A Novel Synthetic Route to 2-Arylalkanoic Acids by a Ruthenium-Catalyzed Chemoselective Oxidation of Furan Rings

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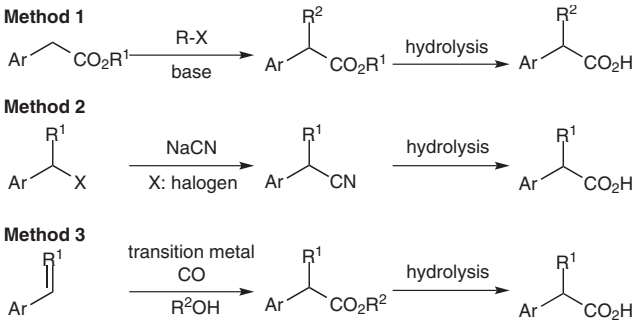
Abstract: An efficient two-step synthesis of 2-arylalkanoic acids from 1-arylalkanols is described. Firstly, 1-arylalkylfuran derivatives were synthesized in high yields by the metal triflate catalyzed Friedel–Crafts alkylation of 2-methylfuran with 1-arylalkanols without employing anhydrous conditions. The chemoselective oxidation of the furan ring in 1-arylalkylfurans to carboxylic acid was then investigated. In a solvent system of hexane–EtOAc/H_2O (1:3:4), the furan ring was selectively oxidized with 7 equivalents of $NaIO_4$ by using 0.5 mol% $RuCl_3$ as catalyst to give 2-arylalkanoic acids in good yields. The selectivity of ruthenium oxidation was controlled by the solvent ratio of hexane–EtOAc.

Key words: Friedel–Crafts alkylation, 1-arylalkylfurans, ruthenium tetroxide, chemoselective oxidation, carboxylic acids

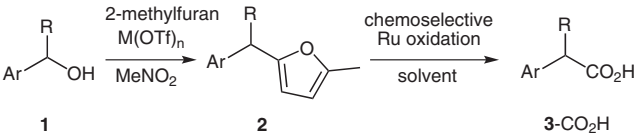
2-Arylalkanoic acids are known to be a very important class of nonsteroidal anti-inflammatory agents, and many synthetic methods have been reported.[1] The alkylation of aryl acetates is the most direct synthetic method though the starting compounds are not widely available (Scheme 1, Method 1). The introduction of a carboxylic group is also achieved by the reaction of CN^- or CO, which are extremely hazardous reagents, with halides or olefins (Scheme 1, Methods 2 and 3).

We have recently developed a metal triflate catalyzed Friedel–Crafts-type benzylation system.[2] This method provides a variety of 1-arylalkylfuran derivatives **2** from readily and commercially available 1-arylalkanols **1**. Chemoselective oxidation of furan ring in **2** over an aromatic ring was expected to be a useful synthetic method for 2-arylalkanoic acids **3**-CO_2H. (Scheme 2)

Sharpless and co-workers reported an efficient ruthenium oxidation system using a catalytic amount of ruthenium salt and several equivalents of $NaIO_4$ in CCl_4–MeCN–H_2O,[3] and this procedure effectively oxidized alcohols, olefins, and benzene rings.[4] For the synthesis of carboxylic acids, ruthenium catalyzed oxidation of aromatic rings is a very useful method.[5] Especially, furan derivatives are extensively employed as a precursor of carboxylic acids.[6] However, the substrates for the ruthenium oxidation have been limited to furans bearing nonaromatic substituents or bearing electron-deficient, relatively inert, aromatic groups.



Scheme 1 Synthetic methods for 2-arylalkanoic acids



Scheme 2 RuO_4-catalyzed chemoselective oxidation of furan rings

Chemoselective oxidation of alcohols,[7] benzene rings,[8] and olefins[9] over benzene rings were observed only in some cases. In addition, only a few examples were known for the chemoselective oxidation of a furan ring over a benzene ring.[10]

In contrast, chemoselective oxidations of olefins have been studied more often than aromatic compounds. These investigations are categorized into three approaches: the addition of ligands,[11] selection of a co-oxidant,[12] and selection of a reaction solvent.[13]

Improvement of the solvent system for the aromatic ring oxidation was also reported in the noncompetitive case. A halogen-free solvent system, EtOAc–MeCN–H_2O, has been used for a benzene ring oxidation.[14] In some cases, a simple EtOAc/H_2O solvent system is better than the CCl_4–MeCN–H_2O solvent system for the oxidation of a benzene ring.[15]

In this work, various types of new 1-arylalkylfurans **2** were synthesized from 1-arylalkanols **1** with 2-methylfuran. And the chemoselective oxidation of furan rings was examined with the aim to lower the environmental impact of the oxidation reaction by a solvent approach.

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Synthesis of Furan Derivatives

The reactions of 1-arylalkanols **1** and 2-methylfuran were performed using 0.5 mol% of La, Yb, Sc, and Hf trifluoromethanesulfonates[16] at 20, 40, and 60 °C in $MeNO_2$. The optimization of the reaction conditions was easily attained through catalyst-temperature screening experiments.[17] The results of the reactions of 1-phenylcyclohexanol (**1a**) and 2-methylfuran to give **2a** are summarized in Table 1. The reaction at 20 °C gave tertiary-alkylated furan **2a** in moderate yields with the recovery of the starting alcohol **1a**. The best yield of **2a** (96%) was obtained in the $Yb(OTf)_3$-catalyzed reaction at 40 °C.

A considerable amount of 1-phenylcyclohexene was obtained in the $Hf(OTf)_4$-catalyzed reaction at 60 °C via the decomposition of the benzylic cation.

The generality of this benzylation of 2-methylfuran was subsequently explored with a variety of benzylic alcohols **1a–r**. The results are summarized in Table 2. Tertiary alcohols **1b** and **1k** were highly reactive, and the mild reaction conditions were better to prevent the formation of olefinic by-products. The formation of dimerized ether derivatives[2] was not observed for the reaction of tertiary alcohols. The electron-donating alkoxy groups in **1d**, **1e**, **1m**, and **1o** efficiently increased the yields. Primary benzylic protecting groups, BnO and CbzNH, were stable during the reaction. Electron-deficient 4-chloro derivative **1i** was considerably less reactive than the alkyl derivative **1g**, and the addition of $Mg(ClO_4)_2$ was effective in increasing the yield. However, the $Hf(OTf)_4$-catalyzed reaction at 60 °C without $Mg(ClO_4)_2$ gave **2i** in only 24% without recovery of **1i**.

The addition of such an inorganic salt increases the ionic strength of the reaction medium and could stabilize[18] the benzylic cation. The addition of $Mg(ClO_4)_2$ was also effective for the reaction of **1g**, **1l**, **1n**.

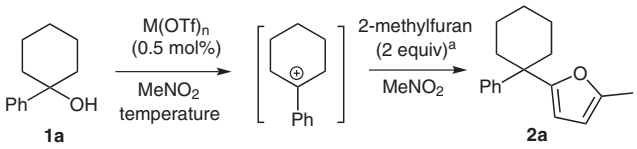
The reaction of (*S*)-ferrocenylethanol (**1r**, 100% ee) gave the desired furan derivative (*S*)-**2r** in 93% yield and 100% ee. 1-Ferrocenylethyl cations are known to be rotationally stable, and the substitution reaction of a leaving group of 1-ferrocenylethyl compounds occur with the retention of configuration in many cases.[19]

The reuse of the catalyst was examined with **1a** under the optimized reaction conditions [$Yb(OTf)_3$, 40 °C]. The catalyst was recycled by extraction with water from the reaction mixture. In the first run, **2a** was isolated in 97% yield, and the yields of the second and third runs were 96% and 94%, respectively.

Chemoselective Oxidation of the Furan Ring

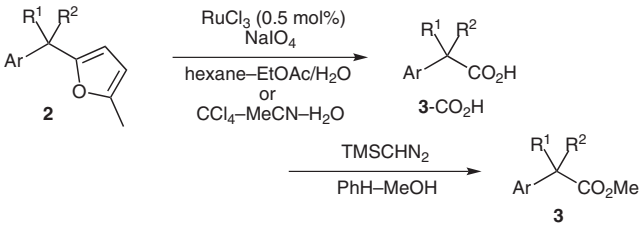
A furan ring is more electron-rich than the majority of the alkyl-substituted benzenes and naphthalenes. The chemoselective oxidation of a furan ring may be possible with the careful tuning of the oxidation conditions. To control the reactivity of active ruthenium species, we employed a hexane–EtOAc/H_2O solvent system with variable ratios. The addition of less polar hexane may decrease the rate of the oxidation, and slower oxidation may increase the selectivity of the oxidation reaction. The reaction is outlined in Scheme 3.

