Novel Rhodium-Catalyzed Reaction of Thiazolidine Derivatives with Carbodiimides

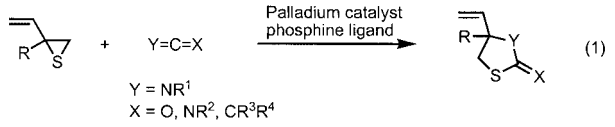
Hai-Bing Zhou, Chune Dong, and Howard Alper*[a]

Abstract: A new, simple, and regioselective synthesis of thiazolidinimine derivatives based on the rhodium-catalyzed reaction of readily available thiazolidines with carbodiimides is described. This methodology provides direct access to a large variety of thiazolidinimine derivatives, possibly via a novel regiospecific insertion of carbodiimides into one of two ring carbon–nitrogen bonds, as well as a metal-catalyzed imine elimination process.

Keywords: carbodiimides · heterocycles · P ligands · rhodium · thiazolidine

Introduction

The synthesis of five-membered heterocyclic rings by metal-catalyzed ring-expansion reactions of heterocyclic compounds has attracted considerable attention in recent years, because of the potential biological activity of some of the products.[1] The usual heterocyclic substrates for this type of reaction with heterocumulenes are small rings, such as oxiranes[2] and aziridines;[3] the reaction results in the formation of 1,3-oxazolidine and imidazolidine derivatives in good to excellent isolated yields. This reaction usually occurs when a substrate having π-electrons (e.g., phenyl) or a vinyl substituent is located at the 2-position of the strained ring system, but not with simple alkylheterocycles. One of us recently reported the first example of the ring expansion of thiiranes catalyzed by palladium to form thiazolidinimine derivatives.[4] Some thiazolidine and thiazolidinimine moieties are found in molecules possessing biological activity.[5] For a variety of reasons including concerns about the inconvenient access to thiiranes, and the benefits of having alternative procedures available for metal-catalyzed synthetic transformations, we have been developing new methods for the formation of functionalized thiazolidine derivatives from economical and readily available sources. Because of the supposed poisoning of the catalyst by the organic-sulfur reactant,[6,7] there are few examples of ring-expansion reactions catalyzed by transition-metal complexes.[8] There are no examples, to our knowledge, of the cyclization of a heterocycle containing two different heteroatoms with carbodiimides. The question arises as to what degree of selectivity of ring-opened cycloaddition occurs into rings containing two heteroatoms. In particular, the regioselectivity of the ring expansion reaction (insertion into carbon–nitrogen versus carbon–sulfur bonds of an N,S-containing heterocycle) is a matter of considerable interest. Herein, we describe the first rhodium-catalyzed rearrangement and cyclization reaction of thiazolidines with carbodiimides for the formation of thiazolidinimine derivatives. Moreover, this methodology uses simple thiazolidines as substrates, which could be readily prepared by alkylation of commercial available thiazolidines. The cyclization occurred under relatively mild reaction conditions (i.e., 90–130 °C and 5 psi N_2). While the anticipated cyclization likely occurs, the reaction proceeds in a novel manner, affording thiazolidinimines in high yield. An unusual imine elimination step may be part of the overall process. The scope of the cyclization was successfully extended to simple unactivated thiazolidines and to functionalized thiazolidinimines.



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Results and Discussion

The palladium-catalyzed reaction of 2-vinylpyrrolidine with heterocumulenes results in the formation of seven-mem-

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Selected X-ray data compound **3d**.

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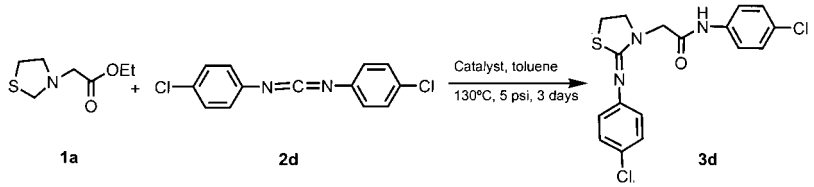
bered ring heterocycles.[9,10] We anticipated that thiazolidines would also afford seven-membered ring heterocycles on reaction with heterocumulenes. Our initial attempts to realize the cyclization of thiazolidine **1a** with aryl isocyanates failed, with starting materials recovered and a complex mixture of unknown compounds formed. When a carbodiimide was used as the reactant, for example, in the reaction of 3-[(ethoxycarbonyl)methyl]thiazolidine (**1a**) with bis(*p*-chlorophenyl)carbodiimide (**2d**), in the presence of catalytic amounts of palladium acetate and dppf at 130 °C for 3 d, the thiazolidinimine **3d** was isolated in 22 % yield (Table 1, entry 2). Dual-site functionalization occurred in this transformation, that is, formation of the thiazolidinimine moiety by rearrangement and cyclization of the thiazolidine ring and amide group formation by the amidation of the ester substituent in the reactant thiazolidine **1a**.

Table 1. Reaction of 3-[(ethoxycarbonyl)methyl]-thiazolidine (**1a**) with bis(*p*-chlorophenyl)carbodiimide **2d** catalyzed by a metal complex.[a]



1a **2d** **3d**

Entry	Catalyst [mol %]	Conv. [%][b]	**3d**, Yields [%][c]
1	$[Pd(OAc)_2]/PPh_3$ (15/60)	10	0
2	$[Pd(OAc)_2]$/dppf (15/30)	31	22
3	$[Pd(OAc)_2]$/dppp (15/30)	11	8
4	$[Pd(OAc)_2]$/dpppentane (15/30)	10	6
5	$[PdCl_2(PhCN)_2]$ (20)	8	<5
6	$[PdCl_2(MeCN)_2]$ (20)	7	<3
7	$[Rh(cod)Cl]_2$/dppf (10/30)	65	59
8	$[Rh(cod)Cl]_2/PPh_3$ (10/60)	58	50
9	$[Rh(cod)Cl]_2$/dpppentane (10/30)	38	30
10	$[Rh(cod)Cl]_2$/dppp (10/30)	42	38
11	$[Rh(cod)Cl]_2$/dppe (10/30)	31	28
12	$[Rh(cod)Cl]_2/P(t\text{Bu})_3$ (10/60)	<10	0
13	$[Rh(cod)Cl]_2/P(O)Ph_3$ (10/60)	<10	0
14	$[Rh(cod)Cl]_2$ (10)	<10	0

[a] The catalyst was dissolved in dry toluene, followed by addition of **1a** and **2d**, the mixture was transferred in a glass autoclave by syringe and stirred under 5 psi at 130 °C. [b] The conversion was determined by GC, using biphenyl as an internal standard, or was calculated based on the crude ^{1}H NMR of the mixture. [c] Isolated yield after preparative TLC and based on the thiazolidine **1a** used.

