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Diastereoselectivity in the Intermolecular Pauson-Khand Reaction of Chiral 2-Alkynoates

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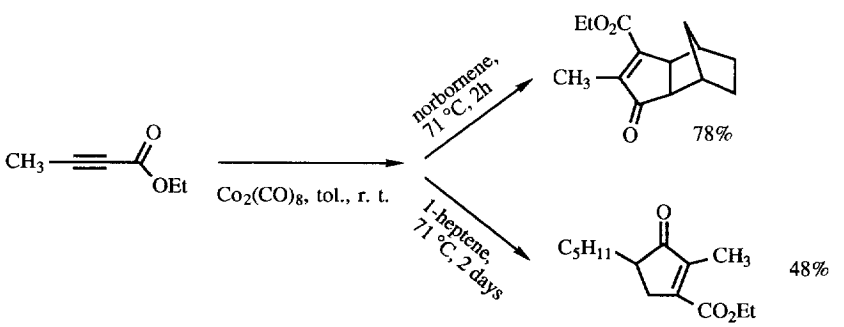
Abstract: Chiral 2-alkynoates have been readily prepared by condensation of several cyclohexyl- or camphor-based alcohols with 2-alkynoic acids or the corresponding acid chlorides. The hexacarbonyldicobalt complexes obtained therefrom reacted with olefins to afford the corresponding Pauson-Khand cyclopentenone adducts in good yields, with high regioselectivity, and with variable degrees of diastereoselectivity. In some instances, the degree of stereocontrol is superior to that observed for alkoxyacetylenes, so that the viability of an enantioselective approach to the intermolecular Pauson-Khand reaction of electron-deficient alkynes is demonstrated for the first time.

Introduction

The Pauson-Khand reaction, a cobalt-mediated carbonylative cocyclization of alkynes and alkenes, is nowadays generally recognized as one of the most effective methods for cyclopentenone synthesis.[1,2] Although the Pauson-Khand reaction can accomodate a broad structural range of alkynes, an important exception has been the case of 2-alkynoates. In effect, Pauson[3] reported some ten years ago that the hexacarbonyldicobalt complex of methyl propiolate did not give the expected adduct when treated with norbornene. Following this observation, no related example appeared in the literature until 1992, when Krafft and co-workers[4] described the successful intermolecular Pauson-Khand reaction of ethyl tetrolate (2-butynoate) with norbornene and 1-heptene (Scheme 1).[5] In this case, the corresponding cyclopentenones were obtained in good yields and with complete regioselectivity. The failure of the experiment reported by Pauson[3] was probably due to the lack of alkyne substitution, since the *intramolecular* cyclization of 3-butenyl propiolate took place only with low yield, in sharp contrast to the behaviour of the corresponding tetrolate or phenylpropiolate.[4] On the other hand, the exclusive formation of 3-ethoxycarbonylcyclopentenones was explained by Krafft[4] as an effect of the alkyne polarization.



Scheme 1

In the past few years, we have been examining the Pauson-Khand cyclization of *O*-alkyl ynol and enol ethers derived from chiral alcohols,[6] and as a result of these studies we have developed practical enantioselective approaches to both the intramolecular[7] and the intermolecular[8] versions of the Pauson-Khand reaction.[9] We wish to describe here the results of an extensive investigation of the intermolecular Pauson-Khand reaction of alkynecarboxylic esters derived from chiral alcohols, in the context of a program devoted to the exploration of the applicability of electron-deficient alkynes in stereoselective transition-metal mediated cyclizations.

Results and Discussion

We selected for our study a set of chiral secondary alcohols, having either the cyclohexyl (**1a-c**) or camphor (**1d-h**) skeleton. All of these alcohols are either commercially available in enantiopure form or can be readily obtained according to published procedures (**1b**,[10] **1c**,[11] **1d**,[12] **1e**,[12] **1f**,[13] **1g**,[14] **1h**[15]). (Figure 1).

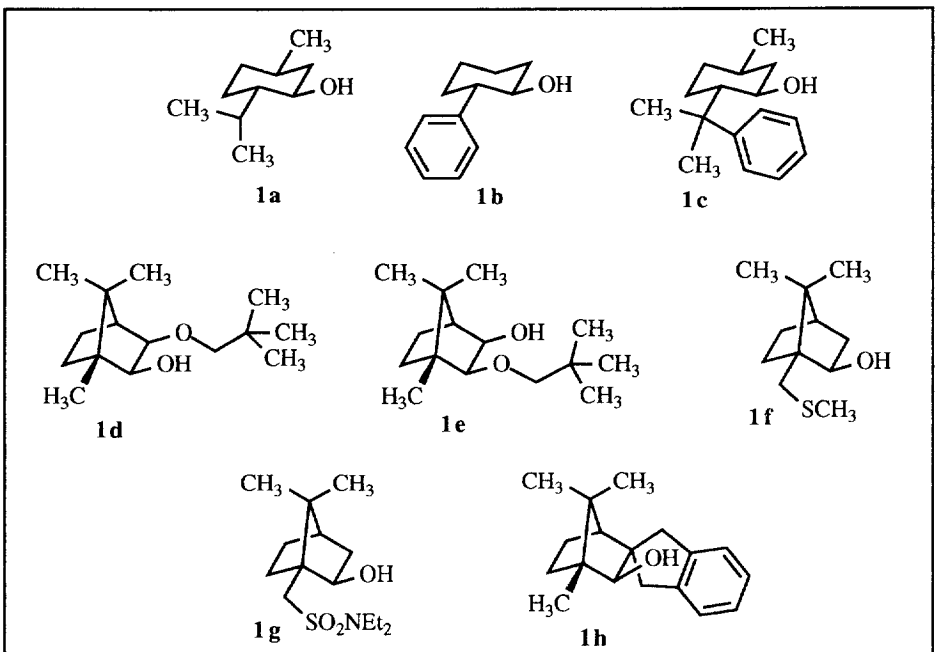


Figure 1

These alcohols were subsequently converted into the corresponding phenylpropiolate (**2a-h**), tetrolate (**3b**, **3c**) or propiolate (**4c**) esters by means of one of the following general methodologies: i) Dicyclohexylcarbodiimide-mediated coupling with phenylpropiolic or tetrolic acid under catalysis of 4-dimethylaminopyridine,[16] ii) reaction with phenylpropiolyl chloride in the presence of silver cyanide,[12] or iii) direct Fischer esterification with the conditions described by Rahm and Jurczak for the preparation of (-)-menthyl propiolate.[17] (See Table 1).

Table 1. 2-Alkynoates from Chiral Alcohols **1a-h**.

ROH ⟶ R'—≡—CO_2R

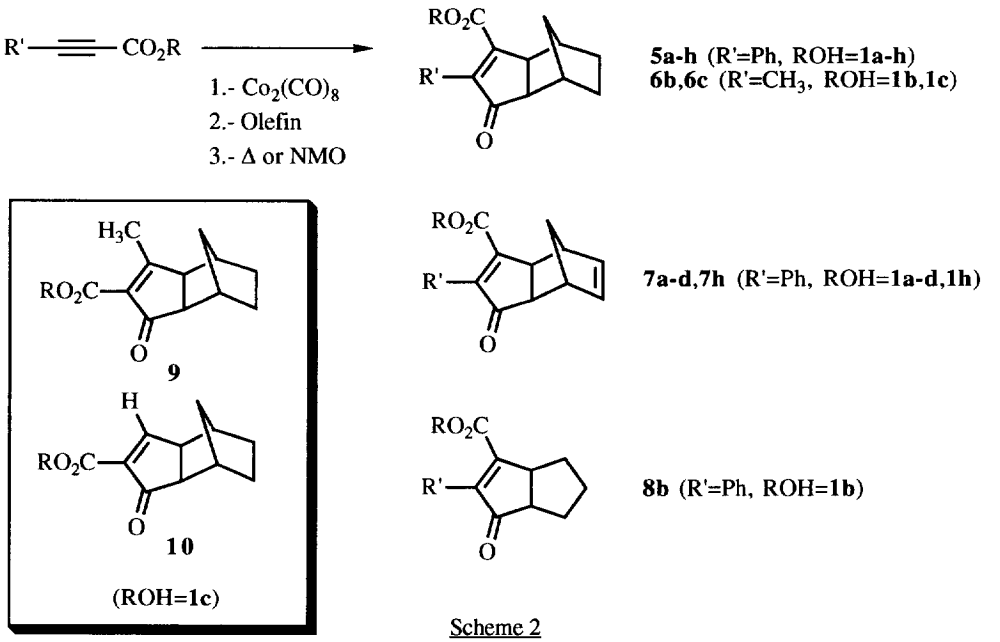
Alcohol	Methodology[a]	Alkynoate	Yield (%)
1a	A	**2a** (R'=C_6H_5)	83
1b	A	**2b** (R'=C_6H_5)	70
	A	**3b** (R'=CH_3)	90
1c	A	**2c** (R'=C_6H_5)	81
	A	**3c** (R'=CH_3)	81
	A	**4c** (R'=H)	12
	C		79
1d	A	**2d** (R'=C_6H_5)	0
	B		92
	A	**3d** (R'=CH_3)	0
	B		0
	C		0
1e	B	**2e** (R'=C_6H_5)	94
1f	A	**2f** (R'=C_6H_5)	46
1g	A	**2g** (R'=C_6H_5)	0
	B		34
1h	B	**2h** (R'=C_6H_5)	53

[a]Method A: 2-alkynoic acid, DCCI, DMAP cat., CH_2Cl_2, 0°C to R.T.; Method B: 2-alkynoyl chloride, AgCN, benzene, reflux; Method C: 2-alkynoic acid, *p*TsOH cat., benzene, reflux.

An inspection of the Table shows that while the relatively mild dicyclohexylcarbodiimide method is suitable to effect the esterification of cyclohexane-based alcohols **1a-c**, the less reactive camphor-derived alcohols **1d-h** require in general the use of the harsher conditions of the silver cyanide procedure. It is worth noting that due to the instability of both propiolyl and tetrolyl chloride, the only esters prepared from the camphor-based alcohols belong to the phenylpropiolate series **2d-h**, since these acid chlorides do not survive the reaction conditions. In a similar way, all attempts of acid-catalized esterification of the hindered alcohols **1d-h** with propiolic or tetrolic acids resulted only in extensive polymerization of the alkyne.

