Supporting Information for the Paper

Iron-catalyzed domino indole fluorination/allenic aza–Claisen rearrangement

Benito Alcaide,*[a] Pedro Almendros,*[b] Sara Cembellín,[a] Teresa Martínez del Campo,*[a] and Alejandro Muñoz*[a]

[a]Grupo de Lactamas y Heterociclos Bioactivos, Departamento de Química Orgánica I, Unidad Asociada al CSIC, Facultad de Química, Universidad Complutense de Madrid, 28040-Madrid, Spain

[b]Instituto de Química Orgánica General, IQOG-CSIC, Juan de la Cierva 3, 28006-Madrid, Spain

E-mail: alcaideb@quim.ucm.es; Palmendros@iqog.csic.es

General methods: 1H NMR, 19F NMR, and 13C NMR spectra were recorded on a Bruker Avance-300 or Varian VRX-300S. NMR spectra were recorded in CDCl3 or C6D6 solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (1H, 0.0 ppm), or CDCl3 (1H, 7.27 ppm; 13C, 76.9 ppm), or C6D6 (1H, 7.16 ppm; 13C, 128.0 ppm). Low and high resolution mass spectra were taken on an AGILENT 6520 Accurate-Mass QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. All commercially available compounds were used without further purification.

2-Substituted indoles were commercially available except 2-(4-tolyl)-1H-indole and 2-(4-tert-butylphenyl)-1H-indole, which were readily obtained as described in the literature: G.-p. Lu, C. Cai, Synlett 2012, 23, 2992.
Scheme S1 Synthesis of 1-(buta-2,3-dienyl)-2-substituted-1H-indoles 2a–m.

Scheme S2 Treatment of 2-(allenyl)-2-phenyl-3,3-difluorindoline 3a under metal-catalyzed conditions.

General Procedure for the Preparation of 1-(Prop-2-ynyl)-2-substituted-1H-indoles 1. Sodium hydride (1.5 mmol) was added to a solution of the appropriate 2-substituted indole (1.0 mmol) in DMF (15 mL) at 0 °C. After 1 h stirring at rt the solution was cooled at 0 °C and propargyl bromide (1.5 mmol) was added. The
reaction was stirred at rt until disappearance of the starting material (TLC). Then water (10 mL) was added, before being being extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried (MgSO₄) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave analytically pure compounds. Spectroscopic and analytical data for some representative pure forms of 1 follow.

1-(Prop-2-ynyl)-2-phenyl-1H-indole 1a. From 1.0 g (5.17 mmol) of 2-phenyl-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 1a (1.01 g, 82%) as a colorless oil; ¹H-NMR (300 MHz, CDCl₃, 25 °C) δ: 7.65 (m, 3H), 7.53 (m, 4H), 7.32 (td, 1H, J = 7.0, 1.2 Hz), 7.21 (td, 1H, J = 7.8, 1.0 Hz), 6.61 (s, 1H), 4.85 (d, 2H, J = 2.5 Hz), 2.39 (t, 1H, J = 2.5 Hz); ¹³C-NMR (75 MHz, CDCl₃, 25 °C) δ: 140.9, 137.6, 132.2, 130.6, 129.3 (2C), 128.7 (2C), 128.2, 122.1, 120.7, 120.5, 110.0, 102.5, 78.9, 72.7, 34.1; IR (CHCl₃, cm⁻¹): v 3291; HRMS (ES): calcd for C₁₇H₁₃N [M⁺]: 231.1042; found: 231.1042.

1-(Prop-2-ynyl)-2-(4-chlorophenyl)-1H-indole 1b. From 250 mg (1.10 mmol) of 2-(4-chlorophenyl)-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 1b (213 mg, 73%) as a colorless oil; ¹H-NMR (300 MHz, CDCl₃, 25 °C) δ: 7.55 (d, 1H, J = 7.7 Hz), 7.12 (m, 1H), 6.49 (s, 1H), 4.70 (d, 2H, J = 2.5 Hz), 2.29 (t, 1H, J = 2.5 Hz); ¹³C-NMR (75 MHz, CDCl₃, 25 °C) δ: 139.6; 137.6; 13.3; 131.8; 130.6; 130.4; 129.0 (2C); 128.1; 122.4; 120.8; 120.6; 110.0; 102.8; 78.7; 73.0; 34.0; IR (CHCl₃, cm⁻¹): v 3293; HRMS (ES): calcd for C₁₇H₁₂ClN [M⁺]: 265.0652; found: 265.0657.

1-(Prop-2-ynyl)-2-(4-fluorophenyl)-1H-indole 1c. From 200 mg (0.9 mmol) of 2-(4-fluorophenyl)-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 1c (136 mg, 61%) as a colorless oil; ¹H-NMR (300 MHz, CDCl₃, 25 °C) δ: 7.73 (d, 1H, J = 7.7 Hz), 7.38 (m, 5H), 7.22 (td, 1H, J = 7.1, 1.2 Hz), 7.12 (m, 1H), 6.49 (s, 1H), 4.70 (d, 2H, J = 2.5 Hz), 2.29 (t, 1H, J = 2.5 Hz); ¹³C-NMR (75 MHz, CDCl₃, 25 °C) δ: 139.6; 137.6; 13.3; 131.8; 130.6; 130.4; 129.0 (2C); 128.1; 122.4; 120.8; 120.6; 110.0; 102.8; 78.7; 73.0; 34.0; IR (CHCl₃, cm⁻¹): v 3293; HRMS (ES): calcd for C₁₇H₁₂ClN [M⁺]: 265.0652; found: 265.0657.
6.63 (s, 1H), 4.86 (d, 2H, J = 2.5 Hz), 2.45 (t, 1H, J = 2.5 Hz); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 139.8, 137.5, 131.0, 130.9, 128.3 (2C), 122.3, 120.7, 116.0, 115.9, 115.7, 115.6, 110.0, 109.9, 105.6, 78.8, 33.9; $^{19}$F NMR (282 MHz, CDCl$_3$, 25 °C): δ = −113.5 (s, 1F); IR (CHCl$_3$, cm$^{-1}$): ν 3292; HRMS (ES): calcd for C$_{17}$H$_{12}$FN $[M]^+$: 249.0948; found: 249.0943.

1-(Prop-2-ynyl)-2-(4-methylphenyl)-1H-indole 1d. From 207 mg (0.99 mmol) of 2-(4-methylphenyl)-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent gave compound 1d (151 mg, 62%) as a colorless oil; $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.55 (d, 1H, J = 7.9 Hz), 7.38 (m, 3H), 7.16 (m, 4H), 6.47 (d, 1H, J = 0.4 Hz), 4.73 (d, 2H, J = 2.5 Hz); 2.35 (s, 3H), 2.27 (t, 1H, J = 2.5 Hz); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 141.1, 138.2, 137.5, 130.5, 129.5 (2C), 129.2 (2C), 128.4, 122.0, 120.6, 120.5, 110.0, 102.2, 79.0, 72.7, 34.1, 21.4; IR (CHCl$_3$, cm$^{-1}$): ν 3290; HRMS (ES): calcd for C$_{18}$H$_{15}$N $[M]^+$: 245.1198; found: 245.1201.

1-(Prop-2-ynyl)-2-(4-tert-butylphenyl)-1H-indole 1e. From 310 mg (1.24 mmol) of 2-(4-tert-butylphenyl)-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 1e (184 mg, 52%) as a colorless oil; $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.52 (d, 2H, J = 8.6 Hz), 7.45 (m, 2H), 7.20 (m, 1H), 7.08 (m, 3H), 6.48 (d, 1H, J = 0.7 Hz), 4.75 (d, 2H, J = 2.5 Hz), 2.30 (t, 1H, J = 2.5 Hz); 1.31 (s, 9H); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 151.3, 150.1, 141.0, 137.6, 137.1, 129.0, 127.6, 125.7, 122.0, 120.6, 120.5, 110.0, 102.2, 90.7, 79.1, 72.7, 34.8, 34.1, 31.4 (3C); IR (CHCl$_3$, cm$^{-1}$): ν 3291; HRMS (ES): calcd for C$_{21}$H$_{21}$N $[M]^+$: 287.1668; found: 287.1684.

1-(Prop-2-ynyl)-2-(naphthalen-2-yl)-1H-indole 1f. From 200 mg (0.82 mmol) of 2-(naphthalen-2-yl)-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 1f (135 mg, 59%) as a colorless oil; $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 8.00 (s, 1H), 7.69 (m, 2H), 7.64 (m, 3H), 7.43 (d, 1H, J = 8.1 Hz), 7.27 (m, 4H), 6.64 (d, 1H, J = 0.5 Hz), 4.30 (d, 2H,
$J = 2.5 \text{ Hz}$), 1.83 (t, 1H, $J = 2.5 \text{ Hz}$); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 140.9, 138.4, 133.9, 133.3, 130.3, 130.2, 129.1, 128.7, 128.6, 128.5, 127.2, 126.7, 126.6, 122.6, 121.2, 121.0, 110.5, 103.6, 79.3, 72.8, 33.9; IR (CHCl$_3$, cm$^{-1}$): ν 3292; HRMS (ES): calcd for C$_{21}$H$_{15}$N [M$^+$]: 287.1198; found: 287.1207.

5-Methyl-1-(prop-2-ynyl)-2-(4-methylphenyl)-1H-indole 1g. From 247 mg (1.12 mmol) of 5-methyl-2-(4-methylphenyl)-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 1g (166 mg, 57%) as a colorless solid; mp 108–109 °C (n-hexane/ethyl acetate); $^1$H-NMR (300 MHz, acetone-d$_6$, 25 °C) δ: 7.52 (d, 2H, $J = 8.2$ Hz, Ar), 7.43 (d, 1H, $J = 8.3$ Hz, Ar), 7.36 (m, 1H, Ar), 7.34 (d, 2H, $J = 8.5$ Hz, Ar), 7.06 (dd, 1H, $J = 8.3$, 1.2 Hz, Ar), 6.46 (d, 1H, $J = 0.7$ Hz, Ar), 4.92 (d, 1H, $J = 2.5$ Hz, NCH$_2$), 2.90 (t, 1H, $J = 2.5$ Hz, ≡CH), 2.41 (s, 3H, Me), 2.40 (s, 3H, Me); $^{13}$C-NMR (75 MHz, acetone-d$_6$, 25 °C) δ: 141.8, 138.8, 137.2, 130.5, 130.3 (Ar, 2CH), 130.0, 129.8, 129.7 (Ar, 2CH), 124.2 (Ar, CH), 121.0 (Ar, CH), 110.9 (Ar, CH), 102.5 (Ar, CH), 80.3, 74.1 (≡CH), 34.5 (NCH$_2$), 21.6 (Me), 21.3 (Me); IR (CHCl$_3$, cm$^{-1}$): ν 2919, 1474, 1330, 1163, 823, 789, 643; HRMS (ES): calcd for C$_{19}$H$_{17}$N [M$^+$]: 259.1355; found: 259.1354.

