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# $RuH_2(CO)(PPh_3)_3$-catalyzed arylation of aromatic esters using arylboronates via C–H bond cleavages

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ABSTRACT

The $RuH_2(CO)(PPh_3)_3$-catalyzed C–H functionalization of aromatic esters with 5,5-dimethyl-2-aryl-[1,3,2]dioxaborinanes (arylboronates) gave the *ortho* arylation products. This coupling reaction can be performed with various combinations of isopropyl benzoate derivatives and arylboronates. Introduction of $CF_3$ group in the aromatic ring increased the reactivity of the esters. Pinacolone effectively served as an acceptor of a hydride generated by C–H bond cleavage, and the amount of pinacolone used also affected the yield of the arylation product.

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## 1. Introduction

Construction of biaryl structures by transition metal-catalyzed intermolecular C–H arylation has been extensively studied in order to develop efficient alternatives of conventional cross-couplings between preactivated arenes [1–7]. Since Catellani and Chiusoli reported an interesting coupling of norbornene and aryl bromides [2a], there have been developed a variety of C–H arylations such as Ar–H/Ar–X (X = halides and pseudohalides) [3,4], Ar–H/Ar–metal [5,6], and Ar–H/Ar–H [7,8] couplings. Directing groups have often been employed to achieve high regioselectivity and efficiency for the arylation of benzene derivatives [4,6,8].

We have developed $RuH_2(CO)(PPh_3)_3$-catalyzed *ortho* arylation of aromatic ketones with 5,5-dimethyl-2-aryl-[1,3,2]dioxaborinanes (arylboronates) [6b,c]. In this coupling reaction, pinacolone serves as both a solvent and a scavenger of hydride generated by C–H bond cleavage. We envisioned that application of aromatic esters in place of aromatic ketones to the arylation would provide an efficient route to other important classes of functionalized biaryl molecules. For example, 2,6-diarylbenzoic acids, which are widely recognized as useful supporting ligands [9] and hydrogen-bonding scaffolds [10], should be easily prepared from aromatic esters. Herein, we describe catalytic synthesis of *o*-arylbenzoates by $RuH_2(CO)(PPh_3)_3$-catalyzed coupling of aromatic esters and arylboronates.

## 2. Results and discussion

The arylation was first examined using several alkyl 2-methylbenzoate **1** and phenylboronate **2a** (Table 1). When the reaction of methyl ester **1a** with **2a** was performed with 5 mol% $RuH_2(CO)(PPh_3)_3$ (**3**) in refluxing pinacolone for 7 h, *ortho* phenylation product **4a** was formed in 21% GC yield (entry 1). Use of ethyl ester **1b** did not improve the yield significantly (entry 2). However, the phenylation of isopropyl ester **1c** gave the corresponding product **4c** in 75% GC yield (entry 3). Increase of the steric bulk of the directing group to *tert*-butoxycarbonyl group resulted in reduction of the product yield (entry 4). To investigate the electronic effect of the directing group, hexafluoroisopropyl ester **1e** was used as a substrate, but no desired product was observed (entry 5) [11]. Therefore, isopropyl esters were chosen as substrates for further examination.

Next, we examined the arylation of 2-(trifluoromethyl)benzoate **5**. The reaction of ester **5** with **2a** for 7 h led to the formation of *ortho* phenylation product **6a** in 92% GC yield, which is higher than the yield obtained with a substrate bearing a relatively electron-donating ($CH_3$) group (Table 1, entry 3). This indicates that the presence of electron-withdrawing groups on the aromatic ring of the ester substrates promotes the arylation, and a similar trend

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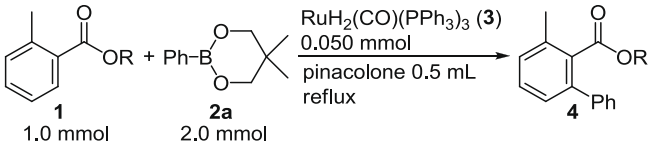
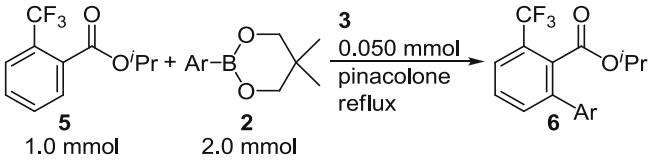
**Table 1**
Phenylation of 2-methylbenzoate **1**.




