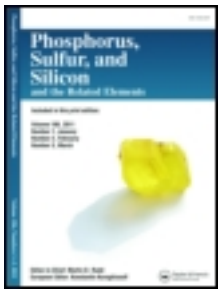

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis and bioactivity of some novel 5-arylmethylideneamino-1,3,4-thiadiazole-2-ylthioacetanilide derivatives

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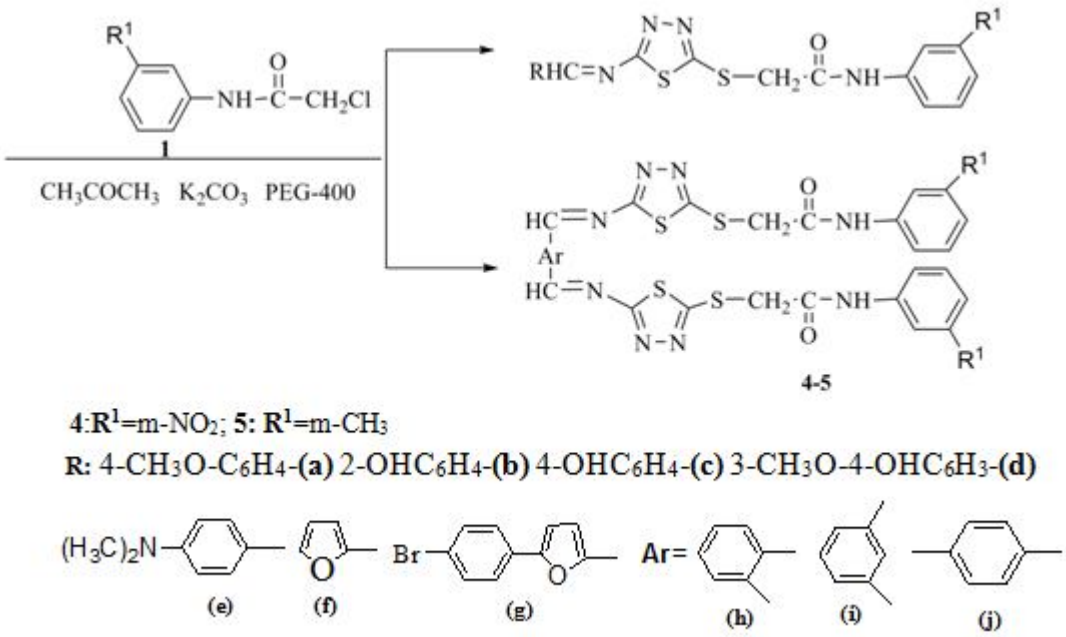

ABSTRACT: *Some novel of 5-arylmethylideneamino-1,3,4-thiadiazole-2-ylsulfanyl acetamide derivatives were synthesized by the S-alkylation of 5-arylmethylideneamino-2-mercapto-1,3,4-thiadiazoles with chloroacetyl anilide under*

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solid-liquid phase transfer catalysis using polyethylene glycol-400 (PEG-400) catalyst in the presence of potassium carbonate. Some of the title compounds were investigated for plant growth-regulating activity. They were found to enhance root elongation remarkably at a low concentration.

KEYWORDS: 5-arylmethyl**id**eneamino-1,3,4-thiadiazole-2-ylthioacetamides; phase transfer catalysis; bioactivity

INTRODUCTION

1,3,4-Thiadiazole and its heterocyclic derivatives are an important class of bioactive molecules that are widely used because of their membrane affinity as well as anticancer,[1] anti-*Helicobacter pylori*,[2] antibacterial,[3] CNS depressing, anticonvulsant,[4] antimicrobial,[5] anti-inflammatory,[6] carbonic anhydrase inhibiting, and corrosion inhibiting activities.[7] These compounds have been used in dyes and pharmaceuticals,[8] and used as building blocks for the synthesis of organic semiconductors.[9] They also serve as useful rigid subunits in macrocyclic receptors or molecular recognition[10,11] and plant growth-regulating activity.[12] Thus, given the wide application range of 1,3,4-thiadiazole and its heterocyclic derivatives in the fields of industrial, agricultural, and medicinal chemistry, they are increasingly gaining the attention of scientists.

A literature survey reveals that some Schiff compounds containing a 1,3,4-thiadiazole ring have good biological activities.[13] Other studies show that the incorporation of various substitutes into heterocyclic ring systems considerably augments the biological activities, and that amide agents

also have good bioactivity.[14,15] In view of these findings and in continuation of our research[16] we designed and synthesized a novel series of amide-substituted fused Schiff 1,3,4-thiadiazole systems as potential biological agents based on cumulative activity. Their plant growth-regulating activities were then examined.

