Supporting Information for
Benzofurazan N-Oxides as Mild Reagents for the Generation of \(\alpha\)-Imino Gold Carbenes: Synthesis of Functionalized 7-Nitroindoles

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**General Methods.** All reactions were carried out under Argon unless noted. DCM, DCE were distilled from CaH$_2$. Toluene was distilled from sodium and benzophenone. THF was distilled from sodium and benzophenone or purified using Innovative Technology Solvent Purifier (for the synthesis of substrates). MeCN was purified using Innovative Technology Solvent Purifier. Unless noted, all commercial reagents were used without further purification. (Acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) hexafluoroantimonate (catalyst A), Gold complex D was purchased from Aldrich Chemical Company. AgSbF$_6$ was purchased from Stream Chemicals. Gold complex B was prepared by stirring the [Au(L)Cl] complex and AgSbF$_6$ in MeCN at room temperature overnight. Gold complex C$^2$ and PPh$_3$AuCl$^3$ were prepared according to the published methods. AuBr$_3$ was purchased from Alfa Aesar.

$^1$H and $^{13}$C NMR spectra were recorded at room temperature in CDCl$_3$ (containing 0.03% TMS) or DMSO-$d_6$ (containing 0.03% TMS), on Varian XL-400 MHz spectrometer, Agilent 400 MHz NMR spectrometer or Bruker 400 MHz NMR spectrometer. $^1$H NMR spectra was recorded at 400 MHz, $^{13}$C NMR spectra was recorded at 100 MHz. $^1$H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) in CDCl$_3$ or DMSO-$d_6$ (δ = 2.50 ppm) as internal reference; $^{13}$C NMR spectra was recorded with CDCl$_3$ (δ = 77.00 ppm) or DMSO-$d_6$ (δ = 39.52 ppm) as internal reference. High-resolution mass spectra were obtained by using Agilent Technologies 6224 TOF LC/MS. IR spectra were obtained by using a Nicolet iS10 spectrometer. Melting points were measured using a SGW-4 microscopic melting point apparatus and were uncorrected. Single crystal X-ray diffraction data were collected at 296(2) K for 3b, 293(2) K for 3p, 193(2) K for 11, 12b and 173(2) K for 7a, 8a on a Bruker APEX-II diffractometer or Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å).

Yanmides and propargyl esters were synthesized according to the published methods. The spectral data of known compounds were in agreement with that reported in the literature. For the synthesis of new yanmides 1j, 1o and propargyl ester 10b see the following:
**N-((2-Bromophenyl)ethyl)-N,4-dimethylbenzenesulfonamide (1j).** \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.89 (d, \(J = 8.0\) Hz, 2H), 7.53 (d, \(J = 7.6\) Hz, 1H), 7.39-7.35 (m, 3H), 7.26-7.21 (m, 1H), 7.12-7.08 (m, 1H), 3.19 (s, 3H), 2.44 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.89, 133.11, 132.48, 132.19, 129.80, 128.63, 127.79, 126.90, 124.91, 124.63, 88.25, 68.21, 39.23, 21.59. IR (neat): 2953, 2920, 2851, 2233, 1597, 1459, 1366, 1188, 1168, 1089, 963, 813, 758, 706, 685, 657 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{16}\)H\(_{15}\)BrNO\(_2\)S [M+H]\(^+\): 364.0001, found 364.0008.

To a solution of 7-hydroxy-3-(4-methoxyphenyl)-4H-chromen-4-one (4.292 g, 16 mmol) in DCM (60 mL) was added pyridine (2.6 mL, 32 mmol). Then Tf\(_2\)O (3.2 mL, 19.2 mmol, diluted with 30 mL DCM) was added dropwise to the mixture at 0 °C. The resulting solution was warmed up to room temperature and stirred for 1 h. Then the mixture was quenched with saturated ammonium chloride solution, extracted with dichloromethane, washed with saturated CuSO\(_4\) solution, brine and dried over anhydrous Na\(_2\)SO\(_4\). The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: dichloromethane = 1:1) to afford **s2-1o**
which was directly used in the following reaction.

To a solution of the above s2-1o in triethylamine (16 mL) and DMF (40 mL) were added ethynyltrimethylsilane (1.886 g, 19.2 mmol) and Pd(PPh₃)₂Cl₂ (673.8 mg, 0.96 mmol) at room temperature under Argon. Then the mixture was stirred at 50 °C for 3.5 h. After the starting material was consumed, the reaction mixture was quenched with 3 N HCl solution, extracted with dichloromethane, washed with water and brine followed by drying over anhydrous Na₂SO₄. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1) to afford compound s3-1o which was directly used in the following reaction.

To a solution of the above s3-1o in MeOH (100 mL) was added K₂CO₃ (663.4 mg, 4.8 mmol) at room temperature and stirred for 2 h. Then the mixture was quenched with water and MeOH was evaporated under the reduced pressure. The residue was extracted with dichloromethane, washed with brine and dried over anhydrous Na₂SO₄. The solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel (eluent: petroleum ether: dichloromethane = 2:1) to afford s4-1o in 38% (3 steps) isolated yield (1.68 g) as a white solid.

To a solution of s4-1o (552.6 mg, 2.0 mmol) in acetone (15 mL) were added N-bromosuccinimide (427.2 mg, 2.4 mmol) and AgNO₃ (34.0 mg, 0.2 mmol) at room temperature. The mixture was stirred at the same temperature for 24 h. The solution was diluted with petroleum ether and filtered through evaporated under the reduced pressure and the residue was quenched with saturated NH₄Cl solution, extracted with dichloromethane, washed with brine and dried over anhydrous Na₂SO₄. The solution was evaporated under the reduced pressure and the residue was filtered through celite. After solvent evaporation, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:3:1 to 10:4:1 to 10:10:1) to afford s5-1o in 92% yield (651.0 mg) as a light yellow solid.

To a dry flask were added N-methylmethanesulfonamide (163.7 mg, 1.5 mmol), anhydrous toluene (15 mL), CuSO₄·5H₂O (37.5 mg, 0.15 mmol), 1,10-phenanthroline (54.1 mg, 0.3 mmol) and K₂CO₃ (414.6 mg, 3.0 mmol). Then s5-1o (639.3 mg, 1.8 mmol) was
added, and the resulting mixture was stirred at 80 °C for 13 h under an atmosphere of argon. When the reaction was complete, the crude mixture was cooled down to room temperature, filtered through celite and washed with ethyl acetate. After solvent evaporation, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 2:1:1) to afford compound 1o (449.1 mg, 78%) as a light yellow solid.

7-Ethynyl-3-(4-methoxyphenyl)-4H-chromen-4-one (s4-1o). M.p. 184-186 °C. 1H NMR (400 MHz, CDCl₃) δ 8.24 (d, J = 8.4 Hz, 1H), 7.98 (s, 1H), 7.59 (s, 1H), 7.50-7.48 (m, 3H), 6.97 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H), 3.31 (s, 1H); 13C NMR (100 MHz, CDCl₃) δ 175.78, 159.66, 155.61, 152.58, 130.01, 128.51, 127.33, 126.45, 125.24, 124.33, 123.68, 121.63, 113.97, 81.92, 80.96, 55.28. IR (neat): 3269, 3011, 2958, 2833, 2105, 1640, 1630, 1617, 1552, 1509, 1428, 1351, 1292, 1244, 1226, 1176, 1100, 1045, 1025, 887, 881, 823, 802, 790, 696 cm⁻¹. HRMS (ESI) calcd for C₁₈H₁₃O₃ [M+H]+: 277.0859, found 277.0855.

