Supporting Information for Publication

Regioselective One-Pot, Three-Component Synthesis of Substituted 2H-Indazoles from 2-Nitroarylaldehyde, Alkyne and Amine Catalyzed by CuBr/Zn(OTf)₂ System

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General experimental methods: Solvents were distilled before use. All starting materials were used as received without further purification unless otherwise indicated. The combined organic layers were dried over Na$_2$SO$_4$. Solvents were evaporated under reduced pressure. All yields given refer to isolated yields. $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ on 600, 400 and 150, 100 MHz NMR spectrometer, respectively using TMS as internal standard. HRMS spectra were recorded using a TOF mass spectrometer. IR spectra were recorded either neat or as film on KBr pellets on a FT-IR spectrometer. Melting points were measured in open capillary tubes and are uncorrected. For thin-layer chromatography (TLC) silica gel GF$_{254}$ was used. Column chromatography was carried out using silica gel 60-120 mesh. X-ray analysis was done on single crystal X-ray diffractometer. All the reactions were performed under nitrogen atmosphere.

General procedure for the Synthesis of 2H-Indazoles: To a mixture of CuBr (30 mol%), o-nitrobenzaldehyde (0.5 mmol), and Zn(OTf)$_2$ (10 mol%) in 3 mL of dry toluene, amine (0.55 mmol) and alkyne (1.0mmol) were added by dissolving in 5 mL of toluene and the reaction mixture was refluxed for specified time. After completion of the reaction, the reaction was cooled, the solvent was removed under rotary evaporator, diluted with water and then extracted with ethyl acetate. The organic layer was further washed with brine solution for 2-3 times. The combined organic layers were dried over Na$_2$SO$_4$ and concentrated in rotary evaporator. The crude was subjected to column chromatography over silica gel to give the corresponding product.

2-(3,4-Dimethoxyphenethyl)-3-(phenylethynyl)-2H-indazole (4a):

Red solid; mp118-120 °C; R$_f$ (hexane/EtOAc 4:1) 0.52; yield 159 mg, 83%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.74 (t, J = 9.2 Hz, 2 H), 7.53 (s, 2 H), 7.40 (s, 3 H), 7.73 (t, J = 7.6 Hz, 1 H), 7.17 (t, J = 7.2 Hz, 1 H), 6.74 (s, 2 H), 6.43 (s, 1 H), 4.77 (t, J = 6.8 Hz, 2 H), 3.79 (s, 3 H), 3.56 (s, 3 H), 3.27 (t, J = 6.8 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.0, 148.2, 148.0, 131.6, 130.4, 129.2, 128.6, 126.7, 124.2, 122.8, 122.3, 120.9, 120.1, 119.1, 117.9, 112.0, 111.5, 100.3, 77.0, 55.9, 55.6, 53.6, 36.7; IR (KBr, neat) 2925, 2853, 1592, 1516, 1464, 1263, 1238, 1156, 1139, 1028, 751, 690 cm$^{-1}$; HRMS (ESI) calcd. for C$_{25}$H$_{23}$N$_2$O$_2$ (M + H)$^+$ 383.1754, found 383.1761.
2-(3,4-Dimethoxyphenethyl)-6-nitro-3-(phenylethynyl)-2H-indazole (4b):

Yellow solid; mp 160-162 °C; Rf (hexane/EtOAc 7:3) 0.50; yield 160 mg, 75%; 1H NMR (400 MHz, CDCl3): δ 8.75 (s, 1 H), 7.98 (d, J = 9.2 Hz, 1 H), 7.84 (d, J = 9.2 Hz, 1 H), 7.55 (d, J = 7.6 Hz, 2 H), 7.43 (d, J = 5.6 Hz, 3 H), 6.75-6.69 (m, 2 H), 6.48 (s, 1 H), 4.84 (t, J = 6.8 Hz, 2 H), 3.80 (s, 3 H), 3.60 (s, 3 H), 3.31 (t, J = 7.2 Hz, 2 H); 13C NMR (100 MHz, CDCl3): δ 149.2, 148.3, 147.3, 146.3, 131.8, 129.9, 129.8, 128.9, 126.4, 121.7, 121.6, 121.0, 120.7, 116.7, 116.0, 112.0, 111.7, 101.5, 75.7, 56.1, 55.8, 54.4, 36.6; IR (KBr, neat) 2923, 1561, 1529, 1519, 1503, 1346, 1267, 1235, 1159, 1029, 837, 754 cm⁻¹; HRMS (ESI) calcd. for C25H22N3O4 (M + H)⁺ 428.1605, found 428.1613.

