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Anomalous Reaction of $Rh_2(OAc)_4$-Generated Transient Carbonyl Ylides: Chemoselective Synthesis of Epoxy-Bridged Tetrahydropyranone, Oxepanone, Oxocinone, and Oxoninone Ring Systems

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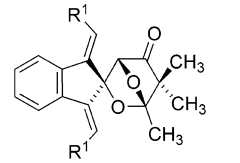
Received October 19, 2006



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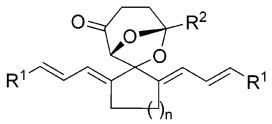

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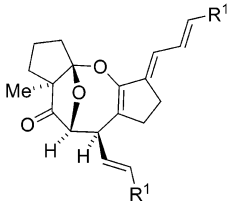

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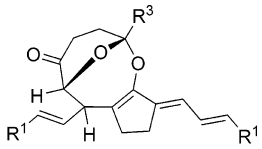

epoxyoxonin-5(6H)-one

A series of symmetrical and unsymmetrical α,*β*-unsaturated ketones such as arylmethylidenecycloalkanones (**16**, **19**), bis(arylmethylidene)cycloalkanones (**21**, **23**, **27**), bisdiphenylnonatetraenones (**30**), and bis(phenylpropenylidene)cycloalkanones (**33**, **38**, **42**) were synthesized and subjected to the rhodium(II)-catalyzed tandem cyclization−cycloaddition reactions with various α-diazo ketones. These reactions afforded spiro epoxy-bridged tetrahydropyranone, spiro epoxy-bridged oxepanone (**41**, **43**), epoxyoxocin-4(5*H*)-one (**35**, **37**), and epoxyoxonin-5(6*H*)-one (**40**) frameworks starting from relatively simple precursors. The regio- and stereochemistry and solid-state architecture arrangements of several products were characterized by single-crystal X-ray structure analysis. The cycloaddition of carbonyl ylides with the compounds having both C═O and C═C groups was found to be chemo- and regioselective. Interestingly, an unusual ring enlargement of cycloadducts **34**, **36**, and **41** derived from C═O group addition was observed, affording epoxyoxocin-4(5*H*)-one and epoxyoxonin-5(6*H*)-one frameworks. Examples for the tandem cyclization−cycloaddition−ring enlargement reaction were also described. The rhodium(II)-generated carbonyl ylides behaved anomalously, furnishing the cycloadducts as a result of the cycloaddition of carbonyl ylides to C═O group despite the presence of C═C groups.

Introduction

α-Diazo ketones are resourceful derivatives, and they serve as very useful intermediates; they continue to be a subject of considerable interest and investigation in synthetic organic chemistry. Rhodium(II) carbenoids, derived from the reaction of α-diazo ketones with a catalytic amount of dirhodium(II) complex, undergo a wide range of synthetically important transformations[1,2] such as ylide formation, cyclopropanation, and insertion reaction. Transition-metal-generated carbonyl ylides, derived from α-diazo ketones, have been broadly used in 1,3-dipolar cycloaddition chemistry.[3] Starting from pretty simple α-diazo ketone precursors, the tandem cyclization−cycloaddition strategies have been applied to the stereocontrolled synthesis

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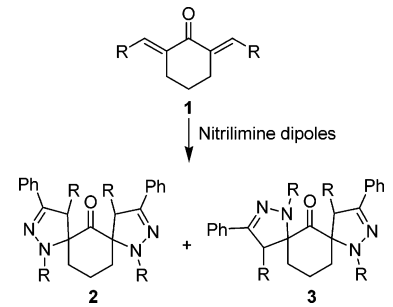
10.1021/jo0621726 CCC: $37.00
Published on Web 01/23/2007

of a variety of oxygen-containing five- or six-membered or complex polycyclic molecules. This chemistry allows for the convenient generation of various five- or six-membered-ring carbonyl ylides, which can be trapped by C=C or C=O bonds. Natural products such as brevicomin,[4] illudins,[5] epoxysorbicillinol,[6] zaragozic acid[7] and many alkaloids[8] have been skillfully synthesized on the basis of the tandem process of cyclization−cycloaddition of rhodium(II) carbenoid. Highly functionalized oxa-bridged units are found as subunits of various biologically important and complex natural products, e.g., ionophore antibiotics[9] and marine toxins.[10] Further, the dioxabicycloalkane unit is present in many oxygen-rich bioactive natural molecules, e.g., frontalin,[11a] sporol,[11b] loukacinols,[11c] amberketal,[11d] isogosterones,[11e] xanthane epoxide,[11f] and austalide B.[11g] The stereoselective synthetic methodology to several oxacyclic compounds has gained considerable attention[12] in recent years.

SCHEME 1



Generally, the chemistry of 1,3-dipolar cycloaddition of various dipoles with dipolarophiles having both C=C and C=O bonds has been scarcely reported. Along this line, there are few reports on the reactions of 1,3-dipoles such as nitrilimines,[13] azomethine ylides,[14] and nitrile oxides[15] furnishing products arise only from C=C groups. For example, 1,3-dipolar cycloaddition reaction of nitrilimines afforded products[13a] exclusive to both exocyclic C=C bonds of 2,6-bis(arylmethylidene)cyclohexanones (Scheme 1). The reactions of carbonyl ylide dipoles with dipolarophiles having both C=C and C=O bonds have also been demonstrated[5,16] to furnish products arising from C=C groups. For example, reactions of carbonyl ylides with dipolarophiles such as α-methylene ketones[16] underwent only C=C cycloaddition. Similar reaction with cycloalkenones[17] afforded both C=O and C=C cycloaddition products without regioselectivity. In continuation of our research program on the reactivity profile[18] of carbonyl ylides, we herein illustrate our investigations on the chemoselective reactions of cyclic carbonyl ylide 1,3-dipoles derived from α-diazo ketones with various symmetrical and unsymmetrical α,β-unsaturated ketones.

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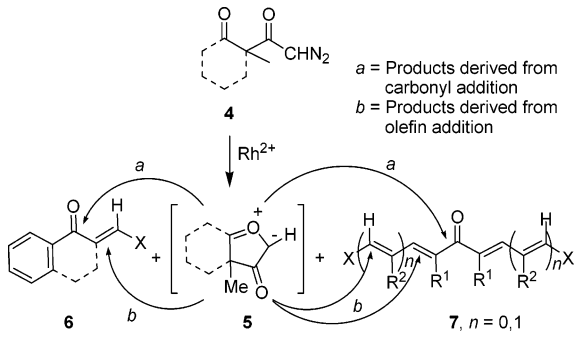
SCHEME 2



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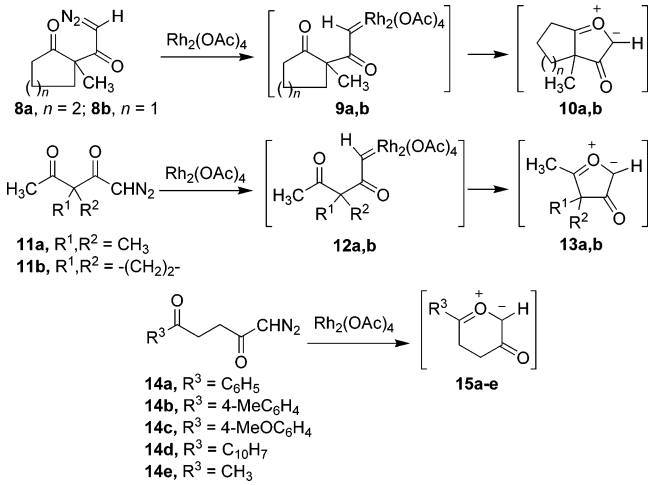
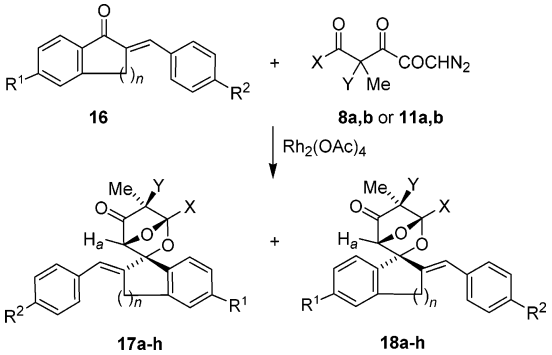


The rhodium(II) acetate dimer catalyzed reactions of α-diazo ketones of type **4** are known to afford the carbonyl ylide dipole intermediates (Scheme 2). The mechanism involved in this processes is the generation of rhodium(II) carbenoid from α-diazo ketone **4** followed by a transannular cyclization of the electrophilic carbenoid on to the neighboring carbonyl group resulting transient cyclic carbonyl ylide **5**, which would cycloadd competitively to dipolarophiles of type **6**, **7**. The general representation of the cycloaddition of carbonyl ylides with dipolarophiles **6**, **7** (Scheme 2) emphasizes their propensity for different modes of 1,3-dipolar cycloaddition. The expected products in these reactions may be either as a result of C═C or C═O cycloaddition, which will result a mixture of isomers.