N-((3-(4-Methoxyphenyl)-4-oxo-4H-chromen-7-yl)ethynyl)-N-methylmethanesulfonamide (1o). 1H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 8.4 Hz, 1H), 7.96 (s, 1H), 7.48 (t, J = 8.8 Hz, 3H), 7.37 (d, J = 8.0 Hz, 1H), 6.97 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H), 3.35 (s, 3H), 3.16 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 175.78, 159.63, 155.81, 152.47, 130.01, 128.11, 127.37, 126.33, 125.15, 123.81, 123.39, 119.70, 113.96, 86.96, 69.04, 55.28, 39.09, 37.35. IR (neat): 3068, 2995, 2935, 2838, 2237, 1616, 1510, 1428, 1367, 1344, 1291, 1242, 1183, 1164, 1152, 1024, 986, 959, 900, 881, 852, 824, 777 cm⁻¹. HRMS (ESI) calcd for C₂₀H₁₈NO₅S [M+H]+: 384.0900, found 384.0910.
1-(Naphthalen-2-yl)prop-2-yn-1-yl benzoate (10b). $^1\text{H}$ NMR (400 MHz, CDCl$_3$) δ 8.10-8.07 (m, 3H), 7.87-7.80 (m, 3H), 7.71-7.69 (m, 1H), 7.53-7.37 (m, 5H), 6.88 (d, $J = 2.4$ Hz, 1H), 2.75 (d, $J = 2.4$ Hz, 1H). $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$) δ 165.30, 133.73, 133.42, 133.29, 132.96, 129.85, 129.49, 128.67, 128.35, 128.25, 127.65, 127.14, 126.68, 126.43, 124.91, 80.21, 75.95, 65.96. IR (neat): 3295, 3058, 2123, 1723, 1600, 1452, 1325, 1285, 1272, 1249, 1174, 1094, 1068, 1025, 932, 902, 864, 820, 760, 747, 714, 678 cm$^{-1}$. HRMS (ESI) calcd for C$_{20}$H$_{14}$NaO$_2$ [M+Na]$^+$: 309.0886, found 309.0891.

General procedure for the synthesis of 7-nitroindole 3.

Typical procedure for the synthesis of 3a.

To a Schlenk tube were added $N$-methyl-$N$-(phenylethynyl)methanesulfonamide 1a (75.3 mg, 0.36 mmol), DCE (3 mL), benzofurazan oxide 2a (40.8 mg, 0.3 mmol) and catalyst A (11.6 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at room temperature for 4.5 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1 to 5:1:1) to afford 3a in 95% yield (98.9 mg) as a yellow solid.
N-Methyl-N-(7-nitro-3-phenyl-1H-indol-2-yl)methanesulfonamide (3a). M.p. 216-218 °C. 
$^1$H NMR (400 MHz, CDCl$_3$) δ 10.19 (s, 1H), 8.17 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.55-7.49 (m, 4H), 7.46-7.42 (m, 1H), 7.21 (t, $J = 8.0$ Hz, 1H), 3.36 (s, 3H), 2.77 (s, 3H); 
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.56, 132.45, 131.89, 130.07, 129.52, 129.06, 127.97, 127.84, 126.69, 120.39, 119.67, 114.40, 39.11, 39.02. IR (neat): 3369, 3089, 2927, 1517, 1481, 1406, 1336, 1309, 1222, 1146, 1005, 968, 910, 890, 806, 742, 714 cm$^{-1}$. HRMS (ESI) calcd for C$_{16}$H$_{10}$N$_{4}$O$_{4}$S [M+NH$_4$]$^+$: 363.1122, found 363.1128.

\[\text{N-Methyl-N-(7-nitro-3-phenyl-1H-indol-2-yl)methanesulfonamide (3a). M.p. 216-218 °C.} \]

\[\text{$^1$H NMR (400 MHz, CDCl$_3$) δ 10.19 (s, 1H), 8.17 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.55-7.49 (m, 4H), 7.46-7.42 (m, 1H), 7.21 (t, $J = 8.0$ Hz, 1H), 3.36 (s, 3H), 2.77 (s, 3H);} \]

\[\text{$^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.56, 132.45, 131.89, 130.07, 129.52, 129.06, 127.97, 127.84, 126.69, 120.39, 119.67, 114.40, 39.11, 39.02. IR (neat): 3369, 3089, 2927, 1517, 1481, 1406, 1336, 1309, 1222, 1146, 1005, 968, 910, 890, 806, 742, 714 cm$^{-1}$. HRMS (ESI) calcd for C$_{16}$H$_{10}$N$_{4}$O$_{4}$S [M+NH$_4$]$^+$: 363.1122, found 363.1128.} \]

N,4-Dimethyl-N-(7-nitro-3-phenyl-1H-indol-2-yl)benzenesulfonamide (3b). Following the typical procedure, 0.3 mmol scale, N,4-dimethyl-N-(phenylethynyl)benzenesulfonamide 1b (102.7 mg, 0.36 mmol), 9 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at 50 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1 to 5:1:1 to 1:1:1 to 0:1:1) afforded the title product as a yellow solid in 78% (98.9 mg) isolated yield. M.p. 253-255 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.04 (s, 1H), 8.21 (d, $J = 8.0$ Hz, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.31-7.27 (m, 4H), 7.23-7.18 (m, 4H), 3.31 (s, 3H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 143.50, 135.48, 133.42, 132.58, 131.76, 129.57, 129.08, 128.53, 127.71, 127.17, 126.92, 126.02, 120.07, 119.62, 114.39, 38.65, 21.03. IR (neat): 3371, 3092, 2914, 1516, 1479, 1404, 1337, 1306, 1219, 1158, 1103, 1089, 1076, 1005, 886, 804, 792, 775, 739, 710, 689 cm$^{-1}$. HRMS (ESI) calcd for C$_{22}$H$_{20}$N$_{3}$O$_{4}$S [M+H]$^+$: 422.1169, found 422.1176.

\[\text{N,4-Dimethyl-N-(7-nitro-3-phenyl-1H-indol-2-yl)benzenesulfonamide (3b). Following the typical procedure, 0.3 mmol scale, N,4-dimethyl-N-(phenylethynyl)benzenesulfonamide 1b (102.7 mg, 0.36 mmol), 9 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at 50 °C for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1 to 5:1:1 to 1:1:1 to 0:1:1) afforded the title product as a yellow solid in 78% (98.9 mg) isolated yield. M.p. 253-255 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.04 (s, 1H), 8.21 (d, $J = 8.0$ Hz, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.31-7.27 (m, 4H), 7.23-7.18 (m, 4H), 3.31 (s, 3H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 143.50, 135.48, 133.42, 132.58, 131.76, 129.57, 129.08, 128.53, 127.71, 127.17, 126.92, 126.02, 120.07, 119.62, 114.39, 38.65, 21.03. IR (neat): 3371, 3092, 2914, 1516, 1479, 1404, 1337, 1306, 1219, 1158, 1103, 1089, 1076, 1005, 886, 804, 792, 775, 739, 710, 689 cm$^{-1}$. HRMS (ESI) calcd for C$_{22}$H$_{20}$N$_{3}$O$_{4}$S [M+H]$^+$: 422.1169, found 422.1176.} \]

N-Methyl-N-(7-nitro-3-phenyl-1H-indol-2-yl)benzenesulfonamide (3c). Following
N-methyl-4-nitro-N-(phenylethynyl)benzenesulfonamide 1c (113.8 mg, 0.36 mmol), 3 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at room temperature for 5 h. The mixture was filtered to obtain the solid, which was washed with ethyl acetate to afford 3c as a yellow solid in 42% (57.0 mg) isolated yield. M.p. 285-287 ºC. \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 12.40 (s, 1H), 8.21 (d, \(J = 8.0\) Hz, 1H), 8.08 (d, \(J = 8.8\) Hz, 2H), 7.95 (d, \(J = 7.6\) Hz, 1H), 7.72 (d, \(J = 8.4\) Hz, 2H), 7.30-7.19 (m, 6H), 3.53 (s, 3H). \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) \(\delta\) 149.53, 144.42, 132.68, 131.60, 129.23, 128.99, 128.55, 128.47, 127.94, 126.78, 126.17, 124.18, 120.38, 119.70, 114.88, 39.80. IR (neat): 3390, 3095, 1603, 1534, 1511, 1480, 1408, 1359, 1341, 1308, 1182, 1163, 1089, 1005, 891, 854, 802, 776, 738, 713, 705, 688 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{21}\)H\(_{16}\)N\(_4\)NaO\(_6\)S [M+Na]\(^+\): 475.0683, found 475.0689.

