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Transfer Hydrodehalogenation of Organic Halides Catalyzed by Ruthenium(II) Complex

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ABSTRACT:

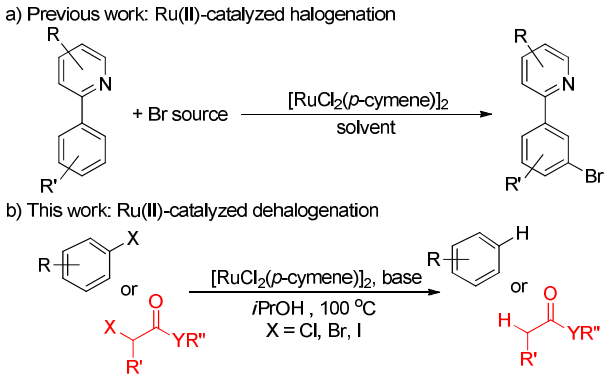
A simple and efficient Ru(II)-catalyzed transfer hydrodehalogenation of organic halides using isopropanol solvent as the hydride source was reported. This methodology is applicable for hydrodehalogenation of a variety of aromatic halides and α-haloesters and amides without additional ligand, and quantitative yields were achieved in many cases. The potential synthetic application of this method was demonstrated by efficient gram scale transformation with catalyst loading as low as 0.5 mol%.

1. INTRODUCTION

Organic halides are widely used as solvents and starting materials for numerous chemical transformations, and the efficient formation of C-X (X = halogen atom) bonds has been actively studied by organic chemists. However, many organic halides are classified as pollutants due to their persistent deleterious effects.[1] Thus, the dehalogenation is equally important from the environmental perspective. The catalytic hydrodehalogenation represents an efficient approach for transforming C-X bonds into C-H bond.[2] While traditionally the H_2 is used as the hydride source in such transformations,[3] simpler processes under transfer hydrogenation conditions have been developed in recent years.[4] In this regard, great progress has been made by homogeneous catalytic systems of palladium,[4,5] rhodium,[6] iron,[7] ruthenium,[8] and other transition metals.[9] However, one drawback of existed methods is that phosphine or other auxiliary ligands, which are toxic, air-senstitive, and difficult to synthesis, are generally required for efficient transformation. Hence, development of novel catalytic process for efficient hydrodehalogenation is highly desirable.

In recent years, Ru(II) complex in the form of $[RuCl_2(p\text{-cymene})]_2$ has been found highly effective for catalyzing a number of organic transformations, and the C-X bonds are tolerable in many of these reactions.[10] More recently, interesting regioselective C-H bond halogenations under Ru catalysis were disclosed by several groups,[11-13] including the $[RuCl_2(p\text{-cymene})]_2$-catalyzed *meta*-brominations of 2-phenylpyridines by the groups of Huang[11] and Greaney (Scheme 1a).[12] While preceding reports seem to

suggest that the C-X bonds are inert under the effect of $[RuCl_2(p\text{-cymene})]_2$ complex, we proposed that the reverse transformation should be possible under certain conditions. Herein an efficient Ru(II)-catalyzed transfer hydrodehalogenation of aromatic halides and α-haloesters is reported (Scheme 1b), in which the cheap and commercially available $[RuCl_2(p\text{-cymene})]_2$ is used as the catalyst combined with isopropanol acting both as solvent and hydrogen donor.



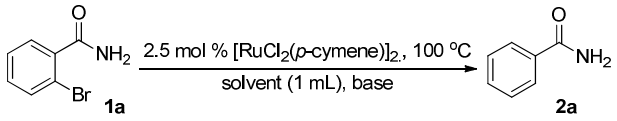
Scheme 1. Ru(II)-catalyzed C-H Halogenation and C-X Hydrodehalogenation

2. RESULTS AND DISCUSSION

Our study started with the condition optimization for transformation of 2-bromobenzamide (**1a**) into benzamide (**2a**) (Table 1). Previous studies found that the formic acid and its salts are reliable hydride donor for transfer hydrogenation reactions.[14] The reaction of **1a** was initially conducted using 2.5 mol % $[RuCl_2(cymene)]_2$ as the catalyst in the presence of 0.5 mL HCOOH/Et_3N (molar ratio 5 : 2) as the hydrogen donor and 0.5 mL H_2O as solvent at 100 °C for 12 h, and the desired hydrodebromination product was obtained in 46% yield (entry 1). Following this result, different conditions were screened to improve the efficiency of the reaction. While only trace amount of product was observed when using $[RuI_2(p\text{-cymene})]_2$ as the catalyst (entry 2), the **2a** could be afforded in 71% yield by reaction at a higher catalyst loading (5 mol %) and prolonging time (24 h) (entry 3). Changing the molar ratio of HCOOH/Et_3N to 1:1 did not lead to a better result (entry 4), and only 33% yield was obtained when using 2.5 mol % $RuCl_2(PPh_3)_3$ as the catalyst (entry 5). Considering alcoholic species could be used both as solvent and hydrogen donor for transfer hydrogenation, the conditions by combination of 1 mL *i*PrOH and 1.2 equiv of base were screened. Lower yields were obtained in systems with Cs_2CO_3 and NaOAc (entries 6 and 7) in

comparison with the reaction in entry 1. However, notable promotion effects were observed with other bases including Et_3N (64%, entry 8), *t*BuOK (70%, entry 9), K_2CO_3 (79%, entry 10), and KOH (79%, entry 11). The results in entries 10 and 12 showed that the yield decreased dramatically when the reaction was run at a lower temperature, indicating heating at 100 °C is necessary for high yield. Among the reactions, the best result was achieved by reaction in *i*PrOH solvent with CsOAc as the additive, which afforded **2a** in 89% yield (entry 13). Both Ru(II) catalyst and CsOAc additive are crucial for triggering the reaction, as no reaction was observed in the absence of Ru catalyst (entry 14) or base (entry 15). Therefore, 2.5 mol % $[RuCl_2(cymene)]_2$ and 1.2 equiv of CsOAc in *i*PrOH solvent at 100 °C was established as the optimal condition for the reduction of benzamide derivatives.