With the requisite chiral 2-alkynoate esters in hand, we proceeded to investigate their cobalt-induced cycloaddition with three representative olefins: norbornene, norbornadiene, and cyclopentene. The corresponding intermediate hexacarbonyldicobalt complexes were readily (with the sole exception of the propiolate **4c**) obtained by addition of octacarbonyldicobalt to a solution of the alkyne, and without isolation were reacted with the desired olefin under nitrogen until complete disappearence of the complex (as judged by TLC), by using one of these reaction conditions: a) Heating in toluene at 40-80 °C ; b) refluxing in acetonitrile;[5c] c) portionwise treatment with 6-10 equivalents of *N*-methylmorpholine-*N*-oxide monohydrate in methylene chloride at 0 °C, as described by Krafft,[4,18] to give the expected[4] *exo*-3-alkoxycarbonylcyclopentenones in good to excellent yields. Only in the reaction of (8-phenylmenthyl)-2-

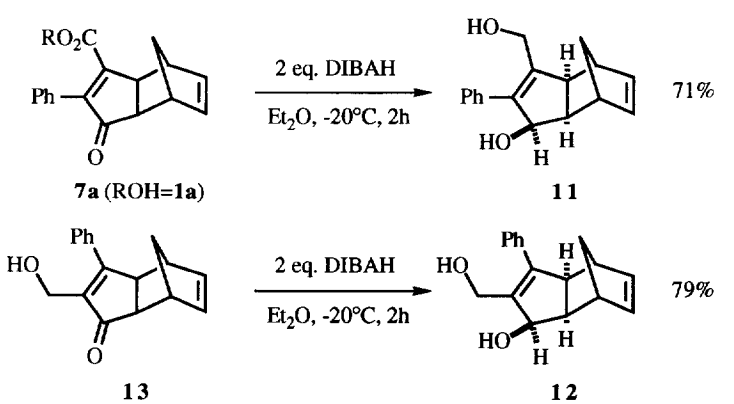
butynoate (**3c**) and propiolate (**4c**) with norbornene we isolated in low yields the regioisomeric 1,3-dicarbonyl adducts **9** and **10**, respectively (Scheme 2 and Table 2).



Scheme 2

The regiochemistry of the Pauson-Khand cycloadducts could be established in the following manner:

When the diastereomeric mixture of cyclopentenones **7a** was treated with two equivalents of diisobutylaluminum hydride in diethyl ether at -20 °C, the diastereomerically pure diol **11** could be isolated in good yield (Scheme 3). The spectral analysis of this compound showed that it was a regioisomer of the diol **12**, which was obtained when the tricyclic hydroxyketone **13** (whose regio- and stereochemistry had been previously determined in our laboratory)[19] was subjected to the same reaction conditions. Comparison of analytical data showed that all of the adducts **5**, **7** and **8** had the 1,4-dicarbonyl regiochemistry shown in Scheme 2.



Scheme 3

Table 2. Yields[a] and Diastereomeric Ratios[b] in the Pauson-Khand Reactions of 2-Alkynoates.

Entry	Alkynoate	Olefin[c]	Conditions[d]	Time (h)	Product	Yield (%)	Diast. ratio
1	**2a**	NBE	Tol, 70°C	2.5	**5a**	64	(1.7:1)
2		NBE	Acn	1		98	(1.1:1)
3		NBE	NMO	2		100	(1.15:1)
4		NBD	Tol, 60°C	4	**7a**	83	(1:1)
5	**2b**	NBE	Tol, 70°C	2.5	**5b**	97	(1.6:1)
6		NBD	Tol, 60°C	3.5	**7b**	95	(1:1)
7		CPE	Tol, 80°C	57	**8b**	41	(1.2:1)
8		CPE	Acn	140		65	(1.2:1)
9		CPE	NMO	12		46	(1.1:1)
10	**2c**	NBE	Tol, 60°C	4	**5c**	88	(2:1)
11		NBD	Tol, 60°C	1	**7c**	88	(1.3:1)
12	**2d**	NBE	Tol, 60°C	10	**5d**	67	(3:1)
13		NBE	NMO	e		70	(1:1)
14		NBD	Tol, 40°C	30	**7d**	60	(1.3:1)
15	**2e**	NBE	Tol, 60°C	3.5	**5e**	89	(2.2:1)
16	**2f**	NBE	Tol, 50°C	3.5	**5f**	57	(1.2:1)
17		NBE	NMO	14		72	(1:1)
18		NBE	NMO[f]	f		65	(1.2:1)
19	**2g**	NBE	Tol, 60°C	8	**5g**	60	(1.2:1)
20	**2h**	NBE	Tol, 55°C	15.5	**5h**	61	(1:1)
21		NBD	Tol, 45°C	38	**7h**	59	(1:1)
22	**3b**	NBE	Tol,40°C	18	**6b**	78	(1:1)
23		NBE	NMO	e		92	(1.8:1)
24	**3c**	NBE	Tol, 55°C	8	**6c**	77	(3.7:1)
25		NBE	NMO	e	**6c**	88	(2.3:1)
					9	12	(1.7:1)
26	**4c**	NBE	Tol, 50°C	15	**10**	26	(1.3:1)

[a]Isolated yield from the starting 2-alkynoate after chromatographic purification. [b]By ^{13}C NMR and/or HPLC (Nucleosyl 100CN column, hexane/isopropyl alcohol as eluent). [c]NBE= norbornene, NBD= norbornadiene, CPE= cyclopentene. [d]Conditions: Tol, XX°C= heating of the preformed complex in toluene solution at the specified temperature in the presence of excess olefin; Acn= complex and excess olefin refluxed in acetonitrile solution; NMO: chemical activation of the complex by *N*-methylmorpholine-*N*-oxide in dichloromethane solution (see text). [e]In this case, the reaction was complete after portionwise addition of 10 eq NMO at 0°C. [f]6 eq of NMO were added in one portion at -20°C, the solution was slowly warmed to room temperature by removal of the cooling bath and stirred overnight.

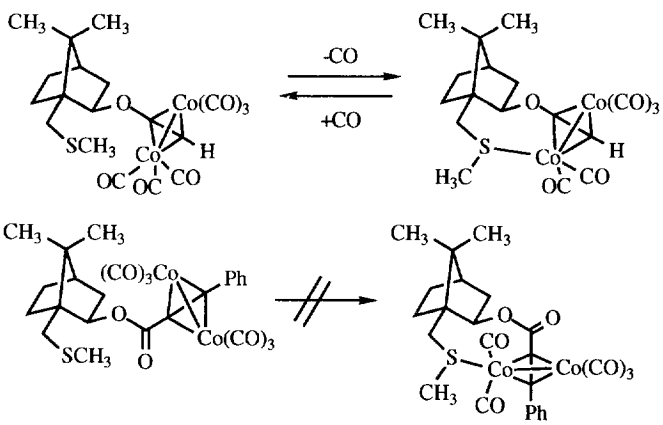
On the other hand, the regiochemistry of the Pauson-Khand adducts **6c** and **9** was deduced from inspection of their ^{13}C NMR and UV spectra. In effect, the major cycloadduct **6c** exhibited at the same time a longer wavelength absorption in the UV spectrum and a smaller chemical shift difference between olefinic carbons in comparison with the minor isomer **9**, indicative of the presence of the linearly conjugated 3-

alkoxycarbonylcyclopentene moiety in the former. By the same token, the regiochemistry of the remaining adducts **6b** and **10** must be that depicted in Scheme 2. Relevant spectroscopic data of the Pauson-Khand products can be found in the experimental section.

Some general trends regarding the stereoselectivity of the process are revealed by inspection of Table 2.

i) Among the cyclohexyl-based auxiliaries, (-)-8-phenylmenthol (**1c**) gives the best diastereoselectivities (see entries 10, 11 and 24 of the Table), while both menthol (**1a**) and *trans*-2-phenylcyclohexanol (**1b**) yield lower product ratios. A different behaviour is found in the intermolecular Pauson-Khand reaction of chiral *O*-alkyl ynol ethers,[8b] where the effectiveness of the auxiliary increases in the order **1a** < **1c** < **1b**.

ii) For the camphor-derived alcohol auxiliaries, the diastereoselectivity decreases in the order **1d** > **1e** > **1f** = **1g** > **1h** (see entries 12, 15, 16, 19 and 20). These results are again at variance with the behaviour showed by the corresponding alkoxyethynes: In effect, while the hexacarbonyldicobalt acetylene complexes derived from **1d**, **1e** and **1h** react with norbornene (under thermal conditions) essentially without diastereoselection,[8b] the 10-methylthioisoborneol-derived complex exhibits an outstanding selectivity, ascribable to the intermediate formation of a chelated intermediate.[8c,20] In the case of alkynoate **2f** we were not able to observe the formation of any chelated species either by thermal or oxidative (NMO) treatment of the hexacarbonyl complex (see Scheme 4), and the derived products were formed with very low diastereoselectivities (see entries 16, 17 and 18).



Scheme 4

iii) In accordance with the results reported by Pauson[3] and Krafft,[4] the unsubstituted propiolate **4c** gave poor yields of Pauson-Khand cycloadducts. In effect, when reacted thermally with norbornadiene, only traces of an unidentified ketonic product could be isolated after total decomposition of the (rather unstable) dicobalt complex. This same complex reacted with excess norbornene to give, in low yield and with marginal diastereoselectivity (see entry 26), the tricyclic 1,3-dicarbonyl adduct **10**. The effect of the alkyl- or aryl-substitution at the alkyne is not very clear (compare entries 5/22 and 10/24).

iv) The reaction of a given 2-alkynoate with the more reactive olefin norbornadiene is always less stereoselective than with norbornene, as occurs with the alkoxyacetylenes.[8] Cyclopentene shows intermediate stereoselectivity (see for instance entries 5, 6, 7, 10 and 11).

v) With respect to the influence of reaction conditions, it can be readily seen that for a given olefin-alkynoate pair, heating in an inert solvent (toluene) under nitrogen atmosphere gives always the best diastereoselectivities. Reflux in a coordinating solvent (acetonitrile) improves the yields but does not ameliorate the diastereoselectivity (compare entries 1/2 and 7/8). Even more surprisingly, chemical activation by means of *N*-methylmorpholine-*N*-oxide produces in all instances higher yields and greatly reduced diastereoselectivities, although the reaction temperature is substantially (by some sixty degrees) lower. The only exception to this rule appears to be the reaction of tetrolate **3b** with norbornene (entries 22 and 23). This diminution of the stereoselectivity associated to the use of *N*-oxide promoters is at variance with the initial observations of Schreiber,[18a] but not without precedent.[18b,21] In any case, it is clear that the role of the amine oxide cannot exclusively be that of accelerating the creation of a vacant coordination site in the cobalt-carbonyl cluster.

An intriguing issue of the present study lies in the aforementioned observation that in the case of both 8-phenylmenthol **1c** and neopentyloxyisoborneol **1d** the stereoselectivities obtained in the Pauson-Khand cyclization of the derived 2-alkynoates are greater than those observed for the corresponding *O*-alkyl ynol ethers, although in the former derivatives the stereogenic centers of the auxiliary are one C-C bond farther from the acetylene moiety. An explanation of this fact would be premature at this point; however it is worth noting that the dicobalt complexes of 2-alkynoates could have a conformational mobility similar if not inferior to that of the alkoxyethyne complexes. In fact, inspection of molecular models show that an *s-cis, syn* conformation is probably the most stable one for the alkynoate complexes (Figure 2).[22]

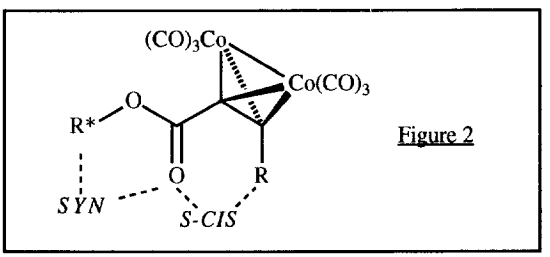


Figure 2

In conclusion, we have shown that it is possible to obtain a reasonable degree of stereocontrol in the cobalt-mediated cocyclizations of 2-alkynoates with olefins through the use of chiral alcohols as auxiliaries. Studies on the intermolecular Pauson-Khand reaction of other chiral electron-deficient alkynes are in progress in our laboratory and will be reported in due course.

