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Asymmetric Intramolecular Pauson–Khand Reaction Mediated by a Remote Sulfenyl or Sulfinyl Group

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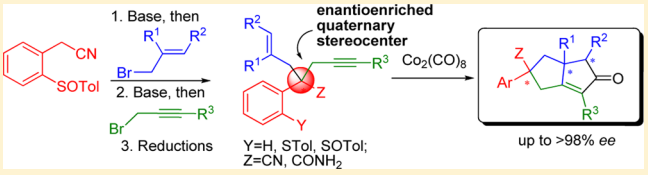
Supporting Information

ABSTRACT: In this work, we report the use of the asymmetric intramolecular Pauson–Khand reactions of 4-aryl-4-cyano-1,6-enynes for obtaining enantiomerically enriched bicyclo[3.3.0]octenones, and the influence of both the quaternary stereocenter and the sulfur functions located at *ortho*-position of the aryl group, on their stereoselectivity and reactivity. The sulfenyl derivatives bearing substituted or unsubstituted triple bonds and mono- and disubstituted alkene moieties afford bicyclo[3.3.0]octenones in high yields with complete diastereocontrol. These results are explained by assuming the association of the lone electron pair at sulfur to the Co–alkyne complexes.



INTRODUCTION

Over the last decades, the Pauson–Khand (PK) reaction has developed into a powerful tool in organic synthesis.[1,2] This formal [2 + 2 + 1] cycloaddition of an alkene and an alkyne with carbon monoxide, obtained typically from $Co_2(CO)_8$, affords cyclopentenone derivatives, which are useful scaffolds for further synthetic transformations. The intramolecular variant of the PK reaction is particularly interesting since it produces two fused rings and three new carbon–carbon bonds in one synthetic step, representing one of the best methodologies so far reported for the synthesis of bicyclo[3.3.0]-octenones and bicyclo[4.3.0]nonenones from 1,6- and 1,7-enynes, respectively.[3] This synthetic utility explains why the asymmetric version of this cyclization, controlled by a chiral fragment present at the substrate,[4] or by an external chiral promoter[5] or ligand,[6] has been so extensively investigated. However, the best stereoselectivities so far reported were achieved by using chiral auxiliaries as the source of asymmetric induction.[7]

In this context, the influence of the sulfinyl group directly bonded to one of the reactive multiple bonds of the substrate has been studied.[8,9] Its efficiency is not too high when located at the alkyne fragment due to regio and stereoselective problems (equation a, Scheme 1),[8] but it affords much better results when the *t*-BuSO group is joined to the alkene moiety (equation b, Scheme 1),[9] presumably due to the interaction of the lone electron pair at sulfur with the Co–alkyne complex. This is one of the best reported methods in the asymmetric PK field despite its moderate yields and limited scope from structural (it is restricted to terminal alkynes and 2-substituted sulfinylethylenes) and stereochemical viewpoint (it is only useful for preparing bicycloalkenones with one stereogenic center because the second one, bonded to the sulfinyl group, disappears when the auxiliary is removed). The later problem is likely to be overcome by using a remote sulfinyl group as a chiral auxiliary, easily removable without affecting the enantiomeric purity of the resulting adducts. In this context, we have recently reported a stereodivergent synthesis of enantiomerically enriched α,α-dialkyl phenylacetonitriles,[10] which could be easily adapted to the preparation of compounds **I**–**III** (equation c, Scheme 1). We reasoned that these compounds could be appropriate models for studying the influence of several factors on the PK reaction course. First, the sulfinyl group of **II** is not directly bonded to the double bond, and its distance to the triple bond suggests an efficient interaction with the Co–alkyne complex, affording a seven- or eight-membered intermediate cobaltocycle. Second, it should be easily transformed into a sulfenyl group (compounds **III**), which has proved to be highly efficient in reactions involving sulfur-coordination to metals.[11] Finally, **I**–**III** have a quaternary stereogenic center, which presumably would improve the reactivity by a Thorpe–Ingold's effect,[12] but whose influence on the stereoselectivity of the intramolecular PK reactions has never been investigated, basically due to the difficulties inherent to their preparation (in most of the studied cases the quaternary carbon atom is bonded to two methyl or alkoxycarbonyl groups). In this work we describe the synthesis of substrates **I**–**III** and their behavior under the PK reaction conditions (Scheme 2) in order to evaluate the influence of the remote sulfinyl group (as well as its sulfenyl derivative) and the quaternary stereocenter on the reactivity and diastereoselecitvity.

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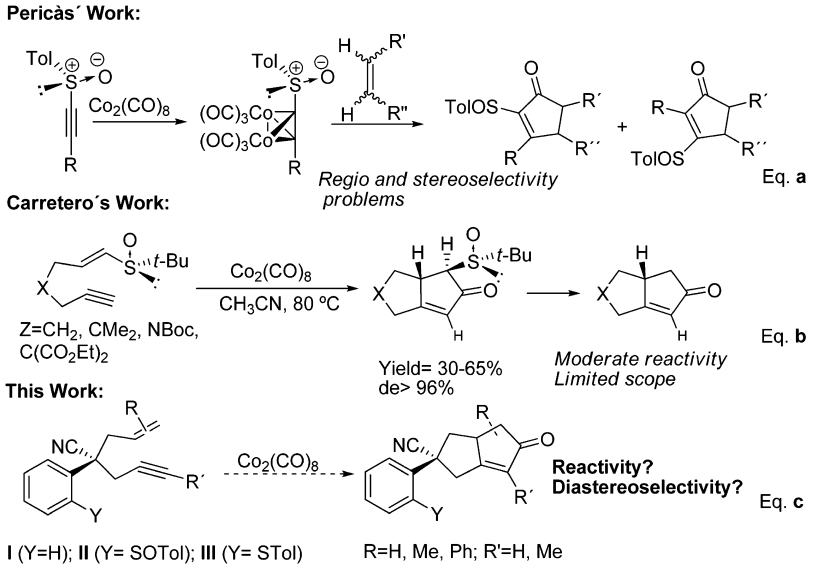
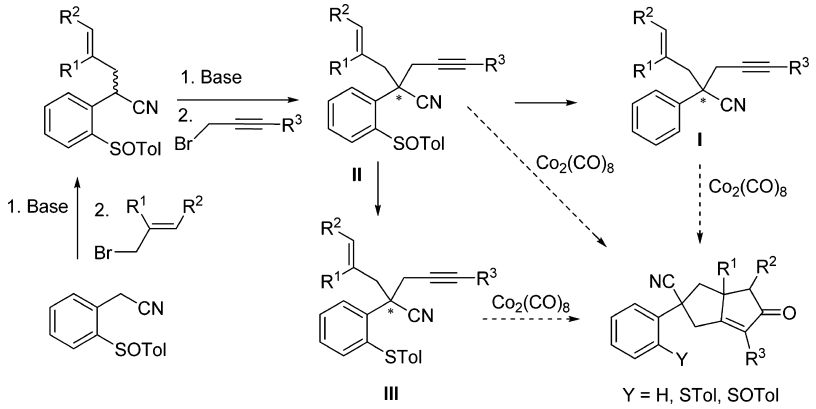
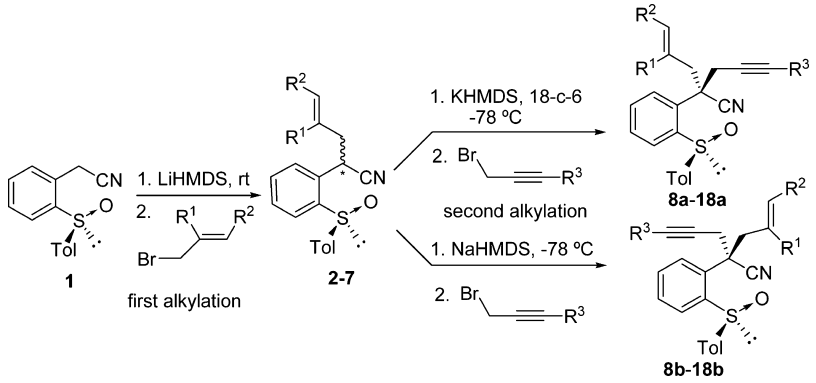
Scheme 1. Different Approaches for the Application of the Sulfinyl Group to the PK Reaction



Scheme 2. Synthetic Proposal for Obtaining Bicyclo[3.3.0]Octenones from Enynes Bearing an All-Carbon Quaternary Stereocenter and/or a Remote Sulfinyl or Sulfenyl Group



Scheme 3. Synthesis of the 1,6-Enynes Epimeric at C-4 (8−18) by Diastereodivergent Dialkylation of (*S*)-[2-(*p*-Tolylsulfinyl)phenyl]acetonitrile (1)



RESULTS AND DISCUSSION

Synthesis and Reactivity of Sulfinyl Enynes II. The synthesis of 4-[2-(*p*-tolylsulfinyl)phenyl]-1,6-enynes **II** (compounds **8**-**18**) was accomplished following the methodology for stereoselective dialkylation of (*S*)-[2-(*p*-tolylsulfinyl)phenyl] acetonitrile (**1**)[10] by using allyl and propargyl halides as electrophiles (Scheme 3).

Although the preparation of the two enynes epimeric at the quaternary center could be achieved by inverting the sequence of the steps 1 and 2 (introducing the allyl group before the propargyl, or vice versa), this strategy would not be advisable for terminal alkynes with acidic protons. Therefore, we prepared both epimeric series of enynes following the sequence depicted in Scheme 1 and taking advantage of the

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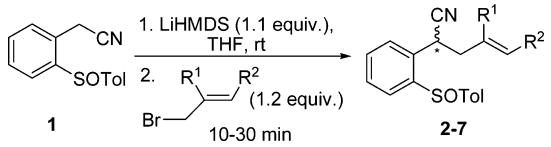
diastereodivergent course of the second alkylating step depending on the reaction conditions. It allows the use of the presumably more reactive propargyl halides in the second alkylation step, which had been reported to be more sensitive to steric effects.[10]

We first prepared the alkenyl derivatives indicated in Table 1, with mono- (**2**), di- (**3**–**6**), and trisubstituted (**7**) double bonds, by reaction of (*S*)-[2-(*p*-tolylsulfinyl)phenyl]acetonitrile (**1**) with LiHMDS (1.1 equiv) in THF and allyl bromides (1.2 equiv), commercially available (entries 1, 2, 3 and 5) or easily prepared following reported procedures (entries 4[13] and 6[14]). After chromatographic purification, the olefins **2**–**7** were obtained in 71–78% yields (Table 1) as almost equimolecular epimeric mixtures at the tertiary benzylic carbon, which was not unexpected from our previous results.[10]

Table 1. Monoalkylation Reaction of Nitrile 1 with Allyl Bromides



1 2-7

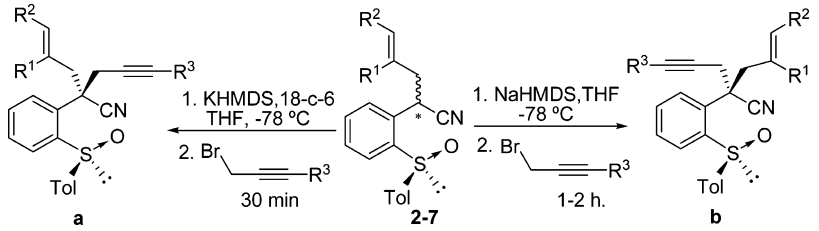
entry	product	R^1	R^2	yield (%)	d.r.
1	**2** + **2′**	H	H	77	50:50
2	**3** + **3′**	Me	H	72	50:50
3	**4** + **4′**	H	Me	78	50[a]:50[a]
4	**5** + **5′**	Ph	H	72	60:40
5	**6** + **6′**	H	Ph	75	50:50
6	**7** + **7′**	Me	Ph	71	50[b]:50[b]

[a]Obtained as a 80:20 mixture of *E*/*Z* isomers, coincident with the *E*/*Z* ratio of the starting allyl bromide. [b]Obtained as a 86:14 mixture of *E*/*Z* isomers, coincident with the *E*/*Z* ratio of the starting allyl bromide.

The reactions of **2**–**7** with propargyl bromide or 1-bromobut-2-yne afforded the 4-[2-(*p*-tolylsulfinyl)phenyl]-1,6-enynes **8**–**18** as diastereomerically enriched mixtures of epimers at the benzylic carbon (**a**, **b**) depending on the experimental conditions (Table 2). The configuration of the predominant diastereoisomer in the obtained diastereomeric mixtures was dependent on the reaction conditions. As it had been previously demonstrated,[10] diastereoisomers **a** were obtained preferentially in those reactions performed with KHMDS/18-crown-6 ether, whereas epimers **b** were predominant in those processes carried out with NaHMDS, which required longer reaction times. In all the cases the stereocontrol (d.r. values ranging between 80:20 and 90:10) as well as the yields (68–94%) were high regardless of the nature of the counterion.

The behavior of the simplest and presumably more reactive sulfinylenyne (**8a**) was evaluated under the different experimental conditions classically reported for the PK cycloadditions. When performed thermally in refluxing acetonitrile, the formation of the enyne–cobalt complex was detected by TLC of the reaction mixture but led finally to decomposition products. The addition of chemical promoters (Me_2S or molecular sieves) afforded the desired cycloadducts **19aA** + **19aB**, but better diastereoselectivity and yield were obtained by performing the reaction with $Co_2(CO)_8$ (1.2 equiv) in anhydrous CH_2Cl_2 at room temperature, in the presence of 8 equiv of *N*-methylmorpholine *N*-oxide (NMO) as an additive. Under these conditions a 72:28 diastereomeric mixture of sulfinyl bicyclo[3.3.0]octenones **19aA** + **19aB** was obtained in 79% yield after 5 min reaction time (Table 3, entry 1). This result was not improved by lowering the temperature, but longer reaction times were required for the reaction to reach completion. Thus, a similar diastereomeric ratio of 70:30 was

Table 2. Quaternization of 2-Allyl-[2-(*p*-tolylsulfinyl)phenyl]acetonitriles 2–7 with Different Propargyl Bromides



a 2-7 b

product	d.r.	yield (%)	substrate (R^1, R^2)	reagent (R^3)	yield (%)	d.r.	product
8a	80:20	80	**2** + **2′** (H, H)	H	84	20:80	**8b**
9a	87:13	69	**2** + **2′** (H, H)	Me	76	12:88	**9b**
10a	89:11	87	**3** + **3′** (Me, H)	H	85	13:87	**10b**
11a	90:10	79	**3** + **3′** (Me, H)	Me	81	20:80	**11b**
12a	88:12[a]	76	**4** + **4′** (H, Me)	H	78	10:90[a]	**12b**
13a	90:10[a]	80	**4** + **4′** (H, Me)	Me	78	10:90[a]	**13b**
14a	90:10[a]	94	**5** + **5′** (Ph, H)	H	80	18:82[a]	**14b**
15a	89:11[a]	94	**5** + **5′** (Ph, H)	Me	80	20:80[a]	**15b**
16a	87:13[a]	83	**6** + **6′** (H, Ph)	H			
17a	86:14[a,b]	80	**7** + **7′** (Me, Ph)	H			
18a	82:18[c]	68[d]	**7** + **7′** (Me, Ph)	Me			

[a]Diastereoisomeric mixture that could not be separated by flash column cromatography. [b]A (77:9):14 mixture of three diastereoisomers was obtained from the 86:14 mixture of the starting *E*/*Z* allyl derivative **7** + **7′**. Probably minor *Z* enyne derived from **7′** could not be detected in the ^{1}H NMR spectrum of the crude mixture. [c]A (74:8):18 mixture of three diastereoisomers was obtained from an 82:18 mixture of the starting *E*/*Z* allyl derivative **7** + **7′**. Probably minor *Z* enyne derived from **7′** could not be detected in the ^{1}H NMR spectrum of the crude mixture. [d]Isolated yield for compound **18a**.

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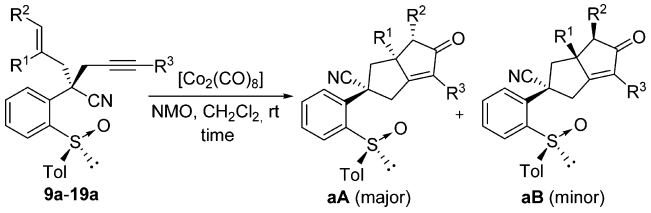
Table 3. Pauson–Khand reaction of Homochiral Sulfinyl 1,6-Enynes 8a–18a



entry	substrate (R^1, R^2, R^3)	time	product	d.r.[a]	yield (%)[b]
1	**8a** (H, H, H)	5 min	**19aA** + **19aB**	72:28	79
2	**9a** (H, H, Me)	5 min	**20aA** + **20aB**	70:30	70
3	**10a** (Me, H, H)	10 min	**21aA** + **21aB**	81:19	65
4	**11a** (Me, H, Me)	10 min	**22aA** + **22aB**	78:22	76
5	**12a** (H, Me, H)[c]	1.5 h	**23aA** + **23aB**	80:20	74
6	**13a** (H, Me, Me)[d]	1.5 h	**24aA** + **24aB**	82:18	80
7	**14a** (Ph, H, H)[c]	12 h	**25aA** + **25aB**	>98:<2	56
8	**15a** (Ph, H, Me)[c]	12 h	**26aA** + **26aB**	>98:<2	58
9	**16a** (H, Ph, H)[d]	3.5 h	**27aA** + **27aB**	>98:<2	74
10	**17a** (Me, Ph, H)			n.r.	n.r.
11	**18a** (Me, Ph, Me)			n.r.	n.r.

[a]Diastereomeric ratio determined by integration of well-separated signals of the ^{1}H NMR spectra. [b]Yield of the diastereomeric mixture. [c]90:10 mixture of epimers **a** + **b** (diastereomeric ratio **aA**:**aB** corresponds to the adducts derived from major epimer **a**). [d]87:13 mixture of epimers **a** + **b** (diastereomeric ratio **aA**:**aB** corresponds to the adducts derived from major epimer **a**).

obtained both at 0 °C (reaction time 60 min) and at −40 °C (reaction time 4.5 h).

Next, the scope of this intramolecular PK cycloaddition was surveyed with all the previously synthesized 1,6-enynes **8**–**18** of the epimeric homochiral series denoted as **a**. The obtained results are collected in Table 3. The reactions of **8a** and **9a**, with no substituents on the olefinic fragment, are those proceeding more rapidly (reaction time 5 min), though with moderate diastereoselectivities (d.r. values ca. 70:30), regardless of the substitution pattern on the alkynyl chain (Table 3, entries 1 and 2). A slight improvement in the stereoselectivity (d.r. values ca. 80:20) and a decrease in the reactivity (10 min were needed for the reaction to reach completion) were detected for substrates **10a** and **11a** bearing a *gem*-disubstituted terminal double bond (R^1 = Me; Table 3, entries 3 and 4). The level of the stereoselectivity was similar (d.r. values ca. 80:20), but the reactivity was severely eroded (reaction times were 1.5 h) for **12a** and **13a** (R^2 = Me; Table 3, entries 5 and 6). In all these cases the role of the substituent at the triple bond (R^3) proved to be scarcely relevant. A dramatic improvement in the stereoselectivity was detected in the reactions of those substrates with R^1 or R^2 = Ph (Table 3, entries 7–9), which afforded only one diastereomerically pure bicyclo[3.3.0]-octenone in moderate to good yields. The reactivity of these substrates was clearly lower, but the negative influence of the phenyl group was even higher when it was an R^1 substituent (reaction of **16a** required 3.5 h, whereas **14a** and **15a** required 12 h). As it was the case in the previous cases, the influence of the R^3 group was negligible. Finally, the cycloaddition failed with enynes **17a** and **18a**, both with trisubstituted double bonds (Table 3, entries 10 and 11).

