Cascade double isocyanide insertion and C-N coupling of 2-iodo-2'-isocyano-1,1'-biphenyls

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1. General Information

All the solvents and reagents were purchased from commercial suppliers. $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 MHz or/and 500 MHz Bruker FT-NMR spectrometers. All chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, $J$, are reported in Hertz (Hz). High Resolution Mass (MS) analysis was obtained using on a LC/MSD TOF spectrometer system with Electrospray Ionization (ESI). Melting points were measured on a Mel-Temp apparatus and are uncorrected. IR was recorded on a Bruker Tensor 27 FT-IR spectrometer. Reactions were monitored by thin-layer chromatography (TLC) carried out on commercial silica gel plates (GF254) under UV light. Flash chromatography was performed on silica gel 60 (200–300 mesh).
2. Synthesis and Characterization of the Starting Materials

2.1 Preparation of 2'-nitro-[1,1'-biphenyl]-2-amines
The above 2'-nitro-[1,1'-biphenyl]-2-amines were prepared by following a reported procedure. In a 250 mL Schlenk flask, 1-bromo-2-nitrobenzene (1.0 equiv,
2.0-6.0 mmol) and 2-aminophenylboronic acid pinacol esters (1.2 equiv) were charged under the protection of argon. Then, dimethoxyethane (80 mL) and NaHCO$_3$ aqueous solution (5.0 equiv, 1.0 mol/L) were added to the above flask and was degassed for 30 minutes. Pd(PPh$_3$)$_4$ (5 mol %) was added, then the mixture was heated to 90 °C and stirred for 12 hours (monitored by TLC). After completion of the reaction, it was cooled to room temperature. The reaction mixture was extracted with ethyl acetate (50 mL×3) and the combined organic phase was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/30 to 1/10) to afford the desired 2'-nitro-[1,1'-biphenyl]-2-amines.

2.2 Iodination of 2'-nitro-[1,1'-biphenyl]-2-amines

The above 2'-nitro-[1,1'-biphenyl]-2-amines were prepared by following a reported procedure.$^2$ A mixture of 2'-nitro-[1,1'-biphenyl]-2-amines (1.0 equiv, 1.0-5.0 mmol), water (72 mL), and conc. hydrochloric acid (12 mL) was warmed at 60-70 °C
until a clear solution was obtained. Then the mixture was diazotized at 5 °C with sodium nitrite (1.6 equiv) in water (12 mL). After stirring for 30 minutes, a solution of potassium iodine (3.0 equiv) in the minimum amount of water was rapidly added and the mixture was cautiously warmed up to its boiling point and refluxed for 6 hours. After completion of the reaction (monitored by TLC), it was cooled to room temperature. The mixture was quenched by adding saturated aqueous sodium thiosulfate solution and pH was regulated with saturated sodium hydroxide aqueous solution to 8-10. After extraction with ethyl acetate (30 mL×3) and the combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/30) to afford the desired product.

![Chemical structure](image)

The above 2'-nitro-[1,1'-biphenyl]-2-amines were prepared by following a reported procedure.³ A mixture of 2'-nitro-[1,1'-biphenyl]-2-amines (1.0 equiv, 1.0-5.0 mol), water (30 mL), and conc. hydrochloric acid (5 mL) was warmed at 60-70 °C until a clear solution was obtained. Then the mixture was diazotized at 5 °C with sodium nitrite (1.2 equiv) in water (5 mL). After stirring for 30 minutes, the resulting solution was poured into a solution of potassium iodine (2.0 equiv) and iodine (0.3 equiv) and the mixture was cautiously warmed up to its boiling point. After completion of the reaction (monitored by TLC), it was cooled to room temperature. The mixture was quenched by adding saturated aqueous sodium thiosulfate solution and pH was regulated with saturated sodium hydroxide aqueous solution to 8-10. The solution was extracted with ethyl acetate (10 mL×3) and the combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was
purified by flash chromatography (ethyl acetate/petroleum ether = 1/30) to afford the desired product.
2.3 Preparation of 2'-iodo-[1,1'-biphenyl]-2-amines
The above 2'-nitro-[1,1'-biphenyl]-2-amines were prepared by following a
reported procedure. A mixture of 2-iodo-2'-nitro-1,1'-biphenyl (1.0 equiv, 1.0-4.0 mmol), anhydrous tin (II) chloride (4.0 equiv), and concentrated hydrochloric acid (4.0 equiv) in absolute ethanol (15 mL) were refluxed for 7 hours. After completion of the reaction (monitored by TLC), it was cooled to room temperature and pH was regulated with saturated sodium hydroxide aqueous solution to 8-10. The mixture was filtered through diatomaceous earth. The filtrate was extracted with ethyl acetate (30 mL×3) and the combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/10) to afford the desired product.
2.4 Preparation of substituted 2-iodo-2'-isocyano-1,1'-biphenyl

The above substituted 2-iodo-2'-isocyano-1,1'-biphenyl were prepared by following a reported procedure with minor changes. A mixture of
2'-iodo-[1,1'-biphenyl]-2-amine (1.0 equiv, 0.3-2.0 mmol) and formic acid (15 mL) was refluxed for 5 hours. After completion of the reaction (monitored by TLC), the mixture was concentrated under reduced pressure to afford crude product as a yellow oil for next step without further purification.

The crude product was dissolved in dichloromethane (20 mL) and NEt₃ (3.0 equiv) and cooled to 0 °C by ice bath. To the above mixture was added phosphory chloride (1.1 equiv) dropwise. After stirring for an hour, the reaction temperature was warmed to room temperature and the mixture was stirred for another hour. When the reaction was completed, the resulting mixture was cooled to 0 °C and aqueous saturated solution of sodium carbonate (10 mL) was added dropwise to quench the reaction. After vigorous stirring for an hour, the mixture was extracted with ethyl acetate (10 mL×3) and the combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/50) to afford the desired product.

3. Optimization of Reaction Condition and General Procedures

3.1 Optimization of Reaction Condition for the Synthesis of 3a

Table S1. Optimization of the Reaction Conditions

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\(a\) Reaction conditions: an aqueous solution of base (0.12 mmol) in water (0.15 mL) was added to a mixture of 1a (0.1 mmol), [Pd] (10 mol%), [Cu] (20 mol%) in solvent (1.5 mL) via syringe bump within 15 minutes and stirred for 30 minutes, at 23 °C, in Ar. \(b\) The yields were determined by \(^1\)H NMR using CH\(_2\)Br\(_2\) as internal standard. \(c\) PPh\(_3\) (0.01 mmol) was used. \(d\) At 40 °C. \(e\) At 60 °C. \(f\) 0.5 equiv base was used. \(g\) 2.0 equiv base was used. \(h\) Pd(OAc)\(_2\) (5 mol%), CuI (20 mol%) were used. \(i\) Pd(OAc)\(_2\) (2 mol%), CuI (20 mol%) were used. \(j\) Pd(OAc)\(_2\) (10 mol%), CuI (15 mol%) were used. \(k\) Pd(OAc)\(_2\) (10 mol%), CuI (10 mol%) were used. \(l\) Pd(OAc)\(_2\) (10 mol%), CuI (10 mol%) were used. \(m\) Pd(OAc)\(_2\) (2 mol%), CuI (20 mol%) were used. \(n\) Pd(OAc)\(_2\) (2 mol%), CuI (15 mol%) were used. \(o\) CuI was added to the mixture after addition of
aqueous solution of K₂CO₃ when the substrate was consumed completely.

3.2 Procedures for the Synthesis of 2a

To a solution of 1a (1.0 equiv, 0.1 mmol) in anhydrous DMSO (1.5 mL) was added Pd(OAc)₂ (2 mol%). The tube was then evacuated and backfilled with argon for 3 times and stirred at 23 °C for 15 minutes. Then an aqueous solution of K₂CO₃ (1.2 equiv) in H₂O (0.15 mL) was added to the mixture via syringe bump with a duration time of 15 minutes and stirred for 30 minutes. After completion of the reaction (monitored by TLC), the mixture was washed with saturated aqueous NH₄Cl solution. The solution was extracted with ethyl acetate (10 mLx3) and the combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/50-1/30) to afford the desired product 2a.

3.3 General Procedures for the Synthesis of 3

To a 10 mL oven-dried Schlenk tube was added 1 (1.0 equiv, 0.1 mmol), Pd(OAc)₂ (2 mol%) and anhydrous DMSO (1.5 mL). The tube was then evacuated and backfilled with argon for 3 times and stirred at 23 °C. Then an aqueous solution of K₂CO₃ (1.2 equiv) in H₂O (0.15 mL) was added to the mixture via syringe bump with a duration time of 15 minutes and stirred for 30 minutes to 4 hours. After complete consumption of 1 (monitored by TLC), CuI (20 mol%) was added to the mixture and stirred for 30 minutes. The mixture was washed with saturated aqueous NH₄Cl solution. The solution was extracted with ethyl acetate (10 mLx3) and the combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/50-1/30) to afford the desired product 3.
4. X-ray Crystallography of 3a

Crystallographic data for compound 3a (CCDC-1582339) has been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).

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Data completeness= 0.989             Theta(max)= 65.780
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S = 1.214                          Npar= 262
5. Characterization Data

2’-Nitro-[1,1’-biphenyl]-2-amine (S3a)
Yellow oil (1112.8 mg, 85% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J = 13.5$ Hz, 1H), 7.67-7.64 (m, 1H), 7.54-7.50 (m, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.21-7.18 (m, 1H), 6.99 (d, $J = 7.5$ Hz, 1H), 6.84-6.80 (m, 1H), 6.77 (d, $J = 12.0$ Hz, 1H), 3.16 (br, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 150.16, 144.02, 134.06, 133.20, 133.10, 129.83, 129.58, 128.98, 124.66, 123.70, 119.2, 116.20; HRMS (ESI) calcd for C$_{12}$H$_{11}$N$_2$O$_2$ [M+H]$^+$ 215.0815, found 215.0819.

5-Methyl-2’-nitro-[1,1’-biphenyl]-2-amine (S3b)
Yellow solid (1162.8 mg, 64% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.94 (dd, $J = 0.8$ Hz, $J = 8.0$ Hz, 1H), 7.66-7.62 (m, 1H), 7.53-7.49 (m, 1H), 7.44 (dd, $J = 0.8$ Hz, $J = 8.4$ Hz, 1H), 7.01 (dd, $J = 1.6$ Hz, $J = 8.0$ Hz, 1H), 6.80 (d, $J = 1.2$ Hz, 1H), 6.69 (d, $J = 8.0$ Hz, 1H), 2.98 (br, 2H), 2.25 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 149.76, 141.15, 133.89, 132.78, 132.76, 130.06, 129.57, 128.48, 128.11, 124.22, 123.52, 116.05, 20.34; HRMS (ESI) calcd for C$_{13}$H$_{13}$N$_2$O$_2$ [M+H]$^+$ 229.0972, found 229.0962.

5-Isopropyl-2’-nitro-[1,1’-biphenyl]-2-amine (S3c)
Yellow oil (1126.4 mg, 74% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95-7.93 (m, 1H),
7.66-7.62 (m, 1H), 7.52-7.47 (m, 2H), 7.07 (dd, \( J = 1.6 \) Hz, \( J = 8.4 \) Hz, 1H), 6.85 (d, \( J = 1.6 \) Hz, 1H), 6.72 (d, \( J = 8.4 \) Hz, 1H), 3.20 (br, 2H), 2.87-2.77 (m, 1H), 1.21 (d, \( J = 6.8 \) Hz, 6H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 149.96, 141.50, 139.47, 134.15, 132.84, 132.76, 128.52, 127.45, 127.21, 124.27, 123.36, 116.08, 33.18, 24.17;

HRMS (ESI) calcd for C\(_{15}\)H\(_{17}\)N\(_2\)O\(_2\) [M+H]\(^+\) 257.1285, found 257.1282.

