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Direct Coupling of Arylacetonitriles and Primary Alcohols to α-Alkylated Arylacetamides with Complete Atom Economy Catalyzed by a Rhodium Complex–Triphenylphosphine–Potassium Hydroxide System

Feng Li,[a,*] Xiaoyuan Zou,[a] and Nana Wang[a]

[a] Key Laboratory for Soft Chemistry and Functional Materials, Ministry of Education, Nanjing University of Science and Technology, Nanjing 210 094, People's Republic of China
Fax: (+86)-25-8443-1939; e-mail: fengli@njust.edu.cn

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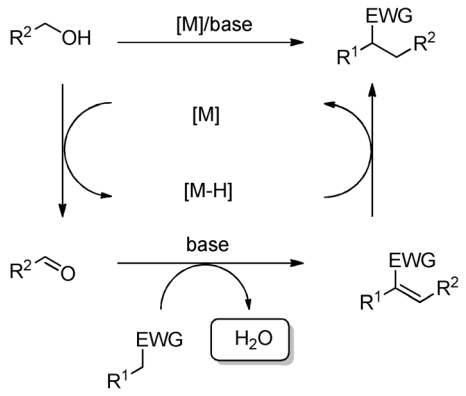
Abstract: A direct synthesis of α-alkylated arylacetamides from arylacetonitriles and primary alcohols has been accomplished for the first time. In the presence of the rhodium complex $[Rh(cod)Cl]_2$/triphenylphosphine/potassium hydroxide system, the desired α-alkylated arylacetamides were obtained in 74–92% yield under microwave conditions. The experimental results in this paper are in sharp contrast with previous reports, where the coupling of arylacetonitriles and primary alcohols produced the α-alkylated arylacetonitriles. Mechanistic investigations show that arylacetonitriles are first α-alkylated with primary alcohols to produce α-alkylated arylacetonitriles, which are further hydrated with the water resulting from the α-alkylation step to produce α-alkylated arylacetamides. More importantly, this research shows the potential of developing completely atom-economical reactions that involve the hydrogen autotransfer (or hydrogen borrowing) process.

Keywords: alcohols; complete atom economy; homogeneous catalysis; nitriles; rhodium

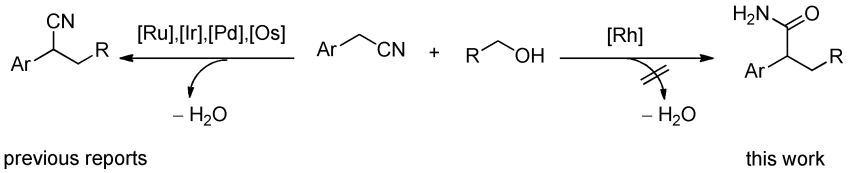
Introduction

Maximizing the atom efficiency and minimizing the waste generation of a reaction are the most significant and challenging goals of modern organic synthesis.[1] In recent years, much attention has been focused on the construction of C–C bonds, which are the essential link in all organic molecules, *via* reactions of enolates with the activation of alcohols as electrophiles based on the hydrogen autotransfer (or hydrogen borrowing) process using ruthenium, iridium or other transition metal catalysts.[2,3] In this process, alcohols are first dehydrogenated to form aldehydes with the generation of metal hydride species, followed by condensation between enolates. The resulting aldehydes produce unsaturated intermediates, which are further hydrogenated by the metal hydride species that is formed in the dehydrogenation step of alcohols, to produce α-alkylated products (Scheme 1). Despite significant advances, such transformations are not completely atom-economical reactions because water is generated as a by-product in this process.

We have reported a series of iridium-catalyzed transformations with the activation of alcohols as electrophiles.[4] As part of our continuing interest in this field, we explored the potential of rhodium complexes as catalysts. Herein, we wish to demonstrate



Scheme 1. Transition metal-catalyzed C–C bond-forming reactions based on the hydrogen autotransfer (or hydrogen borrowing) process.



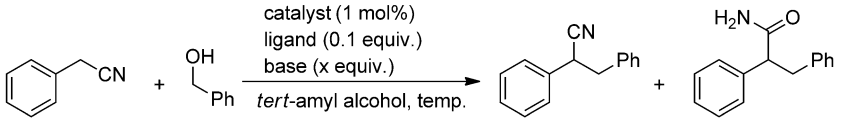
Scheme 2. Transition metal-catalyzed coupling of arylacetonitriles and alcohols.

the first example of the direct coupling of arylacetonitriles and primary alcohols to afford α-alkylated arylacetamides with complete atom economy (Scheme 2, *right*). The experimental results of this paper are in sharp contrast with previous reports.[5] Several groups have reported the coupling of arylacetonitriles and primary alcohols to afford the α-alkylated arylacetonitriles catalyzed by ruthenium,[5a,b] palladium,[5b] iridium[5c] and osmium complexes[5d] (Scheme 2, *left*). The α-alkylated arylacetamides are ubiquitous structural motifs in many natural products and pharmaceutically active compounds,[6] and they are used as the key synthetic intermediates to construct biologically active compounds.[7] Traditional methods to synthesize α-alkylated arylacetamides suffer from being multistep reactions from arylacetic acids or their esters as the starting materials, using of a large amount of hazardous reagents and generating a large amount of harmful by-products.[6,7]

Results and Discussion

Our initial experiment focused on the rhodium-catalyzed coupling of phenylacetonitrile (**1a**) and benzyl alcohol (**2a**). In the presence of $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadienyl) (1 mol%), DPPM [bis(diphenylphosphino)methane] (0.1 equiv.) and KOH (0.4 equiv.), the reaction of **1a** and **2a** was performed at 130 °C in *tert*-amyl alcohol (anhydrous, ≥99%) for 17 h. This reaction generated the α-alkylated product **3aa** in 76% yield and 2,3-diphenylpropanamide **4aa** in 24% yield (Table 1, entry 1). Using PCy_3 (tricyclohexylphosphine) as an alternative ligand, a similar result was also observed (Table 1, entry 2). To our surprise, the product **4aa** could be obtained in 95% yield when PPh_3 was used as the ligand (Table 1, entry 3). Using K_2CO_3 or K_3PO_4, instead of KOH, the reactions produced only **3aa** (Table 1, entries 4 and 5). When $[Cp^*RhCl_2]_2$ or $Rh(acac)(CO)_2]$ was used as the catalyst, the product **4aa** was formed in only moderate yields (Table 1, entries 6 and 7). The reaction of **1a** and **2a** proceeded in the presence of the

Table 1. Reactions of phenylacetonitrile **1a** with benzyl alcohol **2a** under various conditions.[a]

