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Article

Isothioureas, Ureas, and Their *N*-Methyl Amides from 2-Aminobenzothiazole and Chiral Amino Acids

Supplementry material

Table S1. Complementary data of SMe-isothiourea carboxylates **5a–f** and their methyl esters **8a–f**.

Compound	Yield (%)	Physical Appearance	M. P. (°C)	IR (cm^{-1})	$[\alpha]^{d}_{20}$ (g/mL)*	Elemental Analysis Found (Calculated)		
						C	H	N
5a.3H_2O	95	White powder	210 (dc)	3469 1643, 1548	-----	36.60 (36.97)	3.18 (2.80)	12.17 (16.76)
5b.2H_2O	81.4	Ionic liquid	-----	3488 1710, 1594	+77° ($1.87x10^{-2}$)	41.28 (40.79)	4.30 (3.39)	11.86 (11.90)
5c.1/2H_2O	86	White powder	250 (dc)	3480 1614, 1550	+194° (2.64x10-2)	53.29 (52.57)	3.30 (3.61)	11.25 (10.82)
5d.3.5H_2O	62	White powder	------	3482 1745, 1592	-12° ($2.07x10^{-2}$)	47.04 (47.36)	4.80 (3.51)	9.08 (9.21)
5e.H_2O	67	Ionic liquid	------	3475 1738, 1560	------	48.69 (46.36)	4.63 (5.03)	12.17 (11.62)
5f.1.5H_2O	65	Ionic liquid	------	3486 1743, 1557	------	50.14 (47.32)	5.014 (5.49)	11.70 (10.95)
8a	83	White crystals	145-146	3474, 1745, 1551	-----	49.10 (48.81)	4.14 (4.40)	14.46 (14.23)
8b	80	White crystals	100-101	3446 1731, 1586	+147° ($1.93x10^{-2}$)	51.04 (50.32)	4.76 (4.83)	13.14 (13.54)
8c	75	White crystals	133-134	3470 1740, 1548	+260° ($1.42x10^{-2}$)	57.86 (58.22)	4.18 (4.58)	11.04 (11.32)
8d	56	White crystals	84-85	3466 1745, 1554	-34° ($2.73x10^{-2}$)	59.91 (59.22)	4.84 (4.93)	10.95 (10.91)
8e	49	Viscous liquid	----	3472 1738, 1560	-62° $2.06x10^{-2}$	53.41 (53.18)	5.63 (5.72)	12.46 (12.08)
8f	51	Viscous liquid	----	3457, 1567	+183° $2.57x10^{-2}$	54.70 (54.89)	5.98 (5.82)	11.96 (11.89)

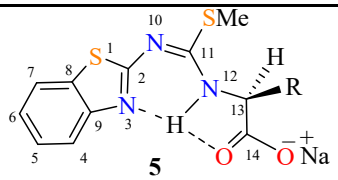
*For compounds 5b–d, ethanol was used and for compounds 8b–d, chloroform was used.

Table S2. X-ray crystal data of compounds **8a**, **8b**, **8c**, and **13f**.

Compound	8a	8b	8c	13f
Unit Cell				
Cell axes [Å], a	8.0071(2)	7.4317(4)	37.7609(10)	9.1259(7)
b	22.7687(6)	8.5528(5)	8.3648(3)	7.1737(5)
c	8.3736(2)	12.1825(5)	5.7818(2)	14.8854(10)
Cell angles, α	90.000(0)	90.000(0)	90.000(0)	90.000(0)
β	115.327(1)	97.806(4)	90.000(0)	98.254(7)
γ	90.000(0)	90.000(0)	90.000(0)	90.000(0)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	P 2_1/c	P 2_1	P 2_1 2_1 2	P 2_1
Molecular Formula	$C_{12}H_{13}N_3O_2S_2$	$C_{12}H_{14}N_2S_2O_2$	$C_{18}H_{17}N_3O_2S_2$	$C_{17}H_{23}N_3O_2S_2$
Density (g cm^{-1})	1.42	1.34	1.35	1.26