5-Fluoro-2'-nitro-[1,1'-biphenyl]-2-amine (S3d)

Yellow solid (1368.8 mg, 90% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.00 (d, \( J = 8.0 \) Hz, 1H), 7.70-7.67 (m, 1H), 7.57-7.54 (m, 1H), 7.44 (d, \( J = 7.5 \) Hz, 1H), 6.94-6.90 (m, 1H), 6.75 (dd, \( J = 2.5 \) Hz, \( J = 8.0 \) Hz, 1H), 6.75 (dd, \( J = 5.0 \) Hz, \( J = 9.0 \) Hz, 1H), 3.33 (br, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 156.31 (d, \( J = 236.3 \) Hz), 149.55, 139.94, 133.25, 132.77, 132.66, 129.20, 124.65, 124.60, 116.98 (d, \( J = 7.6 \) Hz), 116.18 (d, \( J = 22.1 \) Hz), 115.95 (d, \( J = 23.3 \) Hz); \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): -126.33 (s, 1F); HRMS (ESI) calcd for C\(_{12}\)H\(_{10}\)FN\(_2\)O\(_2\) [M+H]\(^+\) 233.0721, found 233.0712.

5-chloro-2'-nitro-[1,1'-biphenyl]-2-amine (S3e)

Yellow oil (1513.9 mg, 86% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.96 (d, \( J = 2.4 \) Hz, 1H), 7.63 (dd, \( J = 2.0 \) Hz, \( J = 8.0 \) Hz, 1H), 7.42 (d, \( J = 8.4 \) Hz, 1H), 7.23-7.19 (m, 1H), 6.96 (dd, \( J = 1.6 \) Hz, \( J = 7.6 \) Hz, 1H), 6.84-6.80 (m, 1H), 6.76 (d, \( J = 7.2 \) Hz, 1H), 3.28 (br, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 150.30, 143.96, 134.71, 134.26, 133.37, 132.47, 130.14, 129.51, 124.87, 122.49, 119.32, 116.33; HRMS (ESI) calcd for C\(_{12}\)H\(_{10}\)ClN\(_2\)O\(_2\) [M+H]\(^+\) 249.0425, found 249.0431.
4-Methyl-2'-nitro-[1,1'-biphenyl]-2-amine (S3f)

Yellow oil (570.0 mg, 51% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.93 (dd, $J = 0.8$ Hz, $J = 8.0$ Hz, 1H), 7.65-7.61 (m, 1H), 7.52-7.48 (m, 1H), 7.48-7.44 (m, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.64 (d, $J = 8.0$ Hz, 1H), 6.60 (s, 1H), 3.27 (br, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 150.32, 143.82, 139.84, 134.08, 133.22, 133.07, 129.47, 128.77, 124.58, 120.92, 120.18, 116.90, 21.62; HRMS (ESI) calcd for C$_{13}$H$_{13}$N$_2$O$_2$+ [M+H]$^+$ 229.0972, found 229.0965.

4-Methoxy-2'-nitro-[1,1'-biphenyl]-2-amine (S3g)

Yellow oil (1683.6 mg, 86% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.90 (d, $J = 7.5$ Hz, 1H), 7.64-7.61 (m, 1H), 7.51-7.47 (m, 1H), 7.45 (dd, $J = 0.5$ Hz, $J = 7.5$ Hz, 1H), 6.90 (d, $J = 8.5$ Hz, 1H), 7.39 (dd, $J = 2.5$ Hz, $J = 8.5$ Hz, 1H), 6.32 (d, $J = 2.0$ Hz, 1H), 3.79 (s, 3H), 3.55 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 160.93, 150.24, 145.01, 133.49, 133.18, 132.74, 130.33, 128.46, 124.30, 116.18, 104.69, 101.49, 55.24; HRMS (ESI) calcd for C$_{13}$H$_{13}$N$_2$O$_3$+ [M+H]$^+$ 245.0921, found 245.0914.

2'-Methyl-6'-nitro-[1,1'-biphenyl]-2-amine (S3j)

Yellow oil (1140.0 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.69 (d, $J = 8.0$ Hz, 1H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.42-7.38 (m, 1H), 7.22-7.18 (m, 1H), 6.86-6.84 (m, 1H), 6.81-6.77 (m, 2H), 3.25 (br, 2H), 2.16 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 151.40, 144.38, 141.08, 134.25, 132.57, 129.74, 129.08, 128.63, 122.06, 121.50, 119.15, 115.98, 20.23; HRMS (ESI) calcd for C$_{13}$H$_{13}$N$_2$O$_2$+ [M+H]$^+$ 229.0972, found...
2'-Methoxy-6'-nitro-[1,1'-biphenyl]-2-amine (S3k)

Yellow solid (1122.4 mg, 92% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.50-7.44 (m, 2H), 7.21-7.18 (m, 2H), 6.92 (d, \(J = 7.2\) Hz, 1H), 6.81-6.78 (m, 2H), 3.81 (s, 3H), 3.20 (br, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 158.15, 151.61, 144.60, 129.64, 129.45, 122.19, 118.82, 118.67, 115.78, 115.65, 114.77, 56.64; HRMS (ESI) calcd for C\(_{13}\)H\(_{13}\)N\(_2\)O\(_3\)\(^+\) [M+H]\(^+\) 245.0921, found 245.0921.

5'-Methyl-2'-nitro-[1,1'-biphenyl]-2-amine (S3l)

Yellow oil (809.2 mg, 65% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.89 (d, \(J = 8.5\) Hz, 1H), 7.29 (d, \(J = 8.5\) Hz, 1H), 7.23 (s, 3H), 7.19-7.16 (m, 1H), 6.96 (dd, \(J = 1.5\) Hz, \(J = 7.5\) Hz, 1H), 6.81-6.79 (m, 1H), 6.75 (d, \(J = 8.0\) Hz, 1H), 3.50 (br, 2H), 2.45 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 147.40, 144.21, 143.72, 133.88, 133.30, 129.33, 129.22, 129.16, 124.60, 123.93, 118.81, 115.81, 21.40; HRMS (ESI) calcd for C\(_{13}\)H\(_{13}\)N\(_2\)O\(_2\)\(^+\) [M+H]\(^+\) 229.0972, found 229.0973.

5'-Fluoro-2'-nitro-[1,1'-biphenyl]-2-amine (S3m)

Yellow oil (1044.0 mg, 90% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.05-8.02 (m, 1H), 7.23-7.15 (m, 3H), 6.98 (dd, \(J = 1.2\) Hz, \(J = 7.6\) Hz, 1H), 6.85-6.81 (m, 1H), 6.77 (d, \(J = 8.0\) Hz, 1H).
= 8.0 Hz, 1H), 3.36 (br, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 164.34 (d, \(J = 256.3\) Hz), 145.78, 143.40, 137.05 (d, \(J = 8.8\) Hz), 129.85, 128.91, 127.15 (d, \(J = 10.0\) Hz), 122.52, 119.63 (d, \(J = 23.8\) Hz), 118.97, 116.03, 115.60 (d, \(J = 22.9\) Hz); \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): -103.95 (s, 1F); HRMS (ESI) calcd for C\(_{12}\)H\(_{10}\)FN\(_2\)O\(_2\) [M+H]\(^{+}\) 233.0721, found 233.0717.

\[
\begin{align*}
\text{6'-Nitro-[1,1':3',1'"-terphenyl]-2-amine (S3n)}
\end{align*}
\]

Yellow oil (2262.0 mg, 85% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 8.08\) (d, \(J = 8.5\) Hz, 1H), 7.73 (dd, \(J = 1.5\) Hz, \(J = 8.5\) Hz, 1H), 7.68 (d, \(J = 1.5\) Hz, 1H), 7.64 (d, \(J = 7.5\) Hz, 2H), 7.50-7.47 (m, 2H), 7.45-7.42 (m, 1H), 7.24-7.21 (m, 1H), 7.06-7.05 (m, 1H), 6.87-6.84 (m, 1H), 6.80 (d, \(J = 8.0\) Hz, 1H), 3.54 (br, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 148.42, 146.12, 143.77, 138.55, 134.51, 131.38, 129.58, 129.30, 129.22, 128.93, 127.42, 127.04, 125.22, 123.72, 118.95, 115.94; HRMS (ESI) calcd for C\(_{18}\)H\(_{15}\)N\(_2\)O\(_2\) [M+H]\(^{+}\) 291.1128, found 291.1124.

\[
\begin{align*}
\text{4'-Methyl-2'-nitro-[1,1'-biphenyl]-2-amine (S3o)}
\end{align*}
\]

Yellow oil (1231.2 mg, 90% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.77\) (d, \(J = 0.4\) Hz, 1H), 7.46 (dd, \(J = 0.8\) Hz, \(J = 7.6\) Hz, 1H), 7.33 (d, \(J = 7.6\) Hz, 1H), 7.21-7.16 (m, 1H), 6.98-6.96 (m, 1H), 6.82-6.78 (m, 1H), 6.76 (d, \(J = 8.0\) Hz, 1H), 3.35 (br, 2H), 2.48 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 149.90, 144.13, 139.54, 134.00, 132.82, 131.02, 129.67, 129.63, 124.97, 123.73, 119.12, 116.08, 21.28; HRMS (ESI) calcd for C\(_{18}\)H\(_{13}\)N\(_2\)O\(_2\) [M+H]\(^{+}\) 229.0972, found 229.0966.
5'-Methoxy-2'-nitro-[1,1'-biphenyl]-2-amine (S3p)

Yellow oil (1220.0 mg, 83% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.48 (s, 1H), 7.35 (d, $J$ = 8.5 Hz, 1H), 7.20-7.17 (m, 2H), 6.97 (d, $J$ = 7.5 Hz, 1H), 6.81-6.78 (m, 1H), 6.76 (d, $J$ = 8.0 Hz, 1H), 3.91 (s, 3H), 3.54 (br, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 159.52, 150.30, 144.11, 133.64, 129.64, 129.33, 125.72, 123.34, 119.45, 118.86, 115.79, 109.31, 56.01; HRMS (ESI) calcd for C$_{13}$H$_{13}$N$_2$O$_3$ $^{[M+H]}$ 245.0921, found 245.0918.

3'-Methyl-2'-nitro-[1,1'-biphenyl]-2-amine (S3r)

Yellow oil (1208.4 mg, 88% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46-7.42 (m, 1H), 7.32 (dd, $J$ = 0.4 Hz, $J$ = 7.6 Hz, 1H), 7.28 (d, $J$ = 7.6 Hz, 1H), 7.20-7.15 (m, 1H), 6.99 (dd, $J$ = 1.2 Hz, $J$ = 7.6 Hz, 1H), 6.79-6.74 (m, 2H), 3.44 (br, 2H), 2.39 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 152.12, 144.42, 131.96, 131.03, 130.59, 130.43, 130.12, 129.63, 122.11, 118.88, 116.2017.83; HRMS (ESI) calcd for C$_{13}$H$_{13}$N$_2$O$_2$ $^{[M+H]}$ 229.0972, found 229.0969.

5-Fluoro-5'-methyl-2'-nitro-[1,1'-biphenyl]-2-amine (S3s)

Yellow oil (1230.0 mg, 83% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.94 (d, $J$ = 8.4 Hz, 1H), 7.33 (d, $J$ = 8.4 Hz, 1H), 7.21 (s, 1H), 6.93-6.88 (m, 1H), 6.75-6.68 (m, 2H), 3.44 (br, 2H), 2.47 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 156.31 (d, $J$ = 236.3 Hz), 147.14, 144.60, 139.92, 133.02 (d, $J$ = 30.0 Hz), 129.69, 125.19 (d, $J$ = 7.6 Hz), 125.09. 

S21
124.81, 116.83 (d, $J = 8.8$ Hz), 115.91 (d, $J = 7.9$ Hz), 115.73 (d, $J = 9.0$ Hz), 21.45; 
$^{19}$F NMR (470 MHz, CDCl$_3$): -126.43 (s, 1F); HRMS (ESI) calcd for C$_{13}$H$_{12}$FN$_{2}$O$_2$ [M+H]$^+$ 247.0877, found 247.0867.

