Homoallyl Alcohol as Allylation Reagent for Termination of Catellani-Lautens Reaction via Retro-Allylation

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1. General remarks

The desired product was purified by flash column chromatography, silica gel (200~300 mesh). ¹H NMR spectra and ¹³C NMR spectra were recorded on 400 MHz in CDCl₃ and TMS as internal standard. All products were further characterized by HRMS (high resolution mass spectra). Copies of their ¹ H NMR and ¹³C NMR spectra are provided. For *N*-benzoyloxyamines 2^1 and homoallyl alcohol 3^2 was prepared based on reported procedures and NMR data have matched to literatures. All reactions were heated by oil bath. HRMS analysis of compounds was performed with a time-of-flight mass spectrometer (micrOTOF-Q, Bruker Daltonik, Germany).

2. General procedure for the preparation of the products 4

An oven-dried Schlenk tube under a nitrogen atmosphere was charged aryl iodide **1** (0.3 mmol, 1.0 equiv), *N*-benzoyloxyamine **2** (0.6 mmol, 2.0 equiv), homoallyl alcohol **3** (1.2 mmol, 4.0 equiv), PdCl₂ (10 mol %), P(*p*-Me-C₆H₄)₃ (20 mol%), N¹ (0.60 mmol, 2.0 equiv), Cs₂CO₃ (1.20 mmol, 4.0 equiv), solvent (2.0 mL). The mixture was stirred at 35 °C for 30 mins and then stirred at 110 °C for 24 h. The resulting mixture was cooled to room temperature and filtered through Celite eluting with EtOAc. The volatiles were evaporated under reduced pressure and the residue was purified by silica gel flash chromatography to afford the desired products **4**. **3. Spectral data of compound 4**



4-(3-methyl-2-(2-methylallyl)phenyl)morpholine; Rf=0.31(peterolium ether/ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 54mg, 78%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.09-7.05(m, 1H), 6.92-6.87(m, 2H), 4.62(s, 1H), 4.20(s, 1H), 3.73(t, *J*=4.4Hz, 4H), 3.39(s, 2H), 2.80-2.78(m, 4H), 2.17(s, 3H), 1.75(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 151.8, 144.2, 138.8, 133.8, 126.7, 126.1, 117.8, 109.6, 67.6, 53.3, 35.6, 23.7, 19.6; HRMS(ESI) m/z:[M+H]⁺ calcd for C₁₅H₂₂NO 232.1696; found 232.1698.



4-(3-isopropyl-2-(2-methylallyl)phenyl)morpholine; Rf=0.32(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 53mg, 68%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ: 7.18-7.14(m, 1H), 7.03-7.01(m, 1H), 6.90(dd, *J*=1.2Hz, 8.0Hz, 1H), 4.64(t, *J*=1.6Hz, 1H), 4.19(d, *J*=1.2Hz, 1H), 3.73(t, *J*=4.4Hz, 4H), 3.44(s, 2H), 2.98-2.91(m, 1H), 2.80-2.77(m, 4H), 1.78(s, 3H), 1.11(s, 3H), 1.09(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ: 151.6, 149.4, 145.7, 132.2, 127.1, 121.4, 117.7, 109.9, 67.7, 53.4, 34.7, 29.2, 24.1, 23.9; HRMS(ESI) m/z: [M+H]⁺ calcd for C₁₇H₂₆NO 260.2009; found 260.2006.



4-(2-(2-methylallyl)-[1,1'-biphenyl]-3-yl)morpholine; Rf=0.30(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 55mg, 63%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.34-7.25(m, 6H), 7.20(dd, *J*=1.2Hz, 8.0Hz, 1H), 7.03(dd, *J*=1.2Hz, 7.2Hz, 1H), 4.63(s, 1H), 4.15(s, 1H), 3.80(t, *J*=4.4Hz, 4H), 3.36(s, 2H), 2.90(t, *J*=4.4Hz, 4H), 1.61(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 152.0, 146.1, 144.1, 142.2, 134.2, 129.0, 127.7, 126.7, 126.6, 120.6, 110.3, 67.7, 53.5, 35.9, 23.6; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₀H₂₄NO 294.1852; found 294.1847.



