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Brønsted-acid-catalyzed coupling of electron-rich arenes with substituted allylic and secondary benzylic alcohols

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Abstract—*p*-Toluenesulfonic acid and triflic acid catalyze efficiently the coupling of electron-rich arenes with allylic and benzylic alcohols. Reactions are conducted under mild conditions, in air, and in the absence of solvent.

1. Introduction

Arenes and heteroarenes have proven to be quite attractive targets because of the extensive use of these compounds in the dyestuff, perfume, flavor, agriculture, and pharmaceutical industries. The coupling of allylic and benzylic groups with arenes can be seen as electrophile–nucleophile combinations, arenes being the nucleophiles and allylic or benzylic compounds being the electrophiles. Mild methodologies for such coupling include the Mo(II)-catalyzed allylic substitution of allylic alcohols or acetates with electron-rich aromatics,[1] the use of lanthanide and actinide triflates,[2] cooperative catalysts in heterobimetallic regime,[3] the Rh- and Ir-catalyzed allylations of electron-rich arenes with allylic tosylates,[4] and heterogeneous catalysts.[5]

Recently, a significant advance, due to Beller et al., has been seen in the use of sub-stoichiometric amounts of transition-metal compounds for arylation of benzylic alcohols and carboxylates.[6] Nevertheless, interest in metal-free and solvent-free reactions is progressing because of both economical concerns and increased environmental awareness.[7] Therefore, Brønsted acids have received recent attention as a simple alternative to toxic and precious metals, and the formation of C–X bonds (X=C, N, O, S) has been reported by different groups. Various Brønsted acids have been found to catalyze the addition of nitrogen and oxygen nucleophiles to olefins.[8] The formation of carbon–carbon bonds was reported via the cyclization of siloxy alkynes,[9] intermolecular Friedel–Crafts reactions using aliphatic alcohols,[10] methylenecyclopropane,[11] acetals,[12] aldehydes[13] and imines,[14] alkylation of anilines with styrenes,[15] acylation of aromatic compounds,[16] addition of 1,3-dicarbonyl compounds to alkenes and alcohols,[17] and nucleophilic substitution of propargylic alcohols.[18]

Direct arylation of allylic and benzylic alcohols under conditions leading to water as the only by-product would represent a green process. Surprisingly, such a simple approach has not been described with electron-rich arenes, probably because homogeneous Brønsted acids were not found to be effective catalysts in Friedel–Crafts reactions, in the past.[19,20] However, while this work was in progress, Sanz et al. have reported a similar procedure in organic medium for the nucleophilic substitution of alcohols.[21] Herein, we report a parallel approach, which tolerates substrates that were previously regarded as incompatible with strong Brønsted acids.

2. Results and discussion

According to the literature, the alkylation of π-electron-rich heteroaromatics, such as furans, by the standard Friedel–Crafts approach was impractical because the Brønsted and Lewis acid catalysts employed induced ring opening and polymerization.[19] While studying the arylation of (*E*)-4-phenylbut-3-en-2-ol (**1a**) with 5 equiv of 2-methylfuran (**2a**), we observed that Brønsted acids can be good catalysts under mild conditions (Table 1). While no reaction occurred in the presence of CH_3CO_2H (20 mol %) in dry CH_2Cl_2, a mixture of **3aa** and **4aa** (**3aa**/**4aa**, 80/20) was obtained in 60% yield with HCl as the catalyst (entries 1 and 2). Using CF_3CO_2H instead of HCl increased the yield, especially when the reaction was carried out without solvent (entries 3 and 4). Stronger acids shortened the reaction time to 1 h

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Keywords: Brønsted acid; Friedel–Crafts; Solvent free; Green chemistry.
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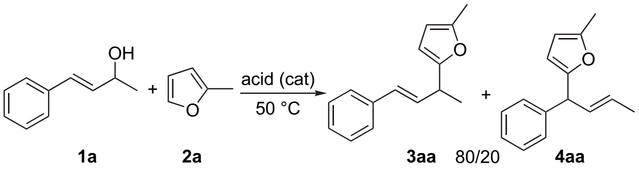
Table 1. Reaction of 2-methylfuran with (*E*)-4-phenylbut-3-en-2-ol[a]



Entry	Catalyst (mol %)	Solvent	Time (h)	Yield of **3aa**+**4aa** (%)
1	CH_3CO_2H (20)	CH_2Cl_2	8	0
2	HCl (20)	CH_2Cl_2	8	60
3	CF_3CO_2H (20)	CH_2Cl_2	8	82
4	CF_3CO_2H (20)		8	87
5	H_2SO_4 (5)		1	83
6	CF_3SO_3H (5)		1	87
7	*p*-$TolSO_3H\cdot H_2O$ (5)		1	87
8[b]	*p*-$TolSO_3H\cdot H_2O$ (5)		2	80
9	*p*-$TolSO_3H\cdot H_2O$ (20)		1	75
10	*p*-$TolSO_3H\cdot H_2O$ (1)		2	61

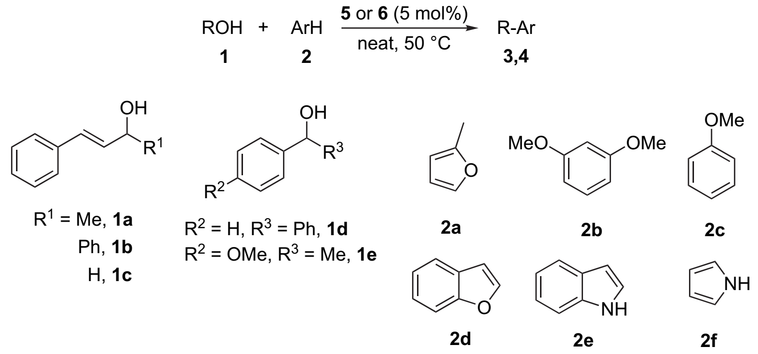
[a] Reaction conditions: **1a** (1.0 mmol), **2a** (5.0 mmol), solvent (0 or 1 mL), 50 °C.

