New Thioureides of the 2-phenethylbenzoic Acid with Potential Antimicrobial Activity. V

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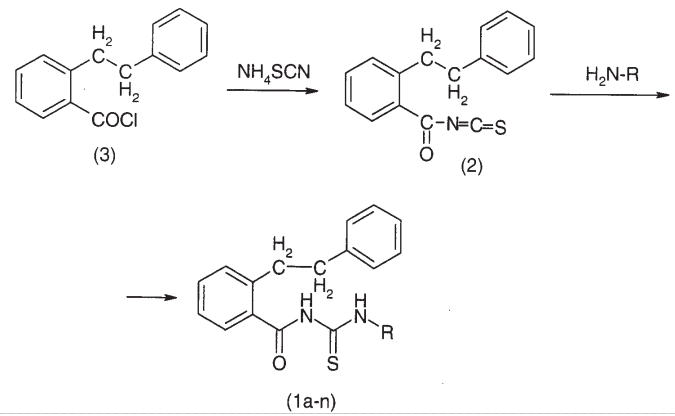
In this paper we presents the synthesis and characterization of fourteen new thioureides of the 2-phenethylbenzoic acid with potential antimicrobial activity by the addition of some primary aromatic amines to the 2-phenethylbenzoyl isothiocyanate. The elemental analysis and the NMR (^1H and ^{13}C) and IR spectroscopy data confirmed the chemical structures and the purity of the compounds.

Keywords: thioureea derivatives, 2-phenethylbenzoic acid, ^1H-NMR, ^{13}C-NMR

In therapy practice are there many substances having thioureide structure with antimicrobian, antiviral antifungal and various others pharmacological properties (anthelmintic, antidiabetic, anticonvulsivant, diuretic) [1-3]. This lead us to synthesized thioureides of the 2-phenethylbenzoic acid [4-14]. The present paper represents a continuation of our research and presents the synthesis and the characterization of new fourteen compounds belonging to this class.

Experimental part

In order to obtain the news compounds (1a-n) we used the addition of some primary aromatic amines to the 2-phenethylbenzoylisothiocyanate (2). This was obtained by the condensation of the 2-phenethylbenzoyl chloride (3) with ammonium thiocyanate in anhydrous acetone (scheme 1). The synthesis of the 2-phenethylbenzoic acid and its chloride was described in a previous paper [5].



Scheme 1. The synthesis of the new thioureides

The general synthesis of the new thioureides (1a-n)

To a solution of 0.01 mol (2.45 g) 2-phenethylbenzoylchloride in 10 mL of anhydrous acetone was added a solution of 0.01 mol (0.76 g) of ammonium thiocyanate in 10 mL anhydrous acetone.

The acetone was dried by refluxing and distiled over potassium carbonate and the ammonium thiocyanate by heating at 100°C.

The reaction mixture was refluxed for an hour, cooled at room temperature and 0.01 mol of the primary aromatic amine in 5- 10 mL dry acetone was added. After refluxing for another hour, the reaction mixture was cooled and poured into 500 mL ice water when separated the crude products.

Analytic tests

The melting points are uncorrected and were determined in open capillary tubes on an Electrothermal 9100 apparatus. The elemental analysis was effected using a Perkin Elmer CHNS/O Analyser Series II 2400 apparatus.

The NMR spectra were recorded on a Varian Unity Inova 400 instrument, at room temperature, operating at 400 MHz for ^1H and 100 MHz for ^{13}C, the new compounds were dissolved in DMSO-d_6 and tetramethylsilane was used as internal standard. The coupling constants values are reported in hertz and the splitting patterns are abbreviated as following: s(singlet), d(doublet), t(triplet), m(multiplet), b(broad).

The IR spectra were performed using a Brucker Vertex 70 apparatus.

Results and conclusions

Following the synthesis of new compounds with antimicrobial activity were synthesized fourteen thioureides of the 2-phenethylbenzoic acid. There were established the conditions in order to obtain the compound with good yields and high purity. The new compounds have been characterized by some physical properties, while the elemental analysis and the spectral parameters (IR, ^1H-NMR, ^{13}C-NMR) confirmed the chemical structures.