| Entry | Substrate | *R* | Time (h) | Product | GC yield (%) |
|---|---|---|---|---|---|
| 1 | **1a** | Me | 7 | **4a** | 21 |
| 2 | **1b** | Et | 7 | **4b** | 23 |
| 3 | **1c** | $^{i}$Pr | 7 | **4c** | 75 |
| 4 | **1d** | $^{t}$Bu | 7 | **4d** | 32 |
| 5 | **1e** | $CH(CF_3)_2$ | 3 | – | ND |

**Table 2**
Arylation of 2-(trifluoromethyl)benzoate **5**.




| Entry | Arylboronate | Pinacolone (mL) | Time (h) | Product | Yield (%) |
|---|---|---|---|---|---|
| 1 | **2a** (*R* = Ph) | 0.5 | 7 | **6a** | 92[a] |
| 2 | **2a** | 0.5 | 2 | **6a** | 69[b] |
| 3 | **2a** | 1.0 | 2 | **6a** | 83[b] |
| 4 | **2a** | 2.0 | 3 | **6a** | 84[b] |
| 5 | **2b** (*R* = 4-$MeOC_6H_4$) | 1.0 | 3 | **6b** | 78 |
| 6 | **2c** (*R* = 2-$MeC_6H_4$) | 1.0 | 3 | **6c** | 74 |

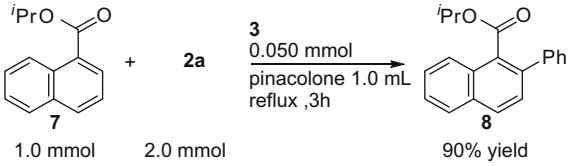
[a] GC yield.
[b] Determined based on $^{1}$H NMR spectra of **6a** isolated as a mixture with starting material **5**.

was also observed for *ortho* alkylation of aromatic esters with alkenes catalyzed by **3** [12]. It is worthy to note that, in the arylation of aromatic ketones, introduction of a $CF_3$ group at an *ortho* position of a substrate resulted in decrease of the yield, because increased electrophilicity facilitated undesired reduction of the substrate and the product and prevented the selective trapping of hydrides by pinacolone [6c].

In order to improve the reaction rate, the amount of pinacolone used was then investigated. As already mentioned above, pinacolone is not only a solvent but also a reagent. Considering its function as a reagent, increase of the amount may improve the activity. When the reaction was performed with 0.5 mL of pinacolone for 2 h, product **6a** was obtained in 69% yield. Increase of the amount of pinacolone to 1.0 mL actually improved the product yield to 83%. The phenylation in 2.0 mL of pinacolone afforded a comparable yield (84%) of **6a** in 3 h. Based on the results, 1.0 mL of pinacolone was used to explore the reaction of other substrates (see Table 2).

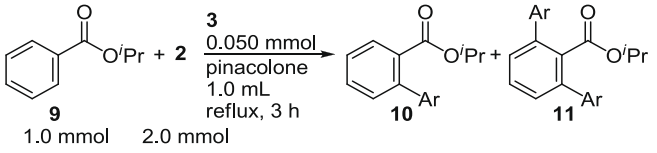
The arylation of ester **5** was also performed with other arylboronates. The reaction using 4-methoxyphenylboronate **2b** provided the corresponding product **6b** in 78% yield. *Ortho*-substituted phenylboronate **2c** can be used for this reaction and product **6c** was obtained in 74% yield, even though the methyl substituent should create severe steric congestion. As previously reported, arylboronate **2c** was also applicable for the arylation of aromatic ketones catalyzed by **3** [6b,c].

1-Naphthoate **7** also showed high reactivity for the arylation. The reaction of ester **7** with **2a** for 3 h afforded product **8**, of which a phenyl group was introduced selectively at 2-position, in 90% yield (Scheme 1).



