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Synthesis of new thiophene, furan and pyridine substituted 1,2,4,5-oxadiazaboroles

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Abstract

Twenty-two new 3,4,5-trisubstituted 1,2,4,5-oxadiazaboroles were prepared by the cyclocondensation reaction of *N*-substituted thiophene, furan and pyridine carboxamidoximes with phenylboronic acid in refluxing toluene in good yields. The structures of the new oxadiazaboroles were elucidated by means of spectral measurements (IR, ^{1}H, ^{13}C, ^{11}B NMR, MS, X-ray) and physical data (melting points, elemental compositions by HRMS).

Keywords: Oxadiazaboroles; Cyclocondensation; Amidoxime; Thiophene; Furan; Pyridine

1. Introduction

Amidoximes are versatile precursors of many heterocyclic compounds of pharmaceutical importance [1,2]. On the other hand, aryl boronic acids and their esters are highly popular as synthetic intermediates in organic synthesis for their ease of conversion to other functional groups (such as phenols and aryl halides) with well-known reactivity [3–6]. To our best knowledge, a literature survey of oxadiazaboroles from amidoxime and phenyl boronic acid reveals that only a limited number of reports were given in the 1960s and 1970s, and no spectral data were supplied for those heterocycles [7–10]. As an ongoing research on assembling amidoxime-based heterocyclic compounds, we report here the preparation and mass spectra of new thiophene, furan and pyridine substituted 1,2,4,5-oxadiazaboroles.

2. Experimental

2.1. Materials and general methods

All reactions were performed under dry argon or nitrogen atmosphere. Aldehydes, *N*-chlorosuccinimide and primary amines were purchased from Merck and Fluka. Phenylboronic acid was purchased from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on Bruker and Varian spectrometers (300 and 400 MHz for proton, 75 and 100 MHz for carbon). ^{11}B NMR spectra of the samples (1–19 mg) were recorded on a Bruker Avance 500 spectrometer (Bruker Bio Spin Scandinavia AB, Täby, Sweden) equipped with a BBO-5 mm-Zgrad probe with $CDCl_3$ as the solvent and referenced to a standard 15% BF_3–Et_2O sample (0.00 ppm frequency given by Bruker software). The spectra were recorded at 160.46 MHz by non-decoupled single pulse excitation with a 30° pulse angle and 1000–10 000 scans. IR spectra were recorded on a JASCO 430 FT/IR instrument (as KBr pellets). Mass spectra were measured on an Agilent GC 6890N gas chromatograph with mass detector MS 5975. High resolution mass spectra of the compounds were measured on a VG ZabSpec mass spectrometer (Micromass, Manchester, UK) equipped with

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the Opus V3.3X program package. Melting points were determined on a Meltemp apparatus and were uncorrected. Flash column chromatography was performed on Silica Gel (Merck, 230–400 Mesh ASTM). TLC was done using pre-coated plates with a fluorescent indicator (Merck 5735). The stain solutions of permanganate, *p*-anisaldehyde and iodine were used for visualization of the TLC spots.

Thiophene-2-carboxaldehyde oxime, furan-2-carbaldehydeoxime, thiophene-2-hydroximoyl chloride, 5-chloro-thiophene-2-hydroximoyl chloride, 5-chloro-furan-2-hydroximoyl chloride, *N*-(*p*-methoxyphenyl)thiophene-2-carboxamidoxime and *N*-*p*-tolylthiophene-2-carboxamidoxime were prepared by utilizing literature procedures described previously [12–17].

2.2. Synthesis of N-substituted amidoximes

2.2.1. N-Phenyl-5-chloro-thiophene-2-carboxamidoxime (**3a**)

To a solution of 5-chloro-thiophene-2-hydroximoyl chloride (**2a**) (0.98 g, 6.06 mmol) in chloroform (20 mL) was added dropwise aniline (1.13 g, 12.1 mmol) in chloroform with constant stirring at room temperature. The reaction mixture was stirred for 2 d. The precipitate was filtered and the solution was evaporated under reduced pressure. The residual solid was subjected to flash column chromatography (eluant: hexane:ethyl acetate; 1:3) to give *N*-phenyl-5-chloro-thiophene-2-carboxamidoxime (**3a**), 0.78 g, yield: 65%. M.p. 131–133 °C. R_f: 0.42 (hexane:ethyl acetate; 3:1). IR (KBr, *v*: cm^{-1}): 3368 (N–H), 3204–3099 (broad, NOH), 1630 (C=N). ^1H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ 9.98 (broad s, 1H), 7.20 (broad s, 1H), 6.95 (t, 1H), 6.82 (d, $J = 7.4$ Hz, 2H), 6.65 (d, $J = 3.9$ Hz, 1H), 6.61 (d, $J = 3.9$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 145.13, 140.00, 132.62, 130.00, 128.40, 127.06, 125.93, 122.46, 121.20, 119.92. MS (*m*/*z*,%): 252 (M^+,32), 235 (76), 220 (16), 200 (12), 143 (23), 93 (100), 77 (31), 65 (22), 51 (14).

2.2.2. N-(4-Methylphenyl)-5-chloro-thiophene-2-carboxamidoxime (**3c**)

Colourless needles (hexane–ethyl acetate). Yield: 50%. M.p. 132–134 °C. R_f: 0.54 (hexane:ethyl acetate; 3:1). IR (KBr, *v*: cm^{-1}): 3363 (N–H), 3213–3171 (broad, NOH), 1627 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.41 (s, 1H, NOH), 7.29 (s, 1H, NH), 6.98 (d, $J = 7.9$ Hz, 2H), 6.78 (d, $J = 7.6$ Hz, 2H), 6.70 (m, 1H), 6.60 (m, 1H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 146.05, 137.66, 132.98, 130.34, 129.42, 127.46, 126.25, 122.35, 20.83. MS (*m*/*z*,%): M–H_2O, 248 (100), 213 (47), 77 (11).

2.2.3. N-(4-Methoxyphenyl)-5-chloro-thiophene-2-carboxamidoxime (**3e**)

White plates (hexane–ethyl acetate). Yield: 65%. M.p. 140–142 °C. R_f: 0.45 (hexane:ethyl acetate; 3:1). IR (KBr, *v*: cm^{-1}): 3344 (N–H), 3234–3111 (broad, NOH), 1631 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.32 (s, 1H, NOH), 7.23 (s, 1H, NH), 6.86 (m, 2H), 6.76 (m, 2H), 6.67 (m, 1H), 6.52 (m, 1H), 3.76 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 156.37, 146.66, 133.12, 132.87, 130.42, 127.52, 126.21, 124.98, 114.13, 55.49. MS (*m*/*z*,%): M–H_2O, 264 (100), 249 (88), 221 (21).

