Radical Cascade Reactions

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Stereoselective Synthesis of Highly Functionalized Indanes and Dibenzocycloheptadienes through Complex Radical Cascade Reactions**

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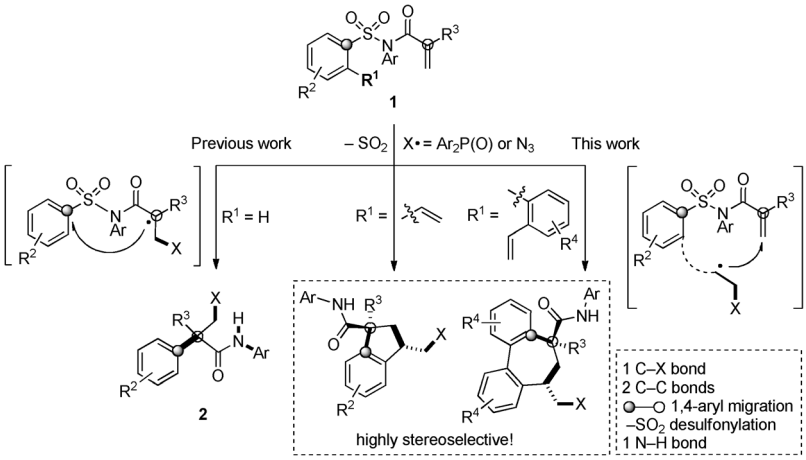
Abstract: *Two highly stereoselective radical-mediated syntheses of densely functionalized indanes and dibenzocycloheptadienes from ortho-vinyl- and ortho-vinylaryl-substituted N-(arylsulfonyl)-acrylamides, respectively, are presented here. The chemoselective addition of in situ generated radicals (X·) onto the styrene moieties triggers an unprecedented reaction cascade, resulting in the formation of one new C–X bond and two new C–C bonds, a formal 1,4-aryl migration, and the extrusion of SO_2 to generate an amidyl radical intermediate. This intermediate, upon H abstraction, leads to the observed 5- and 7-membered ring carbocyclic products, respectively, in a highly efficient manner.*

Alkenes are privileged motifs in organic synthesis because of their potential for the flexible introduction of functional groups across the C=C π system. Alkene difunctionalizations ranging from classical dioxygenation,[1] aminooxygenation,[2] or aminohalogenation[3] to more recently developed diazidation,[4] azidooxygenation,[5] azidohalogenation,[6] or phosphonofluorination[7] reactions mediated by metallic or organo-catalysts have been developed. In this context, the carbofunctionalization of alkenes has received increasing attention. Thus, carbo-trifluoromethylation,[8] carbo-phosphonylation,[9] and carbo-azidation[10] reactions have been recently described. In most cases, these transformations proceed in an intramolecular fashion and oxindoles are obtained from *N*-aryl acrylamide substrates. Although a wide variety of reaction conditions have been applied in these transformations, the addition of an in situ generated cation or radical to the acrylate moiety seems to be at the outset of these processes. Our group has recently reported the addition of a variety of radicals to the double bond of *N*-(aryl)(arylsulfonyl)acrylamide substrates **1** to generate α-aryl-β-functionalized amides **2** bearing a quaternary stereocenter through a novel one-pot radical addition/aryl migration/desulfonylation cascade.[11] We envisioned that the introduction of a more activated alkene at the *ortho* position of the arylsulfonyl group could control the chemoselectivity of the initial radical addition to the C=C π system,[12] thus triggering an unprecedented reaction cascade to access densely functionalized carbocycles (Scheme 1).



Scheme 1. Aryl-heterofunctionalization of activated alkenes.

