Tetrahedron 75 (2019) 665–673

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Base-promoted aromatic [3,3] sigmatropic rearrangement of *N*-acyl-*O*-arylhydroxylamine derivatives

Eiji Tayama [a, *], Kazuki Hirano [b]

[a] Department of Chemistry, Faculty of Science, Niigata University, Niigata, 950-2181, Japan
[b] Graduate School of Science and Technology, Niigata University, Niigata, 950-2181, Japan

ARTICLE INFO

Article history:
Received 12 November 2018
Received in revised form
20 December 2018
Accepted 27 December 2018
Available online 28 December 2018

Keywords:
Sigmatropic rearrangement
α-Arylations
Amide enolates
Hydroxamic acids
Hydroxylamines

ABSTRACT

The base-promoted aromatic [3,3] sigmatropic rearrangement of *N*-acyl-*O*-arylhydroxylamines giving α-(2-hydroxyphenyl)amides was successfully demonstrated. The substrates were prepared from *N*-substituted hydroxylamines by *N*-acylation followed by copper(I)-mediated *O*-arylation with boronic acids. Treatment of the substrates with lithium hexamethyldisilazide (LiHMDS) in THF at 0 °C to room temperature generated the corresponding amide enolates. The aromatic [3,3] rearrangement of the enolates provided the desired products in moderate to good yields. A crossover experiment produced only intramolecular products and clarified that the reaction proceeds via the aromatic [3,3] sigmatropic rearrangement, not a bond-cleavage–recombination process. Our method is a formal α-arylation of amides.

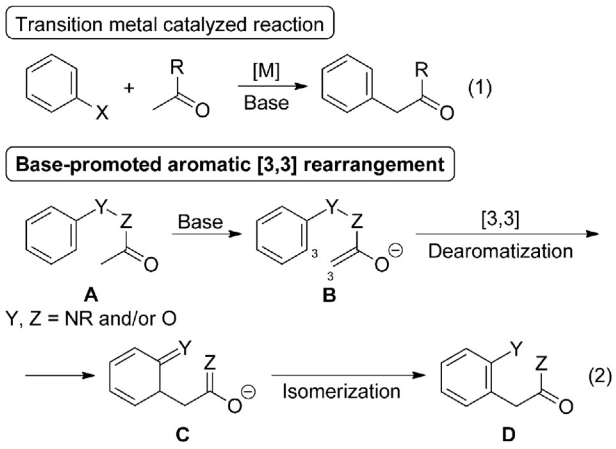
1. Introduction

Aromatic sigmatropic rearrangement is a unique synthetic transformation that enables the formation of carbon–carbon (C–C) bonds between aromatic (sp^2) and aliphatic (sp^3) carbons under simple and mild conditions [1]. However, applications as a synthetic method have been limited in a specific area because of the narrow substrate scopes. For example, in the α-arylation of α-carbonyl compounds, the transition metal catalyzed reactions have been studied by many researchers and advanced greatly because of the wide substrate scopes (Scheme 1, Eq. (1)) [2]. On the other hand, a similar transformation could be drawn by a base-promoted aromatic [3,3] sigmatropic rearrangement (Eq. (2)). The [3,3] rearrangement of an enolate **B**, generated from carbonyl compound **A**, into the dearomatized intermediate **C** followed by isomerization, provides the formal α-arylated product **D**. To achieve this transformation, a Y–Z bond, as in **A**, should be easily cleavable, such as a nitrogen–nitrogen (N–N) or a nitrogen–oxygen (N–O) bond, to obtain the driving force to generate the energetically unfavorable dearomatized intermediate **C**. This requirement results in the narrow substrate scope although the Fischer indole synthesis [3], which involves an N–N bond cleavage, is one of the well-known examples of the aromatic sigmatropic rearrangement [4–7]. In addition, their heteroatom–heteroatom bonds frequently make the preparation of the substrates difficult or complicated. Therefore, the development of an efficient synthetic route to substrates and successful rearrangement are necessary to show the synthetic utility of the aromatic sigmatropic rearrangements.

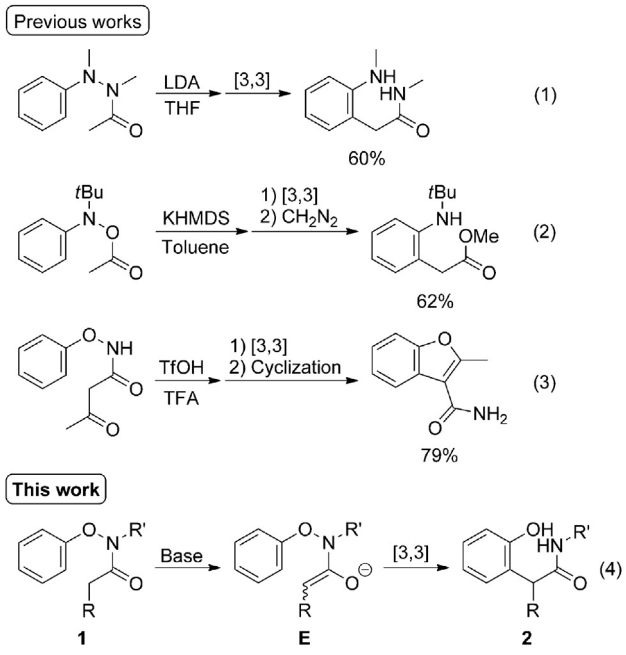
Previously, Endo et al. studied the series of these rearrangements involving an N–N or N–O bond cleavage, e.g., the rearrangements of *N*-acyl-*N*′-arylhydrazines [8] (Scheme 2, Eq. (1) and *O*-acyl-*N*-arylhydroxylamines [9] (Eq. (2))) giving α-(2-aminophenyl)carbonyl derivatives. Their group also reported an acid-catalyzed rearrangement of *N*-acetoacetyl-*O*-arylhydroxylamines to provide benzofuran derivatives [10] by a [3,3] rearrangement of the enol followed by acid-catalyzed intramolecular cyclization (Eq. (3)). These reactions under the acidic conditions gave cyclized products such as indoles or benzofuran derivatives. Surprisingly, to the best of our knowledge, the base-promoted rearrangement of *N*-acyl-*O*-arylhydroxylamines **1** to afford α-(2-hydroxyphenyl)carbonyl derivatives **2** has never been reported (Eq. (4)). Thus, we started to study the rearrangement. Substrate preparations, optimization reaction conditions, scope and limitations were described.

* Corresponding author.
E-mail address: tayama@chem.sc.niigata-u.ac.jp (E. Tayama).

https://doi.org/10.1016/j.tet.2018.12.058
0040-4020/



Scheme 1. α-Arylation of carbonyl compounds.

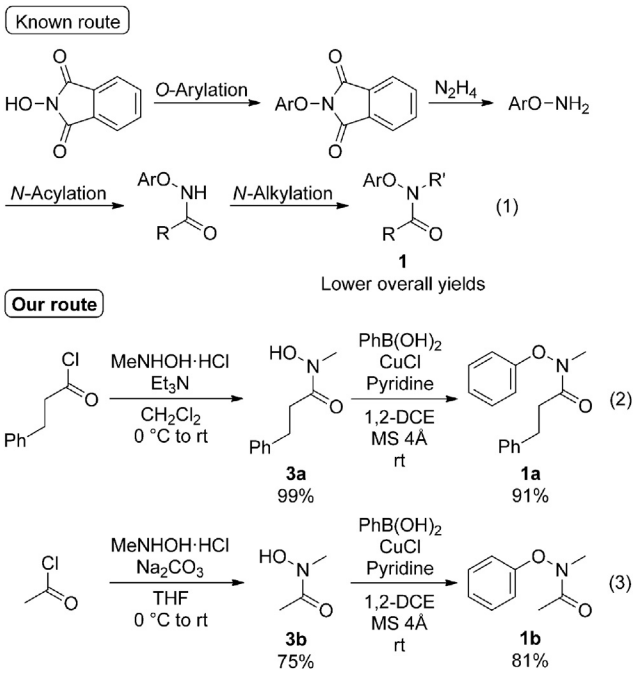


Scheme 2. Aromatic [3,3] rearrangement of hydrazine and hydroxylamine derivatives.

2. Results and discussion

First, we prepared substrate **1** from *N*-hydroxyphthalimide in 4 steps according to the literature [11] depicted in Scheme 3, Eq. (1). However, the overall yields of **1** were unsatisfactory in many cases [12]. Thus, we improved the preparative route, and the representative examples are shown as Eqs. (2) and (3). Compounds **1a** and **1b** were prepared by *N*-acylation of *N*-methylhydroxylamine followed by *O*-arylation [13]. Since compound **3b** is very soluble in H_2O, a condition of *N*-acetylation was modified to avoid extractive workup.

