Stereoselective Inter- and Intramolecular Pauson–Khand Reactions of *N*-(2-Alkynoyl) Derivatives of Chiral Oxazolidin-2-ones

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A complete account of the intermolecular and intramolecular Pauson–Khand reactions of *N*-(2-alkynoyl) derivatives of chiral 2-oxazolidinones is presented. The intermolecular Pauson–Khand reactions with norbornene or norbornadiene take place under mild conditions and in high yields. Phenyl- or trimethylsilylpropiolate derivatives lead to the exclusive formation of 1,4-dicarbonyl regioisomers, while mixtures of 1,3- and 1,4-regioisomers are obtained with tetrolate derivatives. The diastereoselectivity of the reaction, determined by the substitution pattern of the oxazolidinone moieties, can be very high (up to 17.5:1 *dr*) for the formation of 1,4-dicarbonyl regioisomers, and the diastereomeric products can often be separated by column chromatography. Under the appropriate conditions, the intramolecular Pauson–Khand reactions of oxazolidinone-derived enynes can also take place with very good yields, but with low diastereoselectivities. The absolute configurations of several adducts have been determined, and the stereochemical outcome of the reaction has been rationalized.

Introduction

The increasing recognition of the potential of the cobalt-mediated carbonylative alkyne−alkene cocyclization (usually known as the Pauson−Khand reaction)[1] and related processes[2] in the synthesis of 2-cyclopentenones has been accompanied by an interest in the search for asymmetric versions of this useful process. To this end, and leaving aside the use of chiral substrates,[3] several strategies have been adopted. The first attempts to develop an enantioselective version of the Pauson−Khand reaction involved the treatment of the prochiral hexacarbonyldicobalt−phenylacetylene complex with optically active phosphanes such as (*R*)-glyphos to generate a pair of diastereomeric complexes that, after separation, reacted with norbornene to give the corresponding intermolecular adduct in high enantiomeric excess.[4] In spite of some valuable improvements on the initially reported methodology,[5] this approach is of limited practical use, because of the difficult separation and the facile thermal interconversion of the phosphane-substituted complexes.[6] In a conceptually related approach, the use of chiral nonracemic amine oxides to activate selectively one of the enantiotopic cobalt atoms of an achiral complex leads to 2-cyclopentenones of low enantiomeric purities.[7] Recently, Buchwald and Hicks have uncovered an enantioselective intramolecular Pauson−Khand-type reaction, catalyzed by the Brintzinger-type titanocene (*S*,*S*)-[ethylenebis(tetrahydroindenyl)]Ti(CO)$_2$, that leads to the efficient formation of bicyclo[3.3.0]oct-1(2)-en-3-ones in high enantiomeric excesses (72−96% ee).[8] On the other hand, the use of chiral alcohols or thiols as temporary stereochemical controllers in Pauson−Khand reactions has been extensively investigated in our research group in the past years.[9−15] In the intramolecular process, high levels of diastereoselectivity have been attained both with *trans*-2-phenylcyclohexanol [as an (*E*)-enol ether][9] and with 3-(neopentyloxy)isoborneol (as an ynol ether),[10] and the resulting adducts have been put to use in the enantioselective synthesis of natural products.[9a,11] The extension of this approach to intermolecular Pauson−Khand reactions is however not straightforward. In effect, the reaction of acetylenic ethers[12] or thioethers[13] derived from the above-mentioned chiral alcohols with strained olefins takes place with low to moderate stereoselectivity. In order to enhance the diastereoselectivity of the process, it has been necessary to resort to the hexacarbonyldicobalt complexes of (2*R*)-10-(alkylthio)isobornyloxyalkynes. The sulfur substituent in these compounds, upon conversion into a pentacarbonyl species, chelates preferentially one of the diastereotopic cobalt atoms, thus allowing a more efficient transfer of chirality to the C_2Co_2 cluster. The resulting complexes react with strained olefins at −20°C with high diastereoselectivities (84−92% de).[14][15]

With the aim of finding an alternative and operationally simple solution to the problem of diastereocontrol in Pauson−Khand cycloadditions, we decided to investigate the use of chiral derivatives of alkynecarboxylic acids.[16] In our initial studies in this field, we found that the intermolecular Pauson−Khand reactions of the phenylpropiolate or tetrolate esters derived from several cyclohexyl- or camphor-based chiral alcohols took place in good yields, with good regioselectivity and with low to moderate diastereoselectivities (up to 3.7:1 diastereomer ratio in the *N*-methylmorpholine *N*-oxide promoted[17] Pauson−Khand reaction of (−)-8-phenylmenthyltetrolate with norbornene).[18] An

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analysis of these results suggested that the failure to attain higher stereoselectivities should be ascribed to the conformational mobility of the carboxyl group, and that the replacement of an ester linkage by a conformationally more rigid amide bond, together with a judicious choice of the chiral auxiliary, would lead to a more efficient steric shielding of a precise cobalt atom in the starting complex. In order to avoid the possible complications arising from the presence of two different rotamers of the amide bond, enantiomerically pure C_2-symmetric secondary amines would appear to be convenient chiral auxiliaries for this application. Taking into account, however, the relatively difficult preparation of these compounds,[19] we initiated our studies with the *N*-(2-alkynoyl) derivatives of substituted oxazolidin-2-ones, the readily available and widely used class of chiral controllers developed almost twenty years ago in the laboratories of D. A. Evans.[20][21] We present in this paper a complete account of our work in this field, which has uncovered a new, straightforward approach for the preparation of enantiomerically pure cyclopentenone derivatives.[22]

Results and Discussion

Synthesis of the Substrates for the Pauson–Khand Cyclizations

We selected for our studies a set of diversely substituted chiral oxazolidinones (Figure 1). Oxazolidinones **1a–c** were chosen in order to evaluate the effect of the steric bulk of the subsitutent at C-4 on the diastereoselectivity of the process, whereas **1d** and **1e** were selected with the aim of ascertaining the possibility of chelation of the cobalt atoms in the intermediate complex by the alkylthio substituent.[14] Both **1a** and **1b** are commercially available; the remaining oxazolidinones were prepared according to known literature procedures (ref.[23] for **1c** and ref.[24] for **1d** and **1e**). As shown in Figure 1, all oxazolidinones have the same relative configuration around C-4 (4*S* for **1a–d**, 4*R* for **1e**). The enantiomer of **1b** was used in the preparation of some derivatives (**6b** and **7b**, see below).

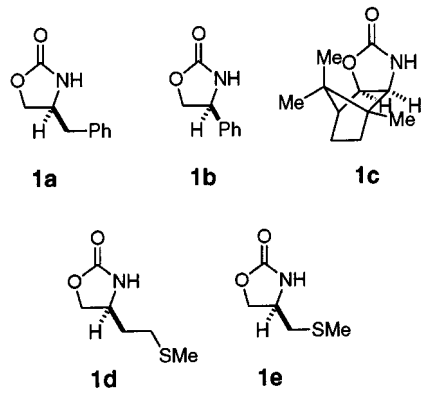


Figure 1. Chiral oxazolidin-2-ones used in this work

The 2-alkynoic acids **2i–v** (Figure 2) were also chosen to cover a wide range of steric and electronic situations. 3-Trimethylsilyl-2-propynoic acid **2iii** was obtained by chromic acid oxidation of 3-trimethylsilyl-2-propyn-1-ol.[25] The known[26] enynecarboxylic acids **2iv** and **2v** were accessed by the original procedure shown in Scheme 1.

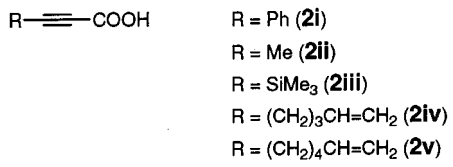
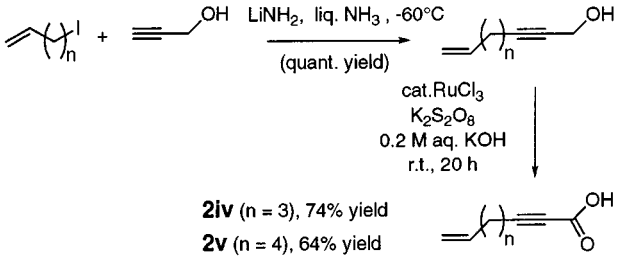


Figure 2. 2-Alkynoic acids used in this work

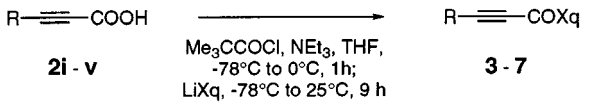


Scheme 1. Preparation of enynecarboxylic acids **2iv–v**

After some experimentation, we found that the coupling of the chiral oxazolidinones **1a–e** with the 2-alkynoic acids **2i–v** could be conveniently performed in one step by the low temperature attack of the lithium salt of the oxazolidinone on a mixed alkynoic–pivalic anhydride prepared in situ, according to the procedure reported by Evans[27] (Scheme 2). The desired *N*-(2-alkynoyl) derivatives **3a–e**, **4a–c**, **5b**, **6a,b** and **7a–c,e** were prepared by this method in moderate to good yields (36–88% isolated yields). In some cases, variable amounts of a secondary product arising from attack of the lithiated heterocycle on the pivaloyl moiety of the mixed anhydride were also isolated from the reaction. It is worth noting that before our work, 2-alkynoyl derivatives of chiral oxazolidinones were virtually unknown.[28]

Yield and Stereoselectivity in the Pauson–Khand Reactions of *N*-(2-Alkynoyl)oxazolidinones 3–7

With the desired compounds in our hands, we undertook the study of their Pauson–Khand reactions. We shall discuss first the results obtained with the phenylpropiolate derivatives **3a–e** (Scheme 3 and Table 1). The reactions were performed in order to render unnecessary the isolation of the hexacarbonyldicobalt complexes. Thus, a solution of the alkynoate (in toluene, acetonitrile or dichloromethane, depending on the experimental protocol chosen) was treated with a slight excess of octacarbonyldicobalt. After stirring for one hour at room temperature, the formation of the complex was complete in all cases. The olefin (norbornene or norbornadiene) was added, and the reaction was promoted either thermally or by addition of *N*-methylmorpholine *N*-oxide at low temperature. Contrary to the general behaviour of alkynes, the temperature of the reaction was generally low. Thus, in several instances (Entries 4, 5, 7 and

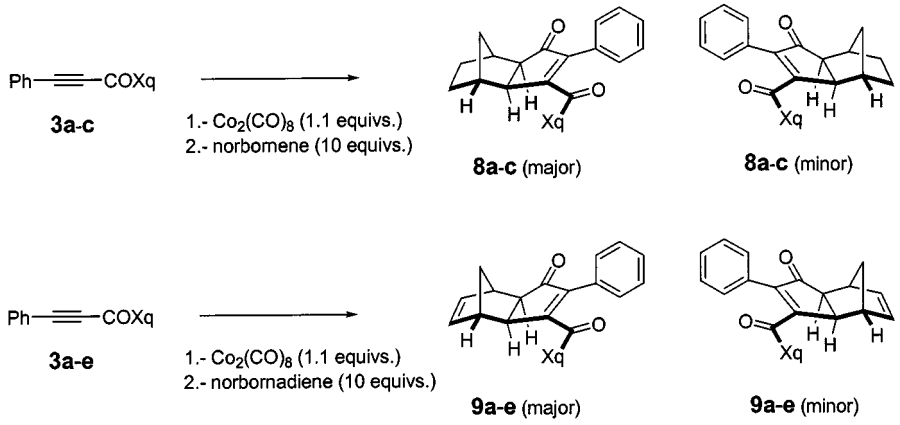


Acid	HXq	*N*-(2-Alkynoyl)oxazolidininone (% yield)
2i	**1a**	**3a** (62%)
2i	**1b**	**3b** (79%)
2i	**1c**	**3c** (62%)
2i	**1d**	**3d** (53%)
2i	**1e**	**3e** (74%)
2ii	**1a**	**4a** (88%)
2ii	**1b**	**4b** (87%)
2ii	**1c**	**4c** (79%)
2iii	**1b**	**5b** (69%)
2iv	**1a**	**6a** (48%)
2iv	*ent*-**1b**	**6b** (55%)
2v	**1a**	**7a** (55%)
2v	*ent*-**1b**	**7b** (69%)
2v	**1c**	**7c** (55%)
2v	**1e**	**7e** (36%)

Scheme 2. Preparation of *N*-(2-alkynoyl)oxazolidinones **3**−**7**

9 of Table 1) the formation of the cyclopentenone under thermal conditions took place at room temperature, and *N*-oxide-promoted reactions could be run at temperatures as low as −20°C (Entry 6). The optimized yields of the Pauson−Khand adducts were uniformly high (81−100%). The process turned out to be completely regioselective, and led to the exclusive formation of the 1,4-dicarbonyl compounds **8** or **9**. This behaviour is totally parallel to that of the phenylpropiolate esters.[18] As expected, the *exo*/*endo* selectivity with respect to the olefin was also complete, and all of the adducts had an *exo* stereochemistry. The diastereoselectivity of the process was found to be completely dependent on the substitution pattern of the oxazolidinone, increasing in the order **3a** < **3b** < **3c**. There appears therefore to be a clear correlation between the steric bulk of the C-4 substituent of the oxazolidinone and the diastereomeric excess of the Pauson−Khand product. The stereoselectivity of the reaction was also affected, albeit in a lower degree, by the nature of the olefin (norbornadiene turned out to be more selective than norbornene) and by the experimental conditions (see Entries 1−3, 5−6 and 10−12 of Table 1). The hexacarbonyldicobalt complexes of both **3d** and **3e** were investigated in order to ascertain whether in this case the methylthio group was able to chelate one of the cobalt atoms. In fact, we were not able to observe the formation of any chelated species either by heating or by treating with *N*-methylmorpholine *N*-oxide, and the corresponding Pauson−Khand products were formed with relatively low stereoselectivities. In any case, the moderate increase in diastereoselectivity observed when the reactions were run under *N*-oxide-mediated conditions (Entries 12 and 14 in Table 1) would be compatible with the existence of a parallel, minor reaction pathway involving a highly unstable, sulfur-chelated complex. An important observation, from the practical point of view, is that the diastereomer adducts obtained from **3b** and **3c** were readily separable by simple column chromatography on silica gel. Thus, for instance, the major adduct arising from the reaction of **3c** with norbornene was obtained in stereochemically pure form in 83% yield directly from the reaction mixture. Thanks to these favourable chromatographic properties, even the products arising from the commercially available oxazolidinone **1b** can be readily obtained in enantiomerically pure form (cf. 66% isolated yield for the major isomer of the reaction of **3b** with norbornadiene).

The Pauson−Khand cycloadditions of the trimethylsilylpropiolate derivatives were found to be hampered by the presence of the bulky silyl substituent. Thus, the reaction of the complex obtained from **5b** with norbornene under thermal conditions was extremely slow, and the expected adduct **10b** was obtained in only 10% yield (as a 3.5:1 diastereomeric mixture) after 68 h at 80°C. In fact, in order to obtain higher yields, it was necessary to use the more reactive olefin norbornadiene in the presence of *N*-methylmorpholine *N*-oxide and under an oxygen atmosphere (Scheme 4). The regioselectivity of the reaction was again complete, leading to the exclusive formation of 1,4-dicarbonyl regioisomers, but the diastereomeric purities of



Scheme 3. Intermolecular Pauson−Khand reactions of *N*-(phenylpropiolyl)oxazolidinones **3**

Table 1. Intermolecular Pauson–Khand cycloadditions of *N*-(phenylpropiolyl)oxazolidinones **3a–e**

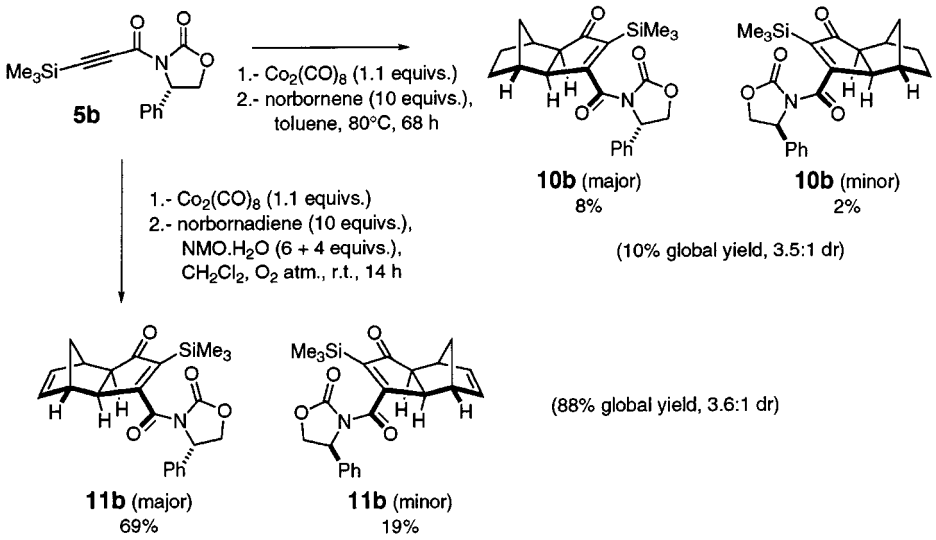
Entry	Alkyne	Olefin	Reaction conditions	Adduct	Yield (%)	dr
1	**3a**	norbornene	toluene, 40°C, 19 h	**8a**	74	1:1[a]
2	**3a**	norbornene	CH_3CN, 55°C, 18 h	**8a**	79	1.2:1[a]
3	**3a**	norbornene	NMO·H_2O (10 equiv.), CH_2Cl_2, 0°C to room temp., 15 h	**8a**	81	1.8:1[a]
4	**3a**	norbornadiene	toluene, room temp., 24 h	**9a**	97	1:1[a]
5	**3b**	norbornene	toluene, room temp., 20 h	**8b**	91	4.3:1[b]
6	**3b**	norbornene	NMO (7.5 equiv.), CH_2Cl_2, −20°C, 24 h	**8b**	100	3.8:1[b]
7	**3b**	norbornadiene	toluene, room temp., 21 h	**9b**	96	5.2:1[b]
8	**3c**	norbornene	toluene, 45°C, 42 h	**8c**	100	9.2:1[b]
9	**3c**	norbornadiene	toluene, room temp., 21 h	**9c**	97	14:1[b]
10	**3d**	norbornadiene	toluene, 60°C, 3 h	**9d**	96	2.2:1[b]
11	**3d**	norbornadiene	CH_3CN, 80°C, 3 h	**9d**	93	1.8:1[b]
12	**3d**	norbornadiene	NMO·H_2O (6 equiv.), CH_2Cl_2, 0°C to room temp., 3 h	**9d**	75	2.9:1[b]
13	**3e**	norbornadiene	toluene, 60°C, 3 h	**9e**	93	2.7:1[b]
14	**3e**	norbornadiene	NMO·H_2O (3 equiv.), CH_2Cl_2, 0°C to room temp., 3 h	**9e**	53	3.1:1[b]

[a] Diastereomer ratios calculated by ^{13}C-NMR spectroscopy. – [b] Diastereomer ratios calculated by HPLC.