Herein we report the realization of this concept with a highly efficient stereoselective synthesis of indanes and dibenzocycloheptadienes from *ortho*-vinyl- and *ortho*-vinylaryl-substituted *N*-(arylsulfonyl)acrylamides. Benzylic radicals generated upon addition of carbon- or heteroatom-centered radicals (X·) across the styrene system undergo an 8- or 10-*endo-trig* cyclization, which results in the formation of a $C(sp^3)$–X and a $C(sp^3)$–$C(sp^3)$ bond. A second $C(sp^3)$–$C(sp^2)$ bond involving a formal 1,4 migration of the arylsulfonyl group takes place prior to the elimination of SO_2 to deliver the observed products in a highly stereoselective fashion. The indane core is present in a large number of natural products[13,14] and dibenzocycloheptadiene moieties constitute the main scaffold of colchicine alkaloids, com-

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pounds with antimitotic, antitumor, and antivascular activity.[15] Despite the interesting biological properties of both types of molecules, the assembly of highly functionalized derivatives in a stereoselective manner has proved to be highly challenging, with a few exceptions.[13b,16]

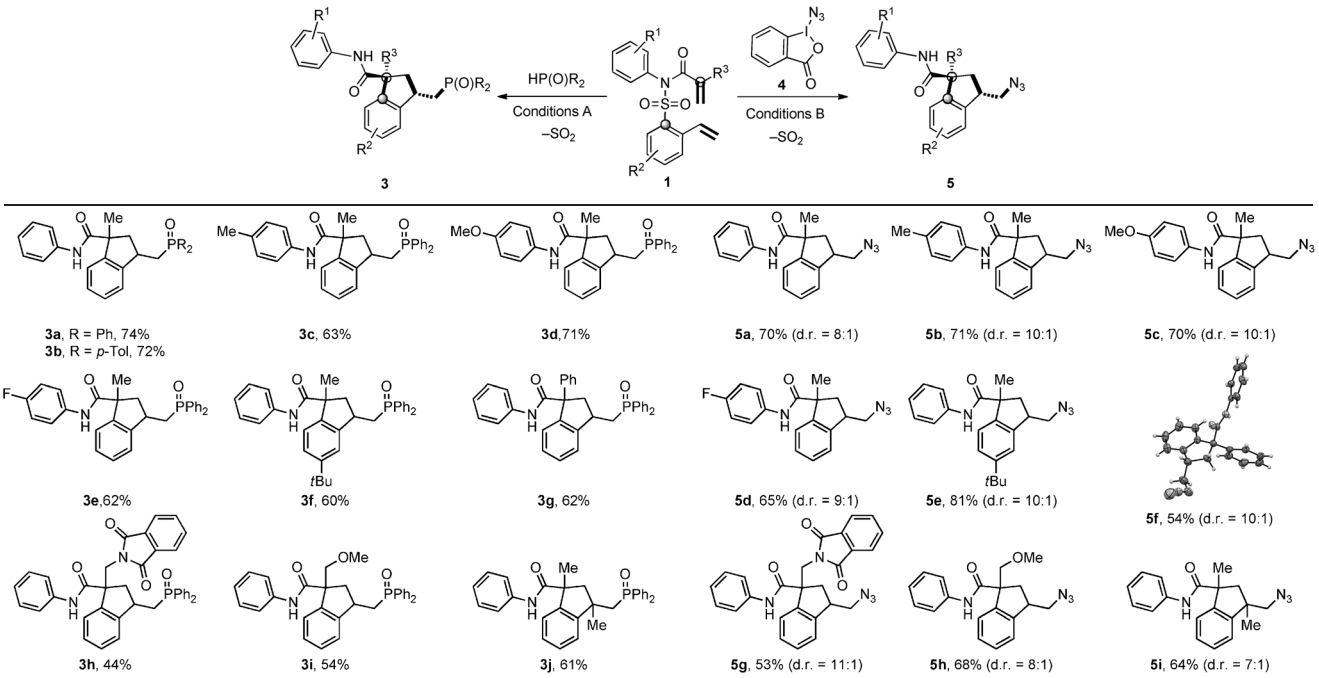
Our study commenced with the reaction of *ortho*-vinyl-substituted *N*-(arylsulfonyl)acrylamides derivatives **1** (Table 1). First, we optimized the reaction conditions for the in situ generation of a phosphonyl radical.[17] When we carried out the reaction of **1a** in the presence of 10 mol% of $AgNO_3$ and two equivalents of $Ph_2P(O)H$ in acetonitrile at 80°C, we were pleased to find the clean formation of indane **3a** in 74% yield. The process is highly stereoselective, as only one diastereoisomer could be detected in the reaction mixture. With the aim of introducing an azido group that could be used for subsequent derivatization of these compounds, the reaction of **1a** was carried out in the presence of reagent **4**[5b] at 60°C in dichloromethane, furnishing indane **5a** in 70% yield. The reaction was also highly stereoselective, affording a mixture of diastereoisomers in a ratio of 8:1.