With substrate **1** in hand, we started to investigate the base-promoted [3,3] rearrangement using **1a** as a model compound (Table 1). First, a reaction of **1a** with 1.2 equivalents of LDA was examined in THF at 0 °C for 1 h. The [3,3] rearranged product **2a** was obtained in 26% yield with recovery of **1a** in 36% yield (Entry 1). The yield of **2a** was improved to 47% by extending the reaction time to 3 h (Entry 2). When the reaction temperature was raised to room

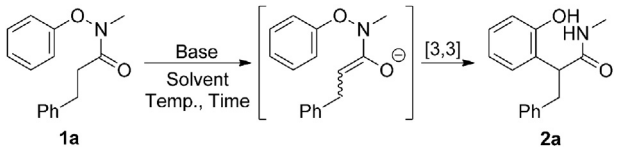


Scheme 3. Representative examples for preparation of **1**.

temperature after the addition of LDA, the yield of **2a** was decreased to 36% (Entry 3). Undesirable deprotonation and/or side reactions might have proceeded. Thus, the α-deprotonation with LDA was carried out at 0 °C for 1 h; then, the temperature was raised to room temperature, and the mixture was reacted for 3 h for the desired [3,3] rearrangement (Entry 4). As expected, the yield of **2a** was improved to 57%. Longer reaction time (6 h) did not show further improvements (Entry 5). The use of excess amounts of LDA (2.5 equivalents) lowered the yield of **2a** with no recovery of **1a** (Entry 6). The reaction in Et_2O showed low reactivity (Entry 7). Although the exact reason is unclear at present, the use of a bulkier base LiTMP (lithium 2,2,6,6-tetramethylpiperidide) did not afford **1a** at all (Entry 8). However, when the reaction was carried out with lithium hexamethyldisilazide (LiHMDS), the reaction proceeded more cleanly with LDA. The desired **2a** was obtained in 77% yield with the recovery of **1a** in 3% yield (Entry 9). The less basicity of LiHMDS than LDA would prevent undesirable side reactions. The use of sodium and potassium hexamethyldisilazide (NaHMDS, KHMDS) or TMEDA as an additive for LiHMDS did not show further improvements (Entries 10–12).

With optimized conditions (Table 1, Entry 9) in hand, we prepared various *N*-acyl-*O*-arylhydroxylamines **1** and subjected them to certain conditions to define the substrate scope and limitations of this reaction (Table 2). First, the reactions of three different *N*-acyl derivatives **1b**–**d** (R^1 = H, Me, Ph) were examined to clarify effects of sterically factor of α-substituent or acidity of α-proton (Entries 1–3). The corresponding products **2b**–**d** were obtained in moderate yields with the recovery of the substrate **1**. A clear difference was not observed. Next, substituent effects on the *O*-aryl moiety were investigated. Reactions of *para*-methyl-, phenyl-, methoxy-, and fluoro-derivatives **1e**–**h** proceeded to provide **2e**–**h** in reasonable yields (Entries 4–7, 68–88%). However, the reaction of *para*-cyano-derivative **1i** resulted in low yield of **2i** (30%) without recovery of **1i** (Entry 8). As a side product, 4-cyanophenol derived by N–O bond cleavage was isolated in 19% yield. In analogy with **1e**, reactions of *N*-acetyl- and *N*-phenylacetyl-derivatives **1j**–**k** afforded **2j**–**k** (Entries 9, 10). When unsymmetrical *O*-(2-

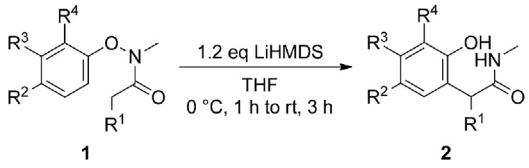
Table 1
Optimization of reaction conditions in the [3,3] rearrangement of **1a**.



Entry	Base (eq.)	Solvent	Temp. Time	Yield (%)[a,b]
1	LDA (1.2)	THF	0 °C, 1 h	26
2	LDA (1.2)	THF	0 °C, 3 h	47
3	LDA (1.2)	THF	0 °C, add. to rt, 3 h	36
4	LDA (1.2)	THF	0 °C, 1 h to rt, 3 h	57
5	LDA (1.2)	THF	0 °C, 1 h to rt, 6 h	58
6	LDA (2.5)	THF	0 °C, 1 h to rt, 3 h	36
7	LDA (1.2)[c]	Et_2O	0 °C, 1 h to rt, 3 h	35
8	LiTMP (1.2)[d]	THF	0 °C, 1 h to rt, 3 h	0
9	LiHMDS (1.2)[e]	THF	0 °C, 1 h to rt, 3 h	77
10	NaHMDS (1.2)[e]	THF	0 °C, 1 h to rt, 3 h	70
11	KHMDS (1.2)[f]	THF	0 °C, 1 h to rt, 3 h	53
12	LiHMDS (1.2)[e] + TMEDA (1.2)	THF	0 °C, 1 h to rt, 3 h	61

[a] Isolated yield.
[b] Recovery of **1a**, Entry 1: 36%; Entry 2: 25%; Entry 6: 0%; Entry 7: 57%; Entry 8: 99%; Entry 9: 3%; Entry 11: 38%; Entry 12: 20%.
[c] Prepared from diisopropylamine and n-butyllithium in Et_2O.
[d] Prepared from 2,2,6,6-tetramethylpiperidine and n-butyllithium in THF.
[e] Commercially available 1.0 M THF solution.
[f] Commercially available 0.5 M KHMDS toluene solution.

Table 2
Base-promoted aromatic [3,3] rearrangement of **1**.

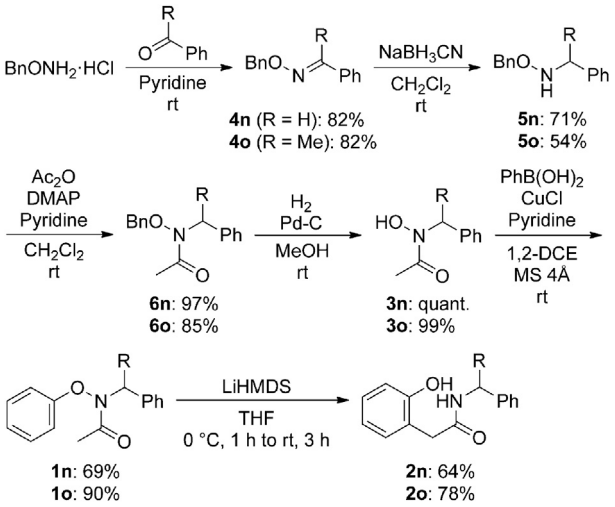


Entry	R^1	R^2	R^3	R^4		Yield (%)[a,b]
1	H	H	H	H	**b**	78
2	Me	H	H	H	**c**	62
3	Ph	H	H	H	**d**	65
4	CH_2Ph	Me	H	H	**e**	88
5	CH_2Ph	Ph	H	H	**f**	68
6	CH_2Ph	OMe	H	H	**g**	77
7	CH_2Ph	F	H	H	**h**	86
8	CH_2Ph	CN	H	H	**i**	30
9	H	Me	H	H	**j**	68
10	Ph	Me	H	H	**k**	90
11	CH_2Ph	H	H	Me	**l**	91
12	CH_2Ph	H	Me	Me	**m**	84

[a] Isolated yield.
[b] Recovery of **1**, Entry 1: 16%; Entry 2: 34%; Entry 4: 5%; Entry 5: 13%; Entry 6: 12%; Entry 7: 10%; Entry 8: 0%; Entry 9: 18%; Entry 11: 8%.

methylphenyl)- (**1l**) and *O*-(2,3-dimethylphenyl)- (**1m**) derivatives were subjected to the reaction, the [3,3] rearrangement proceeded with an unsubstituted *ortho*-position of the *O*-aryl to afford **2l** and **2m** in good yields (Entries 11, 12).

To show further substrate scope on the *N*-substituent, as in substrate **1**, *N*-benzylic derivatives **1n** and **1o** were prepared, and their reactions were examined (Scheme 4). Reductive amination of benzaldehyde or acetophenone with *O*-benzylhydroxylamine via formation of *O*-benzyl oximes **4** gave *N*-benzylic-*O*-benzylhydroxylamines **5** in moderate yields. *N*-Acylation to **6** followed by hydrogenolysis of benzyl ether afforded *N*-benzylic hydroxamic acids **3** in excellent yields [14]. Cu(I)-mediated *O*-arylation under

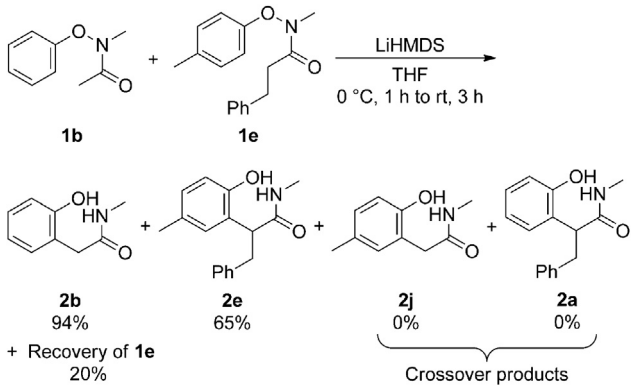


Scheme 4. Preparations and the reactions of *N*-benzylic derivatives **1n** and **1o**.

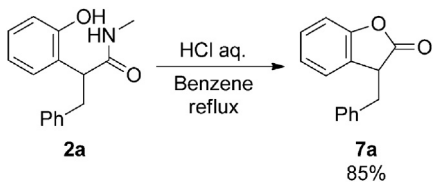
the same conditions provided the desired substrates **1** in acceptable overall yields (**1n**: 39%, **1o**: 34%). The base-promoted [3,3] rearrangement of **1n** and **1o** gave the corresponding α-(2-hydroxyphenyl)acetamide **2n** (64% yield) and **2o** (78% yield), respectively.

A crossover experiment was examined to clarify a mechanism of this reaction (Scheme 5). When an equimolar mixture of **1b** and **1e** was treated with LiHMDS, only the intramolecular products **2b** and **2e** were produced without formation of the intermolecular products **2j** and **2a**. This observation suggests that the products **2** are formed via the concerted aromatic [3,3] sigmatropic rearrangement of amide enolate **E** depicted in Scheme 2, Eq. (4), not a bond-cleavage–recombination process.

The product **2a** was easily converted into 3-benzyl benzofuran-2(3*H*)-one **7a** by acid-mediated cyclization [15] (Scheme 6). Our method would be an efficient synthetic route to various types of 3-



Scheme 5. A crossover experiment between **1b** and **1e**.

