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Copper-Mediated Coupling of Boronic Acids, Amines, and Carbon Disulfide: An Approach to Organic Dithiocarbamates

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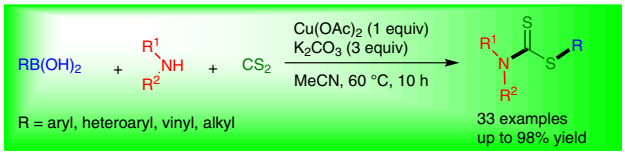

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Abstract An efficient copper-mediated three-component coupling reaction of boronic acids, amines, and carbon disulfide has been developed, which provides a new approach to a wide range of functionalized dithiocarbamates in good to excellent yields. The present methodology has many advantages, such as mild reaction conditions, easily available substrates, wide substrate scope, and high functional-group tolerance.

Key words amine, boron, copper, coupling, multicomponent reaction

Organic dithiocarbamates constitute an important class of compounds that are known to have a wide range of biological activities and thus have attracted much attention in the field of pharmaceuticals and therapeutics in recent years (Figure 1).[1] Moreover, they have been used as versatile synthetic intermediates in organic synthesis,[2] as linkers in solid-phase organic synthesis,[3] and as radical chain transfer agents in reversible addition fragmentation chain transfer (RAFT) polymerizations.[4]

Since conventional methods for the synthesis of dithiocarbamates involve the use of toxic thiophosgene and its derivatives, there is high demand for new and green protocols that allow the synthesis of this type of compounds with low toxic and easily available reagents as starting materials.[5] In the past decades, many elegant alternative processes have been developed.[6–11] Especially, one-pot three-component reactions of amines, carbon disulfide, and electrophiles have been extensively investigated for the construction of different dithiocarbamates (Scheme 1, a). The electrophiles previously used for this purpose include organic halides,[7] α,β-unsaturated compounds,[8] alcohols,[9] aryl diazonium fluoroborate,[10] and *N*-tosylhydrazones.[11] These reactions proceed through the in situ generation of the dithiocarbamate anion via the reaction of amines and carbon disulfide followed by the reaction with electrophiles. Although great progress has been made, the development of a general route to dithiocarbamates with wide substrate scope and high functional-group tolerance still remains a challenge.

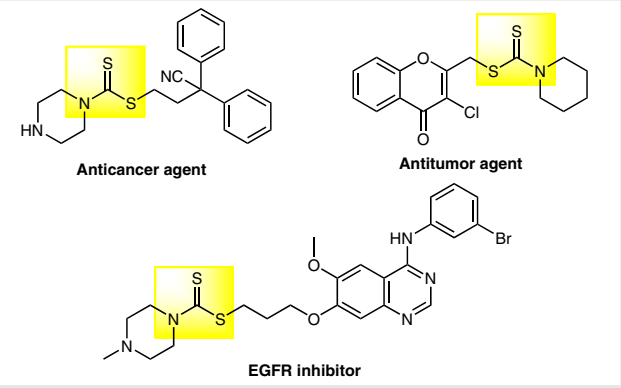
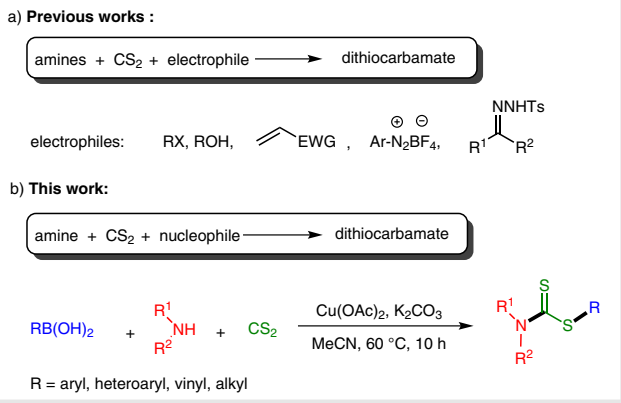


