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ARTICLE TYPE

Expedient Synthesis of Nitrovinyl Substituted Bicyclo[2.2.2]octenone Scaffolds

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A simple and rapid oxidative acetalization and Diels–Alder protocol of nitrovinyl substituted guaiacols has been developed to synthesize nitrovinyl-bearing bicyclo[2.2.2]octenone derivatives. The electron-deficient nature of the *in situ* generated orthoquinone monoketals renders [4 + 2] cycloaddition facile with electron-rich and conjugative dienophiles. The 4-alkenyl masked *o*-benzoquinone is relatively more reactive than its 3-alkenyl counterpart. The 3-alkenyl masked *o*-benzoquinone undergoes dimerization partially even in the presence of external dienophile.

Introduction

Over the past two decades, the hypervalent iodine chemistry received considerable attention in organic synthesis.[1,2] The selective and mild oxidizing properties of these reagents made them very useful and routinely used reagents. These reagents can be used as both dehydrogenating as well as oxygenating reagents. The hypervalent iodine reagents are environmentally benign, non-toxic and alternative to toxic heavy metal oxidants in many of the organic transformations to construct complex molecules. In particular, the hypervalent iodine reagents are valuable for the generation of masked *o*-benzoquinones (MOBs) and benzoquinone monoimines.[3] The generation of these MOBs rely on the oxidative dearomatization of 2-alkoxyphenols in the presence of hypervalent iodine reagents such as diacetoxyiodobenzene (DIB) or phenyliodonium bis(trifluoroacetate) (PIFA) in alcoholic solvents. The linearly conjugative cyclohexadienones are utilized as key intermediates in the synthesis of many natural products.[4] The highly reactive MOBs can act as dienes as well as dienophiles in Diels–Alder reaction. Though these transiently generated MOBs undergo self-dimerization in the absence of external dienophiles, valuable bicyclo[2.2.2]octenone synthons can be obtained in excellent regio- and stereo-selectivities with external dienophiles. The Diels–Alder reaction of MOBs has been exploited as a key step in the total synthesis of many biologically active molecules.[4] The most recent examples of total synthesis based on the MOB strategy are (±)-eremopetasidione,[4a] the tetracyclic lycopodium alkaloid (±)-magellanine,[4b] (±)-penicillones A and B,[4c] (+)-eudesmadien-12,6-olide,[4d] (+)-frullanolide,[4d] (+)-chamaecypanone C.[4e] The MOBs can also undergo Michael- and *anti*-Michael type addition reactions with various nucleophiles.[5] Recently, we have explored the Diels–Alder reactivity of stable 4-halo MOBs[6] and benzoxazole core containing MOBs[7] for the synthesis of various densely functionalized bicyclo[2.2.2]octenone derivatives.

Nitrostyrenes are ubiquitous structural motifs which are involved in the synthesis of heterocyclic compounds[8] and medicinal substances.[9] Nitrostyrenes readily undergo reactions such as [3 + 2] cycloaddition[10] and Michael addition.[11]

Results and Discussion

Inspired by the applications of nitrostyrenes as well as bicyclo[2.2.2]octenones, we were interested to develop a protocol for the synthesis of nitrovinyl bearing bicyclo[2.2.2]octenones using the Diels–Alder strategy of the transiently generated orthoquinone monoketals and to know whether the inner diene **A** and/or the outer diene **B** of the MOBs participate in the Diels–Alder reaction with alkenes[12] (Figure 1).

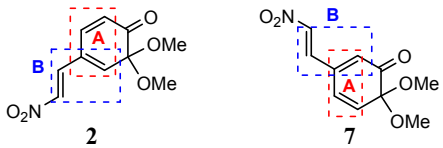

Figure 1 Inner and outer dienes of nitrovinyl substituted ortho-quinone monoketals **2** and **7**.

Considering the electron-deficient nature of the *in situ* generated nitrovinyl *o*-benzoquinone monoketals, we have selected electron-rich dienophiles for the [4 + 2] cycloaddition. As a prelude to our objective, the reaction between (*E*)-2-methoxy-4-(2'-nitrovinyl)phenol (**1**) and ethyl vinyl ether (**3a**) in methanol, in the presence of DIB was carried out (Method A) to furnish the Diels–Alder adduct **4a** as yellow liquid in remarkable yield of 95%.

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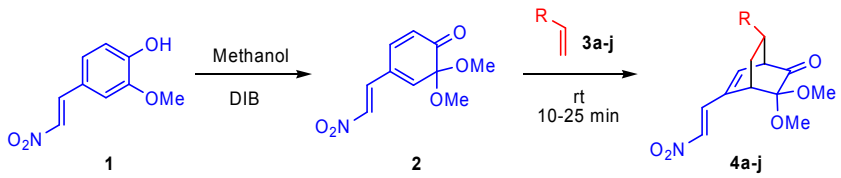
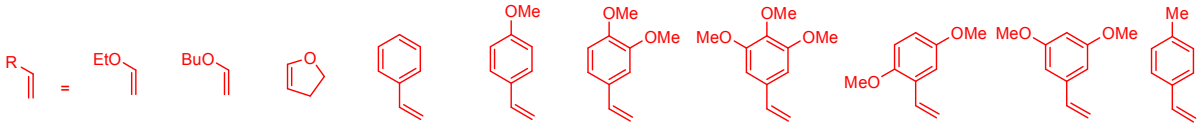
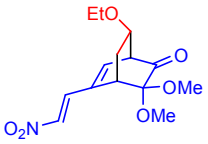
Table 1 Reactions of (*E*)-2-methoxy-4-(2-nitrovinyl)phenol (**1**) with **3a-j**[a,b]



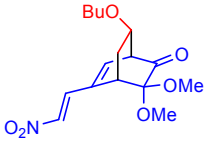
1 2 4a-j



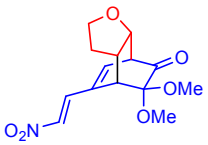
3a **3b** **3c** **3d** **3e** **3f** **3g** **3h** **3i** **3j**



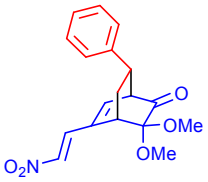
4a (95%)
(Method A, 10 min)



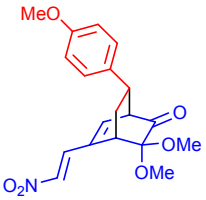
4b (94%)
(Method A, 10 min)



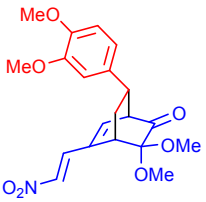
4c (93%)
(Method A, 10 min)



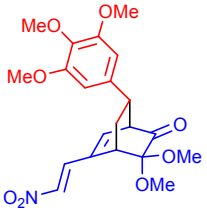
4d (92%)
(Method A, 10 min)



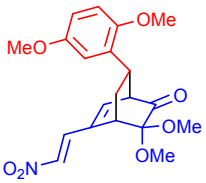
4e (78%)
(Method B, 25 min)



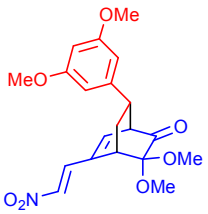
4f (73%)
(Method B, 25 min)



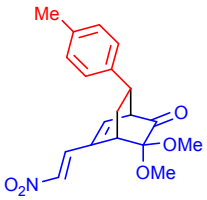
4g (74%)
(Method B, 25 min)



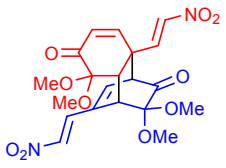
4h (86%)
(Method B, 25 min)



4i (65%)
(Method B, 25 min)



4j (60%)
(Method B, 25 min)



5

[a]Method A: To the solution of methoxyphenol **1** (0.5 mmol) and dienophile **3** (5 mmol) in MeOH (5 mL), solid DIB (1.2 mmol) was added portion-wise and allowed to stir at rt for further 10 min. Method B: To the solution of methoxyphenol **1** (0.5 mmol) and dienophile **3** (5 mmol) in MeOH (2 mL), DIB (1.2 mmol) in MeOH (10 mL) was added drop-wise for 10 min and then allowed to stir at rt for further 15 min. [b]isolated yields.

To expand the scope of the reaction, we extended the present Diels–Alder strategy of MOB **2** generated from 2-methoxyphenol **1** with dienophiles such as butyl vinyl ether (**3b**), 2,3-dihydrofuran (**3c**), styrene (**3d**) and 4-methoxystyrene (**3e**). For this purpose, we dearomatized the 2-methoxyphenol **1** in the presence of dienophiles **3b–3d** in methanol using DIB and stirred at room temperature. The reactions reached completion in 10 min, to furnish the corresponding Diels–Alder adducts **4b–4d** in excellent yields. In the case of 4-methoxystyrene (**3e**), when reactions were carried out under Method A conditions, the yield of the Diels–Alder cycloadduct **4e** was slightly decreased to 67%. Alternatively, we carried out the reaction by Method B in which to a solution of methoxyphenol **1** and styrene derivative **3e** in methanol was added methanolic DIB solution drop-wise for 15 min at room temperature, and the reaction mixture was further stirred for 10 min at room temperature to obtain the corresponding Diels–Alder adduct **4e** in improved yield of 78%. Similarly, the reactions of **1** with the styrenes **3f–3j** bearing methoxy and methyl groups performed the nitrovinyl bicyclo[2.2.2]octenones **4f–4j** in Method B (Table 1).

