Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 8117–8127

TETRAHEDRON

A facile regioselective construction of spiro epoxy-bridged tetrahydropyranone frameworks

S. Muthusamy,[a,*] S. Arulananda Babu[a] and M. Nethaji[b]

[a]*Department of Organic Chemistry, Central Salt and Marine Chemicals Research Institute, GB Marg, Bhavnagar 364 002, India*
[b]*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India*

Received 9 April 2003; revised 28 July 2003; accepted 22 August 2003

This paper is dedicated with best wishes to Professor Goverdhan Mehta on the occasion of his 60th birthday

Abstract—Investigations on the reactivity profile of the transient five-membered-ring cyclic carbonyl ylides, generated from α-diazo ketones, in the presence of the C═O group of various simple ketones and symmetrical/unsymmetrical 1,2-diones were carried out. The reaction of α-diazo ketones with 1,2-naphthoquinone furnished interesting diastereomeric cycloadducts in which both the C═O groups acted as dipolarophilic sites. The similar reaction in the presence of several isatin derivatives afforded novel spiro dioxa-bridged indole derivatives as a mixture of diastereomers. The single crystal X-ray structure analysis manifestly revealed the mode of cycloaddition and the stereochemistry of two of the diastereomers. A diverse set of novel spiro epoxy-bridged tetrahydropyranone frameworks have been constructed in good yield via the tandem cyclization–cycloaddition of α-diazo ketones with the C═O group as heterodipolarophile in a regioselective manner.

1. Introduction

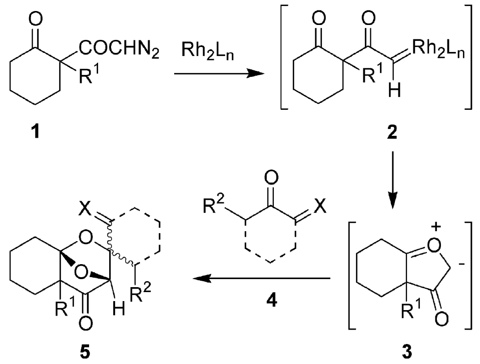
1,3-Dipolar cycloaddition to multiple C–C bonds constitutes a versatile synthetic technique for the stereoselective construction of complex five-membered carbo- or heterocyclic frameworks that can be synthetically manoeuvred to obtain natural product skeletons.[1] The 1,3-dipolar cycloaddition chemistry involving diazo carbonyl compounds is an interesting tool to synthesize novel oxa-polycyclic compounds.

α-Diazo carbonyl compounds have found numerous applications in synthetic organic chemistry and they have served as very useful intermediates for the synthesis of various complex molecules.[2] Diversity in reactions and the unique many bond forming capabilities are notable features of the rhodium carbenoids that can be generated from α-diazo ketones. Especially, the chemistry of tandem rhodium(II)-induced cyclization-1,3-dipolar cycloaddition of α-diazo ketones to C–C multiple bonds has been extensively studied to synthesize epoxy-bridged polycyclic compounds.[2a,3] The epoxy-bridged tetrahydropyranone units are recognized as common structural units in naturally occurring bioactive molecules such as brevicomins,[4] zaragozic acid,[5] frontalin,[6] amberketal,[7] austalide B,[8] loukacinols,[9] xanthane epoxide,[10] sporol[11] and isogosterones.[12] Especially, spiro compounds containing one or more heteroatoms represent an important group of naturally occurring substances characterized by their pronounced biological importance.

In recent years, we have been actively involved in tandem cyclization–cycloaddition methodology and the regio- and stereoselective studies of transient carbonyl ylides to synthesize a variety of new epoxy-bridged polycyclic frameworks.[13] Even though the chemistry of rhodium(II)-generated carbonyl ylides with C═C bonds is well documented, the reaction of carbonyl ylides with heterodipolarophiles has not been much explored.[2a,3] Very limited reports are available on the cycloaddition reactions of transient carbonyl ylides with the C═O group. Ibata and co-workers have initially reported[14] that the reaction of *o*-(diazoacetyl)benzoates in the presence of $Cu(acac)_2$ with carbonyl groups gave 1:1 *exo*/*endo* products and 2:1 cycloadducts. Recently, the reactions of α-diazo ketones with carbonyl compounds such as *o*-quinones,[15] aldehyde,[16] isatins,[17] arylidenetetralones[18] and 2,6-bis(arylmethylidene) cycloalkanones[13a] were reported. The reaction of carbonyl ylides with *p*-benzoquinone was reported[19] to furnish both the C═C and C═O addition products without selectivity. We have also reported[20] a comprehensive study on the stereoselective construction of epoxy-bridged tetrahydropyranone polycyclic frameworks via the cycloaddition of carbonyl ylides with various carbonyl groups of aldehydes or ketones. In continuation of our research interest on the reactions of α-diazo ketones, we herein report our

Keywords: carbonyl ylides; cycloaddition; α-diazo ketones; diones; rhodium(II) acetate catalyst; spiro compounds.
* Corresponding author. Tel.: +91-278-2567760; fax: +91-278-2567562; e-mail: smuthus@yahoo.com

0040–4020/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2003.08.041



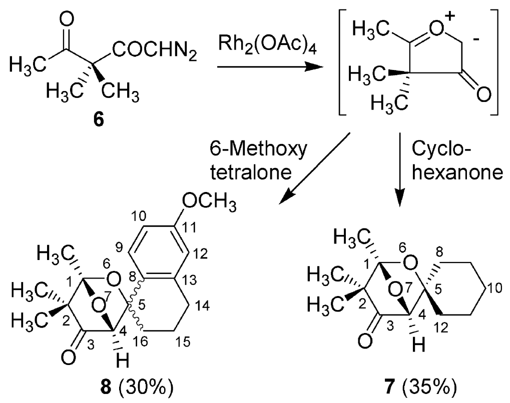
Scheme 1.

regioselective studies on the reactions of transient carbonyl ylides in the presence of the C=O group of symmetrical/unsymmetrical 1,2-diones to synthesize a new class of spiro epoxy-bridged tetrahydropyranone frameworks.

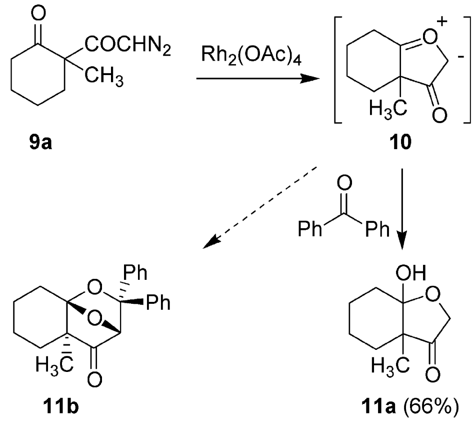
2. Results and discussion

Based on our earlier work, the rhodium(II) carboxylate-catalyzed tandem cyclization–cycloaddition reactions of α-diazo ketone involves the generation of rhodium carbenoid **2** from the α-diazo ketone **1**. This is followed by the transannular cyclization of the electrophilic carbenoid **2** on to the adjacent carbonyl group to give the transient cyclic carbonyl ylide **3**, which can cycloadd to the C=O group of a substrate (Scheme 1). This tactic affords a regioselective tool for the synthesis of oxygen-rich spiro polycyclic frameworks in a single mode of operation.

It was envisaged that the treatment of α-diazo ketones **6** or **9** in the presence of rhodium(II) acetate dimer could lead to the formation of respective five-membered-ring cyclic carbonyl ylides based on our earlier work.[13] Initially, we studied the reaction of these transient carbonyl ylides in the presence of simple cyclic ketones before studying diketone systems. Reactions of α-diazo ketone **6** with cyclic ketones such as cyclohexanone and 6-methoxy-1-tetralone in the presence of $Rh_2(OAc)_4$ catalyst were carried out to afford the corresponding cycloadducts **7**,**8** in 35 and 30% yields, respectively (Scheme 2). The ^{1}H NMR spectrum of the respective crude reaction mixture for these reactions revealed the formation of only one cycloadduct (**7**) and a



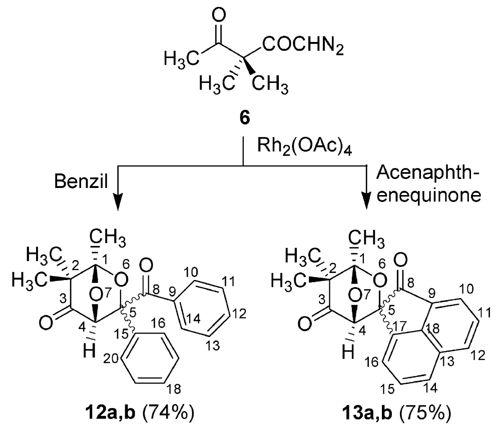
Scheme 2.



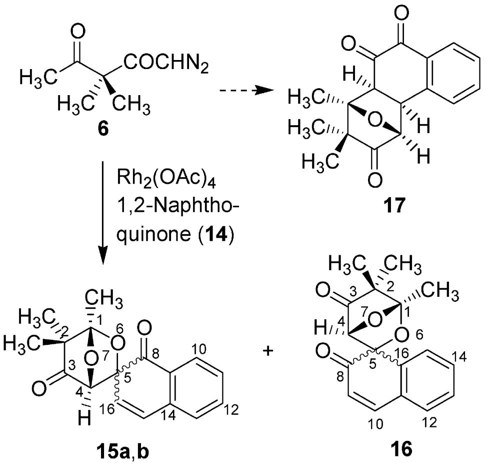
Scheme 3.

mixture of diastereomers in the ratio of 1:6.6 (**8**). Surprisingly, treatment of α-diazo ketone **6** with 2-adamantanone did not afford any cycloaddition product. Similarly, the reaction of fused five-membered-ring cyclic carbonyl ylide **10**, generated from α-diazo ketone **9a** tethered on cyclohexanone ring system, with benzophenone in the presence of $Rh_2(OAc)_4$ did not afford the expected cycloadduct **11b**. Instead, the fused furanone[21] **11a** (66%) was isolated under the experimental conditions (Scheme 3). We have not observed the formation any 2:1 cycloadducts from these reactions.

