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An odorless thia-Michael addition using Bunte salts as thiol surrogates†

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A newly developed C–S bond formation process *via* acid-catalyzed thia-Michael addition has been demonstrated. The protocol, in which Bunte salts generated from odorless, inexpensive sodium thiosulfate and organic halides are used as the thiol precursors, provides an efficient approach for the synthesis of β-sulfido carbonyl compounds.

Introduction

Bunte salts are conveniently prepared by the reaction of odorless and inexpensive sodium thiosulfate with alkyl halides, which are easy to handle crystalline solids, even with highly lipophilic organic moieties, and generally have little to no odor.[1] Various nucleophiles such as thiols,[2] Na_2S,[3] cyanide[4] or Grignard reagents[1c] could react with Bunte salts to yield disulfides, trisulfides, thiocyanates and sulfides respectively. Meanwhile, these compounds also exhibit nucleophilicity under acidic conditions to produce thiols.[5] Therefore, we envisage that electrophiles such as α,β-unsaturated ketones can be attacked by thiol *in situ* formed by the hydrolysis of Bunte salts under acidic conditions (Scheme 1).

In the last decades, sulfur-based compounds have received wide-spread attention due to their potential as novel pharmaceutical, agricultural and chemical agents.[6] Moreover, organic sulfur compounds are essential in materials science, in which the sulfur constituent can have profound effects on the physical, electronic, and surface properties of the resultant materials.[7] The construction of sulfur-containing compounds *via* simple C–S bond-forming reactions is of utmost importance in synthetic and catalytic research fields.[8] The thia-Michael addition is one of most useful approaches for the construction of C–S bonds, so there have been significant efforts towards the development of methodologies for this transformation.[9]

Nevertheless, most of these strategies require malodorous and expensive thiols as starting materials. Because of their potent stench and air sensitivity, the use of thiol as the starting materials, particularly on a large scale operation, is highly undesirable. In order to solve the issue, several odorless protocols have been reported through the *in situ* generation of odorless *S*-alkylisothiouronium salts in place of thiols, which are formed by organic halides and thiourea.[9c,10] Although various electron-deficient alkenes could proceed smoothly under odorless and mild conditions, more sterically hindered substrates such as chalcone fail to yield the desired products, and a stoichiometric amount of base is required.[10]

More recently, various attempts have been made to employ odorless disulfides and *N*-(organothio)succinimides for the synthesis of sulfocompound, but these reagents should be pre-generated from thiols.[11] Iranpoor's and our group have reported several transformations for C–S bonds formation using thiourea as an odorless sulfur source,[12] meanwhile a series of sulfur transfer reactions by *in situ* formation of Bunte salts from sodium thiosulfate and organic halides have also been achieved.[13] With our interest in exploring novel odorless means for construction of C–S bonds, we found odorless Bunte salts could react with steric α,β-unsaturated ketones under acidic conditions with good yields.

Results and discussion

As a representative example, the sulfur-Michael addition of **1a** and **2a** was chosen to optimize the reaction conditions (Table 1). After screening different solvent, methanol emerged as the best choice (entry 4). No reaction took place without acid (entry 9). Various Brønsted acids were employed to further improve the yield. Both $HN(Tf)_2$ (trifluoromethanesulfonimide) and TsOH (*p*-toluenesulfonic acid) were equally effective in this model reaction (entries 4 and 13). TsOH is much cheaper than $HN(Tf)_2$, so TsOH was selected as the catalyst for further studies. The amount of TsOH was also optimized, and 20 mol% of TsOH was the best option (entry 15). Finally, satisfactory yield could be obtained *via* heating the reaction to 80 °C.

