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Bicyclic Cyclopentenones *via* the Combination of an Iridium-Catalyzed Allylic Substitution with a Diastereoselective Intramolecular Pauson–Khand Reaction

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Abstract: Enantioselective syntheses of bicyclic cyclopentenones are described. Key steps are an iridium-catalyzed allylic substitution and an intramolecular diastereoselective Pauson–Khand reaction. The diastereoselectivity of the Pauson–Khand reaction was found to be crucially dependent on the unit connecting the propargylic and the olefinic parts of the precursor. Very high degrees of diastereoselection were obtained with an NBoc unit as connector. This methodology has been illustrated by application within an enantioselective formal total synthesis of (−)-α-kainic acid.

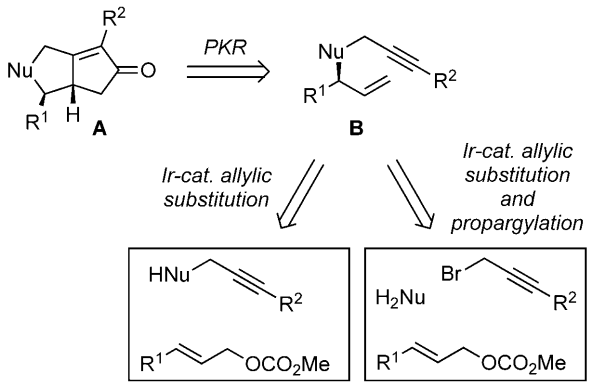
Keywords: alkaloids; alkyne ligands; allylic substitution; asymmetric catalysis; iridium; Pauson–Khand reaction

Introduction

Cyclopentenones are of interest as building blocks for biologically active cyclopentanoids.[1] In relation to this, the Pauson–Khand (PK) reaction is perhaps the most useful method for the direct synthesis of cyclopentenones,[2] as testified by numerous applications in natural product synthesis.[3] Asymmetric PK reactions have been based on the use of chiral auxiliaries,[4] chiral metal complexes,[5] or chiral promotors.[6] In addition, diastereoselective PK reactions with chiral cyclization precursors have been reported.[3c,7]

Jeong et al.[8] have published syntheses of bicyclic cyclopentenones **A** (Scheme 1) based on generation of the precursor **B**, $R^1 = H$, by a Pd-catalyzed allylic substitution and cyclization of **B** in an Rh-catalyzed PK reaction; both steps were accomplished in a domino fashion with a two-metal catalyst system.[9] Additionally, Evans et al. were able to achieve an ingenious domino allylic alkylation[10]/PK reaction with a single Rh catalyst.[11]

We became interested in the Jeong–Evans approach because of a long-standing interest in the PK reaction,[3e–k,5a,f,6a,b,12] biologically active cyclopentanoids[13] and allylic substitutions. In relation to this and following on from the previous studies, there remained one



Scheme 1. Retrosynthetic analysis.

area for development and improvement: asymmetric catalysis. We envisioned an enantioselective approach to cyclopentenones **A** by combining the intramolecular PK reaction of 1,6-enynes **B** with an Ir-catalyzed allylic substitution.[14] The latter could be carried out either directly by reaction of an allylic carbonate with a nucleophile containing a propargylic moiety (Scheme 1, *left box*) or by a two-step sequence involving an Ir-catalyzed allylic substitution followed by propargylation (*right box*). Both of these approaches were required, since Ir-catalyzed allylic substitution proceeds with low selectivity in the cases where $R^2 =$ H. Allylic substitutions with substituted propargylic derivatives, $R^2 \neq$ H, have only recently been reported to give excellent selectivities following work by You and from our own laboratories in a synthesis of (−)-α-kainic acid.[3f,15] We now describe in detail the development of our Ir-catalyzed allylic substitution/PK system and, in turn, the application of this developed strategy in a formal synthesis of (−)-α-kainic acid (Figure 1).

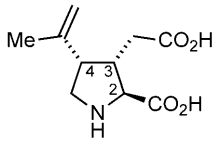


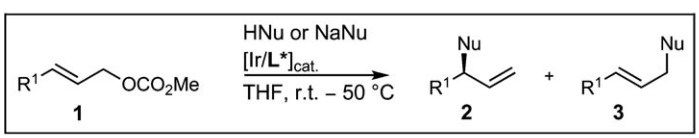
Figure 1. (−)-α-Kainic acid.

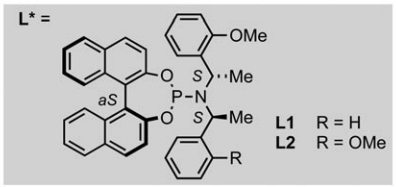
Results and Discussion

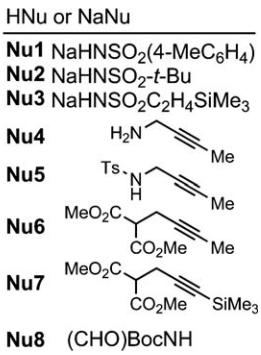
Ir-catalyzed allylic substitution techniques were introduced in 1997.[16] Today enantiomeric excesses of >90% can be achieved routinely.[14] The commonly applied catalyst is prepared from a mixture of $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) and a phosphoramidite by reaction with base, which effects C–H activation. The phosphoramidite ligands **L1** and **L2**, used in our work, were introduced by Alexakis.[17]

As nucleophiles, sodium salts of sulfonamides (**Nu1**–**Nu3**), propargylic amines (**Nu4**[3f] and **Nu5**[18]), and malonates tethered with alkyne moieties (**Nu6** and **Nu7**) were employed (Table 1). If not stated otherwise, reactions were carried out with 2 mol% of

Table 1. Ir-catalyzed allylic substitution.[a]



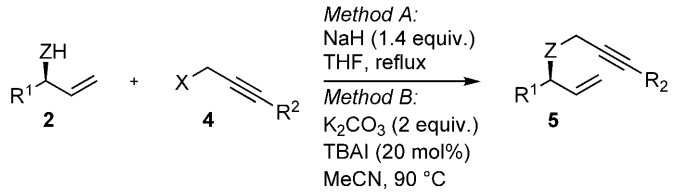




Entry	L*	R^1	HNu or NaNu (equiv.)		Temp.	Time [h]	Ratio[b] **2:3**		**2** Yield[c] [%]	*ee*[d] [%]
1	*ent*-**L2**	Ph	**Nu1**	2.5	50 °C	2	90:10	*ent*-**2a**	75	98
2	*ent*-**L1**	*n*-Pr	**Nu1**	2.5	50 °C	3	91:9	*ent*-**2b**	61	93
3	**L2**	Ph	**Nu2**	2.5	50 °C	1	94:6	**2c**	67	97
4	*ent*-**L1**	*n*-Pr	**Nu2**	2.5	50 °C	1	93:7	*ent*-**2d**	66	92
5	**L2**	Ph	**Nu3**	1.2	50 °C	2	77:23[e]	**2e**	60	97
6	**L2**	Ph	**Nu4**	1.2	rt	8.5	n.d.	**2f**	60	99
7	**L2**	Ph	**Nu5**	1.2	rt	6	93:7	**2g**	88	98
8	*ent*-**L1**	Ph	**Nu5**	1.2	50 °C	5	87:13	*ent*-**2g**	83	96
9	**L2**	Ph	**Nu6**	1.2	r.t.	5	93:7	**2h**	72	99
10	**L2**	Ph	**Nu7**	1.2	r.t.	3	95:5	**2i**	69	99
11	**L2**	CH_2OTAM[f]	**Nu8**	1.2	40 °C	1.5	81:19	**2j**	62	98

[a] $[Ir/L^*]_{cat.} = [Ir(COD)Cl]_2$ (2 mol%), **L*** (4 mol%), TBD (8 mol%).
[b] Determined by ^{1}H NMR of the crude product.
[c] Isolated branched product.
[d] Determined by chiral HPLC or chiral GC.
[e] Ratio between **2** and (**3** + diallylated branched product).
[f] TAM = *tert*-amyl.

Table 2. Propargylation of chiral sulfonamides, allylamines and malonates.



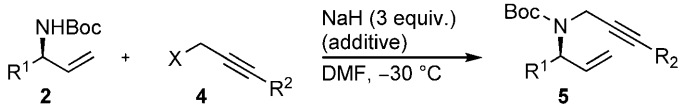
Entry		**2**[a]			**4**			Method	Time [h]	Product **5**	
		R^1	Z		X	R^2	(equiv.)				Yield [%]
1	*ent*-**2a**	Ph	$NSO_2(4\text{-}MeC_6H_4)$	**4a**	Br	H	10	B	2	*ent*-**5a**	93
2	*ent*-**2b**	*n*-Pr	$NSO_2(4\text{-}MeC_6H_4)$	**4a**	Br	H	10	B	2.5	*ent*-**5b**	98
3	*ent*-**2c**	Ph	NSO_2tBu	**4a**	Br	H	10	B	6	*ent*-**5c**	97
4	*ent*-**2e**	Ph	$NSO_2C_2H_4SiMe_3$	**4a**	Br	H	10	B	2	*ent*-**5d**	92
5	**2k**	Ph	NCH_2Ph	**4a**	Br	H	30	A	4	**5e**	89
6	**2l**	Ph	$C(CO_2Me)_2$	**4a**	Br	H	2.4	A	12	**5f**	82
7[b]	*ent*-**2m**	Ph	$N(4\text{-}MeOC_6H_4)$	**4a**	Br	H	9	B	19	*ent*-**5g**	91
8[b]	*ent*-**2m**	Ph	$N(4\text{-}MeOC_6H_4)$	**4d**	OMs	Me	3.3	B	48	*ent*-**5h**	67
9[b]	*ent*-**2n**	CH_2OTr	$N(4\text{-}MeOC_6H_4)$	**4a**	Br	H	9	B	24	*ent*-**5i**	84
10[b]	*ent*-**2n**	CH_2OTr	$N(4\text{-}MeOC_6H_4)$	**4d**	OMs	Me	3	B	48	*ent*-**5j**	76

[a] Enantiomeric purities of the used starting materials: **2k** (92% *ee*), **2l** (95% *ee*), *ent*-**2m** (96% *ee*), *ent*-**2n** (94% *ee*).
[b] Experiment carried out at 60 °C with K_2CO_3 (1.2 equiv.) and without TBAI (TBAI = tetrabutylammonium iodide, Tr = triphenylmethyl).

$[Ir(COD)Cl]_2$, 4 mol% of ligand (**L1** or **L2**) and 8 mol% of TBD (TBD = 1,5,7-triazabicyclo[4.4.0]dec-5-ene) in THF. With the sulfonamide salt nucleophiles, **Nu1–Nu3**, the carbonates **1a**[17b] and **1b**[19] provided the branched products **2** in good yields (60–75%) and high enantiomeric excesses of 92–98% *ee* (Table 1, entries 1–5). Reactions with the nucleophiles **Nu4**–**Nu7** were carried out under "salt-free" conditions,[20] and provided even better results (Table 1, entries 6–10). The reaction with *N*,*N*-diacylamine **Nu8**[20] and carbonate **1c** proceeded at 40 °C with a good branched to linear ratio and delivered the desired product **2j** with 98% *ee* (Table 1, entry 11).

The propargylation of amines[21] and sulfonamides[22] with propargylic bromides or mesylates was carried out according to reported general procedures. For the sulfonamides **2a–c** and **2e** a protocol of Sylvester and Chirik,[21b] which was improved by nucleophilic catalysis with TBAI, was used (Table 2, en-

Table 3. Popargylation of *N*-Boc-allylamines.



Entry		**2**[a]		**4**			Additive (equiv.)	Time [h]	Product **5**	
		R^1		X	R^2	(equiv.)				Yield [%]
1	*ent*-**2o**	Ph	**4a**	Br	H	10	–	14	*ent*-**5k**	93
2	**2o**	Ph	**4d**	OMs	Me	3	–	48	**5l**	22
3	*ent*-**2o**	Ph	**4b**	Br	Me	10	–	2.5	*ent*-**5l**	86
4	*ent*-**2o**	Ph	**4c**	Br	$SiMe_3$	10	–	4	*ent*-**5m**	83
5	**2p**	$CH_2OTBDPS$[e]	**4b**	Br	Me	10	15-crown-5 (3)[b]	5	**5n**	82
6[c]	**2p**	$CH_2OTBDPS$	**4b**	Br	Me	10	15-crown-5 (3)[b]	5	**5n**	82
7	**2q**[d]	CH_2OTAM	**4b**	Br	Me	10	15-crown-5 (3)[b]	2.75	**5o**	94

[a] Enantiomeric purities of the used starting materials: *ent*-**2o/2o** (95% *ee*), **2p** (96% *ee*), **2q** (98% *ee*).
[b] No conversion was observed without 15-crown-5.
[c] Experiment carried out at –20 °C.
[d] The formyl group of **2j** was cleaved with a catalytic amount of KOH in MeOH to give **2q** in quantitative yield.
[e] Boc = *tert*-butoxycarbonyl, TBDPS = *tert*-butyldiphenylsilyl.

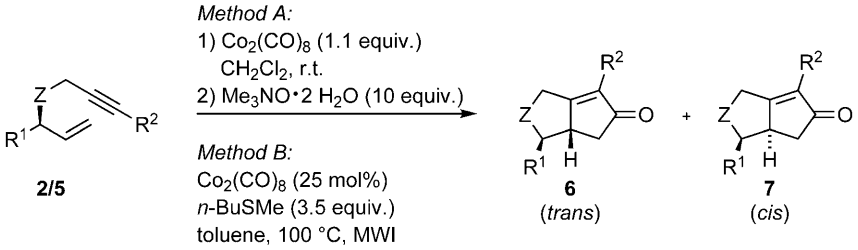
tries 1–4). Reaction times could be shortened to <6 h and yields of **5a–5d** improved to 92–98%.

With the allylamine **2k**[23] and sodiomalonate **2l**[23] as nucleophiles, the yields of the 1,6-enynes **5e** and **5f** (Table 2, entries 5 and 6) were slightly lower (82–89%). For the PMP-protected allylamines **2m**[24] and **2n**[25] the *N*-alkylations were carried out with propargyl bromide (**4a**) and the mesylate **4d**[26] (Table 2, entries 7–10). With the latter the reaction times were much longer than with the bromide, and the yields were slightly lower.

The propargylation of the *N*-Boc-allylamines **2** initially met with difficulties because of a [1,3]-H-shift of the product **5** to give an enamide. Formation of potassium amides with KO-*t*-Bu or KHMDS in conjunction with etheral solvents failed to give good results. Finally, the combination of NaH and DMF and a reaction temperature of -30 °C was found to be the method of choice. Under these optimized conditions the 1,6-enynes **5k–5m** were obtained in 83–93% yield (Table 3, entries 1, 3 and 4),[27] however when the mesylate **4d** was used with **2o**[27] (Table 3, entry 2) the yield were only 22%. The carbamates **2p**[28] and **2q** failed to react under these conditions. However, addition of 15-crown-5 initiated a fast reaction (Table 3, entries 5–7). Attempted alkylation of a carbamate **2** ($R^1 = n$-Pr) with propargyl bromide (**4a**) only gave rise to mixtures of unidentified product.

Despite the emergence of a series of Ti-,[5d,29] Ir-,[5e,30] and Rh-mediated[9b,31] PK methods, work within the laboratory of one us[12] has focused on the development of a series of Co-based techniques, and,

Table 4. Intramolecular Pauson–Khand reactions.



Entry	Starting Material	R^1	Z	R^2	Method	Time [h]	Ratio[a] *trans*/*cis*		**6**+**7** Yield [%]
1	**5a**	Ph	$NSO_2(4\text{-}MeC_6H_4)$	H	A	3.5	78:22	**a**	68
2	*ent*-**5b**	*n*-Pr	$NSO_2(4\text{-}MeC_6H_4)$	H	A	21	66:34	*ent*-**b**	69
3	**2g**	Ph	$NSO_2(4\text{-}MeC_6H_4)$	Me	A	4.5	69:31	**c**	72
4	**5c**	Ph	NSO_2-*t*-Bu	H	A	3.5	82:18	**d**	65
5	**5c**	Ph	NSO_2-*t*-Bu	H	B	0.33	71:29	**d**	85
6	*ent*-**5d**	Ph	$NSO_2C_2H_4SiMe_3$	H	A	3	95:05	*ent*-**e**	50
7[b]	**5e**	Ph	NBn[g]	H	B	0.17	100:0	**f**	72
8	**5f**	Ph	$C(CO_2Me)_2$	H	A	19.5	97:03	**g**	82
9[c]	**5f**	Ph	$C(CO_2Me)_2$	H	B	0.33	96:04	**g**	59
10[d]	**5g**	Ph	$N(4\text{-}MeOC_6H_4)$	H	A	6	100:0	**h**	66
11[b]	**5g**	Ph	$N(4\text{-}MeOC_6H_4)$	H	B	0.17	100:0	**h**	56
12	*ent*-**5h**	Ph	$N(4\text{-}MeOC_6H_4)$	Me	A	4	100:0	*ent*-**i**	59
13	*ent*-**5i**	CH_2OTr	$N(4\text{-}MeOC_6H_4)$	H	A	3.5	100:0	*ent*-**j**	42
14	*ent*-**5j**	CH_2OTr	$N(4\text{-}MeOC_6H_4)$	Me	A	6	100:0	*ent*-**k**	39
15	*ent*-**5k**	Ph	NBoc	H	A	7	100:0	*ent*-**l**	64
16	*ent*-**5k**	Ph	NBoc	H	B	0.17	100:0	*ent*-**l**	44
17	*ent*-**5l**	Ph	NBoc	Me	A	16	66:34	*ent*-**m**	46
18	*ent*-**5m**	Ph	NBoc	TMS	A	8.5	100:0	*ent*-**n**	82
19[e]	**5n**	$CH_2OTBDPS$	NBoc	Me	A	24	100:0	**o**	49
20[f]	**5n**	$CH_2OTBDPS$	NBoc	Me	A	48	90:10	**o**	51
21	**5o**	CH_2OTAM	NBoc	Me	A	9	n.d.	**p**	64

[a] Determined by ^{1}H NMR of the filtered crude product or isolation of the diastereoisomers.
[b] 20 mol% $Co_2(CO)_8$ and 1.2 equiv. *n*-BuSMe were used.
[c] *n*-DodSMe was used as promotor.
[d] $NMO{\cdot}H_2O$ was used as promotor.
[e] 5 equiv. $Me_3NO{\cdot}2\,H_2O$ were added at -10 °C, the mixture warmed up to room temperature, and this procedure repeated.
[f] 10 equiv. $Me_3NO{\cdot}2\,H_2O$ were added at -10 °C and the mixture warmed up to room temperature.
[g] Bn = benzyl, Tr = triphenylmethyl.

indeed, the establishment of new catalytic methods.[32] Accordingly, the intramolecular Pauson–Khand reactions[2] of the 1,6-enynes were carried out in stoichiometric (Table 4, method A) or catalytic mode (Table 4, method B).[32] In the former, amine *N*-oxides ($Me_3NO{\cdot}2\,H_2O$ or $NMO{\cdot}H_2O$)[33] were used as promotors, in the latter, sulfides (*n*-BuSMe[34] or *n*-DodSMe[35]) were used as promotors in a closed microwave vessel (Table 4, entries 5, 7, 9, 11 and 16).

The diastereomeric cyclopentenones were obtained in moderate to good yields (39–85%). The major compound in all experiments was the *trans*-isomer **6** (Table 4). The relative configurations of several cyclopentenones were determined by X-ray crystal structure analysis (Figure 2). Configurations of all other compounds were assigned by analogy.