2-(3,4-Dimethoxyphenethyl)-3-(phenylethynyl)-6-(trifluoromethyl)-2H-indazole (4c):

Pale yellow solid; mp 94-96 °C; Rf (hexane/EtOAc 7:3) 0.55; yield 178 mg, 79%; 1H NMR (400 MHz, CDCl3): δ 8.08 (s, 1 H), 7.83 (d, J = 8.4 Hz, 1 H), 7.57-7.53 (m, 2 H), 7.42 (s, 3 H), 7.33 (d, J = 8.4 Hz, 1 H), 6.75-6.70 (m, 2 H), 6.45 (s, 1 H), 4.81 (t, J = 6.8 Hz, 2 H), 3.80 (s, 3 H), 3.58 (s, 3 H), 3.29 (t, J = 6.8 Hz, 2 H); 13C NMR (150 MHz, CDCl3): δ 149.2, 148.2, 146.7, 131.7, 130.1, 129.6, 129.1 (q, J = 33.0 Hz), 128.8, 125.2, 124.6 (q, J = 271.5 Hz), 122.0, 121.5, 121.0, 120.0, 118.6, 116.5 (q, J = 4.5 Hz), 112.0, 111.6, 101.0, 76.2, 56.0, 55.7, 54.0, 36.7; 19F NMR (376 MHz, C6F6/CDCl3): δ 99.44. IR (KBr, neat) 2934, 2202, 1516, 1463, 1337, 1253, 1160, 1121, 1045, 808, 755, 688 cm⁻¹; HRMS (ESI) calcd. for C26H22F3N2O2 (M + H)⁺ 451.1628, found 451.1628.

5-Chloro-2-(3,4-dimethoxyphenethyl)-3-(phenylethynyl)-2H-indazole (4d):

Pale yellow solid; mp 83-85 °C; Rf (hexane/EtOAc 4:1) 0.51; yield 148 mg, 71%; 1H NMR (400 MHz, CDCl3): δ 7.71 (s, 1 H), 7.68 (d, J = 9.2 Hz, 1 H), 7.54-7.51 (m, 2 H), 7.43-7.39 (m, 3 H), 7.28-7.24 (m, 1 H), 6.75-6.69 (m, 2 H), 6.46 (s, 1 H), 4.75 (t, J = 7.2 Hz, 2 H), 3.80 (s, 3 H), 3.59 (s, 3 H), 3.27 (t, J = 7.2 Hz, 2 H); 13C NMR (100 MHz, CDCl3): δ 149.5, 148.5, 146.9, 132.0, 130.5, 130.0, 129.8, 129.1, 128.4, 124.9, 122.4, 121.3, 119.8, 119.4, 119.3, 112.3, 112.0, 101.1, 76.7, 56.3, 56.0, 54.1, 37.0; IR (KBr, neat) 2932, 2834, 1515, 1463, 1327, 1263, 1237,
5-(Benzyloxy)-2-(3,4-dimethoxyphenethyl)-3-(phenylethynyl)-2H-indazole (4e):

