Base Mediated Benzannulation of α-Cyano Crotonates with Ynones: Facile Synthesis of Benzonitriles and Fluorenes

Maneesh Kumar Reddy Singaman^lab, Attunuri Nagireddy^lab and Maddi Sridhar Reddy*^ab

^aDepartment of OSPC, CSIR-Indian Institute of Chemical Technology, Habsiguda, Hyderabad 500007, India. Academy of Scientific and Innovative Research, New Delhi 110001, India. ^bAnalytical Department, CSIR-IICT, Hyderabad-500007.

*E-mail: msreddy@iict.res.in, msreddy@cdri.res.in

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I. General Information and methods.

All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded with a 300, 400 or 500 MHz spectrometer for $^1$H NMR, 100 or 125 MHz for $^{13}$C NMR spectroscopy. Chemical shifts are reported relative to the residual signals of tetramethylsilane in CDCl$_3$ or deuterated solvent CDCl$_3$ for $^1$H and $^{13}$C NMR spectroscopy. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m). HRMS were recorded by using QTof mass spectrometer. Column chromatography was performed with silica gel (100–200 mesh) as the stationary phase. All reactions were monitored by using TLC.

Ynones 1 were prepared following literature procedures.$^1$ Starting materials 2a-j were prepared from literature procedures.$^3$

II. General Procedure A for the preparation of starting materials:

Starting materials 2a-j were prepared from literature procedures.$^3$

![Diagram of reaction](image)

To a mixture of acetophenone I (1 g, 8.33 mmol, 1 equiv), ethyl cyano acetate 2 (1.13 g, 10 mmol, 1.2 equiv) and ammonium acetate (770 mg, 10 mmol, 1.2 equiv) in toluene (10 mL) was added acetic acid (1.43 mL, 25 mmol, 3 equiv) under N$_2$ atmosphere. The reaction contents were refluxed for 6-10 hours. Upon completion, reaction mixture was concentrated under reduced pressure and the crude material was purified on silica gel using 1-15% EtOAc/hexane.

Methyl 2-cyano-3-(4-cyanophenyl)but-2-enoate (2c): 911 mg of 2c was obtained from 1g (6.9 mmol) of 1c following general procedure A. Yield 55%; brownish oil; R$_f$ = 0.4 (SiO$_2$, EtOAc:Hexane, 1:99); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 – 7.74 (m, 2H), 7.73 – 7.68 (m, 1H), 7.60 – 7.44 (m, 3H), 7.29 – 7.25 (m, 1H), 4.36 (q, $J$ = 7.1 Hz, 2H), 4.12 (q, $J$ = 7.1 Hz, 1H), 2.69 (s, 3H), 2.54 (s, 1H), 1.41 – 1.37 (t, 2H), 1.18 (t, $J$ = 9.0, 5.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.5, 167.9, 161.6, 144.5, 143.6, 132.6, 132.2, 128.6, 128.3, 127.8, 126.8, 126.38, 118.1, 117.9, 115.3, 114.8, 114.0, 113.0, 107.6, 106.9, 63.0, 62.5, 24.8, 22.9, 14.1, 13.8; HRMS (QToF) calcd for C$_{14}$H$_{13}$N$_2$O$_2$ [M+H]$^+$ 241.0977 found 241.0956.
Ethyl 3-[(1,1'-biphenyl)-4-yl]-2-cyanobut-2-enoate (2d): 742 mg of 2d was obtained from 1g (5.1 mmol) of Id following general procedure A. Yield 50%; colourless solid; \(R_f = 0.5\) (SiO\(_2\), EtOAc:Hexane, 2:98); \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 7.69 – 7.65\ (m, 2H), 7.61\ (ddd, \(J = 6.0, 3.7, 1.6\) Hz, 4H), 7.57 – 7.53 (m, 2H), 7.49 – 7.42 (m, 3H), 7.41 – 7.35 (m, 1H), 7.28 – 7.24 (m, 1H), 4.35 (q, \(J = 7.1\) Hz, 2H), 4.13 (q, \(J = 7.1\) Hz, 1H), 2.73 (s, 3H), 2.58 (s, 1H), 1.39 (t, \(J = 7.1\) Hz, 3H), 1.15 (t, \(J = 7.1\) Hz, 1H); \(^13C\) NMR (100 MHz, CDCl\(_3\)) \(\delta 171.8\), 169.3, 162.3, 161.4, 143.3, 142.4, 139.9, 139.8, 138.8, 137.6, 128.8, 127.9, 127.8, 127.2, 127.0, 127.0, 126.9, 126.8, 116.3, 115.6, 115.8, 105.8, 104.7, 62.0, 61.9, 26.7, 23.1, 14.0, 13.7; HRMS (QToF) calcd for C\(_{19}\)H\(_{18}\)NO\(_2\) [M+H\(^+\)] 292.1338 found 292.1328.

Methyl 2-cyano-3-(4-phenoxyphenyl)but-2-enoate (2e): 652 mg of 2e was obtained from 1g (4.7 mmol) of Ie following general procedure A. Yield 45%; brownish oil; \(R_f = 0.5\) (SiO\(_2\), EtOAc:Hexane, 8:92); \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 7.48 – 7.43\ (m, 2H), 7.41 – 7.35\ (m, 3H), 7.21 – 7.13\ (m, 2H), 7.09 – 6.95 (m, 6H), 4.33 (q, \(J = 7.1\) Hz, 2H), 4.14 (d, \(J = 7.1\) Hz, 1H), 2.68 (s, 3H), 2.54 (s, 1H), 1.38 (t, \(J = 7.1\) Hz, 3H), 1.19 (t, \(J = 7.1\) Hz, 1H); \(^13C\) NMR (100 MHz, CDCl\(_3\)) \(\delta 171.6\), 168.9, 162.5, 161.7, 159.9, 159.2, 155.6, 134.2, 132.8, 130.0, 129.4, 128.5, 124.4, 120.1, 119.9, 117.7, 117.6, 116.6, 115.9, 105.4, 104.2, 62.0, 61.9, 26.7, 23.2, 14.1, 13.8; HRMS (QToF) calcd for C\(_{19}\)H\(_{18}\)NO\(_3\) [M+H\(^+\)] 308.1287 found 308.1278.

(E)-(2-(3-cyano-4-ethoxy-4-oxobut-2-en-2-yl)cyclopenta-2,4-dien-1-yl)(cyclopenta-2,4-dien-1-yl)iron (2j): 850 mg was obtained from 1g (4.4 mmol) of 1j following general procedure A. Yield 60%; pink solid; \(R_f = 0.5\) (SiO\(_2\), EtOAc:Hexane, 2:98); \(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta 5.04\ (dd, \(J = 4.1, 2.1\) Hz, 2H), 4.63 (dd, \(J = 4.8, 2.8\) Hz, 2H), 4.32 – 4.25 (q, 2H), 4.24(s, 4H), 2.68(s, 6H), 1.39 – 1.33 (t, \(J = 3.3\) Hz, 3H); \(^13C\) NMR (100 MHz, CDCl\(_3\)) \(\delta 172.3\), 163.3, 118.5, 98.0, 81.3, 72.6, 70.7, 70.5, 61.5, 21.8, 14.2; HRMS (QToF) calcd for C\(_{17}\)H\(_{18}\)NO\(_2\)Fe [M+H\(^+\)] 324.0687 found 324.0677.

Ethyl (E)-2-cyano-2-(2,3-dihydro-1H-inden-1-ylidene)acetate(4) was prepared following literature procedures.\(^3\)

To a mixture of indanone 1 (1g, 7.6 mmol, 1 equiv), ethyl cyano acetate 2 (0.97 ml, 9.1 mmol, 1.2 equiv) and ammonium acetate (702 mg, 9.1 mmol, 1.2 equiv) in toluene (10 mL) was added acetic acid (1.3 mL, 23 mmol, 3 equiv) under N\(_2\) atmosphere. The reaction contents were refluxed for 6-10hours. Upon completion, reaction mixture was concentrated under reduced pressure and the crude material was purified on silica gel using 3% EtOAc/hexaneto get 4 as sticky white solid (850 mg).
III. General procedure and characteristic data of final compounds

(A) General procedure B for the synthesis of final compounds (3) taking Synthesis of 3aa as an Example.