N-(2-Phenethylbenzoyl)-N'-(2-bromo-phenyl) thiourea: **1a; R = -$C_6H_4Br(2)$**

White, microcrystalline powder, m.p.127°-128°C (isopropanol), yield 63.3%, $C_{22}H_{19}BrN_2OS$.

^1H-NMR(dmso-d6, δ ppm, J Hz): 12.10(vbs, 2H, NH); 7.92(dd,1H, H-19, 1.5, 8.1); 7.74(dd, 1H, H-22, 1.3, 8.1); 7.54(dd, 1H, H-7, 1.4, 7.6); 7.49÷7.14(m, 10H, H-arom); 3.03(m, 2H, H-8, syst. A_2B_2); 2.87(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 180.17(C-16); 171.02(C-1); 141.41(Cq); 139.89(Cq); 133.92(Cq); 119.22(Cq); 132.70(CH); 131.00(CH); 130.06(CH); 128.72(CH); 128.59(CH); 128.37(C-12-14); 128.32(C-11-15); 128.15(CH); 127.92(CH); 126.01(CH); 125.95(CH); 37.40 (C-8); 35.33(C-9).

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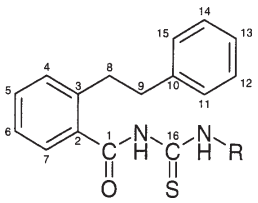
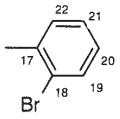
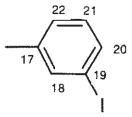
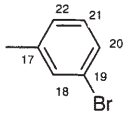
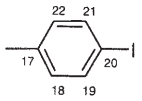
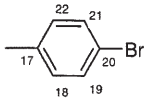
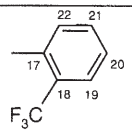
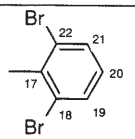
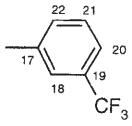
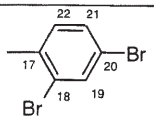
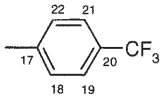
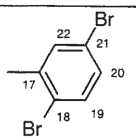
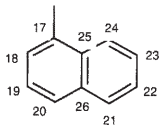
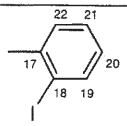
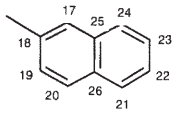
Table 1
THE STRUCTURE OF THE COMPOUNDS (1a-n) AND THE NOTATIONS USED FOR THE PROTONS CHEMICAL SHIFTS ASSIGNMENT



Compound	R	Compound	R
1a		1h	
1b		1i	
1c		1j	
1d		1k	
1e		1l	
1f		1m	
1g		1n	

FT-IR(ATR in solid, ν cm^{-1}): 3212m; 3058m; 3023m; 2923w; 2869w; 1673ms; 1599w; 1574m; 1527vs; 1457m; 1440s; 1322m; 1286m; 1249s; 1161s; 1117m; 1062w; 1025w; 958w; 863w; 843w; 791w; 764w; 741m; 717m; 692s; 659m; 613w; 524m; 477w; 445w.

Calculated %: C 60.14; H 4.36; N 6.38; S 7.30. Experimental %: C 60.29; H 4.35; N 6.41; S 7.34.

N-(2-Phenethylbenzoyl)-N'-(3-bromo-phenyl) thiourea: **1b; R = -$C_6H_4Br(3)$**

White, microcrystalline powder, m.p.102°-103°C (isopropanol), yield 62.6%, $C_{22}H_{19}BrN_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.50(vbs, 2H, NH); 8.08(t, 1H, H-18, 1.8); 7.62(dt, 1H, H-20, 8.1, 1.8); 7.53(dd, 1H, H-7, 1.4, 7.6); 7.49÷7.14(m, 10H, H-arom); 3.03(m, 2H, H-8, syst. A_2B_2); 2.87(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 179.20(C-16); 170.67(C-1); 141.40(Cq); 139.97(Cq); 139.71(Cq); 133.96(Cq), 121.01(Cq); 130.96(CH); 130.60(CH); 130.00(CH); 128.92(CH); 128.39(C-12-14); 128.31(C-11-15); 126.27(CH); 126.84(CH); 125.98(CH); 125.89(CH); 123.52(CH); 37.20 (C-8); 34.99(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3167m; 3024m; 2962m; 2863w; 1675s; 1587m; 1522vs; 1470s; 1446s; 1425m; 1333s; 1296m; 1257s; 1167s; 1064m; 993m; 951w; 865w; 796w; 774m; 683s; 662m; 642w; 584w; 561w; 539w; 511w; 480w; 453w; 433w.

