Synthesis of a New Class of Bisheterocycles from Phenacylsulfonylacetic Acid Methyl Ester

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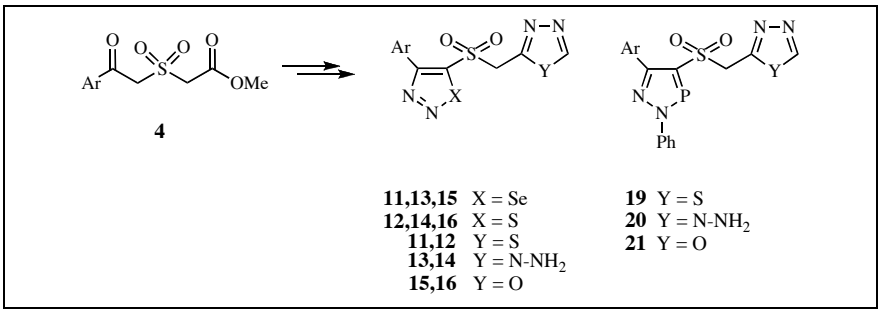

Novel bisheterocycles, 1,2,3-selenadiazoles, thiadiazoles and 2*H*-diazaphospholes in combination with oxadiazoles, thiadiazoles and triazoles were prepared from phenacylsulfonylacetic acid methyl ester.

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INTRODUCTION

Among different heterocyclic systems oxadiazoles, thiadiazoles and triazoles gained importance in both chemical and pharmaceutical purposes. A number of these compounds show analgesic, antidepressive, anticonvulsive and bactericidal activity [1]. Molecules having 1,3,4-thiadiazole unit attached to the nitrogen of a lactam type heterocycle possess phytosanitary activity [2-5]. Besides 1,2,3-selenadiazoles, thiadiazoles and 2*H*-diazaphospholes possess varied physiological properties [6-10]. In fact, the exploitation of a simple molecule with different functionalities for the synthesis of heterocycles is a worthwhile contribution in the field of organic syntheses. Phenacylsulfonylacetic acid methyl esters are valuable synthetic intermediates in a variety of synthetic transformations and useful as building blocks to construct vulnerable heterocycles [11-12]. In continuation of our studies in the synthesis of biologically potent heterocycles, herein we wish to report novel bis heterocycles *viz.,* selenadiazoles, thiadiazoles and 2*H*-diazaphospholes in combination with oxadiazoles, thiadiazoles and triazoles.

RESULTS AND DISCUSSION

In our earlier communication, we have reported the synthesis of 1,2,3-selenadiazoles, thiadiazoles and 2*H*-diazaphospholes by exploiting α-ketomethylene group in phenacylsulfonylacetic acid methyl ester [13] (Scheme 1). In continuation of our efforts to develop bis heterocycles the ester functionality in (4-aryl[1,2,3]selenadiazole-5-sulfonyl)acetic acid methyl ester (**3**), (4-aryl[1,2,3]thiadiazole-5-sulfonyl)acetic acid methyl ester (**4**) and (2-phenyl-5-aryl-2*H*-[1,2,3]diazaphosphole-4-sulfonyl)acetic acid methyl ester (**6**) was used to develop oxadiazoles, thiadiazoles and triazoles. Treatment of **3**, **4** and **6** with hydrazine hydrate produced the corresponding acid hydrazide, (4-aryl[1,2,3]selenadiazole-5-sulfonyl)acetic acid hydrazide (**7**), (4-aryl[1,2,3]thiadiazole-5-sulfonyl)-acetic acid hydrazide (**8**) and (2-phenyl-5-aryl-2*H*-[1,2,3]diazaphosphole-4-sulfonyl)acetic acid hydrazide (**17**) (Table 1). The IR spectra of these compounds displayed absorption bands around 1670 cm^{-1} for *CO*NH, 1325-1342 and 1122-1152 cm^{-1} for SO_2 and in the regions 3312-3322 and 3220-3230 cm^{-1} for NH and NH_2, respectively. Besides these, the compounds **7** and **8** displayed an absorption band at 1626-1638 cm^{-1} for C=C and compound **17** at 1565-1600 cm^{-1} for CN (Table 2). The ^{1}H NMR spectra of **7a**, **8a** and **17a** displayed broad signals in the regions 9.41-9.47 and 5.16-5.24 ppm for NH and NH_2, which disappeared on deuteration. In addition, a singlet was observed at 4.72, 4.70 and 4.64 ppm in **7a**, **8a** and **17a**, respectively, for methylene protons (Table 3). The potassium dithiocarbazate of the acid hydrazide, **9**, **10** and **18** were prepared from **7**, **8** and **17** on treatment with carbon disulfide in the presence of KOH under ultrasonic conditions. The carbodithioates on heating in the presence of acetic acid produced 5′-(4-aryl[1,2,3]selenadiazole-5-sulfonylmethyl)-[1′,3′,4′]thiadiazole-2′-thiol (**11**), 5′-(4-aryl[1,2,3]thiadiazole-5-sulfonylmethyl)-[1′,3′,4′]thiadiazole-2′-thiol (**12**) and 5′-(2-phenyl-5-aryl-2*H*-[1,2,3]diazaphosphole-4-sulfonyl-methyl)thiadiazole-2′-thiol (**19**). Treatment of **9**, **10** and **18** with hydrazine hydrate gave 4′-amino-5′-(4-aryl-[1,2,3]selenadiazole-5-sulfonylmethyl)-4′*H*-[1′,2′,4′]-triazole-3′-thiol (**13**), 4′-amino-5′-(4-aryl[1,2,3]-thiadiazole-5-sulfonylmethyl)-4′*H*-[1′,2′,4′]triazole-3′-thiol (**14**) and