2'-Methoxy-5-methyl-6'-nitro-[1,1'-biphenyl]-2-amine (S3t)

Yellow oil (851.0 mg, 56% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48-7.42 (m, 2H), 7.18 (dd, $J = 1.6$ Hz, $J = 7.6$ Hz, 1H), 7.01-6.99 (m, 1H), 6.72-6.69 (m, 2H), 3.82 (s, 3H), 3.43 (br, 2H), 2.23 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 158.24, 151.76, 124.28, 130.25, 130.01, 129.42, 128.00, 122.54, 119.08, 116.10, 115.72, 114.78, 56.76, 24.94, 20.49; HRMS (ESI) calcd for C$_{14}$H$_{15}$N$_2$O$_3$ [M+H]$^+$ 259.1077, found 259.1072.

2-Iodo-2'-nitro-1,1'-biphenyl (S4a)

Yellow solid (1352.0 mg, 80% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.11 (d, $J = 8.0$ Hz, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.70-7.67 (m, 1H), 7.60-7.57 (m, 1H), 7.43-7.39 (m, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.22 (d, $J = 9.0$ Hz, 1H), 7.10-7.07 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 148.46, 143.70, 139.45, 139.30, 133.29, 133.76, 129.76, 129.19, 128.46, 124.78, 98.41; HRMS (ESI) calcd for C$_{12}$H$_9$INO$_2$ [M+H]$^+$ 325.9672, found 325.9673.

2-Iodo-5-methyl-2'-nitro-1,1'-biphenyl (S4b)
Yellow solid (915.3 mg, 54% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.09 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 4.0$ Hz, 1H), 7.69-7.65 (m, 1H), 7.58-7.54 (m, 1H), 7.31-7.29 (m, 1H), 7.03 (d, $J = 1.2$ Hz, 1H), 6.92-6.90 (m, 1H), 2.32 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 148.13, 143.08, 139.15, 138.66, 138.18, 132.86, 132.44, 130.45, 129.65, 128.90, 124.37, 93.94, 20.92; HRMS (ESI) calcd for C$_{13}$H$_{11}$INO$_2^+$ [M+H]$^+$ 339.9829, found 339.9828.

\[ \text{2-Iodo-5-isopropyl-2'-nitro-1,1'-biphenyl (S4c)} \]

Yellow oil (917.5 mg, 59% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.08 (d, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.68-7.66 (m, 1H), 7.58-7.55 (m, 1H), 7.32 (d, $J = 7.5$ Hz, 1H), 7.07 (s, 1H), 6.97 (d, $J = 8.0$ Hz, 1H), 2.92-2.84 (m, 1H), 1.25-1.23 (m, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): 149.49, 148.52, 143.35, 139.58, 139.06, 133.14, 132.84, 129.22, 128.11, 127.58, 124.65, 94.60, 33.98, 24.07, 24.06; HRMS (ESI) calcd for C$_{15}$H$_{15}$INO$_2^+$ [M+H]$^+$ 368.0142, found 368.0163.

\[ \text{5-Fluoro-2-ido-2'-nitro-1,1'-biphenyl (S4d)} \]

Yellow solid (960.4 mg, 47% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.14 (d, $J = 8.4$ Hz, 1H), 7.84 (dd, $J = 5.6$ Hz, $J = 8.8$ Hz, 1H), 7.73-7.69 (m, 1H), 7.63-7.59 (m, 1H), 7.28 (d, $J = 7.8$ Hz, 1H), 6.98 (dd, $J = 2.8$ Hz, $J = 8.8$ Hz, 1H), 6.89-6.84 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 162.73 (d, $J = 247.5$ Hz), 147.76, 145.26 (d, $J = 7.5$ Hz), 140.15 (d, $J = 7.5$ Hz), 138.10 (d, $J = 1.3$ Hz), 133.25, 132.08, 129.48, 124.64, 116.77 (d, $J = 51.5$ Hz), 116.60 (d, $J = 53.1$ Hz), 91.14 (d, $J = 3.8$ Hz); $^{19}$F NMR (470 MHz, CDCl$_3$): -113.87 (s, 1F); HRMS (ESI) calcd for C$_{12}$H$_8$FINO$_2^+$ [M+H]$^+$ 343.9578,
found 343.9592.

\[
\begin{align*}
\text{5-chloro-2-iodo-2'-nitro-1,1'-biphenyl (S4e)} \\
\text{Yellow solid (853.9 mg, 39% yield). }^1\text{H NMR (400 MHz, CDCl}\_3): \delta 8.09 (d, J = 2.4 \\
\text{Hz, 1H}), 7.90 (dd, J = 0.8 Hz, J = 8.0 Hz, 1H), 7.64 (dd, J = 2.0 Hz, J = 8.0 Hz, 1H), \\
7.42-7.38 (m, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.17 (dd, J = 1.6 Hz, J = 7.6 Hz, 1H), \\
7.11-7.07 (m, 1H); ^13\text{C NMR (125 MHz, CDCl}\_3): 148.68, 142.55, 139.39, 137.81, \\
135.24, 133.87, 133.45, 130.09, 129.17, 128.59, 122.02, 98.31; HRMS (ESI) calcd for \\
\text{C}_{12}\text{H}_8\text{ClINO}_2^+ [M+H]^+ 359.9283, found 359.9279.
\end{align*}
\]

\[
\begin{align*}
\text{2-Iodo-4-methyl-2'-nitro-1,1'-biphenyl (S4f)} \\
\text{Yellow solid (440.7 mg, 53% yield). }^1\text{H NMR (400 MHz, CDCl}\_3): \delta 8.08-8.06 (m, \\
1H), 7.76 (s, 1H), 7.66-7.64 (m, 1H), 7.58-7.56(m, 1H), 7.31-7.29 (m, 1H), 7.22-7.20 \\
(m, 1H), 7.09 (d, J = 7.6 Hz, 1H), 2.36 (s, 3H); ^13\text{C NMR (125 MHz, CDCl}\_3): 148.67, \\
140.62, 139.95, 139.76, 139.31, 133.15, 132.95, 129.30, 129.22, 128.83, 124.68, \\
98.25; HRMS (ESI) calcd for C_{13}\text{H}_{11}\text{INO}_2^+ [M+H]^+ 339.9829, found 339.9859.
\end{align*}
\]

\[
\begin{align*}
\text{2-Iodo-4-methoxy-2'-nitro-1,1'-biphenyl (S4g)} \\
\text{Yellow oil (340.8 mg, 14% yield). }^1\text{H NMR (500 MHz, CDCl}\_3): \delta 8.06 (d, J = 0.5 Hz, \\
1H), 7.67-7.64 (m, 1H), 7.57-7.53 (m, 1H), 7.45 (d, J = 2.5 Hz, 1H), 7.31 (dd, J = 1.0
\end{align*}
\]
Hz, $J = 8.0$ Hz, 1H), 7.11 (d, $J = 8.5$ Hz, 1H), 6.95 (dd, $J = 2.5$ Hz, $J = 8.0$ Hz, 1H), 3.83 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 159.49, 148.72, 138.77, 135.47, 132.99, 132.77, 129.31, 128.94, 124.40, 124.32, 114.32, 98.22, 55.64; HRMS (ESI) calcd for C$_{13}$H$_{11}$INO$_3^+$ [M+H]$^+$ 355.9778, found 355.9775.

2'-Iodo-2-methyl-6-nitro-1,1'-biphenyl (S4j)
Pale yellow solid (1525.5 mg, 90% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.94 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.55 (d, $J = 7.5$ Hz, 1H), 7.47-7.44 (m, 1H), 7.43-7.40 (m, 1H), 7.13 (d, $J = 7.5$ Hz, 1H), 7.10-7.07 (m, 1H), 2.06 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 149.25, 142.23, 139.63, 139.43, 138.10, 134.95, 129.67, 129.19, 128.90, 128.74, 122.09, 99.35, 20.68; HRMS (ESI) calcd for C$_{13}$H$_{11}$INO$_2^+$ [M+H]$^+$ 339.9829, found 339.9871.

2'-Iodo-2-methoxy-6-nitro-1,1'-biphenyl (S4k)
Pale yellow solid (887.5 mg, 50% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.93-7.91 (m, 1H), 7.61-7.59 (m, 1H), 7.54-7.50 (m, 1H), 7.41-7.37 (m, 1H), 7.21 (d, $J = 8.0$ Hz, 1H), 7.14-7.12 (m, 1H), 7.09-7.05 (m, 1H), 3.81 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 157.69, 149.56, 139.11, 138.78, 129.65, 129.48, 129.31, 128.03, 127.88, 115.85, 115.38, 99.77, 56.60; HRMS (ESI) calcd for C$_{13}$H$_{14}$INO$_3^+$ [M+H]$^+$ 355.9778, found 355.9767.
2'-Iodo-5-methyl-2-nitro-1,1'-biphenyl (S4l)

Yellow solid (644.1 mg, 52% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.90 (dd, $J = 0.8$ Hz, $J = 8.0$ Hz, 1H), 7.42-7.38 (m, 1H), 7.36 (dd, $J = 1.6$ Hz, $J = 8.4$ Hz, 1H), 7.21-7.19 (m, 1H), 7.10-7.05 (m, 2H), 2.47 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 145.82, 144.38, 143.86, 139.27, 138.90, 132.91, 129.64, 129.30, 128.82, 128.14, 124.71, 98.15, 21.50; HRMS (ESI) calcd for C$_{13}$H$_{11}$INO$_2$ $^{[M+H]}^+$ 339.9829, found 339.9821.

5-Fluoro-2'-iodo-2-nitro-1,1'-biphenyl (S4m)

Pale yellow oil (1303.4 mg, 78% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.19 (dd, $J = 5.2$ Hz, $J = 9.2$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.44-7.40 (m, 1H), 7.28-7.23 (m, 1H), 7.20 (dd, $J = 1.2$ Hz, $J = 7.6$ Hz, 1H), 7.13-7.09 (m, 1H), 7.01 (dd, $J = 2.4$ Hz, $J = 8.4$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 164.34 (d, $J = 256.3$ Hz), 144.20, 142.43, 142.13 (d, $J = 10.0$ Hz), 139.03, 129.75, 128.53, 128.23, 127.38 (d, $J = 10.0$ Hz), 119.43 (d, $J = 22.5$ Hz), 116.05 (d, $J = 22.5$ Hz), 97.38; $^{19}$F NMR (470 MHz, CDCl$_3$): -103.39 (s, 1F); HRMS (ESI) calcd for C$_{12}$H$_8$FINO$_2$ $^{[M+H]}^+$ 343.9578, found 343.9546.

2-Iodo-6'-nitro-1,1':3',1''-terphenyl (S4n)
Yellow oil (1082.7 mg, 34% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.20 (d, $J = 8.4$ Hz, 1H), 7.95-7.93 (m, 1H), 7.77 (dd, $J = 2.0$ Hz, $J = 8.4$ Hz, 1H), 7.65-7.64 (m, 2H), 7.51-7.40 (m, 5H), 7.26 (dd, $J = 2.0$ Hz, $J = 7.6$ Hz, 1H), 7.12-7.08 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 146.69, 146.00, 143.56, 139.70, 138.97, 138.41, 130.99, 129.41, 129.13, 128.93, 128.81, 128.14, 127.37, 127.30, 125.20, 98.12; HRMS (ESI) calcd for C$_{18}$H$_{13}$INO$_2$ [M+H]$^+$ 401.9985, found 401.9995.

![Structure 1](image1)

2'-Iodo-4-methyl-2-nitro-1,1'-biphenyl (S4o)

Yellow oil (915.3 mg, 50% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.92-7.90 (m, 2H), 7.49 (dd, $J = 0.8$ Hz, $J = 8.0$ Hz, 1H), 7.41-7.37 (m, 1H), 7.21-7.17 (m, 2H), 7.09-7.05 (m, 1H), 2.51 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 148.17, 143.73, 139.98, 139.20, 136.65, 134.07, 132.46, 129.61, 129.30, 128.43, 125.08, 98.80, 21.40; HRMS (ESI) calcd for C$_{13}$H$_{11}$INO$_2$ [M+H]$^+$ 339.9829, found 339.9837.