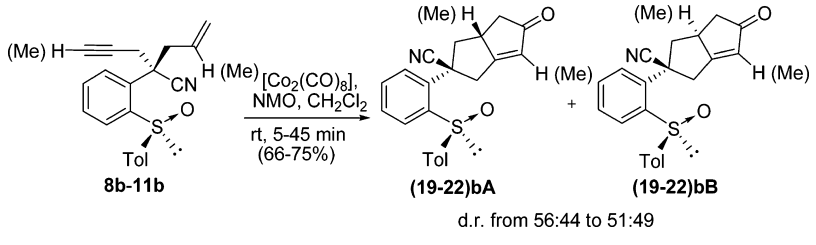
The impossibility of obtaining good crystals from any of the synthesized bicyclo[3.3.0]octenones prevented us from unequivocally assigning their absolute configuration by X-ray analysis. However, the relative configuration of adducts **aA** and **aB** was established by bidimensional ^{1}H NMR experiments (see the Supporting Information) by assuming that the configuration of the benzylic carbon atom of the starting compounds **8a**–**18a** is known (on the basis of the stereochemical behavior of the quaternization reactions[10]) and that it is preserved during the cycloadditions. The absolute configuration [2*R*,3a*S*,(S)*S*] was then assigned to the major cycloadducts **aA** and [2*R*,3a*R*,(S)*S*] to the minor isomers **aB**, as depicted in Table 3.

We also performed a parallel study on the behavior of the epimeric 1,6-enynes of the homochiral series **b**, which were similarly treated under PK conditions (Scheme 4). Compounds **8b** (R^1, R^2, R^3 = H) and **9b** (R^1, R^2 = H, R^3 = Me) exhibited a reactivity similar to that observed for their corresponding **a** isomers but the stereoselectivity was practically nonexistent. A similarly low selectivity was detected for compounds **10b** (R^1 = Me, R^2, R^3 = H) and **11b** (R^1, R^3 = Me, R^2 = H), but the reaction rate was significantly lower than that of the **a** isomers. The rest of the 1,6-enynes, **12b**–**16b** and **18b** were recovered unaltered after long reaction times under similar conditions. The absolute configuration of the products resulting from the PK reaction of the enynes **b** (**19bA**–**22bA** and **19bB**–**22bB**), as indicated in Scheme 4, was assigned by ^{1}H NMR (see the Supporting Information).

Synthesis and Reactivity of 1–6 Enynes I. Differences in reactivity and stereoselectivity of the epimeric sulfinyl enynes **II** should be due to the contribution of the two stereogenic elements present in their structures. In order to know the relative influence of each one, we decided to study the behavior of the enynes **I** (compounds **28**–**30**), with the stereogenic quaternary center as the only stereogenic element, whose influence had never been considered due to the difficulties associated to the preparation of this type of substrates. Removal of the sulfinyl group of compounds **8a**, **10a** and **12a** was performed with *t*-BuLi[15] in THF at −78 °C, affording nitriles **28**, **29** and **30** in high yields (Scheme 5).

When **28** was treated under the usual PK reaction conditions [$Co_2(CO)_8$, NMO in CH_2Cl_2] at room temperature, it afforded, in only five minutes, a mixture of cycloadducts **31A** and **31B** in high yield but with practically no stereoselectivity

Scheme 4. Pauson–Khand Reactions of Homochiral Sulfinyl 1,6-Enynes (Series b)



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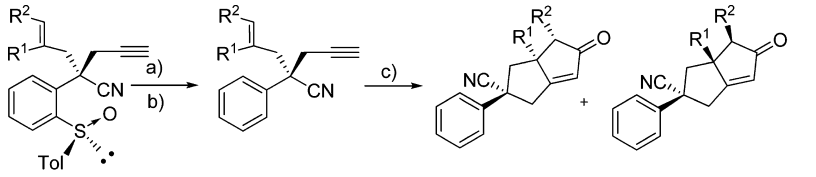
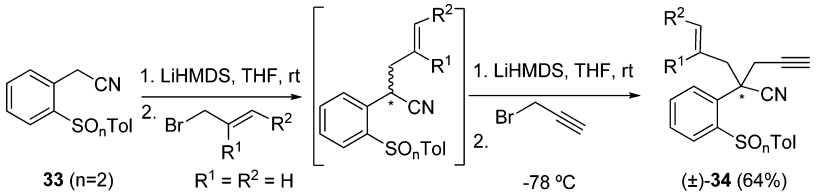
Scheme 5. Synthesis and Pauson–Khand Reactions of 1,6-Enynes 28–30



Reaction conditions:
a) *t*-BuLi (1.5 equiv.),THF, -78 ºC, 30 min. b) NH_4Cl; c) $[Co_2(CO)_8]$/ NMO, CH_2Cl_2, rt.

Scheme 6. Synthesis of Racemic Sulfone 34 and Thioethers 36–38



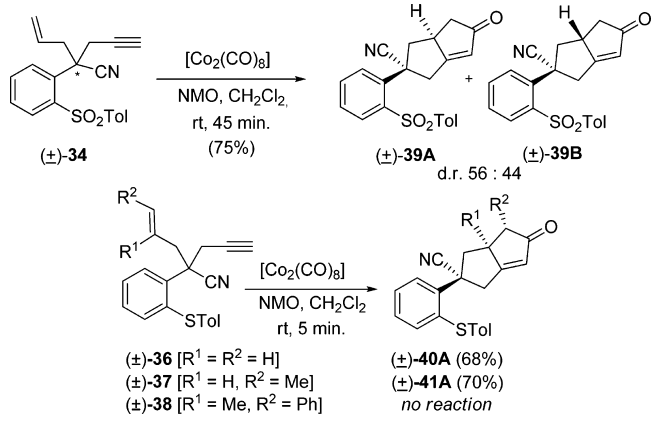
(Scheme 5). By contrast, when starting from **29**, the influence of the quaternary center on the stereoselectivity was significant, and a 90:10 mixture of **32A** and **32B** was obtained after 30 min of reaction. Compound **30** did not react under the PK conditions, and therefore we did not prepare more desulfinylated enynes. The different d.r. values obtained in these reactions show that the influence of the quaternary benzylic carbon atom depends on the nature of the substituents at the allylic fragment.

Despite that the comparison of the results collected in Table 3 for substrate **12a** (entry 5) with those depicted in Scheme 5 for desulfinylated enyne **30** could suggest a positive influence of the sulfinyl group on the reactivity, it is not so clear if we compare the results obtained for **10a** (entry 3) and **29**. For substrates evolving more rapidly, **8a** and **28**, this effect was demonstrated by performing a competitive assay by treating **8a** (1.0 equiv) and **28** (1.0 equiv) with $Co_2(CO)_8$ (1.3 equiv) in anhydrous CH_2Cl_2 at room temperature. Further addition of NMO provided a 67:33 mixture of adducts (**19aA** + **19aB**) and (**31A** + **31B**).

Synthesis and Reactivity of Sulfenyl (1,6)-Enynes III. The low reactivity and stereoselectivity of the sulfoxides of the series **b** with respect to those of the series **a**, under similar PK conditions, indicates that both features are associated to the relative configuration of the enyne, suggesting the existence of some interaction of the sulfinyl group with the metal in the transition state,[6c–g] which is only possible for compounds of the series **a**. In order to unequivocally establish which of the two basic centers, the lone electron pair at sulfur or the sulfinyl oxygen atom, were involved in this interaction, we studied the behavior of thioethers (which lack the oxygen atom) and sulfones (without any lone electron pair at sulfur), the benzylic carbon being the only stereogenic element in both compounds. We first prepared these compounds in their racemic form by using the sequence indicated in Scheme 6. Racemic sulfonyl 1,6-enyne **34** was obtained from **33** (prepared by MPCBA oxidation of its corresponding sulfoxide **1**) following a two-step quaternization process of the benzylic carbon similar to that used for preparing sulfoxides (Scheme 6). A similar procedure starting from thioether **35** provided sulfenyl 1,6-enines with mono- (**36**), di- (**37**), and trisubstituted (**38** as mixture *Z*:*E* 85:15) double bonds.

Under PK conditions compound **34** exhibited a lower reactivity than that of the corresponding sulfinyl derivatives (**8a** or **8b**) or the desulfinylated compound (**28**) and produced a mixture of racemic cycloadducts **39A** + **39B** with practically no stereocontrol (Scheme 7). Contrarily, under similar conditions

Scheme 7. Behavior of Racemic Sulfone 34 and Thioethers 36, 37, And 38 under PK Reaction Conditions



thioether **36** reacted immediately in a completely stereoselective manner, only yielding one diastereoisomer **40A**. A similar behavior was observed for **37**, which only afforded cycloadduct **41A** in 5 min. The relative configuration of racemic adducts **39A**, **39B**, **40A** and **41A** was established from their ^1H NMR spectra. By contrast, thioether **38** did not react under the usual PK reaction conditions. The comparison of these results with those obtained from the sulfoxides of similar structure **8a**, **12a** and **17a** (Table 3) allowed us to conclude that the

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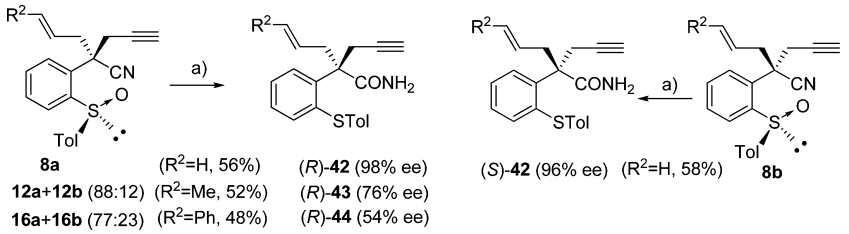
Scheme 8. Reduction of the Sulfoxides 8a, 8b, 12a, and 16a

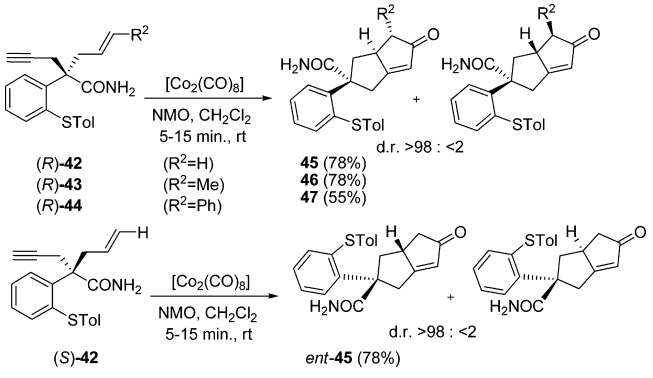


thioethers react with complete stereoselectivity and their reactivity is much higher. These results are indicative of an important role of the lone electron pair at sulfur (more easily available in thioethers) in the course of the PK reactions.

Consequently, the best strategy for obtaining the optically pure bicyclo[3.3.0]octenones would consist first in employing the sulfinyl group for creating the quaternary stereogenic carbon (Table 2), and then transforming compounds **8**–**18** into their corresponding thioethers, which would be finally treated under PK reaction conditions to afford the desired adducts. In order to assess the feasibility of this strategy, we chose three sulfinyl 1,6-enynes of the series **a** (**8a**, **12a**, and **16a**) and one of the series **b** (**8b**) as the substrates for the reduction of the sulfur function. After several unsuccessful trials, the reduction of the sulfinyl group was performed by treatment with $BF_3{\cdot}OEt_2$ and NaI in anhydrous CH_3CN.[16] The reactions were clean, but under these conditions, concomitant sulfinyl reduction and cyano hydrolysis took place (Scheme 8).[17] The resulting sulfenyl carboxamides were obtained in satisfactory yields (50–60%) taking into account that the conversions were not complete (ca. 70%) and the unreacted sulfinyl nitriles could be recovered. As expected, the amides resulting from **8a** and **8b** are enantiomers [(*R*)-**42** and (*S*)-**42**]. Enantiomeric ratio of the obtained (*R*)-**43**, measured with chiral HPLC, is 88:12, in complete agreement with the same d.r. of the mixture **12a** and **12b** used as the starting product. Analogously, the reaction of a 77:23 mixture of **16a** and **16b** yielded (*R*)-**44** with 54% ee (Scheme 8).

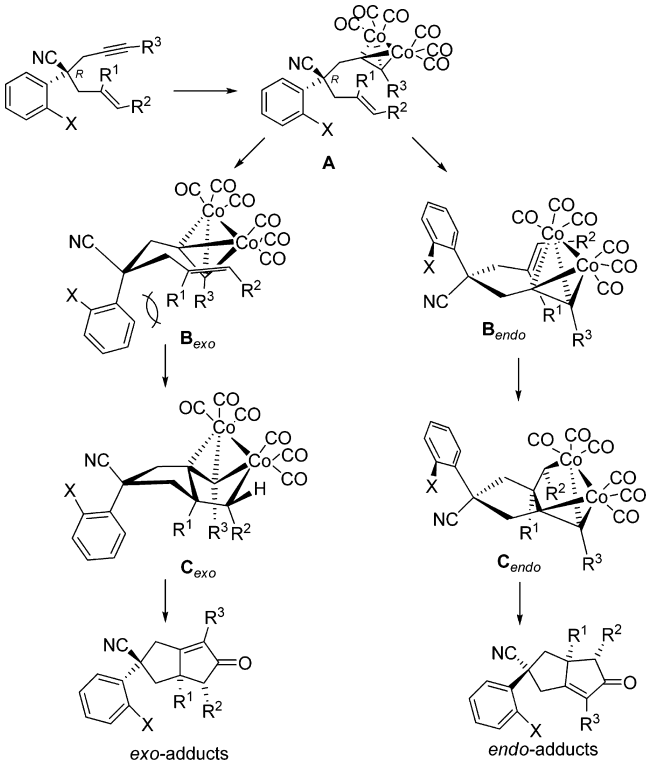
The sulfenyl carboxamides (*R*)-**42** and (*S*)-**42** evolved with a complete control of the stereoselectivity only affording one bicyclo[3.3.0]octenone (**45** and *ent*-**45**, respectively) in high yields (Scheme 9), in contrast with the moderate or low stereocontrol that had been observed in the evolution of their sulfinyl precursors **8a** (d.r. 72:28, entry 1, Table 3) and **8b** (d.r. 56:44, Scheme 4). Analogously, the fast (5–10 min) and completely stereoselective reactions of (*R*)-**43** and (*R*)-**44**, yielding **46** and **47**, respectively (de >98%, Scheme 9), contrasts with the slower (90 min) and less stereoselective (d.r. 80:20) reaction of the sulfinyl precursors **12a** (entry 5, Table 3) and the much lower reactivity of **16a** (3.5 h, entry 6, Table 3). All these results demonstrate that the thioethers are better substrates than the sulfoxides (regardless of their relative configuration) in the assayed PK reactions. The relative configuration of the newly created stereogenic carbon atoms at adducts **45**–**47** was determined from their ^{1}H NMR spectra. Bearing in mind that the previously established configuration of the benzylic carbon for substrates **42**–**44** had been previously established, the absolute configuration of the resulting adducts (**45**–**47**) could, therefore, be assigned.

Scheme 9. Pauson–Khand Reactions of Sulfenyl 1,6-Enynes 42–44



Mechanistic Proposal. Our mechanistic proposal accounting for the experimental results is depicted in Schemes 10 and 11. The alkyne–cobalt complex **A** may follow two alternative pathways, dependent on the C–Co bond chosen by the olefin π-system to become inserted. In the approach $\mathbf{B}_{exo}$, the aryl containing the X group (H, STol, SOTol, SO_2Tol) occupies a pseudoaxial placement far from the cobalt atoms and obviously

Scheme 10. Stereochemical Pathway Accounting for the Stereoselectivity of the PK Reactions of Desulfinylated and Sulfonyl Enynes



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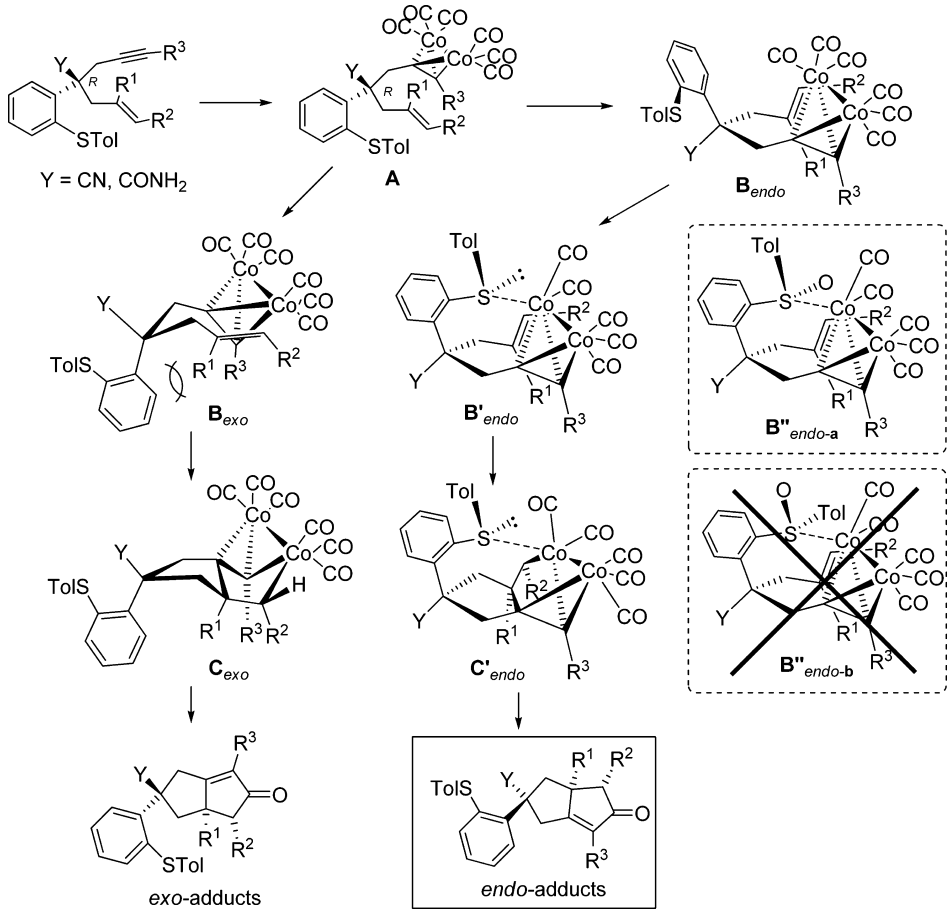
Scheme 11. Stereochemical Pathway Accounting for the Stereoselectivity of the PK Reactions of Sulfenyl and Sulfinyl Enynes



cannot interact with the metal. The same is true for the $\mathbf{B}_{endo}$ approach when X cannot interact with the metal, which is the case when X = H, SO_2Tol (they lack the lone electron pairs) and SOTol (epimers **b**, vide infra). In these cases, the olefin insertion in the suitable C−Co bond will produce the intermediates $\mathbf{C}_{exo}$ and $\mathbf{C}_{endo}$, which will evolve into the *exo* and *endo* adducts, respectively, by reductive elimination and decomplexation. Intermediates $\mathbf{B}_{exo}$ and $\mathbf{B}_{endo}$ (as well as $\mathbf{C}_{exo}$ and $\mathbf{C}_{endo}$) must be similar in energy when R^1 = H (because of the low magnitude of the interactions between the metal complex and the Ar and CN groups), and very low stereoselectivity should be expected. When R^1 = Me, the steric repulsion Ar/Me could become important and justify the differences in the stereoselectivity observed for cyclization of **28** and **29** (Scheme 5) or **8a** and **10a** (Table 3). Even more important will be the interaction Ar/Ph in compounds **14a** and **15a**, thus explaining their much higher stereoselectivity with respect to **10a** and **11a** (Table 3). In all the cases, the reactivity must decrease substantially when R^1 and R^2 are not hydrogen, due to their interactions with the metal complex in both *exo* and *endo* approaches.

When X = STol, the sulfur atom can stabilize the *endo* approach strongly by forming the $\mathbf{B'}_{endo}$ intermediate (Scheme 11) from $\mathbf{B}_{endo}$, by association of the lone electron pair at sulfur with the Co, displacing a CO molecule. Intermediate $\mathbf{B'}_{endo}$ must be much more stable than $\mathbf{B}_{exo}$, which would explain the higher reactivity and the exclusive formation of the *endo* adducts in reactions from thioethers.

