Evaluation of the Regioselectivity in Pauson–Khand Reactions of Substituted Norbornenes and Diazabicyclo[2.2.1]heptanes with Terminal Alkynes

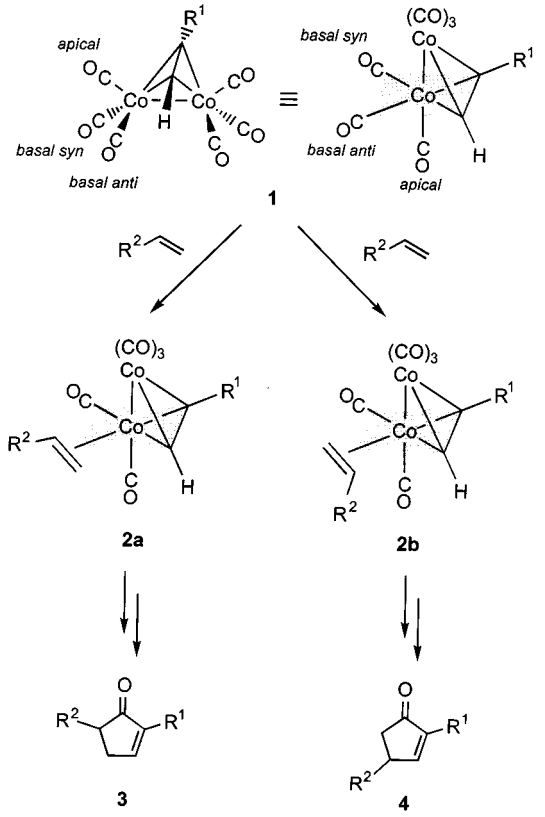
Volker Derdau,[a] Sabine Laschat,*[a] and Peter G. Jones[b]

Dedicated to Professor Wilfried A. König on the occasion of his 60th birthday

Keywords: Pauson–Khand reaction / Cyclopentenones

1-Methyl-norbornene ester **9** and 1-methyl-2,3-diazabicyclo[2.2.1]heptene ester **10** were employed in intermolecular Pauson–Khand reactions with various terminal alkynes **11a–f** to give the dimethyl 1-methyltricyclo[5.2.1.$0^{5,9}$]dec-7-en-6-one 2,3-dicarboxylates **12** and **13,** and diethyl 2,3-diaza-1-methyltricyclo[5.2.1.$0^{5,9}$]dec-7-en-6-one 2,3-dicarboxylates **14** and **15**, respectively. Whereas the co-cyclization of norbornene **9** with alkynes **11** bearing small substituents R resulted in the preferred formation of **12** (**12**:**13** ≤ 85:15), regioisomer **13** was obtained as the major product when sterically bulky alkynes were employed (**12**:**13** ≥ 6:94). For 2-methyl-3-butyn-2-ol **11e** a strong temperature dependency of the regioselectivity was found. The ratio of regioisomers (**12e**:**13e**) changed from 95:5 at –25 °C to 12:88 at 120 °C in toluene. In contrast, reactions with 2,3-diazanorbornene **10** showed only moderate regioselectivities in favour of **14** (**14**:**15** ≤ 69:31), regardless of the temperature and the size of R. The observed regioselectivities support a mechanism for the Pauson–Khand reaction in which the *apical* rather than the *basal anti* oriented carbon monoxide ligand of cobalt alkyne complex **1** is replaced by the alkene.

Transition-metal-catalysed co-cyclizations, in particular the Pauson–Khand reaction, can be considered as valuable tools in organic synthesis. The Pauson–Khand reaction, a cobalt-mediated co-cyclization of an alkyne, an alkene, and CO to give a cyclopentenone, has been elaborated in detail, and many applications have been reported,[1] especially in the field of natural product synthesis. It has also been found that other transition metals such as Fe,[2] Ru,[3] Rh,[4] Ni,[5] Cr,[6] Mo,[7] W,[8] Ti,[8] and Zr[9] can be used for the same purpose. According to the commonly accepted mechanism,[10] the co-cyclization is initiated by the formation of cobalt alkyne complex **1** with a tetrahedral Co_2C_2 core (Scheme 1). Under thermal conditions, or in the presence of amine *N*-oxide promoters,[11] it is assumed that complex **1** undergoes decarbonylation at the *basal* carbon monoxide, which is orientated *anti* relative to R^1, followed by coordination of an alkene to give alkene complexes **2a**, and **b**. The regioselectivity with respect to the alkene is due to steric hindrance in the insertion step **2a** → **3** versus **2b** → **4**. The less hindered face of the alkene is inserted into the less hindered Co–C bond. For alkenes with sufficiently large substituents R^2, conformation **2b**, and thus cyclopentenone **4**, is preferred. However, with most alkenes mixtures of regioisomers **3** and **4** are obtained. The sequence is completed by the insertion of carbon monoxide and extrusion of



Scheme 1

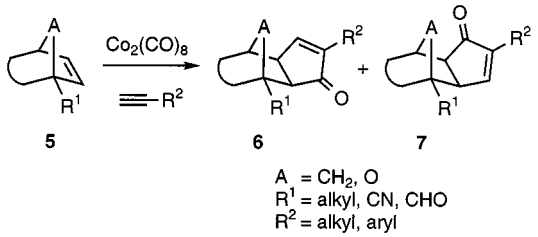
$Co_2(CO)_6$ to give the regioisomeric cyclopentenones **3** and **4**. There are several ways to overcome the regioselectivity problem. If the reaction is performed intramolecularly, only one regioisomer is possible for steric reasons. Another

[a] Institut für Organische Chemie, Technische Universität Braunschweig,
Hagenring 30, D-38106 Braunschweig, Germany
Fax: (internat.) +49(0)531/391–5388
[b] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig,
Hagenring 30, D-38106 Braunschweig, Germany
Fax: (internat.) +49(0)531/391–5387

  1434–193X/00/0204–0681 $ 17.50+.50/0

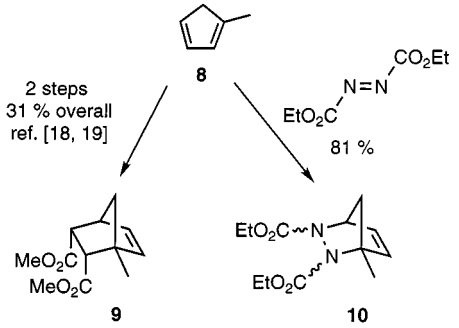
method, recently introduced by Krafft, utilises alkenes tethered to soft donor ligands.[12] The increased regioselectivity observed for these systems was explained by the coordination of the heteroatom to cobalt prior to insertion, thereby fixing the conformation of the alkene in favour of **2b**.

In a different approach one might use bridged bicyclic alkenes. It is well-known from the work of Pauson that the reaction of norbornene is completely *exo*-face selective.[13] Surprisingly, little work has been done on unsymmetrically substituted bridged bicyclic alkenes **5** (Scheme 2). Modest regioselectivity in favour of regioisomer **6** was observed by Schore for 1-methyl-5-norbornen-2-one.[14] However, employing 1-methyl-8-oxabicyclo[3.2.1]oct-6-ene derivatives in the co-cyclization, resulted in the formation of compound **7** as the major regioisomer.[15,16]



Scheme 2

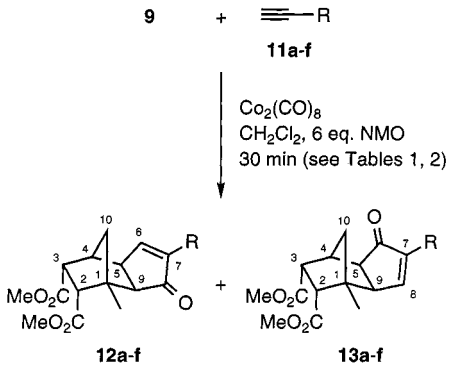
In order to explore the regioselectivity issue in more detail, we employed 1-methyl-substituted *endo*-norbornene ester **9** and 2,3-diazabicyclo[2.2.1]heptene ester **10** (Scheme 3) in intermolecular Pauson–Khand reactions. Compounds **9** and **10** were chosen as substrates, because their ester groups should provide sufficient steric hindrance to suppress *endo*-attack completely, and should allow further functionalization of the Pauson–Khand products. Furthermore, **9** and **10** are easily available by cycloaddition reactions, and they are expected to be highly reactive in the co-cyclization. Since no direct structural information on complexes **2a** and **b** has been obtained until now, we hoped to gain insight as to whether the *basal anti* coordination site, or alternatively the *apical* site, of **1** is involved in the co-cyclization of bicyclic alkenes. Our experimental results with **9** and **10,** and the mechanistic consequences for the Pauson–Khand reaction in general are described below.



