

Supporting Information

The sequential reactions of tetrazoles with bromoalkynes for the synthesis of (Z)-N-(2-bromo-1-vinyl)-N-arylcyanamides and 2-arylindoles

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1. General considerations

All reactions were carried out under air. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) in CDCl_3 or DMSO as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^1H NMR data are reported as follows: δ , chemical shift; coupling constants (J are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). IR spectra were recorded as thin films or as solids in KBr pellets on a Perkin-Elmer FT210 spectrophotometer. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.

2. Typical procedures for the reactions

2.1 Typical procedure for the addition reaction of phenol to bromoalkyne

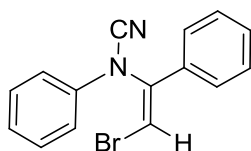
A 10 mL of reaction tube was charged with 1-phenyl-1*H*-tetrazole (**1a**, 0.50 mmol), phenylethynyl bromide (**2a**, 0.75 mmol), Ag_2O (23.2 mg, 0.10 mmol) and DMSO (2.0 mL). The reaction vessel was placed in an oil bath. After the reaction was carried out at 130 °C for 12 h [Ace pressure tube was highly recommended to be employed for safety consideration], it was cooled to room temperature, extracted with EtOAc (3×5.0 mL). The organic layers were combined, dried over MgSO_4 , and concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate= 9:1 to 12:1) to give the desired product **3a**.

2.2 Typical procedure for the palladium-catalyzed intramolecular cyclization of (*Z*)-*N*-(2-bromo-1-vinyl)-*N*-arylcyanamides

A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar charged with (*Z*)-*N*-(2-bromo-1-phenylvinyl)-*N*-phenylcyanamide (**3a**, 0.50 mmol), $\text{Pd}(\text{OAc})_2$ (2.8

mg, 0.025 mmol), K_2CO_3 (138.2 mg, 1.0 mmol), and NMP (2.0 mL). The reaction vessel was placed in an oil bath. After the reaction was carried out at 140 °C for 8 h [Ace pressure tube was highly recommended to be employed for safety consideration], it was cooled to room temperature, extracted with EtOAc (3×5.0 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1 to 9:1) to give the desired product **4a**.

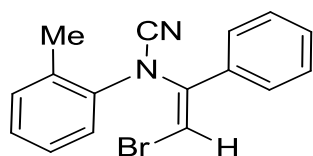
3. Characterization data for the products



3a: (Z)-N-(2-Bromo-1-phenylvinyl)-N-phenylcyanamide

Yellow solid, m.p. 65–66 °C.

1H NMR (400 MHz, $CDCl_3$) δ : 7.48–7.46 (m, 2H), 7.38–7.36 (m, 3H), 7.34–7.32 (m, 2H), 7.14–7.10 (m, 3H), 7.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 139.61, 138.28, 133.20, 130.09, 129.75, 129.31, 126.28, 124.56, 116.71, 110.30, 108.17. IR (KBr, cm^{-1}): 2226 ($\nu_{C\equiv N}$). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{15}H_{12}BrN_2$: 299.0184, Found: 299.0182.

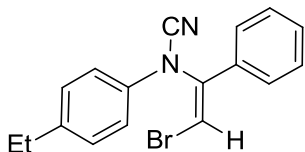


3b: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(p-tolyl)cyanamide

Yellow oil.

1H NMR (400 MHz, $CDCl_3$) δ : 7.47–7.45 (m, 2H), 7.38–7.36 (m, 3H), 7.13 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.95 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 139.79, 135.82, 134.36, 133.33, 130.26, 130.01, 129.25, 126.35, 116.85, 110.59, 107.64, 20.67. IR (neat): 2224 ($\nu_{C\equiv N}$). HRMS (ESI) ($[M+H]^+$) Calcd. for

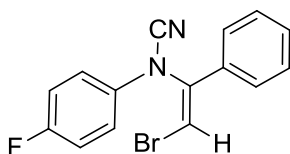
C₁₆H₁₄BrN₂: 313.0340, Found: 313.0340.



3c: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(4-ethylphenyl)cyanamide

Yellow solid, m.p. 43–44 °C.

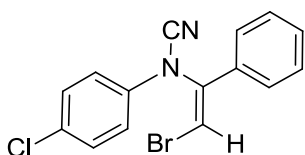
¹H NMR (400 MHz, CDCl₃) δ: 7.49–7.46 (m, 2H), 7.38–7.36 (m, 3H), 7.16–7.14 (m, 2H), 7.05–7.03 (m, 2H), 6.96 (s, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H);
¹³C NMR (100 MHz, CDCl₃) δ: 140.67, 139.83, 135.99, 133.38, 129.99, 129.24, 129.07, 126.34, 116.86, 110.58, 107.72, 28.04, 15.36. IR (KBr, cm⁻¹): 2221 (ν_{C≡N}). HRMS (ESI) ([M+H]⁺) Calcd. for C₁₇H₁₆BrN₂: 327.0497, Found: 327.0493.