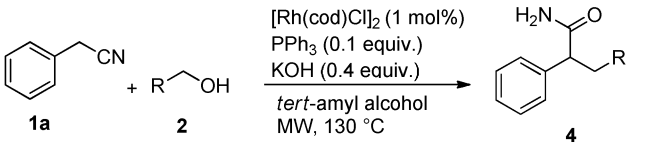


1a **2a** **3aa** **4aa**

Entry	Catalyst	Base	x	Ligand	Temp.	Time	Yield[b]	
							3aa	**4aa**
1	$[Rh(cod)Cl]_2$	KOH	0.4	DPPM	130	17	76	24
2	$[Rh(cod)Cl]_2$	KOH	0.4	PCy_3	130	17	85	15
3	$[Rh(cod)Cl]_2$	KOH	0.4	PPh_3	130	17	5	95
4	$[Rh(cod)Cl]_2$	K_2CO_3	0.4	PPh_3	130	17	17	0
5	$[Rh(cod)Cl]_2$	K_3PO_4	0.4	PPh_3	130	17	90	0
6	$[Cp^*RhCl_2]_2$	KOH	0.4	PPh_3	130	17	46	54
7	$[Rh(acac)(CO)_2]$	KOH	0.4	PPh_3	130	17	58	42
8	**$[Rh(cod)Cl]_2$**	**KOH**	**0.4**	**PPh_3**	**130**	**2**	**4**	**96[c]**
9	$[Rh(cod)Cl]_2$	KOH	0.3	PPh_3	130	2	22	78[c]
10	$[Rh(cod)Cl]_2$	KOH	0.4	PPh_3	120	2	14	86[c]

[a] *Reaction conditions:* **1a** (1 mmol), **2a** (1.1 mmol), catalyst (1 mol%), ligand (0.1 equiv.), base (x equiv.), *tert*-amyl alcohol (1 mL), 130 °C, 17 h.
[b] Yield was determined based on the ^1H NMR spectrum of the crude reaction mixture with 1,3,5-trimethoxybenzene as the internal standard.
[c] MW.

Table 2. Reactions of phenylacetonitrile (**1a**) with various alcohols (**2**).[a]



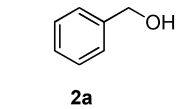
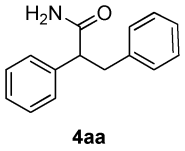
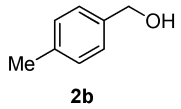
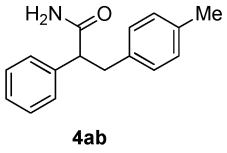
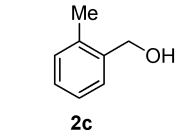
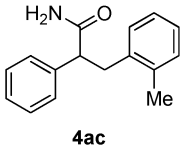
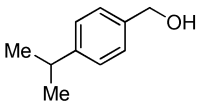
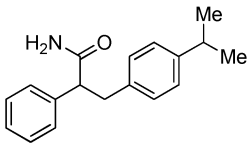
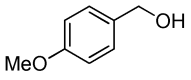
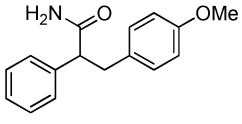
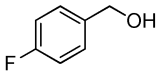
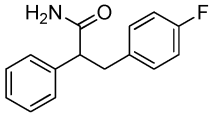
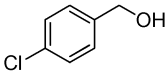
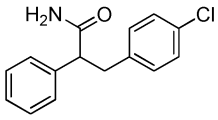
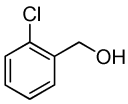
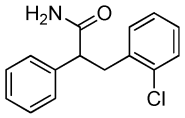
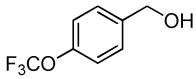
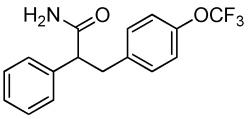
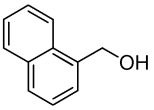
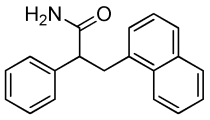
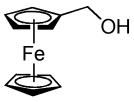
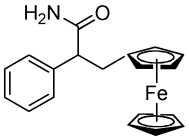
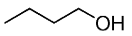
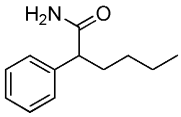
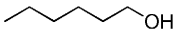
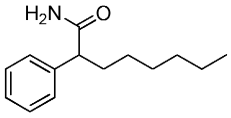
Entry	Alcohol	Product	Yield [%][b]
1	 **2a**	 **4aa**	90
2	 **2b**	 **4ab**	85
3	 **2c**	 **4ac**	82
4	 **2d**	 **4ad**	80
5	 **2e**	 **4ae**	83
6	 **2f**	 **4af**	88
7	 **2g**	 **4ag**	81
8	 **2h**	 **4ah**	88
9	 **2i**	 **4ai**	91

Table 2. (Continued)

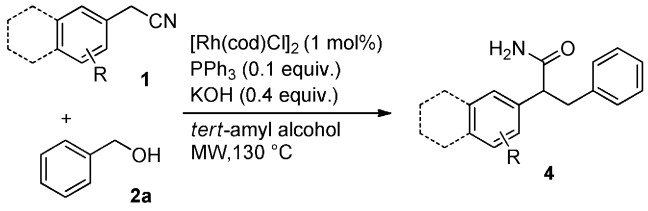
Entry	Alcohol	Product	Yield [%][b]
10	 **2j**	 **4aj**	87
11	 **2k**	 **4ak**	79
12	 **2l**	 **4al**	74[c]
13	 **2m**	 **4am**	76[c]

[a] *Reactions conditions:* **1a** (1 mmol), **2** (1.1 mmol), $[Rh(cod)Cl]_2$ (1 mol%), PPh_3 (0.1 equiv.), KOH (0.4 equiv.), *tert*-amyl alcohol (1 mL), MW, 130 °C, 2 h.
[b] Isolated yield.
[c] **2** (2 mmol).

$[Rh(cod)Cl]_2/PPh_3$/KOH system in a focused, single-mode microwave synthesizer (Discover CEM, USA, 300 W) for 2 h to produce **4aa** in 96% yield (Table 1, entry 8). Apparently, microwave irradiation could accelerate the reaction process. Any attempt to decrease the amount of base and reduce the reaction temperature resulted in relatively low yields of product **4aa** (Table 1, entries 9 and 10).

With the established optimal reaction conditions (Table 1, entry 8), the coupling of **1a** and various alcohols (**2**) was examined, and these results are summarized in Table 2. In analogy to the case of benzyl alcohol (**2a**) (Table 2, entry 1), the reactions with benzylic alcohols that have an electron-donating group, such as methyl (**2b**, **2c**), isopropyl (**2d**) and methoxy (**2e**) groups, generated the desired products (**4ab–4ae**) in 80–85% yields (Table 2, entries 2–5). The coupling with benzylic alcohols that have a halogen atom, such as fluoro (**2f**) and chloro (**2g**, **2h**) generated the corresponding products **4af–4ah** in 81–88% yields (Table 2, entries 6–8). The benzylic alcohol with a strong electron-deficient trifluoromethoxy group (**2i**) was also proven to be a suitable substrate, and the desired product (**4ai**) was obtained in 91% yield (Table 2, entry 9). Furthermore, a high catalytic activity was ob-

Table 3. Reactions of a series of arylacetonitriles (**1**) with benzyl alcohol (**2a**).[a]