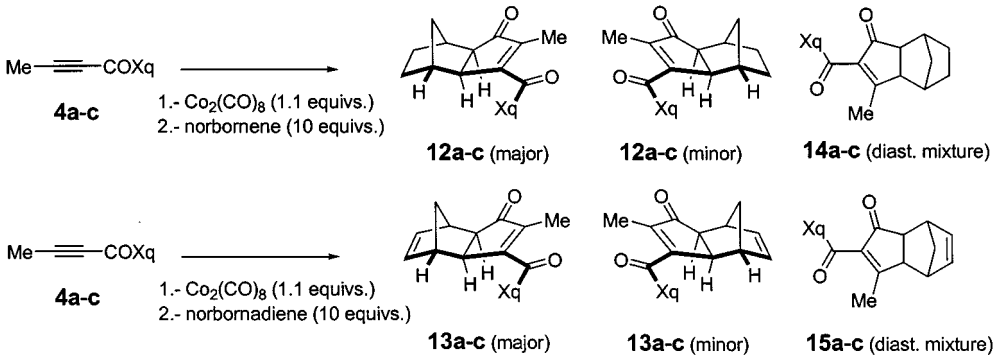
these adducts were somewhat lower than those of the corresponding products obtained from **3b**. Gratifyingly enough, the two diastereomers were again readily separable by column chromatography, and the major isomer of **11b** was obtained in 69% yield after chromatographic purification.

The most outstanding feature of the Pauson–Khand reactions of the tetrolic acid derivatives **4a–c** (Scheme 5 and Table 2) was the isolation of the 1,3-dicarbonyl adducts **14** and **15** along with the 1,4-dicarbonyl regioisomers **12** and **13**, respectively. This lack of regioselectivity stands in sharp contrast with the behaviour of tetrolate esters in the Pauson–Khand reaction,[16][18] since these compounds give almost exclusively the 1,4-dicarbonyl regioisomers.[29][30]

This differential behaviour cannot be easily explained by electronic effects, since the the triple bond of *N*-(tetrolyl)oxazolidinones is more polarized than that of tetrolate esters (as evidenced by the chemical shifts of the sp-carbon atoms in their ^{13}C-NMR spectra). This, as suggested by Krafft,[29] would in any case render the Pauson–Khand cycloaddition more regioselective, by favouring the formation of the 1,4-dicarbonyl regioisomer. The observed regiochemical outcome should therefore be ascribed to the larger steric hindrance exerted by the oxazolidone moiety. In general, these reactions took place at moderate temperatures (when run under thermal conditions) and the overall yields of the adducts were very good (especially in the case of the *N*-oxide-promoted reactions). In the case of the 1,4-dicarbonyl regioisomers **12** and **13**, the diastereoselectivity of the process was largely determined by the steric volume of the oxazolidinone substituents. Once again, the camphor-derived oxazolidinone **1c** produced the highest diastereomer ratios (up to 17.5:1). On the other hand, the formation of the 1,3-dicarbonyl regioisomers **14** and **15** was much less stereoselective, and only moderate diastereomer ratios (up to 5.1:1) could be achieved with the tetrolate **4c**. Although in some instances the diastereomeric pairs corresponding to each adduct were separable by chromatography, the formation of four products rendered the isolation of stereoisomerically pure products very difficult. For this reason, the regioselectivity of the process was established by ^{1}H- and ^{13}C-NMR



Scheme 4. Intermolecular Pauson–Khand reactions of *N*-(trimethylsilylpropiolyl)oxazolidone **5b**



Scheme 5. Intermolecular Pauson−Khand reactions of *N*-(tetrolyl)oxazolidinones **4a−c**

spectroscopy, whereas the diastereomer ratios were determined by ^{13}C-NMR spectroscopy and by HPLC.

The unexpected formation of relatively large amounts of 1,3-dicarbonyl regioisomers in the intermolecular Pauson−Khand reactions of the tetrolate derivatives **4a−c** prompted us to investigate the intramolecular Pauson−Khand cyclizations of the enynes **6** and **7**, which for geometrical reasons should lead to the exclusive formation of the 1,3-dicarbonyl regioisomers. The dicobalt carbonyl complexes derived from both **6a** and **6b** did not lead to the formation of the expected bicyclic enones under a variety of reaction conditions (heating in toluene or acetonitrile, *N*-oxide mediated activation), and gave only complex mixtures of unidentified products. Only when using DMSO as a promoter[31] did the Pauson−Khand cyclization of **6b** produce an unstable product (whose ^{1}H-NMR spectrum was consistent with structure **16b**) in low yield (Scheme 6).

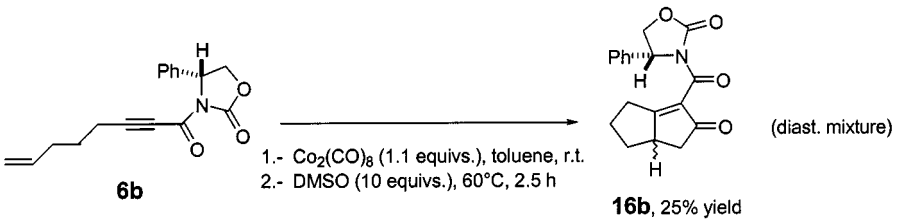
The Pauson−Khand cyclization of the 8-nonen-2-ynoate derivatives **7** was more successful, although an extensive investigation of the reaction conditions was necessary in order to achieve satisfactory yields (Scheme 7 and Table 3). Thus, heating the hexacarbonyldicobalt complex of **7a** in toluene gave a moderate yield of the bicyclononenone derivative **17a**, but without any diastereoselectivity (Entry 1 of Table 3). Neither the yield nor the stereoselectivity were improved by running the reaction in refluxing acetonitrile (Entry 2) or under *N*-oxide-promoted conditions (Entry 3). On the other hand, the use of dimethyl sulfoxide and dimethyl sulfide as reaction activators[31] resulted in a dramatic enhancement of the yield of **17a**, although the diastereoselectivity remained essentially zero (Entry 4). Enynes **7b** (Entries 5−8) and **7c** (Entries 9−11) showed a similar behaviour, and in both cases heating of the complex in toluene in the presence of dimethyl sulfoxide afforded the expected product in 80% yield. Although, as we had initially surmised, the Pauson−Khand cyclization of **7c** showed the highest levels of diastereoselectivity in the series, the diastereomer ratios attained were rather low (up to 2:1), and the two products were not easily separable by column chromatography. Finally, the cyclization of **7e** (Entries 12 and 13 of the Table 3) did not show any evidence of significant involvement of an internally chelated intermediate complex.

In any case, the high-yield preparation of compounds **17a−c** represents a direct route to 9-acylbicyclo[4.3.0]non-1(9)-en-8-one derivatives. It is worth noting that the presence of an amide bond in the precursor appears to be important in order to attain synthetically useful yields. Thus, the Pauson−Khand cyclization of methyl 8-nonen-2-ynoate

Table 2. Intermolecular Pauson−Khand cycloadditions of *N*-(tetrolyl)oxazolidinones **4a−c**

Entry	Alkyne	Olefin	Reaction conditions	Adduct	Yield (%)[a]	dr[b]
1	**4a**	norbornene	toluene, room temp., 70 h	**12a**	25	1.9:1
				14a	45	1:1
2	**4a**	norbornene	NMO (6 equiv.), CH_2Cl_2, −20°C, 14 h	**12a**	40	2.0:1
				14a	60	1.2:1
3	**4a**	norbornadiene	toluene, 0°C, 14 h; room temp., 48 h	**13a**	36	2.0:1
				15a	44	1.2:1
4	**4b**	norbornene	toluene, room temp., 20 h	**12b**	46	7.6:1
				14b	27	1:1
5	**4b**	norbornene	NMO (6 equiv.), CH_2Cl_2, −20°C, 18 h	**12b**	62	7.9:1
				14b	38	1.1:1
6	**4b**	norbornadiene	toluene, room temp., 72 h	**13b**	53	7.6:1
				15b	23	1.9:1
7	**4c**	norbornene	toluene, 40°C, 8 h	**12c**	29	9.3:1
				14c	40	4.4:1
8	**4c**	norbornadiene	toluene, room temp., 96 h	**13c**	34	17.5:1
				15c	38	5.1:1

[a] Yields of the regioisomers estimated by ^{1}H- and ^{13}C-NMR spectroscopy of reaction mixtures. − [b] Diastereomer ratios calculated by ^{13}C-NMR spectroscopy and by HPLC of partially purified reaction mixtures.



6b **16b**, 25% yield

Scheme 6. Intramolecular Pauson−Khand reaction of oxazolidinone **6b**

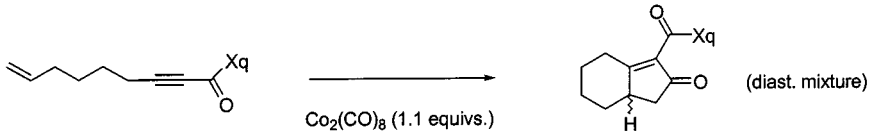
(**18**) afforded the known[32] oxo ester **19** in only 21% yield (Scheme 8).

Determination of Absolute Configurations

The geometry of the asymmetric induction in the intermolecular Pauson−Khand reactions of alkynes **3** and **5** could be unambiguously determined by a combination of chemical correlation and chiroptical methods.

Firstly, in order to establish the stereoisomeric relationship between the diastereomer pairs obtained in the cycloadditions (i.e., to definitely rule out the possibility of *exo*/*endo* isomerism), we proceeded to submit both isomers of adduct **9b** to the $LiOH/H_2O_2$-mediated oxazolidone hydrolysis procedure developed by Evans.[33] Both compounds afforded opposite enantiomers of the same oxo acid **20** (as shown by the opposite values of the rotation), in which nucleophilic epoxidation of the cyclopentenone double bond had also taken place (Scheme 9).

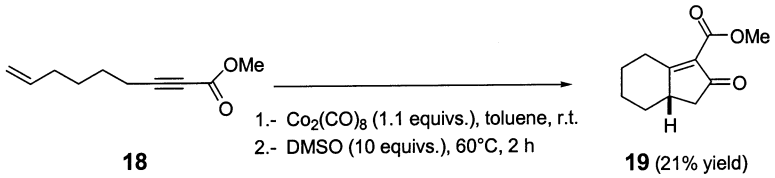
In order to determine the absolute configuration of the major diastereomer of **9b**, we converted it into the known allyl ester **21**. To this end, we dissolved it in anhydrous allyl alcohol and heated it at 150°C in a sealed tube in the presence of titanium tetraisopropoxide, according to the meth-



7a
7b
7c
7e

17a (HXq = **1a**)
17b (HXq = *ent*-**1b**)
17c (HXq = **1c**)
17e (HXq = **1e**)

Scheme 7. Intramolecular Pauson−Khand reactions of oxazolidinones **7a−e**



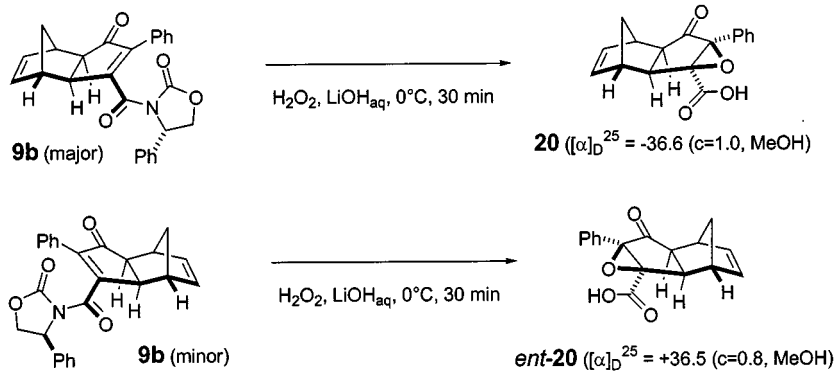
18 **19** (21% yield)

Scheme 8. Intramolecular Pauson−Khand reaction of ester **18**

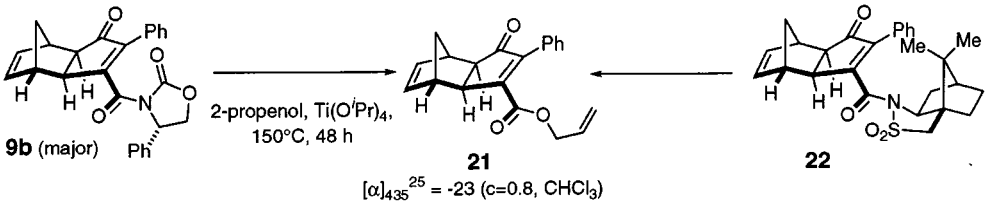
Table 3. Intramolecular Pauson−Khand cycloadditions of *N*-(8-nonen-2-ynoyl)oxazolidinones **7a−c,e**

Entry	Alkyne	Reaction conditions	Adduct	Yield (%)	dr[a]
1	**7a**	toluene, 60°C, 4 h	**17a**	43	1:1
2	**7a**	CH_3CN, 80°C, 3 h	**17a**	34	1:1
3	**7a**	NMO·H_2O (2.5 equiv.), CH_2Cl_2, 0°C to room temp., 1 h	**17a**	8	1:1
4	**7a**	toluene, DMSO (10 equiv.), DMS (10 equiv.), 60°C, 3 h	**17a**	92	1:1
5	**7b**	toluene, 50°C, 2.5 h	**17b**	50	1:1
6	**7b**	CH_3CN, 80°C, 3 h	**17b**	12	1:1
7	**7b**	NMO·H_2O (5 equiv.), CH_2Cl_2, 0°C to room temp., 1 h	**17b**	69	1:1
8	**7b**	toluene, DMSO (10 equiv.), 60°C, 2.5 h	**17b**	80	1.2:1
9	**7c**	toluene, 60°C, 2.5 h	**17c**	60	2:1
10	**7c**	NMO.H_2O (6 equiv.), CH_2Cl_2, 0°C to room temp., 1 h	**17c**	75	1.6:1
11	**7c**	toluene, DMSO (10 equiv.), 60°C, 2.5 h	**17c**	80	1.9:1
12	**7e**	toluene, 60°C, 4 h	**17e**	50	1.1:1
13	**7e**	toluene, DMSO (10 equiv.), 60°C, 3 h	**17e**	59	1.1:1

[a] Diastereomer ratios calculated by HPLC.



Scheme 9. Hydrolysis of adducts **9b**



Scheme 10. Determination of the absolute configuration of **9b**

odology described by Oppolzer.[34] After chromatographic purification, the levorotatory ester **21** was obtained in moderate yield (43%, Scheme 10). Because the same compound was obtained from **22**, whose stereochemistry had been elucidated by single-crystal X-ray diffraction,[35] we concluded that the sense of asymmetric induction in the Pauson−Khand reactions of **4b** must have been that assumed throughout this work.

The absolute configuration of the major stereoisomer of **11b** could also be elucidated, showing that the sense of the asymmetric induction is independent of the substituent of the triple bond. As shown in Scheme 11, catalytic hydrogenation of this compound produced both the saturation of the two olefinic bonds of the substrate and the reductive cleavage of the trimethylsilyl group, affording in quantitative yield the polycyclic ketone **23**. Treatment of this compound with $LiOH/H_2O_2$[33] allowed for the isolation of the tricyclic oxo acid **24**. The relative configuration of the stereogenic centers was established by careful analysis of the ^{1}H-NMR spectrum of the methyl ester **25**, showing that, as expected, the hydrogenation of the tetrasubstituted double bond had taken place at the less hindered face. The circular dichroism spectrum of **24** showed two negative Cotton effects at λ = 219 nm and 300 nm, corresponding to the n→π* transitions of the carboxyl and of the carbonyl groups, respectively. Application of the empirical sector rules[36] for both types of functional groups (Figure 3) is only consistent with a (1*R*,2*S*,3*R*,6*R*,7*S*) configuration of the stereogenic centers in **24**, and therefore in the major isomer of **11b**.

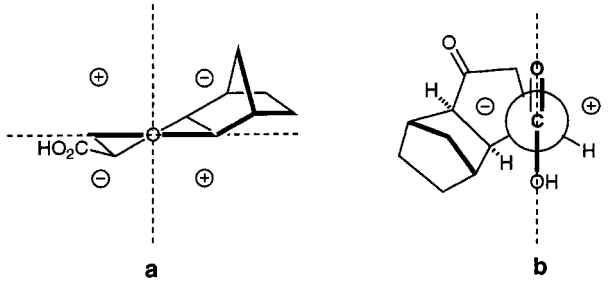
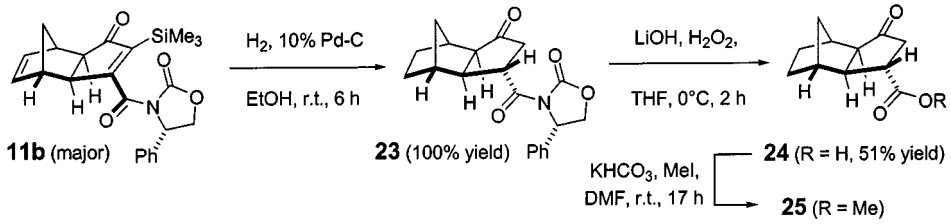


Figure 3. (a) Octant rule projection (rear sectors) of oxo acid **24**; (b) Newman projection of the preferred conformation of oxo acid **24** according to the empirical sector rule for the CD of chiral carboxylic acids at 210 nm

Models for Stereoselectivity

It is generally assumed that the Pauson−Khand reaction takes place by a complex multistep mechanism, involving at



Scheme 11. Determination of the absolute configuration of **11b**

least the existence of five transient reaction intermediates beyond the initial hexacarbonyldicobalt–acetylene complex.[1e,37,38] Although this fact renders the rationalization of the observed diastereoselectivities very difficult,[14b] we have found that the absolute configurations of the major adducts obtained in the inter- and intramolecular Pauson–Khand reactions of chirally substituted alkynes can be consistently predicted simply by analyzing the conformational preferences of the starting complex and assuming that the coordination of the olefin takes place preferentially at the more accessible of the two diastereotopic cobalt atoms and with an orientation that minimizes the steric interactions in the resulting complex.[10,14b]

We have therefore undertaken a study of the conformational preferences of the hexacarbonyldicobalt complexes derived from the *N*-(2-alkynoyl)oxazolidinones, by means of the semiempirical PM3(tm) procedure, which incorporates parameterization for transition metals to the original PM3 method,[39] as implemented in the SPARTAN package of programs.[40] As we have previously noticed,[14b] PM3(tm) reproduces with remarkable accuracy both the structure (bond lengths and bond angles) and the conformation of hexacarbonyldicobalt complexes of alkynes as determined by single-crystal X-ray diffraction. As a result of these studies, we have found that the *N*-(2-alkynoyl)oxazolidinine-derived complexes present in general a similar lowest energy conformation, which is energetically well separated (by more than 5 kcal mol^{-1}) from the next stable conformation (see Figure 4). In this conformation, the amide carbonyl eclipses the other alkyne substituent, while at the same time the oxazolidinone carbonyl adopts an *anti* relationship with respect to it.[21] In this way, the oxazolidinones having an (*S*) configuration at C-4 place the substituent on this carbon in a region of space that is close to the *pro-R* cobalt(tricarbonyl) moiety of the cluster. The six positions occupied by the CO ligands become clearly differentiated from the steric point of view.

