Supporting Information for

C-H arylation of azaheterocycles: A direct ligand-free and Cu-catalyzed approach using diaryliodonium salts

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Table of contents

1. General materials and methods 2
2. 2,5-Diaryl-1,3,4-oxadiazoles 2
   (i) Optimization of reaction conditions for 2,5-diaryl-1,3,4-oxadiazoles
   (ii) Typical experimental procedure for 2,5-diaryl-1,3,4-oxadiazoles
   (iii) Analytical data for 2,5-diaryl-1,3,4-oxadiazoles
3. 2,5-Diaryl-1,3,4-thiadiazoles 6
   (i) Optimization of reaction conditions for 2,5-diaryl-1,3,4-thiadiazoles
   (ii) Typical experimental procedure for 2,5-diaryl-1,3,4-thiadiazoles
   (iii) Analytical data for 2,5-diaryl-1,3,4-thiadiazoles
4. 2-Arylbenzoxazoles 8
   (i) Typical experimental procedure for 2-arylbenzoxazoles
   (ii) Analytical data for 2-arylbenzoxazoles
5. 2-Arylbenzothiazoles 11
   (i) Optimization of reaction conditions for 2-arylbenzothiazoles
   (ii) Typical experimental procedure for 2-arylbenzothiazoles
   (iii) Analytical data for 2-arylbenzothiazoles
6. References 13
7. NMR spectra of isolated 2,5-diaryl-1,3,4-oxadiazoles and 2,5-diaryl-1,3,4-thiadiazoles 15
8. NMR spectra of isolated 2-arylbenzoxazoles and 2-arylbenzothiazoles 38
1. General Materials and Methods:

All the laboratory reagents were obtained commercially. The progress of the reaction was monitored by thin layer chromatography, which was performed on Merck precoated plates (silica gel 60, F_{254}, 0.25mm) and it was visualized by fluorescence quenching under hand-UV lamp (254 nm). The column chromatography was performed using 100-200 mesh silica gel. The solvents were evaporated using Buchi rotary evaporator. Microwave reactions were carried out in CEM DISCOVER instrument. Melting points were determined using E-Z melting point apparatus and were uncorrected. $^1$H and $^{13}$C spectra were recorded using Bruker-Avance II (400, 100 MHz) spectrometer. The coupling constants (J) were given in Hz, chemical shift (δ) in ppm. TMS was used as an internal standard. The proton multiplicities were described as: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet and m = multiplet. Mass spectra were obtained using Hewlett Packard HP 5973 quadrupole Mass Selective Detector with interface for 6890 series GC. All the oxadiazoles 3^{1a}, thiadiazole 4^{1b}, diaryliodonium salts 5^{a-o}^{1c-f}, benzoxazoles 8^{1g} and benzothiazole 9^{1g} were synthesized by the known literature procedures.

2. 2,5-Diaryl-1,3,4-oxadiazoles

(i) Optimization of reaction conditions for 2,5-diaryl-1,3,4-oxadiazoles

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$^a$ A mixture of 3a (1 equiv.), 5a (1 equiv.), Cu catalyst (20 mol %), base (3 equiv.) was stirred in DMSO for 15 min. at rt. $^b$ Conventional heating at 100 °C for 18-24 h. $^c$ reaction under microwave irradiation at 100 °C for 30 min. $^d$ stirring at rt for 10-15 min, NR = no reaction.
(ii) Typical experimental procedure for 2,5-diaryl-1,3,4-oxadiazoles (6a)

To a stirred solution of oxadiazole 3a (100 mg, 0.684 mmol) and CuBr (20 mg, 0.136 mmol) in DMSO (2 mL), t-BuOLi (164 mg, 2.05 mmol) was charged and continued stirring at room temperature for 5 min. Then the required amount of diphenyliodonium triflate 5a (294 mg, 0.684 mmol) was added portion wise and stirred at room temperature for 15 min. Completion of the reaction was confirmed by the TLC (4:1 hexane:ethylacetate). Then the resulting reaction mixture was added to ice-cold water and extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with ammonia solution, brine and dried over anhydrous Na2SO4 and the solvent was removed in vacuo. The obtained crude product was purified by column chromatography using EtOAc/hexane (10%) as an eluent to afford 6a in 89% yield.

(iii) Analytical data for 2,5-diaryl-1,3,4-oxadiazoles (6a-q)

2,5-Diphenyl-1,3,4-oxadiazole (6a)25: White solid (135 mg, 89%), mp 138 °C. 1H NMR (400 MHz, DMSO-δ6) δ 8.15-8.13 (m, 4H), 7.69-7.63 (m, 6H); 13C NMR (100 MHz, DMSO-δ6) δ 164.46, 132.55, 129.78, 127.19, 123.78; GC-MS m/z calcd. for C14H10N2O : 222.1, found: 222.0

2-(4'-Methylphenyl)-5-phenyl-1,3,4-oxadiazole (6b)25: White solid (63 mg, 79%), mp 125-126 °C. 1H NMR (400 MHz, CDCl3) δ 8.15-8.13 (m, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.54-7.52 (m, 3H), 7.34 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 164.83, 164.20, 142.36, 131.62, 129.64, 128.81, 126.90, 123.82, 121.20, 21.49; GC-MS m/z calcd. for C15H12N2O : 236.1, found: 236.0

