CHAPTER II

EXPERIMENTAL

All starting materials were obtained from commercial suppliers, and were used without further purification. All solvents were used directly without drying, except for dimethyl sulfoxide (DMSO), which was dried with 4 Å molecular sieves from Sigma-Aldrich. Calcium carbide was ground before use. Analytical thin-layer chromatography (TLC) was performed on Kieselgel F_{254} pre-coated plastic TLC plates from EM science. Visualization was performed with a 254 nm ultraviolet lamp. Gel column chromatography was carried out with aluminium oxide (90 active neutral, 70-230 mesh) from Merck and silica gel (60, 230-400 mesh) from ICN Silitech. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian or Bruker 400 MHz for ^{1}H and Bruker 100 MHz for ^{13}C in $CDCl_3$ or $(CD_3)_2SO$ solution. Chemical shifts of ^{1}H and ^{13}C NMR were referenced to $CDCl_2$ (δ 7.26 for ^{1}H, δ 77.00 for ^{13}C) and $(CD_3)_2SO$ (δ 2.50 for ^{1}H, δ 39.43 for ^{13}C). Coupling constants (*J*) were reported in Hertz (Hz). Splitting patterns were designated as s (singlet), d (doublet), t (triple), q (quartet), bs (broad singlet), m (multiplet). Mass spectra were performed by Micromass Quattro micro ™ API.

2.1 Preparation of aryloximes

2.1.1 Synthesis of oximes

General procedure for the preparation of oximes (Table 3.1): Ketones (1.0 equiv), hydroxylamine hydrochloride (2.0 equiv) were mixed with ethanol (10mL/mmol of ketone) in a round bottomed flask with a magnetic stir bar. Pyridine (1.8 equiv) was added to the mixture and was refluxed reaction for 4 h. Ethanol was removed by evaporation. To the resulting, residue was added water and the mixture was stirred in an ice bath until the oxime crystallized. The solid was filtered off and washed with cold water and dried with air. The product was recrystallized from hexane, giving the solid crystals.

Acetophenone oxime (1b): synthesized according to the general procedure from acetophenone (5.00 g, 41.6 mmol), hydroxylamine hydrochloride (5.78 g, 83.2 mmol) and pyridine (5.0 mL, 62.4 mmol) to afford 4.51 g (33.0 mmol, 80%) of oxime **1b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.63 (2H,d, *J*=4.8 Hz), 7.42-7.35 (3H, m), 2.29 (3H, s).

1-*p*-Tolylethanone oxime (2b): synthesized according to the general procedure from 1-*p*-tolylethanone (1.00 g, 74.5 mmol), hydroxylamine hydrochloride

(1.04 g, 14.9 mmol) and pyridine (0.9 mL, 11.2 mmol) to afford 0.97 g (6.5 mmol, 87%) of oxime **2b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.54 (2H, d, *J*=6.5 Hz), 7.20 (2H, d, *J*=8.0 Hz), 2.37 (3H, s), 2.31 (3H, s).

1-(4-Hydroxyphenyl)ethanone oxime (3b): synthesized according to the general procedure from 1-(4-hydroxyphenyl)ethanone (5.00 g, 36.7 mmol), hydroxylamine hydrochloride (5.14 g, 74.0 mmol) and pyridine (4.5 mL, 55.5 mmol) to afford 2.87 g (19.0 mmol, 52%) of oxime **3b** as a white solid: ^{1}H NMR (400 MHz, DMSO): δ ppm 10.85 (1H, s), 9.61 (1H, s), 7.45 (2H, d, *J* = 8.6 Hz), 6.73 (2H, d, *J* = 8.7 Hz), 2.06 (3H, s).

1-(4-Methoxyphenyl)ethanone oxime (4b): synthesized according to the general procedure from 1-(4-methoxyphenyl)ethanone (5.00 g, 33.0 mmol), hydroxylamine hydrochloride (4.58 g, 66.0 mmol) and pyridine (4.0 mL, 49.5 mmol) to afford 5.07 g (31.8 mmol, 92 %) of oxime **4b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.59 (2H, d, *J*=8.7 Hz), 6.91 (2H, d, *J*=8.9 Hz), 3.83 (3H, s), 2.27 (3H, s).

1-(4-Butoxyphenyl)ethanone oxime (5b): synthesized according to the general procedure from 1-(4-butoxyphenyl)ethanone (2.62 g, 13.6 mmol), hydroxylamine hydrochloride (1.95 g, 27.3 mmol) and pyridine (2.0 mL, 24.5 mmol) to afford 2.69 g (13.0 mmol, 95%) of oxime **5b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.56 (2H, d, *J*=8.8 Hz), 6.89 (2H, d, *J*=8.9 Hz), 3.98 (2H, t, *J*=6.5 Hz), 2.27 (3H, s), 1.82-1.72 (2H, m), 1.55-1.43 (2H, m), 0.97 (3H, t, *J*=7.4 Hz).

1-(4-(Benzyloxy)phenyl)ethanone oxime (6b): synthesized according to the general procedure from 1-(4-(benzyloxy)phenyl)ethanone (1.00 g, 4.4 mmol), hydroxylamine hydrochloride (0.61 g, 8.8 mmol) and pyridine (0.6 mL, 7.9 mmol) to afford 0.82 g (3.4 mmol, 76%) of oxime **6b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.73 (2H, d, *J*=8.9 Hz), 7.47-7.32 (5H, m), 7.03 (2H, d, *J*=9.3 Hz), 5.12 (2H, s), 2.45 (3H, s).

***(E)*-4-(1-(Hydroxyimino)ethyl)phenyl-4-methylbenzenesulfonate (7b)**: synthesized according to the general procedure from 4-acetylphenyl-4-methylbenzenesulfonate (2.00 g, 8.9 mmol), hydroxylamine hydrochloride (0.96 g, 8.8 mmol) and pyridine (0.8 mL, 10.3 mmol) to afford 1.95 g (6.4 mmol, 93%) of oxime **7b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.89 (2H, d, *J*=8.9 Hz), 7.71 (2H, d, *J*=8.3 Hz), 7.32 (2H, d, *J*=8.0 Hz), 7.08 (2H, d, *J*=6.9 Hz), 2.57 (3H, s), 2.45 (3H, s).

