Supporting information

Alkenes as synthetic equivalents of alkynes: combining cyclizations and fragmentation to design one-pot synthesis of quinolines from o-alkenyl arylisocyanides

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1. General Information

Unless otherwise noted, all $^1$H NMRs were run on 400 MHz and 600 MHz spectrometer in CDCl$_3$ and all $^{13}$C NMR were run on 100 MHz and 150 MHz spectrometer in CDCl$_3$. Proton chemical shifts are given relative to the residual proton signal of CDCl$_3$ (7.26 ppm). Carbon chemical shifts were internally referenced to CDCl$_3$ (77.23 ppm) signal. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained on a Perkin Elmer Lambda 950 or Perkin Elmer Spectrum 100; absorptions are reported in reciprocal centimeters. High resolution mass spectra (HRMS) were obtained on a JEOL TheMSroute JMS-600H with Agilent 6890 Series GC System.

2. Materials

Acetonitrile, Toluene and THF were obtained from a SPS-4 Solvent Purification System. Hexanes for column chromatography and preparatory thin layer chromatography were distilled prior to use. Dichloromethane was dried using 4 Å molecular sieves and stored under N$_2$ prior to use. All other solvents were used as purchased. Column chromatography was performed using silica gel (60 Å) and preparatory thin layer chromatography was performed using a 1000 μm glass backed plate containing UV dye. Phenylboronic acid (Acros Organics), 4-tolylphenylboronic acid (Matrix), isobutylboronic acid (Matrix), 4-cyanophenylboronic acid (Matrix), 4-fluorophenylboronic acid (Matrix), thiophen-2-ylboronic acid (Matrix), pyridine-4-boronic acid (Matrix), 3,5-dimethoxyphenylboronic acid (Aldrich), 2-bromophenylboronic acid (Matrix), naphthalen-1-ylboronic acid (Matrix), Mn(acac)$_3$ (Aldrich), Mn(OAc)$_3$·2H$_2$O (Acros Organics), were obtained from commercial suppliers and used as received.

3. Synthesis of Isocyanides

**Preparation of Wittig salt – phenethyltriphenylphosphoniumbromide, W1**

\[
\begin{align*}
\text{Br} & \quad \text{Toluene} \\
\text{PPh}_3 & \quad \text{Phosphine} \\
\text{Ph} & \quad \text{Phenethyltriphenylphosphoniumbromide, W1}
\end{align*}
\]

(2-bromoethyl)benzene (10.0mmol) was added dropwise into a solution of triphenylphosphine (10.0mmol) in toluene at room temperature. The solution was stirred for 48 hours in refluxing toluene. The resulting oily substance was collected and washed with hexane. Product was obtained as off white solid. Yield: 92%.

**Preparation of Wittig salt – phenethyltriphenylphosphoniumbromide, W2**

\[
\begin{align*}
\text{Br} & \quad \text{Toluene} \\
\text{PPh}_3 & \quad \text{Phosphine} \\
\text{Ph} & \quad \text{Phenethyltriphenylphosphoniumbromide, W2}
\end{align*}
\]

Benzyl bromide (10.0mmol) was added dropwise into a solution of triphenylphosphine (10.0mmol) in toluene at room temperature. The solution was stirred for 48 hours in refluxing toluene. The separated solid was filtered through a Buchner funnel and the residue was washed with hexane. The product was obtained as off white solid. Yield: 88%. 

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Preparation of Wittig salt – butyltriphenylphosphonium iodide, W3

\[
\begin{align*}
\text{Iodobutane (12.0mmol) was added dropwise into a solution of triphenylphosphine (10.0mmol) in toluene in a pressure tube at room temperature. It was stirred for 48 hours at 120 °C. The separated solid was filtered through a Buchner funnel and the residue was washed with hexane. The product was obtained as off white solid. Yield: 85%.}
\end{align*}
\]

Preparation of Wittig salt – (2-bromobenzyl)triphenylphosphonium bromide, W4

\[
\begin{align*}
(2\text{-bromoethyl})\text{benzene (10.0mmol) was added dropwise into a solution of triphenylphosphine (10.0mmol) in toluene in a pressure tube at room temperature. It was stirred for 48 hours at 120 °C. The separated solid was filtered through a Buchner funnel and the residue was washed with hexane. The product was obtained as off white solid. Yield: 89%}
\end{align*}
\]
Synthesis of 1-nitro-2-(3-phenylprop-1-enyl)benzene, 1a

To a solution of the Wittig salt W1 (3.5 mmol) in anhydrous THF (10 mL) at -78 °C was added slowly n-BuLi (3 mL of a 1.5M solution in hexane, 3.0 mmol). After 45 min, a solution of 2-nitrobenzaldehyde (3.5 mmol) in THF (10 mL) was added dropwise. The resulting solution was stirred for 1 h at -78 °C and then at room temperature for 12 h and quenched with saturated NH₄Cl solution. The aqueous phase was extracted with Et₂O (3 × 30 mL), and the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude was purified by column chromatography (hexane) on silica gel affording (E : Z = 1:3, 75%) as dark yellow oil.

1H NMR (400 MHz, CDCl₃) δ 8.12 – 8.05 (m, 3H), 7.96 – 7.90 (m, 1H), 7.65 – 7.58 (m, 4H), 7.58 – 7.55 (m, 1H), 7.50 – 7.19 (m, 27H), 6.98 (t, J = 10.4 Hz, 1H), 6.92 (d, J = 11.4 Hz, 3H), 6.39 (dt, J = 15.5, 7.0 Hz, 1H), 6.08 (dt, J = 11.4, 7.7 Hz, 3H), 3.64 (dd, J = 7.0, 1.0 Hz, 2H), 3.50 (dd, J = 7.7, 0.8 Hz, 6H). Spectral data match those previously reported.

HRMS (ESI): Calcd for C₁₅H₁₃NO₂Na 262.0844, Found: 262.0845

Synthesis of 4-fluoro-1-nitro-2-(3-phenylprop-1-en-1-yl)benzene (E:Z, 1:3), 2a

Substrate 2a was synthesized following the procedure for 1a from 5-fluoro-2-nitrobenzaldehyde and Wittig salt W1. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give the title compound (E:Z = 1:3, 83%) as a light brown oil. Rf = 0.44 (hexanes/EtOAc 10:1). 1H NMR (400 MHz, CDCl₃) δ 8.14 (dd, J = 8.7, 5.1 Hz, 1H), 8.00 (dd, J = 9.1, 5.2 Hz, 1H), 6.37 (d, J = 15.5 Hz, 1H), 6.09 (dt, J = 11.4, 7.7 Hz, 1H), 3.62 (d, J = 6.7 Hz, 1H), 3.48 (d, J = 7.6 Hz, 2H). 13C NMR (101 MHz, CDCl₃) δ 165.7, 163.2, 139.5, 136.0, 135.9, 132.9, 128.8, 128.8, 128.3, 128.3, 127.8, 127.7, 126.7, 126.5, 126.2, 126.0, 118.7, 118.5, 115.3, 115.1, 39.6, 34.5. HRMS (ESI): Calcd for C₁₃H₁₂FNNaO₂ 280.0742, Found: 280.0744

