# PIFA-Mediated Esterification Reaction of Alkynes with Alcohols via Oxidative Cleavage of Carbon Triple Bonds

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**Supporting Information** 



**ABSTRACT:** A metal-free esterification of alkynes via  $C \equiv C$  triple bond cleavage has been developed. In the presence of phenyliodine bis(trifluoroacetate), a diverse range of alkyne and alcohol substrates undergoes triple bond cleavage to produce carboxylic ester motifs in moderate to good yields. The transformation is proposed to proceed via hydroxyethanones and ethanediones as intermediates on the basis of mechanistic studies and exhibits a broad substrate scope and good functional group tolerance.

## ■ INTRODUCTION

Carbon-carbon bond cleavage has attracted much attention and is considered as one of the most challenging goals in organic synthesis because of the inherent stability of the carbon-carbon linkages.<sup>1</sup> It is conceptually different from conventional organic synthesis because the existing molecular skeletons can be reorganized through this strategy to construct valuable desired structural units. Among them, various significant and useful processes involving C-C single and double bond cleavage have been extensively developed,<sup>2,3</sup> and the resulting compounds from those methods take a privileged position in the fields of agrochemicals, pharmaceuticals, and materials. However, the cleavage of the C-C triple bond remains very underdeveloped. Most studies on C-C triple bond cleavage, such as alkyne-ligand scission on metal complexes and oxidative cleavage, involved the use of stoichiometric organometallic reagents and oxidants,<sup>4</sup> thereby making their application less desirable. Recently, considerable efforts have been made to approach this goal through transition-metal catalysis, except for metathesis of alkynes.<sup>5</sup> In 2001, Jun reported catalytic C-C triple bond cleavage via the rhodium-catalyzed hydroimino acylation.<sup>6</sup> Subsequently, Yamamoto described the cleavage of divnes through rutheniumcatalyzed hydroamination.<sup>7</sup> Liu discovered that ethynyl alcohol could catalytically be split into alkene and CO by a ruthenium complex. Liu reported the gold-catalyzed cleavage of C-C triple bonds via cascade cyclization/oxidative cleavage.<sup>8</sup> Jiang recently reported the palladium-catalyzed oxidative cleavage of the C-C triple bond with molecular oxygen promoted by Lewis acid.9 Very recently, Jiao developed a silver-catalyzed nitrogenation of alkynes with azidotrimethylsilane (TMSN<sub>3</sub>) as

the nitrogen source through C-C triple bond cleavage.<sup>10</sup> Our group also reported a manganese-catalyzed oxidative rearrangement of internal alkynes to give one-carbon-shorter ketones using molecular oxygen as a terminal oxidant.<sup>11</sup> However, most of the above approaches suffered from harsh reaction conditions, limited substrate scope, and use of precious and/ or toxic metal complex which led to the difficult purification of the desired products from heavy transition-metal impurities. Thus, it is challenging to update these processes for green and sustainable organic synthesis. In this context, C-C triple bond cleavage under metal-free conditions is undoubtedly the ideal and promising route to address the aforementioned challenges. In fact, examples for metal-free cleavage of C-C triple bond cleavage are rare. For example, Tanaka reported a nucleophilic attack on chloro(phenyl)ethyne by azide ion in which some byproducts are formed via the cleavage of the C-C triple bond.<sup>12</sup> Later, Ochiai presented the iodomesitylene-catalyzed oxidative cleavage of C-C triple bonds using m-chloroperbenzoic acid as a terminal oxidant.<sup>13</sup> More recently, Yanada reported the N-iodosuccinimide-mediated direct cleavage of alkynes to nitriles using TMSN<sub>3</sub> as the nitrogen source.<sup>14</sup> Despite some advances, the development of a new, efficient, and safe metal-free method is still highly desirable. Herein, we describe a novel and convenient protocol for the cleavage of C-C triple bonds in the presence of phenyliodine bis(trifluoroacetate) (PIFA) under mild conditions in which alkyne is split into carboxylic ester in various alcohols.

