Recognition of chiral carboxylates by 1,3-disubstituted thioureas with 1-arylethyl scaffolds

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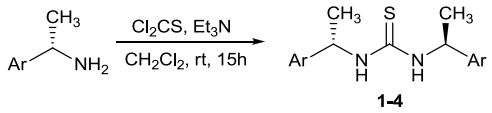
1. General Methods

Al starting materials were purchased from Aldrich, dichloromethane used in the reactions was distilled from P_2O_5. Flash column chromatography was carried out with silica gel 60 (0.4/0.63 mm, 230-400 mesh), TLC was performed with silica gel F_{254} plates. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. ^1H and ^{13}C NMR were recorded on a Jeol Eclipse 300 at 300 MHz and 75 MHz respectively. Chemical shifts (δ) are in ppm downfield from TMS and coupling constants are in Hertz. Optical rotations were measured at r.t. on a Perkin-Elmer 343 polarimeter. Mass spectra were obtained with a Jeol JMS-SX 102A or a Jeol JMS-AX 505 HA mass spectrometer.

2. Synthesis of chiral thioureas.

I. General procedure for the synthesis of thioureas **1-4**.



1-4

In a round bottomed flask 5 mmol (1 equiv.) of the chiral amine was dissolved in 10 mL of dry dichloromethane under nitrogen atmosphere. The solution was cooled to 0 °C and added 0.76 mL (5.5 mmol, 1.1 equiv.) of triethylamine followed by the slow addition of 0.19 mL (2.5 mmol, 0.5 equiv.) of thiophosgene. It was warmed to room temperature and stirred for 15 h. The reaction mixture was quenched by the addition of 10 mL of HCl 1M solution. The phases were separated and the organic layer washed with brine. It was dried ($NaSO_4$ anh.) and concentrated to dryness. It was further purified by flash chromatography hexane:AcOEt (9:1) to obtain a white solid in most cases if a yellowish product was obtained it was recrystallized from MeOH.

1,3-Bis((S)-1-phenylethyl)thiourea, **1**.

Yield 85 % White solid, mp = 193-196 °C, $[\alpha]_D^{20°C}$= +98.9° (c=1, $CHCl_3$)

Lit.[1] 199-200 °C, $[\alpha]_D^{20°C}$= +114.2° (c=1.05, $CHCl_3$).

^1H NMR ($CDCl_3$, 300 MHz): δ 1.46 (d, *J* = 6.8 Hz, 6H), 5.05 (br, 2H), 6.11 (br, 2H), 7.00-7.28 (m, 10H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.3, 54.2, 125.7, 127.7, 129.0, 142.3, 180.1.

MS-EI (m/z): 284 (M^+, 53),179 (12), 120 (100), 105(46), 77 (13), 28 (11)

HRMS-FAB: m/z [M^+] calcd for $C_{17}H_{20}N_2S$: 284.1347; found: 284.1341

1,3-Bis((S)-1-(1-naphthyl)ethyl)thiourea, **2**.

Yield: 82% , white solid, mp: 178-182°C, $[\alpha]_D^{20°C}$= +157.7.° (c = 1, $CHCl_3$).

Lit.[1] 163-164 °C, $[\alpha]_D^{20°C}$= +171.3° (c=0.75, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 300MHz): δ 1.58 (d. *J*=6.6 Hz, 6H), 5.76 (br, 4H), 7.04 (t, *J*=7.6 Hz, 4H), 7.39-7.48 (m. 4H), 7.53 (d, *J*=9.0 Hz, 2H), 7.70-7.78 (m, 2H), 7.89-7.97 (m, 2H)
^{13}C NMR ($CDCl_3$, 75MHz): δ: 21.7, 50.5, 122.6, 125.1, 125.7, 126.6, 128.3, 128.9, 130.1, 133.7, 136.8, 179.7.

MS-EI (m/z): 384 (M^+, 53), 171 (29), 170 (100), 156 (23), 155(90), 154 (28), 153 (30), 129 (26), 128 (22), 84 (17).

HRMS-FAB: m/z [M^+] calcd for $C_{25}H_{24}N_2S$: 384.1660; found: 384.1662

1,3-Bis((S)-1-(9-anthracenyl)ethyl)thiourea, **3**.

Yield: 75% , white solid, mp : 134 – 137 °C, $[\alpha]_D^{20°C}$= -70.1° (c = 1, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 300MHz): δ 1.75 (d, *J* = 6.5 Hz, 6H), 6.30 (br, 4H), 7.00-7.28 (br, 8H), 7.50-7.75 (br, 4H), 7.76-8.08 (br, 6H)

^{13}C NMR ($CDCl_3$, 75MHz): δ 21.7, 50.4, 123.0, 124.5, 126.2, 128.2, 128.4, 129.4, 131.1, 181.1

MS-EI (m/z): 484 (M^+, 18), 220 (20), 206 (35), 205 (100), 204 (53), 203 (54), 202 (34), 179 (15), 178 (38), 101 (15).

HRMS-FAB: m/z [M^+] calcd for $C_{33}H_{28}N_2S$: 484.1973; found: 484.1983

1,3-Bis((S)-1,2,3.4-tetrahydronaphtalen-1-yl)thiourea, **4**.

Yield: 38% (it was also obtained 25 % of the isothiocyanate), white solid, mp: 180-181 °C, $[\alpha]_D^{20°C}$=-71.2° (c=1, $CHCl_3$)

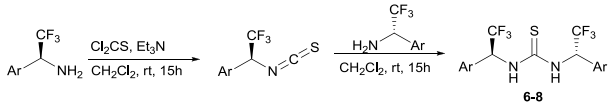
^{1}H NMR ($CDCl_3$, 300MHz): δ 1.65-18.1 (m, 6H), 1.92-2.12 (m, 2H), 2.64-2.81 (m, 4H), 5.14-5.55 (br, 2H), 5.93-6.19 (br, 2H), 7.01-7.1 (m, 2H), 7.11-7.22 (m, 4H), 7.27-7.40 (m, 2H).

^{13}C NMR ($CDCl_3$, 75MHz): δ 20.2, 29.2, 29.8, 52.7, 126.5, 127.7, 128.8, 129.3, 135.9, 137.6, 180.2.

MS-EI (m/z): 337(M^++1, 36), 336 (M^+, 52), 207 (26), 205 (54), 147 (22), 146 (100), 131 (85), 130 (44), 129 (35), 128 (16), 91 (18), 77 (18).

