A fast and simple method for the acylation of alcohols with acid chlorides promoted by metallic samarium

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Acylation of primary, secondary, allyl and benzyl alcohols with acid chlorides promoted by samarium metal under neutral condition gave carboxylic acid esters in good to excellent yields. Acylation of a tertiary alcohol did not occur under the same reaction conditions.

Keywords: samarium, acylation, alcohol, acid chloride

Carboxylic acid esters are well known for their applications in organic synthesis and their activity in the field of medicine. The commonly employed synthetic method is the acylation of alcohols with acid chlorides. In general, the acylations occur by the reaction in the presence of a base such as pyridine, TMEDA or triethylamine.[1] Further, various catalysts have been developed for the acylation of alcohols with acid chlorides such as zinc chloride[2] or alumina.[3] However, to the best of our knowledge, only a few methods have been reported for the acylation of alcohols with acid halides promoted by a metal under neutral conditions.[4]

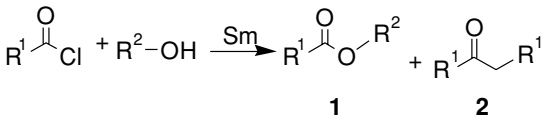
The use of samarium diiodide as a strong and versatile one-electron-transfer reducing agent and a catalyst in organic synthesis has been explored widely since it was introduced by Kagan's group.[5] Although samarium diiodide is a useful reducing agent and catalyst, its application to organic synthesis is limited in some extent due to its sensitivity to air. Metallic samarium, however, is stable in air. The chemistry of samarium metal with its strong reducing power in organic synthesis has received increasing attention in recent years.[6] However, no literature has been reported on samarium metal as a catalyst. Here we report a fast, simple and general method for the acylation of alcohols with acid chlorides using metallic samarium as a promoting agent under neutral conditions. Samarium, without any activation or pretreatment, can promote the reaction of various alcohols with acid chlorides to afford the corresponding carboxylic acid esters **1** together with a small amount of by-product **2** (Scheme 1).

First, we examined the acylation of benzyl alcohol as a model substrate with *p*-chlorobenzoyl chloride (Scheme 2). Results are collected in Table 1. Treatment of benzyl alcohol with *p*-chlorobenzoyl chloride in the presence of 2/3 equivalent of samarium in anhydrous acetonitrile at room temperature for 3 minutes did not afford the desired benzyl *p*-chlorobenzoate (Table 1, Entry 6), however, the reaction was drastically improved at 70 ºC to result in the formation of 88% of **1f** (Table 1, Entry 4) with 3% of by-product 1,2-bis-(4-chlorophenyl)ethanone **2b**. When one equivalent of samarium was used, a similar acylation was completed to give **1f** in 71% yield (Table 1, Entry 5), whereas only a trace of **1f** was obtained using 1/3 equivalent of samarium (Table 1, Entry 3). Nevertheless, in the absence of samarium, no product was generated under the same reaction conditions (Table 1, Entries 1 and 2). These results showed that samarium is a very effective promoting agent for the acylation of benzyl alcohol with *p*-chlorobenzoyl chloride. We have also investigated the influence of solvent on the reaction of *p*-chlorobenzoyl chloride with benzyl alcohol. When the reaction was carried out with 2/3 equivalent of samarium in benzene or tetrahydrofuran at room temperature for 3 min, no product was observed and the reaction at 70 °C gave complex mixtures. A high yield of benzyl *p*-chlorobenzoate and a highly efficient reaction are found only using 2/3 equivalent of samarium in anhydrous acetonitrile at 70 °C.

Table 1 Samarium-promoted acylation of benzyl alcohol with *p*-chlorobenzoyl chloride

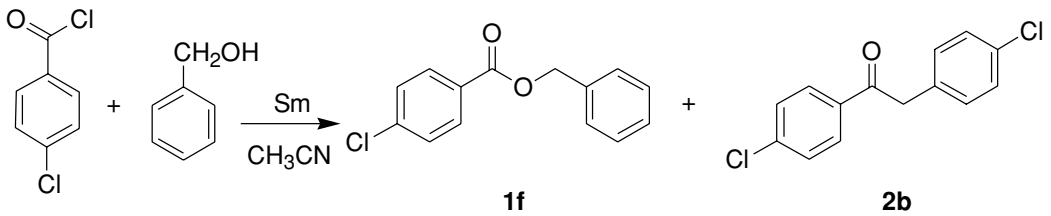
Entry	Sm/ equiv.	Temperature /°C	Time /min	Yield of **1f**/%[a]	Yield of **2b**/%[a]
1	None	rt	3	0	0
2	None	70	3	0	0
3	1/3	70	3	Trace	0
4	2/3	70	3	88	3
5	1	70	3	71	5
6	2/3	rt	3	0	0

[a]Isolated yield.