In this paper, we report a mild and efficient method for the synthesis of 1,3,4-thiadiazole-5-ylthioacetamide derivatives using the environmentally friendly polyethylene glycol-400 (PEG-400) as a catalyst.

RESULTS AND DISCUSSION

The reaction sequence leading to the formation of the title compounds are shown in Scheme 1. 2-Chloroacetanilide **1** can be obtained in good to excellent yield according to our previous work.[17] 2-Amino-5-mercapto-1,3,4-thiadiazoles **2** were prepared in good yield according to literature,[18] and then reacted with aldehydes to give corresponding 5-arylmethylideneamino-2-mercapto-1,3,4-thiadiazoles **3**.

5-Arylmethylideneamino-1,3,4-thiadiazole-2-ylthioacetamide derivatives **4** and **5** were synthesized from **1** and **3** by refluxing with K_2CO_3 and PEG-400 in acetone for 1.5 h. This method had the advantages of simple operation, short reaction times, and high yields.

EXPERIMENTAL

All regents were purchased and used without further purification. Melting points were measured on an X-4 digital melting-point apparatus and uncorrected. IR spectra were recorded in KBr on an

Alpha Centauri FT-IR spectrophotometer, and ^{1}HNMR spectra were recorded on a Mercuryplux-400, Varian instrument (400 MHz) using DMSO-d_6 as solvent (operating at 400MHz for ^{1}H, and 100MHz for ^{13}C) and TMS as an internal reference. Elemental analysis was performed on a PE-2400 CHN instrument.

General procedure for the synthesis of 5-arylmethylideneamino-1,3,4-thiadiazole -2-ylthioacetanilide derivatives

The syntheses of **4** and **5** were carried out by adding K_2CO_3 (2 mmol) to a mixture of **3** (2 mmol) and 15 ml of acetone. The resulting mixture was then stirred at ambient temperature until **3** completely dissolved. After sequentially adding PEG-400 (0.2 mmol) and **1** (2 mmol), the mixture was refluxed for 1.5 h. After evaporating and reclaiming the solvent in a vacuum, the crude products were obtained and the mixture was cooled to ambient temperature. The crude product was then filtered and washed with 10 mL of distilled water three times. The pure products were acquired by recrystallization from DMF-EtOH-H_2O. The chemical structure of all title compounds were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and elemental analyses. The Supplemental Materials contains a representative ^{1}H and ^{13}C NMR spectrum for 5e (Figures S 1 and S 2)

Physical and Spectroscopic Data for the Title Compounds

4a, N-(3-nitrophenyl)-5-(4-methyloxyphenylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide. Yield 90%, m.p. 192-194 ºC. IR (KBr): 3249 (N-H), 1686 (C=O), 1562 (CH=N), 1391 (S-CH_2), 674 cm^{-1} (C-S-C). ^{1}H NMR : δ 3.74 (s, 3H, OCH_3), 4.37 (s, 2H, SCH_2),

7.24 (m, 8H, ArH), 8.80 (s, 1H, CH=N), 10.76 (s, 1H, NH). ^{13}C NMR (DMSO-d_6, 100MHz): δ 192.0, 168.2, 164.2, 163.1, 160.1, 148.7, 140.5, 132.5, 131.0, 127.9, 125.8, 118.8, 115.3, 114.8, 55.9, 39.6. Anal. Calcd. For $C_{18}H_{15}N_5O_4S_2$: C, 50.34; H, 3.52; N, 16.31. Found: C, 50.31; H, 3.55; N, 16.29.

4b, N-(3-nitrophenyl)-5-(2-hydroxyphenylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide. Yield 90%, m.p. 228-230 ºC. IR (KBr): 3436 (O-H), 3285 (N-H), 1661 (C=O), 1530 (CH=N), 1386 (S-CH_2), 672 cm^{-1} (C-S-C). ^{1}H NMR : δ 4.36 (s, 2H, SCH_2), 7.47 (m, 8H, ArH), 8.63 (s, 1H, CH=N), 8.78 (s, 1H, OH), 10.92 (s, 1H, NH). ^{13}C NMR : δ 170.0, 167.0, 166.1, 160.7, 160.3, 148.3, 139.9, 130.7, 130.4, 129.2, 125.1, 122.3, 118.1, 116.9, 116.5, 113.2, 38.6. Anal. Calcd. For $C_{17}H_{13}N_5O_4S_2$: C, 49.15; H, 3.15; N, 16.86. Found: C, 49.17; H, 3.11; N, 16.88.

