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Diels–Alder reactions of masked *o*-benzoquinones with acrylonitrile

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Abstract—Regioselective Diels–Alder reactions of masked *o*-benzoquinones (MOBs) **2a–i** derived from the corresponding 2-methoxyphenols **1a–i** with acrylonitrile leading to highly functionalized bicyclo[2.2.2]octenone derivatives in high yields are described.

1. Introduction

The Diels–Alder cycloaddition reaction occupies a position of particular prominence among the carbon–carbon bond forming reactions. Its widespread application is the introduction of up to four new contiguous asymmetric centers with good yields, high selectivity and predictability.[1]

Recently, the Diels–Alder reactions of 6,6-dialkoxycyclohexa-2,4-dienones generically known as masked *o*-benzoquinones (MOBs) are extensively studied.[2] The excellent selectivities observed in the Diels–Alder reactions of MOBs coupled with the synthetic utility of the cycloadducts made these MOBs very attractive Diels–Alder partners. MOBs can be easily generated in situ by the oxidation of the corresponding 2-methoxyphenols with hypervalent iodine reagents such as (diacetoxy)iodobenzene (DAIB) and phenyliodonium(III) bis(trifluoroacetate) in the presence of an alcohol. In view of the high propensity of most of these MOBs to undergo facile dimerization,[3] they are usually trapped in situ by reactive π-components to provide various highly functionalized bicyclic and tricyclic ring systems via inter- and intramolecular Diels–Alder reactions, respectively.[2] The Diels–Alder reactions of MOBs with several dienophiles including methyl acrylate, methyl methacrylate, methyl vinyl ketone (dienophiles bearing electron-withdrawing group),[4] styrene, benzyl vinyl ether, phenyl vinyl sulfide, dihydrofuran (dienophiles bearing electron-donating group)[5] and heteroaromatics like furans,[6] pyrroles,[7] thiophene[8] were extensively studied in this laboratory and it was found that these cycloadditions proceeded in highly regio- and stereoselective manner.

It is well known that a nitrile group, which is a useful and important functionality in organic synthesis can be transformed into various functional groups such as carboxylic acid, amide, amine, aldehyde, ketone, alcohol, etc. A nitrile was transformed into a methyl group in the synthesis of (+/−)-scopadulin an antiviral aphidicolane diterpene.[9] During the synthetic study of epolactaene, a nitrile was transformed to an amide functionality.[10] In the Diels–Alder reaction of 2-cyano-2-cyclohexenone, a nitrile group was used as an activating group which could be easily removed or replaced by an alkyl group. This strategy was successfully used by Liu and co-workers in the synthesis of *cis*-clerodane diterpenoids.[11] A 1,3-dipolar cycloaddition reaction of acrylonitrile to *N*-benzyl-3-hydroxypyridinium bromide was used as a key step in the total synthesis of Bao Gong Teng A, a natural antiglaucoma compound.[12] Intrigued by the synthetic potential of a nitrile functionality and highly reactive MOB building blocks, we have investigated the Diels–Alder reactions of acrylonitrile with various MOBs and contemplated that their cycloadducts would be of potentially useful synthetic intermediates. Herein we report the details of our studies on these Diels–Alder reactions.

2. Results and discussion

At the outset, the Diels–Alder reaction of the reactive MOB **2a**, generated in situ from methyl vanillate (**1a**) was studied as a representative example. Thus, MOB **2a** was slowly generated in the presence of acrylonitrile by adding DAIB over a period of 6 h (Method A) to afford a 1.1:1 mixture of *endo*–*exo* isomers **3a** and **4a** along with 45% of dimer **5a** (Scheme 1). However, when the in situ generation of MOB

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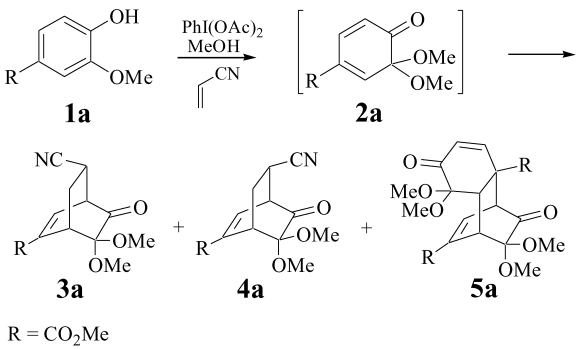


Scheme 1.

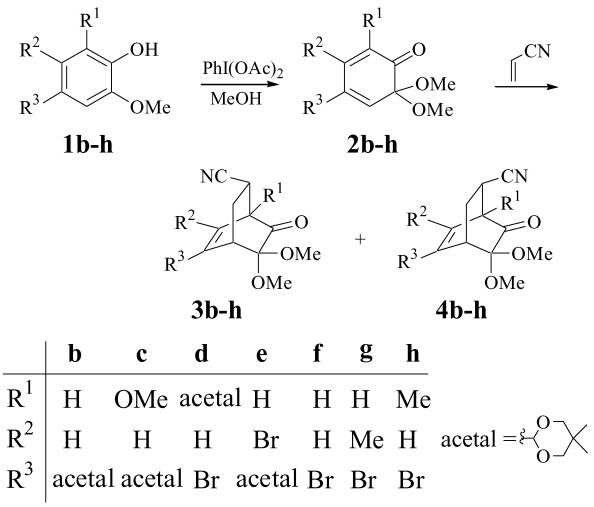
2a was attempted by adding **1a** to a mixture of acrylonitrile and DAIB in methanol (Method B), a white solid was obtained, presumably due to the polymerization of acrylonitrile.

To circumvent this problem, MOB **2a** was first generated at 0°C, confirmed by the disappearance of the starting phenol **1a** on TLC that implies the complete consumption of DAIB, and acrylonitrile was then added in one portion. The reaction was brought to room temperature (Method C) and stirring was continued until the reaction was complete (disappearance of MOB on TLC). However, the reaction was found to be sluggish. Alternatively, the same procedure was repeated at 50°C (Method D) and 100°C (Method E), where enhancement in the reaction rate was observed in both cases. Nevertheless, two stereoisomers **3a** and **4a** were isolated in poor yields along with a considerable amount of dimer **5a** (Scheme 1, Table 1). For this reason we envisioned that the isolable MOBs could be utilized in the present study where (i) the propensity to dimerization of these MOBs is less (ii) even the presence of traces of DAIB can be avoided and also (iii) the Diels–Alder reaction can be carried out without the solvent (neat) thereby enhancing the rate of the reaction by increase of concentration. Accordingly, several MOBs **2b–i** were prepared from the corresponding 2-methoxyphenols **1b–i**, following the procedure developed in our laboratory[13] and purified by flash chromatography (ethyl acetate–hexanes 1:4) (Scheme 2).