HRMS-FAB: m/z [M^+] calcd for $C_{21}H_{24}N_2S$: 336.1660; found: 336.1659

II. General procedure for the synthesis of thioureas **5**-**8**.



NOTE: general procedure for thioureas **1**-**4** can be applied but in some cases considerable amount of the isothiocyanate obtained so we decided a two steps approach to get more reproducible results.

In a round bottomed flask 2 mmol (1 equiv.) of the chiral amine was dissolved in 10 mL of dry dichloromethane under nitrogen atmosphere. The solution was cooled to 0 °C and added 0.58 mL (4.4 mmol, 2.2 equiv.) of triethylamine followed by the slow addition of 0.15 mL (2 mmol, 2 equiv.) of thiophosgene. It was warmed to room temperature and stirred for 15 h. The reaction mixture was quenched by the addition of 10 mL of HCl 1M solution. The phases were separated and the organic layer washed with brine. It was dried ($NaSO_4$ anh.) and concentrated to dryness. It was purified by a short column with hexane:AcOEt (9:1) as eluant to obtain a pale yellow liquid which was assigned as the thioisocyanate with a crude yield above 90% in all cases.

Considering 2 mmol of the isothiocyanate it was dissolved in 5 mL of dry dichloromethane and added 2.1 mmol (1.05 equiv.) of the chiral amine and stirred at room temperature overnight. It was concentrated and purified by flash chromatography with hexane:ethyl acetate (9:1 to 4:6) to obtain the thiourea.

1-(3,5-Bis(trifluoromethyl)phenyl)-3-(1-(*S*)-phenylethyl)thiourea, **5**.

Employing the second part of the general procedure II

Yield: 95%, white solid, m.p. 133-135 °C, $[\alpha]_D^{20°C}$= +15.2 (C = 1, $CHCl_3$)

Lit.[3] for (*R*) isomer:130.5-133 ˚C (hexane-CH_2Cl_2), $[\alpha]_D^{26}$ -16.4 (C = 1.0, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.60 (d, J=6.8, 3H), 5.37 (br, 1H), 6.59 (br, 1H), 7.30-7.45 (m, 5H), 7.66 (s, 3H), 7.89 (br, 1H).

^{13}C (75 MHz, $CDCl_3$): δ 22.2 (br), 54.9, 119.5 (h, J=3.7 Hz), 122.9 (q, 272 Hz), 124.0-124.2 (m), 126.2, 128.5, 129.5, 132.9 (q, J=32.3 Hz), 139.18, 141.4, 180.1.

MS-EI(m/z): 392(M^+,42), 229(21), 120(26), 110(20), 105(100), 104(23), 77(21)

HRMS-FAB: m/z [M^++H] calcd for $C_{17}H_{15}N_2F_6S$: 393.0860; found: 393.0854

1,3-Bis((*S*)-2,2,2-trifluoro-1-phenylethyl)thiourea, **6**.

Yield: 74%, white solid m.p. 198-200 °C, $[\alpha]_D^{20°C}$= +4.8 (C=1, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.14-6.24 (m, 2H), 6.65 (d, *J* = 6.5Hz, 2H), 7.27-7.44 (m, 10H).

^{13}C (75 MHz, $CDCl_3$): δ 59.8(q, J = 31Hz), 124.2 (q, *J* = 280.5 Hz), 127.9, 129.2, 129.6, 132.1, 183.4.

MS-EI(m/z): 392(M^+,92), 59(19), 256(35), 254(39), 228(37), 227(36), 226(30), 225(25), 218(18), 197(18), 185(17), 183(16), 174(75), 170(21), 169(18), 160(15), 129(20), 110(15), 109(45), 77(20)

HRMS-FAB: m/z [M^+] calcd for $C_{17}H_{14}N_2F_6S$: 392.0776; found: 392.0782

1,3-Bis((S)-2,2,2-trifluoro-1-(1-naphthyl)ethyl)thiourea, **7**.

Yield: 67% white solid, m.p. 220-222 °C, $[\alpha]_D^{20°C}$= -8.2 (C = 1, $CHCl_3$),

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20-7.38 (m, 2H), 7.52-7.75 (m, 8H), 8.02-8.13 (m, 4H), 8.28 (d, J = 8.5 Hz, 2H), 9.15 (d, J = 9.3 Hz, 2H).

^{13}C (75 MHz, $CDCl_3$): δ 54.1 (q, J = 30.2 Hz), 122.9, 125.0 (q, *J* = 280.5 Hz), 125.0, 125.5, 126.3, 127.3, 128.9, 129.3, 129.9, 130.9, 133.4, 184.1.

MS-EI(m/z): 492(M^+,95), 224(56), 210(21), 209(26), 189(28), 186(18), 160(100), 159(18), 156(21), 129(29), 127(18)

HRMS-FAB: m/z [M^+] calcd for $C_{25}H_{18}N_2F_6S$: 492.1102; found: 492.1096.

1,3-Bis((S)-2,2,2-trifluoro-1-(9-anthracenyl)ethyl)thiourea, **8**.

Yield: 63% white solid, m.p. 213-215 °C, $[\alpha]_D^{20°C}$= -5.0 (C = 1, $CHCl_3$),

^{1}H NMR (300 MHz, DMSO-*d*6): δ 7.50-7.86 (m, 8H), 7.91-8.10 (m, 2H), 8.10-8.30 (m, 4H), 8.30-8.69 (m, 4H), 8.82 (s, 2H), 9.64 (d, *J*=8.3 Hz, 2H).

^{13}C NMR (75 MHz, DMSO-*d6*): δ 55.2 (q, *J*=31.8 Hz), 123.5, 124.4, 125.1, 126.7-127.9 (m), 129.4, 129.8, 130.7, 131.3, 185.1.

MS-EI(m/z): 592 (M^+,36), 317(20), 274(22), 260(18), 259(100), 236(18), 210(17), 209(48), 207(17), 178(24), 161(23).

HRMS-FAB: m/z [M^+] calcd for $C_{33}H_{22}N_2F_6S$: 592.1408; found: 592.1412.