![Structure 2](image2)

2'-Iodo-5-methoxy-2-nitro-1,1'-biphenyl (S4p)

Pale yellow oil (710.0 mg, 40% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.91 (d, $J = 7.5$ Hz, 1H), 7.61 (s, 1H), 7.40-7.37 (m, 1H), 7.20 (s, 3H), 7.08-7.05 (m, 1H), 3.94 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 159.76, 148.67, 143.36, 138.96, 133.26, 131.63, 129.32, 129.28, 128.19, 119.52, 109.17, 99.15, 56.03; HRMS (ESI) calcd for C$_{13}$H$_{11}$INO$_3$ [M+H]$^+$ 355.9778, found 355.9756.

![Structure 3](image3)
2'-Iodo-3-methyl-2-nitro-1,1'-biphenyl (S4r)

Yellow oil (1084.8 mg, 61% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J = 8.0$ Hz, 1H), 7.45-7.42 (m, 1H), 7.36-7.34 (m, 2H), 7.25-7.23 (m, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.08-7.05 (m, 1H), 2.40 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 150.53, 141.50, 139.33, 136.67, 131.17, 130.01, 129.99, 129.83, 129.61, 129.28, 128.01, 98.97, 17.78; HRMS (ESI) calcd for C$_{13}$H$_{11}$INO$_2$ $^+$ [M+H]$^+$ 339.98, found 339.9834.

![Structure 2'-Iodo-3-methyl-2-nitro-1,1'-biphenyl (S4r)](image)

5-Fluoro-2-iodo-5'-methyl-2'-nitro-1,1'-biphenyl (S4s)

Yellow oil (821.1 mg, 46% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.07 (d, $J = 8.5$ Hz, 1H), 7.83 (dd, $J = 5.5$ Hz, $J = 9.0$ Hz, 1H), 7.38 (dd, $J = 1.0$ Hz, $J = 8.5$ Hz, 1H), 7.06 (d, $J = 1.0$ Hz, 1H), 6.98-6.95 (m, 1H), 6.86-6.83 (m, 1H), 2.48 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 162.74 (d, $J = 247.5$ Hz), 145.70 (d, $J = 8.0$ Hz), 145.44, 144.68, 140.04 (d, $J = 7.8$ Hz), 138.20, 132.51, 129.97, 124.82, 116.68 (d, $J = 21.5$ Hz), 116.39 (d, $J = 22.8$ Hz), 91.16 (d, $J = 3.8$ Hz), 21.42; $^{19}$F NMR (470 MHz, CDCl$_3$): -114.05 (s, 1F); HRMS (ESI) calcd for C$_{13}$H$_{10}$FINO$_2$ $^+$ [M+H]$^+$ 357.9735, found 357.9745.

![Structure 5-Fluoro-2-iodo-5'-methyl-2'-nitro-1,1'-biphenyl (S4s)](image)

2-Iodo-2'-methoxy-5-methyl-6'-nitro-1,1'-biphenyl (S4t)

Yellow solid (553.5 mg, 46% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (d, $J = 8.0$ Hz, 1H), 7.58 (dd, $J = 0.8$ Hz, $J = 8.4$ Hz, 1H), 7.53-7.49 (m, 1H), 7.21-7.19 (m, 1H), 6.94 (d, $J = 1.6$ Hz, 1H), 6.89 (dd, $J = 1.6$ Hz, $J = 8.4$ Hz, 1H), 3.81 (s, 3H), 2.30 (s, 3H), 1.95 (s, 3H).
3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 157.78, 149.71, 138.86, 138.56, 138.13, 130.51, 130.27, 129.62, 127.96, 115.87, 115.40, 95.82, 56.70, 21.05; HRMS (ESI) calcd for C$_{14}$H$_{13}$INO$_3$ $^{+}$ [M+H]$^+$ 369.9935, found 369.9945.

![Image of 2'-Iodo-[1,1'-biphenyl]-2-amine (S5a)]

2'-Iodo-[1,1'-biphenyl]-2-amine (S5a)

Colorless oil (354.0 mg, 30% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.99-7.97 (m, 1H), 7.45-7.41 (m, 1H), 7.33-7.31 (m, 1H), 7.25-7.20 (m, 1H), 7.09-7.05 (m, 1H), 6.99-6.97 (m, 1H), 6.86-6.84 (m, 1H), 6.78 (d, $J = 8.4$ Hz, 1H), 3.19 (br, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 144.50, 143.57, 139.84, 131.00, 130.74, 130.43, 129.55, 129.49, 129.00, 118.61, 115.87, 100.96; HRMS (ESI) calcd for C$_{12}$H$_{11}$IN$^+$ [M+H]$^+$ 295.9931, found 295.9926.

![Image of 2'-Iodo-5'-methyl-[1,1'-biphenyl]-2-amine (S5b)]

2'-Iodo-5'-methyl-[1,1'-biphenyl]-2-amine (S5b)

Yellow oil (309.0 mg, 40% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.84 (d, $J = 10.0$ Hz, 1H), 7.24-7.20 (m, 1H), 7.15 (d, $J = 1.0$ Hz, 1H), 6.98-6.97 (m, 1H), 6.90 (dd, $J = 1.2$ Hz, $J = 8.0$ Hz, 1H), 6.85-6.82 (m, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 3.52 (br, 2H), 2.34 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 143.99, 143.32, 139.27, 138.80, 131.58, 130.54, 130.31, 130.12, 129.11, 118.32, 115.56, 96.40, 20.96; HRMS (ESI) calcd for C$_{13}$H$_{13}$IN$^+$ [M+H]$^+$ 310.0087, found 310.0076.

![Image of 2'-Iodo-5'-isopropyl-[1,1'-biphenyl]-2-amine (S5c)]

2'-Iodo-5'-isopropyl-[1,1'-biphenyl]-2-amine (S5c)
Colorless oil (674.0 mg, 87% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88 (d, $J = 8.0$ Hz, 1H), 7.26-7.20 (m, 2H), 7.01-6.94 (m, 2H), 6.86-6.82 (m, 1H), 6.79 (dd, $J = 0.4$ Hz, $J = 8.0$ Hz, 1H), 3.27 (br, 2H), 2.95-2.85 (m, 1H), 1.26 (d, $J = 7.2$ Hz, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): 150.09, 144.27, 143.61, 139.61, 130.92, 130.49, 129.37, 129.30, 127.95, 118354, 115300, 9700, 3402, 241, 2410; HRMS (ESI) calcd for C$_{15}$H$_{17}$IN$^+$ [M+H]$^+$ 338.0400, found 338.0401.

$5'$-Fluoro-2'-iodo-[1,1'-biphenyl]-2-amine (S5d)

Colorless oil (719.9 mg, 84% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.91-7.88 (m, 1H), 7.23-7.19 (m, 1H), 7.06 (dd, $J = 3.0$ Hz, $J = 9.0$ Hz, 1H), 6.94 (dd, $J = 1.5$ Hz, $J = 7.5$ Hz, 1H), 6.84-6.80 (m, 2H), 6.76 (d, $J = 8.0$ Hz, 1H), 3.33 (br, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 163.22 (d, $J = 247.5$ Hz), 146.23 (d, $J = 8.8$ Hz), 143.08, 140.75 (d, $J = 8.8$ Hz), 129.74 (d, $J = 41.6$ Hz), 129.36, 118.40, 118.05 (d, $J = 21.4$ Hz), 116.78 (d, $J = 21.5$ Hz), 115.74, 93.59 (d, $J = 1.3$ Hz); $^{19}$F NMR (470 MHz, CDCl$_3$): -113.49 (s, 1F); HRMS (ESI) calcd for C$_{12}$H$_{10}$FIN$^+$ [M+H]$^+$ 313.9836, found 313.9829.

$5'$-chloro-2'-iodo-[1,1'-biphenyl]-2-amine (S5e)

Colorless oil (590.0 mg, 74% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J = 0.8$ Hz, 1H), 7.45-7.41 (m, 1H), 7.28-7.26 (m, 1H), 7.09-7.05 (m, 1H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.80-6.76 (m, 2H), 3.12 (br, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 144.83, 143.37, 139.98, 134.92, 131.54, 131.03, 129.87, 129.12, 128.93, 118.58, 115.50, 100.81; HRMS (ESI) calcd for C$_{12}$H$_{10}$ClIN$^+$ [M+H]$^+$ 329.9541, found 329.9547.
2'-Iodo-4'-methyl-[1,1'-biphenyl]-2-amine (S5f)

Colorless oil (339.9 mg, 85% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (s, 1H), 7.26-7.17 (m, 3H), 6.97-6.95 (m, 1H), 6.84-6.80 (m, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 3.17 (br, 2H), 2.36 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 143.52, 141.21, 140.00, 139.39, 130.40, 130.33, 129.61, 129.11, 118.33, 115.55, 100.55, 20.62; HRMS (ESI) calcd for C$_{13}$H$_{13}$IN$^+$ [M+H]$^+$ 310.0087, found 310.0080.

2'-Iodo-4'-methoxy-[1,1'-biphenyl]-2-amine (S5g)

Pale yellow solid (182.3 mg, 57% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.5 (d, $J = 2.4$ Hz, 1H), 7.22-7.18 (m, 2H), 6.99-6.95 (m, 2H), 6.83-6.80 (m, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 3.83 (s, 3H), 3.41 (br, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 159.31, 143.80, 136.43, 130.89, 130.70, 130.10, 129.10, 124.61, 118.28, 115.48, 114.91, 100.70, 55.66; HRMS (ESI) calcd for C$_{13}$H$_{13}$INO$^+$ [M+H]$^+$ 326.0036, found 326.0036.

2'-Iodo-6-methyl-[1,1'-biphenyl]-2-amine (S5j)

Colorless oil (1266.9 mg, 91% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.00 (d, $J = 8.0$ Hz, 1H), 7.46-7.43 (m, 1H), 7.23 (d, $J = 7.5$ Hz, 1H), 7.12-7.09 (m, 1H), 7.07-7.04 (m, 1H), 6.70 (d, $J = 7.5$ Hz, 1H), 6.63 (d, $J = 8.0$ Hz, 1H), 3.22 (br, 2H), 1.92 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 143.75, 143.68, 140.02, 136.97, 130.94, 130.65, 129.47, 128.99, 120.24, 113.30, 101.69, 20.51; HRMS (ESI) calcd for C$_{13}$H$_{13}$IN$^+$ [M+H]$^+$ 310.0087, found 310.0076.
2'-Iodo-6-methoxy-[1,1'-biphenyl]-2-amine (S5k)

Colorless oil (357.5 mg, 44% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.98 (d, \(J = 8.0\) Hz, 1H), 7.46-7.42 (m, 1H), 7.28-7.26 (m, 1H), 7.20-7.16 (m, 1H), 7.07-7.03 (m, 1H), 6.43 (dd, \(J = 8.0\) Hz, \(J = 13.2\) Hz, 2H), 3.71 (s, 3H), 2.58 (br, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 157.46, 144.67, 140.83, 139.50, 131.25, 129.49, 129.07, 128.75, 119.38, 108.51, 102.17, 101.12, 55.76; HRMS (ESI) calcd for \(\text{C}_{13}\text{H}_{13}\text{INO}^+\ [M+H]^+\) 326.0036, found 326.0030.

2'-Iodo-5-methyl-[1,1'-biphenyl]-2-amine (S5l)

Colorless oil (370.8 mg, 64% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.97 (d, \(J = 8.0\) Hz, 1H), 7.43-7.40 (m, 1H), 7.30 (dd, \(J = 1.0\) Hz, \(J = 7.5\) Hz, 1H), 7.07-7.02 (m, 2H), 6.80 (s, 1H), 6.70 (d, \(J = 8.0\) Hz, 1H), 3.00 (br, 2H), 2.29 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 144.38, 140.69, 139.40, 130.66, 130.53, 130.45, 129.67, 129.07, 128.59, 127.48, 115.70, 100.53, 20.42; HRMS (ESI) calcd for \(\text{C}_{13}\text{H}_{13}\text{IN}^+\ [M+H]^+\) 310.0087, found 310.0089.