2.2.4. N-(4-Chlorophenyl)-5-chloro-thiophene-2-carboxamidoxime (**3f**)

Light yellow needles (hexane–ethyl acetate). Yield: 73%. M.p. 97–99 °C. R_f: 0.50 (hexane:ethyl acetate; 3:2). IR (KBr, *v*: cm^{-1}): 3382 (N–H), 3215 (broad, NOH), 1626 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.64 (s, 1H, NOH), 7.66 (s, 1H, NH), 7.14 (d, $J = 9.2$ Hz, 2H), 7.03 (d, $J = 9.2$ Hz, 2H), 6.79 (d, $J = 6.7$ Hz, 1H), 6.73 (d, $J = 4.9$ Hz, 1H), 6.66 (d, $J = 4.1$ Hz, 1H), 6.59 (d, $J = 9.1$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 145.80, 145.15, 139.26, 132.74, 130.76, 128.99, 128.78, 127.67, 127.49, 126.41, 122.61, 116.20. MS (*m*/*z*,%): M–H_2O, 268 (100), 233 (40), 198 (5).

2.2.5. N-(4-Bromophenyl)-5-chloro-thiophene-2-carboxamidoxime (**3g**)

Yield: 84%. M.p. 143–145 °C. R_f: 0.61 (hexane:ethyl acetate; 3:2). IR (KBr, *v*: cm^{-1}): 3387 (N–H), 3235 (broad, NOH), 1630 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.60 (s, 1H, NOH), 7.54 (d, $J = 7.0$ Hz, 1H, NH), 7.27 (m, 2H), 6.72 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 145.46, 139.57, 132.35, 131.90, 131.20, 127.74, 126.50, 123.20, 115.73.MS (*m*/*z*,%): M–H_2O, 314 (100), 279 (47), 198 (12).

2.2.6. N-(4-Iodophenyl)-5-chloro-thiophene-2-carboxamidoxime (**3h**)

Yield: 50%. M.p. 141–144 °C. R_f: 0.50 (hexane:ethyl acetate; 3:1). IR (KBr, *v*: cm^{-1}): 3394 (N–H), 3217 (broad, NOH), 1636 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.63 (s, 1H, NOH), 7.56 (s, 1H, NH), 7.44 (m, 2H), 6.78–6.61 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 144.84, 140.48, 137.58, 132.74, 130.76, 127.46, 126.43, 123.06, 122.02, 85.40. MS (*m*/*z*,%): M–H_2O, 362 (100), 346 (14), 219 (35), 144 (16).

2.2.7. N-(1-Naphthyl)-5-chloro-thiophene-2-carboxamidoxime (**3i**)

Yield: 65%. M.p. 168–170 °C. R_f: 0.44 (hexane:ethyl acetate; 3:1). IR (KBr, *v*: cm^{-1}): 3381 (N–H), 3224–3103 (broad, NOH), 1632 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.61 (s, 1H, NOH), 8.20 (m, 1H), 7.85 (m, 1H), 7.62–7.26 (m, 5H), 6.95 (d, $J = 7.3$ Hz, 1H), 6.60 (d, $J = 1.1$ Hz, 1H), 6.45 (d, $J = 1.1$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 146.98, 136.14, 134.22, 133.05, 130.18, 128.94, 128.34, 126.91, 126.39, 126.33, 126.17, 125.47, 124.71, 122.25, 121.06. MS (*m*/*z*,%): M–H_2O, 284 (100), 249 (18), 140 (6).

*2.2.8. N-Phenyl-5-chloro-furan-2-carboxamidoxime (**3j**)*

Yield: 20%. M.p. 147–149 °C. R_f: 0.29 (hexane:ethyl acetate; 3:1). IR (KBr, *v*: cm^{-1}): 3384 (N–H), 3119–2945 (broad NOH), 1627 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.52 (s, 1H, NOH), 7.47 (s, 1H, NH), 7.18 (m, 2H), 6.97 (m, 1H), 6.75 (d, $J = 8.2$, 6.48 Hz, 1H), 6.21 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 145.24, 142.39, 140.24, 136.95, 128.85, 122.58, 120.28, 113.44, 107.91. MS (*m*/*z*,%): M–H_2O, 218 (100), 190 (53), 155 (68).

*2.2.9. N-(4-Methylphenyl)-5-chloro-furan-2-carboxamidoxime (**3k**)*

Yield: 40%. M.p. 157–159 °C. R_f: 0.23 (hexane:ethyl acetate; 3:1). IR (KBr, *v*: cm^{-1}): 3384 (N–H), 3089–2970 (broad, NOH), 1624 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.31 (s, 1H, NOH), 7.18 (s, 1H, NH), 6.97 (d, $J = 7.9$ Hz, 2H), 6.66 (d, $J = 8.4$ Hz, 2H), 6.40 (d, $J = 1.4$ Hz, 1H), 6.16 (d, $J = 1.6$ Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 145.23, 142.81, 137.59, 136.82, 132.29, 129.39, 120.89, 113.47, 107.82, 20.75. MS (*m*/*z*,%): M–H_2O, 232 (100), 204 (51), 169 (56).

*2.2.10. N-(4-Methoxyphenyl)-5-chloro-furan-2-carboxamidoxime (**3l**)*

Yield: 22%. M.p. 141–143 °C. R_f: 0.32 (hexane:ethyl acetate; 3:2). IR (KBr, *v*: cm^{-1}): 3363 (N–H), 3191–3155 (broad, NOH), 1641 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.34 (s, 1H, NOH), 7.28 (s, 1H, NH), 6.75 (dd, $J = 9.3$ 6.7 Hz, 4H), 6.25 (d, $J = 3.5$ Hz, 1H), 6.16 (d, $J = 3.2$ Hz, 1H), 3.80 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 155.97, 145.14, 143.39, 136.72, 133.19, 123.56, 114.04, 113.55, 107.74, 55.42. MS (*m*/*z*,%): M–H_2O, 248 (100), 233 (54), 220 (14), 205 (28).

*2.2.11. N-(4-Chlorophenyl)-5-chloro-furan-2-carboxamidoxime (**3m**)*

Yield: 30%. M.p. 142–144 °C. R_f: 0.29 (hexane:ethyl acetate; 3:1). IR (KBr, *v*: cm^{-1}): 3382 (N–H), 3127–3094 (broad, NOH), 1622 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.60 (s, br, 1H, NOH), 7.63 (s, 1H, NH), 7.14 (d, $J = 8.7$ Hz, 2H), 6.65 (d, $J = 8.7$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 145.00, 141.81, 139.15, 137.11, 128.67, 127.10, 121.26, 113.59, 108.00. MS (*m*/*z*,%): M–H_2O, 254 (100), 183 (22), 155 (31), 127 (75).

*2.2.12. N-(4-Bromophenyl)-5-chloro-furan-2-carboxamidoxime (**3n**)*

Yield: 44%. M.p. 163–164 °C. R_f: 0.66 (hexane:ethyl acetate; 3:1). IR (KBr, *v*: cm^{-1}): 3382 (N–H), 3087–2970 (broad, NOH), 1625 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.57 (s, 1H, NOH), 8.20 (s, 1H, NH), 7.20 (d, $J = 6.4$ Hz, 2H), 6.60 (d, $J = 7.3$ Hz, 2H), 6.55 (dd, $J = 3.5$ 1.1 Hz, 1H), 6.30 (dd, $J = 3.2$, 1.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6): δ 145.10, 141.59, 139.73, 137.06, 131.55, 121.44, 120.21, 114.45, 113.48, 108.00. MS (*m*/*z*,%): M–H_2O, 298 (100), 270 (35), 233 (27), 189 (22).