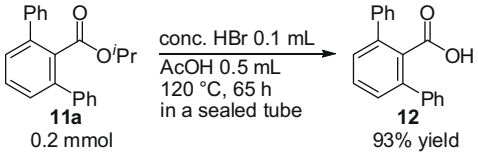

**Scheme 1.**

**Table 3**
Arylation of unsubstituted benzoate **9**.

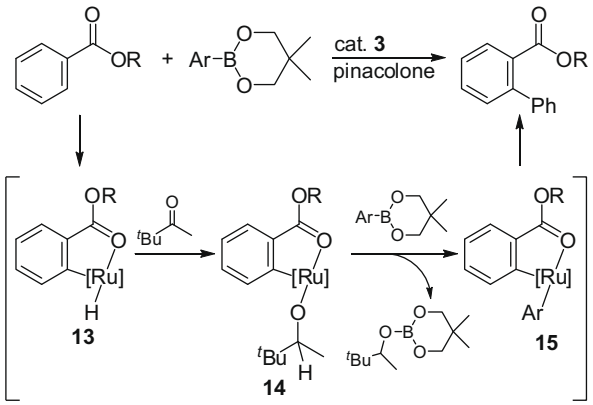



| Entry | Arylboronate | Yield of **10**[a] | | Yield of **11**[a] | |
|---|---|---|---|---|---|
| 1 | **2a** (*R* = Ph) | **10a** | 19% | **11a** | 58% |
| 2 | **2b** (*R* = 4-$MeOC_6H_4$) | **10b** | 27% | **11b** | 37% |
| 3 | **2d** (*R* = 4-$MeC_6H_4$) | **10d** | 26% | **11d** | 38% |

[a] Isolated yield.




**Scheme 2.**




**Scheme 3.** Proposed mechanism of the arylation of aromatic esters.

Unsubstituted benzoate **9** has two *ortho* C–H bonds, and both can be arylated in the reaction. The reaction of **9** with phenylboronate **2a** afforded 1:1 and 1:2 coupling products, **10a** and **11a**, which was isolated in 19% and 58% yields, respectively (Table 3, entry 1). The arylations of **9** with **2b** and **2d** also provided both mono- and di-arylation products (entries 2 and 3). In all cases, 2,6-diarylated benzoate esters were the major products.

Removal of the isopropyl group was also examined. When ester **11a** was treated with conc. HBr in AcOH [13] was performed in a sealed tube at 120 °C for 65 h, hydrolysis took place cleanly, and 2,6-diphenylbenzoic acid (**12**) [14] was isolated in 93% yield (see Scheme 2).

The arylation of aromatic esters described here is considered to proceed via a similar mechanism to the previously-reported

arylation of aromatic ketones [6b,c]. Coordination of the ester moiety of an ester substrate to a ruthenium center, followed by oxidative addition of a C–H bond, leads to formation of five-membered ruthenacycle **13**. Hydroruthenation of the carbonyl group of pinacolone results in alkoxyruthenium complex **14**. Transmetalation between **14** and arylboronates **2** gives intermediate **15**. Reductive elimination provides the coupling product and regenerates the catalytically active ruthenium species (see Scheme 3).

## 3. Conclusion

In summary, aromatic esters were coupled with arylboronates by a catalytic amount of $RuH_2(CO)(PPh_3)_3$ to form *ortho* arylated benzoate derivatives. Isopropyl esters particularly gave high yields of the products. Introduction of electron-withdrawing $CF_3$ group increased the product yield, and the amount of pinacolone used also affected the reaction rate. Finally, 2,6-diarylation product **11a** was successfully hydrolyzed to the corresponding carboxylic acid. The arylation method for aromatic esters reported here provides a new entry for convenient synthesis of functionalized biaryl molecules including highly hindered benzoic acids.