3. General procedure for ^{1}H NMR titrations

In a NMR tube was dissolved 0.005 mmol of the chiral thiourea in 0.5 mL of DMSO-d_6. It was acquired the ^{1}H NMR and the chemical shift of the NH accounted as free thiourea. The titration was carried out by the consecutive additions of tetrabutyl ammonium carboxylate stock solution until the chemical shift of the NH reached a steady value which was accounted as the thiourea-carboxylate adduct. With the data of concentrations and chemical shifts during the titration was obtained he binding constant with WINEQNMR2.[3]

Te stock solution of tetrabutylammonium carboxylate was prepared in a dram vial with 0.1 mmol of the acid dissolved in 1 mL of tetrabutylammonium hydroxide (0.1 M in iPrOH and MeOH), shaken for 2 minutes and concentrated to dryness before the addition of 0.5 mL of DMSO-d_6. The whole stock solution is composed of 20 equiv. of carboxylate but in the case of higher amount of carboxylate needed, a new stock of tetrabutyl ammonium carboxylate was prepared the same as before but instead of dissolving it in DMSO-d_6 it was dissolved with the whole amount of the thiourea solution with the 20 equiv. of carboxylate.

4. Bibliography

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5. Titration of thioureas with $AcONBu_4$

Figure 1. Titration of thiourea **1** with tetrabutylammonium acetate.

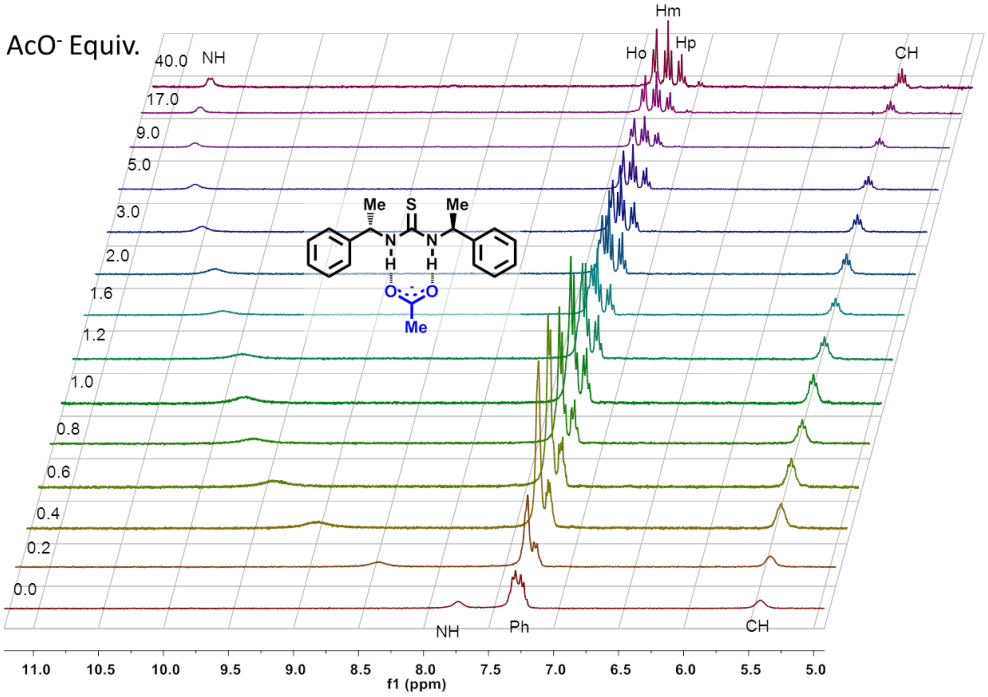


Figure 2. Titration of thiourea **2** with tetrabutylammonium acetate.

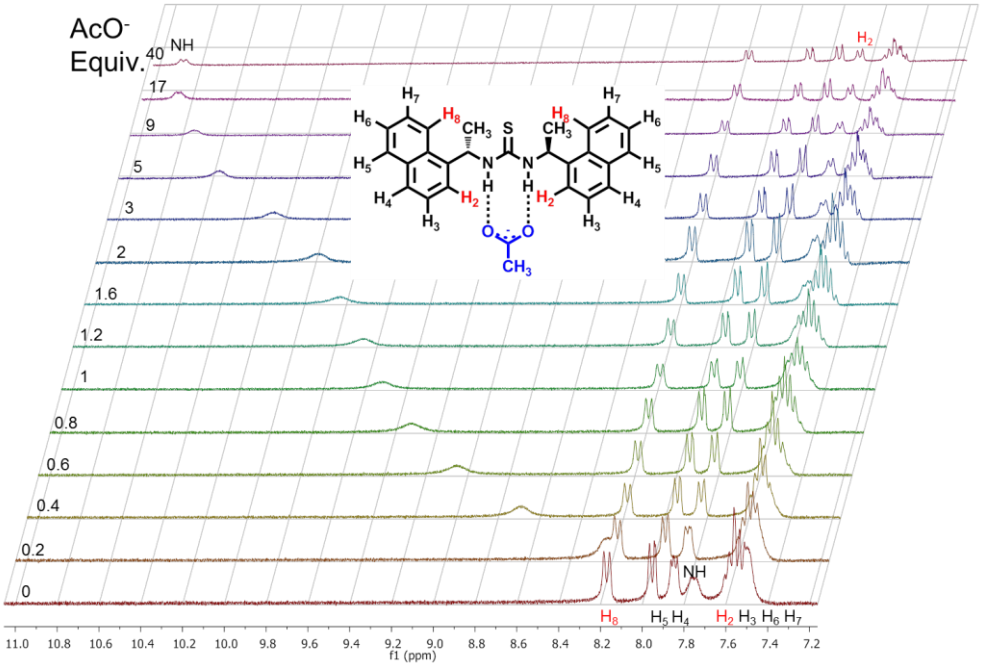


Figure 3. Comparison between free thiourea **2** and supramolecular adduct.

