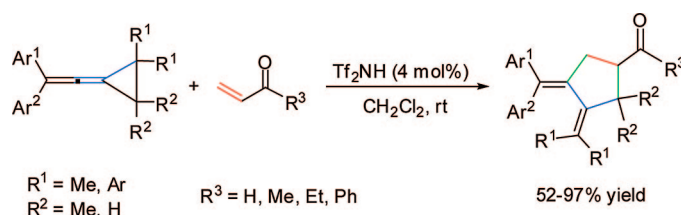# JOC*Article*

A Catalytic Method for the Preparation of Polysubstituted Cyclopentanes: [3+2] Cycloaddition of Vinylidenecyclopropanes with Activated Olefins Catalyzed by Triflic Imide

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[3+2] Cycloadditions of vinylidenecyclopropanes (VDCPs) with electron-deficient olefins, such as methyl vinyl ketone (MVK) and acrylaldehyde, proceed smoothly in the presence of a catalytic amount of triflic imide (Tf$_2$NH) to give the corresponding functionalized cyclopentanes in good to high yields.

Introduction

Five-membered carbocyclic rings appear in the most classes of organic materials including pharmaceutical agents, polymers, natural products, and catalysts.[1] Thus far, numerous methods and strategies for the construction of five-membered carbocyclic rings have been reported by traditional reactions such as Michael addition,[2] Aldol reaction,[3] Wittig reaction,[4] free radical cyclization,[5] and rearrangement of some special compounds,[6] as well as by cyclizations in the presence of metal complexes.[7] Moreover, some other synthetic strategies, such as [3+2], [4+1], and [2+2+1] cycloadditions, are also available for the synthesis of five-membered carbocyclic rings. Among these methodologies, [3+2] cycloadditions—both concerted and stepwise—represent convergent strategies for the formation of the cyclopentane nucleus.[8] In recent years, many efforts have been focused on donor−acceptor (D−A) substituted cyclopropanes[9,10] utilized as equivalents of a three carbon 1,3-dipole unit for the formation of five-membered carbocycles. In the presence of Lewis[9b,c] or Brønsted acids,[11] donor−acceptor cyclopropanes undergo ring-opening to yield 1,3-zwitterions which react with electron-rich olefins or alkynes to furnish multisubstituted five-membered carbocyclic rings.

Vinylidenecyclopropanes (VDCPs) **1** are some of the most remarkable organic compounds which have an allene moiety connected by a cyclopropane ring and yet are thermally stable and reactive substances in organic synthesis. Significant pioneering work has been done for this particular kind of organic compounds;[12] however, few reports on the cycloaddition of VDCPs to form five-membered carbocyclic rings have been

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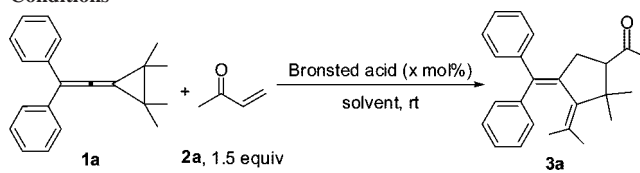
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reported so far.[13] In contrast to cycloaddition reactions involving the donor−acceptor cyclopropanes with electron-rich olefins, we are pleased to disclose in this paper a novel strategy to construct the cyclopentane nucleus from VDCPs and electron-deficient olefins in the presence of Tf$_2$NH.[14]

Results and Discussion

At the outset of this study, the [3+2] cycloaddition of VDCP **1a** with 1.5 equiv of methyl vinyl ketone (MVK) **2a** was examined by using several Brønsted acids in dichloromethane and the results of these experiments are presented in Table 1. Treatment of VDCP **1a** with MVK **2a** in the presence of triflic imide (Tf$_2$NH, 10 mol %) in CH$_2$Cl$_2$ at room temperature (25 °C) for 1 h afforded the polysubstituted cyclopentane **3a** in 95% yield (Table 1, entry 1). However, using other Brønsted acids, such as trifluoromethanesulfonic acid (TfOH), *p*-methylbenzenesulfonic acid (*p*-TSA), and methanesulfonic acid (MeSO$_3$H), resulted in **3a** in lower yields and most of **1a** was recovered, although TfOH is very effective in the [3+2] cycloaddition reactions of diarylvinylidenecyclopropanes with nitriles[12c] (Table 1, entries 2−4). Since Tf$_2$NH as the strong Brønsted acid is very effective in some catalytic carbon−carbon bond-forming reactions,[15−18] the employed amount of Tf$_2$NH was examined in this cycloaddition. It was found that using 4.0 mol % of

