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Scope and limitation of the nickel-catalyzed coupling reaction between lithium borates and mesylates

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Abstract

Coupling reaction of aryl borates and mesylates derived from phenols and enols was studied. Mesylates with an electron-withdrawing group or ring were highly reactive at room temperature in the presence of $NiCl_2(PPh_3)_2$ to furnish the coupling products in good yields. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Biaryl; Borate; Coupling; Mesylate; Nickel-catalyst

1. Introduction

Aryl bromides and iodides **1** (X = Br, I) are substrates usually employed in the transition metal-catalyzed coupling reaction with organometallics **2** (Eq. (1)). The reaction has provided successful results in organic synthesis and material science, and is now recognized as one of the most reliable carbon–carbon bond forming reactions [1]. Although aryl halides of a simple structure are available by several methods or directly from commercial sources, preparation of aryl halides with a complex structure encounters difficulty. Phenol derivatives such as sulfonates and phosphonates are attractive alternatives for the halides as they can be prepared under milder conditions

$$\underset{\mathbf{1}}{\text{Ar–X}} + \underset{\mathbf{2}}{\text{R–m}} \xrightarrow[\text{cat.}]{} \underset{\mathbf{3}}{\text{Ar–R}} \quad (1)$$

X:Br, I, OTf (standard substrates)

X:OMs, OTs (substrates of the present study)

than halides, and furthermore phenols allow flexibility in their preparation and manipulation. Among them, triflates **1** (X = OTf) have been studied well, and their high reactivity in the coupling reaction has produced successful applications [2,3]. However, the unstable nature of the triflates and higher price of the triflating reagents reduce the advantage of using triflates in the coupling reaction, thus prompting an investigation of alternative sulfonates.

Aryl mesylates and tosylates are convenient substitutes for triflates. So far, mesylate couplings were first published by Percec et al. [4], then by Kobayashi and Mizojiri [5], and recently by Miyaura and coworkers [6]. Percec and Miyaura studied aryl boronic acids as organometallics **2**, the reagents developed by Suzuki and Miyaura for coupling reactions using the various types of substrates [7–9]. Among the palladium and nickel complexes Percec examined, the latter showed a somewhat higher catalytic activity, though the yields are moderate in most cases with the best ligand of dppf under forcing conditions of the higher temperatures (65 °C in THF or 90–100 °C in dioxane). Later, Miyaura improved the yields and provided a number of entries of the mesylate coupling, though the high reaction temperature was left unimproved. According to Percec, the results are ascribed to the slow oxidative addition of the mesylates **1** (X = OMs) to Ni(0) complexes. However, there is likely to be slow transmetalation with the boronic acids, which is responsible for the requirement of the high reaction temperature.

Recently, we have found that lithium organoborates **5** with a transferring aryl or alkenyl group (R^T) and a dummy methyl ligand are more reactive reagents than the classical reagents in the coupling with allyl esters **4** (Scheme 1) [10]. Nickel complexes catalyze the reaction much more efficiently than palladium complexes, and overnight stirring at or below room temperature is