Formula weight	295.4	309.4	371.5	365.5
No. Form. Units Z	4	2	4	2
Reflection Data				
No. Meas.	69781	12823	11370	34167
No. Uniq.	3699	3790	3698	5060
No. Obs.	3100	3099	3472	2485
Current Refinement				
No. Refln.	3699	3790	3698	5060
No. Param.	172	182	226	218
Delta-rho (eÅ^{-3}] max, min	0.290, -0.176	0.180, -0.133	0.197, -0.171	0.180, -0.231
R_all, R_obs	0.051, 0.039	0.050, 0.036	0.040, 0.036	0.137, 0.050
wR2_all, wR2_obs	0.111, 0.101	0.086, 0.078	0.100, 0.097	0.144, 0.110

Table S3. ^{1}H NMR data of compounds **5a–f** (DMSO-d_6).



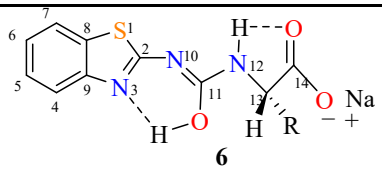
5

Comp.	H4	H5	H6	H7	N12H	SMe	C13H	R
5a	7.76 (d, 7.1)	7.32 (t, 7.6)	7.17 (t,7.2)	7.63 (d, 8.2)	10.66 (br)	2.44 (s)	3.62 (d, 3.8)	3.63 (d, 3.8)
5b	7.75 (d, 7.9)	7.31 (t, 7.6)	7.15 (t, 7.3)	7.63 (d, 8.0)	10.95 (d, 5.6)	2.42 (s)	3.91 (q, 7.6)	1.38 (d, 6.8)
5c	7.80 (d, 7.6)	no ob	no ob	7.63 (d, 7.9)	11.42 (d, 6.2)	2.31 (s)	4.78 (d, 6.2)	7.2-7.3 (m)
5d	7.76 (d, 7.9)	7.32 (t, 7.5)	no ob	7.54 (d, 7.9)	10.74 (d, 5.8)	2.36 (s)	4.12 (d, 3.8)	7.2, 3.14 (m, ddd, 13.6, 6.5, 5.0)
5e	7.77 (d, 7.0)	7.32 (d, 8.2, 7.0)	7.17 (d, 7.0, 7.6))	7.55 (d, 8.2)	10.87 (d, 8.8)	2.42 (s)	3.81 (dd, 4.1, 4.7, 3.5)	2.2, 0.9, 1.0 (m, d, d, 7.0)
5f	7.77 (d, 7.0)	7.31 (t, 7.6, 5.5)	7.17 8d, 7.6, 4.1)	7.57 (d, 8.2)	10.86 (d, 8.2)	2.35 (s)	3.90 (m)	1.66, 1.6, 0.92, 0.87 (m, m, d,d, 7.1, 6.4)

Table S4. ^{13}CNMR data of compounds **5a–f** (DMSO-d_6).

Comp.	C2	C4	C5	C6	C7	C8	C9	C11	SCH_3	C13	C14	R
5a	163.6	126.1	123.4	121.6	120.4	132.9	151.8	171.6	14.1	48.1	169.7	----
5b	163.2	126.1	123.5	121.5	120.6	131.8	151.7	174.0	14.1	55.1	171.6	20.7
5c	163.6	126.1	123.5	121.7	120.6	131.9	151.9	171.3	14.1	63.9	169.8	139.7
5d	164.4	126.1	123.5	121.6	120.4	131.6	151.6	172.5	14.0	61.2	171.3	56.5
5e	164.4	126.1	123.4	121.6	120.3	131.6	151.6	172.9	14.0	65.3	171.6	31.9, 19.9, 18.7
5f	163.8	126.0	123.3	121.5	120.3	131.5	151.5	173.7	13.9	58.7	171.5	43.3, 31.1, 25.1, 23.1

Table S5. ^{1}H NMR data of compounds **6a–f** (DMSO-d_6).



