

**Supporting Information**

**“Carbon Dioxide-Mediated Metal-Free Oxidation of Allylic Alcohols to Esters”**

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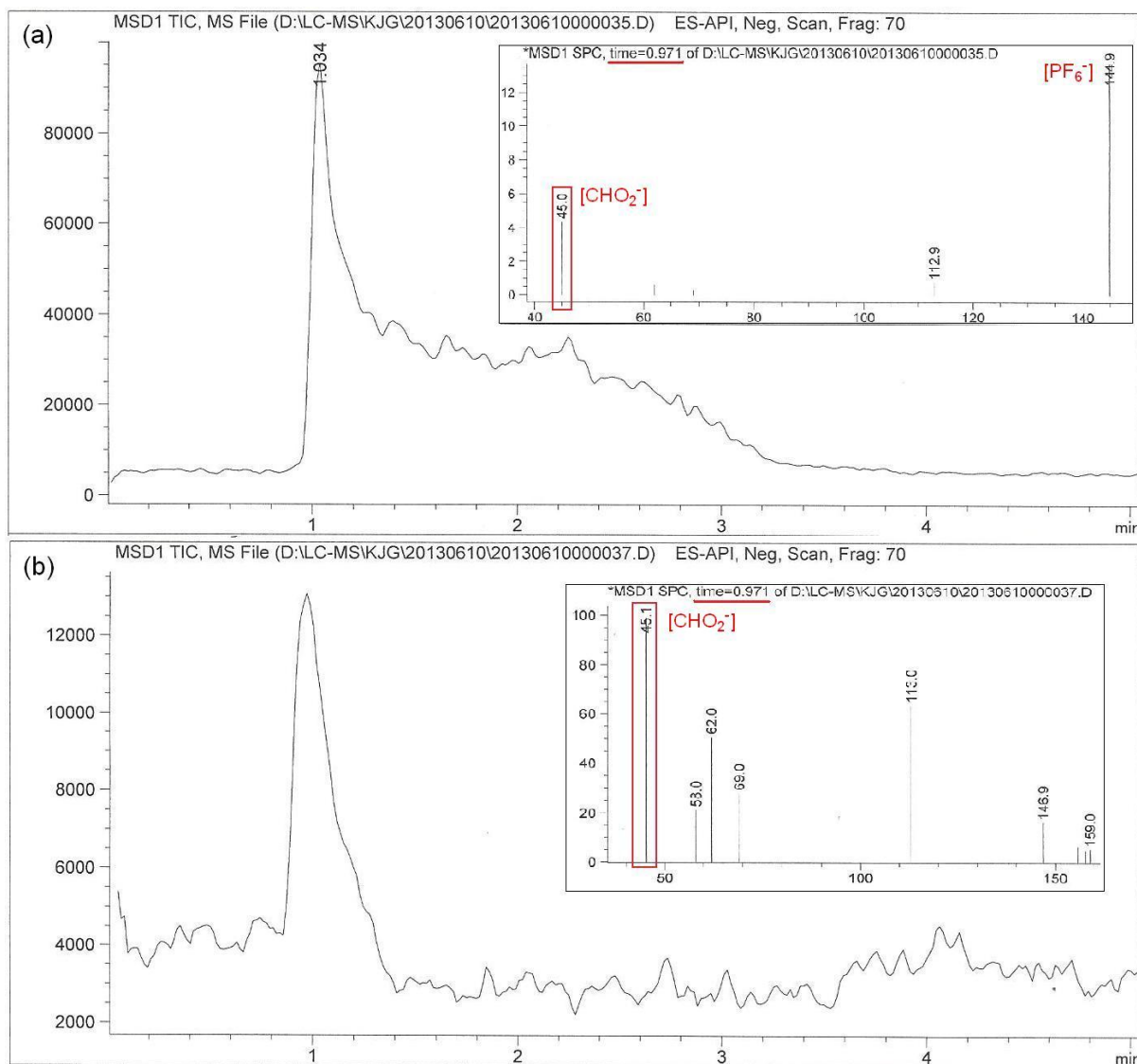
## Experimental section

**General.** Anhydrous solvents were transferred by an oven dried syringe. Dichloromethane was distilled from calcium hydride. Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded with a Varian Mercury plus (400 MHz) spectrometer. Chemical shifts are reported in delta ( $\delta$ ) units, part per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded with a Varian Mercury plus (100 MHz) spectrometer. Chemical shifts are reported in delta ( $\delta$ ) units, part per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform.

**Representative procedure method A:** Cinnamyl alcohol (**1a**, 67.1 mg, 0.5 mmol) was added to the mixture of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 38.1 mg, 0.25 mmol) and 1-n-butyl-3-methylimidazolium hexafluorophosphate bmimPF<sub>6</sub> (1ml). A slow stream of CO<sub>2</sub> was passed through this solution for 10 minutes. Then, dichloromethane (0.1 ml) was added (For method B, no dichloromethane was added). The mixture was stirred over 18h at 100 °C under CO<sub>2</sub> atmosphere. The reaction mixture was extracted from the ionic liquid phase with ethyl ether (20 ml x 8). The organic layer was evaporated under reduced pressure and purified by flash column chromatography (silica gel) (2% Ether/hexane) to obtain cinnamyl 3-phenylpropanoate (**1b**) 40.6 mg (61%).

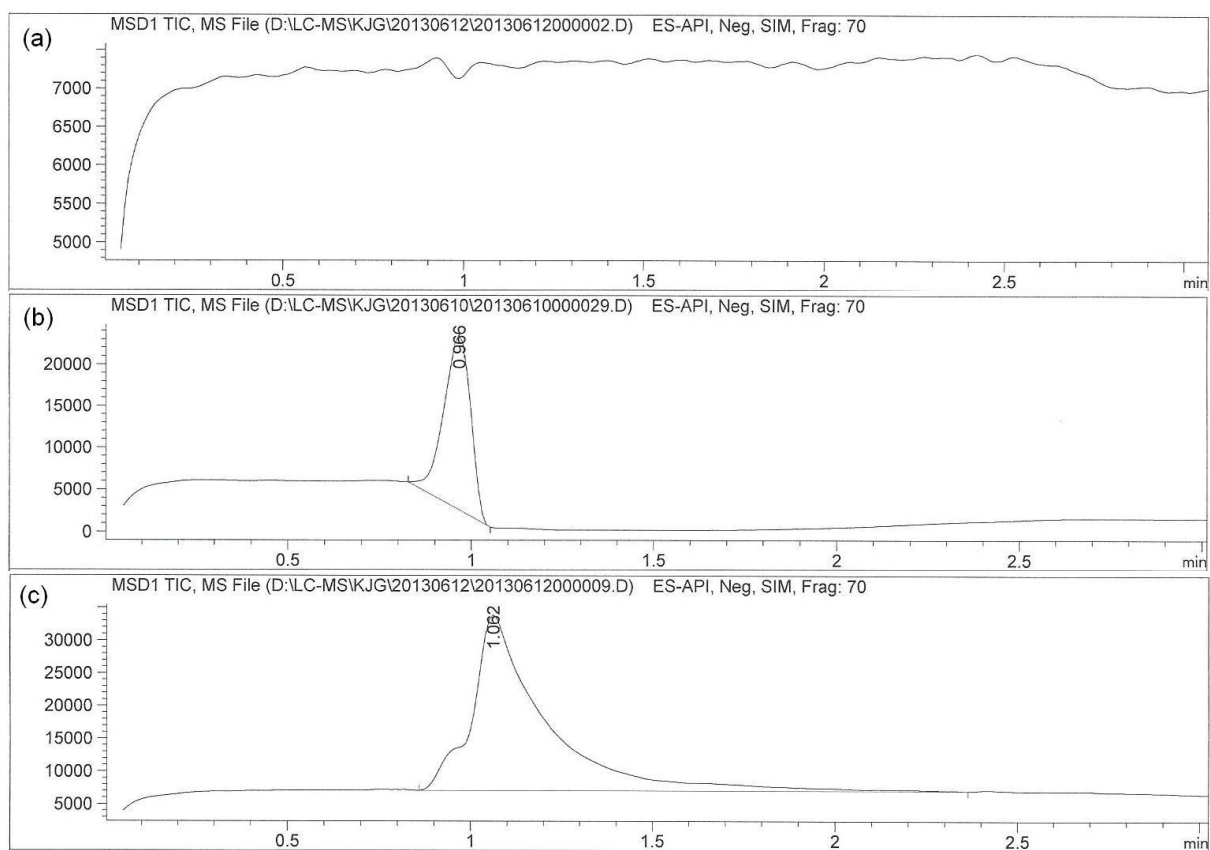
### Confirmation of formic acid by LC-MS analysis

