

**A highly efficient $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -catalysed intramolecular [3+2]
cycloaddition for the synthesis of
3,4-dihydrobenzopyrano[3,4-*c*]pyrazoles**

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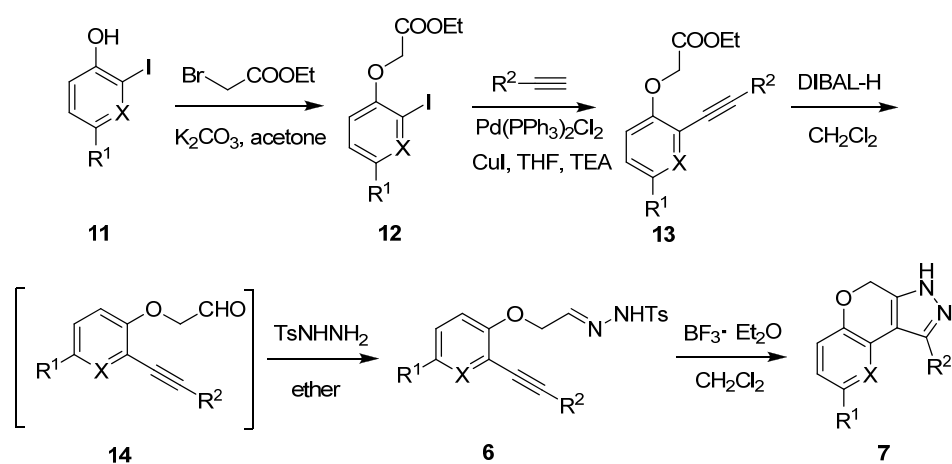
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1. General information

Flash chromatography was performed with freshly distilled solvents. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using CDCl_3 as solvent. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Solvents were purified using the following method. THF was dried over sodium for 4 h and distilled under N_2 atmosphere. CH_2Cl_2 was dried over CaH_2 for 4 h and distilled under N_2 atmosphere. Other solvents and materials were used as received. All the reactions were carried out under N_2 .

2. General procedure for the synthesis of compound 7



X = N, CH; R^1 = H, CH_3 , Br, *t*-Bu; R^2 = Ph, *p*- MeC_6H_4 , *p*- MeOC_6H_4 , *n*-Bu, 2-thiophene, Cyclopropyl

In a 250 mL of three necked flask was added **11** (20.0 mmol), K_2CO_3 (40.0 mmol), acetone (100 mL) and ethyl 2-bromoacetate (30.0 mmol). After refluxing overnight, cooled to r.t., solid was filtrated. The filtrate is concentrated in vacuum affording **12**, which was used in next step without further purification.

In a 250 mL of oven dried three necked flask was added **12** (10.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.2 mmol), CuI (0.4 mmol) under N_2 , then THF (30 mL) and Et_3N (30 mL) was added successively. The reaction mixture was heated to 45 °C, and then terminal alkyne (20.0 mmol) was added dropwise. After the addition, the resulting solution was stirred for additional 3 h, then cooled down to r.t., filtrated, the filtrate was concentrated in vacuum and purified by silica gel column chromatography, affording pure compound **13**.

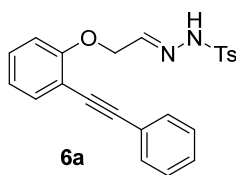
Compound **13** (9.0 mmol) was dissolved in CH_2Cl_2 (30 mL) under N_2 , then cooled to -78 °C, and DIBAL-H (1M in hexane, 9 mL) was added dropwise. After the addition, the solution was stirred at -78 °C for additional 2 h. After the completion of reaction, methanol (9 mL) was added and

stirred for additional 5 min, then poured into ice-water, acidified with diluted HCl to pH 5-6, extracted with CH₂Cl₂ for 3 times. The organic layers were combined and washed with brine, dried over Na₂SO₄, concentrated in vacuum to give **14**, which was used in next step without further purification.

Compound **14** (4.0 mmol) was dissolved in ether (15 mL), 2 drops diluted HCl was added, and the mixture was then cooled in ice-water. After addition of TsNHNH₂ (4.0 mmol) in portions within 5 min, white solid formed, which was then filtrated and washed with cooled ether, dried in vacuum affording compound **6**.

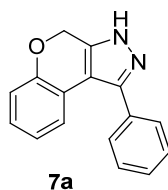
Compound **6** (1.0 mmol) was dissolved in CH₂Cl₂ (10 mL), cooled with ice-water. A solution of BF₃·Et₂O (48% in ether, 0.1 mL, 0.3 mmol) in CH₂Cl₂ (2 mL) was then added in dropwise. After the addition, the resulting solution was stirred at 0 °C for 3 h. The reaction was then quenched with saturated NaHCO₃ (5 mL), and extracted with CH₂Cl₂ for 3 times, washed with brine, dried over Na₂SO₄, concentrated in vacuum. The residue was purified by silica gel column chromatography to give pure tricyclic fused-pyrazole **7**.

3. Analytic data of 6, 7 and 13



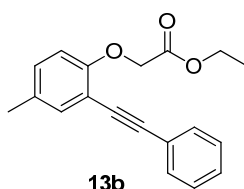
(E)-4-Methyl-N'-(2-(2-(phenylethynyl)phenoxy)ethylidene)benzenesulfonohydrazide (6a)

White solid (91%); m.p. = 105-106 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 11.49 (br s, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.50-7.36 (m, 9H), 7.27-7.23 (m, 1H), 7.00-6.96 (m, 2H), 4.72 (d, *J* = 4.0 Hz, 2H), 2.36 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ 158.2, 145.5, 143.4, 136.0, 133.1, 131.2, 130.1, 129.6, 128.7, 128.6, 127.1, 122.6, 121.1, 112.9, 111.8, 93.2, 85.8, 67.3, 21.0; IR (film): 3198, 1442, 1367, 1344, 1307, 1224, 1014, 918, 753, 687, 577 cm⁻¹; HRMS-ESI (*m/z*) calcd. for C₂₃H₂₀N₂O₃SNa [M+Na]⁺ 427.1092, found: 427.1095.