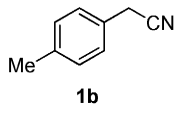
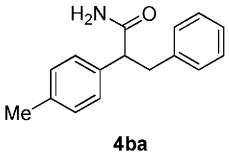
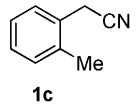
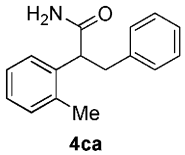
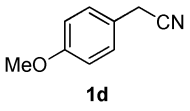
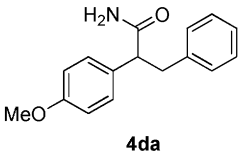
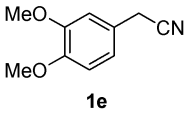
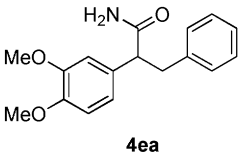
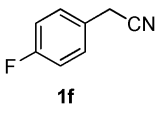
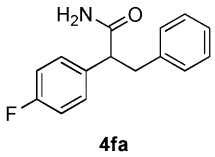
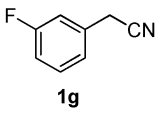
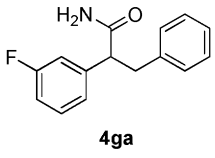
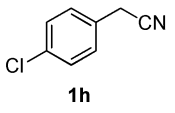
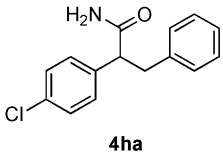
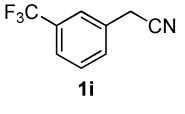
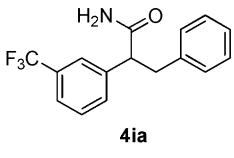
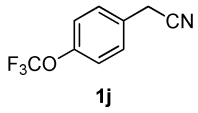
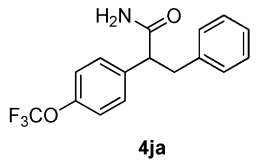
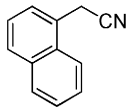
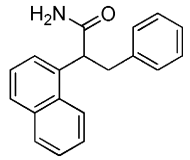
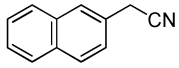
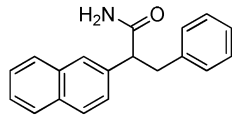
Entry	Arylacetonitrile	Product	Yield [%][b]
1	 **1b**	 **4ba**	83
2	 **1c**	 **4ca**	84
3	 **1d**	 **4da**	80
4	 **1e**	 **4ea**	91
5	 **1f**	 **4fa**	92
6	 **1g**	 **4ga**	89
7	 **1h**	 **4ha**	83
8	 **1i**	 **4ia**	84

Table 3. (Continued)

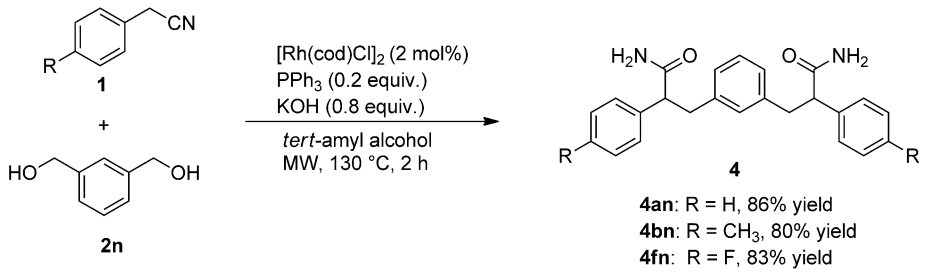
Entry	Arylacetonitrile	Product	Yield [%][b]
9	 **1j**	 **4ja**	90
10	 **1k**	 **4ka**	82
11	 **1l**	 **4la**	88

[a] *Reactions conditions:* **1** (1 mmol), **2a** (1.1 mmol), $[Rh(cod)Cl]_2$ (1 mol%), PPh_3 (0.1 equiv.), KOH (0.4 equiv.), *tert*-amyl alcohol (1 mL), MW, 130 °C, 2 h.

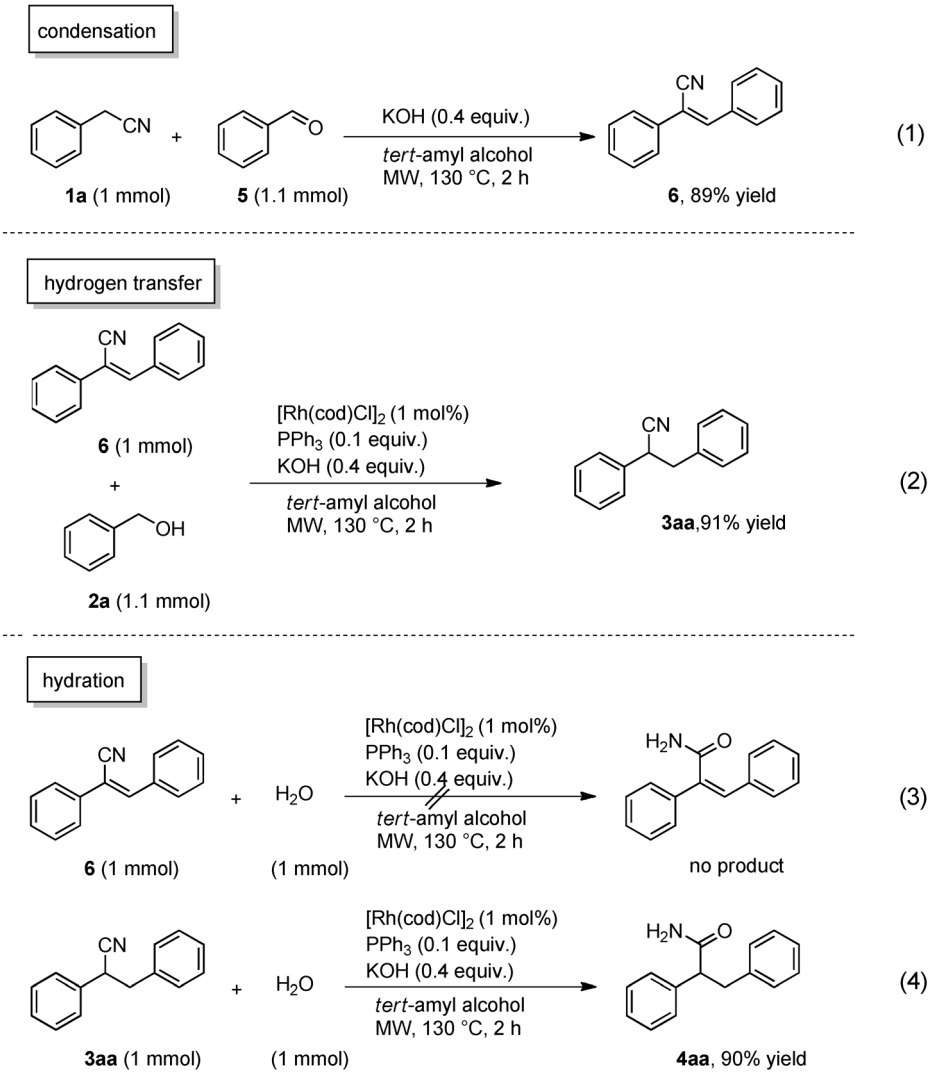
[b] Isolated yield.

served in the transformations of naphthalenemethanol (**2j**) and ferrocenemethanol (**2k**) (Table 2, entries 10 and 11). This coupling reaction was also applied to aliphatic alcohols such as 1-butanol (**2l**) and 1-hexanol (**2m**), which generated the desired products **4al** and **4am** in 74% and 76% yield, respectively, although the addition of 2 equiv. of alcohols was required (Table 2, entries 12 and 13). However, no reaction occurred when secondary alcohols with high steric hindrance, such as cyclohexanol and cyclopentanol, were used as the substrates.