With the optimized conditions in hands, a series of Bunte salts and various α,β-unsaturated ketones were applied in the reaction to establish the scope and generality of the protocol (Scheme 2). Steric α,β-unsaturated ketones including chalcones, benzylidene acetone and (*E*)-4-(thiophen-2-yl)but-3-en-2-one could react with different Bunte salts to afford corresponding

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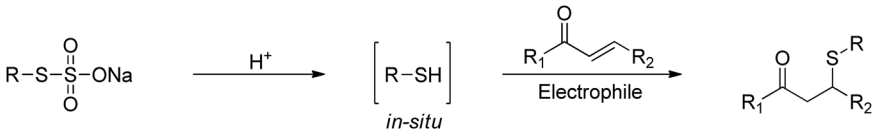
† Electronic supplementary information (ESI) available: More experimental entails, characterization data and copies of ^1H NMR, ^{13}C NMR spectra of all products. See DOI: 10.1039/c5ra01381j



Scheme 1 Working hypothesis: thia-Michael addition using Bunte salts as the thiol equivalents.

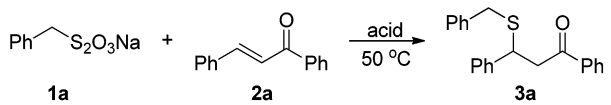
products. Excellent yields would be gained using electron-deficient terminal alkenes to yield the addition products (**3d**, **3e**) at lower temperature (40 °C). Benzyl, allyl and cyclohexyl Bunte salts were also employed in the protocol successfully, and the cyclohexyl Bunte salt leaded to a lower yield (46%) due to sterically hindered effects (**3g**). It should be noted that ethyloxycarbonylmethyl Bunte salt did not result in the desired product, but generate **3h** *via* an additionally transesterification with MeOH. The substituented groups on chalcones had no obvious influence on the reaction (**3k–m**).

Because sodium *S*-aryl sulfothioate can't be hydrolyzed under optimized conditions, no desired product was found when aryl Bunte salts such as phenyl and 4-toluene Bunte salts, were employed in the protocol. To further broaden the scope of the approach, thia-Michael additions of Bunte salts with *N*-substituented maleimides were achieved under optimized conditions (Scheme 3). *N*-Benzyl, methyl and ethyl maleimide reacted smoothly with Bunte salts in good to excellent yields. In the case of *N*-phenyl maleimide, no Michael addition occurred. Undesired products generated from the ring-opening of *N*-phenyl maleimide was observed. Similarly, **3q** was formed *via* Michael addition of ethyloxycarbonylmethyl Bunte salt with *N*-benzyl maleimide, following a transesterification with MeOH.

To further optimize the reaction conditions, attempts were also made to realize thia-Micheal additions *via* a one-pot process from benzyl chloride, $Na_2S_2O_3$ and α,β-unsaturated ketones (Scheme 4). Although the results were also satisfactory, the one-pot process required excess benzyl chloride (3 equiv.) and $Na_2S_2O_3$ (4 equiv.) which leaded to unnecessary waste of substrates.

Finally, a proposed mechanism for the reaction was also illustrated in Scheme 5. TsOH may play a dual role in the reaction: (i) TsOH promotes the hydrolysis of Bunte salts to form thiol *in situ*;[5a] (ii) TsOH actives α,β-unsaturated ketones to form carbonium ion intermediate **I**, following a nucleophilic attack by thiol to afford the final product.

Table 1 Optimization of the reaction conditions[a]



Entry	Solvent	Acid	Yield[b] (%)
1	CH_2Cl_2	TsOH	Trace
2	MeCN	TsOH	63
3	H_2O	TsOH	nr
4	MeOH	TsOH	71
5	EtOH	TsOH	68
6	DMSO	TsOH	nr
7	DMF	TsOH	nr
8	Toluene	TsOH	16
9	MeOH	—	nr
10	MeOH	HCl	27
11	MeOH	$HClO_4$	38
12	MeOH	H_2SO_4	52
13	MeOH	$HN(Tf)_2$	76
14	MeOH	TsOH[c]	72
15	MeOH	TsOH[d]	69 (88)[e]
16	MeOH	TsOH[f]	34

[a] Reaction conditions: **1a** 0.60 mmol, **2a** 0.50 mmol, acid 0.50 mmol, solvent 1 mL, 6 h, 50 °C. [b] GC yields. [c] 0.5 equiv. of TsOH was used. [d] 0.2 equiv. of TsOH was used. [e] The reaction temperature is 80 °C, isolated yield. [f] 0.1 equiv. of TsOH was used.