Scheme 1

To determine the general utility of this method, the acylation of various alcohols with acid chlorides was studied using the above optimised reaction conditions. The result showed that the acylation of various alcohols with acid chlorides occurred rapidly. Some representative results are summarised in Table 2. Various alcohols can react quickly with aroyl chlorides and aliphatic acyl chlorides to form the corresponding carboxylic esters in good to excellent yields. Only the acylation of *t*-butanol with acid chlorides did not occur under the same



Scheme 2

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Table 2 Samarium-promoted acylation of various alcohols with acyl chlorides

Entry	R^1	R^2	Time/min	Yield of **1**/% [a,b]	Yield of **2**/% [a,b]
1	Ph	$PhCH_2$	3	92 (**1a**)	Trace (**2a**)
2	Ph	*n*-C_5H_{11}	3	76 (**1b**)	8 (**2a**)
3	Ph	*i*-Pr	3	75 (**1c**)	3 (**2a**)
4	Ph	*t*-Bu	3	0 (**1d**)	0 (**2a**)
5	Ph	Cinnamyl	3	77 (**1e**)	Trace (**2a**)
6	*p*-ClC_6H_4	$PhCH_2$	3	88 (**1f**)	3 (**2b**)
7	*p*-ClC_6H_4	*n*-C_5H_{11}	3	83 (**1g**)	2 (**2b**)
8	*p*-ClC_6H_4	*i*-Pr	3	79 (**1h**)	10 (**2b**)
9	*p*-ClC_6H_4	*t*-Bu	3	0 (**1i**)	0 (**2b**)
10	*p*-ClC_6H_4	Cinnamyl	3	76 (**1j**)	Trace (**2b**)
11	*p*-MeC_6H_4	$PhCH_2$	2	86 (**1k**)	6 (**2c**)
12	*p*-MeC_6H_4	*n*-C_5H_{11}	2	92 (**1l**)	1 (**2c**)
13	*p*-MeC_6H_4	*i*-Pr	3	89 (**1m**)	2 (**2c**)
14	*p*-MeC_6H_4	*t*-Bu	3	0 (**1n**)	0 (**2c**)
15	*p*-MeC_6H_4	Cinnamyl	3	69 (**1o**)	Trace (**2c**)
16	*p*-$MeOC_6H_4$	$PhCH_2$	2	93(**1p**)	
17	*p*-$MeOC_6H_4$	*n*-C_5H_{11}	2	95 (**1q**)	
18	*p*-$MeOC_6H_4$	*i*-Pr	2	96 (**1r**)	
19	*p*-$MeOC_6H_4$	*t*-Bu	2	0 (**1s**)	
20	*p*-$MeOC_6H_4$	Cinnamyl	5	66 (**1t**)	
21	*p*-O_2N C_6H_4	$PhCH_2$	3	39 (**1u**)	
22	*p*-O_2N C_6H_4	*n*-C_5H_{11}	3	26 (**1v**)	
23	*p*-O_2N C_6H_4	*i*-Pr	4	18 (**1w**)	
24	*p*-O_2N C_6H_4	*t*-Bu	5	0 (**1x**)	
25	$PhCH_2$	$PhCH_2$	2	92 (**1y**)	
26	$PhCH_2$	*n*-C_5H_{11}	2	97 (**1z**)	
27	$PhCH_2$	*i*-Pr	3	89 (**1A**)	
28	$PhCH_2$	*t*-Bu	3	0 (**1B**)	
29	$PhCH_2$	Cinnamyl	2	73 (**1C**)	
30	PhCH=CH	$PhCH_2$	2	77 (**1D**)	
31	PhCH=CH	*n*-C_5H_{11}	2	76 (**1E**)	
32	PhCH=CH	*i*-Pr	3	86 (**1F**)	
33	PhCH=CH	*t*-Bu	3	0 (**1G**)	
34	PhCH=CH	Cinnamyl	5	62 (**1H**)	