Results and Discussion

To study the effect of carbonyl ylides with symmetrical or unsymmetrical α,*β*-unsaturated carbonyl compounds, the required starting materials were prepared[19] from the commercially available materials. α-Diazo ketones **8a**,**b** and **11a**,**b** (Scheme 3) were prepared on the basis of the literature reports.[20] The respective transient five-membered cyclic carbonyl ylides **10a**,**b** or **13a**,**b** could be successfully generated by nucleophilic attack of carbonyl oxygen to the highly electrophilic carbenoid center present in rhodium(II) carbenoids **9a**,**b** or **12a**,**b** (Scheme 3). In order to generate six-membered-ring carbonyl ylides **15a**−**e**, we have also synthesized the appropriate α-diazo ketones **14a**−**e**.[20]

TABLE 1. Synthesis of Spiro Epoxy-Bridged Tetrahydropyranones



							yield[a] (%)	
entry	X	Y	*n*	R^1	R^2	product	**17**	**18**
1	−$(CH_2)_3$−		2	H	H	**a**	17[b]	26[b]
2	−$(CH_2)_4$−		2	H	H	**b**	21	33
3	−$(CH_2)_4$−		2	OCH_3	OCH_3	**c**	41	20
4	−$(CH_2)_4$−		2	OCH_3	Cl	**d**	40	20
5	−$(CH_2)_4$−		1	H	Cl	**e**	49[c]	
6	CH_3	CH_3	2	OCH_3	OCH_3	**f**	39	25
7	CH_3	CH_3	2	OCH_3	Cl	**g**	36	27
8	CH_3	CH_3	2	H	CH_3	**h**	23	36

[a] Yields (unoptimized) denote the isolated yield of diastereomers obtained in the reactions. [b] For spectral data, see ref 21. [c] Inseparable diastereomeric mixture.

Initially, the reaction of an equimolar amount of α-diazo ketone **8b** tethered to a cyclopentanone ring, and 2-benzylideneindan-1-one (**16**) with 1 mol % of rhodium(II) acetate dimer catalyst at room temperature under an argon atmosphere afforded only the C═O addition products[21] **17a** and **18a** in 17 and 26% yields (Table 1), respectively. These diastereomers were successfully isolated and characterized. We next demonstrated that the reaction of α-diazo ketone **8a** tethered to a cyclohexanone ring with 2-benzylidene-1-tetralone (**16**) also afforded **17b** (21%) and **18b** (33%) as diastereomers. The products were obtained in both reactions as a mixture of diastereomers in the ratio of 2:3 based on the NMR experiment of the crude reaction mixture.

In order to firmly ascertain the above chemo- and regioselective 1,3-dipolar cycloaddition reactions of carbonyl ylides **10a**,**b** with arylmethylidenecycloalkanones, the single-crystal X-ray analyses[22] of the representative diastereomers of the above two reactions (**17a**, **18b**) were performed. The crystal structure analyses of **17a** and **18b** clearly revealed that the carbonyl ylide derived from respective diazo ketones **8a**,**b** underwent regio- and chemoselective cycloaddition to C═O group of the arylmethylidenecycloalkanones. The stereochemistry of other diastereomers **17b** and **18a** was tentatively assigned as the opposite diastereomer on the basis of their similarity in spectral data.

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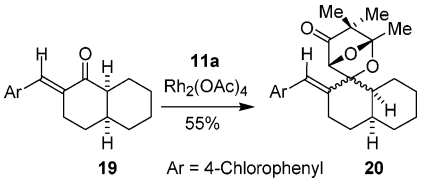
(22) For the single-crystal X-ray analyses of compounds **17a**, **18b**, and **22a**,**b**, see the Supporting Information.

SCHEME 4



The reaction of an equimolar amount of α-diazo ketone **8a** and the appropriate arylmethylidenecycloalkanones **16** derived from 6-methoxytetralone or 1-indanone with rhodium(II) acetate dimer catalyst also afforded only the C═O addition products **17c**−**e** and **18c**−**e** (Table 1) as diastereomers. Similarly, reactions involving other five-membered-ring carbonyl ylides, generated from acyclic α-diazo ketone **11a**, with various substituted arylmethylidenecycloalkanones **16** were performed to furnish **17f**−**h**/**18f**−**h**, and the results are described in Table 1. In all of the above reactions, the diastereomeric mixtures were successfully separated and characterized according to the interrelated spectral data. In particular, the ^{1}H NMR spectrum of compounds **17a**−**h** exhibited characteristic singlet resonance around δ 4.50, whereas their diastereomers **18a**−**h** exhibited around δ 4.70 for the bridgehead proton (H_a). ^{13}C NMR and DEPT-135 analyses of compounds **17a**−**h** showed a peak around 87−89 ppm, whereas compounds **18a**−**h** around 84−86 ppm for OCH carbon.

Consequently, we performed a similar reaction using α-diazo ketone **11a** with α,*β* unsaturated ketone **19** having an *exo*-methylene group derived from *cis*-1-decalone in the presence of rhodium(II) acetate dimer catalyst to furnish the cycloadduct **20** as a inseparable diastereomeric mixture in a ratio of 1:2 (Scheme 4). This reaction also afforded the cycloadduct as a result of cycloaddition of carbonyl ylide to C═O group of **19**.

After studying the 1,3-dipolar cycloaddition reactions with arylmethylidene cycloalkanones, we investigated the detailed reactions of carbonyl ylides derived from α-diazo ketones **8**, **11** with a variety of bis(arylmethylidene)acyclo/cycloalkanones **21**. To this end, the reaction of an equimolar amount of α-diazo ketone **8a** and bis(arylmethylidene)cyclohexanone **21** with $Rh_2(OAc)_4$ catalyst afforded[23] the spiro-dioxabicyclo[2.2.1]alkane system **22a** in 70% yield with complete regio- and chemoselectivity (Table 2).

To obtain evidence for the anomalous behavior and chemo- and regioselective 1,3-dipolar cycloaddition reactions of carbonyl ylide to carbonyl group of multiple *π*-bonded substrates **21**, we performed the single-crystal X-ray analysis of the cycloadduct **22a**. The proposed structure of the cycloadduct **22a** was corroborated unequivocally on the basis of the single-crystal X-ray analysis.[22] The crystal structure analysis clearly showed that the carbonyl ylide **8a** underwent cycloaddition regio- and chemoselectively to the C═O group of bis(arylmethylidene)-cyclohexanone **21**.

Engrossed by the above results, we next generalized this interesting anomalous behavior to obtain diverse spiro-dioxabicyclo[2.2.1]alkane systems. For this purpose, we have chosen several substituted bis(arylmethylidene)acyclo/cycloalkanones **21**. The reaction of α-diazo ketone **11a** with **21** furnished the spirocyclic system **22b** in 71% yield. The single-crystal X-ray analysis[22] and spectral data confirmed the structure and stereochemistry of product **22b**. Reaction of α-diazo ketones **8a**, **11a** and cyclopropane substituted α-diazo ketone **11b** with **21** was performed in the presence of rhodium(II) acetate dimer catalyst to afford the highly functionalized cycloadducts **22c**−**h** in good yields with high degree of regio-, chemo-, and stereocontrol (Table 2). Surprisingly, neither electron-withdrawing nor electron-donating groups (Me/OMe/Cl) as substituents in the aromatic ring of **21** (R^1/R^2/R^3) altered the reaction profile (Table 2). Interestingly, the yield of products **22a-h** was quantitative based on the recovery of the starting materials **21**. Similarly, the reaction of diazo compound **11a** with dibenzylideneinden-2-one **23** derived from 2-indanone afforded the corresponding cycloadduct **24** in 72% yield (Scheme 5).

We have also performed the reactions using diazo ketones **8a** and **11a** with heteroarylmethylidene ketones to afford the products **25** and **26** in good yield (Scheme 6). Thus, the formation of interesting cycloadducts derived from C═O group was observed in a chemoselective manner. It has been reported that the C═C bond of the furan ring is known to undergo cycloaddition with isomünchnone dipoles.[24] It is worth mentioning that the furan as well as thiophene rings remained intact in our experiments.

Further, we performed the above reactions using unsymmetrical bis(arylmethylidene)cyclohexanone. Thus, we carried out the reaction of **8a** with unsymmetrical benzylidenecyclohexanone **27**, prepared by the base condensation reaction of cyclohexanone with an equimolar mixture of benzaldehyde and 4-methylbenzaldehyde, to afford the cycloadduct **28**. This observation is in line with arylmethylidenecycloalkanones as described in Scheme 1. Further, the acyclic α-diazo ketone **11a** treated with **27** furnishing the cycloadduct **29** (Scheme 7). The diastereomers of the above cycloadducts **28** and **29** are obtained in a ratio of 2:1 and could not be separated.

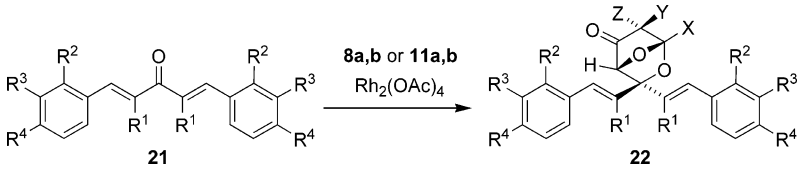
Next, we investigated a series of symmetrical α,*β*-unsaturated ketones having extended C═C bonds. Thus, we carried out the reaction of diazo ketone **11a** with bis-diphenylnonatetraenone **30** in the presence of $Rh_2(OAc)_4$ catalyst affording the cycloadduct **31** as a single product (74%) in a chemoselective manner. Subsequently, we performed the reaction of diazo ketone **8a** with **30**, affording a mixture of cycloadducts **32a**,**b** in a ratio of 4:1 on the basis of the NMR data of crude reaction mixture (Scheme 8). The structure of the major cycloadduct **32a** was confirmed on the basis of the characteristic signal for the oxa-bridged OCH proton at 4.44 ppm and a signal at 212.6 ppm belonging to the carbonyl group in the ^{1}H and ^{13}C NMR spectra, respectively. The structure of the minor cycloadduct **32b** was confirmed as the C═C bond cycloaddition product based on the observation of two signals at 215.7 and 198.9 ppm for two different C═O groups in the ^{13}C NMR spectrum. Furthermore, the regio- and stereoselectivity of the cycloadduct **32b** was also established by the comparison of splitting patterns in ^{1}H NMR spectrum with the cycloadduct **32a**. The ^{1}H NMR spectrum of **32b** exhibited H8 proton at 4.56 ppm (d, J = 6.0 Hz) and H9 proton at 3.12 ppm (d, J = 6.0 Hz). H10 proton of **32b** showed as multiplet around 3.79−3.69 ppm and proton H18 was observed at 5.82 ppm (dd, J_1 = 15.0, J_2 = 9.0 Hz). This pattern clearly reveals that the reaction of ylide **10a** underwent cycloaddition to the terminal C═C bond of diphenylnonatetraenone **30** having *trans*-geometry. As reported,[25] the reactions

(23) Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.* **2002**, *43*, 3931−3934.

