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Studies on the Pauson–Khand reaction of alkynyl sulfoxides. Unexpectedly easy racemization of their dicobalt hexacarbonyl complexes

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Abstract

The scope and limitations of the Pauson–Khand reactions of alkynyl sulfoxides with strained alkenes have been studied. (*S*)-1-Hexynyl *p*-tolyl sulfoxide and (*S*)-2-phenylethynyl *p*-tolyl sulfoxide afforded β-(*p*-tolylsulfinyl)enones in moderate yields and low diastereoselectivities. The diastereomeric mixtures were easily separated by column chromatography and the sulfinyl group could be cleaved by a sequence involving reduction to sulfide, carbonyl reduction and enol thioether hydrolysis to afford 1,3-rearranged enantiomerically enriched α-butyl and α-phenyl enones. The absolute configuration of the Pauson–Khand adducts was determined by X-ray diffraction. The decreased enantiomeric excess of the final products uncovered an unprecedented low temperature racemization of the hexacarbonyl dicobalt complexes of alkynyl sulfoxides.

1. Introduction

The cobalt mediated carbonylative co-cyclization of an alkyne and an alkene, known as the Pauson–Khand reaction,[1] is nowadays a well established methodology for the construction of five membered rings. In the last decade, our group has been engaged in the development of enantioselective versions of this useful reaction using the chiral auxiliary approach.[2–6] Among these, we have developed several methodologies in which a chiral inductor, covalently bonded to the alkyne participating in the process, is able to control the diastereoselectivity in intermolecular Pauson–Khand reactions. Up to now, we have explored for this purpose the use of ethynyl ethers **I**[3] and 2-alkynoates **II**[4] derived from chiral

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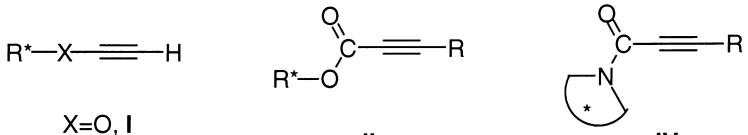
alcohols, ethynyl thioethers **III**[5] derived from chiral thiols, and 2-alkynoyl amides **IV**[6] derived from chiral oxazolidones and sultams. For some of these systems, excellent levels of diastereoselectivity have been achieved in spite of the fact that in all of these compounds the nearest stereogenic center in the inductor is four or five bonds away from the newly created stereogenic center in the Pauson–Khand adducts.

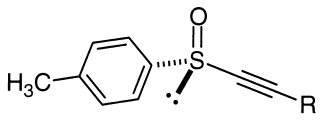


Unlike the above mentioned acetylenic derivatives, alkynyl sulfoxides **1** possess the stereogenic center directly bonded to the acetylenic carbon. This property, combined with the easy availability of enantiopure sulfoxides and the chemical versatility of sulfinyl compounds,[7] made alkynyl sulfoxides **1** very attractive substrates for stereocontrolled Pauson–Khand reactions. We report herein our results on the use of chiral enantiomerically pure alkynyl sulfoxides as steric controllers for intermolecular Pauson–Khand reactions.

2. Results and discussion

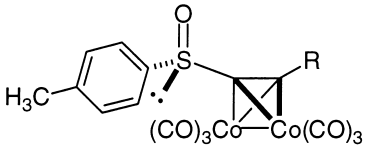
2.1. Syntheses of the cobalt hexacarbonyl complexes of acetylenic sulfoxides

Enantiomerically pure alkynyl sulfoxides **1a**–**d** covering a range of sterically and electronically different substituents were selected for our study. Compounds **1a**–**c** were prepared on a multigram scale by a modification of the Andersen method,[8] developed by Huda,[9] whereas ethynylsulfoxide **1d** (R=H) was prepared by desilylation of **1a**.[9]



1a R = $SiMe_3$
1b R = n-C_4H_9
1c R = Ph
1d R = H

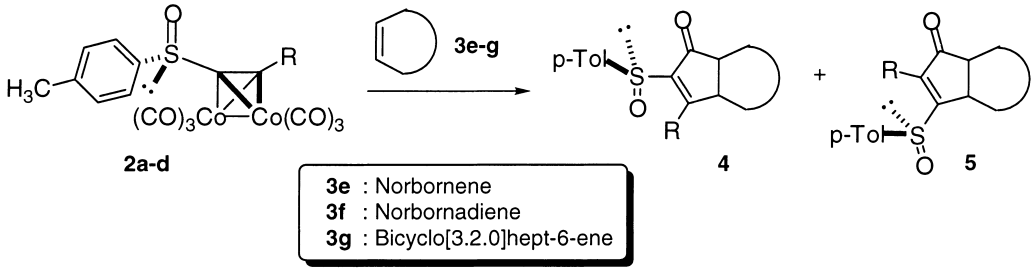
The formation of the hexacarbonyl dicobalt complexes **2a**–**c** took place uneventfully by stirring **1a**–**c** with octacarbonyl dicobalt in toluene at room temperature. In the case of 1-hexynylsulfoxide **1b** the cobalt complex **2b** was isolated in 82% yield although we decided, for practical reasons, not to purify the cobalt complexes and to submit the crude solution to the Pauson–Khand reaction conditions. Conversely, the formation of the cobalt complex of ethynyl sulfoxide **1d** was problematic due to the easy polymerization of the starting material in the presence of $Co_2(CO)_8$. Since our attempts to desilylate the cobalt complex of **1a** were unsuccessful, the polymerization of **1d** was partially alleviated by preparing the complex at low temperature (0°C).



2a R = $SiMe_3$
2b R = n-C_4H_9
2c R = Ph
2d R = H

2.2. Pauson–Khand reactions

The Pauson–Khand reaction of cobalt complexes **2a–d** with strained alkenes **3g–e** to afford the two regioisomeric bicyclic enones **4** and **5** was studied next (Scheme 1 and Table 1).



Scheme 1.

The trimethylsilyl derivative **2a** was completely reluctant to undergo the Pauson–Khand reaction, probably due to the steric shielding provoked by the trimethylsilyl group, and no traces of cycloaddition adducts were detected by TLC when a toluene solution of **2a** was heated with norbornene for 36 h at 70°C (entry 1).

Sulfoxide **1d** represents the opposite situation in steric shielding of the triple bond. When this sulfoxide was converted into the corresponding dicobalt hexacarbonyl complex **2d** (CH_2Cl_2, 0°C) and treated with 10 equiv. of norbornene and 6 equiv. of *N*-methylmorpholine *N*-oxide (NMO) at −78°C the α-sulfinyl cyclopentenone **4de**† was isolated from the crude reaction although only in 9% yield and almost without any diastereoselectivity (Scheme 1, Table 1; entry 9).