Pale yellow semisolid; Rf (hexane/EtOAc 4:1) 0.51; yield 73 mg, 30%; 1H NMR (400 MHz, CDCl3): δ 7.66 (d, J = 9.2 Hz, 1 H), 7.56–7.53 (m, 2 H), 7.49 (d, J = 7.2 Hz, 2 H), 7.43–7.34 (m, 6 H), 7.11 (d, J = 8.8 Hz, 1 H), 7.04 (s, 1 H), 6.75 (s, 2 H), 6.45 (s, 1 H), 5.11 (s, 2 H), 4.73 (t, J = 7.6 Hz, 2 H), 3.81 (s, 3 H), 3.58 (s, 3 H), 3.26 (t, J = 7.2 Hz, 2 H); 13C NMR (150 MHz, CDCl3): δ 155.5, 149.2, 148.1, 145.0, 137.1, 131.7, 130.6, 129.2, 128.8, 128.7, 128.2, 127.9, 124.5, 122.6, 121.7, 121.0, 119.5, 118.4, 112.2, 111.6, 100.3, 98.3, 77.4, 70.6, 56.1, 55.7, 53.6, 36.8; IR (KBr, neat) 2925, 2850, 1633, 1516, 1464, 1262, 1236, 1189, 1027, 807, 756 cm⁻¹; HRMS (ESI) calcd. for C32H29N2O3 (M + H)+ 489.2173, found 489.2171.

2-(3,4-Dimethoxyphenethyl)-3-(phenylethynyl)-2H-indazol-5-yl acetate (4f):

Pale yellow semisolid; Rf (hexane/EtOAc 7:3) 0.54; yield 77 mg, 35%; 1H NMR (400 MHz, CDCl3): δ 7.75 (d, J = 9.2 Hz, 1 H), 7.54-7.51 (m, 2 H), 7.45-7.38 (m, 4 H), 7.06 (d, J = 8.8 Hz, 1 H), 6.76-6.72 (m, 2 H), 6.48 (s, 1 H), 4.77 (t, J = 7.2 Hz, 2 H), 3.80 (s, 3 H), 3.61 (s, 3 H), 3.27 (t, J = 7.6 Hz, 2 H), 2.34 (s, 3 H); 13C NMR (150 MHz, CDCl3): δ 155.5, 149.2, 148.1, 145.0, 137.1, 131.7, 130.6, 129.2, 128.8, 128.7, 128.2, 127.9, 124.5, 122.6, 121.7, 121.0, 119.5, 118.4, 112.2, 111.6, 100.3, 98.3, 77.4, 70.6, 56.1, 55.7, 53.6, 36.8; IR (KBr, neat) 2925, 2850, 1633, 1516, 1464, 1262, 1236, 1189, 1027, 807, 756 cm⁻¹; HRMS (ESI) calcd. for C27H23N2O3 (M + H)+ 441.1809, found 441.1811.

2-(3,4-Dimethoxyphenethyl)-3-((p-tolylethynyl)-2H-indazole (4g):

Red solid; mp 74-76 °C; Rf (hexane/EtOAc 4:1) 0.55; yield 119 mg, 60%; 1H NMR (400 MHz, CDCl3): δ 7.72 (t, J = 7.6 Hz, 2 H), 7.41 (d, J = 7.6 Hz, 2 H), 7.31 (t, J = 8.0 Hz, 1 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.14 (t, J = 7.2 Hz, 1 H), 6.73 (s, 2 H), 6.43 (s, 1 H), 4.75 (t, J = 7.2 Hz, 2 H), 3.79 (s, 3 H), 3.55 (s, 3 H), 3.25 (t, J = 7.2 Hz, 2 H), 2.39 (s, 3 H); 13C NMR (100 MHz, CDCl3): δ 149.1, 148.2, 148.0, 139.6, 131.6, 130.5, 129.5, 126.7, 124.1, 122.7, 121.0, 120.2, 119.4, 119.3,
117.9, 112.0, 111.5, 100.6, 76.4, 56.0, 55.7, 53.6, 36.7, 21.8; IR (KBr, neat) 2925, 2853, 1625, 1515, 1464, 1263, 1238, 1139, 1028, 815, 748 cm⁻¹; HRMS (ESI) calcd. for C₂₆H₂₅N₂O₂ (M + H)⁺ 397.1911, found 397.1915.