(24) Padwa, A.; Hertzog, D. L.; Nadler, W. R. *J. Org. Chem.* **1994**, *59*, 7072−7084.

(25) Muthusamy, S.; Krishnamurthi, J.; Suresh, E. *Synlett* **2005**, 3002−3004.

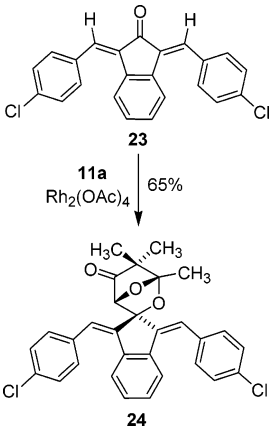
TABLE 2. Synthesis of Novel Spiro-dioxabicyclo[2.2.1]alkanes 22



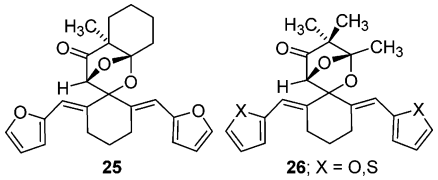
entry	R^1	X	Y	Z	R^2	R^3	R^4	compd	yield[a] of **22** (%)
1	$-(CH_2)_3-$	$-(CH_2)_4-$		CH_3	H	H	Cl	**a**	70
2	$-(CH_2)_3-$	CH_3	CH_3	CH_3	H	H	Cl	**b**	71
3	$-(CH_2)_2-$	$-(CH_2)_4-$		CH_3	$-CH=CHCH=CH-$		H	**c**	74
4	$-(CH_2)_2-$	CH_3	CH_3	CH_3	$-CH=CHCH=CH-$		H	**d**	75
5	$-(CH_2)_2-$	CH_3	CH_3	CH_3	H	H	Me	**e**	71
6	$-(CH_2)_3-$	CH_3	$-(CH_2)_2-$		H	H	H	**f**	73
7	H	CH_3	CH_3	CH_3	H	H	OMe	**g**	75
8	H	CH_3	CH_3	CH_3	H	H	Me	**h**	77

[a] Yields (unoptimized) refer to isolated and pure compounds **22**.

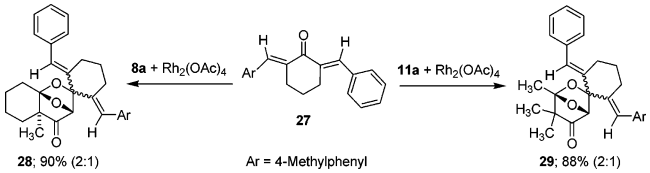
SCHEME 5



SCHEME 6



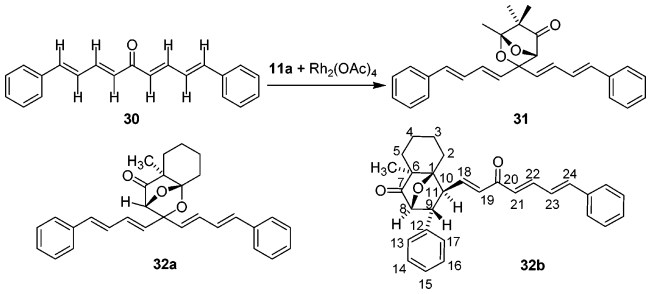
SCHEME 7



with *N*-tosylimines by us, the terminal C=C bond of diphenylnonatetraenone **30** preferably approach the *syn* face to the bridgehead methyl group of five-membered-ring carbonyl ylide **10a**, furnishing the cycloadduct **32b** with complete diastereoselectivity.

We next carried out a similar experiment that involved the reaction of α-diazo ketone **8b** tethered to a cyclopentane ring and bis-(phenylpropenylidene)cyclopentanone **33a** in the presence of rhodium(II) acetate dimer catalyst. ^{1}H NMR spectral analysis of the crude reaction mixture showed a characteristic singlet resonance signal at 4.32 ppm for H-7 proton, which revealed the presence of the corresponding C=O cycloaddition

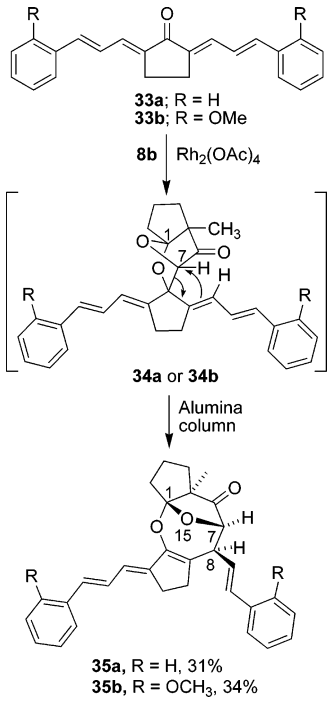
SCHEME 8



product **34a**. Upon neutral alumina column purification of the crude reaction mixture, we observed the formation of the new product **35a**, which was not present in the crude reaction mixture of ^{1}H NMR spectrum. The initially formed product **34a** was not traceable, and we have isolated the product **35a** in 31% yield (Scheme 9). This reaction revealed that the initially formed C=O addition product is not stable and ring-enlarged to **35a**. The IR spectrum showed a strong band at 1754 cm^{-1}. Characteristically, the ^{13}C and DEPT-135 NMR spectra showed the signals at 83.4 and 49.9 ppm for C-7 and C-8 carbons. Moreover, to confirm the stereochemistry of the ring-enlarged product **35a**, the single-crystal X-ray analysis[22] was performed. The styrenyl substituent present in the *exo* position and the dihedral angle between the H7 and H8 protons is found to be 63.5° in the ring-enlarged product **35a**. The observed angle (C1−O15−C7) of oxido-bridge in compound **35a** is 109.7°. Therefore, the formation of ring-enlarged product **35a** was confirmed on the basis of the characteristic singlet resonance at 4.32 ppm for the H7 proton. Similarly, another ring-enlarged product **35b** was obtained from the diazo ketone **8b** and the methoxy-substituted bis(phenylpropenylidene)cyclopentanone **33b**. Interestingly, the α-diazo ketone **8b** underwent tandem cyclization−cycloaddition−ring-expansion reaction, furnishing 2,5-epoxycyclopenta[*b*]oxocin-4(5*H*)-ones **35**.

Encouraged by the result obtained in these reactions, the reaction of an acyclic diazo ketone **11a** and bis(phenylpropenylidene)cyclopentanone **33a** in the rhodium(II) acetate catalyst was performed. ^{1}H NMR spectral analysis of the crude reaction mixture showed the characteristic singlet resonance at 4.32 ppm for H-4 proton of the spiro-dioxabridged cycloadduct **36a** (Table 3). Followed by the neutral alumina column, chromatographic purification of the crude reaction mixture furnished the product **37a** (23%). Similar to the above reaction, we were unable to

SCHEME 9

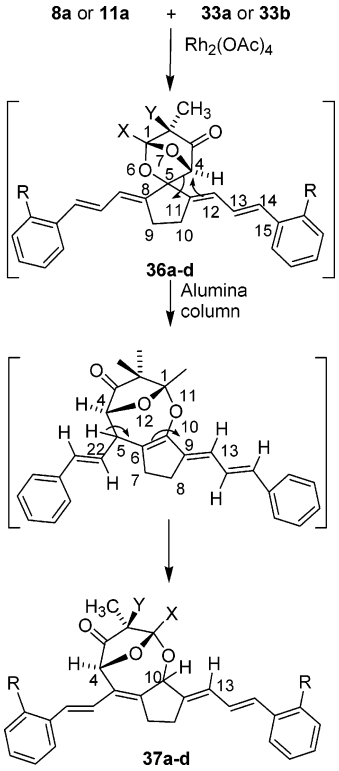


isolate the cycloadduct **36a** by column chromatography. The ^{1}H NMR spectrum showed a singlet at 5.00 and a doublet at 5.34 ppm for H4 and H10 protons, respectively. Characteristically, the ^{13}C and DEPT-135 spectra showed two CH carbon signals at 76.2 and 72.6 ppm for C-4 and C-10 carbons, respectively. The structure of **37a** was assigned as shown in Table 3. This may be due to the initially formed cycloadduct **36a** underwent the ring enlargement followed by 1,3-proton shift. In order to generalize the above interesting process, we have also performed the reactions using diazo ketones **8a** and **11a** with **33** to afford the novel 2,5-epoxycyclopenta[*b*]oxocin-4(5*H*)-ones **37b**−**d**. Fascinatingly, this process involves the tandem cyclization−cycloaddition−ring expansion−proton migration reaction.

To support the mechanistic details for the above ring-enlargement reactions (Scheme 9 and Table 3), we attempted to isolate the initially formed cycloadducts **34**/**36** using silica gel or alumina column chromatographic purification. To this end, we have successfully isolated the representative cycloadduct **36a** in 75% yield using flash neutral alumina column within 15 min duration. Then, we performed the further reaction of the isolated cycloadduct **36a**. Thus, reactions of **36a** with alumina, mild acidic conditions, and Lewis acids or bases such as K_2CO_3, Et_3N afforded only the decomposed material. On the other hand, the cycloadduct **36a** was subjected again to neutral alumina column to furnish the ring-enlarged compound **37a** in 30% yield (Scheme 10). Hence, we determined that the product **37a** arose from the initially formed cycloadduct **36a**.

