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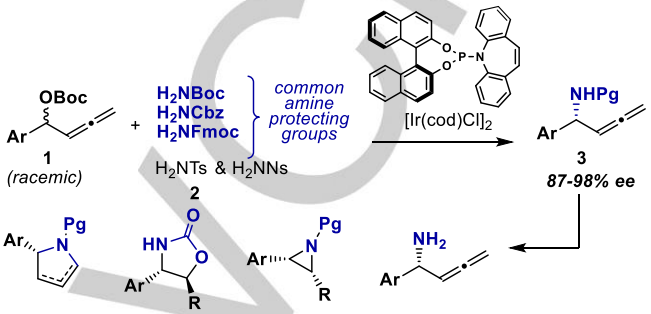
Ir-Catalyzed Enantioconvergent Synthesis of Diversely Protected Allenylic Amines Employing Ammonia Surrogates

Fabian Glatz, David A. Petrone and Erick M. Carreira*

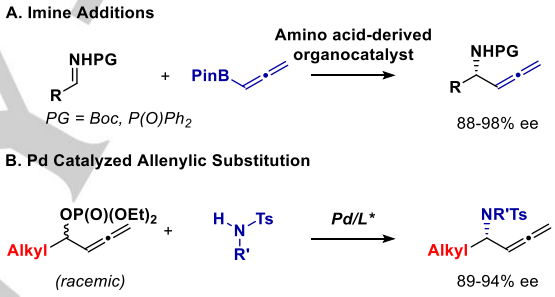
Abstract: The first iridium catalyzed, enantioconvergent amination of allenylic carbonates is reported. This process utilizes various commercially available carbamates and sulfonamides to generate allenylic amines including commonly employed protected groups (Boc, Fmoc, Cbz, Ts, Ns) in 62-82% yield and 87-98% ee. The products generated via this scalable procedure serve as effective linchpins for the rapid, enantiospecific synthesis of a wide range of complex structures.

Allenes have long been versatile platforms for reaction discovery and development.[1] They form the basis of a number of widely used transformations which include: cyclizations,[2a-c] annulations,[2d] photocycloadditions,[2e] hydroheterofunctionalizations,[2f-h] and rearrangements.[2i-k] Their ease of preparation, combined with their broad applications in stereoselective catalysis has greatly increased their utility as building blocks in organic synthesis.[1] Additionally, a number of allene natural products displaying biological activity have been isolated, and pharmacologically active anthropogenic allenes have been designed as suicide inhibitors of enzyme activity.[3] A particularly interesting class of compounds are optically active allenylic amines **3**, as they can be used as effective linchpins in the synthesis of diverse heterocycles (Scheme 1).[4-6] However, the asymmetric synthesis of these amines remains greatly underdeveloped by comparison to their allylic analogs.[7] Herein, we report the development of an Ir-catalyzed enantioconvergent amination of allenylic carbonates **1** with ammonia equivalents to give **3** (Scheme 1). A key feature is that end users can choose from a list of common amine protecting groups on the products, such as Boc, Cbz, Fmoc as well as Ts, and Ns.

Modern, catalytic approaches to optically active protected allenylic amines and their derivatives may be classified according to the starting materials employed. In the first of these, additions to *N*-Boc- or *N*-phosphinoylimines by allene-boronate nucleophiles furnish allenylic amides stereoselectively (Scheme 2A).[8a,b] The second is the subject of a single publication in which Ma and co-workers have reported the use of Pd/BIPHEP as a catalyst for the substitution of racemic alkyl substituted allenylic phosphates to give *N*-alkyl *p*-toluenesulfonamides in 89-94% ee (Scheme 2B).[8c] Although it is state-of-the art, the scope is restricted to alkyl derived substrates and employs *N*-



Scheme 1. Enatioconvergent synthesis of allenylic amines and applications.