4c, N-(3-nitrophenyl)-5-(4-hydroxyphenylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide. Yield 95%, m.p. 175-176 ºC. IR (KBr): 3336 (O-H), 3295 (N-H), 1687 (C=O), 1521 (CH=N), 1348 (S-CH_2), 670 cm^{-1} (C-S-C). ^{1}H NMR : δ 4.36 (s, 2H, SCH_2), 7.17 (m, 8H, ArH), 8.00 (s, 1H, CH=N), 8.84 (s, 1H, OH), 10.32 (s, 1H, NH). ^{13}C NMR : δ 170.0, 168.2, 166.7, 160.8, 160.1, 148.0, 139.9, 130.4, 129.9, 127.7, 125.1, 118.1, 116.0, 113.2, 38.9. Anal. Calcd For $C_{17}H_{13}N_5O_4S_2$: C, 49.15; H, 3.15; N, 16.86. Found: C, 49.13; H, 3.17; N, 16.83.

4d, N-(3-nitrophenyl)-5-(3-methyloxy-4-hydroxyphenylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide. Yield 87%, m.p. 216-218 ºC. IR (KBr): 3433 (O-H), 3289

(N-H), 1653 (C=O), 1579 (CH=N), 1386 (S-CH_2), 699 cm^{-1} (C-S-C). ^{1}H NMR : δ 3.80 (s, 3H, OCH_3), 4.37 (s, 2H, SCH_2), 7.45 (m, 7H, ArH), 8.64 (s, 1H, CH=N), 8.73 (s, 1H, OH), 10.91(s, 1H, NH). ^{13}C NMR : δ 174.6, 168.7, 166.1, 161.5, 152.9, 148.2, 148.0, 139.8, 130.4, 126.9, 125.9, 125.1, 118.2, 115.7, 113.3, 111.1, 56.0, 38.8. Anal. Calcd. For $C_{18}H_{15}N_5O_5S_2$: C, 48.53; H, 3.39; N, 15.72. Found: C, 48.51; H, 3.42; N, 15.70.

4e, N-(3-nitrophenyl)-5-(4-N,N-dimethylaminophenylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide. Yield 90%, m.p.>270 ºC. IR (KBr): 3241 (N-H), 1616 (C=O), 1584 (CH=N), 1352 (S-CH_2), 687 cm^{-1} (C-S-C). ^{1}H NMR : δ 3.36 (s, 6H, CH_3), 4.37 (s, 2H, SCH_2), 7.36 (m, 8H, ArH), 8.61 (s, 1H, CH=N), 10.90 (s, 1H , NH). ^{13}C NMR : δ 175.2, 167.9, 165.3, 160.4, 153.9, 151.8, 130.3, 129.9, 123.6, 121.5, 115.5, 114.6, 114.4, 64.7, 40.1, 38.8. Anal. Calcd. For $C_{19}H_{18}N_6O_3S_2$: C, 51.57; H, 4.10; N, 18.99. Found: C, 51.54; H, 4.12; N, 18.97.

4f, N-(3-nitrophenyl)-5-(2-furylmethylideneamino)-1,3,4-thiadiazole- 2-ylthioacetamide. Yield 90%, m.p. 212-214 ºC. IR (KBr): 3253 (N-H), 1681 (C=O), 1549 (CH=N), 1393 (S-CH_2), 679 cm^{-1} (C-S-C). ^{1}H NMR : δ 4.37 (s, 2H, SCH_2), 7.18 (m, 3H, Furyl), 7.80 (m, 4H, ArH), 9.06 (s, 1H, CH=N), 10.91 (s, 1H, NH). ^{13}C NMR : δ 176.7, 171.0, 166.7, 149.1, 148.0, 146.5, 143.9, 139.9, 130.4, 125.1, 118.2, 113.2, 109.9, 109.5, 38.9. Anal. Calcd. For $C_{15}H_{11}N_5O_4S_2$: C, 46.27; H, 2.85; N, 17.99. Found: C, 46.25; H, 2.88; N, 17.97.

4g, N-(3-nitrophenyl)-5-(5-(4-bromophenyl)-2-furylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide. Yield 88%, m.p. 234-235 ºC. IR (KBr): 3245 (N-H), 1688

(C=O), 1594 (CH=N), 1385 (S-CH_2), 673 cm^{-1} (C-S-C). ^{1}H NMR : δ 4.37 (s, 2H, SCH_2), 7.67 (m, 2H, Furyl), 7.85 (m, 8H, ArH), 8.70 (s, 1H, CH=N), 10.83 (s, 1H, NH). ^{13}C NMR : δ 169.1, 166.3, 162.3, 155.1, 148.4, 148.0, 142.1, 139.8, 133.5, 130.4, 130.3, 128.2, 127.4, 124.6, 118.2, 113.2, 109.3, 104.6, 38.9. Anal. Calcd. For $C_{21}H_{14}N_5O_4S_2Br$: C, 46.33; H, 2.59; N, 12.86. Found: C, 46.31; H, 2.61; N, 12.83.