The reactivity of carbonyl ylide dipoles **10a** and **13a** with the methyl-substituted bis(phenylpropenylidene)cyclopentanone **38** was further examined. Thus, we performed the rhodium(II)-catalyzed reactions of α-diazo ketones **8a**, **11a** with **38** to afford the corresponding C═O cycloaddition products **39a**,**b** (Scheme 11) as the major product and only trace quantity of the corresponding ring-enlarged product. The reason for the absence of the ring-enlarged product may be due to the presence of methyl substituent on the phenylpropenylidene part.

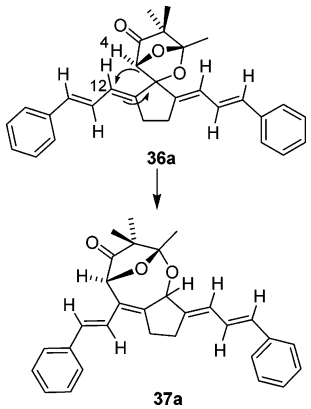
TABLE 3. Synthesis of 2,5-Epoxycyclopenta[*b*]oxocin-4(5*H*)-ones 37



entry	X	Y	R	product **37**	yield[a] (%)
1	CH_3	CH_3	H	**a**	23
2	CH_3	CH_3	OCH_3	**b**	35
3	$-(CH_2)_4-$		H	**c**	28
4	$-(CH_2)_4-$		OCH_3	**d**	32

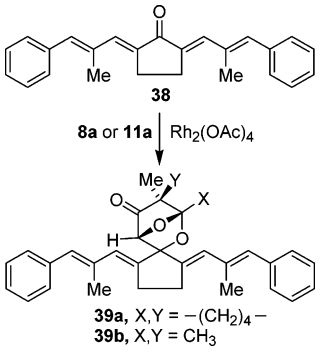
[a] Yields (unoptimized) refer to isolated and pure compounds **37**.

SCHEME 10



Finally, we investigated the reactions of six-membered-ring carbonyl ylides **15**. Toward this, we performed the reaction of α-diazo ketone **14a** with bis-(phenylpropenylidene)cyclopentanone **33b** in the presence of rhodium(II) acetate dimer catalyst at room temperature (Table 4). The purification using neutral alumina column chromatography afforded the products **40a** (major) and **41a** (minor). The ratio of the above products was found to be 3:1 based on the NMR data of the crude reaction mixture. The pure isolated product **41a** was again subjected to neutral alumina column chromatography but failed to obtain the ring-enlarged product **40a**.

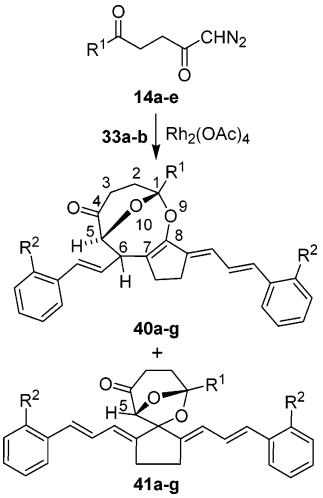
SCHEME 11



Having examined the reaction between **33b** and **14a**, we turned our attention to carry out the reactions of various α-diazo ketones **14b**−**d** tethered to substituted aryl, naphthyl rings with **33**. The reactions of α-diazo ketones **14b**−**d** with dipolarophile **33** afforded the ring-enlarged products **40b**−**e** with a trace quantity of **41**, whereas the α-diazo ketone **14e**, derived from levulinic acid, with **33a,b** afforded only the cycloadducts **41f**,**g**. The presence of methoxy substituent on **33b** enhances the yield of ring-enlarged product **40a**, and the methoxy substituent on diazo ketone **14c** reduces the yield of **40d**. The ring-enlarged products **40** and cycloadducts **41** were obtained on the basis of the phenyl or methyl substituent present on the six-membered-ring carbonyl ylide intermediates **15**.

After studies with bis(phenylpropenylidene)cyclopentanone with five- and six-membered-ring carbonyl ylide dipoles, we investigated the similar reactions with bis(phenylpropenylidene)-cyclohexanone **42**. The reaction of compound **42a** with α-diazo ketones **8a**,**b** and **11a** in the presence of rhodium(II) acetate dimer catalyst afforded the cycloadducts **43a**−**c** in good yield (Table 5). The spectral data manifestly confirmed the proposed structure of the cycloadducts **43**. Similarly, the reaction of six-membered-ring carbonyl ylide derived from **14a** with **42b** also furnished the cycloadduct **43d**. In all of the above reactions, the five- and six-membered-ring carbonyl ylides underwent cycloaddition exclusively to C═O group of compound **42**. No observation of the ring-enlarged products such as **35**, **37**, and **40** was observed.

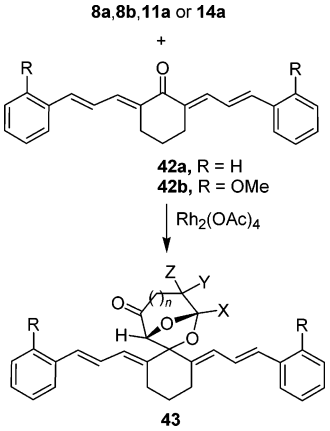
TABLE 4. Synthesis of 2,6-Epoxycyclopenta[*b*]oxonin-5(6*H*)-ones 40



entry	R^1	R^2	product	yield[a] (%) 40	41
1	phenyl	OCH_3	**a**	42	10
2	phenyl	H	**b**	36	trace
3	4-methylphenyl	OCH_3	**c**	34	trace
4	4-methoxyphenyl	OCH_3	**d**	28	trace
5	1-naphthyl	OCH_3	**e**	32	trace
6	methyl	H	**f**		38
7	methyl	OCH_3	**g**		47

[a] Yields (unoptimized) refer to isolated and pure compounds **40** and **41**.

TABLE 5. Synthesis of Spiroepoxy-Bridged Compounds 43



entry	product **43**	*n*	R	X	Y	Z	yield[a] (%)
1	**a**	0	H	$-(CH_2)_4-$		CH_3	74
2	**b**	0	H	$-(CH_2)_3-$		CH_3	69
3	**c**	0	H	CH_3	CH_3	CH_3	74
4	**d**	1	OMe	Ph	H	H	44

[a] Yields (unoptimized) refer to isolated and pure compounds **43**.

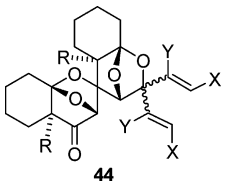


FIGURE 1.

It is notable that the ring-expansion occurred only with the reaction of diazo ketone and bis-(phenylpropenylidene)cyclopentanone **33** via tandem cyclization−cycloaddition−ring enlargement reaction. This indicates that the presence of the cyclopentane ring present in the spirocyclic compounds **34**, **36** and **41** may provide the more strain compared to the cyclohexane ring present in **43**. No ring-expansion of the cycloadducts obtained from all other α,*β*-unsaturated ketones utilized in this study was observed. Under similar experimental conditions, the above experiments can lead to 2:1 cycloadducts[3a] **44** (Figure 1) or products via competitive cyclopropanation/C−H insertion,[26] but we did not observe any such products.

Conclusion

In summary, we have demonstrated that the rhodium(II)-generated carbonyl ylides underwent anomalous 1,3-dipolar cycloaddition to the C═O group of various α,*β*-unsaturated ketones such as arylmethylidenecycloalkanones, symmetrical and unsymmetrical bis(arylmethylidene)acyclo/cycloalkanones,

1,9-diphenylnonatetraen-5-ones, and bis(phenylpropenylidene)-cycloalkanones with high degrees of chemo- and regioselectivity. Interestingly, the tandem cyclization−cycloaddition−ring enlargement process was developed from the rhodium(II)-catalyzed reactions of diazo ketones with the extended π-bonded systems. Besides the well-known C═C cycloaddition processes, carbonyl ylides underwent cycloaddition to C═O group despite the presence of C═C bonds in chemoselective manner. Based on the tandem cyclization−cycloaddition process, a novel stereoselective method has been developed for the synthesis of diverse and structurally complex spiro epoxy-bridged tetrahydropyranone, spiro epoxy-bridged oxepanone, epoxyoxocin-4(5*H*)-one, and epoxyoxonin-5(6*H*)-one frameworks.

Experimental Section

General Procedure for the Rhodium(II)-Catalyzed Cycloaddition Reaction of α-Diazo Ketones with α,β-Unsaturated Ketones. To an oven-dried flask containing an anhydrous dichloromethane solution (dried over phosphorus pentoxide) of the appropriate α-diazo ketone (1.1 mmol) and an appropriate α,β-unsaturated ketone (1 mmol) was added 0.5−1.0 mol % of rhodium(II) acetate dimer catalyst under an argon atmosphere at room temperature. The progress of the reaction was monitored by TLC until the disappearance of the starting diazo ketones. The solvent was removed under reduced pressure and the resulting residue purified using silica gel/neutral alumina column chromatography (EtOAc−hexane mixture as eluent) to afford the respective epoxy-bridged spirocycles.

