$_3$), 1.34 (s, 3H, CH$_3$), 1.52 (s, 3H, CH$_3$), 4.33 (s, 1H), 4.82 (s, 1H), 5.47 (s, 1H), 6.79–6.97 (m, 4H, Ar), 7.07–7.28 (m, 12H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 22.0, 23.2, 40.0, 115.9, 116.3, 119.2, 121.9, 122.06, 122.13, 122.8, 127.6, 127.8, 127.9, 128.5, 128.8, 129.1, 130.6, 131.3, 132.2, 132.8, 133.2, 135.3, 141.1, 141.5, 141.8, 142.3, 142.8, 150.6, 151.2. IR (CH$_2$Cl$_2$) ν 3076, 3039, 2924, 2853, 1902, 1715, 1601, 1575, 1481, 1451, 1367, 1322, 1257, 1218, 1091, 905, 751 cm^{-1}. MS (ESI) *m/e* 523.1 (M$^+$+1). HRMS (MALDI) calcd for C$_{34}$H$_{29}$OCl$_2$: 523.1583, found: 523.1590.

4.3.5. Compound ***3e***. A white solid, mp: 180–182 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 1.22 (s, 3H, CH$_3$), 1.34 (s, 3H, CH$_3$), 1.52 (s, 3H, CH$_3$), 4.33 (s, 1H), 4.83 (s, 1H), 5.46 (s, 1H), 6.80–6.96 (m, 4H, Ar), 7.03–7.28 (m, 10H, Ar), 7.40–7.43 (m, 2H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 22.0, 23.3, 29.7, 40.0, 116.0, 116.3, 119.2, 120.5, 121.0, 121.9, 122.07, 122.14, 122.8, 127.8, 127.9, 128.5, 129.1, 130.5, 130.9, 131.6, 131.7, 133.2, 135.3, 141.1, 141.9, 142.2, 142.3, 142.8, 150.6, 151.2. IR (CH$_2$Cl$_2$) ν 3076, 2964, 2923, 2852, 1715, 1601, 1574, 1482, 1450, 1362, 1322, 1258, 1218, 1010, 905, 750 cm^{-1}. MS (ESI) *m/e* 613.0 (M$^+$+1). HRMS (MALDI) calcd for C$_{34}$H$_{29}$OBr$_2$: 611.0581, found: 611.0580.

4.3.6. Compound ***3f***. (A *E*/*Z* mixture, ratio=4:1). A white solid, mp: 130–132 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 1.09 (s, 2.4H, CH$_3$), 1.17 (s, 0.6H, CH$_3$), 1.34 (s, 2.4H, CH$_3$), 1.53 (s, 0.6H, CH$_3$), 1.54 (s, 0.6H, CH$_3$), 1.70 (s, 2.4H, CH$_3$), 1.95 (s, 2.4H, CH$_3$), 2.30 (s, 0.6H, CH$_3$), 4.02 (s, 0.2H), 4.37 (s, 0.2H), 4.59 (s, 0.8H), 4.95 (s, 0.8H), 5.36 (s, 0.2H), 5.50 (s, 0.8H), 6.75–6.97 (m, 4H, Ar), 7.04–7.21 (m, 10H, Ar), 7.27–7.44 (m, 3H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 21.7, 21.9, 22.0, 22.3, 23.3, 23.4, 23.5, 40.2, 43.1, 115.8, 116.0, 116.1, 116.2, 116.3, 119.4, 121.9, 122.0, 122.3, 122.4, 122.6, 123.9, 125.4, 125.7, 125.9, 126.1, 127.0, 127.1, 127.2, 127.3, 127.4, 127.60, 127.64, 127.8, 128.2, 128.8, 129.2, 129.3, 129.5, 129.8, 130.6, 130.7, 130.9, 131.0, 131.3, 132.5, 133.6, 133.7, 135.5, 136.7, 137.0, 138.9, 141.2, 141.6, 141.8, 142.0, 142.49, 142.53, 142.8, 142.9, 143.2, 150.9, 151.4, 152.9, 153.0. IR (CH$_2$Cl$_2$) ν 3057, 3013, 2922, 2852, 1716, 1600, 1574, 1481, 1451, 1367, 1326, 1259, 1218, 1096, 905, 752 cm^{-1}. MS (%) *m/e* 468 (M$^+$, 21.60), 453 (1.18), 425 (2.07), 287 (13.83), 215 (2.08), 181 (100.00), 165 (1.87), 152 (3.20). HRMS (EI) calcd for C$_{35}$H$_{32}$O: 468.2453, found: 468.2451.