3-((4-(tert-Butyl)phenyl)ethynyl)-2-(3,4-dimethoxyphenethyl)-2H-indazole (4h):

Pale yellow semisolid; Rₛ (hexane/EtOAc 4:1) 0.56; yield 125 mg, 57%; §H NMR (600 MHz, CDCl₃): δ 7.76-7.71 (m, 2 H), 7.48 (d, J = 7.8 Hz, 2 H), 7.42 (d, J = 7.8 Hz, 2 H), 7.33 (t, J = 7.8 Hz, 1 H), 7.16 (t, J = 7.2 Hz, 1 H), 6.75 (s, 2 H), 6.48 (s, 1 H), 4.77 (t, J = 7.8 Hz, 2 H), 3.81 (s, 3 H), 3.58 (s, 3 H), 3.28 (t, J = 7.2 Hz, 2 H), 1.35 (s, 9 H); §C NMR (150 MHz, CDCl₃): δ 152.9, 149.2, 148.3, 148.1, 131.5, 130.5, 126.8, 125.8, 124.2, 122.8, 121.0, 120.2, 119.5, 119.5, 118.0, 112.1, 111.6, 100.7, 76.5, 56.1, 55.7, 53.7, 36.8, 35.2, 31.4 (3C); IR (KBr, neat) 2920, 1630, 1516, 1464, 1263, 1028, 747, 600 cm⁻¹; HRMS (ESI) calcd. for C₂₉H₃₁N₂O₂ (M + H)⁺ 439.2380, found 439.2385.

3-((4-Chlorophenyl)ethynyl)-2-(3,4-dimethoxyphenethyl)-2H-indazole (4i):

Colorless solid; mp 112-114 °C; Rₛ (hexane/EtOAc 4:1) 0.52; yield 129 mg, 62%; §H NMR (400 MHz, CDCl₃): δ 7.76 (d, J = 9.2 Hz, 1 H), 7.70 (d, J = 8.4 Hz, 1 H), 7.44 (d, J = 8.8 Hz, 2 H), 7.39-7.32 (m, 2 H), 7.17 (t, J = 6.8 Hz, 1 H), 6.75–6.70 (m, 2 H), 6.38 (s, 1 H), 4.76 (t, J = 7.6 Hz, 2 H), 3.80 (s, 3 H), 3.55 (s, 3 H), 3.27 (t, J = 7.6 Hz, 2 H); §C NMR (150 MHz, CDCl₃): δ 149.1, 148.4, 148.1, 135.4, 132.8, 130.5, 129.1 (2C), 126.9, 124.4, 123.1, 121.0, 120.9, 120.1, 118.1, 112.1, 111.6, 99.2, 78.1, 56.1, 55.7, 53.8, 36.8; IR (KBr, neat) 2916, 2844, 1633, 1516, 1468, 1263, 1027, 789, 748 cm⁻¹; HRMS (ESI) calcd. for C₂₉H₂₃ClN₂O₂ (M + H)⁺ 417.1364, found 417.1364.

3-((4-Bromophenyl)ethynyl)-2-(3,4-dimethoxyphenethyl)-2H-indazole (4j):

Pale yellow semisolid; mp104-106 °C; Rₛ (hexane/EtOAc 4:1) 0.53; yield 150 mg, 65%; §H NMR (400 MHz, CDCl₃): δ 7.76 (d, J = 8.8 Hz, 1 H), 7.70 (d, J = 8.0 Hz, 1 H), 7.53 (d, J = 8.4 Hz, 2 H), 7.38-7.31 (m, 3 H), 7.17 (t, J = 7.2 Hz, 1 H), 6.75–6.69 (m, 2 H), 6.38 (s, 1 H), 4.76 (t, J = 7.2 Hz, 2 H), 3.79 (s, 3 H), 3.55 (s, 3 H), 3.27 (t, J = 7.6 Hz, 2 H); §C NMR (100 MHz, CDCl₃): δ 149.1, 148.3, 148.1, 132.9, 132.0, 130.4, 126.8, 124.3, 123.6, 123.0, 121.3, 120.9,
120.0, 118.9, 118.1, 112.1, 111.6, 99.2, 78.2, 56.0, 55.7, 53.7, 36.7; IR (KBr, neat) 2932, 1624, 1515, 1463, 1263, 1139, 1010, 821, 747 cm$^{-1}$; HRMS (ESI) calcd. for C$_{25}$H$_{22}$BrN$_2$O$_2$ (M + H)$^+$ 461.0859, found 461.0856.