Table 1

Physical and Analytical Data of Compounds **7-21**

Compound.	Mp (°C)	Ar	Yield %	Molecular Formula	Analysis % Calcd. /Found		
					C	H	N
7a	135-137	Ph	76	$C_{10}H_{10}N_4O_3SSe$ (345.24)	-	-	-
7b	126-128	4-MePh	78	$C_{11}H_{12}N_4O_3SSe$ (359.26)	-	-	-
7c	140-142	4-ClPh	72	$C_{10}H_9ClN_4O_3SSe$ (379.68)	-	-	-
8a	149-151	Ph	75	$C_{10}H_{10}N_4O_3S_2$ (298.34)	-	-	-
8b	143-145	4-MePh	70	$C_{11}H_{12}N_4O_3S_2$ (312.37)	-	-	-
8c	158-160	4-ClPh	73	$C_{10}H_9ClN_4O_3S_2$ (332.79)	-	-	-
11a	164-166	Ph	71	$C_{11}H_8N_4O_2S_3Se$ (403.36)	32.75 (32.82)	2.00 (1.98)	13.89 (13.95)
11b	158-160	4-MePh	68	$C_{12}H_{10}N_4O_2S_3Se$ (417.39)	34.53 (34.60)	2.41 (2.44)	13.42 (13.47)
11c	171-173	4-ClPh	66	$C_{11}H_7ClN_4O_2S_3Se$ (437.81)	30.18 (30.13)	1.61 (1.60)	12.80 (12.86)
12a	180-182	Ph	72	$C_{11}H_8N_4O_2S_4$ (356.47)	37.06 (37.14)	2.26 (2.29)	15.72 (15.68)
12b	176-178	4-MePh	67	$C_{12}H_{10}N_4O_2S_4$ (370.49)	38.90 (38.99)	2.72 (2.70)	15.12 (15.19)
12c	191-193	4-ClPh	69	$C_{11}H_7ClN_4O_2S_4$ (390.91)	33.80 (33.72)	1.80 (1.83)	14.33 (14.37)
13a	168-170	Ph	68	$C_{11}H_{10}N_6O_2S_2Se$ (401.33)	32.92 (32.99)	2.51 (2.50)	20.94 (21.02)
13b	155-157	4-MePh	65	$C_{12}H_{12}N_6O_2S_2Se$ (415.35)	34.70 (34.76)	2.91 (2.94)	20.23 (20.32)
13c	177-179	4-ClPh	64	$C_{11}H_9ClN_6O_2S_2Se$ (435.77)	30.32 (30.36)	2.08 (2.10)	19.29 (19.38)
14a	180-182	Ph	66	$C_{11}H_{10}N_6O_2S_3$ (354.43)	37.28 (37.25)	2.84 (2.88)	23.71 (23.76)
14b	171-173	4-MePh	63	$C_{12}H_{12}N_6O_2S_3$ (368.46)	39.12 (39.21)	3.28 (3.25)	22.81 (22.89)
14c	186-188	4-ClPh	68	$C_{11}H_9ClN_6O_2S_3$ (388.88)	33.97 (33.90)	2.33 (2.37)	21.61 (21.68)
15a	154-156	Ph	70	$C_{11}H_8N_4O_3S_2Se$ (387.3)	34.11 (34.07)	2.08 (2.06)	14.47 (14.52)
15b	147-149	4-MePh	65	$C_{12}H_{10}N_4O_3S_2Se$ (401.32)	35.91 (36.00)	2.51 (2.49)	13.96 (14.02)
15c	161-163	4-ClPh	68	$C_{11}H_7ClN_4O_3S_2Se$ (421.74)	31.33 (31.37)	1.67 (1.70)	13.28 (13.35)
16a	166-167	Ph	74	$C_{11}H_8N_4O_3S_3$ (340.4)	38.81 (38.90)	2.37 (2.35)	16.46 (16.52)
16b	159-161	4-MePh	69	$C_{12}H_{10}N_4O_3S_3$ (354.43)	40.67 (40.72)	2.84 (2.80)	15.81 (15.85)
16c	175-177	4-ClPh	67	$C_{11}H_7ClN_4O_3S_3$ (374.85)	35.25 (35.21)	1.88 (1.90)	14.95 (14.99)
17a	165-167	Ph	72	$C_{16}H_{15}N_4O_3PS$ (374.35)	-	-	-
17b	161-163	4-MePh	74	$C_{17}H_{17}N_4O_3PS$ (388.38)	-	-	-
17c	177-179	4-ClPh	76	$C_{16}H_{14}ClN_4O_3PS$ (408.8)	-	-	-
19a	195-197	Ph	69	$C_{17}H_{13}N_4O_2PS_3$ (466.92)	43.73 (43.79)	2.59 (2.63)	12.00 (12.08)
19b	188-190	4-MePh	71	$C_{18}H_{15}N_4O_2PS_3$ 446.51	48.42 (48.38)	3.39 (3.37)	12.55 (12.50)
19c	212-213	4-ClPh	67	$C_{17}H_{12}ClN_4O_2PS_3$ 432.48	47.21 (47.27)	3.03 (3.07)	12.95 (12.99)
20a	210-212	Ph	70	$C_{17}H_{15}N_6O_2PS_2$ 430.44	47.44 (47.51)	3.51 (3.48)	19.52 (19.60)

Table 1 (continued)

Compound.	Mp (°C)	Ar	Yield %	Molecular Formula	Analysis % Calcd. /Found		
					C	H	N
20b	198-200	4-MePh	73	$C_{18}H_{17}N_6O_2PS_2$ 444.47	48.64 (48.60)	3.86 (3.90)	18.91 (18.88)
20c	218-220	4-ClPh	75	$C_{17}H_{14}ClN_6O_2PS_2$ (464.89)	43.92 (43.97)	3.04 (3.02)	18.08 (18.14)
21a	187-189	Ph	67	$C_{17}H_{13}N_4O_3PS_2$ (416.41)	49.03 (48.96)	3.15 (3.14)	13.45 (13.50)
21b	183-185	4-MePh	63	$C_{18}H_{15}N_4O_3PS_2$ (430.44)	50.23 (50.30)	3.51 (3.55)	13.02 (13.08)
21c	206-208	4-ClPh	65	$C_{17}H_{12}ClN_4O_3PS_2$ (450.86)	45.29 (45.22)	2.68 (2.72)	12.43 (12.40)

