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Article

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Acyloxylation of 1,4-dioxanes and 1,4-dithianes catalyzed by a copper-iron mixed oxide

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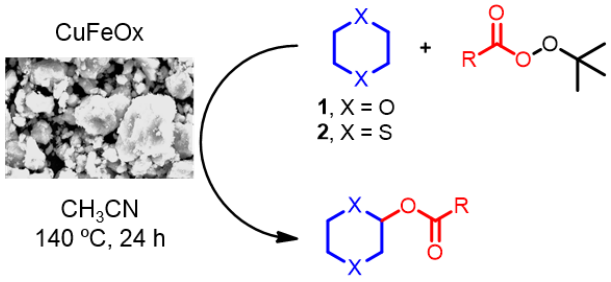


ABSTRACT: The use of a copper-iron mixed oxide as a heterogeneous catalyst for the efficient synthesis of α-acyloxy- 1,4-dioxanes and 1,4-dithianes employing *t*-butyl peroxyesters is reported. The preparation and characterization of the catalyst are described. The effect of the heteroatoms and a plausible mechanism are discussed. The method is operationally simple and involves low-cost starting materials affording products in good to excellent yields.

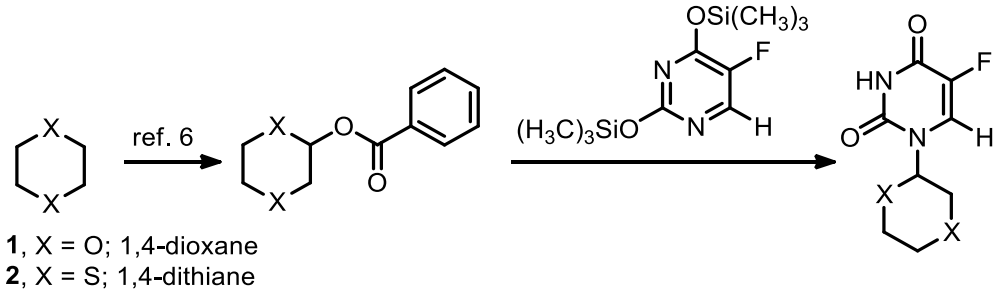
INTRODUCTION

The direct activation of C-H bonds has experienced a significant progress in the field of organic synthesis in the last decade.[1] This kind of transformation poses important challenges such as overcoming the inert nature of most C-H bonds or the control of site selectivity.[2] Some substrates, however, present the appropriate features for a successful C-H activation. The introduction of a

new oxygenated functional group at sp^3 C-H located α to an ethereal oxygen is feasible due the relatively weak dissociation energy of this type of bonds.[3] Recently, the preparation of α-acyloxy ethers has been the subject of study by the Fu and Yuan group[4] and the Patel group.[5]

In contrast, the preparation of their α-acyloxy thioethers siblings has received scarce attention. In 1982, Szarek and Hronowsky reported the preparation of 1,4-dithian-2-yl benzoate in 26% yield, as an intermediate in the preparation of new pyrimidine nucleoside analogues with improved antitumor activity as surrogates of 5-fluorouracil (5-FUra).[6] To the best of our knowledge no other α-acyloxy dithiane has been prepared.

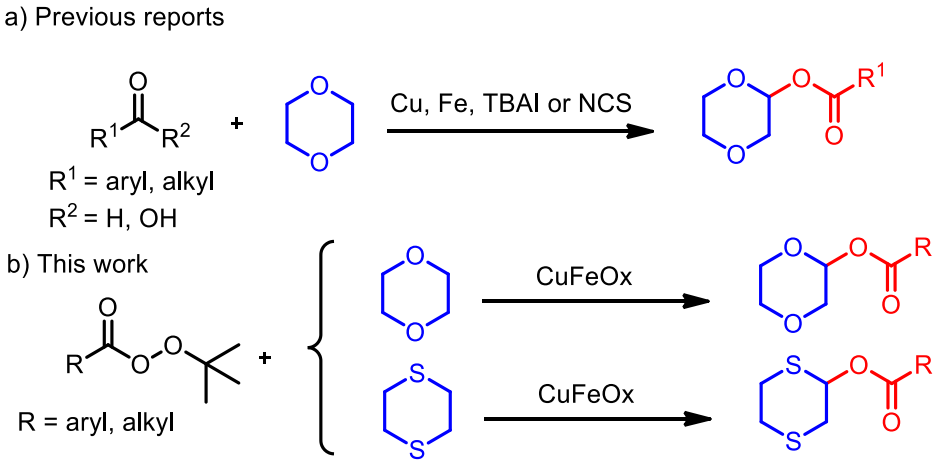
Scheme 1. Preparation of pyrimidine nucleosides by Szarek and Hronowsky.



1, X = O; 1,4-dioxane
2, X = S; 1,4-dithiane

Previous reports oriented to the synthesis of α-acyloxy ethers have based their success in the use of transition-metal catalysts, such as Cu[7] and Fe[8] or by the employment of TBAI[9] or NCS[10] (Scheme 2a). Copper and iron are considered as *low-risk* metals in terms of supply and toxicity,[11] which represents an advantage over other metals such as those belonging to the platinum group. In this article, we present the use of a copper-iron mixed oxide (CuFeOx henceforth), which effectively catalyses the introduction of an acyloxy group α to the oxygen or sulfur atoms in 1,4-dioxanes and 1,4-dithianes (Scheme 2b).

Scheme 2. Preparation of 1,4-dioxane and 1,4-dithiane benzoates.



Although mixed oxides have proved to be of help in catalysis of oxidation reactions,[12] their use in the field of organic synthesis has been rather limited. Recently, we have reported the allylic oxidation of alkenes and the γ-hydroxylation of enones by employing a copper-aluminum mixed oxide.[13] This approach permits the synergistic action of two different metal centres over a substrate. Moreover, it allows the heterogeneization of a process usually performed in homogeneous way.

RESULTS AND DISCUSSION

The preparation was carried out following our method for the synthesis of a copper-aluminum mixed oxide (for details about preparation and characterisation of the catalyst see Supporting Information).[13b,14] To ensure the reproducibility of the CuFeOx preparation, it was submitted to a characterization process. Observation by SEM revealed that the catalyst presented the form of a fine powder, with some irregularities in morphology and size, but in general consisting of micron-sized well-rounded grains. This study was complemented by granulometric measurements, which showed a distribution particle size in volume with relative maxima at approx. 0.8, 9 and 40 μm,

that fitted quite well with the size of the particles observed by SEM. In addition, a textural study was performed using N_2 physisorption that indicated the mesoporous character of the solid.

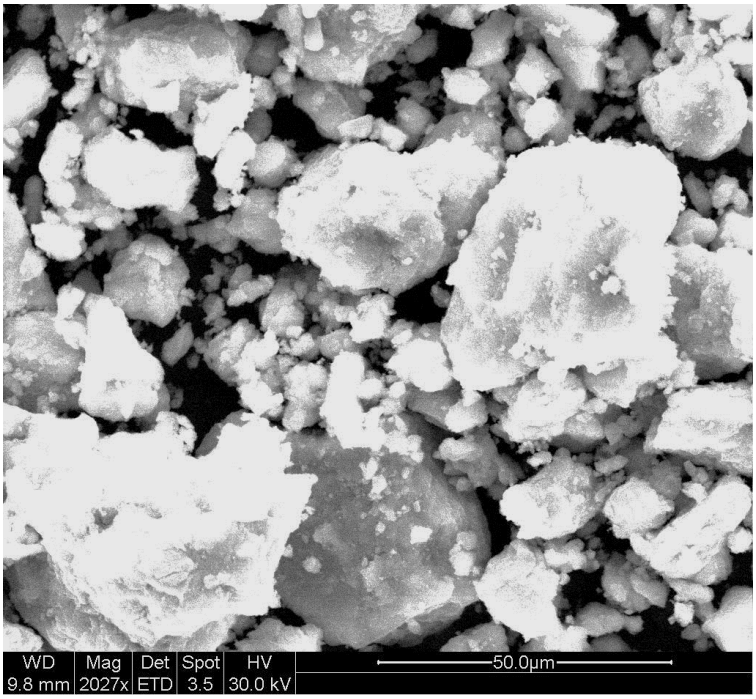


Figure 1. Typical scanning electron micrograph of the CuFeOx catalyst.The raw X-ray diffraction diagram of the sample showed the presence of crystalline CuO, tenorite phase. However, the use of Rietveld analysis allowed detecting other phases such as copper hydroxycarbonates (malachite and azurite) and spinel $CuFe_2O_4$ mixed oxide. The relatively lower intensity of iron-containing phases can be reasonably related to the intrinsic limitations of the XRD technique, which prevent from detecting amorphous phases (the synthesis method followed does not favour obtaining crystalline materials) and underestimate iron-related phases due to the well-known Cu Kα absorption effect of this element.

There was a good agreement between compositional analysis data obtained by ICP, XRF and EDS, so indicating the homogeneity of the sample both at massive and micron-surface levels

(Table 1). Moreover, they are relatively consistent with the Cu/Fe atomic ratio selected for catalyst preparation and the formation of a copper-iron mixed oxide.

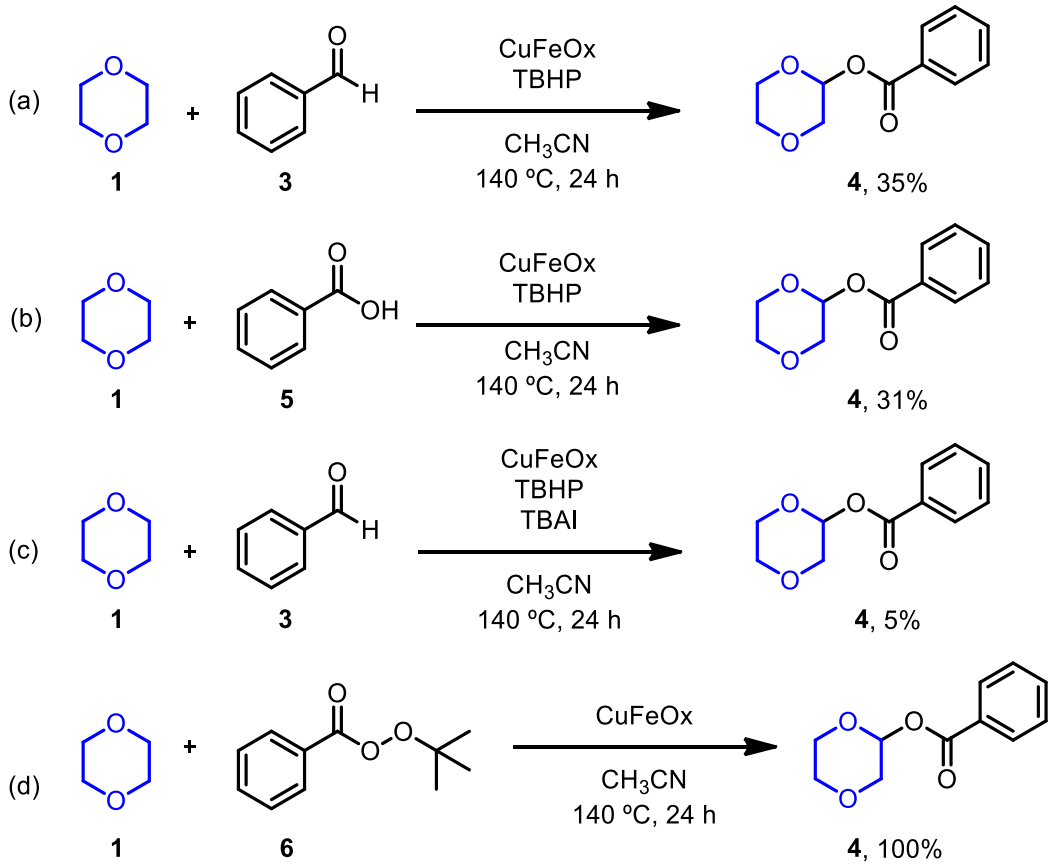
Table 1. Compositional analysis (wt.%) of the CuFeOx sample by means of induced coupled plasma spectroscopy, X-ray fluorescence and energy-dispersive X-ray spectroscopy

Technique	Cu	Fe	O
ICP	47.1±0.3	17.2±0.1	not applicable
XRF	51.5	22.4	24.0
EDS[a]	52.7±3.0	18.1±1.5	22.2

[a]Data correspond to the average of values obtained for four different areas analysed in spot mode.

Once the catalyst was characterized, we focused on the reaction of 1,4-dioxane **1** either with benzaldehyde **3** or benzoic acid **5**, using TBHP as the oxidant. The yields were moderate, affording the corresponding benzoyloxy 1,4-dioxane **4** in 35% and 31% yield, respectively (Table 2, entries a and b).

Table 2. Preliminary assays[a,b]



[a]Reaction conditions: 1,4-dioxane **1** (5.0 mmol), CuFeOx (30 mg, 8.9 mol% Cu), CH_3CN (2 mL), 140 °C, 24 h. (a) Benzaldehyde **3** (2.5 mmol), TBHP (70% aqueous, 7.5 mmol). (b) Benzoic acid **5** (2.5 mmol), TBHP (70% aqueous, 7.5 mmol). (c) Benzaldehyde **3** (2.5 mmol), TBHP (70% aqueous, 7.5 mmol), TBAI (0.5 mmol). (d) TBPB **6** (2.5 mmol). [b]GC yield.

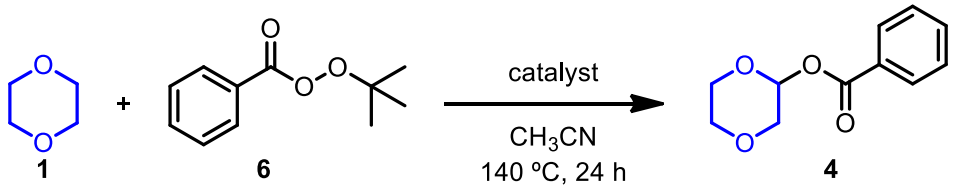
Recently, Wan et al have demonstrated that treatment of an aldehyde with TBAI and TBHP leads to the corresponding peroxyester that is *in situ* used as an oxidant in a Kharasch-Sosnovsky oxidation of an olefin.[15] In our case, the treatment of 1,4-dioxane **1** and benzaldehyde **3** with TBAI in the presence of CuFeOx was negative, leading only to a mere 5% yield (Table 2, entry c).

However, when we employed *t*-butyl peroxybenzoate (TBPB) as the oxidant, the reaction proceeded quantitatively (Table 2, entry d).

To assess the efficiency of CuFeOx as a catalyst, various copper sources were subsequently tested in our benchmark reaction shown in Table 3. It was observed that in the absence of CuFeOx (entry 1), the product **4** was formed in only 4% yield. The use of $Cu(OAc)_2 \cdot H_2O$ (entry 3) resulted in 44% yield, and the mixture of CuFeOx precursors, $CuCl_2$ and $FeCl_3 \cdot 6H_2O$ (entry 4) provided 65% yield. Other commercial oxides and chlorides, such as Cu_2O, CuO, $CuCl_2$, and $FeCl_3 \cdot 6H_2O$ (entries 5-8) were also tested, producing the desired product in moderate yields. Entries 2 and 9-11 confirm the important role of the temperature, displaying a dramatic drop of yield below 100 ºC.

Given that the use of TBPB **6** conducted to the desired α-benzoyloxy 1,4-dioxane **4** in quantitative yield, we thought that the use of different peroxyesters would allow us to prepare different α-acyloxy ethers.

Table 3. Search for the optimal catalyst.[a]



1 + **6** → **4**

Entry	catalyst	Yield[i] (%)
1	-	4
2[b]	CuFeOx	100
3[c]	$Cu(OAc)_2 \cdot H_2O$	44
4[d]	$CuCl_2 + FeCl_3 \cdot H_2O$	65
5[c]	Cu_2O	72
6[c]	CuO	32
7[c]	$CuCl_2$	53
8[e]	$FeCl_3 \cdot 6H_2O$	46
9[b,f]	CuFeOx	3

10[b,g]	CuFeOx	90
11[b,h]	CuFeOx	92

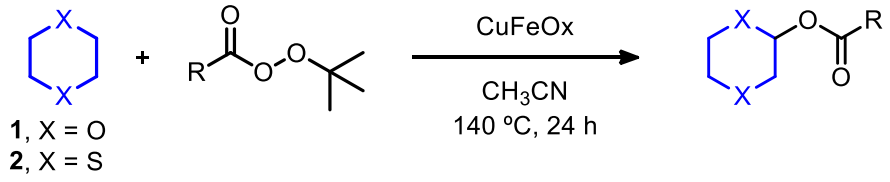
[a]Reaction conditions: 1,4-dioxane **1** (5.0 mmol), TBPB **6** (2.5 mmol), CH_3CN (2 mL), 140 ºC, 24 h. [b]Catalyst (30 mg, 8.9 mol% Cu, 3.7 mol% Fe). [c]Catalyst (8.9 mol% Cu). [d]$CuCl_2$ (17 mg) and $FeCl_3 \cdot 6H_2O$ (13 mg). [e]Catalyst (3.7 mol% Fe). [f]80 ºC. [g]100 ºC. [h]120 ºC. [i]Determined by GC.

The above-mentioned report by Wan et al describes a facile preparation of *t*-butyl peroxyesters from aldehydes catalyzed by TBAI.[15] This methodology was found to be very reproducible, robust, and suited for our purposes. Thus, we proceeded to the preparation of different peroxyesters that were reacted with 1,4-dioxane **1** in the presence of CuFeOx (Table 4). Gratifyingly, the reaction of aromatic peroxyesteres furnished the corresponding α-aryl esters **7-10** in good yields. The nature of the group attached to the aromatic ring of the peroxyester seemed not to affect the outcome, providing good yields either in the presence of donor or acceptor groups. The use of lineal *t*-butyl peroxyesters was also possible, as demonstrated by the formation of 1,4-dioxan-2-yl octanoate **11**. The use of *t*-butyl 2-thienylperoxycarboxylate led to the corresponding ester **12** in a good 73% yield. A 1-naphthyl group could be introduced in the starting peroxyester providing the desired product **13** in 52% yield. An interesting case was that of the peroxyester prepared from cinnamaldehyde, that underwent a coupling reaction with a concomitant decarboxylative process furnishing 1,4-dioxane derivative **14**. This kind of transformation has been previously reported by Li[16] and Han[17] groups in processes catalized by CuO and $Fe(acac)_3$, respectively.

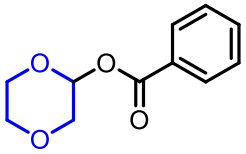
The exploration of the scope continued with 1,4-dithiane **2**. Its behavior was parallel to that already described for 1,4-dioxane **1**. Thus, the respective aryl esters **15**-**19** were prepared with good to excellent yields. The yields of **20** and **21** were nevertheless significantly lower than those of **11**

and **12**. The naphthyl derivative **22** was obtained in 53% yield, a value similar to that obtained for **13**. The main difference was observed in the treatment with the cinnamic acid peroxyester, where the decarboxylation was not observed, and the expected acyloxylated 1,4-dithiane **23** was produced in 26% yield.

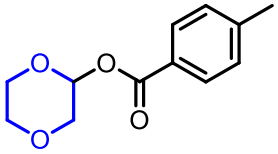
Table 4. Scope of 1,4-dioxane and 1,4-dithiane derivatives.[a,b]



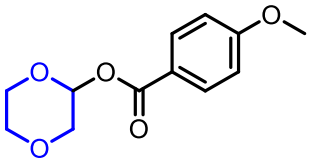
1, X = O
2, X = S



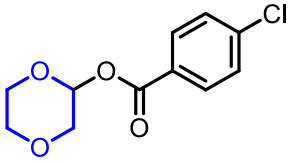
4, 100% (73%)



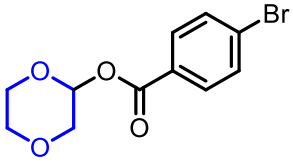
7, 89% (81%)



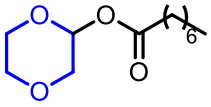
8, 100% (85%)



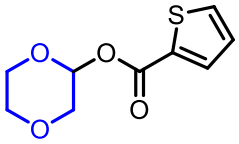
9, 94% (83%)



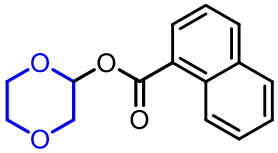
10, 100% (79%)



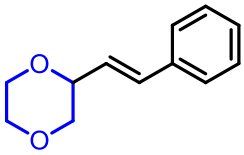
11, 65% (51%)



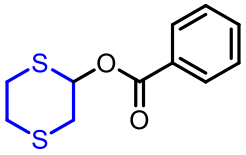
12, 91% (73%)



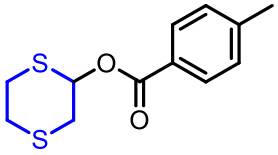
13, 67% (52%)



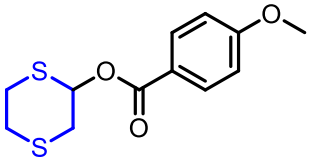
14, 21% (27%)



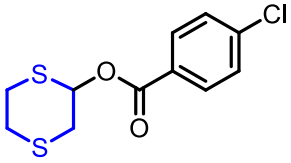
15, 87% (80%)



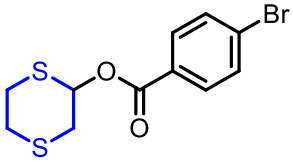
16, 98% (89%)



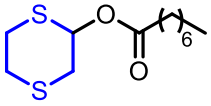
17, 93% (83%)



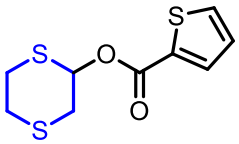
18, 76% (85%)



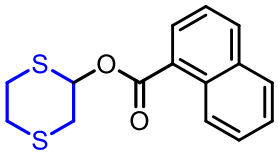
19, 97% (90%)



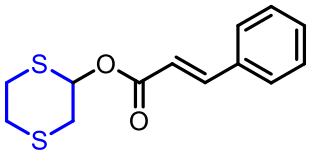
20, 25% (23%)



21, 36% (41%)



22, 55% (53%)

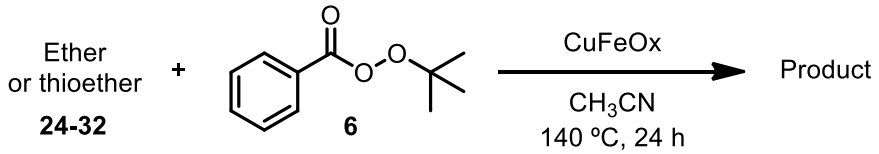


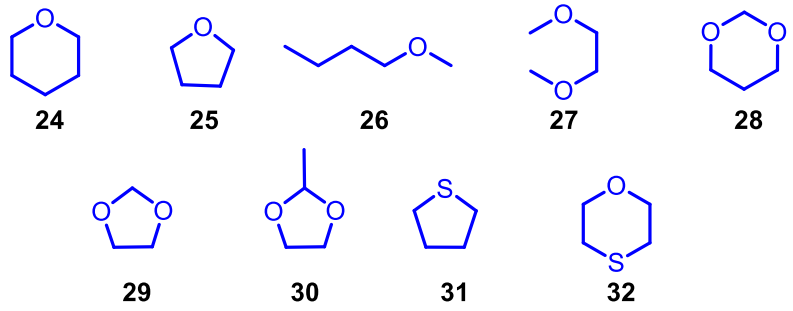
23, 42% (26%)

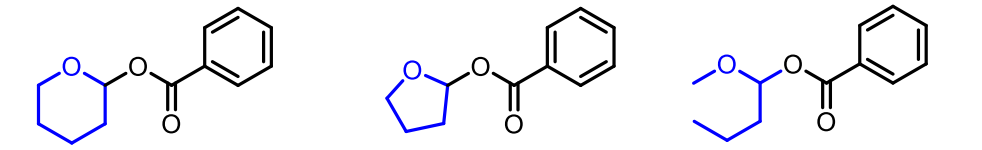
[a]Reaction conditions: 1,4-dioxane **1** (5.0 mmol) or 1,4-dithiane **2** (2.0 mmol), peroxyester (2.5 mmol for **4** and **6-14** or 1.0 mmmol for **15-23**), CuFeOx (30 mg, 8.9 mol% Cu for **4** and **6-14** or 12 mg, 8.9 mol% Cu for **15-23**), CH_3CN (2 mL) for **4** and **6-14** or CH_3CN (1 mL) and CH_2Cl_2 (1 mL) for **15-23**, 140 ºC, 24 h. [b]GC yield (yield).

A general inspection of Table 4 indicates that the presence of two heteroatoms, either sulfur or oxygen, provides a suitable system for the acyloxylation reaction to take place. We found convenient to evaluate the behaviour of substrates bearing just one heteroatom. The results are displayed in Table 5. Cyclic ethers such as tetrahydropyran **24** and tetrahydrofuran **25** led only to traces of the corresponding benzoyloxy esters. Additionally, linear butyl methyl ether **26** provided the regioisomers **35a** and **35b** in a poor 23% overall yield (in a 1:3.6 ratio). A slightly better yield (30%) was obtained when a linear substrate bearing two oxygen atoms in 1,4-relative positions **27** was used. These results suggest that the presence of two oxygen atoms favors the reaction.

Table 5. Role of the substitution pattern in the ether or thioether.[a,b]



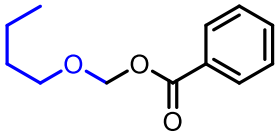




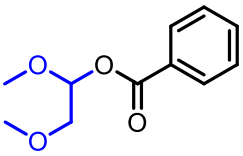
33, trace

34, trace

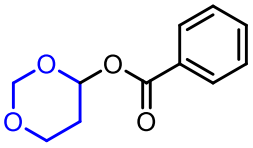
35a, 9% (5%)[c]



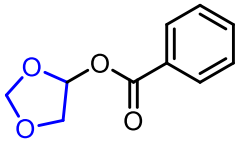
35b, 15% (18%)[c]



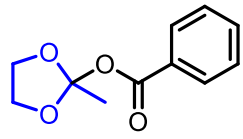
36, 37% (30%)



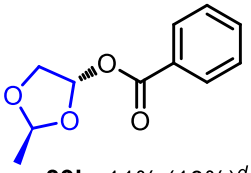
37, trace



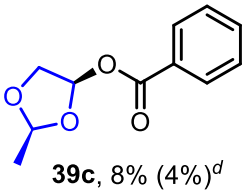
38, 16% (15%)



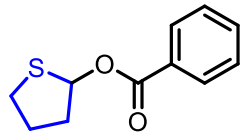
39a, 54% (52%)[d]



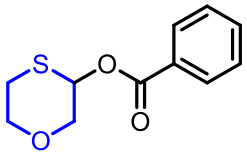
39b, 11% (10%)[d]



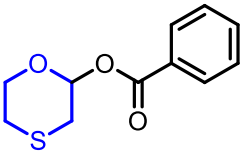
39c, 8% (4%)[d]



40, 47% (46%)



41a, 63% (55%)[e]



41b, 18% (15%)[e]

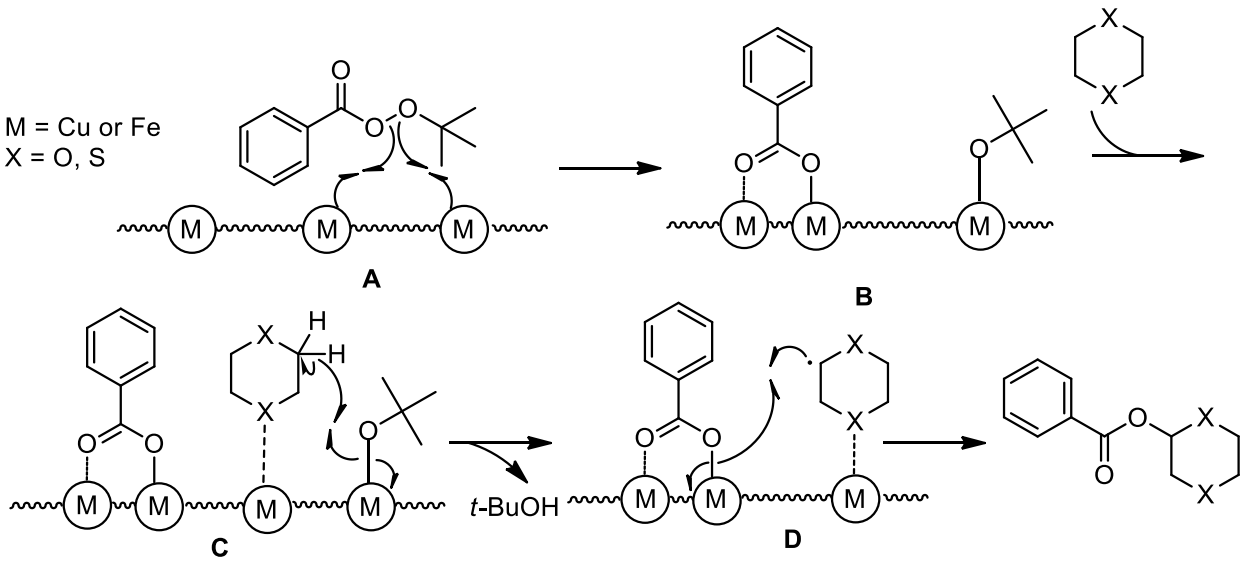
[a]Reaction conditions: ethers **24-30** (5.0 mmol), tetrahydrothiophene **31** (2.0 mmol) or 1,4-oxathiane **32** (5.0 mmol) and TBPB (2.5 mmol for **24-30** and **32** or 1.0 mmmol for **31**), CuFeOx (30 mg, 8.9 mol% Cu for **24-30** and **32** or 12 mg, 8.9 mol% Cu for **31**), CH_3CN (2 mL) for **24-30** or CH_3CN (1 mL) and CH_2Cl_2 (1 mL) for **31** and **32**, 140 ºC, 24 h. [b]GC yield (yield). [c]**35a** and **35b** formed in the same reaction (23% overall yield). [d]**39a**-**39c** formed in the same reaction (66% overall yield). [e]**41a** and **41b** formed in the same reaction (70% overall yield).

The importance of the relative location of the oxygen atoms was further investigated (Table 5). Although 1,3-dioxane **28** and 1,3-dioxolane **29** performed poorly, 2-methyl-1,3-dioxolane **30** furnished compounds **39a**-**39c** in an overall yield of 66% (in a 13:2.5:1 ratio). This fact could be explained in terms of relative stability of **29** and **30** (the acetals of formaldehyde and acetaldehyde, respectively) under the reaction conditions. Additionally, the tertiary nature of the resulting radical intermediate (*vide infra*) involved in the formation of **39a** explains this result. Eventually, it is required the presence of two oxygen atoms, preferably in a 1,4-relative position, for the reaction to proceed properly. It is noteworthy that, in contrast to tetrahydrofuran **25**, tetrahydrothiophene **31** produced **40** in 46% yield. This seems to be in accordance with the higher activating ability of the sulfur atom.[18] This idea was supported by the fact that 1,4-oxathiane **32** underwent the acyloxylation mainly at the α-position of the sulfur atom, leading to **41a** and **41b** in a 3.7:1 ratio (70% overall yield).

The radical nature of the mechanism was confirmed with a control reaction, employing 1,4-dioxane **1** as substrate and TBPB as the oxidant in the presence of 2,6-di-*t*-butyl-4-methylphenol (BHT), which led to the formation of **4** in just 2 % yield.

Although CuFeOx presents a multicomponent nature which makes difficult to precise the origin of its activity, there are precedents of the use of copper-iron mixed oxides such as $CuFe_2O_4$ in heterogeneous conditions in oxidative couplings.[19] A proposal of a plausible mechanism is depicted in Scheme 3. Decomposition of TBPB can be favored by the presence of the metallic centers (**A**). The solid provides a surface suitable for the formation of radicals and the encounter of the different species (**B**). The presence of the *t*-butoxyl radical would induce the formation of the radical at the α-position of the ether or thiother (**C**). The higher yields obtained when two heteroatoms are present in the ether or the thioether suggest the coordination of one of these heteroatoms to a metallic center. The other oxygen or sulfur atom would activate its contiguous position by electron donation to the σ* orbital of the C-H bond.[20] The possibility of backbonding from the metal to the sulfur atom[21] would explain that one sulfur atom is enough for the reaction to proceed in contrast to when only one oxygen atom is present. Once the radical is formed, the coupling with the acyloxy moiety would take place, affording the corresponding product (**D**).

Scheme 3. Plausible mechanism



CONCLUSION

This work is an interesting example of the use of mixed oxides as catalysts for the activation of C-H bonds. In particular, the acyloxylation at the α-position of ethers and thioethers can be performed employing copper-iron mixed oxides in an efficient and clean way. In addition, there are limited precedents of the use of organic peroxides in heterogeneous catalysis.[22] On the other hand, although the acyloxylation of 1,4-ethers has recently been subject of study, the use of the related 1,4-thioethers has not been reported, with the exception of Szarek and Hrownosky paper. Last but not least important, the presence of sulfur atoms in a substrate generally restricts the use of metallic catalysts due to catalyst poisoning.[23] This fact limits the application of C-H activation reactions in the search of sulfur-based heterocyclic drugs. In this sense, the use of copper-iron mixed oxides provides an efficient alternative to overcome this problem.

EXPERIMENTAL SECTION

General Information. NMR spectra were recorded on 400 MHz or 500 MHz spectrometers using standard pulse sequences. Spectra were referenced to the internal chloroform ($CHCl_3$, δ = 7.25 ppm for ^{1}H-NMR, δ = 77.0 ppm for ^{13}C-NMR). GC analyses were performed using a DB-5 column. Octadecane was employed as internal standard and analyses were run in triplicate. Reactions were monitored through TLC on commercial silica gel plates precoated with silica gel. Visualization of the developed plate was performed by fluorescence quenching and aqueous ceric ammonium molybdate or anisaldehyde stains. HPLC purification was carried out using a 1×25 cm silica gel column (10 μm particle size). Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded using NaCl plates and data are reported in cm^{-1}. Mass spectra were recorded on a UPLC-QTOF mass spectrometer.

Compositional analysis of the copper-iron mixed oxide was studied by means of both inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-Ray fluorescence (XRF). Textural characteristics were investigated by means of N_2 physisorption at -196 ºC. The experiment was performed with a sample which was first subjected to a heating treatment under high vacuum at 150 ºC for 2 h. The recorded isotherms were used to obtain the specific surface area, S_{BET}, and the porosity using the BET and BJH data treatment, respectively. Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) compositional data were obtained with a scanning electron microscope using a nominal resolution of 3 nm. Particle size distribution was obtained employing a granulometer operating with laser diffraction over a previously centrifuged dispersion of the sample (3 min sonicated) in water. Results were obtained from the average of the three tests performed to ensure reproducibility of the measurements. Structural study was carried out with X-ray diffraction (XRD) at room temperature using a powder

diffractometer operating with Cu Kα radiation. The 2θ angle ranged from 3º to 75º with a step of 0.05º and a counting time of 1 s. The Rietveld method was applied to the XRD data using the FULLPROF program.[24]

Catalyst Preparation.[13b] The preparation of the copper-iron mixed oxide (CuFeOx) was carried out following our method for the synthesis of copper-aluminum mixed oxide, which is based on that described by Guida et al[14] for the synthesis of hydrotalcites. To this end, a solution of Na_2CO_3 (1.27 g) and NaOH (5.20 g) in water was added dropwise for 1.5 h over a solution containing $CuCl_2$ (5.00 g) and $FeCl_3 \cdot 6H_2O$ (4.00 g) in water (50 mL). The suspension turned dark brown and it was stirred at 70 ºC for 22 h. The mixture was then filtered and the precipitate washed with warm water (3 × 200 mL). The solid was dried in an oven at 105 ºC for 24 h, after which time it was ground until a fine powder was obtained. The solid was left exposed to air for 72 h prior to use.

General Procedure for the Synthesis of Peroxyesters. All peroxyesters have been prepared according to the literature procedure.[15] The following two peroxyesters have been synthesized for the first time.

(*E*) *t*-butyl 3-phenylprop-2-eneperoxoate. Colorless oil (894 mg, 20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 16.0 Hz, 1H), 7.36 (dd, J = 6.7, 2.9 Hz, 2H), 7.25–7.21 (m, 3H), 6.27 (d, J = 16.0 Hz, 1H), 1.24 (s, 9H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.7, 145.5, 133.5, 130.3, 128.5, 127.7, 112.7, 83.1, 25.7; IR (film) ν_{max} 3063, 2936, 2983, 1755, 1634, 1450, 1367, 1190, 1108, 980, 763 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{16}O_3Na$ $[M+Na]^+$ 243.0997; found 243.0997.

***t*-butyl octaneperoxoate.** Colorless oil (804 mg, 18%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (t, J = 7.5 Hz, 2H), 1.64 (tt, J = 7.5, 7.5 Hz, 2H), 1.30 (s, 9H), 1.29–1.20 (m, 8H), 0.85 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 171.1, 83.2, 31.6, 31.3, 29.0, 28.8,

26.1, 25.0, 22.5, 14.0; IR (film) ν_{max} 2957, 2930, 2859, 1779, 1467, 1367, 1191, 854 cm^{-1}; HRMS (ESI): calcd. for $C_8H_{15}O_3$ $[M\text{-}t\text{Bu}]^-$ 159.1021; found 159.1015.

General Procedure for the Acyloxylation of Ethers and 1,4-Oxathiane. 30 mg of CuFeOx was suspended in 2 mL of acetonitrile in a sealed tube and it was stirred for 5 min. Then, ether (5.0 mmol) and *t*-butyl peroxyester (2.5 mmol) were added and the reaction mixture was stirred at 140 ºC (Caution: a considerable pressure can be developed). After 24 h, an aliquot was taken and analysed by GC (using octadecane as an internal standard). The solvent was evaporated under reduced pressure and the crude was purified by SEPHADEX column chromatography (methanol as an eluent). For 1,4-oxathiane, 2 mL of acetonitrile/dichloromethane (1:1) was employed as a solvent.

General Procedure for the Acyloxylation of Thioethers. 12 mg of CuFeOx was suspended in 1 mL of acetonitrile in a sealed tube and it was stirred for 5 min. Then, thioether (2.0 mmol) and *t*-butyl peroxyester (1.0 mmol, dissolved in 1 mL of dichloromethane) were added and the reaction mixture was stirred at 140 ºC (Caution: a considerable pressure can be developed). After 24 h, an aliquot was taken and analysed by GC (using octadecane as an internal standard). The solvent was evaporated under reduced pressure and the crude was purified by silica gel column chromatography (mixtures of EtOAc/hexanes as eluents).

1,4-dioxan-2-yl benzoate (4). Colerless oil (380 mg, 73%); ^{1}H NMR (500 MHz, $CDCl_3$) δ8.11 (d, J = 7.6 Hz, 2H), 7.58 (tt, J = 7.5, 1.8 Hz, 1H), 7.45 (dd, J = 7.9, 7.9 Hz, 2H), 6.09 (br s, 1H), 4.21 (ddd, J = 11.8, 6.6, 6.6 Hz, 1H), 3.89–3.87 (m, 2H), 3.83–3.80 (m, 2H), 3.66 (ddd, J = 5.2, 2.6, 2.6 Hz, 1H); ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ165.2, 133.3, 129.9, 129.7, 128.4, 89.8, 67.8, 66.1, 61.7; IR (film) ν_{max} 2973, 2858, 1731, 1601, 1453, 1259, 1155, 881, 711 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{12}O_4Na$ $[M+Na]^+$ 231.0633; found 231.0640.

1,4-dioxan-2-yl 4-methylbenzoate (7). Yellowish oil (450 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.07 (br s, 1H), 4.20 (ddd, J = 12.0, 6.5, 6.5 Hz, 1H), 3.89–3.86 (m, 2H), 3.83–3.79 (m, 2H), 3.66 (ddd, J = 5.3, 2.6, 2.6 Hz, 1H), 2.41 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 165.3, 144.2, 129.9, 129.1, 126.9, 89.6, 67.9, 66.1, 61.8, 21.7; IR (film) ν_{max} 2974, 2857, 1726, 1612, 1277, 1087, 883, 754 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{13}O_4$ $[M-H]^-$ 221.0814; found 221.0818.

1,4-dioxan-2-yl 4-methoxybenzoate (8). White amorphous solid (506 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 6.05 (br s, 1H), 4.18 (ddd, J = 11.8, 5.5, 5.5 Hz, 1H), 3.86–3.85 (m, 2H), 3.84 (s, 3H), 3.81–3.78 (m, 2H), 3.65 (ddd, J = 5.3, 2.7, 2.7 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.9, 163.7, 132.0, 122.0, 113.7, 89.5, 67.9, 66.1, 61.8, 55.4; IR (film) ν_{max} 2972, 2856, 1720, 1607, 1512, 1257, 1170, 1088, 1020, 913, 883, 771 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{14}O_5Na$ $[M+H]^+$ 261.0739; found 261.0736.

1,4-dioxan-2-yl 4-chlorobenzoate (9). White amorphous solid (504 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 6.07 (br s, 1H), 4.19 (ddd, J = 11.8, 6.6, 6.6 Hz, 1H), 3.88–3.87 (m, 2H), 3.83–3.81 (m, 2H), 3.67 (ddd, J = 5.1, 2.6, 2.6 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.4, 139.9, 131.2, 128.8, 128.1, 90.0, 67.7, 66.1, 61.8; IR (film) ν_{max} 2960, 2856, 1718, 1594, 1236, 1152, 1087, 882, 758 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{10}O_4{}^{35}Cl$ $[M-H]^-$ 241.0268; found 241.0258, calcd. for $C_{11}H_{10}O_4{}^{37}Cl$ $[M-H]^-$ 243.0238; found 243.0250.

1,4-dioxan-2-yl 4-bromobenzoate (10). White amorphous solid (567 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 6.07 (br s, 1H), 4.19 (ddd, J = 13.3, 6.6, 6.6 Hz, 1H), 3.88–3.86 (m, 2H), 3.83–3.81 (m, 2H), 3.67 (ddd, J = 5.2, 2.6, 2.6 Hz, 1H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.5, 131.8, 131.4, 128.6, 90.0, 67.8, 66.1, 61.8; IR (film)

ν_{max} 2974, 2863, 1727, 1589, 1260, 1068, 880, 746 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{11}O_4{}^{79}BrNa$ $[M+Na]^+$ 308.9738; found 308.9749, calcd. for $C_{11}H_{11}O_4{}^{81}BrNa$ $[M+Na]^+$ 310.9718; found 308.9756.

1,4-dioxan-2-yl octanoate (11). Yellow oil (294 mg, 51%); ^1H NMR (400 MHz, $CDCl_3$) δ 5.83 (br s, 1H), 4.08 (ddd, *J* = 12.3, 6.5, 6.5 Hz, 1H), 3.78–3.66 (m, 4H), 3.60 (ddd, *J* = 5.5, 2.8, 2.8 Hz, 1H), 2.36 (t, *J* = 7.6 Hz, 2H), 1.63 (tt, *J* = 14.5, 14.5 Hz, 3H), 1.31–1.19 (m, 8H), 0.85 (t, *J* = 6.7 Hz, 3H). $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 172.5, 89.0, 67.7, 66.0, 61.7, 34.3, 31.6, 29.0, 28.8, 24.7, 22.5, 14.0. IR (film) ν_{max} 2958, 2930, 2857, 1747, 1456, 1232, 1147, 1069, 917, 856, 756 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{21}O_4$ $[M-H]^-$ 229.1440; found 229.1441.

1,4-dioxan-2-yl-thiophene-2-carboxylate (12). Yellow oil (391 mg, 73%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.59 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.04 (br s, 1H), 4.20 (ddd, *J* = 11.8, 7.1, 5.9 Hz, 1H), 3.86–3.85 (m, 2H), 3.81–3.79 (m, 2H), 3.65 (ddd, *J* = 5.3, 2.6, 2.6 Hz, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 160.8, 134.1, 133.2, 127.8, 89.9, 67.7, 66.0, 61.8; IR (film) ν_{max} 3103, 2975, 2858, 1715, 1418, 1256, 1062, 1013, 909, 750 cm^{-1}; HRMS (ESI) calcd. for $C_9H_9O_4S$ $[M-H]^-$ 213.0222; found 213.0226.

1,4-dioxan-2-yl 1-naphthoate (13). White amorphous solid (336 mg, 52%); ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 8.7 Hz, 1H), 8.35 (dd, *J* = 7.3, 1.3 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.63 (ddd, *J* = 8.4, 8.4, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.51 (dd, *J* = 8.2, 7.4 Hz, 1H), 6.21 (br s, 1H), 4.26 (ddd, *J* = 11.8, 6.2, 6.2 Hz, 1H), 3.96–3.95 (m, 2H), 3.86–3.83 (m, 2H), 3.71 (ddd, *J* = 5.2, 2.6, 2.6 Hz, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 165.8, 134.0, 133.8, 131.5, 130.9, 128.5, 128.0, 126.2, 126.1, 125.7, 124.4, 89.8, 67.9, 66.1, 61.8; IR (film) ν_{max} 2973, 2856, 1721, 1510, 1233, 1131, 1067, 883, 783 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{13}O_4$ $[M-H]^-$ 257.0814; found 257.0815.

2-styryl-1,4-dioxane (14). Yellowish amorphous solid (128 mg, 27%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 7.1 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.25 (tt, J = 6.5, 1.3 Hz, 1H), 6.69 (d, J = 16.1 Hz, 1H), 6.09 (dd, J = 16.1, 6.2 Hz, 1H), 4.25 (dddd, J = 10.1, 6.2, 2.8, 1.4 Hz, 1H), 3.89–3.80 (m, 3H), 3.75 (br dd, J = 11.6, 2.6 Hz, 1H), 3.66 (ddd, J = 11.5, 10.8, 3.2 Hz, 1H), 3.42 (dd, J = 11.5, 10.0 Hz, 1H); ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 136.3, 132.6, 128.5, 127.8, 126.5, 125.1, 76.0, 70.9, 66.6, 66.3; IR (film) ν_{max} 3026, 2968, 2868, 1452, 1118, 967, 923, 870, 746, 695 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{15}O_2$ $[M+H]^+$ 191.1072; found 191.1079.

1,4-dithian-2-yl benzoate (15). Yellowish amorphous solid (192 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 8.4, 1.4 Hz, 2H), 7.58 (tt, J = 6.8, 1.3 Hz, 1H), 7.46 (dd, J = 7.8, 7.8 Hz, 2H), 6.06 (dd, J = 5.0, 1.9 Hz, 1H), 3.44–3.37 (m, 2H), 3.10 (dd, J = 11.7, 11.7 Hz, 1H), 3.01 (dd, J = 14.2, 5.1 Hz, 1H), 2.81–2.70 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 164.9, 133.3, 129.8, 129.7, 128.4, 67.7, 33.5, 28.0, 26.2; IR (film) ν_{max} 3063, 2911, 1721, 1601, 1451, 1324, 1265, 1095, 1069, 965, 917, 710 cm^{-1}; HRMS (ESI): calcd. for $C_{11}H_{12}O_2S_2Na$ $[M+Na]^+$ 263.0176; found 263.0145.

1,4-dithian-2-yl 4-methylbenzoate (16). White amorphous solid (226 mg, 89%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 6.06 (br s, 1H), 3.41 (br s, 2H), 3.04 (br s, 2H), 2.77 (br s, 2H), 2.41 (s, 3H); ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$): δ 165.0, 144.1, 129.9, 129.2, 127.1, 68.1, 38.7, 28.1, 23.0, 21.7; IR (film) ν_{max} 2913, 1718, 1612, 1265, 1092, 914, 749 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{14}O_2S_2Na$ $[M+Na]^+$ 277.0333; found 277.0340.

1,4-dithian-2-yl 4-methoxybenzoate (17). White amorphous solid (224 mg, 83%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, J = 9.0 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 6.04 (br d, J = 3.7 Hz, 1H), 3.85 (s, 3H), 3.42–3.37 (m, 2H), 3.10–2.98 (m, 2H), 2.79–2.72 (m, 2H); ^{13}C{^{1}H}NMR (126 MHz, $CDCl_3$) δ 164.6, 163.7, 131.9, 122.1, 113.7, 67.6, 55.4, 33.6, 28.1, 26.3; IR (film) ν_{max} 2913,

2839, 1715, 1606, 1511, 1258, 1093, 1029, 967, 847, 769 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{14}O_3S_2Na$ $[M+Na]^+$ 293.0282; found 293.0288.

1,4-dithian-2-yl 4-chlorobenzoate (18). Yellowish amorphous solid (234 mg, 85%); ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 6.05 (br d, J = 4.9 Hz, 1H), 3.44–3.37 (m, 2H), 3.10 (dd, J = 12.5, 12.5 Hz, 1H), 3.00 (dd, J = 14.2, 5.0 Hz, 1H), 2.81–2.71 (m, 2H); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 164.1, 139.8, 131.2, 128.8, 128.2, 68.1, 33.5, 28.1, 26.2; IR (film) ν_{max} 2956, 2913, 1723, 1594, 1264, 1092, 1014, 964, 915, 757 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{11}O_2S_2{}^{35}ClNa$ $[M+Na]^+$ 296.9787; found 296.9790, calcd. for $C_{11}H_{11}O_2S_2{}^{37}ClNa$ $[M+Na]^+$ 298.9757; found 298.9755.

1,4-dithian-2-yl 4-bromobenzoate (19). White amorphous solid (287 mg, 90%); ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 6.05 (br d, J = 3.6 Hz, 1H), 3.42–3.37 (m, 2H), 3.15–2.93 (m, 2H), 2.87–2.73 (m, 2H); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 164.3, 131.8, 131.4, 128.7, 128.6, 68.2, 33.4, 28.0, 26.3; IR (film) ν_{max} 2912, 1725, 1590, 1398, 1263, 1096, 1011, 963, 753 cm^{-1}; HRMS (ESI) calcd. for $C_7H_4O_2{}^{79}Br$ $[M-C_4H_7S_2]^-$ 198.9395; found 198.9391, calcd. for $C_7H_4O_2{}^{81}Br$ $[M-C_4H_7S_2]^-$ 200.9374; found 200.9372.

1,4-dithian-2-yl octanoate (20). Yellow oil (60 mg, 23%); ^1H NMR (500 MHz, $CDCl_3$) δ 5.82 (dd, J = 5.2, 1.9 Hz, 1H), 3.33–3.27 (m, 2H), 3.10–2.97 (m, 1H), 2.88 (dd, J = 14.1, 5.2 Hz, 1H), 2.76–2.69 (m, 2H), 2.39 (t, J = 7.6 Hz, 2H), 1.65 (tt, J = 14.7, 14.7 Hz, 2H), 1.31–1.25 (m, 8H), 0.87 (t, J = 5.2 Hz, 3H); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 172.4, 67.4, 34.4, 33.3, 31.6, 29.0, 28.9, 28.0, 26.3, 24.9, 22.6, 14.0; IR (film) ν_{max} 2955, 2927, 2857, 1740, 1466, 1153, 966, 725 cm^{-1}; HRMS (ESI) calcd. for $C_{12}H_{22}O_2S_2Na$ $[M+Na]^+$ 285.0959; found 285.0954.

1,4-dithian-2-yl thiophene-2-carboxylate (21). Yellowish amorphous solid (101 mg, 41%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J = 3.8, 1.3 Hz, 1H), 7.60 (dd, J = 5.0, 1.3 Hz, 1H), 7.12

(dd, *J* = 5.0, 3.8 Hz, 1H), 6.03–6.01 (m, 1H), 3.42–3.37 (m, 2H), 3.08 (dd, *J* = 11.8, 11.8 Hz, 1H), 3.00 (dd, *J* = 14.2, 5.2 Hz, 1H), 2.80–2.71 (m, 2H). $^{13}C\{^{1}H\}$NMR (126 MHz, $CDCl_3$) δ 160.6, 134.1, 133.2, 133.1, 127.8, 68.2, 33.4, 28.0, 26.3; IR (film) ν_{max} 3099, 2911, 1709, 1523, 1416, 1253, 1072, 961, 744 cm^{-1}; HRMS (ESI) calcd. for $C_9H_{10}O_2S_3Na$ $[M+Na]^+$ 268.9741; found 268.9734.

1,4-dithian-2-yl 1-naphthoate (22). Yellowish amorphous solid (154 mg, 53%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.05 (d, *J* = 8.7 Hz, 1H), 8.40 (dd, *J* = 7.3, 1.3 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.90–7.88 (m, 1H), 7.64 (ddd, *J* = 8.6, 5.6, 1.4 Hz, 1H), 7.56–7.52 (m, 2H), 6.20–6.19 (m, 1H), 3.50–3.43 (m, 2H), 3.16–3.09 (m, 2H), 2.83–2.75 (m, 2H); $^{13}C\{^{1}H\}$NMR (126 MHz, $CDCl_3$) δ 165.7, 133.9, 133.8, 131.4, 131.1, 128.6, 128.0, 126.3, 126.3, 125.8, 124.5, 68.1, 33.6, 28.1, 26.3; IR (film) ν_{max} 3051, 2911, 1716, 1510, 1237, 1191, 1126, 995, 780 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{14}O_2S_2Na$ $[M+Na]^+$ 313.0333; found 313.0347.

1,4-dithian-2-yl cinnamate (23). Yellow amorphous solid (69 mg, 26%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.56–7.54 (m, 2H), 7.40–7.38 (m, 3H), 6.53 (d, *J* = 16.0 Hz, 1H), 5.97 (dd, *J* = 5.2, 2.0 Hz, 1H), 3.40–3.35 (m, 2H), 3.07 (dd, *J* = 11.5, 11.5 Hz, 1H), 2.98 (dd, *J* = 14.2, 5.2 Hz, 1H), 2.80–2.72 (m, 2H); $^{13}C\{^{1}H\}$NMR (126 MHz, $CDCl_3$) δ 165.4, 146.0, 134.2, 130.5, 128.9, 128.2, 117.4, 67.7, 33.4, 28.0, 26.3; IR (film) ν_{max} 3060, 2911, 1713, 1636, 1336, 1151, 977, 768 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{14}O_2S_2Na$ $[M+Na]^+$ 289.0333; found 289.0342.

1-Methoxybutyl benzoate and Butoxymethyl benzoate (35a and 35b) (as a mixture of regioisomers). Colorless oil (120 mg, 23%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12–8.03 (m, 4H), 7.59–7.54 (m, 2H), 7.48–7.42 (m, 4H), 6.02 (t, *J* = 5.4 Hz, 1H), 5.54 (s, 2H), 3.72 (t, *J* = 6.6 Hz, 2H), 3.47 (s, 3H), 1.83–1.79 (m, 2H), 1.64–1.58 (m, 2H), 1.51–1.44 (m, 2H), 1.42–1.35 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$NMR (126 MHz, $CDCl_3$) δ 166.3, 166.0,

133.1, 133.1, 130.1, 129.95, 129.7, 129.5, 128.4, 128.4, 100.4, 90.0, 70.4, 56.7, 36.5, 31.5, 19.1, 17.3, 13.8, 13.7; HRMS (ESI) calcd. for $C_{12}H_{16}O_3Na$ $[M+Na]^+$ 231.0997; found 231.0994 for **35a**, calcd. for $C_{12}H_{16}O_3Na$ $[M+Na]^+$ 231.0997; found 231.0993 for **35b**.

1,2-dimethoxyethyl benzoate (36). Colorless oil (158 mg, 30%); ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.4, 1.3 Hz, 2H), 7.56 (tt, J = 7.4, 7.4 Hz, 1H), 7.43 (dd, J = 8.0, 7.6 Hz, 2H), 6.12 (dd, J = 5.2, 4.6 Hz, 1H), 3.62 (dd, J = 10.7, 5.3 Hz, 1H), 3.59 (dd, J = 10.7, 4.6 Hz, 1H), 3.52 (s, 3H), 3.41 (s, 3H); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 166.0, 133.3, 129.8, 129.5, 128.3, 97.4, 72.7, 59.5, 57.1; IR (film) ν_{max} 2940, 1724, 1452, 1273, 1093, 926, 713 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{14}O_4Na$ $[M+Na]^+$ 233.0790; found 233.0783.

1,3-dioxolan-4-yl benzoate (38). Colorless oil (73 mg, 15%); ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.59–7.56 (m, 1H), 7.43 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.58 (dd, *J* = 4.1, 1.9 Hz, 1H), 5.19 (br s, 1H), 5.15 (br s, 1H), 4.17 (dd, *J* = 9.5, 4.2 Hz, 1H), 4.12 (dd, *J* = 9.5, 1.9 Hz, 1H); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 165.8, 133.5, 129.8, 129.4, 128.4, 95.9, 94.6, 70.7; IR (film) ν_{max} 2881, 1728, 1452, 1271, 1092, 922, 712 cm^{-1}; HRMS (ESI) calcd. for $C_{10}H_{10}O_4Na$ $[M+Na]^+$ 217.0477; found 217.0470.

2-methyl-1,3-dioxolan-2-yl benzoate (39a). Colorless oil (270 mg, 52%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.52 (tt, *J* = 6.8, 1.3 Hz, 1H), 7.39 (dd, *J* = 7.8, 7.8 Hz, 2H), 4.48–4.46 (m, 2H), 4.38–4.35 (m, 2H), 2.04 (s, 3H); $^{13}C\{^1H\}$NMR (120 MHz, $CDCl_3$) δ 170.6, 166.1, 133.0, 129.6, 129.5, 128.2, 62.5, 62.0, 20.6; IR (film) ν_{max} 2960, 1743, 1722, 1452, 1375, 1278, 1232, 1062, 712 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{12}O_4Na$ $[M+Na]^+$ 231.0633; found 231.0628.

***trans*-2-methyl-1,3-dioxolan-4-yl benzoate (39b).** Colorless oil (52 mg, 10%); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58 (tt, *J* = 6.9,1.3 Hz, 1H), 7.44 (dd, *J* = 8.0, 8.0

Hz, 2H), 6.57 (dd, *J* = 4.8, 2.7 Hz, 1H), 5.37 (q, *J* = 4.8 Hz, 1H), 4.37 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.01 (dd, *J* = 9.5, 2.7 Hz, 1H), 1.45 (d, *J* = 4.9 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, CDCl3) δ165.8, 133.5, 129.8, 129.5, 128.4, 102.4, 95.5, 71.0, 19.2; IR (film) ν_{max} 2994, 2894, 1729, 1452, 1272, 1158, 1057, 981, 712 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{12}O_4Na$ $[M+Na]^+$ 231.0633; found 231.0626.

***cis*-2-methyl-1,3-dioxolan-4-yl benzoate (39c).** Colorless oil (21 mg, 4%); ^{1}H NMR (400 MHz, $CDCl_3$) δ8.05 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58 (tt, *J* = 6.9,1.3 Hz, 1H), 7.45 (dd, *J* = 7.9, 7.9 Hz, 2H), 6.52 (d, *J* = 3.6 Hz, 1H), 5.31 (q, *J* = 4.9 Hz, 1H), 4.32 (d, *J* = 9.8 Hz, 1H), 4.02 (dd, *J* = 9.8, 3.7 Hz, 1H), 1.51 (d, *J* = 4.9 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, CDCl3) δ165.9, 133.4, 129.8, 129.7, 128.4, 104.6, 94.9, 71.6, 21.2; IR (film) ν_{max} 2999, 2884, 1726, 1272, 1157, 1067, 1024, 981, 712 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{12}O_4Na$ $[M+Na]^+$ 231.0633; found 231.0634.

Tetrahydrothiophen-2-yl benzoate (40). Yellowish amorphous solid (96 mg, 46%); ^{1}H NMR (500 MHz, $CDCl_3$) δ8.01 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.56–7.52 (m, 1H), 7.43–7.40 (m, 2H), 6.42 (dd, *J* = 4.8, 1.4 Hz, 1H), 3.07 (ddd, *J* = 9.8, 7.1, 2.3 Hz, 1H), 2.86 (ddd, *J* = 10.4, 10.4, 6.2 Hz, 1H), 2.46–2.42 (m, 1H), 2.31–2.24 (m, 1H), 2.21–2.11 (m, 1H), 2.06–1.98 (m, 1H); $^{13}C\{^{1}H\}$NMR (126 MHz, $CDCl_3$) δ166.0, 133.0, 130.1, 129.6, 128.3, 83.6, 37.4, 32.4, 28.4; IR (film) ν_{max} 2961, 2936, 1717, 1451, 1269, 1096, 1025, 921, 710 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{12}O_2SNa$ $[M+Na]^+$ 231.0456; found 231.0453.

1,4-oxathian-3-yl benzoate (41a). White amorphous solid (308 mg, 55%); ^{1}H NMR (500 MHz, $CDCl_3$) δ8.12 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.57 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.45 (dd, *J* = 7.8, 7.8 Hz, 2H), 5.79 (br s, 1H), 4.27 (br s, 1H), 4.24 (br s, 1H), 4.02 (dd, *J* = 12.6, 1.7 Hz, 1H), 3.86 (ddd, *J* = 11.8, 11.8, 2.0 Hz, 1H), 3.39–3.34 (m, 1H), 2.30 (br d, *J* = 13.6 Hz, 1H); $^{13}C\{^{1}H\}$NMR (126 MHz, $CDCl_3$) δ165.35, 133.3, 129.9, 129.8, 128.4, 71.2, 68.7, 68.0, 23.5; IR (film) ν_{max} 3063,

2952, 2854, 1719, 1451, 1262, 1097, 1008, 711 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{12}O_3SNa$ $[M+Na]^+$ 247.0405; found 247.0404.

1,4-oxathian-2-yl benzoate (41b). White amorphous solid (84 mg, 15%); ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, J = 8.4, 1.3 Hz, 2H), 7.58–7.56 (m, 1H), 7.45 (dd, J = 7.7., 7.7 Hz, 2H), 6.17 (br s, 1H), 4.35 (br s, 1H), 4.01 (br s, 1H), 2.83 (br s, 2H), 2.64 (br s, 2H); $^{13}C\{^1H\}$NMR (126 MHz, $CDCl_3$) δ 164.7, 133.4, 129.86, 129.5, 128.4, 91.2, 66.0, 29.5, 25.8; IR (film) ν_{max} 3063, 2920, 1728, 1452, 1269, 1062, 955 cm^{-1}; HRMS (ESI) calcd. for $C_{11}H_{12}O_3SNa$ $[M+Na]^+$ 247.0405; found 247.0402.

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Notes

The authors declare no competing financial interest.

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ASSOCIATED CONTENT

Supporting information

Physical characterization of the catalyst and NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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