The presence of formic acid, which was supposed to be generated in the course of reactions, was confirmed by LC/MS (Agilent 6120 single quadrupole mass spectrometer with electrospray ionization in the negative ion mode). Samples were eluted on a poroshell 120 EC-C<sub>18</sub> column (4.6×50 mm, 2.7 μm) using a mixture of acetonitrile/water (80:20) with a flow rate of 0.5 mL/min was used. For the CO<sub>2</sub>-mediated oxidation reaction of cinnamyl alcohol in bmimPF<sub>6</sub>, this gave ions at *m/z* 45 (CHO<sub>2</sub><sup>-</sup>) which corresponds to the deprotonated ion of formic acid (HCO<sub>2</sub>H, MW46.02), and at *m/z* 145 as expected for PF<sub>6</sub><sup>-</sup> ion from bmim solvent (Figure S1 (a)). For the authentic sample of formic acid, the deprotonated ion (*m/z* 45) was strongly appeared at 0.971 min, which was determined as a standard retention time.



**Figure S1.** Elution profiles for (a) reaction mixture and (b) formic acid, and corresponding mass spectra eluted at 0.971 min.

Because of the limited quantity of formic acid available in reaction mixture and inseparability with  $\text{PF}_6^-$  ion, LC-MS analysis using selected ion monitoring, which was set to acquire the signal  $\text{CHO}_2^-$  ion, was then carried out.<sup>1</sup> A control sample (acetonitrile) didn't show any noticeable peak at a retention time around 1 min (Figure S2). For the reaction mixture and formic acid samples, broad major peak was detected between 0.9 and 1.5 min, thus indicating that formic acid was generated as byproduct in the course of  $\text{CO}_2$ -mediated oxidation reactions



**Figure S2.** LC-MS analyses using selected ion monitoring ( $m/z$  54.0). (a) acetonitrile, (b) reaction mixture of cinnamyl alcohol and (c) formic acid.

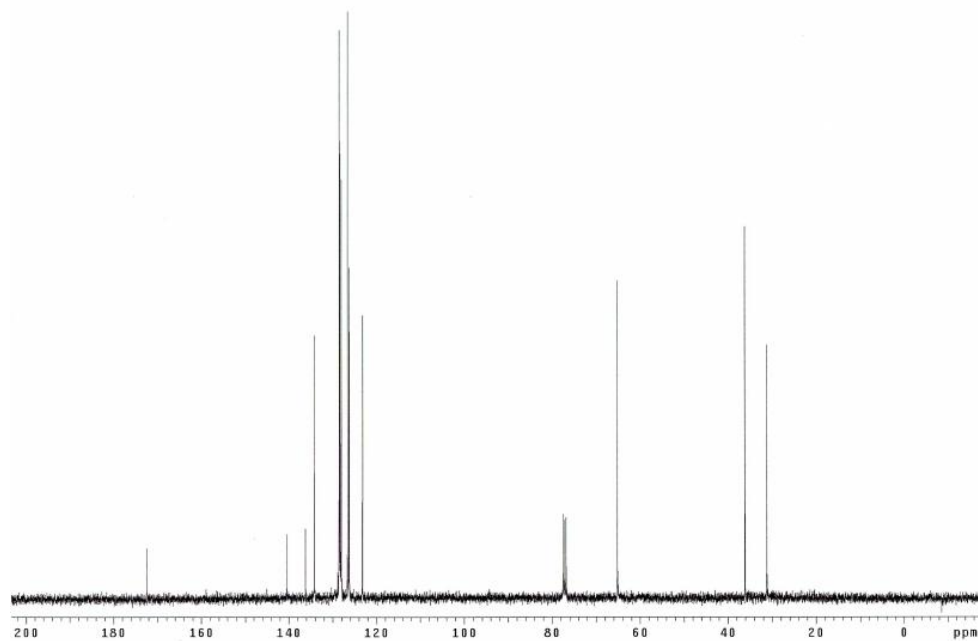
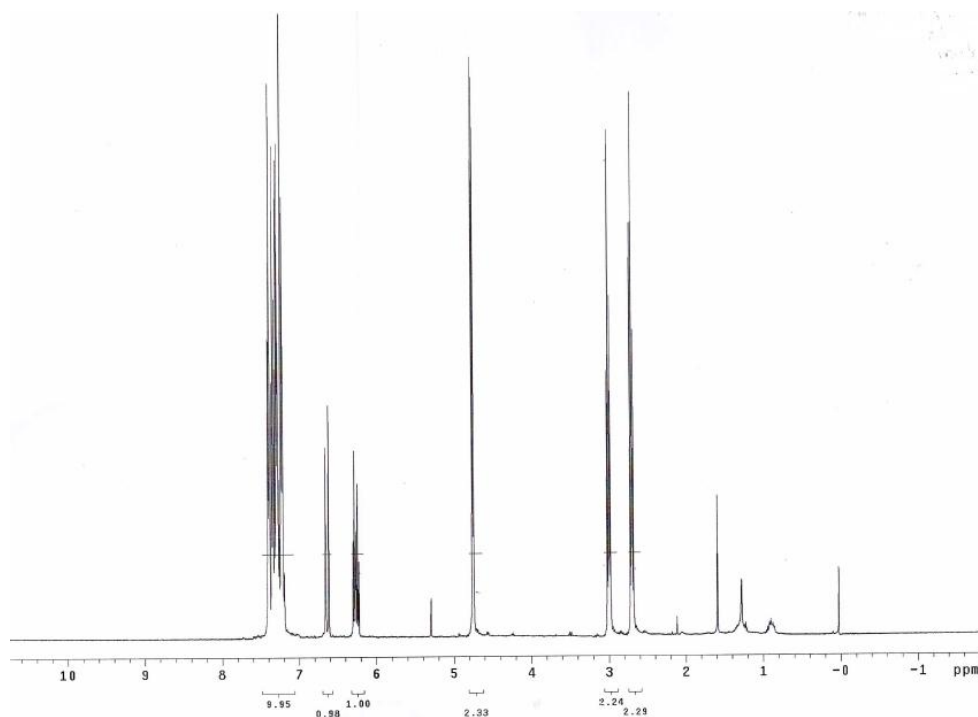
**Cinnamyl 3-phenylpropanoate (Table 1, 1b)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.30 (m, 10H), 6.63 (d, 1H,  $J = 16.4$  Hz), 6.26 (m, 1H), 4.75 (d, 2H,  $J = 6.0$  Hz), 3.00 (t, 2H,  $J = 7.2$  Hz), 2.70 (t, 2H,  $J = 7.2$  Hz) ppm

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.5, 140.4, 136.2, 134.1, 128.6, 128.5, 128.3, 128.0, 126.6, 126.3, 123.2, 65.2, 36.1, 31.2 ppm