Scheme 3

As shown in Scheme 3, *endo*-norbornene ester **9** was prepared by a thermal Diels–Alder reaction of 1-methyl-cyclopentadiene **8**[17] with maleic anhydride, followed by subsequent esterification.[18,19] In a similar fashion, racemic 1-methyl-2,3-diazabicyclo[2.2.1]heptene ester **10** was obtained from **8** and diethyl diazodicarboxylate.[20]

Norbornene ester **9** was then employed in NMO-promoted Pauson–Khand reactions with terminal alkynes **11** to give regioisomeric enones **12** and **13** (Scheme 4, Table 1). Selectivities between 60:40 and 65:35 in favour of regioisomer **12** were obtained for alkynes with small alkyl and phenyl substituents (entries 1, 2, and 4). In case of the hydroxyethyl-substituted alkyne **11f** the selectivity increased to 85:15 (entry 6). However, for the sterically demanding alkynes **11c** and **e**, the regioselectivity was reversed, giving **13** as the major regioisomer (entries 3 and 5). Surprisingly, the selectivities of **11c** and **e** were completely different (**12c/13c** 6:94, **12e/13e** 48:52) despite their similar steric bulk. In contrast to the other alkynes, compound **11e** produced large variations in the regioselectivies, depending on the reaction conditions. In order to study this phenomenon in more detail, Pauson–Khand reactions of **11e** with norbornene derivative **9** were performed at various temperatures (Table 2). At low temperatures, formation of **12e** was preferred. The highest regioselectivity (**12e/13e** 90:10) was obtained at –20 °C in CH_2Cl_2 (entry 1). Upon increasing temperature the selectivity decreased, and at 40 °C in CH_2Cl_2 it was reversed in favour of regioisomer **13e** (48:52, entry 5). When THF was used as the solvent and the temperature was further raised to 70 °C, a remarkable increase of the selectivity was observed in favour of **13e** (**12e/13e** 19:81, entry 7). In order to rule out solvent effects,[21] the co-cyclizations were carried out in toluene at various temperatures. In agreement with the previous results, regioisomer **12e** was obtained at –25 °C as the major product with high selectivity (**12e/13e** 95:5, entry 8). At room temperature the ratio has already switched in favour of **13e** (**12e/13e** 23:77, entry 9). Performing the co-cyclizations at elevated temper-



11 - 13	R
a	*n*-Prop
b	*n*-Pent
c	*t*-Bu
d	Ph
e	$C(CH_3)_2OH$
f	CH_2CH_2OH

Scheme 4

Table 1. Pauson–Khand reaction of norbornene ester **9** with various alkynes **11a–f** (Reaction conditions: 1 equiv. of $Co_2(CO)_8$, CH_2Cl_2, 6 equiv. of NMO, 25 °C, 30 min); ratio of regioisomers was determined by capillary GC of the crude products

Entry	Alkyne **11**	R	Yield [%]	Products	Product ratio 12 : **13**	
(1)	**a**	*n*Prop	31	**12a**, **13a**	60	40
(2)	**b**	*n*Pent	49	**12b**, **13b**	65	35
(3)	**c**	*t*Bu	9	**12c**, **13c**	6	94
(4)	**d**	Ph	56	**12d**, **13d**	61	39
(5)	**e**	$C(CH_3)_2OH$	42	**12e**, **13e**	48	52
(6)	**f**	CH_2CH_2OH	28	**12f**, **13f**	85	15

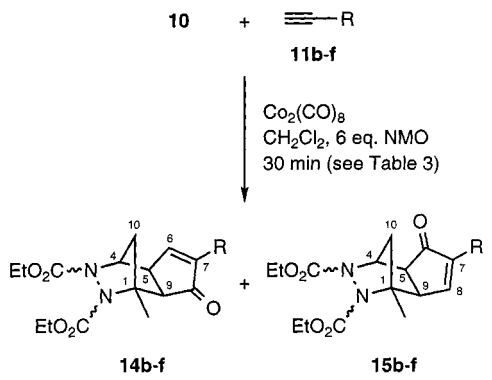
atures (120 °C) resulted in further increase in the selectivity (**12e/13e** 12:88, entry 11). It should be noted that both thermal and NMO-promoted co-cyclizations gave very similar ratios of regioisomers, but increased yields were obtained in the presence of NMO (entries 6, 7, 10, and 11).[22–24]

Table 2. Pauson–Khand reaction of norbornene ester **9** with alkyne **11e** at various temperatures (Reaction conditions: 1 equiv. of $Co_2(CO)_8$, solvent, NMO)

Entry	Solvent	Temp. [°C]	NMO [equiv.]	Time [h]	Yield [%]	Product ratio **12e** : **13e**	
(1)	CH_2Cl_2	–20	6	3	24	90	10
(2)	CH_2Cl_2	0	6	2	25	88	12
(3)	CH_2Cl_2	20	6	2	34	81	19
(4)	CH_2Cl_2	40	0	2	–[a]	–	–
(5)	CH_2Cl_2	40	6	2	42	48	52
(6)	THF	70	0	2	19	12	88
(7)	THF	70	6	2	46	19	81
(8)	toluene	–25	6	4	61	95	5
(9)	toluene	20	6	4	59	23	77
(10)	toluene	120	0	2	27	13	87
(11)	toluene	120	6	2	48	12	88

[a] No conversion of **11e** was observed.

Next, 2,3-diaza-norbornene derivative **10** was used in the Pauson–Khand reaction with alkynes **11b–f** to give enones **14**, and **15** (Scheme 5). The results in Table 3 show that the size of the alkyne substituent has only a small influence on the regioselectivity, which is 1.5–2.2:1 in favour of regioisomer **15**. Only the phenyl acetylene **11d** reacted completely unselectively (entry 3). No significant temperature dependency of the regioselectivity in the co-cyclization of alkyne **11e** with alkene **10** was observed.[22–24]



Scheme 5

Table 3. Pauson–Khand reaction of 2,3-diazanorbornene ester **10** with various alkynes **11b–f** (Reaction conditions: 1 equiv. of $Co_2(CO)_8$, CH_2Cl_2, 6 equiv. of NMO, 25 °C, 30 min); ratio of regioisomers was determined by capillary GC of the crude products

Entry	Alkyne **11**	R	Yield [%]	Products	Product ratio **14** : **15**	
(1)	**b**	*n*Pent	65	**14b**, **15b**	69	31
(2)	**c**	*t*Bu	58	**14c**, **15c**	61	39
(3)	**d**	Ph	54	**14d**, **15d**	50	50
(4)	**e**	$C(CH_3)_2OH$	57	**14e**, **15e**	62	38
(5)	**f**	CH_2CH_2OH	54	**14f**, **15f**	60	40

The constitution of products **12–15** was established by COSY and CH-correlations. The relative configurations of **12–14** were determined by NOE experiments. Thus, irradiation of the ^1H NMR signal for 5-H in **12b** produced enhancements of 4-H and 9-H, and irradiation of the bridgehead methyl group resulted in enhancements of 2-H and 9-H. In contrast, for isomer **13b**, enhancements of 9-H and 1-H were observed upon irradiation of (C-1)CH_3. The NMR assignments were supported by an X-ray crystal structure determination of the *tert*-butyl derivative, **13c** (Figure 1).[25] Irradiation of the ^1H NMR signal for the bridgehead

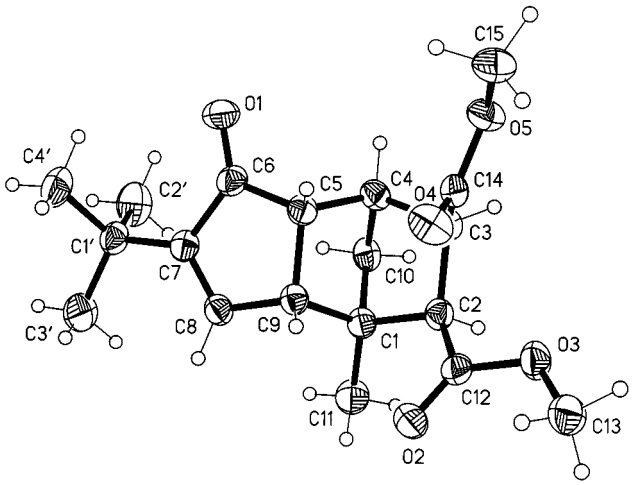
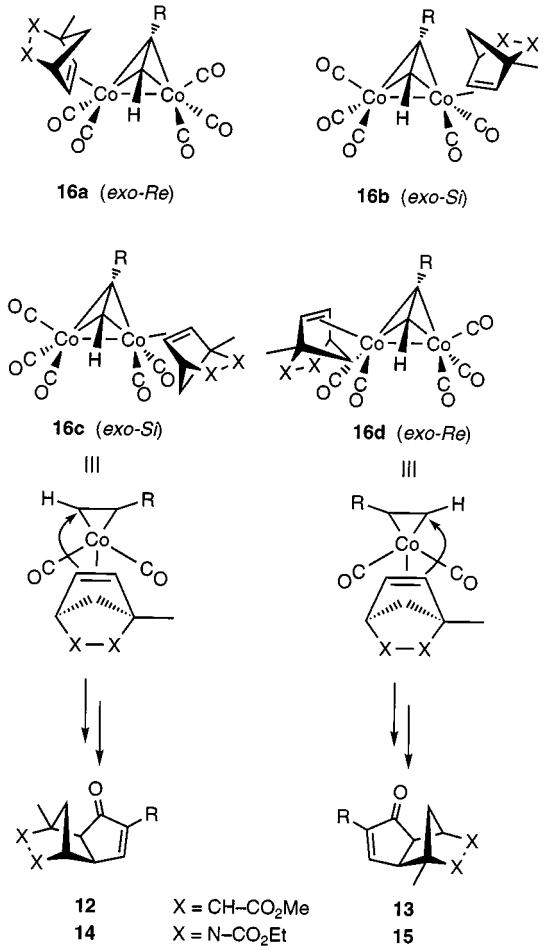


