Electronic Supplementary Material (ESI) for RSC Advances.

An Approach to the Synthesis of 4-Aryl and 5-Aryl Substituted Thiazole-2(3H)-thiones Employing Flow Processing

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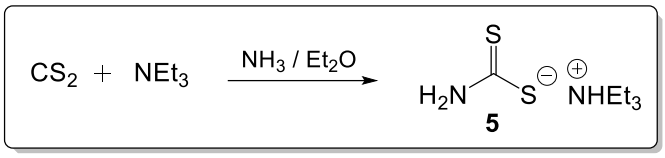
Supporting Information

General Information for experimental studies

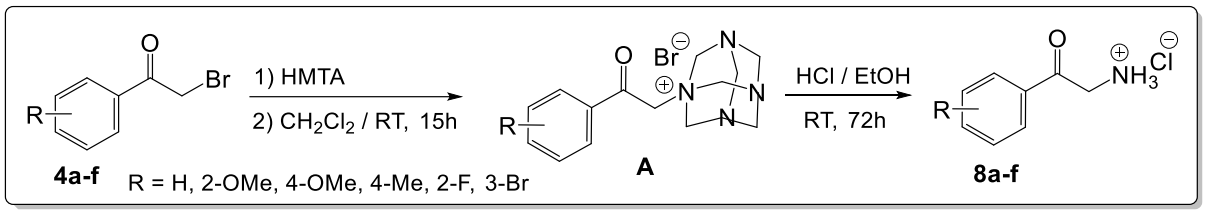
Reagents and solvents were purchased from ABCR, Acros, Aldrich, Fluka, or VWR, all at ACS grade and used without purification unless otherwise indicated. All solvents were of HPLC grade and were stored over molecular sieves. Melting points (mp) were measured by a Büchi B-545 apparatus, in open capillaries. Infrared spectra were recorded on a Perkin Elmer spectrum II FT-IR System using an ATR module and characteristic band positions are expressed in cm^{-1}. NMR spectra were recorded on a JEOL (FNM EX-400) at 400 MHz for ^{1}H, and 100 MHz for ^{13}C acquisitions. All ^{13}C measurements were obtained with hydrogen decoupling. Chemical shifts δ are reported in ppm relative to residual solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constants (Hz), integration. Analytical LC/MS analyses were performed on an Agilent 1100 series HPLC coupled with an MSD Trap SL system using UV detection at 254 and 361 nm. Mass spectra were recorded using electron spray ionization (ESI) operating in positive mode, unless stated otherwise. The following method was applied: injection of 10 µL of a 20 $\mu g.mL^{-1}$ acetonitrile solution onto a C_{18} 3.5 µm ZorbaxSB column (100 mm × 3 mm); separation using a gradient (flow rate of 0.5 $mL.min^{-1}$) of acetonitrile in acetic acid (0.1% v/v in water) from 5% to 95% acetonitrile over 5 min, holding for 3 min, then reversing to 5% acetonitrile within 0.1 min and holding for an additional 5.4 min. High resolution ESI mass spectra (HRMS) were performed on a Bruker maXis Q-TOF in positive ionization mode.

Preparation of triethylammonium dithiocarbamate:

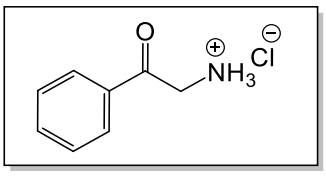


To a well-stirred solution of carbon disulfide (5 mmol, 1 equiv) and triethylamine (5 mmol, 1 equiv) in diethyl ether (12.5 mL) was added ammonia solution 2M (5 mmol, 1 equiv) at 0 °C. The mixture was allowed to warm to room temperature, and stirred overnight. The solid obtained was then filtered and quickly rinsed with 3 × 10 mL of diethyl ether. The product was used promptly without any purification. Yield: 86%; mp: 102 °C. ^{1}H NMR (400 MHz, CD_3OD): 3.26 (m, 6H), 1.34 (m, 9H). ^{13}C NMR (100 MHz, CD_3OD): 217.66, 46.55, 8.65. IR (cm^{-1}): 3305, 3144, 2941, 1610, 1316, 1214, 844.

Synthesis of α aminoacetophenone hydrochlorides:

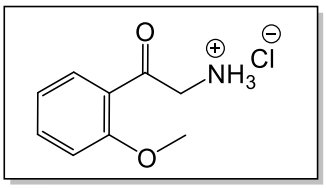


To a 50-mL round-bottom flask equipped with a stir bar was added the appropriate α-bromo acetophenone (10 mmol) and dichloromethane (25 mL). Hexamethylenetetramine (HMTA) (10 mmol) was added to this solution and the resulting mixture was allowed to stir for 15 hours at room temperature and monitored by thin-layer chromatography (TLC) using ethyl acetate / cyclohexane (1:9) as eluent. The precipitate formed was filtered through Celite® eluting with dichloromethane, dried and then dissolved in a mixture (25 mL) of 30% HCl in EtOH and allowed to stir for 72 hours at room temperature. After this time, the solution was filtered and the filtrate concentrated *in vacuo* by rotary evaporation yielding the crude α aminoacetophenone hydrochloride. Further purification was accomplished by recrystallization in ethanol (5mL) to give the pure compounds **8a-f**.



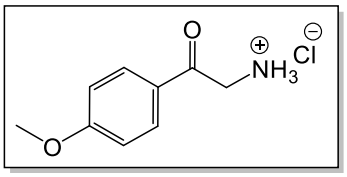
2-Phenyl-2-oxo-ethyl-ammonium chloride (8a): prepared according to the general procedure using 2-bromoacetophenone – mp: 189 °C, Yield: 93%.

IR (cm^{-1}): ν_{NH3} = 3321, $\nu_{C=O}$ = 1665.
^{1}H NMR (400 MHz, CD_3OD): 4.60 (s, 2H, CH_2NH_3), 8.02 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.69 (m, 1H, Ar*H*), 7.56 (m, 2H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 44.91 (CH_2NH_3), 127.94, 128.86, 133.72, 134.46 ($4CH_{Ar}$, C_{Ar}), 191.92 (C=O).



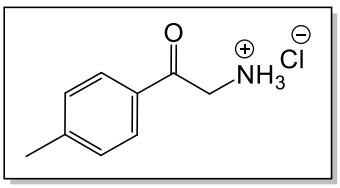
2-(2-Methoxyphenyl)-2-oxo-ethyl-ammonium chloride (8b) prepared according to the general procedure using 2-bromo-2'-methoxyacetophenone – mp: 171 °C, Yield: 68%.

IR (cm^{-1}): ν_{NH3} = 3390, $\nu_{C=O}$ = 1670.
^{1}H NMR (400 MHz, CD_3OD): 4.42 (s, 2H, *C*$H_2$$NH_3$), 3.99 (s, 3H, O*C*$H_3$), 7.96 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.24 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.10 (m, 1H, Ar*H*), 7.64 (m, 1H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 49.08 (*C*$H_2$$NH_3$), 55.02 (O*C*$H_3$), 112.25, 120.72, 123, 130.38, 136.14 (4*C*H_{Ar}, *C*$_{Ar}$), 160.49 (*C*-OCH_3), 191.57 (C=O).



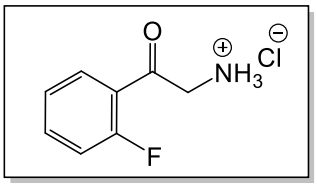
2-(4-Methoxyphenyl)-2-oxo-ethyl-ammonium chloride (8c): prepared according to the general procedure using 2-bromo-4'-methoxyacetophenone – mp: 183 °C, Yield: 88%.

IR (cm^{-1}): ν_{NH3} = 3272, $\nu_{C=O}$ = 1683.
^{1}H NMR (400 MHz, CD_3OD): 4.56 (s, 2H, *C*$H_2$$NH_3$), 3.86 (s, 3H, O*C*$H_3$), 7.07 (d, *J* = 8.8 Hz, 2H, Ar*H*), 8.01 (d, *J* = 8.8 Hz, 2H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 44.44 (*C*$H_2$$NH_3$), 54.93 (O*C*$H_3$), 114.04 (2*C*$H_{Ar}$), 126.56 (*C*$_{Ar}$), 130.39 (2*C*$H_{Ar}$), 165.05 (*C*-$OCH_3$), 190.13 (C=O).



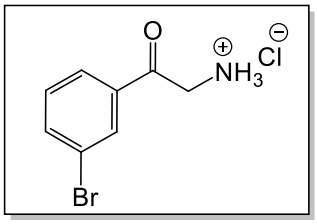
2-(*p*-Tolyl)-2-oxo-ethyl-ammonium chloride (8d): prepared according to the general procedure using 2-bromo-4'-methylacetophenone – mp: 191 °C, Yield: 92%.

IR (cm^{-1}): ν_{NH3} = 3298, $\nu_{C=O}$ = 1681.
^{1}H NMR (400 MHz, CD_3OD): 4.59 (s, 2H, *C*$H_2$$NH_3$), 2.42 (s, 3H, *C*$H_3$), 7.38 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.93 (d, *J* = 8.4 Hz, 2H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 20.45 (*C*H_3), 44.77 (*C*$H_2$$NH_3$), 128.07 (2*C*$H_{Ar}$), 129.45 (2*C*$H_{Ar}$), 131.25(*C*$_{Ar}$), 145.89 (*C*-$CH_3$), 191.40 (C=O).



2-(2-Fluorophenyl)-2-oxo-ethyl-ammonium chloride (8e): prepared according to the general procedure using 2-bromo-2'-fluoroacetophenone – mp: 147 °C, Yield: 66%.

IR (cm^{-1}): ν_{NH3} = 3307, $\nu_{C=O}$ = 1677.
^{1}H NMR (400 MHz, CD_3OD): 4.48 (s, 2H, *C*H_2NH_3), 7.29-7.39 (m, 2H, Ar*H*), 7.74 (m, 1H, Ar*H*), 7.10 (m, 1H, Ar*H*), 8.03 (m, 1H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 48.34 (*C*H_2NH_3), 116.16 (d, *J* = 22.6 Hz), 121.87 (d, *J* = 3.6 Hz), 124.97 (d, *J* = 11.6 Hz), 130.24 (d, *J* = 7.6 Hz), 136.80 (d, *J* = 38 Hz), 161.50 (d, *J* = 248.58 Hz), 189.47 (C=O).
^{19}F NMR (376 MHz, CD_3OD): -109.98 (s).

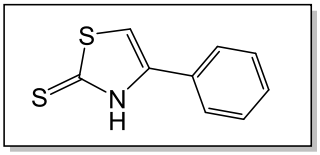


2-(3-Bromophenyl)-2-oxo-ethyl-ammonium chloride (8f): prepared according to the general procedure 2-bromo-3'-bromoacetophenone – mp: 234 °C, Yield: 86%.

IR (cm^{-1}): ν_{NH3} = 3355, $\nu_{C=O}$ = 1701.
^{1}H NMR (400 MHz, CD_3OD): 4.79 (s, 2H, *C*H_2NH_3), 8.15 (s, 1H, Ar*H*), 7.50 (m, 1H, Ar*H*), 7.84 (d, *J* = 8 Hz, 1H, Ar*H*), 8.00 (d, *J* = 8 Hz, 1H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 45.11 (*C*H_2NH_3), 122.79 (*C*-Br), 126.92, 130.65, 130.80, 135.57, 137.15 (4*CH*$_{Ar}$, *C*$_{Ar}$), 191.06 (C=O).

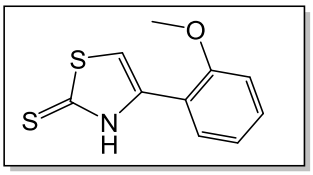
Synthesis of 4-aryl-substituted thiazole-2(3H)-thiones:

*Preparation of 4-Phenylthiazole-2(3H)-thione (**1a**)*: Two stock solutions were prepared – Solution A: Triethylammonium dithiocarbamate (1.2 mmol) in ethanol (20 mL); Solution B: 2-bromoacetophenone (1 mmol) in ethanol (20 mL). A combination of a Vapourtec R2 Pump Module and a Vapourtec R4 Reactor Module was employed for the reaction. The flow system was equipped with two 10-mL volume stainless-steel coils in series coil 1 and coil 2). Two pumps were employed (pump A and pump B), the outlets of which were joined to a T-piece and the outlet of the T-piece attached to the "reagent in" port of the first reactor coil. The "reagent out" port of the second reactor coil was attached to a cartridge containing Amberlyst 15 and the exit of the cartridge directly interfaced with a 100 psi back pressure regulator after which there was a short length of tubing leading to a collection vessel. The flow system was primed using the equipment manufacturer's suggested start-up sequence. The entire system was flushed with ethanol for 5 min at a flow rate of 0.5 mL / min on each pump. The flow rate of each pump was then decreased to 0.2 mL / min (giving a combined flow rate of 0.4 mL / min) and the reactor coils heated to 25 °C (coil 1) and 40 °C (coil 2). Once at the target temperatures, the flow was then changed from solvent to reagents by means of a switch on the flow unit. Solution A was pumped by pump A and solution B by pump B. The reaction mixture was then flowed through the two coils and the cartridge containing Amberlyst 15 and the product collected. Once the requisite volume of reagents had been loaded in to the first reactor coil, the flow was changed back to solvent and the system run until the remainder of the reaction mixture has passed through the entire configuration. Once all the product had exited the unit, the flow of ethanol solvent was stopped. The contents of the collection vessel were decanted into a round bottom flask, and the organic solvent removed using rotary evaporation, leaving behind crystalline product **1a**.



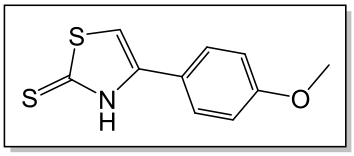
4-Phenylthiazole-2(3H)-thione (1a): mp: 187 °C, Yield: 92%.

IR (cm^{-1}): ν_{NH} = 3144, $\nu_{C=C}$ = 1594, ν_{C-N} = 1523, $\nu_{C=S}$ = 1314.
^{1}H NMR (400 MHz, CD_3OD): 6.98 (s, 1H, C=*CH*-S), 7.61 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.43 (m, 3H, Ar*CH*),
^{13}C NMR (100 MHz, CD_3OD): 108.61(C=*CH*-S), 125.67, 128.87, 129.02, 129.13 (C_{Ar}), 142.39 (Ar*C*=CH-S), 190.85 (C=S).
LC/MS: Tr = 5.4 min, *m/z* $[M+H]^+$ 194.1.



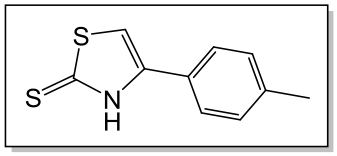
4-(2-Methoxyphenyl)thiazole-2(3H)-thione (1b): prepared from 2-bromo-2'-methoxyacetophenone – mp: 129 °C, Yield: 91%.

IR (cm^{-1}): ν_{NH} = 3137, $\nu_{C=C}$ = 1591, ν_{C-N} = 1483, $\nu_{C=S}$ = 1295.
^{1}H NMR (400 MHz, CD_3OD): 3.87 (s, 3H, O*CH*$_3$)), 6.96 (s, 1H, C=*CH*-S), 7.11 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.46 (d, *J* =7.2 Hz, 1H, Ar*H*), 7.01 (m, 1H, Ar*H*), 7.40 (m, 1H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 55.86 (O*CH*$_3$), 109.85 (C=*CH*-S), 111.68, 116.75, 121.15, 128.38, 131.18 (4*CH*$_{Ar}$, C_{Ar}), 139.06 (*C*-OCH_3), 155.73 (Ar*C*=CH-S), 188.57 (C=S).
LC/MS: Tr = 6.1 min, *m/z* $[M+H]^+$ 224.1.



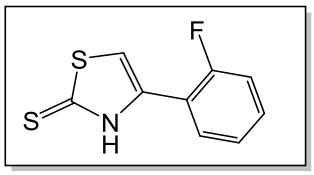
4-(4-Methoxyphenyl)thiazole-2(3H)-thione (1c): prepared from 4-methoxy-2'-methoxyacetophenone – mp: 178 °C, Yield: 96%.

IR (cm^{-1}): ν_{NH} = 3113, $\nu_{C=C}$ =1607, ν_{C-N} =1504, $\nu_{C=S}$ = 1310.
^{1}H NMR (400 MHz, CD_3OD): 3.81 (s, 3H, O*CH*$_3$), 6.83 (s, 1H, C=*CH*-S), 7.52 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.97 (d, *J* = 8.8 Hz, 2H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 54.53 (O*CH*$_3$), 106.75 (C=*CH*-S), 114.16 (2*CH*$_{Ar}$), 121.59 (*C*$_{Ar}$), 127.14 (2*CH*$_{Ar}$), 142.35 (*C*-OCH_3), 160.75 (Ar*C*=CH-S), 190.61 (C=S).
LC/MS: Tr = 5.9 min, *m/z* $[M+H]^+$ 224.1



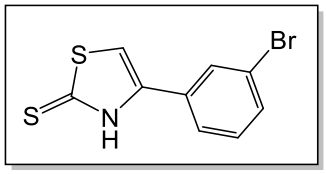
4-(*p*-Tolyl)thiazole-2(3H)-thione (1d): prepared from 2-bromo-4'-methylacetophenone – mp: 187 °C, Yield: 91%.

IR (cm^{-1}): ν_{NH} = 3130, $\nu_{C=C}$ = 1589, ν_{C-N} = 1505, $\nu_{C=S}$ = 1308.
^{1}H NMR (400 MHz, CD_3OD): 2.35 (s, 3H, *CH*$_3$), 6.92 (s, 1H, C=*CH*-S), 7.24 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.47 (d, *J* = 8.4 Hz, 2H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 19.96 (*CH*$_3$), 107.80 (C=*CH*-S), 125.58 (2*CH*$_{Ar}$), 126.24 (2*CH*$_{Ar}$), 129.45 (*C*$_{Ar}$), 139.51 (*C*-CH_3), 142.50 (Ar*C*=CH-S), 190.68 (C=S).
LC/MS: Tr = 6.3 min, *m/z* $[M+H]^+$ 208.1



4-(2-Fluorophenyl)thiazole-2(3H)-thione (1e): prepared from 2-bromo-2'-fluoroacetophenone – mp: 134 °C, Yield: 89%.

IR (cm^{-1}): ν_{NH} = 3189, $\nu_{C=C}$ = 1564, ν_{C-N} = 1458, $\nu_{C=S}$ = 1332, 1060.
^{1}H NMR (400 MHz, CD_3OD): 7.02 (s, 1H, C=*CH*-S), 7.27 (m, 2H, Ar*H*), 7.43 (m, 1H, Ar*H*), 7.58 (m, 1H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 112.46 (d, *J* = 7.6 Hz, C=*CH*-S), 116.16 (d, *J* = 22.7 Hz, *CH*=C-F), 118.44 (d, *J* = 12.7 Hz), 124.65, 128.78 (d, *J* = 3.7 Hz), 131.09, 136.03 (d, *J* = 8.7 Hz), 160.81 (d, *J* = 250.5 Hz), 190.28 (C=S).
^{19}F NMR (376 MHz, CD_3OD): -116.07 (s).
LC/MS: Tr = 5.9 min, *m/z* $[M+H]^+$ 212.1

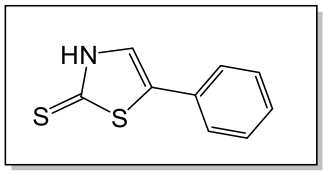


4-(3-Bromophenyl)thiazole-2(3H)-thione (1f): prepared from 2-bromo-3'-bromoacetophenone – mp: 167 °C, Yield: 94%.

IR (cm^{-1}): ν_{NH} = 3155, $\nu_{C=C}$ = 1596, ν_{C-N} = 1474, $\nu_{C=S}$ = 1265.
^{1}H NMR (400 MHz, CD_3OD): 7.08 (s, 1H, C=*CH*-S), 7.82 (s, 1H, Ar*H*), 7.58 (d, *J* = 8 Hz, 1H, Ar*H*), 7.54 (d, *J* = 8 Hz, 1H, Ar*H*), 7.35 (m, 1H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 110.01 (C=*CH*-S), 122.74 (*C*-Br), 124.43, 128.52, 130.61, 132 (4CH_{Ar}), 140.55 (C_{Ar}), 153.47 (Ar*C*=CH-S), 191.06 (C=S).
HRMS (ESI) m/z calculated for calculated for $C_9H_5NS_2Br$ $[M+H]^+$: 269.9052, found 271.9027.

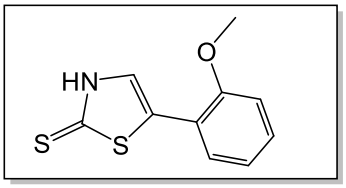
Synthesis of 5-aryl-substituted thiazole-2(3H)-thiones:

*Preparation of 5-Phenylthiazole-2(3H)-thione (**7a**)*: Two stock solutions were prepared – Solution A: 2-Phenyl-2-oxo-ethyl-ammonium chloride (**8a**) (4 mmol) in ethanol (20 mL); Solution B: Carbon disulfide. The flow system was equipped with two cartridges, one containing Amberlyst A21 (cartridge 1) and one containing Amberlyst A15 (cartridge 2). Two pumps were employed (pump A and pump B), the outlets of which were joined to a T-piece and the outlet of the T-piece attached to the inlet port of cartridge 1. The outlet port of cartridge 1 was connected to the inlet port of cartridge 2 and the exit of cartridge 2 directly interfaced with a 100 psi back pressure regulator after which there was a short length of tubing leading to a collection vessel. The flow system was primed using the equipment manufacturer's suggested start-up sequence. The entire system was flushed with ethanol for 5 min at a flow rate of 0.5 mL / min on each pump. The flow rate of each pump was then decreased to 0.05 mL / min (giving a combined flow rate of 0.1 mL / min) and cartridges heated to 80 °C (cartridge 1) and 40 °C (cartridge 2). Once at the target temperatures, the flow was then changed from solvent to reagents by means of a switch on the flow unit. Solution A was pumped by pump A and solution B by pump B. The reaction mixture was then flowed through the system and the product collected. Once the requisite volume of reagents had been loaded in to the first reactor coil, the flow was changed back to solvent and the system run until the remainder of the reaction mixture has passed through the entire configuration. Once all the product had exited the unit, the flow of ethanol solvent was stopped. The contents of the collection vessel were decanted into a round bottom flask, and the organic solvent removed using rotary evaporation, leaving behind crystalline product **8a**.



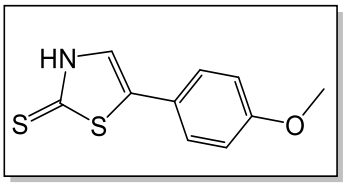
5-Phenylthiazole-2(3H)-thione (7a): prepared from **8a** – mp: 208 °C, Yield: 89%.

IR (cm^{-1}): ν_{NH} = 3132, $\nu_{C=C}$ = 1614, ν_{C-N} = 1477, $\nu_{C=S}$ = 1315.
^{1}H NMR (400 MHz, CD_3OD): 7.48 (s, 1H, C=*CH*-NH), 7.33-7.43 (m, 3H, Ar*CH*), 7.61 (d, *J* = 8.8 Hz, 2H, Ar*CH*).
^{13}C NMR (100 MHz, CD_3OD): 109.63 (Ar*C*-S), 125.77, 129.22, 129.40, 131.25 (5CH_{Ar}, C_{Ar}), 141.57 (C=*CH*-NH), 178.53 (C=S).
LC/MS: Tr = 5.6 min, *m/z* $[M+H]^+$ 194.2.
HRMS (ESI) m/z calculated for calculated for $C_9H_8NS_2$ $[M+H]^+$: 194.0098, found 194.0104



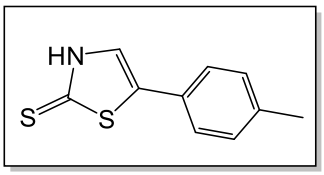
5-(2-Methoxyphenyl)thiazole-2(3H)-thione (7b): prepared from **8b** – mp: 188 °C, Yield: 84%.