2-(4'-Methoxyphenyl)-5-phenyl-1,3,4-oxadiazole (6c)25: White solid (75 mg, 75%), mp 147 °C. 1H NMR (400 MHz, CDCl3) δ 8.13-8.11 (m, 2H), 8.09 (d, J = 8.8 Hz 2H), 7.54-7.52 (m, 3H), 7.05 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 164.55, 164.14, 162.37, 131.50, 129.06, 128.72, 126.84, 124.02, 116.46, 114.53, 55.24; GC-MS m/z calcd. for C15H12N2O : 252.1, found: 252.0

2-(4'-Chlorophenyl)-5-phenyl-1,3,4-oxadiazole (6d)25: Off white solid (79 mg, 89%), mp 161 °C. 1H NMR (400 MHz, CDCl3) δ 8.15-8.08 (m, 4H), 7.58-7.50 (m, 5H); 13C NMR (101 MHz, CDCl3) δ 161.15, 160.21, 134.43, 128.30, 125.84, 125.54, 124.60, 123.38, 120.09, 118.81; GC-MS m/z calcd. for C14H8ClN2O : 256.0, found: 256.0
2-(4'-Bromophenyl)-5-phenyl-1,3,4-oxadiazole (6e): White solid (90 mg, 88%), mp 171 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 (dd, $J$ = 7.6, 1.5 Hz, 2H), 8.03 (d, $J$ = 8.5 Hz, 2H), 7.70 (d, $J$ = 8.5 Hz, 2H), 7.58-7.54 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.77, 163.89, 132.46, 131.84, 129.14, 128.33, 126.99, 126.54, 123.73, 122.80; GC-MS m/z calcd. for C$_{14}$H$_8$BrN$_2$O : 300.0, found: 300.0

2-(4'-Fluorophenyl)-5-phenyl-1,3,4-oxadiazole (6f): Light pink solid (72 mg, 88%), mp 154 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.17-8.11 (m, 4H), 7.56-7.54 (m, 3H), 7.27-7.21 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 207.30, 166.05, 164.64, 163.81, 163.57, 131.84, 129.19, 129.13, 126.94, 123.80, 120.29, 116.58, 116.35; GC-MS m/z calcd. for C$_{14}$H$_8$FN$_2$O : 240.1, found: 240.0

Methyl-4'-(5-phenyl-1,3,4-oxadiazol-2-yl)benzoate (6g): White solid (67 mg, 70%), mp 171 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.29-8.21 (m, 4H), 8.21-8.16 (m, 2H), 7.63-7.54 (m, 3H), 3.99 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.13, 165.10, 163.86, 132.84, 130.22, 129.18, 127.71, 127.08, 126.87, 123.67, 52.32. GC-MS m/z calcd. for C$_{16}$H$_8$N$_2$O$_3$ : 280.1, found: 280.0

2-(4'-Nitrophenyl)-5-phenyl-1,3,4-oxadiazole (6h): Yellow solid (70 mg, 77%), mp 207 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.46-8.40 (m, 2H), 8.39-8.33 (m, 2H), 8.18 (dd, $J$ = 8.1, 1.5 Hz, 2H), 7.65-7.53 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.48, 162.96, 149.50, 132.26, 129.43, 129.28, 127.82, 127.24, 124.45, 123.24.

2-(4'-Methoxyphenyl)-5-(4''-nitrophenyl)-1,3,4-oxadiazole (6i): Yellow solid (60 mg, 75%), mp 250 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.42-8.38 (m, 2H), 8.33-8.29 (m, 2H), 8.12-8.08 (m, 2H), 7.08-7.04 (m, 2H), 3.90 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.53, 162.83, 162.37, 149.43, 129.61, 128.95, 127.67, 124.34, 115.68, 114.72, 55.59. GC-MS m/z calcd. for C$_{15}$H$_{11}$N$_3$O$_3$ : 297.1, found: 297.0

2-(4'-Chlorophenyl)-5-(4''-nitrophenyl)-1,3,4-oxadiazole (6j): Yellow solid (65 mg, 81%), mp 238 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.45-8.27 (m, 4H), 8.16-8.01 (m, 2H), 7.62-7.47 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.79, 162.94, 149.66, 138.80, 129.71, 129.24, 128.43, 127.87, 124.49, 121.80. GC-MS m/z calcd. for C$_{16}$H$_{12}$ClN$_3$O$_3$ : 301.0, found: 301.0
2-(4'-Methoxyphenyl)-5-(4''-methylphenyl)-1,3,4-oxadiazole (6k): Off white solid, yield 78%, mp 138 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.06 (d, $J = 8.9$ Hz, 2H), 8.00 (d, $J = 8.1$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 8.9$ Hz, 2H), 3.87 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 164.18, 162.43, 142.20, 130.40, 128.95, 126.98, 121.20, 116.21, 115.32, 55.93, 21.61; GC-MS m/z calcd. for C$_{16}$H$_{14}$N$_2$O$_2$: 266.1, found: 266.0

2-(4'-Chlorophenyl)-5-(4''-methylphenyl)-1,3,4-oxadiazole (6l): White solid (74 mg, 88%), mp 209 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.11-7.99 (m, 4H), 7.64-7.39 (m, 4H), 2.42 (s, 3H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 164.78, 163.34, 142.62, 137.23, 130.26, 129.87, 128.58, 126.95, 122.65, 120.67, 21.69; GC-MS m/z calcd. for C$_{16}$H$_{11}$ClN$_2$O: 270.1, found: 270.0