Table 1 Reactions of **1a** with 2-Methylfuran



Temp (°C)	Time (h)	GC yield of **2a** (%) La	Yb	Sc	Hf
20	24	45	56	63	67
40	13	92	**96**	81 (1 h)	77 (1 h)
60	1.5	94	94	75 (0.5 h)	65 (0.5 h)

[a] The use of 2 equiv of 2-methylfuran was better suited for the reproducibility of the chemical yields because of the low boiling point of 2-methylfuran.



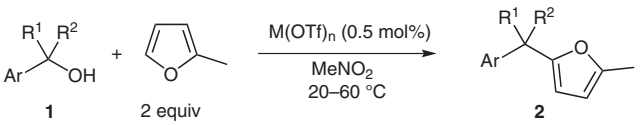
Scheme 3 Ruthenium-catalyzed chemoselective oxidation of furan derivatives

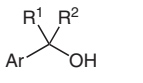
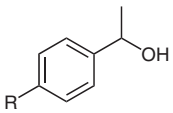
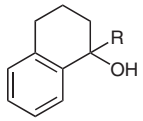
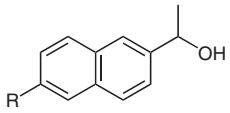
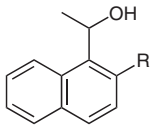
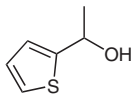
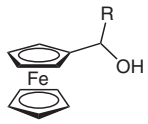
The furan derivative **2** was dissolved in hexane–EtOAc or CCl_4–MeCN, and 0.25 mol/L of $NaIO_4$ solution in water was added. After stirring the mixture at 20 °C for 5–10 min, 0.1 mol/L of $RuCl_3$ solution in water was added, and the mixture vigorously stirred at 20 °C for 24 hours. After the extraction of the carboxylic acid with EtOAc, esterification with trimethylsilyldiazomethane ($TMSCHN_2$) gave the desired ester **3**.

Examination of the Solvent Ratio of Hexane–EtOAc

First, we examined the chemoselective oxidation of **2m** that had the 2-methylfuran and 2-methoxynaphthalene moieties. This compound is a challenging substrate because **2m** has a large electron-rich aromatic ring, and the desired product **3m**-CO_2H is one of the pharmaceutically important classes of nonsteroidal anti-inflammatory agents,[20] naproxen. The oxidation was performed with 7 equivalents of $NaIO_4$ using 0.5 mol% of $RuCl_3$ as catalyst in a two-phase system of hexane–EtOAc/H_2O at 20 °C.

Table 2 Reaction of 1-Arylalkanols **1** with 2-Methylfuran



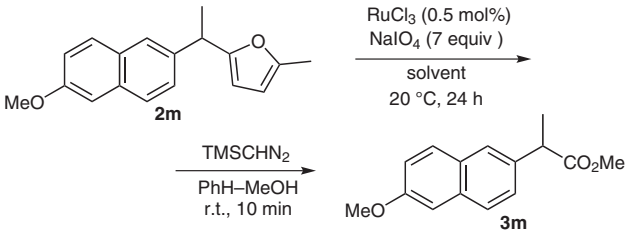
		R	Catalyst 0.5 mol%	Temp (°C)	Time (h)		Yield (%)[a]
	**1a**	R^1, R^2 = -$(CH_2)_5$-	$Yb(OTf)_3$	40	14	**2a**	97
	1b	R^1 = R^2 = Me	$Yb(OTf)_3$	60	2	**2b**	99
	1c	R^1 = H, R^2 = Ph	$Sc(OTf)_3$	60	0.5	**2c**	93
	**1d**	MeO	$Yb(OTf)_3$	40	23	**2d**	95
	1e	BnO	$Yb(OTf)_3$	60	0.08	**2e**	99[b]
	1f	CbzNH	$La(OTf)_3$	40	9	**2f**	93
	1g	Me	$Yb(OTf)_3$[c]	40	1	**2g**	90 (78)[d]
	1h	Ph	$Hf(OTf)_4$	60	1	**2h**	91
	1i	Cl	$Yb(OTf)_3$[c]	40	24	**2i**	58 + 5[e] (47 + 4[e])[d]
	**1j**	H	$La(OTf)_3$	60	0.75	**2j**	99
	1k	Me	$Sc(OTf)_3$	20	0.33	**2k**	93
	**1l**	H	$Yb(OTf)_3$[c]	40	0.5	**2l**	84 (75)[f]
	1m	MeO	$Yb(OTf)_3$	20	4	**2m**	99
	**1n**	H	$Yb(OTf)_3$[c]	40	0.5	**2n**	88 (75)[f]
	1o	MeO	$Sc(OTf)_3$	20	2	**2o**	91
	**1p**	–	$Hf(OTf)_4$	20	0.5	**2p**	84
	**1q**	H	$Hf(OTf)_4$[g]	20	0.5	**2q**	79
	1r	Me	$La(OTf)_3$[g]	20	0.17	**2r**	94
	(*S*)-**1r**[h]	Me	$La(OTf)_3$[g]	20	0.5	(*S*)-**2r**[h]	93

[a] Isolated yield.
[b] GC yield.
[c] $Mg(ClO_4)_2$ (0.2 equiv) was added.
[d] $Yb(OTf)_3$, 60 °C, without $Mg(ClO_4)_2$.
[e] A regioisomer was obtained.
[f] $La(OTf)_3$, 60 °C, without $Mg(ClO_4)_2$.
[g] One mol% of catalyst was used.
[h] 100% ee.

The reaction in the conventional CCl_4–MeCN–H_2O (2:2:3) solvent system gave **3m** in only 20% yield, and **2m** was recovered in 12%. This result indicates that the oxidation was nonselective, and not only the furan ring but also the naphthalene ring also consumed $NaIO_4$. The best solvent system for the oxidation of **2m** was hexane–EtOAc/H_2O (1:3:4), and the yield of **3m** was 65%. The addition of an excess amount of hexane decreased the yields, and 12% of **2m** was recovered in the reaction using the hexane–EtOAc/H_2O (3:1:4) system (Table 3).

The oxidation of **2m** with $KBrO_3$, NaOCl, H_2O_2, and *t*-BuOOH was also examined in hexane–EtOAc/H_2O (1:3:4). In the reaction with $KBrO_3$, NaOCl, and *t*-BuOOH, more than 90% of **2m** disappeared, but the yields of **3m** were less than 5%. And 88% of **2m** was recovered in the reaction with H_2O_2. Interestingly, the reaction of **2m** with *t*-BuOOH gave 6-methoxy-2-acenaphthone, a methylketone-type degradation product,[21] as the main product in 25% yield. This degradation might have occurred via the C–H oxidation of **2m**.[22]

Table 3 Oxidation of **2m** in Hexane–EtOAc/H_2O or CCl_4–MeCN–H_2O



Solvent	hexane–EtOAc/H_2O				CCl_4–MeCN–H_2O
Ratio	3:1:4	2:2:4	1:3:4	0:4:4	2:2:3
Yield (%)[a]	15	58	**65**	46	20

[a] GC yield.

Examination of the Equivalents of $NaIO_4$

Next, we investigated the requirement of $NaIO_4$ equivalents for the oxidative conversion of a furan ring to a carboxylic acid. To accurately estimate the requirement of $NaIO_4$, we used the compound **2j** with a less electron-rich aromatic ring that was expected to have a better chemoselectivity than **2m**. After the optimization of the solvent ratio to hexane–EtOAc/H_2O (1:3:4) for **2j**, 1–8 mol equivalents of $NaIO_4$ was examined for the oxidation reaction (Table 4).

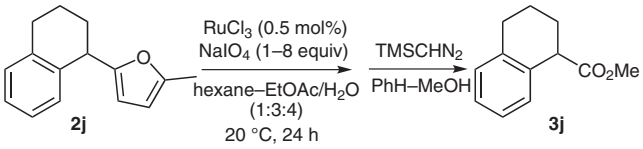
The yields of the desired product **3j** increased from 7 to 86% as the amount of $NaIO_4$ was increased from 1 to 6 mol equivalents. Although the starting compound **2j** almost disappeared when 5 mol equivalents of $NaIO_4$ was used, the best yield was observed for more than 6 mol equivalents of $NaIO_4$. These results indicated that the net requirement of $NaIO_4$ for the oxidative conversion of the furan ring to the carboxylic acid would be 6 mol equivalents.