Scheme 2. Catalytic enantioselective strategies to protected allenylic amines.

tolylsulfonamides as nucleophiles. As such it underscores the need for further development of these reaction types, which have otherwise been extensively studied in the allylic series, to include a broader range of amine nucleophiles.[9-11]

Our group has recently examined and reported Ir-(*P,olefin*) catalyzed alkylation of racemic allenylic carbonates with organozinc reagents.[12] Since metal-catalyzed reactions of allenylic electrophiles have not been studied extensively, we have embarked on expanding the versatility of the catalyst system to include access to other adducts, such as allenylic amines.[10d,e] Because *tert*-butyl carbamate is among the most widely employed nitrogen protecting group, we examined the use of $BocNH_2$ as a nucleophile in the initial screening process. The use of this inexpensive, crystalline, and commercially available nitrogen source would lead to *N*-Boc allenylic amines, which can be conveniently deprotected under mild acidic conditions or transformed into more complex scaffolds, as shown below. Evaluation of a range of parameters led to the identification of optimal outcomes for the reaction of interest (Table 1). A system comprising $[Ir(cod)Cl]_2$ (2 mol%), (*P,olefin*)-ligand (*S*)-**L**$_1$ (8 mol%), $ZnCl_2$ (10 mol%) and $BocNH_2$ (1.1 equiv) in PhMe/THF (4:1) at 23 ºC for 13 h provided product (*R*)-**3a** in 76% isolated yield and 96% ee.[13,14]

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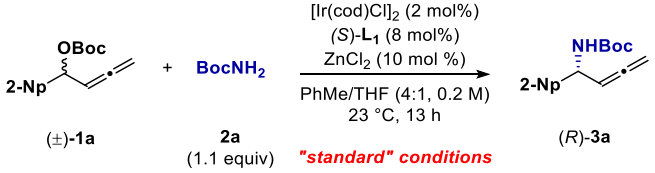
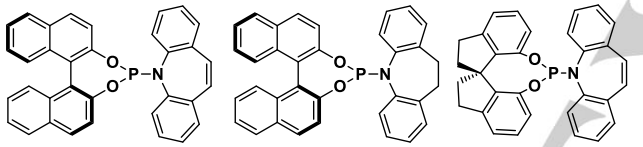
Table 1. Screening of reaction parameters for the Ir-catalyzed amination.[a]



(±)-**1a** | **2a** (1.1 equiv) | *"standard" conditions* | (*R*)-**3a**

Entry	Deviation from the "standard" conditions	Yield [%][b]	ee [%][c]
1	**None**	**82 (76)[d]**	**96**
2	Commercial $ZnCl_2$ solution(0.5 M THF)	80	96
3	THF instead of THF/PhMe	76	94
4	no $[Ir(cod)Cl]_2$	0	-
5	no (*S*)-**L₁**	4	-
6	no $ZnCl_2$	0	-
7	**L₂** instead of **L₁**	0	-
8	**L₃** instead of **L₁**	27	90
9	[Pd]/**L₄**[e]	0	0

[a] Reactions were conducted on 0.2 mmol scale. [b] Determined by ^1H NMR analysis of the unpurified reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard. [c] Determined by HPLC analysis using a chiral stationary phase. [d] Conducted on 0.5 mmol scale. Isolated yield in parentheses [e] $[Pd(allyl)Cl]_2$ (2.5 mol%), (*R*)-**L₄** (6 mol%), DBU (2 equiv), $BocNH_2$ (2 equiv) *o*-xylene, 0 °C, 80 h. 2-Np = 2-naphthyl.