Reaction of α-Diazo Ketone 8a with (2*E*)-6-Methoxy-2-(4-methoxybenzylidene)-3,4-dihydronaphthalen-1(2*H*)-one (16). Preparation of Compounds 17c and 18c. A mixture of **16** (235 mg, 0.81 mmol) and α-diazo ketone **8a** (145 mg, 0.81 mmol) was allowed to react with $Rh_2(OAc)_4$ (3.6 mg 1.0 mol %) in anhydrous CH_2Cl_2 (20 mL) for 3.0 h according to the general procedure to afford the diastereomers **17c** and **18c** in 41% (148 mg) and 20% (72 mg) yield, respectively. **17c:** colorless solid; mp 167−169 °C (CH_2Cl_2/hexane); IR (KBr) 2932, 1760, 1609, 1511, 1494, 1288, 1251, 1051, 1027 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.44 (d, J = 8.6 Hz, 1H), 7.11 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.79−6.75 (m, 2H), 6.61 (d, J = 2.5 Hz, 1H), 4.57 (s, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.05−2.87 (m, 2H), 2.58−2.36 (m, 2H), 2.09−1.31 (m, 8H), 1.24 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 212.1, 160.0, 159.0, 137.6, 136.0, 133.4, 130.7, 131.1, 127.7, 124.7, 114.5, 114.2, 113.8, 113.2, 89.0, 85.9, 55.9, 53.7, 33.2, 29.9, 27.2, 24.9, 23.8, 20.7, 15.3; MS (EI, 70 eV) *m*/*z* 446 (9, M^+), 335 (70), 295 (100), 293 (29), 266 (7), 123 (55), 83 (53). Anal. Calcd for $C_{28}H_{30}O_5$: C, 75.31; H, 6.72. Found: C, 75.06; H, 6.77. **18c:** colorless solid; mp 129−131 °C (CH_2Cl_2/hexane); IR (KBr) 2946, 1766, 1607, 1510, 1498, 1463, 1258, 1179, 1039 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.42 (d, J = 8.6 Hz, 1H), 7.27 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.73−6.69 (m, 3H), 4.74 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 2.99−2.74 (m, 4H), 2.33−1.28 (m, 8H), 1.26 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 212.6, 159.9, 158.8, 139.1, 136.6, 130.9, 128.6, 125.9, 125.2, 114.1, 113.9, 111.8, 86.5, 85.0, 55.9, 55.8, 54.3, 33.3, 28.6, 27.4, 25.9, 23.7, 20.6, 15.0; MS (EI, 70 eV) *m*/*z* 446 (7, M^+), 336 (17), 335 (75), 295 (100), 279 (11), 123 (65). Anal. Calcd for $C_{28}H_{30}O_5$: C, 75.31; H, 6.72. Found: C, 75.37; H, 6.70.

Reaction of α-Diazo Ketone 8a with (2*E*,5*E*)-2,5-Bis(1-naphthylmethylene)cyclopentanone (21). Synthesis of Compound 22c. A mixture of **21** (180 mg, 0.5 mmol) and α-diazo ketone **8a** (90 mg, 0.5 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.2 mg, 1.0 mol %) in anhydrous CH_2Cl_2 (15 mL) for 3.5 h at room temperature under an argon atmosphere according to the general method to afford product **22c** (190 mg, 74%) as a colorless solid: mp 168−170 °C (CH_2Cl_2/hexane); IR (KBr) 2938, 2861, 1760, 1442 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.31 (d, J = 7.4 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.83−7.71 (m, 4H), 7.55−7.16 (m, 10H), 4.64 (s, 1H), 2.70−2.68 (m, 2H), 2.57−2.35 (m, 3H), 2.21−1.50 (m, 7H), 1.40 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 212.0, 143.6, 140.7, 134.6, 134.2, 134.1, 132.4, 132.1, 129.1, 128.9, 128.2, 128.1, 127.2, 126.8, 126.7, 126.6, 126.4, 125.8, 125.7, 124.9, 122.9, 122.7, 114.5, 91.0, 87.5, 54.2, 32.8, 27.4, 25.9, 25.4, 23.5, 20.3, 14.7; MS (FD^+) *m*/*z* 512 (M^+). Anal. Calcd for $C_{36}H_{32}O_3$: C, 84.34; H, 6.29. Found: C, 84.67; H, 6.33.

Reaction of α-Diazo Ketone 11a with (1*E*,3*E*,6*E*,8*E*)-1,9-Diphenylnona-1,3,6,8-tetraen-5-one (30). Synthesis of Compound 31. A mixture of **30** (157 mg, 0.55 mmol) and α-diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with $Rh_2(OAc)_4$ (1.2 mg, 0.5 mol %) in anhydrous CH_2Cl_2 (10 mL) for 3.5 h at room temperature under an argon atmosphere according to the general method to afford product **31** (147 mg, 65%) as a colorless viscous oil: IR (neat) 3028, 2995, 1766, 1448, 1394, 1266, 1131 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.40−7.18 (m, 10H), 6.88−6.43 (m, 6H), 5.85 (d, J = 15.0 Hz, 1H), 5.74 (d, J = 15.0 Hz, 1H), 4.39 (s, 1H), 1.64 (s, 3H), 1.11 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 213.0, 137.7, 137.4, 134.9, 134.4, 133.8, 132.5, 129.2, 129.1, 128.5, 128.4, 127.2, 127.1, 115.0, 87.2, 83.8, 54.3, 22.2, 18.6, 15.7; MS (FD^+) *m*/*z* 412 (M^+). Anal. Calcd for $C_{28}H_{28}O_3$: C, 81.52; H, 6.84. Found: C, 81.71; H, 6.89.

Reaction of α-Diazo Ketone 8a with (1*E*,3*E*,6*E*,8*E*)-1,9-Diphenylnona-1,3,6,8-tetraen-5-one (30). Synthesis of Compounds 32a and 32b. A mixture of **30** (145 mg, 0.5 mmol) and α-diazo ketone **8a** (90 mg, 0.5 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.2 mg) in anhydrous CH_2Cl_2 (15 mL) for 3.0 h at room temperature under an argon atmosphere according to the general method to afford products **32a** (89.0 mg, 41%) and **32b** (55.0 mg, 25%). **32a**: colorless viscous oil; IR (neat) 3027, 2939, 1763, 1448, 1376, 1285, 1045 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.40−7.18 (m, 10H), 6.87−6.43 (m, 6H), 5.85 (d, J = 15.0 Hz, 1H), 5.75 (d, J = 15.0 Hz, 1H), 4.44 (s, 1H), 2.17−2.11 (m, 1H), 1.97−1.24 (m, 7H), 1.14 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 212.6, 134.9, 134.4, 133.8, 132.5, 129.2, 128.5, 128.4, 127.2, 127.1, 114.0, 87.4, 83.9, 53.6, 32.4, 27.6, 23.7, 20.7, 15.5; MS (FD^+) *m*/*z* 438 (M^+). Anal. Calcd for $C_{30}H_{30}O_3$: C, 82.15; H, 6.90. Found: C, 82.20; H, 6.97. **32b**: colorless viscous oil; IR (neat) 2935, 2862, 1756, 1678, 1652, 1615, 1584, 1450, 1265 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.46−7.23 (m, 11H), 7.05−6.83 (m, 2H), 6.47 (d, J = 15.0 Hz, 2H), 5.82 (dd, J_1 = 15.0, J_2 = 9.0 Hz, 1H), 4.56 (d, J = 6.0 Hz 1H), 3.79−3.69 (m, 1H), 3.12 (d, J = 6.0 Hz, 1H), 2.03−1.22 (m, 8H), 1.25 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 215.7, 198.9, 144.0, 143.2, 137.0, 136.5, 134.7, 130.2, 129.9, 129.5, 129.3, 129.2, 129.1, 128.4, 127.9, 127.0, 124.8, 92.1, 84.8, 58.4, 51.7, 48.7, 31.6, 27.1, 22.7, 20.6, 16.1; MS (FD^+) *m*/*z* 438 (M^+). Anal. Calcd for $C_{30}H_{30}O_3$: C, 82.15; H, 6.90. Found: C, 82.05; H, 6.91.

Reaction of α-Diazo Ketone 8b with (2*E*,6*E*)-2,5-Bis[(2*E*)-3-phenylprop-2-en-1-ylidene]cyclopentanone (33a). Synthesis of Compound 35a. A mixture of **33a** (160 mg, 0.51 mmol) and α-diazo ketone **8b** (85 mg, 0.51mmol) was allowed to react with $Rh_2(OAc)_4$ (2.2 mg) in anhydrous CH_2Cl_2 (15 mL) for 3 h at room temperature under an argon atmosphere. The solvent was removed under reduced pressure and the resulting residue purified using neutral alumina column chromatography (EtOAc/hexane, 3:97) to afford compound **35a** (57 mg, 31%) as a pale yellow solid: mp 177−179 °C (CH_2Cl_2/hexane); IR (KBr) 3057, 3028, 2976, 1754, 1449, 1324, 1266, 1166 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.36−7.12 (m, 10H), 6.85 (dd, J_1 =15.0 Hz, J_2 = 11.0 Hz, 1H), 6.51 (dd, J_1 = 15.0 Hz, J_2 = 11.0 Hz, 2H), 6.44−6.16 (m, 2H), 4.43 (s,

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1H), 3.27 (d, J = 8.4 Hz, 1H), 2.62−2.21 (m 6H), 2.05−1.70 (m 4H), 1.02 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 218.0, 150.1, 144.1, 138.4, 137.2, 132.7, 131.8, 129.0, 128.1, 127.6, 127.1, 126.9, 126.6, 122.4, 120.6, 117.8, 83.4, 54.3, 49.9, 37.5, 36.6, 31.6, 25.0, 21.4, 16.8; MS (EI) m/z 451 (33, M + 1), 450 (100, M^+), 394 (8), 353 (32), 197 (27), 97 (74). Anal. Calcd for $C_{31}H_{30}O_3$: C, 82.64; H, 6.71. Found: C, 82.66; H, 6.70.