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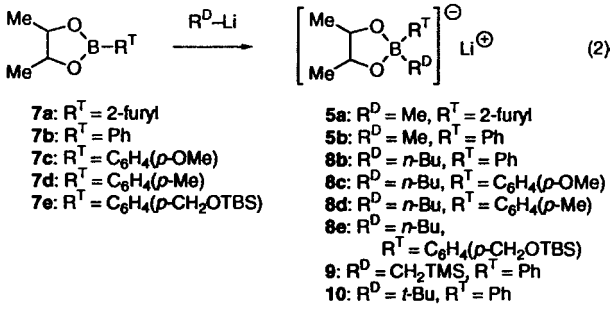
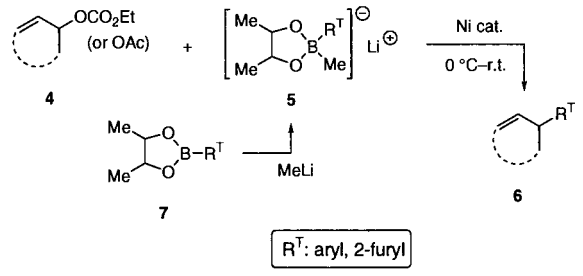
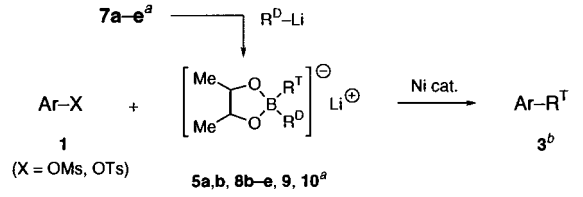
sufficient for completion of the allylic coupling. In addition, the neutral and stable nature of boronate esters **7**, the precursors of **5**, allows easy purification by chromatography and/or distillation and storage for a long period of time without any decomposition. We envisioned that the inherent high reactivity of borates **5** coupled with a nickel-catalyst would accelerate the transmetalation in the coupling reaction of mesylates and tosylates derived from phenols and enols. As communicated previously [5], the coupling was found to proceed at room temperature with the finding that the modified borates **8** possessing the dummy Bu ligand have the highest reactivity, whereas the original borates **5** with the Me ligand show rather moderate reactivity (Scheme 2, Fig. 1, Eq. (2)). These results indicate that the transmetalation is the rate-determining step in the mesylate coupling as we have proposed above. Herein, we report a full account of the coupling reaction.





Scheme 1. Allylic coupling with the highly reactive borates **5**.



Scheme 2. Summary of the present study. [a]R^T and R^D in the boronates **7a**–**e** and borates **5a**,**b**, **8b**–**e**, **9**, **10**: see Eq. (2); [b]**3a**: *p*-$MeO_2CC_6H_4$–(2-furyl), **3b**: *p*-$MeO_2CC_6H_4$–C_6H_5. For other **3**, see Table 2.

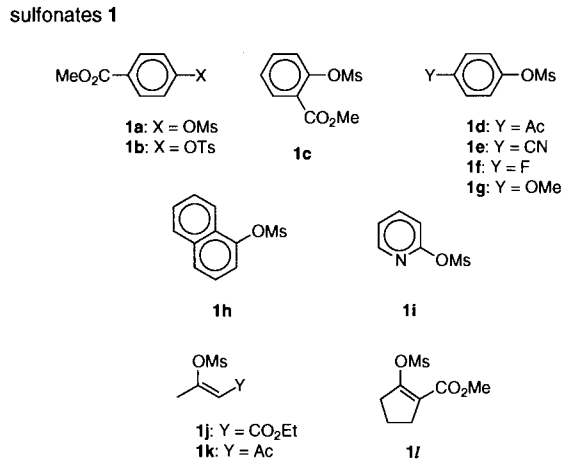
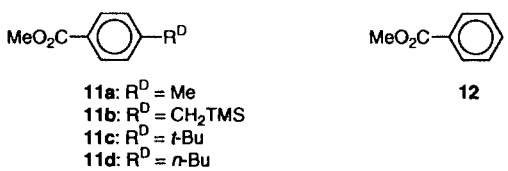


Fig. 1. Sulfonates **1** examined in Scheme 2.

2. Results and discussion

Initially, *p*-methoxycarbonylphenyl mesylate (**1a**) [11] was selected as a representative sulfonate, and the coupling was investigated with the borates **5a** (R^T = 2-furyl) and **5b** (R^T = Ph). Methyllithium (three equivalents) was added to a mixture of $NiCl_2(PPh_3)_2$ or $NiCl_2$(dppf) (10 mol%) and the boronate precursor **7a** (R^T = 2-furyl) or **7b** (R^T = Ph) (four equivalents) in THF to generate the Ni(0) catalyst and borate **5a** or **5b** (15–30 min, 0 °C–room temperature), and, after addition of **1a**, reaction was carried out at room temperature overnight. Furylborate **5a** underwent smooth coupling with mesylate **1a** furnishing *p*-$MeO_2CC_6H_4$–(2-furyl) (**3a**) [12] in good yield (Table 1, entries 1 and 2). To the best of our knowledge, this is the first example that the oxidative addition of mesylates to the Ni(0) species and the subsequent transmetalation proceeded at room temperature at reasonable rates. On the other hand, phenylborate **5b** under similar conditions to **1a** resulted in incomplete coupling and poor product-selectivity yielding *p*-$MeO_2CC_6H_4$–C_6H_5 (**3b**) 9e in 24–32% yield and the by-product **11a** in fairly large quantity (entries 3 and 4). Attempted reactions at higher temperatures and/or in other solvents such as DMF, MeCN did not improve the reactivity or the product-selectivity. We imputed the unsatisfying result to the poor transmetalating ability of the phenyl group from boron to nickel.