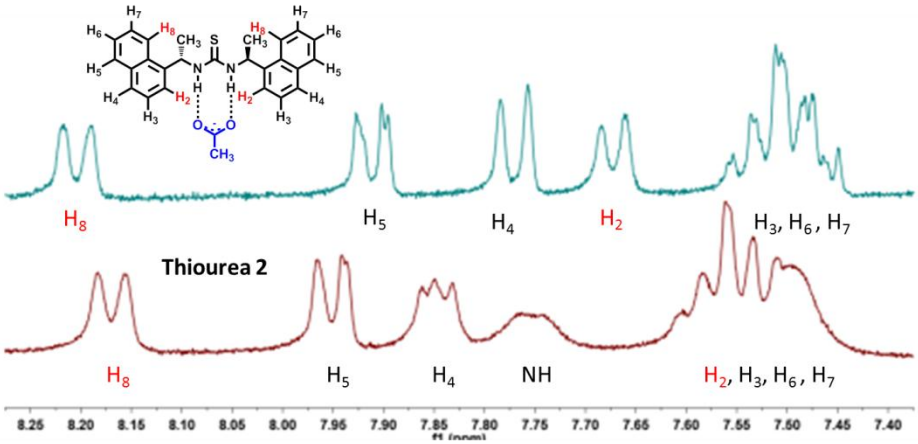


Figure 4. Titration of thiourea **3** with tetrabutylammonium acetate.

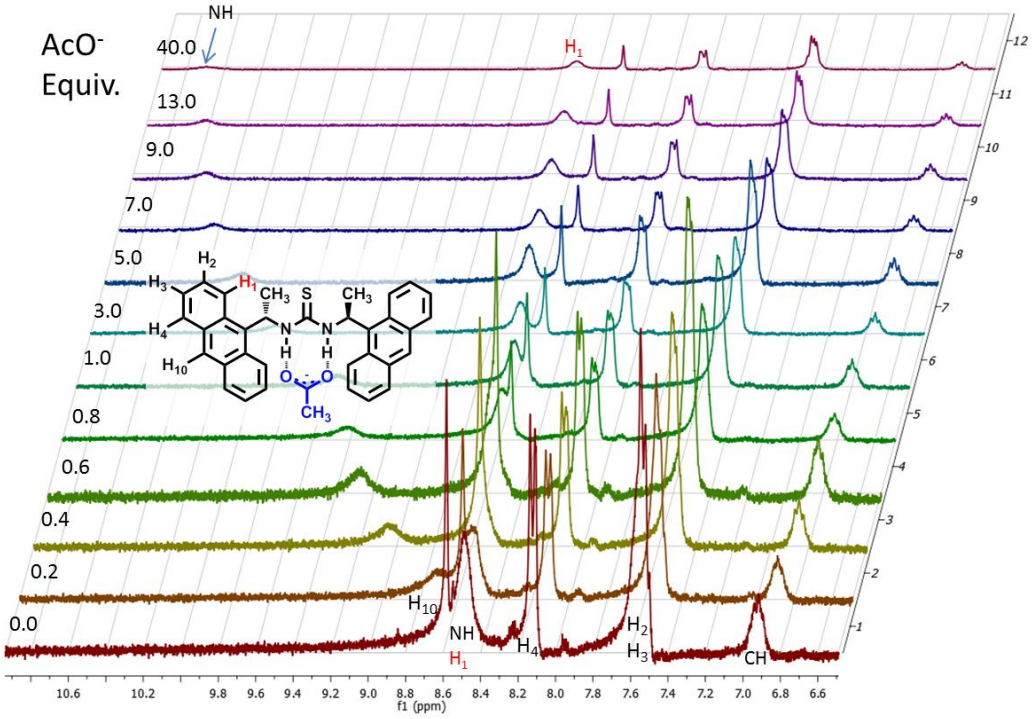


Figure 5. Titration of thiourea **4** with tetrabutylammonium acetate.

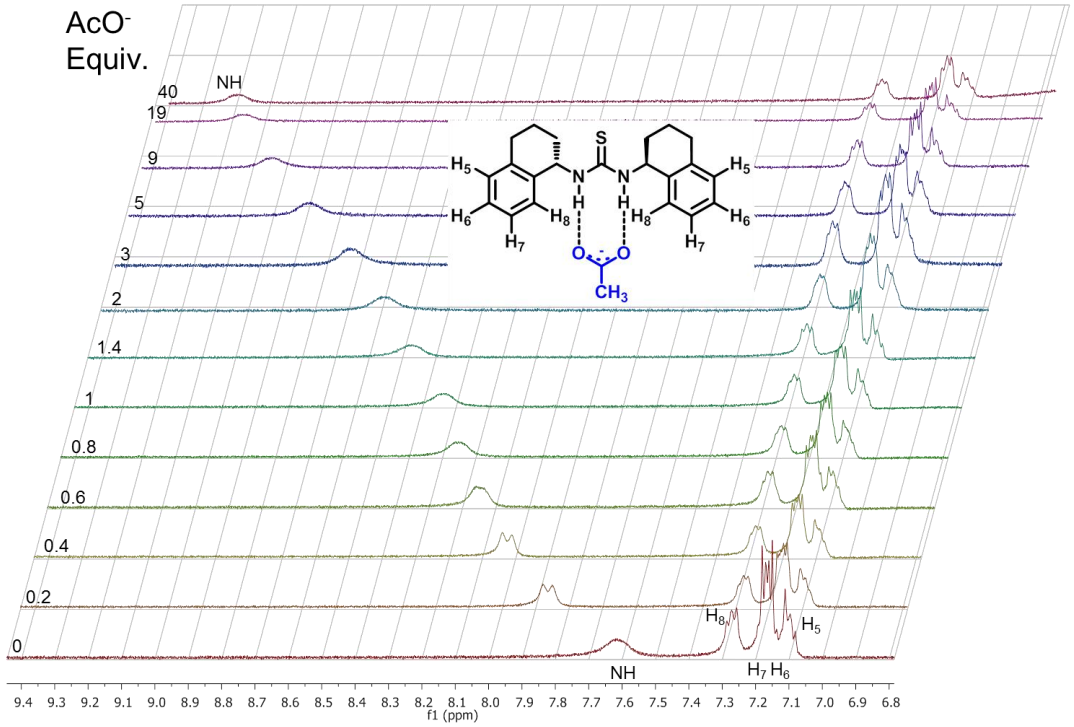


Figure 6. Titration of thiourea **5** with tetrabutylammonium acetate.

