

**Packing modes in some mono- and disubstituted phenylpropionic acids.  
Repeated occurrence of the rare *syn,anti*-catemer**

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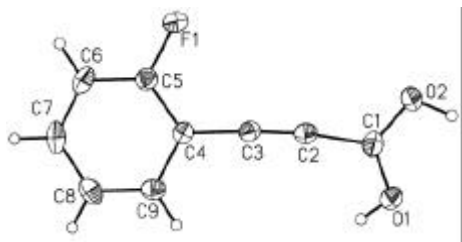
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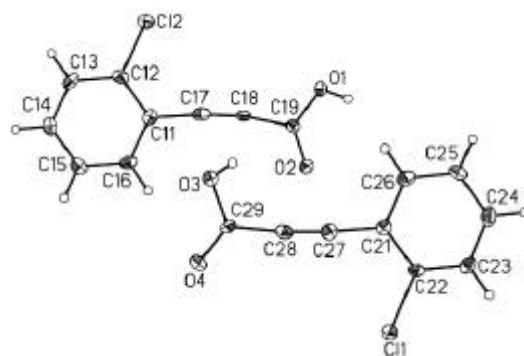
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**Supplementary Material**  
**(7 pages)**

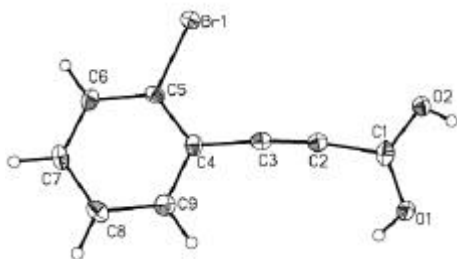
ORTEP diagram of all new acids are shown below. Ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii:



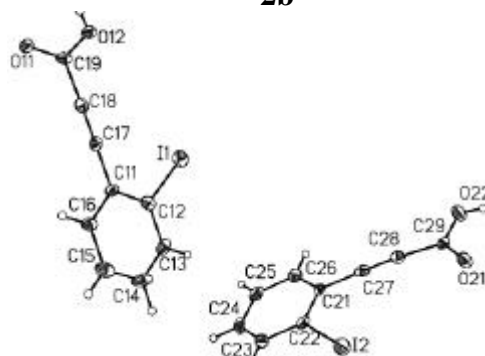
**2a**



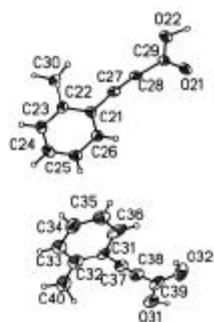
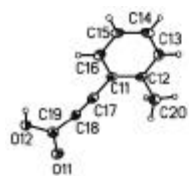
**2b**



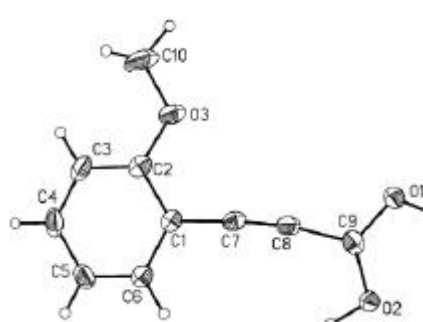
**2c**



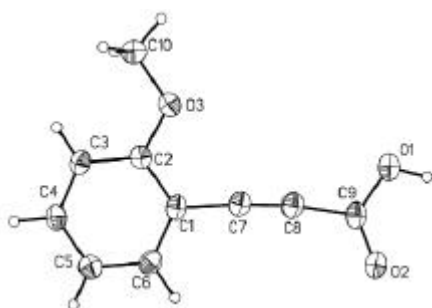
**2d**



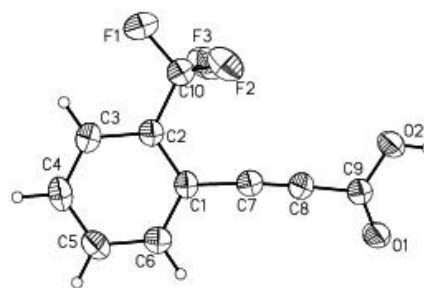
**2e**



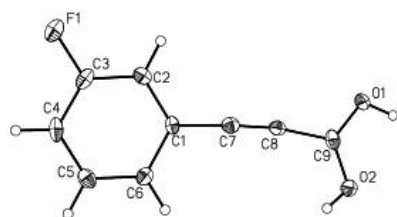
**2f (catemer)**



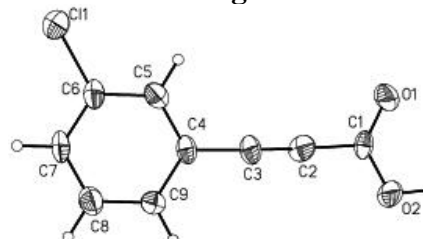
**2f (dimer)**



**2g**



**3a**



**3b**



Spectroscopic details of all new compounds:

All the compounds were characterized with NMR and IR spectra. NMR were recorded at either 400 or 200 MHz on a Bruker ACF instrument. IR spectra were recorded on a Jasco 5300 spectrophotometer. The details of the pure acids are given below:

**2-Fluorophenylpropionic acid (2a).** IR ( $\text{cm}^{-1}$ ): 2216, 1697;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.65 (m, 1H),  $\delta$  7.50 (m, 1H),  $\delta$  7.16 (m, 2H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.43,  $\delta$  161.33,  $\delta$  157.87,  $\delta$  134.78,  $\delta$  133.19,  $\delta$  124.34,  $\delta$  116.17,  $\delta$  84.52,  $\delta$  82.3. Melting point: 109°C.

**2-Chlorophenylpropionic acid (2b).** IR ( $\text{cm}^{-1}$ ): 2214.48, 1693.65;  $^1\text{H}$  NMR (400 MHz,  $\text{MeOH-d}_4 + \text{CDCl}_3$ ):  $\delta$  7.6 (m, 1H),  $\delta$  7.45 (m, 2H),  $\delta$  7.3 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{MeOH-d}_4 + \text{CDCl}_3$ ):  $\delta$  155.33,  $\delta$  137.03,  $\delta$  134.52,  $\delta$  131.48,  $\delta$  129.46,  $\delta$  126.62,  $\delta$  119.88,  $\delta$  85.18,  $\delta$  82.19. Melting point: 132-134°C.

**2-Bromophenylpropionic acid (2c).** IR ( $\text{cm}^{-1}$ ): 2210.62, 1697.51;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.6 (m, 2H),  $\delta$  7.3 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.23,  $\delta$  134.03,  $\delta$  132.52,  $\delta$  129.48,  $\delta$  126.46,  $\delta$  122.62,  $\delta$  119.85,  $\delta$  89.18,  $\delta$  81.19. Melting point: 120-123°C.

**2-Iodophenylpropionic acid (2d).** IR ( $\text{cm}^{-1}$ ): 2206.76, 1682.08;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.5 (m, 2H),  $\delta$  7.2 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.78,  $\delta$  139.23,  $\delta$  134.65,  $\delta$  132.00,  $\delta$  128.04,  $\delta$  126.14,  $\delta$  101.34,  $\delta$  89.68,  $\delta$  82.69. Melting point: 146-147°C.

**2-Methylphenylpropionic acid (2e).** IR ( $\text{cm}^{-1}$ ): 2195.19, 1691.72;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.14 -  $\delta$  7.58 (m, 4H),  $\delta$  2.32 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{MeOH-d}_4$ ):  $\delta$  155.47,  $\delta$  141.81,  $\delta$  138.61,  $\delta$  132.90,  $\delta$  130.67,  $\delta$  125.69,  $\delta$  119.24,  $\delta$  84.43,  $\delta$  84.31,  $\delta$  19.20. Melting point: 90-93°C.

**2-Methoxyphenylpropionic acid (2f).** IR ( $\text{cm}^{-1}$ ): 2200.76, 1695.58;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  13.75 (s, 1H),  $\delta$  7.51 -  $\delta$  7.46 (m, 2H),  $\delta$  7.12 - 6.96 (m, 2H),  $\delta$  3.51 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  161.15,  $\delta$  155.43,  $\delta$  134.20,  $\delta$  131.89,  $\delta$  120.08,  $\delta$  110.60,  $\delta$  108.39,  $\delta$  84.18,  $\delta$  82.85,  $\delta$  55.05. Melting point: 130°C.

**2-(Trifluoromethyl)phenylpropionic acid (2g).** IR ( $\text{cm}^{-1}$ ): 2226.05, 1712.94;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  7.69 -  $\delta$  7.87 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  164.25,  $\delta$  154.39,  $\delta$  135.75,  $\delta$  133.31,  $\delta$  131.16,  $\delta$  129.20,  $\delta$  126.85,  $\delta$  117.34,  $\delta$  86.59,  $\delta$  79.79. Melting point: 141°C.