Since the reactivity of the borates in the allylic coupling was raised substantially by a more electron-donating dummy alkyl ligand than the Me ligand, phenylborates with the CH_2TMS, *t*-Bu, or *n*-Bu ligand

Table 1
Nickel-catalyzed reaction of sulfonates (**1a** or **1b**) with furylborate (**5a**) or phenylborate (**5b**, **8b**, **9**, or **10**) [a]

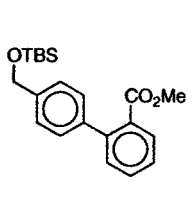
Entry	Sulfonate	Borate [b]			Ni catalyst	Temperature (°C)	Time (h)	Yield [c] of product **3** [e]		Ratio [d]
		Number	R^D	R^T						**3**:**11** [f]
1	**1a**	**5a**	Me	2-furyl	$NiCl_2(PPh_3)_2$	20	11	**3a**	82	100:0
2	**1a**	**5a**	Me	2-furyl	$NiCl_2$(dppf)	20	14	**3a**	91	100:0
3	**1a**	**5b**	Me	Ph	$NiCl_2(PPh_3)_2$	20	11	**3b**	24 [g]	57:43
4	**1a**	**5b**	Me	Ph	$NiCl_2$(dppf)	20	11	**3b**	32 [g]	55:45
5	**1a**	**9**	CH_2TMS	Ph	$NiCl_2(PPh_3)_2$	20	12	**3b**	84	90:10
6	**1a**	**10**	*t*-Bu	Ph	$NiCl_2(PPh_3)_2$	20	12	**3b**	40	45:55
7	**1a**	**8b**	*n*-Bu	Ph	$NiCl_2(PPh_3)_2$	20	12	**3b**	95	>95:<5
8 [h]	**1a**	**8b**	*n*-Bu	Ph	$NiCl_2(PPh_3)_2$	20	12	**3b**	93	>95:<5
9	**1a**	**8b**	*n*-Bu	Ph	$NiCl_2$(dppf)	20	12	**3b**	60 [g]	>95:<5
10	**1a**	**8b**	*n*-Bu	Ph	$NiCl_2(PPh_3)_2$	60	6	**3b**	90	>95:<5
11	**1b**	**5a**	Me	2-furyl	$NiCl_2(PPh_3)_2$	20	11	**3a**	21 [g]	50:50
12	**1b**	**5a**	Me	2-furyl	$NiCl_2$(dppf)	20	14	**3a**	33 [g]	70:30
13	**1b**	**9**	CH_2TMS	Ph	$NiCl_2(PPh_3)_2$	20	12	**3b**	17 [g]	85:15
14	**1b**	**8b**	*n*-Bu	Ph	$NiCl_2(PPh_3)_2$	20	14	**3b**	83	>95:<5

[a] Reactions were carried out at room temperature overnight using the sulfonate and three equivalents of the borate in the presence of 10 mol% of the nickel-catalyst unless otherwise noted.
[b] Borates were prepared in situ from the corresponding boronate esters (**7a** or **7b**) and R^D–Li (0 °C, 15 min).
[c] Isolated yields.
[d] Determined by ^{1}H-NMR (300 MHz) spectroscopy.
[e] **3a**: *p*-$MeO_2CC_6H_4$–(2-furyl). **3b**: *p*-$MeO_2CC_6H_4$–C_6H_5.
[f] One of **11a**–**d**.
[g] Starting mesylate was recovered.
[h] Reaction was carried out with 1.5 equivalents of **8b**.

