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First sonochemical, simple and solvent-free synthesis of chiral *tert*-butanesulfinimines using silica supported *p*-toluenesulfonic acid

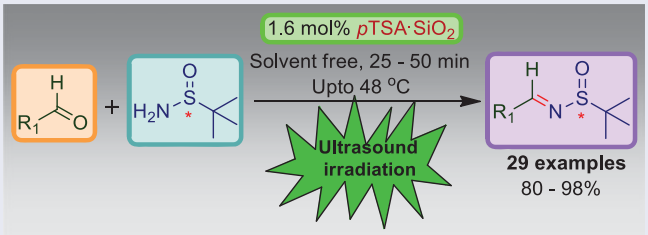
Rama Moorthy Appa[a], Jangam Lakshmidevi[a], Sana Siva Prasad[a], Baitinti Muralidhar[b], Bandameeda Ramesh Naidu[a], Manchala Narasimhulu[a], and Katta Venkateswarlu[a]

[a]Laboratory for Synthetic and Natural Products Chemistry, Department of Chemistry, Yogi Vemana University, Kadapa, India; [b]Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore, India

ABSTRACT

A solvent-free, versatile procedure has been developed for the effective synthesis of *tert*-butanesulfinylimines of a variety of aldehydes using chiral *tert*-butanesulfinamides under green, sonochemical conditions. This method utilizes silica supported *p*-toluenesulfonic acid (*p*TSA·SiO_2) as an efficient, safer and inexpensive catalyst under aerobic conditions. The practicable simplicity, easy preparation of the catalyst from readily available substances, high substrate scope, excellent yields of products in short reaction times and environmentally benign (solvent-free sonochemical) conditions are the exceptional assets of this finding.

GRAPHICAL ABSTRACT



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pTSA·SiO_2; *tert*-butanesulfinimines; aldehydes; sonochemical synthesis; solvent-free condition

Introduction

The synthesis induced by the application of ultrasound has been evidenced as prominent green chemical technology in most of the studies. This synthesis frequently associates with the saving of energy (about 92% of energy saving over conventional heating[1]), large increase in the yield of the products in shorter times, decrease or elimination of the use of toxic, volatile and expensive organic solvents, and formation of cleaner products with little or no by-products.[2] Besides easy handling, unique

CONTACT Venkateswarlu Katta kvenkat@yogivemanauniversity.ac.in Laboratory for Synthetic and Natural Products Chemistry, Department of Chemistry, Yogi Vemana University, Kadapa 516 005, India.

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mechanism and large scope for the invention of potential synthetic methods are the inborn futures of ultrasound-assisted synthesis.

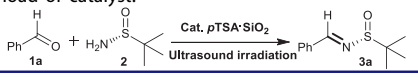
The chiral *tert*-butanesulfinylimines developed by Ellman et al. become prevailed substrates in organic synthesis. These are proved as effective auxiliaries in several reports for making chiral amine-containing precursors and biologically significant complex molecules.[3] Moreover, (*S*)- and (*R*)-*tert*-butanesulfinamides and (*S*)- and (*R*)-α-methylbenzylamines are widely accepted chiral ammonia equivalents among all the chiral amine substrates.[4] In the beginning, Ellman et al. synthesized *tert*-butanesulfinimines by $MgSO_4$ catalyzed condensation of chiral *tert*-butanesulfinamides with aldehydes.[5] In addition to the condensation of sulfinamides with carbonyl compounds, oxidative condensation of alcohols, thiols, ethers, sulfides and disulfides with *tert*-butanesulfinamides[6] are the other and less widely used approach for the construction of chiral *tert*-butanesulfinimines. But, due to the wide scope of catalysts and substrates, the condensation of aldehydes with sulfinamides is a simple and routine practice to access these imines.[6b] In this connection, $CuSO_4$,[7] $Ti(OEt)_4$,[7,8] Cs_2CO_3,[9] $KHSO_4$,[10] $Yb(OTf)_3$,[11] NaOH/^{t}BuOK,[12] BnZnBr,[13] Amberlist-15,[14] pyrrolidine-4Å MS,[15] $TiCl_4$,[16] $B(OCH_2CF_3)_3$,[17] $B(O^iPr)_3$,[18] TPA,[19] HBF_4·DEE[20] and I_2[21] were also developed as catalysts in addition to $MgSO_4$. Nevertheless, these methods required toxic and expensive organic solvent as media and many of these require a large quantity of catalysts (up to 3 mol ratios). Hence, it is highly inevitable to develop mild and convenient protocols for the synthesis of *tert*-butanesulfinimines.