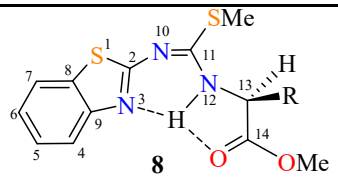
6

Comp.	H4	H5	H6	H7	OH	N12H	C13H	R
6a	7.80 (d, 7.1)	7.30 (d, 7.5)	7.60 (d, 7.5)	7.10 (d, 7.6)	no ob no ob	7.7 (t, 4.0)	3.6 (d, 4.0)	3.6 ----
6b	7.81 (d, 7.9)	7.31 (t, 7.3)	7.15 (t, 7.3)	7.59 (d, 7.9)	11.9 (br)	7.75 (d, 4.5)	3.94 (dq, 6.7)	1.29 (d, 6.7)
6c	7.87 (d, 7.6)	no ob	no ob	7.80 (d, 7.9)	11.85 (br)	8.3 (d, 6.2)	4.99 (d, 6.8)	7.1-7.4 (m)
6d	7.80 (d, 7.6)	7.30 (t, 7.0)	no ob	7.60 (d, 7.9)	12.0 (br)	8.0 (br)	4.25 (dd, 6.4)	2.98, 3.1, 7.2 (d, d, 13.1, 12.3, m)
6e	8.12 (d, 7.6)	7.63 (t, 7.0)	7.46 (t, 7.6)	7.94 (d, 7.6)	no ob	8.11 (d, (8.2)	4.37 (dd, 8.2)	2.48, 1.20, 1.22 (m, d, d, 7.1)
6f	7.80 (d, 7.6)	7.30 (t, 8.2)	7.13 (t, 7.6)	7.60 (d, 8.2)	12.3 (br)	7.90 (d, 8.2)	4.14 (m,br)	1.60, 1.50, 0.84, 0.86 (m, m, d, d, 6.4, 7.1)

Table S6. ^{13}CNMR data of compounds **6a–f** (DMSO-d_6).

Comp.	C2	C4	C5	C6	C7	C8	C9	C11	C13	C14	R
6a	157.8	119.0	121.1	121.5	125.5	132.0	150.1	175.1	45.1	164.4	----
6b	154.0	120.2	121.7	122.9	126.2	132.2	150.0	176.3	51.4	161.0	20.7
6c	153.4	120.0	121.5	122.7	126.5	131.9	149.7	172.5	60.0	160.5	143.1
6d	153.6	119.9	121.6	122.8	126.1	131.9	149.6	173.6	56.4	160.5	38.4, 126.0
6e	155.1	119.8	121.4	122.3	125.8	131.9	149.9	176.1	60.3	161.6	31.8, 20.2, 18.4
6f	154.3	119.9	121.4	122.5	125.9	131.9	149.8	177.3	53.9	160.9	43.6, 25.0, 23.7, 22.9

Table S7. ^{1}HNMR data of compounds **8a–d** ($CDCl_3$).



8

Comp.	H4	H5	H6	H7	N12H	SMe	C13H	R	OMe
8a	7.72 (d, 8.5)	7.34 (t, 7.9)	7.21 (t, 7.6)	7.69 (d, 9.3)	10.80 * (br)	2.55 (s)	4.23 (s)	4.23 (s)	3.83 (s)
8b	7.72 (d, 8.6)	7.34 (t, 8.4)	7.25 (t, 8.5)	7.69 (d, 8.5)	11.20 (br)	2.54 (s)	4.49 (q, 6.8)	1.61 (d, 7.0)	3.81 (s)
8c	7.80 (d, 7.8)	no ob	7.24 (t, 7.6)	7.72 (d, 7.6)	12.04 (br)	2.50 (s)	5.47 (br)	7.4-7.5 (m)	3.79 (s)
8d	7.68	no ob	no ob	7.66	11.23	2.36	4.70	3.28, 3.26, 7.2	3.75