3d: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(4-fluorophenyl)cyanamide

Yellow solid, m.p. 84–85 °C.

¹H NMR (400 MHz, CDCl₃) δ: 7.46–7.44 (m, 2H), 7.39–7.37 (m, 3H), 7.11–7.08 (m, 2H), 7.04–7.00 (m, 2H), 6.96 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 159.67 (d, *J*_{CF} = 243.3 Hz), 139.83, 134.40 (d, *J*_{CF} = 2.93 Hz), 133.04, 130.19, 129.34, 126.35, 118.65 (d, *J*_{CF} = 8.2 Hz), 116.61 (d, *J*_{CF} = 23.2 Hz), 110.32, 107.75. IR (KBr, cm⁻¹): 2225 (ν_{C≡N}). HRMS (ESI) ([M+H]⁺) Calcd. for C₁₅H₁₀BrFN₂: 317.0090, Found: 317.0085.

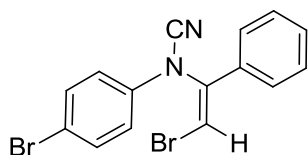


3e: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(4-chlorophenyl)cyanamide

Yellow solid, m.p. 93–94 °C.

¹H NMR (400 MHz, CDCl₃) δ: 7.46–7.44 (m, 2H), 7.39–7.37 (m, 3H), 7.30–7.28 (m, 2H), 7.07–7.05 (m, 2H), 7.01 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 139.26, 136.84,

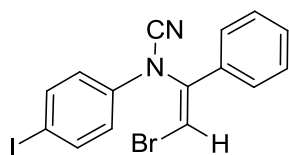
132.71, 130.15, 129.87, 129.70, 129.29, 126.08, 117.89, 109.76, 108.36. IR (KBr, cm^{-1}): 2225 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{10}\text{BrClN}_2$: 332.9794, Found: 332.9792.



3f: (Z)-N-(2-bromo-1-phenylvinyl)-N-(4-bromophenyl)cyanamide

Yellow solid, m.p. 95–96 °C.

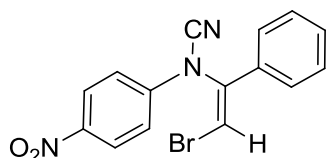
^1H NMR (400 MHz, CDCl_3) δ : 7.46–7.44 (m, 2H), 7.44–7.43 (m, 2H), 7.41–7.38 (m, 3H), 7.02 (s, 2H), 6.99 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 139.37, 137.54, 132.84, 132.76, 130.29, 129.42, 126.19, 118.33, 117.50, 109.76, 108.53. IR (KBr, cm^{-1}): 2224 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{11}\text{Br}_2\text{N}_2$: 376.9289, Found: 376.9288.



3g: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(4-iodophenyl)cyanamide

Yellow solid, m.p. 100–101 °C.

^1H NMR (400 MHz, CDCl_3) δ : 7.64–7.62 (m, 2H), 7.45–7.43 (m, 2H), 7.41–7.36 (m, 3H), 7.02 (s, 1H), 6.89 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 139.28, 138.65, 138.30, 132.84, 130.28, 129.42, 126.16, 118.57, 109.64, 108.60, 87.88. IR (KBr, cm^{-1}): 2232 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{10}\text{BrIN}_2$: 424.9150, Found: 424.9148.

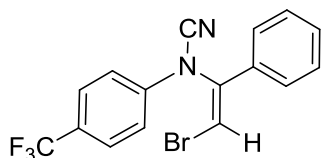


3h: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(4-nitrophenyl)cyanamide

Yellow solid, m.p. 104–105 °C.

^1H NMR (400 MHz, CDCl_3) δ : 8.24–8.22 (d, $J = 9.2$ Hz, 2H), 7.47–7.45 (m, 2H),

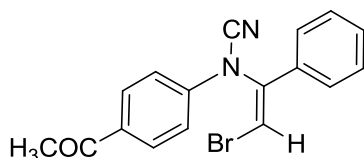
7.44–7.41 (m, 3H), 7.23 (d, $J = 9.1$ Hz, 2H), 7.18 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 144.21, 143.78, 138.86, 132.26, 130.66, 129.66, 125.91, 125.80, 116.29, 110.04, 108.66. IR (KBr, cm^{-1}): 2227 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{10}\text{BrN}_3\text{O}_2$: 344.0035, Found: 344.0036.