\(N\)-benzyl-4-methyl-N-(7-nitro-3-phenyl-1H-indol-2-yl)benzenesulfonamide (3d).

Following the typical procedure, 0.3 mmol scale, \(N\)-benzyl-4-methyl-N-(phenylethynyl)benzenesulfonamide 1d (130.1 mg, 0.36 mmol), 3 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at room temperature for 8 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 30:2:1 to 20:2:1) afforded the title product as a yellow solid in 80% (120.1 mg) isolated yield. M.p. 182-184 ºC. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.86 (s, 1H), 8.11 (d, \(J = 8.0\) Hz, 1H), 7.76 (d, \(J = 8.0\) Hz, 1H), 7.69 (d, \(J = 8.0\) Hz, 2H), 7.36-7.30 (m, 3H), 7.26-7.22 (m, 2H), 7.14-7.09 (m, 4H), 7.00-6.99 (m, 2H), 6.74 (d, \(J = 7.2\) Hz, 2H), 4.54 (s, 2H), 2.49 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.66, 135.45, 135.05, 132.37, 131.43, 130.09, 130.05, 129.92, 129.29, 128.51, 128.39, 128.24, 128.00, 127.56, 127.51, 126.67, 120.04, 119.42, 114.40, 53.55, 21.62. IR (neat): 3356, 3089, 3055, 3029, 1631, 1571, 1508, 1493, 1480, 1410, 1362, 1337, 1302, 1225, 1187, 1165, 862, 803, 788, 770, 758, 734, 708,
697, 679, 655 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{28}\)H\(_{27}\)N\(_4\)O\(_4\)S [M+NH\(_4\)]\(^+\): 515.1748, found 515.1748.

\[\text{N-Methyl-N-(7-nitro-3-(p-tolyl)-1H-indol-2-yl)methanesulfonamide (3e). Following the typical procedure, 0.3 mmol scale, N-methyl-N-(p-tolylethynyl)methanesulfonamide 1e (80.4 mg, 0.36 mmol), 3 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: petroleum ether: dichloromethane = 10:1 to 5:1:1) afforded the title product as a yellow solid in 90\% (96.5 mg) isolated yield. M.p. 213-215 °C.}\]

\[\text{\(\delta\) } ^1\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 10.16 \text{ (s, 1H), 8.15 (d, } J = 7.6 \text{ Hz, 1H), 7.88 (d, } J = 7.6 \text{ Hz, 1H), 7.38 (d, } J = 7.6 \text{ Hz, 2H), 7.33 (d, } J = 8.0 \text{ Hz, 2H), 7.19 (t, } J = 8.0 \text{ Hz, 1H), 3.34 (s, 3H), 2.78 (s, 3H), 2.44 (s, 3H).} \text{\(\delta\) } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{) } \delta 137.85, 132.61, 132.33, 130.32, 129.77, 129.40, 128.79, 127.86, 126.72, 120.34, 119.62, 114.25, 39.05, 38.93, 21.26. IR (neat): 3388, 3351, 3011, 2924, 1634, 1566, 1509, 1486, 1403, 1337, 1308, 1223, 1184, 1154, 977, 961, 894, 832, 818, 807, 799, 726, 712 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{17}\)H\(_{18}\)N\(_3\)O\(_4\)S [M+H]\(^+\): 360.1013, found 360.1015.}\]

\[\text{\(\text{N-(3-(4-Methoxyphenyl)-7-nitro-1H-indol-2-yl)-N-methylmethanesulfonamide (3f). Following the typical procedure, 0.3 mmol scale, N-((4-methoxyphenyl)ethynyl)-N-methylmethanesulfonamide 1f (86.1 mg, 0.36 mmol), 3 mL}\]
DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1 to 5:1:1) afforded the title product as a yellow solid in 86% (97.1 mg) isolated yield. M.p. 206-208 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.13 (s, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 8.4$ Hz, 2H), 7.20 (t, $J = 8.0$ Hz, 1H), 7.06 (d, $J = 8.4$ Hz, 2H), 3.89 (s, 3H), 3.35 (s, 3H), 2.79 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.33, 132.58, 132.23, 130.69, 130.41, 127.84, 126.68, 123.90, 120.36, 119.60, 114.51, 114.02, 55.33, 39.02, 38.96. IR (neat): 3341, 3092, 3019, 2943, 2828, 1510, 1483, 1337, 1316, 1305, 1245, 1180, 1146, 992, 961, 888, 838, 802, 714, 663 cm$^{-1}$. HRMS (ESI) calcd for C$_{17}$H$_{21}$N$_4$O$_5$S [M+NH$_4$]$^+$: 393.1227, found 393.1233.

N-(3-(4-Fluorophenyl)-7-nitro-1H-indol-2-yl)-N-methylmethanesulfonamide (3g). Following the typical procedure, 0.3 mmol scale, N-((4-fluorophenyl)ethynyl)-N-methylmethanesulfonamide 1g (81.8 mg, 0.36 mmol), 9 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at 50 °C for 2.5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1 to 5:1:1 to 5:1:2) afforded the title product as a yellow solid in 88% (95.4 mg) isolated yield. M.p. 253-255 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.35 (s, 1H), 8.22 (d, $J = 8.0$ Hz, 1H), 7.99 (d, $J = 7.6$ Hz, 1H), 7.62-7.59 (m, 2H), 7.38-7.29 (m, 3H), 3.34 (s, 3H), 3.03 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 161.45 (d, $J_{C-F} = 243.1$ Hz), 133.86, 132.70, 131.23 (d, $J_{C-F} = 7.4$ Hz), 129.48, 128.44 (d, $J_{C-F} = 3.0$ Hz), 127.63, 125.99, 120.13, 119.70, 115.74 (d, $J_{C-F} = 20.8$ Hz), 113.85, 38.34. One carbon (CH$_3$) merged with DMSO-$d_6$. IR (neat): 3375, 3348, 3320, 3016, 2932, 1569, 1509, 1484, 1338, 1312, 1221, 1155, 967, 895, 842, 802, 728, 713 cm$^{-1}$. HRMS (ESI) calcd for C$_{16}$H$_{15}$FN$_3$O$_4$S [M+H]$^+$: 364.0762, found
1 mmol scale reaction of 1g.

To a Schlenk tube were added N-((4-fluorophenyl)ethynyl)-N-methylmethanesulfonamide 1g (1.2 mmol, 272.7 mg), DCE (30 mL), benzofurazan oxide 2a (136.1 mg, 1 mmol) and catalyst A (0.05 mmol, 38.6 mg) under Argon. After the reaction mixture was stirred at 50 °C for 2.5 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1 to 4:1:2) to afford 3g in 85% yield (308.1 mg) as a light yellow solid.

\[
\text{3h}
\]

\textit{N-}(3-(4-Chlorophenyl)-7-nitro-1H-indol-2-yl)-\textit{N}-methylmethanesulfonamide} (3h). Following the typical procedure, 0.3 mmol scale, N-((4-chlorophenyl)ethynyl)-\textit{N}-methylmethanesulfonamide 1h (87.7 mg, 0.36 mmol), 3 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1 to 5:1:1) afforded the product, which was further purified by column chromatography on basic Al₂O₃ (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:1 to 3:1:1 to 1:1:1) to afford as a yellow solid in 66% (75.1 mg) isolated yield. M.p. 255-257 °C. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d₆}) \(\delta\) 12.37 (s, 1H), 8.21 (d, \(J = 8.4\) Hz, 1H), 8.00 (d, \(J = 7.6\) Hz, 1H), 7.59-7.54 (m, 4H), 7.31 (t, \(J = 8.0\) Hz, 1H), 3.33 (s, 3H), 3.04 (s, 3H). \textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d₆}) \(\delta\) 133.98, 132.76, 131.93, 131.08, 130.96, 129.25, 128.87, 127.62, 126.07, 120.20, 119.84, 113.66, 38.34. One carbon (CH₃) merged
with DMSO-\textit{d}_6. IR (neat): 3327, 3097, 2932, 1733, 1631, 1568, 1516, 1493, 1484, 1338, 1310, 1300, 1155, 1088, 1008, 993, 958, 889, 835, 820, 803, 739, 714, 670 cm\textsuperscript{-1}. HRMS (ESI) calcd for C\textsubscript{16}H\textsubscript{18}ClN\textsubscript{4}O\textsubscript{4}S [M+NH\textsubscript{4}]\textsuperscript{+}: 397.0732, found 397.0734.