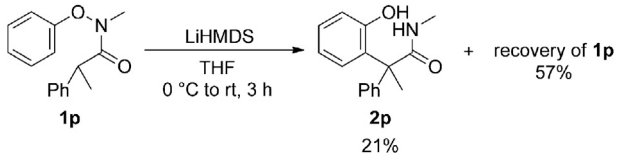


Scheme 6. Conversion of **2a** into benzofuranone derivative **7a**.

substituted benzofuran-2(3*H*)-one derivatives which would be valuable building blocks for biologically active compounds [16].

Finally, we attempted construction of an all-carbon quaternary stereocenter by this [3,3] rearrangement to explore further synthetic applications (Scheme 7). When a reaction of α,α-disubstituted **1p** was carried out under the same conditions, the desired **2p** was obtained in only 21% yield with the recovery of **1p** in 57% yield. Longer reaction time and higher reaction temperature (50 °C) did not improve the yield of **2p**. The [3,3] rearrangement might be inhibited because of steric reasons.

In conclusion, we have demonstrated the base-promoted aromatic [3,3] sigmatropic rearrangement of *N*-acyl-*O*-arylhydroxylamines **1** to afford α-(2-hydroxyphenyl)amides **2** in moderate to good yields [17]. The reaction proceeds via a formation of amide enolate generated from **1** with LiHMDS followed by [3,3] rearrangement between an enolate double bond and an aromatic double bond. This transformation would be a formal α-arylation of amide without using a transition metal catalyst. The scope and limitations of this rearrangement were also investigated. A crossover experiment suggested that the reaction proceeds via a concerted aromatic [3,3] sigmatropic process, not a bond-cleavage–recombination. Efficient synthetic routes into substrates **1** via copper(I)-mediated *O*-arylation of *N*-acylhydroxylamine with boronic acids are also provided. Our results would expand the synthetic utility of aromatic sigmatropic rearrangements.



Scheme 7. An attempt of construction of all-carbon quaternary stereocenter by [3,3] rearrangement of **1p**.

3. Experimental section

General: Infrared spectra (IR) were recorded on a Perkin Elmer Spectrum GX FT-IR or a JASCO FT/IR-4600 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a Varian (^{1}H: 400 MHz, ^{13}C: 100 MHz) or a Bruker spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz). Me_4Si (δ 0 ppm) was used as an internal standard in $CDCl_3$ and DMSO-d_6 for ^{1}H NMR. The residual protons (δ 2.05 ppm) were used as an internal standard in acetone-d_6 for ^{1}H NMR. $CDCl_3$ (δ 77.00 ppm) or DMSO-d_6 (δ 39.51 ppm) were used as an internal standard for ^{13}C NMR. The splitting patterns are denoted as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad peak. High-resolution mass spectra (ESI) were measured on a Thermo Fisher Scientific LC/FT-MS spectrometer. Reactions involving air- or moisture-sensitive compounds were conducted in appropriate round-bottomed flasks with a magnetic stirring bar under an argon atmosphere. Anhydrous tetrahydrofuran (THF) was purchased from KANTO Chemical Co., Inc., Japan. Anhydrous diethyl ether (Et_2O) was obtained by distillation from sodium benzophenone under an argon atmosphere prior to use. LiHMDS, NaHMDS, and KHMDS solution were purchased from Sigma-Aldrich. TMEDA was distilled from KOH under an argon atmosphere. For thin layer chromatography (TLC) analysis throughout this work, Merck TLC plates (silica gel 60 F_{254}) were used. The products were purified by preparative column chromatography on silica gel (60N, spherical neutral) purchased from KANTO Chemical Co., Inc., Japan.

3.1. Representative procedure for the preparation of N-methyl-N-phenoxy-3-phenylpropanamide (*1a*)

(Step 1) A solution of *N*-methylhydroxylamine hydrochloride (164 mg, 1.96 mmol) and triethylamine (0.51 mL, 3.7 mmol) in CH_2Cl_2 (23 mL) was treated with 3-phenylpropionyl chloride (0.24 mL, 1.6 mmol) at 0 °C. After stirring for 1 h at 0 °C and for 1 h at room temperature. The resulting mixture was treated with saturated aq. NH_4Cl and extracted with EtOAc. The combined extracts were washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 1/1 as the eluent) gave *N*-hydroxy-*N*-methyl-3-phenylpropanamide (**3a**) (284 mg, 99% yield) as a colorless oil. (Step 2) A mixture of **3a** (122 mg, 0.681 mmol), phenylboronic acid (196 mg, 1.61 mmol), pyridine (61 μL, 0.75 mmol), copper(I) chloride (77 mg, 0.78 mmol), and MS 4 Å (0.22 g) in 1,2-dichloroethane (3.4 mL) was stirred for 48 h at room temperature under an air atmosphere. The color of the mixture was changed from brown into green. The resulting mixture was filtered through a pad of Celite and the filtrate was evaporated. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 5/1 as the eluent) to afford **1a** (158 mg, 91% yield) as a yellow oil. IR (film) ν_{max} 3061, 3027, 2931, 2869, 1678, 1591, 1484, 1454, 1414, 1381, 1331, 1202, 1178, 1157, 1097, 1073, 1022, 998, 946, 922, 893, 858, 813, 752, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDC1_3$) δ 7.35–7.27 (2H, m, ArH), 7.27–7.19 (2H, m, ArH), 7.19–7.11 (3H, m, ArH), 7.06 (1H, tt, J = 7.4, 1.0 Hz, ArH), 6.94–6.88 (2H, m, ArH), 3.27 (3H, s, NCH_3), 2.95 (2H, t, J = 7.8 Hz, CH_2), 2.70 (2H, t, J = 7.8 Hz, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 157.4, 140.8, 129.8, 128.31, 128.30, 126.0, 123.2, 112.7, 34.1, 34.0, 30.3 ppm; HRMS (ESI): $[M + H]^+$, found 256.1327. $C_{16}H_{18}NO_2$ requires 256.1332.

3.2. Representative procedure for the preparation of N-methyl-N-phenoxyacetamide (*1b*)

(Step 1) A solution of *N*-methylhydroxylamine hydrochloride (194 mg, 2.32 mmol) and Na_2CO_3 (0.49 g, 4.6 mmol) in THF (3.9 mL)

was treated with acetyl chloride (0.15 mL, 2.1 mmol) at 0 °C and stirred for 14 h at room temperature. The resulting mixture was evaporated and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 1/1 as the eluent) to give *N*-hydroxy-*N*-methylacetamide (**3b**) (141 mg, 75% yield) as a colorless oil. (Step 2) A mixture of **3b** (251 mg, 2.82 mmol), phenylboronic acid (693 mg, 5.68 mmol), pyridine (0.25 mL, 3.1 mmol), copper(I) chloride (291 mg, 2.94 mmol), and MS 4 Å (0.65 g) in 1,2-dichloroethane (14 mL) was stirred for 48 h at room temperature under an air atmosphere. The resulting mixture was filtered through a pad of Celite and the filtrate was evaporated. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 4/1 as the eluent) to afford **1b** (377 mg, 81% yield) as a colorless oil. IR (film) ν_{max} 3061, 3041, 3016, 2976, 2933, 1681, 1592, 1484, 1412, 1378, 1344, 1293, 1203, 1179, 1158, 1138, 1075, 1036, 1023, 998, 947, 894, 813, 756, 691 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.40–7.33 (2H, m, Ph), 7.10 (1H, tt, J = 7.4, 1.1 Hz, Ph), 7.02–6.97 (2H, m, Ph), 3.29 (3H, s, NCH_3), 2.10 (3H, s, $COCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 157.4, 129.9, 123.3, 112.8, 33.9, 20.3 ppm; HRMS (ESI): $[M + H]^+$, found 166.0861. $C_9H_{12}NO_2$ requires 166.0863.

3.3. *N*-Methyl-*N*-phenoxypropionamide (**1c**)

Prepared from propanoyl chloride by the same procedure with **1a** (75% overall yield). Yellow oil; IR (film) ν_{max} 3062, 3041, 2979, 2940, 2880, 1684, 1591, 1484, 1416, 1377, 1293, 1202, 1178, 1158, 1111, 1074, 1051, 1022, 926, 893, 816, 753, 691 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.39–7.32 (2H, m, Ph), 7.09 (1H, tt, J = 7.2, 1.1 Hz, Ph), 7.01–6.96 (2H, m, Ph), 3.30 (3H, s, NCH_3), 2.40 (2H, q, J = 7.6 Hz, CH_2CH_3), 1.10 (3H, t, J = 7.6 Hz, CH_2CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 157.6, 129.9, 123.2, 112.7, 34.2, 25.6, 8.4 ppm; HRMS (ESI): $[M + H]^+$, found 180.1017. $C_{10}H_{14}NO_2$ requires 180.1019.

3.4. *N*-Methyl-*N*-phenoxy-2-phenylacetamide (**1d**)

Prepared from phenylacetyl chloride by the same procedure with **1a** (63% overall yield). Purple oil; IR (film) ν_{max} 3062, 3030, 2975, 2934, 1677, 1591, 1483, 1455, 1411, 1375, 1289, 1199, 1157, 1115, 1089, 1023, 1002, 948, 893, 814, 755, 736, 693 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.38–7.31 (2H, m, ArH), 7.29–7.17 (5H, m, ArH), 7.09 (1H, tt, J = 7.4, 1.0 Hz, ArH), 6.99–6.94 (2H, m, ArH), 3.70 (2H, s, CH_2), 3.29 (3H, s, NCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 157.3, 134.1, 129.9, 129.4, 128.3, 126.8, 123.3, 112.9, 39.5, 34.2 ppm; HRMS (ESI): $[M + H]^+$, found 242.1167. $C_{15}H_{16}NO_2$ requires 242.1176.

