Electronic Supplementary Information

Robustness of thioamide $\{\cdots H–N–C=S\}_2$ synthon: synthesis and the effect of substituents on the formation of layered to cage-like supramolecular networks in coumarin-thiosemicarbazone hybrids

Aminah Hameed,[a] Zahid Shafiq,[a] Muhammad Yaqub,[a] Mazhar Hussain,[a] Hafiz Badar-ud-Din Ahmad,[a] Muhammad Nawaz Tahir[b] and Muhammad Moazzam Naseer[c,*]

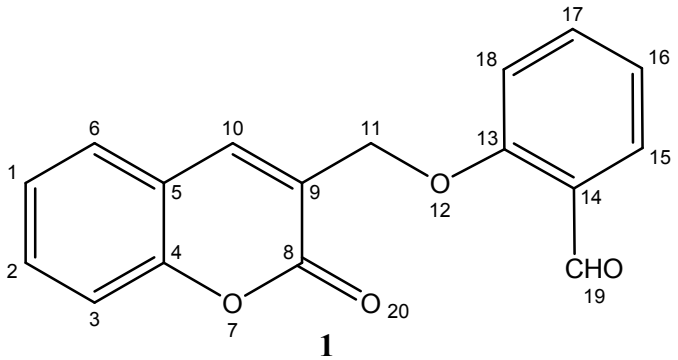
[a]*Institute of Chemical Sciences, Organic Chemistry Division, Bahauddin Zakariya University, Multan 60800, Pakistan*

[b]*Department of Physics, University of Sargodha, Sargodha, Pakistan*

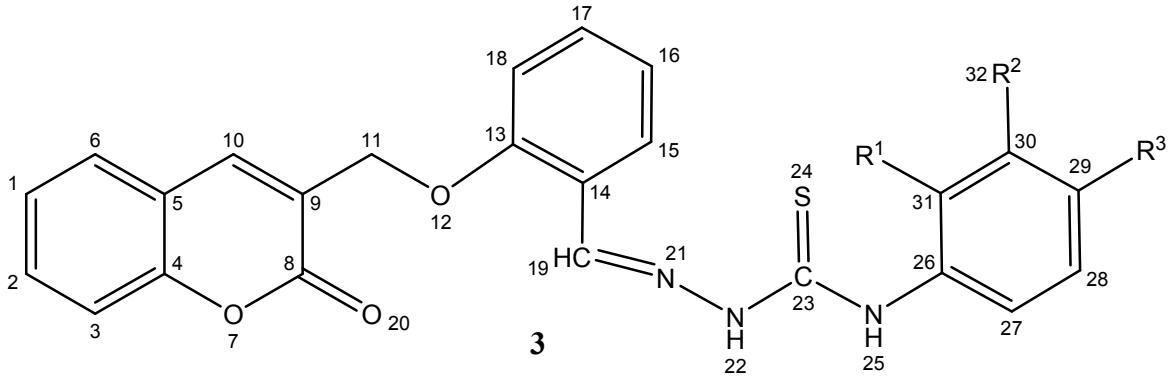
[c]*Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan*

[*]Corresponding author: Fax: +92 51 90642241. Tel.; +92 51 90642129;
E-mail: moazzam@qau.edu.pk (M.M. Naseer), zahidshafiq25@hotmail.com (Z. Shafiq)

Table of Contents



1



3

3a: R^1, R^3 = H, R^2 = CH_3

3b: R^1, R^3 = H, R^2 = OCH_3

3c: R^1, R^3 = Cl, R^2 = H

Figure S1. The atom labelling scheme for the description of ^{1}H and ^{13}C NMR chemical shift values