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## RESULTS AND DISCUSSION

Recently, we reported the phenyliodonium diacetate (PIDA)mediated direct synthesis of benzonitriles from styrenes through oxidative cleavage of C-C double bonds in the presence of NH<sub>4</sub>HCO<sub>3</sub>.<sup>15</sup> When the reaction was extended to phenylacetylene, benzonitrile was obtained in only 10% yield. We questioned whether a stronger oxidant PIFA was utilized in place of PIDA that would directly convert phenylacetylene into the desired benzonitrile. When phenylacetylene was carried out with 5.5 equiv of PIFA and 6.0 equiv of NH4HCO3 in CH<sub>3</sub>OH/H<sub>2</sub>O at 60 °C for 12 h, much to our surprise, we found that the product isolated in 46% yield was actually methyl benzoate 2a, not the expected benzonitrile (<5% yield). This unexpected result prompted us to do further investigation. Initially, we chose phenylacetylene in a model reaction to test different reaction conditions. Selected data from this study are listed in Table 1. First, when the reaction was conducted in the

Table 1. Initial Studies toward C-C Triple Bond Cleavage

	)== + сн <sub>з</sub> он 1а	oxidant temp.	$\rightarrow$	2a						
entry	oxidant (equiv)	temp (°C)	<i>t</i> (h)	yield $(\%)^a$						
1	PIFA (2.0)	60	12	36						
2	none	60	12	0						
3	PIFA (2.0)	60	15	43						
4	PIFA (2.0)	60	20	38						
5	PIFA (2.5)	60	15	59						
6	PIFA (3.0)	60	15	74						
7	PIFA (3.5)	60	15	84						
8	PIFA (4.0)	60	15	78						
9	PIDA (3.5)	60	15	<5						
10	PIFA (3.5)	50	15	68						
11	PIFA (3.5)	rt	15	24						
12	PIFA (3.5)	70	15	72						
$13^{b}$	PIFA (3.5)	60	15	81						
<sup>*</sup> Yields are determined by GC. <sup>b</sup> Under N <sub>2</sub> .										

presence of 2.0 equiv of PIFA in CH<sub>3</sub>OH at 60 °C for 12 h, methyl benzoate 2a was obtained in 36% yield (Table 1. entry 1). Control experiments showed that the reaction did not proceed in the absence of PIFA (Table 1, entry 2). Prolonging the reaction time to 15 h increased the yield of 2a to 43% (Table 1, entry 3), whereas further increase of the reaction time did not improve the yield (Table 1, entry 4). The best yield (84%) was achieved when increasing the amount of PIFA to 3.5 equiv (Table 1, entries 5-7), while further increase of PIFA dropped the yield (Table 1, entry 8). We are confident that trace metals are not the cause of the transformation, as reactions performed in new, acid-washed flasks provided a yield similar to those performed in old flasks. Furthermore, reagents from different commercial sources perform similarly. Substituting the oxidant PIFA with PIDA led to very little product (Table 1, entry 9). To achieve a reasonable reaction rate, heating was required (Table 1, entries 10 and 11). Increasing the reaction temperature to 70 °C decreased the yield to 72% (Table 1, entry 12). In addition, methyl benzoate 2a was obtained in 81% yield when the reaction was carried out under an atmosphere of  $N_2$  (Table 1, entry 3). On the basis of these results, we determined the optimized conditions to be PIFA (3.5 equiv), CH<sub>3</sub>OH (1 mL), 60 °C, 15 h. However, when

styrene was subjected to the optimized conditions, methyl benzoate was not detected by GC-MS.

