Chemospecific and diastereoselective synthesis of bis-dioxabicyclo[2.2.1]heptanone ring systems

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This paper is dedicated to Prof. S. Swaminathan in recognition of his outstanding contributions to organic chemistry

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Abstract

Chemospecific and diastereoselective methods for the construction of bis-dioxabicyclo[2.2.1]heptanone ring systems using $Rh_2(OAc)_4$-catalyzed tandem reactions of α-diazo ketones with keto-functional groups as dipolarophiles are described. Diketone functionalities were utilized to undergo highly efficient tandem cyclization-cycloaddition to furnish the bis-dioxabicyclo[2.2.1]heptanone spirocycles. This process served both as a simple and superior method for multi bond formation in a single synthetic operation.

Keywords: Carbonyl ylides, 1,3-dipolar cycloaddition, diazo ketones, rhodium(II) acetate, dioxabicyclo[2.2.1]heptanone ring systems

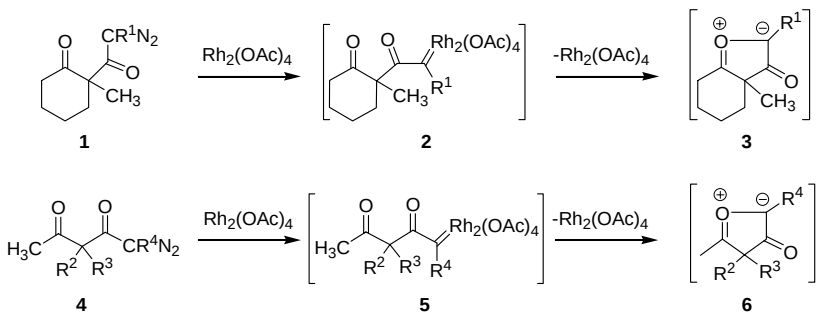
Introduction

Achieving the maximum pertinent complexity increase while minimizing the number of steps is an ideal in synthetic organic chemistry.[1] Reactions leading to multi C-C bond formations through tandem processes, which can rapidly generate the molecular complexity in a controlled and predictable manner, is a contemporary theme in modern organic synthesis and finds application in accessing newer entities. Tandem processes of diverse nature, promoted through catalysis, thermal or photochemical activation have already proven their utility in organic synthesis and found many applications in the acquisition of complexity in the form of functionalized carbo- and heterocyclic systems. Reactions based on carbenoid transformations are among the synthetically most useful to increase the molecular complexity.[2,3] Rhodium(II) carbenoid generated from α-diazo carbonyl compounds and their subsequent reactions play an important role in synthetic organic chemistry to design various polycyclic compounds with regio- and stereocontrol. This methodology serves as an important protocol to construct bonds for the

synthesis of complex molecules[3] and various natural products[4] with atom economy. Thus, this methodology generates considerable interest and intensive investigation in synthetic organic chemistry. Metallo-carbenoid cyclization with a carbonyl group represents a most important method for the generation of carbonyl ylides from α-diazo carbonyl compounds and their subsequent 1,3-dipolar cycloaddition reactions with C=C bonds have been well documented.[3] From a survey of the literature, only a few examples are known for the 1,3-dipolar cycloaddition of carbonyl ylides with heterodipolarophiles such as carbonyl group. For example, reactions of five- or six-membered-ring cyclic carbonyl ylides with *o*-quinones,[5] *p*-benzoquinones,[6,7] 1,2-diketones[8] and other carbonyl compounds[9] have been studied to afford 1:1, 2:1 or 3:1 cycloadducts without any selectivity in the presence of copper or rhodium catalysts. These tandem cyclization-cycloaddition protocols have been successfully utilized in the synthesis of important biologically active compounds such as brevicomins[10] and zaragozic acid A[11] using propionaldehyde and glyoxalate as heterodipolarophiles, respectively. Furthermore, the dioxabicyclo[2.2.1]heptanone skeleton is present in a wide range of natural products and exists as part of polycyclic frameworks e.g. loukacinols,[12] xanthane epoxide,[13] and isogosterones.[14] But the chemistry and the selectivity of these reactions have not been investigated well. The control of the stereoselectivity in the cycloaddition reactions of carbonyl ylides poses a challenge with the prospect of applications towards the synthesis of natural products. In continuation of our interest in the synthesis of highly substituted epoxy-bridged poly- or spirocyclic frameworks,[6,8,15] we recently reported on the chemoselective synthesis of multiple dioxabicyclo[2.2.1]heptanone ring systems.[16] We herein report the detailed investigation on the tandem cyclization–[3+2]-cycloaddition reactions of five-membered-ring carbonyl ylides for the synthesis of bis-dioxabicyclo[2.2.1]heptanone ring systems.

Results and Discussion

It was envisaged that the reaction of α-diazo ketones such as **1** or **4** with $Rh_2(OAc)_4$ could generate the corresponding rhodium carbenoids **2** or **5** based on our earlier work.[6] The respective transient five-membered-ring cyclic carbonyl ylides **3** or **6** could successfully be generated by nucleophilic attack of ring oxygen atom to electron deficient rhodium-carbenoid carbon atom present in intermediates **2** or **5** (Scheme 1).



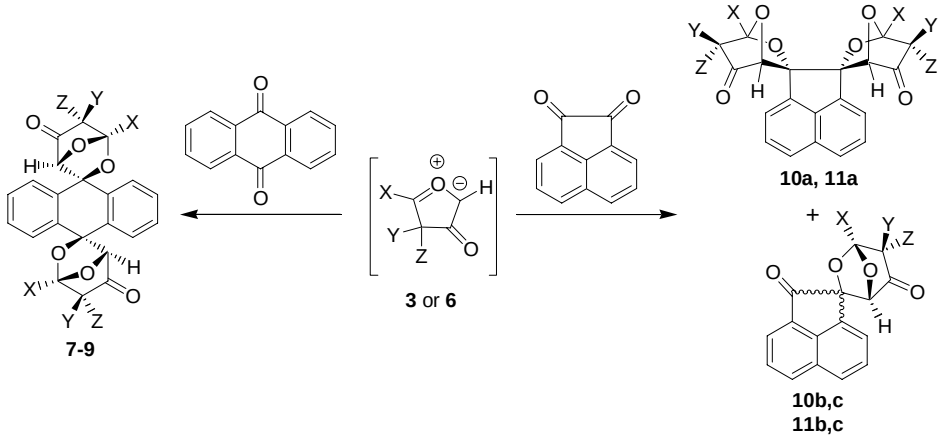
Scheme 1

Thus, the required starting materials of type **1** or **4** were prepared according to the literature procedure[6] and the tandem cyclization-cycloaddition reactions of the diazo ketones **1** or **4** with the keto-functional groups as heterodipolarophile have been investigated (Table 1).