Next, we investigated the reaction of α-diazo ketone **6** with acyclic/cyclic symmetrical 1,2-diones such as benzil and acenaphthenequinone, which afforded the cycloadducts **12/13**, respectively. The cycloadducts **12a** and **12b** as well as **13a** and **13b** were separated by repetitive column chromatography and characterized as diastereomers (Scheme 4). The diastereomeric ratio in the crude reaction mixture for compound **12** and **13** is found to be 1:1.5 and 1:1, respectively. The presence of a singlet resonance signal for the bridgehead H-4 proton (OC*H*) in the ^{1}H NMR spectra of compounds **7**,**8**/**12**,**13** clearly indicated the regioselective formation of epoxy-bridged cycloadducts. The other expected regioisomeric products were not observed and it can conveniently be explained on the basis of the chemical shift value for the bridgehead OC*H* proton, which would be at much more downfield than the observed value for OC*H* (around 4.35–4.85) protons in



Scheme 4.



Scheme 5.

regioisomers **7**,**8/12**,**13**. The H-4 proton of the cycloadduct **12b** surprisingly appeared at 5.68 ppm, which may be due to deshielding of the proton by the 'ring current effect' of the phenyl or benzoyl substituent. The outcome of these reactions is similar to our previous observation of the chemoselective reaction of carbonyl ylide with arylidenetetralones,[18] which also led to cycloadducts as diastereomers.

In order to find the synthetic utility of α-diazo ketones, the rhodium(II)-induced carbenoid cyclization–cycloaddition sequence was extended using an unsymmetrical 1,2-dione, so as to probe the regio- and stereoselective aspects of the reaction. Towards this, α-diazo ketones **6**,**9a** were allowed to react with 1,2-naphthoquinone. To a solution containing α-diazo ketone **6** and 1,2-naphthoquinone (**14**) in dry DCM was added a catalytic amount of $Rh_2(OAc)_4$ and the reaction was monitored by TLC. The ^1H NMR of the crude reaction mixture showed a mixture of four diastereomers in the ratio of 1:1:2:3. Column chromatographic purification of the reaction mixture afforded three products **15a**,**b** and **16** in 31, 9 and 23% yield, respectively. The product **16** was isolated as a mixture of diastereomers in the ratio of 1:2.2. The ^1H, ^{13}C NMR and dept-135 spectra of these products revealed the presence of CH signals for C-3 and C-4 carbons and the absence of one carbonyl group of 1,2-naphthoquinone. All these products formed in this reaction are from the cycloaddition of carbonyl ylide with one of the C═O groups present in dipolarophile **14** and no detectable amount of C═C addition product **17** was observed (Scheme 5). Presumably, due to asymmetry present in dipolarophile **14**, each carbonyl group might produce a mixture of diastereomers **15** and **16**. The FT-IR spectra showed the presence of two strong bands for two different carbonyl groups present in compounds **15**,**16**. Independent spectral analyses of these three products have shown the presence of a signal around 4.5 ppm in the ^1H NMR for H-4 proton and 111 ppm in the ^{13}C NMR spectra for C-1 carbon[22] clearly confirmed the formation of the dioxa-bridged compounds of type **15**,**16**. The spectral analyses revealed that these cycloadducts are present as isomers and the characterization of the stereochemistry is a challenging task. The single-crystal X-ray analysis of compound **15a** helped us to unambiguously characterize the stereochemistry and the ORTEP view is shown in Figure 1. The observed angle of the oxa-bridge (C4–O7–C1) in compound **15a** is 96.66°. ^{13}C NMR spectral analysis of the above three products revealed that the C-3 carbon exhibited a peak around 211 ppm. The other carbonyl group (C-8) appeared at 196.3, 196.2 for products **15a,b**, respectively. The diastereomeric mixture **16** showed a peak at around 198 ppm for the C-8 carbon and the structure of other isomers **15b**,**16** was tentatively assigned. All the above said evidence revealed that the carbonyl ylide chemoselectively cycloadds with the C═O group resulting in a mixture of diastereomers.

It is relevant to mention that the reaction of carbonyl ylide **3** with 1,4-naphthoquinone furnished both C═C and C═O addition products without any selectivity.[19a] It has been reported[15a] that unsymmetrical dipolarophiles such as 3-methoxy-4,6-bis(1,1-diphenylmethyl)-1,2-benzoquinone react with 1-diazo-5-phenyl-2,5-pentanedione to afford the C═O addition products but the diastereomers were not observed.

A subsequent experiment was performed using α-diazo ketone **9a** with 1,2-naphthoquinone in the presence of $Rh_2(OAc)_4$ as described above in a similar manner. The ^1H NMR or the crude reaction mixture showed a mixture of four diastereomers in the ratio of 1:2:3:5. The column purification of the crude reaction mixture furnished only three products **18a**,**b** and **19** in 30, 8 and 19% yields, respectively. The compound **19** was isolated as a mixture of diastereomers in the ratio of 1:3.4. This reaction also did not afford the expected, interesting C═C addition product **20**, having a steroid skeleton (Scheme 6). The ^1H, ^{13}C NMR spectral analyses showed that these isomers consist of a spiro dioxa-bridged system. The ^{13}C NMR of these isomers exhibited a peak around 211 ppm for the C-7 carbon. The other carbonyl group (C-12) appeared at 196.3 and 196.9 ppm for cycloadducts **18a,b**, respectively. The

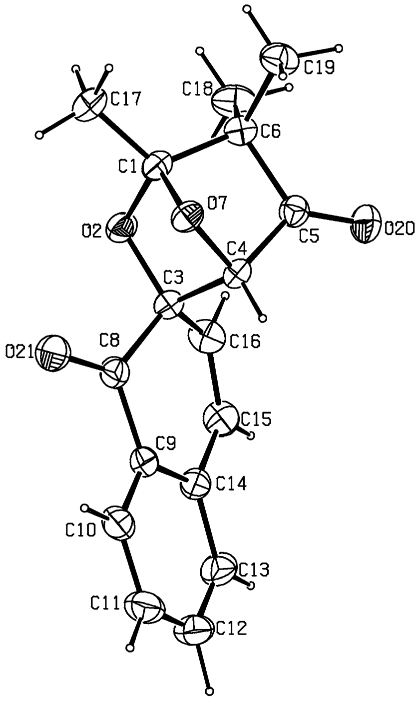
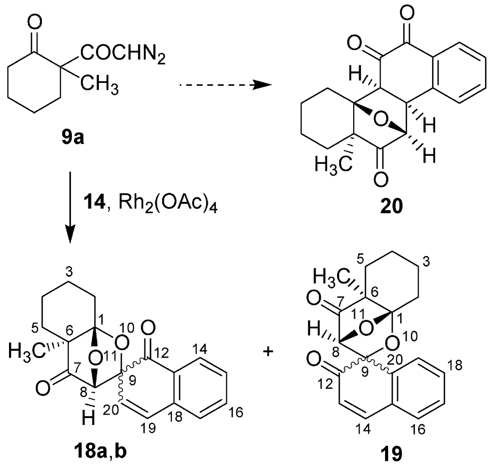


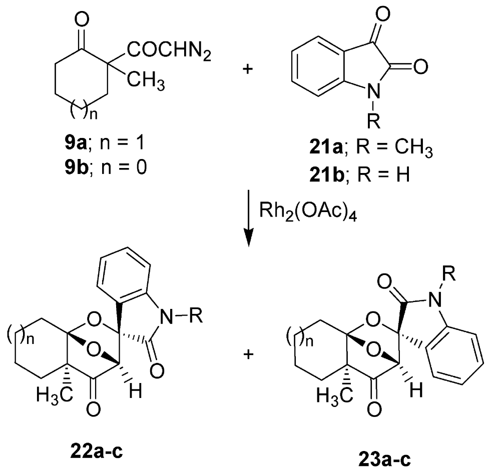
Figure 1. ORTEP diagram of the diastereomer **15a**.



Scheme 6.

diastereomeric mixture **19** showed a peak at around 198 ppm, which we have tentatively assigned to the C-12 carbon. On the basis of the characteristic pattern in the ^{1}H and ^{13}C NMR, the structure of these three compounds isolated in this reaction was tentatively assigned as **18a**, **18b** and **19**.

After studying the reaction with 1,2-naphthoquinone, we were interested in further illustrating the tandem cyclization–cycloaddition reactions using an unsymmetrical heterocyclic 1,2-dione. To this end, the required isatin derivatives **21a–e** were assembled through alkylation of isatin using sodium hydride. To a solution containing α-diazo ketone **9a** and diketone **21a** was added 1 mol% of $Rh_2(OAc)_4$ catalyst under an argon atmosphere and stirred for 3 h at room temperature. Concentration of the reaction mixture and purification through column chromatography afforded products **22a**,**23a** in 53 and 34% yield, respectively.



Scheme 7.

Table 1. Reaction of α-diazo ketones **9a**,**b** with isatins **21a**,**b**

R	*n*	Time (h)	Yield[a] (%)	
CH_3	1	4	**22a** (53)	**23a** (34)
CH_3	0	3.5	**22b** (43)	**23b** (29)
H	1	3	**22c** (46)	**23c** (30)

[a] Yields (unoptimized) refer to isolated and chromatographically pure compounds **22**,**23**.

The respective FT-IR spectrum of compounds **22a**,**23a** indicated the presence of keto and amide carbonyl groups. The ^{1}H NMR spectrum of compounds **22a**,**23a** showed characteristic peak at 4.53 and 4.69 ppm for the bridgehead (OC*H*) proton, respectively. The respective ^{13}C and dept-135 spectral analyses of compounds **22a**,**23a** exhibited signals for seven quaternary, five CH, four CH_2 and two CH_3 carbons. On the basis of similarity in spectral data of **22a**,**23a**, it is clear that the above reaction afforded two cycloaddition products, which exist as diastereomers having dioxa-bridged system (Scheme 7, Table 1). To generalize this reaction, we have carried out some more experiments utilizing diazo ketones **9a**,**b** with isatins **21a**,**b** and all these reactions afforded the diastereomeric products **22b**,**c/23b**,**c** in very good yields as a result of cycloaddition of carbonyl ylide to the C=O group present in the 3-position of isatin **21**.

In order to confirm the exact stereochemistry of products in the above reaction, we have carried out the single-crystal X-ray analysis of the diastereomer **23c** (Fig. 2), which undoubtedly established the stereochemistry of the compound **23c** and the mode of cycloaddition of carbonyl ylide towards isatin **21b**. The observed angle of oxa-bridge (C10–O11–C3) in the spiro molecule **23c** is 96.4°. On the basis of the crystal structure of **23c**, the structure of the other isomer **22c** has appropriately been established.