*2.2.13. N-(4-Iodophenyl)-5-chloro-furan-2-carboxamidoxime (**3o**)*

Yield: 26%. M.p. 165–167 °C. R_f: 0.58 (hexane:ethyl acetate; 3:1). IR (KBr, *v*: cm^{-1}): 3385 (N–H), 3082–2962 (broad, NOH), 1627 (C=N). ^1H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ 9.50 (broad s, 1H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.36 (broad s, 1H), 6.50 (d, $J = 8.5$ Hz, 2H), 6.46 (d, $J = 3.3$ Hz, 1H), 6.13 (d, $J = 3.3$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 144.58, 141.56, 140.01, 137.39, 137.17, 121.79, 120.52, 113.61, 107.88, 84.96. MS (*m*/*z*,%): M–H_2O (100), 316 (22), 281 (12), 217 (9), 189 (32), 172 (12), 154 (14), 127 (12).

*2.2.14. N-(1-Naphthyl)-5-chloro-furan-2-carboxamidoxime (**3p**)*

Yield: 30%. M.p. 128–129 °C. R_f: 0.49 (hexane:ethyl acetate; 3:2). IR (KBr, *v*: cm^{-1}): 3365 (N–H), 3143 (broad, NOH), 1636 (C=N). ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 10.56 (s, 1H, NOH), 8.16 (d, $J = 6.7$ Hz, 1H), 7.85 (d, $J = 7.6$ Hz, 1H), 7.60 (d, $J = 8.2$ Hz, 1H), 7.55–7.50 (m, 1H), 7.42 (s, 1H, NH), 7.28 (t, 1H), 6.87 (d, $J = 7.3$ Hz, 1H), 6.21 (d, $J = 3.5$ Hz, 1H), 6.05 (d, $J = 3.5$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6):δ 145.10, 141.59, 139.73, 137.06, 131.55, 121.44, 120.21, 114.45, 113.48, 108.00. MS (*m*/*z*,%): M–H_2O, 268 (100), 240 (42), 205 (54), 152 (17).

2.3. Synthesis of oxadiazaboroles

*2.3.1. 4,5-Diphenyl-3-(5-chloro-2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (**5a**)*

A mixture of *N*-phenyl-(5-chloro-thiophene)-2-carboxamidoxime (**3a**) (150 mg, 0.68 mmol) and phenylboronic acid (**4**) (92 mg, 0.76 mmol) in toluene (10 mL) was refluxed under an inert atmosphere in the presence of molecular sieves (4 Å) overnight. After extracted with acetone and filtering, the solvent was evaporated under reduced pressure. The crude product was crystallized from hexane–ethylacetate mixture to give **5a** as colorless needles, 140 mg, Yield: 67%. M.p. 164–166 °C. R_f: 0.41 (hexane:ethyl acetate; 3:2). IR (KBr, ν_{max}: cm^{-1}): 1601 (C=N), 1452 (B–N), 1372 (B–O), 1109, 767, 701. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.53–7.49 (m, 5H), 7.40–7.38 (m, 2H), 7.34–7.24 (m, 4H), 6.70 (dd, $J = 4.10$ Hz, 2.05 Hz, 1H), 6.53 (dd, $J = 4.10$ Hz, 2.05 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 155.51, 136.92, 134.36, 134.01, 131.44, 130.30, 129.64, 129.05, 128.68, 128.29, 126.68, 125.49. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.3. MS (*m*/*z*,%): 338 (M^+,100), 234 (15), 179 (20), 103 (11), 91 (7), 77 (15), 51 (6); HRMS calcd for $C_{17}H_{12}BN_2OSCl$: 338.0452; found: 338.0460.

*2.3.2. 5-Phenyl-3-(2-thienyl)-4-(4-methylphenyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (**5b**)*

Yield: 45%. M.p. 222–224 °C (hexane:ethyl acetate). R_f: 0.54 (hexane:ethyl acetate; 3:2). IR (KBr, ν_{max}: cm^{-1}): 1604, 1566, 1514 (C=N), 1444 (B–N), 1369 (B–O), 1121, 1024, 822, 724. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.54 (d, $J = 7.91$ Hz, 2H) 7.43–7.17 (m, 8H), 6.92–6.89 (m, 1H), 6.82 (d, $J = 3.51$ Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.31, 138.79, 134.36, 134.16, 131.02, 130.40, 129.36, 128.64, 128.23, 127.99, 127.20, 126.73, 21.33. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$):δ 32.4. MS (*m*/*z*,%): 318 (M^+,100), 214 (15), 193 (23), 116 (7), 105 (8), 91 (5), 77 (8); HRMS calcd for $C_{18}H_{15}BN_2OS$: 318.0998; found: 318.1002.

*2.3.3. 4-(4-Methylphenyl)-5-phenyl-3-(5-chloro-2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (**5c**)*

Yield: 65%. M.p. 210–212 °C (hexane). R_f: 0.38 (hexane:ethyl acetate; 2:1). IR (KBr, *v*: cm^{-1}): 1600, 1572, 1514 (C=N), 1452 (B–N), 1369 (B–O), 1111, 823, 698. ^1H NMR (300 MHz, $CDCl_3$): δ 7.98–6.55 (m, 11H), 2.20 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.18, 139.08, 134.18, 133.93, 133.71, 133.20, 131.12, 130.64, 129.25, 128.83, 128.01, 127.95, 127.39, 126.59, 125.24, 122.04, 21.27. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.2 MS (*m*/*z*,%): 352 (M^+,100), 248 (11), 193 (25), 116 (11), 105 (8), 77 (11). HRMS calcd for $C_{18}H_{14}BN_2OSCl$: 352.0608; found: 352.0626.

*2.3.4. 4-(4-Methoxyphenyl)-5-phenyl-3-(2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (**5d**)*

Yield: 70%. M.p. 161–163 °C (hexane–ethylacetate). R_f: 0.15 (hexane:ethyl acetate; 3:2). IR (KBr, ν_{max}: cm^{-1}): 1610, 1570, 1515 (C=N), 1444 (B–N), 1370 (B–O), 1256, 1030, 841, 705. ^1H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, $J = 7.32$ Hz, 4H), 7.40–7.21 (m, 4H), 7.00–6.86 (m, 4H), 3.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.86, 156.70, 134.38, 131.30, 129.79, 129.59, 128.96, 128.26, 127.49, 126.92, 115.15, 55.79. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.2. MS (*m*/*z*,%): 334 (M^+,100), 230 (6), 216 (25), 209 (30), 194 (12), 121 (15), 77 (9). HRMS calcd for $C_{18}H_{15}BN_2O_2S$: 334.0947; found: 334.0978.

