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ORIGINAL PAPER

Copper-catalyzed synthesis of thiazolidine derivatives via multicomponent reaction of terminal alkynes, elemental sulfur, and aziridines

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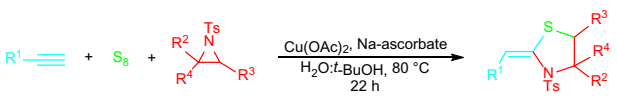
Abstract
An atom-economic catalytic multicomponent reaction between terminal alkynes, elemental sulfur, and aziridines has been reported. In this transformation, alkyne thiolate derived from the reaction of terminal alkynes and elemental sulfur in the presence of CuOTf/DBU reacted with aziridines to afford thiazolidine derivatives.

Graphical abstract



Keywords Thiazolidine · Aziridine · Terminal alkyne · Copper salt · Elemental sulfur

Introduction

Terminal alkynes could serve both as nucleophile and electrophile in organic synthesis and are known as potentially useful substrates in synthesis of heterocyclic compounds [1–3]. In this regards, conversion of terminal alkynes to the corresponding acetylides has attracted enormous interest. Of the various methods documented, those involving metal salts in catalytic or stoichiometric quantities have preeminence. The additions of aluminum, boron, and zinc alkynylides to Michael acceptors have been well documented [4–9]. Recently, catalytic metalation of terminal alkynes opened up possibilities for the effective use of metal-acetylide in complex molecule synthesis [10–12]. Due to the high activity of Cu, metal-acetylide synthesis has been extensively studied on Cu-based catalysts [13–16]. Carreira and co-workers reported the conjugate addition reaction of terminal alkynes catalytic in copper [17]. The additions are not only novel, but also constitute the first example of the conjugate addition reaction of an acetylide catalytic in copper. They also reported a method for the in situ metalation of terminal alkynes and their subsequent reaction with C=O and C=N electrophiles [18, 19]. Recently, a cooperative Brønsted acid/metal catalytic system for the enantioselective alkynylation of α-imino esters has been developed [20]. This catalytic model also opened up possibilities for the usage of copper-acetylide in multicomponent reactions [21–25]. In spite of metal-acetylide importance in addition reactions, the number of available reports featuring the reaction of such substrates with heterocumulene remains scarce. Ghazanfarpour reported an interesting multicomponent reaction using terminal alkynes, carbon disulfide, and oxiranes [26]. Samzadeh-Kermani also described a reaction involving terminal alkynes, isothiocyanates, and oxiranes using

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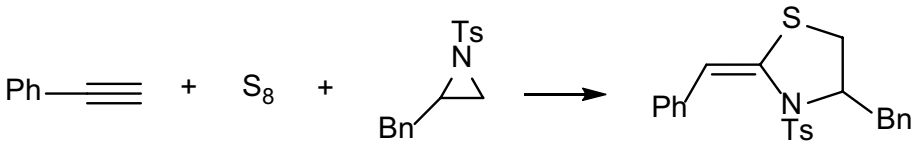
silver salt as the catalyst [27]. Same group reported a three-component reaction between terminal alkynes, elemental sulfur, and oxiranes using sodium hydride to form sodium acetylide [28]. This reaction suffered from the limitation such as requiring strong base. These finding encouraged us to examine the efficiency of elemental sulfur in reaction with alkynes and aziridines using copper salts to form thiazolidine derivatives.

Results and discussion

To test our hypothesis and identify systems capable of mediating this transformation, we considered performing the reaction employing phenyl acetylene (**1a**), elemental sulfur (**2**), and aziridine **3a** using CuI and $(i\text{-Pr})_2$EtN in MeCN. Selected results from our screening experiments are summarized in Table 1. After 22 h of stirring at 80 °C, the desired product **4a** was obtained only in 14% yield together with 1,4-diphenylbuta-1,3-diyne **5** in 39% yield (Table 1, entry 1). This compound must be generated through oxidative Glaser coupling of Cu(I) acetylides [29]. It is worth mentioning that no compounds arising from the direct reaction of copper acetylide and aziridine are detected by crude NMR analysis. Other copper salts also promoted the reaction, however the yields were comparatively lower (Table 1, entries 2–6). It was delightedly found that 10 mol % loading of *N*-heterocyclic carbene copper(I) catalyst (IPr)CuCl (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was turned out to effectively suppress the Glaser coupling