Figure 1 Representative organic dithiocarbamates with pharmaceutical activity

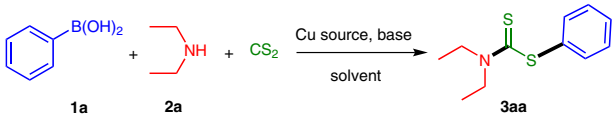


Scheme 1 Methods for the synthesis of organic dithiocarbamates

Organoboronic acids, which have low toxicity and are readily available and easy to handle, have been widely used as coupling partners for the carbon–carbon bond and carbon–heteroatom bond-formation reactions,[12] such as the palladium-catalyzed Suzuki–Miyaura coupling reaction[13] and the copper-mediated Chan–Evans–Lam coupling reaction.[14] However, to the best of our knowledge, they have never been explored for the synthesis of organic dithiocarbamates. As part of our continuing interest in the development of new multicomponent reactions for the construction of functional molecules,[15] herein, we wish to report an efficient copper-mediated three-component coupling reaction of boronic acids, amines, and carbon disulfide, which provides a new route to a wide range of dithiocarbamtates, including alkyl, (hetero)aryl, and vinyl dithiocarbamates (Scheme 1, b).

Initially, the reaction of phenylboronic acid (**1a**), diethylamine (**2a**), and CS_2 was selected as the model reaction for the optimization of reaction conditions, and the results are summarized in Table 1. To our delight, when the reaction was conducted in the presence of one equivalent of $Cu(OAc)_2$ and three equivalents of K_2CO_3 in acetonitrile at 60 °C under air atmosphere for ten hours, the desired product, phenyl diethylcarbamodithioate (**3aa**), was formed in an excellent yield (Table 1, entry 1). An evaluation of other copper sources showed that CuCl could also mediate the reaction efficiently, while $CuSO_4$, $Cu(OTf)_2$, CuI, or Cu_2O exhibited no or lower efficacy (Table 1, entries 2–6). It should be noted that when the reaction was conducted with other metal salts such as $Pd(OAc)_2$ and $NiCl_2$, no desired product was detected (Table 1, entries 7 and 8). Further screening of bases revealed that Na_2CO_3 was also capable of promoting the reaction to give the desired product in 94% yields while replacement of K_2CO_3 with other bases such as NaOH, DMAP, or pyridine resulted in low yield or no trace of the desired product (Table 1, entries 9–12). It was found that the solvent have a significant influence on the reaction. Acetonitrile was proven to be the most suitable solvent for the reaction while CH_2Cl_2, toluene, 1,4-dioxane, DMSO, and H_2O gave inferior results (Table 1, entries 13–17). Both 1 equivalent of $Cu(OAc)_2$ and 3 equivalents of K_2CO_3 are necessary for the reaction completion. Decreasing the loading of the copper salt or the base would dramatically decrease the yield (Table 1, entries 18 and 19). It should be pointed out that the reaction required an air atmosphere to proceed; if the reaction was carried out in nitrogen, the yield of the product was very low (Table 1, entry 20). Further optimization revealed that decreasing the reaction temperature from 60 °C to 35 °C led to a sharp decrease in the yield of **3aa** (Table 1, entry 21). The effect of the mole ratio of reactants was also investigated. A 1:5:2 molar ratio of **1a**/**2a**/CS_2 proved to be the optimal. Lower yield was obtained when the reaction was performed in a molar ratio of **1a**/**2a**/CS_2 = 1:1:1 or 1:2:2 under otherwise identical conditions (Table 1, entries 22 and 23).

Table 1 Optimization of the Reaction Conditions[a]