To a 15 mL Schlenk tube was added ynone 1a (103 mg, 0.5 mmol, 1 equiv), α-cyano crotonates 2a (129 mg, 0.6 mmol, 2 equiv) and KOtBu (112 mg, 1 mmol, 2 equiv) in 1-butanol (3 mL) and the reaction mixture was stirred at room temperature under open air until the complete conversion of starting material (60-90 min). The reaction mixture was concentrated under reduced pressure, washed with hexane (2 times) and the remaining solid was dissolved in 20% EtOAc/Hexane and filtered through a small silica bed. Filtrate was concentrated to get the desired solids in purified form. In case of 3ea, 3i-3la, 3sa, 3ua and 3aj, the reaction contents were concentrated under reduced pressure and the crude material was purified on silica gel using EtOAc/hexane to get the desired product.

5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3aa): 149 mg was obtained from 1a (103 mg, 0.5 mmol) and 2a following general procedure B. Yield 90%; greyish white solid; mp 163−166 °C; Rf = 0.53 (SiO2, EtOAc:Hexane, 1:99); 1H NMR (400 MHz, CDCl3) δ 7.70 – 7.68 (m, 3H), 7.66 (q, J = 2.3 Hz, 3H), 7.64 (q, J = 2.0 Hz, 2H), 7.54 (t, J = 1.8 Hz, 1H), 7.53 – 7.47 (m, 7H), 7.47 – 7.43 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 147.3, 145.1, 139.0, 138.7, 129.1, 129.0, 128.7, 128.6, 127.5, 127.3, 118.0, 109.0; IR (KBr) ν 3049, 2431, 2223, 1962, 1595, 1498, 891, 768, 702 cm⁻¹; HRMS (QToF) calcd for C25H18N [M+H]+ 332.1439 found 332.1440.

5'-(p-tolyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (3ba): 152 mg was obtained from 1b (110 mg, 0.5 mmol) and 2a following general procedure B. Yield 88%; pale yellow solid; mp 132−135 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 1:99); 1H NMR (300 MHz, CDCl3) δ 7.69 (d, J = 5.6 Hz, 4H), 7.66 (s, 2H), 7.61 (s, 1H), 7.59 – 7.55 (m, 2H), 7.54 (s, 2H), 7.50 (d, J = 8.5 Hz, 3H), 7.31 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H);
$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 147.2, 144.9, 138.8, 138.7, 136.0, 129.8, 128.9, 128.6, 128.5, 127.2, 127.1, 118.1, 108.6, 21.1; IR (KBr) ν 3033, 2917, 2309, 2222, 2130, 1596, 769, 703 cm$^{-1}$; HRMS (QToF) caleld for C$_{26}$H$_{20}$N [M+H]$^+$ 346.1596 found 346.1597.

5'-phenyl-[1,1':3',1'':4'',1''''-terphenyl]-6'-carbonitrile (3ca): 165 mg was obtained from 1c (141 mg, 0.5 mmol) and 2a following general procedure B. Yield 81%; colourless solid; mp 193–195 °C; $R_f$ = 0.45 (SiO$_2$, EtOAc:Hexane, 1:99); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 – 7.74 (m, 2H), 7.73 (d, $J$ = 8.5 Hz, 2H), 7.68 (d, $J$ = 1.5 Hz, 2H), 7.66 (s, 2H), 7.65 (s, 3H), 7.57 – 7.55 (m, 1H), 7.54 (s, 1H), 7.52 (s, 2H), 7.51 – 7.49 (m, 1H), 7.49 (d, $J$ = 3.0 Hz, 3H), 7.47 (d, $J$ = 3.4 Hz, 1H), 7.39 (t, $J$ = 7.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.4, 144.5, 141.6, 140.1, 138.6, 137.7, 129.0, 128.8, 128.7, 128.6, 127.7, 127.3, 127.0, 118.0, 109.0; IR (KBr) ν 2928, 2308, 2223, 1597, 1505, 770, 703 cm$^{-1}$; HRMS (QToF) caleld for C$_{31}$H$_{22}$N [M+H]$^+$ 408.1752 found 408.1760.

5'-(4-(tert-butyl)phenyl)-[1,1':3',1'':4'',1''''-terphenyl]-2'-carbonitrile (3da): 159 mg was obtained from 1d (131 mg, 0.5 mmol) and 2a following general procedure B. Yield 82%; brownish solid; mp 135–138 °C; $R_f$ = 0.55 (SiO$_2$, EtOAc:Hexane, 1:99); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.71 (s, 2H), 7.68 (d, $J$ = 1.4 Hz, 2H), 7.65 (d, $J$ = 1.1 Hz, 3H), 7.62 (s, 1H), 7.56 (d, $J$ = 2.0 Hz, 1H), 7.54 (s, 3H), 7.51 (s, 3H), 7.49 – 7.45 (m, 1H), 1.39 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 152.0, 147.2, 144.9, 138.7, 136.0, 129.0, 128.6, 128.6, 127.2, 127.0, 126.0, 118.1, 108.6, 34.6, 31.2; IR (KBr) ν 2966, 2307, 2223, 1595, 1510, 1381, 771, 703 cm$^{-1}$; HRMS (QToF) caleld for C$_{29}$H$_{20}$N [M+H]$^+$ 388.2065 found 388.2072.

5'-phenethyl-[1,1':3',1'':4'',1''''-terphenyl]-2'-carbonitrile (3ea): 129 mg was obtained from 1e (155 mg, 0.5 mmol) and 2a following general procedure B. Yield 72%; colourless gum; $R_f$ = 0.6 (SiO$_2$, EtOAc:Hexane, 1:99); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 – 7.53 (m, 4H), 7.51 – 7.50 (m, 1H), 7.49 (q, $J$ = 1.5 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.32 (dd, $J$ = 7.5, 4.4, 1.2 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.24 (s, 2H), 7.18 (dd, $J$ = 5.2, 3.1 Hz, 2H), 3.09 – 3.03 (m, 2H), 3.02 – 2.97 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.8, 146.5, 140.6, 138.7, 129.1, 128.9, 128.5, 126.2, 118.1, 107.9, 37.9, 37.3; IR (neat) ν 2926, 2300, 2221, 1597, 1502, 1291, 770, 704 cm$^{-1}$; HRMS (QToF) caleld for C$_{27}$H$_{22}$N [M+H]$^+$ 360.1752 found 360.1745.

5'-(3-fluorophenyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (3fa): 136 mg was obtained from 1f (224mg, 0.5 mmol) and 2a following general procedure B. Yield 78%; brownish solid; mp 195–198 °C; $R_f$ = 0.55 (SiO$_2$, EtOAc:Hexane, 1:99); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.66 (d, $J$ = 3.4 Hz, 4H), 7.63 (s, 2H), 7.56 (d, $J$ = 2.3 Hz, 1H), 7.53 (s, 2H), 7.49 (d, $J$ = 7.9 Hz, 3H), 7.46 (s, 2H), 7.37 (d, $J$ = 9.9 Hz, 1H), 7.14 (ddd, $J$ = 11.4, 7.1, 4.5 Hz,
1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 147.5, 143.8, 141.3, 141.2, 130.7, 130.6, 129.0, 128.9, 128.7, 127.5, 123.0, 117.9, 115.7, 115.5, 114.4, 114.2, 109.6; IR (KBr) ν 3108, 3051, 2301, 2222, 1593, 1499, 771, 700 cm$^{-1}$; HRMS (QToF) caled for C$_{25}$H$_{17}$NF [M+H]$^+$ 350.1345 found 350.1346.