According to the accepted mechanism of the Pauson–Khand reaction, the olefin displaces one of these COs, giving a complex in which both the alkyne and the alkene moieties are bonded to cobalt. Further evolution of this complex (insertion of the complexed olefin into a carbon–cobalt bond giving a five-membered cobaltacycle, followed by insertion of carbon monoxide and by reductive elimination of a hexacarbonyldicobalt fragment) leads to the final cyclopentenone product.[1][37] Let us now analyze in some detail the regio- and stereochemical issues of the different possible complexes obtained upon coordination of norbornene or norbornadiene to the six nonequivalent positions of an (*S*)-*N*-(2-alkynoyl)oxazolidinine–hexacarbonyldicobalt complex in the conformation depicted in Figure 4 (see Figure 4b for the nomenclature used).

Binding of the olefin to any of the two equatorial sites proximal to the R alkyne substituent ($eq_{\beta R}$ and $eq_{\beta S}$) would lead to the formation of a 1,3-dicarbonyl cyclopentenone regioisomer. When R = phenyl or trimethylsilyl, this possibility appears to be precluded for steric reasons, and only when R = Me are these regioisomers observed. It is easily seen that the oxazolidinone substituents do not provide an effective differentiation between the two diastereotopic (pro-*R* and pro-*S*) sites, which accounts for the low diastereomer ratios obtained for adducts **14** and **15**. In sharp

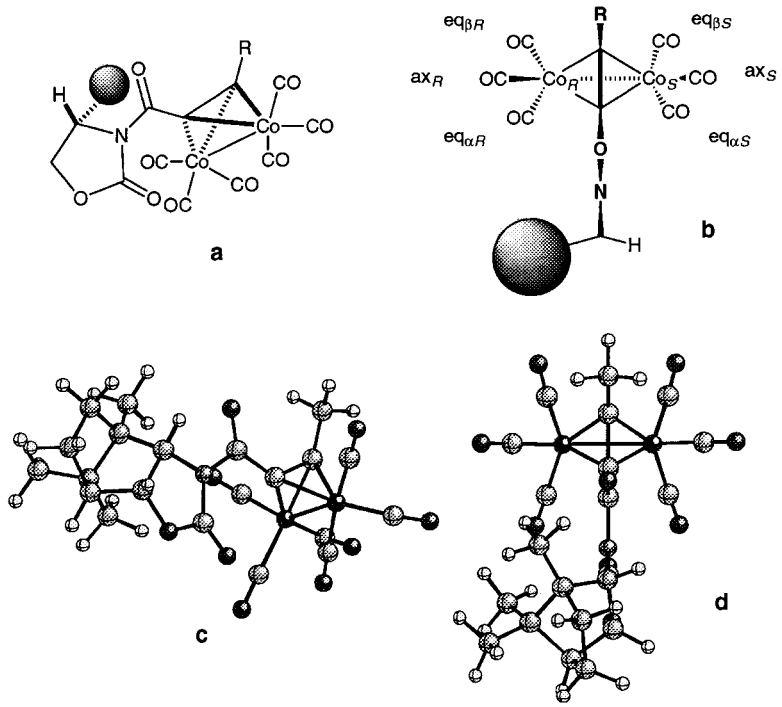


Figure 4. Schematic representation of the lowest energy conformation of hexacarbonyldicobalt complexes of *N*-(2-alkynoyl)oxazolidinones (a: lateral view; b: dorsal view, showing the six diastereotopic CO ligands); PM3(tm)-optimized minimum energy conformer of the hexacarbonyldicobalt complex of **4c** (c: lateral view; d: dorsal view)

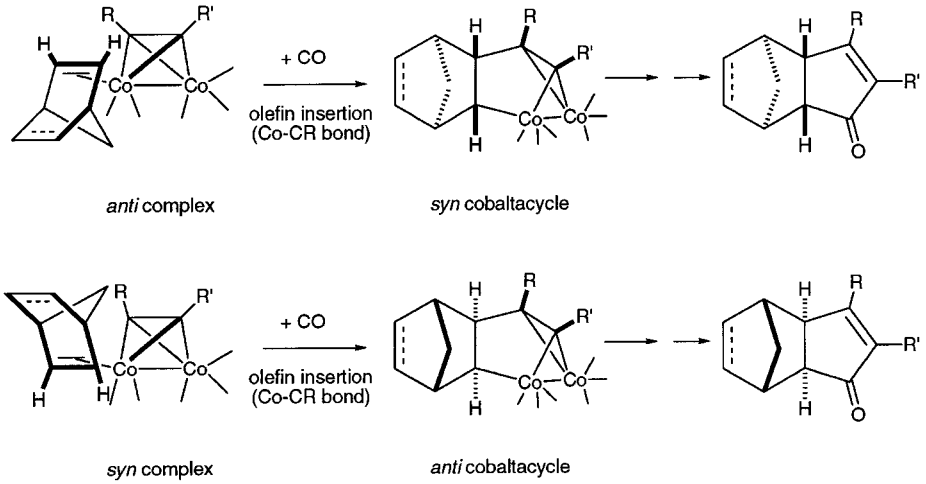


Figure 5. Two possible orientations (*anti* or *syn*) of a norbornene or norbornadiene molecule bonded to a carbonyldicobalt acetylene complex, leading to opposite enantiomers of the final cyclopentenone adduct

contrast to this, and especially in the case of oxazolidinone **1c** derivatives (see Figure 4d), coordination of the olefin to an $eq_{\alpha R}$ site can be appreciably hindered, so that the preferred equatorial site of coordination leading to a 1,4-dicarbonyl regioisomer appears to be the $eq_{\alpha S}$ one. On the other hand, if the olefin occupies an axial site, an inspection of the molecular models reveals that only in the case of very bulky oxazolidinone substituents can a preferential coordination to the ax_S site be expected.

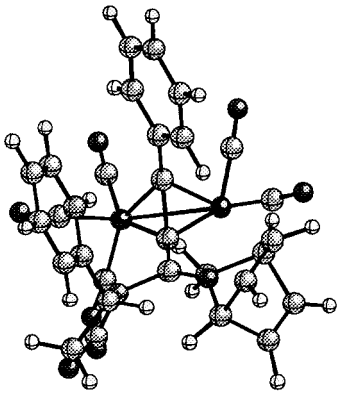
Another factor determining the preferred configuration of the Pauson−Khand adduct is the orientation of the coordinated olefin in the complex. Assuming that coordination takes place exclusively from the *exo* face of norbornene or norbornadiene, there are two possible orientations (Figure 5). In the first of these, which we shall refer to as an *anti* orientation, the methylene bridge points away from the alkyne substituents; in the other possible orientation (*syn*), the methylene bridge points towards the alkyne substituents. In the case of coordination to an axial site, the last arrangement is much more sterically hindered than the other, and in fact PM3(tm) calculations in model systems indicate that only the *anti* orientation can be adopted by the olefin. If the alkene (norbornene or norbornadiene) occupies an equatorial site next to a relatively bulky alkyne substituent, both orientations are, in principle, possible.

Finally, it is important to note that the stereoelectronic requirement for the evolution of these olefin-substituted complexes to the cobaltacycle intermediates is a *syn*-periplanar arrangement of the olefin C=C bond and the carbon−cobalt bond participating in the metathesis step.

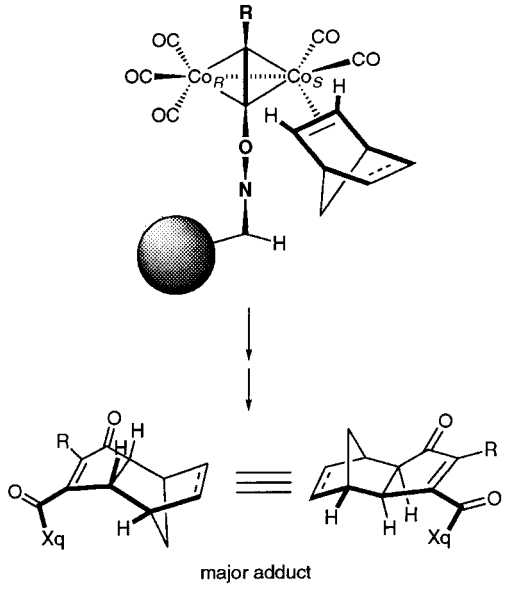
Bearing all these considerations in mind, we undertook a systematic study, at the PM3(tm) level of theory, of the norbornadiene-substituted pentacarbonyldicobalt complexes derived from the (*S*)-*N*-(phenylpropionyl)oxazolidinone **3b**, taken as a representative example. To our satisfaction, we found that among the lowest energy complexes, only that resulting from the coordination of norbornadiene to the $eq_{\alpha S}$ site with an *anti* orientation (Figure 6a) presents an essentially zero (2.8°) dihedral angle between the coordinated double bond and the $C_2-Co_{pro\text{-}S}$ bond, so that the preferential formation of the major diastereomer appears to take place by the intermediacy of this stable complex, in which the olefin moiety is present in a reactive conformation. Increasing the steric size of the oxazolidinone substituent should reinforce the preferential coordination of the olefin to the pro-*S* cobalt, in accordance with the experimentally observed stereochemical trends. Therefore, the diastereoselectivity of the reaction is primarily determined by the prochirality of the cobalt atom of the C_2Co_2 cluster to which the olefin coordinates (which is in turn dependent on the configuration of the oxazolidinone moiety), and the formation of the major diastereomers in the intermolecular Pauson−Khand reactions of alkynoates **3**, **4** and **5** can be explained by the preferred coordination of the olefin, adopting an *exo-anti* orientation, to a $eq_{\alpha S}$ site in the initially formed hexacarbonyldicobalt complex (Figure 6b).

Summary and Outlook

The intermolecular Pauson−Khand reactions of *N*-(2-alkynoyl) derivatives of chiral oxazolidin-2-ones with strained olefins such as norbornene or norbornadiene take place under mild conditions and in high yields, indicating that these polarized alkynes are extremely good substrates for this process. The regioselectivity of the reaction depends on the substitution pattern of the alkyne; thus, the use of phenyl- or trimethylsilylpropiolate derivatives leads to the exclusive formation of 1,4-dicarbonyl regioisomers, while regioisomer mixtures are obtained with tetrolate derivatives. The diastereoselectivity of the reaction is controlled by the substitution pattern of the oxazolidinone moieties, and very high diastereomer ratios (up to 17.5:1) can be achieved in the formation of 1,4-dicarbonyl regioisomers. Moreover, the diastereomer products can in many cases be separated by simple column chromatography, so that stereoisomerically pure adducts can be easily obtained. With respect to the intramolecular Pauson−Khand reactions of oxazolidinone-



a



b

Figure 6. (a) PM3(tm)-optimized structure of the norbornadiene–dicobaltpentacarbonyl complex derived from **3b**, with the olefin coordinated to the eq_{α} site of the pro-*S* cobalt; (b) schematic representation showing that the evolution of such a complex leads to the formation of the major diastereomer

derived enynes, we have found that under adequate reaction conditions, the cyclization of 8-nonen-2-ynoate derivatives takes place with very good yields, albeit with marginal diastereoselectivities, in what constitutes a convenient synthetic route to 9-acylbicyclo[4.3.0]non-1(9)-en-8-ones.

The absolute configurations of the major diastereomers of several adducts obtained in intermolecular Pauson–Khand reactions have been unambiguously determined by a combination of chemical correlation and chiroptical methods, thus allowing a connection to be established between the sense of the asymmetric induction of the process and the stereochemistry of the oxazolidinone moiety. Moreover, a study of the conformational preferences of the hexacarbonyldicobalt complexes derived from *N*-(2-alkynoyl)oxazolidinones, by means of the semiempirical PM3(tm) procedure, has shown that the stereochemical outcome of the reaction can be explained by the preferential coordination of the olefin to an equatorial site of the more accessible of the two diastereotopic cobalt atoms [the pro-*S* one for a (4*S*)-oxazolidinone]. Moreover, the olefin adopts an *exo-anti* orientation that minimizes the steric interactions in the resulting complex and, at the same time, guarantees the fulfillment of the stereoelectronic requirements of the first, product-determining, carbon–carbon bond-forming step. In summary, the use of readily available chiral oxazolidinones as a chiral controller for Pauson–Khand cycloadditions constitutes a synthetically valuable methodology for the preparation of highly enantiomerically pure cyclopentenone derivatives, while allowing for a rationalization of the stereochemical outcome of the reaction.

Experimental Section

General Methods: Melting points were determined in open-ended capillary tubes on a Büchi–Tottoli apparatus or on a Reichert–Thermovar Köfler apparatus and are uncorrected. – Optical rotations were measured at room temperature (23°C) with a Perkin–Elmer 241 MC automatic polarimeter (concentration in g/100 mL). – Infrared spectra: Perkin–Elmer 681 or Nicolet FT-IR 510 spectrometer using film NaCl or KBr pellet techniques. – ^{1}H- and ^{13}C-NMR spectra: Varian Gemini-200 or Varian Unity-300 spectrometer in $CDCl_3$ or CD_3OD with tetramethylsilane or chloroform as an internal standard (s = singlet, d = doublet, t = triplet, q = quadruplet, dt = double triplet, m = multiplet, b = broad and bd = broad doublet). Chemical shifts are expressed in δ (ppm) units downfield to TMS. The multiplicity in ^{13}C-NMR spectra was determined by means of DEPT techniques. – Mass spectra: Hewlett–Packard HP-5988A at 70 eV ionizing voltage . Ammonia or methane were used for chemical ionization (CI). MS spectra are presented as *m*/*z* (% rel. int.). High-resolution mass spectra were performed by the "Servicio de Espectrometría de Masas, Universidad de Córdoba". Elemental analyses were performed by the "Servei d'Anàlisis Elementals del CSIC de Barcelona". – THF used in the reactions was dried by distillation over metallic sodium and benzophenone. Dichloromethane, DMF and acetonitrile were distilled from calcium hydride and toluene was dried with metallic sodium. All reactions were carried out in oven-dried glassware under pre-purified nitrogen. LiCl was dried in vacuo at 150°C for 5 h before use. – The course of all the reactions described here could be conveniently monitored by TLC (Merck DC-Alufolien Kieselgel 60 F_{254}). – Silica gel (J. T. Baker, 70–230 mesh) was used for column chromatography. – HPLC analyses: Hewlett–Packard 1050 liquid chromatograph using a 4.6 mm i.d. × 25 cm Nucleosil 120 5C18 column (Scharlau, Barcelona, Spain) or a 4.6 mm i.d. × 25 cm Nucleosil 120 5C18 column (Scharlau, Barcelona, Spain), ϕ = flow. – Oxazolidinones **1a**,**b**, phenylpropiolic acid and 2-butynoic acid are commercially available (Fluka or Aldrich) and were used as received. Oxazolidinones **1c**–**e** were prepared according to literature procedures.[23][24]

7-Octen-2-ynoic Acid (2iv): To a mechanically stirred solution of potassium hydroxide (11.2 g, 0.20 mol), potassium peroxydisulfate (10.0 g, 37 mmol) and ruthenium trichloride (0.040 g, 0.17 mmol) in water (1 L),[42] 1.0 g (8.1 mmol) of 7-octen-2-yn-1-ol (obtained by lithium amide-mediated alkylation of propargyl alcohol with 5-iodo-1-pentene)[43] were added in a single portion. The resulting

mixture was stirred at room temperature for 20 h. After washing with dichloromethane (1 × 250 mL) in order to remove the unchanged alcohol, the aqueous phase was acidified with concentrated aqueous HCl and extracted with dichloromethane (3 × 250 mL). The combined organic phases were dried with $MgSO_4$. Evaporative distillation of the solvent gave 0.81 g of pure acid **2iv** as an oil.[26] − IR (NaCl film): $\tilde{\nu}$ = 3200 (br), 2936, 2240, 1684, 1414, 1281, 1074, 993, 916, 789, 715 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.7 (t, $^3J_{(H,H)}$ = 7.1 Hz, 2 H), 2.15 (m, 2 H), 2.37 (t, $^3J_{(H,H)}$ = 7.2 Hz, 2 H), 5.0−5.2 (m, 2 H), 5.7−6.0 (m, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 18.5 (CH_2), 26.9 (CH_2), 33.0 (CH_2), 73.4 (C), 92.3 (C), 116.3 (CH_2), 137.5 (CH), 158.3 (C). − EM (CI NH_3): *m/z* = 156 (74) $[M + 18]^+$, 173 (100) $[M + 35]^+$.

8-Nonen-2-ynoic Acid (2v): To a mechanically stirred solution of potassium hydroxide (11.2 g, 0.20 mol), potassium peroxydisulfate (10.2 g, 38 mmol) and ruthenium trichloride (0.040 g, 0.17 mmol) in water (1 L),[42] 8-nonen-2-yn-1-ol (1.0 g, 7.2 mmol, obtained by lithium amide-mediated alkylation of propargyl alcohol with 6-iodo-1-hexene)[43] was added in a single portion. The resulting mixture was stirred at room temperature for 20 h. After washing with dichloromethane (1 × 250 mL) in order to remove the unchanged alcohol, the aqueous phase was acidified with concentrated aqueous HCl and extracted with dichloromethane (3 × 250 mL). The combined organic phases were dried with $MgSO_4$. Evaporative distillation of the solvent gave 0.70 g of pure acid **2v** as an oil;[26] IR (NaCl film): $\tilde{\nu}$ = 3100 (br), 2936, 2240, 1684, 1412, 1277, 1076, 993, 912, 758, 733 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.4−1.7 (m, 4 H), 2.1 (m, 2 H), 2.37 (t, $^3J_{(H,H)}$ = 7.0 Hz, 2 H), 5.0−5.2 (m, 2 H), 5.7−6.0 (m, 1 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 19.1 (CH_2), 27.2 (CH_2), 28.4 (CH_2), 33.5 (CH_2), 73.2 (C), 92.6 (C), 115.4 (CH_2), 138.6 (CH), 158.6 (C). − EM (CI NH_3): *m/z* (%) = 170 (100) $[M + 18]^+$, 187 (82) $[M + 35]^+$.