1-Phenyl-3,4-dihydrochromeno[3,4-c]pyrazole (7a)

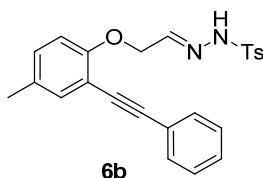
White solid (86%); m.p. = 170-172 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.63 (m, 2H), 7.54-7.52 (m, 3H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.12-7.08 (m, 1H), 7.01-6.99 (m, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 4.85 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 152.5, 146.4, 138.9, 130.1, 129.4, 129.2, 128.6, 127.6, 122.9, 122.0, 119.7, 117.5, 109.5, 63.9; IR (film): 3147, 3070, 2920, 1434, 1207, 1133, 1097, 1030, 750, 700, 559 cm⁻¹; HRMS-EI (*m/z*) calcd. for C₁₆H₁₂N₂O [M]⁺ 248.0950, found: 248.0952.



Ethyl 2-(4-methyl-2-(phenylethynyl)phenoxy)acetate (13b).

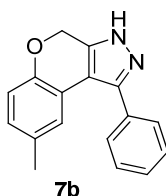
Yellow oil (86%); ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.54 (m, 2H), 7.35-7.30 (m, 4H), 7.07-7.04

(m, 1H), 6.74 (d, $J = 8.0$ Hz, 1H), 4.70 (s, 2H), 4.25 (q, $J = 7.2$ Hz, 2H), 2.28 (s, 3H), 1.28 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 156.5, 134.0, 131.7, 131.3, 130.2, 128.3, 128.2, 123.6, 113.5, 113.4, 93.7, 85.6, 66.8, 61.3, 20.4, 14.2; IR (film): 2981, 2925, 2212, 1759, 1501, 1442, 1297, 1197, 1114, 1071, 805, 758, 692 cm^{-1} ; HRMS-EI (m/z) calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_3$ $[\text{M}]^+$ 294.1256, found: 294.1257.



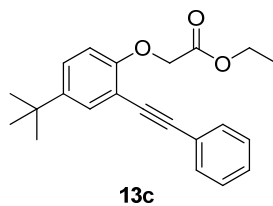
4-Methyl-N'-(2-(4-methyl-2-(phenylethynyl)phenoxy)ethylidene)benzenesulfonohydrazide (6b)

White solid (67%); m.p. = 112-114 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 11.47 (br s, 1H), 7.71 (d, $J = 8.4$ Hz, 2H), 7.51-7.49 (m, 2H), 7.44-7.42 (m, 4H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 1.6$ Hz, 1H), 7.02 (dd, $J = 8.8, 1.6$ Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 4.67 (d, $J = 4.8$ Hz, 2H), 2.37 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.6, 146.1, 143.9, 136.6, 133.8, 131.7, 131.1, 130.5, 130.2, 129.2, 129.1, 127.6, 123.2, 113.5, 112.1, 93.4, 86.5, 68.0, 21.5, 20.2; IR (film): 3192, 1501, 1369, 1347, 1311, 1228, 1167, 1022, 811, 758, 689, 579 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 419.1429, found: 419.1428.



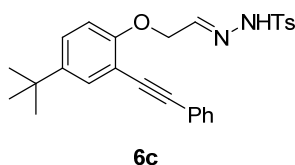
8-Methyl-1-phenyl-3,4-dihydrochromeno[3,4-c]pyrazole (7b)

White solid (91%); m.p. = 169-171 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.63-7.61 (m, 2H), 7.52-7.50 (m, 3H), 7.16 (s, 1H), 6.91 (s, 2H), 5.12 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.4, 146.7, 138.9, 131.2, 130.1, 129.4, 129.1, 128.5, 128.1, 123.4, 119.5, 117.3, 109.5, 63.8, 20.9; IR (film): 3154, 3065, 2920, 1493, 1440, 1234, 1210, 1009, 819, 767, 698, 553 cm^{-1} ; HRMS-EI (m/z) calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}]^+$ 262.1106, found: 262.1104.



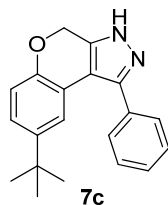
Ethyl 2-(4-*tert*-butyl-2-(phenylethynyl)phenoxy)acetate (13c)

Light yellow solid (90%); m.p. = 72-73 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.59-7.57 (m, 2H), 7.53 (m, 1H), 7.34-7.27 (m, 4H), 6.77 (d, $J = 8.4$ Hz, 1H), 4.73 (s, 2H), 4.27 (q, $J = 7.2$ Hz, 2H), 1.31-1.27 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 156.3, 144.6, 131.7, 130.7, 128.3, 128.2, 126.7, 123.6, 112.9, 112.8, 93.4, 86.0, 66.6, 61.4, 34.2, 31.4, 14.2; IR (film): 2960, 1756, 1523, 1298, 1257, 1222, 816, 762, 693 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{22}\text{H}_{25}\text{O}_3$ $[\text{M}+\text{H}]^+$ 337.1804, found: 337.1801.



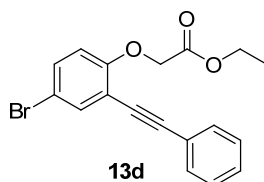
(*E*)-N'-(2-(4-*tert*-butyl-2-(phenylethynyl)phenoxy)ethylidene)-4-methylbenzenesulfonylhydrazide (6c)

White solid (63%); m.p. = 119-120 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 11.47 (br s, 1H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.51-7.38 (m, 9H), 7.23 (dd, $J = 8.8, 2.0$ Hz, 1H), 6.88 (d, $J = 8.8$ Hz, 1H), 4.69 (d, $J = 4.8$ Hz, 2H), 2.37 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.6, 146.2, 143.9, 136.6, 131.8, 131.7, 130.3, 130.2, 129.2, 129.1, 127.7, 127.5, 123.3, 113.1, 111.7, 93.2, 86.8, 68.0, 34.3, 31.6, 21.5; IR (film): 3163, 2957, 1501, 1344, 1240, 1161, 1070, 1018, 890, 804, 753, 689, 581, 583 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 461.1899, found: 461.1894.



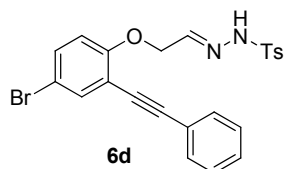
8-Tert-butyl-1-phenyl-3,4-dihydrochromeno[3,4-c]pyrazole (7c)

White solid (90%); m.p. = 168-169 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.67-7.63 (m, 2H), 7.53-7.49 (m, 3H), 7.39 (d, J = 3.2 Hz, 1H), 7.11 (dd, J = 10.8, 2.8 Hz, 1H), 6.91 (d, J = 11.2 Hz, 1H), 4.91 (s, 2H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.1, 146.6, 144.5, 138.5, 129.9, 129.3, 128.9, 128.3, 124.4, 120.0, 118.8, 116.7, 109.7, 63.9, 34.2, 31.3; IR (film): 3153, 3063, 2956, 2903, 2867, 1492, 1439, 1360, 1235, 1215, 1008, 820, 767, 700 cm^{-1} ; HRMS-EI (m/z) calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}$ [M] $^+$ 304.1576, found: 304.1574.



