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COMMUNICATION

CuI-catalyzed tandem synthesis of thioethers using aryl halides, electron-deficient alkenes, and sodium *iso*-propyl xanthogenate

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A ligand-free, CuI-catalyzed protocol was developed for the one-step preparation of Michael adducts of aromatic thiols in high yields by reacting a mixture of an aryl halide and an electron-deficient alkene with sodium *iso*-propyl xanthogenate.

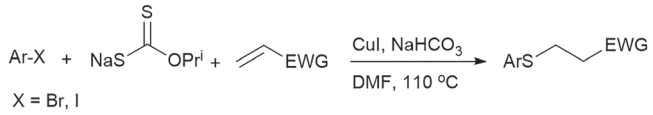
KEYWORDS
aryl halide, CuI, sodium *iso*-propyl xanthogenate, thia-Michael addition

1 | INTRODUCTION

Thioether functionality is an important motif found in a large number of natural products and biologically interesting compounds.[1] A variety of bioactive thioethers have been studied as drug candidates against drug-resistant bacteria,[2] HIV infection,[3] allergies,[4] asthma,[4] coronary artery disease,[4] schizophrenia,[5] bipolar disorder,[5] major depressive disorder,[5] and so on.[6] Synthetically, they are precursors of chiral sulfoxides, which are useful tools in asymmetric carbon–carbon and carbon–heteroatom bond formation.[7] They can be oxidized to sulfones for stabilizing a radical or anion on the α-carbon atom.[8] Removal of the sulfur moiety after the completion of the procedure by reductive desulfurization provides access to sulfur-free products.[9]

Alkyl aryl thioethers can be prepared by cross-coupling of aliphatic thiols with aryl derivatives bearing a leaving group catalyzed by transition metals[10] or by treating aryl mercaptans with a variety of reactants, including alkyl halides,[11] alkenes,[12] and electron-deficient alkenes.[13] The use of foul-smelling thiols is a major difficulty of these strategies. Furthermore, because of their oxidizing tendency, few aryl mercaptans are commercially available[14] and they should be primarily synthesized from aryl halides via a few malodorous procedures.

The conjugate addition of aryl mercaptans to electron-deficient alkenes as an efficient strategy for preparing aryl alkyl thioethers has been widely studied in organic synthesis.[13] These studies have been mainly focused on finding new catalysts and optimizing reaction conditions.[13] As mentioned earlier, aryl mercaptans are rare, smelly, and unpleasant chemicals. To overcome such drawbacks, researchers have developed alternative protocols for preparing thia-Michael adducts by *in situ* generation of aryl thiols using different strategies. In this regard, electron-deficient alkenes have been treated with aryl sulfonyl chloride together with Zn,[15] or diaryl disulfides along with $[BnEt_3N]_2MoS_4$,[16] or a reducing reagent such as In,[17] InI,[18] Zn,[19] Se,[20] Sm,[21] Fe,[22] or PPh_3.[23] Here we introduce an efficient ligand-free CuI-catalyzed one-step synthesis of thia-Michael adducts of aryl mercaptans by treating a mixture of an aryl halide and an electron-deficient alkene with sodium *iso*-propyl xanthogenate in dimethylformamide (DMF) at 110°C (Scheme 1).



SCHEME 1 One-pot, non-sequential synthesis of thia-Michael products. DMF, dimethylformamide; EWG, electron withdrawing group

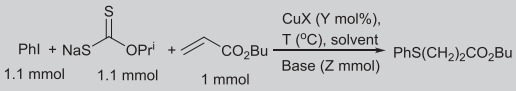
2 | RESULTS AND DISCUSSION

To start our study, different solvents were screened for reaction of iodobenzene (1.2 mmol), butyl acrylate (1 mmol), and sodium *iso*-propyl xanthogenate (1.3 mmol) in the presence of $NaHCO_3$ (2 mmol) and CuI (20 mol%) at 110°C for 24 hr. The results are summarized in Table 1.