2-(3,4-Dimethoxyphenethyl)-3-((4-nitrophenyl)ethynyl)-2H-imidazole (4k):

Yellow solid; mp 154-156 °C; R$_f$(hexane/EtOAc 7:3) 0.55; yield 173 mg, 81%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.25 (d, $J$ = 8.4 Hz, 2 H), 7.79 (d, $J$ = 8.4 Hz, 1 H), 7.71 (d, $J$ = 8.0 Hz, 1 H), 7.63 (d, $J$ = 8.8 Hz, 2 H), 7.37 (t, $J$ = 8.0 Hz, 1 H), 7.22 (t, $J$ = 7.2 Hz, 1 H), 6.72 (s, 2 H), 6.33 (s, 1 H), 4.79 (t, $J$ = 6.8 Hz, 2 H), 3.77 (s, 3 H), 3.53 (s, 3 H), 3.29 (t, $J$ = 6.8 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.1, 148.3, 148.2, 147.5, 133.6, 132.1, 130.3, 129.2, 127.0, 124.7, 123.9, 123.6, 120.9, 119.8, 118.3, 112.1, 111.5, 98.4, 82.2, 56.0, 55.7, 53.9, 36.7; IR (KBr, neat) 2927, 2851, 2202, 1592, 1516, 1463, 1262, 1140, 1107, 1028, 855, 748, cm$^{-1}$; HRMS (ESI) calcd. for C$_{25}$H$_{22}$N$_3$O$_2$ (M + H)$^+$ 428.1605, found 428.1600.

2-Phenethyl-3-(phenylethynyl)-2H-indazole (4l):

Red solid; mp 70-72 °C; R$_f$(hexane/EtOAc 4:1) 0.60; yield 126 mg, 78%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77-7.73 (m, 2 H), 7.58-7.54 (m, 2 H), 7.43-7.40 (m, 3 H), 7.36-7.16 (m, 7 H), 4.80 (t, $J$ = 8.0 Hz, 2 H), 3.35 (t, $J$ = 8.0 Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.3, 137.9, 131.7, 129.2, 129.0, 128.9, 128.8, 127.0, 126.7, 124.3, 122.9, 122.4, 120.1, 118.9, 118.1, 100.6, 77.1, 53.5, 37.2; IR (KBr, neat) 2926, 1518, 1493, 1464, 1364, 1283, 1076, 747, 689 cm$^{-1}$; HRMS (ESI) calcd. for C$_{23}$H$_{19}$N$_2$ (M + H)$^+$ 323.1543, found 323.1550.

2-Benzyl-3-(phenylethynyl)-2H-indazole (4m):

Colorless solid; mp 78-80 °C; R$_f$(hexane/EtOAc 9:1) 0.62; yield 74 mg, 48%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.76 (t, $J$ = 7.6 Hz, 2 H), 7.58-7.54 (m, 2 H), 7.40-7.27 (m, 9 H), 7.19 (t, $J$ = 7.6 Hz, 1 H), 5.76 (s, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.4, 136.2, 131.7, 129.3, 129.0, 128.8, 128.7, 128.3, 128.2, 126.8, 124.7, 123.0, 122.4, 120.2, 118.3, 101.0, 77.5, 55.9; IR (KBr, neat) 2952, 2852, 1518, 1493, 1455, 1443, 1283, 1172, 1097, 748, 706, 689 cm$^{-1}$; HRMS (ESI) calcd. for C$_{22}$H$_{17}$N$_2$ (M + H)$^+$ 309.1386, found 309.1396.

