

## Supporting Information

**Table 2. Density functional theory predicted normal modes for *S*-ethyl  
4-oxybenzoate thioester anion**

| Frequency<br>(cm <sup>-1</sup> ) | Raman<br>activity | Normal Modes  | Observed in 4-HBA-CoA |         |
|----------------------------------|-------------------|---|-----------------------|---------|
|                                  |                   |   | pH 10.5               | pH 9.0  |
| 1634.1                           | 288               | C=O stretch in O=C-S + ring quadrant stretch (v 8a) + C(4)-O stretch (v 7a) | 1625 br               | 1627 br |
| 1581.2                           | 392               | ring quadrant stretch (v 8a) + C=O stretch in O=C-S + C(4)-O stretch (v 7a) | 1574 s                | 1574 s  |
| 1545.5                           | 17                | C(4)-O stretch (v 7a) + ring semicircle stretch (v 19a)                     | 1530 m                | 1532 m  |
| 1482.0                           | 27                | ring quadrant stretch (v 8b)  |                       |         |
| 1479.4                           | 4                 | CH <sub>3</sub> asym. bend  |                       |         |
| 1468.8                           | 16                | CH <sub>3</sub> asym. bend  |                       |         |
| 1456.3                           | 18                | CH <sub>2</sub> scissor   |                       |         |
| 1450.0                           | 21                | ring semicircle stretch (v 19b)   |                       |         |
| 1398.6                           | 21                | ring semicircle stretch (v 19a) + C(4)-O stretch (v 7a)                     |                       |         |
| 1384.3                           | 1                 | CH <sub>3</sub> sym. bend   |                       |         |
| 1293.3                           | 5                 | ring C-H in-plane bend + ring C(1)-C(O) bend (v 3)                          |                       |         |

|        |    |   |         |         |
|--------|----|---|---------|---------|
| 1273.5 | 8  | CH <sub>2</sub> wag   |         |         |
| 1237.0 | 35 | ring C-H in-plane bend (v 14) +<br>C(4)-O in-plane bend                       | 1234 br | 1226 br |
| 1228.6 | 87 | ring X-sensitive mode (v 7a') : C(1)-C(O)<br>stretch + ring C-H in-plane bend | 1234 br | 1226 br |
| 1224.7 | 4  | CH <sub>2</sub> twist   |         |         |
| 1147.3 | 23 | ring C-H in-plane bend (v 9a)   | 1159 m  | 1157 m  |
| 1085.6 | 0  | ring C-H in-plane bend (v 15)   |         |         |
| 1044.0 | 10 | CH <sub>3</sub> rock in ethyl   |         |         |
| 1024.7 | 4  | CH <sub>2</sub> twist   |         |         |
| 968.3  | 11 | C-C stretch in ethyl  |         |         |
| 960.7  | 11 | ring in-plane bend + C-H in-plane bend (v 18a)                                |         |         |
| 949.3  | 2  | ring C-H out-of-plane bend (v 17a)  |         |         |
| 922.1  | 2  | ring C-H out-of-plane bend (v 5)  | 926 w   | 924 w   |
| 853.6  | 5  | ring breathing mode (v 1)<br>+ C(1)-C-S asym. stretch                         | 836 m   | 830 m   |
| 824.9  | 1  | ring C-H out-of-plane bend (v 11)   |         |         |
| 792.2  | 52 | ring in-plane bend (v 13)   | 791 w   | 790 w   |
| 768.1  | 2  | ring C-H out-of-plane bend (v 10a)  |         |         |
| 762.6  | 0  | CH <sub>2</sub> rock + CH <sub>3</sub> rock                                   |         |         |
| 684.1  | 0  | ring out-of-plane bend (v 4)  |         |         |
| 674.0  | 33 | S-C stretch + CH <sub>3</sub> rock  | 655 m   | 656 m   |
| 629.2  | 14 | C-S stretch + ring in-plane bend (v 6b)                                       | 630 m   | 623 m   |

|       |    |   |       |
|-------|----|---|-------|
| 612.8 | 0  | ring C(1)-C(O) out-of-plane bend (v 16b)        |       |
| 600.4 | 11 | ring in-plane bend (v 6b) + C-S stretch         | 604 w |
| 489.5 | 3  | O-C-S in-plane bend + ring in-plane bend (v 6a) |       |
| 461.7 | 2  | ring out-of-plane bend (v 16b')                 |       |
| 444.7 | 1  | ring in-plane bend (v 9b)                       |       |
| 404.2 | 1  | ring out-of-plane bend (v 16a)                  |       |