General Procedure for the Preparation of 2-Alkynoate Derivatives of 4-Substituted Oxazolidin-2-ones: To a cold (−78°C) solution of the 2-alkynoic acid (0.69 mmol) in 4.5 mL of anhydrous THF, were added freshly distilled pivaloyl chloride (0.09 mL, 0.71 mmol), followed by Et_3N (0.1 mL, 0.72 mmol). The mixture was stirred at −78°C for 15 min, at 0°C for 45 min, and then recooled to −78°C. In a separate flask, *n*BuLi (0.1 mL, 0.72 mmol, 1.76 M solution in hexanes) was added to a solution of the chiral oxazolidinone (0.69 mmol) in 2 mL of anhydrous THF at −78°C, stirred for 15 min, and transferred by means of a cannula to the flask containing the mixed pivalic-2-alkynoic anhydride at the same temperature. The mixture was allowed to warm to room temperature and stirred until TLC analysis showed that the reaction was complete. The reaction was quenched with 2 M aq. $KHSO_4$ (15 mL) and extracted with AcOEt (3 × 20 mL). The combined organic phases were washed with brine (20 mL) and dried with $MgSO_4$. After filtration, the solvent was eliminated in vacuo and the residue was purified by column chromatography on silica gel, eluting with 10 to 20% hexane/AcOEt mixtures. Detailed specific procedures for the preparation of compounds **3a−c**, **4a−c** and **5b**, together with the corresponding spectral and analytical data, have been given elsewhere.[41]

(4*S*)-4-(2-Methylsulfanylethyl)-3-(3-phenylprop-2-ynoyl)oxazoli-din-2-one (3d): Prepared by the general procedure from oxazolidinone **1a** (0.55 g, 3.42 mmol) and from **2i** (0.50 g, 3.42 mmol) in 53% yield (0.525 g); White solid. − IR (NaCl film): $\tilde{\nu}$ = 3287, 2919, 2220, 1786, 1659, 1572, 1491, 1333, 1242, 1032, 912, 692, 656 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 2.10 (s, 3 H), 1.80−2.70 (m, 4 H), 4.22 (dd, $^3J_{(H,H)}$ = 8.2 Hz, $^3J'_{(H,H)}$ = 2.4 Hz, 1 H), 4.46 (t, $^3J_{(H,H)}$ = 8 Hz, 1 H), 4.70 (m, 1 H), 7.30−7.80 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 15.3 (CH_3), 29.1 (CH_2), 31.1 (CH_2), 53.5 (CH), 67.1 (CH_2), 80.5 (C), 94.7 (C), 119.6 (C), 128.6 (CH), 131.1 (CH), 133.3 (CH), 150.7 (C), 152.0 (C). − MS (CI NH_3): *m/z* (%) = 290 (10) $[M + 1]^+$, 307 (100) $[M + 18]^+$. − HRMS: $C_{15}H_{15}NO_3S$ ($[M]^+$), calcd. 289.0773; found 289.0753.

(4*R*)-4-Methylsulfanylmethyl-3-(3-phenylprop-2-ynoyl)oxazolidin-2-one (3e): Prepared by the general procedure from oxazolidinone **1e** (0.30 g, 2.0 mmol) and from **2i** (0.30 g, 2.0 mmol) in 74% yield (0.41 g); white solid. − IR (NaCl film): $\tilde{\nu}$ = 2975, 2215, 1790, 1659, 1491, 1352, 1229, 1111, 1030, 760, 690 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 2.10 (s, 3 H), 2.70 (dd, $^3J_{(H,H)}$ = 16 Hz, $^3J'_{(H,H)}$ = 8 Hz, 1 H), 3.00 (dd, $^3J_{(H,H)}$ = 16 Hz, $^3J_{(H,H)}$ = 2.4 Hz, 1 H), 4.39 (m, 2 H), 4.70 (m, 1 H), 7.30−7.80 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 15.9 (CH_3), 35.6 (CH_2), 53.3 (CH), 66.7 (CH_2), 80.9 (C), 94.9 (C), 119.5 (C), 128.6 (CH), 130.1 (CH), 133.3 (CH), 150.7 (C), 151.8 (C). − MS (CI NH_3): *m/z* (%) = 276 (4) $[M + 1]^+$, 293 (63) $[M + 18]^+$. − HRMS: $C_{14}H_{14}NO_3S$ ($[M + 1]^+$), calcd. 276.0694; found 276.0689.

(4*S*)-3-(8-Octen-2-ynoyl)-4-benzyloxazolidin-2-one (6a): Prepared by the general procedure from oxazolidinone **1a** (0.12 g, 0.72 mmol) and from **2iv** (0.10 g, 0.72 mmol) in 48% yield (0.104 g). Pale yellow oil. IR (NaCl film): $\tilde{\nu}$ = 2929, 2220, 1792, 1653, 1456, 1356, 1211, 1092, 916 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.80 (t, $^3J_{(H,H)}$ = 7 Hz, 2 H), 2.25 (m, 2 H), 2.48 (t, $^3J_{(H,H)}$ = 7.2 Hz, 2 H), 2.80 (dd, $^3J_{(H,H)}$ = 16 Hz, $^3J'_{(H,H)}$ = 4 Hz, 1 H), 3.30 (dd, $^3J_{(H,H)}$ = 4 Hz, $^3J'_{(H,H)}$ = 16 Hz, 1 H), 4.20 (t, $^3J_{(H,H)}$ = 4 Hz, 2 H), 4.70 (m, 1 H), 5.00−5.20 (m, 2 H), 5.70−5.90 (m, 1 H), 7.20−7.50 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 18.6 (CH_2), 26.5 (CH_2), 33.5 (CH_2), 37.6 (CH_2), 55.1 (CH), 65.9 (CH_2), 73.7 (C), 99.6 (C), 115.8 (CH_2), 127.4 (CH), 129.0 (CH), 129.4 (CH), 134.9 (C), 137.1 (CH), 150.3 (C), 151.6 (C).

(4*R*)-3-(8-Octen-2-ynoyl)-4-phenyloxazolidin-2-one (6b): Prepared by the general procedure from oxazolidinone *ent*-**1b** (0.495 g, 3.6 mmol) and from **2iv** (0.50 g, 3.6 mmol) in 55% yield (0.56 g). Pale yellow oil. $[\alpha]_D^{25}$ = −4.8 (c = 1.05, $CHCl_3$). − IR (NaCl film): $\tilde{\nu}$ = 2928, 2220, 1798, 1660, 1456, 1389, 1356, 1211, 1092, 915, 701 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): 1.70 (t, $^3J_{(H,H)}$ = 8 Hz, 2 H), 2.10−2.30 (m, 2 H), 2.44 (t, $^3J_{(H,H)}$ = 7 Hz, 2 H), 4.25 (dd, $^3J_{(H,H)}$ = 10 Hz, $^3J'_{(H,H)}$ = 4 Hz, 1 H), 4.70 (t, $^3J_{(H,H)}$ = 8 Hz, 1 H), 4.90−5.10 (m, 2 H), 5.40 (dd, $^3J_{(H,H)}$ = 10 Hz, $^3J'_{(H,H)}$ = 3 Hz, 1 H), 5.70−5.90 (m, 1 H), 7.20−7.40 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 18.5 (CH_2), 26.4 (CH_2), 29.5 (CH_2), 57.5 (CH), 69.8 (CH_2), 73.5 (C), 98.5 (C), 115.7 (CH_2), 126.0 (CH), 128.8 (CH), 129.2 (CH), 137.2 (CH), 138.2 (C), 150.5 (C), 151.8 (C). − MS (CI-NH_3): *m/z* (%) = (301(100) $[M + 18]^+$, 302 (20) $[M + 19]^+$. − HRMS: $C_{17}H_{18}NO_3$ ($[M + 1]^+$), calcd. 284.1287; found 284.1260.

(4*S*)-3-(8-Nonen-2-ynoyl)-4-benzyloxazolidin-2-one (7a): Prepared by the general procedure from oxazolidinone **1a** (0.116 g, 0.65 mmol) and from **2v** (0.10 g, 0.65 mmol) in 55% yield (0.11 g). Pale yellow oil. $[\alpha]_D^{25}$ = + 46.2 (*c* = 1.05 $CHCl_3$). − IR (NaCl film): $\tilde{\nu}$ = 2930, 2220, 1796, 1663, 1456, 1389, 1354, 1315, 1211, 1092, 1013, 914, 758, 733, 702 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.40−1.80 (m, 4 H), 2.05 (m, 2 H), 2.45 (t, $^3J_{(H,H)}$ = 7 Hz, 2 H), 2.80 (dd, $^3J_{(H,H)}$ = 16 Hz, $^3J'_{(H,H)}$ = 4 Hz, 1 H), 3.30 (dd, $^3J_{(H,H)}$ = 4 Hz, $^3J'_{(H,H)}$ = 16 Hz, 1 H), 4.17 (t, $^3J_{(H,H)}$ = 3.6 Hz, 2 H), 4.70 (m, 1 H), 4.90−5.10 (m, 2 H), 5.70−5.90 (m, 1 H), 7.00−7.50 (m, 5 H). − ^{13}C NMR (50 MHz,

$CDCl_3$, 23°C, TMS): δ = 19.1 (CH_2), 26.7 (CH_2), 27.8 (CH_2), 33.0 (CH_2), 37.5 (CH_2), 55.0 (CH), 65.8 (CH_2), 73.5 (C), 99.4 (C), 114.7 (CH_2), 127.3 (CH), 128.9 (CH), 129.3 (CH), 134.9 (C), 138.1 (CH), 150.3 (C), 152.0 (C). − MS (CI-CH_4): *m/z* (%) = 312 (100) $[M + 1]^+$, 340 (22) $[M + 29]^+$. − HRMS: $C_{19}H_{22}NO_3$ ($[M + 1]^+$), calcd. 312.1620; found 312.1600.

(4*R*)-3-(8-Nonen-2-ynoyl)-4-phenyloxazolidin-2-one (7b): Prepared by the general procedure from oxazolidinone *ent*-**1b** (0.55 g, 3.6 mmol) and from **2v** (0.50 g, 3.3 mmol) in 69% yield (0.67 g). Pale yellow oil. $[\alpha]_D^{25} = -3.38$ (*c* = 1.34, $CHCl_3$). − IR (NaCl film): $\tilde{\nu}$ = 2931, 2220, 1792, 1669, 1559, 1541, 1506, 1458, 1383, 1327, 1198, 1090, 1040 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.40−1.70 (m, 4 H), 2.00 (m, 2 H), 2.40 (t, $^3J_{(H,H)}$ = 7.6 Hz, 2 H), 4.26 (dd, $^3J_{(H,H)}$ = 2.4 Hz, $^3J'_{(H,H)}$ = 10 Hz, 1 H), 4.66 (t, $^3J_{(H,H)}$ = 8 Hz, 1 H), 4.90−5.10 (m, 2 H), 5.20 (dd, $^3J_{(H,H)}$ = 10 Hz, $^3J'_{(H,H)}$ = 2.4 Hz, 1 H), 5.70−5.90 (m, 1 H), 7.20−7.40 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 19.2 (CH_2), 26.7 (CH_2), 27.9 (CH_2), 33.0 (CH_2), 57.5 (CH), 69.8 (CH_2), 73.5 (C), 98.7 (C), 114.8 (CH_2), 126.0 (CH), 128.8 (CH), 129.2 (CH), 138.2 (CH), 138.3 (C), 150.3 (C), 151.2 (C). − MS (CI CH_4): *m/z* (%) = 298 (100) $[M + 1]^+$, 326 (16) $[M + 29]^+$. − HRMS: $C_{18}H_{20}NO_3$ ($[M + 1]^+$), calcd. 298.1443; found 298.1443.

(1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-(8-nonen-2-ynoyl)-3-oxa-5-aza-tricyclo[5.2.1.0^{2,6}]decan-4-one (7c): Prepared by the general procedure from oxazolidinone **1c** (0.26 g, 1.3 mmol) and from **2v** (0.20 g, 1.3 mmol) in 55% yield (0.24 g). Pale yellow oil. $[\alpha]_D^{25} = +9.8$ (*c* = 1.70, $CHCl_3$). − IR (NaCl film): $\tilde{\nu}$ = 2959, 2220, 1792, 1669, 1559, 1541, 1506, 1456, 1375, 1308, 1194, 1053 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 0.90 (s, 3 H), 0.96 (s, 3 H), 1.01 (s, 3 H), 1.10−2.20 (m, 11 H), 2.45 (t, $^3J_{(H,H)}$ = 7 Hz, 2 H), 4.44 (dd, $^3J_{(H,H)}$ = 3.2 Hz, $^3J''_{(H,H)}$ = 8 Hz, 2 H), 4.90−5.10 (m, 2 H), 5.70−5.90 (m, 1 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 12.0 (CH_3), 19.2 (CH_3), 19.7 (CH_3), 22.7 (CH_2), 22.8 (CH_2), 26.8 (CH_2), 27.9 (CH_2), 33.1 (CH_2), 33.2 (CH_2), 46.4 (C), 47.6 (CH), 50.1 (C), 65.9 (CH), 74.2 (C), 81.3 (CH), 99.1 (C), 114.8 (CH_2), 138.2 (CH), 151.9 (C), 153.6 (C). − MS (CI CH_4): *m/z* (%) = 330 (100) $[M + 1]^+$, 358 (13) $[M + 29]^+$.

(4*R*)-4-Methylsulfanylmethyl-3-(non-8-en-2-ynoyl)oxazolidin-2-one (7e): Prepared by the general procedure from oxazolidinone **1e** (0.28 g, 2.0 mmol) and from **2v** (0.31 g, 2 mmol) in 36% yield (0.21 g). Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 2925, 2222, 1796, 1663, 1429, 1387, 1350, 1314, 1200, 1097, 735 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.50−1.70 (m, 4 H), 2.00−2.30 (m, 2 H), 2.20 (s, 3 H), 2.45 (t, $^3J_{(H,H)}$ = 6.6 Hz, 2 H), 2.70 (dd, $^3J_{(H,H)}$ = 8 Hz, $^3J'_{(H,H)}$ = 12 Hz, 1 H), 3.00 (dd, $^3J_{(H,H)}$ = 8 Hz, $^3J_{(H,H)}$ = 2.2 Hz, 1 H), 4.20−4.50 (m, 2 H), 4.55−4.70 (m, 1 H) 4.90−5.10 (m, 2 H), 5.70−5.90 (m, 1 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 15.8 (CH_3), 19.2 (CH_2), 26.8 (CH_2), 27.9 (CH_2), 33.0 (CH_2), 35.5 (CH_2), 53.2 (CH), 66.5 (CH_2), 73.6 (C), 99.0 (C), 114.8 (CH_2), 138.2 (CH), 150.1 (C), 152.2 (C). − MS (CI NH_3): *m/z* (%) = 282 (2) $[M + 1]^+$, 299 (100) $[M + 18]^+$.

General Procedures for the Intermolecular Pauson−Khand Reaction of *N*-(2-Alkynoyl)oxazolidinones with Norbornadiene and Norbornene

Thermal Reaction in Toluene: To a stirred solution of a *N*-(2-alkynoyl)oxazolidinone (0.33 mmol) in anhydrous toluene (5 mL), octacarbonyldicobalt (0.36 mmol) was added in one portion, and the resulting dark-coloured solution was stirred at room temperature for 1 h, after which time the formation of the hexacarbonyldicobalt complex was complete (TLC). The mixture was purged with nitrogen and a solution of the olefin (3.28 mmol) in toluene (2 mL) was added dropwise. The reaction mixture was then stirred at a specific temperature (25−45°C, see Table 1) during 12−96 h until complete disappearance of the complex. The reaction mixture was filtered through Celite and submitted to column chromatography on silica gel, eluting with 15−30% hexane/diethyl ether mixtures.

Thermal Reaction in Acetonitrile: A solution of the *N*-(2-alkynoyl)oxazolidinone (0.33 mmol) in dry acetonitrile (5 mL) was introduced by syringe into a flask containing solid octacarbonyldicobalt (0.36 mmol). The resulting solution was stirred at room temperature for 1 h; at this point, an additional amount (0.36 mmol) was added and the stirring was continued until TLC analysis showed that the formation of the complex was complete. The mixture was purged with nitrogen and a solution of the olefin (3.28 mmol) in acetonitrile (2 mL) was added dropwise, and the resulting solution was heated until complete disappearance of the complex. The reaction mixture was filtered through Celite and submitted to column chromatography on silica gel, eluting with 15−30% hexane/diethyl ether mixtures.

Tertiary Amine *N*-Oxide-Mediated Reaction: To a stirred solution of the *N*-(2-alkynoyl)oxazolidinone (0.33 mmol) in anhydrous dichloromethane (5 mL), octacarbonyldicobalt (0.36 mmol) was added in one portion and the resulting dark-coloured solution was stirred at room temperature for 1 h, after which time the formation of the hexacarbonyldicobalt complex was complete (TLC). The mixture was purged with nitrogen and a solution of the olefin (3.28 mmol) in dichloromethane (5 mL) was added dropwise. The mixture was externally cooled with ice. Solid *N*-methylmorpholine *N*-oxide monohydrate (1.96 mmol) was added in one portion and the reaction mixture was allowed to attain room temperature by removal of the cooling bath. After stirring at room temperature until the complete disappearance of the complex, the mixture was filtered through Celite and submitted to column chromatography on silica gel, eluting with 15−30% hexane/diethyl ether mixtures.

(4*S*)-3-{(1*R,2*S**,6*R**,7*S**)-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carbonyl}-4-benzyloxazolidin-2-one (8a):** Obtained as a 1:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (40°C, 19 h) from (4*S*)-3-(3-phenyl-2-propynoyl)-4-benzyloxazolidin-2-one (**3a**, 0.100 g, 0.328 mmol), octacarbonyldicobalt (0.124 g, 0.361 mmol) and norbornene (0.308 g, 3.28 mmol) in 74% overall yield (0.104 g). Obtained as a 1.2:1 diastereomeric mixture by thermal Pauson−Khand in acetonitrile (55°C, 18 h) from **3a** (0.100 g, 0.328 mmol), octacarbonyldicobalt (0.124 g, 0.361 mmol) and norbornene (0.308 g, 3.28 mmol) in 79% overall yield (0.110 g). Obtained as a 1.8:1 diastereomeric mixture by tertiary amine *N*-oxide-mediated reaction (room temperature, 15 h) from **3a** (0.100 g, 0.328 mmol), *N*-methylmorpholine *N*-oxide monohydrate (0.445 g, 3.28 mmol), octacarbonyldicobalt (0.124 g, 0.361 mmol) and norbornene (0.308 g, 3.28 mmol) in 81% overall yield (0.113 g). − IR (NaCl film): $\tilde{\nu}$ = 3060, 3020, 2960, 2870, 1740, 1705, 1360, 1270, 1195, 1100, 700 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.15−1.80 (m, 6 H), 2.40−2.60 (m, 4 H), 3.15 (d, $^3J_{(H,H)}$ = 5 Hz, 1 H), 3.30−3.45 (m, 1 H), 3.90−4.15 (m, 2 H), 4.60−4.70 (m, 1 H), 7.17−7.33 (m, 10 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS) *major diastereomer:* δ = 28.5 (CH_2), 28.9 (CH_2), 32.0 (CH_2), 37.3 (CH_2), 38.0 (CH), 40.0 (CH), 49.0 (CH), 54.2 (CH), 54.9 (CH), 66.6 (CH_2), 127.6 (CH), 128.3 (CH), 128.8 (CH), 129.1 (CH), 129.4 (CH), 130.0 (C), 134.5 (C), 145.1 (C), 153.0 (C), 166.9 (C), 169.9 (C), 207.6 (C); *minor diastereomer:* δ = 28.5 (CH_2), 28.9 (CH_2), 32.0 (CH_2), 37.7 (CH_2), 38.0 (CH), 40.0 (CH), 49.1 (CH), 54.2 (CH), 54.9 (CH), 66.9 (CH_2), 127.6 (CH), 128.3 (CH), 128.8 (CH), 129.1 (CH), 129.4 (CH), 130.0 (C), 134.5 (C), 166.9 (C), 169.9 (C), 207.6 (C). − MS (CI-NH_3): *m/z* (%) =

428 (24) [M + 1]$^+$, 445 (100) [M + 18]$^+$. − HRMS: $C_{27}H_{25}NO_4$ ([M]$^+$), calcd. 427.1784; found 427.1790.