Figure 1. X-ray crystal structure of cyclopentenone **13c**.[25] Ellipsoids correspond to 50% probability. Selected bond lengths [Å] and angles [°]:C(1)–C(10) 1.541(3), C(1)–C(2) 1.546(3), C(1)–C(9) 1.557(3), C(2)–C(3) 1.564(3), C(3)–C(4) 1.551(3), C(4)–C(10) 1.532(3), C(4)–C(5) 1.540(3), C(5)–C(6) 1.515(3), C(5)–C(9) 1.543(3), C(6)–O(1) 1.217(3), C(6)–C(7) 1.480(3), C(7)–C(8) 1.335(3), C(8)–C(9) 1.504(3), C(10)–C(1)–C(2) 99.07(17), C(11)–C(1)–C(9) 115.34(19), C(10)–C(1)–C(9) 100.89(17), C(2)–C(1)–C(9) 108.66(17), C(1)–C(2)–C(3) 104.44(17), C(4)–C(3)–C(2) 102.03(17), C(10)–C(4)–C(3) 101.83(17), C(5)–C(4)–C(3) 108.80(18), C(6)–C(5)–C(4) 112.73(18), C(6)–C(5)–C(9) 104.95(17), C(4)–C(5)–C(9) 103.38(17), C(7)–C(6)–C(5) 108.86(18), C(8)–C(7)–C(6) 108.0(2), C(7)–C(8)–C(9) 114.8(2), C(8)–C(9)–C(5) 103.27(17), C(8)–C(9)–C(1) 113.21(18), C(5)–C(9)–C(1) 103.94(17), C(4)–C(10)–C(1) 95.52(17)

methyl group (11-H) in **14b** resulted in enhancements of 9-H and 10-H, and irradiation of 4-H produced enhancements of 5-H, 6-H, and 10-H.

In order to rationalize the regioselectivities observed for bicyclic alkenes **5**, Schore has proposed a mechanism[16] in which *exo* attack of the alkene at the *basal anti* coordination site of the cobalt cluster **1** results in the formation of four different insertion products. According to his rationale, a *pseudo-1,3-diaxial* interaction between a carbon monoxide ligand and the angular methyl group is the most important factor governing the regioselectivity. However, this mechanism does not explain the dependence of the regioselectivity on the steric bulk of the alkyne and the reaction temperature, which was observed with alkene **9**.

In principle, replacement of each of the three different carbon monoxide ligands by the alkene is possible.[26] However, according to our experimental results, coordination at the *apical* position and subsequent insertion seem to be most likely. As shown in Scheme 6, *exo* attack of **9** (or **10**) either at the *Re*- or *Si*-face of prochiral complex **1** and substitution of the *apical* carbon monoxide leads to four different alkene complexes **16a**–**d**. Note that there are two different *exo*-*Re* and *exo*-*Si*-approaches, respectively, with the methylene bridge being orientated towards the tetrahedral Co_2C_2 core (**16a** and **b**) or the carbon monoxide ligands (**16c** and **d**). Major steric interactions are probably involved in two different steps of the co-cyclization, that is (1) coordination of the alkene followed by formation of **16a**–**d**, and (2) insertion of the alkene to give regioisomeric cyclopentenones **12**–**15**. Concerning the coordination step, complexes **16a** and **b** should be strongly disfavoured due to steric interactions between the methylene bridge and the Co_2C_2 core. In case of 2,3-diazanorbornene **10** (X = NCO_2Et) complexes **16a** and **b** should be even more disfavoured because one of the azo ester groups collides with the alkyne substituent. The destabilisation is further increased in **16b** by steric hindrance between the angular methyl group and the alkyne substituent. Between **16c** and **d**, complex **16c** should be disfavoured in the coordination step because of steric interactions between the angular methyl group and the alkyne substituent. However, for the insertion step the opposite preference is expected, i.e. **16c** is more likely to undergo insertion than **16d**. As mentioned above, insertion of the alkene preferably takes place at the least hindered Co–CH bond, avoiding other steric constraints. Consequently, in **16c** the less substituted end of the alkene is connected first to the alkyne CH, whereas in **16d** the more substituted alkene carbon atom is connected to CH. This means that under kinetic conditions, and in the presence of small substituents, the discrimination between **16c** and **16d** in the coordination step is not as important as the irreversible insertion step favouring **16c**, which yields **12**. Under thermodynamic conditions, and/or the presence of bulky alkynes, **16d** is the preferred coordination geometry, yielding **13** after insertion. The different behaviour of 2,3-diazanorbornene **10** as compared to norbornene **9** is probably caused by the increased flexibility of the methylene bridge and the bridgehead methyl group in **10**. This should decrease the energy differences between **16a**–**d**, because the less rigid methylene bridge should be able to "flip back", thus decreasing steric interactions with the cobalt cluster, and making the influence of R on the coordination and/or insertion step less predominant.



Scheme 6

Our modification to the mechanism is further supported by recent results from Greene and co-workers.[27] The authors reported the preparation of novel dicobalttetracarbonylalkyne complexes with bridging diphosphanylamine ligands, and their successful utilisation in the Pauson–Khand reactions. X-ray crystal structures of these complexes clearly showed that the *basal anti* oriented carbon monoxides in phenyl acetylene complex **1** were replaced by the bidentate ligand. Consequently, the co-cyclization must have occurred at the *apical* position.

Concerning the temperature dependent reversal of the selectivity of **12e** and **13e**, an alternative mechanistic rationale involving a chelation effect must be considered. In contrast to sulfur and nitrogen containing alkynes where chelation effects have been studied in detail by NMR,[12,28] no experimental evidence has been reported until now for hydroxy-substituted alkynes.

In conclusion, the present study employing norbornene ester **9** and 2,3-diazanorbornene ester **10** in intermolecular Pauson–Khand reactions with terminal alkynes **11** supports

a modified mechanistic scheme of the co-cyclization in which coordination of the *apical* position rather than the *basal anti* position by the alkene takes place. For further improvement of the regioisomeric ratios it might be useful to increase the steric bulk of the angular substituent at the bicyclic alkene. Experiments towards this goal and the functionalization of products **12**–**15** are currently under investigation.

Experimental Section

General: All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. Analytical TLC was performed on precoated Merck Si 254 F plates (0.25 mm thickness) and the products were visualised by UV. Flash chromatography[29] was carried out with Merck silica gel 60 (230–400 mesh). – NMR spectra: Bruker AM 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz). Multiplets in ^{13}C NMR spectra were assigned with the aid of DEPT experiments. – IR: Nicolet 320 FT-IR spectrometer. – MS: Finnigan Model MAT 8430 (EI). – 1-Methyl-cyclopentadiene **8** was prepared according to ref.[17] and norbornene ester **9** was prepared by thermal Diels–Alder reaction as described in ref.[18,19]

Diethyl 1-Methyl-2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (10): To a solution of diethyl diaza-dicarboxylate (10.5 g, 0.06 mol) in Et_2O (30 mL) was added freshly distilled 1-methyl-cyclopentadiene (15.2 g, 0.19 mol) and the mixture was stirred for 3 d at room temp. After removal of the solvent in vacuo the crude product was purified by flash chromatography on SiO_2 (hexanes/ethyl acetate 5:1) to yield 12.4 g (81%) of a pale yellow oil. – IR (film): $\tilde{\nu}$ = 1742 cm^{-1}, 1702. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.49 (d, *J* = 5.4 Hz, 1 H, 6-H), 6.41 (dd, *J* = 5.4/3.0 Hz, 1 H, 5-H), 5.19–5.17 (m, 1 H, 4-H), 4.31–4.15 (m, 4 H, OC*H*$_2$CH$_3$), 1.96 (s, 3 H, 8-H), 1.73 (dd, *J* = 1.6/8.6 Hz, 1 H, 7-H$_a$), 1.67 (dd, *J* = 0.9/8.6 Hz, 1 H, 7-H$_b$), 1.31–1.24 (m, 6 H, OCH$_2$C*H*$_3$). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0 (COO), 158.4 (COO), 143.2, 133.7 (C-5, C-6), 75.5 (C-1), 64.4 (C-4), 62.4 (O*C*H$_2$CH$_3$), 62.1 (O*C*H$_2$CH$_3$), 55.2 (C-7), 18.1 (C-8), 14.4 (OCH$_2$*C*H$_3$), 14.3 (OCH$_2$*C*H$_3$). – MS (EI) *m*/*z* (%): 254 (24) [M$^+$], 209 (4), 182 (11), 135 (7), 109 (6), 94 (14), 80 (100). – $C_{12}H_{18}N_2O_4$: calcd. 254.1266, found 254.1262 (MS). – $C_{12}H_{18}N_2O_4$ (254.29): calcd. C 56.68, H 7.13, N 11.02; found: C 56.67, H 7.15; N 10.78.

General Procedure for the Pauson–Khand Reaction of Terminal Alkynes with Bicyclic Alkenes: To a solution of $Co_2(CO)_8$ (342 mg, 1.00 mmol) in CH_2Cl_2 (5 mL) was added alkyne **11** (1.00 mmol) and the resulting solution was stirred at rt for 20 min. After the evolution of carbon monoxide ceased, the bicyclic alkene (1.20 mmol) was added and stirring was continued for 10 min. Then *N*-methylmorpholine *N*-oxide (705 mg, 6.00 mmol) was added in small portions and the mixture was stirred for 30 min. The solvent was evaporated and the mixture was purified by flash chromatography.