Table 1
Intermolecular Pauson–Khand reactions of cobalt complexes **2a–d** with alkenes **3e–g**

	Cobalt complex	Alkene	React. conditions[a] (temperature, time)	Products (overall yield, d.r.)
1	**2a**	**3e**	A, 70°C, 36h	(0%)
2	**2b**	**3f**	A, 65 °C, 27h	**5bf** (46%, 1.6:1)[b]; **6bf** (23%, 2.9:1)[c]
3	**2b**	**3f**	B, NMO•H_2O, 0°C	**5bf** (15%, 1:1)[b]; **6bf** (31%, 4.6:1)[c]
4	**2b**	**3e**	A, 65 °C, 27h	**5be** (34%, 1.8:1)[c]
5	**2b**	**3e**	B, NMO•H_2O, 0°C	**5be** (4%)[c]
6	**2b**	**3g**	A, 65°C, 12h	**5bg** (32%, 2:1)[c]; **6bg** (33%, 1.2:1)[c]
7	**2c**	**3e**	A,70°C, 12h; 100°C, 7h	**5ce** (53%, 2.6:1)[c]
8	**2c**	**3e**	B,TMANO, -78°C to r.t	**5ce** (10%, 1:1)[c]
9	**2d**	**3e**	B, -78°C to r.t.	**4de** (9%, 1.2:1)

[a] Conditions A: stirring the pre-formed dicobalt hexacarbonyl complex in hexanes or toluene at the specified temperature. Conditions B: addition of amine N-oxide to the solution of the dicobalt hexacarbonyl complex in methylene chloride at the specified temperature.
[b] By HPLC. [c] ^{13}C NMR.

† In this article the polycyclic cyclopentenones are indicated by a number and a two letter code: the first letter refers to the R group coming from the starting sulfoxide; the second describes the fragment arising from the alkene counterpart.

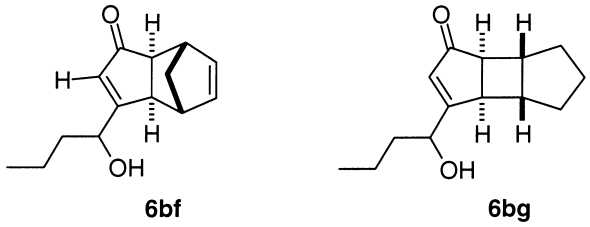
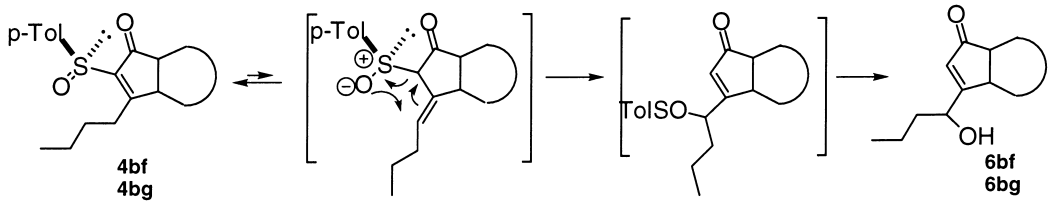


Figure 1.

To our satisfaction, the cyclization of complex **2b** with norbornadiene (**3f**) proceeded cleanly under thermal conditions affording a mixture of cyclopentenones in 69% overall yield (Table 1). The major product of the reaction was the Pauson–Khand adduct **5bf**, with the sulfoxide group placed β to the carbonyl. Thus, the presence of the *n*-butyl substituent provokes a reversal in the regiochemical preferences of the reaction. Although the process took place with low diastereoselectivity, both diastereomers were easily separable by column chromatography.

The regioisomeric adduct **4bf** was not found in the crude product. Instead, the hydroxy cyclopentenone **6bf**, which probably arises from this putative Pauson–Khand adduct, was isolated in a 23% yield. Fig. 1 shows the proposed relative ring stereochemistry of this adduct assuming an *exo*-attack to the olefin as is usual in Pauson–Khand reactions.

A tentative mechanism to explain the presence of **6bf** would involve an isomerization of the double bond followed by a sulfoxide–sulfenate rearrangement (Scheme 2).[10] However, other mechanisms such as a rearrangement of a radical pair intermediate[11] produced by homolytic cleavage of the carbon–sulfur could also be considered.



Scheme 2.

The nowadays widely used *N*-oxide promoted conditions for this reaction[12] were also tried. Unfortunately, both the yield and the diastereomeric ratio of the Pauson–Khand adduct **5bf** were lower than under thermal activation, although they were both higher for the by-product **6bf** (entry 3).

Using norbornene as a reacting olefin, the yield of the Pauson–Khand adduct **5be** was lower than using norbornadiene under both thermal and *N*-oxide reaction conditions (entries 4 and 5). In this case, neither the regioisomeric Pauson–Khand adduct **4be** nor the by-product arising from its decomposition **6be** could be isolated from the crude. On the other hand, the use of a more strained alkene such as bicyclo[3.2.0]hept-6-ene **3g** gave, under thermal conditions, a higher overall yield of cyclopentenones (entry 6). A nearly 1:1 mixture of the Pauson–Khand adduct **5bg** and the tricyclic alcohol **6bg** (Fig. 1) was obtained, the diastereomeric excess of **5bg** being in any case modest (2:1 dr).

The Pauson–Khand reaction using the cobalt complex **2c** prepared from 2-phenylethynyl *p*-tolyl sulfoxide was studied next (entries 7 and 8). Once again, only the thermal conditions afforded good yields of the cycloadduct **5ce**. Due to the higher steric hindrance of the phenyl group relative to *n*-butyl the reaction was completely regioselective and, consequently, the yield of the Pauson–Khand adduct **5ce** increased. Moreover, the selectivity increased up to a 2.6:1 mixture of easily separable diastereomers.

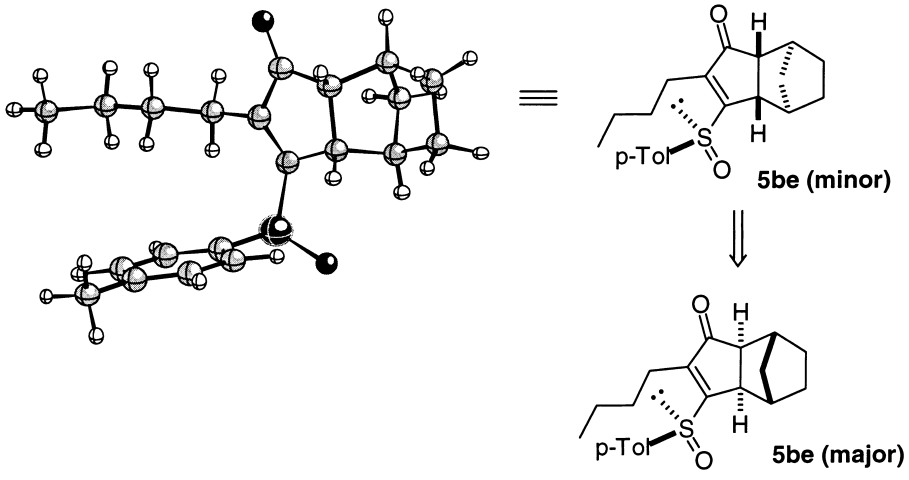


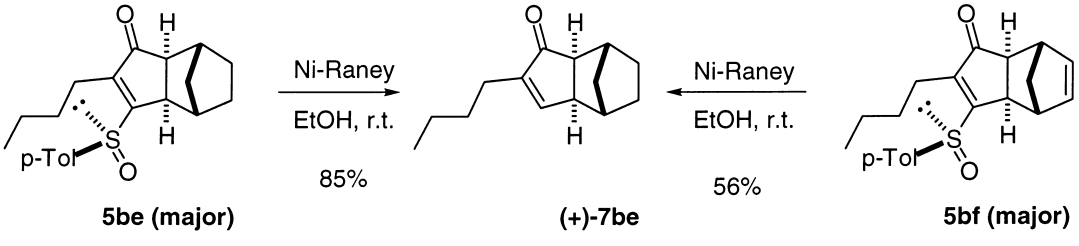
Figure 2.