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2-Allyl-3-(phenylethynyl)-2H-indazole (4n):

Pale yellow semi solid; R_f (hexane/EtOAc 9:1) 0.59; yield 76 mg, 59%; ^1H NMR (400 MHz, CDCl_3): δ 7.77 (t, J = 8.4 Hz, 2 H), 7.61-7.58 (m, 2 H), 7.43-7.40 (m, 3 H), 7.35-7.31 (m, 1 H), 7.20-7.16 (m, 1 H), 6.19–6.09 (m, 1 H), 5.34–5.28 (m, 2 H), 5.21 (d, J = 6.0 Hz 2 H); ^13C NMR(150 MHz, CDCl_3): δ 148.4, 132.3, 131.7, 129.3, 128.8, 126.8, 124.7, 123.0, 122.5, 120.1, 119.2, 118.9, 118.3, 100.9, 77.2, 54.6; IR (KBr, neat) 2924, 2853, 1529, 1465, 1364, 1218, 1091, 927, 748, 689 cm^{-1}; HRMS (ESI) calcd. for C_{18}H_{15}N_2 (M + H)^+ 259.1230, found 259.1236.

2-Cyclohexyl-3-(phenylethynyl)-2H-indazole (4o):

Pale yellow semi solid; R_f (hexane/EtOAc 9:1) 0.61; yield 99 mg, 66%; ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, J = 8.8 Hz, 2 H), 7.62-7.58 (m, 2 H), 7.45-7.39 (m, 3 H), 7.31 (t, J = 8.0 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1 H), 4.82–4.74 (m, 1 H), 2.22-2.12 (m, 4 H), 2.32-1.95 (m, 2 H), 1.82-1.76 (m, 1 H), 1.57-1.34 (m, 3 H); ^13C NMR (100 MHz, CDCl_3): δ 147.9, 131.6, 129.2, 128.8, 126.4, 124.4, 122.7, 120.0, 118.2, 117.7, 100.8, 77.5, 61.4, 33.2, 25.9, 25.5; IR (KBr, neat) 2931, 2854, 1452, 1352, 1280, 1010, 746, 868 cm^{-1}; HRMS (ESI) calcd. for C_{21}H_{21}N_2 (M + H)^+ 301.1699, found 301.1696.

2-Isopropyl-3-(phenylethynyl)-2H-indazole (4p):

Pale yellow semi solid; R_f (hexane/EtOAc 9:1) 0.62; yield 83 mg, 64%; ^1H NMR (600 MHz, CDCl_3): δ 7.80-7.77 (m, 2 H), 7.62 (t, J = 4.2 Hz, 2 H), 7.44-7.39 (m, 3 H), 7.33 (t, J = 7.8 Hz, 1 H), 7.18 (t, J = 7.8 Hz, 1 H), 5.26–5.20 (m, 1 H), 1.71 (d, J = 7.2 Hz, 6 H); ^13C NMR (150 MHz, CDCl_3): δ 147.9, 131.6, 129.2, 128.8, 126.4, 124.5, 122.7, 122.6, 120.0, 118.2, 117.6, 100.8, 77.3, 53.8, 22.9; IR (KBr, neat) 2923, 1641, 1459, 1347, 1276, 1235, 1082, 746, 689 cm^{-1}; HRMS (ESI) calcd. for C_{18}H_{17}N_2 (M + H)^+ 261.1386, found 261.1389.

