Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information (I): Procedures and Physical Data

CuI Catalyzed Sulfonylation of Organozinc Reagents with Sulfonyl Halides

Ying Fu,*[,a] Wenbo Zhu,[a] Xingling Zhao,[a] Helmut Hügel,[b] Zhouqiang Wu,[a] Yuhu Su,[a] Zhengyin Du,[a*] Danfeng Huang[a] and Yulai Hu[a]

†. *College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu 730070, P. R. China.*

‡. *Health Innovations Research Institute & School of Applied Sciences, RMIT University Melbourne, 3001 Australia.*

fuying@iccas.ac.cn and zhengyin_du@nwnu.edu.cn

General methods:

All the reactions were carried out under argon or nitrogen atmosphere. All glassware were dried in oven and kept in a vacuum dryer with fresh phosphorus pentoxide. THF was dried by distillation from sodium benzophenone under nitrogen and stored under nitrogen. Organic sulfonyl chlorides were dried in a vacuum dryer with fresh phosphorus pentoxide overnight before use. NEt_3 and N,N,N',N'-tetramethylethylenediamine (TMEDA) were distilled from calcium hydride and stored under a nitrogen atmosphere. Organic halides were all dried by $CaCl_2$ before use. The magnesium ribbon is cleaned by sand paper in glove box under nitrogen atmosphere, cut into pieces and used immediately.

^{1}H NMR (400 MHz), and ^{13}C NMR (100 MHz) were recorded on Bruker AV400 NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) with TMS as an internal standard. Column chromatography was performed on silica gel 300-400 mesh. Analytical thin layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). IR spectra were recorded as KBr disks on an Alpha Centauri FT-IR spectrometer.

General Procedure A: preparation of aryl and alkyl zinc reagents

To a dry, three-necked 100 mL round-bottomed flask equipped with an argon inlet, a thermometer, and an addition funnel was added magnesium turnings (0.36 g, 15.0 mmol), $ZnCl_2$ (1.36 g, 10.0 mmol) and a small piece of iodine added. After changed the air in the reaction system to argon or nitrogen atmosphere, 5 mL of THF was added and the reaction mixture was stirred until the brown colour disappeared. Organo halides (12.0 mmol) in THF (10 mL) was then added under ice-water bath and the reaction mixture was stirred overnight, allowing the reaction temperature raise to room temperature.

General Procedure B: Preparation of benzyl zinc chlorides

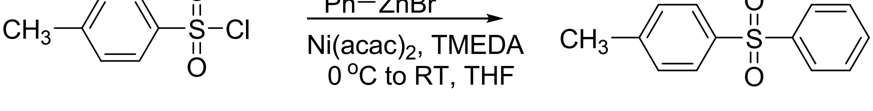
To a dry, three-necked 100 mL round-bottomed flask equipped with an argon inlet, a thermometer, and an addition funnel was added zinc powder (0.99 g, 15.0 mmol). After changed the air to argeon, 1,2-Dibromoethane (150 mg) was then added, and the mixture was heated until evolution of soaplike bubbles of ethylene and darkening of the zinc surface indicated activation. After the reaction mixture cooled to room temperature, a solution of the benzylic chloride (10 mmol) in 10 mL of THF was then added dropwise (1 drop/5-10 s). The reaction mixture was stirred at 30-40 °C until TLC analysis showed that the starting material was completely consumed (4-12 h).

General Procedure C: CuI catalyzed nucleophilic addition of organozinc reagents to sulfonyl halides

The organozinc reagent prepared above was added to an ice-water bath cooled solution of sulfonyl halides (5.0 mmol), CuI (0.19 g, 1.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol) in THF (20 mL). After all of the organozinc reagent was added, the reaction mixture was then stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. Sulfones were obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. All products were characterized by IR, ^1H NMR, and ^{13}C NMR.

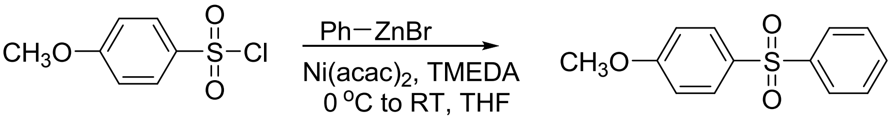
Synthesis and characterization of products

3a: 4-Tolyl phenyl sulfone



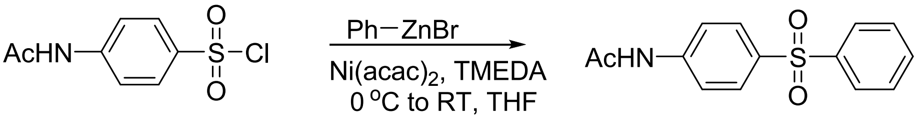
According to general procedure C: The previously prepared phenyl zinc bromide reagent was slowly added to an ice-water bath cooled solution of 4-toluene sulfonyl chloride (0.95g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (20 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours and then quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.05 g, 4.5 mmol, 90 %) after purification on silica gel (10:1~3:1 petroleum ether : EtOAc). Mp : 121-123 ^{o}C (lit[1]: 121 ^{o}C). IR (KBr) ν (cm^{-1}): 3128, 2961, 2858, 1592, 1491, 1447, 1399, 1306, 1151, 1105, 814, 727, 686. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.40 (s, 3H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.49 (tdd, *J* = 7.2, 2.4, 0.8 Hz, 2H), 7.55 (tdd, *J* = 7.2, 2.4, 1.2 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.93 (ddd, *J* = 8.0, 2.4, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.57, 127.47, 127.69, 129.20, 129.90, 132.98, 138.59, 141.93, 144.15.

3b: 1-methoxy-4-(phenylsulfonyl)benzene[1]



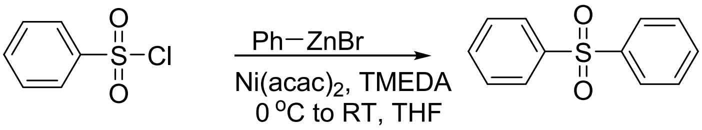
According to general procedure B: The previously prepared phenyl zinc bromide reagent was slowly added to an ice-water bath solution of 4-toluene sulfonyl chloride (1.03 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.08 g, 4.35 mmol, 87 %) after purification on silica gel (10:1~3:1 petroleum ether : EtOAc). mp 90-92 ^{o}C (lit:[2] 92-93^{o}C). IR (KBr) *ν* (cm^{-1}): 2925, 2853, 1591, 1497, 1445, 1316, 1300, 1264, 115, 1106, 835, 802, 730. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 3.84 (s, 3H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.45-7.58 (m, 3H), 7.86-7.94 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 55.60, 114.15, 127.25, 129.15, 129.83, 132.79, 133.03, 142.28, 163.31.