IR (cm^{-1}): ν_{NH} = 3165, $\nu_{C=C}$ = 1605, ν_{C-N} = 1470, $\nu_{C=S}$ = 1308.
^{1}H NMR (400 MHz, CD_3OD): 3.91 (s, 3H, O*CH*$_3$), 7.34 (s, 1H, C=*CH*-NH), 7.65 (d, *J* = 8.4 Hz, 1H, Ar*CH*), 7.05 (d, *J* = 8.4 Hz, 1H, Ar*CH*), 7.00 (m, 1H, Ar*CH*), 7.30 (m, 1H, Ar*CH*).
^{13}C NMR (100 MHz, CD_3OD): 54.65 (O*CH*$_3$), 110.67 (Ar*C*-S), 114.10, 115.8, 120.86, 124.55, 129.39 (4*CH*$_{Ar}$, C_{Ar}), 145.30 (C=*CH*-NH), 155.36 (*C*-OCH_3), 177.55 (C=S).
HRMS (ESI) m/z calculated for calculated for $C_{10}H_{10}NOS_2$ $[M+H]^+$: 224.0204, found 224.0201



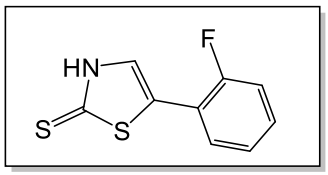
5-(4-Methoxyphenyl)thiazole-2(3H)-thione (7c): prepared from **8c** – mp: 216 °C, Yield: 87%.

IR (cm^{-1}): ν_{NH} = 3136, $\nu_{C=C}$ = 1619, ν_{C-N} = 1461, $\nu_{C=S}$ = 1316.
^{1}H NMR (400 MHz, CD_3OD): 3.65 (s, 3H, O*CH*$_3$), 6.83 (s, 1H, C=*CH*-NH), 7.33 (d, *J* = 9.2 Hz, 2H, Ar*H*), 6.74 (d, *J* = 9.2 Hz, 2H, Ar*H*).
^{13}C NMR (100 MHz, CD_3OD): 54.45 (O*CH*$_3$), 108.92 (Ar*C*-S), 114.17 (2*CH*$_{Ar}$), 119.32 (C_{Ar}), 124.93 (2*CH*$_{Ar}$), 149.07 (C=*CH*-NH), 160.39 (*C*-OCH_3), 178.15 (C=S).
HRMS (ESI) m/z calculated for calculated for $C_{10}H_{10}NOS_2$ $[M+H]^+$: 224.0204, found 224.0211



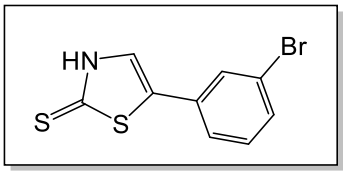
5-(*p*-Tolyl)thiazole-2(3H)-thione (7d): prepared from **8d** – mp: 224 °C, Yield: 88%.

IR (cm^{-1}): ν_{NH} = 3132, $\nu_{C=C}$ = 1611, ν_{C-N} = 1477, $\nu_{C=S}$ = 1315.
^{1}H NMR (400 MHz, CD_3OD): 2.33 (s, 3H, *CH*$_3$), 7.38 (s, 1H, C=*CH*-NH), 7.22 (d, *J* = 8.4 Hz, 2H, Ar*CH*), 7.47 (d, *J* = 8.4 Hz, 2H, Ar*CH*).
^{13}C NMR (100 MHz, CD_3OD): 20.02 (*CH*$_3$), 109.93 (Ar*C*-S), 123.26, 123.96, 129.34 (4*CH*$_{Ar}$, C_{Ar}), 138.92 (*C*-CH_3), 149.06 (C=*CH*-NH), 178.37 (C=S).
HRMS (ESI) m/z calculated for calculated for $C_{10}H_{10}NS_2$ $[M+H]^+$: 208.0255, found 208.0257



5-(2-Fluorophenyl)thiazole-2(3H)-thione (7e): prepared from **8e** – mp; 185 °C, Yield: 76%.

IR (cm^{-1}): ν_{NH} = 3134, $\nu_{C=C}$ = 1608, ν_{C-N} = 1479, $\nu_{C=S}$ = 1309.
^{1}H NMR (400 MHz, CD_3OD): 7.39 (s, 1H, C=*CH*-NH), 7.72 (m, 1H, Ar*CH*), 7.18-7.36 (m, 3H, Ar*CH*).
^{13}C NMR (100 MHz, CD_3OD): 177.86, 158.52 (d, *J* = 252.8 Hz), 143.72, 130.29 (d, *J* = 8.7 Hz), 125.92 (d, *J* = 2.4 Hz), 124.96 (d, *J* = 2.9 Hz), 115.90 (d, *J* = 20.7 Hz), 114.85 (d, *J* = 12.7 Hz), 114.04 (d, *J* = 13.8 Hz)
^{19}F NMR (376 MHz, CD_3OD): -114.31 (s).
HRMS (ESI) m/z calculated for calculated for $C_9H_7FNS_2$ $[M+H]^+$: 212.0003, found 212.0011

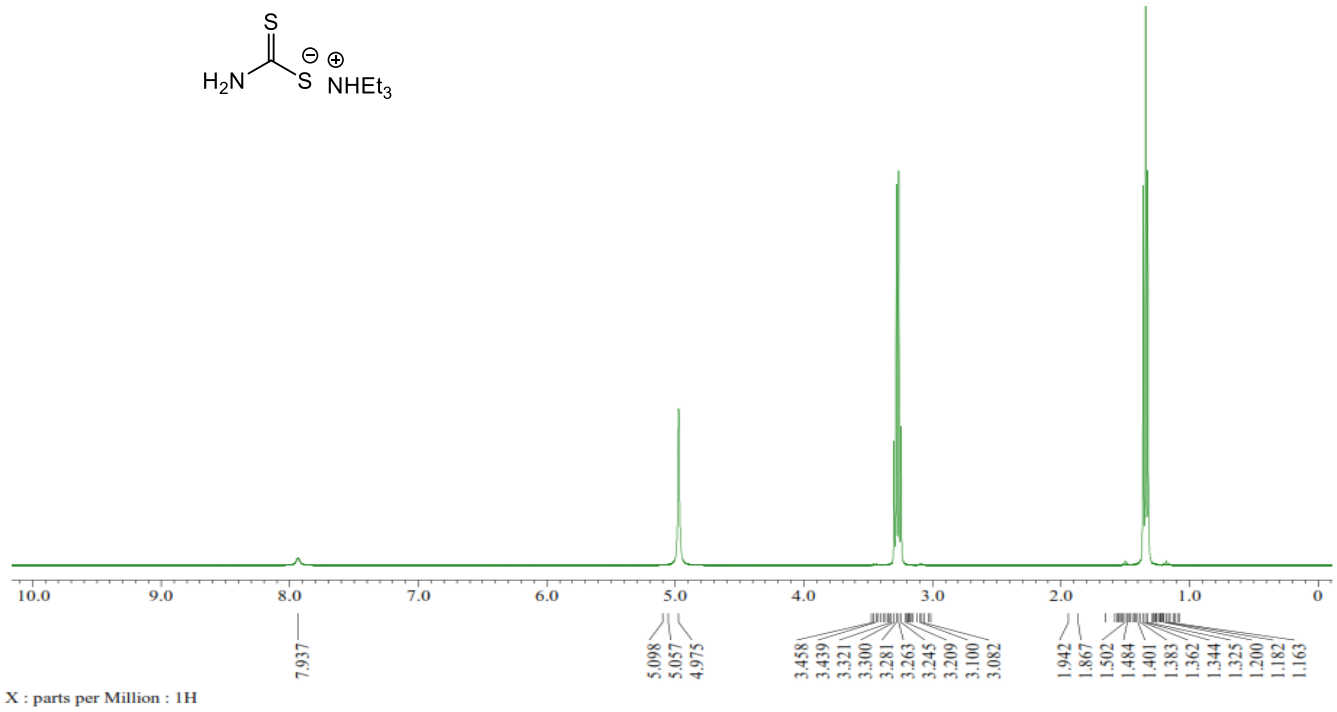


5-(3-Bromophenyl)thiazole-2(3H)-thione (7f): prepared from **8f** – mp: 236 °C, Yield: 84%.

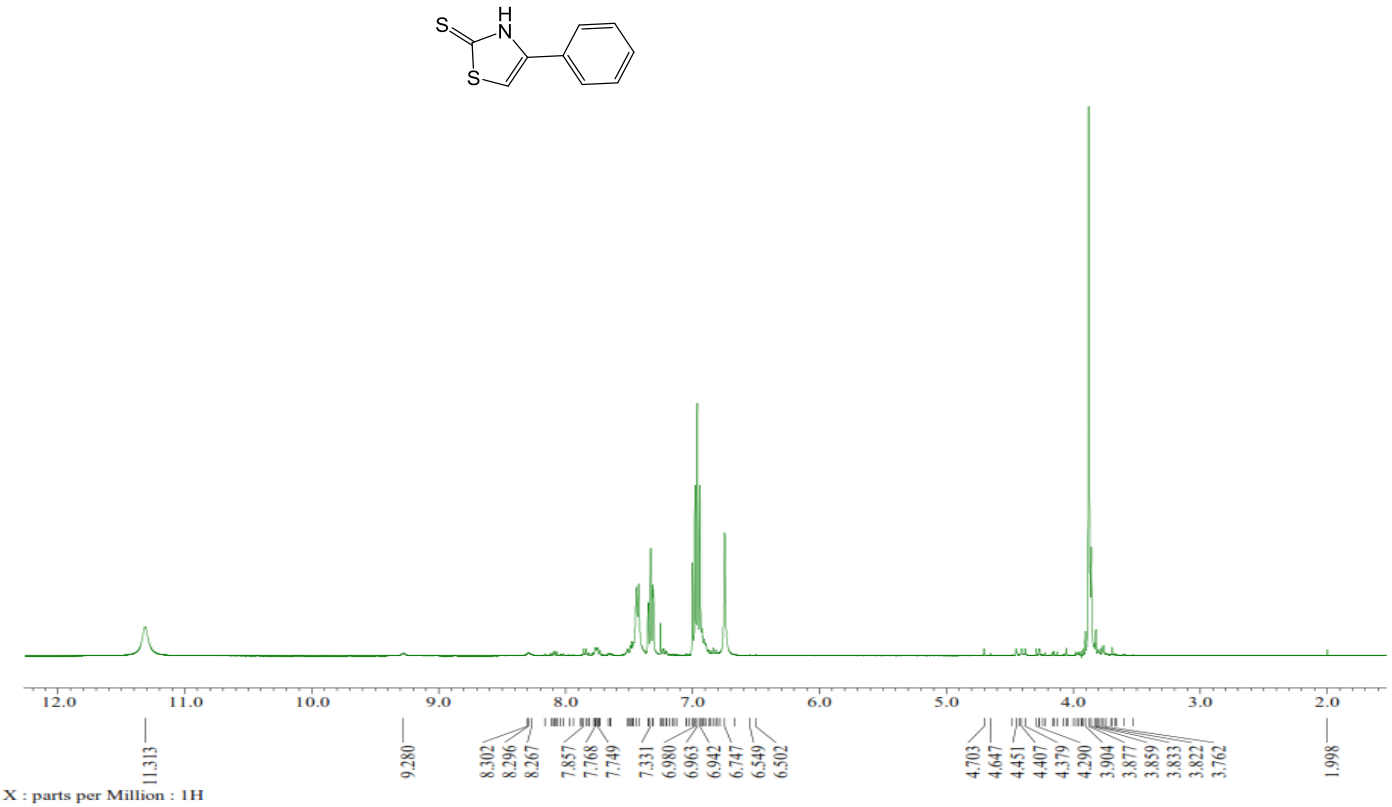
IR (cm^{-1}): ν_{NH} = 3128, $\nu_{C=C}$ = 1617, ν_{C-N} = 1485, $\nu_{C=S}$ = 1287.
^{1}H NMR (400 MHz, CD_3OD): 7.74 (s, 1H, Ar*CH*), 7.54 (s, 1H, C=*CH*-NH), 7.56 (d, *J* = 7.2 Hz, 1H, Ar*CH*), 7.45 (d, *J* = 7.2 Hz, 1H, Ar*CH*), 7.30 (m, 1H, Ar*CH*).
^{13}C NMR (100 MHz, CD_3OD): 112.09 (Ar*C*-S), 121.86 (*C*-Br), 125.92, 128.78, 130.57, 131.27, 146.86 (4CH_{Ar}, C_{Ar}), 158 (C=*CH*-NH), 178.88 (C=S).
HRMS (ESI) m/z calculated for calculated for $C_9H_7BrNS_2$ $[M+H]^+$: 271.9203, found 271.9207.

^{1}H-NMR Spectra of compounds synthesized:

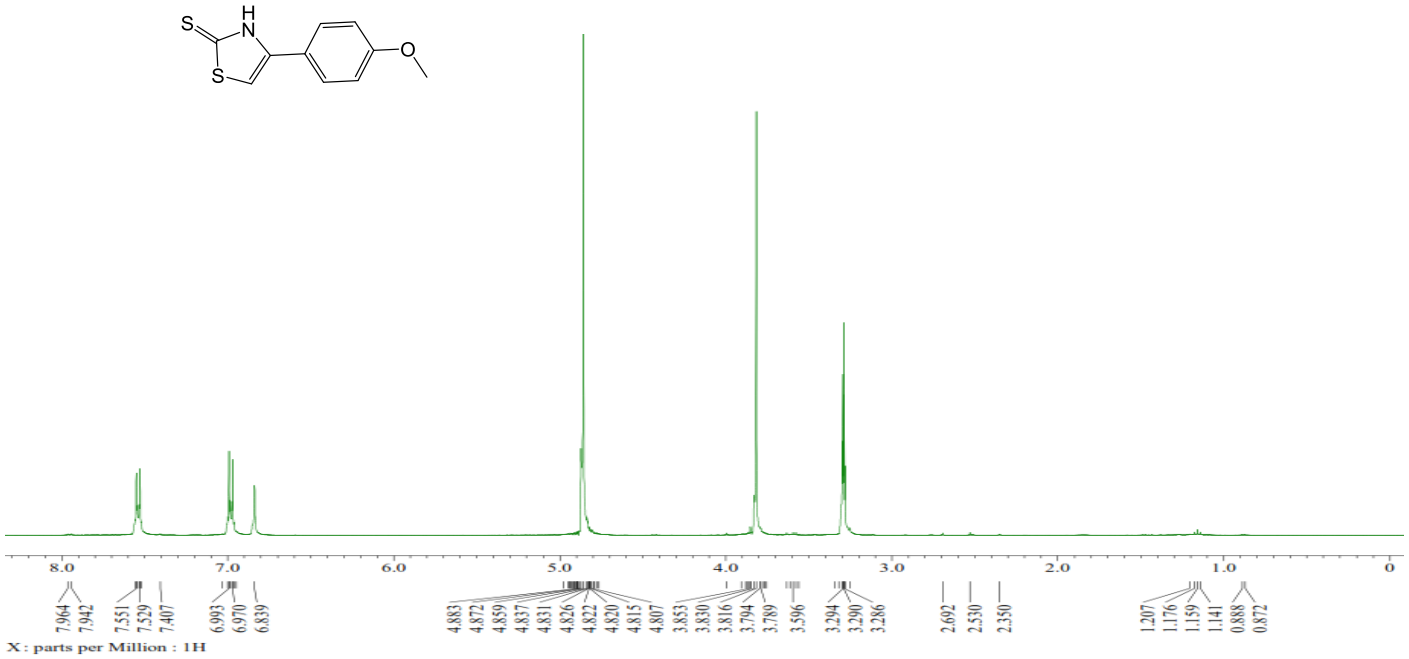
Triethylammonium dithiocarbamate (5)



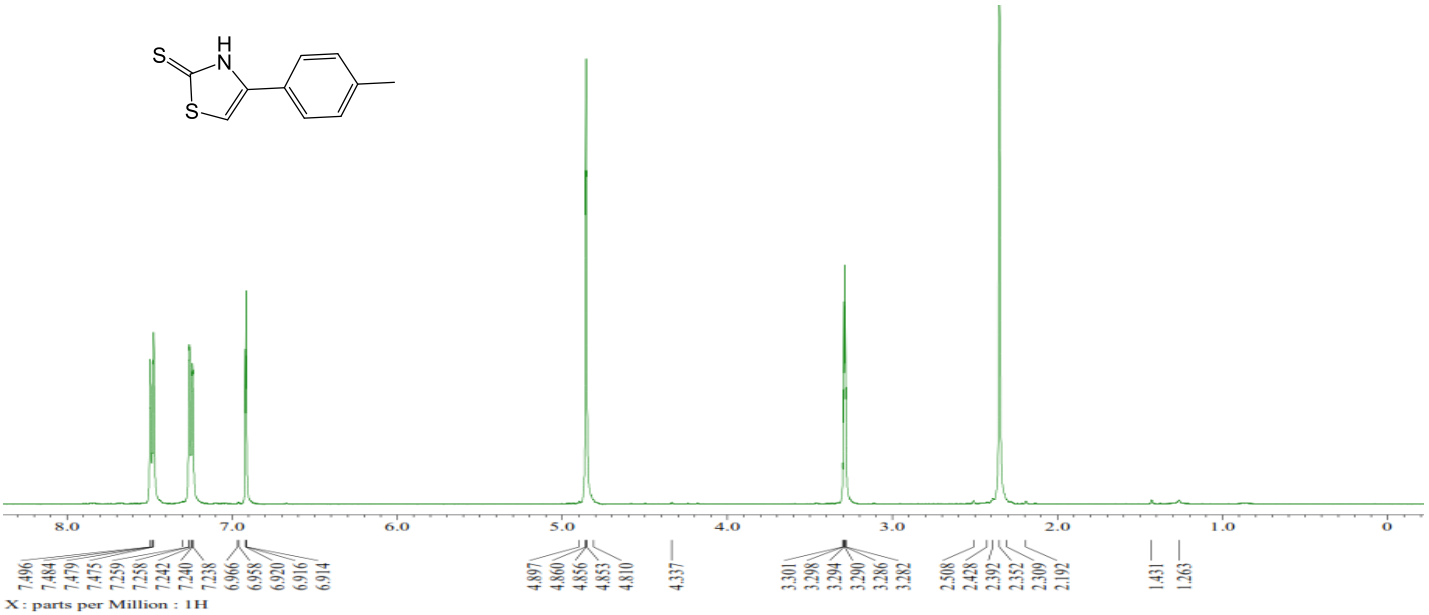
4-Phenylthiazole-2(3H)-thione (1a)



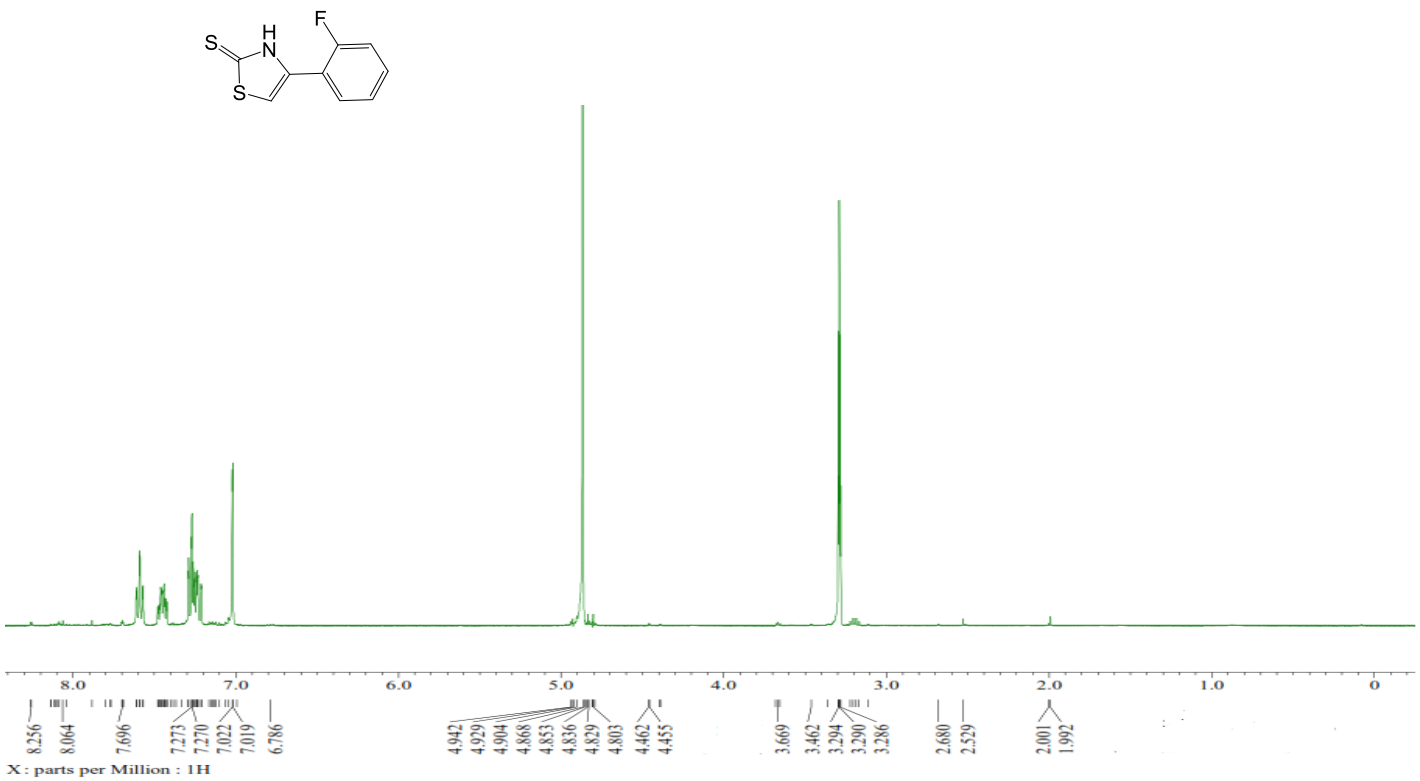
4-(4-Methoxyphenyl)thiazole-2(3H)-thione (1c)