4.3.7. Compound ***3g***. (A *E*/*Z* mixture, ratio=1.2:1.0). A white solid, mp: 133–135 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 1.22 (s, 1.65H, CH$_3$), 1.23 (s, 1.35H, CH$_3$), 1.26 (s, 1.65H, CH$_3$), 1.30 (s, 1.35H, CH$_3$), 1.41 (s, 1.65H, CH$_3$), 1.43 (s, 1.35H, CH$_3$), 2.25 (s, 1.35H, CH$_3$), 2.33 (s, 1.65H, CH$_3$), 4.12 (s, 0.55H), 4.17 (s, 0.45H), 4.66 (s, 0.55H), 4.68 (s, 0.45H), 5.55 (s, 0.45H), 5.60 (s, 0.55H), 6.81–6.98 (m, 5H, Ar), 7.09–7.18 (m, 6H, Ar), 7.22–7.38 (m, 6H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 21.1, 21.2, 21.8, 21.9, 22.8, 22.9, 23.19, 23.22, 40.16, 40.22, 115.8, 116.0, 118.7, 118.8, 121.85, 121.89, 122.0, 122.26, 122.32, 123.1, 123.2, 126.1, 126.6, 127.2, 127.5, 127.6, 128.0, 128.6, 129.01, 129.05, 129.1, 129.2, 129.27, 129.32, 129.4, 129.5, 130.1, 130.2, 132.5, 132.6, 135.0, 135.1, 135.7, 136.4, 139.8, 140.1, 140.77, 140.83, 143.05, 143.15, 143.3, 143.4, 143.88, 143.94, 150.8, 151.4. IR (CH$_2$Cl$_2$) ν 3075, 3022, 2921, 2853, 1715, 1601, 1574, 1481, 1450, 1367, 1322, 1258, 1217, 1096, 905, 751 cm^{-1}. MS (%) *m/e* 468 (M$^+$, 21.60), 441 (1.18), 425 (2.07), 371 (4.31), 287 (13.72), 272 (3.57), 257 (4.38), 181 (100.00). HRMS (EI) calcd for C$_{35}$H$_{32}$O: 468.2453, found: 468.2449.

4.3.8. Compound ***3h***. A white solid, mp: 154–156 °C. ^{1}H NMR (CDCl$_3$, 400 MHz, TMS) δ 1.23 (s, 3H, CH$_3$), 1.29 (s, 3H, CH$_3$), 1.40 (s, 3H, CH$_3$), 2.24 (s, 3H, CH$_3$), 2.31 (s, 3H, CH$_3$), 4.13 (s, 1H), 4.66 (s, 1H), 5.59 (s, 1H), 6.80–6.97 (m, 6H, Ar), 7.07–7.18 (m, 6H, Ar), 7.26–7.36 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$, 100 MHz, TMS) δ 21.1, 21.2, 21.8, 22.9, 23.2, 40.3, 115.8, 116.0, 118.6, 121.8, 121.9, 122.4, 123.3, 127.5, 127.6, 127.9, 129.1, 129.3, 129.5, 130.0, 132.4, 135.1, 135.6, 136.3, 139.6, 141.0, 141.1, 143.1, 143.2, 150.9, 151.5. IR (CH$_2$Cl$_2$) ν 3075, 3021, 2969, 2921, 2854, 1738, 1717, 1601, 1575, 1481, 1450, 1366, 1323, 1258, 1217, 1095, 905, 751 cm^{-1}. MS (ESI) *m/e* 483.1 (M$^+$+1). HRMS (MALDI) calcd for C$_{36}$H$_{35}$O: 483.2695, found: 483.2682.

4.3.9. Compound ***3i***. A colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz, TMS) δ 1.24 (s, 3H, CH$_3$), 1.31 (s, 3H, CH$_3$), 1.43 (s, 3H, CH$_3$), 3.72 (s, 3H, OCH$_3$), 3.77 (s, 3H, OCH$_3$), 4.15 (s, 1H), 4.69 (s, 1H), 5.60 (s, 1H), 6.68 (2H, d, *J*=8.8 Hz, Ar), 6.86–6.88 (m, 6H, Ar), 7.14–7.16 (m, 4H, Ar), 7.29–7.34 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$, 100 MHz, TMS) δ 21.8, 22.9, 23.1, 40.1, 55.0, 55.2, 112.5, 114.0, 115.8, 115.9, 118.7, 121.8, 121.9, 122.4, 123.4, 127.47, 127.54, 128.9, 129.4, 130.6, 131.2, 132.2, 135.3, 136.3, 136.6, 139.3, 142.7, 143.2, 150.7, 151.4, 157.8, 158.3. IR (CH$_2$Cl$_2$) ν 3033, 2998, 2906, 2835, 1715, 1604, 1575, 1508, 1481, 1450, 1366, 1322, 1246, 1173, 1096, 904, 752 cm^{-1}. MS (ESI) *m/e* 515.2 (M$^+$+1). HRMS (MALDI) calcd for C$_{36}$H$_{35}$O$_3$: 515.2583, found: 515.2581.

