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Full Paper

Rh^I-Catalyzed Stille-Type Coupling of Diazoesters with Aryl Trimethylstannanes

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A Rh^I-catalyzed cross-coupling of diazoester with arylstannane was developed. This reaction represents the first Stille-type coupling that uses a diazo compound as the coupling partner. The reaction is operationally simple and can be carried out under mild conditions, thus providing an alternative approach for the synthesis of α-aryl esters. Rh^I–carbene migratory insertion process is suggested to be involved as the key step in this Stille-type coupling.

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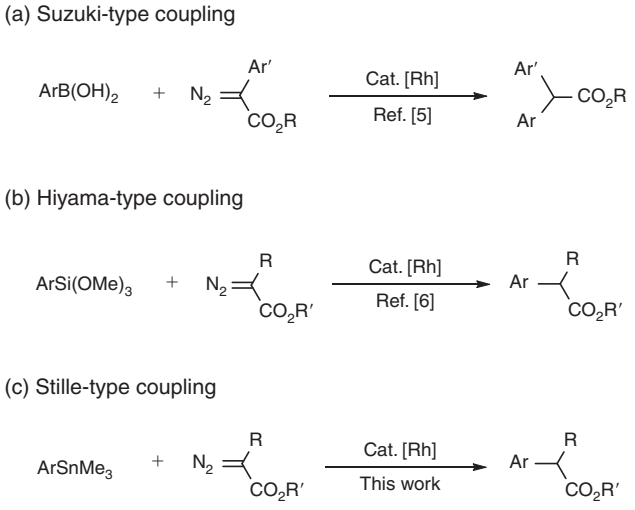
Introduction

Transition metal-catalyzed cross-coupling reactions represent one of the most important methods for the construction of carbon–carbon bond in organic synthesis. Through the extensive studies conducted over the past decades, various cross-coupling partners have been explored. Recently, diazo compounds, as a novel type of coupling partner, have drawn significant attention since the seminal work of Van Vranken and coworkers.[1,2] The distinct feature of these reactions is the formation of metal–carbene intermediate and subsequent migratory insertion process that are the basis of the development of a series of novel cross-coupling reactions.[3] In addition to the palladium- and copper-catalyzed reactions, rhodium-catalyzed coupling reactions of diazo compounds have been investigated. In this context, in 2011, Yu and coworkers reported a Rh^I-catalyzed cross-coupling of aryl diazoesters with aryl boronates, followed by in situ benzylation. The reaction afforded quaternary α,α-diaryl carboxylic acid esters.[4] Subsequently, Ghorai and Anbarasan reported the Rh^I-catalyzed cross-coupling of aryl boronic acids with diazoacetates to give α-aryl carboxylic acid esters (Scheme 1a).[5] Very recently, we have successfully achieved the Rh^I-catalyzed Hiyama-type coupling of arylsiloxanes with a range of diazoesters, affording an alternative methodology for the synthesis of α-aryl carboxylic acid esters (Scheme 1b).[6]

On the other hand, the Stille coupling represents a well-established methodology for building C–C bond in modern organic synthesis.[7] Due to the excellent functional group compatibility, the Stille coupling is widely used in total synthesis, especially for later-stage C–C bond forming transformations.[8] In addition, we have recently developed a Sandmeyer-type stannylation reaction in which aryl trimethylstannanes can be easily prepared from aryl amines.[9] As a continuation of our study in carbene chemistry and the interest of developing new transformation of aryl organotin regents,[10] we conceived that aryl trimethylstannanes might couple with diazo compounds under the catalysis of Rh^I complex. Herein, we report the Rh^I-catalyzed cross-coupling reaction of aryl trimethylstannanes with diazoesters (Scheme 1c). To the best of our knowledge, this reaction represents the first example whereby diazo compounds are used as coupling partners in Stille-type coupling.[11]

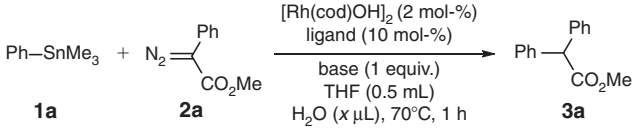


Scheme 1. Rh^I-catalyzed cross-coupling reactions with diazo compounds.