Table 1. Generation of five-membered-ring cyclic carbonyl ylides **3** or **6** from α-diazo ketones **1** or **4**

Entry	α-diazo ketone	R^1	R^2	R^3	R^4
1	**1a** or **3a**	H	-	-	-
2	**1b** or **3b**	COOEt	-	-	-
3	**4a** or **6a**	-	CH_3	CH_3	H
4	**4b** or **6b**	-	CH_3	CH_3	COOEt
5	**4c** or **6c**	-	$-(CH_2)_2-$		H

Initially, we studied the reaction of cyclic diazo ketones **1** with the compound having two keto-groups placed in 1,4-fashion on a rigid cyclic system. For this purpose, an excess of cyclohexane fused diazo ketone **1a** was added to a dichloromethane solution containing anthraquinone and a catalytic amount of $Rh_2(OAc)_4$ under an argon atmosphere. The reaction afforded the symmetric bis-cycloadduct **7** in 60% yield (Scheme 2). The formation of bis-dioxabicyclo[2.2.1]heptanone ring system **7** in a chemospecific and diastereoselective manner was confirmed by spectral and crystallographic analyses. Similarly, the reaction of diazo ketone **4a** and cyclopropane fused acyclic diazo ketone **4c** with anthraquinone afforded the respective symmetric bis-cycloadducts **8** and **9**[16] in good yields (Scheme 2, Table 2) as a single isomer.



Scheme 2

Consequently, we chose acenaphthenequinone as another dipolarophile, where keto-groups are placed in 1,2-fashion to investigate the above reaction in the presence of excess diazo ketones

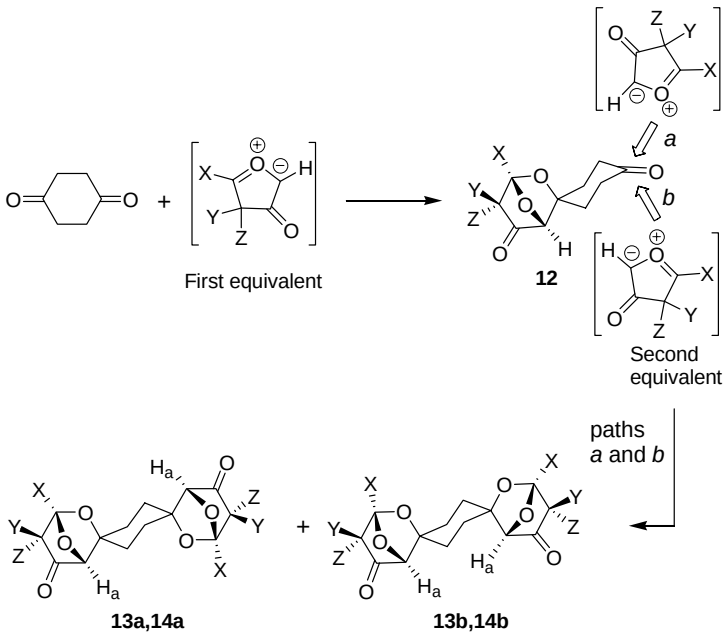
1a and **4a**. Thus, we performed the reaction of excess α-diazo ketone **1a** with acenaphthenequinone in the presence of $Rh_2(OAc)_4$ to furnish bis-dioxabicyclo[2.2.1]heptanone ring system **10a** as a minor isomer along with mono-dioxabicyclo[2.2.1]heptanone ring systems **10b,c** as a diastereomeric mixture. And the crude nmr spectrum showed the formation of products in the ratio of 1:1:1.5. Similarly, diazo ketone **4a** with acenaphthenequinone afforded bis-epoxy-bridged cycloadduct **11a** as a minor isomer along with mono-epoxy-bridged cycloadducts **11b,c** as a diastereomeric mixture and the crude nmr spectrum showed the formation of products in the ratio of 1:1:1.5. The bis-cycloadducts **10a** and **11a** were obtained only in poor (20 and 25%) yields even in the presence of excess diazo ketones. A reason for this may be due to steric hindrance arising from the proximity of an already installed dioxabicyclo[2.2.1]heptanone ring system.

Table 2. Reaction of carbonyl ylides **3** or **6** with anthraquinone and acenaphthenequinone

Entry	X	Y	Z	Product	Yield (%)[a]
1	$-(CH_2)_4-$		CH_3	**7**	60
2	CH_3	CH_3	CH_3	**8**	70
3	CH_3	$-(CH_2)_2-$		**9**	75[b]
4	$-(CH_2)_4-$		CH_3	**10a**	20[c]
5	CH_3	CH_3	CH_3	**11a**	25[c]

[a] Yields (unoptimized) refer to isolated and chromatographically pure compounds. [b] Ref.16. [c] Only the yield of bis-cycloadduct is provided.

After studying the tandem reaction of diazo ketones with 1,2- and 1,4-diketo functionalities placed on a rigid ring system, we extended the reaction of cyclic carbonyl ylides **3** and **6** with substrates having 1,4-diketo-functionalities on a flexible ring system. Thus, an excess of diazo ketone **1a** was reacted with 1,4-cyclohexanedione in the presence of a catalytic amount of $Rh_2(OAc)_4$ under an argon atmosphere. The crude reaction mixture was investigated by ^{1}H NMR spectroscopy, which indicated formation of the bis-dioxabicyclo[2.2.1]heptanone ring system as a mixture of diastereomers in the ratio of 1:3. These diastereomers were separated by column chromatography to afford products **13a** and **13b** in 45 and 17% yield, respectively (Scheme 3, Table 3). The IR spectrum of compound **13a** showed a band at 1763 cm^{-1} for the presence of a keto-functionality in a strained ring. The ^{1}H NMR spectrum of compound **13a** exhibited two singlets for both the bridgehead protons (H_a) at 4.23 and 4.21 ppm. Characteristically, ^{13}C NMR spectrum of the product **13a** showed a single resonance at 87.2, 214.1 ppm for the bridgehead[17] (C-H_a) and the carbonyl (C=O) carbons, respectively. Further, the single crystal X-ray crystallographic analysis[18] of compound **13a** (Figure 1) clearly revealed that the stereochemistry of the interesting bis-cycloadduct **13a** has the *trans*-geometry on cyclohexane ring system. Based on the interrelated spectroscopic analyses, the minor isomer was tentatively assigned as bis-cycloadduct **13b** with *cis*-geometry.