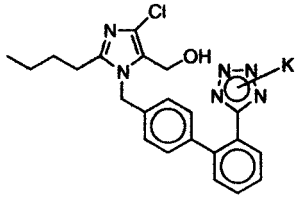
were investigated for the phenylation of mesylate **1a**. The CH_2TMS ligand considerably improved the yield and the product-selectivity (entry 5), while only the yield was increased moderately by the *t*-Bu ligand (entry 6). The best results were provided by borate **8b** with the *n*-Bu ligand, furnishing **3b** in 95% yield with high product-selectivity of **3b**–**11d** (>95:<5) (entry 7). Although the reaction was run with three equivalents of borate **8b**, similar efficiency was recorded with 1.5 equivalents of **8b** (entry 8). Regarding the catalyst, $NiCl_2(PPh_3)_2$ provided a better result than $NiCl_2$(dppf) (entry 7 vs. 9). In the examination with borate **8b**, methyl benzoate (**12**), a likely product via β-hydride elimination of the *n*-Bu ligand, was not detected by ^{1}H-NMR spectroscopy. Even at an elevated temperature the side reaction was not observed at all (entry 10).

Coupling of tosylate **1b** with furylborate **5a** and phenylborates **8b** and **9** was investigated under similar conditions described above. Among the entries examined (entries 11–14), $NiCl_2(PPh_3)_2$ showed higher catalytic activity than $NiCl_2$(dppf), and the best result was obtained with phenylborate of the *n*-Bu ligand (**8b**) (entry 14). However, tosylate **1b** was somewhat less reactive than mesylate **1a**.

Next, the best conditions explored for production of **3a** and **3b** were applied to other combinations of mesylates and borates. The aryl mesylates we investigated were **1a**, sterically more congested mesylate **1c**, phenyl mesylates with an electron-withdrawing or -donating substituent at the *p*-position (**1d**–**f**, **1g**), 1-naphthalenyl mesylate **1h**, 2-pyridyl mesylate **1i**. In addition, mesylates **1j**–**1l** derived from the enols were also studied. Results of the coupling of these mesylates with 2-furylborate **5a**, phenylborate **8b**, and/or substituted phenylborates **8c**–**e** are presented in Table 2. Reaction of mesylate **1a** with borates **8c** and **8d** proceeded at room temperature to furnish **3c** and **3d**, respectively, with good efficiency (the yield and the product-selectivity) (entries 1 and 2). The substituent (CO_2Me) near the reaction site in mesylate **1c** did not interfere with the efficiency producing **3e**–**g** (entries 3–5). Product **3g** would be a precursor of the angiotensin II receptor antagonists such as DuP 753 [13].



3g



DuP 753

Mesylates with an electron-withdrawing substituent such as acetyl (Ac) and cyano (CN) groups were shown to be good mesylates (entries 6–8) as **1a** and **1c**. On the other hand, fluorine–mesylate **1f** required a high temperature of 60 °C for the completion of the coupling (entry 9), while methoxy–mesylate **1g** was a poor sub-

strate even at 60 °C (entry 10). These results indicate that the electron-withdrawing nature is indispensable for a mesylate being a reactive substrate. With this conclusion, it is not surprising that mesylates **1h** and **1i** produced **3m** and **3o** in 93 and 91% yields, respectively (entries 11 and 12) because of the presence of the electron-withdrawing ring.

Finally, mesylates derived from enols were subjected to the reaction at room temperature overnight. The coupling products **3o** as a mixture of *Z* and *E* isomers [14], **3p** with the *E* stereochemistry [15], and **3q** were isolated in high yields (entries 13–15).

3. Conclusions

In conclusion, we have shown that the coupling of aryl mesylates with lithium borates takes place efficiently at room temperature in the presence of a nickel-catalyst, furnishing coupling products in high yields. Although the mesylates we examined possess an electron-withdrawing group or ring, the mesylate methodology will open economical routes to biologically important biaryl compounds.

4. Experimental

Infrared (IR) spectra were determined using a JASCO FT/IR-230 spectrometer and are reported in wave numbers (cm^{-1}). ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were measured on a Varian Gemini-300 in $CDCl_3$ using Me_4Si ($\delta = 0$ ppm) and the center line of $CDCl_3$ triplet ($\delta = 77.1$ ppm) as internal standards, respectively.

Methyllithium (MeLi) in Et_2O and *n*-butyllithium (*n*-BuLi) in C_6H_{14} were prepared as a 0.75–2.76 M solution by the usual procedures and stocked under Ar. The boronate esters were prepared by the method published [10a].