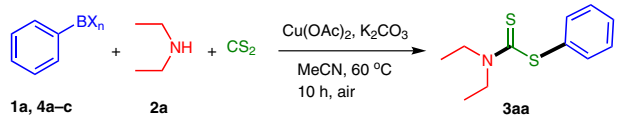
1a **2a** **3aa**

Entry	Cu source	Base	Solvent	Yield (%)[b]
1	$Cu(OAc)_2$	K_2CO_3	MeCN	96 (88)
2	CuCl	K_2CO_3	MeCN	93
3	$CuSO_4$	K_2CO_3	MeCN	trace
4	$Cu(OTf)_2$	K_2CO_3	MeCN	trace
5	CuI	K_2CO_3	MeCN	63
6	Cu_2O	K_2CO_3	MeCN	23
7	$Pd(OAc)_2$	K_2CO_3	MeCN	N.D.[c]
8	$NiCl_2$	K_2CO_3	MeCN	N.D.
9	$Cu(OAc)_2$	Na_2CO_3	MeCN	94
10	$Cu(OAc)_2$	NaOH	MeCN	N.D.
11	$Cu(OAc)_2$	DMAP	MeCN	33
12	$Cu(OAc)_2$	pyridine	MeCN	N.D.
13	$Cu(OAc)_2$	K_2CO_3	CH_2Cl_2	86
14	$Cu(OAc)_2$	K_2CO_3	toluene	88
15	$Cu(OAc)_2$	K_2CO_3	1,4-dioxane	58
16	$Cu(OAc)_2$	K_2CO_3	DMSO	trace
17	$Cu(OAc)_2$	K_2CO_3	H_2O	N.D.
18[d]	$Cu(OAc)_2$	K_2CO_3	MeCN	18
19[e]	$Cu(OAc)_2$	K_2CO_3	MeCN	25
20[f]	$Cu(OAc)_2$	K_2CO_3	MeCN	10
21[g]	$Cu(OAc)_2$	K_2CO_3	MeCN	9
22[h]	$Cu(OAc)_2$	K_2CO_3	MeCN	43
23[i]	$Cu(OAc)_2$	K_2CO_3	MeCN	52

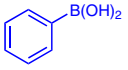
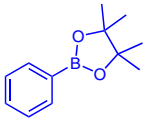
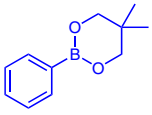
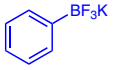
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (2.5 mmol), CS_2 (1.0 mmol), Cu source (1.0 mmol), and base (1.5 mmol) in solvent (4 mL), under air at 60 °C for 10 h.
[b] GC yield with dodecane as internal standard. Number in parentheses is the yield of isolated product. [c] N.D. = Not detected.
[d] With 0.5 equiv of $Cu(OAc)_2$.
[e] With 1.5 equiv of K_2CO_3.
[f] The reaction was conducted under N_2 atmosphere.
[g] At 35 °C.
[h] The reaction was conducted with 0.5 mmol of **2a** and 0.5 mmol of CS_2.
[i] The reaction was conducted with 1.0 mmol of **2a** and 1.0 mmol of CS_2.

In order to evaluate the reactivity of other organoboron compounds in the three-component coupling reaction, phenylboronic acid pinacol ester (**4a**), phenylboronic acid neopentylglycol ester (**4b**), and potassium phenyltrifluoroborate (**4c**) were employed as the coupling partner to react with **2a** and CS_2 under the identical reaction conditions. The results in Table 2 revealed that phenylboronic acid ester **4b** could also work well to give the desired product in excellent yield (Table 2, entry 3), while **4a** and **4c** gave low or no yield (Table 2, entries 2 and 4).

Table 2 Reactivity of other Organoboron Compounds[a]