2-Phenyl-5-(thiophen-2'-yl)-1,3,4-oxadiazole (6m): Yellow solid (66 mg, 85%), mp 114-115 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.14-8.09 (m, 2H), 7.85-7.79 (m, 1H), 7.61-7.50 (m, 4H), 7.19 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.01, 160.83, 131.79, 130.11, 129.80, 129.10, 126.97, 125.26, 123.72; GC-MS m/z calcd. for C$_{12}$H$_{10}$N$_2$O$_2$: 228.0, found: 228.0

2-(4'-Methoxyphenethyl)-5-phenyl-1,3,4-oxadiazole (6n): Yellow liquid (50 mg, 74%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (dd, $J = 7.7, 1.4$Hz, 1H), 7.51-7.46 (m, 2H), 7.16-7.11 (m, 3H), 6.85-6.81 (m, 3H), 3.76 (s, 3H), 3.22 (t, $J = 7.7$ Hz, 1H), 3.12 (t, $J = 7.5$ Hz, 1H), 2.90 (t, $J = 7.7$ Hz, 1H), 2.64 (t, $J = 7.8$ Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.62, 158.28, 132.43, 129.46, 129.29, 129.17, 126.96, 114.28, 114.14, 55.48, 35.50, 29.52; GC-MS m/z calcd. for C$_{17}$H$_{16}$N$_2$O$_2$: 280.1, found: 280.0

2-(3'-Methylphenyl)-5-phenyl-1,3,4-oxadiazole (6o): Light pink solid, (56 mg, 70%), mp 92 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20-8.15 (m, 2H), 8.01-7.94 (m, 2H), 7.59-7.54 (m, 3H), 7.47-7.37 (m, 2H), 2.49 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 164.77, 164.53, 138.99, 132.56, 131.69, 129.08, 129.00, 127.47, 126.94, 124.10, 124.01, 123.81, 21.41. GC-MS m/z calcd. for C$_{15}$H$_{12}$N$_2$O: 236.1, found: 236.0
2-(2',4'-Dimethoxyphenyl)-5-phenyl-1,3,4-oxadiazole (6p): White solid (41 mg, 60%), mp 85°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 (d, \(J = 8.0\) Hz, 2H), 7.94 (d, \(J = 8.6\) Hz, 1H), 7.51-7.49 (m, 3H), 6.61 (d, \(J = 8.6\) Hz, 1H), 6.57 (s, 1H), 3.96 (s, 3H), 3.87 (s, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.76, 163.42, 159.45, 131.88, 131.40, 129.05, 126.95, 124.42, 106.11, 105.62, 99.20, 56.22, 55.73. GC-MS m/z calcd. for C\(_{18}\)H\(_{14}\)N\(_2\)O\(_3\) : 282.1, found: 282.0

2-(Mesityl)-5-phenyl-1,3,4-oxadiazole (6q): White solid (7 mg, 8%), mp 93 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.14-8.08 (m, 2H), 7.58-7.48 (m, 3H), 7.00 (s, 2H), 2.36 (s, 3H), 2.33 (s, 6H). GC-MS m/z calcd. for C\(_{17}\)H\(_{16}\)N\(_2\)O : 264.1, found: 264.0

3. 2,5-Diaryl-1,3,4-thiadiazoles

(i) Optimization of reaction conditions for 2,5-diaryl-1,3,4-thiadiazoles

Table 2 Optimization for the arylation of 2-phenyl-1,3,4-thiadiazole 4 using 5a\(^a\)

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\(^a\) A mixture of 4 (1 equiv.), 5a (1 equiv.), Cu catalyst (30 mol%), base (3.5 equiv) was stirred in DMF for 15 min. at rt. \(^b\) stirring at rt for 10-15 min, NR = no reaction

(ii) Typical experimental procedure for 2,5-diaryl-1,3,4-thiadiazoles (7a)

To a stirred solution of thiadiazole 4 (100 mg, 0.617 mmol) and CuBr (26.4 mg, 0.136 mmol) in DMF (2 mL), \(t\)-BuOLi (172 mg, 2.16 mmol) was charged and stirred at room temperature for 5 min. Then appropriate amount of diaryliodonium triflate 5a (265 mg, 0.617 mmol) was added in portions. The reaction mixture was stirred at room temperature for 15 min. Completion of the reaction was confirmed by TLC (4:1 hexane:ethylacetate). Then the resulting reaction mixture was added to ice-cold water and extracted with EtOAc (3 x 5 mL). The combined organic layer was washed with ammonia, brine solution.
and dried over Na₂SO₄. The solvent was removed and the obtained crude product was purified by column chromatography eluting with 10% EtOAc/hexane to afford 7a in 83% yield.

(iii) Analytical data for 2,5-diaryl-1,3,4-thiadiazoles (7a-f)

**2,5-Diphenyl-1,3,4-thiadiazole (7a)**: White solid (121 mg, 83%), mp 132 °C. ¹H NMR (400 MHz, DMSO-δ₆) δ 8.18-8.13 (m, 4H), 7.70-7.62 (m, 6H); ¹³C NMR (101 MHz, DMSO-δ₆) δ 164.48, 132.55, 129.92, 127.19, 123.77.