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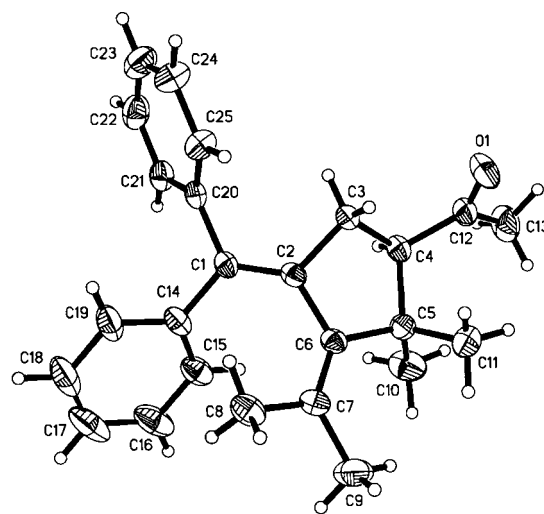(16) Othman, R. B.; Bousquet, T.; Othman, M.; Dalla, V. *Org. Lett.* **2005**, *7*, 5335–5337.

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entry[a]	Brønsted acid	x	solvent	time	yield (%)[b] of **3a**
1[c]	Tf$_2$NH	10	CH$_2$Cl$_2$	1 h	95
2[c]	TfOH	10	CH$_2$Cl$_2$	12 h	16
3[d]	*p*-TSA	10	CH$_2$Cl$_2$	48 h	8
4[e]	MeSO$_3$H	10	CH$_2$Cl$_2$	48 h	11
5	Tf$_2$NH	4	CH$_2$Cl$_2$	1 h	97(95)[f]
6	Tf$_2$NH	4	toluene	4 h	68
7	Tf$_2$NH	4	acetonitrile	4 h	_[g]
8	Tf$_2$NH	4	THF	4 h	_[g]
9	Tf$_2$NH	4	Et$_2$O	4 h	3
10[h]	Tf$_2$NH	4	CH$_2$Cl$_2$	10 min	94
11[i]	*Tf$_2$NH*	*4*	*CH$_2$Cl$_2$*	*10 min*	*97*
12[j]	Tf$_2$NH	4	CH$_2$Cl$_2$	1 h	95

[a] Reaction conditions: VDCP (0.18 mmol) and MVK (1.5 equiv) were dissolved in dry solvent (2.0 mL), Bronsted acid (*x* mol %) was added, then the mixtures were stirred for different times at room temperature. [b] Isolated yield. [c] 50% of **1a** was recovered. [d] 62% of **1a** was recovered. [e] 58% of **1a** was recovered. [f] The mixture was stirred for 10 min. [g] **3a** was not detected by TLC plates. [h] 2.0 equiv of MVK was added. [i] 1.2 equiv of MVK was added. [j] 1.0 equiv of MVK was added. MVK = methyl vinyl ketone.

FIGURE 1. ORTEP drawing of **3a**.

Tf$_2$NH as the catalyst afforded **3a** in 97% yield within 1 h and 95% yield within 10 min, respectively (Table 1, entry 5). The examination of solvent effects revealed that the reaction was much more sluggish in toluene, producing **3a** in 68% yield within 4 h (Table 1, entry 6). When the reaction was carried out in polar solvents, such as acetonitrile, tetrahydrofuran (THF), and ether, either no reaction occurred or **3a** was obtained in low yield (Table 1, entries 7−9). With use of 2.0, 1.2, and 1.0 equiv of MVK in CH$_2$Cl$_2$ at room temperature (25 °C), the

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TABLE 2. The Cycloaddition Reactions of 1 with 2a under the Optimal Conditions

entry[a]	R¹/R²/R³	time(h)	yield(%)[b] 3	yield(%)[b] 4 and 4'
1	Me/H/Me **1b**	0.5	**3b**, 82	**4b**, 13
2	Me/H/H **1c**	0.5	**3c**, 75	**4c+4c'**, 25[f]
3	Me/Me/H **1d**	0.5	**3d**, 52	**4d+4d'**, 38[g]
4	MeO/H/MeO **1e**	0.5	**3e**, 51	
5	Cl/H/Cl **1f**	2	**3f**, 90	
6	F/H/F **1g**	2	**3g**, 91	
7[c]	Cl/H/H **1h**	2	**3h**, 81	
8[d]	Cl/Cl/H **1i**	2	**3i**, 80	
9[e]	F/H/H **1j**	2	**3j**, 95	
10	**1k**	2	**3k**, 31	