Solid acid catalysts especially those based on silica support are widely used in organic synthesis and have substantial benefits like easy preparation from inexpensive materials, simple separation of the catalyst after the completion of the reaction by filtration, the possibility of recyclability and high substrate selectivity.[22] In the green chemistry point-of-view, the synthetic process may be green when no (toxic) solvent is employed.[23] The ecological pollution may be decreased by the application of solvent-free conditions in synthesis since about 85% of the chemicals used in pharmaceutical industry are solvents and their recovery rate is hardly about 50–80%.[24] Inspired by this ideology, we report herein a convenient and effective method for the synthesis of chiral *tert*-butanesulfinyl aldimines in the presence of silica supported *p*-tlouenesulfonic acid (*p*TSA·SiO_2) as an efficient catalyst under solvent-free and aerobic conditions. Furthermore, this is the first report to use ultrasound for the synthesis of *tert*-butanesulfinimines under solvent-free conditions. For the best of our knowledge, there are only a few reports exists for the use of *p*TSA·SiO_2 as a sole catalyst and all of them deals the dehydration of secondary and tertiary alcohols.[25] This protocol further establishes the scope of the catalysis of *p*TSA·SiO_2.

Results and discussion

Initially we have studied the imine formation reaction of benzaldehyde (**1a**) (1 mmol) with (*R*)-*tert*-butanesulfinamide (**2**) (1.05 mmol) under ultrasound irradiation using *p*TSA·SiO_2 (100 mg, 1.6 mol%)[25] in 5 ml of THF, DCM or methanol and found 73%, 50% and 35% of (*R*)-*tert*-butanesulfinylimine (**3a**) in 1 h (Table 1, entries 1–3). No improvement was observed by increasing catalyst load to 2.0 mol% (Table 1, entries 4–6).

Table 1. Influence of solvent and load of catalyst.[a]



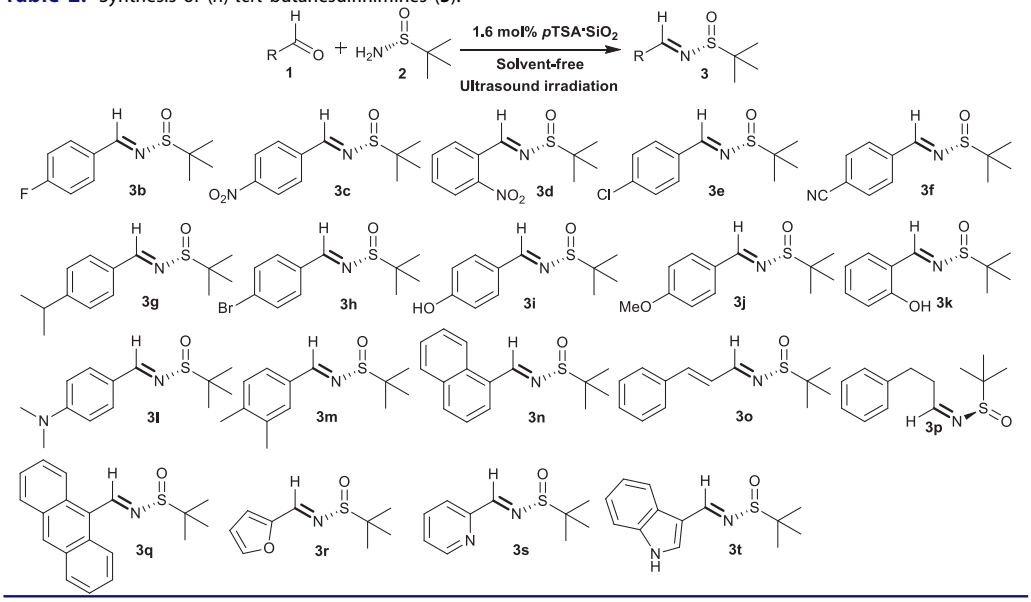
Sl. No.	Catalyst load	Solvent	Time (min)	Isolated yield
1	1.6 mol%	THF	60	73
2	1.6 mol%	DCM	60	50
3	1.6 mol%	Methanol	60	35
4	2.0 mol%	THF	60	74
5	2.0 mol%	DCM	60	53
6	2.0 mol%	Methanol	60	35
7	2.0 mol%	Et_2O	60	32
8	2.0 mol%	EtOAc	60	15
9	2.0 mol%	Toluene	60	43
10	2.0 mol%	DMSO	60	15
11	2.0 mol%	DMF	60	15
12	2.0 mol%	Ethanol	60	18
13[b]	2.0 mol%	THF	180	15
14[b]	2.0 mol%	–	180	12
15[c]	2.0 mol%	THF	90	79
16[d]	2.0 mol%	THF	60	88
17[e]	2.0 mol%	THF	60	89
18[d]	2.0 mol%	–	90	78
19	0.8 mol%	–	60	38
20	1.2 mol%	–	60	62
21	1.6 mol%	–	30	98
22	2.0 mol%	–	30	98