With the optimized reaction conditions in hand, we next sought to define the scope of alkynes and alcohols. As shown in Table 2. various substituents with different electronic features at the phenyl ring showed good to excellent reactivity. Phenylacetylenes bearing electron-donating substituents (Me, Et, Pr, Bu, and MeO) afforded the desired products in 62-86% yield (Table 2, entries 2-8), while phenylacetylenes with electronwithdrawing substituents worked well to produce the corresponding benzoic esters in 65-76% yield (Table 2, entries 9-11). Notably, F (2i), Cl (2j), Br (2k), and MeO (2h) substituents on the phenyl ring were well-tolerated, which enables a potential application in further functionalization.<sup>16</sup> The experimental results indicated that methyl 4-ethynylbenzoate provided the corresponding ester in 63% yield, while 3-hydroxyphenylacetylene and 4-aminophenylacetylene gave a black complex mixture, and the corresponding product was not detected by GC-MS (Table 2, entries 12-14). 3-Ethynylthiophene, which a heteroaryl-substituted substrate, could also be converted into the desired product in 63% yield (Table 2, entry 15). To our delight, aliphatic alkynes readily undergo cleavage reaction to generate the expected carboxylic esters in good yields (Table 2, entries 16 and 17, 83 and 78% yield). In addition, symmetrical and unsymmetrical internal alkynes were included in this study. The symmetrical internal alkynes produced the same product in moderate yields (Table 2, entries 18 and 19, 90 and 72% yield), while the unsymmetrical internal alkynes were cleaved to two different products (Table 2, entries 20-23, 53-62% yield). Moreover, reaction of phenylacetylene with diverse alcohols such as ethanol, *n*-propyl alcohol, *i*-propyl alcohol, and *n*-butyl alcohol proceeded smoothly to provide the corresponding benzoic esters in moderate yields (Table 2, entries 24-27, 65-78% yield). As expected, 4-methylphenylacetylene also efficiently reacted with ethanol to give the desired ethyl 4-methylbenzoate in 74% yield (Table 2, entry 28).

To investigate the possible one-carbon product resulting from terminal alkynes, reaction of phenylacetylene was carried out in methanol under the optimized conditions. After the reaction, dimethoxymethane as another product was detected in the solvent by GC-MS. Likewise, diethoxymethane as another product was also detected by GC-MS in the reaction of phenylacetylene with ethanol. However, under the optimized conditions, treatment of phenylacetylene with *i*-propyl alcohol, *n*-propyl alcohol, and *n*-butyl alcohol provided *i*-propyl formate, *n*-propyl formate, and *n*-butyl formate as another product, respectively (for details, see the Supporting Information).

To get more information on the reaction mechanism, control experiments with possible intermediates were designed and investigated. The reactions performed well in the presence of BHT (2,6-di-*tert*-butyl-4-methylphenol), producing the desired product methyl benzoate **2a** in 78% yield, which may exclude a radical process in this transformation (Scheme 1a). Furthermore, when benzyl alcohol **4**, benzaldehyde **5**, and benzoic acid **6** were employed as the substrates, the reactions provided the desired ester **2a** in 12, 16, and <1% yield, respectively (Scheme 1b–d). These results might exclude **4**, **5**, or **6** as the possible intermediates of this metal-free C–C triple bond cleavage reaction. The above results indicate that the ester products **2** and **3** should be generated simultaneously in the reaction processes.

Table 2. Substrate Scope of the Oxidative Esterification of Alkynes with Various Alcohols<sup>a</sup>