**IR** (neat,  $\text{cm}^{-1}$ ): 3028, 1734, 1603, 1451

**HRMS**:  $\text{C}_{18}\text{H}_{18}\text{O}_2$  Calcd : 266.1307,  $[\text{M}]^+$  Found : 266.1309



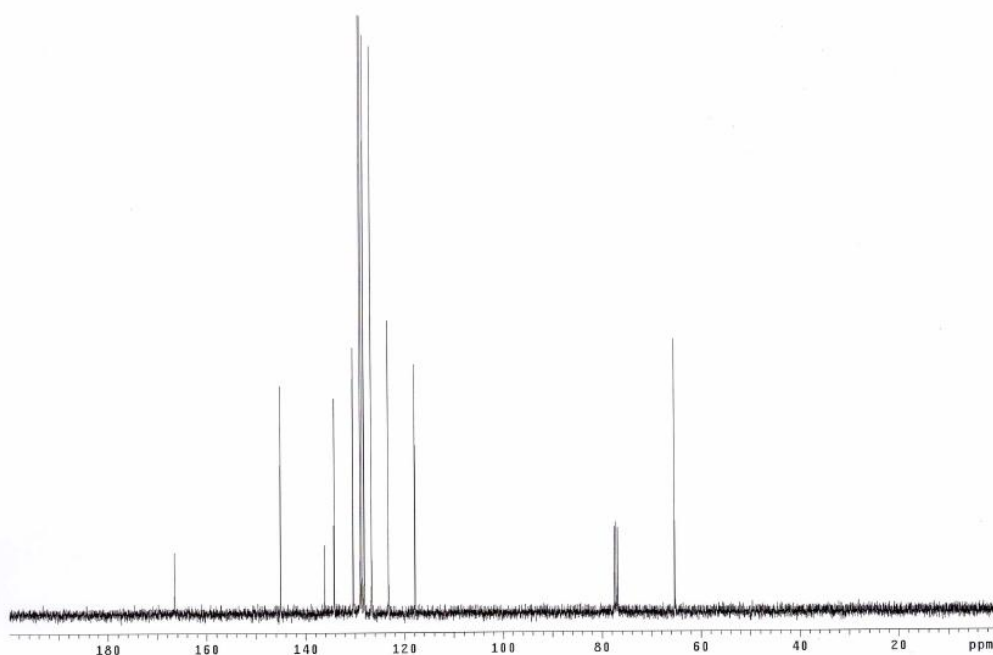
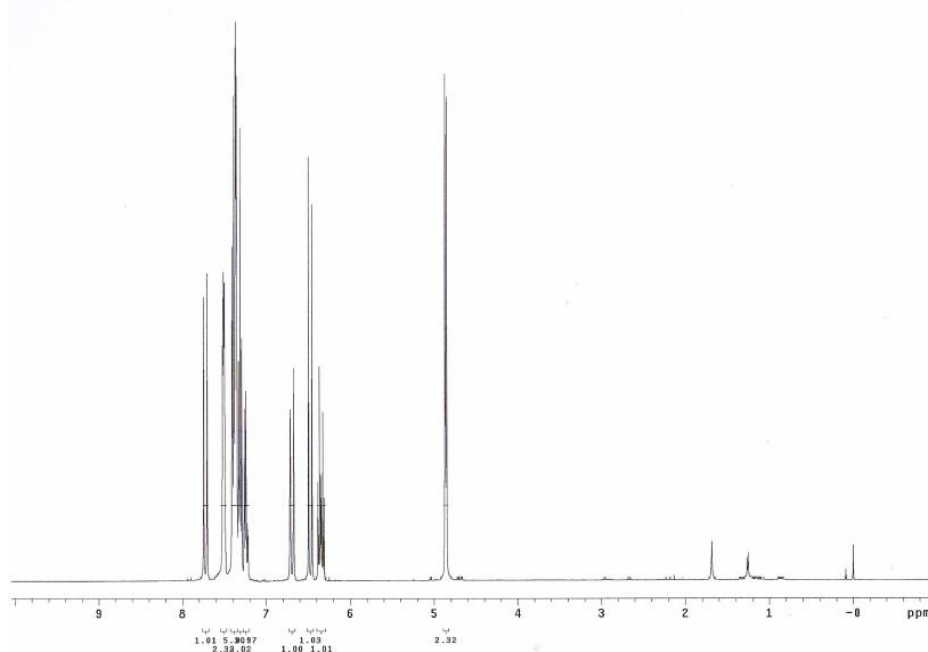
**Cinnamyl cinnamate (Table 1, 1c)** : The representative experimental method B (O<sub>2</sub> was injected instead of CO<sub>2</sub> as an oxidant) was applied to compound **1a** (67.1 mg, 0.5 mmol) to yield product **1b** (26.4 mg, 40%) and **1c** (17.4 mg, 26%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.73 (d, 1H, *J* = 17.2 Hz), 7.53 (m, 2H), 7.39 (m, 5H), 7.32 (m, 2H), 7.26 (m, 1H), 6.70 (d, 1H, *J* = 16.0 Hz), 6.48 (d, 1H, *J* = 16.0 Hz), 6.36 (m, 1H), 4.87 (d, 2H, *J* = 6.8 Hz) ppm

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 166.6, 145.0, 136.1, 134.3, 134.2, 130.3, 128.9, 128.6, 128.1, 126.6, 123.2, 117.8, 65.3 ppm

**IR** (neat, cm<sup>-1</sup>): 2930, 1734, 1588, 1488, 1156

**HRMS**: C<sub>18</sub>H<sub>16</sub>O<sub>2</sub> Calcd : 264.1150, [M]<sup>+</sup> Found : 264.1148



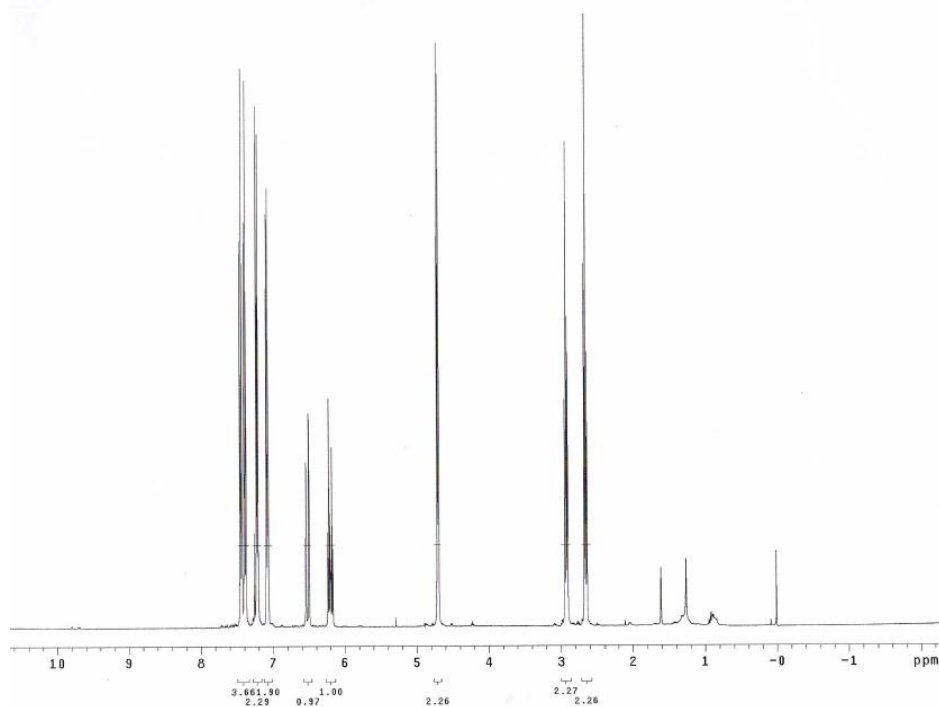
**(E)-3-(4-Bromophenyl)allyl 3-(4-bromophenyl)propanoate (Table 2, 2b)** : The representative experimental method A was applied to compound **2a** (106.0 mg, 0.5 mmol) to yield product **2b** (54.9 mg, 52%).