The behavior of the sulfoxides depends on their relative configuration. Epimers **b** cannot form $\mathbf{B''}_{endo\text{-}b}$ because of the strong steric repulsion of the tolyl group with the alkene fragment (right, Scheme 11), and therefore they would evolve according to the model depicted in Scheme 10, with low reactivity and stereoselectivity. By contrast, epimers **a** could form $\mathbf{B''}_{endo\text{-}a}$ (right, Scheme 11), although the magnitude of its stabilization with respect to $\mathbf{B}_{exo}$ would be less important than that existing for thioethers due to the lower association ability of the sulfinyl sulfur and the steric repulsion of the oxygen with the alkene fragment. Therefore, both reactivity and stereoselectivity of epimers **a** are intermediate between those of thioethers and desulfinylated compounds.

CONCLUSIONS

From the above results, we can conclude that a variety of differently substituted bicyclo[3.3.0]octenones, bearing up to three carbon stereocenters, two of which are quaternary in some of the cases, has been synthesized in high yields with good to excellent diastereocontrol from 1,6-enynes bearing remote sulfenyl or sulfinyl functions. The stereoselectivity of these Pauson−Khand reactions was markedly dependent on the coexistence in the substrate of a quaternary stereogenic carbon and a sulfur atom bearing a coordinating lone electron pair. The presence of the chiral sulfinyl group has proved crucial for the efficient asymmetric generation of the benzylic quaternary stereogenic carbons present at the starting 1,6-enynes. Thioethers, obtained by reduction of the sulfoxides, are much

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more efficient for controlling the stereoselectivity (only one diastereoisomer is obtained) and for increasing the reactivity.

EXPERIMENTAL SECTION

General Procedures. NMR spectra were registered (300 and 75 MHz for ^{1}H and ^{13}C NMR, respectively) in $CDCl_3$ solutions. ^{13}C NMR spectra were acquired on a broad band decoupled mode. Melting points were measured in open capillary tubes. Mass spectra (MS) were determined by EI, FAB and ESI, as indicated in each case. High resolution mass spectra (HRMS) were performed by using a magnetic-sector mass analyzer (for FAB ionization mode) or time-of-flight (TOF) mass analyzer (for EI and ESI ionization modes), as indicated for each compound. All reactions were carried out in anhydrous solvents under argon atmosphere. Commercially available anhydrous tetrahydrofuran (THF) and ethyl ether (Et_2O) were dried over 4 Å molecular sieves. Analytical thin layer chromatography (TLC) was performed using precoated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or $KMnO_4$ dip. Flash column chromatography was performed using silica gel (230−400 mesh). The enantiomeric excess (ee) of products was determined by chiral stationary phase HPLC. Commercially available $Co_2(CO)_8$ and NMO were used without further purification.

General Procedure for the Synthesis of 2-Allyl-2-[2-(*p*-tolylsulfinyl)phenyl]acetonitriles (2−7). To a solution of (*S*)-2-[2-(*p*-tolylsulfinyl)phenyl]acetonitrile (255.3 mg, 1 mmol) in anhydrous THF (10 mL) at rt under argon was added LHMDS (1 M in THF) (1.2 mL, 1.2 mmol). The mixture was stirred at rt for 10 min, and then 1.4 mmol of the corresponding allyl halide was added dropwise. The reaction was monitored by TLC. Upon transformation of the starting material, the reaction was hydrolyzed with saturated aqueous NH_4Cl (5 mL). The mixture was extracted with Et_2O (3 × 5 mL), dried (Na_2SO_4), and the solvent was evaporated. The diastereoisomeric mixture was purified by flash column chromatography using the eluent indicated in each case.

[2*S*,(S)*S*] and [2*R*,(S)*S*]-2-[2-(*p*-Tolylsulfinyl)phenyl]pent-4-enenitrile (2 + 2′). The diastereoisomeric mixture **2** + **2′** was obtained using allyl bromide as the electrophile. The reaction mixture was stirred at rt for 10 min. The crude 50:50 mixture of **2** + **2′** was purified by flash column chromatography using AcOEt−hexane (1:1) as the eluent. Yield: 77% (227 mg, colorless oil); IR (film) 3055, 2923, 2241, 1493, 1083, 1038, 759 cm^{-1}; ^{1}H NMR [diastereoisomeric mixture (50:50)] δ 7.91−7.87 (m, 2H), 7.55−7.45 (m, 6H), 7.44 and 7.27 (AA′BB′ system, 4H), 7.42 and 7.26 (AA′BB′ system, 4H), 5.84−5.66 (m, 2H, 2CH), 5.21−5.04 (m, 4H, $2CH_2$), 4.52−4.44 (m, 2H, 2CH), 2.62−2.49 (m, 2H, 2CH), 2.44−2.30 (m, 1H), 2.23 (s, 6H), 2.25−2.16 (m, 1H) ppm; ^{13}C NMR [diastereoisomeric mixture (50:50)] δ 142.4, 142.2 (2C), 141.7, 140.8, 140.7, 134.9, 133.9, 132.1 (2C), 132.0, 131.8, 130.4 (2C), 130.3 (2C), 129.7, 129.5, 129.2, 128.8, 127.2, 126.3, 125.7 (2C), 125.3 (2C), 119.9, 119.7, 119.6, 119.4, 39.3, 39.2, 32.6, 32.2, 21.3 (2C) ppm; MS (ESI+) *m*/*z* 295 (100); HRMS (EI+) calcd. for $C_{18}H_{18}NOS$ [M + H]$^+$ 295.1031, found 295.1033.

[2*S*,(S)*S*] and [2*R*,(S)*S*]-4-Methyl-2-[2-(*p*-tolylsulfinyl)phenyl]-pent-4-enenitrile (3 + 3′). The diastereoisomeric mixture **3** + **3′** was obtained using commercial 3-bromo-2-methylprop-1-ene as the electrophile. The reaction mixture was stirred at rt for 10 min. The crude 50:50 mixture of **3** + **3′** was purified by flash column chromatography using AcOEt−hexane (1:2) as the eluent. Yield: 72% (222 mg, colorless oil); IR (film) 3078, 2922, 2241, 1650, 1492, 1083, 1035, 761 cm^{-1}; ^{1}H NMR [diastereoisomeric mixture (50:50)] δ 7.80−7.77 (m, 1H), 7.74−7.71 (m, 1H), 7.54−7.49 (m, 2H), 7.47−7.38 (m, 2H), 7.37−7.26 (m, 2H), 7.24−7.04 (m, 8H), 6.28 (m, 2H, 2CH), 6.24 (m, 2H, 2CH), 4.64 (dd, *J* 5.4 and 9.9 Hz, 1H), 4.54 (dd, *J* 6.5 and 8.7 Hz, 1H), 2.62−2.55 (m, 2H, 2CH), 2.50−2.30 (m, 2H, 2CH), 2.26 (s, 6H), 1.81 (d, *J* 1.3 Hz, 3H), 1.76 (d, *J* 1.2 Hz, 3H) ppm; ^{13}C NMR [diastereoisomeric mixture (50:50)] δ 142.4, 142.3, 141.9, 141.7, 140.8, 140.7, 137.3, 137.1, 135.8, 134.2, 132.8, 132.4, 132.3, 132.1, 130.5 (2C), 130.3 (2C), 130.1, 130.0, 129.7, 129.6, 129.1, 128.8 (2C), 128.7, 128.5, 128.1 (2C), 128.0 (2C), 127.9, 126.6, 126.5, 126.1, 125.5 (2C), 125.4 (2C), 119.7, 119.5, 46.2, 46.0, 32.2, 31.5, 21.3 (2C), 17.7, 17.6 ppm; MS (ESI+) *m*/*z* 310 [M + H] $^+$ (100), 292 (17); HRMS (EI+) calcd. for $C_{19}H_{20}NOS$ 310.1266, found 310.1269.

[2*S*,(S)*S*,4*E*], [2*R*,(S)*S*,4*E*], [2*S*,(S)*S*,4*Z*] and [2*R*,(S)*S*,4*Z*]-2-[2-(*p*-Tolylsulfinyl)phenyl]-hex-4-enenitrile [(*E*)-4 + (*E*)-4′ + (*Z*)-4 + (*Z*)-4′]. The diastereoisomeric mixture **4** + **4′** was obtained using commercial 1-bromobut-2-ene (*E*/*Z* mixture of 80:20) as the electrophile. The reaction mixture was stirred at rt for 15 min. The crude 40:40:10:10 mixture of (*E*)-**4** + (*E*)-**4′** + (*Z*)-**4** + (*Z*)-**4′**, which could not be isolated diastereomerically pure, was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. Yield: 78% (241 mg, colorless oil); IR (film) 3078, 2974, 2243, 1643, 1473, 1083, 1035, 758 cm^{-1}; ^{1}H NMR [diastereoisomeric (*E*)-**4** + (*E*)-**4′** mixture (50:50)] δ 7.88−7.85 (m, 2H), 7.59−7.47 (m, 6H), 7.42 and 7.26 (AA′BB′ system, 4H), 7.40 and 7.26 (AA′BB′ system, 4H), 5.68−5.51 (m, 2H, 2CH), 5.46−5.29 (m, 2H, 2CH), 4.47−4.40 (m, 2H, 2CH), 2.63−2.41 (m, 2H, 2CH), 2.40−2.28 (m, 1H), 2.35 (s, 6H), 2.21−2.14 (m, 1H), 1.66 (d, *J* 6.4 Hz, 3H), 1.63 (d, *J* 7.0 Hz, 3H) ppm; ^{1}H NMR [representative signals for diastereoisomers (*Z*)-**4** + (*Z*)-**4′**] δ 5.77−5.53 (m, 4H), 4.50−4.30 (m, 2H, 2CH), 2.65−2.50 (m, 2H), 2.22−2.10 (m, 2H), 1.50 (d, *J* 6.8 Hz, 3H), 1.45 (d, *J* 6.8 Hz, 3H) ppm; ^{13}C NMR [diastereoisomeric (*E*)-**4** + (*E*)-**4′** mixture (50:50)] δ 142.5, 142.1, 142.0, 141.9. 135.1, 134.1, 131.9, 131.8 (2C), 130.8, 130.4, 130.3, 130.2 (2C), 130.1 (2C), 129.5, 129.3, 129.0, 128.7, 127.0, 126.1, 125.7 (2C), 125.6, 125.2, 124.7, 124.4, 119.8, 119.6, 38.3, 38.2, 33.8, 32.8, 21.3 (2C), 17.7 (2C) ppm; ^{13}C NMR [representative signals for diastereoisomers (*Z*)-**4** + (*Z*)-**4′**] δ 142.7, 142.1, 135.3, 134.1, 132.1, 129.7, 129.5, 128.9, 128.7, 127.4, 126.1, 123.8, 123.5, 53.4, 32.6, 32.3, 30.8, 12.8 (2C) ppm; MS (FAB+) *m*/*z* 310 [M + H]$^+$ (100), 292 (17); HRMS (EI+) calcd. for $C_{19}H_{20}NOS$ [M + H]$^+$ 310.1266, found 310.1274.

[2*S*,(S)*S*] and [2*R*,(S)*S*]-4-Phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-pent-4-enenitrile (5 + 5′). The diastereoisomeric mixture **5** + **5′** was obtained using commercial 3-bromo-2-phenylprop-1-ene as the electrophile. The reaction mixture was stirred at rt for 30 min. The crude 60:40 mixture of **5** + **5′** was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. Yield: 72% (267 mg, colorless oil); IR (film) 3050, 2922, 2241, 1639, 1473, 1083, 1035, 810 cm^{-1}; ^{1}H NMR [diastereoisomeric mixture (60:40)] δ 8.10−8.07 (m, 1H), 7.97−7.93 (m, 1H), 7.72−7.60 (m, 7H), 7.56−7.42 (m, 9H), 7.40 and 7.28 (2 × AA′BB′ system, 8H), 5.55 (m, 1H), 5.54 (m, 1H), 5.41 (m, 1H), 5.38 (m, 1H), 4.65 (dd, *J* 6.9 and 8.8 Hz, 1H), 4.36 (dd, *J* 5.5 and 10.1 Hz, 1H), 3.26 (dd, *J* 5.3 and 14.1 Hz, 1H), 3.09 (dd, *J* 10.1 and 14.1 Hz, 1H), 3.08−2.97 (m, 2H), 2.41 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR [diastereoisomeric mixture (60:40)] δ 143.6, 143.2, 142.4, 142.2, 142.0, 141.6, 140.5, 140.4, 139.2, 138.9, 135.2, 133.2, 132.3, 131.7, 130.2 (2C), 130.1 129.8, 129.4, 129.1, 128.6 (2C), 128.4, 128.3, 128.2, 127.8, 127.7, 126.5 (2C), 126.4 (2C), 125.6 (3C), 125.2, 125.1 (2C), 119.3, 118.8, 117.1, 116.3, 41.8, 40.8, 32.3, 31.8, 21.3 (2C) ppm; MS (FAB+) *m*/*z* 372 [M + H]$^+$ (100), 307 (26), 165 (32); HRMS (FAB+) calcd. for $C_{24}H_{22}NOS$ [M + H]$^+$ 372.1422, found 372.1428.

[2*S*,(S)*S*,4*E*] and [2*R*,(S)*S*,4*E*]-5-Phenyl-2-[2-(*p*-tolylsulfinyl)-phenyl]pent-4-enenitrile (6 + 6′). The diastereoisomeric mixture **6** + **6′** was obtained using commercial cinnamyl bromide as the electrophile. The reaction mixture was stirred at rt for 30 min. The crude 50:50 mixture of **6** + **6′** was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. Yield: 75% (278 mg, colorless oil); IR (film) 3049, 2930, 2241, 1639, 1473, 1083, 1035, 750 cm^{-1}; ^{1}H NMR [diastereoisomeric mixture (50:50)] δ 7.86−7.80 (m, 2H), 7.54−7.47 (m, 5H), 7.43−7.36 (m, 3H), 7.29−7.17 (m, 16H), 6.43 (d, *J* 15.4 Hz, 1H), 6.30 (d, *J* 15.7 Hz, 1H), 6.16−6.00 (m, 2H, 2CH), 4.57−4.49 (m, 2H, 2CH), 3.19−3.16 (m, 1H), 2.73−2.64 (m, 1H), 2.62−2.50 (m, 1H), 2.44−2.36 (m, 1H), 2.34 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR [diastereoisomeric mixture (50:50)] δ 142.2, 142.1, 136.4, 136.3, 135.8, 135.7, 135.0, 134.9, 134.6, 134.0, 132.2, 132.1, 130.4 (2C), 130.3 (2C), 130.0, 129.7, 129.5, 129.2, 128.9, 128.7, 128.6, 128.5, 128.4, 127.9, 127.8, 127.4, 126.6, 126.5, 126.4 (2C), 126.3 (2C), 125.9, 125.7 (2C), 125.4 (2C), 123.3, 123.0, 122.4, 121.8, 38.7 (2C), 33.2, 32.6, 21.4 (2C) ppm; MS (ESI+)

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m/*z* 372 [M + H]$^+$ (100), 65 (16); HRMS (FAB+) calcd. for $C_{24}H_{22}NOS$ [M + H]$^+$ 372.1422, found 372.1426.

[2*S*,(S)*S*,4*E*], [2*R*,(S)*S*,4*E*], [2*S*,(S)*S*,4*Z*] and [2*R*,(S)*S*,4*Z*]-4-Methyl-5-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile [(*E*)-7 + (*E*)-7′ + (*Z*)-7 + (*Z*)-7′]. The diastereoisomeric mixture 7 + 7′ was obtained using 3-bromo-2-methyl-1-phenylprop-1-ene[12] (*E*/*Z* mixture of 86:14) as the electrophile. The reaction mixture was stirred at rt for 30 min. The crude 42:42:8:8 mixture of (*E*)-7 + (*E*)-7′ + (*Z*)-7 + (*Z*)-7′, which could not be isolated diastereomerically pure, was purified by flash column chromatography using AcOEt−hexane (1:2) as the eluent. Yield: 71% (273 mg, white solid); IR (KBr) 3054, 3019, 2241, 1596, 1441, 1083, 1033, 753 cm^{-1}; ^{1}H NMR [diastereoisomeric (*E*)-7 + (*E*)-7′ mixture (50:50)] δ 7.88−7.79 (m, 2H), 7.61−7.56 (m, 2H), 7.54−7.48 (m, 3H), 7.43−7.35 (m, 4H), 7.31−7.15 (m, 15H), 6.34 (m, 1H), 6.32 (m, 1H), 4.71 (dd, *J* 5.4 and 9.9 Hz, 1H), 4.61 (dd, *J* 6.4 and 8.6 Hz, 1H), 2.69−2.64 (m, 2H, 2CH), 2.58−2.39 (m, 2H, 2CH), 2.32 (s, 6H), 1.86 (d, *J* 15.8 Hz, 3H), 1.85 (d, *J* 15.8 Hz, 3H) ppm; ^{1}H NMR [representative signals for diastereoisomers (*Z*)-7 + (*Z*)-7′] δ 7.68−7.62 (m, 2H), 6.50 (m, 1H), 6.48 (m, 1H), 4.77 (dd, *J* 5.8 and 10.4 Hz, 1H), 4.57 (dd, *J* 7.1 and 9.1 Hz, 1H), 2.93−2.83 (m, 2H), 2.59−2.38 (m, 2H), 1.93 (d, *J* 10.4 Hz, 3H), 1.92 (d, *J* 10.2 Hz, 3H) ppm; ^{13}C NMR [diastereoisomeric (*E*)-7 + (*E*)-7′ mixture (50:50)] δ 142.4, 142.3, 141.9, 141.7, 140.8, 140.7, 137.3, 137.1, 135.8, 134.2, 132.8, 132.4, 132.3, 132.1, 130.4 (2C), 130.3 (2C), 130.1, 130.0, 129.8, 129.6, 129.5, 129.1, 128.3, 128.0 (3C), 128.7, 128.5, 128.1 (2C), 128.0 (2C), 127.9, 126.6, 126.5, 125.5, 125.4, 119.7, 119.5, 46.2, 46.0, 32.2, 31.5, 21.4, 21.3, 17.7, 17.6 ppm; ^{13}C NMR [representative signals for diastereoisomers (*Z*)-7 + (*Z*)-7′] δ 142.7, 141.8, 140.9, 137.4, 137.2, 135.9, 133.6, 132.9, 131.9, 130.7, 129.9, 129.1, 128.6, 128.2, 128.0, 126.7, 125.6, 125.3, 119.4, 37.9, 37.8, 30.8, 30.3, 23.6, 22.9 ppm; MS (FAB+) *m*/*z* 386 [M + H]$^+$ (100), 211 (30); HRMS (FAB+) calcd. for $C_{25}H_{24}NOS$ [M + H]$^+$ 386.1579, found 386.1567.

General Procedure for the Synthesis of 2-Allyl-2-propargyl-2-[2-(*p*-tolylsulfinyl)phenyl]acetonitriles (8−18). To a solution of the corresponding 2-allyl-2-[2-(*p*-tolylsulfinyl)phenyl]acetonitrile (0.13 mmol) and 18-crown-6 ether (42.0 mg, 0.16 mmol) in anhydrous THF (1 mL) at −78 °C under argon was added KHMDS (0.5 M in toluene) (0.320 mL, 0.16 mmol). The mixture was stirred at −78 °C for 10 min, and then 0.14 mmol of the corresponding propargyl bromide was added dropwise. The resulting mixture was stirred at −78 °C. The reaction was monitored by TLC. Upon transformation of the starting material, the reaction was hydrolyzed with saturated aqueous NH_4Cl (5 mL). The mixture was extracted with CH_2Cl_2 (3 × 5 mL), dried (Na_2SO_4), and the solvent was evaporated. The diastereoisomeric mixture was purified by flash column chromatography using as the eluent a mixture of AcOEt/hexane as indicated in each case. The same experimental procedure was employed when NHMDS was used as the base.