The characterization of diastereomers was extended for other reactions as given below. Diastereomers **22a–c** exhibited a distinctive pattern of aromatic protons with similar chemical shift values and multiplicity in the ^{1}H NMR spectra; doublet (1H, J=7.5 Hz), triplet (1H, J=7.5 Hz), triplet (1H, J=7.5 Hz) and doublet (1H, J=7.5 Hz). On the other hand, the ^{1}H NMR spectra of diastereomers

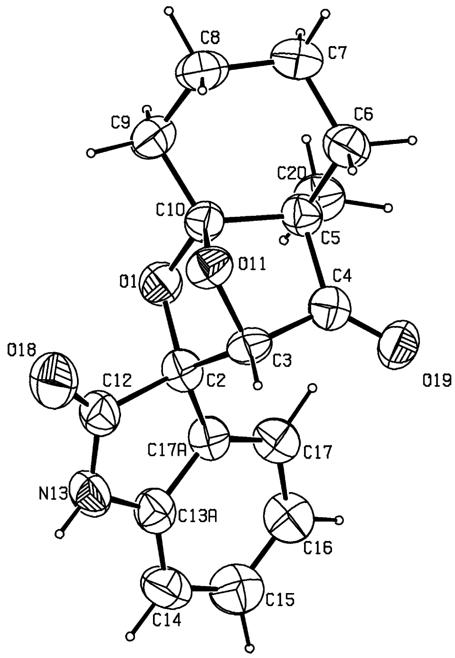
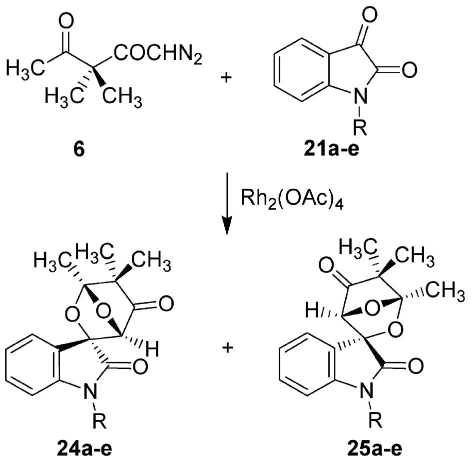


Figure 2. ORTEP diagram of the diastereomer **23c**.



Scheme 8.

Table 2. Reaction of α-diazo ketone **6** with isatins **21a–e**

R	Time (h)	Yield[a] (%)	
CH_3	4	**24a** (50)	**25a** (36)
H	4	**24b** (62)	**25b** (22)
$CH_2C_6H_5$	3.5	**24c** (49)	**25c** (35)
CH_2COOEt	3	**24d** (68)	**25d** (26)
$CH(CH_3)COOEt$	3	**24e** (45)[b]	**25e** (33)[c]

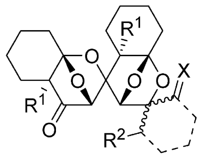
[a] Yields (unoptimized) refer to isolated and chromatographically pure compounds **24**,**25**.
[b] Obtained as stereoisomers in the ratio of 1:2.6
[c] Obtained as stereoisomers in the ratio of 1:1.3

23a–c exhibited the presence of a set of multiplets (for three protons) and a doublet (1H, J=7.5 Hz) for aromatic protons. The characteristic multiplicity pattern of aromatic protons in diastereomers **22a–c** was different from **23a–c**. On the basis of multiplicity pattern and the X-ray structure of compound **23c**, the stereochemistry of other isomers **22a–c** was assigned.

In line with the above study, similar experiments were carried out using α-diazo ketone **6**. Treatment of α-diazo ketone **6** with **21a–e** in the presence of a catalytic amount of $Rh_2(OAc)_4$ furnished the respective diastereomers **24a–e**/**25a–e** in very good yield (Scheme 8, Table 2). These reactions also afforded the respective diastereomeric cycloaddition products in a chemoselective manner as obtained in Scheme 7. Diastereomers **24**,**25** were separated using column chromatography. Typically, the diastereomers **24a–e** and **25a–e** exhibited a similar spectral pattern to compounds **22** and **23** as discussed above. The isolated cycloadducts **24e** and **25e** were obtained as a mixture of inseparable isomers in the ratio of 1:2.6 and 1:1.3, respectively, due to the substitution on N-atom having an additional stereocenter. Based on the spectral pattern with characteristic multiplicity of aromatic protons, interrelated spectral data and X-ray structure analysis of isomer **23c**, the stereochemistry of diastereomers **24**,**25** was tentatively assigned. The transient five-membered-ring carbonyl ylide underwent reaction with isatin derivatives **21a–e** to afford two diastereomers with the C=O group present in the 3-position of isatin in all the experiments carried out in the present work. We have not observed any product resulting from the cycloaddition of the transient carbonyl ylide with the C=O group present in the 2-position of isatin **21** and this was further confirmed based on the presence of amide carbonyl quaternary carbon signal in ^{13}C NMR spectra of all the cycloadducts. It is relevant to mention that the reaction of 5- or 6-membered-ring carbonyl ylide with isatin afforded[17] only one stereoisomer as a result of the cycloaddition to the C=O group present in 3-position of isatin. But, the present study revealed the formation of diastereomeric products in all the reactions of carbonyl ylides with 1,2-diones.

The above studies showed that cyclohexanone and 6-methoxy-1-tetralone are relatively less reactive towards the carbonyl ylide compared to 1,2-diones (benzil, acenaphthenequinone, 1,2-naphthoquinone and isatins). However, we were interested to compare the reactivity of an equimolar amount of α-diazo ketone with a mixture of both ketone and 1,2-dione. For this purpose, we have carried out the reaction of α-diazo ketone **6** with an equimolar mixture of both cyclohexanone and benzil in the presence of $Rh_2(OAc)_4$. The ^1H NMR spectral analysis revealed the formation of cycloadducts **7** (9%) and **12a**,**b** (66%). Similarly, we have carried out the reaction of α-diazo ketone **6** with an equimolar mixture of both cyclohexanone and isatin derivative **21c** in the presence of $Rh_2(OAc)_4$. The ^1H NMR spectral analysis showed only the formation of cycloadducts **24c**,**25c** (75%) and no formation of the cycloadduct **7**. These analyses indicated that the transient carbonyl ylide selectively reacted with activated ketones such as 1,2-diones rather than simple ketones.

It is attractive to note that starting from relatively simple precursors, the rhodium(II)-catalyzed reactions gave complex spiro dioxa-bridged polycyclic ring systems. In these tandem cycloaddition–cyclization reactions, a new C–C and two C–O bonds were created which in turn distinctly generated three new stereocenters. The amount of $Rh_2(OAc)_4$ catalyst was maintained at 1 mol% to perform all our experiments. All of these reactions underwent smoothly to furnish a diverse set of spiro epoxy-bridged tetrahydropyranone frameworks. We have not observed any 2:1 cycloadducts[4,14] similar to compound **26** from ylide **3** and products from either potential competitive C–H insertion[23] or cyclopropanation[24] reactions.



26

3. Conclusion

In summary, we have established the reactivity profiles of the transient five-membered-ring cyclic carbonyl ylides in the presence of various symmetrical/unsymmetrical 1,2-diones as heterodipolarophiles to afford spiro epoxy-bridged tetrahydropyranone derivatives as diastereomers in good yields. Diverse and structurally complex spiro dioxabicyclo[2.2.1]alkane ring systems were synthesized with complete regiocontrol. This tandem cyclization–cycloaddition process with the carbonyl group as the hetero-dipolarophile will be an attractive and useful method to synthesize naturally existing oxygen-rich spiro heterocyclic compounds.

4. Experimental

4.1. General

The melting points are uncorrected. The FT-IR spectra were recorded on a Perkin–Elmer Spectrum GX FT-IR spectrophotometer using KBr or neat method unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 200 (200 and 50.3 MHz, respectively) spectrometer and referenced to TMS. Carbon types were determined from DEPT ^{13}C NMR experiments. Chemical shift (δ) values are reported as parts per million (ppm). Mass analyses were performed on Jeol DX-303 (with an ionizing voltage of 70 eV) and Jeol M Station 700 (FD^+ method in absolute dichloromethane) mass spectrometers. Elemental analyses were performed on a Perkin–Elmer Model 2400 analyzer. Diffraction data for the compound is collected on a Bruker Smart CCD diffractometer with graphite monochromatized Mo K_α radiation (λ=0.71703 Å) at room temperature using the program SMART[25] and processed by SAINT.[26] Absorption correction was applied by SADABS.[27] The structure was solved by direct methods and refined using full-matrix least-squares/difference Fourier techniques using SHELXL 97.[28] All the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located from the difference Fourier map or placed at idealized positions and refined as riding atoms with the relative isotropic parameters to which they are attached. All reactions were carried out under an argon atmosphere. Analytical thin layer chromatography (TLC) was performed on silica/alumina plates and components were visualized by observation under iodine or by sulfuric acid charring. Column chromatography was performed on neutral alumina/silica gel (100–200 mesh). Care has been taken to avoid light during the course of reaction in the synthesis of α-diazo ketones and their further conversion. Dry dichloromethane was prepared using P_2O_5. α-Diazo ketones involved in this work were prepared according to our earlier work.[13b]

4.2. General procedure for the synthesis of N-protected isatins 21

To a suspension of sodium hydride (12 mmol) in dry DMF (10 mL) was added solution of isatin (10 mmol) in DMF (5 mL) at 0°C under an inert atmosphere and allowed to stir for 20 min. To this reaction mixture was added the appropriate alkyl halide (12 mmol) dropwise and stirred for 1 h at 0°C and 3 h at room temperature. After this period of time 25 mL of water was added and extracted using chloroform (3×30 mL). The combined organic layers were washed with brine solution and concentrated under reduced pressure. The resulted crude reaction mixture was purified using silica gel column chromatography to afford the respective N-protected isatins in very good yields.

4.2.1. Ethyl (2,3-dioxo-2,3-dihydroindol-1-yl)acetate (21d). Orange solid, mp 116–118°C (chloroform/hexane); [Found: C, 61.70; H, 4.71; N, 5.94. $C_{12}H_{11}NO_4$ requires C, 61.80; H, 4.75; N, 6.01%]; ν_{max} (KBr) 1744, 1616, 1470, 1345, 1213 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.64–7.57 (2H, m, =C*H*), 7.15 (1H, t, *J*=7.5 Hz, =C*H*), 6.83 (1H, d, *J*=7.5 Hz, =C*H*), 4.50 (2H, s, NCH_2), 4.24 (2H, q, *J*=7.1 Hz, OCH_2), 1.28 (3H, t, *J*=7.1 Hz, CH_2CH_3); δ_C (50.3 MHz, $CDCl_3$) 183.1 (quat-C), 167.2 (*C*OO), 158.5 (quat-C), 150.8 (quat-C), 139.0 (=*C*H), 125.9 (=*C*H), 124.6 (=*C*H), 118.0 (quat-C), 110.7 (=*C*H), 62.6 (OCH_2), 41.7 (NCH_2), 14.5 (CH_3).