4h, N,N'-di(3-nitrophenyl)-5,5'-(1,2-phenylenedimethylideneamino-1,3,4-thiadiazole-2-ylthioacetamide). Yield 78%, m.p. 164-165 ºC. IR (KBr): 3265 (N-H), 1629 (C=O), 1530 (CH=N), 1347 (S-CH_2), 669 cm^{-1} (C-S-C). ^{1}H NMR : δ 4.36 (s, 4H, SCH_2), 7.69 (m, 12H, ArH), 8.65 (s, 2H, CH=N), 10.90 (s, 2H, NH). ^{13}C NMR : δ 173.1, 168.2, 165.2, 160.1, 148.6, 139.5, 134.1, 131.8, 130.1, 129.3, 127.7, 116.4, 115.5, 38.7. Anal. Calcd. For $C_{28}H_{20}N_{10}O_6S_4$: C, 46.66; H, 2.80; N, 19.43. Found: C, 46.68; H, 2.82; N, 19.40.

4i N,N'-di(3-nitrophenyl)-5,5'-(1,3-phenylenedimethylideneamino-1,3,4-thiadiazole-2-ylthioacetamide). Yield 78%, m.p. 182-184 ºC. IR (KBr): 3280 (N-H), 1696 (C=O), 1529 (CH=N), 1351 (S-CH_2), 694 cm^{-1} (C-S-C). ^{1}H NMR : δ 4.36 (s, 4H, SCH_2), 7.69 (m, 12H, ArH), 8.65 (s, 2H, CH=N), 10.90 (s, 2H, NH). ^{13}C NMR : δ 172.5, 168.6, 164.1, 160.3, 148.9, 139.4, 133.9, 131.6, 129.0, 128.8, 128.5, 127.7, 116.7, 115.1, 38.9. Anal. Calcd. For $C_{28}H_{20}N_{10}O_6S_4$: C, 46.66; H, 2.80; N, 19.43. Found: C, 46.64; H, 2.78; N, 19.46.

5a, N-(3-methylphenyl)-5-(4-methyloxyphenylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide. Yield 81%, m.p. 165-167 ºC. IR (KBr): 3187 (N-H), 1665

(C=O), 1561 (CH=N), 1378 (S-CH_2), 699 cm^{-1} (C-S-C). ^{1}H NMR : δ 2.31 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 4.86 (s, 2H, SCH_2), 7.16 (m, 8H, ArH), 8.12 (s, 1H, CH=N), 10.13 (s, 1H, NH). ^{13}C NMR : δ 182.0, 168.2, 164.2, 163.1, 160.1, 140.5, 138.5, 130.2, 128.7, 126.2, 124.9, 121.3, 118.8, 114.4, 55.9, 38.6, 21.3. Anal. Calcd. For $C_{19}H_{18}N_4O_2S_2$: C, 57.27; H, 4.55; N, 14.06. Found: C, 57.29; H, 4.52; N, 14.08.

5b, N-(3-methylphenyl)-5-(2-hydroxyphenylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide. Yield 68%, m.p. 122-124 ºC. IR (KBr): 3432(O-H), 3262 (N-H), 1659 (C=O), 1551 (CH=N), 1369 (S-CH_2), 686 cm^{-1} (C-S-C). ^{1}H NMR : δ 2.31 (s, 3H, CH_3), 4.39 (s, 2H, SCH_2), 6.98 (m, 8H, ArH), 8.53 (s, 1H, CH=N), 8.77 (s, 1H, OH), 10.95 (s, 1H, NH). ^{13}C NMR : δ 175.0, 167.3, 166.7, 162.7, 160.3, 149.4, 138.7, 138.1, 130.4, 128.6, 124.3, 122.3, 119.7, 116.3, 116.5, 113.2, 38.7, 21.2. Anal. Calcd. For $C_{18}H_{16}N_4O_2S_2$: C, 56.23; H, 4.19; N, 14.57. Found: C, 56.20; H, 4.22; N, 14.55.

5c, N-(3-methylphenyl)-5-(4-hydroxyphenylmethylideneamino)-1,3,4-thiadiazole -2-ylthioacetamide. Yield 82%, m.p. 154-155 ºC. IR (KBr): 3330(O-H), 3286 (N-H), 1654 (C=O), 1503 (CH=N), 1318 (S-CH_2), 682 cm^{-1} (C-S-C). ^{1}H NMR : δ 2.28 (s, 3H, CH_3), 3.97 (s, 2H, SCH_2), 7.15 (m, 8H, ArH), 8.05 (s, 1H, CH=N), 8.86 (s, 1H, OH), 10.15 (s, 1H, NH). ^{13}C NMR : δ 170.0, 167.0, 165.7, 160.7, 160.3, 138.7, 138.1, 130.4, 128.6, 124.3, 122.3, 119.7, 118.2, 116.3, 38.7, 21.2. Anal. Calcd. For $C_{18}H_{16}N_4O_2S_2$: C, 56.23; H, 4.19; N, 14.57. Found: C, 56.25; H, 4.21; N, 14.54.