[2*R*,(S)*S*] and [2*S*,(S)*S*]-2-(Prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)-phenyl]pent-4-enenitrile (8a + 8b). The diastereoisomeric mixture **8a** + **8b** was obtained using a 50:50 mixture of [2*S*,(S)*S*] and [2*R*,(S)*S*]-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**2** + **2′**) as the substrate and propargyl bromide (80% solution in toluene) as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 60 min. The crude 80:20 mixture of **8a** + **8b** was purified by flash column chromatography using AcOEt−hexane (1:2) as the eluent. **Diastereoisomer [2*R*,(S)*S*]-8a** (yellow solid): Yield 62% (27 mg); mp 85−87 °C (CH_2Cl_2−hexane); $[\alpha]^{20}_D$ −160.3 (*c* 0.5, $CHCl_3$); IR (KBr) 3299, 2940, 2236, 1436, 1042, 1015, 759 cm^{-1}; ^{1}H NMR δ 7.79−7.76 (m, 1H), 7.60−7.53 (m, 1H), 7.55 and 7.27 (AA′BB′ system, 4H), 7.51−7.44 (m, 2H), 5.73−5.59 (m, 1H), 5.29−5.21 (m, 2H), 3.24−3.13 (m, 3H), 3.06 (dd, *J* 7.6 and 14.1 Hz, 1H), 2.37 (s, 3H), 2.20 (t, *J* 2.5 Hz, 1H) ppm; ^{13}C NMR δ 145.7, 141.3, 141.0, 135.9, 131.8, 130.4, 130.2, 130.1, 129.9 (2C), 127.4, 125.7 (2C), 121.8 (2C), 77.6, 73.9, 45.4, 44.0, 28.6, 21.3 ppm; MS (FAB+) *m*/*z* 334 [M + H] $^+$ (100); HRMS (FAB+) calcd. for $C_{21}H_{20}NOS$ [M + H]$^+$ 334.1266, found 334.1270. **Diastereoisomer [2*S*,(S)*S*]-8b** (yellow solid): Yield 18% (8 mg); mp 108−110 °C (CH_2Cl_2−hexane); $[\alpha]^{20}_D$ −145.9 (*c* 0.8, $CHCl_3$); ^{1}H NMR δ 7.71−7.66 (m, 2H), 7.55−7.39 (m, 2H), 7.51 and 7.27 (sistema AA′BB′ system, 4H), 5.86−5.70 (m, 1H), 5.34−5.11 (m, 2H), 5.24−3.02 (m, 4H), 2.38 (s, 3H), 2.12 (t, *J* 2.6 Hz, 1H) ppm; ^{13}C NMR δ 144.9, 141.2, 140.7, 135.8, 131.8, 130.5, 130.3 (2C), 129.9 (2C), 128.7, 125.5 (2C), 121.6, 121.2, 77.3, 73.9, 47.5, 42.6, 31.5, 21.3 ppm.

[2*R*,(S)*S*] and [2*S*,(S)*S*]-2-(But-1-inyl)-2-[2-(*p*-tolylsulfinyl)-phenyl]pent-4-enenitrile (9a + 9b). The diastereoisomeric mixture **9a** + **9b** was obtained using a 50:50 mixture of [2*S*,(S)*S*] and [2*R*,(S)*S*]-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**2** + **2′**) as the substrate and 1-bromobut-2-ine as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 60 min. The crude 87:13 mixture of **9a** + **9b** was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. **Diastereoisomer [2*R*,(S)*S*]-9a** (colorless oil): Yield 62% (28 mg); $[\alpha]^{20}_D$ −149.5 (*c* 0.6, $CHCl_3$); IR (film) 2921, 2236, 1641, 1453, 1082, 1044, 760 cm^{-1}; ^{1}H NMR δ 7.72−7.64 (m, 2H), 7.55−7.38 (m, 2H), 7.54 and 7.27 (AA′BB′ system, 4H), 5.82−5.71 (m, 1H), 5.34−5.19 (m, 2H), 3.16−2.98 (m, 4H), 2.37 (s, 3H), 1.70 (t, *J* 2.4 Hz, 3H) ppm; ^{13}C NMR δ 144.9, 141.2, 141.1, 136.3, 131.7, 130.8, 130.1 (2C), 129.9 (2C), 128.6, 125.5 (2C), 121.7, 121.3, 81.6, 72.4, 48.0, 42.7, 32.2, 21.3, 3.4 ppm; MS (ESI+) *m*/*z* 348 [M + H]$^+$ (100); HRMS (ESI+) calcd. for $C_{22}H_{22}NOS$ [M + H]$^+$ 348.1421, found 348.1416. **Diastereoisomer [2*S*,(S)*S*]-9b** (colorless oil): Yield 7% (3 mg); $[\alpha]^{20}_D$ −63.7 (*c* 0.7, $CHCl_3$); ^{1}H NMR δ 7.79−7.76 (m, 1H), 7.58−7.53 (m, 1H), 7.56 and 7.27 (AA′BB′ system, 4H), 7.52−7.42 (m, 2H), 5.73−5.59 (m, 1H), 5.25−5.19 (m, 2H), 3.17−3.01 (m, 4H), 2.38 (s, 3H), 1.78 (t, *J* 2.4 Hz, 3H) ppm; ^{13}C NMR δ 145.7, 141.2, 141.1, 136.4, 131.7, 130.4, 130.1, 129.8 (3C), 127.5, 125.7 (2C), 122.2, 121.4, 81.5, 72.6, 45.7, 43.9, 29.0, 21.3, 3.5 ppm.

[2*R*,(S)*S*] and [2*S*,(S)*S*]-4-Methyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (10a + 10b). The diastereoisomeric mixture **10a** + **10b** was obtained using a 50:50 mixture of [2*S*,(S)*S*] and [2*R*,(S)*S*]-4-methyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**3** + **3′**) as the substrate and propargyl bromide (80% solution in toluene) as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 30 min. The crude 89:11 mixture of **10a** + **10b** was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. **Diastereoisomer [2*R*,(S)*S*]-10a** (colorless oil): Yield 79% (36 mg); $[\alpha]^{20}_D$ −132.5 (*c* 1.2, $CHCl_3$); IR (film) 2955, 2236, 1528, 1472, 1083, 1047, 810, 756 cm^{-1}; ^{1}H NMR δ 7.75−7.72 (m, 1H), 7.60−7.43 (m, 3H), 7.59 and 7.28 (AA′BB′ system, 4H), 5.01 (m, 1H), 4.86 (m, 1H), 3.31−3.13 (m, 2H), 3.21 and 3.05 (coupled AB system, *J* 2.3 and 14.6 Hz, 2H), 2.38 (s, 3H), 2.23 (t, *J* 2.3 Hz, 1H), 1.64 (m, 3H) ppm; ^{13}C NMR δ 144.5, 141.3, 140.8, 138.7, 136.1, 131.8, 130.4, 130.3, 130.0 (2C), 129.9, 125.6 (2C), 121.5, 118.0, 77.7, 73.9, 48.5, 46.7, 32.9, 23.5, 21.3 ppm; MS (FAB+) *m*/*z* 348 [M + H]$^+$ (100), 310 (32); HRMS (FAB+) calcd. for $C_{22}H_{22}NOS$ [M + H]$^+$ 348.1422, found 348.1415. **Diastereoisomer [2*S*,(S)*S*]-10b** (colorless oil): Yield 8% (3 mg); $[\alpha]^{20}_D$ −120.7 (*c* 1.8, $CHCl_3$); ^{1}H NMR δ 7.81−7.78 (m, 1H), 7.73−7.70 (m, 1H), 7.52−7.43 (m, 2H), 7.51 and 7.28 (AA′BB′ system, 4H), 4.96 (m, 1H), 4.93 (m, 1H), 3.28 and 3.08 (AB system, *J* 14.4 Hz, 2H), 3.26 and 3.05 (coupled AB system, *J* 2.5 and 16.0 Hz, 2H), 2.39 (s, 3H), 2.13 (t, *J* 2.5 Hz, 1H), 1.67 (m, 3H) ppm; ^{13}C NMR δ 144.7, 141.4, 140.5, 138.7, 136.1, 131.8, 130.4, 130.3 (2C), 129.9, 129.4, 125.6 (2C), 121.6, 118.2, 77.6, 73.8, 48.6, 46.8, 33.0, 23.6, 21.3 ppm. MS (FAB+) *m*/*z* 348 [M + H]$^+$ (100), 310 (32); HRMS (FAB +) calcd. for $C_{22}H_{22}NOS$ [M + H]$^+$ 348.1422, found 348.1412.

[2*R*,(S)*S*] and [2*S*,(S)*S*]-2-(2-But-1-inyl)-4-methyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (11a + 11b). The diastereoisomeric mixture **11a** + **11b** was obtained using a 50:50 mixture of [2*S*,(S)*S*] and [2*R*,(S)*S*]-4-methyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**3** + **3′**) as the substrate and 1-bromobut-2-ine as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 60 min. The crude 90:10 mixture of **11a** + **11b** was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. **Diastereoisomer [2*R*,(S)*S*]-11a** (colorless oil): Yield 71% (33 mg); $[\alpha]^{20}_D$ −88.2 (*c* 2.0, $CHCl_3$); IR (film) 2920, 2236, 1645, 1471, 1082, 1047, 810, 754 cm^{-1}; ^{1}H NMR δ 7.78−7.71 (m, 2H), 7.52 and 7.27 (AA′BB′ system, 4H), 7.51−7.44

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(m, 2H), 4.93 (m, 1H), 4.91 (m, 1H), 3.25 and 3.05 (AB system, *J* 14.4 Hz, 2H), 3.18 and 3.08 (coupled AB system, *J* 2.5 and 12.8 Hz, 2H), 2.38 (s, 3H), 1.70 (t, *J* 2.5 Hz, 3H), 1.65 (m, 3H) ppm; ^{13}C NMR δ 144.5, 141.2 (2C), 138.9, 136.5, 131.7, 130.2, 130.1, 129.9 (2C), 129.3, 125.6 (2C), 121.9, 117.7, 81.6, 72.7, 49.0, 46.7, 33.6, 23.5, 21.3, 3.4 ppm; MS (FAB+) *m*/*z* 362 $[M + H]^+$ (100); HRMS (FAB+) calcd. for $C_{23}H_{24}NOS$ $[M + H]^+$ 362.1601, found 362.1622. **Diastereoisomer [2*S*,(S)*S*]-11b** (colorless oil): Yield 8% (4 mg); $[\alpha]^{20}_D$ −132.5 (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 7.75−7.72 (m, 1H), 7.61−7.55 (m, 1H), 7.59 and 7.28 (AA′BB′ system, 4H), 7.49−7.43 (m, 2H), 4.98 (m, 1H), 4.84 (m, 1H), 3.20−3.06 (m, 2H), 3.18 and 3.02 (AB system, *J* 14.4 Hz, 2H), 2.38 (s, 3H), 1.79 (t, *J* 2.4 Hz, 3H), 1.63 (s, 3H) ppm; ^{13}C NMR δ 146.1, 141.1, 141.0, 138.9, 137.1, 131.7, 130.1, 129.9, 129.8 (2C), 127.3, 125.7 (2C), 122.9, 117.7, 81.6, 72.9, 47.4, 44.9, 29.4, 23.6, 21.3, 3.6 ppm.

[2*R*,(S)*S*,4*E*] and [2*S*,(S)*S*,4*E*]-2-(Prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]hex-4-enenitrile (12a + 12b). The diastereoisomeric mixture **12a** + **12b** was obtained using a 40:40:10:10 mixture of [2*S*,(S)*S*,4*E*], [2*R*,(S)*S*,4*E*], [2*S*,(S)*S*,4*Z*] and [2*R*,(S)*S*,4*Z*]-2-[2-(*p*-tolylsulfinyl)phenyl]-hex-4-enenitrile [(*E*)-**4** + (*E*)-**4′** + (*Z*)-**4** + (*Z*)-**4′**] as the substrate and propargyl bromide (80% solution in toluene) as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 30 min. The crude mixture was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. An 88:12 mixture of **12a** + **12b** was obtained, whereas the products derived from (*Z*)-**4** and (*Z*)-**4′** could not be isolated. Yield (**12a** + **12b** mixture): 76% (34 mg, colorless oil); IR (film) 2940, 2236, 1648, 1438, 1083, 1047, 810, 755 cm^{-1}; ^{1}H NMR (**12a** + **12b** mixture) δ 7.70−7.66 (m, 4H), 7.51 and 7.27 (AA′BB′ system, 8H), 7.52−7.41 (m, 4H), 5.81−5.70 (m, 2H), 5.47−5.37 (m, 2H), 3.30−3.18 (m, 4H), 3.17−3.02 (m, 4H), 2.37 (s, 6H), 2.06 (t, *J* 2.5 Hz, 1H), 1.65 (d, *J* 7.0 Hz, 3H), 1.59 (d, *J* 6.2 Hz, 3H) ppm; ^{13}C NMR (**12a** + **12b** mixture) δ 144.9, 141.2, 140.8, 136.2, 132.7, 131.8, 130.3, 130.2, 129.9 (2C), 128.7, 125.5 (2C), 123.0, 121.5, 77.7, 77.6, 73.7, 47.9, 47.5, 41.8, 36.1, 31.4, 21.3 (2C), 18.0, 13.4 ppm; MS (FAB+) *m*/*z* 348 $[M + H]^+$ (100), 310 (32); HRMS (FAB+) calcd. for $C_{22}H_{22}NOS$ $[M + H]^+$ 348.1422, found 348.1418.

[2*R*,(S)*S*,4*E*] and [2*S*,(S)*S*,4*E*]-2-(But-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]hex-4-enenitrile (13a + 13b). The diastereoisomeric mixture **13a** + **13b** was obtained using a 40:40:10:10 mixture of [2*S*,(S)*S*,4*E*], [2*R*,(S)*S*,4*E*], [2*S*,(S)*S*,4*Z*] and [2*R*,(S)*S*,4*Z*]-2-[2-(*p*-tolylsulfinyl)phenyl]-hex-4-enenitrile [(*E*)-**4** + (*E*)-**4′** + (*Z*)-**4** + (*Z*)-**4′**] as the substrate and 1-bromobut-2-ine as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 90 min. The crude mixture was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. A 90:10 mixture of **13a** + **13b** was obtained, whereas the products derived from (*Z*)-**4** and (*Z*)-**4′** could not be isolated. Yield (**13a** + **13b** mixture): 80% (37.5 mg, colorless oil); IR (film) 3058, 2950, 2235, 1532, 1438, 1082, 1045, 812, 754 cm^{-1}; ^{1}H NMR (**13a** + **13b** mixture) δ 7.74−7.69 (m, 2H), 7.66−7.64 (m, 2H), 7.53 and 7.27 (AA′BB′ system, 8H), 7.58−7.40 (m, 4H), 5.77−5.68 (m, 1H), 5.70−5.58 (m, 1H), 5.46−5.39 (m, 1H), 5.40−5.25 (m, 1H), 3.26−2.92 (m, 4H), 2.38 (s, 6H), 1.76 (t, *J* 2.4 Hz, 1H), 1.69 (t, *J* 2.2 Hz, 1H), 1.65 (d, *J* 6.3 Hz, 3H) ppm; ^{13}C NMR (**13a** + **13b** mixture) δ 144.9, 141.2, 141.0, 136.6, 132.2, 131.6, 130.1, 130.0, 129.9 (3C), 128.6, 125.6, 125.5 (2C), 123.3, 121.9, 81.4, 72.5, 48.4, 47.8, 43.0, 41.8, 36.1, 32.0, 21.2 (2C), 17.9, 13.3, 3.5, 3.3 ppm; MS (FAB+) *m*/*z* 362 $[M + H]^+$ (100), 338 (11); HRMS (FAB+) calcd. for $C_{23}H_{24}NOS$ $[M + H]^+$ 362.1601, found 362.1573.

[2*R*,(S)*S*] and [2*S*,(S)*S*]-4-Phenyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (14a + 14b). The diastereoisomeric mixture **14a** + **14b** was obtained using a 60:40 mixture of [2*S*,(S)*S*] and [2*R*,(S)*S*]-4-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**5** + **5′**) as the substrate and propargyl bromide (80% solution in toluene) as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 2 h. The crude 90:10 mixture of **14a** + **14b** was purified by flash column chromatography using AcOEt−hexane (1:4) as the eluent. Yield (mixture **14a** + **14b**): 94% (50 mg, colorless oil). **Diastereoisomer [2*R*,(S)*S*]-14a** (data from a 90:10 mixture of **14a** + **14b**): IR (film) 3058, 2854, 2236, 1718, 1447, 1083, 1029, 810, 755 cm^{-1}; ^{1}H NMR δ 7.67−7.62 (m, 2H), 7.50 and 7.26 (AA′BB′ system, 4H), 7.39−7.35 (m, 2H), 7.33−7.21 (m, 5H), 5.38 (m, 1H), 5.29 (m, 1H), 3.67 and 3.60 (AB system, *J* 14.8 Hz, 2H), 3.16 (coupled AB system, *J* 2.6 and 17.2 Hz, 2H), 2.38 (s, 3H), 2.06 (t, *J* 2.6 Hz, 1H) ppm; ^{13}C NMR δ 144.0, 142.9, 141.3, 140.6, 140.5, 136.3, 131.7, 130.2, 130.1, 129.9 (2C), 129.3, 128.4 (2C), 128.3, 127.8, 126.7 (2C), 125.6 (2C), 120.5, 77.8, 73.9, 49.7, 43.3, 32.4, 21.3 ppm; MS (FAB+) *m*/*z* 410 $[M + H]^+$ (100); HRMS (FAB+) calcd. for $C_{27}H_{24}NOS$ $[M + H]^+$ 410.1579, found 410.1578. **Diastereoisomer [2*S*,(S)*S*]-14b** (data from a 18:82 mixture of **14a** + **14b**): ^{1}H NMR δ 7.67−7.64 (m, 1H), 7.59 and 7.26 (AA′BB′ system, 4H), 7.38−7.20 (m, 8H), 5.31 (m, 1H), 5.22 (m, 1H), 3.66 and 3.64 (AB system, *J* 18.7 Hz, 2H), 2.99 (m, 2H), 2.35 (s, 3H), 2.19 (t, *J* 2.5 Hz, 1H) ppm; ^{13}C NMR δ 145.9, 142.1, 141.1, 140.9, 140.8, 136.1, 131.4, 130.2, 130.1, 129.9 (2C), 128.4 (2C), 127.8, 126.7, 126.5 (2C), 125.5 (2C), 122.2, 120.6, 78.0, 74.0, 45.2, 44.8, 28.4, 21.3 ppm; MS (FAB+) *m*/*z* 410 $[M + H]^+$ (100), 372 (90); HRMS (FAB+) calcd. for $C_{27}H_{24}NOS$ $[M + H]^+$ 410.1579, found 410.1566.

[2*R*,(S)*S*,4*E*] and [2*S*,(S)*S*,4*E*]-2-(But-2-inyl)-4-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (15a + 15b). The diastereoisomeric mixture **15a** + **15b** was obtained using a 60:40 mixture of [2*S*,(S)*S*] and [2*R*,(S)*S*]-4-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**5** + **5′**) as the substrate and 1-bromobut-2-ine as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 2 h. The crude 89:11 mixture of **15a** + **15b** was purified by flash column chromatography using AcOEt−hexane (1:4) as the eluent. Yield (mixture **15a** + **15b**): 94% (51.6 mg, white solid). **Diastereoisomer [2*R*,(S)*S*]-15a** (data from an 89:11 mixture of **15a** + **15b**): IR (KBr) 3019, 2962, 2236, 1718, 1450, 1082, 1029, 810, 755 cm^{-1}; ^{1}H NMR δ 7.69−7.62 (m, 1H), 7.61−7.58 (m, 1H), 7.50 and 7.26 (AA′BB′ system, 4H), 7.39−7.20 (m, 7H), 5.38 (m, 1H), 5.29 (m, 1H), 3.63 and 3.58 (AB system, *J* 17.6 Hz, 2H), 3.09 (coupled AB system, *J* 2.3 and 16.8 Hz, 2H), 2.38 (s, 3H), 1.65 (t, *J* 2.6 Hz, 3H) ppm; ^{13}C NMR δ 144.2, 143.2, 141.2 (2C), 140.7, 136.8, 131.5 (2C), 129.9, 129.8 (2C), 129.4, 128.3 (2C), 127.7, 126.8 (2C), 125.8 (2C), 121.1, 119.8, 81.6, 72.9, 50.1, 44.4, 33.2, 21.2, 3.3 ppm; MS (FAB+) *m*/*z* 424 $[M + H]^+$ (100), 307 (15); HRMS (FAB+) calcd. for $C_{28}H_{26}NOS$ $[M + H]^+$ 424.1735, found 424.1735. **Diastereoisomer [2*S*,(S)*S*]-15b** (data from a 20:80 mixture of **15a** + **15b**): ^{1}H NMR δ 7.68−7.61 (m, 1H), 7.60 and 7.26 (AA′BB′ system, 4H), 7.36−7.20 (m, 8H), 5.38 (s, 1H), 5.27 (s, 1H), 3.67−3.60 (m, 2H), 2.99 (m, 2H), 2.37 (s, 3H), 1.75 (t, *J* 2.4 Hz, 3H) ppm; ^{13}C NMR δ 146.0, 142.5, 141.2, 141.0, 140.8, 136.8, 131.3, 130.1, 130.0, 129.8 (2C), 128.3 (2C), 127.7, 127.2, 126.6 (2C), 125.7 (2C), 122.6, 120.2, 81.6, 73.0, 45.7, 44.7, 29.1, 21.3, 3.5 ppm; MS (FAB+) *m*/*z* 424 $[M + H]^+$ (100), 372 (40); HRMS (FAB+) calcd. for $C_{28}H_{26}NOS$ $[M + H]^+$ 424.1735, found 424.1737.

