Supporting Information

Carbazole based Electron Donor Acceptor (EDA) Catalysis for the Synthesis

of biaryls and aryl-heteroaryl compounds.

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Materials and Methods

General. All reactions dealing with air and moisture-sensitive compounds were carried out in dry reaction vessels under a nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. ¹H nuclear magnetic resonance (NMR) spectra were recorded on Bruker (300, 400, 500 MHz) NMR spectrometers. ¹H NMR spectra are reported in parts per million (ppm) downfield from an internal standard tetramethylsilane. UV-Vis. spectra were recorded on Evolution 201 thermo scientific spectrometer using cuvettes with 1 cm path length. Melting points were determined using a capillary melting point apparatus and are uncorrected.

Materials. Unless otherwise noted, materials were purchased from TCI, Merck, SRL, and other commercial suppliers and were used as received. Anhydrous DMSO (≥99%) was purchased from Merck without further purification.

General procedures.

Synthesis of 2,3,4,9-tetrahydro-1H-carbazole (Cat.18):



Phenyl hydrazine hydrochloride (1.71 g, 1.2 mmol) and cyclohexanone (1 g, 1 mmol) were dissolved in 10 ml of glacial acetic acid. The reaction mixture was refluxed for 2 hours. After the completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature and poured into water. The crude product was extracted with ethyl acetate dried over Na₂SO₄ and evaporated under reduced pressure to provide a crude brown solid. The solid thus obtained was further purified by column chromatography.

Synthesis of 4-bromobenzenediazonium tetrafluoroborate (17a):

Sodium nitrite (0.4 g, 5.82 mmol) dissolved in 1 ml of water was slowly added to the cold mixture of aniline (1 g, 5.82 mmol) and 45% of HBF₄ (1.53 g, 17.45 mmol) in 3 ml of water. The mixture was stirred for 1 h and the precipitate was collected by filtration and re-dissolved in minimum amount of acetone. Then the diazonium salt was re-crystallized using methyl tert-butyl ether (MTBE). The same procedure was followed by preparation of other diazonium salts.⁴

Arylation of furan with 4-bromobenzenediazonium tetrafluoroborate (12a):

Heteroarene **10a** (0.25 g, 0.37 mmol) and catalyst **18** (6 mg, 0.037 mmol) were dissolved in 0.5 ml DMSO in ice water. Then the 4-bromobenzenediazonium tetrafluoroborate **17a** (0.1 g, 0.37 mmol) dissolved in 0.5 ml of DMSO was added to cold mixture of heteroarene and catalyst

under N₂ atmosphere for about 20 minutes. After completion of the addition the reaction stirred at dark condition for 14 h. Then the reaction mixture was quenched with dichloromethane and water. Organic layer was separated and dried using sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography using hexane to afford the compound 12a. The same procedure was using other biheteroaryl (thiophene and pyrrole) compounds.⁵

Arylation of arenes with benzene diazonium tetrafluoroborate (12o):

Catalyst **18** (8.5 mg, 0.052 mmol) dissolved in 0.1 ml of DMSO drop wise added to the solution of benzene diazonium salt (0.1 g, 0.52 mmol) and benzene (1 ml) under N_2 atmosphere stirred at room temperature for 14 h. Then the reaction mixture was quenched with dichloromethane and water. Organic layer was separated and dried using sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography using hexane to afford the biaryl compound.²

¹H NMR DATA for catalyst, hetero and biaryl compounds:



2,3,4,9-tetrahydro-1H-carbazole: White solid, Yield = 86% (1.53g), R_f = 0.5 (5% of Ethylacetate in Hexanes), m.p. = 96 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.62 (br s, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 6.6

Hz, 1H), 7.13-7.03 (m, 2H), 2.70 (t, J = 6.0 Hz, 4H), 1.88 (d, J = 4.2 Hz, 4H) ppm. The spectra was identical to the existing literature data.¹