4.3.10. Compound ***3j***. (A *E*/*Z* mixture, ratio=1:1). A white solid, mp: 140–141 °C. ^{1}H NMR (CDCl$_3$, 300 MHz, TMS) δ 1.22 (s, 1.5H, CH$_3$), 1.23 (s, 1.5H, CH$_3$), 1.30 (s, 1.5H, CH$_3$), 1.32 (s, 1.5H, CH$_3$), 1.43 (s, 1.5H, CH$_3$), 1.54 (s, 1.5H, CH$_3$), 4.20 (s, 0.5H), 4.31 (s, 0.5H), 4.71 (s, 0.5H), 4.80 (s, 0.5H), 5.51 (s, 0.5H), 5.56 (s, 0.5H), 6.80–7.01 (m, 6H, Ar), 7.09–7.21 (m, 7H, Ar), 7.24–7.37 (m, 4H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz, TMS) δ 21.9, 22.0, 22.9, 23.3, 40.0, 40.2, 114.2 (d, $J_{\mathrm{C-F}}$=21.2 Hz), 115.4 (d, $J_{\mathrm{C-F}}$=21.2 Hz), 115.87, 115.92, 116.1, 116.2, 118.9, 119.1, 121.97, 122.01, 122.05, 122.1, 122.3, 123.1, 123.2, 126.3, 126.9, 127.3, 127.66, 127.74, 127.8, 128.66, 128.71, 128.9, 129.2, 129.3, 129.4, 130.1, 131.0 (d, $J_{\mathrm{C-F}}$=7.7 Hz), 131.6 (d, $J_{\mathrm{C-F}}$=7.7 Hz), 132.8, 135.0, 135.5, 139.5 (d, $J_{\mathrm{C-F}}$=5.6 Hz), 139.7 (d, $J_{\mathrm{C-F}}$=2.9 Hz), 140.8, 141.4, 142.2, 142.6, 142.8, 143.3, 143.5, 143.7, 150.7, 150.9, 151.3, 151.4, 161.2 (d, $J_{\mathrm{C-F}}$=244.7 Hz), 161.6 (d, $J_{\mathrm{C-F}}$=245.2 Hz). IR (CH$_2$Cl$_2$) ν 3075, 2906, 2853, 1715, 1601, 1574, 1504, 1481, 1450, 1367, 1322, 1258, 1222, 1096, 905, 751 cm^{-1}. MS (ESI) *m/e* 473.5 (M$^+$+1). HRMS (MALDI) calcd for C$_{34}$H$_{30}$OF: 473.2276, found: 473.2275.

4.4. The procedure for the reaction of VDCP 1a with DDQ in DCE

Under argon atmosphere, vinylidenecyclopropane 1a (0.2 mmol) and was added into a Schlenk tube, and then the solvent of DCE (2.0 mL) was added. The reaction mixture was stirred at 0 °C for a while until the solid substrates dissolved, then, DDQ (0.4 mmol) was added under argon. The reaction was stirred at 0 °C for 20 min. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO$_2$) to give the corresponding products **3a′** in moderate to good yields.

4.4.1. Compound ***3a′***. A white solid, mp: 142–144 °C. ^{1}H NMR (CDCl$_3$, 400 MHz, TMS) δ 1.47 (s, 3H, CH$_3$), 1.69 (s, 3H, CH$_3$), 1.84 (s, 3H, CH$_3$), 3.84–3.85 (m, 1H), 4.65–4.66 (m, 1H), 7.11–7.14 (m, 2H, Ar), 7.43–7.44 (m, 3H, Ar), 7.60–7.68 (m, 2H, Ar), 7.76–7.79 (m, 1H, Ar), 8.35–8.37 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 22.1, 22.7, 115.17, 115.22, 116.0, 116.7, 118.0, 125.9, 127.6, 127.7, 128.3, 129.0, 129.4, 130.0, 130.4, 131.3, 133.7, 134.0, 135.9, 136.1, 139.2, 141.9, 145.2. IR (CH_2Cl_2) ν 2925, 2854, 2228, 1721, 1557, 1489, 1442, 1372, 1104, 1029, 765, 701 cm^{-1}. MS (%) *m*/*e* 348 (M$^+$, 94.19), 333 (58.04), 318 (9.49), 306 (10.66), 292 (100.00), 265 (28.14), 240 (6.60), 81 (22.33). Anal. Calcd for $C_{25}H_{20}N_2$: C, 86.17; H, 5.79; N, 8.04. Found: C, 86.05; H, 5.80; N, 7.96.