[2*R*,(S)*S*,4*E*] and [2*S*,(S)*S*,4*E*]-5-Phenyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (16a + 16b). The diastereoisomeric mixture **16a** + **16b** was obtained using a 60:40 mixture of [2*S*,(S)*S*] and [2*R*,(S)*S*]-5-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**6** + **6′**) as the substrate and propargyl bromide (80% solution in toluene) as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 30 min. The crude 87:13 mixture of **16a** + **16b** was purified by flash column chromatography using AcOEt−hexane (1:4) as the eluent. Yield (mixture **16a** + **16b**): 83% (44.1 mg, yellow oil); IR (film) 3030, 2860, 2236, 1718, 1596, 1447, 1083, 1029, 754 cm^{-1}; ^{1}H NMR (**16a** + **16b** mixture) δ 7.80−7.76 (dd, *J* 3.4 and 5.9 Hz, 1H), 7.70−7.67 (m, 5H), 7.55−7.39 (m, 9H), 7.29−7.18 (m, 11H), 6.62 (d, *J* 15.7 Hz, 1H), 6.48 (d, *J* 15.7 Hz, 1H), 6.11 (m, 1H), 5.95 (m, 1H), 3.38−3.16 (m, 8H), 2.34 (s, 6H), 2.19 (t, *J* 2.6 Hz, 1H), 2.10 (t, *J* 2.6 Hz, 1H) ppm; ^{13}C NMR (**16a** + **16b** mixture) δ 145.6, 144.9, 141.3 (2C), 140.9, 140.7, 136.4, 136.3, 136.2, 136.0, 135.9, 131.9, 131.8, 130.4 (2C), 130.1, 129.9 (3C), 128.7, 128.6, 128.5 (2C), 127.9, 127.8, 127.4, 126.5 (2C), 126.4 (2C), 125.8 (2C), 125.5 (2C), 121.9, 121.7, 121.3, 121.1, 77.6, 77.2, 74.1, 74.0, 48.0, 45.7, 43.3, 42.2, 31.6, 28.6, 21.3 (2C) ppm; MS

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(FAB+) m/z 410 $[M + H]^+$ (100), 109 (12); HRMS (FAB+) calcd. for $C_{27}H_{24}NOS$ $[M + H]^+$ 410.1573, found 410.1566.

[2*R*,(S)*S*,4*E*], [2*S*,(S)*S*,4*E*], and [2*R*,(S)*S*,4*Z*]-4-Methyl-5-phenyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (17a + 17b + 17c). The diastereoisomeric mixture **17a** + **17b** + **17c** was obtained using a 40:40:10:10 mixture of [2*S*,(S)*S*,4*E*], [2*R*,(S)*S*,4*E*], [2*S*,(S)*S*,4*Z*], and [2*R*,(S)*S*,4*Z*]-4-methyl-5-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile [(*E*)-7 + (*E*)-7′ + (*Z*)-7 + (*Z*)-7′] as the substrate and propargyl bromide (80% solution in toluene) as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 2 h. The crude mixture was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. A 75:16:9 mixture of **17a** + **17b** + **17c** was obtained. Yield (**17a** + **17b** mixture): 80% (44 mg, colorless oil); IR (film) 3019, 2854, 2236, 1718, 1596, 1447, 1083, 1029, 810, 754 cm^{-1}. ^1H NMR (**17a** + **17b** mixture) δ 7.82 (dd, J 1.7 and 7.6 Hz, 1H), 7.70 (dd, J 2.1 and 7.3 Hz, 1H), 7.50 and 7.25 (AA′BB′ system, 4H), 7.51−7.38 (m, 2H), 7.26−7.21 (m, 2H), 7.13−7.08 (m, 3H), 6.60 (m, 1H), 6.49 (m, 1H), 3.60 and 3.25 (AB system, J 14.4 Hz, 2H), 3.38 and 3.22 (AB system, J 16.5 Hz, 2H), 3.34 (coupled AB system, J 2.5 and 17.1 Hz, 2H), 2.99−2.96 (m, 2H), 2.38 (s, 3H), 2.37 (s, 3H), 2.13 (t, J 2.5 Hz, 1H), 1.92 (t, J 2.4 Hz, 1H), 1.77 (m, 3H), 1.67 (m, 3H) ppm; ^{13}C NMR (**17a** + **17b** mixture) δ 144.6, 141.4, 140.9, 137.3, 136.4, 132.5, 131.9, 131.6, 130.5, 130.3, 130.0 (2C), 129.5, 128.9 (2C), 128.0 (2C), 126.6, 125.6 (2C), 121.4, 121.3, 77.9, 77.6, 74.0, 73.7, 49.8, 48.2, 49.6, 41.5, 32.8, 30.8, 21.3 (2C), 19.1, 19.0 ppm; MS (FAB+) m/z 424 $[M + H]^+$ (100), 307 (22); HRMS (FAB+) calcd. for $C_{28}H_{26}NOS$ $[M + H]^+$ 424.1735, found 424.1747. **Diastereoisomer [2*R*,(S)*S*,4*Z*]-17c** (data from a diastereoisomeric mixture **17a** + **17b** + **17c**): ^1H NMR δ 7.85−7.82 (m, 1H), 7.83−7.81 (m, 1H), 7.62 and 7.19 (AA′BB′ system, 4H), 7.57−7.42 (m, 3H), 7.34−7.21 (m, 4H), 6.40 (m, 1H), 3.37 and 3.20 (AB system, J 13.9 Hz, 2H), 3.27−3.25 (m, 2H), 2.38 (s, 3H), 2.26 (t, J 2.4 Hz, 1H), 1.78 (s, 3H) ppm.

[2*R*,(S)*S*,4*E*], [2*S*,(S)*S*,4*E*], and [2*R*,(S)*S*,4*Z*]-2-(But-2-inyl)-4-methyl-5-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]hex-4-enenitrile (18a + 18b + 18c). The diastereoisomeric mixture **18a** + **18b** + **19c** was obtained using a 40:40:10:10 mixture of [2*S*,(S)*S*,4*E*], [2*R*,(S)*S*,4*E*], [2*S*,(S)*S*,4*Z*], and [2*R*,(S)*S*,4*Z*]-4-methyl-5-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile [(*E*)-7 + (*E*)-7′ + (*Z*)-7 + (*Z*)-7′] as the substrate and 1-bromobut-2-ine as the electrophile, in the presence of KHMDS/18-crown-6 ether. The reaction mixture was stirred for 2 h. The crude 72:16:12 mixture of **18a** + **18b** + **18c** was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. **Diastereoisomer [2*R*,(S)*S*,4*E*]-18a** (colorless oil): Yield 68% (38.6 mg); $[\alpha]^{20}_D$ −70.1 (c 1.6, $CHCl_3$); IR (film) 3058, 2854, 2236, 1689, 1447, 1082, 1027, 810, 755 cm^{-1}; ^1H NMR δ 7.78−7.71 (m, 2H), 7.52 and 7.11 (AA′BB′ system, 4H), 7.49−7.44 (m, 2H), 7.29−7.11 (m, 5H), 6.48 (m, 1H), 3.36 and 3.20 (AB system, J 14.4 Hz, 2H), 3.26 (coupled AB system, J 2.5 and 14.5 Hz, 2H), 2.38 (s, 3H), 1.77−1.76 (m, 3H), 1.71 (t, J 2.5 Hz, 3H) ppm; ^{13}C NMR δ 144.7, 141.3, 141.2, 137.4, 136.8, 132.2, 131.9, 131.7, 130.2, 130.0, 129.9 (2C), 129.4, 128.9 (2C), 127.9 (2C), 126.5, 125.7 (2C), 121.9, 81.7, 72.9, 50.1, 49.8, 33.5, 21.3, 19.2, 3.4 ppm; MS (FAB+) m/z 438 $[M + H]^+$ (100); HRMS (FAB+) calcd. for $C_{29}H_{28}NOS$ $[M + H]^+$ 438.1892, found 438.1881. **Diastereoisomers [2*S*,(S)*S*,4*E*]-18b** and [2*R*,(S)*S*,4*Z*]-**18c**: ^1H NMR (significative signals from a diastereoisomeric mixture **18a** + **18b** + **18c**) δ 7.69−7.65 (m, 1H), 6.58 (m, 1H), 6.36 (m, 1H), 2.24 (t, J 2.3 Hz, 3H), 1.98 (t, J 2.4 Hz, 3H) ppm.

(*R*)-2-Phenyl-2-(prop-2-inyl)-pent-4-enenitrile (28). To a solution of 50 mg (0.15 mmol) of [2*R*,(S)*S*]-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**8a**) in anhydrous THF (1.5 mL) at −78 °C under argon was added *t*-BuLi (1.7 M in hexanes) (0.13 mL, 0.23 mmol). The mixture was stirred at −78 °C for 30 min. The reaction was hydrolyzed with saturated aqueous NH_4Cl (1.0 mL). The organic layer was dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by flash column chromatography using AcOEt−hexane (1:6) as the eluent. Yield: 62% (18.1 mg, colorless oil); $[\alpha]^{20}_D$ +11.5 (c 0.7, $CHCl_3$); ^1H NMR δ 7.49−7.34 (m, 5H), 5.74−5.60 (m, 1H), 5.24−5.20 (m, 1H), 5.18−5.15 (m, 1H), 2.92−2.73 (m, 4H), 2.13 (t, J 2.6 Hz, 1H) ppm; ^{13}C NMR δ 137.0, 131.1, 128.8 (2C), 128.3, 126.1 (2C), 121.0, 120.7, 77.9, 72.9, 46.6, 42.9, 30.3 ppm; MS (EI+) m/z 195 $[M]^+$ (18), 154 (81), 127 (100); HRMS (EI+) calcd. for $C_{14}H_{13}N$ 195.1048, found 195.1048.

(*R*,*E*)-2-Phenyl-2-(prop-2-yn-1-yl)hex-4-enenitrile (29). To a solution of 50 mg (0.15 mmol) of [2*R*,(S)*S*]-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**10a**) in anhydrous THF (1.5 mL) at −78 °C under argon was added *t*-BuLi (1.7 M in hexanes) (0.13 mL, 0.23 mmol). The mixture was stirred at −78 °C for 30 min. The reaction was hydrolyzed with saturated aqueous NH_4Cl (1.0 mL). The organic layer was dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by flash column chromatography using AcOEt−hexane (1:6) as the eluent. Yield: 65% (19.1 mg, colorless oil); $[\alpha]^{20}_D$ +8.0 (c 0.7, $CHCl_3$); ^1H NMR δ 7.29−7.21 (m, 5H), 4.80 (dt, J 12.1, 3.0 Hz, 1H), 4.71 (d, J 6.1 Hz, 1H), 2.85−2.81 (m, 2H), 2.85−2.81 (m, 2H), 2.70−2.56 (m, 2H), 2.07 (t, J 3.0 Hz, 1H), 1.50 (d, J 9.0 Hz, 3H) ppm; ^{13}C NMR δ 139.8, 139.5, 128.8, 128.3, 126.2, 117.1, 116.2. 78.2, 72.9, 48.8, 46.1, 31.3, 23.6 ppm. HRMS (EI+) calcd. for $C_{15}H_{15}N$ 209.1204, found 209.1197.

(*R*,*E*)-2-Phenyl-2-(prop-2-yn-1-yl)hex-4-enenitrile (30). To a solution of 50 mg (0.15 mmol) of [2*R*,(S)*S*]-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**12a**) in anhydrous THF (1.5 mL) at −78 °C under argon was added *t*-BuLi (1.7 M in hexanes) (0.13 mL, 0.23 mmol). The mixture was stirred at −78 °C for 30 min. The reaction was hydrolyzed with saturated aqueous NH_4Cl (1.0 mL). The organic layer was dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by flash column chromatography using AcOEt−hexane (1:6) as the eluent. Yield: 58% (18.2 mg, colorless oil); $[\alpha]^{20}_D$ +9.7 (c 0.42, $CHCl_3$); ^1H NMR δ 7.40−7.19 (m, 5H), 5.60−5.71 (m, 1H), 5.29−5.20 (m, 1H), 2.82−2.75 (m, 2H), 2.04 (t, J 3.0 Hz, 1H), 1.58 (t, J 6.1 Hz, 3H) ppm; ^{13}C NMR δ 139.4, 128.8 (2C), 128.3, 126.2, 121.6, 117.1, 78.2, 72.9, 46.5, 31.3, 29.7, 23.6 ppm.

(±)-2-(Prop-2-inyl)-2-[2-(*p*-tolylsulfonyl)phenyl]pent-4-enenitrile (34). It was prepared from 2-[2-(*p*-tolylsulfonyl)phenyl]-acetonitrile (**33**) by successive allylation and propargylation reactions, using allyl bromide and propargyl bromide as the electrophiles, respectively. Overall yield (two steps): 64% (133.8 mg, colorless oil); ^1H NMR δ 7.94 (dd, J 1.1 and 8.0 Hz, 1H), 7.88 (dd, J 1.4 and 8.0 Hz, 1H), 7.80 and 7.33 (AA′BB′ system, 4H), 7.58 (dt, J 1.4 and 7.5 Hz, 1H), 7.44 (dt, J 1.2 and 8.0 Hz, 1H), 5.72−5.62 (m, 1H), 5.28−5.15 (m, 2H), 3.63 (dd, J 2.6 and 17.2 Hz, 1H), 3.46 (dd, J 6.5 and 14.1 Hz, 1H), 3.32 (dd, J 2.6 and 17.2 Hz, 1H), 3.10 (dd, J 6.5 and 14.1 Hz, 1H), 2.43 (s, 3H), 2.00 (t, J 2.6 Hz, 1H) ppm; ^{13}C NMR δ 144.5, 140.3, 138.8, 135.8, 133.6, 132.9, 131.8, 131.5, 129.8 (2C), 128.9, 127.7 (2C), 121.5, 120.8, 78.5, 72.9, 49.3, 42.4, 29.2, 21.6 ppm; MS (ESI+) m/z 350 $[M + H]^+$ (100), 312 (30); HRMS (FAB+) calcd. for $C_{21}H_{20}NO_2S$ $[M + H]^+$ 350.1209, found 350.1193.

2-[2-(*p*-Tolylsulfenyl)phenyl]acetonitrile (35). To a solution of 4-methylbenzenethiol (890 mg, 3.6 mmol) in anhydrous DMF (5.0 mL) at rt was added 2-iodophenylacetonitrile (874 mg, 3.6 mmol), potassium carbonate (506 mg, 3.6 mmol) and Cu(0) (228 mg, 3.6 mmol). The mixture was stirred at reflux for 18 h. The reaction was monitored by TLC. Upon transformation of the substrate, the mixture was cooled at rt and filtered through a Celite pad. The solution was washed with aqueous 1 N HCl (5.0 mL). The aqueous layer was extracted with AcOEt (4 × 5 mL), dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by flash column chromatography using AcOEt−hexane (1:6) as the eluent. Yield: 54% (464 mg, yellow oil); ^1H NMR δ 7.69−7.66 (m, 1H), 7.52−7.39 (m, 3H), 7.38−7.28 (m, 4H), 3.99 (s, 2H), 2.46 (s, 3H) ppm; ^{13}C NMR δ 137.5, 134.5, 133.2, 131.4, 130.2 (2C), 129.8 (2C), 129.0, 128.9, 128.5, 128.3, 117.4, 22.2, 20.9 ppm; MS (EI+) m/z $[M^+]$ 239 (100), 197 (87); HRMS (ESI+) calcd. for $C_{15}H_{13}NS$ 239.0769, found 239.0779.

(±)-2-[2-(*p*-Tolylsulfenyl)phenyl]pent-4-enenitrile. It was prepared by following the general procedure described for allylation. Allyl bromide was used as the electrophile and **35** as the substrate. The reaction mixture was stirred at rt for 30 min. The crude product was purified by flash column chromatography using AcOEt−hexane (1:6) as the eluent. Yield: 76% (27.6 mg, yellow oil); ^1H NMR δ 7.75−7.69

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(m, 1H), 7.47−7.44 (m, 3H), 7.40−7.26 (m, 4H), 7.85 (m, 1H), 5.37−5.24 (m, 2H), 4.70 (dd, *J* 6.9 and 7.7 Hz, 1H), 3.49 (dd, *J* 6.9 and 14.3 Hz, 1H), 3.06 (dd, *J* 7.7 and 14.3 Hz, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR δ 137.5, 136.6, 134.8, 132.5, 131.4, 131.3, 130.5 (2C), 130.2 (2C), 128.5, 128.4, 128.3, 120.3, 119.8, 38.9, 35.0, 21.0 ppm; MS (EI +) *m*/*z* [M]$^+$ 279 (22), 211 (100); HRMS (ESI+) calcd. for $C_{18}H_{17}NS$ 279.1082, found 279.1095.

(±)-2-[2-(*p*-Tolylsulfenyl)phenyl]hex-4-enenitrile. It was prepared by following the general procedure described for allylation. Commercial 1-bromobut-2-ene (80:20 mixture of *E*/*Z*) was used as the electrophile and **35** as the substrate. The reaction mixture was stirred at rt for 30 min. The crude product was purified by flash column chromatography using AcOEt−hexane (1:6) as the eluent. Yield: 64% (24.4 mg, yellow oil); ^{1}H NMR δ 7.66−7.64 (m, 1H), 7.41−7.38 (m, 3H), 7.34−7.25 (m, 4H), 5.72−5.58 (m, 2H), 5.59 (dd, *J* 6.3 and 7.9 Hz, 1H), 3.30 (dd, *J* 6.7 and 14.3 Hz, 1H), 2.93 (dd, *J* 7.6 and 14.3 Hz, 1H), 2.41 (s, 3H), 1.71 (d, *J* 7.6 Hz, 3H) ppm; ^{13}C NMR δ 137.4, 137.3, 136.9, 133.6, 130.5, 130.4 (2C), 130.3 (2C), 129.6, 128.8, 128.4, 127.0, 125.1, 120.6, 37.9, 35.6, 21.0, 17.9 ppm; MS (EI+) *m*/*z* [M]$^+$ 293 (15), 211 (100); HRMS (ESI+) calcd. for $C_{19}H_{19}NS$ 293.1238, found 293.1225.

