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Tetrel, Chalcogen, and Charge-Assisted Hydrogen Bonds in 2-((2-Carboxy-1-(substituted)-2-hydroxyethyl)thio) Pyridin-1-ium Chlorides

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Abstract: Reaction of 2-chloro-2-(diethoxymethyl)-3-substitutedoxirane or 1-chloro-1-(substituted) -3,3-diethoxypropan-2-one with pyridine-2-thiol in EtOH at 25 °C yields 3-(diethoxymethyl)-3-hydroxy-2-substituted-2,3-dihydrothiazolo[3,2-a]pyridin-4-ium chlorides, which subsequently, in MeCN at 85°C, transforms into ring-opening products, 2-((2-carboxy-1-(substituted) -2-hydroxyethyl)thio)pyridin-1-ium chlorides. The tetrel (C···O) and chalcogen (S···O) bonds are found in the structures of **5** and **6**, respectively. Compound **6** is also present in halogen bonding with a short O···Cl distance (3.067 Å). Both molecules are stabilized in crystal by tetrel, chalcogen, and multiple charge-assisted hydrogen bonds.

Keywords: noncovalent interactions; tetrel bonding; chalcogen bonding; charge-assisted hydrogen bonding

1. Introduction

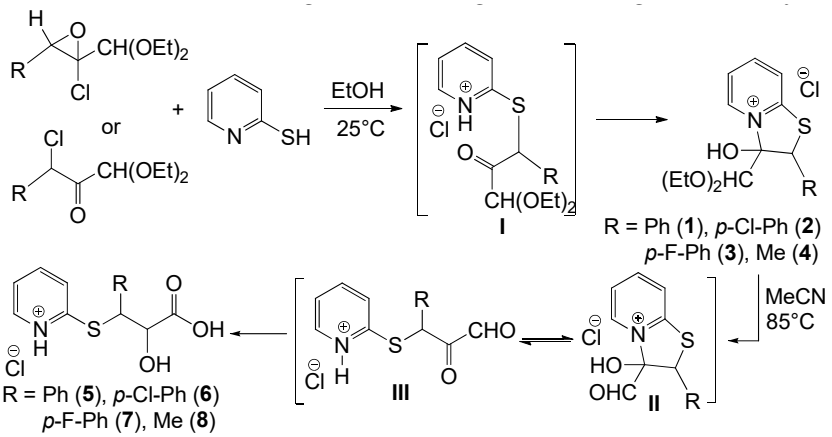
Aerogen, halogen, chalcogen, pnicogen, tetrel, and icosagen bonds, also called σ-hole bonds, where an atom of group 18, 17, 16, 15, 14, or 13, respectively, lies in a region of the positive electrostatic potential, acting as an electrophilic species towards a nucleophilic (negative) region(s) in another or in the same molecule, constitute recently explored noncovalent interactions [1–10]. In comparison to the commonly known hydrogen and halogen bonding, the aerogen, chalcogen, pnicogen, tetrel, and icosagen bonds are quite new, having been extensively studied in recent years from theoretical and experimental points of view. These weak interactions can also be used in the synthesis, catalysis, and design of materials. For instance, due to directionality, tunability, multiplicity, hydrophobicity, and donor atom size [10], chalcogen bonds can direct asymmetric organic reactions [11], stabilize organic radicals [12], be used in molecular recognitions [13–15], support thermodynamic isomers [16], stabilize five-membered intermediates in catalysis [17–19], etc. as a planar geometric synthon [8,9].

Furthermore, all types of chalcogen bonding, viz. negative charge-assisted, positive charge-assisted, conventional (or "neutral"), and resonance-assisted, have been well employed in crystal growth and design [10].

On the other hand, the charge-assisted hydrogen bonding (CAHB), viz. interactions of the X(+)-H···Y(−) type with the X-H donor belonging to a cation and the Y acceptor belonging to an anion, constitutes a particularly powerful tool used in the synthesis and design of new compounds [9,20,21]. CAHBs can control a great variety of synthetic operations involving molecules with groups exhibiting acid-base properties [20,21]. Due to the strength and directionality of the CAHB, this type of noncovalent interaction has an impact on the synthesis of coordination compounds [9], crystal engineering [20–23], etc. In most cases, due to the additional electrostatic interactions involved, CAHBs are stronger in comparison to normal hydrogen bonds.