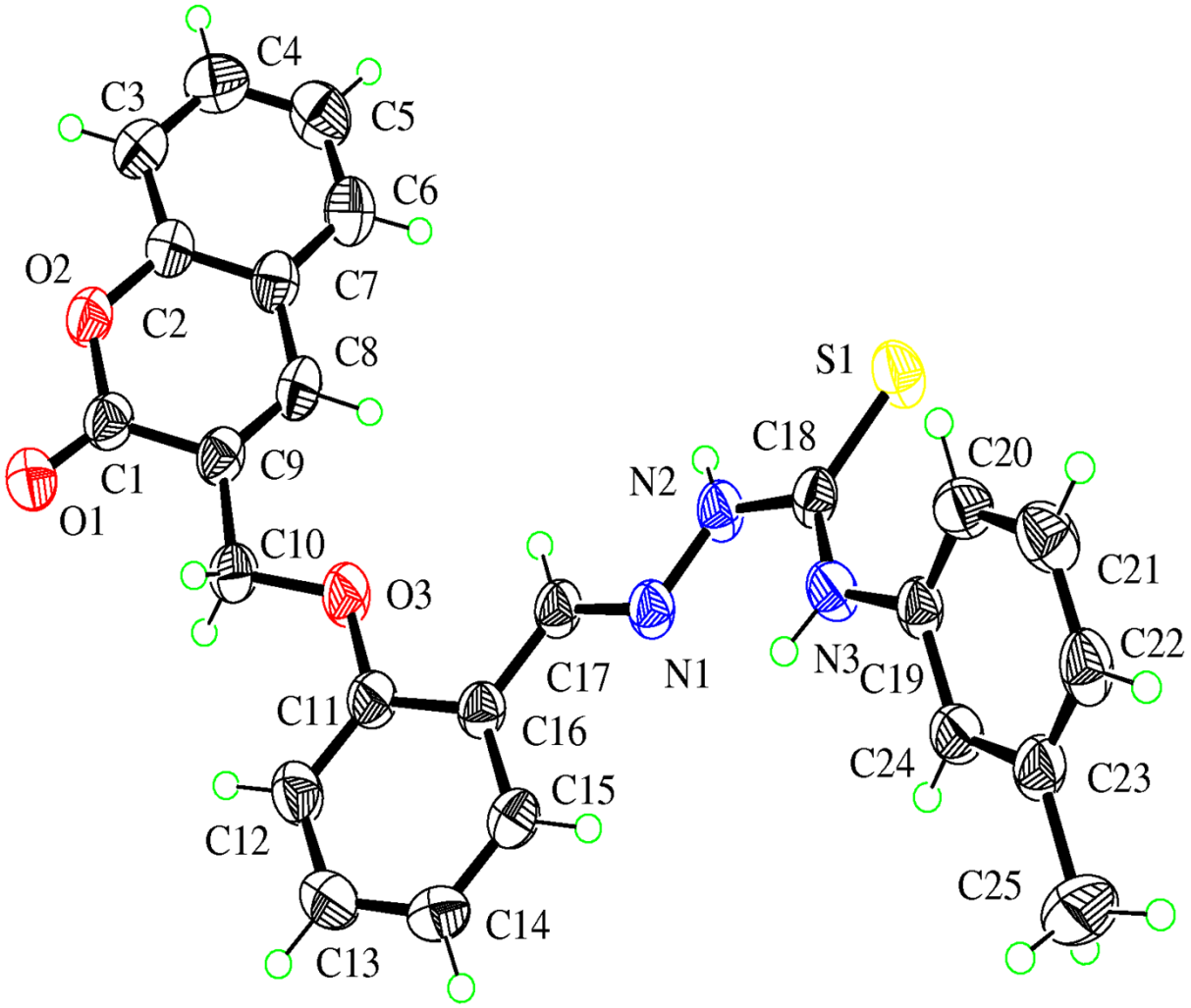


Figure S2. X-ray crystal structure (ORTEP) of compound **3a**. Selected bond lengths (Å): S(1)-C(18) 1.6810(13); O(1)-C(1) 1.2067(18); O(2)-C(1) 1.3699(17); O(2)-C(2) 1.3792(17); O(3)-C(11) 1.3747(16); O(3)-C(10) 1.4204(16); N(1)-C(17) 1.2774(16); N(1)-N(2) 1.3754(15); N(2)-C(18) 1.3574(17); N(2)-H(2) 0.8600; N(3)-C(18) 1.3394(16); N(3)-C(19) 1.4221(16); N(3)-H(3A) 0.8600. Selected bond angles (°): C(1)-O(2)-C(2) 122.12(11); C(11)-O(3)-C(10) 115.82(11); C(17)-N(1)-N(2) 117.72(11); C(18)-N(2)-N(1) 118.94(10); C(18)-N(2)-H(2) 120.5; N(1)-N(2)-H(2) 120.5; C(18)-N(3)-C(19) 130.94(11); C(18)-N(3)-H(3A) 114.5; C(19)-N(3)-H(3A) 114.5; O(1)-C(1)-O(2) 117.52(13); O(1)-C(1)-C(9) 124.60(14); O(2)-C(1)-C(9) 117.87(12); O(2)-C(2)-C(3) 116.76(12); O(2)-C(2)-C(7) 120.65(13).