Scheme 1

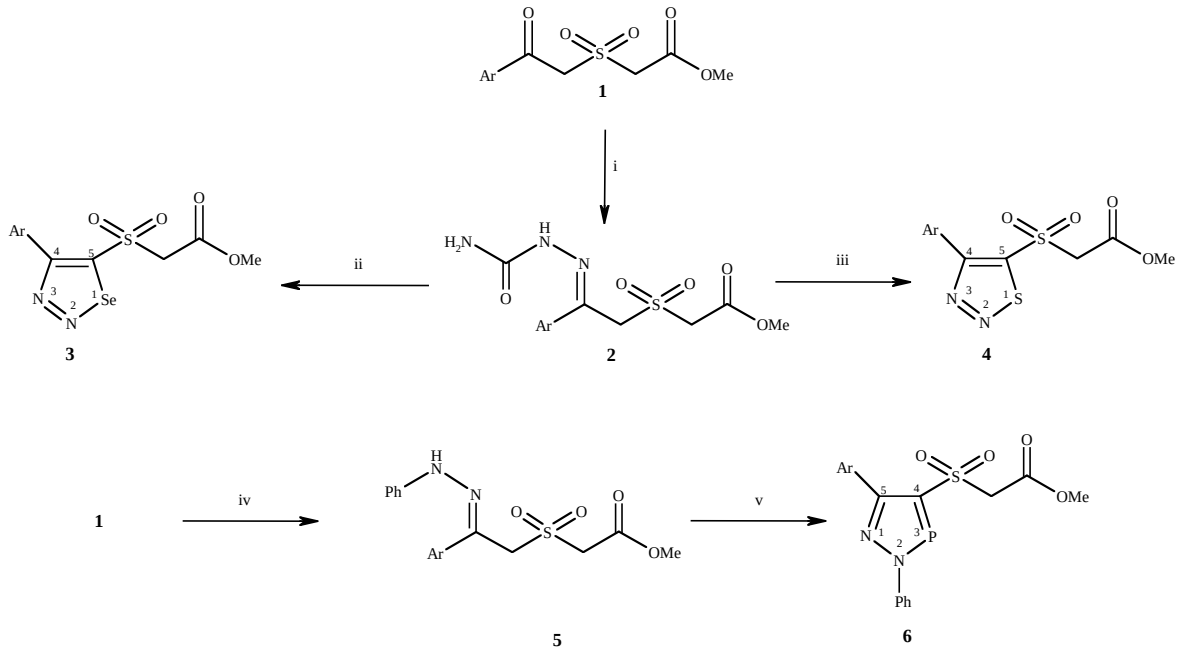


Table 2

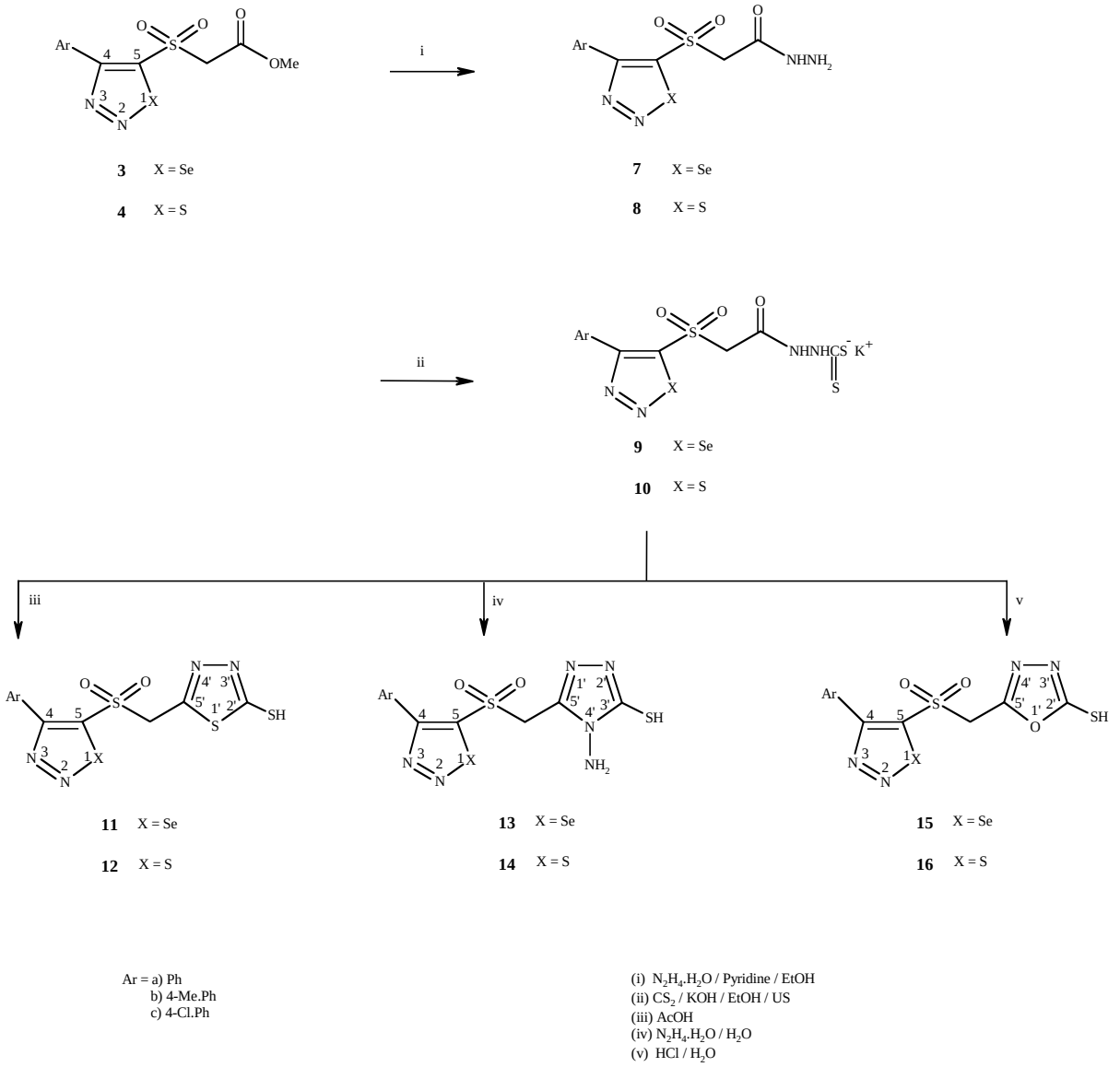
IR Data of Compounds **7-21**

Comp. No.	IR (cm^{-1})								
	C-Se/S	C=C	SO_2	N=N	C=O	C=N	SH	NH	NH_2
7a	722	1638	1329 1127	1443	1664	-	-	3316	3224
7b	724	1635	1325 1130	1435	1668	-	-	3314	3222
7c	729	1632	1333 1122	1446	1670	-	-	3318	3227
8a	714	1626	1326 1138	1452	1662	-	-	3320	3226
8b	722	1628	1332 1143	1437	1665	-	-	3315	3223

Table 2 (continued)

Comp. No.	IR (cm^{-1})								
	C-Se/S	C=C	SO_2	N=N	C=O	C=N	SH	NH	NH_2
8c	725	1636	1342 1139	1449	1669	-	-	3322	3229
11a	723	1631	1337 1144	1445	-	1568	2556	-	-
11b	726	1624	1331 1142	1433	-	1563	2553	-	-
11c	728	1637	1346 1150	1448	-	1572	2560	-	-
12a	715	1635	1336 1148	1451	-	1564	2558	-	-
12b	720	1638	1334 1135	1439	-	1561	2554	-	-
12c	724	1633	1334 1150	1444	-	1573	2562	-	-
13a	721	1628	1328 1139	1433	-	1566	2555	-	3243
13b	727	1632	1337 1141	1443	-	1575	2552	-	3245
13c	730	1637	1349 1146	1438	-	1578	2557	-	3249
14a	711	1632	1326 1143	1450	-	1567	2554	-	3244
14b	716	1629	1335 1148	1437	-	1573	2556	-	3247
14c	720	1635	1342 1150	1446	-	1582	2562	-	3252
15a	723	1625	1337 1144	1448	-	1568	2557	-	-
15b	726	1630	1336 1129	1437	-	1565	2553	-	-
15c	728	1636	1334 1152	1452	-	1575	2561	-	-
16a	715	1634	1330 1139	1445	-	1566	2555	-	-
16b	724	1628	1331 1154	1436	-	1563	2552	-	-
16c	727	1639	1338 1149	1447	-	1577	2557	-	-
17a	-	-	1325 1126	-	1665	1600	-	3314	3220
17b	-	-	1332 1134	-	1668	1565	-	3312	3224
17c	-	-	1328 1152	-	1672	1574	-	3318	3227
19a	-	-	1335 1151	-	-	1568	2558	-	-
19b	-	-	1338 1137	-	-	1567	2555	-	-
19c	-	-	1343 1132	-	-	1572	2565	-	-
20a	-	-	1337 1143	-	-	1560	2552	-	3240
20b	-	-	1329 1146	-	-	1558	2555	-	3245
20c	-	-	1344 1135	-	-	1567	2566	-	3248
21a	-	-	1327 1133	-	-	1570	2557	-	-
21b	-	-	1332 1139	-	-	1574	2554	-	-
21c	-	-	1339 1125	-	-	1577	2562	-	-

Scheme 2



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7 X = Se
8 X = S

9 X = Se
10 X = S

11 X = Se
12 X = S

13 X = Se
14 X = S

15 X = Se
16 X = S

4′-amino-5′-(2-phenyl-5-aryl-2*H*-[1,2,3]diazaphosphole-4-sulfonylmethyl)-4′*H*-[1′,2′,4′]triazole-3′-thiol (**20**). However, acid catalysed hydrolysis of **9**, **10** and **18** resulted in 5′-(4-aryl[1,2,3]selenadiazole-5-sulfonyl-methyl)-[1′,3′,4′]oxadiazole-2′-thiol (**15**), 5′-(4-aryl-[1,2,3]-thiadiazole-5-sulfonyl-methyl)-[1′,3′,4′]oxadiazole-2′-thiol (**16**) and 5′-(2-phenyl-5-aryl-2*H*-[1,2,3]diaza-phosphole-4-sulfonylmethyl)-[1′,3′,4′]oxadiazole-2′-thiol (**21**) (Schemes 2, 3 and Table 1). The IR spectra of **11**-**16** and **19-21** displayed an absorption band at 1558-1582 for C=N and at 1326-1349 and 1125-1154 cm^{-1} for SO_2. Apart from these the bands due to C=C were also observed at 1624-1639 cm^{-1} for **11-16**, whereas **13**, **14** and **20** showed a broad band at 3240-3252 cm^{-1} for NH_2 (Table 2). The ^1H NMR spectra of these compounds displayed a singlet at 10.12-10.61 for SH and another singlet at 4.62-4.79 ppm for methylene protons besides signals due to aromatic protons. Compounds **13**, **14**, and **20** also displayed a broad singlet at 5.60-5.68 ppm for NH_2, which disappeared on deuteration. The structures of the compounds **11-16** and **19-21** were further confirmed by ^{13}C NMR spectra (Table 3).