[b] **2a** (1.1 mmol).

and the best results were obtained with 5 mol % of triflic acid (**5**) or monohydrated *p*-toluenesulfonic acid (**6**) (entries 6 and 7). The use of only a slight excess of **2a** had little impact on the yield (entry 8), but higher acid concentration led to some decomposition (entry 9). The process was less efficient with 1 mol % of acid (entry 10). Regioselectivity was close to that observed in the Mo(II)-catalyzed coupling of **2a** with (*E*)-4-phenylbut-3-en-2-yl acetate.[1b] Indeed, the Brønsted acid conditions led mainly to the formation of the C–C bond between the 5-position of the furan ring and the methyl terminus of the allyl moiety. Note that this reaction is not sensitive to air or moisture and can be used with furan derivatives, which is a rare feature of Friedel–Crafts-type chemistry.[6]

We were interested in the reactivity of other alcohols and arenes (Table 2). Triflic acid (**5**)[22] and monohydrated *p*-toluenesulfonic acid (**6**) were selected as catalysts. Allylic alcohols, such as (*E*)-4-phenylbut-3-en-2-ol (**1a**), (*E*)-1,3-diphenylprop-2-en-1-ol (**1b**), and cinnamyl alcohol (**1c**) react with **2a**, 1,3-dimethoxybenzene (**2b**), anisole (**2c**), and

Table 2. Reactions of allylic and benzylic alcohols with arenes[a]



Entry	1	2	Catalyst	*t* (h)	Product	Yield (%)
1	**1a**	**2b**	**5**	1	**3ab/4ab** (85/15)	86
2	**1a**	**2c**	**5**	2	**3ac**	80
3	**1a**	**2d**	**5**	2	**3ad/4ad** (95/5)	80
4[b,c]	**1a**	**2e**	**6**	2	**3ae/4ae** (45/55)	55
5	**1a**	**2f**	**6**	2	**3af/4af** (75/25)	62
6	**1b**	**2a**	**5**	1	**3ba**	95
7	**1b**	**2b**	**5**	1	**3bb**	80
8	**1b**	**2c**	**5**	2	**3bc**	83
9	**1b**	**2d**	**5**	2	**3bd**	85
10[b,c]	**1b**	**2e**	**6**	2	**3be**	95
11	**1b**	**2f**	**6**	2	**3bf**	83
12[b]	**1c**	**2a**	**6**	2	**3ca/4ca** (75/25)	71
13	**1c**	**2b**	**6**	2	**3cb/4cb** (90/10)	70
14	**1c**	**2c**	**6**	2	**3cc**	73[d]
15	**1c**	**2d**	**6**	2	**3cd**	64
16	**1d**	**2a**	**5**	9	**3da**	90
17	**1d**	**2b**	**5**	9	**3db**	70
18	**1d**	**2c**	**6**	9	**3dc**	92
19	**1d**	**2d**	**6**	9	**3dd**	86
20[b]	**1e**	**2a**	**6**	2	**3ea**	81
21	**1e**	**2b**	**6**	2	**3eb**	78
22	**1e**	**2c**	**6**	2	**3ec**	68
23	**1e**	**2d**	**6**	2	**3ed**	87
24[b,c]	**1e**	**2e**	**5**	2	**3ee**	66
25	**1e**	**2f**	**5**	2	**3ef**	69

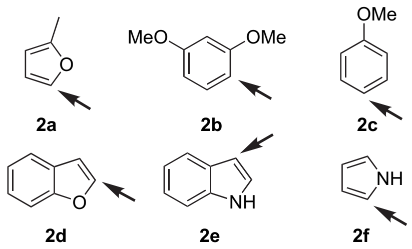
[a] Reaction conditions: alcohol (1.0 mmol), arene (5.0 mmol), catalyst (0.05 mmol), 50 °C.

[b] Performed in dry CH_2Cl_2 (1 mL).

[c] Performed with 1.0 equiv of arene.

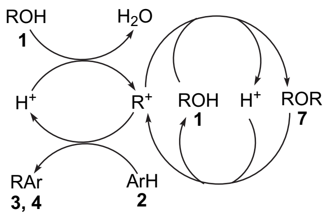
[d] Isolated with traces of a by-product corresponding probably to 1-cinnamyl-2-methoxybenzene.

benzofuran (**2d**) in good to excellent yields and short reaction times. The reaction of **2a**, **2b**, and **2d** with **1a** and **1c** exhibited good to high regioselectivity at the less hindered terminus of the allylic moiety (entries 1, 3, 12, 13, and 15). In all cases, the trans-configuration of the double bond was preserved. Arenes were alkylated regioselectively as observed in other processes (Scheme 1).[23] Note that **2c** reacted with **1a** with high selectivity through the *p*-position of the aromatic ring at the methyl terminus of the allyl moiety (entry 2). Indole (**2e**) and pyrrole (**2f**) also react with **1a** and **1b** in moderate to excellent yields (entries 4, 5, 10, and 11), with regioselectivity similar to that observed in other processes (Scheme 1),[24] but no reaction was observed with **1c**. Benzylic alcohols such as benzhydrol (**1d**) and 1-(4-methoxyphenyl)ethanol (**1e**) also reacted with arenes **2a–d** (entries 16–23) and anisole (**2c**) affording solely the *p*-isomers **3dc** and **3ec**. Compound **1d** gave no reaction with indole (**2e**) and pyrrole (**2f**) while **1e** reacted in fair yields (entries 24 and 25).



Scheme 1. Regioselectivities observed with **2**.

Scheme 2 shows plausible pathways for the reaction. We have observed the formation of bis(diphenylmethyl) ether (**7d**) during the reaction of **1d** with **2a**. Reaction of **7d** with **2a** in the presence of **5** required 8 h to afford **3da** in 95%. The coupling probably proceeds through the formation of a stabilized carbocation, which can react with **2** to produce **3** and **4**, or with **1** to give ether **7**. The latter can regenerate the carbocation and **1** via acid catalysis. The similar reactivity of **1d** and **7d** and the longer reaction time observed compared to the other examples indicate that the stability of **7d** slows down the reaction, probably via steric effects. The absence of reactivity of **1d** with **2e** and **2f** also shows that other factors affect the efficiency of the process.



Scheme 2. Plausible pathways for the acid-catalyzed reaction.

3. Conclusion

In summary, we have shown that *p*-toluenesulfonic acid and triflic acid are efficient catalysts for the direct coupling of phenyl-substituted allylic alcohols and secondary benzylic alcohols with electron-rich arenes under mild conditions. The reaction is operationally simple and can be performed in the absence of solvents. Of special interest are the *para*-selectivity observed with anisole and the tolerance of furans, indole, and pyrrole usually classified as 'acid-sensitive' compounds. This metal-free and solvent-free method, which gives water as the only side product, represents a clean and environmental friendly alternative to the already established use of metallic catalysts.

4. Experimental section

4.1. General information

All reagents used were commercially available and of high purity grade. Allylic and benzylic alcohols were obtained by reduction of ketones with $NaBH_4$ in MeOH. CH_2Cl_2 was distilled over CaH_2 under argon. Column chromatography was conducted over silica gel of 40–63 μm. NMR spectroscopy was performed with a 250 MHz apparatus in $CDCl_3$ and referenced to TMS.