4.5. General procedure for the reactions of 3 in the presence of in the presence of $BF_3 \cdot OEt_2$ (10 mol %) at 70 °C

Under argon atmosphere, **3** (1.0 M in DCE) was dissolved in DCE in a Schlenk tube, then, $BF_3 \cdot OEt_2$ (10 mol %) was inserted into the tube. The reaction mixture was stirred at 70 °C until the reaction completed within 3 h. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding products **4** in moderate to good yields.

*4.5.1. Compound **4a**.* A white solid, mp: 188–190 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.27 (3H, d, *J*=7.6 Hz, CH_3), 0.38 (3H, d, *J*=6.8 Hz, CH_3), 0.91 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.76–1.87 (m, 1H), 6.54 (dd, *J*=8.0, 2.0 Hz, 1H, Ar), 6.68 (dd, *J*=7.6, 1.2 Hz, 1H, Ar), 6.79–6.89 (m, 2H, Ar), 7.09–7.23 (m, 6H, Ar), 7.27–7.39 (m, 7H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.7, 21.0, 24.2, 33.5, 59.7, 116.4, 116.9, 120.2, 122.6, 122.9, 123.4, 123.8, 125.0, 126.1, 127.2, 127.3, 128.0, 128.1, 128.2, 128.6, 128.9, 129.5, 132.8, 133.3, 135.6, 135.7, 145.6, 152.98, 153.04, 154.5, 158.2. IR (CH_2Cl_2) ν 3068, 2960, 2901, 2869, 1598, 1571, 1476, 1441, 1243, 750, 698 cm^{-1}. MS (%) *m*/*e* 454 (M$^+$, 87.02), 439 (78.16), 411 (100.00), 397 (71.36), 381 (13.24), 303 (25.44), 269 (16.52), 181 (38.48). HRMS (EI) calcd for $C_{34}H_{30}O$: 454.2297, found: 454.2296.

*4.5.2. Compound **4b**.* A white solid, mp: 175–177 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.27 (3H, d, *J*=7.2 Hz, CH_3), 0.37 (3H, d, *J*=7.2 Hz, CH_3), 0.89 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.74–1.84 (m, 1H), 6.53 (dd, *J*=7.8, 1.5 Hz, 1H, Ar), 6.66 (dd, *J*=7.8, 1.5 Hz, 1H, Ar), 6.82–6.93 (m, 3H, Ar), 7.01–7.14 (m, 5H, Ar), 7.21–7.36 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.7, 21.0, 21.1, 24.1, 33.4, 59.6 (d, J_{C-F}=1.7 Hz), 112.7 (d, J_{C-F}=23.0 Hz), 114.3 (d, J_{C-F}=22.5 Hz), 115.1 (d, J_{C-F}=20.8 Hz), 116.5, 117.1, 120.8, 120.9, 122.7, 122.8, 123.0, 123.1, 128.4, 129.3, 130.4 (d, J_{C-F}=7.8 Hz), 131.4 (d, J_{C-F}=3.4 Hz), 132.5, 133.7, 141.1 (d, J_{C-F}=1.7 Hz), 152.8, 152.9, 156.2, 156.3, 158.06, 158.11, 162.0 (d, J_{C-F}=245.06 Hz), 162.1 (d, J_{C-F}=243.8 Hz). IR (CH_2Cl_2) ν 2960, 2924, 2870, 1602, 1572, 1506, 1477, 1439, 1234, 1156, 886, 836, 754 cm^{-1}. MS (%) *m*/*e* 490 (M$^+$, 100.00), 475 (37.58), 447 (64.75), 433 (33.09), 339 (15.39), 286 (9.30), 273 (6.55), 181 (16.32). HRMS (EI) calcd for $C_{34}H_{28}OF_2$: 490.2108, found: 490.2112.

