**Palladium-Catalyzed C-H Activation/Intramolecular Amination Reaction: A New
Route to 3-Aryl/Alkylindazoles**

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Supporting Information

1. General

All reactions were carried out under Ar atmosphere unless otherwise noted. Ethanol was distilled from sodium under Ar atmosphere. Dimethyl sulfoxide (DMSO) was distilled from CaH₂ under Ar atmosphere. Melting points were measured with a Yazawa micro melting point apparatus and uncorrected. IR spectra were recorded on a SHIMADZU FTIR-8400. ¹H-NMR spectra were recorded on JEOL JNM-AL400 (400 MHz) or JNM-ECA600 (600 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are given from TMS (0 ppm) and coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sep = septet, dd = double doublet, dt = double triplet, td = triple doublet, ddd = double double doublet, m = multiplet, br.s = broad singlet, and br = broad signal. ¹³C-NMR spectra were recorded on JEOL JNM-AL400 (100 MHz) or JNM-ECA600 (150 MHz) spectrometer and chemical shifts (δ) are given from ¹³CDCl₃ (77.0 ppm) and ¹³C₆D₆ (128.0 ppm). Mass spectra and high resolution mass spectra were measured on JEOL JMS-DX303 and MS-AX500 instruments, respectively. FAB-mass spectra was measured on JEOL JMS-700 instrument. Elemental analyses were performed by Yanaco CHN CORDER MT-6.

2. Preparation of Starting Materials

General Procedure for the Preparation of Hydrazones

Acetyl chloride was slowly added to ethanol (1 mL) at 0°C and stirred for 30 min at the same temperature. The reaction mixture was warmed to room temperature and stirred for another 30 min. The resulting mixture and a ethanol solution of the ketone were added to a ethanol solution of 4-methylphenylsulfonylhydrazide, then heated under reflux. The reaction mixture was treated with saturated aqueous NaHCO_3 and extracted with ethyl acetate. The combined organic layer was washed with brine and dried over MgSO_4 . The solvent was evaporated and the residue was purified by silica gel column chromatography.

Benzophenone 4-Methylphenylsulfonylhydrazone (**1**)

According to the general procedure, a mixture of benzophenone (1.5 g, 8.2 mmol), acetyl chloride (1.3 g, 16.5 mmol), and 4-methylphenylsulfonylhydrazide (3.6 g, 19.8 mmol) in ethanol (40 mL) was heated under reflux for 40 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **1** (2.4 g, 82%) as a colorless solid.

mp 182-183°C (colorless prisms from hexane-acetone, lit.¹⁾ mp 184-185°C);

IR ν (film, cm^{-1}) 3209, 1169, 772, 694, 667;

^1H -NMR (400 MHz, CDCl_3) δ 2.43 (3H, s), 7.10-7.13 (2H, m), 7.25-7.34 (5H, m), 7.44 (2H, d, $J = 6.8$ Hz), 7.50-7.54 (4H, m), 7.85 (2H, d, $J = 8.4$ Hz);

^{13}C -NMR (100 MHz, CDCl_3) δ 21.7, 127.5, 127.8, 128.1, 128.2, 129.6, 129.7, 129.8, 130.0,

131.0, 135.4, 136.3, 144.0, 154.1;

MS m/z 350 (M^+ , 23.4), 195 (100);

HRMS calcd for $C_{20}H_{18}N_2O_2S$ 350.1089, found 350.1081.

4,4'-Dimethoxybenzophenone 4-Methylphenylsulfonylhydrazone (3a)

According to the general procedure, a mixture of 4,4'-dimethoxybenzophenone (0.16 g, 0.66 mmol), acetyl chloride (0.25 g, 3.3 mmol), and 4-methylphenylsulfonylhydrazide (0.37 g, 2.0 mmol) in ethanol (7 mL) was heated under reflux for 40 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (2:1)] to afford **3a** (0.19 g, 69%) as a light brown solid.

mp 138-140°C (light brown plates from hexane-ethyl acetate, lit.²⁾ mp 136-137°C);

IR ν (film, cm^{-1}) 3200, 1252, 1161, 837, 662;

1H -NMR (400 MHz, $CDCl_3$) δ 2.42 (3H, s), 3.79 (3H, s), 3.87 (3H, s), 6.79 (2H, d, J = 8.8 Hz), 7.00 (2H, d, J = 8.0 Hz), 7.05 (2H, d, J = 8.8 Hz), 7.32 (2H, d, J = 8.8 Hz), 7.37 (2H, d, J = 8.8 Hz), 7.50 (1H, s), 7.84 (2H, d, J = 8.0 Hz);

^{13}C -NMR (100 MHz, $CDCl_3$) δ 21.7, 55.3, 55.4, 113.5, 115.0, 123.0, 127.8, 129.1, 129.47, 129.50, 129.8, 135.5, 143.9, 154.2, 160.5, 160.9;

MS m/z 410 (M^+ , 14.5), 255 (100);

HRMS calcd for $C_{22}H_{22}N_2O_4S$ 410.1301, found 410.1301.

4,4'-Dimethylbenzophenone 4-Methylphenylsulfonylhydrazone (3b)

According to the general procedure, a mixture of 4,4'-dimethylbenzophenone (32.3 mg, 0.15 mmol), acetyl chloride (60.3 mg, 0.77 mmol), 4-methylphenylsulfonylhydrazide (85.8 mg, 0.46 mmol), and MgSO₄ (63.5 mg, 0.53 mmol) in ethanol (4 mL) was heated under reflux for 45 min. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to afford **3b** (43.4 g, 75%) as a colorless solid.

mp 150-152°C (colorless prisms from hexane-ethyl acetate);

IR ν (film, cm⁻¹) 3202, 1171, 824, 667;

¹H-NMR (400 MHz, CDCl₃) δ 2.33 (3H, s), 2.42 (6H, s), 6.97 (2H, d, J = 8.0 Hz), 7.08 (2H, d, J = 8.0 Hz), 7.29-7.34 (6H, m), 7.50 (1H, s), 7.83 (2H, d, J = 8.4 Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 21.3, 21.4, 21.7, 127.5, 127.8, 128.1, 128.8, 129.5, 130.3, 133.8, 135.5, 139.9, 140.0, 143.9, 154.6;

MS m/z 378 (M⁺, 16.6), 223 (100);

HRMS calcd for C₂₂H₂₂N₂O₂S 378.1402, found 378.1405.

3,3'-Dimethoxybenzophenone 4-Methylphenylsulfonylhydrazone (**3c**)

According to the general procedure, a mixture of 3,3'-dimethoxybenzophenone (0.12 g, 0.52 mmol), acetyl chloride (0.20 g, 2.6 mmol), and 4-methylphenylsulfonylhydrazide (0.19 g, 1.0 mmol) in ethanol (5 mL) was heated under reflux for 1 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3c** (0.17 g, 80%) as a colorless solid.

mp 103-105°C (colorless plates from hexane-ethyl acetate);

IR ν (film, cm⁻¹) 3198, 1169, 872, 667;

¹H-NMR (400 MHz, CDCl₃) δ 2.42 (3H, s), 3.77 (3H, s), 3.79 (3H, s), 6.60 (1H, d, J = 2.4 Hz), 6.65 (1H, d, J = 8.0 Hz), 6.88 (1H, dd, J = 8.0, 2.4 Hz), 6.97 (1H, d, J = 8.0 Hz), 7.01 (1H, dd, J = 8.0, 2.4 Hz), 7.07 (1H, t, J = 2.4 Hz), 7.18 (1H, t, J = 8.0 Hz), 7.32 (2H, d, J =

8.2 Hz), 7.41 (1H, t, $J = 8.0$ Hz), 7.58 (1H, s), 7.85 (2H, d, $J = 8.2$ Hz);
 ^{13}C -NMR (100 MHz, CDCl_3) δ 21.6, 55.2, 55.4, 112.6, 113.5, 115.6, 115.7, 120.1, 120.4, 127.9, 129.1, 129.6, 131.0, 132.3, 135.5, 137.6, 144.1, 153.8, 159.4, 160.5;
 MS m/z 410 (M^+ , 6.4), 255 (100);
 HRMS calcd for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$ 410.1301, found 410.1293.

3-Methoxy-3'-nitrobenzophenone 4-Methylphenylsulfonylhydrazone (3d)

3-Methoxyphenylmagnesium bromide (0.77 M solution in THF, 1.9 mL, 1.5 mmol) was added to a solution of 3-nitrobenzaldehyde (0.20 g, 1.3 mmol) in THF (7 mL) at -78°C and stirred for 35 min at the same temperature. Saturated aqueous NH_4Cl (5 mL) was added to the reaction mixture and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with water (5 mL) and brine (5 mL), and dried over MgSO_4 . The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to give 3-methoxy- α -(3-nitrophenyl)benzyl alcohol (0.33 g, 95%) as a colorless oil.

^1H -NMR (400 MHz, CDCl_3) δ 2.68 (1H, br), 3.78 (3H, s), 5.86 (1H, s), 6.82-6.84 (1H, m), 6.91-6.93 (2H, m), 7.24-7.29 (1H, m), 7.45-7.51 (1H, m), 7.69 (1H, d, $J = 6.4$ Hz), 8.09 (1H, d, $J = 8.4$ Hz), 8.27 (1H, s);
 ^{13}C -NMR (100 MHz, CDCl_3) δ 55.3, 75.2, 112.2, 113.5, 118.8, 121.2, 122.4, 129.3, 129.9, 132.3, 144.3, 145.6, 148.2, 159.8.

A mixture of the above alcohol (0.29 g, 1.1 mmol) and activated MnO_2 (1.5 g, 17.3 mmol) in dichloromethane (10 mL) was stirred for 30 min at room temperature. The reaction mixture was diluted with methanol and filtered through a pad of Celite[®]. The filtrate was evaporated under reduced pressure and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to give

3-methoxy-3'-nitrobenzophenone (0.29 g, 99%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 3.88 (3H, s), 7.19 (1H, dd, $J = 8.0, 2.6$ Hz), 7.31 (1H, d, $J = 8.0$ Hz), 7.36 (1H, s), 7.43 (1H, t, $J = 8.0$ Hz), 7.70 (1H, t, $J = 8.0$ Hz), 8.14 (1H, d, $J = 8.0$ Hz), 8.44 (1H, m), 8.63 (1H, s);

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 55.3, 114.1, 119.3, 122.4, 124.3, 126.3, 129.3, 135.1, 137.2, 138.7, 147.7, 159.5, 193.4.