[a]Yield of isolated product. [b]All products listed in Table 2 exhibited spectroscopic data in agreement with literature values.

reaction conditions because of the steric effect. The reactions of *p*-nitrobenzoyl chloride with *n*-pentanol, isopropanol, or benzyl alcohol gave the corresponding esters in 18–39% yields under the same reaction conditions. Carbon–carbon double bonds, chloro, alkoxyl and nitro groups of the substrates were not reduced under the reaction conditions and have no influence on the rate of acylation. We also observed that part of the samarium metal was converted into a trivalent samarium salt. Furthermore, a small amount of by-product 1, 2-diarylethanone **2** was isolated from the acylation of *n*-pentanol, isopropanol, benzyl or cinnamyl alcohol with aroyl chlorides. However, interestingly, no by-product **2** was observed in the acylation of *n*-pentanol, isopropanol, benzyl or cinnamyl alcohol with *p*-methoxybenzoyl chloride or *p*-nitrobenzoyl chloride.

The present methodology for the acylation of alcohols with acid chlorides offers distinct advantages over the existing methods.[1,4] These include the excellent selectivity, the faster reaction rate, no activation or pretreatment of the samarium metal, the applicability to a wider range of substrates and the neutral conditions.

Though the mechanism of this reaction is not clear at present, we surmise that the efficiency of this reaction might result from the polar carbonyl group complexing to the surface of the samarium and an increase the electrophilic character of the carbonyl groups. In addition, the formation mechanism of the by-product **2** could be described as shown in Fig. 1. An electron transfer from samarium to an aroyl chloride gives the corresponding aroyl free radical and self-coupling gives 1,2-diarylethane-1,2-dione **3**. A C–O double bond of **3** is reduced to a single one to lead to intermediate **4** and this bond is then cleaved by a second samarium to give

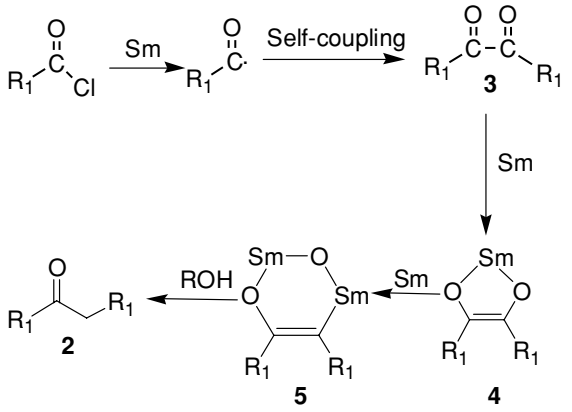

Fig. 1

intermediate **5**. Abstraction of the hydrogen of alcohol affords 1,2-diarylethanone **2**.

In conclusion, we have developed an interesting new method for the synthesis of carboxylic acid esters in good to excellent yields by the acylation of primary, secondary, allyl and benzyl alcohols with a series of acid chlorides promoted by samarium metal in acetonitrile and the acylation was completed within a few minutes. Acylation of a tertiary alcohol did not occur under the same reaction conditions. the present method is very fast, simple and applicable for the preparation of a variety of carboxylic acid esters. Regardless of the exact mechanistic details of the present acylations, the data presented herein reveal the utility of samarium metal for these acylations. Examination of the use of this method is currently underway and the results of these studies will be reported in due course.

Experimental

Column chromatography was performed on silica gel (200–300 mesh). Microanalyses were obtained using a Carlo-Erba 1106. ^{1}H NMR spectra were measured in $CDCl_3$ and recorded on a Bruker AM300 (300MHz) spectrometer and the chemical shifts are reported in ppm with TMS as an internal standard. IR spectra were measured with a Perkin Elmer FT-IR-1600 spectrometer. Mass spectra were determined with a HP 5989A mass spectrometer. Melting points are uncorrected. All reagents and solvents were purchased from commercial sources. Acid chlorides were distilled before use. Acetonitrile was distilled over CaH_2.

General procedure

Samarium powder (0.43 g, 2.86 mmol) was placed in a well-dried three-necked round bottom flask containing a magnetic stirrer. The anhydrous acetonitrile (2 ml) was added via a syringe under a nitrogen atmosphere. The suspension was heated with stirring to 70 °C, and then the acid chloride (4.30 mmol) and the alcohol (4.30 mmol) were added successively. The stirring continued for the given time (Table 2). The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was quenched with saturated sodium bicarbonate solution and then filtered and washed with dichloromethane. The organic layer was separated and the water layer was extracted with dichloromethane (70 ml × 3). The combined extracts were dried with anhydrous magnium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (250:1) to afford the corresponding carboxylic acid esters in good to excellent yields. All the products were reported in the literature and were identified by IR, ^{1}H NMR or mass spectra.