3i: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(4-(trifluoromethyl)phenyl)cyanamide

Yellow oil.

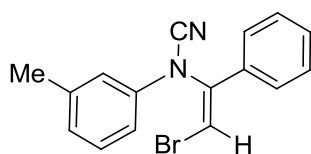
^1H NMR (400 MHz, CDCl_3) δ : 7.61 (d, $J = 8.6$ Hz, 2H), 7.48–7.46 (m, 2H), 7.41–7.40 (m, 3H), 7.22 (d, $J = 8.6$ Hz, 2H), 7.12 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 141.33, 139.09, 132.64, 130.43, 129.53, 127.15 (q, $J = 3.8$ Hz), 126.66 (d, $J = 33.1$ Hz), 126.49, 126.03, 125.13, 122.43, 116.32, 109.34 (q, $J = 10.6$ Hz). IR (neat): 2229 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{11}\text{BrF}_3\text{N}_2$: 367.0058, Found: 367.0055.



3j: (Z)-N-(4-Acetylphenyl)-N-(2-bromo-1-phenylvinyl)cyanamide

Yellow oil.

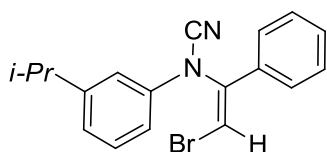
^1H NMR (400 MHz, CDCl_3) δ : 7.96–7.94 (m, 2H), 7.47–7.45 (m, 2H), 7.42–7.36 (m, 3H), 7.19–7.16 (m, 2H), 7.11 (s, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.29, 142.27, 139.11, 133.40, 132.70, 130.37, 129.49, 126.02, 116.01, 109.36, 109.28, 26.43. IR (neat): 2228 ($\nu_{\text{C}\equiv\text{N}}$), 1680 ($\nu_{\text{C}=\text{O}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{17}\text{H}_{13}\text{BrN}_2\text{O}$: 341.0290, Found: 341.0285.



3k: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(m-tolyl)cyanamid

Yellow solid, m.p. 81–82 °C.

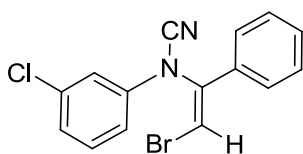
^1H NMR (400 MHz, CDCl_3) δ : 7.49–7.46 (m, 2H), 7.39–7.37 (m, 3H), 7.20 (t, $J = 7.9$ Hz, 1H), 6.99 (br, 2H), 6.93 (d, $J = 7.5$ Hz, 1H), 6.88–6.86 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 140.01, 139.67, 138.22, 133.32, 130.02, 129.49, 129.28, 126.25, 125.43, 117.27, 113.81, 110.43, 108.11, 21.49. IR (KBr, cm^{-1}): 2221 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{14}\text{BrN}_2$: 313.0340, Found: 313.0335.



3l: (Z)-N-(2-bromo-1-phenylvinyl)-N-(3-iso-propylphenyl)cyanamide

Yellow oil.

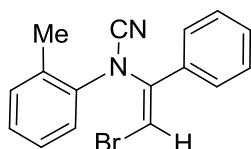
^1H NMR (400 MHz, CDCl_3) δ : 7.49–7.47 (m, 2H), 7.38–7.36 (m, 3H), 7.27–7.21 (m, 1H), 7.03 (s, 1H), 7.00–7.98 (m, 2H), 6.92–6.90 (m, 1H), 2.92–2.85 (m, 1H), 1.21 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 150.98, 139.81, 138.21, 133.44, 130.01, 129.61, 129.27, 126.37, 122.73, 115.02, 114.18, 110.46, 107.90, 34.09, 23.76. IR (neat): 2222 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{18}\text{H}_{18}\text{BrN}_2$: 341.0653, Found: 341.0651.



3m: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(3-chlorophenyl)cyanamide

Yellow solid, m.p. 72–73 °C.

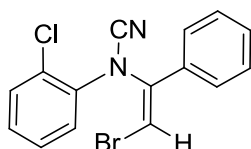
^1H NMR (400 MHz, CDCl_3) δ : 7.47–7.45 (m, 2H), 7.40–7.39 (m, 3H), 7.28–7.24 (m, 1H), 7.14 (s, 1H), 7.11–7.09 (m, 1H), 7.05 (s, 1H), 7.03–7.00 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 139.48, 139.11, 135.62, 132.69, 130.73, 130.24, 129.37, 126.04, 124.69, 116.71, 114.68, 109.55, 108.89. IR (KBr, cm^{-1}): 2227 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{10}\text{BrClN}_2$: 332.9794, Found: 332.9789.



