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Rhodium generated carbonyl ylides with *p*-quinones: synthesis of oxa-bridged polycyclic systems

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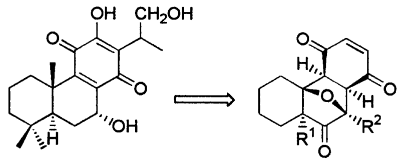
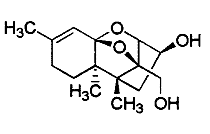
Abstract—A series of α-diazo carbonyl compounds tethered to substituted cyclopentanone and cyclohexanone units with different tether lengths have been synthesized using diazomethane solution or methanesulphonyl azide. The above synthesized α-diazo carbonyl compounds with rhodium(II) acetate dimer furnish cyclic five- or six-membered-ring carbonyl ylide dipoles, which undergo facile 1,3-dipolar cycloaddition with *p*-quinones to furnish various novel oxa-bridged polycyclic systems **10**, **13** and **11**, **14** as C═C and C═O addition products of *p*-quinones. Very interesting unusual cyclization product, tri-oxapolycyclic compounds **12** and **15** were also obtained. Single-crystal X-ray analyses of **11a**, **12d** and **14a** are reported to firmly establish the structure and stereochemistry of the oxa-bridged polycyclic systems. The molecules **11a** and **14a** exhibit novel C–H···O hydrogen bonding motif in the crystal structure. On the other hand, the molecule **12d** revealed both O–H···O and C–H···O motifs in the solid-state architecture. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The tandem cyclization–cycloaddition chemistry of rhodium carbenoids has been developed as a general approach[1] to oxa-bridged ring systems. 1,3-Dipolar cycloaddition offers a versatile route[2] for the construction of a variety of complex five-membered heterocycles that are synthetically useful compounds. The carbonyl ylide 1,3-dipolar cycloaddition reactions have been applied to the synthesis of variety of natural products such as illudin[3] (sesquiterpene), phorbol esters[4] (diterpene), vindoline[5] (alkaloid) and brevicomin[6] (pheromone).



1 **10**



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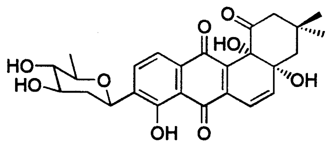
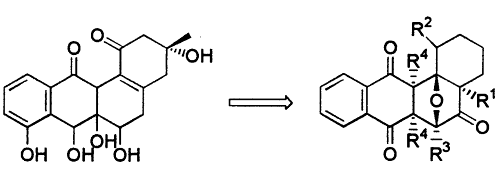
Moreover, the oxa-tetracyclic compounds having benzoquinone skeleton **10** are potential intermediates and can be applied in the synthesis of diterpenoids like abietane quinones[7] such as **1**. Dioxa-bridged ring systems are present in the natural molecules like brevicomin,[6] amberketal,[8] zaragozic acid A[9] and oxygenated sesquiterpenes like sambucinol[10] **2**. The angularly condensed tetracyclic skeleton **13** are important intermediates and can be utilized in the synthesis of angucycline[11] antibiotics which obtained recently much attention due to their wide range of biological activity and their interesting chemical structures especially aquayamycin **3a** and elmycin A **3b**.



3a



3b **13**

As a consequence of our interest in the synthesis of new oxa-polycyclic systems,[12] we became aware that the only one recent report[13] available on the dipolar cycloaddition of carbonyl ylides with *p*-quinones. As an approach to oxygenated sesquiterpenoids and angucycline antibiotics, starting from cycloalkanoic acids **5**, we herein report our

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Keywords: benzoquinone; carbonyl ylides; dipolar cycloaddition; diazo compounds; naphthoquinones; rhodium acetate catalyst.

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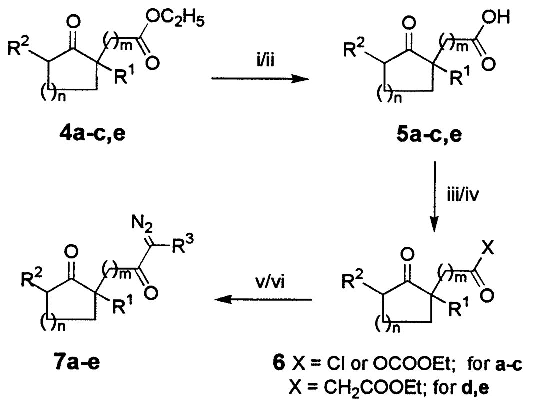


Substrate	n	m	R¹	R²	R³
a	2	0	CH_3	H	H
b	1	0	CH_3	H	H
c	2	1	H	H	H
d	2	0	CH_3	H	COOEt
e	2	1	H	CH_3	COOEt

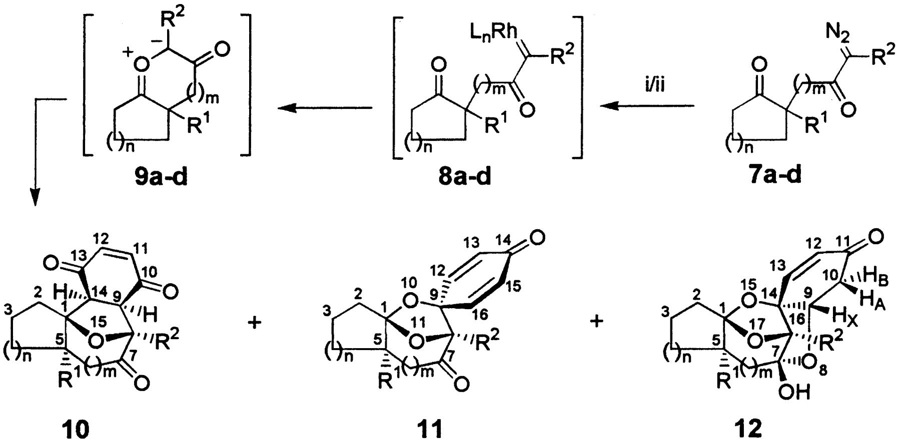
Scheme 1. Reagents for substrates **a**–**c**: (i) 5% aq. KOH, rt; (iii) $(COCl)_2$, Ether or ClCOOEt, NEt_3, Ether; (v) CH_2N_2, Ether; reagents for substrate **d**,**e**: (ii) 5% aq. KOH, rt; (iv) (a) $(COCl)_2$, Ether; (b) *i*-PrMgBr, $EtOOCCH_2COOH$, DCM–THF (1:5); (vi) MsN_3, NEt_3, DCM.

detailed studies on the reaction of various carbonyl ylides with *p*-quinones as bifunctional dipolarophiles towards the synthesis of complex and valuable oxa-bridged polycyclic systems in a tandem manner.

2. Results and discussion

It was envisaged that the reaction of diazo ketones such as **7** with rhodium(II) acetate dimer, can generate metallo-carbenoid **8** based on our earlier[12] work. The highly electrophilic carbenoid center[1] present in **8** can be attacked by the lone pair of electrons on the ring carbonyl oxygen to form five- or six-membered-ring carbonyl ylides **9**. For investigating the intramolecular formation and intermolecular cycloaddition of the carbonyl ylides **9** in tandem fashion with *p*-quinones as dipolarophile, the requisite starting materials **7** were prepared from commercially available materials.

Mild hydrolysis of 2-carbethoxy-2-methyl cyclohexanone (**4a**) was carried out to afford 1-methyl-2-oxocyclohexanecarboxylic acid **5a**. Treatment of **5a** with oxalyl chloride at room temperature afforded the corresponding acid chloride **6a**, which on reaction with freshly prepared ethereal diazomethane containing triethylamine at 0°C furnished the α-diazo ketone **7a** in 92% yield as a thick yellow oil (Scheme 1). The same sequence of reactions on 2-carbethoxy-2-methyl cyclopentanone (**4b**) furnished α-diazo ketone **7b** in good yield. Treatment of 2-(2-oxocyclohexane)acetic acid (**5c**) with ethyl chloroformate and triethylamine resulted in a white suspension at room temperature and the formed mixed anhydride **6c** was then treated with freshly prepared ethereal diazomethane at 0–10°C furnished α-diazo ketone **7c**. The reaction of 1-methyl-2-oxocyclohexanecarboxylic acid (**5a**) with oxalyl chloride furnished the corresponding acid chloride, which on reaction[14] with excess Mg-complex of dianion of monoethyl malonate in a mixture of DCM–THF (1:5) afforded the active methylene compound **6d**. The diazo



Substrate	n	m	R¹	R²	Product Yield[a](%)		
					10	11	12
a	2	0	CH_3	H	6	18	35
b	1	0	CH_3	H	5	15	29
c	2	1	H	H	5	15	25
d	2	0	CH_3	COOEt	4	17	27

[a]Yields (unoptimised) refer to isolated and chromatographically pure compounds of **10**,**11** and **12**.

Scheme 2. Reagents for substrates **a**–**c**: (i) $Rh_2(OAc)_4$, *p*-benzoquinone, DCM or C_6H_6, rt; reagents for substrate **d**: (ii) $Rh_2(OAc)_4$, *p*-benzoquinone, C_6H_6, reflux.

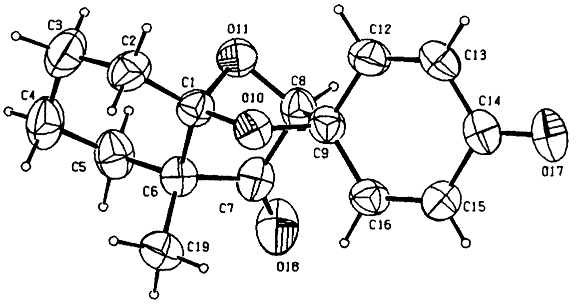


Figure 1. ORTEP view of spiro dioxa-tricyclic compound **11a**.

transfer reaction[15] of the above substrate **6d** was carried out using mesyl azide–triethylamine to give the corresponding diazo compound **7d**. Similar to compound **7d**, the reactions were carried out to obtain diazo compound **7e** from ethyl 3-methyl-2-oxocyclohexanoneacetate (**4e**) (Scheme 1). The characteristic absorption in FT-IR spectra around 2100 cm^{-1} and a singlet resonance in ^{1}H NMR spectra around δ 5.3 in compounds **7a–e** confirm the presence of diazo functionality. All these diazo compounds were stable for chromatographic purification and spectroscopic characterization purposes.

