Asymmetric Synthesis

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N-(Diazoacetyl)oxazolidin-2-thiones as Sulfur-Donor Reagents: Asymmetric Synthesis of Thiiranes from Aldehydes**

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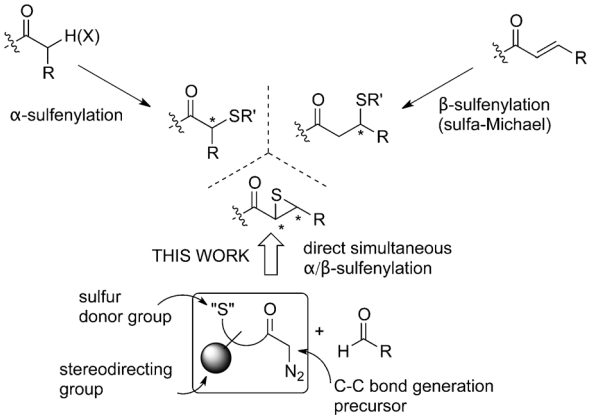
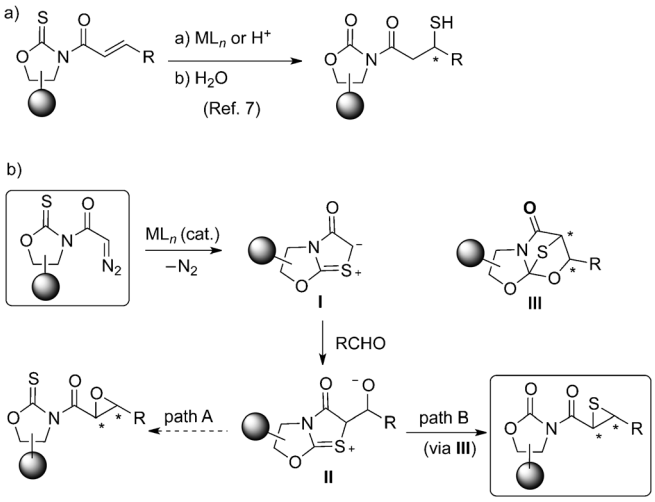
Sulfur-containing compounds are widespread among natural products and bioactive substances, and also useful ligands in asymmetric catalysis.[1] Therefore considerable efforts have been devoted to develop stereocontrolled C–S bond-forming procedures.[2] Two common approaches consist of the electrophilic sulfenylation of enolates or equivalents[3] and the conjugate addition of S nucleophiles to Michael acceptors;[4] these routes afford S-functionalized carbonyls at either the α or β position. Methods to access α,β-thioepoxy carbonyls[5] would not only provide versatile adducts S-functionalized at both the α and β position, but also imply generation of two contiguous stereocenters (Scheme 1). However, as far as we are aware there is virtually no method for achieving such a goal in a direct and stereocontrolled fashion.[6] Herein, we describe *N*-(diazoacetyl)oxazolidin-2-thiones as new sulfur-donor reagents that in combination with aldehydes and a Rh^{II} catalyst are capable of producing α,β-thioepoxy carbonyls in a highly stereoselective manner.

Inspired by the ability of the oxazolidin-2-thione group to act as both an intramolecular sulfur-donor reagent and a stereodirecting group (Scheme 2a),[7] we envisaged that *N*-(diazoacetyl)oxazolidin-2-thiones might serve as both C–C and C–S bond-forming reagents while controlling the reaction stereochemistry. The assumption was that thiocarbonyl ylide **I** (Scheme 2b), generated from *N*-(diazoacetyl)oxazolidin-2-thione upon treatment with a metal catalyst,[8] would react with an aldehyde to afford the zwiterionic intermediate **II**, which may follow either path A or B to provide either epoxide or thioepoxide product. Although path A (epoxide formation) seemed to be the preferred route for both sulfide ylides[9] and carbonyl ylides,[10] and implies no sulfur transfer, we speculated that path B might also be possible, likely through rearrangement of intermediate **III**.



Scheme 1. Common strategies for the stereoselective sulfenylation of carbonyls at the α or β position, and our proposal for the direct simultaneous α and β sulfenylation.