EXPERIMENTAL

General. Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. The purity of compounds was checked by TLC (silica gel H, BDH, ethyl

Table 3

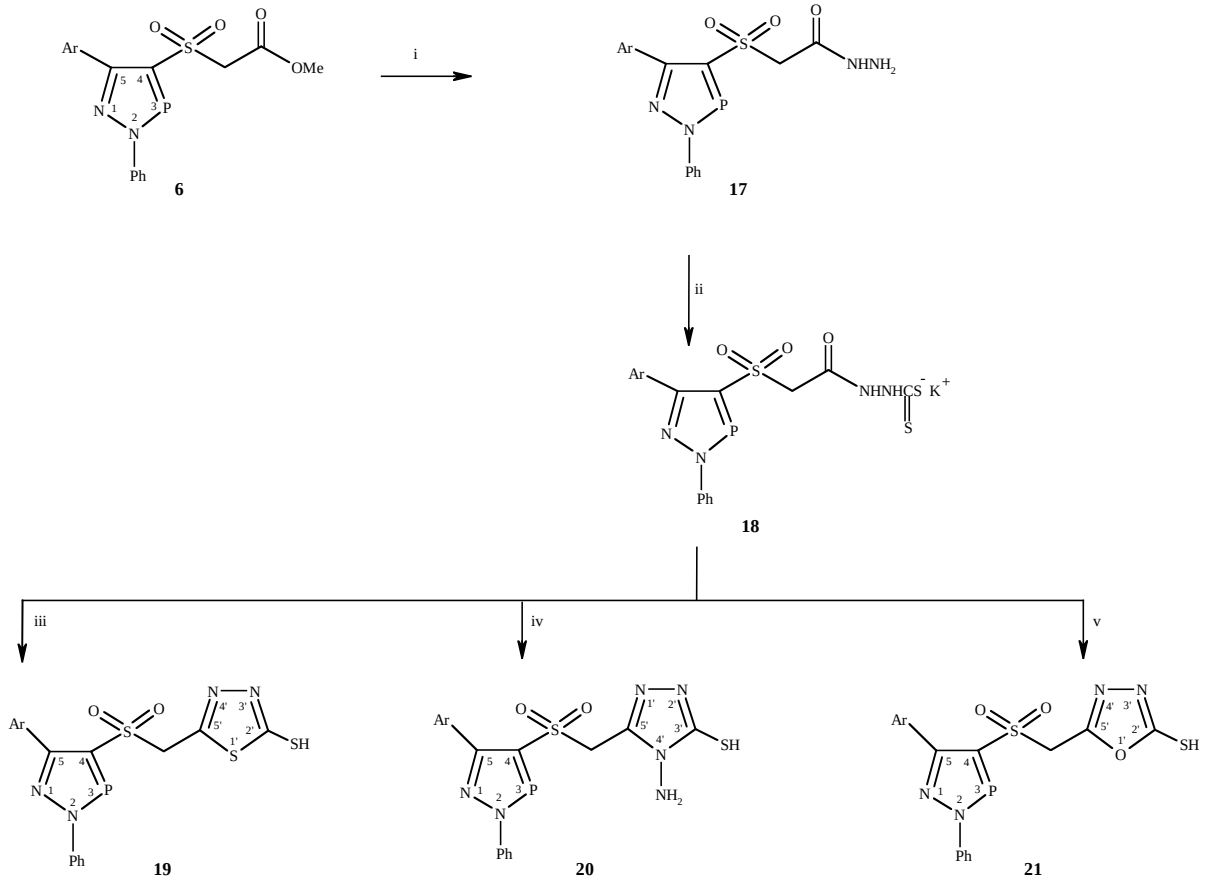
^{1}H and ^{13}C NMR Data of Compounds **7-21**

