Supplementary Information

Rhodium-catalyzed hydroarylation of alkynes via tetrazole-directed C–H activation

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1. General information:

All chemicals were used as received without further purification unless stated otherwise. $^1$H NMR and $^{13}$C NMR spectra were recorded at ambient temperature on a 400 MHz NMR spectrometer (100 MHz for $^{13}$C). NMR experiments are reported in $\delta$ units, parts per million (ppm) and were referenced to CDCl$_3$ (7.26 or 77.0 ppm) as the internal standard. The coupling constants $J$ are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

Experimental procedure for the reaction: Under air, a 20 mL Schlenk tube equipped with a stir bar was charged with tetrazole 1 (0.1 mmol), alkyne 2 (0.3 mmol), benzoic acid (0.025 mmol), Cp*Rh(CH$_3$CN)$_3$(SbF$_6$)$_2$ (2 mol%), acetic acid (2 mL) and sealed. The reaction mixture was stirred at 80 °C for 14 h. After the completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-EtOAc as the eluent to give the desired product 3.

Intermolecular competition experiment with 1a-d5: A 20 mL of Schlenk tube equipped with a stir bar was charged with 2-methyl-5-phenyl-2H-tetrazole 1a and d$_5$-1a (1:1 0.2 mmol), 1,2-diphenylethyne 2a (0.6 mmol), benzoic acid (0.05 mmol), Cp*Rh(CH$_3$CN)$_3$(SbF$_6$)$_2$ (0.004 mmol) in 2 mL of AcOH. The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 80 °C for 15 min in oil bath. After that, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give product 3aa and d$_3$-3aa in 18% yield. The mixture was analyzed using $^1$H NMR spectrometer. As shown in Figure S1, the ratio of 3aa and d$_3$-3aa is nearly 1:1.

$^1$H NMR of 3aa and d$_3$-3aa (CDCl$_3$, 400 MHz): $\delta$ 7.50-7.45 (m, 3H), 7.09-7.03 (m, 11H), 6.95-6.93 (m, 4H), 6.85-6.83 (m, 3.51H), 6.62 (s, 2H), 3.85 (s, 3H).

Recovered materials 1a' of $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.14-8.12(m, 0.81H), 7.50-7.47(m, 1.10H), 4.39 (s, 3H). m/z = 160, 161, 162, 163, 164, 165.
Scheme S1 Intermolecular competition experiment with 1a-d5:

Figure S1 The $^1$H NMR spectrum of the KIE results
2. Experimental characterization data for compounds

5-(2,6-Bis((E)-1,2-diphenylvinyl)phenyl)-2-methyl-2H-tetrazole (3aa): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:25) give 3aa (47.6 mg, 92% yield) as white solid. mp 182-184 °C. 1H NMR (CDCl₃, 400 MHz): δ 7.54-7.47 (m, 3H), 7.13-7.05 (m, 12H), 6.98-6.96 (m, 4H), 6.88 (d, J = 6.4 Hz, 4H), 6.65 (s, 2H), 3.85 (s, 3H); 13C NMR (CDCl₃, 100 MHz): δ 163.8, 146.2, 141.6, 139.9, 137.2, 131.5, 129.9, 129.8, 129.6, 129.4, 127.9, 126.8, 38.7. IR (KBr, cm⁻¹): 3074, 3051, 3018, 2955, 2922, 2851, 2360, 2341, 1519, 1489, 1443, 1406, 1357, 1186, 1078, 1029. HRMS (ESI) calcd for C₃₆H₂₉N₄ ([M + H]+): 517.2387. Found: 517.2363.
5-(2,6-Bis((E)-1,2-diphenylvinyl)-4-methoxyphenyl)-2-methyl-2H-tetrazole (3da): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) give 3da (51.1 mg, 93% yield) as white solid. mp 174-176 °C. 1H NMR (CDCl₃, 400 MHz): δ 7.10-7.04 (m, 14H), 6.99-6.95 (m, 4H), 6.87 (d, 2H, J = 6.4 Hz), 3.83 (s, 3H); 13C NMR (CDCl₃, 100 MHz): δ 163.7, 160.1, 147.6, 141.7, 139.8, 137.1, 131.3, 129.9, 129.4, 127.8, 126.8, 119.3, 115.3, 55.5, 38.6. IR (KBr, cm⁻¹): 3078, 3049, 3018, 2962, 2918, 2853, 2358, 2341, 1445, 1356, 1204, 1032. HRMS (ESI) calcd for C₃₇H₃₁N₄O ([M + H]⁺): 547.2492. Found: 547.2482.