Table 1. Screening of the Reaction Conditions[a]



Entry	Solvent (Hydrogen donor)	Base	Time (h)	Yield (%)[b]
1	F/T(5:2) + H_2O[c]	-	12	46
2	F/T(5:2) + H_2O[c,d]	-	12	trace
3	F/T(5:2) + H_2O[c,e]	-	24	71
4	F/T(1:1) + H_2O[f]	-	24	63
5	F/T(1:1) + H_2O[f,g]	-	24	33
6	*i*PrOH	Cs_2CO_3	12	31
7	*i*PrOH	NaOAc	12	37
8	*i*PrOH	Et_3N	12	64
9	*i*PrOH	*t*BuOK	12	70
10	*i*PrOH	K_2CO_3	12	79
11	*i*PrOH	KOH	12	58
12[h]	*i*PrOH	K_2CO_3	12	34
13	*i*PrOH	CsOAc	12	89
14	*i*PrOH	-	12	NR
15[i]	*i*PrOH	CsOAc	12	NR

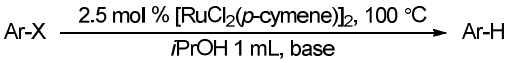
[a]Reaction conditions: **1a** (0.2 mmol), catalyst (2.5 mol %), base (1.2 equiv), solvent (1 mL) at 100 °C. [b]Isolated yields. [c]HCOOH/Et_3N (molar ratio 5:2, 0.5 mL) + H_2O (0.5 mL). [d]$RuI_2(p\text{-cymene})]_2$ was used.[e]5 mol % catalyst. [f]HCOOH/Et_3N (molar ratio 1:1, 0.5 mL) + H_2O (0.5 mL). [g]$RuCl_2(PPh_3)_3$ was used. [h]At 90 °C. [i]Without catalyst.

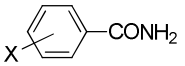
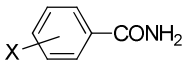
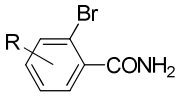
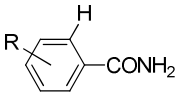
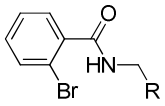
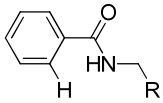
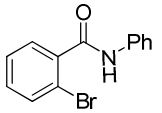
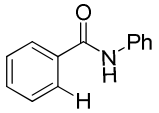
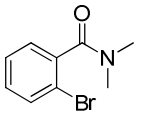
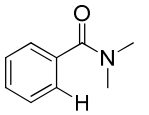
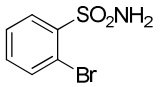
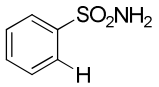
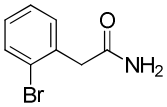
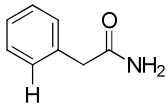
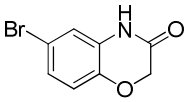
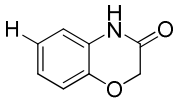
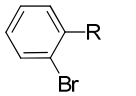
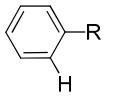
With the optimal reaction conditions in hand, the scope of the Ru-catalyzed dehalogenation for a series of aryl halides bearing different electronic and steric properties was then expanded (Table 2). As expected, the reduction of C-I bond is more efficient than the reduction of C-Br bond in **2a**, and 98% yield was

obtained for reaction of 2-iodobenzamide (entry 2). The position of the bromo substituent does not disturb the reaction, as both 3-bromo and 4-bromo benzamides could be reduced effectively (entries 3 and 4). The results in entries 5 and 6 suggested that introduction of an electron-donating group at C4 has promoting effect but the steric effect at C5 may lower down the reaction efficiency. Interestingly, the substituent on the nitrogen atom of the 2-bromobenzamide may have influence on the reaction efficiency, thus higher yield was obtained for 2-bromo-*N*-ethylbenzamide than *N*-benzyl-2-bromobenzamide (entries 7 and 8). The debrominations of 2-bromo-*N*-phenylbenzamide and 2-bromo-*N*,*N*-dimethylbenzamide occurred more efficiently when 1.2 equiv *t*BuOK was used instead of CsOAc (entries 9 and 10). The superiority of using *t*BuOK as an additive was also observed in reactions of other aryl halides as indicated in Table 2. Good yields were achieved for other amide derivatives such as 2-bromobenzenesulfonamide, 2-(2-bromophenyl)acetamide, and 6-bromo-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one (entries 11-13). Similarly, the reaction of methyl 2-bromobenzoate afforded the debromination product in 75% yield (entry 14). The current reaction is compatible with both acidic and basic substrates, thus good yields were obtained from brominated benzoic acid, indole, and aniline derivatives (entries 15-19). The relatively low yield for reaction of 3-bromopyridin-2-amine may be attributed to its strong chelating effect to Ru(II) catalyst (entry 20). The reaction works well for halogenated benzene, naphthalene, and 9*H*-fluorene substrates (entries 21-25), and quantitative yields were obtained in several cases. The substrate scope could be further expanded to chloro- or bromo-substituted anisoles, phenol, biphenyl, xylene, and others (entries 26-40), showing the compatibility of different functional groups in this transformation.