We further extended this methodology for the reaction of 2-methoxyphenol **1** with electron-deficient dienophiles such as methyl vinyl ketone and methyl acrylate. Unfortunately, in this case, the reaction ended up with the formation Diels–Alder dimer **5** in 72 and 78%, respectively, instead of the Diels–Alder adducts indicating that these dienophiles are not sufficiently electron-rich to drive the Diels–Alder reaction with electron-deficient MOB **2**. To evaluate the propensity of dimerization of the MOB **2**, the oxidation of methoxyphenol **1** was performed in the absence of external dienophile and the reaction afforded the Diels-Alder dimer **5** in 10 min in 94% yield after silica gel column chromatography.

We extended our investigations with more reactive MOB **7** generated *in situ* from the oxidation of (*E*)-2-methoxy-5-(2'-nitrovinyl)phenol (**6**). The reaction of **6** was first carried out with electron-rich dienophile ethyl vinyl ether (**3a**) by Method A and the reaction produced exclusively dimer **9**. This may be due to the high reactivity of MOB **7** generated by the oxidative dearomatization of methoxyphenol **6**. Therefore, dilution technique to maintain large ratio of dienophile to MOB was used throughout the reaction to minimize the dimerization and to increase the yield of Diels–Alder adduct **8a**. Thus to a methanolic solution of **6** in the presence of ethyl vinyl ether **3a**, was added drop-wise a solution of DIB in dry methanol for 15 minutes at 0 ^{o}C. The reaction was further continued for 30 min at room temperature. After usual work up and purification, the Diels–Alder adduct **8a** was obtained in 33% yield along with dimer **9** in 28%.

The present Diels-Alder protocol of MOB **7** was further tested with dienophiles **3b-3l**. In all these cases, the reaction reached completion to furnish the corresponding Diels–Alder adducts **8b-8l** in 27-70% along with the dimer **9**. The reaction of **6 w**ith styrenes **3e, 3f** and **3h** afforded the cycloadducts **8e**, **8f** and **8h** in 67–70% yield and the dimer **9** could not be isolated (Table 2). Interestingly, the electron-deficient dienophiles methyl vinyl ketone (**3k**) and methyl acrylate (**3l**) drove the MOB **7** to undergo the Diels–Alder reaction to produce the bicyclo[2.2.2]octenones **8k** and **8l** in appreciable amount along with the dimer **9** in good amount. However, in the reaction between **6** and **3k**, the cycloadduct **8k** and dimer **9** were too close for the separation on column chromatography. Upon subjecting the residue to preparatory TLC, **8k** was isolated in 24% yield in almost pure form. Furthermore, the oxidation of methoxyphenol **6** was employed in the absence of external dienophile to furnish the Diels-Alder dimer **9** of the *in situ* generated MOB **7** in 45 min in 82% yield after silica gel column chromatography.

The cycloadducts were obtained as racemic mixture of a single diastereomer in each case. The assigned structures of all nitrovinyl bicyclo[2.2.2]octenones were confirmed by the collective data obtained from IR, ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR, DEPT and HRMS spectral analysis. To identify the chemical shifts of protons and carbon atoms, we have carried out the 2-D NMR experiments such as ^{1}H–^{1}H COSY, heteronuclear multiple quantum correlation (HMQC) on cycloadduct **8a**. ^{1}H–^{1}H COSY shows the correlations between protons H_1–H_7, H_4–H_{8a}, H_4–H_5, H_5–H_1, H_7–H_1, H_{8a}–H_{8b} and H_9–H_{10}. The CH connectivities between C_1–H_1, C_2–H_2, C_4–H_4, C_5–H_5, C_7–H_7, C_8–H_{8a}, C_8–H_{8b}, C_9–H_9 and C_{10}–H_{10} are revealed by HMQC spectrum of **8a**. The protons H-1 and H-4 resonate in the range of δ 3.27–3.79 and 3.13–3.56 ppm, respectively (Table SI-2 in supplementary material). The coupling constants of H-4–H-8*b* or H-4–H-8a are observed predominantly in the range of J = 2.5–3.0 Hz, which are in agreement with the assigned *ortho*-regiochemistry. The proton H-8a resonates in the range of δ 1.30–1.86 ppm and H-8b resonate at downfield in the range of δ 2.30–3.40 ppm (Table SI-2 in supplementary material). The higher chemical shift of H-8b may be attributed predominantly to the magnetic anisotropic effect of *exo*-methoxy group of ketal function which is lying in its proximity. The coupling constants (J = 6.0–6.5 Hz) between H-8a–H-7, and those (J = 8.0–10.0 Hz) H-7 between H-8b–H-7 reveals the *cis* relationship of the protons H–8b and which confirms the assigned *endo*-stereochemistry. The cycloadducts exhibited IR absorptions at 1730–1746 cm^{-1}, a characteristic absorption of carbonyl function of bicyclo[2.2.2]octenones derived from MOBs. In the ^{13}C NMR of the Diels–Alder adducts, the ring carbonyl carbon appears at around 199–200 ppm and the ketal quaternary carbon appears at around 93–94 ppm. Among the bridge-head carbons C-1 (δ 50–57 ppm) and C-4 (δ 31–40 ppm), the former which is positioned next to the ring carbonyl resonates downfield (Table SI-3 in supplementary material).

The assigned regio- and stereo-selectivities are further established by the single crystal X-ray analysis of the adduct **4h** (Figure 2).[13] The single crystals of **4h** were grown by slow evaporation of solvent from solution in methanol/hexane (1:9). The analysis of the crystal structure has illustrated the *ortho* regiochemistry and *endo* stereochemistry as shown in Figure 2. The regio-, stereo- and site-selectivity of the dimerization is in harmony with the literature precedents.[6a,7,14]

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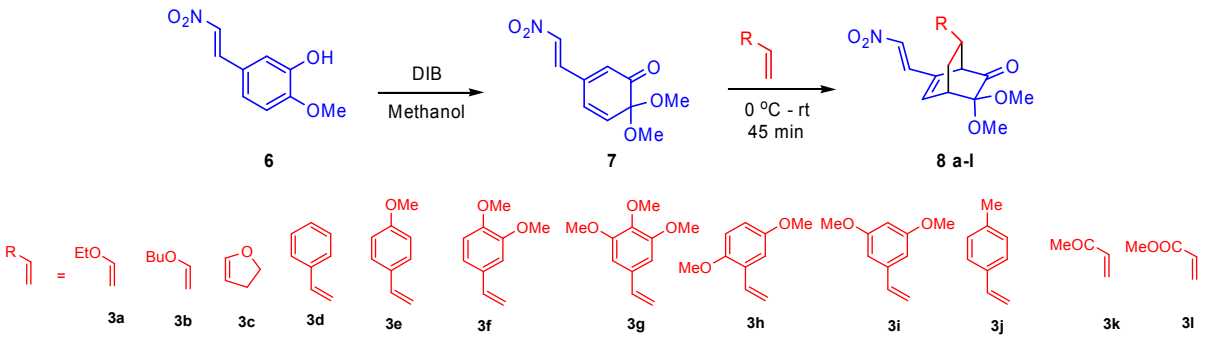
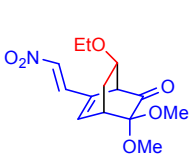
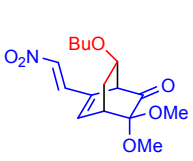
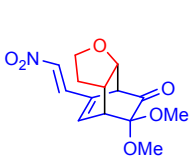
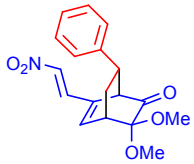
Table 2 Reactions of (*E*)-2-methoxy-5-(2-nitrovinyl)phenol (**6**) with **3a-l**[a,b]

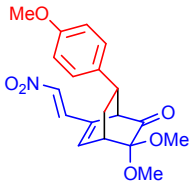


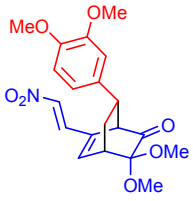

8a (33%)
9 (28%)

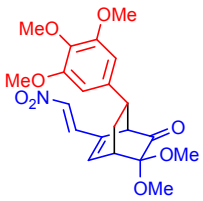

8b (46%)
9 (28%)