## 4. Experimental

### 4.1. General procedure for the arylation of aromatic esters

An apparatus consisting of a 10 mL two-necked round-bottomed flask, a reflux condenser and a magnetic stirring bar was flame-dried, and then cooled to room temperature under a flow of nitrogen. Catalyst **3**, arylboronate **2**, ester and pinacolone were added to the flask. The resulting mixture was refluxed (oil bath temperature 135 °C) under nitrogen. After cooled to room temperature, the reaction mixture was passed through a basic alumina column (Merck, aluminum oxide 90 active basic (0.063–0.200 mm), i.d. 30 mm, length 50 mm) with 2% ethyl acetate in hexane to remove unreacted arylboronate. The arylation product was isolated by silica gel column chromatography (Merck, silica gel 60 (230–400 mesh ASTM)). Further purification of the product was performed by GPC, if necessary.

### 4.2. Analytical data

#### 4.2.1. Compound ***4a***

Colorless liquid $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.40 (s, 3H), 3.58 (s, 3H), 7.20–7.24 (m, 2H), 7.31–7.42 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 19.6, 51.7, 127.2, 127.3, 128.1, 128.2, 129.1, 129.4, 133.1, 135.4, 140.1, 140.9, 170.2. IR (neat): 2949, 1730, 1591, 1462, 1436, 1270, 1239, 1123, 1092, 1067, 797, 760, 701 cm$^{-1}$. MS *m*/*z* (% relative intensity): 227 (13), 226 ($M^+$, 73), 196 (15), 195 (100), 194 (48), 167 (17), 166 (15), 165 (49), 152 (34), 82 (16). Anal. Calc. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.64; H, 6.25%.

#### 4.2.2. Compound ***4b***

Colorless liquid $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.96 (t, *J* = 7.3 Hz, 3H), 2.41 (s, 3H), 4.05 (q, *J* = 7.3 Hz, 2H), 7.19–7.24 (m, 2H), 7.30–7.40 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 13.6, 19.6, 60.8, 127.2, 127.3, 128.2, 128.4, 129.1, 129.3, 133.4, 135.4, 140.2, 141.0, 169.7. IR (neat): 3060, 2980, 2932, 1724, 1590, 1462, 1445, 1365, 1266, 1238, 1173, 1124, 1092, 1067, 1015, 797, 760, 701 cm$^{-1}$. MS *m*/*z* (% relative intensity): 241 (11), 240 ($M^+$, 65), 196 (16), 195 (100), 194 (48), 167 (14), 166 (14), 165 (42), 152 (29). Anal. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.05; H, 6.72%.

#### 4.2.3. Compound ***4c***

Colorless liquid $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 0.99 (d, *J* = 6.2 Hz, 6H), 2.41 (s, 3H), 4.97 (septet, *J* = 6.2 Hz, 1H), 7.18–7.22 (m, 2H), 7.31–7.38 (m, 6H). $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$ = 19.7, 21.4, 68.5, 127.1, 127.2, 128.1, 128.4, 129.0, 129.1, 133.6, 135.0, 139.9, 140.8, 169.0. IR (neat): 3060, 3027, 2979, 2933, 1720, 1590, 1496, 1463, 1384, 1374, 1273, 1180, 1130, 1108, 1090, 1066, 917, 851, 794, 760, 701 cm$^{-1}$. MS *m*/*z* (% relative intensity): 254 ($M^+$, 50), 212 (60), 196 (13), 195 (85), 194 (100), 167 (14), 166 (17), 165 (50), 152 (32). Anal. Calc. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.01; H, 7.10%.

#### 4.2.4. Compound ***4d***

Colorless liquid $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.27 (s, 9H), 2.42 (s, 3H), 7.14–7.24 (m, 2H), 7.28–7.40 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 19.5, 27.7, 81.5, 127.1, 127.1, 128.0, 128.7, 128.7, 129.0, 134.7, 134.8, 139.8, 141.0, 168.6. IR (neat): 2977, 2931, 1720, 1461, 1392, 1368, 1287, 1258, 1242, 1172, 1126, 1092, 1067, 848, 782, 760, 701 cm$^{-1}$. MS *m*/*z* (% relative intensity): 268 ($M^+$, 10), 213 (15), 212 (100), 195 (61), 194 (91), 166 (11), 165 (30), 152 (19), 57 (25). Anal. Calc. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.79; H, 7.57%.