[a] Reaction conditions: **1** (0.18 mmol) and MVK (1.2 equiv) were dissolved in CH₂Cl₂ (2 mL) and Tf₂NH (2 mg, 4 mol %) was added, then the mixtures were stirred for different times at room temperature. [b] Isolated yield. [c] E- or Z-isomeric mixture = 3:2. [d] E- or Z-isomeric mixture = 3:1. [e] E- or Z-isomeric mixture = 3:2. [f] **4c:4c'** = 2:1. [g] **4d:4d'** > 99:1.

reaction proceeded smoothly to give **3a** in 94%, 97%, and 95% yield within 10 min or 1 h, respectively (Table 1, entries 10−12).

The structure of **3a** has been further confirmed by X-ray diffraction and its CIF data have been presented in the Supporting Information (Figure 1).[19]

With these optimal conditions in hand, we next examined the scope and limitations of this interesting cycloaddition reaction using a variety of vinylidenecyclopropanes **1** and the results of these experiments are shown in Table 2. As for VDCPs **1f−j** bearing electron-withdrawing groups on the benzene rings, the cycloaddition reaction proceeded smoothly to provide the corresponding five-membered carbocyclic products **3f−j** in good to excellent yields within 2 h (Table 2, entries 5−9). In the case of the unsymmetrical VDCPs **1h−j**, the cycloadducts **3h−j** were obtained as E- or Z-isomeric mixtures (Table 2, entries 7−9). However, as for vinylidenecyclopropanes **1b−d** bearing moderately electron-donating methyl groups on the benzene rings, the cycloaddition reaction proceeded more rapidly to afford the expected products **3b−d** in moderate to good yields (82%, 75%, and 52%, respectively) along with another byproduct **4b**,[20] **4c** (**4c′**), and **4d** (**4d′**) in low yields (13%, 25%, and 38%, respectively), indicating that electron-rich aromatic ring facilitates such cycloaddition and the subsequent intramolecular Friedel−Crafts reaction (Table 2, entries 1−3). In the case of
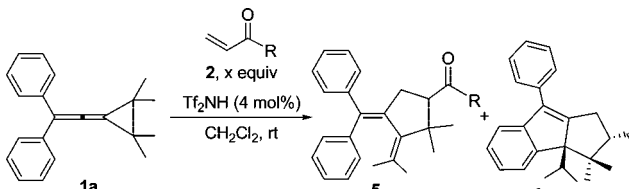
the unsymmetrical VDCPs **1c** and **1d**, **4b** and **4c** were obtained as the major regiochemical isomers of the side product mixtures because the aromatic ring containing more electron-donating methyl groups facilitates such intramolecular Friedel−Crafts reaction (Table 2, entries 2 and 3). Using vinylidenecyclopropane **1e** bearing a strongly electron-donating methoxy group on the benzene ring as the substrate afforded the expected product **3e** in 51% yield along with some other byproducts (Table 2, entry 4). As for the substrate **1k**, the corresponding cycloadduct **3k** was obtained in 31% yield, presumably due to that the replacement of a phenyl group with a methyl group would reduce the nucleophilicity of the allenic moiety and did not facilitate such cycloaddition (Table 2, entry 10).[21]
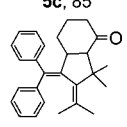
Next, on the basis of above results, we attempted to utilize some other electron-deficient olefins **2** to react with **1a** under similar conditions and the results are summarized in Table 3. The cycloaddition of **1a** with acrylaldehyde **2b** proceeded very smoothly within 1 h, providing the corresponding cycloadduct **5a** in 88% yield (Table 3, entry 1). In the reaction of **1a** with ethyl vinyl ketone **2c** and phenyl vinyl ketone **2d**, the expected cycloadducts **5b** and **5c** were obtained in 92% and 85% yield along with the byproduct **6b** and **6c** in 6% and 10% yield, respectively, under identical conditions (Table 3, entries 2 and 3). Moreover, **1a** could also react with 2-cyclohexen-1-one (**2e**; 10 equiv) smoothly to give cycloadduct **5d** in 56% yield, although a large excess amount of **2e** was required (Table 3, entry 4). However, as for the multisubstituted olefins, such as pent-3-en-2-one (**2f**) and 3-methylbut-3-en-2-one (**2g**), complex product mixtures were obtained under the standard reaction