5-Methoxy-1-(prop-2-ynyl)-2-(4-methylphenyl)-1H-indole 1h. From 159 mg (0.67 mmol) of 5-methoxy-2-(4-methylphenyl)-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 1h (127 mg, 69%) as a colorless solid; mp 115–116 °C (n-hexane/ethyl acetate); $^1$H-NMR (300 MHz, acetone-d$_6$, 25 °C) δ: 7.51 (d, 2H, $J = 8.2$ Hz, Ar), 7.44 (d, 1H, $J = 8.8$ Hz, Ar), 7.33 (d, 2H, $J = 7.9$ Hz, Ar), 7.10 (d, 1H, $J = 2.5$ Hz, Ar), 6.89 (dd, 1H, $J = 8.8$, 2.5 Hz, Ar), 6.48 (s, 1H, Ar), 4.90 (d, 1H, $J = 2.5$ Hz, NCH$_2$), 3.81 (s, 3H, OMe), 2.90 (t, 1H, $J = 2.5$ Hz, ≡CH), 2.40 (s, 3H, Me); $^{13}$C-NMR (75 MHz, acetone-d$_6$, 25 °C) δ: 155.8, 142.3, 138.8, 133.9, 130.5, 130.3 (Ar, 2CH), 129.9, 129.8, 129.7 (Ar, 2CH), 112.7 (Ar, CH), 111.8 (Ar, CH), 103.0 (Ar, CH), 102.8 (Ar, CH), 80.3, 74.1 (≡CH), 55.9 (OMe), 34.6 (NCH$_2$), 21.3 (Me); IR (CHCl$_3$, cm$^{-1}$): ν 2852, 1619, 1474, 1216, 824, 740, 651; HRMS (ES): calcd for C$_{19}$H$_{17}$NO [M$^+$]: 275.1304; found: 275.1319.
5-Fluoro-1-(prop-2-ynyl)-2-(4-methylphenyl)-1H-indole 1i. From 168 mg (0.75 mmol) of 5-fluoro-2-(4-methylphenyl)-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 1i (94 mg, 48%) as a colorless solid; mp 113–114 °C (n-hexane/ethyl acetate); $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.46 (d, 2H, $J = 8.2$ Hz, Ar), 7.38 (m, 1H, Ar), 7.28 (d, 2H, $J = 8.0$ Hz, Ar), 7.19 (d, 1H, $J = 2.5$ Hz, Ar), 6.98 (m, 1H, Ar), 6.48 (s, 1H, Ar), 4.80 (d, 1H, $J = 2.6$ Hz, NCH$_2$), 2.41 (s, 3H, Me), 2.38 (t, 1H, $J = 2.5$ Hz, =CH); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 159.9, 156.8, 142.6, 138.4, 134.0, 130.3, 129.5 (Ar, 2CH), 129.0 (Ar, 2CH), 119.0 (Ar, CH), 109.9 (Ar, CH), 105.7 (Ar, CH), 101.9 (Ar, CH), 78.7, 73.7 (=CH), 34.1 (NCH$_2$), 21.3 (Me); IR (CHCl$_3$, cm$^{-1}$): ν 2921, 1621, 1472, 1197, 824, 783, 645; HRMS (ES): calcd for C$_{18}$H$_{14}$FN [M$^+$]: 263.1104; found: 263.1107.

5-Nitro-2-phenyl-1-(prop-2-ynyl)-1H-indole 1j. From 200 mg (0.84 mmol) of 5-nitro-2-phenyl-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 1j (181 mg, 78%) as a colorless solid; mp 119–120 °C (n-hexane/ethyl acetate); $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 8.60 (d, 1H, $J = 2.2$ Hz, Ar), 8.20 (dd, 1H, $J = 9.1$, 2.3 Hz, Ar), 7.57 (m, 6H, Ar), 6.74 (s, 1H, Ar), 4.87 (d, 2H, $J = 2.5$ Hz, NCH$_2$), 2.46 (t, 1H, $J = 2.5$ Hz, =CH); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 144.1, 142.4, 140.1, 130.9, 129.3 (Ar, 2CH), 129.1 (Ar, CH), 129.0 (Ar, 2CH), 127.5, 117.7 (Ar, CH), 117.6 (Ar, CH), 110.0 (Ar, CH), 104.3 (Ar, CH), 77.7, 73.7 (=CH), 34.4 (NCH$_2$); IR (CHCl$_3$, cm$^{-1}$): ν 2923, 1612, 1472, 1197, 824, 783, 645; HRMS (ES): calcd for C$_{17}$H$_{12}$N$_2$O$_2$ [M$^+$]: 276.0893; found: 276.0888.

2-Phenyl-1-(prop-2-ynyl)-1H-indole-5-carbonitrile 1k. From 120 mg (0.54 mmol) of 2-phenyl-1H-indole-5-carbonitrile, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound 1k (95 mg, 69%) as a pale yellow solid; mp 115–116 °C (n-hexane/ethyl acetate); $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.88 (t, 1H, $J = 0.8$ Hz, Ar), 7.44 (m, 7H, Ar), 6.54 (s, 1H, Ar), 4.75 (d, 1H, $J = 2.5$ Hz, NCH$_2$), 2.34 (t, 1H, $J = 2.5$ Hz, =CH); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C)
δ: 143.2, 138.9, 131.0, 129.3 (Ar, 2CH), 128.9 (Ar, CH), 128.9 (Ar, 2CH), 128.0, 126.0 (Ar, CH), 125.0 (Ar, CH), 120.6, 110.9 (Ar, CH), 103.6, 102.9 (Ar, CH), 77.8, 73.6 (=CH), 34.2 (NCH2); IR (CHCl3, cm⁻¹): ν 2919, 1613, 1467, 1170, 820, 760, 670; HRMS (ES): calcd for C18H12N2 [M]+: 256.0995; found: 256.1007.

1-(Prop-2-ynyl)-2-methyl-1H-indole 1l. From 1.0 g (7.63 mmol) of 2-methyl-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 1l (769 mg, 61%) as a colorless oil; ¹H-NMR (300 MHz, CDCl3, 25 °C) δ: 7.47 (d, 1H, J = 7.7 Hz), 7.28 (d, 1H, J = 8.2 Hz), 7.10 (m, 2H), 6.21 (br s, 1H), 4.74 (d, 2H, J = 2.5 Hz), 2.42 (s, 3H), 2.19 (t, 1H, J = 2.5 Hz); ¹³C-NMR (75 MHz, CDCl3, 25 °C) δ: 136.5, 136.0, 128.3, 120.9, 119.8 (2C), 108.8, 100.9, 78.2, 72.1, 32.3, 12.5; IR (CHCl3, cm⁻¹): ν 3295; HRMS (ES): calcd for C12H11N [M]+: 169.0885; found: 169.0888.

2,5-Dimethyl-1-(prop-2-ynyl)-1H-indole 1m. From 500 mg (3.44 mmol) of 2,5-dimethyl-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 1m (485 mg, 77%) as a colorless solid; mp 110–111 °C (n-hexane/ethyl acetate); ¹H-NMR (300 MHz, acetone-d₆, 25 °C) δ: 7.30 (d, 1H, J = 8.3 Hz, Ar), 7.23 (s, 1H, Ar), 6.93 (d, 1H, J = 8.3 Hz, Ar), 6.15 (s, 1H, Ar), 4.94 (d, 1H, J = 2.5 Hz, NCH2), 2.79 (t, 1H, J = 2.5 Hz, =CH), 2.46 (s, 3H, Me), 2.37 (s, 3H, Me); ¹³C-NMR (75 MHz, acetone-d₆, 25 °C) δ: 137.2, 136.2, 129.7, 129.1, 122.9 (Ar, CH), 120.3 (Ar, CH), 109.7 (Ar, CH), 101.1 (Ar, CH), 80.0, 73.4 (=CH), 32.8 (NCH2), 21.6 (Me), 12.6 (Me); IR (CHCl3, cm⁻¹): ν 2943, 1632, 1471, 1234, 820, 763, 675; HRMS (ES): calcd for C13H13N [M]+: 183.1078; found: 183.1041.

5-Methoxy-2-methyl-1-(prop-2-ynyl)-1H-indole 1n. From 500 mg (3.10 mmol) of 5-methoxy-2-methyl-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 1n (315 mg, 51%) as a colorless solid; mp 119–120 °C (n-hexane/ethyl acetate); ¹H-NMR (300 MHz, acetone-d₆, 25 °C) δ: 7.31 (d, 1H, J = 8.9 Hz, Ar), 6.97 (d, 1H, J = 2.3 Hz, Ar), 6.76
(dd, 1H, J = 8.9, 2.5 Hz, Ar), 6.17 (s, 1H, Ar), 4.94 (d, 1H, J = 2.5 Hz, NCH₂), 3.77 (s, 3H, OMe), 2.80 (t, 1H, J = 2.5 Hz, =CH), 2.45 (s, 3H, Me); ¹³C-NMR (75 MHz, acetone-d₆, 25 °C) δ: 155.3, 137.7, 132.6, 129.9, 111.1 (Ar, CH), 110.6 (Ar, CH), 102.7 (Ar, CH), 101.3 (Ar, CH), 79.9, 73.4 (≡CH), 55.9 (OMe), 32.9 (NCH₂), 12.6 (Me); IR (CHCl₃, cm⁻¹): ν 2958, 1483, 1201, 849, 779; HRMS (ES): calcd for C₁₃H₁₃NO [M]+: 199.0991; found: 199.1004.

5-Chloro-2-methyl-1-(prop-2-ynyl)-1H-indole 1o. From 500 mg (3.08 mmol) of 5-chloro-2-methyl-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 1o (444 mg, 71%) as a colorless solid; mp 127–128 °C (n-hexane/ethyl acetate); ¹H-NMR (300 MHz, acetone-d₆, 25 °C) δ: 7.47 (s, 1H, Ar), 7.45 (d, 1H, J = 8.6 Hz, Ar), 7.10 (dd, 1H, J = 8.8, 2.2 Hz, Ar), 6.26 (s, 1H, Ar), 5.00 (d, 1H, J = 2.5 Hz, NCH₂), 2.85 (t, 1H, J = 2.5 Hz, =CH), 2.49 (d, 3H, J = 0.9 Hz, Me); ¹³C-NMR (75 MHz, acetone-d₆, 25 °C) δ: 139.2, 136.1, 130.5, 125.7, 121.4 (Ar, CH), 119.7 (Ar, CH), 111.4 (Ar, CH), 101.2 (Ar, CH), 79.4, 73.9 (≡CH), 33.0 (NCH₂), 12.6 (Me); IR (CHCl₃, cm⁻¹): ν 2911, 1621, 1478, 1190, 827, 763, 640; HRMS (ES): calcd for C₁₂H₁₀NCl [M]+: 203.0496; found: 203.0502.

5-Bromo-2-methyl-1-(prop-2-ynyl)-1H-indole 1p. From 400 mg (1.90 mmol) of 5-bromo-2-methyl-1H-indole, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 1p (359 mg, 76%) as a colorless oil; ¹H-NMR (300 MHz, CDCl₃, 25 °C) δ: 7.66 (d, 1H, J = 1.6 Hz, Ar), 7.26 (m, 2H, Ar), 6.24 (s, 1H, Ar), 4.79 (d, 2H, J = 2.5 Hz, NCH₂), 2.49 (s, 3H, Me), 2.30 (t, 1H, J = 2.5 Hz, =CH); ¹³C-NMR (75 MHz, CDCl₃, 25 °C) δ: 137.4, 135.1, 130.0, 123.7 (Ar, CH), 122.3 (Ar, CH), 113.1, 110.3 (Ar, CH), 100.5 (Ar, CH), 77.7, 72.5 (≡CH), 32.5 (NCH₂), 12.5 (Me); IR (CHCl₃, cm⁻¹): ν 2965, 1497, 1254, 850; HRMS (ES): calcd for C₁₂H₁₀BrN [M]+: 246.9991; found: 246.9994.