With the optimized reaction conditions for both processes in hand, we set out to explore the scope of these transformations. Other aromatic phosphine oxides could also be introduced, as shown by the isolation of compound **3b** in 72% yield. Acrylamide substrates bearing electron-donating (methyl and methoxy) or electron-withdrawing groups (fluorine) at the *para* position of the aromatic ring that is directly bound to the nitrogen atom produced the corresponding phosphonylated indanes **3c–e** in good yields. Substitution at the arylsulfonyl moiety was also tolerated, as shown by the efficient conversion of **1f** into compound **3f**.

The substitution pattern on the acrylic moiety was also investigated. Substrates bearing a phenyl, methyl-*N*-phthalimide, or methoxymethyl group at the internal position of the alkene were transformed into the corresponding indanes **3g–i** in moderate yields. Indane **3j** with two quaternary centers was generated when a 1,1-disubstituted styrene substrate was used. In contrast, no reaction was observed for substrates bearing internal olefins at either the acrylic or styrenic position.

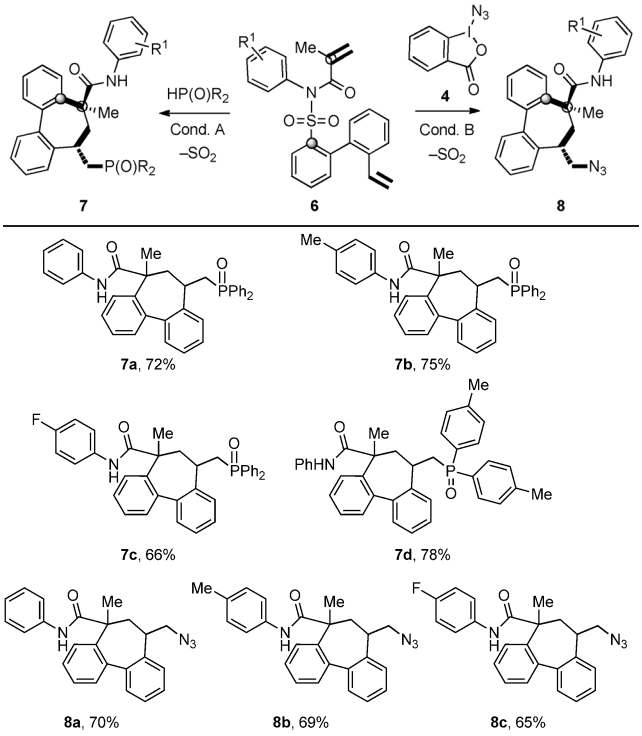
In the reaction cascades introducing an azide group, the corresponding indane products that stem from the variation of the electronic properties at the amide moiety **5b–i** were obtained with comparable efficiency to that observed for **5a**. In all cases, high stereoselectivities were observed with diastereomeric ratios between 11:1 and 8:1. Substrates with substituents at the terminal positions of both alkene moieties and N-alkyl-substituted substrates proved to be unreactive under these conditions. The structure of the product **5f** was confirmed by X-ray diffraction analysis, which proved the relative *trans* configuration between the azidomethyl substituent and the amide moiety.[18] We envisioned that extending the conjugation on the *ortho* substituents in the arylsulfonyl group could build up additional molecular complexity. We thus set out to investigate the reaction of *ortho*-vinyl benzene substituted substrates **6**. To our delight, under the conditions reported in Table 1, phosphonylated dibenzocycloheptadienes **7a–d** were obtained in good yields as

Table 1: Scope of the indane synthesis.[a,b,c,d]



[a] Reaction conditions A: **1** (1 equiv), $R_2P(O)H$ (2 equiv), $AgNO_3$ (10 mol%), MeCN (0.05 M), 80°C, 14 h. Reaction conditions B: **1** (1 equiv), **4** (2 equiv), CH_2Cl_2 (0.05 M), 60°C, 14 h. [b] Yields of isolated product after column chromatography on silica gel are reported for the single (**3**) or major (**5**) diastereoisomer. [c] Diastereoisomeric ratios were determined by ^1H NMR spectroscopy of the reaction crude. [d] We assumed that the stereochemistry of the obtained products is the same as the one shown in the scheme heading this table.