**2-(4'-Methylphenyl)-5-phenyl-1,3,4-thiadiazole (7b)**: White solid (56 mg, 72%), mp 122 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.15-8.13 (m, 2H), 8.03 (d, J = 8.1 Hz, 2H), 7.55-7.52 (m, 3H), 7.34 (d, J = 8.1 Hz, 2H), 2.45 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 164.71, 164.32, 142.29, 131.62, 129.73, 128.99, 126.81, 124.06, 121.18, 21.57.

**2-(4'-Methoxylphenyl)-5-phenyl-1,3,4-thiadiazole (7c)**: White solid, (64 mg, 78%), mp 136 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.16-8.13 (m, 2H), 8.11-8.06 (dd, J = 8.96, 2.1 Hz, 2H), 7.56-7.55 (m, 3H), 7.07(dd, J = 8.96, 2.1 Hz, 2H), 3.91 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 164.55, 164.16, 162.39, 131.54, 128.98, 128.73, 126.80, 124.08, 116.42, 114.48, 55.24.

**2-(4'-Chlorophenyl)-5-phenyl-1,3,4-thiadiazole (7d)**: White solid (70 mg, 84%), mp 180 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.04-8.00 (m, 2H), 7.99-7.95 (m, 2H), 7.54-7.47 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 168.33, 166.88, 137.24, 131.27, 130.03, 129.49, 129.24, 129.09, 128.70, 127.98.

**2-(4'-Bromophenyl)-5-phenyl-1,3,4-thiadiazole (7e)**: White solid (80 mg, 82%), mp 152 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.14 (dd, J = 7.5, 1.9 Hz, 2H), 8.12-8.06 (m, 2H), 7.59-7.53 (m, 4H), 7.52 (d, J = 1.6 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 160.99, 160.09, 134.43, 128.30, 125.90, 125.54, 124.60, 123.38, 120.09, 118.69.

**2-(4'-Fluorophenyl)-5-phenyl-1,3,4-thiadiazole (7f)**: White solid (60 mg, 80%), mp 158 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.17-8.13 (m, 4H), 7.70-7.62 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 164.48, 132.55, 129.92, 127.19, 123.77.
2-(4-Fluorophenyl)-5-phenyl-1,3,4-thiadiazole (7f): White solid (65 mg, 83%), mp 173 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.06-8.00 (m, 4H), 7.54-7.52 (m, 3H), 7.22 (t, $J$ = 8.6 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.72, 163.18, 131.20, 130.12, 129.98, 129.90, 129.23, 127.95, 116.53, 116.31. GC-MS m/z calcd. for C$_{13}$H$_8$FN$_2$: 256.0, found: 256.0

4. 2-Arylbenzoxazoles

(i) Typical experimental procedure for 2-arylbenzoxazoles (10a)

To the oven dried 10 mL round bottomed flask, benzoxazole evaporated and crude product was obtained. The pure 0.136 mmol) and DMSO (2 mL) were added. Then t-BuOLi (201 mg, 2.52 mmol) was charged and stirred at room temperature for 5 min. Then diphenyliodonium triflate was added to ice-cold water and extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with ammonia and brine solutions, and dried over Na$_2$SO$_4$. The combined organic layer was evaporated and crude product was obtained. The pure 10a was isolated in 89% yield by column chromatography using 10% EtOAc/Hexane as an eluent.

(ii) Analytical data for 2-arylbenzoxazoles (10a-n)

![2-Phenylbenzoxazole](image1)

2-Phenylbenzoxazole (10a)$^{15}$: White solid (145 mg, 89%), mp 102 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.28-8.25 (m, 2H), 7.79-7.77 (m, 1H), 7.60-7.58 (m, 1H), 7.51-7.35 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.09, 150.85, 142.06, 137.74, 129.99, 129.91, 129.74, 129.23, 127.95, 127.59, 124.68, 120.13, 110.59; GC-MS m/z calcd. for C$_{14}$H$_8$NO : 195.1, found: 195.0

![2-(4'-Methylphenyl)benzoxazole](image2)

2-(4'-Methylphenyl)benzoxazole (10b)$^{16}$: White solid (69 mg, 79%), mp 113 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 (d, $J$ = 8.4 Hz, 2H), 7.79-7.76 (m, 1H), 7.59-7.53 (m, 1H), 7.37-7.35 (m, 2H), 2.44 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.33, 150.72, 142.20, 142.08, 129.63, 127.62, 124.88, 124.50, 124.43, 119.99, 110.73, 21.74; GC-MS m/z calcd. for C$_{14}$H$_{11}$NO : 209.1, found: 209.0

![2-(4'-Chlorophenyl)benzoxazole](image3)

2-(4'-Chlorophenyl)benzoxazole (10c)$^{16}$: White solid, (79 mg, 83%), mp 148 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, $J$ = 8.4 Hz, 2H), 7.79-7.76 (m, 1H), 7.59-7.53 (m, 1H), 7.35-7.32 (m, 2H), 2.44 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.09, 150.85, 142.06, 137.74, 129.22, 128.88, 125.69, 125.37, 124.77, 119.94, 110.65; GC-MS m/z calcd. for C$_{15}$H$_8$ClNO : 229.0, found: 229.0
2-(4'-Bromophenyl)benzoxazole (10d): Off white solid (102 mg, 89%), mp 158 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J = 8.0$ Hz, 2H), 7.79-7.76 (m, 1H), 7.68 (d, $J = 8.0$ Hz, 2H), 7.60-7.57 (m, 1H), 7.38-7.36 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.02, 150.70, 142.02, 132.23, 129.00, 126.17, 126.11, 125.39, 124.77, 120.13, 110.65; GC-MS m/z calcd. for C$_{13}$H$_8$BrNO : 273.0, found: 273.0

