DOI: 10.1002/ejoc.201101463

Sulfur–Nitrogen and Carbon–Nitrogen Bond Formation by Intermolecular Imination and Amidation without Catalyst

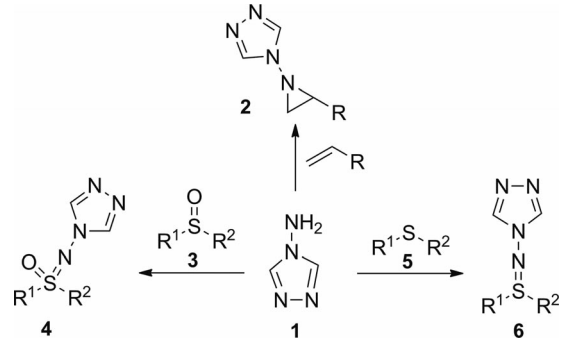
Wen Bo Ma,[a] Sheng Nan Li,[a][‡] Zhong Hua Zhou,[a] Heng Shui Shen,[a] Xue Li,[a] Qiu Sun,[a] Ling He,*[a] and Ying Xue*[b]

Keywords: Nitrogen heterocycles / Nitrenes / Reaction mechanisms / Insertion / C-N coupling / S-N coupling

Imination and amidation of sulfides, sulfoxides, and olefins using 4*H*-1,2,4-triazole-4-amine as a nitrogen source with $PhI(OAc)_2$ as an oxidant were achieved in moderate to high yields without the addition of a catalyst. The carbon–nitrogen and sulfur–nitrogen bond forming reactivity is consistent with a nitrene insertion mechanism in which the reactivity generally increases with decreasing N–H bond dissociation energy of the nitrogen source and increasing oxidation potential of the oxidant.

Introduction

An efficient and convenient procedure for the direct formation of sulfur–nitrogen and carbon–nitrogen bonds is a powerful synthetic approach[1] to regioselective functionalization of sulfides, sulfoxides,[2] and hydrocarbons.[3–5] Such processes are increasingly attractive as synthetic routes to aziridines,[3] amides, or imines, the derivatives of which have been used as building blocks for the construction of heterocyclic compounds and the preparation of chiral ligands. Furthermore, such an approach can play a key role in the preparation of many pharmacologically active compounds.[5o,5p] Stereogenic sulfur atoms can be used as building blocks in bioactive molecules and pseudopeptides, chiral auxiliaries for asymmetric synthesis, and ligands for enantioselective metal catalysis.[6] Most synthetic methods, however, depend upon the use of toxic and potentially explosive reagents such as hydrazoate[7] and *O*-mesitylenesulfonyl-hydroxylamine,[8] and typically require expensive metal-based catalysts.[9–12] Amidation reactions involving nitrogen-heterocycle-containing nitrogen sources are rare.[13] Thus, establishing a reaction system that functions in the absence of catalyst and using 4-amino-4*H*-1,2,4-triazole as a nitrogen source should be significant for the development of an efficient and convenient methodology for the formation of nitrogen-containing compounds. Many kinds of natural products, pharmaceutical compounds, and insecticides are heterocyclic molecules that contain a polyazole unit.[14] It is thus important to synthesize polyazoles derivatives through a convenient route with high yields.[14i] With this aim in mind and because of our interest in synthesizing potentially bioactive nitrogenous compounds, we decided to study a new reaction system for the insertion reaction to olefins, sulfoxides, and sulfides using 4-amino-4*H*-1,2,4-triazole as nitrogen source. In this paper, we present the first examples of the intermolecular imination of sulfides and expand the intermolecular imination of sulfoxides and the aziridination of alkenes through the direct use of 4-amino-4*H*-1,2,4-triazole as nitrogen source and $PhI(OAc)_2$ as oxidant under mild conditions (Scheme 1).

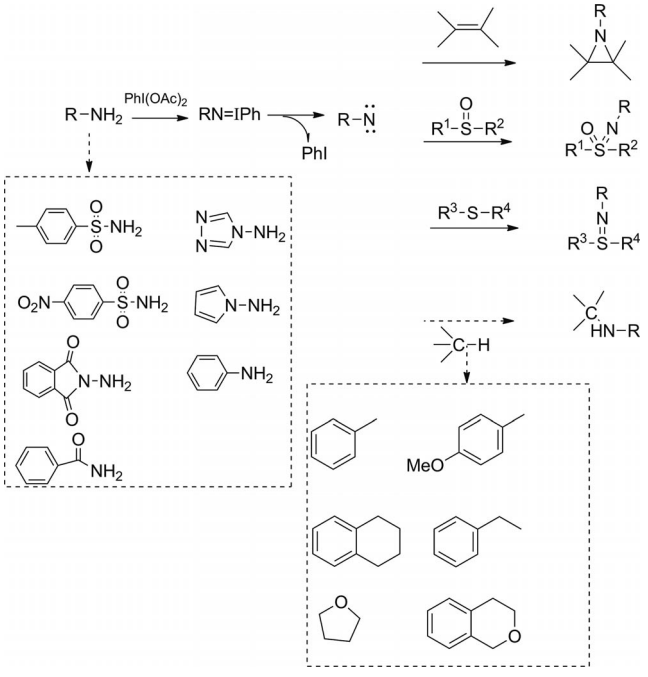


Scheme 1. Functionalization of olefins and sulfides using 4-amine-4*H*-1,2,4-triazole as nitrogen source.

With our interest in synthesizing potentially bioactive nitrogenous compounds and in the construction of new sulfur–nitrogen and carbon–nitrogen bonds, we focused on

[a] Key Laboratory of Drug-Targeting and Drug-Delivery Systems of the Ministry of Education, Department of Medicinal Chemistry, West China School of Pharmacy, Sichuan University,
Chengdu, Sichuan 610041, P. R. of China
Fax: +86-28-85502940
E-mail: lhe2001@sina.com
[b] College of Chemistry, Sichuan University,
Chengdu 610064, P. R. of China
E-mail: yxue@scu.edu.cn
[‡] Joint first author.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201101463.

expanding the scope of nitrogen sources and optimizing the amidation reaction. Only a few suitable nitrogen sources have been reported in the literature, such as trifluoroacetamide, 4-nitrobenzene-sulfonamide or *p*-tosylamide[4,9] *N*-tosyliminophenyl-iodinane (PhI=NTs),[5] Bromamine-T[15] or Chloroamine-T, 2-amino-isoindoline-1,3-dione, and azide[16] compounds. Investigations on their chemistry, particularly with regard to reactions with alkenes, sulfoxides, and sulfides, which could provide valuable insight into the reactivity of amidation reactions, are thus important. To gain further insight into the mode of C–H bond amidation and the formation of sulfur–nitrogen bonds, it was considered of interest to examine the effect of N–H bond dissociation energies of nitrogen sources. The dissociation energies of the N–H bond, to the best of our knowledge, have not hitherto been probed in the context of amidation reactions. Thus, in this paper, we report the effect of bond dissociation energies of N–H bonds on amidation reactions. In addition, the effect of the oxidant on the nitrogen source and substrate was also studied. Furthermore, the intermolecular amidation of sulfides, olefins, and saturated C–H bonds with a series of nitrene sources was also examined and their relative reactivity was compared (Scheme 2). These studies have led to an improvement in the efficiency of amidation reactions and to the discovery of nitrene-transfer reaction rules for the insertion of N–R units into a variety of substrates. We have exploited the insertion reaction to develop a novel metal-catalyst-free imination of sulfides and aziridination of olefins. This metal-free approach continues a tendency toward green chemistry for the formation of C–N and S–N bonds.



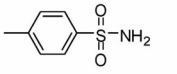
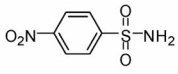
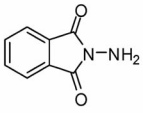
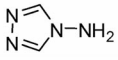
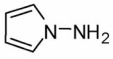
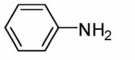
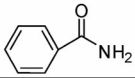
Scheme 2. Nitrene source and substrates employed for the amidation and imination by nitrene insertion.