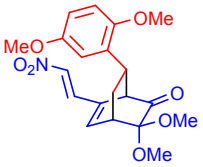

8c (33%)
9 (31%)

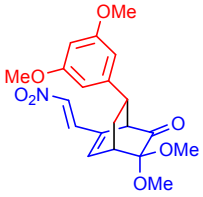

8d (48%)
9 (29%)

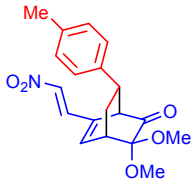

8e (67%)

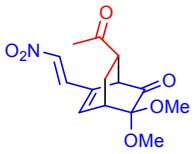

8f (70%)

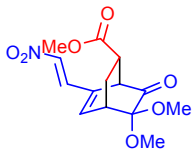

8g (50%)
9 (22%)

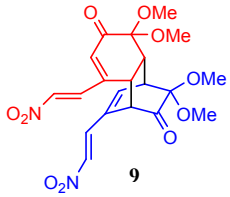

8h (70%)


8i (49%)
9 (32%)


8j (56%)
9 (24%)


8k (24%)
9 (42%,)


8l (27%)
9 (57%)


9

[a] Method B: To the solution of methoxyphenol **6** (0.5 mmol) and dienophile **3** (5 mmol) in MeOH (2 mL), DIB (1.5 mmol) in MeOH (15 mL) was added drop-wise at 0 °C for 15 min and then allowed to stir at rt for further 30 min. [b] isolated yields.

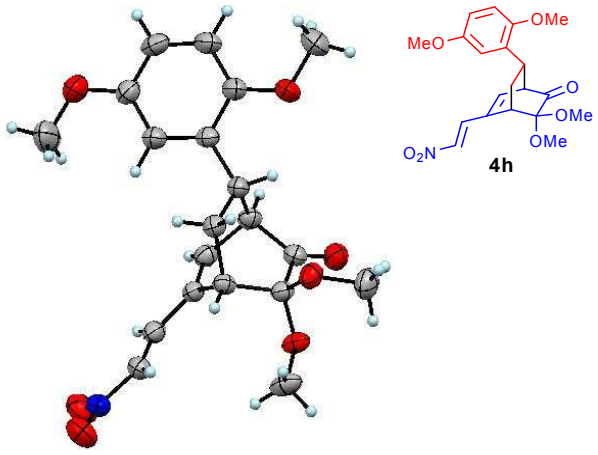
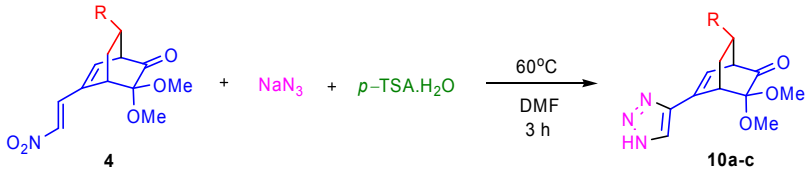


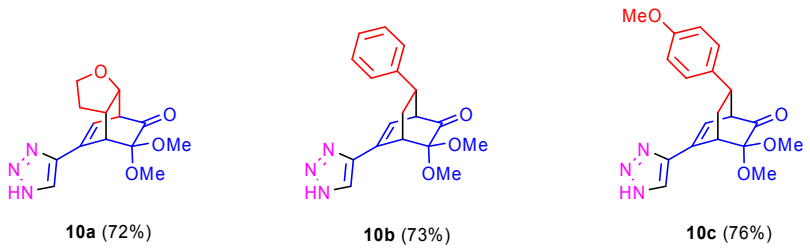
Figure 2 Single crystal X-ray structure of cycloadduct **4h**.

Further functionalization of some of the nitrovinyl bicyclo[2.2.2]octenones 1,3-dipolar cycloaddition was carried out to afford triazole-substituted bicyclo[2.2.2]octenones. The recently reported literature procedure described for the *p*-TSA–mediated 1,3-dipolar cycloadditions of nitroolefins with sodium azide was followed for this purpose.[15] Thus the cycloadducts **4c–4e**, when treated with sodium azide under the catalytic influence of *p*-TSA, furnished the 1,2,3-triazole-bearing cycloadducts **10a–10c** through [3 + 2] cycloaddition (Table 3).

It is noteworthy that the inner diene moiety **A** of the MOBs **2** and **7** participate in the cycloaddition and the outer diene moiety **B** did not take part in the present reaction (Figure 1). Apparently, the electronic nature of the 2-nitrovinyl group positioned at carbon-4 of MOB **2** influenced the cycloaddition reaction in the formation of Diels–Alder adducts **4** or the dimer **5**. During the competition between external dienophile **3** (leading to **4**) and dienophilic MOB **2** (leading to dimer **5**), the steric factors favour the formation of bicyclo[2.2.2]octenones **4**. The differences in such steric effects are less in the reaction of MOB **7**, bearing 2-nitrovinyl group at carbon-3, while competing with external dienophile **3** (leading to **8**) and dienophilic MOB **7** (leading to dimer **9**).

Table 3 [3+2] Cycloaddition reactions of bicyclo[2.2.2]ocetnones **4c-e**[a,b]





a) All the reactions were carried out with bicyclo[2.2.2]octenone derivative **4** (0.3 mmol), sodium azide (0.45 mmol) and 5 mol% of *p*-TSA in DMF (2 mL) at 60 °C. b) Pure and isolated yields.

Conclusion

In summary, we have demonstrated an efficient Diels–Alder cycloaddition of *in situ* generated nitrovinyl substituted orthobenzoquinone monoketals with a variety of 2π-components providing the title compounds with diverse functionalities. The reactivity of novel MOBs, investigated in this study, is noteworthy and these results add up to the known chemistry of MOBs. Further exploration of the reactivity of orthobenzoquinone monoketals and monoimines is in progress in our laboratory.

Experimental

General Methods

All solvents and reagents were purchased at the highest commercially quality and used without further purification. Reactions were monitored by Thin layer chromatography on Merck pre-coated 0.25 mm silica gel plates (60F–254) using UV light as visualizing agent and/or iodine as developing agent. Preparative thin-layer chromatography (TLC) carried out on 0.25

mm E. RANKEM silica gel "G" on glass plate using visualizing in iodine chamber, Melting points are uncorrected. IR spectra of the compounds were recorded on a Thermo Nicolet FT-IR Nexus^{TM} and are expressed as wavenumbers (cm^{-1}). NMR spectra were recorded in $CDCl_3$ and using TMS as internal standard on Brüker AMX-500 instrument. HRMS were recorded on a Brüker micrOTOF^{TM}-Q-II mass spectrometer (ESI–MS). Chemical shifts of ^{1}H NMR spectra were given in parts per million with respect to TMS and the coupling constant *J* was measured in Hz. The signals from solvent $CDCl_3$, 7.26 and 77.0 ppm are set as the reference peaks in ^{1}H and ^{13}C NMR spectra, respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = double doublet, ddd = doublet of doublet of doublet, td = triplet of doublet, dt = doublet of triplet, dq = doublet of quartet, t = triplet, q = quartet, m = multiplet.

*Reactions of nitrovinyl-guaiacol **1** with alkenes:*

Method A: To a solution of nitrovinyl-guaiacol **1** (0.097 g, 0.5 mmol) and dienophile (**3**, 5 mmol, 10 equiv) in dry MeOH (5 mL) solid diacetoxyiodobenzene (DIB, 0.193 g, 0.6 mmol, 1.2 equiv.) was added portion-wise at room temperature and stirred for 10 min. After the completion of the reaction, as indicated by the TLC, the solvent was evaporated and the crude reaction mixture was purified by silica gel column chromatography by using ethyl acetate (10–20%) in hexanes as an eluting system to afford pure bicyclo[2.2.2]octenones **4a-d**.

Method B: To a stirred solution of nitrovinyl-guaiacol **1** (0.097 g, 0.5 mmol) and an alkene **3** (5 mmol, 10 equiv) in dry MeOH (2 mL), a dry methanolic solution (10 mL) of diacetoxyiodobenzene (DIB, 0.193 g, 0.6 mmol, 1.2 equiv) was added drop-wise at 0 ^{o}C during 10 min and then the contents were stirred further for 15 min at room temperature. After completion of the reaction, as indicated by the TLC, the solvent was evaporated and the crude reaction mixture was purified by silica gel column chromatography by using ethyl acetate (10–30%) in hexanes as an eluent to furnish the Diels–Alder cycloadducts **4e-j**.

*Reactions of nitrovinyl-guaiacol **6** with alkenes:*

Method B: To a stirred solution of nitrovinyl-guaiacol **6** (0.097 g, 0.5 mmol) and an alkene **3** (5 mmol, 10 equiv) in dry MeOH (2 mL), a dry methanolic solution (15 mL) of diacetoxyiodobenzene (DIB, 0.241 g, 0.75 mmol, 1.5 equiv) was added drop-wise at 0 ^{o}C during 15 min and then the contents were stirred further for 30 min at room temperature. After completion of the reaction, as indicated by the TLC, the solvent was evaporated and the crude reaction mixture was purified by silica gel column chromatography by using ethyl acetate (10–30%) in hexanes as an eluent to furnish the Diels–Alder cycloadduct **8** and dimer **9**.