		R <sub>1</sub> R <sub>2</sub>	+ R <sub>3</sub> -OH	PhI(OCC	$OCF_3)_2$		3 + R.	R R	
		1				2	12	3	
Entry	Alkyne	R <sub>3</sub> -OH	Product	Yield (%)	Entry	Alkyne	R <sub>3</sub> -OH	Product	Yield (%)
1		≡ MeOH	соом	e 82	16	1p	MeOH ≻		83 <sup>b</sup>
2		≡ MeOH -	- Соом	e <sup>78</sup>	17		MeOH ·		78 <sup>b</sup>
3		≡ MeOH	Д-соом	e 74 2c	18 <sup>c</sup> 〈		MeOH		90
4	Et-	≡ MeOH E	/ t-∕{_}_COON	<b>/le</b> 68	19 <sup>c</sup>	<u> </u>	≻ MeOH	COOMe 2s	72 <sup>b</sup>
5	Pr-	≡ MeOH P	r-<	2d	20 <sup>c</sup>	() <u> </u>	MeOH {		62 <sup>b</sup>
6	Bu-	≡ MeOHΒι	и-Соом	2e le <sup>62</sup> 2f			ſ		58 <sup>b</sup>
7		≡ MeOH 🦄	соом	le <sup>64</sup> 2g	21 <sup>c</sup>	< <u> </u>	t MeOH	COOMe 3u	57 <sup>b</sup>
8 <b>N</b>	leO-	≡ MeOH M	eo-{	0Me 86 2h	22 <sup>c</sup>	( )	r MeOH		53 <sup>b</sup>
9	F-	≡ MeOH I	=-{	le 65 2i		\ <b>─</b> ∕ 1v	l	COOMe 3v	52 <sup>b</sup>
10		≡ MeOH C	I{_}-coon	¶e 73 2j	23 <sup>c</sup>	————————————————————————————————————	u MeOH		54 <sup>b</sup>
11	Br	≡ MeOH B	r-{_}-COON	le 76 2k		₩ 1w	(		54 <sup>5</sup>
12	$\rightarrow$	⊖ ■ MeOH		∕le <sub>63</sub>	24		EtOH		78
M 13		' MeO ≡ MeOH		/e 0	25		<i>n</i> PrOH		72
	) <sup>∕</sup> 1m HO		но	2m	26		<i>i</i> PrOH		67
14	H <sub>2</sub> N-	≡ MeOH H	2N- <coo< td=""><td>Me <sup>0</sup> 2n</td><td>27</td><td>✓</td><td><i>n</i>BuOH</td><td>COOBu</td><td>65 /</td></coo<>	Me <sup>0</sup> 2n	27	✓	<i>n</i> BuOH	COOBu	65 /
15	S 10	≡ MeOH	sू∕–соом	e 63 20	28	{	EtOH-		74

<sup>*a*</sup>Reaction conditions: alkynes (0.3 mmol), PIFA (3.5 equiv), R<sub>2</sub>-OH (1 mL), 60 °C, 15 h. <sup>*b*</sup>GC yields. <sup>*c*</sup>Reaction conditions: alkynes (0.3 mmol), PIFA (5.0 equiv), CH<sub>3</sub>OH (1 mL), 65 °C, 15 h. <sup>*d*</sup>3t was detected by GC-MS.

The results in Table 2 show that the ester products 2 and 3 were produced in similar yields. The data of Table 3 indicate that the ester products 2 are stable under the standard conditions because all the recovered yields of 2 are nearly 100% (Table 3). The above results further support the hypothesis that a pathway for the simultaneous formation of ester products 2 and 3 may be involved in the reaction processes.

To further probe the mechanism, we also tried to catch some intermediates by GC-MS. During the reaction, two key intermediates,  $\alpha$ -hydroxyacetophenone 7 and 1-phenyl-1,2-propanedione 8, were observed, respectively, by GC-MS in the initial stage of phenylacetylene and 1-phenylpropyne reaction (see the Supporting Information). Both species can be directly transformed into the desired methyl benzoate in good yields in the presence of PIFA (Scheme 1e,f). Furthermore, phenylglyoxal was subjected to the standard reaction conditions, and the desired methyl benzoate was obtained in good yield (Scheme 1g). The data indicate that the cleavage reaction proceeds via 7, 8, and 9 as intermediates.

Based on these preliminary results and related reports,<sup>17</sup> a plausible mechanism for this cleavage is proposed (Scheme 2). Initially, the alkyne is activated by the PIFA to form A.<sup>17i,j</sup> Subsequent attack by trifluoroacetate anion generates complexe **B**,<sup>171</sup> which was supported by the isolation of byproduct  $\alpha$ -methoxyacetophenone **10** (Scheme 1h), and the intermediate **B** could form the cyclic intermediate **C**, which had also been

proposed by Li et al.<sup>17i</sup> and Gade et al.<sup>17j</sup> in a similar hypervalent iodine(III) species/alkene system. The cyclic cation is further converted into hydroxyethanone D,<sup>17m</sup> which undergoes oxidation to afford ethanedione E.<sup>17n</sup> Further oxidative fragmentation of E would produce the desired 2 with the formation of 3 as another product. However, when  $R_2$  was hydrogen and  $R_3$  was methyl or ethyl, the E undergoes cleavage to produce the desired 2 with the formation of acetal G as another product.