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*RS*,9*RS*)-1-Methyl-8-oxo-7-propyltricyclo[5.2.1.0^{5,9}]dec-6-ene-2,3-dicarboxylate (12a). Flash chromatography on SiO_2 (Et_2O) yielded 58 mg (18%) of **12a** as the first fraction and 42 mg (13%) of **13a** as the second fraction. Colourless oil; IR (film): $\tilde{\nu}$ = 1741 cm^{-1}, 1697. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11–7.10 (m, 1 H, 6-H), 3.61, 3.58 (s, 6 H, OCH$_3$), 3.42–3.39 (m, 1 H, 5-H), 3.07 (dd, *J* = 11.8/3.8 Hz, 1 H, 3-H), 2.84 (d, *J* = 11.8 Hz, 1 H, 2-H), 2.36–2.34 (m, 2 H, 4-H, 9-H), 2.09–2.05 (m, 2 H, 1'-H), 1.46–1.37 (m, 2 H, 2'-H), 1.28 (s, 3 H, 11-H), 1.16 (d, *J* = 10.8 Hz, 1 H, 10-H$_a$), 0.97 (d, *J* = 10.8 Hz, 2 H, 10-H$_b$), 0.85 (t, *J* = 3.3 Hz, 3 H, 3'-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.6 (CO), 172.1 (COO), 171.8 (COO), 158.2 (C-6), 149.7 (C-7), 52.9 (C-2), 51.6 (OCH$_3$), 51.3 (OCH$_3$), 50.8 (C-9), 50.0 (C-1), 47.2 (C-3), 43.1 (C-5), 41.0 (C-4), 39.3 (C-10), 26.7 (C-1'), 21.0 (C-2'), 16.4 (C-11), 13.7 (C-3'). – MS (EI) *m*/*z* (%): 320 (81) [M$^+$], 289 (42), 260 (45), 228 (21), 201 (29), 175 (100), 145 (52), 113 (56), 91 (25). – $C_{18}H_{24}O_5$: calcd. 320.1624, found 320.1617 (MS).

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*SR*,9*SR*)-1-Methyl-6-oxo-7-propyltricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (13a). Colourless oil. – IR (film): $\tilde{\nu}$ = 1741 cm^{-1}, 1698. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.14 (m, 1 H, 8-H), 3.60, 3.58 (s, 6 H, OCH$_3$), 3.34–3.33 (m, 1 H, 9-H), 3.21 (dd, *J* = 11.8/4.4 Hz, Hz, 3-H), 2.74 (d, *J* = 11.8 Hz, 1 H, 2-H), 2.70–2.69 (m, 1 H, 5-H), 2.65 (d, *J* = 4.4 Hz, 1 H, 4-H), 2.18–2.13 (m, 2 H, 1'-H), 1.53–1.44 (m, 2 H, 2'-H), 1.26 (s, 3 H, 11-H), 1.19 (d, *J* = 10.9 Hz, 1 H, 10-H$_a$), 0.99 (d, *J* = 10.9 Hz, 1 H, 10-H$_b$), 0.91 (t, *J* = 7.3 Hz, 3 H, 3'-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.7 (CO), 172.1 (COO), 171.7 (COO), 157.9 (C-8), 150.0 (C-7), 52.2 (C-2), 51.7 (OCH$_3$), 51.2 (OCH$_3$), 49.6 (C-5), 48.8 (C-1), 48.0 (C-3), 44.6 (C-9), 41.9 (C-4), 39.4 (C-10), 26.8 (C-1'), 20.9 (C-2'), 16.9 (C-11), 13.7 (C-3'). – MS (EI) *m*/*z* (%) 320 (64) [M$^+$], 289 (39), 260 (58), 228 (27), 201 (18), 175 (100), 137 (11), 113 (11), 91 (10). – $C_{18}H_{24}O_5$: calcd. 320.1624, found 320.1617 (MS).

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*RS*,9*RS*)-1-Methyl-6-oxo-7-*n*-pentyltricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (12b). Flash chromatography on SiO_2 (hexanes/ethyl acetate 5:1) yielded 110 mg (32%) of **12b** as the first fraction and 60 mg (17%) of **13b** as the second fraction. Colourless oil; IR (film): $\tilde{\nu}$ = 1740 cm^{-1}, 1734, 1698. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.16 (m, 1 H, 6-H), 3.67, 3.65 (s, 6 H, OCH$_3$), 3.48 (s, 1 H, 5-H), 3.13 (dd, *J* = 11.8/3.8 Hz, 1 H, 3-H), 3.00 (d, *J* = 11.8 Hz, 1 H, 2-H), 2.42–2.40 (m, 2 H, 4-H, 9-H), 2.16–2.12 (m, 2 H, 1'-H), 1.48–1.41 (m, 2 H, 2'-H), 1.36 (s, 3 H, 11-H), 1.35–1.25 (m, 4 H, 3'-H, 4'-H), 1.22 (d, *J* = 10.8 Hz, 1 H, 10-H$_a$), 1.03 (d, *J* = 10.8 Hz, 1 H, 10-H$_b$), 0.89 (t, *J* = 7.3 Hz, 3 H, 5'-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.7 (CO), 172.1 (COO), 171.8 (COO), 158.0 (C-6), 150.0 (C-7), 53.0 (C-2), 51.6 (OCH$_3$), 51.4 (OCH$_3$), 50.8 (C-9), 50.0 (C-1), 47.3 (C-3), 43.1 (C-5), 41.0 (C-4), 39.4 (C-10), 31.5, 27.4, 24.6, 22.3 (C-1', C-2', C-3', C-4'), 16.5 (C-11), 13.9 (C-5'). – MS (EI) *m*/*z* (%): 348 (20) [M$^+$], 316 (18), 288 (16), 260 (9), 229 (10), 203 (23), 193 (18), 165 (8), 145 (36), 133 (16), 113 (47), 105 (16), 91 (14), 80 (100). – $C_{20}H_{28}O_5$: calcd. 348.1937, found 348.1929 (MS). – $C_{20}H_{28}O_5$ (348.19): calcd. C 68.94, H 8.10; found: C 68.91, H 8.15.

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*SR*,9*SR*)-1-Methyl-6-oxo-7-*n*-pentyltricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (13b). Colourless oil. – IR (film): $\tilde{\nu}$ = 1743 cm^{-1}, 1741, 1699. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20–7.19 (m, 1 H, 8-H), 3.65, 3.64 (s, 6 H, CO_2CH_3), 3.38 (s, 1 H, 9-H), 3.27 (dd, *J* = 11.8/4.4 Hz, 3-H), 2.80 (d, *J* = 11.8 Hz, 1 H, 2-H), 2.70–2.69 (m, 1 H, 5-H), 2.66 (d, *J* = 4.4 Hz, 1 H, 4-H), 2.19–2.15 (m, 2 H, 1'-H), 1.49–1.42 (m, 2 H, 2'-H), 1.33–1.21 (s, 7 H, 11-H, 3'-H, 4'-H), 1.19 (d, *J* = 10.9 Hz, 1 H, 10-H$_a$), 0.99 (d, *J* = 10.9 Hz, 1 H, 10-H$_b$), 0.88 (t, *J* = 7.3 Hz, 3 H, 5'-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.7 (CO), 172.1 (COO), 171.7 (COO), 157.7 (C-8), 150.3 (C-7), 52.2 (C-2), 51.7 (OCH$_3$), 51.3 (OCH$_3$), 49.6 (C-5), 48.8 (C-1), 48.0 (C-3), 44.6 (C-9), 41.9 (C-4), 39.4 (C-10), 31.4, 27.4, 24.7, 22.3 (C-1', C-2', C-3', C-4'), 16.9 (C-11), 13.9 (C-5'). – MS (EI) *m*/*z* (%): 348 (51) [M$^+$], 316 (55), 288 (49), 260 (24), 229 (21), 203 (100), 175 (10), 145 (20), 137 (11), 113 (17), 91 (17). – $C_{20}H_{28}O_5$: calcd. 348.1937, found

348.1929 (MS). – $C_{20}H_{28}O_5$ (348.19): calcd. C 68.94, H 8.10; found: C 68.93, H 8.08.

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*RS*,9*RS*)-7-*tert*-Butyl-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (12c). GC-MS (EI) *m/z* (%): 334 (32) [M$^+$], 319 (30), 303 (8), 287 (2), 274 (13), 259 (5), 242 (2), 227 (7), 218 (11), 199 (4), 189 (100), 175 (23), 161 (25), 145 (73), 133 (28), 119 (12), 113 (76), 105 (19).

