

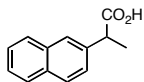
Catherine M. Williams, Jeffrey B. Johnson, and Tomislav Rovis

*Department of Chemistry, Colorado State University  
Fort Collins, Colorado 80523*

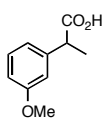
### ***Supporting Information***

**General Methods.** All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. Tetrahydrofuran (THF) was purged with argon and passed through two columns of neutral alumina. Column chromatography was performed using EM Science silica gel 60 (230-400 mesh.) Thin layer chromatography was performed using EM Science 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light,  $\text{KMnO}_4$ , aqueous ceric ammonium molybdate or bromocresol green dyes followed by heating. Unless otherwise noted, starting materials are commercially available from Sigma Aldrich and were utilized without further purification. Styrenes **4a** and **9a** were obtained by treatment of commercially available acid with  $\text{TMSCHN}_2$ . Styrene **10a** was obtained by treatment of the corresponding acid with DCC/ $\text{BnOH}$ . Styrenes **4a**, **12a**, **15a** were prepared by coupling with the corresponding aryl bromide via the procedure reported by Molander.<sup>24</sup>  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Varian 300 MHz spectrometer at ambient temperature unless otherwise noted.

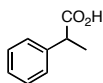
**General Hydrocarboxylation Procedure** will be illustrated with a specific example.  $\text{Ni}(\text{acac})_2$  (10.0 mg, 0.04 mmol) and  $\text{Cs}_2\text{CO}_3$  (26 mg, 0.08 mmol) were weighed into an oven-dried 10 mL round bottom flask which was sealed with a septum, evacuated and refilled with argon two times. The solid was dissolved in THF (1 mL) and 4- $\text{CF}_3$ -styrene (60  $\mu\text{L}$ , 0.4 mmol) was added via syringe. The flask sparged with  $\text{CO}_2$  from a balloon three times. Finally,  $\text{Et}_2\text{Zn}$  (100  $\mu\text{L}$ , 0.97 mmol) was added via syringe. The reaction was allowed to stir at room temperature. After 10 hours, the reaction was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc ( $2 \times 10$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and the solvent was evaporated under low pressure to yield the crude product. The crude material was dissolved in acetone, adsorbed onto silica gel, and purified by column chromatography.



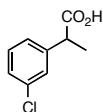
**$\alpha$ -(2-Naphthyl)propionic acid (X).** According to the general procedure for the general hydrocarboxylation procedure, THF (1 mL) was added to a flask containing 2-vinylnaphthalene (**3a**) (62 mg, 0.4 mmol), Ni(acac)<sub>2</sub> (10 mg, 0.04 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (26 mg, 0.08 mmol). After switching to a CO<sub>2</sub> atmosphere and addition of Et<sub>2</sub>Zn (100  $\mu$ L, 0.97 mmol), the reaction was allowed to stir at 23 °C for 12 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc (3  $\times$  5 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under low pressure to provide the crude product. The acid was purified by column chromatography (19:1:1 Hexanes:EtOAc:AcOH) to provide a yellow oil (48 mg, 0.24 mmol, 60%). Spectral data matched literature description.<sup>1</sup>



**2-(3-methoxyphenyl)propionic acid (X).** According to the general procedure for the general hydrocarboxylation procedure, 3-vinylanisole (**X**) (55  $\mu$ L, 0.4 mmol) was added to a THF solution (1 mL) containing Ni(acac)<sub>2</sub> (10 mg, 0.04 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (26 mg, 0.08 mmol). After switching to a CO<sub>2</sub> atmosphere and addition of Et<sub>2</sub>Zn (100  $\mu$ L, 0.97 mmol), the reaction was stirred at 23 °C for 12 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc (3  $\times$  5 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under low pressure to provide the crude product. The acid was purified by column chromatography (19:1:1 Hexanes:EtOAc:AcOH) to provide a pale yellow oil (66 mg, 0.36 mmol, 92%). Spectral data matched literature description.<sup>2</sup>



**2-phenylpropionic acid (X).** According to the general procedure for the general hydrocarboxylation procedure, styrene (**X**) (50  $\mu$ L, 0.4 mmol) purified according to X, was added to a THF solution (1 mL) containing Ni(acac)<sub>2</sub> (20 mg, 0.08 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (52 mg, 0.16 mmol). After switching to a CO<sub>2</sub> atmosphere and addition of Et<sub>2</sub>Zn (100  $\mu$ L, 0.97 mmol), the reaction was stirred at 23 °C for 12 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc (3  $\times$  5 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under low pressure to provide the crude product. The acid was purified by column chromatography (19:1:1 Hexanes:EtOAc:AcOH) to provide a clear oil (33 mg, 0.22 mmol, 56%). Spectral data matched literature description.<sup>3</sup>



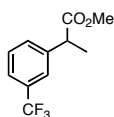
**2-(3-chlorophenyl)propionic acid (X).** According to the general procedure for the general hydrocarboxylation procedure, 3-chlorostyrene (**X**) (51  $\mu$ L, 0.4

<sup>1</sup> Clericuzio, M.; Degani, I.; Dughera, S.; Fochi, R. *Synthesis*. **2002**, 7, 921.

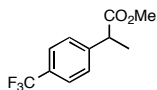
<sup>2</sup> Kübler, W.; Petrov, O.; Winterfeldt, E.; Ernst, L.; Schomburg, D. *Tetrahedron*, **1988**, 44, 4371.

<sup>3</sup> *JOC*, **1986**, 51, 4354.

mmol) was added to a THF solution (1 mL) containing Ni(acac)<sub>2</sub> (10 mg, 0.04 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (26 mg, 0.08 mmol). After switching to a CO<sub>2</sub> atmosphere and addition of Et<sub>2</sub>Zn (100 μL, 0.97 mmol), the reaction was stirred at 23 °C for 12 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under low pressure to provide the crude product. The acid was purified by column chromatography (19:1:1 Hexanes:EtOAc:AcOH) to provide a clear oil (50 mg, 0.27 mmol, 68%). Spectral data matched literature description.<sup>4</sup>



**2-(3-trifluoromethylphenyl)propionic acid methyl ester (X).** According to the general procedure for the general hydrocarboxylation procedure, 3-chlorostyrene (X) (51 μL, 0.4 mmol) was added to a THF solution (1 mL) containing Ni(acac)<sub>2</sub> (10 mg, 0.04 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (26 mg, 0.08 mmol). After switching to a CO<sub>2</sub> atmosphere and addition of Et<sub>2</sub>Zn (100 μL, 0.97 mmol), the reaction was stirred at 23 °C for 12 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under low pressure to provide the crude product. The acid was converted to the corresponding ester by refluxing in methanol with catalytic sulfuric acid. The ester was purified by column chromatography (95:5 hexanes:EtOAc) to provide the desired ester as a clear oil (73 mg, 0.32 mmol, 79%). Spectral data matched literature description.<sup>5</sup>

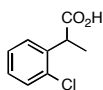


**2-(4-Trifluoromethyl-phenyl)-propionic acid methyl ester (X).** According to the general procedure for the general hydrocarboxylation procedure, 4-trifluoromethylstyrene (X) (60 μL, 0.4 mmol) was added to a THF solution (1 mL) containing Ni(acac)<sub>2</sub> (10 mg, 0.04 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (26 mg, 0.08 mmol). After switching to a CO<sub>2</sub> atmosphere and addition of Et<sub>2</sub>Zn (100 μL, 0.97 mmol), the reaction was stirred at 23 °C for 12 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under low pressure to provide the crude product. The acid was converted to the corresponding ester by dissolving the oil in 1:1 MeOH:benzene and treating the solution with TMSCHN<sub>2</sub>. The ester was purified by column chromatography (95:5 hexanes:EtOAc) to provide the desired ester as a clear oil (85 mg, 0.37 mmol, 92% yield). R<sub>f</sub> = 0.38 (9:1 hexanes:EtOAc). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.58 (2H, d, J = 7.5 Hz), 7.42 (2H, d, J = 7.5 Hz), 3.79 (1H, q, J = 7.5 Hz), 3.67 (3H, s), 1.52 (3H, d, J = 7.5 Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 174.4, 144.6, 129.6 (q, J<sub>C-F</sub> = 41.5 Hz), 128.1,

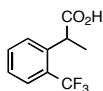
<sup>4</sup> Page, P.; McKenzie, M.; Allin, M.; Clair, S. *Tetrahedron*, **1997**, *53*, 13149.