Synthesis of 1-nitro-2-styrylbenzene, 3a

Substrate 3a was synthesized following the procedure for 1a from 2-nitrobenzaldehyde and Wittig salt W2. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 0.7:1, 81%) of the title compound as a light brown oil. Rf = 0.44 (hexanes/EtOAc 10:1). 1H NMR (400 MHz, CDCl₃) δ 8.14 – 8.06 (m, 1H), 7.97 (dd, J = 8.1, 0.9 Hz, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.64 – 7.52 (m, 2H), 7.45 – 7.24 (m, 1H), 7.21 – 7.15 (m, 3H), 7.13 – 7.04 (m, 3H), 6.91 (d, J = 12.1 Hz, 1H), 6.78 (d, J = 12.1 Hz, 1H). 13C NMR (101 MHz, CDCl₃) δ 136.6, 136.0, 134.0, 134.0, 133.8, 133.8, 133.2, 133.2, 132.4, 132.0, 129.3, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.7, 127.2, 126.6, 126.0, 124.9, 124.8, 123.7. HRMS (ESI): Calcd for C₁₄H₁₀NO₂ 225.0790, Found: 225.0801
Synthesis of 1-nitro-2-(pent-1-en-1-yl)benzene, 4a

Substrate 4a was synthesized following the procedure for 1a from 2-nitrobenzaldehyde and Wittig salt W3. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 1:2, 73%) of the title compound as a light brown oil. Rf = 0.73 (hexanes/EtOAc 10:1). 1H NMR (400 MHz, CDCl3) δ 7.93 (dd, J = 8.2, 1.0 Hz, 1H), 7.86 – 7.76 (m, 1H), 7.60 – 7.43 (m, 2H), 7.41 – 7.24 (m, 3H), 6.80 (d, J = 15.7 Hz, 1H), 6.66 (d, J = 11.6 Hz, 1H), 6.74 (d, J = 11.6, 7.5 Hz, 1H), 2.20 (qd, J = 7.3, 1.5 Hz, 1H), 2.03 (qd, J = 7.5, 1.7 Hz, 1H), 1.57 – 1.43 (m, 1H), 1.42 – 1.31 (m, 2H), 0.93 (t, J = 7.4 Hz, 2H), 0.83 (t, J = 7.4 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 136.6, 134.5, 133.8, 132.8, 132.6, 131.9, 128.3, 127.6, 127.3, 125.1, 125.0, 124.3, 124.3, 35.2, 34.8, 30.4, 22.7, 22.2, 13.6, 13.6. HRMS (ESI): Calcd for C11H12NO2 191.0942, Found: 191.0942

Synthesis of 2-(3-phenylprop-1-en-1-yl)aniline, 1b

Aniline 1b was prepared by reduction of nitro group following a method reported by Bowman and co-workers. To a solution of 1a (1.5 g, 6.2 mmol) in 20 ml of absolute ethanol was added 20 ml of glacial acetic acid and 1.8 g (31 mmol) of iron powder. The mixture was heated to reflux. After 6 h, the crude mixture was cooled and filtered through a pad of Celite. The filtrate was concentrated in vacuo. Purification by flash chromatography on silica gel (Hexanes:EtOAc) afforded 1b as a dark brown oil 1.1 g (E:Z = 1:3, 85%). 1H NMR (400 MHz, CDCl3) δ 7.34 – 7.04 (m, 31H), 6.81 – 6.69 (m, 7H), 6.67 (ddd, J = 8.0, 1.0 Hz, 1H), 6.49 (d, J = 15.5 Hz, 1H), 6.44 (d, J = 11.1 Hz, 3H), 6.24 (dt, J = 15.5, 6.9 Hz, 1H), 5.99 (dt, J = 11.1, 7.5 Hz, 3H), 3.69 (s, 6H), 3.58 (d, J = 7.0 Hz, 3H), 3.52 (d, J = 7.5 Hz, 6H). 13C NMR (CDCl3, 100 MHz) 144.8, 143.4, 136.2, 133.4, 130.2, 129.8, 128.9, 128.8, 128.6, 126.9, 126.5, 123.0, 121.0, 120.5, 56.6, 35.5, 31.5, 21.6. HRMS (ESI): Calcd for C15H15N 209.1250, Found: 209.1260 Spectral data match those previously reported.

Synthesis of 4-fluoro-2-(3-phenylprop-1-en-1-yl)aniline, 2b

Substrate 2b was synthesized following the procedure for 1b from 2a. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 1:3, 78%) of the title compound as a brown oil. Rf = 0.44 (hexanes/EtOAc 10:1). 1H NMR (400 MHz, CDCl3) δ 6.99 (dt, J = 9.5, 3.2 Hz, 1H), 6.67 (ddd, J = 8.4, 4.8, 1.4 Hz, 1H), 6.64 – 6.58 (m, 1H), 6.45 (d, J = 15.2 Hz, 1H), 6.40 (d, J = 11.4 Hz, 1H), 6.32 – 6.20 (m, 1H), 6.09 – 5.96 (m, 1H), 3.52 (d, J = 7.2 Hz, 1H). 13C NMR (CDCl3, 101 MHz) 157.1, 154.8, 140.4, 133.8, 132.4, 128.8, 128.7, 128.7, 128.7, 128.5, 128.4, 126.4, 126.3, 126.1, 125.3, 124.0, 123.9, 116.2, 116.1, 115.9, 114.9, 114.7, 39.7, 34.8. HRMS (ESI): Calcd for C15H15FN 228.1188, Found: 228.1199
Synthesis of 2-styrylaniline, 3b

Substrate 3b was synthesized following the procedure for 1b from 3a. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 0.7:1, 86%) of the title compound as a dark oil. Rf = 0.44 (hexanes/EtOAc 10:1). 1H NMR (400 MHz, CDCl3) δ 7.68 (dd, J = 8.1, 0.9 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.45 (dd, J = 7.7, 1.6 Hz, 2H), 7.41 – 7.25 (m, 6H), 7.18 (d, J = 16.1 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 6.92 – 6.85 (m, 1H), 6.85 – 6.78 (m, 3H), 6.68 (d, J = 12.1 Hz, 1H), 3.84 (s, 4H). 13C NMR (101 MHz, CDCl3) δ 144.0, 143.7, 137.5, 136.6, 131.5, 130.0, 129.5, 128.7, 128.7, 128.6, 128.4, 127.5, 127.4, 127.1, 126.4, 126.4, 124.2, 123.6, 123.0, 119.0, 118.3, 116.2, 115.4. HRMS (ESI): Calcd for C14H14N 196.1126, Found: 196.1141

Synthesis of 2-(pent-1-en-1-yl)aniline, 4b

Substrate 4b was synthesized following the procedure for 1b from 4a. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 1:2, 88%) of the title compound as a light brown oil. Rf = 0.44 (hexanes/EtOAc 10:1). 1H NMR (400 MHz, CDCl3) δ 7.37 – 7.28 (m, 1H), 7.21 – 7.04 (m, 1H), 6.90 – 6.65 (m, 1H), 6.54 – 6.42 (m, 1H), 6.35 (d, J = 11.3 Hz, 1H), 6.14 (dd, J = 9.1, 6.9, 2.2 Hz, 1H), 5.85 (dd, J = 9.5, 7.4, 2.1 Hz, 1H), 3.71 (s, 1H), 2.38 – 2.05 (m, 1H), 1.66 – 1.40 (m, 1H), 1.21 – 0.85 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 144.0, 143.4, 134.8, 133.1, 129.8, 128.0, 127.9, 127.4, 125.5, 125.0, 124.5, 123.4, 119.0, 118.0, 116.0, 115.6, 115.1, 35.6, 30.7, 23.0, 22.7, 13.9, 13.8. HRMS (ESI): Calcd for C11H16N 162.1282, Found: 162.1295