## CONCLUSION

In summary, we have demonstrated that the metal-free cleavage of C-C triple bonds proceeds efficiently in various alcohols in the presence of phenyliodine bis(trifluoroacetate) (PIFA), affording carboxylic esters in moderate to good yields. This transformation exhibits broad substrate scope and good functional group tolerance. Mechanistic studies show that the cleavage reaction proceeds via hydroxyethanones and ethanediones as intermediates. Further investigation of the detailed mechanism and relevant reactions is currently underway.

#### EXPERIMENTAL SECTION

**General Comments.** All reagents and solvent used were obtained commercially and used without further purification unless indicated otherwise. All products were characterized by GC-MS, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. Mass spectra were measured on a mass instrument (EI).

#### Scheme 1. Control Experiments



Analyses of the yield and conversion of phenylacetylene were performed by gas phase chromatography, using a RTX-5 capillary column and a framei onization detector (FID). <sup>1</sup>H NMR spectra were recorded on 400 MHz in CDCl<sub>3</sub>, and <sup>13</sup>C {<sup>1</sup>H} NMR spectra were recorded on 100 MHz in CDCl<sub>3</sub> using TMS as internal standard. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quintet), and m (multiplet), and coupling constants (*J*) are reported in hertz. Copies of <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra are provided as Supporting Information.

General Procedure for the Esterification Reaction of Alkynes with Alcohols. A 10 mL sealed tube was charged with alkynes (0.3 mmol), PIFA (1.05 mmol, 451.5 mg), and alcohols (1 mL). The reaction was stirred at 60 °C for 15 h. The reaction mixture was then allowed to cool to room temperature, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the corresponding carboxylic esters.

**Methyl Benzoate (2a):**<sup>9</sup> Obtained as colorless oil from 1a, 1r, 1t, 1u, 1v, and 1w in 82% (33.5 mg), 90% (36.7 mg), 62% (25.3 mg), 58% (23.7 mg), 53% (21.6 mg), and 54% (22.0 mg) yield, respectively; flash chromatography (petroleum ether/ethyl acetate, 12/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  3.90 (s, 3 H), 7.42 (t, *J* = 8.0 Hz, 2 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  52.0, 128.4, 129.6, 130.2, 132.9, 167.1 ppm. All spectral data correspond to those given in the literature.





"Reaction conditions: 2 (0.3 mmol), PIFA (3.5 equiv), CH<sub>3</sub>OH (1 mL), 60 °C, 15 h.

**Methyl 4-Methylbenzoate (2b):**<sup>9</sup> Following general procedure, the product was isolated as colorless oil in 78% (35.1 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 10/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  2.38 (s, 3 H), 3.88 (s, 3 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.92 (d, *J* = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  21.6, 52.0, 127.3, 129.0, 129.5, 143.5, 167.1 ppm. All spectral data correspond to those given in the literature.

**Methyl 3-Methylbenzoate (2c):**<sup>18a</sup> Following general procedure, the product was isolated as colorless oil in 74% (33.3 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 20/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  2.38 (s, 3 H), 3.89 (s, 3 H), 7.29–7.36 (m, 2 H), 7.82–7.85 (m, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  21.2, 52.0, 126.7, 128.2, 130.0, 130.1, 133.6, 138.1, 167.2 ppm. All spectral data correspond to those given in the literature.

**Methyl 4-Ethylbenzoate (2d):**<sup>18b</sup> Following general procedure, the product was isolated as colorless oil in 68% (33.5 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 15/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.25 (t, J = 8.0 Hz, 3 H), 2.70 (q, J = 8.0 Hz, 2H), 3.90 (s, 3 H), 7.26 (d, J = 8.0 Hz, 2 H), 7.96 (d, J = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  15.4, 29.0, 52.0, 127.6, 127.9, 129.7, 149.8, 167.2 ppm. All spectral data correspond to those given in the literature.

**Methyl 4-Propylbenzoate (2e):**<sup>18c</sup> Following general procedure, the product was isolated as colorless oil in 67% (35.8 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 20/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.93 (t, J = 8.0 Hz, 3 H), 1.60–1.69 (m, 2 H), 2.62 (t, J = 8.0 Hz, 2H), 3.89 (s, 3 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.95 (d, J = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  13.7, 24.2, 38.0, 52.0, 127.6, 128.4, 129.6, 148.2, 167.2 ppm. All spectral data correspond to those given in the literature.