According to the general procedure, a mixture of 3-methoxy-3'-nitrobenzophenone (0.28 g, 1.1 mmol), acetyl chloride (0.43 g, 5.4 mmol), and 4-methylphenylsulfonylhydrazide (0.40 g, 2.2 mmol) in ethanol (6 mL) was heated under reflux for 1.5 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3d** (0.24 g, including impurities), which was further purified by recrystallization from hexane-ethyl acetate to afford **3d** as a single isomer in a pure form (0.23 g, 49%).

mp 193-194°C (colorless prisms from hexane-ethyl acetate);

IR ν (film, cm^{-1}) 3200, 1529, 1348, 1169, 814, 746, 687, 664;

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.45 (3H, s), 3.83 (3H, s), 6.64 (1H, s), 6.69 (1H, d, $J = 8.0$ Hz), 7.08 (1H, dd, $J = 8.0, 2.6$ Hz), 7.37 (2H, d, $J = 8.2$ Hz), 7.475 (1H, t, $J = 8.0$ Hz), 7.480 (1H, t, $J = 8.0$ Hz), 7.74 (1H, s), 7.81 (1H, d, $J = 8.0$ Hz), 7.88 (2H, d, $J = 8.2$ Hz), 8.18 (1H, d, $J = 8.0$ Hz), 8.23 (1H, s);

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 21.7, 55.5, 113.5, 116.0, 119.9, 122.2, 124.2, 127.9, 129.2, 129.7, 130.9, 131.4, 132.9, 135.0, 138.1, 144.5, 148.2, 151.1, 160.7;

MS m/z 425 (M^+ , 0.81), 270 (96.1), 269 (100), 224 (53.1);

HRMS calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_5\text{S}$ 425.1046, found 425.1061;

Anal. calcd for $\text{C}_{21}\text{H}_{19}\text{N}_3\text{O}_5\text{S}$: C, 59.28; H, 4.50; N, 9.88. found: C, 59.12; H, 4.40; N, 9.68.

3'-Cyano-3-methoxybenzophenone 4-Methylphenylsulfonylhydrazone (**3e**)

3-Methoxyphenylmagnesium bromide (0.60 M solution in THF, 11 mL, 6.6 mmol) was added to a solution of 3-bromobenzaldehyde (0.94 g, 5.1 mmol) in THF (20 mL) at 0°C and stirred for 15 min at room temperature. Saturated aqueous NH₄Cl (10 mL) was added to the reaction mixture and the aqueous phase was extracted with ethyl acetate (10 mL x 3). The combined organic solution was washed with water (10 mL) and brine (10 mL), and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give 3-bromo- α -(3-methoxyphenyl)benzyl alcohol (1.5 g, quant.) as a colorless oil.

¹H-NMR (400 MHz, CDCl₃) δ 3.62 (1H, s), 3.66 (3H, s), 5.55 (1H, s), 6.74 (1H, td, J = 8.0, 2.1 Hz), 6.81-6.84 (2H, m), 7.07 (1H, t, J = 8.0 Hz), 7.14-7.19 (2H, m), 7.30 (1H, d, J = 8.0 Hz), 7.47 (1H, s).

A mixture of the above alcohol (1.5 g, 5.2 mmol) and activated MnO₂ (13.0 g, 149.5 mmol) in dichloromethane (30 mL) was stirred for 1 h at room temperature. The reaction mixture was diluted with methanol and filtered through a pad of Celite[®]. The filtrate was evaporated under reduced pressure and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give 3-bromo-3'-methoxybenzophenone (1.3 g, 86%) as a colorless solid.

¹H-NMR (400 MHz, CDCl₃) δ 3.83 (3H, s), 7.12 (1H, dd, J = 8.2, 2.6 Hz), 7.27-7.38 (4H, m), 7.66-7.69 (2H, m), 7.92 (1H, s);

¹³C-NMR (100 MHz, CDCl₃) δ 55.4, 114.1, 119.0, 122.4, 122.6, 128.3, 129.2, 129.6, 132.5, 135.0, 137.9, 139.2, 159.4, 194.5.

A mixture of the above benzophenone (0.52 g, 1.8 mmol), Pd₂(dba)₃ (97.2 mg, 0.11 mmol), dppf (0.24 g, 0.43 mmol), CuCN (0.63 g, 7.1 mmol), and Et₄NCN (0.28 g, 1.8 mmol) in dioxane (10 mL) was heated under reflux for 4.5 h. The reaction mixture was filtered through a pad of Celite[®] and the filtrate was washed with saturated aqueous NaHCO₃ (10 mL x 3) and brine (10 mL x 1), and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to give 3'-cyano-3-methoxybenzophenone (0.41 g, 98%) as a yellow solid.

IR ν (film, cm^{-1}) 2232, 1663, 1288, 1246, 745;

^1H -NMR (400 MHz, CDCl_3) δ 3.86 (3H, s), 7.18 (1H, ddd, $J = 8.0, 2.4, 1.0$ Hz), 7.28 (1H, dt, $J = 8.0, 1.0$ Hz), 7.33 (1H, m), 7.41 (1H, t, $J = 8.0$ Hz), 7.63 (1H, t, $J = 7.8$ Hz), 7.86 (1H, dt, $J = 7.8, 1.4$ Hz), 8.03 (1H, dt, $J = 7.8, 1.4$ Hz), 8.07 (1H, t, $J = 1.4$ Hz);

^{13}C -NMR (100 MHz, CDCl_3) δ 55.1, 112.3, 113.9, 117.5, 118.9, 122.2, 128.9, 129.1, 132.8, 133.3, 134.8, 137.0, 138.0, 159.2, 193.4;

MS m/z 237 (M^+ , 85.9), 135 (100);

HRMS calcd for $\text{C}_{15}\text{H}_{11}\text{NO}_2$ 237.0790, found 237.0774.

According to the general procedure, a mixture of 3'-cyano-3-methoxybenzophenone (0.13 g, 0.55 mmol), acetyl chloride (0.22 g, 2.7 mmol), and 4-methylphenylsulfonylhydrazide (0.20 g, 1.1 mmol) in ethanol (5 mL) was heated under reflux for 75 min. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3e** as a mixture of two isomers (0.21 g, 94%). The ratio of two isomers was determined by ^1H -NMR spectrum (major isomer : minor isomer = 7.7 : 1), and recrystallization gave the single isomer (major isomer).

major isomer: mp 174-175°C (colorless scales from hexane-ethyl acetate);

IR ν (film, cm^{-1}) 3236, 2226, 1165, 907, 868, 806, 669;

^1H -NMR (400 MHz, CDCl_3) δ 2.45 (3H, s), 3.83 (3H, s), 6.60 (1H, s), 6.66 (1H, d, $J = 8.0$ Hz), 7.07 (1H, dd, $J = 8.0, 2.4$ Hz), 7.36 (2H, d, $J = 8.2$ Hz), 7.41 (1H, t, $J = 8.0$ Hz), 7.47 (1H, t, $J = 8.0$ Hz), 7.60 (1H, d, $J = 8.0$ Hz), 7.66 (1H, s), 7.72-7.74 (2H, m), 7.85 (2H, d, $J = 8.2$ Hz);

^{13}C -NMR (100 MHz, CDCl_3) δ 21.7, 55.5, 112.6, 113.5, 116.0, 118.3, 119.8, 127.8, 129.1, 129.7, 130.9, 130.98, 130.99, 131.2, 131.4, 132.8, 137.4, 144.4, 151.2, 160.7;

MS m/z 405 (M^+ , 2.0), 250 (100), 249 (90.9);

HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$ 405.1147, found 405.1138;

Anal. calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$: C, 65.17; H, 4.72; N, 10.36. found: C, 65.19; H, 4.84; N, 10.34.

3'-Ethoxycarbonyl-3-methoxybenzophenone 4-Methylphenylsulfonylhydrazone (3f)

A mixture of 3-bromo-3'-methoxybenzophenone (0.74 g, 2.5 mmol), $\text{Pd}_2(\text{dba})_3$ (0.11 g, 0.51 mmol), dppp (0.31 g, 0.76 mmol), Et_3N (4 mL), and EtOH (4 mL) in DMSO (8 mL) was heated at 70°C for 44 h. The reaction mixture was filtered through a pad of Celite[®] and the filtrate was washed with H_2O (10 mL x 1), saturated aqueous NaHCO_3 (10 mL x 1), 3 N HCl (10 mL x 1), and brine (10 mL x 1), and dried over MgSO_4 . The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (19:1 to 4:1)] to give 3'-ethoxycarbonyl-3-methoxybenzophenone (0.41 g, 98%) as a yellow solid.

