Supporting Information for

**Stereoselective Hydroxycarbonylation of Vinyl Bromides to
 α,β -Unsaturated Carboxylic Acids in Ionic Liquid [BMIM]PF₆**

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Table of Contents

(1) General considerations	S2
(2) NMR spectral data	S2-S3
(3) References	S4
(4) Copies of the NMR Spectra for the products	S5-S14

General Considerations: Unless otherwise noted, all the starting materials were commercially available and used without further purification. For ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, the chemical shift values were relative to CDCl_3 and DMSO-d_6 . All the products were known, and gave spectra in accord with authentic values in the literatures. Vinyl monobromides **1b-1i**¹ and vinyl diacids **6a** and **6b**² were prepared by literature methods.

NMR Spectral Data

2-Phenyl-2-propenoic acid (5a)³: ^1H NMR (CDCl_3 , 300 MHz) δ 10.10 (br, 1H), 7.45-7.37 (m, 5H), 6.56 (s, 1H), 6.04 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 172.5 (COOH), 140.7, 136.2, 129.7, 128.6, 128.5, 128.3.

3-Methyl-2-butenic acid (5b)⁴: ^1H NMR (CDCl_3 , 300 MHz) δ 11.22 (br, 1H), 5.71 (s, 1H), 2.18 (s, 3H), 1.94 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 172.5 (COOH), 159.9, 115.8, 27.9, 20.6.

(E)-3-(Naphth-1-yl)-2-propenoic acid (2h)⁵: ^1H NMR (DMSO-d_6 , 300 MHz) δ 12.57 (br, 1H), 8.39 (d, J = 15.5 Hz, 1H), 8.20 (d, J = 8.1, 1H), 8.03-7.94 (m, 3H), 7.66-7.53 (m, 3H), 6.60 (d, J = 15.8, 1H).

(E)-p-Methoxycinnamic acid (2d)⁵: ^1H NMR (CDCl_3 , 300 MHz) δ 7.75 (d, J = 15.9 Hz, 1H), 7.62 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.33 (d, J = 15.9 Hz, 1H).

(E)-p-Chlorocinnamic acid (2f)⁵: ^1H NMR (DMSO-d_6 , 300 MHz) δ 12.45 (br, 1H), 7.73 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 15.9 Hz, 1H), 7.47 (d, J = 15.9 Hz, 2H), 6.55 (d, J = 16.0 Hz, 1H).

(E)-o-Methylcinnamic acid (2g)⁵: ^1H NMR (CDCl_3 , 300 MHz) δ 10.48 (br, 1H), 8.16 (d, J = 15.7 Hz, 1H), 7.65 (d, J = 7.0 Hz, 1H), 7.36-7.27 (m, 3H), 6.45 (d, J = 15.8 Hz,

1H), 2.38 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 172.5 (COOH), 144.9, 138.1, 131.0, 130.7, 126.8, 126.6, 118.3, 19.9.

2-Methyl-3-phenyl-2-propenoic acid (E/Z = 2.04 : 1.00) (2i)⁶: ^1H NMR (CDCl_3 , 300 MHz) δ 8.76 (br, 3.04H), 7.84 (s, 2.04H), 7.44-7.30 (m, 15.2H), 6.87 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 174.4 (COOH), 141.3, 137.9, 135.7, 130.0, 128.9, 128.6, 128.5, 128.2, 128.0, 127.6.

(E)-o-Methoxycinnamic acid (2e)⁷: ^1H NMR (DMSO-d_6 , 300 MHz) δ 12.24 (br, 1H), 7.84 (d, J = 16.1 Hz, 1H), 7.67 (d, J = 7.0 Hz, 1H), 7.42-7.38 (m, 1H), 7.09-6.95 (m, 2H), 6.51 (d, J = 16.1 Hz, 1H), 3.86 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 168.0 (COOH), 157.8, 138.8, 131.9, 128.5, 122.5, 120.8, 119.3, 111.7, 55.7.

(E)-p-Methylcinnamic acid (2b)⁵: ^1H NMR (CDCl_3 , 300 MHz) δ 7.78 (d, J = 15.9 Hz, 1H), 7.46 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 6.42 (d, J = 16.0 Hz, 1H).

(E)-Cinnamic acid (2a)⁸: ^1H NMR (CDCl_3 , 300 MHz) δ 7.80 (d, J = 16.0 Hz, 1H), 7.59-7.55 (m, 2H), 7.44-7.41 (m, 3H) 6.48 (d, J = 16.0 Hz, 1H); MS (EI) m/z 147 ($\text{M}^+ - 1$, 100%), 148 (M^+ , 77%), 102, 23%.

(1E, 3E)-1, 4-Diphenyl-1, 3-butadiene (3a)⁹: ^1H NMR (CDCl_3 , 300 MHz) δ 7.50 (d, J = 7.5 Hz, 4H), 7.42-7.37 (m, 4H), 7.31-7.28 (m, 2H), 7.07-6.97 (m, 2H), 6.78-6.68 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 137.4, 132.9, 129.4, 128.8, 127.7, 126.5; MS (EI) m/z 206 (M^+).

(E)-3-(Thiophen-2-yl)-2-propenoic acid (2c)⁷: ^1H NMR (CDCl_3 , 300 MHz) δ 11.45 (bs, 1H), 7.91 (d, J = 15.6 Hz, 1H), 7.45 (d, J = 5.1 Hz, 1H), 7.32 (dd, J = 0.5, 3.6 Hz, 1H), 7.10 (dd, J = 3.7, 5.1 Hz, 1H), 6.26 (d, J = 15.6 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75 MHz) δ 172.6 (COOH), 139.5, 139.3, 131.8, 129.5, 128.4, 116.1; MS (EI) m/z 154 (M^+).

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¹H NMR spectrum of **3a**

¹³C{¹H} NMR spectrum of **3a**

¹H NMR spectrum of **2c** (Table 1)

¹³C{¹H} NMR spectrum of **2c** (Table 1)

¹H NMR spectrum of **2b** (Table 1)

¹H NMR in CDCl₃

¹H NMR spectrum of **2d** (Table 2)

¹H NMR in CDCl₃

¹H NMR spectrum of **2e** (Table 2)

¹³C{¹H} NMR spectrum of **2e** (Table 2)

^1H NMR spectrum of **2g** (Table 2)

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2g** (Table 2)

¹H NMR spectrum of **2f** (Table 2)

¹H NMR in DMSO

¹H NMR spectrum of **2h** (DMSO-d₆) (Table 2)

¹H NMR in DMSO

¹H NMR spectrum of **2i** (Table 2)

¹H NMR in CDCl₃

¹³C{¹H} NMR spectrum of **2i** (Table 2)

¹³C NMR in CDCl₃

^1H NMR spectrum of **5a** (Table 3)

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5a** (Table 3)

^1H NMR spectrum of **5b** (Table 3)

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5b** (Table 3)