This dehalogenation reaction could also be applied to α-halocarbonyl compounds (Table 3). The esters and amides containing both secondary (**1b**, **1c**, **1d**, and **1f**) and primary bromide (**1e**) at the α carbon of the carbonyl group undergo debromination reaction smoothly under current conditions. Dehalogenation of C-Cl and C-I bonds containing amide and esters was also tested. The yield for formation of **2f** from amide **1g** (X = Cl) is comparable to that from **1f** (X = Br). Product **2h** could be generated in good yields from reactions of ester derivatives **1h** (X = Cl) and **1i** (X = I), with the latter one being slightly more efficient. It should be noted that the debromination of α-bromoketones are possible, but reduction of the carbonyl group occurs concurrently. Alkyl bromides such as (bromomethylene)dibenzene and (4-bromobutyl)benzene are not compatible because substitution reactions occur more easily than hydrodehalogenation in presence of CsOAc. Controlled experiments found that no desired dehalogenation product could be obtained in absence of Ru(II) or base additive in cases of α-halocarbonyl compounds.

Table 2. Dehalogenation of Aromatic Halides[a]



Entry	Ar-X	Product	Yield (%)[b]
1	 X = 2-Br		88
2	X = 2-I		98
3	X = 3-Br		83
4	X = 4-Br		93
5	 R = 4-Me		96
6	R = 5-Me		74
7	 R = Me		93
8	R = Ph		78
9[c]			89
10[c]			93
11[d]			79
12			90
13			72
14	 R = CO_2Me		[75]
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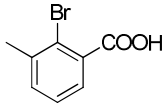
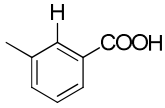
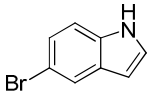
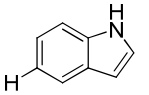
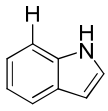
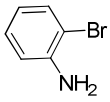
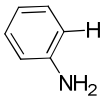
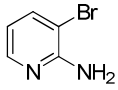
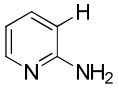
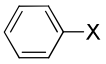
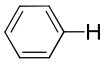
16			93
17			70

Entry	Ar-X	Product	Yield (%)[b]
18			65
19[c]			[67]
20			40
21[c]	 X = Cl		(88)
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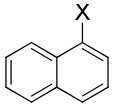
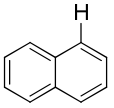
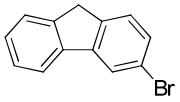
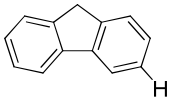
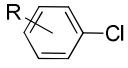
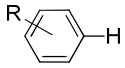
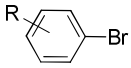
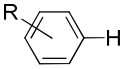
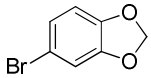
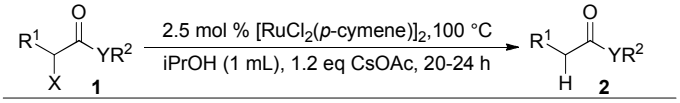
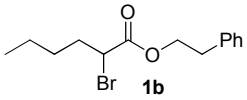
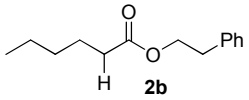
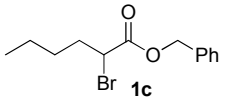
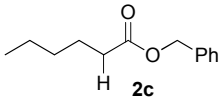
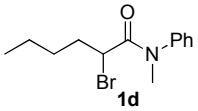
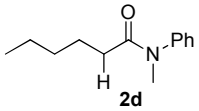
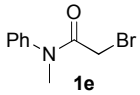
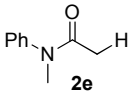
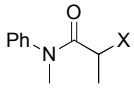
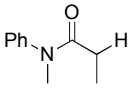
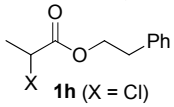
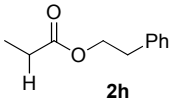
23[c]	 X = Br		[90]
24[c]	X = I		[83]
25[c]			>99
26[c]	 R = 2-OMe		[72]
27[c]	R = 3-OMe		[70]
28[c]	R = 4-OMe		[62]
29[c]	 R = 2-OMe		[93]
30[c]	R = 4-OMe		[94]
31[c]	R = 4-nBu		[93]
32[c]	R = 4-NMe_2		[>99]
33[c]			[88]
34[c]	R = 3,5-diMe		[89]
35[c]	R = 2,6-diMe		[75]
36[c]	R = 2-Ph		96
37[c]	R = 4-Ph		96
38[c]	R = 2-OH		[81]
39[c]	R = 3-OH		[88]
40[c]			[86]

[a] Standard condition: ArX (0.2 mmol), $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %), CsOAc (1.2 equiv) in *i*PrOH (1 mL) for 20-24 h. [b] Values in parenthesis and square bracket were determined by GC and GC-MS, respectively; All others are isolated yields. [c] *t*BuOK was used instead of CsOAc. [d] 0.5 mL HCOOH/Et_3N (molar ratio 1:1) + 0.5 mL H_2O was used.