**3-Fluorophenylpropionic acid (3a):** IR (cm<sup>-1</sup>): 2222.20, 1697.51; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.5-6.7 (m, 4H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ<sup>1</sup> 164.82, δ 159.87, δ 157.88, δ 130.41, δ 129.15, δ120.18, δ118.48, δ 87.19, δ 80.59. Melting point: 108°C.

**3-Chlorophenylpropionic acid (3b):** IR (cm<sup>-1</sup>): 2218.34, 1689.80; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.67 (s, 1H), δ 7.47-7.29 (m, 3H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ157.48, δ134.68, δ132.89, δ131.38, δ131.23, δ129.93, δ120.90, δ 86.94, δ 80.69. Melting point: 143-145°C.

**3-Bromophenylpropionic acid (3c):** IR (cm<sup>-1</sup>): 2214.48, 1685.94; <sup>1</sup>H NMR (200 MHz, MeOH-d<sub>4</sub>): δ 7.64 (s, 1H), δ 7.41-δ 7.14(m, 3H); <sup>13</sup>C NMR (50 MHz, MeOH-d<sub>4</sub>): δ 159.19, δ 139.21, δ 137.59, δ 135.26, δ133.97, δ126.15, δ 125.71, δ 87.77, δ 85.73. Melting point: 155-159°C.

**3-Iodophenylpropionic acid (3d):** IR (cm<sup>-1</sup>): 2210.62, 1672.43; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.76 (s, 1H), δ 7.61(m, 2H), δ6.97(m, 1H); <sup>13</sup>C NMR (50 MHz, MeOH-d<sub>4</sub>): δ 146.87, δ 132.8, δ 131.56, δ 123.63, δ122.10, δ113.73, δ 85.01, δ 75.07, δ 73.49. Melting point: 182-184°C.

**3-Methylphenylpropionic acid (3e):** IR (cm<sup>-1</sup>): 2210.62, 1685.94; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 7.30 (s, 1H), δ 7.41 (m, 3H), δ 2.37 (s, 3H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 158.43, δ 138.53, δ 138.53, δ 133.76, δ 132.06, δ 130.41, δ 128.55, δ 118.93, δ 84.85, δ 80.17, δ 21.12. Melting point: 135°C.

**2,3-Difluorophenylpropionic acid (5a):** Yield 70%. IR (cm<sup>-1</sup>): 2229.91, 1699.44; <sup>1</sup>H NMR (200 MHz, MeOH-d<sub>4</sub>): δ 7.43- δ 6.80 (m, 3H); <sup>13</sup>C NMR (50 MHz, MeOH-d<sub>4</sub>): δ 166.66, δ 161.52, δ 157.34, δ 133.11, δ130.80, δ127.31, δ 111.47, δ 99.19, δ 89.06 Melting point: 150 - 151°C.

**2,4-Difluorophenylpropionic acid (5b):** Yield 50%. IR (cm<sup>-1</sup>): 2222.20, 1699.44; <sup>1</sup>H NMR (400 MHz, MeOH-d<sub>4</sub>): δ 7.74 (m, 1H), δ 7. 42 (m, 1H), δ 7. 20 (m, 1H); <sup>13</sup>C NMR (100 MHz, MeOH-d<sub>4</sub>): δ 162.35, δ 157.23, δ 134.23, δ 129.23, 123.04, δ 118.69, δ 98.59, δ 83.76, δ 83.03. Melting point: 152-155°C.

**2,5-Difluorophenylpropionic acid (5c):** Yield 72%. IR (cm<sup>-1</sup>): 2229.91, 1699.44; <sup>1</sup>H NMR (400 MHz, MeOH-d<sub>4</sub>): δ 7.58 (m, 1H), δ 7. 39(m, 2H); <sup>13</sup>C NMR (100 MHz, MeOH-d<sub>4</sub>): δ 162.70, δ 160.52, δ 135.81, 128.02, δ 120.40, δ 116.97, δ 109.29, δ 85.08, δ 80.74; Melting point: 94°C -96°C.

**3,4-Difluorophenylpropionic acid (5d):** Yield 65%. IR (cm<sup>-1</sup>): 2227.98, 1691.72; <sup>1</sup>H NMR (400 MHz, MeOH-d<sub>4</sub>): δ 7.64 (m, 1H), δ 7.58 (m, 2H). <sup>13</sup>C NMR (100 MHz, MeOH-d<sub>4</sub>): δ

157.52,  $\delta$  150.25,  $\delta$  142.38,  $\delta$  130.37,  $\delta$  126.21,  $\delta$  122.37,  $\delta$  118.25,  $\delta$  86.16,  $\delta$  80.28; Melting point: 137-139°C.