The pH of the aqueous phase of the reaction mixture was slightly acidic (pH 3–4). The hydrolysis of ethyl acetate could have occurred during the reaction, and the generated ethanol consumes $NaIO_4$.[23] In addition, the consumption of $NaIO_4$ by the nonselective oxidation was also considered. We chose 7 mol equivalents of $NaIO_4$ and examined the oxidation of furan derivatives **2**. The results are summarized in Table 5.

The optimization of the solvent ratio of hexane–EtOAc/H_2O was attained for all furan derivatives **2a**–**r**, and the best solvent ratio and the best yield are indicated in Table 5. The yield data of the oxidation reaction in the CCl_4–MeCN–H_2O (2:2:3) solvent system are also shown for comparison.

The desired 2-arylalkanoic acid esters **3a**–**p** were obtained in moderate to good yields both in the hexane–EtOAc/H_2O and CCl_4–MeCN–H_2O systems. In all the productive cases, the yields of the oxidation of **2a**–**p** in the hexane–EtOAc/H_2O system giving **3a**–**p** were better than those in

Table 4 $NaIO_4$ Equivalents for Furan Ring Oxidation



$NaIO_4$ (equiv)	1	2	3	4	5	6	7	8
Yield of **3j** (%)[a]	7	22	35	53	80	86	85	86
Recovery of **2j** (%)	92	70	44	20	1	0	0	0

[a] GC yield.

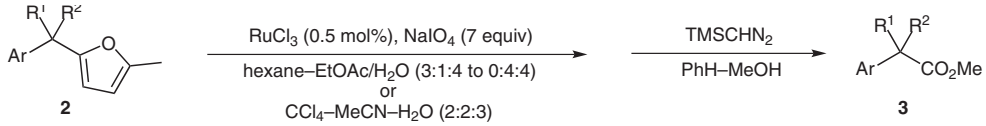
the CCl_4–MeCN–H_2O system. In the majority of the cases, the best solvent ratio was hexane–EtOAc/H_2O (1:3:4). The oxidation of **2a**, **2b**, and **2k**, which have quaternary carbons, proceeded smoothly, and the best yields were obtained for the solvent ratio of hexane–EtOAc/H_2O (2:2:4). This solvent ratio was also effective for the oxidation of unsubstituted naphthalene derivatives (**2l** and **2n**). A marked difference in the solvent effect was observed for the oxidation of electron-rich naphthalene derivatives **2m** and **2o** and thienyl derivative **2p**. The selective oxidation of **2o** was difficult even with the use of 6 or 7 mol equivalents of $NaIO_4$. A methoxy group at the *ortho* position might have inhibited the catalytic cycle, because 22% of **2o** was recovered under the reaction using 7 equivalents of $NaIO_4$. The ferrocene ring reacted more rapidly than the furan ring under the reaction conditions. The nonselective oxidation reaction consumed a considerable amount of $NaIO_4$, and **2q** and **2r** were recovered.

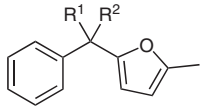
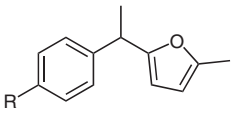
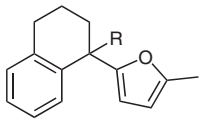
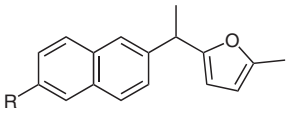
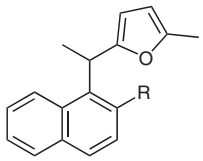
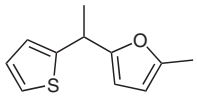
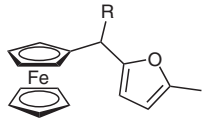
Ruthenium tetroxide is known to oxidize a methylene group at the alpha position of a heteroatom.[3,24] Benzyl ethers are additionally sensitive to oxidation under the conditions employed by Sharpless than the benzene rings. In our case, the BnO and CbzNH moieties of **2e** and **2f** were stable, and the furan ring was chemoselectively oxidized[25] under the reaction conditions.

The origin of chemoselectivity can be rationalized by considering the solubility of the products. After a more electron-rich furan ring is predominantly oxidized, the generated carboxylic acid shifts into an aqueous phase.[26] Ruthenium tetroxide is soluble in the organic phase. In our solvent system, the oxidation would occur in the hexane–EtOAc phase. The solubility of the carboxylic acid can be controlled by the ratio of hexane–EtOAc. The hexane-rich solvent is preferred for the migration of the carboxylic acid to the aqueous phase, but it reduces the concentration of ruthenium tetroxide in the organic phase. In the Sharpless procedure, a more polar MeCN solvent helps the inactive ruthenium-carboxylate complex return to the catalytic cycle. A considerably more polar dimethylformamide was also been employed for the same reason.[27] Therefore, the rate of oxidation in the less polar hexane-rich solvent decreases, and a considerable amount of the starting material was recovered in our case.

In summary, various types of 1-arylalkylfurans **2** were easily synthesized in high yields from secondary and ter-

Table 5 Ruthenium-Oxidation of Furan Derivatives **2**



		R		hexane–EtOAc/H_2O		CCl_4–MeCN–H_2O (2:2:3)
				Ratio	Yield (%)[a]	Yield (%)[a]
	**2a**	R^1, R^2 = -$(CH_2)_5$-	**3a**	2:2:4	**81**	60
	2b	R^1 = R^2 = Me	**3b**	2:2:4	**88**	65
	2c	R^1 = H, R^2 = Ph	**3c**	1:3:4	**87**	80
	**2d**	MeO	**3d**	1:3:4	**92**	87
	2e	BnO	**3e**	1:3:4	**96**	86
	2f	CbzNH	**3f**	1:3:4	**86**	85
	2g	Me	**3g**	1:3:4	**74**	68
	2h	Ph	**3h**	1:3:4	**89**	78
	2i	Cl	**3i**	2:2:4	**77**	71
	**2j**	H	**3j**	1:3:4	**85**	73
	2k	Me	**3k**	2:2:4	**90**	59
	**2l**	H	**3l**	2:2:4	**80**	51
	2m	MeO	**3m**	1:3:4	**65**	21
	**2n**	H	**3n**	2:2:4	**88**	70
	2o	MeO	**3o**	2:2:4	**27**[b]	8
	**2p**	–	**3p**	0:4:4	**51**	11
	**2q**	H	**3q**	3:1:4 – 0:4:4	**0**	0
	2r	Me	**3r**		**0**	0

[a] GC yield.
[b] Isolated yield.

tiary arylalkanols **1** by a metal triflate catalyzed Friedel–Crafts reaction with 2-methylfuran. The furan derivatives **2** were chemoselectively oxidized into arylalkanoic acid derivatives **3** by the $RuCl_3$–$NaIO_4$ catalytic system in hexane–EtOAc/H_2O. The chemoselectivity of the ruthenium oxidation was controlled by the hexane–EtOAc ratio. The ratio of hexane–EtOAc can be easily optimized for various types of arylalkylfuran derivatives, and in the majority of the cases, the best ratio was hexane–EtOAc/H_2O = 1:3:4. This procedure can be a good alternative to the conventional CCl_4–MeCN–H_2O solvent system for furan ring oxidation in view of the yields and environmental requirements.