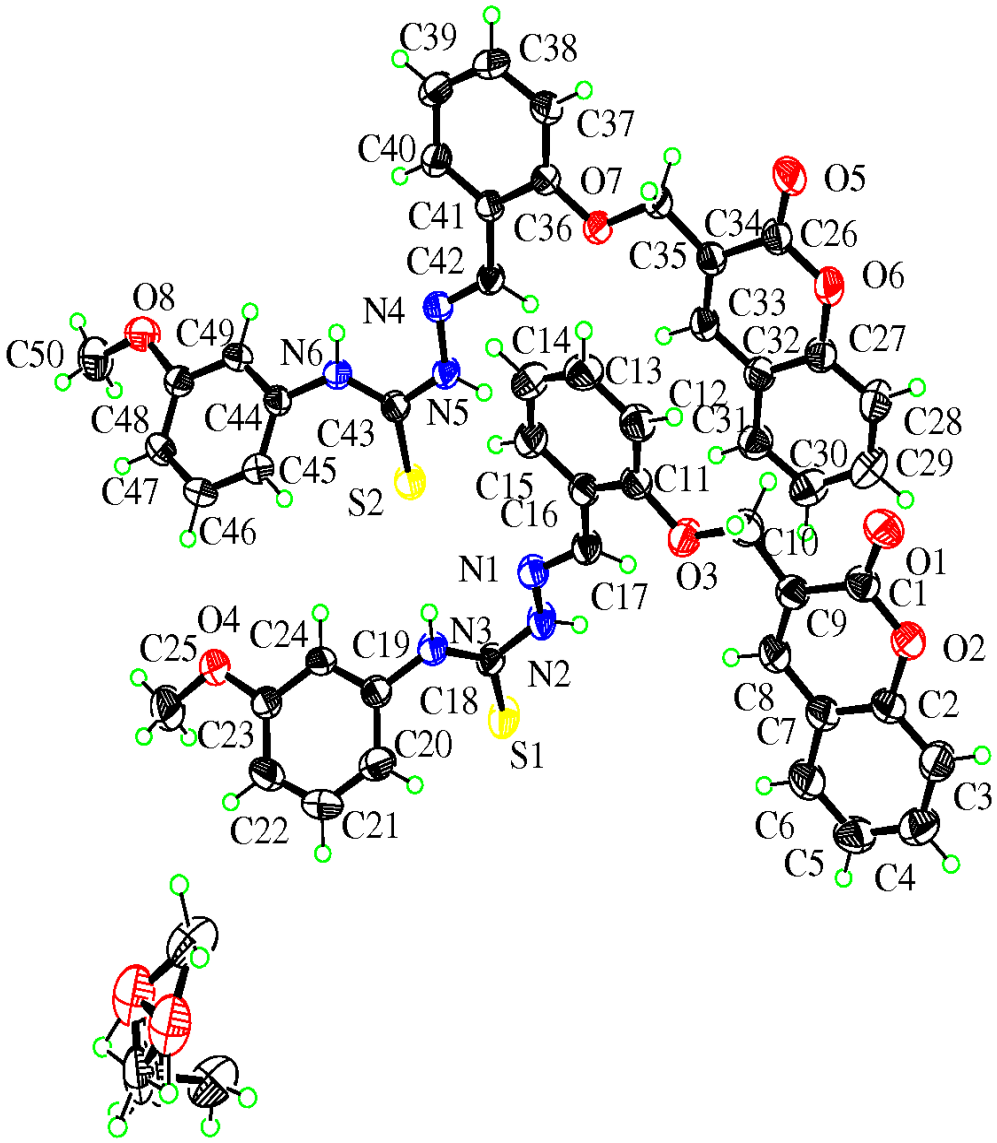


Figure S3. X-ray crystal structure (ORTEP) of compound **3b**. Selected bond lengths (Å): Conformer A = S(1)-C(18) 1.6816(18); O(1)-C(1) 1.203(2); O(2)-C(1) 1.364(2); O(2)-C(2) 1.379(2); O(3)-C(11) 1.373(2); O(3)-C(10) 1.414(2); O(4)-C(23) 1.374(2); O(4)-C(25) 1.418(3); N(1)-C(17) 1.272(2); N(1)-N(2) 1.375(2); N(2)-C(18) 1.344(2); N(2)-H(2) 0.8600; N(3)-C(18) 1.330(2); N(3)-C(19) 1.423(2); N(3)-H(3A) 0.8600; Conformer B = S(2)-C(43) 1.6807(18); O(5)-C(26) 1.209(2); O(6)-C(26) 1.366(2); O(6)-C(27) 1.384(2); O(7)-C(36) 1.369(2); O(7)-C(35) 1.416(2); O(8)-C(48) 1.371(2); O(8)-C(50) 1.416(3); N(4)-C(42) 1.274(2); N(4)-N(5) 1.3734(19); N(5)-C(43) 1.348(2); N(5)-H(5A) 0.8600; N(6)-C(43) 1.342(2); N(6)-C(44) 1.415(2); N(6)-H(6A) 0.8600. Selected bond angles (°):Conformer A = C(1)-O(2)-C(2) 121.99(15); C(11)-O(3)-C(10) 117.54(14); C(23)-O(4)-C(25) 117.59(17); C(17)-N(1)-N(2) 115.85(15); C(18)-N(2)-N(1) 120.13(15); C(18)-N(2)-H(2) 119.9; N(1)-N(2)-H(2) 119.9; C(18)-N(3)-C(19) 124.00(15); C(18)-N(3)-H(3A) 118.0; C(19)-N(3)-H(3A) 118.0; O(1)-C(1)-O(2) 117.47(18); O(1)-C(1)-C(9) 124.70(19); O(2)-C(1)-C(9) 117.81(17); C(3)-C(2)-O(2) 117.06(18);