3.5. *N*-Methyl-3-phenyl-*N*-(*p*-tolyloxy)propanamide (**1e**)

Prepared by the same procedure with **1a** using *p*-tolylboronic acid instead of phenylboronic acid (76% overall yield). Yellow oil; IR (film) ν_{max} 3061, 3028, 2924, 2867, 1676, 1605, 1500, 1452, 1413, 1381, 1331, 1291, 1200, 1179, 1160, 1101, 1072, 1032, 1012, 946, 923, 816, 779, 750, 700 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.27–7.20 (2H, m, ArH), 7.19–7.08 (5H, m, ArH), 6.80 (2H, ddd, J = 8.8, 2.5, 2.5 Hz, ArH), 3.26 (3H, s, NCH_3), 2.94 (2H, t, J = 7.7 Hz, CH_2), 2.69 (2H, t, J = 7.7 Hz, CH_2), 2.30 (3H, s, $ArCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 155.2, 140.9, 132.7, 130.2, 128.33, 128.30, 126.0, 112.6, 33.9, 30.3, 20.4 ppm (one overlapping peak); HRMS (ESI): $[M + H]^+$, found 270.1484. $C_{17}H_{20}NO_2$ requires 270.1489.

3.6. *N*-([1,1′-Biphenyl]-4-yloxy)-*N*-methyl-3-phenylpropanamide (**1f**)

Prepared by the same procedure with **1a** using 4-biphenylboronic acid instead of phenylboronic acid (56% overall yield). White solid, mp 74–75 °C; IR (KBr) ν_{max} 3059, 3031, 2962, 2930, 1672, 1602, 1513, 1484, 1449, 1416, 1380, 1338, 1265, 1216, 1186, 1155, 1097, 1075, 1033, 1002, 947, 910, 857, 831, 761, 700 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.56–7.50 (4H, m, ArH), 7.45–7.39 (2H, m, ArH), 7.33 (1H, tt, J = 7.4, 1.4 Hz, ArH), 7.27–7.21 (2H, m, ArH), 7.20–7.13 (3H, m, ArH), 6.98 (2H, ddd, J = 8.8, 2.6, 2.6 Hz, ArH), 3.31 (3H, s, NCH_3), 2.97 (2H, t, J = 7.9 Hz, CH_2), 2.73 (2H, t, J = 7.9 Hz, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 156.9, 140.9, 140.1, 136.5, 128.8, 128.6, 128.40, 128.37, 127.1, 126.8, 126.1, 113.2, 34.2, 34.1, 30.4 ppm; HRMS (ESI): $[M + H]^+$, found 332.1637. $C_{22}H_{22}NO_2$ requires 332.1645.

3.7. *N*-(4-Methoxyphenoxy)-*N*-methyl-3-phenylpropanamide (**1g**)

Prepared by the same procedure with **1a** using 4-methoxyphenylboronic acid instead of phenylboronic acid (15% overall yield). Pale brown oil; IR (film) ν_{max} 3061, 3026, 3000, 2933, 2835, 1675, 1602, 1501, 1454, 1441, 1415, 1382, 1296, 1245, 1196, 1103, 1073, 1034, 1004, 947, 922, 828, 778, 750, 700 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.28–7.22 (2H, m, ArH), 7.20–7.13 (3H, m, ArH), 6.84 (4H, s, ArH), 3.78 (3H, s, OCH_3), 3.26 (3H, s, NCH_3), 2.95 (2H, t, J = 7.9 Hz, CH_2), 2.71 (2H, t, J = 7.9 Hz, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 155.6, 151.2, 141.0, 128.40, 128.38, 126.0, 114.9, 114.0, 55.7, 34.0, 33.9, 30.4 ppm; HRMS (ESI): $[M + H]^+$, found 286.1430. $C_{17}H_{20}NO_3$ requires 286.1438.

3.8. *N*-(4-Fluorophenoxy)-*N*-methyl-3-phenylpropanamide (**1h**)

Prepared by the same procedure with **1a** using 4-fluorophenylboronic acid instead of phenylboronic acid (75% overall yield). Yellow oil; IR (film) ν_{max} 3064, 3027, 2933, 2870, 1678, 1603, 1498, 1453, 1413, 1381, 1331, 1230, 1185, 1114, 1095, 1073, 1031, 1006, 946, 923, 833, 781, 749, 700 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.28–7.22 (2H, m, ArH), 7.21–7.12 (3H, m, ArH), 7.04–6.96 (2H, m, ArH), 6.89–6.82 (2H, m, ArH), 3.26 (3H, s, NCH_3), 2.95 (2H, t, J = 7.8 Hz, CH_2), 2.69 (2H, t, J = 7.8 Hz, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 159.8, 157.4, 155.3 (d, J = 2 Hz), 140.8, 128.4, 127.3 (d, J = 231 Hz), 116.4 (d, J = 24 Hz), 114.1 (d, J = 8 Hz), 34.12, 34.06, 30.3 ppm; HRMS (ESI): $[M + H]^+$, found 274.1235. $C_{16}H_{17}FNO_2$ requires 278.1238.

3.9. *N*-(4-Cyanophenoxy)-*N*-methyl-3-phenylpropanamide (**1i**)

Prepared by the same procedure with **1a** using 4-cyanophenylboronic acid instead of phenylboronic acid (38% overall yield). Colorless oil; IR (film) ν_{max} 3100, 3063, 3027, 2934, 2871, 2227, 1682, 1601, 1495, 1453, 1413, 1379, 1327, 1296, 1218, 1160, 1110, 1073, 1031, 1010, 945, 921, 839, 777, 752, 701 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.62 (2H, ddd, J = 9.0, 2.4, 2.4 Hz, ArH), 7.25 (2H, dddd, J = 7.1, 7.1, 1.5, 1.5 Hz, ArH), 7.18 (1H, tt, J = 7.1, 1.5 Hz, ArH), 7.15–7.11 (2H, m, ArH), 7.01 (2H, ddd, J = 9.0, 2.4, 2.4 Hz, ArH), 3.28 (3H, s, NCH_3), 2.95 (2H, t, J = 7.8 Hz, CH_2), 2.66 (2H, t, J = 7.8 Hz, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 160.7, 140.4, 134.4, 128.4, 128.3, 126.1, 118.2, 113.7, 106.9, 34.7, 34.1, 30.2 ppm; HRMS (ESI): $[M + H]^+$, found 281.1280. $C_{17}H_{17}N_2O_2$ requires 281.1285.

3.10. *N*-Methyl-*N*-(*p*-tolyloxy)acetamide (**1j**)

Prepared by the same procedure with **1b** using *p*-tolylboronic acid instead of phenylboronic acid (53% overall yield). Yellow oil; IR (film) ν_{max} 3031, 2925, 2871, 1678, 1606, 1502, 1413, 1376, 1344, 1290, 1200, 1162, 1138, 1037, 1000, 947, 818, 767, 735, 700 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.18–7.12 (2H, m, ArH), 6.87 (2H, ddd, J = 8.8, 2.5, 2.5 Hz, ArH), 3.27 (3H, s, NCH_3), 2.32 (3H, s, $ArCH_3$), 2.09 (3H, s, $COCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 155.3, 132.7,

130.3, 112.6, 35.8, 20.4, 20.2 ppm; HRMS (ESI): $[M + H]^+$, found 180.1016. $C_{10}H_{14}NO_2$ requires 180.1019.

3.11. N-Methyl-2-phenyl-N-(p-tolyloxy)acetamide (**1k**)

Prepared from phenylacetyl chloride by the same procedure with **1a** using *p*-tolylboronic acid instead of phenylboronic acid (66% overall yield). White solid, mp 48–49 °C; IR (KBr) ν_{max} 3082, 3059, 3033, 2983, 2917, 2864, 1675, 1603, 1500, 1453, 1406, 1377, 1327, 1286, 1199, 1176, 1159, 1108, 1088, 1029, 1011, 969, 948, 906, 851, 826, 747, 737, 699 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.30–7.18 (5H, m, ArH), 7.14 (2H, d, $J = 8.6$ Hz, ArH), 6.87 (2H, d, $J = 8.6$ Hz, ArH), 3.69 (2H, s, CH_2), 3.27 (3H, s, NCH_3), 2.33 (3H, s, $ArCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 155.2, 134.2, 132.8, 130.3, 129.4, 128.3, 126.7, 112.8, 39.4, 34.1, 20.5 ppm; HRMS (ESI): $[M + H]^+$, found 256.1327. $C_{16}H_{18}NO_2$ requires 256.1332.

3.12. N-Methyl-3-phenyl-N-(o-tolyloxy)propanamide (**1l**)

Prepared by the same procedure with **1a** using *o*-tolylboronic acid instead of phenylboronic acid (62% overall yield). Colorless oil; IR (film) ν_{max} 3061, 3027, 2928, 2864, 1676, 1604, 1587, 1484, 1454, 1414, 1380, 1341, 1303, 1218, 1172, 1113, 1095, 1073, 1044, 986, 946, 924, 859, 848, 831, 751, 700 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.28–7.21 (2H, m, ArH), 7.20–7.11 (5H, m, ArH), 6.97 (1H, ddd, $J = 7.4$, 7.4, 0.8 Hz, ArH), 6.83 (1H, d, $J = 8.0$ Hz, ArH), 3.29 (3H, s, NCH_3), 2.95 (2H, t, $J = 8.0$ Hz, CH_2), 2.69 (2H, t, $J = 8.0$ Hz, CH_2), 2.24 (3H, s, $ArCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 155.2, 140.9, 131.5, 128.4, 127.2, 126.0, 124.5, 122.9, 110.5, 34.2, 33.9, 30.5, 15.7 ppm (one overlapping peak); HRMS (ESI): $[M + H]^+$, found 270.1483. $C_{17}H_{20}NO_2$ requires 270.1489.