**3,5-Difluorophenylpropionic acid (5e):** Yield 60%. IR ( $\text{cm}^{-1}$ ): 2233.77, 1695.58;  $^1\text{H}$  NMR (400 MHz,  $\text{MeOH-d}_4$ ):  $\delta$  7.94 (m, 1H),  $\delta$  7.57 (m, 2H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  160.5,  $\delta$  150.10,  $\delta$  127.45,  $\delta$  135.71,  $\delta$  128.4,  $\delta$  93.3,  $\delta$  82.04. Melting point: 155°C.

**2,6-Difluorophenylpropionic acid (5f):** Yield 60%. IR ( $\text{cm}^{-1}$ ): 2233.77, 1680.15;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.86- $\delta$  7.38 (m, 3H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.66,  $\delta$  161.52,  $\delta$  157.34,  $\delta$  133.11,  $\delta$  111.47,  $\delta$  99.19,  $\delta$  89.06. Melting point: 103°C-108°C.

**2,3-Dichlorophenylpropionic acid (6a):** Yield 65%. IR ( $\text{cm}^{-1}$ ): 2228.31, 1695.23;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.49- $\delta$  7.13 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.63,  $\delta$  135.93,  $\delta$  133.91,  $\delta$  132.87,  $\delta$  131.28,  $\delta$  129.95,  $\delta$  120.70,  $\delta$  86.84,  $\delta$  84.03. Melting point: 170°C-171°C.

**2,4-Dichlorophenylpropionic acid (6b):** Yield 65%. IR ( $\text{cm}^{-1}$ ): 2218.34, 1695.58;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.61 (s, 1H),  $\delta$  7.49 (d, 1H),  $\delta$  7.30 (d, 1H).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.72,  $\delta$  158.10,  $\delta$  135.68,  $\delta$  130.71,  $\delta$  127.35, 121.56,  $\delta$  116.46,  $\delta$  87.98,  $\delta$  80.04. Melting point: 183-184°C.

**2,5-Dichlorophenylpropionic acid (6c):** Yield 60%. IR ( $\text{cm}^{-1}$ ): 2220.27, 1684.01;  $^1\text{H}$  NMR (400 MHz,  $\text{MeOH-d}_4$ ):  $\delta$  7.69 (s, 1H),  $\delta$  7.33 (d, 1H),  $\delta$  7.25 (d, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{MeOH-d}_4$ ):  $\delta$  154.40,  $\delta$  135.12,  $\delta$  133.54,  $\delta$  132.55,  $\delta$  132.07,  $\delta$  131.68,  $\delta$  121.34,  $\delta$  85.87,  $\delta$  79.41; Melting point: 175-180°C.

**3,4-Dichlorophenylpropionic acid (6d):** Yield 65%. IR ( $\text{cm}^{-1}$ ): 2231.84, 1718.73;  $^1\text{H}$  NMR (400 MHz,  $\text{MeOH-d}_4$ ):  $\delta$  7.57 (s, 1H),  $\delta$  7.38 (d, 1H),  $\delta$  7.28 (d, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{MeOH-d}_4$ ):  $\delta$  155.00,  $\delta$  135.08,  $\delta$  134.10,  $\delta$  132.78,  $\delta$  131.71,  $\delta$  130.59,  $\delta$  119.61,  $\delta$  83.73,  $\delta$  80.23. Melting point: 183°C-184°C.

**3,5-Dichlorophenylpropionic acid (6e):** Yield 65%. IR ( $\text{cm}^{-1}$ ): 2231.84, 1697.51;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.89 (s, 1H),  $\delta$  7.39 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{MeOH-d}_4$ ):  $\delta$  154.89,  $\delta$  135.20,  $\delta$  130.47,  $\delta$  127.72,  $\delta$  126.25,  $\delta$  82.18,  $\delta$  81.23.

**2,6-Dichlorophenylpropionic acid (6f):** Yield 65%. IR ( $\text{cm}^{-1}$ ): 2235.70, 1695.58;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.72 (d, 2H),  $\delta$  6.63 (d, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{MeOH-d}_4$ ):  $\delta$  158.45,  $\delta$  142.00,  $\delta$  135.60,  $\delta$  131.77,  $\delta$  128.23,  $\delta$  93.78,  $\delta$  81.75. Melting point: 145-148°C.