3c: N-(4-(phenylsulfonyl)phenyl)acetamide



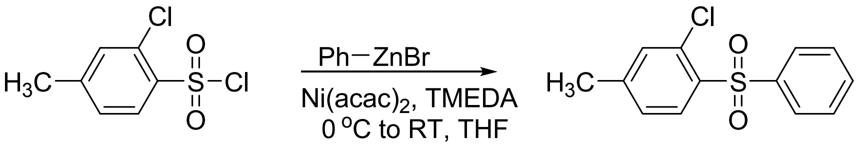
According to general procedure B: The previously prepared phenyl zinc bromide reagent was slowly added to an ice-water bath solution of solution of 4-toluene sulfonyl chloride (1.03 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.20 g, 4.85 mmol, 97 %) after purification on silica gel (1:1~3:1 petroleum ether : EtOAc). Mp: mp: 194-196 °C (lit[3]: 191-193 °C). IR (KBr) ν (cm^{-1}): 3292, 3032, 1707, 1589, 1526, 1402, 1315, 1302, 1259, 1151, 1107, 840,738, 688, 621. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.19 (s, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 6.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.66 (s, 1H, NH), 7.86 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 24.63, 119.56, 127.37, 128.91, 129.28, 133.13, 135.90, 141.68, 142.53, 168.82.

3d: diphenyl sulfone



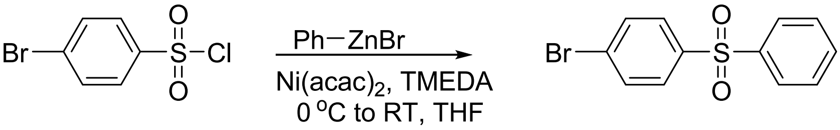
According to general procedure B: The previously prepared phenyl zinc bromide reagent was slowly added to an ice-water bath cooled solution of benzenesulfonyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.95 g, 4.35 mmol, 87 %) after purification on silica gel (5:1~3:1 petroleum ether : EtOAc). m.p.: 124-126°C (lit[2]: 122-124 °C). IR (KBr) *ν* (cm^{-1}): 2992, 2853, 2224, 1647, 1595, 1444, 1401, 1314, 1280, 1140, 1112, 1071, 928, 857. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.46-7.60 (m, 6H), 7.93-7.97 (m, 4H),. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 127.61, 129.23, 133.14, 141.53.

3e: 4-chloro-1-methyl-2-(phenylsulfonyl)benzene



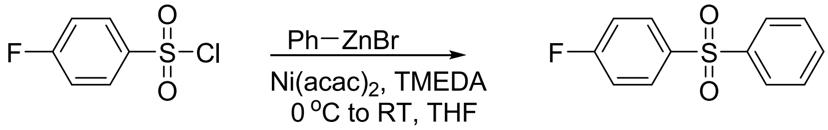
According to general procedure B: The previously prepared phenyl zinc bromide reagent was slowly added to an ice-water bath cooled solution of 2-chloro-4-methylbenzene-1-sulfonyl chloride (1.12 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.09 g, 4.10 mmol, 82 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). Mp: 89-91 °C (lit[4]: 90-91 °C). IR (KBr) *ν* (cm^{-1}): 2926, 2855, 1491, 1460, 1412, 1306, 1161, 1122, 891, 845, 766; ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 2.41 (s, 3H), 7.23 (d, J = 1.6 Hz, 1H), 7.40 (ddd, J = 8.8, 2.4, 0.8 Hz, 1H), 7.51 (tq, J = 7.6, 1.2 Hz, 2H), 7.60 (tt, J = 7.6, 1.2 Hz, 1H), 7.83-7.87 (m, 2H), 8.16 (d, J = 8.8 Hz, 1H).^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 20.06, 126.66, 127.63, 129.13, 130.92, 132.51, 133.26, 137.40, 139.84, 140.83.

3f: 4-Bromodiphenyl sulfone



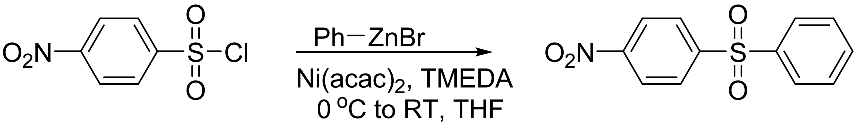
According to general procedure B: The previously prepared phenyl zinc bromide reagent was slowly added to an ice-water bath cooled solution of 4-bromobenzenesulfonyl chloride (1.28 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH$_4$Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.28 g, 4.30 mmol, 86 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). Mp: 102-104 °C. (lit[2]: 98-99 °C). IR (KBr) ν(cm^{-1}): 2924, 2854, 1570, 1470, 1443, 1317, 1155, 1104, 1064, 1003, 743, 686.^{1}H NMR (CDCl$_3$) δ (ppm): 7.52 (tt, J = 7.6, 1.2 Hz, 2H), 7.59 (tt, J = 7.6, 1.2 Hz, 1H), 7.65 (dt, J = 8.4, 2.0 Hz, 2H), 7.80 (dt, J = 8.8, 2.0 Hz, 2H), 7.91-7.95 (m, 2H). ^{13}C NMR (CDCl$_3$) δ (ppm): 127.62, 128.44, 129.16, 129.39, 132.57, 133.43, 140.62, 141.10.

3g: 4-Fluorodiphenyl sulfone



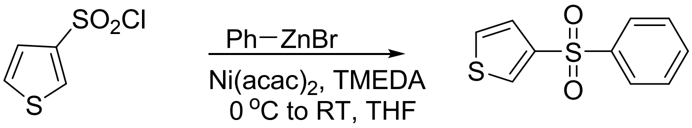
According to general procedure B: The previously prepared phenyl zinc bromide reagent was slowly added to an ice-water bath cooled solution of 4-fluorobenzenesulfonyl chloride (0.97 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH$_4$Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.91 g, 3.85 mmol, 77 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). Mp: 110-112 °C (lit[2]: 112-113 °C). IR (KBr) ν(cm^{-1}): 2925, 2865, 1585, 1492, 1447, 1403, 1317, 1152., 1101, 839. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.18 (tt, J = 8.8, 2.0 Hz, 2H), 7.52 (tt, J = 7.2, 2.0 Hz, 2H), 7.58 (tt, J = 7.6, 2.0 Hz, 1H), 7.91-8.0 (m, 4H). ^{13}C NM**R (**100 MHz, CDCl$_3$) δ (ppm): 116.58 (d, *J* = 22.6 Hz, 2C), 127.54, 129.35, 130.40, 130.50, 133.30, 137.61, 141.41, 165.40 (d, *J* = 254.3 Hz, CF).

3h: 4-Nitrodiphenyl sulfone



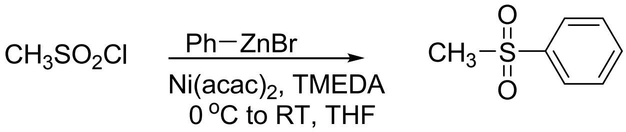
According to general procedure B: The previously prepared phenyl zinc bromide reagent was slowly added to an ice-water bath cooled solution of 4-nitrobenzenesulfonyl chloride (1.11 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.95 g, 360 mmol, 72 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). Mp: 139-142 °C (lit[2]: 143-145 °C). IR (KBr) ν (cm^{-1}): 2926, 2866, 1607, 1528, 1450, 1396, 1355, 1154, 1103, 759. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56 (tdd, *J* = 7.6, 2.8, 1.6 Hz, 2H), 7.65 (tt, *J* = 7.6, 1.6 Hz, 1H), 7.97 (t, *J* = 1.6 Hz, 1H), 7.98-8.00 (m, 1H). ^{13}C **NMR** (100Hz, $CDCl_3$): 124.51, 128.01, 128.95, 129.67, 134.11, 139.97, 147.33, 150.30.