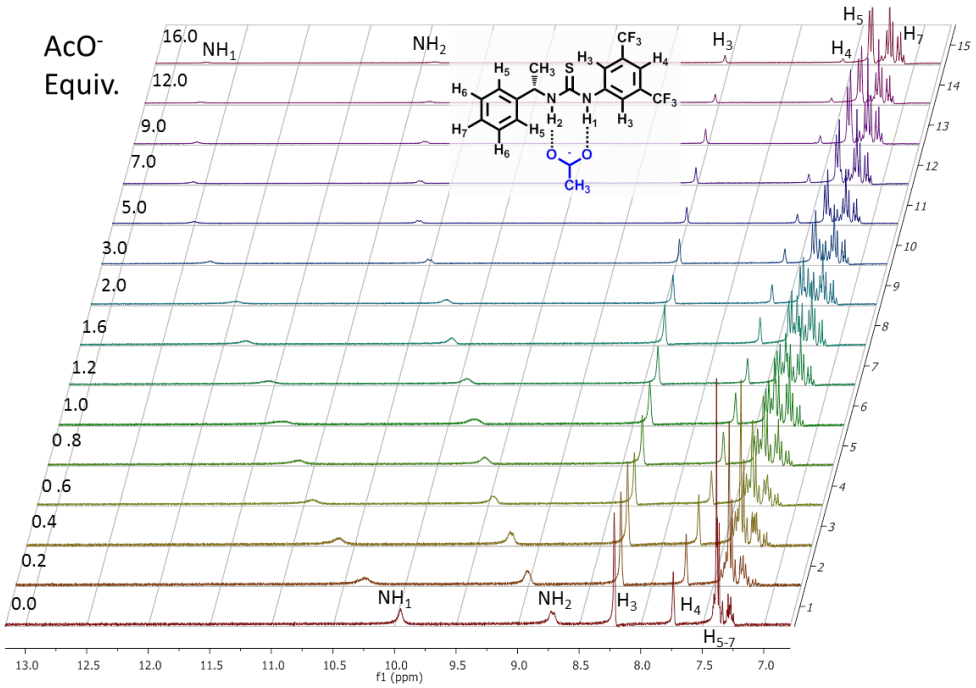


Figure 7. Titration of thiourea **6** with tetrabutylammonium acetate.

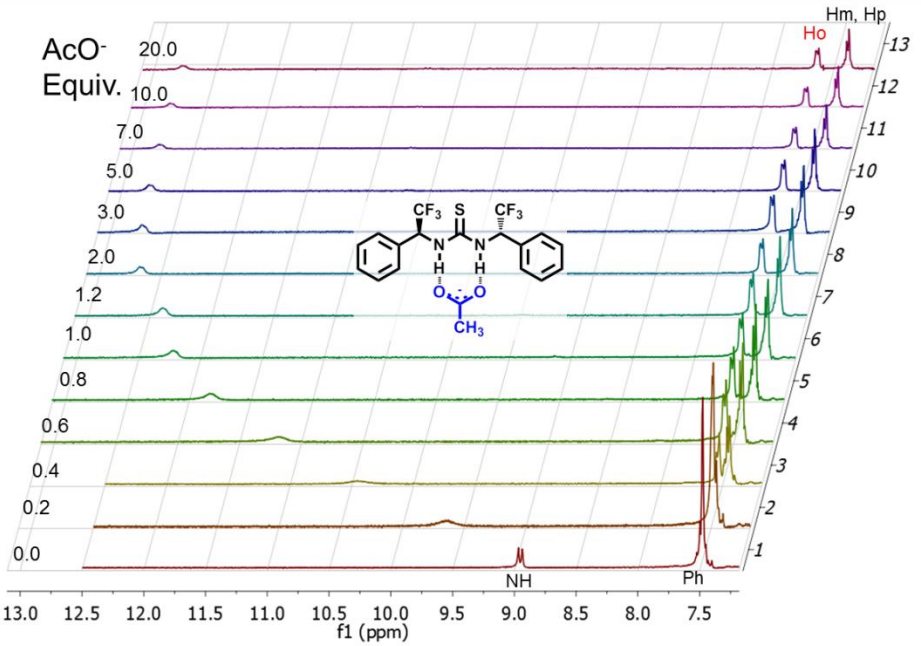


Figure 8. Titration of thiourea **7** with tetrabutylammonium acetate.

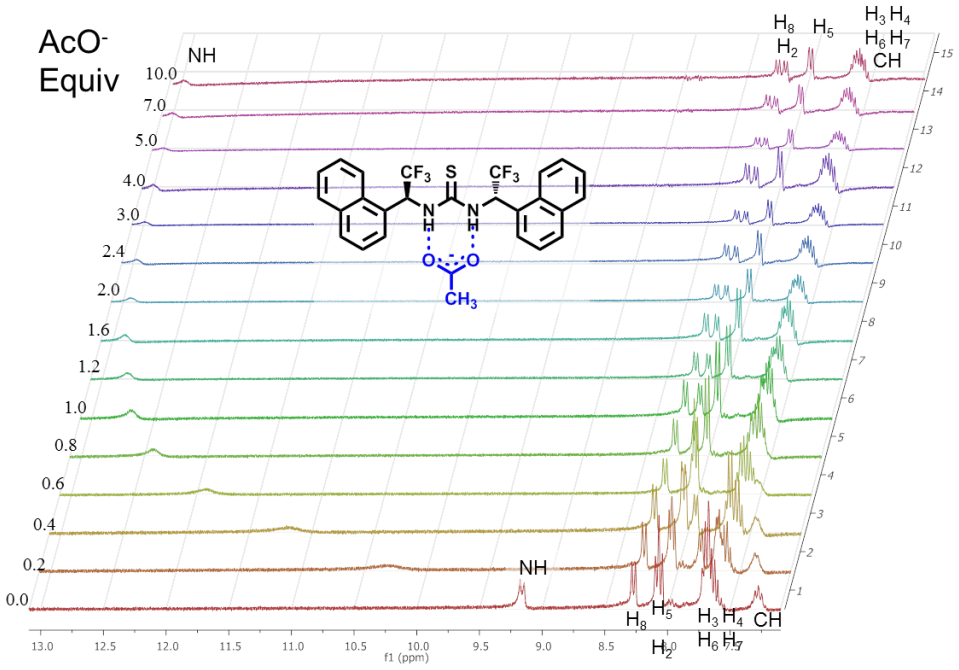
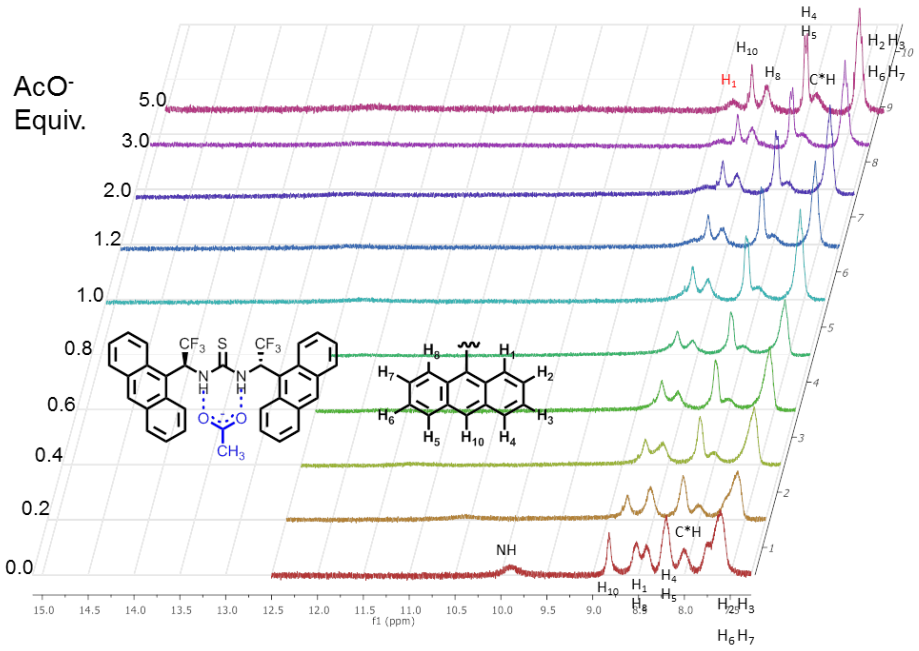