2-(4-bromophenyl)furan: White solid, Yield = 83%, $R_f = 0.94$ (Hexanes), m.p. = 62 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.55-7.51 (m, 4H), 7.48-7.46 (m, 1H), 6.65 (d, J = 3.3 Hz, 1H), 6.47 (dd, J = 3.3 Hz, J = 1.8 Hz, 1H)

ppm. The spectra was identical to the existing literature data.⁴



2-phenylfuran: Colourless liquid, Yield = 61%, $R_f = 0.84$ (Hexanes); ¹**H NMR** (300 MHz, CDCl₃) δ 7.67 (d, J = 7.2 Hz, 2H), 7.46 (d, J = 1.2 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 7.27-7.23 (m, 1H), 6.65 (d, J = 3.3 Hz, 1H),

6.46 (dd, J = 3.3 Hz, 1.8 Hz, 1H) ppm. The spectra was identical to the existing literature data.⁷



2-(4-fluorophenyl)furan: Colourless liquid, Yield = 65%, $R_f = 0.92$ (Hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.66 (m, 2H), 7.45 (d, J = 1.5 Hz, 1H), 7.07 (t, J = 8.9 Hz, 2H), 6.58 (d, J = 3.3 Hz, 1H), 6.47 (dd, J = 3.3

Hz, 1.8 Hz, 1H) ppm. The spectra was identical to the existing literature data.



2-(4-chlorophenyl)furan: White solid, Yield = 81%, R_f = 0.96 (Hexanes),
m.p. = 58 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.59 (d, J = 8.4 Hz, 2H), 7.45
(d, J = 1.2 Hz, 1H), 7.34 (d, J = 8.7 Hz, 2H), 6.64 (d, J = 3.3 Hz, 1H), 6.46

(dd, J = 3.3 Hz, 1.8 Hz, 1H) ppm. The spectra was identical to the existing literature data.⁷



2-(4-nitrophenyl)furan: Yellow solid, Yield = 72%, $R_f = 0.44$ (5% of Ethyl acetate in Hexanes), m.p. = 102 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.25 (d, J = 9.0 Hz, 2H), 7.79 (d, J = 9.0 Hz, 2H), 7.58 (d, J = 1.5 Hz,

1H), 6.89 (d, J = 3.3 Hz, 1H), 6.56 (dd, J = 3.3 Hz, 1.8 Hz, 1H) ppm. The spectra was identical to the existing literature data.⁷



2-(4-(trifluoromethyl)phenyl)furan: White solid, Yield = 74%, $R_f = 0.95$ (Hexanes), m.p. = 50 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.76 (d, J = 7.1 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.52-7.51 (m, 1H), 6.77 (d, J = 3.3

Hz, 1H), 6.50 (dd, *J* = 3.3 Hz, 1.8 Hz, 1H) ppm.



4-(furan-2-yl)benzonitrile: Pale orange solid, Yield = 77%, $R_f = 0.46$ (10 % of Ethyl acetate in Hexanes), m.p. = 52 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.76-7.73 (m, 2H), 7.67-7.64 (m, 2H), 7.54 (d, *J* = 1.5 Hz, 1H),

6.82 (d, J = 3.3 Hz, 1H), 6.53 (dd, J = 3.3 Hz, 1.8 Hz, 1H) ppm The spectra was identical to the existing literature data.⁷



2-(4-methoxyphenyl)furan: White solid, Yield = 42%, $R_f = 0.88$ (Hexanes), m.p. = 68 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, J = 9.0

Hz, 2H), 7.43-7.42 (m, 1H), 6.92 (d, J = 9.0 Hz, 2H), 6.51 (d, J = 3.3 Hz, 1H), 6.43 (dd, J = 3.3 Hz, 1.8 Hz, 1H) 3.83 (s, 3H) ppm The spectra was identical to the existing literature data.⁷



2-(p-tolyl)furan: White semi solid, Yield = 35%, $R_f = 0.76$ (Hexanes); ¹H **NMR** (300 MHz, CDCl₃) δ 7.49 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 1.8 Hz, 1H), 7.11 (d, J = 8.1 Hz, 2H), 6.52 (d, J = 3.3 Hz, 1H), 6.39-6.37 (dd, J =

3.3 Hz, 2.1 Hz, 1H), 2.29 (s, 3H) ppm. The spectra was identical to the existing literature data.⁴



2-(2-bromophenyl)furan: Pale yellow liquid, Yield = 41%, $R_f = 0.94$ (Hexanes); ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 4.8 Hz, 1H), 7.67 (d, *J* = 4.8 Hz, 1H), 7.55 (d, *J* = 0.9, 1H), 7.38 (t, *J* = 4.5 Hz, 1H), 7.19 (d, *J* =