Ethyl 2-(4-bromo-2-(phenylethynyl)phenoxy)acetate (13d)

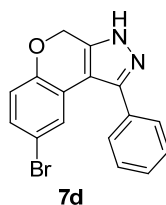
Yellow solid (91%); m.p. = 39-41 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.62-7.62 (m, 1H), 7.56-7.54 (m, 2H), 7.36-7.33 (m, 4H), 6.69 (d, J = 8.8 Hz, 1H), 4.70 (s, 2H), 4.26 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.4, 157.7, 136.0, 132.3, 131.8, 128.7, 128.4, 123.1, 115.8, 114.8, 113.9, 95.3, 84.1, 66.6, 61.6, 14.3; IR (film): 3477, 1716, 1496, 1307, 1268, 1235, 1118, 1019, 799, 751, 685 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{18}\text{H}_{15}\text{BrO}_3\text{Na}$ [$\text{M}+\text{Na}$] $^+$ 381.0102, found: 381.0106.



(E)-N'-(2-(4-bromo-2-(phenylethynyl)phenoxy)ethylidene)-4-methylbenzenesulfonohydrazide (6d)

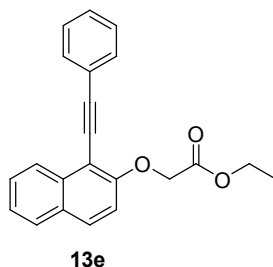
White solid (56%); m.p. = 136-137 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.48 (br s, 1H), 7.69-7.64 (m, 3H), 7.53-7.51 (m, 2H), 7.45-7.44 (m, 3H), 7.41-7.34 (m, 4H), 6.90 (d, J = 9.2 Hz,

1H), 4.73 (d, $J = 4.8$ Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 157.9, 145.4, 143.9, 136.5, 135.3, 133.0, 131.8, 130.2, 129.5, 129.2, 127.6, 122.7, 115.4, 114.5, 112.5, 95.0, 84.8, 68.0, 21.5; IR (film): 3180, 1479, 1345, 1310, 1225, 1166, 1015, 882, 811, 756, 686, 578, 535 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{23}\text{H}_{20}\text{BrN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 483.0378, found: 483.0378.



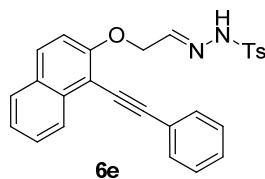
8-Bromo-1-phenyl-3,4-dihydrochromeno[3,4-c]pyrazole (7d)

White solid (89%); m.p. = 189-191 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.59-7.52 (m, 5H), 7.39 (d, $J = 2.4$ Hz, 1H), 7.15 (dd, $J = 8.8, 2.8$ Hz, 1H), 6.83 (d, $J = 8.8$ Hz, 1H), 4.85 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.5, 146.3, 139.3, 130.2, 129.8, 129.4, 129.3, 128.3, 125.4, 121.6, 119.2, 114.3, 108.5, 63.9; IR (film): 3151, 3061, 2903, 1513, 1468, 1432, 1392, 1262, 1236, 1213, 809, 787, 700 cm^{-1} ; HRMS-EI (m/z) calcd. for $\text{C}_{16}\text{H}_{11}\text{BrN}_2\text{O}$ $[\text{M}]^+$ 326.0055, found: 326.0056.



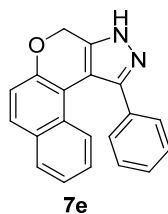
Ethyl 2-(1-(phenylethynyl)naphthalen-2-yloxy)acetate (13e)

White solid (82%); m.p. = 54-56 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.38 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 9.2$ Hz, 2H), 7.67 (d, $J = 7.6$ Hz, 2H), 7.57-7.55 (m, 1H), 7.44-7.35 (m, 4H), 7.19 (d, $J = 9.2$ Hz, 1H), 4.91 (s, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.28 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 157.6, 134.5, 131.7, 130.1, 129.4, 128.4, 128.4, 128.2, 127.5, 125.6, 124.9, 123.7, 115.5, 108.2, 99.7, 83.6, 67.4, 61.4, 14.2; IR (film): 3082, 2976, 1764, 1588, 1508, 1274, 1207, 1107, 1027, 802, 747 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{22}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 353.1154, found: 353.1149.



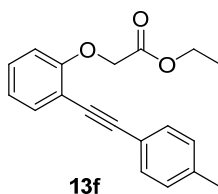
(E)-4-Methyl-N'-(2-(1-(phenylethynyl)naphthalen-2-yloxy)ethylidene)benzenesulfonohydrazide (6e)

White solid, (72%); m.p. = 129-130 °C; ^1H NMR (400 MHz, DMSO- d_6) δ 11.52 (br s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 9.2 Hz, 1H), 7.70-7.63 (m, 5H), 7.53-7.48 (m, 5H), 7.36 (d, J = 9.2 Hz, 1H), 7.31 (d, J = 7.6 Hz, 2H), 4.91 (d, J = 4.8 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 157.9, 146.0, 143.9, 136.5, 134.0, 131.7, 130.9, 130.1, 129.3, 129.2, 128.8, 128.3, 127.5, 125.1, 125.0, 123.3, 115.2, 106.2, 99.2, 84.4, 68.5, 21.4; IR (film): 3190, 1345, 1308, 1270, 1167, 1035, 1019, 914, 809, 749, 687, 582, 599 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 455.1429, found: 455.1436.



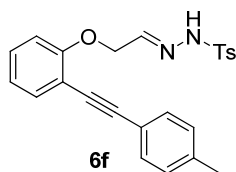
1-Phenyl-3,4-dihydrobenzo[5,6]chromeno[3,4-c]pyrazole (7e)

White solid (90%); m.p. = 222-224 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.43-7.24 (m, 8H), 6.94 (t, J = 7.6 Hz, 1H), 4.99 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.3, 148.9, 139.2, 131.0, 130.3, 129.0, 128.7, 128.5, 128.4, 128.4, 128.1, 126.7, 125.2, 123.9, 118.8, 114.5, 109.1, 64.1; IR (film): 3281, 1492, 1475, 1227, 1041, 989, 818, 766, 748, 720, 697 cm^{-1} ; HRMS-EI (m/z) calcd. for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}]^+$ 298.1106, found: 298.1107.