As shown in Table 3, the coupling of a series of arylacetonitriles (**1**) and benzyl alcohol (**2a**) was investigated. The transformations of phenylacetonitriles with one or two electron-donating groups, such as methyl (**1b**, **1c**), methoxy (**1d**) and dimethoxy (**1e**), led to the corresponding products (**4ba–4ea**) in 80–91% yields (Table 3, entries 1–4). The reactions of phenylacetonitriles with a halide atom such as fluoro (**1f**, **1g**) and chloro (**1h**) groups generated the desired products (**4fa–4ha**) in 83–92% yields (Table 3, entries 5–7). Furthermore, phenylacetonitriles with a strong electron-withdrawing group such as trifluoromethyl (**1i**) and trifluoromethoxy (**1j**) moieties were successfully converted to the corresponding products (**4ia** and **4ja**) in 84% and 90% yields, respectively (Table 3, entries 8 and 9). In the case of 1-naphthalenylacetonitrile (**1k**) and 2-naphthalenylacetonitrile (**1l**), the desired products **4ka** and **4la** were isolated in



Scheme 3. Transformations of arylacetonitriles with a diol.

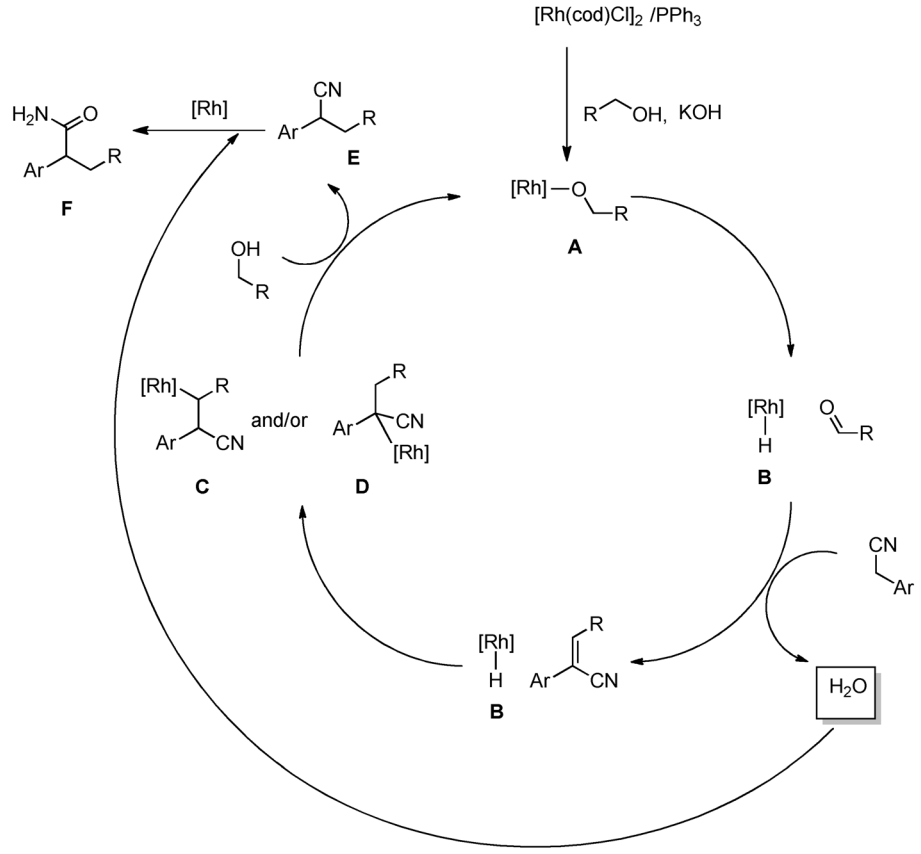


Scheme 4. Mechanistic experiments.

82% and 88% yields, respectively (Table 3, entries 10 and 11).

The transformations of arylacetonitriles with a diol were also investigated (Scheme 3). The reactions of phenylacetonitrile derivatives **1a**, **1b** and **1f** with 1,3-benzenedimethanol (**2n**) generated the desired products in 80–86% yield.

To obtain information on the reaction mechanism, a series of experiments was performed. In the presence of KOH, the condensation between phenylacetonitrile (**1a**) and benzaldehyde (**5**) occurred at 130 °C for 2 h to generate the unsaturated product **6** in 89% yield [Scheme 4, Eq, (1)]. Then, the catalytic hydrogenation of the resulting **6** with benzyl alcohol (**2a**) as



Scheme 5. Proposed mechanism of the reaction.

the hydrogen source was investigated. In the presence of $[Rh(cod)Cl]_2$ (1 mol%), PPh_3 (0.1 equiv.) and KOH (0.4 equiv.), the reaction of **6** with **2a** was performed for 2 h to obtain the product **3aa** in 91% yield [Scheme 4, Eq. (2)]. Finally, the hydration of **6** and **3aa** was examined. When the $Rh(cod)Cl]_2/PPh_3$/KOH system was used, the reaction of **6** with an equimolar amount of water was performed for 2 h, and no product was detected [Scheme 4, Eq. (3)]. It was found that **3aa** could be converted to the product **4aa** in 90% yield under identical reaction conditions [Scheme 4, Eq. (4)]. It is speculated that α,β-unsaturated nitriles are more stable than saturated nitriles under these reaction conditions due to the conjugative effect.

A possible mechanism was proposed to account for this direct coupling of arylacetonitriles and primary alcohols to afford α-alkylated arylacetamides (Scheme 5). The initial step of the reaction involves the formation of alkoxo rhodium species **A** through the reaction of $[Rh(cod)Cl]_2$ and alcohols under the acceleration of the base. By means of the β-hydrogen elimination of the alkoxo rhodium species **A**, the rhodium hydride species **B** and aldehydes are generated. The base-catalyzed Knoevenagel condensation between arylacetonitriles and the resulting aldehydes occurs to produce α,β-unsaturated nitriles and water. Furthermore, the addition of rhodium hydride into the C=C double bond of α,β-unsaturated nitriles produces species **C**. The α-alkylated arylacetonitriles **D** are released, and the catalytically active alkoxo rhodium species **A** are regenerated *via* the reaction of species **C** with alcohols. Finally, the hydration of α-alkylated arylacetonitriles **D** with the water, that results from the Knoevenagel condensation step, produces α-alkylated arylacetamides **E**.[8]

Conclusions

In summary, we have demonstrated the first example of the direct synthesis of α-alkylated arylacetamides from arylacetonitriles and alcohols. In the presence of a rhodium complex $[Rh(cod)Cl]_2$/triphenylphosphine/potassium hydroxide system, α-alkylated arylacetamides could be obtained in 74–92% yield under microwave conditions. The mechanistic investigations show that arylacetonitriles are first α-alkylated with alcohols to produce α-alkylated arylacetonitriles, which are further hydrated with the resulting water through an α-alkylation step to produce α-alkylated arylacetamides. More importantly, this study demon-

strates the potential of developing completely atom-economical reactions that involve the hydrogen auto-transfer (or hydrogen borrowing) process.