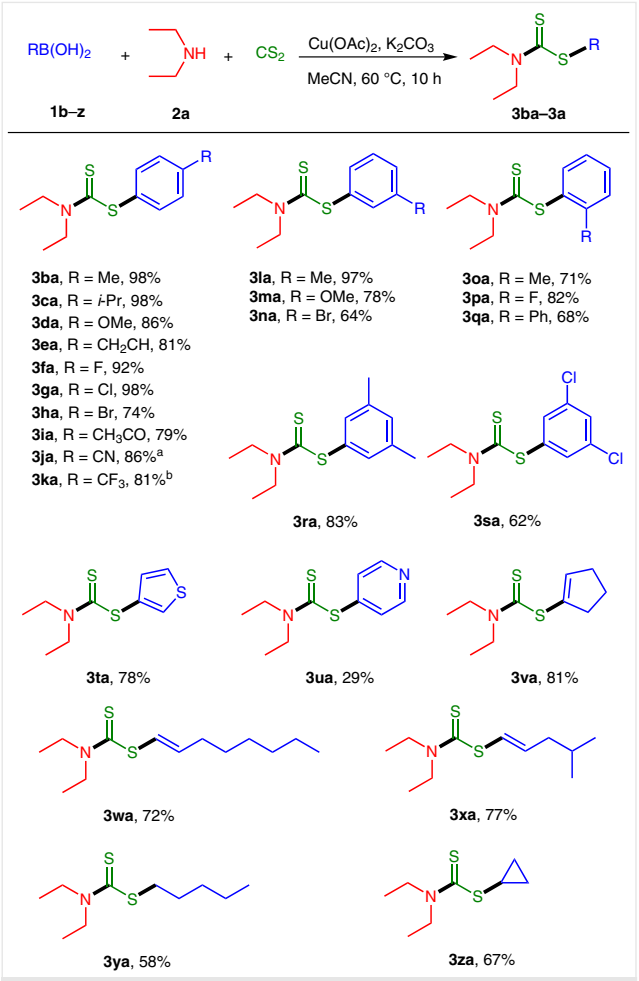
1a, 4a–c 2a 3aa

Entry	Organoboron compound		Yield (%)[b]
1		**1a**	96
2		**4a**	15
3		**4b**	91
4		**4c**	0

[a] Reaction conditions: organoboron reagent (0.5 mmol), **2a** (2.5 mmol), CS_2 (1.0 mmol), $Cu(OAc)_2$ (1.0 mmol), K_2CO_3 (1.5 mmol), MeCN (4 mL), 60 °C, 10 h, air.
[b] GC yield with dodecane as internal standard.

With the optimized reaction conditions in hand, we then examined the scope and generality of this copper-mediated three-component coupling reaction with various boronic acids (Scheme 2).[16,17] Gratifyingly, a variety of arylboronic acids bearing electron-rich or electron-poor substituents, such as alkyl, alkoxyl, alkenyl, halides, ketone, cyano, and trifluoromethyl, underwent the reaction with **2a** and CS_2 to furnish the corresponding products (**3ba–qa**) in good to excellent yields, although in some cases higher temperatures were required. The results also showed that *ortho* substitution decrease the yield of the expected product, probably due to steric hindrance effect (**3ba** and **3la** vs. **3oa**; **3fa** vs. **3pa**). Besides monosubstituted boronic acids, the bis-substituted ones such as **1r** and **1s** could also undergo the reaction smoothly. Remarkably, boronic acids containing a heteroaryl moiety, such as 3-thienylboronic acid (**1t**) and 4-pyridineboronic acid (**1u**), were compatible with the reaction conditions, although the later gave the desired product **3ua** in a lower yield. It should be pointed out that these compounds are difficult to be synthesized by previously reported methods.

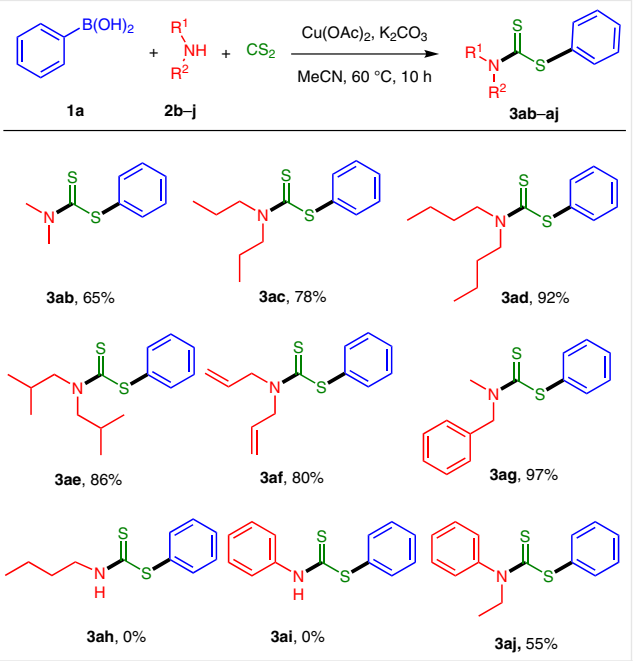
Pleasingly, vinylboronic acids **1v–x** could be efficiently transformed into the desired products (**3va–xa**) in good yields. It is noteworthy that the reactions of vinylboronic acids are highly stereospecific, as the (*E*)-vinylboronic acids **1w** and **1x** gave the corresponding (*E*)-vinyl dithiocarbamates as the sole product without the formation of *Z* isomers. In contrast, the approaches previously developed for