Identifying features in the ^{1}H NMR spectra characteristic of **3d** include the singlet for the methylene proton between the sulfur and nitrogen atoms, and the signals for the ester ethyl group disappear, while the singlet due to the acetamide is shifted downfield by approximately 1 ppm. The ^{13}C NMR spectrum displays a signal for the carbon of the imine of the thiazolidinimine at 162 ppm. Molecular ion peaks consistent with the structure are observed in the mass spectrum. The structure of thiazolidinimine **3d** was also unambiguously established by X-ray determination (Figure 1).[11] We then investigated optimization of the reaction of **1a** with **2d** by using different reaction conditions.

We found that treatment of the thiazolidine **1a** with bis(*p*-chlorophenyl)carbodiimide (**2c**) in the presence of a catalytic amount of $[Pd(OAc)_2]$ and phosphine ligands such as PPh_3, dppp or dpppentane, affords thiazolidinimine **2d** in up to 8 % yield, along with the recovery of some of the starting material. However, increased loading of the catalyst did not improve the yield at all (Table 1, entries 1, 3 and 4). When $[PdCl_2(PhCN)_2]$ or $[PdCl_2(MeCN)_2]$ was used as the catalyst, only traces of the product was observed (Table 1, entries 5 and 6). In comparison, use of a rhodium complex and a phosphine ligand always afforded the desired product in relatively higher yield.

To optimize the present catalytic reaction, various phosphine ligands were systematically tested for the reaction of **1a** with **2d**. The bidentate phosphine ligand dppf shows the highest catalytic activity. For example, reaction of **1a** with **2d** in the presence of 10 mol % $[Rh(cod)Cl]_2$ and 30 mol % of dppf gave **3a** in 59 % yield and 65 % conversion at 130 °C for 3 d (Table 1, entry 7). In addition, we used PPh_3 as the added ligand, which has similar basicity to dppf, in the reaction of **1a** with **2d**. Use of 10 mol % $[Rh(cod)Cl]_2$ and 60 mol % of PPh_3 gave **3d** in 58 % conversion and 50 % yield respectively (Table 1, entry 8). Use of the more basic bidentate phosphine ligands dpppentane, dppp or dppe for the rhodium catalyzed reaction afforded **3d** in modest yields, that is, 30, 38, and 28 % yields, respectively (Table 1, entries 9, 10 and 11). No products were observed by using a trialkylphosphine such as tri-*n*-butylphosphine or triphenylphosphine oxide (Table 1, entries 12 and 13). It should be noted that simply heating **1a** with **2d** in the presence of a catalytic quantity of $[Rh(cod)Cl]_2$, but in the ab-

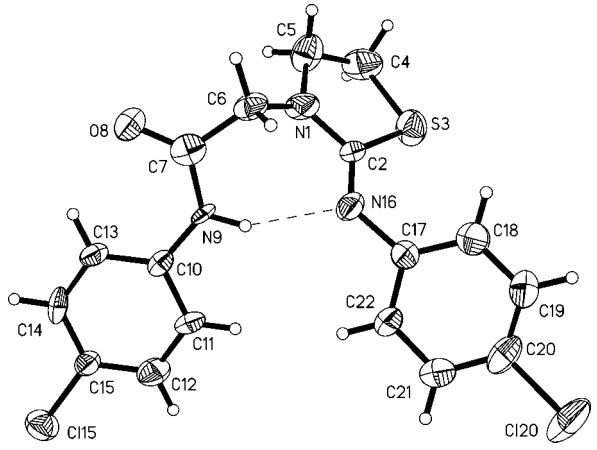


Figure 1. ORTEP of **3d**.

sence of a phosphine ligand, gave only starting material and some decomposition (Table 1, entry 14). Based on the reactions conditions above, we concluded that the catalytic system consisting of $[Rh(cod)Cl]_2$ and dppf is preferred for this reaction. Having established the reaction conditions affording the desired product **3d**, we next investigated the reaction of thiazolidines **1a–c** with the carbodiimides **2a–f**.

The nature of the carbodiimide has a significant effect upon the reaction course. When diphenylcarbodiimide **1a** was used, product **3a** was obtained in 60% yield and 81% conversion in 72 h at 130°C (Table 2, entry 1). When carbodiimides containing electron-withdrawing substituents on the aromatic ring (i.e., **2b–f**) were used for the reaction with **1a**, the strength of the electron-withdrawing substituent on the aryl carbodiimide significantly affected the outcome of the reaction. For example, reaction of **1a** with bis(chlorophenyl)carbodiimides **2b–d**, proceeded smoothly and afforded thiazolidinimines **3b–d** in moderate yields (40–59%) (Table 2, entries 2, 3 and 4). However, for bis(*p*-bromophenyl)carbodiimide (**2e**), the reaction only occurred at the thiazolidine ring site, gave thiazolidinimine **3e** in 25% yield, without the amidation reaction at the ester position (Table 2, entry 5). Use of more reactive bis(*p*-nitrophenyl)carbodiimide (**2f**), which has an increased electron-withdrawing strength, in the reaction with **1a**, rather than the thiazolidinimine, gave the imidazolidinimine **4f** in 42% yield and 52% conversion (Table 2, entry 6). It is conceivable that a thioketene elimination process occurred instead of imine elimination.

Table 2. Reactions of thiazolidine **1** with carbodiimides **2** catalyzed by 10 mol% $[Rh(cod)Cl)]_2$ and 30 mol% dppf in toluene.[a]

