Supporting Information

Intramolecular of C–N Bond Addition of Amides to Alkynes using Platinum-Catalyst

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General Information. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL JMT-400/54/SS (JASTEC, 400 MHz) and JEOL JNM α -500 (500 MHz) spectrometers. ^1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CHCl_3 at 7.24 ppm integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ^{13}C NMR spectra reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77 ppm. IR spectra were recorded on a SHIMADZU FTIR-8200A spectrometer; absorptions are reported in cm^{-1} . High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer. Column chromatography was carried out employing Silica gel 60 N (spherical, neutral, 40~100 μm , KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm pre-coated plate Kieselgel 60 F₂₅₄ (Merck). All manipulations were conducted under an argon atmosphere using standard Schlenk techniques.

Materials. Anhydrous benzene, toluene, *p*-xylene (WAKO), PdCl_2 (Kawaken fine chemicals), PtCl_2 , $\text{PtCl}_2(\text{CH}_3\text{CN})_2$, PtBr_2 , PtCl_4 (Aldrich) were purchased and used as received. , Mesitylene (TCI) and anisole (KANTO) were used after distillation (with CaH_2) and stocked under inert atmosphere (Ar, MS4Å). All the alkynylamides **1** and $\text{Pd}(\text{PPh}_3)_4$ were prepared according to the literature procedure. All other compounds used were commercially available.

Representative procedure for the preparation of alkynylamides (1)

Synthesis of *N*-acetyl-*N*-methyl- 2-(3,3-dimethyl-1-butyryl)aniline **1a**

(1) To a solution of 2-iodoaniline (20.8g, 95.0mmol) in CH_2Cl_2 (200mL) were successively added pyridine (11.5mL, 142.2mmol) and acetic anhydride (13.5mL, 143.1mmol) dropwise at 0 °C with stirring. Then the reaction mixture was allowed to warm to room temperature and stirred. After the reaction completed, water was added and the mixture was extracted with CH_2Cl_2 . Combined organic layers were washed with brine and dried over MgSO_4 . Concentrated crude *N*-acyl-2-iodoaniline was used without further purification as a starting material of the following step.

(2) To a solution of *N*-acyl-2-iodoaniline (crude, ca. 95mmol) in EtOH (200mL) were added

potassium carbonate (39.4g, 300.3mmol) and the reaction progress was methyl iodide (17.7mL, 284.3mmol). The reaction mixture was stirred at room temperature and monitored by TLC. After complete consumption of the starting material, water was added and the resulting mixture was extracted with CH_2Cl_2 . Combined organic layers were washed with brine and dried over MgSO_4 . Obtained crude mixture was purified by column chromatography (silica gel, hexane/ethyl acetate = 5/1) to give *N*-acetyl-*N*-methyl-2-iodoaniline (15.1g, 99% (two steps)).

(3) To a solution of *N*-acetyl-*N*-methyl-2-iodoaniline (2.75g, 10.0mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.46g, 0.4mmol) and CuI (0.15g, 0.8mmol) in DMF (2.5mL) were successively added 3,3-dimethyl-1-butyne (1.85mL, 15.0mmol) and Et_2NH (10mL). The resulting solution was warmed to 40 °C and stirred at the same temperature. After the reaction completed, saturated aqueous $\text{NH}_4\text{Cl}/\text{NH}_3$ was added and the product was extracted with CH_2Cl_2 . Combined organic layers were washed with brine and dried over MgSO_4 . Concentrated crude product was purified by column chromatography (silica gel, toluene/ethyl acetate = 200/1~2/1) to afford *N*-acetyl-*N*-methyl-2-(3,3-dimethyl-1-butyryl)aniline **1a** (1.87g, 82%).

Typical procedure for the PtCl_2 -catalyzed acylation of alkynes

To a mixture of PtCl_2 (13.3mg, 0.05mmol, handle under argon) and *N*-acetyl-*N*-methyl-2-(3,3-dimethyl-1-butyryl)aniline **1a** (114.7mg, 0.50mmol) was added anisole (1.0mL, 0.5M) at room temperature and the mixture was warmed immediately to 80 °C. After complete consumption of the starting material which was monitored by TLC, the reaction mixture was cooled to room temperature and filtered through a short SiO_2 pad and the filtrate was concentrated. The residue was purified by column chromatography (silica gel, toluene/ethyl acetate = 200/1~10/1) to afford 3-acetyl-2-dimethylethyl-*N*-methyldole **2a** (71.8mg, 63%) and 2-dimethylethyl-*N*-methyldole **3a** (26.7mg, 29%).

Analytical Data

***N*-Acetyl-*N*-methyl-2-(3,3-dimethyl-1-butyryl)aniline (1a):** white crystal; ^1H NMR (399.65 MHz, CDCl_3) δ 1.28 (9H, s), 1.80 (3H, s), 3.19 (3H, s), 7.14 (1H, dd, $J = 7.8, 1.6$ Hz), 7.24 (1H, ddd, $J = 7.8, 7.8, 1.6$ Hz), 7.29 (1H, ddd, $J = 7.8, 7.8, 1.6$ Hz), 7.42 (1H, dd, $J = 7.8, 1.6$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 21.97, 28.15, 30.78, 35.92, 74.86 (alkyne), 104.13 (alkyne), 123.22, 127.69, 127.74, 128.75, 132.68, 145.77, 170.48 (CO); IR (KBr) 2968-2870, 2239 (CC, alkyne), 1663 (CO, amide), 1375, 1298, 777, 756 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$: C, 78.55; H, 8.36; N, 6.11. Found: C, 78.17; H, 8.40; N, 5.96; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$ (M^+) 229.1461. Found 229.1462.

***N*-Acetyl-*N*-methyl-2-(1-pentyryl)aniline (1b):** pale yellow oil; ^1H NMR (399.65 MHz, CDCl_3) δ 0.98 (3H, t, $J = 7.4$ Hz), 1.56 (2H, tq, $J = 7.4, 7.4$ Hz), 1.79 (3H, s), 2.33 (2H, t, $J =$

7.4 Hz), 3.18 (3H, s), 7.13 (1H, dd, $J = 7.8, 1.6$ Hz), 7.23 (1H, ddd, $J = 7.8, 7.8, 1.6$ Hz), 7.28 (1H, ddd, $J = 7.8, 7.8, 1.6$ Hz), 7.43 (1H, dd, $J = 7.8, 1.6$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 13.50, 21.46, 22.02, 22.09, 35.96, 76.37 (alkyne), 95.81 (alkyne), 123.17, 127.73, 128.72, 133.08, 145.52, 170.42 (CO); IR (neat) 2964, 2933, 2230 (CC, alkyne), 1668 (CO, amide), 1489, 1377, 772, 754 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}$: C, 78.09; H, 7.96; N, 6.51. Found: C, 77.85; H, 8.16; N, 6.37; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{18}\text{NO}$ ($\text{M}+\text{H}^+$) 216.1383. Found 216.1384.