Results and Discussion

At the beginning of this study, phenyl trimethylstannane (**1a**) and phenyl diazoester (**2a**) were chosen as the model substrates

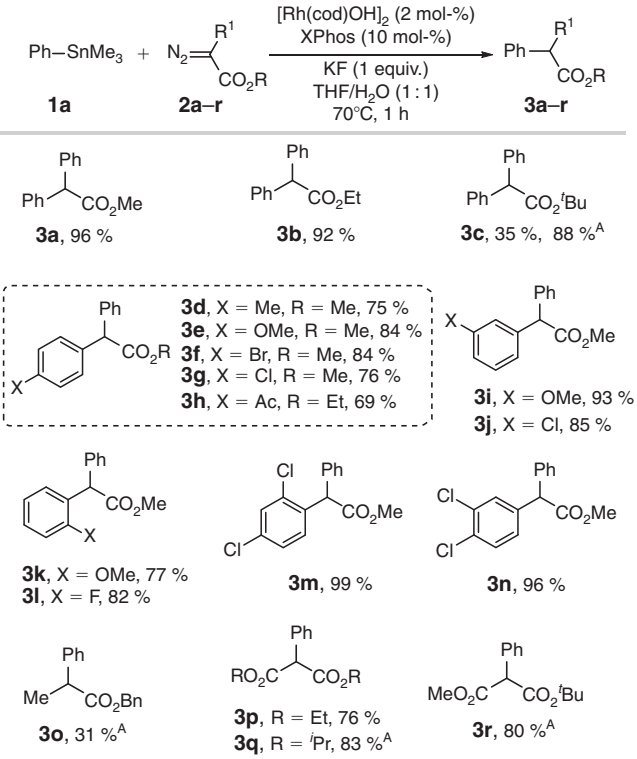
Table 1. Optimization of conditions of the Rh^I-catalyzed coupling between 1a and 2a[A]



1a 2a 3a

Entry	Ligand	1a : 2a	H_2O [μL]	Base	Yield [%][B]
1	None	1 : 1	0	None	N.R.[C]
2	None	1 : 1	50	None	<5
3	None	1 : 1	50	CsF	Trace
4	None	1 : 1	50	TBAF[D]	Trace
5	None	1 : 1	50	KF	15
6	$PCy_3 \cdot HBF_4$	1 : 1	50	KF	41
7	XPhos	1 : 1	50	KF	48
8	BINAP[E]	1 : 1	50	KF	19
9	PPh_3	1: 1	50	KF	17
10	XPhos	1.2 : 1	50	KF	60
11	XPhos	1 : 1.2	50	KF	55
12	XPhos	1.2 : 1	100	KF	75
13	XPhos	1.2 : 1	250	KF	94
14	XPhos	1.2 : 1	500	KF	96
15[F]	XPhos	1.2 : 1	500	KF	85
16	XPhos	1.2 : 1	500	None	57

[A]The reaction was carried out on a 0.1 mmol scale with 2 mol-% of [Rh(cod)OH]$_2$, 10 mol-% of ligand, and 1 equiv. of base at 70°C for 1 h.
[B]Yields correspond to isolated products by column chromatography.
[C]N.R.: no reaction.
[D]Used as 1 M solution in THF.
[E]The amount BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) used was 5 mol-%.
[F]The amounts of [Rh(cod)OH]$_2$ and XPhos used were 1 mol-% and 5 mol-%, respectively .

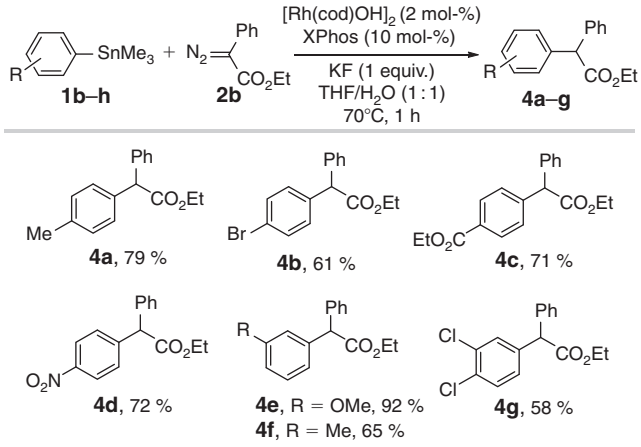


Scheme 2. Reaction scope of diazoesters. Unless otherwise noted, the reaction conditions are the same as those stated in entry 14 of Table 1. Yields correspond to the products isolated by column chromatography. [A]THF (0.75 mL) and H_2O (0.25 mL) were used as the mixed solvent.