*2.3.5. 4-(4-Methoxyphenyl)-5-phenyl-3-(5-chloro-2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (**5e**)*

M.p. 169–170 °C (66%) (hexane–ethylacetate). R_f: 0.29 (hexane:ethyl acetate; 2:1). IR (KBr, *v*: cm^{-1}): 1610, 1514 (C=N), 1454 (B–N), 1369 (B–O), 1255, 839, 700. ^1H NMR (300 MHz, $CDCl_3$): δ 7.54–6.60 (m, 11H), 3.84 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.82, 155.44, 134.22, 133.99, 134.40, 131.17, 129.38, 128.92, 128.84, 128.07, 127.44, 126.60, 125.28, 115.12, 55.56. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.2. MS (*m*/*z*,%): 368 (M^+,100), 264 (6), 249 (16), 209 (34), 194 (16), 121 (16), 77 (12). HRMS calcd for $C_{18}H_{14}BN_2O_2SCl$: 368.0558; found: 368.0575.

*2.3.6. 4-(4-Chlorophenyl)-5-phenyl-3-(5-chloro-2-thienyl)-4,5-dihydro-1,2,4,5- oxadiazaborole (**5f**)*

M.p. 158–160 °C (hexane) (75%). R_f: 0.50 (hexane:ethyl acetate; 3:2). IR (KBr, ν_{max}: cm^{-1}): 1600, 1571, 1525 (C=N), 1493, 1449 (B–N), 1370 (B–O), 1093, 829, 701. ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.40 (m, 6H), 7.31–7.25 (m, 4H), 6.66 (dd, $J = 5.0$, 1.76 Hz, 1H), 6.58 (dd, $J = 3.9$, 1.46 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.23, 135.51, 135.23, 134.31, 131.61, 130.54, 129.96, 129.19, 128.40, 126.81, 125.08. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.2. MS (*m*/*z*,%): 372 (M^+,100), 268 (14), 233 (9), 213 (26), 137 (15), 125 (11), 96 (12), 77 (14), 51 (5). HRMS calcd for $C_{17}H_{11}BN_2OSCl_2$: 372.0062; found: 372.0056.

*2.3.7. 4-(4-Bromophenyl)-5-phenyl-3-(5-chloro-2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (**5g**)*

Yield: 75%. M.p. 177–179 °C (hexane–ethyl acetate). R_f: 0.61 (hexane:ethyl acetate; 3:2). IR (KBr, ν_{max}: cm^{-1}): 1602, 1568, 1510 (C=N), 1488, 1455 (B–N), 1366 (B–O), 1105, 1073, 941, 835, 695. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.65 (d, $J = 0.88$ Hz, 1H), 7.63 (m, 1H), 7.49–7.26 (m, 6H), 7.22 (d, $J = 0.88$ Hz, 1H), 7.20 (m, 1H), 6.74 (dd, $J = 2.34$, 1.17 Hz, 1H), 6.56 (dd, $J = 2.34$, 1.17 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.15, 136.04, 134.32, 133.53, 131.62, 130.28, 129.21, 128.41, 126.84, 125.07, 123.23. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.3. MS (*m*/*z*,%): 418 (M^+,100), 314 (12), 257 (14), 181 (8), 169 (8), 143 (12), 102 (18), 90 (12), 77 (15), 63 (8), 51 (8). HRMS calcd for $C_{17}H_{11}BN_2OSBrCl$: 415.9557; found: 415.9567.

*2.3.8. 4-(4-Iodophenyl)-5-phenyl-3-(5-chloro-2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (**5h**)*

Yield: 52%. M.p. 184–186 °C (hexane–ethyl acetate). R_f: 0.50 (hexane:ethyl acetate; 3:2). IR (KBr, ν_{max}: cm^{-1}): 1603, 1597, 1508 (C=N), 1485, 1455 (B–N), 1368 (B–O), 1103, 942, 829, 695. ^1H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, $J = 7.6$ Hz, 2H), 7.49–7.25 (m, 6H), 7.07 (d, $J = 7.6$ Hz, 2H), 6.74 (d, $J = 3.5$ Hz, 1H), 6.55 (d, $J = 3.4$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.10, 139.49, 136.72, 134.32, 134.27, 131.62, 130.49, 129.23, 128.41, 126.86, 125.05, 94.76. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.2. MS (*m*/*z*,%): 464 (M^+,100), 360 (12), 305 (26), 229 (7), 198 (7), 151 (9), 102 (15), 90 (17), 77 (11), 63 (7). HRMS calcd for $C_{17}H_{11}BN_2OSClI$: 463.9418; found: 463.9409.

*2.3.9. 4-(1-Naphthyl)-5-phenyl-3-(5-chloro-2-thienyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (**5i**)*

Yield: 46%. M.p. 132–134 °C (hexane–ethyl acetate). R_f: 0.54 (hexane:ethyl acetate; 3:2). IR (KBr, ν_{max}: cm^{-1}): 1599, 1522, 1508 (C=N), 1434 (B–N), 1369 (B–O), 1106, 800, 776, 696. ^1H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, $J = 7.9$ Hz, 1H), 8.00 (d, $J = 7.9$ Hz, 1H), 7.74–7.16 (m, 11H), 6.53 (dd, $J = 1.76$, 0.88 Hz, 1H), 6.39 (dd, $J = 1.76$, 0.88 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.11,

134.57, 134.22, 133.89, 133.13, 131.48, 131.11, 130.19, 128.90, 128.68, 128.28, 128.24, 127.46, 126.79, 126.62, 125.99, 125.23, 122.52. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.8. MS (*m*/*z*,%): 388 (M^+,100), 249 (26), 229 (69), 153 (25), 140 (18), 126 (11), 115 (12), 77(9), 51 (5). HRMS calcd for $C_{21}H_{14}BN_2OSCl$: 388.0608; found: 388.0607.

2.3.10. 3-(5-Chloro-2-furyl)-4,5-diphenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5j**)

Yield: 50%. M.p. 114–116 °C (benzene–petroleum ether). R_f: 0.29 (hexane:ethyl acetate; 3:1). IR (KBr, ν_{max}: cm^{-1}): 1598, 1534 (C=N), 1498, 1484 (B–N), 1375 (B–O), 1138, 1024, 790, 699. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52–7.23 (m, 11H), 6.07 (dd, $J = 2.34$, 1.17 Hz, 1H), 5.87 (dd, $J = 3.66$, 1.17, 0.88 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.63, 140.20, 139.68, 136.99, 134.40, 131.45, 130.15, 129.20, 128.30, 128.27, 115.70, 108.22. MS (*m*/*z*,%): 322 (M^+,100), 285 (15), 258 (31), 179 (18), 166 (35), 154 (44), 128 (15), 103 (35), 77 (34), 64 (10), 51 (13). HRMS calcd for $C_{17}H_{12}BN_2O_2Cl$: 322.0680; found: 322.0709.