According to the general procedure, a mixture of 3'-ethoxycarbonyl-3-methoxybenzophenone (0.30 g, 1.0 mmol), acetyl chloride (0.41 g, 5.2 mmol), and 4-methylphenylsulfonylhydrazide (0.39 g, 2.1 mmol) in ethanol (10 mL) was heated under reflux for 1 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3f** as a mixture of two isomers (0.21 g, 94%). The ratio of two isomers was determined by ^1H -NMR spectrum (major isomer : minor isomer = 33 : 1), and recrystallization gave the single isomer (major isomer).

major isomer: mp 180-182°C (colorless prisms from hexane-ethyl acetate);

IR ν (film, cm^{-1}) 3186, 1717, 1267, 1169;

^1H -NMR (400 MHz, CDCl_3) δ 1.40 (3H, t, $J = 7.2$ Hz), 2.44 (3H, s), 3.78 (3H, s), 4.39 (2H, q, $J = 7.2$ Hz), 6.88-6.90 (2H, m), 7.02 (1H, s), 7.19 (1H, t, $J = 8.0$ Hz), 7.33-7.35 (3H, m), 7.44 (1H, s), 7.61 (1H, t, $J = 8.0$ Hz), 7.79 (1H, s), 7.86 (2H, d, $J = 8.0$ Hz), 8.18 (1H, d, $J = 8.0$ Hz);

^{13}C -NMR (100 MHz, CDCl_3) δ 14.4, 21.7, 55.3, 61.5, 112.6, 115.7, 120.4, 127.9, 129.2, 129.3, 129.6, 129.9, 131.1, 131.4, 132.1, 132.5, 135.2, 137.4, 144.2, 152.8, 159.4, 165.3;

MS m/z 452 (M^+ , 4.5), 269 (100);

HRMS calcd for $C_{24}H_{24}N_2O_5S$ 452.1406, found 452.1408;

Anal. calcd for $C_{24}H_{24}N_2O_5S$: C, 63.70; H, 5.35; N, 6.19. found: C, 63.73; H, 5.38; N, 6.16.

3-Hydroxybenzophenone 4-Methylphenylsulfonylhydrazone (**3g**)

According to the general procedure, a mixture of 3-hydroxybenzophenone (0.36 g, 1.8 mmol), acetyl chloride (0.71 g, 9.0 mmol), and 4-methylphenylsulfonylhydrazide (0.67 g, 3.6 mmol) in ethanol (15 mL) was heated under reflux for 8 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (2:1)] to afford **3g** (0.75 g, including impurities), which was further purified by recrystallization from hexane-ethyl acetate to afford **3g** (0.39 g, 60%) as an inseparable mixture of two isomers. The ratio of two isomers was determined by HPLC as 2.4 : 1.

IR ν (film, cm^{-1}) 3437, 3179, 1321, 1161, 839, 772, 704, 669;

1H -NMR/ ^{13}C -NMR: only a 1H -NMR spectrum of *E*-/*Z*-mixture was obtained;

MS m/z 366 (M^+ , 10.6), 211 (100);

HRMS calcd for $C_{20}H_{18}N_2O_3S$ 366.1038, found 366.1034;

Anal. calcd for $C_{20}H_{18}N_2O_3S$: C, 65.55; H, 4.95; N, 7.64. found: C, 65.30; H, 5.04; N, 7.70.

3-Aminobenzophenone 4-Methylphenylsulfonylhydrazone (**3h**)

According to the general procedure, a mixture of 3-aminobenzophenone (0.20 g, 1.0 mmol), acetyl chloride (0.40 g, 5.1 mmol), and 4-methylphenylsulfonylhydrazide (0.38 g,

2.0 mmol) in ethanol (5 mL) was heated under reflux for 45 min. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (2:1)] to afford **3h** (0.20 g, 54%) as an inseparable mixture of two isomers. The ratio of two isomers was determined by HPLC as 1.7 : 1.

IR ν (film, cm^{-1}) 3381, 3215, 1167, 754, 704, 667;

$^1\text{H-NMR}/^{13}\text{C-NMR}$: only a $^1\text{H-NMR}$ spectrum of *E*-/*Z*-mixture was obtained;

MS m/z 365 (M^+ , 5.4), 210 (100);

HRMS calcd for $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_2\text{S}$ 365.1198, found 365.1199;

Anal. calcd for $\text{C}_{20}\text{H}_{19}\text{N}_3\text{O}_2\text{S}$: C, 65.73; H, 5.24; N, 11.50. found: C, 65.51; H, 5.04; N, 11.41.

3-Methoxybenzophenone 4-Methylphenylsulfonylhydrazone (**3i**)

According to the general procedure, a mixture of 3-methoxybenzophenone (0.29 g, 1.4 mmol), acetyl chloride (0.54 g, 6.9 mmol), and 4-methylphenylsulfonylhydrazide (0.51 g, 2.8 mmol) in ethanol (10 mL) was heated under reflux for 45 min. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3i** as a mixture of two isomers (0.47 g, 90%). The ratio of two isomers was determined by $^1\text{H-NMR}$ spectrum (major isomer : minor isomer = 1.3 : 1), and each isomer was obtained by recrystallization from hexane-diethyl ether.

major isomer: mp 156-158°C (colorless needles from hexane-diethyl ether, lit.³⁾ mp 157°C);

IR ν (film, cm^{-1}) 3198, 1169, 814, 694, 669;

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.43 (3H, s), 3.80 (3H, s), 6.61 (1H, m), 6.66 (1H, dt, J = 7.6, 1.0 Hz), 7.02 (1H, ddd, J = 8.4, 2.6, 1.0 Hz), 7.25-7.34 (6H, m), 7.43 (1H, t, J = 8.0 Hz), 7.46 (1H, m), 7.57 (1H, s), 7.85 (2H, d, J = 8.4 Hz);

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 21.7, 55.4, 113.4, 115.6, 120.0, 127.4, 127.8, 128.1, 129.6,

129.8, 130.9, 132.2, 135.4, 136.1, 144.0, 153.9, 160.4;

MS m/z 380 (M^+ , 5.9), 225 (100);

HRMS calcd for $C_{21}H_{20}N_2O_3S$ 380.1194, found 380.1204.

minor isomer: mp 122-123°C (colorless prisms from hexane-diethyl ether);

IR ν (film, cm^{-1}) 3200, 1169, 816, 789, 702, 665;

1H -NMR (400 MHz, $CDCl_3$) δ 2.43 (3H, s), 3.77 (3H, s), 6.88 (1H, dd, $J = 8.0, 2.4$ Hz), 6.94 (1H, dd, $J = 7.6, 0.8$ Hz), 7.05 (1H, s), 7.10-7.12 (2H, m), 7.18 (1H, t, $J = 8.2$ Hz), 7.32 (2H, d, $J = 8.4$ Hz), 7.49-7.52 (4H, m), 7.85 (2H, d, $J = 8.4$ Hz);

^{13}C -NMR (100 MHz, $CDCl_3$) δ 21.7, 55.3, 112.6, 115.6, 120.4, 127.9, 128.2, 129.1, 129.6, 129.7, 130.0, 131.0, 135.4, 137.7, 144.1, 153.9, 159.3;

MS m/z 380 (M^+ , 9.1), 225 (100);

HRMS calcd for $C_{21}H_{20}N_2O_3S$ 380.1195, found 380.1189.

3-Chlorobenzophenone 4-Methylphenylsulfonylhydrazone (**3j**)

According to the general procedure, a mixture of 3-chlorobenzophenone (0.19 g, 0.86 mmol), acetyl chloride (0.34 g, 4.3 mmol), and 4-methylphenylsulfonylhydrazide (0.32 g, 1.7 mmol) in ethanol (10 mL) was heated under reflux for 10.5 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3j** (0.25 g, 76%) as an inseparable mixture of two isomers. The ratio of two isomers was determined by 1H -NMR spectrum (major isomer : minor isomer = 2 : 1).

IR ν (film, cm^{-1}) 3200, 1167, 885, 779, 760, 694, 665;

1H -NMR/ ^{13}C -NMR: only a 1H -NMR spectrum of E/Z -mixture was obtained;

MS m/z 386 ($M^+ + 2$, 8.2), 384 (M^+ , 19.6), 229 (100);

HRMS calcd for $C_{20}H_{17}^{35}ClN_2O_2S$ 384.0699, found 384.0694.

Anal. calcd for $C_{20}H_{17}ClN_2O_2S$: C, 62.41; H, 4.45; N, 7.28. found: C, 62.57; H, 4.47; N,

7.29.

3-Bromobenzophenone 4-Methylphenylsulfonylhydrazone (3k)

According to the general procedure, a mixture of 3-bromobenzophenone (0.58 g, 2.2 mmol), acetyl chloride (0.87 g, 11.0 mmol), and 4-methylphenylsulfonylhydrazide (0.82 g, 4.4 mmol) in ethanol (15 mL) was heated under reflux for 1.5 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3k** (0.61 g, 64%) as a mixture of two isomers. Recrystallization gave the single isomer (major isomer).

major isomer: mp 198-200°C (colorless prisms from hexane-ethyl acetate);

IR ν (film, cm^{-1}) 3190, 1169, 795, 775, 760, 667;

^1H -NMR (400 MHz, CDCl_3) δ 2.44 (3H, s), 7.10 (1H, d, $J = 7.6$ Hz), 7.24 (2H, d, $J = 8.0$ Hz), 7.28-7.37 (4H, m), 7.39-7.43 (3H, m), 7.46 (1H, s), 7.66 (1H, d, $J = 8.0$ Hz), 7.86 (2H, d, $J = 8.0$ Hz);

^{13}C -NMR (100 MHz, CDCl_3) δ 21.7, 123.9, 126.8, 127.4, 127.9, 128.2, 129.6, 130.0, 131.0, 131.2, 133.1, 133.2, 135.2, 135.8, 144.2, 152.4;

MS m/z 430 ($\text{M}^+ + 2$, 8.1), 428 (M^+ , 7.8), 165 (100);

HRMS calcd for $\text{C}_{20}\text{H}_{17}^{81}\text{BrN}_2\text{O}_2\text{S}$ 430.0173, found 430.0155, calcd for $\text{C}_{20}\text{H}_{17}^{79}\text{BrN}_2\text{O}_2\text{S}$ 428.0194, found 428.0180;

Anal. calcd for $\text{C}_{20}\text{H}_{17}\text{BrN}_2\text{O}_2\text{S}$: C, 55.95; H, 3.99; N, 6.52. found: C, 55.98; H, 4.02; N, 6.52.

3-Nitrobenzophenone 4-Methylphenylsulfonylhydrazone (**3l**)

According to the general procedure, a mixture of 3-nitrobenzophenone (0.50 g, 2.2 mmol), acetyl chloride (0.87 g, 11.0 mmol), and 4-methylphenylsulfonylhydrazide (0.82 g, 4.4 mmol) in ethanol (12 mL) was heated under reflux for 1 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3l** (0.84 g, 97%) as an inseparable mixture of two isomers. The ratio of two isomers was determined by HPLC as 2 : 1 ~ 3 : 1.