Diastereomer ratios, *trans*-**6**/*cis*-**7**, varied considerably (66:34 to 100:0). With the exception of **5d**, the sul-

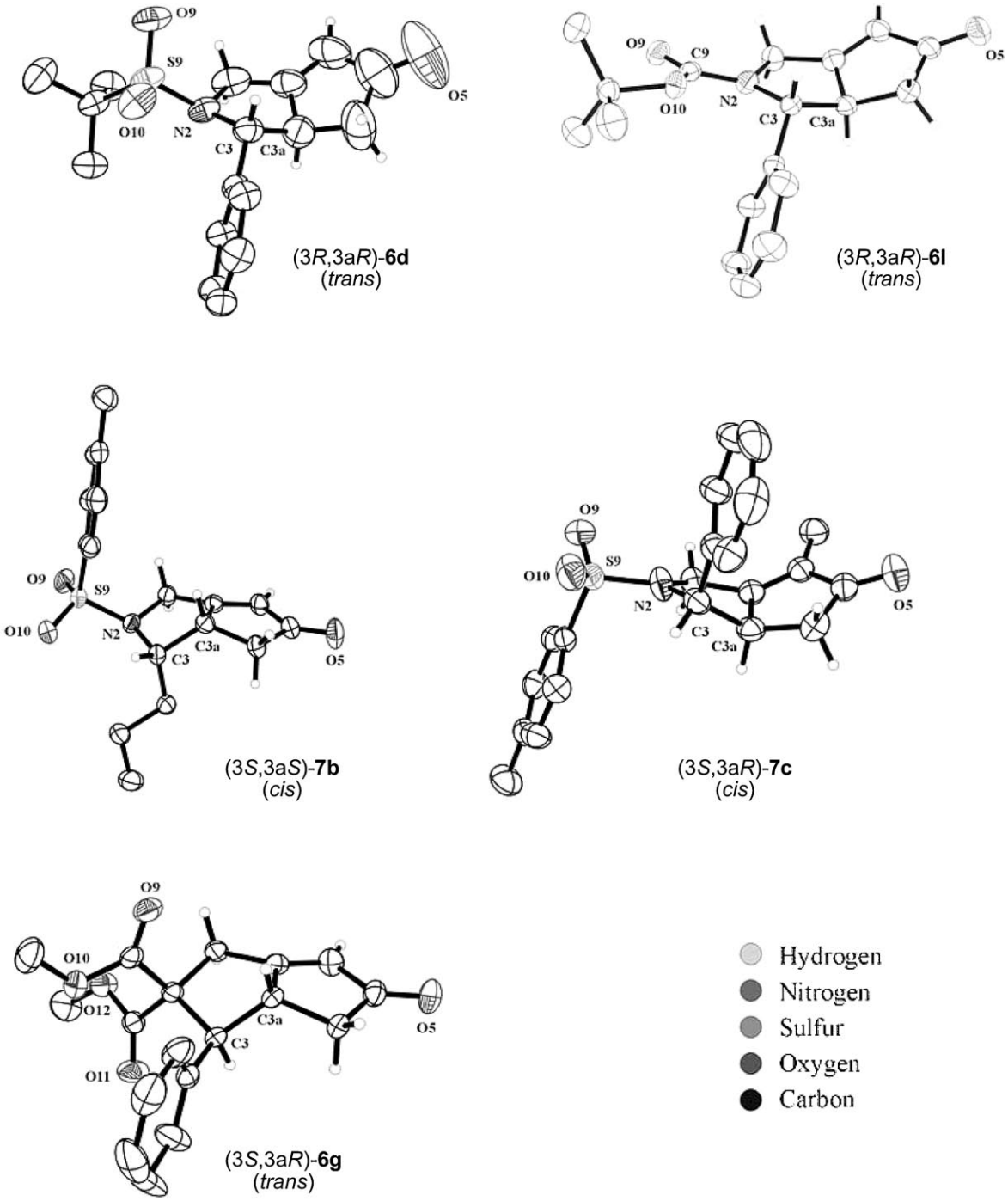


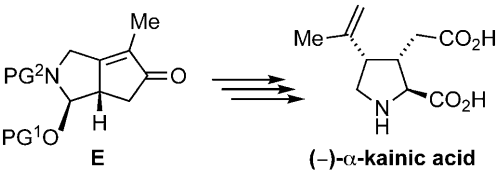
Figure 2. X-ray crystal structures of cyclopentenones; for colored pictures see Supporting Information.

fonamides (Table 4, entries 1–6) gave rise to low or moderate levels of diastereoselection.[36] In all other cases, perfect to high diastereoselectivity was obtained. An exception is the product from the Boc-protected **5l**. The diastereoselectivity of the products **6**/**7p** could not be determined precisely (~80:20 by weight), due to the instability of **7p** under the conditions used for high temperature NMR. The relatively low degree of diastereoselection for sulfonamides was previously observed in conjunction with a synthesis of (−)-α-kainic acid.[37]

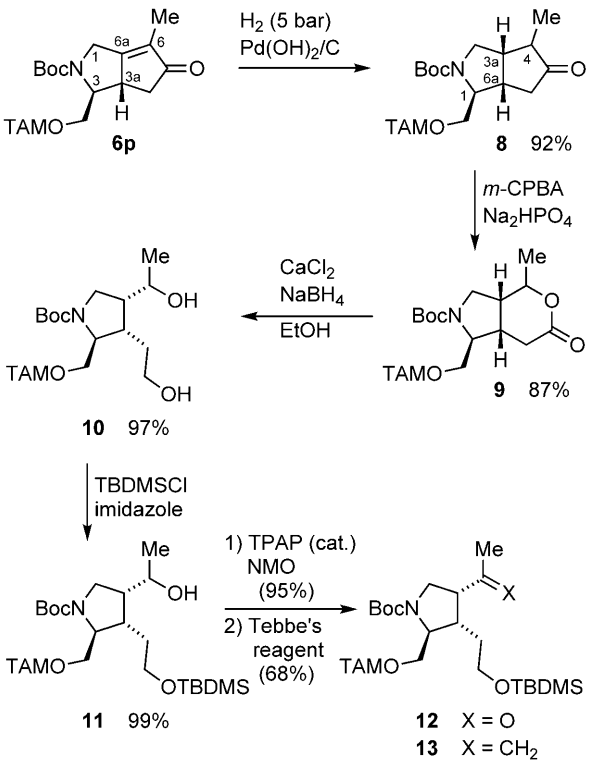
The result that *N*-Boc-protected amines give high degrees of diastereoselectivity was of interest in conjunction with a synthesis of the aforementioned neuropharmacologic agent, (−)-α-kainic acid (Scheme 2). Previously, syntheses of this compound based on the PK reaction have been accomplished; however, a problematic aspect of these published approaches has been the generally low diastereoselectivity of the PK cyclization.[37,38] After recognizing the possibility to control and enhance the diastereoselectivity of the PK annulation based on the *N*-protecting group PG^2, we became interested in a synthesis according to Scheme 2. Several protecting group strategies were explored. The TAM protecting group seemed to be very useful, because it is stable in all transformations. Furthermore, we planned to oxidize the TAM ether to a TAM ester under conditions developed by Sharpless et al.[39] which worked in pretests. Unfortunately, this route failed on later steps. In relation to this, we have reported one successful total synthesis of (−)-α-kainic acid very recently;[3f] here we describe results on an approach, which has led to a formal total synthesis of the same target.

Catalytic hydrogenation of **6p** gave the saturated ketone **8** in 92% yield as a single diastereoisomer (Scheme 3). Subsequent Baeyer–Villiger oxidation[40] with *m*-CPBA, buffered with Na_2HPO_4, in CH_2Cl_2 furnished the lactone **9** in 87% yield.

Opening of lactones of the type represented by **9** with methoxide[41] or MeOH/Et_3N[42] is known to proceed with low yield because of reversibility. We decided to reduce the lactone. This was cleanly effected with *in situ* formed $Ca(BH_4)_2$[43] in ethanol to give the diol **10** in 97% yield. This was reacted with TBDMSCl (*t*-$BuMe_2SiCl$) selectively at the primary OH group to give the alcohol **11** in almost quantitative yield. Ley–Griffith oxidation[44] furnished the



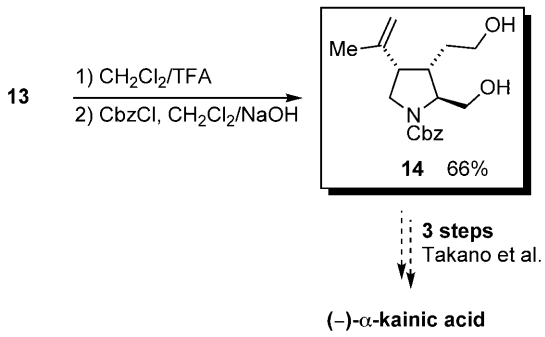
Scheme 2. Approach to (−)-α-kainic acid.



Scheme 3. Synthesis of olefin **13**.

methyl ketone **12**, which was transformed under non-basic conditions into the olefin **13** by reaction with Tebbe's reagent.[45] No epimerization occurred in this step.

Further steps of the synthesis are described in Scheme 4. In spite of the sensitivity of the 2-propenyl moiety to acid, complete deprotection proceeded smoothly under carefully controlled conditions with CH_2Cl_2/TFA (8:1). Reaction of the resultant aminodiol with CbzCl in CH_2Cl_2/1 M NaOH gave the carbamate **14** in 66% yield over two steps. The spectral data of this compound matched those reported by Takano et al.[46]



Scheme 4. Completion of the formal total synthesis of (−)-α-kainic acid.

Conclusions

In summary, the methods reported here allow the efficient syntheses of bicyclic cyclopentenones based on Ir-catalyzed allylic substitutions, which proceeded with up to excellent enantio- and regioselectivity, and highly diastereoselective Pauson–Khand reactions. This methodology has also been illustrated by application within an enantioselective formal total synthesis of (−)-α-kainic acid.

Experimental Section

General Remarks

All reactions were carried out under an atmosphere of argon with dry solvents. Melting points: open glass capillaries on a Büchi Tottoli apparatus. Optical rotation: Perkin–Elmer 241 polarimeter or a Perkin–Elmer 341 polarimeter using a mercury lamp (578 nm); the optical rotation at the sodium-D-line was calculated according the Drude equation. ^{1}H and ^{13}C NMR spectra: Bruker DRX 200, DRX 300, DPX 400 or a DRX 500; chemical shifts relative to residual non-deuterated solvent peaks (^{1}H NMR: $CDCl_3$ $\delta = 7.26$, toluene-d_8 $\delta = 2.09$, benzene-d_6 $\delta = 7.16$; ^{13}C NMR: $CDCl_3$ $\delta = 77.2$, toluene-d_8 $\delta = 20.4$, benzene-d_6 $\delta = 128.1$). HR-MS: JEOL JMS-700 (FAB+) or FT-ICR-MS (ESI+). TLC: Macherey & Nagel Polygram Sil G/UV precoated sheets, visualization of spots by treatment with aqueous $KMnO_4$. HPLC: Hewlett Packard 1090 or 1100 equipped with columns Chiralcel OD-H (25 cm × 0.46 cm) with precolumn OD-H (5 cm × 0.46 cm), Chiralpak AD-H (25 cm × 0.46 cm) with precolumn AD-H (5 cm × 0.46 cm) or Daicel Chiralcel OJ-H (25 cm × 0.46 cm) with precolumn OJ (10 cm × 0.4 cm). GC: Chrompack Chirasil-Dex permethyl β-cyclodextrin (50 m × 0.25 mm, 25 μm film thickness). Flash column chromatography: Fluka silica gel 60 (0.032–0.062 mm). Preparative HPLC: Gilson 305 instrument coupled with a Knauer UV/VIS filter photometer and a silica gel Latek column (250 × 21 mm, 5 μm). Microwave experiments: CEM Discover labmate™ instrument. GC/MS: HP 5890 Series II Plus model, coupled with an HP 5972 mass selective detector and an HP 1 cross-linked methyl silicone column (25 m × 0.2 mm, 0.33 μm) [temperature program: 50 °C 1 min, heating rate 20 °C/min (10 min), 250 °C 14 min; injection temperature 250 °C]. Elemental analysis: Microanalytical Laboratory of the Organisch-Chemisches Institut, Universität Heidelberg.

General Procedure 1: Iridium-Catalyzed Allylic Substitution

Success with the following procedure requires dry THF (< 35 μg of H_2O/mL, Karl Fischer titration). Under argon, in a dried (heatgun) Schlenk tube a solution of $[Ir(COD)Cl]_2$ (2 mol%), **L*** (4 mol%) and TBD (8 mol%) (stored in a desiccator over KOH) in dry THF (1 M to 2 M) was stirred for 5–10 min at room temperature when a white precipitate was formed at the glass wall near the surface of the solution. The allylic carbonate (1.0 equiv.) and after further 5 min the nucleophile (1.2–2.5 equiv.) were added. The mixture was stirred until TLC or GC/MS monitoring indicated complete conversion. The solvent was removed under reduced pressure, and the residue was analyzed with respect to content of branched and linear products by ^{1}H NMR. The pure reaction products were obtained by column chromatography on silica gel (petroleum ether/ethyl acetate).

General Procedure 2: Propargylation of Sulfonamides

Under an atmosphere of argon, K_2CO_3 (2 equiv.) was added to a solution of the sulfonamide (1.0 equiv.) in dry MeCN (0.07 M), and the mixture was stirred for 15 min at room temperature. Then TBAI (20 mol%) was added, and the mixture was heated at 90 °C. The propargylic bromide (10 equiv.) was added dropwise to the hot suspension and conversion monitored by TLC or GC/MS. When full conversion was reached, saturated NH_4Cl was added, and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate).

General Procedure 3: Propargylation of Carbamates

Under an atmosphere of argon a solution of the carbamate (1.0 equiv.) in dry DMF (0.09 M) was cooled to −30 °C. The propargylic bromide (5–10 equiv.) and 15-crown-5 (3 equiv.) were added, and the mixture was stirred for 10 min. Then NaH (2–3 equiv.) was added portionwise (usually 2 × 1.5 or 2 × 1 equiv.) in intervals of 0.5 h. The suspension turned from yellowish to dark brown, and stirring was continued at −30 °C until TLC or GC/MS monitoring showed full consumption of the starting material. Saturated aqueous NH_4Cl was added, and the mixture was allowed to warm up to room temperature. The aqueous phase was extracted with Et_2O, and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate).

General Procedure 4: Intramolecular Pauson–Khand Reaction

Under an atmosphere of argon a solution of the enyne (1.0 equiv.) and $Co_2(CO)_8$ (1.05–1.1 equiv.) in dry CH_2Cl_2 (0.06 M) was stirred at room temperature until TLC monitoring indicated full conversion. Then $Me_3NO{\cdot}2H_2O$ (3–10 equiv.) and, if necessary, an additive (celite or powdered molecular sieves 4 Å) were added in one portion. Stirring was continued until TLC monitoring showed complete consumption of the cobalt-alkyne complex. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate).

General Procedure 5: Microwave-Promoted Catalytic Intramolecular Pauson–Khand Reaction

In an oven-dried microwave vessel the enyne (1 equiv.) was dissolved in toluene (0.09–0.15 M). *n*-BuSMe (1.2–3.5 equiv.) and $Co_2(CO)_8$ (20–25 mol%) were added, and the vessel was closed immediately while gas was evolving. Microwave

irradiation was started as quickly as possible and continued for 10–20 min at 100 °C. The black reaction mixture was directly subjected to column chromatography on silica gel (petroleum ether/ethyl acetate).

4-Methyl-*N*-[(1*R*)-1-phenylprop-2-en-1-yl]benzenesulfonamide (*ent*-2a) (Table 1, entry 1)

GP1 was carried out with $[Ir(COD)Cl]_2$ (107 mg, 0.16 mmol), (*R*,*R*,*aR*)-**L2** (192 mg, 0.32 mmol), TBD (89 mg, 0.64 mmol), cinnamyl methyl carbonate (**1a**) (1.54 g, 8.00 mmol), the sodium salt of *p*-toluenesulfonamide (**Nu1**) (3.80 g, 20.0 mmol) and dry THF (4 mL); reaction time: 2 h at 50 °C; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**1a**) = 0.77, R_f(**2a**) = 0.55, $KMnO_4$]; ratio **2a**:**3a** = 90:10 (^{1}H NMR). Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) afforded *ent*-**2a** as yellowish needles; yield: 1.72 g (6.00 mmol, 75%); mp 98.5–99.5 °C (lit.[47] 97–99 °C); $[\alpha]_D^{20}$: +42.8 (*c* 1.04, $CHCl_3$); lit.[48] $[\alpha]_D^{20}$: +52.8 (*c* 1.15, $CHCl_3$); HPLC (Daicel Chiralcel OD-H 4.6 × 250 mm with precolumn OD-H 10 × 4 mm, *n*-hexane/*i*-PrOH 90:10, flow = 0.5 mL/min, λ = 220 nm): t_R[(+)-(*R*)-**2a**] = 18.2 min, t_R[(−)-(*S*)-**2a**] = 22.1 min; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.39 (s, 3H), 4.87 (d, *J* = 7.3 Hz, 1H), 4.92–4.96 (m, 1H), 5.12 (ddd, *J* = 16.7 Hz, *J* = 1.0 Hz, *J* = 1.0 Hz, 1H), 5.14 (ddd, *J* = 10.7 Hz, *J* = 1.3 Hz, *J* = 1.3 Hz, 1H), 5.87 (ddd, *J* = 16.5 Hz, *J* = 10.8 Hz, *J* = 5.7 Hz, 1H), 7.08–7.12 (m, 2H), 7.18–7.24 (m, 5H), 7.62–7.66 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.6, 60.0, 117.0, 127.2, 127.4, 127.9, 128.8, 129.6, 137.3, 137.8, 139.5, 143.4; MS (FAB+): *m/z* = 288.1 $[M+H]^+$, calcd. for $C_{16}H_{18}NO_2S$: 288.1.

Analytical data for 4-methyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]benzenesulfonamide (3a)[49]: Yellowish solid; mp 103–104 °C (lit.[49] 109–110 °C); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.33 (s, 3H), 3.67 (ddd, *J* = 6.3 Hz, *J* = 6.3 Hz, *J* = 1.0 Hz, 2H), 4.61 (t, *J* = 5.5 Hz, 1H), 5.92 (dt, *J* = 15.8 Hz, *J* = 6.3 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 7.12–7.23 (m, 7H), 7.69–7.72 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.6, 45.6, 124.2, 126.5, 127.3, 128.1, 128.7, 129.9, 133.2, 136.2, 137.2, 143.7; GC/MS: t_R = 19.3 min, *m/z* = 287 $[M]^+$.

4-Methyl-*N*-[(1*S*)-1-propylprop-2-en-1-yl]benzenesulfonamide (*ent*-2b)[50] (Table 1, entry 2)

GP1 was carried out with $[Ir(COD)Cl]_2$ (13.4 mg, 20 μmol), (*R*,*R*,*aR*)-**L1** (22.9 mg, 40 μmol), TBD (11.1 mg, 80 μmol), (2*E*)-hex-2-en-1-yl methyl carbonate (**1b**) (158 mg, 1.00 mmol), the sodium salt of *p*-toluenesulfonamide (**Nu1**) (483 mg, 2.50 mmol) and dry THF (0.5 mL); reaction time: 3 h at 50 °C; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**1b**) = 0.54, R_f(**2b**) = 0.32, $KMnO_4$]; ratio **2b**:**3b** = 91:09 (^{1}H NMR). Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) afforded *ent*-**2b** as colorless needles; yield: 154 mg (0.61 mmol, 61%); mp 51–52 °C; $[\alpha]_D^{20}$: +14.2 (*c* 0.56, $CHCl_3$); HPLC (Daicel Chiralcel OD-H 4.6 × 250 mm with precolumn OD-H 10 × 4 mm, *n*-hexane/*i*-PrOH 90:10, flow = 0.5 mL/min, λ = 215 nm): t_R[(−)-(*R*)-**2b**] = 13.8 min, t_R[(+)-(*S*)-**2b**] = 15.4 min; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.81 (t, *J* = 7.3 Hz, 3H), 1.18–1.32 (m, 2H), 1.39–1.47 (m, 2H), 2.40 (s, 3H), 3.69–3.78 (m, 1H), 4.89 (d, *J* = 7.9 Hz, 1H), 4.96 (ddd, *J* = 16.6 Hz, *J* = 0.9 Hz, *J* = 0.9 Hz, 1H), 4.96 (ddd, *J* = 10.1 Hz, *J* = 0.9 Hz, *J* = 0.9 Hz, 1H), 5.52 (ddd, *J* = 17.0 Hz, *J* = 10.3 Hz, *J* = 6.7 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.72–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.7, 18.6, 21.6, 37.8, 56.2, 115.8, 127.3, 129.6, 138.0, 138.3, 143.2; HR-MS (FAB+): *m/z* = 254.1197 $[M+H]^+$, calcd. for $C_{13}H_{20}NO_2S$: 254.1215.