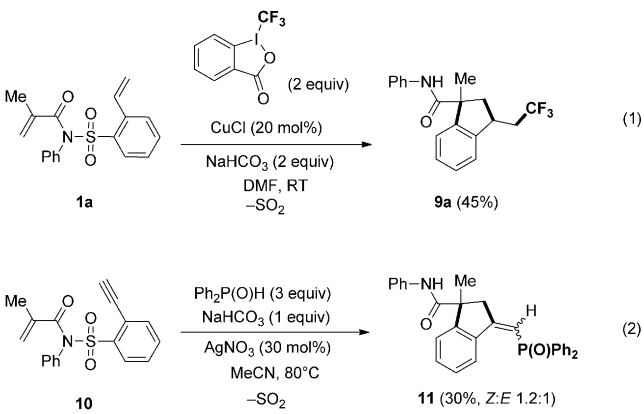
Table 2: Scope of the dibenzocycloheptadiene synthesis.[a,b,c]

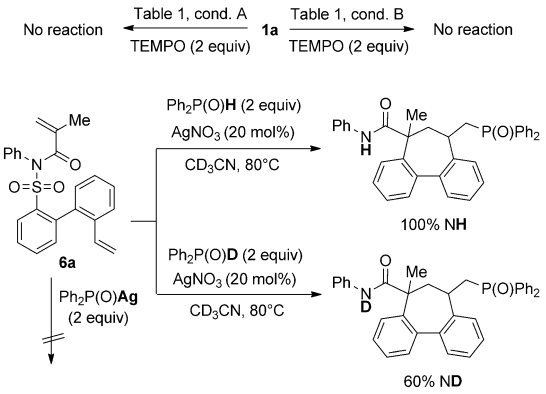


[a] Reaction conditions A and B: same as described in Table 1. [b] Yields of isolated products after column chromatography on silica gel are reported. [c] We assumed that the stereochemistry of the obtained products is the same as that shown in the scheme heading this table.

single diastereoisomers (Table 2). As in the previous case, the azidation reaction could be carried out in the absence of metal, so that azido-substituted dibenzocycloheptadienes **8a**–**c** were obtained in a completely stereoselective fashion.

To expand the synthetic utility of this methodology, the introduction of a trifluoromethyl group was attempted on substrate **1a** using CuCl as catalyst and 1-trifluoromethyl-1,2-benziodoxol-3-(1*H*)-one (Togni's reagent).[19] The corresponding trifluoromethylated indane **9a** could be isolated in 45% yield [Eq. (1)]. Interestingly, when the styrene unit was replaced by an acetylene group, the corresponding phosphonylated indene **11** could be isolated as a mixture of *Z*/*E* isomers (1.2:1) in 30% yield [Eq. (2)]. The structure of *Z*-**11** was confirmed by X-Ray diffraction analysis.[17,18]