4-(3-methoxy-2-(2-methylallyl)phenyl)morpholine; Rf=0.27(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 57mg, 77%; white solid; ¹H NMR(400MHz, CDCl₃) δ : 7.14-7.10(m, 1H), 6.69-6.68(m, 1H), 6.61(d, *J*=8.0Hz, 1H), 4.58-4.57(m, 1H), 4.29(s, 1H), 3.73(t, *J*=4.4Hz, 4H), 3.71(s, 3H), 3.35(s, 2H), 2.80-2.78(m,

4H), 1.73(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 158.7, 152.7, 145.1, 127.3, 123.8, 112.7, 109.0, 106.7, 67.5, 55.7, 53.1, 32.8, 23.6; HRMS(ESI) m/z: [M+H]⁺ calcd for C₁₅H₂₂NO₂ 248.1645; found 248.1651.



4-(3-(benzyloxy)-2-(2-methylallyl)phenyl)morpholine; Rf=0.28(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 74mg, 76%; white solid; ¹H NMR(400MHz, CDCl₃) δ: 7.32(d, *J*=7.2Hz, 2H), 7.28-7.25(m, 2H), 7.22-7.18(m, 1H), 7.10-7.06(m, 1H), 6.68(d, *J*=7.6Hz, 1H), 6.63(d, *J*=8.4Hz, 1H), 4.95(s, 2H), 4.61(s, 1H), 4.35(s, 1H), 3.73-3.71(m, 4H), 3.41(s, 2H), 2.80(t, *J*=4.4Hz, 4H), 1.73(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ: 157.7, 152.8, 145.0, 137.6, 128.3, 127.5, 127.3, 126.9, 124.1, 112.9, 109.2, 107.9, 69.9, 67.5, 53.1, 33.0, 23.6; HRMS(ESI) m/z: [M+Na]⁺ calcd for C₂₁H₂₅NO₂Na 346.1778; found 346.1783



Methyl 2-(2-methylallyl)-3-morpholinobenzoate; Rf=0.32(peterolium ether/ ethyl acetate, 10:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 20:1); 40mg, 48%; yellow solid; ¹H NMR(400MHz, CDCl₃) δ : 7.56-7.54(m, 1H), 7.29-7.26(m, 2H), 4.66(s, 1H), 4.21(s, 1H), 3.86(s, 2H), 3.84-3.81(m, 7H), 2.88-2.86(m, 4H), 1.79(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 168.7, 152.4, 146.2, 136.3, 132.7, 126.8, 125.9, 124.0, 109.5, 67.4, 53.2, 51.9, 34.7, 23.7; HRMS(ESI) m/z: [M+Na]⁺ calcd for C₁₆H₂₁NO₃Na 298.1414; found 298.1424.



4-(3-(((tert-butyldimethylsilyl)oxy)methyl)-2-(2-methylallyl)phenyl)morpholine

Rf=0.28(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 69mg, 64%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.25(d, *J*=7.2Hz, 1H), 7.19(t, *J*=7.6Hz, 1H), 6.99(d, *J*=8.0Hz, 1H), 4.62-4.61(m, 3H), 4.20(s, 1H), 3.73(t, *J*=4.4Hz, 4H), 3.39(s, 2H), 2.80-2.77(m, 4H), 1.74(s, 3H), 0.87(s, 9H), 0.01(s, 6H); ¹³C NMR(100MHz, CDCl₃) δ : 151.4, 144.5, 141.4, 131.8, 126.9, 122.5, 119.1, 109.8, 67.6, 62.5, 53.3, 34.3, 25.9, 23.6, 18.4, -5.3; HRMS(ESI) m/z: [M+Na]⁺ calcd for C₂₁H₃₅NO₂SiNa 384.2329; found 384.2336.



2-(2-methylallyl)-3-morpholinobenzyl acetate; Rf=0.31(peterolium ether/ ethyl acetate, 8:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 15:1); 50mg, 58%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.16-7.12(m, 1H), 6.99(d, *J*=8.0Hz, 1H), 6.95(d, *J*=7.6Hz, 1H), 4.63(d, *J*=1.2Hz, 1H), 4.18(s, 1H), 3.73(t, *J*=4.4Hz, 4H), 3.58(s, 3H), 3.53(s, 2H), 3.44(s, 2H), 2.79(t, *J*=4.4Hz, 4H), 1.75(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 172.3, 152.1, 144.6, 134.9, 134.1, 127.1, 126.4, 119.5, 110.1, 67.5, 53.2, 51.9, 38.6, 35.2, 23.6; HRMS(ESI) m/z:[M+Na]⁺ calcd for C₁₇H₂₃NO₃Na 312.1570; found 312.1579