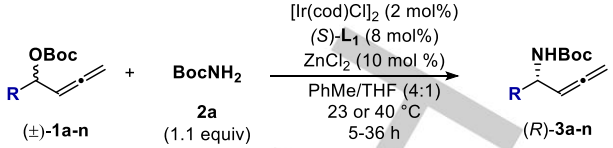


(*S*)-**L₁** (*S*)-**L₂** (*R*)-**L₃**

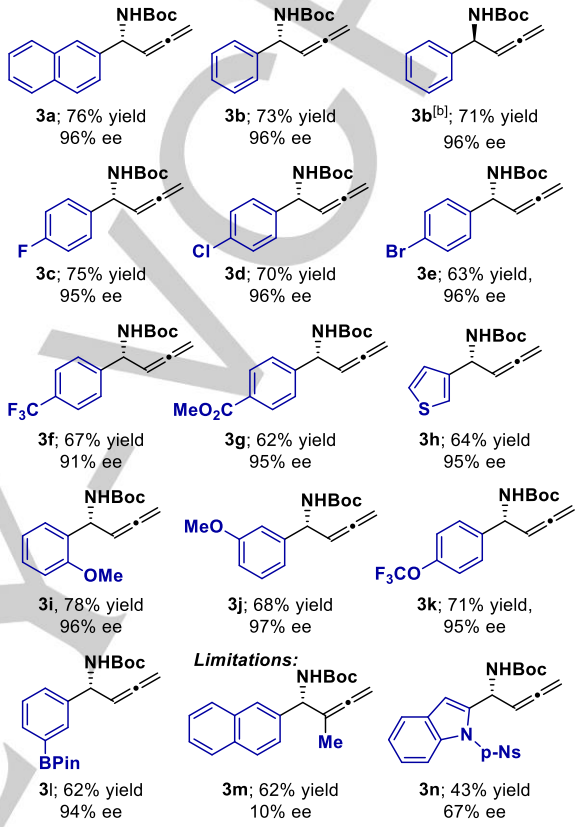
(*R*)-**L₄** = (*R*)-*3,4,5-(MeO)₃-MeOBIPHEP (ref 8c)*

We highlight in Table 1 additional observations that are noteworthy. The replacement of a freshly prepared THF solution of $ZnCl_2$ with a commercially available 0.5 M solution of $ZnCl_2$ in THF led only to a slight decrease in yield, while the ee remained unchanged (entry 2). Replacing the PhMe/THF solvent mixture with a THF-only solvent system led to slight decrease in both yield and ee (entry 3). Additionally, control experiments confirmed that all three components ($[Ir(cod)Cl]_2$, (*S*)-**L₁** and $ZnCl_2$) are crucial to the success of the reaction (entries 4-6). Structural permutations of ligand (*S*)-**L₁** led to less satisfactory outcomes. For example, no product was observed when employing ligand (*S*)-**L₂** which possesses a saturated iminostilbene moiety (entry 7). Furthermore, the more rigid SPINOL derived (*P,olefin*) ligand (*R*)-**L₃** gave the product in significantly reduced yield and enantioselectivity (entry 8). Finally, the reaction conditions reported by Ma and co-workers for amination of allenylic phosphates did not lead to product formation when $BocNH_2$ was used as the nucleophile with **3a** (entry 9).[8c] With the optimized conditions in hand, the scope of the newly developed allenylic amination was explored (Table 2). Phenyl substituted (*R*)-**3b** was obtained in similar yield (73%) and identical ee (96%) to **3a**. Furthermore, enantiomer (*S*)-**3b** was obtained in 71% yield and 96% ee when (*R*)-**L₁** was employed. Allenylic amines (*R*)-**3c**-**3e** possessing 4-haloarenes were generated in 63-75% yield and

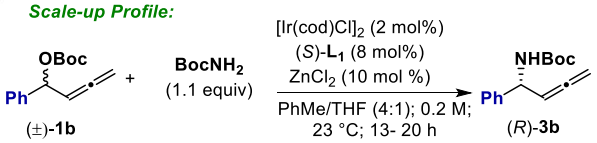
Table 2. Scope of Ir-catalyzed enantioconvergent amination.[a]



(±)-**1a-n** | **2a** (1.1 equiv) | (*R*)-**3a-n**



Scale-up Profile:



(±)-**1b** | (*R*)-**3b**

✓1.00 g (4 mmol) 739 mg (74%) 95% ee
✓10.0 g (40 mmol) 7.63 g (77%) 96% ee

[a] Reaction conditions: [Ir] = 4 mol%, (*S*)-**L₁** = 8 mol%, (±)-**1** (0.5 mmol), $BocNH_2$ (1.1 equiv), $ZnCl_2$ = 10 mol%, PhMe/THF (4:1, v:v) ([(±)-**1**] = 0.2 M), unless otherwise noted. Isolated yields provided. Enantiomeric excess values (ee) were determined by SFC or HPLC analysis using chiral stationary phases. [b] (*R*)-**L₁** was used.