Figure 9. Titration of thiourea **8** with tetrabutylammonium acetate.



6. Graphs of equivalent of carboxylate and NH chemical shift

Figure 10. Chemical shift of NH of thioureas **1-4** during titration with tetrabutylammonium acetate.

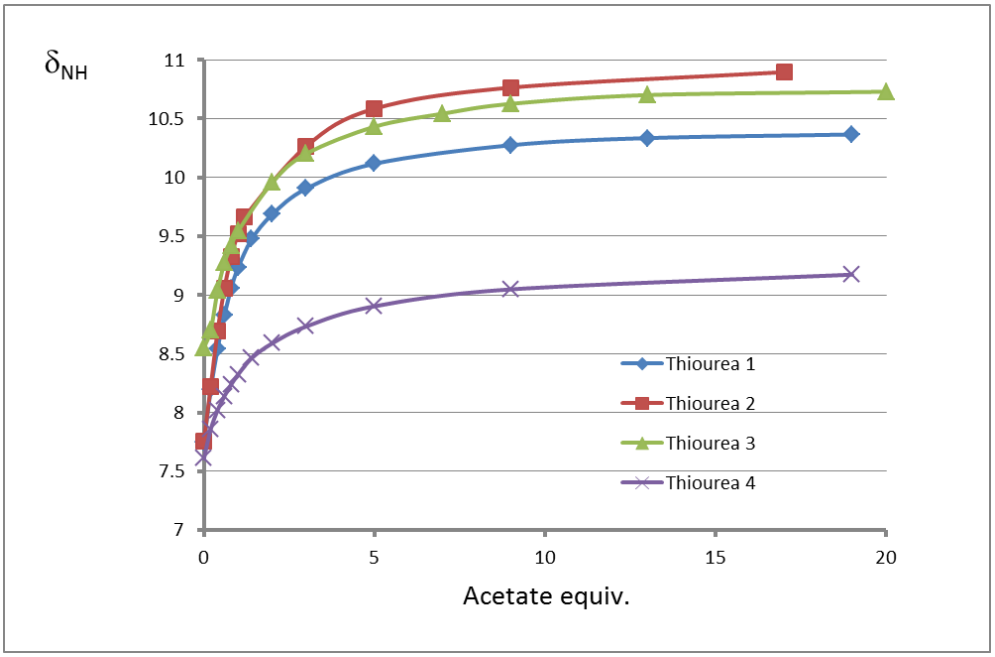


Figure 11. Chemical shift of NH of thioureas **5-8** during titration with tetrabutylammonium acetate.

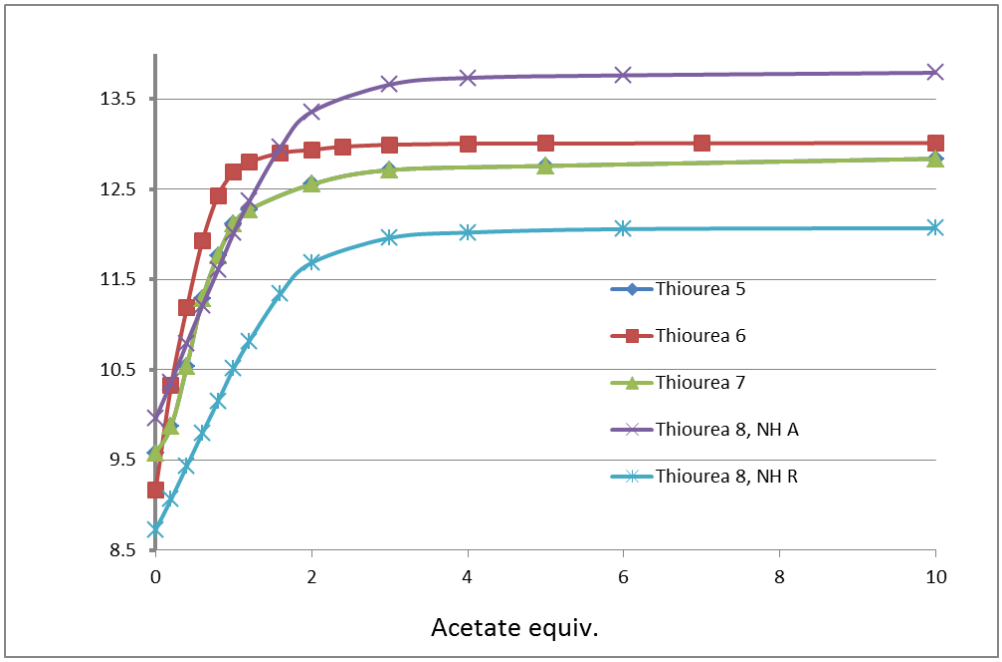


Figure 12. Chemical shift of NH of thioureas **1-4** during titration with (*S*) and (*R*) tetrabutylammonium mandelate.