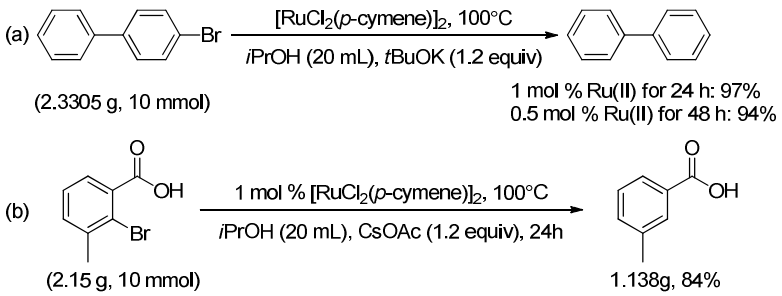
Table 3. Dehalogenation of Aliphatic Halides



Substrate	Product	Yield (%)
 **1b**	 **2b**	78
 **1c**	 **2c**	66
 **1d**	 **2d**	43
 **1e**	 **2e**	82[a]
 **1f** (X = Br))	 **2f**	54[b]
1g (X = Cl)	**2f**	51[b]
 **1h** (X = Cl)	 **2h**	67%
1i (X = I)	**2h**	71%

[a] K_2CO_3 was used as a base by reaction at 100 °C for 18 h. [b] *t*BuOK was used as a base by reaction at 90 °C for 20 h.

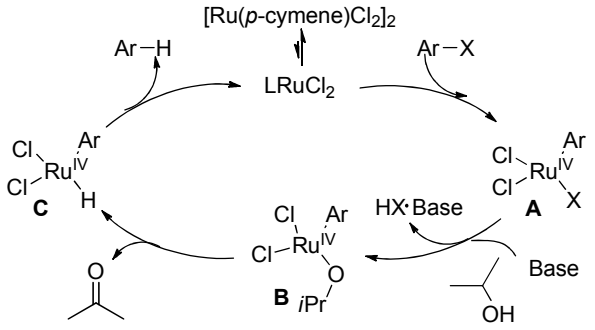
To demonstrate the synthetic utility of this reaction, gram-scale reactions were carried out (Scheme 2). When 4-bromo-1,1'-biphenyl was used (Scheme 2a), almost quantitative yields of debromination product could be achieved with low catalyst loadings (1 mol % and 0.5 mol %), albeit longer reaction times are required for these cases. Gram scale reaction could also be successfully applied for debromination of sterically more crowded substrate 2-bromo-3-methylbenzoic acid (Scheme 2b), which affords 3-methylbenzoic acid in 84% yield with 1 mol % of Ru(II) dimmer.



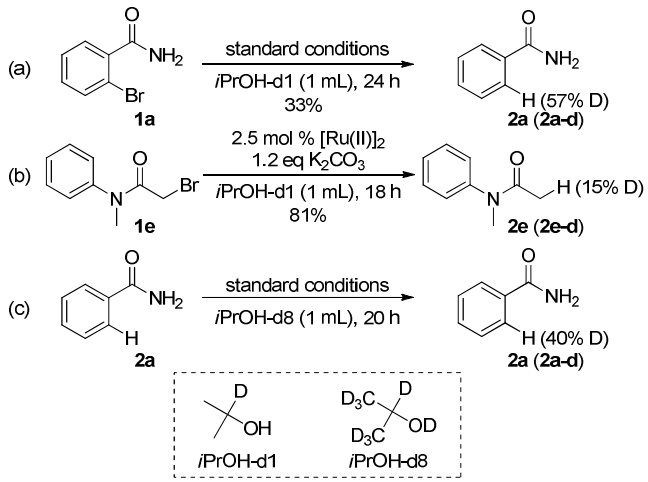
Scheme 2. Gram-scale Synthesis with Low Catalyst Loadings

On the basis of previous reports,[15] a plausible mechanism of this Ru(II)-catalyzed hydrodehalogenation reaction is proposed (Scheme 3). Upon dissociation of the dimmeric ruthenium(II) catalyst, oxidative addition of the halide to Ru(II) monomer would generate a ruthenium(IV) complex **A** in the first step. Probably this is the rate-determining step of the whole reaction because the reduction reactivity was found to follow the order of C-I > C-Br > C-Cl. Then, under the mediation of base additive, an isopropyloxide ligand could be introduced into intermediate **B** by reaction of **A** with the isopropanol solvent. From isopropyloxide intermediate **B**, β-hydride elimination may afford the ruthenium(IV)-hydride complex **C** and an acetone concurrently. Finally, reductive elimination from **C** would form the hydrodehalogenation product and regenerate the active Ru(II) species.

Although a full mechanistic investigation is not available at present, experimental support of the plausible mechanism above was achieved by reactions of **1a** and **1e** in monodeuterated *i*PrOH (*i*PrOH-d1, Scheme 4). The debromoation of **1a** in *i*PrOH-d1 was much slower and yielded only 33% of products **2a** and **2a-d** after 24 h (Scheme 4a), while the reaction of **1e** afforded **2e** and **2e-d** in 81% yield after 18 h (Scheme 4b). These suggested that the transfer hydrogenation of aromatic and aliphatic C-Br bonds should have different kinetic properties. The ratio of the introduced deuterium was lower than expected, which should be resulted from reversible C-H bond cleavage in the debrominated products, as supported by observation of **2a-d** when stirring **2a** in *i*PrOH-d8 under the standard conditions (Scheme 4c). In short, the introduction of deuterium into products **2a-d** and **2e-d** in *i*PrOH-d1 is consistent with the transfer of hydrogen from isopropanol solvent.



Scheme 3. Plausible Mechanism



Scheme 4. Experiments in Deuterated *i*PrOH

3. CONCLUSION

In summary, we have developed a simple and efficient hydrodehalogenation reaction of aryl halides and α-bromocarbonyl compounds by Ru(II) catalysis under transfer hydrogenation conditions. This method is featured with cheap and commercially available $[RuCl_2(cymene)]_2$ catalyst without any additional ligand, simple reaction condition with isopropanol acting both as the solvent and as the hydrogen source, broad substrate scope including a variety of aromatic halides and α-haloesters and amides, and efficient scaled-up synthesis with low catalyst loading. Novel transformations based on transfer hydrogenation are undergoing in our laboratory.