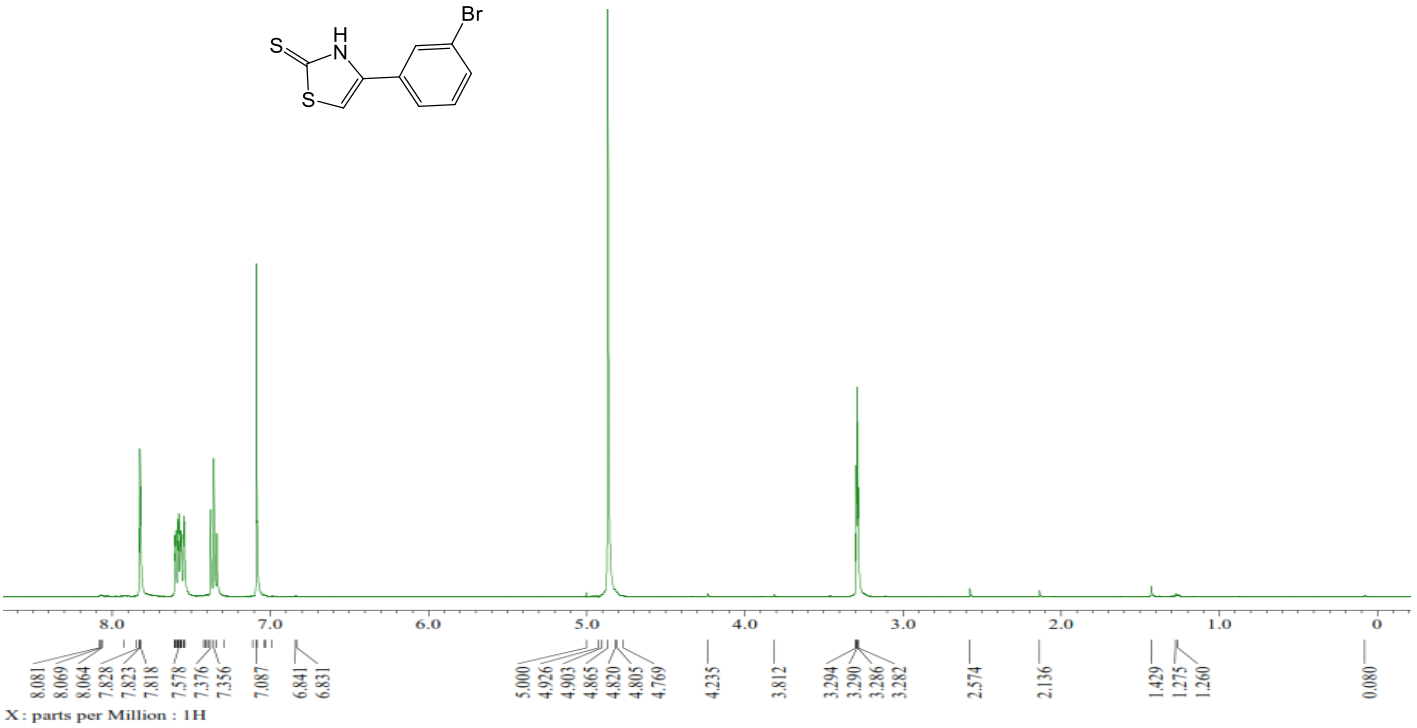
4-(*p*-Tolyl)thiazole-2(3H)-thione (1d)



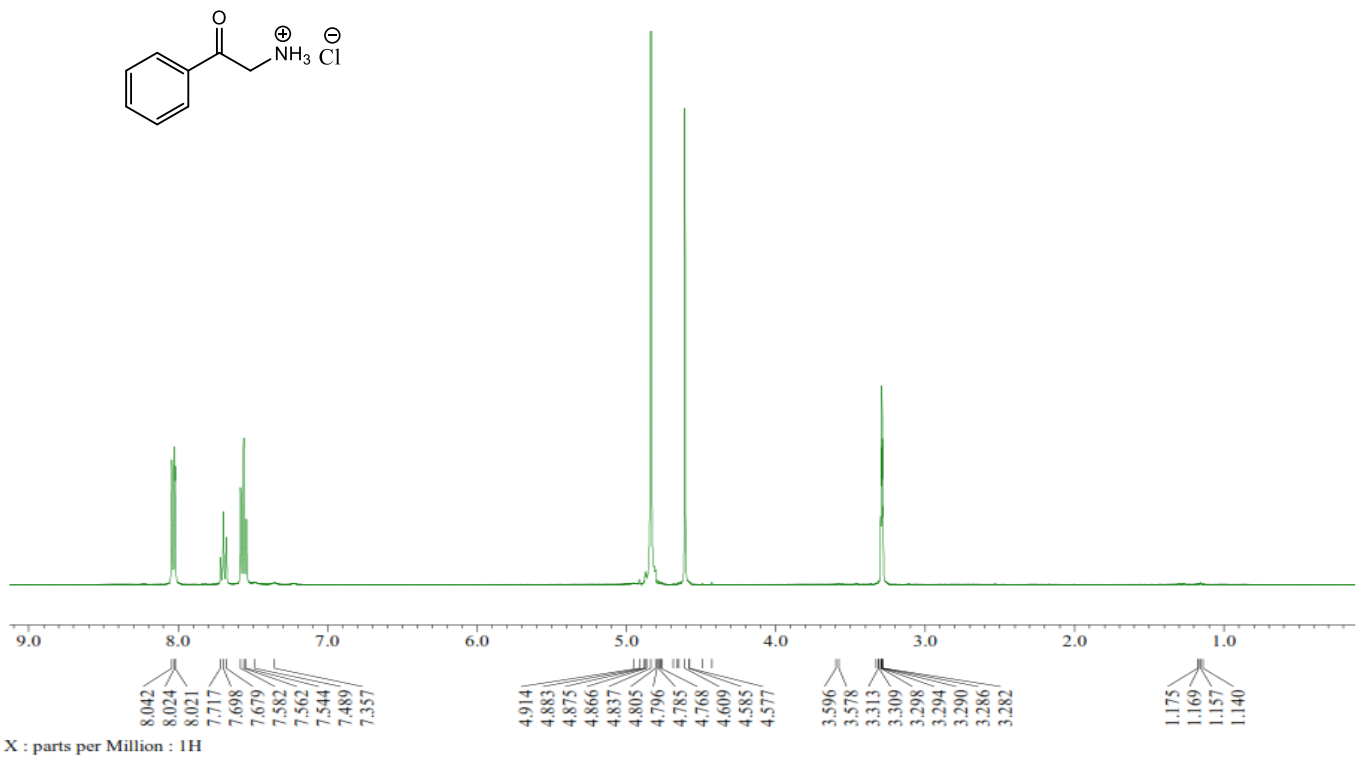
4-(2-Fluorophenyl)thiazole-2(3H)-thione (1e)



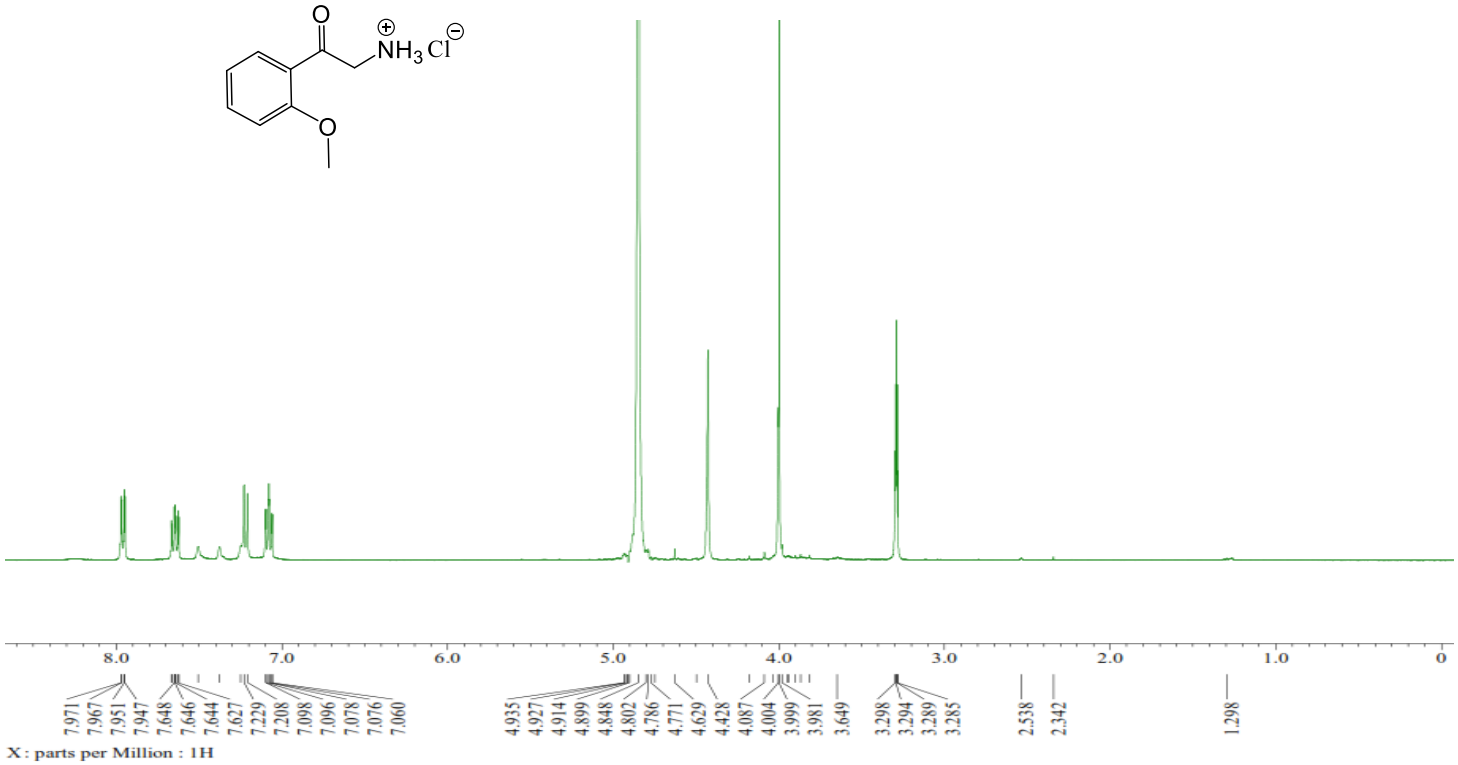
4-(3-Bromophenyl)thiazole-2(3H)-thione (1f)



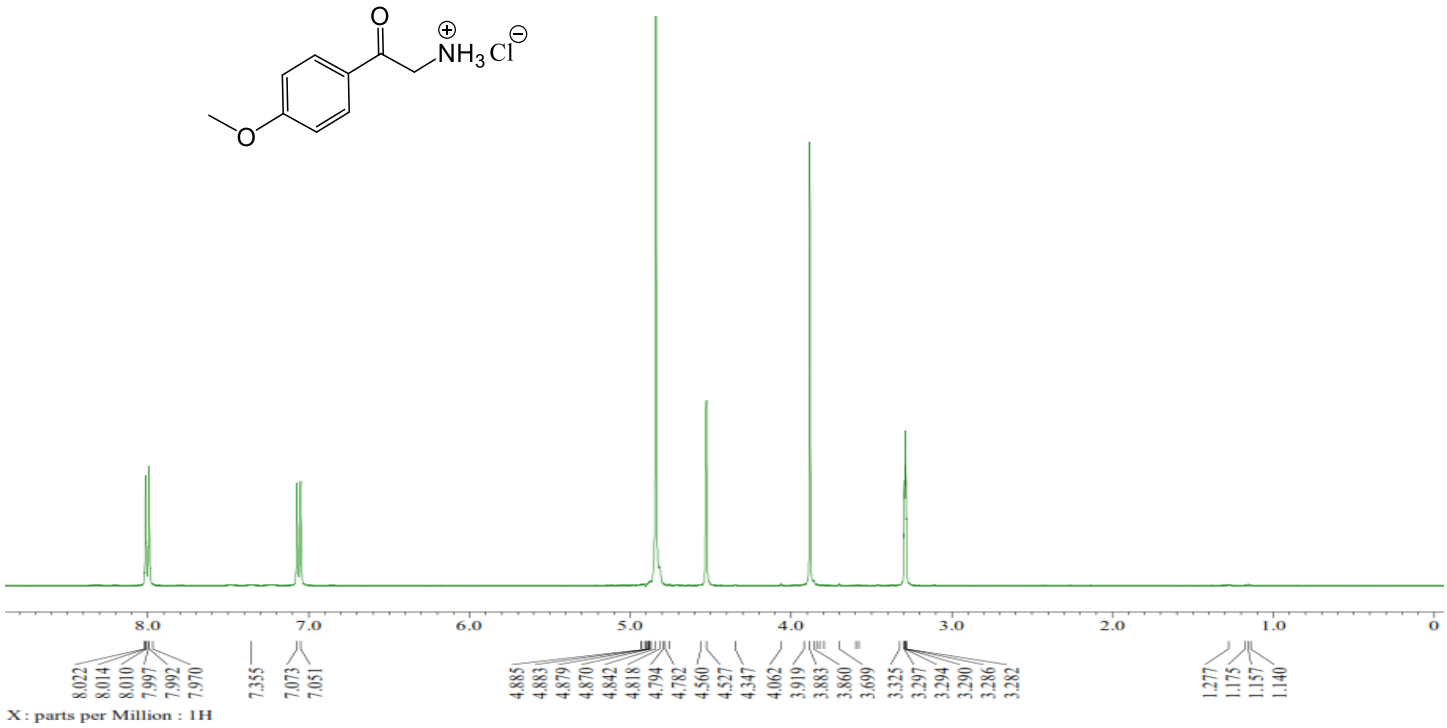
2-Phenyl-2-oxo-ethyl-ammonium chloride (8a)



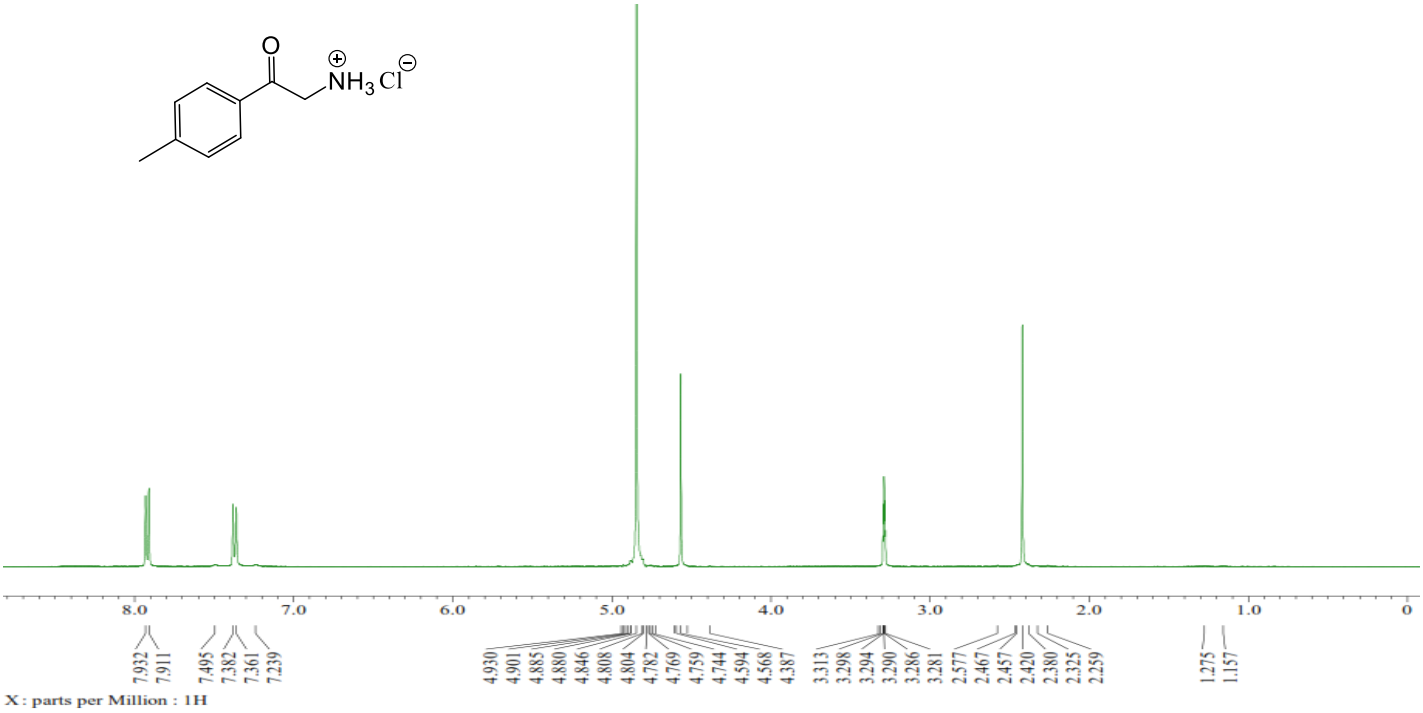
2-(2-Methoxyphenyl)-2-oxo-ethyl-ammonium chloride (8b)



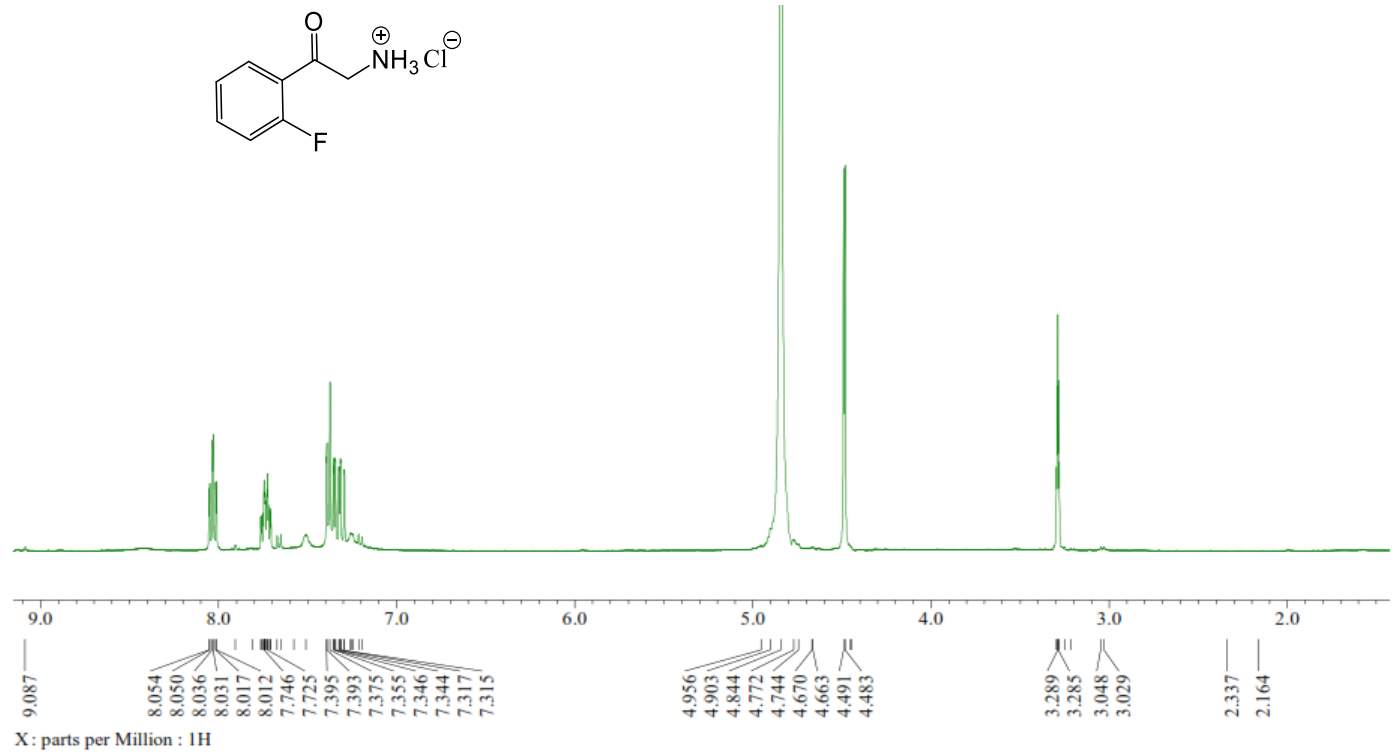
2-(4-Methoxyphenyl)-2-oxo-ethyl-ammonium chloride (8c)



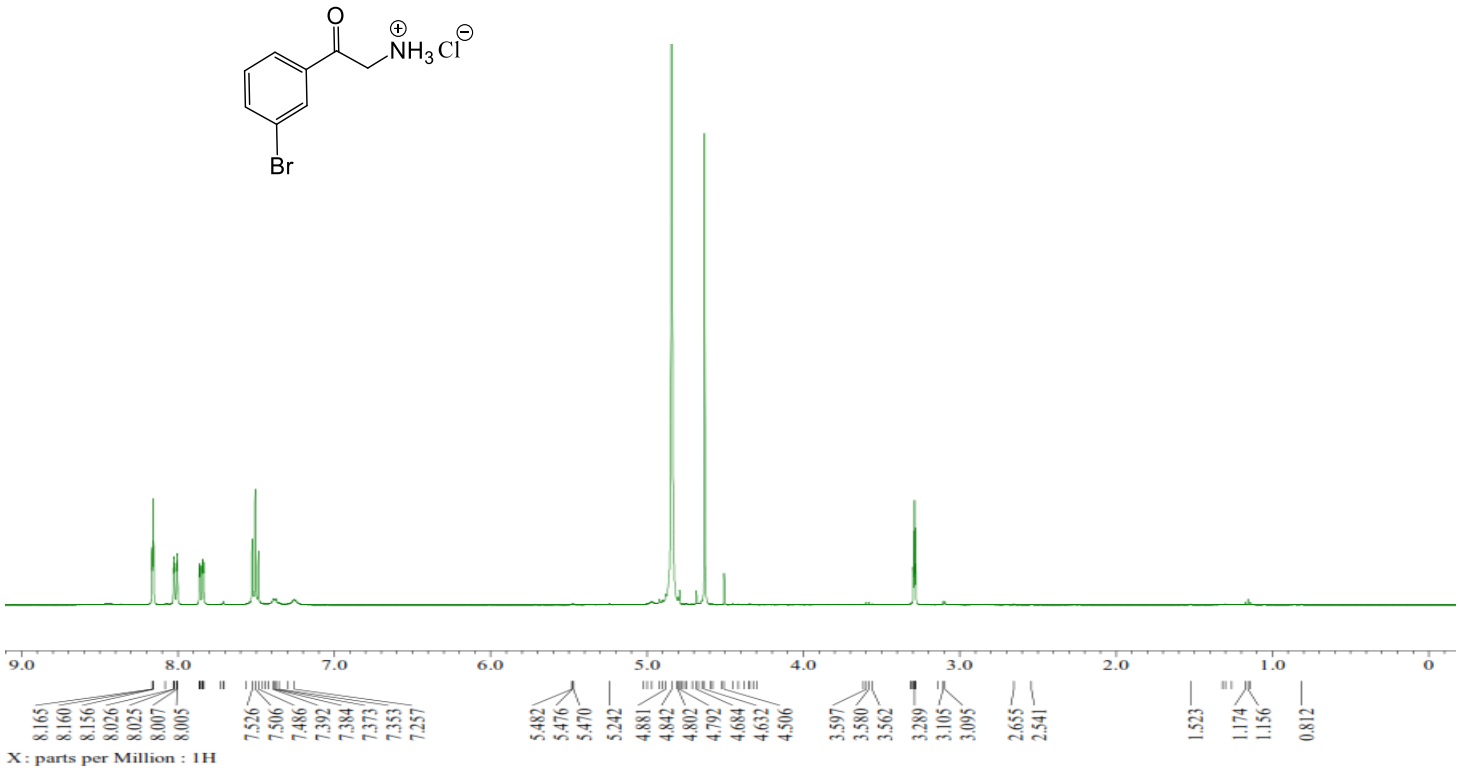
2-(*p*-Tolyl)-2-oxo-ethyl-ammonium chloride (8d)