2-Methyl-5-nitro-1-(prop-2-ynyl)-1H-indole 1q. From 500 mg (2.84 mmol) of 2-methyl-5-nitro-1H-indole, and after chromatography of the residue using
hexanes/ethyl acetate (5:1) as eluent gave compound 1q (404 mg, 66%) as a colorless solid; mp 97–99 °C (n-hexane/ethyl acetate); \(^1\)H-NMR (300 MHz, CDCl\(_3\), 25 °C) \(\delta\): 8.45 (d, 1H, \(J = 2.2\) Hz, Ar), 8.08 (dd, 1H, \(J = 9.1, 2.2\) Hz, Ar), 7.35 (d, 1H, \(J = 9.1\) Hz, Ar), 6.44 (s, 1H, Ar), 4.85 (d, 2H, \(J = 2.5\) Hz, NCH\(_2\)), 2.52 (s, 3H, Me), 2.35 (t, 1H, \(J = 2.5\) Hz, \(\equiv CH\)); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\), 25 °C) \(\delta\): 141.9, 139.6, 139.3, 127.5, 116.8 (Ar, CH), 108.7 (Ar, CH), 103.1 (Ar, CH), 77.4, 73.2 (\(\equiv CH\)), 32.9 (NCH\(_2\)), 12.7 (Me); IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 2956, 1490, 1234, 832; HRMS (ES): calcd for C\(_{12}\)H\(_{10}\)N\(_2\)O\(_2\) [\(M^+\): 214.0736; found: 214.0733.

**General Procedure for the Cu-Catalyzed Reaction of 1-(Prop-2-ynyl)-2-substituted-1\(H\)-indoles 1. Preparation of 1-(Buta-2,3-dienyl)-2-substituted-1\(H\)-indoles 2.** A well stirred solution of (CH\(_2\)O)\(_n\) (0.5 mmol), Cul (0.1 mmol), the appropriate 1-(prop-2-ynyl)-2-substituted-1\(H\)-indole (0.2 mmol), and \(N,N\)-diisopropylethylamine (Hüning's base) (0.36 mmol) in dioxane (1 mL) was refluxed under argon atmosphere. When the reaction was complete as monitored by TLC, it was cooled to RT. Water (5 mL) was added before being extracted with ethyl acetate (3 x 15 mL). The organic phase was washed with water (2 x 5 mL), dried (MgSO\(_4\)) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure compounds 1. Spectroscopic and analytical data for some representative pure forms of 2 follow.

**1-(Buta-2,3-dienyl)-2-phenyl-1\(H\)-indole 2a.** From 266 mg (1.15 mmol) of alkyne 1a, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 2a (236 mg, 84%) as a colorless oil; \(^1\)H-NMR (300 MHz, CDCl\(_3\), 25 °C) \(\delta\): 7.67 (d, 1H, \(J = 7.7\) Hz), 7.57 (t, 1H, \(J = 2.0\) Hz), 7.55 (m, 1H), 7.45 (m, 4H), 7.27 (td, 1H, \(J = 7.0, 1.2\) Hz), 7.18 (td, 1H, \(J = 7.8, 0.9\) Hz), 6.58 (br s, 1H), 5.33 (m, 1H), 4.78 (d, 2H, \(J = 2.8\) Hz), 4.77 (s, 2 H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\), 25 °C) \(\delta\): 208.5, 141.3, 137.7, 132.8, 129.4 (2C), 128.5 (2C), 128.2, 128.0, 121.7, 120.5, 120.0, 110.3, 102.2, 88.1, 77.3, 42.9; IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 1956; HRMS (ES): calcd for C\(_{18}\)H\(_{15}\)N [\(M^+\): 245.1198; found: 245.1199.
1-(Buta-2,3-dienyl)-2-(4-chlorophenyl)-1H-indole 2b. From 290 mg (1.10 mmol) of alkyne 1b, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 2b (224 mg, 73%) as a colorless oil; \(^1\)H-NMR (300 MHz, CDCl\(_3\), 25 °C) \(\delta\): 7.67 (d, 1H, \(J = 7.7\) Hz), 7.57 (t, 1H, \(J = 2.0\) Hz), 7.55 (m, 1H), 7.45 (m, 4H), 7.27 (td, 1H, \(J = 7.0, 1.2\) Hz), 7.18 (td, 1H, \(J = 7.8, 0.9\) Hz), 6.58 (br s, 1H), 5.33 (m, 1H), 4.78 (d, 2H, \(J = 2.8\) Hz), 4.77 (s, 2H); \(^1\)3C-NMR (75 MHz, CDCl\(_3\), 25 °C) \(\delta\): 208.5, 141.3, 137.7, 132.8, 129.4 (2C), 128.5 (2C), 128.2, 128.0, 121.7, 120.5, 120.0, 110.3, 102.2, 88.1, 77.3, 42.9; IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 1954; HRMS (ES): calcd for C\(_{18}\)H\(_{14}\)ClN [\(M^+\)]: 279.0809; found: 279.0812.

1-(Buta-2,3-dienyl)-2-(4-fluorophenyl)-1H-indole 2c. From 200 mg (0.90 mmol) of alkyne 1c, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 2c (136 mg, 64%) as a colorless oil; \(^1\)H-NMR (300 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\): 7.70 (d, 1H, \(J = 7.0\) Hz), 7.27 (m, 3H), 7.21 (m, 2H), 6.82 (t, 2H, \(J = 8.6\)Hz), 6.50 (s, 1H), 4.89 (q, 1H, \(J = 5.9\) Hz), 4.39 (m, 2H), 4.21 (m, 2H); \(^1\)3C-NMR (75 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\): 208.4, 141.3, 137.7, 129.4, 128.9, 127.8, 122.3, 121.1, 120.6, 115.8, 115.5, 110.6, 102.9, 88.4, 77.7, 42.5; \(^1\)9F NMR (282 MHz, C\(_6\)D\(_6\), 25 °C): \(\delta\) = –113.5 (s, 1F); IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 1955; HRMS (ES): calcd for C\(_{18}\)H\(_{14}\)FN [\(M^+\)]: 263.1104; found: 263.1108.

1-(Buta-2,3-dienyl)-2-(4-methylphenyl)-1H-indole 2d. From 150 mg (0.61 mmol) of alkyne 1d, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound 2d (96 mg, 61%) as a colorless oil; \(^1\)H-NMR (300 MHz, CDCl\(_3\), 25 °C) \(\delta\): 7.54 (m, 1H), 7.32 (m, 3H), 7.12 (m, 4H, 6.44 (d, 1H, \(J = 0.8\) Hz), 5.22 (m, 1H), 4.65 (m, 4H), 2.34 (s, 3H); \(^1\)3C-NMR (75 MHz, CDCl\(_3\), 25 °C) \(\delta\): 208.6, 141.4, 138.0, 137.7, 129.9, 129.3 (2C), 129.2 (2C), 128.3, 121.6, 120.5, 120.0, 110.3, 101.9, 88.2, 77.4, 42.9, 21.3; IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 1955; HRMS (ES): calcd for C\(_{19}\)H\(_{17}\)N [\(M^+\)]: 259.1355; found: 259.1365.

1-(Buta-2,3-dienyl)-2-(4-tert-butylphenyl)-1H-indole 2e. From 149 mg (0.52 mmol) of alkyne 1e, and after chromatography of the residue using hexanes/ethyl
acetate (70:1) as eluent gave compound 2e (88 mg, 56%) as a colorless oil; $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.55 (m, 2H), 7.35 (m, 3H), 7.10 (m, 3H), 6.45 (d, 1H, J = 0.7 Hz), 5.21 (m, 1H), 4.66 (m, 4H), 1.30 (s, 9H); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 208.6, 151.1, 141.4, 137.7, 130.3, 129.1 (2C), 125.5 (2C), 121.6, 120.5, 119.9, 110.3, 101.9, 91.0, 88.3, 77.3, 43.0, 34.7, 31.4 (3C); IR (CHCl$_3$, cm$^{-1}$): ν 1954; HRMS (ES): calcd for C$_{22}$H$_{23}$N [$M^+$]: 301.1824; found: 301.1822.

1-(Buta-2,3-dienyl)-2-(naphthalen-2-yl)-1H-indole 2f. From 133 mg (0.47 mmol) of alkyne 1f, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 2f (64 mg, 51%) as a colorless oil; $^1$H-NMR (300 MHz, C$_6$D$_6$, 25 °C) δ: 7.92 (s, 1H), 7.75 (m, 1H), 7.64 (m, 3H), 7.56 (dd, 1H, J = 6.9, 1.5 Hz), 7.31 (m, 5H), 6.70 (s, 1H), 5.00 (q, 1H, J = 6.4 Hz), 4.43 (m, 2H), 4.35 (m, 2H); $^{13}$C-NMR (75 MHz, C$_6$D$_6$, 25 °C) δ: 208.5, 141.3, 138.6, 133.8, 133.3, 130.8, 129.2, 128.6 (2C), 128.5, 128.4, 127.5, 126.7, 126.5, 122.3, 121.2, 120.6, 110.6, 103.4, 88.6, 77.3, 42.9; IR (CHCl$_3$, cm$^{-1}$): ν 1958; HRMS (ES): calcd for C$_{22}$H$_{17}$N [$M^+$]: 295.1355; found: 295.1358.

1-(Buta-2,3-dienyl)-5-methyl-2-(4-methylphenyl)-1H-indole 2g. From 126 mg (0.49 mmol) of alkyne 1g, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 2g (112 mg, 84%) as a colorless oil; $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.17 (d, 2H, J = 8.0 Hz, Ar), 7.04 (m, 4H, Ar), 6.81 (dd, 1H, J = 8.5, 1.8 Hz, Ar), 6.20 (d, 1H, J = 0.6 Hz, Ar), 5.05 (m, 1H, =CH), 4.51 (m, 2H, =CH$_2$), 4.45 (m, 2H, NCH$_2$), 2.23 (s, 3H, Me), 2.18 (s, 3H, Me); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 208.5, 141.4, 137.8, 136.0, 130.5, 129.9, 129.1 (Ar, 2CH), 129.0 (Ar, 2CH), 128.5, 123.1 (Ar, CH), 120.0 (Ar, CH), 109.9 (Ar, CH), 101.3 (Ar, CH), 88.2 (=CH), 77.4 (=CH$_2$), 42.9 (NCH$_2$), 21.4 (Me), 21.3 (Me); IR (CHCl$_3$, cm$^{-1}$): ν 2920, 1957, 1474, 1341, 849, 827, 790; HRMS (ES): calcd for C$_{20}$H$_{19}$N [$M^+$]: 273.1511; found: 273.1523.

1-(Buta-2,3-dienyl)-5-methoxy-2-(4-methylphenyl)-1H-indole 2h. From 142 mg (0.52 mmol) of alkyne 1h, and after chromatography of the residue using
hexanes/ethyl acetate (20:1) as eluent gave compound 2h (116 mg, 78%) as a colorless oil; $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.39 (d, 2H, $J = 8.2$ Hz, Ar), 7.28 (m, 1H, Ar), 7.26 (m, 2H, Ar), 7.08 (d, 1H, $J = 2.6$ Hz, Ar), 6.88 (m, 1H, Ar), 6.43 (d, 1H, $J = 0.6$ Hz, Ar), 5.27 (m, 1H, =CH), 4.72 (m, 2H, =CH$_2$), 4.66 (m, 2H, NCH$_2$), 3.86 (s, 3H, OMe), 2.41 (s, 3H, Me); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 208.5, 154.4, 141.9, 137.8, 132.9, 130.4, 129.8, 129.2 (Ar, 2CH), 129.1 (Ar, 2CH), 111.7 (Ar, CH), 111.0 (Ar, CH), 102.1 (Ar, CH), 101.4 (Ar, CH), 88.2 (=CH), 77.3 (=CH$_2$), 55.9 (OMe), 43.0 (NCH$_2$), 21.3 (Me); IR (CHCl$_3$, cm$^{-1}$): v 2932, 1960, 1472, 1367, 852, 830, 784; HRMS (ES): calcd for C$_{20}$H$_{19}$NO $[M]^+$: 289.1461; found: 289.1466.