Experimental Section

General Experimental Details

High-resolution mass spectra (HR-MS) were obtained on a HPLC-Q-Tof MS(Micro) spectrometer and are reported as *m*/*z* (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$. Melting points were measured on a X-6 micro-melting apparatus (Beijing Tech Instrument Co., Ltd). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 500 MHz using a Bruker Avance 500 spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane or ppm relative to the center of the singlet at 7.26 ppm for $CDCl_3$ and 2.50 ppm for DMSO-d_6. Coupling constants *J* values are reported in Hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 125 MHz using a Bruker Avance 500 spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for $CDCl_3$ and 39.5 ppm for DMSO-d_6. ^{13}C NMR spectra were routinely run with broadband decoupling.

tert-Amyl alcohol (anhydrous, ≥99%), which was purchased from Sigma–Aldrich Co., was used as the solvent for all reactions. Liquid alcohols and arylacetonitriles were stirred for 24 h over CaH_2 and distilled under high vacuum just before use. Solid alcohols, arylacetonitriles and phosphine ligands were treated on a vacuum line with a cold trap using liquid nitrogen as a coolant before use. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates.

General Procedure for the Synthesis of α-Alkylated Arylacetamides *via* Rhodium-Catalyzed Coupling of Arylacetonitriles with Alcohols under Microwave Irradiation (Table 2 and Table 3)

Nitrile **1** (1 mmol), alcohol **2** (1.1 mmol), $[Rh(cod)Cl]_2$ (0.01 mmol, 1 mol%), PPh_3 (0.1 mmol, 0.1 equiv.), KOH (0.4 equiv.) and *tert*-amyl alcohol (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 2 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

2,3-Diphenylpropanamide (4aa):[9] brown solid; yield: 203 mg (90%); mp 126–127 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.24 (m, 5H, ArH), 7.21 (t, *J* = 7.3 Hz, 2H, ArH), 7.15 (t, *J* = 7.3 Hz, 1H, ArH), 7.10 (d, *J* = 7.8 Hz, 2H, ArH), 5.37 (br s, 1H, NH), 5.30 (br s, 1H, NH), 3.64 (t, *J* = 7.5 Hz, 1H, CH), 3.54 (dd, *J* = 13.6 Hz and 7.6 Hz, 1H, CH), 2.99 (dd, *J* = 13.7 Hz and 7.9 Hz, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.4, 139.4, 139.3, 128.9, 128.6, 128.2, 127.9, 127.3, 126.1, 54.5, 39.2.

2-Phenyl-3-*para*-tolylpropanamide (4ab):[10] yellow solid; yield: 202 mg (85%); mp 150–151 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.24 (m, 5H, ArH), 7.03–6.99 (m, 4H, ArH), 5.33 (br s, 1H, NH), 5.29 (br s, 1H, NH), 3.62 (t, *J* = 7.6 Hz, 1H, CH), 3.49 (dd, *J* = 13.6 Hz and 7.5 Hz, 1H, CH), 2.96 (dd, *J* = 13.6 Hz and 7.2 Hz, 1H, CH), 2.28 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.4, 139.4, 136.3, 135.6, 128.9, 128.8, 128.7, 128.0, 127.3, 54.8, 38.9, 21.0.

2-Phenyl-3-*ortho*-tolylpropanamide (4ac): brown solid; yield: 195 mg (82%); mp 150–151 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32–7.26 (m, 5H, ArH), 7.11–7.00 (m, 4H, ArH), 5.37 (br s, 1H, NH), 5.29 (br s, 1H, NH), 3.62 (t, *J* = 7.2 Hz, 1H, CH), 3.54 (dd, *J* = 13.9 Hz and 7.5 Hz, 1H, CH), 2.99 (dd, *J* = 13.9 Hz and 7.2 Hz, 1H, CH), 2.25 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.2, 139.6, 137.6, 136.2, 130.2, 129.6, 128.7, 128.0, 127.4, 126.3, 125.8, 53.4, 36.5, 19.4; HR-MS-EI (70 eV): *m*/*z* = 262.1204, calcd. for $C_{16}H_{17}NONa$ $[M+Na]^+$: 262.1208.

3-(4-Isopropylphenyl)-2-phenylpropanamide (4ad): yellow solid; yield: 214 mg (80%); mp 140–141 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.25 (m, 5H, ArH), 7.09–7.04 (m, 4H, ArH), 5.29 (br s, 2H, NH_2), 3.63 (t, *J* = 7.5 Hz, 1H, CH), 3.42 (dd, *J* = 13.8 Hz and 8.1 Hz, 1H, CH), 2.96 (dd, *J* = 13.9 Hz and 6.9 Hz, 1H, CH), 2.84 (sept, *J* = 6.9 Hz, 1H, CH), 1.21 (d, *J* = 6.9 Hz, 6H, 2xCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.2, 146.7, 139.6, 136.8, 128.8, 128.8, 128.0, 127.4, 126.3, 54.8, 38.9, 33.6, 24.0; HR-MS-EI (70 eV): *m*/*z* = 290.1529, calcd. for $C_{18}H_{21}NONa$ $[M+Na]^+$: 290.1521.

3-(4-Methoxyphenyl)-2-phenylpropanamide (4ae): yellow solid; yield: 212 mg (83%); mp 161–162 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.41 (br s, 1H, NH), 7.35 (d, *J* = 7.6 Hz, 1H, ArH), 7.28 (t, *J* = 7.4 Hz, 2H, ArH), 7.20 (t, *J* = 7.1 Hz, 1H, ArH), 7.08 (d, *J* = 8.1 Hz, 2H, ArH), 6.79–6.77 (m, 3H, 2xArH and NH), 3.70–3.67 (m, 4H, CH and CH_3), 3.22 (dd, *J* = 13.4 Hz and 9.8 Hz, 1H, CH_2), 2.77 (dd, *J* = 13.6 Hz and 5.9 Hz, 1H, CH_2); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.0, 157.5, 140.8, 131.8, 129.8, 128.1, 127.7, 126.6, 113. 5, 54.9, 53.1, 37.8; HR-MS-EI (70 eV): *m*/*z* = 278.1170, calcd. for $C_{16}H_{17}NO_2Na$ $[M+Na]^+$: 278.1157.

3-(4-Fluorophenyl)-2-phenylpropanamide (4af):[10] brown solid; yield: 214 mg (88%); mp 123–124 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33–7.25 (m, 5H, ArH), 7.03 (t, *J* = 6.7 Hz, 2H, ArH), 6.89 (t, *J* = 8.5 Hz, 2H, ArH), 5.39 (br s, 1H, NH), 5.30 (br s, 1H, NH), 3.59 (t, *J* = 7.4 Hz, 1H, CH), 3.50 (dd, *J* = 13.7 Hz and 7.5 Hz, 1H, CH), 2.96 (dd, *J* = 13.6 Hz and 7.6 Hz, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 161.4 (d, $J_{C,F}$ = 243.2 Hz), 139.1, 135.1, 130.4 (d, $J_{C,F}$ = 7.7 Hz), 128.8, 128.0, 127.5, 115.0 (d, $J_{C,F}$ = 20.8 Hz), 54.9, 38.5.

3-(4-Chlorophenyl)-2-phenylpropanamide (4ag): yellow solid; yield: 211 mg (81%); mp 177–178 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.43 (br s, 1H, NH), 7.35 (d, *J* = 7.6 Hz, 2H, ArH), 7.30–7.27 (m, 4H, ArH), 7.22–7.18 (m, 3H, ArH), 6.81 (br s, 1H, NH), 3.71 (dd, *J* = 9.1 Hz and 6.3 Hz, 1H, CH), 3.26 (dd, *J* = 13.6 Hz and 9.3 Hz, 1H, CH_2), 2.85 (dd, *J* = 13.6 Hz and 6.2 Hz, 1H, CH_2); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 173.7, 140.5, 139.0, 130.7, 130.6, 128.2, 128.0, 127.7, 126.7, 52.6, 37.9; HR-MS-EI (70 eV): *m*/*z* = 282.0658, calcd. for $C_{15}H_{14}NOClNa$ $[M+Na]^+$: 282.0662.