5-Fluoro-2'-iodo-[1,1'-biphenyl]-2-amine (S5m)

Colorless oil (594.7 mg, 50% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.97 (d, \(J = 8.0\) Hz, 1H), 7.45-7.41 (m, 1H), 7.30-7.27 (m, 1H), 7.10-7.06 (m, 1H), 6.96-6.91 (m, 1H),
6.74-6.69 (m, 2H), 2.71 (br, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 155.90 (d, \(J = 235.0\) Hz), 143.16, 139.55 (d, \(J = 20.0\) Hz), 131.19 (d, \(J = 7.5\) Hz), 130.51, 129.57, 128.77, 116.59 (d, \(J = 7.5\) Hz), 116.46 (d, \(J = 7.5\) Hz), 115.72 (d, \(J = 22.1\) Hz), 99.92; \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): -126.82 (s, 1F); HRMS (ESI) calcd for C\(_{12}\)H\(_{10}\)FIN\(^{+}\) [M+H]\(^{+}\) 313.9836, found 3313.9829.

\[ \text{2''-Iodo-[1,1':3',1''-terphenyl]-4'-amine (S5n)} \]
Yellow oil (704.9 mg, 71% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 8.01\) (dd, \(J = 1.0\) Hz, \(J = 8.0\) Hz, 1H), 7.60-7.58 (m, 2H), 7.51-7.49 (m, 1H), 7.47-7.44 (m, 1H), 7.41-7.37 (m, 3H), 7.28-7.26 (m, 2H), 7.10-7.07 (m, 1H), 6.86 (d, \(J = 8.5\) Hz, 1H), 3.35 (br, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 144.12, 142.81, 140.95, 139.71, 131.32, 130.81, 130.64, 129.41, 128.96, 128.78, 128.74, 127.79, 126.46, 126.40, 115.98, 100.70; HRMS (ESI) calcd for C\(_{18}\)H\(_{15}\)IN\(^{+}\) [M+H]\(^{+}\) 372.0244, found 372.0239.

\[ \text{2'-Iodo-4-methyl-[1,1'-biphenyl]-2'-amine (S5o)} \]
Colorless oil (741.6 mg, 90% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.97\) (dd, \(J = 0.8\) Hz, \(J = 8.0\) Hz, 1H), 7.44-7.39 (m, 1H), 7.31-7.29 (m, 1H), 7.07-7.03 (m, 1H), 6.87 (d, \(J = 7.6\) Hz, 1H), 6.67 (d, \(J = 7.6\) Hz, 1H), 6.62 (s, 1H), 3.11 (br, 2H), 2.33 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 144.53, 143.30, 139.78, 139.44, 131.19, 130.29, 129.44, 128.97, 128.19, 119.61, 116.57, 101.32, 21.57; HRMS (ESI) calcd for C\(_{13}\)H\(_{13}\)IN\(^{+}\) [M+H]\(^{+}\) 310.0087, found 310.0077.
2'-Iodo-5-methoxy-[1,1'-biphenyl]-2-amine (S5p)

Green solid (552.5 mg, 84% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.97\) (dd, \(J = 1.2\) Hz, \(J = 8.0\) Hz, 1H), 7.43-7.39 (m, 1H), 7.31 (dd, \(J = 2.0\) Hz, \(J = 7.6\) Hz, 1H), 7.07-7.02 (m, 1H), 6.89 (d, \(J = 8.4\) Hz, 1H), 6.41 (dd, \(J = 2.4\) Hz, \(J = 8.4\) Hz, 1H), 6.33 (d, \(J = 2.4\) Hz, 1H), 3.82 (s, 3H), 3.42 (br, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 160.61, 144.52, 144.06, 139.54, 131.18, 131.09, 129.15, 128.68, 123.81, 104.00, 101.70, 100.95, 55.20; HRMS (ESI) calcd for C\(_{13}\)H\(_{13}\)INO\(^+\) [M+H]\(^+\) 326.0036, found 326.0040.

\[
\begin{align*}
\text{NH}_2
\end{align*}
\]

2'-Iodo-3-methyl-[1,1'-biphenyl]-2-amine (S5r)

Colorless oil (463.5 mg, 49% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.99\) (d, \(J = 3.0\) Hz, 1H), 7.44-7.41 (m, 1H), 7.32 (dd, \(J = 1.5\) Hz, \(J = 7.5\) Hz, 1H), 7.13 (d, \(J = 7.5\) Hz, 1H), 7.08-7.05 (m, 1H), 6.86 (d, \(J = 7.5\) Hz, 1H), 6.79-6.76 (m, 1H), 3.43 (br, 2H), 2.23 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 144.61, 141.54, 139.63, 131.09, 129.15, 123.81, 104.00, 101.70, 100.95, 55.20; HRMS (ESI) calcd for C\(_{13}\)H\(_{13}\)IN\(^+\) [M+H]\(^+\) 310.0087, found 310.0083.

\[
\begin{align*}
\text{NH}_2
\end{align*}
\]

5'-Fluoro-2'-iodo-5-methyl-[1,1'-biphenyl]-2-amine (S5s)

Colorless oil (654.0 mg, 89% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.90\) (dd, \(J = 5.5\) Hz, \(J = 9.0\) Hz, 1H), 7.07-7.03 (m, 2H), 6.85-6.81 (m, 1H), 6.78 (d, \(J = 1.0\) Hz, 1H), 6.70 (d, \(J = 8.0\) Hz, 1H), 3.25 (br, 2H), 2.29 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 163.25 (d, \(J = 247.5\) Hz), 146.52 (d, \(J = 7.5\) Hz), 140.69 (d, \(J = 8.8\) Hz), 140.60, 130.22 (d, \(J = 12.5\) Hz), 129.58, 127.74, 118.10 (d, \(J = 21.3\) Hz), 116.70 (d, \(J = 21.5\) Hz), 115.98, 93.53, 20.48; \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): -113.77 (s, 1F); HRMS (ESI)
calcd for C_{13}H_{12}F\text{IN}^+ [M+H]^+ 327.9993, found 327.9986.

![Chemical Structure](image)

2'-Iodo-6-methoxy-5'-2qmehtyl-[1,1'-biphenyl]-2-amine (S5t)

Pale yellow solid (440.7 mg, 85% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.85 (d, $J = 8.0$ Hz, 1H), 7.19-7.15 (m, 1H), 7.10 (d, $J = 2.0$ Hz, 1H), 6.88 (dd, $J = 2.0$ Hz, $J = 8.0$ Hz, 1H), 6.42 (dd, $J = 8.0$ Hz, $J = 13.0$ Hz, 2H), 3.73 (s, 3H), 3.14 (br, 2H), 2.34 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 157.50, 144.77, 140.58, 139.25, 138.80, 132.05, 130.23, 129.43, 119.44, 108.56, 101.19, 98.00, 55.85, 21.03; HRMS (ESI) calcd for C_{14}H_{15}NO+ [M+H]$^+ 340.0193$, found 340.0203.

![Chemical Structure](image)

2-Iodo-2'-isocyano-1,1'-biphenyl (1a)

Green solid (244.0 mg, 67% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J = 8.0$ Hz, 1H), 7.49-7.43 (m, 4H), 7.31-7.27 (m, 2H), 7.15-7.10 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 167.27, 142.57, 141.94, 139.71, 131.11, 130.34, 130.23, 129.46, 129.29, 128.61, 127.30, 125.95, 98.95; HRMS (ESI) calcd for C_{13}H_{11}NO$^+$ [M+H]$^+ 305.9774$, found 305.9776.

![Chemical Structure](image)

2-Iodo-2'-isocyano-5-methyl-1,1'-biphenyl (1b)

Green solid (191.4 mg, 61% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 8.4$ Hz, 1H), 7.49-7.41 (m, 3H), 7.29-7.27 (m, 1H), 7.09 (d, $J = 1.6$ Hz, 1H), 6.95 (dd, $J = 1.6$ Hz, $J = 8.0$ Hz, 1H), 2.35 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 166.78, 142.00,
141.67, 139.06, 138.31, 131.00, 130.75, 130.72, 129.06, 128.80, 126.90, 94.42, 20.89; HRMS (ESI) calcd for C₁₄H₁₁IN⁺ [M+H]⁺ 319.9931, found 319.9925.

\[
\text{2-Iodo-2'}\text{-isocyano-5-isopropyl-1,1'-biphenyl (1c)}
\]
Green oil (381.7 mg, 57% yield). \(^1\)H NMR (500 MHz, CDCl₃): \(\delta\) 7.87 (d, \(J = 8.0\ Hz, 1H\)), 7.49-7.42 (m, 3H), 7.32 (d, \(J = 7.5\ Hz, 1H\)), 7.14 (s, 1H), 7.00 (d, \(J = 8.0\ Hz, 1H\)), 2.96-2.87 (m, 1H), 1.27 (d, \(J = 1.0\ Hz, 1H\)); \(^{13}\)C NMR (125 MHz, CDCl₃): 167.18, 149.65, 142.26, 142.14, 139.54, 131.28, 129.36, 129.13, 128.73, 128.67, 127.31, 125.98, 95.06, 34.07, 24.16, 24.05; HRMS (ESI) calcd for C₁₆H₁₅IN⁺ [M+H]⁺ 348.0244, found 348.0244.

\[
\text{5-Fluoro-2-iodo-2'}\text{-isocyano-1,1'-biphenyl (1d)}
\]
Green solid (419.9 mg, 69% yield). \(^1\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.92 (dd, \(J = 5.6\ Hz, J = 8.8\ Hz, 1H\)), 7.49-7.48 (m, 3H), 7.29-7.26 (m, 1H), 7.04 (dd, \(J = 3.2\ Hz, J = 8.8\ Hz, 1H\)), 6.93-6.88 (m, 1H); \(^{13}\)C NMR (125 MHz, CDCl₃): 167.46, 162.74 (d, \(J = 247.5\ Hz\)), 161.75, 143.98 (d, \(J = 7.5\ Hz\)), 140.64 (d, \(J = 8.0\ Hz\)), 140.52, 130.44, 129.33 (d, \(J = 11.3\ Hz\)), 127.04, 117.60 (d, \(J = 15.0\ Hz\)), 117.41 (d, \(J = 16.3\ Hz\)), 91.70 (d, \(J = 3.8\ Hz\)); \(^{19}\)F NMR (470 MHz, CDCl₃): -113.61 (s, 1F); HRMS (ESI) calcd for C₁₃H₈FIN⁺ [M+H]⁺ 323.9680, found 323.9670.
5-chloro-2-iodo-2'-isocyano-1,1'-biphenyl (1e)

Green solid (202.8 mg, 34% yield). $^1$H NMR (500 MHz, CDCl$_3$): 7.98 (dd, $J = 1.0$ Hz, $J = 8.0$ Hz, 1H), 7.49-7.43 (m, 3H), 7.26-7.23 (m, 2H), 7.15-7.12 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 168.94, 141.47, 140.40, 139.82, 134.89, 132.23, 130.65, 130.20, 129.93, 128.73, 127.32, 98.81; HRMS (ESI) calcd for C$_{13}$H$_8$ClIN+ [M+H]$^+$ 339.9384, found 339.9379.

![Chemical structure of 5-chloro-2-iodo-2'-isocyano-1,1'-biphenyl (1e)](image)

2-Iodo-2'-isocyano-4-methyl-1,1'-biphenyl (1f)

Green oil (159.5 mg, 50% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (s, 1H), 7.47-7.39 (m, 3H), 7.28 (d, $J = 8.4$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.14 (d, $J = 8.0$ Hz, 1H), 2.37 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 166.91, 141.65, 140.27, 139.91, 139.36, 131.07, 129.58, 129.19, 129.12, 128.85, 126.97, 125.85, 98.52, 20.72; HRMS (ESI) calcd for C$_{14}$H$_{11}$IN+ [M+H]$^+$ 319.9931, found 319.9924.