(19) The crystal data of **3a** have been deposited in CCDC with number 671319. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax +44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk).
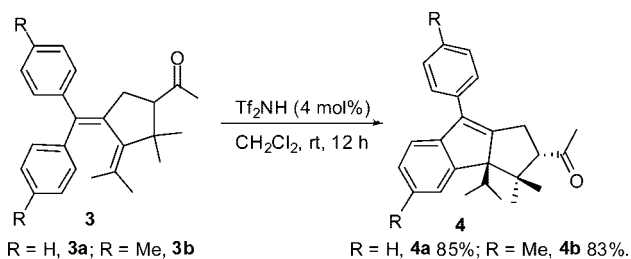
(20) The stereochemistry of **4b** has been further confirmed by X-ray diffraction and its CIF data have been presented in the Supporting Information (CCDC 691928). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax +44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk).

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TABLE 3. The Cycloaddition Reactions of 1 with 2 under Modified Conditions

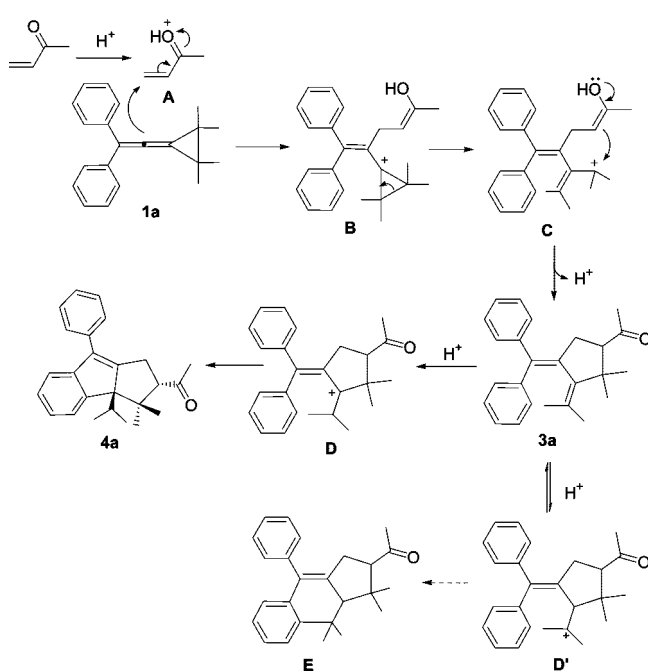| entry[a]	R	x	time (min)	yield (%)[b] 5	yield (%)[b] 6
1	H, **2b**	1.5	60	**5a**, 88	
2	Et, **2c**	2.0	20	**5b**, 92	**6b**, 6
3	Ph, **2d**	1.5	30	**5c**, 85	**6c**, 10
4	**2e**	10.0	60	**5d**, 56	
5	**2f**	2.0	180	complex	
6	**2g**	2.0	180	complex	

[a] Reaction conditions: **1a** (0.18 mmol) and **2** (*x* equiv) were dissolved in CH$_2$Cl$_2$ (2 mL) and Tf$_2$NH (2 mg, 4 mol %) was added, then the mixtures were stirred for different times at room temperature. [b] Isolated yield.

SCHEME 1. The Transformation of 3 to 4 in the Presence of Tf$_2$NH

R = H, **3a**; R = Me, **3b**   R = H, **4a** 85%; R = Me, **4b** 83%.

conditions, presumably due to the steric hindrance[22,23] (Table 3, entries 5 and 6). It should be noted that some other electron-deficient olefins, such as acrylic acid, methyl acrylate, and acrylonitrile, could not react with vinylidenecyclopropanes under the standard conditions.