Synthesis of N-(2-(3-phenylprop-1-en-1-yl)phenyl)formamide, 1c

A solution of aniline 1b (1.3 g, 6.4 mmol) and ethyl formate (3 ml) in anhydrous THF (10 ml) was added dropwise to a suspension of NaH (60% in mineral oil, 0.5 g, 14 mmol) in anhydrous THF (5 ml). The resulting mixture was stirred at r.t. for 24 h, then the reaction was quenched with cold water (5 mL). The solvents were removed under reduced pressure, and the residue was dissolved in ethyl acetate/water (20/5 mL). The aqueous phase was extracted with ethyl acetate (3 x 20 mL), the combined organic extracts were dried over anhydrous Na2SO4 and evaporated. The residue was washed thoroughly with hexane (3 x 30 mL) and dried in vacuo to give 1.3 g (E : Z = 1:3, 87%) of the title compound as a dark yellow liquid that slowly crystallized. 1H NMR (CDCl3, 400 MHz, inseparable mixture of rotamers & E:Z isomers): 1H NMR (400 MHz, CDCl3) δ 8.64 (d, J = 11.3 Hz, 1H), 8.49 (d, J = 11.2 Hz, 1H), 8.39 (dd, J = 6.6, 1.7 Hz, 1H), 8.36 – 8.26 (m, 2H), 7.99 (d, J = 10.9 Hz, 1H), 7.91 (dd, J = 8.1, 0.9 Hz, 1H), 7.81 (s, 1H), 7.56 (d, J = 4.8 Hz, 1H), 7.50 (dd, J = 7.5, 1.7 Hz, 1H), 7.43 (dd, J = 7.7, 1.4 Hz, 1H), 7.39 – 7.08 (m, 24H), 6.63
(dd, $J = 23.0, 15.6$ Hz, 1H), 6.51 (dd, $J = 11.2, 4.6$ Hz, 2H), 6.40 – 6.24 (m, 1H), 6.12 (ddt, $J = 17.2, 11.2, 7.6$ Hz, 2H), 3.49 (d, $J = 7.6$ Hz, 2H), 3.44 (d, $J = 7.6$ Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.8, 159.2, 139.8, 135.1, 134.6, 134.6, 134.5, 130.4, 129.5, 128.6, 128.5, 128.3, 128.2, 127.0, 126.4, 126.3, 125.3, 125.1, 125.0, 124.4, 121.5, 119.5, 119.3, 77.5, 77.2, 76.9, 39.7, 34.7, 34.6. HRMS (ESI): Calcd for C$_6$H$_{15}$NNaO 260.1051, Found: 260.1057. Spectral data match those previously reported.$^4$

**Synthesis of N-(2-stryrylphenyl)formamide, 3c**

Substrate 3c was synthesized following the procedure for 1c from 3b. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 0.7:1, 85%) of the title compound as an off white solid. $R_f = 0.41$ (hexanes/EtOAc 2:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 9.07 (d, $J = 11.0$ Hz, 1H), 8.55 – 8.43 (m, 2H), 8.43 – 8.35 (m, 2H), 8.19 (d, $J = 7.9$ Hz, 1H), 8.14 (d, $J = 1.9$ Hz, 1H), 8.03 (d, $J = 11.0$ Hz, 1H), 7.90 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.70 – 7.60 (m, 2H), 7.55 (ddd, $J = 5.6, 4.2, 0.9$ Hz, 3H), 7.49 (dd, $J = 7.9, 0.9$ Hz, 2H), 7.40 – 6.92 (m, 40H), 6.73 (dd, $J = 12.1$, 3.0 Hz, 3H), 6.51 (dd, $J = 12.1$, 5.4 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 164.1, 162.8, 160.1, 159.2, 136.9, 136.8, 135.9, 135.8, 134.1, 134.0, 133.9, 133.8, 133.5, 133.4, 131.9, 131.8, 130.8, 130.4, 129.8, 129.4, 129.3, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 127.8, 126.8, 126.7, 126.6, 126.4, 126.3, 125.6, 125.5, 125.1, 124.8, 124.8, 123.9, 123.3, 122.7, 122.2, 121.9, 119.9. HRMS (ESI): Calcd for C$_{15}$H$_{13}$NNaO 246.0895, Found: 246.0868.

**Synthesis of N-(2-(pent-1-en-1-yl)phenyl)formamide, 4c**

Substrate 4c was synthesized following the procedure for 1c from 4b. The crude product was purified by flash chromatography (Hexanes:EtOAc, 4:1) to give (E:Z = 1:2, 90%) of the title compound as a light brown oil. $R_f = 0.5$ (hexanes/EtOAc 4:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.61 (d, $J = 11.4$ Hz, 1H), 8.48 (d, $J = 11.2$ Hz, 1H), 8.40 (dd, $J = 5.6, 1.3$ Hz, 1H), 8.23 (d, $J = 8.2$ Hz, 1H), 8.00 – 7.83 (m, 1H), 7.60 (s, 1H), 7.46 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.38 (d, $J = 7.7$ Hz, 1H), 7.30 – 7.05 (m, 1H), 6.50 (t, $J = 14.7$ Hz, 1H), 6.34 (d, $J = 11.4$ Hz, 1H), 6.15 (ddt, $J = 22.6, 15.6, 6.9$ Hz, 1H), 5.97 – 5.77 (m, 1H), 2.27 – 2.14 (m, 1H), 2.12 – 1.98 (m, 1H), 1.50 (ddd, $J = 14.7, 7.4, 4.6$ Hz, 1H), 1.39 (dq, $J = 14.7, 7.4$ Hz, 1H), 0.95 (td, $J = 7.4, 4.1$ Hz, 1H), 0.87 (td, $J = 7.4, 4.7$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.8 162.8, 159.1, 144.1, 137.1, 136.6, 135.3, 134.5, 134.3, 133.3, 131.4, 130.5, 129.5, 129.2, 128.1, 127.8, 127.8, 127.5, 127.3, 127.0, 126.3, 125.4, 125.0, 124.6, 124.3, 124.2, 124.1, 123.9, 123.4, 121.9, 121.2, 119.0, 35.4, 35.4, 30.6, 30.6, 22.6, 22.4, 22.4, 13.8, 13.8. HRMS (ESI) Calcd for C$_{11}$H$_{16}$NO 190.1279, Found: 190.1261.