(±)-2-(Prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)phenyl]pent-4-enenitrile [(±)-36]. It was prepared by following the general procedure described for propargylation. (±)-2-[2-(*p*-Tolylsulfenyl)phenyl]pent-4-enenitrile was used as the substrate and propargyl bromide (80% solution in toluene) as the electrophile, in the presence of LiHMDS (1.0 M in THF). The reaction mixture was stirred at rt for 30 min. The crude **(±)-36** was purified by flash column chromatography using AcOEt−hexane (1:6) as the eluent. Yield: 62% (25.5 mg, yellow oil); ^{1}H NMR δ 7.43−7.40 (m, 1H), 7.38−7.31 (m, 3H), 7.30−7.23 (m, 4H), 5.88 (m, 1H), 5.42−5.26 (m, 2H), 3.60−3.39 (m, 3H), 3.21−3.11 (m, 1H), 2.46 (s, 3H), 2.22 (t, *J* 2.6 Hz, 1H) ppm; ^{13}C NMR δ 137.4, 136.1, 135.6, 134.7, 132.3, 131.5, 130.9 (2C), 130.2 (2C), 129.3, 129.1, 127.5, 126.5, 120.5, 78.4, 72.8, 47.7, 41.2, 27.6, 21.0 ppm; MS (EI+) *m*/*z* [M]$^+$ 317 (24), 236 (100); HRMS (ESI+) calcd. for $C_{21}H_{19}NS$ 317.1238, found 317.1235.

(±)-2-(Prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)phenyl]hex-4-enenitrile [(±)-37]. It was prepared by following the general procedure described for propargylation. (±)-2-[2-(*p*-Tolylsulfenyl)phenyl]hex-4-enenitrile was used as the substrate and propargyl bromide (80% solution in toluene) as the electrophile, in the presence of LiHMDS (1.0 M in THF). The reaction mixture was stirred at rt for 30 min. The crude **(±)-37** was purified by flash column chromatography using AcOEt−hexane (1:6) as the eluent. Yield: 51% (21.8 mg, yellow oil); ^{1}H NMR δ 7.64−7.58 (m, 1H), 7.30−7.21 (m, 4H), 7.16−7.09 (m, 3H), 5.65 (m, 1H), 5.34 (m, 1H), 3.41−3.28 (m, 2H), 3.19−3.12 (m, 1H), 3.01−2.89 (m, 1H), 2.36 (s, 3H), 2.07 (t, *J* 2.5 Hz, 1H), 1.65 (d, *J* 6.4 Hz, 3H) ppm; ^{13}C NMR δ 137.3, 136.5, 135.6, 134.8, 132.6, 131.7 (2C), 131.6, 130.1 (2C), 129.3, 128.9, 127.4, 123.9, 121.5, 78.5, 72.6, 47.7, 40.2, 27.4, 21.0, 18.0 ppm; MS (EI+) *m*/*z* [M + H]$^+$ 331 (23), 211 (100); HRMS (ESI+) calcd. for $C_{22}H_{21}NS$ [M + H]$^+$ 331.1425, found 331.1429.

(±)-(*E*/*Z*)4-Methyl-5-phenyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)phenyl]pent-4-enenitrile [(±)-38]. It was prepared by following the general procedure described for propargylation. A mixture 86:14 (±)-(*E*/*Z*)-4-methyl-5-phenyl-2-(2-(*p*-tolylsulfenyl)-phenyl)pent-4-enenitrile was used as the substrate and propargyl bromide (80% solution in toluene) as the electrophile, in the presence of LiHMDS (1.0 M in THF). The reaction mixture was stirred at rt for 30 min. The crude **(±)-38** was purified by flash column chromatography using AcOEt−hexane (1:6) as the eluent. Yield: 51% (27.0 mg, yellow oil); ^{1}H NMR (86:14 *E*/*Z* mixture) δ 7.82 (dd, *J* 1.7 and 7.6 Hz, 1H), 7.70 (dd, *J* 2.1 and 7.3 Hz, 1H), 7.50 and 7.25 (AA′BB′ system, 4H), 7.51−7.38 (m, 2H), 7.26−7.21 (m, 2H), 7.13−7.08 (m, 3H), 6.61 (m, 1H), 6.47 (m, 1H), 3.60 and 3.25 (AB system, *J* 14.4 Hz, 2H), 3.38 and 3.22 (AB system, *J* 16.5 Hz, 2H), 3.34 (coupled AB system, *J* 2.5 and 17.1 Hz, 2H), 2.99−2.96 (m, 2H), 2.24 (s, 3H), 2.22 (s, 3H), 2.13 (t, *J* 2.5 Hz, 1H), 1.92 (t, *J* 2.4 Hz, 1H), 1.74 (m, 3H), 1.63 (m, 3H) ppm; ^{13}C NMR (*E*/*Z* mixture) δ 144.5, 141.2, 140.9, 137.3, 136.4, 132.5, 131.9, 131.6, 130.5, 130.3, 130.0 (2C), 129.5, 128.9 (2C), 128.0 (2C), 126.6, 125.6 (2C), 121.4, 121.3, 77.9, 77.6, 74.0, 73.7, 49.8, 48.2, 49.6, 41.5, 32.8, 30.8, 20.2, 20.1, 19.1, 18.9 ppm.

General Procedure for the Synthesis of 2-Allyl-2-propargyl-2-[2-(*p*-tolylsulfenyl)phenyl]acetamides (42−44). To a solution of corresponding 2-allyl-2-propargyl-2-[2-(*p*-tolylsulfinyl)phenyl]-acetonitrile (0.18 mmol, 1.0 equiv) in anhydrous CH_3CN (3.0 mL) at rt under argon was dropwise added $BF_3{\cdot}OEt_2$ (0.23 mmol, 1.3 equiv). The mixture was stirred at rt for 30 min, and then NaI (0.19 mmol, 1.1 equiv) was added. The resulting mixture was stirred at rt for 4.5 h. The reaction was monitored by TLC. Upon transformation of the starting material, the reaction was hydrolyzed with saturated aqueous $NaHSO_3$ (2.0 mL) and washed with saturated aqueous $NaHCO_3$ (3 × 3.0 mL). The mixture was extracted with CH_2Cl_2 (3 × 5 mL), dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent.

(*R*)-2-(Prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)phenyl]pent-4-enamide [(*R*)-42]. It was obtained using [2*R*,(S)*S*]-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**8a**) as the substrate. Yield: 56% (33.7 mg, white solid); mp 109−111 °C (CH_2Cl_2−hexane); IR (KBr) 2115, 1669, 1492, 1368, 807 cm^{-1}; $[\alpha]^{20}_D$ −13.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 7.50 (dd, *J* 1.5 and 8.0 Hz, 1H), 7.32 (dt, *J* 1.5 and 7.7 Hz, 1H), 7.27−7.18 (m, 2H), 7.12 and 7.07 (AA′BB′ system, 4H), 5.74−5.54 (m, 1H), 5.32 (br s, 2H), 5.25−5.18 (m, 1H), 5.15−5.11 (m, 1H), 3.26−3.16 (m, 1H), 3.15 (coupled AB system, *J* 2.3 and 17.3 Hz, 2H), 2.82 (dd, *J* 7.0 and 13.6 Hz, 1H), 2.30 (s, 3H), 1.92 (t, *J* 2.7 Hz, 1H) ppm; ^{13}C NMR δ 175.6, 141.1, 136.8, 136.7, 135.4, 132.9, 130.5 (2C), 129.9 (3C), 128.9, 128.5, 127.1, 119.1, 80.9, 71.6, 53.6, 40.5, 25.2, 21.0 ppm; MS (ESI+) *m*/*z* 336 [M + H]$^+$ (20), 319 (100), 292 (55); HRMS (ESI+) calcd. for $C_{21}H_{22}NOS$ [M + H]$^+$ 336.1423, found 336.1416.

(*S*)-2-(Prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)phenyl]pent-4-enamide [(*S*)-42]. It was obtained using [2*S*,(S)*S*]-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**8b**) as the substrate. Yield: 58% (34.9 mg, white solid); $[\alpha]^{20}_D$ +7.7 (*c* 0.9, $CHCl_3$); HPLC enantiomer (*R*)-**42** t_R = 19.5 min and enantiomer (*S*)-**42** t_R = 26.9 min in Daicel CHIRALPAK OD column [eluent hexane/*i*-PrOH (90:10)]; flow = 1 mL/min]; ee = 96% for (*S*)-**42**.

(2*R*,4*E*)-2-(Prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)phenyl]hex-4-enamide (43). It was obtained using a diastereoisomeric 88:12 mixture of [2*R*,(S)*S*,4*E*] and [2*S*,(S)*S*,4*E*]-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]hex-4-enenitrile (**12a** + **12b**) as the substrate, with a conversion of 70%. Yield: 52% (32.5 mg, colorless oil); ee 76%; ^{1}H NMR δ 7.57−7.49 (m, 1H), 7.34−7.25 (m, 2H), 7.23−7.17 (m, 1H), 7.12 and 7.06 (AA′BB′ system, 4H), 5.64 (m, 1H), 5.36−5.29 (m, 3H), 3.23−3.02 (m, 3H), 2.76 (dd, *J* 6.4 and 13.5 Hz, 1H), 2.30 (s, 3H), 1.90 (t, *J* 2.6 Hz, 1H), 1.66 (d, *J* 6.4 Hz, 3H) ppm; ^{13}C NMR δ 175.8, 141.3, 136.8, 135.3, 133.4, 130.5 (2C), 129.9 (2C), 129.8, 129.0, 128.5, 128.4, 127.1, 125.2, 81.2, 71.4, 53.4, 39.4, 25.1, 21.0, 18.1 ppm; MS (ESI) *m*/*z* [M − H]$^-$ 348 [M − H]$^-$ (100), 109 (13); HRMS (ESI) calcd. for $C_{22}H_{24}NOS$ [M − H]$^-$ 348.1416, found 348.1403.

(2*R*,4*E*)-5-Phenyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)-phenyl]pent-4-enamide (44). It was obtained using a diastereoisomeric 77:23 mixture of [2*R*,(S)*S*,4*E*] and [2*S*,(S)*S*,4*E*]-5-phenyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**16a** + **16b**) as the substrate, with a conversion of 70%. A 30% of unreacted **16a** + **16b** was recovered. Yield: 48% (33.3 mg, yellow oil); ^{1}H NMR (data from a **44** + **16** mixture) δ 7.56−7.44 (m, 2H), 7.37−7.19 (m, 7H), 7.14 and 7.07 (AA′BB′ system, 4H), 6.53 (d, *J* 15.7 Hz, 1H), 6.01 (m, 1H), 5.37 (br s, 2H), 3.37−3.13 (m, 3H), 3.02 (dd, *J* 7.1 and 13.7 Hz, 1H), 2.30 (s, 3H), 1.96 (t, *J* 2.6 Hz, 1H) ppm; ^{13}C NMR (data from a **44** + **16** mixture) δ 176.4, 141.3, 136.9, 136.4, 136.0, 135.4, 133.9, 133.3, 130.5 (2C), 130.4, 129.9 (2C), 128.7 (2C), 127.5 (2C), 125.8 (2C), 125.5, 121.7, 81.0, 71.8, 54.1, 39.6, 25.6, 21.0 ppm; MS (FAB+) *m*/*z* 410 [M + H]$^+$ (100), 109 (10); HRMS (FAB+) calcd. for $C_{27}H_{24}NOS$ [M + H]$^+$ 410.1573, found 410.1573.

General Procedure for Pauson−Khand Reaction. To a solution of $[Co_2(CO)_8]$ (60 mg, 0.21 mmol) in anhydrous CH_2Cl_2 (1.0 mL) at rt was added a solution of the corresponding 1,6-enyne

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(0.17 mmol) in anhydrous CH_2Cl_2 (0.5 mL). The mixture was stirred at rt for 1.5 h, and then *N*-methylmorpholine *N*-oxide (NMO) (160 mg, 1.3 mmol) was added dropwise onto the freshly prepared cobalt complex solution. The resulting mixture was stirred at rt. The reaction was monitored by TLC. Upon transformation of the complex, the mixture was filtered through a Celite pad, and the solvent was evaporated. The diastereoisomeric mixture was purified by flash column chromatography using as the eluent a mixture of AcOEt/hexane as indicated in each case.

[2*R*,3a*S*,(S)*S*] and [2*R*,3a*R*,(S)*S*]-5-Oxo-2-[2-(*p*-tolylsulfinyl)-phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (19aA + 19aB). The diastereoisomeric mixture **19aA** + **19aB** was obtained using [2*R*,(S)*S*]-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**8a**) as the substrate. The reaction mixture was stirred for 5 min. The crude 72:28 mixture of **19aA** + **19aB** was purified by flash column chromatography using AcOEt−hexane (1:1) as the eluent. Yield (**19aA** + **19aB** mixture): 79% (48.5 mg, white solid); IR (KBr) 3058, 2972, 2231, 1704, 1631, 1083, 1030, 755 cm^{-1}; ^1H NMR (**19aA** + **19aB** mixture) δ 7.66−7.60 (m, 6H), 7.50−7.41 (m, 2H), 7.48 and 7.30 (AA′BB′ system, 8H), 6.07 (m, 1H), 6.02 (m, 1H), 4.41 and 3.33 (AB system, *J* 19.0 Hz, 2H), 4.11 and 3.64 (AB system, *J* 20.0 Hz, 2H), 3.69−3.55 (m, 1H), 3.41−3.30 (m, 2H), 3.05 (dd, *J* 6.3 and 11.6 Hz, 1H), 2.82 (dd, *J* 6.3 and 17.7 Hz, 1H), 2.71 (dd, *J* 6.8 and 17.8 Hz, 1H), 2.39 (s, 6H), 2.34−2.26 (m, 1H), 2.30 (dd, *J* 3.3 and 17.7 Hz, 1H), 2.18 (dd, *J* 12.1 and 12.2 Hz, 1H) ppm; ^{13}C NMR (**19aA** + **19aB** mixture) δ 207.9, 207.8, 182.1, 181.9, 146.6, 146.4, 141.5, 141.4, 140.0, 139.8, 138.4, 138.3, 137.6, 132.2, 132.1, 131.2, 130.7 (2C), 130.4, 130.0 (4C), 129.9, 126.7, 125.6, 125.2, 125.0 (4C), 124.2, 124.0, 46.4, 44.6, 44.2, 44.0, 42.7, 42.6, 42.0, 41.5, 21.3 (2C) ppm; MS (ESI+) *m*/*z* 362 $[M + H]^+$, 327 (33); HRMS (ESI+) calcd. for $C_{22}H_{20}NO_2S$ 362.1218 $[M + H]^+$, found 362.1209.

[2*S*,3a*R*,(S)*S*] and [2*S*,3a*S*,(S)*S*]-5-Oxo-2-[2-(*p*-tolylsulfinyl)-phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (19bA + 19bB). The diastereoisomeric mixture **19bA** + **19bB** was obtained using [2*S*,(S)*S*]-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]-pent-4-enenitrile (**8b**) as the substrate. The reaction mixture was stirred for 5 min. The crude 56:44 mixture of **19bA** + **19bB** was purified by flash column chromatography using AcOEt−hexane (1:1) as the eluent. Yield (**19bA** + **19bB** mixture): 75% (46.0 mg). **Diastereoisomer [2*S*,3a*R*,(S)*S*]-19bA** (colorless oil): $[\alpha]^{20}_D$ −16.1 (*c* 1.0, $CHCl_3$); IR (film) 3058, 2972, 2231, 1704, 1631, 1083, 1030, 755 cm^{-1}; ^1H NMR δ 7.82−7.79 (m, 1H), 7.65−7.62 (m, 1H), 7.55−7.49 (m, 2H), 7.44 and 7.29 (AA′BB′ system, 4H), 6.09 (m, 1H), 3.77 and 3.50 (AB system, *J* 19.0 Hz, 2H), 3.67−3.60 (m, 1H), 3.25 (dd, *J* 6.9 and 12.3 Hz, 1H), 2.78 (dd, *J* 6.3 and 17.8 Hz, 1H), 2.39 (s, 3H), 2.21 (dd, *J* 3.2 and 17.8 Hz, 1H), 2.04 (dd, *J* 12.1 and 12.2 Hz, 1H) ppm; ^{13}C NMR δ 208.0, 181.7, 145.0, 141.8, 140.5, 137.1, 132.3, 130.6, 130.5, 130.1 (2C), 126.8, 126.5, 125.9 (2C), 123.2, 48.0, 45.8, 45.4, 42.1, 41.8, 21.3 ppm; MS (ESI+) *m*/*z* 362 $[M + H]^+$; HRMS (ESI+) calcd. for $C_{22}H_{20}NO_2S$ $[M + H]^+$ 362.1218, found 362.1209. **Diastereoisomer [2*S*,3a*S*,(S)*S*]-19bB** (colorless oil): $[\alpha]^{20}_D$ −101.7 (*c* 0.6, $CHCl_3$); ^1H NMR δ 7.71−7.68 (m, 1H), 7.49−7.33 (m, 3H), 7.63 and 7.31 (AA′BB′ system, 4H), 6.20 (m, 1H), 3.76 and 3.50 (AB system, *J* 17.6 Hz, 2H), 3.45−3.39 (m, 1H), 3.19−3.09 (m, 1H), 2.76−2.68 (m, 2H), 2.40 (s, 3H), 2.32 (dd, *J* 3.2 and 17.5 Hz, 1H) ppm; ^{13}C NMR δ 208.1, 180.5, 146.4, 141.9, 140.1, 137.5, 132.0, 131.0, 130.9, 130.0 (2C), 127.3, 125.5, 125.4 (2C), 124.1, 45.8, 45.4, 43.5, 43.1, 40.1, 21.3 ppm; MS (ESI+) *m*/*z* 362 $[M + H]^+$ (100); HRMS (ESI+) calcd. for para $C_{22}H_{20}NO_2S$ $[M + H]^+$ 362.1218, found 362.1208.

[2*R*,3a*S*,(S)*S*] and [2*R*,3a*R*,(S)*S*]-6-Methyl-5-oxo-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (20aA + 20aB). The diastereoisomeric mixture **20aA** + **20aB** was obtained using [2*R*,(S)*S*]-2-(but-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**9a**) as the substrate. The reaction mixture was stirred for 5 min. The crude 70:30 mixture of **20aA** + **20aB** was purified by flash column chromatography using AcOEt−hexane (1:1) as the eluent. Yield (**20aA** + **20aB** mixture): 70% (44.6 mg, colorless oil); IR (film) 2921, 2851, 2231, 1708, 1669, 1456, 1082, 1035, 760 cm^{-1}; ^1H NMR (**20aA** + **20aB** mixture) δ 7.67−7.61 (m, 6H), 7.50−7.40 (m, 6H), 7.31−7.26 (m, 4H), 4.30 and 3.20 (AB system, *J* 18.9 Hz, 2H), 4.05 and 3.55 (AB system, *J* 18.2 Hz, 2H), 3.55−3.40 (m, 1H), 3.36 (dd, *J* 6.7 and 13.0 Hz, 1H), 3.20−3.10 (m, 1H), 3.01 (dd, *J* 5.9 and 11.5 Hz, 1H), 2.83 (dd, *J* 6.1 and 18.0 Hz, 1H), 2.76 (dd, *J* 6.1 and 17.9 Hz, 1H), 2.39 (s, 6H), 2.27 (dd, *J* 2.9 and 17.9 Hz, 1H), 2.24 (dd, *J* 3.0 and 17.9 Hz, 1H), 2.10 (dd, *J* 12.3 and 12.4 Hz, 1H), 2.09 (dd, *J* 12.8 and 12.9 Hz, 1H), 1.76 (s, 3H), 1.70 (s, 3H) ppm; ^{13}C NMR (**20aA** + **20aB** mixture) δ 208.0, 207.9, 174.3, 174.1, 146.7, 146.5, 141.4, 141.3, 140.2, 139.9, 138.8, 137.8, 134.4 (2C), 132.2, 132.1, 131.2, 130.6, 130.3, 129.9 (2C), 129.8 (2C), 125.6, 125.2 (2C), 125.1 (2C), 124.7, 124.2, 46.4, 43.9, 43.7, 42.8, 42.3, 42.2, 42.0, 41.7, 41.2, 40.7, 21.3 (2C), 8.6, 8.5 ppm; MS (ESI+) *m*/*z* 376 $[M + H]^+$ (100), 364 (62); HRMS (ESI+) calcd. for $C_{23}H_{22}NO_2S$ $[M + H]^+$ 376.1365, found 376.1373.