[a]Reaction conditions: 1a (1.0 mmol) and 2 (1.05 mmol), catalyst – pTSA·SiO_2, solvent (5 mL) under ultrasound irradiation.
[b]Reaction was conducted under no ultrasound irradiation at room temperature.
[c]Reaction was conducted 70 °C without ultrasound irradiation.
[d]Reaction was conducted 80 °C with no ultrasound irradiation.
[e]Reaction was conducted 90 °C with no ultrasound irradiation.

We further investigated the influence of the solvents on present conversion by using non-polar solvents such as diethyl ether, ethyl acetate and toluene (Table 1, entries 7–9) and polar solvents such as DMSO, DMF and ethanol (Table 1, entries 10–12). These results indicated that the solvent, THF is suitable among the studied using 1.6 mol% of pTSA·SiO_2 (Table 1, entry 1). To understand the influence of ultrasound on the current conversion we have conducted the reaction of **1a** with **2** in THF or without THF at room temperature and at different temperatures in the absence of ultrasound (Table 1, entries 13–18). Very low yields of chiral sulfinylimine, **3a** (15% and 12%) was observed at room temperature in THF and solvent-free conditions in 3 h (Table 1, entries 13, 14). The formation of high yield of **3a** (88%) was observed at 80 °C in THF in 1 h and no improvement of the yield was observed by an increase of temperature (Table 1, entries 16, 17). This reaction was formed 78% of the yield of **3a** in 1.5 h in solvent-free and ultrasound-free conditions at 80 °C (Table 1, entry 18).

The reaction was found to proceed to give excellent yield (98%) of **3a** in the absence of solvent in 0.5 h in the presence of 1.6 mol% of pTSA·SiO_2 under ultrasound irradiation (Table 1, entry 21). No improvement of the yield of **3a** was found when increased the catalyst load to 2.0 mol% (Table 1, entry 22) and incompleteness of the reaction was observed with 0.8 mol% and 1.2 mol% of catalyst (Table 1, entries 19, 20). Furthermore, the literature procedures require 10 mol% to 3 mol ratio of the catalysts for the condensation of *tert*-butanesulfinamides with aldehydes[5,7–21] and hence, the present method is remarkable by the use of very low catalyst load as 1.6 mol%.

Table 2. Synthesis of (*R*)-*tert*-butanesulfinimines (**3**).[a]