Initially, we investigated the Rh(II) catalyzed behavior of above synthesized α-diazo ketones **7** with *p*-benzoquinone as a dipolarophile. The reaction of α-diazo ketone **7a** and an excess amount of *p*-benzoquinone with 1 mol% Rh$_2$(OAc)$_4$ catalyst in dry benzene was carried out under an argon atmosphere at room temperature for 8 h followed by neutral alumina column chromatographic purification of the crude reaction mixture afforded three products **10a**, **11a** and **12a** (Scheme 2). These products were characterized from their interrelated spectral data including single-crystal X-ray analysis as novel oxa-bridged polycyclic compounds in 59% overall yield.

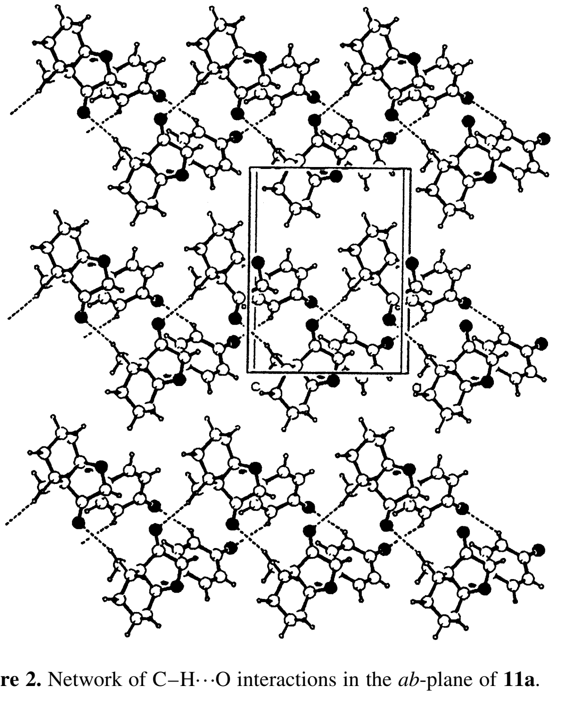


Figure 2. Network of C–H···O interactions in the *ab*-plane of **11a**.

The FT-IR spectrum of compound **10a** exhibited characteristic peaks at 1763 and 1677 cm^{-1} indicating carbonyl group in oxa-bridged and benzoquinone ring systems, respectively. The ^{1}H NMR spectrum of product **10a** exhibited a characteristic singlet resonance at δ 1.17, 4.80 for the methyl and bridgehead (H8) proton, two doublets at δ 3.10 and 3.18 due to adjacent H9 and H14 protons, two doublets at δ 6.78 and 6.84 for quinone ring protons (H11, H12) and a multiplet around δ 1.20–1.85 due to four methylene groups. ^{13}C NMR and dept-135 spectra of product **10a** showed peaks for one sp^3 carbon, four sp^2 carbons, four sp carbons and five quaternary carbons that confirmed the proposed structure **10a**. In the structure **10a**, sp^2 carbons C11 and C12 of benzoquinone ring appeared as a single peak in ^{13}C spectrum. Typically, on the basis of the lack of coupling between the bridgehead (H8) proton and H9 proton clearly indicates the *exo*-stereochemistry for the product **10a**.

The FT-IR spectrum of compound **11a** exhibited characteristic peaks at 1762 and 1673 cm^{-1} indicating carbonyl group in dioxa-bridged and benzoquinone ring system, respectively. The ^{1}H NMR spectrum of product **11a** exhibited a characteristic singlet resonance at δ 1.24, 4.50 for the methyl and bridgehead (H8) proton, a multiplet around δ 1.30–2.08 for four methylene groups and four double doublets at δ 6.25, 6.32, 6.50, 6.87 due to quinone ring protons. The ^{13}C NMR and dept-135 spectra of product **11a** showed peaks for one sp^3 carbon, four sp^2 carbons, five sp carbons and five quaternary carbons that confirmed the proposed structure **11a**.

The FT-IR spectrum of compound **12a** exhibited characteristic peaks at 3326 and 1662 cm^{-1} indicating the presence of hydroxy group and carbonyl group of benzoquinone ring system, respectively. The ^{1}H NMR spectrum of product **12a** exhibited a characteristic singlet resonance at δ 1.04, 2.93, 4.70 for the methyl, hydroxy and bridgehead (H16) proton, doublets at δ 6.06, 6.56 for olefin protons. Three double doublets for H9 (labeled as H$_X$) and two H10 protons (labeled as H$_A$ and H$_B$) of compound **12a** (Scheme 2) indicate ABX pattern of a conformationally locked six-membered ring with three different coupling constants (*J*) of 16.1, 11.5 and 6.8 Hz. Based on an axial and an equatorial coupling constant analysis, these double doublets were characterized for the proton H$_A$ at δ 2.53, H$_B$ at δ 3.10 and H$_X$ at δ 4.42. The presence of hydroxy group at δ 2.93 was further confirmed by deuterium exchange studies. The ^{13}C NMR spectrum of product **12a** showed peaks for one sp^3 carbon, five sp^2 carbons, four sp carbons and five quaternary carbons that confirmed the proposed structure **12a**.

The stereochemical assignments of the methyl group at the ring juncture, spiro dioxa-tricyclic and trioxa-pentacyclic ring system of the products were unambiguously established by single-crystal X-ray analyses of product **11a** (Fig. 1) and **12d** (Fig. 3). In compound **11a**, the observed angle of oxa-bridge (C1–O11–C8) is 96.03°. The presence of methyl group at the ring juncture (C6) in compound **11a**, *endo* with respect to oxido bridge (C1–O11–C8) and the same stereochemistry is tentatively assigned for other products based on their similarity in spectral data. Packing

Table 1. Hydrogen-bonding geometry in **11a**, **12d** and **14a**

Substrate	*D*–H···*A*	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A* (deg)
11a	C15–H15···O17	2.557	3.207	133.6
11a	C19–H193···O18	2.547	3.519	164.9
12d	O19–H19···O22	2.036	2.872	152.5
12d	C24–H242···O20	2.574	3.552	157.6
14a	C8–H8···O22	2.240	3.269	150.0

arrangement of compound **11a** (Fig. 2) clearly shows that molecules are self-assembled by novel C–H···O type[16] hydrogen bonding (Table 1). Each molecule has got two donors (namely C15 and C19) and two acceptors (namely O17 and O18). Molecules are assembled by C–H···O hydrogen bonding as zigzag polymeric chain propagating along *a*-axis and such polymeric chains are packed along *b*-axis.

The formation of trioxa-pentacyclic system was explicitly confirmed by single-crystal X-ray analysis of compound **12d**. In compound **12d**, the observed angle of oxa-bridge (C1–O17–C16) is 96.6° (Fig. 3). The angles of oxygen atoms O8 and O15 which were located in five-membered rings in the angle of 110.4 and 106.4°. Similar to compound **11a**, the methyl group at the ring juncture (C6) in compound **12d**, *endo* with respect to oxido bridge (C1–O17–C16). Interestingly, the solid-state structure of compound **12d** (Fig. 4) is mainly governed by two types of hydrogen bonding interactions (Table 1), namely O–H···O and C–H···O. In this compound, the hydroxy group (O19) and the ester methylene group (C24) act as donor and the ester carbonyl oxygen (O22) and the benzoquinone ring carbonyl oxygen (O20) act as acceptor. Such interactions held molecules as a linear polymeric chain along *a*-axis and such polymeric chains are packed along *b*-axis.

In order to generalize, the Rh(II) catalyzed behavior of various diazo compounds **7b**,**d** and **7c** were also studied (Scheme 2) to form respective five- and six-membered-ring carbonyl ylides which further undergoes 1,3-dipolar cycloaddition in the presence of an excess *p*-benzoquinone to furnish the oxa-tetracyclic systems **10**, spiro dioxa-tricyclic systems **11** and trioxa-pentacyclic systems **12** as C=C, C=O and C=O bond addition followed by cyclization product, respectively.

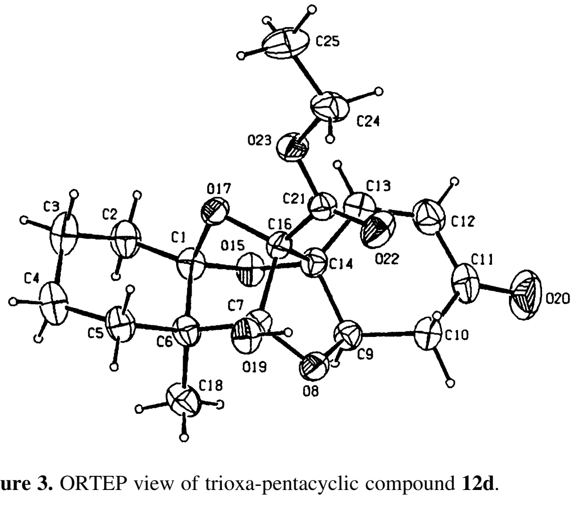


Figure 3. ORTEP view of trioxa-pentacyclic compound **12d**.

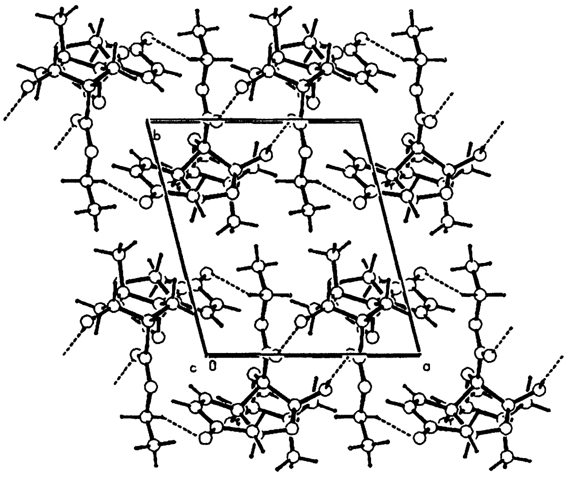
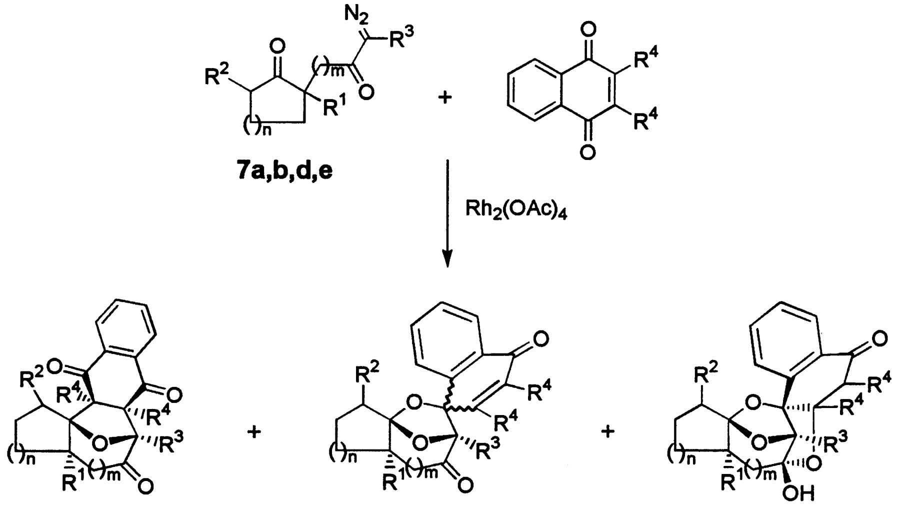


Figure 4. Network of O–H···O and C–H···O interactions in the *ab*-plane of **12d**.