3i: 3-thienyl phenyl sulfone



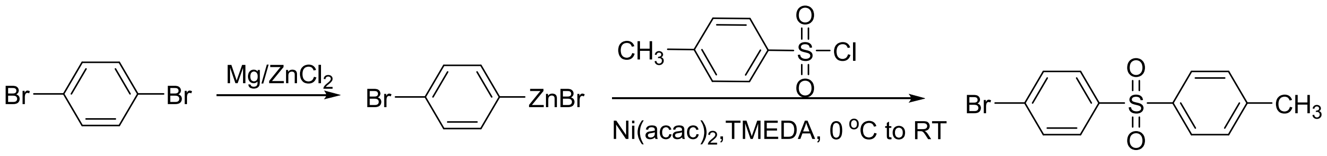
According to general procedure B: The previously prepared phenyl zinc bromide reagent was slowly added to an ice-water bath cooled solution of thiophene-3-sulfonyl chloride (0.91 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.74 g, 3.3 mmol, 66 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). Mp: 113-115 °C (lit[5]:115-117 °C). IR (KBr) *ν* (cm^{-1}): 2924, 2854, 1502, 1445, 1399, 1312, 1150, 1103, 744, 684. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 7.09 (dd, *J* = 5.2, 4.0 Hz, 1H), 7.49-7.55 (m, 2H), 7.59 (tt, *J* = 7.2, 2.4 Hz, 1H), 7.65 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.70 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.98-8.02 (m, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 127.64, 128.46, 129.19, 129.41, 132.59, 133.45, 140.64, 141.11.

3j: methylsulfonylbenzene



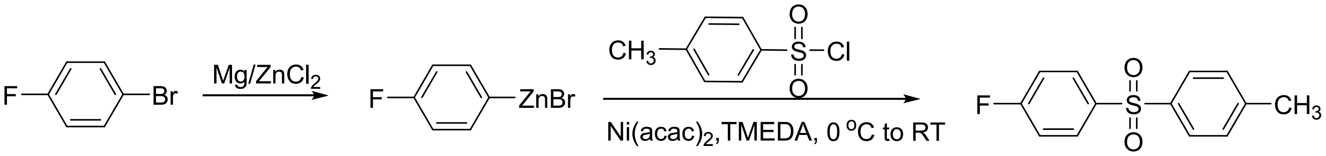
According to general procedure B: The previously prepared phenyl zinc bromide reagent was slowly added to an ice-water bath cooled solution of methanesulfonyl chloride (0.57 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.53 g, 3.4 mmol, 68 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). m.p.: 86-88 ℃ (lit[6]. 87 °C). IR (KBr) ν(cm^{-1}): 2925, 2856, 1452, 1403, 1327, 1290, 1149, 1085, 746, 686. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.19 (s, 3H), (7.16, ddd, J = 5.2, 4.0, 0.8 Hz, 1H), 7.70-7.75 (m, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 46.09, 127.86, 133.45, 133.63, 141.74.

8a: 1-bromo-4-tosylbenzene



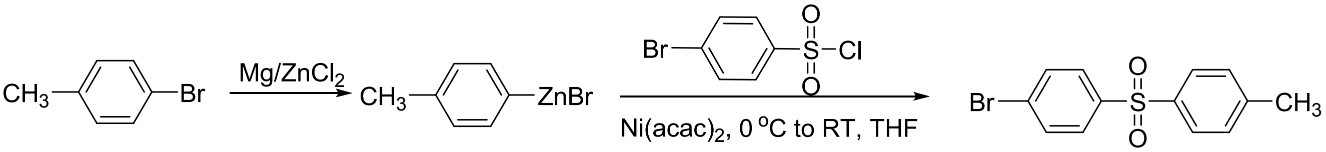
4-Bromophenyl zinc bromide was prepared by reaction of 1,4-dibromobenzene (2.83g, 12 mmol), magnesium turnings (0.36 g, 15.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) according to method to the general procedure A which was then slowly added to an ice-water bath cooled solution of 4-tosyl chloride (0.95 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.06 g, 3.4 mmol, 68 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). mp: 134-136 °C (lit[7]: 135-136 °C). IR (KBr) ν(cm^{-1}): 2924, 2856, 1592, 1447, 1396, 1306, 1153, 1105, 1069, 816, 727, 684. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.40 (s, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.56, 127.48, 127.70, 129.20, 129.90, 132.97, 138.61, 141.95, 144.14.

8b: 1-fluoro-4-tosylbenzene



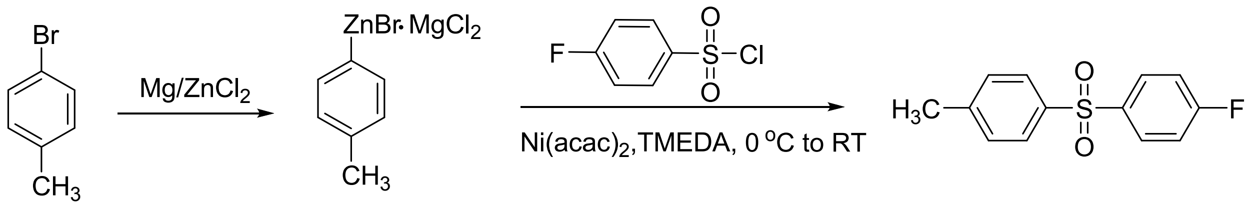
4-Fluorophenyl zinc bromide was prepared by reaction of 1-bromo-4-fluorobenzene (2.10 g, 12 mmol), magnesium turnings (0.36 g, 15.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) according to method to the general procedure A which was then slowly added to an ice-water bath cooled solution of 4-tosyl chloride (0.95 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.79 g, 3.15 mmol, 63 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). Mp: 112-114 °C (lit[7]: 94.5 °C). IR (KBr), ν (cm^{-1}): 2924, 2855, 1588, 1491, 1453, 1404, 1324, 1152, 1101, 839, 811, 710, 675. ^1H NMR (400MHz, $CDCl_3$) δ (ppm): 2.40 (s, 3H), 7.16 (tt, J = 8.4, 1.6 Hz, 2H), 7.28-7.31 (m, 1H), 7.31-7.33 (m, 1H), 7.81 (dt, J = 6.4, 1.6 Hz, 2H), 7.92-7.97 (m, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.56, 116.48 (d, J = 22.5 Hz), 127.59, 129.96, 130.22, 130.31, 138.44, 144.32, 167.70 (d, J = 231.9 Hz).

