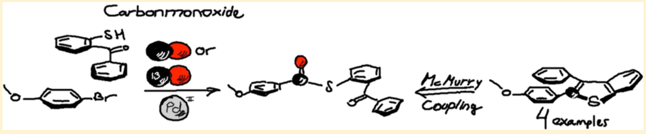
JOC The Journal of Organic Chemistry
Featured Article
pubs.acs.org/joc

Palladium-Catalyzed Thiocarbonylation of Aryl, Vinyl, and Benzyl Bromides

Mia N. Burhardt, Andreas Ahlburg, and Troels Skrydstrup*

Center for Insoluble Protein Structures, Department of Chemistry and Interdisciplinary Nanoscience Center, Aarhus University, Gustav Wieds vej 14, 8000 Aarhus C, Denmark

Supporting Information

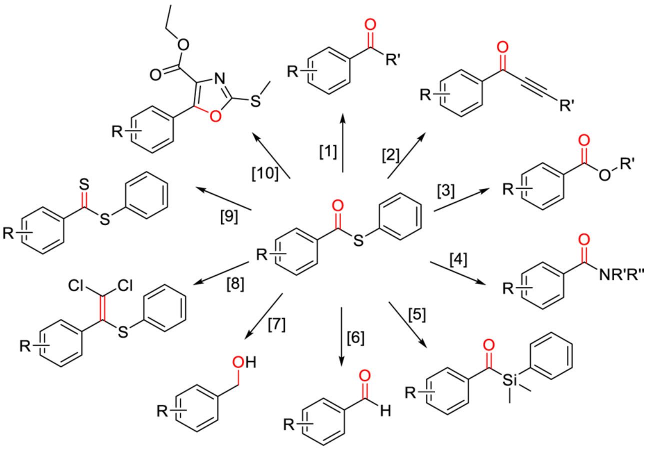


ABSTRACT: A catalytic protocol for synthesis of thioesters from aryl, vinyl, and benzyl bromides as well as benzyl chlorides was developed using only stoichiometric amounts of carbon monoxide, produced from a solid CO precursor inside a two-chamber system. As a catalytic system, the combination of bis(benzonitrile) palladium(II) chloride and Xantphos furnished the highest yields of the desired compounds, along with the weak base, NaOAc, in anisole at 120 °C. The choice of catalytic system as well as solvent turned out to be important in order to ensure a high chemoselectivity in the reaction. Both electron-rich and electron-deficient aryl bromides worked well in this reaction. Addition of 1 equiv of sodium iodide to the reaction improved the chemoselectivity with the electron-deficient aryl bromides. The thiol scope included both aryl and alkyl thiols, including 2-mercaptobenzophenones, whereby a thiocarbonylation followed by a subsequent McMurry coupling yielded differently substituted benzothiophenes. It was demonstrated that the methodology could be applied for ^{13}C introduction into the thiophene ring.

INTRODUCTION

Thioesters are common intermediates in biochemistry, in many cases acting as an important class of acyl donors. In organic chemistry, thioesters represent excellent building blocks for a number of synthetic transformations. These air-stable acyl donors are tolerant to column purification on silica gel and therefore easier to handle than the corresponding acyl halides. Furthermore, substitution of the sulfur-containing leaving group with a variety of nucleophiles can be achieved under relatively mild reaction conditions. Examples of the applications of thioesters in organic synthesis are illustrated in Scheme 1.

Scheme 1. Examples of the Application of Thioesters as Building Blocks in Organic Synthesis



Fukuyama and co-workers developed a chemoselective protocol for the synthesis of ketones from thioesters using Pd-catalysis and a zinc aryl or alkyl species.[1] Different procedures have also been developed for the preparation of acetylene ketones,[2] esters,[3] amides,[4] and acylsilanes[5] from thioesters. Furthermore, it is possible to reduce this carboxylic acid derivative selectively to either an aldehyde or alcohol depending on the conditions used while leaving other functional groups such as esters and amides untouched.[6,7] Sekiya and Lawesson demonstrated that the oxygen atom of a thioester can be replaced by a CCl_2 group or sulfur.[8,9] The benzodithioate products can be further exploited for synthesis of different sulfur-containing heterocycles. Furthermore, it is possible to synthesize 2-methylthio-1,3-oxazoles from both aryl- and alkylthioesters using *N*-(ethoxycarbonylmethyl)-iminodithiocarbonate.[10]

Palladium complexes catalyze a number of carbonylation reactions yielding a large variety of carbonyl-containing compounds, depending on the applied coupling partners.[11] However, Pd-catalyzed thiocarbonylations have not been explored as intensively as the other carbonylation reactions, possibly because of the fear for poisoning of the catalyst with thiol nucleophiles. Nevertheless, Hartwig and co-workers demonstrated that with the appropriate catalyst composition, it is possible to overcome this obstacle for Pd-catalyzed thioarylations.[12] Over the last 15 years, the group of Alper has developed an extensive number of Pd-catalyzed thiocarbony-

Special Issue: Mechanisms in Metal-Based Organic Chemistry

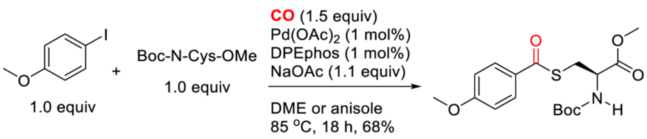
Received: May 7, 2014
Published: June 12, 2014

dx.doi.org/10.1021/jo5009965 | *J. Org. Chem.* 2014, 79, 11830−11840

lation reactions with a variety of unsaturations.[13] But in 2008, they reported the first examples of the thiocarbonylation of aryl iodides employing 5 mol % of a Pd-catalyst in a phosphonium salt ionic liquid as solvent under a CO pressure of 14 bar.[14] Later in 2010, another protocol was published by the Lei group as part of mechanistic studies for the Pd-catalyzed alkoxycarbonylation. They were able to prepare a small range of thioesters with 2 mol % of a Pd catalyst, with sodium thiolates as the nucleophiles in a RSH/THF solvent mixture, and in the presence of 10 bar of CO.[15,16] In 2013, we published an alternative protocol using only 1.5 equiv of carbon monoxide and 1.0 equiv of thiol. Just 1 mol % of a $Pd(OAc)_2$/DPEphos mixture was applied as the catalytic system with NaOAc as the base and dimethoxyethane (DME) or anisole as the solvent (Scheme 2).[17] The choice of solvent for this reaction was dependent on the electronic character of the aryl ring substituents of the electrophilic coupling partner. In order to avoid the manipulation of carbon monoxide from a cylinder, this gas was produced from the solid CO-precursor, 9-methylfluorene-9-carbonyl chloride (COgen), by a Pd-catalyzed decarbonyation using a two-chamber reactor (CO-ware) to separate the CO-producing reaction from the CO-consuming carbonylation reaction.[18,19] This technique has been exploited for a wide variety of Pd-catalyzed carbonylation protocols;[20] as only a slight stoichiometric excess of CO is applied with this glassware, the methodology is highly adaptable for ^{13}C- or ^{14}C-isotope labeling.[21]

Scheme 2. Previously Identified Conditions for the Pd-Catalyzed Thiocarbonylation of Aryl Iodides[17]

Previous work:



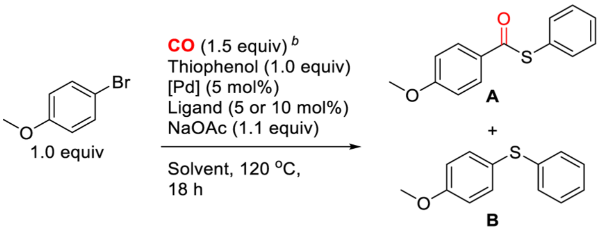
Unfortunately, our previously reported conditions for the thiocarbonylation of aryl iodides were unsuitable for transforming the more attractive aryl bromides into their corresponding thioesters. Hence, in this paper, we describe our studies to identify a suitable catalyst and reaction conditions that include these more interesting substrates to the scope of Pd-catalyzed thiocarbonylation reactions. Furthermore, we report that the methodology is suitable for the thiocarbonylation of vinyl and benzyl bromides, as well as benzyl chlorides. Finally, we disclose that this new thiocarbonylation protocol can be combined with a concomitant McMurry coupling for the successful synthesis of benzothiophenes, including their selective ^{13}C-isotope labeling.

■ RESULTS AND DISCUSSION

Our starting point for the optimization of the thiocarbonylation of aryl bromides began with the conditions identified for the same transformation with the aryl iodides (Scheme 2), using equimolar amounts of *p*-bromoanisole and thiophenol as test substrates, though with a Pd loading of 5 mol %.

As no conversion of the aryl bromide was observed using these conditions (entry 1, Table 1), higher boiling solvents other than DME were tested in order to increase the reaction temperature. Neither the use of diglyme, toluene, benzotrifluoride, nor dioxane led to any conversion of the starting material at 100 °C over a period of 18 h (see the Supporting Information). With anisole as the solvent, we observed a small reactivity leading to a 25% conversion at 100 °C (entry 2) and a 3:1 selectivity for the thioester **A** over the direct coupling product **B**. After heating to 120 °C, diglyme led to the direct coupling product, whereas a better selectivity of again 3:1 for the thioester was observed with anisole as the solvent (entries 3 and 4).