4-(3,4-dimethyl-2-(2-methylallyl)phenyl)morpholine; Rf=0.32(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 60mg, 82%; white solid; ¹H NMR(400MHz, CDCl₃) δ : 6.95(d, *J*=5.2Hz, 1H), 6.83(d, *J*=5.6Hz, 1H), 4.62(s, 1H), 4.18(s, 1H), 3.72-3.70(m, 4H), 3.43(s, 2H), 2.75-2.74(m, 4H), 2.16(s, 3H), 2.04(s, 3H), 1.75(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 149.9, 144.6, 137.1, 133.8, 132.6, 128.2, 117.4, 109.8, 67.7, 53.4, 35.8, 23.7, 20.4, 15.9; HRMS(ESI) m/z: [M+H]⁺ calcd for C₁₆H₂₄NO 246.1852; found 246.1858



4-(4-chloro-3-methyl-2-(2-methylallyl)phenyl)morpholine; Rf=0.30(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 56mg, 70%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.18-7.15(m, 1H), 6.85(d, *J*=8.4Hz, 1H), 4.65-4.64(m, 1H), 4.17(d, *J*=0.8Hz, 1H), 3.73-3.71(m, 4H), 3.42(s, 2H), 2.76-2.74(m, 4H), 2.19(s, 3H), 1.76(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 150.5, 143.9, 136.4, 135.9, 130.5, 127.5, 118.9, 110.1, 67.5, 53.2, 36.3, 23.7, 16.8; HRMS(ESI) m/z:[M+H]⁺ calcd for C₁₅H₂₁ClNO 266.1306; found 266.1314.



4-(3,5-dimethyl-2-(2-methylallyl)phenyl)morpholine; Rf=0.31(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 59mg, 80%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 6.71(s, 2H), 4.61(s, 1H), 4.22(s, 1H), 3.72(t, *J*=4.4Hz, 4H), 3.33(s, 2H), 2.78-2.76(m, 4H), 2.22(s, 3H), 2.12(s, 3H), 1.74(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 151.7, 144.4, 138.6, 136.1, 130.5, 126.9, 118.4, 109.5, 67.6, 53.3, 35.4, 23.6, 21.1, 19.5; HRMS(ESI) m/z:[M+H]⁺ calcd for C₁₆H₂₄NO 246.1852; found 246.1854.



4-(5-chloro-3-methyl-2-(2-methylallyl)phenyl)morpholine; Rf=0.30(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 41mg, 52%; yellow oil; ¹H NMR(400MHz, CDCl₃) δ : 6.86(d, *J*=2.4Hz, 2H), 4.63-4.62(m, 1H), 4.18(s, 1H), 3.73-3.71(m, 4H), 3.31(s, 2H), 2.76(t, *J*=4.4Hz, 4H), 2.13(s, 3H), 1.74(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 152.9, 143.7, 140.4, 132.1, 131.8, 125.8, 118.3, 109.8, 67.4, 53.1, 35.4,

23.6, 19.5; HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{21}CINO$ 266.1306; found 266.1310.



4-(3-methyl-2-(2-methylallyl)-5-nitrophenyl)morpholine Rf=0.31(peterolium ether/ ethyl acetate, 10:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 20:1); 48mg, 58%; yellow oil; ¹H NMR(400MHz, CDCl₃) δ : 7.75-7.74(m, 2H), 4.67(d, *J*=1.2Hz, 1H), 4.14(s, 1H), 3.78-3.75(m, 4H), 3.42(s, 2H), 2.84(t, *J*=4.4Hz, 4H), 2.27(s, 3H), 1.79(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 152.7, 146.7, 142.8, 141.6, 140.4, 120.5, 113.0, 110.4, 67.3, 53.0, 36.1, 23.8, 19.9; HRMS(ESI) m/z: [M+Na]⁺ calcd for C₁₅H₂₀N₂O₃Na 299.1366; found 299.1362.