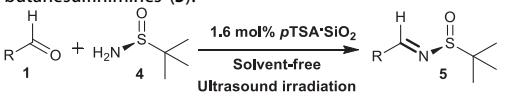


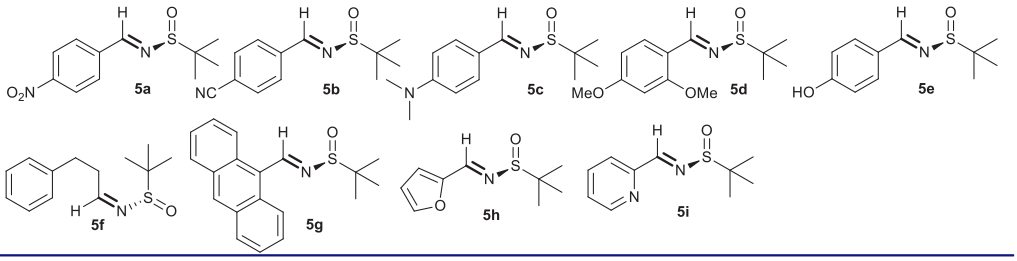
Sl. No.	R	Time (min)	Product (3)	Isolated yield (%)
1	4-fluorophenyl (**1b**)	25	**3b**	98
2	4-nitrophenyl (**1c**)	30[b]	**3c**[20]	97
3	2-nitrophenyl (**1d**)	45[b]	**3d**[21]	92
4	4-chlorophenyl (**1e**)	30[b]	**3e**[21]	95
5	4-cyanophenyl (**1f**)	30	**3f**[20]	95
6	4-isopropylphenyl (**1g**)	35	**3g**[6a]	95
7	4-bromophenyl (**1h**)	30[b]	**3h**[20]	95
8	4-hydroxyphenyl (**1i**)	50	**3i**	92
9	4-methoxyphenyl (**1j**)	40	**3j**[7]	92
10	2-hydroxyphenyl (**1k**)	50	**3k**[20]	90
11	4-*N*,*N*-dimethylaminophenyl (**1l**)	45[b]	**3l**	91
12	3,4-dimethylphenyl (**1m**)	50	**3m**[6a]	80
13	1-naphthyl (**1n**)	50	**3n**[21]	89
14	*trans*-styryl (**1o**)	30	**3o**[21]	96
15	2-phenylethyl (**1p**)	35	**3p**[20]	92
16	9-anthracenyl (**1q**)	50[b]	**3q**	87
17	2-furyl (**1r**)	40	**3r**[7]	95
18	2-pyridyl (**1s**)	30	**3s**[7]	94
19	3-indolyl (**1t**)	50[b]	**3t**	93

[a]Reaction conditions: **1** (1.0 mmol) and **2** (1.05 mmol), catalyst – *p*TSA·SiO_2 (1.6 mol%), under ultrasound irradiation.
[b]Few drops of water was added to make the reaction contents wet.

With the optimized conditions in hand, the method was tested for an array of aldehydes (**1**) and the results are listed in Table 2. The aromatic aldehydes with electron withdrawing groups such as fluoro, nitro, chloro, and cyano show excellent yields (92–98%) of imines under present experimental conditions (Table 2, entries 1–5). Aromatic aldehydes with electron releasing groups such as isopropyl, bromo, hydroxyl, methoxy, *N*,*N*-dimethyl groups also displayed high yields of products (90–95%) in 30–50 min (Table 2, entries 6–11). Disubstituted benzaldehyde (3,4-dimethylbenzaldehyde, **1m**) provides good yield (80%) of imine, **3 m** in 50 min (Table 2, entry 12). Aliphatic aldehydes such as *trans*-cinnamaldehyde (**1o**) and 3-phenylpropanal (**1p**) show high conversion into imines under *p*TSA·SiO_2 catalysis (Table 2, entries 14, 15). Naphthalene-1-carbaldehyde (**1n**) and anthracene-9-carbaldehyde (**1q**) were also found

Table 3. Synthesis of (*S*)-*tert*-butanesulfinimines (**5**).[a]





Sl. No.	R	Time (min)	Product (3)	Isolated yield (%)
1	4-nitrophenyl (**1c**)	30[b]	**5a**[10]	96
2	4-cyanophenyl (**1f**)	30	**5b**	95
3	4-*N*,*N*-dimethylaminophenyl (**1l**)	40[b]	**5c**[10]	90
4	2,4-dimethoxyphenyl (**1u**)	50[b]	**5d**	82
5	4-hydroxyphenyl (**1i**)	50	**5e**[19]	90
6	2-phenylethyl (**1p**)	50	**5f**[10]	92
7	9-anthracenyl (**1q**)	50[b]	**5g**[19]	89
8	2-furyl (**1r**)	35	**5h**[10]	95
9	2-pyridyl (**1s**)	35	**5i**[10]	90