Results and Discussion

Effects of N–H Bond Dissociation Energies of Nitrene Source

We investigated the effect of N–H dissociation energies on the reactivity of the amidation reaction. Styrene was employed as a model substrate for the amidation in dichloromethane with $PhI(OAc)_2$ as oxidant at room temperature without any catalyst. Amines **n3** and **n4** (Table 1, entries 3 and 4) were the most effective for the amidation, but the reaction hardly proceeded using amines **n1** or **n2** (Table 1, entries 1 and 2) as nitrogen source under the same reaction condition, unless under catalysis.[17] The aziridination of styrene in dichloromethane using amines **n5** or **n6** (Table 1, entries 5 and 6) as nitrogen sources only resulted in the formation of oxidized mixtures of amines. When amine **n7** was treated with $PhI(OAc)_2$ under identical conditions, the reaction rate was fast and only Hoffman rearrangement product (aniline) was obtained in the reaction system. It is thus clear that the N–H dissociation energies effect on the reaction may be primarily linked with the stability of the nitrogen source in the reaction system. Next, the reaction may be linked with magnitude of N–H dissociation energies (Figure 1).

Table 1. Calculated bond dissociation energies at different levels of theory [kcal/mol].

Entry	Amine		Method 1[a]	Method 2[b]
1		n1	210.6	215.5
2		n2	212.9	217.9
3		n3	174.2	181.3
4		n4	176.8	183.9
5		n5	168.1	175.4
6		n6	207.6	217.4
7		n7	204.7	209.6

[a] At UB3LYP/6-31+G(d,p) level of theory. [b] At UB3P86-6-311++G(2df,2p)//UB3L YP/6-31+G(d,p) level of theory.

All the calculations were performed using Gaussian 03 program.[18] Geometry optimization was carried out without any constraint at the UB3LYP/6-31+G(d,p)[19,20] level of theory (Method 1). Each optimized structure was confirmed by harmonic frequency analysis at the same calculational level as a true minimum with no imaginary fre-

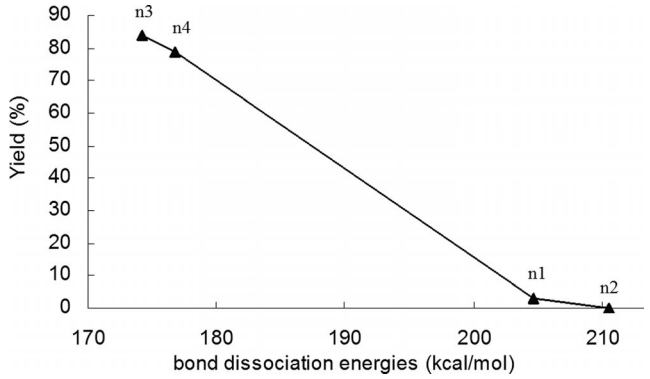


Figure 1. Influence of the bond dissociation energies on yield. The reactivity of the amidation reaction increases with decreasing bond dissociation energies. The amidation of styrene carried out in the absence of a catalyst at 0–30 °C for 20 h using CH_2Cl_2 as solvent, $PhI(OAc)_2$ as oxidant, and **n1**–**n7** as nitrogen source.

quency. The frequency calculations without scaling also provided thermodynamic quantities such as the zero-point vibrational energy, thermal correction, enthalpies, Gibbs free energies, and entropies at a temperature of 298.15 K and pressure of 101325 Pa. The single-point calculations at the UB3P86-6-311++G(2df,2p) level[20] were performed on the basis of the geometrical structures optimized at the B3LYP/6-31+G(d,p) level (Method 2). Note that the enthalpies of each species obtained were calculated using the electronic energies obtained using Methods 1 and 2 added to the enthalpy correction obtained in the B3LYP/6-31+G(d,p) method, respectively. The bond dissociation energies (BDEs) of N–H were calculated as the enthalpy change of the following reaction at 298.15 K and 101.325 kPa.[21]

$$RNH_2^{(g)} \rightarrow :NR^{(g)} + 2H^{\cdot(g)} \quad (1)$$

That is:

$$BDE = H(:NR^{(g)}) + 2H(H^{\cdot(g)}) - H(RNH_2^{(g)}) \quad (2)$$

Effect of Oxidant

Besides $PhI(OAc)_2$, oxidants $PhI(OCOCF_3)_2$, PhI=O, MnO_2, HgO, *m*-chloroperoxybenzoic acid (*m*-CPBA), *N*-bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) were also employed in the amidation or imination reaction. $PhI(OAc)_2$ and $PhI(OCOCF_3)_2$ were the most effective for the imination of sulfides and aziridination of olefins under similar conditions.

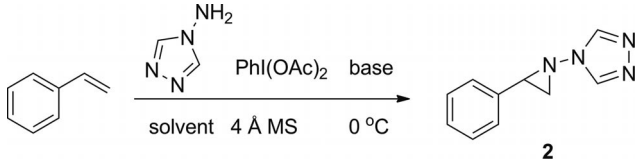
Effect of Substrate

The effect of substrates was investigated using several different substrates under strictly identical conditions. When substrates such as sulfides, olefins, allylic saturated hydrocarbons, ethers, and arenes were treated with the $PhI(OAc)_2$/RNH_2/CH_2Cl_2 system under a nitrogen atmosphere, the activity of allylic saturated hydrocarbons, ethers, and arenes for amidation reactions was low and only starting materials were recovered after reaction times of several hours. However, interestingly, only sulfides and olefins were found to react regioselectively in the imination of sulfides and aziridination of olefins under similar conditions.

Aziridination of Olefins

To evaluate the efficiency of the oxidant and solvent, the aziridination reaction of styrene with 4-amino-4*H*-1,2,4-triazole using PhI $(OAc)_2$ as oxidant was studied by using different molecular ratios, base, and solvents; the results are shown in Table 2. Our studies showed that the best yields were obtained when 4 equiv. $PhI(OAc)_2$ was employed as the oxidant with a substrate/base/$PhI(OAc)_2$/4-amino-4*H*-1,2,4-triazole ratio of 1:6.0:4.0:4.0, in the presence of powdered molecular sieves (4 Å) in CH_2Cl_2 at 0 °C for 20 h; under these conditions, the aziridine derivatives were obtained with moderate to high yield.

Table 2. Optimization of reaction conditions.



Entry	Base	Ratio (I:II:III:IV)[a]	Solvent	% Yield[b]
1	–	1:2.0:2.0:2.0	CH_2Cl_2	47
2	Al_2O_3	1:2.0:2.0:2.0	CH_2Cl_2	53
3	K_2CO_3	1:2.0:2.0:2.0	CH_2Cl_2	64
4	*t*BuOK	1:2.0:2.0:2.0	CH_2Cl_2	51
5	*t*BuOK	1:4.5:3.0:3.0	CH_2Cl_2	75
6	*t*BuOK	1:6.0:4.0:4.0	CH_2Cl_2	79
7	*t*BuOK	1:7.5:5.0:5.0	CH_2Cl_2	74
8	*t*BuOK	1:6.0:4.0:4.0	CH_3CN	32
9	*t*BuOK	1:6.0:4.0:4.0	$ClCH_2CH_2Cl$	61
10	*t*BuOK	1:6.0:4.0:4.0	THF	trace
11	*t*BuOK	1:6.0:4.0:4.0	DMF	trace
12	*t*BuOK	1:6.0:4.0:4.0	DMSO	trace

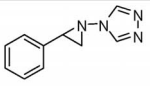
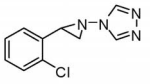
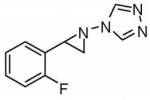
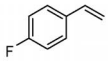
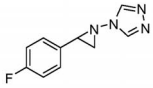
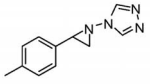
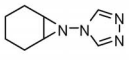
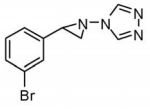
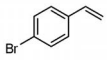
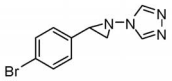
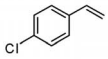
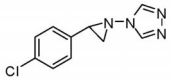
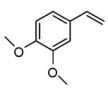
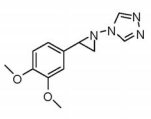
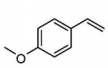
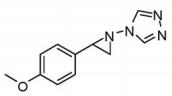
[a] Reagents and conditions: I (alkene)/II (base)/III [$PhI(OAc)_2$]/IV (4-amino-4*H*-1,2,4-triazole), solvent (10 mL), 0 °C, 20 h. [b] Isolated yield.