5'- (4-bromophenyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (3ga)$^2$: 157 mg was obtained from 1g (142 mg, 0.5 mmol) and 2a following general procedure B. Yield 77%; puffy white solid; mp 167−170 °C; R$_f$ = 0.55 (SiO$_2$, EtOAc:Hexane, 2:98); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.65 (s, 4H), 7.62 (d, $J$ = 5.8 Hz, 4H), 7.55 (s, 2H), 7.53 (s, 3H), 7.50 (s, 2H), 7.47 (d, $J$ = 7.4 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 147.5, 143.8, 138.4, 137.9, 132.2, 129.0, 128.8, 128.7, 127.2, 123.2, 117.8, 109.4; IR (KBr) ν 3047, 2308, 2222, 1597, 1497, 769, 706 cm$^{-1}$; HRMS (TOF) calcd for C$_{25}$H$_{17}$NBr [M+H]$^+$ 410.0544 found 410.0546.

5'- (3,5-dimethoxyphenyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (3ha): 162 mg was obtained from 1h (133 mg, 0.5 mmol) and 2a following general procedure B. Yield 83%; pale white solid; mp 213−216 °C; R$_f$ = 0.5 (SiO$_2$, EtOAc:Hexane, 9:91); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.67 (s, 2H), 7.66 (d, $J$ = 1.4 Hz, 2H), 7.64 (s, 2H), 7.55 (d, $J$ = 1.5 Hz, 1H), 7.53 (s, 1H), 7.51 (s, 1H), 7.50 (s, 2H), 7.48 (dd, $J$ = 6.6, 3.2 Hz, 1H), 6.79 (d, $J$ = 2.2 Hz, 2H), 6.54 (t, $J$ = 2.1 Hz, 1H), 3.85 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.3, 147.2, 145.0, 141.1, 138.6, 129.0, 128.7, 128.6, 127.5, 117.9, 109.2, 105.6, 100.5, 55.5; IR (KBr) ν 3009, 2304, 2223, 1598, 1499, 771, 702 cm$^{-1}$; HRMS (QToF) calcd for C$_{27}$H$_{22}$NO$_2$ [M+H]$^+$ 392.1651 found 392.1648.

5'- (cyclohex-1-en-1-yl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (3ia): 117 mg was obtained from 1i (105 mg, 0.5 mmol) and 2a following general procedure B. Yield 70%; colourless gel; R$_f$ = 0.55 (SiO$_2$, EtOAc:Hexane, 1:99); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 (t, $J$ = 1.8 Hz, 4H), 7.60 – 7.58 (m, 1H), 7.52 (t, $J$ = 1.8 Hz, 2H), 7.50 (q, $J$ = 1.6 Hz, 1H), 7.48 (d, $J$ = 1.4 Hz, 1H), 7.48 – 7.46 (m, 2H), 7.46 – 7.43 (m, 1H), 6.38 – 6.34 (m, 1H), 2.46 (dtd, $J$ = 8.5, 4.2, 2.3 Hz, 2H), 2.29 – 2.23 (m, 2H), 1.85 – 1.78 (m, 2H), 1.72 – 1.66 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.7, 146.4, 139.0, 135.3, 128.9, 128.7, 128.5, 125.3, 118.2, 107.9, 27.1, 26.0, 22.7, 21.8; IR (neat) ν 2991, 2304, 2226, 1598, 1495, 771, 703 cm$^{-1}$; HRMS (QToF) calcd for C$_{25}$H$_{22}$N [M+H]$^+$ 336.1752 found 336.1753.

5'- cyclohexyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3ja): 111 mg was obtained from 1j (106 mg, 0.5 mmol) and 2a following general procedure B. Yield 66%; colourless liquid; R$_f$ = 0.6 (SiO$_2$, EtOAc:Hexane, 1:99); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.62 – 7.58 (m, 4H), 7.51 (t, $J$ = 1.8 Hz, 1H), 7.50 (t, $J$ = 1.9 Hz, 2H), 7.48 (t, $J$ = 1.9 Hz, 1H), 7.46 (t, $J$ = 1.5 Hz, 1H), 7.44

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(dt, J = 2.7, 2.0 Hz, 1H), 7.31 (s, 2H), 2.65 (tt, J = 11.6, 3.1 Hz, 1H), 1.96 (d, J = 11.9 Hz, 2H), 1.88 (d, J = 12.5 Hz, 2H), 1.82 – 1.75 (m, 1H), 1.52 (dd, J = 12.5, 2.8 Hz, 1H), 1.45 (dd, J = 14.6, 6.3 Hz, 2H), 1.39 (dt, J = 12.6, 3.0 Hz, 1H), 1.28 (tt, J = 10.7, 3.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.0, 146.9, 139.0, 129.0, 128.5, 127.6, 118.3, 107.7, 44.8, 34.0, 26.6, 25.9; IR (neat) ν 2995, 2224, 1595, 1498, 771, 704 cm$^{-1}$; HRMS (QToF) calcd for C$_{25}$H$_{24}$N [M+H]$^+$ 338.1909 found 338.1917.

5'-cyclopentyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3ka): 94 mg was obtained from 1k (99 mg, 0.5mmol) and 2a following general procedure B. Yield 58%; colourless liquid; R$_f$ = 0.6 (SiO$_2$, EtOAc:Hexane, 1:99); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.62 – 7.58 (m, 4H), 7.54 – 7.52 (m, 1H), 7.50 (s, 2H), 7.49 – 7.42 (m, 3H), 3.18 – 3.05 (m, 1H), 2.20 – 2.10 (m, 2H), 1.85 (dd, J = 8.0, 5.3 Hz, 2H), 1.80 – 1.63 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 151.8, 146.7, 138.9, 129.0, 128.5, 127.8, 118.2, 107.6, 46.0, 34.5, 25.5; IR (neat) ν 2958, 2226, 1595, 1498, 771, 703 cm$^{-1}$; HRMS (QToF) calcd for C$_{24}$H$_{22}$N [M+H]$^+$ 324.1752 found 324.1756.

5'-butyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3la): 81 mg was obtained from 1l (93 mg, 0.5 mmol) and 2a following general procedure B. Yield 52%; colorless liquid; R$_f$ = 0.6 (SiO$_2$, EtOAc:Hexane, 1:99); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, J = 1.6 Hz, 1H), 7.62 (q, J = 1.9 Hz, 2H), 7.54 (t, J = 1.7 Hz, 1H), 7.52 (d, J = 1.6 Hz, 2H), 7.50 (t, J = 1.8 Hz, 1H), 7.49 (t, J = 1.4 Hz, 1H), 7.46 (dt, J = 2.6, 1.9 Hz, 1H), 7.33 (s, 2H), 0.99 (t, J = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.9, 146.7, 138.8, 129.0, 128.9, 128.4, 118.2, 107.5, 35.7, 33.0, 22.3, 13.8; IR (neat) ν 2950, 2224, 1597, 1500, 771, 704 cm$^{-1}$; HRMS (QToF) calcd for C$_{23}$H$_{22}$N [M+H]$^+$ 312.1752 found 312.1756.

5'-(thiophen-3-yl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (3ma): 133 mg was obtained from 1m (106 mg, 0.5 mmol) and 2a following general procedure B. Yield 79%; amorphous powder; mp 152–155 °C; R$_f$ = 0.6 (SiO$_2$, EtOAc:Hexane, 2:98); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.69 (s, 2H), 7.65 (d, J = 1.4 Hz, 5H), 7.63 (s, 1H), 7.55 – 7.54 (m, 2H), 7.53 (s, 1H), 7.51 (s, 1H), 7.49 (dd, J = 6.4, 2.1 Hz, 1H), 7.46 (d, J = 2.6 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.4, 140.2, 139.4, 138.6, 128.9, 128.7, 128.6, 127.1, 126.6, 126.0, 122.8, 118.0, 108.6; IR (KBr) ν 3109, 2965, 2303, 2224, 1597, 1505, 773, 704 cm$^{-1}$; HRMS (QToF) calcd for C$_{23}$H$_{16}$NS [M+H]$^+$ 338.1003 found 338.1003.
4-methyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3na): 143 mg was obtained from 1n (110 mg, 0.5 mmol) and 2a following general procedure B. Yield 83%; greyish white solid; mp 145−148 °C; Rf = 0.53 (SiO2, EtOAc:Hexane, 1:99); 1H NMR (500 MHz, CDCl3) δ 7.69 – 7.65 (m, 4H), 7.64 (s, 1H), 7.56 – 7.47 (m, 7H), 7.43 (dd, J = 8.3, 6.3 Hz, 1H), 7.33 (d, J = 7.9 Hz, 2H), 2.44 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 147.4, 147.3, 145.0, 139.1, 138.7, 135.8, 129.3, 129.0, 129.0, 128.9, 128.7, 128.6, 127.4, 127.3, 118.2, 108.9, 21.2; IR (KBr) ν 2962, 2917, 2223, 1517, 769, 703 cm⁻¹; HRMS (QToF) calcd for C26H20N [M+H]+ 346.1596 found 346.1598.