95-96% ee. Due to their lower reactivity in comparison to **3a**, these substrates required heating to 40 °C for full conversion. Substrates possessing strongly electron-withdrawing groups in the para position of the arene were tolerated, and the corresponding products (*R*)-**3f** and (*R*)-**3g** were obtained in 62% and 67% yield along with 92% and 95% ee, respectively. Furthermore, a series of aryl ethers [(*R*)-**3i-k**] were obtained in 68-78% yield and 95-97% ee. Thiophene **1h** furnished product (*R*)-**3h** in 64% yield and 95% ee. Boronate-substituted substrate **1l** gave product (*R*)-**3l** in 62% yield and 94% ee. Some limitations of this transformation were also uncovered. Hence, 1,1-disubstituted

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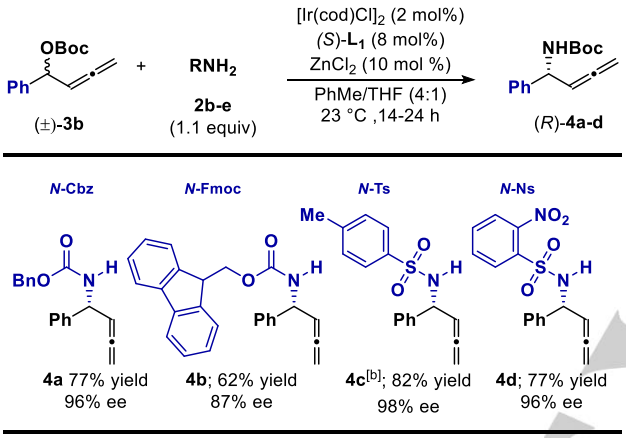
allene (*R*)-**3m** was only obtained in 62% yield and 10% ee, while indole (*R*)-**3n** was isolated in 43% yield and 67% ee. Our attempts with carbonates of alkyl allenyl carbinols were unsuccessful.[15] Our results with aryl substituted allenylic carbonates thus complement those reported by Ma employing *N*-tosyl amides and Pd-catalysis, in which only alkyl substituted allenylic substrates were reported.

We investigated the scalability of this transformation by conducting experiments on both 1.00 g (4.06 mmol) and 10.0 g (40.6 mmol) scale with (±)-**1b** as substrate (Table 2 bottom). In these instances, the results were in agreement with those obtained when the reaction was conducted on 0.5 mmol scale, and product was obtained in 74% and 77% isolated yields and 95% and 96% ee, respectively.

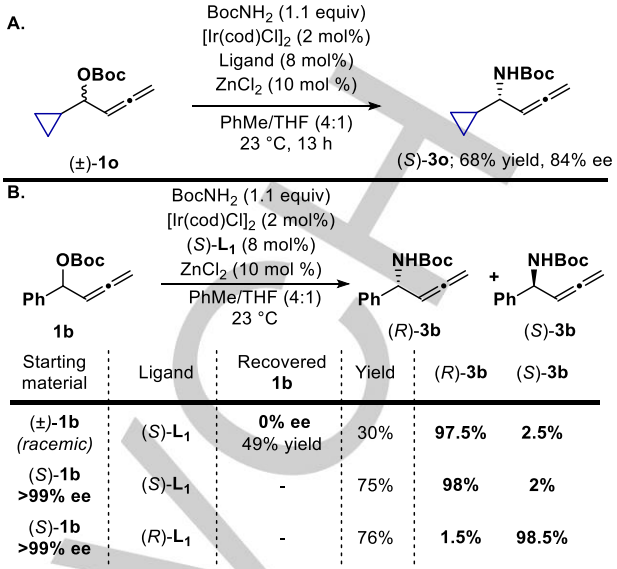
Table 3 Scope of protected ammonia equivalents in Ir-catalyzed amination.[a]



[a] Reaction conditions: [Ir] = 4 mol%, (*S*)-$\mathbf{L_1}$ = 8 mol**%,** (±)-**1b** (0.5 mmol), RNH_2 (1.1 equiv), $ZnCl_2$ = 10 mol%, PhMe/THF (4:1, v:v) ([(±)-**1b**] = 0.2 M), 23 °C Isolated yields provided. Enantiomeric excess values (ee) were determined by HPLC analysis using chiral stationary phases. [b] reaction conducted on 2 mmol scale.

We then proceeded to examine other protected ammonia equivalents in the context of the allenylic amination reaction. Conveniently, the conditions determined to be optimal for $BocNH_2$ extended well to these other nucleophiles, which led to a diverse series of *N*-protected allenylic amides (Table 3). For example, when benzyl carbamate ($CbzNH_2$) or $FmocNH_2$ were used, products (*R*)-**4a** and (*R*)-**4b** were isolated in 77% yield/96% ee and 62% yield/87% ee, respectively. Furthermore, *p*-tolylsulfonamide ($TsNH_2$) gave product (*R*)-**4c** in 82% yield and 98% ee while *o*-nitobenzenesulfonamide (*o*-$NsNH_2$) afforded (*R*)-**4d** in 77% yield and 96% ee.