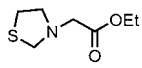
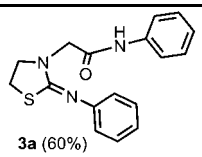
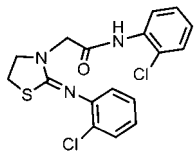
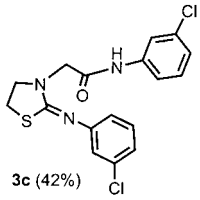
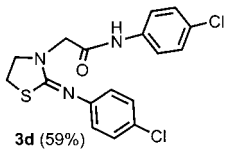
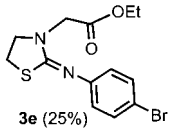
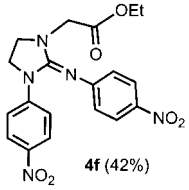
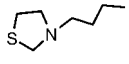
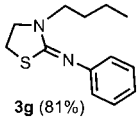
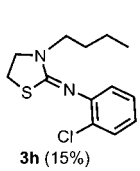
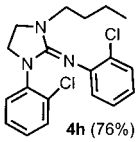
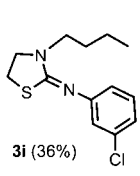
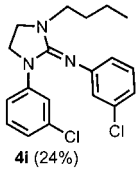
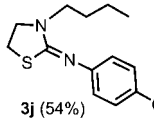
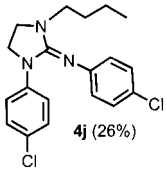
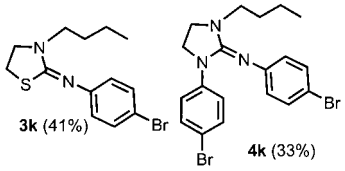
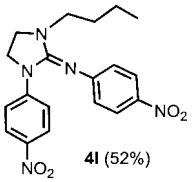
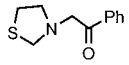
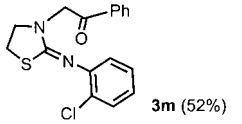
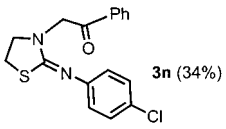
Entry	**1**	**2** [ArN=C=NAr]	*T* [°C]	*t* [h]	Conv.[b] [%]	Product yield [%][c]
1	 **1a**	**2a** (Ar = Ph)	130	72	81	 **3a** (60%)
2		**2b** (Ar = *o*-ClC_6H_4)	140	48	56	 **3b** (43%)
3		**2c** (Ar = *m*-ClC_6H_4)	130	72	51	 **3c** (42%)
4		**2d** (Ar = *p*-ClC_6H_4)	130	72	65	 **3d** (59%)
5		**2e** (Ar = *p*-BrC_6H_4)	125	48	34	 **3e** (25%)
6		**2f** (Ar = *p*-$NO_2C_6H_4$)	90	48	52	 **4f** (42%)
7	 **1b**	**2a**	130	72	91	 **3g** (81%)
8		**2b**	130	72	98	 **3h** (15%)  **4h** (76%)
9		**2c**	130	72	65	 **3i** (36%)  **4i** (24%)
10		**2d**	130	72	85	 **3j** (54%)  **4j** (26%)

Table 2. (Continued)

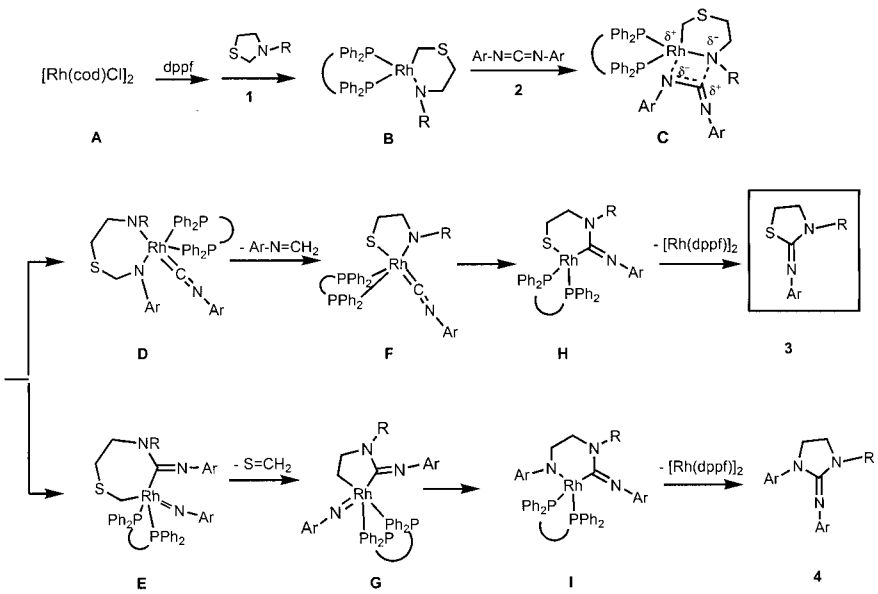
Entry	1	2 [ArN=C=NAr]	T [°C]	t [h]	Conv.[b] [%]	Product yield [%][c]
11		**2e**	130	72	95	 **3k** (41%) **4k** (33%)
12		**2f**	100	48	63	 **4l** (52%)
13	 **1c**	**2b**	100	48	81	 **3m** (52%)
14		**2d**	100	48	51	 **3n** (34%)

[a] The catalyst was dissolved in dry toluene, followed by addition of **1** and **2**, the mixture was transferred in a glass autoclave by syringe and stirred under 5 psi at specified temperature. [b] The conversion was determined by GC, by using biphenyl as an internal standard, or was calculated based on the crude ^{1}H NMR of the mixture. [c] Isolated yield after preparative TLC and based on the thiazolidine **1** used.

We next investigated the reaction of 3-butylthiazolidine **1b** with carbodiimides **2a–f** by using reaction conditions similar to those described above. Reaction of **1b** with **2a–f** was efficient and the products usually were isolated in reasonable yields. Reaction of **1b** with diphenylcarbodiimide **2a** only gave the thiazolidinimine **3g** in 81% yield and 91% conversion (Table 2, entry 7). For reaction of bis(chlorophenyl)carbodiimides **2b–d** with **1b**, the position of the chloro substituent on the aryl carbodiimides has a significant effect on product formation. For example, reaction of **1b** with bis(*o*-chlorophenyl)carbodiimide **2b** gave the imidazolidinimine **4h** as the major product in 76% yield and 98% conversion, accompanied by 15% of thiazolidinimine **3h** (Table 2, entry 8). However, placing a chloro substituent at the *meta*- or *para*-position of the aryl carbodiimides (e.g., **2c** and **2d**), afforded both thiazolidinimines **3i** and **3j** in 36 and 54% yield, as well as imidazolidinimines **4i** and **4j** in 24 and 26% yield, respectively (Table 2, entries 9 and 10). Analogous to the reaction of **1b** with **2c** and **2d**, bis(*p*-bromophenyl)carbodiimide (**2e**), in the reaction with **1b**, gave thiazolidinimine **3k** and imidazolidinimine **4k** in 41 and 33% yield, respectively (Table 2, entry 11). Reaction of **1b** with bis(*p*-nitrophenyl)carbodiimide **2f** led to the exclusive formation of the imidazolidinimine **4l** in 52% yield and 63% conversion (Table 2, entry 12).