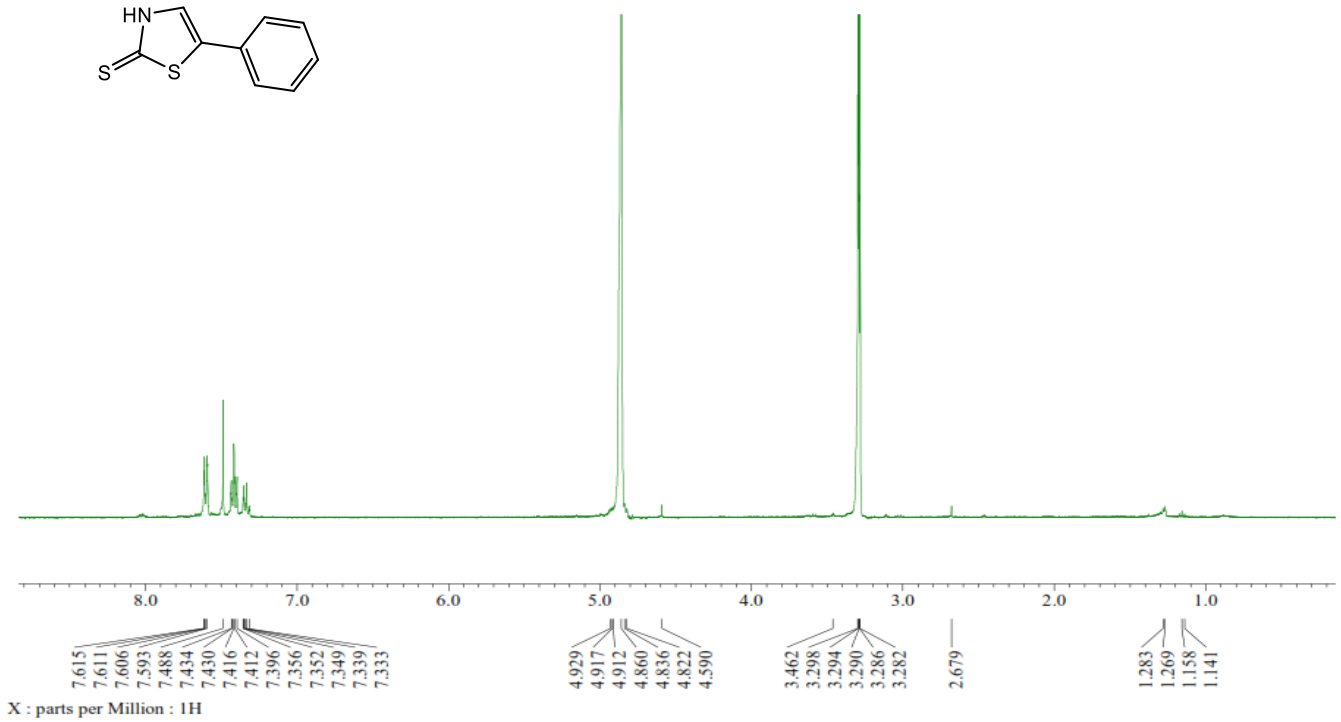
2-(2-Fluorophenyl)-2-oxo-ethyl-ammonium chloride (8e)



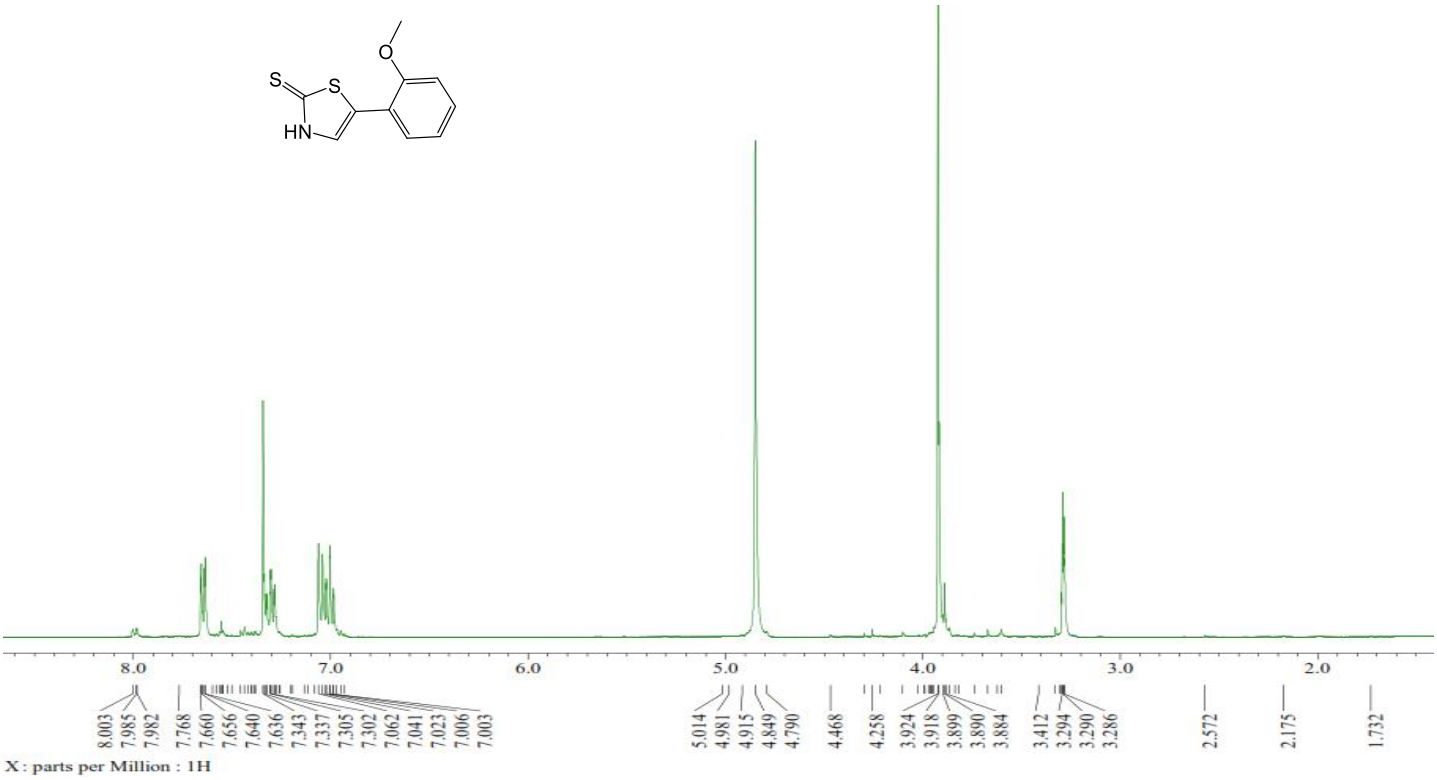
2-(3-Bromophenyl)-2-oxo-ethyl-ammonium chloride (8f)



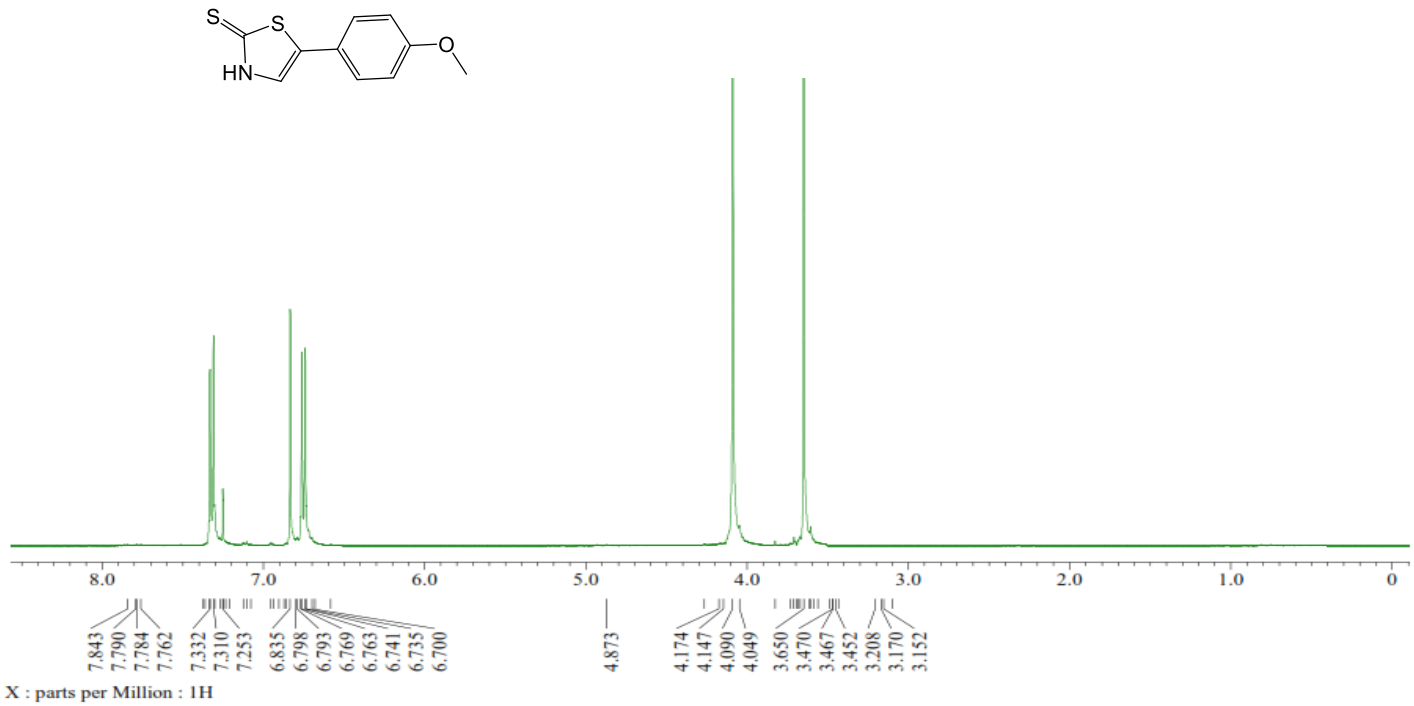
5-Phenylthiazole-2(3H)-thione (7a)



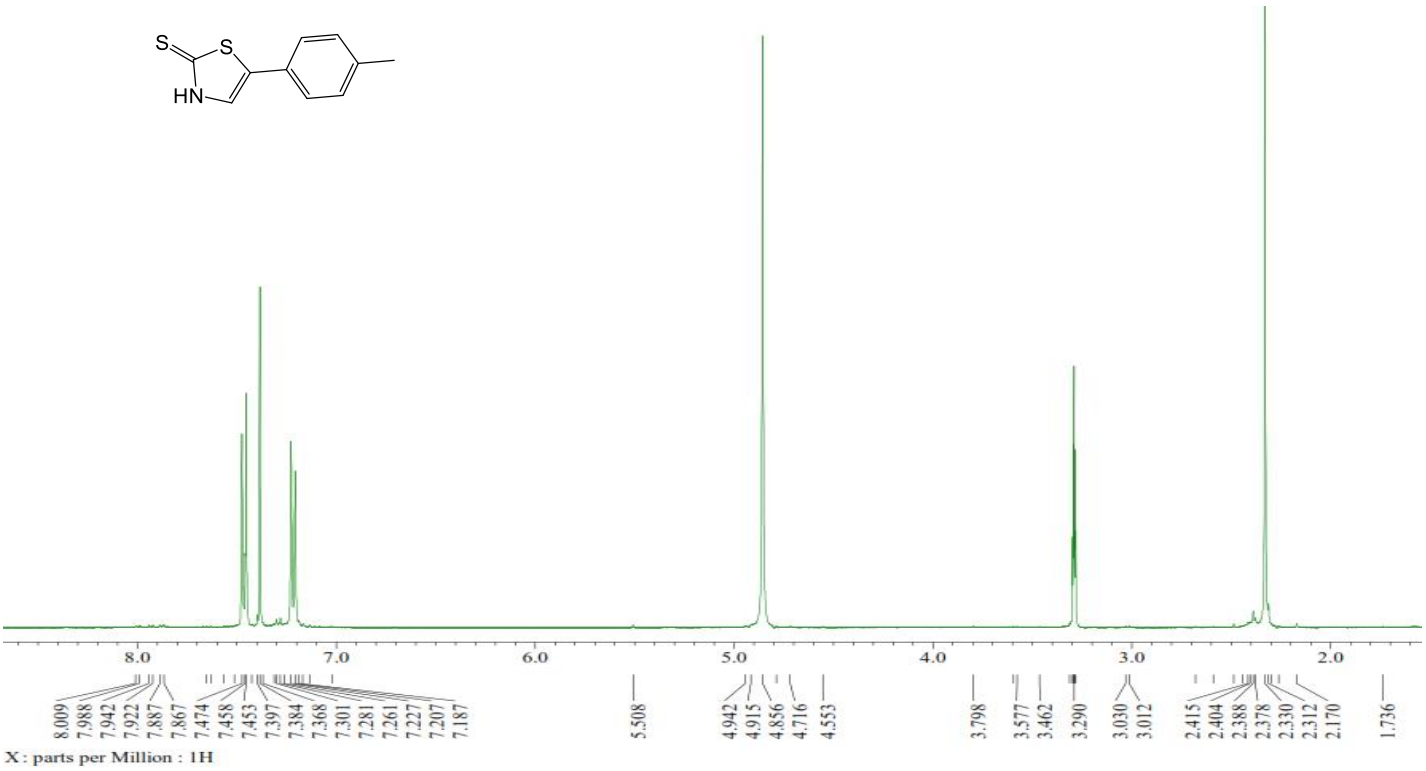
5-(2-Methoxyphenyl)thiazole-2(3H)-thione (7b)



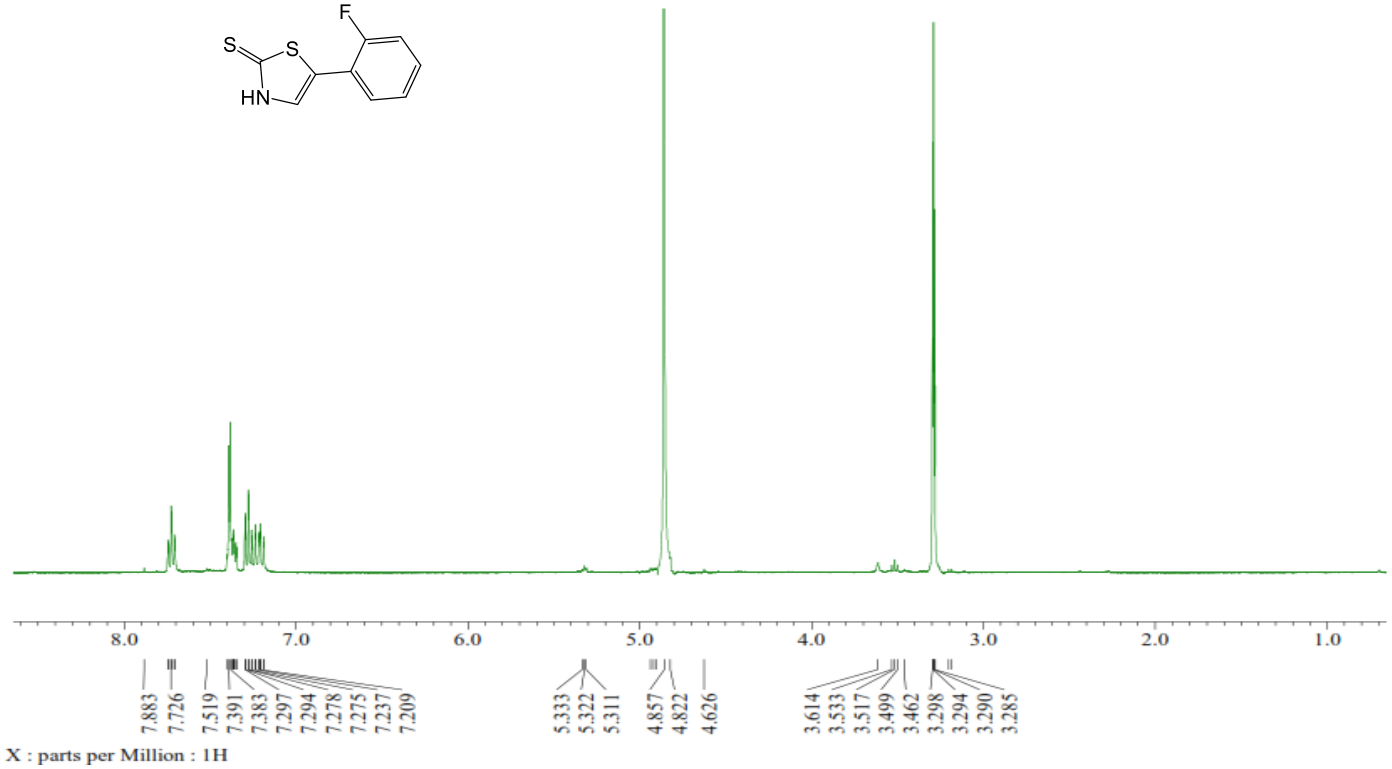
5-(4-Methoxyphenyl)thiazole-2(3H)-thione (7c)



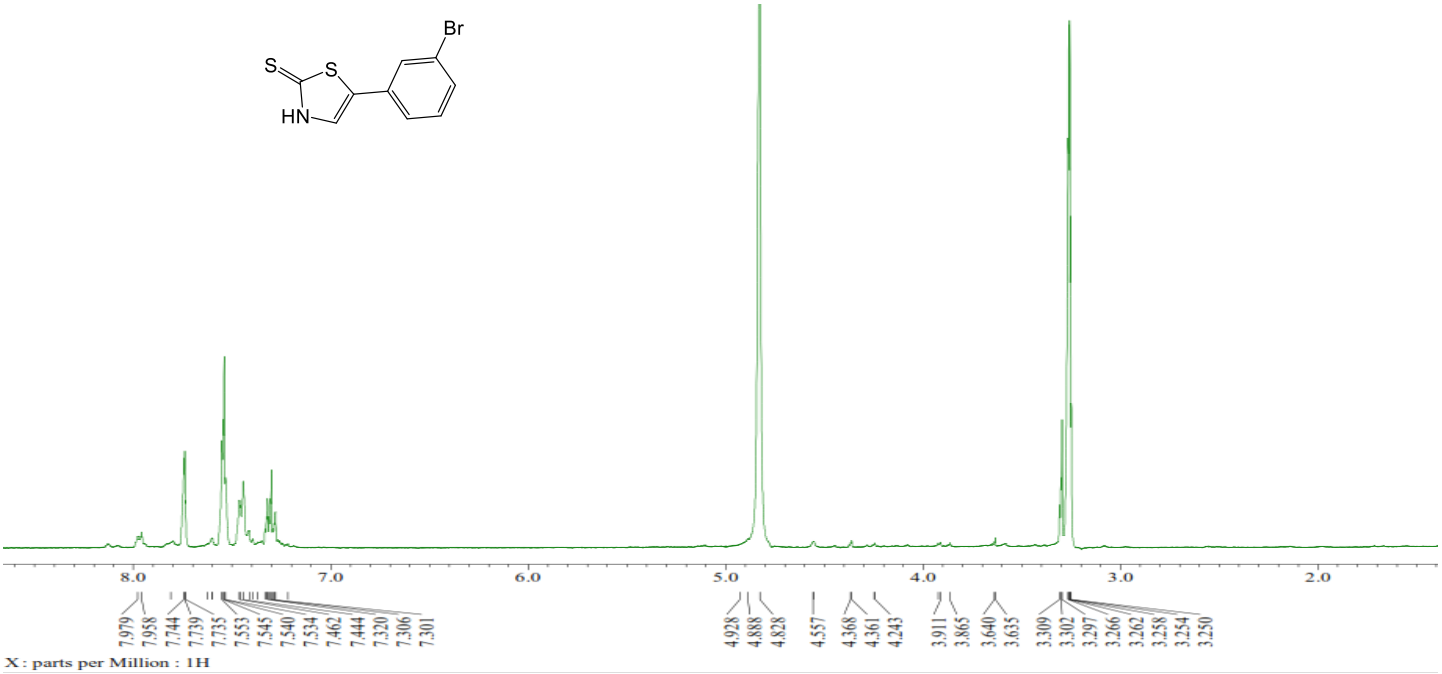
5-(*p*-Tolyl)thiazole-2(3H)-thione (7d)



5-(2-Fluorophenyl)thiazole-2(3H)-thione (7e)

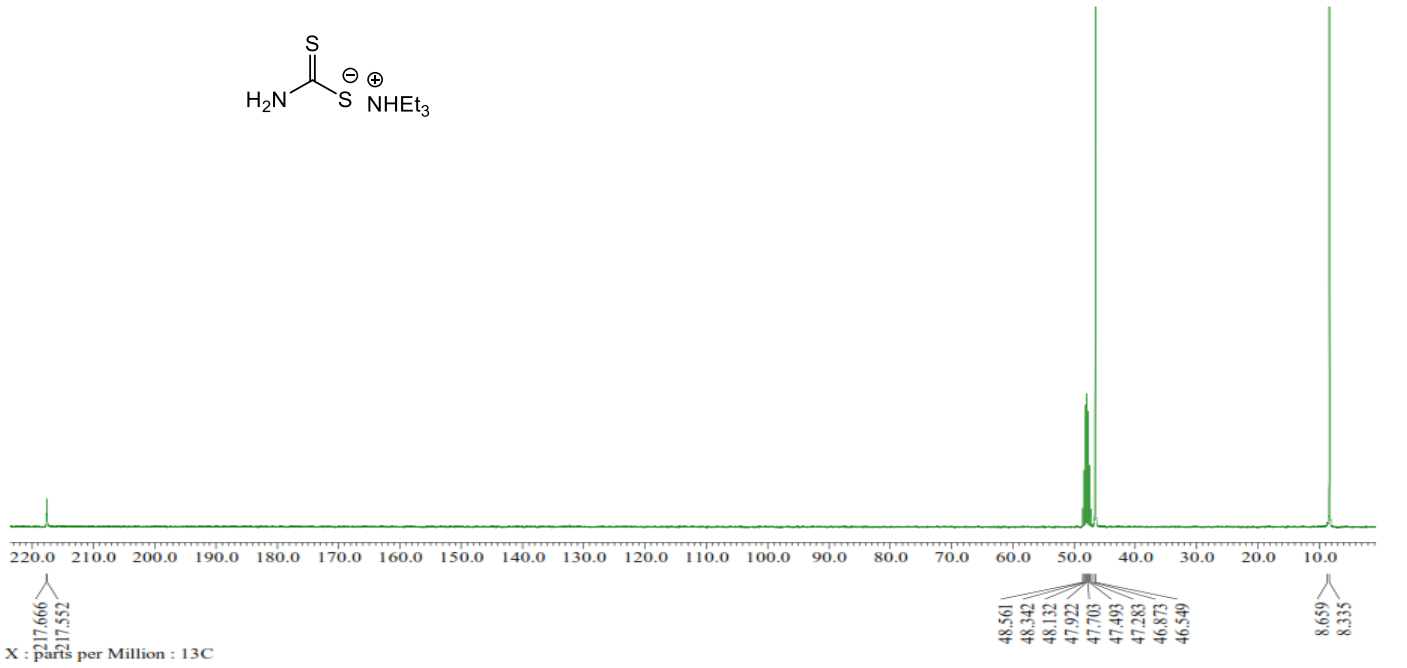


5-(3-Bromophenyl)thiazole-2(3H)-thione (7f)