After obtaining various new oxa-bridged compounds using *p*-benzoquinone, we extended the investigation of Rh(II) catalyzed behavior of the tandem cyclization–cycloaddition sequence of α-diazo carbonyl compounds **7** with various 1,4-naphthoquinones as dipolarophiles. The reaction of α-diazo ketone **7a** and an excess amount of 1,4-naphthoquinone with 1 mol% of $Rh_2(OAc)_4$ catalyst in dry benzene was carried out under an argon atmosphere at room temperature for 9 h followed by neutral alumina column chromatographic purification of the crude reaction mixture afforded three products **13a**, **14a** and **15a** (Scheme 3). These products were characterized based on their interrelated spectral data, which showed similar trend exhibited by *p*-benzoquinone reactions. The reaction of α-diazo compounds **7b**, **7d** and **7e** with naphthoquinone as well as 2,3-dichloro-1,4-naphthoquinone was carried out under similar experimental conditions afforded the corresponding cycloadducts as described above. The product **13** forms an important skeleton of angucycline antibiotics **3a** and **3b**, which we constructed by 1,3-dipolar cycloaddition methodology instead of usual Diels–Alder reaction[17] approach. In contrast to the previous observation,[13] the reaction of carbonyl ylide with 1,4-naphthoquinone which provided only C=C cycloadduct; we could also observe a considerable amount of interesting C=O cycloadducts **14** which were well characterized including single-crystal X-ray analysis (Fig. 5). Moreover, we could get major amount of novel C=O cycloadducts (**14b** and **14e**) in comparison with C=C cycloadducts when we used 2,3-dichloro-1,4-naphthoquinone as a dipolarophile. We could not observe the interesting tri-oxa hexacyclic compound type **15** when chloro substituent is present over the double bond of naphthoquinone.

The formation of C=O addition product of 1,4-naphthoquinone was unequivocally established by single-crystal X-ray analysis of product **14a** (Fig. 5). In compound **14a**, the observed angle of oxa-bridge (C1–O11–C8) is 96.32° (Fig. 5). Similar to benzoquinone cycloadducts; the methyl group at the ring juncture (C6) in compound **14a**, *endo* with respect to oxido bridge (C1–O11–C8). The solid-state structure of compound **14a** viewed down *c*-axis (Fig. 6) and is mainly governed by only C–H···O type hydrogen



13 14 15

Diazo compound	Products 13-15	n	m	R^1	R^2	R^3	R^4	Product Yield[a](%)		
								13	14	15
7a	a	2	0	CH_3	H	H	H	33	14	7
7a	b	2	0	CH_3	H	H	Cl	4	30	-
7b	c	1	0	CH_3	H	H	H	24	8	5
7d	d	2	0	CH_3	H	COOEt	H	25	5	8
7e	e	2	1	H	CH_3	COOEt	Cl	5	40	-

[a]Yields (unoptimised) refer to isolated and chromatographically pure compounds of **13**,**14** and **15**.

Scheme 3.

bonding interaction (Table 1). In this compound, the bridgehead sp carbon (C8) act as donor and the carbonyl oxygen (O22) present in the dioxa-bridged ring system act as an acceptor. The molecules are arranged in layers along *b*-axis, with strong C–H···O interactions between the adjacent layers to create two-dimensional sheet like architecture in *ab*-plane.

Typically the quantity of the catalyst was maintained at 1 mol% for performing all our experiments. Identical results were obtained with all diazo carbonyl compounds **7a**–**d** in the cycloaddition of *p*-benzoquinone, irrespective of the substituent, the formation of five- or six-membered-ring carbonyl ylides from the α-diazo carbonyl compounds. The products **10**, **11** and **12** were obtained in the range of 1:3:6 ratio in almost all reactions, clearly indicates the preference for C=O than C=C cycloadduct in the case of *p*-benzoquinone as a dipolarophile. The ^{1}H NMR spectra showed ABX pattern for H8 and two H9 protons of compound **12b** but the same could not be observed in compounds **12c** and **12d**. The *exo*-stereochemistry was assigned to compounds **10** and **13** on the basis of a lack of coupling between the bridgehead hydrogens.

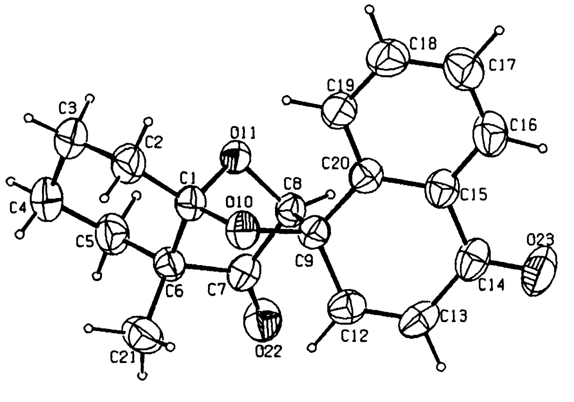


Figure 5. ORTEP view of spirodioxa-pentacyclic compound **14a**.

The formation of products **10** and **11** can conveniently be explained as C=C and C=O addition products of *p*-benzoquinone with the carbonyl ylide dipole **9**. The formation of the product **12** and **15** may be explained from the further reaction of a water molecule with already formed C=O addition product **11** and **14** under the experimental conditions. Moreover, we have not isolated any C–H insertion product[18] during the course of this reaction. Padwa[19] has studied the reactions of carbonyl ylides with benzaldehydes and other aldehydes as dipolarophiles, which afforded the corresponding dioxa-bicyclic systems. The dipolar cycloaddition of the six-membered carbonyl ylide to the *o*-quinone system was reported[20] to afford the product via cycloaddition of carbonyl ylide with C=O group of *o*-quinone. Also it is very interesting to note that the reactions of carbonyl ylides with α,β-unsaturated ketones like arylidenetetralones,[12b] chemoselectively lead to spiro dioxa-ring systems as the only C=O addition product.

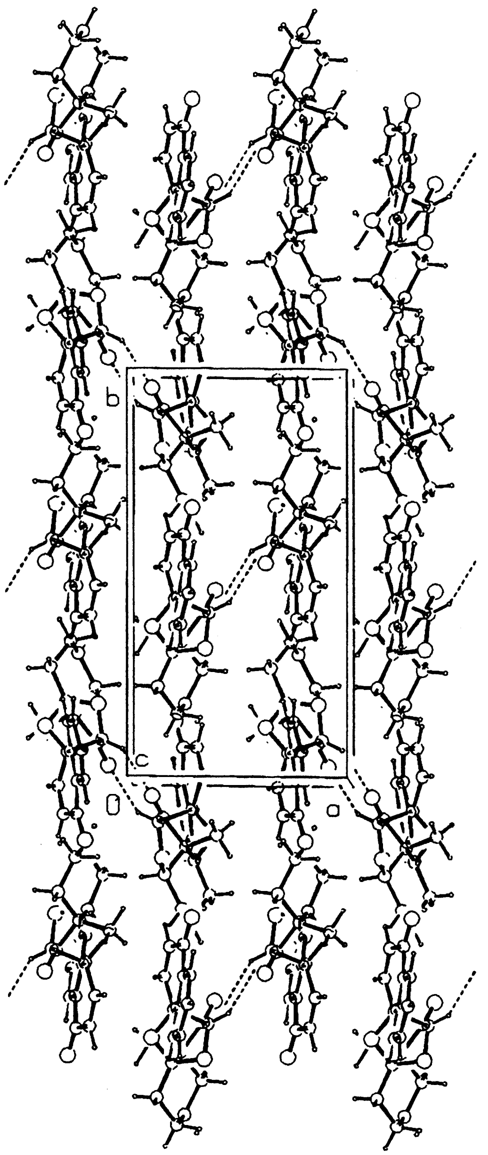


Figure 6. Network of C–H···O interaction in the *ab*-plane of **14a**.

But cyclic α,β-unsaturated ketones, a route to pterosin family of sesquiterpenes afforded[2] only cycloadduct with electron deficient C=C not C=O bond. It is well known[21] that Diels–Alder cycloaddition reactions lead to specifically C=C cycloadditions of *p*-quinones. 1,3-Dipolar cycloaddition reactions of isomunchnone dipoles to 1,4-naphthoquinone resulted[22] only C=C addition products. The dipolar cycloaddition of five-membered carbonyl ylides with *p*-benzoquinones appeared[13] very recently where five-membered carbonyl ylides produced both C=C and C=O addition products of *p*-benzoquinone and the product ratio is mainly the solvent and catalyst dependent. We have made an interesting observation in this work; the dipolar cycloaddition of various carbonyl ylides **9** to *p*-benzoquinone and 2,3-dichloro-1,4-naphthoquinone produced more of C=O cycloadduct than the electron deficient C=C cycloadduct; in the case of 1,4-naphthoquinone major amount of C=C cycloadduct obtained in addition to C=O cycloadduct. It is worth noting, both the C=C and C=O bonds of *p*-quinones show dipolarophilic activity towards five- as well as six-membered-ring carbonyl ylides, lead to various oxa-polycyclic systems.