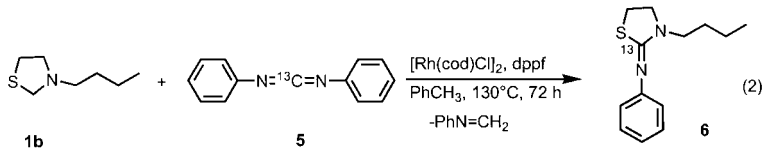
When 3-(benzoylmethyl)thiazolidine (**1c**) was treated with carbodiimide **2b** and **2d** under the same conditions, the desired products **3m** and **3n** were isolated in 52 and 34% yield, respectively (Table 2, entries 13 and 14). Some unidentified products were also formed in these reactions.

A possible mechanism for the reaction is illustrated in Scheme 1. The first step may involve the oxidative addition of the rhodium complex to the thiazolidine **1** would form the Rh^{II} complex **B**.[12] Subsequent cycloaddition of **B** to the carbodiimide **2**, possibly via a four-membered transition state **C**, may afford intermediate **D** or **E**.[13] Migratory insertion of aryl imido into the Rh–C bond of **C** would give **D**. Competitive insertion of carbene into the Rh–N bond of **C** would give **E**. Subsequent imine elimination of **D** would give the intermediate **F** and alternatively, thioketene elimination of **E** would lead to the intermediate **G**. Insertion of carbene or aryl imido into the Rh–N or Rh–C bond of **F** or **G** may give



Scheme 1. Possible mechanism for the formation of **3**.

H or **I**, followed by reductive elimination to form **3** or **4**, and regenerate the catalyst. It seems reasonable to assume that the imino carbon of **3** or **4** is derived from the carbodiimide. To clarify this point, ^{13}C enriched diphenylcarbodiimide **5** was prepared from benzoic-carboxy-^{13}C acid. Treatment of this acid with sodium azide by using cyanuric chloride in the presence of 4-methylmorpholine afforded labeled benzoyl azide in 80% yield.[14] The benzoyl azide underwent thermal rearrangement in refluxing benzene to form the labeled phenyl isocyanate.[15] After completion of the reaction (GC), the phosphine catalyst[16] was added and the mixture was stirred at 65°C for 3 h. The solvent was removed and the residue was distilled under reduced pressure to afford pure labeled diphenylcarbodiimide **5**. When **5** was treated with 3-butylthiazolidine **1b** using conditions identical to those for the unlabeled reaction {[Rh(cod)Cl]$_2$, $PhCH_3$, dppf, 130°C, 3 d}, the ^{13}C-labeled thiazolidinimine **6** was obtained in 90% conversion and 78% yield [Eq. (2)].



The ^{13}C NMR spectrum of **6** (in $CDCl_3$) clearly shows that the product contains ^{13}C at the 2-position (δ 158.8 (^{13}C=N)) (Figure 2), which is a very weak peak in ^{13}C NMR of **3g** (Figure 3). The mass spectrum gave an intense molecular ion at *m*/*e* 235. Therefore, the ^{13}C-labeling experiment demonstrated that the source of the new atom in **6** is the imido group of **5**.

In conclusion, we have achieved a facile direct synthesis of thiazolidinimine derivatives from readily available alkylthiazolidines. The reported catalyst system is tolerant to a variety of thiazolidines and carbodiimides, making the procedure valuable for the synthesis of interesting heterocycles of potential pharmaceutical use.

Experimental Section

All reactions and manipulations of chemicals were carried out using standard Schlenk techniques under an atmosphere of argon. Alkylthiazolidines[8] and carbodiimides[16] were prepared according to the literature. Toluene was dried over Na prior to use. All NMR spectra were recorded using $CDCl_3$ as the solvent with reference to residual $CHCl_3$ (^1H at 7.24 ppm and ^{13}C at 77.0 ppm). Infrared spectra were recorded on a Fourier transform spectrometer and are reported in wavenumbers (cm^{-1}).

General procedure for the rhodium-catalyzed cycloaddition reaction of alkylthiazolidines (1a–c) with carbodiimides 2: [Rh(cod)Cl]$_2$ (14.8 mg, 0.03 mmol, 10 mol% to **1**) was weighed into a Schlenk tube under a stream of argon, and dry toluene (3 mL) was added. Dppf (49.86 mg, 30 mol%) was then added, followed by **1a**, **1b**, or **1c** (0.3 mmol) and then carbodiimide **2** (0.45 mmol). The mixture was transferred in a glass autoclave and stirred under 5 psi of N_2 at a given temperature. The progress of the reaction was monitored by GC and the crude product was purified by silica chromatography using hexane/ethyl acetate 10:1 to 1:1 to afford thiazolidinimine **3** or imidazolidinimine **4**. Further purification was effected using preparative TLC.

***N*-Phenyl-2-(2-phenyliminothiazolidin-3-yl)-acetamide (3a)**: 60% yield; colorless oil; IR (neat): $\tilde{\nu}$=3290, 3056, 2937, 2867, 1672, 1612, 1587, 1546, 1496, 1442, 1294, 1248, 1190, 1142, 1026, 758, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=3.21 (t, J=6.9 Hz, 2H), 3.78 (t, J=6.9 Hz, 2H), 4.26 (s, 2H), 6.97–7.52 (m, 10H), 9.46 (b, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1, 161.1, 150.5, 137.9, 129.2, 129.0, 124.2, 123.9, 121.9, 119.7, 52.8, 52.1, 27.2; MS (70 eV, EI): *m*/*z* (%): 311 (10) [M^+]; EI-HRMS: *m*/*z*: calcd for $C_{17}H_{17}N_3OS$: 311.109249; found: 311.10776.