Calculated %: C 60.14; H 4.36; N 6.38; S 7.30. Experimental %: C 59.98; H 4.25; N 6.41; S 7.24.

N-(2-Phenethylbenzoyl)-N'-(4-bromo-phenyl) thiourea: **1c; R = -$C_6H_4Br(4)$**

White, microcrystalline powder, m.p.162°-163°C (isopropanol), yield 61.5%, $C_{22}H_{19}BrN_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.50(vbs, 2H, NH); 7.69(d, 2H, H-19-21, 8.8); 7.61(d, 2H, H-18-22, 8.8); 7.52(dd, 1H, H-7, 1.4, 7.6); 7.45(td, 1H, H-13, 7.6, 1.5); 7.33(t, 2H, H-12-14, 7.6); 7.30÷7.14(m, 5H, H-arom); 3.03(m, 2H, H-8, syst. A_2B_2); 2.88(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 179.07(C-16); 170.67(C-1); 141.38(Cq); 139.94(Cq); 137.49(Cq); 134.94(Cq); 118.45(Cq); 131.53(CH); 130.96(CH); 129.99(CH); 128.38(C-12-14); 128.32(C-11-15); 128.27(CH); 126.44(CH); 125.98(CH); 125.89(CH); 37.20 (C-8); 34.99(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3156m; 3025m; 2956w; 2933m; 2864w; 1673s; 1587m; 1525vs; 1486s; 1454m;

1333s; 1251s; 1067m; 1042w; 1007w; 943w; 884w; 863w; 841w; 826w; 813w; 752m; 726m; 699s; 676m; 650w; 622w; 608w; 580w; 526w; 499w.

Calculated %: C 60.14; H 4.36; N 6.38; S 7.30. Experimental %: C 60.01; H 4.39; N 6.21; S 7.39.

N-(2-Phenethylbenzoyl)-N'-(2,6-dibromo-phenyl) thiourea: **1d; R = -$C_6H_3Br_2$(2,6)**

White, microcrystalline powder, m.p.181°-182°C (n-butanol), yield 77.8%, $C_{22}H_{18}Br_2N_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.10(bs, 2H, NH); 7.74 (d, 2H, H-19-21, 8.3); 7.52(dd, 1H, H-7, 1.3, 7.6); 7.47(td, 1H, H-13, 1.5, 7.6); 7.38÷7.15(m, 8H, H-arom); 3.03(m, 2H, H-8, syst. A_2B_2); 2.86(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 180.39(C-16); 170.68(C-1); 141.34(Cq); 139.63(Cq); 134.18(Cq); 134.08(Cq); 124.04(Cq); 132.25(CH); 130.91(CH); 130.49(CH);

130.03(CH); 128.38(CH); 128.36(C-11-15); 128.29(C-12-14); 127.87(CH); 126.00(CH); 37.31 (C-8); 35.29(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3125m; 3020m; 2931m; 2863m; 1669s; 1599w; 1509vs; 1488vs; 1448s; 1432s; 1319m; 1257m; 1200m; 1153vs; 1064m; 951m; 864w; 842w; 768m; 746m; 721m; 696m; 656w; 612w; 570w; 523w; 451w.

Calculated %: C 50.99; H 3.50; N 5.41; S 6.19. Experimental %: C 60.17; H 3.54; N 5.38; S 6.26.

N-(2-Phenethylbenzoyl)-N'-(2,4-dibromo-phenyl) thiourea: **1e; R = -$C_6H_3Br_2$(2,4)**