Melting points were measured on a Yanako MP-J3 melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Jeol JNM-AL400 and JNM-AL300 spectrometers in $CDCl_3$. IR spectra were recorded on Hitachi 260-10 and Jasco FT/IR 4100 spectrometers. Low- and high-resolution mass spectra (LRMS, GC-LRMS, HRMS, and GC-HRMS) were measured with a JMS-700 mass spectrometer. Optical rotation was measured on a Jasco P-1020 polarimeter. High performance liquid chromatography (HPLC) was carried out with a Jasco PU-2089 pump equipped

with a Jasco UV-2075 and JASCO CD-2095 spectrophotometer. GC analysis was performed with a Shimadzu GC-14A, GC-2014 (flame ionization detection) with Phenomenex ZB-1 (100% methylpolysiloxane, 30 m length, 0.25 mm inner diameter, 0.50 mm film thickness). Elemental analyses were done with a Yanako CHN Corder MT-6, PerkinElmer Model 240B elemental analyzer. Preparative TLC was performed on Wakogel B5-F. Column chromatography was performed on silica gel 60 (40–50 mm, Kanto Chemical). For analytical TLC, precoated F_{254} silica gel 60 plates (Merck) were used. $RuCl_3$ was purchased from Wako Pure Chemical Industries. The syntheses of **1e**, **1k**, **1m**, **1o**, **1p**, **2j**, **2k**, **2l**, **2m**, **2o**, and **2p** are reported in the literature.[2]

Optimizing Reaction Conditions; Typical Procedure Using 1-Phenylcyclohexanol (1a)

A nitromethane solution (10 mL) of 1-phenylcyclohexanol (**1a**; 1.772 g, 10.05 mmol, 1.005 mol/L) and nitrohexane (339 mg, 2.59 mmol, as an internal standard, 0.2–0.4 mol/L) was prepared. The solution was mixed with catalysts and 2-methylfuran in 20 mL test tubes equipped with glass stoppers as follows at 20 °C: 2.5 mg of $La(OTf)_3$, 832 μL of the solution, and 151 μL of 2-methylfuran; 2.1 mg of $Yb(OTf)_3$, 680 μL of the solution, and 123 μL of 2-methylfuran; 2.1 mg of $Sc(OTf)_3$, 861 μL of the solution, and 156 μL of 2-methylfuran; 2.7 mg of $Hf(OTf)_4$, 698 μL of the solution, and 127 μL of 2-methylfuran. The reactions at 40 and 60 °C were carried out in the same manner. The mixtures in the test tubes were stirred at the corresponding temperatures. The reactions were followed by TLC. After the complete consumption of **1a** (and the symmetrical ethers for secondary benzylic alcohols), 35 μL of the reaction mixture was filtered through a short silica gel pad with 1 mL of EtOAc to remove insoluble materials. The filtrates were analyzed by GC and GC-MS. The programmed GC analysis temperature condition was 150 °C for 2 min, 10 °C/min, and 260 °C for 17 min. The yields were determined using the calibration line prepared from nitrohexane and **2a** using GC.

Reuse of the Catalyst; Typical Procedure for 2-Methyl-5-(1-phenylcyclohexyl)furan (2a)

To a mixture of $Yb(OTf)_3$ (10.5 mg, 17.0 μmol) and **1a** (621 mg, 3.52 mmol) in $MeNO_2$ (3.52 mL) was added 2-methylfuran (635 μL, 7.03 mmol) at r.t. The resulting mixture was stirred at 40 °C for 14 h using a Dimroth condenser with a rubber balloon stopper. After cooling to r.t., the $Yb(OTf)_3$ catalyst was extracted with H_2O (6 × 3 mL) (upper phase) from the reaction mixture of $MeNO_2$ solution (lower phase). When the phase separation became difficult, a small amount of $CHCl_3$ was added. The trace amount of contaminated $MeNO_2$ in the aqueous phase was extracted with EtOAc (2 × 5 mL) and combined with the $MeNO_2$ layer. The combined organic layers were concentrated under reduced pressure, and the resulting oil was purified by column chromatography (silica gel, hexane–EtOAc, 20:1) to afford **2a** (817 mg, 97%) as colorless needles; mp 38–41 °C; R_f = 0.53 (hexane–EtOAc, 4:1).

IR (neat): 2910, 2850, 1600, 1550, 1490, 1450, 1220, 1120, 1020, 970, 780, 750, 700 cm^{-1}.

^1H NMR (400 MHz): δ = 7.29–7.13 (5 H, m), 5.94 (1 H, d, J =3.2 Hz), 5.88–5.87 (1 H, m), 2.33–2.28 (2 H, m), 2.22 (3 H, s), 2.05–1.99 (2 H, m), 1.60–1.35 (6 H, m).

^{13}C NMR (100 MHz): δ = 158.1, 150.1, 147.7, 128.0, 126.2, 125.6, 106.7, 105.6, 44.4, 35.9, 26.2, 23.1, 13.7.

MS (EI, 70 eV): m/z (%) = 240 (M^+, 97), 184 (20), 171 (25), 155 (10), 141 (11), 115 (13).

HRMS-EI: m/z calcd for $C_{17}H_{20}O$ $[M]^+$: 240.1514; found: 240.1516.

Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 85.24; H, 8.64.

The aqueous extract was concentrated under a reduced pressure and dried under vacuum (1 Torr) at r.t. for 10 min and then heated for 3 min using a heating gun at ca. 200 °C to give a white to light-brown crystalline $Yb(OTf)_3$ catalyst. The catalyst was used for the next run. For the second run, **1a** (612 mg, 3.48 mmol), $MeNO_2$ (3.48 mL) and 2-methylfuran (627 μL, 6.95 mmol) were stirred at 40 °C for 14 h. After chromatographic purification, 802 mg of **2a** (96%) was obtained. For the third run, **1a** (626 mg, 3.55 mmol), $MeNO_2$ (3.40 mL), and 2-methylfuran (641 μL, 7.10 mmol) were stirred at 40 °C for 14 h. After chromatographic purification, 799 mg (94%) of **2a** was obtained.

Furan Derivatives; 2-Methyl-5-(1-phenylcyclohexyl)furan (2a); Typical Procedure

To a mixture of $Sc(OTf)_3$ (30.4 mg, 61.8 μmol) and **1a** (2.179 g, 12.37 mmol) in $MeNO_2$ (12.19 mL) was added 2-methylfuran (2.23 mL, 24.7 mmol) at r.t. The resulting mixture was stirred at 40 °C for 1 h using a Dimroth condenser with a rubber balloon stopper. After filtering the mixture through a short silica gel pad with EtOAc (70 mL), the filtrate was concentrated under a reduced pressure and the residue was purified by column chromatography (silica gel, hexane–EtOAc, 10:1) to afford **2a** (2.730 g, 92%) as a colorless liquid (Table 2).

The analytical and spectral data of **2a** are given above.

2-Methyl-5-(2-phenyl-2-propyl)furan (2b)

Pure **2b** was obtained by column chromatography (hexane–EtOAc, 30:1) as a colorless oil; R_f = 0.77 (hexane–EtOAc, 4:1).

IR (neat): 2960, 1450, 1230, 1030, 790, 770, 700 cm^{-1}.

^1H NMR (400 MHz): δ = 7.28–7.17 (5 H, m), 5.96 (1 H, d, J = 4.0 Hz), 5.87–5.86 (1 H, m), 2.22–2.21 (3 H, m), 1.61 (6 H, s).

^{13}C NMR (100 MHz): δ = 160.3, 150.4, 148.0, 127.9, 125.82, 125.76, 105.6, 105.0, 40.2, 28.7, 13.7.

MS (EI, 70 eV): m/z (%) = 200 (M^+, 26), 185 (100).

HRMS-EI: m/z calcd for $C_{14}H_{16}O$ $[M]^+$: 200.1201; found: 200.1204.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.87; H, 8.12.

2-Diphenylmethyl-5-methylfuran (2c)[28]

Pure **2c** was obtained by column chromatography (hexane–EtOAc, 10:1) as a colorless oil; R_f = 0.67 (hexane–EtOAc, 10:1).

IR (neat): 3030, 1600, 1490, 1450, 1220, 1020, 780, 750, 700 cm^{-1}.

^1H NMR (300 MHz): δ = 7.31–7.15 (10 H, m), 5.88–5.86 (1 H, m), 5.74–5.73 (1 H, m), 5.38 (1 H, s), 2.24 (3 H, s).

^{13}C NMR (100 MHz): δ = 154.6, 151.3, 141.9, 128.6, 128.2, 126.5, 109.0, 105.8, 51.0, 13.8.

EI-MS: m/z (%) = 248 (M^+, 100), 205 (81), 171 (85).

HRMS-EI: m/z calcd for $C_{18}H_{16}O$ $[M]^+$: 248.1201; found: 248.1206.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.83; H, 6.67.

2-[1-(4-Methoxyphenyl)ethyl]-5-methylfuran (2d)[28]

Pure **2d** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.83 (hexane–EtOAc, 10:1).

IR (neat): 2940, 1610, 1500, 1450, 1240, 1220, 1170, 1030, 1020, 830, 780 cm^{-1}.

^1H NMR (300 MHz): δ = 7.16–7.10 (2 H, m with doublet character), 6.86–6.81 (2 H, m with doublet character), 5.88–5.83 (2 H, m), 4.01 (1 H, q, J = 7.2 Hz), 3.78 (3 H, s), 2.22 (3 H, s), 1.53 (3 H, d, J = 7.2 Hz).