Reaction of α-Diazo Ketone 8b with (2*E*,6*E*)-2,5-Bis[(2*E*)-3-(2-methoxyphenyl)prop-2-en-1-ylidene]cyclopentanone (33b). Synthesis of Compound 35b. A mixture of **33b** (185 mg, 0.51 mmol) and α-diazo ketone **8b** (85 mg, 0.51 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.2 mg) in anhydrous CH_2Cl_2 (15 mL) for 3 h at room temperature under an argon atmosphere. The solvent was removed under reduced pressure and the resulting residue purified using neutral alumina column chromatography (EtOAc/hexane, 3:97) to afford compound **35b** (73 mg, 34%) as a pale yellow solid: mp 184−186 °C (CH_2Cl_2/hexane); IR (KBr) 3052, 3022, 2977, 1752, 1447, 1326, 1263, 1167 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49−7.43 (m, 2H), 7.25−7.12 (m, 2H), 6.92−6.81 (m, 7H), 6.35−6.18 (m, 2H), 4.46 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.29 (d, J = 8.7 Hz, 1H), 2.52−2.30 (m, 4H), 1.99−1.65 (m, 6H) 1.02 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 217.6, 156.5, 149.3, 143.1, 129.6, 128.5, 127.9, 127.0, 126.8, 126.6, 126.0, 125.6, 121.7, 120.6, 120.5, 120.0, 117.8, 110.8, 83.1, 55.3, 53.6, 49.9, 36.9, 36.0, 31.0, 24.4, 20.8, 15.6; MS (EI) m/z 510 (100, M^+), 413 (18), 389 (8), 361 (10), 283 (12), 227 (13), 121 (42), 91 (22), 55 (11). Anal. Calcd for $C_{33}H_{34}O_5$: C, 77.62; H, 6.71. Found: C, 77.69; H, 6.74.

Reaction of α-Diazo Ketone 11a with (2*E*,6*E*)-2,5-Bis[(2*E*)-3-phenylprop-2-en-1-ylidene]cyclopentanone (33a). Synthesis of Compound 36a. A mixture of **33a** (172 mg, 0.55 mmol) and α-diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.2 mg) in anhydrous CH_2Cl_2 (15 mL) for 3.5 h at room temperature under an argon atmosphere. The solvent was removed under reduced pressure and the resulting residue purified using neutral alumina flash column chromatography (EtOAc/hexane, 7:93) within 15 min duration to afford compound **36a** (179 mg, 75%) as a pale yellow solid: mp 168−170 °C (CH_2Cl_2/hexane); IR (KBr) 2921, 1757, 1599, 1495, 1448, 1360, 1384, 1270, 1154, 960 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.43−7.17 (m, 10H), 6.94−6.77 (m, 2H), 6.66−6.46 (m, 2H), 6.36−6.20 (m, 2H), 4.32 (s, 1H), 2.84−2.50 (m, 4H), 1.77 (s, 3H), 1.34 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 212.0, 143.2, 138.8, 138.1, 137.9, 134.2, 133.9, 129.2, 128.2, 127.0, 125.6, 125.2, 125.1, 124.8, 114.8, 90.2, 87.3, 54.7, 25.11, 24.6, 23.0, 17.8, 15.5; MS (FD$^+$) m/z 438 (M^+). Anal. Calcd for $C_{30}H_{30}O_3$: C, 82.16; H, 6.90. Found: C, 82.43; H, 6.94.

Reaction of α-Diazo Ketone 11a with (2*E*,6*E*)-2,5-Bis[(2*E*)-3-phenylprop-2-en-1-ylidene]cyclopentanone (33a). Synthesis of Compound 37a. A mixture of **33a** (172 mg, 0.55 mmol) and α-diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.2 mg) in anhydrous CH_2Cl_2 (15 mL) for 3.5 h at room temperature under an argon atmosphere. The solvent was removed under reduced pressure and the resulting residue purified using neutral alumina column chromatography (EtOAc/hexane, 5:95) to afford compound **37a** (55 mg, 23%) as a pale yellow solid: mp 200−202 °C (CH_2Cl_2/hexane); IR (KBr) 2917, 1759, 1593, 1493, 1446, 1384, 1270, 965 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41−7.14 (m, 10H), 6.87−6.81 (m, 1H), 6.61 (d, J = 15.0 Hz, 1H), 6.53 (d, J = 15.0 Hz, 1H), 6.30−6.14 (m, 2H), 5.34 (t, J = 7.0 Hz, 1H), 5.00 (s, 1H), 2.83−2.82 (m, 2H), 2.50−2.48 (m, 2H), 1.49 (s, 3H), 1.20 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 215.4, 154.7, 147.7, 139.6, 138.6, 137.1, 131.6, 131.5, 129.1, 128.4, 127.7, 127.6, 127.1, 127.0, 126.7, 118.7, 110.4, 76.2, 72.6, 53.6, 32.2, 29.0, 21.6, 17.6, 16.9; MS (FD$^+$) m/z 438 (M^+). Anal. Calcd for $C_{30}H_{30}O_3$: C, 82.16; H, 6.90. Found: C, 82.31; H, 6.98.

Reaction of α-Diazo Ketone 11a with (2*E*,6*E*)-2,5-Bis[(2*E*)-3-(2-methoxyphenyl)prop-2-en-1-ylidene]cyclopentanone (33b). Synthesis of Compound 37b. A mixture of **33b** (197 mg, 0.55 mmol) and α-diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.2 mg) in anhydrous CH_2Cl_2 (15 mL) for 3.0 h at room temperature under an argon atmosphere. The solvent was removed under reduced pressure and the resulting residue purified using neutral alumina column chromatography (EtOAc/hexane, 5:95) to afford compound **37b** (96 mg, 35%) as a pale yellow solid: mp 212−214 °C (CH_2Cl_2/hexane); IR (KBr) 2911, 1757, 1597, 1490, 1444, 1384, 1273, 965 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49 (d, J = 7.8 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.24−7.12 (m, 2H), 6.95−6.84 (m, 7H), 6.30 (d, J = 8.0 Hz, 1H), 6.22 (d, J = 8.0 Hz, 1H), 5.34 (d, J = 4.0 Hz, 1H), 5.09 (s, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 2.83−2.47 (m, 4H), 1.48 (s, 3H), 1.21 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 215.4, 157.4, 157.1, 154.7, 147.7, 139.6, 138.6, 137.1, 131.6, 131.5, 129.1, 128.4, 127.7, 127.1, 127.0, 126.7, 120.9, 119.4, 108.4, 76.4, 73.2, 55.9, 55.8, 52.6, 32.7, 32.3, 29.1, 28.9, 23.3, 21.1, 14.5; MS (FD$^+$) m/z 498 (M^+). Anal. Calcd for $C_{32}H_{34}O_5$: C, 77.08; H, 6.87. Found: C, 77.30; H, 6.90.

Reaction of α-Diazo Ketone 8a with (2*E*,6*E*)-2,5-Bis[(2*E*)-3-phenylprop-2-en-1-ylidene]cyclopentanone (33a). Synthesis of Compound 37c. A mixture of **33a** (155 mg, 0.5 mmol) and α-diazo ketone **8a** (90 mg, 0.5 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.2 mg) in anhydrous CH_2Cl_2 (20 mL) for 2.5 h at room temperature under an argon atmosphere. The solvent was removed under reduced pressure and the resulting residue purified using neutral alumina column chromatography (EtOAc/hexane, 4:96) to afford compound **37c** (65 mg, 28%) as a viscous oil: IR (neat) 2932, 1759, 1592, 1447, 1274, 1161, 1072 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36−7.17 (m, 10H), 6.87 (d, J = 15.0 Hz, 1H), 6.60 (d, J = 15.0 Hz, 1H), 6.50 (d, J = 15.0 Hz, 1H), 6.30−6.17 (m, 2H), 5.35 (d, J = 4.0 Hz, 1H), 5.11 (s, 1H), 2.83−2.82 (m, 2H), 2.49−2.48 (m, 2H), 2.22 (d, J = 8.0 Hz, 1H), 1.75−1.18 (m, 7H), 1.23 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 214.8, 155.0, 147.7, 139.6, 138.7, 137.1, 131.8, 131.4, 129.2, 128.4, 127.9, 127.6, 127.2, 126.8, 118.9, 108.7, 76.5, 72.6, 52.9, 32.9, 32.3, 29.4, 29.0, 23.4, 21.1, 14.5; MS (FD$^+$) m/z 464 (M^+). Anal. Calcd for $C_{32}H_{32}O_3$: C, 82.73; H, 6.94. Found: C, 82.91; H, 6.98.

Reaction of α-Diazo Ketone 8a with (2*E*,6*E*)-2,5-Bis[(2*E*)-3-(2-methoxyphenyl)prop-2-en-1-ylidene]cyclopentanone (33b). Synthesis of Compound 37d. A mixture of **33b** (178 mg, 0.5 mmol) and α-diazo ketone **8a** (90 mg, 0.5 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.2 mg) in anhydrous CH_2Cl_2 (20 mL) for 3.0 h at room temperature under an argon atmosphere. The solvent was removed under reduced pressure and the resulting residue purified using neutral alumina column chromatography (EtOAc/hexane, 6:94) to afford **37d** (86 mg, 32%) as a pale yellow solid: mp 230−232 °C (CH_2Cl_2/hexane); IR (neat) 2929, 1761, 1593, 1445, 1276, 1159, 1071 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.48 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.24−7.12 (m, 2H), 6.94−6.86 (m, 7H), 6.31 (d, J = 8.0 Hz, 1H), 6.23 (d, J = 8.0 Hz, 1H), 5.36 (d, J = 4.0 Hz, 1H), 5.10 (s, 1H), 3.83 (s, 6H), 2.81−2.47 (m, 4H), 2.24 (d, J = 8.0 Hz 1H), 1.68−1.42 (m, 7H), 1.22 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 214.8, 157.4, 157.1, 154.0, 147.0, 139.0, 129.6, 129.4, 128.5, 127.7, 126.8, 126.6, 125.9, 121.2, 119.5, 108.5, 76.4, 73.2, 56.0, 52.8, 32.8, 32.3, 29.3, 28.9, 23.3, 21.0, 14.4; MS (FD$^+$) m/z 524 (M^+). Anal. Calcd for $C_{34}H_{36}O_5$: C, 77.84; H, 6.92. Found: C, 77.80; H, 6.88.