Scheme 2 Substrate scope of boronic acids. *Reagents and conditions*: **1** (0.5 mmol), **2a** (2.5 mmol), CS_2 (1.0 mmol), $Cu(OAc)_2$ (1.0 mmol), K_2CO_3 (1.5 mmol), MeCN (4 mL), 60 °C, 10 h, air. Isolated yields are given. [a] The reaction was conducted at 80 °C. [b] The reaction was conducted at 100 °C.

the synthesis of (*E*)-vinyl dithiocarbamates from vinyl bromides usually generated *Z* isomers as minor byproducts.[6b,7c] Furthermore, extension of our protocol to more challenging alkylboronic acid substrates to synthesize alkyl dithiocarbamates was also successful. For instance, both pentylboronic acid (**1y**) and cyclopropylboronic acid (**1z**) could enter into the reaction smoothly, affording the corresponding products **3ya** and **3za** in satisfactory yields under the optimized conditions.

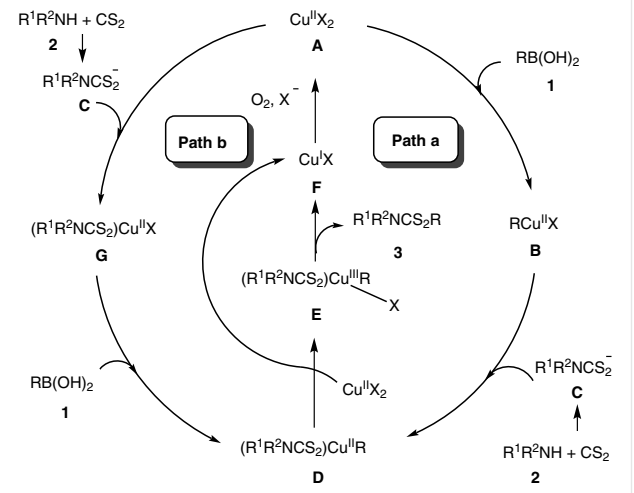
Subsequently, the scope of amines was examined (Scheme 3). A variety of secondary amines (**2b–g**) were capable of taking part in the reaction, furnishing the corresponding products **3ab–ag** in good to excellent yields. However, the reaction of primary amine, such as *n*-butylamine (**2h**), generated the corresponding thiourea as the major product, and the desired dithiocarbamate product was not detected. To our surprise, although aniline (**2i**) could not



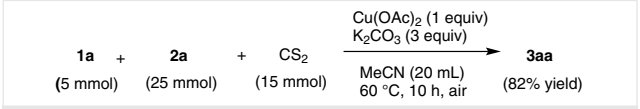
Scheme 3 Substrate scope of amines. *Reagents and conditions*: **1a** (0.5 mmol), **2** (2.5 mmol), CS_2 (1.0 mmol), $Cu(OAc)_2$ (1.0 mmol), K_2CO_3 (1.5 mmol), MeCN (4 mL), 60 °C, 10 h, air. Isolated yields are given.

participate in the reaction, *N*-ethylaniline was a suitable substrate for the reaction, giving rise to the desired product **3aj** in a satisfactory yield.

In order to highlight the practicability and reliability of our new protocol, an amplifying experiment was performed. As can be seen from Scheme 4, the dithiocarbamate product **3aa** could be obtained in a high yield (82%) upon isolation when the reaction was conducted on a 5 mmol scale (Equation 1).



Scheme 4 Proposed reaction mechanism



Equation 1

On the basis of the above results and previous reports,[7–11,18,19] a plausible mechanism is illustrated in Scheme 4. Initially, transmetalation of boronic acid **1** with copper(II) species **A** generated **B**, which then underwent coordination exchange with the in situ generated dithiocarbamate anion **C** to give complex **D**. Upon disproportionation with copper(II), complex **D** was oxidized to copper(III) species **E**. A following reductive elimination produced the final product **3** along with a copper(I) species **F**, which would be oxidized by O_2 to regenerate copper(II) species **A** to close the cycle (path a). Alternatively, the reaction might proceed through path b, in which coordination exchange of species **A** with dithiocarbamate anion **C** occurred first to give intermediate **G**. Subsequent transmetalation of **G** with boronic acid **1** would also afford complex **D**.