**Methyl 4-Butylbenzoate (2f):**<sup>18d</sup> Following general procedure, the product was isolated as colorless oil in 62% (35.7 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 20/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.92 (t, J = 8.0 Hz, 3 H), 1.31–1.37 (m, 2 H), 1.56–1.62 (m, 2 H), 2.64 (t, J = 8.0 Hz, 2 H), 3.89 (s, 3 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.95 (d, J = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  13.9, 22.3, 33.3, 35.7, 52.0, 127.5, 128.4, 129.6, 148.4, 167.1 ppm. All spectral data correspond to those given in the literature. **Methyl 4-Pentylbenzoate (2g):**<sup>18e</sup> Following general procedure,

Methyl 4-Pentylbenzoate (2g):<sup>18e</sup> Following general procedure, the product was isolated as colorless oil in 64% (39.5 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 20/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.88 (t, J = 8.0 Hz, 3 H), 1.30–1.34 (m, 4 H), 1.60–1.65 (m, 2 H), 2.64 (t, J = 8.0 Hz, 2H), 3.89 (s, 3 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.95 (d, J = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz) δ 14.0, 22.5, 30.8, 31.4, 35.9, 51.9, 127.5, 128.4, 129.6, 148.5,

### Scheme 2. Proposed Reaction Mechanism



167.2 ppm. All spectral data correspond to those given in the literature.

**Methyl 4-Methoxybenzoate (2h):**<sup>9</sup> Following general procedure, the product was isolated as colorless solid in 86% (42.8 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 15/1); mp = 47–49 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  3.86 (s, 3 H), 3.88 (s, 3 H), 6.92 (d, J = 8.0 Hz, 2 H), 7.99 (d, J = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  51.9, 55.4, 113.6, 122.6, 131.6, 163.6, 166.9 ppm. All spectral data correspond to those given in the literature.

**Methyl 4-Fluorobenzoate (2i):**<sup>18a</sup> Following general procedure, the product was isolated as colorless oil in 65% (30.0 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 15/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  3.89 (s, 3 H), 7.05–7.11 (m, 2 H), 8.01–8.05 (m, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  52.2, 115.4 (d,  $J_{C-F} =$ 22.2 Hz), 126.3(d,  $J_{C-F} =$  3.0 Hz), 132.0 (d,  $J_{C-F} =$  9.1 Hz), 165.7 (d,  $J_{C-F} =$  254.5 Hz), 166.1 ppm. All spectral data correspond to those given in the literature.

**Methyl 4-Chlorobenzoate (2j):**<sup>18f</sup> Following general procedure, the product was isolated as colorless oil in 73% (37.3 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 50/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  3.85 (s, 3 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.91 (d, *J* = 12.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  52.1, 128.6, 128.7, 131.0, 139.4, 166.3 ppm. All spectral data correspond to those given in the literature.

**Methyl 4-Bromobenzoate (2k):**<sup>9</sup> Following general procedure, the product was isolated as colorless solid in 76% (49.0 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 15/1); mp = 74–76 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  3.91 (s, 3 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.90 (d, *J* = 12.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  52.3, 128.1, 129.0, 131.1, 137.7, 166.4 ppm. All spectral data correspond to those given in the literature.

**Dimethyl Terephthalate (2l)**:<sup>181</sup> Following general procedure, the product was isolated as colorless solid in 63% (36.7 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 10/1); mp = 137–139 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  3.92 (s, 6 H), 8.07 (s, 4 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  52.4, 129.5, 133.8, 166.2 ppm. All spectral data correspond to those given in the literature.

**Methyl 4-Thiophenecarboxylate (20):**<sup>18g</sup> Following general procedure, the product was isolated as colorless oil in 63% (26.8 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 15/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  3.87 (s, 3 H), 7.31 (s, 1 H), 7.53 (d, *J* = 8.0 Hz, 1 H), 8.11 (s, 1 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  51.9, 126.0, 127.9, 132.7, 133.5, 163.3 ppm. All spectral data correspond to those given in the literature.