Reaction of α-Diazo Ketone 8a with (2*E*,5*E*)-2,5-Bis[(2*E*)-2-methyl-3-phenylprop-2-en-1-ylidene]cyclopentanone (38). Synthesis of Compound 39a. A mixture of **38** (150 mg, 0.44 mmol) and α-diazo ketone **8a** (80 mg, 0.44 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.2 mg) in anhydrous CH_2Cl_2 (20 mL) for 3.0 h at room temperature under an argon atmosphere according to the general method to afford **39a** (202 mg, 73%) as a pale yellow solid: mp 178−180 °C (CH_2Cl_2/hexane); IR (KBr) 2934, 1764, 1708, 1447, 1046, 1009, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31−7.18 (m, 10H), 6.51 (s, 1H), 6.39 (s, 1H), 6.20 (s, 2H), 4.41 (s, 1H), 2.86−2.53 (m, 4H), 2.31−2.27 (m, 1H), 2.06 (s, 3H), 2.00

(s, 3H), 1.84−1.39 (m, 7H), 1.31 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 211.6, 139.6, 138.5, 138.3, 136.5, 135.5, 134.9, 131.8, 131.3, 129.6, 129.3, 128.8, 128.6, 127.0, 114.1, 91.1, 87.3, 54.8, 33.0, 27.3, 26.1, 20.5, 19.2, 18.9, 14.7; MS (EI) *m*/*z* 492 (15, M^+), 474 (4), 401 (5), 353 (10), 145 (31), 105 (100), 77 (60), 55 (65), 43 (98). Anal. Calcd for $C_{34}H_{36}O_3$: C, 82.89; H, 7.37. Found: C, 82.80; H, 7.46.

Reaction of α-Diazo Ketone 11a with (2*E*,5*E*)-2,5-Bis[(2*E*)-2-methyl-3-phenylprop-2-en-1-ylidene]cyclopentanone (38). Synthesis of Compound 39b. A mixture of **38** (150 mg, 0.44 mmol) and α-diazo ketone **11a** (68 mg, 0.44 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.0 mg) in anhydrous CH_2Cl_2 (15 mL) for 2.0 h at room temperature under an argon atmosphere according to the general method to afford compound **39b** (142 mg, 69%) as a pale yellow solid: mp 178−180 °C (CH_2Cl_2/hexane); IR (KBr) 2928, 1764, 1699, 1597, 1445, 1108, 699 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30−7.17 (m, 10H), 6.51 (s, 1H), 6.38 (s, 1H), 6.22 (s, 1H), 6.18 (s, 1H), 4.36 (s, 1H), 2.85−2.59 (m, 4H), 2.06 (s, 3H),1.99 (s, 3H), 1.75 (s, 3H), 1.29 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 211.9, 139.5, 138.4, 138.2, 136.4, 135.5, 134.8, 131.7, 131.3, 129.6, 129.3, 128.5, 126.9, 114.8, 91.0, 87.0, 54.3, 25.08, 25.9, 22.9, 19.1, 18.3, 17.5, 15.4; MS (EI) *m*/*z* 466 (6, M^+), 444 (5), 422 (4), 235 (2), 145 (8), 122 (30), 105 (100), 77 (72), 43 (62). Anal. Calcd for $C_{32}H_{34}O_3$: C, 82.37; H, 7.34. Found: C, 82.52; H, 7.30.

Reaction of α-Diazo Ketone 14a with (2*E*,6*E*)-2,5-Bis[(2*E*)-3(2-methoxyphenyl)prop-2-en-1-ylidene]cyclopentanone (33b). Preparation of Compounds 40a and 41a. A mixture of **33b** (200 mg, 0.53 mmol) and α-diazo ketone **14a** (120 mg, 0.59 mmol) was allowed to react with $Rh_2(OAc)_4$ (3.0 mg) in anhydrous CH_2Cl_2 (20 mL) for 4.0 h according to the general procedure to afford the diastereomers **40a** and **41a** in 42% (117 mg) and 10% (35 mg) yield, respectively. **40a**: colorless solid; mp 186−188 °C (CH_2Cl_2/hexane); IR (KBr) 2933, 1734, 1602, 1590, 1487, 1244, 1178, 1023, 755 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.59−7.49 (m, 3H), 7.41−7.25 (m, 8H), 6.98−6.85 (m, 5H), 6.58 (d, J = 15.6 Hz, 1H), 6.36−6.23 (m, 1H), 4.35 (s, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 3.54 (d, J = 10.6 Hz, 1H), 2.73−2.68 (m, 4H), 2.33−1.86 (m, 4H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 204.6, 157.4, 156.9, 144.0, 137.5, 135.1, 133.1, 132.3, 130.3, 128.9, 128.1, 127.4, 127.3, 127.1, 125.7, 125.2, 124.9, 124.7, 124.4, 120.7, 120.5, 111.0, 86.9, 62.1, 57.1, 55.4, 55.3, 33.7, 31.3, 25.6, 24.3; MS (EI) *m*/*z* 546 (6, M^+), 386 (12), 373 (4), 226 (16), 200 (14), 169 (38), 155 (75), 125 (100), 99 (44), 55 (68), 45 (62). Anal. Calcd for $C_{36}H_{34}O_5$: C, 79.10; H, 6.27. Found: C, 79.38; H, 6.31. **41a**: colorless solid; mp 147−149 °C (CH_2Cl_2/hexane); IR (KBr) 2941, 1729, 1610, 1594, 1489, 1244, 1177, 1024, 750 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.80−7.76 (m, 2H), 7.56−7.46 (m, 4H), 7.40−7.14 (m, 4H), 6.98−6.76 (m, 6H), 6.52−6.56 (m, 2H), 5.96 (d, J = 15 Hz, 1H), 4.39 (s, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 2.91−2.46 (m, 8H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 203.2, 156.8, 142.4, 140.1, 138.3, 128.6, 128.3, 127.9, 126.8, 126.5, 125.9, 125.0, 124.0, 123.0, 120.7, 120.6, 111.0, 109.4, 90.8, 88.0, 55.4, 35.7, 33.1, 24.1, 23.9; MS (EI) *m*/*z* 546 (10, M^+), 373 (5), 226 (10), 204 (15), 169 (45), 155 (65), 125 (100), 99 (75), 45 (55). Anal. Calcd for $C_{36}H_{34}O_5$: C, 79.10; H, 6.27. Found: C, 79.22; H, 6.30.

Reaction of α-Diazo Ketone 14a with (2*E*,6*E*)-2,5-Bis[(2*E*)-3-phenylprop-2-en-1-ylidene]cyclopentanone (33a). Synthesis of Compound 40b. A mixture of **33a** (250 mg, 0.80 mmol) and α-diazo ketone **14a** (165 mg, 0.81 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.0 mg) in anhydrous CH_2Cl_2 (15 mL) for 3.5 h at room temperature under an argon atmosphere according to the general method to afford **40b** (140 mg, 36%) as a pale yellow solid: mp 203−205 °C (CH_2Cl_2/hexane); IR (KBr) 2931, 1719, 1594, 1486, 1245, 1179, 1024, 748 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.55−7.20 (m, 15H), 7.05−6.73 (m, 3H), 6.35−6.14 (m, 2H), 4.34 (s, 1H), 3.52 (d, J = 9.1 Hz, 1H), 2.73−2.62 (m, 4H), 2.41−1.82 (m, 4H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 204.5, 143.8, 142.4, 141.2, 139.7, 137.1, 136.5, 136.4, 136.1, 134.3, 133.6, 132.6, 129.2, 128.9, 128.7, 128.6, 128.2, 128.0, 127.2, 127.1, 126.3, 124.7, 124.4, 124.2, 123.3, 86.8, 62.1, 56.9, 33.6, 30.8, 25.6, 24.2; MS (EI) *m*/*z* 486 (3, M^+), 468 (5), 363 (4), 313 (20), 161 (16), 119 (35), 105 (100), 83 (62), 55 (48). Anal. Calcd for $C_{34}H_{30}O_3$: C, 83.92; H, 6.21. Found: C, 83.74; H, 6.28.

Reaction of α-Diazo Ketone 14b with (2*E*,6*E*)-2,5-Bis[(2*E*)-3(2-methoxyphenyl)prop-2-en-1-ylidene]cyclopentanone (33b). Synthesis of Compound 40c. A mixture of **33b** (220 mg, 0.59 mmol) and α-diazo ketone **14b** (140 mg, 0.64 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.0 mg) in anhydrous CH_2Cl_2 (18 mL) for 3.5 h at room temperature under an argon atmosphere according to the general method to afford product **40b** (113 mg, 34%) as a pale yellow solid: mp 212−214 °C (CH_2Cl_2/hexane); IR (KBr) 2937, 1726, 1607, 1592, 1488, 1246, 1176, 1025, 751 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.51−7.36 (m, 4H), 7.28−7.13 (m, 6H), 6.97−6.85 (m, 5H), 6.61−6.53 (m, 1H), 6.28−6.24 (m, 1H), 4.33 (s, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 3.51 (d, J = 10.6 Hz, 1H), 2.66−2.61 (m, 4H), 2.34 (s, 3H), 2.14−1.61 (m, 4H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 204.8, 157.5, 156.9, 141.2, 137.4, 136.6, 135.1, 133.2, 132.1, 130.3, 128.8, 127.4, 125.7, 125.3, 124.9, 124.4, 120.7, 120.5, 111.1, 86.9, 62.1, 57.2, 55.5, 55.4, 33.8, 31.3, 25.6, 24.3, 21.0; MS (FD$^+$) *m*/*z* 560 (M^+). Anal. Calcd for $C_{37}H_{36}O_5$: C, 79.26; H, 6.47. Found: C, 79.25; H, 6.50.