Table 1 Optimization of reaction conditions



1a **2** **3a** **4a**

Entry	Catalyst	Additive	Solvent	Yield/%
1	CuI	$(i\text{-Pr})_2$EtN	MeCN	14 (39)[a]
2	Cu_2O	$(i\text{-Pr})_2$EtN	MeCN	23 (31)[a]
3	CuBr	$(i\text{-Pr})_2$EtN	MeCN	11 (54)[a]
4	CuCl	$(i\text{-Pr})_2$EtN	MeCN	Traces (53)[a]
5	$Cu(OAc)_2$	$(i\text{-Pr})_2$EtN	MeCN	14 (42)[a]
6	$Cu(OTf)_2$	$(i\text{-Pr})_2$EtN	MeCN	25 (58)[a]
7	(IPr)CuCl	$(i\text{-Pr})_2$EtN	MeCN	40 (11)[a]
8	$Cu(SO_4)_2$	Na-ascorbate	H_2O:*t*-BuOH	59 (traces)[b]
9	$CuCl_2$	Na-ascorbate	H_2O:*t*-BuOH	46 (11)[b]
10	$Cu_2(CO_3)$	Na-ascorbate	H_2O:*t*-BuOH	38 (18)[b]
11	$Cu_3(PO4)_2$	Na-ascorbate	H_2O:*t*-BuOH	49 (15)[b]
12	$Cu(acac)_2$	Na-ascorbate	H_2O:*t*-BuOH	61
13	$Cu(OAc)_2$	Na-ascorbate	H_2O:*t*-BuOH	76
14	$Cu(OTf)_2$	Na-ascorbate	H_2O:*t*-BuOH	15 (21)[b]
15	$Fe(OTf)_3$	$(i\text{-Pr})_2$EtN	MeCN	(41)[b]
16	$In(OTf)_3$	$(i\text{-Pr})_2$EtN	MeCN	(52)[b]
17	$Pd(OAc)_2$	$(i\text{-Pr})_2$EtN	MeCN	35
18	$AuCl_3$	$(i\text{-Pr})_2$EtN	MeCN	72
19	AgOAc	$(i\text{-Pr})_2$EtN	MeCN	–
20	CuI	$(i\text{-Pr})_2$EtN	PEG-400	(45)[b]
21	$Cu(OAc)_2$	Na-ascorbate	H_2O:*t*-BuOH	80[c]

Reaction conditions: **1a** (1.2 mmol), **2** (0.3 mmol), **3a** (1.0 mmol), catalyst (0.3 mmol), base (1.5 mmol) or additive (0.6 mmol), in 3 cm^3 solvent or 3 cm^3 H_2O/*t*-BuOH (6:1) at 80 °C for 22 h

[a]The digit in parentheses refer to the yield of Glaser coupling product **5**

[b]The digit in parentheses refer to the yield of the direct coupling by-product

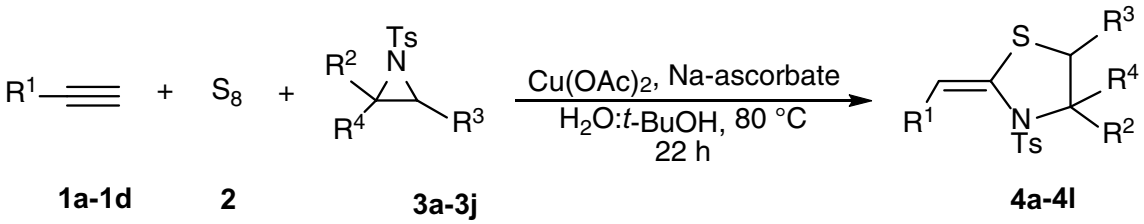
[c]The reaction conducted with $Cu(OAc)_2$ (0.2 mmol) and Na-ascorbate (0.4 mmol)

by-product formation (Table 1, entry 7). We also examined the Cu(II)/ascorbate system for in situ preparation of Cu(I) alkynyl specie [30]. The result was dramatically improved when the reaction was performed in the presence of $CuSO_4$ pentahydrate and sodium ascorbate however, a traces amounts of the direct coupling side-product of acetylide and aziridine was also detected (Table 1, entry 8). A Cu(II)/ascorbate screen showed that $Cu(OAc)_2$ gave superior yields in comparison to other copper (II) salts (Table 1, entries 9–14). These results demonstrated that the insertion of elemental sulfur into copper-acetylide species proceeds significantly faster than that of aziridine using $Cu(OAc)_2$. Lewis acids like $Fe(OTf)_3$ and $In(OTf)_3$ were not efficient in carrying out the desired transformation (Table 1, entries 15 and 16). A moderate yield of the product was achieved when $Pd(OAc)_2$ was employed as the catalyst (Table 1, entry 17) while, $AuCl_3$ provided a high yield of **4a** in 16 h (Table 1, entry 18). Importantly, there was no product formation using AgOAc as the catalyst (Table 1, entry 19).