Scheme 3

Table 3. Reaction of carbonyl ylides **3a** or **6a** with 1,4-cyclohexanedione

Entry	X	Y	Z	Product	Yield[a] %	Stereochemistry on cyclohexane ring
1	-$(CH_2)_4$–		CH_3	**13a**	45	*trans*
				13b	17	*cis*
2	CH_3	CH_3	CH_3	**14a**	23	*trans*
				14b	45	*cis*

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

It is apparent that two consecutive 1,3-dipolar cycloaddition reactions took place with carbonyl groups of 1,4-cyclohexanedione rather than at the carbonyl groups present on dioxabicyclo[2.2.1]heptane ring system of the initially formed dioxabicyclo[2.2.1]heptane ring system of the mono-cycloadduct **12** to eventually yield the bis-cycloadducts **13a,b** in a chemospecific manner. After the first cycloaddition, the keto-group present on the cyclohexane ring of product **12** (obtained via mono-cycloaddition of carbonyl ylide **3a**) constitutes a platform, which led to two possible reaction pathways as shown in Scheme 3. *Route a* shows that the reaction of the carbonyl ylide dipole via equatorial addition to the keto-group of compound **12** leads to the *trans* isomer **13a**. The alternative pathway, *route b*, indicates reaction of the carbonyl ylide dipole via axial addition to the keto-group of compound **12** to furnish the *cis*-isomer **13b**.

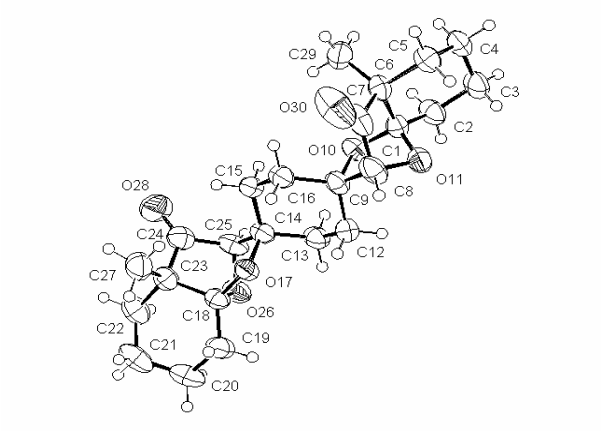


Figure 1. ORTEP diagram of compound **13a**.

A similar reaction was performed with diazo ketone **4a** to afford products **14a,b** in 23 and 45% yield, respectively. The spectroscopic analyses revealed that the products **14a,b** were derived from the double cycloaddition of carbonyl ylides to the carbonyl groups of 1,4-cyclohexanedione as a diastereomeric mixture in the ratio of 1:2. The stereochemistry of product **14b** is unequivocally confirmed as the *cis*-geometry on cyclohexane ring system based on the single-crystal X-ray analysis[19] (Figure 2). The stereochemistry of compound **14a** is tentatively assigned as the *trans*-geometry based on the interrelated spectral analysis. Interestingly, we did not observe any other cycloadducts arising from the carbonyl groups present in the oxa-norboranane ring system.

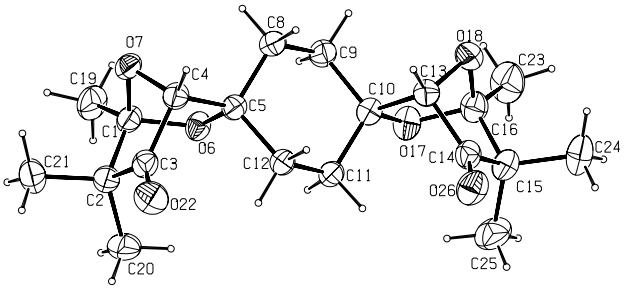


Figure 2. ORTEP diagram of compound **14b**.

The *trans*- and *cis*-isomers were predominant, when the diazo ketones **1a** and **4a** employed, respectively (Table 3). A reason for this may be due to the preference of approach of the respective carbonyl ylide intermediates **3a** and **6a** (path *a* and *b*, Scheme 3). This interesting observation encouraged us to further investigate to achieve a single isomer. To this end, we planned to replace H_a in products **13** and **14** by an ethyl ester group. Thus, reaction was

conducted between 1,4-diketocyclohexane and diazo ketone **1b**. Interestingly, this reaction afforded bis-cycloadduct **16a** as a single isomer in good yield (Scheme 4, Table 4). Single-crystal X-ray crystallographic analysis[20] of bis-cycloadduct **16a** confirmed its *trans*-geometry. Similarly, the reaction of diazo ketone **4b** having ester functionality also furnished compound **17a** as a single isomer and its stereochemistry is also assigned the *trans*-geometry based on the spectral similarities to **16a**.