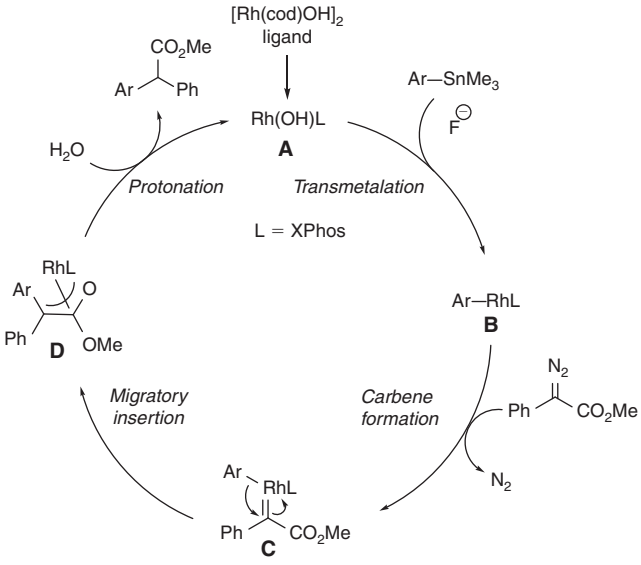
to optimize the reaction conditions (Table 1). Using the reaction conditions of previously reported Hiyama-type coupling,[6] the two substrates were first heated at 70°C for 1 h in the presence of 2 mol-% [Rh(cod)OH]$_2$ (cod = 1,5-cyclooctadiene). However, none of the target product **3a** could be detected through gas chromatography–mass spectrometry (GC–MS) analysis, and both starting materials remained unreacted in large quantities (entry 1). The addition of H_2O to the reaction system was found to slightly promote the reaction (entry 2). We considered that a suitable base might accelerate the transmetalation of organotin reagent to rhodium centre and thus promote the coupling reaction. Then, a series of bases were screened; KF could afford the target coupling product in 15 % isolated yield (entry 5), whereas other stronger bases, such as CsF and TBAF (tetra-*n*-butylammonium fluoride), were not effective (entries 3 and 4). Similarly to our previously reported Hiyama-type coupling,[6] the introduction of electron-rich ligand PCy_3 (tricyclohexylphosphine) to the reaction system significantly promoted the reaction, and the yield could be improved to 41 % (entry 6). By further screening the ligands, it was found that XPhos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) was superior to PCy_3 for the reaction, affording **3a** in slightly improved yields (entries 6–9). Adjusting the ratio of the two substrates could further improve the yields (entries 10 and 11). Finally, we found that the amount of H_2O was crucial to this transformation, and the yield was significantly improved by increasing the amount of H_2O (entries 12–14). Thus, the yield could be improved to 96 % when a 1 : 1 ratio of the THF/H_2O was used as the solution (entry 14). The reaction worked well when the catalyst loading was reduced to 1 mol-%, and the product could still be isolated in 85 % yield (entry 15). In addition, when we removed KF from the reaction system, the reaction yield was only 57 % (entry 16).

With the optimized reaction conditions in hand, we then inspected the reaction scope of this Stille-type coupling. The diazoester component was first tested with phenyl trimethylstannane (**1a**) under the established reaction conditions (Scheme 2). The variation of the ester moiety on the diazo compounds has some effects on the transformation (**3a**–**c**). For both methyl and ethyl ester diazo compounds, the reactions are efficient under the above reaction conditions (**3a**, **3b**). For the more hydrophobic *tert*-butyl ester diazo compound, the ratio of H_2O in the solution system should be reduced, and under the modified conditions, the yield could be improved from 35 % to 88 % (**3c**). The position and electron property of the substituent on the aryl diazo esters show marginal influence on this transformation, and the corresponding products are obtained in 69–99 % yields (**3d**–**n**). It should be noted that the *ortho*-substituted diazo compounds work well in this reaction (**3k**–**m**), and this Rh^I-catalyzed Stille-type coupling is well tolerated with chloro (**3g**, **3j**, **3m, 3n**), bromo (**3f**), and ketone (**3h**) functional groups.