<sup>5</sup> Durandetti, M; Gosmini, C.; Périchon, J. *Tetrahedron*, **2007**, *63*, 1146.

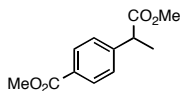
125.7 (q,  $J_{C-F} = 4$  Hz), 125.6, 52.4, 45.5, 18.7. IR (NaCl) 1740, 1327, 1166, 1124  $\text{cm}^{-1}$ . HRMS (FAB+) calcd for  $\text{C}_{11}\text{H}_{12}\text{F}_3\text{O}_2$ , 233.0789. Found 233.0785.



**2-(2-Chlorophenyl)-propionic acid (X).** According to the general procedure for the general hydrocarboxylation procedure, 2-Cl-styrene (**X**) (51  $\mu\text{L}$ , 0.4 mmol) was added to a THF solution (1 mL) containing  $\text{Ni}(\text{acac})_2$  (10 mg, 0.04 mmol) and  $\text{Cs}_2\text{CO}_3$  (26 mg, 0.08 mmol). After switching to a  $\text{CO}_2$  atmosphere and addition of  $\text{Et}_2\text{Zn}$  (100  $\mu\text{L}$ , 0.97 mmol), the reaction was allowed to stir at 23  $^\circ\text{C}$  for 12 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc ( $3 \times 5$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated under low pressure to provide the crude product. The desired acid was purified by column chromatography (19:1:1 hexanes:EtOAc:AcOH) to provide the desired ester as a white solid (48 mg, 0.26 mmol, 65% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.27 (m, 4H), 4.23 (q, 1H,  $J = 7.0$  Hz), 1.49 (d, 3H,  $J = 7.0$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  180.5, 137.9, 134.0, 129.8, 128.7, 77.2, 42.3, 17.5. IR (NaCl,  $\text{CDCl}_3$ ) 2983, 2229, 1707, 1476, 1234, 1035  $\text{cm}^{-1}$ . HRMS (FAB+) calcd for **X**. Found **X**.

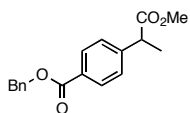


**2-(2-(trifluoromethyl)phenyl)-propionic acid (X).** According to the general procedure for the general hydrocarboxylation procedure, 2- $\text{CF}_3$ -styrene (**X**) (59  $\mu\text{L}$ , 0.4 mmol) was added to a THF solution (1 mL) containing  $\text{Ni}(\text{acac})_2$  (10 mg, 0.04 mmol) and  $\text{Cs}_2\text{CO}_3$  (26 mg, 0.08 mmol). After switching to a  $\text{CO}_2$  atmosphere and addition of  $\text{Et}_2\text{Zn}$  (100  $\mu\text{L}$ , 0.97 mmol), the reaction was allowed to stir at 23  $^\circ\text{C}$  for 12 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc ( $3 \times 5$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated under low pressure to provide the crude product. The desired acid was purified by column chromatography (19:1:1 hexanes:EtOAc:AcOH) to provide the desired ester as a clear oil (75 mg, 0.35 mmol, 87% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.63 (d, 1H,  $J = 7.9$  Hz), 7.5 (m, 2H), 7.3 (m, 1H), 4.17 (q, 1H,  $J = 7.0$  Hz), 1.50 (d, 3H,  $J = 7.0$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  179.1, 139.0, 132.4, 128.4, 126.1, 125.8, 123.1, 77.2, 40.8, 19.3. IR (NaCl,  $\text{CDCl}_3$ ) 2997, 1711, 1314, 1244, 1158, 1037  $\text{cm}^{-1}$ . HRMS (FAB+) calcd for **X**. Found **X**.



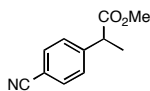
**4-(1-Methoxycarbonyl-ethyl)-benzoic acid methyl ester (X).** According to the general procedure for the general hydrocarboxylation procedure, 4- $\text{CO}_2\text{Me}$ -styrene (**X**) (65 mg, 0.4 mmol) was added to a THF solution (1 mL) containing  $\text{Ni}(\text{acac})_2$  (10 mg, 0.04 mmol) and  $\text{Cs}_2\text{CO}_3$  (26 mg, 0.08 mmol). After switching to a  $\text{CO}_2$  atmosphere and addition of  $\text{Et}_2\text{Zn}$  (100  $\mu\text{L}$ , 0.97 mmol), the reaction was stirred at 23  $^\circ\text{C}$  for 12 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc ( $2 \times 10$  mL). The combined organic layers were dried over

MgSO<sub>4</sub> and concentrated under low pressure to provide the crude product. The acid was converted to the corresponding ester by dissolving the oil in 1:1 MeOH:benzene and treating the solution with TMSCHN<sub>2</sub>. The ester was purified by column chromatography (95:5 hexanes:EtOAc) to provide the desired ester as a clear oil (99 mg, 0.33 mmol, 84% yield). R<sub>f</sub> = 0.25 (9:1 hexanes:EtOAc). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.98 (2H, d, *J* = 6.6 Hz), 7.35 (2H, d, *J* = 6.6 Hz), 3.89 (3H, s), 3.77 (1H, q, *J* = 7.2 Hz), 3.65 (3H, s), 1.50 (3H, d, *J* = 7.2 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 174.6, 167.0, 145.8, 130.2, 129.3, 127.8, 52.4, 52.3, 45.6, 18.6. IR (NaCl, CDCl<sub>3</sub>) 1736, 1720, 1610, 1455, 1273 cm<sup>-1</sup>. HRMS (FAB<sup>+</sup>) calcd for C<sub>12</sub>H<sub>15</sub>O<sub>4</sub><sup>+</sup>, 223.0965. Found 223.0972.



**4-(1-Methoxycarbonyl-ethyl)-benzoic acid benzyl ester (X).**

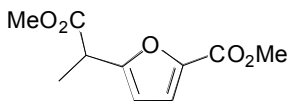
According to the general procedure for the general hydrocarboxylation procedure, 4-CO<sub>2</sub>Bn-styrene (**X**) (79 mg, 0.4 mmol) was added to a THF solution (1 mL) containing Ni(acac)<sub>2</sub> (10 mg, 0.04 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (26 mg, 0.08 mmol). After switching to a CO<sub>2</sub> atmosphere and addition of Et<sub>2</sub>Zn (100 μL, 0.97 mmol), the reaction was stirred at 23 °C for 16 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under low pressure to provide the crude product. The acid was converted to the corresponding ester by dissolving the oil in 1:1 MeOH:benzene and treating the solution with TMSCHN<sub>2</sub>. The ester was purified by column chromatography (95:5 hexanes:EtOAc) to provide the desired ester as a clear oil (120 mg, 0.32 mmol, 81% yield). R<sub>f</sub> = 0.24 (9:1 hexanes:EtOAc). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 8.04 (d, 2H, *J* = 8.1 Hz), 7.47-7.30 (m, 7H), 5.36 (s, 2H), 3.78 (q, 1H, *J* = 7.2 Hz), 3.66 (s, 3H), 1.52 (d, 3H, *J* = 7.2 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 174.3, 166.1, 145.7, 136.0, 130.1, 129.0, 128.5, 128.2, 128.1, 127.6, 66.6, 52.2, 45.4, 18.4. IR (NaCl, CDCl<sub>3</sub>) 1721, 1608, 1436, 1315, 1280 cm<sup>-1</sup>. HRMS (FAB<sup>+</sup>) calcd for C<sub>18</sub>H<sub>19</sub>O<sub>4</sub><sup>+</sup>, 299.1278. Found 299.1277.