#### 4.2.5. Compound ***6a***

Colorless liquid $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 1.01 (d, *J* = 6.2 Hz, 6H), 4.98 (septet, *J* = 6.2 Hz, 1H), 7.35–7.43 (m, 5H), 7.53–7.57 (m, 2H), 7.67–7.71 (m, 1H). $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$ = 21.2, 69.6, 123.5 (q, *J* = 273 Hz), 124.8 (q, *J* = 4.5 Hz), 127.4 (q, *J* = 32 Hz), 127.9, 128.2, 128.6, 129.2, 132.0 (q, *J* = 2.2 Hz), 133.3, 139.0, 141.1, 166.5. IR (neat) 2983, 1733, 1467, 1456, 1375, 1328, 1280, 1197, 1171, 1141, 1103, 1067, 1047, 809, 763, 702 cm$^{-1}$. MS *m*/*z* (% relative intensity): 308 ($M^+$, 45), 267 (11), 266 (72), 265 (12), 250 (18), 249 (100), 245 (17), 230 (14), 229 (74), 201 (47), 152 (21). Anal. Calc. for $C_{17}H_{15}F_3O_2$: C, 66.23; H, 4.90. Found: C, 65.93; H, 4.83%.

#### 4.2.6. Compound ***6b***

White solid; mp 63–64 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.06 (d, *J* = 6.3 Hz, 6H), 3.84 (s, 3H), 5.02 (septet, *J* = 6.3 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.47–7.58 (m, 2H), 7.61–7.71 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.2, 55.3, 69.5, 113.7, 123.6 (q, *J* = 274 Hz), 124.6 (q, *J* = 5.0 Hz), 127.4 (q, *J* = 32 Hz), 129.2, 129.9, 131.5, 132.1 (q, *J* = 2.1 Hz), 133.5, 140.1, 159.6, 166.8. IR (KBr): 1722, 1611, 1517, 1453, 1382, 1285, 1262, 1250, 1195, 1178, 1168, 1142, 1117, 1101, 1067, 1046, 1029, 826, 812 cm$^{-1}$. MS *m*/*z* (% relative intensity): 339 (14), 338 ($M^+$, 73), 297 (16), 296 (100), 279 (26), 259 (44), 139 (14). HRMS–ESI: *m*/*z* $[M + Na]^+$ calc. for $C_{18}H_{17}F_3NaO_3$: 361.1028; found 361.1021.

#### 4.2.7. Compound ***6c***

Colorless liquid $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.87 (d, *J* = 6.3 Hz, 3H), 1.01 (d, *J* = 6.3 Hz, 3H), 2.11 (s, 3H), 4.87 (septet, *J* = 6.3 Hz, 1H), 7.10–7.21 (m, 2H), 7.21–7.31 (m, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.54 (dd, *J* = 7.6 Hz, 7.9 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.1, 20.8, 21.2, 69.3, 123.6 (q, *J* = 274 Hz), 124.9 (q, *J* = 4.8 Hz), 125.2, 127.4 (q, *J* = 32 Hz), 128.3, 128.9, 129.6, 129.8, 132.6 (q, *J* = 2.2 Hz), 133.4 (q, *J* = 1.2 Hz), 136.4, 138.2, 140.8, 166.2. IR (neat): 2983, 1733, 1455, 1376, 1328, 1279, 1192, 1171, 1139, 1102, 1065, 1053, 810, 762 cm$^{-1}$. MS (% relative intensity): 322 ($M^+$, 21), 280 (28), 263 (43), 262 (100), 261 (11), 243 (15), 235 (15), 234 (57), 215 (27), 214 (11), 193 (11), 166 (21), 165 (76). HRMS–ESI: *m*/*z* $[M + Na]^+$ calc. for $C_{18}H_{17}F_3NaO_2$: 345.1078; found 345.1079.