4.2.2. Ethyl 2-(2,3-dioxo-2,3-dihydroindol-1-yl)propionate (21e). Red thick oil; [Found: C, 63.18; H, 5.24; N, 5.74. $C_{13}H_{13}NO_4$ requires C, 63.15; H, 5.30; N, 5.67%]; ν_{max} (neat) 2928, 1742, 1611, 1470, 1360 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.65–7.58 (2H, m, =C*H*), 7.16 (1H, t, *J*=7.5 Hz, =C*H*), 6.92 (1H, d, *J*=8.5 Hz, =C*H*), 5.15 (1H, q, *J*=7.3 Hz, NC*H*), 4.23 (2H, q, *J*=7.1 Hz, OCH_2), 1.71 (3H, d, *J*=7.3 Hz, CHCH_3), 1.24 (3H, t, *J*=7.1 Hz, CH_2CH_3); δ_C (50.3 MHz, $CDCl_3$) 183.0 (quat-C), 169.6 (*C*OO), 158.0 (quat-C), 149.8 (quat-C), 138.6 (=*C*H), 125.7 (=*C*H), 124.6 (=*C*H), 118.1 (quat-C), 111.8 (=*C*H), 62.4 (OCH_2), 49.6 (N*C*H), 14.5 (CH_3), 14.3 (CH_3).

4.3. General procedure for the $Rh_2(OAc)_4$ catalyzed reaction of α-diazo ketones with carbonyl compounds

In an oven-dried flask containing a solution of an equimolar mixture of α-diazo carbonyl compound (0.5 mmol) and the appropriate carbonyl compound (0.5 mmol) in a freshly dried DCM was added 1 mol% of rhodium(II) acetate dimer catalyst under an argon atmosphere at room temperature. The reaction mixture was stirred and monitored by TLC until the disappearance of the starting material, α-diazo ketone. The solvent was removed under reduced pressure and the crude residue was purified using silica gel/neutral alumina column (EtOAc/hexane) to afford the respective cycloadducts.

4.3.1. Reaction of α-diazo ketone 6 with cyclohexanone, synthesis of compound 7. A mixture of cyclohexanone (55 mg, 0.55 mmol) and α-diazo ketone **6** (85 mg, 0.55 mmol) was allowed to react with 2.4 mg of $Rh_2(OAc)_4$ in dry DCM (6 mL) for 3 h according to the general procedure to afford 43 mg (35%) of the cycloadduct **7** as a colorless thick oil; [Found: C, 69.71; H, 8.94. $C_{13}H_{20}O_3$ requires C, 69.61; H, 8.99%]; ν_{max} (neat) 2937, 1767, 1447, 1394, 1380, 1287, 1131 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 4.28 (1H, s, OC*H*), 1.78–1.42 (10H, m), 1.50 (3H, s, CH_3), 1.07 (6H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 215.1 (*C*=O), 113.5 (quat-C), 86.0 (O*C*H), 81.8 (quat-C), 54.0 (quat-C), 36.0 (CH_2), 33.2 (CH_2), 25.8 (CH_2), 23.7 (CH_2), 23.4 (CH_2), 21.8 (CH_3), 18.5 (CH_3), 16.0 (CH_3); *m*/*z* 224 (M^+).

4.3.2. Reaction of α-diazo ketone 6 with 6-methoxy-1-tetralone, synthesis of compound 8. A mixture of 6-methoxy-1-tetralone (95 mg, 0.55 mmol) and α-diazo ketone **6** (85 mg, 0.55 mmol) was allowed to react with 2.4 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 3 h according to the general procedure to afford 50 mg (30%) of the cycloadduct **8** as a mixture of diastereomers, (ratio of stereoisomers in the crude reaction mixture is 1:6.6, data for predominant isomer is given) colorless thick oil; [Found: C, 71.81; H, 7.37. $C_{18}H_{22}O_4$ requires C, 71.50; H, 7.33%]; ν_{max} (neat) 2996, 2938, 1764, 1613, 1494, 1275, 1260 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.57 (1H, d, J=9.6 Hz, arom-H), 6.76 (1H, dd, J_1=9.6 Hz, J_2=2.6 Hz, arom-H), 6.59 (1H, d, J=2.6 Hz, arom-H), 4.35 (1H, s, OCH), 3.77 (3H, s, OCH_3), 2.84–2.77 (2H, m), 2.06–1.75 (4H, m), 1.70 (3H, s, CH_3), 1.19 (3H, s, CH_3), 1.13 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 214.1 (C=O), 159.8 (quat-C), 138.6 (quat-C), 132.1 (quat-C), 129.8 (=CH), 114.2 (quat-C), 113.7 (=CH), 112.5 (=CH), 88.8 (OCH), 81.3 (quat-C), 55.7 (OCH$_3$), 53.9 (quat-C), 32.6 (CH$_2$), 29.5 (CH$_2$), 22.4 (CH$_3$), 20.7 (CH$_3$), 18.9 (CH$_3$), 15.4 (CH$_3$); m/z 302 (M$^+$).

4.3.3. Reaction of α-diazo ketone 6 with benzil, synthesis of compounds 12a,b. A mixture of benzil (270 mg, 1.3 mmol) and α-diazo ketone **6** (200 mg, 1.3 mmol) was allowed to react with 5.7 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 3.5 h according to the general procedure to afford 190 mg (44%) of **12a** and 130 mg (30%) of **12b**.

Compound **12a**. Pale yellow solid, mp 190–192°C (ethyl acetate/hexane); [Found: C, 74.92; H, 6.03. $C_{21}H_{20}O_4$ requires C, 74.98; H, 5.99%]; ν_{max} (KBr) 1773, 1674, 1596, 1448, 1394, 1306, 1270, 1131, 1112 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.99–7.94 (2H, m, arom-H), 7.67–7.63 (2H, m, arom-H), 7.47–7.25 (6H, m, arom-H), 4.85 (1H, s, OCH), 1.79 (3H, s, CH_3), 1.09 (3H, s, CH_3), 0.81 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 210.4 (C=O), 196.5 (C=O), 138.6 (quat-C), 134.7 (quat-C), 134.0 (=CH), 130.8 (=CH), 129.2 (=CH), 128.9 (=CH), 128.6 (=CH), 125.8 (=CH), 116.6 (quat-C), 91.3 (quat-C), 88.5 (OCH), 53.3 (quat-C), 21.9 (CH$_3$), 18.9 (CH$_3$), 15.8 (CH$_3$); m/z 336 (M$^+$, 10), 161 (100), 149 (18), 121 (18), 105 (95), 98 (16), 77 (55), 58 (88%).

Compound **12b**. Pale yellow solid, mp 127–129°C (ethyl acetate/hexane); [Found: C, 75.07; H, 5.97. $C_{21}H_{20}O_4$ requires C, 74.98; H, 5.99%]; ν_{max} (KBr) 1769, 1672, 1595, 1467, 1447, 1397, 1253, 1113 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.12–8.08 (2H, m, arom-H), 7.61–7.22 (8H, m, arom-H), 5.68 (1H, s, OCH), 1.52 (3H, s, CH_3), 1.08 (3H, s, CH_3), 1.05 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 211.6 (C=O), 197.6 (C=O), 135.3 (quat-C), 134.2 (quat-C), 133.3 (=CH), 130.8 (=CH), 129.2 (=CH), 129.1 (=CH), 128.4 (=CH), 126.7 (=CH), 116.6 (quat-C), 92.1 (quat-C), 87.3 (OCH), 54.5 (quat-C), 21.9 (CH$_3$), 18.1 (CH$_3$), 15.4 (CH$_3$); m/z 336 (M$^+$, 3), 294 (4), 231 (100), 224 (40), 165 (50), 161 (99), 135 (34), 106 (62), 91 (64), 89 (73%).

4.3.4. Reaction of α-diazo ketone 6 with acenaphthenequinone, synthesis of compounds 13a,b. A mixture of acenaphthenequinone (234 mg, 1.3 mmol) and α-diazo ketone **6** (200 mg, 1.3 mmol) was allowed to react with 5.7 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 2.5 h according to the general procedure to afford 160 mg (40%) of **13a** and 140 mg (35%) of **13b**.

Compound **13a**. Colorless solid, mp 215–217°C (ethyl acetate/hexane); [Found: C, 74.21; H, 5.19. $C_{19}H_{16}O_4$ requires C, 74.01; H, 5.23%]; ν_{max} (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, OCH), 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 (=CH), 132.3 (quat-C), 131.0 (quat-C), 129.9 (quat-C), 129.0 (=CH), 128.9 (=CH), 127.0 (=CH), 123.1 (=CH), 123.0 (=CH), 116.2 (quat-C), 86.0 (OCH), 83.7 (quat-C), 55.9 (quat-C), 22.5 (CH$_3$), 18.7 (CH$_3$), 15.2 (CH$_3$); m/z 308 (M$^+$, 10), 307 (16), 129 (19), 111 (17), 98 (30), 81 (32), 69 (62), 57 (100%).

Compound **13b**. Colorless solid, mp 133–135°C (chloroform/hexane); [Found: C, 73.89; H, 5.26. $C_{19}H_{16}O_4$ requires C, 74.01; H, 5.23%]; ν_{max} (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, OCH), 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 (=CH), 131.6 (quat-C), 131.0 (quat-C), 129.7 (=CH), 128.9 (=CH), 126.7 (=CH), 122.7 (=CH), 122.0 (=CH), 116.5 (quat-C), 87.5 (OCH), 86.1 (quat-C), 54.7 (quat-C), 22.7 (CH$_3$), 18.8 (CH$_3$), 15.7 (CH$_3$); m/z 308 (M$^+$, 58), 307 (80), 223 (59), 196 (50), 139 (45), 111 (42), 97 (64), 96 (51), 80 (49), 69 (100%).

4.3.5. Reaction of α-diazo ketone 6 with 1,2-naphthoquinone, synthesis of compounds 15a/b,16. A mixture of 1,2-naphthoquinone (205 mg, 1.3 mmol) and α-diazo ketone **6** (200 mg, 1.3 mmol) was allowed to react with 5.7 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 3.5 h according to the general procedure to afford 115 mg (31%) of **15a**, 33 mg (9%) of **15b** and 90 mg (25%) of **16**.