**Synthesis of 1-isocyano-2-(3-phenylprop-1-en-1-yl)benzene, 1d**

\[ \text{NC} \quad \text{Bn} \]
To a solution of N-formyl amide 6b (0.35 g, 1.4 mmol) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (3.0 mL) was added at 0 °C diisopropylamine (0.5 ml, 3.5 mmol), then dropwise over a period of 5 min POCl\textsubscript{3} (0.2 mL, 1.9 mmol) was added. The mixture was stirred at 0 °C for 1 h, then a saturated solution of Na\textsubscript{2}CO\textsubscript{3} (2mL) was added slowly. The mixture was transferred into a separatory funnel, diluted with CH\textsubscript{2}Cl\textsubscript{2} (20mL), the organic phase was washed with a half-saturated solution of Na\textsubscript{2}CO\textsubscript{3} (10mL) and brine(10mL), then dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and evaporated. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give 0.24 g (E : Z = 1:3, 75\%) of the title compound as a brown oil. R\textsubscript{f} = 0.53 (hexanes/EtOAc 10:1).

**1H NMR (400 MHz, CDCl\textsubscript{3})** δ 7.57 (d, J\textsubscript{pp} = 7.7 Hz, 1H), 7.48 – 7.22 (m, 8H), 6.86 (d, J\textsubscript{pp} = 15.8 Hz, 1H), 6.74 (d, J\textsubscript{pp} = 11.5 Hz, 3H), 6.57 – 6.44 (m, 1H), 6.15 (d, J\textsubscript{pp} = 11.5 Hz, 3H), 3.66 (d, J\textsubscript{pp} = 7.1 Hz, 2H), 3.62 (d, J\textsubscript{pp} = 7.6 Hz, 6H).

**13C NMR (100 MHz, CDCl\textsubscript{3})** δ 166.6, 139.6, 139.2, 134.0, 133.9, 133.9, 133.7, 129.6, 129.2, 128.9, 128.6, 128.5, 128.4, 128.2, 127.8, 127.6, 126.9, 126.8, 126.3, 126.2, 125.7, 124.9, 124.9, 39.5, 34.6.

**HRMS (ESI):** Calcd for C\textsubscript{16}H\textsubscript{13}N\textsubscript{2} 219.1052, Found: 219.1052.

**Synthesis of 4-fluoro-1-isocyano-2-(3-phenylprop-1-en-1-yl)benzene, 2d**

![Chemical Structure](image)

Substrate 2d was synthesized following the procedure for 1d. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 1:3, 76%) of the title compound as a light brown oil. R\textsubscript{f} = 0.44 (hexanes/EtOAc 10:1). **1H NMR (400 MHz, CDCl\textsubscript{3})** δ 7.60 (d, J\textsubscript{pp} = 7.4 Hz, 1H), 7.49 – 7.23 (m, 12H), 6.93 – 6.82 (m, 1H), 6.76 (d, J\textsubscript{pp} = 11.5 Hz, 1H), 6.55 (t, J\textsubscript{pp} = 11.4 Hz, 1H), 6.17 (dt, J\textsubscript{pp} = 11.5, 7.6 Hz, 1H), 3.68 (d, J\textsubscript{pp} = 7.6 Hz, 2H).

**13C NMR (100 MHz, CDCl\textsubscript{3})** δ 166.6, 139.8, 139.3, 134.1, 134.0, 129.7, 129.3, 129.0, 128.7, 128.6, 128.5, 128.4, 128.2, 127.8, 127.6, 126.9, 126.8, 126.3, 126.2, 125.7, 124.9, 124.9, 39.5, 34.6. **HRMS (ESI):** Calcd for C\textsubscript{15}H\textsubscript{12}FN 237.0952, Found: 237.0960

**Synthesis of 1-isocyano-2-styrylbenzene, 3d**

![Chemical Structure](image)

Substrate 3d was synthesized following the procedure for 1d from 3c. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (E:Z = 0.7:1, 76%) of the title compound as a light brown oil. R\textsubscript{f} = 0.44 (hexanes/EtOAc 10:1). **1H NMR (400 MHz, CDCl\textsubscript{3})** δ 7.73 (d, J\textsubscript{pp} = 7.9 Hz, 1H), 7.58 (d, J\textsubscript{pp} = 7.7 Hz, 1H), 7.46 – 7.13 (m, 15H), 6.83 (d, J\textsubscript{pp} = 12.2 Hz, 1H), 6.68 (d, J\textsubscript{pp} = 12.2 Hz, 1H). **13C NMR (101 MHz, CDCl\textsubscript{3})** δ 167.2, 166.7, 136.4, 136.1, 134.5, 133.7, 133.6, 132.6, 130.0, 129.4, 128.8, 128.8, 128.6, 128.3, 128.3, 128.0, 128.0, 127.7, 127.2, 127.0, 126.9, 125.4, 124.5, 122.0, 49.0, 49.0, 21.6, 21.5. **HRMS (ESI):** Calcd for C\textsubscript{15}H\textsubscript{11}F 205.0891, Found: 205.0844

**Synthesis of 1-isocyano-2-(pent-1-en-1-yl)benzene, 4d**

![Chemical Structure](image)
Substrate 4d was synthesized following the procedure for 1d from 4c. The crude product was purified by flash chromatography (Hexanes:EtOAc 10:1) to give (E:Z = 1:2, 81%) of the title compound as a light brown oil. Rf = 0.44 (hexanes/EtOAc 10:1). 1H NMR (400 MHz, CDCl3) δ 7.53 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 6.8, 2.5 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.26 – 7.14 (m, 1H), 6.67 (d, J = 15.8 Hz, 1H), 6.50 (dd, J = 11.6, 1.5 Hz, 1H), 6.34 (dt, J = 15.7, 7.0 Hz, 1H), 5.88 (dt, J = 11.6, 7.4 Hz, 1H), 2.21 (dqd, J = 22.2, 7.3, 1.5 Hz, 1H), 1.57 – 1.39 (m, 1H), 0.92 (dt, J = 24.1, 7.4 Hz, 1H).

13C NMR (101 MHz, CDCl3) δ 166.5, 166.3, 136.4, 135.7, 134.5, 134.2, 129.8, 129.2, 128.8, 127.4, 127.3, 126.9, 126.7, 125.6, 124.0, 123.8, 35.3, 30.7, 22.7, 22.3, 13.7, 13.7.

HRMS (ESI): Calcd for C12H13N171.1048, Found: 171.1061

Synthesis of N-(4-methyl-2-(3-phenylprop-1-en-1-yl)phenyl)formamide, 5a

Following the same procedure described above for the synthesis of formylamine 1c, the corresponding N-(2-bromo-4-methylphenyl)formamide was prepared and used in a procedure outlined by Bin Li and co-workers5. To a solution of trans-3-phenyl-1-propenylboronic acid (0.365 g, 2.25 mmol), Pd(PPh3)4 (0.173 g, 0.15 mmol) and K2CO3 (0.828 g, 6 mmol) in 20 mL of toluene, 8 mL of absolute ethanol, and 4 mL of H2O was added N-(2-bromo-4-methylphenyl)formamide (0.310 g, 1.5 mmol). The mixture was then purged with N2 and refluxed for 24 h. The reaction was then cooled to room temperature and 20 mL of H2O were added and the resulting phases were separated. The resulting aqueous phase was extracted with 3 x 10 mL ethyl acetate. The resulting organic phases were then washed with water (1 x 20 mL) followed by a saturated solution of brine (1 x 20 mL). The resulting organic phase was then dried using Na2SO4 and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc 5:1 as eluent) to give the desired products 5a (60%). 1H NMR (400 MHz, CDCl3) δ 8.38 (dd, J = 28.2, 6.3 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.39 – 7.28 (m, 2H), 7.28 – 7.19 (m, 2H), 7.11 – 6.94 (m, 1H), 6.58 (dd, J = 30.3, 15.6 Hz, 1H), 6.38 – 6.21 (m, 1H), 3.56 (t, J = 7.1 Hz, 1H), 2.31 (d, J = 15.6 Hz, 2H). 13C NMR (101 MHz, CDCl3) δ 164.1, 139.7, 136.2, 135.4, 133.1, 131.1, 131.0, 128.8, 128.7, 128.6, 128.6, 127.7, 127.4, 126.4, 125.5, 122.5, 39.7, 39.6, 21.0, 21.0. HRMS (ESI): Calcd for C17H17NNaO274.1207, Found: 274.1216