In conclusion, we have demonstrated the formation of five- and six-membered-ring carbonyl ylides and the subsequent [3+2]-cycloaddition with *p*-quinones furnished the C=C, C=O addition products and followed by very interesting cyclization of C=O addition product in tandem fashion which were characterized as novel oxa-polycyclic systems. Single-crystal X-ray analyses described the interesting network involving both C–H···O and O–H···O hydrogen bonding interactions observed in the solid-state structure of oxa-bridged polycyclic systems. This tandem cyclization–cycloaddition method provides ready access to complex functionalized oxa-bridged carbon networks as intermediates for the synthesis of naturally existing molecules in a single step operation.

3. Experimental

Melting points are uncorrected. IR spectra were recorded on a Perkin–Elmer Spectrum GX FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 200 (200 and 50.3 MHz, respectively) spectrometer and referenced to TMS. Carbon types were determined from DEPT ^{13}C NMR experiments. Mass analyses were performed on Finnigan MAT 8230 (with an ionizing voltage of 70 eV) and Jeol M Station 700 (FD$^+$ method in absolute dichloromethane) mass spectrometer. Elemental analyses were performed on a Perkin–Elmer Model 2400 analyzer. X-ray crystallographic analyses were carried out in an Enraf Nonius CAD-4 diffractometer with Mo·K$_\alpha$ radiation. All solvents were purified by distillation. Thin layer chromatography was performed on silica/alumina plates and components were visualized by observation under iodine or by sulphuric acid charring. Column chromatography was performed on neutral alumina. Care has been taken to avoid light during the course of reaction in the synthesis of diazo compounds and its further conversion.

3.1. General procedure[12a] for the synthesis of diazo ketones 7

3.1.1. For substrates 7a,b. Cycloalkanone ester **4** (12 mmol) was carefully hydrolyzed using 5% aqueous potassium hydroxide solution (20 mL) with stirring at room temperature. The reaction was monitored by TLC and continued until the disappearance of the starting material. The reaction mixture was extracted with ether (3×10 mL), acidified the aqueous layer (pH=5) and extracted with ether (3×15 mL). The organic phase was concentrated under reduced pressure at room temperature to obtain the corresponding keto acids **5**. Freshly distilled oxalyl chloride (20 mmol) was added dropwise to a stirring solution of the appropriate acid (10 mmol, **5a**,**b**) in dry ether (25 mL) at 25°C, and the stirring was continued for 2 h. The solution was evaporated under reduced pressure, the crude residual acid chloride was dissolved in freshly prepared dry ether (100 mL) and used for next step without further purification. The crude acid chloride solution was added dropwise over 0.5 h period to a stirring solution of freshly prepared diazomethane (13 mmol) and freshly distilled triethylamine (10 mmol) in dry ether (50 mL) at 0°C, and the stirring was continued for 2 h. The mixture was filtered and the filtrate evaporated. Chromatography of the residue through a short silica gel column (prewashed by ethyl acetate) led to the corresponding diazo ketone **7a**,**b** with 10% ethyl acetate–hexane elution.

3.1.2. For substrate 7c. To a solution containing 1 equiv. (10 mmol) of keto acid **5c** in freshly prepared dry ether (100 mL) was added 1.2 equiv. of freshly distilled ethyl chloroformate followed by the slow addition of 1.5 equiv. of dry triethylamine. The resulting mixture was stirred at room temperature for 45 min and the solid that formed was filtered under inert atmosphere. The filtrate was added to freshly prepared ethereal diazomethane solution (20 mmol) and then the mixture stirred for 12 h at 0°C, after this duration allowed to warm to 10°C for a period of 2 h under an argon atmosphere. The solvent was removed under reduced pressure and the residue purified as described above to obtain **7c**.

3.1.3. For substrate 7d and 7e. To a solution of freshly distilled monoethyl malonate (35 mmol) in dry dichloromethane (8 mL) was added dropwise a solution of isopropylmagnesium bromide (70 mmol) in tetrahydrofuran (50 mL) until propane has been evolved. The temperature rises to 40–50°C. The green-colored solution was then cooled in an ice/salt bath and crude appropriate acid chloride obtained from the corresponding acid **5a** and **5e** (14 mmol) in dichloromethane (2 mL) was added dropwise with efficient stirring. The stirring continued for 1 h, the cooling bath was removed and the resultant mixture poured into cold 10% hydrochloric acid (20 mL). After cessation of the carbon dioxide evolution the clear solution was extracted with ethyl acetate (3×20 mL), washed with saturated sodium bicarbonate (30 mL) and brine solution. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel to afford the corresponding active methylene compound **6d** and **6e**.

To a solution containing 1 equiv. of active methylene compound **6d**,**e** and 1.2 equiv. of freshly distilled methanesulphonyl azide in dry dichloromethane (5 mL) was added 2 equiv. of freshly distilled triethylamine under an argon atmosphere at room temperature. The reaction was monitored by TLC until the disappearance of starting material. The solvent was removed under reduced pressure at room temperature and the residue subjected to short neutral alumina column chromatography to get pure diazo ketone **7d**,**e** with 15% ethyl acetate–hexane elution.

3.2. General procedure for the rhodium(II) catalyzed cycloaddition reaction of α-diazo ketones 7 with *p*-quinones

Method A: In an oven-dried flask, a solution containing 1 equiv. of the appropriate diazo carbonyl compound (1.5 mmol) and 2 equiv. of *p*-quinone was taken in dry benzene (dried over sodium) or dichloromethane (dried over phosphorous pentoxide, 25 mL). To this reaction mixture was added 1 mol% of rhodium acetate dimer under an argon atmosphere at room temperature. The reaction mixture was allowed to stir and followed by TLC until the disappearance of the starting material. The solvent was removed under reduced pressure and the crude residue was purified by neutral alumina column afforded three products **10/13**, **11/14** and **12/15** with ethyl acetate–hexane elution in the range of 1:16/1:25, 1:8 and 1:1/1:3, respectively.

Method B: The procedure was followed as in method A using dry benzene as solvent and the reaction mixture was allowed to reflux under an argon atmosphere. The refluxing was continued till the disappearance of the starting material and purified by alumina column as described above.

3.2.1. Reaction of α-diazo ketone 7a with *p*-benzoquinone. A mixture of *p*-benzoquinone (300 mg, 2.8 mmol) and diazo ketone **7a** (250 mg, 1.4 mmol) was allowed to react with rhodium acetate dimer (6.1 mg) in benzene solution (10 mL) at room temperature under an argon atmosphere for 8 h according to the general method A to afford three products **10a**, **11a** and **12a** in 59% overall yield. **10a**: 22 mg (6%), thick oil; [Found: C, 69.25; H, 6.16. $C_{15}H_{16}O_4$ requires C, 69.22; H, 6.20%]; ν_{max} (neat) 2928, 2859, 1763, 1677, 1611, 1459, 1378, 1279, 1252, 996 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.84 (1H, d, *J*=10.4 Hz), 6.78 (1H, d, *J*=10.4 Hz), 4.80 (1H, s, H8), 3.18 (1H, d, *J*=8.4 Hz), 3.10 (1H, d, *J*=8.4 Hz), 1.85–1.20 (8H, m), 1.17 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 214.0 ($C{=}O$), 191.5 ($C{=}O$), 191.3 ($C{=}O$), 142.9 ($={C}H$), 92.6 (quat-C), 85.7 (OCH), 57.6 (quat-C), 52.0 (CH), 51.2 (CH) 30.9 (CH_2), 27.4 (CH_2), 22.6 (CH_2), 20.1 (CH_2), 16.5 (CH_3); *m*/*z* 260 (M^+, 39), 232 (34), 204 (32), 162 (86), 149 (64), 123 (49), 95 (46), 82 (58), 41 (100%). **11a**: 65 mg (18%), colorless solid, mp 147–149°C (chloroform–hexane); [Found: C, 69.18; H, 6.23. $C_{15}H_{16}O_4$ requires C, 69.22; H, 6.20%]; ν_{max} (KBr) 2945, 2866, 1762, 1673, 1633, 1377, 1095, 1048, 978 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.87 (1H, dd, *J*=10.2, 3.0 Hz), 6.50 (1H, dd, *J*=10.2, 3.0 Hz), 6.32 (1H, dd, *J*=10.2, 1.9 Hz), 6.25 (1H, dd, *J*=10.2, 1.9 Hz), 4.50 (1H, s, H8), 2.08–1.30 (8H, m), 1.24 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 211.5 ($C{=}O$), 184.5 ($C{=}O$), 147.2 ($={C}H$), 143.0 ($={C}H$), 132.7 ($={C}H$), 129.5 ($={C}H$), 115.8 (quat-C), 87.5 (OCH), 76.3 (quat-C), 54.8 (quat-C), 31.8 (CH_2), 27.5 (CH_2), 23.5 (CH_2), 20.2 (CH_2), 15.1 (CH_3); *m*/*z* 260 (M^+, 3), 167 (3), 149 (28), 123 (100), 95 (41), 81 (46), 55 (58%). **12a**: 135 mg (35%), colorless solid, mp 172–174°C (chloroform–hexane); [Found: C, 64.74; H, 6.52. $C_{15}H_{18}O_5$ requires C, 64.70; H, 6.49%]; ν_{max} (KBr) 3326, 2962, 2935, 1662, 1510, 1380, 1259, 1064, 1037, 987 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.56 (1H, d, *J*=10.2 Hz), 6.06 (1H, d, *J*=10.2 Hz), 4.70 (1H, s, H16), 4.42 (1H, dd, *J*=11.5, 6.8 Hz), 3.10 (1H, dd, *J*=16.1, 6.8 Hz), 2.93 (1H, s, O*H*), 2.53 (1H, dd, *J*=16.1, 11.5 Hz), 2.04–1.15 (8H, m), 1.04 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 196.3 ($C{=}O$), 146.5 ($={C}H$), 130.9 ($={C}H$), 113.6 (quat-C), 112.5 (quat-C), 87.7 (OCH), 84.4 (quat-C), 77.4 (OCH), 52.4 (quat-C), 45.7 (CH_2), 31.5 (CH_2), 26.8 (CH_2), 23.6 (CH_2), 21.6 (CH_2), 13.8 (CH_3); *m*/*z* 278 (M^+, 29), 151 (13), 123 (23), 112 (100), 111 (29), 95 (23), 83 (34%).