4.2. General procedure

A 50 mL round-bottomed flask was charged with alcohol (1.0 mmol), arene (5.0 mmol) and, in some cases, solvent (1 mL). The acid (0.05 mmol) was added at room temperature ($PTSA\cdot H_2O$) or at 0 °C (CF_3SO_3H). The mixture was heated (oil bath, 50 °C) for the appropriate time. After cooling to room temperature, saturated $NaHCO_3$ solution (5 mL) was added and the mixture was extracted with Et_2O (5× 5 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The excess of arene was removed by distillation and the product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 98/2, then petroleum ether/ethyl acetate 95/5).

Caution: addition of triflic acid to 2-methylfuran gives a violent reaction. The following procedure should be used:

4.3. Typical procedure with triflic acid and 2-methylfuran

A 50 mL round-bottomed flask was charged with alcohol (1.0 mmol) and CH_2Cl_2 (1 mL) if required and cooled with an ice water bath. CF_3SO_3H (0.05 mmol, 4.0 μL) was added dropwise in order to prevent the accumulation of a colored gum, followed by the arene (5.0 mmol). The mixture was heated (oil bath, 50 °C) for the appropriate time. The work-up was carried out as for the above general procedure.

4.3.1. (*E*)-1-Phenyl-3-(2-methylfuran-5-yl)-1-butene (3aa) and (*E*)-4-phenyl-4-(2-methylfuran-5-yl)-2-butene (4aa).[1b] Colorless oil. Compound **3aa**: ^1H NMR (measured in a mixture with **4aa**): δ=1.33 (d, J=7.0 Hz, 3H, CH_3CH), 2.18 (s, 3H, CH_3-*furan*), 3.55 (quint, J=7.0 Hz, 1H, CHCH$_3$), 5.80–5.84 (m, 2H, =CH-*furan*), 6.20 (dd, J= 15.9 Hz, J=7.2 Hz, 1H, CH=CH–CH), 6.36 (d, J= 15.9 Hz, 1H, ArCH=CH), 7.05–7.35 (m, 5H, Ar). Compound **4aa**: ^1H NMR (measured in a mixture with **3aa**): δ=1.63 (ddd, J=6.4 Hz, J=1.5 Hz, J=0.9 Hz, 3H,

CH_3CH=CH), 2.15 (s, 3H, CH_3-*furan*), 4.53 (d, *J*=7.5 Hz, 1H, Ar*CH*), 5.41 (dqd, *J*=12.9 Hz, *J*=6.4 Hz, *J*=1.1 Hz, CH=*CH*CH$_3$), 5.75–5.84 (m, 1H, CH*CH*=CH), 5.85–5.93 (m, 2H, =*CH-furan*), 7.05–7.35 (m, 5H, Ar).

4.3.2. (*E*)-1-Phenyl-3-(2,4-dimethoxyphenyl)-1-butene (3ab) and (*E*)-4-phenyl-4-(2,4-dimethoxyphenyl)-2-butene (4ab). Pale yellow oil. Compound **3ab**: ^{1}H NMR (measured in a mixture with **4ab**): δ=1.38 (d, *J*=7.0 Hz, 3H, CH_3CH), 3.72 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.92–4.06 (m, 1H, *CH*CH$_3$), 6.32–6.47 (m, 4H, *CH*=*CH*, Ar), 7.00–7.34 (m, 6H, Ar). ^{13}C NMR (measured in a mixture with **4ab**): δ=20.2, 34.8, 55.3, 55.4, 98.8, 104.2, 126.2, 126.6, 126.9, 127.9, 128.0, 128.5, 135.3, 138.0, 157.8, 159.3. Compound **4ab**: ^{1}H NMR (measured in a mixture with **3ab**): δ=1.69 (dd, *J*=6.4 Hz, *J*=0.9 Hz, 3H, CH_3CH), 3.65 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 5.00 (d, *J*=7.0 Hz, 1H, Ar*CH*), 5.25–5.45 (m, 1H, CH=*CH*CH$_3$), 5.80–5.95 (m, 1H, CH*CH*=CH), 6.32–6.47 (m, 2H, Ar), 7.00–7.34 (m, 6H, Ar). IR (**3ab**/**4ab**, film): ν=3024, 2998, 2960, 2834, 1612, 1587, 1504, 1465, 1293, 1260, 1208, 1179, 1157, 1133, 1037, 968 cm^{-1}. GC–MS (EI): t_R (**4ab**)=10.8; *m*/*z* (%)=268 (94) [M$^+$], 253 (74), 237 (46), 207 (55), 129 (63), 115 (100); t_R (**3ab**)=11.9; *m*/*z* (%)=268 (40) [M$^+$], 253 (100), 237 (24), 115 (54). ESHRMS: calcd for $C_{18}H_{21}O_2$: 269.1542. Found: 269.1546.

4.3.3. (*E*)-1-Phenyl-3-(4-methoxyphenyl)-1-butene (3ac).[1b] Colorless oil. ^{1}H NMR: δ=1.35 (d, *J*=7.0 Hz, 3H, CH_3), 3.44–3.57 (m, 1H, *CH*CH$_3$), 3.69 (s, 3H, OCH_3), 6.26–6.30 (m, 2H, Ar*CH*=*CH*), 6.73–6.80 (m, 2H, Ar), 7.05–7.30 (m, 7H, Ar).

4.3.4. (*E*)-1-Phenyl-3-(benzofuran-2-yl)-1-butene (3ad) and (*E*)-4-phenyl-(benzofuran-2-yl)-2-butene (4ad). Pale yellow gum. Compound **3ad**: ^{1}H NMR (measured in a mixture with **4ad**): δ=1.63 (d, *J*=7.0 Hz, 3H, CH_3), 3.91 (quint, *J*=7.0 Hz, 1H, *CH*CH$_3$), 6.45 (dd, *J*=15.9 Hz, *J*=7.1 Hz, 1H, ArCH=*CH*), 6.52–6.55 (m, 1H, O–C=*CH*), 6.61 (d, *J*=15.9 Hz, Ar*CH*=CH), 7.20–7.62 (m, 9H, Ar). ^{13}C NMR (measured in a mixture with **4ad**): δ=19.0, 37.2, 101.5, 111.1, 120.6, 122.7, 123.5, 126.4, 127.5, 128.7, 128.9, 130.5, 131.3, 137.3, 154.9, 161.7. Compound **4ad**: ^{1}H NMR (selected data measured in a mixture with **3ad**): δ=1.80–1.86 (m, 3H, CH_3), 4.88 (d, *J*=7.2 Hz, 1H, Ar*CH*), 5.58–5.74 (m, 1H, *CH*CH$_3$), 5.90–6.06 (m, 1H, *CH*=CHCH$_3$). IR (**3ad**/**4ad**, pellets): ν=3026, 2967, 2930, 1580, 1493, 1453, 1296, 1254, 1168, 1103, 1033, 1010, 966, 943 cm^{-1}. GC–MS (EI): t_R (**4ad**)=10.4; *m*/*z* (%)=248 (80) [M$^+$], 233 (100), 115 (77); t_R (**3ad**)=11.3; *m*/*z* (%)=248 (98) [M$^+$], 233 (100), 115 (97). Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49; Found: C, 86.65; H, 6.63.