***N*-Acetyl-*N*-methyl-2-cyclohexylethynylaniline (1c):** pale yellow crystal; ^1H NMR (399.65 MHz, CDCl_3) δ 1.24-1.39 (3H, m), 1.40-1.56 (3H, m), 1.63-1.75 (2H, m), 1.78-1.89 (2H, m), 1.81 (3H, s), 2.50-2.60 (1H, m), 3.20 (3H, s), 7.14 (1H, dd, $J = 7.3, 1.6$ Hz), 7.24 (1H, ddd, $J = 7.3, 7.3, 1.6$ Hz), 7.29 (1H, ddd, $J = 7.3, 7.3, 1.9$ Hz), 7.43 (1H, dd, $J = 7.3, 1.9$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 22.01, 24.82, 25.79, 29.70, 32.48, 35.96, 76.18, 100.01, 123.26, 127.69, 127.74, 128.70, 132.89, 145.64, 170.46 (CO); IR (KBr) 2932, 2855, 2224 (CC, alkyne), 1661 (CO, amide), 1379, 1298, 1144, 777, 758 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}$ (M^+) 255.1618. Found 255.1609. Calcd for $\text{C}_{17}\text{H}_{22}\text{NO}$ ($\text{M}+\text{H}^+$) 256.1696. Found 256.1696.

***N*-Acetyl-*N*-methyl-2-(4-methoxyphenyl)ethynylaniline (1d):** pale yellow solid; ^1H NMR (399.65 MHz, CDCl_3) δ 1.87 (3H, s), 3.26 (3H, s), 3.80 (3H, s), 6.84 (2H, d, $J = 9.0$ Hz), 7.21 (1H, dd, $J = 7.3, 1.8$ Hz), 7.30 (1H, ddd, $J = 7.3, 7.3, 1.8$ Hz), 7.42 (2H, d, $J = 9.0$ Hz), 7.55 (1H, dd, $J = 7.3, 1.8$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 22.06, 36.15, 55.24, 83.76 (alkyne), 94.75 (alkyne), 113.97, 114.42, 122.83, 127.80, 127.84, 129.06, 132.49, 133.06, 145.38, 159.85, 170.57 (CO); IR (KBr) 3064-2837, 2216 (CC, alkyne), 1660 (CO, amide), 1605, 1508, 1248, 1026, 831, 775, 748 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2$: C, 77.38; H, 6.14; N, 5.02. Found: C, 77.21; H, 6.29; N, 4.85; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2$ (M^+) 279.1254. Found 279.1256.

***N*-Acetyl-*N*-methyl-2-(4-methylphenyl)ethynylaniline (1e):** pale yellow crystal; ^1H NMR (399.65 MHz, CDCl_3) δ 1.87 (3H, s), 2.35 (3H, s), 3.27 (3H, s), 7.13 (2H, d, $J = 8.2$ Hz), 7.22 (1H, dd, $J = 7.4, 1.6$ Hz), 7.32 (1H, ddd, $J = 7.4, 7.4, 1.6$ Hz), 7.36 (1H, ddd, $J = 7.4, 7.4, 1.9$ Hz), 7.57 (1H, dd, $J = 7.4, 1.9$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 21.52, 22.08, 36.19, 84.31 (alkyne), 94.84 (alkyne), 119.26, 122.69, 127.86, 129.05, 129.27, 131.46, 132.69, 138.87, 138.88, 145.53, 170.53 (CO); IR (KBr) 3071-2918, 2218 (CC, alkyne), 1661 (CO, amide), 1485, 1385, 1306, 820, 779 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}$: C, 82.09; H, 6.51; N, 5.32. Found: C, 82.09; H, 6.66; N, 5.16; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}$ (M^+) 263.1305. Found 263.1307.

***N*-Acetyl-*N*-methyl-2-phenylethynylaniline (1f):** pale yellow solid; ^1H NMR (399.65 MHz, CDCl_3) δ 1.88 (3H, s), 3.28 (3H, s), 7.23 (1H, dd, $J = 7.8, 1.6$ Hz), 7.29-7.36 (3H, m), 7.33 (1H, ddd, $J = 7.8, 7.8, 1.6$ Hz), 7.38 (1H, ddd, $J = 7.8, 7.8, 2.1$ Hz), 7.45-7.53 (2H, m), 7.59 (1H, dd, $J = 7.8, 2.1$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 22.12, 36.24, 84.91 (alkyne), 94.59 (alkyne),

122.35, 122.53, 127.91, 127.92, 128.32, 128.67, 129.52, 131.58, 132.82, 145.67, 170.57 (CO); IR (KBr) 3080-2934, 2218 (CC, alkyne), 1661 (CO, amide), 1497, 1381, 1302, 1144, 777, 758 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}$: C, 81.89; H, 6.07; N, 5.62. Found: C, 81.78; H, 6.24; N, 5.50; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}$ (M^+) 249.1148. Found 249.1151.

***N*-Acetyl-*N*-methyl-2-phenylethynylaniline-*d*₃ (1f-*d*₃)**: white solid; ^1H NMR (399.65 MHz, CDCl_3) δ 3.28 (3H, s), 7.23 (1H, dd, $J = 7.8, 1.6$ Hz), 7.29-7.36 (3H, m), 7.33 (1H, ddd, $J = 7.8, 7.8, 1.6$ Hz), 7.38 (1H, ddd, $J = 7.8, 7.8, 2.1$ Hz), 7.45-7.53 (2H, m), 7.59 (1H, dd, $J = 7.8, 2.1$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 21.32 (septet, $^1J(\text{C}, \text{D}) = 19.9$ Hz), 36.12, 84.47 (alkyne), 94.51 (alkyne), 122.28, 122.45, 127.83, 127.86, 128.25, 128.60, 129.47, 131.50, 132.74, 145.59, 170.48 (CO); IR (KBr) 3055, 3030, 2930, 2221 (CC, alkyne), 1651 (CO, amide), 1497, 1373, 1308, 1150, 777, 758 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{12}\text{D}_3\text{NO}$ (M^+) 252.1336. Found 252.1338.