Synthesis of N-(2-(1H-inden-3-yl)phenyl)formamide, 6a
Following the same procedure described above for the synthesis of formylamine 1c, the corresponding N-(2-iodo-phenyl)formamide was prepared and used in a procedure similar to that outlined by Bin Li and co-workers4. To a solution of (1H-inden-3-yl)boronic acid (0.490g, 3.04mmol), Pd(PPh3)4 (0.233g, 0.20mmol) and K2CO3 (1.12g, 8.08mmol) in 20 mL of toluene, 8 mL of absolute ethanol, and 4 mL of H2O was added N-(2-iodo-phenyl)formamide (0.500g, 2.02mmol). The mixture was then purged with N2 and refluxed for 24 h. The reaction was then cooled to room temperature and 20 mL of H2O were added and the resulting phases were separated. The resulting aqueous phase was extracted with 3 x 10 mL ethylacetate. The resulting organic phases were then washed with water (1 x 20 mL) followed by a saturated solution of brine (1 x 20 mL). The resulting organic phase was then dried using Na2SO4 and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc 5:1 as eluent) to give the desired products 6a (64%) as a brown oil that slowly crystallized.

\[ \text{H NMR (600 MHz, CDCl}_3\text{)} \delta 8.62 (dd, J = 11.3, 2.2 Hz, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.24 – 8.10 (m, 1H), 7.77 – 7.67 (m, 1H), 7.63 – 7.52 (m, 1H), 7.48 (s, 1H), 7.44 – 7.37 (m, 1H), 7.37 – 7.28 (m, 2H), 7.26 – 7.12 (m, 1H), 6.61 (dt, J = 20.2, 1.9 Hz, 1H), 3.60 (dd, J = 7.8, 1.5 Hz, 1H).

\[ \text{C NMR (151 MHz, CDCl}_3\text{)} \delta 161.9, 159.1, 144.1, 143.9, 143.8, 141.5, 140.9, 143.7, 134.5, 134.0, 133.9, 130.7, 129.8, 129.0, 128.8, 126.6, 126.6, 126.5, 126.6, 125.6, 125.1, 124.5, 124.3, 124.2, 121.3, 120.5, 120.2, 118.0, 38.8. \]

HRMS (ESI): Calcd for C16H13NNaO 258.0894, Found: 258.0896

**Synthesis of 1-isocyano-4-methyl-2-(3-phenylprop-1-en-1-yl)benzene, 5b**

Substrate 5b was synthesized following the procedure for 1d from 5a, (79%). \[ \text{H NMR (600 MHz, CDCl}_3\text{)} \delta 7.35 – 7.29 (m, 1H), 7.26 – 7.18 (m, 1H), 7.00 (dd, J = 8.1, 1.0 Hz, 1H), 6.76 (d, J = 15.7 Hz, 1H), 6.44 (dt, J = 15.7, 7.1 Hz, 1H), 3.60 (d, J = 7.1 Hz, 1H), 2.32 (s, 1H).

\[ \text{C NMR (151 MHz, CDCl}_3\text{)} \delta 139.6, 139.5, 133.6, 133.6, 128.7, 128.7, 128.7, 128.6, 126.9, 126.5, 126.3, 125.2, 39.7, 21.7. \]

HRMS (ESI): Calcd for C17H15NNaO 233.1204, Found: 233.1216

**Synthesis of 3-(2-isocyanophenyl)-1H-indene, 6b**

Substrate 6b was synthesized following the procedure for 1d from 6a, (78%). \[ \text{H NMR (600 MHz, CDCl}_3\text{)} \delta 7.59 – 7.56 (m, 1H), 7.54 (dd, J = 10.6, 3.9 Hz, 1H), 7.48 (dd, J = 12.0, 4.4 Hz, 1H), 7.41 (dd, J = 10.7, 4.6 Hz, 1H), 7.34 – 7.27 (m, 1H).

\[ \text{C NMR (151 MHz, CDCl}_3\text{)} \delta 144.0, 143.7, 140.1, 134.8,
133.4, 130.1, 129.4, 128.5, 128.0, 126.3, 125.3, 124.3, 120.3, 38.9. HRMS (ESI): Calcd for C_{16}H_{11}N
217.0891, Found: 217.0885

### Synthesis of ethyl-3-(2-isocyanophenyl)acrylate, 7b

![Chemical Reaction Diagram]

To prepare substrate 7a, to a one neck round bottom flask was added a magnetic stir bar, 2-iodoaniline (9.636 g, 44 mmol), ethyl acrylate (17.6 g, 176 mmol), Pd(OAc)$_2$ (1 g, 4.45 mmol), P(o-tolyl)$_3$ (2.7 g, 8.9 mmol), Triethylamine (15 mL), and CH$_3$CN. The mixture was then purged with N$_2$ and refluxed for 24 h. The reaction was then cooled to room temperature and 20 mL of H$_2$O were added and the resulting phases were separated. The resulting aqueous phase was extracted with 3 x 10 mL ethyl acetate. The resulting organic phases were then washed with water (1 x 20 mL) followed by a saturated solution of brine (1 x 20 mL). The resulting organic phase was then dried using Na$_2$SO$_4$ and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc 10:1 as eluent) to give the desired products 7a (92%) as a dark yellow oil that slowly crystallized. Substrate 7b (63%) was prepared by formylation followed by subsequent dehydration of Aniline 7a following the method described above for substrate 1c, 1d. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, $J = 16.1$ Hz, 1H), 7.77 – 7.56 (m, 1H), 7.50 – 7.31 (m, 1H), 6.51 (d, $J = 16.0$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 1H), 1.41 – 1.25 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.9, 166.1, 137.7, 130.9, 130.8, 129.7, 127.8, 127.0, 122.6, 77.5, 77.2, 76.9, 61.0, 14.4. HRMS (EI): Calcd for C$_{12}$H$_{11}$NO$_2$
201.0790, Found: 201.0796

### 3-(2-aminophenyl)prop-2-en-1-ol, 8a

![Chemical Reaction Diagram]

S11
Substrate 8a was prepared by DIBAL reduction of substrate 7a. To a flame dried round bottom flask was added aniline 7a (3.06g, 16mmol), magnetic stir bar and dry THF (20 mL). The resulting mixture was placed into an ice bath under an inert atmosphere of N₂. To the resulting solution was added drop wise diisobutyl aluminum hydride (37 mL, 1M solution). The resulting mixture was allowed to stir for 8 h under N₂. Upon completion of the reaction, MeOH and H₂O were added (10 mL) and allowed to stir for another 2 h. The resulting mixture was then filtered and the resulting phases were separated. The aqueous phase was extracted with 3 x 10 mL ethyl acetate. The resulting organic phases were then washed with water (1 x 20 mL) followed by a saturated solution of brine (1 x 20 mL). The resulting organic phase was then dried using Na₂SO₄ and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc  6:1 as eluent) to give the desired products 8a (87%) as a yellow oil.