3n: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(o-tolyl)cyanamide

Yellow solid, m.p. 75–76 °C.

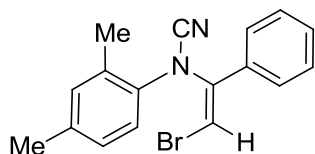
^1H NMR (400 MHz, CDCl_3) δ : 7.47–7.45 (m, 2H), 7.37–7.35 (m, 3H), 7.27–7.24 (m, 1H), 7.18–7.14 (m, 3H), 6.47 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 142.52, 137.27, 133.78, 132.72, 132.12, 130.07, 128.95, 127.47, 127.38, 127.25, 123.50, 111.35, 101.41, 18.28. IR (KBr, cm^{-1}): 2221 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{14}\text{BrN}_2$: 313.0340, Found: 313.0339.



3o: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(2-chlorophenyl)cyanamide

Yellow oil.

^1H NMR (400 MHz, CDCl_3) δ : 7.51–7.49 (m, 2H), 7.38–7.36 (m, 2H), 7.35–7.33 (m, 3H), 7.25–7.23 (m, 1H), 7.19–7.15 (m, 1H), 6.54 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 141.90, 135.47, 133.34, 131.33, 130.17, 128.98, 128.95, 128.57, 128.00, 127.45, 125.26, 110.27, 102.08. IR (neat): 2227 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{10}\text{BrClN}_2$: 332.9794, Found: 332.9791.

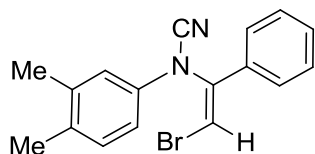


3p: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(2,4-dimethylphenyl)cyanamide

Yellow solid, m.p. 95–96 °C.

^1H NMR (400 MHz, CDCl_3) δ : 7.47–7.45 (m, 2H), 7.37–7.35 (m, 3H), 7.06–7.03 (m, 1H), 6.96–6.94 (m, 2H), 6.45 (s, 1H), 2.42 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 142.49, 137.20, 136.98, 133.85, 131.89, 130.02, 129.46, 128.93, 128.30, 127.37, 123.86, 111.47, 101.26, 20.83, 17.81. IR (KBr, cm^{-1}): 2221 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI)

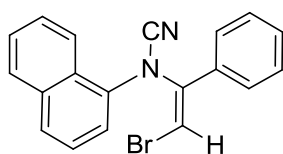
([M+H]⁺) Calcd. for C₁₇H₁₆BrN₂: 327.0497, Found: 327.0492.



3q: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(3,4-dimethylphenyl)cyanamide

Yellow solid, m.p. 86–87 °C.

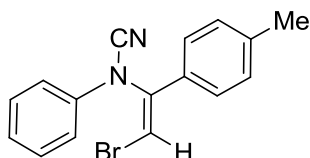
¹H NMR (400 MHz, CDCl₃) δ: 7.48–7.46 (m, 2H), 7.38–7.36 (m, 3H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.97–6.95 (m, 2H), 6.81–6.78 (s, 1H), 3.00 (s, 3H), 2.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 139.81, 138.34, 136.00, 133.45, 133.04, 130.64, 129.94, 129.22, 126.32, 118.03, 114.21, 110.69, 107.64, 19.96, 18.99. IR (KBr, cm⁻¹): 2222 (ν_{C≡N}). HRMS (ESI) ([M+H]⁺) Calcd. for C₁₇H₁₆BrN₂: 327.0497, Found: 327.0497.



3r: (Z)-N-(2-Bromo-1-phenylvinyl)-N-(naphthalen-1-yl)cyanamide

Yellow solid, m.p. 139–141 °C.

¹H NMR (400 MHz, DMSO) δ: 8.31 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.62–7.60 (m, 1H), 7.58–7.54 (m, 3H), 7.51–7.47 (m, 1H), 7.28–7.27 (m, 3H), 7.23 (s, 1H); ¹³C NMR (100 MHz, DMSO) δ: 142.24, 134.61, 134.27, 133.55, 130.40, 129.31, 129.25, 128.81, 127.91, 127.81, 127.40, 127.24, 126.18, 121.92, 121.84, 112.07, 104.62. IR (KBr, cm⁻¹): 2223 (ν_{C≡N}). HRMS (ESI) ([M+H]⁺) Calcd. for C₁₉H₁₃BrN₂: 349.0340, Found: 349.0336.

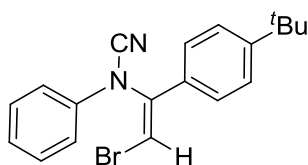


3s: (Z)-N-(2-Bromo-1-(p-tolyl)vinyl)-N-phenylcyanamide

White solid, m.p. 109–110 °C.