2.3. Absolute configuration of the major diastereomers

The diastereomeric mixtures of the Pauson–Khand adducts **5be–bf** and **5ce** could be separated by column chromatography, affording diastereomerically pure β-sulfinylenones. The removal of the sulfoxide group from these enones would afford enantiomerically pure cyclopentenones if no racemization took place along the process. Since these products were highly crystalline it was possible to perform X-ray diffraction analyses. The minor diastereomer of **5be** crystallized nicely from hexane–ether. The X-ray diffraction of these crystals confirmed the assigned structure and revealed the stereochemical relationship between the sulfoxide and the other stereogenic centers in the molecule.

Thus, taking into account the known absolute configuration of the starting acetylenic sulfoxide, the stereochemistry of the diastereomers of the Pauson–Khand adduct **5be** must be the one depicted in Fig. 2.

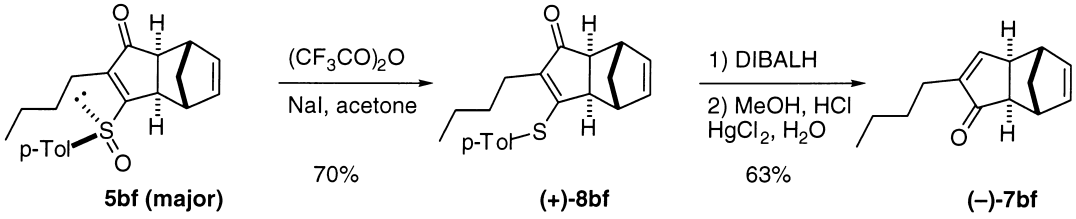
In order to remove the chiral auxiliary from these adducts, a reductive treatment with Raney-Ni was performed: the major diastereomers of β-sulfinylenones **5be** and **5bf** afforded on reductive desulfinylation the same bicyclic enone (+)-**7be**[13] due to the simultaneous reduction of the double bond in **5bf**. In this way the stereochemistry of **5bf** could also be firmly established, as well as the relationship between the sign of the optical rotation and the absolute configuration of enone **7be** (Scheme 3).



Scheme 3.

The concomitant reduction of the double bond during the cleavage of the sulfoxide led us to look for more selective, alternative protocols. Whereas the reductive elimination of sulfinyl groups α to a carbonyl is well documented,[7c] the references concerning cleavage of a sulfoxide β to an enone are scarce.[14] In our hands, reductive treatments involving the use of sodium[15] or aluminium[16] amalgams or of samarium iodide[17] led to complex mixtures where the corresponding sulfide was the major product. After some experimentation we found that the following reaction sequence afforded the corresponding 1,3-

rearranged enones in good yields: (a) sulfoxide reduction to sulfide; (b) carbonyl reduction by DIBALH; and (c) enol thioether hydrolysis with concomitant dehydration of one of the so formed β-hydroxy carbonyl system. Thus, starting from the major diastereomer **5bf**, sulfide (+)-**8bf** could be prepared in 70% yield by reduction with sodium iodide and trifluoroacetic anhydride.[18] This sulfide was then submited to DIBALH reduction and hydrolysis in the presence of mercuric salts[19] to afford enone (−)-**7bf** in 63% yield (Scheme 4). In so doing, the absolute configuration of this enone, already known in racemic form,[20,21] was unambiguously established.



Scheme 4.

On the other hand, from a hexane–ether solution of the major diastereomer of **5ce** a few crystals suitable for X-ray diffraction were collected. The crystalline cell showed the presence of both enantiomers, thus indicating that the crystals corresponded to a racemate. However, the relative configuration between the sulfoxide and the bicyclic system could be determined and the absolute configuration of the major adduct was assigned assuming that the sulfur atom had the same configuration as in the starting sulfoxide (Fig. 3).

The optimized protocol for the removal of the sulfoxide group was also applied to the major adduct **5ce** leading to the enantiomerically enriched bicyclic enone (+)-**7ce** with a similar overall yield (Scheme 5). Enone **7ce**, prepared by Pauson–Khand reaction of phenylacetylene and norbornene, has served as an example in many methodological studies of the reaction[21,22] including the seminal work of Pauson et al.[23] Moreover, it has been prepared in enantiomerically pure form by asymmetric Pauson–Khand reactions[24] although its absolute stereochemistry could not be determined. Now, the relationship between the sign of its rotatory power and configuration has been established for the first time.

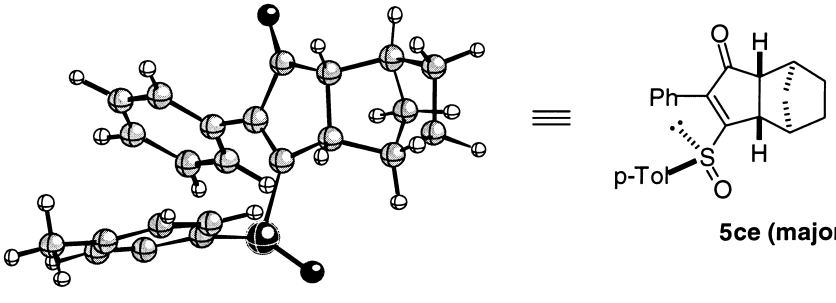
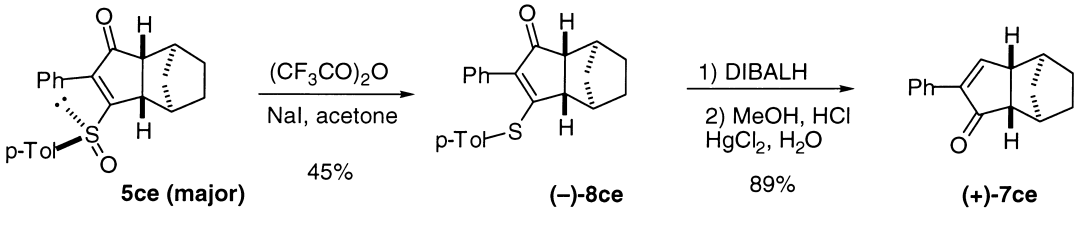


Figure 3.



Scheme 5.

The same sequence of reactions was also applied to the minor diastereomers of **5bf** and **5ce** and leading to the enantiomeric enones (+)-**7bf** and (−)-**7ce**, respectively.

2.4. Enantiomeric excess of the adducts

The optical purity of enones **7bf** and **7ce** was analyzed by GC using a Cyclodex-β column. As suspected after the X-ray analysis of the adduct **5ce**, these compounds were not enantiomerically pure. The enantiomeric excess of (−)-**7bf** was 71% and only 25% ee in the case of (+)-**7ce**, clearly indicating that a racemization process had occurred along the sequences.

The enantiomeric excess of **7be**, obtained by direct desulfurization with Raney-Ni, was also measured and turned out to be 75% ee. The observation of partial racemization irrespective of the desulfinylation conditions employed tends to indicate that the racemization did not take place during the removal of the sulfoxide through a symmetrical intermediate, but at the cobalt carbonyl complex stage or during the Pauson–Khand reaction. A polarimetric study of the enantiomeric excess of the cobalt carbonyl complex **5b** showed that this compound is configurationally unstable and racemizes at an appreciable rate even at room temperature. A linear relationship (R^2=0.971) between ln c and t indicated that the racemization follows a first order kinetics and, therefore, the mechanism should consist of a single unimolecular step. The measured rate constant at 25°C was 2.8 10^{-6} s^{-1}. This means that starting from an enantiomerically pure toluene solution of **5b**, after 7 h at room temperature, the enantiomeric excess would be only 86% ee.