1-(Buta-2,3-dienyl)-5-fluoro-2-(4-methylphenyl)-1H-indole 2i. From 80 mg (0.30 mmol) of alkyne 1i, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 2i (69 mg, 83%) as a colorless solid; mp 106–107 °C (n-hexane/ethyl acetate); $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 7.42 (d, 2H, $J = 8.0$ Hz, Ar), 7.28 (m, 4H, Ar), 6.98 (dd, 1H, $J = 9.0$, 2.6 Hz, Ar), 6.48 (s, 1H, Ar), 5.30 (m, 1H, =CH), 4.77 (m, 2H, =CH$_2$), 4.70 (m, 2H, NCH$_2$), 2.44 (s, 3H, Me); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 208.5, 159.7, 156.6, 142.9, 138.2, 134.2, 130.5, 129.5 (Ar, 2CH), 129.3 (Ar, 2CH), 110.8 (Ar, CH), 109.6 (Ar, CH), 105.3 (Ar, CH), 101.7 (Ar, CH), 88.0 (=CH), 77.5 (=CH$_2$), 43.0 (NCH$_2$), 21.3 (Me); IR (CHCl$_3$, cm$^{-1}$): v 2934, 1952, 1476, 1376, 846, 823, 776; HRMS (ES): calcd for C$_{19}$H$_{16}$FN $[M]^+$: 277.1261; found: 277.1260.

1-(Buta-2,3-dienyl)-5-nitro-2-phenyl-1H-indole 2j. From 129 mg (0.47 mmol) of alkyne 1j, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 2j (93 mg, 68%) as a colorless solid; mp 121–122 °C (n-hexane/ethyl acetate); $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) δ: 8.59 (d, 1H, $J = 2.2$ Hz, Ar), 8.15 (dd, 1H, $J = 9.1$, 2.2 Hz, Ar), 7.51 (m, 5H, Ar), 7.42 (d, 1H, $J = 9.1$ Hz, Ar), 6.71 (s, 1H, Ar), 5.31 (m, 1H, =CH), 4.76 (m, 4H, =CH$_2$ + NCH$_2$); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) δ: 208.5, 144.5, 142.0, 140.4, 131.4, 129.3 (Ar, 2CH), 128.9 (Ar, CH), 128.8 (Ar, 2CH), 127.3, 117.6 (Ar, CH), 117.3 (Ar, CH), 110.1 (Ar, CH), 104.1 (Ar, CH), 87.6 (=CH), 78.1 (=CH$_2$), 43.0 (NCH$_2$); IR (CHCl$_3$, cm$^{-1}$): v...
2970, 1947, 1475, 1387, 838, 808, 753; HRMS (ES): calcd for C_{18}H_{14}N_{2}O_{2} \[M]^+\: 290.1049; found: 290.1053.

1-(Buta-2,3-dienyl)-2-phenyl-1H-indole-5-carbonitrile 2k. From 80 mg (0.31 mmol) of alkyne 1k, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 2k (61 mg, 72%) as a colorless solid; mp 113–114 °C (n-hexane/ethyl acetate); \(^1\)H-NMR (300 MHz, CDCl\(_3\), 25 °C) \(\delta\): 7.97 (s, 1H, Ar), 7.50 (m, 7H, Ar), 6.61 (s, 1H, Ar), 5.30 (qu, 1H, \(J = 6.6\) Hz, =CH), 4.75 (m, 4H, =CH\(_2\) + NCH\(_2\)); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\), 25 °C) \(\delta\): 208.4, 143.5, 139.1, 131.5, 129.3 (Ar, 2CH), 128.7 (Ar, CH), 128.7 (Ar, 2CH), 127.8, 125.8 (Ar, CH), 124.5 (Ar, CH), 120.8, 111.0 (Ar, CH), 102.9, 102.6 (Ar, CH), 87.6 (=CH), 78.0 (=CH\(_2\)), 42.9 (NCH\(_2\)); IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 2959, 1956, 1470, 1350, 840, 813, 756; HRMS (ES): calcd for C\(_{19}\)H\(_{14}\)N\(_2\) \[M]^+\: 270.1151; found: 270.1157.

1-(Buta-2,3-dienyl)-2-methyl-1H-indole 2l. From 350 mg (2.12 mmol) of alkyne 1l, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 2l (303 mg, 78%) as a colorless oil; \(^1\)H-NMR (300 MHz, CDCl\(_3\), 25 °C) \(\delta\): 7.44 (d, 1H, \(J = 7.5\) Hz), 7.20 (d, 1H, \(J = 8.0\) Hz), 7.06 (td, 1H, \(J = 6.7\) Hz, 1.0 Hz), 6.99 (t, 1H, \(J = 7.0\) Hz), 6.12 (br s, 1H), 5.14 (q, 1H, \(J = 6.4\) Hz), 4.70 (m, 2H), 4.60 (m, 2H), 2.35 (s, 3H); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\), 25 °C) \(\delta\): 208.6, 136.6, 136.3, 128.2, 120.7, 120.5, 119.7, 109.0, 100.2, 87.5, 77.4, 41.8, 12.7; IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 1956; HRMS (ES): calcd for C\(_{13}\)H\(_{13}\)N \[M]^+\: 183.1042; found: 183.1042.

1-(Buta-2,3-dienyl)-2,5-dimethyl-1H-indole 2m. From 178 mg (0.97 mmol) of alkyne 1m, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 2m (100 mg, 52%) as a colorless oil; \(^1\)H-NMR (300 MHz, CDCl\(_3\), 25 °C) \(\delta\): 7.36 (s, 1H, Ar), 7.22 (d, 1H, \(J = 8.3\) Hz, Ar), 7.02 (dd, 1H, \(J = 8.2, 1.2\) Hz, Ar), 6.05 (s, 1H, Ar), 5.26 (m, 1H, \(J = 6.6\) Hz, =CH), 4.83 (m, 2H, =CH\(_2\)), 4.73 (m, 2H, NCH\(_2\)), 2.49 (s, 3H, Me), 2.47 (s, 3H, Me); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\), 25 °C) \(\delta\): 208.5, 136.5, 135.0, 128.5, 128.4, 122.0 (Ar, CH), 119.5 (Ar,
1-(Buta-2,3-dienyl)-5-methoxy-2-methyl-1H-indole 2n. From 180 mg (0.90 mmol) of alkyne 1n, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 2n (151 mg, 79%) as a colorless oil; $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) $\delta$: 7.18 (d, 1H, $J = 8.8$ Hz, Ar), 7.02 (d, 1H, $J = 2.5$ Hz, Ar), 6.81 (dd, 1H, $J = 8.8$, 2.5 Hz, Ar), 6.19 (s, 1H, Ar), 5.23 (qu, 1H, $J = 6.5$ Hz, =CH), 4.80 (m, 2H, =CH$_2$), 4.66 (m, 2H, NCH$_2$), 3.86 (s, 3H, OMe), 2.43 (d, 3H, $J = 0.6$ Hz, Me); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) $\delta$: 208.5, 153.9, 136.9, 131.8, 128.5, 110.2 (Ar, CH), 109.6 (Ar, CH), 101.9 (Ar, CH), 99.9 (Ar, CH), 87.5 (=CH), 77.0 (=CH$_2$), 55.9 (OMe), 41.9 (NCH$_2$), 12.7 (Me); IR (CHCl$_3$, cm$^{-1}$): $\nu$ 2954, 1956, 1475, 1369, 843, 821, 758; HRMS (ES): calcd for C$_{14}$H$_{15}$N [$M^+$]: 197.1198; found: 197.1205.

1-(Buta-2,3-dienyl)-5-chloro-2-methyl-1H-indole 2o. From 355 mg (1.74 mmol) of alkyne 1o, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 2o (327 mg, 86%) as a colorless oil; $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) $\delta$: 7.48 (d, 1H, $J = 1.9$ Hz Ar), 7.19 (d, 1H, $J = 8.8$ Hz, Ar), 7.09 (dd, 1H, $J = 8.6$, 2.0 Hz, Ar), 6.20 (s, 1H, Ar), 5.22 (qu, 1H, $J = 6.5$ Hz, =CH), 4.79 (m, 2H, =CH$_2$), 4.66 (m, 2H, NCH$_2$), 2.44 (s, 3H, Me); $^{13}$C-NMR (75 MHz, CDCl$_3$, 25 °C) $\delta$: 208.5, 137.8, 135.0, 129.1, 125.0, 120.7 (Ar, CH), 119.1 (Ar, CH), 109.9 (Ar, CH), 99.9 (Ar, CH), 87.2 (=CH), 77.4 (=CH$_2$), 41.9 (NCH$_2$), 12.7 (Me); IR (CHCl$_3$, cm$^{-1}$): $\nu$ 2953, 1954, 1474, 1360, 842, 810, 782; HRMS (ES): calcd for C$_{13}$H$_{12}$NCl [$M^+$]: 213.1148; found: 213.1146.

1-(Buta-2,3-dienyl)-5-bromo-2-methyl-1H-indole 2p. From 327 mg (1.32 mmol) of alkyne 1p, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 2p (301 mg, 87%) as a colorless oil; $^1$H-NMR (300 MHz, CDCl$_3$, 25 °C) $\delta$: 7.64 (d, 1H, $J = 1.7$ Hz, Ar), 7.22 (dd, 1H, $J = 8.6$, 1.8 Hz, Ar), 7.15 (d, 1H, $J = 8.6$ Hz, Ar), 6.20 (s, 1H, Ar), 5.21 (qu, 1H, $J = 6.4$ Hz, =CH), 4.79
1-(Buta-2,3-dienyl)-2-methyl-5-nitro-1H-indole 2q. From 380 mg (1.77 mmol) of alkyne 1q, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound 2q (289 mg, 72%) as a colorless solid; mp 96–97 °C (n-hexane/ethyl acetate); \(^1\)H-NMR (300 MHz, CDCl\(_3\), 25 °C) \(\delta\): 8.45 (d, 1H, \(J = 2.2\) Hz, Ar), 8.05 (dd, 1H, \(J = 9.0, 2.2\) Hz, Ar), 7.27 (d, 1H, \(J = 9.1\) Hz, Ar), 6.41 (s, 1H, Ar), 5.26 (m, 1H, \(J = 6.0\) Hz, =CH), 4.78 (m, 2H, =CH\(_2\)), 4.72 (dt, 2H, \(J = 6.0, 2.9\) Hz, NCH\(_2\)), 2.47 (d, 3H, \(J = 0.5\) Hz, Me); \(^{13}\)C-NMR (75 MHz, CDCl\(_3\), 25 °C) \(\delta\): 208.4, 141.5, 140.0, 139.6, 127.3, 116.7 (Ar, CH), 116.4 (Ar, CH), 108.7 (Ar, CH), 102.6 (Ar, CH), 86.9 (=CH), 77.9 (=CH\(_2\)), 42.1 (NCH\(_2\)), 12.8 (Me); IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 2968, 1967, 1430, 1348, 832; HRMS (ES): calcd for C\(_{13}\)H\(_{12}\)N\(_2\)O\(_2\) \([M]^+\): 228.0893; found: 228.0904.