*4.2.8. Compound* ***8***

Colorless liquid $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.03 (d, $J$ = 6.3 Hz, 6H), 5.12 (septet, $J$ = 6.3 Hz, 1H), 7.34–7.46 (m, 3H), 7.46–7.61 (m, 5H), 7.87–7.92 (m, 1H), 7.92–7.97 (m, 1H), 7.97–8.02 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.4, 69.0, 124.9, 126.2, 127.4, 127.4, 127.5, 128.1, 128.3, 128.8, 129.6, 129.9, 130.5, 132.3, 137.9, 141.0, 168.9. IR (neat): 3058, 2979, 1718, 1495, 1464, 1447, 1375, 1284, 1238, 1181, 1167, 1143, 1105, 1086, 1029, 1012, 916, 836, 823, 762, 747, 702 cm$^{-1}$. MS (% relative intensity): 291 (16), 290 ($M^+$, 77), 249 (12), 248 (70), 247 (26), 232 (22), 231 (100), 203 (36), 202 (72), 201 (14), 200 (13), 101 (11). Anal. Calc. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 83.01; H, 6.35%.

*4.2.9. Compound* ***10a***

Colorless liquid $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.01(d, $J$ = 6.3 Hz, 6H), 4.97 (septet, $J$ = 6.3 Hz, 1H), 7.28–7.44 (m, 7H), 7.47–7.54 (m, 1H), 7.77–7.83 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.3, 68.5, 127.0, 127.0, 127.9, 128.4, 129.5, 130.5, 130.8, 131.9, 141.5, 142.2, 168.4. IR (neat): 2980, 1718, 1476, 1451, 1373, 1283, 1243, 1132, 1108, 1047, 748, 700 cm$^{-1}$. MS $m/z$ (% relative intensity): 240 ($M^+$, 48), 198 (45), 197 (39), 182 (20), 181 (100), 153 (25), 152 (41), 151 (11). Anal. Calc. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.72; H, 6.76%.

*4.2.10. Compound* ***10b***

Colorless liquid $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.06 (d, $J$ = 6.3 Hz, 6H), 3.84 (s, 3H), 4.94 (septet, $J$ = 6.3 Hz, 1H), 6.98 (d, $J$ = 8.8 Hz, 2H), 7.24 (d, $J$ = 8.8 Hz, 2H), 7.32–7.47 (m, 2H), 7.49–7.59 (m, 1H), 7.65–7.74 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.4, 55.3, 68.5, 113.5, 126.7, 129.4, 129.6, 130.6, 130.8, 131.9, 133.9, 141.7, 159.0, 168.6. IR (neat): 2980, 2935, 1714, 1612, 1518, 1480, 1466, 1444, 1373, 1284, 1248, 1179, 1132, 1107, 1085, 1047, 1037, 833, 764 cm$^{-1}$. MS $m/z$ (% relative intensity): 271 (17), 270 ($M^+$, 95), 229 (15), 228 (100), 227 (17), 212 (14), 211 (63), 168 (21), 167 (11), 140 (15), 139 (27), 106 (12). Anal. Calc. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.24; H, 6.76%.

*4.2.11. Compound* ***10d***

Colorless liquid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.05(d, $J$ = 6.3 Hz, 6H), 2.39 (s, 3H), 4.99 (septet, $J$ = 6.3 Hz, 1H), 7.16–7.23 (m, 4H), 7.31–7.41 (m, 2H), 7.45–7.53 (m, 1H), 7.74–7.80 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.1, 21.4, 68.5, 126.9, 128.3, 128.7, 129.4, 130.5, 130.8, 131.9, 136.8, 138.6, 142.2, 168.5. IR (neat): 3024, 2979, 2935, 1714, 1599, 1518, 1480, 1467, 1446, 1386, 1373, 1350, 1334, 1287, 1245, 1182, 1132, 1108, 1046, 918, 854, 820, 761, 709 cm$^{-1}$. MS $m/z$ (% relative intensity): 255 (16), 254 ($M^+$, 86), 213 (12), 212 (82), 211 (47), 196 (22), 195 (100), 181 (20), 167 (18), 166 (18), 165 (46), 152 (37). Anal. Calc. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.56; H, 7.18%.