When using styrene as a substrate, with a substrate/base/$PhI(OAc)_2$/4-amino-*4H*-1,2,4-triazole molecular ratio of 1:2.0:2.0:2.0, the product 4-(2-phenylaziridin-1-yl)-4*H*-1,2,4-triazole was obtained with 53% yield (Table 2, entry 2). The reactivity of aziridination increased with increasing amounts of 4-amino-4*H*-1,2,4-triazole and $PhI(OAc)_2$. The yield was dramatically raised to 79% (Table 2, entry 6) by using 4-amino-4*H*-1,2,4-triazole as nitrogen source and $PhI(OAc)_2$ as oxidant, with alkene/*t*BuOK/$PhI(OAc)_2$/4-amino-4*H*-1,2,4-triazole in a molecular ratio of 1:6.0:4.0:4.0. Upon examining the effect of bases, it was found that *t*BuOK was more effective than other bases at lower temperature. When the effect of temperature on the aziridination reaction was also tested, it was found that the amidation reaction was best performed at 0 °C; when the temperature was increased to 30 °C, the yield of 4-(2-phen-

ylaziridin-1-yl)-4*H*-1,2,4-triazole decreased to trace amounts. In addition, the use of molecule sieves (4 Å) was found to be helpful for the aziridination reactions. Finally, it was established that dichloromethane was more effective than other solvents under identical reaction conditions.

To test the universality of the reaction system, several different olefins were examined. Most substrates gave the corresponding product with moderate to high yields (Table 3, entries 1, 4, 5, and 9–11). However, use of styrene derivatives with electron-withdrawing substituents in the *ortho*-position resulted in low yields (Table 3, for example, entries 2 and 3) under identical conditions. Cyclohexene did not give the product with high yield in the reaction system (Table 3, entry 6).

Table 3. Aziridination of olefins.[a]

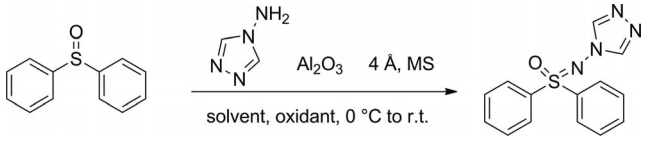
Entry	Substrate	Product		Yield, %[b]
1			**2a**	79
2			**2b**	45
3			**2c**	32
4			**2d**	75
5			**2e**	80
6			**2f**	38
7			**2g**	38
8			**2h**	48
9			**2i**	63
10			**2j**	56
11			**2k**	85

[a] Reagents and conditions: alkenes/4-amino-4*H*-1,2,4-triazole/PhI(OAc)$_2$/*t*BuOK ratio 1:4.0:4.0:6.0, CH_2Cl_2 (10 mL), 0 °C, 20 h. [b] Isolated yield.

Imination of Sulfoxides and Sulfides with 4-Amino-4*H*-1,2,4-triazole

Sulfoxide and sulfide derivatives can also undergo an insertion reaction with 4-amino-4*H*-1,2,4-triazole as nitrogen source to give the corresponding 4-(2-phenylaziridin-1-yl)-4*H*-1,2,4-triazole derivatives, which can play a key role in the synthesis of bioactive compounds. Thus, we examined the insertion reaction of 4-amino-4*H*-1,2,4-triazole with a series of sulfoxides and sulfides in CH_2Cl_2. At the beginning of this work, to evaluate the efficiency of the oxidant and solvent, the imination reaction of diphenyl sulfoxide with 4-amino-4*H*-1,2,4-triazole was studied by using a range of oxidants and solvents; the results were shown in Table 4. It was found that only PhI(OAc)$_2$ and PhI(OCOCF$_3$)$_2$ could be used as oxidant for the imination of sulfoxides; other oxidants, such as PhI=O, MnO_2 and HgO, were much less effective.

Table 4. Optimization of oxidant and solvent.[a]



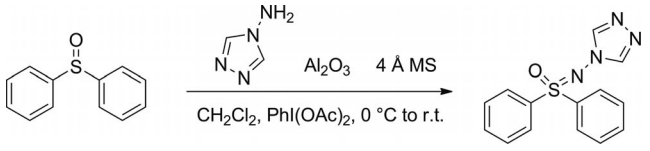
Entry	Solvent	Oxidant	% Yield[b] (conv.)
1	DMF	PhI(OAc)$_2$	85 (33)
2	CH_2Cl_2	PhI(OAc)$_2$	91 (39)
3	CH_3CN	PhI(OAc)$_2$	88 (35)
4	THF	PhI(OAc)$_2$	trace
5	dioxane	PhI(OAc)$_2$	trace
6	CH_2Cl_2	PhI(OCOCF$_3$)$_2$	90 (39)
7	CH_2Cl_2	PhI=O	trace
8	CH_2Cl_2	MnO_2	–
9	CH_2Cl_2	HgO	–

[a] Reagents and conditions: substrate/4-amino-4*H*-1,2,4-triazole/oxidant ratio 1:3.0:3.0, 0 °C to room temp., 2 h. [b] Isolated yield.

With the same procedure, several molecular ratios of substrate/4-amino-4*H*-1,2,4-triazole/PhI(OAc)$_2$, and reaction times were tested in CH_2Cl_2 in the presence of Al_2O_3 and 4 Å molecule sieves; the results are listed in Table 5. Increasing the molecular ratio of substrate/4-amino-4*H*-1,2,4-triazole/PhI(OAc)$_2$ lead to an increase in substrate conversion and product yield (Table 5, entries 5–7). Furthermore, the use of excess PhI(OAc)$_2$ was found to be favorable to the yield. When using sulfinyldibenzene (**3c**) as a substrate with **3c**/4-amino-4*H*-1,2,4-triazole/PhI(OAc)$_2$ in a molecular ratio of 1:1.5:1.5, the product dibenzyl-*N*-(1,2,4-triazol-4-yl)sulfoximine was obtained with 77% yield (Table 5, entry 2). The yield was increased to 89% (Table 5, entry 5) by adding 4-amino-4*H*-1,2,4-triazole/PhI (OAc)$_2$ to 3–4 equiv. Therefore, the results shown in Table 5 demonstrate that the reactivity of imination increases with the amount of 4-amino-4*H*-1,2,4-triazole/PhI(OAc)$_2$. We also examined the effect of temperature, and it was found that longer reaction times were needed to achieve similar yields at lower temperatures (Table 5, entry 1). Increase in temperature (60 °C)

led to a decrease in reaction yield (Table 5, entry 4). The inclusion of Al_2O_3 and molecular sieves (4 Å) were found to be helpful for the imination reactions.

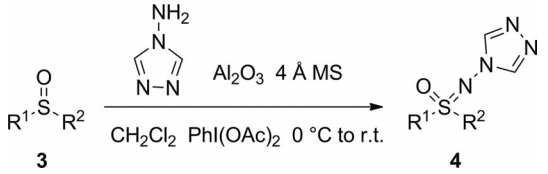
Table 5. Optimization of imination reaction conditions with sulfoxides.