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*SR*,9*SR*)-7-*tert*-Butyl-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (13c). Flash chromatography on SiO_2 (hexanes/ethyl acetate 5:1) yielded 30 mg (9%) of a colourless solid; m.p. 84.3° C. – IR (film): $\tilde{\nu}$ = 1743 cm^{-1}, 1741, 1699. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 3.0 Hz, 1 H, 8-H), 3.66 (s, 6 H, OCH_3), 3.34–3.33 (m, 1 H, 9-H), 3.28 (dd, *J* = 11.8/4.3 Hz, 1 H, 3-H), 2.80 (d, *J* = 11.8 Hz, 1 H, 2-H), 2.68–2.65 (m, 2 H, 5-H, 4-H), 1.27 (s, 3 H, 11-H), 1.18 (s, 9 H, 2'-H, 10-H_a), 1.17 (d, *J* = 10.9 Hz, 1 H, 10-H_a), 0.99 (d, *J* = 10.9 Hz, 1 H, 10-H_b). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.8 (CO), 172.1 (COO), 171.7 (COO), 158.0 (C-8), 155.8 (C-7), 52.2 (C-2), 51.7 (OCH_3), 51.3 (OCH_3), 50.6 (C-5), 48.8 (C-1), 48.0 (C-3), 43.4 (C-9), 42.0 (C-4), 39.2 (C-10), 32.0 (C-1'), 28.3 (C-2'), 16.9 (C-11); MS (EI) *m/z* (%) 334 (M$^+$, 84), 319 (19), 303 (40), 287 (12), 274 (45), 259 (16), 242 (23), 227 (13), 215 (12), 189 (100), 175 (24), 137 (9), 113 (11), 91 (9). – $C_{19}H_{26}O_5$: calcd. 334.1780, found 334.1773 (MS). $C_{19}H_{26}O_5$ (334.40): calcd. C 68.24, H 7.84, found C 67.36, H 7.98. – X-ray structure analysis of **13c**: $C_{19}H_{26}O_5$, M_r = 334.40, crystal size 0.7 × 0.3 × 0.1 mm, monoclinic, space group $P2_1/c$, *a* = 11.521(2) Å, *b* = 12.219(2) Å, *c* = 12.677(3) Å, β = 96.16(2)°, *V* = 1774.3(6) Å^3, $\rho_{calcd.}$ = 1.252 Mg m^{-3}, *T* = 143 K, *Z* = 4, λ = 0.71073 Å. Siemens P4 diffractometer, 4048 reflections collected, 3.03 ≤ θ ≤ 25.05°, 3129 independent reflections, 223 refined parameters, R1 = 0.0508, wR2 = 0.1154. Program used: SHELXL-97. See ref.[25]

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*RS*,9*RS*)-1-Methyl-6-oxo-7-phenyltricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (12d). Flash chromatography on SiO_2 (hexanes/ethyl acetate 5: 1) yielded 120 mg (34%) of **12d** as the first fraction and 80 mg (22%) of **13d** as the second fraction. Colourless oil; IR (film): $\tilde{\nu}$ = 1741 cm^{-1}, 1737, 1700. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.68 (m, 3 H, 6-H, 2'-H), 7.41–7.33 (m, 3 H, 3'-H, 4'-H), 3.71 (s, 3 H, OCH_3), 3.69–3.65 (m, 4 H, 5-H, OCH_3), 3.18 (dd, *J* = 11.8/3.8 Hz, 1 H, 3-H), 2.96 (d, *J* = 11.8 Hz, 1 H, 2-H), 2.63–2.62 (m, 1 H, 9-H), 2.54–2.53 (m, 1 H, 4-H), 1.42 (s, 3 H, 11-H), 1.38 (d, *J* = 10.8 Hz, 1 H, 10-H_a), 1.12 (d, *J* = 10.8 Hz, 1 H, 10-H_b). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.5 (CO), 172.1 (COO), 171.8 (COO), 159.7 (C-6), 146.5 (C-7), 131.4 (C-1'), 128.5 (C-4'), 128.4, 127.4 (C-2', C-3'), 53.0 (C-2), 52.3 (OCH_3), 51.9 (OCH_3), 51.5 (C-9), 50.5 (C-1), 47.3 (C-3), 42.8 (C-5), 41.2 (C-4), 39.6 (C-10), 16.5 (C-11). – MS (EI) *m/z* (%): 354 (100) [M$^+$], 323 (38), 294 (56), 262 (36), 235 (31), 210 (69), 165 (23), 128 (16), 113 (18), 102 (8), 91 (9). – $C_{21}H_{22}O_5$: calcd. 354.1467, found 354.1461 (MS). – $C_{21}H_{22}O_5$ (354.40): calcd. C 71.17, H 6.26; found: C 71.14, H 6.26.

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*SR*,9*SR*)-1-Methyl-6-oxo-7-phenyltricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (13d). Colourless oil. – IR (film): $\tilde{\nu}$ = 1739 cm^{-1}, 1700. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 3.2 Hz, 1 H, 8-H), 7.66–7.61 (m, 2 H, *o*-H), 7.34–7.25 (m, 3 H, *m*-H, *p*-H), 3.62 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 3.60–3.58 (m, 1 H, 9-H), 3.26 (dd, *J* = 11.8/4.3 Hz, 1 H, 3-H), 2.85–2.84 (m, 1 H, 5-H), 2.78 (d, *J* = 11.8 Hz, 1 H, 2-H), 2.72 (d, *J* = 4.3 Hz, 1 H, 4-H), 1.28 (s, 3 H, 11-H), 1.27–1.25 (m, 1 H, 10-H_a), 1.02 (d, *J* = 10.9 Hz, 1 H, 10-H_b). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.5 (CO), 172.1 (COO), 171.7 (COO), 159.4 (C-8), 146.9 (C-7), 131.3 (C-i), 128.5, 128.4, 127.0 (C-o, C-m, C-p), 52.3 (C-2), 51.8 (OCH_3), 51.4 (OCH_3), 50.7 (C-5), 49.3 (C-1), 48.0 (C-3), 44.3 (C-9), 42.3 (C-4), 39.7 (C-10), 17.0 (C-11). – MS (EI) *m/z* (%): 354 (100) [M$^+$], 323 (41), 294 (65), 262 (46), 235 (29), 210 (87), 156 (20), 128 (17), 115 (13), 80 (12). – $C_{21}H_{22}O_5$: calcd. 354.1467, found 354.1461 (MS). – $C_{21}H_{22}O_5$ (354.40): calcd. C 71.17, H 6.26; found: C 71.18, H 6.24.

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*RS*,9*RS*)-7-(2-Hydroxyisopropyl)-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (12e). Flash chromatography on SiO_2 (Et_2O) yielded 67 mg (20%) of **12e** as the first fraction and 74 mg (22%) of **13e** as the second fraction. Colourless oil; IR (film): $\tilde{\nu}$ = 3442 cm^{-1}, 1741, 1700. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (s, 1 H, 6-H), 3.79 (s, 1 H, OH), 3.67 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3), 3.50 (s, 1 H, 5-H), 3.15 (dd, *J* = 11.8/3.7 Hz, 1 H, 3-H), 2.90 (d, *J* = 11.8 Hz, 1 H, 2-H), 2.51 (d, *J* = 3.6 Hz, 1 H, 4-H), 2.44 (s, 1 H, 9-H), 1.42, 1.40 (s, 6 H, 2'-H, 3'-H), 1.35 (s, 3 H, 11-H), 1.26 (d, *J* = 10.8 Hz, 1 H, 10-H_a), 1.06 (d, *J* = 10.8 Hz, 1 H, 10-H_b). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.5 (CO), 171.9 (COO), 171.7 (COO), 156.7 (C-6), 154.5 (C-7), 69.7 (C-1'), 52.8 (C-2), 51.7 (OCH_3), 51.7 (OCH_3), 51.5 (C-9), 50.1 (C-1), 47.2 (C-3), 42.7 (C-5), 40.9 (C-4), 39.3 (C-10), 28.7 (C-2', C-3'), 16.4 (C-11). – MS (EI) *m/z* (%): 336 (4) [M$^+$], 321 (100), 305 (21), 289 (17), 258 (20), 226 (12), 199 (14), 174 (23), 145 (27), 131 (8), 113 (26), 91 (11). – $C_{18}H_{24}O_6$: calcd. 336.1573, found 336.1566 (MS).

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*SR*,9*SR*)-7-(2-Hydroxyisopropyl)-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (13e). Colourless oil. – IR (film): $\tilde{\nu}$ = 3569 cm^{-1}, 3491, 1739, 1719, 1685. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, *J* = 3.0 Hz, 1 H, 8-H), 3.68–3.65 (m, 7 H, OH, OCH_3), 3.41–3.39 (m, 1 H, 5-H), 3.28 (dd, *J* = 11.8/4.1 Hz, 1 H, 3-H), 2.82–2.80 (m, 2 H, 2-H, 9-H), 2.68 (d, *J* = 4.1 Hz, 1 H, 4-H), 1.43, 1.42 (s, 6 H, 2'-H, 3'-H), 1.28 (s, 3 H, 11-H), 1.24 (d, *J* = 10.8 Hz, 1 H, 10-H_a), 1.05 (d, *J* = 10.8 Hz, 1 H, 10-H_b). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.2 (CO), 172.0 (COO), 171.6 (COO), 156.4 (C-6), 155.0 (C-7), 69.7 (C-1'), 52.3 (C-2), 51.7 (OCH_3), 51.4 (OCH_3), 50.5 (C-9), 48.9 (C-1), 47.9 (C-3), 44.2 (C-5), 41.9 (C-4), 39.3 (C-10), 28.8, 28.7 (C-2', C-3'), 16.9 (C-11). – MS (EI) *m/z* (%) 336 (M$^+$, 5), 321 (100), 289 (31), 258 (29), 226 (19), 199 (12), 173 (44), 145 (23), 137 (12), 113 (19), 107 (22), 91 (17). – $C_{18}H_{24}O_6$: calcd. 336.1573, found 336.1566 (MS).