Compd. No.	^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)
7a	4.72 (s, 2H, SO_2-CH_2), 5.17 (bs, 2H, NH_2), 7.46-7.95 (m, 5H, Ar-H), 9.45 (bs, H, NH)	57.2 (SO_2-CH_2), 156.5 (C-5), 157.4 (C-4), 170.8 (C=O), 127.6, 129.7, 131.2, 134.8 (aromatic carbons)
7b	2.38 (s, 3H, Ar-CH_3), 4.63 (s, 2H, SO_2-CH_2), 5.12 (bs, 2H, NH_2), 7.38-7.92 (m, 4H, Ar-H), 9.37 (bs, H, NH)	20.8 (Ar-CH_3), 56.7 (SO_2-CH_2), 156.1 (C-5), 157.8 (C-4), 168.5 (C=O), 126.5, 128.3, 130.9, 134.4 (aromatic carbons)
7c	4.76 (s, 2H, SO_2-CH_2), 5.21 (bs, 2H, NH_2), 7.49-7.97 (m, 4H, Ar-H), 9.52 (bs, H, NH)	57.5 (SO_2-CH_2), 155.7 (C-5), 157.2 (C-4), 170.2 (C=O), 127.8, 129.9, 132.3, 135.2 (aromatic carbons)
8a	4.70 (s, 2H, SO_2-CH_2), 5.24 (bs, 2H, NH_2), 7.42-7.93 (m, 5H, Ar-H), 9.41 (bs, H, NH)	56.9 (SO_2-CH_2), 151.4 (C-5), 154.7 (C-4), 160.2 (C=O), 126.7, 127.4, 131.6, 134.8 (aromatic carbons)
8b	2.34 (s, 3H, Ar-CH_3), 4.67 (s, 2H, SO_2-CH_2), 5.26 (bs, 2H, NH_2), 7.40-7.92 (m, 4H, Ar-H), 9.45 (bs, H, NH)	21.6 (Ar-CH_3), 56.5 (SO_2-CH_2), 152.2 (C-5), 154.5 (C-4), 159.3 (C=O), 125.8, 126.7, 130.9, 134.5 (aromatic carbons)
8c	4.69 (s, 2H, SO_2-CH_2), 5.28 (bs, 2H, NH_2), 7.45-7.89 (m, 4H, Ar-H), 9.47 (bs, H, NH)	57.6 (SO_2-CH_2), 151.9 (C-5), 153.2 (C-4), 160.7 (C=O), 126.4, 127.9, 132.6, 135.2 (aromatic carbons)
11a	4.70 (s, 2H, SO_2-CH_2), 7.42-7.93 (m, 5H, Ar-H) 10.26 (s, H, SH)	58.1 (SO_2-CH_2), 155.5 (C-5), 158.3 (C-4), 163.2 (C-2'), 168.4 (C-5'), 127.3, 129.8, 131.5, 134.7 (aromatic carbons)
11b	2.29 (s, 3H, Ar-CH_3), 4.65 (s, 2H, SO_2-CH_2), 7.34-7.89 (m, 4H, Ar-H) 10.12 (s, H, SH)	21.9 (Ar-CH_3), 56.9 (SO_2-CH_2), 154.7 (C-5), 158.1 (C-4), 162.8 (C-2'), 167.6 (C-5'), 126.2, 128.5, 131.3, 134.6 (aromatic carbons)
11c	4.73 (s, 2H, SO_2-CH_2), 7.46-7.93 (m, 4H, Ar-H) 10.29 (s, H, SH)	57.8 (SO_2-CH_2), 156.8 (C-5), 157.6 (C-4), 163.5 (C-2'), 168.7 (C-5'), 127.6, 129.9, 132.4, 135.3 (aromatic carbons)
12a	4.68 (s, 2H, SO_2-CH_2), 7.39-7.91 (m, 5H, Ar-H) 10.27 (s, H, SH)	56.8 (SO_2-CH_2), 152.7 (C-5), 154.3 (C-4), 162.4 (C-2'), 168.2 (C-5'), 127.1, 129.5, 131.6, 134.9 (aromatic carbons)
12b	2.24 (s, 3H, Ar-CH_3), 4.62 (s, 2H, SO_2-CH_2), 7.37-7.86 (m, 4H, Ar-H) 10.13 (s, H, SH)	22.4 (Ar-CH_3), 56.3 (SO_2-CH_2), 151.7 (C-5), 153.1 (C-4), 162.8 (C-2'), 167.6 (C-5'), 126.2, 128.5, 131.3, 134.6 (aromatic carbons)
12c	4.75 (s, 2H, SO_2-CH_2), 7.46-7.96 (m, 4H, Ar-H) 10.32 (s, H, SH)	57.5 (SO_2-CH_2), 152.6 (C-5), 154.8 (C-4), 163.3 (C-2'), 168.5 (C-5'), 127.5, 129.7, 132.1, 134.9 (aromatic carbons)
13a	4.73 (s, 2H, SO_2-CH_2), 5.64 (bs, 2H, NH_2), 7.46-7.98 (m, 5H, Ar-H), 10.34 (s, H, SH)	57.9 (SO_2-CH_2), 155.3 (C-5), 158.4 (C-4), 163.6 (C-5'), 145.8 (C-3'), 127.3, 129.8, 131.9, 134.8 (aromatic carbons)
13b	2.27 (s, 3H, Ar-CH_3), 4.71 (s, 2H, SO_2-CH_2), 5.60 (bs, 2H, NH_2), 7.41-7.89 (m, 4H, Ar-H), 10.44 (s, H, SH)	21.8 (Ar-CH_3), 57.6 (SO_2-CH_2), 154.1 (C-5), 157.2 (C-4), 165.5 (C-5'), 147.5 (C-3'), 126.8, 128.8, 131.6, 134.4 (aromatic carbons)
13c	4.79 (s, 2H, SO_2-CH_2), 5.66 (bs, 2H, NH_2), 7.43-7.87 (m, 4H, Ar-H), 10.61 (s, H, SH)	58.2 (SO_2-CH_2), 155.9 (C-5), 157.7 (C-4), 163.8 (C-5'), 146.4 (C-3'), 127.5, 130.6, 132.4, 135.2 (aromatic carbons)