Entry	T [°C]	Molar ratio of substrate/ N-source/$PhI(OAc)_2$	Time [h]	% Yield (conv.)
1	0	1:1.5:1.5	10	75 (30)
2	r.t.	1:1.5:1.5	2	77 (31)
3	40	1:1.5:1.5	2	67 (27)
4	60	1:1.5:1.5	2	48 (13)
5	r.t.	1:3.0:3.0	2	91 (39)
6	r.t.	1:4.0:4.0	2	87 (40)
7	r.t.	1:5.0:5.0	2	89 (38)

To test the universality of the metal-catalyst-free reaction system, we applied several sulfoxides and sulfides to the imination reaction. Almost all the substrates gave the corresponding products with good yields, however, the conversions were moderate (Tables 6 and 7, entries 1, 2, and 4). In addition, the conversion of sulfinyldibenzene (Table 6, entry 3) was increased from 39 to 63% in the presence of *t*BuOK at 0 °C for 4 h. Nevertheless, other sulfoxides gave more than 90% conversion and only trace amounts of corresponding products **4** under these reaction conditions. The nucleophilic sulfides showed higher reactivity than sulfoxides, giving the corresponding sulfilimines in good yields (Table 7, entries 3, 5, 6, 7, and 8) under the same reaction conditions. From these results, we can conclude that this method could provide a convenient way to prepare sulfoximines and sulfilimines from either sulfoxides or sulfides through the use of simple, commercially available reagents by a metal-catalyst-free imination reaction.

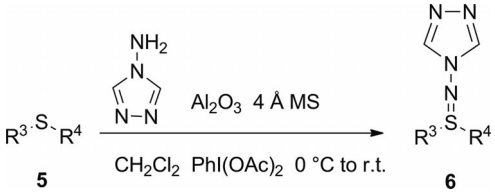
Table 6. Imination of sulfoxides with 4-amino-4*H*-1,2,4-triazole.[a]



Entry	R^1	R^2	Product	% Yield[b] (conv.)
1	Me	Me	**4a**	51
2	Bu	Bu	**4b**	89 (52)
3	Ph	Ph	**4c**	91 (63)[c]
4	Bn	Bn	**4d**	97 (48)
5	Ph	Me	**4e**	86 (52)
6	Ph	Bu	**4f**	71 (51)
7	Ph	Bn	**4g**	84 (56)
8	hexyl	hexyl	**4h**	84 (51)
9		$(-CH_2CH_2-)_2$	**4i**	96 (55)
10	Ph	*p*-C_6H_4-NO_2	**4j**	81 (52)
11	Ph	CH_2CH_2CN	**4k**	91 (65)

[a] Reagents and conditions: sulfoximine/4-amino-4*H*-1,2,4-triazole/$PhI(OAc)_2$/Al_2O_3 ratio 1.0:3.0:3.0:4.0, CH_2Cl_2 (10 mL), room temperature, 2 h. [b] Isolated yield. [c] The reaction was performed with sulfoximine/4-amino-4*H*-1,2,4-triazole/$PhI(OAc)_2$/*t*BuOK ratio 1.0:3.0:3.0:3.0, CH_2Cl_2, 0 °C, 4 h.

Table 7. Imination of sulfides derivatives.[a]



Entry	R^3	R^4	Product	% Yield[b] (conv.)
1	phenothiazine (PHT)		**6a**	85 (40)
2	Bu	Bu	**6b**	85 (52)
3	Ph	Bn	**6c**	98 (67)
4	Ph	allyl	**6d**	77 (51)
5	Ph	*p*-C_6H_4-NO_2	**6e**	95 (75)
6	Ph	Bu	**6f**	93 (74)
7	Ph	*o*-C_6H_4-NO_2	**6g**	91 (65)
8	(*p*-$COOCH_3$)Ph	Me	**6h**	88 (100)
9	Ph	Py	**6i**	40 (66)

[a] Reagents and conditions: sulfoximine/4-amino-*4H*-1,2,4-triazole/$PhI(OAc)_2$/Al_2O_3 ratio 1.0:3.0:3.0:4.0, CH_2Cl_2 (10 mL), room temperature, 2 h. [b] Isolated yield.

C–H Functionalization Reaction

The intermolecular amidation of saturated C–H bonds using 4-amino-4*H*-1,2,4-triazole as a nitrene source was also examined. Thus, α-saturated C–H bonds of ethers and allylic sp^3 C–H bonds of hydrocarbons such as tetrahydrofuran, 3,4-dihydro-1*H*-isochromene, 1,2,3,4-hydronaphthalene, and toluene were used as substrates with a substrate/4-amino-4*H*-1,2,4-triazole/$PhI(OAc)_2$ molecular ratio of 1:3.0:3.0 in CH_2Cl_2 at room temp. for 24 h under a nitrogen atmosphere. Unfortunately, activities for the C–H insertion reaction were low, and only starting materials were recovered. With the same procedure, several oxidants, such as HgO, MnO_2, $PhI(CF_3CO)_2$, and PhI=O were tested, however, the formation of amidation product was still not observed.

Conclusions

We have demonstrated a convenient and efficient procedure for the formation of sulfur–nitrogen bonds (Table 6, entries 3 and 11, Table 7, entries 3, and 5–8) and carbon–nitrogen bonds (Table 3, entries 1, 4, 5, 9, and 11) by direct reaction with 4-amino-4*H*-1,2,4-triazole using $PhI(OAc)_2$ as oxidant in the absence of a catalyst under mild conditions. These methods utilize the infrequently used nitrene-transfer reaction and subsequent insertion to introduce polyazoles units into carbon–carbon double bonds and sulfides. The nitrene insertion reactivity correlates with calculated decreases in N–H bond dissociation energies. Further investigation into the pharmacological activity of these sulfox-

imines, sulfilimines, and aziridines compounds, and into the synthesis and application of chiral alkyl-aryl-*N*-(1,2,4-triazol-1-yl)sulfoximines are underway and will be reported in due course.

Experimental Section

General: All reactions were performed under a nitrogen atmosphere. Unless specified, all reagents were purchased from commercial sources. Molecular sieves (4 Å) were dried at 200 °C and cooled under reduced pressure prior to use. Solvents were purified according to standard procedures. Silica gel F254 plates were used for thin-layer chromatography (TLC); the spots were examined under UV light at 254 nm and then developed in an iodine vapor. Flash chromatography was performed on silica gel. ^{1}H NMR spectra were recorded with Bruker AC-E 200 MHz and Varian Mercury 400 MHz spectrometers with tetramethylsilane (TMS) as internal standard and with chemical shifts (ppm) recorded relative to TMS. The HRMS (ESI) spectra were recorded with a Bruker Daltonics Data analysis 3.2 mass spectrometer.

Synthesis of Aziridine. General Procedure 1 (GP1): A mixture of alkene (1.0 mmol), 4-amino-4*H*-1,2,4-triazole (4.0 mmol), $PhI(OAc)_2$ (4.0 mmol), *t*BuOK (6.0 mmol), molecular sieves (4 Å), and CH_2Cl_2 (8 mL) was stirred under a nitrogen atmosphere at 0 °C for approximately 20 h in a flame-dried flask. After consumption of the starting material (the reaction was monitored by TLC), the mixture was concentrated under reduced pressure. The resulting product was purified by flash column chromatography ($CHCl_3$/CH_3OH, 50:1).

4-(2-Phenylaziridin-1-yl)-4*H*-1,2,4-triazole (2a): Following GP1 using styrene and 4-amino-4*H*-1,2,4-triazole gave **2a** (79% yield) as a pale-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 2 H), 7.45–7.28 (m, 5 H), 3.54–3.51 (m, 1 H), 2.97 (dd, *J* = 8.2, 2.4 Hz, 1 H), 2.78 (dd, *J* = 8.2, 2.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 135.1, 128.8, 128.6, 126.4, 46.4, 41.2 ppm. HRMS: calcd. for $C_{10}H_{11}N_4$ [M + H]$^+$ 187.0984; found 187.0980.

4-[2-(2-Chlorophenyl)aziridin-1-yl]-4*H*-1,2,4-triazole (2b): Following GP1 using 1-chloro-2-vinylbenzene and 4-amino-4*H*-1,2,4-triazole gave **2b** (45% yield) as a pale-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (s, 2 H), 7.50–7.40 (m, 1 H), 7.38–7.22 (m, 3 H), 3.95–3.82 (m, 1 H), 3.01 (dd, *J* = 8.0, 2.0 Hz, 1 H), 2.81 (dd, *J* = 8.0, 2.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDC1_3$): δ = 139.1, 134.4, 132.5, 129.8, 129.5, 127.3, 127.2, 44.3, 40.0 ppm. HRMS: calcd. for $C_{10}H_9ClN_4$ [M + H]$^+$ 221.0594; found 221.0595.