(1*S,4*R**,7*S**)-(*E*)-7-Ethoxy-3,3-dimethoxy-5-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (4a):** *Method A*. Reaction time: 10 min. Yield: 0.141 g (95%) as viscous yellow liquid. IR (KBr): ν_{max} 2920, 1734, 1631, 1521, 1380, 1104, 1055 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 13.5 Hz, 1H), 7.26 (d, *J* = 13.5 Hz, 1H), 6.62 (d, *J* = 6.0 Hz, 1H), 4.06–4.03 (m, 1H), 3.77 (dd, *J* = 2.5, 6.0 Hz, 1H), 3.53–3.47 (m, 1H), 3.42–3.36 (m, 1H), 3.32 (s, 3H), 3.27 (s, 3H), 3.23 (q, *J* = 3.0 Hz, 1H), 2.48 (ddd, *J* = 3.0, 8.5, 14.0 Hz, 1H), 1.36 (td, *J* = 3.5, 14.0 Hz, 1H), 1.14 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.2 (*C*=O), 138.6 (*C*), 136.9 (*C*H), 135.9 (*C*H), 135.9 (*C*H), 93.1 (*C*), 74.8 (*C*H), 64.4 (CH_2), 55.4 (*C*H), 50.9 (CH_3), 49.3 (CH_3), 38.5 (*C*H), 29.6 (CH_2), 15.0 (CH_3) ppm. HRMS (ESI+): *m/z* calcd for $C_{14}H_{19}NO_6Na$ $[M + Na]^+$: 320.1104, found 320.1104.

(1*S,4*R**,7*S**)-(*E*)-7-butoxy-3,3-dimethoxy-5-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (4b):** *Method A*. Reaction time: 10 min. Yield: 0.152 g (94%) as viscous yellow liquid. IR (KBr): ν_{max} 2956, 1743, 1629, 1518, 1453, 1342, 1101, 1054 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 13.5 Hz, 1H), 7.27 (d, *J* = 13.5 Hz, 1H), 6.62 (d, *J* = 6.0 Hz, 1H), 4.05–4.03 (m, 1H), 3.79 (dd, *J* = 2.5, 6.0 Hz, 1H), 3.47 –3.40 (m, 1H), 3.34 (s, 3H), 3.29 (s, 3H), 3.25–3.23 (m, 1H), 2.50 (ddd, *J* = 2.5, 8.0, 13.5 Hz, 1H), 1.50–1.47(m, 2H), 1.40–1.25 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.3 (*C*=O), 138.7 (*C*), 137.0 (*C*H), 136.0 (*C*H), 93.3 (*C*), 75.1 (*C*H), 69.0 (CH_2), 55.5 (*C*H), 51.1 (OCH_3), 49.5 (OCH_3), 38.7, (*C*H), 31.6 (CH_2), 29.7 (CH_2), 19.2 (CH_2), 13.7 (CH_3) ppm. HRMS (ESI+): *m/z* calcd for $C_{16}H_{23}NO_6Na$ $[M + Na]^+$: 348.1417, found 348.1415.

(1*R,2*R**,6*R**,7*S**)-(*E*)-11-(2-nitrovinyl)-8,8-dimethoxy-3-oxa-tricyclo[5.2.2.0^{2,6}]undec-10-en-9-one (4c):** *Method A*. Reaction time: 10 min. Yield: 0.137 g (93%) as viscous yellow liquid. IR (KBr): ν_{max} 2949, 1740, 1629, 1521, 1343, 1084, 1036 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 13.5 Hz, 1H), 7.25 (d, *J* = 13.5 Hz, 1H), 6.67 (dd, *J* = 0.5, 6.5 Hz, 1H), 4.39 (dd, *J* = 3.0, 8.0 Hz, 1H), 3.84 (dt, *J* = 2.5, 8.0 Hz, 1H), 3.79 (dd, *J* = 3.0, 6.0 Hz, 1H), 3.57–3.51 (m, 1H), 3.37 (s, 3H), 3.34 (t, *J* = 2.0 Hz, 1H), 3.28 (s, 3H), 3.00 (dq, *J* = 3.5, 8.5 Hz, 1H), 2.15–2.09 (m, 1H), 1.39–1.31 (m, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 198.8 (*C*=O), 137.6 (*C*), 137.2 (*C*H), 137.0 (*C*H), 136.7 (*C*H), 92.8 (*C*), 78.9 (*C*H), 68.8 (CH_2), 56.4 (*C*H), 51.0 (CH_2), 49.5 (CH_2), 43.1 (*C*H), 37.7 (*C*H), 30.0 (CH_2) ppm. HRMS (ESI+): *m/z* calcd for $C_{14}H_{17}NO_6Na$ $[M + Na]^+$: 318.0948, found 318.0945.

(1*S,4*R**,7*S**)-(*E*)-7-phenyl-3,3-dimethoxy-5-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (4d):** *Method A*. Reaction time: 10 min. Yield: 0.151 g (92%) as viscous yellow liquid. IR (KBr): ν_{max} 2945, 1730, 1629, 1559, 1341, 1130, 1062 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 13.5 Hz, 1H), 7.35 (d, *J* = 13.5 Hz, 1H), 7.31–7.26 (m, 2H), 7.25–7.23 (m, 1H), 7.08–7.05 (m, 2H), 6.71 (dd, *J* = 1.5, 6.5 Hz, 1H), 3.53 (t, *J* = 8.0 Hz, 1H), 3.49 (dd, *J* = 1.5, 6.5 Hz, 1H), 3.44 (s, 3H), 3.42–3.40 (m, 1H), 3.35 (s, 3H), 2.63 (ddd, *J* = 3.0, 10.0, 13.5 Hz, 1H), 1.65 (ddd, *J* = 3.0, 6.5, 13.5 Hz, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.4 (*C*=O), 142.8 (*C*), 139.7 (*C*), 137.1 (*C*H), 136.9 (*C*H), 135.7 (*C*H), 128.7 (*C*H), 127.2 (*C*H), 127.1 (*C*H), 93.3 (*C*), 56.8 (*C*H), 50.9 (CH_3), 49.8 (CH_3), 40.8 (*C*H), 39.9 (*C*H), 29.3 (CH_2) ppm. HRMS (ESI+): *m/z* calcd for $C_{18}H_{19}NO_5Na$ $[M + Na]^+$: 352.1155, found 352.1155.

(1*S,4*R**,7*S**)-(*E*)-7-(4-methoxyphenyl)-3,3-dimethoxy-5-(2-nitro vinyl)bicyclo[2.2.2]oct-5-en-2-one (4e):** *Method B*.

Reaction time: 25 min. Yield: 0.140 g (78%) as viscous yellow liquid. IR (KBr): ν_{max} 3099, 2977, 2946, 2842, 1733, 1628, 1515, 1458, 1345, 1247, 1184, 1087, 1028 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 13.5 Hz, 1H), 7.33 (d, *J* = 13.5 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 3.50–3.45 (m, 1H), 3.45–3.43 (m, 1H), 3.43 (s, 3H), 3.39–3.37 (m, 1H), 3.34 (s, 3H), 2.64–2.56 (m, 1H), 1.60–1.56 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5 (*C*=O), 158.6 (*C*), 139.7 (*C*), 137.1 (*C*), 137.1 (*C*), 135.7 (*C*H), 134.8 (*C*H), 128.2 (*C*H), 114.1 (*C*H), 93.3 (*C*), 57.3 (CH_3), 55.2 (*C*H), 50.9 (CH_3), 49.8 (CH_3), 40.2 (*C*H), 39.9 (*C*H), 29.3 (CH_2) ppm. HRMS (ESI+): *m/z* calcd for $C_{19}H_{21}NO_6Na$ $[M + Na]^+$: 382.1261, found 382.1261.