3.2.2. Reaction of α-diazo ketone 7b with *p*-benzoquinone. A mixture of *p*-benzoquinone (195 mg, 1.8 mmol) and diazo ketone **7b** (150 mg, 0.9 mmol) was allowed to react with rhodium acetate dimer (4.0 mg) at room temperature under an argon atmosphere in dry dichloromethane (10 mL) for 4.5 h according to the general method A to afford three products **10b**, **11b** and **12b** in 49% overall yield. **10b**: 11 mg (5%), thick oil; [Found: C, 68.36; H, 5.77. $C_{14}H_{14}O_4$ requires C, 68.28; H, 5.73%]; ν_{max} (neat) 2930, 2860, 1766, 1680, 1561, 1457, 1346, 1143, 1044, 997 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 6.90 (1H, d, *J*=10.4 Hz), 6.85 (1H, d, *J*=10.4 Hz), 4.76 (1H, s, H7), 3.17 (1H, d, *J*=8.4 Hz), 3.09 (1H, d, *J*=8.4 Hz), 2.34–2.00 (4H, m), 1.64–1.26 (2H, m), 1.19 (3H, s, C*H*$_3$); δ_C (50.3 MHz, CDCl$_3$) 211.8 (*C*=O), 189.1 (*C*=O), 189.0 (*C*=O), 143.3 (=*C*H), 143.2 (=*C*H), 102.2 (quat-C), 82.8 (O*C*H), 58.3 (quat-C), 51.8 (*C*H), 49.9 (*C*H), 33.7 (*C*H$_2$), 27.9 (*C*H$_2$), 23.0 (*C*H$_2$), 18.0 (*C*H$_3$); *m*/*z* 246 (M$^+$, 34), 218 (32), 148 (82), 95 (47), 55 (63), 41 (100%). **11b**: 33 mg (15%), colorless solid, mp 141–143°C (chloroform–hexane); [Found: C, 68.21; H, 5.69. $C_{14}H_{14}O_4$ requires C, 68.28; H, 5.73%]; ν_{max} (KBr) 2947, 2858, 1758, 1677, 1634, 1398, 1123, 1099, 1041, 996 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 6.83 (1H, dd, *J*=10.2, 3.0 Hz), 6.53 (1H, dd, *J*=10.2, 3.0 Hz), 6.34 (1H, dd, *J*=10.2, 1.9 Hz), 6.26 (1H, dd, *J*=10.2, 1.9 Hz), 4.51 (1H, s, H7), 2.34–1.85 (4H, m), 1.65–1.25 (2H, m) 1.13 (3H, s, C*H*$_3$); δ_C (50.3 MHz, CDCl$_3$) 211.7 (*C*=O), 184.6 (*C*=O), 147.0 (=*C*H), 143.0 (=*C*H), 132.8 (=*C*H), 129.9 (=*C*H), 115.6 (quat-C), 87.0 (O*C*H), 76.0 (quat-C), 58.3 (quat-C), 33.9 (*C*H$_2$), 27.8 (*C*H$_2$), 23.6 (*C*H$_2$), 18.9 (*C*H$_3$); *m*/*z* 246 (M$^+$). **12b**: 69 mg (29%), colorless solid, mp 180–182°C (chloroform–hexane); [Found: C, 63.62; H, 6.08. $C_{14}H_{16}O_5$ requires C, 63.63; H, 6.11%]; ν_{max} (KBr) 3434, 2961, 1685, 1561, 1458, 1340, 1142, 1061, 1001, 977 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 6.50 (1H, d, *J*=10.2 Hz), 6.04 (1H, d, *J*=10.2 Hz), 4.71 (1H, s, H15), 4.44 (1H, dd, *J*=11.6, 6.7 Hz), 3.20 (1H, s, O*H*), 3.12 (1H, dd, *J*=16.3, 6.7 Hz), 2.58 (1H, dd, *J*=16.3, 11.6 Hz), 2.40–1.78 (4H, m), 1.67–1.25 (2H, m), 1.07 (3H, s, C*H*$_3$); δ_C (50.3 MHz, CDCl$_3$) 197.0 (*C*=O), 146.7 (=*C*H), 131.1 (=*C*H), 113.3 (quat-C), 112.5 (quat-C), 87.6 (O*C*H), 84.9 (quat-C), 78.0 (O*C*H), 57.9 (quat-C), 46.0 (*C*H$_2$), 33.6 (*C*H$_2$), 27.0 (*C*H$_2$), 23.6 (*C*H$_2$), 18.6 (*C*H$_3$); *m*/*z* 264 (M$^+$, 26), 137 (13), 109 (27), 98 (100), 83 (33%).

3.2.3. Reaction of α-diazo ketone 7c with *p*-benzoquinone. A mixture of *p*-benzoquinone (220 mg, 2.0 mmol) and diazo ketone **7c** (180 mg, 1.0 mmol) was allowed to react with rhodium acetate dimer (4.4 mg) in dry dichloromethane (10 mL) at room temperature under an argon atmosphere for 2.5 h according to the general method A to afford three products **10c**, **11c** and **12c** in 45% overall yield. **10c**: 13 mg (5%), thick oil; [Found: C, 69.31; H, 6.26. $C_{15}H_{16}O_4$ requires C, 69.22; H, 6.20%]; ν_{max} (neat) 2930, 2910, 1731, 1675, 1611, 1460, 1270, 1253, 1035, 913 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 6.90 (1H, d, *J*=10.4 Hz), 6.85 (1H, d, *J*=10.4 Hz), 4.68 (1H, s, H9), 3.27 (1H, d, *J*=8.4 Hz), 3.20 (1H, d, *J*=8.4 Hz), 2.80–1.24 (11H, m); δ_C (50.3 MHz, CDCl$_3$) 202.7 (*C*=O), 193.0 (*C*=O), 192.9 (*C*=O), 143.0 (=*C*H), 142.8 (=*C*H), 92.7 (quat-C), 86.2 (O*C*H), 52.3 (*C*H), 51.3 (*C*H), 43.4 (*C*H), 41.6 (*C*H$_2$), 36.2 (*C*H$_2$), 31.1 (*C*H$_2$), 24.9 (*C*H$_2$), 23.8 (*C*H$_2$); *m*/*z* 260 (M$^+$, 29), 204 (31), 149 (61), 123 (47), 95 (43), 55 (62), 41 (100%). **11c**: 39 mg (15%), colorless solid, mp 145–147°C (chloroform–hexane); [Found: C, 69.30; H, 6.16. $C_{15}H_{16}O_4$ requires C, 69.22; H, 6.20%]; ν_{max} (KBr) 2938, 2861, 1730, 1675, 1634, 1396, 1174, 1083, 1051, 915 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 6.89 (1H, dd, *J*=10.2, 3.0 Hz), 6.52 (1H, dd, *J*=10.2, 3.0 Hz), 6.36 (1H, dd, *J*=10.2, 1.9 Hz), 6.24 (1H, dd, *J*=10.2, 1.9 Hz), 4.18 (1H, s, H9), 2.76–2.55 (1H, m), 2.20–1.14 (10 H, m); δ_C (50.3 MHz, CDCl$_3$) 201.2 (*C*=O), 184.5 (*C*=O), 147.7 (=*C*H), 141.1 (=*C*H), 133.3 (=*C*H), 128.6 (=*C*H), 111.6 (quat-C), 87.5 (quat-C), 86.9 (O*C*H), 43.2 (*C*H), 41.5 (*C*H$_2$), 35.7 (*C*H$_2$), 31.1 (*C*H$_2$), 24.9 (*C*H$_2$), 23.8 (*C*H$_2$); *m*/*z* 260 (M$^+$, 16), 243 (4), 162 (3), 152 (12), 151 (74), 139 (7), 133 (8), 95 (100%). **12c**: 70 mg (25%), colorless solid, mp 187–189°C (ethyl acetate-hexane); [Found: C, 64.74; H, 6.48. $C_{15}H_{18}O_5$ requires C, 64.74; H, 6.52 %]; ν_{max} (KBr) 3431, 2940, 2860, 1676, 1511, 1469, 1221, 919 cm^{-1}; δ_H (200 MHz, CDCl$_3$/DMSO-d$_6$) 8.75 (1H, s, O*H*), 6.62 (1H, d, *J*=10.2 Hz), 6.12 (1H, d, *J*=10.2 Hz), 4.87 (1H, s, H17), 4.78 (1H, t, *J*=8.0 Hz), 3.17–2.96 (2H, m), 2.76–1.24 (11H, m); δ_C (50.3 MHz, CDCl$_3$/DMSO-d$_6$) 200.7 (*C*=O), 149.3 (=*C*H), 133.5 (=*C*H), 112.3 (quat-C), 108.7 (quat-C), 87.9 (O*C*H), 86.4 (quat-C), 80.8 (O*C*H), 51.5 (*C*H), 47.3 (*C*H$_2$), 39.1 (*C*H$_2$), 35.1 (*C*H$_2$), 28.6 (*C*H$_2$), 27.1 (*C*H$_2$), 27.0 (*C*H$_2$); *m*/*z* 278 (M$^+$).