4-[2-(2-Fluorophenyl)aziridin-1-yl]-4*H*-1,2,4-triazole (2c): Following GP1 using 1-fluoro-2-vinylbenzene and 4-amino-4*H*-1,2,4-triazole gave **2c** (32% yield) as a pale-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 2 H), 7.41–7.33 (m, 1 H), 7.21–7.11 (m, 3 H), 3.81–3.74 (m, 1 H), 3.01 (dd, *J* = 8.4, 2.4 Hz, 1 H), 2.76 (dd, *J* = 5.6, 2.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.3, 130.4, 127.2, 124.5, 123.2, 115.6, 115.4, 41.3, 39.6 ppm. HRMS: calcd. for $C_{10}H_{10}FN_4$ [M + H]$^+$ 205.0889; found 205.0895.

4-[2-(4-Fluorophenyl)aziridin-1-yl]-4*H*-1,2,4-triazole (2d): Following GP1 using 1-fluoro-4-vinylbenzene and 4-amino-4*H*-1,2,4-triazole gave **2d** (75% yield) as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 2 H), 7.32–7.22 (m, 2 H), 7.16–7.04 (m, 2 H), 3.56–3.48 (m, 1 H), 2.96 (dd, *J* = 8.0, 2.4 Hz, 1 H), 2.75 (dd, *J* = 8.0, 2.0 Hz, 1 H) ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ = 159.0, 134.4, 126.0, 123.2, 123.1, 110.8, 110.6, 40.7, 36.3 ppm. HRMS: calcd. for $C_{10}H_{10}FN_4$ [M + H]$^+$ 205.0889; found 205.0883.

4-[2-(*p*-Tolyl)aziridin-1-yl]-4*H*-1,2,4-triazole (2e): Following GP1 using 1-methyl-4-vinylbenzene and 4-amino-4*H*-1,2,4-triazole gave **2e** (80% yield) as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 2 H), 7.24–7.00 (m, 4 H), 3.50–3.45 (m, 1 H), 2.93 (dd, *J* = 8.2, 2.4 Hz, 1 H), 2.77 (dd, *J* = 8.2, 2.4 Hz, 1 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1, 138.6, 131.8, 129.5, 126.3, 46.5, 41.1, 21.2 ppm. HRMS: calcd. for $C_{11}H_{13}N_4$ [M + H]$^+$ 201.1140; found 201.1134.

7-(4*H*-1,2,4-Triazol-4-yl)-7-azabicyclo[4.1.0]heptane (2f): Following GP1 using cyclohexene and 4-amino-4*H*-1,2,4-triazole gave **2f** (38% yield) as a pale-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 2 H), 2.80–2.74 (m, 2 H), 2.14–2.04 (m, 2 H), 2.0–1.89 (m, 2 H), 1.48–1.36 (m, 2 H), 1.34–1.24 (m, 2 H) ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ = 139.3, 72.8, 44.5, 19.5 ppm. HRMS: calcd. for $C_8H_{12}N_4Na$ [M + Na]$^+$ 187.0960; found 187.0958.

4-[2-(3-Bromophenyl)aziridin-1-yl]-4*H*-1,2,4-triazole (2g): Following GP1 using 1-bromo-3-vinylbenzene and 4-amino-4*H*-1,2,4-triazole gave **2g** (38% yield) as a pale-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 2 H), 7.54–7.44 (m, 2 H), 7.32–7.20 (m, 2 H), 3.56–3.48 (m, 1 H), 3.00 (dd, *J* = 8.0, 2.4 Hz, 1 H), 2.76 (dd, *J* = 8.0, 2.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0, 137.3, 131.5, 130.2, 129.1, 125.0, 122.7, 45.4, 41.4 ppm. HRMS: calcd. for $C_{10}H_{10}BrN_4$ [M + H]$^+$ 265.0089; found 265.0086.

4-[2-(4-Bromophenyl)aziridin-1-yl]-4*H*-1,2,4-triazole (2h): Following GP1 using 1-bromo-4-vinylbenzene and 4-amino-4*H*-1,2,4-triazole gave **2h** (48% yield) as a pale-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (s, 2 H), 7.41 (dd, *J* = 6.8, 1.6 Hz, 2 H), 7.19 (dd, *J* = 6.8, 1.6 Hz, 2 H), 3.51–3.49 (m, 1 H), 2.99 (dd, *J* = 8.4, 2.4 Hz, 1 H), 2.74 (dd, *J* = 8.4, 2.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 134.1, 131.9, 128.0, 122.5, 45.7, 41.4 ppm. HRMS: calcd. for $C_{10}H_{10}BrN_4$ [M + H]$^+$ 265.0089; found 265.0081.

4-[2-(4-Chlorophenyl)aziridin-1-yl]-4*H*-1,2,4-triazole (2i): Following GP1 using 1-chloro-4-vinylbenzene and 4-amino-4*H*-1,2,4-triazole gave **2i** (63% yield) as a pale-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 2 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.23 (d, *J* = 8.2 Hz, 2 H), 3.54–3.50 (m, 1 H), 2.99 (dd, *J* = 8.2, 2.4 Hz, 1 H), 2.73 (dd, *J* = 8.2, 2.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 134.4, 133.7, 128.9, 127.7, 45.7, 41.4 ppm. HRMS: calcd. for $C_{10}H_9ClN_4$ [M + H]$^+$ 221.0594; found 221.0590.

4-[2-(3,4-Dimethoxyphenyl)aziridin-1-yl]-4*H*-1,2,4-triazole (2j): Following GP1 using 1,2-dimethoxy-4-vinylbenzene and 4-amino-4*H*-1,2,4-triazole gave **2j** (56% yield) as a pale-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 2 H), 6.98–6.90 (m, 2 H), 6.80–6.76 (m, 1 H), 3.96–3.86 (m, 6 H), 3.52–3.47 (m, 1 H), 2.94 (dd, *J* = 8.0, 2.4 Hz, 1 H), 2.78 (dd, *J* = 5.6, 2.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 145.1, 142.7, 137.5, 122.9, 111.3, 103.9, 56.0, 55.7, 47.0, 40.5 ppm. HRMS: calcd. for $C_{12}H_{15}N_4O_2$ [M + H]$^+$ 247.1195; found 247.1183.

4-[2-(4-Methoxyphenyl)aziridin-1-yl]-4*H*-1,2,4-triazole (2k): Following GP1 using 1-methoxy-4-vinylbenzene and 4-amino-4*H*-1,2,4-triazole gave **2k** (85% yield) as a pale-brown solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.83 (s, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 8.4 Hz, 2 H), 3.76 (m, 4 H), 3.16 (dd, *J* = 8.4, 2.4 Hz, 1 H), 2.85 (dd, *J* = 8.0, 2.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 139.1, 127.6, 126.7, 114.2, 55.3, 46.3, 40.9 ppm. HRMS: calcd. for $C_{12}H_{15}N_4O_2$ [M + H]$^+$ 247.1195; found 247.1183.

Synthesis of Sulfoximines and Sulfilimines. General Procedure 2 (GP2): A mixture of sulfide or sulfoxide (1.0 mmol), 4-amino-4*H*-1,2,4-triazole (3.0 mmol), $PhI(OAc)_2$ (3.0 mmol), Al_2O_3 (4.0 mmol)

and molecular sieves (4 Å, 0.2 g), in a dried flask, CH_2Cl_2 (8 mL) was stirred under a nitrogen atmosphere at 0 °C in a flame-dried flask. The reaction was stirred at 0 °C to room temperature for 2–4 h. After consumption of the starting material (reaction monitored by TLC) the reaction mixture was concentrated under reduced pressure. The resulting product was purified by flash column chromatography ($CHCl_3$/CH_3OH, 25:1) to give the product.

Dimethyl-*N*-(1,2,4-triazol-4-yl)sulfoximine (4a): Following GP2 using dimethyl sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4a** (43 mg, 51% yield) as a gray powder. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 8.42 (s, 2 H), 3.32 (s, 6 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 143.7, 38.4 ppm. HRMS (ESI): calcd. for $C_4H_9N_4OS$ [M + H]$^+$ 161.0497; found 161.0492.