O(2)-C(2)-C(7) 120.67(17); O(3)-C(10)-C(9) 108.45(15); O(3)-C(10)-H(10A) 110.0; O(3)-C(10)-H(10B) 110.0; O(3)-C(11)-C(12) 124.21(19); O(3)-C(11)-C(16) 115.03(16); N(1)-C(17)-C(16) 120.38(17); N(1)-C(17)-H(17) 119.8; N(3)-C(18)-N(2) 116.51(16); Conformer B = C(26)-O(6)-C(27) 121.74(15); C(36)-O(7)-C(35) 116.99(13); C(48)-O(8)-C(50) 118.31(16); C(42)-N(4)-N(5) 115.56(14); C(43)-N(5)-N(4) 121.03(14); C(43)-N(5)-H(5A) 119.5; N(4)-N(5)-H(5A) 119.5; C(43)-N(6)-C(44) 126.35(15); C(43)-N(6)-H(6A) 116.8; C(44)-N(6)-H(6A) 116.8; O(5)-C(26)-O(6) 117.13(17); O(5)-C(26)-C(34) 124.81(18); O(6)-C(26)-C(34) 118.06(16); C(28)-C(27)-O(6) 117.00(18); O(6)-C(27)-C(32) 120.77(17); O(7)-C(35)-C(34) 109.00(15); O(7)-C(35)-H(35A) 109.9; O(7)-C(35)-H(35B) 109.9; O(7)-C(36)-C(37) 124.09(17); O(7)-C(36)-C(41) 115.40(15); N(4)-C(42)-C(41) 121.00(16); N(4)-C(42)-H(42) 119.5; N(6)-C(43)-N(5) 115.71(15).