methyl 3-methyl-4-(2-methylallyl)-5-morpholinobenzoate; Rf=0.30(peterolium ether/ ethyl acetate, 10:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 20:1); 61mg, 70%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.57(d, *J*=2.4Hz, 2H), 4.63-4.62(m, 1H), 4.14(s, 1H), 3.82(s, 3H), 3.74(t, *J*=4.4Hz, 4H), 3.40(s, 2H), 2.82-2.80(m, 4H), 2.20(s, 3H), 1.76(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 167.2, 151.9, 143.4, 139.4, 139.1, 128.4, 127.1, 119.0, 109.9, 67.4, 53.2, 51.9, 35.8, 23.7, 19.6; HRMS(ESI) m/z: [M+Na]⁺ calcd for C₁₇H₂₃NO₃Na 312.1570; found 312.1576.



methyl 3-(benzyloxy)-4-(2-methylallyl)-5-morpholinobenzoate Rf=0.27(peterolium ether/ ethyl acetate, 10:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 20:1); 86mg, 75%; yellow oil; ¹H NMR(400MHz, CDCl₃) δ : 7.39(d, *J*=1.2Hz, 1H), 7.35-7.33(m, 3H), 7.29(t, *J*=6.8Hz, 2H), 7.24-7.21(m, 1H), 5.01(s, 2H), 4.61(s, 1H), 4.29(s, 1H), 3.83(s, 3H), 3.75-3.73(m,

4H), 3.42(s, 2H), 2.83(t, *J*=4.4Hz, 4H), 1.73(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ: 167.0, 157.6, 152.7, 144.2, 137.0, 129.7, 129.2, 128.4, 127.7, 127.0, 114.4, 109.6, 108.5, 70.1, 67.4, 53.0, 52.1, 33.3, 23.6; HRMS(ESI) m/z: [M+Na]⁺ calcd for C₂₃H₂₇NO₄Na 404.1832; found 404.1836



4-(4,5-dimethoxy-3-methyl-2-(2-methylallyl)phenyl)morpholine; Rf=0.31(peterolium ether/ ethyl acetate, 15:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 30:1); 56mg, 64%; yellow oil; ¹H NMR(400MHz, CDCl₃) δ : 6.53(s, 1H), 4.60(s, 1H), 4.19(s, 1H), 3.78(s, 3H), 3.73-3.72(d, *J*=4.4Hz, 4H), 3.67(s, 3H), 3.33(s, 2H), 2.77-2.75(m, 4H), 2.01(s, 3H), 1.73(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 151.0, 147.5, 144.6, 144.0, 132.3, 127.0, 109.5, 102.5, 67.6, 60.2, 55.6, 53.4, 35.4, 23.5, 12.1; HRMS(ESI) m/z:[M+H]⁺ calcd for C₁₇H₂₆NO₃ 292.1907; found 292.1914



4-(1-(2-methylallyl)naphthalen-2-yl)morpholine Rf=0.30(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 69mg, 86%; white solid; ¹H NMR(400MHz, CDCl₃) δ : 7.78(d, *J*=8.4Hz, 1H), 7.71-7.66(m, 2H), 7.38-7.27(m, 3H), 4.66-4.65(m, 1H), 4.15(d, *J*=0.8Hz, 1H), 3.84(s, 2H), 3.79-3.77(m, 4H), 2.90-2.88(m, 4H), 1.83(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 148.4, 145.0, 133.5, 131.0, 129.6, 128.1, 127.8, 125.8, 125.2, 124.4, 119.8, 111.1, 67.6, 53.0, 34.9, 23.8; HRMS(ESI) m/z: [M+H]⁺ calcd for C₁₈H₂₂NO 268.1696; found 268.1695



4-(2-methoxy-3-(2-methylallyl)pyridin-4-yl)morpholine Rf=0.27(peterolium ether/ ethyl acetate,

10:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 20:1); 51mg, 68%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.92(d, *J*=5.6Hz, 1H), 6.50(d, *J*=5.6Hz, 1H), 4.63(s, 1H), 4.32(s, 1H), 3.83(s, 3H), 3.75-3.72(m, 4H), 3.20(s, 2H), 2.90-2.87(m, 4H), 1.74(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 163.8, 159.7, 145.2, 143.8, 114.2, 109.6, 108.2, 67.1, 53.6, 51.8, 33.2, 23.6; HRMS(ESI) m/z: [M+H]⁺ calcd for C₁₄H₂₁N₂O₂ 249.1598; found 249.1593