Apart from aryl diazoesters, other types of diazo compounds were investigated (Scheme 2, **3o**–**r**). For alkyl diazoester, this reaction is sluggish even under the modified reaction conditions, and the product **3o** was obtained in 31 % yield only. To our delight, diazomalonates are good substrates for this reaction. Both symmetric and asymmetric diazomalonates are converted into the corresponding products (**3p**–**r**) in good yields.



Scheme 3. Reaction scope of aryl trimethylstannane. The reaction conditions are the same as those stated in entry 14 of Table 1. Yields correspond to the products isolated by column chromatography.



Scheme 4. Proposed reaction mechanism.

Next, the scope of aryl trimethylstannanes was inspected with reaction of aryl diazoester **1b**–**h** under the optimized reaction conditions (Scheme 3). Aryl trimethylstannanes bearing electron-rich (to give products **4a**, **4e, 4f**) and electron-withdrawing (to give products **4b**–**d**, **4g**) groups are all suitable substrates for this transformation, providing the corresponding products in 58–92 % yields. Again, halogen substituents are fully compatible under the current reaction conditions (**4b**, **4g**), thus affording the possibility for further transformations. Other sensitive groups, such as ester and nitro moieties, could also tolerate the reaction conditions (**4c**, **4d**).

A mechanism is proposed for the Rh^I-catalyzed Stille-type coupling reaction (Scheme 4). First, the active rhodium species **A** is generated through ligand exchange, which then undergoes base-assisted transmetalation with aryl trimethylstannane with the aid of base to form aryl rhodium species **B**.[12] According to our control experiment (Table 1, entry 16), KF could significantly improve the reaction yield. One possibility was that KF accelerates the transmetalation step, probably via tin ate complex formation.[7] Intermediate **B** then reacts with diazo substrate to give rhodium–carbene species **C** with extrusion of a molecule of N_2 gas.[13,14] Subsequently, an oxa-π-allyl Rh^I intermediate **D** is generated through migratory insertion of the rhodium–carbene species.[14] Finally, protonation of the intermediate **D** affords the coupling product and regenerates the active rhodium species **A**, from which water is indispensable for this transformation.

Conclusions

In summary, we have developed a Rh^I-catalyzed Stille-type cross-coupling of diazoester with aryl trimethylstannane. Aryl organotin reagents are successfully applied in the coupling of diazoesters under the catalytic action of Rh^I complex for the construction of C–C bonds. Rhodium carbene migratory insertion is proposed to be involved in this Stille-type coupling. This reaction shows good functional group compatibility for both coupling partners and the yields are generally good for most examples, thus providing an alternative methodology for the synthesis of α-aryl esters.[15]

Experimental

General Experimental Procedures

All solvents and reagents were purchased from commercial suppliers and used without further purification. Column chromatography was performed on 200–300 mesh silica gal. ^{1}H NMR spectra were recorded on a Bruker ARX 400 (400 MHz) and the data are referenced relative to tetramethylsilane (TMS) at δ_H 0.00 ppm. The ^{1}H NMR data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) J (Hz), integration, and assignment. The ^{13}C NMR spectra were recorded on a Bruker ARX 400 MHz (100 MHz) and are referenced relative to $CDCl_3$ at δ_C 77.0 ppm. The infrared (IR) spectra were recorded on a Thermo Electron Corporation Nicolet AVATAR 300 FT-IR spectrometer; the data are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were recorded on a Bruker Apex IV FTMS spectrometer. The high-resolution mass spectrometry (HRMS) measurements were performed on a FT-ICR mass analyzer.