4.3.5. (*E*)-1-Phenyl-3-(indol-3-yl)-1-butene (3ae) and (*E*)-4-phenyl-(indol-3-yl)-2-butene (4ae).[1b] Pale yellow gum. Compound **3ae**: ^{1}H NMR (measured in a mixture with **4ae**): δ=1.54 (d, *J*=7.0 Hz, 3H, CH_3), 3.90 (quint, *J*=7.0 Hz, 1H, *CH*CH$_3$), 6.42–6.48 (m, 2H, Ar*CH*=*CH*), 6.87–6.91 (m, 1H, *CH*–NH), 6.94–7.40 (m, 9H, Ar), 7.73 (br s, 1H, NH). Compound **4ae**: ^{1}H NMR (measured in a mixture with **3ae**): δ=1.67–1.73 (m, 3H, CH_3), 4.87 (d, *J*=7.5 Hz, 1H, Ar*CH*), 5.50 (dq, *J*=15.1 Hz, *J*=6.3 Hz, 1H, *CH*CH$_3$), 5.93 (dd, *J*=15.1 Hz, *J*=7.6 Hz, 1H, *CH*=CHCH$_3$), 6.74–6.78 (m, 1H, *CH*–NH), 6.94–7.40 (m, 8H, Ar), 7.66 (d, *J*=7.8 Hz, 1H, Ar), 7.73 (br s, 1H, NH).

4.3.6. (*E*)-1-Phenyl-3-(pyrrol-2-yl)-1-butene (3af) and (*E*)-4-phenyl-(pyrrol-3-yl)-2-butene (4af). Pale yellow oil. Compound **3af**: ^{1}H NMR (measured in a mixture with **4af**): δ=1.40 (d, *J*=6.9 Hz, 3H, CH_3CH), 3.58 (quint, *J*=6.9 Hz, 1H, *CH*CH$_3$), 5.93–5.98 (m, 1H, *CH-pyrrole*), 6.05–6.13 (m, 1H, *CH-pyrrole*), 6.19 (dd, *J*=15.8 Hz, *J*=7.8 Hz, CH=*CH*–CH), 6.40 (d, *J*=15.9 Hz, Ar*CH*=CH), 6.58–6.68 (m, 1H, *CH-pyrrole*), 7.10–7.34 (m, 5H, Ar), 7.92 (br s, 1H, NH). ^{13}C NMR (measured in a mixture with **4af**): δ=19.7, 36.3, 104.3, 108.4, 117.0, 126.3, 127.5, 128.4, 128.6, 128.7, 129.5, 133.9. Compound **4af**: ^{1}H NMR (measured in a mixture with **3af**): δ=1.65 (ddd, *J*=6.4 Hz, *J*=1.5 Hz, *J*=0.7 Hz, 3H, CH_3CH), 4.56 (d, *J*=7.7 Hz, 1H, Ar*CH*), 5.46 (dqd, *J*=15.0 Hz, *J*=6.4 Hz, *J*=1.0 Hz, CH*CH*=CH), 5.71–5.85 (m, 2H, CH=*CH*CH$_3$, *CH-pyrrole*), 6.05–6.13 (m, 1H, *CH-pyrrole*), 6.58–6.68 (m, 1H, *CH-pyrrole*), 7.10–7.34 (m, 5H, Ar) 7.75 (br s, 1H, NH). IR (**3af**/**4af**, film): ν=3432, 3025, 2967, 2930, 1561, 1493, 1449, 1115, 1093, 1207, 967 cm^{-1}. GC–MS (EI): t_R (**4af**)=8.5; *m*/*z* (%)=197 (94) [M$^+$], 182 (42), 156 (58), 128 (74), 115 (100); t_R (**3af**)=9.3; *m*/*z* (%)=197 (94) [M$^+$], 182 (80), 115 (100). ESHRMS: calcd for $C_{14}H_{16}N$: 198.1283. Found: 198.1275.

4.3.7. 5-((*E*)-1,3-Diphenylallyl)-2-methylfuran (3ba). Pale yellow oil. ^{1}H NMR: δ=2.24 (s, 3H, CH_3), 4.84 (d, *J*=7.2 Hz, 1H, CH=CH*CH*Ar), 5.88–5.99 (m, 2H, =*CH-furan*), 6.38 (d, *J*=15.9 Hz, 1H, Ar*CH*=CH), 6.56 (dd, *J*=15.9 Hz, *J*=7.2 Hz, 1H, ArCH=*CH*CH), 7.16–7.40 (m, 10H, Ar). ^{13}C NMR: δ=13.7, 48.6, 106.2, 107.6, 126.5, 126.9, 127.5, 128.4, 128.6, 128.7, 130.2, 131.5, 137.2, 141.5, 151.5, 154.4. IR (pellets): ν=3025, 2885, 1598, 1556, 1494, 1450, 1216, 1154, 1027, 961 cm^{-1}. GC–MS (EI): t_R=11.7; *m*/*z* (%)=274 (80) [M$^+$], 231 (48), 215 (42), 192 (78), 115 (100). Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61; Found: C, 87.75; H, 6.68.

4.3.8. 1-((*E*)-1,3-Diphenyl-2-propenyl)-2,4-dimethoxybenzene (3bb). Pale yellow oil. ^{1}H NMR: δ=3.75 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 5.22 (d, *J*=7.1 Hz, 1H, CH=CH*CH*Ar), 6.25 (d, *J*=15.9 Hz, 1H, Ar*CH*=CH), 6.42–6.50 (m, 2H, Ar), 6.66 (dd, *J*=15.9 Hz, *J*=7.0 Hz, 1H, ArCH=*CH*CH), 7.07 (d, *J*=8.9 Hz, 1H, Ar), 7.15–7.40 (m, 10H, Ar). ^{13}C NMR: δ=46.6, 55.4, 55.6, 99.0, 104.2, 124.5, 126.2, 126.4, 127.2, 128.3, 128.6, 128.7, 130.0, 130.9, 132.9, 137.7, 143.9, 158.0, 159.6. IR (pellets): ν=3024, 2999, 2934, 2833, 1610, 1586, 1503, 1451, 1292, 1260, 1207, 1176, 1156, 1116, 1035, 969 cm^{-1}. GC–MS (EI): t_R=18.8; *m*/*z* (%)=330 (10) [M$^+$], 192 (28), 165 (44), 115 (48), 91 (77), 77 (100). ESHRMS: calcd for $C_{23}H_{23}O_2$: 331.1698. Found: 331.1701.