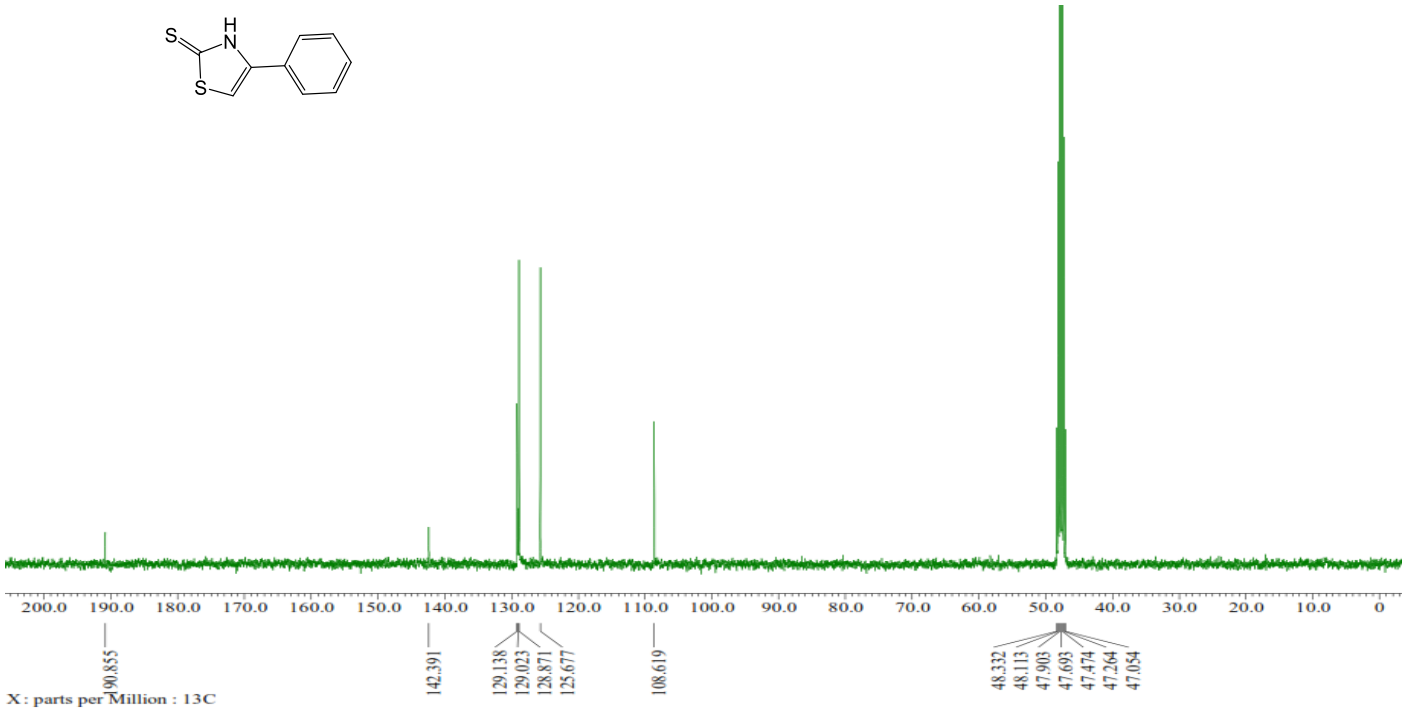


^{13}C-NMR spectra of compounds synthesized:

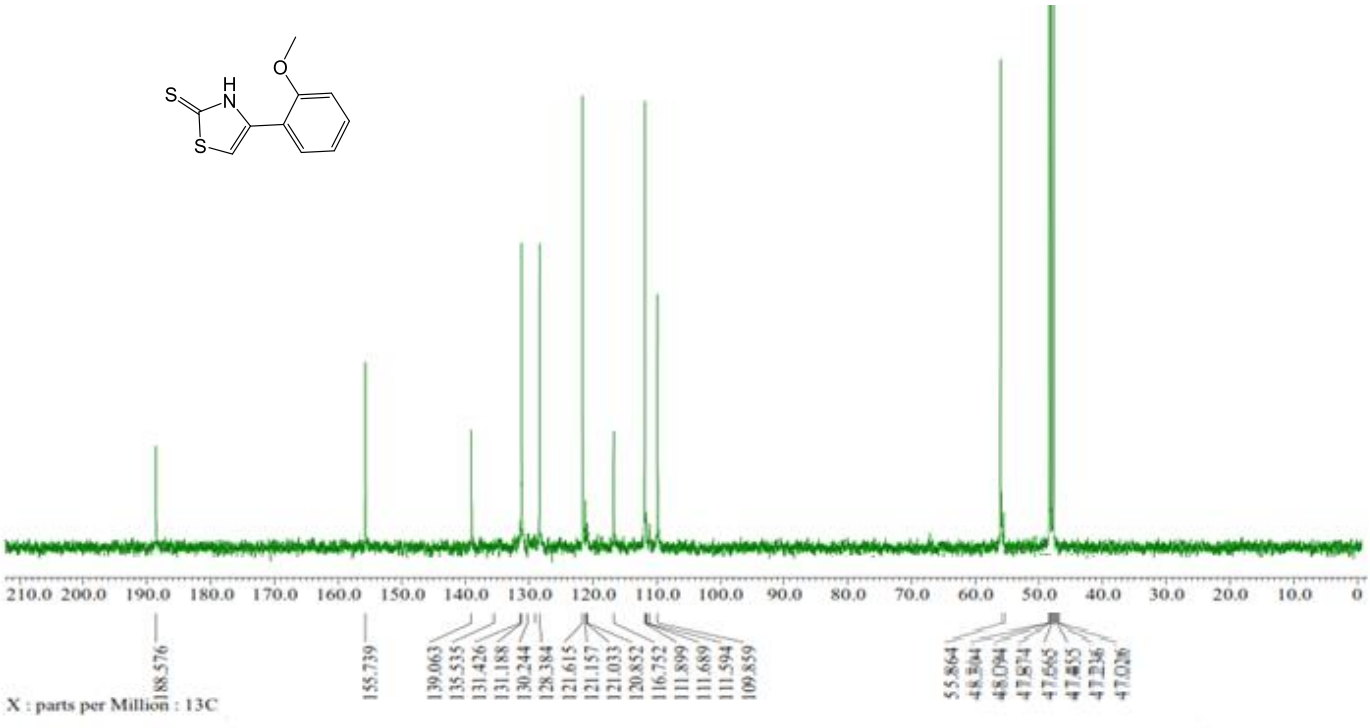
Triethylammonium dithiocarbamate (5)



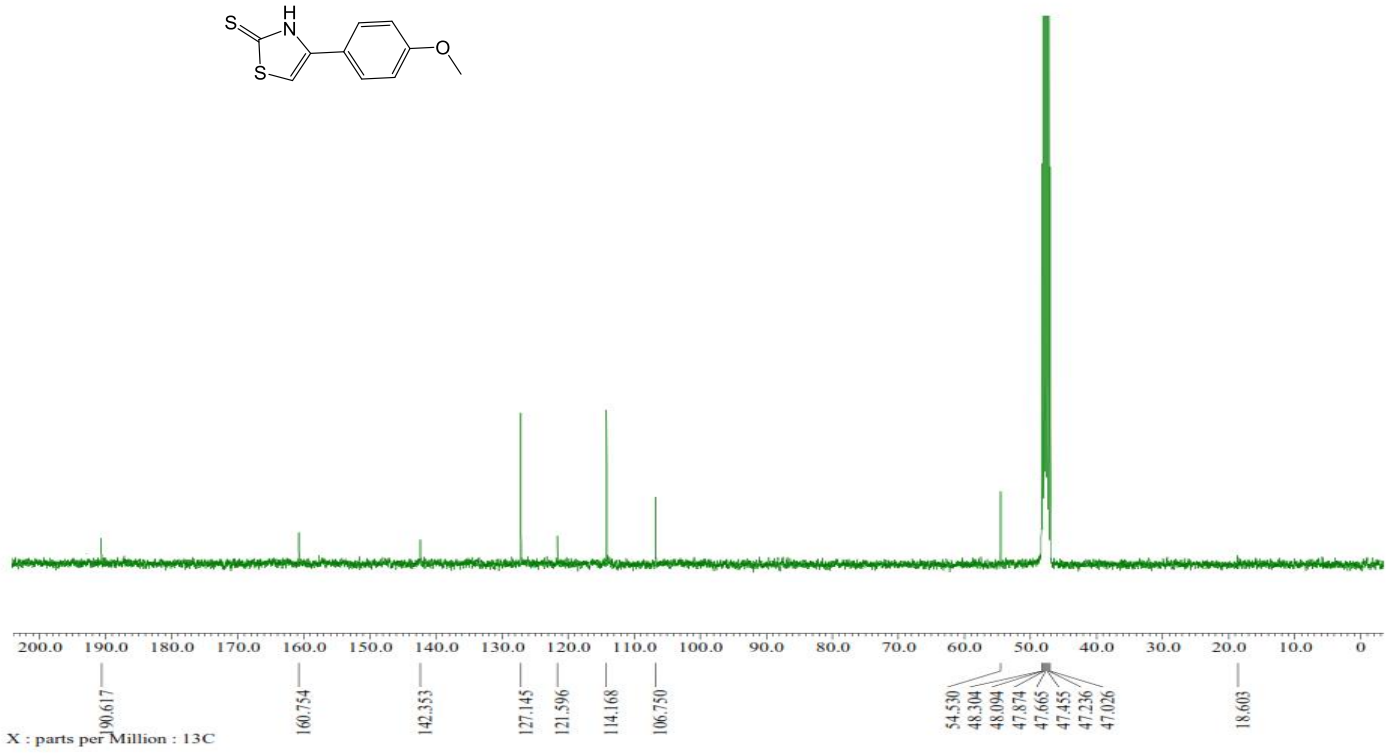
4-Phenylthiazole-2(3H)-thione (1a)



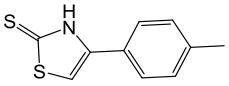
4-(2-Methoxyphenyl)thiazole-2(3H)-thione (1b)



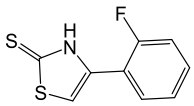
4-(4-Methoxyphenyl)thiazole-2(3H)-thione (1c)



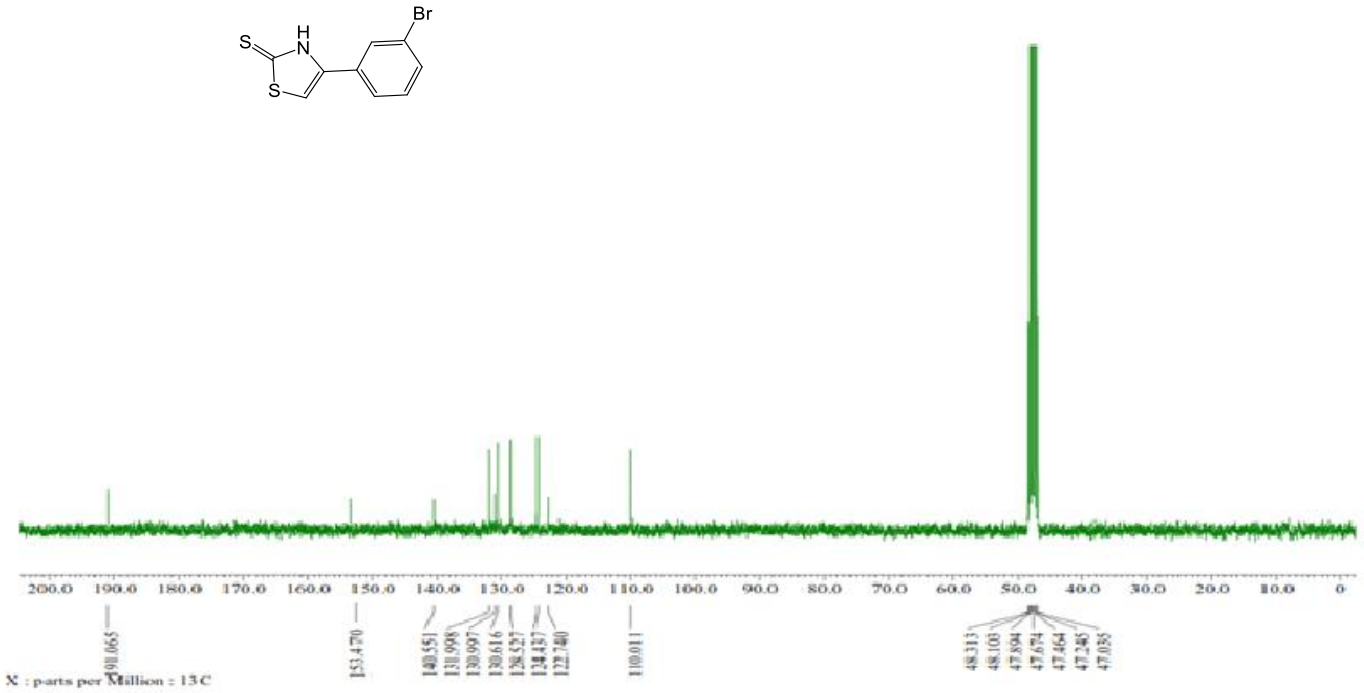
4-(*p*-Tolyl)thiazole-2(3H)-thione (1d)



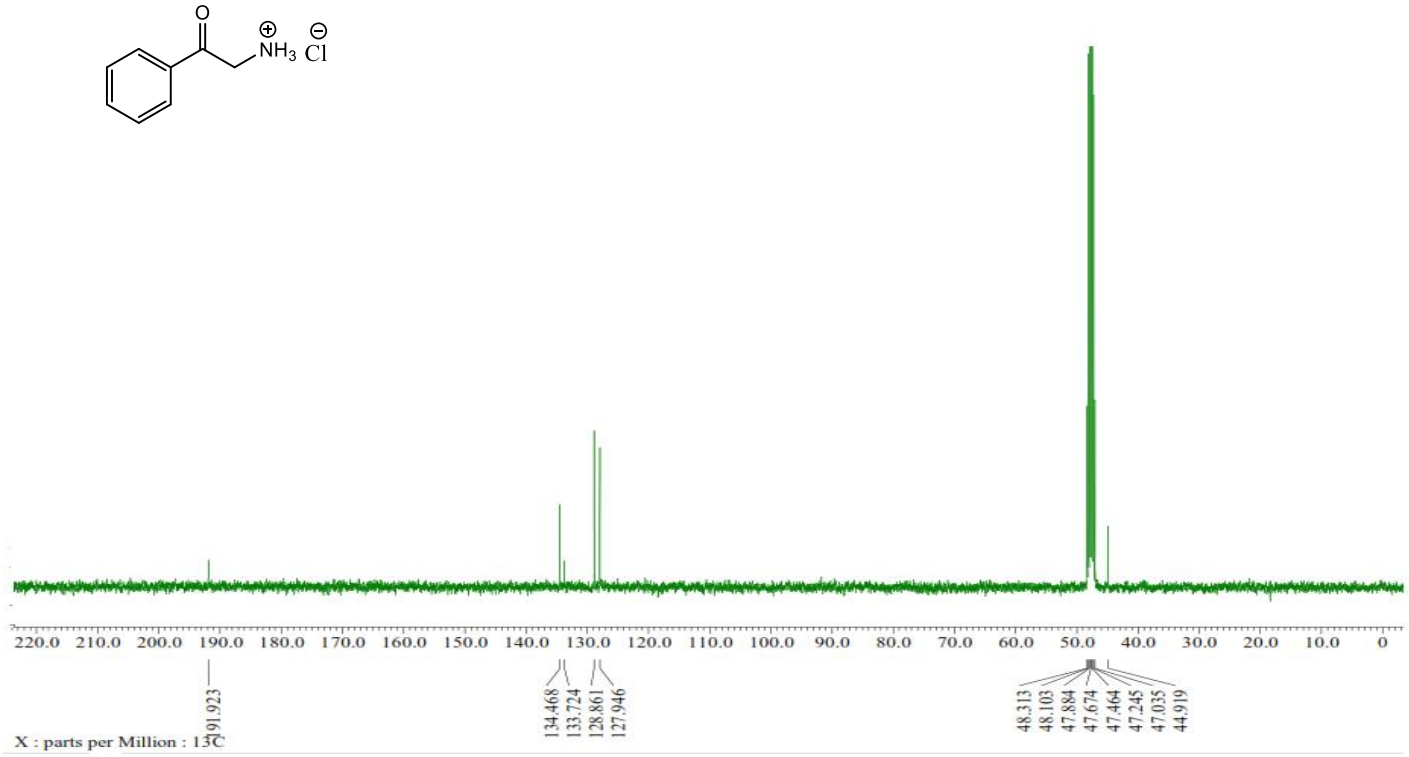
4-(2-Fluorophenyl)thiazole-2(3H)-thione (1e)



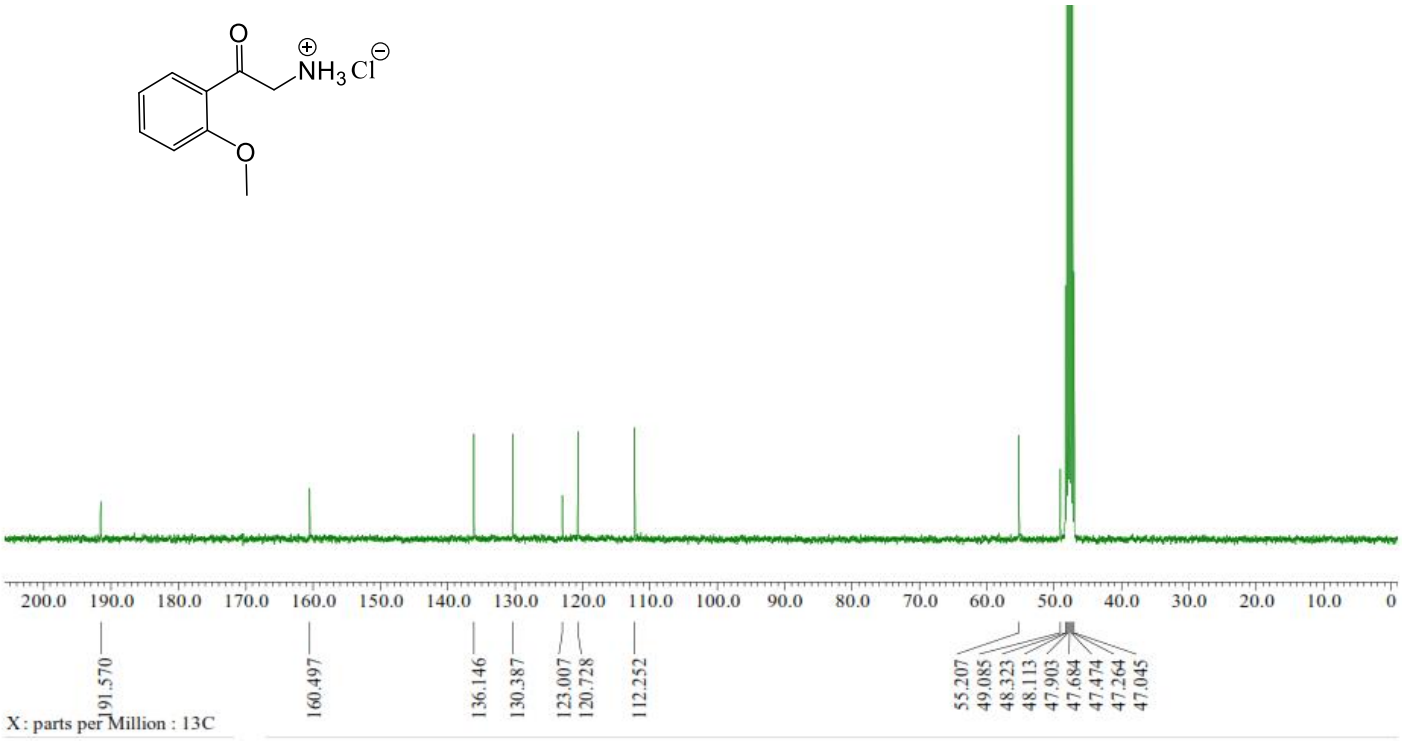
4-(3-Bromophenyl)thiazole-2(3H)-thione (1f)



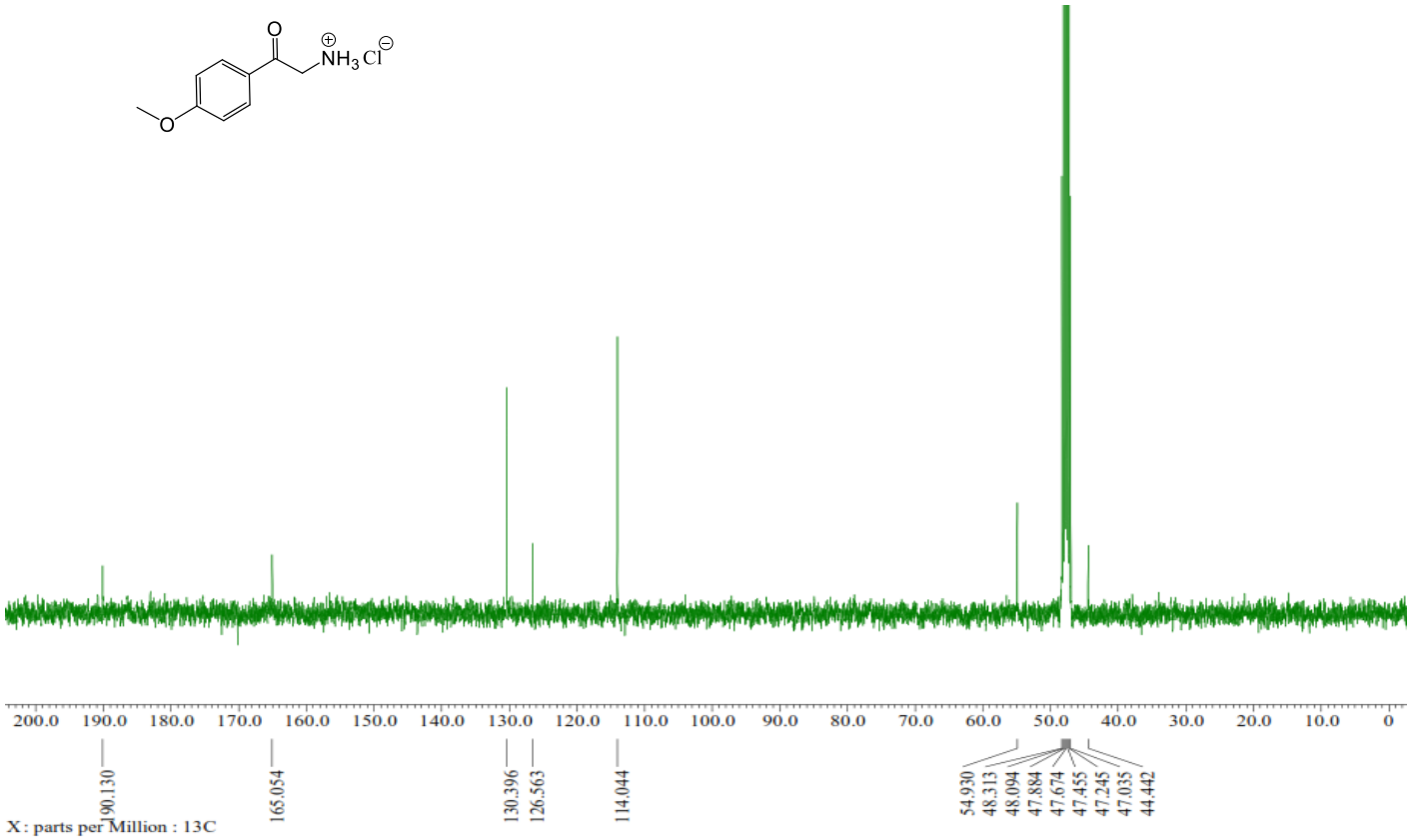
2-Phenyl-2-oxo-ethyl-ammonium chloride (8a)