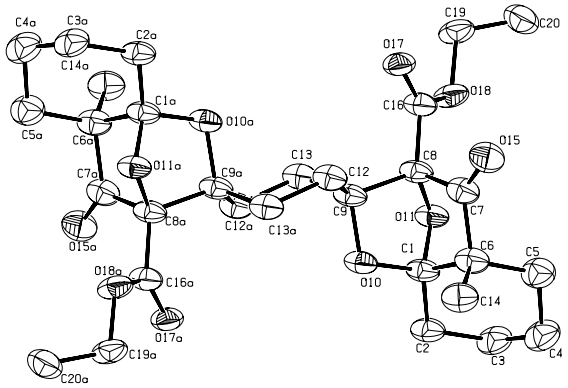
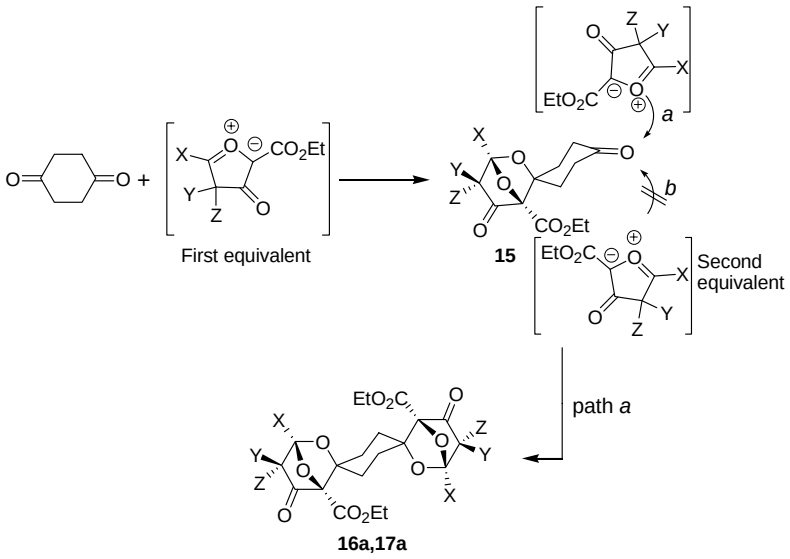


Figure 3. ORTEP diagram of compound **16a**.



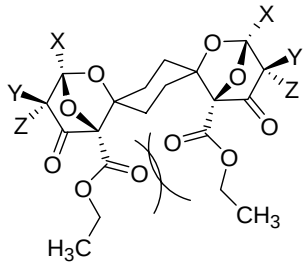
Scheme 4

Table 4. Reaction of carbonyl ylides **3b** or **6b** with 1,4-cyclohexanedione

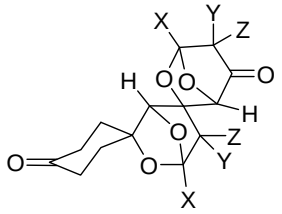
Entry	X	Y	Z	Product	Yield (%)[a]
1	$-(CH_2)_4-$		CH_3	**16a**	75
2	CH_3	CH_3	CH_3	**17a**	78

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

The formation of the alternative *cis*-isomers of type **16b** and **17b** (Figure 4) have been ruled out in the above reactions (Scheme 4) because of the prevailing steric hindrance when the ester substituent present in compound **15** completely restricts the axial approach of carbonyl ylide dipole. Thus, multiple tandem reactions of diazo ketones **1b** and **4b** having the ester substituent afforded the bis-cycloadducts **16a** and **17a** in good yield via equatorial addition of carbonyl ylide dipole with high stereoselectivity and chemospecificity. Essentially, in all the above reactions, there was no formation of such 2:1 or 3:1 cycloadducts such as compound **18** (Figure 4) even in the presence of an excess amount of diazo ketone.



16b,17b, Presence of steric interaction



18, Possible 2:1 cycloadduct

Figure 4

In conclusion, tandem reactions of diazo ketones were demonstrated on examples having 1,2- and 1,4-diketo-functionalities placed on rigid as well as flexible frameworks. The transient five-membered-ring carbonyl ylides generated from α-diazo ketones underwent 1,3-dipolar cycloaddition reactions with keto-functionality to afford various bis-dioxabicyclo[2.2.1]heptanone ring systems in a chemospecific and diastereoselective manner. In this process, construction of many stereocenters and up to 6 chemical bonds is attained in a single synthetic operation.

Experimental Section

General Procedures. The melting points are uncorrected. The FT-IR spectra were recorded using KBr method unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were (200 MHz and 50.3 MHz, respectively) referenced to TMS. Carbon types were determined from DEPT ^{13}C NMR experiments. Mass analyses were performed with an ionizing voltage of 70 eV or FD^{+} method unless otherwise stated. All reactions were carried out under an argon atmosphere and glasswares were dried in an oven before using for catalytic diazo decomposition reaction. Care has been taken to avoid light during the course of catalytic decomposition of α-diazo ketones. Dry benzene or dichloromethane has been used as solvent for α-diazo ketone decomposition reaction. Analytical thin layer chromatography (TLC) was performed on alumina plates and components were visualized by observation under iodine and UV-Light. Column

chromatography was performed on a silica gel (100-200 mesh) column unless otherwise stated. Benzene was dried over sodium.

Typical procedure. Method A. To an oven-dried flask, a solution containing the appropriate carbonyl compound (1 mmol) and 0.5 mol% of rhodium(II) acetate dimer in 15 mL of dry dichloromethane (dried over phosphorous pentoxide) was degassed using argon. To this reaction mixture, a solution of appropriate α-diazo ketone **1** (R^1=H) or **4** (R^4=H) (3 mmol) in dry dichloromethane was added very slowly over a period of 1 h. The progress of the reaction was monitored by TLC. The solvent was removed under reduced pressure and the resulting residue purified using silica gel column chromatography (hexane/EtOAc) unless otherwise stated to afford the respective bis-cycloadducts.

Method B. Reactions utilizing α-diazo ketones **1b** and **4b** were performed in dry benzene (dried over sodium) at reflux. The procedure was further followed as described above. All new compounds exhibited spectral data consistent with their structures.