1a: Oil (lit.[7] 18–20 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.15 (d, *J* = 8.1 Hz, 2H), 7.58–7.38 (m, 8H), 5.43 (s, 2H); IR (KBr) 3065, 3032, 2950, 1720, 1601, 1497, 1451, 1270, 1109 cm^{-1}.

1b: Oil (lit.[8]); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.04 (d, *J* = 8.4 Hz, 2H), 7.56–7.40 (m, 3H), 4.31 (t, *J* = 6.9 Hz, 2H), 1.79–1.72 (m, 2H), 1.47–1.26 (m, 4H), 0.92 (t, *J* = 6.9 Hz, 3H); IR (KBr) 3064, 3033, 2957, 2931, 2871, 1721, 1602, 1491, 1451, 1272, 1110 cm^{-1}.

1c: Oil (lit.[9]); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.04 (d, *J* = 8.1 Hz, 2H), 7.54–7.40 (m, 3H), 5.26 (m, 1H), 1.37 (d, *J* = 5.7 Hz, 6H); IR (KBr) 3063, 2980, 2925, 1716, 1603, 1491, 1466, 1451, 1275, 1104 cm^{-1}.

1e: M.p. 38–39 °C (lit.[10] 39–40 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.09 (d, *J* = 8.1 Hz, 2H), 7.59–7.21 (m, 8H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.45–6.36 (m, 1H), 4.98 (d, *J* = 7.5 Hz, 2H); IR (KBr) 3060, 3026, 2938, 1719, 1600, 1494, 1450, 1269, 1116 cm^{-1}; Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9. Found; C, 80.4; H, 5.8.

In the cases of **1f** to **1w** below AA'xx' systems are involved in the aromatic ^{1}H NMR region and the *J* values quoted are ($J_{2,3}$ +$J_{2,5}$) values.

1f: Oil (lit.[11] 26–27 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.01 (d, *J* = 8.79 Hz, 2H), 7.46–7.34 (m, 7H), 5.36 (s, 2H); IR (KBr) 3065, 3033, 2926, 2853, 1722, 1594, 1496, 1454, 1270, 1102 cm^{-1}.

1g[4]**:** ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.96 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 4.31 (t, *J* = 6.3 Hz, 2H), 1.78–1.36 (m, 6H), 0.93 (t, *J* = 7.5 Hz, 3H); IR (KBr) 2957, 2932, 2871, 1723, 1595, 1488, 1466, 1272, 1114 cm^{-1}; Anal. Calcd for $C_{12}H_{15}ClO_2$: C, 63.5; H, 6.6. Found; C, 63.6; H, 6.6.

1h: Oil (lit.[9]); ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.93 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 5.22 (m, 1H), 1.33 (d, *J* = 6 Hz, 6H). IR (KBr) 2981, 2936, 1718, 1594, 1488, 1468, 1275, 1102 cm^{-1}.

1j: M.p. 44–46 °C (lit.[12] 46 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.01 (d, *J* = 8.7 Hz, 2H), 7.41–7.22 (m, 7H), 6.72 (d, *J* = 15.6 Hz, 1H), 6.42–6.33 (m, 1H), 4.95 (d, *J* = 6.6 Hz, 2H). IR (KBr) 3026, 2947, 1721, 1595, 1488, 1449, 1268, 1117 cm^{-1}.

1k: M.p. 45–46 °C (lit.[7] 46.5 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.03 (d, *J* = 8.1 Hz, 2H), 7.48–7.25 (m, 7H), 5.39 (s, 2H), 2.43 (s, 3H). IR (KBr) 3064, 3034, 2951, 1719, 1612, 1498, 1455, 1271, 1103 cm^{-1}.

1l: ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.93 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.29 (t, *J* = 6.9 Hz, 2H), 2.42–1.39 (m, 6H), 0.93 (t, *J* = 7.2 Hz, 3H); IR (KBr) 2957, 2931, 2872, 1719, 1612, 1458, 1273, 1107 cm^{-1}; Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.6; H, 8.7. Found; C, 75.5; H, 8.6.