In summary, we have successfully developed an efficient method for the synthesis of organic dithiocarbamates through a copper-mediated three-component coupling reaction of boronic acids, amines, and carbon disulfide. A variety of boronic acids, including aryl, heteroaryl, vinyl, and alkyl boronic acids, could be applied to the protocol, affording the corresponding products in good to excellent yields. The present methodology has many advantages, such as mild reaction conditions, easily available substrates, wide substrate scope, and high functional-group tolerance. Further investigations into the mechanism and exploration of additional active catalytic system for this and related coupling reaction are underway in our laboratory.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560561.

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(16) **Typical Procedure for the Synthesis of Compound 3aa**
A 25 mL dried Schlenk tube was charged with boronic acid **1a** (0.5 mmol), diethylamine (**2a**, 2.5 mmol), CS_2 (1.0 mmol), $Cu(OAc)_2$ (1.0 mmol), K_2CO_3 (1.5 mmol), and MeCN (4 mL) at room temperature. The reaction mixture was stirred at 60 °C for 10 h under air. After the reaction was completed, the mixture was cooled to room temperature and filtered through a plug of Celite. The filtrate was then concentrated in vacuo to afford the crude product, which was then subjected to chromatography on silica gel with hexanes–EtOAc (20:1) to give the desired product **3aa** as a pale yellow oil; 88% isolated yield (96% GC yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (q, *J* = 8.0 Hz, 5 H), 4.04 (q, *J* = 4.0 Hz, 2 H), 3.86 (q, *J* = 8.0 Hz, 2 H), 1.40 (t, *J* = 8.0 Hz, 3 H), 1.30 (t, *J* = 8.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.78, 137.00, 131.47, 129.79, 128.87, 49.71, 47.14, 12.61, 11.46. IR (KBr): 3055, 2978, 2932, 1485, 1444, 1414, 1067, 1009, 978, 915, 826, 744, 685, 505 cm^{-1}. MS (EI): *m/z* = 225[M$^+$], 152, 141, 116 (100), 109, 88. ESI-HRMS: *m/z* calcd for $C_{11}H_{15}NS_2Na$ [M + Na]$^+$: 248.0538; found: 248.0543.
(17) **Analytical Data of Two New Compounds**
4-Isopropylphenyl Diethylcarbamodithioate (3ca)
Colorless solid (123.5 mg, 98%); mp 80–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 4.01 (q, *J* = 8.0 Hz, 2 H), 3.83 (q, *J* = 8.0 Hz, 2 H), 2.99–2.90 (m, 1 H), 1.36 (t, *J* = 6.0 Hz, 3 H), 1.27 (d, *J* = 4.0 Hz, 9 H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.02, 150.51, 136.73, 128.18, 126.99, 49.57, 46.97, 33.66, 23.54, 12.53, 11.37. IR (KBr): 2962, 2870, 1592, 1486, 1414, 1265, 1205, 1142, 1101, 976, 827, 548 cm^{-1}. MS (EI): *m/z* = 267[M$^+$], 135, 116 (100), 91, 88. ESI-HRMS: *m/z* calcd for $C_{14}H_{21}NS_2Na$ [M + Na]$^+$: 290.1008; found: 290.1014.
Phenyl Dipropylcarbamodithioate (3ac)
Yellow oil (98.7 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.39 (m, 5 H), 3.90 (t, *J* = 6.0 Hz, 2 H), 3.72 (t, *J* = 8.0 Hz, 2 H), 1.88–1.74 (m, 4 H), 1.01 (t, *J* = 6.0 Hz, 3 H), 0.92 (t, J = 6.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.27, 136.93, 131.57, 129.69, 128.81, 56.92, 54.71, 20.81, 19.47, 11.09. IR (KBr): 2968, 2871, 1482, 1410, 1238, 1194, 1145, 986, 745, 686, 503 cm^{-1}. MS (EI): *m/z* = 253 [M$^+$], 153, 144 (100), 109, 102, 77, 60. ESI-HRMS: *m/z* calcd for $C_{13}H_{19}NS_2Na$ [M + Na]$^+$: 276.0851; found: 276.0853.
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