2-(4'-Fluorophenyl)benzoxazole (10e): Off white solid (78 mg, 88%), mp 97 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.28-8.25 (m, 2H), 7.78-7.76 (m, 1H), 7.59-7.56 (m, 1H), 7.37-7.35 (m, 2H), 7.26-7.20 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.08, 163.57, 150.75, 142.06, 129.89, 129.80, 126.68, 123.53, 123.50, 120.00, 116.32, 116.10, 110.32. GC-MS m/z calcd. for C$_{13}$H$_8$FNO : 213.1, found: 213.0

2-(4'-Methoxyphenyl)benzoxazole (10f): White solid (68 mg, 72%), mp 98 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (dd, $J = 8.9, 2.1$ Hz, 3H), 7.91-7.84 (m, 1H), 7.50-7.43 (m, 1H), 7.38-7.34 (m, 1H), 7.03 (dd, $J = 8.8, 2.0$ Hz, 2H), 3.88 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.27, 162.02, 134.53, 129.03, 126.70, 124.37, 122.88, 121.67, 114.31, 55.68, 7.71. GC-MS m/z calcd. for C$_{14}$H$_{11}$NO : 225.0, found: 225.0

2-(Naphthalen-1'-yl)benzoxazole (10g): Pale yellow solid (68 mg, 67%), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.50 (dd, $J = 8.6, 1.1$ Hz, 1H), 8.47 (dd, $J = 7.3, 1.2$ Hz, 1H), 8.07 (d, $J = 8.2$ Hz, 1H), 7.97 (d, $J = 8.2$ Hz, 1H), 7.94-7.89 (m, 1H), 7.74-7.71 (m, 1H), 7.69-7.59 (m, 3H), 7.46-7.41 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.84, 150.20, 142.33, 133.98, 132.33, 130.71, 129.35, 128.69, 127.94, 126.48, 126.29, 125.30, 124.97, 123.65, 120.30, 110.54. GC-MS m/z calcd. for C$_{17}$H$_{11}$NO : 245.1, found: 245.0

2-(2'-Methoxyphenyl)benzoxazole (10h): White solid (68 mg, 72%), mp 54 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J = 9.3$ Hz, 1H), 7.87-7.80 (m, 1H), 7.63-7.57 (m, 1H), 7.53 (t, $J = 7.1$ Hz, 1H), 7.39-7.32 (m, 2H), 7.14-7.10 (m, 2H), 4.04 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.45, 150.26, 142.15, 132.66, 131.29, 124.96, 124.29, 120.73, 120.13, 111.91, 110.38, 56.21. GC-MS m/z calcd. for C$_{14}$H$_{11}$NO$_2$ : 225.1, found: 225.0
2-(2'-Nitrophenyl)benzoxazole (10i): Yellow solid (80 mg, 80%), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (dd, $J = 7.6$, 1.5 Hz, 1H), 7.87 (dd, $J = 7.7$, 1.4 Hz, 1H), 7.83-7.78 (m, 1H), 7.75-7.63 (m, 2H), 7.59-7.52 (m, 1H), 7.43-7.35 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.64, 154.10, 137.06, 135.04, 132.19, 129.30, 128.70, 126.57, 125.39, 123.33, 121.68. GC-MS m/z calcd. for C$_{13}$H$_8$N$_2$O$_3$ : 240.1, found: 240.0

2-(4'-Chlorophenyl)-5-methylbenzoxazole (10j): White solid (77 mg, 85%), mp 151 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J = 8.5$ Hz, 2H), 7.56-7.42 (m, 4H), 7.17 (d, $J = 8.2$ Hz, 1H), 2.49 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 175.10, 162.69, 149.62, 142.94, 138.20, 135.14, 129.86, 129.42, 127.20, 126.57, 120.93, 110.57, 22.15; GC-MS m/z calcd. for C$_{14}$H$_{10}$ClNO : 243.0, found: 243.0

5-(Methyl-2-phenyl)benzoxazole (10k): White solid (66 mg, 85%), mp 102 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.25-8.23 (m, 2H), 7.55-7.44 (m, 5H), 7.17-7.15 (m, 1H), 2.49 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.07, 148.99, 142.25, 134.30, 131.38, 128.88, 127.57, 127.26, 126.24, 119.94, 109.95, 21.35; GC-MS m/z calcd. for C$_{14}$H$_{11}$NO : 209.1, found: 209.0

5-(Chloro-2-phenyl)benzoxazole (10l): White solid (60 mg, 80%), mp 105 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (dd, $J = 7.6$, 1.5 Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.51 (d, $J = 1.9$ Hz, 1H), 7.28 (s, 1H), 7.22 (dd, $J = 8.1$, 0.9 Hz, 1H), 2.54 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.64, 154.10, 137.06, 135.04, 132.19, 129.30, 128.70, 126.57, 125.39, 123.33, 121.68; GC-MS m/z calcd. for C$_{13}$H$_8$ClNO : 229.0, found: 229.0