1-(3-methyl-2-(2-methylallyl)phenyl)-4-phenylpiperidine Rf=0.27(peterolium ether /ethyl acetate, 30:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 60:1); 52mg, 57%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.26-7.19(m, 4H), 7.15-7.11(m, 1H), 7.07-7.03(m, 1H), 6.94(d, *J*=7.6Hz, 1H), 6.85(d, *J*=7.2Hz, 1H), 4.63(s, 1H), 4.26(s, 1H), 3.41(s, 2H), 3.08(d, *J*=12.0Hz, 2H), 2.71-2.63(m, 2H), 2.57-2.49(m, 1H), 2.17(s, 3H), 1.83-1.78(m, 4H), 1.76(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 153.0, 146.5, 144.3, 138.7, 133.8, 128.4, 126.9, 126.5, 126.1, 125.6, 117.7, 109.4, 54.1, 42.5, 35.8, 34.3, 23.6, 19.7; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₂H₂₈N 306.2216; found 306.2220.



methyl 1-(3-methyl-2-(2-methylallyl)phenyl)piperidine-4-carboxylate; Rf=0.30 (peterolium ether/ ethyl acetate, 6:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 12:1); 43mg, 50%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.05-7.01(m, 1H), 6.88-6.83(m, 2H), 4.61(d, *J*=1.6Hz, 1H), 4.21(d, *J*=1.2Hz, 1H), 3.62(d, *J*=2.8Hz, 3H), 3.35(s, 2H), 3.01-2.98(m, 2H), 2.58-2.52(m, 2H), 2.36-2.28(m, 1H), 2.16(s, 3H), 1.90-1.86(m, 2H), 1.83-1.76(m, 2H), 1.74(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 175.8, 152.6, 144.3, 138.7, 133.8, 126.5, 125.7, 117.7, 109.4, 52.8, 51.6, 41.0, 35.6, 29.1, 23.6, 19.7; HRMS(ESI) m/z: [M+H]⁺calcd for C₁₈H₂₆NO₂ 288.1958; found 288.1966



4-methoxy-1-(3-methyl-2-(2-methylallyl)phenyl)piperidine; Rf=0.30(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 42mg, 54%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.04(t, *J*=7.6Hz, 1H), 6.90(d, *J*=7.6Hz, 1H), 6.84(d, *J*=7.2Hz, 1H), 4.62(d, *J*=1.2Hz, 1H), 4.22(s, 1H), 3.37(s, 2H), 3.31(s, 3H), 3.27-3.21(m, 1H), 2.99-2.94(m, 2H), 2.62-2.56(m, 2H), 2.17(s, 3H), 1.94-1.91(m, 2H), 1.75(s, 3H), 1.65-1.57(m, 2H); ¹³C NMR(100MHz, CDCl₃) δ : 152.6, 144.3, 138.7, 133.9, 126.4, 125.7, 117.8, 109.3, 55.5, 51.0, 35.7, 31.9, 23.6, 19.7; HRMS(ESI) m/z: [M+H]⁺ calcd for C₁₇H₂₆NO 260.2009; found 260.2013.



8-(3-methyl-2-(2-methylallyl)phenyl)-1,4-dioxa-8-azaspiro[4.5]decane; Rf=0.32(peterolium ether/ethyl acetate, 15:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 30:1); 55mg, 64%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.02(t, *J*=7.6Hz, 1H), 6.93(d, *J*=8.0Hz, 1H), 6.84(d, *J*=7.2Hz, 1H), 4.62-4.61(m, 1H), 4.22(d, *J*=1.2Hz, 1H), 3.91(s, 4H), 3.38(s, 2H), 2.85(t, *J*=5.6Hz, 4H), 2.16(s, 3H), 1.76(d, *J*=5.6Hz, 4H), 1.74(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 152.4, 144.2, 138.6, 133.8, 126.5, 125.7, 118.0, 109.4, 107.1, 64.2, 51.2, 35.8, 35.7, 23.5, 19.7; HRMS(ESI) m/z:[M+H]⁺ calcd for C₁₈H₂₆NO₂ 288.1958; found 288.1963.