Experimental

Melting points were determined in open ended capillary tubes on a Büchi-Tottoli apparatus or on a Reichert-Thermovar Köfler apparatus and are uncorrected. Infrared spectra were measured with a Perkin-Elmer 681 or Nicolet FT-IR 510 spectrometer using film NaCl or KBr pellet techniques; the peak intensity is designated s (strong), m (medium), or w (weak). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, on a Varian Gemini-200 or on a Varian Unity-300 spectrometer with tetramethylsilane or chloroform as an internal standard. Chemical shifts are expressed in δ (PPM) units downfield by TMS. The multiplicity in ^{13}C NMR spectra was determined by means of DEPT techniques. Mass spectra were recorded at 70 eV ionizing voltage on a Hewlett-Packard HP-5988A apparatus. Ammonia was used for chemical ionization (CI). MS spectra are presented as *m/z* (% rel. int.). Optical rotations were measured with a Perkin-Elmer 241 MC automatic polarimeter. UV-VIS spectra were measured in hexane solution, on a Perkin-Elmer Lambda 5 spectrophotometer. 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 was distilled over calcium hydride and toluene over metallic sodium. All reactions were carried out in oven-dried glassware under an atmosphere of pre-purified nitrogen. The course of all of the reactions described 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 were carried out with a Hewlett-Packard 1050 liquid chromatograph using a 4.6 mm i.d. x 25 cm Nucleosyl 100 5CN column (Scharlau, Barcelona, Spain).

General Procedures for the Preparation of 2-Alkynoate Esters.

Method A:[16] To a stirred, ice-cooled solution of a chiral alcohol **1** (3.73 mmol) and a 2-alkynoic acid (3.43 mmol) in anhydrous dichloromethane (3 mL), a solution of dicyclohexylcarbodiimide (0.705 g, 3.43 mmol) and 4-dimethylaminopyridine (4 mg, 0.036 mmol) in anhydrous dichloromethane (3 mL) was added dropwise. The resulting mixture was stirred at 0°C during 3-5 h and at room temperature for 1 h. The resulting precipitate was filtered out and thoroughly washed with dichloromethane; the solvent was eliminated *in vacuo* and the residue was purified by column chromatography on silica gel, eluting with 3 to 5% hexane/diethyl eher mixtures.

Method B:[12] To a stirred solution of a chiral alcohol **1** (0.42 mmol) and phenylpropiolyl chloride[23] (207 mg, 1.26 mmol) in dry benzene (2 mL) was added AgCN (79 mg, 0.59 mmol). The resulting mixture was stirred at reflux temperature between 21 and 165 h (until the alcohol was consumed). The silver chloride precipitate was filtered out and washed with diethyl ether, and the combined filtrate and washings were subsequently washed with saturated aqueous $NaHCO_3$ and brine. After drying ($MgSO_4$) the solvents were eliminated *in vacuo* and the crude product was purified by column chromatography on silica gel eluting with 1 to 3% hexane/diethyl ether mixtures.

Method C:[17] A solution of (-)-8-phenylmenthol **1c** (916 mg, 3.95 mmol), propiolic acid (300 mg, 4.28 mmol) and *p*-toluenesulfonic acid (7 mg, 0.04 mmol) in anhydrous benzene (3.2 mL) was refluxed for 95 h in a Dean-Stark apparatus. After dilution with diethyl ether, the resulting mixture was washed with saturated aqueous $NaHCO_3$ and with brine. After drying ($NaSO_4$) the solvents were eliminated *in vacuo* and the crude product was purified by column chromatography on silica gel eluting with 5% hexane/ethyl acetate, to afford 0.89 g (79% yield) of propiolate **4c** (*v. infra*).

(-)-Menthyl phenylpropiolate, 2a: Prepared by method A from **1a** in 83% yield (0.811 g). White solid. mp 62-64°C; IR (KBr): 3380, 3060, 2960 (s), 2920, 2870, 2230 (s), 1705 (s), 1490, 1460, 1440, 1280, 1190, 1170, 980, 755, 690 cm^{-1}; ^1H NMR (200 MHz): 0.78-0.82 (3H, d, J=5.5 Hz), 0.90-0.94 (6H, d, J=6 Hz), 1.20 (2H, m), 1.60 (5H, m), 2.0 (2H, m), 4.85 (1H, td, J= 11.3, 5.1 Hz), 7.4 (3H, m), 7.6 (2H, m); ^{13}C NMR (50 MHz): 16.7 (CH_3), 21.2 (CH_3), 22.5 (CH_3), 23.8 (CH_2), 26.6 (CH), 31.9 (CH), 34.6 (CH_2), 41.2 (CH_2), 47.4 (CH), 76.9 (CH), 81.5 (Cq), 86.3 (Cq), 120.0 (Cq), 129.0 (CH), 130.9 (CH), 133.5 (CH), 154.0 (Cq); MS (CI): 285 ($[M+1]^+$, 100%), $[\alpha]^{25}_D$ = -54.7 (c=0.92, $CHCl_3$); Anal. calcd for $C_{19}H_{24}O_2$: C, 80.28%; H, 8.45%. Found: C, 80.31%; H, 8.54%.

(*trans*-2-Phenylcyclohexyl) phenylpropiolate, 2b: Prepared by method A from **1b** in 70% yield (0.860 g). White solid. mp 95-97°C; IR (KBr): 3370, 3050, 3020, 2920(s), 2840, 2200 (s), 1690 (s), 1480, 1440, 1265, 1180, 1160, 1000, 910, 750, 695 cm^{-1}; ^1H NMR (200 MHz): 1.30-2.00 (7H, m), 2.10-2.20 (1H, m), 2.65-2.85 (1H, td, J=11.9, 4.0 Hz), 5.25 (1H, td, J=10.5, 5.2 Hz), 7.24-7.45 (10H, m); ^{13}C NMR (50 MHz): 24.2 (CH_2), 25.6 (CH_2), 31.1 (CH_2), 33.9 (CH_2), 49.3 (CH), 78.7 (CH), 80.6 (Cq), 85.8 (Cq), 120.0 (Cq), 126.5 (CH), 127.4 (CH), 128.3 (CH), 130.4 (CH), 132.8 (CH), 142.5 (Cq), 154.0 (Cq); MS (CI)= 305 ($[M+1]^+$, 20%), 322 ($[M+18]^+$, 100%); Anal. calcd for $C_{21}H_{20}O_2$: C, 82.89%; H, 6.58%. Found: C, 83.04%; H, 6.66%.

[(-)-8-Phenylmenthyl] phenylpropiolate, 2c: Prepared by method A from **1c** in 81% yield (0.851 g). Colorless oil. IR (film NaCl): 3090, 3060, 3020, 2960 (s), 2920, 2870, 2230 (s), 1705 (s), 1495, 1450, 1285, 1195, 1180, 1100, 760, 690 cm^{-1}; ^1H NMR (200 MHz): 0.88 (3H, d, J= 6.8 Hz), 0.80-1.20 (4H, m), 1.28 (3H, s), 1.38 (3H, s), 1.50-1.70 (2H, m), 1.90-2.10 (2H, m), 4.80-5.00 (1H, td, J=9.8, 4.7 Hz), 7.20-7.50 (10H, m); ^{13}C NMR (50 MHz): 21.6 (CH_3), 25.8 (CH_3), 26.6 (CH_2), 27.0 (CH_3), 31.2 (CH), 34.3 (CH_2), 39.6 (Cq), 41.3 (CH_2), 50.4 (CH), 76.3 (CH), 80.8 (Cq), 85.4 (Cq), 120.0 (Cq), 125.0 (CH), 125.4 (CH), 128.0 (CH), 128.3 (CH), 130.3 (CH), 132.9 (CH), 151.0 (Cq), 154.0 (Cq); MS (CI)= 361 ($[M+1]^+$, 6%), 378 ($[M+18]^+$, 100%); $[\alpha]^{25}_D$ = +39.1 (c=3, $CHCl_3$).

[*(1R,2S,3R,4S)*-3-(2,2-Dimethylpropoxy)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl] phenylpropiolate, 2d: Prepared by method B from **1d** in 92% yield (0.363 g). Colorless oil. IR (film NaCl): 3060, 3040, 2960 (s), 2880, 2230 (s), 1710 (s), 1290, 1190, 1105, 1040, 760, 690 cm^{-1}; ^1H NMR (200 MHz): 0.84 (3H, s), 0.89 (9H, s), 0.95 (3H, s), 1.17 (3H, s), 1.40-1.80 (4H, m),1.85 (1H, d, J=4.8 Hz), 2.98 (1H, d, J=8.0 Hz), 3.13 (1H, d, J=8.0 Hz), 3.50 (1H, d, J=6.8 Hz), 4.70 (1H, d, J=6.9 Hz), 7.30-7.60 (5H, m); ^{13}C NMR (50 MHz): 11.3 (CH_3), 20.5 (CH_3), 21.2 (CH_3), 23.7 (CH_2), 26.8 (CH_3x3), 32.0 (Cq), 33.5 (CH_2), 47.3 (Cq), 47.8 (Cq), 47.9 (CH), 81.1 (CH_2), 82.0 (Cq), 83.2 (CH), 83.4 (CH), 85.6 (Cq), 120.0 (Cq), 128.4 (CH), 130.2 (CH), 132.8 (CH), 154.0 (Cq); MS (CI)= 369 ($[M+1]^+$, 10%), 386 ($[M+18]^+$, 100%); $[\alpha]^{25}_D$=-49.2 (c=2.8, $CHCl_3$).

[*(1S,2R,3S,4R)*-3-(2,2-Dimethylpropoxy)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl] phenylpropiolate, 2e: Prepared by method B from **1e** in 94% yield (0.144 g). Colorless oil. IR (film NaCl): 3380, 3060, 3030, 2960 (s), 2880, 2240 (s), 1710 (s), 1480, 1450, 1295, 1190, 1115, 760, 690 cm^{-1}; ^1H NMR (200 MHz): 0.81 (3H, s), 0.92 (3H, s), 0.93 (9H, s), 1.05 (1H, m), 1.17 (3H, s), 1.40-1.80 (3H, m), 1.88 (1H, d, J=4.7 Hz), 3.05-3.08 (1H, d, J=7.7 Hz), 3.13-3.17 (1H, d, J=7.7 Hz), 3.32 (1H, d, J=6.8 Hz), 4.80 (1H, d, J= 6.7 Hz), 7.3-7.6 (5H, m); ^{13}C NMR (50 MHz): 11.4 (CH_3), 20.6 (CH_3), 20.9 (CH_3), 24.1 (CH_2), 26.8 (CH_3x3), 32.3 (Cq), 33.0 (CH_2), 47.0 (Cq), 49.1 (CH), 49.8 (Cq), 80.0 (CH), 81.5 (Cq), 83.2 (CH_2), 86.2 (Cq), 87.0 (CH), 120.0 (Cq), 128.4 (CH), 130.3 (CH), 132.8 (CH), 154.5 (Cq); MS (CI)= 369 ($[M+1]^+$, 2%), 386 ($[M+18]^+$, 100%); $[\alpha]^{25}_D$=+7.3 (c=3.5, $CHCl_3$).