^{13}C NMR (100 MHz): δ = 157.9, 157.3, 150.5, 136.5, 128.1, 113.7, 105.6, 105.2, 55.3, 38.5, 20.9, 13.7.

MS (EI, 70 eV): *m*/*z* (%) = 216 (M^+, 26), 201 (100).

HRMS-EI: *m*/*z* calcd for $C_{14}H_{16}O_2$ $[M]^+$: 216.1150; found: 216.1147.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.68; H, 7.27.

2-[1-(4-Benzyloxyphenyl)ethyl]-5-methylfuran (2e)

Pure **2e** was obtained by column chromatography (hexane–EtOAc, 40:1) as a colorless oil; R_f = 0.77 (hexane–EtOAc, 4:1).

IR (neat): 2960, 1610, 1510, 1460, 1380, 1240, 1220, 1180, 1020, 830, 790, 720, 700 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.43–7.28 (5 H, m), 7.14–7.10 (2 H, m with doublet character), 6.91–6.89 (2 H, m with doublet character), 5.87–5.83 (2 H, m), 5.02 (2 H, s), 4.01 (1 H, q, *J* = 7.2 Hz), 2.21 (3 H, s), 1.53 (3 H, d, *J* = 7.3 Hz).

^{13}C NMR (100 MHz): δ = 157.3, 157.2, 150.5, 137.0, 136.8, 128.4, 128.2, 127.7, 127.3, 114.6, 105.6, 105.3, 70.1, 38.5, 20.9, 13.7.

MS (EI, 70 eV): *m*/*z* (%) = 292 (M^+, 59), 277 (58), 91 (100).

HRMS-EI: *m*/*z* calcd for $C_{20}H_{20}O_2$ $[M]^+$: 292.1463; found: 292.1471.

Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.12; H, 6.96.

Benzyl 4-(1-Hydroxyethyl)phenylcarbamate (1f)

To a solution of benzyl 4-acetylphenylcarbamate[29] (5.190 g, 19.27 mmol) in propan-2-ol (19.3 mL) and THF (19.3 mL) was added $NaBH_4$ (365 mg, 9.64 mmol) at r.t. The mixture was stirred for 1 h. To the mixture was then added MeOH (10 mL) and after stirring for 1 h, another portion of $NaBH_4$ (185 mg, 4.90 mmol) was added and stirred for 1 h. The whole was concentrated, and the residue was partitioned between H_2O (100 mL) and EtOAc (100 mL). The aqueous phase was extracted with EtOAc (2 × 100 mL). The combined organic layers were washed with brine (1 × 100 mL), dried over $MgSO_4$, filtered, and the filtrate was concentrated to give a colorless solid (5.130 g, 98%). The solid was recrystallized from propan-2-ol to afford colorless prisms; mp 101–102 °C; R_f = 0.32 (hexane–EtOAc, 1:1).

IR (KBr): 3441, 3253, 1699, 1601, 1539, 1419, 1239, 1048, 741 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.40–7.25 (9 H, m), 6.76 (1 H, br), 5.18 (2 H, s), 4.84 (1 H, q, *J* = 6.4 Hz), 1.91(1 H, br), 1.46 (3 H, d, *J* = 6.6 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 271 (M^+, 22), 253 (16), 212 (22), 148 (17), 91 (100).

HRMS-EI: *m*/*z* calcd for $C_{16}H_{17}NO_3$ $[M]^+$: 271.1208; found: 271.1209.

Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.99; H, 6.38; N, 5.25.

Benzyl *N*-[4-(1-(5-Methyl-2-furyl)ethyl)phenyl]carbamate (2f)

Pure **2f** was obtained by column chromatography (hexane–EtOAc, 15:1) as a colorless oil; R_f = 0.45 (hexane–EtOAc, 4:1).

IR (neat): 3330, 2960, 1710, 1600, 1530, 1420, 1320, 1220, 1070, 1030, 840, 790, 750, 710 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.25 (7 H, m), 7.15 (2 H, d, *J* = 8.4 Hz), 6.63 (1 H, br), 5.88 (1 H, d, *J* = 2.8 Hz), 5.85–5.84 (1 H, m), 5.19 (2 H, s), 4.02 (1 H, q, *J* = 6.8 Hz), 2.21 (3 H, s), 1.53 (3 H, d, *J* = 6.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 153.2, 150.6, 139.7, 135.9, 135.8, 128.5, 128.2, 128.1, 127.8, 118.8, 105.6, 150.4, 67.0, 38.7, 20.7, 13.7.

MS (EI, 70 eV): *m*/*z* (%) = 335 (M^+, 8), 227 (28), 212 (100), 108 (10), 91 (17).

HRMS-EI: *m*/*z* calcd for $C_{21}H_{21}NO_3$ $[M]^+$: 335.1521; found: 335.1517.

Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31. Found: C, 75.38; H, 6.47.

2-Methyl-5-[1-(4-Methylphenyl)ethyl]furan (2g)

Pure **2g** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.57 (hexane–EtOAc, 4:1).

IR (neat): 2970, 2930, 1570, 1520, 1460, 1230, 1020, 805, 790 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.12–7.08 (4 H, m), 5.89–5.88 (1 H, m), 5.85–5.84 (1 H, m), 4.02 (1 H, q, *J* = 7.2 Hz), 2.31 (3 H, s), 2.21 (3 H, s), 1.54 (3 H, d, *J* = 7.2 Hz).

^{13}C NMR (100 MHz): δ = 157.2, 150.5, 141.4, 135.7, 128.9, 127.0, 105.6, 105.3, 39.0, 21.1, 20.9, 13.7.

MS (EI, 70 eV): *m*/*z* (%) = 200 (M^+, 29), 185 (100).

HRMS-EI: *m*/*z* calcd for $C_{14}H_{16}O$ $[M]^+$: 200.1201; found: 200.1203.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.81; H, 8.19.

2-[1-(4-Biphenylyl)ethyl]-5-methylfuran (2h)

Pure **2h** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.63 (hexane–EtOAc, 10:1).

IR (neat): 2960, 1560, 1480, 1220, 1020, 840, 780, 770, 740, 700 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.58–7.56 (2 H, m with doublet character), 7.53–7.51 (2 H, m with doublet character), 7.44–7.39 (2 H, m with triplet character), 7.40–7.27 (3 H, m), 5.95 (1 H, d, *J* = 2.8 Hz), 5.88–5.87 (1 H, m), 4.11 (1 H, q, *J* = 7.2 Hz), 2.44 (3 H, s), 1.60 (3 H, d, *J* = 7.2 Hz).

^{13}C NMR (100 MHz): δ = 156.8, 150.7, 143.5, 140.9, 139.2, 128.6, 127.6, 127.0, 126.91, 126.90, 105.7, 105.5, 39.0, 20.8, 13.7.

MS (EI, 70 eV): *m*/*z* (%) = 262 (M^+, 33), 247 (100).

HRMS-EI: *m*/*z* calcd for $C_{19}H_{18}O$ $[M]^+$: 262.1358; found: 262.1362.

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 87.08; H, 7.00.

2-[1-(4-Chlorophenyl)ethyl]-5-methylfuran (2i)

A mixture of **2i** and **2i′** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.67 (hexane–EtOAc, 4:1).

IR (neat) (mixture of **2i** and **2i′**): 2970, 1570, 1500, 1230, 1100, 1020, 840, 790 cm^{-1}.

^{1}H NMR (300 MHz,): δ = 7.26–7.23 (2 H, m), 7.15–7.11 (2 H, m), 5.91–5.89 (1 H, m), 5.86–5.85 (1 H, m), 4.03 (1 H, q, *J* = 7.2 Hz), 2.21 (3 H, s), 1.53 (3 H, d, *J* = 6.9 Hz).

^{13}C NMR (100 MHz): δ = 156.3, 150.8, 142.8, 131.9, 128.5, 128.4, 105.67, 105.63, 38.8, 20.7, 13.7.

GC-MS (EI, 70 eV): *m*/*z* (%) = 222 (M^+ + 2, 28), 220 (77), 207 (78), 205 (100), 141 (14).

GC-HRMS-EI: *m*/*z* calcd for $C_{13}H_{13}ClO$ $[M]^+$: 220.0655; found: 220.0658.

Anal. Calcd for $C_{13}H_{13}ClO$ (mixture of **2i** and **2i′**): C, 70.75; H, 5.94. Found: C, 70.75; H, 6.11.