Table 1. Diels–Alder reactions of MOB **2a** with acrylonitrile

Entry	Method[a] (temp)	Time[b] (h)	Adduct			
			Yield[c] (%)			Ratio[d]
			3a	**4a**	**5a**	**3a–4a**
1	A (0°C)	1	10	6	45	1.1:1
2	B[e] (0°C)	–	–	–	–	–
3	C (rt)	12	8	6	60	1.2:1
4	D (50°C)	2	15	11	48	1.2:1
5	E (100°C)	0.5	22	15	34	1.2:1

All the reactions were carried out at 1 mM of **1a** and 25 mM of acrylonitrile.
[a] See Section 3.
[b] In entry 1, it indicates the reaction time after the addition of DAIB. In entries 3–5, it indicates the reaction time after the addition acrylonitrile to in situ generated MOB.
[c] The yields are of isolated products.
[d] The ratios are of the stereoisomers and were determined from the ^{1}H NMR analysis of the crude reaction mixture.
[e] Polymerization of acrylonitrile was observed.



Scheme 2.

The solvent was evaporated, dienophile (25 equiv.) was added, and the reaction was performed at appropriate temperature (Methods C–E) as shown in Table 2. In each case, no dimers of MOBs were observed, and the two stereoisomers **3** (*ortho*, *endo*-) and **4** (*ortho*, *exo*-) were obtained as indicated by the ^{1}H NMR (400 MHz) spectra of the crude products. The reactions proceeded regioselectively, **3** being the major products (Scheme 2, Table 2). When MOBs **2a–d** and **2i** were used, the resulted isomers could be separated by column chromatography unlike in the cases of MOBs **2e–h** which afforded an inseparable mixtures. However, **4e** (*ortho*, *exo*-), **3g** (*ortho*, *endo*-), **3h** (*ortho*, *endo*-) could be obtained in their pure states by recrystalization from their mixtures of stereoisomers. It is interesting to note that the non-dimerizing MOB **2i** gave two regioisomers *ortho*, *endo*-**3i** and *meta*, *endo*-**6i**, respectively, **3i** being the major adduct (Scheme 3).

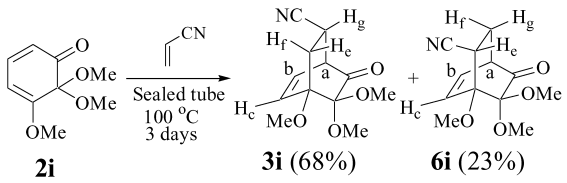
The structures of all the products were assigned on the basis of their IR, ^{1}H and ^{13}C NMR, DEPT, and low- and high-resolution mass spectral analyses. For all the cycloadducts, satisfactory elemental analyses were obtained. For most of the high-resolution mass spectra recorded in electron impact mode (70 eV), the peaks corresponding to the molecular ion (M^+) could not be seen; instead the peaks corresponding to M^+-28 were observed, indicating the extrusion of CO resulted from facile fragmentation. All the cycloadducts exhibited IR absorptions at 2240–2340 and 1745–1758 cm^{-1}, due to the characteristic features of nitrile and carbonyl functional groups, respectively. All the compounds showed ^{13}C resonance at about δ 194.5–197.8 and δ 118.0–120.8 also revealing the presence of carbonyl and nitrile groups, respectively. Further, the peak corresponding to the CH attached to nitrile carbon was observed at about δ 23.5–31.6 and the quarternary carbon with two methoxy groups was found to be present at δ 92.8–95.1. The olefinic carbons were observed at δ 119.0–147.0 depending on the substitutions on the double bond.

The regiochemistry of **3c**,**3d**,**4c** and **4d** was confirmed by NOE studies (Fig. 1). In the case of **3c**, saturation of both the –OMe gave rise to increase in the signal intensity of H_e (0.18%) while saturation of H_d brought about a significant

Table 2. Diels–Alder reactions of MOBs **2b–i** with acrylonitrile

Entry	Phenol	MOB	Method[a] (temp)	Time	Adducts		
					Yield %[b]		Ratio[c]
					endo-**3**	*exo*-**4**	*endo*-**3**–*exo*-**4**
1	**1b**	**2b**	C (rt)	18.5 h	**3b**/55	**4b**/29	1.9:1
2	**1b**	**2b**	D (50°C)	8 h	**3b**/61	**4b**/30	2:1
3	**1b**	**2b**	E (100°C)	1 h	**3b**/57	**4b**/30	2:1
4	**1c**	**2c**	C (rt)	6 h	**3c**/60	**4c**/17	3:1
5	**1c**	**2c**	D (50°C)	25 min	**3c**/72	**4c**/19	3:1
6	**1c**	**2c**	E (100°C)	5 min	**3c**/72	**4c**/21	3:1
7	**1d**	**2d**	C (rt)	12.5 h	**3d**/68	**4d**/25	2.5:1
8	**1d**	**2d**	D (50°C)	4 h	**3d**/56	**4d**/36	1.6:1
9	**1d**	**2d**	E (100°C)	35 min	**3d**/56	**4d**/32	1.6:1
10	**1e**	**2e**	C (rt)	17 h	**3e**+**4e**/92		1.3:1
11	**1e**	**2e**	D (50°C)	4 h	**3e**+**4e**/95		1.3:1
12	**1e**	**2e**	E (100°C)	1 h	**3e**+**4e**/88		1.3:1
13	**1f**	**2f**	C (rt)	21 h	**3f**+**4f**/92		1.4:1
14	**1f**	**2f**	D (50°C)	6.5 h	**3f**+**4f**/80		1.5:1
15	**1f**	**2f**	E (100°C)	2 h 40 min	**3f**+**4f**/92		1.4:1
16	**1g**	**2g**	C (rt)	14 h	**3g**+**4g**/75		1:1
17	**1g**	**2g**	D (50°C)	2.5 h	**3g**+**4g**/80		1:1
18	**1g**	**2g**	E (100°C)	7 min	**3g**+**4g**/70		1:1
19	**1h**	**2h**	C (rt)	8 h	**3h**+**4h**/85		5:1
20	**1h**	**2h**	D (50°C)	1 h	**3h**+**4h**/74		2.7:1
21	**1h**	**2h**	E (100°C)	10 min	**3h**+**4h**/70		2:1
22	**1i**	**2i**	C (rt)	48 h	–[d]		–[d]
23	**1i**	**2i**	D (50°C)	48 h	–[d]		–[d]
24	**1i**	**2i**	(100°C)[e]	3 Days	**3i**/68	**6i**/23	3:1[f]

All the reactions were carried out at 1 mM of MOB **2** and 25 mM of acrylonitrile.
[a] See Section 3.
[b] The yields are of isolated products; and the yields in entries 10–21 represent the combined yields of inseparable *endo*- and *exo*-isomers.
[c] The ratios of stereoisomers were determined from the ^{1}H NMR of crude reaction mixture.
[d] The starting material (85–90%) was recovered.
[e] The reaction was carried out in a sealed tube.
[f] The ratio of the regioisomers **3i** and **6i**, respectively.