On the other hand, α-hydroxy carboxylic acids are versatile and powerful intermediates for the synthesis of various chiral compounds with unique properties [24–27]. Furthermore, the functionalization of α-hydroxy carboxylic acids with 2-tiopyridine (expected chalcogen bond donor) moiety can increase their bioactivity, donor sites towards coordination, etc.

Hence, on the basis of the above considerations, in this work we synthesized 2-tiopyridine functionalized α-hydroxy carboxylic acids (e.g., 2-((2-carboxy-2-hydroxy-1-arylethyl)thio) pyridin-1-ium chlorides (Scheme 1), having tetrel, chalcogen, and charge-assisted hydrogen bonds.



Scheme 1. Synthesis of 2-((2-carboxy-2-hydroxy-1-arylethyl) thio)pyridin-1-ium chlorides.

2. Results and Discussion

Reaction of 2-chloro-2-(diethoxy- methyl)-3-substituted-oxirane or 1-chloro-1-(substituted)-3,3-diethoxypropan-2-one, which proved to be convenient reagents in the synthesis of interesting heterocyclic systems [25–28], with pyridine-2-thiol in EtOH at 25°C yields 3-(diethoxymethyl)-3-hydroxy-2-substituted-2,3-dihydro-thiazolo[3,2-a]pyridin-4-ium chlorides (**1–4**), which subsequently, in MeCN at 85°C, transforms into ring-opening products, 2-((2-carboxy-1-(substituted)-2-hydroxyethyl)thio)pyridin-1-ium chlorides (**5–8**), having tetrel, chalcogen, and charge-assisted hydrogen bonds (Figures 1–4). Additionally, the use of the dihalogen functionalized substrate 2-chloro-3-(4-chlorophenyl)-2-(diethoxymethyl) oxirane or 1-chloro-1-(4-chloro-phenyl)-3,3-diethoxypropan-2-one leads to halogen bonding in the reaction product **6** (Figure 5).

Due to the thermodynamic stability of **1–4**, the expected acyclic products, 2-((1-(substituted)-3,3-diethoxy-2-oxopropyl)thio)pyridin-1-ium chlorides (**I**), were not observed (Scheme 1). The structures of **1–4** were fully characterized by ^{1}H and ^{13}C NMR, ESI-MS, as well as elemental and X-ray analysis (for **1**). In the ^{1}H NMR spectra of **1–4,** the *CHS* and *OH* protons are observed at δ 4.37–4.54 and 9.64–9.98, respectively. Elemental analyses (see ESI section) and ESI-MS peaks at 332.21 [*Mr*-Cl^{-}]$^{+}$ (**1**), 366.08 [*Mr*-Cl^{-}]$^{+}$ (**2**), 350.10 [*Mr*-Cl^{-}]$^{+}$ (**3**), and 270.25 [*Mr*-Cl^{-}]$^{+}$