14a	4.65 (s, 2H, SO_2-CH_2), 5.65 (bs, 2H, NH_2), 7.37-7.85 (m, 5H, Ar-H), 9.43 (bs, 2H, NH_2), 10.28 (s, H, SH)	56.3 (SO_2-CH_2), 151.4 (C-5), 154.1 (C-4), 163.3 (C-5'), 145.9 (C-3'), 126.1, 129.3, 131.7, 134.6 (aromatic carbons)
14b	2.29 (s, 3H, Ar-CH_3), 4.70 (s, 2H, SO_2-CH_2), 5.63 (bs, 2H, NH_2), 7.43-7.91 (m, 4H, Ar-H), 10.36 (s, H, SH)	22.5 (Ar-CH_3), 58.4 (SO_2-CH_2), 152.3 (C-5), 154.5 (C-4), 166.7 (C-5'), 144.7 (C-3'), 127.8, 129.9, 132.6, 135.3 (aromatic carbons)
14c	4.76 (s, 2H, SO_2-CH_2), 5.68 (bs, 2H, NH_2), 7.33-7.89 (m, 4H, Ar-H), 10.45 (s, H, SH)	57.9 (SO_2-CH_2), 152.6 (C-5), 154.9 (C-4), 164.7 (C-5'), 146.5 (C-3'), 127.6, 130.8, 132.7, 135.4 (aromatic carbons)
15a	4.71 (s, 2H, SO_2-CH_2), 7.40-7.91 (m, 5H, Ar-H) 10.29 (s, H, SH)	57.5 (SO_2-CH_2), 155.4 (C-5), 157.6 (C-4), 163.5 (C-2'), 168.7 (C-5'), 127.5, 130.4, 132.3, 134.9 (aromatic carbons)
15b	2.24 (s, 3H, Ar-CH_3), 4.68 (s, 2H, SO_2-CH_2), 7.39-7.89 (m, 4H, Ar-H) 10.26 (s, H, SH)	22.4 (Ar-CH_3), 56.8 (SO_2-CH_2), 155.3 (C-5), 157.7 (C-4), 162.3 (C-2'), 167.5 (C-5'), 126.3, 128.1, 131.5, 134.4 (aromatic carbons)
15c	4.75 (s, 2H, SO_2-CH_2), 7.41-7.92 (m, 4H, Ar-H) 10.32 (s, H, SH)	57.8 (SO_2-CH_2), 156.7 (C-5), 157.9 (C-4), 164.1 (C-2'), 168.8 (C-5'), 127.8, 130.3, 132.8, 135.5 (aromatic carbons)
16a	4.73 (s, 2H, SO_2-CH_2), 7.45-7.96 (m, 5H, Ar-H) 10.34 (s, H, SH)	57.4 (SO_2-CH_2), 152.6 (C-5), 155.9 (C-4), 163.3 (C-2'), 167.7 (C-5'), 126.9, 130.2, 132.5, 135.3 (aromatic carbons)
16b	2.28 (s, 3H, Ar-CH_3), 4.71 (s, 2H, SO_2-CH_2), 7.41-7.88 (m, 4H, Ar-H) 10.28 (s, H, SH)	21.9 (Ar-CH_3), 56.6 (SO_2-CH_2), 153.1 (C-5), 154.5 (C-4), 161.7 (C-2'), 167.3 (C-5'), 126.4, 128.9, 131.8, 134.8 (aromatic carbons)
16c	4.77 (s, 2H, SO_2-CH_2), 7.47-7.94 (m, 4H, Ar-H) 10.38 (s, H, SH)	56.6 (SO_2-CH_2), 151.5 (C-5), 154.8 (C-4), 162.7 (C-2'), 168.5 (C-5'), 127.5, 129.7, 132.9, 135.2 (aromatic carbons)
17a	4.64 (s, 2H, SO_2-CH_2), 5.16 (bs, 2H, NH_2), 7.60-7.83 (m, 10H, Ar-H), 9.47 (bs, H, NH)	61.3 (SO_2-CH_2), 146.5 (C-5), 158.9 (C-4), 164.6 (C=O), 128.8, 129.4, 129.7, 130.5, 132.7, 133.3, 134.7, 135.2 (aromatic carbons)
17b	2.35 (s, 3H, Ar-CH_3), 4.62 (s, 2H, SO_2-CH_2), 5.13 (bs, 2H, NH_2), 7.62-7.85 (m, 9H, Ar-H), 9.43 (bs, H, NH)	22.3 (Ar-CH_3), 58.7 (SO_2-CH_2), 148.5 (C-5), 159.2 (C-4), 164.9 (C=O), 127.7, 128.5, 129.4, 130.1, 131.4, 131.6, 132.7, 133.5 (aromatic carbons)
17c	4.67 (s, 2H, SO_2-CH_2), 5.19 (bs, 2H, NH_2), 7.65-7.89 (m, 9H, Ar-H), 9.43 (bs, H, NH)	61.9 (SO_2-CH_2), 147.4 (C-5), 157.8 (C-4), 163.8 (C=O), 127.4, 128.1, 128.7, 129.8, 131.7, 132.8, 133.6, 135.3 (aromatic carbons)
19a	4.72 (s, 2H, SO_2-CH_2), 7.62-7.86 (m, 10H, Ar-H), 10.29 (s, H, SH)	61.5 (SO_2-CH_2), 146.7 (C-5), 159.2 (C-4), 161.4 (C-2'), 168.5 (C-5'), 128.5, 129.6, 129.9, 130.7, 132.7, 133.3, 134.7, 135.4 (aromatic carbons)
19b	2.29 (s, 3H, Ar-CH_3), 4.68 (s, 2H, SO_2-CH_2), 7.64-7.89 (m, 9H, Ar-H), 10.22 (s, H, SH)	22.3 (Ar-CH_3), 60.6 (SO_2-CH_2), 146.3 (C-5), 158.7 (C-4), 162.1 (C-2'), 168.3 (C-5'), 128.3, 129.4, 129.5, 130.4, 132.6, 133.5, 134.5, 134.9 (aromatic carbons)