Dibutyl-*N*-(1,2,4-triazol-4-yl)sulfoximine (4b): Following GP2 using dibutyl sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4b** (47 mg, 89% yield, 52% conversion) as a gray powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 2 H), 3.23–3.06 (m, 4 H), 1.88–1.78 (m, 4 H), 1.54–1.45 (m, 4 H), 0.99 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 49.1, 24.7, 21.7, 13.4 ppm. HRMS (ESI): calcd. for $C_{10}H_{21}N_4OS$ [M + H]$^+$ 245.1436; found 245.1432.

Diphenyl-*N*-(1,2,4-triazol-4-yl)sulfoximine (4c): Following GP2 using diphenyl sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4c** (83 mg, 91% yield, 63% conversion) as a gray powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 2 H), 8.05–8.03 (m, 4 H), 7.69–7.65 (m, 2 H), 7.57–7.61 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 135.5, 134.6, 130.0, 128.7 ppm. HRMS (ESI): calcd. for $C_{14}H_{13}N_4OS$ [M + H]$^+$ 285.0810; found 285.0805.

Dibenzyl-*N*-(1,2,4-triazol-4-yl)sulfoximine (4d): Following GP2 using dibenzyl sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4d** (71 mg, 97% yield, 48% conversion) as a pale-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 2 H), 7.52–7.43 (m, 6 H), 7.33–7.27 (m, 4 H), 4.38 (s, 4 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 148.5, 136.7, 134.1, 133.9, 132.3, 61.0 ppm. HRMS (ESI): calcd. for $C_{16}H_{17}N_4OS$ [M + H]$^+$ 313.1123; found 313.1119.

Methylphenyl-*N*-(1,2,4-triazol-4-yl)sulfoximine (4e): Following GP2 using methyl phenyl sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4e** (53 mg, 86% yield, 52% conversion) as a gray powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (s, 2 H), 7.92 (d, J = 8.0 Hz, 2 H), 7.71 (t, J = 7.6 Hz, 1 H), 7.63 (t, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9, 135.1, 134.6, 130.3, 128.8, 40.9 ppm. HRMS (ESI): calcd. for: $C_9H_{11}N_4OS$ [M + H]$^+$ 223.0654; found 223.0648.

Butylphenyl-*N*-(1,2,4-triazol-4-yl)sulfoximine (4f): Following GP2 using butyl phenyl sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4f** (41 mg, 71% yield, 51% conversion) as a gray solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 1 H), 7.88 (d, J = 7.6 Hz, 2 H), 7.71 (t, J = 7.2 Hz, 1 H), 7.62 (t, J = 7.6 Hz, 2 H), 3.53–3.45 (m, 1 H), 3.37–3.29 (m, 1 H), 1.93–1.84 (m, 1 H), 1.72–1.65 (m, 1 H), 1.50–1.40 (m, 1 H), 0.93 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 134.8, 133.7, 130.2, 129.2, 52.6, 23.8, 21.4, 13.4 ppm. HRMS (ESI): calcd. for $C_{14}H_{22}N_2O_2SNa$ [M + Na]$^+$ 305.1294; found 305.1284.

Benzylphenyl-*N*-(1,2,4-triazol-4-yl)sulfoximine (4g): Following GP2 using phenyl benzyl sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4g** (60 mg, 84% yield, 56% conversion) as a pale-brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (s, 2 H), 7.66 (d, J = 8.0 Hz, 3 H), 7.52 (t, J = 8.0 Hz, 2 H), 7.38 (t, J = 7.6 Hz, 1 H), 7.29 (t, J = 7.6 Hz, 2 H),7.10 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 134.9, 132.4, 131.4, 129.9, 129.9, 129.8, 128.9, 125.4, 59.7 ppm. HRMS (ESI): calcd. for $C_{15}H_{15}N_4OS$ [M + H]$^+$ 299.0966; found 299.0961.

Dihexyl-*N*-(1,2,4-triazol-4-yl)sulfoximine (4h): Following GP2 using dihexyl sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4h** (58 mg, 84% yield, 51% conversion) as a gray solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (s, 2 H), 3.20–3.02 (m, 4 H), 1.89–1.76 (m, 4 H), 1.47–1.40 (m, 4 H), 1.33–1.25 (m, 8 H), 0.91–0.88 (t, J = 6.4 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 49.3, 31.0, 28.0, 22.7, 22.2, 13.8 ppm. HRMS (ESI): calcd. for $C_{14}H_{29}N_4OS$ [M + H]$^+$ 301.2062; found 301.2057.

Tetramethylene-*N*-(1,2,4-triazol-4-yl)sulfoximine (4i): Following GP2 using tetramethylenesulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4i** (101 mg, 96% yield, 55% conversion) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 8.19 (s, 1 H), 3.41 (m, 2 H), 3.11 (m, 2 H), 2.35 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.8, 143.1, 49.9, 23.8 ppm. HRMS (ESI): calcd. for $C_6H_{11}N_4OS$ [M + H]$^+$ 187.0654; found 187.0648.

(4-Nitrophenyl)phenyl-*N*-(1,2,4-triazol-4-yl)sulfoximine (4j): Following GP2 using 4-nitrophenyl phenyl sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4j** (39 mg, 81% yield, 52% conversion) as a gray solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (d, J = 8.4 Hz, 2 H), 8.23 (d, J = 8.4 Hz, 2 H), 8.16 (s, 2 H), 8.06 (d, J = 8.0 Hz, 2 H), 7.79–7.72 (m, 1 H), 7.66–7.62 (t, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 143.4, 140.9, 135.8, 133.7, 130.9, 130.8, 129.5, 125.6, 125.5 ppm. HRMS (ESI): Calcd. for $C_6H_{11}N_4OS$ [M + H]$^+$ 330.0661; found 330.0658.

3-[*N*-(4*H*-1,2,4-Triazol-4-yl)phenylsulfonimidoyl]propanenitrile (4k): Following GP2 using 3-(phenylsulfinyl)propanitrile sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **4k** (62 mg, 91% yield, 65%conversion) as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 2 H), 7.96 (m, 2 H), 7.79 (m, 1 H), 7.69 (m, 2 H), 3.92–3.84 (m, 1 H), 3.70–3.62 (m, 1 H), 3.11–2.94 (m, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 143.4, 135.5, 132.1, 130.4, 130.1, 117.6, 46.7, 11.4 ppm. HRMS (ESI): calcd. for $C_{11}H_{12}N_5OS$ [M + H]$^+$ 262.0763; found 262.0738.

***N*-Butyl-*N*-(1,2,4-triazol-4-yl)-10*H*-phenothiazine (6a):** Following GP2 using phenothiazine and 4-amino-4*H*-1,2,4-triazole gave **6a** (45 mg, 85% yield, 40% conversion) as a purple solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.02 (d, J = 7.6 Hz, 2 H), 7.74 (t, J = 7.6 Hz, 2 H), 7.40 (d, J = 8.0 Hz, 2 H), 7.33 (t, J = 8.4 Hz, 2 H), 6.83 (s, 2 H), 3.55 (m, J = 8.0 Hz, 2 H), 1.56–1.52 (m, 2 H), 1.47–1.41 (m, 2 H), 0.97–0.94 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5, 141.5, 133.9, 131.9, 122.9, 115.1, 113.2, 48.3, 28.9, 19.8, 13.7 ppm. HRMS (ESI): calcd. for $C_{18}H_{20}N_5S$ [M + H]$^+$ 338.1439; found 338.1436.

Dibutyl-*N*-(1,2,4-triazol-4-yl)sulfilimine (6b): Following GP2 using dibutyl sulfides and 4-amino-4*H*-1,2,4-triazole gave **6b** (77 mg, 85% yield, 52% conversion) as a brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (s, 2 H), 2.82–2.75 (m, 2 H), 2.58–2.51 (m, 2 H), 1.91–1.77 (m, 4 H), 1.61–1.44 (m, 4 H), 1.01 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8, 45.3, 25.6, 21.8, 13.6 ppm. HRMS (ESI): calcd. for $C_{10}H_{21}N_4S$ [M + H]$^+$ 229.1487; found 229.1480.