5-(4,6-bis((E)-1,2-Diphenylvinyl)benzo[d][1,3]dioxol-5-yl)-2-methyl-2H-tetrazole (3ea): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) give 3ea (48.7 mg, 87% yield) as white solid. mp 65-66 °C. 1H NMR (CDCl₃, 400 MHz): δ 7.12-7.05 (m, 12H), 6.97-6.92 (m, 9H), 6.71 (s, 1H), 6.56 (s, 1H), 6.02 (s, 2H), 3.83 (s, 3H); 13C NMR (CDCl₃, 100 MHz): δ 163.5, 148.4, 141.3, 140.7, 140.0, 137.1, 136.6, 134.6, 133.3, 131.2, 129.9, 129.7, 129.4, 129.3, 127.8, 126.9, 109.8, 101.6, 38.7. IR (KBr, cm⁻¹): 3078, 3053, 3020, 2957, 2918, 2853,

5-(4-Bromo-2,6-bis((E))-1,2-diphenylvinyl)phenyl)-2-methyl-2H-tetrazole (3fa): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gives 3fa (52.5 mg, 88% yield) as white solid. mp 80-82 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.65 (s, 2H), 7.12-7.05 (m, 12H), 6.95-6.93 (m, 4H), 6.84 (d, $J = 6.4$ Hz, 4H), 6.64 (s, 2H), 3.84 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 163.0, 147.9, 140.3, 139.3, 136.7, 132.4, 132.2, 129.8, 129.4, 128.0, 127.9, 127.1, 127.0, 125.8, 123.8, 38.7. IR (KBr, cm$^{-1}$): 3078, 3055, 3022, 2956, 2927, 2852, 2358, 2329, 1598, 1574, 1504, 1404, 1355, 1223, 1157, 1095, 1038, 1012. HRMS (ESI) calcd for C$_{36}$H$_{28}$BrN$_4$ ([M + H]$^+$): 595.1492. Found: 595.1487.

5-(2,6-Bis((E))-1,2-diphenylvinyl)-4-fluorophenyl)-2-methyl-2H-tetrazole (3ga): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gives 3ga (47.2 mg, 88% yield) as white solid. mp 143-145 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.12-7.06 (m, 12H), 6.96 (s, 4H), 6.86 (d, $J = 6.4$ Hz, 4H), 6.64 (s, 2H), 3.85 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 163.1, 148.5 (d, $J_{C-F} = 8.2$ Hz), 140.6, 139.4, 136.7, 132.1, 129.8, 129.4, 127.9 (d, $J_{C-F} = 7.1$ Hz), 127.0, 116.7 (d, $J_{C-F} = 21.6$ Hz), 38.7. IR (KBr, cm$^{-1}$): 3055, 3022, 2956, 2869, 2854, 2358, 2329, 1587, 1491, 1445, 1409, 1356, 1182, 1136, 1117, 1076, 1029. HRMS (ESI) calcd for C$_{36}$H$_{28}$FN$_4$ ([M + H]$^+$): 535.2293. Found: 535.2285.

5-(2,6-Bis((E))-1,2-diphenylvinyl)-4-(trifluoromethyl)phenyl)-2-methyl-2H-tetrazole (3ha): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) gives 3ha (50.6 mg, 86% yield) as white solid. mp 156-158 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.75 (s, 2H), 7.11-7.04 (m, 12H), 6.97-6.95 (m, 4H), 6.82 (d, $J = 6.8$ Hz, 4H), 6.88 (s, 2H), 3.85 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 162.7, 147.1, 140.4, 139.1, 136.6, 132.6, 131.6 (q, $J = 137.9$ Hz), 129.8, 129.4, 128.0, 127.9, 127.2, 127.1, 126.2 (q, $J = 3.5$ Hz), 38.7. IR (KBr, cm$^{-1}$): 3078, 3055, 3022, 2957, 2928, 2359, 2332, 1526, 1491, 1445, 1423, 1342, 1315, 1249, 1186, 1163, 1132, 1089, 1078. HRMS (ESI) calcd for C$_{37}$H$_{28}$F$_3$N$_4$ ([M + H]$^+$): 585.2261. Found: 585.2233.