Compound **15a**. Pale yellow solid, mp 147–149°C (chloroform/hexane); [Found: C, 71.89; H, 5.70. $C_{17}H_{16}O_4$ requires C, 71.81; H, 5.67%]; ν_{max} (KBr) 1770, 1698, 1595, 1448, 1388, 1131 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.93 (1H, d, J=7.5 Hz, =CH), 7.61–7.53 (1H, m, =CH), 7.40–7.19 (2H, m, =CH), 6.67 (1H, d, J=10.0 Hz, =CH), 5.84 (1H, d, J=10.0 Hz, =CH), 4.52 (1H, s, OCH), 1.78 (3H, s, CH_3), 1.24 (3H, s, CH_3), 1.13 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 211.6 (C=O), 196.3 (C=O), 137.0 (quat-C), 135.0 (=CH), 130.7 (=CH), 129.5 (=CH), 129.4 (=CH), 128.2 (=CH), 127.9 (=CH), 116.7 (quat-C), 84.6 (OCH), 84.2 (quat-C), 55.1 (quat-C), 21.9 (CH$_3$), 18.5 (CH$_3$), 14.8 (CH$_3$); m/z 284 (M$^+$, 22), 227 (16), 185 (100), 172 (68), 171 (86), 131 (61), 115 (44), 97 (59), 77 (15%).

4.3.6. X-Ray crystal structure analysis. Crystal data for the compound 15a. $C_{17}H_{16}O_4$, M=284.30, 0.30×0.25×0.25 mm^3, rectangular, $P21/n$, a=6.1918(13) Å, b=16.309(3) Å, c=14.344(3) Å, β=93.936(4)°, V=1445.1(5) Å^3, T=293(2) K, R_1=0.0423, wR_2=0.1322 on observed data, z=4, D_{calcd}=1.307 g cm^{-3}, $F(000)$=600, absorption coefficient=0.093 mm^{-1}, λ=0.7107 Å, 2847 reflections were collected on a SMART APEX CCD diffractometer, 2393 observed reflections ($I\geq 2\sigma(I)$). The largest difference peak and hole=0.186 and −0.297e Å^{-3}, respectively.

Compound **15b**. Colorless solid, mp 123–125°C (ethyl acetate/hexane); [Found: C, 71.79; H, 5.61. $C_{17}H_{16}O_4$ requires C, 71.81; H, 5.67%]; ν_{max} (KBr) 1766, 1690, 1596, 1470, 1450, 1395, 1305, 917 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.93 (1H, d, *J*=7.5 Hz, =C*H*), 7.58–7.55 (1H, m, =C*H*), 7.38–7.19 (2H, m, =C*H*), 6.62 (1H, d, *J*=10.0 Hz, =C*H*), 6.22 (1H, d, *J*=10.0 Hz, =C*H*), 4.44 (1H, s, OC*H*), 1.67 (3H, s, C*H*$_3$), 1.45 (3H, s, C*H*$_3$), 1.14 (3H, s, C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 210.6 (*C*=O), 196.2 (*C*=O), 137.1 (quat-C), 136.0 (=*C*H), 134.7 (=*C*H), 130.5 (quat-C), 129.4 (=*C*H), 128.4 (=*C*H), 128.2 (=*C*H), 117.2 (quat-C), 89.5 (O*C*H), 85.6 (quat-C), 55.4 (quat-C), 22.8 (*C*H$_3$), 18.5 (*C*H$_3$), 16.1 (*C*H$_3$); *m*/*z* 284 (M$^+$).

Compound **16**. Mixture of stereoisomers in the ratio of 1:2.2, (data for predominant isomer is given) Orange–red solid, mp 165–167°C (ethyl acetate/hexane); [Found: C, 71.91; H, 5.63. $C_{17}H_{16}O_4$ requires C, 71.81; H, 5.67%]; ν_{max} (KBr) 2929, 1769, 1697, 1615, 1471, 1395, 1304 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.60–7.32 (4H, m, =C*H*), 6.17–6.10 (2H, m, =C*H*), 4.36 (1H, s, OC*H*), 1.84 (3H, s, C*H*$_3$), 1.40 (3H, s, C*H*$_3$), 1.13 (3H, s, C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 211.3 (*C*=O), 198.4 (*C*=O), 145.0 (=*C*H), 141.2 (quat-C), 130.7 (quat-C), 130.1 (=*C*H), 130.0 (=*C*H), 129.5 (=*C*H), 128.7 (=*C*H), 125.9 (=*C*H), 117.6 (quat-C), 90.9 (O*C*H), 90.2 (quat-C), 54.9 (quat-C), 22.9 (*C*H$_3$), 17.6 (*C*H$_3$), 15.1 (*C*H$_3$); *m*/*z* 284 (M$^+$).

4.3.7. Reaction of α-diazo ketone 9a with 1,2-naphthoquinone, synthesis of compounds 18a/b,19. A mixture of 1,2-naphthoquinone (200 mg, 1.3 mmol) and α-diazo ketone **9a** (225 mg, 1.3 mmol) was allowed to react with 5.7 mg of $Rh_2(OAc)_4$ in dry DCM (15 mL) for 3.5 h according to the general procedure to afford 120 mg (30%) of **18a**, 30 mg (8%) of **18b** and 75 mg (19%) of **19**.

Compound **18a**. Pale yellow solid, mp 151–153°C (chloroform/hexane); [Found: C, 73.60; H, 5.89. $C_{19}H_{18}O_4$ requires C, 73.53; H, 5.85%]; ν_{max} (KBr) 2940, 1763, 1692, 1595, 1450, 1377, 1290, 1229, 1094 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.94–7.90 (1H, m, =C*H*), 7.61–7.53 (1H, m, =C*H*), 7.40–7.32 (1H, m, =C*H*), 7.20 (1H, d, *J*=7.5 Hz, =C*H*), 6.67 (1H, d, *J*=10.0 Hz, =C*H*), 5.87 (1H, d, *J*=10.0 Hz, =C*H*), 4.58 (1H, s, OC*H*), 2.43–1.48 (8H, m), 1.27 (3H, s, C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 211.0 (*C*=O), 196.3 (*C*=O), 137.0 (quat-C), 135.3 (=*C*H), 130.6 (=*C*H), 129.7 (=*C*H), 129.5 (quat-C), 129.4 (=*C*H), 128.2 (=*C*H), 128.0 (=*C*H), 115.8 (quat-C), 84.9 (O*C*H), 84.2 (quat-C), 54.4 (quat-C), 32.1 (*C*H$_2$), 26.7 (*C*H$_2$), 23.6 (*C*H$_2$), 20.5 (*C*H$_2$), 15.4 (*C*H$_3$); *m*/*z* 310 (M$^+$, 35), 198 (16), 184 (21), 170 (100), 160 (29), 131 (51), 123 (61), 115 (43), 111 (26), 83 (47%).

Compound **18b**. Colorless liquid (data for predominant isomer is given); [Found: C, 73.49; H, 5.79. $C_{19}H_{18}O_4$ requires C, 73.53; H, 5.85%]; ν_{max} (neat) 2939, 1767, 1692, 1596, 1455, 1375, 1297 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.93 (1H, d, *J*=7.5 Hz, =C*H*), 7.73–7.54 (1H, m, =C*H*), 7.47–7.26 (1H, m, =C*H*), 7.20 (1H, d, *J*=7.5 Hz, =C*H*), 6.11 (1H, d, *J*=10.0 Hz, =C*H*), 6.19 (1H, d, *J*=10.0 Hz, =C*H*), 4.49 (1H, s, OC*H*), 2.13–1.15 (8H, m), 1.48 (3H, s, C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 210.0 (*C*=O), 196.9 (*C*=O), 137.0 (quat-C), 135.8 (=*C*H), 136.5 (=*C*H), 130.4 (quat-C), 129.2 (=*C*H), 128.2 (=*C*H), 128.0 (=*C*H), 116.2 (quat-C), 89.6 (O*C*H), 85.5 (quat-C), 54.6 (quat-C), 34.1 (*C*H$_2$), 27.8 (*C*H$_2$), 23.8 (*C*H$_2$), 20.5 (*C*H$_2$), 15.1 (*C*H$_3$); *m*/*z* 310 (M$^+$).

Compound **19**. Mixture of stereoisomers in the ratio of 1:3.4, (data for predominant isomer is given) orange–red solid, mp 187–189°C (ethyl acetate/hexane); [Found: C, 73.47; H, 5.89. $C_{19}H_{18}O_4$ requires C, 73.53; H, 5.85%]; ν_{max} (KBr) 2942, 1765, 1684, 1374, 1031 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.58–7.54 (1H, m, =C*H*), 7.44–7.31 (3H, m, =C*H*), 6.17–6.12 (2H, m, =C*H*), 4.39 (1H, s, OC*H*), 2.42–1.50 (8H, m), 1.46 (3H, s, C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 210.8 (*C*=O), 198.3 (*C*=O), 144.9 (=*C*H), 141.1 (quat-C), 130.4 (quat-C), 130.1 (=*C*H), 130.0 (=*C*H), 129.4 (=*C*H), 128.6 (=*C*H), 125.9 (=*C*H), 116.6 (quat-C), 91.2 (O*C*H), 86.3 (quat-C), 54.3 (quat-C), 32.8 (*C*H$_2$), 26.9 (*C*H$_2$), 23.8 (*C*H$_2$), 20.4 (*C*H$_2$), 14.3 (*C*H$_3$); *m*/*z* 310 (M$^+$).

4.3.8. Reaction of α-diazo ketone 9a with 21a, synthesis of compounds 22a,23a. A mixture of **21a** (160 mg, 1.0 mmol) and α-diazo ketone **9a** (180 mg, 1.0 mmol) was allowed to react with 4.4 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 4 h according to the general procedure to afford 166 mg (53%) of **22a** and 105 mg (34%) of **23a**.

Compound **22a**. Colorless solid, mp 222–224°C (ethyl acetate/hexane); [Found: C, 69.09; H, 6.12; N, 4.49. $C_{18}H_{19}NO_4$ requires C, 69.00; H, 6.11; N, 4.47%]; ν_{max} (KBr) 2940, 1768, 1717, 1612, 1473, 1377, 1353, 1095 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.50 (1H, d, *J*=7.5 Hz, =C*H*), 7.35 (1H, t, *J*=7.5 Hz, =C*H*), 7.08 (1H, t, *J*=7.5 Hz, =C*H*), 6.81 (1H, d, *J*=7.5 Hz, =C*H*), 4.53 (1H, s, OC*H*), 3.16 (3H, s, NC*H*$_3$), 2.18–1.18 (8H, m), 1.46 (3H, s, C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 209.3 (*C*=O), 172.2 (N*C*=O), 143.4 (quat-C), 131.0 (=*C*H), 128.4 (quat-C), 125.2 (=*C*H), 123.8 (=*C*H), 115.3 (quat-C), 108.9 (=*C*H), 88.4 (quat-C), 87.3 (O*C*H), 53.5 (quat-C), 32.8 (*C*H$_2$), 27.3 (*C*H$_2$), 26.9 (*C*H$_3$), 23.7 (*C*H$_2$), 20.4 (*C*H$_2$), 15.6 (*C*H$_3$); *m*/*z* 313 (M$^+$, 31), 187 (47), 162 (21), 152 (26), 123 (100), 111 (39), 95 (34), 83 (48), 69 (29), 67 (26%).