(4*S*)-3-{(1*R,2*R**,6*S**,7*S**)-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carbonyl}-4-benzyloxazolidin-2-one (9a):** Obtained as a 1:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (room temperature, 24 h) from (4*S*)-3-(3-phenyl-2-propynoyl)-4-benzyloxazolidin-2-one (**3a**, 92 mg, 0.302 mmol), octacarbonyldicobalt (0.113 g, 0.332 mmol) and norbornadiene (0.278 g, 3.020 mmol) in 97% overall yield (0.125 g). − IR (NaCl film): $\tilde{\nu}$ = 3060, 3040, 2980, 1795, 1710, 1690, 1370, 1260, 1215, 1100, 760, 735, 705 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.50−1.70 (m, 2 H), 2.10−2.30 (m, 1 H), 2.62 −2.65 (d, $^3J_{(H,H)}$ = 5.5 Hz, 1 H), 2.90−3.15 (m, 2 H), 3.18−3.21 (d, $^3J_{(H,H)}$ = 5.5 Hz, 1 H), 3.30−3.50 (m, 1 H), 3.90−4.10 (m, 2 H), 4.55−4.60 (m, 1 H), 6.25−6.33 (m, 2 H), 7.30−7.34 (m, 10 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS) *first diastereomer:* δ = 37.7 (CH_2), 42.0 (CH_2), 43.0 (CH), 44.6 (CH), 48.7 (CH), 53.0 (CH), 54.8 (CH), 66.9 (CH_2), 127.4 (CH), 127.5 (CH), 128.2 (CH), 128.3 (CH), 128.9 (CH), 129.3 (CH), 130.0 (C), 134.6 (C), 137.7 (CH), 138.2 (CH), 146.1 (C), 152.8 (C), 168.0 (C), 170.1 (C), 205.9 (C); *second diastereomer:* δ = 37.4 (CH_2), 42.0 (CH_2), 43.0 (CH), 44.6 (CH), 48.6 (CH), 53.0 (CH), 54.8 (CH), 66.7 (CH_2), 127.4 (CH), 127.5 (CH), 128.0 (CH), 128.3 (CH), 128.9 (CH), 129.3 (CH), 130.0 (C), 134.6 (C), 137.7 (CH), 138.2 (CH), 146.1 (C), 152.8 (C), 168.0 (C), 170.1 (C), 205.9 (C). − MS (CI-NH_3): *m*/*z* (%) = 426 (18) [M + 1]$^+$, 443 (100) [M + 18]$^+$. − HRMS: $C_{27}H_{23}NO_4$ ([M]$^+$), calcd. 425.1627; found 425.1625.

(4*S*)-3-{(1*R,2*S**,6*R**,7*S**)-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]-dec−3-ene-3-carbonyl}-4-phenyloxazolidin-2-one (8b):** Obtained as a 4.3:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (room temperature, 20 h) from (4*S*)-3-(3-phenyl-2-propynoyl)-4-phenyloxazolidin-2-one (**3b**, 0.100 g, 0.344 mmol), octacarbonyldicobalt (0.129 g, 0.378 mmol) and norbornene (0.323 g, 3.44 mmol) in 91% overall yield (0.114 g). Column chromatography afforded 0.085 g (60% yield) of the major diastereomer and 0.014 g (10% yield) of the minor diastereomer. Obtained as a 3.8:1 diastereomeric mixture by tertiary amine *N*-oxide-mediated reaction (−20°C, 24 h) from **3b** (0.109 g, 0.375 mmol), octacarbonyldicobalt (0.141 g, 0.412 mmol), anhydrous *N*-methylmorpholine *N*-oxide (0.250 g, 2.25 mmol), and norbornene (0.353 g, 3.75 mmol) in 100% overall yield (0.155 g). Column chromatography allowed the isolation of 84 mg (54%) of the pure major diastereomer. *Major diastereomer*: $[\alpha]_D^{25}$ = +6.4 (*c* = 1.8, $CHCl_3$). − IR (NaCl film): $\tilde{\nu}$ = 3060, 3030, 2960, 2870, 1790, 1705, 1490, 1385, 1360, 1320, 1200, 1040, 760, 710, 700 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 0.80−1.64 (m, 6 H), 2.00−2.20 (m, 1 H), 2.40−2.60 (m, 2 H), 3.03−3.06 (d, $^3J_{(H,H)}$ = 5.6 Hz, 1 H), 4.15−4.25 (m, 1 H), 4.40−4.60 (m, 1 H), 5.34−5.42 (m, 1 H), 7.25−7.37 (m, 10 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 28.4 (CH_2), 28.8 (CH_2), 31.9 (CH_2), 37.8 (CH), 39.9 (CH), 49.2 (CH), 54.2 (CH), 57.4 (CH), 70.4 (CH_2), 126.3 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 128.9 (C), 129.1 (CH), 129.2 (CH), 130.0 (C), 146.0 (C), 152.0 (C), 162.0 (C), 166.5 (C), 207.6 (C). − MS (CI NH_3): *m*/*z* (%) = 414 (20) [M + 1]$^+$, 431 (100) [M + 18]$^+$. − $C_{26}H_{23}NO_4$: calcd. C 75.53, H 5.61, N 3.39; found C 75.14, H 5.84, N 3.23. − HPLC (Nucleosyl C-18): t_R = 21.84 min (φ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 240 nm). − *Minor diastereomer:* ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 28.4 (CH_2), 28.8 (CH_2), 31.9 (CH_2), 37.8 (CH), 40.0 (CH), 49.1 (CH), 54.2 (CH), 57.4 (CH), 70.4 (CH_2), 126.3 (CH), 128.2 (CH), 128.7 (2CH), 128.9 (C), 129.1 (CH), 129.2 (CH), 130.0 (C), 146.0 (C), 152.0 (C), 162.0 (C), 166.5 (C), 207.6 (C). − HPLC (Nucleosil C-18): t_R = 21.02 min (φ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 240 nm).

(4*S*)-3-{(1*R,2*R**,6*S**,7*S**)-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carbonyl}-4-phenyloxazolidin-2-one (9b):** Obtained as a 5.2:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (room temperature, 21 h) from **3b** (0.096 g, 0.330 mmol), octacarbonyldicobalt (0.124 g, 0.363 mmol) and norbornadiene (0.304 g, 3.30 mmol) in 96% overall yield (0.130 g). Column chromatography afforded 0.090 g (66% yield) of the pure major diastereomer. *Major diastereomer* (1*S*, 2*S*, 6*R*, 7*R*): m.p. 78−80°C (hexane/dichloromethane). $[\alpha]_D^{25}$ = +26.0 (*c* = 2.2, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3070, 3040, 2980, 1795, 1710, 1640, 1390, 1335, 1270, 1205, 1100, 1040, 1010, 960, 770, 730, 710 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.35−1.55 (m, 2 H), 2.59−2.61 (m, 2 H), 3.05 (m, 1 H), 3.15−3.18 (d, $^3J_{(H,H)}$ = 5.6 Hz, 1 H), 4.18−4.26 (m, 1 H), 4.47−4.58 (t, $^3J_{(H,H)}$ = 8.2 Hz, 1 H), 5.34−5.42 (m, 1 H), 6.15−6.35 (m, 2 H), 7.35−7.39 (m, 10 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 42.0 (CH_2), 42.8 (CH), 44.6 (CH), 48.7 (CH), 53.0 (CH), 57.4 (CH), 70.5 (CH_2), 126.3 (CH), 128.4 (2CH), 128.8 (CH), 129.1 (CH), 129.2 (CH), 129.4 (C), 129.9 (C), 137.7 (CH), 138.2 (CH), 145.0 (C), 152.1 (C), 161.8 (C), 166.2 (C), 206.0 (C). − MS (CI-NH_3): *m*/*z* (%) = 412 (9) [M + 1]$^+$, 429 (100) [M + 18]$^+$. − $C_{26}H_{21}NO_4$: calcd. C 75.90, H 5.14, N 3.40; found C 75.71, H 5.09; N. 3.41. − HPLC (Nucleosyl C-18): t_R = 20.01 min (φ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 240 nm). *Minor diastereomer* (1*R*, 2*R*, 6*S*, 7*S*): ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 42.0 (CH_2), 42.8 (CH), 44.8 (CH), 48.7 (CH), 53.0 (CH), 57.6 (CH), 70.5 (CH_2), 126.3 (CH), 128.3 (2CH), 128.7 (CH), 129.1 (CH), 129.2 (CH), 129.4 (C), 129.9 (C), 137.7 (CH), 138.2 (CH), 145.0 (C), 152.1 (C), 161.8 (C), 166.2 (C), 206.0 (C). − HPLC (Nucleosil C-18): t_R = 19.06 min. (φ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 240 nm).

(1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-{(1*R,2*S**,6*R**,7*S**)-5-oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carbonyl}-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]decan-4-one (8c):** Obtained as a 9.2:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (45°C, 42 h) from the corresponding *N*-alkynoyloxazolidinone **3c** (0.060 g, 0.19 mmol), octacarbonyldicobalt (0.070 g, 0.20 mmol) and norbornene (0.175 g, 1.86 mmol) in 100% overall yield (0.092 g). Column chromatography afforded 0.076 g (92% yield) of pure major diastereomer. *Major diastereomer:* m.p. 81−83°C (hexane-dichloromethane). − $[\alpha]_D^{25}$ = −41.9 (*c* = 0.98, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3060, 3030, 2960, 2880, 1790, 1705, 1280, 1195, 1050, 770, 715, 700 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 0.92 (s, 3 H), 1.05 (s, 3 H), 0.86−1.90 (m, 13 H), 2.10−2.65 (m, 4 H), 3.10−3.50 (d, $^3J_{(H,H)}$ = 5.5 Hz, 1 H), 4.30−4.45 (d, $^3J_{(H,H)}$ = 10 Hz, 1 H), 4.45−4.57 (d, $^3J_{(H,H)}$ = 10 Hz, 1 H), 7.26−7.32 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 16.2 (CH_3), 19.4 (CH_3), 22.6 (CH_3), 22.7 (CH_2), 28.3 (CH_2), 28.9 (CH_2), 32.0 (CH_2), 33.3 (CH_2), 37.9 (CH), 39.6 (CH), 46.5 (C), 47.6 (CH), 49.1 (CH), 50.2 (C), 54.1 (CH), 62.8 (CH), 82.3 (CH), 128.3 (CH), 128.5 (CH), 128.6 (CH), 130.0 (C), 142.7 (C), 153.7 (C), 163.0 (C), 167.0 (C), 207.5 (C). − MS (CI-CH_4): *m*/*z* (%) = 446 (94) [M + 1]$^+$, 474 (16) [M + 29]$^+$, 486 (7) [M + 41]$^+$. − $C_{28}H_{31}NO_4$: calcd. C 75.83, H 7.05, N 3.16; found C 76.01, H 6.91; N. 3.00. HPLC (Nucleosil C-18): t_R = 21.56 min (φ = 0.8 mL/min, MeOH/H_2O 75:25, λ = 240 nm). *Minor diastereomer:* HPLC (Nucleosil C-18): t_R = 19.45 min (φ = 0.8 mL/min, MeOH/H_2O 75:25, λ = 240 nm).

(1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-{(1*R,2*R**,6*S**,7*S**)-5-oxo-4-phenyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carbonyl}-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]decan-4-one (9c):** Obtained as a 14:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (room temperature, 21 h) from the *N*-(alkynoyl)oxazolidinone **3c** (0.057 g, 0.18 mmol), octacarbonyldicobalt (0.067 g, 0.19 mmol) and norbornadiene (0.162 g, 1.76 mmol) in 97% overall yield (0.076

g). Column chromatography afforded 0.070 g (89% yield) of the major diastereomer as a white solid. M.p. 90−95°C (hexane/dichloromethane). − $[\alpha]_D^{25}$ = −18.7 (*c* = 1.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3060, 3040, 2970, 2940, 1795, 1710, 1290, 1280, 1200, 1050, 760 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 0.86−0.98 (m, 6 H), 1.06 (s, 3 H), 1.20−2.15 (m, 7 H), 2.00−2.62 (d, $^3J_{(H,H)}$ = 4.6 Hz, 1 H), 2.80−2.85 (m, 1 H), 3.13−3.16 (m, 1 H), 3.17−3.20 (d, $^3J_{(H,H)}$ = 5.6 Hz, 1 H), 4.34−4.38 (d, $^3J_{(H,H)}$ = 8.6 Hz, 1 H), 4.46−4.49 (d, $^3J_{(H,H)}$ = 8.6 Hz, 1 H), 6.20−6.28 (m, 2 H), 7.20−7.40 (m, 5 H). − ^{13}C NMR (75 MHz, C_6D_6, 50°C, TMS): δ = 12.3 (CH_3), 19.4 (CH_3), 22.5 (CH_3), 22.6 (CH_2), 33.2 (CH_2), 42.0 (CH_2), 42.8 (CH), 44.4 (CH), 46.4 (C), 47.5 (CH), 48.5 (CH), 50.1 (C), 52.8 (CH), 65.4 (CH), 82.3 (CH), 128.2 (CH), 128.4 (CH), 128.6 (CH), 130.5 (C), 137.8 (CH), 138.1 (CH), 144.5 (C), 152.0 (C), 163.0 (C), 167.5 (C), 205.9 (C). − MS (CI-NH_3): *m/z* (%) = 444 (100) $[M + 1]^+$, 472 (100) $[M + 29]^+$, 484 (6) $[M + 41]^+$. − $C_{28}H_{29}NO_4$: calcd. C 75.82, H 6.59, N 3.16; found C 76.11, H 6.87; N. 3.00. − HPLC (Nucleosil C-18): t_R = 19.73 min (ϕ = 0.8 mL/min, MeOH/H_2O 75:25, λ = 240 nm).

(4*S*)-4-Methylsulfanylethyl-3-(5-oxo-4-phenyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carbonyl)oxazolidin-2-one (9d): Obtained as a 2.2:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (60°C, 3 h) from (4*S*)-4-methylsulfanylethyl-3-(3-phenylprop-2-ynoyl)oxazolidin-2-one **3d** (0.066 g, 0.23 mmol), norbornadiene (0.21 g, 2.3 mmol) and octacarbonyldicobalt (0.080 g, 0.25 mmol) in 93% overall yield (0.067 g). Obtained as a 2.9:1 diastereomeric mixture by tertiary amine *N*-oxide-mediated reaction (room temperature, 3 h) from **3e** (0.050 g, 0.17 mmol), octacarbonyldicobalt (0.067 g, 0.2 mmol), *N*-methylmorpholine *N*-oxide monohydrate (0.138 g, 1.05 mmol) and norbornadiene (0.165 g, 1.8 mmol) in 75% overall yield (0.055 g). Obtained as a 1.8:1 diastereomeric mixture by thermal Pauson−Khand reaction in acetonitrile (80°C, 3 h) from **3e** (0.052 g, 0.18 mmol), norbornadiene (0.165 g, 1.8 mmol) and octacarbonyldicobalt (0.067 g, 0.2 mmol) in 93% overall yield (0.069 g). Pale yellow oil. IR (NaCl film): $\tilde{\nu}$ = 3060, 2975, 1788, 1705, 1632, 1493, 1445, 1368, 1323, 1279, 1213, 1097, 810, 762, 700 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.40−2.70 (m, 10 H), 2.80−3.30 (m, 3 H), 4.10−4.30 (m, 2 H), 4.60 (m, 1 H), 6.30 (m, 2 H), 7.20−7.50 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 16.2 (CH_3), 29.0 (CH_2), 36.5 (CH_2), 42.0 (CH_2), 43.0 (CH), 44.7 (CH), 48.7 (CH), 48.8 (CH), 53.1 (CH), 67.4 (CH_2), 128.2 (CH), 128.3 (CH), 129.0 (CH), 137.7 (CH), 138.2 (CH); (quaternary carbons could not be observed). − MS (CI-NH_3): *m/z* (%) = 410 (24) $[M + 1]^+$, 427 (100) $[M + 18]^+$. − HRMS: $C_{23}H_{23}NO_4S$ ($[M]^+$), calcd. 409.1348; found 409.1367. − HPLC (Nucleosil C-18): $t_{R(minor)}$ = 25.4 min, $t_{R(major)}$ = 27.0 min, (ϕ = 0.8 mL/min, MeOH/H_2O = 60:40, λ = 254 nm).

(4*R*)-4-Methylsulfanylmethyl-3-(5-oxo-4-phenyltricyclo[5.2.1.0^{2,6}]-deca-3,8-diene-3-carbonyl)oxazolidin-2-one (9e): Obtained as a 2.7:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (60°C, 3 h) from (4*R*)-4-methylsulfanylmethyl-3-(3-phenylprop-2-ynoyl)oxazolidin-2-one (**3e**, 0.050 g, 0.18 mmol), norbornadiene (0.168 g, 1.8 mmol) and octacarbonyldicobalt (0.065 g, 0.20 mmol) in 93% overall yield (0.067 g). Obtained as a 3.1:1 diastereomeric mixture by tertiary amine *N*-oxide-mediated reaction (room temperature, 3 h) from **3e** (0.10 g, 0.37 mmol), octacarbonyldicobalt (0.13 g, 0.40 mmol), *N*-methylmorpholine *N*-oxide monohydrate (0.15 g, 1.11 mmol) and norbornadiene (0.33 g, 3.7 mmol) in 53% overall yield (0.077 g). Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 2979, 1790, 1705, 1634, 1495, 1445, 1366, 1323, 1279, 1209, 1099, 1001, 754, 702 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.40−1.70 (m, 2 H), 2.00−2.30 (m, 5 H), 2.50−2.70 (m, 1 H), 2.80−3.30 (m, 3 H), 4.10−4.30 (m, 2 H), 4.40−4.60 (m, 1 H), 6.29 (s, 2 H), 7.20−7.50 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 16.2 (CH_3), 36.5 (CH_2), 42.0 (CH_2), 43.0 (CH), 44.7 (CH), 48.7 (CH), 48.8 (CH), 53.1 (CH), 67.4 (CH_2), 128.2 (CH), 128.3 (CH), 129.0 (CH), 137.7 (CH), 138.2 (CH); (quaternary carbons could not be observed). − MS (CI NH_3): *m/z* (%) = 413 (100) $[M + 18]^+$. − HRMS: $C_{22}H_{21}NO_4S$ ($[M]^+$), calcd. 395.1191; found 395.1188. − HPLC (Nucleosil C-18): $t_{R(minor)}$ = 21.2 min, $t_{R(major)}$ = 22.8 min, (ϕ = 0.8 mL/min, MeOH/H_2O = 60:40, λ = 254 nm).