Scheme 2. Working hypothesis for stereoselective thiirane synthesis by sulfur transfer with concomitant C–C bond formation.

Starting thione diazo compounds were readily prepared by reaction of oxazolidin-2-thiones with 2-(2-tosylhydrazono)acetyl chloride in yields of 47–67%. Initial screening of catalysts and reaction conditions revealed that both Rh^{II} and Cu^{II} salts catalyzed the reaction of **1** with benzaldehyde in CH_2Cl_2 at 0°C to afford thiirane **5a** in yields from 50% to 62% upon isolation and *cis*/*trans* ratios from 85:15 to 88:12

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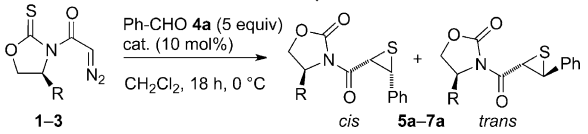
(Table 1, entries 1, 2, and 7). Remarkably, in both cases no oxirane product was detected in the corresponding crude reaction mixtures.[10] This process is thus particularly significant in that the new C–S σ-bond formation occurs in detriment of the C–O σ-bond and with concomitant generation of two contiguous stereocenters. The nature of the counterion of the transition metal salt used has an influence on the catalytic activity: both $Rh_2(OAc)_4{\cdot}2H_2O$ and $Cu(acac)_2$ were active and induced good reaction yields, whereas no reaction at all was observed with either $Rh_2(OCOCF_3)_4$ or $Cu(OTf)_2$ salts (Table 1, entries 1, 2, and 7 vs. 5 and 8). The use of other divalent metal salts such as $CoCl_2$, $FeCl_2{\cdot}H_2O$, and $Pd(OAc)_2$, which are potentially capable of inducing ylide formation, led to sluggish reactions or no reaction at all (Table 1, entries 6, 10, 13).

On the other hand, some metals in the oxidation state +1 were also effective catalysts. For instance, although no reaction was observed with AgOTf, both CuCl and AuCl promoted the reaction to give product **5a** with *cis*/*trans* ratios of 91:9 and 99:1, respectively, albeit in these cases the yields were low (Table 1, entries 12, 9, and 11). Further optimization of the reaction conditions with $Rh_2(OAc)_4{\cdot}2H_2O$ as catalyst indicated that a lower (2 mol%) catalyst loading could be used and the *cis*/*trans* ratio could be improved by lowering the temperature (up to 97:3 *cis*/*trans* ratio; Table 1, entries 3 and 4). Finally, diazo-oxazolidinethiones **2** and **3**, bearing a *tert*-butyl and a phenyl substituent, respectively, were also tolerated, although in the case of the phenyl analogue **3** a relatively lower yield and selectivity was observed (Table 1, entries 14 and 15).

Table 1: Screening of catalysts for the reaction of *N*-(diazoacetyl)-2-oxazolidinethiones **1**–**3** and benzaldehyde.[a]

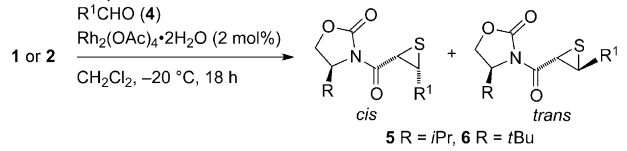


Entry	R	Substrate	Catalyst	*T* [°C]	Prod.	*cis*/*trans*[b]	Yield [%][c]
1	*i*Pr	**1**	$Rh_2(OAc)_4$	0	**5a**	86:14	50
2	*i*Pr	**1**	$Rh_2(OAc)_4{\cdot}2H_2O$	0	**5a**	88:12	62
3	*i*Pr	**1**	$Rh_2(OAc)_4{\cdot}2H_2O$	−10	**5a**	94:6	64[d]
4	*i*Pr	**1**	$Rh_2(OAc)_4{\cdot}2H_2O$	−20	**5a**	97:3	62[d]
5	*i*Pr	**1**	$Rh_2(OCOCF_3)_4$	0	**5a**	–	0[e]
6	*i*Pr	**1**	$CoCl_2$	0	**5a**	–	0
7	*i*Pr	**1**	$Cu(acac)_2$	0	**5a**	85:15	53
8	*i*Pr	**1**	$Cu(OTf)_2$	0	**5a**	–	0[e]
9	*i*Pr	**1**	CuCl	0	**5a**	91:9	40
10	*i*Pr	**1**	$FeCl_2{\cdot}4H_2O$	0	**5a**	–	0[e]
11	*i*Pr	**1**	AuCl	0	**5a**	99:1	18
12	*i*Pr	**1**	AgOTf	0	**5a**	–	0[e]
13	*i*Pr	**1**	$Pd(OAc)_2$	0	**5a**	–	17
14	*t*Bu	**2**	$Rh_2(OAc)_4{\cdot}2H_2O$	−20	**6a**	94:6	60[d]
15	Ph	**3**	$Rh_2(OAc)_4{\cdot}2H_2O$	−20	**7a**	92:8	45[d]