3.2.4. Reaction of α-diazo ketone 7d with *p*-benzoquinone. A mixture of *p*-benzoquinone (170 mg, 1.6 mmol) and diazo ketone **7d** (200 mg, 0.8 mmol) was allowed to react with rhodium acetate dimer (3.5 mg) in dry benzene (10 mL) for 3 h at reflux under an argon atmosphere according to the general method B to afford three products **10d**, **11d** and **12d** in 48% overall yield. **10d**: 11 mg (4%), colorless solid, mp 142–144°C (chloroform–hexane); [Found: C, 64.98; H, 6.03. $C_{18}H_{20}O_6$ requires C, 65.05; H, 6.07%]; ν_{max} (KBr) 2930, 2857, 1763, 1751, 1676, 1612, 1459, 1378, 1279, 1105, 1035 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 6.83 (1H, d, *J*=10.4 Hz), 6.78 (1H, d, *J*=10.4 Hz), 4.24 (2H, q, *J*=7.2 Hz, OC*H*$_2$), 3.15 (1H, d, *J*=8.4 Hz), 3.07 (1H, d, *J*=8.4 Hz), 2.20–1.22 (8H, m), 1.17 (3H, t, *J*=7.2 Hz, CH$_2$C*H*$_3$), 1.13 (3H, s, C*H*$_3$); δ_C (50.3 MHz, CDCl$_3$) 206.0 (*C*=O), 194.8 (*C*=O), 194.6 (*C*=O), 172.5 (*C*OO), 142.8 (=*C*H), 142.6 (=*C*H), 93.0 (quat-C), 89.9 (quat-C), 62.9 (O*C*H$_2$), 55.3 (quat-C), 52.3 (*C*H), 52.0 (*C*H), 31.9 (*C*H$_2$), 27.4 (*C*H$_2$), 23.2 (*C*H$_2$), 20.1 (*C*H$_2$), 15.8 (*C*H$_3$), 14.3 (*C*H$_3$); *m*/*z* 332 (M$^+$, 16), 304 (34), 190 (87), 177 (66), 149 (46), 41 (100%). **11d**: 45 mg (17%), colorless solid, mp 153–155°C (chloroform–hexane); [Found: C, 65.11; H, 6.09. $C_{18}H_{20}O_6$ requires C, 65.05; H, 6.07%]; ν_{max} (KBr) 2393, 2870, 1775, 1751, 1674, 1635, 1382, 1303, 1141, 1099, 1107, 990 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 6.78 (1H, dd, *J*=10.2, 3.0 Hz), 6.53 (1H, dd, *J*=10.2, 3.0 Hz), 6.36 (1H, dd, *J*=10.2, 1.9 Hz), 6.27 (1H, dd, *J*=10.2, 1.9 Hz), 4.23 (2H, q, *J*=7.2 Hz, OC*H*$_2$), 2.14–1.24 (8H, m), 1.30 (3H, s, C*H*$_3$), 1.18 (3H, t, *J*=7.2 Hz, CH$_2$C*H*$_3$); δ_C (50.3 MHz, CDCl$_3$) 205.8 (*C*=O), 184.5 (*C*=O), 175.0 (*C*OO), 144.4 (=*C*H), 142.5 (=*C*H), 132.7 (=*C*H), 131.0 (=*C*H), 114.0 (quat-C), 93.9 (quat-C), 82.5 (quat-C), 63.0 (O*C*H$_2$) 55.2 (quat-C), 32.0 (*C*H$_2$), 27.4 (*C*H$_2$), 23.2 (*C*H$_2$), 20.1 (*C*H$_2$), 15.3 (*C*H$_3$), 14.3 (*C*H$_3$); *m*/*z* 332 (M$^+$, 3), 224 (43), 206 (59), 178 (8), 123 (100), 95 (16%). **12d**: 75 mg (27%), colorless solid, mp 174–176 °C (chloroform–hexane); [Found: C, 61.69; H, 6.28. $C_{18}H_{22}O_7$ requires C, 61.71; H, 6.33%]; ν_{max} (KBr) 3438, 2970, 1704, 1685, 1373, 1339, 1253, 1152, 1108, 1056, 1029 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 6.47 (1H, d, *J*=10.2 Hz), 6.08 (1H, d, *J*=10.2 Hz), 4.51 (1H, dd, *J*=10.2, 8.2 Hz), 4.35 (2H, q, *J*=7.2 Hz, *OCH*$_2$), 3.70 (1H, s, O*H*), 3.25–2.90 (2H, m), 2.20–1.35

(8H, m), 1.31(3H, t, J=7.2 Hz, CH_2CH_3), 1.09 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 196.3 (C=O), 166.4 (COO), 142.9 (=CH), 132.5 (=CH), 112.4 (quat-C), 112.1 (quat-C), 92.3 (quat-C), 85.8 (quat-C), 77.0 (OCH), 63.1 (OCH_2), 52.6 (quat-C), 43.3 (CH_2), 31.4 (CH_2), 26.6 (CH_2), 23.4 (CH_2), 21.3 (CH_2), 14.6 (CH_3), 13.8 (CH_3); m/z 350 (M^+, 9), 295 (3), 249 (5), 195 (7), 157 (15), 139 (25), 121 (100), 83 (12), 65 (16%).

3.2.5. Reaction of α-diazo ketone 7a with 1,4-naphthoquinone. A mixture of 1,4-naphthoquinone (320 mg, 2.0 mmol) and diazo ketone **7a** (180 mg, 1.0 mmol) was allowed to react with rhodium acetate dimer (4.4 mg) in dry benzene (10 mL) for 9 h at room temperature under an argon atmosphere according to the general method A to afford three products **13a**, **14a** and **15a** in 54% overall yield. **13a**: 102 mg (33%), colorless solid, mp 141–143°C (chloroform–hexane); [Found: C, 73.51; H, 5.89, $C_{19}H_{18}O_4$ requires C, 73.53; H, 5.85%]; ν_{max} (KBr) 2936, 2864, 1755, 1682, 1591, 1457, 1301, 1269, 1246, 1170, 996 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.06–8.00 (2H, m, Arom-H), 7.79–7.75 (2H, m, Arom-H), 4.87 (1H, s, OCH), 3.32 (1H, d, J=8.4 Hz), 3.24 (1H, d, J=8.4 Hz), 2.00–1.30 (8H, m), 1.23 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 214.4 (C=O), 195.0 (C=O), 194.1 (C=O), 136.7 (quat-C), 136.2 (quat-C), 135.2 (=CH), 134.9 (=CH), 127.5 (=CH), 127.1 (=CH), 92.9 (quat-C), 86.4 (OCH), 53.0 (CH), 52.3 (CH), 52.2 (quat-C), 30.9 (CH_2), 27.2 (CH_2), 22.6 (CH_2), 20.1 (CH_2), 16.7 (CH_3); m/z 310 (M^+, 84), 281 (100), 263 (87), 253 (70), 212 (28), 199 (26), 172 (37), 148 (27), 134 (78), 133 (97%). **14a**: 43 mg (14%), colorless solid, mp 190–192°C (ethyl acetate–hexane); [Found: C, 73.50; H, 5.82, $C_{19}H_{18}O_4$ requires C, 73.53; H, 5.85%]; ν_{max} (neat) 2945, 2876, 1759, 1670, 1630, 1369, 1085, 1047, 978 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.06–8.02 (1H, m, Arom-H), 7.77–7.73 (1H, m, Arom-H), 7.59–7.43 (2H, m, Arom-H), 6.65 (1H, d, J=10.5 Hz), 6.42 (1H, d, J=10.5 Hz), 4.23 (1H, s, OCH), 2.28–1.32 (8H, m), 1.27 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 211.0 (C=O), 183.3 (C=O), 145.4 (=CH),142.5 (quat-C), 135.5 (quat-C), 132.7 (=CH), 131.5 (=CH), 128.9 (=CH), 127.8 (=CH), 126.7 (=CH), 115.3 (quat-C), 89.4 (OCH), 82.5 (quat-C), 53.1 (quat-C), 31.8 (CH_2), 26.5 (CH_2), 23.1 (CH_2), 19.9 (CH_2), 15.0 (CH_3); m/z 310 (M^+, 4), 308 (4), 247 (3), 184 (16), 152 (42), 123 (100), 122 (95), 95 (23%). **15a**: 23 mg (7%), colorless solid, mp 174–176°C (chloroform–hexane); [Found: C, 69.49; H, 6.13, $C_{19}H_{20}O_5$ requires C, 69.50; H, 6.14%]; ν_{max} (KBr) 3420, 2941, 2807, 1695, 1596, 1452, 1339, 1300, 1253, 1138, 1071, 961 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.96 (1H, d, J=7.6 Hz, Arom-H), 7.75–7.60 (2H, m, Arom-H), 7.46 (1H, d, J=7.5 Hz, Arom-H), 4.71 (1H, s, OCH), 4.67 (1H, dd, J=8.0, 10.5 Hz), 3.53 (1H, s, OH), 3.29 (1H, dd, J=16.3 10.5 Hz), 2.70 (1H, dd, J=16.3, 8.0 Hz), 2.20–1.30 (8H, m), 1.07 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 196.0 (C=O), 137.7 (quat-C), 134.8 (=CH), 132.0 (quat-C), 129.8 (=CH), 129.0 (=CH), 126.5 (=CH), 113.0 (quat-C), 111.9 (quat-C), 87.9 (OCH), 84.5 (quat-C), 77.2 (OCH), 52.9 (quat-C), 44.0 (CH_2), 31.4 (CH_2), 26.6 (CH_2), 23.5 (CH_2), 21.4 (CH_2), 13.9 (CH_3); m/z 328 (M^+).

3.2.6. Reaction of α-diazo ketone 7a with 2,3-dichloro-1,4-naphthoquinone. A mixture of 2,3-dichloro-1,4-naphthoquinone (455 mg, 2.0 mmol) and diazo ketone **7a** (180 mg, 1.0 mmol) was allowed to react with rhodium acetate dimer (4.4 mg) in dry benzene (10 mL) for 12 h at room temperature under an argon atmosphere according to the general method A to afford two products **13b** and **14b** in 34% overall yield. **13b**: 15 mg (4%), pale yellow solid, mp 192–194°C (ethyl acetate-hexane); [Found: C, 60.10; H, 4.19, $C_{19}H_{16}Cl_2O_4$ requires C, 60.18; H, 4.25%]; ν_{max} (KBr) 2940, 2869, 1676, 1677, 1596, 1561, 1297, 1258, 1144, 1035, 1008, 978 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.12–7.99 (2H, m, Arom-H), 7.83–7.62 (2H, m, Arom-H), 4.58 (1H, s, OCH), 2.20–1.32 (8H, m), 1.29 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 210.4 (C=O), 194.2 (C=O), 193.2 (C=O), 136.7 (quat-C), 136.2 (quat-C), 135.2 (=CH), 134.9 (=CH), 127.5 (=CH), 127.1 (=CH), 94.2 (OCH), 92.9 (quat-C), 92.3 (quat-C), 84.5 (quat-C), 54.5 (quat-C), 33.0 (CH_2), 25.5 (CH_2), 22.9 (CH_2), 19.9 (CH_2), 14.6 (CH_3); m/z 379 (M^+, 1), 343 (7), 228 (63), 226 (76), 191 (100), 87 (26%). **14b**: 114 mg (30%), pale yellow solid, mp 214–216°C (ethyl acetate–hexane); [Found: C, 60.28; H, 4.29, $C_{19}H_{16}Cl_2O_4$ requires C, 60.18; H, 4.25%]; ν_{max} (KBr) 2939, 2868, 1762, 1678, 1596, 1561, 1458, 1297, 1258, 1035, 1109 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.16 (1H, d, J=7.6 Hz, Arom-H), 7.78 (1H, d, J=7.8 Hz, Arom-H), 7.59–7.49 (2H, m, Arom-H), 4.18 (1H, s, OCH), 2.23–1.30 (8H, m), 1.30 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 209.1 (C=O), 176.4 (C=O), 148.8 (quat-C), 142.3 (quat-C), 132.4 (=CH), 129.5 (quat-C), 129.3 (=CH), 128.7 (quat-C), 127.9 (=CH), 127.5 (=CH), 117.4 (quat-C), 90.5 (OCH), 83.6 (quat-C), 54.6 (quat-C), 32.7 (CH_2), 26.1 (CH_2), 23.1 (CH_2), 19.6 (CH_2), 14.8 (CH_3); m/z 379 (M^+, 1), 226 (79), 191 (100), 163 (62), 135 (38), 123 (62), 95 (28), 87 (28%).