This unexpected low temperature racemization is completely unprecedented for a non-allylic sulfoxide. It is worth recalling that the racemization by pyramidal inversion in alkyl or aryl sulfoxides takes place at a measurable rates only at temperatures higher than 200°C[25] and in benzylic sulfoxides at 135–155°C.[26] According to the literature precedents, we have envisaged three possible mechanisms for the racemization of the dicobalt hexacarbonyl complexes of alkynyl sulfoxides: (a) homolytic cleavage of the sulfur–carbon bond; (b) pyramidal inversion; and (c) formation of a pentavalent sulfur intermediate followed by Berry pseudorotations. These tentative mechanisms are currently being studied in our laboratories both from the experimental and theoretical point of view. The results of this study will be reported in due course.

In summary, the elaboration of the adducts arising from the Pauson–Khand reaction of alkynyl sulfoxides with strained alkenes has allowed the establishment of the absolute configuration of some synthetically important polycyclic ketones. Moreover, the observed loss of enantiomeric excess in diastereomerically pure Pauson–Khand adducts arising from enantiomerically pure sulfoxides, has been traced to the unprecedented, extremely easy racemization of the dicobalt hexacarbonyl complexes of alkynyl sulfoxides.

3. Experimental

3.1. General

Melting points were determined in an open capillary tube and are uncorrected. Optical rotations were measured at room temperature (23°C) on a Perkin–Elmer 241 MC polarimeter (concentration in g/100 mL). Infrared spectra were recorded on a Perkin–Elmer 681, or on a Nicolet 510 FTIR using an NaCl film technique. ^{1}H NMR were recorded at 200 or 500 MHz (s=singlet, d=doublet, t=triplet, q=quartet, dt=double triplet, m=multiplet and b=broad). ^{13}C NMR were recorded at 50.3 MHz or 125.7 MHz.

Carbon multiplicities have been assigned by DEPT experiments. In all cases, chemical shifts are in ppm downfield of TMS (referenced to an internal standard for ^{1}H NMR, and to the central signal of $CDCl_3$ for ^{13}C NMR). Diastereomeric ratios were determined by ^{13}C NMR. Mass spectra were recorded on a Hewlett–Packard 5890 instrument at 70 eV ionizing voltage; ammonia was used for chemical ionization (CI). THF and diethyl ether were distilled from sodium benzophenone ketyl. All reactions were performed in oven-dried glassware under an N_2 atmosphere. Reaction progress was monitored by TLC (Merck DC-Alufolien Kieselgel 60 F254) eluting with hexanes/ethyl acetate mixtures.

Alkynyl sulfoxides **1a**–**d** were prepared according to the procedures described in the literature.[9] The optical purity of **1b** and **1c** was checked by polarimetry. (+)-(*S*)-1-Hexynyl *p*-tolyl sulfoxide **1b**: $[\alpha]_D^{23}$=+80.3 (*c* 1.3 $CHCl_3$); lit.[9] $[\alpha]_D^{23}$=+77.6 (*c* 1.2 $CHCl_3$). (+)-(*S*)-2-Phenylethynyl *p*-tolyl sulfoxide **1c**: $[\alpha]_D^{23}$=+83.7 (*c* 1.2 $CHCl_3$); lit.[27] $[\alpha]_D^{23}$=+76 (*c* 2.5 $CHCl_3$).

3.2. Thermal Pauson–Khand reaction

3.2.1. General procedure A

To a solution of acetylenic sulfoxide (0.45 mmol) in toluene (10 mL), $Co_2(CO)_8$ (0.48 mmol) was added. The formation of a dark red colored complex was observed and monitored by TLC. After 30 minutes of stirring at room temperature, a solution of the alkene (4.5 mmol) in toluene (5 mL) was added and the reaction mixture was heated at the specified temperature until no dicobalt hexacarbonyl complex could be observed by TLC. The solid suspension was filtered through Celite, and washed thoroughly with CH_2Cl_2. The combined organic extracts were evaporated under vacuum. The crude product was purified by column chromatography on Et_3N pre-treated silica gel (2.5% v/v) eluting with diethyl ether/hexane mixtures of increasing polarity to yield the corresponding cyclopentenone.

3.3. Amine N*-oxide promoted Pauson–Khand reaction*

3.3.1. General procedure B

To a solution of acetylenic sulfoxide (0.09 mmol) in CH_2Cl_2 (25 mL), $Co_2(CO)_8$ (0.1 mmol) was added. The formation of a dark red colored complex was observed and monitored by TLC. After 30 minutes of stirring at room temperature, the corresponding alkene was added (0.9 mmol) and the reaction mixture was cooled at −78°C. Then, solid amine *N*-oxide (6–10 equivalents) was added and the reaction was stirred at the specified temperature. The solid suspension was filtered through Celite and washed thoroughly with CH_2Cl_2. The combined organic extracts were evaporated under vacuum. The crude product was purified by column chromatography on Et_3N pre-treated silica gel (2.5% v/v) eluting with diethyl ether/hexane mixtures of increasing polarity to yield the corresponding cyclopentenone.

*3.4. Pauson–Khand reactions of (+)-(*S*)-1-hexynyl* p*-tolyl sulfoxide (**1b**) with norbornadiene*

The general procedure A (65°C for 27 h) using as reagents **1b** (200 mg, 0.9 mmol), toluene (30 mL), $Co_2(CO)_8$ (362 mg, 0.95 mmol) and norbornadiene (828 mg, 9 mmol), afforded 130 mg of **5bf** (46% yield) as a mixture of two diastereomers, separable by chromatography (1.6:1 dr) and 45 mg of **6bf** (23% yield) as a mixture of diastereomers (2.9:1 dr).

The general procedure B using as reagents **1b** (100 mg, 0.45 mmol), CH_2Cl_2 (22 mL), $Co_2(CO)_8$ (163 mg, 0.48 mmol), norbornadiene (414 mg, 4.5 mmol) and $NMO \cdot H_2O$ (605 mg, 4.5 mmol) (added portionwise at 0°C) afforded 23 mg (15%) of **5bf** and 30 mg of **6bf** (31%, 4.6:1 dr).

*3.4.1. (1*S*,2*S*,6*R*,7*R*)-4-Butyl-5-[(*S*)-4-tolylsulfinyl]tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (**5bf**-major)*

$[\alpha]_D^{23}$=−11.7 (*c* 1.4 $CHCl_3$). IR (film) ν=2960, 2880, 1710, 1600, 1085, 1050, 810, 620 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ=7.56, 7.35 (AB, J=8.3 Hz, 4H), 6.13 (s, 2H), 3.05 (d, J=7.7 Hz, 1H), 2.91 (s, 1H), 2.6–2.3 (m, 2H), 2.4 (s, 3H), 1.5–1.2 (m, 8H), 0.93 (t, J=6.9 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=206.3 (C), 170.6 (C), 151.3 (C), 141.7 (C), 138.6 (C), 137.8 (CH), 136.9 (CH), 130.02 (CH), 124.5 (CH), 53.4 (CH), 45.3 (CH), 43.8 (CH), 42.5 (CH), 41.1 (CH_2), 30.5 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.2 (CH_3), 13.6 (CH_3). MS (DIP-CI-NH_3) m/e=358 (M^++18, 100%), 340 (M^+, 1%), 252 (M^+−88, 3%), 236 (M^+−104, 5%). Conditions for HPLC analysis: Nucleosil C_{18} (25 cm) column, 60% CH_3CN, 0.7 mL/min, λ=254 nm, t_R (min)=22.43.