(1*S,4*R**,7*S**)-(*E*)-7-(3,4-dimethoxyphenyl)-3,3-dimethoxy-5-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (4f):** *Method B*. Reaction time: 25 min. Yield: 0.141 g (73%) as yellow solid. MP: 131 °C. IR (KBr): ν_{max} 3099, 2943, 2837, 2842, 1738, 1622, 1514, 1458, 1341, 1260, 1147, 1079, 1029 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 13.5 Hz, 1H), 7.34 (d, *J* = 13.5 Hz, 1H), 6.78–6.74 (m, 1H), 6.69 (d, *J*.= 6.0 Hz, 1H), 6.62–6.55 (m, 2H), 3.84 (s, 3H), 3.84 (s, 3H), 3.50–3.45 (m, 2H), 3.43 (s, 3H), 3.39 (d, *J* = 1.5 Hz, 1H), 3.34 (s, 3H), 2.65–2.55 (m, 1H), 1.65–1.57 (m, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5 (*C*=O), 149.0 (*C*), 148.2 (*C*), 139.8 (*C*), 137.3 (*C*H), 137.1 (*C*H), 135.7 (*C*H), 135.4 (*C*) 118.8 (*C*H), 111.4 (*C*H), 111.1 (*C*H), 93.4 (*C*), 57.3 (*C*H), 55.9 (O*C*H_3), 51.0 (O*C*H_3), 49.9 (O*C*H_3) , 40.6 (*C*H), 40.0 (*C*H), 29.4 (CH_2) ppm. HRMS (ESI+): *m/z* calcd for $C_{20}H_{23}NO_7Na$ $[M + Na]^+$: 412.1366, found 412.1366.

(1*S,4*R**,7*S**)-(*E*)-7-(3,4,5-trimethoxyphenyl)-3,3-dimethoxy-5-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (4g):** *Method B*. Reaction time: 25 min.Yield: 0.155 g (74%) as yellow solid. MP: 187 °C. IR (KBr): ν_{max} 3105, 2937, 2834, 1741, 1625, 1591, 1509, 1463, 1340, 1241, 1129, 1077, 1004 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 13.5 Hz, 1H), 7.34 (d, *J* = 13.5 Hz, 1H), 6.71 (d, *J* = 5.5 Hz, 1H), 6,26 (s, 2H), 3.81 (s, 9H), 3.49–3.45 (m, 2H), 3.43 (s, 3H), 3.39 (d, *J* = 1.5 Hz, 1H), 3.35 (s, 3H), 2.64–2.57 (m, 1H), 1.65–1.58 (m, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.3 (*C*=O), 153.3 (*C*), 139.9 (*C*), 138.5 (*C*), 137.4 (*C*H), 137.3 (*C*), 136.8 (*C*H), 135.4 (*C*H), 104.5 (*C*H), 93.3 (*C*), 60.8 (O*C*H_3), 57.0 (*C*H), 56.2 (*C*H), 51.1 (O*C*H_3), 49.8 (O*C*H_3), 41.2 (*C*H), 40.0 (*C*H), 29.5 (CH_2) ppm. HRMS (ESI+): *m/z* calcd for $C_{21}H_{25}NO_8Na$ $[M + Na]^+$: 442.1472, found 442.1466.

(1*S,4*R**,7*S**)-(*E*)-7-(2,5-dimethoxyphenyl)-3,3-dimethoxy-5-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (4h):** *Method B*. Reaction time: 25 min. Yield: 0.168 g (86%) as orange solid. Mp: 160 °C. IR (KBr): ν_{max} 3107, 2938, 2839, 1741, 1625, 1591, 1464, 1339, 1241, 1129, 1081, 1005 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.70 (d, *J* = 13.5 Hz, 1H), 7.31 (d, *J* = 13.5 Hz, 1H), 6.78–6.74 (m, 1H), 6.72–6.67 (m, 2H), 6.46 (d, *J* = 2.5 Hz, 1H), 3.98 (t, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 3.47 (dd, *J* = 1.5, 6.5 Hz, 1H), 3.43 (s, 3H), 3.36 (d, *J* = 2.0 Hz, 1H), 3.34 (s, 3H), 2.62–2.53 (m, 1H), 1.52 (ddd, J = 2.0, 6.0, 13.0 Hz, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.6 (*C*=O), 153.3 (*C*), 151.1 (*C*), 139.5 (*C*), 137.6 (*C*H), 137.1 (*C*H), 135.9 (*C*H), 132.1 (*C*), 114.5 (*C*H), 111.1 (*C*H), 110.8 (*C*H), 93.5 (*C*), 55.9 (O*C*H_3), 55.7 (O*C*H_3), 55.2 (*C*H), 51.0 (O*C*H_3), 49.9 (O*C*H_3), 39.9 (*C*H), 33.4 (*C*H), 27.8 (CH_2) ppm. HRMS (ESI+): *m/z* calcd for $C_{20}H_{23}NO_7Na$ $[M + Na]^+$: 412.1366, found 412.1368.

(1*S,4*R**,7*S**)-(*E*)-7-(3,5-dimethoxyphenyl)-3,3-dimethoxy-5-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (4i):** *Method B*. Reaction time: 25 min. Yield: 0.126 g (65%) as yellow solid. MP: 166 °C. IR (KBr): ν_{max} 3100, 2950, 2845, 1740, 1600, 1503, 1464, 1335, 1205, 1158, 1055 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 13.5 Hz, 1H), 7.32 (d, *J* = 13.5 Hz, 1H), 6.71 (d, *J* = 6.0 Hz, 1H), 6.32 (s, 1H), 6.21 (s, 2H), 3.76 (s. 6H), 3.48 (d, *J* = 6.5 Hz, 1H), 3.42 (s, 4H), 3.37 (s, 1H), 3.34 (s, 3H), 2.64–2.55 (m, 1H), 1.64–1.56 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.3 (*C*=O), 161.0 (*C*), 145.2 (*C*), 139.7 (*C*), 137.2 (*C*H), 136.8 (*C*H), 135.6 (*C*H), 105.7 (*C*H), 98.3 (*C*H), 93.3 (*C*), 56.7 (*C*H), 55.3 (O*C*H_3), 51.0 (O*C*H_3), 49.8 (O*C*H_3), 41.0 (*C*H), 40.0 (*C*H), 29.3 (CH_2) ppm. HRMS (ESI+): *m/z* calcd for $C_{20}H_{23}NO_7Na$ $[M + Na]^+$: 412.1366, found 412.1366.

(1*S,4*R**,7*S**)-(*E*)-7-(4-methylphenyl)-3,3-dimethoxy-5-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (4j):** *Method B*. Reaction time: 25 min. Yield: 0.102 g (60%) as viscous yellow liquid. IR (KBr): ν_{max} 3101, 2944, 2845, 1740, 1627, 1514, 1338, 1129, 1084 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 13.0 Hz, 1H), 7.35 (d, *J* = 13.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.69 (d, *J* = 6.0 Hz, 1H), 3.52–3.44 (m, 2H), 3.43 (s, 3H), 3.39 (s, 1H), 3.34 (s, 3H), 263–2.57 (m, 1H), 2.31 (s, 3H), 1.62 (dd, *J* = 6.0, 13.0 Hz, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5 (*C*=O), 139.9 (*C*), 139.8 (*C*), 137.2 (*C*H), 137.1 (*C*H), 137.0 (*C*), 135.8 (*C*H), 129.5 (*C*H), 127.2 (*C*H), 93.4 (*C*), 57.1 (*C*H), 51.0 (O*C*H_3), 49.4 (O*C*H_3), 40.6 (*C*H), 40.1 (*C*H), 29.4 (CH_2) 20.9 (CH_3) ppm. HRMS (ESI+): *m/z* calcd for $C_{19}H_{21}NO_5Na$ $[M + Na]^+$: 366.1311, found 366.1310.

(1*S,2*S**,7*R**,8*R**)-7,11-(bis-2-nitrovinyl)-3,3,10,10-tetra methoxytricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione (5):**

To a solution of nitrovinyl-guaiacol **1** (0.097 g, 0.5 mmol) in dry MeOH (5 mL) solid diacetoxyiodobenzene (0.193 g, 0.6 mmol, 1.2 equiv.) was added portion-wise at room temperature and stirred for 10 min. The solution turned to orange-pale brown colour immediately after the addition of DIB. After the completion of the reaction, as indicated by the TLC, the orange-brownish solution was evaporated and the crude reaction mixture was purified by silica gel column chromatography by using ethyl acetate (30–40%) in hexanes as an eluting system to afford pure Diels–Alder dimer **5**.

Reaction time: 10 min. Yield: 0.106 g (94%) as yellow solid. MP: 190 °C. IR (KBr): ν_{max} 2947, 1743, 1708, 1630, 1528, 1511, 1383, 1342, 1135, 1053, 965, 818, 733 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 13.5 Hz, 1H), 7.28 (d, *J* = 5.5 Hz, 1H), 7.21 (d, *J* = 13.5 Hz, 1H), 7.12 (d, *J* = 13.5 Hz, 1H), 6.49 (d, *J* = 6.5 Hz, 1H), 6.19 (d, *J* = 10.0 Hz, 1H), 6.13 (d, *J* = 10.5 Hz, 1H), 3.45–3.42 (m, 1H), 3.48 (s, 3H), 3.47 (s, 3H), 3.33–3.31 (m, 2H), 3.27 (s, 3H), 3.11 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.9 (*C*=O), 190.9 (*C*=O), 144.0 (*C*H), 140.9 (*C*H), 140.7 (*C*H),

138.8 (*C*H), 137.4 (*C*), 137.0 (*C*H), 134.4 (*C*H), 129.2 (*C*H), 97.3 (*C*), 94.0 (*C*), 58.0 (*C*H), 51.0 (O*C*H$_3$), 50.7 (O*C*H$_3$), 50.2 (O*C*H$_3$), 48.9 (O*C*H$_3$), 48.2 (*C*), 43.5 (*C*H), 41.4 (*C*H) ppm. HRMS (ESI+): *m/z* calcd for $C_{20}H_{22}N_2O_{10}Na$ [M + Na]$^+$: 473.1166 , found 473.1164.