Ethyl 4-(2-(N-methylsulfonamido)-7-nitro-1\textit{H}-indol-3-yl)benzoate (3i). Following the typical procedure, 0.3 mmol scale, ethyl 4-((N-methylsulfonamido)ethynyl)benzoate 1\textit{i} (101.3 mg, 0.36 mmol), 3 mL DCE, 2\textit{a} (40.8 mg, 0.33 mmol), PicAuCl\textsubscript{2} (5.9 mg, 0.015 mmol) were stirred at room temperature for 10 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 5:1:1 to 4:1:1) afforded the title product as a yellow solid in 75% (93.8 mg) isolated yield. M.p. 194-196 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 10.35 (s, 1H), 8.22 (d, \(J = 8.4\) Hz, 2H), 8.15 (d, \(J = 8.0\) Hz, 1H), 7.92 (d, \(J = 8.0\) Hz, 1H), 7.62 (d, \(J = 7.6\) Hz, 2H), 7.27-7.22 (m, 1H), 4.44 (q, \(J = 6.8\) Hz, 2H), 3.38 (s, 3H), 2.83 (s, 3H), 1.44 (t, \(J = 7.2\) Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.12, 136.66, 132.84, 132.67, 130.24, 129.84, 129.5, 129.30, 127.63, 126.75, 120.61, 120.06, 113.54, 61.20, 39.29, 39.03, 14.30. IR (neat): 3324, 2979, 2932, 1707, 1610, 1524, 1486, 1338, 1311, 1292, 1266, 1227, 1175, 1151, 1117, 1097, 1005, 994, 960, 890, 868, 806, 740, 720 cm\textsuperscript{-1}. HRMS (ESI) calcd for C\textsubscript{19}H\textsubscript{23}N\textsubscript{4}O\textsubscript{6}S [M+NH\textsubscript{4}]\textsuperscript{+}: 435.1333, found 435.1337.
N-(3-(2-Bromophenyl)-7-nitro-1H-indol-2-yl)-N,4-dimethylbenzenesulfonamide (3j).

Following the typical procedure, 0.3 mmol scale, N-((2-bromophenyl)ethynyl)-N,4-dimethylbenzenesulfonamide 1j (131.1 mg, 0.36 mmol), 3 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at room temperature for 5 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1 to 7:1) followed by recycling preparative HPLC afforded the title product as a yellow solid in 66% (99.2 mg) isolated yield. M.p. 165-167 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 10.25 (s, 1H), 8.17 (d, $J = 8.0$ Hz, 1H), 7.63-7.59 (m, 3H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.22-7.13 (m, 2H), 7.01-6.97 (m, 1H), 6.18 (dd, $J = 7.2$, 1.2 Hz, 1H), 3.02 (s, 3H), 2.49 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.66, 133.87, 133.49, 132.82, 132.74, 132.68, 132.48, 130.05, 129.96, 129.78, 127.64, 127.57, 126.97, 126.04, 125.01, 119.61, 119.48, 111.01, 37.57, 21.56. IR (neat): 3424, 3058, 2943, 2911, 1518, 1472, 1399, 1369, 1349, 1306, 1155, 1088, 990, 887, 802, 790, 763, 729, 679 cm$^{-1}$. HRMS (ESI) calcd for C$_{22}$H$_{19}$BrN$_3$O$_4$S [M+H]$^+$: 500.0274, found 500.0289.

![Structure of 3j](image)

N-Methyl-N-(7-nitro-3-(thiophen-2-yl)-1H-indol-2-yl)methanesulfonamide (3k).

Following the typical procedure, 0.3 mmol scale, N-methyl-N-(thiophen-2-ylethynyl)methanesulfonamide 1k (77.5 mg, 0.36 mmol), 3 mL DCE, 2a (40.8 mg, 0.3 mmol), PicAuCl$_2$ (5.9 mg, 0.015 mmol) were stirred at room temperature for 8 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1 to 5:1:1) afforded the title product as a yellow solid in 60% (63.2 mg) isolated yield. M.p. 192-194 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 10.20 (s, 1H), 8.22 (d, $J = 8.0$ Hz, 1H), 8.09 (d, $J = 8.0$ Hz, 1H), 7.45 (d, $J = 5.2$ Hz, 1H), 7.30-7.25 (m, 2H), 7.22-7.20 (m, 1H), 3.39 (s, 3H), 2.95 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.87, 132.74, 132.19, 129.75, 127.94, 127.84, 127.02, 126.70, 126.03, 120.70, 120.11, 107.33, 39.00, 38.83. IR

![3](image)

**N-Methyl-N-(3-(naphthalen-1-yl)-7-nitro-1H-indol-2-yl)methanesulfonamide (3l).**

Following the typical procedure, 0.3 mmol scale, N-methyl-N-(naphthalen-1-ylethynyl)methanesulfonamide 1l (93.4 mg, 0.36 mmol), 3 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at room temperature for 3 h. Column chromatography on silica gel (elucent: petroleum ether: ethyl acetate: dichloromethane = 20:2:1 to 6:2:1) afforded the title product as a yellow solid in 85% (100.3 mg) isolated yield. M.p. 184-185 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.38 (s, 1H), 8.17 (dd, J = 8.0, 0.8 Hz, 1H), 7.97 (t, J = 9.2 Hz, 2H), 7.62-7.51 (m, 4H), 7.44-7.39 (m, 2H), 7.09 (t, J = 7.6 Hz, 1H), 3.17 (s, 3H), 2.61 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 134.05, 133.73, 132.73, 132.63, 131.40, 129.20, 129.05, 128.99, 128.51, 127.92, 126.66, 126.47, 126.33, 125.65, 125.36, 120.09, 119.63, 111.44, 38.45, 38.35. IR (neat): 3343, 3050, 3008, 2932, 1520, 1486, 1410, 1369, 1340, 1307, 1229, 1148, 1117, 1011, 957, 891, 802, 780, 761, 737, 720, 694 cm⁻¹. HRMS (ESI) calcd for C₂₀H₂₁N₄O₄S [M+NH₄]⁺: 413.1278, found 413.1285.