3,5-dimethyl-1-(3-methyl-2-(2-methylallyl)phenyl)piperidine; Rf=0.4(peterolium ether); Column chromatoghraphy(silica gel; peterolium ether); 45mg, 58%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.02(t, *J*=7.6Hz, 1H), 6.86(d, *J*=8.0Hz, 1H), 6.81(d, *J*=7.6Hz, 1H), 4.63(s, 1H), 4.25(s, 1H), 3.35(s, 2H), 2.90(d, *J*=10.8Hz, 2H), 2.16(s, 3H), 2.03(t, *J*=10.8Hz, 2H), 1.72-1.68(m, 6H), 0.79(s, 3H), 0.77(s, 3H), 0.60-0.50(m, 1H); ¹³C NMR(100MHz, CDCl₃) δ : 153.0, 144.4, 138.6, 133.7, 126.4, 125.3, 117.7, 109.4, 61.2, 42.3, 35.7, 32.1, 23.5, 19.7, 19.4; HRMS(ESI) m/z:[M+H]⁺ calcd for C₁₈H₂₈N 258.2216; found 258.2215.



2,6-dimethyl-4-(3-methyl-2-(2-methylallyl)phenyl)morpholine;Rf=0.34(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 50:1); 64mg, 82%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.06-7.02(m, 1H), 6.87-6.84(m, 2H), 4.63(s, 1H), 4.21(s, 1H), 3.75-3.69(m, 2H), 3.36(s, 2H), 2.88(d, *J*=11.2Hz, 2H), 2.33(t, *J*=10.8Hz, 2H), 2.16(s, 3H), 1.73(s, 3H), 1.10(s, 3H), 1.08(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 151.5, 144.2, 138.7, 133.8, 126.6, 125.9, 117.8, 109.6, 72.3, 59.0, 35.6, 23.6, 19.6, 19.0; HRMS(ESI) m/z:[M+H]⁺ calcd for C₁₇H₂₆NO 260.2009; found 260.2010.



tert-butyl 4-(3-methyl-2-(2-methylallyl)phenyl)piperazine-1-carboxylate;

Rf=0.30(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 74mg, 75%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.06-7.02(m, 1H), 6.86(d, *J*=7.6Hz, 2H), 4.62(s, 1H), 4.19(s, 1H), 3.41(m, 6H), 2.72(s, 4H), 2.16(s, 3H), 1.74(s, 3H), 1.40(s, 9H); ¹³C NMR(100MHz, CDCl₃) δ : 154.9, 151.8, 144.1, 138.7, 133.8, 126.6, 126.1, 117.9, 109.6, 79.5, 52.7, 35.6, 28.4, 23.6, 19.6; HRMS(ESI) m/z:[M+H]⁺ calcd for C₂₀H₃₁N₂O₂ 331.2380; found 331.2378.



tert-butyl4-(3-methyl-2-(2-methylallyl)phenyl)-1,4-diazepane-1-carboxylate;Rf=0.31(peterolium ether/ ethyl acetate, 8:1); Column chromatoghraphy(silica gel; peteroliumether/ethyl acetate, 15:1); 74mg, 72%; yellow oil; ¹H NMR(400MHz, CDCl₃) δ : 7.05-7.00(m, 1H),6.92-6.89(m, 1H), 6.86-6.83(m, 1H), 4.61(s, 1H), 4.13(s, 1H), 3.52-3.39(m, 6H), 2.97-2.87(m, 4H),2.16(s, 3H), 1.80-1.73(m, 5H), 1.41(s, 9H); ¹³C NMR(100MHz, CDCl₃) δ : 155.5, 154.7, 144.0,138.6, 134.1, 126.6, 125.9, 119.7, 109.4, 79.2, 57.6, 56.8, 48.5, 46.1, 35.8, 29.0, 28.5, 23.6, 19.7;HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₁H₃₃N₂O₂ 345.2537; found 345.2551.



4-(3-methyl-2-(3-methylbut-2-en-1-yl)phenyl)morpholine; Rf=0.33(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 60mg, 82%; colourless oil; ¹H NMR(400MHz,CDCl₃) δ : 7.03(t, *J*=7.6Hz, 1H), 6.91-6.86(m, 2H), 4.98-4.95(m, 1H), 3.75(t, *J*=4.4Hz, 4H), 3.42(d, *J*=6.0Hz, 2H), 2.80-2.78(m, 4H), 2.21(s, 3H), 1.70(s, 3H), 1.61(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 151.4, 138.2, 135.9, 131.7, 126.4, 123.3, 117.9, 67.5, 53.4, 26.8, 25.6, 20.0, 18.1; HRMS(ESI) m/z: [M+H]⁺ calcd for C₁₆H₂₄NO 246.1852; found 246.1859