5d, N-(3-methylphenyl)-5-(3-methyloxy-4-hydroxyphenylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide. Yield 78%, m.p. >270 ºC. IR (KBr): 3340(O-H), 3259 (N-H), 1643 (C=O), 1509 (CH=N), 1402 (S-CH_2), 634 cm^{-1} (C-S-C). ^{1}H NMR : δ 2.33 (s, 3H, CH_3), 3.63 (s, 3H, OCH_3), 4.39 (s, 2H, SCH_2), 7.13 (m, 7H, ArH), 8.61 (s, 1H, CH=N), 8.75 (s, 1H, OH), 10.14 (s, 1H, NH). ^{13}C NMR : δ 174.2, 168.5, 165.1, 160.5, 151.5, 148.2, 138.6, 138.1, 128.9, 126.9, 125.9, 122.8, 121.1, 118.2, 117.7, 114.3, 56.2, 38.7, 22.3. Anal. Calcd. For $C_{19}H_{18}N_4O_3S_2$: C, 55.06; H, 4.38; N, 13.52. Found: C, 55.09; H, 4.36; N, 13.49.

5e, N-(3-methylphenyl)-5-(4-N,N-dimethylaminophenylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide. Yield 85%, m.p. 221-222 ºC. IR (KBr): 3204 (N-H), 1611 (C=O), 1580 (CH=N), 1312 (S-CH_2), 637 cm^{-1} (C-S-C). ^{1}H NMR : δ 2.28 (s, 3H, CH_3), 3.33 (s, 6H, CH_3), 4.27 (s, 2H, SCH_2), 7.13 (m, 8H, ArH), 8.61 (s, 1H, CH=N), 10.29 (s, 1H, NH). ^{13}C NMR : δ 175.2, 167.8, 165.1, 160.4, 153.9, 138.6, 138.0, 132.3, 128.6, 124.3, 121.5, 119.6, 116.3, 111.5, 40.1, 38.9, 21.1. Anal. Calcd. For $C_{20}H_{21}N_5OS_2$: C, 58.37; H, 5.14; N, 17.02. Found: C, 58.35; H, 5.17; N, 17.00.

5f, N-(3-methylphenyl)-5-(2-furylmethylideneamino)-1,3,4-thiadiazole- 2-ylthioacetamide. Yield 85%, m.p. >270 ºC. IR (KBr): 3233 (N-H), 1625 (C=O), 1531 (CH=N), 1372 (S-CH_2), 670 cm^{-1} (C-S-C). ^{1}H NMR : δ 2.28 (s, 3H, CH_3), 4.37 (s, 2H, SCH_2), 6.92 (m, 3H, Furyl), 7.36 (m, 4H, ArH), 8.11 (s, 1H, CH=N), 10.61 (s, 1H, NH). ^{13}C NMR : δ 176.1, 170.0, 165.7, 148.2,

146.5, 143.9, 138.6, 138.4, 128.8, 124.2, 121.2, 118.5, 109.8, 109.5, 38.6, 21.3. Anal. Calcd. For $C_{16}H_{14}N_4O_2S_2$: C, 53. 62; H, 3.94; N, 15.63. Found: C, 53. 59; H, 3.96; N, 15.61.

5g, N-(3-methylphenyl)-5-(5-(4-bromophenyl)-2-furylmethylideneamino)-1,3,4-thiadiazole-2-ylthioacetamide). Yield 78%, m.p. >270 ºC. IR (KBr): 3230 (N-H), 1641 (C=O), 1514 (CH=N), 1402 (S-CH_2), 633 cm^{-1} (C-S-C). ^{1}H NMR : δ 2.28 (s, 3H, CH_3), 4.36 (s, 2H, SCH_2), 7.66 (m, 2H, Furyl), 7.84 (m, 8H, ArH), 8.68 (s, 1H, CH=N), 10.63 (s, 1H, NH). ^{13}C NMR : δ 169.0, 165.3, 162.3, 155.1, 148.4, 146.0, 138.5, 138.3, 132.1, 130.1, 129.4, 128.3, 124.2, 123.4, 121.6, 118.2, 107.3, 104.6, 38.6, 21.3. Anal. Calcd. For $C_{22}H_{17}N_4O_2S_2Br$: C, 51.47; H, 3.34; N, 10.91. Found: C, 51.50; H, 3.32; N, 10.94.