(**4**) support the formulations, which are also proved by X-ray crystallography for **1** (Figure 1). The structures of **5** and **6** were also established by X-ray diffraction. In the ^{1}H NMR spectra of **5–8,** the two protons at asymmetric centers (*SCH* and *CHOH*) display two doublets at δ 4.46 and 5.51 (for **5**), 4.45 and 5.52 (for **6**), 4.42 and 5.55 (for **7**) and 4.26 and 4.35 (for **8**) with the vicinal coupling constant J = 3.0 Hz. The mass spectra of these compounds display molecular ion peaks at 276.09 $[C_{14}H_{14}NO_3S]^+$ (**5**), 310.78 [*Mr*-Cl$^-$]$^+$ (**6**), 294.32 [*Mr*-Cl$^-$]$^+$ (**7**), and 214.26 [*Mr*-Cl$^-$]$^+$ (**8**) (see experimental section). These compounds may stabilize as *syn*- or *anti*-isomers, depending on the nature of the involved intermolecular noncovalent interactions (Figures 2–5). For example, **5** is stabilized as a *syn*-isomer whereas **6** is stabilized as an *anti*-isomer in the solid state. In the latter compound also presents an additional halogen bonding with a short O···Cl distance (3.067 Å) that is shorter than twice the sum of the van der Waals radii of the interacting atoms (O + Cl = 1.52 + 1.75 = 3.27 Å) [28] (Figure 5), and with the O···ClC$_{Ar}$ angle of 162.86°. A Cl$^-$ in both compounds provides negative charge-assisted hydrogen bonds with hydroxylic and carboxylic–*OH*, asymmetric *SCH*, and aromatic *CH* protons (Figure 4). Moreover, **5** and **6** contain an intramolecular 1,4 S···O synthon with the distance of 2.814 and 2.958 Å, respectively, suggesting that there is a strong chalcogen bonding between the electron-donating hydroxyl O atom and the acceptor S atom of the thioether, as compared with the sum of the van der Waals radii of 3.32 Å [28]. Moreover, these distances are shorter than the corresponding distance of 3.147 Å to be found in the 1,4 S···O synthon of acetazolamide [29]. The intermolecular S···S chalcogen and C···O tetrel bond distances of 3.482 and 3.176 for **5**, 3.413 and 3.078 Å for **6** (van der Waals radii 1.80(S) + 1.80(S) = 3.60 Å and 1.70(C) + 1.52(O) = 3.22 Å) [28], respectively, also prove strong noncovalent interactions in both compounds (Figures 2 and 3). The O(2)···O(2′) and O(3)···O(3′) distances of 3.405 and 3.324 Å for 5 and 6, respectively, are longer than twice the sum of the van der Waals radii of the interacting atoms (1.52(O) + 1.52(O) = 3.04 Å) [28] (Figure 3). In **6**, an additional intermolecular S···O chalcogen bond distance also falls in the van der Waals region with a high directionality of 168.07° (Figure 2).

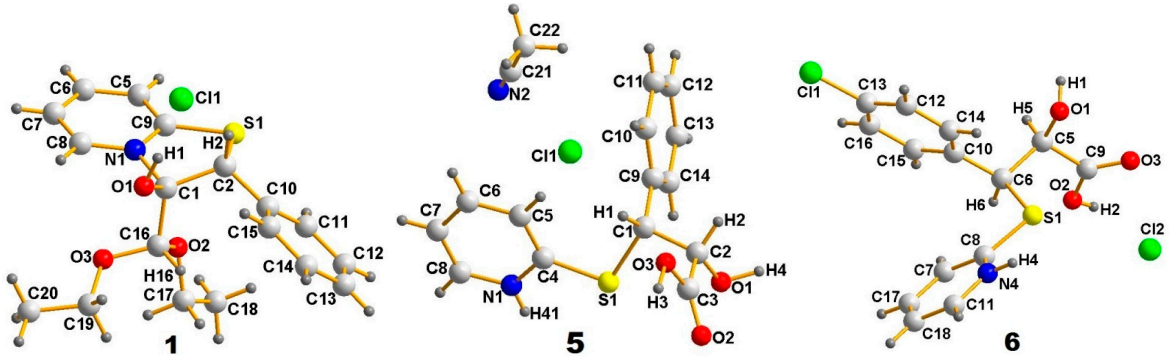


Figure 1. X-ray structure of **1**, **5**, and **6**.