1-(4-aminophenyl)ethanone oxime (8b): synthesized according to the general procedure from 1-(4-aminophenyl)ethanone (5.00 g, 37.0 mmol),

hydroxylamine hydrochloride (5.14 g, 73.9 mmol) and pyridine (5.4 mL, 67.0 mmol) to afford 5.10 g (34.0 mmol, 92%) of oxime **8b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.45 (2H, d, *J* = 8.7 Hz), 6.66 (2H, d, *J* = 8.6 Hz), 2.22 (3H, s).

***(E)*-1-(4-(Dimethylamino)phenyl)ethanone oxime (9b):** synthesized according to the general procedure from 1-(4-(dimethylamino)phenyl)ethanone (1.00 g, 6.1 mmol), hydroxylamine hydrochloride (0.83 g, 11.9 mmol) and pyridine (0.9 mL, 10.8 mmol) to afford 0.66 g (3.7 mmol, 60%) of oxime **9b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.54 (2H, d, *J*=8.,6 Hz), 6.71 (2H, d, *J*=8.5 Hz), 2.99 (6H, s), 2.25 (3H, s).

1-(4-(Methylthio)phenyl)ethanone oxime (10b): synthesized according to the general procedure from 1-(4-(methylthio)phenyl)ethanone (0.50 g, 3.0 mmol), hydroxylamine hydrochloride (0.42 g, 6.0 mmol) and pyridine (0.4 mL, 5.4 mmol) to afford 0.42 g (2.3 mmol, 77%) of oxime 10**b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.56 (2H, d, *J*=8.3 Hz), 7.24 (2H, d, *J*=8.4 Hz), 2.50 (3H, s), 2.29 (3H, s).

1-(4-Fluorophenyl)ethanone oxime (11b): synthesized according to the general procedure from 1-(4-fluorophenyl)ethanone (3.00 g, 21.7 mmol), hydroxylamine hydrochloride (3.06 g, 44.0 mmol) and pyridine (2.6 mL, 32.6 mmol) to afford 3.24 g (21.2 mmol, 97%) of oxime **11b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.21-7.88 (1H, br), 7.61 (2H, m), 7.07 (2H, t, *J* = 8.7 Hz), 2.27 (3H, s).

1-(4-Chlorophenyl)ethanone oxime (12b): synthesized according to the general procedure from 1-(4-chlorophenyl)ethanone (5.00 g, 32.3 mmol), hydroxylamine hydrochloride (4.17 g, 64.6 mmol) and pyridine (3.6 mL, 45.0 mmol) to afford 5.29 g (31.0 mmol, 96%) of oxime 12b as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.60 (2H, d, *J*=8.6 Hz), 7.37 (2H, d, *J*=8.6 Hz), 2.31 (3H, s).

1-(4-Bromophenyl)ethanone oxime (13b). synthesized according to the general procedure from 1-(4-bromophenyl)ethanone (5.00 g, 25.1 mmol), hydroxylamine hydrochloride (3.49 g, 50.2 mmol) and pyridine (3.3 mL, 37.7 mmol) to afford 5.10 g (23.8 mmol, 95%) of oxime 13b as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.51 (4H, d, *J* = 9.3 Hz), 2.26 (3H, s).

1-(4-Iodophenyl)ethanone oxime (14b): synthesized according to the general procedure from 1-(4-iodophenyl)ethanone (2.00 g, 8.1 mmol), hydroxylamine hydrochloride (1.12 g, 16.1 mmol) and pyridine (1.0 mL, 12.2 mmol) to afford 1.97 g (7.5 mmol, 94%) of oxime **14b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.07 (1H, br), 7.71 (2H, d, *J* = 8.5 Hz), 7.36 (2H, d, *J* = 8.4 Hz), 2.25 (3H, s).

1-(4-Nitrophenyl)ethanone oxime (15b). synthesized according to the general procedure from 1-(4-nitrophenyl)ethanone (5.00 g, 30.3 mmol), hydroxylamine hydrochloride (4.17 g, 60.0 mol) and pyridine (3.7 mL, 45.5 mmol) to afford 5.06 g (28.1 mmol, 93%) of oxime **15b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.24 (2H, d, *J*=8.9 Hz), 7.81 (2H, d, *J*=7.8 Hz), 2.33 (3H, s).

***(E)*-4-(1-(Hydroxyimino)ethyl)benzonitrile (16b):** synthesized according to the general procedure from 4-acetylbenzonitrile (2.00 g, 13.8 mmol), hydroxylamine hydrochloride (1.95 g, 27.6 mmol) and pyridine (1.7 mL, 20.7 mmol) to afford 2.02 g (12.6 mmol, 91%) of oxime 16**b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.75 (2H, d, *J*=8.9 Hz), 7.67 (2H, d, *J*=8.7 Hz), 2.29 (3H, s).

1-(Biphenyl-4-yl)ethanone oxime (17b): synthesized according to the general procedure from 1-(biphenyl-4-yl)ethanone (1.00 g, 51.0 mmol), hydroxylamine hydrochloride (0.71 g, 10.2 mmol) and pyridine (0.6 mL, 7.7 mmol) to afford 1.05 g (5.0 mol, 97%) of oxime **17b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.12-7.98 (1H, m), 7.82-7.54 (4H, m), 7.45 (2H, d, *J*=8.0 Hz), 7.38 (2H, d, *J*=6.3 Hz), 2.32 (3H, s).

1-(4-(Pyridin-3-yl)phenyl)ethanone oxime (18b): synthesized according to the general procedure from 1-(4-(pyridin-3-yl)phenyl)ethanone (1.00 g, 8.3 mmol), hydroxylamine hydrochloride (1.15 g, 16.6 mmol) and pyridine (1.0 mL, 12.5 mmol) to afford 1.52 g (7.2 mmol, 87%) of oxime **18b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 9.00 (2H, s), 8.61 (2H, d, *J*=4.2 Hz), 8.04 (2H, d, *J*=8.1 Hz), 7.42 (2H, dd, *J*=8.0, 5.0 Hz), 2.65 (3H, s).

1-(4-(Thiophen-2-yl)phenyl)ethanone oxime (19b): synthesized according to the general procedure from 1-(4-(thiophen-2-yl)phenyl)ethanone (5.00 g, 24.7 mmol), hydroxylamine hydrochloride (3.43 g, 49.4 mmol) and pyridine (3.0 mL, 37.1 mmol) to afford 5.11 g (23.5 mmol, 95%) of oxime **19b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.58 (1H, dd, *J*=5.1, 0.9 Hz), 7.51 (1H, dd, *J*=3.8, 1.1 Hz), 7.28 (2H, d, *J*=5.1 Hz), 7.12 (1H, dd, *J*=5.1, 3.9 Hz), 7.03 (2H, dd, *J*=5.1, 3.7 Hz), 2.38 (3H, s).