[*(1S,2R,4R)*-7,7-Dimethyl-1-methylsulfenylmethylbicyclo[2.2.1]hept-2-yl] phenyl propiolate, 2f: Prepared by method A from **1f** in 46% yield (0.085 g). Colorless oil. IR (film NaCl): 2950 (s), 2880, 2220 (s), 1710 (s), 1285, 1190, 1175, 760, 690 cm^{-1}; ^1H NMR (200 MHz): 0.92 (3H, s), 1.09 (3H, s), 1.40-2.00 (7H, m), 2.14 (3H, s), 2.55 (1H, d, J=12.6 Hz), 2.95 (1H, d, J=12.6 Hz), 4.90-5.05 (1H, m), 7.30-7.70 (5H, m); ^{13}C NMR (50 MHz): 19.0 (CH_3), 20.0 (CH_3), 20.5 (CH_3), 26.8 (CH_2), 31.0 (CH_2), 33.5 (CH_2), 39.0 (CH_2), 45.4 (CH), 48.2 (Cq), 52.6 (Cq), 80.6 (CH), 82.0 (Cq), 86.0 (Cq), 120.0 (Cq), 128.5 (CH), 130.5 (CH), 132.9 (CH), 153.5 (Cq); MS (CI)= 329 ($[M+1]^+$, 15%), 346 ($[M+18]^+$, 100%), 363 ($[M+35]^+$, 6%); $[\alpha]^{25}_D$=-108.1 (c=3.3, $CHCl_3$).

[*(1S,2R,4R)*-1-Diethylsulfamoylmethyl-7,7-dimethylbicyclo[2.2.1]hept-2-yl] phenyl propiolate, 2g: Prepared by method B from **1g** in 34% yield (0.074 g). Colorless oil. IR (film NaCl): 3060, 2960 (s), 2860, 2220 (s), 1785, 1715 (s), 1620, 1450, 1330, 1190, 1050, 1025, 940, 760, 710, 690 cm^{-1}; ^1H NMR (200 MHz): 0.80-1.30 (3H, m), 0.91 (3H, s), 1.15 (3H, s), 1.19 (6H, t, J=5.5 Hz), 1.60-2.10 (4H, m), 2.85 (1H, d, J=13.5 Hz), 3.35 (5H, m), 5.10 (1H, m), 7.40-7.53 (5H, m); ^{13}C NMR (50 MHz): 14.5 (CH_3x2), 20.1 (CH_3), 20.3 (CH_3), 26.9 (CH_2), 29.8 (CH_2), 39.1 (CH_2), 39.5 (Cq), 41.6 (CH_2x2), 44.5 (CH), 49.5 (CH_2), 49.8 (Cq), 80.1 (CH), 81.0 (Cq), 85.0 (Cq), 120.0 (Cq), 128.2 (CH), 129.9 (CH), 130.4 (CH), 130.7 (CH), 153.0 (Cq); MS (CI)= 418 ($[M+1]^+$, 1%), 435 ($[M+18]^+$, 100%); $[\alpha]^{25}_D$=-53.5 (c=1.8, $CHCl_3$).

[*(1R,2S,4S)*-1,7,7-Trimethylspiro(bicyclo[2.2.1]heptan-3,2′-indan)-2-yl] phenyl propiolate, 2h: Prepared by method B from **1h** in 53% yield (0.158 g). Colorless oil. IR (film NaCl): 3060, 3040, 3020, 2980 (s), 2850, 2230 (s), 1710 (s), 1400, 1290, 1190, 1175, 995, 760, 695 cm^{-1}; ^1H NMR (200 MHz): 0.86 (3H, s), 0.92, (3H, s), 1.28 (3H, s), 1.60-1.80 (5H, m), 2.86-2.95 (1H, d, J=15.8 Hz), 2.90-2.92 (1H, d, J=15.5 Hz), 3.18 (1H, d, J=15.6 Hz), 3.45 (1H, d, J=15.8 Hz), 4.76 (1H, s), 7.00-7.60 (9H, m); ^{13}C NMR (50 MHz): 11.8 (CH_3), 21.9 (CH_3), 22.1 (CH_3), 24.0 (CH_2), 33.8 (CH_2), 41.8 (CH_2), 46.4 (CH_2), 49.4 (Cq), 51,1 (Cq), 55.7 (CH), 57.3 (Cq), 80.5 (Cq), 86.0 (Cq), 90.6 (CH), 120.0 (Cq), 123.5 (CH), 123.8 (CH), 126.2 (CH), 128.5 (CH), 130.4 (CH), 132.9 (CH), 141.0 (Cq), 143.4 (Cq), 153.0 (Cq); MS (CI)= 402 ($[M+18]^+$, 100%); $[\alpha]^{25}_D$=+140.7 (c=0.4, $CHCl_3$).

***(trans*-2-Phenylcyclohexyl) 2-butynoate, 3b:** Prepared by method A from **1b** in 90% yield (0.235 g). Colorless oil. IR (film NaCl): 3480, 3060, 3030, 2930 (s), 2860, 2240 (s), 1705 (s), 1450, 1205, 1070, 940, 750, 700 cm^{-1}; ^1H NMR (200 MHz): 1.30-1.90 (7H, m), 1.85 (3H, s), 2.10-2.20 (1H, m), 2.60-2.80 (1H, td, J= 8.7, 4.3 Hz), 5.02-5.15 (1H, td J= 10.6, 4.4 Hz), 7.17-7.27 (5H, m); ^{13}C NMR (50 MHz): 3.7 (CH_3), 24.6 (CH_2), 25.6 (CH_2), 32.0 (CH_2), 34.0 (CH_2), 49.3 (CH), 73.0 (Cq), 77.4 (CH), 85.5 (Cq), 126.4 (CH), 127.3 (CH), 128.2 (CH), 142.5 (Cq), 153.0 (Cq); MS (CI): 243 ($[M+1]^+$, 2%), 260 ($[M+18]^+$, 100%); 277 ($[M+35]^+$, 1%).

[(-)-8-Phenylmenthyl] 2-butynoate, 3c: Prepared by method A from **1c** in 81% yield (0.573 g). White solid. mp 53-55°C; IR (KBr): 3400, 3100, 3085, 3040, 2950 (s), 2860, 2260 (s), 1705 (s), 1610, 1500, 1445, 1205, 1070, 765, 750, 700 cm^{-1}; ^1H NMR (200 MHz): 0.85 (3H, d, J=6.8 Hz), 0.90-1.10

(4H, m), 1.26 (3H, s), 1.35 (3H, s), 1.55 (3H, m), 1.89 (3H, s), 1.90-2.10 (1H, m), 4.85 (1H, td, J= 11.4, 4.5 Hz), 7.10-7.30 (5H, m); ^{13}C NMR (50 MHz): 4.6 (CH_3), 22.6 (CH_3), 27.2 (CH_3), 27.7 (CH_2), 27.8 (CH_3), 32.2 (CH), 35.3 (CH_2), 40.8 (Cq), 42.4 (CH_2), 51.4 (CH), 73.9 (Cq), 77.0 (CH), 86.0 (Cq), 126.0 (CH), 126.4 (CH), 128.9 (CH), 151.6 (Cq), 154.0 (Cq); MS (CI): 299 ($[M+1]^+$, 1%), 316 ($[M+18]^+$, 100%); $[\alpha]^{25}_D$=+10.2 (c=3.3, $CHCl_3$); Anal. calcd for $C_{20}H_{26}O_2$: C, 80.54%; H, 8.73%. Found: C, 80.52%; H, 8.92%.

[(-)-8-Phenylmenthyl] propynoate, 4c: Prepared by method A in 12% yield (0.1 g) and by method C in 79% yield (0.89 g) from **1c.** Colorless oil. IR (film NaCl): 3400, 3260 (s), 3080, 3050, 2950 (s), 2920, 2120 (s), 1710 (s), 1240, 1100, 760, 700 cm^{-1}; ^{1}H NMR (200 MHz): 0.88 (3H, d, J=5.5 Hz), 1.05-1.11 (3H, m), 1.29 (3H, s), 1.37 (3H, s), 1.50-1.60 (3H, m), 1.90-2.10 (2H, m), 2.74 (1H, s), 4.85 (1H, td, J=10.5, 5.0 Hz), 7.27-7.32 (5H, m); ^{13}C NMR (50 MHz): 21.6 (CH_3), 26.3 (CH_3), 26.7 (CH_2), 26.8 (CH_3), 31.3 (CH), 34.2 (CH_2), 40.4 (Cq), 41.3 (CH_2), 50.4 (CH), 74.1 (CH), 75.5 (Cq), 76.9 (CH), 125.4 (CH), 128.0 (CH), 150.4 (Cq), 155.0 (Cq); MS (CI): 302 ($[M+18]^+$, 100%), 319 ($[M+35]^+$, 2%); $[\alpha]^{25}_D$=+0.45 (c=6.3, $CHCl_3$).

General Procedures for the Intermolecular Pauson-Khand Reaction of 2-Alkynoate Esters.

Thermal Reaction in Toluene: To a stirred solution of a 2-alkynoic ester (0.35 mmol) in anhydrous toluene (5 mL) dicobaltoctacarbonyl (133 mg, 0.38 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). A solution of the olefin (3.52 mmol) in toluene (2 mL) was added dropwise, and the reaction mixture was heated at a specified temperature (40-80°C, see Table 2) during 1-57 h (until complete disappearence of the complex; see Table 2), filtered through Celite and directly submitted to column chromatography on silicagel, eluting with 5% hexane/diethyl ether mixture.

Thermal Reaction in Acetonitrile: To 124 mg (0.362 mmol) of solid dicobaltoctacarbonyl a solution of 2-alkynoic ester (0.33 mmol) in freshly distilled acetonitrile (3 mL) was added dropwise. The mixture was stirred at room temperature for 1 h, and additional dicobaltoctacarbonyl was eventually added until total consumption of the starting 2-alkynoate. At this point, an acetonitrile (1 mL) solution of the desired cycloalkene (3.33 mmol) was added dropwise, and the reaction mixture was heated to reflux until complete disappearance of the complex (1 to 140 h; see Table 2). The resulting suspension was filtered through Celite and submitted to column chromatography on silicagel, eluting with 5% hexane/diethyl ether mixture.

Tertiary Amine *N*-Oxide Mediated Reaction:[4] To a stirred solution of a 2-alkynoic ester (0.35 mmol) in anhydrous dichloromethane (5 mL) dicobaltoctacarbonyl (133 mg, 0.38 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). A solution of the olefin (3.52 mmol) in dry dichloromethane (5 mL) was added dropwise, the reaction mixture was externally cooled with ice, solid *N*-methylmorpholino-*N*-oxide monohydrate (97 mg, 0.718 mmol, 2 equiv.) was added in one portion, the reaction mixture was allowed to attain the room temperature by removal of the cooling bath and the extent of the reaction was monitored by TLC. This treatment was repeated until complete disappearence of the complex (6 to 10 equivalents of *N*-oxide). After 2 h of additional stirring at room temperature, the resulting suspension was filtered through Celite, the solvent was eliminated *in vacuo* and the residue was purified by column chromatography on silicagel, eluting with 5% hexane/diethyl ether mixture.