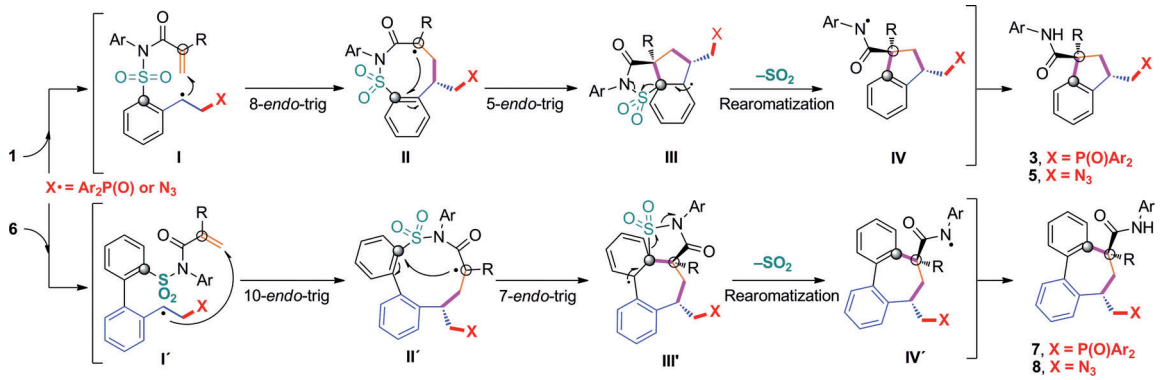


Scheme 2. Control experiments.

To investigate the mechanism of these transformations, control experiments were carried out (Scheme 2). The presence of TEMPO in both phosphonylation and azidation reactions of **1a** strongly inhibited the formation of the expected products, thus supporting the intervention of radicals in these processes. Deuterium-labeling experiments showed $Ph_2P(O)H$ as the key source of hydrogen in the reactions producing carbocycles **3** and **7**.[20] In addition, the stoichiometric reaction of **6a** with Ph_2POAg showed no conversion, thus ruling out the participation of this complex as a productive intermediate.

Based on these experiments, the following mechanism can be proposed (Scheme 3). In the first step, in situ generated radicals (X•) react exclusively with the activated styryl alkene of substrates **1** and **6**, forming a new C(sp^3)–X bond and benzylic stabilized radical intermediates **I** and **I′**, respectively.[12] Depending on the substrate, these intermediates can undergo a rare 8- or 10-*endo-trig* cyclization, generating alkyl α-keto radicals **II** and **II′**. A second 5- or 7-*ipso* cyclization of these radicals onto the carbon atom of the C(sp^2)–SO_2 group takes place in a highly stereoselective manner involving the concomitant 1,4 migration of the aryl sulfonyl group[21,22] in a Smiles-type rearrangement reaction[23] to give intermediates **III** and **III′**. This step sets up the relative *trans* configuration of the phosphonyl- or azidomethyl group and the amide moiety at the quaternary stereocenter of the final products. Rearomatization accompanied by extrusion of SO_2 and H abstraction by the amidyl radical intermediates **IV** and **IV′** delivers the observed indanes **3**/**5** or dibenzocycloheptadienes **7**/**8**, respectively. In the case of the silver-catalyzed phosphonylation reaction, a self-propagating radical cycle operates[11c] without the presence of an oxidant or a Ph_2POAg complex, in contrast to previously described oxidative phosphonylation reactions.[9,24]

In summary, we presented two highly stereoselective radical cascades that produce densely functionalized indanes and dibenzocycloheptadienes from *ortho*-vinyl- and *ortho*-vinylaryl-substituted *N*-(arylsulfonyl)acrylamides, respectively. Control experiments suggest the chemoselective addition of in situ generated heteroatom-centered radicals onto the styrenic olefin as a trigger of an unprecedented sequence of steps, resulting in the formation of a new C–X and two new C–C bonds. In addition, a formal 1,4-aryl migration, the



Scheme 3. Mechanistic proposal.

release of a molecule of SO_2, and the formation of a N–H bond result in the formation of the observed 5- and 7-membered ring carbocyclic products. Applications of these transformations toward the total synthesis of biologically active natural products are currently underway in our laboratory.

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[1] a) H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* **1994**, *94*, 2483–2547; b) Y. Li, D. Song, V. M. Dong, *J. Am. Chem. Soc.* **2008**, *130*, 2962–2964; c) A. Wang, H. Jiang, H. Chen, *J. Am. Chem. Soc.* **2009**, *131*, 3846–3847; d) M.-K. Zhu, J.-F. Zhao, T.-P. Loh, *J. Am. Chem. Soc.* **2010**, *132*, 6284–6285; e) B. C. Giglio, V. A. Schmidt, E. J. Alexanian, *J. Am. Chem. Soc.* **2011**, *133*, 13320–13322.