4. EXPERIMENTAL SECTION

General Information. The bromides were purchased from commercial available resources and were used as received, except for the substrates in entries 5, 6, 9, and 12 in Table 2 and **1b-1i** in Table 3, which were synthesized according to literature methods as detailed below. Solvents were distilled by standard procedures. Column chromatography was performed using 200−300 mesh silica with the proper solvent system according to TLC analysis using UV light to visualize the reaction components. Nuclear magnetic resonance spectra were recorded on a 500 MHz spectrometer (^{1}H: 500 MHz, ^{13}C: 125 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. Abbreviations used in the description of NMR data are as following: s, singlet; br, broad; d, duplet; t, triplet; q, quartet; m, multiplet. High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. Melting points were measured on an X4 melting point apparatus.

Procedures for Synthesis of 2-Bromo-4-methylbenzamide (entry 5, Table 2) and 2-Bromo-5-methylbenzamide (entry 6, Table 2).[16] To a flame-dried flask charged with a magnetic stir bar was added bromo-substituted benzonitrile (3.0 mmol, 1.0 equiv) and *t*BuOK (1.0 g, 9.0 mmol, 3.0 equiv), and dry Toluene (4 mL/mmol). The reaction mixture was stirred at room temperature for 20 h under nitrogen atmosphere. Upon completion, the reaction mixture was diluted with ethyl acetate and filtered. The filtrate was concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to give the desired products.

2-Bromo-4-methylbenzamide **(entry 5, Table 2)**: white solid; (612 mg, 57%); mp 174−176 °C; ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.78 (bs, 1H), 7.49 (bs, 1H), 7.47 (s, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, d_6-DMSO) δ 169.0, 140.7, 136.3, 132.9, 128.4, 128.0, 118.5, 20.3; HRMS (ESI^+): calcd for $C_8H_8BrNONa^+$ ($[M + Na]^+$) 235.9681, found 235.9693.

2-Bromo-5-methylbenzamide **(entry 6, Table 2)**:[17] white solid; mp 196−197 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H), 7.11 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.14 (bs, 1H), 6.04 (bs, 1H), 2.33 (s, 3H).

Procedures for Synthesis of 2-Bromo-N-phenylbenzamide (entry 9, Table 2).[17] To a 20 mL flask charged with a magnetic stir bar, aniline (5 mL) was added drop-wisely to 2-bromobenzoyl chloride (1.10 g, 5.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h. Then the reaction mixture was poured into 30 mL of ethyl acetate and washed with 1N aqueous HCl solution (20 mL x 2), and washed with saturated aqueous $NaHCO_3$ solution (30 mL x 1) and brine (20 mL x 1). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulted solid was purified by flash column chromatography (petroleum ether/EtOAc = 5/1) to afford the desired product as a yellow solid. mp 121−122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.64 – 7.62 (m, 4H), 7.41 – 7.36 (m, 3H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H).

Procedures for Synthesis of 2-(2-Bromophenyl) acetamide (entry 12, Table 2).[18] To a solution of 2-bromophenyl acetonitrile (1.10 g, 5.6 mmol) in *t*BuOH (5.5 mL) was added potassium hydroxide (1.26 g, 22.4 mmol). The mixture was refluxed for 2 h, then allowed to cool to room temperature, quenched with water (15 mL) and extracted with $CHCl_3$ (2 x 30 mL). The organic layers were combined and dried over $MgSO_4$, and then filtered and recrystallised to give the target compound, as determined by GC/MS.

Procedures for Synthesis of Compounds 1b-1d. To a solution of hexanoic acid (580.8mg, 5 mmol), alcohol or amine (5 mmol), DMAP (61.1 mg, 0.5 mmol) in 5 mL DCM was added DIC (6 mmol, 0.93 mL) dropwisely at 0 °C over 5 mins. The reaction was allowed to warm to ambient temperature and stir for 24~48 h. Then the mixture was poured into 30 mL ethyl actate, and washed with saturated $NaHCO_3$ (15 mL x 1), saturated NH_4Cl (15 mL x 1),

and saturated NaCl (15 mL x 1) respectively. The organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography to afford the desired products.

Phenethyl 2-bromohexanoate (**1b, Table 3**):[19] colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33−7.27 (m, 2H), 7.26−7.20 (m, 3H), 4.39 (td, J = 7.0, 3.2 Hz, 2H), 4.18 (t, J = 7.4 Hz, 1H), 2.98 (t, J = 7.0 Hz, 2H), 2.08−1.87 (m, 2H), 1.44−1.22 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H).

Benzyl 2-bromohexanoate (**1c, Table 3**):[19] colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42−7.30 (m, 5H), 5.20 (s, 2H), 4.25 (t, J = 7.4 Hz, 1H), 2.16−2.04 (m, 1H), 2.04−1.94 (m, 1H), 1.50−1.22 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H).

2-Bromo-N-methyl-N-phenylhexanamide (**1d, Table 3**):[19] colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 4.08 (t, J = 7.4 Hz, 1H), 3.31 (s, 3H), 2.20−2.05 (m, 1H), 1.98−1.84 (m, 1H), 1.33−1.15 (m, 4H), 0.85 (t, J = 6.3 Hz, 3H).

Procedures for Synthesis of 2-Bromo-*N*-methyl-*N*-phenylacetamide (1e, Table 3).[20a] To a mixture of N-methylbenzenamine (0.55 mL, 5 mmol) in dichloromethane (40 mL) cooled at 0-5 °C was added a solution of 2-bromoacetyl bromide (0.5 mL, 5.72 mmol) in 20 mL dichloromethane. The reaction mixture was stirred at room temperature for 1 h, then cooled at 0-5 °C and a saturated solution of $NaHCO_3$ (40 mL) was added. The organic layer was washed with a saturated solution of $NaHCO_3$, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography to afford product **1e** as a yellow solid. mp 39−41 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.29 (d, J = 7.3 Hz, 2H), 3.67 (s, 2H), 3.31 (s, 3H).