2-Butyl-3-(phenylethynyl)-2H-indazole (4q):

Pale yellow semi solid; R_f (hexane/EtOAc 9:1) 0.64; yield 96 mg, 70%; ^1H NMR (400 MHz, CDCl_3): δ 7.76 (t, J = 9.6 Hz, 2 H), 7.62-7.59 (m, 2H), 7.43-7.40 (m, 3 H), 7.33 (t, J = 7.2 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1 H), 4.60 (t, J = 7.6 Hz, 2 H), 2.05 (p, J = 7.2 Hz, 2 H), 1.44–1.36 (m, 2
H), 0.98 (t, J = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.1, 131.6, 129.2, 128.8, 126.5, 124.4, 122.8, 122.5, 120.0, 118.8, 118.1, 100.6, 77.4, 51.8, 32.7, 20.1, 13.8; IR (KBr, neat) 2958, 2929, 2871, 2659, 2206, 2107, 1625, 1597, 1492, 1464, 1364, 1284, 1084, 746, 689 cm$^{-1}$; HRMS (ESI) calcd. for C$_{19}$H$_{19}$N$_2$ (M + H)$^+$ 275.1543, found 275.1552.

2-Butyl-3-(p-tolylethynyl)-6-(trifluoromethyl)-2H-indazole (4r):

Pale yellow solid; mp 84-86 °C; R$_f$ (hexane/EtOAc 9:1) 0.58; yield 107 mg, 60%; $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.06 (s, 1 H), 7.86 (d, J = 8.4 Hz, 1 H), 7.50 (d, J = 7.8 Hz, 2 H), 4.62 (t, J = 7.2 Hz, 2 H), 2.41 (s, 3 H), 2.05 (p, J = 7.2 Hz, 2 H), 1.43-1.38 (m, 2 H), 0.98 (t, J = 7.2 Hz, 3 H); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ 146.6, 140.0, 131.7, 129.6, 128.7 (q, J = 33.0 Hz), 125.3, 124.7 (q, J = 270.0 Hz), 121.5, 119.8, 119.0, 118.4, 116.5 (q, J = 4.5 Hz), 101.5, 75.9, 52.2, 32.6, 21.8, 20.0, 13.8; $^{19}$F NMR (376 MHz, C$_6$F$_6$/CDCl$_3$): $\delta$ 99.43; IR (KBr, neat) 2926, 1653, 1455, 1337, 1252, 1164, 1084, 1045, 809 cm$^{-1}$; HRMS (ESI) calcd. for C$_{21}$H$_{20}$F$_3$N$_2$ (M + H)$^+$ 357.1573, found 357.1572.

2-(tert-Butyl)-3-(phenylethynyl)-2H-indazole (4s):

Pale yellow solid; mp 92-94 °C; R$_f$ (hexane/EtOAc 9:1) 0.70; yield 70 mg, 51%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (d, J = 8.4 Hz, 2 H), 7.62-7.58 (m, 2 H), 7.33-7.28 (m, 1 H), 7.17 (t, J = 7.2 Hz, 1 H), 1.97 (s, 9 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.3, 131.3, 129.1, 128.8, 128.7, 126.8, 126.3, 123.0, 122.8, 119.8, 118.4, 101.3, 79.5, 63.1, 30.1; IR (KBr, neat) 2925, 1543, 1456, 1369, 1343, 1261, 1205, 1028, 746, 688, 668 cm$^{-1}$; HRMS (ESI) calcd. for C$_{19}$H$_{19}$N$_2$ (M + H)$^+$ 275.1544, found 275.1544.

2-Octadecyl-3-(phenylethynyl)-2H-indazole (4t):

Pale yellow solid; mp 81-83 °C; R$_f$ (hexane/EtOAc 9:1) 0.78; yield 132 mg, 56%; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 (t, J = 9.2 Hz, 2 H), 7.63-7.58 (m, 2 H), 7.43-7.39 (m, 3 H), 7.32 (t, J = 8.0 Hz, 1 H), 7.17 (t, J = 7.6 Hz, 1 H), 4.59 (t, J = 6.8 Hz, 2 H), 2.09-2.03 (m, 2 H), 1.37-1.21 (m, 30 H), 0.88 (t, J = 7.2 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.1, 131.6, 129.2, 128.8, 126.5, 124.4, 122.8, 122.6, 120.1, 118.7, 118.1, 100.6, 77.4, 52.1, 32.1, 30.7, 29.9 (4C), 29.8 (3C).
29.82, 29.8, 29.7, 29.6, 29.3, 26.8, 22.9, 14.3; IR (KBr, neat) 2920, 2852, 2213, 1641, 1465, 1368, 1279, 1025, 745, 688 cm\(^{-1}\); HRMS (ESI) calcd. for C\(_{33}\)H\(_{47}\)N\(_2\) (M + H)\(^+\) 471.3734, found 471.3721.
$^1$H and $^{13}$C spectra of compound 4a
$^1\text{H}$ and $^{13}\text{C}$ spectra of compound 4b
$^1$H and $^{13}$C spectra of compound 4c
$^1$H and $^{13}$C spectra of compound 4d
$^1$H and $^{13}$C spectra of compound 4e
$^1$H and $^{13}$C spectra of compound 4f