Compound 7. A mixture of anthraquinone (200 mg, 1.0 mmol) and α-diazo ketone **1a** (520 mg, 3 mmol) was allowed to react in the presence of 5.0 mg (1.0 mol %) of $Rh_2(OAc)_4$ in dry DCM (20 mL) for 4 h to afford **7** based on method A. Yield: 341 mg (60%); Orange color solid. mp 214-216 °C (chloroform/hexane). IR (KBr): 2937, 1765, 1456, 1375, 1310, 1044, 996, 764 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.72 (d, *J* = 6.7 Hz, 2H, arom-*H*), 7.61 (d, *J* = 7.5 Hz, 2H, arom-*H*), 7.32-7.26 (m, 4H, arom-*H*), 4.72 (s, 2H, OC*H*), 2.54-2.45 (m, 2H), 2.18-1.55 (m, 14H), 1.48 (s, 6H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 211.2 (*C*=O), 140.4 (*quat*-C), 133.4 (*quat*-C), 128.1 (=*C*H), 127.8 (=*C*H), 126.7 (=*C*H), 126.1 (=*C*H), 114.6 (*quat*-C), 88.5 (O*C*H), 84.5 (*quat*-C), 54.8 (*quat*-C), 33.5 (*C*H_2), 26.7 (*C*H_2), 23.5 (*C*H_2), 20.3 (*C*H_2), 15.1 (*C*H_3). MS (EI, 70 eV), *m/z* 512 (M^+, 0.3), 361 (3), 304 (0.6), 152 (28), 123 (100), 95 (22), 28 (8%). Anal. Calcd for $C_{32}H_{32}O_6$: requires C, 74.98; H, 6.29%. Found: C, 75.15; H, 6.32%.

Compound 8. A mixture of anthraquinone (200 mg, 1.0 mmol) and α-diazo ketone **4a** (440 mg, 3 mmol) was allowed to react in the presence of 5.0 mg (1.0 mol %) of $Rh_2(OAc)_4$ in dry DCM (20 mL) for 4 h to afford **8** based on method A. Yield: 361 mg (70%); Orange color solid. mp 202-204 °C (chloroform/hexane). IR (KBr): 2972, 1767, 1457, 1398, 1304, 1126, 1009, 987, 850, 764 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.70 (d, *J* = 7.1 Hz, 2H, arom-*H*), 7.62 (d, *J* = 7.1 Hz, 2H, arom-*H*), 7.37-7.22 (m, 4H, arom-*H*), 4.65 (s, 2H, OC*H*), 1.92 (s, 6H, CH_3), 1.44 (s, 6H, CH_3), 1.16 (s, 6H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 211.7 (*C*=O), 140.4 (*quat*-C), 133.5 (*quat*-C), 128.2 (=*C*H), 127.9 (=*C*H), 126.9 (=*C*H), 126.1 (=*C*H), 115.4 (*quat*-C), 88.5 (O*C*H), 84.4 (*quat*-C), 55.5 (*quat*-C), 23.5 (*C*H_3), 17.6 (*C*H_3), 15.0 (*C*H_3). MS (FAB), *m/z* 483.2 (M^+, Na) (5), 335 (13), 259 (10), 239 (12), 127 (100), 57 (90%). Anal. Calcd for $C_{28}H_{28}O_6$: requires C, 73.03; H, 6.13%. Found: C, 73.13; H, 6.18%.

Compounds 10a-c. A mixture of acenaphthenequinone (250 mg, 1.3 mmol) and α-diazo ketone **1a** (1.0 g, 6 mmol) was allowed to react in the presence of 5.0 mg (1.0 mol %) of $Rh_2(OAc)_4$ in dry dichloromethane (20 mL) for 3 h to afford bis-cycloadduct **10a** along with mono-cycloadducts **10b** and **10c** in the ratio of 1:1:1.5 based on method A, the pure adducts were

isolated using alumina column chromatography (hexane/EtOAc). Compound **10a**: Yield 133.0 mg (20%); Colorless solid; mp. 207-209 °C (chloroform/hexane); IR (KBr) 2936, 1765, 1463, 1443, 1376, 1100, 1025, 983, 872, 778 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H, arom-*H*), 7.60 (t, *J* = 7.3 Hz, 2H, arom-*H*), 7.26 (d, *J* = 7.1 Hz, 2H, arom-*H*), 4.76 (s, 2H, OC*H*), 2.61-2.56 (m, 2H), 1.96-1.58 (m, 14H), 1.56 (s, 6H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 211.8 (*C*=O), 134.8 (*quat*-C), 130.4 (*quat*-C), 128.1 (*quat*-C), 127.6 (=*C*H), 125.8 (=*C*H), 122.0 (=*C*H), 113.3 (*quat*-C), 91.9 (*quat*-C), 84.7 (O*C*H), 54.2 (*quat*-C), 31.9 (*C*H_2), 25.7 (*C*H_2), 22.9 (*C*H_2), 19.9 (*C*H_2), 14.6 (*C*H_3). MS (FD^+): *m/z* = 486 [M^+]. Anal. Calcd for $C_{30}H_{30}O_6$: requires C, 74.06; H, 6.21%. Found: C, 73.80; H, 6.18%. Compound **10b**: Yield: 206 mg (31%); Colorless solid; mp 223-225 °C (chloroform/hexane); IR (KBr) 2939, 1771, 1728, 1604, 1433l, 1374, 1269, 1044, 1002, 984, 779 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 1H, arom-*H*), 7.94 (d, *J* = 7.0 Hz, 2H, arom-*H*), 7.80 (d, *J* = 7.0 Hz, 1H, arom-*H*), 7.74-7.64 (m, 2H, arom-*H*), 4.58 (s, 1H, OC*H*), 2.27-2.14 (m, 1H), 2.07-1.66 (m, 7H), 1.54 (s, 3H, CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 210.1 (*C*=O), 199.3 (*C*=O), 141.4 (*quat*-*C*), 137.9 *(quat*-*C*), 132.6 (=*C*H), 131.4 (*quat*-*C*), 130.7 (*quat*-*C*), 129.4 (=*C*H), 128.7 (=*C*H), 126.4 (=*C*H), 122.5 (=*C*H), 121.7 (=*C*H), 115.3 (*quat*-*C*), 87.6 (O*C*H), 85.9 (*quat*-*C*), 53.9 (*quat*-*C*), 32.7 (*C*H_2), 27.3 (*C*H_2), 23.7 (*C*H_2), 20.4 (*C*H_2), 15.4 (*C*H_3). MS (FD^+): *m/z* = 334 [M^+]. Anal. Calcd for $C_{21}H_{18}O_4$: requires C, 75.43; H, 5.43%. Found: C, 75.65; H, 5.50%. Compound **10c**: Yield: 127 mg (19%); Colorless solid; mp 186-188 °C (chloroform/hexane); IR (KBr) 2949, 1762, 1722, 1600, 1436, 1374, 1267, 1048, 1006, 913, 788 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.1 Hz, 1H, arom-*H*), 8.01-7.90 (m, 2H, arom-*H*), 7.79-7.40 (m, 2H, arom-*H*), 7.38 (d, *J* = 6.7 Hz, 1H, arom-*H*), 4.73 (s, 1H, OC*H*), 2.45-2.39 (m, 1H), 2.04-1.56 (m, 7H), 1.51 (s, 3H, CH_3); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 210.2 (*C*=O), 199.4 (*C*=O), 142.3 (*quat*-*C*), 132.4 (=*C*H), 132.2 (*quat*-*C*), 130.8 (*quat*-*C*), 129.7 (*quat*-*C*), 128.8 (=*C*H), 128.7 (=*C*H), 126.8 (=*C*H), 123.0 (=*C*H), 122.9 (=*C*H), 115.1 (*quat*-*C*), 87.2 (O*C*H), 86.0 (*quat*-*C*), 55.0 (*quat*-*C*), 32.1 (*C*H_2), 26.7 (*C*H_2), 23.4 (*C*H_2), 20.3 (*C*H_2), 15.2 (*C*H_3). MS (FD^+): *m/z* = 334 [M^+]. Anal. Calcd for $C_{21}H_{18}O_4$: requires C, 75.43; H, 5.43%. Found: C, 75.80; H, 5.34%.