2.3.11. 3-(5-Chloro-2-furyl)-5-phenyl-4-(4-methylphenlyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (**5k**)

Yield: 60%. M.p. 167–168 °C (benzene–petroleum ether). R_f: 0.23 (hexane:ethyl acetate; 3:1). IR (KBr, ν_{max}: cm^{-1}): 1611, 1532, 1515 (C=N), 1485 (B–N), 1376 (B–O), 1138, 1028, 831, 794, 707. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, $J = 7.32$ Hz, 2H), 7.41–7.26 (m, 5H), 7.19 (d, $J = 7.32$ Hz, 2H), 7.03 (d, $J = 8.50$ Hz, 1H), 6.77 (d, $J = 8.20$ Hz, 1H) 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.55, 140.15, 139.42, 138.94, 134.19, 134.10, 131.15, 130.49, 129.64, 128.01, 127.79, 122.80, 115.43, 107.93, 21.29. MS (*m*/*z*,%): 336 (M^+,100), 299 (15), 271 (10), 192 (23), 180 (23), 168 (54), 142 (8), 127 (7), 116 (28), 104 (10), 90 (15), 77 (20), 65 (8), 51 (8). HRMS calcd for $C_{18}H_{14}BN_2O_2Cl$: 336.0837; found: 336.0868.

2.3.12. 3-(5-Chloro-2-furyl)-4-(4-methoxyphenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5l**)

Yield: 65%. M.p. 145–147 °C (hexane–ethyl acetate). R_f: 0.32 (hexane:ethyl acetate; 3:1). IR (KBr, ν_{max}: cm^{-1}): 1612, 1516 (C=N), 1489 (B–N), 1375 (B–O), 1251, 1023, 841, 794, 707. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45–6.90 (m, 10H), 6.00 (dd, $J = 3.52$, 1.76 Hz, 1H), 5.70 (dd, $J = 3.52$, 1.76 Hz, 1H) 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.91, 152.92, 140.36, 139.62, 134.40, 131.43, 129.49, 129.34, 128.28, 115.71, 108.26, 55.83. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.0. MS (*m*/*z*,%): 352 (M^+,100), 209 (27), 194 (16), 184 (30), 133 (21), 121 (10), 103 (11), 90 (13), 77 (15). HRMS calcd for $C_{18}H_{14}BN_2O_3Cl$: 352.0786; found: 352.0800.

2.3.13. 4-(4-Chlorophenyl)-3-(5-chloro-2-furyl)-5-phenyl-4,5-dihydro-1,2,4,5- oxadiazaborole (**5m**)

M.p. 131–133 °C (hexane–dichloroethane) (43%). R_f: 0.29 (hexane:ethyl acetate; 3:1). IR (KBr, ν_{max}: cm^{-1}): 1611, 1530 (C=N), 1496 (B–N), 1373 (B–O), 1139, 1092, 1021, 838, 789, 704. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49–7.26 (m, 10H), 6.12 (dd, $J = 3.33$ Hz, 1.76 Hz, 1.46,1H), 5.98 (dd, $J = 3.52$ Hz, 1.76 Hz, 1.46 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.38, 139.88, 135.60, 135.03, 134.36, 131.63, 130.36, 129.65, 128.39, 115.91, 108.33. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.1. MS (*m*/*z*,%): 356 (M^+,100), 319 (7), 293 (15), 257 (12), 213 (25), 200 (25), 189 (38), 162 (9), 137 (40), 102 (25), 77 (20), 64 (8), 51(9). HRMS calcd for $C_{17}H_{11}BN_2O_2Cl_2$: 356.0291; found: 356.0270.

2.3.14. 4-(4-Bromophenyl)-3-(5-chloro-2-furyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5n**)

Yield: 72%. M.p. 166–168 °C (hexane–ethyl acetate). R_f: 0.66 (hexane:ethyl acetate; 3:2). IR (KBr, ν_{max}: cm^{-1}): 1610, 1530 (C=N), 1492 (B–N), 1374 (B–O), 1210, 1140, 1020, 789, 704. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65 (m, 10H), 6.13 (d, $J = 3.22$ Hz, 1H), 5.99 (dd, $J = 1.76$, 0.88 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.30, 139.92, 139.84, 136.12, 134.37, 133.35, 131.64, 129.96, 128.40, 123.08, 115.90, 108.33. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.0. MS (*m*/*z*,%): 402 (M^+,100), 257 (29), 244 (15), 232 (26), 181 (18), 154 (8), 127 (15), 102 (40), 90 (12), 77 (26), 63 (9), 51 (9). HRMS calcd for $C_{17}H_{11}BN_2O_2BrCl$: 399.9785; found: 399.9796.

2.3.15. 3-(5-Chloro-2-furyl)-4-(4-iodophenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5o**)

Yield: 75%. M.p. 203–205 °C (hexane–ethyl acetate). R_f: 0.58 (hexane:ethyl acetate; 3:2). IR (KBr, ν_{max}: cm^{-1}): 1627, 1583 (C=N), 1482 (B–N), 1367 (B–O), 978, 671. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, $J = 1.17$ Hz, 1H), 7.81 (s, 1H), 7.50–7.24 (m, 6H), 7.08 (d, $J = 1.17$ Hz, 1H), 7.06 (s, 1H), 6.13 (dd, $J = 2.34$, 1.17 Hz, 1H), 5.99 (dd, $J = 2.34$, 1.17 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.27, 139.93, 139.83, 139.31, 136.81, 134.37, 131.63, 130.16, 128.39, 115.92, 108.32, 94.45. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.0. MS (*m*/*z*,%): 448 (M^+,100), 305 (20), 292 (23), 280 (39), 257 (23), 229 (16), 203 (7), 189 (9), 154 (11), 127 (16), 102 (41), 90 (16), 77 (19), 63 (13), 51(9). HRMS calcd for $C_{17}H_{11}BN_2O_2ClI$: 447.9647; found: 447.9683.

2.3.16. 3-(5-Chloro-2-furyl)-4-(1-naphthyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5p**)

Yield: 40%. M.p. 148–150 °C (hexane–dichloroethane). R_f: 0.49 (hexane:ethyl acetate; 3:2). IR (KBr, ν_{max}: cm^{-1}): 1603, 1527 (C=N), 1484 (B–N), 1371 (B–O), 1209, 1143, 1018, 777, 710. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, $J = 8.03$ Hz, 1H), 7.98 (d, $J = 8.03$ Hz, 1H), 7.69–7.12 (m, 11H), 5.87 (s, 1H), 5.39 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.08, 140.00, 139.55, 134.49, 134.26, 133.24, 131.50, 130.79, 129.86, 128.79, 128.26, 125.15, 127.41, 126.27, 125.93, 122.52, 115.32, 108.23. MS (*m*/*z*,%): 372 (M^+,69), 336 (92), 308 (42), 292 (15), 259 (34), 233 (48), 216 (54), 204 (100), 189 (15), 178 (17), 153 (54), 140 (34),

126 (29), 115 (23), 77 (18), 51 (8). HRMS calcd for $C_{21}H_{14}BN_2O_2Cl$: 372.0837; found: 372.0824.