[2*S*,3a*R*,(S)*S*] and [2*S*,3a*S*,(S)*S*]-6-Methyl-5-oxo-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (20bA + 20bB). The diastereoisomeric mixture **20bA** + **20bB** was obtained using [2*S*,(S)*S*]-2-(but-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**9b**) as the substrate. The reaction mixture was stirred for 5 min. The crude 51:49 mixture of **20bA** + **20bB** was purified by flash column chromatography using AcOEt−hexane (2:1) as the eluent. Yield (**20bA** + **20bB** mixture): 66% (42.0 mg). **Diastereoisomer [2*S*,3a*R*,(S)*S*]-20bA** (colorless oil): $[\alpha]^{20}_D$ −91.3 (*c* 1.6, $CHCl_3$); IR (film) 2921, 2851, 2231, 1708, 1669, 1456, 1082, 1035, 760 cm^{-1}; ^1H NMR δ 7.83−7.80 (m, 1H), 7.67−7.64 (m, 1H), 7.54−7.50 (m, 2H), 7.42 and 7.28 (AA′BB′ system, 4H), 3.56 and 3.39 (AB system, *J* 18.6 Hz, 2H), 3.56−3.42 (m, 1H), 3.21 (dd, *J* 6.5 and 11.9 Hz, 1H), 2.79 (dd, *J* 6.3 and 18.0 Hz, 1H), 2.39 (s, 3H), 2.16 (dd, *J* 3.0 and 18.0 Hz, 1H), 1.93 (dd, *J* 12.2 and 12.3 Hz, 1H), 1.76 (s, 3H) ppm; ^{13}C NMR δ 208.2, 174.3, 144.2, 140.8, 140.6, 137.3, 134.4, 132.2, 130.5, 130.3, 130.1 (2C), 126.8, 125.8 (2C), 123.3, 48.1, 46.1, 43.0, 41.2, 41.0, 21.3, 8.6 ppm; MS (ESI+) *m*/*z* 376 $[M + H]^+$ (100); HRMS (ESI+) calcd. for $C_{23}H_{22}NO_2S$ $[M + H]^+$ 376.1365, found 376.1378. **Diastereoisomer [2*S*,3a*S*,(S)*S*]-20bB** (colorless oil): $[\alpha]^{20}_D$ −142.2 (*c* 0.5, $CHCl_3$); ^1H NMR δ 7.72−7.68 (m, 1H), 7.66 and 7.31 (AA′BB′ system, 4H), 7.50−7.46 (m, 2H), 7.44−7.40 (m, 1H), 3.64 and 3.45 (AB system, *J* 17.4 Hz, 2H), 3.12 (m, 1H), 3.03−2.98 (m, 1H), 2.76−2.59 (m, 2H), 2.40 (s, 3H), 2.26 (dd, *J* 3.1 and 17.8 Hz, 1H), 1.86 (s, 3H) ppm; ^{13}C NMR δ 208.3, 172.7, 146.4, 141.4, 140.1, 137.8, 135.1, 131.9, 130.9, 130.1 (2C), 125.7, 125.6 (2C), 124.4, 56.7, 46.1, 45.3, 42.2, 41.2, 39.1, 21.3, 8.9 ppm.

[2*R*,3a*S*,(S)*S*] and [2*R*,3a*R*,(S)*S*]-3a-Methyl-5-oxo-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (21aA + 21aB). The diastereoisomeric mixture **21aA** + **21aB** was obtained using [2*R*,(S)*S*]-4-methyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**10a**) as the substrate. The reaction mixture was stirred for 45 min. The crude 81:19 mixture of **21aA** + **21aB** was purified by flash column chromatography using AcOEt−hexane (2:1) as the eluent. Yield (**21aA** + **21aB** mixture): 65% (41.4 mg, colorless oil); IR (film) 2969, 2927, 2231, 1709, 1634, 1456, 1083, 1035, 812, 756 cm^{-1}; ^1H NMR (**21aA** + **21aB** mixture) δ 7.66−7.58 (m, 2H), 7.59 and 7.31 (AA′BB′ system, 8H), 7.56−7.43 (m, 6H), 6.08 (m, 1H), 5.90 (m, 1H), 4.39 and 3.60 (AB system, *J* 18.6 Hz, 2H), 4.23 and 3.54 (AB system, *J* 15.9 Hz, 2H), 3.10 (d, *J* 14.2 Hz, 1H), 2.91 (d, *J* 12.7 Hz, 1H), 2.57 and 2.46 (AB system, *J* 17.4 Hz, 2H), 2.61−2.44 (m, 4H), 2.39 (s, 6H), 1.68 (s, 3H), 1.65 (s, 3H), 1.27−1.21 (m, 2H) ppm; ^{13}C NMR (**21aA** + **21aB** mixture) δ 207.7, 207.6, 185.8, 184.5, 146.5, 146.2, 141.5, 141.4, 140.2, 139.9, 139.4, 138.2, 132.0, 131.9, 131.0, 130.8, 130.7, 130.6, 130.2 (4C), 125.9, 125.7, 125.4, 125.3, 125.2 (4C), 124.3, 53.4, 52.4, 52.2, 50.6, 49.1, 48.7, 47.7, 45.0, 44.1, 42.8, 42.3, 27.8, 26.1, 21.3 (2C) ppm; MS (ESI+) *m*/*z* 376 $[M + H]^+$ (100); HRMS (ESI+) calcd. for $C_{23}H_{22}NO_2S$ $[M + H]^+$ 376.1365, found 376.1379.

[2*S*,3a*R*,(S)*S*] and [2*S*,3a*S*,(S)*S*]-3a-Methyl-5-oxo-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (21bA + 21bB). The diastereoisomeric mixture **21bA** + **21bB** was obtained using [2*S*,(S)*S*]-4-methyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**10b**) as the substrate. The reaction mixture was stirred for 45 min. The crude 56:44 mixture of

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21bA + 21bB was purified by flash column chromatography using AcOEt−hexane (2:1) as the eluent. Yield (**21bA + 21bB** mixture): 68% (43.3 mg, colorless oil); IR (film) 2969, 2927, 2231, 1709, 1634, 1456, 1083, 1035, 812, 756 cm^{-1}; ^1H NMR (**21bA + 21bB** mixture) δ 7.81−7.78 (m, 1H), 7.71−7.68 (m, 1H), 7.64−7.61 (m, 3H), 7.54−7.45 (m, 4H), 7.42−7.38 (m, 3H), 7.32−7.28 (m, 4H), 6.19 (m, 1H), 6.09 (m, 1H), 3.77 and 3.50 (AB system, *J* 18.6 Hz, 2H), 3.74 and 3.49 (AB system, *J* 17.5 Hz, 2H), 3.45 and 3.25 (AB system, *J* 7.1 Hz, 2H), 3.17 and 3.12 (AB system, *J* 8.8 Hz, 2H), 2.82−2.68 (m, 4H), 2.40 (s, 6H), 2.16 (s, 6H), 2.03 (m, 1H) ppm; MS (ESI+) *m/z* 376 $[M + H]^+$ (100); HRMS (ESI+) calcd. for $C_{23}H_{22}NO_2S$ $[M + H]^+$ 376.1365, found 376.1368.

[2*R*,3a*S*,(S)*S*] and [2*R*,3a*R*,(S)*S*]-3a,6-Dimethyl-5-oxo-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (22aA + 22aB). The diastereoisomeric mixture **22aA + 22aB** was obtained using [2*R*,(S)*S*]-2-(2-but-1-inyl)-4-methyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**11a**) as the substrate. The reaction mixture was stirred for 45 min. The crude 78:22 mixture of **22aA + 22aB** was purified by flash column chromatography using AcOEt−hexane (1:1) as the eluent. Yield (**22aA + 22aB** mixture): 76% (50.3 mg). **Diastereoisomer [2*R*,3a*S*,(S)*S*]-22aA** (colorless oil): $[\alpha]^{20}_D$ −153.4 (*c* 1.0, $CHCl_3$); IR (film) 2966, 2930, 2231, 1709, 1634, 1456, 1082, 1030, 812, 755 cm^{-1}; ^1H NMR δ 7.67−7.58 (m, 1H), 7.60 and 7.31 (AA′BB′ system, 4H), 7.52−7.41 (m, 3H), 4.28 and 3.50 (AB system, *J* 18.2 Hz, 2H), 2.90 and 2.46 (AB system, *J* 12.6 Hz, 2H), 2.58 and 2.44 (AB system, *J* 17.3 Hz, 2H), 2.40 (s, 3H), 1.65 (s, 3H), 1.61 (s, 3H) ppm; ^{13}C NMR δ 207.8, 176.9, 146.3, 141.4, 140.3, 139.7, 133.8, 132.0, 130.8, 130.5, 130.0 (3C), 125.6, 125.3 (2C), 51.8, 49.3, 48.4, 44.5, 41.8, 26.2, 21.3, 8.6 ppm; MS (ESI+) *m/z* 390 $[M + H]^+$ (100), 229 (18); HRMS (ESI+) calcd. for $C_{24}H_{24}NO_2S$ $[M + H]^+$ 390.1522, found 390.1518. **Diastereoisomer [2*R*,3a*R*,(S)*S*]-22aB** (colorless oil): $[\alpha]^{20}_D$ −40.8 (*c* 1.0, $CHCl_3$); ^1H NMR δ 7.70 (dd, *J* 6.9 and 2.2 Hz, 1H), 7.62−7.56 (m, 1H), 7.61 and 7.31 (AA′BB′ system, 4H), 7.54−7.44 (m, 2H), 4.18 and 3.43 (AB system, *J* 15.9 Hz, 2H), 3.12 and 2.50 (AB system, *J* 14.2 Hz, 2H), 2.40 (s, 3H), 1.83 (s, 3H), 1.64 and 1.23 (AB system, *J* 13.2 Hz, 2H), 1.18 (s, 3H) ppm; ^{13}C NMR δ 207.9, 176.6, 146.7, 141.4, 140.4, 138.5, 133.7, 131.9, 131.0, 130.6, 130.0 (2C), 125.3 (3C), 124.7, 51.4, 47.9, 47.0, 45.2, 41.3, 27.8, 21.3, 8.7 ppm; MS (ESI+) *m/z* 390 $[M + H]^+$ (100), 229 (18); HRMS (ESI+) calcd. for $C_{24}H_{24}NO_2S$ $[M + H]^+$ 390.1522, found 390.1540.

[2*S*,3a*R*,(S)*S*] and [2*S*,3a*S*,(S)*S*]-3a,6-Dimethyl-5-oxo-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (22bA + 22bB). The diastereoisomeric mixture **22bA + 22bB** was obtained using [2*S*,(S)*S*]-2-(2-but-1-inyl)-4-methyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**11b**) as the substrate. The reaction mixture was stirred for 45 min. The crude 50:50 mixture of **22bA + 22bB** was purified by flash column chromatography using AcOEt−hexane (1:1) as the eluent. Yield (**22bA + 22bB** mixture): 74% (48.9 mg). **Diastereoisomer [2*S*,3a*R*,(S)*S*]-22bA** (colorless oil): $[\alpha]^{20}_D$ −94.9 (*c* 2.5, $CHCl_3$); IR (film) 2966, 2930, 2231, 1709, 1634, 1456, 1082, 1030, 812, 755 cm^{-1}; ^1H NMR δ 7.62−7.59 (m, 1H), 7.56−7.50 (m, 1H), 7.54 and 7.22 (AA′BB′ system, 4H), 7.48−7.29 (m, 2H), 3.50−3.44 (m, 2H) 3.36 and 2.58 (AB system, *J* 13.9 Hz, 2H), 2.57−2.48 (m, 2H), 2.38 (s, 3H), 1.87 (s, 3H) 1.20 (s, 3H) ppm; ^{13}C NMR δ 208.3, 175.1, 146.8, 141.3, 140.2, 138.5, 133.9, 132.2, 130.7, 130.6, 129.9 (2C), 125.0 (2C), 124.9, 124.5, 52.8, 52.3, 46.5, 45.8, 36.5, 29.4, 21.3, 8.7 ppm. **Diastereoisomer [2*S*,3a*S*,(S)*S*]-22bB** (colorless oil): $[\alpha]^{20}_D$ −168.3 (*c* 2.0, $CHCl_3$); ^1H NMR δ 7.62−7.59 (m, 1H), 7.56 and 7.25 (AA′BB′ system, 4H), 7.50−7.39 (m, 3H), 3.51 and 3.45 (AB system, *J* 14.2 Hz, 2H), 3.39 and 2.61 (AB system, *J* 13.9 Hz, 2H), 2.58 and 2.52 (AB system, *J* 17.3 Hz, 2H), 2.34 (s, 3H), 1.83 (s, 3H), 1.16 (s, 3H) ppm; ^{13}C NMR δ 208.3, 175.1, 146.8, 141.3, 140.2, 138.5, 133.9, 132.2, 130.7, 130.6, 129.9 (2C), 125.0 (2C), 124.9, 124.5, 53.1, 52.3, 46.5, 45.4, 36.5, 30.8, 21.3, 8.5 ppm.

[2*R*,3a*S*,4*S*,(S)*S*] and [2*R*,3a*R*,4*R*,(S)*S*]-4-Methyl-5-oxo-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (23aA + 23aB). The diastereoisomeric mixture **23aA + 23aB** was obtained using a 90:10 mixture of [2*R*,(S)*S*,4*E*] and [2*S*,(S)*S*,4*E*]-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]hex-4-enenitrile (**12a + 12b**) as the substrate. The reaction mixture was stirred for 1.5 h. The crude 80:20 mixture of **23aA + 23aB** was purified by flash column chromatography using AcOEt−hexane (3:1) as the eluent. The products derived from **12b** were not detected in the crude mixture. **Diastereoisomer [2*R*,3a*S*,4*S*,(S)*S*]-23aA**: Yield 59% (37.6 mg, white solid); mp 144−146 °C (CH_2Cl_2−hexane); $[\alpha]^{20}_D$ −216.1 (*c* 1.1, $CHCl_3$); IR (KBr) 2971, 2851, 2231, 1708, 1669, 1459, 1083, 1035, 811, 762 cm^{-1}; ^1H NMR δ 7.66−7.61 (m, 1H), 7.62 and 7.31 (AA′BB′ system, 4H), 7.51−7.43 (m, 3H), 6.03 (m, 1H), 4.41 and 3.31 (AB system, *J* 19.3 Hz, 2H), 3.28−3.23 (m, 1H), 3.10 (dd, *J* 6.5 and 11.7 Hz, 1H), 2.38 (s, 3H), 2.38−2.36 (m, 1H), 2.21 (dd, *J* 11.9 and 12.0 Hz, 1H), 1.36 (d, *J* 7.4 Hz, 1H) ppm; ^{13}C NMR δ 210.1, 179.7, 146.5, 141.5 (2C), 140.1, 137.7, 132.3, 130.8, 130.5, 130.1 (2C), 125.7, 125.3 (2C), 124.0, 52.9, 48.8, 46.5, 42.7, 42.3, 21.4, 13.6 ppm; MS (FAB+) *m/z* 376 $[M + H]^+$ (100), 358 (12), 327 (14), 283 (38); HRMS (FAB+) calcd. for $C_{23}H_{22}NO_2S$ $[M + H]^+$ 376.1371, found 376.1372. **Diastereoisomer [2*R*,3a*R*,4*R*,(S)*S*]-23aB**: Yield 15% (9.6 mg, colorless oil); $[\alpha]^{20}_D$ −84.1 (*c* 1.0, $CHCl_3$); ^1H NMR δ 7.68−7.60 (m, 1H), 7.64 and 7.31 (AA′BB′ system, 4H), 7.55−7.44 (m, 3H), 6.08 (m, 1H), 4.07 and 3.65 (AB system, *J* 18.4 Hz, 2H), 3.39 (dd, *J* 7.0 and 13.6 Hz, 1H), 2.96−2.88 (m, 1H), 2.39 (s, 3H), 2.34 (dq, *J* 3.8 and 7.5 Hz, 1H), 2.25 (dd, *J* 12.5 and 13.6 Hz, 1H), 1.30 (d, *J* 7.5 Hz, 1H) ppm; ^{13}C NMR δ 209.8, 179.3, 146.7, 141.5 (2C), 139.9, 138.3, 132.2, 131.3, 130.8, 130.0 (2C), 125.9, 125.3 (2C), 124.4, 52.5, 49.6, 44.6, 44.3, 41.7, 21.3, 13.6 ppm; MS (ESI+) *m/z* 376 $[M + H]^+$ (100), 358 (12), 327 (14), 283 (38); HRMS (ESI+) calcd. for $C_{23}H_{22}NO_2S$ $[M + H]^+$ 376.1371, found 376.1375.

[2*R*,3a*S*,4*S*,(S)*S*] and [2*R*,3a*R*,4*R*,(S)*S*]-4,6-Dimethyl-5-oxo-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (24aA + 24aB). The diastereoisomeric mixture **24aA + 24aB** was obtained using a 87:13 mixture of [2*R*,(S)*S*,4*E*] and [2*S*,(S)*S*,4*E*]-2-(but-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]hex-4-enenitrile (**13a + 13b**) as the substrate. The reaction mixture was stirred for 1.5 h. The crude 82:18 mixture of **24aA + 24aB** was purified by flash column chromatography using AcOEt−hexane (2:1) as the eluent. The products derived from **13b** were not detected in the crude mixture. Yield (**24aA + 24aB** mixture): 80% (52.9 mg). **Diastereoisomer [2*R*,3a*S*,4*S*,(S)*S*]-24aA** (data from a 90:10 **24aA + 24aB** mixture): IR (film) 2921, 2851, 2231, 1704, 1650, 1459, 1083, 1030, 811, 755 cm^{-1}; ^1H NMR δ 7.68−7.63 (m, 1H), 7.63 and 7.31 (AA′BB′ system, 4H), 7.51−7.44 (m, 3H), 4.30 and 3.20 (AB system, *J* 18.9 Hz, 2H), 3.14−3.03 (m, 2H), 2.40 (s, 3H), 2.34−2.24 (m, 1H), 2.13 (dd, *J* 11.3 and 11.4 Hz, 1H), 1.35 (d, *J* 7.3 Hz, 1H) ppm; ^{13}C NMR δ 210.2, 172.0, 146.5, 141.6, 140.2, 137.8, 133.6, 132.2, 130.7, 130.4, 130.0 (2C), 125.6, 125.1 (2C), 124.2, 50.9, 47.9, 46.5, 42.4, 41.5, 21.3, 13.8, 8.8 ppm; MS (ESI+) *m/z* 390 $[M + H]^+$ (100); HRMS (ESI+) calcd. for $C_{24}H_{24}NO_2S$ $[M + H]^+$ 390.1522, found 390.1523. **Diastereoisomer [2*R*,3a*R*,4*R*,(S)*S*]-24aB** (colorless oil): $[\alpha]^{20}_D$ −40.8 (*c* 1.0, $CHCl_3$); ^1H NMR δ 7.68−7.64 (m, 1H), 7.65 and 7.31 (AA′BB′ system, 4H), 7.54−7.43 (m, 3H), 4.02 and 3.52 (AB system, *J* 18.0 Hz, 2H), 3.38 (dd, *J* 6.7 and 13.4 Hz, 1H), 2.83−2.72 (m, 1H), 2.40 (s, 3H), 2.27 (dq, *J* 3.3 and 7.4 Hz, 1H), 2.15 (dd, *J* 12.4 and 13.4 Hz, 1H), 1.30 (d, *J* 7.4 Hz, 1H) ppm; ^{13}C NMR δ 209.9, 171.6, 146.7, 141.2, 140.0, 138.6, 133.7, 132.1, 131.2, 130.7, 130.1, 129.9 (2C), 125.3 (2C), 124.3, 50.8, 48.7, 44.2, 43.6, 42.0, 21.3, 13.9, 8.9 ppm; MS (ESI+) *m/z* 390 $[M + H]^+$ (100); HRMS (ESI+) calcd. for $C_{24}H_{24}NO_2S$ $[M + H]^+$ 390.1522, found 390.1525.