2-(3',5'-Dichlorophenyl)-6-methylbenzoxazole (10m): White solid (72 mg, 69%), mp 146 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J = 1.9$ Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.51 (d, $J = 1.9$ Hz, 1H), 7.28 (s, 1H), 7.22 (dd, $J = 8.1$, 0.9 Hz, 1H), 2.54 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.81, 151.03, 139.48, 136.56, 135.68, 130.92, 129.97, 126.30, 125.59, 119.68, 110.86, 21.87. GC-MS m/z calcd. for C$_{14}$H$_6$Cl$_2$NO : 277.0, found: 277.0
Methyl-2-(3',5'-dichlorophenyl)benzoxazole-6-carboxylate (10n): White solid (60 mg, 67%), mp 151 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.34 (d, \(J = 1.4\) Hz, 1H), 8.20-8.14 (m, 2H), 7.89 (d, \(J = 8.4\) Hz, 1H), 7.64 (d, \(J = 2.0\) Hz, 1H), 7.46 (dd, \(J = 8.5, 2.1\) Hz, 1H), 4.00 (s, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.52, 162.63, 150.20, 145.33, 138.30, 134.59, 132.61, 131.61, 127.56, 126.55, 120.17, 112.49, 52.60.

GC-MS m/z calcd. for C\(_{13}\)H\(_8\)Cl\(_2\)NO\(_3\): 321.0, found: 321.0

5. 2-Arylbenzothiazoles

(i) Optimization of reaction conditions for 2-arylbenezothiazoles

**Table 3 Optimization for the arylation of benzothiazole (9) using diphenyliodonium triflate (5a)**

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst/ligand</th>
<th>Base</th>
<th>solvent</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^a)</td>
<td>CuI/PPh(_3)</td>
<td>K(_3)PO(_4)</td>
<td>DMSO</td>
<td>NR</td>
</tr>
<tr>
<td>2(^a)</td>
<td>CuBr</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>NR</td>
</tr>
<tr>
<td>3(^b)</td>
<td>CuI/PPh(_3)</td>
<td>K(_3)PO4</td>
<td>DMSO</td>
<td>NR</td>
</tr>
<tr>
<td>4(^b)</td>
<td>CuI/Phen</td>
<td>K(_3)PO4</td>
<td>DMSO</td>
<td>NR</td>
</tr>
<tr>
<td>5(^b)</td>
<td>CuI</td>
<td>Cs(_2)CO(_3)</td>
<td>DMF</td>
<td>NR</td>
</tr>
<tr>
<td>6(^b)</td>
<td>CuI</td>
<td>t-BuOLi</td>
<td>DMF</td>
<td>Trace</td>
</tr>
<tr>
<td>7(^b)</td>
<td>CuBr</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>NR</td>
</tr>
<tr>
<td>8(^b)</td>
<td>CuBr</td>
<td>AgOAc</td>
<td>DMSO</td>
<td>NR</td>
</tr>
<tr>
<td>9(^b)</td>
<td>CuBr</td>
<td>t-BuOLi</td>
<td>DMSO</td>
<td>Trace</td>
</tr>
<tr>
<td>10(^b)</td>
<td>Cu(OAc)(_2)</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>NR</td>
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<td>11(^b)</td>
<td>Cu(OAc)(_2)</td>
<td>AgOAc</td>
<td>DMF</td>
<td>NR</td>
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<td>12(^b)</td>
<td>CuCl(_2)</td>
<td>t-BuOK</td>
<td>DMSO</td>
<td>NR</td>
</tr>
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<td>NaOAc</td>
<td>DMF</td>
<td>NR</td>
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<td>14(^b)</td>
<td>Cu(OTf)(_2)</td>
<td>AgOAc</td>
<td>DMF</td>
<td>NR</td>
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<tr>
<td>15(^b)</td>
<td>Pd(OAc)(_2)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>Trace</td>
</tr>
<tr>
<td>16(^b)</td>
<td>Pd(OAc)(_2)/Cu(OAc)(_2)</td>
<td>K(_2)CO(_3)</td>
<td>DMF</td>
<td>NR</td>
</tr>
<tr>
<td>17(^b)</td>
<td>Pd(OAc)(_2)</td>
<td>t-BuOLi</td>
<td>DMF</td>
<td>Trace</td>
</tr>
<tr>
<td>18(^b)</td>
<td>Pd(OAc)(_2)</td>
<td>AgOAc</td>
<td>DMF</td>
<td>60</td>
</tr>
<tr>
<td>19(^c)</td>
<td>CuBr(_2)</td>
<td>AgOAc</td>
<td>DMF</td>
<td>NR</td>
</tr>
<tr>
<td>20(^c)</td>
<td>CuI</td>
<td>Cs(_2)CO(_3)</td>
<td>DMSO</td>
<td>Trace</td>
</tr>
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<td>CuI</td>
<td>AgOAc</td>
<td>DMSO</td>
<td>NR</td>
</tr>
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<td>22(^c)</td>
<td>CuI</td>
<td>t-BuOLi</td>
<td>DMF</td>
<td>40</td>
</tr>
<tr>
<td>23(^c)</td>
<td>CuI</td>
<td>t-BuOLi</td>
<td>DMSO</td>
<td>40</td>
</tr>
<tr>
<td>24(^c)</td>
<td>CuI</td>
<td>t-BuOLi</td>
<td>PEG-400</td>
<td>NR</td>
</tr>
<tr>
<td>25(^c)</td>
<td>CuI</td>
<td>t-BuOLi</td>
<td>NMP</td>
<td>NR</td>
</tr>
<tr>
<td>26(^c)</td>
<td>CuI</td>
<td>t-BuOLi</td>
<td>DMA</td>
<td>Trace</td>
</tr>
<tr>
<td>27(^c)</td>
<td>CuI</td>
<td>t-BuOLi</td>
<td>1,4-dioxane</td>
<td>85</td>
</tr>
</tbody>
</table>
A mixture of 9 (1 equiv.), 5a (1 equiv.), Cu catalyst (30 mol%), ligand (10 mol%), and base (3.5 equiv.) was stirred in DMSO for 24 h at rt. Conventional heating at 130 °C for 18-24 h. Reaction under microwave irradiation at 130 °C for 25-30 min., NR = no reaction.