Analytical data for *N*-[(2*E*)-hex-2-en-1-yl]-4-methylbenzenesulfonamide (3b)[51]: Colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.83 (t, *J* = 7.3 Hz, 3H), 1.30 (sext, *J* = 7.4 Hz, 2H), 1.90 (dt, *J* = 6.8 Hz, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 3.52 (t, *J* = 5.8 Hz, 2H), 4.47 (t, *J* = 5.5 Hz, 1H), 5.30 (dtt, *J* = 15.2 Hz, *J* = 6.4 Hz, *J* = 1.3 Hz, 1H), 5.30 (dt, *J* = 14.9 Hz, *J* = 6.7 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.7, 21.6, 22.2, 34.3, 45.5, 124.6, 127.3, 129.8, 135.0, 137.2, 143.5; HR-MS (FAB+): *m/z* = 254.1208 $[M+H]^+$, calcd. for $C_{13}H_{20}NO_2S$: 254.1215.

2-Methyl-*N*-[(1*S*)-1-phenylprop-2-en-1-yl]propane-2-sulfonamide (2c) (Table 1, entry 3)

GP1 was carried out with $[Ir(COD)Cl]_2$ (13.4 mg, 20 μmol), (*S*,*S*,*aS*)-**L2** (24.0 mg, 40 μmol), TBD (11.1 mg, 80 μmol), cinnamyl methyl carbonate (**1a**) (192 mg, 1.00 mmol), the sodium salt of 2-methylpropane-2-sulfonamide (**Nu2**) (398 mg, 2.50 mmol) and dry THF (0.5 mL); reaction time: 1 h at 50 °C; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**1a**) = 0.56, R_f(**2c**) = 0.40, $KMnO_4$]; ratio **2c**:**3c** = 94:06 (^{1}H NMR). Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) afforded **2c** as yellow needles; yield: 169 mg (0.67 mmol, 67%); mp 91–92 °C; $[\alpha]_D^{20}$: −37.8 (*c* 0.58, $CHCl_3$); HPLC (Daicel Chiralpak AD-H 4.6 × 250 mm with precolumn AD-H 10 × 4 mm, *n*-hexane/*i*-PrOH 90:10, flow = 0.5 mL/min, λ = 215 nm): t_R[(+)-(*R*)-**2c**] = 13.5 min, t_R[(−)-(*S*)-**2c**] = 19.2 min; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.35 (s, 9H), 4.78 (bd, *J* = 9.4 Hz, 1H), 5.14 (dddd, *J* = 8.8 Hz, *J* = 5.4 Hz, *J* = 1.5 Hz, *J* = 1.5 Hz, 1H), 5.25–5.31 (m, 2H), 6.06 (ddd, *J* = 17.2 Hz, *J* = 10.2 Hz, *J* = 5.5 Hz, 1H), 7.27–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.3, 60.1, 60.4, 116.2, 127.2, 127.8, 128.9, 138.7, 140.8; HR-MS (FAB+): *m/z* = 254.1234 $[M+H]^+$, calcd. for $C_{13}H_{20}NO_2S$: 254.1215; anal. calcd. for $C_{13}H_{19}NO_2S$: C 61.63, H 7.56, N 5.53, S 12.66; found: C 61.83, H 7.44, N 5.46, S 12.43.

Analytical data for 2-methyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]propane-2-sulfonamide (3c): Yellowish solid; mp 73.5–74.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.37 (s, 9H), 3.90 (ddd, *J* = 6.0 Hz, *J* = 6.0 Hz, *J* = 1.1 Hz, 2H), 4.00 (bt, *J* = 5.4 Hz, 1H), 6.17 (dt, *J* = 15.8 Hz, *J* = 6.2 Hz, 1H), 6.51 (d, *J* = 15.8 Hz, 1H), 7.16–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.5, 47.0, 60.1, 125.8, 126.6, 128.1, 128.8, 132.8, 136.3; MS (FAB+): *m/z* = 254.1 $[M+H]^+$, calcd. for $C_{13}H_{20}NO_2S$: 254.1.

2-Methyl-*N*-[(1*R*)-1-propylprop-2-en-1-yl]propane-2-sulfonamide (*ent*-2d) (Table 1, entry 4)

GP1 was carried out with $[Ir(COD)Cl]_2$ (13.4 mg, 20 μmol), (*R*,*R*,*aR*)-**L1** (22.9 mg, 40 μmol), TBD (11.1 mg, 80 μmol), (2*E*)-hex-2-en-1-yl methyl carbonate (**1b**) (158 mg, 1.00 mmol), the sodium salt of 2-methylpropane-2-sulfonamide (**Nu2**) (398 mg, 2.50 mmol) and dry THF (0.5 mL); reaction time: 1 h at 50 °C; TLC monitoring [petroleum ether/ethyl acetate 9:1, R_f(**1b**) = 0.72, R_f(**2c**) = 0.25, $KMnO_4$];

ratio **2d**:**3d** = 93:07 (^{1}H NMR). Column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) afforded *ent*-**2d** as a yellowish oil; yield: 144 mg (0.66 mmol, 66%); $[\alpha]_D^{20}$: +13.6 (*c* 0.75, $CHCl_3$); GC [Chrompack permethyl β-cyclodextrin column (50 m × 0.25 mm), injector temperature 200 °C, temperature program: 110 °C isothermal]: t_R[(−)-(*R*)-**2d**] = 57.4 min, t_R[(+)-(*S*)-**2d**] = 58.6 min; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.92 (t, *J* = 7.2 Hz, 3H), 1.35–1.43 (m, 2H), 1.37 (s, 9H), 1.53–1.60 (m, 2H), 3.86–3.96 (m, 1H), 4.07 (d, *J* = 9.5 Hz, 1H), 5.13 (ddd, *J* = 10.4 Hz, *J* = 1.0 Hz, *J* = 1.0 Hz, 1H), 5.21 (ddd, *J* = 17.2 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 5.78 (ddd, *J* = 16.9 Hz, *J* = 10.4 Hz, *J* = 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 18.9, 24.4, 39.4, 57.2, 59.9, 115.3, 139.1; HR-MS (FAB+): *m/z* = 220.1348 [M+H]$^+$, calcd. for $C_{10}H_{22}NO_2S$: 220.1371; elem. anal. calcd. for $C_{10}H_{21}NO_2S$: C 54.76, H 9.65, N 6.39, S 14.62; found: C 54.59, H 9.59, N 6.36, S 14.85.

Analytical data for *N*-[(2*E*)-hex-2-en-1-yl]-4-methylpropane-2-sulfonamide (3d): Colorless needles; mp 30–31 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.89 (t, *J* = 7.3 Hz, 3H), 1.35–1.42 (m, 2H), 1.39 (s, 9H), 2.00 (dt, *J* = 7.4 Hz, *J* = 7.3 Hz, 2H), 3.72 (ddd, *J* = 6.0 Hz, *J* = 6.0 Hz, *J* = 0.9 Hz, 2H), 3.89 (t, *J* = 5.6 Hz, 1H), 5.49 (dtt, *J* = 15.2 Hz, *J* = 6.2 Hz, *J* = 1.2 Hz, 1H), 5.30 (dt, *J* = 15.2 Hz, *J* = 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 22.3, 24.5, 34.3, 46.9, 60.0, 126.3, 134.5; HR-MS (FAB+): *m/z* = 220.1360 [M+H]$^+$, calcd. for $C_{10}H_{22}NO_2S$: 220.1371.

N-[(1*S*)-1-Phenylprop-2-en-1-yl]-2-(trimethylsilyl)-ethanesulfonamide (2e) (Table 1, entry 5)

GP1 was carried out with $[Ir(COD)Cl]_2$ (13.4 mg, 20 μmol), (*S*,*S*,*aS*)-**L2** (24.0 mg, 40 μmol), TBD (11.1 mg, 80 μmol), cinnamyl methyl carbonate (**1a**) (192 mg, 1.00 mmol), the sodium salt of 2-(trimethylsilyl)ethanesulfonamide (**Nu3**) (244 mg, 1.20 mmol) and dry THF (0.5 mL); reaction time: 2 h at 50 °C; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**1a**) = 0.77, R_f(**2e**) = 0.38, $KMnO_4$]; ratio **2e**:(**3e**+diallylated product) = 77:23 (^{1}H NMR). Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) afforded **2e** as a yellow oil; yield: 140 mg (0.60 mmol, 60%); $[\alpha]_D^{25}$: +19.0 (*c* 1.07, $CHCl_3$); HPLC (Daicel Chiralcel OJ-H 4.6 × 250 mm with precolumn OJ 10 × 4 mm, *n*-hexane/*i*-PrOH 95:05, flow = 0.5 mL/min, λ = 220 nm): t_R[(+)-(*S*)-**2e**] = 19.4 min, t_R[(−)-(*R*)-**2e**] = 22.5 min; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = −0.07 (s, 9H), 0.77–0.97 (m, 2H), 2.60–2.81 (m, 2H), 4.60 (d, *J* = 7.2 Hz, 1H), 5.08 (dd, *J* = 7.3 Hz, *J* = 6.0 Hz, 1H), 5.28 (ddd, *J* = 10.2 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 5.28 (ddd, *J* = 17.1 Hz, *J* = 1.5 Hz, *J* = 0.8 Hz, 1H), 6.02 (ddd, *J* = 16.9 Hz, *J* = 10.2 Hz, *J* = 6.0 Hz, 1H), 7.28–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = −2.0, 10.5, 50.3, 60.0, 117.2, 127.4, 128.4, 129.1, 137.7, 140.1; GC/MS: t_R = 12.6 min, *m/z* = 297 [M]$^+$; elem. anal. calcd. for $C_{14}H_{23}NO_2SSi$: C 56.52, H 7.79, N 4.71, S 10.78; found: C 56.75, H 7.76, N 4.84, S 10.62.

Analytical data for *N*-(3-phenylprop-2-en-1-yl)-2-(trimethylsilyl)ethanesulfonamide (3e): Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.00 (s, 9H), 0.97–1.09 (m, 2H), 2.90–3.01 (m, 2H), 3.89 (dt, *J* = 6.3 Hz, *J* = 1.4 Hz, 1H), 4.28–4.42 (m, 1H), 6.18 (td, *J* = 15.9 Hz, *J* = 6.4 Hz, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 7.21–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = −1.6, 10.8, 45.7, 49.8, 124.9, 126.6, 128.2, 128.7, 133.4, 136.2; GC/MS: t_R = 15.0 min, *m/z* = 297 [M]$^+$.

N-[(1*S*)-1-Phenylprop-2-en-1-yl]but-2-yn-1-amine (2f) (Table 1, entry 6)

GP1 was carried out with $[Ir(COD)Cl]_2$ (13.7 mg, 20 μmol), (*S*,*S*,*aS*)-**L2** (24.2 mg, 40 μmol), TBD (13.1 mg, 94 μmol), cinnamyl methyl carbonate (**1a**) (202 mg, 1.05 mmol), but-2-yn-1-amine (**Nu4**) (88 mg, 1.26 mmol) and dry THF (1 mL); reaction time: 8.5 h at room temperature; TLC monitoring [petroleum ether/diethyl ether 3:1, R_f(**1a**) = 0.32, R_f(**2f**) = 0.18, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/diethyl ether 5:1) afforded **2f** as yellowish oil; yield: 116 mg (0.63 mmol, 60%); $[\alpha]_D^{20}$: −23.6 (*c* 1.06, $CHCl_3$); HPLC (Daicel Chiralpak AD-H 4.6 × 250 mm with precolumn AD-H 10 × 4 mm, *n*-hexane/*i*-PrOH 99:01, flow = 0.5 mL/min, λ = 220 nm): t_R[(+)-(*R*)-**2f**] = 13.6 min, t_R[(−)-(*S*)-**2f**] = 14.5 min; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.65 (bs, 1H), 1.84 (t, *J* = 2.4 Hz, 3H), 3.27 (dq, *J* = 16.6 Hz, *J* = 2.3 Hz, 1H), 3.34 (dq, *J* = 16.6 Hz, *J* = 2.3 Hz, 1H), 4.40 (d, *J* = 7.3 Hz, 1H), 5.13 (ddd, *J* = 10.2 Hz, *J* = 1.4 Hz, *J* = 0.9 Hz, 1H), 5.28 (ddd, *J* = 17.1 Hz, *J* = 1.3 Hz, *J* = 1.3 Hz, 1H), 5.93 (ddd, *J* = 17.3 Hz, *J* = 10.2 Hz, *J* = 7.3 Hz, 1H), 7.24–7.28 (m, 1H), 7.32–7.38 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 3.6, 36.3, 64.5, 77.2, 79.2, 115.6, 127.4, 127.5, 128.6, 140.5, 142.3; HR-MS (EI+): *m/z* = 184.1153 [M+H]$^+$, calcd. for $C_{13}H_{14}N$: 184.1126.

N-But-2-yn-1-yl-4-methyl-*N*-[(1*S*)-1-phenylprop-2-en-1-yl]benzenesulfonamide (2g) (Table 1, entry 7)

GP1 was carried out with $[Ir(COD)Cl]_2$ (13.8 mg, 20 μmol), (*S*,*S*,*aS*)-**L2** (22.6 mg, 38 μmol), TBD (13.2 mg, 95 μmol), cinnamyl methyl carbonate (**1a**) (207 mg, 1.10 mmol), *N*-but-2-yn-1-yl-4-methylbenzenesulfonamide (**Nu5**) (288 mg, 1.30 mmol) and dry THF (1 mL); reaction time: 6 h at room temperature; TLC monitoring [petroleum ether/diethyl ether 3:1, R_f(**1a**) = 0.32, R_f(**2g**) = 0.25, $KMnO_4$]; ratio **2g**:**3g** = 93:07 (^{1}H NMR). Column chromatography on silica gel (petroleum ether/ethyl acetate 7:1) afforded **2g** as a yellow oil; yield: 318 mg (0.94 mmol, 88%); $[\alpha]_D^{20}$: −10.0 (*c* 0.92, $CHCl_3$); HPLC (Daicel Chiralpak AD-H 4.6 × 250 mm with precolumn AD-H 10 × 4 mm, *n*-hexane/*i*-PrOH 90:10, flow = 0.5 mL/min, λ = 220 nm): t_R[(+)-(*R*)-**2g**] = 23.5 min, t_R[(−)-(*S*)-**2g**] = 27.3 min; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.56 (t, *J* = 2.4 Hz, 3H), 2.42 (s, 3H), 3.75 (dq, *J* = 18.2 Hz, *J* = 2.3 Hz, 1H), 4.06 (dq, *J* = 18.2 Hz, *J* = 2.4 Hz, 1H), 5.15 (ddd, *J* = 17.0 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 5.24 (ddd, *J* = 10.3 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 5.61 (d, *J* = 7.5 Hz, 1H), 6.17 (ddd, *J* = 17.2 Hz, *J* = 10.3 Hz, *J* = 7.5 Hz, 1H), 7.24–7.32 (m, 7H), 7.77–7.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 3.5, 21.7, 34.6, 63.8, 74.7, 80.8, 119.1, 127.9, 128.1, 128.3, 128.5, 129.1, 134.4, 138.0, 138.3, 143.1; HR-MS (FAB+): *m/z* = 340.1418 [M+H]$^+$, calcd. for $C_{20}H_{22}NO_2S$: 340.1371; elem. anal. calcd. for $C_{20}H_{21}NO_2S$: C 70.77, H 6.24, N 4.13, S 9.45; found: C 70.67, H 6.37, N 4.13, S 9.37.

Analytical data for *N*-but-2-yn-1-yl-4-methyl-*N*-[(2*E*)-3-phenylprop-2-en-1-yl]benzenesulfonamide (3g): Colorless solid; mp 60–63 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.57 (t, *J* = 2.3 Hz, 3H), 2.43 (s, 3H), 3.96 (dd, *J* = 6.8 Hz, *J* = 0.8 Hz, 2H), 4.06 (q, *J* = 2.2 Hz, 2H), 6.09 (dt, *J* = 15.8 Hz, *J* =

6.8 Hz, 1H), 6.56 (d, $J=15.8$ Hz, 1H), 7.22–7.36 (m, 7H), 7.76–7.79 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=3.4$, 21.6, 36.6, 48.7, 71.9, 81.8, 123.5, 126.6, 128.0, 128.1, 128.7, 129.4, 134.6, 136.4, 136.4, 143.4; HR-MS (ESI+): $m/z=340.1367$ $[M+H]^+$, calcd. for $C_{20}H_{22}NO_2S$: 340.1366; elem. anal. calcd. for $C_{20}H_{21}NO_2S$: C 70.77, H 6.24, N 4.13, S 9.45; found: C 70.64, H 6.18, N 4.25, S 9.64.

Dimethyl But-2-yn-1-yl[(1*S*)-1-phenylprop-2-en-1-yl]-malonate (2h) (Table 1, entry 9)

GP1 was carried out with $[Ir(COD)Cl]_2$ (13.8 mg, 20 μmol), (*S*,*S*,*aS*)-**L2** (24.9 mg, 40 μmol), TBD (13.1 mg, 95 μmol), cinnamyl methyl carbonate (**1a**) (200 mg, 1.04 mmol), dimethyl but-2-yn-1-ylmalonate (**Nu6**) (220 mg, 1.20 mmol) and dry THF (1 mL); reaction time: 5 h at room temperature; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**1a**)=0.36, R_f(**2h**)=0.32, $KMnO_4$]; ratio **2h**:**3h**=93:07 (^{1}H NMR). Column chromatography on silica gel (petroleum ether/ethyl acetate 95:5) afforded **2h** as a yellowish oil; yield: 226 mg (0.75 mmol, 72%); $[\alpha]_D^{20}$: +13.0 (*c* 1.07, $CHCl_3$); HPLC (Daicel Chiralcel OD-H 4.6×250 mm with precolumn OD-H 10×4 mm, *n*-hexane/*i*-PrOH 99:01, flow=0.5 mL/min, $\lambda=220$ nm): t_R[(+)-(*S*)-**2h**]=15.0 min, t_R[(−)-(*R*)-**2h**]=19.2 min; ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta=1.79$ (dd, $J=2.5$ Hz, $J=2.5$ Hz, 3H), 2.49 (dq, $J=16.9$ Hz, $J=2.5$ Hz, 1H), 2.69 (dq, $J=16.8$ Hz, $J=2.5$ Hz, 1H), 3.70 (s, 3H), 3.74 (s, 3H), 4.25 (d, $J=8.1$ Hz, 1H), 5.07 (ddd, $J=16.8$ Hz, $J=1.2$ Hz, $J=1.2$ Hz, 1H), 5.14 (ddd, $J=10.2$ Hz, $J=0.8$ Hz, $J=0.8$ Hz, 1H), 6.42 (ddd, $J=17.0$ Hz, $J=10.3$ Hz, $J=8.1$ Hz, 1H), 7.18–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=3.7$, 25.0, 52.4, 52.6, 52.6, 61.7, 73.9, 79.5, 117.4, 127.4, 128.3, 129.4, 137.6, 139.0, 170.0, 170.2; HR-MS (ESI+): $m/z=301.1434$ $[M+H]^+$, calcd. for $C_{18}H_{21}O_4$: 301.1434.

Analytical data for dimethyl but-2-yn-1-yl[(2*E*)-3-phenylprop-2-en-1-yl]malonate (3h): Yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=1.78$ (dd, $J=2.5$ Hz, $J=2.5$ Hz, 3H), 2.79 (q, $J=2.5$ Hz, 2H), 2.94 (dd, $J=7.6$ Hz, $J=1.1$ Hz, 2H), 3.74 (s, 6H), 6.02 (dt, $J=15.5$ Hz, $J=7.6$ Hz, 1H), 6.49 (d, $J=15.7$ Hz, 1H), 7.18–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=3.6$, 23.4, 36.1, 52.8, 57.7, 73.4, 79.2, 123.6, 126.4, 127.5, 128.6, 134.4, 137.2, 170.6; HR-MS (ESI+): $m/z=301.1435$ $[M+H]^+$, calcd. for $C_{18}H_{21}O_4$: 301.1434.