*4.5.3. Compound **4c**.* (A mixture, ratio=1.2:1). A colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.27 (d, *J*=7.2 Hz, 1.4H), 0.29 (d, *J*=7.2 Hz, 1.6H), 0.36 (d, *J*=7.2 Hz, 1.4H), 0.39 (d, *J*=7.2 Hz, 1.6H), 0.89 (s, 1.6H), 0.90 (s, 1.4H), 1.48 (s, 1.4H), 1.50 (s, 1.6H), 1.74–1.86 (m, 1H), 6.50–6.56 (m, 1H, Ar), 6.64–6.69 (m, 1H, Ar), 6.79–6.93 (m, 2H, Ar), 7.09–7.25 (m, 5H, Ar), 7.28–7.37 (m, 7H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.7, 20.9, 21.1, 21.3, 21.5, 24.1, 33.4, 59.4, 116.2, 116.8, 119.9, 122.6, 122.8, 123.7, 124.1, 125.7, 127.9, 128.0, 128.66, 128.71, 128.8, 129.7, 132.88, 132.94, 133.0, 135.4, 135.8, 136.6, 143.0, 152.88, 152.90, 154.9, 156.7. IR (CH_2Cl_2) ν 2958, 2871, 1600, 1572, 1477, 1442, 1303, 1283, 1244, 750 cm^{-1}. MS (%) *m*/*e* 488 (M$^+$, 100.00), 473 (72.32), 445 (89.70), 431 (66.74), 395 (10.89), 337 (11.52), 197 (17.47), 181 (41.03). HRMS (EI) calcd for $C_{34}H_{29}OCl$: 488.1907, found: 488.1908.

*4.5.4. Compound **4d**.* A white solid, mp: 205–207 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.29 (3H, d, *J*=7.2 Hz, CH_3), 0.37 (3H, d, *J*=7.2 Hz, CH_3), 0.88 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.74–1.83 (m, 1H), 6.52 (dd, *J*=7.8, 1.5 Hz, 1H, Ar), 6.65 (dd, *J*=7.8, 1.5 Hz, 1H, Ar), 6.82–6.94 (m, 2H, Ar), 7.10–7.14 (m, 3H, Ar), 7.19–7.37 (m, 8H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.7, 21.0, 21.1, 24.1, 33.3, 59.7, 116.6, 117.1, 120.9, 122.2, 122.6, 122.8, 123.1, 125.5, 127.7, 128.45, 128.52, 129.3, 130.1, 132.2, 132.3, 133.2, 133.67, 133.72, 133.9, 143.6, 152.78, 152.81, 156.0, 159.0. IR (CH_2Cl_2) ν 2959, 2918, 2869, 1600, 1572, 1479, 1440, 1306, 1284, 1240, 1090, 834, 751 cm^{-1}. MS (%) *m*/*e* 522 (M$^+$, 100.00), 507 (44.31), 479 (50.14), 465 (38.07), 444 (12.89), 337 (7.93), 255 (5.25), 181 (26.29). HRMS (EI) calcd for $C_{34}H_{28}OCl_2$: 522.1517, found: 522.1520.

*4.5.5. Compound **4e**.* A white solid, mp: 207–209 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.29 (3H, d, *J*=7.2 Hz, CH_3), 0.37 (3H, d, *J*=7.2 Hz, CH_3), 0.88 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.73–1.83 (m, 1H), 6.51 (dd, *J*=6.6, 1.2 Hz, 1H, Ar), 6.65 (dd, *J*=6.6, 1.2 Hz, 1H, Ar), 6.83–6.94 (m, 2H, Ar), 7.10–7.28 (m, 8H, Ar), 7.45–7.52 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.7, 20.9, 21.1, 24.1, 33.3, 59.7, 116.6, 117.1, 120.2, 121.3, 121.4, 122.1, 122.5, 122.9, 123.1, 128.3, 128.4, 128.5, 129.3, 130.4, 130.6, 131.4, 132.2, 133.8, 133.9, 134.1, 144.0, 152.76, 152.79, 156.2, 159.0. IR (CH_2Cl_2) ν 2958, 2921, 2868, 2851, 1600, 1571, 1478, 1440, 1284, 1239, 1011, 831, 752 cm^{-1}. MS (%) *m*/*e* 612 (M$^+$, 100.00), 497 (13.50), 569 (21.46), 518 (77.48), 490 (41.35), 475 (9.72), 242 (13.19), 181 (17.98). HRMS (EI) calcd for $C_{34}H_{28}Br_2O$: 610.0507, found: 610.0509.