(1*S,4*R**,7*S**)-(*E*)-7-Ethoxy-3,3-dimethoxy-6-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (8a):** Reaction time: 45 min. Yield: 0.049 g (33%) as yellow solid. MP: 152 ^{o}C. IR (KBr): ν_{max} 3091, 2957, 2916, 2831, 1744, 1698, 1626, 1523, 1459, 1241, 1117, 1056 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 13.5 Hz, 1H), 7.11 (d, *J* = 13.5 Hz, 1H), 7.01 (d, *J* = 6.5 Hz, 1H), 4.06–4.02 (m, 1H), 3.68 (s, 1H), 3.50–3.40 (m, 2H), 3.30 (s, 3H), 3.28 (s, 4H), 2.46 (ddd, *J* = 2.5, 8.5, 14.0 Hz, 1H), 1.37 (td, *J* = 3.5, 14.0 Hz, 1H), 1.12 (t, *J* = 7.0 Hz, 3H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.7 (*C*=O), 144.4 (*C*H), 136.6 (*C*H), 136.5 (*C*H), 130.0 (*C*), 93.5 (*C*), 73.6 (*C*H), 64.7 (*C*H$_2$), 53.9 (CH), 50.7 (O*C*H$_3$), 49.6 (O*C*H$_3$), 39.4 (*C*H), 29.7 (*C*H$_2$), 15.2 (*C*H$_3$) ppm. HRMS (ESI+): *m/z* calcd for $C_{14}H_{19}NO_6Na$ [M + Na]$^+$: 320.1104, found 320.1104.

(1*S,4*R**,7*S**)-(*E*)-7-butoxy-3,3-dimethoxy-6-(2-nitrovinyl)bi -cyclo[2.2.2]oct-5-en-2-one (8b):** Reaction time: 45 min. Yield: 0.076 g (46%) as viscous yellow liquid. IR (KBr): ν_{max} 3090, 2957, 2863, 1744, 1636, 1522, 1459, 1342, 1259, 1101, 1054 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 13.5 Hz, 1H), 7.09 (d, *J* = 13.5 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 1H), 4.01–3.97 (m, 1H), 3.67 (s, 1H), 3.40–3.28 (m, 2H), 3.26 (s, 3H), 3.25 (s, 1H), 3.24 (s, 3H), 2.44–2.38 (m, 1H), 1.44–1.36 (m, 2H), 1.34–1.30 (m, 1H), 1.25–1.19 (m, 2H), 0.81 (t, *J* = 7.5, 3H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.8 (*C*=O), 144.5 (*C*H), 136.6 (*C*H), 130.1 (*C*), 93.6 (*C*), 73.8 (*C*H), 69.2 (*C*H$_2$), 53.9 (*C*H), 50.6 (O*C*H$_3$), 49.6 (O*C*H$_3$), 39.4 (*C*H), 31.7 (*C*H$_2$), 29.6 (*C*H$_2$), 19.2 (*C*H$_2$), 13.7 (*C*H$_3$) ppm. HRMS (ESI+): *m/z* calcd for $C_{16}H_{23}NO_6Na$ [M + Na]$^+$: 348.1417, found 348.1413.

(1*R,2*R**,6*R**,7*S**)-(*E*)-10-(2-nitrovinyl)8,8-dimethoxy-3-oxa-tricyclo[5.2.2.0^{2,6}]undec-10-en-9-one (8c):** Reaction time: 45 min. Yield: 0.049 g (33%) as yellow solid. MP: 136 ^{o}C. IR (KBr): ν_{max} 3099, 2925, 2854, 1746, 1629, 1505, 1452, 1343, 1210, 1138, 1095, 1037 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 13.5 Hz, 1H), 7.16 (d, *J* = 13.5 Hz, 1H), 6.85 (d, *J* = 7.0 Hz, 1H), 4.42 (dd, *J* = 3.5, 8.0 Hz, 1H), 3.82 (dt, *J* = 3.0, 8.0 Hz, 1H), 3.70 (dd, *J* = 2.0, 3.5 Hz, 1H), 3.56–3.50 (m, 1H), 3.40 (dd, *J* = 2.5, 7 Hz, 1H), 3.35 (s, 3H), 3.29 (s, 3H), 2.98−2.93 (m, 1H), 2.08–2.16 (m, 1H), 1.60–1.50 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5 (*C*=O), 142.8 (*C*H), 137.4 (*C*H), 136.1 (*C*H), 131.9 (*C*), 93.3 (*C*), 78.4 (*C*H), 69.0 (*C*H$_2$), 55.1 (*C*H), 50.6 (O*C*H$_3$), 49.7 (O*C*H$_3$), 43.9 (*C*H), 38.5 (*C*H), 30.7 (*C*H$_2$) ppm. HRMS (ESI+): *m/z* calcd for $C_{14}H_{17}NO_6Na$ [M + Na]$^+$: 318.0948, found 318.0948.

(1*S,4*R**,7*S**)-(*E*)-7-phenyl-3,3-dimethoxy-6-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (8d):** Reaction time: 45 min. Yield: 0.078 g (48%) as yellow solid. MP: 128 ^{o}C. IR (KBr): ν_{max} 3090, 2937, 1740, 1629, 1510, 1452, 1337, 1125, 1089, 1057 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 13.0 Hz, 1H), 7.26–7.17 (m, 3H), 7.12 (d, *J* = 7 0 Hz, 1H), 7.06 (d, *J* =7.0 Hz, 2H), 6.63 (d, *J* = 13.5 Hz, 1H), 3.55–3.50 (m, 1H), 3.46–3.43 (m, 1H), 3.41 (s, 3H), 3.34 (s, 3H), 3.33 (s, 1H), 2.56 (ddd, *J* = 2.5, 9.5, 13.0 Hz, 1H), 1.73 (ddd, *J* = 2.5, 6.0, 13.5 Hz, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.8 (*C*=O), 145.4 (*C*H), 142.0 (*C*), 136.7 (*C*H), 136.2 (*C*H), 130.0 (*C*H) 128.8 (*C*H), 127.3, (*C*H), 127.0 (*C*H), 93.5 (*C*), 56.1 (CH), 50.5 (O*C*H$_3$), 49.8 (O*C*H$_3$), 40.6 (CH), 39.4 (*C*H), 28.2 (*C*H$_2$) ppm. HRMS (ESI+): *m/z* calcd for $C_{18}H_{19}NO_5Na$ [M + Na]$^+$: 352.1155, found 352.1143.

(1*S,4*R**,7*S**)-(*E*)-7-(4-methoxyphenyl)-3,3-dimeth-oxy-6-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (8e):** Reaction time: 45 min. Yield: 0.120 g (67%) as viscous yellow liquid. IR (KBr): ν_{max} 3104, 2945, 2834, 1740, 1629, 1514, 1459, 1338, 1250, 1179, 1127, 1091, 1056 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 13.0 Hz, 1H), 7.12 (d, *J* = 7 0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 13.5. Hz, 1H), 3.74 (s, 3H), 3.48 (t, *J* = 8.0 Hz, 1H), 3.44–3.41 (m, 1H), 3.40 (s, 3H), 3.33 (s, 3H), 3.29 (s, 1H), 2.56–2.49 (m, 1H), 1.67 (dd, *J* = 5.0, 13.0 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.0 (*C*=O), 158.7 (*C*H), 145.5 (*C*H), 136.7 (*C*H), 136.3 (*C*H) , 134.0 (*C*), 130.9 (*C*), 128.0 (*C*H), 114.1 (*C*H), 93.5 (*C*), 56.4 (*C*H), 55.1 (O*C*H$_3$), 50.6 (O*C*H$_3$), 49.8 (O*C*H$_3$), 40.5 (*C*H), 38.7 (*C*H), 28.5 (*C*H$_2$) ppm. HRMS (ESI+): *m/z* calcd for $C_{19}H_{21}NO_6Na$ [M + Na]$^+$: 382.1261, found 382.1251.