1m: Oil (lit.[9]); ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.93 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.24 (m, 1H), 2.39 (s, 3H), 1.36 (d, *J* = 6.6Hz, 6H); IR (KBr) 3033, 2980, 2934, 2873, 1715, 1612, 1467, 1452, 1275, 1105 cm^{-1}.

1o[13]**:** ^{1}H NMR(300MHz, $CDCl_3$, δ): 7.97 (d, *J* = 8.1 Hz, 2H), 7.42–7.22 (m, 7H), 6.73 (d, *J* = 15.6 Hz, 1H), 6.44–6.35 (m, 1H), 4.96 (d, *J* = 6.6 Hz, 2H), 2.39 (s, 3H); IR (KBr) 3081, 3058, 3027, 2923, 2875, 1716, 1611, 1497, 1448, 1269, 1103 cm^{-1}; Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.85; H, 6.3. Found; C, 80.9; H, 6.3.

1p: Oil (lit.[7] 26–27 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.05 (d, *J* = 8.7 Hz, 2H), 7.47–7.31 (m, 5H), 6.92 (d, *J*= 8.7 Hz, 2H), 5.35 (s, 2H), 3.84 (s, 3H); IR (KBr) 3064, 3033, 2956, 2936, 2839, 1710, 1606, 1510, 1458, 1256, 1100 cm^{-1}.

1q[14]**:** ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.99 (d, *J*= 9.3 Hz, 2H), 6.91 (d, *J*= 9.3 Hz, 2H), 4.28 (t, *J*= 6.9 Hz, 2H), 3.84 (s, 3H), 1.75–1.38 (m, 6H), 0.93 (t, *J* = 7.5 Hz, 3H); IR (KBr) 2957, 2934, 2871, 1713, 1607, 1511, 1465, 1275, 1257, 1102 cm^{-1}; Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.2; H, 8.1. Found; C, 70.1; H, 8.0.

1r: Oil (lit.[9]); ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.93 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.22 (m, 1H), 3.84 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 6H); IR (KBr) 3074, 2979, 2936, 2841, 1710, 1606, 1511, 1466, 1276, 1257, 1101 cm^{-1}.

1t: M.p. 63–64 °C (lit.[15] 63 °C);^{1}H NMR (300MHz, $CDCl_3$, δ): 7.96 (d, *J* = 9 Hz, 2H), 7.36–7.18 (m, 5H), 6.85 (d, *J* = 9 Hz, 2H), 6.65 (d, *J* = 16.2 Hz, 1H), 6.35–6.60 (m, 1H), 4.88 (d, *J* = 6.6 Hz, 2H), 3.79 (s, 3H); IR (KBr) 3081, 3059, 3026, 2925, 2852, 1719, 1599, 1511, 1494, 1449, 1248, 1117 cm^{-1}.

1u: M.p. 84 °C (lit.[7] 83–84.5 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.28 (d, *J* = 9 Hz, 2H), 8.23 (d, *J* = 9 Hz, 2H), 7.47–7.39 (m, 5H), 5.40 (s, 2H); IR (KBr) 3062, 2943, 2855, 1711, 1602, 1519, 1456, 1276, 1104 cm^{-1}.

1v: Oil (lit.[16]); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.28 (d, *J* = 9 Hz, 2H), 8.23 (d *J* = 9 Hz, 2H), 4.38 (t, *J* = 6.9 Hz, 2H), 1.83–1.40 (m, 6H), 0.94 (t, *J* = 7.2 Hz, 3H); IR (KBr) 2958, 2928, 2869, 1726, 1606, 1530, 1462, 1276, 1107 cm^{-1}.

1w: M.p. 106–107 °C (lit.[16] 108.5 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.29 (d, *J* = 9 Hz, 2H), 8.22 (d, *J* = 9 Hz, 2H), 5.30 (m, 1H), 1.39 (d, *J* = 6.6 Hz, 6H); IR (KBr) 2925, 2856, 1712, 1604, 1524, 1465, 1280, 1099 cm^{-1}.

1y: M.p. 50–51 °C (lit.[17] 51–52 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.35–7.26 (m, 10H), 5.13 (s, 2H), 3.67 (s, 2H); IR (KBr) 3064, 3032, 2954, 1737, 1603, 1496, 1455, 1259, 1145 cm^{-1}.