2.3.17. 3-(2-Pyridyl)-4-methyl-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5q**)

Yield: 28%. M.p. 76–77 °C hexane–petroleum ether. R_f: 0.18 (hexane:ethyl acetate; 1:3). IR (KBr, *v*: cm^{-1}): 1607, 1587, 1542 (C=N), 1482 (B–N), 1391 (B–O), 1297, 1081, 793, 697. ^1H NMR (300 MHz, $CDCl_3$): δ 8.78–7.44 (m, 9H), 3.67 (s, 3H).^{13}C NMR, (75 MHz, $CDCl_3$) δ: 160.05, 149.24, 147.50, 137.07, 133.88, 130.72, 128.27, 124.76, 124.73, 31.43. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 33.2. MS (*m*/*z*,%): 236 (M^+,100), 160 (9), 133 (25), 105 (100), 78 (29), 51(10). HRMS calcd for $C_{13}H_{12}BN_3O$: 237.1073; found: 237.1075.

2.3.18. 3-(2-Pyridyl)-4-ethyl-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5r**)

Yield: 63%. M.p. 82–83 °C (benzene–petroleum ether). R_f: 0.11 (hexane:ethyl acetate; 2:1). IR (KBr, ν_{max}: cm^{-1}): 1600, 1552 (C=N), 1482 (B–N), 1348 (B–O), 1151, 777, 715. ^1H NMR (300 MHz, $CDCl_3$): δ 8.73–8.71 (m, 1H), 7.96–7.79 (m, 4H), 7.51–7.45 (m, 4H), 4.18 (q, 2H), 1.26 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.07, 149.54, 147.74, 137.29, 133.94, 130.95, 128.53, 124.96, 124.89, 38.40, 17.85. ^{11}B NMR (160.46 MHz, $CDCl_3$-15% $BF_3 \cdot Et_2O$): δ 33.2. MS (*m*/*z*,%): 250 (M^+,54), 236 (8), 174 (52), 147 (31), 105 (100), 78 (40), 51 (11). HRMS calcd for $C_{14}H_{14}BN_3O$: 251.1230; found: 251.1237.

2.3.19. 3-(2-Pyridyl)-4-(1-naphthyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5s**)

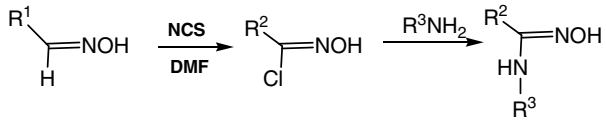
Yield: 51%. M.p. 181–182 °C (hexane–petroleum ether). R_f: 0.31 (hexane:ethyl acetate; 1:3). IR (KBr, *v*: cm^{-1}): 1598, 1525 (C=N), 1473 (B–N), 1374 (B–O), 1151, 824, 768, 694. ^1H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, $J = 4.5$ Hz, 1H), 7.76 (d, $J = 7.7$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.56 (dt, $J = 1.7$, 7.7, 15.5 Hz, 1H), 7.51–7.32 (m, 7H), 7.20 (t, 2H), 7.10 (ddd, $J = 1.0$, 4.8, 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.30, 149.25, 146.17, 136.32, 134.13, 134.10, 134.08, 131.07, 130.84, 128.44, 128.36, 128.29, 127.96, 127.10, 126.46, 125.87, 125.41, 124.37, 124.12, 122.71. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.5. MS (*m*/*z*,%): 349 (M^+,100), 318 (11), 272 (19), 244 (27), 229 (10), 141 (27), 115 (8), 78 (9). HRMS calcd for $C_{22}H_{16}BN_3O$: 349.1386; found: 349.1424.

2.3.20. 3-(4-Pyridyl)-4,5-diphenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5t**)

Yield: 42%. M.p. 213–215 °C (hexane–ethyl acetate). R_f: 0.08 (hexane:ethyl acetate; 2:1). IR (KBr, ν_{max}: cm^{-1}): 1653, 1599 (C=N), 1516 (B–N), 1373 (B–O), 943, 823, 684. ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ 8.22 (d, $J = 5.86$ Hz, 1H), 8.18 (d, $J = 5.56$ Hz, 1H), 7.49 (d, $J = 7.33$ Hz, 1H), 7.24–6.56 (m, 10H), 6.33 (d, $J = 7.62$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.92, 149.35, 134.20, 134.01, 131.24, 129.94, 128.82, 128.09, 127.57, 127.44, 122.90, 122.40, 120.74. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.4. MS (*m*/*z*,%): 299 (M^+,100), 222 (8), 195 (11), 179 (31), 118 (8), 91 (11), 77 (15), 51 (9). HRMS calcd for $C_{18}H_{14}BN_3O$: 299.1230; found: 299.1247.

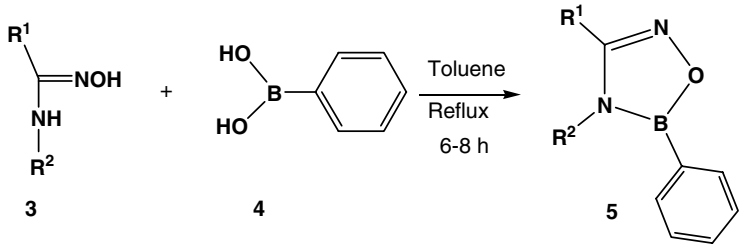
2.3.21. 3-(4-Pyridyl)-4-(4-methylphenyl)-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5u**)

Yield: 80%. M.p. 234–236 °C (hexane–dichloromethane). R_f: 0.18 (hexane:ethyl acetate; 1:2). IR (KBr, ν_{max}: cm^{-1}): 1601, 1587, 1541 (C=N), 1483 (B–N), 1390 (B–O), 1076, 1020, 792, 694. ^1H NMR (400 MHz, DMSO-d_6): δ 8.45 (d, $J = 6.0$ Hz, 1H), 8.12 (s, 1H), 7.84 (s, 1H), 7.76 (d, $J = 6.5$ Hz, 1H), 7.34–7.25 (m, 5H), 6.85 (d, $J = 8.1$ Hz, 1H), 6.54 (d, $J = 8.3$ Hz, 1H), 2.16 (s, 3H).