Procedures for Synthesis of 2-Bromo-N-methyl-N-phenylpropanamide (1f, Table 3).[20b] 2-Bromopropionic acid (0.5 mL, 5.5 mmol) and N-methylbenzenamine (0.65 mL, 6 mmol) were dissolved in 13 mL chloroform and cooled to 0 °C. A solution of N,N'-diisopropylcarbodiimide (0.95 mL, 6 mmol) in 3 mL chloroform was added slowly through a syringe. The reaction mixture was stirred at room temperature for over 1 h. The solid residue was filtered off and washed with chloroform. The filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography. The target was confirmed by GC/MS.

Procedures for Synthesis of 2-Chloro-N-methyl-N-phenylpropanamide (1g, Table 3).[20c] 2-Chloropropionyl chloride (0.485 mL, 5 mmol) was added dropwise to a stirred solution of N-methylbenzenamine (0.54 mL, 5 mmol) and triethylamine (1.04 L, 7.5 mmol) in 35 mL dichloromethane at 0°C, then the reaction mixture was stirred at room temperature overnight. Next, an aqueous solution of HCl (1 M; 15 mL) was added. The organic layer was separated, washed with water (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4 and concentrated. The

residue was purified by column chromatography to afford product **1g** as a faint yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 7.3 Hz, 2H), 4.29 (q, J = 6.6 Hz, 1H), 3.31 (s, 3H), 1.58 (d, J = 6.6 Hz, 3H).

Procedures for Synthesis of Phenethyl 2-chloropropanoate (1h, Table 3).[21a] 2-Chloropropionyl chloride (0.534 mL, 5.5 mmol) was added dropwise to a stirred solution of phenethyl alcohol (0.6 mL, 5 mmol) and pyridine (0.44 mL, 5.5 mmol) in 8 mL dichloromethane at 0 °C, then the reaction mixture was stirred at room temperature overnight. Next, the reaction mixture was diluted with dichloromethane and an aqueous solution of HCl (1 M; 15 mL) was added. The organic layer was separated, washed with water (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography to afford product **1h** as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 5H), 4.43 – 4.33 (m, 3H), 2.98 (t, J = 7.0 Hz, 2H), 1.64 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 137.3, 128.9, 128.6, 126.7, 66.3, 52.5, 34.9, 21.5.

Procedures for Synthesis of Phenethyl 2-iodopropanoate (1i, Table 3).[21b] To a stirred solution of sodium iodide (1.5g, 10 mmol) in acetone (5 mL) was added phenethyl 2-chloropropanoate (1.06g, 5 mmol). The mixture was stirred at 50 °C overnight, and then the solvent was evaporated. The residue was purified by column chromatography to afford product **1i** as a faint yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.21 (m, 5H), 4.46 (q, J = 7.0 Hz, 1H), 4.42 – 4.30 (m, 2H), 2.97 (t, J = 7.1 Hz, 2H), 1.93 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 137.4, 129.0, 128.6, 126.7, 66.2, 34.7, 23.3, 12.9. HRMS (ESI) calcd for $C_{11}H_{14}IO_2^+$ ($[M + H]^+$): 305.0038, found 305.0042.

Typical Procedures for the Ru(II)-catalyzed Dehalogenation. To a flame-dried Schlenk tube changed with a magnetic stirring bar was added $[RuCl_2(cymene)]_2$ (3.1 mg, 0.005 mmol), CsOAc (46.1 mg, 0.24 mmol, 1.2 equiv) or *t*BuOK (26.9 mg, 0.24 mmol, 1.2 equiv), halide (0.2 mmol) and isopropanol (1 mL) under nitrogen atmosphere. The resulting mixture was stirred at 100 °C for 20-24 h. The reaction mixture was cooled to ambient temperature before filtered over silica gel, and then the filtrate was concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc or cyclohexane/dichloromethane/EtOAc) to give the desired dehalogenation products. For reactions that lead to volatile products, an internal standard (dodecane or toluene) was added to the cooled mixture, and the yields were calculated by GC/GC–MS analysis, as were indicated in related tables.

Benzamide (entries 1 – 4, Table 2):[22a] eluent: petroleum ether/EtOAc = 1/1, white solid (entry 1: 21.5 mg, 88%; entry 2: 23.8 mg, 98%; entry 3: 20.3 mg, 83%; entry 4: 22.7 mg, 93%); mp 125−127 °C; ^{1}H NMR (entry 1, Table 2, 500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.29 (bs, 2H); ^{13}C

NMR (entry 1, Table 2, 125 MHz, $CDCl_3$) δ 169.7, 133.5, 132.0, 128.6, 127.4.

^{1}H NMR (entry 2, Table 2, 500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.26 (bs, 2H).

^{1}H NMR (entry 3, Table 2, 500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.3 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 6.18 (bs, 2H).

^{1}H NMR (entry 4, Table 2, 500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.3 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 6.18 (bs, 2H).

4-Methylbenzamide (entry 5, Table 2):[16] eluent: petroleum ether/EtOAc = 1/1, white solid (26.2 mg, 96%); mp 158−161 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.07 (bs, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, d_6-DMSO) δ 167.8, 141.0, 131.5, 128.7, 127.5, 20.9.