**2-(4-Cyano-phenyl)-propionic acid methyl ester (X).**

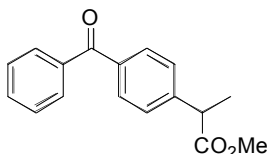
According to the general procedure for the general hydrocarboxylation procedure, 4-CN-styrene (**X**) (71 mg, 0.4 mmol) was added to a THF solution (1 mL) containing Ni(acac)<sub>2</sub> (10 mg, 0.04 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (15 μL, 0.10 mmol). After switching to a CO<sub>2</sub> atmosphere and addition of Et<sub>2</sub>Zn (100 μL, 0.97 mmol) the reaction was stirred at 23 °C for 16 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under low pressure to provide the crude product. The acid was converted to the corresponding ester by dissolving the oil in 1:1 MeOH:benzene and treating the solution with TMSCHN<sub>2</sub>. The ester was purified by column chromatography (95:5 hexanes:EtOAc) to provide the desired ester as a clear oil (46 mg, 0.24 mmol, 61%

yield).  $R_f = 0.28$  (9:1 hexanes:EtOAc).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.63 (d, 2H,  $J = 8.4$  Hz), 7.42 (d, 2H,  $J = 8.4$  Hz), 3.79 (q, 1H,  $J = 7.5$  Hz), 3.69 (s, 3H), 1.52 (d, 3H,  $J = 7.5$  Hz).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  173.8, 145.6, 132.4, 128.4, 118.7, 111.1, 52.3, 45.5, 18.3. IR (NaCl,  $\text{CDCl}_3$ ) 3425, 2229, 1737, 1608, 1210, 1168  $\text{cm}^{-1}$ . HRMS (FAB+) calcd for  $\text{C}_{11}\text{H}_{12}\text{NO}_2^+$ , 190.0868. Found 190.0872.



**5-(1-Methoxycarbonyl-ethyl)-furan-2-carboxylic acid methyl ester (X).** According to the general procedure for the general hydrocarboxylation procedure, 5-Vinyl-furan-2-carboxylic acid

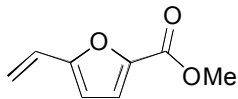
methyl ester (**4a**) (61 mg, 0.4 mmol) was added to a THF solution (1 mL) containing  $\text{Ni}(\text{acac})_2$  (10 mg, 0.04 mmol) and  $\text{Cs}_2\text{CO}_3$  (26 mg, 0.08 mmol). After switching to a  $\text{CO}_2$  atmosphere and addition of  $\text{Et}_2\text{Zn}$  (100  $\mu\text{L}$ , 0.97 mmol) the reaction was stirred at 23  $^\circ\text{C}$  for 16 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc ( $2 \times 10$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated under low pressure to provide the crude product. The acid was converted to the corresponding ester by dissolving the oil in 1:1 MeOH:benzene and treating the solution with  $\text{TMSCHN}_2$ . The ester was purified by column chromatography (9:1 hexanes:EtOAc) to provide the desired ester as a clear oil (56 mg, 0.26 mmol, 66% yield).  $R_f = 0.37$  (9:1 hexanes:EtOAc).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.12 (d, 1H,  $J = 3.2$  Hz), 6.32 (d, 1H,  $J = 3.2$  Hz), 3.90 (q, 1H,  $J = 7.2$  Hz), 3.87 (s, 3H), 3.72 (s, 3H), 1.56 (d, 3H,  $J = 7.2$  Hz).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.1, 159.0, 157.7, 143.6, 119.0, 108.5, 52.5, 51.8, 39.5, 15.9. IR (NaCl,  $\text{CDCl}_3$ ) 2954, 1739, 1521, 1437, 1376, 1308, 1207  $\text{cm}^{-1}$ . HRMS (FAB+) calcd for  $\text{C}_{10}\text{H}_{13}\text{O}_5^+$ , 213.0758. Found 213.0758.



**2-(4-Benzoyl-phenyl)-propionic acid methyl ester (X).**

According to the general procedure for the general hydrocarboxylation procedure, phenyl-(4-vinyl-phenyl)-methanone (**X**) (47 mg, 0.4 mmol) was added to a THF solution (1 mL) containing  $\text{Ni}(\text{acac})_2$  (10 mg, 0.04 mmol) and  $\text{Cs}_2\text{CO}_3$  (26  $\mu\text{L}$ , 0.08 mmol). After switching to a  $\text{CO}_2$  atmosphere and addition of  $\text{Et}_2\text{Zn}$  (100  $\mu\text{L}$ , 0.97 mmol) the reaction was stirred at 23  $^\circ\text{C}$  for 16 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with 1 M HCl (5 mL). After separation, the aqueous layer was extracted with EtOAc ( $2 \times 10$  mL). The combined organic layers were dried over  $\text{MgSO}_4$  and concentrated under low pressure to provide the crude product. The acid was converted to the corresponding ester by dissolving the oil in 1:1 MeOH:benzene and treating the solution with  $\text{TMSCHN}_2$ . The ester was purified by column chromatography (9:1 hexanes:EtOAc) to provide the desired ester as a clear oil (77 mg, 0.29 mmol, 72% yield).  $R_f = 0.31$  (9:1 hexanes:EtOAc).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 7.83-7.75 (m, 4H), 7.63-7.55 (m, 1H), 7.52-7.45 (m, 2H), 7.44-7.39 (m, 2H), 3.82 (q, 1H,  $J = 6.9$  Hz), 3.69 (s, 3H), 1.54 (d, 2H,  $J = 6.9$  Hz).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ): 196.4, 174.5, 145.3,

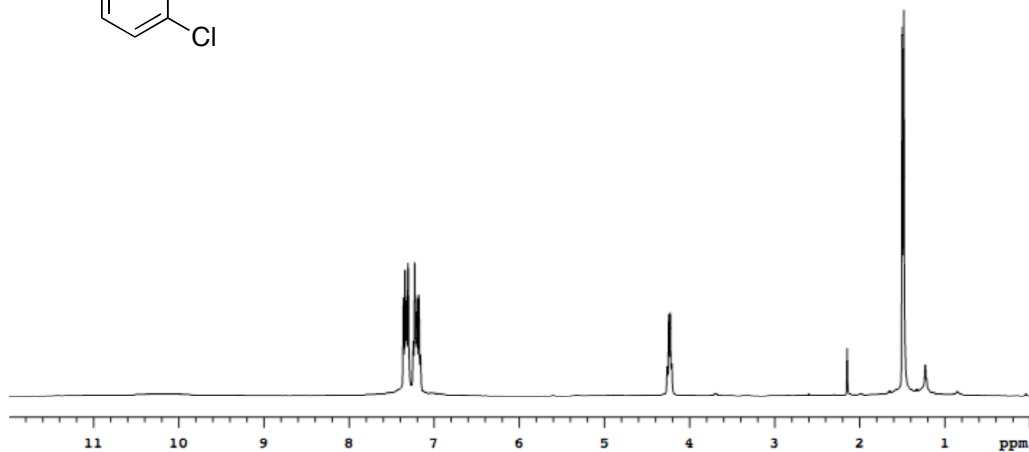
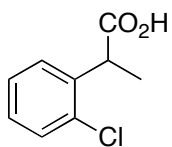
132.6, 130.7, 130.2, 128.5, 127.7, 52.4, 45.6, 18.6. IR (NaCl, CDCl<sub>3</sub>) 2927, 2254, 1732, 1659, 1607, 1456, 1280, 1211 cm<sup>-1</sup>. HRMS (FAB+) calcd for C<sub>17</sub>H<sub>17</sub>O<sub>3</sub><sup>+</sup>, 269.1172. Found 269.1162.