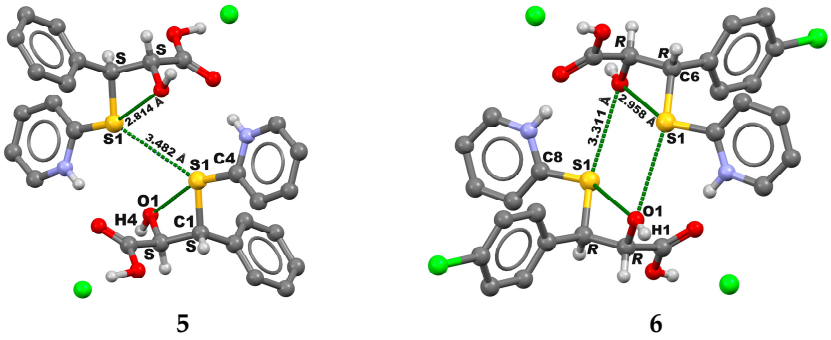
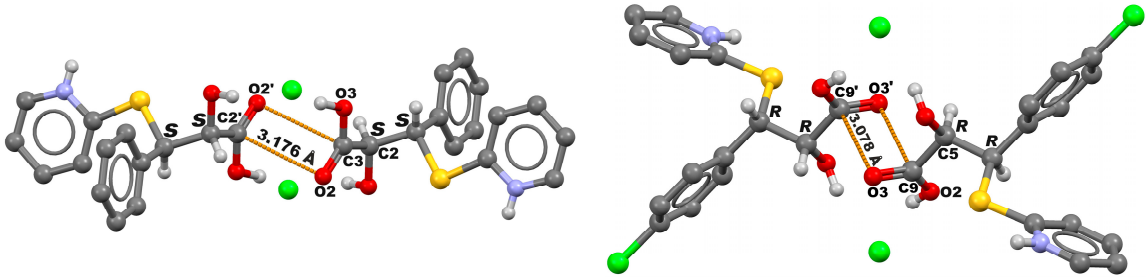
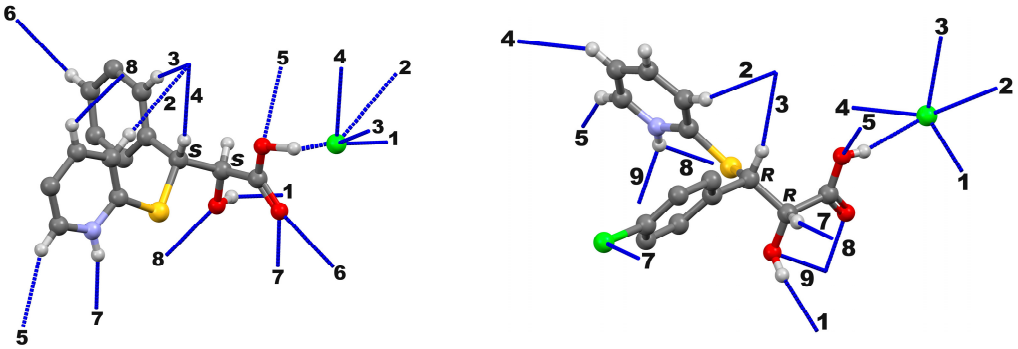


Figure 2. Inter- and intramolecular chalcogen bonds in **5** and **6** (shown as dashed green lines).



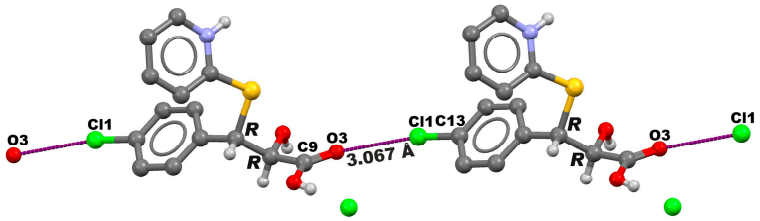
5 6

Figure 3. Tetrel bonds in **5** and **6** (shown as dashed orange lines).



5 6

Figure 4. Hydrogen bonds in **5** and **6** (shown as dashed blue lines).



6

Figure 5. Halogen bonds in **6** (shown as dashed purpura lines).

3. Conclusions

In summary, we report that the ring-opening in 3-(diethoxymethyl)-3-hydroxy-2-substituted-2,3-dihydrothiazolo[3,2-a]pyridin-4-ium chlorides lead to 2-((2-carboxy-1-(substituted)-2-hydroxyethyl)thio)pyridin-1-ium chlorides in MeCN at 85°C. Several types of noncovalent interactions, e.g., tetrel, chalcogen, halogen, and charge-assisted hydrogen bonds are formed to stabilize the obtained products in the solid state. These results offer new opportunities in synthetic operations, and may be useful in the design of new materials.

4. Experimental Section

4.1. Materials and Instrumentation

All the chemicals were obtained from commercial sources (Aldrich) and used as received. Carbon, hydrogen, and nitrogen elemental analyses were conducted using a "2400 CHN Elemental Analyzer" (Perkin-Elmer, MA, USA). The infrared spectra (4000–400 cm^{-1}) were recorded on a Vektor 22 (Bruker, Bremen, Germany) instrument in KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance II + 300 (UltraShield^{TM} Magnet, Bruker, Ettlingen, Germany)

spectrometer operating at 300.130 and 75.468 MHz for proton and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) (Varian, CA, USA) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 psi nebulizer pressure. Scanning was performed from *m/z* 0 to 1100 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V).