![5](image)

**N-Methyl-N-(methylsulfonyl)-N’-(2-nitrophenyl)hex-2-enimidamide (5).** Following the
typical procedure, 0.3 mmol scale, N-(hex-1-yn-1-yl)-N-methylmethanesulfonamide 1m (68.1 mg, 0.36 mmol), 3 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1) afforded the title product as a yellow oil in 31% (30.5 mg, E/Z = 7.0:1) isolated yield. E-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.03 (d, $J$ = 8.0 Hz, 1H), 7.52 (t, $J$ = 7.6 Hz, 1H), 7.19 (t, $J$ = 8.4 Hz, 1H), 6.84 (d, $J$ = 8.0 Hz, 1H), 6.53-6.46 (m, 1H), 5.75 (d, $J$ = 15.6 Hz, 1H), 3.28 (s, 3H), 3.20 (s, 3H), 2.11-2.06 (m, 2H), 1.40-1.31 (m, 2H), 0.82 (t, $J$ = 7.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.83, 148.22, 143.41, 134.18, 125.10, 123.83, 122.79, 120.35, 38.71, 36.16, 34.65, 21.32, 13.48. Partial NMR for Z-isomer: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, $J$ = 8.4 Hz, 1H), 7.47 (d, $J$ = 7.6 Hz, 1H), 7.14 (d, $J$ = 7.2 Hz, 1H), 5.82-5.76 (m, 2H), 3.33 (s, 3H), 3.32 (s, 3H), 2.05-2.01 (m, 2H), 1.26-1.20 (m, 2H), 0.87-0.85 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.45, 140.39, 133.84, 123.68, 123.61, 119.72, 40.84, 34.70, 31.57, 21.61, 13.67. IR (neat): 2958, 2932, 2864, 1646, 1603, 1518, 1342, 1257, 1151, 982, 857, 780, 756, 731, 665 cm$^{-1}$. HRMS (ESI) calcd for C$_{14}$H$_{20}$N$_3$O$_4$S [M+H]$^+$: 326.1169, found 326.1177. Partial $^1$H NMR for Z-isomer in CD$_3$CN: $^1$H NMR (400 MHz, CD$_3$CN) δ 7.95 (d, $J$ = 7.2 Hz, 1H), 7.53 (d, $J$ = 8.0 Hz, 1H), 7.19 (d, $J$ = 8.4 Hz, 1H), 6.90 (d, $J$ = 8.4 Hz, 1H), 5.84 (d, $J$ = 11.2 Hz, 1H), 5.73 (dt, $J$ = 12.0, 7.2 Hz, 1H), 3.27 (s, 3H), 3.26 (s, 3H). The structure of Z-isomer was also confirmed by LC-MS(ESI): calcd for C$_{14}$H$_{20}$N$_3$O$_4$S [M+H]$^+$: 326.1, found 326.1.

3n

$N$-Methyl-$N$-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-7-nitro-1H-indol-2-yl)methanesulfonamide (3n).
Following the typical procedure, 0.3 mmol scale, N-methyl-N-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)ethynyl)methanesulfonamide 1n (138.8 mg, 0.36 mmol), 3 mL DCE, 2a (40.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 3:1:1) afforded the title product as a yellow solid in 97% (152.3 mg) isolated yield. M.p. 261-262 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.25 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 6.4 Hz, 2H), 7.19 (t, J = 8.0 Hz, 1H), 3.35 (s, 3H), 3.01-2.99 (m, 2H), 2.85 (s, 3H), 2.58-2.36 (m, 3H), 2.23-2.00 (m, 4H), 1.71-1.51 (m, 6H), 0.97 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 220.72, 139.56, 137.17, 132.56, 132.26, 130.25, 129.91, 129.17, 127.91, 126.79, 126.68, 125.95, 120.27, 119.56, 114.02, 50.44, 47.91, 44.32, 38.98, 38.92, 38.00, 35.78, 31.52, 29.41, 26.38, 25.60, 21.53, 13.82. IR (neat): 3338, 2927, 2867, 2854, 2917, 2867, 2854, 1734, 1517, 1488, 1372, 1330, 1308, 1233, 1142, 968, 891, 823, 801, 762, 738, 719 cm⁻¹. HRMS (ESI) calcd for C₂₈H₃₅N₃O₅S [M+NH₄]⁺: 539.2323, found 539.2321.

N-(3-(3-(4-Methoxyphenyl)-4-oxo-4H-chromen-7-yl)-7-nitro-1H-indol-2-yl)-N-methylmethanesulfonamide (3o). Following the typical procedure, 0.3 mmol scale, N-((3-(4-methoxyphenyl)-4-oxo-4H-chromen-7-yl)ethynyl)-N-methylmethanesulfonamide 1o (138.0 mg, 0.36 mmol), 6 mL DCE, 2a (40.8 mg, 0.3 mmol), PicAuCl₂ (5.9 mg, 0.015 mmol) were stirred at room temperature for 22 h. Column chromatography on silica gel (eluent: dichloromethane: ethyl acetate = 1:0 to 10:1) afforded the title product as a yellow solid in
53% (82.7 mg) isolated yield. M.p. 252-254 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 12.52 (s, 1H), 8.49 (s, 1H), 8.22 (t, $J = 6.8$ Hz, 2H), 8.13 (d, $J = 8.0$ Hz, 1H), 7.81 (s, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.35 (t, $J = 8.4$ Hz, 1H), 7.01 (d, $J = 8.8$ Hz, 2H), 3.79 (s, 3H), 3.40 (s, 3H), 3.11 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 175.03, 159.10, 155.82, 153.93, 138.23, 134.68, 132.85, 130.09, 128.82, 127.63, 126.38, 126.15, 125.88, 124.00, 123.74, 122.34, 120.34, 120.20, 117.89, 113.65, 113.17, 55.16, 39.25, 38.22. IR (neat): 3369, 3074, 3029, 2937, 2846, 1634, 1620, 1513, 1427, 1404, 1335, 1309, 1295, 1180, 1149, 1015, 958, 885, 829, 803, 732, 719 cm$^{-1}$. HRMS (ESI) calcd for C$_{26}$H$_{22}$N$_3$O$_7$S [M+H]$^+$: 520.1173, found 520.1179.

N-(4-Methoxy-7-nitro-3-phenyl-1H-indol-2-yl)-N-methylmethanesulfonamide (3p).

Following the typical procedure, 0.3 mmol scale, N-methyl-N-(phenylethynyl)methanesulfonamide 1a (75.3 mg, 0.36 mmol), 6 mL DCE, 5-methoxybenzofurazan N-oxide 2b (49.8 mg, 0.3 mmol), catalyst A (11.6 mg, 0.015 mmol) were stirred at room temperature for 17 h. Column chromatography on silica gel (eluent: petroleum ether: diethyl ether: acetone = 8:1:1) afforded the title product 3p as a yellow solid in 60% (68.1 mg) isolated yield. In addition, a mixture of byproduct 3p’ and a hydration product N-methyl-N-(methylsulfonyl)-2-phenylacetamide was also isolated in a combined yield of ca. 12%.

For the characterization of the product 3p: M.p. 230-232 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.15 (s, 1H), 8.20 (d, $J = 9.2$ Hz, 1H), 7.44-7.37 (m, 5H), 6.57 (d, $J = 8.8$ Hz, 1H), 3.81 (s, 3H), 3.29 (s, 3H), 2.58 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.65, 132.96, 131.18, 130.47, 128.51, 127.84, 127.53, 127.28, 123.68, 117.12, 114.98, 100.80, 55.87, 39.37, 38.71. IR (neat): 3324, 3053, 3024, 2951, 2846, 1569, 1489, 1399, 1341, 1324, 1312, 1178, 1152, 1100, 865, 894, 820, 801, 772, 764, 737, 728, 712, 691 cm$^{-1}$. HRMS (ESI) calcd for C$_{17}$H$_{18}$N$_3$O$_7$S [M+H]$^+$: 376.0962, found 376.0967.
It is suggested that $3p'$ is a 7-nitroindole isomer in which the MeO group locates at the C-5 position due to the tautomerization of the substrate $2b$. Pure $3p'$ could be obtained through the reactions performed at different conditions (e.g. 50 °C), and purified by column chromatography on silica gel for several times.