IR ν (film, cm^{-1}) 3200, 1529, 1348, 1167, 854, 814, 775, 733, 691, 665;

$^1\text{H-NMR}/^{13}\text{C-NMR}$: only a $^1\text{H-NMR}$ spectrum of *E*-/*Z*-mixture was obtained;

MS m/z 395 (M^+ , 31.0), 240 (100), 211 (89.9), 194 (98.5);

HRMS calcd for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$ 395.0940, found 395.0924;

Anal. calcd for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$: C, 60.75; H, 4.33; N, 10.63. found: C, 60.61; H, 4.35; N, 10.57.

4-Nitrobenzophenone 4-Methylphenylsulfonylhydrazone (**3m**)

According to the general procedure, a mixture of 4-nitrobenzophenone (0.31 g, 1.3 mmol), acetyl chloride (0.21 g, 2.7 mmol), and 4-methylphenylsulfonylhydrazide (0.50 g, 2.7 mmol) in ethanol (9 mL) was heated under reflux for 22 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3m-E** (0.41 g, 78%) and **3m-Z** (83.0 mg, 16%) as a yellow solid, respectively. Geometries of both isomers were confirmed by NOESY.

E-isomer: mp 139-140°C (yellow plates from hexane-ethyl acetate, lit.⁴⁾ mp 130-138°C);
 IR ν (film, cm^{-1}) 3202, 1520, 1344, 1167, 862, 777, 737, 700, 681, 656;
 ^1H -NMR (600 MHz, C_6D_6) δ 1.87 (3H, s), 6.57 (2H, d, $J = 7.2$ Hz), 6.83 (2H, d, $J = 7.8$ Hz), 6.94-6.98 (3H, m), 7.24 (2H, d, $J = 9.0$ Hz), 7.69 (2H, d, $J = 9.0$ Hz), 7.77 (1H, s), 7.90 (2H, d, $J = 7.8$ Hz);
 ^{13}C -NMR (100 MHz, CDCl_3) δ 21.7, 123.4, 127.8, 128.1, 129.73, 129.75, 129.8, 130.1, 130.6, 135.1, 142.1, 144.5, 148.2, 151.2;
 MS m/z 395 (M^+ , 29.7), 240 (82.8), 211 (99.5), 194 (100);
 HRMS calcd for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$ 395.0940, found 395.0953.

Z-isomer: mp 183-185°C (light yellow plates from hexane-ethyl acetate);
 IR ν (film, cm^{-1}) 3190, 1520, 1348, 1165, 849, 758, 700, 671;
 ^1H -NMR (600 MHz, C_6D_6) δ 1.84 (3H, s), 6.28 (2H, d, $J = 8.7$ Hz), 6.79 (2H, d, $J = 8.1$ Hz), 7.03-7.04 (3H, m), 7.34-7.36 (2H, m), 7.53 (2H, d, $J = 8.7$ Hz), 7.59 (1H, s), 8.02 (2H, d, $J = 8.1$ Hz);
 ^{13}C -NMR (100 MHz, CDCl_3) δ 21.7, 124.8, 127.3, 127.8, 128.4, 129.68, 129.72, 130.3, 135.0, 135.4, 137.8, 144.4, 148.5, 151.8;
 MS m/z 395 (M^+ , 18.7), 240 (77.8), 211 (90.5), 194 (100);
 HRMS calcd for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$ 395.0940, found 395.0942.

4-Methoxybenzophenone 4-Methylphenylsulfonylhydrazone (3n)

According to the general procedure, a mixture of 4-methoxybenzophenone (0.30 g, 1.4 mmol), acetyl chloride (0.22 g, 2.8 mmol), and 4-methylphenylsulfonylhydrazide (0.79 g, 4.2 mmol) in ethanol (15 mL) was heated under reflux for 43 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3n** as an inseparable mixture of two isomers (0.12 g, 22%). The ratio of two isomers was determined by $^1\text{H-NMR}$ spectrum as $E : Z = 1 : 1$. Recrystallization gave the single isomer (E -isomer). Geometries of both isomers were confirmed by NOESY.

IR ν (film, cm^{-1}) 3200, 1161, 837, 775, 700, 664;

MS m/z 380 (M^+ , 18.2), 225 (100);

HRMS calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$ 380.1195, found 380.1196;

Anal. calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$: C, 66.29; H, 5.30; N, 7.36. found: C, 66.29; H, 5.30; N, 7.41.

E -isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.42 (3H, s), 3.78 (3H, s), 6.79 (2H, d, $J = 9.0$ Hz), 7.09 (2H, dd, $J = 6.4, 3.2$ Hz), 7.32 (2H, d, $J = 8.0$ Hz), 7.37 (2H, d, $J = 9.0$ Hz), 7.42 (1H, s), 7.49-7.50 (3H, m), 7.84 (2H, d, $J = 8.0$ Hz);

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 21.6, 55.3, 113.5, 127.8, 128.1, 129.01, 129.04, 129.5, 129.6, 129.9, 131.2, 135.5, 143.9, 154.1, 160.9.

2-Bromobenzophenone 4-Methylphenylsulfonylhydrazone (**3o**)

A mixture of 2-bromobenzoic acid (1.0 g, 5.0 mmol) and thionyl chloride (1.2 g, 10.0 mmol) in chloroform (10 mL) was heated under reflux for 3 h. After the excess thionyl chloride and chloroform had been evaporated, the crude benzoyl chloride was dissolved in benzene (4 mL) and added to a suspension of aluminum chloride (0.75 g, 5.5 mmol) in benzene (8 mL). After being heated under reflux for 6 h, the reaction mixture was quenched with diluted HCl (2 mL). The mixture was extracted with ethyl acetate (20 mL x 3) and the combined organic layer was washed with brine (5 mL), and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to give 2-bromobenzophenone (1.0 g, 77%) as a colorless oil.

IR ν (neat, cm⁻¹) 1670;

¹H-NMR (400 MHz, CDCl₃) δ 7.32-7.44 (3H, m), 7.48 (2H, t, J = 7.5 Hz), 7.59 (1H, d, J = 8.2 Hz), 7.63-7.65 (1H, m), 7.83 (2H, d, J = 7.5 Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 119.3, 127.0, 128.5, 128.8, 130.0, 131.0, 133.0, 133.5, 135.9, 140.4, 195.5;

MS m/z 262 (M⁺+2, 32.0), 260 (M⁺, 31.4), 105 (100);

HRMS calcd for C₁₃H₉⁷⁹BrO 259.9837, found 259.9811.

According to the general procedure, a mixture of 2-bromobenzophenone (1.5 g, 5.7 mmol), acetyl chloride (2.3 g, 28.7 mmol), and 4-methylphenylsulfonylhydrazide (2.1 g, 11.5 mmol) in ethanol (25 mL) was heated under reflux for 43 h. The crude material was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **3o** (1.8 g, 74%, single isomer) as a colorless solid.

mp 125-126°C (colorless prisms from hexane-chloroform, lit.³⁾ mp 126°C);

IR ν (Nujol, cm⁻¹) 3196, 1389, 1167;

¹H-NMR (400 MHz CDCl₃) δ 2.41 (3H, s), 7.10 (1H, d, J = 7.8 Hz), 7.20-7.49 (10H, m),

7.70 (1H, d, $J = 7.8$ Hz), 7.89 (2H, d, $J = 8.3$ Hz);

^{13}C -NMR (100 MHz, CDCl_3) δ 21.7, 121.4, 126.9, 128.0, 128.3, 128.6, 129.4, 129.9, 130.0, 131.5, 132.5, 133.6, 135.0, 135.2, 144.0, 152.0;

MS m/z 430 ($\text{M}^+ + 2$, 9.8), 428 (M^+ , 9.1), 193 (100);

HRMS calcd for $\text{C}_{20}\text{H}_{17}^{79}\text{BrN}_2\text{O}_2\text{S}$ 428.0194, found 428.0182;

Anal. calcd for $\text{C}_{20}\text{H}_{17}\text{BrN}_2\text{O}_2\text{S}$: C, 55.95; H, 3.99; N, 6.52. found: C, 55.83; H, 3.87; N, 6.59.

3. Results of Screenings

3-1. Effect of Pd and Cu

Entry	"Pd" (mol%)	"Cu" (mol%)	Yield (%) ^{a,b}
1	---	---	0 (99)
2	$\text{Pd}(\text{OAc})_2$ (100)	---	18
3	---	$\text{Cu}(\text{OAc})_2$ (100)	0
4	$\text{Pd}(\text{OAc})_2$ (100)	$\text{Cu}(\text{OAc})_2$ (100)	31
5	$\text{Pd}(\text{OAc})_2$ (50)	$\text{Cu}(\text{OAc})_2$ (100)	18 (16)
6	$\text{Pd}(\text{OAc})_2$ (10)	$\text{Cu}(\text{OAc})_2$ (100)	5
7	$\text{Pd}(\text{OAc})_2$ (10)	CuCl_2 (100)	trace
8	$\text{Pd}(\text{OAc})_2$ (10)	CuBr_2 (100)	trace
9	$\text{Pd}(\text{OAc})_2$ (50)	(Benzoquinone) (100)	11 (19)
10	PdCl_2 (50)	$\text{Cu}(\text{OAc})_2$ (100)	0
11	$\text{Pd}(\text{OAc})_2[(o\text{-Tol})_3\text{P}]_2$ (50)	$\text{Cu}(\text{OAc})_2$ (100)	trace
12	$\text{PdCl}_2(\text{dppf})$ (50)	$\text{Cu}(\text{OAc})_2$ (100)	trace
13	$\text{PdCl}_2(\text{dppp})$ (50)	$\text{Cu}(\text{OAc})_2$ (100)	0
14	$\text{PdCl}_2(\text{dppb})$ (50)	$\text{Cu}(\text{OAc})_2$ (100)	0
15	$\text{Pd}_2(\text{dba})_3$ (25)	$\text{Cu}(\text{OAc})_2$ (100)	0
16	$\text{PdCl}_2(\text{COD})_2$ (50)	$\text{Cu}(\text{OAc})_2$ (100)	5 (47)
17	$\text{PdCl}_2(\text{MeCN})_2$ (50)	$\text{Cu}(\text{OAc})_2$ (100)	0

^a Isolated yield. ^b Recovery yield of starting material in parentheses.