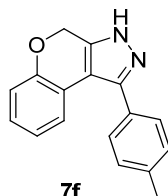
Ethyl 2-(2-(*p*-tolylethynyl)phenoxy)acetate (13f)

Yellow oil (84%); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49-7.44 (m, 3H), 7.22-7.17 (m, 1H), 7.11-7.09 (d, $J = 8.8$ Hz, 2H), 6.93 (t, $J = 7.4$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 4.67 (s, 2H), 4.20 (q, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 1.22 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.7, 158.4, 138.3, 133.6, 131.6, 129.5, 129.1, 121.8, 120.6, 113.8, 113.1, 94.3, 84.9, 66.3, 61.3, 21.5, 14.2; IR (film): 2982, 2924, 1760, 1512, 1488, 1450, 1300, 1197, 1112, 818, 752 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{19}\text{H}_{19}\text{O}_3$ [$\text{M}+\text{H}$] $^+$ 295.1334, found: 295.1329.



(*E*)-4-Methyl-*N'*-(2-(2-(*p*-tolylethynyl)phenoxy)ethylidene)benzenesulfonohydrazide (6f)

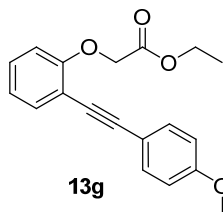
White solid (59%); m.p. = 113-114 $^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, DMSO-d_6) δ 11.48 (br s, 1H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.47-7.36 (m, 6H), 7.24-7.22 (m, 3H), 6.97-6.94 (m, 2H), 4.71 (d, $J = 4.8$ Hz, 2H), 2.36 (s, 3H), 2.34 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, DMSO) δ 158.6, 146.0, 143.9, 138.8, 136.5, 133.5, 131.6, 130.4, 130.1, 129.8, 127.6, 121.6, 120.2, 113.4, 112.5, 93.9, 85.7, 67.8, 21.5, 21.5; IR (film): 3181, 1446, 1347, 1309, 1221, 1165, 1016, 918, 816, 753, 576 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ [$\text{M}+\text{H}$] $^+$ 419.1429, found: 419.1429.



1-*p*-tolyl-3,4-dihydrochromeno[3,4-*c*]pyrazole (7f)

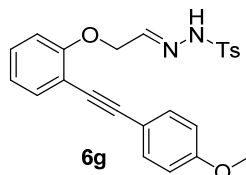
White solid (93%); m.p. = 174-176 $^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.6$ Hz, 2H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 7.6$ Hz, 2H), 7.13 (t, $J = 7.6$ Hz, 1H), 7.03 (d, $J = 8.0$ Hz, 1H), 6.87 (t, $J = 7.4$ Hz, 1H), 4.97 (s, 2H), 2.48 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 152.6, 146.5,

139.4, 139.0, 129.8, 128.3, 127.4, 127.1, 123.0, 121.9, 119.8, 117.5, 109.2, 64.0, 21.4; IR (film): 3148, 3067, 2920, 1522, 1431, 1209, 1027, 820, 753 cm^{-1} ; HRMS-EI (m/z) calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}$ $[\text{M}]^+$ 262.1106, found: 262.1107.



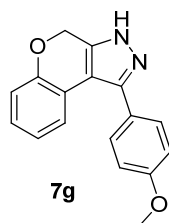
Ethyl 2-(2-((4-methoxyphenyl)ethynyl)phenoxy)acetate (13g)

Yellow oil (89%); ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.48 (m, 3H), 7.25-7.21 (m, 1H), 6.97 (td, $J = 7.6, 0.8$ Hz, 1H), 6.87-6.85 (m, 2H), 6.81 (dd, $J = 8.4, 0.8$ Hz, 1H), 4.72 (s, 2H), 4.25 (q, $J = 7.2$ Hz, 2H), 3.78 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 159.7, 158.3, 133.5, 133.1, 129.3, 121.8, 115.7, 114.0, 113.9, 113.1, 94.1, 84.1, 66.4, 61.3, 55.3, 14.2; IR (film): 2933, 1759, 1606, 1512, 1488, 1449, 1287, 1249, 1198, 1111, 1029, 834, 753 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{19}\text{H}_{19}\text{O}_4$ $[\text{M}+\text{H}]^+$ 311.1283, found: 311.1278.



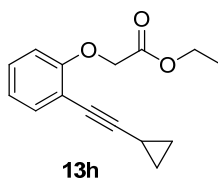
(E)-N'-(2-(2-((4-methoxyphenyl)ethynyl)phenoxy)ethylidene)-4-methylbenzenesulfonohydrazide (6g)

White solid (63%); m.p. = 120-121 $^{\circ}\text{C}$; ^1H NMR (400 MHz, DMSO-d_6) δ 11.49 (br s, 1H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.47-7.44 (m, 4H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.24-7.20 (m, 1H), 7.00-6.94 (m, 4H), 4.71 (d, $J = 4.8$ Hz, 2H), 3.80 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.0, 158.5, 146.0, 143.9, 136.6, 133.4, 133.3, 130.2, 130.2, 127.6, 121.6, 115.2, 114.8, 113.4, 112.8, 93.8, 84.9, 67.9, 55.7, 21.5; IR (film): 3195, 1512, 1452, 1346, 1310, 1250, 1224, 1166, 1016, 831, 757, 703, 577 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$ 435.1379, found: 435.1371.



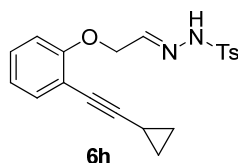
1-(4-Methoxyphenyl)-3,4-dihydrochromeno[3,4-c]pyrazole (7g)

White solid (86%); m.p. = 164-166 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.53-7.51 (d, J = 8.4 Hz, 2H), 7.37-7.35 (m, 1H), 7.12-7.08 (m, 1H), 7.02-6.99 (m, 3H), 6.86 (t, J = 7.6 Hz, 1H), 4.95 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.4, 152.5, 146.3, 138.9, 129.8, 127.4, 122.9, 122.2, 122.0, 119.9, 117.5, 114.5, 109.1, 64.0, 55.4; IR (film): 3143, 2906, 1595, 1515, 1488, 1434, 1295, 1249, 1205, 1095, 1028, 831, 755 cm^{-1} ; HRMS-EI (m/z) calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_2$ $[\text{M}]^+$ 278.1055, found: 278.1059.