2i **3i** (68%) **6i** (23%)

Scheme 3.

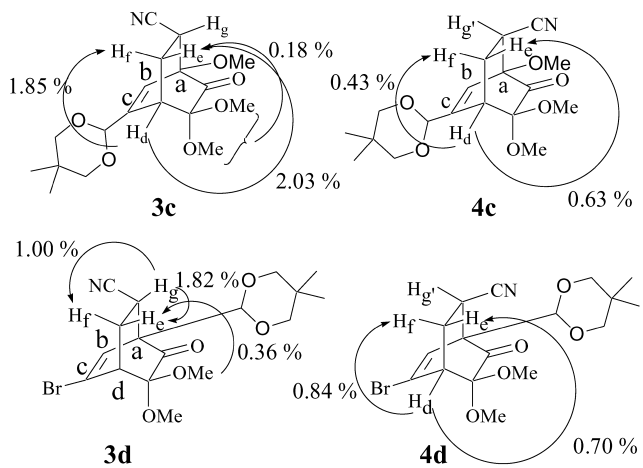
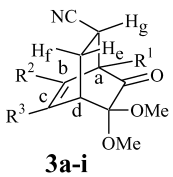


Figure 1. ^{1}H NMR studies of NOE (%) for **3c**,**4c**,**3d**, and **4d**.

NOE in H_f (1.85%) and H_e (2.03%). For **3d**, saturation of –OMe gave rise to the increase in signal intensity of H_e (0.36%) that proves the assigned *ortho*-regio chemistry, while saturation of H_g gave rise to the enhancement in signal intensity of H_e (1.82%) and H_f (1.00%) thus confirming the *endo*-stereochemistry. In the case of **4c**, saturation of H_d brought about significant NOE on the signal intensities of H_f (0.43%) and H_e (0.63%) and for **4d**, when H_d was saturated, the increase in the signal intensity of H_f (0.84%) and H_e (0.70%) was observed proving them to be *ortho*-adducts. The ^{1}H NMR spectra of **3b**,**3c** and **3i** showed long range coupling between H_b and H_g of 0.8, 0.4 and 0.8 Hz, respectively, confirming the given *ortho*,*endo*-assignment. The structures of all the other compounds were confirmed by comparing the chemical shifts [δH_f (*endo*)$<\delta H_f$ (*exo*), δH_e (*endo*)$>\delta H_e$ (*exo*) and δH_g (*endo*)$>\delta H_g$ (*exo*)] and coupling constants [$J_{e,g}/J_{e,g'}$, $J_{f,g}/J_{f,g'}$ and $J_{b,g}$] of a particular set of protons as shown in Table 3 and by decoupling experiments. For the cases where isomers could not be separated, the chemical shifts and coupling constants of H_e, H_f and H_g in the ^{1}H NMR spectra of the mixture of isomers were used for the characterization. Single crystal X-ray crystallography studies of **3h** (Fig. 2)[14] and **4b** (Fig. 3)[15] are fully in consonance with their assigned structures.

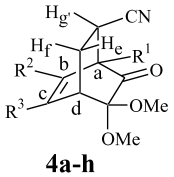
Similarly, in the ^{1}H NMR spectra of **6i**, a long range coupling (J=0.8 Hz) between H_c and H_e, the proton on the carbon with a nitrile function was observed and H_a exhibited coupling constants of 3.6 and 2.8 Hz with the methylene

Table 3. Selected chemical shifts (δ) and coupling constants (J in Hz) of the adducts **3a–i** and **4a–h**



3a-i

ortho, *endo*-



4a-h

ortho, *exo*-

Adduct	H_b	H_e	H_f	$H_g/H_{g'}$	$J_{a,g}$	$J_{b,g}/J_{b,g'}$	$J_{d,e}$	$J_{d,f}$	$J_{e,f}$	$J_{e,g}/J_{e,g'}$	$J_{f,g}/J_{f,g'}$
3a	7.16	2.55	1.69	3.21	2.0	–[a]	2.8	3.2	13.6	8.8	5.6
3b	6.26	2.50	1.67	3.12	2.0	0.8	2.8	2.8	12.4	10.0	6.0
3c	6.32	2.50	1.77	3.18	–	0.4	2.8	3.2	13.2	10.4	5.6
3d	6.43	2.58	1.95	3.30–3.33	–	–[a]	3.2	3.2	13.2	10.2	5.6
3e	–	2.55	1.75	3.17	2.0	–	2.8	2.8	13.2	10.0	6.0
3f	6.43	2.51	1.91	3.14	2.0	–[a]	2.8	2.8	13.2	10.0	5.6
3g	–	2.48	1.91	3.13	2.0	–	2.8	3.2	13.6	9.6	5.2
3h	6.06	2.53	1.98	2.84	–	–[a]	2.8	3.2	13.6	10.0	5.6
3i	6.21	2.58	1.92	3.19	2.0	0.8	–	–	12.4	10.4	5.2
4a	7.05	2.47	1.88	2.85	3.6	–[a]	2.8	3.2	13.2	4.0	12.0
4b	6.15	2.41	1.86	2.82	3.2	–[a]	2.8	2.8	13.2	4.0	12.0
4c	6.26	2.40	1.95	2.95	–	–[a]	3.2	3.2	13.2	4.0	12.4
4d	6.47	2.32	2.12	3.11	–	–[a]	2.8	3.2	13.2	4.4	12.0
4e	–	2.46	1.91	3.01	3.6	–	3.2	2.8	13.2	3.6	11.6
4f	6.30	2.43	2.09	2.91	3.6	–[a]	3.2	2.8	13.6	3.2	12.0
4g	–	2.41	–[b]	2.89	–[b]	–	–[b]	–[b]	13.2	–[b]	–[b]
4h	5.97	2.45	2.16	2.73	–	–[a]	3.2	2.8	13.2	3.2	12.0

[a] No coupling was observed.
[b] Could not be assigned from the ^{1}H NMR of the mixture of two isomers.

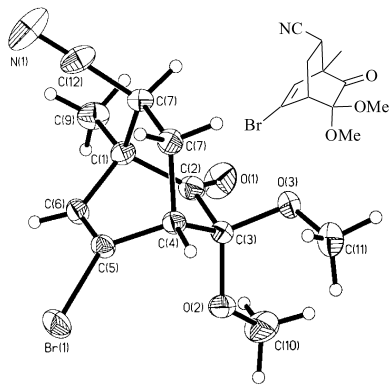


Figure 2. Crystal structure of **3h**.