3-2. Effect of Solvents

Entry	Pd(OAc) ₂ (mol%)	Solvent	Yield (%) ^{a,b}
1	50	Toluene	18 (16)
2	50	Dioxane	19 (0)
3	50	EtOH	23 (53)
4	50	MeCN	73 (0)
5	50	Dichloromethane	15 (23)
6	50	Hexane	16 (trace)
7	50	AcOH	51 (0)
8	50	DMF	55 (0)
9^c	50	DMSO	95 (0)
10^c	30	DMSO	76 (trace)
11 ^c	30	DMSO/AcOH (9:1)	64 (0)

^a Isolated yield. ^b Recovery yield of starting material in parentheses. ^c Carried out in a round bottom flask.

3-3. Effect of Conditions (Temp./Time)

Entry	Pd(OAc) ₂ (mol%)	Conditions	Yield (%) ^{a,b}
1	30	120°C, 12 h	76 (trace)
2	30	100°C, 12 h	64 (12)
3	30	80°C, 12 h	76 (7)
4	30	50°C, 12 h	85 (0)
5	30	rt, 12 h	5 (70)

6	20	50°C, 12 h	58 (30)
7	15	50°C, 36 h	48 (39)
8	10	50°C, 12 h	14 (61)
9	10	50°C, 25 h	55 (41)
10	10	50°C, 62 h	44 (32)

^a Isolated yield. ^b Recovery yield of starting material in parentheses.

3-4. Effect of Oxidants

Entry	Oxidant	Yield (%) ^{a,b}
1	$\text{Cu}(\text{OAc})_2$	58 (30)
2	$\text{Cu}(\text{OAc})_2^c$	58 (32)
3	$\text{Cu}(\text{OTs})_2$	7 (66)
4	$\text{Cu}(\text{OMs})_2$	8 (64)
5	$\text{Cu}(\text{OTf})_2$	13 (60)
6	$\text{Cu}(\text{OCOCF}_3)_2 \cdot \text{H}_2\text{O}$	30 (50)
7	CuSt_2^d	39 (53)

^a Isolated yield. ^b Recovery yield of starting material in parentheses. ^c 200 mol%. ^d $\text{Cu}[\text{OCO}(\text{CH}_2)_{16}\text{Me}]_2$.

3-5. Effect of Concentration

Entry	Concentration	Yield (%) ^{a,b}
1	0.025	55 (35)
2	0.01	50 (39)
3	0.05	55 (41)
4	0.1	14 (66)

5	0.2	13 (50)
6	0.3	17 (34)

^a Isolated yield. ^b Recovery yield of starting material in parentheses.

3-6. Effect of Additives

Entry	$\text{Pd}(\text{OAc})_2$ (mol%)	$\text{Cu}(\text{OAc})_2$ (mol%)	Additive (mol%)	Yield (%) ^{a,b}
1	20	100	---	58 (30)
2	20	200	---	58 (32)
3	20	100	MS4Å (100 mg)	65 (20)
4	20	100	H ₂ O (1 drop)	57 (26)
5	20	100	Bu ₄ NBr (20)	43 (47)
6	20	200	Et ₃ N (300)	43 (44)
7	20	200	Ag ₂ O (100)	63 (32)
8	20	200	AgBr (200)	45 (35)
9	20	200	AgOAc (200)	62 (34)
10	20	200	AgClO ₄ (200)	93 (0)
11	5	200	AgClO ₄ (200)	23 (61)
12	20	200	AgNO ₃ (200)	94 (0)
13	5	200	AgNO ₃ (200)	28 (55)
14	20	200	AgBF ₄ (200)	90 (0)
15	5	200	AgBF ₄ (200)	23 (63)
16	20	200	Ag ₂ CO ₃ (200)	88 (0)
17	5	200	Ag ₂ CO ₃ (200)	14 (70)
18	20	200	AgOSO ₂ CF ₃ (200)	91 (0)
19	5	200	AgOSO ₂ CF ₃ (200)	20 (54)
20	20	200	AgOCOCF₃ (200)	94 (0)
21	5	200	AgOCOCF₃ (200)	58 (37)

^a Isolated yield. ^b Recovery yield of starting material in parentheses.

3-7. Optimization of Pd(OAc)₂/Cu(OAc)₂/AgOCOCF₃ System

Entry	Pd(OAc) ₂ / Cu(OAc) ₂ / AgOCOCF ₃ (mol%)	Yield (%) ^{a,b}
1	20 / 0 / 0	16 (74)
2 ^c	0 / 100 / 0	NR
3	0 / 0 / 200	NR
4	20 / 200 / 0	58 (32)
5	20 / 0 / 200	26 (68)
6	0 / 200 / 200	NR
7	20 / 200 / 200	94 (0)
8	10 / 200 / 200	87 (0)
9	5 / 200 / 200	58 (37)
10	10 / 100 / 100	33 (59)
11	10 / 100 / 200	90 (0)
12	20 ^c / 200 / 0	63 (20)

^a Isolated yield. ^b Recovery yield of starting material in parentheses. ^c Pd(OCOCF₃)₂ was used instead of Pd(OAc)₂.

1-(4-Methylphenylsulfonyl)-3-phenylindazole (2) (Table 1, Entry 11)

A mixture of **1** (50.0 mg, 0.14 mmol), Pd(OAc)₂ (3.2 mg, 0.014 mmol), Cu(OAc)₂ (25.9 mg, 0.14 mmol), and AgOCOCF₃ (63.0 mg, 0.29 mmol) in DMSO (2.9 mL) was stirred at 50°C for 12 h. The reaction mixture was extracted with ethyl acetate (5 mL x 3) and the combined organic layer was washed with brine (10 mL), and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to afford **2** (44.7 mg, 90%) as a colorless solid.

mp 115-116°C (colorless scales from hexane-ethyl acetate, lit.⁵⁾ mp 115-116°C);

IR ν (Nujol, cm^{-1}) 1366, 1174;

^1H -NMR (400 MHz, CDCl_3) δ 2.35 (3H, s), 7.15-7.53 (7H, m), 7.90-7.94 (5H, m), 8.26 (1H, d, $J = 8.5$ Hz);

^{13}C -NMR (100 MHz, CDCl_3) 21.5, 113.5, 121.6, 124.3, 124.4, 127.5, 128.2, 128.8, 129.0, 129.5, 129.7, 131.4, 134.6, 141.8, 145.2, 151.6.

MS m/z 348 (M^+ , 49.3), 193 (100);

HRMS calcd for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ 348.0932, found 348.0887.

4. General Procedure for Pd-Catalyzed C-H Amination of Hydrazones (Tables 2 and 3)

A mixture of hydrazone **3** (1.0 eq.), $\text{Pd}(\text{OAc})_2$ (10 mol%), $\text{Cu}(\text{OAc})_2$ (100 mol%), and AgOCOCF_3 (200 mol%) in DMSO (0.05 M) was stirred at 50°C. The reaction mixture was extracted with ethyl acetate (5 mL x 3) and the combined organic layer was washed with brine (10 mL), and dried over MgSO_4 . The solvent was evaporated and the residue was purified by silica gel column chromatography.

6-Methoxy-3-(4-methoxyphenyl)-1-(4-methylphenylsulfonyl)indazole (**4a**) (Table 2, Entry 1)

According to the general procedure, a mixture of **3a** (50.0 mg, 0.12 mmol), $\text{Pd}(\text{OAc})_2$ (2.7 mg, 0.012 mmol), $\text{Cu}(\text{OAc})_2$ (22.1 mg, 0.12 mmol), and AgOCOCF_3 (53.8 mg, 0.24 mmol) in DMSO (2.4 mL) was stirred for 24 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (3:1)] to afford **4a** (4.6 mg, 9%) and **3a** (15.4 mg, 31%).

mp 160-161°C (colorless prisms from hexane-ethyl acetate);

IR ν (film, cm^{-1}) 1611, 1175, 669;

^1H -NMR (400 MHz, CDCl_3) δ 2.35 (3H, s), 3.86 (3H, s), 3.96 (3H, s), 6.96 (1H, dd, $J = 8.6$, 2.2 Hz), 7.00 (2H, d, $J = 8.8$ Hz), 7.22 (2H, d, $J = 8.0$ Hz), 7.68 (1H, d, $J = 2.2$ Hz), 7.73 (1H, d, $J = 8.6$ Hz), 7.82 (2H, d, $J = 8.8$ Hz), 7.87 (2H, d, $J = 8.0$ Hz);

^{13}C -NMR (100 MHz, CDCl_3) δ 21.7, 55.4, 55.9, 95.7, 114.1, 115.3, 118.5, 122.3, 124.0, 127.5, 129.4, 129.6, 134.7, 143.6, 145.0, 151.4, 160.6, 161.0;

MS m/z 408 (M^+ , 46.3), 253 (100), 225 (33.6);

HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4\text{S}$ 408.1144, found 408.1129.

6-Methyl-3-(4-methylphenyl)-1-(4-methylphenylsulfonyl)indazole (4b) (Table 2, Entry 2)

According to the general procedure, a mixture of **3b** (50.0 mg, 0.13 mmol), $\text{Pd}(\text{OAc})_2$ (3.0 mg, 0.013 mmol), $\text{Cu}(\text{OAc})_2$ (24.0 mg, 0.13 mmol), and AgOCOCF_3 (58.4 mg, 0.26 mmol) in DMSO (2.6 mL) was stirred for 24 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to afford **4b** (26.0 mg, 52%) and **3b** (14.5 mg, 29%).

mp 158-159°C (colorless prisms from hexane-ethyl acetate);

IR ν (film, cm^{-1}) 1377, 1175, 679, 667;

^1H -NMR (400 MHz, CDCl_3) δ 2.34 (3H, s), 2.42 (3H, s), 2.56 (3H, s), 7.18 (1H, d, $J = 8.4$ Hz), 7.21 (2H, d, $J = 8.0$ Hz), 7.29 (2H, d, $J = 8.0$ Hz), 7.77 (1H, d, $J = 8.4$ Hz), 7.79 (2H, d, $J = 8.0$ Hz), 7.88 (2H, d, $J = 8.0$ Hz), 8.04 (1H, s);

^{13}C -NMR (100 MHz, CDCl_3) δ 21.4, 21.5, 22.0, 113.3, 121.2, 122.5, 126.2, 127.5, 128.0, 128.7, 129.4, 129.7, 134.9, 139.5, 139.7, 142.5, 145.0, 151.6;

MS m/z 376 (M^+ , 60.8), 221 (100), 193 (37.7);

HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ 376.1246, found 376.1225.