Our previous work on Ir-catalyzed substitution of allenylic electrophiles indicated that substrate ionization at the allenylic carbon leads to a highly delocalized cation.[12,16] The trends observed in this study are consistent with such an intermediate. To further probe this, cyclopropyl (±)-**1o** was examined as substrate, given the known stability of carbinyl cyclopropyl cabocations (Scheme 3A).[17] Indeed, product (*R*)-**3o** was formed in 68% yield and 84% ee.[18] This result stands in direct contrast



Starting material	Ligand	Recovered **1b**	Yield	(*R*)-**3b**	(*S*)-**3b**
(±)-**1b** *(racemic)*	(*S*)-$\mathbf{L_1}$	**0% ee** 49% yield	30%	**97.5%**	**2.5%**
(*S*)-**1b** **>99% ee**	(*S*)-$\mathbf{L_1}$	-	75%	**98%**	**2%**
(*S*)-**1b** **>99% ee**	(*R*)-$\mathbf{L_1}$	-	76%	**1.5%**	**98.5%**

Scheme 3. Mechanistic studies to probe catalyst vs substrate control.

with those from experiments involving the cyclobutyl homolog, which was expectedly unreactive.[15]

In order to ascertain if the enantioconvergent allenylic amination displayed significant rate differences between enantiomeric starting carbonates, three experiments were conducted (Scheme 3B).[19] Firstly, when the reaction of (±)-**1b** was quenched after 1.5 h at 51% conversion, recovered **1b** (49% yield) was racemic and product (*R*)-**3b** was isolated in 30% yield and 95% ee. This result is consistent with both enantiomeric carbonates (±)-**1b** undergoing consumption at the same rate. Secondly, in separate experiments enantiopure carbonate (*S*)-**1b** was allowed to react under the standard conditions with either (*S*)- or (*R*)- $\mathbf{L_1}$. For both, products were obtained in similar yields (75%/76%) and equally high, but opposite, enantioselectivity (96 and –97% ee). These observations indicate that substrate-dependent kinetic resolution is not operative and that product configuration is solely dictated by the chirality of Ir-catalyst.

The reactivity of the allenes and amines can be leveraged to synthesize useful heterocyclic building blocks (Scheme 4). For example, treatment of Boc-carbamate (*R*)-**3a**[20] with 5 mol% $Pd(PPh_3)_4$ and PhI (1.05 equiv) in the presence of base, furnished oxazolidinone **5** in 77% yield as a single diastereomer and a crystalline solid (see SI for X-ray structure).[21] To the best of our knowledge, there is no precedence for such a transformation involving allenes. By contrast, under similar conditions *N*-Ts (*R*)-**4c** gave aziridine **6** in 82% yield as a single diastereomer and without erosion in ee.[4a] Au-catalyzed cycloisomerization of (*R*)-**3a** using Echavarran's catalyst (**10**) in a 1,2-DCE/PhMe solvent mixture afforded 2,5-dihydropyrrole **7** in 89% yield.[5a] There have been recent reports of the formation of 2,3-dihydropyrroles from protected racemic allenylic amines using a collection of iron catalysts by Bäckvall and Rueping.[6] The use of Fe-catalyst **11** leads to the cycloisomerization of optically active (*R*)-**4c** to isomeric 2,3-dihydropyrrole **9** in 93% yield (98% ee). Finally, enantioenriched primary amine hydrochloride salt **8** was obtained in 88% yield by cleavage of the Boc group (HCl, 1,4-dioxane).[22]