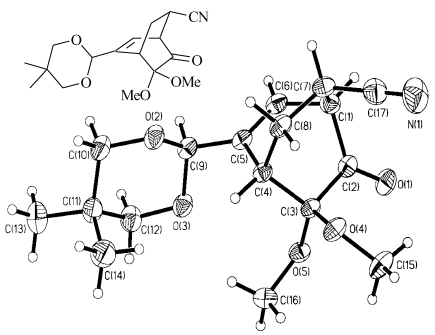


Figure 3. Crystal structure of **4b**.

protons (H_g and H_f) confirming the assigned regio- and stereochemistry (see Scheme 3).

The regioselectivities of the cyloadditions were very high in all the cases except for **2i**, and are in accord with our earlier results[3,5,16] due to the greater influence of the carbonyl functionality than the two methoxy groups present on the MOB moiety. Secondary orbital interactions,[17] if present, do not appear to be particularly important in the control of the *endo*–*exo* selectivity even though in most of cases *endo*-adduct was major. It is clear by comparing the chemical yields as given in Tables 1 and 2 that the Diels–Alder reactivity of MOBs depends on the substituents. It is worth mentioning that MOB **2a**, which exhibited high reactivity with many other dienophiles,[3,6,18] failed to produce **3a** and **4a** in good yields in the cycloaddition with acrylonitrile. The isolable MOBs **2b–h** provided the Diels–Alder cycloadducts in good yields. The non-dimerizing MOB **2i** required harsh conditions to proceed and furnished two regioisomeric adducts; these results are in accordance with our earlier studies.[19] The less stereoselectivities observed in the present study have literature precedents. For example, both cyclopentadiene and 5-bromo-2-pyrone provided the *endo*- and *exo*-isomers in equal amounts in their cycloaddition with acrylonitrile[20,21] while the *o*-quinodimethanes underwent Diels–Alder cycloaddition with acrylonitrile to give a 3:1 *endo*–*exo* mixture.[22] Similarly, less selectivities were observed in the reactions of furan,[23] and furo[3,4-*b*]1,4-benzodioxin with acrylonitrile.[24] Recently, we also observed poor stereoselectivity in the Diels–Alder reactions between 4-triflyloxy-2,6,6-trimethyl-2,4-cyclohexadienone and acrylonitrile.[25]

In conclusion, the Diels–Alder reactions of masked *o*-benzoquinones with acrylonitrile provided an entry to functionalized bicyclo[2.2.2]octenone derivatives in high yields with excellent regioselectivity. Although the stereoselectivities are not up to the anticipated level, the

stereoisomers can be separated in several cases in good chemical yields.

3. Experimental

Acrylonitrile was distilled prior to use. All the reagents were obtained from commercial sources and used without further purification. All the reactions were performed under a nitrogen atmosphere in anhydrous solvents, which were dried prior to use following standard procedures. Reactions were monitored by thin layer chromatography carried out on 0.25 mm E. Merck silica gel Plate (60F-254) using 7% ethanolic phosphomolybdic acid as developing agent. The isomeric distribution of the adducts in each reaction was determined by analyzing the ^{1}H NMR (400 MHz) spectrum of the crude reaction mixture. Standard column chromatography was performed using 230–400 mesh silica gel obtained from E. Merck. Melting points are uncorrected. IR spectra were recorded as films on NaCl plates. ^{1}H and ^{13}C spectra were recorded at 400 and 100 MHz, respectively, in $CDCl_3$ and chemical shifts are reported in δ ppm, using solvent resonance as the internal reference. Mass spectra were recorded in electron-impact mode (70 eV) at NSC Instrumentation Center at Hsinchu, Taiwan. Elemental analyses were performed at NSC Instrumentation Center at Tainan, Taiwan.

3.1. General procedures for Diels–Alder reactions

Procedure A. To a mixture of methyl vanillate (**1a**, 1 mM) and acrylonitrile (25 mM) in MeOH (4 mL) was added DAIB (1.1 mM) in MeOH (6 mL) during a period of 6 h with the aid of a syringe pump at room temperature. The reaction mixture was stirred further for additional 1 h at the same temperature and then all the volatiles were removed under reduced pressure and the residue was subjected to purification by column chromatography on silica gel using a mixture of ethyl acetate and hexanes as eluent to obtain the desired cycloadducts.

Procedure B. To a mixture of acrylonitrile (25 mM) and DAIB (1.1 mM) in MeOH (6 mL) was added methyl vanillate (**1a**, 1 mM) in MeOH (4 mL) during a period of 1 h with the aid of a syringe pump.

Procedure C. To a solution of appropriate 2-methoxyphenol (**1a**–**i**) in anyhydrous MeOH (10 mL) was added DAIB (1.1 mM) at 0°C. After 10 min stirring, MeOH was evaporated and flash column was performed using a mixture of ethyl acetate and hexanes as eluent to obtain the MOB (only in the reaction of phenol **1a**, the MOB **2a** was not isolated due to its high propensity towards dimerization). Solvents were evaporated and acrylonitrile 25 equiv. (acts as solvent also) was added and the reaction mixture was stirred at room temperature for an appropriate period of time as shown in Table 1 and worked up as described in procedure A. Special care should be taken that flash chromatography, evaporation of solvent and addition of acrylonitrile should be done fast (30–45 min duration) or else the prolonged time may lead to the dimerization of MOBs.

Procedure D. The procedure C was repeated while the reaction mixture was dipped in a 50°C preheated oil bath and the reaction was carried for a period of time as shown in Table 1.

Procedure E. The procedure C was repeated while the reaction mixture was dipped in a 100°C preheated oil bath and the reaction was carried for a period of time as shown in Table 1.

3.1.1. (1*S,4*R**,8*S**)-8-Cyano-6,6-dimethoxy-5-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (3a).** Mp 156.9–157.3°C; IR (film) 2952, 2840, 2242, 1749, 1716; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (ddd, J=3.2, 5.2, 13.6 Hz, 1H), 2.55 (ddd, J=2.8, 10.0, 13.6 Hz, 1H), 3.21 (ddd, J=2.0, 5.6, 8.8 Hz, 1H), 3.28 (s, 3H), 3.30 (s, 3H), 3.59 (dd, J=2.0, 6.4 Hz, 1H), 3.81 (s, 3H), 3.83 (dd, J=2.4, 5.2 Hz, 1H), 7.16 (dd, J=2.0, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.84 (CH), 26.42 (CH_2), 38.11 (CH), 50.24 (CH), 50.37 (CH_3), 52.35 (CH_3), 92.75 (C), 119.93 (C), 133.80 (CH), 139.86 (C), 163.54 (C), 197.27 (C); MS (EI, 75 eV) *m/z* (relative intensity) 237 (100), 209 (16), 206 (19), 190 (98), 178 (19), 145 (8), 118 (6), 104 (6), 76 (10); HRMS (EI) calcd for $C_{12}H_{15}NO_4$ (M^+-CO) 237.1001, found 237.1001. Anal. calcd for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.70; N, 5.28. Found: C, 58.83; H, 5.79; N, 5.19.