General Procedure for Rh^I-Catalyzed Stille Coupling

$[Rh(cod)OH]_2$ (0.9 mg, 0.002 mmol, 2 mol-%), XPhos (4.8 mg, 0.01 mmol, 10 mol-%), and KF (5.8 mg, 0.1 mmol) were added successively to a 10-mL Schlenk tube. The reaction tube was degassed thrice with nitrogen gas, followed by the addition of THF (0.5 mL) and deionized water (0.5 mL) using a syringe. The diazoester substrates (0.1 mmol, 1.0 equiv.) and aryl trimethylstannane (0.12 mmol, 1.2 equiv.) were then added successively using a syringe. It should be noted that substrates in a solid form were added to the reaction tube before adding the solvent. The reaction tube was immediately immersed in an oil bath at 70°C with stirring for 1 h. Upon completion of the reaction, the reaction mixture was diluted with petroleum ether (3 mL) and filtered through a short plug of silica gel using petroleum ether/ethyl acetate (5 : 1, 10 mL) as eluent. The solvent was then removed under vacuum to leave a crude mixture, which was purified by silica gel column chromatography to afford the pure product.

*Methyl 2,2-Diphenylacetate (**3a**)*[6]

Yield: 21.7 mg, 96 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.32–7.24 (m, 10H), 5.03 (s, 1H), 3.74 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 172.9, 138.6, 128.6, 128.6, 127.2, 57.0, 52.3.

*Ethyl 2,2-Diphenylacetate (**3b**)*[6]

Yield: 22.1 mg, 92 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.32–7.23 (m, 10H), 5.01 (s, 1H), 4.20 (d, *J* 7.1, 2H), 1.24 (d, *J* 7.1, 3H). δ_C ($CDCl_3$, 100 MHz) 172.4, 138.7, 128.5, 128.5, 127.2, 61.1, 57.1, 14.1.

*tert-Butyl 2,2-Diphenylacetate (**3c**)*[6]

Yield: 23.6 mg, 88 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.30–7.29 (m, 7H), 7.25–7.22 (m, 2H), 4.91 (s, 1H), 1.44 (s, 9H). δ_C ($CDCl_3$, 100 MHz) 171.6, 139.2, 128.6, 128.4, 127.0, 81.2, 58.0, 27.9.

*Methyl 2-Phenyl-2-(p-tolyl)acetate (**3d**)*[6]

Yield: 18.0 mg, 75 %. Yellow oil. δ_H ($CDCl_3$, 400 MHz) 7.30–7.24 (m, 5H), 7.19 (d, *J* 8.0, 2H), 7.12 (d, *J* 8.0, 2H), 4.99 (s, 1H), 3.72 (s, 3H), 2.31 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 173.1, 138.8, 136.9, 135.6, 129.3, 128.5, 128.5, 128.4, 127.2, 56.6, 52.2, 21.0.

*Methyl 2-(4-Methoxyphenyl)-2-phenylacetate (**3e**)*[16]

Yield: 21.6 mg, 84 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.34–7.22 (m, 7H), 6.89–6.84 (m, 2H), 4.98 (s, 1H), 3.78 (s, 3H), 3.73 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 173.2, 158.7, 138.9, 130.7, 129.6, 128.6, 128.4, 127.2, 114.0, 56.1, 55.2, 52.3.

*Methyl 2-(4-Bromophenyl)-2-phenylacetate (**3f**)*[6]

Yield: 25.6 mg, 84 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.43 (d, *J* 8.5, 2H), 7.32–7.26 (m, 5H), 7.18 (d, *J* 8.5, 2H), 4.98 (s, 1H), 3.74 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 172.5, 138.0, 137.6, 131.7, 130.3, 128.7, 128.4, 127.5, 121.4, 56.3, 52.4.

*Methyl 2-(4-Chlorophenyl)-2-phenylacetate (**3g**)*[4]

Yield: 19.7 mg, 76 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.35–7.23 (m, 8H), 5.00 (s, 1H), 3.75 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 172.6, 138.1, 137.1, 133.2, 130.0, 128.7, 128.7, 128.4, 127.5, 56.3, 52.4.