5h N,N'-di(3-methylphenyl)-5,5'-(1,2-phenylenedimethylideneamino-1,3,4-thiadiazole-2-ylthioacetamide). Yield 80%, m.p. >270 ºC. IR (KBr): 3284 (N-H), 1653 (C=O), 1504 (CH=N), 1319 (S-CH_2), 642 cm^{-1} (C-S-C). ^{1}H NMR : δ 2.29 (s, 6H, CH_3), 4.01 (s, 4H, SCH_2), 7.15 (m, 12H, ArH), 8.65 (s, 2H, CH=N), 10.31 (s, 2H, NH). ^{13}C NMR : δ 170.0, 168.2, 165.7, 160.1, 138.6, 138.5, 134.0, 131.2, 130.1, 128.6, 124.2, 121.3, 119.6, 38.7, 21.1. Anal. Calcd. For $C_{30}H_{26}N_8O_2S_4$: C, 54.69; H, 3.98; N, 17.01. Found: C, 54.71; H, 3.95; N, 17.04.

5i N,N'-di(3-methylphenyl)-5,5'-(1,3-phenylenedimethylideneamino-1,3,4-thiadiazole-2-ylthioacetamide). Yield 80%, m.p. 138-140 ºC. IR (KBr): 3293 (N-H), 1670 (C=O), 1548 (CH=N), 1368 (S-CH_2), 688 cm^{-1} (C-S-C). ^{1}H NMR : δ 2.29 (s, 6H, CH_3), 4.26 (s, 4H, SCH_2), 7.48 (m, 12H, ArH), 8.64 (s, 2H, CH=N), 10.40 (s, 2H, NH). ^{13}C NMR : δ 172.5,

168.6, 164.1, 160.3, 138.9, 138.4, 133.9, 131.5, 129.0, 128.9, 128.5, 124.7, 121.2, 118.1, 38.9, 21.2. Anal. Calcd. For $C_{30}H_{26}N_8O_2S_4$: C, 54.69; H, 3.98; N, 17.01. Found: C, 54.66; H, 3.96; N, 17.03.

5j N,N'-di(3-methylphenyl)-5,5'-(1,4-phenylenedimethylideneamino-1,3,4-thiadiazole-2-ylthioacetamide). Yield 82%, m.p. 232-234 ºC. IR (KBr): 3273 (N-H), 1660 (C=O), 1546 (CH=N), 1370 (S-CH_2), 691 cm^{-1} (C-S-C). ^{1}H NMR : δ 2.30 (s, 6H, CH_3), 4.33 (s, 4H, SCH_2), 7.43 (m, 12H, ArH), 8.15 (s, 2H, CH=N), 10.26 (s, 2H, NH). ^{13}C NMR : δ 170.7, 168.6, 166.4, 164.1, 139.4, 138.7, 136.0, 129.3, 128.8, 124.9, 120.3, 117.0, 39.6, 21.9. Anal. Calcd. For $C_{30}H_{26}N_8O_2S_4$: C, 54.69; H, 3.98; N, 17.01. Found: C, 54.67; H, 3.95; N, 17.00.

BIOLOGICAL ACTIVITY

Some of the synthesized compounds were investigated for plant growth regulation activity. The plate culture method was adopted, and the compound solutions were prepared in the concentration of 100, 10, 1, 0.1, 0.01, and 0.001 ppm. Rapeseeds were cultured in a 10 cm flat utensil with 10 mL of different solution and a circular filter paper. Then, the roots were allowed to grow at room temperature. The root length was obtained after 4 d. The percentage plant growth activity was calculated according to the following equation: Percentage plant growth activity = $(N-N_1)/N_1 \times 100\%$, where N is the root length cultured in compound solution, and N_1 is the root length cultured in distilled water under the same condition.

The results, as shown in Table S 1 (Supplemental Materials), indicated that all of the tested compounds displayed good inhibition activities against the root growth of tested weeds at high concentration of 100 ppm, while displayed enhancing root elongation activity at a low concentration of 1 to 0.001 ppm. For example, compound **4f** displayed 36.42% enhancing root a elongation activity at a low concentration of 0.001 ppm. When compared with heteroauxing it is seen that the compounds have obvious inhibition of root elongation at high concentration of 100 ppm, while they show remarkable enhancement in root elongation at the low concentration.

CONCLUSION

In summary, we describe a simple, efficient, straightforward method for the synthesis of N-benzylideneamino-1,3,4-thiadiazole-2-ylsulfanyl acetamide derivatives. The ambient conditions, high reaction rates, excellent product yields, and easy work-up procedure which using of PEG-400 as a phase transfer catalyst not only make this methodology promoter, but also make it significant under the umbrella of environmentally greener and safer processes. In addition, some of the title compounds have considerable promoting activities on the rapeseeds growth.