Although none of the reactions were complete after this period, the reaction in DMF gave the best yield (Table 1, entry 1). It gave the desired product in 54% yield but similar reactions in polyethylene glycol-200 (PEG-200), dimethyl sulfoxide (DMSO), and toluene gave it in 37%, 43%, 40% yields, respectively, after this period. Also, the reactions in H_2O and sodium dodecyl sulfate (SDS) micellar medium completely failed and after the same time period the starting iodobenzenes were recovered unreacted near quantitatively for both reactions.

After choosing DMF as the solvent, we examined several different bases. The bases Na_2CO_3, K_2CO_3, KOH, Et_3N, and NaOH did not give higher yield than $NaHCO_3$ (Table 1, entry 1 vs. 7–12). Subsequently, by changing the amount of $NaHCO_3$ in the reaction, we found that an increase in the amount of $NaHCO_3$ reduces the reaction time and increases the reaction yield. For example, by increasing the amount of $NaHCO_3$ to 4 and 6 equivalents, the starting iodobenzene was completely consumed to give butyl 3-(phenylthio)propanoate in 84% (within 4 hr) and 90% (12 hr) yields, respectively. On the other hand, decreasing the catalyst loading to 10 mol% or the reaction temperature to 100°C reduced the reaction efficiency. Meanwhile, the reaction time or yield was not improved

TABLE 1 Reaction of iodobenzene, sodium *iso*-propyl xanthogenate, and butyl acrylate under different conditions[a]



Entry	Solvent	Base/*Z* (mmol)	CuX/*Y* (mol%)	*t* (hr)	*T* (°C)	Yield (%)
1	DMF	$NaHCO_3$/2	CuI/20	24	110	54
2	DMSO	$NaHCO_3$/2	CuI/20	24	110	43
3	H_2O	$NaHCO_3$/2	CuI/20	24	110	–
3	SDS/H_2O	$NaHCO_3$/2	CuI/20	24	110	–
4	PEG-200	$NaHCO_3$/2	CuI/20	24	110	37
	$PhCH_3$	$NaHCO_3$/2	CuI/20	24	110	40
5	DMF	Na_2CO_3/2	CuI/20	24	110	54
6	DMF	K_2CO_3/2	CuI/20	24	110	53
7	DMF	Et_3N/2	CuI/20	24	110	45
8	DMF	NaOH/2	CuI/20	24	110	50
9	DMF	KOH/2	CuI/20	24	110	52
10	DMF	$NaHCO_3$/4	CuI/20	17	110	84
11	**DMF**	**$NaHCO_3$/6**	CuI/20	**12**	**110**	**90**
12	DMF	$NaHCO_3$/6	CuI/20	12	120	87
13	DMF	$NaHCO_3$/6	CuI/20	24	100	80
14	DMF	$NaHCO_3$/6	CuI/10	24	110	55
15	DMF	$NaHCO_3$/6	CuCl/20	15	110	85
16	DMF	$NaHCO_3$/6	Cu $(OAc)_2$/20	16	110	79

DMF, dimethylformamide; DMSO, dimethyl sulfoxide; PEG-200, polyethylene glycol; SDS, sodium dodecyl sulfate.

[a]Reaction conditions: PhI (1.2 mmol), sodium *iso*-propyl xanthogenate (1.3 mmol), butyl acrylate (1 mmol), solvent (2 ml).

by elevation of temperature from 110 to 120°C or with increasing catalyst loading to 30 mol%. With the optimal reaction conditions in hand, we proceeded to investigate the scope of the reaction for the synthesis of thia-Michael adducts using a range of different aryl halides and electron-deficient alkenes.

The results shown in Table 2 indicate that both aryl iodides and bromides efficiently react with sodium *iso*-propyl xanthogenate and electron-deficient alkenes under reaction conditions to produce thia-Michael adducts in high yields. Iodobenzene reacts completely within 12 hr, but bromobenzene reacts more slowly and is consumed after 19 hr. Also, both *ortho*- and *para*-iodotoluenes react much slower than iodobenzene but in high yields. Also, *para*-bromotoluene reacts more slowly but 4-bromobenzonitrile reacts faster than bromobenzene. Reactions with the participation of 2-bromopyridine proceeded to completion more slowly than with bromobenzene and gave lower yields of Michael products.