4.1. General procedure for the preparations of aryl mesylates and tosylate

To an ice-cold suspension of NaH (0.72 g, 50% in mineral oil, 15 mmol) in THF (10 ml) was added the corresponding phenol or enol (10 mmol) in THF (5 ml). After 15 min, MsCl (1.55 ml, 20 mmol) or a THF (5 ml) solution of TsCl (3.8 g, 20 mmol) was added and the reaction mixture was stirred at room temperature (r.t.) for 3–7 h. The reaction was quenched by addition of saturated NH_4Cl, and the product was extracted with EtOAc several times. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the crude product, which was purified by chromatography on silica gel and/or recrystallization from a solvent indicated. The ^{1}H-NMR spectra of the products **1a**–**g** [11], **1h** [16], and **1i** [17] as well as the ^{13}C-NMR spectra of **1a**, **1c**, **1e**, **1f**, and **1i** were in good agreement with the data reported in the literatures.

Table 2
Nickel-catalyzed coupling of mesylates with borates [a]

Entry	Mesylate	Borate			Temperature (°C)	Time (h)	Product **3** [b]	
		Number	R^D	R^T			Number	Yield (%) [c]
1	**1a**	**8c**	*n*-Bu	C_6H_4(*p*-OMe)	r.t.	12	**3c**	85 [d]
2	**1a**	**8d**	*n*-Bu	C_6H_4(*p*-Me)	r.t.	12	**3d**	85 [d]
3	**1c**	**5a**	Me	2-furyl	r.t.	12	**3e**	94
4	**1c**	**8b**	*n*-Bu	Ph	r.t.	12	**3f**	83 [d]
5	**1c**	**8e**	*n*-Bu	C_6H_4(*p*-CH_2OTBS)	r.t.	12	**3g**	88 [d]
6	**1d**	**5a**	Me	2-furyl	r.t.	12	**3h**	80
7	**1d**	**8b**	*n*-Bu	Ph	r.t.	12	**3i**	95 [d]
8	**1e**	**8b**	*n*-Bu	Ph	r.t.	12	**3j**	80 [d]
9	**1f**	**8c**	*n*-Bu	C_6H_4(*p*-OMe)	60	13	**3k**	82 [d]
10	**1g**	**8d**	*n*-Bu	C_6H_4(*p*-Me)	60	41	**3l**	58 [d,e]
11	**1h**	**8c**	*n*-Bu	C_6H_4(*p*-OMe)	r.t.	13	**3m**	93
12	**1I**	**8b**	*n*-Bu	Ph	r.t.	13	**3n**	91
13	**1j**	**8b**	*n*-Bu	Ph	r.t.	13	**3o**	95 [f]
14	**1k**	**8b**	*n*-Bu	Ph	r.t.	13	**3p**	93 [g]
15	**1l**	**8b**	*n*-Bu	Ph	r.t.	13	**3q**	97

[a] Reactions were carried out using the mesylates and three equivalents of the borates with $NiCl_2(PPh_3)_2$ (10 mol%).
[b] **3**: Ar–R^T of Scheme 2.
[c] Isolated yields.
[d] A trace amount (<5%) of the butyl-coupling product was detected by ^{1}H-NMR spectroscopy.
[e] **1g** was recovered in 38% yield.
[f] Product **3o** was a 1:2 mixture of the (*E*)- and (*Z*)-stereoisomers.
[g] (*E*)-Stereoisomer was obtained exclusively.

*4.1.1. Ethyl (Z)-3-(methylsulfonyloxy)-2-butenoate (**1j**)*

Yield: 53%. Colorless oil. b.p. 160–165 °C (0.5 Torr). IR (neat): ν_{max} 1726, 1676, 1219, 1169, 1136, 1049, 930 cm^{-1}. ^{1}H-NMR $\delta = 1.28$ (t, $J = 7$ Hz, 3H), 2.21 (d, $J = 1$ Hz, 3H), 3.31 (s, 3H), 4.17 (q, $J = 7$ Hz, 2H), 5.60 (d, $J = 1$ Hz, 1H). ^{13}C-NMR $\delta = 14.0$, 22.3, 39.5, 60.3, 110.2, 157.2, 163.1.