***(1R*,2S*,6R*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carboxylic acid (-)-menthyl ester, 5a:** Colorless oil. IR (film NaCl): 3400, 3060, 2950 (s), 2920, 2870, 1715 (s), 1640, 1460, 1250, 1230, 1170, 960, 730, 700 cm^{-1}; ^{1}H NMR (200 MHz): 0.60-1.85 (23 H, m), 1.90-2.10 (1H, m), 2.40 (2H, m), 2.55 (1H, broad s), 2.95-3.05 (1H, m), 4.65-4.81 (1H, m), 7.21-7.35 (5H, m); ^{13}C NMR (50 MHz), major diastereomer: 16.0 (CH_3), 20.6 (CH_3), 21.9 (CH_3), 23.1 (CH_2), 25.9 (CH), 28.3 (CH_2), 28.8 (CH_2), 31.2 (CH), 31.4 (CH_2), 33.9 (CH_2), 38.0 (CH), 39.6 (CH), 40.2 (CH_2), 46.5 (CH), 48.8 (CH), 53.8 (CH), 75.6 (CH), 131.0 (Cq), 147.8 (Cq), 159.7 (Cq), 166.0 (Cq), 208.6 (Cq), minor diastereomer: 15.8 (CH_3), 20.7 (CH_3), 21.9 (CH_3), 22.8 (CH_2), 25.4 (CH), 28.3 (CH_2), 28.8 (CH_2), 31.2 (CH), 31.4 (CH_2), 33.9 (CH_2), 38.0 (CH), 39.6 (CH), 40.4 (CH_2), 46.5 (CH), 48.9 (CH), 53.8 (CH), 75.7 (CH), 131.0 (Cq), 147.2 (Cq), 160.0 (Cq), 166.1 (Cq), 208.6 (Cq); MS (CI): 262 ([(M-$C_{19}H_{24}O_2$)x2+18]$^+$, 100%), 333 ([M-C_7H_7+18]$^+$, 18%), 407 ($[M+1]^+$, 2%), 424 ($[M+18]^+$, 15%).

***(1R*,2S*,6R*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carboxylic acid *trans*-2-phenylcyclohexyl ester, 5b**: Colorless oil. IR (film NaCl): 3070 (w), 3040 (w), 2950 (s), 2880, 1715 (s), 1500, 1450, 1230, 1170, 1130, 1015, 760, 700 cm^{-1}; ^{1}H NMR (200 MHz): 0.80-2.00 (14H, m), 2.10-2.70 (5H, m), 5.05-5.20 (1H, td, J= 10.0, 5.0 Hz), 7.15-7.34 (10H, m); ^{13}C NMR (50 MHz), major diastereomer: 24.6 (CH_2), 25.5 (CH_2), 28.3 (CH_2), 29.1 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 33.7 (CH_2), 37.2 (CH), 39.8 (CH), 48.4 (CH), 49.6 (CH), 53.6 (CH), 77.3 (CH), 126.4 (CH), 127.4 (CH), 127.9 (CH), 128.4 (CH), 128.5 (CH), 130.0 (Cq), 143.0 (Cq), 146.0 (Cq), 159.9 (Cq), 165.9 (Cq), 208.7 (Cq), minor diastereomer: 24.6 (CH_2), 25.6 (CH_2), 28.6 (CH_2), 29.1 (CH_2), 31.1 (CH_2), 32.0 (CH_2), 34.0 (CH_2), 37.6 (CH), 39.9 (CH), 48.6 (CH), 49.8 (CH), 53.6 (CH), 77.3 (CH), 126.5 (CH), 127.3 (CH), 127.9 (CH), 128.3 (CH), 128.5 (CH), 130.0 (Cq), 143.0 (Cq), 146.0 (Cq), 159.4 (Cq), 165.0 (Cq), 208.7 (Cq); MS (CI): 427 ([M+1]$^+$, 60%), 444 ([M+18]$^+$, 100%).

***(1R*,2S*,6R*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carboxylic acid (-)-8-phenylmenthyl ester, 5c**: Colorless oil. IR (film NaCl): 3090 (w), 3060 (w), 3025 (w), 2970 (s), 2940, 2880, 1710 (s), 1445, 1220, 1165, 765, 700 cm^{-1}; ^{1}H NMR (200 MHz): 0.80-2.00 (13H, m), 0.85 (3H, d, J= 6.2 Hz), 1.16 (3H, s), 1.19 (3H, s), 2.15 (1H, d, J= 3.3 Hz), 2.32 (1H, d, J= 6.2 Hz), 2.48 (1H, d, J=3.3 Hz), 2.65 (1H, d, J= 4.2 Hz), 2.75 (1H, d, J= 6.2 Hz), 4.78-4.83 (1H, m), 7.15-7.41 (10H, m); ^{13}C NMR (50 MHz), major diastereomer: 21.7 (CH_3), 25.2 (CH_3), 26.3 (CH_3), 26.4 (CH_2), 28.3 (CH_2), 28.6 (CH_2), 31.2 (CH), 31.4 (CH_2), 34.3 (CH_2), 38.1 (CH), 39.7 (CH), 40.0 (Cq), 41.1 (CH_2), 47.7 (CH), 50.2 (CH), 53.6 (CH), 75.7 (CH), 125.3 (CH), 127.7 (CH), 127.9 (CH), 129.0 (CH), 130.4 (Cq), 150.0 (Cq), 152.0 (Cq), 158.4 (Cq), 164.5 (Cq), 209.2 (Cq), minor diastereomer: 21.7 (CH_3), 25.2 (CH_3), 26.3 (CH_3), 26.4 (CH_2), 28.3 (CH_2), 29.0 (CH_2), 31.1 (CH), 31.4 (CH_2), 34.1 (CH_2), 38.6 (CH), 39.5 (CH), 40.0 (Cq), 41.0 (CH_2), 47.7 (CH), 50.0 (CH), 53.8 (CH), 75.8 (CH), 124.8 (CH), 127.7 (CH), 127.8 (CH), 128.6 (CH), 130.4 (Cq), 150.0 (Cq), 150.9 (Cq), 159.0 (Cq), 165.7 (Cq), 208.7 (Cq); MS (CI): 483 ([M+1]$^+$, 25%), 500 ([M+18]$^+$, 100%); UV (λ_{max}, hexane): 273.4 nm (ε=5800).

***(1R*,2S*,6R*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carboxylic acid *(1R,2S,3R,4S)*-3-(2,2-dimethylpropoxy)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl ester, 5d**: Colorless oil. IR (film NaCl): 3400 (w), 3060 (w), 2960 (s), 2880 (s), 1715 (s), 1480, 1360, 1210, 1165, 1105, 695 cm^{-1}; ^{1}H NMR (200 MHz): 0.76 (6H, s), 0.84 (9H, s), 0.97 (3H, s), 0.70-1.80 (10H, m), 1.85 (1H, d, J=5 Hz), 2.40-2.42 (1H, d, J=5.4 Hz), 2.48-2.52 (1H, m), 2.93-2.97 (1H, d, J=8.4 Hz), 2.80-3.10 (2H, m), 3.11-3.15 (1H, d, 8.4 Hz), 3.48-3.51 (1H, d, J=7.3 Hz), 4.58-4.61 (maj. diast.)-4.62 (min. diast.) (1H, d, 7.1 Hz), 7.26-7.35 (5H, m); ^{13}C NMR (50 MHz), major diastereomer: 11.4 (CH_3), 20.2 (CH_3), 21.1 (CH_3), 23.7 (CH_2), 26.7 (CH_3x3), 28.2 (CH_2), 29.2 (CH_2), 31.3 (CH_2), 31.9 (Cq), 33.6 (CH_2), 39.1 (CH), 40.0 (CH), 47.1 (Cq), 47.7 (CH), 47.9 (Cq), 48.9 (CH), 53.9 (CH), 81.1 (CH_2), 82.4 (CH), 84.2 (CH), 127.9 (CH), 128.6 (CH), 128.9 (CH), 130.6 (Cq), 150.8 (Cq), 157.9 (Cq), 164.4 (Cq), 209.4 (Cq), minor diastereomer: 10.9 (CH_3), 20.4 (CH_3), 21.0 (CH_3), 23.7 (CH_2), 26.7 (CH_3x3), 28.3 (CH_2), 29.1 (CH_2), 31.3 (CH_2), 32.1 (Cq), 33.6 (CH_2), 38.9 (CH), 40.1 (CH), 47.0 (Cq), 47.6 (CH), 47.9 (Cq), 48.6 (CH), 54.0 (CH), 81.2 (CH_2), 82.5 (CH), 83.8 (CH), 127.7 (CH), 128.6 (CH), 129.0 (CH), 130.3 (Cq), 150.1 (Cq), 157.9 (Cq), 164.6 (Cq), 209.4 (Cq); MS (CI): 492 (491.7) ([M+1]$^+$, 4%), 509 (508.7) ([M+18]$^+$, 100%).

***(1R*,2S*,6R*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carboxylic acid *(1S,2R,3S,4R)*-3-(2,2-dimethylpropoxy)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl ester, 5e**: Colorless oil. IR (film NaCl): 3400 (w), 2960 (s), 2880 (s), 1715 (s), 1480, 1400, 1365, 1220, 1170, 1115, 700 cm^{-1}; ^{1}H NMR (200 MHz): 0.78 (6H, s), 0.80 (9H, s), 0.90 (3H, s), 0.70-1.80 (11H, m), 2.40 (1H, d, J=5.2 Hz), 2.55 (1H, broad s), 2.90-3.05 (4H, m), 3.25-3.28 (1H, d, J=6.7 Hz), 4.86-4.89 (maj. diast.)-4.72-4.75 (min. diast.) (1H, d, J=6.8 Hz), 7.25-7.35 (5H, m); ^{13}C NMR (50 MHz), major diastereomer: 11.5 (CH_3), 20.5 (CH_3), 20.8 (CH_3), 24.0 (CH_2), 26.7 (CH_3x3), 28.3 (CH_2), 29.1 (CH_2), 31.5 (CH_2), 32.3 (Cq), 33.2 (CH_2), 38.9 (CH), 40.0 (CH), 46.9 (Cq), 48.6 (CH), 49.6 (CH), 49.9 (Cq), 53.9 (CH), 79.0 (CH), 83.2 (CH_2), 87.8 (CH), 127.8 (CH), 128.7 (CH), 129.0 (CH), 130.3 (Cq), 150.2 (Cq), 158.0 (Cq), 164.5 (Cq), 209.2 (Cq), minor diastereomer: 11.5 (CH_3), 20.2 (CH_3), 20.8 (CH_3), 24.0 (CH_2), 26.7 (CH_3x3), 28.4 (CH_2), 29.1 (CH_2), 31.4 (CH_2), 32.4 (Cq), 33.2 (CH_2), 38.9 (CH), 40.1 (CH), 46.7 (Cq), 48.9 (CH), 49.2 (CH), 49.9 (Cq), 54.0 (CH), 79.6 (CH), 83.4 (CH_2), 87.9 (CH), 127.8 (CH), 128.6 (CH), 129.0 (CH), 130.6 (Cq), 150.2 (Cq), 158.0 (Cq), 164.5 (Cq), 209.2 (Cq); MS (CI): 492 (491.7) ([M+1]$^+$, 4%), 509 (508.7) ([M+18]$^+$, 100%).