	1 R^1	2 R^2	3 R^3
a	2-Thienyl	5-Chloro-2-thienyl	Ph
b	2-Thienyl	2-Thienyl	4-Me-C_6H_4
c	2-Thienyl	5-Chloro-2-thienyl	4-Me-C_6H_4
d	2-Thienyl	2-Thienyl	4-MeO-C_6H_4
e	2-Thienyl	5-Chloro-2-thienyl	4-MeO-C_6H_4
f	2-Thienyl	5-Chloro-2-thienyl	4-Cl-C_6H_4
g	2-Thienyl	5-Chloro-2-thienyl	4-Br-C_6H_4
h	2-Thienyl	5-Chloro-2-thienyl	4-I-C_6H_4
i	2-Thienyl	5-Chloro-2-thienyl	1-Naphthyl
j	2-Furyl	5-Chloro-2-furyl	Ph
k	2-Furyl	5-Chloro-2-furyl	4-Me-C_6H_4
l	2-Furyl	5-Chloro-2-furyl	4-MeO-C_6H_4
m	2-Furyl	5-Chloro-2-furyl	4-Cl-C_6H_4
n	2-Furyl	5-Chloro-2-furyl	4-Br-C_6H_4
o	2-Furyl	5-Chloro-2-furyl	4-I-C_6H_4
p	2-Furyl	5-Chloro-2-furyl	1-Naphthyl
q	2-Pyridyl	2-Pyridyl	Me
r	2-Pyridyl	2-Pyridyl	Et
s	2-Pyridyl	2-Pyridyl	1-Naphthyl
t	4-Pyridyl	4-Pyridyl	Ph
u	4-Pyridyl	4-Pyridyl	4-Me-C_6H_4
v	Ph	Ph	4-Me-C_6H_4

Scheme 1. Structure of the *N*-substituted amidoximes.



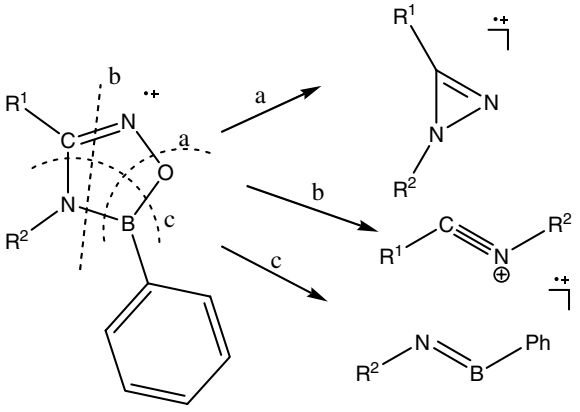
	R^1	R^2		R^1	R^2
5a	5-Chloro-2-thienyl	Ph	**5l**	5-Chloro-2-furyl	4-MeO-C_6H_4
5b	2-Thienyl	4-Me-C_6H_4	**5m**	5-Chloro-2-furyl	4-Cl-C_6H_4
5c	5-Chloro-2-thienyl	4-Me-C_6H_4	**5n**	5-Chloro-2-furyl	4-Br-C_6H_4
5d	2-Thienyl	4-MeO-C_6H_4	**5o**	5-Chloro-2-furyl	4-I-C_6H_4
5e	5-Chloro-2-thienyl	4-MeO-C_6H_4	**5p**	5-Chloro-2-furyl	1-Naphthyl
5f	5-Chloro-2-thienyl	4-Cl-C_6H_4	**5q**	2-Pyridyl	Me
5g	5-Chloro-2-thienyl	4-Br-C_6H_4	**5r**	2-Pyridyl	Et
5h	5-Chloro-2-thienyl	4-I-C_6H_4	**5s**	2-Pyridyl	1-Naphthyl
5i	5-Chloro-2-thienyl	1-Naphthyl	**5t**	4-Pyridyl	Ph
5j	5-Chloro-2-furyl	Ph	**5u**	4-Pyridyl	4-Me-C_6H_4
5k	5-Chloro-2-furyl	4-Me-C_6H_4	**5v**	Ph	4-Me-C_6H_4

Scheme 2. Structure of the 1,2,4,5-oxadiazaboroles.

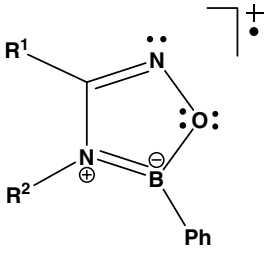
^{13}C NMR (100 MHz, DMSO-d_6): δ 149.85, 148.37, 138.56, 134.45, 130.80, 130.20, 129.32, 128.57, 127.56, 122.45, 120.94, 20.68. ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.2. MS (*m*/*z*,%): 313 (M^+,100), 298 (7), 208 (10), 193 (23), 104 (7), 91(9), 77 (8), 51(6). HRMS calcd for $C_{19}H_{16}BN_3O$: 313.1386; found: 313.1415.

2.3.22. 3,5-Diphenyl-4-(4-methylphenyl)-4,5-dihydro-1,2,4,5-oxadiazaborole (**5v**)

Yield: 85%. M.p. 243–245 °C (hexane–ethyl acetate). R_f: 0.51 (hexane:ethyl acetate; 2:1). IR (KBr, ν_{max}: cm^{-1}): 1600, 1539, 1514 (C=N), 1438 (B–N), 1373 (B–O), 1028, 822, 698. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75–6.69 (m, 14H), 2.46 (s, 3H). ^{11}B NMR (160.46 MHz, $CDCl_3$–15% $BF_3 \cdot Et_2O$): δ 32.3. MS (*m*/*z*,%): 312 (M^+,100), 297 (6), 208 (15), 193 (26), 104 (11), 91(12), 77 (15). HRMS calcd for $C_{20}H_{17}BN_2O$: 312.1434; found: 312.1460.



Scheme 3.



Scheme 4.

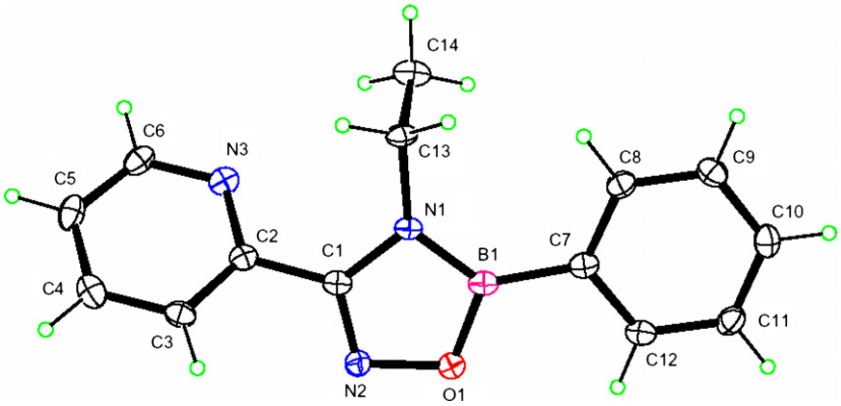


Fig. 1. X-ray ORTEP view of **5r**.

3. Results and discussion

In a recent paper [11] we described the synthesis and protonation equilibria of 4-unsubstituted 1,2,4,5-oxadiazaboroles in non-aqueous media. In the present work we report here the synthesis of some novel 3,4,5-trisubstituted 1,2,4,5-oxadiazaboroles bearing thiophene, furan and pyridine at the 3-position of the heterocyclic ring. The *N*-substituted amidoximes used as the starting compounds were obtained as described in the literature [12–24] (Scheme 1).