White, microcrystalline powder, m.p.165°-166°C (isopropanol), yield 69.0%, $C_{22}H_{18}Br_2N_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.46(s, 1H, NH); 12.02(s, 1H, NH); 8.00(d, 1H, H-19, 2.2); 7.89(d, 1H, H-22, 8.6); 7.67(dd, 1H, H-21, 2.2, 8.6); 7.52(dd, 1H, H-7, 1.4, 7.7); 7.45(td, 1H, H-5,1.4, 7.7); 7.37÷7.22(m, H-arom); 7.18(tt, 1H, H-13, 1.2, 7.6); 3.04(m, 2H, H-8, syst. A_2B_2); 2.89(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 180.35(C-16); 170.89(C-1); 141.36(Cq); 139.93(Cq); 136.66(Cq); 134.60(C-19), 133.74(Cq); 131.56(C-5); 130.92(C-21); 130.28(C-22); 130.05(CH); 128.35(CH); 128.30(CH); 128.17(CH); 126.00(CH); 125.93(CH); 120.59(Cq); 119.93(Cq); 37.33 (C-8); 35.21(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3227m; 3080m; 2966m; 2928m; 2868w; 1671s; 1684s; 1600w; 1561m; 1517vs; 1453s; 1374m; 1317m; 1261m; 1243m; 1163w; 1115s; 1079w; 1060w; 1041m; 942w; 758m; 736w; 710m; 692m; 648w; 526w.

Calculated %: C 50.99; H 3.50; N 5.41; S 6.19. Experimental %: C 51.08; H 3.56; N 5.38; S 6.28

N-(2-Phenethylbenzoyl)-N'-(2,5-dibromo-phenyl) thiourea: **1f; R = -$C_6H_3Br_2$(2,5)**

White, microcrystalline powder, m.p.163°-163,5°C (isopropanol), yield 75.0%, $C_{22}H_{18}Br_2N_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.56(s, 1H, NH); 12.06(s, 1H, NH); 8.22(d, 1H, H-22, 2.2); 7.70(d, 1H, H-19, 8.6); 7.46(dd, 1H, H-20, 2.2, 8.6); 7.52(dd, 1H, H-7, 1.4, 7.7); 7.45(td, 1H, H-5, 1.4, 7.7); 7.37÷7.22(m, H-arom); 7.18(tt, 1H, H-13, 1.2, 7.6); 3.05(m, 2H, H-8, syst. A_2B_2); 2.89(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 180.26(C-16); 170.82(C-1); 141.28(Cq); 139.88(Cq); 138.37(Cq); 133.59(Cq), 131.14(C-5); 131.00(CH); 130.95(CH); 129.97(CH); 128.27(CH); 128.20(CH); 128.10(CH); 125.90(CH); 125.84(CH); 119.79(Cq); 118.47(Cq); 37.25 (C-8); 35.13(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3078m; 3058m; 3017m; 2997w; 2920w; 2872w; 1679s; 1600w; 1578w; 1563m; 1514vs; 1455m; 1395m; 1313m; 1267m; 1244m; 1160s; 1134m; 1080m; 1061m; 1032m; 954w; 804w; 756m; 692m; 661w; 638w; 529w.

Calculated %: C 50.99; H 3.50; N 5.41; S 6.19. Experimental %: C 50.90; H 3.48;N 5.44; S 6.07

N-(2-Phenethylbenzoyl)-N'-(2-iodophenyl)thiourea: **1g; R = -C_6H_4I(2)**

White, microcrystalline powder, m.p.137°-138°C (isopropanol), yield 47.5%, $C_{22}H_{19}IN_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.36(s, 1H, NH); 12.00(s, 1H, NH); 7.95(dd, 1H, H-19, 1.2, 7.6); 7.70(dd, 1H, H-22, 1.5, 7.3); 7.54(dd, 1H, H-7, 1.4, 7.6,); 7.51÷7.14(m, 9H, H-arom); 7.10 (td, 1H, H-20, 1.5, 7.6); 3.06(m, 2H, H-8, syst. A_2B_2); 2.90(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 180.44(C-16); 171.85(C-1); 141.27(Cq); 140.23(Cq); 139.78(Cq); 133.80(Cq); 97.25(C-18), 138.88(CH); 130.92(CH); 129.99(CH);

128.93(CH); 128.84(CH); 128.58(CH); 128.35(C-12-14); 128.25(C-11-15); 128.03(CH); 125.91(CH); 125.87(CH); 37.25 (C-8); 35.13(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3189m; 3058m; 3017m; 2926m; 2866w; 1684s; 1601w; 1568w; 1517vs; 1455m; 1437m; 1317m; 1244m; 1163s; 1112m; 1061w; 1015w; 955w; 826w; 842w; 742m; 714m; 694m; 661m; 609w; 568w; 527w; 465w; 439w.