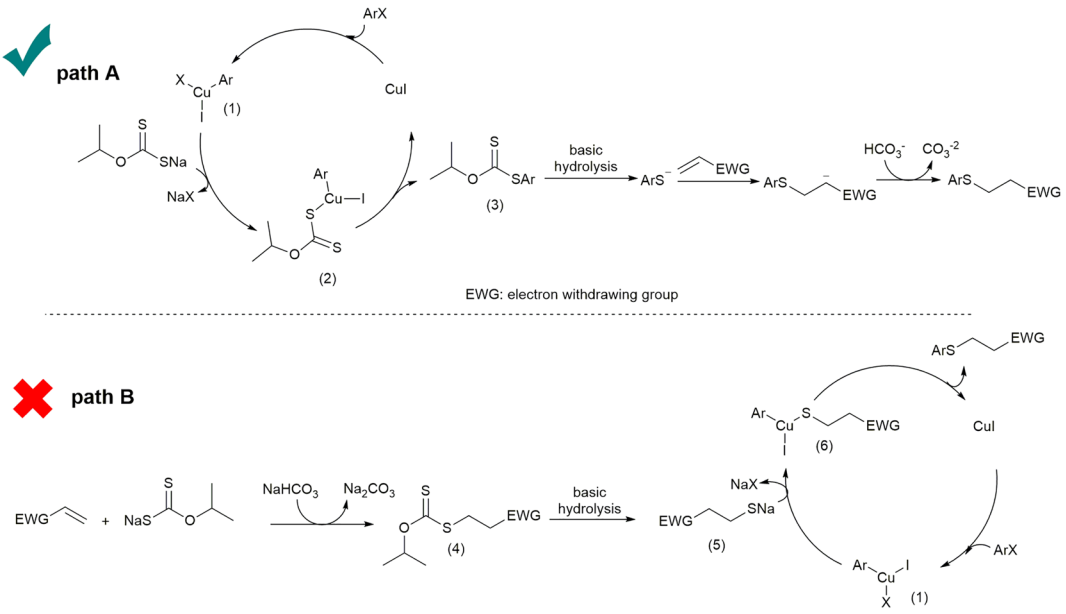
We considered two reasonable pathways for the reaction, marked path A and path B in Scheme 2.

According to path A, CuI undergoes oxidative addition by insertion into the aryl C–X bond to produce Cu(III) intermediate **1**. Next, this intermediate is converted to intermediate **2** by replacing halide (X^-) with xanthogenate on Cu. This step is followed by reductive elimination to give *O*-*iso*-propyl *S*-phenyl carbonodithioate (**3**) along with regeneration of CuI. This intermediate under basic hydrolysis affords aryl thiolate, which in turn undergoes 1,4-addition to an electron-deficient alkene followed by proton capture from bicarbonate to produce the thia-Michael adduct.

According to path B, the conjugate addition of *iso*-propyl xanthogenate to alkene results in the thia-Michael adduct **4**, which subsequently undergoes basic hydrolysis to form the aliphatic thiolate **5**. On the other hand, insertion of Cu into the aryl–X bond generates intermediate **1**, which under treatment with the aliphatic thiolate **5** generates intermediate **6** by replacing halide with thiolate. Finally, a reductive elimination process regenerates CuI catalyst and releases the thia-Michael adduct.

In order to understand the thiol intermediates involved in the process and therefore to approve or reject the proposed mechanisms, a reaction using iodobenzene (1.2 mmol), butyl acrylate (1 mmol), sodium *iso*-propyl xanthogenate (1.3 mmol), $NaHCO_3$ (6 mmol), and CuI (20 mol%) in DMF at 110 oC was conducted in the presence of C_2Cl_6 (1 mmol). Thiols in the presence of C_2Cl_6 undergo fast oxidation to symmetric disulfides.[24] The reaction in the presence of C_2Cl_6 gave only diphenyl disulfide and the starting butyl acrylate was recovered unreacted from the reaction mixture in near-quantitative yield. This finding confirms path A and rejects path B.