2.1 Hz, 1H), 7.15 (t, J = 4.5 Hz, 1H), 6.55 (dd, J = 3.3 Hz, 1.8 Hz, 1H) ppm. The spectra was identical to the existing literature data.⁴



2-(2-nitrophenyl)furan: Yellow semi solid, Yield = 64%, $R_f = 0.47$ (10%) of Ethyl acetate in Hexanes) ; ¹H NMR (300 MHz, CDCl₃) δ 7.71-7.66 (m, 2H), 7.56 (t, J = 4.8 Hz, 1H), 7.51-7.50 (m, 1H), 7.40 (t, J = 4.5 Hz, 1H), 6.67 (d, J = 2.1 Hz, 1H), 6.50-6.49 (m, 1H) ppm. The spectra was identical to the existing

literature data.⁴



2-(furan-2-yl)benzonitrile: Pale orange solid, Yield = 51%, $R_f = 0.47$ (10% of Ethyl acetate in Hexanes), m.p. = 50 °C; ¹H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 1H), 7.70 (d, J = 7.84 Hz, 1H), 7.61 (ddd, J = 7.2 Hz, J = 1.2 Hz, J = 1.5 Hz, 1H), 7.56 (dd, J = 7.8 Hz, 1.2 Hz, 1H), 7.35-7.31 (m, 2H), 6.56 (dd, J = 6.3 Hz, J = 1.8 Hz, 1H) ppm. The spectra was identical to the existing literature data.⁸

2-(3-chlorophenyl)furan: Yellow liquid, Yield = 61%, $R_f = 0.72$ (Hexanes); ¹H NMR (300 MHz, CDCl₃) 7.66 (t, J = 1.8 Hz, 1H), 7.54 (d, J = 8.2 Hz, 1H), 7.48 (d, J = 1.5 Hz, 1H), 7.27 (d, J = 6.6 Hz, 1H), 7.24-7.20 (m, 1H), 6.67 (d, J = 3.6 Hz, 1H), 6.48 (dd, J = 3.3 Hz, 1.8 Hz 1H) ppm. The spectra was identical to the existing literature data.⁴



1,1'-biphenyl: White solid, Yield = 45%, $R_f = 0.82$ (Hexanes), m.p. = 56 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 4.8 Hz, 4H), 7.47 (t, J = 4.5 Hz, 4H), 7.37 (t, J = 4.5 Hz, 2H) ppm. The spectra was identical to

the existing literature data.¹⁰



4-chloro-1,1'-biphenyl: Pale yellow solid, Yield = 55%, $R_f = 0.84$ (Hexanes), m.p. = 58 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.76 (m, 4H), 7.71-7.65 (m, 4H), 7.61 (dt, J = 4.5 Hz, 1H) ppm. The spectra was

identical to the existing literature data.⁶



4-fluoro-1,1'-biphenyl: Orange solid, Yield = 60%, $R_f = 0.83$ (Hexanes), m.p. = 36 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.54 (m, 4H), 7.44 (t, J = 4.2 Hz, 24H), 7.35 (tt, J = 4.5 Hz, 1H), 7.14 (t, J = 5.1 Hz, 2H) ppm.

The spectra was identical to the existing literature data.⁶



4-nitro-1,1'-biphenyl: Orange solid, Yield = 58%, $R_f = 0.46$ (5% fo Ethyl acetate in Hexanes), m.p. = 58 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, J = 6.6 Hz, 2H), 7.75 (d, J = 5.4 Hz, 2H), 7.64 (d, J = 4.5 Hz,

2H), 7.51 (t, J = 4.5 Hz, 2H), 7.46 (t, J = 4.5 Hz, 1H) ppm. The spectra was identical to the existing literature data.⁵