Dimethyl [(1*S*)-1-Phenylprop-2-en-1-yl][3-(trimethylsilyl)prop-2-yn-1-yl]malonate (2i) (Table 1, entry 10)

GP1 was carried out with $[Ir(COD)Cl]_2$ (13.7 mg, 20 μmol), (*S*,*S*,*aS*)-**L2** (24.5 mg, 40 μmol), TBD (13.1 mg, 95 μmol), cinnamyl methyl carbonate (**1a**) (202 mg, 1.05 mmol), dimethyl [3-(trimethylsilyl)prop-2-yn-1-yl]malonate (**Nu7**) (306 mg, 1.26 mmol) and dry THF (1 mL); reaction time: 3 h at room temperature; TLC monitoring [petroleum ether/diethyl ether 9:1, R_f(**1a**)=0.38, R_f(**2i**)=0.35, $KMnO_4$]; ratio **2i**:**3i**=95:05 (^{1}H NMR). Column chromatography on silica gel (petroleum ether/ethyl acetate 95:5) afforded **2i** as a colorless oil; yield: 261 mg (0.73 mmol, 69%); $[\alpha]_D^{20}$: +5.7 (*c* 1.14, $CHCl_3$); HPLC (Daicel Chiralpak AD-H 4.6×250 mm with precolumn AD-H 10×4 mm, *n*-hexane/*i*-PrOH 99.5:0.5, flow=0.5 mL/min, $\lambda=220$ nm): t_R[(+)-(*S*)-**2i**]=13.3 min, t_R[(−)-(*R*)-**2i**]=16.5 min; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=0.17$ (s, 9H), 2.59 (d, $J=17.2$ Hz, 1H), 2.79 (d, $J=17.2$ Hz, 1H), 3.70 (s, 3H), 3.75 (s, 3H), 4.27 (d, $J=8.1$ Hz, 1H), 5.07 (ddd, $J=17.0$ Hz, $J=1.5$ Hz, $J=1.5$ Hz, 1H), 5.14 (ddd, $J=10.3$ Hz, $J=1.3$ Hz, $J=1.3$ Hz, 1H), 6.43 (ddd, $J=17.0$ Hz, $J=10.3$ Hz, $J=8.1$ Hz, 1H), 7.18–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=0.1$, 25.9, 52.5, 52.6, 52.7, 61.7, 88.9, 101.9, 117.6, 127.4, 128.3, 129.5, 137.3, 138.8, 169.8, 169.9; HR-MS (ESI+): $m/z=359.1676$ $[M+H]^+$, calcd. for $C_{20}H_{27}O_4Si$: 359.1673.

Analytical data for dimethyl [(2*E*)-3-phenylprop-2-en-1-yl][3-(trimethylsilyl)prop-2-yn-1-yl]malonate (3i): Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=0.11$ (s, 9H), 2.81 (s, 2H), 2.90 (dd, $J=7.7$ Hz, $J=0.9$ Hz, 2H), 3.69 (s, 6H), 5.96 (dt, $J=15.5$ Hz, $J=7.6$ Hz, 1H), 6.45 (d, $J=15.7$ Hz, 1H), 7.13–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=0.1$, 24.5, 36.1, 52.9, 57.6, 88.6, 101.4, 123.4, 126.4, 127.6, 128.6, 134.7, 137.2, 170.3; HR-MS (ESI+): $m/z=359.1676$ $[M+H]^+$, calcd. for $C_{20}H_{27}O_4Si$: 359.1673.

tert-Butyl {(1*S*)-1-[(1,1-Dimethylpropoxy)methyl]-prop-2-en-1-yl}formylcarbamate (2j) (Table 1, entry 11)

GP1 was carried out with $[Ir(COD)Cl]_2$ (202 mg, 0.30 mmol), (*S*,*S*,*aS*)-**L2** (360 mg, 0.60 mmol), TBD (167 mg, 1.20 mmol), carbonate **1c** (3.24 g, 15.0 mmol), *tert*-butyl formylcarbamate (**Nu8**) (2.61 g, 18.0 mmol) and dry THF (15 mL); reaction time: 1.5 h at 40 °C; TLC monitoring [petroleum ether/ethyl acetate 9:1, R_f(**1c**)=0.42, R_f(**2j**)=0.52, $KMnO_4$]; ratio **2j**:**3j**=81:19 (^{1}H NMR). Column chromatography on silica gel (petroleum ether/ethyl acetate 20:1→9:1) afforded **2j** as a colorless oil; yield: 2.66 g (9.32 mmol, 62%); $[\alpha]_D^{20}$: +10.9 (*c* 0.83, $CHCl_3$); HPLC (Daicel Chiralpak AD-H 4.6×250 mm with precolumn AD-H 10×4 mm, *n*-hexane/*i*-PrOH 99.5:0.5, flow=0.5 mL/min, $\lambda=220$ nm): t_R[(−)-(*R*)-**2j**]=12.7 min, t_R[(+)-(*S*)-**2j**]=13.7 min; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=0.81$ (t, $J=7.5$ Hz, 3H), 1.07, 1.08 (2 s, 6H), 1.43 (dq, $J=7.4$ Hz, $J=2.3$ Hz, 2H), 1.53 (s, 9H), 3.50 (dd, $J=9.0$ Hz, $J=6.1$ Hz, 1H), 3.74 (dd, $J=9.0$ Hz, $J=9.0$ Hz, 1H), 5.02–5.08 (m, 1H), 5.17 (ddd, $J=10.5$ Hz, $J=1.3$ Hz, $J=1.3$ Hz, 1H), 5.20 (ddd, $J=17.4$ Hz, $J=1.3$ Hz, $J=1.3$ Hz, 1H), 6.02 (ddd, $J=17.2$ Hz, $J=10.4$ Hz, $J=6.7$ Hz, 1H), 9.21 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=8.3$, 24.8, 25.1, 28.2, 33.3, 55.1, 61.1, 75.1, 84.0, 117.9, 134.1, 152.5, 163.5; HR-MS (ESI+): $m/z=308.1833$ $[M+Na]^+$, calcd. for $C_{15}H_{27}NO_4Na$: 308.1832.

Analytical data for *tert*-butyl [(2*E*)-4-(1,1-dimethylpropoxy)but-2-en-1-yl]formylcarbamate (3j): Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=0.84$ (t, $J=7.5$ Hz, 3H), 1.12 (s, 6H), 1.48 (q, $J=7.5$ Hz, 2H), 1.52 (s, 9H), 3.82 (dd, $J=5.2$ Hz, $J=1.1$ Hz, 2H), 4.15 (dd, $J=6.0$ Hz, $J=1.0$ Hz, 2H), 5.64 (dtt, $J=15.3$ Hz, $J=6.0$ Hz, $J=1.4$ Hz, 1H), 5.71–5.77 (m, 1H), 9.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta=8.4$, 25.2, 28.2, 32.7, 41.9, 61.4, 75.3, 84.1, 125.1, 132.2, 152.5, 162.8; HR-MS (ESI+): $m/z=308.1835$ $[M+Na]^+$, calcd. for $C_{15}H_{27}NO_4Na$: 308.1832.

tert-Butyl {(1*S*)-1-[(1,1-Dimethylpropoxy)methyl]-prop-2-en-1-yl}carbamate (2q)

KOH (203 mg, 3.62 mmol) was added to a solution of carbamate **2j** (2.58 g, 9.04 mmol) in MeOH (45 mL). The mixture

was stirred for 21 h at room temperature when TLC monitoring [petroleum ether/ethyl acetate 9:1, R_f(**2j**) = 0.44, R_f(**2q**) = 0.37, $KMnO_4$] showed complete conversion of the starting material. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) affording **2q** as a colorless oil; yield: 2.33 g (9.03 mmol, 100%); $[\alpha]_D^{20}$: −35.3 (*c* 1.17, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.84 (t, *J* = 7.5 Hz, 3H), 1.09 (s, 6H), 1.44 (s, 9H), 1.45 (q, *J* = 7.4 Hz, 2H), 3.33 (dd, *J* = 8.8 Hz, *J* = 4.0 Hz, 1H), 3.39 (dd, *J* = 8.8 Hz, *J* = 4.4 Hz, 1H), 4.17 (bs, 1H), 4.89 (bs, 1H), 5.10 (ddd, *J* = 10.4 Hz, *J* = 1.3 Hz, *J* = 1.3 Hz, 1H), 5.19 (ddd, *J* = 17.3 Hz, *J* = 1.3 Hz, *J* = 1.3 Hz, 1H), 5.85 (ddd, *J* = 17.1 Hz, *J* = 10.4 Hz, *J* = 5.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.3, 24.9, 25.0, 28.6, 33.0, 53.3, 63.6, 75.0, 79.4, 115.3, 137.3, 155.7; HR-MS (ESI+): *m/z* = 296.1627 [M+K]$^+$, calcd. for $C_{14}H_{27}NO_3K$: 296.1623.

4-Methyl-*N*-[(1*R*)-1-phenylprop-2-en-1-yl]-*N*-prop-2-yn-1-ylbenzenesulfonamide (*ent*-5a) (Table 2, entry 1)

GP2 was carried out with sulfonamide *ent*-**2a** (104 mg, 0.36 mmol), propargyl bromide (**4a**) (80% in toluene, 230 μL, 3.62 mmol), K_2CO_3 (100 mg, 0.72 mmol), TBAI (26.7 mg, 72.3 μmol) and MeCN (5.7 mL); reaction time: 2 h at 90 °C; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**2a**) = 0.40, R_f(**5a**) = 0.56, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) afforded *ent*-**5a** as a yellowish oil; yield: 109 mg (0.34 mmol, 93%); $[\alpha]_D^{20}$: +15.6 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.99 (t, *J* = 2.5 Hz, 1H), 2.38 (s, 3H), 3.75 (dd, *J* = 18.6 Hz, *J* = 2.5 Hz, 1H), 4.11 (dd, *J* = 18.6 Hz, *J* = 2.5 Hz, 1H), 5.12 (ddd, *J* = 17.0 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 5.21 (ddd, *J* = 10.3 Hz, *J* = 1.0 Hz, *J* = 1.0 Hz, 1H), 5.57 (d, *J* = 7.5 Hz, 1H, 1-H), 6.17 (ddd, *J* = 17.8 Hz, *J* = 10.3 Hz, *J* = 7.5 Hz, 1H), 7.21–7.27 (m, 7H), 7.75 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.7, 34.0, 63.9, 72.8, 79.5, 119.4, 128.0, 128.1, 128.3, 128.7, 129.4, 134.1, 137.8, 138.0, 143.5; HR-MS (FAB+): *m/z* = 326.1221 [M+H]$^+$, calcd. for $C_{19}H_{20}NO_2S$: 326.1215; elem. anal. calcd. for $C_{19}H_{19}NO_2S$: C 70.12, H 5.88, N 4.30, S 9.85; found: C 69.84, H 6.03, N 4.12, S 9.73.

2-Methyl-*N*-[(1*S*)-1-propylprop-2-en-1-yl]-*N*-prop-2-yn-1-ylbenzenesulfonamide (*ent*-5b) (Table 2, entry 2)

GP2 was carried out with sulfonamide *ent*-**2b** (484 mg, 1.91 mmol), propargyl bromide (**4a**) (80% in toluene, 1.26 mL, 19.1 mmol), K_2CO_3 (528 mg, 3.82 mmol), TBAI (141 mg, 0.38 mmol) and MeCN (27 mL); reaction time: 2.5 h at 90 °C; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**2b**) = 0.18, R_f(**5b**) = 0.32, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) afforded *ent*-**5b** as a colorless oil; yield: 548 g (1.88 mmol, 98%); $[\alpha]_D^{20}$: −34.2 (*c* 0.95, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.87 (t, *J* = 7.4 Hz, 3H), 1.22–1.39 (m, 2H), 1.57–1.68 (m, 2H), 2.13 (t, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 3.90 (dd, *J* = 14.1 Hz, *J* = 6.8 Hz, 1H), 4.08 (dd, *J* = 18.5 Hz, *J* = 2.4 Hz, 1H), 4.36 (dd, *J* = 14.1, *J* = 6.8 Hz, 1H), 5.08 (d, *J* = 17.3 Hz, 1H), 5.11 (d, *J* = 10.6 Hz, 1H), 5.69 (ddd, *J* = 16.8 Hz, *J* = 10.7 Hz, *J* = 6.1 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.7, 19.5, 21.5, 32.4, 33.8, 59.7, 72.0, 79.9, 117.7, 127.6, 129.3, 135.9, 137.8, 143.2; HR-MS (FAB+): *m/z* = 292.1361 [M+H]$^+$, calcd. for $C_{16}H_{22}NO_2S$: 292.1371; elem. anal. calcd. for $C_{16}H_{21}NO_2S$: C 65.95, H 7.26, N 4.81, S 11.00; found: C 65.73, H 7.29, N 4.83, S 10.86.

2-Methyl-*N*-[(1*R*)-1-phenylprop-2-en-1-yl]-*N*-prop-2-yn-1-ylpropane-2-sulfonamide (*ent*-5c) (Table 2, entry 3)

GP2 was carried out with sulfonamide *ent*-**2c** (1.60 g, 6.30 mmol), propargyl bromide (**4a**) (80% in toluene, 4.15 mL, 63.0 mmol), K_2CO_3 (1.75 g, 12.6 mmol), TBAI (465 mg, 1.26 mmol) and MeCN (90 mL); reaction time: 6 h at 90 °C; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**2c**) = 0.36, R_f(**5c**) = 0.52, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) afforded *ent*-**5c** as an orange oil; yield: 1.79 g (6.14 mmol, 97%); $[\alpha]_D^{20}$: +3.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.48 (s, 9H), 2.21 (t, *J* = 2.4 Hz, 1H), 3.68 (d, *J* = 17.7 Hz, 1H), 4.23 (d, *J* = 18.7 Hz, 1H), 5.32 (ddd, *J* = 17.1 Hz, *J* = 1.1 Hz, *J* = 1.1 Hz, 1H), 5.43 (ddd, *J* = 10.3 Hz, *J* = 1.0 Hz, *J* = 1.0 Hz, 1H), 5.68 (d, *J* = 7.8 Hz, 1H), 6.48–6.60 (m, 1H), 7.27–7.47 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.9, 34.7, 61.7, 65.4, 72.8, 81.2, 119.4, 128.1, 128.6, 128.7, 135.4, 138.1; HR-MS (FAB+): *m/z* = 292.1384 [M+H]$^+$, calcd. for $C_{16}H_{22}NO_2S$: 292.1371; elem. anal. calcd. for $C_{16}H_{21}NO_2S$: C 65.95, H 7.26, N 4.81, S 11.00; found: C 65.80, H 7.28, N 4.77, S 11.11.

N-[(1*R*)-1-Phenylprop-2-en-1-yl]-*N*-prop-2-yn-1-yl-2-(trimethylsilyl)ethanesulfonamide (*ent*-5d) (Table 2, entry 4)

GP2 was carried out with sulfonamide *ent*-**2e** (195 mg, 0.66 mmol), propargyl bromide (**4a**)(80% in toluene, 420 μL, 6.55 mmol), K_2CO_3 (181 mg, 1.31 mmol), TBAI (48.4 mg, 0.13 mmol) and MeCN (9.3 mL); reaction time: 2 h at 90 °C; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**2e**) = 0.35, R_f(**5d**) = 0.51, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) afforded *ent*-**5d** as a yellowish oil; yield: 209 mg (0.62 mmol, 95%); $[\alpha]_D^{20}$: +5.2 (*c* 0.51, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.03 (s, 9H), 1.11 (m_c, 2H), 2.26 (t, *J* = 2.5 Hz, 1H), 3.09 (m_c, 2H), 3.70 (dd, *J* = 18.7 Hz, *J* = 2.5 Hz, 1H), 4.13 (dd, *J* = 18.7 Hz, *J* = 2.5 Hz, 1H), 5.39 (d, *J* = 17.0 Hz, 1H), 5.44 (d, *J* = 10.3 Hz, 1H), 5.59 (d, *J* = 8.2 Hz, 1H), 6.43 (ddd, *J* = 17.0 Hz, *J* = 10.2 Hz, *J* = 8.2 Hz, 1H), 7.28–7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = −1.9, 10.1, 33.9, 50.7, 64.3, 73.0, 80.5, 119.6, 128.2, 128.8, 135.1, 138.1; HR-MS (FAB+): *m/z* = 336.1419 [M+H]$^+$, calcd. for $C_{17}H_{26}NO_2SSi$: 336.1454; elem. anal. calcd. for $C_{17}H_{25}NO_2SSi$: C 60.85, H 7.51, N 4.17, S 9.56; found: C 60.85, H 7.57, N 4.26, S 9.44.

(1*S*)-*N*-Benzyl-1-phenyl-*N*-prop-2-yn-1-ylprop-2-en-1-amine (5e) (Table 2, entry 5)

Under an atmosphere of argon, the amine **2k** (114 mg, 0.51 mmol) was dropped into a suspension of NaH (17.9 mg, 0.75 mmol) in dry THF (0.7 mL). The reaction mixture was stirred at room temperature for 5 min until a clear solution was formed. Propargyl bromide (**4a**) (80% in toluene,

1.15 mL, 15.3 mmol) was added. The mixture turned brown and turbid and was heated at reflux (4 h) until TLC monitoring [petroleum ether/ethyl acetate 10:1, R_f(**5e**) = 0.57, $KMnO_4$] indicated complete consumption of the starting material. Saturated NH_4Cl solution was added, and the aqueous phase was extracted with Et_2O. The combined organic layers were dried over Mg_2SO_4, filtered and concentrated under vacuum. Column chromatography on silica gel (petroleum ether/ethyl acetate 1:1) afforded **5e** as a colorless oil which crystallized in the refrigerator as small, felt like needles; yield: 117 mg (0.48 mmol, 89%); mp 55–57 °C; $[\alpha]_D^{20}$: +59.2 (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.27 (t, *J* = 2.4 Hz, 1H), 3.18 (dd, *J* = 17.4 Hz, *J* = 2.1 Hz, 1H), 3.39 (dd, *J* = 17.6 Hz, *J* = 1.4 Hz, 1H), 3.59 (d, *J* = 13.4 Hz, 1H), 3.73 (d, *J* = 13.4 Hz, 1H), 4.26 (d, *J* = 9.1 Hz, 1H), 5.15 (dd, *J* = 10.0 Hz, *J* = 1.7 Hz, 1H), 5.39 (dd, *J* = 17.1 Hz, *J* = 1.2 Hz, 1H), 6.01 (ddd, *J* = 16.9 Hz, *J* = 9.3 Hz, *J* = 9.7 Hz, 1H), 7.22–7.39 (m, 8H), 7.48–7.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 38.7, 53.9, 70.5, 73.3, 78.6, 116.7, 127.0, 127.3, 127.9, 128.3, 128.7, 128.9, 139.1, 139.9, 142.4; HR-MS (EI+): *m/z* = 261.1499 $[M]^+$, calcd. for $C_{19}H_{19}N$: 261.1517; elem. anal. calcd. for $C_{19}H_{19}N$: C 87.31, H 7.33, N 5.36; found: C 87.02, H 7.34, N 5.19.

(1*S*)-Dimethyl (1-Phenylprop-2-en-1-yl)(prop-2-yn-1-yl)malonate (5f) (Table 2, entry 6)

Under an atmosphere of argon diester **2l** (712 mg, 2.87 mmol) was dropped into a suspension of NaH (99.4 mg, 4.17 mmol) in dry THF (4 mL). The reaction mixture was stirred at room temperature for 5 min when a clear solution was formed. Then propargyl bromide (**4a**) (80% in toluene, 0.5 mL, 7.00 mmol) was added. The mixture turned brown and turbid and was heated for 12 h at reflux. Saturated NH_4Cl solution was added, and the aqueous phase was extracted with Et_2O. The combined organic layers were dried over Mg_2SO_4, filtered and concentrated under vacuum. Kugelrohr distillation afforded **5f** as a colorless, viscous oil; yield (670 mg, 2.35 mmol, 82%); $[\alpha]_D^{20}$: +37.8 (*c* 1.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.09 (t, *J* = 2.6 Hz, 1H), 2.56 (dd, *J* = 17.1 Hz, *J* = 2.7 Hz, 1H), 2.75 (dd, *J* = 17.2 Hz, *J* = 2.6 Hz, 1H) 3.72 (s, 3H), 3.76 (s, 3H), 4.26 (d, *J* = 8.2 Hz, 1H), 5.06–5.17 (m, 2H), 6.42 (ddd, *J* = 16.9 Hz, *J* = 10.3 Hz, *J* = 8.2 Hz, 1H), 7.17–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.6, 52.4, 52.5, 52.7, 61.4, 71.9, 79.2, 117.7, 127.4, 128.3, 129.2, 137.0, 138.5; HR-MS (EI+): *m/z* = 286.1216 $[M]^+$, calcd. for $C_{17}H_{18}O_4$: 286.1205.