1-(4-(Phenylethynyl)phenyl)ethanone oxime (20b): synthesized according to the general procedure from 1-(4-(phenylethynyl)phenyl)ethanone (0.32 g, 1.5 mmol), hydroxylamine hydrochloride (0.20 g, 2.9 mmol) and pyridine (0.2 mL, 2.3 mmol) to afford 0.27 g (1.1 mmol, 80%) of oxime **20b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.94 (1H, d, *J*=7.3 Hz), 7.79 (1H, d, *J*=8.4 Hz), 7.72 (1H, d, *J*= 6.6 Hz), 7.57 (3H, dd, *J*=16.1, 7.4 Hz), 7.36 (2H, d, *J*=4.2 Hz), 2.45 (3H, s).

4-(1-(Hydroxyimino)ethyl)phenylboronic acid (21b): synthesized according to the general procedure from 4-acetylphenylboronic acid (2.00 g, 12.1 mmol), hydroxylamine hydrochloride (1.67 g, 24.2 mmol) and pyridine (1.5 mL, 18.2 mmol) to afford 1.89 g (10.6 mmol, 87%) of oxime **21b** as a white solid: ^{1}H NMR (400 MHz, DMSO): δ ppm 11.16 (1H, s), 8.24 (1H, s), 7.76 (2H, d, *J* = 7.7 Hz), 7.56 (2H, d, *J* = 8.1 Hz), 2.12 (3H, s).

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanone oxime (22b): synthesized according to the general procedure from 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanone (0.49 g, 2.0 mmol), hydroxylamine hydrochloride (0.28 g, 4.0 mmol) and pyridine (0.3 mL, 3.0 mmol) to afford 0.44 g (1.7 mmol, 84%) of oxime **22b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.84 (2H, d, *J*=2.5 Hz), 7.65 (2H, d, *J*=3.7 Hz), 2.17 (3H, s), 1.35 (12H, s).

1-(Naphthalen-1-yl)ethanone oxime (23b): synthesized according to the general procedure from 1-(naphthalen-1-yl)ethanone (5.00 g, 29.4 mmol), hydroxylamine hydrochloride (5.78 g, 58.8 mmol) and pyridine (3.6 mL, 44.1 mmol) to afford 4.90 g (26.5 mmol, 90%) of oxime **23b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.02(1H, d, *J*=8.0 Hz), 7.88(2H, t, *J*=6.5 Hz), 7.57-7.43(4H, m), 2.38(3H, s).

1-(Naphthalen-2-yl)ethanone oxime (24b): synthesized according to the general procedure from 1-(naphthalen-2-yl)ethanone (2.00 g, 11.8 mmol), hydroxylamine hydrochloride (1.67 g, 23.6 mmol) and pyridine (1.4 mL, 17.7 mmol) to afford 1.98 g (10.7 mmol, 91%) of oxime **24b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.02 (1H, s), 7.81-7.88 (4H, m), 7.50 (2H, dd, *J*=6.2, 3.3 Hz), 2.41 (3H, s).

1-(Anthracen-2-yl)ethanone oxime (25b): synthesized according to the general procedure from 1-(anthracen-2-yl)ethanone (0.50 g, 2.3 mmol), hydroxylamine hydrochloride (0.32 g, 4.5 mmol) and pyridine (0.3 mL, 3.5 mmol) to afford 0.47 g (2.0 mmol, 88%) of oxime **25b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.45 (1H, s), 8.40 (1H, s), 8.22 (1H, s), 8.04-7.97 (2H, m), 7.83 (1H, d, *J*= 8.6 Hz), 7.49-7.52 (2H, m), 2.53 (3H, s).

(3*E*)-4-Phenylbut-3-en-2-one oxime (26b): synthesized according to the general procedure from (*E*)-4-phenylbut-3-en-2-one (5.00 g, 34.2 mmol), hydroxylamine hydrochloride (4.73 g, 68.4 mmol) and pyridine (4.1 mL, 51.3 mmol) to afford 4.82 g (29.9 mmol, 87%) of oxime **26b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.49 (2H, d, *J*=7.5 Hz), 7.41-7.28 (3H, m), 6.94 (2H, q, *J*=16.4 Hz), 2.19 (3H, s).

Cyclohexanone oxime (27b): synthesized according to the general procedure from cyclohexanone (5.00 g, 50.9 mmol), hydroxylamine hydrochloride (5.78 g, 83.2 mmol) and pyridine (6.2 mL, 76.4 mmol) to afford 4.80 g (42.4 mmol, 83%) of oxime **27b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 2.51 (2H, t, *J*=6.2 Hz), 2.26-2.20 (2H, m), 1.73-1.56 (6H, m).

3,4-Dihydronaphthalen-1(2*H*)-one oxime (28b): synthesized according to the general procedure from 3,4-dihydronaphthalen-1*(2H)*-one (1.00 g, 6.8 mmol), hydroxylamine hydrochloride (0.95 g, 13.7 mmol) and pyridine (0.8 mL, 10.2 mmol) to afford 1.04 g (6.5 mmol, 95%) of oxime **28b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.92 (1H, d, *J*=7.8 Hz), 7.29 (1H, dd, *J*=7.5, 0.9 Hz), 7.21 (1H, dd, *J*=10.8, 4.1 Hz), 7.16 (1H, d, *J*=7.5 Hz), 2.83 (2H, t, *J*=6.6 Hz), 2.80-2.73 (2H, m), 1.93-1.83 (2H, m).

1-Cyclohexenylethanone oxime (29b): synthesized according to the general procedure from 1-cyclohexenylethanone (0.50 g, 4.0 mmol), hydroxylamine hydrochloride (0.56 g, 8.1 mmol) and pyridine (0.5 mL, 6.0 mmol) to afford 0.19 g (1.4 mmol, 35%) of oxime **29b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.71 (1H, br), 6.12 (1H, s), 2.20 (2H, s), 2.11 (2H, d, *J*=3.2 Hz), 1.64-1.48 (4H, m).