*4.5.6. Compound **4g**.* (A mixture, ratio=1.2:1). A colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.27 (d, *J*=7.2 Hz, 1.6H, CH_3), 0.29 (d, *J*=7.2 Hz, 1.4H, CH_3), 0.36 (d, *J*=7.2 Hz, 1.6H, CH_3), 0.39 (d, *J*=7.2 Hz, 1.4H, CH_3), 0.90 (s, 1.4H, CH_3), 0.91 (s, 1.6H, CH_3), 1.48 (s, 1.6H, CH_3), 1.49 (s, 1.4H, CH_3), 1.78–1.87 (m, 1H), 2.30 (s, 1.6H, CH_3), 2.37 (s, 1.4H, CH_3), 6.52–6.57 (m, 1H, Ar), 6.67–6.71 (m, 1H, Ar), 6.78–6.96 (m, 2H, Ar), 7.08–7.38 (m, 12H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.7, 21.0, 21.1, 21.3, 21.5, 24.1, 24.2, 33.4, 33.5, 59.5, 59.6, 116.30, 116.34, 116.8, 116.9, 120.0, 120.3, 122.60, 122.62, 122.9, 123.5, 123.6, 123.9, 124.0, 125.0, 125.7, 126.1, 127.1, 127.2, 127.95, 128.00, 128.04, 128.1, 128.4, 128.67, 128,71, 128.75, 128.78, 128.8, 129.0, 129.1, 129.2, 129.5, 129.7, 132.7, 132.9, 133.1, 133.2, 135.47, 135.55, 135.9, 136.8, 142.9, 145.7, 152.88, 152.93, 152.99, 153.04, 154.5, 154.9, 157.2, 157.7. IR (CH_2Cl_2) ν 3026, 2961, 2922, 2870, 1599, 1571, 1477, 1441, 1304, 1283, 1243, 821, 750 cm^{-1}. MS (%) *m*/*e* 468 (M$^+$, 87.65), 453 (77.52), 425 (100.00), 411 (76.81), 395 (14.92), 317 (15.74), 205 (12.76), 181 (29.23). HRMS (EI) calcd for $C_{35}H_{32}O$: 468.2453, found: 468.2460.

*4.5.7. Compound **4h**.* A white solid, mp: 184–186 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.28 (3H, d, *J*=6.9 Hz, CH_3), 0.37 (3H, d, *J*=6.9 Hz, CH_3), 0.90 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.77–1.88 (m, 1H), 2.29 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 6.55 (d, *J*=7.8 Hz, 1H, Ar), 6.70 (d, *J*=7.8 Hz, 1H, Ar), 6.78–6.90 (m, 2H, Ar), 7.07–7.28 (m, 11H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.7, 20.9, 21.1, 21.3, 21.5, 24.1, 33.4, 59.4, 116.2, 116.8, 119.9, 122.6, 122.8, 123.7, 124.1, 125.7, 127.9, 128.0, 128.66, 128.71, 128.8, 129.7, 132.88, 132.94, 133.0, 135.4, 135.8, 136.6, 143.0, 152.88, 152.90, 154.9, 156.7. IR (CH_2Cl_2) ν 3023, 2963, 2919, 2866, 1599, 1572, 1508, 1477, 1441, 1304, 1283, 1244, 756 cm^{-1}. MS (%) *m*/*e* 482 (M$^+$, 100.00), 467 (77.79), 439 (92.01), 425 (90.18), 331 (12.52), 282 (6.57), 212 (5.42), 181 (24.09). HRMS (EI) calcd for $C_{36}H_{34}O$: 482.2610, found: 482.2608.

*4.5.8. Compound **4i**.* A white solid, mp: 182–184 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.28 (3H, d, *J*=7.2 Hz, CH_3), 0.37 (3H, d, *J*=7.2 Hz, CH_3), 0.90 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.81–1.88 (m, 1H), 3.69 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.55 (d, *J*=8.0 Hz, 1H, Ar), 6.70–6.71 (m, 2H, Ar), 6.79–6.90 (m, 5H, Ar), 7.07–7.32 (m, 7H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.6, 21.0, 21.1, 24.0, 33.4, 55.1, 55.5, 59.5, 110.8, 113.0, 113.4, 116.2, 116.8, 120.7, 122.7, 122.9, 123.8, 124.1, 128.0, 128.3, 128.8, 129.6, 129.9, 133.0, 133.1, 134.6, 138.6, 152.89, 152.94, 155.4, 156.1, 158.6, 158.7. IR (CH_2Cl_2) ν 2960, 2932, 2869, 2834, 1611, 1570, 1507, 1476, 1439, 1278, 1245, 1034, 751 cm^{-1}. MS (%) m/e 514 (M^+, 100.00), 499 (47.51), 471 (62.57), 457 (33.69), 441 (8.36), 363 (4.74), 255 (2.38), 181 (12.12). Anal. Calcd for $C_{36}H_{34}O_3$: C, 84.01; H, 6.66. Found: C, 83.93; H, 6.66.