3.13. N-(2,3-Dimethylphenoxy)-N-methyl-3-phenylpropanamide (**1m**)

Prepared from phenylacetyl chloride by the same procedure with **1a** using 2,3-dimethylphenylboronic acid instead of phenylboronic acid (63% overall yield). Colorless oil; IR (film) ν_{max} 3061, 3026, 2924, 2865, 1675, 1605, 1581, 1494, 1466, 1413, 1381, 1340, 1301, 1231, 1175, 1114, 1091, 1058, 1030, 990, 948, 926, 892, 844, 811, 773, 750, 699 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.28–7.21 (2H, m, ArH), 7.20–7.12 (3H, m, ArH), 7.03 (1H, dd, $J = 8.0$, 7.2 Hz, ArH), 6.88 (1H, d, $J = 7.2$ Hz, ArH), 6.70 (1H, d, $J = 8.0$ Hz, ArH), 3.28 (3H, s, NCH_3), 2.95 (2H, t, $J = 7.9$ Hz, CH_2), 2.69 (2H, t, $J = 7.9$ Hz, CH_2), 2.28 (3H, s, $ArCH_3$), 2.14 (3H, s, $ArCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 155.0, 141.0, 138.8, 128.38, 128.35, 126.3, 126.0, 124.6, 122.9, 108.3, 34.1, 33.9, 30.5, 19.7, 11.2 ppm; HRMS (ESI): $[M + H]^+$, found 284.1638. $C_{18}H_{22}NO_2$ requires 284.1645.

3.14. N-Benzyl-N-phenoxyacetamide (**1n**)

A mixture of benzaldehyde (0.38 mL, 3.7 mmol) and *O*-benzylhydroxylamine hydrochloride (774 mg, 4.85 mmol) in pyridine (10.5 mL) was stirred for 14 h at room temperature. The resulting mixture was evaporated and the residue was diluted with H_2O. The mixture was extracted with EtOAc and the combined extracts were washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 10/1 to 5/1 as the eluent) afforded benzaldehyde *O*-benzyl oxime (**4n**) (669 mg, 82% yield) as a colorless oil. (Step 2) A solution of **4n** (662 mg, 2.99 mmol) in CH_2Cl_2 (6.2 mL) was treated with sodium cyanoborohydride (398 mg, 6.33 mmol) at room temperature. The mixture was stirred for 21 h at the same temperature. The resulting mixture was evaporated and the residue was diluted with a 1 M aq. NaOH. The mixture was extracted with CH_2Cl_2 and the combined extracts were dried over Na_2SO_4. Evaporation of volatiles and purification of the residue by chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 1/1 as the eluent) gave *N*,*O*-dibenzylhydroxylamine (**5n**) (455 mg, 71% yield) as a colorless oil. (Step 3) A solution of **5n** (316 mg, 1.48 mmol), DMAP (95 mg, 0.78 mmol), pyridine (0.24 mL, 3.0 mmol), in CH_2Cl_2 (3.0 mL) was treated with acetic anhydride (0.21 mL, 2.2 mmol) at room temperature. After stirring for 2 h at the same temperature, the resulting mixture was treated with saturated aq. $NaHCO_3$ and extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 2/1 as the eluent) afforded *N*-benzyl-*N*-(benzyloxy)acetamide (**6n**) (367 mg, 97% yield) as a colorless oil. (Step 4) A mixture of **6n** (236 mg, 0.924 mmol) and Pd-C (loading: 10 wt%, 20 mg) in MeOH (9 mL) was stirred at room temperature for 3 h under a hydrogen atmosphere. The resulting mixture was filtered through a pad of Celite and the filtrate was evaporated to afford *N*-benzyl-*N*-hydroxyacetamide (**3n**) (152 mg, quant.) as a brown oil. (Step 5) A mixture of **3n** (140 mg, 0.848 mmol), phenylboronic acid (237 mg, 1.94 mmol), pyridine (80 μL, 0.99 mmol), copper(I) chloride (90 mg, 0.91 mmol), and MS 4 Å (0.17 g) in 1,2-dichloroethane (4.2 mL) was stirred for 38 h at room temperature under an air atmosphere. The resulting mixture was filtered through a pad of Celite and the filtrate was evaporated. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 5/1 as the eluent) to afford **1n** (142 mg, 69% yield) as a colorless oil. IR (film) ν_{max} 3062, 3032, 2930, 1676, 1589, 1485, 1435, 1388, 1346, 1244, 1193, 1156, 1083, 1030, 979, 895, 811, 755, 736, 698 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.37–7.25 (7H, m, ArH), 7.08 (1H, tt, $J = 7.4$, 1.2 Hz, ArH), 7.00–6.94 (2H, m, ArH), 4.85 (2H, s, CH_2), 2.11 (3H, s, $COCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 157.4, 135.5, 129.9, 128.9, 128.5, 127.8, 123.3, 113.2, 50.0, 20.7 ppm; HRMS (ESI): $[M + H]^+$, found 242.1170. $C_{15}H_{16}NO_2$ requires 242.1176.

3.15. N-Phenoxy-N-(1-phenylethyl)acetamide (**1o**)

Prepared from acetophenone by the same procedure with **1n**. The yields were depicted in Scheme 4. Colorless oil; IR (film) ν_{max} 3062, 3033, 2983, 2937, 2877, 1683, 1591, 1489, 1455, 1428, 1374, 1337, 1295, 1193, 1156, 1131, 1073, 1025, 981, 935, 914, 893, 832, 822, 781, 755, 700 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.42–7.36 (2H, m, ArH), 7.31–7.18 (5H, m, ArH), 6.98 (1H, t, $J = 7.2$ Hz, ArH), 6.93 (2H, d, $J = 7.6$ Hz, ArH), 5.84 (1H, q, $J = 7.2$ Hz, 1-H), 2.03 (3H, s, $COCH_3$), 1.55 (3H, d, $J = 7.2$ Hz, 2-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 159.5, 139.8, 129.5, 128.2, 127.8, 127.7, 122.7, 120.1, 115.3, 112.8, 56.7, 21.6, 17.2 ppm; HRMS (ESI): $[M + H]^+$, found 256.1326. $C_{16}H_{18}NO_2$ requires 256.1332.

3.16. N-Methyl-N-phenoxy-2-phenylpropanamide (**1p**)

Prepared from 2-phenylpropanoyl chloride by the same procedure with **1a** (63% overall yield). A preparation of 2-phenylpropanoyl chloride is as follows: A solution of 2-phenylpropanoic acid (292 mg, 1.94 mmol) and DMF (15 μL, 0.19 mmol) in CH_2Cl_2 (8 mL) was treated with oxalyl chloride (0.70 mL, 8.3 mmol) at room temperature under an argon atmosphere. The resulting solution was evaporated to provide crude 2-phenylpropanoyl chloride (331 mg, quant.) as a yellow oil. The product was used without purifications. Colorless oil; IR (film) ν_{max} 3061, 3028, 2976, 2932, 2872, 1669, 1592, 1484, 1454, 1411, 1377, 1289, 1199, 1179, 1157, 1117, 1072, 1050, 1022, 993, 928, 892, 821, 752, 717, 697 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.32–7.13 (7H, m, ArH), 7.05 (1H, t, $J = 7.4$ Hz, ArH), 6.88–6.82 (2H, m, ArH), 3.96 (1H, q, $J = 7.0$ Hz, 2-H), 3.25 (3H, s, NCH_3), 1.44 (3H, d, $J = 7.0$ Hz, 3-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 157.4, 140.7, 129.8, 128.4,

127.6, 126.7, 123.1, 112.8, 42.2, 34.4, 19.3 ppm; HRMS (ESI): $[M + H]^+$, found 256.1326. $C_{16}H_{18}NO_2$ requires 256.1332.

3.17. Representative procedure for the base-promoted [3,3] rearrangement of **1a** into 2-(2-hydroxyphenyl)-N-methyl-3-phenylpropanamide (**2a**)

(Table 1, Entry 9) A 1 M LiHMDS THF solution (0.34 mL, 0.34 mmol) was added to a solution of **1a** (70.8 mg, 0.277 mmol) in THF (1.4 mL) at 0 °C under an argon atmosphere. The mixture was stirred for 1 h at 0 °C and for 3 h at room temperature. The resulting mixture was quenched with saturated aq. NH_4Cl and extracted with EtOAc. The combined extracts were washed with brine, dried over Na_2SO_4, and evaporated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 5/1 to 1/1 as the eluent) gave **2a** (54.4 mg, 77% yield) as a yellow gum. IR (film) ν_{max} 3302, 3086, 3028, 2940, 2865, 2783, 2728, 2634, 1636, 1601, 1548, 1490, 1455, 1409, 1308, 1247, 1158, 1105, 1074, 1043, 936, 835, 787, 755, 699 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 10.71 (1H, s, OH), 7.26–7.09 (6H, m, ArH), 6.95 (1H, dd, J = 7.8, 1.2 Hz, ArH), 6.86 (1H, dd, J = 7.2, 1.6 Hz, ArH), 6.75 (1H, ddd, J = 7.8, 7.2, 1.2 Hz, ArH), 5.86 (1H, br, NH), 3.54 (1H, dd, J = 13.2, 9.6 Hz, CH), 3.42 (1H, dd, J = 9.6, 6.2 Hz, CH_2), 3.07 (1H, dd, J = 13.2, 6.2 Hz, CH_2), 2.66 (3H, d, J = 4.8 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 156.2, 138.9, 130.5, 129.3, 128.8, 128.4, 126.5, 124.1, 119.9, 118.8, 57.4, 37.7, 26.6 ppm; HRMS (ESI): $[M + H]^+$, found 256.1327. $C_{16}H_{18}NO_2$ requires 256.1332.