Calculated %: C 54.33; H 3.94; N 5.76; S 6.59. Experimental %: C 54.09; H 4.02;N 5.79; S 6.66.

N-(2-Phenethylbenzoyl)-N'-(3-iodophenyl)thiourea: **1h; R = -C_6H_4I(3)**

White, microcrystalline powder, m.p.105°-106°C (isopropanol), yield 66.1%, $C_{22}H_{19}IN_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.48(s, 1H, NH); 11.86(s, 1H, NH); 8.19(t, 1H, H-18, 1.9); 7.66(dt, 1H, H-21, 1.9, 8.2); 7.53(dd, 1H, H-7, 1.4, 7.6); 7.46(td, 1H, H-13, 1.5, 7.4); 7.34(t, 2H, h-12-14, 7.4); 7.32÷7.13(m, 7H, H-arom); 3.03(m, 2H, H-8, syst. A_2B_2); 2.87(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 179.18(C-16); 170.44(C-1); 141.27(Cq); 139.85(Cq); 139.28(Cq); 133.75(Cq), 93.70(Cq); 134.80(Cq); 132.62(CH); 130.87(CH); 130.49(CH); 129.88(CH); 128.27(C-12-14); 128.20(CH); 128.19(C-11-15); 128.13(CH); 125.86(CH); 125.78(CH); 37.09 (C-8); 34.86(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3169m; 3023m; 2960w; 2920w; 2861w; 1676s; 1582s; 1551m; 1522vs; 1468m; 1446s; 1420m; 1333s; 1296m; 1257s; 1166s; 1063m; 1040w; 991w; 890w; 861w; 794w; 774m; 744s; 693m; 681m; 661m; 644m; 611m; 584w; 561w; 538w; 511w; 479w; 452w; 427w.

Calculated %: C 54.33; H 3.94; N 5.76; S 6.59. Experimental %: C 54.44; H 3.88; N 5.82; S 6.53.

N-(2-Phenethylbenzoyl)-N'-(4-iodophenyl)thiourea: **1i; R = -C_6H_4I(4)**

White, microcrystalline powder, m.p.148°-149°C (isopropanol), yield 54.3%, $C_{22}H_{19}IN_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.50(s, 1H, NH); 11.84(s, 1H, NH); 7.77(d, 2H, H-18-22, 8.8); 7.56(d, 2H, H-18-22, 8.8); 7.52(dd, 1H, H-7, 1.4, 7.6); 7.46(td, 1H, H-13, 1.5, 7.6); 7.34(t, 2H, H-12-14, 7.6); 7.31÷7.14(m, 5H, H-arom); 3.03(m, 2H, H-8, syst. A_2B_2); 2.88(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 178.88(C-16); 170.46(C-1); 141.23(Cq); 139.80(Cq); 137.76(Cq); 137.27(C-19-21); 133.74(Cq); 90.92(C-20); 131.83(CH); 129.83(CH);

128.22(C-12-14); 128.17(C-11-15); 128.11(CH); 126.37(C-18-22); 125.82(CH); 125.73(CH); 37.04 (C-8); 34.82(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3150m; 3049m; 3023m; 2956w; 2930w; 2864w; 1672s; 1581m; 1524vs; 1482s; 1453m; 1393m; 1332s; 1251s; 1168s; 1115w; 1060w; 1003w; 941w; 884w; 862w; 840w; 813w; 753m; 726m; 697s; 674m; 648m; 621w; 604w; 576w; 526w; 497w; 473w.

Calculated %: C 54.33; H 3.94; N 5.76; S 6.59. Experimental %: C 54.19; H 3.97; N 5.75; S 6.63.