Ethyl 2-(2-(cyclopropylethynyl)phenoxy)acetate (13h)

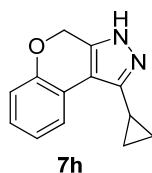
Light yellow oil (82%); ^1H NMR (400 MHz, CDCl_3) δ 7.34 (dd, J = 7.6, 1.6 Hz, 1H), 7.18-7.13 (m, 1H), 6.90-6.86 (m, 1H), 6.73 (dd, J = 8.0, 0.8 Hz, 1H), 4.65 (s, 2H), 4.23 (q, J = 7.2 Hz, 2H), 1.51-1.46 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H), 0.88-0.81 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 158.0, 133.1, 128.1, 121.1, 113.5, 112.4, 97.6, 70.9, 65.7, 60.6, 13.6, 8.19, -0.01; IR (film): 2982, 2929, 2230, 1760, 1492, 1450, 1301, 1128, 1128, 752 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{15}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$ 245.1178, found: 245.1183.



N'-(2-(2-(cyclopropylethynyl)phenoxy)ethylidene)-4-methylbenzenesulfonohydrazide (6h)

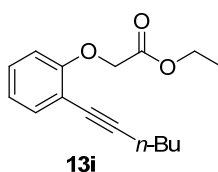
White solid (65%); m.p. = 101-103 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 11.47 (br s, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.41-7.39 (m, 3H), 7.28 (d, J = 7.2 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.90-6.85 (m, 2H), 4.63 (d, J = 4.8 Hz, 2H), 2.39 (s, 3H), 1.54-1.50 (m, 1H), 0.88-0.86 (m, 2H), 0.69-0.69

(m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.7, 146.0, 144.0, 136.5, 133.6, 130.2, 129.4, 127.6, 121.4, 113.2, 113.2, 98.2, 72.2, 67.7, 21.5, 9.0, 0.58; IR (film): 3195, 1492, 1446, 1345, 1311, 1221, 1166, 1009, 814, 752, 576 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 369.1273, found: 369.1262.



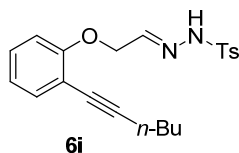
1-Cyclopropyl-3,4-dihydrochromeno[3,4-c]pyrazole (7h)

White solid (87%); m.p. = 154-156 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.6$ Hz, 1H), 7.15-7.11 (m, 1H), 7.04-7.00 (m, 2H), 5.27 (s, 2H), 2.08-2.01 (m, 1H), 1.09-1.04 (m, 2H), 0.84-0.80 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.1, 145.4, 140.2, 127.1, 123.6, 122.0, 120.0, 117.1, 110.5, 64.2, 6.5; IR (film): 3134, 3004, 2934, 2889, 1594, 1523, 1437, 1229, 1200, 1113, 1035, 816, 757 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 213.1028, found: 213.1019.



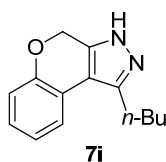
Ethyl 2-(2-(hex-1-ynyl)phenoxy)acetate (13i)

Yellow oil (86%); ^1H NMR (400 MHz, CDCl_3) δ 7.37 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.19-7.15 (m, 1H), 6.93-6.89 (m, 1H), 6.76 (dd, $J = 8.0, 0.8$ Hz, 1H), 4.68 (s, 2H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.45 (t, $J = 7.0$ Hz, 2H), 1.64-1.46 (m, 4H), 1.26 (t, $J = 7.2$ Hz, 3H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.8, 158.4, 133.8, 128.6, 121.7, 114.3, 113.1, 95.1, 76.4, 66.4, 61.2, 30.9, 22.0, 19.4, 14.1, 13.6; IR (film): 2959, 2932, 2232, 1761, 1491, 1450, 1194, 1124, 1074, 752 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{16}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$ 261.1491, found: 261.1492.



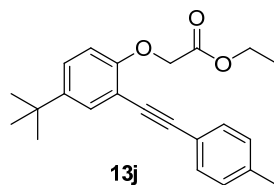
(E)-N'-(2-(2-(hex-1-ynyl)phenoxy)ethylidene)-4-methylbenzenesulfonylhydrazide (6i)

White solid (50%); m.p. = 102-104 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 11.48 (br s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.39-7.37 (m, 3H), 7.30-7.28 (m, 1H), 7.14-7.11 (m, 1H), 6.91-6.86 (m, 2H), 4.62 (d, *J* = 5.2 Hz, 2H), 2.41-2.38 (m, 5H), 1.51-1.39 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ 158.6, 145.8, 143.9, 136.6, 133.5, 130.2, 129.5, 127.6, 121.4, 113.4, 113.2, 95.0, 77.3, 67.8, 30.8, 21.8, 21.5, 19.1, 13.9; IR (film): 3193, 2962, 1492, 1457, 1349, 1311, 1167, 1066, 1009, 921, 748, 676, 575 cm⁻¹; HRMS-ESI (*m/z*) calcd. for C₂₁H₂₅N₂O₃S [M+H]⁺ 385.1586, found: 385.1593.



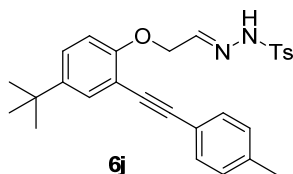
1-Butyl-3,4-dihydrochromeno[3,4-c]pyrazole (7i)

6i (384 mg, 1.0 mmol) was dissolved in CH₂Cl₂ (10 mL), cooled with ice-water. A solution of BF₃·Et₂O (48%, 0.1 mL, 0.3 mmol) in CH₂Cl₂ (2 mL) was added in dropwise. After the addition, the solution was stirred at r.t. for 24 h. The reaction was quenched with saturated NaHCO₃ (5 mL), and extracted with CH₂Cl₂ for 3 times, washed with brine, dried over Na₂SO₄, concentrated in vacuum. The residue was purified by chromatography (PE:EA = 5:1), affording white solid (148 mg, 65%); m.p. = 115-117 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 8.0 Hz, 1H), 7.14-7.10 (m, 1H), 7.02-6.99 (m, 2H), 5.25 (s, 2H), 2.90 (t, *J* = 7.8 Hz, 2H), 1.75-1.67 (m, 2H), 1.46-1.40 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 152.3, 145.6, 139.6, 127.0, 122.9, 122.1, 120.2, 117.4, 108.7, 64.2, 30.7, 25.7, 22.5, 13.8; IR (film): 3135, 3071, 2930, 2857, 1595, 1527, 1461, 1430, 1205, 1117, 1062, 1041, 756 cm⁻¹; HRMS-ESI (*m/z*) calcd. for C₁₄H₁₇N₂O [M+H]⁺ 229.1341, found: 229.1337.