3.1.2. (1*R,2*S**,4*S**)-5-(5,5-Dimethyl-1,3-dioxan-2-yl)-8,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (3b).** Mp 156.8–157.2°C; IR (film) 2954, 2341, 2359, 1745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (s, 3H), 1.21 (s, 3H), 1.67 (ddd, J=2.8, 6.0, 12.4 Hz, 1H), 2.50 (ddd, J=2.8, 10.0, 12.8 Hz, 1H), 3.12 (ddd, J=2.0, 6.8, 10.0 Hz, 1H), 3.28 (s, 3H), 3.31 (s, 3H), 3.43–3.45 (m, 2H), 3.49 (dd, J=5.2, 10.4 Hz, 2H), 3.65 (d, J=11.6 Hz, 2H), 4.96 (s, 1H), 6.26 (dd, J=0.8, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.61 (CH_3), 22.82 (CH_3), 24.60 (CH), 27.19 (CH_2), 30.03 (C), 37.95 (CH), 49.21 (CH_3), 49.43 (CH), 50.09 (CH_3), 76.75 (CH_2), 77.09 (CH_2), 92.85 (C), 99.59 (CH), 120.39 (C), 120.99 (CH), 146.98 (C), 197.60 (C); MS (EI, 75 eV) *m/z* (relative intensity) 293 (100), 207 (32), 203 (25), 160 (28), 144 (17), 133 (30), 132 (23), 91 (30), 69 (46), 28 (30); HRMS (EI) calcd for $C_{17}H_{23}NO_5$ (M^+) 321.1602, found 320.1496. Anal. calcd for $C_{17}H_{23}NO_5$: C, 63.54; H, 7.21; N, 4.36. Found: C, 63.68; H, 7.17; N, 4.14.

3.1.3. (1*S,2*R**,4*S**)-5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1,8,8-trimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (3c).** Mp 119.9–121.9°C; IR (film) 2954, 2244, 1757; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (s, 3H), 1.19 (s, 3H), 1.77 (ddd, J=3.2, 5.6, 13.2 Hz, 1H), 2.50 (ddd, J=2.8, 10.4, 13.2 Hz, 1H), 3.18 (ddd, J=0.4, 8.0, 10.4 Hz, 1H), 3.30 (s, 3H), 3.31 (s, 3H), 3.35 (apparent ddd, J=0.8, 2.8, 7.6 Hz, 1H), 3.49 (dd, J=4.8, 10.8 Hz, 2H), 3.61 (s, 3H), 3.64 (dd, J=8.8, 11.2 Hz, 2H), 4.96 (d, J=0.8 Hz, 1H), 6.32 (d, J=0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.80 (CH_3), 22.99 (CH_3), 27.81 (CH_2), 30.25 (C), 30.80 (CH), 37.38 (CH), 49.92 (CH_3), 50.13 (CH_3), 54.42 (CH_3), 76.67 (CH_2), 77.30 (CH_2), 83.30 (C), 93.48 (C), 99.37 (CH), 119.11 (C), 122.92 (CH), 145.08 (C), 197.77 (C); MS (EI, 75 eV) *m/z* (relative intensity) 323 (26), 308 (18), 292 (53), 237 (28), 222 (70), 202 (42), 190 (73), 163 (78); HRMS (EI) calcd for $C_{17}H_{25}NO_5$ (M^+-CO) 323.1733, found 323.1735.

Anal. calcd for $C_{18}H_{25}NO_6$: C, 61.52; H, 7.17; N, 3.99. Found: C, 61.21; H, 7.18; N, 3.85.

3.1.4. (1*S,2*S**,4*R**)-5-Bromo-1-(5,5-dimethyl-1,3-dioxan-2-yl)-8,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (3d).** Mp 116.3–117.3°C; IR (film) 2955, 2243, 1748, 1611; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 (s, 3H), 1.30 (s, 3H), 1.95 (ddd, *J*=3.2, 5.6, 13.2 Hz, 1H), 2.58 (ddd, *J*=3.2, 10.2, 13.2 Hz, 1H), 3.29 (s, 3H), 3.30–3.33 (m, 2H), 3.68 (dd, *J*=2.8, 11.2 Hz, 1H) 3.35 (s, 3H), 3.47 (d, *J*=11.2 Hz, 1H), 3.55 (d, *J*=10.8 Hz, 1H), 3.75 (dd, *J*=2.4, 10.8 Hz, 1H), 4.99 (s, 1H), 6.43 (d, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.89 (CH_3), 23.22 (CH_3), 24.82 (CH), 27.92 (CH_2), 30.44 (C), 48.26 (CH), 50.41 (CH_3), 50.81 (CH_3), 58.57 (C), 76.66 (CH_2), 76.98 (CH_2), 93.78 (C), 97.79 (CH), 120.01 (C), 125.64 (C), 125.79 (CH), 194.66 (C); MS (EI, 75 eV) *m*/*z* (relative intensity) 371 (100), 285 (91), 256 (6), 206 (21), 115 (12), 69 (32), 43 (23), 29 (8); HRMS (EI) calcd for $C_{16}H_{22}{}^{79}BrNO_4$ (M^+ − CO) 371.0732, found 371.0732, calcd for $C_{16}H_{22}{}^{81}BrNO_4$ 373.0711, found 373.0708. Anal. calcd for $C_{17}H_{22}BrNO_5$: C, 51.01; H, 5.54: N, 3.50. Found: C, 51.51: H, 5.71: N, 3.43.

3.1.5. (1*R,2*S**,4*S**)-6-Bromo-5-(5,5-dimethyl-1,3-dioxan-2-yl)-8,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (3e).** (The selected ^{1}H and ^{13}C NMR data of **3e** presented here were taken from the spectra of isomeric mixture of **3e** and **4e**. All the other data given here belong to the mixture of **3e** and **4e**.)

Mp 127.4–128.5°C; IR (film) 2960, 2859, 2242, 1749, 1104, 1055; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (s, 3H), 1.21 (s, 3H), 1.75 (ddd, *J*=2.8, 6.0, 13.2 Hz, 1H), 2.55 (ddd, *J*=2.8, 10.0, 12.8 Hz, 1H), 3.17 (ddd, *J*=2.0, 6.0, 10.0 Hz, 1H), 3.58–3.69 (m, 5H), 3.72 (dd, *J*=2.8, 2.8 Hz, 1H), 3.29 (s, 3H), 3.33 (s, 3H), 5.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.81 (CH_3), 23.03 (CH_3), 25.35 (CH), 27.55 (CH_2), 30.18 (C), 39.71 (CH), 48.87 (CH_3), 50.52 (CH_3), 59.40 (CH), 77.12 (CH_2), 93.06 (C), 99.11 (CH), 114.19 (C), 119.02 (C), 143.39 (C), 194.54 (C); MS (EI, 75 eV) *m*/*z* (relative intensity) 371 (91), 298 (19), 285 (66), 239 (41), 202 (36), 144 (45), 132 (23), 69 (99), 43 (100); HRMS (EI) calcd for $C_{16}H_{22}{}^{79}BrNO_4$ (M^+−CO) 371.0732, found 371.0734, calcd for $C_{16}H_{22}{}^{81}BrNO_4$ 373.0711, found 373.0716. Anal. calcd for $C_{17}H_{22}BrNO_5$: C, 51.01; H, 5.54; N, 3.50. Found: C, 51.20; H, 5.52; N, 3.69.