*4.1.2. (Z)-4-(Methylsulfonyloxy)-3-penten-2-one (**1k**)*

Yield: 38%. Colorless oil. b.p. 95–98 °C (0.5 Torr). IR (neat): ν_{max} 3024, 1705, 1633, 1358, 1174, 1140, 972, 906, 789 cm^{-1}. ^{1}H-NMR $\delta = 2.21$ (q, $J = 0.9$ Hz, 3H), 2.27 (s, 3H), 3.29 (t, $J = 0.9$ Hz, 3H), 5.84 (s, 1H). ^{13}C-NMR $\delta = 22.2$, 31.5, 39.8, 117.7, 154.1, 194.8.

*4.1.3. Methyl 1-(2′-(methylsulfonyloxy)-1′-cyclopentene)carboxylate (**1l**)*

Yield: 69%. Colorless oil. b.p. 125–128 °C (0.5 Torr). IR (neat): ν_{max} 3022, 1718, 1657, 1165, 816 cm^{-1}. ^{1}H-NMR $\delta = 1.92$–2.04 (m, 2H), 2.60–2.69 (m, 2H), 2.76–2.85 (m, 2H), 3.25 (s, 3H), 3.75 (s, 3H). ^{13}C-NMR $\delta = 19.1$, 29.1, 33.7, 39.1 and 39.4, 51.4 and 51.6, 119.9, 156.8, 163.6.

4.2. General procedure for the coupling reaction

To an ice-cold suspension of the boronate ester **7** (1.08 mmol) and the nickel-catalyst (0.027 mmol) in THF (2 ml) was added the lithium reagent (0.81 mmol) dropwise over 5 min under Ar. The ice bath was removed and the solution was stirred at r.t. for 15 min. The mesylate or tosylate **1** (0.27 mmol) in THF (1 ml) was added to the solution. The reaction was continued at r.t. overnight, and quenched by addition of saturated $NaHCO_3$. The product was extracted with AcOEt several times. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the crude product, which was purified by chromatography on silica gel (C_6H_{14}–AcOEt) to afford the coupling product **3** in the yield given in Tables 1 and 2. The ^{1}H-NMR spectra of the products **3b** [9e], **3f** [9e], **3h** [12b], **3i** [3a,3i,4,9e], **3j** [9e], **3k** [18], **3l** [3g,6,9h,19], **3n** [20], (*E*)-isomer of **3o** [14], and **3p** [15] as well as the ^{13}C-NMR spectra of ***3l*** were in good agreement with the data reported and/or spectra attached in the literatures.

*4.2.1. Methyl 4-(2′-furyl)benzoate (**3a**)*

White crystals. m.p. 120–121 °C (C_6H_{14}) (lit. [12a] 119–120 °C; lit. [12b] 120–121 °C). IR (nujol): ν_{max} 1716, 1277, 1109, 773, 740 cm^{-1}. ^{1}H-NMR $\delta = 3.95$ (s, 3H), 6.52 (dd, $J = 3.5$, 2 Hz, 1H), 6.79 (d, $J = 3.5$ Hz, 1H), 7.53 (d, $J = 2$ Hz, 1H), 7.74 (d, $J = 8.5$ Hz, 2H), 8.03 (d, $J = 8.5$ Hz, 2H). ^{13}C-NMR $\delta = 52.1$, 107.3, 112.1, 123.5, 128.7, 130.2, 134.9, 143.2, 153.2, 166.8.

*4.2.2. Methyl 4-phenylbenzoate (**3b**)*

White crystals. m.p. 115–116 °C (C_6H_{14}) (lit. [4] 116–117 °C) IR (nujol): ν_{max} 1726, 1606, 1277, 1113, 752 cm^{-1}. ^{13}C-NMR $\delta = 52.1$, 126.9, 127.1, 128.0, 128.9, 130.0, 139.8, 145.4, 166.7.