4-bromo-1,1'-biphenyl: Orange solid, Yield = 52%, R_f = 0.86 (Hexanes), m.p. = 58 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.57 (m, 4H), 7.48-7.47 (m, 4H), 7.28-7.26 (m, 1H) ppm. The spectra was identical to the

existing literature data.⁵



4-methoxy-1,1'-biphenyl: solid, Yield = 5%, $R_f = 0.72$ (Hexanes), m.p. =42 °C; ¹H NMR (300 MHz, CDCl₃) δ) δ 7.62-7.59 (m, 4H), 7.45-7.47 (m, 4H), 7.28-7.26 (m, 1H), 3.86 (s, 3H) ppm. The spectra

was identical to the existing literature data. ¹¹



2-(4-chlorophenyl)thiophene: Sandle solid, Yield = 69%, $R_f = 0.94$ (Hexanes), m.p. = 62 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.29-7.28 (m, 2H), 7.07 (t, J = 4.5 Hz,

1H) ppm. The spectra was identical to the existing literature data.⁴



2-(3-chlorophenyl)thiophene: Orange liquid, Yield = 76%, $R_f = 0.84$ (Hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.59 (t, J = 1.8 Hz, 1H), 7.48 (dt, J = 7.2 Hz, 1H), 7.33-7.30 (m, 3H), 7.25 (s, 1H), 7.08 (t, J = 5.1, 1H) ppm.

The spectra was identical to the existing literature data.⁶



2-phenylthiophene 12w: Orange semisolid, Yield = 53%, $R_f = 0.82$ (Hexanes); ¹**H NMR** (500 MHz, CDCl₃) δ 7.64 (d, J = 4.5 Hz, 2H), 7.41 (t, J = 4.5 Hz, 2H), 7.35-7.29 (m, 3H), 7.09 (t, J = 2.7 Hz, 1H) ppm. The

spectra was identical to the existing literature data.⁹



2-(4-bromophenyl)thiophene: Pale pink solid, Yield = 73%, $R_f = 0.86$ (Hexanes), m.p. = 58 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.48-7.47 (m, 4H), 7.29 (d, J = 4.2 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H) ppm. The spectra

was identical to the existing literature data.⁴



2-(4-nitrophenyl)thiophene: Orange solid, Yield = 79%, $R_f = 0.46$ (5% Ethyl acetate in Hexanes), m.p. = 116 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.24 (d, J = 8.7 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.48 (dd, J = 3.9 Hz,

5.1 Hz, 1H), 7.44 (d, J = 5.1 Hz, 1H) ppm. The spectra was identical to the existing literature data.⁴



tert-butyl 2-(4-chlorophenyl)-1H-pyrrole-1-carboxylate: Orange liquid, Yield = 53%, $R_f = 0.48$ (5% of Ethyl actate in Hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.23 (m, 5H), 6.21 (t, J = 1.5 Hz, 2H),

1.59 (s, 9H) ppm. The spectra was identical to the existing literature data.⁶





5-phenylfuran-2-carbaldehyde: Yellow solid, Yield = 33%, $R_f = 0.36$ (10 % of Ethyl acetate in Hexanes), m.p. = 154 °C; ¹H NMR (500 MHz, CDCl₃) δ 9.73 (s, 1H), 8.31 (d, J = 5.4 Hz, 2H), 7.98 (d, J = 5.4 Hz, 2H), 7.37 (d, J = 2.4 Hz, 1H), 7.04 (d, J = 2.4 Hz, 1H) ppm.

The spectra was identical to the existing literature data.⁶



2-(4-fluorophenyl)thiophene : Orange solid, Yield = 71%, $R_f = 0.92$ (Hexanes), m.p. = 38 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.59-7.54 (m, 2H), 7.28-7.23 (m, 2H), 7.10-7.40 (m, 3H) ppm. The spectra was

identical to the existing literature data.²



2,2,6,6-tetramethyl-1-(4-nitrophenoxy)piperidine: White solid, Yield = 62%, $R_f = 0.84$ (Hexanes), m.p. = 112 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.14 (d, J = 9.3 Hz, 2H), 7.26 (bs, 2H), 1.66-1.57 (m, 5H), 1.25 (s, 3H), 0.99 (s, 3H) ppm. The spectra was identical to the

existing literature data.⁶



1-(4-bromophenoxy)-2,2,6,6-tetramethylpiperidine: White solid, Yield = 57%, $R_f = 0.94$ (Hexane), m.p. = 90 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.29 (d, J = 9 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 1.62-1.55 (m, 5H), 1.43-1.38 (m, 1H), 1.21 (s, 6H), 0.98 (s, 6H) ppm.

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¹H NMR spectrum of catalyst, hetero and biaryl compounds





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