*Ethyl 2-(4-Acetylphenyl)-2-phenylacetate (**3h**)*[6]

Yield: 19.5 mg, 69 %. Yellow oil. δ_H ($CDCl_3$, 400 MHz) 7.93–7.90 (m, 2H), 7.42 (d, *J* 8.2, 2H), 7.34–7.28 (m, 5H), 5.06 (s, 1H), 4.22 (d, *J* 7.1, 2H), 2.58 (s, 3H), 1.26 (d, *J* 7.1, 3H). δ_C ($CDCl_3$, 100 MHz) 197.6, 171.8, 144.0, 137.9, 136.0, 128.8, 128.7, 128.6, 128.5, 127.5, 61.4, 57.0, 26.6, 14.1.

*Methyl 2-(3-Methoxyphenyl)-2-phenylacetate (**3i**)*[6]

Yield: 23.8 mg, 93 %. Yellow oil. δ_H ($CDCl_3$, 400 MHz) 7.32–7.23 (m, 6H), 6.90–6.86 (m, 2H), 6.81–6.79 (m, 1H), 5.00 (s, 1H), 3.76 (s, 3H), 3.74 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 172.8, 159.7, 140.0, 138.4, 129.5, 128.6, 128.5, 127.3, 120.9, 114.6, 112.5, 56.9, 55.2, 52.3.

*Methyl 2-(3-Chlorophenyl)-2-phenylacetate (**3j**)*[6]

Yield: 22.1 mg, 85 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.34–7.18 (m, 9H), 4.99 (s, 1H), 3.75 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 172.4, 140.5, 137.9, 134.4, 129.8, 128.8, 128.5, 127.5, 127.5, 126.8, 56.6, 52.4.

*Methyl 2-(2-Methoxyphenyl)-2-phenylacetate (**3k**)*

Yield: 19.6 mg, 77 %. Colourless oil. ν_{max} (film)/cm^{-1} 700, 756, 1245, 1730, 2921. δ_H ($CDCl_3$, 400 MHz) 7.36–7.22 (m, 6H), 7.02 (dd, *J* 1.4, 7.7, 1H), 6.90–6.87 (m, 2H), 5.31 (s, 1H), 3.82 (s, 3H), 3.72 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 173.4, 156.7, 137.6, 129.1, 129.0, 128.5, 128.4, 127.6, 127.1, 120.4, 110.3, 55.5, 52.1, 50.7. HRMS (ESI (electrospray ionization) *m*/*z* 257.1170; calcd for $C_{16}H_{17}O_3$ 257.1172. HRMS (ESI) *m*/*z* 279.0990; calcd for $C_{16}H_{16}NaO_3$ 279.0992.

*Methyl 2-(2-Fluorophenyl)-2-phenylacetate (**3l**)*[6]

Yield: 20.0 mg, 82 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.36–7.21 (m, 7H), 7.10–7.02 (m, 2H), 5.30 (s, 1H), 3.74 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 172.3, 162.4 (d, *J* 246.6), 137.1, 129.9 (d, *J* 3.5), 130.0 (d, *J* 8.2), 128.7, 127.5, 126.2 (d, *J* 14.2), 124.1 (d, *J* 3.5), 115.3 (d, *J* 22.1), 52.4, 49.7 (d, *J* 3.4).

*Methyl 2-(2,4-Dichlorophenyl)-2-phenylacetate (**3m**)*[6]

Yield: 29.2 mg, 99 %. White solid. δ_H ($CDCl_3$, 400 MHz) 7.40 (d, *J* 1.5, 1H), 7.37–7.24 (m, 5H), 7.19–7.14 (m, 2H), 5.42 (s, 1H), 3.74 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 172.0, 136.6, 135.2, 134.8, 133.8, 131.0, 129.3, 128.9, 128.7, 127.7, 127.2, 53.2, 52.6.

*Methyl 2-(3,4-Dichlorophenyl)-2-phenylacetate (**3n**)*[6]

Yield: 28.3 mg, 96 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.41–7.25 (m, 7H), 7.15 (dd, *J* 2.1, 8.4, 1H), 4.96 (s, 1H), 3.75 (s, 3H). δ_C ($CDCl_3$, 100 MHz) 172.1, 138.7, 137.5, 132.6, 131.5, 130.6, 130.4, 128.9, 128.4, 128.0, 127.7, 56.0, 52.5.