The yield of **4a** completely suppressed when we replaced H_2O/*t*-BuOH with polyethylene glycol (PEG) (a known solvent for activating of oxiranes and aziridines [31]) and instead the direct coupling by-product was achieved in moderate yield (Table 1, entry 20). It could be deduced that PEG activates aziridine and consequently the insertion of **3a** into copper acetylide species proceeds faster than that of elemental sulfur. Gratifyingly, we found that the use of lower loadings of Cu(II) and sodium ascorbate resulted in higher yields (Table 1, entry 21).

We next evaluated the scope of this reaction and our results are shown in Table 2. Benzyl-substituted aziridine **3a** afforded the corresponding tosylthiazolidines motif **4a** in good yield (Table 2, entry 1). It was found that *gem-di*substituted aziridine **3b** gave the corresponding product in moderate yield, most likely due to the steric hindrance of alkyl groups (Table 2, entry 2). The desired coupling reactions could be smoothly carried out using simple alkyl-substituted aziridines (Table 2, entries 3 and 4). The *meso* aziridine derived from cyclohexene participated effortlessly

Table 2 Synthesis of functionalized tosylthiazolidines



1a-1d **2** **3a-3j** **4a-4l**

Entry	Alkyne	R^1	Aziridine	R^2, R^3, R^4	Yield/%
1	**1a**	Ph	**3a**	Bn, H, H	**4a**, 80
2	**1a**	Ph	**3b**	*n*-C_3H_7, H, CH_3	**4b**, 68
3	**1a**	Ph	**3c**	*n*-C_4H_9, H, H	**4c**, 87
4	**1a**	Ph	**3d**	*n*-C_6H_{13}, H, H	**4d**, 76
5	**1a**	Ph	**3e**	$-(CH_2)_4-$ H	**4e**, 89
6	**1a**	Ph	**3f**	$-(CH_2)_5-$ H	**4f**, 46
7	**1a**	Ph	**3g**	$-(CH_2)_3-$ H	Traces
8	**1a**	Ph	**3h**	Ph, H, H	**4g**, 90[a]
9	**1a**	Ph	**3i**	Ph, CH_3, H	**4h**, 85[b]
10	**1a**	Ph	**3j**	Ph, H, CH_3	**4i**, 70[a]
11	**1b**	*n*-Pr	**3a**	Bn, H, H	**4j**, 76[c]
12	**1c**	2-furyl	**3a**	Bn, H, H	**4k**, 92
13	**1d**	TMS	**3a**	Bn, H, H	**4l**, 68[d]

For all entries except stated otherwise: **1** (1.2 mmol), **2** (0.3 mmol), **3** (1.0 mmol), $Cu(OAc)_2$ (0.2 mmol), Na-ascorbate (0.4 mmol), in 3 cm^3 H_2O/*t*-BuOH (6:1) at 80 °C for 22 h

[a]The yield of benzylic-attacked product

[b]The yield of both regioisomer

[c]Reaction mixture was stirred for 26 h

[d]Reaction mixture was stirred at 90 °C for 24 h

in this multicomponent reaction and furnished the *trans*-configuration product **4e** in good yield (Table 2, entry 5). Cycloheptene aziridine **3e** afforded the corresponding product in moderate yield while, no the desired reaction took place in the presence of cyclopentene aziridine **3 g**, because of the high strain energy of *trans*-stereochemistry of the product (Table 2, entries 6 and 7). As expected, 2-phenyl-*N*-tosylaziridine (**3 h**) was attacked by sulfur atom at the benzylic position (Table 2, entry 8). For the phenyl- and alkyl-substituted aziridine **3i**, the terminal- and benzylic-attacked products were formed in a ratio of 1:1, likely due to the interference of the electronic and steric effects (Table 2, entry 9). The difference in reactivity was reflected in the reaction of aziridine **3j**, where the attack exclusively occurred at the benzylic position (Table 2, entry 10). In this reaction we could not detect the other plausible regioisomers at all. No obvious decreases in yields was observed when 1-pentyne (**1b**) was used as the substrate (Table 2, entry 11). Heteroaromatic terminal alkyne **1c** engaged proficiently in this transformation (Table 2, entry 12). Trimethylsilylacetylene also gave the corresponding tosylthiazolidines skeleton containing vinylsilane motif in good yield which would be interesting for the synthetic chemists because of vinylsilanes being among the most important organosilicon compounds (Table 2, entry 13).