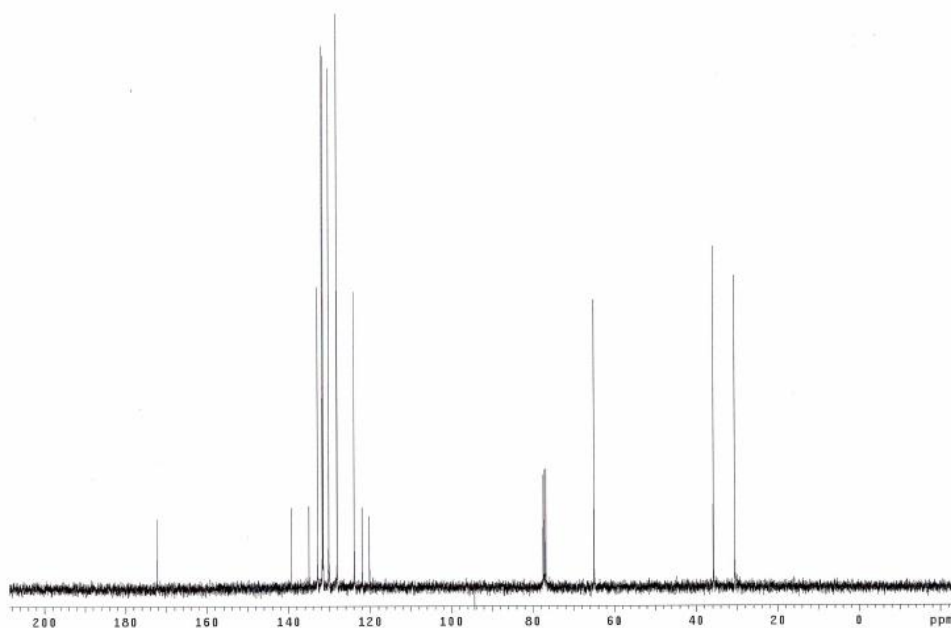
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.45 (d, 2H, *J* = 8.4 Hz), 7.39 (d, 2H, *J* = 8.4 Hz), 7.22 (d, 2H, *J* = 8.8 Hz), 7.08 (d, 2H, *J* = 8.4 Hz), 6.52 (d, 1H, *J* = 15.6 Hz), 6.20 (m, 1H), 4.71 (d, 2H, *J* = 7.6 Hz), 2.93 (t, 2H, *J* = 7.6 Hz), 2.66 (t, 2H, *J* = 7.6 Hz) ppm

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 172.1, 139.3, 135.0, 132.9, 131.7, 131.5, 130.1, 128.1, 123.8, 122.0, 120.1, 65.0, 35.8, 30.5 ppm

**IR** (neat, cm<sup>-1</sup>): 2930, 1734, 1588, 1488, 1156

**HRMS**: C<sub>18</sub>H<sub>16</sub>Br<sub>2</sub>O<sub>2</sub> Calcd : 423.9498, [M]<sup>+</sup> Found : 423.9515





**(E)-3-(4-Methoxyphenyl)allyl 3-(4-methoxyphenyl)propanoate (Table 2, 3b)** : The representative experimental method B was applied to compound **3a** (82.0 mg, 0.5 mmol) to yield product **3b** (34.2 mg, 42%).

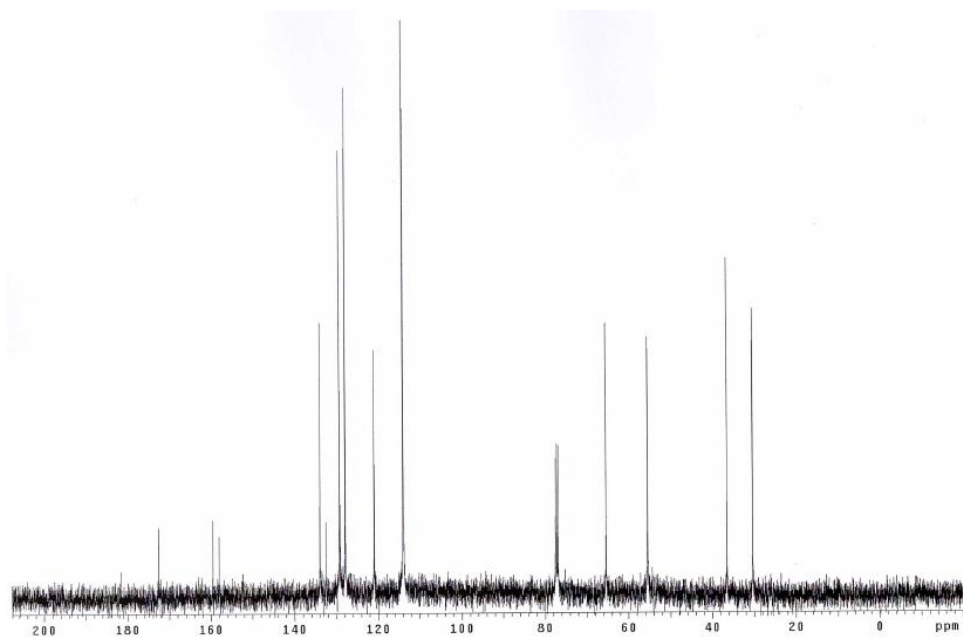
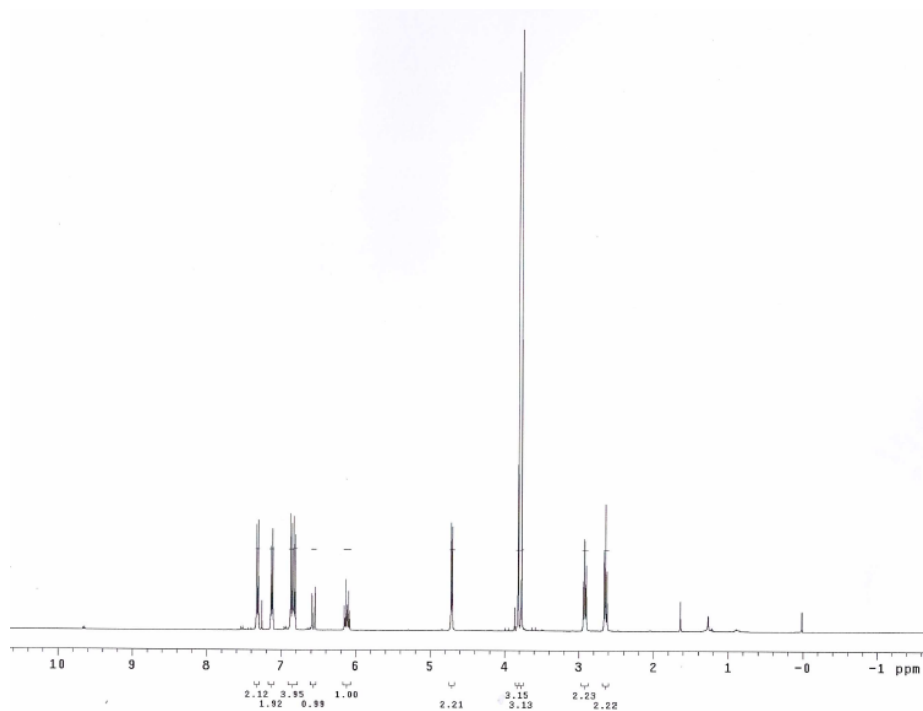
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.32 (d, 2H,  $J = 8.8$  Hz), 7.13 (d, 2H,  $J = 8.8$  Hz), 6.84 (m, 4H), 6.57 (d, 1H,  $J = 15.6$  Hz), 6.12 (m, 1H), 4.71 (d, 2H,  $J = 7.6$  Hz), 3.81 (s, 3H), 3.77 (s, 3H), 2.92 (t, 2H,  $J = 7.6$  Hz), 2.64 (t, 2H,  $J = 7.6$  Hz) ppm

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  172.6, 159.5, 158.0, 133.9, 132.5, 129.2, 129.0, 127.8, 120.9, 114.0, 113.9, 65.4, 55.4, 36.4, 30.4 ppm