(4*S*)-3-{(1*R,2*R**,6*S**,7*S**)-5-Oxo-4-trimethylsilyltricyclo [5.2.1.0^{2,6}]-deca-3,8-diene-3-carbonyl}-4-phenyloxazolidin-2-one (11b):** Obtained as a 3.6:1 diastereomeric mixture by tertiary amine *N*-oxide-mediated Pauson−Khand reaction (oxygen atmosphere, 0°C to room temp., 14 h) from the *N*-alkynoyloxazolidinone **5b** (0.070 g, 0.24 mmol), octacarbonyldicobalt (0.092 g, 0.27 mmol), norbornadiene (0.225 g, 2.44 mmol) and *N*-methylmorpholine *N*-oxide monohydrate (0.330 g, 3.90 mmol, added in two portions) in 88% overall yield (0.097 g). Column chromatography afforded 0.068 g (69% yield) of the major diastereomer (1*S*,2*S*,6*R*,7*R*) and 0.019 g (19% yield) of the minor diastereomer. *Major diastereomer.* White solid, m.p. 72−75°C (hexane/dichloromethane). − $[\alpha]_{435}^{25}$ = −50.3 (*c* = 0.8, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3060, 3040, 1795, 1695, 1600, 1390, 1330, 1250, 1230, 1200, 1100, 1045, 850, 765, 710 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 0.15 (s, 9 H), 1.17−1.40 (m, 2 H), 2.20−2.30 (m, 1 H), 2.41−2.45 (d, $^3J_{(H,H)}$ = 5.5 Hz, 1 H), 2.90−2.97 (m, 1 H), 3.12−3.15 (d, $^3J_{(H,H)}$ = 5.6 Hz, 1 H), 4.35−4.45 (dd, $^3J_{(H,H)}$ = 9.5 Hz, $^3J'_{(H,H)}$ = 5.1 Hz, 1 H), 4.75−4.85 (dd, $^3J_{(H,H)}$ = $^3J'_{(H,H)}$ = 9.5 Hz, 1 H), 5.45−5.55 (dd, $^3J_{(H,H)}$ = 9.5 Hz, $^3J'_{(H,H)}$ = 5.1 Hz, 1 H), 6.30−6.42 (m, 2 H), 7.41−7.46 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = −1.8 (CH_3), 41.9 (CH_2), 42.3 (CH), 44.4 (CH), 52.5 (CH), 53.6 (CH), 57.0 (CH), 70.6 (CH_2), 126.0 (CH), 129.2 (CH), 129.3 (CH), 137.7 (CH), 137.9 (CH), 148.8 (C), 152.6 (C), 167.6 (C), 175.7 (C), 211.6 (C). − MS (CI-CH_4): *m/z* (%) = 392 (55) $[M-15]^+$, 408 (100), $[M + 1]^+$, 436 (18) $[M + 29]^+$, 448 (7) $[M + 41]^+$. − $C_{23}H_{25}NO_4Si$: calcd. C 67.79, H 6.18, N 3.44; found C 67.77, H 6.27; N. 3.26. − HPLC (Nucleosil C-18): t_R = 31.20 min (ϕ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 240 nm). − *Minor diastereomer* (1*R*, 2*R*, 6*S*, 7*S*): $[\alpha]_{435}^{25}$ = +167.9 (*c* = 0.7, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3060, 3040, 1795, 1695, 1600, 1390, 1330, 1250, 1230, 1200, 1100, 1045, 850, 765, 710 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 0.0 (s, 9 H), 1.30−1.45 (m, 2 H), 2.28−2.32 (d, $^3J_{(H,H)}$ = 5.5 Hz, 1 H), 2.75−2.80 (m, 1 H), 2.85−2.95 (m, 2 H), 4.40−4.50 (dd, $^3J_{(H,H)}$ = 9.5 Hz, $^3J'_{(H,H)}$ = 5 Hz, 1 H), 4.70−4.85 (dd, $^3J_{(H,H)}$ = $^3J'_{(H,H)}$ = 9.5 Hz, 1 H), 5.35−5.45 (dd, $^3J_{(H,H)}$ = 9.5 Hz, $^3J'_{(H,H)}$ = 5 Hz, 1 H), 6.13−6.15 (m, 2 H), 7.25−7.40 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = −1.9 (CH_3), 42.1 (CH_2), 43.0 (CH), 44.5 (CH), 53.0 (CH), 53.7 (CH), 57.5 (CH), 70.6 (CH_2), 127.1 (CH), 129.2 (CH), 129.3 (CH), 137.9 (CH), 138.1 (CH), 148.8 (C), 152.6 (C), 167.6 (C), 175.7 (C), 211.6 (C). − HPLC (Nucleosil C-18): t_R = 31.86 min (ϕ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 240 nm).

(4*S*)-3-{(1*R,2*S**,6*R**,7*S**)-4-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carbonyl}-4-benzyloxazolidin-2-one (12a) and (4*S*)-3-{(1*R**,2*S**,6*R**,7*S**)-3-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-4-carbonyl}-4-benzyloxazolidin-2-one (14a):** According to the procedure described above for the thermal Pauson−Khand reaction in toluene, a solution of the complex derived from *N*-(tetrolyl)oxazolidinone **4a** (0.100 g, 0.412 mmol) and octacarbonyldicobalt (0.155 g, 0.453 mmol) was treated with norbornene (0.387 g, 4.12 mmol), and the resulting mixture was stirred at room temperature for 70 h. After chromatographic purification, 0.107 g (71% yield) of a 1:1.8 mixture of the regioisomers **12a** (1.9:1 diastereomeric

mixture) and **14a** (1:1 diastereomeric mixture) were obtained. The tertiary amine *N*-oxide-mediated reaction (dichloromethane, −20°C, 14 h), using **4a** (0.078 g, 0.32 mmol), octacarbonyldicobalt (0.121 g, 0.353 mmol), norbornene (0.301 g, 3.21 mmol) and anhydrous *N*-methylmorpholine *N*-oxide (0.225 g, 1.92 mmol) gave, after chromatographic purification, 0.129 g (100% yield) of a 1:1.5 mixture of the regioisomers **12a** (2.0:1 diasteromer mixture) and **14a** (1.2:1 diastereomeric mixture).

(4*S*)-3-{(1*R,2*S**,6*R**,7*S**)-4-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carbonyl}-4-benzyloxazolidin-2-one (12a, Diastereomeric Mixture):** IR (NaCl film): $\tilde{\nu}$ = 3040, 2960, 2930, 2880, 1795, 1705, 1650, 1365, 1240, 1215, 1115, 705 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$, 23°C, TMS): δ = 1.23−1.32 (m, 4 H), 1.55−1.65 (m, 2 H), 1.76 (s, 3 H), 2.28−2.29 (d, $^3J_{(H,H)}$ = 3.3 Hz, 1 H), 2.33−2.35 (d, $^3J_{(H,H)}$ = 5.1 Hz, 1 H), 2.49−2.50 (d, $^3J_{(H,H)}$ = 3.6 Hz, 1 H), 2.80−3.00 (m, 2 H), 3.45−3.55 (m, 1 H), 4.25−4.36 (m, 2 H), 4.73−4.82 (m, 1 H), 7.26−7.37 (m, 5 H). − ^{13}C NMR (75 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 9.0 (CH_3), 28.4 (CH_2), 28.7 (CH_2), 31.8 (CH_2), 37.7 (CH), 37.9 (CH_2), 39.6 (CH), 49.1 (CH), 53.4 (CH), 55.2 (CH), 67.0 (CH_2), 127.5 (CH), 129.1 (CH), 129.4 (CH), 134.6 (C), 142.3 (C), 152.0 (C), 160.5 (C), 167.4 (C), 209.5 (C); *(minor diastereomer)* 8.9 (CH_3), 28.4 (CH_2), 28.7 (CH_2), 31.8 (CH_2), 37.6 (CH), 37.9 (CH_2), 39.6 (CH), 49.2 (CH), 53.4 (CH), 55.4 (CH), 66.9 (CH_2), 127.5 (CH), 129.1 (CH), 129.4 (CH), 134.6 (C), 142.3 (C), 152.0 (C), 160.5 (C), 167.4 (C), 209.5 (C). − MS (CI-NH_3): *m*/*z* (%) = 366 (24) $[M + 1]^+$, 383 (100) $[M + 18]^+$. − HPLC (Nucleosil C-18): t_R(major diastereomer) = 19.87 min; t_R(minor diastereomer) = 19.24 min; (ϕ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 248 nm).

(4*S*)-3-{(1*R,2*S**,6*R**,7*S**)-3-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-4-carbonyl}-4-benzyloxazolidin-2-one (14a, Diastereomeric Mixture):** IR (NaCl film): $\tilde{\nu}$ = 3040, 2960, 2930, 2880, 1795, 1715, 1680, 1645, 1360, 1235, 1220, 1200, 1120, 705 cm^{-1}. − ^{1}H NMR (300 MHz, $CDCl_3$, 23°C, TMS): δ = 1.20−1.30 (m, 3 H), 1.56−1.62 (m, 3 H), 2.21 (s, 3 H), 2.30−2.35 (m, 1 H), 2.40−2.42 (d, $^3J_{(H,H)}$ = 3.9 Hz, 1 H), 2.49−2.50 (d, $^3J_{(H,H)}$ = 3.6 Hz, 1 H), 2.62−2.63 (d, $^3J_{(H,H)}$ = 5.4 Hz, 1 H), 2.79−2.87 (dd, $^3J_{(H,H)}$ = 13.5 Hz, $^3J'_{(H,H)}$ = 9.9 Hz, 1 H), 3.43−3.49 (dd, $^3J_{(H,H)}$ = 13.5 Hz, $^3J'_{(H,H)}$ = 3.5 Hz, 1 H), 4.15−4.30 (m, 2 H), 4.65−4.80 (m, 1 H), 7.24−7.35 (m, 5 H). − ^{13}C NMR (75 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 16.9 (CH_3), 28.6 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 38.0 (CH_2), 38.0 (CH), 38.8 (CH), 39.0 (CH), 53.9 (CH), 54.6 (CH), 66.7 (CH_2), 127.4 (CH), 129.0 (CH), 129.4 (CH), 135.3 (C), 139.5 (C), 152.0 (C), 167.5 (C), 179.0 (C), 204.5 (C); *(minor diastereomer)* 16.9 (CH_3), 28.4 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 38.0 (CH), 39.0 (CH), 39.6 (CH), 53.8 (CH), 54.6 (CH), 66.7 (CH_2), 127.4 (CH), 129.0 (CH), 129.4 (CH), 135.3 (C), 139.5 (C), 152.0 (C), 167.5 (C), 179.0 (C), 204.5 (C). − HPLC (Nucleosil C-18): t_R(major diastereomer) = 16.40 min; t_R(minor diastereomer) = 15.59 min; (ϕ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 248 nm).

(4*S*)-3-{(1*R,2*R**,6*S**,7*S**)-4-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carbonyl}-4-benzyloxazolidin-2-one (13a) and (4*S*)-3-{(1*R**,2*R**,6*S**,7*S**)-3-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-4-carbonyl}-4-benzyloxazolidin-2-one (15a):** According to the procedure described above for thermal Pauson−Khand reactions in toluene, a solution of the complex derived from *N*-(tetrolyl)oxazolidinone **4a** (0.100 g, 0.412 mmol) and octacarbonyldicobalt (0.155 g, 0.453 mmol) was treated with norbornadiene (0.379 g, 4.12 mmol). The resulting mixture was stirred at 0°C for 7.5 h and at room temperature for 14 h. After chromatographic purification, 0.119 g (80% yield) of a 1:1.2 mixture of the regioisomers **13a** (2.0:1 diastereomeric mixture) and **15a** (1.2:1 diastereomeric mixture) were obtained.

(4*S*)-3-{(1*R,2*R**,6*S**,7*S**)-4-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carbonyl}-4-benzyloxazolidin-2-one (13a, Diastereomeric Mixture):** ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 9.2 (CH_3), 38.0 (CH_2), 42.0 (CH_2), 42.7 (CH), 44.3 (CH), 48.6 (CH), 53.5 (CH), 55.3 (CH), 67.0 (CH_2), 127.4 (CH), 129.0 (CH), 129.1 (CH), 129.4 (CH), 135.2 (C), 138.3 (CH), 143.0 (C), 152.0 (C), 161.5 (C), 167.0 (C), 210.2 (C); *(minor diastereomer)* 9.1 (CH_3), 37.9 (CH_2), 42.0 (CH_2), 42.7 (CH), 44.3 (CH), 48.6 (CH), 53.4 (CH), 55.3 (CH), 66.9 (CH_2), 127.4 (CH), 129.0 (CH), 129.1 (CH), 129.4 (CH), 135.2 (C), 138.3 (CH), 143.0 (C), 152.0 (C), 161.5 (C), 167.0 (C), 210.2 (C). − HPLC (Nucleosil C-18): t_R(major diastereomer) = 16.78 min; t_R(minor diastereomer) = 16.27 min; (ϕ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 248 nm).

(4*S*)-3-{(1*R,2*R**,6*S**,7*S**)-3-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-4-carbonyl}-4-benzyloxazolidin-2-one (15a, Diastereomeric Mixture):** IR (NaCl film): $\tilde{\nu}$ = 3060, 3040, 2980, 1795, 1710, 1680, 1360, 1300, 1215, 1120, 705 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.62 (m, 2 H), 2.23 (s, 3 H), 2.40−2.50 (m, 1 H), 2.75−3.05 (m, 4 H), 3.40−3.55 (dd, $^3J_{(H,H)}$ = 12.5 Hz, $^3J'_{(H,H)}$ = 3.5 Hz, 1 H), 4.15−4.35 (m, 2 H), 4.60−4.80 (m, 1 H), 6.20−6.35 (m, 2 H), 7.26−7.34 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 16.9 (CH_3), 38.0 (CH_2), 42.1 (CH_2), 42.1 (CH), 43.1 (CH), 43.9 (CH), 53.5 (CH), 55.6 (CH), 66.7 (CH_2), 127.4 (CH), 129.0 (2CH), 129.4 (CH), 135.2 (C), 138.3 (CH), 139.0 (C), 152.0 (C), 167.0 (C), 179.0 (C), 212.0 (C); *(minor diastereomer)* 16.9 (CH_3), 38.0 (CH_2), 42.1 (CH_2), 42.1 (CH), 43.6 (CH), 44.0 (CH), 53.5 (CH), 55.2 (CH), 66.7 (CH_2), 127.4 (CH), 129.0 (2CH), 129.4 (CH), 135.2 (C), 138.3 (CH), 139.0 (C), 152.0 (C), 167.0 (C), 179.0 (C), 212.0 (C). − MS (CI-NH_3): *m*/*z* (%) = 364 (13) $[M + 1]^+$, 381 (100) $[M + 18]^+$. − HPLC (Nucleosil C-18): t_R(major diastereomer) = 13.45 min; t_R(minor diastereomer) = 12.93 min; (ϕ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 248 nm).

(4*S*)-3-{(1*R,2*S**,6*R**,7*S**)-4-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carbonyl}-4-phenyloxazolidin-2-one (12b) and (4*S*)-3-{(1*R**,2*S**,6*R**,7*S**)-3-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-4-carbonyl}-4-phenyloxazolidin-2-one (14b):** According to the procedure described above for the thermal Pauson−Khand reaction in toluene, a solution of the complex derived from the *N*-(tetrolyl)oxazolidinone **4b** (0.134 g, 0.585 mmol) and octacarbonyldicobalt (0.220 g, 0.644 mmol) was treated with norbornene (0.550 g, 5.85 mmol), and the resulting mixture was stirred at room temperature for 20 h. After chromatographic purification, 0.150 g (73% yield) of a 1.7:1 mixture of the regioisomers **12b** (7.6:1 diastereomeric mixture) and **14b** (1:1 diastereomeric mixture) was obtained. The tertiary amine *N*-oxide-mediated reaction (dichloromethane, −20°C, 18 h), using **4b** (0.083 g, 0.36 mmol), octacarbonyldicobalt (0.136 g, 0.399 mmol), norbornene (0.338 g, 3.62 mmol) and anhydrous *N*-methylmorpholine *N*-oxide (0.240 g, 2.16 mmol) gave, after chromatographic purification, 0.128 g (100% yield) of a 1.67:1 mixture of the regioisomers **12b** (7.9:1 diastereomeric mixture) and **14b** (1.1:1 diastereomeric mixture).

(4*S*)-3-{(1*R,2*S**,6*R**,7*S**)-4-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carbonyl}-4-phenyloxazolidin-2-one (12b, Diastereomeric Mixture):** IR (NaCl film): $\tilde{\nu}$ = 3060, 3040, 2960, 2920, 2880, 1795, 1700, 1390, 1330, 1220, 1200, 715 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.20−1.30 (m, 4 H), 1.55−1.60 (m, 2 H), 1.75−1.76 (d, $^3J_{(H,H)}$ = 2 Hz, 3 H), 1.85−1.90 (m, 1 H), 2.25−2.35 (d, $^3J_{(H,H)}$ = 5.6 Hz, 1 H), 2.40−2.45 (m, 1 H), 2.90−3.10 (m, 1 H), 4.35−4.45 (dd, $^3J_{(H,H)}$ = 9.5 Hz, $^3J'_{(H,H)}$ = 5 Hz, 1 H), 4.75−4.85 (dd, $^3J_{(H,H)}$ = $^3J'_{(H,H)}$ = 9.5 Hz, 1 H), 5.00−5.12 (dd, $^3J_{(H,H)}$ = 9.5 Hz, $^3J'_{(H,H)}$ = 5 Hz, 1 H), 7.35−7.43 (m, 5 H). −

^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): *(major diastereomer)* δ = 9.0 (CH_3), 28.4 (CH_2), 28.7 (CH_2), 31.7 (CH_2), 37.5 (CH), 39.5 (CH), 49.0 (CH), 53.5 (CH), 57.5 (CH), 70.4 (CH_2), 126.4 (CH), 129.2 (CH), 129.3 (CH), 137.9 (Cq), 142.8 (Cq), 152.0 (Cq), 166.9 (Cq); (two quaternary carbons could not be observed). − MS (CI-NH_3): *m/z* (%) = 352 (23) $[M + 1]^+$, 369 (100) $[M + 18]^+$. − HPLC (Nucleosil C-18): t_R(major diastereomer) = 12.12 min; t_R(minor diastereomer) = 11.73 min; (φ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 248 nm).