3.18. 2-(2-Hydroxyphenyl)-N-methylacetamide (**2b**)

Colorless gum; IR (KBr) ν_{max} 3371, 3068, 3013, 2974, 2937, 2878, 2729, 2628, 1628, 1599, 1510, 1460, 1403, 1313, 1265, 1248, 1183, 1167, 1127, 1106, 1038, 941, 928, 876, 840, 796, 756, 712 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 9.88 (1H, s, OH), 7.16 (1H, ddd, J = 7.9, 7.4, 1.6 Hz, ArH), 7.02 (1H, dd, J = 7.6, 1.6 Hz, ArH), 6.95 (1H, dd, J = 7.9, 1.2 Hz, ArH), 6.82 (1H, ddd, J = 7.6, 7.4, 1.2 Hz, ArH), 6.52 (1H, br, NH), 3.57 (2H, s, CH_2), 2.79 (3H, d, J = 4.8 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 155.9, 130.6, 129.1, 121.5, 120.3, 117.6, 40.4, 26.7 ppm; HRMS (ESI): $[M + H]^+$, found 166.0860. $C_9H_{12}NO_2$ requires 166.0863.

3.19. 2-(2-Hydroxyphenyl)-N-methylpropanamide (**2c**)

Colorless gum; IR (film) ν_{max} 3287, 2974, 2939, 2877, 2730, 2631, 1641, 1601, 1548, 1503, 1489, 1454, 1410, 1373, 1325, 1244, 1159, 1117, 1062, 1026, 1000, 985, 936, 909, 836, 754 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 10.17 (1H, br, OH), 7.16 (1H, ddd, J = 8.0, 7.6, 1.4 Hz, ArH), 6.99 (1H, dd, J = 7.4, 1.4 Hz, ArH), 6.93 (1H, d, J = 8.0 Hz, ArH), 6.81 (1H, dd, J = 7.6, 7.4 Hz, ArH), 6.21 (1H, br, NH), 3.55 (1H, q, J = 7.2 Hz, 2-H), 2.82 (3H, d, J = 5.2 Hz, NCH_3), 1.58 (3H, d, J = 7.2 Hz, 3-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 155.7, 129.2, 128.9, 126.0, 120.1, 118.2, 46.2, 26.7, 16.8 ppm; HRMS (ESI): $[M + H]^+$, found 180.1016. $C_{10}H_{14}NO_2$ requires 180.1019.

3.20. 2-(2-Hydroxyphenyl)-N-methyl-2-phenylacetamide (**2d**)

Colorless gum; IR (KBr) ν_{max} 3419, 3293, 3087, 2942, 2730, 2624, 1633, 1602, 1531, 1493, 1453, 1408, 1275, 1249, 1160, 1093, 1040, 930, 884, 862, 834, 819, 785, 757, 698 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.77 (1H, s, OH), 8.20 (1H, q, J = 4.8 Hz, NH), 7.31–7.24 (2H, m, ArH), 7.24–7.15 (4H, m, ArH), 7.05 (1H, ddd, J = 7.9, 7.3, 1.4 Hz, ArH), 6.78 (1H, dd, J = 7.9, 1.4 Hz, ArH), 6.73 (1H, ddd, J = 7.9, 7.3, 1.4 Hz, ArH), 5.13 (1H, s, CH), 2.60 (3H, d, J = 4.8 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.3, 154.9, 140.1, 129.6, 128.4, 128.1, 127.7, 126.4, 118.7, 115.3, 51.1, 25.9 ppm (one overlapping peak); HRMS (ESI): $[M + H]^+$, found 242.1172. $C_{15}H_{16}NO_2$ requires 242.1176.

3.21. 2-(2-Hydroxy-5-methylphenyl)-N-methyl-3-phenylpropanamide (**2e**)

Colorless gum; IR (KBr) ν_{max} 3313, 3130, 3058, 3025, 2933, 2605, 1636, 1603, 1590, 1499, 1452, 1404, 1373, 1265, 1249, 1154, 1119, 1075, 1030, 897, 858, 817, 783, 699 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 10.43 (1H, s, OH), 7.27–7.21 (2H, m, ArH), 7.18 (1H, tt, J = 7.2, 1.6 Hz, ArH), 7.16–7.11 (2H, m, ArH), 6.96 (1H, dd, J = 8.1, 2.2 Hz, ArH), 6.85 (1H, d, J = 8.1 Hz, ArH), 6.71 (1H, d, J = 2.2 Hz, ArH), 5.84 (1H, br q, J = 4.8 Hz, NH), 3.57 (1H, dd, J = 13.4, 10.1 Hz, CH), 3.38 (1H, dd, J = 10.1, 5.7 Hz, CH_2), 3.02 (1H, dd, J = 13.4, 5.7 Hz, CH_2), 2.65 (3H, d, J = 4.8 Hz, NCH_3), 2.20 (3H, s, $ArCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 153.8, 139.1, 130.9, 129.7, 129.1, 128.8, 128.4, 126.5, 124.0, 118.6, 57.2, 37.7, 26.5, 20.3 ppm; HRMS (ESI): $[M + H]^+$, found 270.1482. $C_{17}H_{20}NO_2$ requires 270.1489.

3.22. 2-(4-Hydroxy-[1,1′-biphenyl]-3-yl)-N-methyl-3-phenylpropanamide (**2f**)

Colorless gum; IR (KBr) ν_{max} 3297, 3131, 3027, 2956, 2932, 2863, 2764, 2464, 1638, 1602, 1482, 1408, 1377, 1292, 1267, 1162, 1122, 1077, 1049, 1027, 904, 858, 834, 771, 762, 698 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.11 (1H, s, OH), 7.92 (1H, q, J = 4.8 Hz, NH), 7.54–7.48 (3H, m, ArH), 7.42 (2H, dd, J = 8.0, 7.4 Hz, ArH), 7.35 (1H, dd, J = 8.4, 2.4 Hz, ArH), 7.28 (1H, tt, J = 7.4, 1.2 Hz, ArH), 7.27–7.18 (4H, m, ArH), 7.15 (1H, tt, J = 7.0, 1.8 Hz, ArH), 6.89 (1H, d, J = 8.4 Hz, ArH), 4.10 (1H, dd, J = 9.2, 6.0 Hz, CH), 3.29 (1H, dd, J = 13.6, 9.2 Hz, CH_2), 2.94 (1H, dd, J = 13.6, 6.0 Hz, CH_2), 2.51 (3H, d, J = 4.8 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.2, 154.7, 140.4, 140.1, 131.0, 128.8, 128.7, 128.1, 127.0, 126.8, 126.4, 126.01, 125.97, 116.1, 47.7, 38.0, 25.8 ppm (one overlapping peak); HRMS (ESI): $[M + H]^+$, found 332.1637. $C_{22}H_{22}NO_2$ requires 332.1645.

3.23. 2-(2-Hydroxy-5-methoxyphenyl)-N-methyl-3-phenylpropanamide (**2g**)

Pale brown gum; IR (film) ν_{max} 3301, 3110, 3028, 3001, 2939, 2833, 1640, 1607, 1544, 1496, 1453, 1433, 1410, 1374, 1297, 1244, 1212, 1180, 1153, 1112, 1067, 1042, 978, 911, 850, 815, 786, 699 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 10.20 (1H, br, OH), 7.26–7.19 (2H, m, ArH), 7.17 (1H, tt, J = 7.2, 1.4 Hz, ArH), 7.14–7.09 (2H, m, ArH), 6.87 (1H, d, J = 8.7 Hz, ArH), 6.71 (1H, dd, J = 8.7, 2.9 Hz, ArH), 6.49 (1H, d, J = 2.9 Hz, ArH), 6.11 (1H, br q, J = 4.8 Hz, NH), 3.67 (3H, s, OCH_3), 3.54 (1H, dd, J = 13.1, 9.4 Hz, CH), 3.43 (1H, dd, J = 9.4, 5.7 Hz, CH_2), 3.06 (1H, dd, J = 13.1, 5.7 Hz, CH_2), 2.64 (3H, d, J = 4.8 Hz, NCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 152.9, 149.8, 138.9, 128.8, 128.4, 126.5, 125.0, 119.1, 116.1, 113.9, 56.5, 55.7, 37.4, 26.5 ppm; HRMS (ESI): $[M + H]^+$, found 286.1431. $C_{17}H_{20}NO_3$ requires 286.1438.

3.24. 2-(5-Fluoro-2-hydroxyphenyl)-N-methyl-3-phenylpropanamide (**2h**)

Colorless gum; IR (film) ν_{max} 3291, 3112, 3029, 2941, 2686, 2621, 1641, 1614, 1545, 1494, 1440, 1411, 1373, 1247, 1182, 1143, 1073, 1030, 1009, 964, 944, 914, 870, 819, 786, 699 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 10.56 (1H, br, OH), 7.26–7.20 (2H, m, ArH), 7.18 (1H, tt, J = 7.0, 1.6 Hz, ArH), 7.13–7.08 (2H, m, ArH), 6.88–6.80 (2H, m, ArH), 6.63 (1H, ddd, J = 9.1, 2.3, 1.0 Hz, ArH), 6.21 (1H, br q, J = 5.2 Hz, NH), 3.55–3.42 (2H, m, CH and CH_2), 3.08 (1H, ddd, J = 15.2, 10.8, 10.8 Hz, CH_2), 2.66 (3H, d, J = 5.2 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 157.5, 155.1, 151.9 (d, J = 2 Hz), 138.5, 128.5, 127.7 (d, J = 209 Hz), 125.2 (d, J = 7 Hz), 119.2 (d, J = 8 Hz), 116.6 (d, J = 23 Hz),

115.3 (d, J = 22 Hz), 55.9, 37.4, 26.6 ppm; HRMS (ESI): $[M + H]^+$, found 274.1232. $C_{16}H_{17}FNO_2$ requires 274.1238.