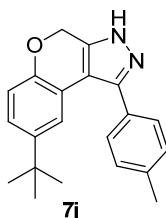
Ethyl 2-(4-*tert*-butyl-2-(*p*-tolylethynyl)phenoxy)acetate (13j)

Light yellow solid (92%); m.p. = 68-69 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 2.8 Hz, 1H), 7.48-7.46 (m, 2H), 7.26 (dd, J = 8.8, 2.8 Hz, 1H), 7.15-7.13 (m, 2H), 6.77 (d, J = 8.8 Hz, 1H), 4.72 (s, 2H), 4.26 (q, J = 7.1 Hz, 2H), 2.36 (s, 3H), 1.30-1.27 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 156.3, 144.7, 138.2, 131.6, 130.7, 129.1, 126.4, 120.5, 113.2, 113.1, 93.6, 85.3, 66.7, 61.3, 34.2, 31.4, 21.5, 14.2; IR (film): 2961, 1761, 1513, 1496, 1198, 1109, 817 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{23}\text{H}_{27}\text{O}_3$ [$\text{M}+\text{H}$] $^+$ 351.1960, found: 351.1963.



(*E*)-N'-(2-(4-*tert*-butyl-2-(*p*-tolylethynyl)phenoxy)ethylidene)-4-methylbenzenesulfonohydrazide (6j)

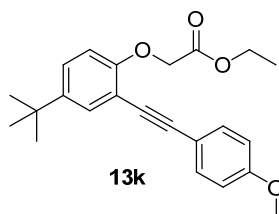
White solid (69%); m.p. = 128-129 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 11.47 (br s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.45-7.38 (m, 6H), 7.24-7.22 (m, 3H), 6.88 (d, J = 8.8 Hz, 1H), 4.69 (d, J = 4.4 Hz, 2H), 2.37 (s, 3H), 2.34 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.5, 146.2, 143.9, 143.8, 138.8, 136.7, 131.6, 130.2, 130.1, 129.8, 127.7, 127.2, 120.3, 113.2, 112.0, 93.4, 86.2, 68.0, 34.2, 31.6, 21.5; IR (film): 3167, 2924, 1450, 1380, 1348, 1246, 1162, 1029, 819, 670 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{28}\text{H}_{29}\text{N}_2\text{O}_3\text{S}$ [$\text{M}-\text{H}$] $^+$ 473.1899, found: 473.1909.



8-*Tert*-butyl-1-*p*-tolyl-3,4-dihydrochromeno[3,4-*c*]pyrazole (7j)

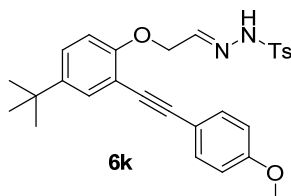
White solid (91%); m.p. = 139-141 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.55 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 2.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.13 (dd, J = 8.4, 2.4 Hz, 1H), 6.94 (d, J = 8.8

Hz, 1H), 4.96 (s, 2H), 2.46 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.3, 146.7, 144.6, 139.3, 138.7, 129.6, 128.2, 127.1, 124.3, 120.2, 119.1, 116.8, 109.6, 64.1, 34.3, 31.4, 21.5; IR (film): 3149, 3063, 2957, 2902, 2866, 1492, 1217, 1134, 1012, 821, 733 cm^{-1} ; HRMS-EI (m/z) calcd. for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}$ [M] $^+$ 318.1732, found: 318.1733.



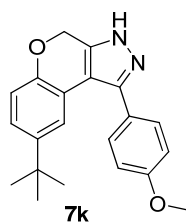
Ethyl 2-(4-*tert*-butyl-2-((4-methoxyphenyl)ethynyl)phenoxy)acetate (13k)

Yellow solid (91%); m.p. = 69-71 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.50 (m, 3H), 7.25 (dd, J = 8.8, 2.4 Hz, 1H), 6.87-6.85 (m, 2H), 6.76 (d, J = 8.8 Hz, 1H), 4.71 (s, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 1.30-1.26 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 159.6, 156.2, 144.6, 133.1, 130.5, 126.3, 115.8, 114.0, 113.2, 113.1, 93.5, 84.6, 66.7, 61.3, 55.3, 34.2, 31.4, 14.2; IR (film): 2961, 1760, 1604, 1512, 1497, 1464, 1287, 1249, 1198, 1109, 1030, 833 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{23}\text{H}_{27}\text{O}_4$ [$\text{M}+\text{H}$] $^+$ 367.1909, found: 367.1906.



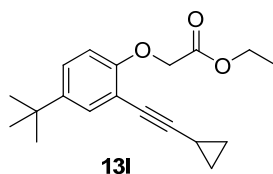
(*E*)-*N'*-(2-(4-*tert*-butyl-2-((4-methoxyphenyl)ethynyl)phenoxy)ethylidene)-4-methylbenzenesulfonohydrazide (6k)

White solid (71%); m.p. = 122-123 $^{\circ}\text{C}$; ^1H NMR (400 MHz, DMSO-d_6) δ 11.47 (br s, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.47-7.39 (m, 6H), 7.21 (dd, J = 8.4, 2.0 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 1H), 4.69 (d, J = 4.4 Hz, 2H), 3.80 (s, 3H), 2.38 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.9, 156.4, 146.3, 143.9, 136.7, 133.3, 130.2, 130.1, 127.7, 127.0, 115.2, 114.8, 113.1, 112.2, 93.4, 85.4, 68.0, 55.7, 34.2, 31.6, 21.5; IR (film): 3185, 2958, 1513, 1452, 1377, 1349, 1289, 1249, 1163, 1031, 816, 669 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_4\text{S}$ [$\text{M}+\text{H}$] $^+$ 491.2005, found: 491.2003.