***N*-Acetyl-*N*-methyl-2-(4-fluorophenyl)ethynylaniline (1g)**: colorless crystal; ^1H NMR (399.65 MHz, CDCl_3) δ 1.87 (3H, s), 3.26 (3H, s), 7.02 (2H, dd, $^3J(\text{H}, \text{H}) = 9.0$ Hz, $^3J(\text{H}, \text{F}) = 9.0$ Hz), 7.23 (1H, dd, $J = 7.7, 1.3$ Hz), 7.33 (1H, ddd, $J = 7.7, 7.7, 1.3$ Hz), 7.38 (1H, ddd, $J = 7.7, 7.7, 1.8$ Hz), 7.46 (2H, dd, $^3J(\text{H}, \text{H}) = 9.0$ Hz, $^4J(\text{H}, \text{F}) = 5.3$ Hz), 7.57 (1H, dd, $J = 7.7, 1.8$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 22.05, 36.17, 84.62 (d, $^5J(\text{C}, \text{F}) = 1.7$ Hz, alkyne), 93.42 (alkyne), 115.62 (d, $^2J(\text{C}, \text{F}) = 22.3$ Hz), 118.42 (d, $^4J(\text{C}, \text{F}) = 4.1$ Hz), 122.31, 127.85, 127.92, 129.57, 132.64, 133.48 (d, $^3J(\text{C}, \text{F}) = 8.2$ Hz), 145.59, 162.57 (d, $^1J(\text{C}, \text{F}) = 249.3$ Hz), 170.53 (CO); IR (KBr) 3069, 2930, 2220 (CC, alkyne), 1661 (CO, amide), 1508, 1217 (C-F), 841, 797, 766, 750 cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{NOF}$: C, 76.37; H, 5.28; N, 5.24. Found: C, 76.37; H, 5.55; N, 5.06; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{14}\text{NOF}$ (M^+) 267.1054. Found 267.1054.

***N*-Acetyl-*N*-methyl-2-(4-trifluoromethylphenyl)ethynylaniline (1h)**: pale yellow oil; ^1H NMR (399.65 MHz, CDCl_3) δ 1.82 (3H, s), 3.22 (3H, s), 7.20 (1H, dd, $J = 7.8, 1.4$ Hz), 7.29 (1H, ddd, $J = 7.8, 7.8, 1.4$ Hz), 7.36 (1H, ddd, $J = 7.8, 7.8, 1.6$ Hz), 7.50 (2H, d, $J = 8.3$ Hz), 7.53 (2H, d, $J = 8.3$ Hz), 7.55 (1H, dd, $J = 7.8, 1.6$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 21.96, 36.14, 87.14 (alkyne), 92.75 (alkyne), 121.73, 123.60 (q, $^1J(\text{C}, \text{F}) = 271.7$ Hz), 125.16 (q, $^3J(\text{C}, \text{F}) = 4.2$ Hz), 126.06 (q, $^4J(\text{C}, \text{F}) = 1.7$ Hz), 127.89, 127.95, 130.13, (q, $^2J(\text{C}, \text{F}) = 32.6$ Hz), 130.14, 131.69, 132.87, 145.83, 170.39 (CO); IR (neat) 3065, 2934, 2222 (CC, alkyne), 1668 (CO, amide), 1614, 1487, 1323 (C-F), 1169 (C-F), 1126 (C-F), 1065, 843, 770, 752 cm^{-1} ; Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{NOF}_3$: C, 68.12; H, 4.45; N, 4.42. Found: C, 67.98; H, 4.61; N, 4.65; HRMS (EI) Calcd for $\text{C}_{18}\text{H}_{14}\text{NOF}_3$ (M^+) 317.1022. Found 317.1024.

***N*-Formyl-*N*-methyl-2-(1-pentynyl)aniline (1i)**: pale yellow oil; ^1H NMR (399.65 MHz, CDCl_3) δ 1.01 (3H, t, $J = 7.1$ Hz), 1.60 (2H, tq, $J = 7.1, 7.1$ Hz), 2.36 (2H, t, $J = 7.1$ Hz), 3.26 (3H, s), 7.12 (1H, dd, $J = 7.6, 1.5$ Hz), 7.24 (1H, ddd, $J = 7.6, 7.6, 1.5$ Hz), 7.30 (1H, ddd, $J =$

7.6, 7.6, 1.5 Hz), 7.46 (1H, dd, $J = 7.6, 1.5$ Hz), 8.26 (1H, s); ^{13}C NMR (100.40 MHz, CDCl_3) δ 13.45, 21.40, 21.93, 32.82, 76.68 (alkyne), 95.98 (alkyne), 121.81, 126.30, 127.24, 128.41, 133.26, 142.89, 162.77 (CO); IR (neat) 3070-2860, 2233 (CC, alkyne), 1682 (CO, amide), 1491, 1340, 1097, 766 cm^{-1} ; Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}$: C, 77.57; H, 7.52; N, 6.96. Found: C, 77.39; H, 7.64; N, 6.91; HRMS (EI) Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}$ (M^+) 201.1148. Found 201.1155. Calcd for $\text{C}_{13}\text{H}_{14}\text{NO}$ ($\text{M}-\text{H}^+$) 200.1070. Found 200.1070.

***N*-Benzoyl-*N*-methyl-2-(1-pentynyl)aniline (1j):** pale yellow oil; ^1H NMR (399.65 MHz, CDCl_3) δ 1.04 (3H, t, $J = 7.3$ Hz), 1.65 (2H, tq, $J = 7.3, 7.3$ Hz), 2.44 (2H, t, $J = 7.3$ Hz), 3.42 (3H, s), 6.89-6.97 (1H, m), 7.03-7.12 (2H, m), 7.11 (2H, dd, $J = 7.3, 7.3$ Hz), 7.18 (1H, t, $J = 7.3$ Hz), 7.28-7.37 (1H, m), 7.32 (2H, d, $J = 7.3$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 13.27, 21.35, 21.85, 36.98, 76.89 (alkyne), 96.11 (alkyne), 122.49, 126.76, 127.10, 127.84, 128.02, 128.35, 129.11, 132.67, 135.82, 145.79, 170.51 (CO); IR (neat) 3060-2872, 2230 (CC, alkyne), 1651 (CO, amide), 1489, 1362, 1094, 791, 768, 752, 714 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}$ (M^+) 277.1461. Found 277.1444. Calcd for $\text{C}_{19}\text{H}_{20}\text{NO}$ ($\text{M}+\text{H}^+$) 278.1539. Found 278.1544.