4.3.9. 1-((*E*)-1,3-Diphenyl-2-propenyl)-4-methoxy-benzene (3bc).[25] Pale yellow oil. ^{1}H NMR: δ=3.79 (s, 3H, OCH_3), 4.95 (d, *J*=7.3 Hz, 1H, CH=CH*CH*Ar), 6.46 (d, *J*=15.8 Hz, 1H, Ar*CH*=CH), 6.80 (dd, *J*=15.8 Hz, *J*=7.4 Hz, 1H, ArCH=*CH*CH), 6.94–7.00 (m, 2H, Ar), 7.22–7.50 (m, 12H).

4.3.10. 2-((*E*)-1,3-Diphenyl-2-propenyl)benzofuran (3bd). White solid, mp 85–87 °C. ^{1}H NMR: δ=4.96 (d, *J*=7.3 Hz, 1H, CH=CH*CH*Ar), 6.34–6.46 (m, 2H, Ar*CH*=CH, O–C=*CH*), 6.58 (dd, J=15.8 Hz, J=7.3 Hz, ArCH=*CH*), 7.10–7.46 (m, 14H, Ar). ^{13}C NMR: δ=48.8, 104.2, 111.3, 120.8, 122.8, 123.8, 126.6, 127.3, 127.8, 128.5, 128.7 (2C), 128.8, 129.1, 132.4, 137.0, 140.5, 155.2, 159.4. IR (pellets): ν=3080, 3028, 3022, 2924, 2875, 2850, 1568, 1579, 1490, 1453, 1254, 1163, 1070, 972, 960 cm^{-1}. GC–MS (EI): t_R=18.3; m/z (%)=310 (32) [M$^+$], 231 (42), 202 (42), 178 (72), 115 (60), 77 (100). Anal. Calcd for ($C_{23}H_{18}O$): C, 89.00; H, 5.85; Found: C, 88.59; H, 5.87.

4.3.11. 3-((*E*)-1,3-Diphenyl-2-propenyl)-1*H*-indole (3be).[26] Pale yellow oil. ^{1}H NMR: δ=5.11 (d, J=7.3 Hz, 1H, CH=CH*CH*Ar), 6.43 (d, J=15.9 Hz, 1H, Ar*CH*=CH), 6.72 (dd, J=15.8 Hz, J=7.3 Hz, ArCH=*CH*CH), 6.86–6.89 (m, 1H, *CH*–NH), 6.96–7.06 (m, 1H, Ar), 7.10–7.46 (m, 13H, Ar), 7.97 (br s, 1H, NH).

4.3.12. 2-((*E*)-1,3-Diphenyl-2-propenyl)-1*H*-pyrrole (3bf). White solid, mp 71–73 °C. ^{1}H NMR: δ=4.86 (d, J=7.5 Hz, 1H, CH=CH*CH*Ar), 5.94–5.99 (m, 1H, *CH-pyrrole*), 6.17 (m, 1H, *CH-pyrrole*), 6.42 (d, J=15.8 Hz, 1H, Ar*CH*=CH), 6.59 (dd, J=15.8 Hz, J=7.5 Hz, ArCH=*CH*CH), 6.67–6.72 (m, 1H, *CH-pyrrole*), 7.16–7.40 (m, 10H, Ar), 7.85 (br s, 1H, NH). ^{13}C NMR: δ=48.1, 106.8, 108.4, 117.4, 126.5, 127.0, 127.6, 128.5, 128.7, 128.8, 131.3, 133.0, 137.1, 142.3. IR (pellets): ν=3386, 3083, 3058, 3029, 1599, 1552, 1491, 1449, 1415, 1396, 1271, 1200, 1112, 1095, 1062, 1027, 977, 959 cm^{-1}. GC–MS (EI): t_R=12.7; m/z (%)=259 (95) [M$^+$], 180 (67), 115 (100), 77 (98). ESHRMS: calcd for $C_{19}H_{18}N$: 260.1447. Found: 259.1439.

4.3.13. (*E*)-1-Phenyl-3-(2-methylfuran-5-yl)-1-propene (3ca) and 3-phenyl-3-(2-methylfuran-5-yl)-1-propene (4ca).[1b] Colorless oil. Compound **3ca**: ^{1}H NMR (measured in a mixture with **4ca**): δ=2.17 (s, 3H, *CH*$_3$), 3.41 (d, J=6.5 Hz, 2H, CH=CH*CH*$_2$), 5.64–5.88 (m, 2H, =*CH-furan*), 6.00–6.28 (m, 1H, ArCH=*CH*CH$_2$), 6.40 (d, J=15.8 Hz, 1H, Ar*CH*=CH), 7.02–7.32 (m, 5H, Ar). Compound **4ca**: ^{1}H NMR (measured in a mixture with **3ca**): δ=2.15 (s, 3H, *CH*$_3$), 4.59 (d, J=7.0 Hz, 1H, Ar*CH*CH=CH$_2$), 4.95 (td, J=17.0 Hz, J=1.4 Hz, 1H, CH=*CH*$_2$), 5.09 (td, J=10.1 Hz, J=1.4 Hz, 1H, CH=*CH*$_2$), 5.64–5.88 (m, 2H, =*CH-furan*), 6.00–6.28 (m, 1H, ArCH*CH*=CH$_2$), 7.02–7.32 (m, 5H, Ar).

4.3.14. (*E*)-1-Phenyl-3-(2,4-dimethoxyphenyl)-1-propene (3cb) and 3-phenyl-3-(2,4-dimethoxyphenyl)-1-propene (4cb).[27] Colorless oil. Compound **3cb**: ^{1}H NMR (measured in a mixture with **4cb**): δ=3.45 (d, J=5.0 Hz, 2H, CH=CH*CH*$_2$Ar), 3.76 (s, 3H, O*CH*$_3$), 3.78 (s, 3H, O*CH*$_3$), 6.30–6.48 (m, 3H, Ar*CH*=*CH*, Ar), 7.00–7.40 (m, 6H, Ar). ^{13}C NMR (measured in a mixture with **4cb**): δ=32.9, 55.3, 55.4, 98.6, 104.0, 121.0, 126.1, 126.9, 128.5, 129.4, 130.2, 130.4, 137.9, 158.2, 159.5. Compound **4cb**: ^{1}H NMR (measured in a mixture with **3ca**): δ=3.70 (s, 3H, O*CH*$_3$), 3.80 (s, 3H, O*CH*$_3$), 4.82–2.96 (m, 1H, CH=*CH*$_2$), 5.06 (d, J=6.6 Hz, 1H, Ar*CH*CH=CH$_2$), 5.12–5.20 (m, 1H, CH=*CH*$_2$), 6.30–6.48 (m, 3H, ArCH*CH*=CH$_2$, Ar), 7.00–7.40 (m, 6H, Ar). IR (**3cb/4cb**, film): ν=3025, 2936, 2834, 1614, 1588, 1505, 1465, 1291, 1208, 1156, 1038, 967 cm^{-1}. GC–MS (EI): t_R (**4cb**)=10.2; m/z (%)=254 (15) [M$^+$], 138 (62), 115 (88), 91 (76), 77 (100); t_R (**3cb**)=11.6; m/z (%)=254 (100) [M$^+$], 223 (48), 178 (40), 138 (44), 115 (100). ESHRMS: calcd for $C_{17}H_{19}O_2$: 255.1285. Found: 255.1383.