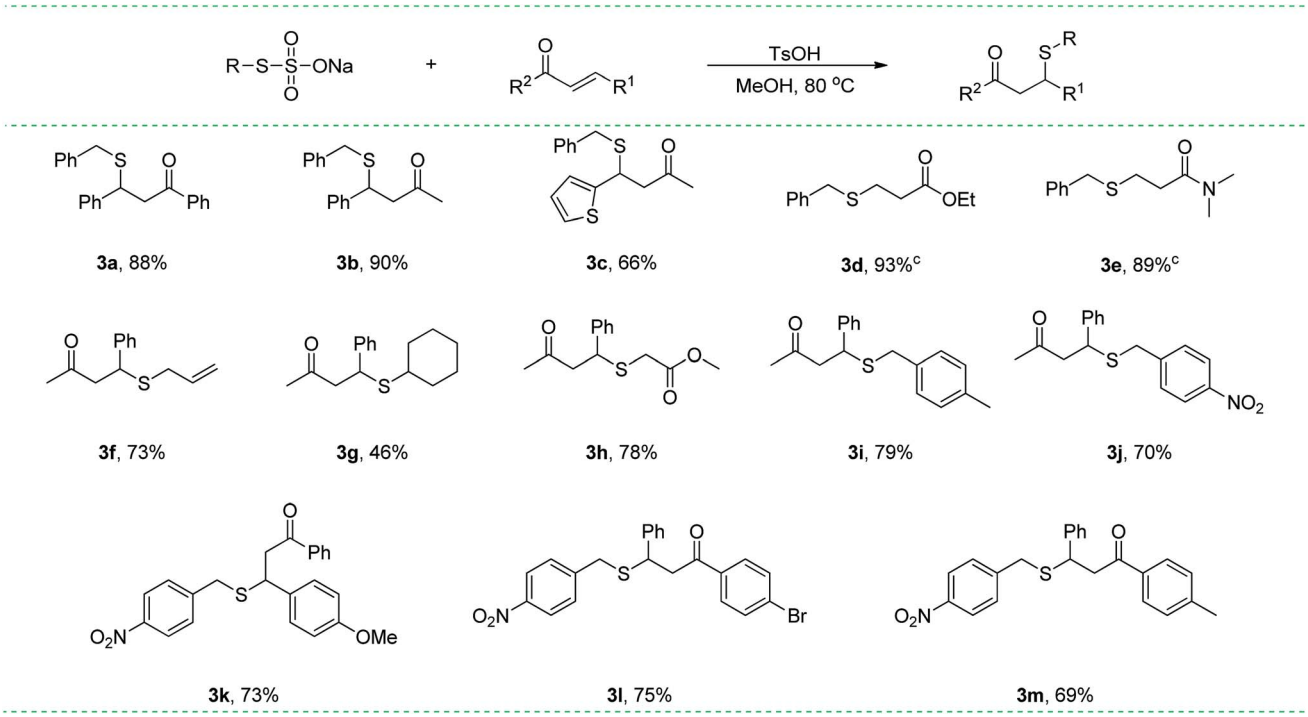
Conclusions

In summary, we have described an efficient and odorless thia-Michael addition by *in situ* formation of thiols from the hydrolysis of Bunte salts under acidic conditions. Steric α,β-unsaturated ketones can also be applied in the system successfully. The procedure uses odorless, inexpensive and easy to handle Bunte salts instead of thiols, making it more suitable for large-scale operations.

