Supporting Information
for DOI: 10.1055/s-0037-1610265
© Georg Thieme Verlag KG Stuttgart · New York 2018
Supporting Information

Na$_2$CO$_3$-catalyzed $O$-Acylation of Phenols for the Synthesis of Aryl Carboxylates with Vinyl Carboxylates as Acyl Reagents

Xiao-Yu Zhou* and Xia Chen*

School of Chemistry and Materials Engineering, Liupanshui Normal University, Liupanshui, 553004, China

Zhouxiaoyu20062006@126.com (X.-Y. Zhou), xia811@live.cn (X. Chen)

Table of Contents
1. General and Materials…………………………………………………….……..……S1
2. The Typical Procedure for Na$_2$CO$_3$-catalyzed $O$-Acylation of Phenols…………….S1-7
3. Copy of NMR for the Aryl Carboxylates……………………………………………………….S8-25

General:

**General:** The chemical shifts for $^1$H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for $^{13}$C NMR were recorded in ppm downfield using the central peak of d-dimethyl sulfoxide (39.6 ppm) or d-chloroform (77.23 ppm) as the internal standard. Coupling constants ($J$) are reported in Hz and refer to apparent peak multiplications. Flash column chromatography was performed on silica gel (200-300 mesh). TLC analysis was performed using glass-backed plates coated with 0.2 mm silica.

**Materials:** All commercially available reagents were used without further purification. The starting materials 1a-1o are commercially available.

The Typical Procedure for Na$_2$CO$_3$-catalyzed $O$-Acylation of Phenols:

- A mixture of phenol 1 (0.50 mmol), Na$_2$CO$_3$ (10.6 mg, 0.10 mmol, 20 mol%) and alkenyl carboxylate (2.0 mmol, 4.0 equiv) in CH$_3$CN (3 mL) was added into a Schlenk flask (25 mL) and stirred at room temperature. The mixture was stirred at 120°C until the reaction was finished. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate 20:1 to 10:1).
naphthalen-2-yl acetate (3aa). Yield: 99%, 92.8 mg, white solid, mp 70-72 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81-7.72 (m, 3H), 7.50 (d, $J = 2.2$ Hz, 1H), 7.45-7.37 (m, 2H), 7.19-7.15 (m, 1H), 2.29 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.7, 148.3, 133.7, 131.4, 129.4, 127.8, 127.6, 126.6, 125.7, 121.1, 118.5, 21.2; HRMS Calcd for C$_{12}$H$_{10}$O$_2$Na: 209.0578 [M+Na]$^+$; found: 209.0582.

naphthalen-2-yl but-2-enoate (3ac). Yield: 82%, 87.3 mg, white solid, mp 52-54 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83-7.76 (m, 3H), 7.55 (d, $J = 2.2$ Hz, 1H), 7.48-7.40 (m, 2H), 7.25-7.15 (m, 2H), 6.11-6.03 (m, 1H), 1.96 (dd, $J = 6.9, 1.7$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.0, 148.4, 147.1, 133.8, 131.4, 129.3, 127.7, 127.6, 126.5, 125.6, 122.1, 121.3, 118.6, 18.3; HRMS Calcd for C$_{14}$H$_{12}$O$_2$Na: 235.0735 [M+Na]$^+$; found: 235.0734.

naphthalen-2-yl propionate (3ad). Yield: > 99%, 101.0 mg, white solid, mp 48-50 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86-7.78 (m, 3H), 7.55 (d, $J = 2.1$ Hz, 1H), 7.51-7.42 (m, 2H), 7.24-7.20 (m, 1H), 2.65 (q, $J = 7.6$ Hz, 2H), 1.30 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.2, 148.4, 133.8, 131.4, 129.4, 127.8, 127.6, 126.5, 125.6, 121.2, 118.5, 27.8, 9.1; HRMS Calcd for C$_{13}$H$_{12}$O$_2$Na: 223.0735 [M+Na]$^+$;
naphthalen-2-yl butyrate (3ae). Yield: > 99%, 106.9 mg, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.78-7.70 (m, 3H), 7.47 (d, $J = 2.2$ Hz, 1H), 7.43-7.34 (m, 2H), 7.16-7.12 (m, 1H), 2.51 (q, $J = 7.4$ Hz, 2H), 1.74 (m, 2H), 1.00 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.4, 148.4, 133.8, 131.4, 129.4, 127.8, 127.6, 126.5, 125.7, 121.2, 118.5, 36.3, 18.5, 13.7; HRMS Calcd for C$_{14}$H$_{14}$O$_2$Na: 237.0891 [M+Na]$^+$; found: 237.0887.