**5-Vinyl-furan-2-carboxylic acid methyl ester (4a).** Following the procedure of Molander<sup>24</sup> 5-Bromo-furan-2-carboxylic acid methyl ester (410 mg, 2.0 mmol) was combined with potassium vinyl trifluoroborate (268 mg, 2.0 mmol), PdCl<sub>2</sub> (7.0 mg, 0.02 mmol), PPh<sub>3</sub> (32 mg, 0.06 mmol) and CsCO<sub>3</sub> (6.0 mmol) in a sealed tube under argon and suspended in 9:1 THF:H<sub>2</sub>O (5 mL). Heating at 85 °C for 24 h and purification by column chromatography (19:1 hexanes:Et<sub>2</sub>O) provided the desired alkene (190 mg, 62% yield). R<sub>f</sub> = 0.24 (19:1 Hex:Et<sub>2</sub>O). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.14 (d, 1H, *J* = 3.6 Hz), 6.54 (dd, 1H, *J* = 11.4, 18.0 Hz), 6.38 (d, 1H, *J* = 3.6 Hz), 5.93 (d, 1H, *J* = 18 Hz), 5.37 (d, 1H, *J* = 11.4 Hz), 3.89 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 159.4, 156.7, 143.5, 124.6, 119.8, 117.1, 109.5, 52.1. IR (NaCl, CDCl<sub>3</sub>) 1727, 1506, 1436, 1302, 1223, 1207, 1141 cm<sup>-1</sup>. HRMS (FAB+) calcd for C<sub>8</sub>H<sub>9</sub>O<sub>3</sub><sup>+</sup>, 153.0552. Found 153.0547.

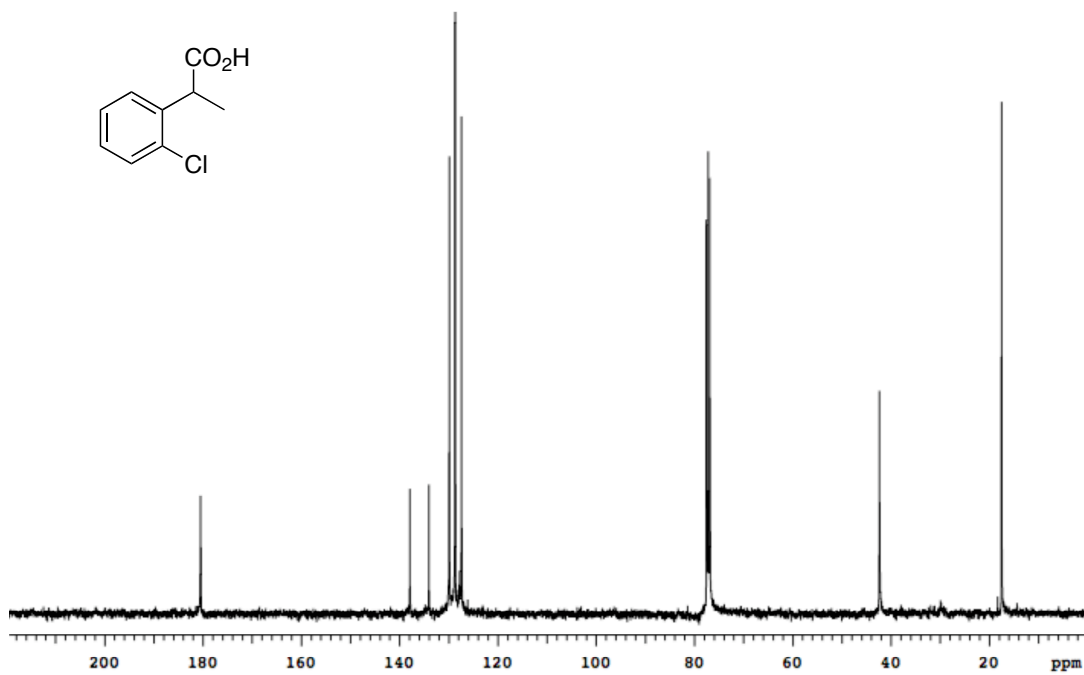
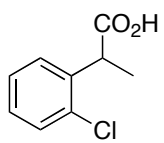
**<sup>1</sup>H-NMR Spectrum for X:**