To clarify the formation route of byproducts **4** and **6**, a control experiment was carried out by treatment of cycloadducts **3a** and **3b** with Tf$_2$NH in CH$_2$Cl$_2$. The corresponding products **4a** and **4b** were provided in 85% and 83% yield, respectively, suggesting that the byproducts **4** and **6** were derived from a further intramolecular Friedel−Crafts reaction of **3** and **5** in the presence of a strong Brønsted acid (Scheme 1).[24]

On the basis of the above results, a plausible reaction mechanism for the cycloaddition of vinylidenecyclopropanes **1** (**1a** as the example) with electron-deficient olefins **2** (MVK as the example) is outlined in Scheme 2. First, MVK is protonated by Tf$_2$NH to

SCHEME 2. A Proposed Mechanism of the Cycloaddition Reaction

generate intermediate **A**, which undergoes a 1,4-nucleophilic addition reaction with the central carbon in the allene moiety of **1a** to give intermediate **B**. Ring opening of cyclopropane in intermediate **B** produces intermediate **C**. Product **3a** is obtained from intermediate **C** through an intramolecular nucleophilic attack. The product **3a** could be further transformed to the product **4a** via intermediate **D**, which was generated from **3a** by protonation, and a subsequent intramolecular Friedel−Crafts reaction. Alternatively, intermediate **D′** can also be given by protonation of **3a**. However, since intermediate **D′** is less stable than the allylic cationic intermediate **D** that is responsible for the formation of **4a**, product **E** is not formed in this reaction system. This is the reason why product **4a** can be exclusively produced in this reaction (Scheme 2).

The generality of this cycloaddition reaction was also examined by using a variety of vinylidenecyclopropanes **7** having two aromatic rings at the cyclopropane under the optimal conditions and the results of these experiments are summarized in Table 4. The corresponding cyclopentane derivatives **8a−f** were obtained in good to excellent yields (67−95%) whether electron-donating or electron-withdrawing groups were introduced on the benzene ring of **7** (Table 4, entries 1−6). The structure of **8a** has been further confirmed by X-ray diffraction and its CIF data have been presented in the Supporting Information.[25]
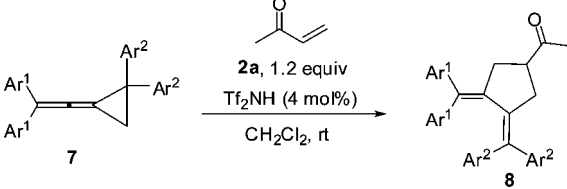
When vinylidenecyclopropane **9** was used to react with MVK, we found that the corresponding five-membered carbocyclic product **10** was formed in 23% yield along with a naphthalene derivative **11** in 20% yield, suggesting that the substituted pattern on the cyclopropane could also significantly affect the reaction outcome. A plausible mechanism of this reaction was outlined in Scheme 3. First, vinylidenecyclopropane **9** produces intermediate **F** via a 1,4-nucleophilic addition to intermediate **A**

(22) Please see the ^{1}H and ^{13}C NMR spectroscopic data of **3a** in the SI and Figure 1 above.

(23) As far as we know, there has been no report in the literature on any skeleton analogy to **3a** having all carbons substituted five-membered carbocycles.

(24) (a) Chavan, S. P.; Thakkar, M.; Kalkote, U. R. *Tetrahedron Lett.* **2007**, *48*, 643–646. (b) Janssen, C. G. M.; Godefroi, E. F. *J. Org. Chem.* **1984**, *49*, 3600–3603.
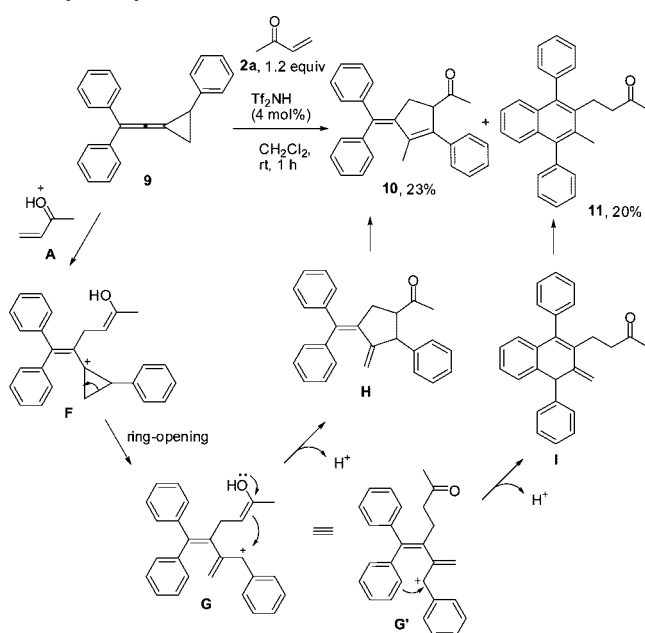
(25) The crystal data of **8a** have been deposited in CCDC with number 678843. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax +44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk).