For the characterization of $N$-(5-Methoxy-7-nitro-3-phenyl-1H-indol-2-yl)-N-methyl-methanesulfonamide ($3p'$): $^1$H NMR (400 MHz, CDCl$_3$) δ 9.87 (s, 1H), 7.83 (d, $J = 2.4$ Hz, 1H), 7.54-7.42 (m, 6H), 3.87 (s, 3H), 3.32 (s, 3H), 2.76 (s, 3H). HRMS (ESI) calcd for C$_{17}$H$_{18}$N$_3$O$_5$S [M+H]$^+$: 376.0962, found 376.0970.

For the characterization of hydration product $N$-methyl-$N$-(methylsulfonyl)-2-phenylacetamide:

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.25-7.37 (m, 5H), 4.01 (s, 2H), 3.29 (s, 3H), 3.08 (s, 3H). The $^1$H NMR is in agreement with that reported.$^5$

Gold-catalyzed reaction of 1,2-diphenylacetylene with $2a$.

To a Schlenk tube were added 1,2-diphenylacetylene (64.2 mg, 0.36 mmol), DCE (3 mL), benzofurazan oxide $2a$ (40.8 mg, 0.3 mmol) and catalyst A (11.6 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at 80 °C for 8 h, the solvent was evaporated
under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 40:1) to give 1,2-diphenylacetylene in 82% yield (52.5 mg) as a white solid.

**Reduction of 7-nitroindole 3a.**

![Reaction Scheme](image)

To a flask were added 7-nitroindole 3a (69.1 mg, 0.2 mmol), EtOH (2 mL), ammonium formate (63.1 mg, 1.0 mmol) and Pd/CaCO$_3$ (21.3 mg, 0.01 mmol, 5% wet.). After the reaction mixture was refluxed for 1 h as monitored by thin-layer chromatography, it was filtered through celite and the solvent was evaporated under the reduced pressure. Then the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 1:1:1 to 1:3:3) to afford 4 in 90% yield (56.7 mg) as a white solid.

**N-(7-Amino-3-phenyl-1H-indol-2-yl)-N-methylmethanesulfonamide (4).** $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.03 (s, 1H), 7.56 (d, $J = 8.0$ Hz, 2H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 1H), 6.86-6.80 (m, 2H), 6.46-6.44 (m, 1H), 5.15 (br, 2H), 3.25 (s, 3H), 2.96 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 134.10, 133.84, 129.66, 128.70, 128.53, 126.15, 126.09, 122.93, 121.07, 112.63, 107.35, 106.01, 38.59, 38.52. IR (neat): 3427, 3359, 3313, 3055, 3013, 2927, 2848, 1630, 1584, 1493, 1443, 1333, 1103, 960, 882, 785, 737, 712, 697 cm$^{-1}$. HRMS (ESI) calcd for C$_{16}$H$_{18}$N$_3$O$_2$S [M+H]$^+$: 316.1114, found 316.1121.

**General procedure for the synthesis of quinoxaline N-oxide 7.**

**Typical procedure for the synthesis of 7a.**
To a Schlenk tube were added N,4-dimethyl-N-(phenylethynyl)benzenesulfonamide 1b (85.6 mg, 0.3 mmol), DCE (3 mL), benzofurazan 6a (72.1 mg, 0.6 mmol) and tBuXPhosAu(MeCN)SbF₆ (13.5 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at room temperature for 18 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:1 to 4:1:0 to 3:1:0) to afford 7a in 56% yield (68.0 mg) as a white solid and 8a in 15% yield (17.8 mg) as a white solid.

![Chemical structure of 7a and 8a](image)

3-((N,4-Dimethylphenyl)sulfonamido)-2-phenylquinoxaline 1-oxide (7a). $^1$H NMR (400 MHz, CDCl₃) δ 8.55 (d, $J$ = 8.4 Hz, 1H), 7.93 (d, $J$ = 8.4 Hz, 1H), 7.81-7.66 (m, 6H), 7.58-7.50 (m, 3H), 7.29 (d, $J$ = 8.0 Hz, 2H), 2.91 (s, 3H), 2.44 (s, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ 150.97, 143.95, 141.87, 140.61, 136.76, 135.00, 131.66, 130.39, 130.21, 129.67, 129.34, 129.19, 128.87, 128.76, 128.41, 119.35, 36.73, 21.52. IR (neat): 3029, 1574, 1482, 1341, 1298, 1163, 1081, 1004, 814, 805, 781, 768, 703, 665 cm⁻¹. HRMS (ESI) calcd for C$_{22}$H$_{20}$N$_3$O$_3$S [M+H]$^+$: 406.1220, found 406.1228.

![Chemical structure of 8a](image)

N,4-Dimethyl-N-(3-phenylquinoxalin-2-yI)benzenesulfonamide (8a). M.p. 189-191 °C. $^1$H NMR (400 MHz, CDCl₃) δ 8.16 (d, $J$ = 8.0 Hz, 1H), 8.00 (d, $J$ = 7.2 Hz, 2H), 7.90 (d, $J$ = 8.8
Hz, 1H), 7.79-7.70 (m, 4H), 7.57-7.51 (m, 3H), 7.31 (d, \(J = 8.0\) Hz, 2H), 3.07 (s, 3H), 2.46 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 153.14, 148.12, 143.88, 141.53, 140.06, 137.35, 134.97, 130.37, 130.08, 129.40, 129.23, 129.18, 128.95, 128.61, 128.30, 36.81, 21.61. IR (neat): 3058, 3026, 2922, 1597, 1438, 1393, 1351, 1223, 1184, 1157, 1066, 850, 814, 803, 771, 745, 692, 669 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{22}\)H\(_{20}\)N\(_3\)O\(_2\)S [M+H]*: 390.1271, found 390.1280.

![Image 7b](image_url)

3-(N-Methylmethylsulfonamido)-2-phenylquinoxaline 1-oxide (7b). Following the typical procedure, 0.3 mmol scale, N-methyl-N-(phenylethynyl)methanesulfonamide 1a (62.8 mg, 0.3 mmol), 3 mL DCE, 6a (72.1 mg, 0.6 mmol), \(^{1}\)BuXPhosAu(MeCN)SbF\(_6\) (13.5 mg, 0.015 mmol) were stirred at room temperature for 18 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5:1 to 2:1) afforded the title product as a white solid in 48% (47.5 mg) isolated yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.56 (dd, \(J = 8.8, 0.4\) Hz, 1H), 8.02 (dd, \(J = 8.8\) Hz, 1.2 Hz, 1H), 7.85-7.81 (m, 1H), 7.77-7.73 (m, 1H), 7.69-7.67 (m, 2H), 7.58-7.49 (m, 3H), 3.19 (s, 3H), 2.96 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 151.17, 141.82, 139.70, 136.82, 131.86, 130.44, 130.12, 129.91, 129.39, 128.56, 128.42, 119.40, 39.41, 36.87. IR (neat): 3000, 2911, 1579, 1482, 1396, 1339, 1295, 1155, 958, 801, 767 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{16}\)H\(_{16}\)N\(_3\)O\(_3\)S [M+H]*: 330.0907, found 330.0915.

![Image 7c](image_url)

3-((N,4-Dimethylphenyl)sulfonamido)-2-(4-fluorophenyl)quinoxaline 1-oxide (7c). Following the typical procedure, 0.3 mmol scale, N-((4-fluorophenyl)ethynyl)-N,4-dimethylbenzenesulfonamide 1p (91.0 mg, 0.3 mmol), 3 mL DCE, 6a (72.1 mg, 0.6 mmol), \(^{1}\)BuXPhosAu(MeCN)SbF\(_6\) (13.5 mg, 0.015 mmol) were stirred
at room temperature for 17 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1 to 5:1 to 4:1) afforded the title product as a white solid in 55% (69.9 mg) isolated yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.55 (d, \(J = 8.4\) Hz, 1H), 7.92 (d, \(J = 8.0\) Hz, 1H), 7.83-7.68 (m, 6H), 7.32 (d, \(J = 8.4\) Hz, 2H), 7.28-7.23 (m, 2H), 2.94 (s, 3H), 2.47 (s, 3H).