In conclusion, we have developed conditions for a one-step copper-catalyzed synthesis of thia-Michael products of aromatic thiols using aryl halides, sodium *iso*-propyl xanthogenate, and diverse electron-deficient alkenes. The method is ligand-free, one-pot, one-step, thiol-free, and simple, giving thia-Michael adducts in good to excellent yields.



SCHEME 2 Two possible reaction pathways. Path A was confirmed by further experiments whereas path B was rejected. EWG, electron withdrawing groups

TABLE 2 Synthesis of Michael adducts by reacting aryl halides, electron-deficient alkenes, and sodium *iso*-propyl xanthogenate[a]

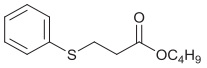
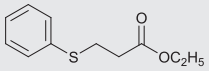
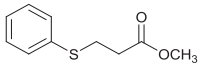
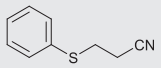
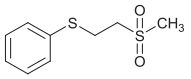
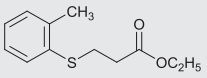
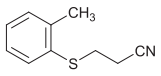
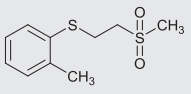
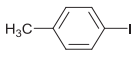
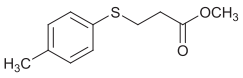
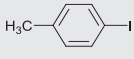
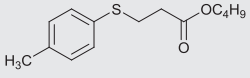
Entry	ArX	Alkene	Product	*T* (hr)	Yield (%)
1		Butyl acrylate		12	89
2		Ethyl acrylate		12	86
3		Methyl acrylate		12	86
4		Acrylonitrile		12	85
5		Methyl vinyl sulfone		12	83
6		Ethyl acrylate		21	85
7		Acrylonitrile		21	84
8		Methyl vinyl sulfone		21	80
9		Methyl acrylate		21	83
10		Butyl acrylate		21	85

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TABLE 2 (Continued)

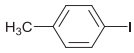
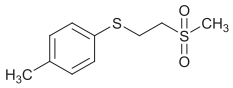
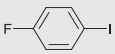
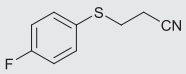
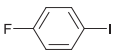
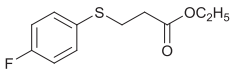
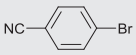
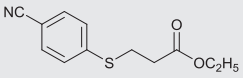
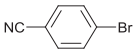
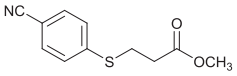
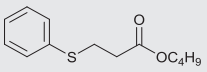
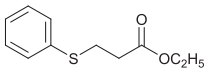
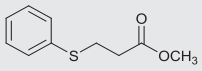
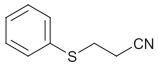
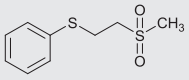
Entry	ArX	Alkene	Product	*T* (hr)	Yield (%)
11		Methyl vinyl sulfone		21	85
12		Acrylonitrile		20	85
13		Ethyl acrylate		20	85
14		Ethyl acrylate		17	85
15		Methyl acrylate		17	85
16		Butyl acrylate		19	86
17		Ethyl acrylate		19	86
18		Methyl acrylate		19	85
19		Acrylonitrile		19	83
20		Methyl vinyl sulfone		19	81

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TABLE 2 (Continued)

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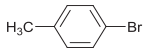
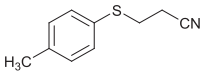
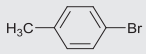
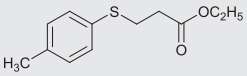
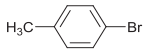
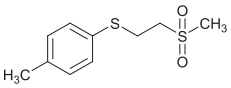
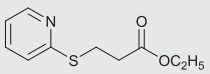
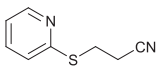
21		Acrylonitrile		28	83
22		Ethyl acrylate		28	84
23		Methyl vinyl sulfone		28	80
24		Ethyl acrylate		24	82
25		Acrylonitrile		24	79

[a]Reaction conditions: aryl halide (1.2 mmol), sodium *iso*-propyl xanthogenate (1.3 mml), electron-deficient alkene (1 mmol), CuI (0.2 mmol), $NaHCO_3$ (6 mmol), DMF (2 ml), 110°C.