Propiophenone oxime (30b): synthesized according to the general procedure from propiophenone (5.00 g, 37.3 mmol), hydroxylamine hydrochloride (5.14 g, 74.6 mmol) and pyridine (4.5 mL, 56.0 mmol) to afford 2.68 g (18.0 mmol, 48%) of oxime **30b** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.65-7.59 (2H, m), 7.42-7.36 (3H, m), 2.83 (2H, q, *J*=7.6 Hz), 1.18 (3H, t, *J*=7.6 Hz).

2.1.2 Preparation of arylketones (5a-7a, 9a, 20a)

4-Butoxyacetophenone (5a)

4-Hydroxyacetophenone (2.0 g, 14.7 mmol) and potassium hydroxide (1.7 g, 3.0 mmol) were stirred in DMF (15 mL). Butyl bromide (3.2 mL, 29.4 mmol) was added dropwise and the reaction was continuously stirred at room temperature for 24 h. The reaction was quenched with water (20 mL), extracted with EtOAc (3 x 20 mL) and washed with brine (3 x 20 mL). The organic layer was dried with anh. $NaSO_4$ filtered, and the solvent was removed under reduce pressure to give ketone **5a** in 93% yield (2.6 g, 0.0135 mol) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.56 (2H, d, *J*=8.8 Hz), 6.89 (2H, d, *J*=8.9 Hz), 3.98 (2H, t, *J*=6.5 Hz), 1.86-1.68 (2H, m), 1.50 (2H, dt, *J*=14.9, 7.4 Hz), 0.97 (3H, t, *J*=7.4 Hz).

4-Benzyloxyacetophenone (6a)

4-Hydroxyacetophenone (0.5 g, 3.7 mmol) and potassium carbonate (1.6 g, 11.8 mmol) were dissolved with DMF (40 mL). Benzyl bromide (0.5 mL, 4.4 mmol) was added and the reaction was stirred at 80 °C for 12 h. The mixture reaction was diluted with water and extracted with EtOAc (3 x 20 mL) and washed with brine (3 x 20 mL). The organic layer was dried by anh.Na_2SO_4 and evaporated under reduce pressure to give product **6a** in 85% yield (0.7 g, 3.1 mmol) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.93 (2H, d, *J*=8.8 Hz), 7.45-7.30 (5H, m), 7.01 (2H, d, *J*=8.8 Hz), 5.13 (2H, s), 2.55 (3H, s).

4-Tosyloxyacetophenone (7a)

4-Hydroxyacetophenone (2.0 g, 15.0 mmol) was dissolved in pyridine (50 mL) and DMAP (1 crystal). Tosyl chloride (5.7 g, 29.9 mmol) was added to the mixture solution and the reaction was heated to 80 °C for 24 h. The mixture was diluted with water (40 mL) and extracted with EtOAc (3 x 40 mL) and washed with brine (2 x 30 mL). The EtOAc layer was dried with anh.$NaSO_4$ and the solvent was removed under reduce pressure to afford product **7a** in 100% yield (4.3 g, 14.8 mmol) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.89 (2H, d. *J*=8.9 Hz), 7.71 (2H, d, *J*=8.3 Hz), 7.32 (2H, d, 8.0 Hz), 7.08 (2H, d, *J*=8.8 Hz), 2.57 (3H, s), 2.45 (3H, s).

(4-(Dimethylamino)phenyl)ethanone (9a)

To a solution of 4-aminoacetophenone (0.5 g, 3.7 mmol) in DMF (5 mL) was added iodomethane (0.5 mL, 8.1 mmol) and K_2CO_3 (1.1 g 8.1 mmol). The mixture was stirred at 60 °C for 24 h and then cooled to room temperature. The solution was quenched with a mixture of ice and water, filtered and washed with water to afford the desired product in 75% yield (1.8 g, 11.0 mmol) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.87 (2H, d, *J*=8.7 Hz), 6.65 (2H, d, *J*=8.8 Hz), 3.06 (6H, s), 2.51 (3H, s).

1-(4-(Phenylethynyl)phenyl)ethanone (20a)

A mixture of 4-iodoacetophenone (500.0 mg, 2.03 mmol), copper (II) iodide (311.5 mg, 3.05 mmol), bis(triphenylphosphine)palladium(II) dichloride (28.8 mg, 0.04 mmol), triphenylphosphine (21.4 mg, 0.08 mmol) as stirred in THF (20 mL) and triethylamine (15 mL). To this mixture was added phenylacetylene (0.34 mL, 3.05 mmol) and the reaction was stirred at room temperature for 4 h. The reaction was filtered and the solid was washed with water. The organic layer was extracted with ammonium chloride (2 x 20 mL) and dried with anh.Na_2SO_4. The residue was

evaporated under reduced pressure and purified by silica column chromatography using 25%EtOAc–hexanes as eluent to afford the product in 71% yield (319.0 mg, 1.45 mmol) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.94 (2H, d, *J*=8.0 Hz), 7.61 (2H, d, *J*=7.7 Hz), 7.55 (2H, s), 7.37 (3H, s), 2.62 (3H, s).

2.2 Trofimov reaction using calcium carbide as a starting material.

2.2.1 Optimization of the reaction conditions

Table 3.2 Effect of solvent: acetophenone oximes **(1b)** 100.0 mg (1.0 equiv), potassium hydroxide (1.5 equiv) and calcium carbide (6.0 equiv) were mixed with 10 mL of solvent and 18-crown-6 in a sealed tube with magnetic stir bar. The mixture was stirred at 100 °C for 15 h. The reaction was cooled to room temperature and diluted with water. The crude product was filtered and extracted with ether (5 x 30 mL). The extracts were washed with brine (2 x 50 mL) and dried with potassium carbonate. The ether was removed under reduced pressure and the crude product was purified by alumina column chromatography using 25% EtOAc–hexanes as eluent to give the 2-phenylpyrrole **(1c)** in corresponding yield.

Table 3.3 Effect of bases: acetophenone oxime **(1b)** 100.0 mg (1.0 equiv), bases (1.5 equiv) and calcium carbide (6.0 equiv) were mixed with 10 mL of DMSO and 18-crown-6 in a sealed tube with magnetic stir bar. The mixture was stirred at 100 °C for 15 h. The reaction was cooled to room temperature and diluted with water. The crude product was filtered and extracted with ether (5 x 30 mL). The extracts were washed with brine (2 x 50 mL) and dried with potassium carbonate. The ether was removed under reduced pressure and the crude product was purified by alumina column chromatography using 25% EtOAc–hexanes as eluent to give the 2-phenylpyrrole **(1c)** in corresponding yield.