\(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.27 (d, \(J_{CF} = 249.0\) Hz), 150.96, 144.14, 141.85, 139.88, 136.73, 134.74, 132.56 (d, \(J_{CF} = 8.4\) Hz), 131.82, 130.57, 129.37, 129.26, 128.76, 124.75 (d, \(J_{CF} = 3.8\) Hz), 119.37, 115.66 (d, \(J_{CF} = 21.3\) Hz), 36.80, 21.56. IR (neat): 3071, 2924, 1600, 1577, 1510, 1483, 1395, 1343, 1295, 1231, 1160, 1116, 1083, 1018, 1003, 906, 833, 811, 767, 730, 664 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{22}\)H\(_{19}\)F\(_3\)N\(_3\)O\(_3\)S [M+H]\(^+\): 424.1126, found 424.1134.

\[
\text{2-(4-Chlorophenyl)-3-((N,4-dimethylphenyl)sulfonamido)quinoxaline 1-oxide (7d).}
\]
Following the typical procedure, 0.3 mmol scale, \(N\)-((4-chlorophenyl)ethynyl)-N,4-dimethylbenzenesulfonamide 1q (95.9 mg, 0.3 mmol), 3 mL DCE, 6a (72.1 mg, 0.6 mmol), \(\text{BuXPhosAu(MeCN)SbF}_6\) (13.5 mg, 0.015 mmol) were stirred at room temperature for 12 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1 to 5:1) afforded the title product as a white solid in 47% (61.7 mg) isolated yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.53 (d, \(J = 8.4\) Hz, 1H), 7.92 (d, \(J = 8.0\) Hz, 1H), 7.80 (t, \(J = 6.8\) Hz, 1H), 7.74 (t, \(J = 8.0\) Hz, 1H), 7.65 (d, \(J = 8.0\) Hz, 4H), 7.52 (d, \(J = 8.4\) Hz, 2H), 7.31 (d, \(J = 8.0\) Hz, 2H), 2.95 (s, 3H), 2.46 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 150.79, 144.15, 141.89, 139.73, 136.69, 135.77, 134.63, 131.87, 131.83, 130.58, 129.38, 129.25, 128.71, 127.32, 119.33, 36.82, 21.56. IR (neat): 3060, 2927, 1781, 1697, 1597, 1571, 1482, 1344, 1293, 1228, 1160, 1090, 1017, 991, 905, 826, 764, 734, 702, 663 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{22}\)H\(_{19}\)ClN\(_3\)O\(_3\)S [M+H]\(^+\): 440.0830, found 440.0835.
3-((N,4-Dimethylphenyl)sulfonamido)-2-(4-methoxyphenyl)quinoxaline 1-oxide (7e).

Following the typical procedure, 0.3 mmol scale, N-((4-Methoxyphenyl)ethynyl)-N,4-dimethylbenzenesulfonamide 1r (94.6 mg, 0.3 mmol), 3 mL DCE, 6a (72.1 mg, 0.6 mmol), 'BuPhosAu(MeCN)SbF₆ (13.5 mg, 0.015 mmol) were stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 10:1:1 to 5:1:1) afforded the title product as a light yellow solid in 17% (22.0 mg) isolated yield. ¹H NMR (400 MHz, CDCl₃) δ 8.57 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 8.4, 1.2 Hz, 1H), 7.81-7.68 (m, 6H), 7.32 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), 2.92 (s, 3H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.60, 151.22, 143.96, 141.65, 140.32, 136.83, 135.26, 131.87, 131.51, 130.37, 129.31, 129.22, 128.88, 120.58, 119.46, 114.00, 55.31, 36.76, 21.62. IR (neat): 3068, 2932, 2835, 1607, 1576, 1513, 1483, 1396, 1290, 1177, 1160, 1083, 1019, 999, 829, 805, 769, 732, 664 cm⁻¹. HRMS (ESI) calcd for C₂₃H₂₂N₃O₄S [M+H]⁺: 436.1326, found 436.1336.

8e was also isolated in 25% (31.6 mg) yield as a white solid.

N-(3-(4-Methoxyphenyl)quinoxalin-2-yl)-N,4-dimethylbenzenesulfonamide (8e). ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 9.2 Hz, 2H), 7.87-7.85 (m, 1H), 7.77-7.68 (m, 4H), 7.32 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H), 3.07 (s, 3H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.71, 152.43, 148.02, 143.83, 141.57, 139.71, 134.98, 130.72, 130.27, 129.70, 129.58, 129.18, 128.98, 128.18, 114.07, 55.32, 36.80, 21.60. IR (neat): 3042, 2961, 2932, 2838, 1611, 1516, 1347, 1255, 1246, 1224, 1172, 1158,
1072, 1031, 995, 830, 812, 803, 775, 755, 675 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{23}\)H\(_{22}\)N\(_3\)O\(_3\)S [M+H]\(^+\): 420.1376, found 420.1385.

2-Cyclopropyl-3-((N,4-dimethylphenyl)sulfonamido)quinoxaline 1-oxide (7f). Following the typical procedure, 0.3 mmol scale, N-(cclopropylethynyl)-N,4-dimethylbenzenesulfonamide 1s (74.8 mg, 0.3 mmol), 3 mL DCE, 6a (72.1 mg, 0.6 mmol), \(\text{^1BuXphos}\text{Au(MeCN)SbF}_6\) (13.5 mg, 0.015 mmol) were stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 20:1:1 to 15:1:1) afforded the title product as a colorless oil in 49% (54.6 mg) isolated yield. \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 8.52-8.49 (m, 1H), 7.80-7.77 (m, 1H), 7.72-7.68 (m, 4H), 7.32 (d, \(J = 8.4\) Hz, 2H), 3.19 (s, 3H), 2.51-2.42 (m, 4H), 1.53-1.49 (m, 2H), 1.29-1.24 (m, 2H). \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 151.86, 144.08, 143.71, 140.69, 136.73, 134.07, 130.79, 130.10, 129.30, 129.06, 128.80, 118.64, 37.02, 21.55, 10.97, 6.65. IR (neat): 3079, 3011, 2943, 1579, 1487, 1345, 1306, 1161, 1012, 911, 804, 777, 762, 727, 678, 666 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{19}\)H\(_{20}\)N\(_3\)S [M+H]\(^+\): 370.1220 found 370.1227.

**Reaction of 1b with 6a at 80 °C.**

![Reaction Scheme](Image)

To a Schlenk tube were added \(N,4\)-dimethyl-\(N\)-(phenylethynyl)benzenesulfonamide 1b (188.3 mg, 0.66 mmol), DCE (3 mL), benzofurazan 6a (36.0 mg, 0.3 mmol) and \(\text{^1BuXphos}\text{Au(MeCN)SbF}_6\) (13.5 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at 80 °C for 7 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column
chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:1) to afford 8a in 66% yield (77.5 mg) as a white solid and 9 in 45% yield (78.9 mg) as a white solid.

\[ \text{N,N'}-(3,4-	ext{Diphenylfuran-2,5-diyl)} \text{bis(N,4-dimethylbenzenesulfonamide)} \] (9). M.p. 200-202 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.59 (d, \( J = 8.4 \) Hz, 4H), 7.25-7.17 (m, 14H), 3.01 (s, 6H), 2.39 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 143.75, 140.20, 134.94, 130.24, 129.42, 129.36, 128.10, 128.07, 127.40, 122.85, 37.62, 21.49. IR (neat): 2982, 2922, 1616, 1603, 1584, 1495, 1443, 1350, 1168, 1150, 1062, 980, 812, 772, 733, 705, 684, 666 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{32}\)H\(_{34}\)N\(_3\)O\(_5\)S\(_2\)[M+NH\(_4\)]\(^+\): 604.1934, found 604.1936.

Reaction of 1b with 7a at 80 °C.