STANDARD IN OBSERVE



### <sup>13</sup>C-NMR Spectrum for X:

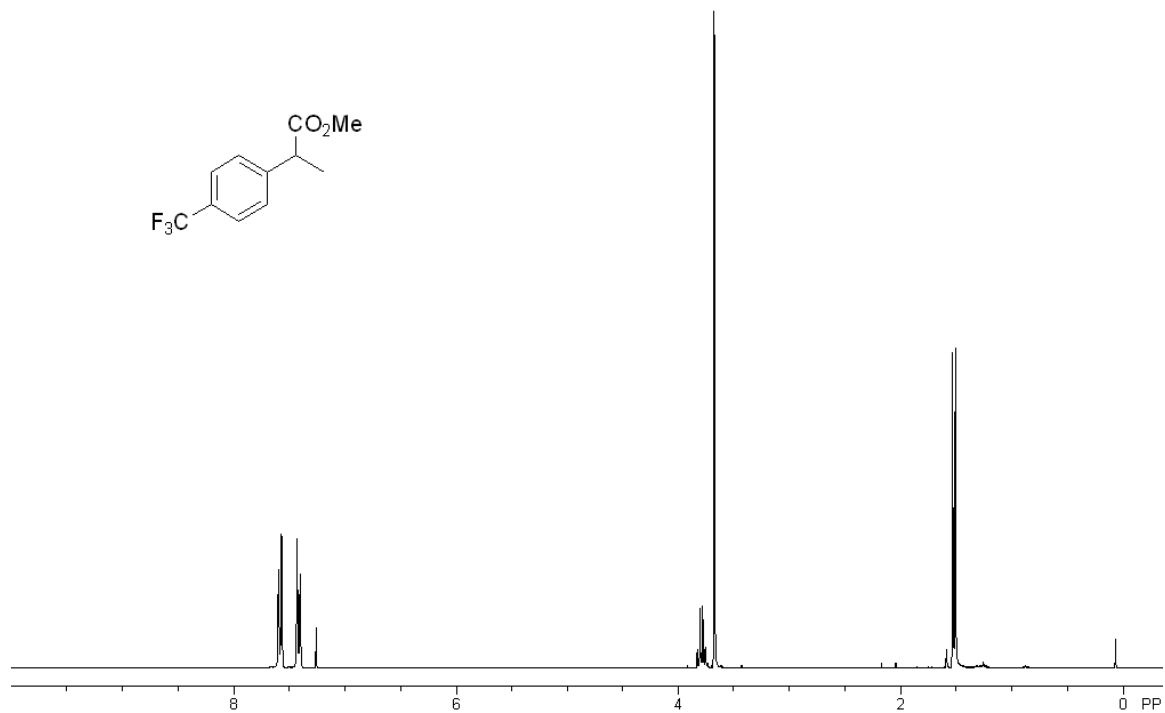
<sup>13</sup>C OBSERVE



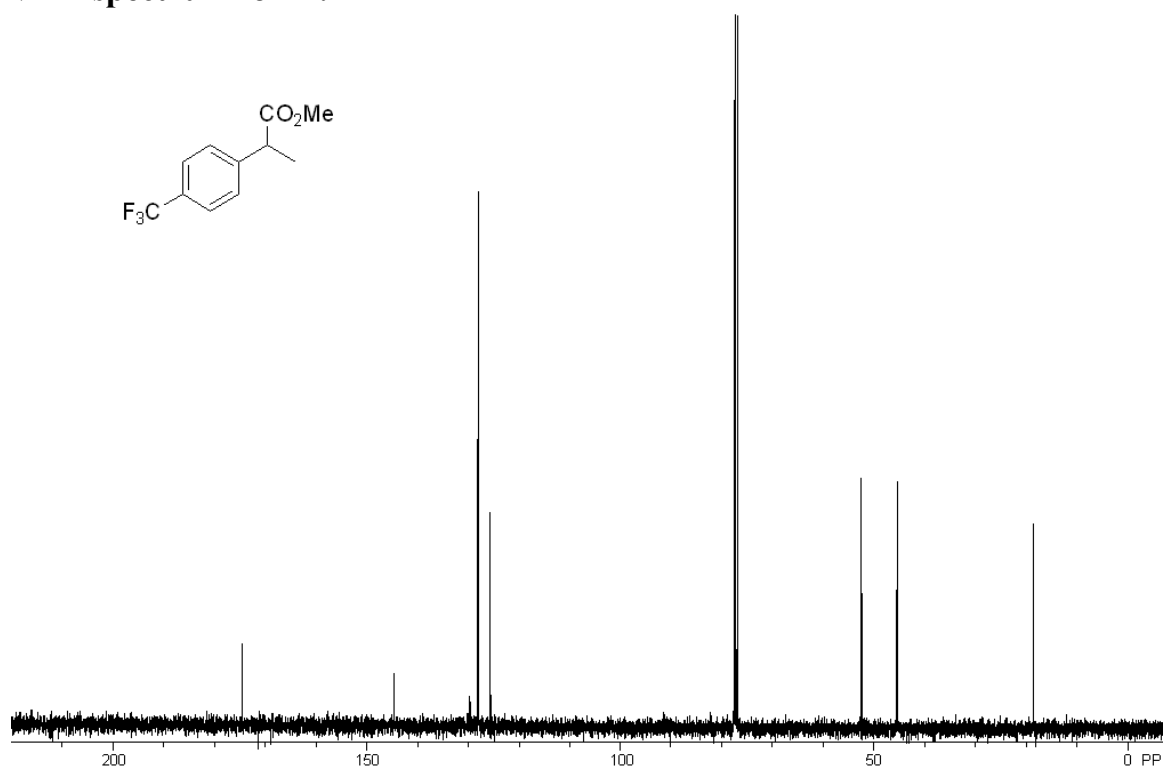




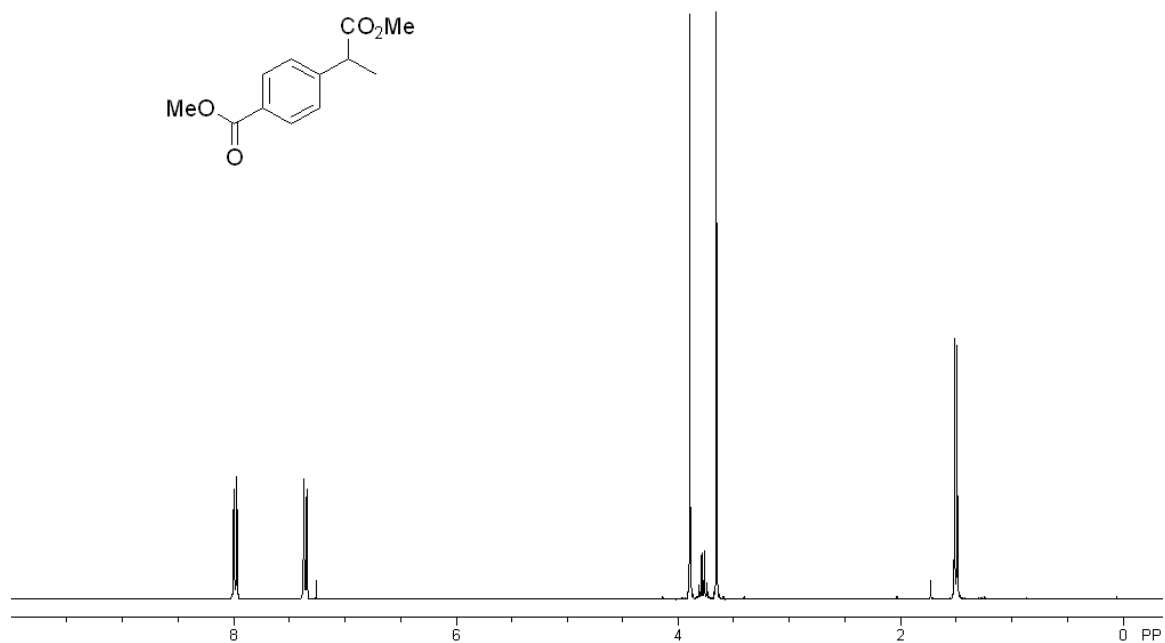
**<sup>1</sup>H NMR spectrum for X:**



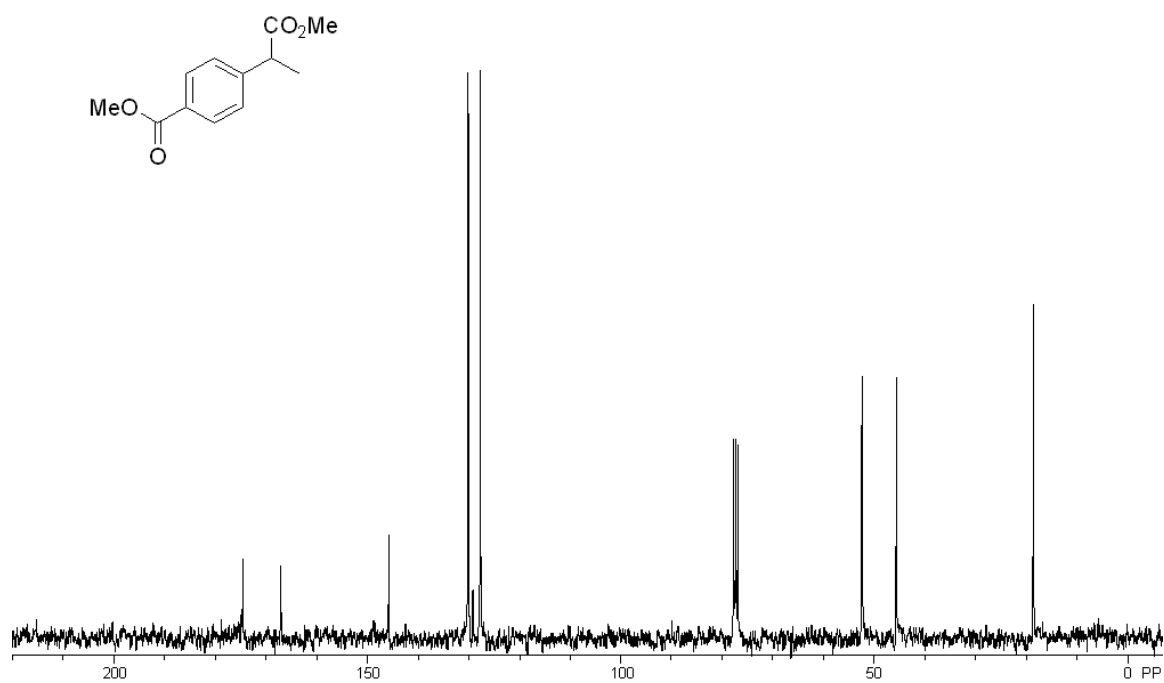