3-[1-(4-Chlorophenyl)ethyl]-5-methylfuran (2i′)

^{1}H NMR (300 MHz): δ = 7.26–7.23 (2 H, m), 7.15–7.11 (2 H, m), 6.22 (1 H, br), 5.90–5.85 (1 H, m), 3.92 (1 H, q, *J* = 7.2 Hz), 2.15 (3 H, s), 1.50 (3 H, d, *J* = 7.5 Hz).

^{13}C NMR (100 MHz): δ = 146.8, 144.6, 139.8, 131.4, 128.4, 128.3, 122.7, 109.8, 35.0, 22.2, 11.9.

GC-MS (EI, 70 eV): *m*/*z* (%) = 222 (M^+ + 2, 11), 220 (34), 207 (32), 205 (100), 141 (8).

GC-HRMS-EI: *m*/*z* calcd for $C_{13}H_{13}ClO$ $[M]^+$: 220.0655; found: 220.0650.

2-Methyl-5-[1-(1-naphthyl)ethyl]furan (2n)

Pure **2n** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.67 (hexane–EtOAc, 4:1).

IR (neat): 2960, 1560, 1450, 1380, 1220, 1020, 780 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.13 (1 H, d, *J* = 8.4 Hz), 7.86 (1 H, d, *J* = 7.6 Hz), 7.72 (1 H, d, *J* = 8.0 Hz), 7.52–7.44 (2 H, m), 7.40 (1 H, t, *J* = 7.7 Hz), 7.27–7.23 (1 H, m), 5.95–5.94 (1 H, m), 5.89–5.87 (1 H, m), 4.90 (1 H, q, *J* = 7.1 Hz), 2.23 (3 H, s), 1.70 (3 H, d, *J* = 7.2 Hz).

^{13}C NMR (100 MHz): δ = 156.8, 150.6, 140.2, 133.8, 131.2, 128.7, 126.9, 125.8, 125.5, 125.2, 124.0, 123.2, 106.3, 105.7, 34.8, 20.4, 13.7.

MS (EI, 70 eV): *m*/*z* (%) = 236 (M^+, 50), 221 (100), 193 (11), 178 (17).

HRMS-EI: *m*/*z* calcd for $C_{17}H_{16}O$ $[M]^+$: 236.1201; found: 236.1200.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.47; H, 7.02.

2-(Ferrocenyl)methyl-5-methylfuran (2q)

Pure **2q** was obtained by preparative TLC (hexane–$CHCl_3$, 4:1) as an orange solid; mp 33–34 °C; R_f = 0.45 (hexane–$CHCl_3$, 4:1).

IR (KBr): 3100, 1568, 1419, 1217, 1105, 1027, 1001, 969, 950, 817, 788, 491 cm^{-1}.

^{1}H NMR (400 MHz): δ = 5.86–5.84 (2 H, m), 4.13–4.06 (9 H, m), 3.61 (2 H, s), 2.27 (3 H, s).

^{13}C NMR (100 MHz): δ = 152.8, 150.1, 106.0, 105.8, 85.7, 68.7, 68.4, 67.4, 28.5, 13.7.

MS (EI, 70 eV): *m*/*z* (%) = 281 (M^+ + 1, 20), 280 (100), 214 (7).

HRMS-EI: *m*/*z* calcd for $C_{16}H_{16}FeO$ $[M]^+$: 280.0551; found: 280.0549.

Anal. Calcd for $C_{16}H_{16}FeO$: C, 68.60; H, 5.76. Found: C, 68.62; H, 5.87.

2-(1-Ferrocenyl)ethyl-5-methylfuran (2r)

Pure **2r** was obtained by preparative TLC (hexane–$CHCl_3$, 4:1) as an orange solid; mp 55–56 °C; R_f = 0.45 (hexane–$CHCl_3$, 4:1).

IR (neat): 3100, 2960, 1560, 1450, 1220, 1105, 1020, 820, 790 cm^{-1}.

^{1}H NMR (400 MHz): δ = 5.84–5.80 (2 H, m), 4.12–4.06 (9 H, m), 3.80 (1 H, q, *J* = 7.2 Hz), 2.27 (3 H, s), 1.53 (3 H, d, *J* = 7.2 Hz).

^{13}C NMR (100 MHz): δ = 157.5, 149.7, 105.6, 104.4, 92.5, 68.6, 67.5, 67.2, 67.0, 66.5, 33.1, 20.2, 13.7.

MS (EI, 70 eV): *m*/*z* (%) = 295 (M^+ + 1, 22), 294 (M^+, 100), 279 (21).

HRMS-EI: *m*/*z* calcd for $C_{17}H_{18}FeO$ $[M]^+$: 294.0707; found: 294.0704.

Anal. Calcd for $C_{17}H_{18}FeO$: C, 69.41; H, 6.17. Found: C, 69.44; H, 6.33.

(*S*)-1-(Ferrocenyl)ethanol [(*S*)-1r]

(*S*)-**1r** was prepared by the (*R*)-oxazaborolidine-catalyzed asymmetric borane reduction of acetylferrocene.[22] The crude product was recrystallized from cyclohexane to afford (*S*)-**1r** with 100% ee.

(*S*)-2-(1-Ferrocenyl)ethyl-5-methylfuran [(*S*)-2r]

100% ee, DAICEL CHIRALCEL OD-H, hexane–propan-2-ol (30:1), 1 mL/min, 254 nm detection; $[\alpha]_D^{26}$ +57.4 (*c* = 0.935, $CHCl_3$).

Ruthenium Oxidation of Furan Derivatives; Methyl 1-Phenyl-1-cyclohexanecarboxylate (3a);[30] Typical Procedures

For GC Analysis

Furan derivative **2a** (20.0 mg, 83.2 μmol) was dissolved in hexane–EtOAc (3:1, 2.33 mL) in a 20 mL test tube. A 0.25 mol/L solution of $NaIO_4$ in H_2O (2.33 mL, 583 μmol, 7 equiv) was added and the mixture was stirred for 5 min at 20 °C. A 0.1 mol/L solution of $RuCl_3 \cdot nH_2O$ (calculated as 3 H_2O) in H_2O (4.2 μL, 0.42 μmol, 0.5 mol%) was added. The mixture was vigorously stirred at 20 °C for 24 h. NaCl was added to saturate the aqueous layer and the mixture was extracted with EtOAc (5 × 2 mL). The combined extracts were dried ($MgSO_4$) and filtered. The filtrate was concentrated under reduced pressure, and the residue was dissolved in benzene–MeOH (2:7, 832 μL). A 2.0 mol/L solution of trimethylsilyldiazomethane ($TMSCHN_2$) in hexane (250 μL, 1.5 equiv) was added, and stirred for 5 min at r.t. A 0.1 mol/L solution of AcOH in MeOH was added to consume the excess of $TMSCHN_2$, and the mixture was concentrated under reduced pressure to give the methyl ester **3a**. Octadecane (13.0 mg, 2/3–3/4 weight of the starting material) was added, and dissolved in EtOAc (26 mL). The solution was analyzed by GC and GC-MS. The yields were determined using the calibration line prepared from octadecane and **3a** using GC. The yield of **3a** was 69%. The carboxylic acids (**3**-CO_2H) can be obtained by preparative TLC (CH_2Cl_2–MeOH, 10:1) after the extraction of the crude products.

1 mmol Scale

Furan derivative **2a** (280.8 mg, 1.168 mmol) was dissolved in hexane–EtOAc (1:1, 32.7 mL) in a 100 mL flask. A 0.25 mol/L solution of $NaIO_4$ in H_2O (32.7 mL, 8.18 mmol, 7 equiv) was added and the mixture was stirred for 10 min at 20 °C. A 0.1 mol/L solution of $RuCl_3 \cdot nH_2O$ (calculated as 3 H_2O) in H_2O (58.4 μL, 5.84 μmol, 0.5 mol%) was added. The mixture was stirred vigorously at 20 °C for 24 h. NaCl was added to saturate the aqueous layer and the mixture was extracted with EtOAc (4 × 40 mL). The combined extracts were dried ($MgSO_4$) and filtered. The filtrate was concentrated under reduced pressure, and the residue was dissolved in benzene–MeOH (2:7, 20 mL). A 2.0 mol/L solution of trimethylsilyldiazomethane ($TMSCHN_2$) in hexane (3.51 mL, 1.5 equiv) was added, and stirred for 10 min at r.t. A 0.1 mol/L solution of AcOH in MeOH was added to consume the excess of $TMSCHN_2$, and the mixture was concentrated under reduced pressure to give crude methyl ester **3a**. Pure **3a** was obtained by column chromatography (hexane–EtOAc, 20:1) as a pale yellow oil; yield: 191.4 mg (75%); R_f = 0.45 (hexane–EtOAc, 10:1).