***N*-(2-Chlorphenyl)-2-[2-(2-chlorophenylimino)-thiazolidin-3-yl]-acetamide (3b)**: 43% yield; colorless oil; IR (neat): $\tilde{\nu}$=3367, 3060, 2943, 2868, 1693, 1609, 1581, 1524, 1469, 1440, 1292, 1238, 1190, 1126, 1057, 1033, 924, 756, 729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=3.29 (t, J=

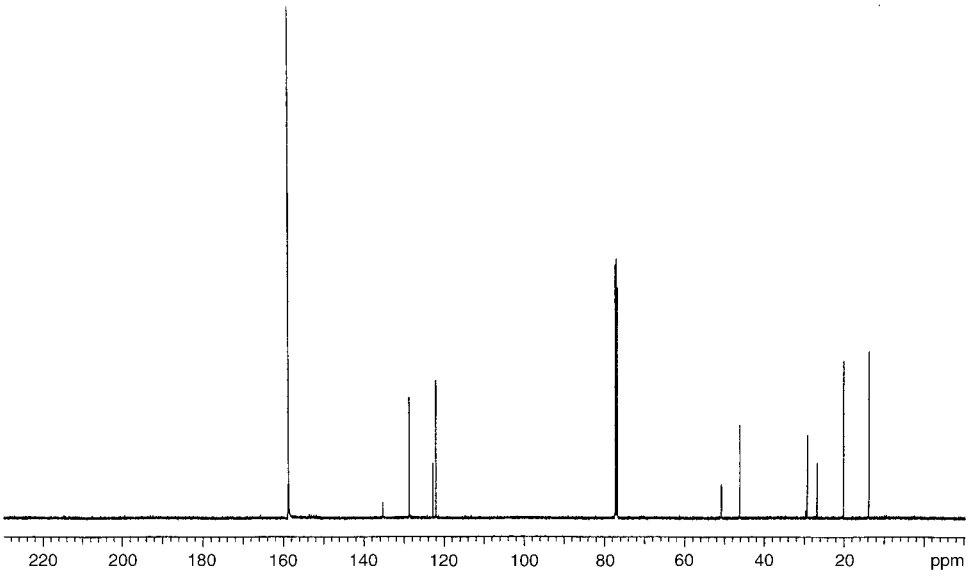


Figure 2. ^{13}C NMR spectrum of **6**.

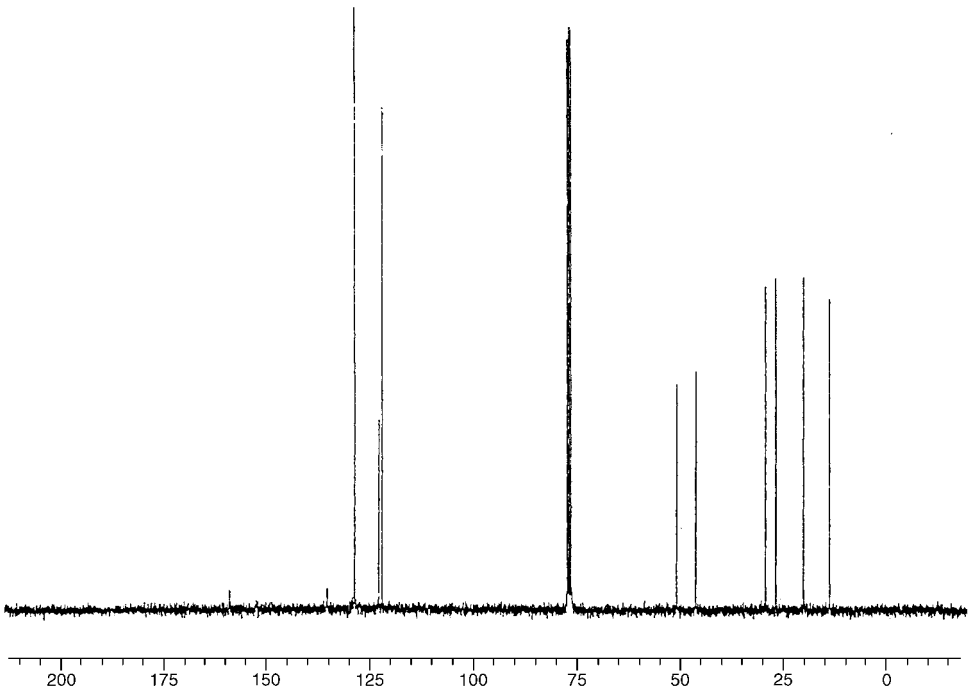


Figure 3. ^{13}C NMR spectrum of **3g**.

6.9 Hz, 2H), 3.84 (t, $J=6.9$ Hz, 2H), 4.40 (s, 2H), 6.96–7.07 (m, 3H), 7.15–7.20 (m, 1H), 7.23–7.28 (m, 1H), 7.32–7.36 (m, 2H), 8.25 (dd, $J=8.2$ Hz, 1H), 9.10 (b, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=166.7$, 162.3, 134.3, 130.5, 129.8, 129.2, 127.9, 127.5, 127.3, 125.4, 124.3, 123.5, 122.8, 52.6, 52.0, 27.5; MS (70 eV, EI): m/z (%): 379 (6) [M^+], 381 (3) [M^++2]; EI-HRMS: m/z: calcd for $C_{17}H_{15}N_3OSCl_2$: 379.031309; found: 379.03269.

***N*-(3-Chlorphenyl)-2-[2-(3-chlorophenylimino)-thiazolidin-3-yl]-acetamide (3c)**: 42% yield; colorless oil; IR (neat): $\tilde{\nu}=3285$, 3065, 2947, 2872, 1678, 1614, 1582, 1481, 1425, 1294, 1190, 1089, 1072, 995, 874, 844, 779, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=3.24$ (t, $J=7.0$ Hz, 2H), 3.79 (t, $J=7.0$ Hz, 2H), 4.23 (s, 2H), 6.83–6.87 (m, 1H), 6.97–6.98 (m, 1H), 7.05–7.07 (m, 2H), 7.18–7.26 (m, 3H), 7.67–7.68 (m, 1H), 9.34 (b, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=166.9$, 161.7, 151.7, 138.8, 134.7, 134.5, 130.2, 130.0, 124.3, 123.9, 122.2, 120.2, 119.8, 117.6, 52.6, 52.1, 27.3; MS (70 eV, EI): m/z (%): 379 (6) [M^+], 381 (23) [M^++2]; EI-HRMS: m/z: calcd for $C_{17}H_{15}N_3OSCl_2$: 379.031309; found: 379.031408.

***N*-(4-Chlorphenyl)-2-[2-(4-chlorophenylimino)-thiazolidin-3-yl]-acetamide (3d)**: 59% yield; colorless needles; m.p. 143–145 °C; IR (neat): $\tilde{\nu}=$ 3273, 3053, 2956, 2869, 1674, 1614, 1583, 1539, 1489, 1400, 1327, 1301, 1240, 1190, 1143, 1089, 1010, 923, 831, 731, 704 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=3.23$ (t, $J=7.0$ Hz, 2H), 3.80 (t, $J=7.0$ Hz, 2H), 4.28 (s, 2H), 6.88–6.91 (m, 2H), 7.23–7.27 (m, 4H), 7.38–7.44 (m, 2H), 9.47 (b, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=166.7$, 162.0, 148.5, 136.4, 129.3, 129.2, 129.1, 129.0, 123.3, 120.8, 52.6, 52.4, 27.3; MS (70 eV, EI): m/z (%): 379 (4) [M^+], 381 (6) [M^++2]; EI-HRMS: m/z: calcd for $C_{17}H_{15}N_3OSCl_2$: 379.031309; found: 379.03159.