[a] The reactions were performed on a 0.30 mmol scale. [b] Determined by ^{1}H NMR spectroscopy. [c] Yield of isolated major isomer after chromatography. [d] Using 2 mol% of catalyst. [e] Extensive decomposition was observed.

We next investigated the scope of the reaction with respect to the aldehyde component. As the results in Table 2 show, reactions of a range of aromatic aldehydes bearing either electron-donating, neutral, or electron-withdrawing substituents all produced the corresponding thiirane product smoothly within 16–18 h at −20 °C. In each case a mixture of *cis*/*trans* isomers was formed from which the major isomer was obtained in 57–75% yield upon isolation. Interestingly, in most cases *cis*-thiirane was obtained as the major isomer (*cis*/*trans* ratio from 97:3 to 82:18; Table 2, entries 1–3, 6–10), whereas in the case of *p*-anisidine, and *p*-*tert*-butyldimethylsilyloxybenzaldehyde, the *trans*-configured thiirane (**5d** and **5e**) was the exclusive product (Table 2, entries 4 and 5). This unusual reversal of the reaction stereochemistry observed for benzaldehydes bearing electron-donating substituents could be explained on the basis of the proposed reaction mechanism (see below). The catalytic generation of thiiranes **5** and **6** also worked for other nonenolizable aldehydes, such as alkynyl and heteroaryl aldehydes (Table 2, entries 11–16). Pyridylcarbaldehyde was an exception (Table 2, entry 17). Assignment of the *cis*/*trans* relative configuration of the formed thiirane ring was primarily made by correlation of the coupling constants between the two vicinal H nucleus in ^{1}H NMR spectroscopy: 7.4 Hz to 7.7 Hz for the *cis*-thiirane

Table 2: Scope of the reaction.[a]

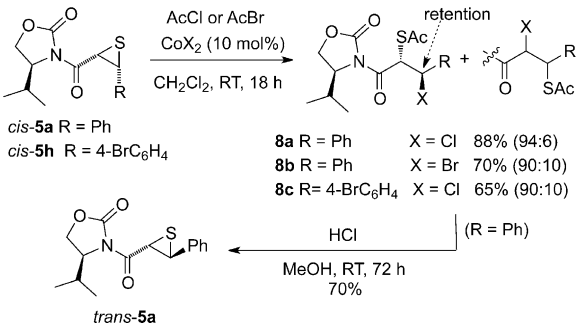


Entry	Substrate	R^1	Product	*cis*/*trans*[b]	Yield [%][c]
1	**1**	Ph	**5a**	93:7	65[d]
2	**1**	4-MeC_6H_4	**5b**	82:18	60
3	**1**	3,5-MeC_6H_3	**5c**	83:17	61
4	**1**	4-$MeOC_6H_4$	**5d**	1:99	61
5	**1**	4-$TBSOC_6H_4$	**5e**	1:99	31[e]
6[f]	**1**	4-ClC_6H_4	**5f**	88:12	63
7	**1**	3-ClC_6H_4	**5g**	86:14	57
8	**1**	4-BrC_6H_4	**5h**	91:9	56
9	**1**	4-$NO_2C_6H_4$	**5i**	92:8	61
10	**1**	4-CNC_6H_4	**5j**	91:9	56
11	**1**	PhC≡C	**5k**	72:28	65
12[g]	**2**	PhC≡C	**6k**	83:17	75
13[h]	**2**	PhC≡C	**6k**	86:14	69
14[g]	**2**	3-ClC_6H_4C≡C	**6l**	85:15	60
15	**1**	3-furyl	**5m**	62:38	n.d.[i]
16[g]	**2**	3-furyl	**6m**	83:17	70
17	**1**	3-pyridyl	**5n**	–	0[j]