Compound **23a**. Colorless solid, mp 207–209°C (ethyl acetate/hexane); [Found: C, 69.12; H, 6.08; N, 4.45. $C_{18}H_{19}NO_4$ requires C, 69.00; H, 6.11; N, 4.47%]; ν_{max} (KBr) 1768, 1716, 1613, 1473, 1377 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.39–7.31 (1H, m, =C*H*), 7.08–7.01 (2H, m, =C*H*), 6.81 (1H, d, *J*=7.5 Hz, =C*H*), 4.69 (1H, s, OC*H*), 3.17 (3H, s, NC*H*$_3$), 2.30–1.46 (8H, m), 1.42 (3H, s, C*H*$_3$); δ_C (50.3 MHz, $CDCl_3$) 209.7 (*C*=O), 174.0 (N*C*=O), 144.8 (quat-C), 131.2 (=*C*H), 126.1 (=*C*H), 123.0 (=*C*H), 122.2 (quat-C), 115.0 (quat-C), 108.9 (=*C*H), 87.0 (quat-C), 85.9 (O*C*H), 54.9 (quat-C), 32.2 (*C*H$_2$), 26.9 (*C*H$_2$), 26.8 (N*C*H$_3$), 23.4 (*C*H$_2$), 20.3 (*C*H$_2$), 15.1 (*C*H$_3$); *m*/*z* 313 (M$^+$).

4.3.9. Reaction of α-diazo ketone 9b with 21a, synthesis of compounds 22b,23b. A mixture of **21a** (160 mg, 1.0 mmol) and α-diazo ketone **11b** (165 mg, 1.0 mmol) was allowed to react with 4.4 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 3.5 h according to the general procedure to afford 129 mg (43%) of **22b** and 87 mg (29%) of **23b**.

Compound **22b**. Colorless solid, mp 225–227°C (ethyl acetate/hexane); [Found: C, 68.10; H, 5.66; N, 4.64.

$C_{17}H_{17}NO_4$ requires C, 68.21; H, 5.72; N, 4.68%]; ν_{max} (KBr) 1767, 1717, 1613, 1473, 1377 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.51 (1H, d, J=7.5 Hz, =C*H*), 7.34 (1H, t, J=7.5 Hz, =C*H*), 7.09 (1H, t, J=7.5 Hz, =C*H*), 6.82 (1H, d, J=7.5 Hz, =C*H*), 4.56 (1H, s, OC*H*), 3.17 (3H, s, NCH_3), 2.10–1.18 (6H, m), 1.32 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 209.2 (*C*=O), 172.3 (N*C*=O), 143.5 (quat-C), 131.1 (=*C*H), 128.3 (quat-C), 125.1 (=*C*H), 123.7 (=*C*H), 115.5 (quat-C), 108.8 (=*C*H), 88.5 (quat-C), 87.5 (O*C*H), 58.6 (quat-C), 34.0 (*C*H_2), 26.9 (*C*H_3), 26.6 (*C*H_2), 23.7 (*C*H_2), 21.3 (*C*H_3); *m/z* 299 (M^+).

Compound **23b**. Colorless solid, mp 209–211°C (ethyl acetate/hexane); [Found: C, 68.19; H, 5.65; N, 4.73. $C_{17}H_{17}NO_4$ requires C, 68.21; H, 5.72; N, 4.68%]; ν_{max} (KBr) 2940, 1768, 1717, 1612, 1473, 1377, 1353 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.37–7.31 (1H, m, =C*H*), 7.08–7.00 (2H, m, =C*H*), 6.81 (1H, d, J=7.5 Hz, =C*H*), 4.70 (1H, s, OC*H*), 3.16 (3H, s, NCH_3), 2.20–1.46 (6H, m), 1.31 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 209.8 (*C*=O), 174.1 (N*C*=O), 144.9 (quat-C), 131.0 (=*C*H), 126.2 (=*C*H), 123.1 (=*C*H), 122.2 (quat-C), 115.2 (quat-C), 108.8 (=*C*H), 87.3 (quat-C), 85.7 (O*C*H), 59.0 (quat-C), 34.0 (*C*H_2), 26.9 (*C*H_3), 26.6 (*C*H_2), 23.7 (*C*H_2), 21.3 (*C*H_3); *m/z* 299 (M^+).

4.3.10. Reaction of α-diazo ketone 9a with 21b, synthesis of compounds 22c,23c. A mixture of **21b** (150 mg, 1.0 mmol) and α-diazo ketone **9a** (180 mg, 1.0 mmol) was allowed to react with 4.4 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 3 h according to the general procedure to afford 139 mg (46%) of **22c** and 90 mg (30%) of **23c**.

Compound **22c**. Colorless solid, mp 230–232°C (ethyl acetate/hexane); [Found: C, 68.40; H, 5.73; N, 4.64. $C_{17}H_{17}NO_4$ requires C, 68.21; H, 5.72; N, 4.68%]; ν_{max} (KBr) 3169, 1770, 1727, 1623, 1470, 1377 cm^{-1}; δ_H (200 MHz, CD_3CN/CD_2Cl_2) 8.67 (1H, br s, N*H*), 7.43 (1H, d, J=7.5 Hz, =C*H*), 7.29 (1H, t, J=7.5 Hz, =C*H*), 7.03 (1H, t, J=7.5 Hz, =C*H*), 6.88 (1H, d, J=7.5 Hz, =C*H*), 4.60 (1H, s, OC*H*), 2.15–1.50 (8H, m), 1.35 (3H, s, CH_3); δ_C (50.3 MHz, CD_3CN/CD_2Cl_2) 208.8 (*C*=O), 173.3 (N*C*=O), 141.1 (quat-C), 130.6 (=*C*H), 128.9 (quat-C), 125.1 (=*C*H), 123.0 (=*C*H), 114.9 (quat-C), 110.3 (=*C*H), 87.1 (O*C*H), 81.6 (quat-C), 53.0 (quat-C), 32.6 (*C*H_2), 26.9 (*C*H_2), 23.4 (*C*H_2), 20.0 (*C*H_2), 14.9 (*C*H_3); *m/z* 299 (M^+, 42), 173 (44), 161 (36), 145 (18), 123 (100), 111 (27), 95 (26), 81 (31), 77 (15), 55 (50%).

Compound **23c**. Colorless solid, mp 240–242°C (ethyl acetate/hexane); [Found: C, 68.31; H, 5.70; N, 4.67. $C_{17}H_{17}NO_4$ requires C, 68.21; H, 5.72; N, 4.68%]; ν_{max} (KBr) 3313, 2938, 1768, 1746, 1619, 1474, 1206 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 9.14 (1H, br s, N*H*), 7.31–7.23 (1H, m, =C*H*), 7.02–6.91 (3H, m, =C*H*), 4.77 (1H, s, OC*H*), 2.36–1.11 (8H, m), 1.43 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 209.7 (*C*=O), 176.8 (N*C*=O), 142.2 (quat-C), 131.4 (=*C*H), 126.5 (=*C*H), 123.2 (=*C*H), 122.7 (quat-C), 115.4 (quat-C), 111.5 (=*C*H), 86.1 (O*C*H), 80.5 (quat-C), 55.1 (quat-C), 32.4 (*C*H_2), 27.0 (*C*H_2), 23.6 (*C*H_2), 20.4 (*C*H_2), 15.3 (*C*H_3); *m/z* 299 (M^+, 23), 153 (20), 139 (21), 123 (100), 119 (24), 111 (56), 97 (38), 85 (36), 83 (54), 67 (51%).

4.3.11. X-Ray crystal structure analysis. Crystal data for the compound 23c. $C_{17}H_{17}NO_4$, M=299.32, 0.30×0.30×0.25 mm^3, monoclinic, $P21/c$, a=10.806(16) Å, b=11.902(18) Å, c=15.36(2) Å, β=107.35(2)°, V=1885(5) Å^3, T=293(2) K, R_1=0.1029, wR_2=0.2227 on observed data, z=4, D_{calcd}=1.055 g cm^{-3}, F(000)=632, absorption coefficient=0.075 mm^{-1}, λ=0.7107 Å, 3279 reflections were collected on a SMART APEX CCD diffractometer, 1716 observed reflections ($I \geq 2\sigma(I)$). The largest difference peak and hole=0.247 and $-0.366e$ Å^{-3}, respectively.

4.3.12. Reaction of α-diazo ketone 6 with 21a, synthesis of compounds 24a,25a. A mixture of **21a** (260 mg, 1.6 mmol) and α-diazo ketone **6** (250 mg, 1.6 mmol) was allowed to react with 7.0 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 4 h according to the general procedure to afford 230 mg (50%) of **24a** and 165 mg (36%) of **25a**.

Compound **24a**. Colorless solid, mp 222–224°C (ethyl acetate/hexane); [Found: C, 66.95; H, 6.01; N, 4.85. $C_{16}H_{17}NO_4$ requires C, 66.89; H, 5.96; N, 4.88%]; ν_{max} (KBr) 1771, 1719, 1613, 1495, 1472, 1377, 1110 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.51 (1H, d, J=7.5 Hz, =C*H*), 7.35 (1H, t, J=7.5 Hz, =C*H*), 7.08 (1H, t, J=7.5 Hz, =C*H*), 6.81 (1H, d, J=7.5 Hz, =C*H*), 4.48 (1H, s, OC*H*), 3.16 (3H, s, NCH_3), 1.70 (3H, s, CH_3), 1.42 (3H, s, CH_3), 1.19 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 209.7 (*C*=O), 172.2 (N*C*=O), 143.6 (quat-C), 131.2 (=*C*H), 128.6 (quat-C), 125.4 (=*C*H), 124.0 (=*C*H), 116.4 (quat-C), 109.0 (=*C*H), 87.2 (O*C*H), 81.7 (quat-C), 54.3 (quat-C), 27.0 (*C*H_3), 22.6 (*C*H_3), 18.9 (*C*H_3), 15.6 (*C*H_3); *m/z* 287 (M^+).