[2-(4-Bromophenylimino)-thiazolidin-3-yl]-acetic acid ethyl ester (3e): 25% yield; colorless oil; IR (neat): $\tilde{\nu}=3057$, 2979, 2929, 2871, 1745, 1614, 1577, 1485, 1442, 1417, 1373, 1296, 1238, 1203, 1097, 1070, 1010, 927, 879, 833, 711 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=1.28$ (t, $J=7.1$ Hz, 1H), 3.16 (t, $J=6.9$ Hz, 2H), 3.80 (t, $J=6.9$ Hz, 2H), 4.24 (q, $J=7.1$ Hz, 2H), 4.44 (br, 2H), 6.89 (d, $J=7.9$ Hz, 2H), 7.37 (d, $J=7.9$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=168.4$, 161.2, 132.0, 131.5, 124.5, 120.2, 61.6, 48.3, 29.7, 27.5, 14.2; MS (70 eV, EI): m/z (%): 342 (100) [M^+], 344 (98) [M^++2]; EI-HRMS: m/z: calcd for $C_{13}H_{15}N_2O_2SBr$: 342.003791; found: 341.99644.

[3-(4-Nitrophenyl)-2-(4-nitrophenylimino)-imidazolidin-1-yl]-acetic acid ethyl ester (4f): 42% yield; colorless oil; IR (neat): $\tilde{\nu}=3379$, 3114, 3080, 2981, 2904, 1741, 1634, 1595, 1573, 1504, 1435, 1323, 1280, 1201, 1101, 1024, 953, 912, 854, 752, 735, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=$ 1.21 (t, $J=7.1$ Hz, 3H), 3.72 (t, $J=7.7$ Hz, 2H), 3.90 (s, 2H), 4.07 (t, $J=$ 7.7 Hz, 2H), 4.14 (q, $J=7.1$ Hz, 2H), 6.77 (d, $J=8.8$ Hz, 2H), 7.41(d, $J=$ 9.1 Hz, 2H), 7.95 (d, $J=8.8$ Hz, 2H), 8.05 (d, $J=9.1$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=168.6$, 150.0, 146.0, 142.9, 141.6, 125.0, 124.5, 121.3, 120.2, 113.3, 61.7, 48.6, 47.5, 46.1, 14.1; MS (70 eV, EI): m/z (%): 413 (100) [M^+]; EI-HRMS: m/z: calcd for $C_{19}H_{19}N_5O_6$: 413.133509; found: 413.1327.

(3-Butyl-thiazolidin-2-ylidene)-phenyl-amine (3g): 81% yield; colorless oil; IR (neat): $\tilde{\nu}=3053$, 2957, 2927, 2860, 1622, 1587, 1489, 1441, 1406, 1377, 1333, 1292, 1234, 1184, 1105, 1070, 1024, 926, 877, 767, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=0.95$ (t, $J=7.3$ Hz, 3H), 1.32–1.44 (m, 2H), 1.57–1.66 (m, 2H), 3.10 (t, $J=6.9$ Hz, 2H), 3.50 (t, $J=7.3$ Hz, 2H), 3.60 (t, $J=6.9$ Hz, 2H), 6.90–6.93 (m, 2H), 6.98–7.02 (m, 1H), 7.22–7.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=158.8$, 135.3, 128.7, 122.9, 122.1, 50.9, 46.3, 29.3, 26.9, 20.1, 13.9; MS (70 eV, EI): m/z (%): 234 (70) [M^+]; EI-HRMS: m/z: calcd for $C_{13}H_{18}N_2S$: 234.11909; found: 234.11907.

(3-Butyl-thiazolidin-2-ylidene)-(2-chlorophenyl)-amine (3h): 15% yield; colorless oil; IR (neat): $\tilde{\nu}=3060$, 2958, 2927, 2858, 1645, 1625, 1581, 1519, 1475, 1440, 1298, 1238, 1126, 1055, 1033, 752, 727, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=0.92$ (t, $J=7.3$ Hz, 3H), 1.33–1.42 (m, 2H), 1.54–1.63 (m, 2H), 3.10 (t, $J=6.9$ Hz, 2H), 3.50 (t, $J=7.3$ Hz, 2H), 3.621 (t, $J=6.9$ Hz, 2H), 6.80–6.98 (m, 3H), 7.15 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.3$, 132.1, 131.5, 128.8, 128.0, 123.6, 120.3, 51.0, 46.3, 29.3, 27.0, 20.1, 13.9; MS (70 eV, EI): m/z (%): 268 (75) [M^+], 270 (28) [M^+ +2]; EI-HRMS: m/z: calcd for $C_{13}H_{17}N_2SCl$: 268.08012; found: 268.0821.

[1-Butyl-3-(2-chlorophenyl)-imidazolidin-2-ylidene]-(2-chlorophenyl)-amine (4h): 76% yield; colorless oil; IR (neat): $\tilde{\nu}=3059$, 2956, 2927, 2869, 1645, 1579, 1481, 1437, 1419, 1367, 1273, 1099, 1053, 1031, 933, 864, 756, 729, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=0.96$ (t, $J=7.4$ Hz, 3H), 1.35–1.46 (m, 2H), 1.60–1.70 (m, 2H), 3.41 (t, $J=6.5$ Hz, 2H), 3.53 (t, $J=7.4$ Hz, 2H), 3.66 (b, 2H), 6.39–6.46 (m, 1H), 6.55–6.69 (m, 2H), 6.83–6.93 (m, 3H), 7.06–7.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 152.1, 146.3, 139.2, 131.8, 129.4, 128.8, 128.4, 127.5, 127.0, 126.6, 126.0, 123.6, 121.0, 48.9, 45.7, 45.2, 29.2, 20.1, 14.0; MS (70 eV, EI): m/z (%): 361 (13) [M^+], 363 (8) [M^++2], 365 (6) [M^++4]; EI-HRMS: m/z: calcd for $C_{19}H_{21}N_3Cl_2$: 361.111245; found: 361.10829.