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*RS*,9*RS*)-7-(2-Hydroxyethyl)-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (12f). GC-MS (EI) *m/z* (%) 322 (7) [M$^+$], 304 (1), 290 (57), 272 (3), 261 (86), 244 (8), 230 (27), 213 (5), 199 (18), 177 (100), 159 (34), 147 (43), 137 (31), 113 (34);

Dimethyl (1*RS*,2*SR*,3*SR*,4*SR*,5*SR*,9*SR*)-7-(2-Hydroxyethyl)-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (13f). Flash chromatography on SiO_2 (Et_2O) yielded 120 mg (24%) of a colourless oil. – IR (film): $\tilde{\nu}$ = 3457 cm^{-1}, 1738, 1733, 1695. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.31 (m, 1 H, 6-H), 3.76–3.64 (m, 9 H, OCH_3, OH, 2'-H), 3.54 (s, 1 H, 5-H), 3.15 (dd, *J* = 11.8/3.7 Hz, 1 H, 3-H), 2.91 (d, *J* = 11.8 Hz, 1 H, 2-H), 2.50–2.47 (m, 3 H, 1'-H, 9-H), 2.44 (d, *J* = 3.7 Hz, 1 H, 4-H), 1.35 (s, 3 H, 11-H), 1.26 (d, *J* = 10.8 Hz, 1 H, 10-H_a), 1.06 (d, *J* = 10.8 Hz, 1 H, 10-H_b). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.8 (CO), 172.0 (COO), 171.8 (COO), 161.0 (C-6), 147.3 (C-7), 61.3 (C-2'), 52.9 (C-2), 51.7 (OCH_3), 51.4 (OCH_3), 50.9 (C-9), 50.1 (C-1), 47.2 (C-3), 43.6 (C-5), 40.9 (C-4), 39.4 (C-10), 29.1 (C-1') 16.4 (C-11). – MS (EI) *m/z* (%): 322 (56) [M$^+$], 291 (61), 261 (100), 231 (22), 177 (63), 159 (20), 145 (37), 131 (16), 113 (44), 105 (10), 91 (18). – $C_{17}H_{22}O_6$: calcd. 322.1416, found 322.1410 (MS).

Diethyl (1*RS*,4*SR*,5*SR*,9*SR*)-2,3-Diaza-1-methyl-6-oxo-7-*n*-pentyltricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (14b). Flash chromatography on SiO_2 (hexanes/ethyl acetate 2:1) yielded 76 mg (20%) of **15b** as the first fraction and 170 mg (45%) of **14b** as the second fraction. Colourless oil; IR (film): $\tilde{\nu}$ = 1747 cm^{-1}, 1704, 1702. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.20 (m, 1 H, 6-H), 4.51 (s, 1 H, 4-H), 4.30–4.15 (m, 4 H, OCH_2CH$_3$), 3.20 (s, 1 H, 5-H), 2.82 (s, 1 H, 9-H), 2.19–2.14 (m, 2 H, 1'-H), 1.84 (s, 3 H, 11-H), 1.49–1.34 (m, 6 H, 2'-H, 3'-H, 10-H), 1.32–1.25 (m, 8 H, 4'-H, OCH$_2$CH_3), 0.90 (t, *J* = 6.8 Hz, 3 H, 5'-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.1 (CO), 158.1 (COO), 157.7 (COO), 154.5 (C-6), 151.4 (C-7), 70.4 (C-1), 62.7, 62.3 (O*C*H$_2$CH$_3$), 59.9 (C-4), 53.8 (C-9), 46.8 (C-5), 39.2 (C-10), 31.5, 27.2, 24.8 (C-1'), 22.3 (C-2', C-3', C-4'), 16.2 (C-11), 14.4, 14.4 (OCH$_2$*C*H$_3$), 13.9 (C-5'). – MS (EI) *m*/*z* (%): 378 (2) [M$^+$], 295 (6), 227 (29), 206 (16), 183 (14), 155 (100), 149 (26), 133 (25), 111 (46), 107 (36), 83 (100), 69 (56). – $C_{20}H_{30}N_2O_5$: calcd. 378.2155, found 378.2146 (MS). – $C_{20}H_{30}N_2O_5$ (378.47): calcd. C 63.47, H 7.99, N 7.40; found: C 63.29, H 7.80, N 7.52.

Diethyl (1*RS*,4*SR*,5*RS*,9*RS*)-2,3-Diaza-1-methyl-7-6-oxo-*n*-pentyltricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (15b). Colourless oil. – IR (film): $\tilde{\nu}$ = 1748 cm^{-1}, 1705. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (s, 1 H, 8-H), 4.63 (s, 1 H, 4-H), 4.29–4.18 (m, 4 H, OCH_2CH$_3$), 3.30 (s, br, 1 H, 9-H), 2.84 (d, *J* = 5.0 Hz, 5-H), 2.20 (t, *J* = 7.9 Hz, 2 H, 1'-H), 1.80 (s, 3 H, 11-H), 1.49–1.44 (m, 4 H, 2'-H, 3'-H), 1.34–1.24 (m, 10 H, 10-H, 4'-H, OCH$_2$CH_3), 0.90 (t, *J* = 6.8 Hz, 3 H, 5'-H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.7 (CO), 158.0 (COO), 155.2 (C-8), 151.2 (C-7), 70.6 (C-1), 62.1 (O*C*H$_2$CH$_3$), 59.7 (C-4), 52.2 (C-5), 49.2 (C-9), 38.9 (C-10), 31.4, 27.2, 24.8, 22.3 (C-1', C-2', C-3', C-4'), 17.1 (C-11), 14.4, 14.4 (OCH$_2$*C*H$_3$), 13.9 (C-5'). – MS (EI) *m*/*z* (%): 378 (9) [M$^+$], 333 (2), 305 (2), 227 (33), 203 (12), 183 (8), 155 (100), 139 (6), 111 (35), 83 (56), 79 (18), 77 (6). – $C_{20}H_{30}N_2O_5$: calcd. 378.2155, found 378.2146 (MS). – $C_{20}H_{30}N_2O_5$ (378.47): calcd. C 63.47, H 7.99, N 7.40; found: C 63.45, H 8.01, N 7.41.

Diethyl (1*RS*,4*SR*,5*SR*,9*SR*)-2,3-Diaza-7-*tert*-butyl-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (14c). Flash chromatography on SiO_2 (hexanes/ethyl acetate 2:1) yielded 82 mg (0.23 mmol) of **15c** as the first fraction and 128 mg (35%) of **14c** as the second fraction. Colourless oil. – IR (film): $\tilde{\nu}$ = 1704 cm^{-1}, 1700. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 3.1 Hz, 1 H, 6-H), 4.50 (s, 1 H, 4-H), 4.30–4.14 (m, 4 H, OCH_2CH$_3$), 3.13 (s, 1 H, 5-H), 2.79 (s, 1 H, 9-H), 1.84 (s, 3 H, 11-H), 1.48, 1.39 (d, *J* = 11.0 Hz, 2 H, 10-H$_a$, 10-H$_b$), 1.32–1.25 (m, 6 H, OCH$_2$CH_3), 1.17 [s, 9 H, C(CH$_3$)$_3$]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.1 (CO), 158.8 (COO), 157.6 (C-7), 152.9 (C-6), 70.4 (C-1), 62.6 (O*C*H$_2$CH$_3$), 62.2 (O*C*H$_2$CH$_3$), 59.9 (C-4), 54.5 (C-9), 45.7 (C-5), 39.0 (C-10), 32.1 [*C*(CH$_3$)$_3$], 28.0 [C(*C*H$_3$)$_3$], 16.1 (C-11), 14.3 (OCH$_2$*C*H$_3$). – MS (EI) *m*/*z* (%): 364 (8) [M$^+$], 319 (1), 291 (2), 227 (24), 189 (10), 155 (100), 139 (6), 111 (45), 91 (7), 83 (78), 79 (5). – $C_{19}H_{28}N_2O_5$: calcd. 364.1998, found 364.1991 (MS).

Diethyl (1*RS*,4*SR*,5*RS*,9*RS*)-2,3-Diaza-7-*tert*-butyl-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (15c). Colourless oil. – IR (KBr): $\tilde{\nu}$ = 1747 cm^{-1}, 1705. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (d, *J* = 2.8 Hz, 1 H, 8-H), 4.62 (s, 1 H, 4-H), 4.26–4.16 (m, 4 H, OCH_2CH$_3$), 3.24 (s, br, 1 H, 9-H), 2.82 (d, *J* = 4.9 Hz, 1 H, 5-H), 1.80 (s, 3 H, 11-H), 1.44–1.36 (m, 2 H, 10-H), 1.31–1.24 (m, 6 H, OCH$_2$CH_3), 1.18 [s, 9 H, C(CH$_3$)$_3$]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.8 (CO), 158.8 (COO), 158.0 (C-7), 153.5 (C-8), 70.7 (C-1), 62.2, 62.0 (O*C*H$_2$CH$_3$), 59.8 (C-4), 53.1 (C-5), 48.1 (C-9), 38.8 (C-10), 32.1 [*C*(CH$_3$)$_3$], 28.1 [C(*C*H$_3$)$_3$], 17.1 (C-11), 14.3 (OCH$_2$*C*H$_3$). – MS (EI) *m*/*z* (%): 364 (5) [M$^+$], 319 (1), 305 (1), 227 (33), 183 (9), 155 (100), 139 (7), 122 (5), 111 (34), 83 (78), 77 (6). – $C_{19}H_{28}N_2O_5$: calcd. 364.1998, found 364.1991 (MS).