4.3.15. (*E*)-1-Phenyl-3-(4-methoxyphenyl)-1-propene (3cc).[1b] Colorless oil. ^{1}H NMR: δ=3.47 (d, J=5.9 Hz, 2H, CH=CH*CH*$_2$Ar), 3.77 (s, 3H, O*CH*$_3$), 6.24–6.48 (m, 2H, Ar*CH*=*CH*), 6.84 (d, J=8.3 Hz, 2H, Ar), 7.10–7.40 (m, 7H, Ar).

4.3.16. (*E*)-1-Phenyl-3-(benzofuran-2-yl)-1-propene (3cd). Pale yellow oil. ^{1}H NMR: δ=3.70 (d, J=6.7 Hz, 2H, CH=CH*CH*$_2$Ar), 6.33 (dt, J=15.8 Hz, J=6.7 Hz, ArCH=*CH*), 6.39–6.43 (m, 1H, O–C=*CH*), 6.52 (d, J=15.9 Hz, Ar*CH*=CH), 7.08–7.50 (m, 9H, Ar). ^{13}C NMR: δ=32.3, 102.9, 111.0, 120.6, 122.7, 123.6, 124.7, 126.4, 127.6, 128.7, 129.0, 132.8, 137.2, 155.0, 157.2. IR (film): ν=3058, 3028, 1598, 1495, 1454, 1422, 1253, 1163, 965 cm^{-1}. GC–MS (EI): t_R=11.1; m/z (%)=234 (100) [M$^+$], 157 (30), 131 (45), 128 (67), 115 (52), 102 (30), 77 (57). Anal. Calcd for ($C_{17}H_{14}O$): C, 87.15; H, 6.02; Found: C, 87.33; H, 6.14.

4.3.17. 2-Benzhydryl-5-methylfuran (3da).[23b] Colorless oil. ^{1}H NMR: δ=2.23 (s, 3H, *CH*$_3$), 5.43 (s, 1H, Ar*CH*), 5.78 (d, J=3.0 Hz, 1H, =*CH-furan*), 5.88 (d, J=3.0 Hz, 1H, =*CH-furan*), 7.12–7.42 (m, 10H, Ar).

4.3.18. 1-((2,4-Dimethoxyphenyl)diphenylmethane (3db). White solid, mp 120–124 °C. ^{1}H NMR: δ=3.60 (s, 3H, O*CH*$_3$), 3.70 (s, 3H, O*CH*$_3$), 5.83 (s, 1H, Ar*CH*), 6.35 (dd, J=8.4 Hz, J=2.4 Hz, 1H, Ar), 6.43 (d, J=2.3 Hz, 1H, Ar), 6.73 (d, J=8.4 Hz, 1H, Ar), 7.00–7.38 (m, 10H, Ar). ^{13}C NMR: δ=49.3, 55.3, 55.6, 98.7, 103.8, 125.3, 126.1, 128.2, 129.5, 130.9, 144.3, 158.1, 159.5. IR (pellets): ν=3056, 2951, 2830, 1611, 1585, 1501, 1467, 1451, 1290, 1259, 1207, 1117, 1045, 835 cm^{-1}. GC–MS (EI): t_R=13.5; m/z (%)=304 (100) [M$^+$], 289 (25), 273 (22), 227 (73), 165 (53), 91 (100). ESHRMS: calcd for $C_{21}H_{21}O_2$: 305.1542. Found: 305.1540.

4.3.19. 1-((4-Methoxyphenyl)diphenylmethane (3dc).[28] White solid, mp 55–57 °C. ^{1}H NMR: δ=3.74 (s, 3H, OCH$_3$), 5.49 (s, 1H, Ar*CH*), 6.77–6.85 (m, 2H, Ar), 6.98–7.32 (m, 12H, Ar).

4.3.20. 2-Benzhydrylbenzofuran (3dd). White solid, mp 110–114 °C. ^{1}H NMR: δ=5.85 (s, 1H, Ar*CH*), 6.54 (s, O–C=*CH*), 7.36–7.86 (m, 14H, Ar). ^{13}C NMR: δ=51.5, 105.8, 111.3, 120.8, 122.8, 123.9, 127.1, 128.6, 128.7, 129.0, 141.2, 155.2, 160.0. IR (pellets): ν=3064, 3027, 1598, 1582, 1494, 1451, 1252, 1163, 1148, 1130, 1104, 1079, 1029, 1004, 957 cm^{-1}. GC–MS (EI): t_R=12.3; m/z (%)=284 (17) [M$^+$], 207 (62), 178 (90), 77 (100). Anal. Calcd for ($C_{21}H_{16}O$): C, 88.70; H, 5.67; Found: C, 88.60; H, 5.77.

4.3.21. 2-(1-(4-Methoxyphenyl)ethyl)-5-methylfuran (3ea).[23b] Pale yellow oil. ^{1}H NMR: δ=1.53 (d, J=7.2 Hz, 3H, ArCH*CH*$_3$), 2.21 (s, 3H, *CH*$_3$*-furan*), 3.76 (s, 3H, O*CH*$_3$), 4.01 (q, J=7.1 Hz, Ar*CH*CH$_3$), 5.85–5.87 (m, 2H, =*CH-furan*), 6.83 (d, J=8.7 Hz, 2H, Ar), 7.13 (d, J=8.7 Hz, 2H, Ar).

4.3.22. 1-Methoxy-4-(1-(2,4-dimethoxyphenyl)ethyl)-benzene (3eb).[29] Colorless oil. ^{1}H NMR: δ=1.52 (d, *J*=7.2 Hz, 3H, CH*CH*$_3$), 3.75 (s, 3H, O*CH*$_3$), 3.76 (s, 3H, O*CH*$_3$), 3.77 (s, 3H, O*CH*$_3$), 4.43 (q, *J*=7.2 Hz, 1H, *CH*CH$_3$), 6.39–6.46 (m, 2H, Ar), 6.80 (d, *J*=8.3 Hz, 2H, Ar), 7.01 (d, *J*=9.1 Hz, 1H, Ar), 7.14 (d, *J*=8.3 Hz, 2H, Ar).