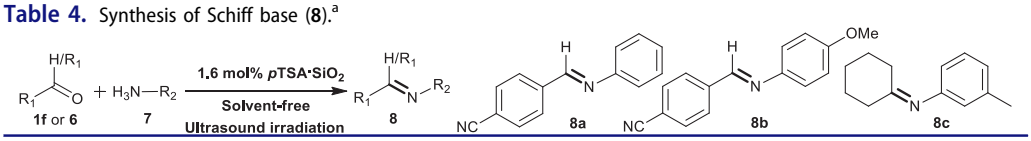
[a]Reaction conditions: **1** (1.0 mmol) and **4** (1.05 mmol), catalyst – *p*TSA·SiO_2 (1.6 mol%), under ultrasound irradiation.
[b]Few drops of water was added to make the reaction contents wet.

as best substrates and yielded **3n** and **3q** with 89% and 87% (Table 2, entries 13,16). Heteroaromatic aldehydes such 2-fural (**1r**), pyridine-2-carbaldehyde (**1s**) and indole-3-carbaldehyde (**1t**) gave excellent yields of their corresponding imines (**3r**–**3t**) in 30–50 min (Table 2, entries 17–19). In some cases like $CuSO_4$,[7] $Yb(OTf)_3$,[11] and I_2[21], the yields of imines of heteroaryl aldehydes was found low.

The reaction for perfect solid system (e.g. in the case of **1c**–**1e**, **1 h**, **1 l**, **1q**, and **1t**) was found to give very low yields of imines under solvent-free conditions, but by making reaction mixture wet by an addition of few drops of water the reaction proceeds to give the best results (Table 2, entries 2–4, 7, 11, 16, 19). This observation evidences the acoustic cavitation mechanism. The mechanism of acoustic cavitation is well studied and is similar to that of reported in Ref.[2b,26]. The mechanism of the condensation of an aldehyde with sulfinamides in the presence of *p*TSA·SiO_2 is assumed to be identical to that of acid catalyzed imine formation from amines and aldehydes, but it can be accelerated by the adiabatic heating of the reactants in acoustic cavitation mechanism.

We then applied this method for the preparation of (*S*)-*tert*-butanesulfinyl aldimines. In this connection a variety of aldehydes such as aromatic aldehydes [4-nitrobenzaldehyde (**1c**), 4-cyanobenzaldehyde (**1f**), 4-*N*,*N*-dimethylaminobenzaldehyde (**1l**), 2,4-dimethoxybenzaldehyde (**1u**), 4-hydroxybenzaldehyde (**1i**) and anthracene-9-carbaldehyde (**1q**)], aliphatic aldehyde [3-phenylpropanal (**1p**)] and heteroaromatic aldehydes [2-fural (**1r**) and pyridine-2-carbaldehyde (**1s**)] are found to reacts rapidly with (*S*)-*tert*-butanesulfinamide (**4**) to provide high yields of imines, **5a**–**5i** (Table 3, entries, 1–9).

Table 4. Synthesis of Schiff base (**8**).[a]



Sl. No.	Carbonyl compound	Amine (7)	Product (8)	Isolated yield (%)
1	4-cyanobenzaldehyde (**1f**)	aniline (**7a**)	**8a**[27]	70
2	4-cyanobenzaldehyde (**1f**)	*p*-anisidine (**7b**)	**8b**	74
3	cyclohexanone (**6**)	*m*-toluidine (**7c**)	**8c**[28]	65

[a]**1f** or **6** (1.0 mmol), **7** (1.05 mmol), *p*TSA·SiO_2 (1.6 mol%) under ultrasound irradiation, time – 2h.

To ensure the formation of chiral enriched sulfinylimines, we measured the optical rotation values of **3c**, **3j** and **3 s** {$[\alpha]_D^{25}$ – 64.64 ($c = 0.1$, $CHCl_3$), $[\alpha]_D^{26}$ – 67.62 ($c = 0.1$, $CHCl_3$) and $[\alpha]_D^{25}$ – 163.00 ($c = 0.1$, $CHCl_3$)}, and are found to be very near to that of reported {$[\alpha]_D^{20}$ – 70 ($CHCl_3$)[21], $[\alpha]_D^{20}$ – 68 ($CHCl_3$)[21] and $[\alpha]_D^{23}$ – 172 ($CHCl_3$)[7]}. It indicates the formation of (*R*)-*tert*-butanesulfinylimines with optical purity. The optical rotation value of enantiomer of **3c**, that is, **5a** was found to be $[\alpha]_D^{25}$ + 65.30 ($c = 0.1$, $CHCl_3$) with almost similar value but with opposite sign indicates the formation of *tert*-butanesulfinylimine with (*S*)-configuration.