4-methoxy-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3oa): 153 mg was obtained from 1o (118 mg, 0.5 mmol) and 2a following general procedure B. Yield 85%; white solid; mp 179−181 °C; Rf = 0.45 (SiO2, EtOAc:Hexane, 3:97); 1H NMR (400 MHz, CDCl3) δ 7.69 – 7.65 (m, 5H), 7.64 (d, J = 1.2 Hz, 1H), 7.61 (d, J = 2.1 Hz, 1H), 7.60 – 7.58 (m, 1H), 7.55 – 7.48 (m, 4H), 7.48 – 7.43 (m, 2H), 7.07 – 7.02 (m, 2H), 3.88 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 160.0, 147.3, 147.0, 145.0, 139.1, 138.7, 132.9, 131.9, 131.0, 130.5, 130.2, 129.0, 129.0, 128.6, 128.6, 127.3, 127.3, 127.1, 118.3, 114.1, 113.8, 108.8, 55.3; IR (KBr) ν 3048, 2217, 1603, 1512, 768, 701 cm⁻¹; HRMS (QToF) calcd for C26H20NO [M+H]+ 362.1545 found 362.1547.

4-fluoro-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3pa): 138 mg was obtained from 1p (112 mg, 0.5 mmol) and 2a following general procedure B. Yield 79%; pale brown solid; mp 195−198 °C; Rf = 0.50 (SiO2, EtOAc:Hexane, 1:99); 1H NMR (400 MHz, CDCl3) δ 7.70 (d, J = 1.8 Hz, 1H), 7.68 (t, J = 1.8 Hz, 1H), 7.66 – 7.60 (m, 6H), 7.56 – 7.49 (m, 4H), 7.48 – 7.41 (m, 2H), 7.22 (ddd, J = 10.6, 5.9, 2.5 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 161.8, 147.4, 146.3, 145.2, 138.9, 138.5, 134.7, 130.9, 130.8, 129.1, 129.0, 128.8, 128.6, 127.6, 127.4, 127.3, 117.9, 115.8, 115.6, 109.0; IR (KBr) ν 2925, 2299, 2227, 1510, 705 cm⁻¹; HRMS (QToF) calcd for C25H17NF [M+H]+ 350.1345 found 350.1335.

4-chloro-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3qa): 141 mg was obtained from 1q (120 mg, 0.5mmol) and 2a following general procedure B. Yield 77%; pale yellowish solid; mp 205−210 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 1:99); 1H NMR (400 MHz, CDCl3) δ 7.71 (d, J = 1.7 Hz, 1H), 7.68 (d, J = 1.5 Hz, 1H), 7.65 (d, J = 1.5 Hz, 3H), 7.63 (d, J = 1.1 Hz, 1H), 7.60 – 7.57 (m, 2H), 7.55 – 7.47 (m, 7H), 7.47 – 7.42 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 147.5, 146.1, 145.3, 138.9, 138.5, 137.1, 135.1, 130.4, 129.2,
2-bromo-4,5-dimethoxy-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3ra): 157 mg was obtained from 1t (172 mg, 0.5 mmol) and 2a following general procedure B. Yield 67%; white solid; mp 189–193 °C; Rf = 0.53 (SiO2, EtOAc:Hexane, 7:93); 1H NMR (400 MHz, CDCl3) δ 7.74 (d, J = 1.6 Hz, 1H), 7.68 (t, J = 6.8 Hz, 4H), 7.64 (d, J = 1.6 Hz, 1H), 7.54 (s, 1H), 7.50 (dd, J = 12.7, 7.6 Hz, 4H), 7.46 – 7.41 (m, 1H), 7.19 (s, 1H), 6.95 (s, 1H), 3.95 (s, 3H), 3.90 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 149.9, 148.3, 146.7, 146.4, 144.8, 138.9, 138.4, 131.4, 129.1, 129.0, 128.8, 128.7, 128.2, 127.8, 127.4, 117.5, 115.7, 113.6, 113.3, 110.6, 56.2, 56.2; IR (KBr) ν 2961, 2307, 2223, 1511, 1460, 767, 699 cm⁻¹; HRMS (QToF) calcd for C27H17NCl [M+H]+ 470.0756 found 470.0761.

2-bromo-5'-(4-ethynylphenyl)-[1,1':3',1''-terphenyl]-2'-carbonitrile (3sa): 136 mg was obtained from 1s (154 mg, 0.5 mmol) and 2a following general procedure B. Yield 63%; pale yellow solid; mp 167–170 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 8:92); 1H NMR (400 MHz, CDCl3) δ 7.75 (dd, J = 7.0, 4.9 Hz, 2H), 7.67 (d, J = 1.6 Hz, 1H), 7.66 – 7.65 (m, 2H), 7.64 (d, J = 2.2 Hz, 1H), 7.61 (t, J = 1.8 Hz, 2H), 7.59 (d, J = 2.0 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.51 (d, J = 1.3 Hz, 1H), 7.50 – 7.48 (m, 1H), 7.46 (t, J = 3.4 Hz, 2H), 7.34 (dt, J = 8.1, 4.7 Hz, 1H), 3.18 (s, 1H); 13C NMR (100 MHz, CDCl3) δ 146.7, 146.5, 143.7, 139.3, 139.0, 138.2, 133.1, 132.8, 131.0, 130.3, 128.9, 128.9, 128.7, 127.8, 127.7, 127.5, 127.2, 122.9, 122.6, 117.1, 110.7, 83.0, 78.7; IR (KBr) ν 3025, 2995, 2316, 2223,2159, 1595, 1389, 767, 703 cm⁻¹; HRMS (QToF) calcd for C27H17NBr [M+H]+ 434.0544 found 434.0541.

5'-(phenylethynyl)-[1,1':3',1''-terphenyl]-4'-carbonitrile (3ta): 140 mg was obtained from 1r (115 mg, 0.5 mmol) and 2a following general procedure B. Yield 79%; off white solid; mp 118–121 °C; Rf = 0.53 (SiO2, EtOAc:Hexane, 1:99); 1H NMR (400 MHz, CDCl3) δ 7.85 (d, J = 1.7 Hz, 1H), 7.69 – 7.64 (m, 6H), 7.63 (d, J = 1.3 Hz, 1H), 7.56 – 7.49 (m, 4H), 7.49 – 7.44(m, 2H), 7.41 – 7.38 (m, 3H); 13C NMR (100 MHz, CDCl3) δ 146.6, 145.0, 138.5, 138.0, 132.0, 129.2, 129.1, 128.9, 128.9, 128.7, 128.4, 128.1, 127.2, 117.2, 112.5, 95.8, 86.2; IR (KBr) ν 3050, 2962, 2223, 1595, 1494,766, 701 cm⁻¹; HRMS(QToF) calcd for C27H18N [M+H]+ 356.1439 found 356.1429.
5’-(3-iodo-1H-indol-2-yl)-[1,1’:3’,1”-terphenyl]-4’-carbonitrile (3ua): 176 mg was obtained from 1u (186 mg, 0.5 mmol) and 2a following general procedure B. Yield 71%; yellow solid; mp 182–185 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 10:90); 1H NMR (400 MHz, CDCl3) δ 8.29 (d, J = 1.5 Hz, 1H), 8.23 (s, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 1.4 Hz, 1H), 7.71 (s, 1H), 7.54 (dd, J = 5.2, 1.3 Hz, 5H), 7.52 – 7.49 (m, 2H), 7.47 – 7.42 (m, 2H), 7.39 (d, J = 7.9 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.25 – 7.21 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 157.2, 144.8, 141.1, 139.7, 139.6, 136.8, 135.8, 134.0, 133.5, 129.8, 129.2, 129.0, 128.5, 128.4, 127.7, 127.3, 126.2, 123.0, 121.9, 118.6, 113.4, 57.4; IR (KBr) ν 3670, 2962, 2367, 2223, 1650, 1509, 766, 701 cm⁻¹; HRMS (QToF) calcd for C27H18N2I [M+H]+ 497.0515 found 497.0516.