4.3.23. 1,1-Bis(4-methoxyphenyl)ethane (3ec).[30] White solid, mp 67–69 °C. ^{1}H NMR: δ=1.58 (d, *J*=7.1 Hz, 3H, CH*CH*$_3$), 3.77 (s, 6H, O*CH*$_3$), 4.06 (q, *J*=7.1 Hz, 1H, *CH*CH$_3$), 6.82 (d, *J*=8.7 Hz, 4H, Ar), 7.12 (d, *J*=8.7 Hz, 4H, Ar).

4.3.24. 2-(1-(4-Methoxyphenyl)ethyl)benzofuran (3ed). White solid, mp 43–45 °C. ^{1}H NMR: δ=1.66 (d, *J*=7.2 Hz, 3H, CH*CH*$_3$), 3.73 (s, 3H, O*CH*$_3$), 4.19 (q, *J*=7.1 Hz, 1H, *CH*CH$_3$), 6.37–6.41 (m, 1H, O–C=*CH*), 6.85 (d, *J*=8.7 Hz, 2H, Ar), 7.14–7.24 (m, 4H, Ar), 7.36–7.52 (m, 2H, Ar). ^{13}C NMR: δ=20.6, 38.9, 55.3, 102.0, 111.1, 114.1, 120.6, 122.6, 123.5, 128.6, 128.8, 135.5, 155.0, 158.5, 162.6. IR (film): ν=2965, 2933, 2835, 1610, 1584, 1512, 1454, 1377, 1299, 1265, 1248, 1175, 1147, 1108, 1069, 1057, 1031, 1009, 934 cm^{-1}. GC–MS (EI): t_R=11.1; *m/z* (%)=252 (35) [M$^+$], 237 (100), 165 (30). Anal. Calcd for ($C_{17}H_{16}O_2$): C, 80.93; H, 6.39; Found: C, 80.71; H, 6.41.

4.3.25. 3-(1-(4-Methoxyphenyl)ethyl)-1*H*-indole (3ee). White solid, mp 137–140 °C. ^{1}H NMR: δ=1.67 (d, *J*=7.1 Hz, 3H, CH*CH*$_3$), 3.76 (s, 3H, O*CH*$_3$), 4.32 (q, *J*=7.1 Hz, *CH*CH$_3$), 6.75–6.85 (m, 2H, Ar), 6.95–7.05 (m, 2H, Ar), 7.10–7.23 (m, 3H, Ar), 7.30–7.40 (m, 2H, Ar), 7.93 (br s, 1H, NH). ^{13}C NMR: δ=22.7, 36.2, 55.3, 111.2, 113.8, 119.3, 119.8, 121.2, 121.8, 122.0, 127.0, 128.5, 136.8, 139.2, 157.8. IR (pellets): ν=3367, 2970, 2863, 1608, 1509, 1459, 1441, 1424, 1338, 1264, 1237, 1178, 1101, 1024 cm^{-1}. GC–MS (EI): t_R=13.4; *m/z* (%)=251 (37) [M$^+$], 236 (100), 192 (27). ESHRMS: calcd for $C_{17}H_{18}NO$: 252.1388. Found: 251.1383.

4.3.26. 2-(1-(4-Methoxyphenyl)ethyl)-1*H*-pyrrole (3ef).[31] Pale yellow oil. ^{1}H NMR: δ=1.49 (d, *J*=7.2 Hz, 3H, CH*CH*$_3$), 3.68 (s, 3H, O*CH*$_3$), 3.94 (q, *J*=7.2 Hz, 1H, *CH*CH$_3$), 5.95–6.00 (m, 1H, *CH-pyrrole*), 6.03–6.09 (m, 1H, *CH-pyrrole*), 6.49–6.55 (m, 1H, *CH-pyrrole*), 6.70–6.79 (m, 2H, Ar), 6.97–7.05 (m, 2H, Ar), 7.60 (br s, 1H, NH).

4.3.27. Preparation of (benzhydryloxy)diphenylmethane (7d).[32] A 50 mL round-bottomed flask was charged with benzhydrol (184 mg, 1.0 mmol), CH_2Cl_2 (1 mL), and CF_3SO_3H (4 μL, 0.05 mmol) at 0 °C. The mixture was heated (oil bath, 50 °C) for 1 h. After cooling to room temperature, saturated $NaHCO_3$ (5 mL) was added and the mixture was extracted with Et_2O (5×5 mL). Organic phase was dried over $MgSO_4$, filtered, solvent was removed under reduced pressure, and the product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 98/2, then petroleum ether/ethyl acetate 95/5) to yield **7d** (152 mg, 0.43 mmol, 87%). ^{1}H NMR: δ=5.32 (s, 2H, *CH*–O), 7.12–7.34 (m, 20H, Ar).