3,5-bis((E))-1,2-diphenylvinyl)-4-(2-methyl-2H-tetrazol-5-yl)benzoic acid (3ia): Flash column chromatography on a silica gel (dichloromethane: ethyl acetate: petroleum ether, 1:1:3) gives 3ia (30.8 mg, 57% yield) as white solid. mp 213-215 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.93
(s, 2H), 7.11-7.02 (m, 12H), 6.83-6.81 (m, 4H), 6.68 (s, 2H), 3.84 (s, 3H); 13C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.8, 162.9, 146.9, 140.7, 139.3, 136.8, 134.3, 132.3, 130.2, 129.9, 129.4, 128.5, 128.0, 127.9, 127.1, 127.0, 38.7. IR (KBr, cm$^{-1}$): 3456, 3294, 3178, 2957, 2923, 2853, 2358, 2341, 1732, 1682, 1655, 1612, 1558, 1445, 1389, 1275. HRMS (ESI) calcd for C$_{37}$H$_{29}$N$_4$O$_2$ ([M + H]$^+$): 561.2285. Found: 561.2277.

(E)-5-(2-(1,2-Diphenylvinyl)-6-methylphenyl)-2-methyl-2H-tetrazole (3ja): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) give 3ja (32.6 mg, 92% yield) as white solid. mp 89-91 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.42-7.35 (m, 2H), 7.29-7.26 (m, 1H), 7.11-7.05 (m, 6H), 7.01-6.98 (m, 2H), 6.87 (d, $J$ = 6.8 Hz, 2H), 6.65 (s, 1H), 4.13 (s, 3H), 2.15 (s, 3H); 13C NMR (CDCl$_3$, 100 MHz): $\delta$ 164.1, 145.9, 142.1, 140.1, 138.6, 137.3, 129.9, 129.6, 129.5, 129.4, 128.1, 127.9, 127.8, 126.8, 39.1, 20.2. IR (KBr, cm$^{-1}$): 3051, 3024, 2955, 2922, 2868, 2358, 2331, 1574, 1522, 1493, 1456, 1441, 1416, 1404, 1356, 1188, 1074, 1038. HRMS (ESI) calcd for C$_{23}$H$_{21}$N$_4$ ([M + H]$^+$): 353.1761. Found: 353.1754.

(E)-5-(2-Chloro-6-(1,2-diphenylvinyl)phenyl)-2-methyl-2H-tetrazole (3ka): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:20) give 3ka (32.9 mg, 88% yield) as white solid. mp 122-124 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.49-7.42 (m, 3H), 7.14-7.06 (m, 6H), 6.99-6.97 (m, 2H), 6.86 (d, $J$ = 6.8 Hz, 2H), 6.66 (s, 1H), 4.13 (s, 3H); 13C NMR (CDCl$_3$, 100 MHz): $\delta$ 162.2, 147.9, 140.7, 139.4, 136.7, 135.3, 132.1, 130.9, 129.9, 129.4, 128.9, 128.8, 128.0, 127.9, 127.1, 127.0, 126.8, 39.2. IR (KBr, cm$^{-1}$): 3076, 3053, 3024, 2953, 2920, 2853, 2359, 2341, 1591, 1558, 1491, 1445, 1406, 1359, 1192, 1074. HRMS (ESI) calcd for C$_{22}$H$_{18}$ClN$_4$ ([M + H]$^+$): 373.1215. Found: 373.1209.

5-(2,6-Bis((E)-1,2-Dip-tolylvinyl)phenyl)-2-methyl-2H-tetrazole (3ab): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:25) give 3ab (49.6 mg, 87% yield) as white solid. mp 79-81 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.51-7.43 (m, 3H), 6.92-6.84 (m, 12H), 6.78 (d, $J$ = 8.0 Hz, 4H), 6.56 (s, 2H), 3.88 (s, 3H), 2.26 (s, 6H), 2.25 (s, 6H); 13C NMR (CDCl$_3$, 100 MHz): $\delta$ 163.9, 146.4, 140.7, 137.3, 136.3, 134.5, 130.9, 129.7, 129.6, 129.4, 129.2, 128.5, 126.6, 38.6, 21.3, 21.2. IR (KBr, cm$^{-1}$): 3076, 3045, 3020, 2953, 2918, 2864, 2358, 2341, 1508, 1456, 1406, 1354, 1182, 1034. HRMS (ESI) calcd for C$_{40}$H$_{37}$N$_4$ ([M + H]$^+$): 573.3013. Found: 573.2997.
5-(2,6-Bis((E)-1,2-bis(4-methoxyphenyl)vinyl)phenyl)-2-methyl-2H-tetrazole (3ac): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:5) gave 3ac (47.1 mg, 74% yield) as white solid. mp 80-82 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.46-7.40 (m, 3H), 6.89 (d, \(J = 8.8\) Hz, 4H), 6.78 (d, \(J = 8.8\) Hz, 4H), 6.63-6.59 (m, 8H), 6.49 (s, 2H), 3.87 (s, 3H), 3.74 (s, 6H), 3.72 (s, 6H), 3.71 (s, 6H); \(^1\)\(^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 164.0, 158.3, 158.2, 146.5, 139.4, 132.7, 131.1, 130.5, 130.3, 129.6, 129.4, 126.5, 113.3, 55.1, 38.6. IR (KBr, cm\(^{-1}\)): 3029, 3001, 2953, 2934, 2907, 2835, 2359, 2322, 1605, 1574, 1508, 1458, 1441, 1418, 1354, 1290, 1248, 1177, 1109, 1034. HRMS (ESI) calcd for C\(_{40}\)H\(_{37}\)N\(_4\)O\(_4\) ([M + H]\(^+\)): 637.2809. Found: 637.2782.