[a] Reaction conditions: **1** (0.5 mmol), **4** (3 equiv, 1.5 mmol), $Rh_2(OAc)_4{\cdot}2H_2O$ (2 mol%), −20 °C, 16–18 h in CH_2Cl_2 (1 mL). [b] Determined by ^{1}H NMR spectroscopy. [c] Yields of isolated compounds **5** or **6** after column chromatography. [d] Reaction carried out at 2 mmol scale. [e] Yield not optimized; partial desilylation occurred during chromatography (SiO_2). [f] 91:9 diastereoselectivity in the presence of 2,2′-bipyridyl as additive. [g] Reaction run at −60 °C. [h] Reaction run at −78 °C. [i] n.d. = not determined. [j] Unchanged starting material recovered.

systems; 4.80 Hz to 4.90 Hz for the *trans* isomer. In addition, an X-ray single-crystal structure analysis of compound *cis*-**5a** confirmed the proposed structure.[11]

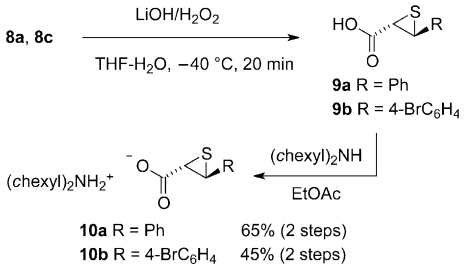
Next, reaction conditions for the selective opening of the thiirane ring and the release of the oxazolidinone auxiliary were explored. For example, treatment of thiiranes *cis*-**5a** and *cis*-**5h** with acetyl chloride in CH_2Cl_2 at room temperature in the presence of $CoCl_2$ (10 mol%), according to the procedure of Iranpoor, Firouzabadi, and Jafari,[12] gave the β-chloro-α-thio imide derivatives **8a** and **8c** in 88% and 65% yields, respectively, after chromatography (Scheme 3). Similarly,



Scheme 3. Thiirane ring opening of adducts **5**.

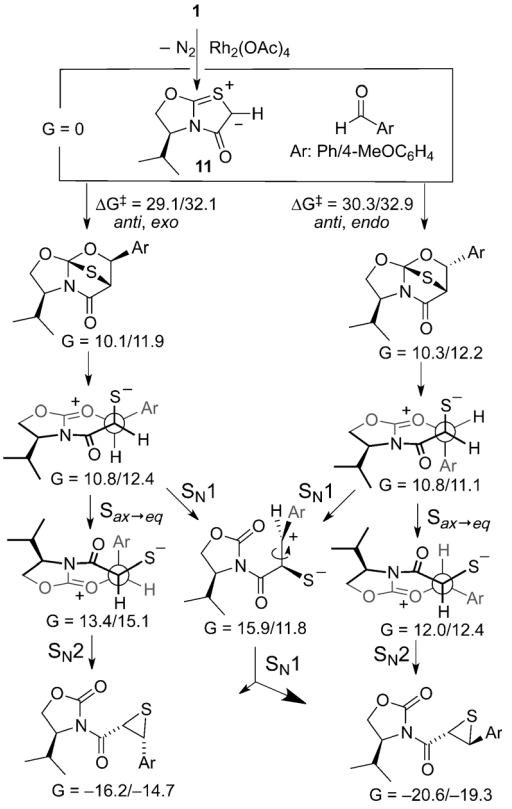
treatment of *cis*-**5a** with acetyl bromide in the presence of $CoBr_2$, as catalyst, afforded the corresponding bromo derivative **8b** in 70% yield upon isolation. In all these three cases a minor amount (6–10%) of the corresponding regioisomeric ring-opening product was also observed in the respective crude reaction mixture. It is important to note that substitution at the β carbon atom during ring opening leading to products **8** occurred with retention of configuration, perhaps by a double inversion pathway involving a transient C–O adduct. Interestingly, acid-promoted cyclization of compounds **8** to restore the thiirane ring took place very efficiently, with inversion of the configuration of β carbon atom. For instance, the treatment of **8a** with methanolic HCl afforded *trans*-**5a** in 70% yield. Accordingly, a two-step thiirane-ring isomerization from *cis* to the more stable *trans* isomer is feasible.