**1H NMR (400 MHz, CDCl₃)** δ 7.24 (dd, J = 7.7, 1.1 Hz, 1H), 7.08 (td, J = 7.9, 1.4 Hz, 1H), 6.84 – 6.72 (m, 1H), 6.70 – 6.57 (m, 2H), 6.17 (dt, J = 15.7, 5.3 Hz, 1H), 4.23 (d, J = 5.4 Hz, 2H), 3.87 (s, 3H).

**13C NMR (101 MHz, CDCl₃)** δ 143.6, 130.2, 128.5, 127.2, 125.9, 123.2, 119.1, 116.4, 77.5, 77.2, 76.9, 63.2.

**HRMS (EI)**: Calcd for (2M + Na) C₁₈H₂₂N₂O₂Na 321.1413, Found: 321.1399

Substrate 8b was obtained by treating 8a (0.110g, 0.737mmols) with NaH (0.02g, 0.8mmol) in dry THF (10 mL). This solution was allowed to stir in an ice bath for 30 min. Then to the solution was added MeI (0.115g, 0.81mmol). The solution was allowed to stir for 1 h, and was monitored by TLC. Upon completion, 5 mL of water was added. The aqueous phase was separated and washed with ethyl acetate (1 x 20 mL). The organic phases were collected and washed with water (1 x 20 mL) followed by saturated solution of brine (1 x 20 mL). The organic phases were separated and dried using Na₂SO₄ and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc, 10:1 as eluent) to give the desired product 8b (60%) as a crème colored oil that slowly crystallized.

**1H NMR (400 MHz, CDCl₃)** δ 7.27 (dd, J = 7.7, 1.3 Hz, 1H), 7.14 – 7.03 (m, 1H), 6.76 (ddd, J = 7.5, 1.1, 0.6 Hz, 1H), 6.72 – 6.54 (m, 1H), 6.17 (dt, J = 15.8, 6.0 Hz, 1H), 4.10 (dd, J = 6.0, 1.5 Hz, 1H), 3.75 (s, 1H), 3.41 (s, 1H).

**13C NMR (101 MHz, CDCl₃)** δ 143.9, 128.7, 128.1, 127.5, 127.5, 123.0, 118.9, 116.1, 77.5, 77.2, 76.9, 73.3, 58.0.

**HRMS (ESI)** calculated for C₁₀H₁₃NO 163.0997, found 163.1003.

**2-(3-methoxyprop-1-en-1-yl)aniline, 8b**

Substrate 8b was obtained by treating 8a (0.110g, 0.737mmols) with NaH (0.02g, 0.8mmol) in dry THF (10 mL). This solution was allowed to stir in an ice bath for 30 min. Then to the solution was added MeI (0.115g, 0.81mmol). The solution was allowed to stir for 1 h, and was monitored by TLC. Upon completion, 5 mL of water was added. The aqueous phase was separated and washed with ethyl acetate (1 x 20 mL). The organic phases were collected and washed with water (1 x 20 mL) followed by saturated solution of brine (1 x 20 mL). The organic phases were separated and dried using Na₂SO₄ and filtered. The solvent was removed under reduced pressure in vacuo and the crude product was purified using flash chromatography on silica gel (n-hexane/EtOAc 6:1 as eluent) to give the desired products 8a (87%) as a yellow oil.

**1H NMR (400 MHz, CDCl₃)** δ 7.24 – 6.72 (m, 1H), 6.70 – 6.57 (m, 2H), 6.17 (dt, J = 15.7, 5.3 Hz, 1H), 4.23 (d, J = 5.4 Hz, 2H), 3.87 (s, 3H).

**13C NMR (101 MHz, CDCl₃)** δ 143.6, 130.2, 128.5, 127.2, 125.9, 123.2, 119.1, 116.4, 77.5, 77.2, 76.9, 63.2. HRMS (EI): Calcd for (2M + Na) C₁₈H₂₂N₂O₂Na 321.1413, Found: 321.1399

**Synthesis of N-(2-(3-methoxyprop-1-en-1-yl)phenyl)formamide, 8c**

Substrate 8c was synthesized following the procedure described for 1c using aniline 8b. The crude residue was washed thoroughly with hexane (3 x 30 mL) and dried in vacuo to give (88%) of the title compound as a light orange liquid that slowly crystallized.

**1H NMR (400 MHz, CDCl₃)** δ 8.52 – 8.33 (m, 11H), 7.85 (d, J = 8.0 Hz, 5H), 7.48 (dd, J = 7.5, 1.6 Hz, 4H), 7.39 (dd, J = 7.8, 1.1 Hz, 3H), 7.30 – 7.16 (m, 7H), 7.12 (t, J = 7.7 Hz, 7H), 6.81 – 6.66 (m, 7H), 6.30 – 6.11 (m, 7H), 4.08 (ddd, J = 4.8, 2.3, 1.0 Hz, 14H), 3.37 (t, J = 1.2 Hz, 21H).

**13C NMR (101 MHz, CDCl₃)** δ 163.9, 159.8, 133.8, 133.5, 130.4, 130.0, 129.9,
129.4, 128.7, 128.3, 127.4, 127.0, 126.6, 126.5, 125.7, 123.8, 122.3, 77.5, 76.9, 72.9, 72.9, 58.3, 58.2.

HRMS(ESI) calculated for C_{11}H_{13}NO_2Na 214.0844, found 214.0856.

**Synthesis of 1-isocyano-2-(3-methoxyprop-1-en-1-yl)benzene, 8d**

![Structural formula](image)

Substrate 8d was synthesized following the procedure for 1a using 8c. The crude product was purified by flash chromatography (Hexanes:EtOAc, 10:1) to give (83%) of the title compound as a light brown oil. R<sub>f</sub> = 0.44 (hexanes/EtOAc 10:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (d, <i>J</i> = 7.8 Hz, 1H), 7.59 (d, <i>J</i> = 7.8 Hz, 1H), 7.45 – 7.33 (m, 2H), 6.94 (d, <i>J</i> = 15.9 Hz, 1H), 6.40 (dt, <i>J</i> = 15.9, 5.8 Hz, 1H), 4.25 – 4.03 (m, 2H), 3.42 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.4, 133.3, 130.9, 129.5, 128.3, 127.3, 126.2, 77.5, 76.9, 72.9, 58.4, 29.8.

690 cm<sup>-1</sup>. HRMS(ESI) calculated for C<sub>11</sub>H<sub>11</sub>N<sub>173.0841</sub>, found 173.0850.