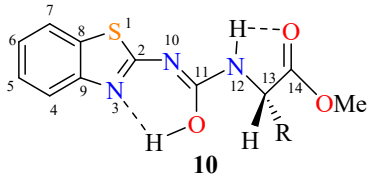
	(d, 8.2)			(d, 9.2)	(br)	(s)	(br)	(s, s, m)	(s)
8e	7.74 (d, 4.9)	7.35 (t, 7.0)	7.21 (t, 7.6)	7.68 (d, 4.7)	11.41 (d, 8.2)	2.54 (dd,8.8,4.7)	4.30 (br)	2.37, 1.12, 1.09 (m, d, d, 7.0)	3.78 (s)
8f	7.70 (d,4.6)	7.35 (t, 8.2)	7.25 (t, 8.3)	7.68 (d, 4.1)	11.20 (br)	2.53 (s)	4.42 (br)	1.82, 1.83, 1.0, 0.98 (m, m, d, d, 6.8)	3.78 (s)

* Observed in DMSO-d_6 for **8a.**

Table S8. ^{13}C NMR data of compounds **8a–d** ($CDCl_3$).

Comp.	C2	C4	C5	C6	C7	C8	C9	C11	SCH_3	C13	C14	R	OMe
8a	164.8	125.6	123.3	121.0	120.6	132.2	151.0	171.7	14.1	52.7	169.1	-	45.0
8b	164.0	125.6	123.3	121.0	120.7	132.1	151.0	171.7	14.0	52.3	172.3	19.3	52.8
8c	164.0	125.7	123.4	121.0	120.8	132.1	151.0	171.6	14.2	60.6	170.2	136.1	53.0
8d	164.2	125.6	123.3	121.0	120.6	132.2	151.0	171.5	14.2	58.2	171.1	39.1	52.6
8e	165.2	125.7	123.4	121.1	123.4	132.2	151.1	172.0	14.2	62.4	171.3	31.9, 19,3, 17.9	52.5
8f	164.6	125.6	123.3	121.0	120.5	132.2	151.0	172.2	14.0	55.4	171.8	42.0,25.0,22.7, 22.1	52.5

Table S9. ^{1}H NMR data of compounds **10a–f** ($CDCl_3$).



10

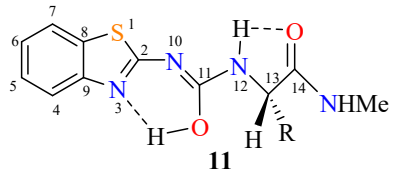
Comp.	H4	H5	H6	H7	OH	N12H	C13H	R	OMe
10a	7.75 (d, 8.1)	7.41 (t, 8,3)	7.27 (t, 8.2)	7.73 (d, 8.1)	11.0 no ob.	7.26 (d, 5.8)	4.2 (d, 5.5)	4.0 (d, 6.0)	3.70 (s)
10b	7.75 (d, 7.6)	7.38 (d, 8.0)	7.24 8d, 7.2)	7.70 (d, 7.6)	no ob.	No ob.	4.66 (q, 7.0)	1.54 (d, 7.1)	3.79 (s)
10c	7.88 (d, 7.6)	no ob	7.23 (d, 7.6)	7.65 (d, 7.6)	no ob.	no ob.	5.5 (s)	7.3-7.5 (m)	3.76 (s)
10d	7.71 (d, 8.2)	7.38 (d, 7.1)	no ob	7.65 d(10.5)	no ob	no ob	4.87 (q, 7.0)	7.15-7.25, 3.20 m, dd (5.8, 5.3)	3.73 (s)
10e	7.71 (d, 7.0)	7.34 (t, 7.0)	7.20 (t, 7.6)	7.69 d(7.0)	no ob	no ob	4.55 (dd, 4.7)	2.0, 0.79, 0.74 (m, d, d, 6.5)	3.74 (s)
10f	7.71 (d, 7.6)	7.35 (t, 7.6)	7.21 (t, 7.6)	7.68 (d, 7.6)	no ob	no ob	4.61 (m)	1.72, 1.67, 0.98, 0.96 (m, m, d, d, 6.5)	3.75 (s)

Table S10. ^{13}CNMR data of compounds **10a–f** ($CDCl_3$).