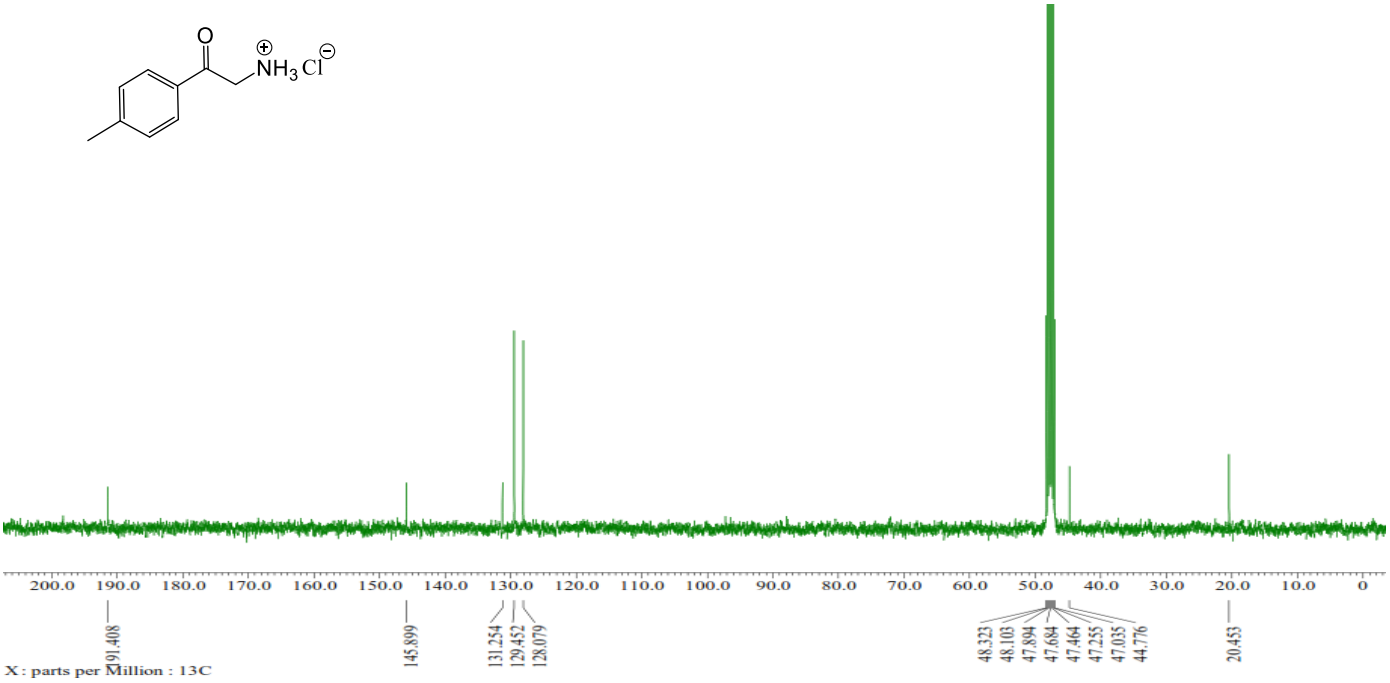
2-(2-Methoxyphenyl)-2-oxo-ethyl-ammonium chloride (8b)



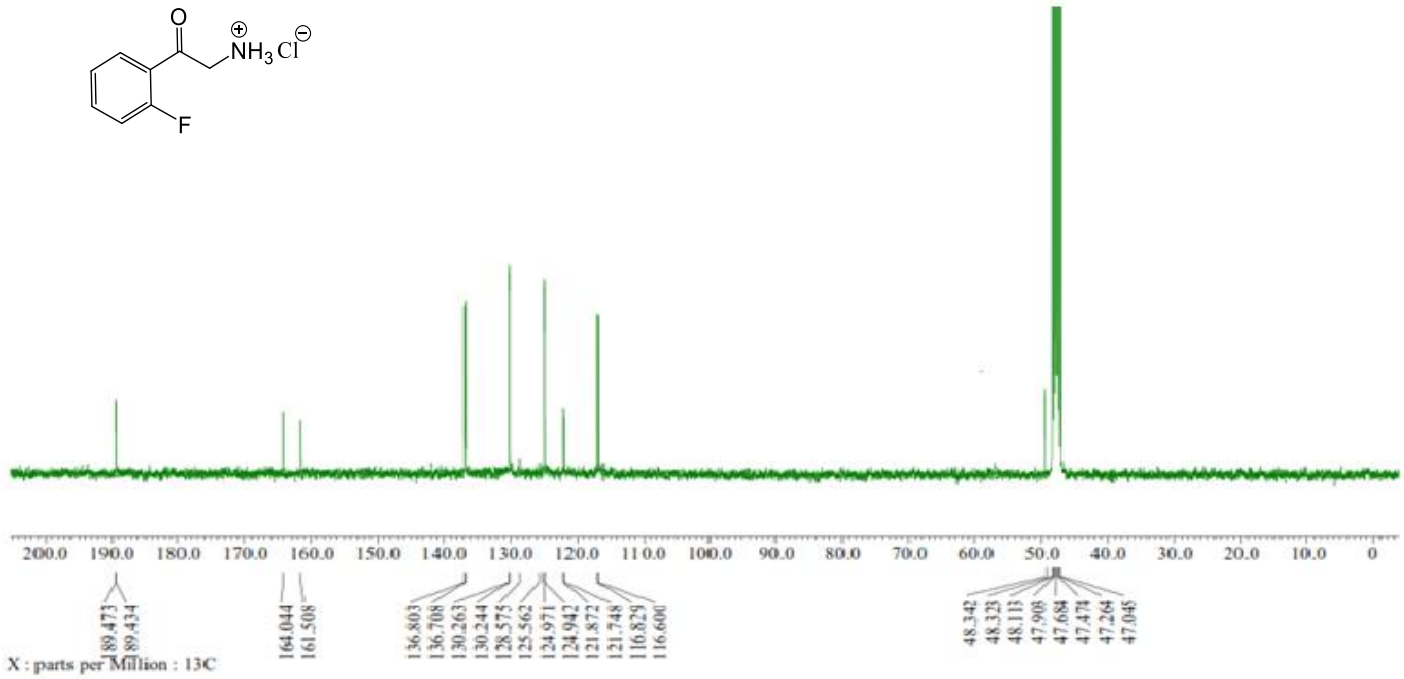
2-(4-Methoxyphenyl)-2-oxo-ethyl-ammonium chloride (8c)



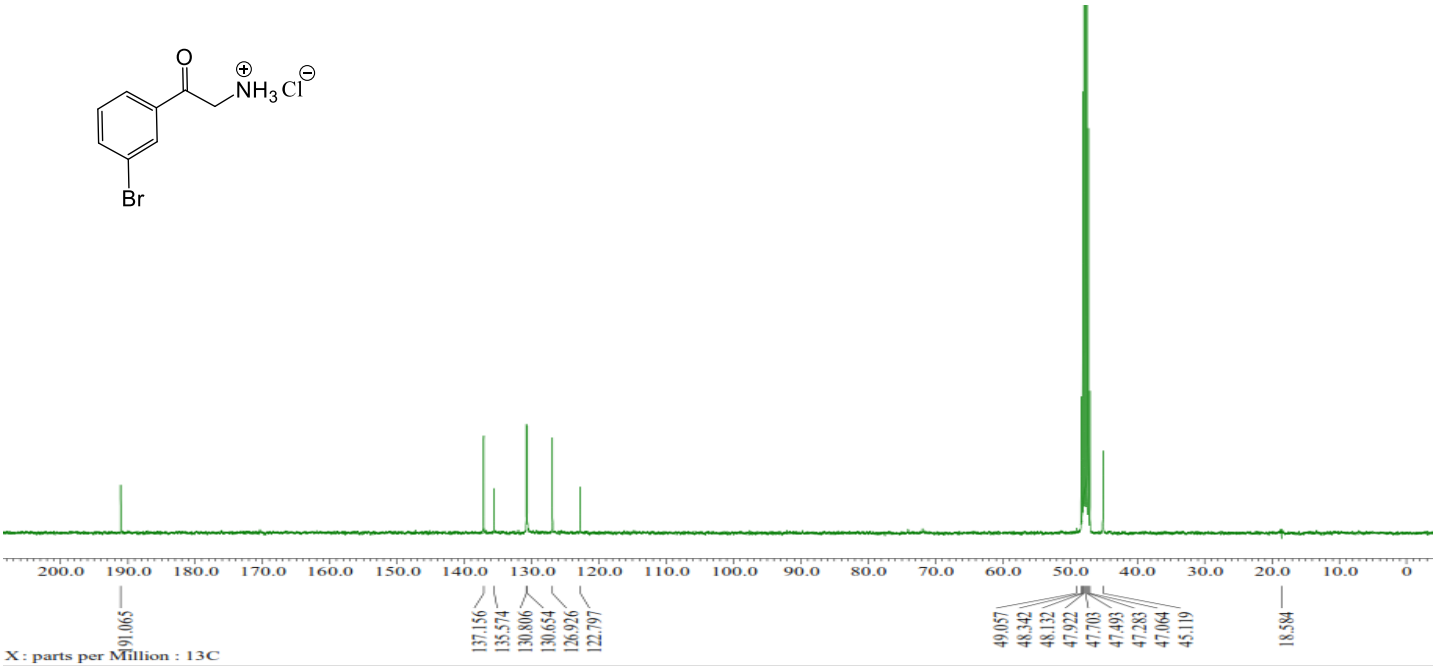
2-(*p*-Tolyl)-2-oxo-ethyl-ammonium chloride (8d)



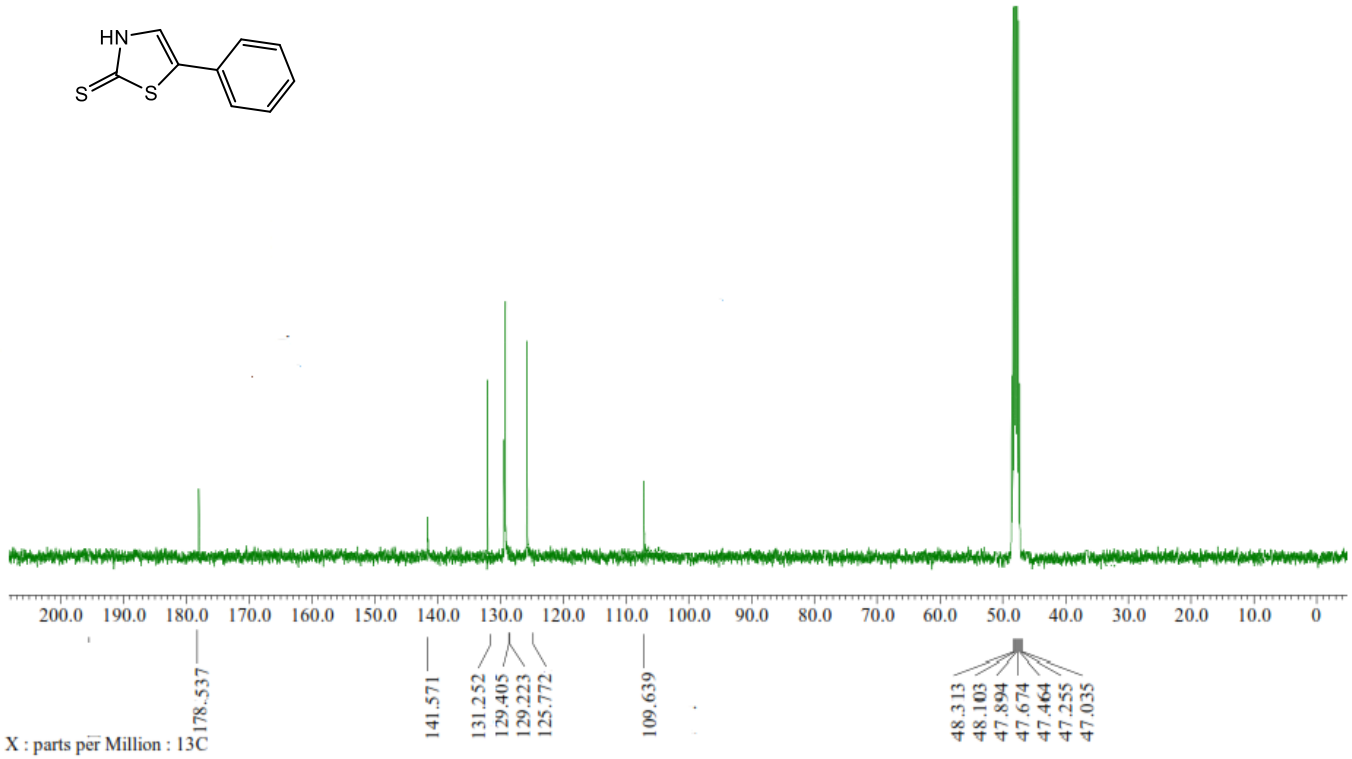
2-(2-Fluorophenyl)-2-oxo-ethyl-ammonium chloride (8e)



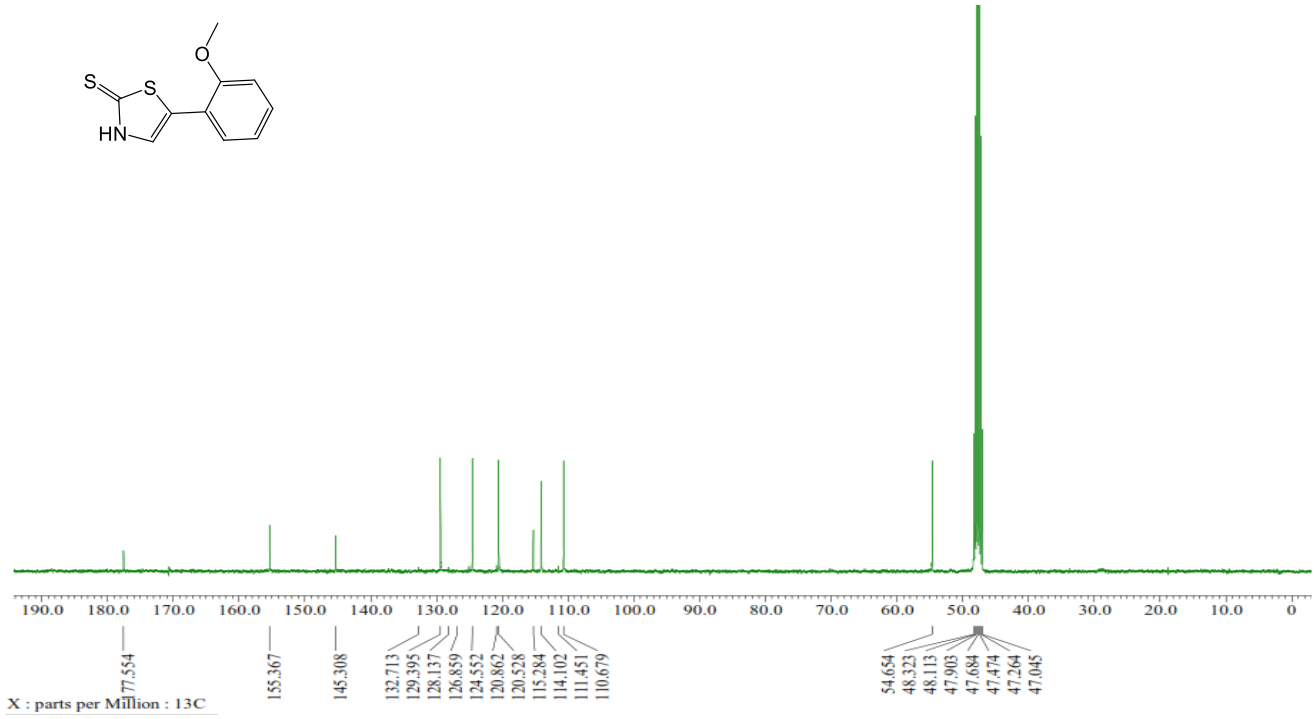
2-(3-Bromophenyl)-2-oxo-ethyl-ammonium chloride (8f)



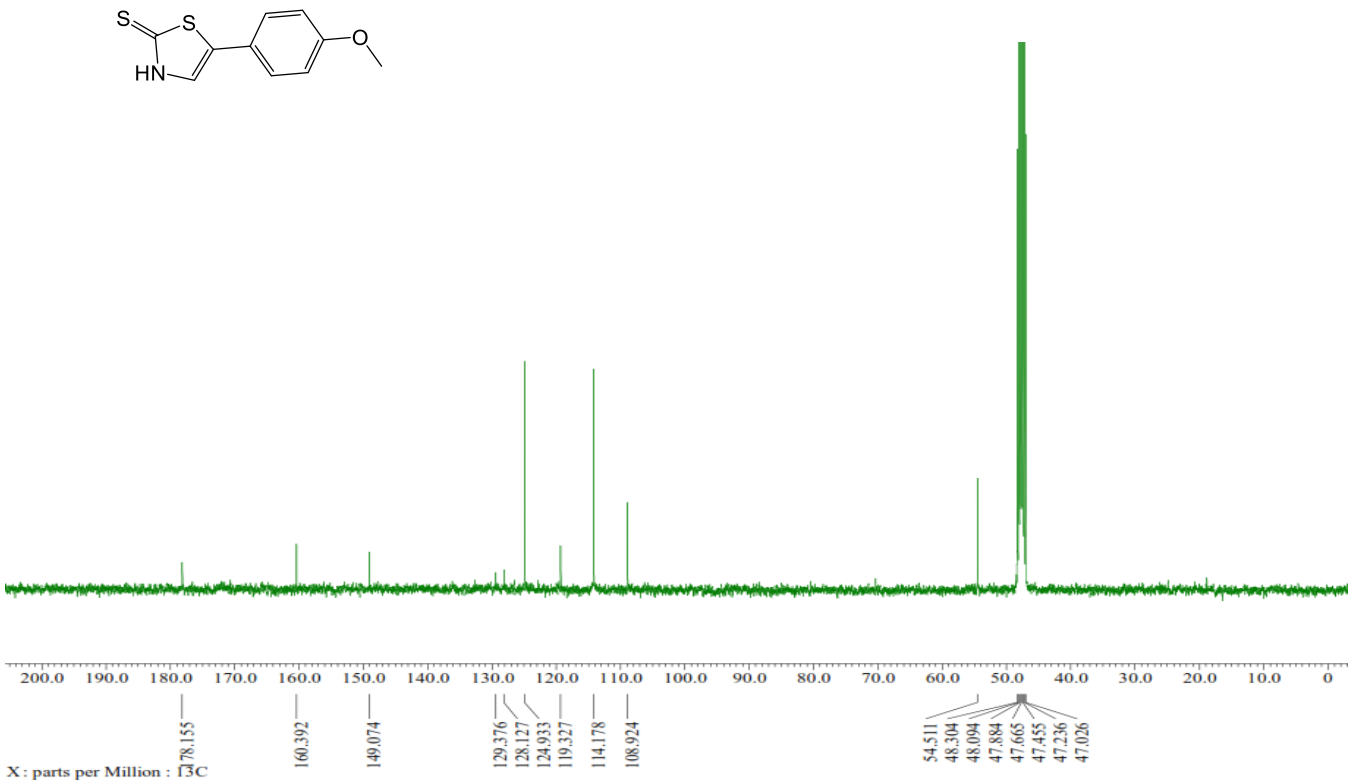
5-Phenylthiazole-2(3H)-thione (7a)



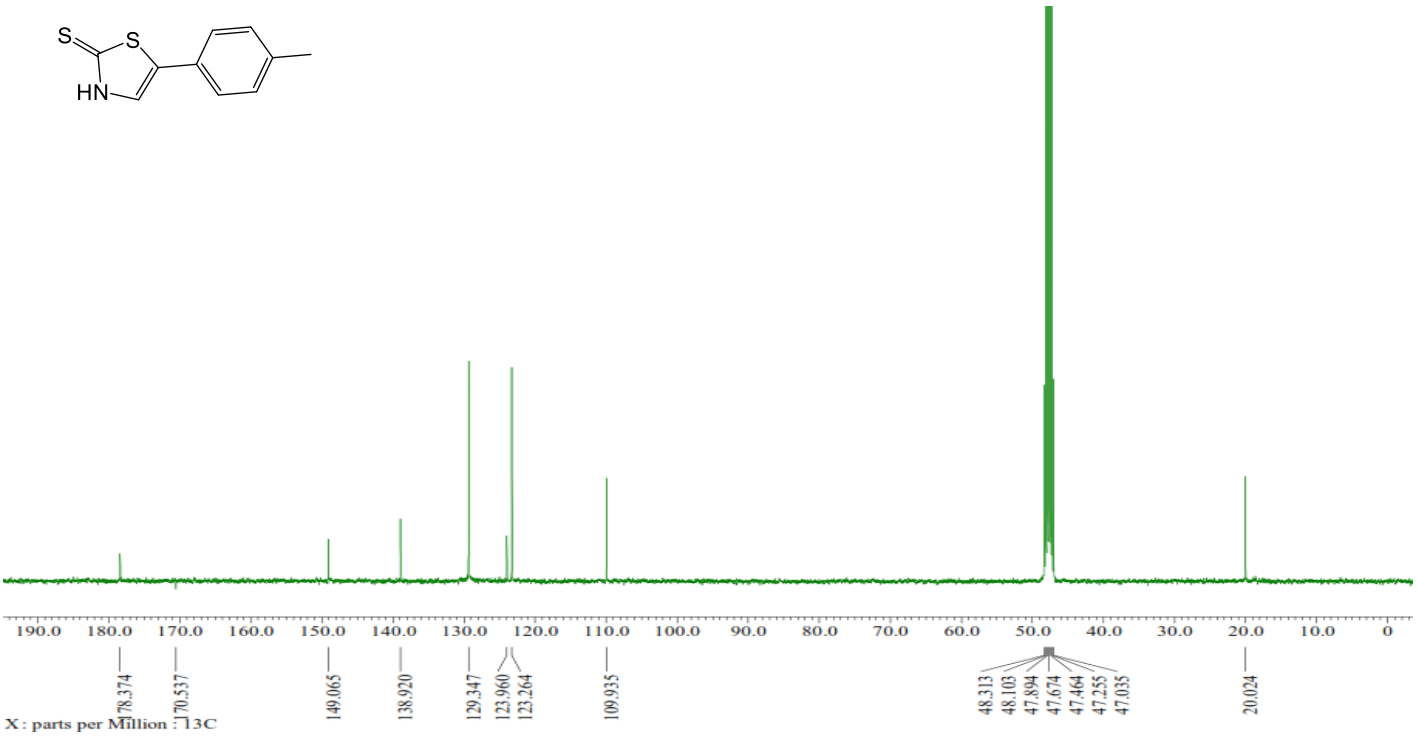
5-(2-Methoxyphenyl)thiazole-2(3H)-thione (7b)