*Benzyl 2-Phenylpropanoate (**3o**)*[6]

Yield: 7.4 mg, 31 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.31–7.22 (m, 10H), 5.10 (AB quart, *J* 12.5, 2H), 3.77 (q, *J* 7.2, 1H), 1.52 (d, *J* 7.2, 3H). δ_C ($CDCl_3$, 100 MHz) 174.3, 140.4, 136.0, 128.6, 128.4, 128.0, 127.8, 127.5, 127.1, 66.4, 45.5, 18.4.

*Diethyl 2-Phenylmalonate (**3p**)*[6]

Yield: 17.9 mg, 76 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.42–7.33 (m, 5H), 4.61 (s, 1H), 4.26–4.17 (m, 4H), 1.26 (t, *J* 7.1, 6H). δ_C ($CDCl_3$, 100 MHz) 168.1, 132.8, 129.2, 128.6, 128.2, 61.8, 57.9, 14.0.

*Diisopropyl 2-Phenylmalonate (**3q**)*[6]

Yield: 22.0 mg, 83 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.41–7.30 (m, 5H), 5.11–5.02 (m, 2H), 4.54 (s, 1H), 1.27–1.22 (m, 12H). δ_C ($CDCl_3$, 100 MHz) 167.7, 133.0, 129.3, 128.5, 128.0, 69.3, 58.4, 21.5.

*1-tert-Butyl 3-Methyl 2-Phenylmalonate (**3r**)*[6]

Yield: 20.0 mg, 80 %. Colourless oil. δ_H ($CDCl_3$, 400 MHz) 7.40–7.32 (m, 5H), 4.55 (s, 1H), 3.75 (s, 3H), 1.45 (s, 9H). δ_C ($CDCl_3$, 100 MHz) 169.0, 167.1, 133.1, 129.2, 128.5, 128.0, 82.4, 58.8, 52.6, 27.8.

*Ethyl 2-Phenyl-2-(p-tolyl)acetate (**4a**)*[17]

Yield: 20.1 mg, 79 %. Yellow oil. δ_H ($CDCl_3$, 400 MHz) 7.31–7.11 (m, 9H), 4.97 (s, 1H), 4.20 (d, *J* 7.1, 2H), 2.32 (s, 3H), 1.25 (t, *J* 7.1, 3H). δ_C ($CDCl_3$, 100 MHz) 172.6, 138.9, 136.8, 135.7, 129.2, 128.5, 128.4, 127.0, 61.1, 56.7, 21.0, 14.1.

*Ethyl 2-(4-Bromophenyl)-2-phenylacetate (**4b**)*

Yield: 19.4 mg, 61 %. White solid. ν_{max} (film)/cm^{-1} 699, 1011, 1151, 1191, 1734. δ_H ($CDCl_3$, 400 MHz) 7.45–7.18 (m, 9H), 4.95 (s, 1H), 4.20 (d, *J* 7.1, 2H), 1.25 (t, *J* 7.1, 3H). δ_C ($CDCl_3$, 100 MHz) 172.0, 138.2, 137.7, 131.6, 130.3, 128.6, 128.4, 127.4, 121.3, 61.3, 56.4, 14.0. HRMS (ESI) *m/z* 319.0330; calcd for $C_{16}H_{16}BrO_2$ 319.0328. HRMS (ESI) *m/z* 341.0150; calcd for $C_{16}H_{15}BrNaO_2$ 341.0148.

*Ethyl 4-(2-Ethoxy-2-oxo-1-phenylethyl)benzoate (**4c**)*

Yield: 22.0 mg, 71 %. Colourless oil. ν_{max} (film)/cm^{-1} 1023, 1106, 1153, 1277, 1720. δ_H ($CDCl_3$, 400 MHz) 8.01–7.99 (m, 2H), 7.40–7.27 (m, 7H), 5.06 (s, 1H), 4.36 (d, *J* 7.1, 2H), 4.22 (d, *J* 7.1, 2H), 1.37 (t, *J* 7.1, 3H), 1.26 (t, *J* 7.1, 3H). δ_C ($CDCl_3$, 100 MHz) 171.8, 166.2, 143.6, 138.0, 129.7, 129.4, 128.6, 128.6, 128.5, 127.4, 61.3, 60.9, 57.0, 14.3, 14.0. HRMS (ESI) *m/z* 313.1435; calcd for $C_{19}H_{21}O_4$ 313.1434. HRMS (ESI) *m/z* 335.1255; calcd for $C_{19}H_{20}NaO_4$ 335.1254.