Reaction of 1-Allenyl-2-phenyl-indole 2a with Selectfluor. From 50 mg (0.20 mmol) of aminoallene 2a, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, 11 mg (20%) of the less polar compound 3a and 4 mg (8%) of the more polar compound 4a were obtained.

1-(Buta-2,3-dienyl)-3-fluoro-2-phenyl-1H-indole 4a. Colorless oil; \(^1\)H-NMR (300 MHz, CDCl\(_3\), 25 °C) \(\delta\): 7.57 (d, 1H, \(J = 7.7\) Hz), 7.38 (m, 6H), 7.14 (m, 2H), 5.16 (q, 1H, \(J = 6.0\) Hz), 4.65 (m, 2H), 4.59 (m, 2H); \(^{19}\)F NMR (282 MHz, CDCl\(_3\), 25 °C): \(\delta = -175.4\) (s, 1F); HRMS (ES): calcd for C\(_{18}\)H\(_{14}\)FN \([M]^+\): 263.1104; found: 263.1118.

General Procedure for the Metal-Catalyzed Reaction of \(N\)-Allenyl-2-aryl Indoles 2a–i and Selectfluor. Synthesis of 2-(Allenyl)-2-aryl-3,3-difluoroinodlines 3a–i. Fe(OTf)\(_3\) or [(Ph\(_3\)P)AuNTf\(_2\)] (0.05 mmol), Selectfluor (2.0 mmol), and NaHCO\(_3\) (2.0 mmol) were sequentially added to a stirred solution of
the corresponding N-allenyl indole 2 (1.0 mmol) in acetonitrile (10 mL) under argon atmosphere. The resulting mixture was stirred at room temperature until disappearance of the starting material (TLC, typically 1 h). After filtration through a pad of Celite, water (5 mL) was added before being extracted with ethyl acetate (3 x 15 mL). The organic layer was dried (MgSO₄) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave adducts 3.

2-(Allenyl)-2-phenyl-3,3-difluorindoline 3a. From 235 mg (0.96 mmol) of N-allenyl indole 2a, and after chromatography of the residue using hexanes/ethyl acetate (15:1) as eluent gave compound 3a (227 mg, 83%) as a colorless oil; ¹H-NMR (300 MHz, CDCl₃, 25 ºC) δ: 7.56 (m, 2H), 7.42 (m, 5H), 6.58 (t, 1H, J = 7.4 Hz), 6.76 (d, 1H, J = 8.0 Hz), 5.18 (q, 1H, J = 6.6 Hz), 4.80 (m, 2H), 3.78 (m, 1H), 3.68 (m, 1H), 3.18 (d, 1H, J = 4.3 Hz); ¹³C-NMR (75 MHz, CDCl₃, 25 ºC) δ: 209.0, 150.2, 134.8, 134.9, 133.4, 129.1 (2C), 128.2, 127.7, 126.3, 124.5, 119.5, 119.0, 108.6, 96.4 (t, J = 89.1 Hz), 87.9, 76.7, 42.3; ¹⁹F NMR (282 MHz, CDCl₃, 25 ºC): δ = −98.44 (d, 1H, J = 317.6 Hz), −110.6 (d, 1F, J = 317.6 Hz); IR (CHCl₃, cm⁻¹): ν 3525, 1955, 1157, 1133; HRMS (ES): calcd for C₁₈H₁₅F₂N [M]⁺: 283.1167; found: 283.1183.

2-(Allenyl)-2-(4-chlorophenyl)-3,3-difluorindoline 3b. From 43 mg (0.15 mmol) of N-allenyl indole 2b, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 3b (32 mg, 66%) as a colorless oil; ¹H-NMR (300 MHz, CDCl₃, 25 ºC) δ: 7.42 (d, 2H, J = 8.6 Hz), 7.34 (m, 2H), 7.28 (d, 2H, J = 8.8 Hz), 6.81 (t, 1H, J = 7.4 Hz), 6.66 (d, 1H, J = 8.1 Hz), 5.07 (q, 1H, J = 6.6 Hz), 4.71 (m, 2H), 3.68 (m, 1H), 3.55 (m, 1H), 3.09 (d, 1H, J = 4.0 Hz); ¹³C-NMR (75 MHz, CDCl₃, 25 ºC) δ: 209.0, 150.0, 135.2, 133.5 (2C), 129.2 (2C), 128.4 (2C), 126.2, 124.5, 122.8, 119.2, 108.8, 95.9 (t, J = 89.1 Hz), 87.8, 76.9, 42.2; ¹⁹F NMR (282 MHz, CDCl₃, 25 ºC): δ = −97.7 (d, 1F, J = 317.6 Hz), −110.2 (d, 1F, J = 263.2 Hz); IR (CHCl₃, cm⁻¹): ν 3525, 1953, 1155, 1135; HRMS (ES): calcd for C₁₈H₁₄ClF₂N [M]⁺: 317.0777; found: 317.0792.
2-(Allenyl)-2-(4-fluorophenyl)-3,3-difluoroindoline 3c. From 70 mg (0.27 mmol) of N-allenyl indole 2c, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 3c (32 mg, 40%) as a colorless oil; $^1$H-NMR (300 MHz, C$_6$D$_6$, 25 °C) δ: 7.42 (m, 2H), 7.31 (dd, 1H, J = 6.0 Hz, J = 1.5 Hz), 7.13 (m, 1H), 6.74 (t, 2H, J = 8.9 Hz), 6.61 (t, 1H, J = 7.4 Hz), 6.56 (d, 1H, J = 8.0 Hz), 4.89 (q, 1H, J = 6.4 Hz), 4.51 (m, 2H), 3.48 (m, 1H), 3.35 (m, 1H), 2.61 (d, 1H, J = 3.5 Hz); $^{13}$C-NMR (75 MHz, C$_6$D$_6$, 25 °C) δ: 209.8, 165.3, 162.0, 133.4, 130.3, 130.2, 127.0, 126.6, 125.9, 124.7, 119.4, 115.4, 115.1, 109.0, 96.3, 88.3, 76.5, 42.2; $^{19}$F NMR (282 MHz, C$_6$D$_6$, 25 °C): δ = –95.5 (d, 1F, J = 263.2 Hz), –111.6 (d, 1F, J = 263.3 Hz), –113.1 (s, 1F); IR (CHCl$_3$, cm$^{-1}$): ν 3524, 1954, 1160, 1130; HRMS (ES): calcd for C$_{18}$H$_{14}$F$_3$N [M$^+$]: 301.1072; found: 301.1089.

2-(Allenyl)-2-(4-methylphenyl)-3,3-difluoroindoline 3d. From 96 mg (0.37 mmol) of N-allenyl indole 2d, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 3d (52 mg, 48%) as a colorless oil; $^1$H-NMR (300 MHz, C$_6$D$_6$, 25 °C) δ: 7.68 (d, 2H, J = 8.2 Hz); 7.47 (dd, 1H, J = 8.0, 1.3 Hz), 7.07 (m, 3H), 6.75 (m, 2H), 5.08 (m, 1H), 4.65 (m, 2H), 3.67 (m, 2H), 2.18 (s, 3H); $^{13}$C-NMR (75 MHz, C$_6$D$_6$, 25 °C) δ: 206.8, 136.6, 131.0, 130.2, 129.2 (2C), 128.3 (2C), 125.5, 124.6, 123.9, 122.4, 119.9, 116.8, 106.6, 86.2, 74.1, 40.1, 18.7; $^{19}$F NMR (282 MHz, C$_6$D$_6$, 25 °C): δ = –96.2 (d, 1F, J = 263.2 Hz), –111.3 (d, 1F, J = 263.2 Hz); IR (CHCl$_3$, cm$^{-1}$): ν 3525, 1952, 1160, 1130; HRMS (ES): calcd for C$_{19}$H$_{17}$F$_2$N [M$^+$]: 297.1323; found: 297.1322.

2-(Allenyl)-2-(4-tert-butylphenyl)-3,3-difluoroindoline 3e. From 48 mg (0.16 mmol) of N-allenyl indole 2e, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 3e (23 mg, 43%) as a colorless oil; $^1$H-NMR (300 MHz, C$_6$D$_6$, 25 °C) δ: 7.54 (d, 2H, J = 8.3 Hz), 7.39 (d, 1H, J = 8.6 Hz); 7.23 (dd, 1H, J = 7.6, 1.6 Hz), 7.16 (d, 2H, J = 8.8 Hz); 6.52 (m, 2H), 4.86 (m, 1H), 4.43 (m, 2H), 3.43 (m, 2H), 1.06 (s, 9H); $^{13}$C-NMR (75 MHz, C$_6$D$_6$, 25 °C) δ: 207.7, 150.7, 142.3, 132.0, 131.1, 127.5, 126.9 (2C), 126.6 (2C),
126.0, 125.1, 124.3 (2C), 124.2, 123.4, 117.8, 107.5, 87.2, 75.1, 41.1, 29.9; ^19F NMR (282 MHz, C_6D_6, 25 °C): δ = –96.0 (d, 1F, J = 263.2 Hz), –110.9 (d, 1F, J = 263.2 Hz); IR (CHCl_3, cm^{-1}): ν 3528, 1954, 1154, 1134; HRMS (ES): calcd for C_{22}H_{23}F_2N [M]^+: 339.1793; found: 339.1790.

2-(Allenyl)-2-(naphthalen-2-yl)-3,3-difluoroindoline 3f. From 60 mg (0.25 mmol) of N-allenyl indole 2f, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 3f (45 mg, 55%) as a colorless oil; ^1H-NMR (300 MHz, C_6D_6, 25 °C) δ: 8.19 (s, 1H), 7.49 (m, 4H), 7.27 (dd, 1H, J = 7.9, 1.4 Hz), 7.12 (m, 3H), 6.53 (d, 2H, J = 7.7 Hz); 4.86 (m, 1H), 4.42 (m, 2H), 3.42 (m, 2H); ^13C-NMR (75 MHz, C_6D_6, 25 °C) δ: 209.2, 134.2, 133.6, 133.5, 133.1, 128.9, 128.3, 128.2 (2C), 127.9, 126.8, 126.4, 125.6 (2C), 124.9, 123.8, 120.5, 119.4, 109.0, 88.5, 76.5, 42.4; ^19F NMR (282 MHz, C_6D_6, 25 °C): δ = –95.4 (d, 1F, J = 268.1 Hz), –110.5 (d, 1F, J = 263.2 Hz); IR (CHCl_3, cm^{-1}): ν 3525, 1951, 1152, 1132; HRMS (ES): calcd for C_{22}H_{17}F_2N [M]^+: 333.1323; found: 333.1337.