3-Methylbenzamide (entry 6, Table 2):[16] eluent: petroleum ether/EtOAc = 1/1, white solid (19.9 mg, 74%); mp 90−93 °C; ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.93 (bs, 1H), 7.71 (s, 1H), 7.68 (t, J = 4.3 Hz, 1H), 7.33 (d, J = 5.0 Hz, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, d_6-DMSO) δ 168.0, 137.4, 134.3, 131.7, 128.0, 124.6, 20.9.

N-Ethylbenzamide (entry 7, Table 2):[22b] eluent: dichloromethane/EtOAc = 20/1, white solid (27.8 mg, 93%); mp 62−65 °C; ^{1}H NMR (500 MHz, d_6-DMSO) δ 8.48 (bs, 1H), 7.84 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 3.33 – 3.24 (m, 2H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, d_6-DMSO) δ 165.9, 134.7, 130.97, 128.2, 127.1, 34.0, 14.8.

N-Benzylbenzamide (entry 8, Table 2):[22b] eluent: petroleum ether/EtOAc = 3/1, white solid (32.7 mg, 78%); mp 102−105 °C; ^{1}H NMR (500 MHz, d_6-DMSO) δ 9.08 (t, J = 5.7 Hz, 1H), 7.91 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.33 (d, J = 4.4 Hz, 4H), 7.27 – 7.21 (m, 1H), 4.50 (d, J = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, d_6-DMSO) δ 166.2, 140.0, 134.3, 131.2, 128.3, 128.3, 127.2, 127.2, 126.7, 42.6.

N-Phenylbenzamide (entry 9, Table 2):[22c] eluent: petroleum ether/EtOAc = 8/1, white solid (35.4 mg, 89%); mp 160−162 °C; ^{1}H NMR (500 MHz, d_6-DMSO) δ 10.26 (s, 1H), 8.01 – 7.90 (m, 2H), 7.80 (d, J = 7.7 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.54 (t, J = 7.4 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, d_6-DMSO) δ 165.5, 139.2, 135.0, 131.5, 128.6, 128.3, 127.6, 123.6, 120.3.

N,N-Dimethylbenzamide (entry 10, Table 2):[22b] eluent: petroleum ether/EtOAc = 2/1, light yellow oil (27.4 mg, 93%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 5H), 3.11 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 136.3, 129.5, 128.3, 127.0, 39.6, 35.3.

Benzenesulfonamide (entry 11, Table 2):[22d] eluent: petroleum ether/EtOAc = 2/1, white solid (25.0 mg, 79%); mp 150−152 °C; ^{1}H NMR (500 MHz; d_6-DMSO) δ 7.88– 7.79 (m, 2H), 7.64 – 7.52 (m, 3H), 7.36 (bs, 2H); ^{13}C

NMR (125 MHz; d_6-DMSO) δ 144.2, 131.7, 128.9, 125.6.

2-Phenylacetamide (entry 12, Table 2):[22e] eluent: petroleum ether/EtOAc = 1/1, white solid (24.0 mg, 90%); mp 91−93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.32 – 7.24 (m, 3H), 5.90 (bs, 1H), 5.44 (bs, 1H), 3.57 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 134.9, 129.4, 129.1, 127.4, 43.3.

2H-Benzo[b][1,4]oxazin-3(4H)-one (entry 13, Table 2):[22f] eluent: petroleum ether/EtOAc = 4/1, white solid (21.4 mg, 72%); mp 170−173 °C; ^{1}H NMR (500 MHz, d_6-DMSO) δ 10.70 (s, 1H), 7.03 – 6.83 (m, 4H), 4.56 (s, 2H); ^{13}C NMR (125 MHz, d_6-DMSO) δ 164.9, 143.2, 127.2, 123.0, 122.3, 116.1, 115.8, 66.7.

Benzoic acid (entry 15, Table 2):[23] eluent: petroleum ether/EtOAc = 5/1, white solid (19.6 mg, 78%); mp 122−124 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.89 (bs, 1H), 8.13 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 133.8, 130.2, 129.4, 128.5.

3-Methylbenzoic acid (entry 16, Table 2):[23] eluent: petroleum ether/EtOAc = 5/1, white solid (25.4 mg, 93%); mp 105−108 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.81 (bs, 1H), 7.92 (d, J = 8.9 Hz, 2H), 7.41 (d, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 138.3, 134.6, 130.7, 129.3, 128.4, 127.4, 21.3.

1H-Indole (entries 17 and 18, Table 2):[24] eluent: petroleum ether/EtOAc = 40/1, white solid (entry 17: 16.6 mg, 70%; entry 18: 15.3 mg, 65%); mp 47−49 °C; ^{1}H NMR (entry 17, Table 2, 500 MHz, $CDCl_3$) δ 7.92 (bs, 1H), 7.64 (dd, J = 7.9, 0.8 Hz, 1H), 7.31 (dd, J = 8.1, 0.8 Hz, 1H), 7.23 – 7.15 (m, 1H), 7.14 – 7.07 (m, 2H), 6.55-6.50 (m, 1H); ^{13}C NMR (entry 17, 125 MHz, $CDCl_3$) δ 135.8, 127.9, 124.2, 122.0, 120.8, 120.0, 111.1, 102.6.

^{1}H NMR (entry 18, Table 2, 500 MHz, $CDCl_3$) δ 8.10 (bs, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.15– 7.08 (m, 1H), 6.60 – 6.52 (m, 1H).

Pyridin-2-amine (entry 20, Table 2):[25] eluent: petroleum ether/EtOAc = 1/5, light yellow oil (7.5 mg, 40%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, J = 5.0, 1.0 Hz, 1H), 7.43 (ddd, J = 8.3, 7.2, 1.9 Hz, 1H), 6.64 (ddd, J = 7.2, 5.1, 0.9 Hz, 1H), 6.50 (d, J = 8.3 Hz, 1H), 4.46 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 148.1, 137.8, 114.0, 108.6.