Compounds 11a-c. A mixture of acenaphthenequinone (250 mg, 1.3 mmol) and α-diazo ketone **4a** (0.8 g, 5 mmol) was allowed to react in the presence of 5.0 mg (1.0 mol %) of $Rh_2(OAc)_4$ in dry dichloromethane (20 mL) for 3 h based on method A to afford bis-cycloadduct **11a** along with mono-cycloadducts **11b** and **11c** in the ratio of 1:1:1.5. The pure adducts were isolated using alumina column chromatography (hexane/EtOAc). Compound **11a**: Yield 150.0 mg (25%); Colorless solid; mp. 218-220 °C (chloroform/hexane); IR (KBr) 2971, 1767, 1466, 1394, 1269, 1129, 1041, 1005, 984, 854, 779 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H, arom-*H*), 7.49 (t, *J* = 7.9 Hz, 2H, arom-*H*), 7.15 (d, *J* = 7.1 Hz, 2H, arom-*H*), 4.67 (s, 2H, OC*H*), 1.78 (s, 6H, CH_3), 1.49 (s, 6H, CH_3), 1.22 (s, 6H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 212.9 (*C*=O), 136.7 (*quat*-C), 135.4 (*quat*-C), 131.0 (*quat*-C), 128.2 (=*C*H), 126.4 (=*C*H), 122.6 (=*C*H), 115.0 (*quat*-C), 92.4 (*quat*-C), 85.3 (O*C*H), 55.5 (*quat*-C), 22.9 (*C*H_3), 18.7 (*C*H_3), 14.4 (*C*H_3). MS (EI, 70 eV), *m/z* 434 (M^+, 3.0), 414 (2), 395 (5), 368 (56), 322 (18), 238 (80), 220 (50), 165 (100), 97 (24%). Anal. Calcd for $C_{26}H_{26}O_6$: requires C, 71.87; H, 6.03%. Found: C,

72.07; H, 6.09%. Compound **11b**: Yield: 214 mg (36%); Colourless solid, m.p. 215-217 °C (Chloroform/hexane, Lit[8] m.p. 215-217 °C); IR (KBr) 1762, 1735, 1398, 1269, 1133, 991 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.03 (1H, d, *J* = 8.1 Hz, arom-*H*), 7.92 (1H, d, *J* = 7.0 Hz, arom-*H*), 7.83 (1H, d, *J* = 8.1 Hz, arom-*H*), 7.70-7.52 (2H, m, arom-*H*), 7.28 (1H, d, *J* = 7.0 Hz, arom-*H*), 4.67 (1H, s, OC*H*), 1.79 (3H, s, CH_3), 1.44 (3H, s, CH_3), 1.23 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 210.8 (*C*=O), 199.5 (*C*=O), 142.4 (*quat*-C), 132.6 (=*C*H), 132.3 (*quat*-C), 131.0 (*quat*-C), 129.9 (*quat*-C), 129.0 (=*C*H), 128.9 (=*C*H), 127.0 (=*C*H), 123.1 (=*C*H), 123.0 (=*C*H), 116.2 (*quat*-C), 86.0 (O*C*H), 83.7 (*quat*-C), 55.9 (*quat*-C), 22.5 (*C*H_3), 18.7 (*C*H_3), 15.2 (*C*H_3). Compound **11c**: Yield: 143 mg (24%); Colourless solid, m.p. 133-135 °C (chloroform/hexane, Lit[8] m.p. 133-135 °C); IR (KBr) 1769, 1731, 1435, 1272, 1134, 989 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.17 (1H, d, *J* = 8.0 Hz, arom-*H*), 7.96 (1H, d, *J* = 8.0 Hz, arom-*H*), 7.86-7.68 (4H, m, arom-*H*), 4.58 (1H, s, OC*H*), 1.82 (3H, s, CH_3), 1.57 (3H, s, CH_3), 1.30 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 210.5 (*C*=O), 199.4 (*C*=O), 141.6 (*quat*-C), 138.2 (*quat*-C), 132.9 (=*C*H), 131.6 (*quat*-C), 131.0 (*quat*-C), 129.7 (=*C*H), 128.9 (=*C*H), 126.7 (=*C*H), 122.7 (=*C*H), 122.0 (=*C*H), 116.5 (*quat*-C), 87.5 (O*C*H), 86.1 (*quat*-C), 54.7 (*quat*-C), 22.7 (*C*H_3), 18.8 (*C*H_3), 15.7 (*C*H_3).