5-Methoxy-3-(3-methoxyphenyl)-1-(4-methylphenylsulfonyl)indazole (4c) (Table 2, Entry 3)

According to the general procedure, a mixture of **3c** (50.0 mg, 0.12 mmol), Pd(OAc)₂ (2.7 mg, 0.012 mmol), Cu(OAc)₂ (22.1 mg, 0.12 mmol), and AgOCOCF₃ (53.8 mg, 0.24 mmol) in DMSO (2.4 mL) was stirred for 16 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **4c** (48.0 mg, 96%).

mp 119-120°C (colorless plates from hexane-ethyl acetate);

IR ν (film, cm⁻¹) 1177, 812, 669;

¹H-NMR (400 MHz, CDCl₃) δ 2.34 (3H, s), 3.85 (3H, s), 3.88 (3H, s), 7.01 (1H, dt, J = 6.8, 2.4 Hz), 7.20-7.25 (4H, m), 7.40-7.42 (3H, m), 7.86 (2H, d, J = 8.4 Hz), 8.14 (1H, d, J = 8.8 Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 21.5, 55.4, 55.8, 102.0, 113.6, 114.5, 115.1, 119.7, 120.5, 125.2, 127.5, 129.7, 129.8, 132.8, 134.5, 137.1, 145.1, 151.4, 157.2, 159.9;

MS m/z 408 (M⁺, 91.3), 253 (100);

HRMS calcd for C₂₂H₂₀N₂O₄S 408.1144, found 408.1127.

5-Methoxy-1-(4-methylphenylsulfonyl)-3-(3-nitrophenyl)indazole (4d) (Table 2, Entry 4)

According to the general procedure, a mixture of **3d** (50.0 mg, 0.12 mmol), Pd(OAc)₂ (2.6 mg, 0.012 mmol), Cu(OAc)₂ (21.3 mg, 0.12 mmol), and AgOCOCF₃ (51.9 mg, 0.24 mmol) in DMSO (2.4 mL) was stirred for 19 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **4d** (49.1 mg, 99%) as a

colorless solid.

mp 194°C (colorless needles from hexane-ethyl acetate);

IR ν (film, cm^{-1}) 1537, 1379, 1348, 1236, 1177, 729, 671;

^1H -NMR (600 MHz, CDCl_3) δ 2.36 (3H, s), 3.88 (3H, s), 7.22 (1H, d, $J = 2.4$ Hz), 7.25-7.27 (3H, m), 7.70 (1H, t, $J = 7.8$ Hz), 7.89 (2H, d, $J = 8.4$ Hz), 8.18 (1H, d, $J = 9.6$ Hz), 8.24 (1H, dt, $J = 7.8, 1.2$ Hz), 8.31 (1H, ddd, $J = 7.8, 2.3, 1.2$ Hz), 8.71 (1H, s);

^{13}C -NMR (150 MHz, CDCl_3) δ 21.6, 55.9, 101.1, 114.7, 120.2, 122.8, 123.9, 124.4, 127.6, 129.9, 130.0, 133.4, 133.8, 134.3, 137.1, 145.5, 148.5, 148.6, 157.5;

MS m/z 423 (M^+ , 100), 268 (54.4);

Anal. calcd for $\text{C}_{21}\text{H}_{17}\text{N}_3\text{O}_5\text{S}$: C, 59.57; H, 4.05; N, 9.92. found: C, 59.37; H, 4.04; N, 9.76.

3-(3-Cyanophenyl)-5-methoxy-1-(4-methylphenylsulfonyl)indazole (4e) (Table 2, Entry 5)

According to the general procedure, a mixture of **3e** (50.0 mg, 0.12 mmol), $\text{Pd}(\text{OAc})_2$ (2.8 mg, 0.012 mmol), $\text{Cu}(\text{OAc})_2$ (22.4 mg, 0.12 mmol), and AgOCOCF_3 (54.5 mg, 0.25 mmol) in DMSO (2.5 mL) was stirred for 10 h. The crude product was purified by silica gel

column chromatography [hexane-ethyl acetate (2:1)] to afford **4e** (48.7 mg, 98%) as a colorless solid.

mp 187-189°C (colorless prisms from hexane-ethyl acetate);

IR ν (film, cm^{-1}) 2232, 1491, 1381, 1238, 1190, 1177, 1086, 883, 802, 752, 669;

^1H -NMR (600 MHz, C_6D_6) δ 1.68 (3H, s), 3.24 (3H, s), 6.58 (2H, d, $J = 8.1$ Hz), 6.78 (1H, t, $J = 7.4$ Hz), 6.81 (1H, s), 7.00 (1H, d, $J = 7.4$ Hz), 7.03 (1H, dd, $J = 9.0, 2.4$ Hz), 7.70 (1H, d, $J = 7.4$ Hz), 7.76 (1H, s), 7.88 (2H, d, $J = 8.1$ Hz), 8.28 (1H, d, $J = 9.0$ Hz);

^{13}C -NMR (150 MHz, C_6D_6) δ 21.0, 55.3, 101.9, 113.9, 115.2, 118.2, 120.1, 124.9, 128.3, 129.5, 129.8, 131.3, 131.8, 132.3, 133.5, 135.7, 137.9, 145.2, 148.9, 157.9;

MS m/z 403 (M^+ , 100), 248 (66.9);

HRMS calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_3\text{S}$ 403.0991, found 403.1003.

Anal. calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3\text{O}_3\text{S}$: C, 65.49; H, 4.25; N, 10.42. found: C, 65.62; H, 4.30; N, 10.38.

3-(3-Ethoxycarbonylphenyl)-5-methoxy-1-(4-methylphenylsulfonyl)indazole (4f)
(Table 2, Entry 6)

According to the general procedure, a mixture of **3f** (50.0 mg, 0.11 mmol), $\text{Pd}(\text{OAc})_2$

(2.5 mg, 0.011 mmol), Cu(OAc)₂ (20.1 mg, 0.11 mmol), and AgOCOCF₃ (48.8 mg, 0.22 mmol) in DMSO (3.0 mL) was stirred for 24 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (6:1)] to afford **4f** (20.3 mg, 41%) and **3f** (25.6 mg, 51%, A : B = 1 : 1).

mp 125°C (colorless plates from hexane-ethyl acetate);

IR ν (film cm⁻¹) 2928, 1720, 1381, 1232, 1177, 1078, 669;

¹H-NMR (600 MHz, C₆D₆) δ 0.97 (3H, t, J = 7.2 Hz), 1.61 (3H, s), 3.23 (3H, s), 4.09 (2H, q, J = 7.2 Hz), 6.50 (2H, d, J = 8.7 Hz), 7.04-7.05 (2H, m), 7.10 (1H, t, J = 8.1 Hz), 7.91 (2H, d, J = 8.7 Hz), 7.96 (1H, d, J = 8.1 Hz), 8.10 (1H, d, J = 8.1 Hz), 8.31 (1H, dd, J = 8.7, 0.9 Hz), 8.74 (1H, s);

¹³C-NMR (600 MHz, C₆D₆), δ 14.1, 21.0, 55.0, 61.0, 101.7, 115.1, 120.1, 125.4, 128.3, 129.2, 129.4, 129.7, 130.4, 131.8, 132.4, 132.7, 135.5, 137.9, 144.8, 150.4, 157.7, 165.7;

MS m/z 450 (M⁺, 100);

HRMS calcd for C₂₄H₂₂N₂O₅S 450.1249, found 450.1242.

5-Hydroxy-1-(4-methylphenylsulfonyl)-3-phenylindazole (**4g-a**) (Table 3, Entry 1)

According to the general procedure, a mixture of **3g** (50.0 mg, 0.14 mmol), Pd(OAc)₂ (3.1 mg, 0.014 mmol), Cu(OAc)₂ (24.8 mg, 0.14 mmol), and AgOCOCF₃ (60.3 mg, 0.27 mmol) in DMSO (2.7 mL) was stirred for 12 h (80°C.) The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (2:1)] to afford **4g-a** (37.2 mg, 75%) as a colorless oil.

IR ν (film, cm⁻¹) 3481, 1373, 1175, 870, 733, 702, 669;

¹H-NMR (400 MHz, CDCl₃) δ 2.29 (3H, s), 5.47 (1H, br.s), 7.15-7.17 (3H, m), 7.25 (1H, d, *J* = 2.0 Hz), 7.34-7.36 (3H, m), 7.74-7.76 (2H, m), 7.82 (2H, d, *J* = 8.4 Hz), 8.06 (1H, d, *J* = 8.8 Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 21.6, 105.5, 114.4, 119.6, 125.4, 127.4, 127.9, 128.6, 129.4, 129.7, 131.0, 134.1, 136.8, 145.2, 151.6, 153.3;

MS *m/z* 364 (M⁺, 98.9), 209 (100), 181 (39.2);

HRMS calcd for C₂₀H₁₆N₂O₃S 364.0881, found 364.0865.

5-Amino-1-(4-methylphenylsulfonyl)-3-phenylindazole (**4h-a**) (Table 3, Entry 2)

According to the general procedure, a mixture of **3h** (50.0 mg, 0.14 mmol), Pd(OAc)₂ (3.1 mg, 0.014 mmol), Cu(OAc)₂ (24.9 mg, 0.14 mmol), and AgOCOCF₃ (60.4 mg, 0.27 mmol) in DMSO (2.7 mL) was stirred for 18 h (80°C). The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (2:1)] to afford **4h-a** (32.9 mg, 66%) as a brown oil.