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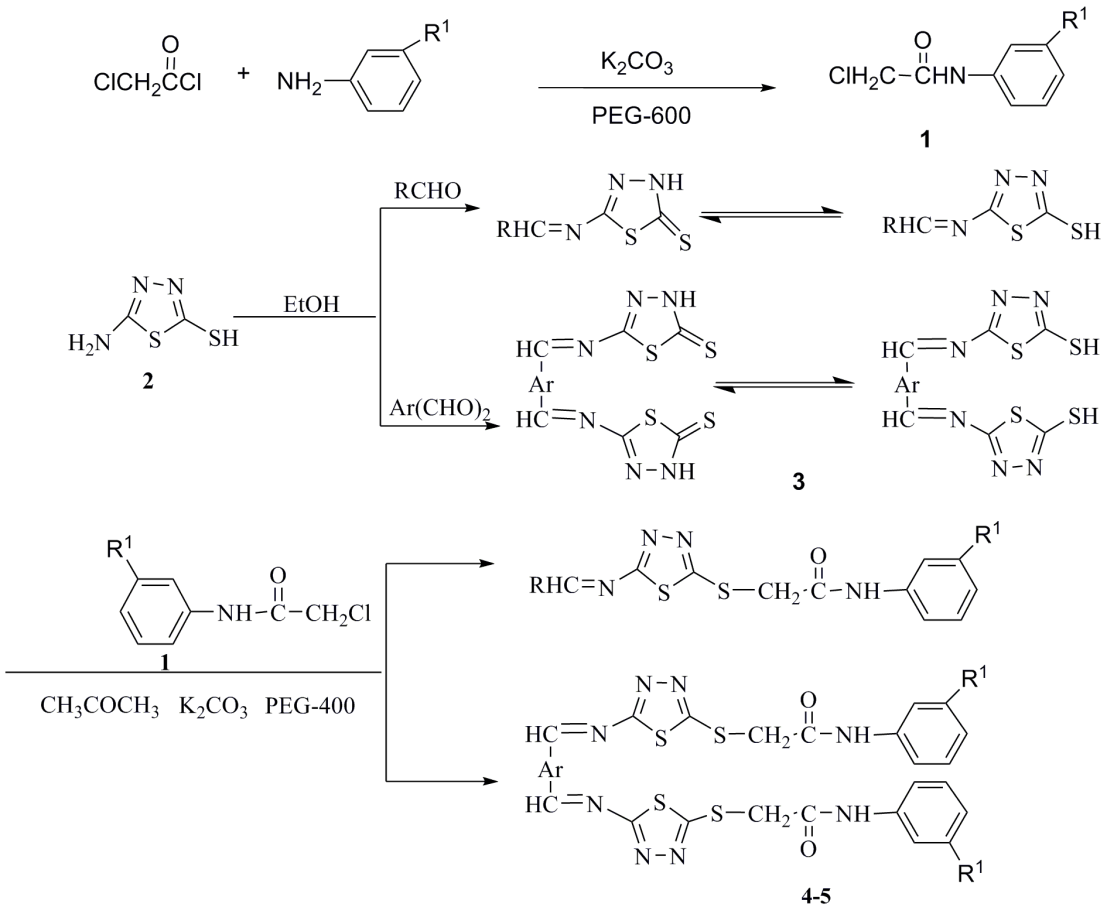
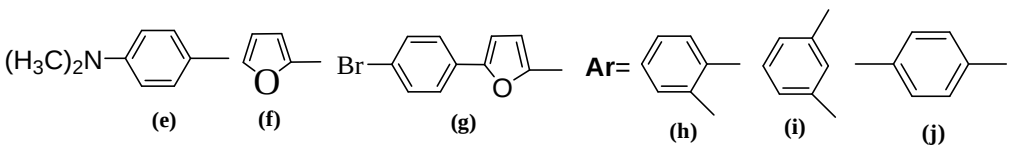


4:**R**^{1}=m-NO_2; **5: R**^{1}=m-CH_3

R: 4-CH_3O-C_6H_4-**(a)** 2-OHC_6H_4-**(b)** 4-OHC_6H_4-**(c)** 3-CH_3O-4-OHC_6H_3-**(d)**



SCHEME 1

Supplemental Materials

Biological Activity

Table S 1: Plant Growth regulating activity (%) data

Compound	Plant growth activity [a] (%)					
	100 mg/L	10 mg/L	1 mg/L	0.1 mg/L	0.01 mg/L	0.001 mg/L
4b	-100	-55.04	41.42	24.08	43.73	10.4
4c	-100	-64.67	36.37	67.24	40.32	21.00
4d	-100	-12.33	15.29	15.88	35.09	4.43
4e	-100	-25.1	44.7	6.17	6.83	4.13
4f	-100	7.58	33.16	29.29	42.15	36.42
4g	-100	-60.89	52.02	30.54	-10.54	-3.08
Heteroauxin	-100	-66.67	-33.66	77.65	73.99	27.15

a The solution was prepared in the proportion of H_2O:DMF=99.5:0.5, and 0.1 g Tween 80 was added to induce dissolution of the compound.