***N*-Phenylacetyl-*N*-methyl-2-(1-pentynyl)aniline (1k):** pale yellow oil; ^1H NMR (399.65 MHz, CDCl_3) δ 0.99 (3H, t, $J = 7.0$ Hz), 1.57 (2H, tq, $J = 7.0, 7.0$ Hz), 2.33 (2H, t, $J = 7.0$ Hz), 3.22 (3H, s), 3.36 (1H, d, $J = 14.8$ Hz), 3.44 (1H, d, $J = 14.8$ Hz), 7.01-7.07 (3H, m), 7.12-7.22 (3H, m), 7.22-7.30 (2H, m), 7.44-7.50 (1H, m); ^{13}C NMR (100.40 MHz, CDCl_3) δ 13.58, 21.50, 22.08, 36.36, 40.89, 76.50 (alkyne), 96.13 (alkyne), 123.46, 126.28, 127.87, 128.00, 128.39, 128.58, 129.14, 133.10, 135.38, 144.98, 170.86 (CO); IR (neat) 3070-2870, 2230 (CC, alkyne), 1663 (CO, amide), 1489, 1450, 1373, 1101, 770, 754, 731, 696 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{21}\text{NO}$ (M^+) 291.1618. Found 291.1617.

***N*-Phenylacetyl-*N*-methyl-2-phenylethynylaniline (1l):** pale yellow oil; ^1H NMR (399.65 MHz, CDCl_3) δ 3.30 (3H, s), 3.43 (1H, d, $J = 14.9$ Hz), 3.52 (1H, d, $J = 14.9$ Hz), 7.02-7.08 (2H, m), 7.10-7.19 (4H, m), 7.34-7.39 (5H, m), 7.42-7.49 (2H, m), 7.57-7.63 (1H, m); ^{13}C NMR (100.40 MHz, CDCl_3) δ 36.56, 41.02, 84.99 (alkyne), 94.84 (alkyne), 122.28, 122.74, 126.29, 128.00, 128.25, 128.49, 128.50, 128.63, 129.06, 129.34, 131.55, 132.76, 135.19, 145.06, 171.02 (CO); IR (neat) 3070-2930, 2220 (CC, alkyne), 1661 (CO, amide), 1497, 1450, 1375, 1128, 1094, 756, 731 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{23}\text{H}_{19}\text{NO}$ (M^+) 325.1461. Found 325.1462.

***N*-Methyl-*N*-trifluoroacetyl-2-(1-pentynyl)aniline (1m):** orange oil; ^1H NMR (399.65 MHz, CDCl_3) δ 1.00 (3H, t, $J = 7.2$ Hz), 1.59 (2H, tq, $J = 7.2, 7.2$ Hz), 2.36 (2H, t, $J = 7.2$ Hz), 3.32 (2.7H, s, s-cis), 3.44 (0.3H, q, $^5J(\text{H}, \text{F}) = 1.8$ Hz, s-trans), 7.15-7.23 (1H, m), 7.26-7.37 (2H, m), 7.42-7.51 (1H, m); ^{13}C NMR (100.40 MHz, CDCl_3) δ 13.31, 21.32, 21.85 (s-trans), 21.92 (s-cis), 37.30 (s-trans), 37.98 (s-cis), 75.75 (alkyne, s-cis), 75.84 (alkyne, s-trans), 95.81 (alkyne,

s-trans), 96.45 (alkyne, s-cis), 116.12 (q, ^1J (C, F) = 287.7 Hz, s-cis), 116.49 (q, ^1J (C, F) = 287.3 Hz), 121.98 (s-trans), 123.44 (s-cis), 126.69 (s-trans), 127.88 (s-cis), 128.16 (s-trans), 128.21 (s-cis), 128.70 (s-trans), 128.77 (s-cis), 132.74 (s-cis), 133.14 (s-trans), 141.52 (s-cis), 143.16 (s-trans), 156.84 (q, ^2J (C, F) = 35.6 Hz, CO); IR (neat) 2966, 2937, 2876, 2233 (CC, alkyne), 1705 (CO, amide), 1491, 1219 (C–F), 1120 (C–F), 1155 (C–F), 1124, 1097, 770, 752 cm^{-1} ; Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{NOF}_3$: C, 62.43; H, 5.24; N, 5.20. Found: C, 62.13; H, 5.40; N, 5.18; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{14}\text{NOF}_3$ (M^+) 269.1022. Found 269.1023.

***N*-Acetyl-4-methoxy-2-(1-pentynyl)-*N*-methylaniline (1n):** pale yellow oil; ^1H NMR (399.65 MHz, CDCl_3) δ 0.98 (3H, t, J = 7.3 Hz), 1.61 (2H, tq, J = 7.1, 7.3 Hz), 2.37 (2H, t, J = 7.1 Hz), 3.19 (3H, s), 3.82 (3H, s), 6.85 (1H, dd, J = 2.9, 8.8 Hz), 6.97 (1H, d, J = 2.9 Hz), 7.07 (1H, d, J = 8.8 Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 13.55, 21.47, 22.01, 22.12, 36.16, 55.54, 76.46, 95.63, 115.05, 117.27, 123.96, 128.66, 138.70, 158.50, 170.96; IR (neat) 2963-2838, 2231, 1665, 1503, 1377, 1031 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ (M^+) 245.1416. Found 245.1413.

***N*-Acetyl-5-methoxy-2-(1-pentynyl)-*N*-methylaniline (1o):** orange solid; ^1H NMR (399.65 MHz, CDCl_3) δ 0.88 (3H, t, J = 7.4 Hz), 1.59 (2H, tq, J = 6.9, 7.4 Hz), 2.37 (2H, t, J = 6.9 Hz), 3.22 (3H, s), 3.82 (3H, s), 6.71 (1H, d, J = 3.7 Hz), 6.83 (1H, dd, J = 3.7, 8.8 Hz), 7.39 (1H, d, J = 8.8 Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 0.88 (3H, t, J = 7.4 Hz), 1.59 (2H, tq, J = 6.9, 7.4 Hz), 2.37 (2H, t, J = 6.9 Hz), 3.22 (3H, s), 3.82 (3H, s), 6.71 (1H, d, J = 3.7 Hz), 6.83 (1H, dd, J = 3.7, 8.8 Hz), 7.39 (1H, d, J = 8.8 Hz); IR (neat) 3112-2843, 2228, 1654, 1601, 1230, 838 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.22; H, 7.81; N, 5.71; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ (M^+) 245.1416. Found 245.1413.

***N*-Methyl-3-acetyl-2-(1,1-dimethylethyl)indole (2a):** white crystal; ^1H NMR (399.65 MHz, CDCl_3) δ 1.52 (9H, s), 2.68 (3H, s), 3.89 (3H, s), 7.13 (1H, dd, J = 8.4, 6.9 Hz), 7.22 (1H, dd, J = 8.4, 6.9 Hz), 7.27 (1H, d, J = 8.4 Hz), 7.45 (1H, d, J = 8.4 Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 30.92, 33.21, 33.77, 33.97, 108.92, 116.69, 118.49, 120.21, 121.88, 125.49, 137.05, 144.53, 203.54 (CO); IR (KBr) 3009-2874, 1676 (CO), 1472, 1346, 1103, 743, 708 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$: C, 78.55; H, 8.36; N, 6.11. Found: C, 78.49; H, 8.37; N, 6.17; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$ (M^+) 229.1461. Found 229.1462.