3.1.6. (1*R,2*S**,4*R**)-5-Bromo-8,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (3f).** (The selected ^{1}H NMR data of **3f** presented here was taken from the spectra of isomeric mixture of **3f** and **4f**. All the other data given here belong to the mixture of **3f** and **4f**.)

Mp 115.4–116.7°C; IR (film) 2947, 2242, 1746; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (ddd, *J*=2.8, 5.6, 13.6 Hz, 1H), 2.51 (ddd, *J*=2.8, 10.0, 13.2 Hz, 1H), 3.14 (ddd, *J*=2.0, 5.6, 9.6 Hz, 1H), 6.43 (dd, *J*=2.4, 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.86 (CH), 26.15 (CH_2), 26.82 (CH_2), 48.72 (CH), 48.87 (CH), 50.30 (CH_3), 50.40 (CH_3), 50.82 (CH_3), 51.59 (CH), 51.68 (CH), 93.21 (C), 93.49 (C), 119.17 (C), 119.93 (C), 124.48 (C), 125.43 (C), 126.87 (C), 196.28 (C); MS (EI, 75 eV) *m*/*z* (relative intensity) 257 (100), 225 (17), 178 (64), 104 (19), 76 (34), 73 (15), 59 (46), 42 (15), 28 (16); HRMS (EI) calcd for $C_{10}H_{12}{}^{79}BrNO_2$ (M^+−CO) 257.0051, found 257.0053, calcd for $C_{10}H_{12}{}^{81}BrNO_2$ 259.0030, found 259.0036. Anal. calcd for $C_{11}H_{12}BrNO_3$: C, 46.18; H, 4.23; N, 4.90. Found: C, 46.22; H, 4.29; N, 5.20.

3.1.7. (1*S,2*S**,4*R**)-5-Bromo-8,8-dimethoxy-6-methyl-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (3g).** Mp 82.9–84.6°C; IR (film) 2946, 2241, 2349, 1747; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (ddd, *J*=3.2, 5.2, 13.6 Hz, 1H), 1.98 (s, 3H), 2.48 (ddd, *J*=2.8, 9.6, 13.6 Hz, 1H), 3.13 (ddd, *J*=2.0, 5.2, 10.0 Hz, 1H), 3.28 (s, 3H), 3.30–3.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.19 (CH_3), 24.86 (CH), 27.28 (CH_2), 48.78 (CH), 50.40 (CH_3), 50.58 (CH_3), 56.56 (CH), 93.67 (C), 119.96 (C), 120.15 (C), 132.18 (C), 196.04 (C); MS (EI, 75 eV) *m*/*z* (relative intensity) 273 (100), 271 (95), 255 (41), 242 (20), 198 (15), 161 (17), 132 (36); HRMS (EI) calcd for $C_{11}H_{14}BrNO_2$ (M^+−CO) 273.0187, found 273.0180.

3.1.8. (1*R,2*S**,4*R**)-5-Bromo-8,8-dimethoxy-1-methyl-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (3h).** Mp 130.7–131.2°C; IR (film) 2955, 2238, 1748; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 3H), 1.98 (ddd, *J*=3.2, 5.6, 13.6 Hz, 1H), 2.53 (ddd, *J*=2.8, 10.0, 13.2 Hz, 1H), 2.84 (dd, *J*=5.6, 10.0 Hz, 1H), 3.29 (s, 3H), 3.32 (apparent dd, *J*=1.6, 3.2 Hz, 1H), 3.35 (s, 3H), 6.06 (d, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.86 (CH_3), 28.32 (CH_2), 31.64 (CH), 48.47 (CH), 50.24 (CH_3), 50.88 (CH_3), 52.75 (C), 93.67 (C), 119.54 (C), 126.01 (C), 129.80 (CH), 197.99 (C); MS (EI, 75 eV) *m*/*z* (relative intensity) 271 (99), 242 (19), 198 (37), 192 (52), 161 (13), 132 (28), 117 (20), 91 (21), 59 (47), 28 (14); HRMS (EI) calcd for $C_{11}H_{14}{}^{79}BrNO_2$ (M^+−CO) 271.0207, found 271.0206, calcd for $C_{11}H_{14}{}^{79}BrNO_2$ 273.0187, found 273.0188.

3.1.9. (1*R,2*S**,4*R**)-4,8,8-Trimethoxy-7-oxobicyclo-[2.2.2]oct-5-en-2-yl cyanide (3i).** Mp 83.6–84.7°C; IR (film) 2948, 2242, 1746; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (dd, *J*=5.2, 12.4 Hz, 1H), 2.58 (ddd, *J*=0.8, 10.4, 12.0 Hz, 1H), 3.10 (dddd, *J*=0.8, 2.0, 5.2, 7.2 Hz, 1H), 3.37 (ddd, *J*=1.2, 2.0, 6.0 Hz, 1H), 3.43 (s, 3H), 3.44 (s, 3H), 3.50 (s, 3H), 6.21 (dd, *J*=6.4, 8.8 Hz, 1H), 6.67 (ddd, *J*=1.2, 1.2, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.50 (CH), 29.85 (CH_2), 48.54 (CH), 51.95 (CH_3), 52.49 (CH_3), 52.84 (CH_3), 60.33 (C), 82.52 (C), 120.27 (C), 122.63 (CH), 139.28 (CH), 196.58 (C); MS (EI, 75 eV) *m*/*z* (relative intensity) 237 (11), 222 (22), 209 (24), 194 (41), 178 (58), 162 (100), 135 (23), 74 (18), 59 (35); HRMS (EI) calcd for $C_{12}H_{15}NO_4$ (M^+) 237.1001, found 237.1004. Anal. calcd for $C_{12}H_{15}NO_4$; C, 60.75; H, 6.37; N, 5.90. Found: C, 61.00; H, 6.71; N, 5.59.