naphthalen-2-yl pivalate (3af). Yield: 86%, 98.3 mg, white solid, mp 66-68 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83-7.75 (m, 3H), 7.50 (d, $J = 2.12$ Hz, 1H), 7.48-7.40 (m, 2H), 7.17 (dd, $J = 8.8$, 2.2 Hz, 1H), 1.38 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.3, 148.8, 133.8, 131.4, 129.3, 127.8, 127.6, 126.5, 121.2, 118.4, 39.2, 27.2; HRMS Calcd for C$_{15}$H$_{16}$O$_2$Na: 251.1048 [M+Na]$^+$; found: 251.1050.

naphthalen-2-yl hexanoate (3ag). Yield: 79%, 96.2 mg, white solid, mp 36-38 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.89-7.81 (m, 3H), 7.59 (d, $J = 2.0$ Hz, 1H), 7.54-7.46 (m, 2H), 7.28-7.24 (m, 1H), 2.64 (t, $J = 7.5$ Hz, 2H), 1.88-1.79 (m, 2H), 1.50-1.40 (m, 4H), 0.98 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.5, 148.4, 133.8,
naphthalen-1-yl acetate (3ba). Yield: 90%, 84.0 mg, white solid, mp 50-52 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84-7.78 (m, 2H), 7.69 (d, $J_1$ = 8.3 Hz, 1H), 7.47-7.38 (m, 3H), 7.20-7.18 (m, 1H), 2.41 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.5, 146.6, 134.7, 128.1, 126.8, 126.45, 126.1, 125.4, 121.1, 118.1, 21.0; HRMS Calcd for C$_{16}$H$_{18}$O$_2$Na: 265.1204 [M+Na]$^+$; found: 265.1205.

naphthalene-1,5-diyl diacetate (3ca). Yield: 47%, 57.0 mg, white solid, mp 159-161 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J_1$ = 8.6 Hz, 2H), 7.52-7.48 (m, 2H), 7.29 (d, $J_2$ = 7.5 Hz, 2H), 2.46 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 169.3, 146.7, 128.1, 126.0, 119.3, 118.8, 21.0; HRMS Calcd for C$_{14}$H$_{12}$O$_4$Na: 267.0633 [M+Na]$^+$; found: 267.0631.

phenyl acetate (3da). Yield: > 99%, 67.9 mg, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36-7.30 (m, 2H), 7.20-7.15 (m, 1H), 7.07-7.01 (m, 2H), 2.23 (s, 3H); $^{13}$C
NMR (101 MHz, CDCl₃) δ 169.4, 150.6, 129.3, 125.7, 121.4, 21.0; HRMS Calcd for C₈H₈O₂Na: 159.0422 [M+Na]+; found: 159.0423.

2-methoxyphenyl acetate (3ea). Yield: > 99%, 83.0 mg, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.17 (ddd, J = 8.3, 7.5, 1.7 Hz, 1H), 7.01 (dd, J = 7.8, 1.7 Hz, 1H), 6.95 – 6.89 (m, 2H), 3.79 (s, 3H), 2.28 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 169.1, 151.1, 139.8, 126.9, 122.8, 120.8, 112.4, 55.8, 20.7; HRMS Calcd for C₉H₁₀O₃Na: 189.0528 [M+Na]+; found: 189.0532.

1,2-phenylene diacetate (3fa). Yield: 77%, 74.9 mg, white solid, mp 62-64 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.21 (m, 2H), 7.19-7.16 (m, 2H), 2.28 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 168.3, 142.1, 126.6, 123.5, 20.7; HRMS Calcd for C₁₀H₁₀O₄Na: 217.0477 [M+Na]+; found: 217.0475.

m-tolyl acetate (3ga). Yield: 76%, 57.3 mg, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.29-7.25 (m, 1H), 7.05 (d, J = 7.6 Hz, 1H), 6.92-6.89 (m, 2H), 2.37 (s, 3H), 2.29 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 169.6, 150.6, 139.6, 129.1, 126.7, 122.2, 118.5,

\[ \text{p-tolyl acetate (3ha). Yield: 98\%, 73.6 mg, colorless oil.} \]
\[ \text{δ} \stackrel{7.16}{\text{(d, } J = 8.2 \text{ Hz, 2H), 6.98-6.93 (m, 2H), 2.33 (s, 3H), 2.27 (s, 3H);} \]
\[ \text{δ} \stackrel{169.8, 148.5, 135.5, 130.0, 121.3, 21.1, 20.9; HRMS Calcd for} \]
\[ \text{C₉H₁₀O₂Na: 173.0578 [M+Na]⁺; found: 173.0578.} \]

1,4-phenylene diacetate (3ia). Yield: 79%, 77.1 mg, white solid, mp 122-124 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.08 (s, 4H), 2.27 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 169.4, 148.0, 122.4, 21.1; HRMS Calcd for C₁₀H₁₀O₄Na: 217.0477 [M+Na]⁺; found: 217.0474.