**<sup>13</sup>C NMR spectrum for X:**



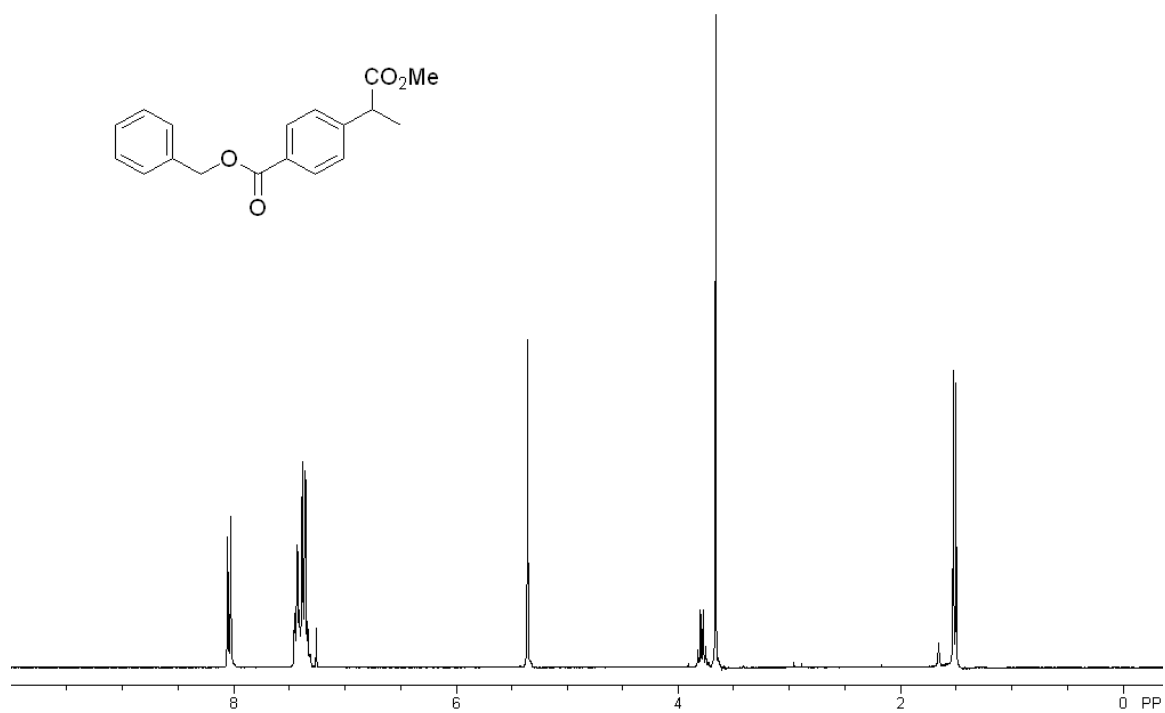
**<sup>1</sup>H NMR spectrum for X:**



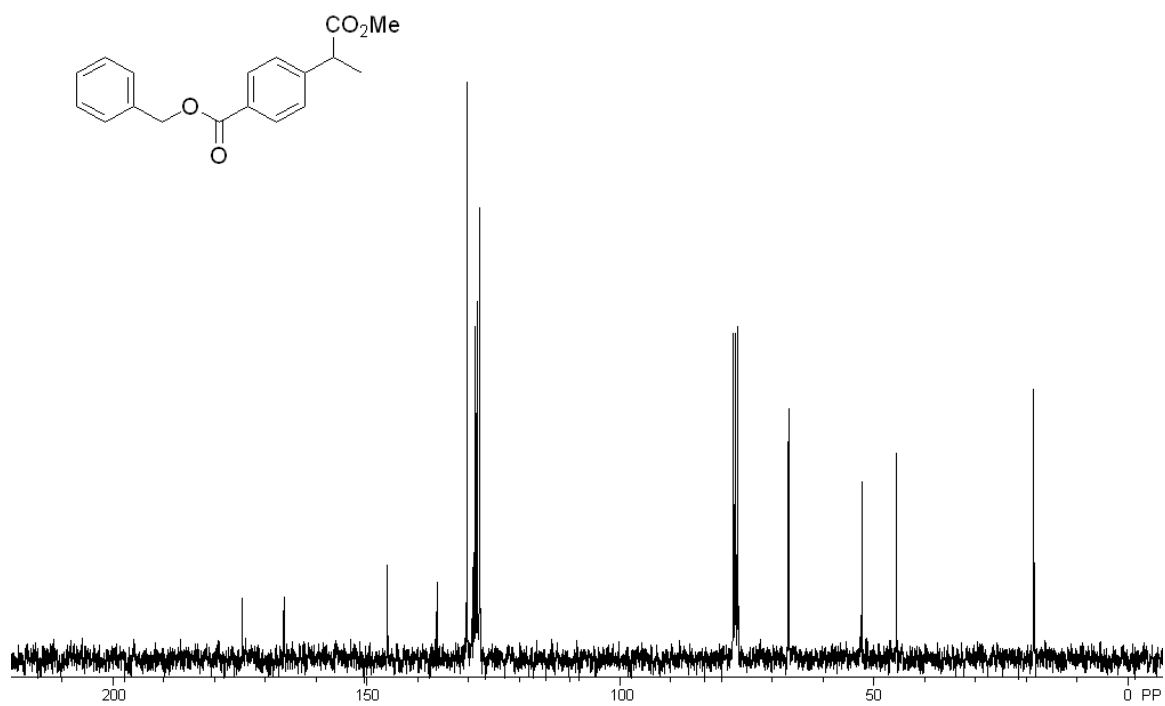
**<sup>13</sup>C NMR spectrum for X:**



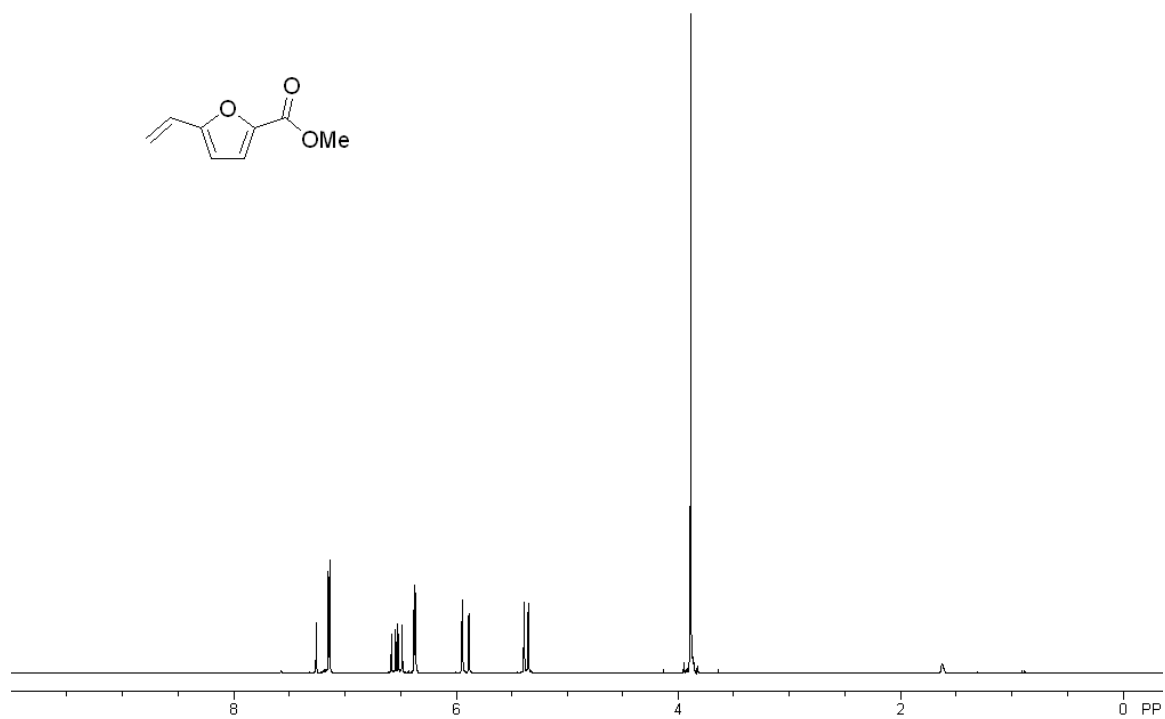
**<sup>1</sup>H NMR spectrum for X:**



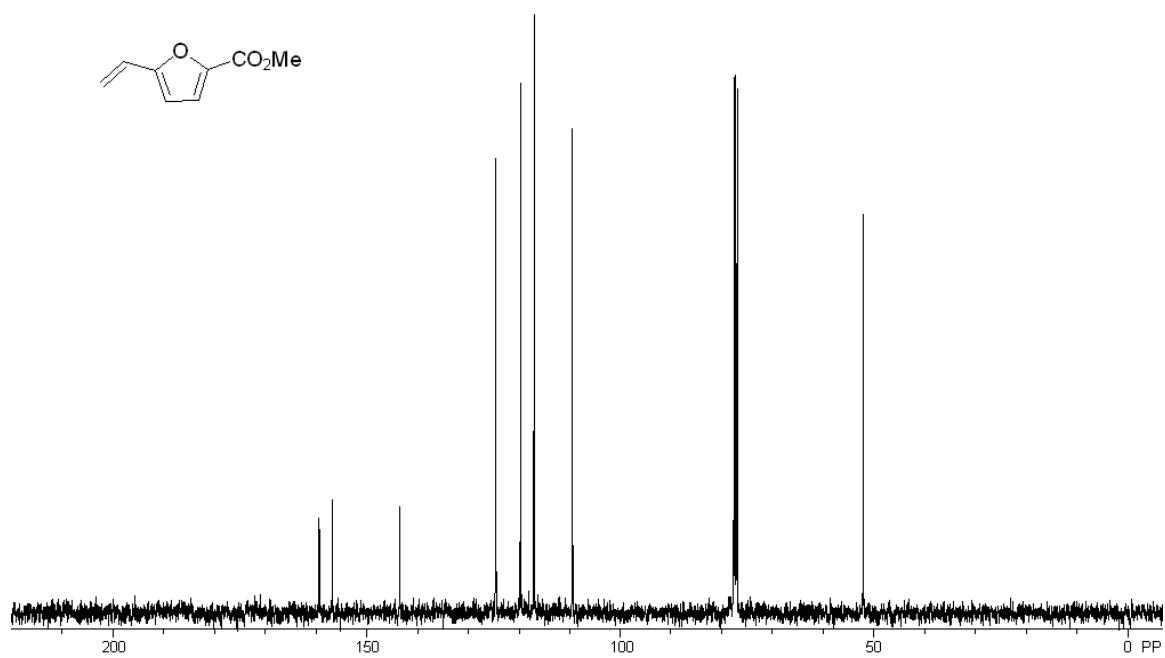