3.25. 2-(5-Cyano-2-hydroxyphenyl)-N-methyl-3-phenylpropanamide (**2i**)

Colorless gum; IR (KBr) ν_{max} 3329, 3127, 3062, 3028, 2941, 2589, 2224, 1640, 1597, 1493, 1454, 1406, 1372, 1288, 1270, 1218, 1158, 1114, 1066, 1030, 914, 832, 788, 770, 699 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 12.12 (1H, s, OH), 7.45 (1H, d, J = 8.6, 2.0 Hz, ArH), 7.27–7.17 (3H, m, ArH), 7.14 (1H, d, J = 2.0 Hz, ArH), 7.10–7.06 (2H, m, ArH), 7.02 (1H, d, J = 8.6 Hz, ArH), 6.31 (1H, br q, J = 4.8 Hz, NH), 3.52 (1H, dd, J = 9.1, 6.9 Hz, CH), 3.44 (1H, dd, J = 13.2, 9.1 Hz, CH_2), 3.07 (1H, dd, J = 13.2, 6.9 Hz, CH_2), 2.71 (3H, d, J = 4.8 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 161.4, 137.8, 135.0, 133.4, 128.7, 128.6, 126.9, 125.2, 120.1, 119.6, 101.9, 56.8, 37.6, 26.6 ppm; HRMS (ESI): $[M + H]^+$, found 281.1279. $C_{17}H_{17}N_2O_2$ requires 281.1285.

3.26. 2-(2-Hydroxy-5-methylphenyl)-N-methylacetamide (**2j**)

Colorless gum; IR (KBr) ν_{max} 3288, 2942, 1636, 1611, 1554, 1510, 1411, 1356, 1266, 1214, 1169, 1113, 1059, 924, 873, 818, 769, 723, 703 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 9.58 (1H, s, OH), 6.97 (1H, d, J = 8.0, 1.8 Hz, ArH), 6.85 (1H, d, J = 8.0 Hz, ArH), 6.82 (1H, d, J = 1.8 Hz, ArH), 6.40 (1H, br, NH), 3.52 (2H, s, CH_2), 2.79 (3H, d, J = 4.4 Hz, NCH_3), 2.23 (3H, s, $ArCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 153.5, 131.0, 129.48, 129.47, 121.3, 117.5, 40.5, 26.7, 20.3 ppm; HRMS (ESI): $[M + H]^+$, found 180.1014. $C_{10}H_{14}NO_2$ requires 180.1019.

3.27. 2-(2-Hydroxy-5-methylphenyl)-N-methyl-2-phenylacetamide (**2k**)

Colorless gum; IR (KBr) ν_{max} 3302, 3111, 3059, 3026, 2941, 2920, 2600, 1638, 1607, 1540, 1499, 1451, 1410, 1375, 1253, 1221, 1160, 1121, 1101, 1078, 1055, 1032, 922, 816, 786, 757, 728, 697 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.55 (1H, s, OH), 8.20 (1H, q, J = 4.4 Hz, NH), 7.31–7.15 (5H, m, ArH), 7.00 (1H, d, J = 1.6 Hz, ArH), 6.86 (1H, dd, J = 8.0, 1.6 Hz, ArH), 6.67 (1H, d, J = 8.0 Hz, ArH), 5.09 (1H, s, CH), 2.60 (3H, d, J = 4.4 Hz, NCH_3), 2.14 (3H, s, $ArCH_3$) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.3, 154.9, 140.1, 129.6, 128.4, 128.1, 127.7, 126.4, 118.7, 115.3, 51.1, 40.0, 25.9 ppm (one overlapping peak); HRMS (ESI): $[M + H]^+$, found 256.1326. $C_{16}H_{18}NO_2$ requires 256.1332.

3.28. 2-(2-Hydroxy-3-methylphenyl)-N-methyl-3-phenylpropanamide (**2l**)

Colorless gum; IR (film) ν_{max} 3322, 3087, 3027, 2923, 2779, 2635, 1630, 1605, 1590, 1494, 1468, 1408, 1379, 1251, 1221, 1160, 1089, 1072, 1030, 998, 909, 846, 767, 745, 699 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 10.81 (1H, s, OH), 7.26–7.19 (2H, m, ArH), 7.17 (1H, tt, J = 7.2, 1.6 Hz, ArH), 7.14–7.08 (2H, m, ArH), 7.05 (1H, ddd, J = 7.2, 1.6, 0.8 Hz, ArH), 6.74 (1H, dd, J = 7.6, 1.6 Hz, ArH), 6.67 (1H, dd, J = 7.6, 7.2 Hz, ArH), 5.92 (1H, br, NH), 3.57 (1H, dd, J = 13.3, 9.9 Hz, CH), 3.41 (1H, dd, J = 9.9, 5.8 Hz, CH_2), 3.04 (1H, dd, J = 13.3, 5.8 Hz, CH_2), 2.61 (3H, d, J = 4.8 Hz, NCH_3), 2.27 (3H, s, $ArCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 154.4, 139.0, 130.5, 128.8, 128.4, 128.2, 127.6, 126.5, 123.6, 119.4, 57.5, 37.6, 26.5, 16.4 ppm; HRMS (ESI): $[M + H]^+$, found 270.1479. $C_{17}H_{20}NO_2$ requires 270.1489.

3.29. 2-(2-Hydroxy-3,4-dimethylphenyl)-N-methyl-3-phenylpropanamide (**2m**)

Colorless gum; IR (KBr) ν_{max} 3318, 3105, 3061, 3028, 2924, 2861, 2732, 1630, 1609, 1577, 1496, 1454, 1409, 1377, 1280, 1257, 1219, 1160, 1086, 1029, 983, 886, 860, 815, 790, 749, 699 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 10.72 (1H, s, OH), 7.27–7.21 (2H, m, ArH), 7.18 (1H, tt, J = 7.4, 1.4 Hz, ArH), 7.15–7.11 (2H, m, ArH), 6.64 (1H, d, J = 7.6 Hz, ArH), 6.59 (1H, d, J = 7.6 Hz, ArH), 5.73 (1H, br q, J = 4.8 Hz, NH), 3.60 (1H, dd, J = 13.4, 10.4 Hz, CH), 3.34 (1H, dd, J = 10.4, 5.6 Hz, CH_2), 3.01 (1H, dd, J = 13.4, 5.6 Hz, CH_2), 2.62 (3H, d, J = 4.8 Hz, NCH_3), 2.24 (3H, s, $ArCH_3$), 2.21 (3H, s, $ArCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 154.1, 139.2, 137.8, 128.8, 128.4, 127.1, 126.5, 126.1, 121.4, 121.1, 57.7, 37.7, 26.5, 20.1, 12.0 ppm; HRMS (ESI): $[M + H]^+$, found 284.1636. $C_{18}H_{22}NO_2$ requires 284.1645.

3.30. N-Benzyl-2-(2-hydroxyphenyl)acetamide (**2n**)

White solid, mp 113–115 °C; IR (KBr) ν_{max} 3306, 3219, 3075, 3030, 2938, 2889, 2713, 1613, 1595, 1557, 1510, 1498, 1456, 1415, 1375, 1362, 1344, 1311, 1270, 1227, 1185, 1101, 1071, 1042, 1028, 1006, 938, 923, 907, 871, 849, 824, 788, 747, 698 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 9.59 (1H, br, OH), 7.33–7.23 (3H, m, ArH), 7.23–7.18 (2H, m, ArH), 7.16 (1H, ddd, J = 7.7, 7.7, 1.4 Hz, ArH), 6.99 (1H, dd, J = 7.7, 1.4 Hz, ArH), 6.94 (1H, dd, J = 7.7, 1.4 Hz, ArH), 6.81 (1H, ddd, J = 7.7, 7.7, 1.4 Hz, ArH), 6.46 (1H, br, NH), 4.38 (2H, d, J = 5.6 Hz, NCH_2), 3.56 (2H, s, CH_2CO) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 155.9, 137.1, 130.5, 129.1, 128.8, 127.75, 127.73, 121.4, 120.4, 117.8, 44.0, 40.7 ppm; HRMS (ESI): $[M + H]^+$, found 242.1171. $C_{15}H_{16}NO_2$ requires 242.1176.

3.31. 2-(2-Hydroxyphenyl)-N-(1-phenylethyl)acetamide (**2o**)

Colorless gum; IR (KBr) ν_{max} 3351, 3066, 3033, 2973, 2927, 2870, 1624, 1596, 1535, 1495, 1455, 1409, 1362, 1347, 1263, 1233, 1178, 1153, 1131, 1098, 1073, 1039, 1013, 954, 926, 910, 864, 846, 789, 749, 698 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 9.83 (1H, br, OH), 7.31–7.20 (5H, m, ArH), 7.14 (1H, ddd, J = 7.6, 7.6, 1.4 Hz, ArH), 6.98 (1H, dd, J = 7.6, 1.4 Hz, ArH), 6.92 (1H, dd, J = 7.6, 1.4 Hz, ArH), 6.80 (1H, ddd, J = 7.6, 7.6, 1.4 Hz, ArH), 6.69 (1H, br d, J = 6.8 Hz, NH), 5.04 (1H dq, J = 6.8, 6.8 Hz, NCH), 3.55 (1H, d, J = 6.4 Hz, CH_2), 3.50 (1H, d, J = 6.4 Hz, CH_2), 1.44 (3H, d, J = 6.8 Hz, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 155.8, 142.3, 130.6, 129.0, 128.7, 127.5, 126.0, 121.5, 120.3, 117.6, 49.4, 40.7, 21.6 ppm; HRMS (ESI): $[M + H]^+$, found 256.1325. $C_{16}H_{18}NO_2$ requires 256.1332.