Diethyl (1*RS*,4*SR*,5*SR*,9*SR*)-2,3-Diaza-1-methyl-6-oxo-7-phenyltricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (14d). Flash chromatography on SiO_2 (hexanes/ethyl acetate 2:1) yielded 105 mg (28%) of **15d** as the first fraction and 103 mg (27%) of **14d** as the second fraction. Colourless oil. – IR (KBr): $\tilde{\nu}$ = 1739 cm^{-1}, 1706. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 3.1 Hz, 1 H, 6-H), 7.70–7.67 (m, 2 H, *m*-H), 7.42–7.33 (m, 3 H, *o*-H, *p*-H), 4.63 (s, 1 H, 4-H), 4.31–4.19 (m, 4 H, OCH_2CH$_3$), 3.35 (s, 1 H, 5-H), 3.04 (s, 1 H, 9-H), 1.90 (s, 3 H, 11-H), 1.57–1.52 (m, 2 H, 10-H), 1.34–1.23 (m, 6 H, OCH$_2$CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.9 (C-8), 157.7 (COO), 155.6 (C-6), 147.5 (C-7), 130.6 (C-i), 129.1 (C-p), 128.5, 127.1 (C-o, C-m), 70.6 (C-1), 62.7, 62.3 (O*C*H$_2$CH$_3$), 60.1 (C-4), 54.9 (C-9), 46.4 (C-5), 39.5 (C-10), 16.2 (C-11), 14.5, 14.4 (OCH$_2$*C*H$_3$). – MS (EI) *m*/*z* (%): 384 (5) [M$^+$], 339 (2), 328 (4), 312 (1), 227 (41), 209 (45), 155 (100), 115 (10), 111 (42), 105 (18), 96 (13), 83 (86), 77 (9). – $C_{21}H_{24}N_2O_5$ (384.43): calcd. C 65.61, H 6.29, N 7.29; found: C 65.66, H 6.40, N 7.15.

Diethyl (1*RS*,4*SR*,5*RS*,9*RS*)-2,3-Diaza-1-methyl-6-oxo-7-phenyltricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (15d). Colourless oil. – IR (KBr): $\tilde{\nu}$ = 1746 cm^{-1}, 1705. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.68 (m, 3 H, *m*-H, 8-H), 7.43–7.38 (m, 3 H, *o*-H, *p*-H), 4.74 (s, 1 H, 4-H), 4.31–4.19 (m, 4 H, OCH_2CH$_3$), 3.45 (s, br, 1 H, 9-H), 3.05 (d, *J* = 5.2 Hz, 1 H, 5-H), 1.89 (s, 3 H, 11-H), 1.57–1.52 (m, 2 H, 10-H), 1.33–1.24 (m, 6 H, OCH$_2$CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.7 (CO), 158.0 (COO), 156.3 (C-7), 147.4 (C-8), 130.5 (C-i), 129.2 (C-p), 128.6, 127.1 (C-o, C-m), 70.9 (C-1), 62.7 (O*C*H$_2$CH$_3$), 62.3 (O*C*H$_2$CH$_3$), 60.0 (C-4), 53.3 (C-5), 48.7 (C-9), 39.4 (C-10), 17.4 (C-11), 14.5, 14.5 (OCH$_2$*C*H$_3$). – MS (EI) *m*/*z* (%): 384 (5) [M$^+$], 368 (1), 340 (2), 312 (3), 254 (11), 227 (41), 209 (7), 183 (10), 155 (100), 139 (6), 128 (7), 111 (35), 105 (14), 95 (6), 83 (90), 80 (17).

Diethyl (1*RS*,4*SR*,5*SR*,9*SR*)-2,3-Diaza-7-(2-hydroxyisopropyl)-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (14e). Flash chromatography on SiO_2 (hexanes/ethyl acetate 1:1) yielded 210 mg (0.57 mmol) of an inseparable mixture of regioisomers **14e**, **15e**. Colourless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 2.9 Hz, 1 H, 6-H), 4.52 (s, 1 H, 4-H), 4.27–4.12 (m, 5 H, OCH_2CH$_3$, OH), 3.18 (s, 1 H, 5-H), 2.86 (s, 1 H, 9-H), 1.84 (s, 3 H, 11-H), 1.48–1.45 (m, 2 H, 10-H), 1.42 [s, 6 H, C(CH_3)OH], 1.39–1.21 (m, 6 H, OCH$_2$CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.3 (CO), 157.6 (C-7), 156.0 (COO), 153.5 (C-6), 70.3 (C-1), 69.5 [*C*(CH$_3$)OH], 62.7, 62.3 (O*C*H$_2$CH$_3$), 59.8 (C-4), 54.6 (C-9), 46.2 (C-5), 39.1 (C-10), 28.5 [*C*(*C*H$_3$)OH], 16.1 (C-11), 14.4, 14.4 (OCH$_2$*C*H$_3$).

Diethyl (1*RS*,4*SR*,5*RS*,9*RS*)-2,3-Diaza-7-(2-hydroxyisopropyl)-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (15e). Colourless oil. – IR (KBr): $\tilde{\nu}$ = 3453 cm^{-1}, 1702. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.30 (m, 1 H, 8-H), 4.60 (s, 1 H, 4-H), 4.27–4.12 (m, 5 H, OCH_2CH$_3$, OH), 3.29 (s, br, 1 H, 9-H), 2.84 (s, 1 H, 5-H), 1.81 (s, 3 H, 11-H),), 1.48–1.45 (m, 2 H, 10-H), 1.42 [s, 6 H, C(CH_3)OH], 1.39–1.21 (m, 6 H, OCH$_2$CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.7 (C-6), 157.7 (C-7), 156.0 (COO), 154.2 (C-8), 70.5 (C-1), 69.6 [*C*(CH$_3$)OH], 62.7, 62.2 (O*C*H$_2$CH$_3$), 59.6 (C-4), 53.1 (C-5), 48.6 (C-9), 38.9 (C-10), 28.3 [*C*(*C*H$_3$)OH], 17.1 (C-11), 14.4, 14.3 (OCH$_2$*C*H$_3$). – MS (EI) *m*/*z* (%): 366 (8) [M$^+$], 313 (3), 293 (2), 272 (1), 254 (7), 227 (17), 207 (12), 183 (9), 176 (24), 155 (100), 122 (16), 111 (47), 97 (24), 83 (96). – $C_{18}H_{26}N_2O_6$: calcd. 366.1791, found 366.1784 (MS).

Diethyl (1*RS*,4*SR*,5*SR*,9*SR*)-2,3-Diaza-7-(2-hydroxyethyl)-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (14f). Flash chromatography on SiO_2 (hexanes/ethyl acetate 1:1) yielded 190 mg (54%) of an inseparable mixture of regioisomers **14f**, **15f**. Colourless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.36 (m, 1 H, 6-H), 4.51 (s, 1 H, 4-H), 4.27–4.12 (m, 4 H, OCH_2CH$_3$), 3.76–3.66 (m, 2 H, CH$_2$CH_2OH), 3.22 (s, 1 H, 5-H), 2.85 (s, 1 H, 9-H), 2.48–2.44 (m, 2 H, CH_2CH$_2$OH), 2.42–2.03 (s, br, 1 H, OH), 1.84 (s, 3 H, 11-H), 1.47–1.42 (m, 2 H, 10-H), 1.29–1.23 (m, 6 H, OCH$_2$CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.8 (CO), 157.7 (COO), 157.2 (C-6), 148.4 (C-7), 70.3 (C-1), 62.7 (O*C*H$_2$CH$_3$), 62.3 (O*C*H$_2$CH$_3$), 60.6 (CH$_2$*C*H$_2$OH), 59.8 (C-4), 53.7 (C-9), 47.2 (C-5), 39.2 (C-10), 28.6 (*C*H$_2$CH$_2$OH), 16.2 (C-11), 14.4, 14.4 (OCH$_2$*C*H$_3$).

Diethyl (1*RS*,4*SR*,5*RS*,9*RS*)-2,3-Diaza-7-(2-hydroxyethyl)-1-methyl-6-oxotricyclo[5.2.1.0^{5,9}]dec-7-ene-2,3-dicarboxylate (15f). Colourless oil. – IR (KBr): $\tilde{\nu}$ = 3476 cm^{-1}, 3319, 1747, 1705. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.30 (m, 1 H, 8-H), 4.60 (s, 1 H, 4-H), 4.27–4.12 (m, 4 H, OCH_2CH$_3$), 3.76–3.66 (m, 2 H, CH$_2$CH_2OH), 3.31 (s, br, 1 H, 9-H), 2.84 (s, 1 H, 5-H), 2.48–2.44 (m, 2 H, CH_2CH$_2$OH), 2.42–2.03 (br s, 1 H, OH), 1.81 (s, 3 H, 11-H), 1.47–1.42 (m, 2 H, 10-H), 1.29–1.23 (m, 6 H, OCH$_2$CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.4 (CO), 158.0 (C-8), 157.8 (COO), 148.2 (C-7), 70.6 (C-1), 62.7 (O*C*H$_2$CH$_3$), 62.3 (O*C*H$_2$CH$_3$), 60.5 (CH$_2$*C*H$_2$OH), 59.7 (C-4), 52.1 (C-5), 49.6 (C-9), 39.0 (C-10), 28.6 (*C*H$_2$CH$_2$OH), 17.1 (C-11), 14.4, 14.4 (OCH$_2$*C*H$_3$). – MS (EI) *m*/*z* (%): 352 (8) [M$^+$], 307 (2), 279 (1), 235 (7), 227 (20), 177 (9), 155 (100), 139 (6), 111 (43), 91 (6), 83 (95), 79 (6). – $C_{17}H_{24}N_2O_6$: calcd. 352.1634, found 352.1628 (MS).

Acknowledgments

Generous financial support by the Deutsche Forschungsgemeinschaft (Gerhard-Hess prize for S.L.) and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Thorsten Sell for investigating the temperature effects.