¹H NMR (400 MHz, CDCl₃) δ: 7.38 (s, 1H), 7.36–7.31 (m, 3H), 7.18–7.16 (m, 2H),

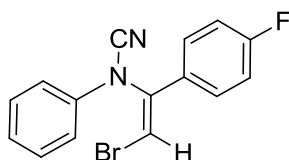
7.15–7.10 (m, 3H), 6.94 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 140.41, 139.64, 138.41, 130.41, 130.01, 129.72, 126.21, 124.49, 116.72, 110.39, 107.06, 21.32. IR (KBr, cm^{-1}): 2225 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{13}\text{BrN}_2$: 313.0340, Found: 313.0336.



3t: (Z)-N-(2-Bromo-1-(4-(tert-butyl)phenyl)vinyl)-N-phenylcyanamide

White solid, m.p. 82–84 °C.

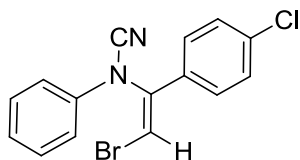
^1H NMR (400 MHz, CDCl_3) δ : 7.41–7.39 (m, 4H), 7.37–7.32 (m, 2H), 7.15–7.11 (m, 3H), 6.97 (s, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 153.53, 139.53, 138.48, 130.31, 129.74, 126.29, 125.94, 124.42, 116.57, 110.42, 107.43, 34.82, 31.11. IR (KBr, cm^{-1}): 2225 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{19}\text{H}_{19}\text{BrN}_2$: 355.0807, Found: 355.0810.



3u: (Z)-N-(2-Bromo-1-(4-fluorophenyl)vinyl)-N-phenylcyanamide

Yellow solid, m.p. 108–109 °C.

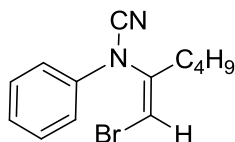
^1H NMR (400 MHz, CDCl_3) δ : 7.48–7.44 (m, 2H), 7.35 (t, $J = 8.2$ Hz, 2H), 7.15–7.12 (m, 2H), 7.10–7.04 (m, 3H), 6.93 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.62 (d, $J = 250.0$ Hz), 138.77, 138.10, 129.79, 129.47 (d, $J = 3.4$ Hz), 128.32 (d, $J = 8.5$ Hz), 124.73, 116.81, 116.49 (d, $J = 22.0$ Hz), 110.10, 107.67 (d, $J = 1.8$ Hz). IR (KBr, cm^{-1}): 2230 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{10}\text{BrFN}_2$: 317.0090, Found: 317.0086.



3v: (Z)-N-(2-Bromo-1-(4-chlorophenyl)vinyl)-N-phenylcyanamide

Yellow solid, m.p. 113–114 °C.

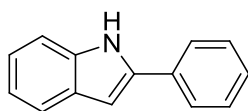
^1H NMR (400 MHz, CDCl_3) δ : 7.41–7.39 (m, 2H), 7.35–7.34 (m, 3H), 7.33–7.32 (m, 1H), 7.15–7.14 (m, 2H), 7.11–7.09 (m, 2H), 7.00 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 138.73, 138.04, 136.18, 131.75, 129.83, 129.60, 127.54, 124.78, 116.76, 110.03, 108.61. IR (KBr, cm^{-1}): 2227 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{10}\text{BrClN}_2$: 332.9794, Found: 332.9792.



3w: (Z)-N-(1-bromohept-1-en-2-yl)-N-phenylcyanamide

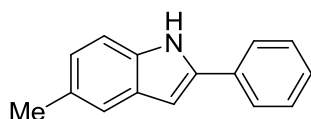
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ : 7.42–7.38 (m, 2H), 7.20–7.16 (m, 1H), 7.13–7.11 (m, 2H), 6.41 (s, 1H), 2.37 (t, $J = 7.4$ Hz, 2H), 1.56–1.50 (m, 2H), 1.32–1.30 (m, 4H), 0.90–0.87 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 140.27, 137.68, 129.74, 124.72, 117.21, 110.38, 106.08, 33.66, 30.92, 26.31, 22.21, 13.82. IR (neat): 2221 ($\nu_{\text{C}\equiv\text{N}}$). HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{14}\text{H}_{17}\text{BrN}_2$: 293.0653, Found: 295.0649.