[2] a) G. Li, H.-T. Chang, K. B. Sharpless, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 451–454; *Angew. Chem.* **1996**, *108*, 449–452; b) E. J. Alexanian, C. Lee, E. J. Sorensen, *J. Am. Chem. Soc.* **2005**, *127*, 7690–7691; c) G. Liu, S. S. Stahl, *J. Am. Chem. Soc.* **2006**, *128*, 7179–7181; d) L. V. Desai, M. S. Sanford, *Angew. Chem. Int. Ed.* **2007**, *46*, 5737–5740; *Angew. Chem.* **2007**, *119*, 5839–5842; e) P. H. Fuller, J.-W. Kim, S. R. Chemler, *J. Am. Chem. Soc.* **2008**, *130*, 17638–17639; f) K. Muñiz, A. Iglesias, Y. Fang, *Chem. Commun.* **2009**, 5591–5593; g) H. M. Lovick, F. E. Michael, *J. Am. Chem. Soc.* **2010**, *132*, 1249–1251; h) T. de Haro, C. Nevado, *Angew. Chem. Int. Ed.* **2011**, *50*, 906–910; *Angew. Chem.* **2011**, *123*, 936–940; i) H. Wang, Y. Wang, D. Liang, L. Liu, J. Zhang, Q. Zhu, *Angew. Chem. Int. Ed.* **2011**, *50*, 5678–5681; *Angew. Chem.* **2011**, *123*, 5796–5799.

[3] a) K. Muñiz, C. H. Hovelmann, E. Campos-Gomez, J. Barluenga, J. M. Gonzalez, J. Streuff, M. Nieger, *Chem. Asian J.* **2008**, *3*, 776–788; b) S. Qiu, T. Xu, J. Zhou, Y. Guo, G. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 2856–2857; c) M. T. Bovino, S. R. Chemler, *Angew. Chem. Int. Ed.* **2012**, *51*, 3923–3927; *Angew. Chem.* **2012**, *124*, 3989–3993; d) X. Ji, H. Huang, W. Wu, H. Jiang, *J. Am. Chem. Soc.* **2013**, *135*, 5286–5289; e) W. Kong, P. Feige, T. de Haro, C. Nevado, *Angew. Chem. Int. Ed.* **2013**, *52*, 2469–2473; *Angew. Chem.* **2013**, *125*, 2529–2533; f) Z. Li, L. Song, C. Li, *J. Am. Chem. Soc.* **2013**, *135*, 4640–4643.

[4] a) R. Chung, E. Yu, C. D. Incarvito, D. J. Austin, *Org. Lett.* **2004**, *6*, 3881–3884; b) D. A. Kamble, P. U. Karabal, P. V. Chouthaiwale, A. Sudalai, *Tetrahedron Lett.* **2012**, *53*, 4195–4198.

[5] a) M. V. Vita, J. Waser, *Org. Lett.* **2013**, *15*, 3246–3249; b) B. Zhang, A. Studer, *Org. Lett.* **2013**, *15*, 4548–4551.

[6] a) P. V. Chouthaiwale, P. U. Karabal, G. Suryavanshi, A. Sudalai, *Synthesis* **2010**, 3879–3882; b) Z. Li, C. Zhang, L. Zhu, C. Liu, C. Li, *Org. Chem. Front.* **2014**, *1*, 100–104.

[7] C. Zhang, Z. Li, L. Zhu, L. Yu, Z. Wang, C. Li, *J. Am. Chem. Soc.* **2013**, *135*, 14082–14085.

[8] E. Merino, C. Nevado, *Chem. Soc. Rev.* **2014**, *43*, 6598–6608, and references therein.

[9] a) M. L. E. N. da Mata, W. B. Motherwell, F. Ujjainwalla, *Tetrahedron Lett.* **1997**, *38*, 137–140; b) M. L. E. N. da Mata, W. B. Motherwell, F. Ujjainwalla, *Tetrahedron Lett.* **1997**, *38*, 141–144; c) C. R. A. Godfrey, P. Hegarty, W. B. Motherwell, M. K. Uddin, *Tetrahedron Lett.* **1998**, *39* 723–726; d) Y.-M. Li, M. Sun, H.-L. Wang, Q.-P. Tian, S.-D. Yang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3972–3976; *Angew. Chem.* **2013**, *125*, 4064–4068; e) Y.-R. Chen, W. L. Duan, *J. Am. Chem. Soc.* **2013**, *135*, 16754–16757.