### 4. Optimization Studies

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<th>Temp, °C</th>
<th>Conv %&lt;sup&gt;a&lt;/sup&gt;</th>
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S13
[a] NMR yield based on 1a using 1,2-dichloroethane as an internal standard. [b] Isolated yield based on 1a

At the outset, we examined the reaction of isocyanide 1a with phenylboronic acid(2a) in the presence of Mn(OAc)₃·2H₂O due to its known ability to generate carbon centered radical with organo boron reagents. The use of Mn(OAc)₃·2H₂O (3 equiv) gave quinoline 3aa in 67% yield at 90 °C for 4 hours (entry 8). There was no other observed byproduct. The oxidant was then varied to Mn(acac)₃ (3 equiv) under similar reaction conditions gave quinoline 3aa in 86% yield. It was then decided to screen conditions using Mn(acac)₃ as our preferred oxidant. The use of more than two equivalents of the manganese salt was required for the complete conversion of 1a (entry 1, 2). Solvent screening showed a preference for non-polar aromatics, along with this reflux was not necessary with only mild heating to observe desired transformation.

5. General procedure for the Mn(III) Mediated radical cyclization with boronic acids

Preparation of the corresponding quinolines followed a similar method reported by Chatani, Tobisu and co-workers⁵. To an oven-dried 10 mL single neck flask, isocyanide (0.1 mmol), phenylboronic acid(0.15mmol), Mn(acac)₃ (0.3 mmol) and toluene (3.0ml) were added sequentially under an inert atmosphere of nitrogen. The mixture was stirred at 90 °C for 4 h under a nitrogen atmosphere. The reaction mixture was then cooled to room temperature and purified by column chromatography on silica gel to afford the desired product.

6. Spectroscopic data for products

6-phenyl-7H-indeno[2,1-c]quinoline, Q2

![Chemical structure of 6-phenyl-7H-indeno[2,1-c]quinoline](image)

1H NMR (600 MHz, CDCl₃) δ 8.76 (d, J = 8.3 Hz, 1H), 8.49 (d, J = 7.8 Hz, 1H), 8.32 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 7.3 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.69 (dd, J = 10.9, 7.6 Hz, 1H), 7.52 (ddd, J = 17.6, 14.4, 7.5 Hz, 3H), 4.18 (s, 1H). 13C NMR (151 MHz, CDCl₃) δ 156.5, 148.5, 145.7, 145.2, 141.0, 140.6, 134.5, 130.9, 129.0, 128.9, 128.9, 128.8, 128.4, 127.5, 126.8, 125.3, 124.5, 124.1, 123.6, 37.9. HRMS (EI): Calcd for C₂₂H₁₆N 294.1282, Found: 294.1298

3-benzylidene-2-phenylindoline, Q3

![Chemical structure of 3-benzylidene-2-phenylindoline](image)

1H NMR (400 MHz, CDCl₃) δ 7.57 (s, 1H), 7.36 (d, J = 7.4 Hz, 3H), 7.28 (d, J = 8.1 Hz, 1H), 7.18 (dd, J = 6.2, 2.5 Hz, 2H), 7.08 (t, J = 6.3 Hz, 6H), 6.96 (t, J = 7.5 Hz, 1H), 6.62 (t, J = 7.6 Hz, 1H), 5.32 (s, 1H). 13C NMR (101 MHz, CDCl₃) δ 145.6, 135.9, 133.4, 129.4, 129.2, 128.5, 128.3, 128.0, 127.8, 125.7, 122.0, 122.0, 121.1, 119.4, 114.9, 110.4, 50.0. HRMS (EI): Calcd for C₂₂H₁₆N 294.1282, Found: 294.1298
3-butyl-2-phenyl-1H-indole, Q4

\[
\begin{align*}
\text{HNMR (600 MHz, CDCl}_3\text{) } & \delta 8.01 (s, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.56 (dd, J = 8.1, 1.0 Hz, 2H), 7.47 (t, J = 7.7 Hz, 3H), 7.39 – 7.36 (m, 2H), 7.22 – 7.18 (m, 1H), 7.16 – 7.12 (m, 1H), 2.94 – 2.83 (m, 2H), 1.72 (dt, J = 15.4, 7.7 Hz, 2H), 1.48 – 1.38 (m, 3H), 0.93 (t, J = 7.4 Hz, 4H). \\
\text{13C NMR (151 MHz, CDCl}_3\text{) } & \delta 138.9, 136.1, 134.2, 130.5, 129.5, 129.0, 128.1, 127.6, 122.3, 119.6, 119.5, 114.3, 110.9, 33.4, 29.9, 24.5, 23.1. \\
\text{HRMS (EI)}: \text{Calcd for C}_{18}H_{18}N 248.1439, \text{Found: 248.1452}
\end{align*}
\]

2-Phenylquinoline(Q1)

\[
\begin{align*}
\text{HNMR (600 MHz, CDCl}_3\text{) } & \delta 8.25 – 8.15 (m, 4H), 7.88 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.48 (t, J = 7.3 Hz, 1H). \\
\text{13C NMR (151 MHz, CDCl}_3\text{) } & \delta 157.5, 148.4, 139.8, 136.9, 129.9, 129.8, 129.5, 129.0, 127.7, 127.6, 127.3, 126.4, 119.2. \\
\text{Spectral data match those previously reported}^6.
\end{align*}
\]

2-(4-Methylphenyl)quinoline(Q5)

\[
\begin{align*}
\text{HNMR (400 MHz, CDCl}_3\text{): } & \delta 2.36 (s, 3H), 7.25, (d, J = 8.3 Hz, 2H), 7.35-7.45, (m, 1H), 7.60-7.75, (m, 3H), 8.00-8.05 (m, 3H), 8.15 (d, J = 4.4 Hz, 1H). \\
\text{13C NMR (101 MHz, CDCl}_3\text{): } & \delta 21.1, 118.5, 125.8, 126.8, 127.2, 127.3, 128.0, 129.3, 129.4, 136.4, 136.6, 139.1, 148.0, 156.9. \\
\text{Spectral data match those previously reported}^6.
\end{align*}
\]

2-isobutylquinoline(Q10)

\[
\begin{align*}
\text{HNMR (CDCl}_3\text{, 400 MHz) } & \delta (ppm): 8.06 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.74 (dd, J = 8.2, 0.8 Hz, 1H), 7.44-7.40 (m, 1H), 7.67-7.63 (m, 1H), 7.20 (d, J = 8.4 Hz, 1H), 2.81 (d, J = 7.4 Hz, 2H), 2.20 (q, J = 6.8 Hz, 1H), 0.95 (s, 6H). \\
\text{13C NMR (CDCl}_3\text{, 101 MHz) } & \delta: 162.2, 148.0, 135.9, 129.2, 128.9, 127.5, 126.7, 125.6, 122.0, 48.3, 29.4, 22.6. \\
\text{Spectral data match those previously reported}^7.
\end{align*}
\]