(1*S,4*R**,7*S**)-(*E*)-7-(3,4-dimethoxyphenyl)-3,3-dimethoxy-6-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (8f):** Reaction time: 45 min. Yield: 0.136 g (70%) as yellow solid. MP: 142 ^{o}C. IR (KBr): ν_{max} 3090, 2926, 2843, 1745, 1623, 1514, 1462, 1334, 1254, 1136, 1091, 1038 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 13.5 Hz, 1H), 7.13 (d, *J* = 6.5 Hz, 1H), 6.75–6.70 (m, 2H), 6.60–6.56 (m, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 3.49–3.43 (m, 2H), 3.41 (s, 3H), 3.35 (s, 3H), 3.33 (s, 1H), 2.56 (t, *J* = 11.5 Hz, 1H), 1.67 (dd, *J* = 5.5, 13.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.9 (*C*=O), 149.0 (*C*), 148.3 (*C*), 145.6, (*C*H) 137.0 (*C*H), 136.3 (*C*H), 134.7 (*C*), 131.1 (*C*), 118.9 (*C*H), 111.3 (*C*H), 110.7 (*C*H), 93.5 (*C*), 56.3 (O*C*H$_3$), 55.9 (O*C*H$_3$), 55.9 (*C*H), 50.7 (O*C*H$_3$), 50.0 (O*C*H$_3$), 40.6 (*C*H), 39.2 (*C*H), 28.9 (*C*H$_2$) ppm. HRMS (ESI+): *m/z* calcd for $C_{20}H_{23}NO_7Na$ [M + Na]$^+$: 412.1366, found 412.1367.

(1*S,4*R**,7*S**)-(*E*)-7-(3,4,5-trimethoxyphenyl-3,3-dimethoxy-6-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (8g):** Reaction time: 45 min. Yield: 0.104 g (50%) as viscous yellow liquid. IR (KBr): ν_{max} 3090, 2938, 2834, 1740, 1628, 1512, 1459, 1340, 1240, 1127, 1095 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 13.5 Hz, 1H), 7.14 (d, *J* = 7 0 Hz, 1H), 6.80 (d, *J* = 13.5 Hz, 1H), 6.26 (s, 2H), 3.77 (s, 3H), 3.75 (s, 6H), 3.46–3.42 (m, 2H), 3.39 (s, 3H), 3.35 (s, 1H), 3.33(s, 3H) 2.59–2.52 (m, 1H), 1.66–1.59 (m, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5 (*C*=O), 153.3 (*C*), 145.6 (*C*H), 138.0 (*C*), 137.2 (*C*H), 137.0 (*C*H), 136.1 (*C*), 131.0 (*C*), 104.2 (*C*H), 93.4 (*C*), 60.8 (O*C*H$_3$), 56.1 (O*C*H$_3$), 55.8 (*C*H), 50.6 (O*C*H$_3$), 49.9 (O*C*H$_3$), 40.5 (*C*H), 39.6 (*C*H), 29.1 (*C*H$_2$) ppm.HRMS (ESI+): *m/z* calcd for $C_{21}H_{25}NO_8Na$ [M + Na]$^+$: 442.1472, found 442.1472.

(1*S,4*R**,7*S**)-(*E*)-7-(2,5-dimethoxyphenyl)-3,3-dimethoxy-6-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (8h):**Reaction time: 45 min. Yield: 0.136 g (70%) as viscous yellow liquid. IR (KBr): ν_{max} 3096, 2946, 2836, 1740, 1628, 1501, 1461, 1339, 1220, 1126, 1093, 1050, cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, *J* = 13.5 Hz, 1H), 7.14 (d, *J* = 6.5 Hz, 1H), 6.78–6.75 (m, 1H), 6.69–6.61 (m, 2H), 6.44 (d, *J* = 1.5 Hz, 1H), 4.07–4.02 (m, 1H), 3.81 (s, 3H), 3.65 (s, 3H), 3.41 (s, 4H), 3.37 (s, 1H), 3.34 (s, 3H), 2.48–2.42 (m, 1H), 1.70–1.65 (m, 1H), ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 200.3 (*C*=O), 153.4 (*C*), 150.9 (*C*), 145.2 (*C*H), 136.6 (*C*H), 136.5 (*C*H), 131.4 (*C*), 130.9 (*C*), 114.2 (*C*H), 111.3 (*C*H), 111.1 (*C*H), 93.8 (*C*), 55.9 (O*C*H_3), 55.6 (O*C*H_3), 54.1 (*C*H), 50.6 (O*C*H_3), 49.9 (O*C*H_3), 40.6 (*C*H), 31.6 (*C*H), 26.5 (*C*H_2) ppm. HRMS (ESI+): *m/z* calcd for $C_{20}H_{23}NO_7Na$ $[M + Na]^+$: 412.1366, found 412.1354.

(1*S,4*R**,7*S**)-(*E*)-7-(3,5-dimethoxyphenyl)-3,3-dimethoxy-5-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (8i): Reaction time:** 45 min. Yield: 0.095 g (49%) as yellow solid. MP: 124 °C. IR (KBr): ν_{max} 3090, 2966, 2842, 1736, 1630, 1598, 1522, 1456, 1345, 1204, 1153, 1096, 1055 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 13.5 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 6.76 (d, *J* = 13.5 Hz, 1H), 6.30 (s, 1H), 6.20 (d, J = 2.0 Hz, 2H), 3.72 (s, 6H), 3.46–3.39 (m, 2H), 3.40 (s, 3H), 3.34 (s, 4H), 2.53 (ddd, *J* = 2.5, 9.5, 13.5 Hz, 1H), 1.68 (ddd, *J* = 2.5, 6.5, 13.5 Hz, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): 199.7 (*C*=O), 160.9 (*C*), 145.4 (*C*H), 144.5 (*C*), 136.9 (*C*H) 136.3 (*C*H), 130.9 (*C*), 105.5 (*C*H), 98.6 (*C*H), 93.5 (*C*), 55.9 (*C*H), 55.2 (O*C*H_3), 50.6 (O*C*H_3), 50.0 (O*C*H_3), 40.5 (*C*H), 39.6 (*C*H), 28.4 (*C*H_2) ppm. HRMS (ESI+): *m/z* calcd for $C_{20}H_{23}NO_7Na$ $[M + Na]^+$: 412.1366, found 412.1366.

(1*S,4*R**,7*S**)-(*E*)-7-(4-methylphenyl)-3,3-dimethoxy-5-(2-nitro vinyl)bicyclo[2.2.2]oct-5-en-2-one (8j):** Reaction time: 45 min. Yield: 0.096 g (56%) as viscous yellow liquid. IR (KBr): ν_{max} 3092, 2945, 2833, 1740, 1629, 1515, 1457, 1338, 1268, 1127, 1091, 1054 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 13.5 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.66 (d, *J* = 13.5 Hz, 1H), 3.52–3.46 (m, 1H), 3.45–3.42 (m, 1H), 3.41 (s, 3H), 3.34 (s, 3H), 3.31 (s, 1H), 2.52–2.50 (m, 1H), 2.28 (s, 3H), 1.73–1.67 (m, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 200.0 (*C*=O), 145.5 (*C*H), 139.0 (*C*), 137.0 (*C*), 136.8 (*C*H), 136.3 (*C*H), 130.9 (*C*), 129.5 (*C*H), 126.9 (*C*H), 93.5 (*C*), 56.3 (*C*H), 50.6 (O*C*H_3), 49.9 (O*C*H_3), 40.6 (*C*H), 39.1 (*C*H), 28.4 (*C*H_2), 20.9 (*C*H_3) ppm. HRMS (ESI+): *m/z* calcd for $C_{19}H_{21}NO_5Na$ $[M + Na]^+$: 366.1311, found 366.1316.

(1*S,4*R**,7*S**)-(*E*)-7-acetyl-3,3-dimethoxy-6-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (8k):** Reaction time: 45 min. Yield: 0.032 g (25%) as viscous yellow liquid. IR (KBr): ν_{max} 3110, 3049, 2947, 2831, 1745, 1709, 1629, 1511, 1451, 1333, 1266, 1193, 1135, 1096, 1050 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, *J* = 13.0 Hz, 1H), 7.31 (d, *J* = 13.5 Hz, 1H), 6.89 (d, *J* = 7.0 Hz, 1H), 3.62 (s, 1H), 3.36 (s, 3H), 3.30 (s, 3H), 3.27 (s, 3H), 3.21–3.16 (m, 1H), 2.46–2.41 (m, 1H), 2.15 (s, 1H), 1.64–1.58 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.9 (*C*=O), 199.6 (*C*=O), 144.2 (*C*H), 137.9 (*C*H), 135.4 (*C*H), 131.5 (*C*), 93.7 (*C*), 50.6 (O*C*H_3), 50.0 (*C*H), 49.4 (O*C*H_3), 46.3 (*C*H), 39.7 (*C*H), 28.0 (*C*H_3), 24.0 (*C*H_2) ppm.