(ii) Typical experimental procedure for 2-arylbenzothiazoles (11a):
Benzoazolone 9 (100 mg, 0.740 mmol), CuI (42 mg, 0.222 mmol) diphenyliodonium triflate 5a (318 mg, 0.740 mmol), t-BuOLi (207 mg, 2.59 mmol) and 1,4-dioxane (2 mL) were charged in a sealed vial and irradiated under microwave (CEM Discover) with P = 200 w/ 100 psi at 130 °C for 30 min. Completion of the reaction was confirmed by the TLC (4:1 hexane:ethylacetate). The solvent was evaporated and purified by column chromatography using 10% EtOAc/hexane as an eluent to obtain 11a in 85% yield.

(iii) Analytical data for 2-arylbenzoxazoles (11a-h)

![2-phenylbenzothiazole (11a)](image)

**2-Phenylbenzothiazole (11a)**: Yellow solid (132 mg, 85%), mp 113 °C. **1H NMR** (400 MHz, CDCl₃) δ 8.12 – 8.07 (m, 3H), 7.92-7.90 (m, 1H), 7.52-7.48 (m, 4H), 7.41-7.37 (m, 1H); **13C NMR** (101 MHz, CDCl₃) δ 168.06, 154.13, 153.09, 135.66, 130.92, 127.05, 126.34, 125.21, 123.27, 121.61, 119.59.

![2-(4'-Methylphenyl)benzothiazole (11b)](image)

**2-(4'-Methylphenyl)benzothiazole (11b)**: Light yellow solid (62 mg, 75%), mp 85 °C. **1H NMR** (400 MHz, CDCl₃) δ 8.10 (d, J = 8.2 Hz, 1H), 8.01 (dd, J = 8.2, 1.7 Hz, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.52-7.48 (m, 1H), 7.40-7.36 (m, 1H), 7.31 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H); **13C NMR** (101 MHz, CDCl₃) δ 168.25, 154.08, 141.44, 134.96, 130.97, 129.73, 127.51, 126.26, 125.02, 123.06, 121.58, 21.34.

![2-(4'-Methoxyphenyl)benzothiazole (11c)](image)

**2-(4'-Methoxyphenyl)benzothiazole (11c)**: Yellow solid (69 mg, 78%), mp 120 °C. **1H NMR** (400 MHz, CDCl₃) δ 8.06 (dd, J = 8.9, 2.0 Hz, 3H), 7.90 (d, J = 7.5 Hz, 1H), 7.52-7.47 (m, 1H), 7.47-7.35 (m, 1H), 7.03 (dd, J = 8.9, 2.0 Hz 2H), 3.90 (s, 3H); **13C NMR** (101 MHz, CDCl₃) δ 167.82, 161.81, 154.09, 134.75, 129.05, 126.40, 126.24, 124.83, 122.82, 121.33, 114.45, 55.23.

![2-(4'-Chlorophenyl)benzothiazole (11d)](image)

**2-(4'-Chlorophenyl)benzothiazole (11d)**: Yellow solid (72 mg, 80%), mp 118 °C. **1H NMR** (400 MHz, CDCl₃) δ 8.08-8.00 (m, 3H), 7.90 (d, J = 8.0 Hz, 1H), 7.53-7.44 (m, 3H), 7.40 (t, J = 8.1 Hz, 1H); **13C NMR** (101 MHz, CDCl₃) δ 166.56, 154.15, 136.96, 135.04, 132.19, 129.30, 128.70, 126.51, 125.44, 123.33, 121.68.
2-(4'-Bromophenyl)benzothiazole (11e)\textsuperscript{5b}: Off white solid (89 mg, 83\%), mp 133 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.10 (d, J = 7.6 Hz, 1H), 7.98 (dd, J = 8.6, 1.9 Hz, 2H), 7.92-7.90 (m, 1H), 7.65 (dd, J = 8.6, 1.9 Hz, 2H), 7.54-7.50 (m, 1H), 7.44-7.40 (m, 1H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 166.70, 154.04, 134.97, 132.52, 132.24, 128.91, 126.53, 125.45, 123.19, 121.68.