(E)-4-(2-(but-2-en-1-yl)-3-methylphenyl)morpholine; Rf=0.31(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 41mg, 59%;

colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.04(t, *J*=7.6Hz, 1H), 6.92(d, *J*=7.6Hz, 1H), 6.87(d, *J*=7.2Hz, 1H), 5.47-5.41(m, 1H), 5.30-5.24(m, 1H), 3.76-3.74(m, 4H), 3.43-3.41(m, 2H), 2.81-2.78(m, 4H), 2.22(s, 3H), 1.56-1.53(m, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 151.6, 138.3, 134.7, 129.2, 126.5, 126.4, 125.1, 118.2, 67.5, 53.4, 30.7, 19.9, 17.9; HRMS(ESI) m/z:[M+H]⁺ calcd for C₁₅H₂₂NO 232.1696; found 232.1699



(E)-4-(3-methyl-2-(3-phenoxyallyl)phenyl)morpholine; Rf=0.29(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 50mg, 54%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.28-7.24(m, 2H), 7.08-7.04(m, 1H), 7.01-6.88(m, 5H), 6.37-6.34(m, 1H), 4.78-4.73(m, 1H), 3.73(t, *J*=4.4Hz, 4H), 3.70-3.68(m, 2H), 2.83-2.80(m, 4H), 2.29(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 157.4, 151.6, 140.2, 138.3, 134.8, 129.7, 126.6, 126.4, 122.6, 118.0, 116.2, 111.2, 67.5, 53.4, 22.9, 19.9; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₀H₂₄NO₂ 310.1802; found 310.1809



(E)-4-(3-methyl-2-(3-phenoxyallyl)phenyl)morpholine Rf=0.29(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 57mg, 62%; colourless oil; ¹H NMR(400MHz,CDCl₃) δ : 7.23-7.18(m, 2H), 7.09-7.05(m, 1H), 6.96-6.93(m, 2H), 6.91-6.89(d, *J*=7.6Hz, 1H), 6.83-6.81(m, 2H), 6.27(dt, *J*=1.6Hz, 12.0Hz, 1H), 5.47-5.41(m, 1H), 3.79-3.77(m, 4H), 3.48(dd, *J*=1.2Hz, 6.4Hz, 2H), 2.85-2.83(m, 4H), 2.31(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 157.3, 151.6, 142.2, 138.0, 134.1, 129.5, 126.9, 126.7, 122.5, 118.6, 116.2, 112.1, 67.6, 53.6, 25.6, 19.9; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₀H₂₄NO₂310.1802; found 310.1799



4-(3-methyl-2-(2-phenylallyl)phenyl)morpholine: Rf=0.31(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 65mg, 74%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ: 7.48-7.46(m, 2H), 7.32-7.28(m, 2H), 7.25-7.22(m, 1H), 7.11(t, *J*=7.6Hz, 1H), 6.96-6.91(m, 2H), 5.18(d, *J*=1.6Hz, 1H), 4.45(d, *J*=1.2Hz, 1H), 3.88(s, 2H), 3.68(t, *J*=4.4Hz, 4H), 2.82-2.80(m, 4H), 2.20(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ: 152.0, 146.7, 142.2, 139.0, 133.5, 128.3, 127.5, 127.0, 126.2, 125.8, 118.0, 111.8, 67.6, 53.3, 33.3, 19.7; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₀H₂₄NO 294.1853; found 294.1851.



4-(3-methyl-2-(2-(p-tolyl)allyl)phenyl)morpholine : Rf=0.32(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 51mg, 55%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.37(d, *J*=8.4Hz, 2H), 7.11(t, *J*=7.6Hz, 3H), 6.96-6.91(m, 2H), 5.17(d, *J*=1.6Hz, 1H), 4.41(d, *J*=1.2Hz, 1H), 3.86(s, 2H), 3.69(t, *J*=4.4Hz, 4H), 2.83-2.81(m, 4H), 2.30(s, 3H), 2.19(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 152.0, 146.4, 139.2, 139.0, 137.3, 133.6, 129.0, 126.9, 126.2, 125.6, 117.9, 111.0, 67.6, 53.3, 33.2, 21.1, 19.7; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₁H₂₆NO 308.2009; found 308.2003.