The structures of the products were confirmed by spectroscopic analyses. For example, the ^{1}H NMR spectrum of **4a** showed characteristic (AB)X spin system for the CH_2-CH H-atoms, together with a (AB)X spin system for the benzylic group. The ^{13}C NMR spectrum of **4a** exhibited 24 signals in agreement with the proposed structure. The mass spectrum of **4a** displayed the molecular ion peak at $m/z = 421$.

Mechanistically, it is conceivable that the reaction involves the initial formation of copper acetylide **6**. The metal acetylide then attacked on elemental sulfur (**2**) to afford intermediate **7** and **8**. This anionic adduct reacts with **3** to afford **9** and finally, cyclization and protonation of this intermediate gives **4** (Scheme 1).

In this report we attempt to develop a novel catalytic multicomponent reaction between terminal alkynes, elemental sulfur, and aziridines. The control experiments showed that the choice of catalyst and the reaction medium had great impact in furnishing the desired transformation. We found that the efficiency and regioselectivity of the ring opening reaction of aziridines is very sensitive to the electronic as well as steric properties of substrates. Alkyl terminal alkyne required a longer reaction times to furnish the reaction with good success. Gratifyingly, the reaction was proved to be general under the optimized conditions, performing well in most of the cases examined.

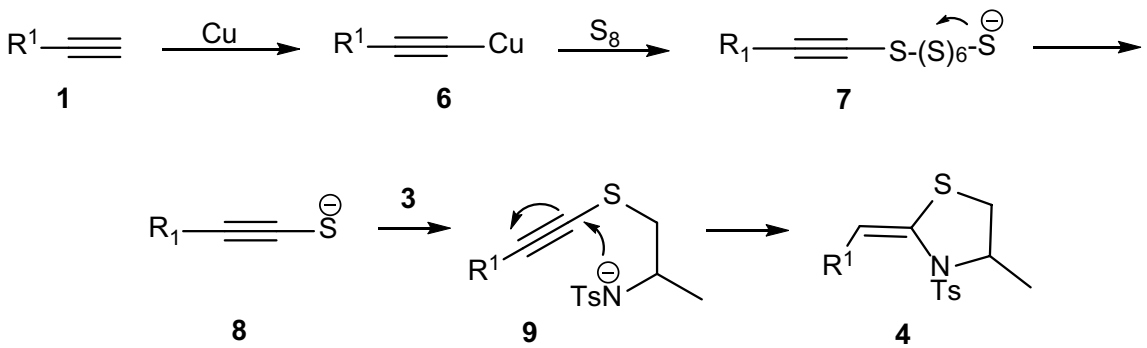
Experimental

Elemental sulfur, catalysts, bases, and solvents were obtained from Merck. All the solvents were purchased from Wako Pure Chemical Industries, and were dried and degassed before use. *N*-Tosylaziridines were prepared using the literature procedures [32]. Melting points were measured with Electrothermal-9100 apparatus. IR spectra were recorded with Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with Bruker DRX-500 AVANCE instrument; in $CDCl_3$ at 500 and 125 MHz, resp; δ in ppm, J in Hz. Mass spectra were recorded with EIMS (70 eV): Finnigan-MAT-8430 mass spectrometer. Elemental analyses (C, H, N) were performed with a Heraeus CHN-*O*-Rapid analyzer. The results agreed favourably with the calculated values. Column chromatography was performed using silica gel 60 (particle size 63–200 µm) (Merck, item number 7734–3). TLC was performed using silica gel 60 (Merck, item number 116,835).

General procedure for the preparation of compounds 4

Amixture of terminal alkyne (1.2 mmol), $Cu(OAc)_2$ (0.2 mmol), Na-ascorbate (0.4 mmol), and elemental sulfur

Scheme 1



(0.3 mmol) in 3 cm^3 H_2O/*t*-BuOH (6:1) was stirred at 25 °C for 30 min. Aziridine (1.0 mmol) was then added and the resulting yellowish mixture was warmed up to 80 °C and stirred for 22–26 h. After completion of the reaction, it was diluted by 5 cm^3 EtOAc and 5 cm^3 of a saturated NH_4Cl solution. The mixture stirred for additional 30 min and two layers were separated. The aqueous layer was then extracted with EtOAc (10 $cm^3 \times 3$). The combined organic layers were washed with 10 cm^3 water and 10 cm^3 brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by chromatography (silica gel, hexane: EtOAc 5:1) to give the pure product.