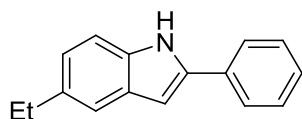
4a: 2-Phenyl-1H-indole^[1]

^1H NMR (400 MHz, CDCl_3) δ : 8.36 (br, 1H), 7.69–7.68 (m, 3H), 7.49–7.45 (m, 2H), 7.43–7.41 (m, 1H), 7.38–7.34 (m, 1H), 7.27–7.23 (m, 1H), 7.20–7.16 (m, 1H), 6.87 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 137.93, 136.87, 132.41, 129.31, 129.04, 127.73, 125.20, 122.38, 120.70, 120.30, 110.96, 100.01.



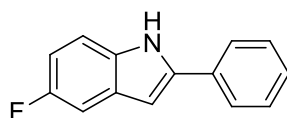
4b: 5-Methyl-2-phenyl-1H-indole^[2]

¹H NMR (400 MHz, CDCl₃) δ: 8.25 (br, 1H), 7.68–7.66 (m, 2H), 7.48–7.44 (m, 3H), 7.36–7.30 (m, 2H), 7.07–7.05 (m, 1H), 6.78 (d, *J* = 1.3 Hz, 1H), 2.49 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 137.98, 135.22, 132.55, 129.59, 129.49, 129.00, 127.58, 125.09, 124.00, 120.33, 110.59, 99.58, 21.49.



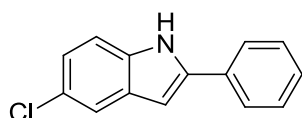
4c: 5-Ethyl-2-phenyl-1H-indole^[3]

¹H NMR (400 MHz, CDCl₃) δ: 8.25 (br, 1H), 7.69–7.67 (m, 2H), 7.50–7.45 (m, 3H), 7.37–7.33 (m, 2H), 7.13–7.11 (s, 1H), 6.82 (s, 1H), 2.83 (q, *J* = 7.4 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 138.05, 136.29, 135.41, 132.60, 129.57, 129.02, 127.59, 125.13, 123.04, 119.12, 110.72, 99.76, 29.06, 16.47.



4d: 5-Fluoro-2-phenyl-1H-indole^[2]

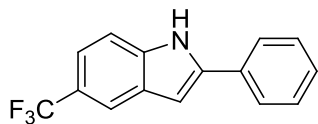
¹H NMR (400 MHz, CDCl₃) δ: 8.34 (br, 1H), 7.67–7.65 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.38–7.34 (m, 1H), 7.33–7.27 (m, 2H), 6.98–6.93 (m, 1H), 6.80 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 158.22 (d, *J*_{CF} = 233.4 Hz), 139.69, 133.35, 132.06, 129.65 (d, *J*_{CF} = 9.8 Hz), 129.08, 128.03, 125.21, 111.47 (d, *J*_{CF} = 9.7 Hz), 110.63 (d, *J*_{CF} = 26.3 Hz), 105.38 (d, *J*_{CF} = 23.4 Hz), 100.08 (d, *J*_{CF} = 4.7 Hz).



4e: 5-Chloro-2-phenyl-1H-indole^[1]

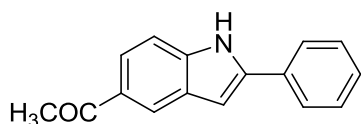
¹H NMR (400 MHz, CDCl₃) δ: 8.38 (br, 1H), 7.67–7.65 (m, 2H), 7.60 (d, *J* = 1.3 Hz, 1H), 7.48–7.45 (m, 2H), 7.38–7.34 (s, 1H), 7.32–7.30 (s, 1H), 7.17–7.14 (m, 1H), 6.77

(d, $J = 1.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 139.31, 135.15, 131.89, 130.35, 129.09, 128.11, 125.87, 125.24, 122.57, 119.98, 111.84, 99.57.



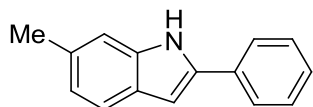
4i: 2-Phenyl-5-(trifluoromethyl)-1H-indole^[2]

^1H NMR (400 MHz, CDCl_3) δ : 8.55 (br, 1H), 7.94 (s, 1H), 7.69–7.67 (m, 2H), 7.50–7.47 (m, 2H), 7.45–7.43 (m, 2H), 7.41–7.37 (m, 1H), 6.90 (d, $J = 1.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 139.68, 138.06, 131.66, 129.16, 128.62, 128.33, 126.66, 125.33, 123.97, 119.00 (d, $J_{\text{CF}} = 3.6$ Hz), 118.31 (d, $J_{\text{CF}} = 4.2$ Hz), 111.07, 100.56.