Reaction of α-Diazo Ketone 14c with (2*E*,6*E*)-2,5-Bis[(2*E*)-3(2-methoxyphenyl)prop-2-en-1-ylidene]cyclopentanone (33b). Synthesis of Compound 40d. A mixture of **33b** (220 mg, 0.59 mmol) and α-diazo ketone **14c** (150 mg, 0.63 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.4 mg) in anhydrous CH_2Cl_2 (20 mL) for 3.5 h at room temperature under an argon atmosphere according to the general method to afford product **40d** (95 mg, 28%) as a pale yellow solid: mp 195−197 °C (CH_2Cl_2/hexane); IR (KBr) 2932, 1727, 1591, 1488, 1462, 1247, 1178, 1028, 752 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.58−7.47 (m, 4H), 7.46−7.25 (m, 6H), 7.01−6.82 (m, 5H), 6.62−6.54 (m, 1H), 6.28−6.25 (m, 1H), 4.32 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.50 (d, J = 10.6 Hz, 1H), 2.89−2.60 (m, 4H), 2.34−1.82 (m, 4H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 204.8, 158.8, 157.5, 156.9, 144.1, 137.7, 137.5, 136.6, 135.1, 133.3, 132.1, 128.7, 127.7, 127.3, 127.1, 125.7, 125.2, 124.9, 124.7, 124.4, 120.7, 120.5, 113, 111.0, 86.9, 62.0, 57.4, 55.4, 55.2, 33.7, 31.2, 27.1, 24.2; MS (FD$^+$) *m*/*z* 576 (M^+). Anal. Calcd for $C_{37}H_{36}O_6$: C, 77.06; H, 6.29. Found: C, 77.12; H, 6.34.

Reaction of α-Diazo Ketone 14d with (2*E*,6*E*)-2,5-Bis[(2*E*)-3(2-methoxyphenyl)prop-2-en-1-ylidene]cyclopentanone (33b). Synthesis of Compound 40e. A mixture of **33b** (250 mg, 0.67 mmol) and α-diazo ketone **14d** (180 mg, 0.71 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.4 mg) in anhydrous CH_2Cl_2 (25 mL) for 4.0 h at room temperature under an argon atmosphere according to the general method to afford compound **40e** (128 mg, 32%) as a pale yellow solid: mp 227−229 °C (CH_2Cl_2/hexane); IR (KBr) 2930, 1726, 1592, 1245, 1178, 1026, 750 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.19−7.82 (m, 5H), 7.67−7.24 (m, 8H), 6.97−6.73 (m, 5H), 6.64−6.6.34 (m, 2H), 4.40 (s, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.43 (d, J = 10.6 Hz, 1H), 2.74−2.61 (m, 4H), 2.48−1.92 (m, 4H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 204.7, 157.5, 157.0, 141.6, 137.6, 135.3, 133.2, 132.6, 132.5, 132.3, 132.2, 130.4, 129.0, 128.9, 128.4, 128.1, 128.0, 127.5, 126.9, 125.8, 125.3, 124.9, 124.7, 123.3, 123.1, 120.7, 120.6, 111.1, 87.1, 62.2, 57.3, 55.5, 55.4, 33.8, 31.2, 25.7, 24.3; HRMS (ESI$^+$, LCMS) for $C_{40}H_{36}O_5$ [(M + Na)$^+$] calcd 619.2465, found 619.2460.

Reaction of α-Diazo Ketone 14e with (2*E*,6*E*)-2,5-Bis[(2*E*)-3-phenylprop-2-en-1-ylidene]cyclopentanone (33a). Synthesis of Compound 41f. A mixture of **33a** (225 mg, 0.72 mmol) and α-diazo ketone **14e** (110 mg, 0.78 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.4 mg) in anhydrous CH_2Cl_2 (15 mL) for 3.0 h at room temperature under an argon atmosphere according to the general method to afford compound **41f** (116 mg, 38%) as a pale yellow solid: mp 136−138 °C (CH_2Cl_2/hexane); IR (KBr) 2940, 1730, 1599, 1487, 1465, 1243, 1110, 1030, 741 cm^{-1}; ^{1}H NMR

(200 MHz, $CDCl_3$) δ 7.45−7.17 (m, 10H), 6.91−6.78 (m, 2H), 6.63−6.50 (m, 2H), 6.33 (d, J = 10.8 Hz, 2H), 4.23 (s, 1H), 2.85−2.64 (m, 4H), 2.54−2.27 (m, 4H), 1.88 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 203.5, 143.4, 139.6, 137.3, 137.1, 133.3, 132.9, 128.5, 127.5, 127.4, 126.3, 124.8, 124.4, 122.3, 121.8, 108.9, 90.2, 88.0, 33.1, 32.1, 24.7, 24.1, 23.6; MS (EI) *m*/*z* 424 (24, M^+), 325 (6), 313 (100), 222 (10), 141 (12), 115 (15), 91 (38), 43 (17). Anal. Calcd for $C_{29}H_{28}O_3$: C, 82.05; H, 6.65. Found: C, 82.01; H, 6.67.

Reaction of α-Diazo Ketone 14e with (2*E*,6*E*)-2,5-Bis[(2*E*)-3(2-methoxyphenyl)prop-2-en-1-ylidene]cyclopentanone (33b). Synthesis of Compound 41g. A mixture of **33b** (225 mg, 0.60 mmol) and α-diazo ketone **14e** (100 mg, 0.71 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.4 mg) in anhydrous CH_2Cl_2 (20 mL) for 4.0 h at room temperature under an argon atmosphere according to the general method to afford product **41g** (137 mg, 47%) as a pale yellow solid: mp 167−169 °C (CH_2Cl_2/hexane); IR (KBr) 2939, 1727, 1597, 1488, 1464, 1245, 1027, 737 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 2H), 7.18 (t, J = 8.1 Hz, 2H), 6.98−6.77 (m, 8H), 6.37 (d, J = 8.7 Hz, 2H), 4.21 (s, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 2.82−2.61 (m, 4H), 2.52−2.20 (m, 4H), 1.86 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 203.7, 156.7, 143.0, 139.0, 129.0, 128.6, 128.5, 128.0, 127.7, 126.4, 125.6, 125.0, 123.0, 122.7, 120.6, 110.9, 109.0, 90.3, 88.1, 55.4, 33.8, 32.2, 24.8, 24.2, 23.7; MS (FD^+) *m*/*z* 484 (M^+). Anal. Calcd for $C_{31}H_{32}O_5$: C, 76.84; H, 6.66. Found: C, 76.50; H, 6.68.

Reaction of α-Diazo Ketone 11a with (2*E*,6*E*)-2,6-Bis[(2*E*)-3-phenylprop-2-en-1-ylidene]cyclohexanone (42a). Synthesis of Compound 43c. A mixture of **42a** (180 mg, 0.55 mmol) and α-diazo ketone **11a** (85 mg, 0.55 mmol) was allowed to react with 2.2 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 4 h at room temperature under an argon atmosphere according to the general method to afford product **43c** (184 mg, 74%) as a pale yellow solid upon purification on silica gel column chromatography (2% EtOAc−hexane): mp 183−185 °C: IR (KBr) 2961, 2936, 1767, 1446, 1392 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41−7.16 (m, 10H), 7.06−6.87 (m, 2H), 6.67−6.39 (m, 4H), 4.79 (s, 1H), 3.11−3.00 (m, 2H), 2.19−2.01 (m, 4H), 1.74 (s, 3H), 1.21 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 213.0, 141.8, 140.1, 138.3, 138.1, 134.0, 133.9, 129.2, 128.1, 127.0, 124.9, 124.3, 124.2, 124.1, 114.8, 89.1, 858, 54.3, 29.1, 28.9, 28.0, 22.5, 17.9, 15.7; MS (EI) *m*/*z* 453 (19, M^{+1}), 452 (39, M^+), 367 (36), 327 (45), 149 (39), 117 (40), 115 (50), 105 (75), 97 (100), 77 (63). Anal. Calcd for $C_{31}H_{32}O_3$: C, 82.27; H, 7.13. Found: C, 82.44; H, 7.17.

Reaction of α-Diazo Ketone 14a with (2*E*,6*E*)-2,6-Bis[(2*E*)-3(2-methoxyphenyl)prop-2-en-1-ylidene]cyclohexanone (42b). Synthesis of Compound 43d. A mixture of **42b** (200 mg, 0.53 mmol) and α-diazo ketone **14a** (110 mg, 0.54 mmol) was allowed to react with $Rh_2(OAc)_4$ (2.4 mg) in anhydrous CH_2Cl_2 (15 mL) for 4.0 h at room temperature under an argon atmosphere according to the general method to afford product **43d** (132 mg, 44%) as a pale yellow solid: mp 220−222 °C (CH_2Cl_2/hexane); IR (KBr) 2930, 1729, 1592, 1487,1245, 1178, 1026, 750 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75 (d, J = 7.5 Hz, 2H), 7.50−7.44 (m, 4H), 7.32−7.09 (m, 9H), 7.03−6.76 (m, 2H), 6.30 (d, J = 15.5 Hz, 1H), 6.02 (d, J = 11.1 Hz, 1H), 4.72 (s, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.03 (d, J = 14.5 Hz, 2H), 2.74−2.42 (m, 4H), 2.35−1.96 (m, 4H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 203.3, 156.6, 139.6, 139.1, 137.7, 128.4, 128.2, 128.0, 126.7, 126.4, 125.4, 125.0, 124.7, 124.3, 123.3, 120.6, 120.5, 110.9, 108.6, 89.9, 86.2, 55.4, 36.2, 33.0, 28.2, 27.6, 27.5; MS (FD^+) *m*/*z* 560 (M^{+1}). Anal. Calcd for $C_{37}H_{36}O_5$: C, 79.26; H, 6.47. Found: C, 79.52; H, 6.41.

Acknowledgment. This research was supported by DST, New Delhi. J.K. thanks CSIR, New Delhi, for a research fellowship.

Supporting Information Available: Experimental details, spectral data for compounds **17b**, **18b**, **17d**−**h**, **18d**−**h**, **20**, **22a**,**b**,**d**−**h**, **24**, **25**, **26a**,**b**, **28**, **29**, and **43a**,**b**, and single-crystal X-ray analyses of compounds **17a**, **18b**, **22a**,**b**, and **35a** with CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0621726