4-Benzyl-2-benzylidene-3-tosylthiazolidine (4a,$C_{24}H_{23}NO_2S_2$) Pale yellow solid; yield: 0.34 g (80%); m.p.: 105–107 °C; IR (KBr): $\bar{\nu}$ = 3032, 2978, 1541, 1364, 1311, 1115 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 2.52 (3H, s, Me), 2.85 (1H, dd, ^2J = 11.2 Hz, ^3J = 9.7 Hz, CH), 3.15 (1H, dd, ^2J = 11.2 Hz, ^3J = 5.1 Hz, CH), 3.34 (1H, dd, ^2J = 10.8 Hz, ^3J = 6.0 Hz, CH), 3.51 (1H, dd, ^2J = 10.8 Hz, ^3J = 5.2 Hz, CH), 3.81–3.87 (1H, m, CH), 5.34 (1H, s, CH), 7.18-7.29 (5H, m, 5 CH), 7.32-7.41 (5H, m, 5 CH), 7.63 (2H, d, ^3J = 6.0 Hz, 2 CH), 7.71 (2H, d, ^3J = 6.7 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 22.6 (Me), 38.4 (CH_2), 40.7 (CH_2), 69.6 (CH), 96.1 (CH), 125.4 (CH), 125.7 (CH), 127.6 (2 CH), 128.1 (2 CH), 128.7 (2 CH), 129.2 (2 CH), 129.6 (2 CH), 130.0 (2 CH), 135.1 (C), 135.6 (C), 138.2 (C), 139.1 (C), 162.3 (C) ppm; MS: *m/z* (%) = 421 (M^+, 1), 266 (16), 174 (50), 155 (39), 91 (100), 77 (52), 54 (42).

2-Benzylidene-4-methyl-4-propyl-3-tosylthiazolidine (4b,$C_{21}H_{25}NO_2S_2$) Yellow oil; yield: 0.36 g (68%); IR (KBr): $\bar{\nu}$ = 3025, 2980, 1556, 1341, 1314, 1122 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.81 (3H, t, ^3J = 6.0 Hz, Me), 1.31–1.40 (4H, m, 2 CH_2), 1.59 (3H, s, Me), 2.54 (3H, s, Me), 3.17 (1H, d, ^2J = 10.4 Hz, CH), 3.31 (1H, d, ^2J = 10.7 Hz, CH), 5.38 (1H, s, CH), 7.28–7.42 (5H, m, 5 CH), 7.60 (2H, d, ^3J = 6.2 Hz, 2 CH), 7.68 (2H, d, ^3J = 6.4 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 15.3 (Me), 15.8 (CH_2), 22.0 (Me), 24.6 (Me), 43.3 (CH_2), 48.7 (CH_2), 70.1 (C), 96.2 (CH), 126.5 (CH), 127.7 (2 CH), 128.3 (2 CH), 128.8 (2 CH), 130.5 (2 CH), 134.1 (C), 135.3 (C), 139.0 (C), 160.5 (C) ppm; MS: *m/z* (%) = 387 (M^+, 4), 232 (24), 1437 (34), 155 (61), 134 (40), 77 (100), 54 (48).

2-Benzylidene-4-butyl-3-tosylthiazolidine (4c,$C_{21}H_{25}NO_2S_2$) Yellow powder; m.p.: 73–75 °C; yield: 0.34 g (87%); IR (KBr): $\bar{\nu}$ = 3021, 2980, 1557, 1387, 1345, 1123 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.89 (3H, t, ^3J = 6.4 Hz, Me), 1.21–1.49 (6H, m, 3 CH_2), 2.47 (3H, s, Me), 3.07 (1H, dd, ^2J = 11.0 Hz, ^3J = 9.7 Hz, CH), 3.26 (1H, dd, ^2J = 11.0 Hz, ^3J = 5.2 Hz, CH), 3.55–3.64 (1H, m, CH), 5.34 (1H, s, CH), 7.25–7.43 (5H, m, 5 CH), 7.59 (2H, d, ^3J = 6.8 Hz, 2 CH), 7.68 (2H, d, ^3J = 6.6 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 14.9 (Me), 24.3 (Me), 25.9 (CH_2), 28.1 (CH_2), 34.7 (CH_2), 40.3 (CH_2), 67.2 (CH), 97.4 (CH), 126.7 (CH), 127.5 (2 CH), 128.4 (2 CH), 128.8 (2 CH), 131.53 (2 CH), 134.8 (C), 135.9 (C), 139.3 (C), 160.3 (C) ppm; MS: *m/z* (%) = 490 (M^+, 1), 230 (21), 155 (62), 142 (43), 77 (100), 54 (53).