4.2. Synthesis of ***1–8***

4.2.1. Synthesis of **1–4**

3-(diethoxymethyl)-3-hydroxy-2-phenyl-2,3-dihydrothiazolo[3,2-a]pyridin-4-ium chloride (1).

2-Chloro-2-(diethoxymethyl)-3-substitutedoxirane (0.75 mmol) or 1-chloro-1-(substituted)-3,3-diethoxypropan-2-one (0.75 mmol) was dissolved in 10 mL ethanol at room temperature and 0.11 g (0.75 mmol) pyridine-2-thiol was added. The reaction mixture was stirred for 15 hours (as monitored by thin layer chromatography TLC), then the solvent was removed under reduced pressure, and the residue was washed with acetone. Recrystallization from ethanol gave pure products.

1: white solid; yield 0.20 g (87%); mp 117–118 °C (EtOH). Anal. Calcd. for $C_{18}H_{22}ClNO_3S$ (*Mr* = 367.89): C, 58.77; N, 3.81; H, 6.03 %. Found: C, 58.69; N, 3.77; H, 5.96 %. MS (ESI) (positive ion mode): *m/z*: 332.21 [*Mr*-Cl^-]$^+$. ^{1}H NMR (300.130 MHz, DMSO-d_6) δ (ppm): 0.98–1.10 (6H, 2-$OCH_2\underline{CH_3}$), 3.70–3.78 (4H, -$O\underline{CH_2}CH_3$), 4.46 (1H, $SC\underline{H}$), 5.52 (1H, $\underline{CH}(OEt)_2$), 7.30–8.44 (9H, Py and Ph), 9.86 (1H, $O\underline{H}$). ^{13}C NMR (75.468 MHz, DMSO-d_6) δ (ppm): 15.14 ($2CH_3$), 51.26 ($S\underline{C}H$), 67.52 ($2CH_2$), 104.45 ($\underline{C}H(OEt)_2$), 122.36 ($\underline{C}_{tert}OH$), 123.05 ($\underline{C}_{py}H$), 128.18 ($C_{ar}H$), 128.46 ($C_{py}H$), 128.91 ($2C_{ar}H$), 128.97 ($2C_{ar}H$), 140.44 ($\underline{C}_{ar}HCH$), 145.98 ($\underline{C}_{py}H$), 146.21 ($\underline{C}_{py}H$), 158.11 ($\underline{C}_{py}S$). IR (KBr): 1640 ν(C=N) cm^{-1}.

2: white solid; yield 0.24 g (87%); mp 147–149 °C (EtOH). Anal. Calcd. for $C_{18}H_{21}Cl_2NO_3S$ (*Mr* = 402.34): C, 53.73; N, 3.48; H, 5.26 %. Found: C, 53.69; N, 3.42; H, 5.19 %. MS (ESI) (positive ion mode): *m/z*: 366.08 [*Mr*-Cl^-]$^+$. ^{1}H NMR (300.130 MHz, DMSO-d_6) δ (ppm): 0.98–1.12 (6H, 2-$OCH_2\underline{CH_3}$), 3.70–3.76 (4H, -$O\underline{CH_2}CH_3$), 4.48 (1H, $SC\underline{H}$), 5.56 (1H, $\underline{CH}(OEt)_2$), 7.28–8.44 (8H, Py and Ph), 9.90 (1H, $O\underline{H}$). ^{13}C NMR (75.468 MHz, DMSO-d_6) δ (ppm): 15.10 ($2CH_3$), 51.22 ($S\underline{C}H$), 67.54 ($2CH_2$), 104.48 ($\underline{C}H(OEt)_2$), 122.34 ($\underline{C}_{tert}OH$), 123.11 ($\underline{C}_{py}H$), 128.29 ($C_{ar}H$), 128.43 ($C_{py}H$), 128.94 ($2C_{ar}H$), 128.96 ($2C_{ar}H$), 140.46 ($\underline{C}_{ar}HCH$), 145.93 ($\underline{C}_{py}H$), 146.27 ($\underline{C}_{py}H$), 158.20 ($\underline{C}_{py}S$). IR (KBr): 1643 ν(C=N) cm^{-1}.