Compounds 13a and 13b. A mixture of cyclohexa-1,4-dione (200 mg, 1.8 mmol) and α-diazo ketone **1a** (1.3 g, 7 mmol) was allowed to react in the presence of 5.0 mg (1.0 mol %) of $Rh_2(OAc)_4$ in dry dichloromethane (20 mL) for 3 h and the procedure followed by method A to afford compounds **13a** and **13b** as a mixture of diastereomers in the ratio of 1:3. The pure diastereomers were separated using alumina column chromatography (hexane/EtOAc). Compound **13a**: Yield: 334 mg (45%); Colorless solid; mp 226-228 °C (chloroform/hexane); IR (KBr) 2932, 1763, 1450, 1376, 1286, 1104, 1028, 957, 867 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.23 (s, 1H, OC*H*), 4.21 (s, 1H, OC*H*), 2.04-1.38 (m, 24H), 1.07 (s, 3H, CH_3), 1.05 (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 214.1 (*C*=O), 113.0 (*quat*-*C*), 87.2 (O*C*H), 80.2 (*quat*-*C*), 53.3 (*quat*-*C*), 32.2 (*C*H_2), 31.9 (*C*H_2), 31.4 (*C*H_2), 30.3 (*C*H_2), 29.0 (*C*H_2), 28.1 (*C*H_2), 23.6 (*C*H_2), 20.7 (*C*H_2), 15.3 (*C*H_3). MS (EI) (%): *m/z* 416 (M^+, 30), 388 (8), 329 (10), 277 (12), 263 (11), 198 (22), 153 (29), 123 (25), 112 (63), 83 (62), 69 (39), 55 (100). Anal. Calcd for $C_{24}H_{32}O_6$: requires C, 69.21; H, 7.74. Found: C, 69.35; H, 7.69%. Compound **13b**: Yield: 126 mg (17%); Colorless solid; mp 203-205 °C (chloroform/hexane); IR (KBr) 2940, 1763, 1448, 1374, 1288, 1227, 1102, 1027, 981, 867 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.28 (s, 2H, OC*H*), 1.95-1.41 (m, 24H), 1.07 (s, 3H, CH_3), 1.06 (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 214.4 (*C*=O), 214.1 (*C*=O), 112.8 (*quat*-*C*), 85.7 (*quat*-*C*), 80.3 (*quat*-*C*), 53.3 (*quat*-*C*), 32.5 (*C*H_2), 32.2 (*C*H_2), 31.8 (*C*H_2), 30.3 (*C*H_2), 29.2 (*C*H_2), 27.9 (*C*H_2), 23.5 (*C*H_2), 20.6 (*C*H_2), 15.3 (*C*H_3). MS (EI) (%): *m/z* 416 (M^+, 45), 388 (5), 329 (10), 277 (12), 263 (20), 198 (14), 153 (28), 123 (35), 112 (62), 83 (63), 69 (39), 55 (100). Anal. Calcd for $C_{24}H_{32}O_6$: requires C, 69.21; H, 7.74. Found: C, 69.38; H, 7.78%.

Compounds 14a and 14b. A mixture of cyclohexa-1,4-dione (200 mg, 1.8 mmol) and α-diazo ketone **4a** (1.1 g, 7 mmol) was allowed to react in the presence of 5.0 mg (1.0 mol %) of $Rh_2(OAc)_4$ in dry dichloromethane (20 mL) for 3 h and the procedure followed by method A to afford products **14a** and **14b** as a diastereomeric mixture in the ratio of 1:2. The pure isomers

were separated using alumina column chromatography (hexane/EtOAc). Compound **14a**: Yield: 150 mg (23%); Colorless solid; mp 228-230 °C (chloroform/hexane); IR (KBr) 2966, 1766, 1440, 1396, 1269, 1127, 997, 855 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.18 (s, 1H, OC*H*), 4.17 (s, 1H, OC*H*), 1.78-1.68 (m, 6H), 1.49 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.44-1.35 (m, 2H), 1.06 (s, 6H, CH_3), 1.04 (s, 3H, CH_3), 1.02 (s, 3H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 214.6 (*C*=O), 114.1 (*quat*-*C*), 86.9 (O*C*H), 80.0 (*quat*-*C*), 54.0 (*quat*-*C*), 32.1 (*C*H_2), 31.2 (*C*H_2), 28.8 (*C*H_2), 27.8 (*C*H_2), 21.9 (*C*H_3), 18.6 (*C*H_3), 16.1 (*C*H_3). MS (EI) *m/z* (%): 364 (M^+, 22), 304 (18), 276 (10), 219 (8), 192 (20), 177 (25), 97 (23), 70 (41), 43 (100). Anal. Calcd for $C_{20}H_{28}O_6$: requires C, 65.91; H, 7.74. Found: C, 66.08; H, 7.79%. Compound **14b**: Yield: 292 mg (45%); Colorless solid; mp 181-183 °C (chloroform/hexane); IR (KBr) 2971, 1764, 1444, 1395, 1268, 1134, 994, 855 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.25 (s, 1H, OC*H*), 4.24 (s, 1H, OC*H*), 1.92-1.53 (m, 8H), 1.49 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.06 (s, 6H, CH_3), 1.03 (s, 6H, CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 214.8 (*C*=O), 214.6 (*C*=O), 113.9 (*quat*-*C*), 85.5 (O*C*H), 80.2 (*quat*-*C*), 54.0 (*quat*-*C*), 32.5 (*C*H_2), 32.2 (*C*H_2), 29.6 (*C*H_2), 29.1 (*C*H_2), 21.9 (*C*H_3), 18.5 (*C*H_3), 16.0 (*C*H_3); MS (EI) *m/z* (%): 364 (M^+, 7), 304 (52), 276 (33), 261 (11), 216 (14), 192 (54), 191 (43), 188 (21), 177 (100), 174 (60), 122 (45), 93 (15), 70 (70), 57 (13); Anal. Calcd for $C_{20}H_{28}O_6$: requires C, 65.91; H, 7.74. Found: C, 66.15; H, 7.72%.