*4.2.3. Methyl 4-(4′-methoxyphenyl)benzoate (**3c**)*

White crystals. m.p. 165–167 °C (C_6H_6–C_6H_{14}). IR (nujol): ν_{max} 1712, 1290, 833, 773, 721 cm^{-1}. ^{1}H-NMR $\delta = 3.86$ (s, 3H), 3.93 (s, 3H), 7.00 (d, $J = 9$ Hz, 2H), 7.57 (d, $J = 9$ Hz, 2H), 7.62 (d, $J = 8.5$ Hz, 2H), 8.08 (d, $J = 8.5$ Hz, 2H). ^{13}C-NMR $\delta = 52.1$, 55.4, 114.5, 126.6, 128.4, 128.5, 130.3, 132.5, 145.4, 160.0, 167.3.

*4.2.4. Methyl 4-(4′-methylphenyl)benzoate (**3d**)*

White crystals. m.p. 111–112 °C (C_6H_{14}) (lit. [21] 115–116 °C). IR (nujol): ν_{max} 1730, 1606, 1275, 1111, 818, 769 cm^{-1}. ^{1}H-NMR (revised data of lit. [6]) δ 2.41 (s, 3H), 3.94 (s, 3H), 7.27 (d, $J = 8$ Hz, 2H), 7.53 (d, $J = 8$ Hz, 2H), 7.65 (d, $J = 9$ Hz, 2H), 8.09 (d, $J = 9$ Hz, 2H). ^{13}C-NMR $\delta = 21.1$, 52.1, 127.0, 127.3, 128.8, 129.8, 130.2, 137.3, 138.3, 145.8, 167.3.

*4.2.5. Methyl 2-(2′-furyl)benzoate (**3e**)*

Colorless oil. IR (neat): ν_{max} 3022, 1726, 1604, 1261, 760 cm^{-1}. ^{1}H-NMR $\delta = 3.85$ (s, 3H), 6.49 (dd, $J = 3.5$, 2 Hz, 1H), 6.58 (dd, $J = 3.5$, 1 Hz, 1H), 7.36 (dt, $J = 1.5$, 8 Hz, 1H), 7.46–7.53 (m, 2H), 7.58–7.68 (m, 2H). ^{13}C-NMR $\delta = 52.4$, 108.1, 111.7, 127.8, 128.3, 129.4, 130.0, 130.3, 131.1, 142.9, 152.7, 169.8.

*4.2.6. Methyl 2-phenylbenzoate (**3f**)*

Colorless oil. IR (neat): ν_{max} 1732, 1282, 1248, 1126, 1092, 746, 700 cm^{-1}. ^{13}C-NMR $\delta = 52.0$, 127.3, 127.4, 128.2, 128.5, 129.9, 130.9, 131.0, 131.4, 141.5, 142.7, 169.4.

*4.2.7. Methyl 2-(4′-((tert-butyldimethyl)-silyloxymethyl)phenyl)benzoate (**3g**)*

Colorless oil. IR (neat): ν_{max} 1724, 1599, 1284, 1253, 1090, 839 cm^{-1}. ^{1}H-NMR $\delta = 0.12$ (s, 6H), 0.95 (s, 9H), 3.62 (s, 3H), 4.78 (s, 2H), 7.25–7.28 (m, 2H), 7.30–7.42 (m, 4H), 7.53 (dt, $J = 1$, 8 Hz, 1H), 7.80 (d, $J = 8$ Hz, 1H). ^{13}C-NMR $\delta = -5.3$, 18.4, 25.9, 52.0, 64.8, 125.9, 127.2, 128.3, 129.9, 130.9, 131.0, 131.4, 140.0, 140.6, 142.5, 169.5.

*4.2.8. 1-(4′-(2″-Furyl)phenyl)ethanone (**3h**)*

White crystals. m.p. 100–101 °C (C_6H_{14}) (lit. [12b] 102–103 °C). IR (nujol): ν_{max} 1670, 1608, 1018, 839 cm^{-1}. ^{13}C-NMR $\delta = 26.6$, 107.5, 112.1, 123.6, 129.0, 135.0, 135.7, 143.3, 153.0, 197.3.

*4.2.9. 1-(4′-Biphenyl)ethanone (**3i**)*

White crystals. m.p. 120–121 °C (C_6H_{14}–C_6H_6) (lit. [3a,4] 119–120 °C). IR (nujol): ν_{max} 1680, 1263, 960,

764, 721 cm^{-1}. ^{13}C-NMR (revised data of lit. [3i]) $\delta = 26.6$, 127.37, 127.42, 128.4, 129.06, 129.10, 136.1, 140.1, 146.0, 197.9.