1z: Oil (lit.[17] 31–32 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.35–7.30 (m, 5H), 4.12 (t, *J* = 6.9 Hz, 2H), 3.64 (s, 2H), 1.67–1.30 (m, 6H), 0.93 (t, *J* = 6.9 Hz, 3H); IR (KBr) 3064, 3031, 2956, 2933, 2872, 1735, 1603, 1496, 1455, 1256, 1158 cm^{-1}.

1A: Oil (lit.[18]);^{1}H NMR (300MHz, $CDCl_3$, δ): 7.35–7.27 (m, 5H), 5.05 (m, 1H), 3.61 (s, 2H), 2H), 1.26 (d, *J* = 6.6 Hz, 6H); IR (KBr) 3064, 3032, 2981, 2935, 1734, 1604, 1496, 1466, 1454, 1260, 1107 cm^{-1}.

1C[19]**:** ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.37–7.22 (m, 10H), 6.58 (d, *J* = 16.2 Hz, 1H), 6.31–6.20 (m, 1H), 4.74 (d, *J* = 6.3 Hz, 2H), 3.66 (s, 2H); IR (KBr) 3083, 3061, 3029, 2943, 1732, 1654, 1601, 1496, 1453, 1256, 1148 cm^{-1}.

1D: Oil (lit.[7] 34 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.78 (d, *J* = 15.9 Hz, 1H), 7.56–7.38 (m, 10H), 6.54 (d, *J* = 15.9 Hz, 1H), 5.30 (s, 2H); IR (KBr) 3084, 3062, 3030, 2951, 2891, 1713, 1637, 1578, 1496, 1450, 1269, 1202, 1163 cm^{-1}.

1E: ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.68 (d, *J* = 15.9 Hz, 1H), 7.52–7.34 (m, 5H), 6.44 (d, *J* = 15.9 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 1.72–1.35 (m, 6H), 0.92 (t, *J* = 6.9 Hz, 3H); IR (KBr) 3061, 2956, 2931, 2860, 1713, 1638, 1578, 1496, 1450, 1268, 1170 cm^{-1}; Anal. Calcd for $C_{13}H_{18}O_2$: C, 77.0; H, 8.2. Found; C, 76.8; H, 8.2.

1F[20]**:** ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.67 (d, *J* = 16.2 Hz, 1H), 7.55–7.38 (m, 5H), 6.43 (d, *J* = 16.2 Hz, 1H), 5.15 (m, 1H), 1.37 (d, *J* = 6.6 Hz, 6H); IR (KBr) 3083, 3061, 3028, 2979, 2935, 2874, 1710, 1638, 1578, 1496, 1466, 1450, 1272, 1202, 1175, 1109 cm^{-1}.

1H: M.p. 42–43 °C (lit.[21] 44–44.5 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.74 (d, *J* = 15.9 Hz, 1H), 7.57–7.25 (m, 10H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.46–6.35 (m, 1H), 4.89 (d, *J* = 6.3 Hz, 2H); IR (KBr) 3082, 3059, 3027, 2941, 2878, 1712, 1637, 1599, 1496, 1449, 1268, 1202, 1164, 1110 cm^{-1}.

2a: M.p. 52–53 °C (lit.[22] 54–55 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 8.01 (d, *J* = 8.4 Hz, 2H), 7.58–7.25 (m, 8H), 4.28 (s, 2H); IR (KBr) 2924, 2853, 1683, 1599, 1491, 1452 cm^{-1}.

2b: M.p. 113–115 °C (lit.[23] 112–113 °C); ^{1}H NMR (300MHz, $CDCl_3$, δ): 7.93 (d, *J* = 9 Hz, 2H), 7.44 (d, *J* = 9 Hz, 2H), 7.32–7.16 (m, 4H), 4.23 (s, 2H); IR (KBr) 2924, 1690, 1587, 1491, 1458 cm^{-1}; *m/z* (%): 264 (M^+, 2.87), 139 (100), 125 (7.91), 111 (21.22).

2c: M.p. 100–102 °C (lit.[24] 101–103 °C); ^{1}H NMR(300MHz, $CDCl_3$, δ): 7.94 (d, *J* = 8.4 Hz, 2H), 7.43–7.14 (m, 6H), 4.21 (s, 2H), 2.39 (s, 3H), 2.31 (s, 3H); IR (KBr) 3062, 3004, 1685, 1599, 1582, 1449 cm^{-1}.

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