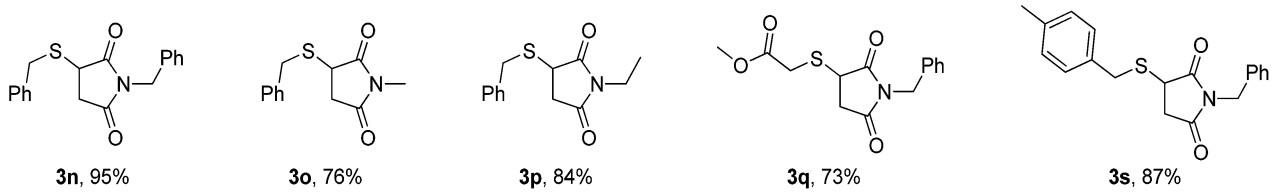
Experimental section

General

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are identified by appropriate technique such as MS, ^{1}H NMR, and compared with previously reported data. All unknown compounds are characterized by ^{1}H NMR, ^{13}C NMR, MS and elemental analyses. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Finnigan TSQ Quantum-MS instrument in the electrospray ionization (ESI) mode. ^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm. Elemental analyses are performed on a Yanagimoto MT3CHN recorder. GC analyses are performed on an Agilent 7890A instrument (column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H_2, FID detection). GC/MS data was recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies).



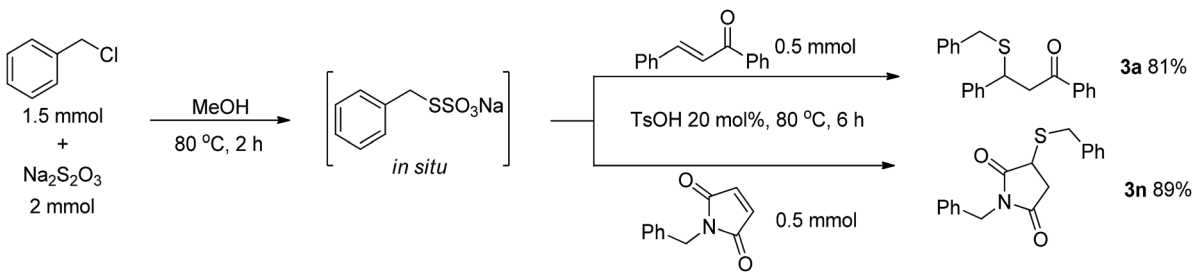
Scheme 2 The thia-Michael addition of Bunte salts and α,β-unsaturated ketones.[a,b] [a]Reaction conditions: **1** 0.60 mmol, **2** 0.50 mmol, TsOH 0.10 mmol, MeOH 1 mL, 6 h, 80 °C. [b]Isolated yields. [c]Reaction conditions: **1** 0.60 mmol, **2** 0.50 mmol, TsOH 0.10 mmol, CH_2Cl_2 1 mL, 6 h, 40 °C.



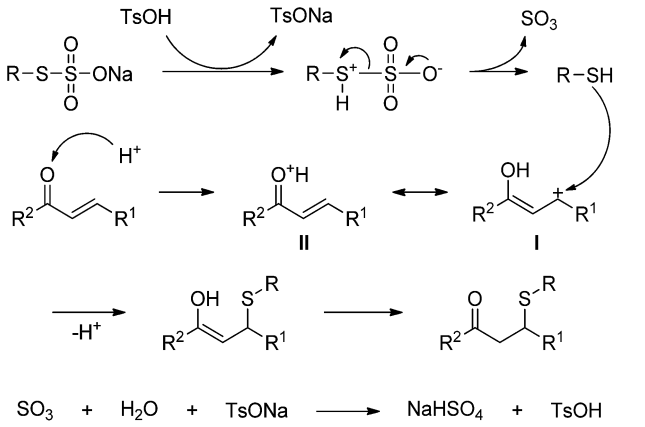
Scheme 3 The thia-Michael additions of Bunte salts with *N*-substituented maleimide.