4.2.10. 4-Phenylbenzenecarbonitrile (**3j**)

White crystals. m.p. 82–84 °C (C_6H_{14}) (lit. [22] 86 °C). IR (nujol): ν_{max} 2225, 1604, 1113, 1078, 847 cm^{-1}. ^{13}C-NMR $\delta = 111.1$, 119.1, 127.4, 127.9, 128.8, 129.3, 132.8, 139.4, 145.9.

4.2.11. 4′-Methoxyphenyl-1-naphthalene (**3m**)

White crystals. m.p. 111–112 °C (EtOH) (lit. [23] 116–116.5 °C). IR (nujol): ν_{max} 1608, 1244, 1174, 1107, 1032 cm^{-1}. ^1H-NMR $\delta = 3.91$ (s, 3H), 7.06 (dt, $J = 9$, 2.5 Hz, 2H), 7.41–7.58 (m, 6H), 7.84–7.98 (m, 3H). ^{13}C-NMR $\delta = 55.4$, 113.8, 125.6, 125.9, 126.1, 126.2, 127.1, 127.5, 128.4, 131.3, 132.0, 133.3, 134.0, 140.1, 159.1.

4.2.12. 2-Phenylpyridine (**3n**)

Colorless oil. IR (neat): ν_{max} 1585, 1468, 1448, 1425, 746, 694 cm^{-1}. ^{13}C-NMR $\delta = 120.7$, 122.2, 127.1, 128.9, 129.1, 136.9, 139.6, 149.9, 157.7.

4.2.13. Ethyl 3-phenyl-2-butenoate (**3o**)

4.2.13.1. (E)-isomer. Colorless oil. IR (neat): ν_{max} 1712, 1628, 1273, 1165, 1043, 768, 694 cm^{-1}. ^1H-NMR (updated data of lit. [14]) $\delta = 1.32$ (t, $J = 7$ Hz, 3H), 2.58 (d, $J = 1$ Hz, 3H), 4.22 (q, $J = 7$ Hz, 2H), 6.14 (q, $J = 1$ Hz, 1H), 7.34–7.43 (m, 3H), 7.45–7.52 (m, 2H). ^{13}C-NMR $\delta = 14.3$, 17.9, 59.9, 117.3, 126.5, 128.7, 129.1, 142.4, 155.7, 167.1.

4.2.13.2. (Z)-isomer. Colorless oil. IR (neat): ν_{max} 1724, 1639, 1275, 1230, 1161, 1047, 768, 698 cm^{-1}. ^1H NMR $\delta = 1.08$ (t, $J = 7$ Hz, 3H), 2.17 (d, $J = 1$ Hz, 3H), 4.00 (q, $J = 7$ Hz, 2H), 5.91 (q, $J = 1$ Hz, 1H), 7.17–7.23 (m, 2H), 7.29–7.33 (m, 3H). ^{13}C-NMR $\delta = 13.9$, 27.1, 59.8, 117.9, 126.9, 127.9, 128.0, 141.0, 155.6, 166.1.

4.2.14. (E)-4-Phenyl-3-penten-2-one (**3p**)

Colorless oil. IR (neat): ν_{max} 1682, 1601, 1356, 1182, 758, 696 cm^{-1}. ^{13}C-NMR $\delta = 18.3$, 32.3, 124.7, 126.6, 128.7, 129.3, 142.7, 154.1, 199.2.

4.2.15. Methyl 1-(2′-phenyl-1′-cyclopentene)carboxylate (**3q**)

Colorless oil. IR (neat): ν_{max} 1720, 1435, 1354, 1228, 1047, 756, 696 cm^{-1}. ^1H-NMR $\delta = 1.99$ (quintet, $J =$ 7.5 Hz, 2H), 2.79–2.90 (m, 4H), 3.62 (s, 3H), 7.36–7.41 (m, 5H). ^{13}C-NMR $\delta = 21.9$, 35.1, 40.1, 51.2 (br peak), 127.8, 127.9, 128.0, 128.9, 137.1, 153.8, 166.8.

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