(1*S,4*R**,7*S**)-(*E*)-7-methoxycarbonyl-3,3-dimethoxy-6-(2-nitrovinyl)bicyclo[2.2.2]oct-5-en-2-one (8l):** Reaction time: 45 min. Yield: 0.042 g (27%) as viscous yellow liquid. IR (KBr): ν_{max} 3101, 2955, 2919, 2845, 1740, 1632, 1521, 1440, 1342, 1263, 1128, 1096, 1057cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 13.5 Hz, 1H), 7.22 (d, *J* = 13.5 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 3.74–3.67 (m, 2H), 3.65 (s, 3H), 3.34 (s, 3H), 3.30 (s, 3H), 3.18–3.13 (m, 1H), 2.39–2.32 (m, 1H), 1.86–1.80 (m, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 199.3 (*C*=O), 172.3 (*C*=O), 145.4 (*C*H), 137.5 (*C*H), 135.4 (*C*H), 131.1 (*C*), 93.6 (*C*), 52.5 (O*C*H_3), 50.6 (O*C*H_3), 50.1 (*C*H), 49.8 (O*C*H_3), 39.7 (*C*H), 38.7 (*C*H), 24.1 (*C*H_2) ppm. HRMS (ESI+): *m/z* calcd for $C_{14}H_{17}NO_7Na$ $[M + Na]^+$: 334.0897, found 334.0877.

(1*S,2*S**,7*R**,8*R**)-6,12-(bis-2-nitrovinyl)-3,3,10,10-tetramethoxytricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione (9)**

To a solution of nitrovinyl-guaiacol **6** (0.097 g, 0.5 mmol) in dry MeOH (5 mL) solid diacetoxyiodobenzene (0.193 g, 0.6 mmol, 1.2 equiv.) was added portion-wise at room temperature. The solution was turned to orange-pale brown colour immediately after the addition of DIB and slowly changed into yellowish turbid solution. After the completion of the reaction in 45 min, as indicated by the TLC, the solvent was evaporated and the crude reaction mixture was purified by silica gel column chromatography by using ethyl acetate (30–50%) in hexanes as an eluting system to afford pure Diels–Alder dimer **9** as yellow solid.

Reaction time: 45 min. MP: 207 °C. Yield: 0.092 g (82%) as yellow solid.^{1}H NMR (500 MHz, $CDCl_3$): δ 8.0 (d, *J* = 14.0 Hz, 1H), 7.75 (d, *J* = 13.5 Hz, 1H), 7.63 (dd, *J* = 2.5, 14.0 Hz, 2H), 7.00 (d, *J* = 6.0 Hz, 1H), 6.60 (s, 1H), 4.21 (d, *J* = 6.5 Hz, 1H), 3.88 (s, 1H), 3.40 (s, 3H), 3.29 (s, 3H), 3.26 (d, *J* = 6Hz, 1H), 3.20 (d, *J* = 8Hz, 1H), 3.16 (s, 3H), 2.92 (s, 3H) ppm.^{13}C NMR (125 MHz, DMSO): δ 199.2 (*C*=O), 191.8 (*C*=O), 146.6 (*C*), 143.4 (*C*H), 142.9 (*C*H), 138.0 (*C*H), 135.3 (*C*H), 134.5 (*C*H), 133.5 (*C*H), 133.4 (*C*H), 97.6 (*C*), 93.4 (*C*), 51.2 (*C*H), 49.9 (O*C*H_3), 49.3 (O*C*H_3), 49.0 (O*C*H_3), 47.9 (O*C*H_3), 40.3 (*C*H), 37.6 (*C*H), 36.1 (*C*H) ppm. HRMS (ESI +): calcd for $C_{20}H_{22}N_2O_{10}$ $[M + Na]^+$ 473.1166 Found: 473.1152.

*Synthesis of triazole-substituted bicyclo[2.2.2]*octenones **10a-c**

Nitroolefin (**4c-e**, 0.3 mmol) and NaN_3 (0.45 mmol) were stirred in DMF (3 mL). Then *p*-TsOH (0.15 mmol) was carefully added to the mixture and the contents were allowed to stir at 60 °C in air for 3 h. After completion of the reaction, as detected by TLC, the reaction mixture was cooled to room temperature, quenched with H_2O (10 mL) and extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhyd. Na_2SO_4 and evaporated *in vacuo*. The residue was purified by silica gel column chromatography by using ethyl acetate (10–30%) in hexanes to furnish the trizoles **10a-c**.

(1*R,2*R**,6*R**,7*S**)-(*E*)-8,8-dimethoxy-11-(1*H*-1,2,3-triazol-4-yl)-3-oxatricyclo[5.2.2.0^{2,6}]undec-10-en-9-one (10a**): This product was obtained from **4c**. Reaction time: 3 h. Yield: 0.063 g (72%) as viscous yellow liquid. IR (KBr): ν_{max} 3447, 2949, 1732, 1632, 1512, 1459, 1250, 1180, 1135, 1096, 1057, 912, 829, 730, 530 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (s, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 4.01 (s, 1H), 3.82 (t, *J* = 8.0 Hz, 1H), 3.72–3.69 (m, 1H), 3.56 (q, *J* = 7.5 Hz, 1H), 3.38 (s, 3H), 3.27 (s, 3H), 3.08 (q, *J* = 8.5 Hz, 1H), 2.10–2.06 (m, 1H), 1.52–1.42 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.4 (*C*=O), 145.8 (*C*), 134.5 (*C*H$_2$), 130.0 (*C*H), 121.7 (*C*H), 93.5 (*C*), 78.9(*C*H), 69.2 (*C*H$_2$), 54.9 (*C*H), 50.7 (O*C*H$_3$), 50.0 (O*C*H$_3$), 44.3(*C*H), 38.4 (*C*H), 30.2 (*C*H$_2$) ppm.

(1*S,4*R**,7*S**)-(*E*)-7-phenyl-3,3-dimethoxy-5-(1*H*-1,2,3-triazol-4-yl)bicyclo[2.2.2]oct-5-en-2-one (10b):** This product was obtained from **4d**. Reaction time: 3 h. Yield: 0.071 g (73%) as viscous yellow liquid. IR (KBr): ν_{max} 3257, 2954, 1733,1603, 1453, 1324, 1209, 1136, 1096, 987, 909, 1054, 842, 765, 701, 616 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.25–7.22 (m, 1H), 7.20 (d, *J* = 6.5 Hz, 2H), 7.14 (d, *J* = 7.0 Hz, 2H), 6.54 (d, *J* = 5.5 Hz, 1H), 4.02 (s, 1H), 3.53 (t, *J* = 7.0 Hz, 1H), 3.46 (s, 3H), 3.41 (d, *J* = 6.0 Hz, 1H), 3.36 (s, 3H), 2.70–2.63 (m, 1H), 1.75–1.70 (m, 1H) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 201.1 (*C*=O), 145.1 (*C*), 143.7 (*C*), 137.1 (*C*), 128.6 (*C*H), 127.4 (*C*H), 126.8 (*C*H), 121.1 (*C*H), 93.9 (*C*), 55.1 (CH), 50.5 (O*C*H$_3$), 50.2 (O*C*H$_3$), 41.3 (*C*H), 40.3 (*C*H), 29.9 (*C*H$_2$) ppm. HRMS (ESI+): *m/z* calcd for $C_{18}H_{19}N_3O_3Na$ [M + Na]$^+$: 348.1318, found 348.1318.

(1*S,4*R**,7*S**)-(*E*)-7-(4-methoxyphenyl)-3,3-dimethoxy-5-(1*H*-1,2,3-triazol-4-yl)bicyclo[2.2.2]oct-5-en-2-one (10c):** This product was obtained from **4e**. Reaction time: 3 h. Yield: 0.080 g (76%) as viscous yellow liquid. IR (KBr): ν_{max} 3439, 2929, 2857, 1737, 1632, 1452, 1218, 1143, 1095, 1047, 908, 848, 730, 600 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 2H), 6.54 (d, *J* = 6.5 Hz, 1H), 4.03 (s, 1H), 3.78 (s, 3H), 3.52–3.50 (m, 1H), 3.48 (s, 3H), 3.39 (s, 1H), 3.37 (s, 3H), 2.69–2.64 (m, 1H), 1.73–1.68 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.1 (*C*=O), 158.5 (*C*), 144.7, 137.1 (*C*), 135.9 (*C*), 128.5 (*C*H), 121.2 (*C*H), 114.0 (*C*H), 93.5 (*C*), 55.6 (*C*H), 55.3 (O*C*H$_3$), 50.6 (O*C*H$_3$), 50.2 (O*C*H$_3$), 41.4 (*C*H), 39.7 (*C*H), 30.1 (*C*H$_2$) ppm.

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†Electronic Supplementary Information (ESI) available: [Copies of ^{1}H & ^{13}C NMR Spectra of all products, 2D NMR spectra of compound **8a**, Selected ^{1}H and ^{13}C NMR chemical shifts of the cycloadducts **4a-j** and **8a-k**]. See DOI: 10.1039/x0xx00000x

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Expedient Synthesis of Nitrovinyl Substituted Bicyclo[2.2.2]octenone Scaffolds

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