4-(2-(4-chlorophenyl)allyl)-3-methylphenyl)morpholine : Rf=0.34(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 65mg,

66%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ: 7.41-7.38(m, 2H), 7.27-7.25(m, 2H), 7.12(t, J=7.6Hz, 1H), 6.97-6.91(m, 2H), 5.18(d, J=1.2Hz, 1H), 4.49(d, J=1.2Hz, 1H), 3.84(s, 2H), 3.69-3.67(m, 4H), 2.81-2.79(m, 4H), 2.19(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ: 152.0, 145.7, 140.5, 138.9, 133.3, 133.2, 128.4, 127.2, 127.1, 126.4, 118.2, 112.4, 67.6, 53.4, 33.1, 19.8; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₀H₂₃CINO 328.1463; found 328.1462.



4-(3-methyl-2-(2-(naphthalen-1-yl)allyl)phenyl)morpholine: Rf=0.32(peterolium ether/ ethyl acetate, 20:1); Column chromatoghraphy(silica gel; peterolium ether/ethyl acetate, 40:1); 52mg, 51%; colourless oil; ¹H NMR(400MHz, CDCl₃) δ : 7.91(s, 1H), 7.81-7.75(m, 3H), 7.64-7.61(m, 1H), 7.45-7.37(m, 2H), 7.15-7.11(m, 1H), 6.98-6.93(m, 2H), 5.36(d, *J*=1.2Hz, 1H), 4.57(d, *J*=1.2Hz, 1H), 4.01(s, 2H), 3.69(t, *J*=4.4Hz, 4H), 2.85-2.83(m, 4H), 2.24(s, 3H); ¹³C NMR(100MHz, CDCl₃) δ : 152.0, 146.4, 139.2, 139.0, 133.6, 133.3, 132.8, 128.2, 127.8, 127.5, 127.0, 126.3, 126.2, 125.9, 124.4, 124.3, 118.0, 112.4, 67.6, 53.4, 33.2, 19.8; HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₄H₂₆NO 344.2009; found 344.2007.



4-(2-(2-cyclohexylallyl)-3-methylphenyl)morpholine: Rf=0.33(peterolium ether/ ethyl acetate, 20:1); NMR yield, HRMS(ESI) m/z: [M+H]⁺ calcd for C₂₀H₃₀NO 300.2322; found 300.2323.

4. References

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2. (a) Bunnelle, W. H.; Rafferty, M. A.; Hodges, S. L. Aldol-equivalent elaboration of sterically hindered ketiones: methallylmagnesium chloride as a synthon for acetone enolate, *J. Org. Chem*, **1987**, *52*, 1603; (b) Iwasaki, M.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. Pd(OAc)₂/P(^eC₆H₁₁)₃-Catalyzed Allylation of Aryl Halides with Homoallyl Alcohols via Retro-Allylation, *J. Am. Chem. Soc*, **2007**, *129*, 4463.

5. The crystal structure of product 4-5



Bond precision:	C-C = 0.0059 A	Wavelength=1.54184			
Cell:	a=12.4334(3) alpha=90	b=7.2808(2) beta=90	c=40.6710(13) gamma=90		
Temperature:	293 K		-		
	Calculated	Reported	l		
Volume	3681.75(18)	3681.75(3681.75(18)		
Space group	Pbca	Pbca	Pbca		
Hall group	-P 2ac 2ab	-P 2ac 2	-P 2ac 2ab		
Moiety formula	C21 H25 N O2	C21 H25	C21 H25 N O2		
Sum formula	C21 H25 N O2	C21 H25	C21 H25 N O2		
Mr	323.42	323.42	323.42		
Dx,g cm-3	1.167	1.167	1.167		
Z	8	8	8		
Mu (mm-1)	0.583	0.583	0.583		
F000	1392.0	1392.0			
F000'	1395.88				
h,k,lmax	15,8,50	15,8,50			
Nref	3584	3520	3520		
Tmin, Tmax	0.993,0.994	0.567,1.000			
Tmin'	0.988				
Correction method= # Reported T Limits: Tmin=0.567 Tmax=1.000 AbsCorr = MULTI-SCAN					
Data completeness= 0.982 Theta(max) = 71.490					
R(reflections) = 0.0800(2902) wR2(reflections) = 0.1971(3520)					
S = 1.110 Npar= 234					

6. ¹H, ¹³C spectra for compound 4







0 -1





























































