TABLE 4. The Cycloaddition Reaction of 7 with 2a under the Optimal Conditions

entry[a]	Ar¹/Ar²	time (h)	yield (%)[b] of 8
1	C_6H_5/C_6H_5, **7a**	1	**8a**, 76
2	p-FC_6H_4/p-MeC_6H_4, **7b**	1	**8b**, 79
3	C_6H_5/p-FC_6H_4, **7c**	1	**8c**, 82
4	p-MeC_6H_4/C_6H_5, **7d**	1	**8d**, 95
5	p-ClC_6H_4/C_6H_5, **7e**	1	**8e**, 71
6	p-FC_6H_4/C_6H_5, **7f**	1	**8f**, 67

[a] Reaction conditions: VDCP **7** (0.18 mmol) and MVK (1.2 equiv) were dissolved in CH_2Cl_2 (2 mL) and Tf_2NH (2 mg, 4 mol%) was added, then the mixtures were stirred for 1 h at room temperature. [b] Isolated yield.

SCHEME 3. The Reaction Mechanism of 9 with MVK 2a Catalyzed by Tf_2NH

similarly as shown in Scheme 2, which is then transformed to intermediate **G** via a ring-opening process. Subsequent cyclization of **G** gives intermediate **H**, which undergoes isomerization to furnish product **10**. Alternatively, intermediate **G′**, which is an equivalent of intermediate **G**, can afford intermediate **I** via an intramolecular Friedel−Crafts reaction. Similarly, subsequent aromatization of intermediate **I** furnishes product **11**. The structure of **11** was unambiguously determined by X-ray diffraction and its CIF data have been summarized in the Supporting Information.[26]

Conclusion

We have developed an efficient method for the [3+2] cycloaddition reactions of vinylidenecyclopropanes **1** and **7** with electron-deficient olefins **2** to provide a variety of cyclopentane-containing derivatives **3** and **8** in moderate to excellent yields catalyzed by Tf_2NH under mild conditions. Efforts are in progress to elucidate further mechanistic details of these reactions and to understand their scope and limitations.

Experimental Section

General Remarks. ¹H NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. Infrared spectra were measured on a spectrometer. Mass spectra were recorded by the EI method, and HRMS was measured on a Kratos Analytical Concept mass spectrometer (EI or MALDI). Satisfactory CHN microanalyses were obtained with an analyzer. Melting points are uncorrected. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out with use of 300−400 mesh silica gel at increased pressure.

General Procedure for the Cycloaddition of 1 with MVK. Vinylidenecyclopropanes (VDCPs) **1** (0.18 mmol) and MVK (15 mg, 0.22 mmol, 1.2 equiv) were dissolved in CH_2Cl_2 (3 mL), then Tf_2NH (2 mg, 4 mol %) was added. The mixture was stirred for 0.5 to 2 h at room temperature (25 °C). The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel column with petroleum ether−EtOAc (40: 1) as an eluent.

1-(4-(Diphenylmethylene)-2,2-dimethyl-3-(propan-2-ylidene)cyclopentyl)ethanone, 3a: white solid, mp 150−152 °C; ¹H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.04 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 2.30 (br s, 1H, CH), 2.67−2.72 (m, 2H, CH_2), 7.13−7.16 (m, 5H, Ar), 7.20−7.29 (m, 5H, Ar). ¹³C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.3, 23.0, 25.8, 28.9, 31.7, 34.5, 42.9, 63.5, 126.0, 126.7, 127.6, 127.9, 128.7, 130.4, 130.5, 137.2, 139.9, 140.1, 143.9, 144.1, 209.8. IR (CH_2Cl_2) ν 3077, 3021, 2966, 2926, 2717, 1706, 1597, 1491, 1442, 1358, 1212, 1151, 1073, 1031, 770, 699, 586 cm⁻¹. MS (%) m/e 344 (M⁺, 13), 329 (9), 246 (11), 232 (19), 231 (100), 216 (12), 165 (5), 91 (3), 43 (4). Anal. Calcd. for $C_{25}H_{28}O$: C, 87.16; H, 8.19. Found: C, 87.18; H, 8.01.

Supporting Information Available: Detailed description of experimental procedures, full characterization of new compounds **3**, **4**, **5**, **6**, **8**, **10**, and **11** shown in tables and schemes, and X-ray crystal analysis data of **3a**, **4b**, **8a**, and **11** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) The crystal data of **11** have been deposited in CCDC with number 678269. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax +44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk).