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ARTICLE

One-pot and Odorless Thia-Michael Reaction by Copper Ferrite Nanoparticles Catalyzed Reaction of Elemental Sulfur, Aryl Halides and Electron-deficient Alkenes

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In this article, we report a non-odorous protocol for the high yielding generation of aryl-alkyl sulfides from the reaction of aryl iodides, bromides and boronic acids with elemental sulfur and electron-deficient alkenes catalyzed by copper ferrite nanoparticles. The catalyst could be easily separated by an external magnetic bar and recycled for consecutive runs with preserving its catalytic activity.

Introduction

Aryl sulfide moieties are present in the structure of various numbers of medicines which are employed for Alzheimer, Parkinson, diabetes, immune and inflammatory diseases.[1] Therefore, reactions leading to generation of carbon–sulfur bonds formation is of importance for the synthesis of numerous pharmaceutically and biologically active compounds. Among the different types of reactions leading to carbon-sulfur bonds, the thia-Michael addition is one of the most versatile and practical ones for preparation of sulfides bearing varieties of functional groups such as –CN, -$CONH_2$, -OH, -COOR, etc.[2] The resultant β-sulfido carbonyl compounds from the reaction of aliphatic or aromatic thiols with α,β-unsaturated ketones provides a strategy for the chemoselective protection of C=C bonds.[3] These compounds work as starting materials for the generation of β-acylvinyl cation equivalents and homoenolate equivalents. Thia-Michael reaction proceeds in the presence of both acidic and basic catalysts for the direct addition of thiols to Michael acceptors. In literature, ionic liquids such as molten tetrabutyl ammonium bromide[4] or 1-pentyl-3-methyl imidazolium bromide,[5] heterogeneous catalysts such as KF/Al_2O_3,[6] perchloric acid impregnated on silica gel,[7] montmorillonite clay[8] and heteropolyacids,[9] silica sulfuric acid,[10] borax, boric acid,[11] and Nafion SAC-13[12] are reported to catalyze direct addition of thiols to α,β-unsaturated compounds. By the discovery of copper-catalyzed Ullmann coupling reaction[13] an important achievement was attained for the construction of sp^2 carbon-sulfur bond in organic synthesis. However, the Ullmann coupling reactions are known to suffer from high reaction temperatures and low functional group tolerance. Moreover, the C–S coupling reactions are mostly carried out in the presence of expensive, toxic, flammable organic solvents and their disposal becomes a serious problem for the chemical industries[13]. In recent years, serious attention has been paid to reduce the aforementioned problems. For this purpose, the catalytic activity of different transition metals such as palladium,[14] nickel,[15] cobalt,[16] copper,[17] indium,[18] iron,[19] and manganese salts[20] have been studied under milder reaction conditions.

Although these efforts have solved some of the mentioned problems associated with classic Ullmann reaction, however, main drawback which is the use of volatile and foul smelling thiols is still a real obstacle. Therefore, introduction of new strategies for catalytic aryl carbon–sulfur bond formation leading to more economical, more competent and eco-friendly protocols have been under severe considerations. Along this line of efforts, recently our group reported odorless carbon-sulfur bond formation reactions in water and polyethylene glycol.[21] After appearance of these reports, many researchers have become interested in odorless C-S bond formation reactions and published articles in this respect.[22] However, despite the efficiency of the reported methods, they are applicable to alkyl and benzyl halides under homogeneous reaction conditions in which the catalysts are not recoverable.

In addition, in all the reported protocols, less attention has been paid to the development of the odorless thia-Michael reaction.[24] In recent years, preparation of magnetically separable catalysts has been well explored.[25] Among the different magnetic compounds, $CuFe_2O_4$ NPs has shown versatile catalytic activities in different organic transformations.[26] Recently, $CuFe_2O_4$ NPs as a heterogeneous catalyst for odorless thia etherification reaction has been reported.[27] Very recently, palladium nanoparticles in the presence of $CuFe_2O_4$ has been also reported as a magnetically separable heterogeneous catalyst for cyanation of aryl halides[28] and Sonogashira coupling reaction.[29]

Among the reported sulfur surrogates, elemental sulfur is one of the easily available and a cheap sulfur source for the formation of thiolate moiety[23] and as the result for C-S bond formation. Now in this context, new efficient and odorless strategy for thia-Michael reaction using magnetically separable $CuFe_2O_4$NPs catalyzed one-pot reaction of aryl halides, elemental sulfur and *α,β*-unsaturated compounds to generate different aryl alkyl sulfides is described.

Results and discussion

$CuFe_2O_4$NPs was synthesized by a procedure reported in the literature using $Fe(NO_3)_3.9H_2O$ and $Cu(NO_3)_2.3H_2O$ salts.[26n] The structure of $CuFe_2O_4$NPs was characterized using transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis. TEM image of $CuFe_2O_4$NPs showed the average size of particles to be in the range of 40-60 nm and XRD revealed the characteristic peaks related to $CuFe_2O_4$NPs according to JCPDS file No. 34-0425.25.

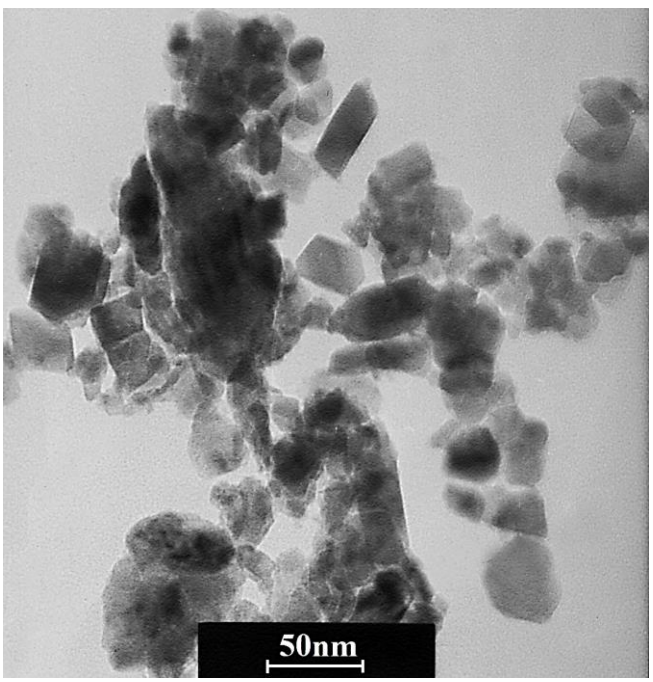


Fig 1. TEM image of the prepared $CuFe_2O_4$NPs

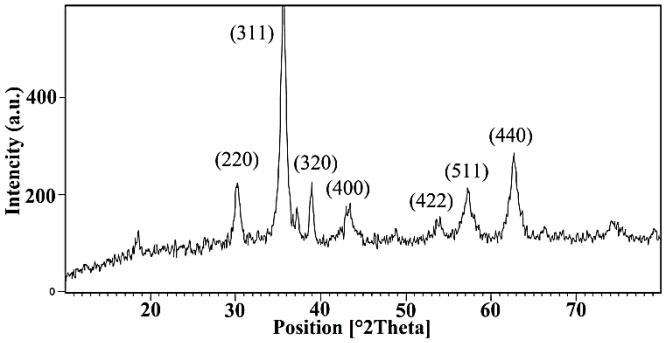
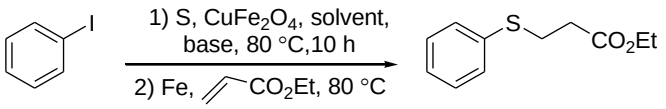


Fig. 2 XRD pattern of the prepared $CuFe_2O_4$NPs.

Preliminary, the reaction of iodobenzene with elemental sulfur powder, Fe powder and *n*-butyl acrylate in the presence of the catalyst was selected as a model reaction to optimize the reaction conditions with respect to solvents and bases (Table 1).

Table 1. Optimization of the reaction conditions[a] using iodobenzene with elemental sulfur and *n*-butyl acrylate as a model reaction.[a]



80 °C, 5 h

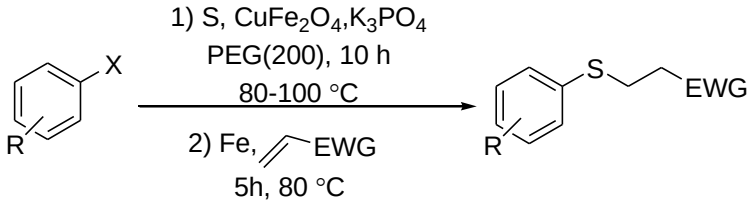
Entry	Solvent	base	Yield(%)[b]
1	DMF	K_2CO_3	58
2	DMF	K_3PO_4	75
3	Toluene	K_2CO_3	2
4	Toluene	K_3PO_4	10
5	H_2O	K_2CO_3	30
6	PEG (200)	K_2CO_3	84
7	Dioxane	K_2CO_3	6
8	CH_3CN	K_2CO_3	8
9	PEG (200)	NaOAc	24
10	PEG (200)	DABCO	5
11	**PEG (200)**	**K_3PO_4**	**94**
12	PEG (200)	K_3PO_4	6[c]
13	H_2O	K_3PO_4	35

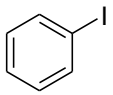
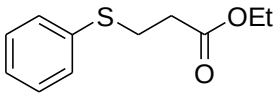
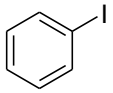
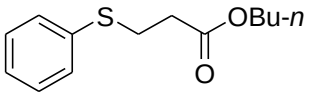
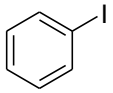
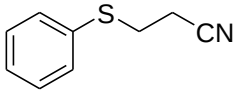
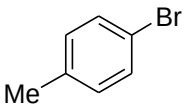
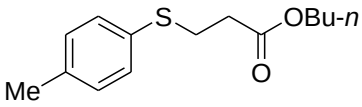
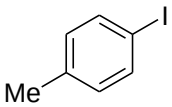
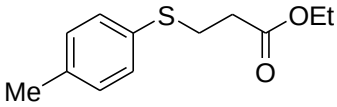
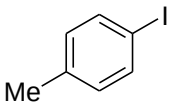
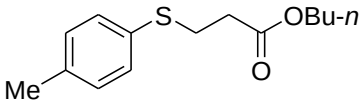
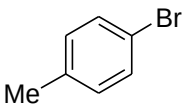
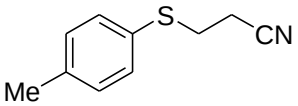
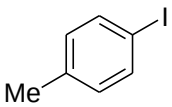
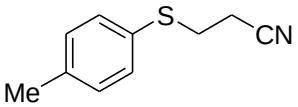
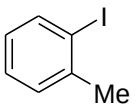
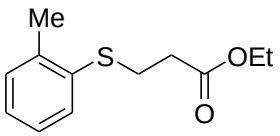
[a] Reactions were performed on a 0.5 mmol scale. [b] Yields were determined by GC. [c] Reaction in the absence of $CuFe_2O_4$ NPs.

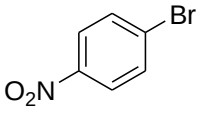
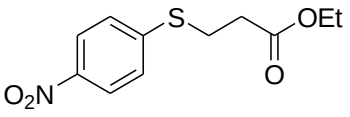
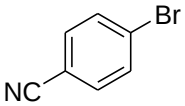
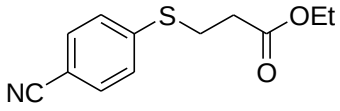
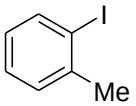
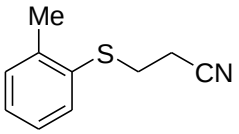
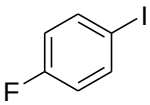
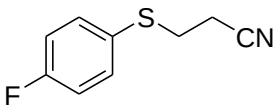
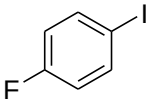
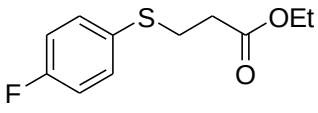
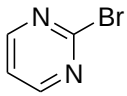
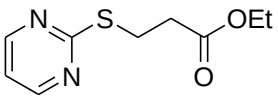
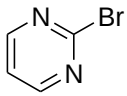
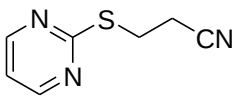
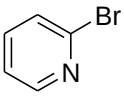
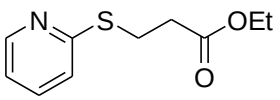
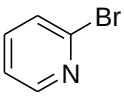
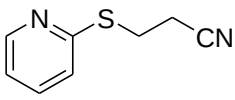
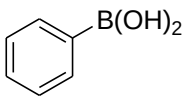
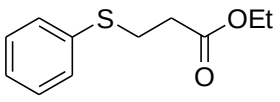
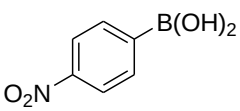
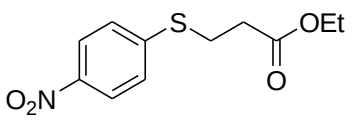
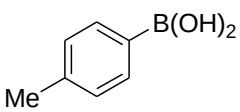
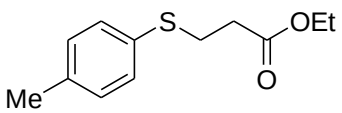
The results of Table 1 indicate that using PEG (200) as a safe and eco-friendly solvent and K_3PO_4 as a base at 80 °C is the most efficient reaction conditions. Study of the model reaction under optimized reaction conditions in the absence of catalyst afforded only 6% GC yield (Table 1, entry 12). The scope of the reaction was further expanded for the reactions of structurally varied aryl compounds [I, Br, $B(OH)_2$] with sulfur element and *α,β*-unsaturated compounds under the obtained optimized reaction conditions (Table 2). The results of Table 2 indicate that aryl iodides were reacted efficiently and the desired sulfides were obtained in excellent yields. However, the reaction of aryl bromides at 80 °C was sluggish therefore; the reaction temperature was raised to 100 °C. Under this condition, the reaction of aryl bromides was performed well and the corresponding aryl alkyl sulfides were obtained in high to excellent yields. In addition, the reactions of arylboronic acid derivatives were also studied under the optimized conditions at 80 °C. The reactions were proceeded smoothly to produce the desired aryl alkyl sulfides in high yields (Table 2). The presence of electron withdrawing groups at the *para*-position of the aryl halides give higher yields compared to electron

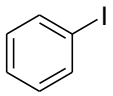
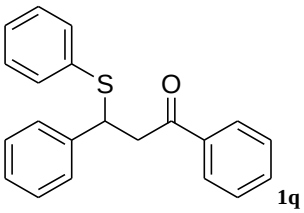
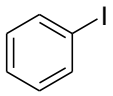
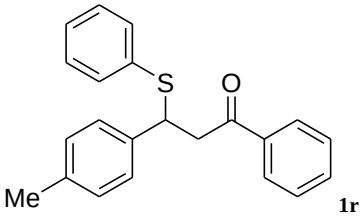
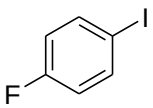
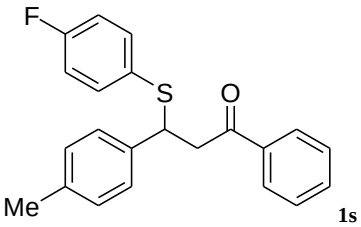
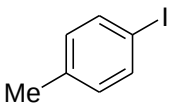
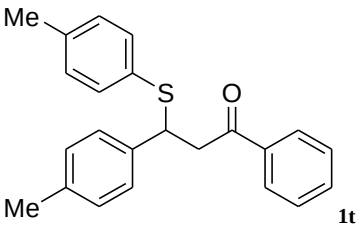
donating groups at the *para*-position. Also, results of Table 2 indicated that structurally different electron-deficient alkenes such as ethyl acrylate, *n*-butyl acrylate, acrylonitrile, chalcone, and 4-methylchalcone were reacted efficiently as thia-Michael acceptors. However, our studies show that the protocol was not successful for aryl chlorides even at higher temperatures.

Table 2. Thia-Michael addition reaction of aryl compounds with electron-deficient alkenes for the synthesis of aryl alkyl sulfides using sulfur element as a sulfur surrogate catalyzed by $CuFe_2O_4$.



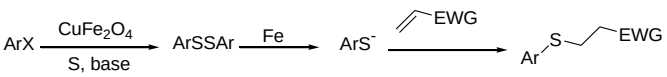
Entry	ArX	Michael acceptor	Product	Isolated Yield (%)[a]
1		Ethyl acrylate	 **1a**	86
2		*n*-Butyl acrylate	 **1b**	84
3		Acrylonitrile	 **1c**	87
4		*n*-Butyl acrylate	 **1d**	80 (2)[b]
5		Ethyl acrylate	 **1e**	81
6		*n*-Butyl acrylate	 **1d**	84
7		Acrylonitrile	 **1f**	84
8		Acrylonitrile	 **1f**	83
9		Ethyl acrylate	 **1g**	77

10		Ethyl acrylate	 **1h**	91
11		Ethyl acrylate	 **1i**	89
12		Acrylonitrile	 **1j**	80
13		Acrylonitrile	 **1k**	92
14		Ethyl acrylate	 **1l**	87
15		Ethyl acrylate	 **1m**	86
16		Acrylonitrile	 **1n**	89
17		Ethyl acrylate	 **1o**	79
18		Acrylonitrile	 **1p**	82
19		Ethyl acrylate	 **1a**	80
20		Ethyl acrylate	 **1h**	87
21		*n*-Butyl acrylate	 **1e**	82

22		Chalcone	 **1q**	80
23		4-Methylchalcone	 **1r**	74
24		4-Methylchalcone	 **1s**	75
25		4-Methylchalcone	 **1t**	72

[a] Reaction condition: $CuFe_2O_4$ (12 mg, 5 mol%), ArX (1 mmol), S (48 mg, 3 mmol), Fe (1 mmol), alkene (1.5 mmol) and PEG 200 (2 mL). [b] GC yield in the absence of catalyst.

We believe a reasonable reaction pathway of the reaction is similar with the reported mechanism in which, in the first step, the reaction of aryl compounds with sulfur in the presence of the catalyst and a base proceeded with the formation of diaryl disulfides.[23d] In the second step, cleavage of S-S bond by the addition of iron powder occurs to produce the thiolate moiety[30] that easily reacts with the electron deficient alkenes (Scheme1).



Scheme 1. Proposed reaction pathway

The stability and reusability are significant factors for assessing the performance of the heterogeneous catalysts. We have studied recyclability of the catalyst for the reaction of iodobenzene with elemental sulfur and ethyl acrylate under optimized reaction conditions. After completion of reaction, the catalyst was easily separated by an external magnet which after washing with diethyl ether and drying, was charged again into another batch of the reaction. The recycling process was repeated for 5 consecutive runs with small drops in catalytic activity (Figure. 3).

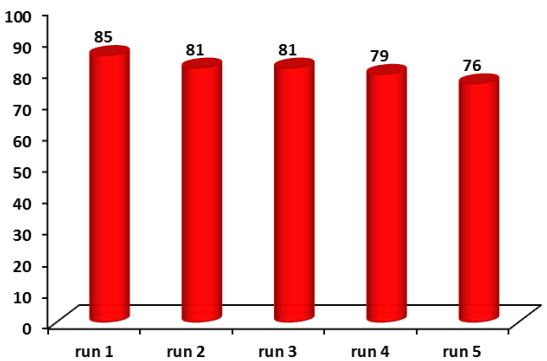
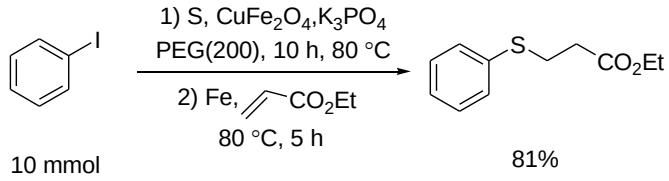


Fig. 3. The recycling of $CuFe_2O_4$NPs for the reaction of iodobenzene with elemental sulfur and ethyl acrylate under the optimized reaction conditions.

The procedure is also suitable for laboratory large scale operation. For this purpose, 10 mmol (2.04g) of iodobenzene was reacted under the optimized condition to give the desired aryl alkyl sulfide in 81% isolated yield as presented in Scheme 2.



Scheme 2. The laboratory large scale operation using iodobenzene, sulfur element, the catalyst and ethyl acrylate in PEG (200).

Conclusions

In conclusion, in this report, we have introduced a new strategy for the synthesis of aryl-alkyl sulfides from the reaction of aryl iodides, bromides and boronic acids with elemental sulfur and electron-deficient alkenes using iron powder as a reducing agent catalyzed by copper ferrite nanoparticles under none odorous conditions. The strong points of the introduced protocol are: a) separation of the catalyst from the reaction mixture by an external magnetic field makes the isolation of the products from the reaction mixture an easy process, b) the use of a cheap and a highly available sulfur powder as the source of sulfur atom makes the process more attractive from economical points of views, c) the protocol is applicable for large-scale operation, d) the catalyst is recyclable which has been applied in several consecutive runs without noticeable change in its catalytic activity and e) the reactions were proceeded under non-odorous conditions in PEG (200) as an eco-friendly media. We believe this protocol is a highly useful addition to the available non-odorous procedures for the high yielding preparation of aryl-alkyl sulfides. By this protocol, aryl chlorides which are much cheaper than their corresponding bromides and iodides do not undergo the reaction. This may be considered as a weak point of the presented procedure.

Experimental:
All chemicals were purchased from Sigma-Aldrich, Acros and Merck Chemical Companies and were used without further purification. Column chromatography was carried out on silica gel 60 Merck (230-240 mesh) in glass columns (2 or 3 cm diameter) using 15-30 grams of silica gel per one gram of the crude mixture. ^{1}H NMR was recorded at 400 MHz and ^{13}C NMR was recorded at 100 MHz in $CDCl_3$ using TMS as internal standard. X-ray diffraction (XRD) was recorded on Philips X'PertPro. The size of the particles of the catalyst was determined by transmission electron microscopy using Philips CM-120 instrument.

General procedure for the preparation of aryl alkyl sulfides from aryl compounds
$CuFe_2O_4$ (12 mg, 5 mol%), aryl compound (1 mmol), S (3 mmol), and PEG(200) (2 mL) were added to a flask equipped with a magnetic bar. The resulting mixture was vigorously stirred magnetically for 10 h at 80 °C for aryl iodides and boronic acids and at 100 °C for aryl bromides. Then, iron powder (1 mmol) and the alkene (1.5 mmol) were added and the resulting mixture was stirred for 5 h. After completion of the reaction (5 h), the resulting reaction mixture was cooled to room temperature. The catalyst was separated by an external magnet from the mixture and the produced crude product was extracted with EtOAc which after flash column chromatography on silica gel (EtOAc/*n*-hexane) afforded the highly pure aryl alkyl sulfides in 72-92 isolated yields (Table 2).

1a: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.39 (m, 2H), 7.34-7.30(m, 2H), 7.25-7.21 (m,1H), 4-19-4.14 (m, 2H), 3.19 (t, 2H, *J*= 7.6), 2.64 (t, 2H, *J*= 7.6), 1.28 (t, 3H, *J*= 6.8).^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.76, 135.30, 130.11, 129.04, 126.56, 60.74, 34.48, 29.08, 14.21.

1b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, 2H, *J*= 7.2), 7.34-7.31 (m, 2H), 7.26-7.22 (m, 1H), 4.11 (t, 2H, *J*= 6.8), 3.20 (t, 2H, *J*= 7.2), 2.65 (t, 2H, 7.2), 1.67-1.59 (m, 2H), 1.45-1.35 (m, 2H), 0.96 (t, 3H, *J*= 7.2).^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.88, 135.28, 130.09, 129.05, 126.56, 64.68, 34.46, 30.62, 29.09, 19.15, 13.74.

1c: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, 2H, *J*= 7.2), 7.38-7.29 (m, 3H), 3.14 (t, 2H, *J*= 7.2), 2.61 (t, 2H, *J*= 7.2).^{13}C NMR ($CDCl_3$, 101 MHz): δ 133.19, 131.44, 129.45, 127.78, 118.10, 30.26, 18.29.

1d: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (d, 2H, *J*= 8), 7.14 (d, 2H, *J*= 8), 4.10 (t, 2H, *J*= 6.4), 3.14 (t, 2H, *J*= 7.2), 2.62 (t, 2H, *J*= 7.2), 2.35 (s, 3H), 1.66-1.59 (m, 2H), 1.44-1.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.93, 136.82, 131.05, 129.82, 64.60, 34.45, 30.64, 29.82, 21.07, 19.l6, 13.75.

1e: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (d, 2H, *J*= 8), 7.13 (d, 2H, *J*= 8), 4.18-4.13 (m, 2H), 3.14 (t, 2H, *J*= 7.2), 2.61 (d, 2H, *J*= 7.6), 2.34 (s, 3H), 1.27 (t, 2H, *J*= 6.8). ^{13}C NMR ($CDCl_3$, 101 MHz): 171.83, 136.82, 131.42, 131.05, 129.82, 60.68, 34.54, 29.78, 21.07, 14.23.

1f: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (d, 2H, *J*= 7.6), 7.18 (d, 2H, *J*= 7.6), 3.09 (t, 2H, *J*= 7.2), 2.58 (d, 2H, *J*= 7.2), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.21, 132.29, 130.21, 129.35, 118.17, 30.89, 21.16, 18.26.

1g: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, 2H, *J*= 8), 7.22-7.13 (m, 3H), 4.20-4.15 (m, 2H), 3.18 (t, 7.2), 2.66 (t, 2H, *J*= 7.6), 2.41 (s, 3H), 1.29 (t, 3H, *J*= 6.8).^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.83, 138.41, 134.58, 130.30,129.08, 126.52, 126.34, 60.76, 34.32, 28.25, 20.47, 14.23.

1h: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17 (d, 2H, *J*= 8.8), 7.39 (d, 2H, *J*= 8.8), 4.23-4.18 (m, 2H), 3.33 (t, 2H, *J*= 7.2), 2.74 (t,

2H, *J*=7.2), 1.30 (t, 2H, *J*= 6.8).^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.19, 146.39, 126.61, 124.13, 61.14, 33.63, 27.05, 14.

1i: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, 2H, *J*= 8.4), 7.36 (d, 2H, *J*=8.4), 4.22-4.16 (m, 2H), 3.28 (t, 2H, *J*= 7.2), 2.70 (t, 3H, *J*= 7.2), 1.29 (t, 3H, *J*= 7.2).^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.25, 143.62, 132.41, 127.33, 118.77, 108.74, 61.06, 33.75, 27.09, 14.20.

1j: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.36 (m, 1H), 7.27-7.17 (m, 3H), 3.14-3.09 (m, 2H), 2.63-2.58 (m, 2H), 2.47 (s, 3H).^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.70, 132.44, 130.82, 130.80, 127.67, 126.83, 118.17, 29.39, 20.60, 18.12.

1k: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.46 (m, 2H), 7.10-7.05 (m, 2H), 3.09 (t, 3H, *J*= 7.2), 2.59 (t, 2H, *J*= 7.2).^{13}C NMR ($CDCl_3$, 101 MHz): δ 164.0, 161.53, 134.72, 134.64, 128.13, 128.09, 117.91, 116.74, 116.52, 31.37, 18.31.

1l: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.37 (m, 2H), 7.03-6.98 (m, 2H), 4.16-4.11 (m, 2H), 3.11 (t, 2H, *J*= 7.2), 2.58 (t, 2H, *J*= 7.2), 1.25 (t, 3H, *J*= 7.2).^{13}C NMR ($CDCl_3$, 101 MHz): δ 171.64, 163.34, 160.88, 133.38, 133.30, 130.08, 130.05, 60.74, 34.44, 30.37, 14.18.

1m: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (d, 2H, *J*= 4.8), 7.01-6.98 (m, 1H), 4.22-4.17 (m, 2H), 3.41 (t, 2H, *J*= 7.2), 2.83 (t, 2H, *J*= 7.2), 1.29 (t, 3H, *J*= 6.8).^{13}C NMR ($CDCl_3$, 101 MHz): δ 172.02, 171.94, 157.35, 116.60, 60.74, 34.37, 25.91, 14.24.

1n: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57(d, 2H, *J*= 4.8), 7.07-7.05 (m, 1H), 3.41 (t, 2H, *J*= 7.2), 2.91 (t, 2H, *J*= 7.2). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 170.63, 157.62, 118.37, 117.18, 26.64, 18.34.

1o: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.45 (d, 1H, *J*= 4.4), 7.52-7.48 (m, 2H), 7.19 (d, 1H, *J*= 8.4), 7.02-6.99 (m, 1H), 4.22-4.16 (m, 2H), 3.46 (t, 2H, *J*= 7.2), 2.80 (t, 2H, *J*= 7.2), 1.29 (t, 3H, *J*= 6.8).^{13}C NMR ($CDCl_3$, 101 MHz): δ 172.16, 158.23, 149.44, 136.03, 122.45, 119.51, 60.68, 34.74, 24.99, 14.24.

1p: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.45 (d, 1H, *J*= 4.4), 7.56-7.51 (m, 1H), 7.22 (d, 1H, *J*= 8), 7.07-7.04 (m, 1H), 3.45 (t, 3H, *J*= 7.2), 2.89 (t, 2H, *J*= 7.2).^{13}C NMR ($CDCl_3$, 101 MHz): δ 156.62, 149.59, 136.28, 122.70, 120.02, 118.67, 25.56, 18.75.

1q: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, 2H, *J*= 7.6), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 2H), 7.39-7.37 (m, 4H), 7.31-7.20 (m, 6H), 5.0 (t, 1H, *J*=7.6), 3.74-3.58 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 197.04, 141.20, 136.74, 134.26, 133.31, 132.78, 128.89, 128.65, 128.50, 128.10, 127.84, 127.57, 127.41, 48.23, 44.71.

1r: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, 2H, *J*= 8), 7.56-7.52 (m, 1H), 7.44-7.45 (m, 2H), 7.34-7.32 (m, 2H), 7.23-7.05 (m, 5H), 7.06 (d, 2H, *J*= 7.6) 4.93 (dd, 1H, *J*= 8.4, *J*= 6,), 3.6-3.51 (m, 2H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 196.93, 137.86, 136.79, 136.42, 134.25, 133.2, 122.21, 129.0, 128.77, 128.52, 127.85, 127.48, 127.3, 47.64, 44.47, 20.95.

1s: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.94 (d, 2H, *J*= 7.2), 7.61-7.57 (m, 1H), 7.49-7.46 (m, 2H), 7.35-7.32 (m, 2H), 7.27-7.21 (m, 2H), 7.11-7.10 (m, 2H), 6.98-6.94 (m, 2H), 4.89 (t, *J*= 6.8, 1H), 3.70-3.57 (m, 2H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 196.97, 163.92, 161.45, 138.08, 137.13, 136.76, 135.87, 135.79, 133.34, 129.22, 128.68, 128.12, 127.69, 116.06, 115.84, 48.88, 44.48, 21.16.

1t: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, 2H, *J*= 6.8), 7.60-7.55 (m, 1H), 7.48-7.44 (m, 2H), 7.31-7.27 (m, 4H), 7.13-7.09 (m, 4H), 4.94 (dd, 1H, *J*= 8.4, *J*= 6), 3.72-3.56 (m, 2H), 2.34 (s, 3H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 197.28, 138.24, 137.75, 136.99, 136.82, 133.33, 133.23, 130.71, 129.71, 129.20, 128.62, 128.12, 127.71, 48.35, 44.73, 21.20, 21.18.

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Notes and references
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