*3.4.2. (1*R*,2*R*,6*S*,7*S*)-4-Butyl-5-[(*S*)-4-tolylsulfinyl]tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (**5bf**-minor)*

$[\alpha]_D^{23}$=−12.4 (*c* 1.0 $CHCl_3$). IR (film) ν=2960, 2880, 1710, 1600, 1500, 1085, 1050, 810 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ=7.55, 7.35 (AB, J=8.1 Hz, 4H), 6.3–6.1 (m, 2H), 3.42 (s, 1H), 2.92 (s, 1H), 2.43 (s, 3H), 2.68, 2.25 (AB, J=7.7 Hz, 2H), 1.45–1.26 (m, 8H), 0.94 (t, J=6.5 Hz, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=207.3 (C), 171 (C), 150.1 (C), 140.2 (C), 138.8 (CH), 136.6 (CH), 130.1 (CH), 124.3 (CH), 53.4 (CH), 45.3 (CH), 43.8 (CH), 42.5 (CH), 41.1 CH_2). 30.5 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.2 (CH_3), 13.6 (CH_3). MS (DIP-CI-NH_3) m/e=358 (M^++18, 33%), 341 (M^++1, 2%), 236 (M^+−104, 100%). Conditions for HPLC analysis: Nucleosil C_{18} (25 cm) column, 60% CH_3CN, 0.7 mL/min, λ=254 nm, t_R (min)=23.30.

*3.4.3. 5-(1-Hydroxybutyl)tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (**6bf**)*

IR (film) ν=3450 (b), 2970, 2880, 1775, 1700, 1610, 730, 715 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ=6.24 (s, 1H), 4.55 (m, 1H), 2.94 (s, 1H), 2.78 (m, 1H), 2.38 (d, J=5 Hz, 1H), 2.09 (a, 1H), 1.75–1.3 (m, 9H), 0.98 (t, J=7 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ=209.1 (C), 184.9 (C), 138.2 (CH, minor), 137.8 (CH), 137.6 (CH), 137.3 (CH, minor), 132.9 (CH, minor), 132.1 (CH), 70.6 (CH), 70.5 (CH, minor), 53.6 (CH), 49.6 (CH), 43.4 (CH, minor), 43.2 (CH), 42.9 (CH, minor), 42.4 (CH), 41.4 (CH_2), 41.1 (CH_2, minor), 37.9 (CH_2), 18.6 (CH_2, minor), 18.4 (CH_2), 13.8 (CH_3). MS (DIP-EI) m/e=218 (M^+, 5%), 175 (M^+−43, 22%), 146 (M^+−72, 43%), 117 (M^+−101, 57%), 91 (M^+−127, 100%).

3.5. Pauson–Khand reactions of 1-hexynyl p*-tolyl (+)-(*S*)-sulfoxide (**1b**) with norbornene*

The general procedure A (65°C for 27 h) using as reagents **1b** (100 mg, 0.45 mmol), toluene (15 mL), $Co_2(CO)_8$ (163 mg, 0.48 mmol) and norbornene (423 mg, 4.5 mmol) afforded 52 mg of **5be** as a mixture of two diastereomers separable by chromatography (34%, 1.8:1 dr).

The general procedure B using as reagents **1b** (200 mg, 0.91 mmol), CH_2Cl_2, of $Co_2(CO)_8$ (342 mg, 0.1 mmol), norbornene (428 mg, 4.5 mmol) and NMO (640 mg, 0.54 mmol) afforded 14 mg (4%) of **5be**.

*3.5.1. (1*R*,2*S*,6*R*,7*S*)-4-Butyl-5-[(*S*)-4-tolylsulfinyl]tricyclo[5.2.1.0^{2,6}]dec-4-en-3-one (**5be**-major)*

$[\alpha]_D^{23}$=+29.4 (*c* 1.1 acetone). IR (film) ν=2950, 2870, 1705, 1085, 1050, 810 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ=7.54, 7.34 (AB, J=8.5 Hz, 4H), 2.86, 2.23 (AB, J=6 Hz, 2H), 2.61–2.46 (m, 2H), 2.43 (s, 3H), 2.4 (s, 1H), 1.93 (s, 1H), 1.56–1.19 (m, 8H), 0.93 (t, J=7 Hz, 3H), 0.81–0.79 (m, 2H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ=207.9 (C), 170.7 (C), 150.4 (C), 141.9 (C), 138.9 (C), 124.7 (CH), 130.1 (CH), 54.5 (CH), 46.2 (CH), 39.4 (CH), 37.8 (CH), 31.2 (CH_2), 30.6 (CH_2), 28.5 (CH_2), 28.2 (CH_2), 23.4 (CH_2), 22.8 (CH_2), 21.3 (CH_3), 13.7 (CH_3). MS (DIP-EI) m/e=342 (M^+, 2%), 325 (M^+−17, 100%), 283 (M^+−59, 21%), 203 (M^+−139, 2%).

*3.5.2. (1*S*,2*R*,6*S*,7*R*)-4-Butyl-5-[(*S*)-4-tolylsulfinyl]tricyclo[5.2.1.0 ^{2,6}]dec-4-en-3-one (**5be**-minor)*

$[\alpha]_D^{23}$=−24.5 (*c* 1.71 acetone). IR (film) ν=2980, 2890, 1725, 1095, 1060, 820 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.54, 7.35 (AB, J=8 Hz, 4H), 2.92 (d, J=4 Hz, 1H), 2.57, 2.12 (AB, J=5.5 Hz, 2H), 2.47–2.45 (m, 2H), 2.43 (s, 3H), 2.41 (d, J=4 Hz, 1H), 1.63–1.11 (m, 10H), 0.94 (t, J=7 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ=208.8 (C), 170.4 (C), 150.2 (C), 142.06, (C) 138.9 (C), 130.3 (CH), 124.6 (CH), 54.7 (CH), 46.6 (CH), 39.15 (CH), 39.3 (CH), 31.6 (CH_2), 30.6 (CH_2), 28.9 (CH_2), 28.2 (CH_2), 23.8 (CH_2), 22.9 (CH_2), 21.5 (CH_3), 13.8 (CH_3). MS (DIP-EI) m/e=342 (M^+, 12%), 325 (M^+−17, 100%), 283 (M^+−59, 25%), 251 (M^+−91, 1%), 139 (M^+−203, 13%).

*3.6. Pauson–Khand reaction of (+)-(*S*)-1-hexynyl* p*-tolyl sulfoxide (**1b**) with bicyclo[3.2.0]hept-6-ene*

The general procedure A (65°C for 12 h) using as reagents **1b** (200 mg, 0.9 mmol), toluene (20 mL), $Co_2(CO)_8$ (362 mg, 0.95 mmol) and bicyclo[3.2.0]hept-6-ene (846 mg, 9 mmol) in toluene (10 mL) afforded 110 mg (32%, 2:1 dr) of 4-butyl-5-[(*S*)-*p*-tolylsulfinyl]tricyclo[5.3.0.0^{2,6}]dec-4-en-3-one **5bg** and 65 mg (33%) of 5-(1-hydroxybutyl)tricyclo[5.3.0.0^{2,6}]dec-4-en-3-one **6bg** (1.2:1 dr).