(4*S*)-3-{(1*R,2*S**,6*R**,7*S**)-3-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-4-carbonyl}-4-phenyloxazolidin-2-one (14b, Diastereomeric Mixture):** IR (NaCl film): ṽ = 3060, 3040, 2970, 2940, 2880, 1795, 1710, 1690, 1640, 1380, 1200, 1120, 700 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.20−1.35 (m, 4 H), 1.45−1.65 (m, 2 H), 2.12 (s, 3 H), 2.30−2.65 (m, 4 H), 4.20−4.30 (dd, $^3J_{(H,H)}$ = 9.6 Hz, $^3J'_{(H,H)}$ = 5 Hz, 1 H), 4.70−4.83 (dd, $^3J_{(H,H)}$ = $^3J'_{(H,H)}$ = 9.6 Hz, 1 H), 5.40−5.50 (dd, $^3J_{(H,H)}$ = 9.6 Hz, $^3J'_{(H,H)}$ = 5 Hz, 1 H), 7.35−7.45 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 16.8 (CH_3), 28.4 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 38.0 (CH), 38.9 (CH), 53.9 (CH), 54.6 (CH), 58.0 (CH), 70.4 (CH_2), 126.0 (CH), 128.9 (CH), 129.2 (CH); *(minor diastereomer)* 16.8 (CH_3), 28.4 (CH_2), 29.2 (CH_2), 31.8 (CH_2), 38.1 (CH), 39.1 (CH), 53.8 (CH), 54.6 (CH), 58.1 (CH), 70.4 (CH_2), 126.0 (CH), 128.9 (CH), 129.2 (CH); (quaternary carbon signals could not be observed). HPLC (Nucleosil C-18): t_R(major diastereomer) = 10.64 min; t_R(minor diastereomer) = 10.53 min; (φ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 248 nm).

(4*S*)-3-{(1*R,2*R**,6*S**,7*S**)-4-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carbonyl}-4-phenyloxazolidin-2-one (13b) and (4*S*)-3-{(1*R**,2*R**,6*S**,7*S**)-3-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-4-carbonyl}-4-phenyloxazolidin-2-one (15b):** According to the procedure described above for the thermal Pauson−Khand reaction in toluene, a solution of the complex derived from the *N*-(tetrolyl)oxazolidinone **4b** (0.085 g, 0.37 mmol) and octacarbonyldicobalt (0.140 g, 0.408 mmol) was treated with norbornadiene (0.341 g, 3.71 mmol), and the resulting mixture was stirred at room temperature for 72 h. After chromatographic purification, 0.098 g (76% yield) of a 2.4:1 mixture of the regioisomers **13b** (7.6:1 diastereomeric mixture) and **15b** (1.9:1 diastereomeric mixture) were obtained.

(4*S*)-3-{(1*R,2*R**,6*S**,7*S**)-4-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carbonyl}-4-phenyloxazolidin-2-one (13b, Diastereomeric Mixture):** IR (NaCl film): ṽ = 3060, 3030, 2980, 2880, 1795, 1705, 1390, 1330, 1275, 1210, 1120, 1065, 710 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.20−1.35 (m, 2 H), 1.76 (s, 3 H), 2.35−2.45 (m, 2 H), 3.10−3.15 (m, 1 H), 3.90−3.95 (m, 1 H), 4.35−4.45 (dd, $^3J_{(H,H)}$ = 9.6 Hz, $^3J'_{(H,H)}$ = 5.6 Hz, 1 H), 4.75−4.85 (dd, $^3J_{(H,H)}$ = $^3J'_{(H,H)}$ = 9.6 Hz, 1 H), 5.52−5.62 (dd, $^3J_{(H,H)}$ = 9.6 Hz, $^3J'_{(H,H)}$ = 5.6 Hz, 1 H), 6.19−6.21 (m, 2 H), 7.35−7.55 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 9.2 (CH_3), 41.9 (CH_2), 42.5 (CH), 44.2 (CH), 48.4 (CH), 52.3 (CH), 57.5 (CH), 70.4 (CH_2), 126.4 (CH), 129.3 (CH), 129.4 (CH), 137.6 (CH), 137.8 (C), 138.0 (CH), 142.5 (C), 152.0 (C), 160.0 (C), 166.5 (C). − MS (CI-NH_3): *m/z* (%) = 350 (15) $[M + 1]^+$, 367 (100) $[M + 18]^+$. − HPLC (Nucleosil C-18): t_R(major diastereomer) = 11.16 min; t_R(minor diastereomer) = 10.90 min; (φ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 248 nm).

(4*S*)-3-{(1*R,2*R**,6*S**,7*S**)-3-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-4-carbonyl}-4-phenyloxazolidin-2-one (15b, Diastereomeric Mixture):** ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 16.9 (CH_3), 42.0 (CH_2), 43.2 (CH), 44.0 (CH), 48.7 (CH), 53.3 (CH), 58.2 (CH), 70.5 (CH_2), 126.4 (CH), 129.3 (CH), 129.4 (CH), 137.6 (CH), 137.8 (C), 138.2 (CH); (quaternary carbon signals could not be observed). − HPLC (Nucleosil C-18): t_R(major diastereomer) = 9.80 min; t_R(minor diastereomer) = 9.36 min; (φ = 0.8 mL/min, MeOH/H_2O 65:35, λ = 248 nm).

(1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-{(1*R,2*S**,6*R**,7*S**)-4-methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carbonyl}-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]decan-4-one (12c) and (1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-{(1*R**,2*S**,6*R**,7*S**)-3-methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-4-carbonyl}-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]decan4-one (14c):** According to the procedure described above for the thermal Pauson−Khand reaction in toluene, a solution of the complex derived from the *N*-(tetrolyl)oxazolidinone **4c** (0.073 g, 0.28 mmol) and octacarbonyldicobalt (0.105 g, 0.308 mmol) was treated with norbornene (0.262 g, 2.79 mmol), and the resulting mixture was stirred at 40°C for 40 h. After chromatographic purification, 0.073 g (68% yield) of a 1:1.4 mixture of the regioisomers **12c** (9.3:1 diastereomeric mixture) and **14c** (4.4:1 diastereomeric mixture) were obtained.

(1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-{(1*R,2*S**,6*R**,7*S**)-4-methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carbonyl}-3-oxa-5-azatricyclo-[5.2.1.0^{2,6}]decan-4-one (12c, Diastereomeric Mixture):** IR (NaCl film): ṽ = 2960, 2920, 2870, 1780, 1700, 1680, 1390, 1370, 1325, 1285, 1200, 1140, 1050, 800, 760, 720, 685 cm^{-1}. − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 8.9 (CH_3), 12.1 (CH_3), 19.8 (CH_3), 22.8 (CH_3), 22.7 (CH_2), 28.8 (CH_2), 29.2 (CH_2), 31.9 (CH_2), 33.2 (CH_2), 37.9 (CH), 46.6 (C), 47.7 (CH), 49.0 (CH), 50.2 (C), 53.6 (CH), 54.6 (CH), 65.2 (CH), 81.8 (CH), 142.9 (C), 152.0 (C), 164.9 (C), 209.9 (C). − MS (CI-CH_4): *m/z* (%) = 384 (100) $[M + 1]^+$, 412 (21) $[M + 29]^+$, 424 (10) $[M + 41]^+$. − HPLC (Nucleosil C-18): t_R(major diastereomer) = 14.61 min; t_R(minor diastereomer) = 13.68 min; (φ = 0.8 mL/min, MeOH/H_2O 75:25, λ = 240 nm).

(1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-{(1*R,2*S**,6*R**,7*S**)-3-methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-4-carbonyl}-3-oxa-5-azatricyclo-[5.2.1.0^{2,6}]decan-4-one (14c, Diastereomeric Mixture):** ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 12.3 (CH_3), 16.7 (CH_3), 19.8 (CH_3), 22.8 (CH_3), 22.7 (CH_2), 28.8 (CH_2), 29.2 (CH_2), 31.8 (CH_2), 33.3 (CH_2), 37.9 (CH), 39.2 (CH), 46.6 (Cq), 47.7 (CH), 50.1 (C), 53.6 (CH), 54.6 (CH), 65.2 (CH), 81.8 (CH), 152.0 (C), 209.9 (C); (some quaternary carbon signals could not be observed). − HPLC (Nucleosil C-18): t_R(major diastereomer) = 11.79 min; t_R(minor diastereomer) = 11.74 min; (φ = 0.8 mL/min, MeOH/H_2O 75:25, λ = 240 nm).

(1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-{(1*R,2*R**,6*S**,7*S**)-4-methyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carbonyl}-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]decan-4-one (13c) and (1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-{(1*R**,2*R**,6*S**,7*S**)-3-methyl-5-oxotricyclo[5.2.1.0^{2,6}]-deca-3,8-diene-4-carbonyl}-3-oxa-5-azatricyclo [5.2.1.0^{2,6}]decan-4-one (15c):** According to the procedure described above for the thermal Pauson−Khand reaction in toluene, a solution of the complex derived from the*N*-(tetrolyl)oxazolidinone **4c** (0.076 g, 0.29 mmol) and octacarbonyldicobalt (0.110 g, 0.32 mmol) was treated with norbornadiene (0.267 g, 2.91 mmol), and the resulting mixture was stirred at room temperature for 96 h. After chromatographic purification, 0.080 g (72% yield) of a 1.1:1 mixture of the regioisomers **13c** (17.5:1 diastereomeric mixture) and **15c** (5.1:1 diastereomeric mixture) were obtained.

(1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-{(1*R,2*R**,6*S**,7*S**)-4-methyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carbonyl}-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]decan-4-one (13c, Diastereomeric Mixture):** ^{13}C NMR (75 MHz $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 9.0 (CH_3), 12.3 (CH_3), 19.8 (CH_3), 22.7 (CH_3), 22.8 (CH_2), 32.3

(CH_2), 42.0 (CH_2), 44.0 (CH), 46.6 (C), 47.7 (CH), 48.4 (CH), 50.2 (C), 52.4 (CH), 53.3 (CH), 65.2 (CH), 82.2 (CH), 137.7 (CH), 138.2 (CH), 143.9 (C), 154.3 (C), 164.0 (C), 167.7 (C), 208.5 (C). − MS (CI-CH_4): *m/z* (%) = 382 (100) $[M + 1]^+$, 410 (20) $[M + 29]^+$, 422 (10) $[M + 41]^+$. − HPLC (Nucleosil C-18): t_R(major diastereomer) = 13.68 min; t_R(minor diastereomer) = 12.80 min; (ϕ = 0.8 mL/min, MeOH/H_2O 75:25, λ = 240 nm).

(1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-{(1*R,2*R**,6*S**,7*S**)-3-methyl-5-oxotricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene-4-carbonyl}-3-oxa-5-azatricyclo[5.2.1.$0^{2,6}$]decan-4-one (15c, Diastereomeric Mixture):** ^{13}C NMR (75 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 12.3 (CH_3), 16.8 (CH_3), 19.8 (CH_3), 22.7 (CH_3), 22.8 (CH_2), 32.3 (CH_2), 42.0 (CH_2), 42.8 (CH), 44.0 (CH), 46.6 (C), 47.7 (CH), 50.2 (C), 52.4 (CH), 53.3 (CH), 65.2 (CH), 81.9 (CH), 137.7 (CH), 138.2 (CH), 153.8 (C), 178.5 (C), 208.5 (C); (some quaternary carbon signals could not be observed). − HPLC (Nucleosil C-18): t_R(major diastereomer) = 10.75 min; t_R(minor diastereomer) = 10.64 min; (ϕ = 0.8 mL/min, MeOH/H_2O 75:25, λ = 240 nm).

General Procedure for the Intramolecular Pauson−Khand Reaction of *N*-(8-Nonen-2-ynoyl)oxazolidin-2-ones

Thermal Reaction in Toluene: To a stirred 0.005 M solution of a *N*-(8-nonen-2-ynoyl)oxazolidin-2-one (1 mmol) in anhydrous toluene, octacarbonyldicobalt (1.1 mmol) was added in one portion, and the resulting dark-coloured solution was stirred at room temperature for 30 min, after which time the formation of the hexacarbonyldicobalt complex was complete (TLC). The mixture was purged with nitrogen and was heated at the specified temperature during 1−4 h, the resulting suspension was filtered throught Celite, the solvent was eliminated in vacuo and the residue was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures.

Thermal Reaction in Acetonitrile: To 1.1 mmol of octacarbonyldicobalt a 0.07 M solution of a *N*-(8-nonen-2-ynoyl)oxazolidin-2-one (1 mmol) in freshly distilled acetonitrile was added dropwise. The resulting mixture was stirred at room temperature for 30 min, and additional octacarbonyldicobalt was eventually added until total consumption of the *N*-(8-nonen-2-ynoyl)oxazolidin-2-one. At this point, the reaction mixture was purged with nitrogen and was heated at reflux until complete disappearance of the complex. The resulting suspension was filtered through Celite, the solvent was eliminated in vacuo and the residue was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures.

Tertiary Amine *N*-Oxide-Mediated Reaction: To a stirred 0.007 M solution of a *N*-(8-nonen-2-ynoyl)oxazolidin-2-one (1 mmol) in anhydrous dichloromethane, was added octacarbonyldicobalt (1.1 mmol) in one portion, and the resulting dark-coloured solution was stirred at room temperature for 30 minutes, after which time the formation of the hexacarbonyldicobalt complex was complete (TLC). The reaction mixture was purged with nitrogen and was externally cooled with ice. *N*-Methylmorpholine *N*-oxide monohydrate (2 mmol) was added in one portion, the reaction mixture was allowed to attain room temperature by removal of the cooling bath and the extent of the reaction was monitored by TLC. This treatment was repeated until the complete disappearance of the complex. After 2 h of additional stirring at room temperature, the resulting suspension was filtered through Celite, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures.

DMS/DMSO-Promoted Thermal Reaction in Toluene: To a stirred 0.005 M solution of a *N*-(8-nonen-2-ynoyl)oxazolidin-2-one (1 mmol) in anhydrous toluene octacarbonyldicobalt (1.1 mmol) was added in one portion, and the resulting dark-coloured solution was stirred at room temperature for 30 min, after which time the formation of the hexacarbonyldicobalt complex was complete (TLC). The reaction mixture was purged with nitrogen and then 10 mmol of DMS and/or 10 mmol of DMSO were added dropwise. The reaction mixture was heated at specified the temperature during 1−4 h. The resulting suspension was filtered through Celite, the solvent was removed in vacuo and the residue was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures.

(4*S*)-4-Benzyl-3-(2-oxo-3,3a,4,5,6,7-hexahydro-2*H*-indene-1-carbonyl)oxazolidin-2-one (17a): Obtained as a 1:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (60°C, 4 h) from (4*S*)-3-(8-nonen-2-ynoyl)-4-benzyloxazolidin-2-one **7a** (0.10 g, 0.32 mmol) and octacarbonyldicobalt (0.13 g, 0.38 mmol) in 43% overall yield (0.046 g). Obtained as a 1:1 diastereomeric mixture by thermal Pauson−Khand reaction in acetonitrile (80°C, 3 h) from **7a** (0.15 g, 0.48 mmol) and octacarbonyldicobalt (0.20 g, 0.58 mmol) in 34% overall yield (0.055 g). Obtained as a 1:1 diastereomeric mixture by DMS/DMSO-promoted Pauson−Khand reaction in toluene (60°C, 3 h) from **7a** (0.10 g, 0.32 mmol), octacarbonyldicobalt (0.13 g, 0.38 mmol), DMSO (0.24 g, 3.2 mmol) and DMS (0.198 g, 3.2 mmol) in 92% overall yield (0.10 g). Obtained as a 1:1 diastereomeric mixture by tertiary amine *N*-oxide-mediated reaction (room temperature, 1 h) from **7a** (0.24 g, 0.77 mmol), octacarbonyldicobalt (0.29 g, 0.85 mmol), and *N*-methylmorpholine *N*-oxide monohydrate (0.27 g, 1.93 mmol) in 8% overall yield (0.021 g). Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 2935, 1788, 1713, 1684, 1645, 1447, 1362, 1323, 1308, 1209, 1115, 889, 825, 760, 704 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.20−1.60 (m, 4 H), 1.80−2.40 (m, 4 H), 2.50−3.00 (m, 4 H), 3.20 (m, 1 H), 4.10 m, 2 H), 4.70 (m, 1 H), 7.20−7.40 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 25.1 (CH_2), 26.7 (CH_2), 29.7 (CH_2), 34.7 (CH_2), 37.9 (CH_2), 41.2 (CH) 41.7 (CH_2), 55.2 (CH), 66.5 (CH_2), 127.3 (CH), 128.9 (CH), 129.4 (CH), 135.2 (C), 152.3 (C), 164.0 (C), 183.1 (C); (two quaternary carbon signals could not be observed). − MS (CI-NH_3): *m/z* (%) = 357 (100) $[M + 18]^+$. − HRMS: $C_{20}H_{22}NO_4$ ($[M + 1]^+$), calcd. 340.1549; found 340.1561. − HPLC (Nucleosil C-18): t_{R1} = 118 min, t_{R2} = 121 min, (ϕ = 0.8 mL/min, MeOH/H_2O = 42:58, λ = 254 nm).