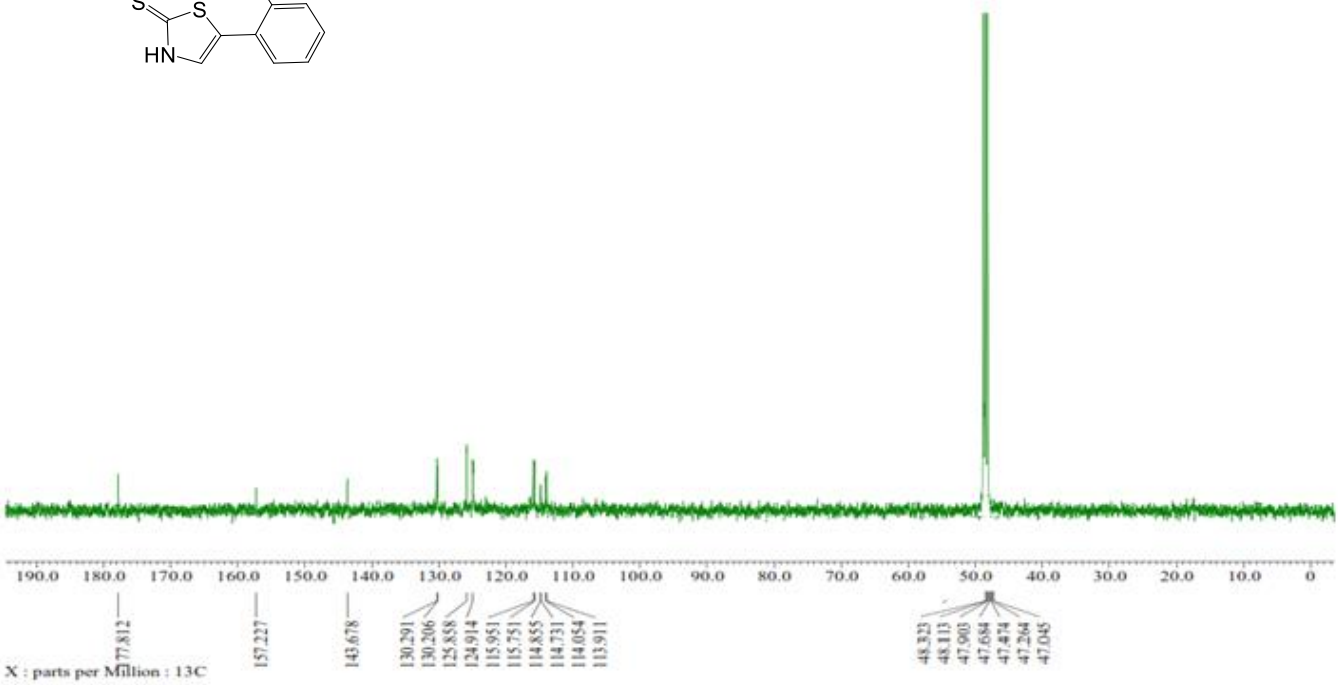
5-(4-Methoxyphenyl)thiazole-2(3H)-thione (7c)



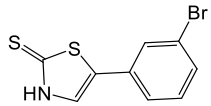
5-(*p*-Tolyl)thiazole-2(3H)-thione (7d)

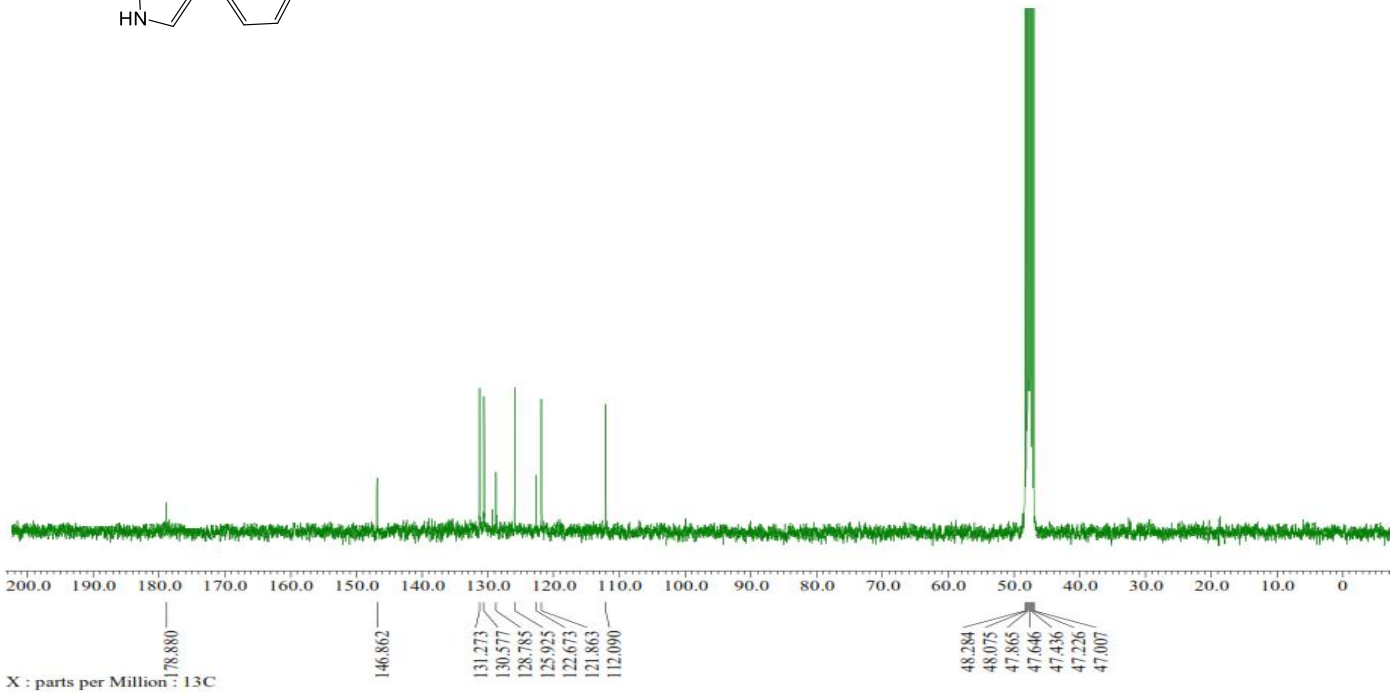


5-(2-Fluorophenyl)thiazole-2(3H)-thione (7e)



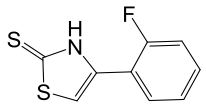
5-(3-Bromophenyl)thiazole-2(3H)-thione (7f)

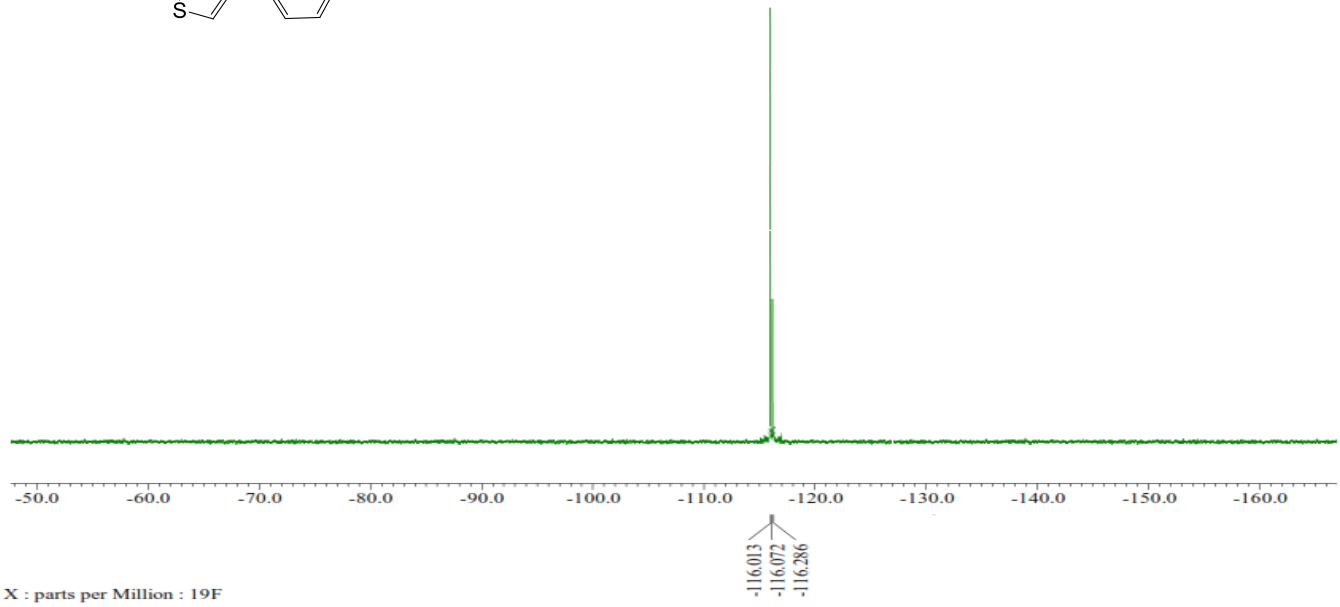




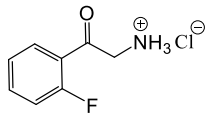
^{19}F-NMR spectra of compounds synthesized:

4-(2-Fluorophenyl)thiazole-2(3H)-thione (1e)

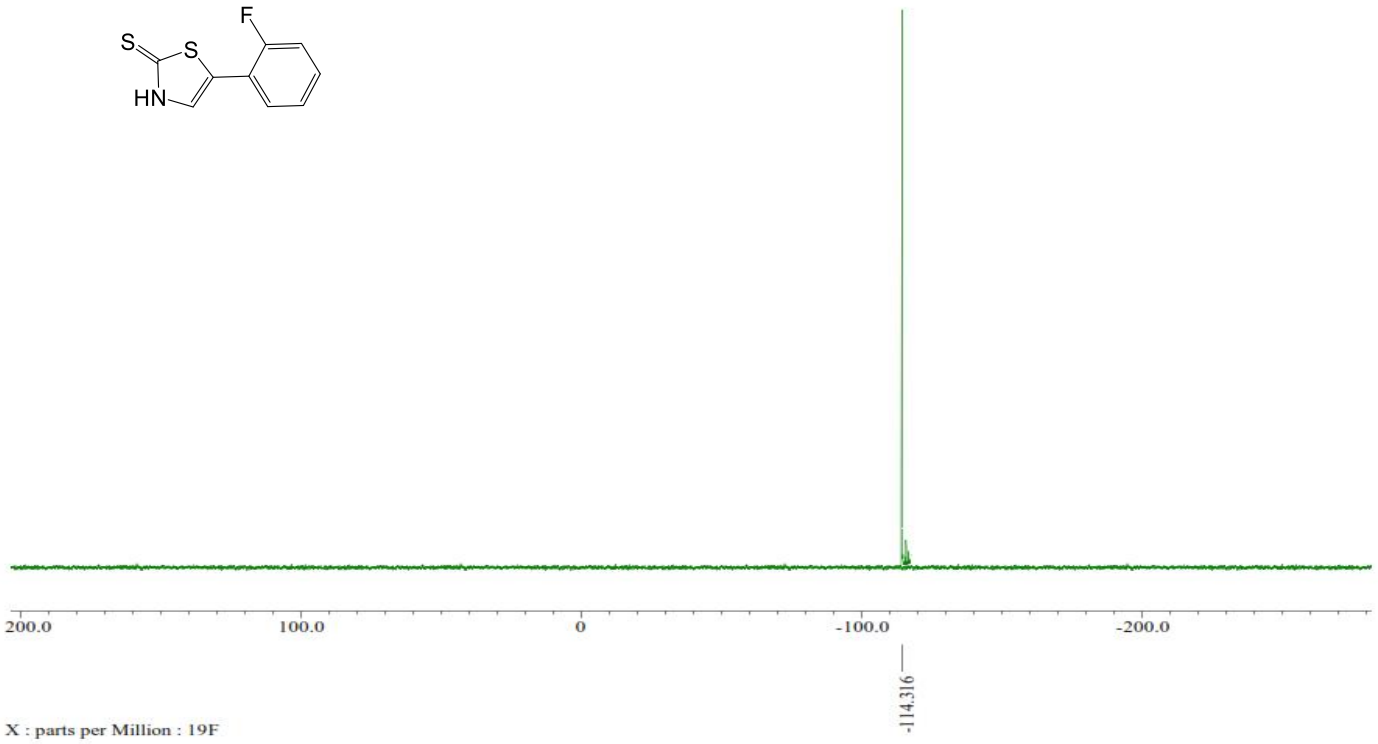




2-(2-Fluorophenyl)-2-oxo-ethyl-ammonium chloride (8e)



5-(2-Fluorophenyl)thiazole-2(3H)-thione (7e)



General considerations for calculations:

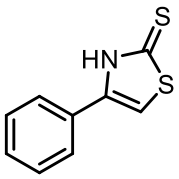
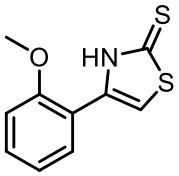
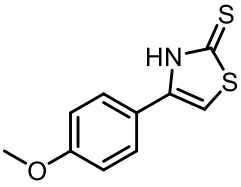
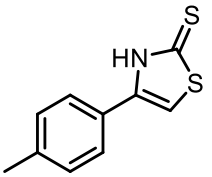
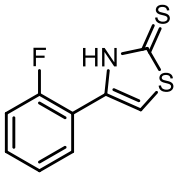
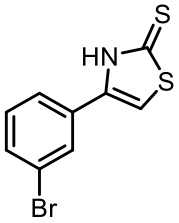
Calculations were performed using Gaussian 09.[1] All optimized geometries were calculated using PBEPBE,[2] an exchange correlation functional, with the 6-311g(d,p) level of theory.[3,4,5] Stationary points were characterized by frequency calculations at 298 K, with structures at energy minima showing no negative frequencies. Electronic energies are obtained by the sum of electronic and zero-point energies. The zero-point energy correction factor was obtained using frequency analysis. All energy values shown is this supporting information are in Hartrees.

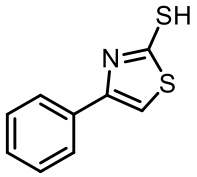
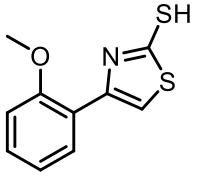
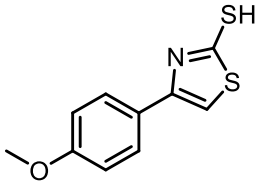
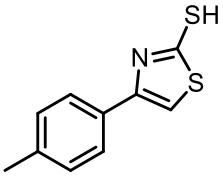
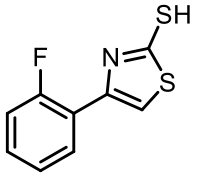
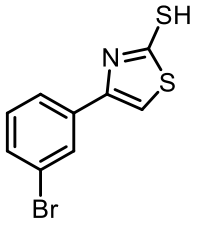
Complete Citation for Gaussian 09:

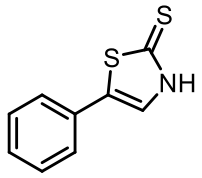
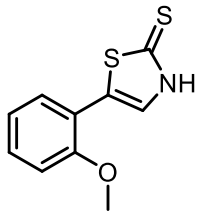
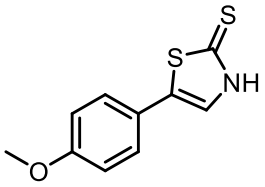
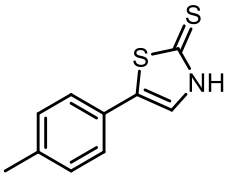
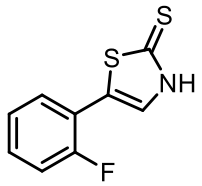
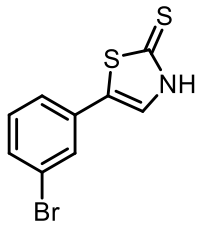
Gaussian 09, Revision **A.02**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

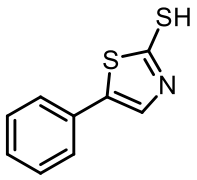
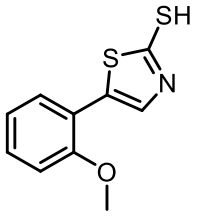
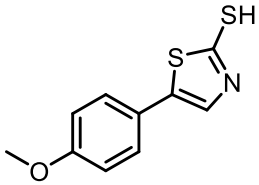
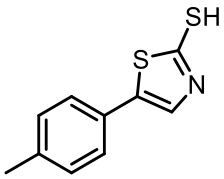
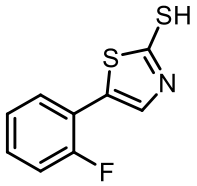
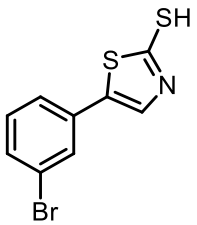
1. M. J. Frisch, et al. Gaussian 09, revision B.02; Gaussian, Inc.:Wallingford, CT, 2009
2. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
3. R. Krishnan, J. S. Binkley, R. Seeger, and A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654.
4. M. Balti, B. Norberg, M. L. Efrit, S. Lanners, and J. Wouters, *Acta Crystallogr. C Struct. Chem.*, 2016, **72**, 421-425.
5. A. Carletta, C. Meinguet, J. Wouters, and A. Tilborg, *Cryst.Growth Des.*, 2015, **15**, 2461-2473.

Summary of zero-point corrections to the electronic energies from optimization and frequency calculations of stationary points:

Identifier	Compound	Correction to zero-point energy[a]	SCF energy[a]
1a		0.134873	-1197.586401
1b		0.166536	-1312.013985
1c		0.166244	-1312.012988
1d		0.16129	-1236.857366
1e		0.126878	-1296.767026
1f		0.124787	-3770.725952

Identifier	Compound	Correction to zero-point energy[a]	SCF energy[a]
2a		0.131007	-1197.572777
2b		0.162307	-1311.993109
2c		0.162426	-1311.999061
2d		0.15741	-1236.843392
2e		0.12293	-1296.748522
2f		0.120938	-3770.714608

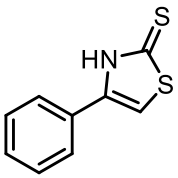
Identifier	Compound	Correction to zero-point energy[a]	SCF energy[a]
7a		0.134953	-1197.586359
7b		0.166532	-1312.01288
7c		0.166342	-1312.012721
7d		0.161404	-1236.857193
7e		0.127005	-1296.768277
7f		0.124893	-3770.7264

Identifier	Compound	Correction to zero-point energy[a]	SCF energy[a]
10a		0.131123	-1197.570836
10b		0.162678	-1311.996644
10c		0.162455	-1311.996807
10d		0.157559	-1236.842757
10e		0.12314	-1296.751262
10f		0.121084	-3770.710999

[a] Values in Hartrees

Cartesian Coordinates of Stationary Points

1a



Coordinates (from last standard orientation):

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C	-2.88758900	0.23074300	0.57004500
C	-2.47551600	1.54385800	0.32948400
C	-1.21200400	1.80527400	-0.23861300
C	-0.37522600	0.71726200	-0.55829600
C	-0.79586500	-0.59276600	-0.32597500
H	-2.37551000	-1.86773800	0.43027200
H	-3.87173400	0.04576700	1.00613000
H	-3.15707000	2.36909600	0.55219500
H	0.61995200	0.90774400	-0.96649900
H	-0.13344300	-1.42464400	-0.57543600
C	-0.77192000	3.18114800	-0.50527900
C	0.03154300	3.62609400	-1.51630900
C	-0.78974000	5.50914600	-0.01266200
H	0.46122100	3.03339500	-2.31826300
N	-1.20869700	4.23598500	0.29376800
H	-1.75025000	4.09728700	1.14459800
S	0.23924900	5.35924500	-1.45969500
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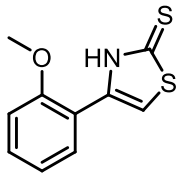
1b



Coordinates (from last standard orientation):

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C	-0.72364200	0.73695200	-1.33816300
C	-0.97224800	-0.62908700	-1.20906100
H	-1.81516000	-0.69881800	2.08947600
H	-0.37845000	1.13091000	-2.29611600
H	-0.84124700	-1.29051200	-2.06714200
C	-0.63966200	3.06686100	-0.48127800
C	-0.67052500	3.72987700	-1.67961100
C	-0.09592300	5.25467500	0.27191300
H	-0.92117200	3.32078400	-2.65321700
N	-0.31860500	3.93464300	0.56011400
H	-0.32617800	3.61641800	1.52843700
S	-0.28907000	5.42071800	-1.49253500
S	0.27449500	6.46874300	1.34405100
H	-1.56292700	-2.20834500	0.15140600
O	-1.38761700	1.97112900	2.03954500
C	-1.83151100	1.47841300	3.30819500
H	-2.83530200	1.02900700	3.22988900
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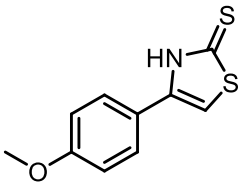
1c



Coordinates (from last standard orientation):

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C	-1.24072100	1.84512800	-0.23531400
C	-0.44470700	0.72046800	-0.54696000
C	-0.89003700	-0.56729400	-0.28394500
H	-3.93424300	0.19798300	1.09047100
H	-3.15555100	2.46440700	0.57866700
H	0.54765500	0.86796500	-0.97905200
H	-0.27475400	-1.43850600	-0.51560600
C	-0.76860200	3.20041200	-0.53855200
C	0.03067900	3.60650200	-1.56958300
C	-0.71145700	5.53709800	-0.08582600
H	0.42945400	2.99043500	-2.36972800
N	-1.16042100	4.28195700	0.24925300
H	-1.68793000	4.17286700	1.11296000
S	0.29025900	5.33509500	-1.54291400
S	-1.02294500	6.95580800	0.71792200
O	-2.48704700	-2.07953200	0.53503400
C	-3.75260200	-2.34466400	1.14310800
H	-3.81605700	-3.43583400	1.22852200
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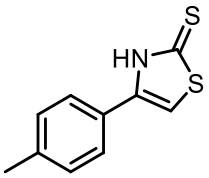
1d



ATOM	X	Y	Z
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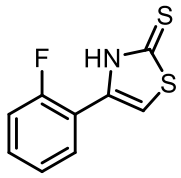
C	-1.16749800	1.80571100	-0.24519500
C	-0.79564200	0.79847300	-1.15754000
C	-1.22239300	-0.51590500	-0.97895200
H	-3.04337800	-0.12481200	1.86716500
H	-2.25975100	2.19438000	1.59394900
H	-0.18503500	1.05910000	-2.02525000
H	-0.92191000	-1.27868900	-1.70283500
C	-0.69917200	3.18543500	-0.42504800
C	0.48076900	3.61303100	-0.96448200
C	-0.98369200	5.53339300	-0.15890500
H	1.29594300	2.99404100	-1.32681900
N	-1.47220500	4.25992500	0.01153300
H	-2.41908800	4.14923500	0.36847900
S	0.61310900	5.35476100	-0.92759200
S	-1.73440900	6.95514800	0.25060600
C	-2.53478900	-2.29509700	0.26492500
H	-2.86105200	-2.49358900	1.29591800
H	-3.39414800	-2.49361400	-0.39782400
H	-1.75111500	-3.02331100	0.00670800

1e



Coordinates (from last standard orientation):

ATOM	X	Y	Z
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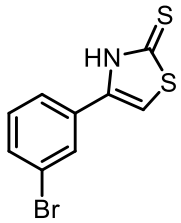
C	-1.18974500	1.81603600	-0.18744600
C	-0.64603200	0.74458600	-0.93173100
C	-1.06276800	-0.57041600	-0.73741000
H	-3.40967300	-0.00647700	1.68913700
H	0.10457400	0.96507600	-1.69300400
H	-0.62004900	-1.37013600	-1.33379400
C	-0.70468500	3.18670900	-0.39145200
C	0.48726800	3.55672000	-0.95301400
C	-0.93515500	5.54984300	-0.26613200
H	1.28287100	2.90301700	-1.29659100
N	-1.45638800	4.30263400	-0.02667800
H	-2.35670900	4.22591800	0.44204900
S	0.65591200	5.28864100	-1.03070200
S	-1.63238900	7.01295700	0.08181400
H	-2.39503700	-1.88934500	0.35658700
F	-2.77296400	2.46146700	1.49090600