***N*-Methyl-3-acetyl-2-propylindole (2b):** pale yellow oil; ^1H NMR (399.65 MHz, CDCl_3) δ 1.05 (3H, t, J = 7.4 Hz), 1.67 (1H, ddq, J = 10.0, 8.0, 7.4 Hz), 1.67 (1H, ddq, J = 8.0, 7.4, 5.6 Hz), 2.68 (3H, s), 3.18 (1H, dd, J = 10.0, 5.6 Hz), 3.18 (1H, dd, J = 8.0, 8.0 Hz), 7.22-7.28 (2H, m), 7.30-7.36 (1H, m), 7.90-7.97 (1H, m); ^{13}C NMR (100.40 MHz, CDCl_3) δ 14.18, 22.45, 27.80, 29.34, 31.61, 109.51, 113.38, 120.53, 121.75, 121.76, 126.19, 136.48, 149.21, 193.83 (CO); IR (neat) 2963, 2932, 2872, 1645 (CO), 1514, 1472, 1402, 1215, 1101, 970, 746 cm^{-1} ; HRMS (EI)

Calcd for $C_{14}H_{17}NO$ (M^+) 215.1305. Found 215.1306.

***N*-Methyl-3-acetyl-2-cyclohexylindole (2c):** pale yellow oil; ^1H NMR (399.65 MHz, $CDCl_3$) δ 1.22-1.52 (3H, m), 1.75-1.82 (3H, m), 1.83-1.92 (2H, m), 1.93-2.06 (2H, m), 2.69 (3H, s), 3.85 (3H, s), 3.91-4.04 (1H, m), 7.21-7.27 (2H, m), 7.29-7.34 (1H, m), 7.84-7.90 (1H, m); ^{13}C NMR (100.40 MHz, $CDCl_3$) δ 25.89, 26.90, 29.53, 31.72, 32.21, 36.43, 109.40, 113.71, 120.41, 121.53, 121.70, 126.21, 136.75, 151.69, 194.87 (CO); IR (neat) 2928, 2853, 1645 (CO), 1504, 1472, 1099, 745 cm^{-1} ; HRMS (EI) Calcd for $C_{17}H_{21}NO$ (M^+) 255.1618. Found 255.1620.

***N*-Methyl-3-acetyl-2-(4-methoxyphenyl)indole (2d):** white solid; ^1H NMR (399.65 MHz, $CDCl_3$) δ 1.98 (3H, s), 3.48 (3H, s), 3.89 (3H, s), 7.05 (2H, d, $J = 8.4$ Hz), 7.27-7.35 (3H, m), 7.30 (2H, d, $J = 8.4$ Hz), 8.46-8.53 (1H, m); ^{13}C NMR (100.40 MHz, $CDCl_3$) δ 30.10, 30.69, 55.31, 109.31, 114.14, 115.76, 122.50, 123.06, 123.07, 123.73, 126.55, 131.37, 136.42, 146.35, 160.38, 194.44 (CO); IR (KBr) 2963, 2926, 2839, 1638 (CO), 1464, 1431, 1398, 1250, 1028, 930, 858, 837, 758 cm^{-1} ; HRMS (EI) Calcd for $C_{18}H_{17}NO_2$ (M^+) 279.1254. Found 279.1256.

***N*-Methyl-3-acetyl-2-(4-methylphenyl)indole (2e):** white solid; ^1H NMR (399.65 MHz, $CDCl_3$) δ 1.98 (3H, s), 2.48 (3H, s), 3.48 (3H, s), 7.25-7.38 (3H, m), 7.28 (2H, d, $J = 8.4$ Hz), 7.35 (2H, d, $J = 8.4$ Hz), 8.47-8.54 (1H, m); ^{13}C NMR (100.40 MHz, $CDCl_3$) δ 21.46, 30.14, 30.75, 109.31, 115.72, 122.55, 122.59, 123.09, 126.58, 128.91, 129.39, 129.96, 136.48, 139.56, 146.57, 194.46 (CO); IR (KBr) 3045, 2922, 1624 (CO), 1468, 1394, 1101, 934, 829, 750 cm^{-1} ; HRMS (EI) Calcd for $C_{18}H_{17}NO$ (M^+) 263.1305. Found 263.1307.

***N*-Methyl-3-acetyl-2-phenylindole (2f):** pale yellow solid; ^1H NMR (399.65 MHz, $CDCl_3$) δ 1.96 (3H, s), 3.48 (3H, s), 7.30-7.36 (3H, m), 7.38-7.44 (2H, m), 7.51-7.58 (3H, m), 8.48-8.55 (1H, m); ^{13}C NMR (100.40 MHz, $CDCl_3$) δ 30.09, 30.76, 109.33, 115.69, 122.57, 123.16, 126.49, 128.65, 128.82, 129.48, 130.06, 131.95, 136.45, 146.24, 194.28 (CO); IR (neat) 3055, 2926, 1634 (CO), 1466, 1394, 1099, 934, 748, 704 cm^{-1} ; HRMS (EI) Calcd for $C_{17}H_{15}NO$ (M^+) 249.1148. Found 249.1150.; Registry No. 62367-64-0.

***N*-Methyl-3-acetyl-2-phenylindole- d_3 (2f- d_3):** pale yellow solid; ^1H NMR (399.65 MHz, $CDCl_3$) δ 3.48 (3H, s), 7.30-7.36 (3H, m), 7.38-7.44 (2H, m), 7.51-7.58 (3H, m), 8.48-8.55 (1H, m); ^{13}C NMR (100.40 MHz, $CDCl_3$) δ 29.34 (septet, $^1J(C, D) = 19.9$ Hz), 30.75, 109.33, 115.72, 122.58, 123.16, 126.49, 128.65, 128.82, 129.48, 130.06, 131.94, 136.45, 146.25, 194.37 (CO); IR (KBr) 3065, 2920, 1616 (CO), 1470, 1387, 1107, 928, 745, 704 cm^{-1} ; HRMS (EI) Calcd for $C_{17}H_{12}D_3NO$ (M^+) 252.1336. Found 252.1337.