***(1R*,2S*,6R*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carboxylic acid (1S,2R,4R)-7,7-dimethyl-1-methylsulfenylmethylbicyclo[2.2.1]hept-2-yl ester, 5f**: Colorless oil. IR (film NaCl): 3400 (w), 3060 (w), 2960 (s), 2880 (s), 1710 (s), 1450, 1350, 1320, 1220 (s), 1150, 765, 735, 700 cm^{-1}; ^{1}H NMR (200 MHz): 0.41 (maj. diast.)-0.70 (min. diast.) (3H, s), 0.77 (maj. diast.)-0.83 (min. diast.) (3H, s), 1.10-1.90 (13H, m), 2.03 (maj. diast.)-2.06 (min. diast.) (3H, s), 2.30 (1H, d, J= 11.4 Hz), 2.40-2.70 (4H, m), 3.04-3.06 (maj. diast.)-2.91-2.94 (min. diast.) (1H, d, J=5.4 Hz), 4.95 (1H, m), 7.32-7.36 (5H, m); ^{13}C NMR (50 MHz), major diastereomer: 17.3 (CH_3), 19.0 (CH_3), 20.2 (CH_3), 26.8 (CH_2), 28.4 (CH_2), 28.8 (CH_2), 31.1 (CH_2), 31.6 (CH_2), 33.6 (CH_2), 37.9 (CH), 38.1 (CH_2), 39.9 (CH), 45.2 (CH), 47.9 (Cq), 48.8 (CH), 52.2 (Cq), 53.7 (CH), 79.6 (CH), 128.1 (CH), 128.6 (CH), 128.8 (CH), 130.0 (Cq), 148.0 (Cq), 160.0 (Cq), 165.9 (Cq), 208.6 (Cq), minor diastereomer: 17.4 (CH_3), 19.6 (CH_3), 20.3 (CH_3), 26.8 (CH_2), 28.4 (CH_2), 29.2 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 33.6 (CH_2), 38.4 (CH), 38.6 (CH_2), 40.0 (CH), 45.2 (CH), 48.0 (Cq), 49.1 (CH), 53.4 (Cq), 53.9 (CH), 80.0 (CH), 128.0 (CH), 128.6 (CH), 128.8 (CH), 130.0 (Cq), 146.8 (Cq), 158.8 (Cq), 165.1 (Cq), 208.8 (Cq); MS (CI): 451 ([M+1]$^+$, 15%), 468 ([M+18]$^+$, 100%).

***(1R*,2S*,6R*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carboxylic acid *(1S,2R,4R)*-1-(diethyl)-sulfamoylmethyl-7,7-dimethylbicyclo[2.2.1]hept-2-yl ester, 5g**: Colorless oil. IR (film NaCl): 3080 (w), 2970 (s), 2880, 1710 (s), 1450, 1340, 1205, 1170, 1150, 1020, 940, 730, 700 cm^{-1}; ^{1}H NMR (200 MHz): 0.77 (maj. diast.)-0.38 (min. diast.) (3H, s), 0.80-2.00 (22H, m), 2.35-2.60 (3H, m), 2.85-3.25 (7H, m), 5.10 (1H, m), 7.35 (5H, broad s); ^{13}C NMR (50 MHz), major diastereomer: 14.5 (CH_3 x2), 19.0 (CH_3), 20.2 (CH_3), 26.9 (CH_2), 28.4 (CH_2), 28.8 (CH_2), 30.3 (CH_2), 31.6 (CH_2), 37.8 (CH), 38.8 (CH_2), 39.8 (CH), 41.4 (CH_2x2), 44.4 (CH), 48.8 (CH), 49.1 (Cq), 49.5 (CH_2), 53.8 (CH), 79.5 (CH), 128.2 (CH), 128.6 (CH), 128.8 (CH), 130.1 (Cq), 147.0 (Cq), 159.8 (Cq), 165.0 (Cq), 208.7 (Cq), minor diastereomer: 14.5 (CH_3 x2), 19.0 (CH_3), 20.2 (CH_3), 26.9 (CH_2), 28.4 (CH_2), 29.2 (CH_2), 30.3 (CH_2), 31.3 (CH_2), 38.6 (CH), 38.9 (CH_2), 40.2 (CH), 41.6 (CH_2x2), 44.4 (CH), 48.9 (CH), 49.1 (Cq), 49.7 (CH_2), 54.2 (CH), 79.4 (CH), 128.2 (CH), 128.6 (CH), 128.8 (CH), 130.1 (Cq), 147.0 (Cq), 160.0 (Cq), 165.5 (Cq), 208.7 (Cq); MS (CI): 558 (557.76) ([M+18]$^+$, 100%).

***(1R*,2S*,6R*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carboxylic acid *(1R,2S,4S)*-1,7,7-trimethylspiro(bicyclo[2.2.1]heptan-3,2'indan)-2-yl ester, 5h**: Colorless oil. IR (film NaCl): 3040, 3020, 2940 (s), 2880 (s), 1720 (s), 1250, 1210, 1170, 750, 700 cm^{-1}; ^{1}H NMR (200 MHz): 0.73 (maj. diast.)-0.56 (min. diast.) (3H, s), 0.87 (maj. diast.)-0.83 (min. diast.) (3H, s), 0.99 (maj. diast.)-0.95 (min. diast.) (3H, s), 1.05-1.40 (6H, m), 1.55-1.70 (7H, m), 2.35-2.58 (1H, m), 2.69-2.72 (1H, d, J=5.4 Hz), 2.76-2.96 (2H, m), 3.13-3.37 (2H, m), 4.72 (maj. diast.)-4.67 (min. diast.) (1H, s), 6.80-7.30 (9H, m); ^{13}C NMR (50 MHz), major diastereomer: 12.1 (CH_3), 21.5 (CH_3), 21.8 (CH_3), 24.0 (CH_2), 28.3 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 34.1 (CH_2), 38.5 (CH), 39.7 (CH), 42.0 (CH_2), 47.0 (CH_2), 49.0 (CH), 49.3 (Cq), 51.3 (Cq), 53.8 (CH), 56.0 (CH), 56.9 (Cq), 90.4 (CH), 123.2 (CH), 126.1 (CH), 126.2 (CH), 128.0 (CH), 128.5 (CH), 130.1 (Cq), 141.1 (Cq), 143.3 (Cq), 149.0 (Cq), 158.2 (Cq), 164.6 (Cq), 208.6 (Cq), minor diastereomer: 11.7 (CH_3), 21.5 (CH_3), 21.8 (CH_3), 23.9 (CH_2), 28.3 (CH_2), 29.1 (CH_2), 31.3 (CH_2), 34.0 (CH_2), 38.6 (CH), 40.0 (CH), 41.8 (CH_2), 46.8 (CH_2), 48.4 (CH), 49.2 (Cq), 51.6 (Cq), 53.9 (CH), 56.1 (CH), 56.9 (Cq), 90.5 (CH), 124.0 (CH), 126.1 (CH), 126.5 (CH), 128.1 (CH), 128.6 (CH), 130.1 (Cq), 141.4 (Cq), 143.3 (Cq), 149.0 (Cq), 159.1 (Cq), 165.3 (Cq), 208.6 (Cq); MS (CI): 507 ([M+1]$^+$, 2%), 524 ([M+18]$^+$, 100%).

***(1R*,2S*,6R*,7S*)*-4-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carboxylic acid *trans*-2-phenylcyclohexyl ester, 6b**: Colorless oil. IR (film NaCl): 3400 (w), 3070 (w), 3030 (w), 2940 (s), 2880 (s), 1705 (s), 1450, 1220, 1175, 750, 700 cm^{-1}; ^{1}H NMR (200 MHz): 1.79 (3H, broad s), 1.20-2.05 (14H, m), 2.10 (1H, d, J=6.5 Hz), 2.20-2.90 (4H, m), 5.05-5.22 (1H, m), 7.15-7.35 (5H, m); ^{13}C NMR (50 MHz), major diastereomer: 9.4 (CH_3), 24.6 (CH_2), 25.6 (CH_2), 28.2 (CH_2), 28.8 (CH_2), 31.1 (CH_2), 32.3 (CH_2), 33.4 (CH_2), 37.9 (CH), 39.4 (CH), 48.2 (CH), 50.0 (CH), 53.1 (CH), 77.2 (CH), 126.4 (CH), 127.4 (CH), 128.2 (CH), 142.6 (Cq), 148.4 (Cq), 155.4 (Cq), 164.6 (Cq), 211.2 (Cq), minor diastereomer: 9.2 (CH_3), 24.6 (CH_2), 25.6 (CH_2), 28.1 (CH_2), 29.1 (CH_2), 30.9 (CH_2), 32.2 (CH_2), 33.9 (CH_2), 37.5 (CH), 39.4 (CH), 48.0 (CH), 49.8 (CH), 53.1 (CH), 77.1 (CH), 126.4 (CH), 127.2 (CH), 128.4 (CH), 143.1 (Cq), 149.0 (Cq), 155.4 (Cq), 164.6 (Cq), 211.2 (Cq); MS (CI): 365 ([M+1]$^+$, 15%), 382 ([M+18]$^+$, 100%).

***(1R*,2S*,6R*,7S*)*-4-Methyl-5-oxotricyclo[5.2.1.0^{2,6}]dec-3-ene-3-carboxylic acid (-)-8-phenylmenthyl ester, 6c**: Colorless oil. IR (film NaCl): 3400 (w), 3090 (w), 3060 (w), 2960 (s),

2880 (s), 1705 (s), 1450, 1220, 1180, 770, 735, 700 cm^{-1}; ^1H NMR (200 MHz): 0.89-0.92 (3H, d, J=6.4 Hz), 1.20 (3H, s), 1.30 (3H, s), 1.91 (3H, s), 0.80-2.05 (14H, m), 2.10-2.60 (4H, m), 4.95-5.10 (1H, td, J=11.4, 5 Hz), 7.12-7.30 (5H, m); ^{13}C NMR (50 MHz), major diastereomer: 9.6 (CH_3), 21.7 (CH_3), 23.6 (CH_3), 26.3 (CH_2), 28.6 (CH_2), 28.8 (CH_2), 29.0 (CH_3), 31.2 (CH_2), 31.8 (CH), 34.4 (CH_2), 37.9 (CH), 39.3 (CH), 39.6 (Cq), 41.7 (CH_2), 47.6 (CH), 50.3 (CH), 53.1 (CH), 74.7 (CH), 124.8 (CH), 125.1 (CH), 127.9 (CH), 148.7 (Cq), 151.8 (Cq), 156.4 (Cq), 164.1 (Cq), 211.5 (Cq), minor diastereomer: 9.9 (CH_3), 21.7 (CH_3), 24.4 (CH_3), 26.4 (CH_2), 28.6 (CH_2), 28.8 (CH_2), 29.0 (CH_3), 31.2 (CH_2), 31.8 (CH), 34.3 (CH_2), 38.4 (CH), 39.3 (CH), 39.6 (Cq), 42.2 (CH_2), 48.8 (CH), 50.5 (CH), 53.2 (CH), 74.8 (CH), 125.0 (CH), 125.1 (CH), 127.7 (CH), 148.4 (Cq), 151.2 (Cq), 156.0 (Cq), 165.1 (Cq), 211.5 (Cq); MS (CI): 421 ($[M+1]^+$, 22%), 438 ($[M+18]^+$, 100%). UV (λ_{max}, hexane): 248.0 nm (ε=9900), 206.0 nm (ε=11190).