3.32. 2-(2-Hydroxyphenyl)-N-methyl-2-phenylpropanamide (**2p**)

White solid, mp 53–57 °C; IR (KBr) ν_{max} 3360, 3060, 3026, 2984, 2941, 1805, 1632, 1599, 1534, 1493, 1463, 1447, 1407, 1381, 1292, 1245, 1208, 1187, 1159, 1129, 1112, 1080, 1031, 1015, 888, 854, 822, 787, 755, 699 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) δ 10.31 (1H, s, OH), 7.69 (1H, br, NH), 7.30 (1H, dd, J = 8.0, 1.2 Hz, ArH), 7.27–7.16 (4H, m, ArH), 7.09–7.04 (2H, m, ArH), 6.88 (1H, dd, J = 8.0, 1.2 Hz, ArH), 6.86 (1H, dd, J = 8.0, 1.2 Hz, ArH), 6.80 (1H, dd, J = 8.0, 1.2 Hz, ArH), 2.83 (3H, d, J = 4.8 Hz, NCH_3), 1.88 (3H, s, 3-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 156.8, 144.6, 129.5, 128.4, 127.4, 127.0, 126.6, 119.7, 119.6, 55.3, 27.6, 27.2 ppm (one overlapping peak); HRMS (ESI): $[M + H]^+$, found 256.1327. $C_{16}H_{18}NO_2$ requires 256.1332.

3.33. Cyclization of **2a** into 3-benzylbenzofuran-2(3H)-one (**7a**)

A solution of **2a** (253 mg, 0.991 mmol) in benzene (22 mL) was treated with a 1 M HCl aq. (2.2 mL) and the mixture was refluxed for 2 days. The resulting mixture was cooled to room temperature, treated with saturated aq. NH_4Cl, and extracted with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and evaporated. The residue was purified by chromatography on silica gel (*n*-hexane/

EtOAc = 15/1 to 10/1 as the eluent) to afford **7a** (189 mg, 85% yield) as a white solid, mp 55–57 °C. IR (KBr) ν_{max} 3082, 3060, 3028, 2932, 2916, 2885, 1799, 1620, 1600, 1495, 1478, 1462, 1444, 1336, 1324, 1295, 1229, 1174, 1155, 1123, 1080, 1061, 1032, 1016, 988, 960, 941, 923, 889, 873, 812, 753, 710, 699 cm^{-1}; ^1H NMR (400 MHz, $CDC1_3$) δ 7.32–7.21 (4H, m, ArH), 7.18–7.13 (2H, m, ArH), 7.05–6.99 (1H, m, ArH), 7.03 (1H, d, J = 8.0 Hz, ArH), 6.82–6.77 (1H, m, ArH), 4.00 (1H, dd, J = 9.2, 4.8 Hz, 3-H), 3.50 (1H, dd, J = 13.8, 4.8 Hz, CH_2Ph), 3.03 (1H, dd, J = 13.8, 9.2 Hz, CH_2Ph) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 153.6, 136.6, 129.3, 128.8, 128.5, 127.1, 126.6, 124.8, 123.8, 110.6, 44.9, 37.1 ppm; HRMS (ESI): $[M + H]^+$, found 225.0909. $C_{15}H_{13}O_2$ requires 255.0910.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2018.12.058.

References

[1] For a review: T.J. Snape, in: J. Mortier (Ed.), Arene Chemistry: Reaction Mechanisms and Methods for Aromatic Compounds, Wiley, 2016, pp. 485–510. Chap. 18.

[2] For reviews: (a) C.C.C. Johansson, T.J. Colacot, Angew. Chem. Int. Ed. 49 (2010) 676–707;
(b) D.A. Culkin, J.F. Hartwig, Acc. Chem. Res. 36 (2003) 234–245.

[3] For reviews: (a) B. Robinson, Chem. Rev. 69 (1969) 227–250;
(b) B. Robinson, Chem. Rev. 63 (1963) 373–401.

[4] Recent examples of aromatic sigmatoropic rearrangements involving N–N bond cleavage: (a) T.J. Seguin, T. Lu, S.E. Wheeler, Org. Lett. 17 (2015) 3066–3069;
(b) S. Huang, L. Kötzner, C.K. De, B. List, J. Am. Chem. Soc. 137 (2015) 3446–3449;
(c) L. Kötzner, M.J. Webber, A. Martínez, C.D. Fusco, B. List, Angew. Chem. Int. Ed. 53 (2014) 5202–5205;
(d) C.K. De, F. Pesciaioli, B. List, Angew. Chem. Int. Ed. 52 (2013) 9293–9295;
(e) G. Li, H. Gao, C. Keene, M. Devonas, D.H. Ess, L. Kürti, J. Am. Chem. Soc. 135 (2013) 7414–7417;
(f) A. Martínez, M.J. Webber, S. Müller, B. List, Angew. Chem. Int. Ed. 52 (2013) 9486–9490.

[5] For a review of aromatic sigmatoropic rearrangements involving N–O bond cleavage: A.A. Tabolin, S.L. Ioffe Chem. Rev. 114 (2014) 5426–5476.

[6] Recent examples of aromatic sigmatoropic rearrangements involving N–O bond cleavage: (a) S. Shaaban, V. Tona, B. Peng, N. Maulide, Angew. Chem. Int. Ed. 56 (2017) 10938–10941;
(b) T. Tomakinian, C. Kouklovsky, G. Vincent, Synlett 26 (2015) 1269–1275;
(c) H. Gao, Q. Xu, C. Keene, L. Kürti 20 (2014) 8883–8887;
(d) N. Takeda, M. Ueda, S. Kagehira, H. Komei, N. Tohnai, M. Miyata, T. Naito, O. Miyata, Org. Lett. 15 (2013) 4382–4385;
(e) H. Wang, L.L. Anderson, Org. Lett. 15 (2013) 3362–3365;
(f) H. Gao, D.H. Ess, M. Yousufuddin, L. Kürti, J. Am. Chem. Soc. 135 (2013) 7086–7089.

[7] Aromatic sigmatoropic rearrangements involving heteroatom–heteroatom bond cleavage. A review: (a) T. Yanagi, K. Nogi, H. Yorimitsu, Tetrahedron Lett. 59 (2018) 2951–2959. See also recent examples:;
(b) L.L. Baldassari, A.C. Mantovani, S. Senoner, B. Maryasin, N. Maulide, D.S. Lüdtke, Org. Lett. 20 (2018) 5881–5885;
(c) L. Shang, Y. Chang, F. Luo, J. He, X. Huang, L. Zhang, L. Kong, K. Li, B. Peng, J. Am. Chem. Soc. 139 (2017) 4211–4217;
(d) D. Kaldre, B. Maryasin, D. Kaiser, O. Gajsek, L. González, N. Maulide, Angew. Chem. Int. Ed. 56 (2017) 2212–2215.

[8] Y. Endo, T. Uchida, K. Shudo, Tetrahedron Lett. 38 (1997) 2113–2116.

[9] (a) Y. Endo, T. Uchida, S. Hizatate, K. Shudo, Synthesis (1994) 1096–1105;
(b) Y. Endo, S. Hizatate, K. Shudo, Tetrahedron Lett. 32 (1991) 2803–2806. See also the related works reported by other groups:;
(c) N. Duguet, A.M.Z. Slawin, A.D. Smith, Org. Lett. 11 (2009) 3858–3861;
(d) Z. Mao, S.W. Baldwin, Org. Lett. 6 (2004) 2425–2428;
(e) P.S. Almeida, S. Prabhakar, A.M. Lobo, M.J. Marcelo-Curto, Tetrahedron Lett. 32 (1991) 2671–2674.

[10] Y. Endo, K. Namikawa, K. Shudo, Tetrahedron Lett. 27 (1986) 4209–4212. The related works: see ref. 5.

[11] Representative examples: (a) Y. Wu, Z. Chen, Y. Yang, W. Zhu, B. Zhou, J. Am. Chem. Soc. 140 (2018) 42–45;
(b) Y. Li, Y. Tang, X. He, D. Shi, J. Wu, S. Xu, Chem. Eur. J. 23 (2017) 7453–7457;
(c) X. Wang, A. Lerchen, T. Gensch, T. Knecht, C.G. Daniliuc, F. Glorius, Angew. Chem. Int. Ed. 56 (2017) 1381–1384;
(d) J. Davies, T.D. Svejstrup, D.F. Reina, N.S. Sheikh, D. Leonori, J. Am. Chem. Soc. 138 (2016) 8092–8095;
(e) P. Duan, Y. Yang, R. Ben, Y. Yan, L. Dai, M. Hong, Y. Wu, D. Wang, X. Zhang, J. Zhao, Chem. Sci. 5 (2014) 1574–1578;
(f) Y. Shen, G. Liu, Z. Zhou, X. Lu, Org. Lett. 15 (2013) 3366–3369.

[12] The yields reported previously: see ref. 11d–f.

[13] For a review: Y. Jiao, X. Ma, G. Su, D. Mo Synthesis 49 (2017) 933–959.

[14] G.E. Keck, T.T. Wager, S.F. McHardy, Tetrahedron 55 (1999) 11755–11772.

[15] M.A.J. Miah, M.P. Sibi, S. Chattopadhyay, O.B. Familoni, V. Snieckus, Eur. J. Org. Chem. (2018) 440–446.

[16] Recent examples of synthesis of 3-substituted benzofuran-2(3*H*)-one derivatives: (a) H. Li, H. Ai, J. Qi, J. Peng, X. Wu, Org. Biomol. Chem. 15 (2017) 1343–1345;
(b) H. Wang, B. Dong, Y. Wang, J. Li, Y. Shi, Org. Lett. 16 (2014) 186–189.

[17] To demonstrate advantage of our reaction system, we examined an acid-mediated [3,3] rearrangement of **1a** (TFA, 0 °C to rt, 3 h) according to the previous work (ref. 10). The reaction gave a complicated mixture. The desired [3,3] rearranged **2a** and cyclized **7a** were not obtained.