Table 3.4 Effect of temperature: acetophenone oximes **(1b)** 100.0 mg (1.0 equiv), bases (1.5 equiv) and calcium carbide (6.0 equiv) were mixed with 10 mL of DMSO and 18-crown-6 in a sealed tube with magnetic stir bar. The mixture was stirred at 100°C and hearted for 15 h. The reaction was cooled to room temperature and diluted with water. The crude product was filtered and extracted with ether (5 x 30 mL). The extracts were washed with brine (2 x 50 mL) and dried with potassium carbonate. The ether was removed under reduced pressure and the crude product was purified by alumina column chromatography using 25% EtOAc–hexanes as eluent to give the 2-phenylpyrrole **(1c)** in corresponding yield.

Table 3.5 (entries 2-3) Effect of additive: acetophenone oximes **(1b)** 100.0 mg (1.0 equiv), potassium hydroxide (1.5 equiv) and calcium carbide (6.0 equiv) were mixed with 10 mL of DMSO and additives (3 mol%) in a sealed tube with magnetic stir bar. The mixture was stirred at 100 °C for 15 h. The reaction was cooled to room temperature and diluted with water. The crude product was filtered and extracted with ether (5 x 30 mL). The extracts were washed with brine (2 x 50 mL) and dried with potassium carbonate. The ether was removed under reduced pressure and the crude product was purified by alumina column chromatography using 25% EtOAc–hexanes as eluent to give the 2-phenylpyrrole **(1c)** in corresponding yield.

Table 3.5 (entries 4-6) Effect of equivalent of CaC_2 and base: acetophenone oxime (1b) 100.0 mg (1.0 equiv), potassium hydroxide (1.5 equiv) and calcium carbide (6.0 equiv) were mixed with 10 mL of DMSO and 3 mol% of 18-crown-6 in a sealed tube with magnetic stir bar. The mixture was stirred at 100 °C for 15 h. The reaction was cooled to room temperature and diluted with water. The crude product was filtered and extracted with ether (5 x 30 mL). The extracts were washed with brine (2 x 50 mL) and dried with potassium carbonate. The ether was removed under reduced pressure and the crud product was purified by alumina column chromatography using 25% EtOAc–hexanes as eluent to give the 2-phenylpyrrole **(1c)** in corresponding yield.

Table 3.6 Effect of water: acetophenone oximes **(1b)** 100.0 mg (1.0 equiv), potassium hydroxide (1.5 equiv) and calcium carbide (6.0 equiv) were mixed with 10 mL of DMSO : water and 18-crown-6 (3 mol%) in a sealed tube with a magnetic stir bar. The mixture was stirred at 100 °C for 15 h. The reaction was cooled in room temperature and diluted dropwise with water. The crude product was filtered and extracted with ether (5 x 30 mL). The extracts were washed with brine (2 x 50 mL) and dried with potassium carbonate. The ether was removed under reduced pressure and the crude product was purified by alumina column chromatography using 25% EtOAc–hexanes as eluent to give the 2-phenylpyrrole **(1c)** in corresponding yield.

2.2.2 Screening of 2-aryloximes

General procedure for screening 2-aryloximes via Trofimov reaction using calcium carbide as starting material: acetophenone oximes (1.0 equiv), potassium hydroxide (1.5 equiv), calcium carbide (6.0 equiv) and 18-crown-6 were mixed with DMSO as solvent in condition A or (50:1) DMSO/water as the solvent in condition B in a sealed tube with magnetic stir bar. The mixture was stirred at 100 °C for overnight.

The reaction was cooled to room temperature and diluted dropwise with water. The product was filtered and extracted into ether (5 x 30 mL). The extracts were washed with brine (2 x 50 mL) and dried with potassium carbonate. The ether was removed under reduced pressure and the crude product was purified with alumina column chromatography using 25% EtOAc–hexanes as eluent to give the desired compound.

2-Phenylpyrrole (1c): synthesized according to general procedure from **1b** (100.0 mg, 0.74 mmol), potassium hydroxide (63.1 mg, 1.13 mmol), and calcium carbide (474.3 mg, 7.40 mmol) dissolved in DMSO (10 mL) to afford **1c** (67.0 mg, 0.47 mmol. 65%) as a pink solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.45 (1H, br s,), 7.48 (2H, d, *J*=7.4 Hz), 7.37 (2H, t, *J*=7.6 Hz), 7.22 (1H, d, *J*=7.8 Hz), 6.87 (1H, s), 6.53 (1H, s), 6.31 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.8, 132.2, 128.9, 128,9, 126.2, 123.7 123.7, 118.9, 110.1, 106.0.

2-Phenylvinylpyrrole (1c'): yield 10.3 mg (0.06 mmol, 8%) of **1c'** as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.37-7.19 (4H, m), 7.05 (1H, s), 6.84 (1H, dd, *J*=15.7, 8.8 Hz), 6.21 (2H, d, *J*=16.3 Hz), 5.11 (1H, d, *J*=15.7 Hz), 4.63 (1H, d, *J*=8.9 Hz).

3-Methyl-2-phenylpyrrole (2c): synthesized according to general procedure from **30b** (100.0 mg, 0.67 mmol), potassium hydroxide (56.7 mg, 1.01 mmol), and calcium carbide (257.7 mg, 4.02 mmol) dissolved in DMSO (10 mL) to afford **2c** (23.2 mg, 0.15 mmol. 22%) as a purple oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.15 (1H, br s), 7.46-7.32 (5H, m), 7.26 (1H, s), 6.78 (1H, s), 6.16 (1H, s), 2.29 (3H, s).

3-Methyl-2-phenylvinylpyrrole (2c'): yield 13.5 mg (0.07 mmol, 11%) as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.47-7.38 (3H, m), 7.29 (3H, d, *J*=7.5 Hz), 7.05 (1H, d, *J*=2.2 Hz), 6.72 (1H, dd, *J*=15.6, 8.9 Hz), 6.18 (1H, s), 5.06 (1H, d, *J*= 15.7 Hz), 4.55 (1H, d, *J*=8.9 Hz), 2.06 (3H, s).