3.1.10. (1*S,4*R**,8*R**)-8-Cyano-6,6-dimethoxy-5-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (4a).** Mp 123.4–124.5°C; IR (film) 2507, 1870, 1819; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (ddd, *J*=2.8, 11.2, 13.2 Hz, 1H), 2.47 (ddd, *J*=3.2, 3.6, 13.6 Hz, 1H), 2.85 (ddd, *J*=3.6, 4.0, 12.0 Hz, 1H), 3.29 (s, 3H), 3.39 (s, 3H), 3.55 (dd, *J*=3.2, 6.8 Hz, 1H), 3.78 (s, 3H), 3.85 (dd, *J*=2.8, 5.2 Hz, 1H), 7.05 (dd, *J*=2.0, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.93 (CH), 25.78 (CH_2), 38.03 (CH), 49.82 (CH_3), 50.34 (CH_3), 50.50

(CH), 52.35 (CH_3), 92.98 (C), 119.29 (C), 134.74 (CH), 139.67 (C), 163.52 (C), 196.73 (C); MS (EI, 75 eV) *m/z* (relative intensity) 237 (46), 209 (14), 206 (17), 190 (100), 146 (10), 104 (8), 77 (19); HRMS (EI) calcd for $C_{12}H_{15}NO_4$ (M^+-CO) 237.1001, found 237.0996.

3.1.11. (1*R,2*R**,4*S**)-5-(5,5-Dimethyl-1,3-dioxan-2-yl)-8,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (4b).** Mp 143.7–144.4°; IR (film) 2954, 2240, 1745; ^1H NMR (400 MHz, $CDCl_3$) δ 0.73 (s, 3H), 1.18 (s, 3H), 1.86 (ddd, *J*=2.8, 12.0, 14.4 Hz, 1H), 2.41 (ddd, *J*=2.8, 4.0, 13.2 Hz, 1H), 2.82 (ddd, *J*=3.2, 3.6, 12.0 Hz, 1H), 3.32 (s, 3H), 3.36 (s, 3H), 3.41 (dd, *J*=3.2, 6.8 Hz, 1H), 3.45–3.50 (m, 3H), 3.63 (ddd, *J*=2.4, 4.0, 11.2 Hz, 2H), 4.91 (d, *J*=0.8 Hz, 1H), 6.15 (ddd, *J*=1.2, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.78 (CH_3), 22.96 (CH_3), 25.09 (CH), 26.59 (CH_2), 30.20 (C), 38.08 (CH), 49.27 (CH_3), 49.56 (CH), 50.27 (CH_3), 76.67 (CH_2), 77.30 (CH_2), 93.42 (C), 99.79 (CH), 120.04 (C), 122.20 (CH), 146.87 (C), 197.48 (C); MS (EI, 75 eV) *m/z* (relative intensity) 293 (100), 207 (47), 160 (38), 133 (25), 90 (18), 74 (15), 69 (34), 43 (36), 32 (10), 28 (39); HRMS (EI) calcd for $C_{17}H_{23}NO_5$ (M^+) 320.1498, found 321.16. Anal. calcd for $C_{17}H_{23}NO_5$: C, 63.54; H, 7.21; N, 4.36. Found: C, 63.29; H, 7.18; N, 4.20.

3.1.12. (1*S,2*S**,4*S**)-5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1,8,8-trimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (4c).** Mp 115–116.8°C; IR (film) 3020, 2959, 2348, 1758; ^1H NMR (400 MHz, $CDCl_3$) δ 0.74 (s, 3H), 1.18 (s, 3H), 1.95 (ddd, *J*=3.2, 12.4, 13.2 Hz, 1H), 2.40 (ddd, *J*=3.2, 4.0, 13.2 Hz, 1H), 2.95 (dd, *J*=4.0, 12.0 Hz, 1H), 3.32 (s, 3H), 3.38 (s, 3H), 3.48 (dd, *J*=3.2, 10.4 Hz, 2H), 3.59 (s, 3H), 3.64 (d, *J*=11.2 Hz, 2H), 4.91 (d, *J*=0.8 Hz, 1H), 6.26 (dd, *J*=0.8, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.68 (CH_3), 22.88 (CH_3), 27.11 (CH_2), 30.17 (C), 31.05 (CH), 37.28 (CH), 49.47 (CH_3), 50.05 (CH_3), 54.15 (CH_3), 76.93 (CH_2), 77.27 (CH_2), 83.71 (C), 93.26 (C), 99.23 (CH), 118.62 (C), 122.31 (CH), 145.60 (C), 196.34 (C); MS (EI, 75 eV) *m/z* (relative intensity) 323 (92), 292 (25), 268 (58), 222 (85), 190 (63), 182 (100), 147 (43), 109 (26), 69 (71), 41 (35); HRMS (EI) calcd for $C_{17}H_{25}NO_5$ (M^+-CO) 323.1733, found 323.1730. Anal. calcd for $C_{18}H_{25}NO_6$: C, 61.52; H, 7.17; N, 3.99. Found: C, 61.48; H, 7.21; N, 4.14.

3.1.13. (1*S,2*R**,4*R**)-5-Bromo-1-(5,5-dimethyl-1,3-dioxan-2-yl)-8,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (4d).** Mp 125.2–126.8°C; IR (film) 2957, 2241, 1749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.73 (s, 3H), 1.17 (s, 3H), 2.12 (ddd, *J*=3.2, 12.0, 15.2 Hz, 1H), 2.32 (ddd, *J*=2.8, 4.4, 13.2 Hz, 1H), 3.11 (dd, *J*=4.4, 12.0 Hz, 1H), 3.32 (dd, *J*=3.2, 5.6 Hz, 1H), 3.35 (s, 3H), 3.37 (s, 3H), 3.52–3.66 (m, 4H), 5.04 (s, 1H), 6.47 (d, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.45 (CH_3), 22.94 (CH_3), 26.35 (CH_2), 26.75 (CH), 30.06 (C), 48.29 (CH), 49.97 (CH_3), 50.58 (CH_3), 59.30 (C), 76.52 (CH_2), 76.83 (CH_2), 93.93 (C), 97.00 (CH), 118.30 (C), 124.65 (C), 125.78 (CH), 194.54 (C); MS (EI, 75 eV) *m/z* (relative intensity) 371 (100), 285 (99), 256 (7), 206 (35), 178 (8), 115 (23), 69 (53), 59 (36), 29 (9); HRMS (EI) calcd for $C_{16}H_{22}{}^{79}BrNO_4$ (M^+-CO) 371.0732, found 371.0732, calcd for $C_{16}H_{22}{}^{81}BrNO_4$ 373.0711, found 373.0712. Anal. calcd for $C_{17}H_{22}BrNO_5$: C, 51.01; H, 5.54: N, 3.50. Found: C, 51.22: H, 5.81: N, 3.36.