5’-(furan-2-yl)-[1,1’:3’,1”-terphenyl]-4’-carbonitrile (3va): 112 mg was obtained from 1v (98 mg, 0.5 mmol) and 2a following general procedure B. Yield 70%; grey solid; mp 105–110 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 2:98); 1H NMR (500 MHz, CDCl3) δ 8.13 (d, J = 1.8 Hz, 1H), 7.70 (t, J = 1.7 Hz, 1H), 7.69 – 7.68 (m, 1H), 7.62 (t, J = 1.8 Hz, 1H), 7.58 (dt, J = 1.7, 1.1 Hz, 1H), 7.54 (t, J = 1.8 Hz, 1H), 7.52 (d, J = 2.2, 1.5 Hz, 1H), 7.51 (d, J = 1.5 Hz, 1H), 7.50 (dd, J = 2.9, 1.5 Hz, 1H), 7.49 (t, J = 1.9 Hz, 1H), 7.46 (dd, J = 2.5, 0.9 Hz, 1H), 7.44 (t, J = 2.3 Hz, 1H), 7.43 (t, J = 1.2 Hz, 1H), 6.60 (dd, J = 3.6, 1.8 Hz, 1H); 13C NMR (125 MHz, CDCl3) δ 149.9, 147.8, 145.3, 143.3, 139.0, 134.8, 129.0, 128.7, 128.6, 127.3, 127.2, 123.5, 118.4, 112.3, 111.2, 104.6; IR (KBr) ν 3012, 2998, 2304, 2228, 1542, 1265, 767, 710 cm⁻¹; HRMS (QToF) calcd for C23H16NO [M+H]+ 322.1232 found 322.1234.

5’-(thiophen-2-yl)-[1,1’:3’,1”-terphenyl]-4’-carbonitrile (3wa): 123 mg was obtained from 1w (106 mg, 0.5 mmol) and 2a following general procedure B. Yield 73%; greyish white solid; mp 149–152 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 2:98); 1H NMR (400 MHz, CDCl3) δ 7.80 (d, J = 1.7 Hz, 1H), 7.69 – 7.67 (m, 2H), 7.66 – 7.65 (m, 1H), 7.64 (d, J = 1.6 Hz, 2H), 7.63 – 7.62 (m, 1H), 7.55 – 7.52 (m, 2H), 7.50 (dd, J = 3.9, 1.5 Hz, 2H), 7.47 (ddd, J = 7.1, 6.4, 2.2 Hz, 3H), 7.19 (dd, J = 5.1, 3.7 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ 147.9, 145.3, 139.6, 139.3, 138.8, 138.5, 129.1, 128.9, 128.8, 128.6, 128.1, 128.1, 127.7, 127.4, 127.3, 118.1, 108.1; IR (KBr) ν 3013, 2959, 2302, 2228, 1542, 766, 710 cm⁻¹; HRMS (QToF) calcd for C23H16NS [M+H]+ 338.1003 found 338.1010.

4-chloro-5’-phenyl-[1,1’:3’,1”-terphenyl]-2’-carbonitrile (3ab): 142 mg was obtained from 1a (106 mg, 0.5 mmol) and 2b following general procedure B. Yield 78%; puffy white solid; mp 205–208 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 1:99); 1H NMR (500 MHz, CDCl3) δ 149.1, 146.4, 139.6, 139.4, 138.7, 129.2, 128.9, 128.7, 128.5, 128.1, 127.7, 127.5, 127.3, 118.1, 108.1; 13C NMR (100 MHz, CDCl3) δ 114.9, 114.3, 113.9, 112.2, 111.2, 104.6; IR (KBr) ν 3012, 2959, 2302, 2228, 1542, 766, 710 cm⁻¹; HRMS (QToF) calcd for C23H16NS [M+H]+ 338.1003 found 338.1010.
7.71 (d, J = 1.8 Hz, 1H), 7.67 (t, J = 1.7 Hz, 1H), 7.66 – 7.64 (m, 3H), 7.64 – 7.63 (m, 1H), 7.61 – 7.59 (m, 1H), 7.59 – 7.57 (m, 1H), 7.54 (t, J = 1.7 Hz, 1H), 7.53 (d, J = 1.6 Hz, 1H), 7.51 (dd, J = 4.0, 1.7 Hz, 2H), 7.49 (dd, J = 4.8, 2.7 Hz, 3H), 7.47 – 7.43 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 147.5, 146.0, 145.3, 138.8, 138.4, 137.0, 135.0, 130.3, 129.1, 128.9, 128.8, 128.7, 127.3, 117.8, 108.9; IR (KBr) ν 2962, 2306, 2221, 1597, 1495, 768, 701 cm⁻¹; HRMS (QToF) caled for C₂₅H₁₇ClN [M+H]⁺ 366.1050 found 366.1043.

5'-phenyl-[1,1':3',1''-terphenyl]-2',4-dicarbonitrile (3ac): 139 mg was obtained from 1a (106 mg, 0.5 mmol) and 2c following general procedure B. Yield 78%; colourless solid; mp 228–232 °C; Rᵣ = 0.53 (SiO₂, EtOAc:Hexane, 1:99); ¹H NMR (500 MHz, CDCl₃) δ 7.84 – 7.81 (m, 2H), 7.78 – 7.75 (m, 3H), 7.67 (t, J = 1.8 Hz, 1H), 7.66 (d, J = 1.7 Hz, 2H), 7.64 (q, J = 2.0 Hz, 1H), 7.63 – 7.62 (m, 1H), 7.56 – 7.50 (m, 4H), 7.50 – 7.45 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 147.7, 145.6, 145.2, 143.1, 138.5, 138.1, 132.4, 129.8, 129.2, 129.0, 128.9, 128.7, 128.5, 127.3, 127.2, 118.4, 117.5, 112.6, 108.7; IR (KBr) ν 3022, 2359, 2223, 1595, 1251, 740, 670 cm⁻¹; HRMS (QToF) caled for C₂₆H₁₇N₂ [M+H]⁺ 357.1392 found 357.1386.

5'-phenyl-[1,1':3',1''-quaterphenyl]-2'-carbonitrile (3ad): 163 mg was obtained from 1a (106 mg, 0.5 mmol) and 2d following general procedure B. Yield 80%; colourless solid; mp 193–196 °C; Rᵣ = 0.55 (SiO₂, EtOAc:Hexane, 1:99); ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 2.0 Hz, 5H), 7.72 – 7.70 (m, 2H), 7.69 (s, 2H), 7.57 – 7.53 (m, 2H), 7.49 – 7.43 (m, 4H), 7.41 – 7.37 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 147.4, 146.95, 145.1, 141.6, 140.4, 139.0, 138.7, 137.5, 129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 127.6, 127.5, 127.4, 127.3, 127.1, 118.1, 108.8; IR (KBr) ν 3037, 2221, 1696, 1595, 1222, 765, 700 cm⁻¹; HRMS (QToF) caled for C₃₁H₂₂N [M+H]⁺ 408.1752 found 408.1747.