3-(2-Chlorophenyl)-2-phenylpropanamide (4ah): yellow solid; yield: 229 mg (88%); mp 179–180 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.47 (br s, 1H, NH), 7.40 (d, J = 7.1 Hz, 1H, ArH), 7.35 (d, J = 7.4 Hz, 2H, ArH), 7.29 (t, J = 7.3 Hz, 2H, ArH), 7.23–7.20 (m, 4H, ArH), 6.84 (br s, 1H, NH), 3.82 (t, J = 7.3 Hz, 1H, CH), 3.35 (m, 1H, CH), 2.96 (dd, J = 13.6 Hz and 5.4 Hz, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 173.5, 140.7, 137.2, 133.3, 131.3, 129.2, 128.3, 128.1, 127.6, 126.9, 126.8, 50.6, 36.4; HR-MS-EI (70 eV): m/z = 282.0664, calcd. for $C_{15}H_{14}NONaCl$ $[M+Na]^+$: 282.0662.

2-Phenyl-3-[4-(trifluoromethoxy)phenyl]propanamide (4ai): light yellow solid; yield: 280 mg (91%); mp 155–156 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.25 (m, 5H, ArH), 7.10 (d, J = 8.7 Hz, 2H, ArH), 7.05 (d, J = 8.2 Hz, 2H, ArH), 5.36 (br s, 1H, NH), 5.30 (br s, 1H, NH), 3.60 (t, J = 7.3 Hz, 1H, CH), 3.54 (dd, J = 13.4 Hz and 7.4 Hz, 1H, CH), 2.98 (dd, J = 13.5 Hz and 7.3 Hz, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.6, 147.7, 139.0, 138.2, 130.3, 128.9, 128.0, 127.7, 120.8, 120.4 (q, J_{C-F} = 255.5 Hz), 54.7, 38.6; HR-MS-EI (70 eV): m/z = 332.0878, calcd. for $C_{16}H_{14}NO_2F_3Na$ $[M+Na]^+$: 332.0874.

3-(Naphthalen-1-yl)-2-phenylpropanamide (4aj): brown solid; yield: 240 mg (87%); mp 150–151 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06 (d, J = 8.1 Hz, 1H, ArH), 7.86 (d, J = 7.6 Hz, 1H, ArH), 7.69 (d, J = 8.1 Hz, 1H, ArH), 7.51 (m, 2H, ArH), 7.32–7.26 (m, 6H, ArH), 7.17 (d, J = 6.7 Hz, 1H, ArH), 5.27 (br s, 1H, NH), 5.21 (br s, 1H, NH), 4.06 (dd, J = 13.8 Hz and 7.5 Hz, 1H, CH_2), 3.82 (t, J = 7.0 Hz, 1H, CH), 3.42 (dd, J = 14.0 Hz and 6.7 Hz, 1H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.0, 139.7, 135.3, 133.9, 131.6, 128.9, 128.8, 127.9, 127.5, 127.4, 127.1, 126.0, 125.4, 123.4, 53.5, 36.5; HR-MS-EI (70 eV): m/z = 298.1201, calcd. for $C_{19}H_{17}NONa$ $[M+Na]^+$: 298.1208.

3-(Ferrocenemethyl)-2-phenylpropanmide (4ak): brown solid; yield: 264 mg (79%); mp 117–118 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (t, J = 7.3 Hz, 2H, ArH), 7.27–7.25 (m, 3H, ArH), 5.26 (br s, 2H, NH), 4.10 (br s, 1H, ferrocene H), 4.08 (s, 5H, ferrocene H), 4.01 (br s, 1H, ferrocene H), 3.95 (br s, 1H, ferrocene H), 3.78 (br s, 1H, ferrocene H), 3.43(t, J = 7.17 Hz, 1H, CH), 3.28 (dd, J = 7.25 Hz and 7.3 Hz, 1H, CH_2), 2.77 (dd, J = 7.3 Hz and 7.45 Hz, 1H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.3, 139.7, 128.7, 127.8, 127.4, 85.9, 68.9, 68.8, 68.6, 67.4, 67.3, 55.3, 33.9; HR-MS-EI (70 eV): m/z = 356.0721, calcd. for $C_{19}H_{19}FeNONa$ $[M+Na]^+$: 356.0714.

2-Phenylhexanamide (4al):[10] light yellow solid; yield: 141 mg (74%); mp 94–95 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.26 (m, 5H, ArH), 5.41 (br s, 1H, NH), 5.34 (br s, 1H, NH), 3.37 (t, J = 7.3 Hz, 1H, CH), 2.19–2.11 (m, 1H, CH), 1.82–1.75 (m, 1H, CH), 1.38–1.13 (m, 4H, 2×CH_2), 0.86 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.4, 140.0, 128.8, 127.9, 127.2, 52.8, 32.6, 29.8, 22.5, 13.9.

2-Phenyloctanamide (4am): white solid; yield: 167 mg (76%); mp 85–86 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 5H, ArH), 5.40 (br s, 1H, NH), 5.34 (br s, 1H, NH), 3.37 (t, J = 7.6 Hz, 1H, CH), 2.18–2.11 (m, 1H, CH_2), 1.81–1.74 (m, 1H, CH_2), 1.35–1.14 (m, 8H, 4×CH_2), 0.85 (t, J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.3, 140.0, 128.8, 127.9, 127.2, 52.8, 32.9, 31.6, 29.1, 27.6, 22.5, 14.0; HR-MS-EI (70 eV): m/z = 242.1527, calcd. for $C_{14}H_{21}NONa$ $[M+Na]^+$: 242.1521.

3-Phenyl-2-*para*-tolylpropanamide (4ba): light yellow solid; yield: 198 mg (83%); mp 138–139 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21 (t, J = 7.32 Hz, 2H, ArH), 7.17–7.14 (m, 3H, ArH), 7.11 (t, J = 6.90 Hz, 4H, ArH), 5.26 (br s, 2H, NH_2), 3.91 (t, J = 7.32 Hz, 1H, CH), 3.53 (dd, J = 7.35 Hz and 7.30 Hz, 1H, CH), 2.98 (dd, J = 7.30 Hz and 7.90 Hz, 1H, CH), 2.32 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.41, 139.59, 137.06, 136.33, 129.44, 128.93, 128.20, 127.83, 126.12, 54.31, 39.23, 21.01; HR-MS-EI (70 eV): m/z = 262.1211, calcd. for $C_{16}H_{17}NONa$ $[M+Na]^+$: 262.1208.

3-Phenyl-2-*ortho*-tolylpropanamide (4ca): yellow solid; yield: 201 mg (84%); mp 142–143 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, J = 7.5 Hz, 1H, ArH), 7.26–7.11 (m, 6H, ArH), 7.07 (d, J = 7.1 Hz, 2H, ArH), 5.34 (br s, 1H, NH), 5.20 (br s, 1H, NH), 3.91 (t, J = 7.3 Hz, 1H, CH), 3.57 (dd, J = 13.7 Hz and 6.7 Hz, 1H, CH), 2.96 (dd, J = 13.6 Hz and 7.9 Hz, 1H, CH), 2.16 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.4, 139.6, 137.6, 136.1, 130.6, 128.9, 128.2, 127.5, 127.3, 126.6, 126.2, 50.4, 38.8, 19.6; HR-MS-EI (70 eV): m/z = 262.1206, calcd. for $C_{16}H_{17}NONa$ $[M+Na]^+$: 262.1208.