5-Methyl-2-(allenyl)-2-(4-methylphenyl)-3,3-difluoroindoline 3g. From 49 mg (0.18 mmol) of N-allenyl indole 2g, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 3g (29 mg, 52%) as a colorless oil; ^1H-NMR (300 MHz, C_6D_6, 25 °C) δ: 7.59 (d, 2H, J = 8.2 Hz, Ar), 6.97 (d, 3H, J = 7.9 Hz, Ar), 6.85 (s, 1H, Ar), 6.66 (m, 1H, Ar), 5.22 (m, 1H, J = 6.4 Hz, =CH), 4.53 (m, 2H, =CH_2), 3.97 (m, 1H, CH_H), 3.71 (m, 1H, CH_H), 2.77 (d, 1H, J = 3.2 Hz, NH), 2.06 (s, 3H, Me), 1.84 (s, 3H, Me); ^13C-NMR (75 MHz, C_6D_6, 25 °C) δ: 209.1, 139.1 (Ar, CH), 138.9, 133.9, 132.8, 131.1, 129.3 (Ar, 2CH), 128.4 (Ar, 2CH), 125.3 (Ar, CH), 121.0, 120.7, 109.0 (Ar, CH), 97.1, 88.8 (=CH), 76.5 (=CH_2), 42.7 (CH_2), 21.1(Me), 20.5 (Me); ^19F NMR (282 MHz, C_6D_6, 25 °C): δ = –94.7 (d, 1F, J = 268.1 Hz), –111.7 (d, 1F, J = 263.2 Hz); IR (CHCl_3, cm^{-1}): ν 2925, 1713, 1501, 1328, 1272, 1095, 857, 823; HRMS (ES): calcd for C_{20}H_{16}F_2N [M]^+: 311.1480; found: 311.1487.
5-Methoxy-2-(allenyl)-2-(4-methylphenyl)-3,3-difluorooindoline 3h. From 56 mg (0.19 mmol) of N-allenyl indole 2h, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 3h (26 mg, 42%) as a colorless oil; \(^1\)H-NMR (300 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\): 7.63 (d, 2H, \(J = 8.2\) Hz, Ar), 7.03 (m, 1H, Ar), 6.99 (d, 2H, \(J = 8.0\) Hz, Ar), 6.92 (m, 1H, Ar), 6.58 (d, 1H, \(J = 8.6\) Hz, Ar), 5.03 (m, 1H, \(J = 6.3\) Hz, =CH), 4.55 (m, 2H, =CH\(_2\)), 3.55 (m, 1H, CH\(_H\)), 3.47 (m, 1H, CH\(_H\)), 3.23 (s, 3H, OMe), 2.71 (d, 1H, \(J = 3.4\) Hz, NH), 2.07 (s, 3H, Me); \(^13\)C-NMR (75 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\): 209.1, 154.1, 145.0, 139.0, 132.7, 129.2 (Ar, 4CH), 128.9, 120.5 (Ar, CH), 113.0, 110.4 (Ar, CH), 109.4 (Ar, CH), 97.3, 88.9 (=CH), 76.4 (=CH\(_2\)), 55.5 (OMe), 43.0 (CH\(_2\)), 21.1(Me); \(^{19}\)F NMR (282 MHz, C\(_6\)D\(_6\), 25 °C): \(\delta = -96.0\) (d, 1F, \(J = 263.3\) Hz), \(-113.1\) (d, 1F, \(J = 268.1\) Hz); IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 2926, 1706, 1495, 1276, 1073, 825; HRMS (ES): calcd for C\(_{20}\)H\(_{19}\)F\(_2\)NO \([M]^+: 327.1429\); found: 327.1434.

5-Fluoro-2-(allenyl)-2-(4-methylphenyl)-3,3-difluorooindoline 3i. From 32 mg (0.12 mmol) of N-allenyl indole 2i, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 3i (16 mg, 44%) as a colorless oil; \(^1\)H-NMR (300 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\): 7.52 (d, 2H, \(J = 8.2\) Hz, Ar), 6.99 (m, 1H, Ar), 6.97 (d, 2H, \(J = 7.9\) Hz, Ar), 6.81 (m, 1H, Ar), 6.33 (m, 1H, Ar), 4.92 (m, 1H, \(J = 6.4\) Hz, =CH), 4.51 (m, 2H, =CH\(_2\)), 3.51 (m, 1H, CH\(_H\)), 3.45 (m, 1H, CH\(_H\)), 2.63 (d, 1H, \(J = 3.1\) Hz, NH), 2.06 (s, 3H, Me); \(^13\)C-NMR (75 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\): \(-96.0\) (d, 1F, \(J = 263.3\) Hz), \(-113.1\) (d, 1F, \(J = 268.1\) Hz); IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 2924, 1700, 1492, 1266, 1187, 843, 814; HRMS (ES): calcd for C\(_{19}\)H\(_{16}\)F\(_3\)N \([M]^+: 315.1229\); found: 315.1243.

2-(Buta-2,3-dienyl)-3,3-difluoro-5-nitro-2-phenyllindoline 3j. From 47 mg (0.16 mmol) of N-allenyl indole 2j, 49 mg (92%) of compound 3j was obtained as a pale yellow solid; mp 123–124 °C (n-hexane/ethyl acetate); \(^1\)H-NMR (300 MHz, C\(_6\)D\(_6\), 25
°C) δ: 8.15 (d, 1H, J = 1.8 Hz, Ar), 7.98 (dd, 1H, J=8.9, 2.3 Hz, Ar), 7.41 (m, 2H, Ar), 7.12 (m, 3H, Ar), 6.06 (d, 1H, J = 9.1 Hz, Ar), 4.74 (qu, 1H, J = 6.4 Hz, =CH), 4.48 (m, 2H, =CH₂), 3.30 (m, 2H, CH₂), 3.03 (br s, 1H, NH); ¹³C-NMR (75 MHz, C₆D₆, 25 °C) δ: 209.1, 154.4 (t, J = 24.0 Hz, C), 140.4, 134.2, 130.2, 129.8 (Ar, 2CH), 128.9 (Ar, CH), 127.9 (Ar, 2CH), 125.0, 121.7 (Ar, CH), 120.0 (t, J = 102.5 Hz, C), 107.3 (Ar, CH), 97.1 (dd, J = 124.3, 89.4 Hz, Ar, C), 87.3 (=CH), 77.1 (=CH₂), 41.7(CH₂); ¹⁹F NMR (282 MHz, C₆D₆, 25 °C): δ = –97.9 (d, 1F, J = 251.1 Hz), –108.5 (d, 1F, J = 252.3 Hz); IR (CHCl₃, cm⁻¹): ν 2930, 1622, 1507, 1328, 1269, 1099, 758, 707; HRMS (ES): calcd for C₁₈H₁₄F₂N₂O₂ [M⁺]: 328.1017; found: 328.1038.

2-(Buta-2,3-dienyl)-3,3-difluoro-2-phenylindoline-5-carbonitrile 3k. From 30 mg (0.11 mmol) of N-allenyl indole 2k, 33 mg (97%) of compound 3k was obtained as a colorless solid; mp 118–119 °C (n-hexane/ethyl acetate); ¹H-NMR (300 MHz, C₆D₆, 25 °C) δ: 7.48 (d, 2H, J = 7.7 Hz, Ar), 7.11 (m, 3H, Ar), 7.03 (s, 1H, Ar), 7.00 (d, 1H, J = 9.3 Hz, Ar), 6.13 (d, 1H, J = 8.3 Hz, Ar), 4.79 (m, 1H, J = 6.4 Hz, =CH), 4.48 (m, 2H, =CH₂), 3.33 (m, 3H, CH₂ + NH); ¹³C-NMR (75 MHz, C₆D₆, 25 °C) δ: 209.1, 152.9 (t, J = 26.2 Hz, Ar, C), 137.7 (Ar, CH), 134.5 (d, J = 10.9 Hz, Ar, C), 129.6 (Ar, CH), 128.9 (Ar, CH), 128.6 (Ar, 2CH), 128.3 (Ar, CH), 127.9 (Ar, 2CH), 125.5 (t, J = 113.5 Hz, Ar, C), 120.8 (t, J = 102.5 Hz, Ar, C), 119.0, 108.6 (Ar, CH), 101.8, 96.7 (dd, J = 124.3, 89.4 Hz, Ar, C), 87.4 (=CH), 76.9 (=CH₂), 41.8 (CH₂); ¹⁹F NMR (282 MHz, C₆D₆, 25 °C): δ = –96.9 (d, 1F, J = 251.9 Hz), –109.4 (d, 1F, J = 251.9 Hz); IR (CHCl₃, cm⁻¹): ν 2858, 2224, 1626, 1499, 1178, 1097, 856, 735; HRMS (ES): calcd for C₁₉H₁₄F₂N₂ [M⁺]: 308.1119; found: 308.1112.

Procedure for the Iron-Catalyzed Reaction of 1-(Allenyl)-2-methyl-1H-indoles 2l–q and Selectfluor. Synthesis of 2-(Allenyl)-3,3-difluoro-2-methyl indolines 3l, 3m, and 3o–q. Fe(OTf)₃ (0.0715 mmol), Selectfluor (2.86 mmol), and NaHCO₃ (2.86 mmol) were sequentially added at 0 °C to a stirred solution of the appropriate N-allenyl-2-methyl indole 2 (1.43 mmol) in acetonitrile (14 mL) under argon atmosphere. The resulting mixture was stirred at 0 °C until disappearance of the...
starting material (TLC, 5 min). After filtration through a pad of Celite, water (7 mL) was added before being extracted with ethyl acetate (3 x 20 mL). The organic layer was dried (MgSO₄) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave adducts 3.

2-(Buta-2,3-dienyl)-2-methyl-3,3-difluoroindoline 3l. From 88 mg (0.48 mmol) of aminoallene 2l, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 3l (50 mg, 47%) as a colorless oil; ¹H-NMR (300 MHz, C₆D₆, 25 °C) δ: 7.35 (d, J = 7.4 Hz, Ar), 7.07 (t, J = 7.6 Hz, Ar), 6.56 (d, J = 8.0 Hz, Ar), 6.38 (d, J = 8.0 Hz, Ar), 4.91 (m, J = 6.5 Hz, −CH), 4.52 (m, 2H, −CH₂), 3.50 (m, 2H, CH₂), 2.11 (br s, 1H, NH), 1.32 (d, 3H, J = 2.9 Hz, Me); ¹³C-NMR (75 MHz, C₆D₆, 25 °C) δ: 209.0, 149.4, 133.3 (Ar, CH), 124.5 (Ar, CH), 123.8, 120.1, 118.7 (Ar, CH), 108.4 (Ar, CH), 93.4 (dd, J = 115.7, 93.8 Hz, Ar, C), 88.4 (t, =CH), 76.5 (t, =CH₂), 40.6 (CH₂), 18.2 (d, J = 30.6 Hz, Me); ¹⁹F NMR (282 MHz, C₆D₆, 25 °C): δ = −107.7 (d, 1F, J = 268.2 Hz), −108.9 (d, 1F, J = 268.2 Hz); IR (CHCl₃, cm⁻¹): ν 2930, 1623, 1480, 1249, 1065, 843, 814; HRMS (ES): calcd for C₁₃H₁₃F₂N [M⁺]: 221.1010; found: 221.1021.