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## Supporting Information

**Table 3. Density functional theory predicted normal modes of  
S-ethyl 4-(dimethylamino)benzoate thioester**

| Frequencies<br>( $\text{cm}^{-1}$ ) | Raman<br>activities | Normal Modes  | Observed in 4-DMABA-CoA |
|-------------------------------------|---------------------|---|-------------------------|
| 1698.7                              | 125                 | C=O stretch + 8b (ring C=C stretch)                             | 1699 w                  |
| 1639.5                              | 583                 | 8a (ring C=C stretch)   | 1589 s                  |
| 1579.3                              | 24                  | 8b (ring C=C stretch) + C=O                                     |                         |
| 1554.7                              | 4                   | 19a (ring C=C stretch) + N-C(4) stretch                         |                         |
| 1535.7                              | 17                  | 19a (ring C=C stretch) + CH <sub>3</sub> asym. bend in N-methyl | 1543 m                  |
| 1522.2                              | 4                   | CH <sub>3</sub> asym. bend in N-methyl                          |                         |
| 1510.8                              | 5                   | CH <sub>3</sub> asym. bend in ethyl                             |                         |
| 1504.1                              | 16                  | CH <sub>3</sub> asym. bend in ethyl                             |                         |
| 1501.1                              | 25                  | CH <sub>3</sub> asym. bend in N-methyl                          |                         |
| 1492.1                              | 5                   | CH <sub>3</sub> asym. bend in N-methyl                          |                         |
| 1491.1                              | 17                  | CH <sub>3</sub> sym. bend in N-methyl                           | 1490 sh                 |
| 1485.8                              | 13                  | CH <sub>2</sub> scissor   |                         |
| 1465.9                              | 8                   | 19b (ring C=C stretch) + CH <sub>3</sub> sym. bend in N-methyl  |                         |
| 1448.3                              | 9                   | CH <sub>3</sub> sym. bend in N-methyl + 19b                     | 1444 m                  |
| 1423.4                              | 2                   | CH <sub>3</sub> sym. bend in ethyl                              |                         |
| 1386.7                              | 96                  | 7a (N-C(4) stretch + ring C-H in-plane bend)                    | 1378 m                  |

|        |     |   |        |
|--------|-----|---|--------|
| 1365.6 | 0   | 3 (ring C-H in-plane bend) + C-N-C asym. stretch                                |        |
| 1342.6 | 2   | 14 (ring C-H in-plane bend)   |        |
| 1305.2 | 10  | CH <sub>2</sub> wag   |        |
| 1268.8 | 1   | C-N-C asym. stretch + 14  |        |
| 1257.2 | 6   | CH <sub>2</sub> twist + CH <sub>3</sub> rock                                    |        |
| 1252.9 | 49  | 7a' (C-CO stretch + ring C-H in-plane bend)                                     | 1251 m |
| 1202.9 | 69  | 9a (C-H in-plane bend)  |        |
| 1189.3 | 151 | 9a + CH <sub>3</sub> rock in N-methyl + N-C stretch<br>+ ring C-H in-plane bend | 1184 s |
| 1154.9 | 4   | 15 (ring C-H in-plane bend)   |        |
| 1137.8 | 3   | CH <sub>3</sub> rock in N-methyl  |        |
| 1135.5 | 54  | CH <sub>3</sub> rock in N-methyl  | 1132 w |
| 1076.3 | 0.5 | CH <sub>3</sub> rock in N-methyl  |        |
| 1073.1 | 11  | CH <sub>3</sub> rock in ethyl + C-C stretch in ethyl                            |        |
| 1056.6 | 3   | CH <sub>2</sub> rock + CH <sub>3</sub> rock                                     |        |
| 1012.8 | 12  | 18a (ring in-plane bend)  |        |
| 998.3  | 9   | C-C stretch in ethyl  |        |
| 976.3  | 0   | 17a (ring C-H out-of-plane bend)  |        |
| 957.8  | 5   | 13 (ring in-plane bend)   |        |
| 949.7  | 0   | 5 (ring C-H out-of-plane bend)  |        |
| 912.7  | 4   | 1 (ring breath) + C-S stretch   |        |
| 826.0  | 0   | 11 (ring C-H out-of-plane bend)   |        |
| 804.1  | 1   | 10a (ring C-H out-of-plane bend)  |        |

|       |    |  |           |
|-------|----|--|-----------|
| 781.2 | 0  | CH <sub>2</sub> rock + CH <sub>3</sub> rock in ethyl |           |
| 760.0 | 45 | C-S stretch + 1 (ring breath)                        | 756 m     |
| 732.5 | 3  | 4 (ring out-of-plane bend)                           |           |
| 680.3 | 37 | S-C stretch  | 680 w, br |
| 646.1 | 4  | 6b (ring in-plane bend) + C-S stretch                | 640 w     |
| 643.2 | 1  | 16b (ring out-of-plane bend)                         |           |
| 622.5 | 4  | 6b' (ring in-plane bend) + C-S stretch               | 617 w     |
| 532.5 | 2  | 6a (ring out-of-plane bend)                          |           |
| 507.2 | 1  | 16b' (ring out-of-plane bend)                        |           |
| 483.0 | 2  | 9b (ring in-plane bend)                              |           |
| 455.6 | 0  | C-N-C bend   |           |
| 428.4 | 0  | 16a (ring out-of-plane bend)                         |           |
| 397.4 | 0  | O=C-S bend + C-N-C bend                              |           |

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