To a Schlenk tube were added N,4-dimethyl-N-(phenylethynyl)benzenesulfonamide 1b (125.6 mg, 0.44 mmol), DCE (2 mL), quinoxaline oxide 7a (81.1 mg, 0.2 mmol) and \(^t\)BuXPhosAu(MeCN)SbF\(_6\) (9.0 mg, 0.01 mmol) under Argon. After the reaction mixture was stirred at 80 °C for 2.5 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate: dichloromethane = 15:1:1) to afford 8a in 84% yield (65.3 mg) as a white solid and 9 in 52% yield (61.1 mg) as a white solid.

Reaction of propargyl ester 10a with 2a.
To a Schlenk tube were added 1-phenylprop-2-yn-1-yl benzoate 10a (106.3 mg, 0.45 mmol), DCE (3 mL), benzofurazan N-oxide 2a (40.8 mg, 0.3 mmol) and IPrAuNTf₂ (13.0 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at room temperature for 6 h as monitored by thin-layer chromatography, the mixture was filtered through silica gel. Then the solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1 to 5:1) to afford 11 in 22% yield (24.1 mg) as a red solid.

\((1Z,3^R,4^R,5^Z)-1,4\text{-Bis}(2\text{-nitrophenyl)amino}\)-3,6-diphenylhexa-1,5-diene-2,5-diyl dibenzoate (11). M.p. 94-96 °C. \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 9.67 (d, \(J = 10.4\) Hz, 1H), 8.28 (d, \(J = 7.2\) Hz, 1H), 8.16 (d, \(J = 7.6\) Hz, 2H), 8.12-8.08 (m, 2H), 7.83 (d, \(J = 7.6\) Hz, 2H), 7.65 (t, \(J = 7.6\) Hz, 1H), 7.60-7.47 (m, 7H), 7.41-7.26 (m, 8H), 7.21-7.16 (m, 3H), 6.76-6.69 (m, 4H), 6.14 (s, 1H), 5.29-5.26 (m, 1H), 4.58 (d, \(J = 4.4\) Hz, 1H). \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 165.08, 163.98, 145.42, 143.78, 139.50, 136.79, 136.19, 135.12, 134.42, 134.06, 133.75, 133.01, 132.88, 132.54, 130.23, 129.91, 129.14, 128.87, 128.77, 128.71, 128.51, 128.44, 128.21, 128.14, 127.79, 126.73, 126.42, 118.54, 118.05, 116.79, 116.12, 115.83, 114.17, 57.32, 50.22. IR (neat): 3346, 3058, 3029, 2919, 2848, 1727, 1613, 1576, 1499, 1449, 1420, 1347, 1236, 1152, 1057, 1023, 741, 705 cm\(^{-1}\). HRMS (ESI) calcd for C\(_{44}\)H\(_{34}\)N\(_4\)NaO\(_8\) [M+Na]\(^+\): 769.2269, found 769.2291.
Proposed reaction mechanism for the formation of 11.

In the reaction of propargyl ester 10a with benzofurazan N-oxide 2a, gold-carbene intermediate Int-S1 is initially generated through 1,2-acyloxy migration. Then attack of benzofurazan N-oxide 2a to Int-S1 gives intermediate Int-S2. This is followed by ring fragmentation to afford Int-S3, which is attacked by intermediate Int-S2 to provide Int-S5. Deprotonation and ring fragmentation of Int-S5 gives Int-S6. Attack of a hydride ion, possibly is pushed out from the intermediate Int-S5 to afford Int-S6 (Int-S6 to Int-S7, see eq S2), to imine moiety in Int-S6 followed by protonation forms product 11.

Reaction of propargyl ester 10a with 6a.

To a Schlenk tube were added 1-phenylprop-2-yn-1-yl benzoate 10a (106.3 mg, 0.45 mmol), DCE (3 mL), benzofurazan 6a (36.0 mg, 0.3 mmol) and IPrAuNTf$_2$ (13.0 mg, 0.015 mmol) under Argon. After the reaction mixture was stirred at 80 °C for 5 h as monitored by thin-layer chromatography, the solvent was evaporated under the reduced pressure and the
residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to afford **12a** in 39% yield (41.5 mg) as a white solid.

![Structure of 12a](image)

2-(2-Phenylacetyl)-1H-benzo[d]imidazol-1-yl benzoate (12a). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.21-8.19 (m, 2H), 7.97-7.95 (m, 1H), 7.71-7.66 (m, 1H), 7.53 (t, $J = 8.0$ Hz, 2H), 7.48-7.38 (m, 3H), 7.35-7.29 (m, 4H), 7.26-7.22 (m, 1H), 4.60 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 189.61, 163.63, 140.92, 137.24, 134.85, 133.34, 132.38, 130.57, 129.98, 128.91, 128.52, 127.28, 127.04, 125.55, 124.50, 122.44, 109.30, 45.74. IR (neat): 3066, 3037, 2932, 1776, 1686, 1603, 1480, 1453, 1335, 1230, 1211, 1046, 1035, 1007, 999, 837, 761, 738, 724, 697, 691, 677, 660 cm$^{-1}$. HRMS (ESI) calcd for C$_{22}$H$_{17}$N$_2$O$_3$ [M+H]$^+$: 357.1234, found 357.1244.

![Structure of 12b](image)

2-(2-(Naphthalen-2-yl)acetyl)-1H-benzo[d]imidazol-1-yl benzoate (12b). Following the typical procedure, 0.3 mmol scale, 1-(naphthalen-2-yl)prop-2-yn-1-yl benzoate **10b** (128.8 mg, 0.45 mmol), 3 mL DCE, **6a** (36.0 mg, 0.3 mmol), IPrAuNTf$_2$ (13.0 mg, 0.015 mmol) were stirred at room temperature for 2 h. Column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 20:1) afforded the title product as a white solid in 30% (36.4 mg) isolated yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.21-8.19 (m, 2H), 7.99-7.97 (m, 1H), 7.80-7.77 (m, 4H), 7.68 (t, $J = 7.6$ Hz, 1H), 7.54-7.39 (m, 8H), 4.76 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 189.69, 163.67, 140.95, 137.30, 134.88, 133.43, 132.43, 132.42, 130.91, 130.59, 128.93, 128.80, 128.15, 127.97, 127.68, 127.60, 127.35, 125.99, 125.72, 125.54, 124.56, 122.49, 109.34, 45.92. IR (neat): 3055, 1778, 1689, 1600, 1484, 1330, 1228, 1157, 1112, 1031, 992, 791, 762, 739, 699, 674 cm$^{-1}$. HRMS (ESI) calcd for C$_{26}$H$_{19}$N$_2$O$_3$ [M+H]$^+$: 407.1390,
Proposed reaction mechanism for the formation of 12.⁷

In the reaction of benzofurazan 6a with propargyl ester 10, gold-carbene intermediate Int-S1 is initially generated through 1,2-acyloxy migration. Int-S1 reacts with benzofurazan 6a through a [4+1] process to give the intermediate Int-S9. Then ring-opening followed by attack of O⁺ to the ester moisty provides the product 12.

References:


(5) Karad, S. N.; Bhunia, S.; Liu, R.-S. Retention of Stereochemistry in Gold-Catalyzed


Figure S1. X-ray crystal structure of compound 3b

Figure S2. X-ray crystal structure of compound 3p

Figure S3. X-ray crystal structure of compound 7a
Figure S4. X-ray crystal structure of compound 8a

Figure S5. X-ray crystal structure of compound 9

Figure S6. X-ray crystal structure of compound 11
Figure S7. X-ray crystal structure of compound 12b
$\text{Br}$

$\text{Ts}$

$\text{Me}$

$1j$
3j

[Chemical structure image]

[Graphical representation of the spectrum with various ppm values]
NO₂

H

Ms

N

Me

3I
5, (E/Z = 7.0:1)
5, ($E/Z = 7.0:1$)
3p' (possible structure)