3 | EXPERIMENTAL SECTION

General procedure: An aryl halide (1.2 mmol), a Michael acceptor (1 mmol), CuI (0.2 mmol), and $NaHCO_3$ (6 mmol) were added to a mixture of sodium *iso*-propyl xanthogenate (1.3 mmol) in DMF (2 ml). The reaction mixture was stirred at 110°C until the aryl halide was consumed. After that, the mixture was diluted with H_2O (0.5 ml) and extracted with 1:1 *n*-hexane/ethyl acetate (4 × 1 ml). The organic extracts were combined, concentrated, and purified by chromatography on silica gel using *n*-hexane or a suitable mixture of *n*-hexane/EtOAc as eluent to obtain pure product.

The NMR spectra of products are shown in the supporting information file.

Butyl 3-(phenylthio)propanoate (Table 2, entries 1 and 16): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.41–7.39 (m, 2H), 7.35–7.31 (m, 2H), 7.26–7.22 (m, 1H), 4.12 (t, J = 6.7 Hz, 2H), 3.20 (t, J = 7.4 Hz, 2H), 2.66 (t, J = 7.4 Hz, 2H), 1.67–1.60 (m, 2H), 1.45–1.36 (m, 2H), 0.96 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):171.9, 135.3, 130.1, 129.9, 126.6, 64.7, 34.5, 30.6, 29.1, 19.2, 13.7.

Ethyl 3-(phenylthio)propanoate (Table 2, entries 2 and 17): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.40–7.37 (m, 2H), 7.34–7.28 (m, 2H), 7.25–7.21 (m, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.19 (t, J = 7.4 Hz, 2H), 2.64 (t, J = 7.4 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.7, 135.3, 130.1, 129.0, 126.5, 60.7, 34.42, 29.0, 14.2.

Methyl 3-(phenylthio)propanoate (Table 2, entries 3 and 18): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40–7.35 (m, 2H), 7.33–7.27 (m, 2H), 7.23–7.17 (m, 1H), 3.67 (s, 3H), 3.17 (t, J = 7.1 Hz, 2H), 2.63 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.3, 135.4, 130.3, 129.2, 126.7, 51.9, 34.4, 29.2.

3-(Phenylthio)propanenitrile (Table 2, entries 4 and 19): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47–7.44 (m, 2H), 7.40–7.30 (m, 3H), 3.15 (t, J = 7.2 Hz, 2H), 2.62 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 133.3, 131.5, 129.5, 127.9, 118.2, 30.3, 18.4.

(2-(Methylsulfonyl)ethyl)(phenyl)sulfane (Table 2, entries 5 and 20): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.46–7.31 (m, 5H), 3.40–3.33 (m, 2H), 3.31–3.23 (m, 2H), 2.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 133.3, 130.7, 129.5, 127.6, 54.5, 41.4, 26.5.

Ethyl 3-(*o*-tolylthio)propanoate (Table 2, entry 6): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37–7.35 (m, 1H), 7.23–7.14 (m, 3H), 4.18 (q, J = 7.1 Hz, 2H), 3.19 (t, J = 7.4 Hz, 2H), 2.67 (t, J = 7.4 Hz, 2H), 2.42 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.8, 138.4, 134.6, 130.3, 129.1, 126.5, 126.4, 60.8, 34.3, 28.3, 20.5, 14.2.

3-(*o*-Tolylthio)propanenitrile (Table 2, entry 7): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39–7.36 (m, 1H), 7.29–7.20 (m, 3H), 3.14 (t, J = 7.2 Hz, 2H), 2.61 (t, J = 7.2 Hz, 2H), 2.47 (3, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.6, 132.4, 130.8, 130.7, 127.6, 126.8, 118.1, 29.3, 20.5, 18.1.

(2-(Methylsulfonyl)ethyl)(*o*-tolyl)sulfane (Table 2, entry 8): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.39–7.34 (m, 1H), 7.28–7.19 (m, 3H), 3.37–3.22 (m, 4H), 2.97 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 139.0, 132.6, 130.8, 129.8, 127.4, 126.9, 54.3, 41.3, 25.5, 20.5.