(*R*)-(4-Methoxyphenyl)(1-phenylprop-2-en-1-yl)prop-2-yn-1-ylamine (*ent*-5g) (Table 2, entry 7)

GP2 was carried out with *ent*-**2m** (201 mg, 0.84 mmol), propargyl bromide (**4a**) (80% in toluene, 0.82 mL, 12.8 mmol), K_2CO_3 (145 mg, 1.05 mmol) and MeCN (5 mL); reaction time: 19 h at 60 °C; TLC monitoring [petroleum ether/ethyl acetate 20:1, R_f(**2m**) = 0.23, R_f(**5g**) = 0.33, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 40:1) afforded *ent*-**5g** as a pale yellow oil; yield: 212 mg (0.76 mmol, 91%); $[\alpha]_D^{23}$: −27.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.12 (t, *J* = 2.3 Hz, 1H), 3.68 (s, 3H), 3.78 (dd, *J* = 15.0 Hz, *J* = 2.4 Hz, 1H), 3.87 (dd, *J* = 17.8 Hz, *J* = 2.4 Hz, 1H), 5.06–5.22 (m, 3H), 5.98 (ddd, *J* = 17.2 Hz, *J* = 9.9 Hz, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 7.15–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 41.0, 55.4, 67.5, 72.3, 80.5, 114.0, 117.3, 121.8, 127.2, 128.0, 128.5, 138.1, 141.1, 142.2, 154.4; HR-MS (EI+): *m/z* = 277.1471 $[M]^+$, calcd. for $C_{19}H_{19}NO$: 277.1467; elem. anal. calcd. for $C_{19}H_{19}NO$: C 82.28, H 6.90, N 5.05; found: C 82.05, H 6.87, N 4.97.

(*R*)-*N*-But-2-yn-1-yl-4-methoxy-*N*-(1-phenylprop-2-en-1-yl)aniline (*ent*-5h) (Table 2, entry 8)

GP2 was carried out with *ent*-**2m** (525 mg, 2.19 mmol), but-2-yn-1-yl methanesulfonate (**4d**) (1.06 g, 7.14 mmol), K_2CO_3 (360 mg, 2.61 mmol) and MeCN (11 mL); reaction time: 48 h at 60 °C; TLC monitoring [petroleum ether/ethyl acetate 20:1, R_f(**2m**) = 0.19, R_f(**5h**) = 0.31, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 40:1) afforded *ent*-**5h** as a pale yellow oil; yield: 428 mg (1.47 mmol, 67%); $[\alpha]_D^{20}$: +4.0 (*c* 1.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.77 (t, *J* = 2.3 Hz, 3H), 3.70–3.86 (m, 2H), 3.72 (s, 3H), 5.12–5.24 (m, 3H), 6.06 (ddd, *J* = 17.2 Hz, *J* = 10.0 Hz, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 7.18–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 3.6, 40.9, 55.5, 67.3, 75.7, 79.7, 114.0, 117.2, 120.9, 127.1, 128.0, 128.4, 138.1, 141.1, 142.5, 153.8; HR-MS (EI+): *m/z* = 291.1606 $[M]^+$, calcd. for $C_{20}H_{21}NO$: 291.1623.

(*R*)-(4-Methoxyphenyl)-prop-2-yn-1-yl-[1-(trityloxy)-but-3-en-1-yl]amine (*ent*-5i) (Table 2, entry 9)

GP2 was carried out with the amine *ent*-**2n** (873 mg, 2.00 mmol), propargyl bromide (**4a**) (80% in toluene, 1.97 mL, 17.7 mmol), K_2CO_3 (347 mg, 2.51 mmol) and MeCN (8 mL); reaction time: 24 h at 60 °C; TLC monitoring [petroleum ether/ethyl acetate 20:1, R_f(**2n**) = 0.19, R_f(**5i**) = 0.31, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 40:1) afforded *ent*-**5i** as a pale yellow oil; yield: 816 mg (1.72 mmol, 86%); $[\alpha]_D^{26}$: +11.5 (*c* 0.96, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.06 (t, *J* = 2.3 Hz, 1H), 3.28 (dd, *J* = 9.4 Hz, *J* = 6.1 Hz, 1H), 3.33 (dd, *J* = 9.4 Hz, *J* = 6.1 Hz, 1H), 3.75 (s, 3H), 3.83 (t, *J* = 2.1 Hz, 2H), 4.35 (q, *J* = 5.8 Hz, 1H), 5.18–5.24 (m, 2H), 5.89 (ddd, *J* = 17.8 Hz, *J* = 10.2 Hz, *J* = 5.6 Hz, 1H), 6.78 (d, *J* = 9.2 Hz, 2H), 6.86 (d, *J* = 9.2 Hz, 2H), 7.17–7.39 (m, 15H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 37.6, 55.6, 62.3, 63.8, 71.5, 86.8, 114.4, 117.6, 118.2, 127.0, 127.7, 128.77, 135.8, 142.3, 143.9, 153.1; HR-MS (EI+): *m/z* = 473.2388 $[M]^+$, calcd. for $C_{33}H_{31}NO_2$: 473.2355.

(*R*)-But-2-yn-1-yl(4-methoxyphenyl){1-[(trityloxy)-methyl]prop-2-en-1-yl}amine (*ent*-5j) (Table 2, entry 10)

GP2 was carried out with amine *ent*-**2n** (1.02 g, 2.34 mmol), but-2-yn-1-yl methanesulfonate (**4d**) (1.96 g, 13.3 mmol), K_2CO_3 (725 mg, 5.25 mmol) and MeCN (5 mL); reaction time: 48 h at 60 °C; TLC monitoring [petroleum ether/ethyl acetate 20:1, R_f(**2n**) = 0.13, R_f(**5j**) = 0.23, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 40:1) afforded *ent*-**5j** as a pale yellow oil; yield: 871 mg (1.79 mmol, 76%); $[\alpha]_D^{26}$: +12.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.69 (t, *J* = 2.2 Hz, 3H), 3.26–3.36

(m_c, 2H), 3.73–3.79 (m, 2H), 3.75 (s, 3H), 4.37 (dt, J = 5.8 Hz, J = 5.8 Hz, 1H), 5.16–5.22 (m, 2H), 5.91 (ddd, J = 16.7 Hz, J = 11.2 Hz, J = 5.5 Hz, 1H), 6.76–6.86 (m, 4H), 7.17–7.27 (m, 10H), 7.36–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 3.6, 37.7, 55.6, 62.0, 63.7, 78.9, 86.7, 114.3, 117.3, 117.5, 126.9, 127.7, 128.7, 135.9, 142.6, 144.0, 152.6; HR-MS (EI+): m/z = 487.2474 $[M]^+$, calcd. for $C_{34}H_{33}NO_2$: 487.2511.

tert-Butyl [(1*R*)-1-Phenylprop-2-en-1-yl]prop-2-yn-1-ylcarbamate (*ent*-5k) (Table 3, entry 1)

GP3 was carried out with carbamate *ent*-**2o** (500 mg, 2.14 mmol), propargyl bromide (**4a**) (80% in toluene, 1.4 mL, 21.4 mmol), NaH (154 mg, 6.43 mmol) and dry DMF (25 mL); reaction time: 14 h at −30 °C; GC/MS monitoring [t_R(**2o**) = 9.6 min, t_R(**5k**) = 10.4 min]. Column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) afforded *ent*-**5k** as a colorless oil; yield: 543 mg (2.00 mmol, 93%); $[\alpha]_D^{20}$: +40.6 (c 1.38, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.42 (s, 9H), 2.10 (s, 1H), 3.76 (d, J = 16.7 Hz, 1H), 4.03 (d, J = 17.0 Hz, 1H), 5.28 (ddd, J = 17.1 Hz, J = 1.2 Hz, J = 1.2 Hz, 1H), 5.37 (ddd, J = 10.3 Hz, J = 1.2 Hz, J = 1.2 Hz, 1H), 5.69 (bs, 1H), 6.23 (ddd, J = 17.1 Hz, J = 10.3 Hz, J = 6.8 Hz, 1H), 7.24–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 28.4, 34.4, 62.3, 70.7, 80.8, 80.9, 118.5, 127.5, 127.8, 128.5, 135.1, 139.7, 155.1; HR-MS (FAB+): m/z = 272.1646 $[M+H]^+$, calcd. for $C_{17}H_{22}NO_2$: 272.1651.

tert-Butyl But-2-yn-1-yl[(1*R*)-1-phenylprop-2-en-1-yl]carbamate (*ent*-5l) (Table 3, entry 3)

GP3 was carried out with carbamate *ent*-**2o** (80.0 mg, 0.34 mmol), 1-bromobut-2-yne (**4b**) (456 mg, 3.43 mmol), NaH (25.0 mg, 1.03 mmol) and dry DMF (3.8 mL); reaction time: 2.5 h at −30 °C; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**2o**) = 0.40, R_f(**5l**) = 0.48, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) afforded *ent*-**5l** as a colorless oil; yield: 84.0 mg (0.29 mmol, 86%); $[\alpha]_D^{20}$: +44.8 (c 0.99, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.39 (s, 9H), 1.74 (t, J = 2.4 Hz, 3H), 3.75 (d, J = 17.3 Hz, 1H), 4.03 (bd, J = 16.8 Hz, 1H), 5.26 (ddd, J = 17.1 Hz, J = 1.4 Hz, J = 1.4 Hz, 1H), 5.35 (ddd, J = 10.3 Hz, J = 1.3 Hz, J = 1.3 Hz, 1H), 5.69 (bs, 1H), 6.25 (ddd, J = 17.2 Hz, J = 10.3 Hz, J = 7.0 Hz, 1H), 7.22–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 3.6, 28.5, 35.1, 62.4, 76.1, 78.5, 80.4, 118.2, 127.3, 127.6, 128.3, 135.5, 140.2, 155.2; HR-MS (ESI+): m/z = 286.1803 $[M+H]^+$, calcd. for $C_{18}H_{24}NO_2$: 286.1802.

tert-Butyl [(1*R*)-1-Phenylprop-2-en-1-yl][3-(trimethylsilyl)prop-2-yn-1-yl]carbamate (*ent*-5m) (Table 3, entry 4)

GP3 was carried out with carbamate *ent*-**2o** (140 mg, 0.60 mmol), (3-bromoprop-1-yn-1-yl)(trimethyl)silane (**4c**) (940 μL, 6.00 mmol), NaH (43.0 mg, 1.80 mmol) and dry DMF (6.7 mL); reaction time: 4 h at −30 °C; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**2o**) = 0.46, R_f(**5m**) = 0.54, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) afforded *ent*-**5m** as a brownish oil; yield: 171 mg (0.50 mmol, 83%); $[\alpha]_D^{20}$: +46.2 (c 0.58, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.05 (s, 9H), 1.34 (bs, 9H), 3.73 (d, J = 17.5 Hz, 1H), 3.93 (bs, 1H), 5.22 (ddd, J = 17.1 Hz, J = 1.3 Hz, J = 1.3 Hz, 1H), 5.28 (ddd, J = 10.3 Hz, J = 1.3 Hz, J = 1.3 Hz, 1H), 5.61 (bs, 1H), 6.16 (ddd, J = 17.1 Hz, J = 10.3 Hz, J = 6.7 Hz, 1H), 7.16–7.28 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = −0.1, 28.5, 35.6, 62.2, 80.6, 87.3, 103.1, 118.3, 127.4, 127.9, 128.4, 135.3, 139.9, 155.2; HR-MS (FAB+): m/z = 344.2014 $[M+H]^+$, calcd. for $C_{20}H_{30}NO_2Si$: 344.2046.

tert-Butyl [(1*S*)-1-({[*tert*-Butyl(diphenyl)silyl]oxy}methyl)prop-2-en-1-yl]but-2-yn-1-ylcarbamate (5n) (Table 3, entry 5)

GP3 was carried out with carbamate **2p** (8.64 g, 20.3 mmol), 1-bromobut-2-yne (**4b**) (27.0 g, 203 mmol), 15-crown-5 (13.4 g, 60.9 mmol), NaH (1.46 g, 60.9 mmol) and dry DMF (225 mL); reaction time: 5 h at −30 °C; TLC monitoring [petroleum ether/ethyl acetate 9:1, R_f(**2p**) = 0.31, R_f(**5n**) = 0.38, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) afforded **5n** as a colorless oil; yield: 7.94 g (16.7 mmol, 82%); $[\alpha]_D^{20}$: −5.1 (c 1.31, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz, 50 °C): δ = 1.09 (s, 9H), 1.47 (s, 9H, 1.74 (t, J = 2.3 Hz, 3H), 3.86 (dd, J = 10.3 Hz, J = 6.4 Hz, 1H), 3.94 (dd, J = 10.3 Hz, J = 7.0 Hz, 1H), 3.95–4.08 (m, 2H), 4.56 (bs, 1H), 5.18–5.23 (m, 2H), 5.96 (ddd, J = 17.7 Hz, J = 10.3 Hz, J = 5.8 Hz, 1H), 7.37–7.47 (m, 6H), 7.67–7.72 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz, 50 °C): δ = 3.5, 19.5, 27.1, 28.7, 35.3, 60.6, 64.7, 76.5, 80.2, 117.1, 127.8, 129.8, 133.9, 135.2, 135.8, 155.2; HR-MS (FAB+): m/z = 478.2740 $[M+H]^+$, calcd. for $C_{29}H_{40}NO_3Si$: 478.2772.

tert-Butyl But-2-yn-1-yl{(1*S*)-1-[(1,1-dimethylpropoxy)methyl]prop-2-en-1-yl}carbamate (5o) (Table 3, entry 7)

GP3 was carried out with carbamate **2q** (2.30 g, 8.94 mmol), 1-bromobut-2-yne (**4b**) (11.9 g, 89.4 mmol), 15-crown-5 (5.90 g, 26.8 mmol), NaH (643 mg, 26.8 mmol) and dry DMF (100 mL); reaction time: 2 h 45 min at −30 °C; TLC monitoring [petroleum ether/ethyl acetate 9:1, R_f(**2q**) = 0.34, R_f(**5o**) = 0.40, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 30:1→20:1→9:1) afforded **5o** as a colorless oil; yield: 2.59 g (8.38 mmol, 94%); $[\alpha]_D^{20}$: −5.3 (c 0.46, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz, 50 °C): δ = 0.85 (t, J = 7.5 Hz, 3H), 1.11 (s, 6H), 1.46 (s, 9H), 1.47 (q, J = 7.5 Hz, 2H), 1.77 (t, J = 2.4 Hz, 3H), 3.52 (dd, J = 9.1 Hz, J = 6.2 Hz, 1H), 3.60 (dd, J = 9.1 Hz, J = 6.6 Hz, 1H), 3.91 (d, J = 17.3 Hz, 1H), 4.02 (d, J = 17.0 Hz, 1H), 4.40 (bs, 1H), 5.16 (ddd, J = 10.6 Hz, J = 1.5 Hz, J = 1.5 Hz, 1H), 5.20 (ddd, J = 17.5 Hz, J = 1.4 Hz, J = 1.4 Hz, 1H), 5.96 (ddd, J = 17.3 Hz, J = 10.6 Hz, J = 5.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz, 50 °C): δ = 3.5, 8.3, 24.9, 25.0, 28.7, 33.4, 35.8, 59.5, 62.5, 75.0, 76.7, 78.0, 80.0, 116.5, 135.8, 155.2; HR-MS (ESI+): m/z = 310.2382 $[M+H]^+$, calcd. for $C_{18}H_{32}NO_3$: 310.2377.

(3*S*,3a*S*)-2-[(4-Methylphenyl)sulfonyl]-3-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (6a) (Table 4, entry 1)

GP4 was carried out with enyne **5a** (76.0 mg, 0.23 mmol), $Co_2(CO)_8$ (88.0 mg, 0.26 mmol) and dry CH_2Cl_2 (3.5 mL);

reaction time: 1.5 h; TLC monitoring {petroleum ether/ethyl acetate 4:1, R_f(**5a**) = 0.47, R_f[**5a-$Co_2(CO)_6$**] = 0.61, $KMnO_4$}. Then $Me_3NO{\cdot}2H_2O$ (256 mg, 2.30 mmol) and 4 Å MS were added; reaction time: 2 h at room emperature; TLC monitoring {petroleum ether/ethyl acetate 1:1, R_f[**5a-$Co_2(CO)_6$**] = 0.90, R_f(**6a/7a**) = 0.25, $KMnO_4$}. Column chromatography on silica gel (petroleum ether/ethyl acetate 1:1 + Et_3N) afforded cyclopentenones **6a/7a** as a mixture of diastereoisomers in a ratio of 78:22; yield: 55.0 mg (0.16 mmol, 68%). An analytically pure sample of the major (3*S*,3a*S*)-isomer **6a** could be obtained after preparative HPLC as colorless needles; mp 148–149 °C; $[\alpha]_D^{20}$: −196.1 (*c* 1.09, $CHCl_3$); ^{1}H NMR (benzene-d_6, 300 MHz): δ = 1.54 (dd, *J* = 17.7 Hz, *J* = 3.7 Hz, 1H), 1.80 (dd, *J* = 17.7 Hz, *J* = 6.6 Hz, 1H), 1.87 (s, 3H), 2.47–2.54 (m, 1H), 3.72 (d, *J* = 9.8 Hz, 1H), 3.93 (ddd, *J* = 16.3 Hz, *J* = 1.5 Hz, *J* = 1.5 Hz, 1H), 4.20 (d, *J* = 16.1 Hz, 1H), 5.39–5.40 (m, 1H), 6.72 (d, *J* = 8.0 Hz, 2H), 7.03–7.11 (m, 5H), 7.47 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (benzene-d_6, 75 MHz): δ = 21.1, 39.2, 49.6, 54.5, 69.7, 125.5, 127.4, 128.0, 128.1, 128.6, 129.5, 136.0, 139.8, 143.4, 174.7, 205.1; HR-MS (FAB+): *m/z* = 354.1180 $[M+H]^+$, calcd. for $C_{20}H_{20}NO_3S$: 354.1164; elem. anal. calcd. for $C_{20}H_{19}NO_3S$: C 67.97, H 5.42, N 3.96, S 9.07; found: C 67.87, H 5.60, N 3.80, S 8.82.

(3*S*,3a*S*)-2-[(4-Methylphenyl)sulfonyl]-3-propyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*ent*-6b) (Table 4, entry 2)

GP4 was carried out with enyne *ent*-**5b** (396 mg, 1.36 mmol), $Co_2(CO)_8$ (511 mg, 1.50 mmol) and dry CH_2Cl_2 (23 mL); reaction time: 3 h; TLC monitoring {petroleum ether/ethyl acetate 4:1, R_f(**5b**) = 0.42, R_f[**5b-$Co_2(CO)_6$**] = 0.54, $KMnO_4$}. Then $Me_3NO{\cdot}2H_2O$ (1.56 g, 14.0 mmol) was added; reaction time: 4.5 h at room temperature; TLC monitoring {petroleum ether/ethyl acetate 1:1, R_f[**5b-$Co_2(CO)_6$**] = 0.90, R_f(**6b/7b**) = 0.52, $KMnO_4$}. Column chromatography on silica gel (petroleum ether/ethyl acetate 2:1) afforded cyclopentenones *ent*-**6b**/*ent*-**7b** as a mixture of diastereoisomers in a ratio of 66:34; yield: 301 mg (0.94 mmol, 69%). Analytically pure samples of the major (3*S*,3a*S*)-isomer *ent*-**6b** and the minor (3*S*,3a*R*)-isomer *ent*-**7b** could be obtained after preparative HPLC.