***N*-Methyl-3-acetyl-2-(4-fluorophenyl)indole (2g):** colorless solid; ^1H NMR (399.65 MHz,

CDCl₃) δ 1.99 (3H, s), 3.48 (3H, s), 7.24 (2H, dd, ^3J (H, H) = 8.9 Hz, ^3J (H, F) = 8.9 Hz), 7.29-7.35 (3H, m), 7.38 (2H, dd, ^3J (H, H) = 8.9 Hz, ^4J (H, F) = 5.9 Hz), 8.43-8.49 (1H, m); ^{13}C NMR (100.40 MHz, CDCl₃) δ 30.24, 30.74, 109.42, 115.926 (d, ^2J (C, F) = 22.4 Hz), 115.929, 122.50, 122.66, 123.30, 126.38, 127.87 (d, ^4J (C, F) = 4.1 Hz), 132.06 (d, ^3J (C, F) = 8.2 Hz), 136.47, 144.92, 163.24 (d, ^1J (C, F) = 249.3 Hz), 193.98 (CO); IR (KBr) 3067, 2928, 1634 (CO), 1468, 1398, 1221 (C–F), 1165, 864, 760 cm⁻¹; HRMS (EI) Calcd for C₁₇H₁₄NOF (M⁺) 267.1054. Found 267.1053.

N-Methyl-3-acetyl-2-(4-trifluoromethylphenyl)indole (2h): colorless crystal; ^1H NMR (399.65 MHz, CDCl₃) δ 2.03 (3H, s), 3.49 (3H, s), 7.30-7.39 (3H, m), 7.55 (2H, d, J = 8.2 Hz), 7.81 (2H, d, J = 8.2 Hz), 8.40-8.47 (1H, m); ^{13}C NMR (100.40 MHz, CDCl₃) δ 30.42, 30.83, 109.57, 115.94, 122.39, 122.74, 123.45, 123.66 (q, ^1J (C, F) = 271.7 Hz), 125.54 (q, ^3J (C, F) = 3.6 Hz), 126.33, 130.71, 131.48 (q, ^2J (C, F) = 32.3 Hz), 135.84, 136.64, 144.04, 193.62 (CO); IR (KBr) 3063, 2958, 1638 (CO), 1466, 1396, 1323 (C–F), 1167 (C–F), 1119 (C–F), 1070, 868, 758 cm⁻¹; HRMS (EI) Calcd for C₁₈H₁₄NOF₃ (M⁺) 317.1022. Found 317.1025.

N-Methyl-3-formyl-2-propylindole (2i): pale red oil; ^1H NMR (399.65 MHz, CDCl₃) δ 1.03 (3H, t, J = 7.4 Hz), 1.72 (2H, tq, J = 7.4, 7.4 Hz), 3.06 (2H, t, J = 7.4 Hz), 3.71 (3H, s), 7.25-7.33 (3H, m), 8.24-8.30 (1H, m), 10.14 (1H, s); ^{13}C NMR (100.40 MHz, CDCl₃) δ 13.75, 23.31, 26.13, 29.69, 109.21, 113.94, 120.85, 122.63, 122.94, 125.47, 136.88, 151.57, 183.89 (CO); IR (neat) 3100-2700, 1651 (CO), 1472, 1393, 1126, 1047, 748 cm⁻¹; HRMS (EI) Calcd for C₁₃H₁₅NO (M⁺) 201.1148. Found 201.1148.

N-Methyl-3-benzoyl-2-propylindole (2j): colorless solid; ^1H NMR (399.65 MHz, CDCl₃) δ 1.02 (3H, t, J = 7.6 Hz), 1.73 (1H, ddq, J = 9.9, 8.2, 7.6 Hz), 1.73 (1H, ddq, J = 8.2, 7.6, 6.1 Hz), 3.05 (1H, dd, J = 9.9, 6.1 Hz), 3.05 (1H, dd, J = 8.2, 8.2 Hz), 3.75 (3H, s), 7.05 (1H, dd, J = 8.0, 8.0 Hz), 7.19 (1H, dd, J = 8.0, 8.0 Hz), 7.22 (1H, d, J = 8.0 Hz), 7.32 (1H, d, J = 8.0 Hz), 7.45 (2H, dd, J = 7.4, 7.4 Hz), 7.55 (1H, t, J = 7.4 Hz), 7.78 (2H, d, J = 7.4 Hz); ^{13}C NMR (100.40 MHz, CDCl₃) δ 14.00, 22.94, 27.47, 29.62, 109.16, 113.02, 120.76, 121.07, 121.74, 126.82, 127.96, 128.73, 131.13, 136.36, 141.35, 148.79, 192.49 (CO); IR (neat) 3061, 2957, 2872, 1624 (CO), 1518, 1400, 1231, 1018, 905, 748, 738, 708 cm⁻¹; HRMS (EI) Calcd for C₁₉H₁₉NO (M⁺) 277.1461. Found 277.1456.

N-Methyl-3-phenylacetyl-2-propylindole (2k): colorless solid; ^1H NMR (399.65 MHz, CDCl₃) δ 1.07 (3H, t, J = 7.5 Hz), 1.70 (2H, tq, J = 7.5, 7.5 Hz), 3.20 (2H, t, J = 7.5 Hz), 3.72 (3H, s), 4.41 (2H, s), 7.25-7.42 (8H, m), 8.02-8.10 (1H, m); ^{13}C NMR (100.40 MHz, CDCl₃) δ 14.20, 22.41, 27.95, 29.38, 49.43, 109.68, 113.05, 120.59, 121.83, 121.87, 125.75, 126.33, 128.25, 129.60, 135.33, 136.60, 149.88, 193.47 (CO); IR (KBr) 3030-2870, 1614 (CO), 1495, 1452,

1404, 1217, 1086, 748, 781 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{NO}$: C, 82.43; H, 7.27; N, 4.81. Found: C, 82.15; H, 7.51; N, 4.77; HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{21}\text{NO}$ (M^+) 291.1618. Found 291.1620.

***N*-Methyl-3-phenylacetyl-2-phenylindole (2l):** pale yellow solid; ^1H NMR (399.65 MHz, CDCl_3) δ 3.49 (3H, s), 3.59 (2H, s), 6.95 (2H, d, $J = 7.2$ Hz), 7.13 (1H, t, $J = 7.2$ Hz), 7.19 (2H, dd, $J = 7.2, 7.2$ Hz), 7.29-7.37 (3H, m), 7.39-7.45 (2H, m), 7.50-7.58 (3H, m), 8.48-8.53 (1H, m); ^{13}C NMR (100.40 MHz, CDCl_3) δ 30.81, 47.68, 109.38, 115.33, 122.69, 123.28, 126.04, 126.88, 127.92, 128.76, 129.25, 129.60, 129.61, 130.23, 131.86, 135.56, 136.59, 145.83, 194.05 (CO); IR (KBr) 3070-2890, 1688 (CO), 1466, 1433, 1389, 1080, 930, 760, 704 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{23}\text{H}_{19}\text{NO}$ (M^+) 325.1461. Found 325.1462.