2-(Buta-2,3-dienyl)-3,3-difluoro-5-methyl-2-methylindoline 3m. From 40 mg (0.20 mmol) of aminoallene 2m, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent gave compound 3m (23 mg, 48%) as a colorless oil; ¹H-NMR (300 MHz, C₆D₆, 25 °C) δ: 7.16 (s, 1H, Ar), 6.92 (d, J = 8.5 Hz, Ar), 4.96 (m, 1H, J = 6.5 Hz, =CH), 4.55 (m, 2H, =CH₂), 3.53 (m, 2H, CH₂), 2.01 (s, 3H, Me), 1.35 (d, 3H, J = 3.7 Hz, Me); ¹³C-NMR (75 MHz, C₆D₆, 25 °C) δ: 209.0 147.5 (t, J = 26.1 Hz, Ar, C), 133.8 (Ar, CH), 124.9 (Ar, CH), 123.9, 120.3 (t, J = 106.9 Hz, Ar, C), 108.5 (Ar, CH), 93.7 (dd, J = 115.6, 93.8 Hz, Ar, C), 88.6 (t, =CH), 76.4 (t, =CH₂), 40.9 (CH₂), 20.5 (Me), 18.1 (d, J = 30.5 Hz, Me); ¹⁹F NMR (282 MHz, C₆D₆, 25 °C): δ = −107.8 (d, 1F, J = 267.9 Hz), −109.3 (d, 1F, J = 268.2 Hz); IR (CHCl₃, cm⁻¹): ν 2937, 1713, 1470, 1245, 1157, 823; HRMS (ES): calcd for C₁₄H₁₅F₂N₂ [M⁺]: 235.1167; found: 235.1189.
2-(Buta-2,3-dienyl)-5-chloro-3,3-difluoro-2-methylindoline 3o. From 67 mg (0.31 mmol) of aminoallene 2o, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 3o (33 mg, 41%) as a colorless oil; \(^{1}\)H-NMR (300 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\): 7.29 (d, 1H, \(J = 1.7\) Hz, Ar), 7.02 (d, 1H, \(J = 8.6\) Hz, Ar), 6.06 (d, 1H, \(J = 8.5\) Hz, Ar), 4.81 (m, 1H, \(J = 6.4\) Hz, =CH), 4.49 (m, 2H, =CH\(_2\)), 3.36 (m, 2H, CH\(_2\)), 2.02 (br s, 1H, NH), 1.25 (dd, 3H, \(J = 3.6, 0.9\) Hz, Me); \(^{13}\)C-NMR (75 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\): 208.9, 147.8 (t, \(J = 25.0\) Hz, Ar, C), 133.2 (Ar, CH), 126.2, 124.7 (Ar, CH), 123.1 (d, \(J = 150.5\) Hz, Ar, C), 121.2 (t, \(J = 100.4\) Hz, Ar, C), 109.5 (Ar, CH), 93.5 (dd, \(J = 111.2, 93.8\) Hz, Ar, C), 87.9 (=CH), 76.8 (=CH\(_2\)), 40.4 (CH\(_2\)), 18.2 (dd, \(J = 28.3, 6.5\) Hz, Me); \(^{19}\)F NMR (282 MHz, C\(_6\)D\(_6\), 25 °C): \(\delta\) = –108.0 (d, 1F, \(J = 268.2\) Hz), –109.2 (d, 1F, \(J = 268.2\) Hz); IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 2926, 1614, 1483, 1256, 1069, 851, 808; HRMS (ES): calcd for C\(_{13}\)H\(_{12}\)NClF\(_2\) \([M]^+\): 255.0620; found: 255.0637.

2-(Buta-2,3-dienyl)-5-bromo-3,3-difluoro-2-methylindoline 3p. From 80 mg (0.31 mmol) of aminoallene 2p, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 3p (38 mg, 42%) as a colorless oil; \(^{1}\)H-NMR (300 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\): 7.44 (dd, 1H, \(J = 3.3, 1.6\) Hz, Ar), 7.14 (m, 1H, Ar), 6.02 (d, 1H, \(J = 8.5\) Hz, Ar), 4.80 (m, 1H, \(J = 6.4\) Hz, =CH), 4.49 (dt, 2H, \(J = 6.3, 3.0\) Hz, NCH\(_2\)), 3.36 (m, 2H, CH\(_2\)), 2.11 (br s, 1H, NH), 1.23 (dd, 3H, \(J = 3.5, 0.9\) Hz, Me); \(^{13}\)C-NMR (75 MHz, C\(_6\)D\(_6\), 25 °C) \(\delta\): 208.9, 148.2 (t, \(J = 26.0\) Hz, Ar, C), 136.0 (Ar, CH), 126.1, 122.8, 121.9 (t, \(J = 100.4\) Hz, Ar, C), 110.0 (Ar, CH), 93.4 (dd, \(J = 113.5, 94.1\) Hz, Ar, C), 87.9 (=CH), 76.8 (=CH\(_2\)), 40.3 (CH\(_2\)), 18.2 (d, \(J = 28.8\) Hz, Me); \(^{19}\)F NMR (282 MHz, C\(_6\)D\(_6\), 25 °C): \(\delta\) = –107.9 (d, 1F, \(J = 251.8\) Hz), –109.1 (d, 1F, \(J = 251.6\) Hz); IR (CHCl\(_3\), cm\(^{-1}\)): \(\nu\) 2924, 1610, 1472, 1254, 1084, 853, 802; HRMS (ES): calcd for C\(_{13}\)H\(_{12}\)NBrF\(_2\) \([M]^+\): 299.0115; found: 299.0137.

2-(Buta-2,3-dienyl)-3,3-difluoro-5-nitro-2-methylindoline 3q. From 73 mg (0.32 mmol) of aminoallene 2q, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent gave compound 3q (49 mg, 57%) as a
colorless oil; $^1$H-NMR (300 MHz, C$_6$D$_6$, 25 °C) δ: 8.18 (dd, 1H, J = 3.8, 1.8 Hz, Ar), 7.91 (dd, 1H, J = 9.0, 2.3 Hz, Ar), 5.85 (dd, 1H, J = 9.0, 1.2 Hz, Ar), 4.72 (m, 1H, J = 6.5 Hz, =CH), 4.49 (m, 2H, =CH$_2$), 3.35 (m, 2H, CH$_2$), 2.41 (br s, 1H, NH), 1.22 (d, 3H, J = 4.0 Hz, Me); $^{13}$C-NMR (75 MHz, C$_6$D$_6$, 25 °C) δ: 208.9, 153.0 (t, J = 24.0 Hz, Ar, C), 139.7, 130.2 (Ar, CH), 125.1, 121.5 (Ar, CH), 119.5 (t, J = 103.4 Hz, Ar, C), 106.8 (Ar, CH), 93.7 (dd, J = 119.0, 91.2 Hz, Ar, C), 87.1 (=CH), 77.4 (=CH$_2$), 39.8 (CH$_2$), 18.6(d, J = 28.8 Hz, Me); $^{19}$F NMR (282 MHz, C$_6$D$_6$, 25 °C): δ = −106.7 (d, 1F, J = 252.9 Hz), −108.4 (d, 1F, J = 252.9 Hz); IR (CHCl$_3$, cm$^{-1}$): ν 2932, 1702, 1490, 1242, 1150, 830; HRMS (ES): calcd for C$_{13}$H$_{12}$N$_2$O$_2$F$_2$ [M]$^+$: 266.0861; found: 266.0851.

**Procedure for the Iron-Catalyzed Reaction of 1-(Allenyl)-2-methyl-1H-indoles 2l–q and Selectfluor. Synthesis of 2-(Allenyl)-3,3-difluoro-2-(fluoromethyl)indolines 5l, 5m, and 5o–q.** Fe(OTf)$_3$ (0.0715 mmol), Selectfluor (5.00 mmol), and NaHCO$_3$ (5.00 mmol) were sequentially added to a stirred solution of the appropriate N-allenyl-2-methyl indole 2 (1.43 mmol) in acetonitrile (14 mL) under argon atmosphere. The resulting mixture was stirred at room temperature until disappearance of the starting material (TLC, 5 min). After filtration through a pad of Celite, water (7 mL) was added before being extracted with ethyl acetate (3 x 20 mL). The organic layer was dried (MgSO$_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave adducts 5.

2-(Buta-2,3-dienyl)-3,3-difluoro-2-(fluoromethyl)indoline 5l. From 88 mg (0.48 mmol) of aminoallene 2l, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 5l (55 mg, 48%) as a colorless oil; $^1$H-NMR (300 MHz, C$_6$D$_6$, 25 °C) δ: 7.28 (d, 1H, J = 7.4, 1.2 Hz, Ar), 7.03 (td, 1H, J = 8.2, 1.2 Hz, Ar), 6.53 (t, 1H, J = 7.4 Hz, Ar), 6.37 (d, 1H, J = 8.2 Hz, Ar), 4.91 (m, 1H, J = 6.3Hz, =CH), 4.51 (m, 2H, =CH$_2$), 4.45 (d, 1H, J = 1.5 Hz, CH$_2$F), 4.30 (d, 1H, J = 1.3 Hz, CH$_2$H), 3.61 (m, 1H, CH$_2$H), 3.46 (m, 1H, CHH), 2.62 (br s, 1H, NH); $^{13}$C-NMR (75 MHz, C$_6$D$_6$, 25 °C) δ: 208.9, 150.0, 133.5 (Ar,
(CH), 124.3 (Ar, CH), 123.9, 119.8, 119.1 (Ar, CH), 108.5 (Ar, CH), 91.6 (dd, J = 122.2, 87.3 Hz, Ar, C), 88.3 (=CH), 80.4 (dd, J = 709.1, 37.1 Hz, Ar, CH₂F), 76.7 (=CH₂), 41.1 (CH₂); ¹⁹F NMR (282 MHz, C₆D₆, 25 °C): δ = –103.5 (d, 1F, J = 273.0 Hz), –107.0 (dd, 1F, J = 273.0, 14.6 Hz), –230.5 (d, 1F, J = 14.6 Hz); IR (CHCl₃, cm⁻¹): ν 2930, 1614, 1480, 1260, 1084, 846, 809; HRMS (ES): calcd for C₁₃H₁₂NF₃ [M]⁺: 239.0916; found: 239.0922.

2-(Buta-2,3-dienyl)-3,3-difluoro-2-(fluoromethyl)-5-methylindoline 5m. From 46 mg (0.23 mmol) of aminoallene 2m, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 5m (30 mg, 51%) as a colorless oil; ¹H-NMR (300 MHz, C₆D₆, 25 °C) δ: 7.11 (s, 1H, Ar), 6.88 (d, 1H, J = 7.9 Hz, Ar), 6.35 (d, 1H, J = 8.2 Hz, Ar), 4.96 (m, 1H, J = 6.6Hz, =CH), 4.52 (m, 2H, =CH₂), 4.49 (d, 1H, J = 2.5 Hz, CHHF), 4.33 (d, 1H, J = 2.5 Hz, CHHF), 3.64 (m, 1H, CH₂), 3.50 (m, 1H, CHH), 2.63 (br s, 1H, NH), 1.96 (s, 3H, Me); ¹³C-NMR (75 MHz, C₆D₆, 25 °C) δ: 208.9, 148.0 (t, J = 26.1 Hz, Ar, C), 145.7, 134.1 (Ar, CH), 124.7 (Ar, CH), 124.0, 120.0, 108.5 (Ar, CH), 91.8, 88.5 (=CH), 80.7 (dd, J = 709.1, 39.3 Hz, Ar, C), 76.6 (=CH₂), 41.4 (CH₂), 20.4 (Me); ¹⁹F NMR (282 MHz, C₆D₆, 25 °C): δ = –103.9 (d, 1F, J = 273.0 Hz), –106.6 (dd, 1F, J = 273.0, 9.6 Hz), –230.5 (d, 1F, J = 9.9 Hz); IR (CHCl₃, cm⁻¹): ν 2926, 1708, 1486, 1260, 1157, 828; HRMS (ES): calcd for C₁₄H₁₄NF₃ [M]⁺: 253.1072; found: 253.1077.
2-(Buta-2,3-dienyl)-5-chloro-3,3-difluoro-2-(fluoromethyl)indoline 5o. From 67 mg (0.31 mmol) of aminoallene 2o, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 5o (36 mg, 45%) as a colorless oil; ^1H-NMR (300 MHz, C_6D_6, 25 °C) δ: 7.22 (d, 1H, J = 1.9 Hz, Ar), 6.98 (d, 1H, J = 8.1 Hz, Ar), 6.05 (d, 1H, J = 8.5 Hz, Ar), 4.82 (qu, 1H, J = 6.3Hz, =CH), 4.47 (m, 2H, =CH_2), 4.37 (d, 1H, J = 2.3 Hz, CHHF), 4.21 (d, 1H, J = 2.3 Hz, CHHF), 3.48 (m, 1H, ArH), 3.32 (m, 1H, CH), 2.50 (br s, 1H, NH); ^13C-NMR (75 MHz, C_6D_6, 25 °C) δ: 208.8, 148.8 (t, J = 9.8 Hz, Ar, CH), 133.5 (Ar, CH), 124.5 (Ar, CH), 124.0, 122.9, 121.1, 109.6 (Ar, CH), 92.1 (dd, J = 120.0, 87.3 Hz, Ar, C), 87.8 (=CH), 80.4 (dd, J = 709.1, 37.1 Hz, Ar, CHF), 76.9 (=CH_2), 40.9 (CH_2); ^19F NMR (282 MHz, C_6D_6, 25 °C): δ = –103.5 (d, 1F, J = 273.0 Hz), –108.0 (dd, 1F, J = 273.0, 9.8 Hz), –230.6 (d, 1F, J = 9.8 Hz); IR (CHCl_3, cm⁻¹): ν 2925, 1620, 1488, 1260, 1080, 853, 811; HRMS (ES): calcd for C_{13}H_{11}NClF_3 [M]^+: 273.0526; found: 273.0530.