Benzylphenyl-*N*-(1,2,4-triazol-4-yl)sulfilimine (6c): Following GP2 using phenyl benzyl sulfides and 4-amino-4*H*-1,2,4-triazole gave **6c** (71.1 mg, 98% yield, 67% conversion) as a pale-yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 2 H), 7.70 (s, 1 H), 7.63–7.53 (m, 4 H), 7.39–7.38 (m, 3 H), 7.31–7.28 (m, 2 H), 4.36 (q, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3, 135.3, 132.8, 130.5, 130.1, 129.3, 128.8, 127.3, 55.2 ppm. HRMS (ESI): calcd. for $C_{15}H_{15}N_4S$ [M + H]$^+$ 283.1017; found 283.1021.

Allylbenzyl-*N*-(1,2,4-triazol-4-yl)sulfilimine (6d): Following GP2 using allyl benzyl sulfides and 4-amino-4*H*-1,2,4-triazole gave **6d**

(53 mg, 77% yield, 51% conversion) as a gray solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.72 (s, 2 H), 7.49–7.47 (m, 5 H), 5.89–5.78 (m, 1 H), 5.22–5.14 (m, 2 H), 4.1 (d, J = 6.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 141.8, 134.3, 132.3, 130.0, 129.8, 129.5, 126.1, 64.6 ppm. HRMS (ESI): calcd. for $C_{11}H_{13}N_4S$ [M + H]$^+$ 233.0861; found 233.0863.

(4-Nitrophenyl)phenyl-*N*-(1,2,4-triazol-4-yl)sulfilimine (6e): Following GP2 using phenyl(4-nitrophenyl) sulfides and 4-amino-4*H*-1,2,4-trizaole gave **6e** (110 mg, 95% yield, 75% conversion) as a yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.42 (d, J = 8.8 Hz, 2 H), 7.90 (s, 2 H), 7.85 (d, J = 8.8 Hz, 2 H), 7.71 (m, 1 H), 7.62 (t, J = 7.6 Hz, 2 H), 7.52 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.8, 142.8, 134.8, 130.8, 130.0. 129.7, 128.9, 126.6, 124.0 ppm. HRMS (ESI): calcd. for $C_{14}H_{12}$ N_5O_2S [M + H]$^+$ 314.0712; found 314.0718.

Butylphenyl-*N*-(1,2,4-triazol-4-yl)sulfilimine (6f): Following GP2 using butyl phenyl sulfide and 4-amino-4*H*-1,2,4-triazole gave **6f** (109 mg, 93% yield, 74% conversion) as a yellow-brown solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.83 (s, 2 H), 7.63–7.61 (m, 1 H), 7.58–7.51 (m, 4 H), 3.27–3.20 (m, 1 H), 3.02–2.95 (m, 1 H), 1.88–1.73 (m, 2 H), 1.61–1.45 (m, 2 H), 0.99 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 144.2, 133.0, 130.3, 129.2, 127.6, 45.5, 25.7, 21.7, 13.5 ppm. HRMS (ESI): calcd. for $C_{12}H_{16}N_4S$ [M + H]$^+$ 249.1174; found 249.1175.

***N*-(1,2,4-Triazol)phenyl-(2-nitrophenyl)sulfilimine (6g):** Following GP2 using phenyl (2-nitrophenyl) sulfide and 4-amino-4*H*-1,2,4-triazole gave **6g** (109 mg, 91% yield, 65% conversion) as a pale-yellow solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.78 (d, J = 7.6 Hz, 1 H), 8.48 (s, 1 H), 8.43 (d, J = 8.0 Hz, 1 H), 8.27 (m, 1 H), 7.99 (t, J = 7.8 Hz, 1 H), 7.67 (d, J = 7.2 Hz, 2 H), 7.63–7.56 (m, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.7, 142.9, 134.7, 133.7, 130.7, 130.0, 129.7, 129.1, 128.9, 126.6, 124.0 ppm. HRMS (ESI): calcd. for $C_{14}H_{12}N_5O_2S$ [M + H]$^+$ 314.0712; found 314.0721.

Methyl 4-[Methyl-*N*-(4*H*-1,2,4-triazol-4-yl)sulfinimidoyl]benzoate (6h): Following GP2 procedure using methyl 4-(methylthio)benzoate and 4-amino-4*H*-1,2,4-triazole gave **6h** (63 mg, 88% yield) as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.22 (m, 2 H), 7.82 (s, 2 H), 7.66 (d, J = 8.0 Hz, 2 H), 3.98 (s, 3 H), 2.94 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 165.2, 143.9, 140.4, 134.1, 131.2, 127.2, 52.7, 29.9 ppm. HRMS (ESI): calcd. for $C_{11}H_{13}N_4OS$ [M + H]$^+$ 265.0759; found 265.0755.

Phenylpyrimidinyl-*N*-(1,2,4-triazol-4-yl)sulfilimine (6i): Following GP2 using pyrimidinyl phenyl sulfoxide and 4-amino-4*H*-1,2,4-triazole gave **6i** (97 mg, 40% yield, 66% conversion) as a pale yellow solid. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.03 (s, 1 H), 8.59 (s, 2 H), 7.46–7.41 (m, 2 H), 7.40–7.35 (m, 5 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 142.8, 141.9, 135.4, 134.0, 130.4, 130.0, 129.1, 125.0 ppm. HRMS (ESI): calcd. for $C_{12}H_{10}N_6S$ [M + H]$^+$ 271.0766; found 271.0770.

Supporting Information (see footnote on the first page of this article): Copies of the NMR spectra, the Cartesian coordinates [Å] and calculated energies and the thermal corrections to the enthalpy of the structures optimized at the UB3LYP/6-31+G(d,p) level of theory.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (NSFC) (grant number 21072131).

[1] a) M. M. Díaz-Requejo, P. J. Pérez, *Chem. Rev.* **2008**, *108*, 3379–3394; b) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417–424; c) P. Müller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905–2919; d) C. Florence, H. D. Robert, D. Philippe, *Chem. Commun.* **2009**, 5061–5072.

[2] a) C. R. Johnson, *Acc. Chem. Res.* **1973**, *6*, 341–347; b) M. Reggelin, C. Zur, *Synthesis* **2000**, 1–64; c) H. Okamura, C. Bolm, *Chem. Lett.* **2004**, *33*, 482–487; d) M. C. Carreno, *Chem. Rev.* **1995**, *95*, 1717–1760; e) S. Meehan, R. D. Little, *J. Org. Chem.* **1997**, *62*, 3779–3781.

[3] a) D. Tanner, *Angew. Chem.* **1994**, *106*, 625–646; b) W. McCoull, F. A. Davies, *Synthesis* **2000**, 1347–1365; c) P. Dauban, R. H. Dodd, *Synlett* **2003**, 1571–1586.

[4] a) X. L. Hou, J. Wu, R. Fan, C. H. Ding, Z. B. Luo, L. X. Dai, *Synlett* **2006**, 181–193; b) J. B. Sweeney, *Chem. Soc. Rev.* **2002**, *31*, 247–258; c) B. Zwanenburg, P. Ten Holte, *Top. Curr. Chem.* **2001**, *216*, 93–124; d) R. H. Dodd, *Molecules* **2000**, *5*, 293–298; e) R. S. Atkinson, *Tetrahedron* **1999**, *55*, 1519–1559; f) H. Stamm, *J. Prakt. Chem.* **1999**, *4*, 319–331; g) H. M. I. Osborn, J. Sweeney, *Tetrahedron: Asymmetry* **1997**, *8*, 1693–1715; h) D. Tanner, *Angew. Chem.* **1994**, *106*, 625; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 599–619; i) M. Kasai, M. Kono, *Synlett* **1992**, 778–790.