(3-Butyl-thiazolidin-2-ylidene)-(3-chlorophenyl)-amine (3i): 36% yield; colorless oil; IR (neat): $\tilde{\nu}=3059$, 2956, 2929, 2860, 1612, 1581, 1556, 1467, 1441, 1404, 1290, 1234, 1184, 1105, 1070, 995, 925, 906, 871, 844, 779, 717, 694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta=0.94$ (t, $J=7.3$ Hz, 3H), 1.31–

1.43 (m, 2H), 1.55–1.65 (m, 2H), 3.12 (t, $J=6.9$ Hz, 2H), 3.49 (t, $J=7.3$ Hz, 2H), 3.62 (t, $J=6.9$ Hz, 2H), 6.81 (d, $J=8.1$ Hz, 1H), 6.93–6.98 (m, 2H), 7.15 (t, $J=7.9$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.5$, 134.1, 131.5, 129.7, 122.9, 122.5, 120.5, 51.0, 46.3, 29.3, 26.9, 20.1, 13.9; MS (70 eV, EI): m/z (%): 268 (16) [M^+], 270 (6) [M^++2]; EI-HRMS: m/z: calcd for $C_{13}H_{17}N_2SCl$: 269.08012 (M^++1); found: 269.08100.

[1-Butyl-3-(3-chlorophenyl)-imidazolidin-2-ylidene]-(3-chlorophenyl)-amine (4i): 24% yield; colorless oil; IR (neat): $\tilde{\nu}=3060$, 2958, 2929, 2871, 1633, 1579, 1479, 1409, 1371, 1269, 1112, 1095, 993, 900, 871, 777, 686 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.88$ (t, $J=7.3$ Hz, 3H), 1.23–1.28 (m, 2H), 1.50–1.61 (m, 2H), 3.36 (t, $J=7.3$ Hz, 2H), 3.57 (t, $J=8.0$ Hz, 2H), 3.87 (t, $J=8.0$ Hz, 2H), 6.77 (m, 3H), 6.89–6.92 (m, 2H), 7.03–7.05 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=151.7$, 144.3, 141.8, 134.2, 133.8, 129.5, 129.3, 124.7, 122.7, 122.1, 121.6, 121.0, 120.5, 48.7, 46.7, 45.2, 29.0, 19.9, 13.8; MS (70 eV, EI): m/z (%): 361 (29) [M^+], 363 (18) [M^++2], 365 (8) [M^++4]; EI-HRMS: m/z: calcd for $C_{19}H_{21}N_3Cl_2$: 361.111245; found: 361.1076.

(3-Butyl-thiazolidin-2-ylidene)-(4-chlorophenyl)-amine (3j): 54% yield; colorless oil; IR (neat): $\tilde{\nu}=3032$, 2956, 2929, 2860, 1616, 1583, 1487, 1441, 1408, 1296, 1232, 1184, 1091, 1009, 833, 715, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.94$ (t, $J=7.4$ Hz, 3H), 1.30–1.40 (m, 2H), 1.55–1.65 (m, 2H), 3.11 (t, $J=6.9$ Hz, 2H), 3.49 (t, $J=7.4$ Hz, 2H), 3.60 (t, $J=6.9$ Hz, 2H), 6.85 (d, $J=6.7$ Hz, 2H), 7.19 (dd, $J=6.7$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=159.5$, 150.5, 128.8, 128.1, 123.6, 51.0, 46.3, 29.3, 26.9, 20.1, 13.9; MS (70 eV, EI): m/z (%): 268 (6) [M^+], 270 (3) [M^++2]; EI-HRMS: m/z: calcd for $C_{13}H_{17}N_2Cl$: 269.08012; found: 269.0849 [M^++H].

[1-Butyl-3-(4-chlorophenyl)-imidazolidin-2-ylidene]-(4-chlorophenyl)-amine (4j): 26% yield; colorless oil; IR (neat): $\tilde{\nu}=3033$, 2958, 2929, 2871, 1633, 1583, 1492, 1417, 1404, 1371, 1271, 1114, 1091, 1012, 827, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.87$ (t, $J=7.3$ Hz, 3H), 1.23–1.31 (m, 2H), 1.49–1.59 (m, 2H), 3.37 (t, $J=7.3$ Hz, 2H), 3.57 (t, $J=7.8$ Hz, 2H), 3.86 (t, $J=7.8$ Hz, 2H), 6.74 (t, $J=8.3$ Hz, 2H), 6.98 (m, 2H), 7.03 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=152.3$, 143.2, 137.6, 134.9, 128.8, 128.4, 123.4, 118.3, 49.2, 46.8, 45.2, 29.0, 19.8, 13.8; MS (70 eV, EI): m/z (%): 361 (26) [M^+], 363 (17) [M^++2], 365 (8) [M^++4]; EI-HRMS: m/z: calcd for $C_{19}H_{21}N_3Cl_2$: 361.111245; found: 361.1151.

(3-Butyl-thiazolidin-2-ylidene)-(4-bromophenyl)-amine (3k): 41% yield; colorless oil; IR (neat): $\tilde{\nu}=3055$, 2956, 2927, 2860, 1614, 1577, 1483, 1438, 1409, 1332, 1294, 1234, 1184, 1105, 1068, 1004, 924, 879, 831, 731, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.93$ (t, $J=7.3$ Hz, 3H), 1.31–1.40 (m, 2H), 1.53–1.65 (m, 2H), 3.12 (t, $J=6.9$ Hz, 2H), 3.48 (t, $J=7.3$ Hz, 2H), 3.61 (t, $J=6.9$ Hz, 2H), 6.87 (d, $J=6.8$ Hz, 2H), 7.38 (dd, $J=6.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=154.1$, 132.0, 131.4, 128.3, 124.8, 52.1, 47.4, 29.7, 27.6, 20.1, 14.0; MS (70 eV, EI): m/z (%): 312 (76) [M^+], 314 (77) [M^++2]; EI-HRMS: m/z: calcd for $C_{13}H_{17}N_2SBr$: 312.029613; found: 312.02800.