IR ν (film, cm⁻¹) 3462, 3377, 1626, 1371, 1175, 756, 700, 669;

¹H-NMR (400 MHz, CDCl₃) δ 2.31 (3H, s), 3.81 (2H, br.s), 6.96 (1H, d, *J* = 8.8 Hz), 7.06 (1H, s), 7.18 (2H, d, *J* = 8.0 Hz), 7.42-7.47 (3H, m), 7.83 (4H, m), 8.01 (1H, d, *J* = 8.8 Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 21.6, 104.2, 114.4, 119.3, 125.7, 127.4, 128.0, 128.6, 129.2, 129.6, 131.6, 134.4, 136.3, 143.7, 144.8, 151.2;

MS *m/z* 363 (M⁺, 80.0), 208 (100);

HRMS calcd for C₂₀H₁₇N₃O₂S 363.1041, found 363.1033.

5-Methoxy-1-(4-methylphenylsulfonyl)-3-phenylindazole (4i-a)⁵ and 3-(3-Methoxyphenyl)-1-(4-methylphenylsulfonyl)indazole (4i-b) (Table 3, Entry 3)

According to the general procedure, a mixture of **3i** (50.0 mg, 0.13 mmol, A : B = 1.3 : 1), Pd(OAc)₂ (2.9 mg, 0.013 mmol), Cu(OAc)₂ (23.9 mg, 0.13 mmol), and AgOCOCF₃ (58.1 mg, 0.26 mmol) in DMSO (2.6 mL) was stirred for 21 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **4i-a** (54%) and **4i-b** (27%) as an inseparable mixture (40.4 mg, 81%), and **3i** (1.5 mg, 3% as B). The yields of **4i-a** and **4i-b** were determined by ¹H-NMR spectrum.

4i-a⁵+**4i-b**: IR ν (film, cm⁻¹) 1377, 1236, 1190, 1177, 669;

¹H-NMR/¹³C-NMR: only a ¹H-NMR spectrum of the mixture of **4i-a** and **4i-b** was obtained;

MS *m/z* 378 (M⁺, 94.4), 223 (100);

HRMS calcd for C₂₁H₁₈N₂O₃S 378.1038, found 378.1020.

Anal. calcd for C₂₁H₁₈N₂O₃S: C, 66.65; H, 4.79; N, 7.40. found: C, 66.54; H, 4.93; N, 7.31.

5-Chloro-1-(4-methylphenylsulfonyl)-3-phenylindazole (4j-a) and 3-(3-Chlorophenyl)-1-(4-methylphenylsulfonyl)indazole (4j-b) (Table 3, Entry 4)

According to the general procedure, a mixture of **3j** (50.0 mg, 0.13 mmol, major isomer :

minor isomer = 2 : 1), Pd(OAc)₂ (2.9 mg, 0.013 mmol), Cu(OAc)₂ (23.6 mg, 0.13 mmol), and AgOCOCF₃ (57.4 mg, 0.26 mmol) in DMSO (2.6 mL) was stirred for 20 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to afford **4j-a** (9.4 mg, 19%) and **4j-b** (32.1 mg, 65%).

4j-a: mp 128-129°C (colorless prisms from hexane-ethyl acetate, lit.⁶⁾ mp 119-121°C);

IR ν (film, cm⁻¹) 1385, 1192, 1175, 799, 760, 677, 665;

¹H-NMR (400 MHz, CDCl₃) δ 2.36 (3H, s), 7.25 (2H, d, J = 8.0 Hz), 7.49-7.55 (4H, m), 7.85-7.90 (5H, m), 8.21 (1H, d, J = 8.8 Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 21.6, 114.7, 121.1, 125.4, 127.7, 128.2, 128.9, 129.6, 129.8, 129.9, 130.3, 130.9, 134.4, 140.3, 145.5, 150.9;

MS m/z 384 (M⁺+2, 44.8), 382 (M⁺, 100), 227 (96.4);

Anal. calcd for C₂₀H₁₅ClN₂O₂S: C, 62.74; H, 3.95; N, 7.32. found: C, 62.58; H, 4.09; N, 7.27.

4j-b: mp 163-164°C (colorless needles from hexane-ethyl acetate);

IR ν (film, cm⁻¹) 1381, 1190, 1177, 692, 667;

¹H-NMR (400 MHz, CDCl₃) δ 2.36 (3H, s), 7.24 (2H, d, J = 8.4 Hz), 7.39 (1H, t, J = 7.6 Hz), 7.43-7.44 (2H, m), 7.60 (1H, td, J = 7.8, 0.8 Hz), 7.79-7.81 (1H, m), 7.90-7.92 (4H, m), 8.28 (1H, d, J = 8.4 Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 21.7, 113.6, 121.2, 123.8, 124.6, 126.2, 127.5, 128.1, 129.2, 129.5, 129.8, 130.0, 133.1, 134.5, 134.7, 141.7, 145.3, 150.0;

MS m/z 384 (M⁺+2, 41.9), 382 (M⁺, 100), 318 (72.8), 227 (89.0);

Anal. calcd for C₂₀H₁₅ClN₂O₂S: C, 62.74; H, 3.95; N, 7.32. found: C, 62.87; H, 3.95; N, 7.33.

5-Bromo-1-(4-methylphenylsulfonyl)-3-phenylindazole (**4k-a**) and **3-(3-Bromophenyl)-1-(4-methylphenylsulfonyl)indazole** (**4k-b**) (Table 3, Entry 5)

According to the general procedure, a mixture of **3k** (0.10 g, 0.23 mmol), Pd(OAc)₂ (5.2 mg, 0.023 mmol), Cu(OAc)₂ (42.3 mg, 0.23 mmol), and AgOCOCF₃ (0.10 g, 0.47 mmol) in DMSO (4.7 mL) was stirred for 17 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (19:1)] to afford **4k-a** (33.8 mg, 34%), **4k-b** (44.7 mg, 45%), and **3k** (8.8 mg, 9%).

4k-a: mp 109-110°C (colorless plates from hexane-ethyl acetate);

IR ν (film, cm⁻¹) 1383, 1192, 1175, 673;

¹H-NMR (400 MHz, CDCl₃) δ 2.36 (3H, s), 7.25 (2H, d, J = 8.2 Hz), 7.48-7.54 (3H, m), 7.66 (1H, dd, J = 9.2, 1.4 Hz), 7.85 (2H, dd, J = 7.8, 1.8 Hz), 7.89 (2H, d, J = 8.2 Hz), 8.05 (1H, d, J = 1.4 Hz), 8.15 (1H, d, J = 9.2 Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 21.7, 114.9, 117.7, 124.2, 125.8, 127.5, 128.1, 128.8, 129.7, 129.8, 130.7, 132.0, 134.2, 140.5, 145.5, 150.7;

MS m/z 428 (M⁺+2, 100), 426 (M⁺, 96.4), 364 (50.2), 362 (50.7), 273 (95.5), 271 (95.5), 163 (98.7);

Anal. calcd for C₂₀H₁₅BrN₂O₂S: C, 56.21; H, 3.54; N, 6.56. found: C, 56.21; H, 3.49; N, 6.60.

4k-b: mp 159-160°C (colorless needles from hexane-ethyl acetate);

IR ν (film, cm⁻¹) 1381, 1190, 1177, 750, 685, 667;

¹H-NMR (400 MHz, CDCl₃) δ 2.35 (3H, s), 7.24 (2H, d, J = 8.0 Hz), 7.35-7.40 (2H, m), 7.58-7.61 (2H, m), 7.84 (1H, d, J = 8.0 Hz), 7.88-7.92 (3H, m), 8.06 (1H, s), 8.28 (1H, d, J = 8.4 Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 21.7, 113.6, 121.2, 122.8, 123.8, 124.5, 126.7, 127.5, 129.2, 129.8, 130.2, 130.9, 132.4, 133.3, 134.4, 141.7, 145.3, 149.9;

MS m/z 428 (M⁺+2, 100), 426 (M⁺, 95.2), 364 (61.3), 362 (61.3), 273 (86.2), 271 (86.7), 163 (77.7);

Anal. calcd for C₂₀H₁₅BrN₂O₂S: C, 56.21; H, 3.54; N, 6.56. found: C, 56.21; H, 3.71; N, 6.51.

1-(4-Methylphenylsulfonyl)-3-(3-nitrophenyl)indazole (4l-b) (Table 3, Entry 6)

4l-b

According to the general procedure, a mixture of **3l** (0.10 g, 0.25 mmol), Pd(OAc)₂ (5.7 mg, 0.025 mmol), Cu(OAc)₂ (45.9 mg, 0.25 mmol), and AgOCOCF₃ (0.11 g, 0.51 mmol) in DMSO (5.1 mL) was stirred for 24 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **4l-b** (32.1 mg, 32%) and **3l** (26.0 mg, 26%).

mp 233-234°C (colorless prisms from hexane-ethyl acetate);

IR ν (film, cm⁻¹) 1375, 1348, 1178;

¹H-NMR (400 MHz, CDCl₃) δ 2.37 (3H, s), 7.26-7.28 (2H, m), 7.45 (1H, t, J = 7.7 Hz), 7.64 (1H, t, J = 7.7 Hz), 7.70 (1H, t, J = 8.3 Hz), 7.93 (2H, d, J = 8.4 Hz), 7.94 (1H, d, J = 8.3 Hz), 8.29-8.34 (3H, m), 8.76 (1H, t, J = 2.0 Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 21.7, 113.7, 120.9, 122.9, 123.5, 124.0, 124.9, 127.6, 129.4, 129.9, 133.2, 133.9, 134.4, 141.8, 145.6, 148.5, 148.8;

MS m/z 393 (M⁺, 100), 329 (73.3);

Anal. calcd for C₂₀H₁₅N₃O₄S: C, 61.06; H, 3.84; N, 10.68. found: C, 61.07; H, 3.86; N, 10.49.