Table 3 (continued)

Compd. No.	^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)
19c	4.76 (s, 2H, SO_2-CH_2), 7.68-7.92 (m, 9H, Ar-H), 10.22 (s, H, SH)	61.8 (SO_2-CH_2), 147.5 (C-5), 159.6 (C-4), 162.7 (C-2'), 168.8 (C-5'), 128.9, 129.8, 130.3, 131.6, 132.9, 133.5, 134.8, 135.7 (aromatic carbons)
20a	4.75 (s, 2H, SO_2-CH_2), 5.64 (bs, 2H, NH_2), 7.66-7.89 (m, 10H, Ar-H), 10.24 (s, H, SH)	59.7 (SO_2-CH_2), 146.9 (C-5), 159.6 (C-4), 163.8 (C-5'), 146.2 (C-3'), 128.2, 129.7, 130.4, 130.9, 132.6, 133.8, 134.6, 135.2 (aromatic carbons)
20b	2.32 (s, 3H, Ar-CH_3), 4.73 (s, 2H, SO_2-CH_2), 5.62 (bs, 2H, NH_2), 7.61-7.84 (m, 9H, Ar-H), 10.18 (s, H, SH)	21.9 (Ar-CH_3), 59.2 (SO_2-CH_2), 146.4 (C-5), 159.3 (C-4), 163.5 (C-5'), 145.7 (C-3'), 128.4, 129.6, 130.6, 131.7, 132.8, 134.2, 134.7, 135.4 (aromatic carbons)
20c	4.77 (s, 2H, SO_2-CH_2), 5.66 (bs, 2H, NH_2), 7.69-7.92 (m, 9H, Ar-H), 10.27 (s, H, SH)	60.6 (SO_2-CH_2), 147.4 (C-5), 159.3 (C-4), 162.5 (C-5'), 144.3 (C-3'), 128.4, 129.6, 130.6, 131.7, 132.8, 134.2, 134.7, 135.4 (aromatic carbons)
21a	4.67 (s, 2H, SO_2-CH_2), 7.60-7.85 (m, 10H, Ar-H), 10.16 (s, H, SH)	59.7 (SO_2-CH_2), 146.3 (C-5), 159.4 (C-4), 162.8 (C-2'), 168.7 (C-5'), 127.3, 128.9, 129.8, 131.8, 132.6, 133.5, 134.4, 135.3 (aromatic carbons)
21b	2.26 (s, 3H, Ar-CH_3), 4.63 (s, 2H, SO_2-CH_2), 7.66-7.93 (m, 9H, Ar-H), 10.25 (s, H, SH)	22.5 (Ar-CH_3), 60.4 (SO_2-CH_2), 147.1 (C-5), 159.5 (C-4), 161.7 (C-2'), 167.9 (C-5'), 126.8, 128.4, 129.3, 130.7, 131.9, 133.4, 134.8, 135.1 (aromatic carbons)
21c	4.75 (s, 2H, SO_2-CH_2), 7.65-7.84 (m, 9H, Ar-H), 10.28 (s, H, SH)	60.6 (SO_2-CH_2), 146.9 (C-5), 160.3 (C-4), 163.7 (C-2'), 169.5 (C-5'), 128.2, 130.3, 131.7, 132.8, 133.2, 133.8, 134.7, 135.5 (aromatic carbons)