[1-Butyl-3-(4-bromophenyl)-imidazolidin-2-ylidene]-(4-bromophenyl)-amine (4k): 33% yield; colorless oil; IR (neat): $\tilde{\nu}=3024$, 2956, 2927, 2869, 1633, 1575, 1479, 1417, 1404, 1375, 1321, 1271, 1095, 1070, 1010, 927, 823, 734 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.88$ (t, $J=7.4$ Hz, 3H), 1.25–1.31 (m, 2H), 1.48–1.59 (m, 2H), 3.18 (t, $J=7.4$ Hz, 2H), 3.49 (t, $J=7.9$ Hz, 2H), 3.76 (t, $J=7.9$ Hz, 2H), 6.61 (d, J = 7.9 Hz, 2H), 6.97–7.09 (m, 4H), 7.23 (d, $J=7.9$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=151.8$, 139.1, 131.8, 131.6, 131.4, 129.5, 124.1, 123.9, 118.1, 49.2, 46.9, 45.3, 29.0, 19.8, 13.8; MS (70 eV, EI): m/z (%): 449 (29) [M^+], 451 (58) [M^++2], 453 (26) [M^++4]; EI-HRMS: m/z: calcd for $C_{19}H_{21}N_3Br_2$: 449.010231; found: 449.01198.

[1-Butyl-3-(4-nitrophenyl)-imidazolidin-2-ylidene]-(4-nitrophenyl)-amine (4l): 52% yield; colorless oil; IR (neat): $\tilde{\nu}=3082$, 2958, 2929, 2872, 1633, 1595, 1574, 1500, 1479, 1429, 1321, 1271, 1172, 1139, 1109, 1049, 852, 752, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.81$ (t, $J=7.2$ Hz, 3H), 1.14–1.25 (m, 2H), 1.42–1.49 (m, 2H), 3.21 (t, $J=7.3$ Hz, 2H), 3.68 (t, $J=7.2$ Hz, 2H), 4.05 (t, $J=7.3$ Hz, 2H), 6.87 (d, $J=8.4$ Hz, 2H), 7.44 (d, $J=8.4$ Hz, 2H), 7.96–8.17 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=150.2$, 146.1, 142.6, 126.3, 125.0, 124.5, 121.1, 119.6, 113.3, 60.4, 46.8, 45.0, 28.7, 19.7, 13.6; MS (70 eV, EI): m/z (%): 383 (28) [M^+]; EI-HRMS: m/z: calcd for $C_{19}H_{21}N_5O_4$: 383.159331; found: 383.15924.

2-[2-(2-Chlorophenylimino)-thiazolidin-3-yl]-1-phenyl-ethanone (3m): 52% yield; colorless oil; IR (neat): $\tilde{\nu}=3059$, 2956, 2924, 2872, 1697, 1624, 1582, 1467, 1438, 1350, 1292, 1222, 1180, 1057, 1031, 912, 831, 756, 729, 688 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.25$ (t, $J=6.9$ Hz, 2H), 3.80 (t, $J=6.9$ Hz, 2H), 5.02 (s, 2H), 6.94–6.98 (m, 2H), 7.15 (t, $J=7.5$ Hz, 1H), 7.33 (d, $J=8.0$ Hz, 1H), 7.45 (t, $J=7.8$ Hz, 2H), 7.58 (t, $J=7.3$ Hz, 1H), 8.03–8.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=194.6$, 159.5, 135.1, 133.6, 129.7, 128.9, 128.3, 127.2, 125.5, 121.6, 52.7, 51.6, 27.3; MS (70 eV, EI): m/z (%): 330 (43) [M^+], 332 (15) [M^++2]; EI-HRMS: m/z: calcd for $C_{17}H_{15}N_3Cl_2OSCl$: 330.059384; found: 330.06056.

2-[2-(4-Chlorophenylimino)-thiazolidin-3-yl]-1-phenyl-ethanone (3n): 34% yield; colorless needles; m.p. 95–97°C; IR (neat): $\tilde{\nu}=3059$, 2957, 2923, 2874, 1697, 1620, 1583, 1489, 1439, 1419, 1400, 1294, 1222, 1180, 1144, 1089, 1012, 912, 877, 833, 754, 690 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.27$ (t, $J=6.9$ Hz, 2H), 3.79 (t, $J=6.9$ Hz, 2H), 5.07 (s, 2H), 6.89–6.94 (m, 2H), 7.19 (d, $J=7.9$ Hz, 1H), 7.42–7.49 (m, 2H), 7.60–7.61 (m, 2H), 8.01 (d, $J=7.3$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=194.4$, 161.2, 135.1, 133.4, 129.6, 127.9, 124.2, 125.5, 121.6, 61.7, 48.3, 29.6; MS (70 eV, EI): m/z (%): 330 (50) [M^+], 332 (21) [M^++2]; EI-HRMS: m/z: calcd for $C_{17}H_{15}N_3Cl_2OSCl$: 330.059384; found: 330.05772.

Procedure for the rhodium-catalyzed reaction of 3-butylthiazolidine 1b and ^{13}C diphenylcarbodiimide 5—(3-Butyl-thiazolidin-2-ylidene)[2-^{13}C]-phenyl-amine (6): The reaction procedure was the same as that described in the general procedure. The isolated yield of pure **6** was 78%; colorless oil; IR (neat): $\tilde{\nu}=3056$, 2956, 2854, 1624, 1575, 1493, 1438, 1227, 1176, 1068, 1022, 760 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.97$ (t, $J=7.3$ Hz, 3H), 1.36–1.43 (m, 2H), 1.59–1.66 (m, 2H), 3.14 (t, $J=6.9$ Hz, 2H), 3.50 (t, $J=7.3$ Hz, 2H), 3.60 (t, $J=6.9$ Hz, 2H), 6.92–6.93 (m, 2H), 7.00–7.04 (m, 1H), 7.24–7.28 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=158.8$, 135.3, 128.7, 122.9, 122.1, 50.9, 46.2, 29.3, 26.8, 20.1, 13.9; MS (70 eV, EI): m/z (%): 235 (60) [M^+]; EI-HRMS: m/z: calcd for $C_{13}H_{18}N_2S$: 235.1226; found: 235.1218.

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[11] CCDC-246783 (**3d**) contains the supplementary crystallographic data. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

[12] One reviewer suggested that the Rh moiety would insert in the C–S bond rather than the C–N bond. We proposed that the Rh moiety inserts in C–N bond because our previous study (ref. [8a]) has shown, in the rhodium(I) catalyzed ring expansion carbonylation of thiazolidines, a six-membered-ring heterocycle was obtained with exclusive carbon monoxide insertion into the C2–N bond and no insertion into carbon–sulfur bond. These results indicated that the active rhodium intermediate was generated by oxidative addition of rhodium(I) into the C2–N bond of thiazolidine.

[13] See ref. [8a] for rhodium catalyzed ketene elimination process; b) for an example of the transformation of an imido rhodium complex, see F. Ragaini, S. Cenini, *Organometallics* **1994**, *13*, 1178.

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