[1] Reviews: [1a] N. E. Schore, *Org. React.* **1991**, *40*, 1–90. – [1b] P. L. Pauson, *Tetrahedron* **1985**, *41*, 5855–5860. – [1c] N. Jeong, in *Transition Metals for Organic Synthesis*, C. Bolm, M. Beller, Eds.; Wiley-VCH: New York, 1998, p. 560–577. – [1d] P. L. Pauson, in *Organometallics in Organic Synthesis*, A. de Meijere, H. tom Dieck, Springer Verlag: Berlin, 1987, p. 233. – [1e] N. E. Schore, in *Comprehensive Organic Synthesis*, B. M. Trost, Ed., Pergamon Press: Oxford, 1991, vol. 5, p. 1037–1074. – [1f] N. E. Schore, in *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds., Pergamon Press: Oxford, 1995, vol. 12, p. 703–739. [1g] O. Geis, H.-G. Schmalz, *Angew. Chem.* **1998**, *110*, 955–958; *Angew. Chem. Int. Ed.* **1998**, *37*, 911–914. – [1h] Y. K. Chung, *Coord. Chem. Rev.* **1999**, *188*, 297–341.

[2] [2a] A. J. Pearson, R. A. Dubbert, *J. Chem. Soc., Chem. Commun.* **1991**, 202–203. – [2b] A. J. Pearson, R. A. Dubbert, *Organometallics* **1994**, *13*, 1656–1661. – [2c] H.-J. Knölker, J. Heber, *Synlett* **1993**, 924–926. – [2d] A. J. Pearson, X. Yao, *Synlett* **1997**, 1281–1282.

[3] [3a] T. Kondo, N. Suzuki, T. Okada, T.-A. Misudo, *J. Am. Chem. Soc.* **1997**, *119*, 6187–6188. – [3b] T. Morimoto, N. Chatami, Y. Fukumoto, S. Murai, *J. Org. Chem.* **1997**, *62*, 3762–3763.

[4] [4a] Y. Koga, T. Kobayashi, K. Narasaka, *Chem. Lett.* **1998**, 249–250. – [4b] N. Jeong, S. Lee, B. K. Sung, *Organometallics* **1998**, *17*, 3642–3644. – [4c] Z. Zhao, Y. Ding, *J. Chem. Soc., Perkin Trans. 1* **1998**, 171–172.

[5] [5a] L. Pages, A. Llebaria, F. Camps, E.Molins, C. Miravitelles, J. M. Moreto, *J. Am. Chem. Soc.* **1992**, *114*, 10449–10461. – [5b] K. Tamao, K. Kobayashi, Y. Ito, *J. Am. Chem. Soc.* **1998**, *110*, 1286–1288. – [5c] K. Tamao, K. Kobayashi, Y. Ito, *Synlett* **1992**, 539–546. – [5d] S. L. Buchwald, M. Zhang, *J. Org. Chem.* **1996**, *61*, 4498–4499.

[6] L. Jordi, A. Segundo, F. Camps, S. Picart, J. M. Moreto, *Organometallics* **1993**, *12*, 3795–3797.

[7] D. T. Rutherford, S. D. R. Christie, *Tetrahedron Lett.* **1998**, *39*, 9805–9808.

[8] Z. Zhao, Y. Ding, G. Zhao, *J. Org. Chem.* **1998**, *63*, 9285–9291.

[9] T. Takahashi, Z. Xi, Y. Nishihara, S. Huo, K. Kasai, K. Aoyagi, V. Denisov, E. Negishi, *Tetrahedron* **1997**, *53*, 9123–9134.

[10] See ref.[1f] for details concerning the mechanism of the Pauson–Khand reaction.

[11] [11a] S. Shambayati, W. E. Crowe, S. L. Schreiber, *Tetrahedron Lett.* **1990**, *31*, 5289–5292. – [11b] N. Jeong, Y. K. Chung, B. Y. Lee, H. L. Lee, S. E. Yoo, *Synlett* **1991**, 204–206.

[12] [12a] M. E. Krafft, I. L. Sott, R. H. Romero, S. Feibelmann, C. E. Van Pelt, *J. Am. Chem. Soc.* **1993**, *115*, 7199–7207. – [12b] M. E. Krafft, *J. Am. Chem. Soc.* **1988**, *110*, 968–970. c) M. E. Krafft, C. A. Juliano, I. L. Scott, C. Wright, M. D. Mc Eachin, *J. Am. Chem. Soc.* **1991**, *113*, 1693–1703.

[13] [13a] I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, M. I. Foreman, *J. Chem. Soc., Perkin Trans. 1* **1973**, 977–981. – [13b] I. U. Khand, P. L. Pauson, *J. Chem. Soc., Perkin Trans. 1* **1976**, 30–32.

[14] [14a] S. E. Mac Wherter, V. Sampath, M. M. Olmstead, N. E. Schore, *J. Org. Chem.* **1988**, *53*, 203–205. – [14b] N. E. Schore, S. D. Nadji, *J. Am. Chem. Soc.* **1990**, *112*, 441–442.

[15] [15a] M. E. Price, N. E. Schore, *J. Org. Chem.* **1989**, *54*, 5662–5667. – [15b] M. E. Price, N. E. Schore, *Tetrahedron Lett.* **1989**, *30*, 5865–5868.

[16] B. E. La Belle, M. J. Knudsen, M. M. Olmstead, H. Hope, M. D. Yanuck, N. E. Schore, *J. Org. Chem.* **1985**, *50*, 5215–5222.

[17] J. R. Stille, B. D. Santarsiero, R. H. Grubbs, *J. Org. Chem.* **1990**, *55*, 843–862.

[18] B. Giese, *Chem. Ber.* **1974**, *107*, 819–828.

[19] V. A. Mironow, T. M. Fadeeva, A. U. Stepanyanb, A. A. Akrem, Bu*ll. Acad. Sci, USSR Div. Chem. Sci. (Engl. Transl.)* **1967**, 1633–1636; *Chem. Abstr.* **1967**, *66*, 75500j.

[20] The corresponding ethyl 2,3-diazabicyclo[2.2.1]heptane 2,3-dicarboxylate has already been prepared by Lehn: J. E. Anderson, J. M. Lehn, *Tetrahedron* **1968**, *24*, 123–125.

[21] Solvent-dependencies of the regio- and stereoselectivities in Pauson–Khand reactions were reported by Jeong, Pauson and Kerr:[21a] Y. K. Chung, B. Y. Lee, N. Jeong, M. Hudecek, P. L. Pauson, *Organometallics* **1993**, *12*, 220–223. – [21b] W. J. Kerr, G. G. Kirk, D. Middlemiss, *Synlett* **1995**, 1085–1086.

[22] The moderate yields are due to competing reaction pathways for the cobalt alkyne complex **1**, i.e. (1) decarbonylation followed by insertion of the alkene and (2) thermal or aminoxide-induced decomposition of **1**. If the decarbonylation is too slow compared to the decomposition pathway, most of the alkyne is lost.[23] We were particularly concerned about the cobalt-mediated trimerization of the alkyne[24] as a possible side reaction. However, none of the 1,2,4-trisubstituted benzenes or other by-products could be detected in the co-cyclizations of **9** and **10**. It should also be noted, that the regioisomeric cyclopentenones **12** and **13,** and **14** and **15** neither interconvert nor selectively decompose under the reaction conditions.

[23] Schore observed the formation of benzoquinone, bicyclo[3.3.0]octa-3,6-diene-2,8-dione and several cyclopentadienone-derived products upon treatment of $Co_2(CO)_8$ with acetylene and carbon monoxide at low temperatures. For details see: N. E. Schore, B. E. La Belle, M. J. Knudsen, H. Hope, X.-J. Xu, *J. Organomet. Chem.* **1984**, *272*, 435–446.

[24] K. P. C. Vollhardt, *Angew. Chem.* **1984**, *96*, 525–628; *Angew. Chem. Int. Ed. Engl.* **1984**, *96*, 460–539.

[25] The authors have deposited atomic coordinates for the structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, email: deposit@ccdc.cam.ac.uk upon quoting the reference number CCDC-127376.

[26] Variable temperature ^{13}C NMR studies by Milone revealed that indeed CO scrambling occurred in (alkyne)$Co_2(CO)_6$ complexes and that the interchange of CO ligands is localised at

each cobalt. Thus no evidence for bridging CO was found. See: S. Aime, L. Milone, R. Rossetti, P. L. Stanghellini, *Inorg. Chim. Acta* **1977**, *22*, 135–139.
[27] Y. Gimbert, F. Robert, A. Durif, M.-T. Averbuch, N. Kann, A. E. Greene, *J. Org. Chem.* **1999**, *64*, 3492–3497.
[28] [28a] X. Verdaguer, A. Moyano, M. A. Pericas, A. Riera, V. Bernardes, A. E. Greene, A. Alvarez-Larena, J. F. Piniella, *J. Am. Chem. Soc.* **1994**, *116*, 2153–2154. – [28b] E. Montenegro, M. Poch, A. Moyano, M. A. Pericas, A. Riera, *Tetrahedron Lett.* **1998**, *39*, 335–338. – [28c] X. Verdaguer, J. Vazquez, G. Fuster, V. Bernardes-Genisson, A. E. Greene, A. Moyano, M. A. Pericas, A. Riera, *J. Org. Chem.* **1998**, *63*, 7037–7052.
[29] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.

Received August 11, 1999
[O99496]