9H-Fluorene (entry 25, Table 2):[26a] eluent: petroleum ether, white solid (33.1 mg, >99%); mp 108−111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 7.5 Hz, 2H), 7.52 (d, J = 7.4 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 3.87 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 141.7, 126.8, 125.1, 119.9, 37.0.

1,1'-Biphenyl (entries 36 and 37, Table 2):[26b] eluent: petroleum ether, white solid (entry 36: 29.3 mg, 96%; entry 37: 29.8 mg, 96%); mp 66−68 °C; ^{1}H NMR (entry 36, Table 2, 500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.4 Hz, 4H), 7.43 (t, J = 7.7 Hz, 4H), 7.33 (t, J = 7.4 Hz, 2H); ^{13}C NMR (entry 36, 125 MHz, $CDCl_3$) δ 141.3, 128.8, 127.3, 127.2.

^{1}H NMR (entry 37, Table 2, 500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 4H), 7.43 (t, J = 7.5 Hz, 4H), 7.33 (t, J = 7.3 Hz, 2H).

Phenethyl hexanoate (**2b**):[27a] eluent: petroleum ether/EtOAc = 80/1, colorless liquid (34.5 mg, 78%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, J = 7.5 Hz, 2H), 7.25 – 7.18 (m, 3H), 4.28 (t, J = 7.1 Hz, 2H), 2.93 (t, J = 7.1 Hz,2H), 2.27 (t, J = 7.5 Hz, 2H), 1.66 – 1.52 (m, 2H), 1.34 – 1.21 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 137.9, 128.9, 128.5, 126.5, 64.7, 35.2, 34.3, 31.3, 24.6, 22.3, 13.9.

Benzyl hexanoate (**2c**):[27a] eluent: petroleum ether/EtOAc = 80/1, colorless liquid (27.2 mg, 66%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 5.11 (s, 2H), 2.35 (t, J = 7.6 Hz, 2H), 1.71 – 1.56 (m, 2H), 1.36 – 1.24 (m, 4H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 136.2, 128.6, 128.2, 128.2, 66.1, 34.3, 31.3, 24.7, 22.3, 13.9.

N-Methyl-N-phenylhexanamide (**2d**):[27b] eluent: petroleum ether/EtOAc = 15/1, colorless liquid (16.9 mg, 43%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.18 (d, J = 7.6 Hz, 2H), 3.26 (s, 3H), 2.13 – 1.97 (m, 2H), 1.67 – 1.46 (m, 2H), 1.28 – 1.13 (m, 4H), 0.82 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 144.3, 129.7, 127.7, 127.3, 37.3, 34.1, 31.5, 25.3, 22.4, 13.9.

N-Methyl-N-phenylacetamide (**2e**):[28] eluent: petroleum ether/EtOAc = 10/1, white solid (24.0 mg, 82%); mp 94−95 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.19 (d, J = 7.6 Hz, 2H), 3.27 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 144.7, 129.7, 127.7, 127.1, 37.1, 22.3.

N-Methyl-N-phenylpropionamide (**2f**):[28] eluent: petroleum ether/EtOAc = 10/1, white solid (**2f** from **1f**: 17.6 mg, 54%; **2f** from **1g**: 17.0 mg, 51%); mp 49−52 °C; ^{1}H NMR (**2f** from **1f**, 500 MHz, $CDCl_3$) δ 7.42 (t, J = 7.5 Hz, 2H), 7.33 (t, J = 6.9 Hz, 1H), 7.18 (d, J = 7.5 Hz, 2H), 3.27 (s, 3H), 2.11-2.06 (m, 2H), 1.05 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 144.3, 129.7, 127.6, 127.3, 37.3, 27.5, 9.7.

^{1}H NMR (**2f** from **1g**, 500 MHz, $CDCl_3$) δ 7.42 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.18 (d, J = 7.5 Hz, 2H), 3.27 (s, 3H), 2.08 (q, J = 6.9 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H).

Phenethyl propionate (**2h**):[29] eluent: petroleum ether/EtOAc = 50/1, colorless liquid (**2h** from **1h**: 24.9 mg, 67%; **2h** from **1i**: 25.1 mg, 71%); ^{1}H NMR (**2h** from **1h**, 500 MHz, $CDCl_3$) δ 7.42 – 7.17 (m, 5H), 4.29 (t, J = 7.1 Hz, 2H), 2.94 (t, J = 7.0 Hz, 2H), 2.31 (q, 7.6 Hz, 2H), 1.12 (t, J = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 137.9, 128.9, 128.5, 126.5, 64.8, 35.2, 27.6, 9.1.

^{1}H NMR (**2h** from **1i**, 500 MHz, $CDCl_3$) δ 7.37 – 7.16 (m, 5H), 4.29 (t, J = 7.1 Hz, 2H), 2.93 (t, J = 7.1 Hz, 2H), 2.31 (q, J = 7.6 Hz, 2H), 1.11 (t, J = 7.6 Hz, 3H).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Copies of ^{1}H and ^{13}C NMR spectra for isolated compounds and GC/GC-MS analysis for volatile products.

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Notes

The authors declare no competing financial interest.

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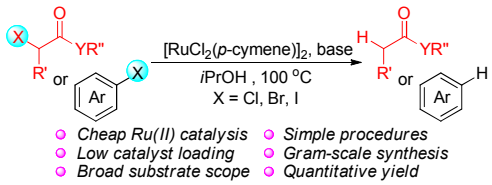
TOC Graphic



- *Cheap Ru(II) catalysis*
- *Low catalyst loading*
- *Broad substrate scope*
- *Simple procedures*
- *Gram-scale synthesis*
- *Quantitative yield*