On the other hand, the removal of the oxazolidinone moiety from thiirane adducts **5** through imide hydrolysis or alcoholysis under standard reaction conditions led to extensive loss of the sulfur atom. This problem could be circumvented by performing imide hydrolysis on the ring-opened adducts **8** instead (Scheme 4). Thus, saponification with $LiOH/H_2O_2$ of adducts **8a** and **8c** proceeded with restoration of the thiirane ring, to afford the corresponding acids **9**, which were isolated as crystalline bench stable dicyclohexylamine salts **10**. In this transformation, oxazolidinone was also formed and it could be recovered, transformed into the thione auxiliary, and recycled.[7] Unambiguous determination of the structure of salt **10b** and compound **8a** by X-ray single-crystal structure analysis[11] further confirmed the identity of the products as well as the stereochemical outcome of the reactions involved.



Scheme 4. Recovery of the auxiliary.

A DFT investigation was carried out at the B3LYP level of theory, and provided support for a plausible pathway for this intriguing thiirane-forming reaction. Calculations predict that the corresponding rhodium carbenoid species[11] formed upon treatment of diazo thione compound **1** with $Rh_2(OAc)_4$, evolves into bicyclic ylide **11** (Scheme 5)[13] with no activation



Scheme 5. Principal reaction pathways found by DFT investigation at the B3LYP level of theory for the Rh-catalyzed reaction between diazocompound **1** and either benzaldehyde or *p*-anisaldehyde. Values of Gibbs energy are given in kcal mol^{-1}.

barrier, probably because of the high charge delocalization exhibited by this particular ylide.[14] According to calculations, subsequent reaction of **11** with either benzaldehyde or *p*-anisaldehyde would generate a unique tricyclic adduct,[15] and among the four possible relative orientations of the ylide and aldehyde component during the cycloaddition, those leading to *anti*, *exo* and *anti*, *endo* isomers are preferred. The

complementary *syn* transition states lie considerably higher in energy because unfavorable interactions between the ylide isopropyl substituent and the incoming aldehyde. The energy differences between *anti*, *exo* and *anti*, *endo* approaches for benzaldehyde and *p*-anisaldehyde, (1.2 and 0.8 kcal mol^{-1}, respectively) would justify preferential formation of the *anti, exo* adduct with expected diastereoselectivities near 90:10. Transformation of these tricyclic high energy intermediates into the final thiirane products would follow a more-or-less downhill energy profile, involving thiirane ring opening, $S_{ax\rightarrow eq}$ conformational switch, and internal S_N2 displacement. Accordingly, from a tricyclic *anti, exo* intermediate the *cis*-configured thiirane would be formed; conversely, from the less-favorable *anti, endo* precursor, the *trans*-thiirane would be formed, a prediction that agrees with the experimentally observed trend for most of the aldehydes tested. Interestingly, calculations also offer a plausible explanation of the reversal of the reaction stereochemistry observed experimentally for *p*-anisaldehyde and other related electron-rich aromatic aldehydes. Indeed, thiirane generation could occur through an alternative S_N1-type pathway, which is about 2.5 kcal mol^{-1} less favorable than the S_N2 pathway for benzaldehyde, but conversely about 3.3 kcal mol^{-1} more favorable than the S_N2 pathway for *p*-anisaldehyde. As expected, S_N1-type cyclization would preferentially lead to the most stable *trans*-thiirane product.

In conclusion, we have reported the first Rh-catalyzed reaction of a diazoacetyl compound with aldehydes that affords thiiranes, instead of oxiranes, as known before. This unusual reactivity relies on the use of *N*-(diazoacetyl)oxazolidin-2-thiones as new chiral sulfur-donor reagents and enables the direct production of optically active thiiranes with very high stereoselectivity. Work towards expanding the scope of this sulfur-transfer protocol is currently underway in our laboratory.