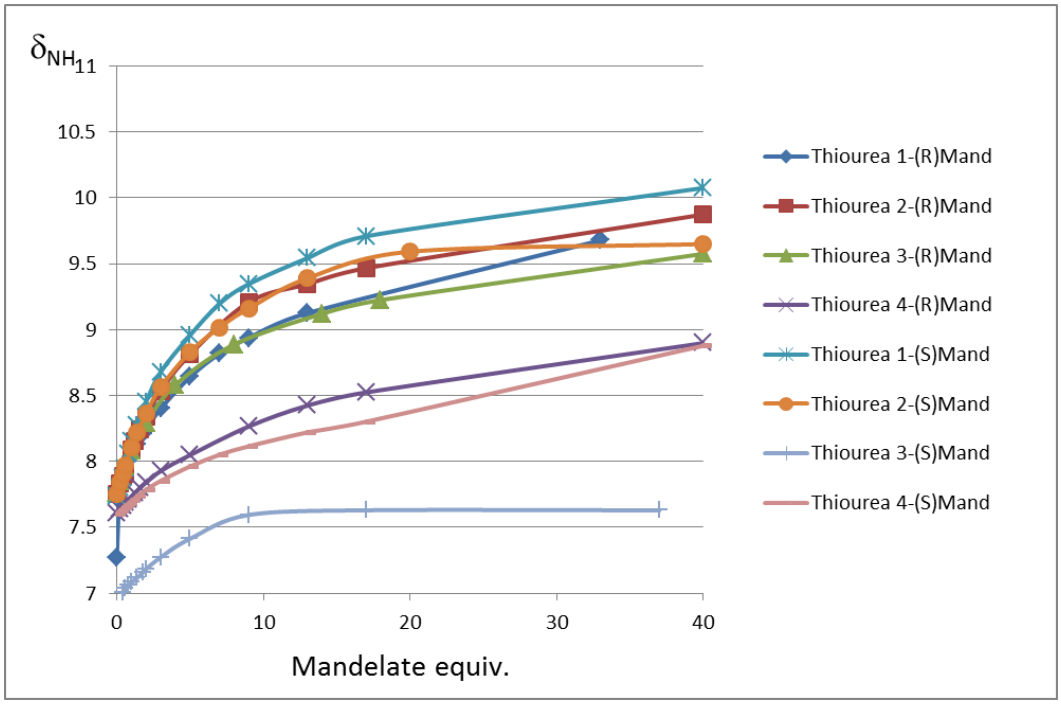
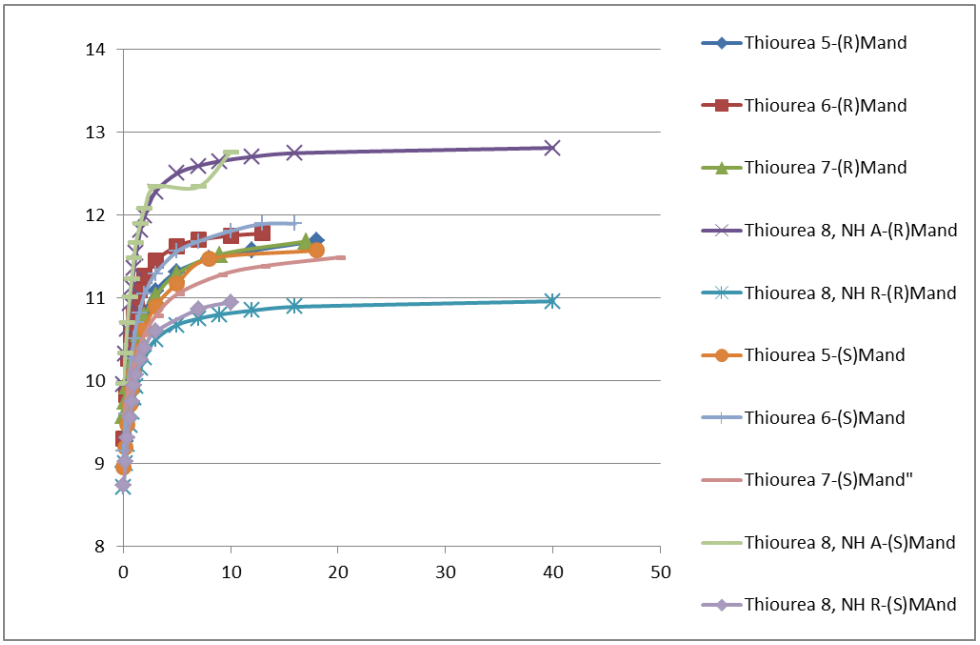


Figure 13. Chemical shift of NH of thioureas **5-8** during titration with (*S*) and (*R*) tetrabutylammonium mandelate.



7. Internal coordinates of the supramolecular adducts of thiourea 8 with mandelates

Computational modeling was performed in Gaussian 03 Revision E.01[5]

Thiourea **8** + (*S*)-Mandelate

B3LYP/6-31G(d,p)

Number of imaginary frequencies = 0

Total enegy + ZPE = -2911.842834 Hartree

C	0.426400	-1.058200	-0.021100
N	-0.703000	-0.738800	-0.712300
N	1.200600	0.016000	0.294600
C	-1.613300	-1.757000	-1.202800
H	-1.001900	-2.659000	-1.253500
C	2.389600	-0.118200	1.115800
H	2.240900	-1.057800	1.649400
H	-4.029900	2.308500	0.541600
C	-4.198700	1.254200	0.739800
H	-2.714000	0.681200	-0.629600
C	-3.437000	0.321000	0.085300
C	-5.427900	-0.464800	1.898900
C	-3.611200	-1.085600	0.310000
C	-5.201300	0.863600	1.669700