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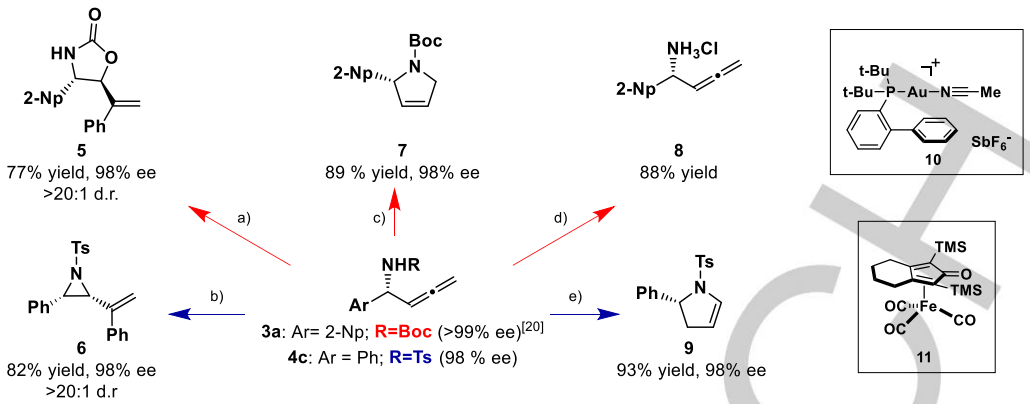

Scheme 4. Synthetic application of amination products, synthesis of nitrogen heterocycles. Reagents and conditions: a) $Pd(PPh_3)_4$ (5 mol%), PhI (1.05 equiv), K_2CO_3 (4 equiv), DMF 70 °C; b) $Pd(PPh_3)_4$ (10 mol%), PhI (4 equiv), K_2CO_3 (4 equiv), 1,4-dioxane, 110 °C; c) **10** (5 mol%), 1,2-DCE/PhMe, 23 °C; d) **11** (5 mol %), TMANO (6 mol %), K_2CO_3 (1 equiv), PhMe, 70 °C; e) HCl, 1,4-dioxane, 23 °C. TMANO = trimethylamine *N*-oxide

In summary, we have developed a highly enantioconvergent protocol for the amination of racemic allenylic carbonates using an Ir-*(P,olefin)* catalyst system for the first time with various, convenient used ammonia equivalents ($BocNH_2$, $FmocNH_2$, $CbzNH_2$, $TsNH_2$, $NsNH_2$). This procedure features mild reaction conditions, readily available catalysts along with racemic starting materials, and is easily scalable. Furthermore, the general product scaffolds can be used as effective linchpins for the streamlined preparation of various building blocks. The synthesis of allenylic amines considerably extends the chemistry of Ir-catalyzed substitution reactions, which should find wide applications.

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Keywords: allenes • amination• enantioconvergent • iridium • heterocycles

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[13] For optimization details, see SI.

[14] The absolute configuration of (*R*)-**3a** was determined by X-ray, see SI.

[15] For details on substrate limitations, see SI

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[19] For examples of Ir-catalyzed kinetic resolutions, see: a) S. Breitler, E. M. Carreira, *J. Am. Chem. Soc.* **2015**, *137*, 5296; b) Y. Sempere, J. L. Alfke, S. L. Rössler, E. M. Carreira, *Angew. Chem. Int. Ed.* **2019**, *58*, 9537; *Angew. Chem.* **2019**, *131*, 9637.

[20] The 96% ee of **3a** (Table 1) was upgraded to >99% by recrystallization from hexanes/ether.

[21] Pd-catalyzed conversion of an achiral allenyl amine to an oxazolidinone in the presence of CO_2 has been reported.[4c] The approach we describe directly converts the optically active, Boc-protected allenyl amide.

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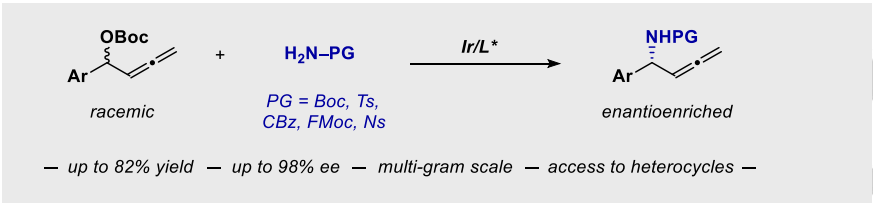

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Ir-Catalyzed Enantioconvergent Synthesis of Diversely Protected Allenylic Amines Employing Ammonia Surrogates

Pick and choose: Ir- catalysis enables the synthesis of diversely protected allenylic amines employing readily available ammonia equivalents. This highly scalable method grants access to these building blocks in high enantiomeric excess. The products obtained may be transformed in to a variety of heterocycles.