General procedures for the synthesis of Bunte salts[1c]

A flask is charged with organic halides (50 mmol), sodium thiosulfate pentahydrate (60 mmol), water (10.0 mL) and MeOH (50 mL). The reaction mixture is stirred and heated to 65 °C. After 16 h at 65 °C, the reaction mixture is cooled to rt, and then concentrated on a rotovap at a bath temperature of 60 °C to remove the MeOH and water. The resultant solid is treated with MeOH (100 mL), heated to 50 °C (most solid dissolves), and filtered to remove excess sodium thiosulfate and sodium bromide. The filtrate is concentrated to a white solid, following trituration of this solid with hexanes, filtration, and drying under vacuum at 50 °C to afford the corresponding Bunte salts.



Scheme 4 Thia-Micheal additions *via* a one-pot process through *in situ* formation of Bunte salts.



Scheme 5 A proposed mechanism for thia-Micheal additions with Bunte salts.

General procedures for thia-Michael additions with Bunte salts and α,β-unsaturated ketones

A mixture of Bunte salts **1** 0.60 mmol, α,β-unsaturated ketones **2** 0.50 mmol, TsOH 0.10 mmol in MeOH (1.0 mL) is stirred at 80 °C for 6 h. Upon completion, the reaction mixture is diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, The volatiles are removed *in vacuo* to afford the crude product. Further column chromatography on silica gel affords the pure desired product **3**.

General procedures for thia-Michael additions *via* a one-pot process from benzyl chloride, $Na_2S_2O_3$ and α,β-unsaturated ketones

A mixture of benzyl chloride 1.5 mmol and $Na_2S_2O_3$ 2.0 mmol in MeOH (1.0 mL) is stirred at 80 °C for 2 h. Then, α,β-unsaturated ketones 0.50 mmol and TsOH 0.10 mmol are added to the mixture. The reaction proceeds at the same temperature for additionally 6 h. Upon completion, the reaction mixture is diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite, the volatiles are removed *in vacuo* to afford the crude product. Further column chromatography on silica gel affords the pure desired product.

Characterization data for unknown compounds

4-((4-Methylbenzyl)thio)-4-phenylbutan-2-one 3i. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 3H), 2.33 (s, 3H), 2.92–2.94 (m, 2H), 3.41–3.51 (dd, J = 37.0, 8.5 Hz, 2H), 4.19–4.22 (t, J = 7.5 Hz, 1H), 7.09 (brs, 4H), 7.24–7.26 (m, 1H), 7.32–7.33 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (1C, Ar-CH_3), 30.6 (1C, O=CCH_3), 35.5 (1C, SCH_2), 44.0 (1C, CH), 50.1 (1C, CH_2C=O), 127.5 (1C, Ar-C), 128.1 (2C, Ar-C), 128.7 (2C, Ar-C), 128.9 (2C, Ar-C), 129.3 (2C, Ar-C), 134.8 (1C, Ar-C), 136.7 (1C, Ar-C), 141.7 (1C, Ar-C), 205.5 (1C, C=O). MS (ESI) m/z: 284.25 $[M + H]^+$. Anal. calcd for $C_{18}H_{20}OS$: C, 76.01%; H, 7.09%. Found: C, 76.36%; H, 7.45%.

4-((4-Nitrobenzyl)thio)-4-phenylbutan-2-one 3j. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02 (s, 3H), 2.93 (d, J = 7.0 Hz, 2H), 3.48–3.57 (dd, J = 34.0, 8.0 Hz, 2H), 4.17–4.19 (t, J = 7.5 Hz, 1H), 7.21–7.31 (m, 7H), 8.08 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.7 (1C, CH_3), 35.2 (1C, SCH_2), 44.2 (1C, CH), 49.9 (1C, CH_2C=O), 123.7 (2C, Ar-C), 127.8 (1C, Ar-C), 128.0 (2C, Ar-C), 129.8 (2C, Ar-C), 141.1 (1C, Ar-C), 146.0 (1C, Ar-C), 147.0 (1C, Ar-C), 205.0 (1C, C=O). MS (ESI) m/z: 314.98 $[M + H]^+$. Anal. calcd for $C_{17}H_{17}NO_3S$: C, 64.74%; H, 5.43%; N, 4.44%. Found: C, 64.38%; H, 5.29%; N, 4.75%.