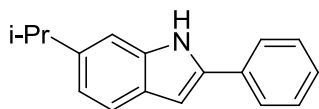
4j: 1-(2-Phenyl-1H-indol-5-yl)ethanone^[4]

^1H NMR (400 MHz, DMSO) δ : 11.93 (br, 1H), 8.26 (m, 1H), 7.89–7.87 (m, 2H), 7.77–7.75 (m, 1H), 7.50–7.45 (s, 3H), 7.35–7.32 (s, 1H), 7.04 (s, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ : 202.57, 144.96, 144.68, 136.84, 134.57, 134.18, 133.36, 133.09, 130.40, 127.56, 126.87, 116.39, 105.41, 31.77.



4k: 6-Methyl-2-phenyl-1H-indole^[5]

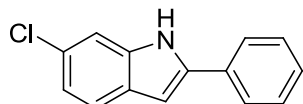
^1H NMR (400 MHz, CDCl_3) δ : 8.22 (br, 1H), 7.67–7.65 (m, 2H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.35–7.31 (m, 1H), 7.20 (s, 1H), 7.00–6.98 (m, 1H), 6.80 (d, $J = 1.3$ Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 137.33, 137.25, 132.59, 132.25, 128.98, 127.45, 127.11, 124.98, 122.07, 120.30, 110.86, 99.85, 21.80.



4l: 6-(*iso*-Propyl)-2-phenyl-1*H*-indole

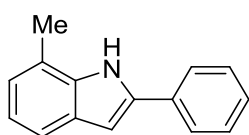
White solid, m.p. 165.5–166.1 °C.

^1H NMR (400 MHz, CDCl_3) δ : 8.24 (br, 1H), 7.69–7.67 (m, 2H), 7.62–7.60 (m, 1H), 7.49 (t, $J = 7.5$ Hz, 2H), 7.38–7.34 (m, 1H), 7.29 (s, 1H), 7.11–7.09 (m, 1H), 6.84 (d, $J = 0.8$ Hz, 1H), 3.12–3.05 (m, 1H), 1.40–1.38 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 143.76, 137.51, 137.29, 132.68, 129.03, 127.51, 127.48, 125.05, 120.44, 119.77, 108.17, 99.89, 34.46, 24.51. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{17}\text{H}_{16}\text{N}$: 235.1361, Found: 235.1360.



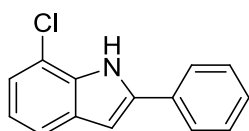
4m: 6-Chloro-2-phenyl-1*H*-indole^[1]

^1H NMR (400 MHz, DMSO) δ : 11.70 (br, 1H), 7.84 (m, $J = 7.6$ Hz, 2H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.42 (s, 1H), 7.34–7.30 (m, 1H), 7.02–7.00 (m, 1H), 6.91 (d, $J = 0.90$ Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ : 139.26, 137.98, 132.23, 129.39, 128.17, 127.91, 126.53, 125.55, 121.82, 120.19, 111.27, 99.26.



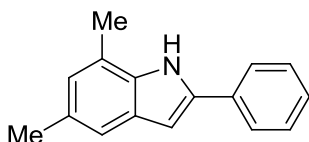
4n: 7-Methyl-2-phenyl-1*H*-indole^[5]

^1H NMR (400 MHz, CDCl_3) δ : 8.26 (br, 1H), 7.77–7.76 (m, 2H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 2H), 7.43–7.40 (m, 1H), 7.19–7.16 (m, 1H), 7.12–7.10 (m, 1H), 6.93 (d, $J = 2.0$ Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 137.74, 136.55, 132.65, 129.08, 128.96, 127.71, 125.29, 123.06, 120.58, 120.16, 118.53, 100.71, 16.77.



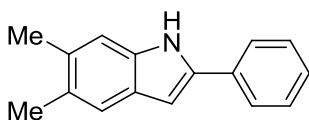
4o: 7-Chloro-2-phenyl-1H-indole^[6]

¹H NMR (400 MHz, CDCl₃) δ: 8.52 (br, 1H), 7.72–7.70 (m, 2H), 7.56–7.54 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.40–7.35 (m, 1H), 7.27–7.21 (m, 1H), 7.11–7.07 (m, 1H), 6.87 (d, *J* = 2.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 138.69, 134.09, 131.81, 130.62, 129.11, 128.18, 125.37, 121.62, 121.04, 119.25, 116.35, 100.82.



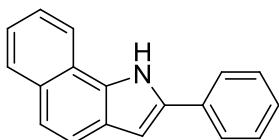
4p: 5,7-Dimethyl-2-phenyl-1H-indole^[7]

¹H NMR (400 MHz, CDCl₃) δ: 8.19 (br, 1H), 7.75–7.74 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 3H), 7.41–7.36 (m, 1H), 6.93 (s, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 2.58 (s, 3H), 2.53 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 137.79, 134.90, 132.79, 129.74, 129.24, 129.03, 127.55, 125.18, 124.84, 119.78, 118.07, 100.24, 21.49, 16.71.