**IR** (neat, cm<sup>-1</sup>): 3391, 1731, 1608, 1512, 1248

**HRMS**: C<sub>20</sub>H<sub>22</sub>O<sub>4</sub> Calcd : 326.1518, [M]<sup>+</sup> Found : 326.1514





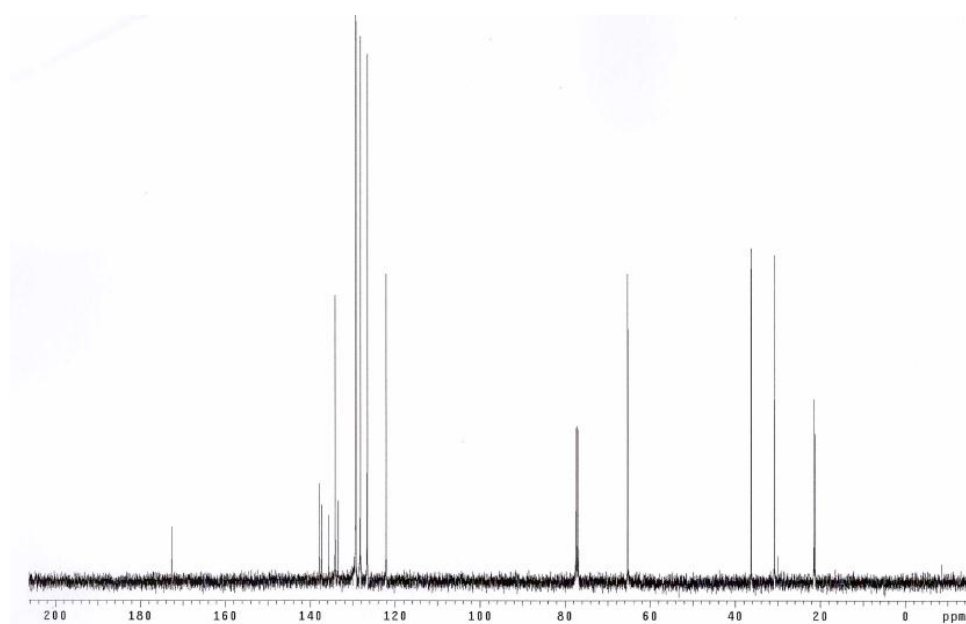
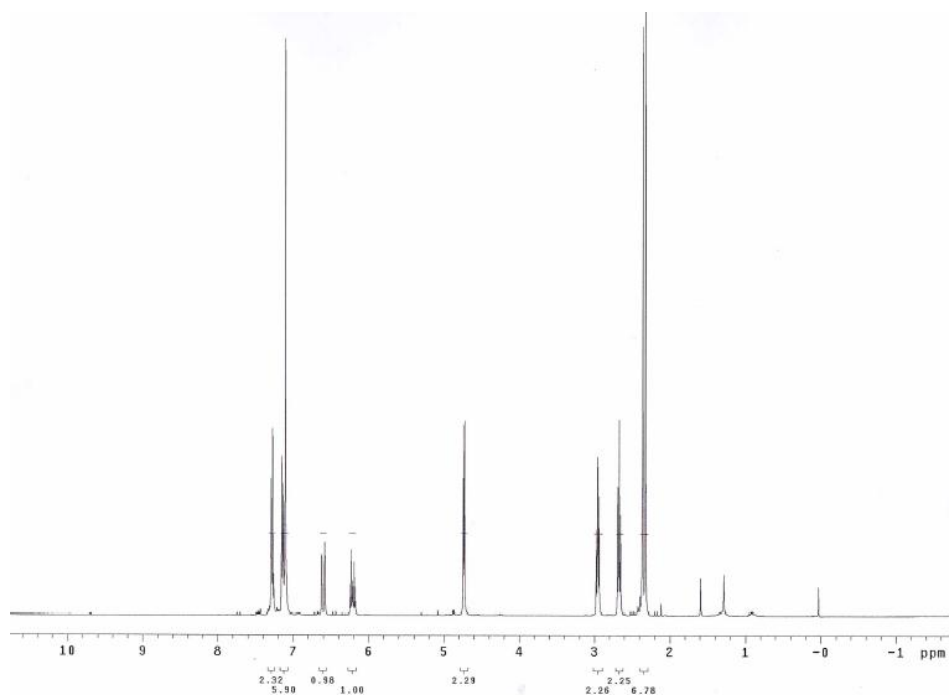
**(E)-3-p-Tolylallyl 3-p-tolylpropanoate (Table 2, 4b)** : The representative experimental method **B** was applied to compound **4a** (74.0 mg, 0.5 mmol) to yield product **4b** (41.9 mg, 57%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.29 (m, 2H,  $J = 7.6$  Hz), 7.13 (m, 6H), 6.60 (d, 1H,  $J = 15.6$  Hz), 6.21 (m, 1H), 4.73 (d, 2H,  $J = 6.0$  Hz), 2.96 (t, 2H,  $J = 7.6$  Hz), 2.67 (t, 2H,  $J = 7.6$  Hz), 2.36 (s, 3H), 2.33 (s, 3H) ppm

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  172.6, 137.9, 137.4, 135.7, 134.2, 133.4, 129.3, 129.2, 128.2, 126.5, 122.2, 65.3, 36.3, 30.8, 21.5, 21.3 ppm

IR (neat,  $\text{cm}^{-1}$ ): 2919, 1723, 1515, 1450, 1147

HRMS:  $\text{C}_{20}\text{H}_{22}\text{O}_2$  Calcd : 294.1620,  $[\text{M}]^+$  Found : 294.1620



**(E)-3-(4-Chlorophenyl)allyl 3-(4-chlorophenyl)propanoate (Table 2, 5b)** : The representative experimental method A was applied to compound **5a** (84.0 mg, 0.5 mmol) to yield product **5b** (44.5 mg, 53%).

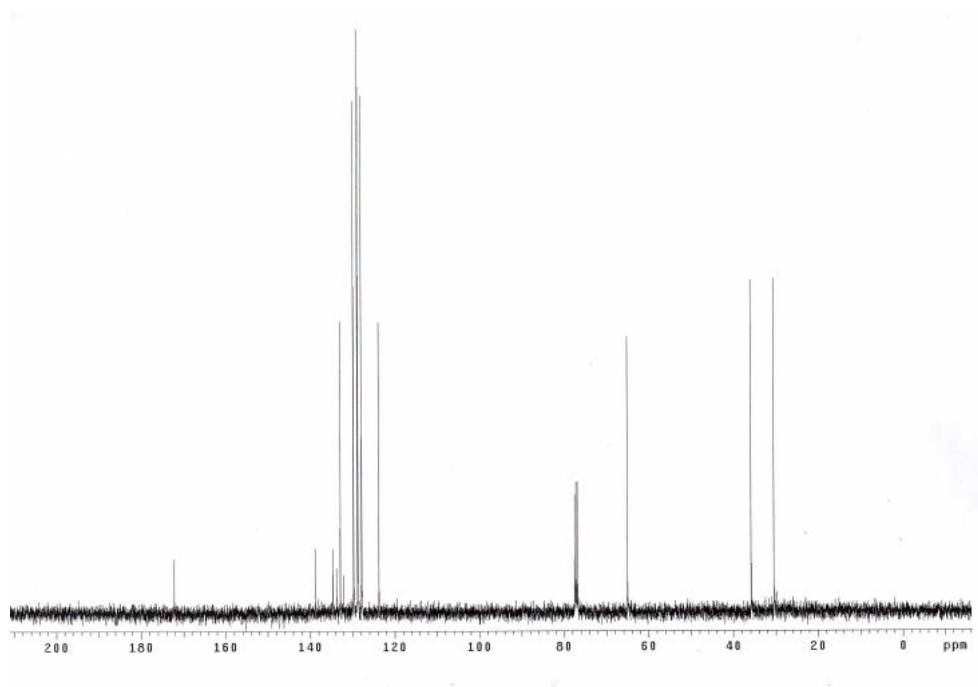
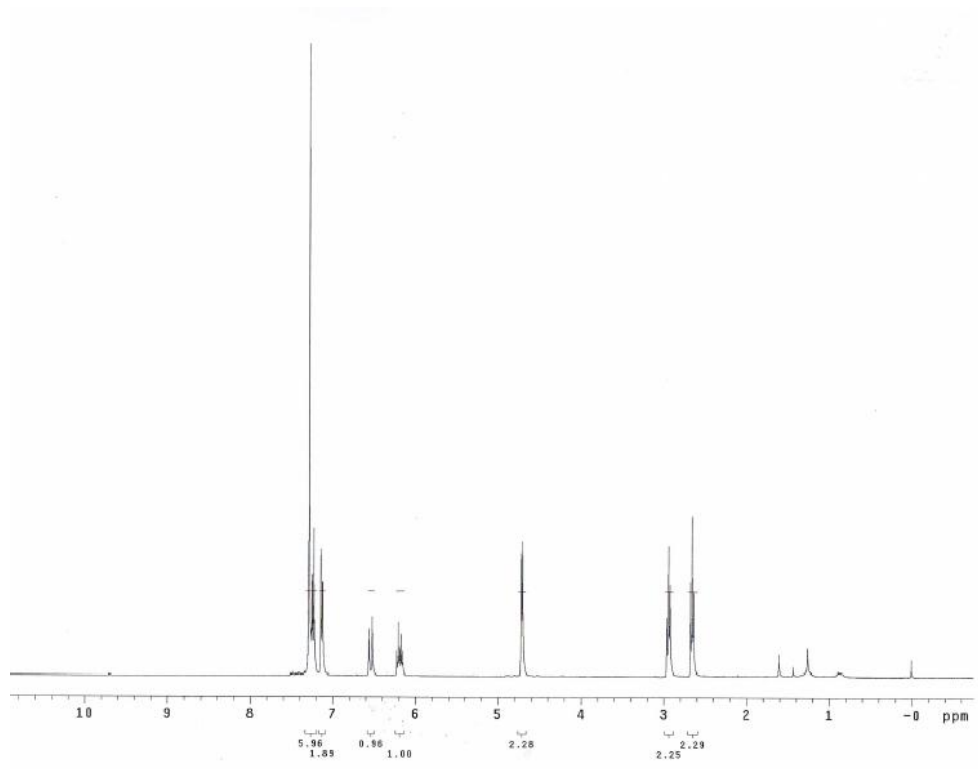
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.25 (m, 6H), 7.13 (d, 2H,  $J = 8.4$  Hz), 6.54 (d, 1H,  $J = 16.0$  Hz), 6.19 (m, 1H), 4.71 (d, 2H,  $J = 7.6$  Hz), 2.93 (t, 2H,  $J = 7.6$  Hz), 2.66 (t, 2H,  $J =$