Note: For the isolation of the methyl ester derivative **3**, the concentration process should be carried out below 30 °C, because some methyl ester derivative **3** is significantly volatile.

IR (neat): 2930, 2860, 1730, 1450, 1310, 1220, 1140, 1000, 740, 700 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.40–7.22 (5 H, m), 3.64 (3 H, s), 2.53–2.45 (2 H, m), 1.78–1.22 (8 H, m).

MS (EI, 70 eV): *m*/*z* (%) = 218 (M^+, 19), 159 (100), 91 (63).

HRMS-EI: *m*/*z* calcd for $C_{14}H_{18}O_2$ $[M]^+$: 218.1307; found: 218.1308.

Methyl 2-Methyl-2-phenylpropionate (3b)[31]
Pure **3b** was obtained by column chromatography (hexane–EtOAc, 20:1) as a pale yellow oil; R_f = 0.53 (hexane–EtOAc, 4:1).

IR (neat): 2950, 1730, 1470, 1450, 1440, 1260, 1200, 1150, 1105, 850, 770, 700 cm^{-1}.

^1H NMR (300 MHz): δ = 7.34–7.22 (5 H, m), 3.65 (3 H, s), 1.58 (6 H, s).

MS (EI, 70 eV): *m*/*z* (%) = 178 (M^+, 24), 119 (100), 91 (40).

HRMS-EI: *m*/*z* calcd for $C_{11}H_{14}O_2$ $[M]^+$: 178.0994; found: 178.0991.

Methyl Diphenylacetate (3c)[32]
Pure **3c** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.33 (hexane–EtOAc, 10:1).

IR (neat): 3030, 1730, 1430, 1280, 1200, 1150, 1010, 750, 700 cm^{-1}.

^1H NMR (300 MHz): δ = 7.82–7.22 (10 H, m), 5.03 (1 H, s), 3.74 (3 H, s).

MS (EI, 70 eV): *m*/*z* (%) = 226 (M^+, 21), 167 (100).

HRMS-EI: *m*/*z* calcd for $C_{15}H_{14}O_2$ $[M]^+$: 226.0994; found: 226.0995.

Methyl 2-(4-Methoxyphenyl)propionate (3d)[33,40]
Pure **3d** was obtained by column chromatography (hexane–EtOAc, 40:1) as a colorless oil; R_f = 0.26 (hexane–EtOAc, 10:1).

IR (neat): 2930, 1730, 1610, 1510, 1460, 1250, 1210, 1170, 1040, 840, 790 cm^{-1}.

^1H NMR (300 MHz): δ = 7.24–7.19 (2 H, m), 6.88–6.84 (2 H, m), 3.79 (3 H, s), 3.67 (1 H, q, *J* = 7.2 Hz), 3.65 (3 H, s), 1.47 (3 H, d, *J* = 7.2 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 194 (M^+, 23), 135 (100).

HRMS-EI: *m*/*z* calcd for $C_{11}H_{14}O_3$ $[M]^+$: 194.0943; found: 194.0939.

Methyl 2-(4-Benzyloxyphenyl)propionate (3e)[33]
Pure **3e** was obtained by column chromatography (hexane–EtOAc, 40:1) as a colorless oil; R_f = 0.53 (hexane–EtOAc, 4:1).

IR (neat): 1730, 1605, 1500, 1450, 1250, 1180, 1020, 830, 740 cm^{-1}.

^1H NMR (400 MHz): δ = 7.43–7.32 (5 H, m), 7.23–7.21 (2 H, m with doublet character), 6.95–6.91 (2 H, m with doublet character), 5.04 (2 H, s), 3.67 (1 H, q, *J* = 7.2 Hz), 3.65 (3 H, s), 1.47 (3 H, d, *J* = 7.2 Hz).

^{13}C NMR (100 MHz): δ = 175.0, 157.7, 136.9, 132.8, 128.44, 128.36, 127.8, 127.3, 114.8, 70.1, 52.0, 44.6, 18.8.

MS (EI, 70 eV): *m*/*z* (%) = 270 (M^+, 38), 211 (11), 91 (100).

HRMS-EI: *m*/*z* calcd for $C_{17}H_{18}O_3$ $[M]^+$: 270.1256; found: 270.1255.

Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.75; H, 6.86.

Methyl 2-[4-(Benzyloxycarbonylamino)phenyl]propionate (3f)
Pure **3f** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless solid; mp 71.5–72.5 °C; R_f = 0.29 (hexane–EtOAc, 4:1).

IR (KBr): 3368, 1739, 1709, 1594, 1536, 1454, 1436, 1417, 1316, 1210, 1172, 1069, 840, 738 cm^{-1}.

^1H NMR (400 MHz): δ = 7.39–7.32 (7 H, m), 7.24–7.22 (2 H, m with doublet character), 6.65 (1 H, br), 5.19 (2 H, s), 3.68 (1 H, q, *J* = 7.2 Hz), 3.65 (3 H, s), 1.47 (3 H, d, *J* = 7.2 Hz).

^{13}C NMR (100 MHz): δ = 174.7, 153.1, 136.6, 135.9, 135.5, 128.5, 128.22, 128.17, 128.0, 118.8, 67.1, 52.1, 44.8, 18.7.

MS (EI, 70 eV): *m*/*z* (%) = 313 (M^+, 18), 210 (25), 205 (29), 146 (100), 128 (16), 108 (14), 91 (55), 79 (12), 77 (10).

HRMS-EI: *m*/*z* calcd for $C_{18}H_{19}NO_4$ $[M]^+$: 313.1314; found: 313.1309.

Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 69.11; H, 6.31; N, 4.12.

Methyl 2-(4-Methylphenyl)propionate (3g)[34]
Pure **3g** was obtained by column chromatography (hexane–EtOAc, 30:1) as a colorless oil; R_f = 0.25 (hexane–EtOAc, 10:1).

IR (neat): 2930, 1730, 1430, 1200, 1160, 1060, 820 cm^{-1}.

^1H NMR (300 MHz): δ = 7.20–7.11 (4 H, m), 3.69 (1 H, q, *J* = 7.2 Hz), 3.65 (3 H, s), 2.33 (3 H, s), 1.48 (3 H, d, *J* = 7.2 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 178 (M^+, 23), 119 (100).

HRMS-EI: *m*/*z* calcd for $C_{11}H_{14}O_2$ $[M]^+$: 178.0994; found: 178.0992.

Methyl 2-(4-Biphenyl)propionate (3h)[35]
Pure **3h** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.29 (hexane–EtOAc, 10:1).

IR (neat): 2940, 1730, 1490, 1210, 760, 700 cm^{-1}.

^1H NMR (300 MHz): δ = 7.58–7.52 (4 H, m), 7.46–7.30 (5 H, m), 3.78 (1 H, q, *J* = 7.2 Hz), 3.69 (3 H, s), 1.54 (3 H, d, *J* = 7.2 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 240 (M^+, 41), 181 (100).

HRMS-EI: *m*/*z* calcd for $C_{16}H_{16}O_2$ $[M]^+$: 240.1150; found: 240.1150.

Methyl 2-(4-Chlorophenyl)propionate (3i)[33]
Pure **3i** was obtained by column chromatography (hexane–EtOAc, 20:1) as a pale yellow oil; R_f = 0.26 (hexane–EtOAc, 10:1).

IR (neat): 2950, 1730, 1490, 1440, 1330, 1210, 1170, 1090, 1020, 830, 770 cm^{-1}.

^1H NMR (300 MHz): δ = 7.71–7.21 (4 H, m), 3.70 (1 H, q, *J* = 7.2 Hz), 3.66 (3 H, s), 1.48 (3 H, d, *J* = 6.9 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 200 (M^+ + 2, 8), 198 (M^+, 24), 141 (34), 139 (100), 103 (38).

HRMS-EI: *m*/*z* calcd for $C_{10}H_{11}ClO_2$ $[M]^+$: 198.0448; found: 198.0445.

Methyl 1,2,3,4-Tetrahydronaphthalene-1-carboxylate (3j)[36]
Pure **3j** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.38 (hexane–EtOAc, 10:1).

IR (neat): 2930, 1720, 1450, 1435, 1250, 1205, 1195, 1060, 1070, 1000, 750 cm^{-1}.