*3.6.1. 4-Butyl-5-[(*S*)-*p*-tolylsulfinyl]tricyclo[5.3.0.0^{2,6}]dec-4-en-3-one (**5bg**)*

IR (film) ν=2960, 2880, 1710, 1600, 1500, 1090, 1050, 815 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ=7.35, 7.59 (AB, J=8 Hz, 4H), 3.05 (m, 1H), 2.7–0.95 (m, 18H), 2.42 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ=208.9 (C), 208.8 (C, minor), 172.5 (C, minor), 171.9 (C), 148.6 (C), 147.6 (C, minor), 142 (C), 137.9 (C), 130.1 (CH, minor), 130.0 (CH), 124.6 (CH, minor), 124.4 (CH), 49.1 (CH), 48.9 (CH, minor), 45.3 (CH), 40.6 (CH, minor), 39.6 (CH, minor), 39.4 (CH), 38.5 (CH), 32.9 (CH_2, minor), 32.8 (CH_2), 32.1 (CH_2), 30.8 (CH_2), 30.3 (CH_2, minor), 24.5 (CH_2, minor), 24.3 (CH_2), 23.7 (CH_2), 22.7 (CH_2), 21.4 (CH_3), 13.8 (CH_3). MS (DIP-CI-NH_3) m/e=360 (M^++18, 6%), 342 (M^+, 2%), 238 (M^+−105, 100%), 222 (M^+−120, 17%).

*3.6.2. 5-(1-Hydroxybutyl)tricyclo[5.3.0.0^{2,6}]dec-4-en-3-one (**6bg**)*

IR (film) ν=3400 (b), 2950, 2860, 1680, 1605 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$) δ=6.28 (major), 6.18 (minor) (s, 1H), 4.56 (m, 1H), 2.95–1.4 (m, 15H), 0.96 (t, J=7 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ=211.9 (C, minor), 211.8 (C), 186.5 (C), 185.9 (C, minor), 129.3 (CH, minor), 129.2 (CH), 70.9 (CH, minor), 69.9 (CH), 49.2 (CH), 49.0 (CH, minor), 44.6 (CH, minor), 44.5 (CH), 44.4 (CH), 43.9 (CH, minor), 40.0 (CH), 38.9 (CH, minor), 37.9 (CH_2), 37.6 (CH_2, minor), 32.8 (CH_2), 32.5 (CH_2), 32.4 (CH_2, minor), 24.7 (CH_2), 24.6 (CH_2, minor), 18.5 (CH_2, minor), 18.4 (CH_2), 13.9 (CH_3), 13.7 (CH_3, minor). MS (DIP-CI-NH_3) m/e=458 ($2M^+$+18, 20%), 441 ($2M^+$+1, 100%), 238 (M^++18, 73%), 221(M^++1, 11%).

*3.7. Pauson–Khand reaction of (+)-(*S*)-2-phenylethynyl* p*-tolyl sulfoxide (**1c**) with norbornene*

The general procedure A (2 h at room temperature, 2 h at 50°C, 12 h at 70°C and 7 h at 100°C) using as reagents **1c** (200 mg, 0.83 mmol), toluene (20 mL), $Co_2(CO)_8$ (310 mg, 0.92 mmol) and norbornene (781 mg, 8.3 mmol) afforded 160 mg of **5ce** (53%, 2.6:1 dr).

The general procedure B using as reagents **1c** (100 mg, 0.42 mmol), CH_2Cl_2 (10 mL), $Co_2(CO)_8$ (150 mg, 0.44 mmol), norbornene (395 mg, 4.2 mmol) and TMANO (189 mg, 2.52 mmol) gave 15 mg (10%) of **5ce** (1:1 dr).

*3.7.1. (1S,2R,6S,7R)-4-Phenyl-5-[(S)-4-tolylsulfinyl]tricyclo[5.2.1.0^{2,6}]dec-4-en-3-one (**5ce**-major)*

$[\alpha]_D^{23}$=−28.9 (*c* 1.3 $CHCl_3$). IR (film) ν=2970, 2890, 1720, 1090, 1060, 700 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ=7.43–7.25 (m, 9H), 3.05 (s, 1H), 2.78, 2.3 (AB, J=5 Hz, 2H), 2.49 (s, 1H), 2.38 (s, 3H), 1.35–1.1 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ=206.7 (C), 175.0 (C), 148.0 (C), 142.9 (C), 139.9 (C), 130.02 (CH), 129.3 (CH), 128.6 (CH), 124.2 (CH), 55.2 (CH), 46.2 (CH), 39.6 (CH), 39.5 (CH), 31.7 (CH_2), 29.1 (CH_2), 28.2 (CH_2), 21.4 (CH_3). MS (DIP-EI) m/e=363 (M^++1, 10%), 362 (M^+, 40%), 314 (M^+−48, 31%), 299 (M^+−63, 14%), 255 (M^+−107, 26%).

*3.7.2. (1R,2S,6R,7S)-4-Phenyl-5-[(S)-4-tolylsulfinyl]tricyclo[5.2.1.0^{2,6}]dec-4-en-3-one (**5ce**-minor)*

$[\alpha]_D^{23}$=−20.9 (*c* 1.1 $CHCl_3$). IR (film) ν=2980, 2900, 1720, 1090, 1060, 840, 710 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$,) δ=7.45–7.15 (m, 9H), 3.34, 2.47 (AB, J=5.8 Hz, 2H), 2.51 (s, 1H), 2.36 (s, 3H), 2.1 (s, 1H), 1.57–1.25 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ=175.2 (C), 148.1 (C), 142.0 (C), 139.5 (C), 129.9 (CH), 129.2 (CH), 128.7 (CH), 124.2 (CH), 54.9 (CH), 46.3 (CH), 40.2 (CH), 38.1 (CH), 31.3 (CH_2), 28.7 (CH_2), 28.3 (CH_2), 21.3 (CH_3). MS (DIP-EI) m/e=363 (M^++1, 10%), 362 (M^+, 40%), 314 (M^+−48, 31%), 299 (M^+−63, 15%), 255 (M^+−107, 27%).

*3.8. (1R,2S,6S,7S)-4-Butyltricyclo[5.2.1.0 ^{2,6}]dec-4-en-3-one [(+)-**7be**]*

(a) To a solution of the adduct **5be**-major (100 mg, 0.3 mmol), in ethanol (10 mL) was added Raney-Ni (50% suspension in water, 1.2 mmol) in ethanol (5 mL). The reaction mixture was stirred at room temperature until no starting material was observed by TLC. The suspension was filtered through Celite, washed thoroughly with CH_2Cl_2 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on Et_3N pre-treated silica gel (2.5% v/v) eluting with diethyl ether/hexane mixtures of increasing polarity to yield 50 mg of (+)-**7be** as an oil (85% yield, 54% ee by GC). $[\alpha]_D^{23}$=+90.1 (*c* 1.4 $CHCl_3$). (b) The same procedure using as reagents **5bf**-major (90 mg 0.3 mmol), ethanol (10 mL) and Raney-Ni (1.2 mmol), afforded 31 mg of (+)-**7be** as an oil (56% yield, 75% ee by GC). $[\alpha]_D^{23}$=+108.3 (*c* 1.5 $CHCl_3$). Conditions for chiral GC analysis: Cyclodex-β (50 m, 0.25 mm ID) column, 150°C, t_R (min)=83.0 (minor), 85.2 (major). IR (film) ν=2950, 2870, 1700, 1630, 1450, 1185, 1050 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ=7.16 (m, 1H), 2.55 (s, 1H), 2.35 (s, 1H), 2,16 (m, 2H), 1.6–1.27 (m, 12H), 0.94 (t, J=7 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ=211.2 (C), 158.6 (CH), 149.3 (C), 53.8 (CH), 48.1 (CH), 38.9 (CH), 37.9 (CH), 30.9 (CH_2), 29.9 (CH_2), 28.9 (CH_2), 28.4 (CH_2), 24.3 (CH_2), 23.4 (CH_2), 13.8 (CH_3). MS (DIP-CI-NH_3) m/e=222 (M^++18, 100%), 205 (M^++1, 45%).