2-*p*-Tolylpyrrole (3c): synthesized according to general procedure from **2b** (100 mg, 0.67 mmol), potassium hydroxide (56.7 mg, 1.01 mmol), and calcium carbide (257.7 mg, 4.02 mmol) dissolved in DMSO (10 mL) to afford **3c** (27.4 mg, 0.17 mmol. 26%) of as a pink solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.24 (1H, br), 7.30 (2H, d, *J*=8.8 Hz), 6.82 (2H, d, *J*=11.7 Hz), 6.72 (1H, s), 6.32 (1H, s), 6.19 (1H, s), 3.73 (3H, s).

2-*p*-Tolylvinylpyrrole (3c'): yield 8.6 mg (0.05 mmol, 7%) as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm δ 7.25-7.19 (3H, m), 7.18 (2H, d, *J*= 1.4 Hz), 6.97 (1H, s), 6.70 (1H, s), 6.68-6.60 (1H, m), 6.09 (2H, d, *J*=9.4 Hz), 4.99 (1H, d, *J*=15.7 Hz), 4.48 (1H, d, *J*=8.9 Hz), 2.21 (3H, s).

2-(4-Methoxyphenyl)pyrrole (4c): synthesized according to general procedure from **3b** (100.0 mg, 0.61 mmol), potassium hydroxide (51.0 mg, 0.91 mmol), and calcium carbide (232.7 mg, 3.63 mmol) dissolved in DMSO (10 mL) to afford **4c** (36.7 mg, 0.21 mmol. 35%) of as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.28 (1H, br s), 7.34 (2H, d, *J*=8.,4 Hz), 6.85 (2H, d, *J*=8.5 Hz), 6.76 (1H, s), 6.34 (1H, s), 6.21 (1H, s), 3.76 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 158.3, 132.2, 126.0, 125.3, 125.3, 118.2, 114.4, 114.4, 109.9, 104.9, 55.35.

2-(4-Methoxyphenyl)vinylpyrrole (4c'): yield 12.1 mg (0.06 mmol, 10%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.30 (2H, d, *J*=8.1 Hz), 7.10 (1H, s), 6.95 (2H, d, *J*=8.1 Hz), 6.87 (1H, dd, *J*=15.7, 8.9 Hz), 6.29 (1H, s), 6.20 (1H, s), 5.15 (1H, d, *J*= 15.7 Hz), 4.67 (1H, d, *J*=8.8 Hz), 3.85 (3H, s).

2-(4-Butoxyphenyl)pyrrole (5c): synthesized according to general procedure from **4b** (100.0 mg, 0.48 mmol), potassium hydroxide (40.4 mg, 0.72 mmol), and calcium carbide (184.6 mg, 2.88 mmol) dissolved in DMSO (10 mL) to afford **5c** (35.8 mg, 0.17 mmol. 34%) as a purple solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.33 (1H, br s), 7.39 (2H, d, *J*=8.6 Hz), 6.90 (2H, d, *J*=8.3 Hz), 6.83 (1H, s), 6.40 (1H, s), 6.27 (1H, s), 3.97 (2H, t, *J*=6.5 Hz), 1.82-1.73 (2H, m), 1.50 (2H, dd, *J*=15.0,7.5 Hz), 0.98 (3H, t, *J*=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 157.9, 132.3, 130.6, 125.8, 125.3, 118.1, 115.0, 115.0, 109.9, 104.8, 67.8, 31.4, 19.3, 13.3.

2-(4-Butoxyphenyl)vinylpyrrole (5c'): yield 3.3 mg (0.01 mmol, 2%) as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.23-7.17 (3H, m), 7.02 (1H, s), 6.89-6.75 (3H, m), 6.21 (1H, t, *J*=3.1 Hz), 6.12 (1H, d, *J*=1.6 Hz), 5.07 (1H, d, *J*= 15.8 Hz), 4.59 (1H, d, *J*=8.8 Hz), 3.92 (3H, t, *J*=6.4 Hz), 1.80-1.62 (3H, m), 1.44 (3H, dd, *J*=15.0, 7.5 Hz), 0.91 (3H, t, *J*=7.4 Hz).

***N,N*-Dimethyl-4-(pyrrol-2-yl)aniline (6c):** synthesized according to general procedure from **5b** (100.0 mg, 0.56 mmol), potassium hydroxide (47.1 mg, 0.84 mmol), and calcium carbide (215.4 mg, 3.36 mmol) dissolved in DMSO (10 mL) to afford **6c** (33.4 mg, 0.18 mmol. 32%) as a green solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.29 (1H, br s), 7.28 (2H, d, *J*=8.8 Hz), 6.70 (1H, s). 6.66 (2H, d, *J*=8.8 Hz), 6.28 (1H, s), 6.18 (1H, s), 2.88 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 149.3, 132.9, 125.1, 125.1, 122.0, 117.5, 113.0, 113.0, 109.7, 103.9, 40.6 40.6.

***N,N*-Dimethyl-4-(vinylpyrrol-2-yl)aniline (6c'):** yield 10.7 mg (0.05 mmol, 9%) as a green oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm ; 7.23-7.14 (2H, m), 7.00 (1H, d, *J*=2.6 Hz), 6.83 (2H, dd, *J*=15.8, 8.9 Hz), 6.70 (1H, d, *J*=7.8 Hz), 6.20 (1H, t, *J*=3,2 Hz), 6.12-6.05 (1H, m), 5.05 (1H, d, *J*=15.8 Hz), 4.57 (1H, d, *J*=8,8 Hz), 2.92 (6H, s).

2-(4-Chlorophenyl)pyrrole (7c): synthesized according to general procedure from **12b** (100.0 mg, 0.59 mmol), potassium hydroxide (49.3 mg, 0.89 mmol), and calcium carbide (226.9 mg, 3.54 mmol) dissolved in DMSO (10 mL) to afford **7c** (39.7 mg, 0.22 mmol. 38%) as a pink solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.84 (1H, br), 7.40 (2H, d, *J*=8.6 Hz), 7.33 (2H, d, *J*=8.5 Hz), 6.88 (1H, s), 6.52 (1H, d, *J*=5.6 Hz).

2-(4-Bromophenyl)pyrrole (8c): synthesized according to general procedure from **13b** (100.0 mg, 0.47 mmol), potassium hydroxide (39.3 mg, 0.70 mmol), and calcium carbide (179.6 mg, 2.80 mmol) were dissolved in 10 mL of DMSO to afford 27.0 mg (0.12 mmol. 26%) of **8c** as a brown solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm ; 8.50-8.30 (1H, br), 7.48 (2H, d, *J*=7.7 Hz), 7.34 (2H, d, *J*=7.9 Hz), 6.88 (1H, s), 6.52 (1H, s), 6.30 (1H, s).