**Ethyl Benzoate (2t):**<sup>9</sup> Following general procedure, the product was isolated as colorless oil in 78% (35.1 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 15/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.39 (t, *J* = 8.0 Hz, 3 H), 4.38 (q, *J* = 8.0 Hz, 2 H), 7.42 (t, *J* = 8.0 Hz, 2 H), 7.54 (t, *J* = 8.0 Hz, 1 H), 8.05 (d, *J* = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  14.3, 60.9, 128.3, 129.5, 130.5, 132.8, 166.6 ppm. All spectral data correspond to those given in the literature.

**Propyl Benzoate (2u):**<sup>18h</sup> Following general procedure, the product was isolated as colorless oil in 72% (35.4 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 15/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.03 (t, J = 8.0 Hz, 3 H), 1.75–1.84 (m, 2 H), 4.28 (t, J = 8.0 Hz, 2 H), 7.44 (t, J = 8.0 Hz, 2 H), 7.55 (t, J = 8.0 Hz, 1 H), 8.05 (d, J = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  10.5, 22.1, 66.5, 128.3, 129.5, 130.5, 132.8, 166.7 ppm. All spectral data correspond to those given in the literature. *i*-**Propyl Benzoate (2v):**<sup>18i</sup> Following general procedure, the

*i*-Propyl Benzoate (2v):<sup>181</sup> Following general procedure, the product was isolated as colorless oil in 67% (33.0 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 15/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.37 (d, *J* = 8.0 Hz, 6 H), 5.23–5.29 (m, 1 H), 7.42 (t, *J* = 8.0 Hz, 2 H), 7.53 (t, *J* = 8.0 Hz, 1 H), 8.04 (d, *J* = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  22.0, 68.3, 128.3, 129.5, 130.9, 132.7, 166.1 ppm. All spectral data correspond to those given in the literature.

**Butyl Benzoate (2w):**<sup>18j</sup> Following general procedure, the product was isolated as colorless oil in 65% (34.7 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 15/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  0.98 (t, J = 8.0 Hz, 3 H), 1.41–1.52 (m, 2 H), 1.71–1.78 (m, 2 H), 4.32 (t, J = 8.0 Hz, 2 H), 7.42 (t, J = 8.0 Hz, 2 H), 7.54 (t, J = 8.0 Hz, 1 H), 8.05 (d, J = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  13.4, 19.3, 30.8, 64.8, 128.3, 129.5, 130.5, 132.8, 166.7 ppm. All spectral data correspond to those given in the literature.

**Ethyl 4-Methylbenzoate (2x):**<sup>9</sup> Following general procedure, the product was isolated as colorless oil in 74% (36.4 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 15/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  1.38 (t, *J* = 8.0 Hz, 3 H), 2.39 (s, 3 H), 4.35 (q, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.93 (d, *J* = 8.0 Hz, 2 H); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  14.4, 21.6, 60.7, 127.8, 129.0, 129.6, 143.4, 166.7 ppm. All spectral data correspond to those given in the literature.

α-Methoxyacetophenone (10):<sup>18k</sup> Following general procedure, the product was isolated as pale yellow oil in 6% (2.7 mg) yield; flash chromatography (petroleum ether/ethyl acetate, 12/1); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 3.52 (s, 3 H), 4.72 (s, 2 H), 4.35 (q, J = 8.0 Hz, 2 H), 7.48 (t, J = 8.0 Hz, 2 H), 7.59 (t, J = 8.0 Hz, 1 H), 7.94 (d, J =

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8.0 Hz, 2 H);  $^{13}$ C { $^{1}$ H} NMR (CDCl<sub>3</sub>, 101 MHz)  $\delta$  59.5, 75.3, 127.8, 128.8, 133.6, 134.8, 196.2 ppm. All spectral data correspond to those given in the literature.

#### ASSOCIATED CONTENT

#### **Supporting Information**

Copies of <sup>1</sup>H and <sup>13</sup>C  $\{^{1}H\}$  NMR spectra for the products. This material is available free of charge via the Internet at http:// pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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