**<sup>13</sup>C NMR spectrum for X:**



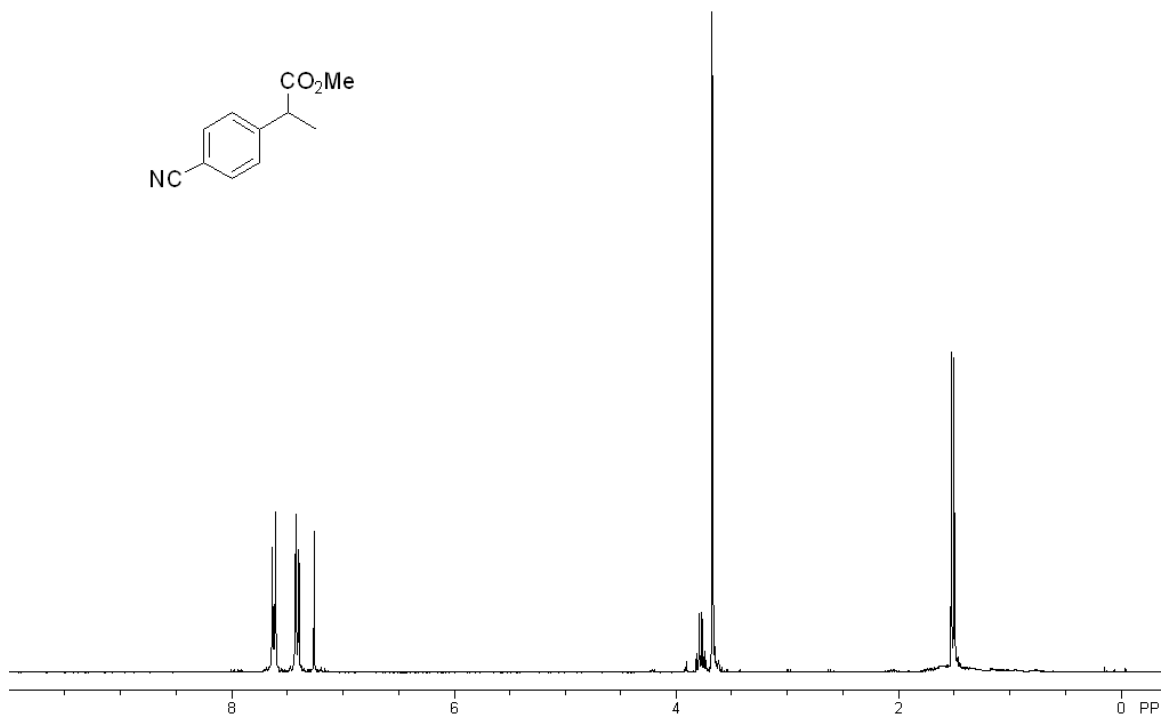
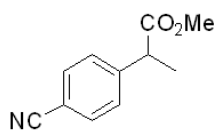
**<sup>1</sup>H NMR spectrum for X:**



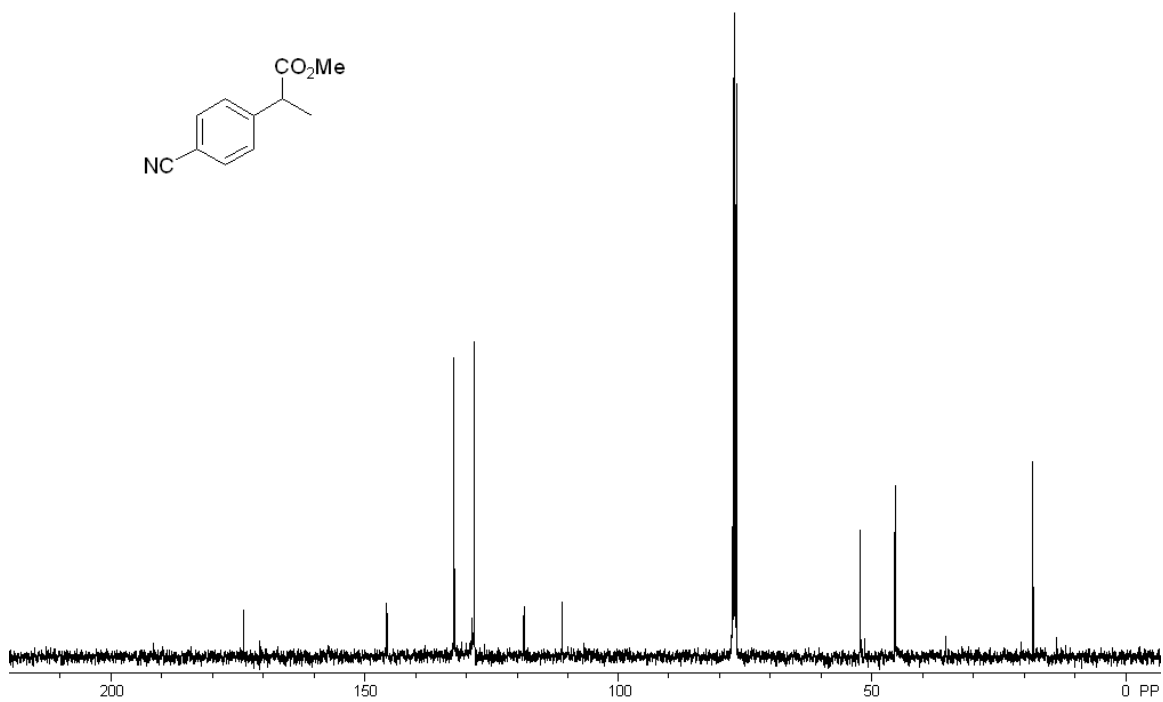
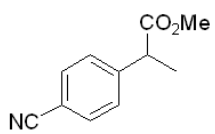
**<sup>13</sup>C NMR spectrum for X:**