^1H NMR (300 MHz): δ = 7.19–7.08 (4 H, m), 3.84 (1 H, t, *J* = 5.9 Hz), 3.71 (3 H, s), 2.89–2.70 (2 H, m), 2.20–1.73 (4 H, m).

^{13}C NMR (100 MHz): δ = 175.1, 137.0, 133.1, 129.2, 129.1, 126.7, 125.6, 52.0, 44.9, 29.2, 26.7, 20.7.

MS (EI, 70 eV): *m*/*z* (%) = 190 (M^+, 20), 131 (100).

HRMS-EI: *m*/*z* calcd for $C_{12}H_{14}O_2$ $[M]^+$: 190.0994; found: 190.0991.

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.53; H, 7.65.

Methyl 1-Methyl-1,2,3,4-tetrahydronaphthalene-1-carboxylate (3k)[37]

Pure **3k** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.42 (hexane–EtOAc, 4:1),

IR (neat): 2920, 1720, 1450, 1440, 1260, 1200, 1120, 770, 740 cm^{-1}.

^1H NMR (300 MHz): δ = 7.23–7.26 (4 H, m), 3.65 (3 H, s), 2.29–2.72 (2 H, m), 2.35–2.26 (1 H, m), 1.94–1.69 (3 H, m), 1.55 (3 H, s).

^{13}C NMR (100 MHz): δ = 177.5, 139.0, 136.2, 129.1, 127.8, 126.3, 1258, 52.2, 46.4, 35.3, 30.0, 27.8, 19.9.

MS (EI, 70 eV): *m*/*z* (%) = 204 (M^+, 13), 145 (100), 129 (10).

HRMS-EI: *m*/*z* calcd for $C_{13}H_{16}O_2$ $[M]^+$: 204.1150; found: 204.1152.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.46; H, 8.16.

Methyl 2-(2-Naphthyl)propionate (3l)[38]

Pure **3l** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.22 (hexane–EtOAc, 10:1).

IR (neat): 2950, 1730, 1440, 1330, 1250, 1200, 1170, 820, 750 cm^{-1}.

^1H NMR (300 MHz): δ = 7.82–7.79 (3 H, m), 7.73–7.74 (1 H, m), 7.49–7.41 (3 H, m), 3.90 (1 H, q, *J* = 7.2 Hz), 3.67 (3 H, s), 1.59 (3 H, d, *J* = 7.2 Hz).

^{13}C NMR (100 MHz): δ = 174.7, 137.8, 133.3, 132.4, 128.2, 127.7, 127.5, 126.01, 125.98, 125.7, 125.6, 52.1, 45.6, 18.7.

MS (EI, 70 eV): *m*/*z* (%) = 214 (M^+, 42), 155 (100).

HRMS-EI: *m*/*z* calcd for $C_{14}H_{14}O_2$ $[M]^+$: 214.0994; found: 214.0991.

Methyl 2-(6-Methoxy-2-naphthyl)propionate (3m)[39]

Pure **3m** was obtained by column chromatography (hexane–EtOAc, 20:1) as colorless fine needles; mp 64–65 °C (propan-2-ol); R_f = 0.41 (hexane–EtOAc, 4:1).

IR (KBr): 2977, 1736, 1605, 1449, 1333, 1332, 1266, 1230, 1198, 1174, 1029, 857, 824, 480 cm^{-1}.

^1H NMR (300 MHz): δ = 7.69 (1 H, d, *J* = 8.4 Hz), 7.69 (1 H, d, *J* = 8.4 Hz), 7.65 (1 H, d, *J* = 0.9 Hz), 7.39 (1 H, dd, *J* = 8.4, 1.8 Hz), 7.15–7.09 (2 H, m), 3.00 (3 H, s), 3.85 (1 H, q, *J* = 7.2 Hz), 3.66 (3 H, s), 1.57 (3 H, d, *J* = 7.2 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 244 (M^+, 52), 185 (100).

HRMS-EI: *m*/*z* calcd for $C_{15}H_{16}O_3$ $[M]^+$: 244.1099; found: 244.1093.

Methyl 2-(1-Naphthyl)propionate (3n)[33,40]

Pure **3n** was obtained by column chromatography (hexane–EtOAc, 20:1) as a colorless oil; R_f = 0.42 (hexane–EtOAc, 4:1).

IR (neat): 2950, 1730, 1440, 1200, 1180, 790 cm^{-1}.

^1H NMR (300 MHz): δ = 8.07 (1 H, d, *J* = 8.1 Hz), 7.88–7.85 (1 H, m), 7.79–7.75 (1 H, m), 7.56–7.48 (2 H, m), 7.47–7.40 (2 H, m), 4.51 (1 H, q, *J* = 7.2 Hz), 3.65 (3 H, s), 1.66 (3 H, d, *J* = 7.2 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 214 (M^+, 34), 155 (100).

HRMS-EI: *m*/*z* calcd for $C_{14}H_{14}O_2$ $[M]^+$: 214.0994; found: 214.0998

Methyl 2-(2-Methoxy-1-naphthyl)propionate (3o)

Pure **3o** was obtained by column chromatography (hexane–EtOAc, 20:1) and preparative TLC (CH_2Cl_2–EtOH, 200:1) as a pale yellow oil; R_f = 0.28 (hexane–EtOAc, 4:1).

IR (neat): 1736, 1263, 1210, 1095, 809, 747 cm^{-1}.

^1H NMR (300 MHz): δ = 7.84 (1 H, d, *J* = 8.7 Hz), 7.80 (1 H, d, *J* = 7.5 Hz), 7.79 (1 H, d, *J* = 9.0 Hz), 7.48 (1 H, dd, *J* = 6.6, 1.5 Hz), 7.34 (1 H, dd, *J* = 6.9, 1.2 Hz), 7.27 (1 H, d, *J* = 9.0 Hz), 4.54 (1 H, q, *J* = 6.9 Hz), 3.92 (3 H, s), 3.63 (3 H, s), 1.54 (3 H, d, *J* = 6.9 Hz).

^{13}C NMR (100 MHz): δ = 175.8, 153.7, 131.9, 129.4, 128.71, 128.70, 126.65, 123.3, 123.1, 122.2, 113.5, 56.6, 51.9, 36.7, 16.3.

MS (EI, 70 eV): *m*/*z* (%) = 244 (M^+, 51), 185 (100), 155 (9).

HRMS-EI: *m*/*z* calcd for $C_{15}H_{16}O_3$ $[M^+]$: 244.1099; found: 244.1102.

Methyl 2-(2-Thienyl)propionate (3p)[38]

A mixture of **3p** and **3p′** was obtained by column chromatography (hexane–EtOAc, 20:1) as a pale yellow oil. The ratio of **3p/3p′** was determined by ^1H NMR spectroscopy; R_f = 0.30 (hexane–EtOAc, 10:1).

IR (neat) (5.3:1 mixture of **3p/3p′**): 1739, 1455, 1435, 1327, 1200, 1171, 1059, 852, 702 cm^{-1}.

^1H NMR (300 MHz): δ = 7.20 (1 H, t, *J* = 3.3 Hz), 6.95 (2 H, d, *J* = 3.0 Hz), 4.02 (1 H, q, *J* = 7.2 Hz), 3.71 (3 H, s), 1.59 (3 H, d, *J* = 7.2 Hz).

^{13}C NMR (100 MHz): δ = 173.7, 142.7, 126.5, 124.6, 124.2, 52.3, 40.8, 19.5.

GC-MS (EI, 70 eV): *m*/*z* (%) = 170 (M^+, 29), 111 (100).

GC-HRMS-EI: *m*/*z* calcd for $C_8H_{10}O_2S$ $[M]^+$: 170.0402; found: 170.0408.

Methyl 2-(4-Iodo-2-thienyl)propionate (3p′)

^1H NMR (300 MHz): δ = 7.08 (1 H, d, *J* = 3.6 Hz), 6.63 (1 H, d, *J* = 3.6 Hz), 3.98 (1 H, q, *J* = 6.9 Hz), 3.71 (3 H, s), 1.55 (3 H, d, *J* = 7.5 Hz).

^{13}C NMR (100 MHz): δ = 173.2, 148.7, 136.3, 126.4, 71.9, 52.4, 41.2, 19.4.

GC-MS (EI, 70 eV): *m*/*z* (%) = 296 (M^+, 39), 237 (100).

GC-HRMS-EI: *m*/*z* calcd for $C_8H_9IO_2S$ $[M]^+$: 295.9368; found: 295.9369.

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