2-Benzylidene-4-hexyl-3-tosylthiazolidine (4d,$C_{23}H_{29}NO_2S_2$) Yellow oil; yield: 0.31 g (76%); IR (KBr): $\bar{\nu}$ = 3023, 2978, 1561, 1371, 1343, 1118 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.87 (3H, t, ^3J = 6.6 Hz, Me), 1.26–1.63 (10H, m, 5 CH_2), 2.52 (3H, s, Me), 3.02 (1H, dd, ^2J = 12.1 Hz, ^3J = 4.9 Hz, CH), 3.27 (1H, dd, ^2J = 12.1 Hz, ^3J = 9.5 Hz, CH), 3.50–3.61 (1H, m, CH), 5.43 (1H, s, CH), 7.26–7.45 (5H, m, 5 CH), 7.63 (2H, d, ^3J = 6.5 Hz, 2 CH), 7.71 (2H, d, ^3J = 6.9 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 15.6 (Me), 24.3 (Me), 24.5 (CH_2), 28.1 (CH_2), 29.5 (CH_2), 34.3 (CH_2), 37.9 (CH_2), 41.6 (CH_2), 65.9 (CH), 96.5 (CH), 126.2 (CH), 127.1 (2 CH), 128.2 (2 CH), 129.4 (2 CH), 130.5 (2 CH), 134.8 (C), 135.9 (C), 139.6 (C), 159.7 (C) ppm; MS: *m/z* (%) = 415 (M^+, 3), 258 (19), 174 (31), 155 (66), 91 (42), 77 (100), 54 (60).

2-Benzylidene-3-tosyloctahydrobenzo[*d*]thiazole (4e,$C_{21}H_{23}NO_2S_2$) Yellow powder; m.p.: 180–182 °C; yield: 0.34 g (89%); IR (KBr): $\bar{\nu}$ = 3032, 2981, 1541, 1347, 1321, 1108 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.21–2.26 (8H, m, 4 CH_2), 2.48 (3H, s, Me), 2.64–2.71 (1H, m, 1 CH), 3.06–3.14 (1H, m, CH), 5.29 (1H, s, CH), 7.27–7.46 (5H, m, 5 CH), 7.61 (2H, d, ^3J = 6.0 Hz, 2 CH), 7.73 (2H, d, ^3J = 6.6 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.1 (CH_2), 24.9 (Me), 27.8 (CH_2), 29.5 (CH_2), 31.6 (CH_2), 45.1 (CH), 64.8 (CH), 98.5 (CH), 126.6 (CH), 127.5 (2 CH), 128.2 (2 CH), 129.1 (2 CH), 130.5 (2 CH), 134.2 (C), 135.7 (C), 139.9 (C), 159.8 (C) ppm; MS: *m/z* (%) = 385 (M^+, 1), 274 (13), 185 (54), 155 (37), 91 (35), 77 (100), 54 (47).

2-Benzylidene-3-tosyloctahydro-2*H*-cyclohepta[*d*]thiazole (4f,$C_{22}H_{25}NO_2S_2$) Yellow powder; m.p.: 173–175 °C; yield: 0.18 g (46%); IR (KBr): $\bar{\nu}$ = 3046, 2971, 1613, 1555, 1341, 1334, 1127 cm^{-1}; ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 1.39–2.01 (10H, m, 5 CH_2), 2.49 (3H, s, Me), 2.51–2.59 (1H, m, 1 CH), 2.87–2.96 (1H, m, CH), 5.36 (1H, s, CH), 7.28–7.474 (5H, m, 5 CH), 7.59 (2H, d, ^3J = 6.6 Hz, 2 CH), 7.69 (2H, d, ^3J = 6.6 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 25.2 (Me), 25.1 (CH_2), 26.3 (CH_2), 26.9 (CH_2), 30.7 (CH_2), 34.8 (CH_2), 49.8 (CH), 69.5 (CH), 97.5 (CH), 126.1 (CH), 127.0 (2 CH), 128.7 (2 CH), 129.1 (2 CH), 130.7 (2 CH), 134.5 (C), 136.1 (C), 140.5 (C), 158.6 (C) ppm; MS: *m/z* (%) = 399 (M^+, 6), 288 (25), 197 (61), 155 (43), 77 (100), 54 (39).