[2*R*,3a*R*,(S)*S*]-5-Oxo-3a-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (25aA). The diastereoisomer **25aA** was obtained using a 90:10 mixture of [2*R*,(S)*S*] and [2*S*,(S)*S*]-4-phenyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)-phenyl]pent-4-enenitrile (**14a + 14b**) as the substrate. The reaction mixture was stirred for 12 h. The crude >98:<2 mixture of **25aA + 25aB** was purified by flash column chromatography using AcOEt−hexane (2:1) as the eluent. The products derived from **14b** were not detected in the crude mixture. Yield (**25aA**): 56% (41.6 mg, colorless oil); $[\alpha]^{20}_D$ −133.2 (*c* 0.8, $CHCl_3$); IR (film) 3019, 2936, 2236, 1709, 1640, 1492, 1083, 1035, 810, 755 cm^{-1}; ^1H NMR δ 7.64−7.60 (m, 1H), 7.52 and 7.23 (AA′BB′ system, 4H), 7.47−7.40 (m, 5H), 7.36−7.30 (m, 3H), 6.27 (m, 1H), 4.45 and 3.63 (AB system, *J* 18.4 Hz, 2H), 3.59 and 2.71 (AB system, *J* 12.7 Hz, 2H), 2.84 and 2.73 (AB

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system, *J* 17.5 Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR δ 211.1, 181.8, 146.6, 142.1 (2C), 141.4, 139.9, 139.4, 132.0, 130.6, 129.9 (2C), 129.8 (2C), 128.9, 128.1, 126.2 (2C), 125.3 (2C), 125.1, 123.1, 58.1, 53.7, 48.5, 44.1, 42.9, 21.3 ppm; MS (ESI+) *m*/*z* 438 [M + H]$^+$ (100), 301 (12), 229 (13); HRMS (ESI+) calcd. for $C_{28}H_{24}NO_2S$ [M + H]$^+$ 438.1522, found 438.1505.

[2*R*,3a*R*,(S)*S*]-6-Methyl-5-oxo-3a-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (26aA). The diastereoisomer **26aA** was obtained using a 90:10 mixture of [2*R*,(S)*S*,4*E*] and [2*S*,(S)*S*,4*E*]-2-(but-2-inyl)-4-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**15a** + **15b**) as the substrate. The reaction mixture was stirred for 12 h. The crude >98:<2 mixture of **26aA** + **26aB** was purified by flash column chromatography using AcOEt−hexane (2:1) as the eluent. The products derived from **15b** were not detected in the crude mixture. Yield (**26aA**): 58% (44.5 mg, colorless oil); $[\alpha]^{20}_D$ −64.2 (*c* 1.7, $CHCl_3$); IR (film) 3040, 2926, 2236, 1715, 1640, 1448, 1085, 1031, 812, 760 cm^{-1}; ^{1}H NMR δ 7.65−7.61 (m, 1H), 7.55 and 7.23 (AA′BB′ system, 4H), 7.45−7.35 (m, 5H), 7.34−7.30 (m, 3H), 4.34 and 3.52 (AB system, *J* 18.3 Hz, 2H), 3.55 and 2.64 (AB system, *J* 12.3 Hz, 2H), 2.83 and 2.74 (AB system, *J* 17.9 Hz, 2H), 2.35 (s, 3H), 1.84 (s, 3H) ppm; ^{13}C NMR δ 207.3, 174.1, 146.6, 142.8, 141.3, 140.1, 139.6, 136.7, 132.0, 130.8, 130.6, 129.8 (2C), 129.1 (2C), 127.9, 126.4 (2C), 125.4, 125.1 (2C), 123.3, 55.9, 52.9, 48.9, 44.4, 41.7, 21.3, 8.8 ppm; MS (ESI+) *m*/*z* 452 [M + H]$^+$ (100), 301 (14), 229 (13); HRMS (ESI+) calcd. for $C_{29}H_{26}NO_2S$ [M + H]$^+$ 452.1678, found 452.1662.

[2*R*,3a*R*,4*R*,(S)*S*]-5-Oxo-4-phenyl-2-[2-(*p*-tolylsulfinyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (27aA). The diastereoisomer **27aA** was obtained using a 87:13 mixture of [2*R*,(S)*S*,4*E*] and [2*S*,(S)*S*,4*E*]-5-phenyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**16a** + **16b**) as the substrate. The reaction mixture was stirred for 3.5 h. The crude >98:<2 mixture of **27aA** + **27aB** was purified by flash column chromatography using AcOEt−hexane (2:1) as the eluent. The products derived from **16b** were not detected in the crude mixture. Yield (**27aA**): 74% (54.9 mg, colorless oil); $[\alpha]^{20}_D$ −223.8 (*c* 1.2, $CHCl_3$); IR (film) 3019, 2936, 2236, 1709, 1640, 1492, 1083, 1035, 810, 755 cm^{-1}; ^{1}H NMR δ 7.68−7.63 (m, 1H), 7.62 and 7.31 (AA′BB′ system, 4H), 7.55−7.44 (m, 3H), 7.43−7.38 (m, 2H), 7.35−7.30 (m, 1H), 7.27−7.24 (m, 2H), 6.14 (m, 1H), 4.50 and 3.41 (AB system, *J* 19.2 Hz, 2H), 3.75 (m, 1H), 3.48 (d, *J* 3.9 Hz, 1H), 3.15 (dd, *J* 6.4 and 11.7 Hz, 1H), 2.40 (s, 3H), 2.41−2.33 (m, 1H) ppm; ^{13}C NMR δ 207.3, 180.0, 146.5, 141.6, 140.0, 137.6, 137.2, 132.3, 130.8, 130.6, 130.1 (2C), 129.0 (2C), 128.4 (2C), 127.5, 125.7, 125.6, 125.1 (2C), 123.8, 60.2, 53.7, 46.4, 42.8, 42.5, 21.3 ppm; MS (ESI+) *m*/*z* 438 [M + H]$^+$ (100); HRMS (ESI+) calcd. for $C_{28}H_{24}NO_2S$ [M + H]$^+$ 438.1522, found 438.1504.

[2*R*,3a*S*] and [2*R*,3a*R*]-5-Oxo-2-phenyl-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (31A + 31B). The diastereoisomeric mixture **31A** + **31B** was obtained using (*R*)-2-phenyl-2-(prop-2-inyl)-pent-4-enenitrile (**28**) as the substrate. The reaction mixture was stirred for 5 min. The crude 56:44 mixture of **31A** + **31B** was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. Yield (**31A** + **31B** mixture): 80% (33.4 mg); IR (film) 2965, 2926, 2234, 1699, 1632, 1448, 1261, 1085, 1031, 872, 700 cm^{-1}; ^{1}H NMR (**31A** + **31B** mixture) δ 7.51−7.46 (m, 2H), 7.45−7.41 (m, 4H), 7.40−7.31 (m, 4H), 6.11 (m, 1H), 6.04 (m, 1H), 3.68 and 3.45 (AB system, *J* 20.0 Hz, 2H), 3.61−3.52 (m, 1H), 3.52 and 3.15 (AB system, *J* 19.1 Hz, 2H), 3.30−3.20 (m, 1H), 2.92 (dd, *J* 6.8 and 12.4 Hz, 1H), 2.81−2.66 (m, 2H), 2.28−2.16 (m, 2H), 1.83 (t, *J* 12.6 Hz, 1H) ppm; ^{13}C NMR (**31A** + **31B** mixture) δ 208.5, 208.4, 183.2, 182.6, 139.8, 138.7, 129.6 (2C), 129.3 (2C), 128.5, 128.4, 126.8, 126.3, 125.7 (2C), 125.6 (2C), 123.5, 123.4, 48.4, 46.5, 46.0, 45.9, 45.4, 44.0, 42.7, 42.6, 41.6, 41.5 ppm; MS (ESI+) *m*/*z* 224 [M]$^+$ (100), 197 (20); HRMS (ESI+) calcd. for $C_{15}H_{13}NO$ [M + Na]$^+$ 246.0889, found 246.0896.

[2*R*,3a*S*] and [2*R*,3a*R*]-3a-Methyl-5-oxo-2-phenyl-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (32A + 32B). The diastereoisomeric mixture **32A** + **32B** was obtained using (*R*,*E*)-2-phenyl-2-(prop-2-yn-1-yl)hex-4-enenitrile (**29**) as the substrate. The reaction mixture was stirred for 5 min. The crude 90:10 mixture of **32A** + **32B** was purified by flash column chromatography using AcOEt−hexane (1:3) as the eluent. Yield (**32A** + **32B** mixture): 72% (29.0 mg); $[\alpha]^{20}_D$ −9.2 (*c* 0.1, $CHCl_3$); ^{1}H NMR (**32A**) δ 7.32−7.25 (m, 5H), 6.11 (m, 1H), 5.92 (s, 1H), 3.68 and 3.22 (AB system, *J* 18.0 Hz, 2H), 3.22−3.57 (AB system, *J* 15.0 Hz, 2H), 2.04−1.97 (m, 1H), 1.48 (d, *J* 9.1 Hz, 3H) ppm; ^{13}C NMR (**32A**) δ 208.3, 186.1, 140.6, 129.6, 128.3, 127.8, 123.9, 53.5, 50.7, 41.2, 30.6, 21.6, 13.1 ppm; HRMS (mixture **32A** + **32B**) (ESI+) calcd. for $C_{16}H_{15}NO$ 237.1154, found 237.1158.

[2*R,3a*S**] and [2*R**,3a*R**]-5-Oxo-2-[2-(*p*-tolylsulfonyl)-phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile [(±)-39A + (±)-39B].** The diastereoisomeric mixture (±)-**39A** + (±)-**39B** was obtained using (±)-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfonyl)phenyl]pent-4-enenitrile (**34**) as the substrate. The reaction mixture was stirred for 20 min. The crude 56:44 mixture of **39A** + **39B** was purified by flash column chromatography using AcOEt−hexane (2:1) as the eluent. Yield (**39A** + **39B** mixture): 75% (48.2 mg, white solid); ^{1}H NMR (**39A** + **39B** mixture) δ 7.96−7.84 (m, 2H), 7.94 and 7.34 (AA′BB′ system, 4H), 7.89 and 7.36 (AA′BB′ system, 4H), 7.68−7.63 (m, 3H), 7.60−7.51 (m, 2H), 7.48−7.40 (s, 1H), 6.07 (s, 1H), 5.96 (m, 1H), 4.47 and 3.30 (AB system, *J* 19.8 Hz, 2H), 3.88 and 3.68 (AB system, *J* 18.6 Hz, 2H), 3.65 (m, 1H), 3.47−3.41 (m, 1H), 3.09 (dd, *J* 6.4 and 11.5 Hz, 1H), 2.79 (dd, *J* 6.4 and 17.9 Hz, 1H), 2.72 (dd, *J* 6.2 and 11.5 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 3H), 2.72 (dd, *J* 11.4 and 13.2 Hz, 1H), 2.25 (dd, *J* 6.4 and 14.4 Hz, 1H), 2.30−2.16 (m, 2H) ppm; ^{13}C NMR (**39A** + **39B** mixture) δ 208.5, 208.4, 183.8, 182.8, 145.0, 144.8, 141.2, 140.8, 139.4, 138.6, 138.1, 137.3, 136.6, 134.0, 133.1, 132.6, 130.0 (2C), 129.9 (2C), 129.3, 129.2, 128.7, 128.2 (2C), 128.0 (2C), 127.4, 126.5, 125.8, 123.1, 123.0, 47.5, 46.0, 45.0, 44.5, 44.4, 44.3, 44.0, 42.7, 42.3, 41.5, 21.6 (2C) ppm; MS (ESI+) *m*/*z* [M + H]$^+$ 378 (100); HRMS (ESI+) calcd. for $C_{22}H_{20}NO_3S$ [M + H]$^+$ 378.1158, found 378.1161.

(±)-[2*R,3a*S**]-5-Oxo-2-[2-(*p*-tolylsulfenyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (40A).** It was obtained using (±)-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)phenyl]pent-4-enenitrile (**36**) as the substrate. The reaction mixture was stirred for 5 min. The crude (±)-**40A** was purified by flash column chromatography using AcOEt−hexane (1:2) as the eluent. Yield: 68% (39.8 mg, colorless oil); ^{1}H NMR δ 7.54−7.48 (m, 1H), 7.30−7.23 (m, 4H), 7.19−7.12 (m, 3H), 5.96 (s, 1H), 4.05 and 3.17 (AB system, *J* 19.1 Hz, 2H), 3.65 (m, 1H), 3.55 (m, 1H), 3.20 (m, 1H), 2.90 (dd, *J* 12.0 and 18.6 Hz, 1H), 2.79 (dd, *J* 6.3 and 17.8 Hz, 1H), 2.35 (s, 3H) ppm; ^{13}C NMR δ 183.8, 137.8, 137.6, 136.8, 134.1, 131.7, 131.4, 131.3 (2C), 130.4, 130.3 (2C), 129.4, 127.5, 126.9, 126.3, 48.4, 45.0, 42.9, 41.7, 41.2, 21.1 ppm; MS (EI+) *m*/*z* [M]$^+$ 345 (67), 318 (100); HRMS (ESI+) calcd. for $C_{22}H_{19}NOS$ 345.1187, found 345.1181.

(±)-[2*R,3a*S**,4*S**]-4-Methyl-5-oxo-2-[2-(*p*-tolylsulfenyl)-phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carbonitrile (41A).** It was obtained using (±)-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)-phenyl]hex-4-enenitrile (**37**) as the substrate. The reaction mixture was stirred for 5 min. The crude (±)-**41A** was purified by flash column chromatography using AcOEt−hexane (1:2) as the eluent. Yield: 70% (42.7 mg, white solid); ^{1}H NMR δ 7.54−7.46 (m, 1H), 7.29−7.20 (m, 4H), 7.19−7.12 (m, 3H), 5.96 (s, 1H), 4.05 and 3.13 (AB system, *J* 19.7 Hz, 2H), 3.25−3.16 (m, 1H), 2.95 (m, 1H), 2.38−2.20 (m, 2H), 2.34 (s, 3H), 1.32 (d, *J* 7.1 Hz, 3H) ppm; ^{13}C NMR δ 183.6, 137.8, 137.7, 136.5, 134.3, 131.7, 131.5, 131.4 (2C), 130.5, 130.3 (2C), 129.6, 127.8, 126.7, 125.3, 52.1, 48.6, 42.8, 41.6, 41.0, 21.0, 13.7 ppm; MS (EI+) *m*/*z* [M]$^+$ 359 (26), 332 (100); HRMS (ESI+) calcd. for $C_{23}H_{21}NOS$ 359.1344, found 359.1336.

[2*R*,3a*S*]-5-Oxo-2-[2-(*p*-tolylsulfenyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carboxamide (45). The diastereoisomer **45** was obtained using (*R*)-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)-phenyl]pent-4-enamide [(*R*)-**42**] as the substrate. The reaction mixture was stirred for 5 min. The crude >98:<2 mixture was purified by flash column chromatography using AcOEt−hexane (3:1) as the eluent. Yield (**45**): 78% (42.3 mg, white solid); mp 144−146 °C (CH_2Cl_2−hexane); $[\alpha]^{20}_D$ −160.1 (*c* 0.6, $CHCl_3$); ^{1}H NMR δ 7.46−7.44 (m, 1H), 7.26 and 7.13 (AA′BB′ system, 4H), 7.24−7.19 (m,

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3H), 5.88 (s, 1H), 5.33 (br s, 1H), 5.18 (br s, 1H), 4.32 and 2.74 (AB system, *J* 20.0 Hz, 2H), 3.47 (m, 1H), 2.76−2.73 (m, 2H), 2.35 (s, 3H), 2.16 (m, 1H), 2.09 (dd, *J* 12.2 and 12.3 Hz, 1H) ppm; ^{13}C NMR δ 210.1, 188.9 (2C), 142.1, 139.8, 138.5, 138.1, 133.0, 132.2 (2C), 130.9, 130.2 (2C), 128.6, 126.9, 126.4, 124.8, 43.8, 42.7, 42.0, 38.8, 21.1 ppm; MS (ESI+) *m*/*z* 364 $[M + H]^+$ (36), 319 (100); HRMS (ESI+) calcd. for $C_{22}H_{22}NO_2S$ $[M + H]^+$ 364.1365, found 364.1378.

[2*R,3a*S**,4*S**]-4-Methyl-5-oxo-2-[2-(*p*-tolylsulfenyl)phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carboxamide (46).** The diastereoisomer **46** was obtained using (2*R*,4*E*)-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)phenyl]hex-4-enamide (**43**) (76% ee) as the substrate. The reaction mixture was stirred for 5 min. The crude >98:<2 mixture was purified by flash column chromatography using AcOEt−hexane (2:1) as the eluent. Yield (**46**): 78% (50.1 mg, white solid); ^{1}H NMR δ 7.47−7.45 (m, 1H), 7.26 and 7.13 (AA′BB′ system, 4H), 7.24−7.19 (m, 3H), 5.87 (m, 1H), 5.26 (br s, 1H), 5.21 (br s, 1H), 4.34 and 2.71 (AB system, *J* 18.6 Hz, 2H), 3.10 (m, 1H), 2.79 (dd, *J* 7.26 and 11.9 Hz, 1H), 2.36−2.30 (m, 1H), 2.35 (s, 3H), 2.12 (dd, *J* 12.3 and 15.4 Hz, 1H) ppm; ^{13}C NMR δ 211.8, 186.6, 186.4, 142.1, 138.5, 138.0, 133.0, 132.2 (2C), 131.0, 130.2 (2C), 128.6, 126.9, 126.4, 123.8, 52.1, 49.2, 42.3, 38.7, 29.6, 21.1, 13.7 ppm; MS (ESI+) *m*/*z* 378 $[M + H]^+$ (20), 333 (100); HRMS (ESI+) calcd. for $C_{23}H_{24}NO_2S$ $[M + H]^+$ 378.1522, found 378.1508.

[2*R,3a*S**,4*R**]-5-Oxo-4-phenyl-2-[2-(*p*-tolylsulfenyl)-phenyl]-1,2,3,3a,4,5-hexahydropentalene-2-carboxamide (47).** The diastereoisomer **47** was obtained using (2*R*,4*E*)-5-phenyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfenyl)phenyl]pent-4-enamide (**44**) as the substrate (54% ee) [unpurified with a 30% of 5-phenyl-2-(prop-2-inyl)-2-[2-(*p*-tolylsulfinyl)phenyl]pent-4-enenitrile (**16**)]. The reaction mixture was stirred for 10 min. The crude >98:<2, along with **32aA**, was purified by flash column chromatography using AcOEt−hexane (2:1) as the eluent. **Diastereoisomer** [2*R**,3a*S**,4*R**]-**47** (data from a 70:30 **47** + **27aA** mixture): ^{1}H NMR δ 7.46−7.44 (m, 1H), 7.38−730 (m, 3H), 7.26 and 7.13 (AA′BB′ system, 4H), 7.28−7.24 (m, 3H), 7.23−7.18 (m, 2H), 6.05 (s, 1H), 5.34 (br s, 1H), 5.20 (br s, 1H), 4.05 and 3.15 (AB system, *J* 18.9 Hz, 2H), 3.42 (d, *J* 3.8 Hz, 1H), 3.36−3.30 (m, 1H), 3.03 (dd, *J* 7.2 and 13.2 Hz, 1H), 2.33 (s, 3H), 2.22 (dd, *J* 12.5 and 12.8 Hz, 1H) ppm; ^{13}C NMR δ 208.5, 185.0, 180.1, 141.3, 138.4, 138.3, 138.0, 133.3, 132.1, 130.2, 130.0 (2C), 129.0 (2C), 128.7, 128.5 (2C), 127.1, 127.0, 126.0, 125.6, 124.1, 60.7, 54.8, 45.0, 41.4, 39.4, 21.1 ppm; MS (ESI+) *m*/*z* 440 $[M + H]^+$ (100); HRMS (ESI+) calcd. for $C_{28}H_{26}NO_2S$ $[M + H]^+$ 440.1678, found 440.1655.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR for 2-allyl-2-[2-(*p*-tolylsulfinyl)-phenylacetonitriles **2**, **4**−**7**; 1,6-enynes **8**−**18**, **28**−**30**, **34**, **36**−**38**, **42**−**44**; adducts **19**−**26**, **31**−**32**, **39**−**41**, **45**−**47**, and **9**−**12** and bidimensional ^{1}H NMR experiments of compounds **23aA** and **23aB**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

In memory of Prof. Alessandro Degl'Innocenti.

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