8c: 1-bromo-4-tosylbenzene (4a)



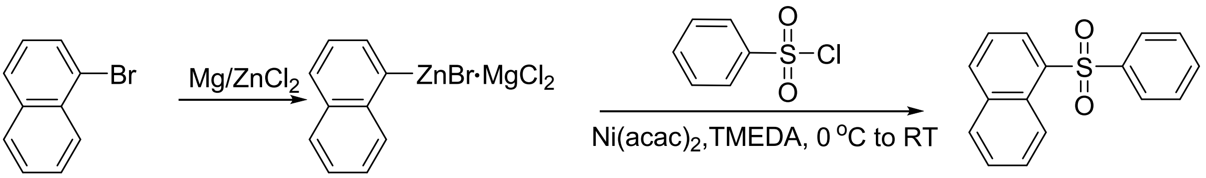
p-Tolylzinc bromide was prepared by reaction of 4-bromotoluene (2.83g, 12 mmol), magnesium turnings (0.36 g, 15.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) according to method to the general procedure A which was then slowly added to an ice-water bath cooled solution of 4-tosyl chloride (0.95 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.06 g, 3.4 mmol, 68 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc).

8d: 1-fluoro-4-tosylbenzene(4b)



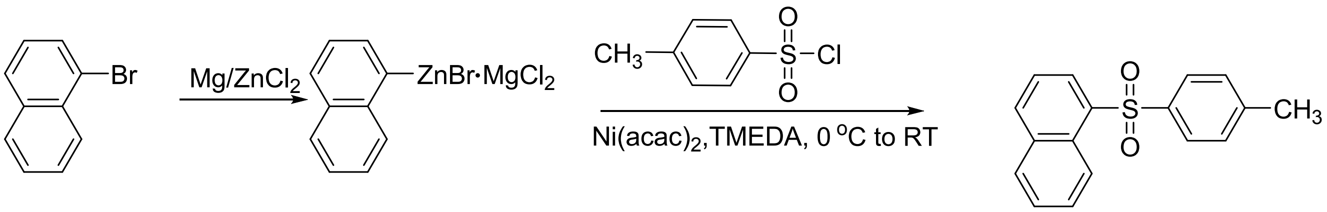
p-Tolylzinc bromide was prepared by reaction of 4-bromotoluene (2.83g, 12 mmol), magnesium turnings (0.36 g, 15.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) according to method to the general procedure A which was then slowly added to an ice-water bath cooled solution of 4-fluoro benzenesulfonylchloride (0.95 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid ((1.02 g, 4.1 mmol, 82 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc).

8f: 1-(phenylsulfonyl)naphthalene



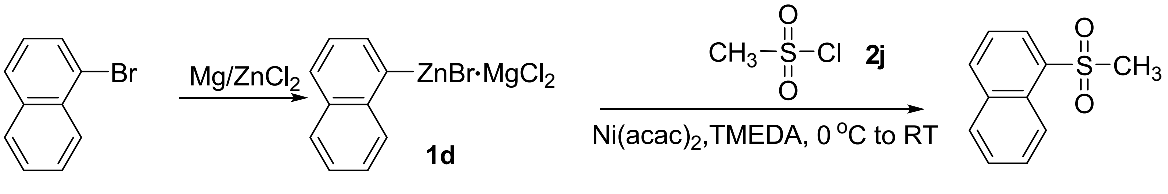
According to general procedure A, reaction of 1-bromonaphthalene (3.10g, 15 mmol), magnesium turnings (0.48 g, 20.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) in THF give the desired □□naphthyl bromide which was then slowly added to an ice-water bath cooled solution of benzenesulfonyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.99 g, 3.7 mmol, 74 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). mp 70-71 °C (lit[8]: 69-71 °C). IR (KBr) ν (cm^{-1}): 2925, 2856, 1586, 1502, 1481, 1447, 1398, 1307, 1140, 1084, 764, 717, 680. ^1H NMR ($CDCl_3$) δ (ppm): 3.23 (s, 3H), 7.59-7.67 (m, 2H), 7.74 (ddd, J = 8.4, 6.8, 1.2 Hz, 1H), 8.00 (dt, J = 8.0, 0.4 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.35 (dd, J = 7.2, 1.2 Hz, 1H), 8.74 (dd, J = 8.4, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 44.25, 123.89, 124.47, 127.03, 128.77, 129.31, 129.67, 134.18, 135.16.

8g: Napthyltolylsulfone



According to general procedure A, reaction of 1-bromonaphthalene (3.10g, 15 mmol), magnesium turnings (0.48 g, 20.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) in THF give the desired □□naphthyl bromide which was then slowly added to an ice-water bath cooled solution of tosyl chloride (0.95 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.11 g, 3.95 mmol, 79 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). mp: 101-103 °C(lit[8]: 102-104 °C). IR (KBr) ν(cm^{-1}): 2924, 2856, 1625, 1592, 1502, 1450, 1400, 1303, 1131, 1083, 808, 772, 687, 648. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.65-8.63 (d, J = 8.5 Hz, 1H), 8.51-8.49 (d, J = 7.4 Hz, 1H), 8.09-8.07 (d, J = 8.2 Hz, 1H), 7.90-7.84 (dd, J = 15.8, 8.4 Hz, 3H), 7.63-7.53 (m, 3H), 7.27-7.25 (t, J = 4.2 Hz, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm): 21.51, 124.33, 124.36, 126.79, 127.43, 128.23, 128.95, 129.70, 134.17, 134.95, 136.09, 138.76, 143.92.

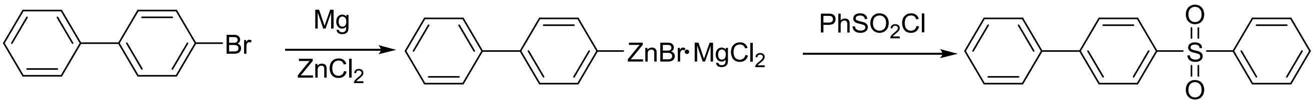
8h: 1-(methylsulfonyl)naphthalene



According to general procedure A, reaction of 1-bromonaphthalene (3.10g, 15 mmol), magnesium turnings (0.48 g, 20.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) in THF give the desired □□naphthyl bromide which was then slowly added to an ice-water bath cooled solution of mesyl chloride (0.59 g, 0.4 ml, 5.2 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.66g, 3.22 mmol, 62 %) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). mp 100-102 °C(lit[9]: 99-101 °C). IR (KBr) ν (cm^{-1}): 2925, 2856, 1558, 1508, 1458, 1399, 1300, 1157, 1120, 809, 770, 670. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.75-8.73 (dd, J = 8.6, 0.8 Hz, 1H), 8.36-8.34 (dd, J = 7.4, 1.3 Hz, 1H), 8.16-8.14 (d, J =8.2Hz, 1H), 8.01-7.99(d, J = 8.2 Hz, 1H), 7.76-

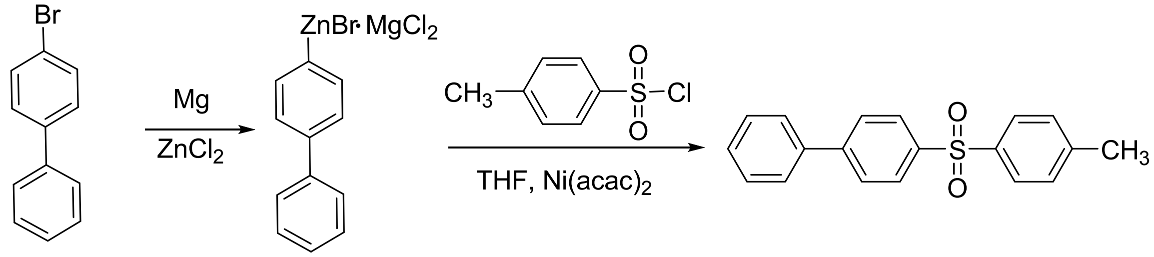
7.71 (ddd, *J* = 8.5, 6.9, 1.4 Hz,1H), 7.67-7.60(m, 2H), 3.23(s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm): 135.16, 134.18, 129.67, 129.31, 128.77, 127.03, 124.47, 123.89, 44.25.