2-Benzylidene-5-phenyl-3-tosylthiazolidine (4g,$C_{23}H_{21}NO_2S_2$) Pale yellow solid; m.p.: 105–107 °C; yield: 0.37 g (90%); IR (KBr): $\bar{\nu}$ = 3021, 2978, 1565, 1344, 1310, 1136 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 2.48 (3H, s, Me), 3.95–4.05 (1H, dd, ^3J = 11.7 Hz, ^3J = 7.1 Hz, CH), 4.38 (1H, dd, ^2J = 12.4 Hz, ^3J = 5.6 Hz, CH), 4.71 (1H, dd, ^2J = 12.4 Hz, ^3J = 9.8 Hz, CH), 5.35 (1H, s, CH), 7.18–7.46 (10H, m, 10 CH), 7.59 (2H, d, ^3J = 6.7 Hz, 2 CH), 7.71 (2H, d, ^3J = 6.5 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.2 (Me), 54.6 (CH), 66.9 (CH), 97.2 (CH), 126.1 (CH), 126.4 (CH), 127.0 (2 CH), 128.3 (2 CH), 128.5 (2 CH), 129.1 (2 CH), 129.5 (2 CH), 130.6 (2 CH), 134.4 (C), 135.9 (C), 138.8 (C), 139.7 (C), 153.6 (C) ppm; MS: *m/z* (%) = 407 (M^+, 7), 296 (22), 294 (57), 155 (44), 77 (100), 54 (48).

2-Benzylidene-4-methyl-5-phenyl-3-tosylthiazolidine (4h,$C_{24}H_{23}NO_2S_2$) Yellow powder; m.p.: 143–145 °C; yield: 0.36 g (85%); IR (KBr): $\bar{\nu}$ = 3026, 2981, 1562, 1361, 1321, 1132 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.38 (3H, d, ^3J = 5.8 Hz, Me), 2.45 (3H, s, Me), 3.60 (1H, d, ^3J = 6.2 Hz, CH), 3.87 (1H, d, ^3J = 6.2 Hz, CH), 5.33 (1H, s, CH), 7.17–7.46 (10H, m, 10 CH), 7.58 (2H, d, ^3J = 6.5 Hz, 2 CH), 7.69 (2H, d, ^3J = 6.7 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 15.6 (Me), 24.3 (Me), 58.4 (CH), 68.4 (CH), 96.5 (CH), 125.3 (CH), 126.1 (CH), 127.2 (2 CH), 127.5 (2 CH), 128.1 (2 CH), 128.9 (2 CH), 129.7 (2 CH), 131.4 (2 CH), 134.2 (C), 134.9 (C), 138.7 (C), 141.3 (C), 151.2 (C) ppm; MS: *m/z* (%) = 421 (M^+, 1), 406 (12), 251 (29), 190 (40), 155 (57), 77 (100).

2-Benzylidene-5-methyl-5-phenyl-3-tosylthiazolidine (4i,$C_{24}H_{23}NO_2S_2$) Yellow powder; m.p.: 102–104 °C; yield: 0.29 g (70%); IR (KBr): $\bar{\nu}$ = 3026, 2982, 1563, 1365, 1334, 1148 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 1.78 (3H, s, Me), 2.45 (3H, s, Me), 4.33 (1H, d, ^2J = 10.6 Hz, CH), 4.65 (1H, d, ^2J = 10.6 Hz, CH), 5.25 (1H, s, CH), 7.18–7.47 (10H, m, 10 CH), 7.61 (2H, d, ^3J = 6.4 Hz, 2 CH), 7.69 (2H, d, ^3J = 6.5 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.2 (Me), 27.3 (Me), 57.3 (C), 68.4 (CH_2), 97.6 (CH), 125.3 (CH), 126.0 (2 CH), 126.3 (CH), 127.7 (2 CH), 128.6 (2 CH), 128.8 (2 CH), 129.3 (2 CH), 130.4 (2 CH), 134.3 (C), 135.7 (C), 139.4 (C), 151.0 (C), 154.8 (C) ppm; MS: *m/z* (%) = 421 (M^+, 6), 406 (15), 344 (31), 266 (42), 155 (64), 77 (100).