Experimental Section

General catalytic procedure for the synthesis of thiiranes **5**–**7**: Rhodium(II) acetate dihydrate (4.8 mg, 0.01 mmol, 2 mol%) was added to a solution of the corresponding diazocompound **1**–**3** (0.50 mmol) and aldehyde **4a**–**p** (3 equiv, 1.5 mmol) in anhydrous CH_2Cl_2 (1.5 mL) at a given temperature, under argon atmosphere. The reaction mixture was stirred for 16–18 h at the same temperature and afterwards quenched with saturated $NaHCO_3$; the organic layer was separated, dried with $MgSO_4$, and filtered. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: AcOEt/hexanes, 1:4) to afford the desired product.

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[1] a) *Organosulfur Chemistry in Asymmetric Synthesis* (Eds.: T. Toru, C. Bolm), Wiley-VCH, Weinheim, **2008**; b) M. Mellah, A. Voituriez, E. Schulz, *Chem. Rev.* **2007**, *107*, 5133 – 5209.

[2] a) D. J. Procter, *J. Chem. Soc. Perkin Trans. 1* **2001**, 335 – 354; for asymmetric synthesis of tertiary thiols and thioethers, see: b) J. Clayden, P. MacLellan, *Beilstein J. Org. Chem.* **2011**, *7*, 582 – 595; for metal-catalyzed C–S bond formation, see: c) T. Kondo, T.-a. Mitsudo, *Chem. Rev.* **2000**, *100*, 3205 – 3220; d) W. Adam, R. M. Bargon, *Chem. Rev.* **2004**, *104*, 251 – 261; e) Y. Zhang, J. Wang, *Coord. Chem. Rev.* **2010**, *254*, 941 – 953.

[3] Leading examples of asymmetric electrophilic α-sulfenylations: Stoichiometric: a) D. A. Evans, K. R. Campos, J. S. Tedrow, F. E. Michael, M. R. Gagné, *J. Am. Chem. Soc.* **2000**, *122*, 7905 – 7920; b) D. Enders, A. Schaadt, *Synlett* **2002**, 498 – 500: organocatalytic: c) M. Marigo, T. C. Wabnitz, D. Fielenbach, K. A. Jørgensen, *Angew. Chem.* **2005**, *117*, 804 – 807; *Angew. Chem. Int. Ed.* **2005**, *44*, 794 – 797; d) G. L. Zhao, R. Rios, J. Vesely, L. Eriksson, A. Cordova, *Angew. Chem.* **2008**, *120*, 8596 – 8600; *Angew. Chem. Int. Ed.* **2008**, *47*, 8468 – 8472; e) L. Fang, A. Lin, H. Hu, C. Zhu, *Chem. Eur. J.* **2009**, *15*, 7039 – 7043; metal catalyzed: f) M. Jereb, A. Togni, *Chem. Eur. J.* **2007**, *13*, 9384 – 9392.

[4] For a review on asymmetric sulfa-Michael additions, see: D. Enders, K. Lüttgen, A. A. Narine, *Synthesis* **2007**, 959 – 980.

[5] For a general review on thiiranes, see: "Thiiranes and Derivatives" M. Saito, J. Nakayama in *Science of Syntheses, Houben-Weyl Methods of Molecular Transformations, Vol. 39* (Eds.: D. Bellus, E. N. Jacobsen, S. V. Ley, R. Noyori, M. Regitz, P. J. Reider, E. Schaumann, I. Shinkai, E. J. Thomas, B. M. Trost, N. Kambe), Thieme, Stuttgart, **2008**, pp. 589 – 658 and Ref. [2d].

[6] Asymmetric synthesis of thiiranes from chiral nonracemic precursors: allenes: a) C. Zhou, C. Fu, S. Ma, *Angew. Chem.* **2007**, *119*, 4457 – 4459; *Angew. Chem. Int. Ed.* **2007**, *46*, 4379 – 4381; oxiranes: b) M. Lee, M. M. Bernardo, S. O. Meroueh, S. Brown, R. Fridman, S. Mobashery, *Org. Lett.* **2005**, *7*, 4463 – 4465; β-thiocyanoalcohols: c) E. Łukowska, J. Plenkiewicz, *Tetrahedron: Asymmetry* **2007**, *18*, 1202 – 1209; synthesis of chiral nonracemic thiiranium ions: d) S. E. Denmark, T. Vogler, *Chem. Eur. J.* **2009**, *15*, 11737 – 11745.