3-(4-Methoxyphenyl)-3-((4-nitrobenzyl)thio)-1-phenylpropan-1-one 3k. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.42 (d, J = 7.0 Hz, 2H), 3.51–3.60 (dd, J = 32, 14 Hz, 2H), 3.79 (s, 3H), 4.39–4.42 (t, J = 7.0 Hz, 1H), 6.84 (d, J = 8.5 Hz, 2H), 7.19–7.36 (m, 7H), 7.81 (d, J = 8.5 Hz, 2H), 8.04 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.4 (1C, SCH_2), 44.7 (1C, CH), 44.9 (1C, CH_2C=O), 55.6 (1C, OCH_3), 113.9 (2C, Ar-C), 123.7 (2C, Ar-C), 127.7 (1C, Ar-C), 128.1 (2C, Ar-C), 128.8 (2C, Ar-C), 129.7 (1C, Ar-C), 129.8 (2C, Ar-C), 130.5 (2C, Ar-C), 141.6 (1C, Ar-C), 146.1 (1C, Ar-C), 146.9 (1C, Ar-C), 163.8 (1C, Ar-C), 195.0 (1C, C=O). MS (ESI) m/z: 407.13 $[M + H]^+$. Anal. calcd for $C_{23}H_{21}NO_4S$: C, 67.79%; H, 5.19%; N, 3.44%. Found: C, 67.81%; H, 5.32%; N, 3.74%.

1-(4-Bromophenyl)-3-((4-nitrobenzyl)thio)-3-phenylpropan-1-one 3l. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.41–3.42 (dd, J = 7.0, 1.0 Hz, 2H), 3.50–3.59 (dd, J = 32.5, 13.5 Hz, 2H), 4.34–4.37 (t, J = 7.0 Hz, 1H), 7.19–7.32 (m, 7H), 7.51 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz, 2H), 8.06 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 35.4 (1C, SCH_2), 44.4 (1C, CH), 45.2 (1C, CH_2C=O), 123.7 (2C, Ar-C), 127.8 (1C, Ar-C), 128.1 (2C, Ar-C), 128.7 (1C, Ar-C), 128.8 (2C, Ar-C), 129.7 (2C, Ar-C), 129.8 (2C, Ar-C), 132.0 (2C, Ar-C), 135.4 (1C, Ar-C), 141.2 (1C, Ar-C), 145.9 (1C, Ar-C), 147.0 (1C, Ar-C), 195.5 (1C, C=O). MS (ESI) m/z: 455.18 $[M + H]^+$. Anal. calcd for $C_{22}H_{18}BrNO_3S$: C, 57.90%; H, 3.98%; N, 3.07%. Found: C, 57.68%; H, 4.17%; N, 2.86%.

3-((4-Nitrobenzyl)thio)-3-phenyl-1-(*p*-tolyl)propan-1-one 3m. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.45–3.47 (dd, J = 7.0, 1.5 Hz, 2H), 3.53–3.62 (dd, J = 32, 14 Hz, 2H), 4.40–4.43 (t, J = 7.0 Hz, 1H), 7.19–7.25 (m, 3H), 7.29–7.36 (m, 6H), 7.75 (d, J = 8.5 Hz, 2H), 8.08 (d, J = 8.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.7 (1C, Ar-CH_3), 35.4 (1C, CH_2S), 44.6 (1C, CH), 45.2 (1C, CH_2C=O), 123.7 (2C, Ar-C), 127.7 (1C, Ar-C), 128.1 (2C, Ar-C), 128.3 (2C, Ar-C) 128.8 (2C, Ar-C), 129.4 (2C, Ar-C), 129.8 (2C, Ar-C), 134.2 (1C, Ar-C), 141.5 (1C, Ar-C), 144.4, 146.1, 147.0, 196.0. MS (ESI) m/z: 391.20 $[M + H]^+$. Anal. calcd for $C_{23}H_{21}NO_3S$: C, 70.56%; H, 5.41%; N, 3.58%. Found: C, 70.29%; H, 5.17%; N, 3.96%.