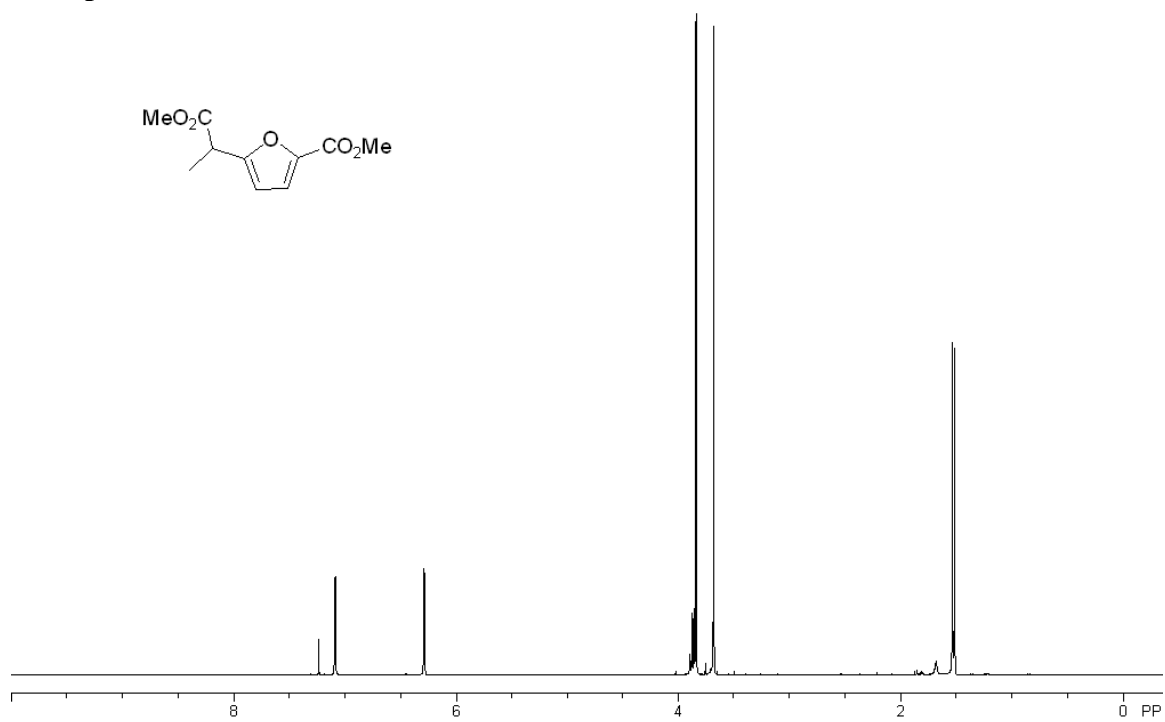
**<sup>1</sup>H NMR spectrum for X:**



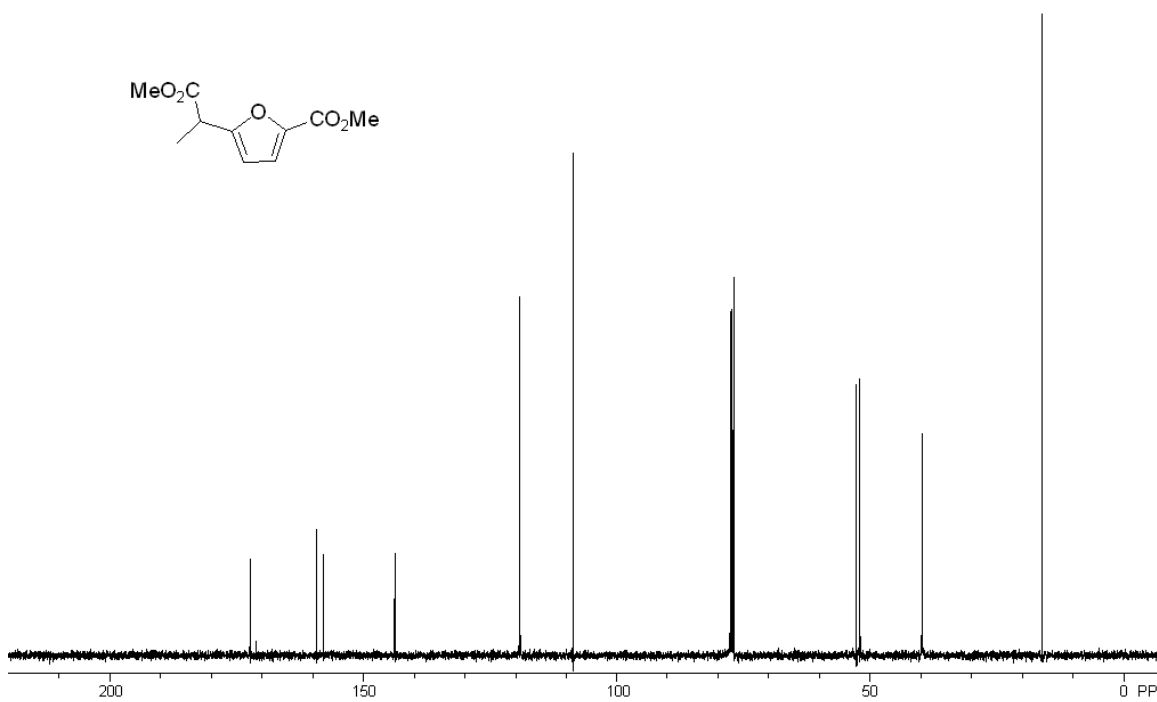
**<sup>13</sup>C NMR spectrum for X:**



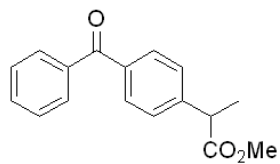
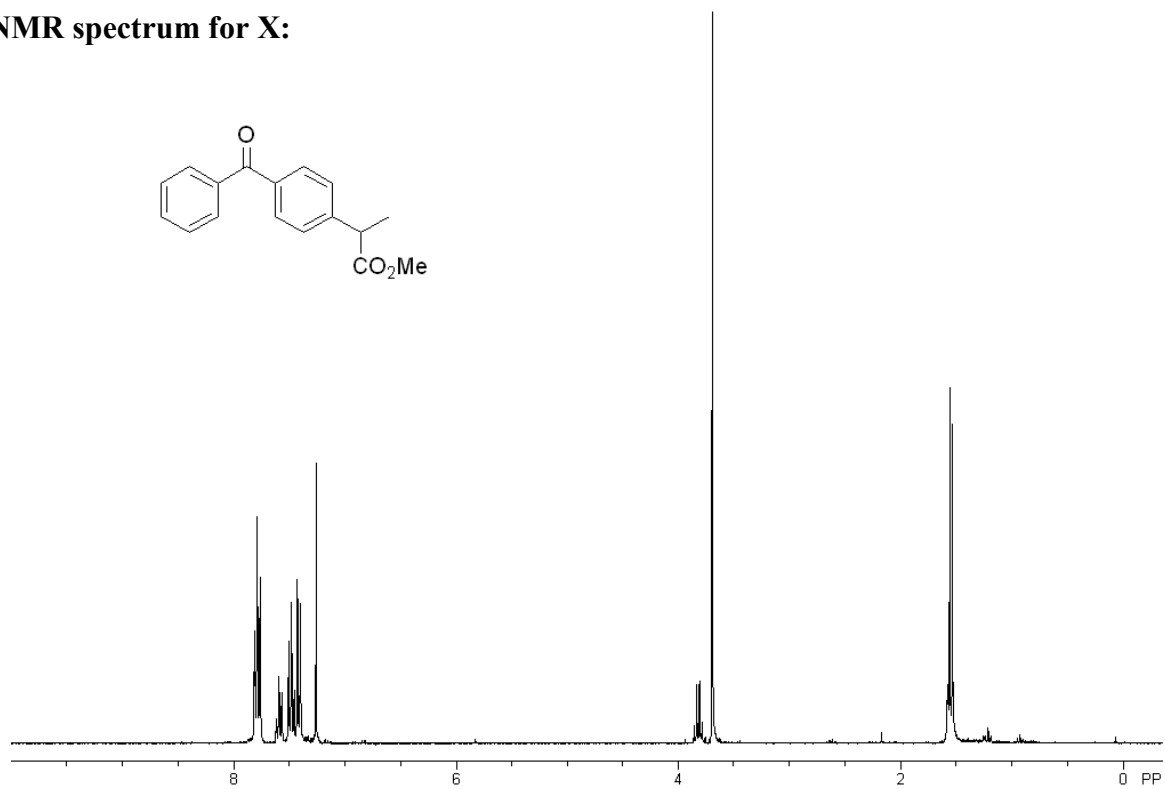
**<sup>1</sup>H NMR spectrum for X:**



**<sup>13</sup>C NMR spectrum for X:**



**<sup>1</sup>H NMR spectrum for X:**



**<sup>13</sup>C NMR spectrum for X:**