Analytical data for *ent*-6b: Yellow solid; mp 124–126 °C; $[\alpha]_D^{20}$: +218.0 (*c* 1.06, $CHCl_3$); ^{1}H NMR (benzene-d_6, 300 MHz): δ = 0.83 (t, *J* = 7.0 Hz, 3H), 0.88–1.01, 1.04–1.18 (2 m, 2H), 1.40 (dd, *J* = 17.0 Hz, *J* = 6.6 Hz, 1H), 1.48–1.60 (m, 1H), 1.86 (s, 3H), 1.97 (dd, *J* = 17.0 Hz, *J* = 6.6 Hz, 1H), 2.02–2.08 (m, 1H), 2.18 (dddd, *J* = 13.5 Hz, *J* = 11.1 Hz, *J* = 5.4 Hz, *J* = 3.5 Hz, 1H), 2.77 (ddd, *J* = 8.9 Hz, *J* = 8.9 Hz, *J* = 3.6 Hz, 1H), 3.72 (ddd, *J* = 16.3 Hz, *J* = 1.5 Hz, *J* = 1.5 Hz, 1H), 3.92 (d, *J* = 16.3 Hz, 1H), 5.24–5.26 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (benzene-d_6, 75 MHz): δ = 14.3, 18.7, 21.1, 37.6, 41.4, 49.5, 49.6, 66.0, 124.6, 127.8, 129.8, 135.4, 143.6, 175.5, 205.6; HR-MS (FAB+): *m/z* = 320.1320 $[M+H]^+$, calcd. for $C_{17}H_{22}NO_3S$: 320.1325; elem. anal. calcd. for $C_{17}H_{21}NO_3S$: C 63.92, H 6.63, N 4.39, S 10.04; found: C 63.78, H 6.62, N 4.33, S 10.27.

Analytical data for *ent*-7b: White solid, which crystallized from benzene-d_6 in the NMR tube as monoclinic crystals, suitable for X-ray crystal structure analysis; mp 100–101 °C; $[\alpha]_D^{20}$: −82.6 (*c* 1.73, $CHCl_3$); ^{1}H NMR (benzene-d_6, 300 MHz): δ = 0.84 (t, *J* = 7.2 Hz, 3H), 0.97–1.10 (m, 1H), 1.16–1.44 (m, 3H), 2.08 (dd, *J* = 18.2 Hz, *J* = 3.6 Hz, 1H), 2.29 (dd, *J* = 18.2 Hz, *J* = 6.5 Hz, 1H), 2.36 (s, 3H), 2.59–2.66 (m, 1H), 4.07 (ddd, *J* = 8.7 Hz, *J* = 8.7 Hz, *J* = 4.4 Hz, 1H), 4.13 (d, *J* = 17.8 Hz, 1H), 4.20 (d, *J* = 17.8 Hz, 1H), 5.94–5.96 (m, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (benzene-d_6, 75 MHz): δ = 13.8, 13.9, 21.5, 31.5, 37.3, 46.8, 47.4, 60.5, 126.6, 127.1, 130.0, 135.3, 143.9, 180.3, 208.3.

(3*S*,3a*S*)-6-Methyl-2-[4-methylphenyl)sulfonyl]-3-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (6c) (Table 4, entry 3)

GP4 was carried out with enyne **2g** (46.0 mg, 0.14 mmol), $Co_2(CO)_8$ (51.0 mg, 0.15 mmol) and dry CH_2Cl_2 (2.3 mL); reaction time: 40 min; TLC monitoring {petroleum ether/ethyl acetate 4:1, R_f(**2g**) = 0.40, R_f[**2g-$Co_2(CO)_6$**] = 0.53, $KMnO_4$}. Then $Me_3NO{\cdot}2H_2O$ (151 mg, 1.36 mmol) was added; reaction time: 4 h at room temperature; TLC monitoring {petroleum ether/ethyl acetate 1:1, R_f[**2g-$Co_2(CO)_6$**] = 0.78, R_f(**6c/7c**) = 0.43, $KMnO_4$}. Column chromatography on silica gel (petroleum ether/ethyl acetate 1:1) afforded cyclopentenones **6c/7c** as a mixture of diastereoisomers in a ratio of 69:31; yield: 36.0 mg (0.10 mmol 72%). Analytically pure samples of the major (3*S*,3a*S*)-isomer **6c** and the minor (3*S*,3a*R*)-isomer **7c** could be obtained after preparative HPLC.

Analytical data for 6c: Yellowish oil; $[\alpha]_D^{20}$: −55.7 (*c* 1.03, $CHCl_3$); ^{1}H NMR (benzene-d_6, 300 MHz): δ = 1.38–1.40 (m, 3H), 1.57 (dd, *J* = 17.7 Hz, *J* = 3.3 Hz, 1H), 1.85 (s, 3H), 1.89 (dd, *J* = 17.7 Hz, *J* = 6.3 Hz, 1H), 2.43–2.52 (m, 1H), 3.76 (d, *J* = 9.6 Hz, 1H), 3.92 (ddd, *J* = 15.7 Hz, *J* = 1.2 Hz, *J* = 1.2 Hz, 1H), 4.35 (d, *J* = 15.7 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 7.05–7.15 (m, 5H), 7.48 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (benzene-d_6, 75 MHz): δ = 8.4, 21.1, 38.6, 48.7, 52.5, 69.8, 127.4, 127.9, 128.6, 129.5, 133.3, 136.3, 140.1, 143.3, 167.2, 205.3; HR-MS (FAB+): *m/z* = 368.1315 $[M+H]^+$, calcd. for $C_{21}H_{22}NO_3S$: 368.1320.

Analytical data for 7c: Crystallized from benzene-d_6 in the NMR tube as orthorhombic crystals, suitable for X-ray crystal structure analysis; mp 203–205 °C; $[\alpha]_D^{20}$: +13.8 (*c* 0.22, $CHCl_3$); ^{1}H NMR (benzene-d_6, 300 MHz): δ = 1.28 (dd, *J* = 18.0 Hz, *J* = 3.4 Hz, 1H), 1.40 (ddd, *J* = 2.5 Hz, *J* = 1.3 Hz, *J* = 1.3 Hz, 3H), 1.84 (dd, *J* = 17.8 Hz, *J* = 6.4 Hz, 1H), 1.88 (s, 3H), 2.50–2.60 (m, 1H), 4.02 (d, *J* = 15.9 Hz, 1H), 4.07 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 9.0 Hz, 1H), 6.59–6.62 (m, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 6.87–6.91 (m, 3H), 7.58 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (benzene-d_6, 75 MHz): δ = 8.6, 21.1, 37.1, 46.7, 47.3, 64.5, 127.0, 127.6, 127.9, 128.6, 129.6, 134.8, 137.9, 143.0, 168.0, 205.8.

(3*S*,3a*S*)-2-(*tert*-Butylsulfonyl)-3-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (6d) (Table 4, entries 4 and 5)

Method A: GP4 was carried out with enyne **5c** (46.0 mg, 0.16 mmol), $Co_2(CO)_8$ (57.0 mg, 0.17 mmol) and dry CH_2Cl_2 (2.5 mL); reaction time: 1.5 h; TLC monitoring {petroleum ether/ethyl acetate 4:1, R_f(**5c**) = 0.69, R_f[**5c-$Co_2(CO)_6$**] = 0.78, $KMnO_4$}. Then $Me_3NO{\cdot}2H_2O$ (176 mg, 1.58 mmol) and 4 Å MS were added; reaction time: 2 h at room temperature;

TLC monitoring {petroleum ether/ethyl acetate 1:1, R_f[**5c-$Co_2(CO)_6$**] = 0.91, R_f(**6d/7d**) = 0.52, $KMnO_4$}. Column chromatography on silica gel (petroleum ether/ethyl acetate 2:1 + Et_3N) afforded cyclopentenones **6d/7d** as a mixture of diastereoisomers in a ratio of 82:18; yield: (33.0 mg, 0.10 mmol, 65%).

Method B: GP5 was carried out with enyne **5c** (102 mg, 0.35 mmol), $Co_2(CO)_8$ (30.0 mg, 87 μmol), *n*-BuSMe (128 mg, 1.23 mmol) and toluene (3.9 mL); reaction time: 20 min at 100 °C. Column chromatography on silica gel [petroleum ether/ethyl acetate 1:1, R_f(**6d/7d**) = 0.37, $KMnO_4$] afforded **6d/7d** as a mixture of diastereoisomers in a ratio of 71:29; yield: 95.0 mg (0.30 mmol, 85%). An enriched sample (*dr* = 96:04) of the major (3*S*,3a*S*)-isomer **6d** could be obtained after preparative HPLC as colorless plates. Crystallization from ethyl acetate/*n*-pentane at room temperature gave monoclinic colorless crystals suitable for X-ray crystal structure analysis; mp 160–162 °C; $[\alpha]_D^{20}$: −103.1 (*c* 0.74, $CHCl_3$); ^{1}H NMR (benzene-d_6, 300 MHz): δ = 0.92 (s, 9H), 1.65 (dd, *J* = 17.7 Hz, *J* = 3.7 Hz, 1H), 1.89 (dd, *J* = 17.7 Hz, *J* = 6.6 Hz, 1H), 2.59–2.65 (m, 1H), 3.43 (ddd, *J* = 14.9 Hz, *J* = 1.5 Hz, *J* = 1.5 Hz, 1H), 4.30 (d, *J* = 9.7 Hz, 1H), 4.52 (d, *J* = 15.0 Hz, 1H), 5.57–5.58 (m, 1H), 6.93–7.13 (m, 5H); ^{13}C NMR (benzene-d_6, 75 MHz): δ = 24.1, 39.7, 51.1, 53.2, 60.2, 69.0, 124.8, 128.2, 128.4, 128.6, 141.3, 175.8, 205.8; HR-MS (FAB+): *m/z* = 320.1340 $[M+H]^+$, calcd. for $C_{17}H_{22}NO_3S$: 320.1320; elem. anal. calcd. for $C_{17}H_{21}NO_3S$: C 63.92, H 6.63, N 4.39, S 10.04; found: C 63.88, H 6.67, N 4.41, S 10.01.

(3*R*,3a*R*)-3-Phenyl-2-{[2-(trimethylsilyl)ethyl]sulfonyl}-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*ent*-6e) (Table 4, entry 6)

GP4 was carried out with enyne *ent*-**5d** (100 mg, 0.30 mmol), $Co_2(CO)_8$ (108 mg, 0.32 mmol) and dry CH_2Cl_2 (4.5 mL); reaction time: 1 h; TLC monitoring [petroleum ether/ethyl acetate 4:1, R_f(**5d**) = 0.64, R_f[**5d-$Co_2(CO)_6$**] = 0.73 $KMnO_4$}. Then $Me_3NO{\cdot}2H_2O$ (333 mg, 3.0 mmol) and 4 Å MS were added; reaction time: 2 h at room temperature; TLC monitoring {petroleum ether/ethyl acetate 1:1, R_f[**5d-$Co_2(CO)_6$**] = 0.93, R_f(**6e/7e**) = 0.63, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 2:1 + Et_3N) afforded cyclopentenones *ent*-**6e**/*ent*-**7e** as a mixture of diastereoisomers in a ratio of 95:05; yield: 54.0 mg (0.15 mmol, 50%). An analytically pure sample of the major (3*R*,3a*R*)-isomer *ent*-**6e** could be obtained after preparative HPLC as colorless foam; $[\alpha]_D^{20}$: +66.2 (*c* 0.87, $CHCl_3$); ^{1}H NMR (benzene-d_6, 300 MHz): δ = −0.27 (s, 9H), 0.78–1.02 (m, 2H), 1.66 (dd, *J* = 17.7 Hz, *J* = 3.8 Hz, 1H), 1.87 (dd, *J* = 17.7 Hz, *J* = 6.5 Hz, 1H), 2.11–2.35 (m, 2H), 2.60–2.68 (m, 1H), 3.74 (ddd, *J* = 16.1 Hz, *J* = 1.5 Hz, *J* = 1.5 Hz, 1H), 4.01 (d, *J* = 10.2 Hz, 1H), 4.58 (d, *J* = 16.0 Hz, 1H), 5.51–5.53 (m, 1H), 7.02–7.11 (m, 5H); ^{13}C NMR (benzene-d_6, 75 MHz): δ = −2.2, 10.2, 39.1, 49.2, 51.2, 54.0, 69.0, 125.7, 128.2, 128.7, 129.0, 139.5, 175.1, 205.3; HR-MS (FAB+): *m/z* = 364.1393 $[M+H]^+$, calcd. for $C_{18}H_{26}NO_3SSi$: 364.1403; elem. anal. calcd. for $C_{18}H_{25}NO_3SSi$: C 59.47, H 6.93, N 3.85, S 8.82; found: C 59.60, H 7.03, N 3.80, S 8.78.

(3*S*,3a*S*)-2-Benzyl-3-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5-(1*H*)-one (6f) (Table 4, entry 7)

GP5 was carried out with enyne **5e** (46.7 mg, 0.18 mmol), $Co_2(CO)_8$ (14.8 mg, 0.04 mmol), *n*-BuSMe (25 μL, 0.20 mmol) and toluene (2 mL); reaction time: 10 min at 100 °C. Column chromatography on silica gel [petroleum ether/ethyl acetate 1:1, R_f(**6f**) = 0.60, $KMnO_4$] afforded **6f** as a yellow oil; yield: 26.7 mg (0.09 mmol, 51%); $[\alpha]_D^{20}$: −157.5 (*c* 1.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.22 (dd, *J* = 17.8 Hz, *J* = 3.1 Hz, 1H), 2.43 (dd, *J* = 17.7 Hz, *J* = 5.7 Hz, 1H), 3.21–3.31 (m, 4H, 3-H), 3.94 (d, *J* = 13.4 Hz, 1H), 4.12 (d, *J* = 17.8 Hz, 1H), 5.93–5.95 (m_c, 1H), 7.21–7.44 (m, 8H), 7.52–7.55 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 39.3, 53.2, 55.1, 57.3, 73.6, 124.9, 127.1, 127.3, 128.1, 128.4, 128.9, 138.5, 140.1, 184.3, 208.8; HR-MS (EI+): *m/z* = 289.1479 $[M]^+$, calcd. for $C_{20}H_{19}NO$: 289.1467.

Dimethyl (3*S*,3a*R*)-5-Oxo-3-phenyl-3,3a,4,5-tetrahydropentalene-2,2(1*H*)-dicarboxylate (6g) (Table 4, entries 8 and 9)

Method A: GP4 was carried out with enyne **5f** (300 mg, 1.05 mmol), $Co_2(CO)_8$ (394 mg, 1.15 mmol) and dry CH_2Cl_2 (17 mL); reaction time: 3.5 h; TLC monitoring {petroleum ether/ethyl acetate 9:1, R_f(**5f**) = 0.32, R_f[**5f-$Co_2(CO)_6$**] = 0.46, $KMnO_4$}. Then $Me_3NO{\cdot}2H_2O$ (349 mg, 3.14 mmol) and celite were added; reaction time: 16 h at room temperature; TLC monitoring {petroleum ether/ethyl acetate 1:1, R_f[**5f-$Co_2(CO)_6$**] = 0.81, R_f(**6g/7g**) = 0.58, $KMnO_4$}. Column chromatography on silica gel (petroleum ether/ethyl acetate 1:1) afforded cyclopentenones **6g/7g** as a mixture of diastereoisomers in a ratio of 97:03; yield: 270 mg (0.86 mmol, 82%).

Method B: GP5 was carried out with enyne **5f** (1.40 g, 4.88 mmol), $Co_2(CO)_8$ (417 mg, 1.22 mmol), *n*-DodSMe (3.70 g, 17.1 mmol) and toluene (20 mL); reaction time: 20 min at 100 °C. Column chromatography on silica gel [petroleum ether/ethyl acetate 1:1, R_f(**6g/7g**) = 0.58, $KMnO_4$] afforded **6g/7g** as a mixture of diastereoisomers in a ratio of 96:04; yield: 907 mg (2.88 mmol, 59%). An enriched sample (*dr* = 97:03) of the major (3*S*,3a*R*)-isomer **6g** could be obtained after preparative HPLC as colorless needles. Crystallization from toluene gave monoclinic crystals, suitable for X-ray crystal structure analysis; mp 138–140 °C; $[\alpha]_D^{20}$: −153.9 (*c* 0.97, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.04 (dd, *J* = 17.9 Hz, *J* = 2.3 Hz, 1H), 2.54 (dd, *J* = 18.3 Hz, *J* = 5.2 Hz, 1H), 3.05 (d, *J* = 18.5 Hz, 1H), 3.19 (s, 3H), 3.59–3.70 (m, 2H), 3.74 (s, 3H), 3.80 (d, *J* = 18.5 Hz, 1H), 5.96 (s, 1H), 7.17–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 36.8, 41.2, 48.0, 52.4, 52.9, 55.0, 65.9, 125.9, 127.8, 128.3, 128.4, 136.6, 170.7, 171.3, 183.3, 209.0; HR-MS (EI+): *m/z* = 314.1171 $[M]^+$, calcd. for $C_{18}H_{18}O_5$: 314.1154; elem. anal. calcd. for $C_{18}H_{28}O_5$: C 68.78, H 5.77; found: C 68.66, H 5.64.

(3*S*,3a*S*)-2-(4-Methoxyphenyl)-3-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (6h) (Table 4, entries 10 and 11)

Method A: GP4 was carried out with enyne **5g** (51.6 mg, 0.19 mmol), $Co_2(CO)_8$ (61.7 mg, 0.18 mmol) and dry CH_2Cl_2 (2.8 mL); reaction time: 3 h. Then $NMO{\cdot}H_2O$ (243 mg, 1.80 mmol) was added; reaction time: 3 h at room tempera-

ture; TLC monitoring [petroleum ether/ethyl acetate 5:1, R_f(**5g**) = 0.47, R_f(**6h**) = 0.08, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 5:1→0:1) afforded cyclopentenone **6h** as a pale yellow oil; yield: 37.9 mg (0.12 mmol, 66%).

Method B: GP5 was carried out with enyne **5g** (57.5 mg, 0.21 mmol), $Co_2(CO)_8$ (13.4 mg, 0.04 mmol), *n*-BuSMe (0.03 mL, 0.025 mmol) and toluene (2.1 mL); reaction time: 10 min at 100 °C. Column chromatography on silica gel (petroleum ether/ethyl acetate 5:1→1:1) afforded **6h** as a yellow oil; yield: 35.7 mg (0.12 mmol, 56%); $[\alpha]_D^{20}$: −20.2 (*c* 0.71, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.35 (dd, *J* = 17.8 Hz, *J* = 3.5 Hz, 1H), 2.47 (dd, *J* = 17.9 Hz, *J* = 6.4 Hz, 1H), 3.19 (bs, 1H), 3.58 (s, 3H), 4.01 (d, *J* = 9.3 Hz, 1H), 4.09 (d, *J* = 16.1 Hz, 1H), 4.81 (d, *J* = 15.8 Hz, 1H), 5.96 (s, 1H), 6.43 (d, *J* = 9.0 Hz, 2H), 6.61 (d, *J* = 9.0 Hz, 2H), 7.16–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 39.6, 53.5, 55.4, 55.5, 69.2, 114.4, 116.0, 124.0, 125.5, 127.6, 129.1, 141.8, 141.9, 152.3, 180.2, 208.0; HR-MS (FAB+): *m/z* = 306.1476 $[M+H]^+$, calcd. for $C_{20}H_{20}NO_2$: 306.1494.