***(1R*,2R*,6S*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carboxylic acid (-)-menthyl ester, 7a**: Colorless oil. IR (film NaCl): 3060 (w), 2960 (s), 2870 (s), 1710 (s), 1450, 1325, 1230, 1155, 1140, 950, 715, 695 cm^{-1}; ^1H NMR (200 MHz): 0.80-1.50 (19 H, m), 2.00 (1H, m), 2.45 (1H, d, J=5 Hz), 2.95 (1H, broad s), 3,15 (2H, m), 4.70-4.85 (1H, m), 6.25 (1H, m), 6.40 (1H, m), 7.31-7.36 (5H, m); ^{13}C NMR (50 MHz), major diastereomer: 16.0 (CH_3), 20.7 (CH_3), 21.9 (CH_3), 23.1 (CH_2), 25.4 (CH), 31.6 (CH), 33.9 (CH_2), 40.4 (CH_2), 41.4 (CH_2), 43.2 (CH), 44.7 (CH), 46.6 (CH), 48.3 (CH), 52.6 (CH), 75.7 (CH), 127.9 (CH), 128.6 (CH), 130.5 (Cq), 137.3 (CH), 138.5 (CH), 148.3 (Cq), 159.6 (Cq), 165.5 (Cq), 208.2 (Cq), minor diastereomer: 15.8 (CH_3), 20.6 (CH_3), 21.9 (CH_3), 22.8 (CH_2), 25.9 (CH), 31.6 (CH), 33.9 (CH_2), 40.2 (CH_2), 41.4 (CH_2), 43.2 (CH), 44.7 (CH), 46.6 (CH), 48.4 (CH), 52.6 (CH), 75.4 (CH), 127.9 (CH), 128.6 (CH), 130.5 (Cq), 137.3 (CH), 138.5 (CH), 147.9 (Cq), 159.4 (Cq), 165.9 (Cq), 208.2 (Cq); MS (CI): 405 ($[M+1]^+$, 41%), 422 ($[M+18]^+$, 100%).

***(1R*,2R*,6S*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carboxylic acid *trans*-2-phenylcyclohexyl ester, 7b**: Colorless oil. IR (film NaCl): 3400, 3060 (w), 3040, 2940 (s), 2860 (s), 1710 (s), 1500, 1450, 1330, 1240, 1170, 1020, 765, 725, 700 cm^{-1}; ^1H NMR (200 MHz): 0.90-1.90 (9H, m), 2.15 (1H, broad s), 2.35 (1H, d, J=5.2 Hz), 2.45-2.75 (2H, m), 2.85 (1H, d, J=5.2 Hz), 2.95 (1H, broad s), 5.05-5.20 (1H, m), 6.05-6.15 (2H, m), 7.15-7.35 (10H, m); ^{13}C NMR (50 MHz), major diastereomer: 24.6 (CH_2), 25.6 (CH_2), 31.6 (CH_2), 33.8 (CH_2), 41.4 (CH_2), 42.4 (CH), 44.4 (CH), 48.0 (CH), 49.7 (CH), 52.6 (CH), 77.3 (CH), 126.5 (CH), 127.4 (CH), 127.9 (CH), 128.4 (CH), 128.5 (CH), 130.0 (Cq), 136.8 (CH), 138.5 (CH), 142.6 (Cq), 147.1 (Cq), 159.1 (Cq), 164.9 (Cq), 207.1 (Cq), minor diastereomer: 24.6 (CH_2), 25.4 (CH_2), 32.0 (CH_2), 34.0 (CH_2), 41.2 (CH_2), 42.8 (CH), 44.5 (CH), 48.1 (CH), 49.8 (CH), 52.6 (CH), 77.4 (CH), 126.6 (CH), 127.4 (CH), 127.9 (CH), 128.3 (CH), 128.5 (CH), 130.2 (Cq), 137.0 (CH), 138.9 (CH), 142.8 (Cq), 147.9 (Cq), 159.8 (Cq), 165.5 (Cq), 207.1 (Cq), MS (CI): 425 ($[M+1]^+$, 38%), 442 ($[M+18]^+$, 100%).

***(1R*,2R*,6S*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carboxylic acid (-)-8-phenylmenthyl ester, 7c**: Colorless oil. IR (film NaCl): 3400 (w), 3060 (w), 3020 (w), 2960 (s), 2920, 2870 (s), 1705 (s), 1600, 1495, 1445, 1230, 1165, 765, 700 cm^{-1}; ^1H NMR (200 MHz): 0.70-1.95 (17H, m), 2.35-2.45 (2H, m), 2.70 (1H, broad s), 2.81 (1H, d, J=5.8 Hz), 2.98 (1H, broad s), 3.19 (1H, broad s), 4.80-4.95 (1H, td, J=11.1, 4.4 Hz), 6.18-6.30 (1H, m), 6.40 (1H, m), 7.08-7.38 (10H, m); ^{13}C NMR (50 MHz), major diastereomer: 21.7 (CH_3), 25.5 (CH_3), 26.4 (CH_2), 27.1 (CH_3), 31.1 (CH), 34.1 (CH_2), 40.5 (Cq), 41.0 (CH_2), 41.4 (CH_2), 43.7 (CH), 44.6 (CH), 48.5 (CH), 49.9 (CH), 52.7 (CH), 75.7 (CH), 125.0 (CH), 125.1 (CH), 127.5 (CH), 127.8 (CH), 128.6 (CH), 129.1 (CH), 130.3 (Cq), 137.1 (CH), 138.9 (CH), 148.0 (Cq), 151.0 (Cq), 158.4 (Cq), 165.4 (Cq), 207.3 (Cq), minor diastereomer: 21.7 (CH_3), 25.0 (CH_3), 26.4 (CH_2), 27.5 (CH_3), 31.2 (CH), 34.3 (CH_2), 40.5 (Cq), 41.2 (CH_2), 41.5 (CH_2), 43.1 (CH), 44.4 (CH), 47.0 (CH), 50.1 (CH), 52.6 (CH), 75.7 (CH), 124.9 (CH), 125.2 (CH), 127.6 (CH), 127.9 (CH), 128.6 (CH), 129.0 (CH), 130.1 (Cq), 137.0 (CH), 138.6 (CH), 148.0 (Cq), 151.4 (Cq), 158.0 (Cq), 163.8 (Cq), 207.6 (Cq); MS (CI): 248 ($[M-C_{16}H_{24}O]^+$, 54%), 498 ($[M+18]^+$, 5%).

***(1R*,2R*,6S*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carboxylic acid *(1R,2S,3R,4S)*-3-(2,2-dimethylpropoxy)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl ester, 7d**: Colorless oil. IR (film NaCl): 3400 (w), 3070 (w), 2960 (s), 2880 (s), 1715 (s), 1480, 1460, 1210, 1170, 1110, 755, 700 cm^{-1}; ^1H NMR (200 MHz): 0.77 (6H, s), 0.84 (9H, s), 0.98 (3H, s), 0.70-1.70 (6H, m), 1.85 (1H, broad s), 2.55 (1H, d, J=5.5 Hz), 2.85-3.18 (4H, m), 3.30 (1H, broad s), 3.50 (1H, d, J=7.5 Hz), 4.60 (maj. diast.)-4.70 (min. diast.) (1H, d, J=7.5 Hz), 6.20-6.30 (1H, m), 6.30-6.40

(1H, m), 7.29-7.38 (5H, m); ^{13}C NMR (50 MHz), major diastereomer: 10.9 (CH_3), 20.2 (CH_3), 21.1 (CH_3), 23.7 (CH_2), 26.7 (CH_3x3), 32.0 (Cq), 33.6 (CH_2), 41.3 (CH_2), 44.0 (CH), 44.7 (CH), 47.0 (Cq), 47.6 (CH), 47.9 (Cq), 48.4 (CH), 52.8 (CH), 81.1 (CH_2), 82.6 (CH), 84.2 (CH), 127.8 (CH), 128.9 (CH), 129.0 (CH), 130.5 (Cq), 137.1 (CH), 138.9 (CH), 150.7 (Cq), 157.5 (Cq), 164.5 (Cq), 207.9 (Cq), minor diastereomer: 11.5 (CH_3), 20.4 (CH_3), 21.1 (CH_3), 23.7 (CH_2), 26.7 (CH_3x3), 31.9 (Cq), 33.6 (CH_2), 41.3 (CH_2), 44.1 (CH), 44.7 (CH), 47.1 (Cq), 47.9 (CH), 47.9 (Cq), 48.2 (CH), 52.8 (CH), 81.0 (CH_2), 82.5 (CH), 83.8 (CH), 127.8 (CH), 128.9 (CH), 129.0 (CH), 130.5 (Cq), 137.1 (CH), 138.8 (CH), 151.5 (Cq), 157.5 (Cq), 164.2 (Cq), 207.9 (Cq); MS (CI): 489 ([M+1]$^+$, 6%), 506 ([M+18]$^+$, 100%).