7.6 Hz) ppm

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.2, 138.8, 134.6, 133.7, 132.9, 132.1, 129.7, 128.8, 128.6, 127.8, 123.7, 65.0, 35.9, 30.5 ppm

IR (neat,  $\text{cm}^{-1}$ ): 2929, 1736, 1594, 1492

HRMS:  $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{O}_2$  Calcd : 334.0527,  $[\text{M}]^+$  Found : 334.0524



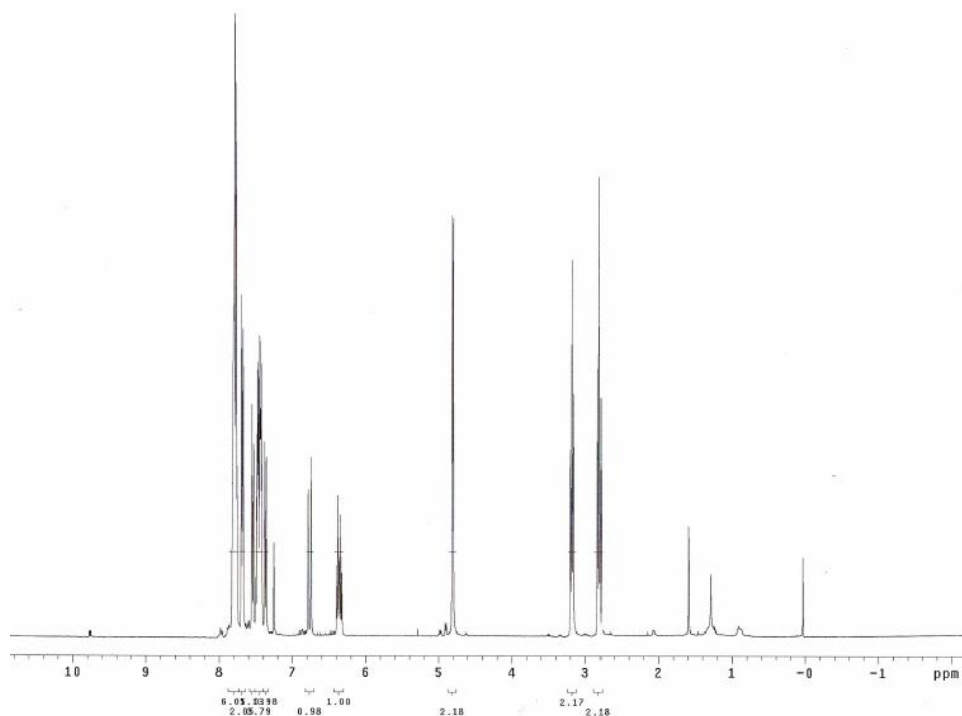
**(E)-3-(Naphthalen-2-yl)allyl 3-(naphthalen-2-yl)propanoate (Table 2, 6b)** : The representative experimental method B was applied to compound **6a** (92.0 mg, 0.5 mmol) to yield product **6b** (43.5 mg, 47%).

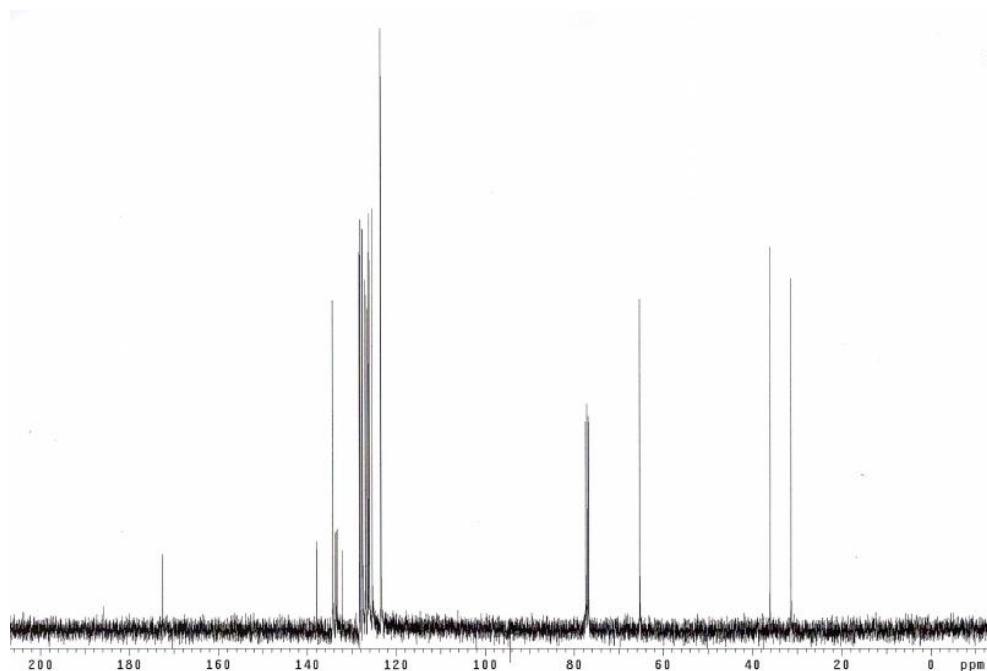
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (m, 6H), 7.70 (d, 2H,  $J = 7.2$  Hz), 7.55 (d, 1H,  $J = 8.4$  Hz), 7.47 (m, 4H), 7.38 (d, 1H,  $J = 8.4$  Hz), 6.77 (d, 2H,  $J = 15.6$  Hz), 6.37 (m, 1H), 4.81 (d, 2H,  $J = 6.4$  Hz), 3.19 (t, 2H,  $J = 7.6$  Hz), 2.93 (t, 2H,  $J = 7.6$  Hz) ppm

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  172.5, 137.9, 134.2, 133.6, 133.5, 133.2, 132.1, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.0, 126.8, 126.5, 126.3, 126.1, 126.0, 125.4, 123.5, 65.3, 36.1, 31.4 ppm