(4*R*)-4-Phenyl-3-(2-oxo-3,3a,4,5,6,7-hexahydro-2*H*-indene-1-carbonyl)oxazolidin-2-one (17b): Obtained as a 1:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (50°C, 2.5 h) from (4*R*)-3-(8-nonen-2-ynoyl)-4-phenyloxazolidin-2-one **7b** (0.10 g, 0.33 mmol) and octacarbonyldicobalt (0.13 g, 0.38 mmol) in 50% overall yield (0.055 g). Obtained as a 1:1 diastereomeric mixture by thermal Pauson−Khand reaction in acetonitrile (80°C, 3 h) from **7b** (0.10 g, 0.33 mmol) and octacarbonyldicobalt (0.13 g, 0.38 mmol) in 12% overall yield (0.026 g). Obtained as a 1.2:1 diastereomeric mixture by DMSO-promoted Pauson−Khand reaction in toluene (60°C, 2.5 h) from **7b** (0.050 g, 0.16 mmol), of octacarbonyldicobalt (0.065 g, 0.19 mmol) and DMSO (0.12 g, 1.6 mmol) in 80% overall yield (0.10 g). Obtained as a 1:1 diastereomeric mixture by tertiary amine *N*-oxide mediated reaction (room temperature, 1 h) from **7b** (0.10 g, 0.33 mmol), octacarbonyldicobalt (0.13 g, 0.38 mmol) and *N*-methylmorpholine *N*-oxide monohydrate (0.116 g, 0.825 mmol) in 69% overall yield (0.075 g). Pale yellow oil. − IR (NaCl film): $\tilde{\nu}$ = 2934, 2859, 1788, 1711, 1688, 1645, 1497, 1458, 1385, 1362 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.00−2.30 (m, 8 H), 2.60−3.00 (m, 3 H),

4.30 (m, 1 H), 4.75 (t, $^3J_{(H,H)}$ = 7.6 Hz, 1 H), 5.50 (m, 1 H), 7.20−7.50 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = *(major diastereomer)* 25.1 (CH_2), 26.7 (CH_2), 29.5 (CH_2), 34.7 (CH_2), 41.2 (CH) 41.7 (CH_2), 57.9 (CH), 70.3 (CH_2), 126.1 (CH), 128.7 (CH), 129.2 (CH); (the quaternary carbon signals could not be observed). − MS (CI NH_3): *m/z* (%) = 326 (22) $[M + 1]^+$, 326 (100) $[M + 18]^+$. − HRMS: $C_{19}H_{20}NO_4$ ($[M + 1]^+$), calcd. 326.1392; found 326.1386. − HPLC (Nucleosil C-18): $t_{R(minor)}$ = 13.0 min, $t_{R(major)}$ = 14.0 min, (ϕ = 0.8 mL/min, MeOH/H_2O = 55:45, λ = 254 nm).

(1*S*,2*R*,6*S*,7*R*)-7,10,10-Trimethyl-5-(2-oxo-3,3a,4,5,6,7-hexahydro-2*H*-indene-1-carbonyl)-3-oxa-5-azatricyclo[5.2.1.0^{2,6}]decan-4-one (17c): Obtained as a 2:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (60°C, 2.5 h) from (1*S*,2*R*,6*S*,7*R*)-7,10,10-trimethyl-5-(8-octen-2-ynoyl)-3oxa-5-azatricyclo[5.2.1.0^{2,6}]-decan-4-one **7c** (0.046 g, 0.14 mmol) and octacarbonyldicobalt (0.06 g, 0.18 mmol) in 60% overall yield (0.030 g). Obtained as a 1.9:1 diastereomeric mixture by DMSO-promoted Pauson−Khand reaction in toluene (60°C, 2.5 h) from **7c** (0.10 g, 0.3 mmol), octacarbonyldicobalt (0.113 g, 0.33 mmol) and DMSO (0.234 g, 3.00 mmol) in 80% overall yield (0.087 g). Obtained as a 1.6:1 diastereomeric mixture by tertiary amine *N*-oxide-mediated reaction (room temperature, 1 h) from **7c** (0.037 g, 0.11 mmol), octacarbonyldicobalt (0.042 g, 0.13 mmol) and *N*-methylmorpholine *N*-oxide monohydrate (0.090 g, 0.65 mmol) in 75% overall yield (0.030 g). Pale yellow oil. − IR (NaCl film): ṽ = 2934, 1784, 1715, 1686, 1647, 1483, 1447, 1360, 1323, 1306, 1285, 1196, 1132, 1086, 1051, 985, 937, 908, 821, 787, 762, 740 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 0.90−2.40 (m, 22 H), 2.60−3.00 (m, 3 H), 4.53 (s, 2 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): *(major diastereomer)* δ = 12.0 (CH_3), 19.7 (CH_3), 22.8 (CH_3), 25.1 (CH_2), 26.7 (CH_2), 29.5 (CH_2), 33.1 (CH_2), 34.5 (CH_2), 41.2 (CH) 41.7 (CH_2), 47.1 (C), 47.7 (CH), 58.1 (C), 65.1 (CH), 81.6 (CH), 154.1 (C), 164.6 (C), 182.1 (C); (two quaternary carbon signals could not be observed). − MS (CI-NH_3): *m/z* (%) = 358 (100) $[M + 1]^+$, 359 (22) $[M + 2]^+$. − HRMS: $C_{21}H_{28}NO_4$ ($[M + 1]^+$), calcd. 358.2018; found 358.2038. − HPLC (Nucleosil C-18): $t_{R(major)}$ = 40.0 min, $t_{R(minor)}$ = 42.0 min, (ϕ = 0.8 mL/min, MeOH/H_2O = 60:40, λ = 254 nm).

(4*R*)-4-Methylsulfanylmethyl-3-(2-oxo-3,3a,4,5,6,7-hexahydro-2*H*-indene-1-carbonyl)oxazolidin-2-one (17e): Obtained as a 1.1:1 diastereomeric mixture by thermal Pauson−Khand reaction in toluene (60°C, 4 h) from (4*R*)-4-methylsulfanylmethyl-3-(non-8-en-2-ynoyl)oxazolidin-2-one **7e** (0.050 g, 0.18 mmol) and octacarbonyldicobalt (0.065 g, 0.2 mmol) in 50% overall yield (0.027 g). Obtained as a 1.1:1 diastereomeric mixture by DMSO-promoted Pauson−Khand reaction in toluene (60°C, 3 h) from **7e** (0.050 g, 0.18 mmol), octacarbonyldicobalt (0.065 g, 0.20 mmol) and DMSO (0.144 g, 1.80 mmol) in 59% overall yield (0.033 g). Pale yellow oil. − IR (NaCl film): ṽ = 2930, 1788, 1713, 1643, 1362, 1323, 1207, 1115, 754, 712 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.20−2.40 (m, 12 H), 2.50−3.20 (m, 4 H) 4.30−4.80 (m, 3 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): *(major diastereomer)* δ = 15.7 (CH_3), 25.0 (CH_2), 26.7 (CH_2), 29.5 (CH_2), 34.1 (CH_2), 35.7 (CH_2), 41.2 (CH) 41.7 (CH_2), 53.3 (CH), 67.1 (CH_2), 183.4 (C); (four quaternary carbon signals could not be observed). − MS (CI-NH_3): *m/z* (%) = 310 (7) $[M + 1]^+$, 327 (41) $[M + 18]^+$. − HRMS: $C_{15}H_{19}NO_4S$ ($[M]^+$), calcd. 309.1035; found 309.1019. − HPLC (Nucleosil C-18): $t_{R(major)}$ = 23.9 min, $t_{R(minor)}$ = 25.2 min, (ϕ = 0.8 mL/min, MeOH/H_2O = 48:52, λ = 254 nm).

Determination of Absolute Configurations

Lithium Hydroxide/Hydrogen Peroxide-Mediated Hydrolysis of Adducts 9b: To a cold (0°C) solution of the major (1*S*,2*S*,6*R*,7*R*) diastereomer of the adduct **9b** (0.100 g, 0.243 mmol) in 4:1 THF/H_2O (2 mL) 30% aq. H_2O_2 (0.14 mL, 1.36 mmol) and a solution of LiOH (0.023 g, 0.54 mmol) in water (0.7 mL) were added dropwise, and the resulting mixture was stirred at the same temperature for 30 min. At this point, a solution of Na_2SO_3 (0.171 g, 1.36 mmol) in water (1.2 mL) was added and the THF was eliminated in vacuo. The resulting mixture was extracted with dichloromethane (2 × 5 mL), cooled at 0°C, acidified (pH = 1) with 6 M aq. HCl and extracted with ethyl acetate (2 × 5 mL). The dichloromethane phase was dried with Na_2SO_4 and the solvent was evaporated to afford 0.040 g (100% yield) of (4*S*)-4-phenyloxazolidin-2-one **1b**. The ethyl acetate phase was dried with $MgSO_4$. Evaporation of the solvent at reduced pressure gave 0.047 g (68% yield) of levorotatory 4-phenyl-5-oxo-3,4-epoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carboxylic acid (−)-**20** as a colourless oil. $[\alpha]_D^{25}$ = −36.6 (*c* = 1.04, MeOH). − IR (NaCl film): ṽ = 3100 (br), 3060, 3040, 2980, 2940, 2880, 1740, 1710, 1240, 1220, 1115, 980, 950, 750, 720, 700 cm^{-1}. − ^{1}H NMR (200 MHz, CD_3OD, 23°C, TMS): δ = 1.48−1.70 (m, 2 H), 2.40−2.53 (dd, $^3J_{(H,H)}$ = 7.5 Hz, $^3J'_{(H,H)}$ = 2.0 Hz, 1 H), 2.63−2.70 (d, $^3J_{(H,H)}$ = 7.5 Hz, 1 H), 3.10−3.20 (m, 1 H), 3.50−3.55 (m, 1 H), 6.35−6.42 (m, 2 H), 7.30−7.45 (m, 5 H). − ^{13}C NMR (50 MHz, CD_3OD, 23°C, TMS): δ = 44.8 (CH_2), 45.2 (CH), 47.9 (CH), 50.2 (CH), 52.8 (CH), 56.9 (C), 73.9 (C), 128.9 (CH), 129.3 (2CH), 130.4 (C), 139.7 (CH), 140.8 (CH), 168.0 (C), 218.3 (C). − MS (CI-CH_4): *m/z* (%) = 283 (100) $[M + 1]^+$, 311 (23) $[M + 29]^+$, 323 (10) $[M + 41]^+$. − In a similar way, the treatment of a solution of the minor (1*R*,2*R*,6*S*,7*S*) diastereomer of **9b** (0.090 g, 0.22 mmol) in 4:1 THF/H2O (1.8 mL) with 30% aq. H_2O_2 (0.13 mL, 1.25 mmol) and LiOH monohydrate (0.021 g, 0.50 mmol) gave 0.041 g (100% yield) of **1b** and 0.035 g (57% yield) of the dextrorotatory acid (+)-**20**, $[\alpha]_D^{25}$ = +36.5 (*c* = 0.67, MeOH).

Titanium(tetraisopropoxide)-Mediated Esterification of 9b (Major Isomer) with Allyl Alcohol: A mixture of 0.100 g (0.243 mmol) of the major diastereomer of **9b**, 2-propen-1-ol (2.4 mL), titanium tetraisopropoxide (0.11 g, 0.36 mmol) and powdered 4-Å molecular sieves (0.061 g) was heated at 150°C under a nitrogen atmosphere for 30 min in a sealed tube. The cold reaction mixture was poured over aq. saturated ammonium chloride solution and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were washed with brine, dried with $MgSO_4$ and the solvent was evaporated to give, after chromatographic purification (SiO_2, hexane/diethyl ether mixtures), 0.032 g (43% yield) of 2-propenyl (1*S*,2*S*,6*R*,7*R*)-4-phenyl-5-oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carboxylate **21** as a colourless solid. m.p. 46−48°C (hexane/dichloromethane). − $[\alpha]_{435}^{25}$ = −22.8 (*c* = 1.6, $CHCl_3$). − IR (KBr): ṽ = 3405, 3062, 2981, 2876, 1712, 1445, 1326, 1230, 1165, 1140, 1077, 987, 957, 715, 696 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.20−1.65 (m, 2 H), 1.50−1.60 (d, $^3J_{(H,H)}$ = 5.5 Hz, 1 H), 3.00−3.11 (m, 2 H), 3.12−3.20 (d, $^3J_{(H,H)}$ = 5.5 Hz, 1 H), 4.64−4.67 (d, $^3J_{(H,H)}$ = 5.8 Hz, 2 H), 5.15−5.21 (m, 2 H), 5.67−5.90 (m, 1 H), 6.22−6.32 (m, 1 H), 6.33−6.43 (m, 1 H), 7.32−7.39 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 41.5 (CH_2), 43.5 (CH), 44.7 (CH), 48.4 (CH), 52.9 (CH), 65.8 (CH_2), 118.9 (CH_2), 127.9 (CH), 128.7 (CH), 128.9 (CH), 130.1 (C), 131.5 (CH), 137.3 (CH), 138.7 (CH), 146.0 (C), 149.5 (C), 158.5 (C), 207.8 (C). − MS (CI-NH_3): *m/z* (%) = 307 (3) $[M + 1]^+$, 324 (100) $[M + 18]^+$, 341 (2) $[M + 35]^+$. − $C_{20}H_{18}O_3$: calcd. C 78.41, H 5.92; found C 78.46, H 6.14.

(4*S*)-3-{(1*R*,2*S*,3*R*,6*R*,7*S*)-5-Oxotricyclo[5.2.1.0^{2,6}]decan-3-carbonyl}-4-phenyloxazolidin-2-one (23): A solution of 0.050 g (0.123 mmol) of the major diastereomer of the adduct **11b** in absolute ethanol (9 mL) was submitted to catalytic hydrogenation (1 atm)

in the presence of 0.030 g of 10% Pd/C for 6 h. The crude mixture was filtered through Celite and the solvent was evaporated in vacuo, affording 0.042 g (100% yield) of the cyclopentanone **23** as a colourless solid. m.p. 174−176°C (hexane/dichloromethane). − $[\alpha]_D^{25}$ = −53.9 (*c* = 1.4, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3080, 3050, 2970, 2880, 1780, 1740, 1705, 1390, 1330, 1255, 1240, 1200, 1110, 760, 715 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.60−1.00 (m, 7 H), 2.20−2.40 (m, 3 H), 2.75−2.90 (m, 2 H), 4.37−4.55 (m, 2 H), 4.70−4.80 (dd, $^3J_{(H,H)}$ = $^3J'_{(H,H)}$ = 10 Hz, 1 H), 5.45−5.55 (dd, $^3J_{(H,H)}$ = 10 Hz, $^3J'_{(H,H)}$ = 2.5 Hz, 1 H), 7.37−7.42 (m, 5 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 27.7 (CH_2), 29.0 (CH_2), 35.2 (CH_2), 39.0 (CH), 40.8 (CH), 40.9 (CH_2), 42.3 (CH), 45.1 (CH), 57.3 (CH), 57.7 (CH), 69.9 (CH_2), 126.8 (CH), 128.8 (CH), 129.0 (CH), 138.8 (C), 153.2 (C), 171.5 (C), 220.2 (C). − MS (CI NH_3): *m/z* (%) = 340 (5) $[M + 1]^+$, 357 (100) $[M + 18]^+$. − $C_{20}H_{21}NO_4$: calcd. C 70.78, H 6.24, N 4.13; found C 70.79, H 6.41; N. 4.12.

(1*R*,2*S*,3*R*,6*R*,7*R*)-5-Oxotricyclo[5.2.1.0^{2,6}]decan-3-carboxylic Acid (24): A solution of the reduced adduct **23** (0.07 g, 0.20 mmol) in THF/H_2O = 4:1 (1.7 mL) was treated at 0°C with 35% aq. H_2O_2 (0.12 mL, 1.14 mmol) and a solution of $LiOH.H_2O$ (0.020 g, 0.45 mmol) in H_2O (0.6 mL). After stirring for 2 h at this temperature, a solution of Na_2SO_3 (0.17 g, 1.30 mmol) in H_2O (1.2 mL) was added and the resulting mixture was extracted with dichloromethane (3 × 10 mL). The aqueous layer was acidified with 6 M aq. HCl until pH = 1 and subsequently extracted with ethyl acetate (3 × 20 mL). Evaporation of the dichloromethane extracts gave 0.040 g (100% yield) of the oxazolidinone **1b**. From the ethyl acetate extracts the carboxylic acid **24** (0.020 g, 51% yield) was obtained as a colourless oil. $[\alpha]_D^{25}$ = −86.4 (*c* = 1.4, MeOH). − IR (NaCl film): $\tilde{\nu}$ = 3100 (br), 2980, 2960, 2900, 1730, 1705, 1420, 1200, 1170, 1140, 820, 700, 655 cm^{-1}. − ^{13}C NMR (75 MHz, CD_3OD, 23°C, TMS): δ = 28.8 (CH_2), 30.1 (CH_2), 36.1 (CH_2), 41.3 (2 CH + CH_2), 42.7 (CH), 46.9 (CH), 58.4 (CH), 176.3 (C), 220.0 (C). − MS (CI-NH_3): *m/z* (%) = 212 (100) $[M + 18]^+$. − CD: [Θ] = −6557 (*c* = 1.23 × 10^{-3} M, MeOH; λ = 299.5 nm).

Methyl (1*R*,2*S*,3*R*,6*R*,7*R*)-5-Oxotricyclo[5.2.1.0^{2,6}]decan-3-carboxylate (25): A solution of the carboxylic acid **24** (0.040 g, 0.19 mmol) in anhydrous DMF (0.3 mL) was treated at 0°C with $KHCO_3$ (0.040 g, 0.37 mmol) and methyl iodide (0.02 mL, 0.29 mmol). After stirring at room temperature for 17 h, H_2O (5 mL) was added and the resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water (10 mL), aqueous 5% Na_2SO_3 solution (10 mL) and brine (10 mL), and dried with Na_2SO_4. The crude residue obtained after evaporation of the solvent was purified by column chromatography on silica gel eluting with 5% hexane/diethyl ether, affording 0.020 g (47% yield) of the methyl ester **25** as a colourless solid. M.p. 87−89°C (hexane/dichloromethane). − $[\alpha]_D^{25}$ = −141.4 (*c* = 0.8, $CHCl_3$). − IR (NaCl film): $\tilde{\nu}$ = 2960, 2880, 1745, 1450, 1370, 1205, 1180, 1055, 1030, 970, 920, 830, 760 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$, 23°C, TMS): δ = 1.11−1.27 (m, 4 H), 1.51−1.56 (m, 2 H), 2.10 (m, 1 H), 2.25−2.27 (d, $^3J_{(H,H)}$ = 8.1 Hz, 1 H), 2.33−2.43 (ddd, $^3J_{(H,H)}$ = 19.5 Hz, $^3J'_{(H,H)}$ = 10.2 Hz, $^3J''_{(H,H)}$ = 1.8 Hz, 1 H), 2.51 (m, 1 H), 2.53−2.59 (m, 1 H), 2.69−2.79 (dd, $^3J_{(H,H)}$ = 19.2 Hz, $^3J'_{(H,H)}$ = 10.5 Hz, 1 H), 3.31−3.41 (ddd, $^3J_{(H,H)}$ = $^3J'_{(H,H)}$ = $^3J''_{(H,H)}$ = 10.5 Hz, 1 H), 3.78 (s, 3 H). − ^{13}C NMR (50 MHz, $CDCl_3$, 23°C, TMS): δ = 27.8 (CH_2), 29.2 (CH_2), 35.3 (CH_2), 40.1 (CH), 41.4 (CH_2), 41.5 (CH), 43.0 (CH), 45.8 (CH), 51.9 (CH_3), 57.1 (CH), 171.0 (C), 220.0 (C). − MS (CI NH_3): *m/z* (%) = 226 (100) $[M + 1]^+$. − $C_{12}H_{16}O_3$: calcd. C 69.21, H 7.74; found C 69.20, H 7.98.

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