4-(quinolin-2-yl)benzonitrile(Q7)

\[
\begin{align*}
\text{HNMR (CDCl}_3\text{, 400 MHz) } & \delta (ppm): 8.46 (d, J = 8.4 Hz, 1H), 8.40 (d, J = 8.4 Hz, 1H), 7.74 (dd, J = 8.2, 1.0 Hz, 1H), 7.44-7.40 (m, 1H), 7.67-7.63 (m, 1H), 7.20 (d, J = 8.4 Hz, 1H), 2.81 (d, J = 7.4 Hz, 2H), 2.20 (q, J = 6.8 Hz, 1H), 0.95 (s, 6H). \\
\text{13C NMR (CDCl}_3\text{, 101 MHz) } & \delta: 162.2, 148.0, 135.9, 129.2, 128.9, 127.5, 126.7, 125.6, 122.0, 48.3, 29.4, 22.6. \\
\text{Spectral data match those previously reported}^7.
\end{align*}
\]
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 – 8.24 (m, 2H), 8.21 – 8.12 (m, 1H), 7.91 – 7.84 (m, 1H), 7.82 – 7.73 (m, 3H), 7.70 – 7.66 (m, 1H), 7.59 (ddd, $J = 8.1$, 6.9, 1.2 Hz, 1H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ: 112.7, 118.5, 118.8, 127.1, 127.5, 128.0, 132.5, 137.2, 143.6, 148.2, 154.8. Spectral data match those previously reported$^8$.

**2-(4-fluorophenyl)quinoline (Q6)**

![Image of 2-(4-fluorophenyl)quinoline](image)

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.22 (d, $J = 8.7$ Hz, 1H), 8.20 – 8.14 (m, 1H), 7.83 (d, $J = 8.6$ Hz, 1H), 7.74 (ddd, $J = 8.4$, 6.9, 1.5 Hz, 1H), 7.54 (ddd, $J = 8.1$, 6.9, 1.1 Hz, 1H), 7.22 (dd, $J = 9.7$, 7.8 Hz, 1H). $^{13}$C NMR (CDCl$_3$, 101 MHz): δ = 163.8, 156.2, 148.2, 136.8, 135.8, 129.7, 129.4, 129.3, 127.4, 126.3, 118.6, 115.7. Spectral data match those previously reported$^7$.

**2-(2-Thienyl)quinoline (Q9)**

![Image of 2-(2-Thienyl)quinoline](image)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.11-7.18 (m, 1H), 7.42-7.47 (m, 2H), 7.61-7.74 (m, 4H), 8.03 (d, $J = 8.1$ Hz, 1H), 8.07 (d, $J = 7.5$ Hz, 1H). $^{13}$C NMR (CDCl$_3$, 101 MHz): δ 117.1, 125.7, 125.9, 127.0, 127.4, 128.0, 128.5, 129.0, 129.7, 136.5, 145.2, 147.9, 152.2. Spectral data match those previously reported$^9$.

**2-(pyridin-4-yl)quinoline (Q13)**

![Image of 2-(pyridin-4-yl)quinoline](image)

$^1$H NMR (CDCl$_3$, 400 MHz) δ: 8.80 (d, $J = 5.7$ Hz, 2H), 8.31 (d, $J = 8.6$ Hz, 1H), 8.21 (d, $J = 8.5$ Hz, 1H), 8.09 (d, $J = 6.0$ Hz, 2H), 7.93 (d, $J = 8.6$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.76-7.80 (m, 1H), 7.61 (t, $J = 7.5$ Hz, 1H). $^{13}$C NMR (CDCl$_3$, 101 MHz): δ: 118.2, 121.4, 127.0, 127.4, 127.6, 129.8, 129.9, 137.0, 146.3, 148.1, 150.3, 154.1. Spectral data match those previously reported$^7$.

**2-(3,5-dimethoxyphenyl)quinolone (Q8)**

![Image of 2-(3,5-dimethoxyphenyl)quinolone](image)

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.22 (d, $J = 8.6$ Hz, 1H), 8.18 (d, $J = 8.5$ Hz, 1H), 7.87 – 7.81 (m, 2H), 7.76 – 7.71 (m, 1H), 7.54 (dd, $J = 11.0$, 3.9 Hz, 1H), 7.33 (d, $J = 2.2$ Hz, 2H), 6.59 (t, $J = 2.2$ Hz, 1H), 3.91 (s, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 161.3, 157.2, 148.3, 142.0, 136.9, 129.9, 129.8, 127.6, 127.5, 126.5, 119.3, 105.8, 101.8, 55.7. HRMS(ESI) calculated for C$_{17}$H$_{15}$NO$_2$Na [M+Na]+m/z 288.0093, found 288.0093.

**2-(2-bromophenyl)quinoline (Q12)**

S16
**1H NMR (400 MHz, CDCl$_3$)** $\delta$ 8.21 (dd, $J = 16.3, 8.4$ Hz, 2H), 7.88 (d, $J = 8.1$ Hz, 1H), 7.76 (ddd, $J = 8.5, 6.9, 1.4$ Hz, 1H), 7.71 (dd, $J = 8.3, 1.8$ Hz, 2H), 7.64 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.62 – 7.56 (m, 1H), 7.46 (td, $J = 7.4, 1.0$ Hz, 1H), 7.31 (td, $J = 7.7, 1.7$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.9, 148.1, 141.8, 135.8, 133.4, 131.7, 130.1, 129.9, 129.8, 127.9, 127.7, 127.3, 127.2, 127.0, 122.9, 122.0, 120.0. Spectral data match those previously reported.$^9$

**2-(naphthalen-1-yl)quinoline (Q11)**

**6-methyl-2-phenylquinoline, (Q17)**

**6-methyl-2-(p-tolyl)quinoline, (Q18)**

**6-fluoro-2-(p-tolyl)quinoline, (Q15)**
1H NMR (600 MHz, CDCl₃) δ 8.15 (dt, J = 4.9, 2.8 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.7 Hz, 1H), 7.49 (td, J = 8.8, 2.8 Hz, 1H), 7.43 (dd, J = 8.8, 2.8 Hz, 1H), 7.34 (dd, J = 7.9, 0.5 Hz, 1H), 2.44 (s, 1H). 13C NMR (151 MHz, CDCl₃) δ 145.5, 139.7, 136.7, 136.2, 132.3, 132.2, 129.8, 129.8, 127.8, 127.5, 120.0, 119.8, 119.7, 110.7, 110.5, 21.5.

6-fluoro-2-phenylquinoline, (Q16)

6-fluoro-2-(4-fluorophenyl)quinoline, (Q14)

1H NMR (600 MHz, CDCl₃) δ 8.15 (ddd, J = 9.5, 7.6, 5.4 Hz, 3H), 7.85 (d, J = 8.6 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.44 (dd, J = 8.7, 2.8 Hz, 1H), 7.25 – 7.18 (m, 2H). 13C NMR (151 MHz, CDCl₃) δ 164.8, 163.2, 161.4, 159.7, 155.8, 145.5, 136.4, 136.4, 135.7, 132.3, 132.2, 129.5, 129.4, 127.8, 127.7, 120.2, 120.1, 119.5, 116.1, 115.9, 110.7, 110.6.
7. Copies of $^1$H and $^{13}$C NMR spectra
+ rotamers
DIPA was left in mixture to prevent acidic hydrolysis by chloroform.
DIPA was left in mixture to prevent acidic hydrolysis by chloroform.
Cocrystallized dichloromethane
8. References