References and notes

1. (a) Nay, B.; Collet, M.; Lebon, M.; Chèze, C.; Vercauteren, J. *Tetrahedron Lett.* **2002**, *43*, 2675–2678; (b) Malkov, A. V.; Davis, S. L.; Baxendale, I. R.; Mitchell, W. L.; Kočovský, P. *J. Org. Chem.* **1999**, *64*, 2751–2764; (c) Malkov, A. V.; Spoor, P.; Vinader, V.; Kočovský, P. *J. Org. Chem.* **1999**, *64*, 5308–5311.
2. (a) Noji, M.; Ohno, T.; Fuji, K.; Futaba, N.; Tajima, H.; Ishii, K. *J. Org. Chem.* **2003**, *68*, 9340–9347; (b) Shiina, I.; Suzuki, M. *Tetrahedron Lett.* **2002**, *43*, 6391–6394; (c) Kotsuki, H.; Oshisi, T.; Inoue, M. *Synlett* **1998**, 255–256; (d) Tsuchimoto, T.; Tobita, K.; Hiyama, T.; Fukuzawa, S.-I. *J. Org. Chem.* **1997**, *62*, 6997–7005.
3. Choudhury, J.; Podder, S.; Roy, S. *J. Am. Chem. Soc.* **2005**, *127*, 6162–6163.
4. Tsukada, N.; Yagura, Y.; Sato, T.; Inoue, Y. *Synlett* **2003**, 1431–1434.
5. Selected recent examples: (a) Okumura, K.; Yamashita, K.; Hirano, M.; Niwa, M. *J. Catal.* **2005**, *234*, 300–307; (b) Rác, B.; Mulas, G.; Csongrádi, A.; Lóki, K.; Molnár, Á. *Appl. Catal.* **2005**, *282*, 255–265; (c) Mantri, K.; Komura, K.; Kubota, Y.; Sugi, Y. *J. Mol. Catal. A: Chem.* **2005**, *236*, 168–175; (d) Macquarrie, D. J.; Tavener, S. J.; Harmer, M. A. *Chem. Commun.* **2005**, 2363–2365; (e) Salavati-Niasari, M.; Hasanalian, J.; Najafian, H. *J. Mol. Catal. A: Chem.* **2004**, *209*, 209–214; (f) Shrigadi, N. B.; Shinde, A. B.; Samant, S. D. *Appl. Catal.* **2003**, *252*, 23–35; (g) Hu, X.; Chuah, G. K.; Jaenicke, S. *Appl. Catal.* **2001**, *217*, 1–9; (h) Choudary, V. R.; Jana, S. K. *J. Catal.* **2001**, *201*, 225–235; (i) Deshpande, A. B.; Bajpai, A. R.; Samant, S. D. *Appl. Catal.* **2001**, *209*, 229–235; (j) Smith, K.; Pollaud, G. M.; Matthews, I. *Green Chem.* **1999**, *1*, 75–81.
6. (a) Mertins, K.; Iovel, I.; Kischel, J.; Zapf, A.; Beller, M. *Adv. Synth. Catal.* **2006**, *348*, 691–695; (b) Iovel, I.; Mertins, K.; Kischel, J.; Zapf, A.; Beller, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3913–3917; (c) Mertins, K.; Iovel, I.; Kishel, J.; Zapf, A.; Beller, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 238–242.
7. (a) Anastas, P. T.; Warner, J. C. *Green Chemistry, Theory and Practice*; Oxford University Press: Oxford, 1998; (b) Lancaster, M. *Green Chemistry, An Introductory Text*; Royal Society of Chemistry: Cambridge, 2002.
8. (a) Rosenfeld, D. C.; Shekhar, S.; Takemiya, A.; Utsunomiya, M.; Hartwig, J. F. *Org. Lett.* **2006**, *8*, 4179–4182; (b) Li, Z.; Zhang, J.; Brouwer, C.; Yang, C.-G.; Reich, N. W.; He, C. *Org. Lett.* **2006**, *8*, 4175–4178; (c) Motokura, K.; Nakagiri, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Jitsukawa, K.; Kaneda, K. *Org. Lett.* **2006**, *8*, 4617–4620.
9. Zhang, L.; Sun, J.; Kozmin, S. A. *Tetrahedron* **2006**, *62*, 11371–11380.
10. Kotsuki, H.; Ohishi, T.; Inoue, M.; Kojima, T. *Synthesis* **1999**, 602–606.
11. Wang, B.-Y.; Jiang, R.-.S.; Li, J.; Shi, M. *Eur. J. Org. Chem.* **2005**, 4002–4008.
12. Fukuzawa, S.-i.; Tsuchimoto, T.; Hiyama, T. *J. Org. Chem.* **1997**, *62*, 151–156.
13. Hashmi, A. S. K.; Schwarz, L.; Rubenbauer, P.; Blanco, M. C. *Adv. Synth. Catal.* **2006**, *348*, 705–708.
14. Shirakawa, S.; Kobayashi, S. *Org. Lett.* **2006**, *8*, 4939–4942.
15. (a) Anderson, L. L.; Arnold, J.; Bergman, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 14542–14543; (b) Cherian, A. E.; Domski, G. J.; Rose, J. M.; Lobkovsky, E. B.; Coates, G. W. *Org. Lett.* **2005**, *7*, 5135–5137.
16. Sarvari, M. H.; Sharghi, H. *Helv. Chim. Acta* **2005**, *88*, 2282–2287.
17. Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2605–2609.

18. Sanz, R.; Martínez, A.; Álvarez-Gutiérrez, J. M.; Rodríguez, F. *Eur. J. Org. Chem.* **2006**, 1383–1386.
19. Darbeau, R. W.; White, E. H. *J. Org. Chem.* **1997**, *62*, 8091–8094.
20. Espeel, P. H.; Janssens, B.; Jacobs, P. A. *J. Org. Chem.* **1993**, *58*, 7688–7693.
21. Sanz, R.; Martínez, A.; Miguel, D.; Álvarez-Gutiérrez, J. M.; Rodríguez, F. *Adv. Synth. Catal.* **2006**, *348*, 1841–1845.
22. Caution: direct addition of triflic acid to 2-methylfuran gives a violent reaction, see Section 4.3 for adapted procedure.
23. (a) For 2-alkylated furans, see Refs. 1b and 6b; (b) For 4-alkylated 1,3-dimethoxybenzenes, see: Hofmann, M.; Hampel, N.; Kanzian, T.; Mayr, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 5402–5405; (c) For 4-alkylated anisoles, see Ref. 1b; (d) For 2-alkylated benzofurans, see: Jaouhari, R.; Dixneuf, P. H. *Inorg. Chim. Acta* **1988**, *145*, 179–180; Colas, C.; Goeldner, M. *Eur. J. Org. Chem.* **1999**, 1357–1366.
24. (a) For 3-alkylated indoles, see Refs. 1b and 21; (b) For 2-alkylated pyrroles, see: Jorapur, Y. R.; Lee, C.-H.; Chi, D. Y. *Org. Lett.* **2005**, *7*, 1231–1234 and references therein.
25. Kabalka, G. W.; Dong, G.; Venkataiah, B. *Org. Lett.* **2003**, *5*, 893–895.
26. Bandini, M.; Melloni, A.; Umani-Ronchi, A. *Org. Lett.* **2004**, *6*, 3199–3202.
27. Bissel, P.; Nazih, A.; Sablong, R.; Lepoittevin, J.-P. *Org. Lett.* **1999**, *1*, 1283–1285.
28. Newcomb, M.; Varick, T. R.; Goh, S.-H. *J. Am. Chem. Soc.* **1990**, *112*, 5186–5193.
29. Ceraulo, L.; Filizzola, F.; Fontana, G.; Lamartina, L.; Natoli, M. *Arkivoc* **2002**, *11*, 123–141.
30. Yonezawa, N.; Hino, T.; Shimizu, M.; Matsuda, K.; Ikeda, T. *J. Org. Chem.* **1999**, *64*, 4179–4182.
31. Schumacher, D. P.; Hall, S. S. *J. Org. Chem.* **1981**, *46*, 5060–5064.
32. Miller, K. J.; Abu-Omar, M. M. *Eur. J. Org. Chem.* **2003**, 1294–1299.