***N*-Methyl-3-trifluoroacetyl-2-propylindole (2m):** colorless solid; ^1H NMR (399.65 MHz, CDCl_3) δ 1.10 (3H, t, $J = 7.3$ Hz), 1.69 (1H, ddq, $J = 10.3, 8.1, 7.3$ Hz), 1.69 (1H, ddq, $J = 8.1, 7.3, 5.8$ Hz), 3.15 (1H, dd, $J = 10.3, 5.8$ Hz), 3.15 (1H, dd, $J = 8.1, 8.1$ Hz), 3.72 (3H, s), 7.27-7.37 (3H, m), 7.98-8.06 (1H, m); ^{13}C NMR (100.40 MHz, CDCl_3) δ 14.12, 21.96, 28.35, 29.77, 107.09, 109.87, 117.23 (q, ^1J (C, F) = 289.3 Hz), 120.59 (q, ^3J (C, F) = 5.3 Hz), 123.02, 124.58, 136.78, 154.87, 174.67 (q, ^2J (C, F) = 35.9 Hz, CO); IR (neat) 2963, 2936, 2876, 1657 (CO), 1491, 1458, 1196 (C-F), 1132 (br, C-F), 1078, 907, 745 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{14}\text{NOF}_3$ (M^+) 269.1022. Found 269.1025.

3-Acetyl-5-methoxy-*N*-methyl-2-propylindole (2n): colorless solid; ^1H NMR (399.65 MHz, CDCl_3) δ 1.02 (3H, t, $J = 7.4$ Hz), 1.63 (2H, tq, $J = 7.4, 7.9$ Hz), 2.62 (3H, s), 3.09 (2H, t, $J = 7.9$ Hz), 3.60 (3H, s), 3.87 (3H, s), 6.87 (1H, dd, $J = 2.2, 9.0$ Hz), 7.16 (1H, d, $J = 9.0$ Hz), 7.47 (1H, d, $J = 2.2$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 14.07, 22.44, 27.88, 29.37, 31.21, 55.72, 103.77, 109.94, 110.78, 113.21, 126.89, 131.56, 149.17, 155.54; IR (neat) 2961-2867, 1851, 1738, 1624, 1608, 1481, 802 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.40; H, 8.09; N, 5.60; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ (M^+) 245.1416. Found 245.1413.

3-Acetyl-6-methoxy-1-methyl-2-propylindole (2o): colorless solid; ^1H NMR (399.65 MHz, CDCl_3) δ 1.03 (3H, t, $J = 7.3$ Hz), 1.61 (2H, tq, $J = 7.3, 7.3$ Hz), 2.62 (3H, s), 3.09 (2H, t, $J = 7.3$ Hz), 3.59 (3H, s), 3.85 (3H, s), 6.75 (1H, d, $J = 2.2$ Hz), 6.88 (1H, dd, $J = 2.2, 8.8$ Hz), 7.81 (1H, d, $J = 8.8$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 14.05, 22.45, 27.71, 29.26, 31.32, 55.52, 93.57, 110.53, 113.17, 120.18, 121.17, 137.25, 148.11, 155.93, 193.54; IR (neat) 2994-2835, 2061, 1866, 615, 1235, 821 cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.34, 8.10, 5.60; HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ (M^+) 245.1416. Found 245.1412.

***N*-Methyl-2-(1,1-dimethylethyl)indole (3a):** pale yellow oil; ^1H NMR (399.65 MHz, CDCl_3) δ 1.54 (9H, s), 3.92 (3H, s), 6.38 (1H, s), 7.10-7.18 (1H, m), 7.19-7.27 (1H, m), 7.29-7.36 (1H, m), 7.57-7.64 (1H, m); ^{13}C NMR (100.40 MHz, CDCl_3) δ 30.24, 30.27, 32.32, 97.94, 108.51, 119.20, 119.86, 120.74, 127.11, 138.52, 148.98; IR (KBr) 2968, 2909, 1529, 1472, 1354, 1313, 781, 731 cm^{-1} ; Registry No. 46275-90-5.

***N*-Methyl-2-propylindole (3b, 3i-k):** white solid; ^1H NMR (399.65 MHz, CDCl_3) δ 1.04 (3H, t, $J = 7.6$ Hz), 1.75 (2H, tq, $J = 7.6, 7.6$ Hz), 2.71 (2H, t, $J = 7.6$ Hz), 3.66 (3H, s), 6.24 (1H, s), 7.05 (1H, dd, $J = 7.6, 7.6$ Hz), 7.14 (1H, dd, $J = 7.6, 7.6$ Hz), 7.25 (1H, d, $J = 7.6$ Hz), 7.52 (1H, d, $J = 7.6$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 14.10, 21.98, 28.98, 29.76, 98.70, 108.63, 119.10, 119.63, 120.36, 127.82, 137.22, 141.15; IR (neat) 2959-2853, 1547, 1468, 1313, 772, 746 cm^{-1} ; Registry No. 133165-98-7.

***N*-Methyl-2-cyclohexylindole (3c):** colorless solid; ^1H NMR (399.65 MHz, CDCl_3) δ 1.24-1.51 (5H, m), 1.74-1.83 (1H, m), 1.83-1.92 (2H, m), 2.00-2.08 (2H, m), 2.64-2.73 (1H, m), 3.69 (3H, s), 6.24 (1H, s), 7.06 (1H, dd, $J = 7.8, 7.8$ Hz), 7.15 (1H, dd, $J = 7.8, 7.8$ Hz), 7.27 (1H, d, $J = 7.8$ Hz), 7.54 (1H, d, $J = 7.8$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 26.24, 24.70, 29.46, 33.25, 35.98, 96.48, 108.65, 119.10, 119.77, 120.42, 127.81, 137.09, 146.61; IR (KBr) 2928, 2849, 1609, 1537, 1468, 1313, 770, 746, 729 cm^{-1} ; Registry No. 68051-20-7.

***N*-Methyl-2-(4-methoxyphenyl)indole (3d):** white solid; ^1H NMR (399.65 MHz, CDCl_3) δ 3.73 (3H, s), 3.88 (3H, s), 6.52 (1H, s), 7.01 (2H, d, $J = 8.6$ Hz), 7.15 (1H, dd, $J = 8.0, 7.5$ Hz), 7.25 (1H, dd, $J = 8.0, 7.5$ Hz), 7.36 (1H, d, $J = 8.0$ Hz), 7.45 (2H, d, $J = 8.6$ Hz), 7.64 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 31.08, 55.35, 100.96, 109.44, 113.88, 119.68, 120.18, 121.29, 125.17, 127.90, 130.51, 138.03, 141.31, 159.31; IR (KBr) 2961, 2932, 2835, 1611, 1499, 1468, 1240, 1180, 1036, 839, 777, 748, 729 cm^{-1} ; Registry No. 61843-43-4.