8i: 4-(phenylsulfonyl)biphenyl



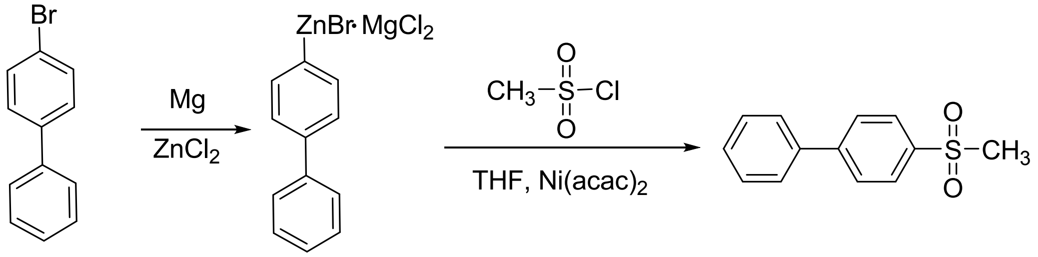
According to general procedure A, reaction of 4-bromobiphenyl (2.80 g, 12 mmol), magnesium turnings (0.36 g, 15.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) in THF give the desired □□naphthyl bromide which was then slowly added to an ice-water bath cooled solution of benzenesulfonyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.11 g, 3.8 mmol,76%) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). Mp: 148-150 °C (lit[10]:148-149 °C). IR (KBr) *ν* (cm^{-1}): 2925, 2856, 1558, 1516, 1473, 1446, 1396, 1310, 1155, 1107, 760. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.40-7.60 (m, 8H), 7.71 (d, *J* = 8.0 Hz, 2H), 8.0 (d, *J* = 8.01 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm): 127.31, 127.61, 127.90, 128.16, 128.55, 129.01, 129.28, 133.16, 139.12, 140.05, 141.67, 146.14.

8j: 4-tosylbiphenyl



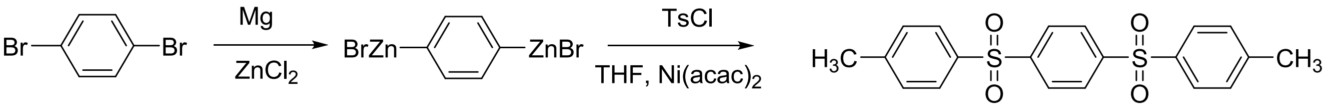
According to general procedure A, reaction of 4-bromobiphenyl (2.80 g, 12 mmol), magnesium turnings (0.36 g, 15.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) in THF give the desired □□naphthyl bromide which was then slowly added to an ice-water bath cooled solution of tosyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.20 g, 3.9 mmol,78%) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). mp 205-206 °C. (lit[11]: 206-207 °C). IR (KBr) ν (cm-1): 2924, 2854, 1592, 1460, 1396, 1304, 1153, 1109, 838, 816, 764, 678, 644. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.40 (s, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.40-7.50 (m, 3H), 7.55 (dt, J = 6.9, 1.5 Hz, 2H), 7.69 (dt, J = 8.7, 2.0 Hz, 2H), 7.87 (dt, J = 8.7, 1.8 Hz, 2H),8.00 (dt, J = 6.7, 2.0 Hz, 2H). ^{13}C NMR (CDCl$_3$) δ (ppm): 29.69, 127.30, 127.67, 127.85, 128.00, 128.50, 129.00, 129.92, 138.74, 139.20, 140.47, 144.14, 145.95.

8k: 4-(methylsulfonyl)biphenyl



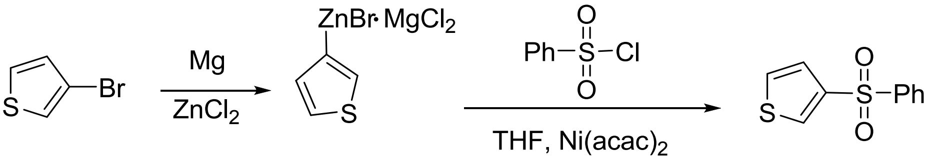
According to general procedure A, reaction of 4-bromobiphenyl (2.80 g, 12 mmol), magnesium turnings (0.36 g, 15.0 mmol) and ZnCl$_2$ (1.36 g, 10.0 mmol) in THF give the desired □□naphthyl bromide which was then slowly added to an ice-water bath cooled solution of mesyl chloride (0.59 g, 0.4 ml, 5.2 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH$_4$Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.77 g, 3.28 mmol, 64%) after purification on silica gel (5:1~2:1 petroleum ether : EtOAc). mp: 138-140 °C (lit[9]: 139-141 °C). IR (KBr) ν (cm^{-1}): 2924, 2855, 1593, 1562, 1458, 1395, 1298, 1150, 1090, 760, 689. ^{1}H NMR (400 Hz, CDCl$_3$) δ (ppm): 3.10 (s, 3H), 7.44 (tt, J = 7.6, 1.6 Hz, 1H), 7.50 (tt, J = 7.2, 1.6 Hz, 2H), 7.61 (ddd, J = 6.8, 2.8, 1.6 Hz, 2H), 7.78 (dt, J = 8.8, 2.0 Hz, 2H), 8.01 (dt, J = 8.8, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 44.62, 127.37, 127.90, 127.97, 128.66, 129.08, 139.09, 146.70.

8l: 1,4-ditosylbenzene



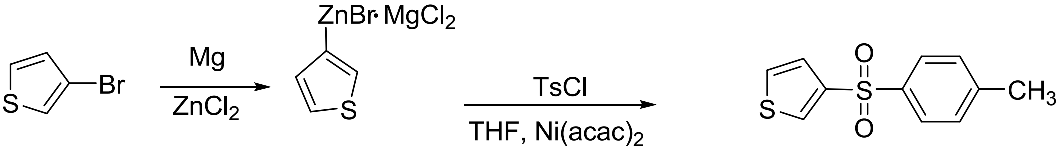
According to general procedure A, reaction of 1,4-dibromobiphenyl (1.89 g, 8 mmol), magnesium turnings (0.48 g, 20.0 mmol) and ZnCl$_2$ (2.04 g, 15.0 mmol) in THF give the desired phenyl 1,4-dizincbromide which was then slowly added to an ice-water bath cooled solution of tosyl chloride (1.76 g, 10.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH$_4$Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.20 g, 3.10 mmol, 62%) after purification on silica gel (5:1~2:1 petroleum ether : EtOAc). IR (KBr) (cm-^{1}): 3075, 2923, 1589, 1491, 1451, 1404, 1323, 1293, 1152, 1104, 841, 812, 677. ^{1}H NMR (400 Hz, $CDCl_3$) δ (ppm): 2.40 (s, 6H), 7.29 (d, *J* = 8.0 Hz, 4H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.80 (t, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.56, 129.00, 130.01, 132.48, 138.10, 140.99, 144.49.