***(1R*,2R*,6S*,7S*)*-5-Oxo-4-phenyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene-3-carboxylic acid *(1R,2S,4S)*-1,7,7-trimethylspiro(bicyclo[2.2.1]heptan-3,2'indan)-2-yl ester, 7h**: Colorless oil. IR (film NaCl): 3060 (w), 2960, 2920 (s), 2860, 1710 (s), 1450, 1215, 1170, 740, 715, 695 cm^{-1}; ^{1}H NMR (200 MHz): 0.75 (maj. diast.)-0.55 (min. diast.) (3H, s), 0.87 (maj. diast.), 0.83 (min. diast.) (3H, s), 0.96 (maj. diast.)-0.93 (min. diast.) (3H, s), 1.20-1.80 (7H, m), 2.48-2.60 (2H, m), 2.78-3.33 (6H, m), 4.81 (maj. diast.)-4.78 (min. diast.) (1H, s), 6.20-6.35 (2H, m), 6.90-7.35 (9H, m); ^{13}C NMR (50 MHz), major diastereomer: 12.1 (CH_3), 21.5 (CH_3), 21.8 (CH_3), 24.0 (CH_2), 34.1 (CH_2), 41.6 (CH_2), 41.9 (CH_2), 43.6 (CH), 44.5 (CH), 46.9 (CH_2), 48.0 (CH), 49.2 (Cq), 51.6 (Cq), 52.7 (CH), 56.1 (CH), 57.0 (Cq), 90.5 (CH), 123.2 (CH), 124.1 (CH), 126.2 (CH), 126.3 (CH), 128.0 (CH), 128.7 (CH), 130.0 (Cq), 137.3 (CH), 138.7 (CH), 141.4 (Cq), 143.3 (Cq), 148.0 (Cq), 159.0 (Cq), 164.5 (Cq), 207.4 (Cq), minor diastereomer: 11.6 (CH_3), 21.5 (CH_3), 21.8 (CH_3), 23.9 (CH_2), 34.0 (CH_2), 41.3 (CH_2), 41.8 (CH_2), 43.4 (CH), 44.7 (CH), 46.8 (CH_2), 48.6 (CH), 49.2 (Cq), 51.3 (Cq), 52.8 (CH), 56.0 (CH), 57.1 (Cq), 90.7 (CH), 123.2 (CH), 124.1 (CH), 126.2 (CH), 126.3 (CH), 128.1 (CH), 128.5 (CH), 130.0 (Cq), 137.3 (CH), 138.7 (CH), 141.0 (Cq), 143.3 (Cq), 148.0 (Cq), 159.5 (Cq), 164.5 (Cq), 207.1 (Cq); MS (CI): 505 ([M+1]$^+$, 1%), 522 ([M+18]$^+$, 100%)

***(1R*,5S*)*-4-Oxo-3-phenylbicyclo[3.3.0]oct-2-ene-2-carboxylic acid *trans*-2-phenylcyclohexyl ester, 8b**: Colorless oil. IR (film NaCl): 3400, 3060 (w), 3020, 2930 (s), 2860 (s), 1710 (s), 1635, 1490, 1450, 1220, 1150, 755, 700 cm^{-1}; ^{1}H NMR (200 MHz): 0.80-2.20 (13H, m), 2.45-2.70 (1H, m), 2.75-2.90 (1H, m), 3.10-3.15 (1H, m), 3.30-3.40 (1H, m), 5.05-5.21 (1H, m), 7.16-7.35 (10H, m); ^{13}C NMR (50 MHz), major diastereomer: 23.8 (CH_2), 24.5 (CH_2), 25.5 (CH_2), 28.5 (CH_2), 30.2 (CH_2), 31.6 (CH_2), 33.6 (CH_2), 44.6 (CH), 49.5 (CH), 50.1 (CH), 77.2 (CH), 126.5 (CH), 127.4 (CH), 127.8 (CH), 128.2 (CH), 128.5 (CH), 128.6 (CH), 130.0 (Cq), 142.6 (Cq), 143.9 (Cq), 161.0 (Cq), 165.8 (Cq), 210.2 (Cq), minor diastereomer: 23.8 (CH_2), 24.5 (CH_2), 25.6 (CH_2), 28.9 (CH_2), 30.2 (CH_2), 32.0 (CH_2), 34.0 (CH_2), 44.7 (CH), 49.7 (CH), 50.3 (CH), 77.2 (CH), 126.5 (CH), 127.4 (CH), 127.8 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 1329.9 (Cq), 142.6 (Cq), 144.2 (Cq), 160.4 (Cq), 165.2 (Cq), 210.2 (Cq); MS (CI): 401 ([M+1]$^+$, 12%), 418 ([M+18]$^+$, 82%).

***(1R*,2S*,6R*,7S*)*-5-Methyl-3-oxotricyclo[5.2.1.0^{2,6}]dec-4-ene-4-carboxylic acid (-)-8-phenylmenthyl ester, 9**: Colorless oil. IR (film NaCl): 2950 (s), 2880 (s), 1740, 1720 (s), 1450, 1330, 1310, 1190, 1025, 770, 705 cm^{-1}; ^{1}H NMR (200 MHz): 0.88 (3H, d, J=6.8 Hz), 0.93-1.20 (7H, m), 1.21 (3H, s), 1.30 (3H, s), 1.40-1.70 (6H, m), 2.04 (3H, s), 2.00-2.50 (5H, m), 4.90-5.10 (1H, td, J=11.4, 4.5 Hz), 7.00-7.26 (5H, m); ^{13}C NMR (50 MHz), major diastereomer: 17.7 (CH_3), 21.8 (CH_3), 25.1 (CH_3), 26.6 (CH_2), 27.6 (CH_3), 28.4 (CH_2), 29.2 (CH_2), 31.3 (CH_2), 31.5 (CH), 34.5 (CH_2), 37.6 (CH), 39.2 (CH), 39.7 (Cq), 41.9 (CH_2), 50.6 (CH), 53.2 (CH), 54.0 (CH), 74.4 (CH), 124.6 (CH), 125.5 (CH), 135.5 (Cq), 151.6 (Cq), 162.2 (Cq), 182.9 (Cq), 204.5 (Cq), minor diastereomer: 17.9 (CH_3), 21.8 (CH_3), 25.6 (CH_3), 26.7 (CH_2), 27.4 (CH_3), 28.3 (CH_2), 29.3 (CH_2), 31.3 (CH_2), 31.7 (CH), 34.5 (CH_2), 37.9 (CH), 39.0 (CH), 39.7 (Cq), 41.8 (CH_2), 50.2 (CH), 53.4 (CH), 54.3 (CH), 74.4 (CH), 124.7 (CH), 127.7 (CH), 135.0 (Cq), 151.4 (Cq), 162.5 (Cq), 184.0 (Cq), 204.5 (Cq); MS (CI): 421 ([M+1]$^+$, 32%), 438 ([M+18]$^+$, 100%). UV (λ_{max}, hexane): 230.0 nm (ε=4910).

***(1R*,2S*,6S*,7S*)*-3-oxotricyclo[5.2.1.0^{2,6}]dec-4-ene-4-carboxylic acid (-)-8-phenylmenthyl ester, 10**: Colorless oil. IR (film NaCl): 3080, 3050, 2950 (s), 2870 (s), 1745, 1720 (s), 1600, 1330, 1300, 1165, 1125, 1025, 760, 700 cm^{-1}; ^{1}H NMR (200 MHz): 0.87 (3H, d, J=6.8 Hz), 1.16 (3H, s), 1.28 (3H, s), 0.85-1.28 (6H, m), 1.40-1.70 (4H, m), 1.90 (3H, m), 2.20 (3H, m), 2.40 (2H, m), 4.95 (1H, m), 7.00-7.26 (6H, m); ^{13}C NMR (50 MHz), major diastereomer: 21.8 (CH_3), 23.0 (CH_3), 26.3 (CH_2), 28.1 (CH_2), 29.3 (CH_2), 29.7 (CH_3), 31.2 (CH), 31.5 (CH_2), 34.5 (CH_2), 37.9 (CH), 39.3 (CH), 41.6 (CH_2), 47.6 (CH), 50.1 (CH), 54.8 (CH), 74.1 (CH), 124.5 (CH), 125.4 (CH), 127.9 (CH),

138.0 (Cq), 152.4 (Cq), 160.0 (Cq), 172.2 (CH), 204.8 (Cq), minor diastereomer: 21.8 (CH_3), 23.2 (CH_3), 26.4 (CH_2), 28.3 (CH_2), 29.3 (CH_2), 29.7 (CH_3), 31.2 (CH), 31.5 (CH_2), 34.5 (CH_2), 37.9 (CH), 39.5 (CH), 41.6 (CH_2), 47.9 (CH), 49.8 (CH), 54.8 (CH), 74.5 (CH), 124.9 (CH), 125.3 (CH), 127.9 (CH), 138.5 (Cq), 152.4 (Cq), 160.5 (Cq), 172.5 (CH), 204.8 (Cq); MS (CI): 407 ($[M+1]^+$, 23%), 424 ($[M+18]^+$, 100%). UV (λ_{max}, hexane): 230.0 nm (ε=7120).

***(1R*,2R*,3R*,6S*,7S*)*-5-Hydroxymethyl-4-phenyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3-ol, 11:** To a stirred solution of cycloadduct **7a** (63 mg, 0.16 mmol) in anhydrous diethyl ether (2.5 mL) were added dropwise at -20°C 0.32 mL (0.32 mmol) of a 1M solution of diisobutylaluminum hydride in hexanes. The mixture was stirred at the same temperature for 30 min., 0.3 mL of dry methanol were added, the cooling bath was removed and stirring was maintained for 1 h at room temperature. The aluminum precipitate was filtered out and thoroughly washed with diethyl ether, and the combined filtrate and washings were washed with brine and dried over magnesium sulfate. The solvent was evaporated at reduced pressure, and the crude residue was purified by column chromatography on silica gel eluting with 20% hexane/ethyl acetate, to afford alcohol **11** (28 mg, 71% yield) as a colorless viscous oil. IR (film NaCl): 3359 (s), 3060 (w), 2970 (s), 2940, 2870, 1600, 1495, 1445, 1330, 1000 (s), 960, 900, 775, 730, 700 cm^{-1}; ^1H NMR (200 MHz): 1.34-1.64 (4H, m), 2.38 (1H, t, J=8.4 Hz), 2.90 (3H, m), 4.20 (1H, d, J=12.8 Hz), 4.40 (1H, d, J=12.6 Hz), 5.20 (1H, d, J=8.4 Hz), 6.20 (2H, s), 7.20-7.40 (5H, m); ^{13}C NMR (50 MHz): 41.7 (CH), 43.0 (CH), 43.1 (CH_2), 43.8 (CH), 53.9 (CH), 58.8 (CH_2), 76.3 (CH), 128.2 (CH), 128.5 (CH), 135.0 (Cq), 137.6 (CH), 138.0 (CH), 141.0 (Cq), 143.8 (Cq); MS (CI): 255 ($[M+1]^+$, 15%), 273 ($[M+18]^+$, 100%)

***(1R*,2R*,3R*,6S*,7S*)*-4-Hydroxymethyl-5-phenyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3-ol, 12:** The tricyclic hydroxyketone **13**[19] (25 mg, 0.10 mmol) was reduced with diisobutylaluminum hydride (0.20 mmol) by the methodology described above to give 20 mg (79% yield) of the crude alcohol **12**, whose spectroscopic data showed that it was a regioisomer of **11**. IR (film NaCl): 3400 (s), 3070 (w), 2940 (s), 2870, 1690, 1080, 1020, 700 cm^{-1}; ^1H NMR (200 MHz): 1.20-1.43 (2H, m), 1.70 (2H, d, J=8.7 Hz), 2.27-2.45 (2H, m), 2.97 (1H, m), 3.10 (1H, d, J=6.9 Hz), 4.31 (2H, m), 5.06 (1H, d, J=8.8 Hz), 6.09-6.14 (1H, m), 6.17-6.21 (1H, m), 7.26-7.35 (5H, m); ^{13}C NMR (50 MHz): 41.5 (CH), 42.9 (CH), 43.1 (CH_2), 44.6 (CH), 56.5 (CH), 59.6 (CH_2), 77.6 (CH), 128.2 (CH), 128.3 (CH), 135.8 (Cq), 137.6 (CH), 138.1 (CH), 140.1 (Cq), 144.0 (Cq); MS (CI): 237 ($[M-OH]^+$, 30%), 254 ($[(M-OH)+18]^+$,100%), 255 ($[M+1]^+$, 20%), 273 ($[M+18]^+$, 42%).

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