The influence of the *p*TSA·SiO_2 catalysis under ultrasound irradiation was also studied for the preparation of imines of carbonyl compounds (Schiff bases). The reaction of carbonyl compounds such as 4-cyanobenzaldehyde (**1f**) or cyclohexanone (**6**) with aromatic amines (**7a**–**7c**) took comparatively extended time (2.0 h) to give good yields (65–74%) of Schiff bases, **8a**–**8c** (Table 4, entries 1–3).

A poor reusability of the catalyst was observed (only 32% of the product was formed) when the catalyst reused on separation by dissolving the reaction mixture of **1a** and **2** in ethyl acetate and filtering the catalyst followed by drying. The reaction mixture was thus added a little amount of silica gel to get free-flowing solid, was loaded directly on the silica gel packed glass column and chromatographed to get the product **3a** with no alteration of yield. This step avoids the catalyst separation step and hence saves from the necessity of toxic organic solvent. In the case of pyrrolidine,[15] $B(OCH_2CF_3)_3$,[17] and $B(OiPr)_3$[18] the catalyst separation step is critical but an additional reagent (hypo) is necessary for I_2 catalysis.[21]

Conclusion

In summary, a versatile, simple and sonochemical method has been developed for the construction of *tert*-butanesulfinylimines of aldehydes and imines from aldehydes and *tert*-butanesulfinamides under solvent-free and aerobic conditions. The current method obeys several principles of green chemistry, such as saving the energy by an application of ultrasound, avoiding the toxic, flammable and expensive organic solvents as reaction media, formation of products with excellent yields by eliminating the formation of by-products (waste), unnecessitating catalyst separation step there by saving the organic solvents and the application of low amounts (1.6 mol%) of solid acid catalyst. This finding further establishes the scope of ultrasound and *p*TSA·SiO_2 in the synthesis of chiral *tert*-butanesulfinyl aldimines.

Experimental

General experimental procedure for the preparation of imines

Aldehyde (**1**) (1.0 mmol), chiral *tert*-butanesulfinamide (**2** or **4**) (1.05 mmol) and *p*TSA·SiO_2 (1.6 mol%) in a round-bottomed flask were sonicated in a bath sonicator. An increase of temperature up to 48 °C was observed during irradiation. After completion (as indicated by TLC), the reaction mixture was added to a little amount of silica gel to obtain a free flowing gel. The gel obtained was loaded on top of a small pad of silica gel loaded in a glass column, which was eluted with a mixture of *n*-hexane and ethyl acetate at varying ratios to obtain pure imine (**3** or **5** or **8**). The structures of the imines were ascertained from their spectral (^{1}H & ^{13}C NMR and MS) data. The data of reported imines were found identical with the literature values. The characterization data of some of the representative compounds are provided here.

Compound 3t

Pale yellow solid. 93% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 9.14 (1 H, brs), 8.76 (1 H, s), 8.32 (1 H, d, $J = 8.6$ Hz), 7.66 (1 H, d, $J = 2.8$ Hz), 7.48 − 7.42 (1 H, m), 7.36 − 7.27 (2 H, m), 1.31 (9 H, s). 13C-NMR (100 MHz, $CDCl_3$) δ: 156.3, 137.0, 132.5, 124.8, 124.0, 122.3, 122.2, 115.2, 111.6, 57.1, 22.5. HRMS (ESI) *m/z*: Calcd for $C_{13}H_{17}N_2OS$ $[M+H]^+$: 249.1056. Found: 249.1056.

Compound 5d

Light Yellow solid. 82% yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.95 (1 H, s), 7.95 (1 H, d, $J = 8.7$ Hz), 6.55 (1 H, d, $J = 8.7$ Hz), 6.45 (1 H, s), 3.87 (6 H, s), 1.24 (9 H, s). 13C-NMR (100 MHz, $CDCl_3$) δ: 164.6, 161.1, 157.8, 129.7, 116.3, 105.9, 97.7, 57.3, 55.5, 55.4, 22.5; HRMS (ESI) *m/z*: $C_{13}H_{20}NO_3S$ $[M+H]^+$: 270.1158. Found: 270.1157.

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ORCID

Katta Venkateswarlu http://orcid.org/0000-0002-1475-1126

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