4-phenoxy-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3ae): 171 mg was obtained from 1a (106 mg, 0.5 mmol) and 2e following general procedure B. Yield 81%; greyish white solid; mp 150–153 °C; Rᵣ = 0.55 (SiO₂, EtOAc:Hexane, 2:98); ¹H NMR (300 MHz, CDCl₃) δ 7.69 (s, 3H), 7.68 (d, J = 1.5 Hz, 2H), 7.66 – 7.64 (m, 2H), 7.62 (s, 1H), 7.57 – 7.50 (m, 4H), 7.49 – 7.44 (m, 2H), 7.40 (t, J = 7.9 Hz, 2H), 7.19 (d, J = 7.4 Hz, 1H), 7.16 – 7.14 (m, 2H), 7.12 (t, J = 2.1 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 158.1, 156.4, 147.4, 146.7, 145.1, 139.0, 138.6, 133.2, 130.5, 129.8, 129.0, 129.0, 128.7, 128.6, 127.4, 127.3, 127.3, 123.8, 119.6, 118.3, 118.1, 108.8; IR (KBr) ν 3029, 2223, 1593, 1495, 1223, 840, 758 cm⁻¹; HRMS (QToF) caled for C₃₁H₂₂NO [M+H]⁺ 424.1701 found 424.1701.
2-methoxy-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3af): 143 mg was obtained from 1a (106 mg, 0.5 mmol) and 2f following general procedure B. Yield 79%; brownish white solid; mp 178-181 °C; \(R_f = 0.45\) (SiO\(_2\), EtOAc:Hexane, 3:97); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.68 (s, 3H), 7.66 (s, 3H), 7.53 (d, \(J = 6.7\) Hz, 1H), 7.49 (d, \(J = 3.4\) Hz, 3H), 7.44 (dd, \(J = 8.6, 2.3\) Hz, 3H), 7.37 (dd, \(J = 7.5, 1.3\) Hz, 1H), 7.12 – 7.04 (m, 2H), 3.89 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 156.6, 146.4, 144.8, 144.3, 139.2, 138.8, 130.9, 130.3, 129.0, 129.0, 128.6, 128.1, 127.7, 127.3, 120.7, 117.9, 111.3, 110.9, 55.6; IR (KBr) \(\nu\) 3017, 2924, 2225, 1598, 1496, 1253, 763, 702 cm\(^{-1}\); HRMS (QToF) calcd for C\(_{26}\)H\(_{20}\)NO [M+H]+ 362.1545 found 362.1541.

3,4-dimethoxy-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (3ag): 152 mg was obtained from 1a (106 mg, 0.5 mmol) and 2g following general procedure B. Yield 78%; white solid; mp 208–211 °C; \(R_f = 0.45\) (SiO\(_2\), EtOAc:Hexane, 6:94); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.66 (t, \(J = 7.9\) Hz, 2H), 7.53 (d, \(J = 6.5\) Hz, 2H), 7.50 (s, 2H), 7.47 (d, \(J = 3.6\) Hz, 2H), 7.43 (t, \(J = 4.9\) Hz, 3H), 7.24 (d, \(J = 1.9\) Hz, 1H), 7.22 – 7.17 (m, 2H), 7.01 (d, \(J = 8.2\) Hz, 1H), 3.96 (d, \(J = 2.8\) Hz, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 149.5, 148.8, 147.4, 147.1, 145.0, 139.1, 138.7, 131.2, 129.1, 129.0, 128.7, 128.6, 127.3, 127.2, 121.6, 118.3, 112.3, 111.2, 108.9, 56.0, 55.9; IR (KBr) \(\nu\) 3016, 2312, 2222, 1596, 1516, 1259, 766, 703 cm\(^{-1}\); HRMS (QToF) calcd for C\(_{27}\)H\(_{22}\)NO\(_2\) [M+H]+ 392.1651 found 392.1649.

5'-(benzo[d][1,3]dioxol-5-yl)-[1,1':3',1''-terphenyl]-4'-carbonitrile (3ah): 139 mg was obtained from 1a (106 mg, 0.5 mmol) and 2h following general procedure B. Yield 74%; greyish white solid; mp 188–191 °C; \(R_f = 0.45\) (SiO\(_2\), EtOAc:Hexane, 3:97); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.66 (ddd, \(J = 7.3, 5.4, 1.5\) Hz, 5H), 7.63 (s, 1H), 7.54 – 7.46 (m, 5H), 7.46 – 7.41 (m, 1H), 7.12 (dd, \(J = 7.0, 1.6\) Hz, 2H), 6.96 – 6.93 (m, 1H), 6.05 (s, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 148.1, 147.8, 147.3, 147.0, 145.0, 139.0, 138.6, 132.5, 129.1, 129.0, 128.7, 128.6, 127.4, 127.3, 123.0, 118.1, 109.5, 108.9, 108.5, 101.4; IR (KBr) \(\nu\) 2966, 2920, 2222, 1599, 1498, 767, 702 cm\(^{-1}\); HRMS (QToF) calcd for C\(_{26}\)H\(_{18}\)NO\(_2\) [M+H]+ 376.1338 found 376.1336.

5'-(pyridin-4-yl)-[1,1':3',1''-terphenyl]-4'-carbonitrile (3ai): 125 mg was obtained from 1a (106 mg, 0.5 mmol) and 2i following general procedure B. Yield 75%; pale yellow solid; mp 193–196 °C; \(R_f = 0.53\) (SiO\(_2\), EtOAc:Hexane, 2:98); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.78 (dd, \(J = 8.7, 0.8\) Hz, 1H), 7.88 (dd, \(J = 8.7, 0.5\) Hz, 1H), 7.49 (d, \(J = 8.0\) Hz, 2H), 7.14 (d, \(J = 8.0\) Hz, 2H), 7.01 (d, \(J = 8.0\) Hz, 2H), 6.98 – 6.93 (m, 1H), 6.59 (s, 1H), 5.95 (s, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 149.5, 148.2, 147.3, 147.0, 145.0, 139.0, 138.6, 132.5, 129.1, 129.0, 128.7, 128.6, 127.4, 127.3, 123.0, 122.7, 118.1, 109.5, 108.9, 108.5, 101.4; IR (KBr) \(\nu\) 2966, 2920, 2222, 1599, 1498, 767, 702 cm\(^{-1}\); HRMS (QToF) calcd for C\(_{26}\)H\(_{18}\)NO\(_2\) [M+H]+ 376.1338 found 376.1336.
4.5, 1.6 Hz, 2H), 7.77 (d, J = 1.8 Hz, 1H), 7.68 (d, J = 1.7 Hz, 2H), 7.67 – 7.64 (m, 2H), 7.64 – 7.63 (m, 1H), 7.58 (dd, J = 4.4, 1.7 Hz, 2H), 7.56 – 7.50 (m, 4H), 7.47 (ddd, J = 8.9, 5.8, 2.4 Hz, 2H); 

13C NMR (100 MHz, CDCl3) δ 150.2, 147.7, 146.2, 145.6, 144.3, 138.5, 138.1, 129.2, 129.0, 128.9, 128.7, 127.3, 127.1, 123.6, 117.4, 108.6; IR (KBr) ν 3031, 2219, 1594, 1550, 764, 699 cm⁻¹; HRMS (QToF) calcd for C24H17N2 [M+H]+ 333.1392 found 333.1396.

(2-(4'-cyano-[1,1':3',1''-terphenyl]-5'-yl)cyclopenta-2,4-dien-1-yl)(cyclopenta-2,4-dien-1-yl)iron (3aj): 167 mg was obtained from 1a (106 mg, 0.5 mmol) and 2j following general procedure B. Yield 76%; pink solid; mp 140−145 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 3:97); 1H NMR (400 MHz, CDCl3) δ 7.89 (d, J = 1.8 Hz, 1H), 7.69 (d, J = 1.5 Hz, 1H), 7.66 (d, J = 1.0 Hz, 1H), 7.63 (d, J = 1.6 Hz, 1H), 7.61 (t, J = 1.7 Hz, 1H), 7.55 – 7.53 (m, 1H), 7.52 (d, J = 1.1 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.49 (d, J = 1.6 Hz, 1H), 7.47 (s, 1H), 7.46 (s, 1H), 5.02 – 5.00 (m, 1H), 4.48 – 4.46 (m, 1H), 4.23 (s, 5H); 13C NMR (100 MHz, CDCl3) δ 147.7, 145.2, 144.4, 139.3, 138.8, 129.1, 129.0, 128.6, 128.5, 128.5, 127.2, 126.9, 126.4, 118.9, 107.5, 82.8, 70.0, 69.7, 69.1; IR (KBr) ν 3040, 2923, 2220, 1596, 1554, 840, 768, 701 cm⁻¹; HRMS (QToF) calcd for C29H22NFe [M+H]+ 440.1102 found 440.1087.