![Chemical structure of 2-Iodo-2'-isocyano-4-methyl-1,1'-biphenyl (1f)](image)

2-Iodo-2'-isocyano-4-methoxy-1,1'-biphenyl (1g)

White solid (100.5 mg, 59% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.50 (s, 1H), 7.47-7.40 (m, 3H), 7.29 (d, $J = 9.0$ Hz, 1H), 7.17 (d, $J = 7.5$ Hz, 1H), 6.99 (d, $J = 8.5$ Hz, 1H), 3.84 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 166.82, 159.83, 141.40, 134.58, 131.37, 130.26, 129.08, 128.81, 126.96, 124.59, 114.47, 98.73, 55.65; HRMS (ESI) calcd for C$_{14}$H$_{11}$INO+ [M+H]$^+$ 335.9880, found 335.9882.

![Chemical structure of 2-Iodo-2'-isocyano-4-methoxy-1,1'-biphenyl (1g)](image)

2'-Iodo-2'-isocyano-6-methyl-1,1'-biphenyl (1j)
Green solid (638.0 mg, 42% yield). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.99 (d, $J = 8.0$ Hz, 1H), 7.49-7.46 (m, 1H), 7.34-7.32 (m, 3H), 7.19 (d, $J = 7.5$ Hz, 1H), 7.15-7.11 (m, 1H), 2.06 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 166.47, 142.16, 141.57, 139.75, 138.45, 131.21, 130.18, 129.80, 129.05, 128.96, 126.31, 124.62, 99.30, 20.61; HRMS (ESI) calcd for C$_{14}$H$_{11}$N$^+$ [M+H]$^+$ 319.9931, found 319.9941.

2'-Iodo-2-isocyno-6-methoxy-1,1'-biphenyl (1k)

White solid (201.0 mg, 54% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.97 (d, $J = 8.0$ Hz, 1H), 7.48-7.44 (m, 1H), 7.42-7.38 (m, 1H), 7.22 (d, $J = 6.8$ Hz, 1H), 7.14-7.09 (m, 2H), 7.02 (d, $J = 8.8$ Hz, 1H), 3.79 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 166.52, 157.32, 139.13, 139.11, 130.97, 130.32, 129.75, 128.30, 126.67, 118.92, 112.13, 99.77, 56.18; HRMS (ESI) calcd for C$_{14}$H$_{11}$NO$^+$ [M+H]$^+$ 335.9880, found 335.9887.

2'-Iodo-2-isocyno-5-methyl-1,1'-biphenyl (1l)

Green solid (223.3 mg, 58% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.97 (dd, $J = 0.8$ Hz, $J = 8.0$ Hz, 1H), 7.46-7.42 (m, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.27-7.22 (m, 2H), 7.13-7.09 (m, 2H), 2.42 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 166.23, 142.47, 141.42, 139.60, 139.38, 131.29, 129.95, 129.61, 128.29, 126.80, 123.18, 98.73, 21.42; HRMS (ESI) calcd for C$_{14}$H$_{11}$N$^+$ [M+H]$^+$ 319.9931, found 319.9932.

5-Fluoro-2'-iodo-2-isocyno-1,1'-biphenyl (1m)
Green oil (468.4 mg, 76% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.99 (d, $J = 8.0$ Hz, 1H), 7.50-7.45 (m, 2H), 7.28-7.26 (m, 1H), 7.17-7.13 (m, 2H), 7.02 (dd, $J = 1.6$ Hz, $J = 8.4$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 167.15, 161.72 (d, $J = 251.3$ Hz), 143.74 (d, $J = 8.8$ Hz), 141.11, 139.46, 130.35, 129.65, 128.82 (d, $J = 9.3$ Hz), 128.35, 121.93, 117.97 (d, $J = 23.5$ Hz), 116.13 (d, $J = 23.0$ Hz), 97.97; $^{19}$F NMR (470 MHz, CDCl$_3$): -108.67 (s, 1F); HRMS (ESI) calcd for C$_{13}$H$_8$F$_{16}$N$^+$ [M+H]$^+$ 323.9680, found 323.9672.

2-Iodo-6'-isocyano-1,1':3',1''-terphenyl (1n)

Green solid (266.7 mg, 37% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.03 (d, $J = 8.0$ Hz, 1H), 7.68-7.63 (m, 3H), 7.56 (s, 2H), 7.50-7.47 (m, 3H), 7.43-7.40 (m, 1H), 7.37 (d, $J = 7.5$ Hz, 1H), 7.17-7.14 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 167.53, 142.15, 142.04, 141.84, 139.45, 139.08, 130.09, 129.99, 129.47, 129.06, 128.35, 128.33, 127.42, 127.39, 127.18, 124.44, 98.73; HRMS (ESI) calcd for C$_{19}$H$_{13}$IN$^+$ [M+H]$^+$ 382.0087, found 382.0082.

2'-Iodo-2-isocyano-4-methyl-1,1'-biphenyl (1o)

Dark green oil (414.7 mg, 56% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J = 1.0$ Hz, 1H), 7.45-7.42 (m, 1H), 7.30-7.25 (m, 3H), 7.18 (d, $J = 7.5$ Hz, 1H), 7.12-7.09 (m, 1H), 2.43 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 166.65, 142.55, 139.63, 139.08, 130.82, 130.38, 130.29, 130.17, 128.55, 127.65, 125.65, 125.63, 99.32, 21.32; HRMS (ESI) calcd for C$_{14}$H$_{11}$IN$^+$ [M+H]$^+$ 319.9931, found 319.9932.
2'-Iodo-2-isocyno-5-methoxy-1,1'-biphenyl (1p)
Green solid (368.5 mg, 68% yield). \(^1^H\) NMR (400 MHz, CDCl\(_3\)): δ 7.96 (dd, \(J = 0.8\) Hz, \(J = 8.0\) Hz, 1H), 7.44-7.40 (m, 1H), 7.28-7.25 (m, 1H), 7.19 (d, \(J = 8.4\) Hz, 1H), 7.12-7.08 (m, 1H), 7.02-6.98 (m, 2H), 3.87 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 167.03, 159.97, 142.39, 139.66, 134.52, 131.98, 130.63, 130.15, 128.57, 126.54, 115.85, 112.27, 99.92, 56.05; HRMS (ESI) calcd for C\(_{14}\)H\(_{11}\)INO\(^+\) [M+H]+ 335.9880, found 335.9882.

2'-Iodo-2-isocyno-3-methyl-1,1'-biphenyl (1r)
Colorless oil (350.9 mg, 76% yield). \(^1^H\) NMR (500 MHz, CDCl\(_3\)): δ 7.97 (d, \(J = 8.0\) Hz, 1H), 7.45-7.42 (m, 1H), 7.37-7.32 (m, 2H), 7.26 (d, \(J = 8.0\) Hz, 1H), 7.12-7.09 (m, 2H), 2.50 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 168.92, 142.83, 141.75, 139.39, 135.42, 130.06, 129.91, 128.65, 128.29, 128.12, 98.77, 19.16; HRMS (ESI) calcd for C\(_{14}\)H\(_{11}\)IN\(^+\) [M+H]+ 319.9931, found 319.9931.

5-Fluoro-2'-ido-2'-isocyno-5'-methyl-1,1'-biphenyl (1s)
Green oil (438.0 mg, 64% yield). \(^1^H\) NMR (500 MHz, CDCl\(_3\)): δ 7.90 (dd, \(J = 5.5\) Hz, \(J = 9.0\) Hz, 1H), 7.36 (d, \(J = 8.0\) Hz, 1H), 7.26-7.24 (m, 1H), 7.07 (s, 1H), 7.01 (dd, \(J = 3.0\) Hz, \(J = 9.0\) Hz, 1H), 6.90-6.86 (m, 1H), 2.42 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 166.70, 162.81 (d, \(J = 248.8\) Hz), 144.26 (d, \(J = 8.8\) Hz), 140.65 (d, \(J = 7.9\) Hz), 140.37, 139.86, 130.96, 130.04, 126.90, 117.50 (d, \(J = 21.3\) Hz), 91.85 (d, \(J = 3.8\) Hz), 21.41; \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): -113.91 (s, 1F); HRMS (ESI) calcd for
C$_{14}$H$_{10}$FIN$^+$ [M+H]$^+$ 337.9836, found 337.9839.

2-Iodo-2'-isocyno-6'-methoxy-5-methyl-1,1'-biphenyl (1t)

Green solid (209.4 mg, 53% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82 (d, $J = 8.0$ Hz, 1H), 7.41-7.37 (m, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 7.05-7.01 (m, 2H), 6.94 (dd, $J = 0.8$ Hz, $J = 8.0$ Hz, 1H), 3.79 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 166.44, 157.44, 138.89, 138.39, 131.17, 130.95, 129.71, 126.77, 119.01, 112.20, 95.68, 56.31, 21.06; HRMS (ESI) calcd for C$_{15}$H$_{13}$INO$^+$ [M+H]$^+$ 350.0036, found 350.0031.

N-(2'-iodo-[1,1'-biphenyl]-2-yl)phenanthridine-6-carboxamide (2a)

White solid (16.3 mg, 65% yield). Mp 219-221 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 10.45 (s, 1H), 9.85 (d, $J = 10.0$ Hz, 1H), 8.75 (d, $J = 8.0$ Hz, 1H), 8.61 (d, $J = 8.0$ Hz, 1H), 8.54-8.53 (m, 1H), 8.14 (d, $J = 7.5$ Hz, 1H), 7.87-7.84 (m, 1H), 7.77-7.74 (m, 1H), 7.70-7.69 (m, 2H), 7.62-7.56 (m, 3H), 7.46 (d, $J = 7.0$ Hz, 1H), 7.29-7.26 (m, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 163.20, 147.79, 143.33, 141.39, 139.73, 135.54, 134.93, 134.00, 131.19, 131.04, 130.43, 129.79, 129.76, 129.31, 129.09, 128.88, 128.84, 128.72, 128.15, 125.73, 124.60, 123.86, 122.10, 121.89, 120.12, 100.92; IR (cm$^{-1}$) 3284, 3114, 1682, 1628, 1579, 1456, 1251, 869, 804, 785, 772, 490; HRMS (ESI) calcd for C$_{26}$H$_{18}$INO$_2^+$ [M+H]$^+$ 501.0458, found 501.0437.
(9H-carbazol-9-yI)(phenanthridin-6-yI)methanone (3a)

White solid (16.7 mg, 90% yield). Mp 202-205 °C. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) 9.09 (d, \(J = 8.5\) Hz, 1H), 9.01 (d, \(J = 8.0\) Hz, 1H), 8.24 (d, \(J = 7.5\) Hz, 2H), 8.16 (d, \(J = 8.0\) Hz, 1H), 8.11-8.08 (m, 2H), 7.94-7.87 (m, 2H), 7.83-7.80 (m, 1H), 7.42-7.36 (m, 3H), 7.30 (br, 3H); \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)): 167.00, 155.26, 143.28, 138.60, 134.00, 133.39, 130.86, 130.72, 129.95, 129.88, 128.47, 127.19, 126.99, 125.42, 125.10, 124.25, 124.15, 123.21, 121.45, 116.29; IR (cm\(^{-1}\)) 3379, 2059, 1675, 1610, 1581, 1489, 1443, 876, 848, 762, 736; HRMS (ESI) calcd for C\(_{26}\)H\(_{17}\)N\(_2\)O\(^+\) [M+H]\(^+\) 373.1335, found 373.1338.

(3-Methyl-9H-carbazol-9-yI)(9-methylphenanthridin-6-yI)methanone (3b)

White solid (19.0 mg, 95% yield). Mp 285-290 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 8.97 (d, \(J = 7.6\) Hz, 1H), 8.89 (s, 1H), 8.18 (d, \(J = 7.6\) Hz, 1H), 8.07 (d, \(J = 8.0\) Hz, 1H), 8.02 (s, 1H), 7.98 (d, \(J = 8.0\) Hz, 1H), 7.89-7.85 (m, 2H), 7.71-7.62 (m, 3H), 7.38 (br, 1H), 7.27 (br, 1H), 7.09 (br, 1H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 166.66, 154.98, 143.39, 142.43, 138.79, 136.63, 133.88, 133.77, 130.80, 130.06, 129.19, 128.38, 128.23, 127.14, 126.99, 126.89, 126.61, 124.46, 124.12, 122.26, 122.15, 121.40, 119.88, 119.64, 22.47, 21.23; IR (cm\(^{-1}\)) 3440, 2956, 2851, 1671, 1583, 1486.
1464, 1447, 1379, 878, 824, 760; HRMS (ESI) calcd for C$_{28}$H$_{21}$N$_{2}$O$^+$ [M+H]$^+$ 401.1648, found 401.1644.