3-(Benzylthio)-1-ethylpyrrolidine-2,5-dione 3p. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18–1.21 (t, J = 7.0 Hz, 3H), 2.39–2.43 (dd, J = 18.5, 1.5 Hz, 1H), 2.94–2.99 (dd, J = 9.0, 4.0 Hz, 1H), 3.49–3.51 (dd, J = 9.0, 3.5 Hz, 1H), 3.55–3.59 (q, J = 7.5 Hz, 2H), 3.87 (d, J = 13.5 Hz, 1H), 4.24 (d, J = 13.5 Hz, 1H), 7.29–7.42 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0 (1C, CH_3), 34.1 (1C, CH_2N), 35.6 (1C, CH_2C=O), 36.0 (1C, SCH_2), 37.4 (1C, CH), 127.7 (1C, Ar-C), 128.8 (2C, Ar-C), 129.3 (2C, Ar-C), 136.9 (1C, Ar-C), 174.7 (1C, C=O), 176.8 (1C, C=O). MS (ESI) m/z: 249.18 $[M + H]^+$. Anal. calcd for $C_{13}H_{15}NO_2S$: C, 62.62%; H, 6.06%; N, 5.62%. Found: C, 62.38%; H, 5.87%; N, 5.37%.

Methyl 2-((1-benzyl-2,5-dioxopyrrolidin-3-yl)thio)acetate 3q. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50–2.54 (dd, J = 19.0, 4.0 Hz, 1H), 3.11–3.17 (q, J = 9.5 Hz, 1H), 3.34–3.37 (d, J = 16.0 Hz, 1H), 3.74 (s, 3H), 3.90–3.93 (d, J = 16.0 Hz, 1H), 4.01–4.04 (dd, J = 9.5, 3.5

Hz, 1H), 4.62–4.70 (q, J = 9.0 Hz, 2H), 7.28–7.37 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 33.0 (1C, SCH_2), 35.5 (1C, $CHCH_2C$=O), 38.4 (1C, CH), 42.8 (1C, Ph-CH_2), 52.8 (1C, OCH_3), 128.2 (1C, Ar-C), 128.8 (4C, Ar-C), 135.2 (1C, Ar-C), 170.1 (1C, O–C=O), 174.1 (1C, N–C=O), 176.1 (1C, N–C=O). MS (ESI) m/z: 293.22 $[M + H]^+$. Anal. calcd for $C_{14}H_{15}NO_4S$: C, 57.32%; H, 5.15%; N, 4.77%. Found: C, 57.65%; H, 5.41%; N, 4.59%.

1-Benzyl-3-((4-methylbenzyl)thio)pyrrolidine-2,5-dione 3s. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.40–2.45 (dd, J = 19.0, 1.5 Hz, 1H), 2.95–3.00 (dd, J = 9.0, 4.0 Hz, 1H), 3.81 (d, J = 13.5 Hz, 1H), 4.17 (d, J = 13.5 Hz, 1H), 4.63–4.71 (q, J = 9.0 Hz, 2H), 7.13–7.14 (d, J = 8.0 Hz, 2H), 7.25–7.40 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (1C, CH_3), 35.6 (1C, CH_2C=O), 35.7 (1C, CH_2S), 37.6 (1C, CH), 42.7 (1C, NCH_2), 128.1 (1C, Ar-C), 128.8 (4C, Ar-C), 129.2 (2C, Ar-C), 129.5 (2C, Ar-C), 133.7 (1C, Ar-C), 135.5 (1C, Ar-C), 137.4 (1C, Ar-C), 174.5 (1C, C=O), 176.6 (1C, C=O). MS (ESI) m/z: 325.12 $[M + H]^+$. Anal. calcd for $C_{19}H_{19}NO_2S$: C, 70.12%; H, 5.88%; N, 4.30%. Found: C, 70.42%; H, 6.01%; N, 4.41%.

Acknowledgements

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