8m: 3-(phenylsulfonyl)thiophene



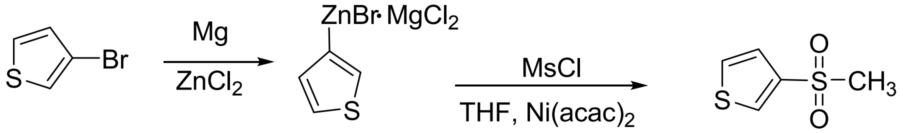
According to general procedure A, reaction of 3-bromothiophene (2.00 g, 12 mmol), magnesium turnings (0.36 g, 15.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) in THF give the desired □□naphthyl bromide which was then slowly added to an ice-water bath cooled solution of benzenesulfonyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.81 g, 3.60 mmol, 72%) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). Mp: 113-115 °C (lit[5]:117-118 °C). IR (KBr) *ν* (cm^{-1}): 2924, 2854, 1502, 1445, 1399, 1312, 1150, 1103, 744, 684. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 7.09 (dd, *J* = 5.2, 4.0 Hz, 1H), 7.49-7.55 (m, 2H), 7.59 (tt, *J* = 7.2, 2.4 Hz, 1H), 7.65 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.70 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.98-8.02 (m, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 127.64, 128.46, 129.19, 129.41, 132.59, 133.45, 140.64, 141.11.

8n: 3-tosylthiophene



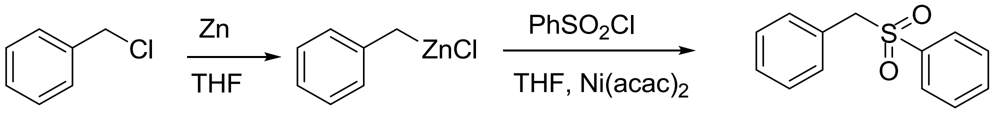
According to general procedure A, reaction of 3-bromothiophene (2.00 g, 12 mmol), magnesium turnings (0.36 g, 15.0 mmol) and $ZnCl_2$ (1.36 g, 10.0 mmol) in THF give the desired □□naphthyl bromide which was then slowly added to an ice-water bath cooled solution of tosyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.89 g, 3.75 mmol, 75%) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). Mp 135-137 °C (lit[5] 136-138 °C). IR (KBr) ν (cm^{-1}): 2925, 2859, 1593, 1497, 1451, 1398, 1315, 1148, 1104, 852, 814, 725, 677, 640. ^{1}H NMR (CDCl$_3$) δ (ppm): 2.10 (s, 3H), 7.07 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.62 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.67 (dd, *J* = 3.6, 1.2 Hz, 1H),7.86 (dt, *J* = 6.8, 1.6 Hz, 2H). ^{13}C NMR (CDCl$_3$) δ (ppm): 21.59, 127.36, 127.72, 129.92, 133.01, 133.51, 139.10, 144.30.

8o: 3-(methylsulfonyl)thiophene[13]



According to general procedure A, reaction of 3-bromothiophene (2.00 g, 12 mmol), magnesium turnings (0.36 g, 15.0 mmol) and ZnCl$_2$ (1.36 g, 10.0 mmol) in THF give the desired □□naphthyl bromide which was then slowly added to an ice-water bath cooled solution of mesyl chloride (0.59 g, 0.4 ml, 5.2 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH$_4$Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.64 g, 3.95 mmol, 76%) after purification on silica gel (10:1~4:1 petroleum ether : EtOAc). IR (KBr) ν (cm^{-1}): 2925, 2855, 1507, 1403, 1311, 1144, 1077, 739, 688, 649. ^{1}H NMR (CDCl$_3$) δ (ppm): 3.19 (s, 3H) , 7.16 (ddd, *J* = 5.2, 4.0, 0.8 Hz, 1H), 7.70-7.75 (m, 2H). ^{13}C NMR (CDCl$_3$) δ (ppm): 46.09, 127.86, 133.45, 133.63, 141.74.

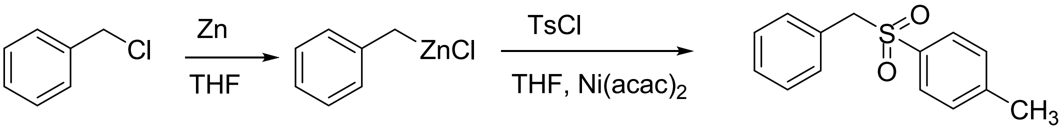
9a: benzyl phenyl sulfone



According to general procedure C: The previously prepared benzyl zinc chloride reagent(General procedure B) was slowly added to an ice-water bath cooled solution of benzenesulfonyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH$_4$Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.82 g, 3.55 mmol, 71 %) after purification on silica gel (10:1~3:1 petroleum ether : EtOAc). Mp[13]: 148-150 °C (lit. 151-155 °C). IR (KBr) ν (cm^{-1}): 2923, 2856, 1539, 1511, 1450, 1399, 1293, 1155, 1125, 1080, 759, 756, 686. ^{1}H NMR (CDCl$_3$) δ (ppm): 4.31 (s, 2H), 7.09 (d, *J* = 7.2

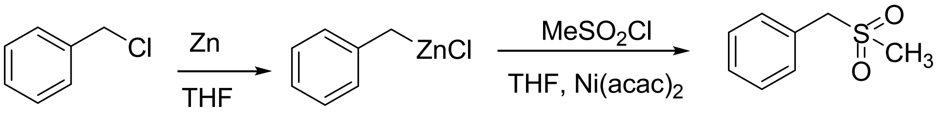
Hz, 2H),7.23-7.33 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.57-7.65 (m, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 62.87, 133.68, 130.79, 128.06, 128.55, 128.61, 128.74, 128.85, 137.88.

9b: benzyl *p*-tolyl sulfone



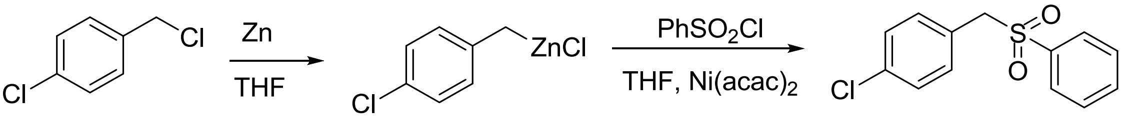
According to general procedure C: The previously prepared benzyl zinc chloride reagent(General procedure B) was slowly added to an ice-water bath cooled solution of benzenesulfonyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.03 g, 3.9 mmol, 78 %) after purification on silica gel (10:1~3:1 petroleum ether : EtOAc). m.p. 140-141°C (lit[14]. 140-141 °C). IR (KBr) ν (cm^{-1}): 2925, 2854, 1493, 1452, 1401, 1308, 1150, 1081, 818, 775, 698, 666. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.44 (s, 3H), 4.25 (s, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 7.23-7.28 (m, 5H), 7.51 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.63, 62.89, 128.65, 128.25, 128.51, 128.61, 129.46, 130.79, 144.63.