(3-Isopropyl-9H-carbazol-9-yl)(9-isopropylphenanthridin-6-yl)methanone (3c)
Pale yellow solid (17.3 mg, 76% yield). Mp 175-179 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ 9.05 (d, J = 7.2 Hz, 1H), 8.89 (s, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.08-8.05 (m, 2H), 8.01 (d, J = 8.4 Hz, 1H), 7.91-7.82 (m, 2H), 7.71-7.68 (m, 1H), 7.41-7.37 (m, 2H), 7.29 (br, 1H), 7.10 (br, 2H), 3.28-3.20 (m, 1H), 2.99-2.93 (m, 1H), 1.36 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.8 Hz, 6H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): 165.92, 154.20, 153.29, 144.92, 142.45, 137.92, 135.85, 133.23, 129.80, 129.52, 128.58, 127.91, 127.31, 126.24, 126.18, 126.11, 125.94, 124.34, 124.12, 123.23, 120.76, 120.34, 120.12, 117.78, 115.46, 114.95, 34.12, 33.16, 23.87, 23.42; IR (cm$^{-1}$) 3362, 2958, 2865, 1634, 1582, 1512, 1460, 1448, 1357, 885, 851, 692; HRMS (ESI) calcd for C$_{32}$H$_{29}$N$_{2}$O$^+$ [M+H]$^+$ 457.2274, found 457.2260.

(3-Fluoro-9H-carbazol-9-yl)(9-fluorophenanthridin-6-yl)methanone (3d)
Pale yallow solid (18.8 mg, 92% yield). Mp 181-185 °C. $^1$H NMR (400 MHz,
DMSO-$d_6$): $\delta$ 9.01-8.99 (m, 1H), 8.95 (dd, $J = 2.4$ Hz, $J = 10.8$ Hz, 1H), 8.32 (dd, $J = 4.8$ Hz, $J = 9.2$ Hz, 1H), 8.26 (d, $J = 6.8$ Hz, 1H), 8.16 (dd, $J = 2.4$ Hz, $J = 8.4$ Hz, 1H), 8.11-8.08 (m, 1H), 7.93-7.90 (m, 2H), 7.73-7.68 (m, 1H), 7.42-7.38 (m, 2H), 7.28-7.23 (m, 3H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): 165.68, 164.20 (d, $J = 352.0$ Hz), 159.42 (d, $J = 239.1$ Hz), 153.49, 142.53, 138.43, 135.96 (d, $J = 10.1$ Hz), 134.26, 130.56, 130.11 (d, $J = 7.3$ Hz), 130.01, 129.14, 128.23, 127.80 (d, $J = 9.9$ Hz), 125.56 (d, $J = 3.4$ Hz), 124.54, 124.03 (d, $J = 4.3$ Hz), 123.90, 121.17, 119.60, 118.22 (d, $J = 24.3$ Hz), 117.17, 115.34, 114.87 (d, $J = 24.6$ Hz), 108.93 (d, $J = 22.9$ Hz), 106.95 (d, $J = 24.4$ Hz); $^{19}$F NMR (470 MHz, CDCl$_3$): -103.64 (s, 1F), -117.74 (s, 1F); IR (cm$^{-1}$) 3392, 2956, 2920, 1674, 1597, 1583, 1459, 1447, 1392, 894, 836, 744, 698; HRMS (ESI) calcd for C$_{26}$H$_{15}$F$_2$N$_2$O$^+$ [M+H]$^+$ 409.1147, found 409.1144.

(3-chloro-9H-carbazol-9-yl)(9-chlorophenanthridin-6-yl)methanone (3e)
Pale yellow solid (15.0 mg, 68% yield). Mp 223-227 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.75 (s, 1H), 8.65-8.63 (m, 1H), 8.17-8.15 (m, 1H), 8.09 (d, $J = 8.8$ Hz, 1H), 7.96-7.94 (m, 2H), 7.86-7.84 (m, 2H), 7.63 (d, $J = 9.2$ Hz, 1H), 7.36-7.21 (m, 5H); $^{13}$C NMR (125 MHz, CDCl$_3$): 116.11, 153.86, 143.36, 138.62, 136.90, 134.93, 130.95, 130.22, 129.15, 129.12, 128.33, 128.01, 127.36, 125.78, 124.53, 123.58, 122.49, 122.42, 121.42, 120.15, 119.78, 117.61, 116.13, 138.82, 130.10, 129.94; IR (cm$^{-1}$) 3065, 2921, 2851, 1674, 1442, 1323, 881, 849, 788, 764, 746, 706; HRMS (ESI) calcd for C$_{26}$H$_{15}$Cl$_2$N$_2$O$^+$ [M+H]$^+$ 441.0556, found 441.0551.
(2-Methyl-9H-carbazol-9-yl)(8-methylphenanthridin-6-yl)methanone (3f)

White solid (18.8 mg, 94% yield). Mp 181-183 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 9.00-8.95 (m, 2H), 8.16 (d, \(J = 7.6\) Hz, 1H), 8.11 (d, \(J = 8.0\) Hz, 1H), 8.08-8.06 (m, 1H), 7.98-7.84 (m, 4H), 7.55 (br, 1H), 7.35-7.31 (m, 1H), 7.29 (d, \(J = 8.0\) Hz, 1H), 7.14 (s, 1H), 6.81 (br, 1H), 3.35 (s, 3H), 2.28 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 167.01, 154.80, 142.96, 139.29, 138.65, 138.48, 138.37, 137.74, 133.71, 131.66, 130.84, 128.94, 128.50, 127.16, 126.65, 126.15, 125.63, 124.77, 124.58, 124.06, 123.53, 122.51, 122.22, 119.61, 119.40, 117.42, 115.94, 22.22, 21.70; IR (cm\(^{-1}\)) 3424, 3057, 2955, 1679, 1602, 1568, 1499, 1459, 877, 826, 742, 703; HRMS (ESI) calcd for C\(_{28}\)H\(_{21}\)N\(_2\)O\(^+\) [M+H]\(^+\) 401.1648, found 401.1652.

(2-Methoxy-9H-carbazol-9-yl)(8-methoxyphenanthridin-6-yl)methanone (3g)

White solid (20.5 mg, 95% yield). Mp 170-173 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 9.03 (d, \(J = 9.6\) Hz, 1H), 8.92 (d, \(J = 8.4\) Hz, 1H), 8.12 (d, \(J = 8.8\) Hz, 2H), 8.04 (d, \(J = 8.0\) Hz, 1H), 7.80-7.86 (m, 1H), 7.82-7.78 (m, 1H), 7.75 (dd, \(J = 9.2\) Hz, \(J = 2.4\) Hz, 1H), 7.53 (d, \(J = 2.4\) Hz, 1H), 7.37-7.34 (m, 2H), 7.19 (br, 2H), 7.04 (d, \(J = 8.8\) Hz, 1H), 3.84 (s, 3H), 3.48 (s, 3H); \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)): 166.26, 159.20, 159.08, 153.21, 141.56, 139.14, 137.87, 129.90, 129.17, 128.80, 127.56, 126.20,
126.14, 125.31, 124.43, 124.39, 123.82, 123.01, 122.72, 121.22, 119.70, 119.44, 115.34, 111.87, 106.13, 100.89, 55.68, 55.08; IR (cm\(^{-1}\)) 3393, 3058, 2921, 1646, 1602, 1500, 1463, 1145, 883, 834, 757, 743, 702; HRMS (ESI) calcd for C\(_{28}\)H\(_{21}\)N\(_2\)O\(_3\)\(^+\) [M+H]\(^+\) 433.1574, found 433.1554.

(4-Methyl-9H-carbazol-9-yl)(1-methylphenanthridin-6-yl)methanone (3j)
Pale yellow solid (14.2 mg, 71% yield). Mp 210-215 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): δ 9.18 (d, \(J = 8.4\) Hz, 1H), 8.26 (d, \(J = 8.0\) Hz, 1H), 8.22 (d, \(J = 8.0\) Hz, 1H), 8.15-8.11 (m, 1H), 8.01-7.99 (m, 1H), 7.89-7.85 (m, 1H), 7.82-7.77 (m, 2H), 7.49-7.35 (m, 3H), 7.23 (br, 3H), 3.25 (s, 3H), 2.86 (s, 3H); \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)): 167.27, 155.34, 144.88, 138.82, 138.68, 136.78, 134.91, 134.12, 133.92, 132.76, 129.85, 129.79, 129.12, 128.19, 128.03, 127.82, 127.53, 127.36, 127.16, 125.46, 125.07, 124.53, 124.16, 123.72, 116.11, 113.76, 27.09, 21.41; IR (cm\(^{-1}\)) 3363, 2957, 2850, 2921, 2850, 1666, 1598, 1583, 1497, 1450, 1347, 781, 740, 670; HRMS (ESI) calcd for C\(_{28}\)H\(_{21}\)N\(_2\)O\(_3\)\(^+\) [M+H]\(^+\) 401.1648, found 401.1659.

(4-Methoxy-9H-carbazol-9-yl)(1-methoxyphenanthridin-6-yl)methanone (3k)
Yellow solid (15.3 mg, 71% yield). Mp 214-222 °C. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)):
δ 9.74 (d, J = 8.5 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.11-8.08 (m, 1H), 7.88-7.85 (m, 1H), 7.83-7.80 (m, 1H), 7.77-7.69 (m, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.45-7.42 (m, 1H), 7.32-7.26 (m, 3H), 7.04 (d, J = 8.0 Hz, 1H), 4.26 (s, 3H), 4.08 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): 167.05, 158.23, 155.84, 155.64, 145.31, 139.71, 137.81, 133.55, 131.55, 128.77, 128.37, 127.90, 127.53, 126.32, 126.23, 124.00, 123.60, 123.52, 123.15, 115.86, 115.69, 115.38, 109.46, 108.88, 105.51, 56.01, 55.58; IR (cm⁻¹) 3365, 2957, 2921, 2850, 1600, 1573, 1487, 1450, 1137, 783, 742, 725; HRMS (ESI) calcd for C_{28}H_{21}N_{2}O_{3}⁺ [M+H]⁺ 433.1547, found 433.1557.