[10] a) P. Renaud, C. Ollivier, P. Panchaud, *Angew. Chem. Int. Ed.* **2002**, *41*, 3460–3462; *Angew. Chem.* **2002**, *114*, 3610–3612; b) P. Panchaud, C. Ollivier, P. Renaud, S. Zigmantas, *J. Org. Chem.* **2004**, *69*, 2755–2759; c) K. Weidner, A. Giroult, P. Panchaud, P. Renaud, *J. Am. Chem. Soc.* **2010**, *132*, 17511–17515; d) K. Matcha, R. Narayan, A. P. Antonchick, *Angew. Chem. Int. Ed.* **2013**, *52*, 7985–7989; *Angew. Chem.* **2013**, *125*, 8143–8147; e) X.-H. Wei, Y.-M. Li, A.-X. Zhou, T.-T. Yang, S.-D. Yang, *Org. Lett.* **2013**, *15*, 4158–4161.

[11] a) W. Kong, M. Casimiro, E. Merino, C. Nevado, *J. Am. Chem. Soc.* **2013**, *135*, 14480–14483; b) W. Kong, M. Casimiro, N. Fuentes, E. Merino, C. Nevado, *Angew. Chem. Int. Ed.* **2013**, *52*, 13086–13090; *Angew. Chem.* **2013**, *125*, 13324–13328; c) W. Kong, E. Merino, C. Nevado, *Angew. Chem. Int. Ed.* **2014**, *53*, 5078–5082; *Angew. Chem.* **2014**, *126*, 5178–5182.

[12] a) P. Renaud, M. Gerster, *Angew. Chem. Int. Ed.* **1998**, *37*, 2562–2579; *Angew. Chem.* **1998**, *110*, 2704–2722; b) *Radicals in Organic Synthesis, Vols. 1 and 2* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**; c) G. J. Rowlands, *Tetrahedron* **2009**, *65*, 8603–8655; d) G. J. Rowlands, *Tetrahedron* **2010**, *66*, 1593–1636; e) G. Bar, A. F. Parsons, *Chem. Soc. Rev.* **2003**, *32*, 251–263; f) M. P. Sibi, S. Manyem, J. Zimmerman, *Chem. Rev.* **2003**, *103*, 3263–3696; g) M. Albert, L. Fensterbank, E. Lacote, M. Malacria in *Topics in Current Chemistry, Vol. 264* (Ed.: A. Gansauer), Springer, Heidelberg, **2006**, pp. 1–62; h) E. Yoshioka, S. Kohtani, K. Sawai, Kentefu, E. Tanaka, H. Miyabe, *J. Org. Chem.* **2012**, *77*, 8588–8604; i) H. Subramanian, Y. Landais, M. P. Sibi in *Comprehensive Organic Synthesis* (Eds.: G. Molander, P. Knochel), 2nd ed., Elsevier, Oxford, **2013**.