***N*-Methyl-2-(4-methylphenyl)indole (3e):** colorless solid; ^1H NMR (399.65 MHz, CDCl_3) δ 2.45 (3H, s), 3.75 (3H, s), 6.56 (1H, s), 7.16 (1H, dd, $J = 7.8, 7.8$ Hz), 7.26 (1H, dd, $J = 7.8, 7.8$ Hz), 7.30 (2H, d, $J = 8.0$ Hz), 7.37 (1H, d, $J = 7.8$ Hz), 7.43 (2H, d, $J = 8.0$ Hz), 7.65 (1H, d, $J = 7.8$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 21.33, 31.15, 101.15, 109.48, 119.71, 120.29, 121.41, 127.91, 129.11, 129.17, 129.84, 137.65, 138.16, 141.54; IR (KBr) 2914, 1499, 1464, 1317, 1007, 773, 750, 735 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{15}\text{N}$ (M^+) 221.1199. Found 221.1200.; Registry No. 51358-08-8.

***N*-Methyl-2-phenylindole (3f, 3l):** white solid; ^1H NMR (399.65 MHz, CDCl_3) δ 3.75 (3H, s), 6.56 (1H, s), 7.13 (1H, dd, $J = 8.1, 8.1$ Hz), 7.24 (1H, dd, $J = 8.1, 8.1$ Hz), 7.36 (1H, d, $J = 8.1$ Hz), 7.40 (1H, t, $J = 7.5$ Hz), 7.46 (2J, dd, $J = 7.5, 7.5$ Hz), 7.51 (2H, d, $J = 7.5$ Hz), 7.63 (1H, d,

$J = 8.1$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 31.20, 101.59, 109.54, 119.77, 120.38, 121.57, 127.75, 127.87, 128.39, 129.28, 132.74, 138.24, 141.45; IR (neat) 3055, 2922, 1470, 1346, 1007, 797, 768, 750, 732, 702 cm^{-1} ; Registry No. 3558-24-5.

***N*-Methyl-2-phenylindole-*d* (3f-*d*):** 57%D; pale yellow solid; ^1H NMR (399.65 MHz, CDCl_3) δ 3.75 (3H, s), 6.56 (0.44H, s), 7.13 (1H, dd, $J = 8.1$, 8.1 Hz), 7.24 (1H, dd, $J = 8.1$, 8.1 Hz), 7.36 (1H, d, $J = 8.1$ Hz), 7.40 (1H, t, $J = 7.5$ Hz), 7.46 (2H, dd, $J = 7.5$, 7.5 Hz), 7.51 (2H, d, $J = 7.5$ Hz), 7.63 (1H, d, $J = 8.1$ Hz).

***N*-Methyl-2-(4-fluorophenyl)indole (3g):** pale yellow solid; ^1H NMR (399.65 MHz, CDCl_3) δ 3.71 (3H, s), 6.52 (1H, s), 7.13 (1H, dd, $J = 8.2$, 8.2 Hz), 7.15 (2H, dd, $^3J(\text{H}, \text{H}) = 8.7$ Hz, $^3J(\text{H}, \text{F}) = 8.7$ Hz), 7.24 (1H, dd, $J = 8.2$, 8.2 Hz), 7.46 (2H, dd, $^3J(\text{H}, \text{H}) = 8.7$ Hz, $^4J(\text{H}, \text{F}) = 5.4$ Hz), 7.62 (1H, d, $J = 8.2$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 31.11, 101.67, 109.54, 115.48 (d, $^2J(\text{C}, \text{F}) = 21.6$ Hz), 119.88, 120.39, 121.70, 127.78, 128.84 (d, $^4J(\text{C}, \text{F}) = 3.3$ Hz), 130.98 (d, $^3J(\text{C}, \text{F}) = 8.3$ Hz), 138.15, 140.35, 162.47 (d, $^1J(\text{C}, \text{F}) = 246.9$ Hz); IR (KBr) 2918, 2853, 1497, 1464, 1219, 843, 797, 733 cm^{-1} ; HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{12}\text{NF}$ (M^+) 225.0948. Found 225.0949.

***N*-Methyl-2-(4-trifluoromethylphenyl)indole (3h):** colorless solid; ^1H NMR (399.65 MHz, CDCl_3) δ 3.76 (3H, s), 6.62 (1H, s), 7.15 (1H, ddd, $J = 8.0$, 7.1, 1.1 Hz), 7.27 (1H, ddd, $J = 8.0$, 7.1, 1.1 Hz), 7.37 (1H, dd, $J = 8.0$, 1.1 Hz), 7.62 (2H, d, $J = 8.6$ Hz), 7.64 (1H, dd, $J = 8.0$, 1.1 Hz), 7.72 (2H, d, $J = 8.6$ Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 31.36, 102.80, 109.70, 120.13, 120.71, 122.29, 124.08 (q, $^1J(\text{C}, \text{F}) = 271.7$ Hz), 125.42 (q, $^3J(\text{C}, \text{F}) = 3.9$ Hz), 127.71, 129.34, 129.68 (q, $^2J(\text{C}, \text{F}) = 32.3$ Hz), 136.31, 138.63, 139.76; IR (KBr) 2926, 1614, 1464, 1325 (C–F), 1169 (C–F), 1113 (C–F), 1069, 854, 791, 733 cm^{-1} ; Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{NF}_3$: C, 69.80; H, 4.40; N, 5.09. Found: C, 69.90; H, 4.54; N, 4.84; HRMS (EI) Calcd for $\text{C}_{16}\text{H}_{12}\text{NF}_3$ (M^+) 275.0916. Found 275.0917.

***N*-Methylacetanilide:** white solid; ^1H NMR (399.65 MHz, CDCl_3) δ 1.86 (3H, s), 3.25 (3H, s), 7.17 (2H, d, $J = 7.1$ Hz), 7.31 (1H, t, $J = 7.1$ Hz), 7.40 (2H, dd, $J = 7.1$, 7.1 Hz); ^{13}C NMR (100.40 MHz, CDCl_3) δ 22.39, 37.10, 126.92, 127.54, 129.56, 144.43, 170.29 (CO); IR (KBr) 3047, 2937, 1666 (CO), 1599, 1499, 1421, 1387, 1298, 1142, 1086, 1030, 970, 775, 710 cm^{-1} ; Registry No. 579-10-2.

Fig 1. nOe Experiments