Comp.	C2	C4	C5	C6	C7	C8	C9	C11	C13	C14	R	OMe
10a	154.3	126. 2	121. 2	120. 2	126. 6	130.7	148.7	169.5	43.0	160. 1	----	51.7
10b	154.2	126. 1	121. 2	120. 1	123. 5	130.9	148.8	173.6	49.1	161. 4	18.5	52.6

10c	153.8	126.1	121.2	120.3	123.5	131.0	149.0	171.4	57.5	161.2	140, 129, 128, 127.1	57.5
10d	153.8	126.4	121.3	119.7	123.7	130.5	148.6	172.2	52.51	161.3	136, 129, 129, 127, 38	54.5
10e	154.2	125.6	120.8	119.9	122.8	131.4	149.2	172.6	57.9	160.5	30.95, 18.94, 17.51	51.9
10f	154.5	126.1	121.2	120.0	123.4	131.1	148.8	173.8	41.3	161.3	41.4, 24.9, 22.8, 21.9	52.4

Table S11. ^{1}H NMR data of compounds **11a–f** ($CDCl_3$).



11

Comp.	H4	H5	H6	H7	OH	N12H	C13H	N14H	R	NMe
11a	7.88 (d, 8.3)	7.36 (t, 7.1)	7.21 (t, 7.6)	7.63 (d, 8.2)	10.8 (br)	7.21 (t, 5.2)	3.79 (d, 5.3)	7.96 (q, 4.1)	3.79 (d, 5.3)	2.62 (d, 4.7)
11b	7.86 (d, 7.5)	7.36 (t, 7.1)	7.21 (t, 7.5)	7.62 (d, 8.0)	no ob.	7.36 (t, 6.3)	4.25 (q, 7.0)	8.1 (q, 4.6)	1.27 (d, 7.0)	2.61 (d, 4.6)
11c	7.84 (d, 8.2)	no ob	7.15 (d, 7.6)	7.61 (d, 7.6)	no ob	7.9 (d, 7.0)	5.37 (d, 7.7))	8.4 (q, 7)	7.2-7.5 (m)	2.61 (d, 4.1)
11d	7.86 (d, 7.7)	7.36 (t, 7.1)	no ob	7.62 (d, 8.0)	10.6 (br)	7.10 (d, 7.9)	4.48 (q, 8.1)	8.17 (q, 4.5)	7.1-7.3(m) 2.95 (ddd, 21.7, 13.7, 6.7)	2.61 (d, 4.5)
11e	7.86 (d, 8.2)	7.35 (t, 7.6)	7.20 (t, 7.6)	7.62 (d, 7.7)	10.6 (br)	7.06 (d, 8.7)	4.14 (dd, 8.7, 5.9)	8.10 (q, 4.6)	1.98, 0.87, 0.83 m, d, d (7.1)	2.6 (d, 4.6)
11f	7.85 (d, 8.3)	7.33 (t, 7.2)	7.18 (t, 7.6)	7.61 (d, 7.9)	10.5 (br)	7.0 (d, 8.2)	4.22 (m)	8.13 (q, 4.7)	1.55, 1.46, 0.87, 0.85 m, m, d, d (2.4)	2.57 (d, 4.7)

Table S12. ^{13}C NMR data of compounds **11a–f** ($CDCl_3$).

Comp.	C2	C4	C5	C6	C7	C8	C9	C11	C13	C14	R	NMe
11a	154.3	126.2	123.1	121.8	120.1	131.8	159.5	169.5	43.0	160.1	---	25.9
11b	153.6	126.3	123.2	121.7	120.1	131.8	149.4	173.0	49.3	160.1	19.8	26.0
11c	153.8	126.1	123.0	121.7	120.1	131.8	149.5	170.5	57.1	160.3	140	26.1
11d	153.6	126.3	123.2	121.8	120.2	131.8	149.5	171.6	54.8	160.0	138, 130, 129, 127, 39	26.0
11e	154.0	126.2	123.1	121.8	120.2	131.8	149.5	171.6	63.3	160.0	30.4, 17.8,17.3	25.5
11f	153.9	126.2	123.0	121.7	120.1	131.9	149.5	172.7	52.1	160.1	42.4, 24.8, 23.3, 22.3	26.0