[5] a) D. A. Evans, M. M. Faul, M. T. Bilodeau, *J. Am. Chem. Soc.* **1994**, *116*, 2742–2753; b) J. U. Jeong, B. Tao, I. Sagasser, H. Henniges, K. B. Sharpless, *J. Am. Chem. Soc.* **1998**, *120*, 6844–6845; c) Z. Li, K. R. Conser, E. N. Jacobsen, *J. Am. Chem. Soc.* **1993**, *115*, 5326–5327; d) T. Siu, A. K. Yudin, *J. Am. Chem. Soc.* **2002**, *124*, 530–531; e) S. M. Au, J. S. Huang, W. Y. Yu, W. H. Fung, C. M. Che, *J. Am. Chem. Soc.* **1999**, *121*, 9120–9132; f) S. I. Ali, M. D. Nikalje, A. Sudalai, *Org. Lett.* **1999**, *1*, 705–707; g) J. C. Antilla, W. D. Wulff, *J. Am. Chem. Soc.* **1999**, *121*, 5099–5100; h) K. Guthikonda, D. J. Bois, *J. Am. Chem. Soc.* **2002**, *124*, 13672–13673; i) H. Kawabata, K. Omura, T. Katsuki, *Tetrahedron Lett.* **2006**, *47*, 1571–1574; j) C. M. Agathe, A. F. Salit, C. Bolm, *Chem. Commun.* **2008**, 5975–5977; k) J. W. W. Chang, M. U. Thi, Z.-Y. Zhang, Y.-J. Xu, W. H. Philip, *Tetrahedron Lett.* **2009**, *50*, 161–164; l) Y. Li, B. Diebl, A. Raith, F. E. Kühn, *Tetrahedron Lett.* **2008**, *49*, 5954–5956; m) Z. Li, R. W. Quan, E. N. Jacobsen, *J. Am. Chem. Soc.* **1995**, *117*, 5889–5890; n) Y. Cui, C. He, *J. Am. Chem. Soc.* **2003**, *125*, 16202–16203; o) A. Raza, Y. Y. Sham, R. Vince, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 5406–5410; p) D. Lu, Y. Y. Sham, R. Vince, *Bioorg. Med. Chem.* **2010**, *18*, 2037–2048.

[6] a) C. Bolm, O. Simic, *J. Am. Chem. Soc.* **2001**, *123*, 3830–3831; b) M. Harmata, S. K. Ghosh, *Org. Lett.* **2001**, *3*, 3321–3323; c) C. Bolm, M. Martin, O. Simic, M. Verrucci, *Org. Lett.* **2003**, *5*, 427–429; d) C. Bolm, M. Verrucci, O. Simic, P. G. Cozzi, G. Raabe, H. Okamura, *Chem. Commun.* **2003**, 2816–2817; e) C. Bolm, M. Martin, G. Gescheidt, C. Palivan, D. Neshchadin, H. Bertagnolli, M. P. Feth, A. Schweiger, G. Mitrikas, J. Harmer, *J. Am. Chem. Soc.* **2003**, *125*, 6222–6227; f) M. Harmata, *Chemtracts* **2003**, *16*, 660–666.

[7] a) C. R. Johnson, C. W. Schroeck, *J. Am. Chem. Soc.* **1973**, *95*, 7418–7423; b) J. Brandt, H. J. Gais, *Tetrahedron: Asymmetry* **1997**, *6*, 909–912; c) T. Bach, C. Körber, *Eur. J. Org. Chem.* **1999**, 1033–1039; d) T. Bach, C. Körber, *Tetrahedron Lett.* **1998**, *39*, 5015–5016.

[8] Y. Tamura, H. Matushima, J. Minamikawa, M. Keda, K. Sumoto, *Tetrahedron* **1975**, *31*, 3035–3040.

[9] a) J. F. K. Müller, P. Vogt, *Tetrahedron Lett.* **1998**, *39*, 4805–4806; b) E. Lacöte, M. Amatore, L. Fensterbank, M. Malacria, *Synlett* **2002**, 116–118; c) C. Ohta, T. Katsuki, *Tetrahedron Lett.* **2001**, *42*, 3885–3888; d) T. Uchida, Y. Tamura, M. Ohba, T. Katsuki, *Tetrahedron Lett.* **2003**, *44*, 7965–7968; e) H. Okamura, C. Bolm, *Org. Lett.* **2004**, *6*, 1305–1307; f) F. Collet, R. H. Dodd, P. Dauban, *Org. Lett.* **2008**, *10*, 5473–5476.

[10] a) M. O. Garcia, C. Bolm, *Org. Lett.* **2006**, *8*, 2349–2352; b) M. O. Garcia, J. Dallimore, P. Plant, C. Bolm, *Org. Lett.* **2009**, *11*, 2429–2432.
[11] a) G. Y. Cho, C. Bolm, *Org. Lett.* **2005**, *7*, 4983–4985; b) H. Nishikori, C. Ohta, E. Oberlin, R. Irie, T. Katsuki, *Tetrahedron* **1999**, *55*, 13937–13946.
[12] a) C. Bolm, K. Muñiz, N. Aguilar, M. Kesselgruber, R. Raabe, *Synthesis* **1999**, 1251–1260; b) H. Takada, K. Ohe, S. Uemura, *Angew. Chem.* **1999**, *111*, 1367; *Angew. Chem. Int. Ed.* **1999**, *38*, 1288–1292; c) J. Nakayama, T. Otani, Y. Sugihara, Y. Sano, A. Ishii, A. Sakamoto, *Heteroatom Chem.* **2001**, *12*, 333–348; d) S. Cren, T. C. Kinahan, C. L. Skinner, H. Tye, *Tetrahedron Lett.* **2002**, *43*, 2749–2751; e) L. Zhang, F. Wang, J. B. Hu, *Org. Lett.* **2009**, *11*, 2109–2112.
[13] a) K. K. Mayer, F. Schroppel, J. Sauer, *Tetrahedron Lett.* **1972**, *13*, 2899–2902; b) L. B. Krasnova, R. M. Hili, O. V. Chernoloz, A. K. Yudin, *ARKIVOC* **2005**, *4*, 26–38.
[14] a) H. T. Ji, W. N. Zhang, Y. J. Zhou, *J. Med. Chem.* **2000**, *43*, 2493–2505; b) J. Heeres, L. J. Backx, C. J. Van, *J. Med. Chem.* **1984**, *27*, 894–900; c) Z. G. Turan, Z. A. Kaplakcikli, M. T. Yildiz, *Eur. J. Med. Chem.* **2005**, *40*, 607–613.; d) L. W. Lawrence Woo, C. Bubert, O. B. Sutcliffe, *J. Med. Chem.* **2007**, *50*, 3540–3560; e) S. Yahiaoui, C. Pouget, C. Fagnere, *Bioorg. Med. Chem. Lett.* **2004**, *14*, 5215–5218; f) M. R. Saberi, T. K. Vinh, S. W. Yee, *J. Med. Chem.* **2006**, *49*, 1016–1022; g) Y. Q. Long, X. H. Jiang, R. Dayam, *J. Med. Chem.* **2004**, *47*, 2561–2573; h) L. Zahajská, V. Klimesová, J. Koci, *Arch. Pharm.* **2004**, *337*, 549–555; i) O. Garcia Mancheno, C. Bolm, *Org. Lett.* **2007**, *9*, 2951–2954.
[15] R. Vyas, G. Y. Gao, J. D. Harden, X. P. Zhang, *Org. Lett.* **2004**, *6*, 1907–1910.
[16] S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem.* **2005**, *117*, 5320; *Angew. Chem. Int. Ed.* **2005**, *44*, 5188–5240.
[17] S. K. Y. Leung, W. M. Tsui, J. S. Huang, C. M. Che, J. L. Liang, N. Y. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 16629–16640.
[18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Etersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 03*, revision D.01, Gaussian, Inc., Pittsburgh, PA, **2005**.
[19] A. D. Beck, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[20] R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, U. K., **1989**.
[21] S. J. Blanksby, G. B. Ellison, *Acc. Chem. Res.* **2003**, *36*, 255–263.

Received: October 7, 2011
Published Online: January 26, 2012