**IR** (neat, cm<sup>-1</sup>): 3384, 1730, 1636, 1155

**HRMS**: C<sub>26</sub>H<sub>22</sub>O<sub>2</sub> Calcd : 366.1620, [M]<sup>+</sup> Found : 366.1619





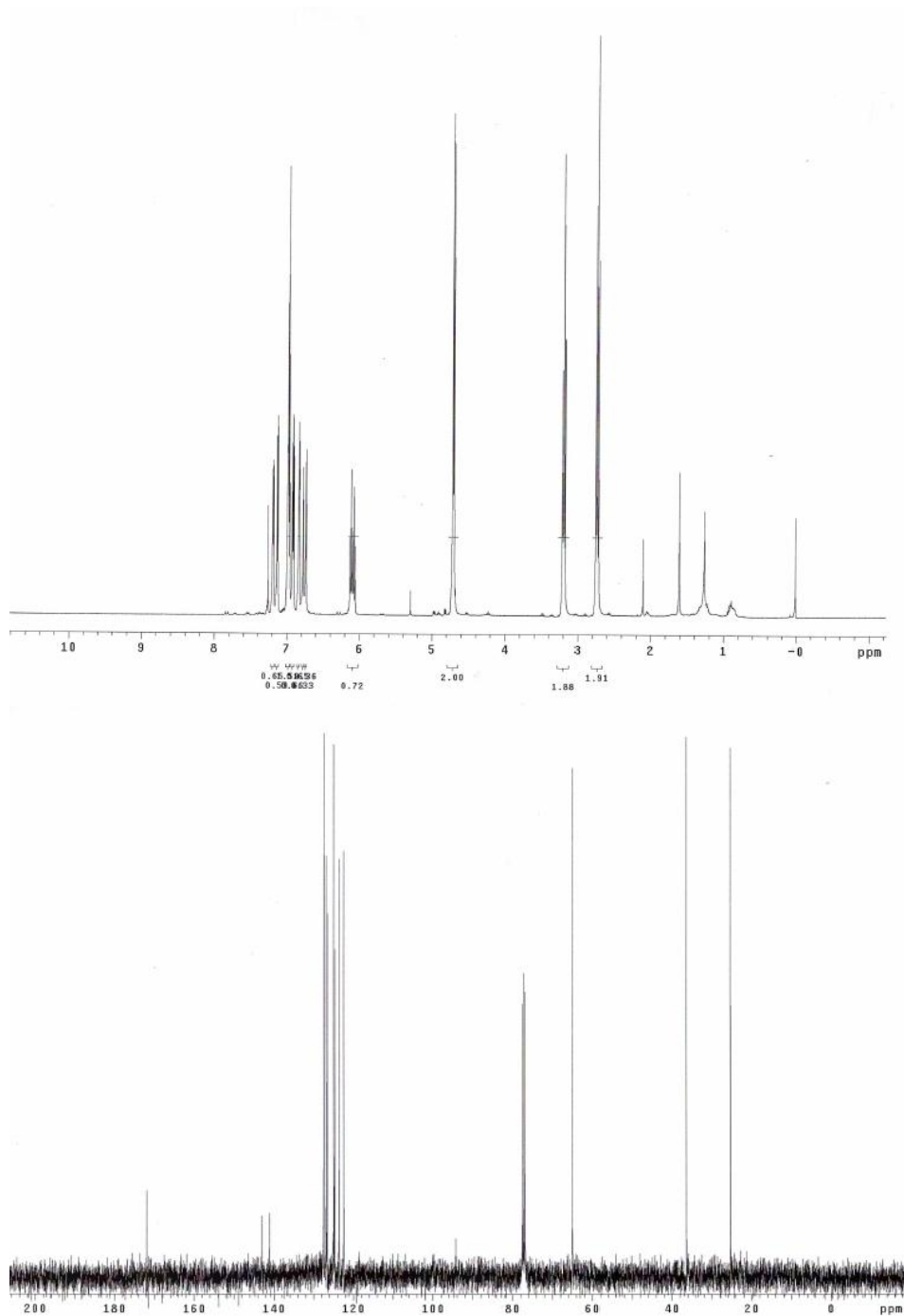
**(E)-3-(Thiophen-2-yl)allyl 3-(thiophen-2-yl)propanoate (Table 2, 7b)** : The representative experimental method B was applied to compound **7a** (70.0 mg, 0.5 mmol) to yield product **7b** (35.0 mg, 50%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.19 (d, 1H,  $J$  = 4.4 Hz), 7.13 (dd, 1H,  $J$  = 1.2, 5.2 Hz), 6.98 (m, 2H), 6.92 (m, 1H), 6.83 (m, 1H), 6.76 (d, 2H,  $J$  = 16.0 Hz), 6.10(m, 1H), 4.71(dd, 2H,  $J$  = 1.6, 6.0 Hz), 3.20(t, 2H,  $J$  = 7.2 Hz), 2.74(t, 2H,  $J$  = 7.6 Hz) ppm

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  172.0, 142.9, 141.1, 127.4, 126.9, 126.6, 125.0, 123.6, 122.4, 65.0, 36.4, 25.4 ppm

**IR** (neat, cm<sup>-1</sup>): 3358, 2359, 1733, 1650, 1165

**HRMS**: C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>S<sub>2</sub> Calcd : 278.0435, [M]<sup>+</sup> Found : 278.0435



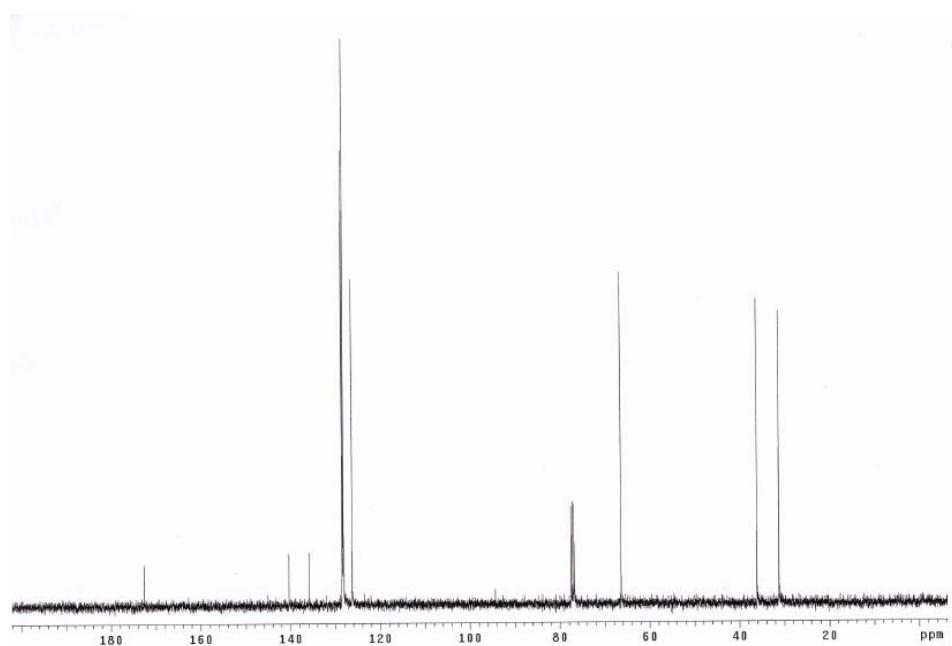
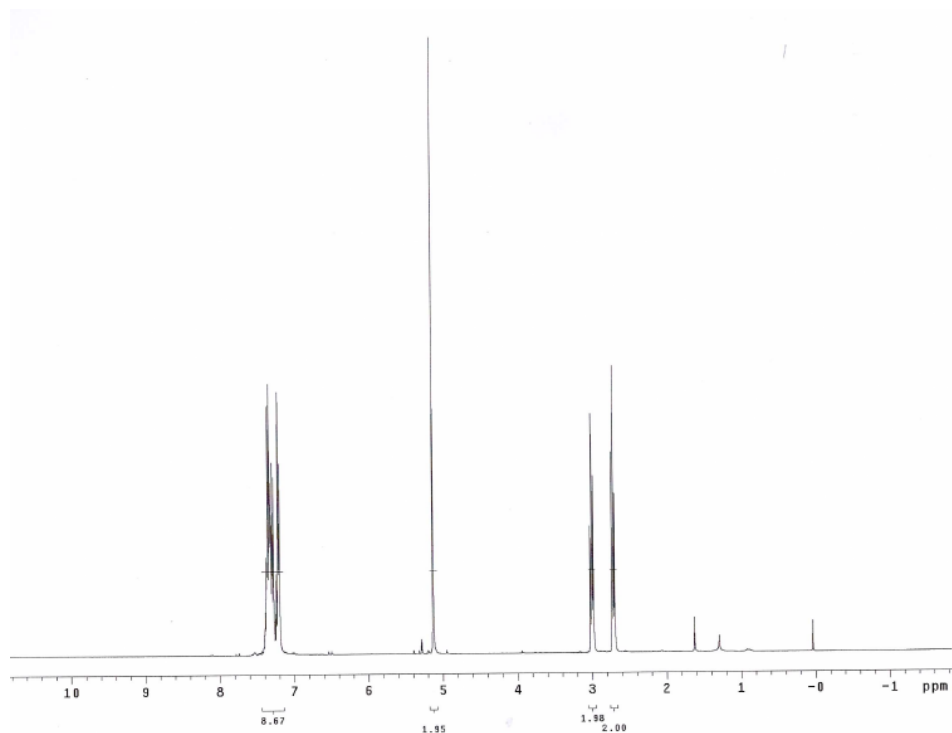
**Benzyl 3-phenylpropanoate (Table 2, 8b)** : The representative experimental method B was applied to compound **1a** (67.1 mg, 0.5 mmol) and **8a** ( 108.1 mg, 1 mmol) to yield product **8b** (22.0 mg, 18%) and **1b** (26.9 mg, 40%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.29(m, 8H), 5.14(s, 2H), 3.00(t, 2H,  $J = 7.6$  Hz), 2.71(t, 2H,  $J = 7.6$  Hz)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  172.6, 140.3, 135.9, 128.5, 128.3, 128.2, 126.2, 66.4, 36.1, 31.2 ppm