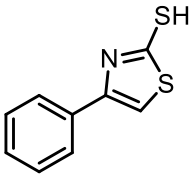
1f



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	-1.76246600	-0.89977200	0.35816000
C	-2.81289700	-0.08393900	-0.07660700
C	-2.62580400	1.27319200	-0.33609500
C	-1.34594800	1.84179400	-0.17809200
C	-0.28244100	1.02557700	0.25624900
C	-0.49682100	-0.32828000	0.52316100
H	0.72439400	1.43887700	0.35077900
H	0.33450400	-0.95434800	0.85406400
C	-1.13788600	3.26538200	-0.47410800
C	-1.76766100	4.02890800	-1.41530900
C	0.00679900	5.32124200	-0.12503500
H	-2.51748000	3.70019700	-2.12877400
N	-0.16886700	3.99821700	0.20789200
H	0.34770300	3.62836900	1.00335700
S	-1.14834400	5.66052400	-1.44029300
S	1.06473700	6.39332500	0.56636400
H	-1.93289900	-1.95665300	0.56418800
H	-3.47002100	1.89607800	-0.63407800
Br	-4.55523500	-0.84139600	-0.29812000

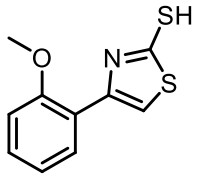
2a



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	-2.13914800	-0.82649900	0.13713800
C	-2.78718300	0.24879700	0.75449500
C	-2.31061800	1.55106500	0.58773700
C	-1.17196800	1.80316800	-0.20251600
C	-0.52800100	0.71284500	-0.82071800
C	-1.00666700	-0.58693300	-0.65178500
H	-2.51253700	-1.84474000	0.26754300
H	-3.67170700	0.07362700	1.37160500
H	-2.80971100	2.39588500	1.06462600
H	0.35474800	0.87734400	-1.44323400
H	-0.49366300	-1.41898200	-1.13994500
C	-0.68758400	3.18691200	-0.36256100
C	0.42532900	3.59209200	-1.07279300
C	-0.83635800	5.37565200	0.01071700
H	1.14026300	2.99519900	-1.63169600
N	-1.38498400	4.22019300	0.24366700
S	0.61916700	5.31311200	-0.99287500
S	-1.52973500	6.86481300	0.66613600
H	-0.59787900	7.69703400	0.13308100

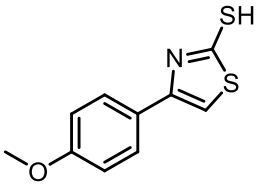
2b



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	-1.16679700	-1.10257900	0.04777300
C	-1.42038400	-0.24788600	1.12747600
C	-1.27080200	1.14091800	0.98207600
C	-0.84293000	1.67960400	-0.26108600
C	-0.60052600	0.79624100	-1.32393900
C	-0.76213100	-0.58632000	-1.18416600
H	-1.74600300	-0.66976100	2.07855700
H	-0.25137900	1.21412100	-2.27141100
H	-0.55777600	-1.25078300	-2.02571600
C	-0.67134800	3.13439500	-0.45892000
C	-1.16274700	3.82445300	-1.54567600
C	0.11144900	5.14343600	0.05622000
H	-1.77815900	3.45507900	-2.36152900
N	0.04856900	3.90189600	0.44432300
S	-0.71555200	5.50077100	-1.46480100
S	0.95442100	6.43242000	0.92975400
H	-1.28826100	-2.18017200	0.18130900
O	-1.54252000	2.04355200	1.96677000
C	-1.95508200	1.54514700	3.23678500
H	-2.90509600	0.98589000	3.16671400
H	-1.18275400	0.89895300	3.68986600
H	-2.10145400	2.43145300	3.86586000
H	1.35849100	5.58156200	1.90885000

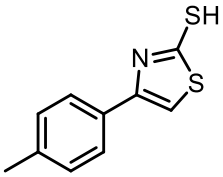
2c



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	-2.21831600	-0.77149800	0.20272300
C	-2.84929900	0.33536300	0.79269100
C	-2.33505900	1.61884300	0.58662100
C	-1.19250000	1.83586700	-0.20236900
C	-0.57263700	0.71007600	-0.78746100
C	-1.07253400	-0.57013200	-0.59127100
H	-3.73834100	0.21161400	1.41198500
H	-2.82261400	2.48152600	1.04333500
H	0.31765100	0.83336100	-1.40869200
H	-0.59469400	-1.44159200	-1.04275000
C	-0.68013400	3.20175500	-0.39653600
C	0.42698700	3.57147400	-1.13564100
C	-0.77379600	5.40039000	-0.05900200
H	1.11635000	2.95107800	-1.70093500
N	-1.34308200	4.26174000	0.20465600
S	0.65908700	5.29062700	-1.08857100
S	-1.42178600	6.91553900	0.58554100
O	-2.62763300	-2.06924700	0.33275400
C	-3.78379200	-2.31932500	1.13113800
H	-3.93358700	-3.40543200	1.10420700
H	-3.63216900	-1.99683600	2.17630500
H	-4.67714800	-1.81685900	0.72018700
H	-0.48383300	7.71856900	0.01969600

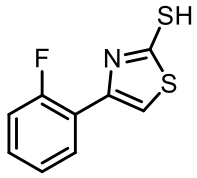
2d



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	-2.03055200	-0.86506400	0.12119100
C	-2.58560700	0.18504700	0.86954300
C	-2.16821400	1.50518700	0.69175100
C	-1.17067900	1.82426300	-0.24846300
C	-0.60656600	0.77233500	-0.99706900
C	-1.02951700	-0.54270400	-0.81349000
H	-3.36063300	-0.03594800	1.60928700
H	-2.60584000	2.31226400	1.28132000
H	0.17898400	0.97806700	-1.72835000
H	-0.57141400	-1.34048300	-1.40552300
C	-0.74496600	3.22423900	-0.42201400
C	0.17992400	3.69655500	-1.33263600
C	-0.83323100	5.38439500	0.10652000
H	0.75174300	3.15127700	-2.07791100
N	-1.30557700	4.20494300	0.38213800
S	0.36974300	5.41435300	-1.18993400
S	-1.37405700	6.81550600	0.99449000
C	-2.50359100	-2.28701800	0.29283300
H	-3.00744900	-2.42915900	1.25998400
H	-3.22247200	-2.56374800	-0.49736900
H	-1.66749800	-3.00071200	0.23417500
H	-0.62499800	7.70467300	0.29230200

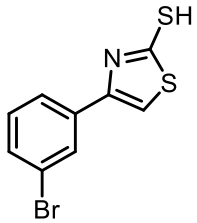
2e



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	-2.08860500	-0.83549300	0.10821800
C	-2.54589300	0.14291400	0.99538900
C	-2.09280900	1.45374100	0.86141100
C	-1.18944200	1.83825200	-0.14679800
C	-0.74953700	0.82924800	-1.02688700
C	-1.18486500	-0.49146300	-0.90377500
H	-3.24395400	-0.08935400	1.80138600
H	-0.07222100	1.10836600	-1.83738300
H	-0.83157300	-1.24806000	-1.60698000
C	-0.70230300	3.22387200	-0.28020300
C	0.59352100	3.55926900	-0.61576000
C	-0.93722800	5.42825300	-0.27265600
H	1.44562000	2.90415900	-0.77531900
N	-1.55256500	4.29768100	-0.08510900
S	0.77441100	5.28126200	-0.70842600
S	-1.79223900	6.96721600	-0.10933000
H	-2.44281200	-1.86357700	0.20813900
F	-2.52427500	2.36914000	1.75814200
H	-0.71646700	7.75139200	-0.38006600

2f

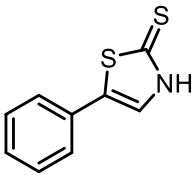


Coordinates (from last standard orientation):

0 1

C	-1.68323100	-0.86629900	0.33737900
C	-2.68805000	-0.12096500	-0.28791900
C	-2.53705000	1.23851600	-0.55347900
C	-1.34418000	1.89330800	-0.18694500
C	-0.32738100	1.14988900	0.44235500
C	-0.50092700	-0.21139000	0.69839800
H	0.59390100	1.66103900	0.72284700
H	0.29523700	-0.77740500	1.18746900
C	-1.14680200	3.33088000	-0.45064200
C	-2.05182800	4.19219100	-1.03632700
C	0.07375400	5.18808200	-0.38599900
H	-3.05416700	3.99393800	-1.40518900
N	0.05572400	3.91995500	-0.08826900
S	-1.39916500	5.79385600	-1.14856300
S	1.42729600	6.28477900	-0.08457900
H	-1.82384000	-1.92927900	0.53479400
H	-3.34607900	1.77972700	-1.04499100
Br	-4.31911500	-0.99121100	-0.79710600
H	2.18508200	5.29944900	0.46354300

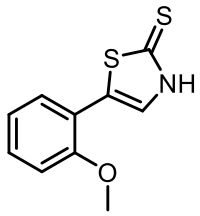
7a



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	0.17419500	2.36296400	4.94658200
C	-0.23261900	3.67845100	4.69035600
C	-0.35719000	4.13516200	3.37784900
C	-0.09477600	3.27588300	2.28908900
C	0.31852700	1.95532600	2.56040900
C	0.45350900	1.50669400	3.87580100
H	0.28060900	2.01087700	5.97481000
H	-0.43765000	4.35929000	5.51972800
H	-0.63428500	5.17527100	3.19018100
H	0.51663100	1.27181600	1.73081400
H	0.77310500	0.47938400	4.06447500
C	-1.07499200	4.73131700	0.44270200
C	-0.25199700	3.74894700	0.91338400
C	-0.11230400	4.13605800	-1.63027900
N	-0.98296500	4.93106200	-0.92010300
H	-1.53734000	5.61618400	-1.42948700
S	0.66472800	3.06403900	-0.44201700
S	0.16167400	4.17375500	-3.26545800
H	-1.78472400	5.31792800	1.02162700

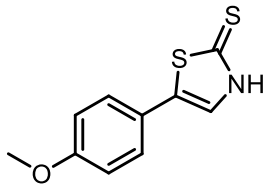
7b



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	-0.69947900	2.82484800	5.18718800
C	-0.86937200	4.16377100	4.83115400
C	-0.88461200	4.51719500	3.48207900
C	-0.73386300	3.56849600	2.44946200
C	-0.55912100	2.20702600	2.83818200
C	-0.54465000	1.85167900	4.19381500
H	-0.99042300	4.93244200	5.59629500
H	-1.01959700	5.56755500	3.21178300
H	-0.41198500	0.80962700	4.48416000
C	-0.65222200	3.27971500	-0.10716200
C	-0.76173700	3.99745200	1.05442100
C	-0.90318200	5.40442500	-1.10964900
N	-0.73009800	4.04860600	-1.25003900
H	-0.66712800	3.66362700	-2.19026200
S	-0.97068100	5.71808400	0.63507900
S	-1.02415500	6.52578600	-2.32772200
H	-0.51698800	2.20762200	-0.18683900
H	-0.68556800	2.52628300	6.23749800
O	-0.41052300	1.29642200	1.82549800
C	-0.22336300	-0.07686600	2.17419400
H	0.69289500	-0.21945000	2.77199800
H	-1.09136200	-0.47473000	2.72695700
H	-0.12276900	-0.61277200	1.22246300

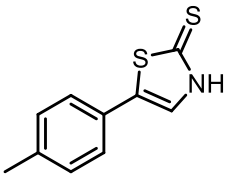
7c



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	0.33298800	2.25018200	4.83852900
C	-0.48988100	3.37271600	4.62005100
C	-0.71094200	3.84091100	3.33254100
C	-0.10753100	3.22072300	2.21326000
C	0.70646900	2.09796600	2.44851800
C	0.92775300	1.60954500	3.73919800
H	-0.96000600	3.84677400	5.48361400
H	-1.38379300	4.68880300	3.18426100
H	1.19528200	1.60106800	1.60650900
H	1.56781800	0.73752600	3.87507000
C	-0.65139000	5.00373300	0.47553300
C	-0.32440700	3.73573000	0.86333800
C	-0.56989500	4.05163100	-1.68504600
N	-0.78800600	5.15267200	-0.89189400
H	-1.01886100	6.03524200	-1.34321000
S	-0.18757600	2.71091200	-0.57953100
S	-0.65207100	3.98284800	-3.34146000
H	-0.77939800	5.86995000	1.12056800
O	0.47763500	1.86701800	6.14011500
C	1.29099500	0.72386100	6.40822300
H	1.26752100	0.59301900	7.49658800
H	0.88850300	-0.18192600	5.92201600
H	2.33338000	0.88362200	6.08147700

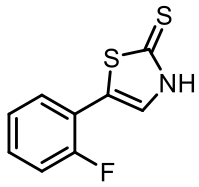
7d



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	0.11450800	2.43557400	4.99915400
C	-0.98336300	3.24017100	4.65408200
C	-1.17449500	3.68697200	3.34587700
C	-0.26868800	3.34000400	2.32427600
C	0.82833400	2.52022900	2.66542100
C	1.01662400	2.08891300	3.97680800
H	-1.69996800	3.53066100	5.42738100
H	-2.02603300	4.33270300	3.11586100
H	1.87616100	1.45461400	4.21218400
C	0.49918800	4.01805400	-0.00807900
C	-0.44884300	3.81700200	0.95379100
C	-1.36637300	4.68975900	-1.29164700
N	-0.00974400	4.47811100	-1.20663300
H	0.56454200	4.68885900	-2.02018500
S	-2.04044500	4.23663400	0.29112900
S	-2.20655500	5.25018700	-2.60783000
H	1.57291100	3.88052600	0.09735800
H	1.52708200	2.19994900	1.88867000
C	0.30450800	1.93076500	6.40734100
H	-0.06840500	0.89744500	6.51087600
H	1.36745800	1.92205900	6.69262900
H	-0.24017100	2.55092800	7.13389800

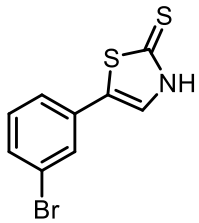
7e



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	0.20111800	2.47800000	4.99591800
C	0.87750600	3.62042000	4.55393900
C	0.72221300	4.06313200	3.24084300
C	-0.10937600	3.38930100	2.31674100
C	-0.76992200	2.24384900	2.80791300
C	-0.63076100	1.78440700	4.11112600
H	1.52963300	4.17125800	5.23403600
H	1.25548600	4.95834500	2.91174100
H	-1.17748600	0.88898800	4.41093400
C	-1.03553900	3.37745100	-0.07351900
C	-0.26076100	3.86277800	0.94584900
C	-0.07575800	5.17623500	-1.26707100
N	-0.92294700	4.09207300	-1.24610100
H	-1.43321800	3.85944300	-2.09582300
S	0.63513600	5.28254100	0.35773600
S	0.22406000	6.18194300	-2.54989600
H	-1.69874700	2.51997300	-0.03235500
H	0.31667100	2.12470500	6.02210300
F	-1.58940000	1.54113100	1.97415200

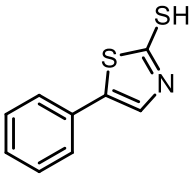
7f



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	0.16812800	2.47674500	4.99289700
C	0.65368100	3.73650400	4.62652600
C	0.53040000	4.19939700	3.31553300
C	-0.08312700	3.40016400	2.32978400
C	-0.55684100	2.12038800	2.69103900
C	-0.43568100	1.68578500	4.00964700
H	1.12887800	4.36701700	5.38108200
H	0.89438700	5.19553400	3.05425900
C	-1.17725100	3.51732100	0.03374000
C	-0.23463600	3.87539800	0.95460400
C	-0.01721800	5.06844200	-1.31775100
N	-1.04313400	4.15962900	-1.17907000
H	-1.67056300	4.01451500	-1.96756100
S	0.85396600	5.07564400	0.23434300
S	0.33860300	5.96994400	-2.66153100
H	-2.00294800	2.82487600	0.18200900
H	0.26132500	2.11265700	6.01621200
H	-0.99270500	1.46011500	1.94047800
Br	-1.09019200	-0.05227600	4.47619900

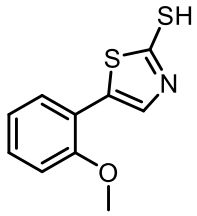
10a



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	0.16437700	2.34747500	4.91937600
C	-0.27423300	3.65393700	4.67136000
C	-0.37843300	4.12766900	3.36280600
C	-0.06222600	3.29476800	2.26737800
C	0.37850000	1.98094000	2.53170700
C	0.49437700	1.51606100	3.84306900
H	0.25339300	1.98205800	5.94467600
H	-0.52266600	4.31533500	5.50468300
H	-0.68503800	5.16009800	3.18126400
H	0.61209900	1.31397000	1.69779500
H	0.83658900	0.49460300	4.02457200
C	-1.06590000	4.75871300	0.40700400
C	-0.20712100	3.79596600	0.89986700
C	-0.08371400	4.30738300	-1.51117200
N	-0.99512700	5.04212800	-0.93193500
S	0.77238700	3.19850400	-0.43548200
S	0.22703300	4.44880300	-3.24560600
H	-1.80677900	5.27687700	1.01651800
H	1.21979100	3.52271600	-3.28486100

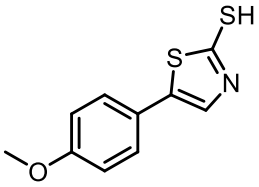
10b



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	-0.78788600	2.76913700	5.20089200
C	-0.97712400	4.11662700	4.88853300
C	-0.95386500	4.51969300	3.55313900
C	-0.73895000	3.61512100	2.49277300
C	-0.55154500	2.24298700	2.83603200
C	-0.57676800	1.83781800	4.17861700
H	-1.14873700	4.85205500	5.67653700
H	-1.12133500	5.57269200	3.31289100
H	-0.43087400	0.78828700	4.43373500
C	-0.82202500	3.42160200	-0.09775200
C	-0.69874900	4.08706100	1.10927000
C	-0.58783200	5.43715300	-0.95769100
N	-0.76549100	4.17355700	-1.24492400
S	-0.47155400	5.80640500	0.75716300
S	-0.46341900	6.73337900	-2.15412900
H	-0.96824500	2.34824700	-0.17720700
H	-0.80638300	2.43134900	6.23930900
O	-0.34574700	1.37737800	1.79775800
C	-0.08879600	0.00601900	2.10113700
H	0.81305400	-0.10679500	2.72712800
H	-0.94947700	-0.46582200	2.60608700
H	0.07726300	-0.48270200	1.13344300
H	-0.59726600	5.86363100	-3.18981000

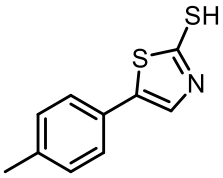
10c



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	0.29945800	2.22258000	4.80316700
C	-0.58292200	3.29528100	4.57158300
C	-0.76525100	3.79056000	3.28757700
C	-0.06330600	3.24792100	2.18516000
C	0.81333700	2.17608900	2.43504600
C	0.99559100	1.65950600	3.72097200
H	-1.12813300	3.71083200	5.42108000
H	-1.48102700	4.59905600	3.12432000
H	1.38398600	1.74422100	1.60877200
H	1.68671700	0.82920800	3.86763900
C	-0.60643200	5.08235000	0.46609400
C	-0.24784200	3.80356000	0.84556400
C	-0.44862300	4.26523900	-1.57329000
N	-0.71949500	5.33532800	-0.87713800
S	-0.03669300	2.83933600	-0.61386200
S	-0.48400300	4.29662700	-3.34174900
H	-0.77751500	5.89700900	1.17036200
O	0.40014400	1.80691900	6.10027700
C	1.27491500	0.71390300	6.37948700
H	1.20314600	0.54597800	7.46075300
H	0.96305900	-0.20129000	5.84610800
H	2.32005800	0.95349600	6.11572300
H	-0.19767800	2.97960000	-3.50924800

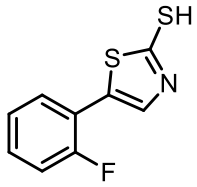
10d



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	0.11287000	2.43626300	4.98405300
C	-0.98651700	3.24607600	4.65578300
C	-1.19033600	3.70133900	3.35255800
C	-0.29997300	3.35552100	2.31619400
C	0.79998300	2.53298500	2.64235900
C	1.00230100	2.09449000	3.94963600
H	-1.69269000	3.53562000	5.43919300
H	-2.04045400	4.35420500	3.13761300
H	1.86500300	1.45954900	4.17175400
C	0.45683100	4.05303200	-0.04074100
C	-0.48284800	3.83531400	0.94652800
C	-1.29259200	4.66401200	-1.22964700
N	0.00694100	4.51343700	-1.25310600
S	-2.06874700	4.23928200	0.29409100
S	-2.26427700	5.24643400	-2.58734500
H	1.52839900	3.90759400	0.09889200
H	1.49056300	2.22035300	1.85584800
C	0.31820300	1.92434900	6.38773900
H	-0.05549700	0.89126000	6.49158900
H	1.38441800	1.91231600	6.66066100
H	-0.21641500	2.54249500	7.12360700
H	-1.17506000	5.35447400	-3.39294300

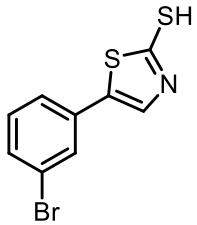
10e



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	0.21027000	2.49894400	4.97912600
C	0.88002400	3.64446100	4.53405900
C	0.72836300	4.07688500	3.21744700
C	-0.08873800	3.39008200	2.28875100
C	-0.74363500	2.24193000	2.78326300
C	-0.60888600	1.79434300	4.09256900
H	1.52074900	4.20712000	5.21553000
H	1.24777000	4.98056800	2.88916900
H	-1.14936200	0.89535100	4.39321300
C	-1.11857500	3.45750900	-0.08725900
C	-0.23454400	3.84110200	0.90765500
C	-0.04670700	4.96605100	-1.28376600
N	-1.01185200	4.08653300	-1.29910600
S	0.82183400	5.09154400	0.24580000
S	0.32239000	5.93163100	-2.71582800
H	-1.88537700	2.69841700	0.04513100
H	0.32043800	2.15376000	6.00873000
F	-1.54650400	1.52223100	1.95376600
H	1.34453600	6.62856000	-2.15466400

10f



Coordinates (from last standard orientation):

ATOM	X	Y	Z
0 1			
C	0.16335200	2.49980300	4.98114800
C	0.68217500	3.74267200	4.60189900
C	0.57506100	4.19278100	3.28533800
C	-0.05150200	3.39719400	2.30381900
C	-0.56163700	2.13534300	2.67980100
C	-0.45699300	1.71423100	4.00448800
H	1.16858300	4.37061400	5.35160800
H	0.96113100	5.17830400	3.01551200
C	-1.16168000	3.52362600	-0.01143000
C	-0.19388000	3.84862000	0.91909000
C	-0.01561700	4.87871900	-1.31457000
N	-1.06034300	4.09644100	-1.25108200
S	0.93932400	4.96641900	0.16876800
S	0.36913400	5.75744900	-2.79777700
H	-2.00683900	2.86686900	0.19709900
H	0.24132900	2.14620200	6.00940900
H	-1.01484400	1.48172800	1.93420800
Br	-1.16144700	0.00061400	4.49071800
H	1.48051600	6.36894000	-2.31222000