Compound 16a. A mixture of cyclohexa-1,4-dione (150 mg, 1.3 mmol) and α-diazo ketone **1b** (1 g, 3 mmol) was allowed to react in the presence of 5.0 mg (1.0 mol %) of $Rh_2(OAc)_4$ in dry benzene (20 mL) for 8 h reflux based on method B to afford compound **16a**. Yield: 563 mg Yield: (75%); Colorless solid. mp 146-148 °C (chloroform/hexane). IR (KBr): 2941, 1778, 1751, 1449, 1380, 1322, 1303, 1174, 1133, 1082, 1048, 982 760 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 4.44-4.25 (m, 4H, OCH_2), 2.04-1.94 (m, 4H), 1.73-1.48 (m, 20H), 1.37 (t, *J* = 7.0 Hz, 6H, CH_3), 1.12 (s, 6H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 207.7 (*C*=O), 207.5 (*C*=O), 163.7 (COO), 110.8 (*quat*-C), 110.0 (*quat*-C), 93.4 (*quat*-C), 92.8 (*quat*-C), 82.0 (*quat*-C), 81.8 (*quat*-C), 62.7 (O*C*H_2), 62.5 (O*C*H_2), 53.5 (*quat*-C), 32.0 (*C*H_2), 30.0 (*C*H_2), 29.7 (*C*H_2), 28.9 (*C*H_2), 28.7 (*C*H_2), 27.9 (*C*H_2), 27.7 (*C*H_2), 23.1 (*C*H_2), 20.4 (*C*H_2), 15.5 (*C*H_3), 14.6 (*C*H_3). MS (EI, 70 eV), *m/z* 560 (M^+,6), 514 (3), 336 (9), 226 (15), 225 (82), 224 (16), 202 (23), 151 (34), 139 (15), 123 (41), 112 (40), 111 (46), 83 (97), 55 (100%). Anal. Calcd for $C_{30}H_{40}O_{10}$: requires C, 64.27; H, 7.19%. Found: C, 64.10; 7.23%.

Compound 17a. A mixture of cyclohexa-1,4-dione (150 mg, 1.3 mmol) and α-diazo ketone **4b** (900 mg, 3 mmol) was allowed to react in the presence of 5.0 mg (1.0 mol %) of $Rh_2(OAc)_4$ in dry benzene (20 mL) for 8 h reflux based on method B to afford compound **17a**. Yield: 530 mg Yield: (78%); Colorless solid. mp 102-104 °C (chloroform/hexane). IR (KBr): 2984, 1780, 1746, 1468, 1399, 1376, 1332, 1268, 1120, 1061, 739 cm^{-1}.^1H NMR (200 MHz, $CDCl_3$): δ 4.44-4.25 (m, 4H, OCH_2), 2.07-2.04 (m, 2H), 1.81-1.66 (m, 6H), 1.51 (s, 6H, CH_3), 1.37 (t, *J* = 7.7 Hz, 6H, CH_3), 1.11 (s, 6H, CH_3), 1.09 (s, 6H, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 208.3 (*C*=O), 208.0 (*C*=O), 163.9 (COO), 163.7 (COO), 112.2 (*quat*-C), 111.4 (*quat*-C), 92.7 (*quat*-C), 82.1 (*quat*-C), 63.0 (O*C*H_2), 62.9 (O*C*H_2), 54.4 (*quat*-C), 30.1 (*C*H_2), 29.9 (*C*H_2), 28.9 (*C*H_2), 28.7 (*C*H_2), 22.1 (*C*H_3), 18.8 (*C*H_3), 16.1 (*C*H_3), 14.8 (*C*H_3). MS (EI, 70 eV), *m/z* 508 (M^+,6), 448 (19), 402

(12), 251 (15), 250 (41), 199 (100), 153 (14), 97 (30), 70 (86), 57 (40%). Anal. Calcd for $C_{26}H_{36}O_{10}$: requires C, 61.40; H, 7.14%. Found: C, 61.51; 7.19%.

Supplementary information

Crystallographic data for **13a**,**14b,16a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-253358 - 253360. Copies of the data can be obtained free of charge on application to 12, Union Road, Cambridge CB2 1EZ, UK. (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. Tables of atomic coordinates, bond lengths and bond angles of bis-dioxabicyclo[2.2.1]heptanone derivatives **13a**,**14b,16a** are provided.

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18. Crystal data for compound **13a**: Colorless rectangular. $C_{24}H_{32}O_6$, M = 416.50, 0.42 × 0.18 × 0.06 mm^3, monoclinic, space group 21/c with a = 13.546(4) Å, b = 8.249(3) Å, c = 19.564(6) Å, V = 2146.1(12) Å^3, T = 293(2) K, R_1 = 0.0570, wR_2 = 0.1257 on observed data, z = 4, D_{calcd} = 1.289 g cm^{-3}, F(000) = 896, Absorption coefficient = 0.092 mm^{-1}, λ = 0.71073 Å, 15789 reflections were collected on a smart apex CCD single crystal diffractometer, 4213 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole = 0.211 and -0.151e Å^{-3}, respectively. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL–97 software.
19. Crystal data for compound **14b**: Colorless rectangular. $C_{20}H_{28}O_6$, M = 364.42, 0.34 × 0.22 × 0.18 mm^3, monoclinic, space group 21/c with a = 14.2634(10) Å, b = 11.3716(8) Å, c = 11.7879(8) Å, V = 1898.6(2) Å^3, T = 273(2) K, R_1 = 0.0458, wR_2 = 0.1211 on observed data, z = 4, D_{calcd} = 1.275 g cm^{-3}, F(000) = 784, Absorption coefficient = 0.093 mm^{-1}, λ = 0.71073 Å, 11196 reflections were collected on a smart apex ccd single crystal CCD diffractometer,

4393 observed reflections ($I \geq 2\sigma$ (I)). The largest difference peak and hole = 0.301 and -0.191e Å^{-3}, respectively. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL–97 software.

20. Crystal data for compound **16a**: Colorless rectangular. $C_{30}H_{40}O_{10}$, M = 560.62, 0.30 × 0.10 × 0.06 mm^3, monoclinic, space group 21/c with a = 12.028(2) Å, b = 7.3281(14) Å, c = 16.693(3) Å, V = 1447.1(5) Å^3, T = 293(2) K, R_1 = 0.0555, wR_2 = 0.1597 on observed data, z = 4, D_{calcd} = 1.287 g cm^{-3}, F(000) = 600, Absorption coefficient = 0.096 mm^{-1}, λ = 0.71073 Å, 8509 reflections were collected on a smart apex ccd single crystal CCD diffractometer, 3360 observed reflections ($I \geq 2\sigma$ (I)). The largest difference peak and hole = 0.363 and -0.285e Å^{-3}, respectively. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL–97 software.