Butyl 3-(*p*-tolylthio)propanoate (Table 2, entry 10): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 4.10 (t, J = 6.7 Hz, 2H), 3.14 (t, J = 7.4 Hz, 2H), 2.62 (t, J = 7.4 Hz, 2H), 2.35 (s, 3H), 1.66–1.59 (m, 2H), 1.44–1.35 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 172.1, 137.0, 131.5, 131.2, 130.0, 64.7, 34.7, 30.8, 29.9, 21.2, 19.3, 13.9.

(2-(Methylsulfonyl)ethyl)(*p*-tolyl)sulfane (Table 2, entries 11 and 23): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.33 (dd, J = 8.2, 1.2 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 3.33–3.17 (m, 4H), 2.93 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):138.0, 131.5, 130.3, 129.6, 54.4, 41.3, 27.2, 21.1.

3-((4-Fluorophenyl)thio)propanenitrile (Table 2, entry 12): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50–7.46 (m, 2H), 7.10–7.06 (m, 2H), 3.10 (t, J = 7.2 Hz, 2H), 2.60 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.1, 161.6, 134.8, 134.7, 128.2, 128.16, 118.0, 116.8, 116.6, 77.5, 77.2, 76.8, 31.4, 18.4.

Ethyl 3-((4-fluorophenyl)thio)propanoate (Table 2, entry 13): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42–7.38 (m, 2H), 7.02 (t, J = 8.7 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.12 (t, J = 7.4 Hz, 2H), 2.59 (t, J = 7.4 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.7, 163.4, 160.9, 133.4, 133.3, 130.1, 130.1, 116.3, 116.0, 60.7, 34.5, 30.4, 14.2.

Ethyl 3-((4-cyanophenyl)thio)propanoate (Table 2, entry 14): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):7.58 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 4.20 (q, J = 7.2 Hz, 2H), 3.29 (t, J = 7.3 Hz, 2H), 2.71 (t, J = 7.3 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.2, 143.5, 132.3, 127.2, 118.7, 108.7, 61.0, 33. 7, 27.0, 14.1.

Methyl 3-((4-cyanophenyl)thio)propanoate (Table 2, entry 15): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 3.72 (s, 3H), 3.24(t, J = 7.2 Hz, 2H), 2.68 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.9, 143.8, 132.6, 127.7, 118.9, 109.0, 52.3, 33.8, 27.3.

3-(*p*-Tolylthio)propanenitrile (Table 2, entry 21): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (d, J = 7.7 Hz, 2H), 7.19 (d, J = 7.7 Hz, 2H), 3.10 (t, J = 7.3 Hz, 2H), 2.59 (t, J = 7.3 Hz, 2H), 2.38 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 138.4, 132.4, 130.4, 129.5, 118.3, 31.0, 21.3, 18.4.

Ethyl 3-(*p*-tolylthio)propanoate (Table 2, entry 22): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.31 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.14 (t, J = 7.4 Hz, 2H), 2.61 (t, J = 7.4 Hz, 2H), 2.34 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.8, 136.7, 131.3, 131.0, 129.7, 60.6, 34.5, 29.7, 21.0, 14.2.

Ethyl 3-(pyridin-2-ylthio)propanoate (Table 2, entry 24): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.45–8.44 (m, 1H), 4.527.48 (m, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.02–6.99 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.46 (t, J = 7.1 Hz, 2H), 2.80 (t, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 172.1, 158.2, 149.4, 135.9, 122.4, 119.5, 60.6, 34.7, 24.9, 14.1.

3-(Pyridin-2-ylthio)propanenitrile (Table 2, entry 25): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.47–8.45 (m, 1H), 7.57–7.53 (m, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.08–7.05 (m, 1H), 3.46 (t, J = 7.1 Hz, 2H), 2.90 (t, J = 7.1 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 156.6, 149.6, 136.3, 122.7, 120.0, 118.7, 25.6, 18.8.

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