(B). General procedure C for the synthesis of final compounds (5) taking Synthesis of 4a as an Example.

To a 15 mL Schlenk tube was added ynene 1a (103 mg, 0.5 mmol, 1 equiv), ethyl (E)-2-cyano-2-(2,3-dihydro-1H-inden-1-ylidene)acetate 4 (136 mg, 0.6 mmol, 2 equiv), KOtBu (112 mg, 1 mmol, 2 equiv) in 1-butanol (3 mL) and the reaction mixture was stirred at room temperature under open air until the complete conversion of starting material (30-60 min). The reaction mixture was concentrated under reduced pressure, washed with hexane (2 times) and the remaining solid was dissolved in 20% EtOAc/Hexane and filtered through a small silica bed. Filtrate was concentrated to get the desired solids in purified form 5a.

1,3-diphenyl-9H-fluorene-4-carbonitrile (5a): 146 mg was obtained from 4 (136 mg, 0.6 mmol) and 1a following general procedure B. Yield 71%; colourless solid; mp 165–168 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 1:99); 1H NMR (400 MHz, CDCl3) δ 8.67 (d, J = 7.7 Hz, 1H), 7.67 (t, J = 1.8 Hz, 1H), 7.66 – 7.65 (m, 1H), 7.59 (d, J = 1.5 Hz, 1H), 7.57 (d, J = 1.0 Hz, 2H), 7.55 – 7.48 (m,
5H), 7.48 – 7.47 (m, 1H), 7.46 (t, J = 1.9 Hz, 1H), 7.44 – 7.42 (m, 2H), 4.00 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.6, 144.6, 144.2, 142.9, 140.9, 139.4, 139.0, 138.4, 129.1, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 127.4, 124.7, 122.8, 118.1, 102.2, 36.3; IR (KBr) ν 3031, 2925, 2221, 2158, 1509, 1387, 769, 704 cm$^{-1}$; HRMS (QToF) calcd for C$_{26}$H$_{18}$N [M+H]$^+$ 344.1439 found 344.1432

1-((1,1’-biphenyl)-4-yl)-3-phenyl-9H-fluorene-4-carbonitrile (5b): 176 mg was obtained from 4 (136 mg, 0.6 mmol) and 1c following general procedure B. Yield 70%; grey solid; mp 199–203 °C; R$_f$ = 0.55 (SiO$_2$, EtOAc:Hexane, 1:99); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.68 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 1.8 Hz, 1H), 7.74 (d, J = 1.9 Hz, 1H), 7.67 (ddd, J = 6.2, 4.4, 3.0 Hz, 6H), 7.60 (d, J = 7.2 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.48 (dd, J = 8.3, 4.0 Hz, 4H), 7.46 – 7.38 (m, 2H), 4.07 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.7, 144.2, 142.5, 141.2, 140.9, 140.3, 139.0, 138.4, 138.2, 129.1, 128.9, 128.6, 127.6, 127.4, 127.3, 127.1, 124.8, 122.8, 118.1, 102.2, 36.4; IR (KBr) ν 3043, 2917, 2220, 1581, 1486, 840, 742 cm$^{-1}$; HRMS (QToF) calcd for C$_{32}$H$_{22}$N [M+H]$^+$ 420.1752 found 420.1747.

1-(3,5-dimethoxyphenyl)-3-phenyl-9H-fluorene-4-carbonitrile (5c): 177 mg was obtained from 4 (136 mg, 0.6 mmol) and 1h following general procedure B. Yield 73%; white solid; mp 213-215 °C; R$_f$ = 0.45 (SiO$_2$, EtOAc:Hexane, 6:94); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.66 (d, J = 7.7 Hz, 1H), 7.66 (dt, J = 3.4, 2.0 Hz, 2H), 7.58 (d, J = 7.3 Hz, 1H), 7.56 – 7.47 (m, 6H), 6.69 (d, J = 2.3 Hz, 2H), 6.55 (t, J = 2.2 Hz, 1H), 4.01 (s, 2H), 3.86 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.9, 145.5, 144.6, 144.2, 142.8, 141.3, 140.9, 139.0, 138.4, 138.2, 129.1, 128.9, 128.6, 127.6, 127.4, 127.1, 124.8, 122.8, 118.1, 106.7, 102.3, 99.9, 55.4, 36.3; IR (KBr) ν 3055, 2308, 2222, 1590, 1493, 1303, 751 cm$^{-1}$; HRMS (QToF) calcd for C$_{28}$H$_{22}$NO$_2$ [M+H]$^+$ 404.1651 found 404.1646.

3-(furan-2-yl)-1-phenyl-9H-fluorene-4-carbonitrile (5d): 124 mg was obtained from 4 (136 mg, 0.6 mmol) and 1v following general procedure B. Yield 62%; brownish white solid; mp 203-206 °C; R$_f$ = 0.53 (SiO$_2$, EtOAc:Hexane, 2:98); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.69 (d, J = 7.8 Hz, 1H), 7.84 (s, 1H), 7.58 (ddd, J = 6.5, 3.7, 1.4 Hz, 3H), 7.55 – 7.46 (m, 5H), 7.46 – 7.41 (m, 2H), 6.60 (dd, J = 3.5, 1.8 Hz, 1H), 3.96 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 150.2, 144.7, 144.2, 143.2, 143.0, 140.8, 139.40, 138.9, 133.2, 128.7, 128.6, 128.3, 127.3, 124.9, 124.7, 122.8, 118.5, 112.2, 110.4, 98.1, 36.3; IR (KBr) ν 2923, 1540, 1471, 1378, 756, 636 cm$^{-1}$; HRMS (QToF) calcd for C$_{24}$H$_{16}$NO[M+H]$^+$ 334.1232 found 334.1224.
1-phenyl-3-(thiophen-2-yl)-9H-fluorene-4-carbonitrile (5e): 126 mg was obtained from 4 (136 mg, 0.6 mmol) and 1w following general procedure B. Yield 60%; greyish white solid; mp 216–219 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 2:98); 1H NMR (400 MHz, CDCl3) δ 8.68 (d, J = 7.7 Hz, 1H), 7.69 (dd, J = 3.6, 1.1 Hz, 1H), 7.58 – 7.55 (m, 3H), 7.55 – 7.52 (m, 3H), 7.51 – 7.46 (m, 3H), 7.45 – 7.42 (m, 1H), 7.20 (dd, J = 5.1, 3.7 Hz, 1H), 3.98 (s, 2H); 13C NMR (100 MHz, CDCl3) δ 145.0, 144.3, 143.1, 141.3, 139.6, 139.1, 138.8, 137.6, 128.8, 128.7, 128.6, 128.4, 128.1, 127.8, 127.4, 127.0, 124.8, 122.9, 118.2, 101.3, 36.3; IR (KBr) ν 3045, 2899, 2222, 1581, 1500, 769, 707 cm⁻¹; HRMS (QToF) calcd for C24H16NS [M+H]+ 350.1003 found 350.0996.

3-(4-chlorophenyl)-1-phenyl-9H-fluorene-4-carbonitrile (5f): 156 mg was obtained from 4 (136 mg, 0.6 mmol) and 1q following general procedure B. Yield 69%; greyish white solid; mp 223–226 °C; Rf = 0.53 (SiO2, EtOAc:Hexane, 2:98); 1H NMR (500 MHz, CDCl3) δ 8.65 (d, J = 7.8 Hz, 1H), 7.61 – 7.55 (m, 5H), 7.54 – 7.50 (m, 3H), 7.50 – 7.48 (m, 2H), 7.38 (s, 1H), 4.00 (s, 2H); 13C NMR (125 MHz, CDCl3) δ 144.8, 144.3, 143.1, 141.4, 139.2, 138.9, 136.9, 134.9, 130.4, 128.9, 128.8, 128.7, 128.5, 128.4, 128.4, 127.5, 124.8, 122.8, 118.0, 102.1, 36.3; IR (KBr) ν 2960, 2222, 1572, 1516, 1382, 762, 672 cm⁻¹; HRMS (QToF) calcd for C26H17ClN [M+H]+ 378.1050 found 378.1044.