N-(2-Phenethylbenzoyl)-N'-(2-trifluoro-methylphenyl)thiourea: **1j ; R= -C_6H_4-CF_3(2)**

White, microcrystalline powder, m.p.93°-96°C (isopropanol), yield 50.0%, $C_{23}H_{19}F_3N_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.59(s, 1H, NH); 12.12(s, 1H, NH); 7.80÷7.86(m, 2H, H-7, H-19); 7.76(td, 1H, H-5, 1.4, 7.7); 7.15÷7.59(m, 10H, H-arom); 3.01(m, 2H, H-8, syst. A_2B_2); 2.86(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 181.59(C-16); 171.40(C-1); 141.42(Cq); 139.90(Cq); 135.90(Cq); 133.70(Cq); 132.93(CH); 132.17(CH); 130.94(CH); 130.19(CH); 128.34(CH); 128.33(CH); 128.18(CH); 127.90(CH); 126.31(q, C-19, 4J(19F-13C) = 5.0 Hz); 126.08(CH); 126.04(CH); 124.59(q, C-18, 2J(19F-13C) = 29.5 Hz); 123.55(q, C-23, J(19F-13C) = 271.8 Hz); 37.53 (C-8); 35.53(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3180w; 3026w; 1680mm; 1586m; 1523s; 1458m; 1318s; 1285s; 1255s; 1179s; 1149s; 1113vs; 1058s; 1036s; 955w; 862w; 758vs; 732vs; 694vs; 665m; 652m; 620m; 593w; 571w; 526w; 473w; 437w.

Calculated %: C 64.47; H 4.47; N 6.54; S 7.48. Experimental %: C 64.53; H 4.49; N 6.42; S 7.43.

N-(2-Phenethylbenzoyl)-N'-(3-trifluoro-methyl phenyl)thiourea: **1k ; R = -C_6H_4- CF_3(3)**

White, microcrystalline powder, m.p.90°-91°C (isopropanol), yield 64.7%, $C_{23}H_{19}F_3N_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.58(s, 1H, NH); 11.92(s, 1H, NH); 8.21(bs, 1H, H-18); 7.86(dt, 1H, H-20, 7.2, 2.1); 7.67(t, 1H, H-21, 7.2); 7.62(m, 1H, H-22); 7.55(d, 2H, H-18-22, 8.8); 7.46(td, 1H, H-13, 1.5, 7.6); 7.33(t, 2H, H-12-14, 7,6); 7.31÷7.14(m, 4H, H-arom); 3.05(m, 2H, H-8, syst. A_2B_2); 2.89(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 179.56(C-16); 170.41(C-1); 141.28(Cq); 139.88(Cq); 138.79(Cq); 133.75(Cq); 131.62(q, C-19, 2J(^{19}F-^{13}C) = 31.5 Hz); 124.35(q, CF_3, J(^{19}F-^{13}C) = 270.5 Hz); 130.91(CH); 129.90(CH); 129.77(CH); 128.63(CH); 128.49(CH); 128.28(C-12-14); 128.18(C-11-15); 125.86(CH); 125.80(CH); 122.72(q, CH); 121.05(q, CH); 37.08 (C-8); 34.83(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3244w; 3140w; 3062w; 3026w; 2925w; 1595m; 1559s; 1503vs; 1450s; 1332s; 1311m; 1242s; 1173w; 1146m; 1113s; 1062m; 1000w; 966w; 914w; 882w; 802m; 778w; 756m; 730m; 698m; 679m; 637w; 598m; 559w; 524m; 451w; 425w.

Calculated %: C 64.47; H 4.47; N 6.54; S 7.48. Experimental %: C 64.39; H 4.52; N 6.55; S 7.51.

N-(2-Phenethylbenzoyl)-N'-(4-trifluoro-methylphenyl)thiourea: **1l ; R = -C_6H_4 -CF_3(4)**

White, microcrystalline powder, m.p.129°-131°C (isopropanol), yield 56.0%, $C_{23}H_{19}F_3N_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 11.91(s, 2H, NH); 7.99(dl,2H, H-19, H-21, 8.5); 7.53(dd, 1H, H-7, 1.2, 7.4); 7.80(d, 2H, H-18, H-22, 8.5); 7.54(dd, 1H, H-7, 1.4, 7.9); 7.47(td, 1H, H-5, 1.4, 7.9); 7.34(d, 2H,H-12, H-14, 8.5); 7.36÷7.14(m, 5H, H-arom); 3.05(m, 2H, H-8, syst. A_2B_2); 2.88(m, 2H, H-9, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 179.43(C-16); 170.68(C-1); 141.75(Cq); 141.44(Cq); 140.07(Cq); 133.85(Cq), 128.37(q, C-19, J(^{19}F-^{13}C) = 30.5 Hz); 122.31 (q, C-23, J(^{19}F-^{13}C) = 272.8 Hz);131.15(CH); 130.10(CH); 128.46(CH); 128.40(CH);

126.55(CH); 126.07(CH); 125.99(CH); 125.88(CH); 124.78(CH); 37.28 (C-8); 35.05(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3134m; 3063m; 3029m; 1670m; 1608w; 1527vs; 1505vs; 1456m; 1409w; 1315vs; 1261m; 1151vs; 1119vs; 1104s; 1061vs; 1016m; 867w; 848w; 797w; 736s; 702m; 671m; 653m; 618w; 592w; 527w.