4-Benzyl-2-butylidene-3-tosylthiazolidine (4j,$C_{21}H_{25}NO_2S_2$) Yellow powder; m.p.: 84–86 °C; yield: 0.29 g (76%); IR (KBr): $\bar{\nu}$ = 3025, 2961, 1567, 1371, 1319, 1145 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 0.88 (3H, t, ^3J = 6.1 Hz, Me), 1.42–1.53 (2H, m, CH_2), 2.26–2.37 (2H, m, CH_2), 2.40 (3H, s, Me), 2.85 (1H, dd, ^2J = 10.7 Hz, ^3J = 5.5 Hz, CH), 3.02 (1H, dd, ^2J = 10.7 Hz, ^3J = 8.9 Hz, CH), 3.19 (1H, dd, ^2J = 10.5 Hz, ^3J = 5.3 Hz, CH), 3.31 (1H, dd, ^2J = 10.5 Hz, ^3J = 8.7 Hz, CH), 3.55–3.63 (1H, m, CH), 4.53 (1H, t, ^3J = 6.1 Hz, CH), 7.17–7.33 (5H, m, 5 CH), 7.39 (2H, d, ^3J = 6.4 Hz, 2 CH), 7.68 (2H, d, ^3J = 6.4 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 15.6 (Me), 24.1 (CH_2), 24.5 (Me), 30.3 (CH_2), 40.4 (CH_2), 43.1 (CH_2), 62.5 (CH), 96.3 (CH), 125.4 (CH), 127.6 (2 CH), 129.2 (2 CH), 129.6 (2 CH), 131.6 (2 CH), 134.9 (C), 138.3 (C), 138.9 (C), 159.7 (C) ppm; MS: *m/z* (%) = 387 (M^+, 4), 296 (24), 155 (50), 141 (49), 91 (100), 77 (80).

4-Benzyl-2-(furan-2-ylmethylene)-3-tosylthiazolidine (4k,$C_{22}H_{21}NO_3S_2$) Pale yellow solid; m.p.: 94–96 °C; yield: 0.38 g (92%); IR (KBr): $\bar{\nu}$ = 3030, 2982, 1664, 1563, 1372, 13,218, 1144 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 2.45 (3H, s, Me), 2.78 (1H, dd, ^2J = 11.2 Hz, ^3J = 5.4 Hz, CH), 2.93 (1H, dd, ^2J = 11.2 Hz, ^3J = 9.7 Hz, CH), 3.15 (1H, dd, ^2J = 12.4 Hz, ^3J = 4.9 Hz, CH), 3.33 (1H, dd, ^2J = 12.4 Hz, ^3J = 8.9 Hz, CH), 3.72–3.79 (1H, m, CH), 5.35 (1H, s, CH), 6.67 (1H, t, ^3J = 6.3 Hz, CH), 6.97 (1H, d, ^3J = 6.7 Hz, CH), 7.16–7.33 (5H, m, 5 CH), 7.40 (2H, d, ^3J = 6.5 Hz, 2 CH), 7.69 (2H, d, ^3J = 6.5 Hz, 2 CH), 7.80 (1H, d, ^3J = 6.3 Hz, CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.3 (Me), 39.1 (CH_2), 45.2 (CH_2), 67.3 (CH), 95.1 (CH), 111.5 (CH), 112.2 (CH), 125.8 (CH), 127.6 (2 CH), 128.1 (2 CH), 129.2 (2 CH), 129.5 (2 CH), 134.1 (C), 137.6 (C), 137.9 (C), 145.7 (CH), 153.6 (C), 164.9 (C) ppm; MS: *m/z* (%) = 411 (M^+, 5), 300 (19), 221 (35), 155 (52), 91 (100), 67 (51).

4-Benzyl-3-tosyl-2-[(trimethylsilyl)methylene]thiazolidine (4l,$C_{21}H_{27}NO_2S_2Si$) Pale yellow solid; m.p.: 78–80 °C; yield: 0.28 g (68%); IR (KBr): $\bar{\nu}$ = 3041, 2971, 1641, 1547, 1326, 1309, 1107 cm^{-1}; ^1H NMR (500.1 MHz, $CDCl_3$): δ = 0.01 (9H, s, 3 Me), 2.44 (3H, s, Me), 2.75 (1H, dd, ^2J = 11.8 Hz, ^3J = 7.1 Hz, CH), 2.93 (1H, dd, ^2J = 11.8 Hz, ^3J = 4.5 Hz, CH), 3.15 (1H, dd, ^2J = 10.8 Hz, ^3J = 8.5 Hz, CH), 3.34 (1H, dd, ^2J = 10.8 Hz, ^3J = 4.9 Hz, CH), 3.76–3.84 (1H, m, CH), 4.78 (1H, s, CH), 7.17–7.30 (5H, m, 5 CH), 7.37 (2H, d, ^3J = 6.7 Hz, 2 CH), 7.69 (2H, d, ^3J = 6.7 Hz, 2 CH) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 1.1 (3 Me), 23.9 (Me), 37.1 (CH_2), 41.8 (CH_2), 69.9 (CH), 84.7 (CH), 126.4 (CH), 128.0 (2 CH), 128.6 (2 CH), 129.5 (2 CH), 129.8 (2 CH), 134.9 (C), 138.6 (C), 139.5 (C), 178.3 (C) ppm; MS: *m/z* (%) = 417 (M^+, 4), 306 (22), 221 (34), 155 (46), 91 (100), 77 (68).

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