*Ethyl 2-(4-Nitrophenyl)-2-phenylacetate (**4d**)*

Yield: 20.4 mg, 72 %. Yellow oil. ν_{max} (film)/cm^{-1} 703, 1153, 1348, 1521, 1734. δ_H ($CDCl_3$, 400 MHz) 8.18–8.16 (m, 2H), 7.51–7.49 (m, 2H), 7.38–7.29 (m, 5H), 5.10 (s, 1H), 4.24 (d, *J* 7.1, 2H), 1.28 (t, *J* 7.1, 3H). δ_C ($CDCl_3$, 100 MHz) 171.3, 147.0, 145.9, 137.3, 129.5, 128.9, 128.4, 127.8, 123.7, 61.6, 56.7, 14.0. HRMS (ESI) *m/z* 286.1074; calcd for $C_{16}H_{16}NO_4$ 286.1074. HRMS (ESI) *m/z* 308.0892; calcd for $C_{16}H_{15}NNaO_4$ 308.0893.

*Ethyl 2-(3-Methoxyphenyl)-2-phenylacetate (**4e**)*[18]

Yield: 24.8 mg, 92 %. Yellow oil. δ_H ($CDCl_3$, 400 MHz) 7.32–7.21 (m, 6H), 6.91–6.87 (m, 2H), 6.81–6.78 (m, 1H), 4.98 (s, 1H), 4.20 (d, *J* 7.1, 2H), 3.76 (s, 3H), 1.25 (t, *J* 7.1, 3H). δ_C ($CDCl_3$, 100 MHz) 172.3, 159.6, 140.1, 138.5, 129.4, 128.5, 127.2, 120.9, 114.4, 112.4, 61.1, 57.0, 55.1, 14.1.

*Ethyl 2-Phenyl-2-(m-tolyl)acetate (**4f**)*

Yield: 16.6 mg, 65 %. Colourless oil. ν_{max} (film)/cm^{-1} 700, 1028, 1147, 1735, 2921. δ_H ($CDCl_3$, 400 MHz) 7.32–7.19 (m, 6H), 7.13–7.06 (m, 3H), 4.97 (s, 1H), 4.20 (d, *J* 7.1, 2H), 2.32 (s, 3H), 1.25 (t, *J* 7.1, 3H). δ_C ($CDCl_3$, 100 MHz) 172.5, 138.8, 138.6, 138.1, 129.2, 128.5, 128.5, 128.4, 127.9, 127.1, 125.5, 61.1, 57.0, 21.4, 14.1. HRMS (ESI) *m/z* 255.1377; calcd for $C_{17}H_{19}O_2$ 255.1380. HRMS (ESI) *m/z* 277.1197; calcd for $C_{17}H_{18}NaO_2$ 277.1199.

*Ethyl 2-(3,4-Dichlorophenyl)-2-phenylacetate (**4g**)*

Yield: 17.9 mg, 58 %. Colourless oil. ν_{max} (film)/cm^{-1} 699, 1011, 1151, 1191, 1734. δ_H ($CDCl_3$, 400 MHz) 7.42–7.27 (m, 7H), 7.16 (dd, *J* 2.1, 8.3, 1H), 4.94 (s, 1H), 4.21 (d, *J* 7.1, 2H), 1.25 (t, *J* 7.1, 3H). δ_C ($CDCl_3$, 100 MHz) 171.6, 138.8, 137.6, 132.5, 131.4, 130.6, 130.4, 128.8, 128.3, 128.0, 127.6, 61.5, 56.0. HRMS (ESI) *m/z* 309.0443; calcd for $C_{16}H_{15}Cl_2O_2$ 309.0444. HRMS (ESI) *m/z* 331.0263; calcd for $C_{16}H_{14}Cl_2NaO_2$ 331.0263.

Supplementary Material

Copies of ^{1}H and ^{13}C NMR spectra for all new products are available on the Journal's website.

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