Supporting Information

Table S1. DFT predicted frequencies (cm^{-1}) of 4-FBA-CoA model compound *S*-ethyl 4-fluorobenzoate thioester between 2000 and 400 cm^{-1}

Mode No.	Frequency	Normal Modes
48	1696.4	thioester C=O stretch + 8b
47	1622.7	8a (ring C=C stretch)
46	1609.2	8b (ring C=C stretch) + C=O stretch
45	1521.7	19a (ring C=C stretch)
44	1499.9	CH_3 asymmetric bend
43	1493.6	CH_3 asymmetric bend
42	1474.8	CH_2 scissor
41	1423.9	19b (ring C=C stretch)
40	1415.1	CH_3 symmetric bend
39	1335.8	3 (ring stretch + ring C-H in-plane bend)
38	1311.2	14 (ring stretch + C-H in-plane bend)
37	1296.2	CH_2 wag
36	1249.9	CH_2 twist + CH_3 rock
35	1237.4	7a (C-F stretch + ring C-H in-plane bend)
34	1202.9	7a' (C1-CO stretch + C-H in-plane bend)
33	1167.3	9a (ring C-H in-plane bend)
32	1114.1	15 (ring C-H in-plane bend)
31	1066.4	ethyl C-C stretch in ethyl + CH_3 rock
30	1050.0	CH_2 rock + CH_3 rock
29	1016.1	18a (ring in-plane bend)
28	980.2	C-C stretch + CH_3 rock + CH_2 wag
27	974.7	17a (ring C-H out-of-plane bend)
26	947.3	5 (ring C-H out-of-plane bend)
25	913.5	ring breathing (mode 1) + C-S stretch
24	846.9	11 (ring C-H out-of-plane bend)
23	816.0	10a (ring C-H out-of-plane bend)
22	814.5	13 (ring in-plane bend) + C-S stretch
21	776.9	CH_2 rock + CH_3 rock
20	708.2	mode 4 (ring out-of-plane bend)
19	672.9	S-C stretch + CH_3 rock
18	641.3	6b (ring in-plane bend)
17	630.3	16b (ring out-of-plane bend)
16	622.1	6b' (ring in-plane bend) + + C-S stretch
15	516.5	6a + O=C-S bend in-plane + C-S-C in-plane bend
14	492.7	16b' (ring out-of-plane bend)
13	438.7	9b (ring in-plane bend)
12	413.4	6a (ring out-of-plane bend)

Table S2. DFT predicted frequencies (cm^{-1}) of 4-NBA-CoA model compound *S*-ethyl 4-nitrobenzoate thioester between 2000 and 400 cm^{-1}.

Mode. No.	Frequency	Normal Mode
54	1696.2	thioester C=O stretch
53	1623.8	8b (ring stretch) + O-N-O asymmetric stretch
52	1616.3	8a (ring stretch)
51	1566.7	O-N-O asymmetric stretch + 8b
50	1502.8	19a (ring stretch)
49	1497.1	Ethyl C-H deformation
48	1491.6	Ethyl C-H deformation
47	1471.0	Ethyl C-H deformation
46	1416.9	19b (ring stretch)
45	1413.8	Ethyl C-H deformation
44	1358.9	O-N-O symmetric stretch
43	1348.5	3 (ring stretch)
42	1311.6	14 (ring stretch)
41	1294.1	Ethyl CH_2 wag
40	1248.0	Ethyl CH_2 twist + CH_3 rock
39	1198.5	7a′ (–C(=O)-C stretch + C-H i.p. bend)
38	1185.4	9a (ring C-H i.p. bend)
37	1119.5	15 (ring C-H i.p. bend)
36	1105.3	7a (N-C stretch + C-H i.p. bend)
35	1065.6	C-C stretch in ethyl
34	1049.7	Ethyl CH_2 rock + CH_3 rock
33	1014.3	18a (ring i.p. bend)
32	990.7	17a (C-H o.o.p bend)
31	978.2	C-C stretch in ethyl
30	972.0	5 (C-H o.o.p. bend)
29	917.5	S-C=O bend + 1
28	868.2	11 (C-H o.o.p. bend)
27	841.3	O-N-O i.p. bend + 1
26	836.7	10a (C-H o.o.p. bend)
25	774.8	Ethyl (CH_2 rock + CH_3 rock)
24	743.8	4
23	717.7	1
22	689.0	16b
21	669.3	S-C stretch
20	629.2	6b
19	621.5	S-C=O o.o.p. bend + 4
18	572.8	S-C-C i.p. bend + 9b
17	519.2	9b
16	471.6	13 + C-S stretch
15	448.3	16b′
14	408.1	16a

Table S3. Complete list of DFT predicted frequencies (cm^{-1}) of Meisenheimer Compound I between 2000 and 400 cm^{-1}.

Mode No.	Frequency	Normal mode
66	1740.0	acetoxy ester C=O stretch
65	1644.3	thioester C=O stretch + 8a-like C=C symmetric stretch
64	1595.0	8a-like C=C symmetric stretch + thioester C=O stretch
63	1524.9	two C=C antisymmetric stretch
62	1483.1	ethyl C-H deformation
61	1471.3	ethyl C-H deformation
60	1462.4	methyl C-H deformation
59	1459.4	8b-like ring quadrant stretch
58	1457.6	methyl C-H deformation
57	1447.7	19a-like ring stretch
56	1434.2	Ethyl C-H deformation
55	1384.2	Ethyl C-H deformation
54	1370.3	methyl C-H deformation
53	1304.2	19b-like ring stretch
52	1285.0	ethyl
51	1277.5	3-like ring stretch
50	1265.5	ethyl
49	1258.3	7a'-like ring bend + C1-C stretch + ring C-H i.p. bend + acetoxy –O-C=O bend
48	1245.6	acetoxy ester –O-C=O bend + 7a'-like ring i.p. bend + C-H i.p. bend
47	1176.4	9a-like ring C-H i.p. bend
46	1101.2	15-like ring C-H i.p. bend
45	1051.2	ethyl
44	1039.5	methyl
43	1038.6	ethyl
42	1009.5	methyl
41	983.5	18a-like ring i.p. bend
40	960.9	ethyl C-C stretch
39	946.9	ring C-H o.o.p. bend
38	939.3	C-O-C bend + 18a
37	920.5	ring C-H o.o.p. bend
36	909.0	13-like ring i.p. bend
35	847.4	1-like ring bend + C-S stretch
34	797.4	ring o.o.p. bend
33	734.7	ring C-H o.o.p. bend
32	733.2	ethyl
31	724.7	ring i.p. bend
30	718.3	ring C-H o.o.p. bend
29	662.2	S-C stretch
28	653.4	acetoxy O-C-C bend + ring i.p. bend + C-F stretch

27	628.8	C-H o.o.p. bend
26	610.5	6b like i.p. bend
25	590.9	acetoxy ester C=O o.o.p. bend
24	573.1	18b-like ring i.p. bend + C-F stretch
23	537.9	ring o.o.p. bend
22	504.4	ring o.o.p. bend