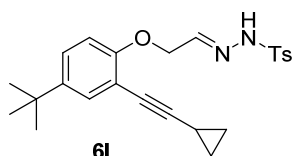
8-Tert-butyl-1-(4-methoxyphenyl)-3,4-dihydrochromeno[3,4-c]pyrazole (7k)

White solid (88%); m.p. = 159-161 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 2.0 Hz, 1H), 7.09 (dd, J = 8.4, 2.0 Hz, 1H), 6.96 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 1H), 4.92 (s, 2H), 3.82 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.4, 150.2, 146.5, 144.6, 138.7, 129.7, 124.3, 122.3, 120.1, 119.2, 116.8, 114.4, 109.4, 64.0, 55.4, 34.3, 31.4; IR (film): 3184, 2958, 2904, 2866, 1519, 1489, 1460, 1435, 1252, 1215, 1178, 832 cm^{-1} ; HRMS-EI (m/z) calcd. for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$ $[\text{M}]^+$ 334.1681, found: 334.1679.



Ethyl 2-(4-tert-butyl-2-(cyclopropylethynyl)phenoxy)acetate (13I)

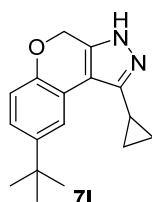
Yellow oil (87%); ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, J = 2.4 Hz, 1H), 7.19 (dd, J = 8.8, 2.8 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 4.66 (s, 2H), 4.26 (q, J = 7.2 Hz, 2H), 1.54-1.47 (m, 1H), 1.31-1.28 (m, 12H), 0.87-0.84 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.0, 156.4, 144.5, 130.8, 125.6, 113.4, 112.9, 97.5, 72.0, 66.6, 61.2, 34.1, 31.3, 14.2, 8.75, 0.54; IR (film): 2962, 1761, 1736, 1499, 1288, 1197, 1156, 1099, 811 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{19}\text{H}_{25}\text{O}_3$ $[\text{M}+\text{H}]^+$ 301.1804, found: 301.1803.



(E)-N'-(2-(4-tert-butyl-2-(cyclopropylethynyl)phenoxy)ethylidene)-4-methylbenzenesulfonohydrazide (6I)

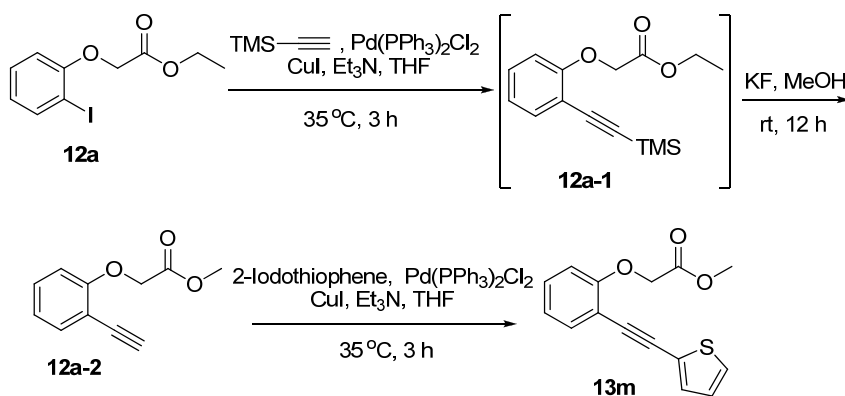
White solid (48%); m.p. = 102-104 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.45 (br s, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 5.0 Hz, 1H), 7.25 (d, J = 2.0 Hz, 1H), 7.12

(dd, $J = 8.8, 2.0$ Hz, 1H), 6.77 (d, $J = 8.8$ Hz, 1H), 4.60 (d, $J = 5.2$ Hz, 2H), 2.40 (s, 3H), 1.54-1.50 (m, 1H), 1.22 (s, 9H), 0.89-0.85 (m, 2H), 0.71-0.67 (m, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 156.6, 146.3, 143.9, 143.6, 136.6, 130.4, 130.2, 127.7, 126.2, 113.0, 112.6, 97.6, 72.7, 67.9, 34.2, 31.6, 21.6, 8.94, 0.57; IR (film): 3154, 2958, 1499, 1343, 1299, 1274, 1161, 1069, 1022, 921, 886, 804, 576 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{24}\text{H}_{29}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 425.1899, found: 425.1898.



8-Tert-butyl-1-cyclopropyl-3,4-dihydrochromeno[3,4-c]pyrazole (71)

Light yellow oil (87%); ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 2.4$ Hz, 1H), 7.14 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.92 (d, $J = 8.4$ Hz, 1H), 5.23 (s, 2H), 2.07-2.03 (m, 1H), 1.34 (s, 9H), 1.10-1.05 (m, 2H), 0.85-0.81 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.9, 145.4, 144.7, 139.8, 124.0, 120.6, 119.3, 116.5, 110.9, 64.2, 34.3, 31.6, 6.42, 6.30; IR (film): 3181, 2960, 2868, 1727, 1496, 1480, 1264, 1233, 1211, 1129, 1008, 820 cm^{-1} ; HRMS-EI (m/z) calcd. for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}$ $[\text{M}]^+$ 268.1576, found: 268.1575.



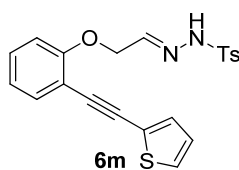
Methyl 2-(2-(thiophen-2-ylethynyl)phenoxy)acetate (13m)

In an oven dried three necked flask was added **12a** (3.0 g, 10.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (70 mg, 0.1 mmol), CuI (57 mg, 0.3 mmol), THF (15 mL) and Et_3N (15 mL) successively. The mixture was heated to 35 $^\circ\text{C}$, and then ethynyltrimethylsilane (2.1 mL, 15.0 mmol) was added dropwise. After the addition, the mixture was stirred for 3 h. The mixture was concentrated in vacuum, and used in next step without further purification.

The residue was dissolved in methanol (50 mL), KF (1.4 g, 24.0 mmol) was added, stirred for 12 h

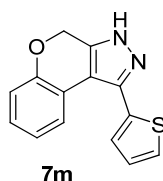
at r.t. Concentrated, and purified by chromatography (PE:EA = 20:1), affording light yellow oil **12a-2** (1.43 g, 75%); ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 7.6$ Hz, 1H), 7.30-7.26 (m, 1H), 6.98-6.95 (m, 1H), 6.79 (d, $J = 8.4$ Hz, 1H), 4.75 (s, 2H), 3.79 (s, 3H), 3.33 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.1, 159.0, 134.4, 130.1, 121.7, 112.5, 112.2, 81.8, 79.6, 66.0, 52.2; IR (film): 3280, 2954, 2107, 1760, 1597, 1489, 1450, 1292, 1211, 1119, 1073, 754 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{11}\text{H}_{10}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 213.0528, found: 213.0519.