C	-4.661100	-1.470800	1.231300
C	-2.829600	-2.091500	-0.316800
H	-5.786600	1.621100	2.183700
H	-5.713400	-3.100400	2.150800
H	-6.200800	-0.788700	2.591900
C	-3.145200	-3.462400	-0.110400
C	-2.468500	-4.548500	-0.762600
C	-4.212700	-3.824700	0.797200
H	-5.332700	-5.436600	1.709800
C	-4.924700	-2.822000	1.454600
C	-2.805700	-5.856500	-0.533700
H	-1.678800	-4.346400	-1.472000
H	-2.266300	-6.644600	-1.051300
C	-3.848300	-6.197300	0.371400
H	-4.098300	-7.240600	0.543500
C	-4.528600	-5.202400	1.016100
H	5.142100	-3.645000	3.196200
C	5.344900	-3.031300	2.323200
H	3.548900	-1.957200	2.549900
C	4.437400	-2.076500	1.946800
C	6.800300	-2.454600	0.493200
C	4.649800	-1.233900	0.803300
C	6.545400	-3.232400	1.587800
C	5.882300	-1.441200	0.073500
C	3.736400	-0.231500	0.376200
H	7.250700	-3.998100	1.899100
H	7.083000	-0.819700	-1.594200
H	7.712900	-2.585800	-0.083400
C	4.072900	0.608100	-0.717700
C	3.266000	1.710500	-1.158000
C	5.302500	0.370800	-1.446200
H	6.559500	0.976500	-3.101900
C	6.163400	-0.647900	-1.038200
C	3.626400	2.476600	-2.235900
H	2.363700	1.983200	-0.632200
H	2.986500	3.302500	-2.532200
C	4.818000	2.212200	-2.965300
H	5.078400	2.828400	-3.821600
C	5.634200	1.188800	-2.571500
C	2.408000	0.948800	2.216700
C	-2.001700	-1.473000	-2.657800
H	0.815400	0.968000	0.128800
H	-0.809900	0.232200	-1.057500
O	0.308500	2.633000	-0.100800
O	-1.147900	1.885100	-1.659200
C	-0.581600	2.785300	-0.972500
C	-1.063000	4.235300	-1.278900
O	-1.868300	4.227100	-2.438800
H	-1.983500	3.267300	-2.601500
S	0.831600	-2.658700	0.407700
H	-0.155200	4.829100	-1.466600
C	-1.786200	4.844400	-0.078700
C	-3.123200	5.994800	2.112600
C	-3.116000	5.262500	-0.195700
C	-1.130100	5.007600	1.150600
C	-1.795300	5.576800	2.235500

C	-3.780700	5.833500	0.892900
H	-3.608800	5.139700	-1.153800
H	-0.109600	4.653700	1.251100
H	-1.275700	5.689400	3.183800
H	-4.814200	6.154500	0.784500
H	-3.638900	6.439000	2.960300
F	-2.676600	-2.534400	-3.169000
F	-2.795000	-0.394300	-2.817000
F	-0.911000	-1.288100	-3.428100
F	3.403300	0.676100	3.100400
F	2.618900	2.203300	1.769300
F	1.253100	0.955900	2.909600

Thiourea **8** + (*R*)-Mandelate

B3LYP/6-31G(d,p)

Number of imaginary frequencies = 0

Total energy + ZPE = -2911.843938Hartree

C	-0.451100	-1.207400	2.010000
N	-1.271900	-0.233800	1.518300
N	0.721200	-0.735300	2.514400
C	-2.531000	-0.554800	0.869100
H	-2.458800	-1.629200	0.698900
C	1.688400	-1.615500	3.146100
H	1.116300	-2.518000	3.362600
H	-2.811200	4.043500	2.873500
C	-3.496400	3.205600	2.971100
H	-2.338500	2.036400	1.670700
C	-3.221500	2.049200	2.288000
C	-5.520900	2.254900	3.873400
C	-4.080000	0.904500	2.356200
C	-4.657400	3.311800	3.785700
C	-5.273700	1.036700	3.165500
C	-3.823400	-0.313600	1.673600
H	-4.857200	4.232900	4.326700
H	-7.074000	0.085300	3.846700
H	-6.421500	2.318500	4.479800
C	-4.780800	-1.364200	1.726500
C	-4.653900	-2.605000	1.013400
C	-5.977000	-1.205500	2.527700
H	-7.824800	-2.105700	3.205500
C	-6.180000	-0.020900	3.235300
C	-5.605300	-3.587800	1.091000
H	-3.791800	-2.787200	0.387500
H	-5.464900	-4.509900	0.534300
C	-6.769300	-3.421300	1.890800
H	-7.510400	-4.214200	1.942700
C	-6.942500	-2.259000	2.588600
H	2.449900	-6.465000	3.649600

C	2.971600	-5.741800	3.029200
H	1.797100	-4.150500	3.746000
C	2.599600	-4.424100	3.076100
C	4.681600	-5.263100	1.403300
C	3.249800	-3.420400	2.280200
C	4.025800	-6.177000	2.179600
C	4.329200	-3.877200	1.430300
C	2.900000	-2.042100	2.296300
H	4.303300	-7.227200	2.152900
H	5.820700	-3.308600	-0.004800
H	5.493400	-5.569400	0.747900
C	3.655000	-1.114000	1.531500
C	3.440400	0.304300	1.555600
C	4.721400	-1.595000	0.676600
H	6.258100	-1.067500	-0.754300
C	5.019900	-2.957000	0.642700
C	4.190800	1.158400	0.789600
H	2.694200	0.741300	2.200900
H	3.999200	2.225400	0.849900
C	5.214700	0.670800	-0.068200
H	5.791400	1.365600	-0.672600
C	5.471500	-0.671000	-0.116400
C	2.087600	-1.087200	4.528900
C	-2.584800	0.035700	-0.543900
H	0.817300	0.290300	2.655500
H	-0.875800	0.715800	1.413200
O	1.079200	1.995600	3.038200
O	-0.263800	2.420500	1.270400
C	0.440200	2.753000	2.268700
C	0.471000	4.283100	2.562600
H	0.254900	4.394300	3.634100
O	-0.554000	4.916600	1.817100
H	-0.796500	4.215300	1.175200
S	-0.860800	-2.864800	1.995900
C	1.847600	4.881500	2.284600
C	4.378900	5.999600	1.782500
C	2.979000	4.422500	2.976400
C	1.999500	5.904100	1.343200
C	3.256400	6.459800	1.093800
C	4.233800	4.976900	2.724300
H	2.864600	3.613300	3.690300
H	1.117200	6.254700	0.819600
H	3.357200	7.254400	0.358200
H	5.102000	4.607100	3.264100
H	5.357600	6.431500	1.588900
F	2.819400	-2.028000	5.180800
F	2.831800	0.036500	4.505200
F	1.001000	-0.834600	5.284900
F	-2.631600	1.384300	-0.585300
F	-1.514900	-0.346400	-1.269600
F	-3.690100	-0.416100	-1.188300