9c: benzyl methyl sulfone



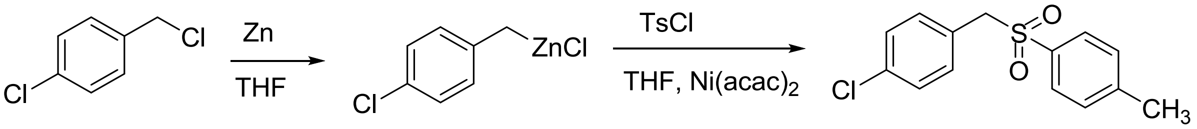
According to general procedure C: The previously prepared benzyl zinc chloride reagent(General procedure B) was slowly added to an ice-water bath cooled solution of mesyl chloride (0.59 g, 0.4 ml, 5.2 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.67 g, 3.27 mmol, 63 %) after purification on silica gel (10:1~3:1 petroleum ether : EtOAc). m.p. 124-126 °C (lit[14]: 125-126.5°C) IR (KBr) ν (cm^{-1}): 2926, 2854, 1494, 1460, 1413, 1303, 1155, 1117, 788, 702. ^{1}H NMR ($CDCl_3$) δ (ppm):, 2.76 (s, 3H), 4.26 (s, 2H), 7.42 (s, 5H). ^{13}C NMR ($CDCl_3$) δ (ppm): 38.97, 61.33 , 128.27, 129.14, 130.47.

9d: 4-chlorobenzyl phenyl sulfone



According to general procedure C: The previously prepared 4-chlorobenzyl zinc chloride reagent(General procedure B) was slowly added to an ice-water bath cooled solution of benzenesulfonyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.09 g, 3.9 mmol, 78 %) after purification on silica gel (10:1~3:1 petroleum ether : EtOAc). Mp 190-192 °C (lit[15]: 189-191 °C). IR (KBr) ν (cm^{-1}): 2925, 2855, 1460, 1408, 1379, 1301, 1151, 1016, 818, 770, 691. ^1H NMR ($CDCl_3$) δ (ppm): 4.27 (s, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 2H),7.60-7.70 (m, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 62.09, 126.59, 128.58, 128.83, 129.02, 132.03, 133.89, 135.06, 137.55.

9e: 4-chlorobenzyl 4'-methylphenyl sulfone

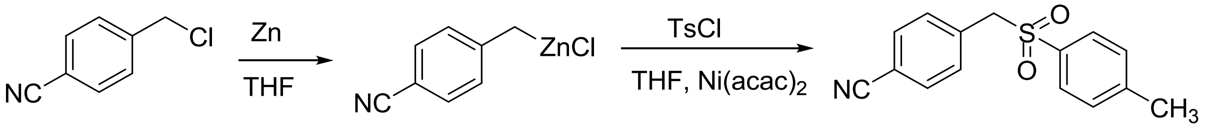


According to general procedure C: The previously prepared 4-chlorobenzyl zinc chloride reagent(General procedure B) was slowly added to an ice-water bath cooled solution of tosyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (1.13 g, 3.9 mmol, 81 %) after purification on silica gel (10:1~3:1 petroleum ether : EtOAc). Mp: 167-169 °C (lit[16]: 170-171 °C). IR (KBr) ν (cm^{-1}): 2923, 2854, 1596, 1489, 1405, 1299, 1279, 1150, 1087, 816, 720. ^1H NMR ($CDCl_3$) δ (ppm): 2.42 (s, 3H), 4.29 (s, 2H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.22-7.36 (m, 4H), 7.50 (dt, *J* = 4.4, 1.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 25.04, 57.49, 122.16, 123.95, 124.14, 124.99, 127.41, 130.06, 130.32, 140.28.

9f: 4-chlorobenzyl methyl sulfone

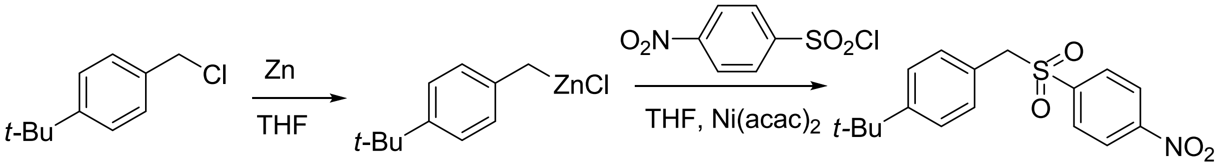
According to general procedure C: The previously prepared 4-chlorobenzyl zinc chloride reagent(General procedure B) was slowly added to an ice-water bath cooled solution of mesyl chloride (0.59 g, 0.4 ml, 5.2 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.77 g, 3.74 mmol, 72 %) after purification on silica gel (10:1~3:1 petroleum ether : EtOAc). Mp: 121-122 °C(lit[17]: 120-122 °C). IR (KBr) ν (cm^{-1}): 2926, 2855, 1491, 1460, 1412, 1306, 1161, 1122, 891, 845, 766, 718, 680. ^1H NMR ($CDCl_3$) δ (ppm): 2.78 (s, 3H), 4.22 (s, 2H), 7.78 (q, J = 7.6 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm): 39.15, 60.45, 126.56, 129.36, 131.78, 135.47.

9g: 4-(tosylmethyl)benzonitrile



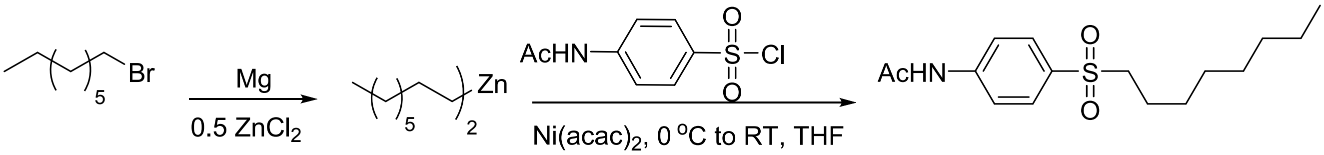
According to general procedure C: The previously prepared 4-cyanobenzyl zinc chloride reagent(General procedure B) was slowly added to an ice-water bath cooled solution of *p*-tosyl chloride (0.88 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.79 g, 2.9 mmol, 58 %) after purification on silica gel (10:1~3:1 petroleum ether : EtOAc). IR (KBr) ν (cm^{-1}): 2951, 2227, 1735, 1608, 1509, 1454, 1381, 1252, 1047, 823, 547. ^1H NMR (400 Hz,$CDCl_3$) (ppm): 8.20(d, J = 8.4 Hz, 1H), 8.00(dm, J = 8.0 Hz, 1H), 7.86 (dt, J = 8.4, 1.6 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.66(d, J = 8.8, 2.0 Hz, 2H), 7.46 (dt, J = 8.0, 0.4 Hz, 2H), 5.16 (s, 2H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.05, 137.50, 134.48, 132.47, 129.93, 129.26, 128.40, 117.15, 102.83, 56.28, 26.38.