3.2.7. Reaction of α-diazo ketone 7b with 1,4-naphthoquinone. A mixture of 1,4-naphthoquinone (315 mg, 2.0 mmol) and diazo ketone **7b** (165 mg, 1.0 mmol) was allowed to react with rhodium acetate dimer (4.4 mg) in dry benzene (10 mL) for 9 h at room temperature under an argon atmosphere according to the general method A to afford three products **13c**, **14c** and **15c** in 37% overall yield. **13c**: 71 mg (24%), colorless solid, mp 164–167°C (chloroform–hexane); [Found: C, 72.99; H, 5.49, $C_{18}H_{16}O_4$ requires C, 72.96; H, 5.44%]; ν_{max} (KBr) 2969, 2930, 1761, 1683, 1590, 1458, 1319, 1300, 1266, 1093, 992, 962 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.08–8.04 (2H, m, Arom-H), 7.81–7.74 (2H, m, Arom-H), 4.61 (1H, s, OCH), 3.47 (1H, d, J=8.4 Hz), 3.40 (1H, d, J=8.4 Hz), 2.34–1.26 (1H, m), 1.99–1.82 (3H, m), 1.65–1.58 (1H, m), 1.34–1.25 (1H, m), 1.17 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 211.5 (C=O), 194.3 (C=O), 193.6 (C=O), 135.9 (quat-C), 135.7 (quat-C), 134.7 (=CH), 134.4 (=CH), 127.2 (=CH), 126.9 (=CH), 104.0 (quat-C), 84.7 (OCH), 58.9 (quat-C), 52.6 (CH), 49.1 (CH), 33.9 (CH_2), 28.2 (CH_2), 22.7 (CH_2), 19.3 (CH_3); m/z 296 (M^+, 8), 268 (100), 267 (68), 250 (77), 239 (45), 221 (23), 197 (19), 159 (34), 119 (21), 104 (64), 93 (35%). **14c**: 24 mg (8%), colorless solid, mp 194–196°C (ethyl acetate–hexane); [Found: C, 72.90; H, 5.49, $C_{18}H_{16}O_4$ requires C, 72.96; H, 5.44%]; ν_{max} (neat) 2933, 2869, 1760, 1668, 1629, 1341, 1081, 1049 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.06–8.01 (1H, m, Arom-H), 7.79–7.29 (1H, m, Arom-H), 7.60–7.40 (2H, m, Arom-H), 6.66 (1H, d, J=10.5 Hz), 6.41 (1H, d, J=10.5 Hz), 4.20 (1H, s, OCH), 2.35–1.83 (4H, m), 1.65–1.26 (2H, m), 1.19 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$)

211.2 (*C*=O), 183.2 (*C*=O), 145.3 (=*C*H), 142.5 (quat-C), 135.7 (quat-C), 132.6 (=*C*H), 131.6 (=*C*H), 128.9 (=*C*H), 127.9 (=*C*H), 126.7 (=*C*H), 115.0 (quat-C), 89.3 (O*C*H), 82.2 (quat-C), 58.6 (quat-C), 33.8 (*C*H_2), 28.1 (*C*H_2), 22.7 (*C*H_2), 19.6 (*C*H_3); *m/z* 296 (M^+). **15c**: 15 mg (5%), colorless solid, mp 167–169°C (chloroform–hexane); [Found: C, 68.87; H, 5.80, $C_{18}H_{18}O_5$ requires C, 68.78; H, 5.77%]; ν_{max} (KBr) 3390, 2931, 1705, 1599, 1453, 1341, 1320, 1251, 1136, 1071, cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.97 (1H, d, *J*=7.5 Hz, Arom-*H*), 7.73–7.62 (2H, m, Arom-*H*), 7.49 (1H, d, *J*=7.5 Hz, Arom-*H*), 4.73 (1H, s, OC*H*), 4.65 (1H, dd, *J*=8.0, 10.5 Hz), 3.42 (1H, s, O*H*), 3.25 (1H, dd, *J*=16.3, 10.5 Hz), 2.72 (1H, dd, *J*=16.3, 8.0 Hz), 2.20–1.30 (6H, m), 1.09 (3H, s, C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 196.6 (*C*=O), 137.0 (quat-C), 134.2 (=*C*H), 132.6 (quat-C), 129.2 (=*C*H), 129.2 (=*C*H), 126.4 (=*C*H), 113.1 (quat-C), 111.6 (quat-C), 87.0 (O*C*H), 84.9 (quat-C), 77.6 (O*C*H), 52.0 (quat-C), 44.4 (*C*H_2), 32.5 (*C*H_2), 27.6 (*C*H_2), 22.2 (*C*H_2), 13.9 (*C*H_3); *m/z* 314 (M^+).

3.2.8. Reaction of α-diazo ketone 7d with 1,4-naphthoquinone. A mixture of 1,4-naphthoquinone (155 mg, 1.0 mmol) and diazo ketone **7d** (125 mg, 0.5 mmol) was allowed to react with rhodium acetate dimer (2.2 mg) in dry benzene (10 mL) for 6.5 h at reflux under an argon atmosphere according to the general method B to afford three products **13d**, **14d** and **15d** in 38% overall yield. **13d**: 48 mg (25%), colorless solid, mp 168–170°C (chloroform–hexane); [Found: C, 69.19; H, 5.74, $C_{22}H_{22}O_6$ requires C, 69.10; H, 5.80%]; ν_{max} (KBr) 3023, 2938, 2863, 1775, 1745, 1682, 1595, 1458, 1376, 1320, 1264, 1241, 1073 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.09–7.99 (2H, m, Arom-*H*), 7.80–7.75 (2H, m, Arom-*H*), 4.43 (2H, q, *J*=7.2 Hz, OC*H*$_2$), 3.62 (1H, d, *J*=8.2 Hz), 3.46 (1H, d, *J*=8.2 Hz), 1.96–1.25 (8H, m), 1.41 (3H, t, *J*=7.2 Hz, CH_2C*H*$_3$) 1.28 (3H, s, C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 207.8 (*C*=O), 194.1 (*C*=O), 192.0 (*C*=O), 163.8 (*C*OO), 144.4 (quat-C), 144.2 (quat-C), 135.1 (=*C*H), 135.0 (=*C*H), 127.5 (=*C*H), 126.8 (=*C*H), 93.8 (quat-C), 90.6 (quat-C), 62.7 (O*C*H_2), 55.0 (*C*H), 53.9 (*C*H), 52.6 (quat-C), 31.0 (*C*H_2), 26.7 (*C*H_2), 22.3 (*C*H_2), 20.0 (*C*H_2), 14.6 (*C*H_3), 14.0 (*C*H_3); *m/z* 382 (M^+, 12), 354 (23), 336 (63), 281 (69), 263 (32), 253 (51), 211 (45), 123 (100), 104 (63), 76 (48%). **14d**: 10 mg (5%), colorless solid, mp 149–153°C (chloroform–hexane); [Found: C, 69.13; H, 5.84, $C_{22}H_{22}O_6$ requires C, 69.10; H, 5.80%]; ν_{max} (neat) 2940, 2879, 1756, 1731, 1669, 1631, 1369, 1089, 1041, 999 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.06–7.85 (2H, m, Arom-*H*), 7.65–7.50 (2H, m, Arom-*H*), 6.72 (1H, d, *J*=10.5 Hz), 6.55 (1H, d, *J*=10.5 Hz), 4.03 (2H, q, *J*=7.2 Hz, OC*H*$_2$), 2.41–1.34 (8H, m), 1.42 (3H, s, C*H*$_3$), 0.91 (3H, t, *J*=7.2 Hz, CH_2C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 211.3 (*C*=O), 184.4 (*C*=O), 163.8 (*C*OO), 145.4 (=*C*H), 142.5 (quat-C), 135.5 (quat-C), 132.7 (=*C*H), 131.5 (=*C*H), 128.9 (=*C*H), 127.8 (=*C*H), 126.7 (=*C*H), 115.0 (quat-C), 90.9 (quat-C), 81.9 (quat-C), 62.5 (O*C*H_2), 52.9 (quat-C), 31.8 (*C*H_2), 26.5 (*C*H_2), 23.1 (*C*H_2), 19.8 (*C*H_2), 14.9 (*C*H_3), 14.0 (*C*H_3); *m/z* 382 (M^+, 1), 224 (27), 158 (6), 123 (100), 95 (23%). **15d**: 32 mg (8%), colorless solid, mp 178–180°C (chloroform–hexane); [Found: C, 65.97; H, 6.10, $C_{22}H_{24}O_7$ requires C, 65.99; H, 6.04%]; ν_{max} (KBr) 3411, 2941, 2868, 1710, 1694, 1596, 1381, 1337, 1300, 1253, 1071, 1012, 961 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.94 (1H, d, *J*=7.3 Hz, Arom-*H*), 7.74–7.61 (2H, m, Arom-*H*), 7.46 (1H, d, *J*=7.3 Hz, Arom-*H*), 4.68 (1H, dd, *J*=8.0, 10.5 Hz), 4.15 (2H, q, *J*=7.2 Hz, OC*H*$_2$), 3.63 (1H, s, O*H*), 3.47–3.21 (2H, m), 2.36–1.20 (8H, m), 1.15 (3H, s, C*H*$_3$) 0.80 (3H, t, *J*=7.2 Hz, CH_2C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 195.0 (*C*=O), 166.5 (*C*OO), 137.6 (quat-C), 134.7 (=*C*H), 132.2 (quat-C), 129.7 (=*C*H), 129.3 (=*C*H), 126.5 (=*C*H), 111.9 (quat-C), 111.7 (quat-C), 93.2 (quat-C), 86.5 (quat-C), 77.1 (O*C*H), 62.6 (O*C*H_2), 52.6 (quat-C), 44.2 (*C*H_2), 31.4 (*C*H_2), 26.5 (*C*H_2), 23.5 (*C*H_2), 21.4 (*C*H_2), 14.0 (*C*H_3), 13.9 (*C*H_3); *m/z* 400 (M^+, 16), 299 (12), 244 (14), 171 (100), 143 (11), 123 (12), 112 (26), 83 (12%).