5-(2,6-Bis((E)-1,2-bis(4-chlorophenyl)vinyl)phenyl)-2-methyl-2H-tetrazole (3ad): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:25) gave 3ad (46.4 mg, 71% yield) as white solid. mp 87-89 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.54-7.45 (m, 3H), 7.05 (t, \(J = 8.4\) Hz, 8H), 6.87 (d, \(J = 8.4\) Hz, 4H), 6.75 (d, \(J = 8.4\) Hz, 4H), 6.58 (s, 2H), 3.90 (s, 3H); \(^1\)\(^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 163.5, 145.5, 140.9, 137.9, 135.1, 135.0, 132.9, 131.2, 130.6, 130.1, 129.9, 128.3, 126.5, 38.8. IR (KBr, cm\(^{-1}\)): 3051, 3028, 2955, 2924, 2853, 2357, 2329, 1591, 1489, 1456, 1398, 1354, 1180, 1092, 1034, 1013. HRMS (ESI) calcd for C\(_{36}\)H\(_{25}\)Cl\(_4\)N\(_4\) ([M + H]\(^+\]): 653.0828. Found: 653.0826.

5-(2,6-Bis((E)-1,2-bis(4-bromophenyl)vinyl)phenyl)-2-methyl-2H-tetrazole (3ae): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:25) gave 3ae (59.9 mg, 72% yield) as white solid. mp 85-87 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.58-7.48 (m, 3H), 7.28-7.22 (m, 4H), 7.15 (s, 2H), 7.01-6.80 (m, 11H), 6.61 (s, 2H), 4.01 (s, 3H); \(^1\)\(^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 163.3, 145.2, 141.4, 141.3, 138.5, 132.4, 132.3, 130.8, 130.2, 130.1, 129.8, 129.6, 128.4, 127.8, 126.7, 122.1, 121.9, 39.0. IR (KBr, cm\(^{-1}\)): 3057, 3011, 2953, 2926, 2852, 2357, 2329, 1589, 1558, 1472, 1418, 1404, 1356, 1157, 1070, 1036. HRMS (ESI) calcd for C\(_{36}\)H\(_{25}\)Br\(_4\)N\(_4\) ([M + H]\(^+\]): 828.8807. Found: 832.8794.

5-(2,6-Bis((E)-1,2-bis(4-fluorophenyl)vinyl)phenyl)-2-methyl-2H-tetrazole (3af): Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1:25) gave 3af (42.2 mg, 72% yield) as white solid. mp 176-178 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.54-7.44 (m, 3H), 6.92-6.88 (m, 4H), 6.82-6.74 (m, 4H), 6.57 (s, 2H), 3.91 (s, 3H); \(^1\)\(^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 163.7, 162.9 (d, \(J_{CF} = 13.1\) Hz), 160.5 (d, \(J_{CF} = 13.2\) Hz), 145.8, 140.3, 135.6 (d, \(J_{CF} = 3.4\) Hz),
132.9 (d, $J_{C,F} = 3.5$ Hz), 131.5 (d, $J_{C,F} = 7.9$ Hz), 130.9 (d, $J_{C,F} = 7.8$ Hz), 130.5, 129.8 (d, $J_{C,F} = 10.0$ Hz), 115.1 (d, $J_{C,F} = 2.0$ Hz), 114.9(d, $J_{C,F} = 2.0$ Hz), 38.8. IR (KBr, cm$^{-1}$): 3078, 3055, 3022, 2956, 2927, 2852, 2356, 2329, 1599, 1573, 1504, 1404, 1356, 1223, 1157, 1095, 1037, 1012. HRMS (ESI) calcd for C$_{36}$H$_{25}$F$_4$N$_4$ ([M + H]$^+$): 589.2010. Found: 589.2005.
3. Copies of the $^1$H NMR and $^{13}$C NMR spectra