*4.2.12. Compound* ***11a***

White solid; mp 125–125.5 °C. $^1$H NMR (270 MHz, $CDCl_3$): $\delta$ = 0.83 (d, $J$ = 6.2 Hz, 6H), 4.75 (septet, $J$ = 6.2 Hz, 1H), 7.34–7.49 (m, 13H). $^{13}$C NMR (67.8 MHz, $CDCl_3$): $\delta$ = 21.1, 65.6, 127.4, 128.1, 128.5, 128.7, 129.0, 133.3, 140.1, 140.4, 168.5. IR (KBr):3059, 2976, 1723, 1584, 1571, 1495, 1454, 1441, 1372, 1282, 1267, 1129, 1099, 1065, 1028, 919, 809, 773, 761, 699 cm$^{-1}$. MS $m/z$ (% relative intensity): 317 (13), 316 ($M^+$, 55), 274 (38), 273 (28), 258 (30), 257 (100), 229 (19), 228 (30), 227 (12), 226 (16). Anal. Calc. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.36; H, 6.34%.

*4.2.13. Compound* ***11b***

White solid; mp 113–114 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.88 (d, $J$ = 6.3 Hz, 6H), 3.83 (s, 6H), 4.80 (septet, $J$ = 6.3 Hz, 1H), 6.89–6.94 (m, 4H), 7.28–7.37 (m, 6H), 7.41–7.48 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.2, 55.3, 68.4, 113.6, 128.5, 128.9, 129.7, 133.0, 133.5, 139.7, 159.1, 168.9. IR (KBr): 1722, 1609, 1515, 1460, 1291, 1270, 1245, 1175, 1101, 1059, 1032, 1020, 827, 802, 775, 568 cm$^{-1}$. MS $m/z$ (% relative intensity): 377 (26), 376 ($M^+$, 100), 335 (13), 334 (58), 333 (11), 318 (13), 317 (49), 202 (13). HRMS–ESI: $m/z$ [M + Na]$^+$ calc. for $C_{24}H_{24}NaO_4$: 399.1572; found 399.1585.

*4.2.14. Compound* ***11d***

White solid; mp 92.5–93 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 0.85 (d, $J$ = 6.3 Hz, 6H), 2.38 (s, 6H), 4.78 (septet, $J$ = 6.3 Hz, 1H), 7.15–7.22 (m, 4H), 7.28–7.35 (m, 6H), 7.42–7.48 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.0, 21.1, 68.4, 128.4, 128.6, 128.8, 129.0, 133.3, 137.0, 137.7, 140.1, 168.8. IR (KBr): 2976, 1727, 1515, 1454, 1280, 1265, 1101, 1063, 819, 800 cm$^{-1}$. MS $m/z$ (% relative intensity):345 (21), 344 ($M^+$, 79), 303 (11), 302 (53), 301 (33), 286 (27), 285 (100), 271 (15), 242 (24), 241 (15), 238 (13). HRMS–ESI: $m/z$ [M + Na]$^+$ calc. for $C_{24}H_{24}NaO_2$: 367.1674; found 367.1684.

*4.3. Synthesis of* ***12***

An apparatus consisting of a 10 mL Schlenk tube, a glass stopper and a magnetic stirring bar was flame-dried, and then cooled to room temperature under a flow of nitrogen. Ester **11a** (63.1 mg, 0.20 mmol), acetic acid (0.50 mL) and hydrobromic acid (48 wt%, 0.10 mL) were added to the tube. The resulting mixture was heated at 120 °C for 65 h under nitrogen atmosphere. After cooled to room temperature, the reaction mixture was dissolved in potassium hydroxide solution and the mixture was extracted with diethyl ether. The water layer was then acidified with dilute hydrochloric acid and the mixture was extracted with diethyl ether. The organic layer was washed with brine and dried over $Na_2SO_4$. Compound **12** was isolated by silica gel column chromatography (eluent: 25% ethyl acetate in hexane).

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