Calculated %: C 64.47; H 4.47; N 6.54; S 7.48. Experimental %: C 64.55; H 4.45; N 6.39; S 7.40

N-(2-Phenethylbenzoyl)-N'-(1-naphthyl)thiourea: **1m; R = 1-$C_{10}H_7$**

White, microcrystalline powder, m.p.157°-158°C (isopropanol), yield 78.0%, $C_{26}H_{22}N_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.61(s, 1H, NH); 12.03(s, 1H, NH); 8.12÷7.84(m, 3H, H-naphtyl); 7.64÷7.16(m, 13H, H-arom); 3.10(t, 2H, H-18, 7.8); 2.94(m, 2H, H-8, syst. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 180.95(C-16); 168.15(C-1); 141.50(Cq); 139.94(Cq); 134.22(Cq); 134.02(Cq), 133.79(Cq); 128.67(Cq); 130.99(CH); 130.05(CH);

128.38(CH); 128.36(CH); 128.31(CH); 128.26(CH); 127.43(CH); 126.73(CH); 126.40(CH); 126.04(CH); 125.94(CH); 125.55(CH); 124.71(CH); 122.10(CH); 37.46(C-8); 35.35(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3165m; 3022m; 2867w; 1675s; 1597w; 1527vs; 1455m; 1395w; 1327m; 1264m; 1179s; 1151m; 1114w; 1063w; 1034w; 952w; 759s; 720m; 695m; 649w; 527w.

Calculated %: C 76.07; H 5.40; N 6.82; S 7.81. Experimental %: C 75.90; H 5.43; N 6.64; S 7.80

N-(2-Phenethylbenzoyl)-N'-(2-naphthyl)thiourea: **1n; R = 2-$C_{10}H_7$**

White, microcrystalline powder, m.p.144°C (isopropanol), yield 79.0%, $C_{26}H_{22}N_2OS$.

^{1}H-NMR(dmso-d6, δ ppm, J Hz): 12.72(s, 1H, NH); 11.85(s, 1H, NH); 8.35(d,1H, H-17, 1.1); 7.97(d, 1H, H-20, 8.8); 7.95(m, 1H, H-24); 7.79(dd, 1H, H-19, 1.2, 8.8); 7.58(m, 1H, H-naphtyl); 7.51(dd, 1H, H-7, 1.4, 7.5); 7.46(td, 1H, H-5, 1.4, 7.30; 7.37÷7.16(m, H-arom); 2.96(m, 2H, H-8, syst. A_2B_2); 2.84(m, 2H, H-9, sist. A_2B_2).

^{13}C-NMR(dmso-d6, δ ppm): 179.17(C-16); 170.73(C-1); 141.33(Cq); 139.87(Cq); 135.57(Cq); 133.89(Cq), 132.88(Cq); 131.30(Cq); 130.91(CH); 129.92(CH);

128.32(CH); 128.26(CH); 128.22(CH); 128.13(CH); 127.71(CH); 127.52(CH); 126.53(CH); 126.01(CH); 125.92(CH); 125.84(CH); 123.77(C-19); 121.57(C-17); 37.3(C-8); 34.94(C-9).

FT-IR(ATR in solid, ν cm^{-1}): 3150m; 3080m; 3043m; 3020m; 2961m; 2921m; 2861m; 1674s; 1582m; 1558s; 1532vs; 1447s; 1335s; 1262s; 220w; 1164s; 1063w; 952w; 890w; 857w; 804m; 743s; 693s; 635m; 608m; 443m.

Calculated %: C 76.07; H 5.40; N 6.82; S 7.81. Experimental %: C 76.19; H 5.37;N 6.80; S 7.93.

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