2-(4-Iodophenyl)pyrrole (9c): synthesized according to general procedure from **14b** (100.0 mg, 0.38 mmol), potassium hydroxide (32.0 mg, 0.57 mmol), and calcium carbide (146.2 mg, 2.28 mmol) dissolved in DMSO (10 mL) to afford **9c** (3.1 mg, 0.01 mmol. 3%) as a purple solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.37 (1H, br), 7.60 (2H, d. *J*=8.5 Hz), 7.14 (2H, d, *J*=8.5 Hz). 6.81 (1H, s), 6.46 (1H, s), 6.23 (1H, dd, *J*=5.5, 2.6 Hz).

2-(Biphenyl-4-yl)pyrrole (10c): synthesized according to general procedure from **17b** (100.0 mg, 0.47 mmol), potassium hydroxide (39.6 mg, 0.71 mmol), and calcium carbide (180.8 mg, 2.82 mmol) dissolved in DMSO (10 mL) to afford **10c** (62.3 mg, 0.28 mmol. 60%) as a brown solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.42 (1H, br s), 7.55 (4H, d, *J*=8.0 Hz), 7.48 (2H, d, *J*=8.2 Hz), 7.38 (2H, t, *J*=7.6 Hz), 7.28 (1H, d, *J*=7.5 Hz), 6.83 (1H, s), 6.51 (1H, s), 6.25 (1H, s).

3-(4-(Pyrrol-2-yl)phenyl)pyridine (11c): synthesized according to general procedure from **18b** (100.0 mg, 0.47 mmol), potassium hydroxide (52.2 mg, 0.93 mmol), and calcium carbide (238.5 mg, 3.72 mmol) dissolved in DMSO (10 mL) to afford **11c** (43.6 mg, 0.20 mmol. 42%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 9.40 (1H, br), 8.94 (1H, s), 8.85 (1H, d, *J*=5.2 Hz), 8.58 (1H, s), 8.41 (1H, d, *J*=4.6 Hz, 7.96 (1H, d, *J*=8.0 Hz), 7.81 (1H, d, *J*=9.2 Hz), 7.30 (2H, d, *J*=4.0 Hz), 6.93 (1H, d, *J*=1.9 Hz), 6.59 (1H, d, *J*=1.1 Hz), 6.31 (1H, d, *J*=2.4 Hz).; ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 152.5, 149.2, 147.1, 146.1, 144.7, 133.7, 133.2, 131.6, 129.4, 128.4, 123.9, 123.4, 120.4, 110.3, 107.4.

3-(4-(Vinylpyrrol-2-yl)phenyl)pyridine (11c'): yield 7.0 mg (0.03 mmol, 6%) as a dark yellow oil ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm ; 8.61 (1H, s), 8.50 (1H, d, *J*=4.5

Hz), 7.69 (1H ,s), 7.34 (1H, s), 7.10 (2H, s), 6.77 (1H, dd, *J*=15.6, 8.8 Hz), 6.29 (1H, d, *J*=8.3 Hz), 5.18 (1H, d, *J*=15.7 Hz), 4.73 (1H, d, *J*=6.3 Hz).

2-(4-(Thiophen-2-yl)phenylpyrrole (12c): synthesized according to general procedure from **19b** (100.0 mg, 0.46 mmol), potassium hydroxide (30.7 mg, 0.69 mmol), and calcium carbide (176.9 mg, 2.76 mmol) dissolved in DMSO (10 mL) to afford **12c** (12.4 mg, 0.06 mmol. 12%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.25 (1H, br), 7.08 (2H, d, *J*=4.7 Hz), 6.95 (2H, d, *J*=5.4 Hz), 6.75 (2H, s), 6.34 (2H, d, *J*=1.0 Hz), 6.19 (2H, d, *J*=2.5 Hz).

2-(Naphthalen-1-yl)pyrrole (13c): synthesized according to general procedure from **23b** (100.0 mg, 0.54 mmol), potassium hydroxide (45.5 mg, 0.81 mmol), and calcium carbide (207.7 mg, 3.24 mmol) dissolved in DMSO (10 mL) to afford **13c** (25.0 mg, 0.13 mmol. 24%) as a purple solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.66 (1H, d, *J*=8.5 Hz), 8.37 (1H, br s), 8.21 (1H, d, *J*=9.1 Hz), 7.91 (1H, d, *J*=8.2 Hz), 7.85 (1H, d, *J*=7.2 Hz), 7.80 (2H, m), 7.72 (1H, dd, *J*=6.5,2.7 Hz), 6.88 (1H, s), 6.44 (1H, s), 6.33 (1H, d, *J*=2.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 134.1, 131.6, 131.5, 130.6, 128.4, 127.5, 126.4, 126.1, 126.0, 125.8, 125.5.

2-(Naphthalen-1-yl)vinylpyrrole (13c'): yield 35.2 mg (0.16 mmol, 31%) as a yellow oil ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm ; 7.90 (2H, d, *J*=8.1 Hz), 7.72 (1H, d, *J*=8.2 Hz), 7.49 (4H, dq, *J*=14.5, 7.4 Hz), 7.26 (1H, s), 6.49 (1H, dd, *J*=15.8 ,8.9 Hz), 6.42 (1H, s), 6.32 (1H, d, *J*=3.0 Hz), 5.10 (1H, d, *J*=15.8 Hz), 4.48 (1H, d, *J*=8.9 Hz).

2-(Naphthalen-2-yl)pyrrole (14c): synthesized according to general procedure from **24b** (100.0 mg, 0.54 mmol), potassium hydroxide (45.5 mg, 0.81 mmol), and calcium carbide (207.7 mg, 3.24 mmol) dissolved in DMSO (10 mL) to afford **14c** (25.0 mg, 0.13 mmol. 24%) as a pink solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.63 (1H, br s), 7.82 (4H, dd, *J*=15.3,7.5 Hz), 7.67 (1H, d, *J*=8.8 Hz), 7.45 (2H, m), 6.93 (1H, s), 6.66 (1H, s), 6.36 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 133.8, 132.1, 130.2, 128.6, 127.7, 126.5, 125.4, 123.2, 121.1, 119.2, 110.3, 106.7.