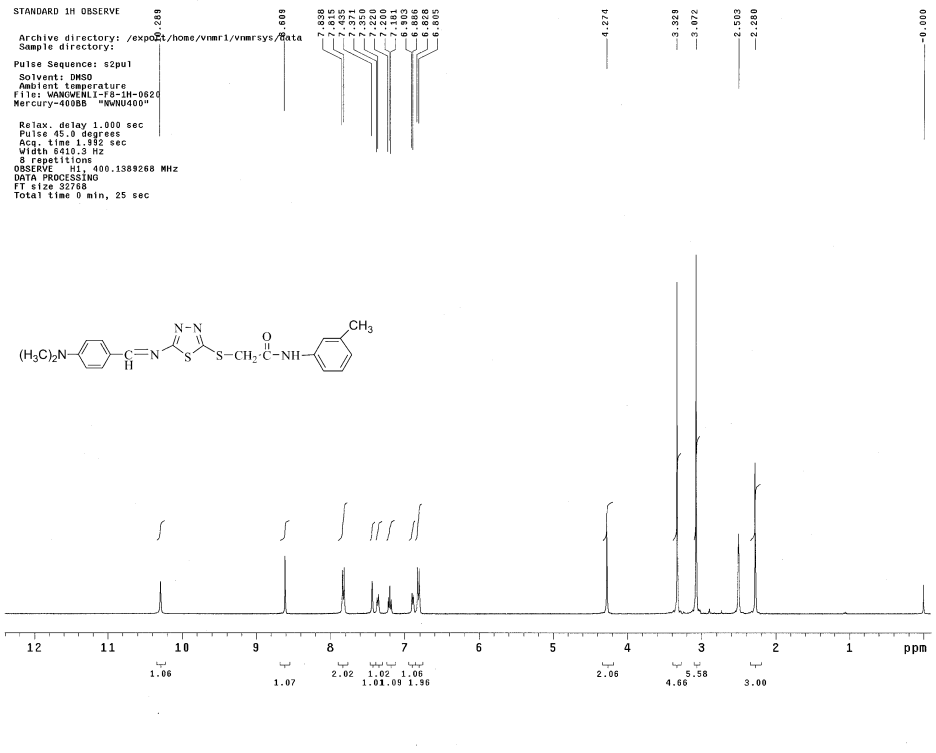


Figure S 1: ^{1}H NMR of 5e

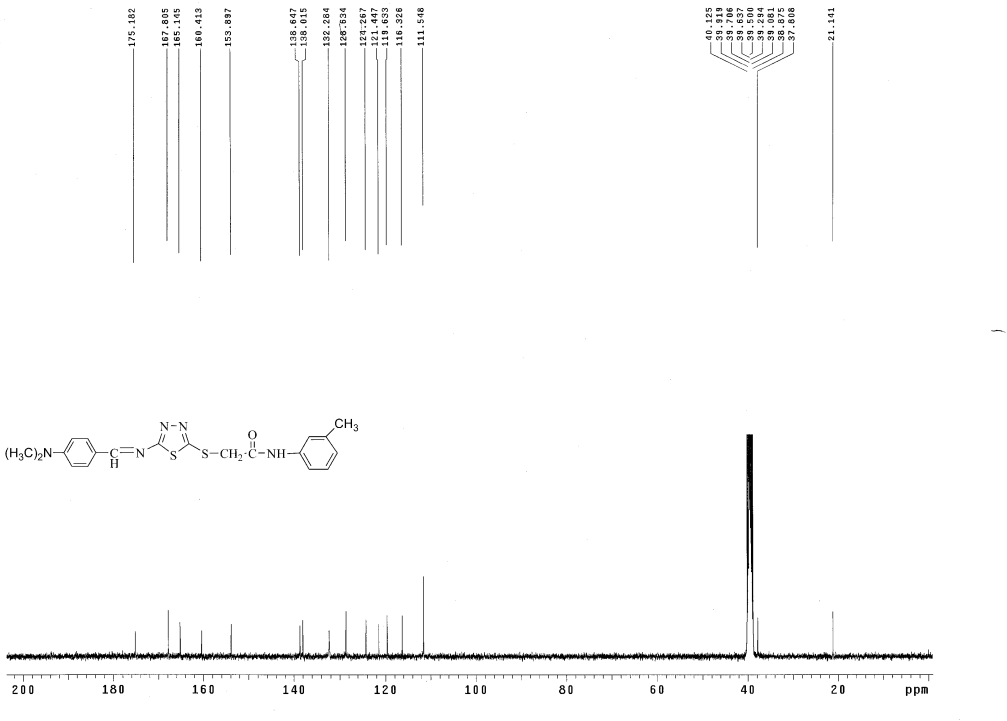


Figure S 2: ^{13}C NMR of 5e