3: white solid; yield 0.22 g (75%); mp 143–144 °C (EtOH). Anal. Calcd. for $C_{18}H_{21}ClFNO_3S$ (*Mr* = 385.88): C, 56.03; N, 3.63; H, 5.49 %. Found: C, 55.96; N, 3.55; H, 5.43 %. MS (ESI) (positive ion mode): *m/z*: 350.10 [*Mr*-Cl^-]$^+$. ^{1}H NMR (300.130 MHz, DMSO-d_6) δ (ppm): 0.96–1.12 (6H, 2-$OCH_2\underline{CH_3}$), 3.72–3.78 (4H, -$O\underline{CH_2}CH_3$), 4.54 (1H, $SC\underline{H}$), 5.60 (1H, $\underline{CH}(OEt)_2$), 7.26–8.48 (8H, Py and Ph), 9.98 (1H, $O\underline{H}$). ^{13}C NMR (75.468 MHz, DMSO-d_6) δ (ppm): 15.09 ($2CH_3$), 51.23 ($S\underline{C}H$), 67.45 ($2CH_2$), 104.47 ($\underline{C}H(OEt)_2$), 122.33 ($\underline{C}_{tert}OH$), 123.14 ($\underline{C}_{py}H$), 128.22 ($C_{ar}H$), 128.53($C_{py}H$), 128.96 ($2C_{ar}H$), 128.99 ($2C_{ar}H$), 140.50 ($\underline{C}_{ar}HCH$), 146.04 ($\underline{C}_{py}H$), 146.30 ($\underline{C}_{py}H$), 158.20 ($\underline{C}_{py}S$). IR (KBr): 1650 ν(C=N) cm^{-1}.

4: white solid; yield 0.27 g (90%); mp 150–152 °C (EtOH). Anal. Calcd. for $C_{13}H_{20}ClNO_3S$ (*Mr* = 305.82): C, 51.06; N, 4.58; H, 6.59 %. Found: C, 51.00; N, 4.47; H, 6.45 %. MS (ESI) (positive ion mode): *m/z*: 270.25 [*Mr*-Cl^-]$^+$. ^{1}H NMR (300.130 MHz, DMSO-d_6) δ (ppm): 1.16–1.20 (6H, 2-$OCH_2\underline{CH_3}$), 1.46 (3H, $\underline{CH_3}$), 3.63–3.77 (4H, -$O\underline{CH_2}CH_3$), 4.37 (1H, $SC\underline{H}$), 5.05 (1H, $\underline{CH}(OEt)_2$), 7.79–8.92 (4H, Py), 9.64 (1H, $O\underline{H}$). ^{13}C NMR (75.468 MHz, DMSO-d_6) δ (ppm): 11.39 (CH_3), 16.42 ($2CH_3$), 43.56 ($S\underline{C}H$), 65.87 ($2CH_2$), 102.54 ($\underline{C}H(OEt)_2$), 121.63 ($\underline{C}_{tert}OH$), 122.19 ($\underline{C}_{py}H$), 140.54 ($\underline{C}_{py}H$), 141.67 ($\underline{C}_{py}H$), 145.65 ($\underline{C}_{py}H$), 157.86 ($\underline{C}_{py}S$). IR (KBr): 1667 ν(C=N) cm^{-1}.

4.2.2. Synthesis of **5–8**

First, 0.50 mmol compound **1**, **2**, **3**, or **4** was dissolved in 15 mL acetonitrile and boiled for 7 hours. After the completion of the reaction (as monitored by TLC), the solvent was removed under reduced pressure, and the residue was recrystallized from a mixture of DMSO/CH_3CN (3/1, *v*/*v*), giving the pure product **5**, **6**, **7** or **8**, respectively.