4-acetylphenyl acetate (3ja). Yield: 98%, 87.3 mg, white solid, mp 46-48 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.97-7.93 (m, 2H), 7.18-7.12 (m, 2H), 2.55 (s, 3H), 2.28 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.9, 168.9, 154.3, 134.7, 129.9, 121.8, 26.6, 21.1; HRMS Calcd for C₁₀H₁₀O₃Na: 201.0528 [M+Na]⁺; found: 201.0530.

4-nitrophenyl acetate (3ka). Yield: 81%, 72.9 mg, light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.86 (m, 2H), 7.22-7.18 (m, 2H), 2.66 (s, 3H), 2.26 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.9, 168.9, 154.3, 134.7, 129.9, 121.8, 26.6, 21.1; HRMS Calcd for C₁₀H₁₀O₃Na: 201.0528 [M+Na]⁺; found: 201.0530.
MHz, CDCl₃) δ 8.20 (d, J = 9.2 Hz, 2H), 7.21 (d, J = 9.2 Hz, 2H), 2.28 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.4, 155.3, 125.2, 122.4, 110.0, 21.1; HRMS Calcd for C₈H₇NO₄Na: 204.0273 [M+Na]⁺; found: 204.0272.

4-acetoxybenzyl acetate (3la). Yield: 27%, 28.1 mg, colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 8.6 Hz, 2H), 7.09-7.03 (m, 2H), 5.06 (s, 2H), 2.27 (s, 3H), 2.07 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.8, 169.4, 150.5, 133.5, 131.2, 129.5, 122.4, 121.7, 65.6, 21.1, 21.0; HRMS Calcd for C₁₁H₁₂O₄Na: 231.0633 [M+Na]⁺; found: 231.0631.

naphthalen-2-ylmethyl acetate (3ma). Yield: 63%, 63.2 mg, white solid, mp 57-59 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, J = 9.1, 3.2 Hz, 4H), 7.50-7.44 (m, 3H), 5.26 (s, 2H), 2.12 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.9, 133.3, 133.2, 133.1, 128.4, 128.0, 127.7, 127.4, 126.30, 126.26, 125.9, 66.5, 21.1; HRMS Calcd for C₁₃H₁₂O₂Na: 223.0735 [M+Na]⁺; found: 223.0731.
3. Copy of NMR for the Aryl Carboxylates

$^1$H-NMR of 3aa

$^{13}$C-NMR of 3aa
$^1$H-NMR of 3ac

$^{13}$C-NMR of 3ac
$^1$H-NMR of 3ad

$^{13}$C-NMR of 3ad
$^1$H-NMR of 3ae

$^{13}$C-NMR of 3ae
$^1$H-NMR of 3af

$^{13}$C-NMR of 3af
$^1$H-NMR of 3ag

$^{13}$C-NMR of 3ag
$^{1}$$H$-NMR of 3ca

$^{13}C$-NMR of 3ca
$^{1}$H-NMR of 3ea

$^{13}$C-NMR of 3ea
**1H-NMR of 3fa**

**13C-NMR of 3fa**
\[ ^1\text{H-NMR of 3ga} \]

\[ \begin{align*}
\text{Chemical Shifts} & \\
\delta & \\
2.30 (t, J=7.1 Hz) & \\
2.58 (t, J=7.1 Hz) & \\
2.66 (t, J=7.1 Hz) & \\
2.78 (t, J=7.1 Hz) & \\
7.68 (d, J=7.1 Hz) & \\
\end{align*} \]

\[ ^{13}\text{C-NMR of 3ga} \]

\[ \begin{align*}
\text{Chemical Shifts} & \\
105.83 & \\
120.14 & \\
118.90 & \\
77.92 & \\
77.92 & \\
119.10 & \\
\end{align*} \]
$^1$H-NMR of 3ha

$^{13}$C-NMR of 3ha
$^1$H-NMR of 3ia

$^{13}$C-NMR of 3ia
$^1$H-NMR of 3ja

$^{13}$C-NMR of 3ja
$^1$H-NMR of 3ka

$^{13}$C-NMR of 3ka
$^{1}H$-NMR of 3la

$^{13}C$-NMR of 3la
$^1$H-NMR of 3ma

$^{13}$C-NMR of 3ma