2-(4'-Fluorophenyl)benzothiazole (11f)\textsuperscript{5a}: Yellow solid (72 mg, 85\%), mp 99 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.11-8.04 (m, 3H), 7.90 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 8.2 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.18 (t, J = 8.6 Hz, 2H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 166.69, 165.73, 163.28, 154.05, 135.08, 129.51, 126.44, 125.27, 123.22, 121.54, 116.08.

2-(2'-Methoxyphenyl)benzothiazole (11g)\textsuperscript{5c}: Yellow solid (65 mg, 73\%), mp 121 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.54 (dd, J = 7.9, 1.7 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.51-7.42 (m, 2H), 7.39-7.34 (m, 1H), 7.16-7.10 (m, 1H), 7.05 (d, J = 8.3 Hz, 1H), 4.03 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 154.05, 135.08, 129.51, 126.44, 125.27, 123.22, 121.54, 116.08. GC-MS m/z calcd. for C\textsubscript{14}H\textsubscript{11}NOS : 241.1, found: 241.0

2-(Thiophen-2'-yl)benzothiazole (11h)\textsuperscript{5d}: Brown solid (62 mg, 78\%), mp 99 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.07 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.65-7.64 (m, 1H), 7.50-7.45 (m, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.13 (t, J = 8.1 Hz, 1H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 161.37, 153.64, 137.35, 134.64, 129.35, 128.68, 128.10, 126.47, 125.27, 122.99, 121.51.
6. References:


7. NMR spectra of isolated 2,5-diaryl-1,3,4-oxadiazoles 6 and 2,5-diaryl-1,3,4-thiadiazoles 7

2,5-Diphenyl-1,3,4-oxadiazole (6a)
2-(4'-Methylphenyl)-5-phenyl-1,3,4-oxadiazole (6b)
2-(4'-Methoxyphenyl)-5-phenyl-1,3,4-oxadiazole (6c)
2-(4'-Chlorophenyl)-5-phenyl-1,3,4-oxadiazole (6d)
2-(4'-Bromophenyl)-5-phenyl-1,3,4-oxadiazole (6e)
2-(4'-Fluorophenyl)-5-phenyl-1,3,4-oxadiazole (6f)
Methyl-4'-(5-phenyl-1,3,4-oxadiazol-2-yl)benzoate (6g)
2-(4'-Nitrophenyl)-5-phenyl-1,3,4-oxadiazole (6h)
2-(4'-Methoxyphenyl)-5-(4''-nitrophenyl)-1,3,4-oxadiazole (6i)
2-(4'-Chlorophenyl)-5-(4''-nitrophenyl)-1,3,4-oxadiazole (6j)
2-(4'-Methoxyphenyl)-5-(4''-methylphenyl)-1,3,4-oxadiazole (6k)
2-(4'-Chlorophenyl)-5-(4''-methylphenyl)-1,3,4-oxadiazole (6l)
2-Phenyl-5-(thiophen-2'-yl)-1,3,4-oxadiazole (6m)
2-(4'-Methoxyphenethyl)-5-phenyl-1,3,4-oxadiazole (6n)
2-(3'-Methylphenyl)-5-phenyl-1,3,4-oxadiazole (6o)
2-(2',4'-Dimethoxyphenyl)-5-phenyl-1,3,4-oxadiazole (6p)
2-(Mesityl)-5-phenyl-1,3,4-oxadiazole (6q)
2,5-Diphenyl-1,3,4-thiadiazole (7a)
2-(4'-Methylphenyl)-5-phenyl-1,3,4-thiadiazole (7b)
2-(4'-Methoxylphenyl)-5-phenyl-1,3,4-thiadiazole (7c)
2-(4'-Chlorophenyl)-5-phenyl-1,3,4-thiadiazole (7d)
2-(4’-Bromophenyl)-5-phenyl-1,3,4-thiadiazole (7e)
2-(4'-Fluorophenyl)-5-phenyl-1,3,4-thiadiazole (7f)
8. NMR spectra of isolated 2-arylbenzoxazoles 10 and 2-arylbenzothiazoles 11

2-Phenylbenzoxazole (10a)
2-(4'-Methylphenyl)benzoxazole (10b)
2-(4′-Chlorophenyl)benzoxazole (10c)
2-(4'-Bromophenyl)benzoxazole (10d)
2-(4'-Fluorophenyl)benzoxazole (10e)
2-(4'-Methoxyphenyl)benzoxazole (10f)
2-(Napthalen-1'yl)benzoxazole (10g)
2-(2'-Methoxyphenyl)benzoxazole (10h)
2-(2'-Nitrophenyl)benzoxazole (10i)
2-(4'-Chlorophenyl)-5-methylbenzoxazole (10j)
5-Methyl-2-phenylbenzoxazole (10k)
5-Chloro-2-phenylbenzoxazole (10l)
2-(3',5'-Dichlorophenyl)-6-methylbenzoxazole (10m)
Methyl-2-(3',5'-dichlorophenyl) benoxazole-6-carboxylate (10n)
2-Phenylbenzothiazole (11a)
2-(4'-Methylphenyl)benzothiazole (11b)
2-(4'-Methoxyphenyl) benzothiazole (11c)
2-(4'-Chlorophenyl)benzothiazole (11d)
2-(4'-Bromophenyl)benzothiazole (11e)
2-(4'-Fluorophenyl)benzothiazole (11f)
2-(2'-Methoxyphenyl)benzothiazole (11g)
2-(Thiophen-2'-yl)benzothiazole (11h)