![Spectral Image]
$^1$H and $^{13}$C spectra of compound 4g
$^1$H and $^{13}$C spectra of compound 4h
$^1$H and $^{13}$C spectra of compound 4j

S19
$^1$H and $^{13}$C spectra of compound 4k
$^1$H and $^{13}$C spectra of compound 41


\[ ^1H \text{ and } ^{13}C \text{ spectra of compound 4m} \]

\[
\text{[Chemical Structure Image]}
\]
$^1$H and $^{13}$C spectra of compound 4n

![Spectra Image]

**S23**
$^1$H and $^{13}$C spectra of compound 4o
$^1$H and $^{13}$C spectra of compound 4p
$^1$H and $^{13}$C spectra of compound 4q

![NMR Spectra](image)
$^1$H, $^{13}$C and $^{19}$F spectra of compound 4r
\(^1\)H and \(^{13}\)C spectra of compound 4s

\[
\begin{align*}
\text{Signal:} & \quad \text{Signal} \\
\text{Pulse:} & \quad \text{Pulse} \\
\text{Accum. time:} & \quad \text{Accum. time} \\
\text{NMR tube:} & \quad \text{NMR tube} \\
\text{Operator:} & \quad \text{Operator} \\
\text{File:} & \quad \text{File} \\
\text{Solvent:} & \quad \text{Solvent} \\
\text{Temp:} & \quad \text{Temp} \\
\text{ chant:} & \quad \text{ chant} \\
\text{Hahn:} & \quad \text{Hahn} \\
\text{MGX:} & \quad \text{MGX} \\
\end{align*}
\]
$^1$H and $^{13}$C spectra of compound 4t
The crystal parameters of compound 4a

<table>
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<tr>
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<th>4a- CCDC1008821</th>
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<tr>
<td><strong>Formula</strong></td>
<td>( \text{C}<em>{25}\text{H}</em>{22}\text{N}<em>{2}\text{O}</em>{2} )</td>
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<tr>
<td><strong>Formula weight</strong></td>
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<td><strong>( T/\text{K} )</strong></td>
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<td><strong>Crystal system</strong></td>
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<td><strong>Space group</strong></td>
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<td><strong>( a/\text{\AA} )</strong></td>
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<tr>
<td><strong>( b/\text{\AA} )</strong></td>
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<tr>
<td><strong>( c/\text{\AA} )</strong></td>
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<td><strong>( \alpha/\text{\degree} )</strong></td>
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<td><strong>( \beta/\text{\degree} )</strong></td>
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<tr>
<td><strong>( \gamma/\text{\degree} )</strong></td>
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<tr>
<td><strong>( V/\text{\AA}^3 )</strong></td>
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<td><strong>( Z )</strong></td>
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<td><strong>Abs. Coeff./mm(^{-1})</strong></td>
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<td><strong>Abs. Correction</strong></td>
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<td><strong>GOF on ( F^2 )</strong></td>
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<td><strong>Final ( R ) indices [I &gt; 2\sigma(I)]</strong></td>
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<td>( wR^2 = 0.0707 )</td>
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<tr>
<td><strong>R indices [all data]</strong></td>
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<td>( wR^2 = 0.0719 )</td>
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ORTEP diagram of 4a