5: white solid; yield 0.08 g (65%); mp 147–148 °C [DMSO/CH_3CN (3/1, *v*/*v*)]. Anal. Calcd. for $C_{30}H_{31}Cl_2N_3O_6S_2$ (*Mr* = 664.62): C, 54.21; N, 6.32; H, 4.70 %. Found: C, 54.18; N, 6.13 H, 4.49 %. MS (ESI) (positive ion mode): *m*/*z*: 276.09 $[C_{14}H_{14}NO_3S]^+$. ^{1}H NMR (300.130 MHz, DMSO-d_6) δ (ppm): 2.06 (CH_3CN), 4.46 and 4.47 (1H, SC<u>H</u>, *J* = 3.00 Hz), 5.51 and 5.52 (C<u>H</u>OH, *J* = 3.00 Hz), 7.21–8.46 (9H, Py and Ph), 10.19 (1H, COO<u>H</u>). ^{13}C NMR (75.468 MHz, DMSO-d_6) δ (ppm): 8.41 (<u>C</u>H_3CN), 50.02 (S<u>C</u>H), 77.25 (<u>C</u>HOH), 115.30 (CH_3<u>C</u>N), 119.95 (<u>C</u>$_{Py}$), 123.37 (<u>C</u>$_{Py}$), 127.89 (2<u>C</u>$_{Ar}$), 130.15 (2<u>C</u>$_{Ar}$), 132.23 (<u>C</u>$_{Ar}$), 137.99 (<u>C</u>$_{Ar}$CH), 140.00 (<u>C</u>$_{Py}$), 148.43 (<u>C</u>$_{Py}$), 157.09 (<u>C</u>$_{Py}$S), 174.01 (<u>C</u>OOH). IR (KBr): 1632 ν(C=N) cm^{-1}.

6: white solid; yield 0.13 g (85%); mp 187–188 °C [DMSO/CH_3CN (3/1, *v*/*v*)]. Anal. Calcd. for $C_{14}H_{13}Cl_2NO_3S$ (*Mr* = 346.23): C, 48.57; N, 4.05; H, 3.78 %. Found: C, 48.39; N, 4.00 H, 3.66 %. MS (ESI) (positive ion mode): *m*/*z*: 310.78 [*Mr*-Cl^-]$^+$. ^{1}H NMR (300.130 MHz, DMSO-d_6) δ (ppm): 4.45 and 4.46 (1H, SC<u>H</u>, *J* = 3.00 Hz), 5.52 and 5.53 (C<u>H</u>OH, *J* = 3.00 Hz), 7.13–8.42 (8H, Py and Ph), 10.24 (1H, COO<u>H</u>). ^{13}C NMR (75.468 MHz, DMSO-d_6) δ (ppm): 50.91 (S<u>C</u>H), 73.85 (<u>C</u>HOH), 120.72 (<u>C</u>$_{Py}$), 123.15 (<u>C</u>$_{Py}$), 128.00 (2<u>C</u>$_{Ar}$), 130.51 (2<u>C</u>$_{Ar}$), 131.90 (<u>C</u>$_{Ar}$–Cl), 138.43 (<u>C</u>$_{Ar}$CH), 139.34 (<u>C</u>$_{Py}$), 147.99 (<u>C</u>$_{Py}$), 156.35 (<u>C</u>$_{Py}$S), 172.83 (<u>C</u>OOH). IR (KBr): 1648 ν(C=N) cm^{-1}.

7: white solid; yield 0.10 g (60%); mp 183–184 °C [DMSO/CH_3CN (3/1, *v*/*v*)]. Anal. Calcd. for $C_{14}H_{13}ClFNO_3S$ (*Mr* = 329.77): C, 50.99; N, 4.25; H, 3.97 %. Found: C, 50.91; N, 4.13 H, 3.85 %. MS (ESI) (positive ion mode): *m*/*z*: 294.32 [*Mr*-Cl^-]$^+$. ^{1}H NMR (300.130 MHz, DMSO-d_6) δ (ppm): 4.42 and 4.43 (1H, SC<u>H</u>, *J* = 3.00 Hz), 5.55 and 5.56 (C<u>H</u>OH, *J* = 3.00 Hz), 7.31–8.40 (8H, Py and Ph), 10.35 (1H, COO<u>H</u>). ^{13}C NMR (75.468 MHz, DMSO-d_6) δ (ppm): 51.28 (S<u>C</u>H), 71.96 (<u>C</u>HOH), 123.86 (<u>C</u>$_{Py}$), 125.30 (<u>C</u>$_{Py}$), 129.92 (2<u>C</u>$_{Ar}$), 131.39 (2<u>C</u>$_{Ar}$), 132.83 (<u>C</u>$_{Ar}$-F), 140.03 (<u>C</u>$_{Ar}$CH), 141.76 (<u>C</u>$_{Py}$), 146.05 (<u>C</u>$_{Py}$), 156.13 (<u>C</u>$_{Py}$S), 171.80 (<u>C</u>OOH). IR (KBr): 1637 ν(C=N) cm^{-1}.