1-(4-Methylphenylsulfonyl)-3-(4-nitrophenyl)indazole (4m-b) (Table 3, Entry 7)

4m-b

According to the general procedure, a mixture of **3m** (50.0 mg, 0.13 mmol, $E : Z = 1 : 1.2$), Pd(OAc)₂ (2.8 mg, 0.013 mmol), Cu(OAc)₂ (23.0 mg, 0.13 mmol), and AgOCOCF₃

(55.9 mg, 0.25 mmol) in DMSO (2.5 mL) was stirred for 24 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **4m-b** (13.2 mg, 27%) and **3m** (13.6 mg, 27%, *E* : *Z* = 1.2 : 1).

mp 237-238°C (light yellow prisms from ethyl acetate);

IR ν (film, cm^{-1}) 1522, 1348, 1192, 681;

^1H -NMR (400 MHz, CDCl_3) δ 2.37 (3H, s), 7.27 (2H, d, J = 8.4 Hz), 7.44 (1H, t, J = 8.2 Hz), 7.63 (1H, t, J = 8.2 Hz), 7.92 (1H, d, J = 8.2 Hz), 7.93 (2H, d, J = 8.4 Hz), 8.12 (2H, d, J = 9.0 Hz), 8.31 (1H, d, J = 8.2 Hz), 8.36 (2H, d, J = 9.0 Hz);

^{13}C -NMR (100 MHz, CDCl_3) δ 21.7, 113.7, 121.0, 123.5, 124.0, 124.9, 127.6, 128.8, 129.4, 129.8, 134.3, 137.7, 141.7, 145.6, 148.1, 148.7;

MS m/z 393 (M^+ , 100), 329 (59.5), 155 (63.8);

HRMS calcd for $\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}_4\text{S}$ 393.0783, found 393.0786.

6-Methoxy-1-(4-methylphenylsulfonyl)-3-phenylindazole (4n-a) and 3-(4-Methoxyphenyl)-1-(4-methylphenylsulfonyl)indazole (4n-b) (Table 3, Entry 8)

According to the general procedure, a mixture of **3n** (50.0 mg, 0.13 mmol, *E* : *Z* = 1 : 0.04), $\text{Pd}(\text{OAc})_2$ (2.9 mg, 0.013 mmol), $\text{Cu}(\text{OAc})_2$ (23.9 mg, 0.13 mmol), and AgOCOCF_3 (58.1 mg, 0.26 mmol) in DMSO (2.6 mL) was stirred for 24 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **4n-a** (3.0 mg, 6%), **4n-b** (8.0 mg, 16%), and **3n** (28.3 mg, 57%, *E* : *Z* = 1 : 1).

4n-a: mp 155-156°C (colorless plates from hexane-ethyl acetate);

IR ν (film, cm^{-1}) 1614, 1366, 1173, 671;

^1H -NMR (400 MHz, CDCl_3) δ 2.35 (3H, s), 3.97 (3H, s), 6.97 (1H, dd, J = 9.0, 2.4 Hz), 7.23 (2H, d, J = 8.2 Hz), 7.44-7.52 (3H, m), 7.69 (1H, d, J = 2.4 Hz), 7.75 (1H, d, J = 9.0

Hz), 7.85-7.90 (4H, m);

^{13}C -NMR (100 MHz, CDCl_3) δ 21.6, 55.8, 95.6, 115.5, 118.5, 122.3, 127.6, 128.2, 128.8, 129.5, 129.8, 131.5, 134.7, 143.7, 145.2, 151.6, 161.1;

MS m/z 378 (M^+ , 62.9), 223 (100), 195 (56.5);

HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$ 378.1039, found 378.1016.

4n-b: 143-145°C (colorless plates from hexane-ethyl acetate, lit.⁵⁾ mp 143-145°C);

IR ν (film, cm^{-1}) 1371, 1256, 1177;

^1H -NMR (400 MHz, CDCl_3) δ 2.31 (3H, s), 3.85 (3H, s), 7.01 (2H, d, $J = 8.8$ Hz), 7.20 (2H, d, $J = 8.0$ Hz), 7.34 (1H, t, $J = 8.0$ Hz), 7.55 (1H, t, $J = 8.0$ Hz), 7.84-7.89 (5H, m), 8.24 (1H, d, $J = 8.0$ Hz);

^{13}C -NMR (100 MHz, CDCl_3) δ 21.6, 55.4, 113.5, 114.2, 121.6, 123.9, 124.2, 124.3, 127.5, 128.9, 129.5, 129.6, 134.6, 141.8, 145.0, 151.4, 160.6;

MS m/z 378 (M^+ , 75.2), 223 (100);

HRMS calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$ 378.1038, found 378.1043.

6-Methoxy-1-(4-methylphenylsulfonyl)-3-phenylindazole (4n-a) and 3-(4-Methoxyphenyl)-1-(4-methylphenylsulfonyl)indazole (4n-b) (Table 3, Entry 9)

According to the general procedure, a mixture of **3n** (40.0 mg, 0.11 mmol, $E : Z = 0.31 : 1$), $\text{Pd}(\text{OAc})_2$ (2.4 mg, 0.011 mmol), $\text{Cu}(\text{OAc})_2$ (19.1 mg, 0.11 mmol), and AgOCOCF_3 (46.4 mg, 0.21 mmol) in DMSO (2.1 mL) was stirred for 24 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **4n-a** (5.5 mg, 14%), **4n-b** (6.9 mg, 17%), and **3n** (20.6 mg, 52%, $E : Z = 1 : 1.3$).

1-(4-Methylphenylsulfonyl)-3-phenylindazole (4o-c=2) (Table 3, Entry 10)

According to the general procedure, a mixture of **3o** (0.10 g, 0.23 mmol), Pd(OAc)₂ (5.2 mg, 0.023 mmol), Cu(OAc)₂ (42.3 mg, 0.23 mmol), and Ag(OCOCF₃) (0.10 g, 0.47 mmol) in DMSO (4.7 mL) was stirred for 14 h. The crude product was purified by silica gel column chromatography [hexane-ethyl acetate (4:1)] to afford **2** (79.8 mg, 98%) as a colorless solid.

5. Synthesis of 3-Alkylindazole (Scheme 1)

2,2-Dimethylpropiophenone 4-Methylphenylsulfonylhydrazone (**5**)

Acetyl chloride (0.15 g, 1.9 mmol) was slowly added to ethanol (1 mL) at 0°C and stirred for 30 min at the same temperature. The reaction mixture was warmed to room temperature and stirred for another 30 min. The resulting mixture and a solution of the 2,2-dimethylpropiophenone (62.1 mg, 0.38 mmol) in ethanol (2 mL) were added to a solution of 4-methylphenylsulfonylhydrazide (0.14 g, 0.77 mmol) in ethanol (2 mL) and heated under reflux for 2 h. The mixture was treated with saturated aqueous NaHCO₃ (5 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with brine (10 mL) and dried over MgSO₄. The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to afford 2,2-dimethylpropiophenone 4-methylphenylsulfonylhydrazone **5** (99.5 mg, 79%, single isomer) as a colorless solid.

mp 159-160°C (colorless needles from hexane-ethyl acetate, lit.⁶⁾ mp 156-158°C);

IR ν (film, cm⁻¹) 3223, 1169;

¹H-NMR (400 MHz, CDCl₃) δ 1.06 (9H, s), 2.45 (3H, s), 6.80-6.82 (2H, m), 6.88 (1H, s),

7.33 (2H, d, $J = 8.4$ Hz), 7.40-7.41 (3H, m), 7.77 (2H, d, $J = 8.4$ Hz);
 ^{13}C -NMR (100 MHz, CDCl_3) δ 21.5, 27.9, 38.4, 127.3, 127.8, 129.1, 129.2, 131.6, 135.3, 143.8, 165.4;
MS m/z 330 (M^+ , 8.9), 119 (100);
HRMS calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$ 330.1402, found 330.1395.

3-*tert*-Butyl-1-(4-methylphenylsulfonyl)indazole

A mixture of 2,2-dimethylpropiophenone 4-methylphenylsulfonylhydrazone (50 mg, 0.15 mmol), $\text{Pd}(\text{OAc})_2$ (3.4 mg, 0.015 mmol), $\text{Cu}(\text{OAc})_2$ (27.5 mg, 0.15 mmol), and AgOCOCF_3 (66.8 mg, 0.30 mmol) in DMSO (3.0 mL) was stirred at 50°C for 24 h. The reaction mixture was extracted with ethyl acetate (5 mL x 3) and the combined organic layer was washed with brine (10 mL), and dried over MgSO_4 . The solvent was evaporated and the residue was purified by silica gel column chromatography [hexane-ethyl acetate (9:1)] to afford 3-*tert*-butyl-1-(4-methylphenylsulfonyl)indazole **6** (32.9 mg, 66%), and hydrazone **5** (16.0 mg, 32%).

mp $146\text{--}147^\circ\text{C}$ (colorless prisms from hexane-ethyl acetate);
IR ν (film, cm^{-1}) 1377, 1177, 712, 665;
 ^1H -NMR (400 MHz, CDCl_3) δ 1.45 (9H, s), 2.33 (3H, s), 7.19 (2H, d, $J = 8.0$ Hz), 7.26 (1H, ddd, $J = 8.1, 7.2, 0.8$ Hz), 7.48 (1H, ddd, $J = 8.4, 7.2, 1.2$ Hz), 7.78-7.82 (3H, m), 8.18 (1H, dd, $J = 8.4, 0.8$ Hz);
 ^{13}C -NMR (100 MHz, CDCl_3) δ 21.6, 29.4, 34.3, 113.7, 122.3, 123.3, 124.2, 127.4, 128.3, 129.4, 134.4, 142.1, 144.7, 161.1;
MS m/z 328 (M^+ , 74.1), 313 (100);
HRMS calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ 328.1246, found 328.1232;
Anal. calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: C, 65.83; H, 6.14; N, 8.53. found: C, 65.83; H, 6.17; N, 8.55.

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