2-(4-Methoxyphenyl)-3-phenylpropanamide (4da):[11] yellow solid; yield: 205 mg (80%); mp 162–164 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22–7.08 (m, 5H, ArH), 7.09 (d, J = 7.8 Hz, 2H, ArH), 6.84 (d, J = 8.5 Hz, 2H, ArH), 5.38 (br s, 1H, NH), 5.30 (br s, 1H, NH), 3.79 (s, 3H, OCH_3), 3.59 (t, J = 7.4 Hz, 1H, CH), 3.51 (dd, J = 13.6 Hz and 7.4 Hz, 1H, CH), 2.96 (dd, J = 13.6 Hz and 7.7 Hz, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.6, 158.8, 139.6, 131.4, 129.1, 129.0, 128.2, 126.1, 114.1, 55.2, 53.9, 39.4.

2-(3,4-Dimethoxyphenyl)-3-phenylpropanamide (4ea): light yellow solid; yield: 260 mg (91%); mp 100–101 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (t, J = 7.3 Hz, 2H, ArH), 7.16 (t, J = 7.3 Hz, 1H, ArH), 7.09 (d, J = 7.0 Hz, 2H, ArH), 6.79–6.78 (m, 3H, ArH), 5.31 (br s, 2H, NH_2), 3.86 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.58 (t, J = 7.4 Hz, 1H, CH), 3.50 (dd, J = 13.8 Hz and 7.3 Hz, 1H, CH), 2.98 (dd, J = 13.6 Hz and 7.6 Hz, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.4, 149.0, 148.3, 139.5, 131.8, 129.0, 128.2, 126.2, 120.3, 111.1, 110.9, 55.83, 55.80, 54.3, 39.4; HR-MS-EI (70 eV): m/z = 308.1269, calcd. for $C_{17}H_{19}NO_3Na$ $[M+Na]^+$: 308.1263.

2-(4-Fluorophenyl)-3-phenylpropanamide (4fa): yellow solid; yield: 224 mg (92%); mp 150–151 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.21 (m, 4H, ArH), 7.17 (t, J = 7.2 Hz, 1H, ArH), 7.08 (d, J = 7.1 Hz, 2H, ArH), 7.00 (t, J = 8.6 Hz, 2H, ArH), 5.39 (br s, 1H, NH), 5.29 (br s, 1H, NH), 3.61 (t, J = 7.6 Hz, 1H, CH), 3.49 (dd, J = 13.7 Hz and 7.6 Hz, 1H, CH), 2.96 (dd, J = 13.6 Hz and 7.6 Hz, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.9, 162.1 (d, $J_{C,F}$ = 244.7 Hz), 139.1, 135.0, 129.6 (d, $J_{C,F}$ = 8.1 Hz), 128.9, 128.3, 126.4, 115.6 (d, $J_{C,F}$ = 21.2 Hz), 54.0, 39.6; HR-MS-EI (70 eV): m/z = 266.0956, calcd. for $C_{15}H_{14}NOFNa$ $[M+Na]^+$: 266.0957.

2-(3-Fluorophenyl)-3-phenylpropanamide (4ga): yellow solid; yield: 216 mg (89%); mp 147–148 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.47 (br s, 1H, NH), 7.35–7.15 (m, 8H, ArH), 7.04 (t, J = 7.9 Hz, 1H, ArH), 6.86 (br s, 1H, NH), 3.79 (t, J = 7.1 Hz, 1H, CH), 3.27 (dd, J = 13.5 Hz and

9.8 Hz, 1H, CH), 2.86 (dd, J=13.3 Hz and 5.9 Hz, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ=173.5, 162.0 (d, $J_{C,F}$=241.6 Hz), 143.5 (d, $J_{C,F}$=7.2 Hz), 139.6, 130.0 (d, $J_{C,F}$=8.2 Hz), 128.8, 128.1, 126.0, 124.0, 114.5 (d, $J_{C,F}$=20.8 Hz), 113.4 (d, $J_{C,F}$=20.8 Hz), 52.4, 38.5; HR-MS-EI (70 eV): m/z=266.0952, calcd. for $C_{15}H_{14}NOFNa$ $[M+Na]^+$: 266.0957.

2-(4-Chlorophenyl)-3-phenylpropanamide (4ha): yellow solid; yield: 215 mg (83%); mp 165–166 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=7.47–7.16 (m, 10H, 9×ArH and NH), 6.86 (br s, 1H, NH), 3.76 (br s, 1H, CH), 3.27 (br s, 1H, CH), 2.85 (br s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ=173.6, 139.6, 131.3, 129.6, 128.8, 128.1, 127.7, 126.6, 126.0, 52.0, 38.5; HR-MS-EI (70 eV): m/z=282.0652, calcd. for $C_{15}H_{14}NOClNa$ $[M+Na]^+$:282.0662.

3-Phenyl-2-[3-(trifluoromethyl)phenyl]propanamide (4ia): brown solid; yield: 247 mg (84%); mp 123–125 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=7.68–7.54 (m, 5H, 4×ArH and NH), 7.22–7.18 (m, 5H, ArH), 6.91 (br s, 1H, NH), 3.89 (br s, 1H, CH), 3.35 (br s, 1H, CH), 2.89 (br s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ=173.3, 142.0, 139.5, 131.9, 129.2, 128.9 (q, $J_{C,F}$=30.8 Hz), 128.8, 128.1, 126.1, 124.3 (q, $J_{C,F}$=271.0 Hz), 124.2, 123.4, 52.4, 38.5; HR-MS-EI (70 eV): m/z=316.0929, calcd. for $C_{16}H_{14}NOF_3Na$ $[M+Na]^+$: 316.0925.

3-Phenyl-2-[4-(trifluoromethoxy)phenyl]propanamide (4ja): yellow solid; yield: 279 mg (90%); mp 160–161 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=7.49–7.17 (m, 10H, 9×ArH and NH), 6.87 (br s, 1H, NH), 3.82 (br s, 1H, CH), 3.30 (br s, 1H, CH), 2.85 (d, J=7.9 Hz, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ=173.6, 147.1, 140.1, 139.7, 129.5, 128.8, 128.1, 126.0, 120.8, 120.1 (q, $J_{C,F}$=254.4 Hz), 52.0, 38.6; HR-MS-EI (70 eV): m/z=332.0867, calcd. for $C_{16}H_{14}NO_2F_3Na$ $[M+Na]^+$: 332.0874.

2-(Naphthalen-1-yl)-3-phenylpropanamide (4ka): light yellow solid; yield: 226 mg (82%); mp 132–133 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.07 (d, J=5.2 Hz, 1H, ArH), 7.89–7.78 (m, 2H, ArH), 7.53–7.43 (m, 4H, ArH), 7.26–7.13 (m, 5H, ArH), 5.27 (m, 2H, NH_2), 4.40 (br s, 1H, CH), 3.74 (br s, 1H, CH), 3.18 (br s, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ=175.2, 139.9, 135.2, 134.1, 131.2, 129.2, 128.9, 128.3, 128.2, 126.6, 126.2, 126.1, 125.8, 125.6, 123.0, 51.0, 38.4; HR-MS-EI (70 eV): m/z=298.1207, calcd. for $C_{19}H_{17}NONa$ $[M+Na]^+$: 298.1208.