(3-Methyl-9H-carbazol-9-yl)(2-methylphenanthridin-6-yl)methanone (3l)

White solid (19.6 mg, 98% yield). Mp 214-218 °C. ¹H NMR (500 MHz, DMSO-d₆): δ 9.05 (d, J = 8.5 Hz, 1H), 8.81 (s, 1H), 8.19 (d, J = 7.5 Hz, 1H), 8.10-8.03 (m, 3H), 7.99 (d, J = 8.0 Hz, 1H), 7.80-7.77 (m, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.40-7.10 (m, 5H), 2.68 (s, 3H), 2.41 (s, 3H); ¹³C NMR (125 MHz, DMSO-d₆): 166.10, 155.52, 140.78, 139.15, 137.98, 135.89, 133.95, 132.82, 132.27, 131.49, 129.76, 129.66, 128.87, 128.57, 127.47, 126.28, 126.16, 124.52, 124.11, 123.34, 122.71, 122.45, 120.51, 120.47, 115.47, 115.18, 21.58, 20.78; IR (cm⁻¹) 3367, 2919, 2851, 1671, 1634, 1585, 1486, 1446, 875, 846, 755, 699; HRMS (ESI) calcd for C_{28}H_{21}N_{2}O⁺ [M+H]⁺ 401.1648, found 401.1643.
(3-Fluoro-9H-carbazol-9-yl)(2-fluorophenanthridin-6-yl)methanone (3m)

Pale yellow solid (14.3 mg, 70% yield). Mp 199-204 °C. 1H NMR (400 MHz, DMSO-\textit{d}_6): δ 9.09 (d, \(J = 8.4\) Hz, 1H), 8.87 (dd, \(J = 2.4\) Hz, \(J = 6.4\) Hz, 1H), 8.26 (d, \(J = 8.0\) Hz, 1H), 8.20-8.14 (m, 3H), 8.13-8.09 (m, 1H), 7.88-7.84 (m, 1H), 7.79-7.74 (m, 1H), 7.42-7.38 (m, 2H), 7.28-7.23 (m, 3H); 13C NMR (125 MHz, CDCl\textsubscript{3}): 166.23, 162.43 (d, \(J = 248.4\) Hz), 160.03 (d, \(J = 241.4\) Hz), 153.91 (d, \(J = 3.0\) Hz), 139.91, 139.12, 134.82, 133.14 (d, \(J = 9.3\) Hz), 133.09 (d, \(J = 4.3\) Hz), 131.89, 129.04, 128.28 (d, \(J = 9.4\) Hz), 127.84, 126.82, 126.23, 126.18 (d, \(J = 4.8\) Hz), 124.26, 123.23, 122.79, 120.14, 118.56 (d, \(J = 24.3\) Hz), 117.74, 116.07, 114.63 (d, \(J = 24.3\) Hz), 107.44 (d, \(J = 23.4\) Hz), 106.04 (d, \(J = 24.1\) Hz); 19F NMR (470 MHz, CDCl\textsubscript{3}): -109.62 (s, 1F), -117.83 (s, 1F); IR (cm\textsuperscript{-1}) 3360, 3050, 2921, 2851, 1666, 1631, 1598, 1581, 1485, 1447, 895, 833, 764, 707; HRMS (ESI) calcd for C\textsubscript{26}H\textsubscript{15}F\textsubscript{2}N\textsubscript{2}O\textsuperscript{+} [M+H]\textsuperscript{+} 409.1147, found 409.1163.

(3-Phenyl-9H-carbazol-9-yl)(2-phenylphenanthridin-6-yl)methanone (3n)

White solid (23.8 mg, 91% yield). Mp > 350 °C. 1H NMR (400 MHz, DMSO-\textit{d}_6): δ 9.33 (d, \(J = 8.4\) Hz, 1H), 9.27 (s, 1H), 8.60 (d, \(J = 1.2\) Hz, 1H), 8.38 (d, \(J = 7.6\) Hz,
1H), 8.20-8.19 (m, 3H), 8.14-8.10 (m, 1H), 8.04 (d, J = 7.2 Hz, 2H), 7.87-7.83 (m, 1H), 7.77 (d, J = 7.6 Hz, 2H), 7.62-7.58 (m, 3H), 7.51-7.45 (m, 5H), 7.39-7.35 (m, 3H); $^{13}$C NMR (125 MHz, DMSO-d$_6$): 166.10, 154.26, 141.85, 140.76, 139.56, 139.35, 138.24, 137.13, 136.70, 133.28, 132.50, 130.66, 129.19, 129.14, 128.93, 128.71, 128.22, 127.85, 127.60, 127.46, 126.94, 126.85, 126.37, 126.28, 124.72, 124.67, 123.90, 122.63, 120.95, 118.58, 115.81, 115.60; IR (cm$^{-1}$) 3439, 2957, 2920, 2851, 1674, 1629, 1468, 1450, 987, 933, 531, 526; HRMS (ESI) calcd for C$_{38}$H$_{25}$N$_2$O$^+$ [M+H]$^+$ 525.1961, found 525.1992.

![Chemical Structure](image)

**(2-Methyl-9H-carbazol-9-yl)(3-methylphenanthridin-6-yl)methanone (3o)**

White solid (18.0 mg, 90% yield). Mp 220-225 °C. $^1$H NMR (400 MHz, DMSO-d$_6$): δ 9.03 (d, J = 8.4 Hz, 1H), 8.89 (d, J = 8.4 Hz, 1H), 8.16-8.04 (m, 4H), 7.91 (s, 1H), 7.79-7.42 (m, 2H), 7.56 (br, 1H), 7.34-7.28 (m, 2H), 7.12 (br, 1H), 6.79 (br, 1H), 2.56 (s, 3H), 2.28 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): 166.21, 154.42, 142.59, 139.85, 138.33, 137.52, 137.38, 133.15, 132.44, 130.76, 129.36, 128.55, 126.92, 126.24, 126.19, 125.79, 124.34, 123.80, 123.16, 123.06, 122.06, 121.90, 120.33, 120.19, 116.28, 114.93, 21.77, 21.02; IR (cm$^{-1}$) 3361, 3032, 2920, 2851, 1678, 1600, 1581, 1499, 1458, 889, 844, 746, 696; HRMS (ESI) calcd for C$_{28}$H$_{21}$N$_2$O$^+$ [M+H]$^+$ 401.1648, found 401.1696.
(3-Methoxy-9H-carbazol-9-yl)(2-methoxyphenanthridin-6-yl)methanone (3p)

White solid (21.2 mg, 98% yield). Mp 200-205 °C. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.97 (d, $J = 8.5$ Hz, 1H), $\delta$ 8.89 (d, $J = 9.0$ Hz, 1H), 8.12-8.08 (m, 3H), 8.05-8.02 (m, 1H), 7.74-7.71 (m, 1H), 7.60 (s, 1H), 7.53 (d, $J = 9.0$ Hz, 1H), 7.36-7.02 (m, 4H), 3.92 (s, 3H), 3.48 (s, 3H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): 166.23, 160.47, 159.13, 154.79, 144.32, 138.98, 137.73, 133.36, 132.56, 127.91, 126.27, 126.25, 126.15, 124.57, 124.53, 122.84, 121.37, 121.30, 119.80, 119.77, 119.49, 118.18, 115.32, 111.93, 110.08, 100.88, 55.67, 55.09; IR (cm$^{-1}$) 3388, 3365, 2920, 1667, 1616, 1583, 1459, 1439, 1121, 886, 853, 765, 699; HRMS (ESI) calcd for C$_{28}$H$_{21}$N$_2$O$_3$ $^+$ [M+H]$^+$ 433.1547, found 433.1549.

(1-Methyl-9H-carbazol-9-yl)(4-methylphenanthridin-6-yl)methanone (3r)

Pale yellow solid (17.6 mg, 88% yield). Mp 183-186 °C. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 9.01 (d, $J = 8.5$ Hz, 1H), 8.74 (d, $J = 8.0$ Hz, 2H), 8.23 (d, $J = 7.5$ Hz, 1H), 8.11-8.06 (m, 2H), 7.95-7.91 (m, 1H), 7.74-7.71 (m, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.59 (d, $J = 7.0$ Hz, 1H), 7.42-7.31 (m, 3H), 7.08 (d, $J = 7.5$ Hz, 1H), 2.01 (s, 3H), 1.72 (s, 3H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): 167.39, 149.98, 140.17, 140.00, 139.54, 138.18, 133.71, 131.81, 130.01, 129.48, 129.41, 128.82, 127.32, 126.83,
126.50, 126.11, 125.34, 124.58, 123.94, 123.33, 122.92, 120.78, 120.48, 117.95, 114.11, 20.34, 16.72; IR (cm$^{-1}$) 3365, 2957, 2920, 2851, 1678, 1595, 1543, 1493, 1468, 1446, 1374, 788, 766; HRMS (ESI) calcd for C$_{28}$H$_{21}$N$_2$O$^+$ [M+H]$^+$ 401.1648, found 401.1649.

(9-Fluoro-2-methylphenanthridin-6-yl)(3-fluoro-6-methyl-9H-carbazol-9-yl)methanone (3s)

White solid (18.1 mg, 83% yield). Mp 234-236 °C. $^1$H NMR (500 MHz, DMSO-d$_6$): δ 8.86 (d, $J = 10.5$ Hz, 1H), 8.79 (s, 1H), 8.23 (s, 3H), 8.05-7.96 (m, 4H), 7.72-7.65 (m, 3H), 7.18-7.05 (m, 3H), 2.64 (s, 3H), 2.36 (s, 3H); $^{13}$C NMR (125 MHz, DMSO-d$_6$): 165.59, 164.01 (d, $J = 250.0$ Hz), 159.37 (d, $J = 238.8$ Hz), 152.55, 140.83, 139.23, 136.55, 135.56 (d, $J = 9.9$ Hz), 134.46, 133.88, 132.12, 129.86 (d, $J = 9.9$ Hz), 129.72, 129.14, 127.77 (d, $J = 9.9$ Hz), 125.67 (d, $J = 3.3$ Hz), 123.84 (d, $J = 3.8$ Hz), 123.26, 120.95, 119.67, 118.02 (d, $J = 24.4$ Hz), 117.15, 115.01, 114.65 (d, $J = 24.5$ Hz), 108.76 (d, $J = 22.8$ Hz), 106.75 (d, $J = 24.4$ Hz), 21.48, 20.70; $^{19}$F NMR (470 MHz, CDCl$_3$): -104.25 (s, 1F), -117.95 (s, 1F); IR (cm$^{-1}$) 3429, 3291, 2951, 2919, 2852, 1679, 1620, 1585, 1457, 1274, 859, 831, 815; HRMS (ESI) calcd for C$_{28}$H$_{19}$F$_2$N$_2$O$^+$ [M+H]$^+$ 437.1460, found 437.1461.
(3-Methoxy-5-methyl-9H-carbazol-9-yl)(1-methoxy-9-methylphenanthridin-6-yl) methanone (3t)

Yellow solid (21.2 mg, 92% yield). Mp 238-241 °C. $^1$H NMR (400 MHz, DMSO-$d_6$): δ 9.49 (s, 1H), 8.07 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.81-7.77 (m, 1H), 7.70-7.68 (m, 1H), 7.60 (dd, J = 1.2 Hz, J = 8.4 Hz, 1H), 7.49 (d, J = 7.6 Hz, 2H), 7.19-6.97 (m, 4H), 4.21 (s, 3H), 4.03 (s, 3H), 2.64 (s, 3H), 2.40 (s, 3H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): 166.24, 158.01, 155.38, 154.96, 144.65, 142.55, 139.03, 135.12, 133.81, 132.95, 129.66, 129.47, 128.44, 127.66, 127.51, 125.80, 125.46, 122.93, 122.48, 120.80, 114.72, 114.57, 114.18, 110.27, 107.85, 106.31, 56.28, 55.84, 22.39, 20.88; IR (cm$^{-1}$) 3392, 3185, 2920, 2850, 1635, 1585, 1506, 1452, 1034, 880, 812, 782, 770, 751; HRMS (ESI) calcd for C$_{30}$H$_{25}$N$_2$O$_3$ $^+[M+H]^{+}$ 461.1860, found 461.1864.

9H-carbazole (4)

Yellow solid (15.0 mg, 90% yield). $^1$H NMR (400 MHz, DMSO-$d_6$): δ 11.22 (s, 1H), 8.10 (d, J = 10.0 Hz, 2H), 7.47 (d, J = 10.5 Hz, 2H), 7.39-7.35 (m, 2H), 7.17-7.13 (m, 2H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): 139.68, 125.45, 122.35, 120.08, 118.43, 110.88; HRMS (ESI) calcd for C$_{12}$H$_{10}$N$^+$ [M+H]$^+$ 168.0808, found 168.0807.
Phenantridine-6-carboxylic acid (5)

Yellow solid (20.5 mg, 92% yield). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.74 (d, $J = 5.0$ Hz, 1H), 8.69 (d, $J = 5.0$ Hz, 1H), 8.64 (s, 1H), 8.21 (s, 1H), 7.97-7.94 (m, 1H), 7.84-7.82 (m, 3H), 6.73 (br, 1H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): 163.99, 144.46, 140.50, 134.36, 132.05, 130.17, 129.96, 129.60, 129.01, 128.92, 126.69, 124.13, 122.46, 122.12; HRMS (ESI) calcd for C$_{14}$H$_{10}$NO$_2$ $^+$ [M+H]$^+$ 224.0706, found 224.0708.

6. References

7. Copies of $^1$H and $^{13}$C NMR Spectra

S3a

S54
3k