Compound **25a**. Colorless solid, mp 207–209°C (ethyl acetate/hexane); [Found: C, 66.81; H, 6.00; N, 4.79. $C_{16}H_{17}NO_4$ requires C, 66.89; H, 5.96; N, 4.88%]; ν_{max} (KBr) 1773, 1730, 1614, 1488, 1468, 1268 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.37–7.29 (1H, m, =C*H*), 7.01–6.97 (2H, m, =C*H*), 6.80 (1H, d, J=7.5 Hz, =C*H*), 4.63 (1H, s, OC*H*), 3.15 (3H, s, NCH_3), 1.73 (3H, s, CH_3), 1.38 (3H, s, CH_3), 1.21 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 210.2 (*C*=O), 173.9 (N*C*=O), 144.9 (quat-C), 131.2 (=*C*H), 135.9 (=*C*H), 122.9 (=*C*H), 122.1 (quat-C), 115.9 (quat-C), 109.0 (=*C*H), 85.6 (O*C*H), 79.8 (quat-C), 55.6 (quat-C), 26.8 (*C*H_3), 22.3 (*C*H_3), 18.4 (*C*H_3), 15.0 (*C*H_3); *m/z* 287 (M^+).

4.3.13. Reaction of α-diazo ketone 6 with 21b, synthesis of compounds 24b,25b. A mixture of **21b** (150 mg, 1.0 mmol) and α-diazo ketone **6** (155 mg, 1.0 mmol) was allowed to react with 4.4 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 4 h according to the general procedure to afford 170 mg (62%) of **24b** and 60 mg (22%) of **25b**.

Compound **24b**. Pale yellow solid, mp 230–232°C (ethyl acetate/hexane); [Found: C, 65.81; H, 5.59; N, 5.14. $C_{15}H_{15}NO_4$ requires C, 65.92; H, 5.53; N, 5.13%]; ν_{max} (KBr) 3284, 1771, 1736, 1620, 1472, 913 cm^{-1}; δ_H (200 MHz, $CD_3CN/CDCl_3$) 8.67 (1H, br s, N*H*), 7.46 (1H, d, J=7.5 Hz, =C*H*), 7.03 (1H, t, J=7.5 Hz, =C*H*), 7.27 (1H, t, J=7.5 Hz, =C*H*), 6.87 (1H, d, J=7.5 Hz, =C*H*), 4.52 (1H, s, OC*H*), 1.69 (3H, s, CH_3), 1.35 (3H, s, CH_3), 1.16 (3H, s, CH_3); δ_C (50.3 MHz, $CD_3CN/CDCl_3$) 209.2

(*C*=O), 173.3 (N*C*=O), 140.7 (quat-C), 130.5 (=*C*H), 128.5 (quat-C), 125.0 (=*C*H), 123.0 (=*C*H), 115.8 (quat-C), 110.4 (=*C*H), 86.6 (O*C*H), 81.4 (quat-C), 53.6 (quat-C), 21.8 (CH_3), 18.1 (CH_3), 14.8 (CH_3); *m/z* 273 (M^+, 16), 203 (18), 161 (100), 126 (16), 97 (58), 69 (15%).

Compound **25b**. Pale yellow solid, mp 245–247°C (ethyl acetate/hexane); [Found: C, 65.89; H, 5.51; N, 5.15. $C_{15}H_{15}NO_4$ requires C, 65.92; H, 5.53; N, 5.13%]; ν_{max} (KBr) 3180, 1774, 1730, 1620, 1469, 1209, 1130 cm^{-1}; δ_H (200 MHz, CD_3CN) 8.67 (1H, br s, N*H*), 7.35–7.25 (1H, m, =C*H*), 6.98–6.88 (3H, m, =C*H*), 4.79 (1H, s, OC*H*), 1.66 (3H, s, CH_3), 1.34 (3H, s, CH_3), 1.17 (3H, s, CH_3); δ_C (50.3 MHz, CD_3CN) 209.9 (*C*=O), 174.6 (N*C*=O), 142.4 (quat-C), 130.7 (=*C*H), 125.7 (=*C*H), 121.7 (=*C*H), 118.1 (quat-C), 115.4 (quat-C), 110.2 (=*C*H), 85.1 (O*C*H), 79.5 (quat-C), 54.9 (quat-C), 21.1 (CH_3), 17.2 (CH_3), 13.9 (CH_3); *m/z* 273 (M^+, 31), 213 (19), 149 (23), 132 (24), 126 (44), 111 (26), 97 (85), 85 (40), 71 (49), 69 (62), 57 (100%).

4.3.14. Reaction of α-diazo ketone 6 with 21c, synthesis of compounds 24c,25c. A mixture of **21c** (260 mg, 1.1 mmol) and α-diazo ketone **6** (170 mg, 1.1 mmol) was allowed to react with 4.8 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 3.5 h according to the general procedure to afford 196 mg (49%) of **24c** and 142 mg (35%) of **25c**.

Compound **24c**. Colorless thick oil; [Found: C, 72.61; H, 5.85; N, 3.82. $C_{22}H_{21}NO_4$ requires C, 72.71; H, 5.82; N, 3.85%]; ν_{max} (KBr) 1773, 1730, 1614, 1487, 1469, 1363, 1268 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.52 (1H, d, *J*=7.5 Hz, =C*H*), 7.26–7.16 (6H, m, =C*H*), 7.03 (1H, t, *J*=7.5 Hz, =C*H*), 6.69 (1H, d, *J*=7.5 Hz, =C*H*), 4.91 (1H, d, *J*=15.5 Hz, NC*H*), 4.76 (1H, d, *J*=15.5 Hz, NC*H*), 4.51 (1H, s, OC*H*), 1.71 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.20 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 209.4 (*C*=O), 172.3 (N*C*=O), 142.5 (quat-C), 135.6 (quat-C), 130.9 (=*C*H), 129.3 (=*C*H), 128.5 (quat-C), 128.3 (=*C*H), 127.8 (=*C*H), 125.4 (=*C*H), 123.9 (=*C*H), 116.5 (quat-C), 110.0 (=*C*H), 87.2 (O*C*H), 81.7 (quat-C), 54.2 (quat-C), 44.6 (NCH_2), 22.5 (CH_3), 18.9 (CH_3), 15.5 (CH_3); *m/z* 363 (M^+).

Compound **25c**. Colorless thick oil; [Found: C, 72.73; H, 5.80; N, 3.82. $C_{22}H_{21}NO_4$ requires C, 72.71; H, 5.82; N, 3.85%]; ν_{max} (KBr) 1771, 1732, 1614, 1489, 1468, 1362, 1269 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.32–7.18 (6H, m, =C*H*), 7.04–6.97 (2H, m, =C*H*), 6.71 (1H, d, *J*=7.5 Hz, =C*H*), 4.96 (1H, d, *J*=15.5 Hz, NC*H*), 4.77 (1H, d, *J*=15.5 Hz, NC*H*), 4.69 (1H, s, OC*H*), 1.78 (3H, s, CH_3), 1.41 (3H, s, CH_3), 1.24 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 210.4 (*C*=O), 173.8 (N*C*=O), 144.1 (quat-C), 135.9 (quat-C), 131.3 (=*C*H), 129.4 (=*C*H), 128.4 (=*C*H), 127.9 (=*C*H), 126.2 (=*C*H), 123.2 (=*C*H), 122.2 (quat-C), 116.3 (quat-C), 110.1 (=*C*H), 86.0 (O*C*H), 80.2 (quat-C), 55.9 (quat-C), 44.6 (NCH_2), 22.5 (CH_3), 18.6 (CH_3), 15.2 (CH_3); *m/z* 363 (M^+).

4.3.15. Reaction of α-diazo ketone 6 with 21d, synthesis of compounds 24d,25d. A mixture of **21d** (285 mg, 1.2 mmol) and α-diazo ketone **6** (190 mg, 1.2 mmol) was allowed to react with 5.3 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 3 h according to the general procedure to afford 300 mg (68%) of **24d** and 115 mg (26%) of **25d**.

Compound **24d**. Pale yellow solid, mp 145–147°C (ethyl acetate/hexane); [Found: C, 63.55; H, 5.85; N, 3.92. $C_{19}H_{21}NO_6$ requires C, 63.50; H, 5.89; N, 3.90%]; ν_{max} (KBr) 1780, 1738, 1612, 1379, 1356, 1231 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.29 (1H, d, *J*=7.5 Hz, =C*H*), 7.06 (1H, t, *J*=7.5 Hz, =C*H*), 6.84 (1H, t, *J*=7.5 Hz, =C*H*), 6.47 (1H, d, *J*=7.5 Hz, =C*H*), 4.25 (1H, s, OC*H*), 4.14 (2H, d, *J*=6.9 Hz, NCH_2), 3.95 (2H, q, *J*=7.1 Hz, OCH_2), 1.45 (3H, s, CH_3), 1.14 (3H, s, CH_3), 0.98 (3H, t, *J*=7.1 Hz, CH_2CH_3), 0.93 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 209.1 (*C*=O), 172.2 (N*C*=O), 167.4 (*C*OO), 142.1 (quat-C), 130.9 (=*C*H), 128.2 (quat-C), 125.4 (=*C*H), 124.0 (=*C*H), 116.4 (quat-C), 109.0 (=*C*H), 87.1 (O*C*H), 81.4 (quat-C), 62.2 (OCH_2), 54.0 (quat-C), 41.9 (NCH_2), 22.3 (CH_3), 18.7 (CH_3), 15.3 (CH_3), 14.4 (CH_3); *m/z* 359 (M^+, 14), 247 (26), 186 (25), 164 (28), 155 (41), 140 (40), 126 (44), 98 (42), 78 (64), 70 (58), 55 (100%).

Compound **25d**. Pale yellow solid, mp 196–198°C (ethyl acetate/hexane); [Found: C, 63.41; H, 5.88; N, 3.89. $C_{19}H_{21}NO_6$ requires C, 63.50; H, 5.89; N, 3.90%]; ν_{max} (KBr) 1767, 1733, 1611, 1491, 1467, 1367, 1239 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.36–7.27 (1H, m, =C*H*), 7.04–7.02 (2H, m, =C*H*), 6.71 (1H, d, *J*=7.5 Hz, =C*H*), 4.70 (1H, s, OC*H*), 4.55 (1H, d, *J*=17.5 Hz, NC*H*), 4.27 (1H, d, *J*=17.5 Hz, NC*H*), 4.20 (2H, q, *J*=7.1 Hz, OCH_2), 1.75 (3H, s, CH_3), 1.40 (3H, s, CH_3), 1.25 (3H, t, *J*=7.1 Hz, CH_3), 1.23 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 210.1 (*C*=O), 174.0 (N*C*=O), 167.6 (*C*OO), 143.6 (quat-C), 131.3 (=*C*H), 126.3 (=*C*H), 123.4 (=*C*H), 122.0 (quat-C), 116.3 (quat-C), 109.1 (=*C*H), 85.9 (O*C*H), 80.1 (quat-C), 62.4 (OCH_2), 55.8 (quat-C), 42.0 (NCH_2), 22.4 (CH_3), 18.5 (CH_3), 15.1 (CH_3), 14.6 (CH_3); *m/z* 359 (M^+, 14), 247 (32), 234 (42), 206 (13), 146 (10), 126 (29), 97 (100), 83 (72%).