IR (neat, cm<sup>-1</sup>): 3030, 1736, 1497, 1159

HRMS: C<sub>16</sub>H<sub>16</sub>O<sub>2</sub> Calcd : 240.1150, [M]<sup>+</sup> Found : 240.1150



**Cinnamyl benzoate (Table 2, 9b)** : The representative experimental procedure B was applied to compound **1a** (67.1 mg, 0.5 mmol) and **9a** (106.1 mg, 0.5 mmol) to yield product **9b** (47.8 mg, 40%) and **1b** (15.8 mg, 24%).

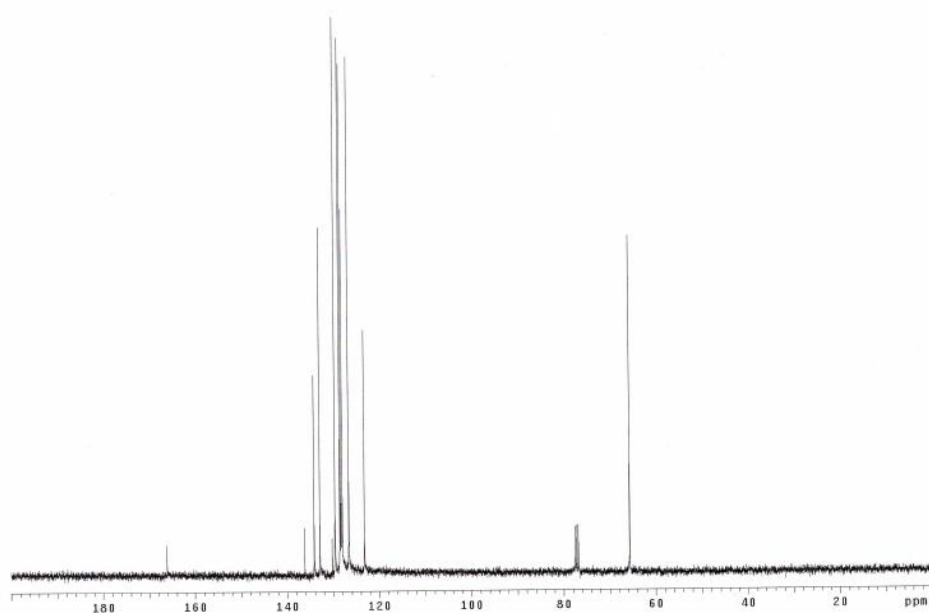
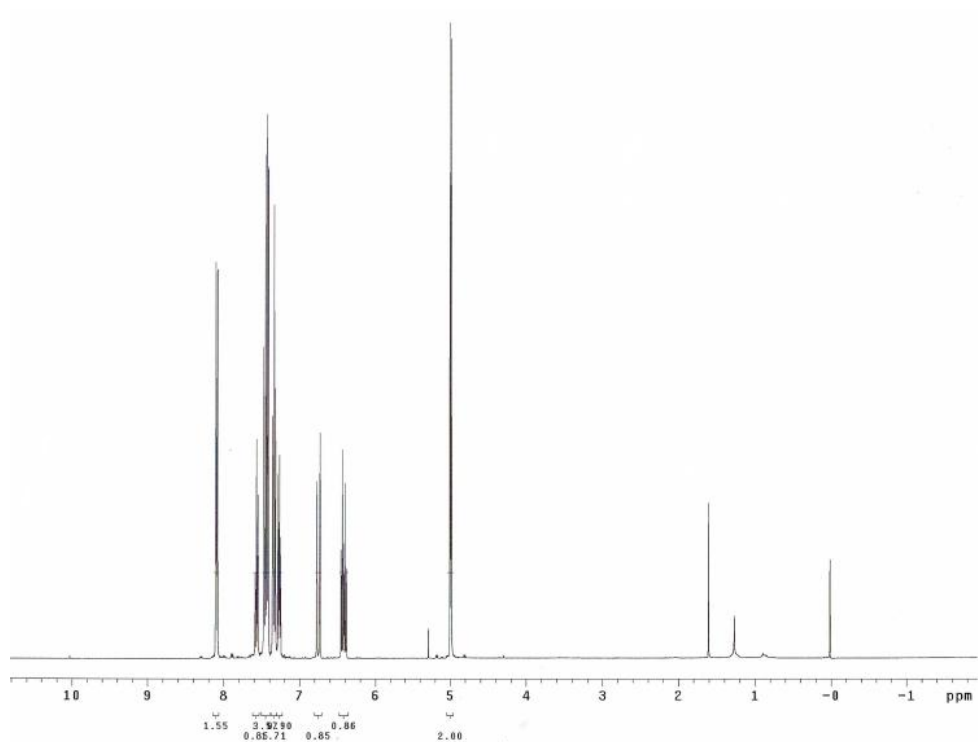
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.12 (m, 1H), 7.58 (m, 1H), 7.46 (m, 4H), 7.35 (m, 2H), 7.28 (m, 1H), 6.77 (d, 1H,  $J$  = 16.0 Hz), 6.43 (m, 1H), 5.01 (dd, 2H,  $J$  = 1.6, 6.0 Hz)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  166.2, 136.2, 134.2, 133.0, 130.2, 129.6, 128.6, 128.3, 128.0,

126.6, 123.3, 65.6 ppm

IR (neat,  $\text{cm}^{-1}$ ): 3416, 1719, 1601, 1450, 1269

HRMS:  $\text{C}_{16}\text{H}_{14}\text{O}_2$  Calcd : 238.0994,  $[\text{M}]^+$  Found : 238.0996





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- <sup>1</sup> (a) Chen, H.; Chen, W.; Gan, L.-S.; Mutlib, A. E. *Drug Metab. Dispos.* **2003**, *31*, 122-132.  
(b) Chauhan, N.; Thackray, S. J.; Rafice, S. A.; Eaton, G.; Lee, M.; Efimov, I.; Basran, J.; Jenkins, P. R.; Mowat, C. G.; Chapman, S. K.; Raven, D. L. *J. Am. Chem. Soc.* **2009**, *131*, 4186-4187.