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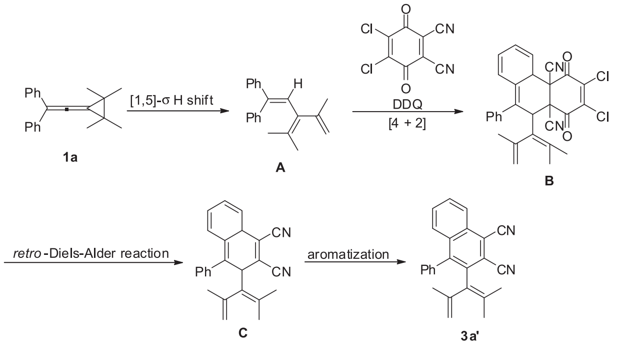
Supplementary data

Spectroscopic charts of the compounds shown in Tables 1–4, X-ray crystal data of **3a**′ and **4i** and the detailed descriptions of experimental procedures. This material is available free of charge via the Internet at the Website. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.07.004.

References and notes

1. For the synthesis of diarylvinylidenecyclopropanes, please see: (a) Isagawa, K.; Mizuno, K.; Sugita, H.; Otsuji, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2283–2285 and references therein; (b) Al-Dulayymi, J. R.; Baird, M. S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1547–1548 For some other papers related to vinylidenecyclopropanes: (c) Maeda, H.; Hirai, T.; Sugimoto, A.; Mizuno, K. *J. Org. Chem.* **2003**, *68*, 7700–7706; (d) Pasto, D. J.; Brophy, J. E. *J. Org. Chem.* **1991**, *56*, 4554–4556 For a recent review, see: (e) Maeda, H.; Mizuno, K. *J. Synth. Org. Chem. Jpn.* **2004**, *62*, 1014–1025.
2. (a) Xu, G.-C.; Liu, L.-P.; Lu, J.-M.; Shi, M. *J. Am. Chem. Soc.* **2005**, *127*, 14552–14553; (b) Shi, M.; Lu, J.-M.; Xu, G.-C. *Tetrahedron Lett.* **2005**, *46*, 4745–4748; (c) Li, Q.-J.; Shi, M.; Timmons, C.; Li, G.-G. *Org. Lett.* **2006**, *8*, 625–628; (d) Shi, M.; Lu, J.-M. *Synlett* **2005**, 2352–2356; (e) Lu, J.-M.; Shi, M. *Org. Lett.* **2007**, *9*, 1805–1808; (f) Lu, J.-M.; Shi, M. *Org. Lett.* **2006**, *8*, 5317–5320; (g) Shi, M.; Li, W. *Tetrahedron* **2007**, *63*, 6654–6660; (h) Shi, M.; Yao, L.-F. *Chem.—Eur. J.* **2008**, *14*, 8725–8731; (i) Lu, J.-M.; Zhu, Z.-B.; Shi, M. *Chem.—Eur. J.* **2009**, *15*, 963–971; (j) Zhu, Z.-B.; Shi, M. *Chem.—Eur. J.* **2008**, *14*, 10219–10222; (k) Shi, M.; Yao, L.-F. *Chem.—Eur. J.* **2008**, *14*, 8725–8731; (l) Lu, J. M.; Shi, M. *J. Org Chem.* **2008**, *73*, 2206–2210; (m) Zhang, Y.-P.; Lu, J.-M.; Xu, G.-C.; Shi, M. *J. Org. Chem.* **2007**, *72*, 509–516; (n) Lu, J.-M.; Shi, M. *Tetrahedron* **2007**, *63*, 7545–7549.
3. (a) Huang, X.; Su, C.-L.; Liu, Q.-Y.; Song, Y.-T. *Synlett* **2008**, 229–231; (b) Fall, Y.; Doucet, H.; Santelli, M. *Tetrahedron Lett.* **2007**, *48*, 3579–3581; (c) Poutsma, M. L.; Ibarbia, P. A. *J. Am. Chem. Soc.* **1971**, *93*, 440–450; (d) Smadja, W. *Chem. Rev.* **1983**, *83*, 263–320; (e) Hendrick, M. E.; Hardie, J. A.; Jones, M., Jr. *J. Org. Chem.* **1971**, *36*, 3061–3062; (f) Sugita, H.; Mizuno, K.; Saito, T.; Isagawa, K.; Otsuji, Y. *Tetrahedron Lett.* **1992**, *33*, 2539–2542; (g) Mizuno, K.; Sugita, H.; Kamada, T.; Otsuji, Y. *Chem. Lett.* **1994**, 449–452 and references cited therein; (h) Sydnes, L. K. *Chem. Rev.* **2003**, *103*, 1133–1150; (i) Akasaka, T.; Misawa, Y.; Ando, W. *Tetrahedron Lett.* **1990**, *31*, 1173–1176; (j) Mizuno, K.; Sugita, H.; Isagawa, K.; Goto, M.; Otsuji, Y. *Tetrahedron Lett.* **1993**, *34*, 5737–5738; (k) Mizuno, K.; Sugita, H.; Hirai, T.; Maeda, H. *Chem. Lett.* **2000**, 1144–1145; (l) Mizuno, K.; Nire, K.; Sugita, H.; Maeda, H. *Tetrahedron Lett.* **2001**, *42*, 2689–2692.
4. Wu, L.; Shi, M.; Li, Y.-X. *Chem.—Eur. J.* **2010**, *16*, 5163–5172.
5. (a) Benfatti, F.; Capdevila, M. G.; Zoli, L.; Benedetto, E.; Cozzi, P. G. *Chem. Commun.* **2009**, 5919–5921; (b) Zhang, Y.; Li, C.-J. *J. Am. Chem. Soc.* **2006**, *128*, 4242–4243.
6. The crystal data of **3a**′ have been deposited in CCDC with number 764682. Empirical Formula: $C_{25}H_{20}N_2$; Formula Weight: 348.43; Crystal Color, Habit: colorless, prismatic; Crystal System: Monoclinic; Lattice Type: Primitive; Crystal size: 0.415×0.360×0.287; Lattice Parameters: a=14.9661 (16) ·, b=8. 1905 (9) ·, c=16.7871 (19) ·, α=90°, β=109.339 (2)°, γ=90°, V=1941.7 (4) ·^{3}; Space group: $P2$ (1)/n; Z=4; D_{calcd}=1.192 g/cm^3; F_{000}=736; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.068, 0.2143.
7. The plausible reaction mechanism of VDCP **1a** reacting with DDQ has been shown belows:



8. (a) Yi, C.-Y.; Liu, S.-X.; Neels, A.; Renaud, P.; Decurtins, S. *Org. Lett.* **2007**, *9*, 1805–1808; (b) Shin, J.-Y.; Patrick, B. O.; Dolphin, D. *Org. Biomol. Chem.* **2009**, *7*, 2032–2035.
9. The crystal data of **4i** have been deposited in CCDC with number 773387. Empirical Formula: $C_{36}H_{34}O_3$; Formula Weight: 514.63; Crystal Color, Habit: colorless, prismatic; Crystal System: Triclinic; Lattice Type: Primitive; Crystal size: 0.362×0.341×0.280; Lattice Parameters: a=9.4647 (10) ·, b=11.3691 (9) ·, c=14.6352 (14) ·, α=84.563 (2)°, β=89.929 (2) °, γ=66.560 (2)°, V=1437.2 (2) ·^{3}; space group: P–1; Z=2; D_{calcd}=1.189 g/cm^3; F_{000}=548; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0777, 0.2452.
10. For the related papers with that a trace of water is required to trigger the first formation of cation B by means of Lewis acid BF_3 ($BF_3+H_2O+Me_2CH{=}CH_2 \rightarrow Me_3CH+BF_3OH^-$). Please see: (a) Evans, A. G.; Holden, D.; Plesch, P.; Polanyi, M.; Skinner, H. A.; Weinberger, M. A. *Nature* **1946**, *157*, 102–103; (b) Evans, A. G.; Meadows, G. W.; Polanyi, M.; Skinner, H. A.; Weinberger, M. A. *Nature* **1946**, *158*, 94–95; (c) Evans, A. G.; Polanyi, M. *J. Chem. Soc.* **1947**, 252–257; (d) Prakash, G. K. S.; Mathew, T.; Hoole, D.; Esterves, P. M.; Wang, Q.; Rasul, G.; Olah, G. A. *J. Am. Chem. Soc.* **2004**, *126*, 15770–15776.