4.3.16. Reaction of α-diazo ketone 6 with 21e, synthesis of compounds 24e,25e. A mixture of **21e** (320 mg, 1.3 mmol) and α-diazo ketone **6** (200 mg, 1.3 mmol) was allowed to react with 5.7 mg of $Rh_2(OAc)_4$ in dry DCM (10 mL) for 3 h according to the general procedure to afford 215 mg (45%) of **24e** and 159 mg (33%) of **25e**.

Compound **24e**. Mixture of stereoisomers in the ratio of 1:2.6, thick oil; [Found: C, 64.32; H, 6.26; N, 3.74. $C_{20}H_{23}NO_6$ requires C, 64.33; H, 6.21; N, 3.75%]; ν_{max} (neat) 2980, 1774, 1732, 1613, 1468, 1396, 1227 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.56 (1H, d, *J*=7.5 Hz, =C*H*), 7.31 (1H, t, *J*=7.5 Hz, =C*H*), 7.09 (1H, t, *J*=7.5 Hz, =C*H*), 6.78 (1H, d, *J*=7.5 Hz, =C*H*), 4.98 (1H, q, *J*=7.3 Hz, NC*H*), 4.49 (1H, s, OC*H*), 4.20 (2H, q, *J*=7.1 Hz, OCH_2), 1.72 (3H, s, CH_3), 1.62 (3H, d, *J*=7.3 Hz, CH_3), 1.41 (3H, s, CH_3), 1.19 (3H, s, CH_3), 1.17 (3H, t, *J*=7.1 Hz, CH_2CH_3); δ_C (50.3 MHz, $CDCl_3$) 209.2 (*C*=O), 171.8 (N*C*=O), 170.1 (*C*OO), 141.4 (quat-C), 130.8 (=*C*H), 128.5 (quat-C), 125.6 (=*C*H), 123.9 (=*C*H), 116.5 (quat-C), 109.8 (=*C*H), 87.2 (O*C*H), 81.4 (quat-C), 62.3 (OCH_2), 54.1 (quat-C), 49.7 (N*C*H), 22.5 (CH_3), 18.8 (CH_3), 15.5 (CH_3), 14.8 (CH_3), 14.4 (CH_3); *m/z* 373 (M^+).

Compound **25e**. Mixture of stereoisomers in the ratio of 1:1.3, thick oil; [Found: C, 64.39; H, 6.26; N, 3.72. $C_{20}H_{23}NO_6$ requires C, 64.33; H, 6.21; N, 3.75%]; ν_{max} (neat) 1770, 1722, 1608, 1488, 1467, 1360, 1217 cm^{-1}; δ_H

(200 MHz, $CDCl_3$) 7.35–7.26 (1H, m, $=$C*H*), 7.04–7.01 (2H, m, $=$C*H*), 6.78 (1H, d, *J*=7.5 Hz, $=$C*H*), 4.95 (1H, q, *J*=7.3 Hz, NC*H*), 4.67 (1H, s, OC*H*), 4.16 (2H, q, *J*=7.1 Hz, OCH_2), 1.76 (3H, s, CH_3), 1.63 (3H, d, *J*=7.3 Hz, CH_3), 1.41 (3H, s, CH_3), 1.28 (3H, s, CH_3), 1.20 (3H, t, *J*=7.1 Hz, CH_3); δ_C (50.3 MHz, $CDCl_3$) 210.0 (*C*=O), 173.5 (N*C*=O), 170.2 (*C*OO), 142.8 (quat-C), 131.0 ($=$*C*H), 126.3 ($=$*C*H), 123.0 ($=$*C*H), 122.1 (quat-C), 116.1 (quat-C), 109.6 ($=$*C*H), 85.8 (O*C*H), 79.9 (quat-C), 62.2 (OCH_2), 55.7 (quat-C), 49.6 (N*C*H), 22.3 (CH_3), 18.3 (CH_3), 15.0 (CH_3), 14.7 (CH_3), 14.5 (CH_3); *m/z* 373 (M^+).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication numbers CCDC 205863 and CCDC 206864. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-(0)1223-336033 or e-mail: deposit@CCDC.cam.ac.uk].

Acknowledgements

This research was supported by Department of Science and Technology, New Delhi. We thank Dr P. K. Ghosh, Director, for his encouragement. S. A. B. thanks CSIR, New Delhi for a Fellowship.

References

1. *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5. Chapters 1–9. *Cycloaddition Reactions in Organic synthesis*; Carruthers, W., Ed.; Pergamon: Oxford, 1990. Gothelf, K. V.; Jorgenson, K. A. *Chem. Rev.* **1998**, *98*, 863–909. Grigg, R. *Chem. Soc. Rev.* **1987**, *16*, 89–121.
2. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds. From Cyclopropanes to Ylides*; Doyle, M. P., McKervey, M. A., Ye, T., Eds.; Wiley: New York, 1998. *Diazo Compounds—Properties and Synthesis*; Regitz, M., Mass, G., Eds.; Academic: New York, 1986. Ye, T.; McKervey, A. *Chem. Rev.* **1994**, *94*, 1091–1160. Miller, D. J.; Moody, C. J. *Tetrahedron* **1995**, *51*, 10811–10843. Padwa, A.; Hornbuckle, S. A. *Chem. Rev.* **1991**, *91*, 263–309. Mass, G. *Top. Curr. Chem.* **1987**, *137*, 75–253.
3. Mehta, G.; Muthusamy, S. *Tetrahedron* **2002**, *58*, 9477–9504. Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223–269. Padwa, A. *Acc. Chem. Res.* **1991**, *24*, 22–28. Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385–5453. Calter, M. A. *Curr. Org. Chem.* **1997**, *1*, 37–70.
4. Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100–3109.
5. Hodgson, D. M.; Bailley, J. M.; Villalonga-Barber, C.; Drew, M. G. B.; Harrison, T. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3432–3443. Kataoka, O.; Kitagaki, S.; Watanabe, N.; Kobayashi, J.; Nakumura, S.; Shiro, M.; Hashimoto, S. *Tetrahedron Lett.* **1998**, *39*, 2371–2374. Koyoma, H.; Ball, R. G.; Berger, G. D. *Tetrahedron Lett.* **1994**, *35*, 9185–9188.
6. Whitesell, J. K.; Buchanan, C. M. *J. Org. Chem.* **1986**, *51*, 5443–5445.
7. Kongkathip, B.; Kongkathip, N.; Janthorn, S.; Virarangsiyakorn, D. *Chem. Lett.* **1999**, 51–52.
8. Paquette, L. A.; Wang, T. Z.; Sivik, M. R. *J. Am. Chem. Soc.* **1994**, *116*, 2665–2666.
9. Loukaci, A.; Kayser, O.; Bindseil, K-U.; Siems, K.; Frevert, J.; Abreu, P. M. *J. Nat. Prod.* **2000**, *63*, 52–56.
10. Mahmoud, A. A. *Phytochemistry* **1997**, *45*, 1633–1638.
11. Corley, D. G.; Rottinghaus, G. E.; Tempesta, M. S. *Tetrahedron Lett.* **1986**, *27*, 427–430.
12. Tomono, Y.; Hirota, H.; Fusetani, N. *J. Org. Chem.* **1999**, *64*, 2272–2275.
13. Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.* **2002**, *43*, 3931–3934. Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Suresh, E.; Dastidar, P.; Jasra, R. V. *Tetrahedron* **2000**, *56*, 6307–6318. Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Suresh, E.; Dastidar, P. *Bull. Chem. Soc. Jpn* **2002**, *75*, 801–811. Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Suresh, E.; Dastidar, P. *Synlett* **2001**, 1407–1410. Muthusamy, S.; Gunanathan, C.; Babu, S. A. *Tetrahedron Lett.* **2001**, *42*, 523–526. Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.* **2002**, *43*, 5981–5984.
14. Ibata, T.; Toyada, *J. Bull. Chem. Soc. Jpn* **1986**, *59*, 2489–2493.
15. Nair, V.; Sheela, K. C.; Sethumadhavan, D.; Dhanya, R.; Rath, N. P. *Tetrahedron* **2002**, *58*, 4171–4177. Nair, V.; Sheela, K. C.; Radhakrishnan, K. V.; Rath, N. P. *Tetrahedron Lett.* **1998**, *39*, 5627–5630.
16. Padwa, A.; Chinn, A. L.; Hornbuckle, S. F.; Zhang, Z. *J. Org. Chem.* **1991**, *56*, 3271–3278.
17. Nair, V.; Sheela, K. C.; Sethumadhavan, D.; Bindu, S.; Rath, N. P.; Eigendorf, G. K. *Synlett* **2001**, 272–274.
18. Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.* **2000**, *41*, 8839–8842.
19. Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Suresh, E.; Dastidar, P.; Jasra, R. V. *Tetrahedron* **2001**, *57*, 7009–7019. Pirrung, M. C.; Kaliappan, K. P. *Org. Lett.* **2000**, *2*, 353–355.
20. Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Ganguly, B.; Suresh, E.; Dastidar, P. *J. Org. Chem.* **2002**, *67*, 8019–8033.
21. Muthusamy, S.; Babu, S. A.; Gunanathan, C.; Jasra, R. V. *Tetrahedron Lett.* **2001**, *42*, 5113–5116.
22. Hellier, D. G.; Liddy, G. *J. Chem. Res. (S)* **1988**, 138–139.
23. 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. Doyle, M. P.; Tauton, J.; Pho, H. Q. *Tetrahedron Lett.* **1989**, *30*, 5397–5400.
24. Davies, H. M. L.; Townsend, R. *J. Org. Chem.* **2001**, *66*, 6595–6603.
25. Bruker AXS, SMART.; Bruker AXS: Madison, WI, USA, 1998.
26. Bruker AXS, SAINT.; Bruker AXS: Madison, WI, USA, 1999.
27. Blessing, R. *Acta Crystallogr. Sect. A* **1995**, *51*, 33–38.
28. Sheldrick, G.M. *SHELXL97, Program for the solution of X-ray crystal structures*; University of Gottingen: Germany, 1997.