8: white solid; yield 0.10 g (60%); mp 174–175°C [DMSO/CH_3CN (3/1, *v*/*v*)]. Anal. Calcd. for $C_9H_{12}ClNO_3S$ (*Mr* = 249.71): C, 43.29; N, 5.61; H, 4.84 %. Found: C, 43.11; N, 5.55 H, 4.77 %. MS (ESI) (positive ion mode): *m*/*z*: 214.26 [*Mr*-Cl^-]$^+$. ^{1}H NMR (300.130 MHz, DMSO-d_6) δ (ppm): 1.42 (CH_3<u>C</u>H), 4.26 and 4.27 (1H, SC<u>H</u>, *J* = 3.00 Hz), 4.34–4.36 (C<u>H</u>OH), 7.25–8.49 (4H, Py), 9.00 (1H, COO<u>H</u>). ^{13}C NMR (75.468 MHz, DMSO-d_6) δ (ppm): 19.13 (<u>C</u>H_3CH), 43.70 (S<u>C</u>H), 73.36 (<u>C</u>HOH), 120.60 (<u>C</u>$_{Py}$), 123.44 (<u>C</u>$_{Py}$), 139.06 (<u>C</u>$_{Py}$), 147.44 (<u>C</u>$_{Py}$), 157.18 (<u>C</u>$_{Py}$S), 173.40 (<u>C</u>OOH). IR (KBr): 1653 ν(C=N) cm^{-1}.

4.3. X-ray Analysis

X-ray diffraction patterns of **1**, **5**, and **6** were collected using a Bruker SMART APEX-II CCD area detector equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at room temperature. Absorption correction was applied by SADABS [30,31]. The structure was solved by direct methods and refined on F^2 by the full-matrix least-squares method using Bruker's SHELXTL-97 [32]. All non-hydrogen atoms were refined anisotropically. The details of the crystallographic data are summarized in Table 1. Crystallographic data for the structural analysis have been deposited to the Cambridge Crystallographic Data Center (CCDC 1536797, 1536798 and 1536799 for **1**, **5**, and **6**, respectively). Copy of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/data_request/cif).

Table 1. Crystallographic data and structure refinement details for **1**, **5**, and **6**.

	1	**5**	**6**
Empirical formula	$C_{18}H_{22}ClNO_3S$	$C_{16}H_{17}ClN_2O_3S$	$C_{14}H_{13}Cl_2NO_3S$
fw	367.87	352.84	346.21
Temperature (K)	295(2)	295(2)	297(2)
Crystal System	monoclinic	triclinic	triclinic
Space group	C 2/c	P-1	P-1
a (Å)	21.1881(9)	8.0318(6)	7.8927(13)
b (Å)	7.3063(2)	9.4358(5)	9.2432(14)
c (Å)	24.64070(10)	11.0398(7)	12.1043(17)
α, °	90	79.935(5)	74.695(11)
β, °	91.942(3)	78.597(6)	82.290(13)
γ, °	90	82.607(6)	82.015(13)
V (Å^3)	3812.35(19)	803.68(9)	839.1(2)
Z	8	2	2
ρ_{calc} (g cm^{-3})	1.282	1.360	1.370
μ(Mo K$_\alpha$) (mm^{-1})	2.923	3.413	4.720
F (000)	1552	343	356
GOOF	0.984	0.969	1.007
R1[a] ($I \geq 2\sigma$)	0.0451	0.0846	0.0608
wR2[b] ($I \geq 2\sigma$)	0.1145	0.2197	0.1664

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

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