2-(Buta-2,3-dienyl)-5-bromo-3,3-difluoro-2-(fluoromethyl)indoline 5p. From 76 mg (0.29 mmol) of aminoallene 2p, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 5p (50 mg, 54%) as a colorless oil; ^1H-NMR (300 MHz, C_6D_6, 25 °C) δ: 7.38 (d, 1H, J = 1.7 Hz, Ar), 7.13 (d, 1H, J = 9.8 Hz, Ar), 6.02 (d, 1H, J = 8.5 Hz, Ar), 4.85 (m, 1H, J = 6.4 Hz, =CH), 4.48 (m, 2H, =CH_2), 4.39 (t, 1H, J = 2.6 Hz, CHF), 4.24 (t, 1H, J = 2.6 Hz, CHF), 3.52 (m, 1H, ArH), 3.34 (m, 1H, CH), 3.02 (br s, 1H, NH); ^13C-NMR (75 MHz, C_6D_6, 25 °C) δ: 208.9, 148.8 (t, J = 26.2 Hz, Ar, C), 136.2 (Ar, CH), 128.0 (Ar, CH), 121.7 (t, J = 25.1 Hz, Ar, C), 110.5, 110.0 (Ar, CH), 92.0 (dd, J = 171.3, 85.5 Hz, Ar, C), 87.8 (=CH), 81.6 (dd, J = 709.9, 37.8 Hz, Ar, CHF), 76.9 (=CH_2), 40.9(CH_2); ^19F NMR (282 MHz, C_6D_6, 25 °C): δ = –102.2 (d, 1F, J = 257.2 Hz), –107.0 (dd, 1F, J = 257.4, 9.6 Hz), –229.4 (d, 1F, J = 9.2 Hz); IR (CHCl_3, cm⁻¹): ν 2923, 1608, 1476, 1256, 1059, 867, 805; HRMS (ES): calcd for C_{13}H_{11}NBrF_3 [M]^+: 317.0021; found: 317.0041.
2-(Buta-2,3-dienyl)-3,3-difluoro-5-nitro-2-(fluoromethyl)indoline 5q. From 50 mg (0.22 mmol) of aminoallene 2q, 57 mg (91%) of compound 5q was obtained as a colorless oil; $^1$H-NMR (300 MHz, C$_6$D$_6$, 25 °C) δ: 8.16 (dd, 1H, J = 3.7, 1.8 Hz, Ar), 7.89 (dd, 1H, J = 9.0, 2.2 Hz, Ar), 5.89 (d, 1H, J = 9.0 Hz, Ar), 4.81 (m, 1H, J = 6.5 Hz, =CH), 4.51 (m, 2H, =CH$_2$), 4.48 (m, 1H, CHF), 4.19 (d, 1H, CHF), 3.51 (m, 1H, CH), 3.35 (m, 1H, CHH); $^{13}$C-NMR (75 MHz, C$_6$D$_6$, 25 °C) δ: 208.9, 153.7, 140.2, 130.3 (Ar, CH), 121.8, 121.1 (Ar, CH), 119.6 (t, J = 101.3 Hz, Ar, C), 107.0 (Ar, CH), 92.3 (dd, J = 205.5, 84.2 Hz, Ar, C), 86.9 (=CH), 80.0 (dd, J = 712.7, 37.3 Hz, Ar, CHF). $^{19}$F NMR (282 MHz, C$_6$D$_6$, 25 °C): δ = –100.9 (d, 1F, J = 258.9 Hz), –110.8 (dd, 1F, J = 258.9, 12.5 Hz), –230.0 (d, 1F, J = 12.3 Hz); IR (CHCl$_3$, cm$^{-1}$): ν 2940, 1680, 1474, 1264, 1080, 846, 800; HRMS (ES): calcd for C$_{13}$H$_{11}$N$_2$O$_2$F$_3$ [M]$^+$: 284.0767; found: 284.0791.

Procedure for the Pd(II)-Catalyzed Cyclization of 2-Allenyl-1H-indoles 3 in Presence of Allyl Bromide. Preparation of 7-allyl-9a-(4-substituted)-10,10-difluoro-6,9,9a,10-tetrahydropyrido[1,2-a]indoles 11. Palladium(II) chloride (0.004 mmol) was added to a stirred solution of the appropriate β-aminoallene 3 (0.08 mmol) and allyl bromide (0.40 mmol) in N,N-dimethylformamide (0.5 mL). The reaction was stirred under argon atmosphere until disappearance of the starting material (TLC, 24 h). Water (0.4 mL) was added before being extracted with ethyl acetate (3 x 4 mL). The organic phase was washed with water (2 x 2 mL), dried (MgSO$_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures gave adducts 11.

10,10-Difluoro-tetrahydropyrido[1,2-a]indole 11a. From 48 mg (0.17 mmol) of β-aminoallene 3a, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 11a (28 mg, 50%) as a colorless oil; $^1$H-NMR (300 MHz, C$_6$D$_6$, 25 °C) δ: 7.66 (d, 2H, J = 7.7 Hz, Ar), 6.93 (m, 6H, Ar), 6.73 (d, 1H, J = 7.9 Hz, Ar), 5.58 (m, 1H, =CH), 4.92 (m, 2H, =CH$_2$), 4.88 (dd, 2H, J = 11.3, 1.4 Hz, CH$_2$), 3.38 (dd, 2H, J = 11.1, 2.9 Hz, CH$_2$), 3.37 (s, 2H, CH$_2$), 2.42 (d, 2H, J = 6.3 Hz, CH$_2$); $^{13}$C-NMR (75 MHz, C$_6$D$_6$, 25 °C) δ: 138.4, 135.5, 135.0 (Ar,
CH), 134.2, 132.2 (Ar, 2CH), 129.1 (Ar, CH), 128.6 (Ar, 2CH), 128.0 (=CH), 126.5 (=CH), 125.9 (Ar, CH), 124.6 (Ar, CH), 120.0 (Ar, CH), 116.4 (=CH₂), 115.6, 114.9, 62.4 (CH₂), 60.7 (CH₂), 33.4 (CH₂); ¹⁹F NMR (282 MHz, C₆D₆, 25 °C): δ = –92.6 (s, 2F); IR (C₆D₆, cm⁻¹): ν 2927, 1703, 1499, 1256, 1180, 840, 810; HRMS (ES): calcd for C₂₁H₁₉F₂N [M⁺]: 323.1480; found: 323.1469.

10,10-Difluoro-tetrahydropyrido[1,2-a]indole 11b. From 26 mg (0.08 mmol) of β-aminoallene 3b, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 11b (13 mg, 46%) as a colorless oil;¹H-NMR (300 MHz, CDCl₃, 25 °C) δ: 7.87 (d, 1H, J = 7.9 Hz), 7.67 (d, 2H, J = 8.5 Hz), 7.50 (t, 1H, J = 7.5 Hz); 7.37 (t, 1H, J = 7.5 Hz), 7.28 (d, 2H, J = 8.6 Hz), 7.22 (d, 1H, J = 8.0 Hz), 5.76 (m, 1H), 5.25 (br s, 1H), 5.05 (m, 2H), 3.47 (br s, 2H), 3.38 (br s, 2H), 2.72 (d, 2H, J = 6.0 Hz); ¹³C-NMR (75 MHz, CDCl₃, 25 °C) δ: 148.9, 138.7, 138.2, 134.6, 133.5, 132.4, 132.3, 131.8, 129.6, 128.5 (2C), 126.2 (2C), 125.2, 124.4, 119.6, 116.6, 78.5, 62.1, 60.6, 33.2; ¹⁹F NMR (282 MHz, CDCl₃, 25 °C): δ = –95.5 (d, 1F, J = 263.2 Hz), –99.7 (s, 2F); IR (C₆D₆, cm⁻¹): ν 2935, 1634, 1474, 1245, 1056, 840; HRMS (ES): calcd for C₁₆H₁₇F₂N [M⁺]: 357.1090; found: 357.1089.

10,10-Difluoro-tetrahydropyrido[1,2-a]indole 11l. From 30 mg (0.14 mmol) of β-aminoallene 3l, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave compound 11l (28 mg, 32%) as a colorless oil;¹H-NMR (300 MHz, C₆D₆, 25 °C) δ: 7.71 (d, 2H, J = 7.8 Hz, Ar), 7.05 (t, 1H, J = 7.3 Hz, Ar), 6.88 (dd, 1H, J = 12.4, 7.8 Hz, Ar), 5.62 (m, 1H, =CH), 4.98 (m, 2H, =CH₂), 4.97 (m, 2H, CH₂), 3.60 (dd, 2H, J = 19.2, 2.7 Hz, CH₂), 3.59 (m, 2H, CH₂), 2.47 (d, 2H, J = 6.0 Hz, CH₂), 2.12 (d, 3H, J = 1.2 Hz, Me); ¹³C-NMR (75 MHz, C₆D₆, 25 °C) δ: 138.9, 135.0 (Ar, CH), 132.3 (=CH), 128.9, 126.9 (=CH), 126.2 (Ar, CH), 125.7 (Ar, CH), 125.1, 124.9, 120.4 (Ar, CH), 116.6 (=CH₂), 63.5 (CH₂), 62.1 (CH₂), 33.4 (CH₂), 23.6 (Me); ¹⁹F NMR (282 MHz, C₆D₆, 25 °C): δ = –99.7 (s, 2F); IR (C₆D₆, cm⁻¹): ν 2935, 1634, 1474, 1245, 1056, 840; HRMS (ES): calcd for C₁₆H₁₇F₂N [M⁺]: 261.1323; found: 261.1348.
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Figure S1 $^1$H NMR evolution of the Selectfluor-promoted gold-catalyzed reaction of 2-(allenyl)-2-aryl-3,3-difluoroindoline 2b; s.m. = starting material 2b; i. = reaction intermediate; p. = product 3b; s. = Selectfluor.
Figure S2 $^{19}$F NMR evolution of the Selectfluor-promoted gold-catalyzed reaction of 2-(allenyl)-2-aryl-3,3-difluoroindoline 2b; i. = reaction intermediate; p. = product 3b; s. = Selectfluor.