4q: 5,6-Dimethyl-2-phenyl-1H-indole^[8]

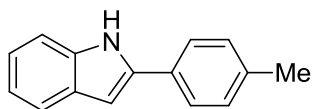
¹H NMR (400 MHz, CDCl₃) δ: 8.15 (br, 1H), 7.66–7.64 (m, 2H), 7.46–7.41 (m, 3H), 7.34–7.30 (m, 1H), 7.18 (s, 1H), 6.75 (d, *J* = 1.0 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 3H); ¹³C NMR (100MHz, CDCl₃) δ: 137.08, 135.93, 132.72, 131.50, 128.95, 128.89, 127.70, 127.31, 124.92, 120.71, 111.30, 99.42, 20.52, 20.07.



4r: 2-Phenyl-1H-benzo[g]indole^[2]

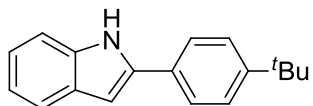
¹H NMR (400 MHz, CDCl₃) δ: 9.07 (br, 1H), 8.10–8.08 (m, 1H), 7.96–7.94 (m, 1H), 7.76–7.72 (m, 3H), 7.58–7.54 (m, 2H), 7.51–7.43 (m, 3H), 7.37–7.33 (m, 1H), 6.98 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 136.28, 132.56, 131.42, 130.62,

129.09, 129.02, 127.41, 125.56, 125.35, 124.99, 123.95, 121.63, 121.20, 120.62, 119.35, 101.72.



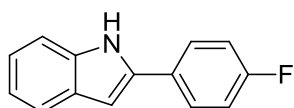
4s: 2-(*p*-Tolyl)-1*H*-indole^[1]

¹H NMR (400 MHz, CDCl₃) δ: 8.30 (br, 1H), 7.67–7.65 (m, 1H), 7.59–7.57 (m, 2H), 7.42–7.40 (m, 1H), 7.29–7.27 (m, 2H), 7.24–7.20 (m, 1H), 7.18–7.14 (m, 1H), 6.82 (s, 1H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 138.09, 137.65, 136.74, 129.72, 129.62, 129.38, 125.09, 122.14, 120.54, 120.22, 110.82, 99.44, 21.23.



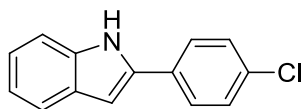
4t: 2-(4-(*tert*-Butyl)phenyl)-1*H*-indole^[9]

¹H NMR (400 MHz, CDCl₃) δ: 8.33 (br, 1H), 7.67–7.64 (m, 2H), 7.62 (s, 1H), 7.51–7.48 (m, 2H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.24–7.20 (m, 1H), 7.17–7.13 (m, 1H), 6.83 (s, 1H), 1.40 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ: 150.91, 138.03, 136.77, 129.61, 129.40, 125.96, 124.93, 122.12, 120.55, 120.19, 110.84, 99.54, 34.67, 31.29.



4u: 2-(4-Fluorophenyl)-1*H*-indole^[1]

¹H NMR (400 MHz, DMSO) δ: 11.53 (br, 1H), 7.91–7.87 (m, 2H), 7.53(d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 8.8 Hz, 2H), 7.13–7.09 (m, 1H), 7.02–6.99 (m, 1H), 6.84 (d, *J* = 0.8 Hz, 1H); ¹³C NMR (100 MHz, DMSO) δ: 162.02 (d, *J*_{CF} = 243.1 Hz), 137.62, 137.20, 129.36 (d, *J*_{CF} = 3.1 Hz), 129.14, 127.44 (d, *J*_{CF} = 8.1 Hz), 122.04, 120.50, 119.88, 116.24 (d, *J*_{CF} = 21.5 Hz), 111.75, 99.13 (d, *J*_{CF} = 1.2 Hz).



4v: 2-(4-Chlorophenyl)-1H-indole^[1]

¹H NMR (400 MHz, DMSO) δ : 11.58 (br, 1H), 7.88–7.86 (m, 2H), 7.54–7.51 (m, 2H), 7.49 (s, 1H), 7.44–7.42 (m, 1H), 7.14–7.10 (m, 1H), 7.03–6.99 (m, 1H), 6.90 (d, $J = 1.0$ Hz, 1H); ¹³C NMR (100 MHz, DMSO) δ : 137.73, 136.85, 132.26, 131.62, 129.33, 129.05, 127.07, 122.33, 120.65, 119.97, 111.83, 99.79.

6. References

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5. ^1H NMR and ^{13}C NMR spectra of the products