3-(4-bromophenyl)-1-phenyl-9H-fluorene-4-carbonitrile (5g): 164 mg was obtained from 4 (136 mg, 0.6mmol) following general procedure B. Yield 65%; brownish white solid; mp 195–198 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 2:98); 1H NMR (400 MHz, CDCl3) δ 8.64 (d, J = 7.5 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.58 – 7.55 (m, 3H), 7.53 (dt, J = 11.8, 3.6 Hz, 4H), 7.49 – 7.41 (m, 3H), 7.38 (s, 1H), 3.98 (s, 2H); 13C NMR (100 MHz, CDCl3) δ 144.8, 144.3, 143.1, 141.4, 139.2, 138.9, 136.9, 134.9, 130.4, 128.9, 128.8, 128.7, 128.5, 128.4, 127.5, 124.8, 122.8, 118.0, 102.0, 36.3; IR (KBr) ν 3050, 2311, 2215, 1585, 747, 698 cm⁻¹; HRMS (QToF) calcd for C26H17BrN [M+H]+ 422.0544 found 422.0540.

4'-methyl-5'-phenyl-[1,1':3',1''-terphenyl]-2'-carbonitrile (5h): 122 mg was obtained from 1a (106 mg, 0.5 mmol) and 2j following general procedure A. Yield 71%; white solid; mp 168–171 °C; Rf = 0.55 (SiO2, EtOAc:Hexane, 1:99); 1H NMR (400 MHz, CDCl3) δ 7.62 (d, J = 1.5 Hz, 1H), 7.60 (s, 1H), 7.54 – 7.50 (m, 2H), 7.49 – 7.41 (m, 3H), 7.39 (dd, J = 6.5, 4.0, 1.7 Hz, 5H), 2.04 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 147.4, 146.8, 143.1, 140.7, 138.8, 138.42.
133.9, 130.6, 129.1, 128.9, 128.7, 128.6, 128.5, 128.3, 127.8, 117.9, 110.9, 18.6; IR (KBr) ν 3049, 2431, 2223, 1962, 1595, 1498, 891, 768, 702 cm⁻¹; HRMS (QToF) calcd for C_{26}H_{20}N [M+H]⁺ 346.1596 found 346.1592.

IV. General Procedure and Characteristic data of derivatives:

(A). General procedure D for the synthesis of derivative (6):

![Chemical structure of (Z)-N'-hydroxy-5'-(p-tolyl)-[1,1':3',1''-terphenyl]-2'-carboximidamide (6)]

Benzonitrile 3ba (0.41 mmol) and 50% hydroxylamine in water (0.3 mL) were added to ethanol at room temperature. The reaction mixture was stirred at reflux for 3 to 4 hours until the complete consumption of starting materials (monitored by TLC). The mixture was concentrated to give the crude product, which was further purified by column chromatography to afford compound 6 as a colourless solid.

(Z)-N'-hydroxy-5'-(p-tolyl)-[1,1':3',1''-terphenyl]-2'-carboximidamide (6): 110 mg was obtained from 3ba (140 mg, 0.6 mmol) following general procedure D. Yield 72%; colourless solid; R_f = 0.55 (SiO₂, EtOAc:Hexane, 35:65); ¹H NMR (400 MHz, DMSO) δ 7.68 (d, J = 7.2 Hz, 2H), 7.50 (d, J = 6.6 Hz, 3H), 7.45 (s, 2H), 7.43 – 7.36 (m, 4H), 7.32 (dd, J = 9.3, 7.4 Hz, 4H), 7.15 (d, J = 7.9 Hz, 2H), 7.07 (s, 1H), 2.27 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 170.1, 140.8, 140.2, 139.8, 139.8, 139.6, 137.8, 136.7, 136.1, 129.2, 129.0, 128.9, 128.8, 128.2, 128.0, 127.5, 127.2, 12.16, 20.9; HRMS (QToF) calcd for C_{26}H_{21}N₂ [M-OH]⁺ 361.1705 found 361.1700.

(B). General procedure E for the synthesis of derivative (7):

![Chemical structure of 3ua and 7]

To a round bottomed flask, nitrile 3ua (0.30 mmol) and caesium carbonate (0.6 mmol) were added in THF and the reaction mixture was stirred at reflux at 60 °C for 4-6 hours until the complete consumption of starting materials (monitored by TLC). The mixture was
concentrated to give the crude product, which was further purified by column chromatography to afford compound 7.

11-iodo-7,9-diphenyl-6H-isoindolo[2,1-a]indol-6-imine (7): 126 mg was obtained from 3ua (150 mg, 0.30 mmol) following general procedure E. Yield 85%; yellow solid; R_f = 0.55 (SiO_2, EtOAc:Hexane, 15:85); \(^1\)HNMR (400 MHz, DMSO) δ 12.27 (s, 1H), 8.02 (d, J = 1.7 Hz, 1H), 7.97 (d, J = 1.7 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.76 (dd, J = 8.1, 1.3 Hz, 2H), 7.58 (ddd, J = 20.7, 9.2, 4.7 Hz, 6H), 7.49 (dt, J = 7.2, 3.1 Hz, 2H), 7.41 (d, J = 7.9 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.23 – 7.18 (m, 1H); \(^13\)C NMR (100 MHz, DMSO) δ 146.8, 144.4, 138.1, 137.9, 136.9, 136.4, 130.6, 129.5, 129.4, 129.3, 129.0, 128.4, 127.7, 123.8, 121.0, 120.9, 117.7, 112.3, 110.1, 61.7; IR (KBr) ν 3454, 2258, 1664, 1032, 770 cm\(^{-1}\); HRMS (QToF) calcd for C\(_{27}\)H\(_{18}\)N\(_2\)I [M+H]^+ 497.0515 found 497.0513.

(C). General procedure F for the synthesis of derivative (8):

To a round bottomed flask, nitrile 4c (0.44 mmol) and sodium hydride (0.88 mmol) were added to THF, the reaction mixture was stirred under open air at room temperature until the complete consumption of nitrile (monitored by TLC). The mixture was concentrated to give the crude product, which was further purified by column chromatography to afford compound 8 as a yellow solid.

1-(3-hydroxy-5-methoxyphenyl)-9-oxo-3-phenyl-9H-fluorene-4-carbonitrile (8): 142 mg was obtained from 4c (177 mg, 0.44 mmol) following general procedure F. Yield 80%; yellow solid; mp 189–193 °C; R_f = 0.55 (SiO_2, EtOAc:Hexane, 10:90); \(^1\)HNMR (400 MHz, CDCl\(_3\)) δ 8.46 (d, J = 7.7 Hz, 1H), 7.70 (d, J = 7.2 Hz, 1H), 7.65 – 7.60 (m, 3H), 7.57 – 7.51 (m, 3H), 7.45 (td, J = 7.5, 0.8 Hz, 1H), 7.37 (s, 1H), 6.67 (d, J = 2.3 Hz, 2H), 6.57 (t, J = 2.3 Hz, 1H), 3.84 (s, 6H; \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ 190.0, 160.4, 150.4, 149.0, 145.4, 140.6, 137.8, 137.1, 135.2, 134.3, 132.7, 130.8, 129.5, 129.0, 128.8, 128.7, 124.4, 122.7, 117.0, 107.2, 103.4, 101.1, 55.4; IR (KBr) ν 3055, 2308, 2222, 1590, 1493, 770 cm\(^{-1}\); HRMS (QToF) calcd for C\(_{28}\)H\(_{20}\)NO\(_3\) [M+H]^+ 418.1443 found 418.1436.
References:


Ph
Ph
CN
n-Bu

31a
3ma