The new oxadiazaboroles **5a**–**v** (Scheme 2) show strong absorptions related to the B–N and B–O stretching vibrations in the 1516–1438 and 1391–1348 cm^{-1} regions in their IR spectra, which are remarkably consistent with the reported values for B–O and B–N stretching frequencies [25]. Iminic carbon chemical shifts of the title oxadiazaboroles in their ^{13}C NMR spectra appeared to resonate in the deshielded region at around 160–149 ppm. When there is a 2-pyridyl group on the number three carbon of the heterocycle, the iminic carbon chemical shifts go to more deshielded lowfield regions. In addition, the ^{11}B NMR spectra of these compounds were measured (the conditions are given in Section 2) and the boron chemical shift frequencies appear between 32.0 and 33.2 ppm, which can be considered as an indication of a trigonal planar sp^2 hybridized boron atom [26,27].

As for the electron impact mass spectra of the oxadiazaboroles; peaks related to the following fragmentations: diaziridine cation in route **a**, nitrilium cation in route **b** and borimide cation in route **c**, would occur (Scheme 3).

Except for compounds **5p** and **5r**, all of the molecular ion peaks have relative abundances of 100%, on account of the following structure which has aromatic stability (Scheme 4).

As a representative view, the X-ray crystal structure and selected atomic parameters are given for compound **5r** (Fig. 1, Tables 1 and 2).

Table 1
Crystallographic data for 3-(2-pyridyl)-4-ethyl-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5r**)

Empirical formula	$C_{14}H_{14}BN_3O$
Formula weight (amu)	251.09
Crystal color, habit	colorless, lath fragment
Crystal dimensions (mm)	0.30 × 0.07 × 0.03
Crystal system	Orthorhombic
Space group	*Pbca*
Cell parameters at T (K)	90
α (Å)	11.600 (2)
b (Å)	10.1778 (17)
c (Å)	21.602 (4)
V (Å^3)	2550.4 (8)
Z	8
D_{calc} (Mg m^{-3})	1.308
Absorption correction	none
θ Range for collection (°)	2.5–27.8
Number of reflections measured	23865
Number of independent reflections	3022
Observed reflections	$X = 2$
$[I > X\sigma(I)]$	2142
Refinement method	full matrix least squares on F^2
Final R indices $[I > X\sigma(I)]$	$X = 2$
	$R[F^2 > 2\sigma(F^2)] = 0.049$
	$wR(F^2) = 0.097$

Table 2
Selected bond distances (Å) and bond angles (°) with estimated standard deviations of 3-(2-pyridyl)-4-ethyl-5-phenyl-4,5-dihydro-1,2,4,5-oxadiazaborole (**5r**)

Bond distances		Bond angles	
O1–B1	1.387 (2)	B1–O1–N2	108.70 (11)
O1–N2	1.4370 (16)	O1–B1–N1	106.64 (13)
N1–C1	1.3796 (19)	O1–B1–C7	120.49 (14)
N1–B1	1.430 (2)	N1–B1–C7	132.86 (14)
N1–C13	1.4764 (18)	C1–N1–B1	104.97 (12)
N2–C1	1.3062 (19)	C1–N1–C13	123.75 (13)
N3–C6	1.344 (2)	B1–N1–C13	131.02 (13)
N3–C2	1.3492 (19)	C1–N2–O1	105.38 (11)
		C6–N3–C2	116.65 (13)
		N2–C1–N1	114.32 (13)
		N2–C1–C2	118.96 (13)
		N1–C1–C2	126.69 (13)
		N3–C2–C3	123.57 (14)
		N3–C2–C1	116.29 (13)

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Appendix A. Supplementary material

CCDC data_MA50 contains the supplementary crystallographic data for **5r**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.11.043.

References

[1] D.N. Nicolaides, E.A. Varella, in: S. Patai (Ed.), The Chemistry of Acid Derivatives, vol. 2, Suppl. B, John Wiley & Sons Ltd., 1992, p. 875.
[2] F. Eloy, R. Lenaers, Chem. Rev. 62 (1962) 55.
[3] K.S. Webb, D. Levy, Tetrahedron Lett. 36 (1995) 5117.
[4] C. Thiebes, G.K.S. Prakash, N.A. Petasis, G. Olah, Synlett (1998) 141.
[5] A. Suzuki, Pure Appl. Chem. 66 (1994) 213.
[6] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457.
[7] A. Dornow, K. Fischer, Chem. Ber. 99 (1966) 68.
[8] A.B. Goel, V.D. Gupta, J. Indian Chem. Soc. 54 (1977) 581.
[9] (a) H.L. Yale, J. Heterocycl. Chem. 8 (1971) 205;
(b) H.L. Yale, J. Heterocycl. Chem. 8 (1971) 193.
[10] P.I. Paetzold, G. Stohr, Chem. Ber. 101 (1968) 2874.
[11] Y. Dürüst, N. Dürüst, M. Akcan, J. Chem. Eng. Data 52 (2007) 718.
[12] Y. Dürüst, C. Altuğ, F. Kılıç, Phosphorus Sulfur Silicon 182 (2007) 299.
[13] N. Dürüst, Y. Dürüst, İ. Meriç, Turk. J. Chem. 26 (2002) 833.
[14] Y. Dürüst, F. Nohut, Synth. Commun. 29 (1999) 1997.
[15] H. Ağırbaş, Y. Dürüst, D. Sümengen, Phosphorus Sulfur Silicon 66 (1992) 321.
[16] Y. Dürüst, N. Dürüst, Synth. Commun. 22 (1992) 209.
[17] Y. Dürüst, H. Ağırbaş, D. Sümengen, Phosphorus Sulfur Silicon 62 (1991) 47.
[18] T.L. Deegan, T.J. Nitz, D. Cebzanov, D.E. Pufko, J.A. Porco Jr., Bioorg. Med Chem. Lett. 9 (1999) 209.
[19] J.B. Hynes, R.F. Gratz, J. Med. Chem. 15 (1972) 198.
[20] H.A. Oskooie, M.M. Heravi, Z. Jaddi, Phosphorus Sulfur Silicon 180 (2005) 1993.
[21] K. Niknam, B. Karami, A.R. Kiasat, Bull. Korean Chem. Soc. 26 (2005) 975.
[22] N. Iranpoor, H. Firouzabadi, G. Aghapour, Synth. Commun. 32 (2002) 2535.
[23] S. Chandrasekhar, K. Gopalaiah, Tetrahedron Lett. 42 (2001) 8123.
[24] T. L Ho, C.M. Wong, Synth. Commun. 5 (1975) 299.
[25] B. Stuart, Infrared Spectroscopy: Fundamentals and Applications, John & Wiley Sons, Inc., Hoboken, NJ, 2004, p. 83.
[26] W. Kliegel, G. Lubkowitz, J.O. Prokriefke, S.J. Rettig, J. Trotter, Can. J. Chem. 79 (2001) 26.
[27] S. Hermanek, Chem. Rev. 92 (1992) 325.