2-(Naphthalen-2-yl)-3-phenylpropanamide (4la): light yellow solid; yield: 243 mg (88%); mp 148–149 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.82–7.70 (m, 4H, ArH), 7.48–7.44 (m, 3H, ArH), 7.26–7.12 (m, 5H, ArH), 5.41 (br s, 1H, NH), 5.34 (br s, 1H, NH), 3.81 (t, J=7.0 Hz, 1H, CH), 3.63 (dd, J=13.5 Hz and 7.5 Hz, 1H, CH), 3.10 (dd, J=13.4 Hz and 7.5 Hz, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ=175.0, 139.4, 136.8, 133.4, 132.6, 129.0, 128.6, 128.3, 127.7, 127.6, 127.0, 126.3, 126.2, 126.0, 125.8, 54.9, 39.2; HR-MS-EI (70 eV): m/z=298.1210, calcd. for $C_{19}H_{17}NONa$ $[M+Na]^+$: 298.1208.

General Procedure for the Rhodium-Catalyzed Coupling of Arylacetonitriles with a Diol under Microwave Irradiation (Scheme 3)

Nitrile **1** (2.2 mmol), alcohol **2n** (1 mmol), $[Rh(cod)Cl]_2$ (0.02 mmol, 2 mol%), PPh_3 (0.2 mmol, 0.2 equiv.), KOH (0.8 equiv.) and *tert*-amyl alcohol (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 2 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

3-[3-(2-Amide-2-phenylethyl)phenyl]-2-phenylpropanamide (4an): white solid; yield: 322 mg (86%); mp 180–181 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=7.42–6.79 (m, 18H, ArH and NH_2), 3.72 (s, 2H, 2×CH), 3.25 (s, 2H, 2×CH), 2.76 (s, 2H, 2×CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ=174.0, 140.8, 139.6, 129.4, 128.1, 127.7, 126.6, 126.4, 52.6, 38.7; HR-MS-EI (70 eV): m/z=395.1742, calcd. for $C_{24}H_{24}N_2O_2Na$ $[M+Na]^+$: 395.1735.

3-{3-[2-Amide-2-(4-methyl)phenylethyl]phenyl}-2-(4-methyl)propanamide (4bn): light yellow solid; yield: 319 mg (80%); mp 188–189 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=7.34 (br s, 2H, 2xNH), 7.22 (d, J=7.5 Hz, 4H, ArH), 7.09–7.02 (m, 6H, ArH), 6.91 (d, J=7.0 Hz, 2H, ArH), 6.73 (br s, 2H, 2×NH), 3.69 (t, J=7.1 Hz, 2H, 2×CH), 3.21 (dd, J=13.2 Hz and 9.8 Hz, 2H, 2×CH), 2.73 (dd, J=13.9 Hz and 5.9 Hz, 2H, 2×CH), 2.25 (s, 6H, 2×CH_3); ^{13}C NMR (125 MHz, DMSO-d_6): δ=174.2, 139.7, 137.8, 135.5, 129.4, 128.7, 127.7, 127.6, 126.4, 52.3, 38.7, 20.6; HR-MS-EI (70 eV): m/z=423.2056, calcd. for $C_{26}H_{28}N_2O_2Na$ $[M+Na]^+$: 423.2048.

3-{3-[2-Amide-2-(4-fluoro)phenylethyl]phenyl}-2-(4-fluoro)propanamide (4fn): yellow solid; yield: 339 mg 83%); mp 192–193 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=7.41–7.35 (m, 6H, 4×ArH and 2×NH), 7.10–7.05 (m, 6H, ArH), 6.91 (s, 2H, ArH), 6.80 (br s, 2H, 2×NH), 3.73 (s, 2H, 2×CH), 3.21 (s, 2H, 2×CH), 2.76 (s, 2H, 2×CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ=174.0, 161.1 (d, $J_{C,F}$=240.5 Hz), 139.4, 136.9, 129.5 (d, $J_{C,F}$=5.8 Hz), 129.4, 127.8, 126.5, 114.8 (d, $J_{C,F}$=20.9 Hz), 51.8, 38.8; HR-MS-EI (70 eV): m/z=431.1553, calcd. for $C_{24}H_{22}N_2O_2F_2Na$ $[M+Na]^+$: 431.1547.

Condensation Between 2-Phenylacetonitrile and Benzaldehyde [Scheme 4, Eq. (1)]

Phenylacetonitrile **1a** (1 mmol), benzaldehyde **5** (1.1 mmol), KOH (0.4 equiv.) and *tert*-amyl alcohol (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 2 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture reaction was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product **6**.

(*Z*)-2,3-Diphenylacrylonitrile (6):[5b] white solid; yield: 183 mg (89%); mp 80–81 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.88 (d, J=7.4 Hz, 2H, ArH), 7.68 (d, J=7.7 Hz, 2H, ArH), 7.54 (s, 1H, CH), 7.51–7.36 (m, 6H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ=142.1, 134.3, 133.6, 130.4, 129.1, 129.06, 128.9, 128.8, 125.9, 117.9, 111.5.

Hydrogen Transfer between (*Z*)-2,3-Diphenylacrylonitrile and Benzyl Alcohol [Scheme 4, Eq. (2)]

Nitrile **6** (1 mmol), **2a** (1.1 mmol), $[Rh(cod)Cl]_2$ (0.01 mmol, 1 mol%), PPh_3 (0.1 mmol, 0.1 equiv.), KOH (0.4 equiv.) and *tert*-amyl alcohol (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 2 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product **3aa**.

2,3-Diphenylpropanenitrile (3aa):[5d] white solid; yield: 188 mg (91%); mp 49–50 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.38$–7.24 (m, 8H, ArH), 7.14 (t, $J = 4.0$ Hz, 2H, ArH), 4.00 (q, $J = 5.0$ Hz, 1H, CH), 3.22–3.11 (m, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 136.2$, 135.2, 129.2, 129.0, 128.6, 128.13, 127.4, 127.3, 120.3, 42.1, 39.7.

Hydration of (*Z*)-2,3-Diphenylacrylonitrile [Scheme 4, Eq. (3)]

Nitrile **6** (1 mmol), H_2O (1 mmol, 1 equiv.), $[Rh(cod)Cl]_2$ (0.01 mmol, 1 mol%), PPh_3 (0.1 mmol, 0.1 equiv.), KOH (0.4 equiv.) and *tert*-amyl alcohol (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 2 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. No hydrated product was found from the ^{1}H NMR spectrum of crude reaction mixture.

Hydration of (*Z*)-2,3-Diphenylpropanenitrile [Scheme 4, Eq.(4)]

Nitrile **3aa** (1 mmol), H_2O (1 mmol, 1 equiv), $[Rh(cod)Cl]_2$ (0.01 mmol, 1 mol%), PPh_3 (0.1 mmol, 0.1 equiv.), KOH (0.4 equiv.) and *tert*-amyl alcohol (1 mL) were added to a microwave vial containing a stirrer bar. The vial was then placed in a focused, single-mode microwave synthesizer (Discover CEM, USA) at 130 °C for 2 h (300 W, sealed reaction vessel), and was then cooled to ambient temperature. The reaction mixture was concentrated under vacuum and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product **4aa** as a brown solid; yield: 202 mg (90%).

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