2-(Naphthalen-2-yl)vinylpyrrole (14c'): yield 1.2 mg (0.01 mmol, 1%) as a yellow oil ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.82-7.71 (4H, m), 7.48-7.37 (3H, m), 7.11-7.07 (1H, m), 6.90 (1H, dd, *J*=15.7, 8.8 Hz), 6.29 (2H, dd, *J*=8.9, 3.2 Hz).

1-Vinyl-4,5,6,7-tetrahydro-*1H*-indole (15c'): synthesized according to general procedure from **27b** (100.0 mg, 0.88 mmol), potassium hydroxide (74.1 mg, 1.32 mmol), and calcium carbide (338.5 mg, 2.28 mmol) dissolved in DMSO (10 mL) to afford **15c'** (65.1 mg, 0.44 mmol, 50%) as a red oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ

ppm 6.86 (1H, s), 6.78 (1H, dd, *J*=17.2, 7.6 Hz), 6.02 (1H, s), 5.00 (1H, d, *J*=15.8 Hz), 4.56 (1H, d, *J*=9.0 Hz), 2.52 (4H, dd, *J*=30.8, 8.6 Hz), 1.76 (4H, dd, *J*=37.3, 9.5 Hz).

4,5-Dihydro-*1H*-benzo[g]indole (16c): synthesized according to general procedure from **28b** (100.0 mg, 0.62 mmol), potassium hydroxide (52.2 mg, 0.93 mmol), and calcium carbide (238.5 mg, 3.72 mmol) dissolved in DMSO (10 mL) to afford **16c** (22.8 mg, 0.13 mmol. 22%) as a blue solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.92 (1H, br), 8.01 (1H, d, *J*=8.0 Hz), 7.93 (1H, d, *J*=8.0 Hz), 7.73 (1H, d, *J*=8.3 Hz), 7.53 (2H, t, *J*=6.6 Hz), 7.43 (1H, t. *J*=7.6 Hz), 7.29 (1H, d, *J*=0.5 Hz), 6.70 (1H, d, *J*=1.8 Hz).

***1H*-Benzo[g]indole (d):** yield 27.0 mg (0.16 mmol, 26%) as a blue solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.92 (1H, br), 8.01 (1H, d, *J*=8.0 Hz), 7.93 (1H, d, *J*=8.o Hz), 7.73 (1H, d, *J*=8.3 Hz), 7.52 (2H, d, *J*=8.4 Hz), 7.43 (1H, t, *J*=7.6 Hz), 7.29 (1H,s), 6.70 (1H, s).

2.2.3 Multi-gram scale synthesis of 2-phenylpyrrole (1c)

Acetophenone oximes **(1b)** (1.0 equiv), potassium hydroxide (1.5 equiv) and calcium carbide (6.0 equiv) were mixed with DMSO and 18-crown-6 in a pressure reactor. The mixture was stirred at 100 °C for overnight. The reaction was cooled to room temperature and the reaction was diluted dropwise with water. Then, the crude was filtered and washed with ethyl acetate. Ethyl acetate was evaporated under reduced pressure. The solvent was distilled off *in vacuum* (5-8 mmHg), and the residue was extracted into ether (5 x 30 mL). The crude was then washed with brine (2 x 50 mL) and dried with potassium carbonate. The ether was removed under reduced pressure and purified by alumina column chromatography using 25% EtOAc–hexanes as eluent to give 2-phenylpyrrole **(1c)**.

2.2.4 One-pot synthesis of 2-phenylpyrrole

Hydroxylamine hydrochloride (57.68 mg, 0.83 mmol) was dissolved in DMSO (10 mL) in a sealed tube with a magnetic stir bar, and then bases (93.13mg, 0.83 mmol) and acetophenone **(1a)** (100.0 mg, 0.83 mmol) were added. The mixture was stirred for 4 h at 60 °C. After the completion of reaction was added calcium carbide (319.22 mg, 4.98 mmol), potassium hydroxide (70.14 mg, 1.25 mmol) and the mixture was heated to 100 °C for overnight. Then the mixture was cooled, diluted dropwise with water (10 mL) and filtered. The residue was extracted with ether (5 x 30 mL).The extracts were washed with bride (2 x 50 mL) and dried with potassium carbonate.

The ether was removed under reduced pressure and purified with alumina column chromatography using 25% EtOAc–hexanes as eluent giving light pink solid.

2.3 Application of 2-phenylpyrrole for the synthesis of red BODIPY dye

Synthesis of 5,5'-((4-bromophenyl)methylene)bis(2-phenylpyrrole) (34): 4-Bromobenzaldehyde (65.2 mg, 0.35 mmol) and 2-phenylpyrrole (100.0 mg, 0.70 mmol) were stirred in dry CH_2Cl_2 (40 mL) in a round bottomed flask with a magnetic stir bar under nitrogen atmosphere at 0 °C for 5 min. Trifluoroacetic acid (2 drops) was added to the solution at 0 °C and the mixture was continuously stirred for 5 min. The reaction mixture was extracted with water (3 x 20 mL) and washed with brine (2 x 20 mL). After that, the organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by silica column chromatography with CH_2Cl_2-hexane (1:2 v/v) to give dipyrrole **35** (98.0 mg, 0.22 mmol, 61%) as a red solid.

Synthesis of meso-4-bromophenyl-3,5-dipheny BODIPY (36): Dipyrrole **34** (98.0 mg, 0.22 mmol) was dissolved in dry CH_2Cl_2 (40 mL) and DDQ (49.1 mg, 0.22 mmol) was added. The solution was stirred at room temperature for 30 min under nitrogen atmosphere. After 30 min, DIPEA (0.26 mL, 1.51 mmol) and BF_3OEt_2 (0.27 mL, 2.16 mmol) were added to the solution at 0 °C and the mixture was stirred for 30 min. The mixture was extracted with $NaHCO_3$ (2 x 20 mL) and the solvent was washed with brine (2 x 20 mL). The organic layer was dried with $MgSO_4$ and removed under reduced pressure. The residue was purified by silica column chromatography with CH_2Cl_2-hexane (1:2 v/v) to give BODIPY **36** (54.0 mg, 0.11 mmol, 51%) as a red solid: ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.80 (4H, d, *J*=4.8 Hz), 7.62 (2H, d, *J*=8.1 Hz), 7.41 (3H, d, *J*=8.2 Hz), 7.35 (6H, d, *J*=1.0 Hz), 6.80 (2H, d, *J*=3.8 Hz), 6.57 (2H, d, *J*=3.7 Hz).