3.1.14. (1*R,2*R**,4*S**)-6-Bromo-5-(5,5-dimethyl-1,3-dioxan-2-yl)-8,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (4e).** Mp 143.1–143.6°C; IR (film) 2956, 2857, 2238, 1744, 1097, 1052; ^1H NMR (400 MHz, $CDCl_3$) δ 0.742 (s, 3H), 1.20 (s, 3H), 1.91 (ddd, *J*=2.8, 11.6, 14.8 Hz, 1H), 2.46 (ddd, *J*=3.2, 3.6, 13.2 Hz, 1H), 3.01 (ddd, *J*=3.6, 3.6, 12.0 Hz, 1H), 3.33 (s, 3H), 3.37 (s, 3H), 3.56 (d, *J*=2.8, 11.2, 17.6 Hz, 2H), 3.60–3.65 (m, 3H), 3.74 (t, *J*=3.2 Hz, 1H), 5.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.81 (CH_3), 23.09 (CH_3), 25.32 (CH), 28.10 (CH_2), 30.21 (C), 39.71 (CH), 49.27 (CH_3), 50.67 (CH_3), 59.25 (CH), 77.09 (CH_2), 77.21 (CH_2), 92.75 (C), 99.17 (CH), 113.25 (C), 119.29 (C), 143.21 (C), 194.94 (C); MS (EI, 75 eV) *m/z* (relative intensity) 371 (11), 370 (54), 287 (59), 267 (18), 240 (50), 145 (24); HRMS (EI) calcd for $C_{16}H_{22}{}^{79}BrNO_4$ (M^+-CO) 399.0681, found 399.0691, calcd for $C_{17}H_{22}{}^{81}BrNO_5$ 401.0601, found 401.0616. Anal. calcd for $C_{17}H_{22}BrNO_5$: C, 51.01; H, 5.54; N, 3.50. Found: C, 50.91; H, 5.57; N, 3.45.

3.1.15. (1*R,2*R**,4*R**)-5-Bromo-8,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (4f).** (The selected ^1H NMR data of **4f** presented here was taken from the spectra of isomeric mixture of **3f** and **4f**.)

^1H NMR (400 MHz, $CDCl_3$) δ 2.09 (ddd, *J*=2.8, 12.0, 14.4 Hz, 1H), 2.43 (ddd, *J*=3.2, 3.2, 13.6 Hz, 1H), 2.91 (ddd, *J*=3.6, 4.0, 12.0 Hz, 1H), 6.30 (dd, *J*=2.4, 6.8 Hz, 1H).

3.1.16. (1*S,2*R**,4*R**)-5-Bromo-8,8-dimethoxy-6-methyl-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (4g).** (The selected ^1H NMR data of **4g** presented here was taken from the spectra of isomeric mixture of **3g** and **4g**.)

Mp 83.5–84.8°C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.86 (s, 3H), 2.07–2.11 (apparent ddd, 1H), 2.41 (ddd, *J*=3.2, 3.2, 13.2 Hz, 1H), 2.89 (ddd, *J*=4.0, 4.0, 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.28 (CH_3), 24.62 (CH_3), 26.85 (CH_2), 48.65 (CH), 50.06 (CH_3), 50.49 (CH), 56.56 (CH), 93.67 (C), 119.96 (C), 120.15 (C), 132.18 (C), 196.04 (C); MS (EI, 75 eV) *m/z* (relative intensity) 273 (99), 256 (33), 242 (20), 192 (69), 132 (30), 90 (36), 59 (59), 43 (19); HRMS (EI) calcd for $C_{11}H_{14}{}^{79}BrNO_2$ (M^+-CO) 271.0207, found 273.0207, calcd for $C_{11}H_{14}{}^{81}BrNO_2$ 273.0187, found 273.0187. Anal. calcd for $C_{12}H_{14}BrNO_3$: C, 48.02; H, 4.70; N, 4.67. Found: C, 47.88; H, 4.89; N, 4.61.

3.1.17. (1*R,2*R**,4*R**)-5-Bromo-8,8-dimethoxy-1-methyl-7-oxobicyclo[2.2.2]oct-5-en-2-yl cyanide (4h).** Mp 118.3–118.9°C; IR (film) 2945, 2240, 1746, 1610; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 3H), 2.16 (ddd, *J*=2.8, 12.0, 14.8 Hz, 1H), 2.45 (ddd, *J*=3.2, 3.2, 13.2 Hz, 1H), 2.73 (dd, *J*=4.0, 12.0 Hz, 1H), 3.33 (d, *J*=4.0 Hz, 1H), 3.36 (s, 3H), 3.37 (s, 3H), 5.97 (d, *J*=2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.90 (CH_3), 27.57 (CH_2), 31.70 (CH), 48.37 (CH), 50.15 (CH_3), 50.76 (CH_3), 53.18 (C), 93.56 (C), 118.69 (C), 126.35 (C), 130.53 (CH), 197.86 (C); MS (EI, 75 eV) *m/z* (relative intensity) 271 (43), 195 (39), 192 (49), 132 (56), 117 (48), 91 (54), 59 (100); HRMS (EI) calcd for $C_{12}H_{14}BrNO_3$ (M^+-CO) 271.0207, found 271.0211. Anal.

calcd for $C_{12}H_{14}BrNO_3$: C, 48.02; H, 4.70; N, 5.01. Found: C, 48.59: H, 4.62: N, 5.01.

3.1.18. Dimer 5a. For the spectral data see Ref. 3.

3.1.19. (1*R,2*S**,4*R**)-1,7,7-trimethoxy-8-oxobicyclo-[2.2.2]oct-5-en-2-yl cyanide (6i).** Mp 80.7–81.5°C; IR (film) 2949, 2341, 2359, 1746; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (ddd, J=3.6, 3.6, 13.6 Hz, 1H), 2.28 (dddd, J=0.8, 2.8, 10.0, 12.8 Hz, 1H), 3.19 (dddd, J=1.2, 2.0, 3.6, 5.6 Hz, 1H), 3.42 (s, 3H), 3.45 (s, 3H), 3.61 (ddd, J=0.8, 3.6, 10.0 Hz, 1H), 3.71 (s, 3H), 6.28 (ddd, J=0.8, 6.4, 8.8 Hz, 1H), 6.56 (ddd, J=0.8, 1.2, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.65 (CH_2), 29.45 (CH), 45.83 (CH), 51.63 (CH_3), 52.86 (CH_3), 54.51 (CH_3), 83.24 (C), 95.13 (C), 120.79 (C), 125.84 (CH), 135.06 (CH), 197.62 (C); MS (EI, 75 eV) *m/z* (relative intensity) 237 (24), 209 (46), 194 (98), 178 (100), 162 (96), 135 (28), 134 (39), 95 (24), 76 (17), 73 (24), 59 (49); HRMS (EI) calcd for $C_{12}H_{15}NO_4$ (M^+) 237.1001, found 237.1005. Anal. calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37: N, 5.90. Found: C, 61.16: H, 6.48: N, 5.75.

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