3.2.9. Reaction of α-diazo ketone 7e with 2,3-dichloro-1,4-naphthoquinone. A mixture of 2,3-dichloro-1,4-naphthoquinone (136 mg, 0.6 mmol) and diazo ketone **7e** (80 mg, 0.3 mmol) was allowed to react with rhodium acetate dimer (1.3 mg) in dry benzene (10 mL) for 5 h at reflux under an argon atmosphere according to the general method B to afford two products **13e** and **14e** in 45% overall yield. **13e**: 14 mg (5%), yellow solid, mp 206–208°C (ethyl acetate–hexane); [Found: C, 59.41; H, 4.85, $C_{23}H_{22}Cl_2O_6$ requires C, 59.37; H, 4.77%]; ν_{max} (KBr) 2930, 2856, 1760, 1734, 1686, 1596, 1570, 1457, 1372, 1308, 1286, 1109 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.10–8.01 (2H, m, Arom-*H*), 7.67–7.52 (2H, m, Arom-*H*), 4.13 (2H, q, *J*=7.2 Hz, OC*H*$_2$), 2.85–2.62 (3H, m), 2.43–1.29 (7H, m), 1.39 (3H, d, *J*=7.6 Hz), 1.09 (3H, t, *J*=7.2 Hz, CH_2C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 204.0 (*C*=O), 189.0 (*C*=O), 188.5 (*C*=O), 172.0 (*C*OO), 141.3 (quat-C), 134.0 (=*C*H), 131.0 (quat-C), 130.1 (=*C*H), 127.7 (=*C*H), 127.5 (=*C*H), 95.2 (quat-C), 86.9 (quat-C), 74.1 (quat-C), 73.1 (quat-C), 63.1 (O*C*H_2), 42.6 (*C*H_2), 37.9 (*C*H), 37.0 (*C*H), 26.0 (*C*H_2), 24.7 (*C*H_2), 16.4 (*C*H_2), 15.8 (*C*H_3), 14.1 (*C*H_3); *m/z* 465 (M^+). **14e**: 111 mg (40%), pale yellow solid, mp 210–213°C (ethyl acetate–hexane); [Found: C, 59.31; H, 4.71, $C_{23}H_{22}Cl_2O_6$ requires C, 59.37; H, 4.77%]; ν_{max} (KBr) 2927, 2854, 1754, 1734, 1683, 1597, 1574, 1457, 1301, 1280, 1104, 906 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.13 (1H, d, *J*=7.8 Hz, Arom-*H*), 7.82 (1H, d, *J*=7.8 Hz, Arom-*H*), 7.66–7.51 (2H, m, Arom-*H*), 3.84 (2H, q, *J*=7.2 Hz, OC*H*$_2$), 2.89–2.65 (3H, m), 2.40–1.33 (7H, m), 1.47 (3H, d, *J*=7.6 Hz), 0.89 (3H, t, *J*=7.2 Hz, CH_2C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 200.7 (*C*=O), 175.6 (*C*=O), 169.0 (*C*OO), 141.3 (quat-C), 133.7 (=*C*H), 130.8 (quat-C), 130.1 (=*C*H), 127.7 (=*C*H), 127.5 (=*C*H), 116.3 (quat-C), 115.3 (quat-C), 95.2 (quat-C), 86.9 (quat-C), 79.1 (quat-C), 63.1 (O*C*H_2), 42.6 (*C*H_2), 37.8 (*C*H), 37.0 (*C*H), 26.2 (*C*H_2), 24.7 (*C*H_2), 16.4 (*C*H_2), 15.8 (*C*H_3), 13.9 (*C*H_3); *m/z* 465 (M^+, 1), 332 (4), 261 (5), 238 (31), 191 (21), 149 (74), 95 (14), 41 (100%).

3.3. X-Ray crystal structure analysis

Crystal data for the compound **11a**: $C_{15}H_{16}O_4$, M=260.28, 0.15×0.09×0.24 mm^3, colorless plates, Monoclinic, $P2_1/a$, a=8.703(4), b=11.678(15), c=12.742(4) Å, β=91.75(3)°, V=1294.4(18) Å^3, T=293(2) K, R_1=0.0610, wR_2=0.1854 on observed data, z=4, D_{calc}=1.336 Mg m^{-3}, F(000)=552, Absorption coefficient=0.097 mm^{-1}, λ=0.7107 Å, 2279 reflections were collected on a CAD-4 diffractometer, 1653 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole=0.308 and −0.444e Å^{-3}, respectively.

Crystal data for the compound **12d**: $C_{18}H_{22}O_7$, M=350.36, 0.20×0.18×0.12 mm^3, colorless plates, Triclinic, $P-1$, a=9.299(3), b=9.930(2), c=10.214(6) Å, α=98.21(3), β=111.98(4), γ=99.48(2)°, V=840.8(6) Å^3, T=293(2) K, R_1=0.0562, wR_2=0.1357 on observed data, z=2, D_{calc}=1.384 Mg m^{-3}, $F(000)$=372, Absorption coefficient=0.107 mm^{-1}, λ=0.7107 Å, 2936 reflections were collected on a CAD-4 diffractometer, 1706 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole=0.252 and −0.382e Å^{-3}, respectively.

Crystal data for the compound **14a**: $C_{19}H_{18}O_4$, M=310.33, 0.20×0.16×0.12 mm^3, colorless plates, Monoclinic, $P2_1/n$, a=9.162(3), b=16.181(9), c=11.086(3) Å, β=110.35(2)°, V=1540.9(11) Å^3, T=293(2) K, R_1=0.0454, wR_2=0.1138 on observed data, z=4, D_{calc}=1.338 Mg m^{-3}, $F(000)$=656, Absorption coefficient=0.093 mm^{-1}, λ=0.7107 Å, 2696 reflections were collected on a CAD-4 diffractometer, 1783 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole=0.156 and −0.182e Å^{-3} respectively. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELX 97.[23] All non-hydrogen atoms were refined anisotropically. Some hydrogens were located on a difference Fourier map and some were stereochemically fixed. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK. The corresponding CCDC numbers are 160621, 160622, 160623 for compounds **11a**, **12d** and **14a**, respectively.

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References

1. Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223–269.
2. (a) Padwa, A., Ed.; *1,3-Dipolar Cycloaddition Chemistry*; Wiley-Interscience: New York, 1984; Vols 1 and 2. (b) Padwa, A. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, p. 1069.
3. (a) Padwa, A.; Curtis, E. A.; Sandanayaka, V. P. *J. Org. Chem.* **1997**, *62*, 1317–1325. (b) McMorris, T. C.; Hu, Y.; Yu, J.; Kelner, M. J. *J. Chem. Soc., Chem. Commun.* **1997**, 315–316. (c) Kinder, Jr., F. R.; Bair, K. W. *J. Org. Chem.* **1994**, *59*, 6965–6967.
4. (a) McMills, M. C.; Zhuang, L.; Wright, D. L.; Watt, W. *Tetrahedron Lett.* **1994**, *35*, 8311–8314. (b) Dauben, W. G.; Dinges, J.; Smith, T. C. *J. Org. Chem.* **1993**, *58*, 7635–7637.
5. Padwa, A.; Price, A. T. *J. Org. Chem.* **1995**, *60*, 6258–6259.
6. Padwa, A.; Chinn, R. L.; Zhi, L. *Tetrahedron Lett.* **1989**, *30*, 1491–1494.
7. Yunlong, X.; Dan, W.; Xiaojie, L.; Jian, F. *Phytochemistry* **1989**, *28*, 189–191.
8. Conner, A. H.; Nagasampagi, B. A.; Rowe, J. W. *Phytochemistry* **1980**, *19*, 1121–1131.
9. (a) Hodgson, D. M.; Bailey, J. M.; Villalonga-Barber, C.; Drew, M. G. B.; Harrison, T. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3432–3443. (b) Wilson, K. E.; Burk, R. B.; Biftn, T.; Ball, R. G.; Hoogsteen, K. *J. Org. Chem.* **1992**, *57*, 7151–7158.
10. Zamir, L. O.; Devor, K. A.; Morin, N.; Sauriol, F. *J. Chem. Soc., Chem. Commun.* **1991**, 1033–1034.
11. Krohn, K.; Rohr, J. *Top. Curr. Chem.* **1997**, *188*, 128–195.
12. (a) Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Suresh, E.; Dastidar, P.; Jasra, R. V. *Tetrahedron* **2000**, *56*, 6307–6318. (b) Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.* **2000**, *41*, 8839–8842. (c) Muthusamy, S.; Gunanathan, C.; Babu, S. A. *Tetrahedron Lett.* **2001**, *42*, 523–526.
13. Pirrung, M. C.; Kaliappan, K. P. *Org. Lett.* **2000**, *2*, 353–355.
14. Pollet, P.; Gelin, S. *Synthesis* **1978**, 142–143.
15. (a) Regitz, M.; Hecker, J.; Leidhergener, K. *Organic Synthesis Collected Volume V*; Wiley: New York, 1973; pp 179–183. (b) Taber, D. F.; Ruckle Jr., R. E.; Hennessy, M. J. *J. Org. Chem.* **1986**, *51*, 4077–4078.
16. Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290–296.
17. (a) Krohn, K.; Khanbabaee, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 99–100. (b) Kim, K.; Sulikowski, G. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2396–2398.
18. (a) Doyle, M. P.; Shanklin, M. S.; Oon, S. M.; Pho, H. Q.; van der Heide, F. R.; Veal, W. R. *J. Org. Chem.* **1988**, *53*, 3384–3386. (b) Doyle, M. P.; Tauton, J.; Pho, H. Q. *Tetrahedron Lett.* **1989**, *30*, 5397–5400.
19. Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100–3109.
20. Nair, V.; Sheela, K. C.; Radhakrishnan, K. V.; Rath, N. P. *Tetrahedron Lett.* **1998**, *39*, 5627–5630.
21. Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon: Oxford, 1990; pp 91–139.
22. Padwa, A.; Prein, M. *Tetrahedron* **1998**, *54*, 6957–6976.
23. Sheldrick, M. *SHELX 97*, Program for the solution of crystal structures, University of Gottingen, Germany, 1997.