*3.9. (1S,2R,6R,7R)-4-Butyltricyclo[5.2.1.0^{2,6}]dec-4-en-3-one [(−)-**7be**]*

The procedure described for (+)-**7be** using as a reagents **5be**-minor (58 mg, 0.17 mmol), ethanol (6 mL) and Raney-Ni (6.3 mmol), afforded 19 mg of (−)-**7be** (56%, 54% ee by GC) as an oil. $[\alpha]_D^{23}$=−72.7 (*c* 1.0 $CHCl_3$). Conditions for chiral GC analysis: Cyclodex-β (50 m, 0.25 mm ID) column, 150°C, t_R (min)=82.5 (major), 84.9 (minor). Spectroscopic data identical to those of (+)-**7be**.

*3.10. (1S,2S,6R,7R)-4-Butyl-5-*p*-tolylsulfanyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one [(+)-**8bf**]*

To a cold (−40°C) suspension of **5bf**-major (73 mg, 0.22 mmol) and NaI (0.70 mmol) in acetone (6.5 mL) was added trifluoroacetic anhydride (1.1 mmol). The reaction mixture was stirred at this temperature until no starting material was observed. The reaction was quenched with sat. Na_2SO_3 and $NaHCO_3$. The acetone was removed under vacuum and the aqueous phase was extracted with diethyl ether. The organic

phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on Et_3N pre-treated silica gel (2.5% v/v) eluting with diethyl ether/hexane mixtures of increasing polarity to yield 50 mg of (+)-**8bf** (70%). $[\alpha]_D^{23}$=+209.1 (*c* 0.1 $CHCl_3$). IR (film) ν=2950, 2870, 1690, 1590, 1490, 810 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ=7.43, 7.19 (AB, J=8.3 Hz, 4H), 6.06, 5.81 (ABXY, J=5.64 Hz, J′=3 Hz, 2H), 3.89 (s, 1H), 2.61 (d, J=5 Hz, 1H), 2.46 (s, 1H), 2.37 (s, 3H), 2.3–2.15 (m, 3H), 1.5–1.3 (m, 6H), 0.90 (t, J=6.9 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ=204.9 (C), 171.4 (C), 142.9 (C), 139.7 (C), 137.5 (CH), 137.3 (CH), 134.9 (CH), 130.04 (CH), 52.8 (CH), 49.7 (CH), 43.8 (CH), 43.1 (CH), 41.1 (CH_2), 29.7 (CH_2), 23.8 (CH_2), 22.8 (CH_2), 21.2 (CH_3), 13.9 (CH_3). MS (DIP-CI-NH_3) m/e=342 (M^++18, 56%), 325 (M^++1, 100%).

*3.11. (1*R,*2*R,*6*S,*7*S*)-4-Butyl-5*-p-*tolylsulfanyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one [(−)-**8bf**]*

The procedure described for (+)-**8bf** starting from **5bf**-minor (50 mg, 0.14 mmol), afforded 15 mg of (−)-**8bf** (33%). $[\alpha]_D^{23}$=−199.1 (*c* 0.9 $CHCl_3$). Spectroscopic data identical to those of (+)-**8bf**.

*3.12. (1*S,*2*R,*6*S,*7*R*)-4-Phenyl-5*-p-*tolylsulfanyltricyclo[5.2.1.0^{2,6}]dec-4-en-3-one [(−)-**8ce**]*

The procedure described for (+)-**8bf** (3 h, −20°C) starting from **5ce**-major (81 mg, 0.23 mmol) gave 36 mg (45%) of (−)-**8ce**. $[\alpha]_D^{23}$=−82.1 (*c* 1.9 $CHCl_3$). IR (film) ν=2940, 2850, 1675, 1550, 1480, 1290, 800, 740, 690 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ=7.51–7.18 (m, 9H), 2.35, 2.65 (AB, J=5.7 Hz, 2H), 2.45 (s, 1H), 2.39 (s, 3H), 2.15 (s, 1H), 1.55–0.80 (m, 6H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ=204.4 (C), 173.5 (C), 140 (C), 135.1 (CH), 130.0 (CH), 128.9 (CH), 128.1 (CH), 127.9 (CH), 54.8 (CH), 50.04 (CH), 39.6 (CH), 39.2 (CH), 31.2 (CH_2), 28.8 (CH_2), 28.2 (CH_2), 21.3 (CH_3) ppm. MS (DIP-CI-NH_3) m/e=364 (M^++18, 100%), 347 (M^++1, 82%).

*3.13. (1*R,*2*S,*6*R,*7*S*)-4-Phenyl-5*-p-*tolylsulfanyltricyclo[5.2.1.0^{2,6}]dec-4-en-3-one [(+)-**8ce**]*

The procedure described for (+)-**8bf** (30 min, −40°C) starting from **5ce**-minor (95 mg, 0.26 mmol) gave 50 mg (55%) of (+)-**8ce**. $[\alpha]_D^{23}$=+34.5 (*c* 1.1 $CHCl_3$). Spectroscopic data identical to those of (−)-**8ce**.

*3.14. (1*R,*2*R,*6*R,*7*S*)-4-Butyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one [(−)-**7bf**]*

To a cold (−60°C) solution of the sulfide (+)-**8bf** (50 mg, 0.15 mmol) in diethyl ether, DIBALH (1.2 mmol, 1 M in hexanes) was added. The reaction was stirred at this temperature until no starting material was observed by TLC. The reaction was quenched by dropwise addition of MeOH and the organic phase was washed with saturated aqueous $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed under vacuum. To the crude (45 mg of alcohol) dissolved in MeOH (6 mL), were added two drops of aqueous 35% HCl, $HgCl_2$ (84 mg, 0.31 mmol) and HgO (32 mg, 0.15 mmol). The reaction was stirred at room temperature until no starting material was observed by TLC (24 h). The solid suspension was filtered through Celite, and washed thoroughly with diethyl ether. The combined organic extracts were evaporated under vacuum. The crude product was purified by column chromatography on Et_3N pre-treated silica gel (2.5% v/v) eluting with diethyl ether/hexane mixtures of increasing polarity to afford 15 mg (63%, 71% ee by GC) of (−)-**7bf**. $[\alpha]_D^{23}$=−58.4 (*c* 0.63 $CHCl_3$). Conditions for chiral GC analysis: Cyclodex-β (50 m, 0.25 mm ID) column, 160°C, t_R (min)=47.05 (major), 47.9 (minor). IR (film) ν=3090, 2980, 2940, 2890,

1705, 1470, 1330, 1220, 1150, 860 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ=7.16 (m, 1H), 6.17–6.31 (m, 2H), 2.90 (s, 1H), 2.69 (m, 2H), 2.28 (d, J=5 Hz, 1H), 2.16 (t, J=7 Hz, 2H, 1.15–1.55 (m, 6H), 0.90 (t, J=7 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ=158.7 (CH), 150.9 (C), 138.3 (CH), 137.0 (CH), 52.5 (CH), 47.6 (CH), 43.6 (CH), 42.9 (CH), 41.2 (CH_2), 29.9 (CH_2), 24.6 (CH_2), 22.5 (CH_2), 13.8 (CH_3). MS (DIP-CI-NH_3) m/e=237 (M^++35, 56%), 220 (M^++18, 100%), 203 (M^++1, 9%).