(3*R*,3a*R*)-2-(4-Methoxyphenyl)-6-methyl-3-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*ent*-6i) (Table 4, entry 12)

GP4 was carried out with enyne *ent*-**5h** (57.0 mg, 0.19 mmol), $Co_2(CO)_8$ (70.0 mg, 0.21 mmol) and dry CH_2Cl_2 (1.9 mL); reaction time: 3 h. Then NMO·H_2O (257 mg, 1.90 mmol) was added; reaction time: 1 h at room temperature; TLC monitoring [petroleum ether/ethyl acetate 5:1, R_f(**5h**) = 0.41, R_f(**6i**) = 0.11, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) afforded cyclopentenone *ent*-**6i** as a pale yellow oil; yield: 35.3 mg (0.11 mmol, 59%); $[\alpha]_D^{20}$: −121.1 (*c* 0.94, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.77 (s, 3H), 2.40 (dd, *J* = 18.0 Hz, *J* = 3.1 Hz, 1H), 2.58 (dd, *J* = 18.1 Hz, *J* = 6.3 Hz, 1H), 3.15 (bs, 1H), 3.67 (s, 3H), 4.02 (d, *J* = 9.2 Hz, 1H), 4.13 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 6.52 (d, *J* = 8.9 Hz, 2H), 6.70 (d, *J* = 9.0 Hz, 2H), 7.24–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 8.6, 39.0, 52.7, 53.2, 55.6, 69.6, 114.4, 115.9, 125.6, 127.6, 129.1, 132.8, 142.1, 142.3, 152.2, 172.6, 208.0; HR-MS (FAB+): *m/z* = 320.1616 $[M+H]^+$, calcd. for $C_{21}H_{22}NO_2$: 320.1651.

(3*R*,3a*R*)-2-(4-Methoxyphenyl)-3-[(trityloxy)methyl]-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*ent*-6j) (Table 4, entry 13)

GP4 was carried out with enyne *ent*-**5i** (57.0 mg, 0.12 mmol), $Co_2(CO)_8$ (41.3 mg, 0.12 mmol) and dry CH_2Cl_2 (1.2 mL); reaction time: 2 h. Then $Me_3NO{\cdot}2H_2O$ (133 mg, 1.2 mmol) was added; reaction time: 1.5 h at room temperature; TLC monitoring [petroleum ether/ethyl acetate 5:1, R_f(**5i**) = 0.43, R_f(**6j**) = 0.17, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) afforded cyclopentenone *ent*-**6j** as a pale yellow oil; yield: 26.2 mg (0.06 mmol, 42%); $[\alpha]_D^{20}$: +5.8 (*c* 1.17, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.49 (dd, *J* = 17.9 Hz, *J* = 2.9 Hz 1H), 2.84 (dd, *J* = 18.1 Hz, *J* = 6.0 Hz, 1H), 3.15 (dd, *J* = 9.4 Hz, *J* = 7.4 Hz, 1H) 3.26–3.33 (m, 2H, 3-H), 3.68 (s, 4H), 3.89 (d, *J* = 15.6 Hz, 1H), 4.51 (d, *J* = 15.3 Hz, 1H), 5.91 (d, *J* = 0.8 Hz, 1H), 6.37 (d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 2H), 7.17–7.38 (m, 15H); HR-MS (FAB+): *m/z* = 515.2275 $[M]^+$, calcd. for $C_{34}H_{31}NO_3$: 501.2304.

(3*R*,3a*R*)-2-(4-Methoxyphenyl)-6-methyl-3-[(trityloxy)methyl]-2,3,3a,4-tetrahydrocyclopenta[*c*]pyrrol-5(1*H*)-one (*ent*-6k) (Table 4, entry 14)

GP4 was carried out with enyne *ent*-**5j** (56.5 mg, 0.12 mmol), $Co_2(CO)_8$ (59.1 mg, 0.17 mmol) and dry CH_2Cl_2 (1.2 mL); reaction time: 2 h. Then $Me_3NO{\cdot}2H_2O$ (147 mg, 1.31 mmol) was added; reaction time: 4 h at room temperature; TLC monitoring [petroleum ether/ethyl acetate 5:1, R_f(**5j**) = 0.42, R_f(**6k**) = 0.17, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 5:1) afforded cyclopentenone *ent*-**6k** as a pale yellow oil; yield: 23.4 mg (0.05 mmol, 39%); $[\alpha]_D^{20}$: +100.0 (*c* 1.17, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.71 (s, 3H), 2.52 (d, *J* = 17.8 Hz, 1H), 2.91 (dd, *J* = 17.7 Hz, *J* = 5.6 Hz, 1H), 3.18–3.27 (m, 3H), 3.72 (bs, 4H), 3.88 (d, *J* = 14.8 Hz, 1H), 4.47 (d, *J* = 14.8 Hz, 1H), 6.41 (d, *J* = 7.6 Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 7.24–7.43 (m, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.7, 41.3, 48.4, 53.1, 55.7, 63.7, 65.6, 87.0, 114.6, 115.7, 127.1, 127.9, 128.6, 132.2, 142.4, 144.0, 152.5, 172.8, 209.3; HR-MS (FAB+): *m/z* = 515.2444 $[M]^+$, calcd. for $C_{35}H_{33}NO_3$: 515.2460.

tert-Butyl (3*R*,3a*R*)-5-Oxo-3-phenyl-3,3a,4,5-tetrahydrocyclopenta[*c*]pyrrole-2(1*H*)-carboxylate (*ent*-6l) (Table 4, entries 15 and 16):

Method A: GP4 was carried out with enyne *ent*-**5k** (168 mg, 0.62 mmol), $Co_2(CO)_8$ (233 mg, 0.68 mmol) and dry CH_2Cl_2 (10 mL); reaction time: 1 h; TLC monitoring {petroleum ether/ethyl acetate 4:1, R_f(**5k**) = 0.49, R_f[**5k-$Co_2(CO)_6$**] = 0.61, $KMnO_4$}. Then $Me_3NO{\cdot}2H_2O$ (688 mg, 6.19 mmol) was added; reaction time: 4 h at room temperature; TLC monitoring {petroleum ether/ethyl acetate 1:1, R_f[**5k-$Co_2(CO)_6$**] = 0.69, R_f(**6l**) = 0.33, $KMnO_4$}. Column chromatography on silica gel (petroleum ether/ethyl acetate 2:1) afforded cyclopentenone *ent*-**6l** as colorless plates; yield: 118 mg (0.39 mmol, 64%).

Method B: GP5 was carried out with enyne *ent*-**5k** (25.0 mg, 92 μmol), $Co_2(CO)_8$ (6.30 mg, 17.6 μmol), *n*-BuSMe (11.5 mg, 111 μmol) and toluene (0.9 mL); reaction time: 10 min at 100 °C. Column chromatography on silica gel [petroleum ether/ethyl acetate 2:1, R_f(**6l**) = 0.33 in petroleum ether/ethyl acetate 1:1, $KMnO_4$] afforded *ent*-**6l** as colorless plates which crystallize from Et_2O at room temperature as orthorhombic crystals, suitable for X-ray crystal structure analysis; yield: 12.0 mg (40.0 μmol, 44%); mp 123–125 °C; $[\alpha]_D^{20}$: +149 (*c* 0.45, $CHCl_3$); ^{1}H NMR (benzene-d_6, 300.13): δ = 1.15 (bs, 9H), 1.75 (dd, *J* = 17.6 Hz, *J* = 3.7 Hz, 1H), 1.95 (dd, *J* = 17.6 Hz, *J* = 6.6 Hz, 1H), 2.38–2.44 (m, 1H), 3.59 (bs, 1H), 3.97 (d, *J* = 16.1 Hz, 1H), 4.18 (d, *J* = 15.7 Hz, 1H), 5.51–5.54 (m, 1H), 6.95–7.14 (m, 5H); ^{13}C NMR (benzene-d_6, 75 MHz): δ = 28.1, 39.5, 48.4, 54.2), 67.5, 79.6, 125.4, 125.9, 127.3, 128.6, 143.7, 154.3, 176.4, 205.9; HR-MS (FAB+): *m/z* = 300.1610 $[M+H]^+$, calcd. for $C_{18}H_{22}NO_3$: 300.1600; elem. anal. calcd. for $C_{18}H_{21}NO_3$: C 72.22, H 7.07, N 4.68; found: C 72.12, H 7.07, N 4.62.

tert-Butyl (3*R*,3a*R*)-6-Methyl-5-oxo-3-phenyl-3,3a,4,5-tetrahydrocyclopenta[*c*]pyrrole-2(1*H*)-carboxylate (*ent*-6m) (Table 4, entry 17):

GP4 was carried out with enyne *ent*-**5l** (76.0 mg, 0.27 mmol), $Co_2(CO)_8$ (100 mg, 0.29 mmol) and dry CH_2Cl_2 (4.5 mL); reaction time: 2 h; TLC monitoring {petroleum ether/ethyl acetate 4:1, R_f(**5l**) = 0.49, R_f[**5l-Co$_2$(CO)$_6$**] = 0.81, $KMnO_4$}. Then $Me_3NO{\cdot}2H_2O$ (688 mg, 6.19 mmol) was added; reaction time: 12 h at room temperature; TLC monitoring {petroleum ether/ethyl acetate 1:1, R_f[**5l-Co$_2$(CO)$_6$**] = 0.93, R_f(**6m/7m**) = 0.51, $KMnO_4$}. Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1→2:1) afforded cyclopentenones *ent*-**6m**/*ent*-**7m** as a mixture of diastereoisomers in a ratio of 66:34; yield: 38.3 mg (0.12 mmol, 46%). An analytically pure sample of the major (3*R*,3a*R*)-isomer *ent*-**6m** could be obtained after preparative HPLC as colorless needles; mp 77–80 °C; $[\alpha]_D^{20}$: +34.9 (*c* 1.39, $CHCl_3$); ^{1}H NMR [benzene-d_6, 300 MHz; mixture of rotamers (ratio 65:35)]: δ = 1.10, 1.14 (2 s, 18H), 1.50 (s, 3H), 1.69 (d, *J* = 2.5 Hz, 3H), 1.75 (dd, *J* = 17.8 Hz, *J* = 3.3 Hz, 2H), 1.98 (dd, *J* = 6.5 Hz, *J* = 6.5 Hz, 1H), 2.04 (dd, *J* = 6.0 Hz, *J* = 6.0 Hz, 1H), 2.36–2.40 (m, 1H), 2.94–2.99 (m, 1H), 3.52 (bs, 1H), 3.68 (bs, 1H), 3.99 (d, *J* = 16.0 Hz, 2H), 4.29 (d, *J* = 16.1 Hz, 2H), 6.89–7.40 (m, 10H); ^{13}C NMR [benzene-d_6, 75 MHz; mixture of rotamers (ratio 65:35)]: δ = 8.6, 8.8, 27.9, 28.1, 38.9, 39.4, 47.4, 49.9, 52.4, 67.6, 68.3, 79.6, 81.3, 125.9, 126.2, 127.3, 127.6, 128.6, 128.8, 133.0, 135.8, 143.3, 143.9, 154.6, 165.7, 169.0, 206.2, 206.7; HR-MS (FAB+): *m/z* = 314.1726 $[M+H]^+$, calcd. for $C_{19}H_{24}NO_3$: 314.1756.

tert-Butyl (3*R*,3a*R*)-5-Oxo-3-phenyl-6-(trimethylsilyl)-3,3a,4,5-tetrahydrocyclopenta[*c*]pyrrole-2(1*H*)-carboxylate (*ent*-6n) (Table 4, entry 18)

GP4 was carried out with enyne *ent*-**5m** (81.0 mg, 0.24 mmol), $Co_2(CO)_8$ (89.0 mg, 0.26 mmol) and dry CH_2Cl_2 (4 mL); reaction time: 5 h; TLC monitoring {petroleum ether/ethyl acetate 9:1, R_f(**5m**) = 0.34, R_f[**5m-Co$_2$(CO)$_6$**] = 0.59, $KMnO_4$}. Then $Me_3NO{\cdot}2H_2O$ (262 mg, 2.36 mmol) was added; reaction time: 3.5 h at room temperature; TLC monitoring {petroleum ether/ethyl acetate 9:1, R_f[**5m-Co$_2$(CO)$_6$**] = 0.59, R_f(**6n**) = 0.17, $KMnO_4$}. Column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) afforded cyclopentenone *ent*-**6n** as colorless needles; yield: 74.0 mg (0.20 mmol, 82%); mp 111–112 °C; $[\alpha]_D^{20}$: +99.4 (*c* 1.96, $CHCl_3$); ^{1}H NMR (benzene-d_6, 300 MHz): δ = 0.25 (s, 9H), 1.16 (bs, 9H), 1.81 (dd, *J* = 17.3 Hz, *J* = 4.4 Hz, 1H), 2.03 (dd, *J* = 17.3 Hz, *J* = 6.8 Hz, 1H), 2.45–2.52 (m, 1H), 3.64 (bd, *J* = 8.8 Hz, 1H), 4.24 (d, *J* = 16.7 Hz), 4.59 (d, *J* = 16.6 Hz), 6.99–7.14 (m, 5H); ^{13}C NMR (benzene-d_6, 75 MHz): δ = −1.3, 28.1, 40.3, 49.4, 56.2, 67.2, 79.6, 125.9, 127.37, 128.6, 144.1, 154.5, 184.1, 209.9; HR-MS (FAB+): *m/z* = 372.2000 $[M+H]^+$, calcd. for $C_{21}H_{30}NO_3Si$: 372.1995; elem. anal. calcd. for $C_{21}H_{29}NO_3Si$: C 67.89, H 7.87, N 3.77; found: C 67.64, H 7.91, N 3.73.

tert-Butyl (3*S*,3a*S*)-3-({[*tert*-Butyl(diphenyl)silyl]oxy}methyl)-6-methyl-5-oxo-3,3a,4,5-tetrahydrocyclopenta[*c*]pyrrole-2(1*H*)-carboxylate (6o) (Table 4, entry 19)

GP4 was carried out with enyne **5n** (6.13 g, 12.8 mmol), $Co_2(CO)_8$ (4.82 g, 14.1 mmol) and dry CH_2Cl_2 (213 mL); reaction time: 2 h; TLC monitoring {petroleum ether/ethyl acetate 9:1, R_f(**5n**) = 0.31, R_f[**5n-Co$_2$(CO)$_6$**] = 0.58, $KMnO_4$}. The reaction mixture was cooled to −10 °C and $Me_3NO{\cdot}2H_2O$ (7.113 g, 64.0 mmol) was added. The suspension was allowed to warm up to room temperature, stirred for 5 h, cooled to −10 °C, and another portion of $Me_3NO{\cdot}2H_2O$ (7.11 g, 64.0 mmol) was added; reaction time: 12 h at room temperature; TLC monitoring {petroleum ether/ethyl acetate 2:1, R_f[**5n-Co$_2$(CO)$_6$**] = 0.55, R_f(**6o**) = 0.33, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 9:1) afforded cyclopentenone **6o** as a yellowish foam; yield: 3.18 g (6.29 mmol, 49%); $[\alpha]_D^{20}$: −60.3 (*c* 0.70, $CHCl_3$); ^{1}H NMR (toluene-d_8, 300 MHz, 90 °C): δ = 1.11 (s, 9H), 1.35 (s, 9H), 1.51 (s, 3H), 1.91 (dd, *J* = 17.6 Hz, *J* = 2.8 Hz, 1H), 2.46 (dd, *J* = 17.6 Hz, *J* = 6.4 Hz, 1H), 2.99–3.07 (m, 1H), 3.15–3.21 (m, 1H), 3.84 (d, *J* = 15.7 Hz, 1H), 4.03 (dd, *J* = 8.8 Hz, *J* = 5.9 Hz, 1H), 4.16 (dd, *J* = 9.8 Hz, *J* = 3.0 Hz, 1H), 4.26 (d, *J* = 15.5 Hz, 1H), 7.20–7.22 (m, 6H), 7.68–7.70 (m, 4H); ^{13}C NMR (toluene-d_8, 75 MHz, 90 °C): δ = 8.4, 19.8, 27.5, 28.8, 41.2, 46.1, 47.6, 65.1, 65.7, 80.0, 128.2, 130.2, 136.1, 136.2, 154.7, 168.8, 205.9; HR-MS (ESI+): *m/z* = 506.2723 $[M+H]^+$, calcd. for $C_{30}H_{40}NO_4Si$: 506.2721.

tert-Butyl (3*S*,3a*S*)-3-[(1,1-Dimethylpropoxy)methyl]-6-methyl-5-oxo-3,3a,4,5-tetrahydrocyclopenta[*c*]-pyrrole-2(1*H*)-carboxylate (6p) (Table 4, entry 21)

GP4 was carried out with enyne **5o** (65.0 mg, 0.21 mmol), $Co_2(CO)_8$ (79.0 mg, 0.23 mmol) and dry CH_2Cl_2 (3.5 mL); reaction time: 4 h; TLC monitoring {petroleum ether/ethyl acetate 9:1, R_f(**5o**) = 0.49, R_f[**5o-Co$_2$(CO)$_6$**] = 0.62, $KMnO_4$}. $Me_3NO{\cdot}2H_2O$ (70 mg, 0.63 mmol) and celite (215 mg) were added; reaction time: 5 h at room temperature; TLC monitoring {petroleum ether/ethyl acetate 4:1, R_f[**5o-Co$_2$(CO)$_6$**] = 0.90, R_f(**6p**) = 0.40, $KMnO_4$]. Column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) afforded cyclopentenone **6p** as a colorless oil; yield: 45.0 mg (0.13 mmol, 64%); $[\alpha]_D^{20}$: −93.0 (*c* 0.7, $CHCl_3$); ^{1}H NMR (toluene-d_8, 400 MHz, 80 °C): δ = 0.81 (t, *J* = 7.5 Hz, 3H), 1.01 (s, 6H), 1.37 (q, *J* = 7.4 Hz, 2H), 1.44 (s, 9H), 1.49–1.50 (m, 3H), 1.89 (dd, *J* = 17.8 Hz, *J* = 3.6 Hz, 1H), 2.42 (dd, *J* = 17.8 Hz, *J* = 6.6 Hz, 1H), 2.78–2.85 (m, 1H), 3.10 (ddd, *J* = 8.8 Hz, *J* = 6.9 Hz, *J* = 3.4 Hz, 1H), 3.39–3.48 (m, 1H), 3.79 (d, *J* = 15.7 Hz, 1H), 3.86 (dd, *J* = 8.7 Hz, *J* = 3.4 Hz, 1H), 4.20 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR (toluene-d_8, 100 MHz, 80 °C): δ = 8.4, 25.1, 25.2, 28.7, 33.8, 41.3, 46.7, 47.5, 63.2, 63.9, 74.9, 79.6, 132.7, 154.6, 169.0, 206.3; HR-MS (ESI+): *m/z* = 338.2328 $[M+H]^+$, calcd. for $C_{19}H_{32}NO_4$: 338.2326.

tert-Butyl (1*S*,3a*S*,6a*S*)-1-[(1,1-Dimethylpropoxy)-methyl]-4-methyl-5-oxohexahydrocyclopenta[*c*]-pyrrole-2(1*H*)-carboxylate (8)

Cyclopentenone **6p** (1.82 g, 5.35 mmol) was dissolved in EtOAc (38 mL) and $Pd(OH)_2/C$ (182 mg, 10 wt%) was added. The black suspension was placed in an autoclave and stirred for 18 h under H_2 (5 bar). The mixture was filtered through a pad of silica (EtOAc) and the filtrate concentrated under vacuum to give **8** as a colorless oil; yield: 1.67 g (4.91 mmol, 92%); $[\alpha]_D^{20}$: +50.5 (*c* 0.80, $CHCl_3$); ^{1}H NMR (toluene-d_8, 300 MHz, 90 °C): δ = 0.82 (t, *J* = 7.3 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H), 1.03 (s, 6H), 1.36–1.43 (m, 2H), 1.40 (s, 9H), 1.61 (dd, *J* = 19.0 Hz, *J* = 8.8 Hz, 1H), 1.92–2.01 (m, 1H), 2.20 (dd, *J* = 19.0 Hz, *J* = 9.5 Hz, 1H), 2.49 (ddd, *J* = 16.1 Hz, *J* = 8.1 Hz, *J* = 0.9 Hz, 1H), 2.73–2.84 (m, 1H), 2.94 (dd, *J* = 11.1 Hz, *J* = 9.4 Hz, 1H), 3.30–3.43 (m, 3H), 3.61–3.66 (m, 1H); ^{13}C NMR (toluene-d_8, 75 MHz, 90 °C): δ = 8.4, 10.6, 25.2, 25.3, 28.8, 33.8, 41.0, 41.4, 43.3, 47.1, 47.7, 62.8, 64.5, 75.2, 79.2, 154.4, 215.1; HR-MS (ESI+): *m/z* = 340.2489 $[M+H]^+$, calcd. for $C_{19}H_{34}NO_4$: 340.2482.