Scheme 3



Ar = a) Ph
b) 4-Me.Ph
c) 4-Cl.Ph

(i) $N_2H_4.H_2O$ / Pyridine / EtOH
(ii) CS_2 / KOH / EtOH / US
(iii) AcOH
(iv) $N_2H_4.H_2O$ / H_2O
(v) HCl / H_2O

acetate-hexane, 1:4). The IR spectra were recorded on a Thermo Nicolet IR 200 FT-IR spectrometer as KBr pellets and the wave numbers were given in cm^{-1}. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$/DMSO-d_6 on a Varian EM-360 spectrometer at 300 and 75.5 MHz, respectively. All chemical shifts are reported in δ (ppm) using TMS as an internal standard. The microanalyses were performed on Perkin-Elmer 240C elemental analyzer. The starting compounds (4-aryl[1,2,3]selenadiazole-5-sulfonyl)acetic acid methyl ester (**3**), (4-aryl[1,2,3]thiadiazole-5-sulfonyl)acetic acid methyl ester (**4**), (2-phenyl-5-aryl-2*H*-[1,2,3]diazaphosphole-4-sulfonyl)acetic acid methyl ester (**6**) were prepared by the literature procedure [13].

(4-Aryl[1,2,3]selenadiazole-5-sulfonyl)acetic acid hydrazide (7), (4-Aryl[1,2,3]thiadiazole-5-sulfonyl)acetic acid hydrazide (8) and (2-Phenyl-5-aryl-2*H*-[1,2,3]diazaphosphole-4-sulfonyl)acetic acid hydrazide (17). General Procedure. To a solution of **3/4/6** (1 mmol) in absolute ethanol, hydrazine hydrate (80%, 4.5 mmol) and pyridine (0.4 mL) were added and stirred for 6 h at room temperature. The resultant solid was collected by filtration and recrystallized from ethanol.

Potassium (4-aryl[1,2,3]selenadiazole-5-sulfonylacetyl)-hydrazine-N'-carbodithio-ate (9), potassium (4-aryl[1,2,3]-thiadiazole-5-sulfonylacetyl)-hydrazine-N'-carbodithioate (10) and potassium (2-phenyl-5-aryl-2*H*-[1,2,3]diazaphosphole-4-sulfonylacetyl)-hydrazine-N'-carbodithioate (18). General Procedure. to a mixture of potassium hydroxide (2 mmol) and 7/8/17 (1 mmol) in absolute ethanol (5 mL), carbon disulfide (4 mmol) was added and sonicated for 12 h. the separated solid was filtered and dried.

5′-(4-Aryl[1,2,3]selenadiazole-5-sulfonylmethyl)-[1′,3′,4′]-thiadiazole-2′-thiol (11) / 5′-(4-Aryl[1,2,3]thiadiazole-5-sulfonylmethyl)-[1′,3′,4′]thiadiazole-2′-thiol (12) / 5′-(2-Phenyl-5-aryl-2*H*-[1,2,3]diazaphosphole-4-sulfonylmethyl)-thiadiazole-2′-thiol (19). General Procedure. The compound **9 / 10 / 18** (1 mmol) in acetic acid (4 mL) was refluxed for 24 h. The contents of the flask were cooled and poured onto crushed ice. The solid obtained was collected by filtration, dried and recrystallized from 2-propanol.

4′-Amino-5′-(4-aryl[1,2,3]selenadiazole-5-sulfonylmethyl)-4′*H*-[1′,2′,4′]triazole-3′-thiol (13), 4′-Amino-5′-(4-aryl-[1,2,3]-thiadiazole-5-sulfonylmethyl)-4′*H*-[1′,2′,4′]triazole-3′-thiol (14) and 4′-Amino-5′-(2-phenyl-5-aryl-2*H*-[1,2,3]diazaphosphole-4-sulfonylmethyl)-4′*H*-[1′,2′,4′]triazole-3′-thiol (20). General Procedure. To a solution of **9/10/18** (1 mmol) in 6 mL of water, hydrazine hydrate (80%, 2 mmol) was added and refluxed for 8-9 h. The contents of the flask were cooled, diluted with water and acidified with 2 mL of acetic acid. The separated solid was collected by filtration, dried and recrystallized from 2-propanol.

5′-(4-Aryl[1,2,3]selenadiazole-5-sulfonylmethyl)-[1′,3′,4′]-oxadiazole-2′-thiol (15), 5′-(4-Aryl[1,2,3]thiadiazole-5-sulfonylmethyl)-[1′,3′,4′]oxadiazole-2′-thiol (16) and 5′-(2-Phenyl-5-aryl-2*H*-[1,2,3]diazaphosphole-4-sulfonylmethyl)-[1′,3′,4′]oxadiazole-2′-thiol (21). General Procedure. The compound **9/10/18** (1 mmol) was dissolved in 6 mL of water and acidified with 1-2 mL of conc. HCl. The regenerated solid was collected by filtration, dried and recrystallized from 2-propanol.

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