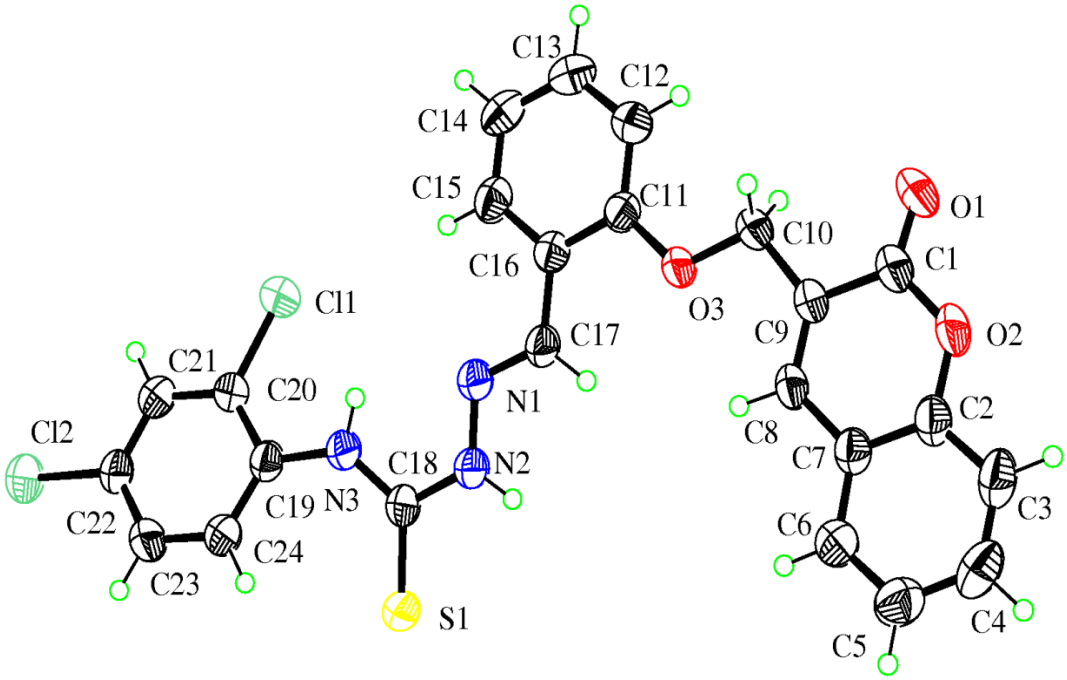


Figure S4. X-ray crystal structure (ORTEP) of compound **3c**. Selected bond lengths (Å): Cl(1)-C(20) 1.742(2); Cl(2)-C(22) 1.738(2); S(1)-C(18) 1.672(2); O(1)-C(1) 1.204(3); O(2)-C(1) 1.374(3); O(2)-C(2) 1.384(3); O(3)-C(11) 1.371(2); O(3)-C(10) 1.420(2); N(1)-C(17) 1.277(2); N(1)-N(2) 1.371(2); N(2)-C(18) 1.361(2); N(2)-H(2) 0.8600; N(3)-C(18) 1.341(2); N(3)-C(19) 1.405(2); N(3)-H(3A) 0.8600. Selected bond angles (°): C(1)-O(2)-C(2) 121.96(15); C(11)-O(3)-C(10) 116.78(14); C(17)-N(1)-N(2) 117.22(16); C(18)-N(2)-N(1) 118.81(15); C(18)-N(2)-H(2) 120.6; N(1)-N(2)-H(2) 120.6; C(18)-N(3)-C(19) 131.28(17); C(18)-N(3)-H(3A) 114.4; C(19)-N(3)-H(3A) 114.4; O(1)-C(1)-O(2) 117.68(18); O(1)-C(1)-C(9) 124.7(2); O(2)-C(1)-C(9) 117.61(18); C(3)-C(2)-O(2) 117.31(19); C(7)-C(2)-O(2) 120.56(18).

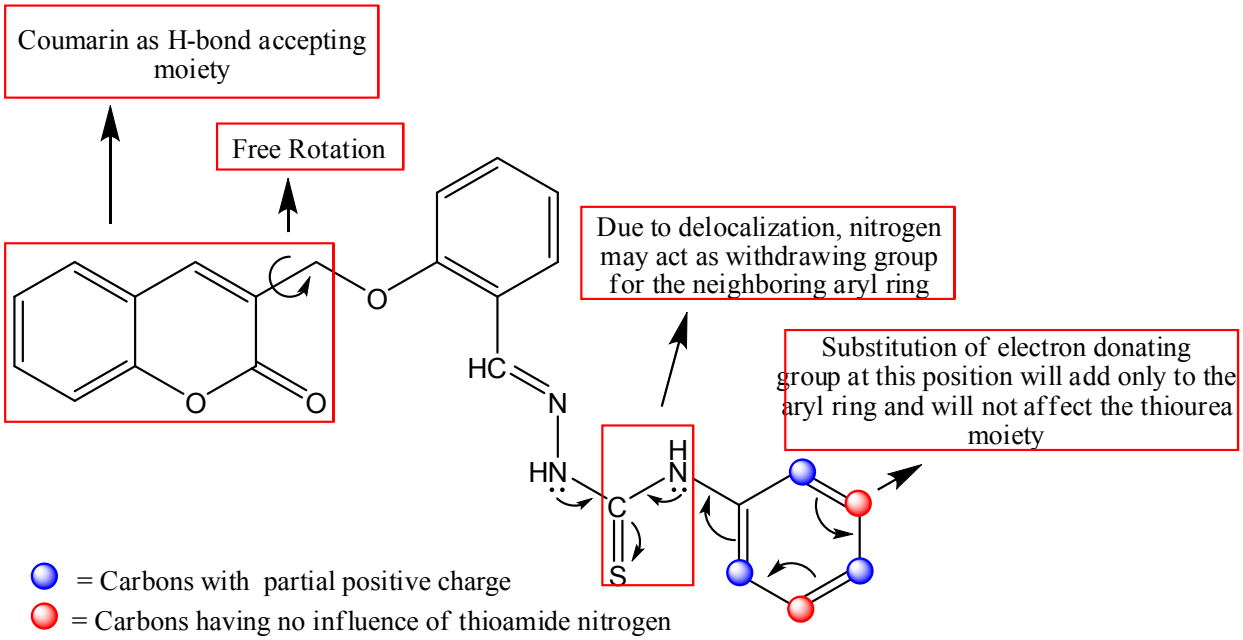


Figure S5. Showing rationale for the design of target molecules (**3a-3c**) and the electronic effect of thiamide moiety on the attached aryl ring.