*3.15. (1S,2S,6S,7R)-4-Butyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one [(+)-**7bf**]*

The procedure described for (−)-**7bf** starting from (−)-**8bf** (15 mg, 0.05 mmol) afforded 7 mg (87%, 71% ee by GC) of (+)-**7bf**. Conditions for chiral GC analysis: Cyclodex-β (50 m, 0.25 mm ID) column, 160°C, t_R (min)=47.2 (minor), 48.02 (major). Spectroscopic data identical to those of (−)-**7bf**.

*3.16. (1R,2S,6S,7S)-4-Phenyltricyclo[5.2.1.0^{2,6}]dec-4-en-3-one [(+)-**7ce**]*

The procedure described for (−)-**7bf** starting from (−)-**8ce** (34 mg, 0.1 mmol) after 24 h afforded 16 mg (89%, 25% ee) of (+)-**7ce**. $[\alpha]_D^{23}$=+15.6 (*c* 1.1 benzene). Conditions for chiral GC analysis: Cyclodex-β (50 m, 0.25 mm ID) column, 150°C, t_R (min)=51.8 (minor), 53.7 (major). IR (film) ν=3020, 2940, 2860, 1690, 1480, 750 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ=7.72–7.64 (m, 3H), 7.38–7.26 (m, 3H), 2.71 (m, 1H), 2.5 (s, 1H), 2.35 (d, J=7 Hz, 1H), 2.28 (s, 1H), 1.8–0.95 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ=208.8 (C), 160.1 (CH), 145.9 (C), 128.2 (CH), 126.9 (CH), 54.8 (CH), 47.6 (CH), 39.3 (CH), 38.2 (CH), 31.2 (CH_2), 29.0 (CH_2), 28.3 (CH_2). MS (DIP-CI-NH_3) m/e=242 (M^++18, 82%), 225 (M^++1, 100%), 224 (M^+, 4%).

*3.17. (1S,2R,6R,7R)-4-Phenyltricyclo[5.2.1.0^{2,6}]dec-4-en-3-one [(−)-**7ce**]*

The procedure described for (−)-**7bf** (24 h) starting from (+)-**8ce** (50 mg, 0.14 mmol) afforded 15 mg (86%, 9% ee by GC) of (−)-**7ce**. $[\alpha]_D^{23}$=−4.2 (*c* 1.1 benzene). Conditions for chiral GC analysis: Cyclodex-β (50 m, 0.25 mm ID) column, 150°C, t_R (min)=51.4 (major), 53.4 (minor). Spectroscopic data identical to those of (+)-**7ce**.

3.18. Pauson–Khand reaction of (+)-(R)-ethynyl p*-tolyl sulfoxide **1d** with norbornene*

To a solution of **1d** (100 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) was added $Co_2(CO)_8$ (205 mg, 0.6 mmol). After 10 min of stirring at room temperature, norbornene (282 mg, 3 mmol) was added and the mixture cooled down to −78°C. NMO (211 mg, 1.8 mmol) was added and the mixture was allowed to warm up to 0°C. Then, it was cooled again to −78°C and more NMO (211 mg, 1.8 mmol) was added. The mixture was allowed to reach room temperature and stirred for 1 h. The crude was evaporated and chromatographed affording 12 mg (9% yield) of **4de** as a mixture of diastereomers (1.2:1 by ^{13}C NMR). IR (film) ν_{max} =2960, 2880, 1700, 1600, cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ=7.95–8 (m, 1H), 7.65, 7.28 (AB, J=8 Hz, 4H), 2.85–2.7 (m, 1H), 2.5–1 (m, 9H), 2.39 (s, 3H). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ=203.7 (C), 163.8 (CH), 142.1 (C, major), 142.2 (C, minor), 129.9 (CH), 125.1 (CH, minor), 124.9 (CH, major), 56.1 (CH, major), 56.0 (CH, minor), 49.2 (CH, major), 48.9 (CH, minor), 39.4 (CH, major), 39.3 (CH, minor), 38.4 (CH, major), 38.5 (CH, minor), 31.5 (CH_2, major), 31.3 (CH_2, minor), 29.1 (CH_2, major), 29.06 (CH_2, minor), 28.1 (CH_2, major), 28.1 (CH_2, minor), 21.5 (CH_3, minor), 21.4 (CH_3, major). EM (CI-NH_3) m/e=321 (M^++35, 1%), 304 (M^++18, 100%), 287 (M^++1, 2%).

3.19. X-Ray diffraction analysis of **5be**-minor

The crytal data for **5be**-minor are as follows. Crystal dimensions: 0.7×0.6×0.4 mm. Empirical formula $C_{21}H_{26}O_2S$. Molecular weight 342.48. The three-dimensional intensity data were collected on a Enraf Nonius CAD4 diffractometer (λ=0.71069 Å) at 293(2) K yielding 3231 independent reflections. Calculated density 1.241 g/cm^3. Crystal system: triclinic. Space group *P*1 (No. 2). Lattice parameters: *a*=8.690(1) Å, *b*=10.517(2) Å, *c*=10.820(1) Å, α=108.35(1)°, β=96.23(1)°, γ=98.18(1)°, *V*=916.6(2) Å^3, *Z*=2, *F*(000)=368. The structure was solved by the direct methods (SHELXS-86)[28] and refined by least-squares on F^2 of all reflections (SHELXL-93).[29] Data/restraints/parameters: 3230/0/217. Goodness-of-fit on F^2: 1.091. Final *R* indices[$I>2\sigma(I)$]: $R(F)$=0.0369, $Rw(F^2)$=0.1005. *R* indices (all data): $R(F)$=0.0426, $Rw(F^2)$=0.1062.

3.20. X-Ray diffraction analysis of **5ce**-major

The crytal data for **5ce**-major are as follows. Crystal dimensions 0.5×0.5×0.2 mm. Empirical formula $C_{23}H_{22}O_2S$. Molecular weight 362.47. The three-dimensional intensity data were collected on a Enraf Nonius CAD4 diffractometer (λ=0.71069 Å) at 293(2) K yielding 1894 independent reflections. Calculated density 1.282 g/cm^3. Crystal system: orthorhombic. Space group $P2_12_12_1$ (No. 19). Lattice parameters: *a*=9.984(1) Å, *b*=10.1864(5) Å, *c*=18.467(3) Å, *V*=1878.1(4) Å^3, *Z*=4, *F*(000)=768. The structure was solved by the direct method (SHELXS-86)[28] and refined by least-squares on F^2 of all reflections (SHELXL-93).[29] Data/restraints/parameters: 1894/0/235. Goodness-of-fit on F^2: 1.075. Final *R* indices [$I>2\sigma(I)$]: $R(F)$=0.0278, $Rw(F^2)$=0.0803. *R* indices (all data): $R(F)$=0.0324, $Rw(F^2)$=0.0816.

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