In an oven dried three necked flask was added 2-iodothiophene (0.88 mL, 8.0 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (72 mg, 0.1 mmol), CuI (38 mg, 0.2 mmol) THF (15 mL) and Et_3N (15 mL) successively. The mixture was heated to 35 $^\circ\text{C}$, and then a solution of **12a-2** (2.66 g, 14.0 mmol) in THF (5 mL) was added dropwise. After the addition, the mixture was stirred for 3 h. The mixture was concentrated in vacuum, the residue was purified by chromatography (PE:EA = 40:1), affording light yellow oil (1.85 g, 85%); ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 7.2$ Hz, 1H), 7.33-7.26 (m, 3H), 7.03-6.99 (m, 2H), 6.82 (d, $J = 8.4$ Hz, 1H), 4.75 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.2, 158.3, 133.5, 132.0, 129.9, 127.4, 127.2, 123.5, 121.9, 113.2, 112.9, 89.2, 87.2, 66.2, 52.3; IR (film): 2956, 2924, 2853, 1714, 1455, 1261, 1201, 1100, 802 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$ 295.0405, found: 295.0403.



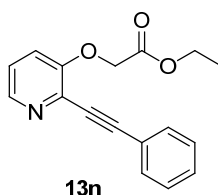
(E)-4-Methyl-N'-(2-(2-(thiophen-2-ylethynyl)phenoxy)ethylidene)benzenesulfonylhydrazide
(6m)

White solid (68%); m.p. = 103-105 $^\circ\text{C}$; ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.47 (br s, 1H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.66 (d, $J = 5.2$ Hz, 1H), 7.47-7.36 (m, 5H), 7.27-7.22 (m, 1H), 7.14-7.12 (m, 1H), 7.00-6.95 (m, 2H), 4.71 (d, $J = 5.2$ Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 158.5, 145.9, 144.0, 136.5, 133.4, 132.8, 130.8, 130.2, 129.2, 128.2, 127.6, 122.7, 121.6, 113.3, 111.9, 89.9, 86.8, 67.8, 21.5; IR (film): 3196, 1443, 1387, 1345, 1307, 1223, 1163, 1012, 918, 815, 754, 707, 577 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}_3\text{S}_2$ $[\text{M}+\text{H}]^+$ 411.0837, found: 411.0837.



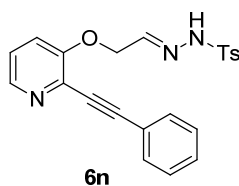
1-(Thiophen-2-yl)-3,4-dihydrochromeno[3,4-c]pyrazole (7m)

Grey solid (88%); m.p. = 174-176 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.42 (br s, 1H), 7.50-7.47 (m, 2H), 7.34 (d, $J = 3.2$ Hz, 1H), 7.18-7.16 (m, 1H), 7.09 (t, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 6.86 (t, $J = 7.6$ Hz, 1H), 4.94 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.5, 145.9, 132.5, 130.3, 128.5, 128.0, 127.9, 127.6, 123.1, 122.1, 119.3, 117.5, 110.8, 63.7; IR (film): 3147, 3074, 2921, 1533, 1408, 1277, 1205, 1122, 1026, 755, 707 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{OS}$ $[\text{M}+\text{H}]^+$ 255.0592, found: 255.0590.



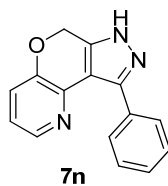
Ethyl 2-(2-(phenylethynyl)pyridin-3-yloxy)acetate (13n)

Yellow oil (81%); ^1H NMR (400 MHz, CDCl_3) δ 7.96-7.95 (m, 1H), 7.40-7.38 (m, 2H), 7.09-7.07 (m, 3H), 6.88-6.87 (m, 2H), 4.47 (s, 2H), 3.93 (q, $J = 7.2$ Hz, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.7, 155.2, 142.6, 133.6, 131.8, 128.8, 128.2, 123.4, 122.4, 119.6, 93.9, 85.4, 65.6, 61.2, 13.9; IR (film): 3057, 2983, 2934, 2221, 1756, 1577, 1492, 1442, 1295, 1201, 1124, 796, 759, 692 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{17}\text{H}_{16}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 282.1130, found: 282.1131.



4-Methyl-N'-(2-(2-(phenylethynyl)pyridin-3-yloxy)ethylidene)benzenesulfonohydrazide (6n)

White solid (50%); m.p. = 84-85 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.20-8.18 (m, 1H), 7.78 (d, $J = 8.0$ Hz, 2H), 7.43-7.38 (m, 3H), 7.31-7.23 (m, 5H), 7.09-7.03 (m, 2H), 4.66 (d, $J = 5.2$ Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.4, 144.3, 142.4, 135.4, 135.2, 133.8, 132.0, 129.7, 129.0, 128.3, 127.9, 123.6, 122.2, 120.0, 94.5, 84.9, 67.9, 21.6; IR (film): 3203, 1573, 1460, 1440, 1366, 1344, 1306, 1276, 1165, 1115, 1004, 757, 578 cm^{-1} ; HRMS-ESI (m/z) calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 406.1225, found: 406.1226.



9-Aza-1-phenyl-3,4-dihydrochromeno[3,4-c]pyrazole (7n)

6n (405 mg, 1.0 mmol) was dissolved in CH₂Cl₂ (10 mL), cooled with ice-water. A solution of BF₃·Et₂O (48%, 1 mL, 3.0 mmol) in CH₂Cl₂ (5 mL) was added in dropwise. After the addition, the solution was stirred at r.t. for 12 h. The reaction was quenched with saturated NaHCO₃ (20 mL), and extracted with CH₂Cl₂ for 3 times, washed with brine, dried over Na₂SO₄, concentrated in vacuum. The residue was purified by chromatography (PE:EA = 5:1), affording light yellow solid (212 mg, 85%); m.p. = 84-85 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 3.6 Hz, 1H), 7.97 (d, *J* = 6.8 Hz, 2H), 7.42-7.35 (m, 3H), 7.22-7.20 (m, 1H), 7.02-6.99 (m, 1H), 5.12 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 148.1, 142.4, 140.6, 140.6 129.3, 128.9, 128.5, 128.4, 123.8, 122.2, 110.1, 64.2; IR (film): 3211, 3058, 2923, 1590, 1517, 1416, 1238, 1198, 1129, 1045, 840, 760 cm⁻¹; HRMS-ESI (*m/z*) calcd. for C₁₅H₁₂N₃O [M+H]⁺ 250.0980, found: 250.0981.