9h: 1-tert-butyl-4-((4-nitrophenylsulfonyl)methyl)benzene



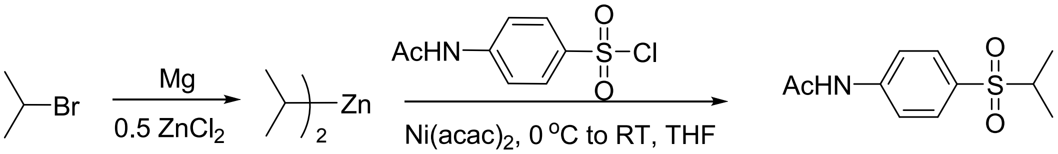
According to general procedure C: The previously prepared *4-tert*-butylbenzyl zinc chloride reagent(General procedure B) was slowly added to an ice-water bath cooled solution of *p*-nitrophenylsulfonyl chloride (1.11 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a yellowish solid (1.05 g, 3.15 mmol, 63 %) after purification on silica gel (10:1~3:1 petroleum ether : EtOAc). IR (KBr) ν (cm^{-1}): 2924, 2864, 1605, 1531, 1462, 1406, 1346, 1300, 1160, 842, 677. ^{1}H NMR (400 Hz,CDCl$_3$) (ppm): 8.28 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 9.2 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H),7.02 (d, *J* =8.4 Hz, 2H), 4.35(s, 2H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm):152.61, 150.71, 143.58, 130.45, 130.13, 126.88, 125.86, 125.50, 123.88, 62.44, 34.67, 31.19.

10a: N-(4-(octylsulfonyl)phenyl)acetamide



Dioctyl zinc reagent, prepared by reaction of *n*-octyl bromide (4.82 g, 25 mmol), magnesium turnings (0.72 g, 30.0 mmol) and ZnCl$_2$ (1.36 g, 10.0 mmol) according to general procedure A, was slowly added to an ice-water bath cooled solution of 4-acetamidobenzene-1-sulfonyl chloride (1.17 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH$_4$Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white syrup (1.16 g, 3.75 mmol, 72 %) after purification on silica gel (5:1~3:1 petroleum ether : EtOAc). IR (KBr) *ν* (cm^{-1}): 3264, 2928, 2856, 1694, 1602, 1516, 1325, 1261, 1142, 860. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.06 (brs, 1H, NH), 7.81 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 3.06 (q, *J* = 8.0 Hz, 2H), 2.21 (s, 3H), 1.55-1.65 (m, 4H), 1.25-1.45 (m, 4H), 0.87 (t, J = 5.2 Hz, 3H). ^{13}C NMR (CDCl$_3$) δ (ppm): 14.03, 22.56, 25.66, 29.08, 29.30, 31.78, 34.35, 37.58, 56.46, 119.26, 129.03, 133.14, 143.26, 169.05.

10b: N-(4-(isopropylsulfonyl)phenyl)acetamide



Diisopropyl zinc reagent, prepared by reaction of isopropyl bromide (3.08 g, 25 mmol), magnesium turnings (0.72 g, 30.0 mmol) and ZnCl$_2$ (1.36 g, 10.0 mmol) according to general procedure A, was slowly added to an ice-water bath cooled solution of 4-acetamidobenzene-1-sulfonyl chloride (1.17 g, 5.0 mmol), TMEDA (2.32 g, 3.0 ml, 20 mmol), CuI (0.19 g, 1.0 mmol)in THF (10 mL). After addition, the reaction mixture was stirred at room temperature for 6 hours. The reaction mixture was quenched by aqueous NH$_4$Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The pure product was obtained as a white solid (0.77 g, 3.2 mmol, 64 %) after purification on silica gel

(10:1~4:1 petroleum ether : EtOAc). mp: 155-157 °C (lit[18]: 157-158 °C). IR (KBr) ν (cm^{-1}): 3344, 2929, 1693, 1598, 1589, 1523, 1319, 1290, 1261, 1138, 840. ^{1}H NMR (CDCl$_3$) δ (ppm): 1.28 (d, J = 7.2 Hz, 6H), 2.23 (s, 3H), 3.10-3.25 (m, 1H), 7.67 (s, 1H, N*H*), 7.10 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H). ^{13}C NMR (CDCl$_3$) δ (ppm): 15.7, 24.6, 29.6, 55.7, 119.3, 130.2, 131.2, 143.0, 168.9.

Referfece:

1. Bandgar, B. P. ; Bettigeri, S. V.; Phopase, J. *Org Lett*. **2004**, *6*, 2105.
2. Umierski, N.; Manolikakes, G. *Org. Lett.*, **2013**, *15*, 188.
3. Zhu, W.; Ma, D. *J. Org. Chem*. **2005**, *70*, 2696.
4. Petrillo, G.; Novi, M.; Garbarino, G.; Dell'Erba, C. *Tetrahedron,* **1986**, *42*, 4007 – 4016.
5. Baarschers, W. H., *Can. J. Chem*. **1976**, *54*, 3056.
6. Villemin, D.; Alloum, A. B.; *Synth. Commun.,* **1990**, *20*, 925.
7. Répichet, S.; Roux, C. L.; Hernandez, P.; Dubac, J.; Desmurs, J.-R. *J. Org. Chem*. **1999**, *64*, 6479.
8. Singh, R.P.; Kamble, R.M.; Chanda, K.L.; Saravanan, P.; Singh, V.K. *Tetrahedron* **2001**, *57*, 241–247.
9. Zhu, W.; Ma, D. *J. Org. Chem.* **2005**, *70*, 2696**.**
10. Cho, S.-D.; Kim, H.-K.; Yim, H.; Kim, M.-R.; Lee, J.-K.; Kim, J.-J.; Yoon, Y.-J.; *Tetrahedron*, **2007**, *63*, 1345.
11. Kar , A.; Sayyed , I. A.; Lo, W. F.; Kaiser , H. M.; Beller , M.; Tse, M. K.; *Org. Lett*., **2007**, *9*, 3405.
12. Truce,W.E. et al.; *Tetrahedron* **1965**, *21*, 2899.
13. Chen, Y.; Lam, Y.; Lai, Y.-H. *Org. Lett.* **2003**, *5,* 1067.
14. Ju, Y.; Kumar , D.; Varma, R. S. *J. Org. Chem*., **2006**, *71*, 6697.
15. Jarvis, B. B.; Saukaitis, J. C. *J. Am. Chem. Soc.* **1973**, *95*, 7708–7715
16. Lia, H.; Wang, H.; Pan Y.; Shi, Y.*; Synth. Commun.,* **1998**, *28*, 409.
17. Russell, G. A.; Pecoraro, J. M. *J. Org. Chem*. **1979**, *44,* 3990.
18. Courtin, A.; *Helvetica Chimica Acta*; **1983**, *66*, 1046.