tert-Butyl (1*S*,3a*R*,7a*S*)-1-[(1,1-Dimethylpropoxy)-methyl]-4-methyl-6-oxohexahydropyrano[3,4-*c*]pyrrole-2(3*H*)-carboxylate (9)

Under an atmosphere of argon cyclopentanone **8** (1.38 g, 4.07 mmol) was dissolved in dry CH_2Cl_2 (40 mL). Na_2HPO_4 (14.4 g, 102 mmol) and *m*-CPBA (1.76 g, 10.2 mmol) were added, and the suspension was stirred at room temperature for 9 h when GC/MS monitoring [t_R(**8**) = 12.6 min, t_R(**9**) = 14.5 min] indicated full consumption of the starting material. Saturated Na_2SO_3 solution (40 mL) was added, and the mixture was stirred at room temperature for 20 min. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (50 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. Column chromatography on silica gel [petroleum ether/ethyl acetate 2:1, R_f(**9**) = 0.18, $KMnO_4$] firnished lactone **9** as a colorless oil which crystallized on standing as colorless needles; yield: 1.28 g (3.61 mmol, 87%); mp 71–73 °C; $[\alpha]_D^{20}$: −86.4 (*c* 0.88, $CHCl_3$); ^{1}H NMR (toluene-d_8, 300 MHz, 90 °C): δ = 0.80 (t, *J* = 7.4 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.99 (s, 6H), 1.36 (q, *J* = 7.5 Hz, 2H), 1.41 (s, 9H), 2.04–2.09 (m, 1H), 2.15–2.25 (m, 2H, 3a-H), 2.39–2.45 (m, 1H), 3.27 (dd, *J* = 10.8 Hz, *J* = 9.1 Hz, 1H), 3.31 (d, *J* = 4.4 Hz, 2H), 3.56 (dd, *J* = 11.2 Hz, *J* = 7.2 Hz, 1H), 3.61–3.63 (m, 1H), 3.78–3.85 (m, 1H); ^{13}C NMR (toluene-d_8, 75 MHz, 90 °C): δ = 8.4, 18.8, 25.1, 25.2, 28.8, 33.8, 33.9, 38.8, 40.7, 45.4, 63.1, 66.4, 73.5, 75.3, 79.5, 154.1, 169.3; HR-MS (ESI+): *m/z* = 356.2441 $[M+H]^+$, calcd. for $C_{19}H_{34}NO_5$: 356.2432.

tert-Butyl (2*S*,3*S*,4*R*)-2-[(1,1-Dimethylpropoxy)-methyl]-4-[(1*S*)-1-hydroxyethyl]-3-(2-hydroxyethyl)-pyrrolidine-1-carboxylate (10)

Lactone **9** (1.18 g, 3.32 mmol) was dissolved in EtOH (66 mL). Freshly powdered $CaCl_2$ (1.11 g, 9.96 mmol) and $NaBH_4$ (754 mg, 19.9 mmol) were added, and the suspension was heated at 50 °C. After stirring for 5 h TLC monitoring [petroleum ether/ethyl acetate 1:2, R_f(**9**) = 0.38, R_f(**10**) = 0.12, $KMnO_4$] indicated full conversion. Water (16 mL) and MeOH (8 mL) were added to give a precipitate. Then 2 M HCl was added (~13 mL) dropwise until the precipitate dissolved. Stirring was continued for further 10 min, and then the aqueous phase was extracted with $CHCl_3$ (3 × 150 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (150 mL), dried over Na_2SO_4 and concentrated under vacuum. Column chromatography on silica gel (petroleum ether/ethyl acetate 2:1→0:1) yielded dialcohol **10** as a colorless, sticky oil; yield: 1.16 g (3.22 mmol, 97%); $[\alpha]_D^{20}$: −30.6 (*c* 2.10, $CHCl_3$); ^{1}H NMR (toluene-d_8, 300 MHz, 90 °C): δ = 0.82 (t, *J* = 7.4 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 1.03 (s, 6H), 1.14–1.25 (m, 1H), 1.40 (q, 2H), 1.45 (s, 9H), 1.47–1.54 (m, 1H), 2.12–2.18 (m, 1H), 2.21–2.29 (m, 1H), 3.18 (dd, *J* = 8.4 Hz, *J* = 8.4 Hz, 1H), 3.30 (dd, *J* = 10.4 Hz, *J* = 10.4 Hz, 1H), 3.49–3.62 (m, 5H), 3.81 (bd, *J* = 7.6 Hz, 1H); ^{13}C NMR (toluene-d_8, 75 MHz, 90 °C): δ = 8.4, 22.9, 25.2, 25.3, 29.0, 31.0, 33.8, 39.8, 47.9, 49.3, 61.2, 62.7, 63.6, 67.8, 75.4, 79.0, 155.1; HR-MS (ESI+): *m/z* = 360.2746 $[M+H]^+$, calcd. for $C_{19}H_{38}NO_5$: 360.2745.

tert-Butyl (2*S*,3*S*,4*R*)-3-(2-{[*tert*-Butyl(dimethyl)silyl]-oxy}ethyl)-2-[(1,1-dimethylpropoxy)methyl]-4-[(1*S*)-1-hydroxyethyl]-3-(2-hydroxyethyl)pyrrolidine-1-carboxylate (11)

Under an atmosphere of argon imidazole (357 mg, 5.25 mmol) was added to a solution of the diol **10** (1.01 g, 2.82 mmol) in dry CH_2Cl_2 (5.2 mL). After stirring for 5 min at room temperature a solution of TBDMSCl (514 mg, 3.41 mmol) in CH_2Cl_2 (5.2 mL) was added dropwise. Stirring was continued for 1 h when TLC monitoring [petroleum ether/ethyl acetate 1:2, R_f(**10**) = 0.12, R_f(**11**) = 0.53, $KMnO_4$] indicated full consumption of the starting material. Saturated $NaHSO_4$ solution (10 mL) was added, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. Column chromatography on silica gel (petroleum ether/ethyl acetate 1:1) afforded silyl ether **11** as a colorless oil; yield: 1.32 g (2.78 mmol, 99%); $[\alpha]_D^{20}$: −32.2 (*c* 1.12, $CHCl_3$); ^{1}H NMR (toluene-d_8, 300 MHz, 90 °C): δ = 0.03 (s, 6H), 0.84 (t, *J* = 7.4 Hz, 3H), 0.92 (s, 9H), 1.04 (s, 6H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.24–1.35 (m, 1H), 1.41 (q, *J* = 7.8 Hz, 2H), 1.45 (s, 9H), 1.52–1.61 (m, 1H), 2.17–2.30 (m, 2H), 3.28–3.35 (m, 2H), 3.50 (dd, *J* = 8.8 Hz, *J* = 3.2 Hz, 1H), 3.53–3.67 (m, 4H), 3.79–3.81 (m, 1H); ^{13}C NMR (toluene-d_8, 75 MHz, 90 °C): δ = −5.0, 8.5, 18.7, 22.9, 25.3, 26.4, 29.0, 31.7, 33.9, 40.0, 48.0, 49.3, 62.4, 62.5, 64.3, 68.0, 75.0, 78.8, 154.9; HR-MS (ESI+): *m/z* = 474.3608 $[M+H]^+$, calcd. for $C_{25}H_{52}NO_5Si$: 474.3609.

tert-Butyl (2*S*,3*S*,4*R*)-4-Acetyl-3-(2-{[*tert*-butyl-(dimethyl)silyl]oxy}ethyl)-2-[(1,1-dimethylpropoxy)-methyl]pyrrolidine-1-carboxylate (12)

Under an atmosphere of argon at room temperature, TPAP (88.6 mg, 0.25 mmol) was added to a solution of alcohol **11** (1.19 g, 2.52 mmol), NMO (679 mg, 5.80 mmol) and powdered 4 Å MS (3.5 g) in dry CH_2Cl_2 (115 mL). The suspension was stirred for 1.5 h when TLC monitoring [petroleum ether/ethyl acetate 2:1, R_f(**11**) = 0.50, R_f(**12**) = 0.80, $KMnO_4$] indicated full conversion of the starting marterial. Celite

was added, and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate 4:1) to afford **12** as a colorless oil; yield: 1.13 g (95%); $[\alpha]_D^{20}$: −21.8 (*c* 1.03, $CHCl_3$); ^{1}H NMR (toluene-d_8, 300 MHz, 90 °C): δ = 0.00, 0.01 (2 s, 6H), 0.83 (t, *J* = 7.5 Hz, 3H), 0.90 (s, 9H), 1.04 (s, 6H), 1.37–1.43 (m, 4H), 1.43 (s, 9H), 1.85 (s, 3H), 2.64–2.68 (m, 1H), 3.18–3.26 (m, 1H), 3.35 (dd, *J* = 11.0 Hz, *J* = 7.7 Hz, 1H), 3.46 (d, *J* = 3.7 Hz, 2H), 3.52 (dd, *J* = 6.0 Hz, *J* = 6.0 Hz, 2H), 3.78 (dd, *J* = 11.3 Hz, *J* = 8.9 Hz, 1H), 3.80–3.85 (m, 1H); ^{13}C NMR (toluene-d_8, 75 MHz, 90 °C): δ = −5.1, 8.4, 18.7, 25.2, 26.3, 28.9, 29.1, 33.1, 33.8, 40.9, 47.1, 53.7, 61.8, 62.6, 63.8, 75.2, 79.1, 154.7, 204.8; HR-MS (ESI+): *m/z* = 472.3472 $[M+H]^+$, calcd. for $C_{25}H_{50}NO_5Si$: 472.3453.

tert-Butyl (2*S*,3*S*,4*R*)-3-(2-{[*tert*-Butyl(dimethyl)silyl]-oxy}ethyl)-2-[(1,1-dimethylpropoxy)methyl]-4-isopropenylpyrrolidine-1-carboxylate (13)

Under an atmosphere of argon, a stirred solution of the methyl ketone **12** (260 mg, 0.55 mmol) in dry THF (2.2 mL) was cooled to −40 °C. Pyridine (49 μL, 0.61 mmol) was added, and stirring was continued for 10 min. A solution of Tebbe's reagent (0.5 M in toluene, 1.43 mL, 0.72 mmol) was added dropwise, and the resulting deep red mixture was allowed to warm up to room temperature over a period of 8 h when GC/MS monitoring [t_R(**12**) = 15.8 min, t_R(**13**) = 14.7 min] indicated full conversion of the starting material. The solution was diluted with Et_2O (50 mL), and 3 M NaOH was added dropwise until gas evolution ceased. The mixture was dried over Na_2SO_4, filtered through a pad of celite (EtOAc), and the filtrate concentrated under vacuum. The crude product was subjected to column chromatography on silica gel [petroleum ether/ethyl acetate 20:1, R_f(**13**) = 0.38 in petroleum ether/ethyl acetate 9:1, $KMnO_4$] to furnish **13** as a yellow oil; yield: 177 mg (0.38 mmol, 68%); $[\alpha]_D^{20}$: −27.5 (*c* 0.57, $CHCl_3$); ^{1}H NMR (toluene-d_8, 300 MHz, 90 °C): δ = 0.03, 0.04 (2 s, 6H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.92 (s, 9H), 1.05 (s, 6H), 1.22–1.34 (m, 1H), 1.42 (q, *J* = 7.33 Hz, 2H), 1.45 (s, 9H), 1.50–1.58 (m, 1H), 1.64 (s, 3H), 2.45–2.50 (m, 1H), 2.92 (dd, *J* = 14.3 Hz, *J* = 7.3 Hz, 1H), 3.45–3.63 (m, 6H), 3.79–3.81 (m, 1H), 4.61, 4.78 (2 s, 2H); ^{13}C NMR (toluene-d_8, 75 MHz, 90 °C): δ = −5.0, 8.5, 18.7, 22.5, 25.3, 26.4, 28.9, 32.4, 33.9, 40.5, 46.9, 49.1, 62.3, 62.7, 64.0, 75.0, 78.9, 111.8, 144.0, 154.8; HR-MS (ESI+): *m/z* = 470.3659 $[M+H]^+$, calcd. for $C_{26}H_{52}NO_4Si$: 470.3660.

Benzyl (2*S*,3*S*,4*S*)-3-(2-Hydroxyethyl)-2-(hydroxymethyl)-4-isopropenylpyrrolidine-1-carboxylate (14)

TFA (100 μL, 1.30 mmol) was added dropwise to a solution of olefin **13** (40.0 mg, 85.1 μmol) in CH_2Cl_2 (800 μL), and the solution stirred for 2.5 h at room temperature. The solvent was removed under reduced pressure, and the residue was dissolved in a biphasic mixture of CH_2Cl_2/1 M NaOH (850 μL, 1:1). *n*-Bu_4NHSO_4 (3.5 mg, 10.2 μmol) and CbzCl (21.8 mg, 12.8 μmol) were added, and the mixture was stirred vigorously at room temperature for 15 h. The phases were separated, and the aqueous phase was extracted with $CHCl_3$ (3 × 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude product was subjected to column chromatography on silica gel [petroleum ether/ethyl acetate 1:2→0:1, R_f(**14**) = 0.12 in petroleum ether/ethyl acetate 1:2, $KMnO_4$] to furnish **14** as a colorless oil; yield: 18.0 mg (56.4 μmol, 66%).

The synthesis of **14** *via* a different route has been described.[46] Our analytical data are in agreement with those reported. $[\alpha]_D^{20}$: −47.6 (*c* 0.76, $CHCl_3$); lit.[46] $[\alpha]_D^{30}$: −43.3 (*c* 0.56, $CHCl_3$); ^{1}H NMR (toluene-d_8, 300 MHz, 90 °C): δ = 1.03–1.14 (m, 1H), 1.20–1.42 (m, 2H), 1.50 (s, 3H), 1.79 (bs, 1H), 2.05–2.18 (m, 1H), 2.62 (dd, *J* = 14.1 Hz, *J* = 7.0 Hz, 1H), 3.33–3.48 (m, 4H), 3.54 (dd, *J* = 10.7 Hz, *J* = 5.2 Hz, 1H), 3.65 (dd, *J* = 10.7 Hz, *J* = 5.3 Hz, 1H), 3.78 (dd, *J* = 8.6 Hz, *J* = 4.9 Hz, 1H), 4.49, 4.70 (2 s, 2H), 5.04 (d, *J* = 12.9 Hz, 1H), 5.09 (d, *J* = 12.8 Hz, 1H), 7.01–7.23 (m, 5H); ^{13}C NMR (toluene-d_8, 75 MHz, 90 °C): δ = 22.3, 31.7, 40.6, 47.1, 49.6, 61.2, 65.7, 65.9, 67.5, 112.4, 128.3, 128.5, 128.8, 137.9, 143.5, 156.4; HR-MS (ESI+): *m/z* = 320.1858 $[M+H]^+$, calcd. for $C_{18}H_{26}NO_4$: 320.1856.

X-Ray Structure Determination for Compounds (3*R*,3a*R*)-6d, (3*S*,3a*R*)-6g, (3*R*,3a*R*)-6l, (3*S*,3a*S*)-7b and (3*S*,3a*R*)-7c

X-ray data were collected on a Bruker APEX (**6l** and **7c**), a Bruker Smart CCD (**6g** and **7b**) area detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and 0.3° ω-scan frames or on an Oxford Xcalibur (**6d**) diffractometer with Cu Nova Microsource and Onyx detector using Cu-Kα radiation (λ = 1.54184 Å) and 1.0° ω-scan frames. Intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[52] based on the Laue symmetry of the reciprocal space. The structure was solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm using the SHELXTL-PLUS (6.10) software package.[53] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and thereafter treated using appropriate riding models. Important crystallographic data are given below.

(3*R*,3a*R*)-6d: $C_{17}H_{21}NO_3S$, M_r = 319.41, colorless plates from ethyl acetate/*n*-pentane, 0.11 × 0.06 × 0.01 mm^3, monoclinic, space group $P2_1$, *a* = 15.3905(3) Å, *b* = 5.9244(1) Å, *c* = 18.5033(4) Å, *V* = 1624.03(5) Å^3, *Z* = 4, μ = 1.87 mm^{-1}, d_x = 1.31 g cm^{-3}, *T* = 200(2) K, 12320 reflections collected (θ_{max} = 72.2°) and merged to 5951 independent data (R_{int} = 0.0325); final *R* indices (all data): R_1 = 0.045, wR_2 = 0.126, 397 parameters, absolute structure parameter = −0.01(2).

(3*S*,3a*R*)-6g: $C_{18}H_{18}O_5$, M_r = 314.32, colorless needles from toluene, 0.42 × 0.30 × 0.20 mm^3, monoclinic, space group $P2_1$, *a* = 8.2078(3) Å, *b* = 7.5808(3) Å, *c* = 13.4314(3) Å, *V* = 816.75(5) Å^3, *Z* = 2, μ = 0.093 mm^{-1}, T_{min}/T_{max} = 0.96 and 0.98, d_x = 1.278 g cm^{-3}, *T* = 200(2) K, 8403 reflections collected (θ_{max} = 27.48°) and merged to 3730 independent data (R_{int} = 0.0299); final *R* indices (all data): R_1 = 0.035, wR_2 = 0.082, 280 parameters.

(3*R*,3a*R*)-6l: $C_{18}H_{21}NO_3$, M_r = 299.36, colorless plates from Et_2O, 0.26 × 0.14 × 0.09 mm^3, orthorhombic, space group $P2_12_12_1$, *a* = 8.768(2) Å, *b* = 13.162(3) Å, *c* = 14.037(3) Å, *V* = 1620.1(7) Å^3, *Z* = 4, μ = 0.08 mm^{-1}, T_{min}/T_{max} = 0.98 and 0.99, d_x = 1.23 g cm^{-3}, *T* = 200(2) K, 17048 reflections collected (θ_{max} = 28.3°) and merged to 4025 independent data (R_{int} =

0.0338); final R indices (all data): $R_1 = 0.052$, $wR_2 = 0.112$, 202 parameters.

(3*S*,3a*S*)-7b: $C_{23}H_{27}NO_3S$, $M_r = 397.52$, colorless crystals from benzene-d_6, $0.32 \times 0.32 \times 0.22$ mm^3, monoclinic, space group $P2_1$, $a = 9.0416(1)$ Å, $b = 9.7826(2)$ Å, $c = 12.1689(2)$ Å, $V = 1043.74(3)$ Å^3, $Z = 2$, $\mu = 0.18$ mm^{-1}, $T_{min}/T_{max} = 0.95$ and 0.96, $d_x = 1.26$ g cm^{-3}, $T = 180(2)$ K, 10492 reflections collected ($\theta_{max} = 27.5°$) and merged to 4216 independent data ($R_{int} = 0.0491$); final R indices (all data): $R_1 = 0.039$, $wR_2 = 0.093$, 256 parameters, absolute structure parameter = 0.06(7).

(3*S*,3a*R*)-7c: $C_{21}H_{21}NO_3S$, $M_r = 367.45$, colorless crystals from benzene-d_6, $0.48 \times 0.36 \times 0.16$ mm^3, orthorhombic, space group $P2_12_12_1$, $a = 7.6978(4)$ Å, $b = 12.7118(7)$ Å, $c = 18.6562(11)$ Å, $V = 1825.56(18)$ Å^3, $Z = 4$, $\mu = 0.20$ mm^{-1}, $T_{min}/T_{max} = 0.91$ and 0.97, $d_x = 1.34$ g cm^{-3}, $T = 298(2)$ K, 19226 reflections collected ($\theta_{max} = 28.4°$) and merged to 4542 independent data ($R_{int} = 0.0250$); final R indices (all data): $R_1 = 0.044$, $wR_2 = 0.110$, 238 parameters, absolute structure parameter = 0.03(8).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 779172 (**6d**), CCDC 779173 (**6g**), CCDC 779174 (**6l**), CCDC 779175 (**7b**) and CCDC 779176 (**7c**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) +44 1223/336–033; e-mail: deposit@ccdc.cam.ac.uk].

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