[13] a) C. Zhong, J. Zhu, J. Chang, X. Sun, *Tetrahedron Lett.* **2011**, *52*, 2815 – 2817; b) F. Klotter, A. Studer, *Angew. Chem. Int. Ed.* **2014**, *53*, 2473 – 2476; *Angew. Chem.* **2014**, *126*, 2505 – 2509.
[14] Y. Murakami, M. Shoji, A. Hirata, S. Tanaka, I. Yokoe, S. Fujisawa, *Arch. Biochem. Biophys.* **2005**, *434*, 326 – 332.
[15] a) S. Sapra, Y. Bhalla, Nandani, S. Sharma, G. Singh, K. Nepali, A. Budhiraja, K. Dhar, *Med. Chem. Res.* **2013**, *22*, 531 – 547; b) N. S. Sitnikov, A. Y. Fedorov, *Russ. Chem. Rev.* **2013**, *82*, 393; c) S. Larsson, N. Ronsted, *Curr. Top. Med. Chem.* **2014**, *14*, 274 – 289.
[16] a) B. Bonnaud, P. Funes, N. Jubault, B. Vacher, *Eur. J. Org. Chem.* **2005**, 3360 – 3369; b) B. Bonnaud, N. Mariet, B. Vacher, *Eur. J. Org. Chem.* **2006**, 246 – 256; c) S. Bhowmik, S. Khanna, K. Srivastava, M. Hasanain, J. Sarkar, S. Verma, S. Batra, *ChemMedChem* **2013**, *8*, 1767 – 1772; d) M. Egi, K. Shimizu, M. Kamiya, Y. Ota, S. Akaia, *Chem. Commun.* **2015**, *51*, 380 – 383.
[17] See the Supporting Information.
[18] CCDC 997143 (**5 f**) and 1010646 (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[19] P. Eisenberger, S. Gischig, A. Togni, *Chem. Eur. J.* **2006**, *12*, 2579 – 2586.
[20] In the reactions with reagent **4**, traces of water in the reaction media could be responsible for the formation of the N–H bond. See Ref. [11c].
[21] a) A. Studer, M. Bossart, *Tetrahedron* **2001**, *57*, 9649 – 9667; b) A. Gheorghe, B. Quiclet-Sire, X. Vila, S. Z. Zard, *Org. Lett.* **2005**, *7*, 1653 – 1656; c) J. Sandoval-Lira, J. M. Hernandez-Perez, F. Sartillo-Piscil, *Tetrahedron Lett.* **2012**, *53*, 6689 – 6693; d) W. Thaharn, D. Soorukram, C. Kuhakarn, P. Tuchinda, V. Reutrakul, M. Pohmakotr, *Angew. Chem. Int. Ed.* **2014**, *53*, 2212 – 2215; *Angew. Chem.* **2014**, *126*, 2244 – 2247.
[22] For additional recent examples of radical-mediated aryl migrations, see: a) P. Gao, Y. W. Shen, R. Fang, X. H. Hao, Z. H. Qiu, F. Yang, X. B. Yan, Q. Wang, X. J. Gong, X. Y. Liu, Y. M. Liang, *Angew. Chem. Int. Ed.* **2014**, *53*, 7629 – 7633; *Angew. Chem.* **2014**, *126*, 7759 – 7763; b) X. W. Liu, F. Xiong, X. P. Huang, L. Xu, P.-F. Li, X.-X. Wu, *Angew. Chem. Int. Ed.* **2013**, *52*, 6962 – 6966; *Angew. Chem.* **2013**, *125*, 7100 – 7104; c) Z.-M. Chen, W. Bai, S. H. Wang, B. M. Yang, Y. Q. Tu, F. M. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 9781 – 9785; *Angew. Chem.* **2013**, *125*, 9963 – 9967; d) H. Egami, R. Shimizu, Y. Usui, M. Sodeoka, *Chem. Commun.* **2013**, *49*, 7346 – 7348.
[23] For a review on Smiles rearrangements, see: a) T. J. Snape, *Chem. Soc. Rev.* **2008**, *37*, 2452 – 2458. See also: b) E. Bacqué, M. El Qacemi, S. Z. Zard, *Org. Lett.* **2005**, *7*, 3817 – 3820; c) A. J. Clark, S. R. Coles, A. Collis, D. R. Fullaway, N. P. Murphy, P. Wilson, *Tetrahedron Lett.* **2009**, *50*, 6311 – 6314; d) V. Rey, A. B. Pierini, A. B. Peñéñory, *J. Org. Chem.* **2009**, *74*, 1223 – 1230; e) M. Pudlo, I. Allart-Simon, B. Tinant, S. Gérard, J. Sapi, *Chem. Commun.* **2012**, *48*, 2442 – 2444.
[24] a) S. Thielges, P. Bisseret, J. Eustache, *Org. Lett.* **2005**, *7*, 681 – 684; b) A. Kondoh, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2007**, *129*, 4099 – 4104; c) C. Huang, X. Tang, H. Fu, Y. Jiang, Y. Zhao, *J. Org. Chem.* **2006**, *71*, 5020 – 5022.