[7] a) C. Palomo, M. Oiarbide, F. Dias, A. Ortiz, A. Linden, *J. Am. Chem. Soc.* **2001**, *123*, 5602 – 5603; b) C. Palomo, M. Oiarbide, F. Dias, R. López, A. Linden, *Angew. Chem.* **2004**, *116*, 3369 – 3372; *Angew. Chem. Int. Ed.* **2004**, *43*, 3307 – 3310; c) C. Palomo, M. Oiarbide, R. López, P. B. González, E. Gómez-Bengoa, J. M. Saá, A. Linden, *J. Am. Chem. Soc.* **2006**, *128*, 15236 – 15247.

[8] For C–S bond formation mediated by sulfur ylides derived from metal carbene, see Ref. [2e]. For metal-catalyzed reactions of α-diazocarbonyl compounds, see: a) M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley-Interscience, New York, **1998**; b) Z. Zhang, J. Wang, *Tetrahedron* **2008**, *64*, 6577 – 6605; c) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704 – 724; d) H. M. L. Davies, J. R. Deton, *Chem. Soc. Rev.* **2009**, *38*, 3061 – 3071; for the generation of thiocarbonyl ylides, see: e) A. Padwa, *Chem. Soc. Rev.* **2009**, *38*, 3072 – 3081.

[9] For a review, see: a) V. K. Aggarwal, M. Crimmin, S. Riches in *Science of Synthesis, Vol. 37* (Ed.: C. J. Forsyth), Thieme, Stuttgart, **2008**, pp. 321 – 406; for leading recent examples, see: b) V. K. Aggarwal, J. P. H. Charmant, D. Fuentes, J. N. Harvey, G. Hynd, D. Ohara, W. Picoul, R. L. Robiette, C. Smith, J.-L. Vasse, C. L. Winn, *J. Am. Chem. Soc.* **2006**, *128*, 2105 – 2114 and references therein. For a mechanistic investigation, see: c) D. R. Edwards, P. Montoya-Peleaz, C. M. Crudden, *Org. Lett.* **2007**, *9*, 5481 – 5484.

[10] a) M. P. Doyle, W. Hu, D. J. Timmons, *Org. Lett.* **2001**, *3*, 933 – 935; b) W.-J. Liu, B.-D. Lv, L.-Z. Gong, *Angew. Chem.* **2009**, *121*, 6625 – 6628; *Angew. Chem. Int. Ed.* **2009**, *48*, 6503 – 6506.

[11] See the Supporting Information for details.

[12] N. Iranpoor, H. Firouzabadi, A. A. Jafari, *Synth. Commun.* **2003**, *33*, 2321 – 2327.

[13] For generation, and subsequent cycloaddition, of thiocarbonyl ylides from the Rh^{II}-catalyzed cyclization of diazothiocarbonyl compounds, see: Ref. [8e] and a) K. T. Potts, E. Houghton, U. P. Singh, *J. Org. Chem.* **1974**, *39*, 3627 – 3631; b) A. Padwa, F. R. Kinder, L. Zhi, *Synlett* **1991**, 287 – 288; c) A. Padwa, A. C. Flick, H. I. Lee, *Org. Lett.* **2005**, *7*, 2925 – 2928.

[14] It has been reported that the treatment of a diazothioamide compound related to **1** with rhodium(II) acetate yielded an stable aromatic mesoionic system: K. T. Potts, P. Murphy, *J. Chem. Soc. Chem. Commun.* **1984**, 1348 – 1349.

[15] An alternative pathway to this tricyclic adduct would involve attack of the thione group onto the epoxide initially generated from the reaction between the aldehyde and the diazocarbonyl moiety. However, the fact that no traces of epoxide product were detected in the reaction mixtures and a 14.4 $kcal\,mol^{-1}$ energy barrier is calculated for such epoxide formation (see Ref. [11]), disfavors the epoxide pathway.