Table 1. Selected Entries from the Optimization Studies for the Pd-Catalyzed Thiocarbonylation of Aryl Bromides

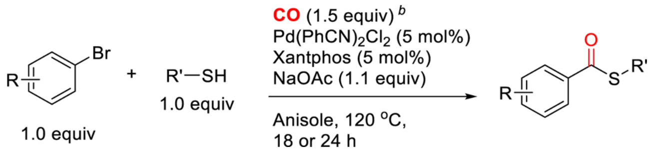


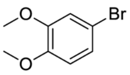
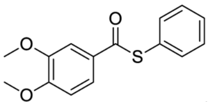
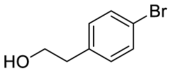
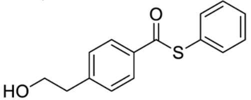
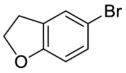
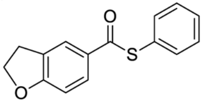
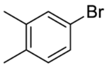
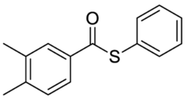
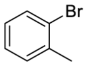
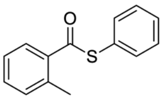
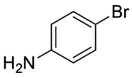
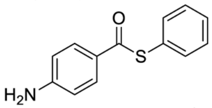
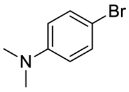
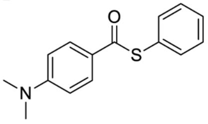
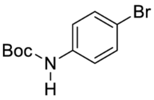
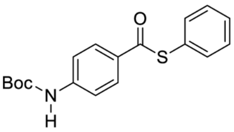
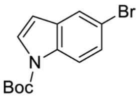
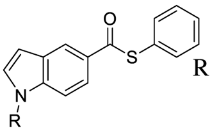
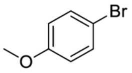
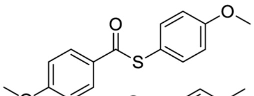
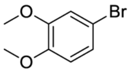
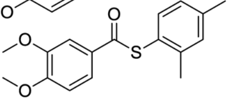
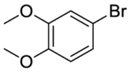
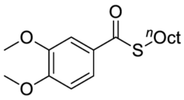
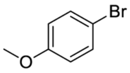
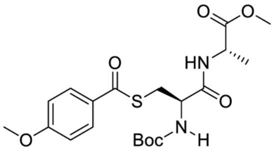
entry	solvent	ligand	[Pd]	conv (%) (yield, %)	A:B ratio
1[c]	DME	DPEphos	$Pd(OAc)_2$	0	
2[d]	anisole	DPEphos	$Pd(OAc)_2$	25 (19)	3:1
3	diglyme	DPEphos	$Pd(OAc)_2$	33	0:1
4	anisole	DPEphos	$Pd(OAc)_2$	55	3:1
5	anisole	Xantphos	$Pd(OAc)_2$	65 (46)	4:1
6	anisole	Xantphos[e]	$Pd(OAc)_2$	>95 (79)	4:1
7	anisole	Xantphos	$Pd(PhCN)_2Cl_2$	>95 (90)	9:1
8[f]	anisole	Xantphos	$Pd(PhCN)_2Cl_2$	>95 (87)	9:1
9[g]	anisole	Xantphos	$Pd(PhCN)_2Cl_2$	58 (58)	1:0
10[d]	anisole	Xantphos	$Pd(PhCN)_2Cl_2$	25 (25)	1:0
11	anisole	Xantphos	$Pd(PhCN)_2Cl_2$[h]	65 (65)	1:0
12	anisole	Xantphos	$Pd(PhCN)_2Cl_2$[i]	80% (64%)	7:1
13[f]	anisole	Xantphos	$Pd(PhCN)_2Cl_2$[j]	>95 (81%)	5:1

[a] Chamber 1: aryl bromide (0.25 mmol), thiol (0.25 mmol), [Pd] (13 μmol), ligand (13 μmol), NaOAc (0.28 mmol), solvent (1.0 mL). [b] Chamber 2: 9-methylfluorene-9-carbonyl chloride (COgen) (0.38 mmol), $Pd(dba)_2$ (13 μmol), $P(^tBu)_3 \cdot HBF_4$ (13 μmol), Cy_2NMe (0.63 mmol), solvent (1.5 mL). [c] The reaction was performed at 85 °C. [d] Reaction performed at 100 °C. [e] Xantphos (25 μmol). [f] Chamber 1: aryl bromide (0.50 mmol), thiol (0.50 mmol), $Pd(PhCN)_2Cl_2$ (25 μmol), Xantphos (25 μmol), NaOAc (0.55 mmol), anisole (2.0 mL). Chamber 2: 1.5 equiv of 9-methylfluorene-9-carbonyl chloride (COgen). [g] The reaction was performed at 110 °C. [h] $PdCl_2(PhCN)_2$ (5.0 μmol), Xantphos (5.0 μmol). [i] Aryl bromide (2.50 mmol), thiol (2.50 mmol), [Pd] (25 μmol), Xantphos (25 μmol), NaOAc (2.75 mmol), anisole (10.0 mL). Chamber 2: 9-methylfluorene-9-carbonyl chloride (COgen) (3.75 mmol), $Pd(dba)_2$ (38 μmol), $P(^tBu)_3 \cdot HBF_4$ (38 μmol), Cy_2NMe (5.63 mmol), anisole (15 mL). [j] Reaction set up without using a glovebox.

A ligand screening was then undertaken, whereby 12 bidentate and 5 monodentate ligands were examined (see the Supporting Information). The reaction proved to be particularly sensitive to the ligand choice, as the only two leading to any conversion of the starting material were DPEphos and Xantphos (entries 4 and 5). Notably, the latter led to a slightly better conversion and selectivity. Xantphos has previously been shown by Buchwald to be an excellent ligand for the Pd-catalyzed aminocarbonylations of aryl bromides under low CO pressure. The exact reasons for the high efficiency for this reaction with Xantphos as a ligand are still not clear, but it appears that the Pd complexes bearing this bidentate ligand can undergo facile interconverion between the *cis*- and *trans*-configurations.[22] We have also later observed the usefulness of

Table 2. Pd-Catalyzed Thiocarbonylation of Electron-Rich Aryl Bromides

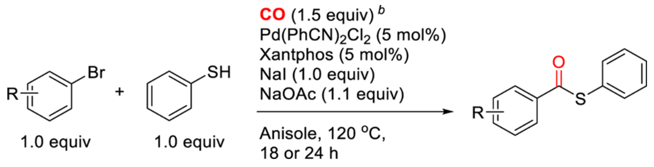


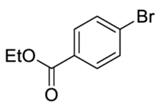
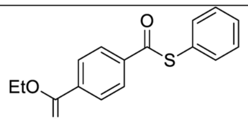
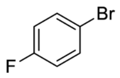
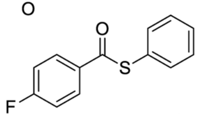
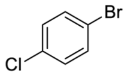
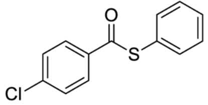
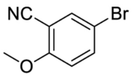
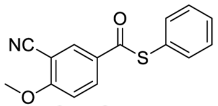
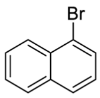
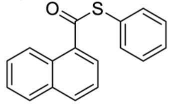
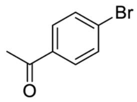
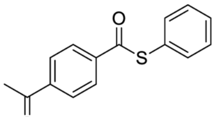
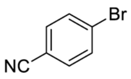
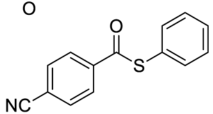
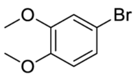
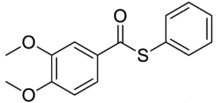
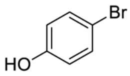
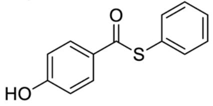
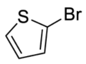
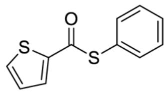
Entry	Substrate	Time [h]	Product	Yield
1		18		81%
2		24		75%
3		18		79%
4		18		98%
5		18		20%
6		24		66%
7		24		78%
8		18		49%
9		18	 R = Boc R = H	27% 48%
10		24		80%
11		18		76%
12		18		88%
13		18		93%

---

[a] Chamber 1: aryl bromide (0.50 mmol), thiol (0.50 mmol), $Pd(PhCN)_2Cl_2$ (25 μmol), Xantphos (25 μmol), NaOAc (0.55 mmol), anisole (2.0 mL). [b] Chamber 2: 9-methylfluorene-9-carbonyl chloride (COgen) (0.75 mmol), $Pd(dba)_2$ (25 μmol), $P(^tBu)_3 \cdot HBF_4$ (25 μmol), Cy_2NMe (1.13 mmol), anisole (3 mL).

Table 3. Substrates Requiring Addition of NaI in the Pd-Catalyzed Thiocarbonylation of Aryl Bromides



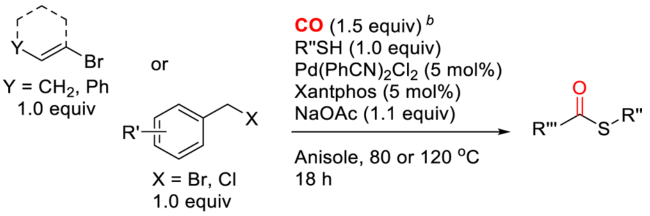
Entry	Substrate	Time [h]	Product	Yield
1		18		74%
2		18		80%
3		18		75%
4		18		70%
5		18		62%
6		18		45%
7		24		26%
8		18		87%
9		24		80%
10		18		75%

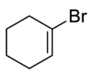
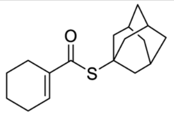
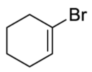
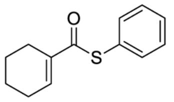
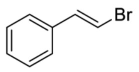
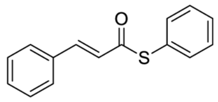
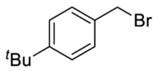
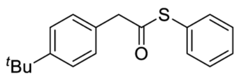
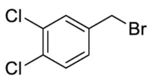
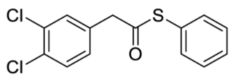
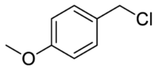
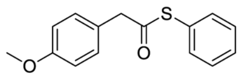
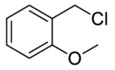
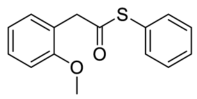
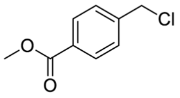
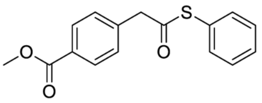
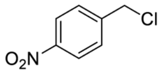
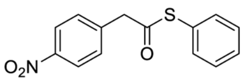
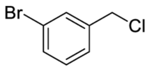
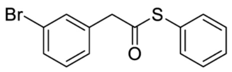
[a] Chamber 1: aryl bromide (0.50 mmol), thiol (0.50 mmol), $Pd(PhCN)_2Cl_2$ (25 μmol), Xantphos (25 μmol), NaOAc (0.55 mmol), NaI (0.50 mmol), anisole (2.0 mL). [b] Chamber 2: 9-methylfluorene-9-carbonyl chloride (COgen) (0.75 mmol), $Pd(dba)_2$ (25 μmol), $P(^tBu)_3\cdot HBF_4$ (25 μmol), Cy_2NMe (1.13 mmol), anisole (3 mL).

Xantphos in other Pd-catalyzed carbonylation reactions with aryl bromides.[17,20a,b,e]

By increasing the Xantphos/$Pd(OAc)_2$ ratio to 2:1, the yield and selectivity could be further improved compared to the test system, providing full conversion and a 79% yield of thioester **A** (entry 6). After testing a number of other palladium complexes (see the Supporting Information), the use of bis(benzonitrile)-dichloropalladium proved to be the best precatalyst for the reaction, leading again to full conversion of the starting material and a 90% yield of the desired product (entry 7). This yield was not affected by an increased gas pressure when the same reaction was run at twice the scale in the same sized glassware (entry 8). On the other hand, when the reaction temperature was lowered to 110 and 100 °C, the conversion decreased to 58%, and 25%, respectively (entries 9 and 10). Decreasing the catalyst loading to 2 mol % also had a dramatic effect on the yield, which dropped to 65% (entry 11). As these optimization studies were run on a 0.25 mmol scale, an attempt was made on a scale 10 times greater in order to see if the catalyst loading could be decreased without affecting the yield and selectivity, as previously demonstrated for other carbonylation protocols.[20e] Unfortunately, with a catalyst loading of 1 mol % the conversion was not complete after the same reaction time of 18 h (entry 12). For the optimization studies discussed so far,

Table 4. Pd-Catalyzed Thiocarbonylation of Vinyl and Benzyl Bromides and Benzyl Chlorides



Entry	Substrate	Temp [°C]	Product	Yield
1		80		62%
2		120		58%
3[c]		120		38%
4		80		62%
5		120		39%
6		60		48%
7		80		56%
8		120		29%
9		80		37%
10		120		24%
11		80		78%
12		80		66%
13		80		71%
14		80		42%
15		80		49%

[a] Chamber 1: bromide (0.50 mmol), thiol (0.50 mmol), Pd(PhCN)$_2$Cl$_2$ (25 μmol), Xantphos (25 μmol), NaOAc (0.55 mmol), anisole (2.0 mL). [b] Chamber 2: 9-methylfluorene-9-carbonyl chloride (COgen) (0.75 mmol), Pd(dba)$_2$ (25 μmol), P(^{t}Bu)$_3$·HBF$_4$ (25 μmol), Cy$_2$NMe (1.13 mmol), anisole (3 mL). [c] NaI (0.50 mmol) added to chamber 1.

all reactions were set up in a glovebox, whereafter heating was performed in a standard fumehood. When a similar reaction on a 0.5 mmol scale as in entry 8 was set up using standard Schlenk techniques, only a slight drop was observed in the product yield (81% yield, entry 13).

As illustrated in Table 2, the above protocol proved efficient for the thiocarbonylation of a series of electron-rich aryl bromides including substituents in the *meta*- or *para*-position with yields attaining 98%. In contrast to that observed with the aryl iodides,[17] the yield dropped drastically with an aryl bromide possessing an *ortho*-substituent as demonstrated with *o*-tolyl bromide (entry 5), which only performed in a 20% yield. Either a free alcohol or an aniline could be tolerated as shown in entries 2 and 6. The corresponding *N*,*N*-dimethyl derivative provided an increased yield of the thioester (entry 7), whereas with the *N*-Boc-protected derivative, we observed a small drop in efficiency of the carbonylation reaction (entry 8). Longer reaction times improved the yield for both aniline and its *N*,*N*-dimethyl-protected version, probably due to a slow oxidative addition into the Ar−Br bond, with these more electron-rich systems. We never observed any formation of either ester or amide byproducts, which is undoubtedly related to the superior nucleophilicity of the thiols. 5-Bromoindole-1-carboxylate was partially deprotected during the course of the carbonylation reaction but gave a combined yield of 75% for the protected and deprotected indole derivative (entry 9). Four additional thiols were tested with *p*-bromoanisole and *m*,*p*-bromoveratrole. Both the electron-rich *p*-methoxybenzenethiol and 2,4-dimethylbenzenethiol performed well, providing good yields of the thioesters (entries 10 and 11), while *n*-octanethiol and the dipeptide sequence Boc-N-Cys-Ala-OMe provided excellent yields of 88 and 93% of the desired products, respectively (entries 12 and 13).

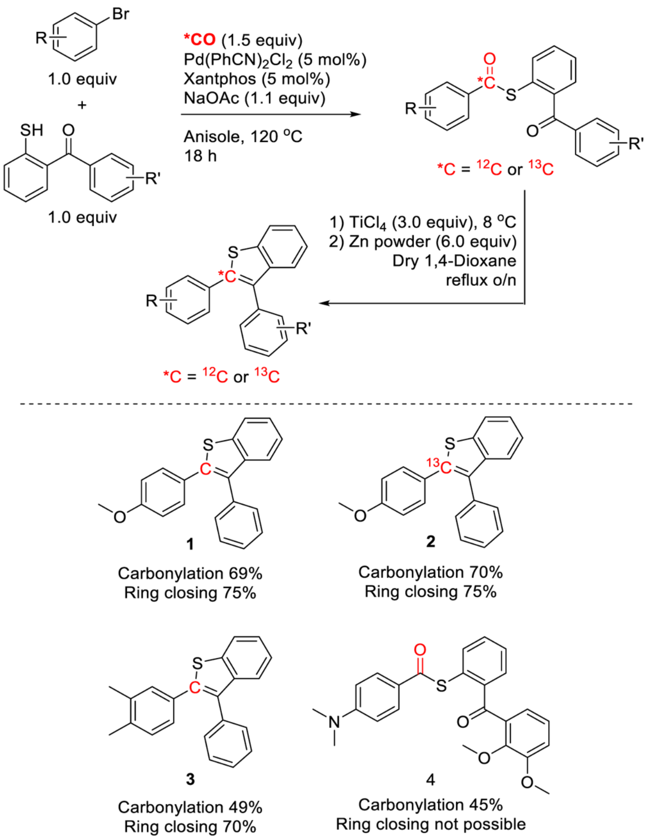
In contrast to the electron-rich aryl bromides, applying this catalytic protocol to the electron-deficient counterparts led to disappointing yields of the desired thioesters and low selectivity with respect to the ratio of thioester vs thioether. These observations may possibly be explained by a mechanism exhibiting a slow CO-insertion step into the Ar−Pd bond.[23] The same effect has been observed in the case of other carbonylation reactions published by us and others.[17,24] To solve this problem, we explored the effect of addition of iodide salts in the carbonylative coupling between ethyl 4-bromobenzoate and thiophenol. These experiments were undertaken on the basis of literature precedence for the beneficial effects of added potassium iodide in the carbonylative Suzuki reaction with aryl bromides.[25] After some experimentation with a few iodide salts, we discovered that the addition of 1.0 equiv of sodium iodide increased the thioester/thioether ratio from 1:1 to 3:1 (see Supporting Information). The two products could easily be separated by column chromatography, and in this way, a 74% yield of the thioester was secured (Table 3, entry 1). We suspect the iodide generates a Pd−I complex replacing the coordinated bromide, thereby facilitating the CO-insertion step in the catalytic cycle. Literature precedence reveals that a Me−Pd−I species performs faster CO insertion than the corresponding bromide analogue.[26] Another possibility could be in situ acid iodide or bromide formation, but according to the work by Quesnel et al.,[27] these species do not form as readily as the corresponding acid chlorides. Furthermore, Xantphos proved to be a less efficient ligand for this transformation. We also attempted to influence the selectivity and thereby the reaction yield by decreasing the temperature to 100 °C. This had a slight effect on the yield, which improved from 50% at 120 °C to 61% at the lower temperature, but the effect was not as pronounced as the addition of sodium iodide to the reaction.

The improved procedure afforded the thioesters from the corresponding aryl bromides in yields up to 87% (Table 3); especially those for the electron-poor aryl bromides could be improved this way. *Para*-substituted haloaryl bromides performed well in the reaction (entry 2 and 3), as did the free *p*-bromophenol (entry 9). Not surprisingly, it turned out to be more difficult to control the selectivity with the aryl bromides carrying more electron-withdrawing groups such as *p*-bromoacetophenone and *p*-bromobenzonitrile, which led to a 45 and 26% yield, respectively (entries 6 and 7). *m*,*p*-Bromoveratrole led to a slightly better yield when NaI was applied to the reaction mixture compared to the reaction without NaI (entry 8, Table 3 compared to entry 1, Table 2).

It was possible to expand the scope of this carbonylation reaction to include vinyl and benzyl bromides as well as benzyl chlorides (Table 4) using the same conditions as for the aryl bromides. However, the yields were in general rather low, and the corresponding thioethers were seen as the major product in most of these reactions. In order to avoid the thioether formation, we examined the effect of decreasing the temperature from 120 °C to 80 or even 60 °C for *p*-*tert*-butylbenzyl bromide (entries 6−8). In general, it turned out to be possible to slow down the rate of the competing side reaction compared to the carbonylation reaction at the lower reaction temperature, except in one (entry 3). The coupling between 1-bromocyclohexene[28] and 1-adamentanethiol afforded the thioester in almost the same yield at 80 and 120 °C (entries 1 and 2), whereas the decrease in the reaction temperature was more influential for the reaction between *β*-bromostyrene and thiophenol, providing a 60% higher yield of the desired product (entries 4 and 5). Not surprisingly, lowering the reaction temperature for the benzyl bromides provided more useful yields of the thioester as illustrated with *p*-*tert*-butylbenzyl bromide (entries 6−8) and 3,4-dichlorobenzyl bromide (entries 9 and 10). At 120 °C, the products from direct coupling were observed as the major compound, most likely by nucleophilic substitution, while the conversion of starting material was less than complete at 60 °C (entry 6). The best carbonylative couplings with these conditions were observed at 80 °C. Hence, for the benzyl chlorides, this same reaction temperature was chosen affording the corresponding thioesters in yields up to 78% (entries 11−15).

Finally, this methodology was applied for the synthesis of benzothiophenes, whereby the formed thioesters were ring closed via a McMurry coupling (Scheme 3). There is literature precedence for the construction of dithienothiophenes from benzothieno[2,3-*b*]thiophene structures, but the reaction has to

Scheme 3. Synthesis and ^{13}C-Isotope Labeling of Benzothiophene via a Sequential Pd-Catalyzed Thiocarbonylation and Subsequent McMurry Coupling



our knowledge never before been performed with *S*-(2-benzoylphenyl) benzothioates.[29] By applying 2- mercaptobenzophenones[30] as nucleophiles in the thiocarbonylation, it was possible to generate the *S*-(2-benzoylphenyl) benzothioate structures **1**−**3** in yields from 45 to 70% by refluxing the prepared thioester with $TiCl_4$ and Zn powder in dry 1,4-dioxane. As illustrated for the synthesis of compound **2**, selective ^{13}C-isotope labeling proved also feasible. Only in the case of thioester **4** did the cyclization fail.

CONCLUSION

In conclusion, we have identified suitable catalytic reaction conditions for promoting the thiocarbonylation of aryl, vinyl, and benzyl bromides as well as benzyl chlorides by applying ex situ generated CO in a two-chamber reactor. Both electron-rich and electron-poor aryl bromides performed well in the reaction, including a couple of heterocyclic bromides.

A catalytic system consisting of Xantphos/bis(benzonitrile) dichloropalladium proved to be the most efficient for the reaction in combination with NaOAc as the base and anisole as the solvent. Screenings demonstrated that the reaction was very ligand selective, but also that the choice of solvent proved highly influential for the efficiency of the coupling.

Finally benzothiophenes could be constructed and selectively ^{13}C-labeled when applying 1-mercaptobenzophenones as nucleophiles in this carbonylation protocol, followed by a McMurry coupling for the ring closure. Because of their versatility as building blocks thioesters are well suited for parallel synthesis of different carboxylic acid derivatives. Installation of the carbonyl group can therefore be performed using the presented procedure, which allows for an easy route to a number of ^{13}C-isotope labeled compounds.

EXPERIMENTAL SECTION

General Methods. Dry solvents were prepared according to standard literature procedures.[31] All other chemicals were used as received from the suppliers unless mentioned otherwise. Starting materials were made according to literature procedures. Flash column chromatography was performed on silica gel 60 (230−400 mesh). ^{1}H and proton-decoupled ^{13}C {^{1}H} NMR spectra were recorded at 400 and 100 MHz. Chemical shifts are reported in ppm downfield to TMS (δ = 0) and referenced to the solvent residual peak,[32] using the following peak pattern abbreviations: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; pent, pentet; sext, sextet; sept, septet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; ddd, doublet of doublet of doublets; ddt, doublet of doublet of triplets, and td, triplet of doublets. HRMS was recorded on a LC TOF (ES).

Equipment Used for the Thiocarbonylation. The thiocarbonylations were performed in a two-chamber reaction vessel with a total volume of 20 mL, using 9-methylfluorene-9-carbonyl chloride as the source of carbon monoxide. The two chambers were loaded in an argon filled glovebox. Chamber 1 was loaded with the reactants for the thiocarbonylation, all thiols were injected into chamber 1 outside the glovebox prior to heating. Chamber 2 was loaded with 1.5 equiv of 9-methylfluorene-9-carbonyl chloride, $Pd(dba)_2$ (3.3 mol %), $P(^tBu)_3\cdot HBF_4$ (3.3 mol %), Anisole and Cy_2NMe (1.13 mmol). The chambers were sealed with a screw cap, 2 mm stabilizing PTFE disc and a 2 mm thick PTFE-lined silicone disc before taking the two chamber vessel out of the glovebox and heating at 120 °C. The glass equipment should be examined for surface damages before use. The equipment should not be operated above 60 psi, and gas release should only take place behind a shield.

General Procedures for the Thiocarbonylation. *Thiocarbonylation Conditions. Chamber 1.* Aryl bromide, allyl bromide, benzyl bromide, or benzyl chloride (0.50 mmol), $Pd(PhCN)_2Cl_2$ (9.6 mg, 25 μmol), Xantphos (14.5 mg, 25 μmol), and NaOAc (45.1 mg, 0.55 mmol) were dissolved in anisole (2.0 mL). In case of the thiol being a solid, thiol (0.5 mmol) was added before sealing of the glassware. Chamber 2: 1.5 equiv of CO was generated in chamber 2. The glassware was then removed from the glovebox, and the thiol (0.50 mmol) was injected into chamber 1 before mixing at 120 °C. After 18 or 24 h, the solvent was removed from chamber 1 in vacuo, and the desired compound was purified by flash chromatography on silica gel using a pentane/CH_2Cl_2 eluent system.

Chamber 2. 1.5 equiv of CO: 9-methylfluorene-9-carbonyl chloride (182 mg, 0.75 mmol), $Pd(dba)_2$ (14.1 mg, 25 μmol), and $P(^tBu)_3\cdot HBF_4$ (7.5 mg, 25 μmol) were dissolved in anisole (3.0 mL). Cy_2NMe (241 μL, 1.13 mmol) was added before the glassware was sealed.

*S-Phenyl 4-Methoxybenzothioate (**A**).*[14] The title compound was isolated as colorless crystals (106 mg, 0.44 mmol, 87%): mp 92.5−93.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, J = 9.2 Hz, 2H), 7.54−7.44 (m, 5H), 6.97 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.5, 164.0, 135.2, 129.7, 129.4, 129.3, 129.1, 127.6, 113.9, 55.5; HRMS (ESI) m/z calcd for $C_{14}H_{12}O_2S$ [M + H^+] 245.0631, found 245.0632.

S-Phenyl 3,4-Dimethoxybenzothioate (Table 2, Entry 1).[33] The title compound was isolated as colorless crystals (111 mg, 0.41 mmol, 81%): mp 110.9−112.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H), 7.53−7.44 (m, 6H), 6.92 (d, J = 8.4 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.7, 153.7, 149.0, 135.1, 129.5, 129.4, 129.2, 127.6, 122.0, 110.3, 109.7, 56.1, 56.0; HRMS (ESI) m/z calcd for $C_{15}H_{14}O_3S$ [M + Na^+] 297.0556, found 297.0554.

S-Phenyl 4-(2-Hydroxyethyl)benzothioate (Table 2, Entry 2). The reaction time was 24 h for the title compound, which was isolated as colorless crystals (97 mg, 0.38 mmol, 75%): mp 66.2−67.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (d, J = (7.9 Hz, 2H), 7.53−7.44 (m, 5H), 7.34 (d, J = 7.2 Hz, 2H), 3.87 (t, J = 6.5 Hz, 2H), 2.92 (t, J = 6.6 Hz, 2H), 1.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.9, 145.3, 135.2, 135.0, 129.6, 129.5, 129.3, 127.8, 127.5, 65.2, 39.2; HRMS (ESI) m/z calcd for $C_{15}H_{14}O_2S$ [M + H^+] 259.0787, found 259.0788.

S-Phenyl 2,3-Dihydrobenzofuran-5-carbothioate (Table 2, Entry 3). The title compound was isolated as colorless crystals (101 mg, 0.40 mmol, 79%): mp 118.5−120.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92−7.89 (m, 2H), 7.54−7.44 (m, 5H), 6.84 (d, J = 8.3 Hz, 2H), 4.66 (t, J = 8.7 Hz, 2H), 3.25 (t, J = 8.7, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.5, 165.0, 135.3, 129.7, 129.5, 129.4, 129.2, 128.0, 127.9, 124.8, 109.4, 72.4, 29.1; HRMS (ESI) m/z calcd for $C_{15}H_{12}O_2S$ [M + H^+] 257.0631, found 257.0630.

S-Phenyl 3,4-Dimethylbenzothioate (Table 2, Entry 4). The title compound was isolated as colorless crystals (119 mg, 0.49 mmol, 98%): mp 88.3−89.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81−7.78 (m, 2H), 7.55−7.51 (m, 2H), 7.49−7.43 (m, 3H), 7.23 (d, J = 7.8 Hz, 2H), 2.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 190.1, 143.6, 137.5, 135.4, 134.8, 130.3, 129.7, 129.5, 128.8, 128.0, 125.5. 20.4, 20.1; HRMS (ESI) m/z calcd for $C_{15}H_{14}OS$ [M + H^+] 243.0838, found 243.0838.

S-Phenyl 2-Methylbenzothioate (Table 2, Entry 5).[17] The title compound was isolated as colorless crystals (22 mg, 0.098 mmol, 20%): mp 45.0−46.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J = 7.6 Hz, J = 0.8 Hz, 1H), 7.55−7.41 (m, 6H), 7.32 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.1, 137.4, 136.8, 134.9, 132.0, 131.7, 129.4, 129.2, 128.6, 128.2, 125.8, 20.8; HRMS (ESI) m/z calcd for $C_{14}H_{12}OS$ [M + H^+] 229.0682, found 229.0680.

S-Phenyl 4-Aminobenzothioate (Table 2, Entry 6). The reaction time was 24 h for the title compound, which was isolated as colorless crystals (76 mg, 0.33 mmol, 66%): mp 157.4−158.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.87 (d, J = 8.6 Hz, 2H), 7.53−7.50 (m, 2H), 7.46−7.43 (m, 3H), 6.65 (d, J = 8.6 Hz, 2H), 4.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.4, 152.0, 135.6, 130.3, 129.5, 129.4, 128.4, 126.9, 114.2; HRMS (ESI) m/z calcd $C_{13}H_{12}NOS$ [M + H^+] 230.0634, found 230.0636.

S-Phenyl 4-(Dimethylamino)benzothioate (Table 2, Entry 7).[34] The reaction time was 24 h for the title compound, which was isolated as colorless crystals (100 mg, 0.39 mmol, 78%): mp 191.9−193.0 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.94 (d, *J* = 9.1 Hz, 2H), 7.54−7.51 (m, 2H), 7.46−7.42 (m, 3H), 6.67 (d, *J* = 9.1 Hz, 2H), 3.07 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 188.0, 154.2, 135.6, 130.0, 129.3, 128.7, 124.3, 111.1, 40.4; HRMS (ESI) *m/z* calcd C$_{15}$H$_{15}$NOS [M + H$^+$] 258.0947, found 258.0947.

S-Phenyl 4-((tert-Butoxycarbonyl)amino)benzothioate (Table 2, Entry 8). The title compound was isolated as colorless crystals (81 mg, 0.25 mmol, 49%): mp 198.3−199.6 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.98 (d, *J* = 8.6 Hz, 2H), 7.53−7.44 (m, 7H), 6.74 (s, 1H), 3.32 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 188.9, 152.2, 135.3, 131.1, 129.5, 129.3, 129.1, 127.7, 117.7, 81.6, 28.4; HRMS (ESI) *m/z* calcd for C$_{18}$H$_{19}$NO$_3$S [M + H$^+$] 330.1158, found 330.1161.

tert-Butyl 5-((Phenylthio)carbonyl)indole-1-carboxylate (Table 2, Entry 9). The reaction yielded the carbonylation products with and without the Boc protection group. The title compound was isolated as colorless solid (48 mg, 0.14 mmol, 27%): mp 97.8−99.8 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.31 (d, *J* = 1.9 Hz, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 8.01 (dd, *J* = 8.7 Hz, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 3.7 Hz, 1H), 7.57−7.54 (m, 2H), 7.50−7.45 (m, 3H), 6.69 (d, *J* = 3.7 Hz, 1H), 1.70 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 189.9, 149.4, 135.3, 131.5, 130.6, 129.5, 129.3, 127.9, 127.7, 123.7, 121.3, 115.3, 108.0, 84.7, 28.3; HRMS (ESI) *m/z* calcd for C$_{20}$H$_{19}$NO$_3$S [M + H$^+$] 354.1158, found 354.1163. The compound without Boc protection (*S*-phenyl indole-5-carbothioate) was isolated as colorless crystals (61 mg, 0.24 mmol, 48%): mp 152.5−154.2 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.57 (br. s, 1H), 8.48 (s, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.60−7.57 (m, 2H), 7.49−7.40 (m, 4H), 7.26−7.22 (m, 1H), 6.71−6.70 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 190.5, 139.0, 135.4, 129.4, 129.3, 129.1, 128.3, 127.6, 126.3, 122.1, 121.6, 111.3, 104.4; HRMS (ESI) *m/z* calcd for C$_{15}$H$_{11}$NOS [M + H$^+$] 254.0635, found 254.0634.

S-(4-Methoxyphenyl) 4-Methoxybenzothioate (Table 2, Entry 10).[35] The reaction time was 24 h for the title compound, which was isolated as colorless crystals (109 mg, 0.40 mmol, 80%): mp 138.0−138.9 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.01 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 189.5, 163.9, 160.7, 136.7, 129.7, 129.4, 118.2, 114.9, 113.9, 55.5, 55.4; HRMS (ESI) *m/z* calcd for C$_{15}$H$_{14}$O$_3$S [M + Na$^+$] 297.0556, found 297.0552.

S-(2,4-Dimethylphenyl) 3,4-Dimethoxybenzothioate (Table 2, Entry 11). The title compound was isolated as a colorless solid (116 mg, 0.38 mmol, 76%): mp 113.2−115.0 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.77 (dd, *J* = 8.4 Hz, *J* = 2.1 Hz, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.20−7.15 (m, 1H), 7.10−7.03 (m, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 188.6, 153.6, 149.0, 142.4, 140.3, 136.3, 131.7, 129.8, 127.5, 123.6, 122.0, 110.3, 109.7, 56.1, 56.0, 21.3, 20.8; HRMS (ESI) *m/z* calcd for C$_{17}$H$_{18}$O$_3$S [M + H$^+$] 303.1050, found 303.1052.

S-Octyl 3,4-Dimethoxybenzothioate (Table 2, Entry 12). The title compound was isolated as a colorless solid (137 mg, 0.44 mmol, 88%): mp 27.8−28.3 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.61 (dd, *J* = 8.4 Hz, *J* = 2.1 Hz, 1H), 7.44 (d, *J* = 2.1 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 6H), 3.01 (t, *J* = 7.4 Hz, 2H), 1.62 (pent, *J* = 7.0 Hz 1H), 1.45−1.17 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 190.7, 153.3, 148.9, 130.3, 121.6, 110.2, 109.4, 56.0, 31.8, 29.7, 29.20, 29.17, 29.1, 29.0, 22.7, 14.1; HRMS (ESI) *m/z* calcd for C$_{17}$H$_{26}$O$_3$S [M + H$^+$] 311.1675, found 311.1677.

(S)-Methyl 2-((R)-2-((tert-Butoxycarbonyl)amino)-3-((4-methoxybenzoyl)thio)propanamido)propanoate (Table 2, Entry 13).[17] The title compound was isolated as a colorless solid (205 mg, 0.47 mmol, 93%): mp 113.3−115.9 °C;; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.93(d, *J* = 9.2 Hz, 2H), 7.05 (br s, 1H), 6.90 (d, *J* = 9.2 Hz, 2H), 5.45 (br. d, *J* = 7.2 Hz, 1H), 4.55 (pent, *J* = 7.2 Hz, 1H), 4.38 (br. s, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.52 (dd, *J* = 14.4 Hz, *J* = 4.4 Hz, 1H), 3.36 (dd, *J* = 14.4 Hz, *J* = 8.0 Hz, 1H), 1.42 (d, *J* = 11.6 Hz, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 190.7, 172.9, 169.9, 169.6, 164.1, 129.7, 129.3, 113.8, 80.4, 55.5, 55.0, 52.4, 48.2, 30.9, 28.2, 18.3; HRMS (ESI) *m/z* calcd for C$_{20}$H$_{28}$N$_2$O$_7$S [M + H$^+$] 441.1690, found 441.1693.

S-(1s,3s)-Adamantan-1-yl Cyclohex-1-enecarbothioate (Table 4, Entries 1 and 2). The reaction was performed at 80 °C. The title compound was isolated as a colorless solid (85 mg, 0.31 mmol, 62%): mp 67.2−69.0 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 6.91 (s, 1H), 2.27−3.04 (m, 13H), 1.80 (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 194.0, 139.6, 137.4, 50.3, 42.2, 36.6, 30.0, 25.9, 24.0, 22.2, 21.7; HRMS (ESI) *m/z* calcd for C$_{17}$H$_{24}$OS [M + H$^+$] 277.1621, found 277.1621.

(E)-S-Phenyl 3-Phenylprop-2-enethioate (Table 4, Entries 4 and 5).[36] The reaction was performed at 80 °C. The title compound was isolated as a colorless solid (74 mg, 0.31 mmol, 62%): mp 75.5−77.2 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.71 (d, *J* = 15.8 Hz, 1H), 7.59−7.41 (m, 10H), 6.82 (d, *J* = 15.7 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 188.0, 141.6, 134.7, 134.1, 130.9, 129.6, 129.3, 129.1, 128.6, 127.8, 124.3; HRMS (ESI) *m/z* calcd for C$_{15}$H$_{12}$OS [M + H$^+$] 241.0687, found 241.0682.

S-Phenyl 2-(4-tert-Butylphenyl)ethanethioate (Table 4, Entries 6−8). The reaction was performed at 80 °C. The title compound was isolated as a colorless oil (80 mg, 0.28 mmol, 56%): ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.42 (br s, 7H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 2H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 195.5, 150.5, 134.5, 130.3, 129.44, 129.40, 129.2, 128.0, 125.8, 49.7, 34.6, 31.5; HRMS (ESI) *m/z* calcd for C$_{18}$H$_{20}$OS [M + H$^+$] 285.1308, found 285.1307.

S-Phenyl 2-(3,4-Dichlorophenyl)ethanethioate (Table 4, Entries 9 and 10). The reaction was performed at 80 °C. The title compound was isolated as a colorless oil (55 mg, 0.19 mmol, 37%): ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.43−7.40 (m, 7H), 7.16 (dd, *J* = 8.2 Hz, *J* = 1.7 Hz, 1H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 194.4, 134.5, 133.4, 132.8, 132.0, 131.6, 130.7, 129.8, 129.4, 129.1, 127.3, 48.9; HRMS (ESI) *m/z* calcd for C$_{14}$H$_{10}$Cl$_2$OS [M + H$^+$] 296.9902, found 296.9906.

S-Phenyl 2-(4-Methoxyphenyl)ethanethioate (Table 4, Entry 11). The reaction was performed at 80 °C. The title compound was isolated as a colorless oil (100 mg, 0.39 mmol, 78%): ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.42 (m, 5H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 195.9, 159.2, 134.5, 130.9, 129.4, 129.2, 128.0, 55.3, 49.3; HRMS (ESI) *m/z* calcd for C$_{15}$H$_{14}$O$_2$S [M + H$^+$] 259.0787, found 259.0786.

S-Phenyl 2-(2-Methoxyphenyl)ethanethioate (Table 4, Entry 12). The reaction was performed at 80 °C. The title compound was isolated as a colorless oil (85 mg, 0.33 mmol, 66%): ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.43−7.27 (m, 7H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.99 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 196.0, 157.9, 134.6, 131.6, 129.3, 129.2, 129.1, 128.4, 122.3, 120.7, 110.7, 55.6, 44.9; HRMS (ESI) *m/z* calcd for C$_{15}$H$_{14}$O$_2$S [M + H$^+$] 259.0787, found 259.0787.

Methyl 4-(2-Oxo-2-(phenylthio)ethyl)benzoate (Table 4, Entry 13). The reaction was performed at 80 °C. The title compound was isolated as a colorless solid (102 mg, 0.36 mmol, 71%): mp 100.0−101.8 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.03 (d, *J* = 8.2 Hz, 2H), 7.42−7.39 (m, 7H), 3.97 (s, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 194.5, 166.8, 138.4, 134.5, 130.1, 129.75, 129.66, 129.5, 129.3, 127.5, 52.2, 50.0; HRMS (ESI) *m/z* calcd for C$_{16}$H$_{14}$O$_3$S [M + H$^+$] 287.0736, found 287.0737.

S-Phenyl 2-(4-Nitrophenyl)ethanethioate (Table 4, Entry 14). The reaction was performed at 80 °C. The title compound was isolated as a yellow solid (58 mg, 0.21 mmol, 42%): mp 63.4−64.6 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 8.21 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.43−7.38 (m, 5H), 4.03 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 193.9, 147.5, 140.6, 134.5, 130.6, 129.9, 129.4, 127.1, 124.0, 49.5; HRMS (ESI) *m/z* calcd for C$_{14}$H$_{11}$NO$_3$S [M + Na$^+$] 296.0352, found 296.0354.

S-Phenyl 2-(3-Bromophenyl)ethanethioate (Table 4, Entry 15). The reaction was performed at 80 °C. The title compound was isolated as a colorless oil (75 mg, 0.25 mmol, 49%): ^{1}H NMR (400

MHz, $CDCl_3$) δ (ppm) 7.40−7.30 (m, 7H), 7.18−7.10 (m, 2H), 3.79 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.7, 135.5, 134.5, 132.7, 130.8, 130.3, 129.7, 129.3, 128.4, 127.5, 122.8, 49.5; HRMS (ESI) *m/z* calcd for $C_{14}H_{11}BrOS$ [M + H$^+$] 306.9787, found 306.9788.

General Procedure for the Thiocarbonylation with NaI as Additive. Thiocarbonyation Conditions. Chamber 1. Aryl bromide or allyl bromide (0.50 mmol), $Pd(PhCN)_2Cl_2$ (9.6 mg, 25 μmol), Xantphos (14.5 mg, 25 μmol), NaI (74.9 mg, 0.50 mmol), and NaOAc (45.1 mg, 0.55 mmol) were dissolved in anisole (2.0 mL). In case of the thiol being a solid, thiol (0.5 mmol) was added before sealing of the glassware. Chamber 2: 1.5 equiv of CO were generated in chamber 2. The glassware was then removed from the glovebox, and the thiol (0.50 mmol) was injected into chamber 1 before mixing at 120 °C. After 18 or 24 h, the solvent was removed from chamber 1 in vacuo, and the desired compound was purified by flash chromatography on silica gel using a pentane/CH_2Cl_2 eluent system.

Chamber 2. 1.5 equiv of CO: 9-methylfluorene-9-carbonyl chloride (182 mg, 0.75 mmol), $Pd(dba)_2$ (14.1 mg, 25 μmol), and $P(^tBu)_3\cdot HBF_4$ (7.5 mg, 25 μmol) were dissolved in anisole (3.0 mL). Cy_2NMe (241 μL, 1.13 mmol) was added before the glassware was sealed.

Ethyl 4-((Phenylthio)carbonyl)benzoate (Table 3, Entry 1).[17] The title compound was isolated as colorless crystals (106 mg, 0.37 mmol, 74%): mp 65.3−66.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, J = 8.8 Hz, 2H), 8.07 (d, J = 8.8 Hz, 2H), 7.54−7.46 (m, 5H), 4.42 (q, J = 7.2 Hz, 2H), 1.42 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.7, 165.6, 139.8, 135.0, 134.8, 129.9, 129.8, 129.4, 127.4, 126.8, 61.5, 14.3; HRMS (ESI) *m/z* calcd for $C_{16}H_{14}O_3S$ [M + H$^+$] 287.0736, found 287.0737.

S-Phenyl 4-Fluorobenzothioate (Table 3, Entry 2). The title compound was isolated as colorless crystals (93 mg, 0.40 mmol, 80%): mp 59.2−60.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.07 (dd, J = 8.5 Hz, J = 5.3 Hz, 2H), 7.62−7.37 (m, 5H), 7.17 (t, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.8, 166.2, (d, J_{C-F} = 255 Hz), 135.2, 133.1 (d, J_{C-F} = 3.0 Hz), 130.2 (d, J_{C-F} = 9.4 Hz) 129.7, 129.4, 127.2, 116.0 (d, J_{C-F} = 22.1 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) −104.09; HRMS (ESI) *m/z* calcd for $C_{13}H_9FOS$ [M + H$^+$] 233.0431, found 233.0430.

S-Phenyl 4-Chlorobenzothioate (Table 3, Entry 3).[14] The title compound was isolated as colorless crystals (93 mg, 0.37 mmol, 75%): mp 81.2−82.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, J = 8.8 Hz, 2H), 7.53−7.46 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.0, 140.1, 135.04, 134.96, 129.7, 129.3, 129.1, 128.8, 126.9; HRMS (ESI) *m/z* calcd for $C_{13}H_9ClOS$ [M + H$^+$] 249.0135, found 249.0141.

S-Phenyl 3-Cyano-4-methoxybenzothioate (Table 3, Entry 4). The title compound was isolated as colorless crystals (94 mg, 0.35 mmol, 70%): mp 113.9−115.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.24 (d, J = 2.3 Hz, 1H), 8.20 (dd, J = 8.8 Hz, J = 2.3 Hz, 1H), 7.51−7.44 (m, 5H), 7.06 (d, J = 8.9 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 187.3, 164.7, 135.1, 133.9, 133.5, 129.8, 129.6, 129.4, 126.6, 115.3, 111.5, 102.5, 56.8; HRMS (ESI) *m/z* calcd for $C_{15}H_{11}NO_2S$ [M + H$^+$] 270.0583, found 270.0585.

S-Phenyl Naphthalene-1-carbothioate (Table 3, Entry 5).[14] The title compound was isolated as colorless crystals (83 mg, 0.31 mmol, 63%): mp 58.8−59.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.55 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.63−7.50 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 192.2, 134.9, 134.7, 133.8, 133.3, 129.6, 129.4, 129.3, 128.4, 128.3, 128.1, 128.0, 126.7, 125.3, 124.5; HRMS (ESI) *m/z* calcd for $C_{17}H_{12}OS$ [M + Na$^+$] 287.0501, found 287.0501.

S-Phenyl 4-Acetylbenzothioate (Table 3, Entry 6).[17] The title compound was isolated as colorless crystals (58 mg, 0.23 mmol, 45%): mp 113.2−114.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, J = 8.7 Hz, 2H), 8.05 (d, J = 8.6 Hz, 2H), 7.53−7.46 (m, 5H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.2, 189.6, 140.6, 139.9, 135.0, 129.8 129.4, 128.6, 127.7, 126.8, 26.9; HRMS (ESI) *m/z* calcd for $C_{15}H_{12}O_2S$ [M + H$^+$] 257.0631, found 257.0633.

S-Phenyl 4-Cyanobenzothioate (Table 3, Entry 7).[37] The reaction time for the title compound was 24 h, which was isolated as colorless crystals (31 mg, 0.13 mmol, 26%): mp 134.2−135.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.11 (d, J = 8.6 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 7.54−7.47 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.4, 140.1, 135.2, 133.0, 130.4, 129.8, 126.6, 118.1, 117.2; HRMS (ESI) *m/z* calcd for $C_{14}H_9NOS$ [M + H$^+$] 240.0478, found 240.0473.

S-Phenyl 3,4-Dimethoxybenzothioate (Table 3, Entry 8).[33] The title compound was isolated as colorless crystals (119 mg, 0.43 mmol, 87%): mp 110.9−112.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (dd, J = 8.4 Hz, J = 2.0 Hz, 1H), 7.53−7.44 (m, 6H), 6.92 (d, J = 8.4 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 188.7, 153.7, 149.0, 135.1, 129.5, 129.4, 129.2, 127.6, 122.0, 110.3, 109.7, 56.1, 56.0; HRMS (ESI) *m/z* calcd for $C_{15}H_{14}O_3S$ [M + Na$^+$] 297.0556, found 297.0554.

S-Phenyl 4-Hydroxybenzothioate (Table 3, Entry 9). The reaction time was 24 h for the title compound, which was isolated as colorless crystals (92 mg, 0.40 mmol, 80%): mp 172.8−174.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (d, J = 8.7 Hz, 2H), 7.53−7.44 (m, 5H), 6.87 (d, J = 8.7 Hz, 2H), 5.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 189.3, 160.7, 135.4, 130.2, 129.7, 129.6, 129.4, 127.6, 115.7; HRMS (ESI) *m/z* calcd for $C_{13}H_{10}O_2S$ [M + H$^+$] 231.0474, found 231.0474.

S-Phenyl Thiophene-2-carbothioate (Table 3, Entry 10).[14] The title compound was isolated as yellow crystals (83 mg, 0.37 mmol, 75%): mp 59.4−60.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (dd, J = 4.0 Hz, J = 1.2 Hz, 1H), 7.67 (dd, J = 5.2 Hz, J = 1.2 Hz, 1H), 7.56−7.43 (m, 5H), 7.16 (dd, J = 4.8 Hz, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 182.0, 141.4, 135.0, 133.2, 131.6, 129.6, 129.2, 128.0, 126.9; HRMS (ESI) *m/z* calcd for $C_{11}H_8OS_2$ [M + Na$^+$] 242.9909, found 242.9906.

S-phenyl Cyclohex-1-enecarbothioate (Table 4 entry 3).[38] The title compound was isolated as a colorless oil (41 mg, 0.19 mmol, 38%): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45−7.39 (m, 5H), 7.13 (s, 1H), 2.37−2.25 (m, 4H), 1.73−1.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 190.9, 139.4, 138.4, 135.2, 129.3, 129.2, 128.1, 26.1, 24.3, 22.1, 21.7; HRMS (ESI) *m/z* calcd for $C_{13}H_{14}OS$ [M + H$^+$] 219.0844, found 219.0839.

2-(4-Methoxyphenyl)-3-phenylbenzo[b]thiophene (1). The thiocarbonylation procedure was followed to make *S*-(2-benzoylphenyl) 4-methoxybenzothioate, which was isolated as colorless crystals (120 mg, 0.35 mmol, 69%): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82−7.79 (m, 4H), 7.66 (d, J = 7.6 Hz, 1H), 7.59−7.47 (m, 4H), 7.38 (t, J = 7.6 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.4, 187.6, 164.1, 144.1, 137.6, 137.1, 133.4, 130.6, 130.3, 129.8, 129.2, 129.1, 128.9, 128.4, 126.2, 113.9, 55.6; HRMS (ESI) *m/z* calcd for $C_{21}H_{16}O_3S$ [M + Na$^+$] 371.0712, found 371.0715. *S*-(2-Benzoylphenyl) 4-methoxybenzothioate (116 mg, 0.33 mmol) was dissolved in dry dioxane (35 mL) and cooled to 0 °C, and $TiCl_4$ (110 μL, 1.0 mmol) was added dropwise under an argon atmosphere. After the mixture was stirred at 8 °C for 0.5 h, Zn powder (131 mg, 2.0 mmol) was added, and the reaction mixture was refluxed overnight. The reaction was quenched with water and the product extracted with Et_2O (3 × 20 mL) and dried with Na_2SO_4. The organic solvent was removed under vacuum, and the desired compound was purified by flash chromatography on silica gel using pentane/CH_2Cl_2 as eluent system. The title compound was isolated as yellow crystals (78 mg, 0.25 mmol, 75%): mp 119.4−121.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.45−7.29 (m, 7H), 7.28 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.3, 141.2, 139.6, 138.7, 135.9, 132.5, 130.9, 130.6, 128.8, 127.4, 126.8, 124.5, 124.4, 123.3, 122.1, 114.0, 55.3; HRMS (ESI) *m/z* calcd for $C_{21}H_{16}OS$ [M + H$^+$] 317.1000, found 317.1003.

[^{13}C]-2-(4-Methoxyphenyl)-3-phenylbenzo[b]thiophene (2). The thiocarbonylation procedure was followed to make [^{13}C]-*S*-(2-benzoylphenyl)4-methoxybenzothioate, which was isolated as colorless crystals (123 mg, 0.35 mmol, 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84−7.79 (m, 4H), 7.66 (d, J = 7.6 Hz, 1H), 7.61−7.48 (m, 4H), 7.39 (t, J = 7.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.3, 187.5 (^{13}C), 164.0 (d, J_{C-C} = 1 Hz), 144.1 (d, J_{C-C} = 1 Hz), 137.6, 137.0, 133.3, 130.5, 130.2, 129.8 (d, J_{C-C} = 4 Hz), 129.2, 129.0 (d, J_{C-C} = 65 Hz), 128.9, 128.4,

126.2 (d, $J_{C-C} = 1$ Hz), 113.8 (d, $J_{C-C} = 5$ Hz), 55.5; HRMS (ESI) *m*/*z* calcd for $C_{20}{}^{13}CH_{16}O_3S$ [M + H$^+$] 350.0926, found 350.0929. [^{13}C]-*S*-(2-Benzoylphenyl)4-methoxybenzothioate (123 mg, 0.35 mmol) was subjected to the same conditions as in the previous McMurry coupling. The title compound was isolated as yellow crystals (79 mg, 0.26 mmol, 75%): mp 119.9−121.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, $J = 8.7$ Hz, 1H), 7.60 (d, $J = 8.8$ Hz, 1H), 7.44−7.33 (m, 7H), 7.28 (dd, $J = 4.1$ Hz, $J = 8.7$ Hz, 2H), 6.81 (d, $J = 8.7$ Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.3, 141.2 (d, $J_{C-C} = 4$ Hz), 139.6 (^{13}C), 138.7 (d, $J_{C-C} = 4$ Hz), 135.9 (d, $J_{C-C} = 3$ Hz), 132.4 (d, $J_{C-C} = 71$ Hz), 130.9 (d, $J_{C-C} = 2$ Hz), 130.6 (d, $J_{C-C} = 3$ Hz), 128.8, 127.4, 126.8 (d, $J_{C-C} = 63$ Hz), 124.5, 124.4 (d, $J_{C-C} = 1$ Hz), 123.3 (d, $J_{C-C} = 6$ Hz), 122.1 (d, $J_{C-C} = 2$ Hz), 114.0 (d, $J_{C-C} = 5$ Hz), 55.3; HRMS (ESI) *m*/*z* calcd for $C_{20}{}^{13}CH_{16}OS$ [M + H$^+$] 318.1028, found 318.1025.

2-(4-Methoxyphenyl)-3-phenylbenzo[b]thiophene ***(3)***. The thiocarbonylation procedure was followed to make *S*-(2-benzoylphenyl) 4-methoxybenzothioate, which was isolated as colorless crystals (85 mg, 0.25 mmol, 49%): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 (d, $J = 7.4$ Hz, 2H), 7.66 (d, $J = 7.4$ Hz, 1H), 7.61−7.47 (m, 6H), 7.39 (t, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 7.8$ Hz, 1H), 2.27 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.9, 188.9, 144.1, 143.4, 137.6, 137.2, 137.1, 134.2, 133.4, 130.6, 130.3, 129.9, 129.3, 129.0, 128.6, 128.4, 126.3, 125.3, 20.1, 19.7; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{18}O_2S$ [M + H$^+$] 347.1100, found 347.1102. *S*-(2-Benzoylphenyl) 4-methoxybenzothioate (85 mg, 0.25 mmol) was subjected to the same conditions as in the previous McMurry coupling. The title compound was isolated as yellow crystals (55 mg, 0.18 mmol, 75%): mp 108.2−109.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (d, $J = 8.6$ Hz, 1H), 7.61 (d, $J = 8.8$ Hz, 1H), 7.42−7.33 (m, 7H), 7.18 (s, 1H), 7.03 (q, $J = 7.9$ Hz, 2H), 2.25 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 141.2, 140.0, 138.8, 136.7, 136.5, 136.0, 132.8, 131.8, 130.9, 130.6, 129.8, 128.7, 127.4, 127.1, 124.48, 124.45, 123.3, 122.2, 19.9, 19.6; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{18}S$ [M + H$^+$] 315.1202, found 315.1204.

S-(2-(2,3-Dimethoxybenzoyl)phenyl) 4-(Dimethylamino)-benzothioate ***(4)***. 4-Bromo-*N*,*N*-dimethylaniline (80 mg, 0.40 mmol), (2,3-dimethoxyphenyl)(2-mercaptophenyl)methanone (110 mg, 0.40 mmol), $Pd(PhCN)_2Cl_2$ (7.7 mg, 20 μmol), Xantphos (11.6 mg, 20 μmol), and NaOAc (36.1 mg, 0.44 mmol) were dissolved in anisole (2.0 mL). Chamber 2: 1.5 equiv of CO was generated in chamber 2. The glassware was then removed from the glovebox, and the contents were mixed at 120 °C. After 18 h, the solvent was removed from chamber 1 in vacuo, and the desired compound was purified by flash chromatography on silica gel using a gradient starting from pentane to CH_2Cl_2 as eluent system. The title compound was isolated a yellow oil (mg, 0.23 mmol, 45%): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, $J = 9.1$ Hz, 2H), 7.65 (dd, $J = 9.2$ Hz, $J = 2.9$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.43 (dt, $J = 6.7$ Hz, $J = 1.9$ Hz, 1H), 7.10 (dd, $J = 6.9$ Hz, $J = 2.4$ Hz, 1H), 7.03−6.97 (m, 2H), 6.58 (d, $J = 9.1$ Hz), 3.82 (s, 3H) 3.58 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.2, 186.7, 153.9, 153.0, 148.5, 144.9, 137.5, 134.0, 130.6, 129.8, 129.5, 128.6, 127.2, 123.9, 123.7, 122.3, 115.8, 110.6, 61.4, 56.1, 40.1; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{23}NO_4S$ [M + H$^+$] 422.1421, found 422.1423.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and copies of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra for all coupling products. This material is available free of charge via the Internet at http://pubs.acs.org

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ts@chem.au.dk.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are deeply appreciative of generous financial support from the Danish National Research Foundation (Grant No. DNRF59), the Villum Foundation, the Danish Council for Independent Research: Technology and Production Sciences, the Carlsberg Foundation, and Aarhus University. We thank Mia Nørreskov Burhardt for the complete design of the cover illustration.

■ REFERENCES

(1) Tokuyama, H.; Yokoshima, S.; Yamashita, T.; Fukuyama, T. *Tetrahedron Lett.* **1998**, *39*, 3189.

(2) Mehta, V. P.; Sharma, A.; Van der Eycken, E. *Org. Lett.* **2008**, *10*, 1147.

(3) Os'kina, I. A.; Vlasov, V. M. *Russ. J. Org. Chem.* **2009**, *4*, 523.

(4) Ueda, M.; Seki, K.; Imai, Y. *Synthesis* **1981**, 991.

(5) Azuma, H.; Okano, K.; Tokuyama, H. *Chem. Lett.* **2011**, *40*, 959.

(6) Fukuyama, T.; Lin, S. C.; Li, L. P. *J. Am. Chem. Soc.* **1990**, *112*, 7050.

(7) Kotsuki, H.; Yoshimura, N.; Ushio, Y.; Ohtsuka, T.; Ochi, M. *Chem. Lett.* **1986**, 1003.

(8) Nagashima, E.; Suzuki, K.; Sekiya, M. *Chem. Pharm. Bull.* **1983**, *31*, 3306.

(9) Yousif, N. M.; Pedersen, U.; Yde, B.; Lawesson, S. O. *Tetrahedron* **1984**, *40*, 2663.

(10) Alvarez-Ibarra, C.; Mendoza, M.; Orellana, G.; Quiroga, M. L. *Synthesis* **1989**, 560.

(11) For some recent reviews, see: (a) Wu, X. F.; Neumann, H.; Beller, M. *Chem. Rev.* **2013**, *113*, 1. (b) Odell, L. R.; Larhed, M. *Synlett* **2012**, 685. (c) Wu, W. F.; Neumann, H.; Beller, M. *Chem. Soc. Rev.* **2011**, *40*, 4986. (d) Brennführer, A.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4114. (e) Magano, J.; Dunetz, J. R. *Chem. Rev.* **2011**, *111*, 2177. (f) Grigg, R.; Mutton, S. P. *Tetrahedron* **2010**, *66*, 5515.

(12) (a) Baranano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937. (b) Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205. (c) Fernandez-Rodriguez, M. A.; Shen, Q. L.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 2180. (d) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534. (e) Fernandez-Rodriguez, M. A.; Hartwig, J. F. *J. Org. Chem.* **2009**, *74*, 1663. (f) Alvaro, E.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 7858.

(13) For other Pd-catalyzed thiocarbonylation reactions developed in the Alper group, see: (a) Xiao, W. J.; Alper, H. *J. Org. Chem.* **1997**, *62*, 3422. (b) Xiao, W. J.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **1998**, *63*, 2609. (c) Xiao, W. J.; Alper, H. *J. Org. Chem.* **1998**, *63*, 7939. (d) Xiao, W. J.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **1999**, *64*, 2080. (e) Xiao, W. J.; Alper, H. *J. Org. Chem.* **1999**, *64*, 9646. (f) Xiao, W. J.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **2000**, *65*, 4138. (g) Xiao, W. J.; Alper, H. *J. Org. Chem.* **2001**, *66*, 6229. (h) Xiao, W. J.; Alper, H. *J. Org. Chem.* **2005**, *70*, 1802. (i) Cao, H.; Xiao, W. J.; Alper, H. *Adv. Synth. Catal.* **2006**, *348*, 1807. (j) Li, C. F.; Xiao, W. J.; Alper, H. *J. Org. Chem.* **2009**, *74*, 888.

(14) Cao, H.; McNamee, L.; Alper, H. *J. Org. Chem.* **2008**, *73*, 3530.

(15) Hu, Y. H.; Liu, J.; Lu, Z. X.; Luo, X. C.; Zhang, H.; Lan, Y.; Lei, A. W. *J. Am. Chem. Soc.* **2010**, *132*, 3153.

(16) Recently Oshima and co-workers showed the possibility of using the iron carbonyl complex $[CpFe(CO)_2]_2$ as a CO precursor for Pd-catalyzed thioarylation of a few simple aryl iodides in varying yields. Nakaya, R.; Yorimitsu, H.; Oshima, K. *Chem. Lett.* **2011**, *40*, 904.

(17) Burhardt, M. N.; Taaning, R. H.; Skrydstrup, T. *Org. Lett.* **2013**, *15*, 948.

(18) COgen is commercially available at: www.sigmaaldrich.com and www.sytracks.com.

(19) Hermange, P.; Lindhardt, A. T.; Taaning, R. H.; Bjerglund, K.; Lupp, D.; Skrydstrup, T. *J. Am. Chem. Soc.* **2011**, *133*, 6061.

(20) (a) Neumann, K. T.; Laursen, S. R.; Lindhardt, A. T.; Bang-Andersen, B.; Skrydstrup, T. *Org. Lett.* **2014**, *16*, 2216. (b) Nielsen, D. U.; Lescot, C.; Gøgsig, T. M.; Lindhardt, A. T.; Skrydstrup, T.

Chem.—Eur. J. **2013**, *19*, 17926. (c) Korsager, S.; Nielsen, D. U.; Taaning, R. H.; Lindhardt, A. T.; Skrydstrup, T. *Chem.—Eur. J.* **2013**, *19*, 17687. (d) Ahlburg, A.; Lindhardt, A. T.; Taaning, R. H.; Modvig, A. E.; Skrydstrup, T. *J. Org. Chem.* **2013**, *78*, 10310. (e) Korsager, S.; Nielsen, D. U.; Taaning, R. H.; Skrydstrup, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 9763. (f) Gøgsig, T. M.; Taaning, R. H.; Lindhardt, A. T.; Skrydstrup, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 798. (g) Burhardt, M. N.; Taaning, R.; Nielsen, N. C.; Skrydstrup, T. *J. Org. Chem.* **2012**, *77*, 5357. (h) Gøgsig, T. M.; Nielsen, D. U.; Lindhardt, A. T.; Skrydstrup, T. *Org. Lett.* **2012**, *14*, 2536 and references cited therein.

(21) Lindhardt, A. T.; Simonssen, R.; Taaning, R. H.; Gøgsig, T. M.; Nilsson, G. N.; Stenhagen, G.; Elmore, C. S.; Skrydstrup, T. *J. Labelled Compd. Radiopharm.* **2012**, *55*, 411.

(22) Martinelli, J. R.; Watson, D. A.; Freckmann, D. M. M; Barder, T. E.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 7102 and references cited therein.

(23) Although we propose that the mechanism involves a slow CO insertion step into the Pd−Ar bond, there is the althernative possibility that CO inserts into the Pd−SR bond as well (see ref 15).

(24) In this case, the product yields obtained with the electron-deficient aryl halides are generally lower than those for the electron-rich substrates. For examples, see: Wu, X. F.; Neumann, H.; Spannenberg, A.; Schulz, T.; Jiao, H. J.; Beller, M. *J. Am. Chem. Soc.* **2010**, *132*, 14596. See also ref 20c,f.

(25) Ishiyama, T.; Kizaki, H.; Hayashi, T.; Suzuki, A.; Miyaura, N. *J. Org. Chem.* **1998**, *63*, 4726.

(26) Ankersmit, H. A.; Witte, P. T.; Kooilman, H.; Lakin, M. T.; Spek, A. L.; Goubitz, K.; Vrieze, K.; vanKoten, G. *Inorg. Chem.* **1996**, *35*, 6053.

(27) Quesnel, J. S.; Arndsen, B. A. *J. Am. Chem. Soc.* **2013**, *135*, 16841.

(28) Protocol for the synthesis of 1-bromocyclohexene: Zhan, F.; Liang, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 1266.

(29) Geng, W. Z.; Wang, H. L.; Wang, Z. T.; Zhang, S. G.; Zhang, W. X.; Xi, Z. F. *Tetrahedron* **2012**, *68*, 5283.

(30) Protocol for the synthesis of 2-mercaptobenzophenones: Katritzky, A. R.; Kirichenko, K.; Ji, Y.; Prakash, I. *Chem. Heterocycl. Compd.* **2002**, *38*, 156.

(31) Perrin, D.; Armarego, W. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

(32) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.

(33) Kuhakarn, C.; Surapanich, N.; Kamtonwong, S.; Pohmakotr, M.; Reutrakul, V. *Eur. J. Org. Chem.* **2011**, *29*, 5911.

(34) Arisawa, M.; Igarashi, Y.; Kobayashi, H.; Yamada, T.; Bando, K.; Ichikawa, T.; Yamaguchi, M. *Tetrahedron* **2011**, *67*, 7846.

(35) Cilento, G. *J. Am. Chem. Soc.* **1953**, *75*, 3748.

(36) Xia, Z.; Lv, X.; Wang, W.; Wang, X. *Tetrahedron Lett.* **2011**, *52*, 4906.

(37) Arnaudov, M. G.; Ivanova, B. B.; Prangova, L. S. *J. Mol. Struct.* **2003**, *661*, 219.

(38) Hewkin, C. T.; Jackson, R. W.; William, C. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3091.