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Synthesis of unsymmetrical pincer CNN palladium complex of 8-dimethylamino-3-ferrocenylmethyl-3-azabicyclo[3.2.1]octane and its catalytic activity in the Suzuki reaction

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Experimental

General

The NMR experiments were carried out using a Bruker Avance^{TM} 400 (400.13 and 100.61 MHz) and Bruker Avance^{TM} 500 (500.13 and 125.7 MHz). ^{1}H chemical shift data are given in units δ relative TMS calibrated with $CHCl_3$ at 7.26 ppm. The multiplicity of a signal is indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets. ^{13}C chemical shifts are given relative TMS calibrated to the solvent, $CDCl_3$ at 77.26 ppm. The assignment of the signals in ^{1}H and ^{13}C NMR spectra has been performed by use of 2D COSY, HMQC and HMBC techniques on the basis of the Bruker program standard library. 2D inverse proton detected heteronuclear shift correlation spectra, gs-HMQC (^{1}H-^{13}C) and gs-HMBC (^{1}H-^{13}C) were obtained using standard pulse sequence from the Bruker library. EI mass spectra were taken on a FINNIGAN POLARIS Q spectrometer at 70 eV and the temperature of the ion chamber was 250° C. IR spectra were recorded on a FT-IR Tensor 37 spectrometer (Bruker) in KBr pellets and FT-IR spectrometer Nicolet Magna 750 (nujol). The TLC on Silufol UV-254 (Merck) was used to follow the course of reactions. 3-Benzyl-8-dimethylamino-3-azabicyclo[3.2.1]octane [S1], ferrocenecarbaldehyde [S2] and $PhB(OH)_2$ [S3] were obtained according to the literature procedures.

*8-Dimethylamino-3-ferrocenylmethyl-3-azabicyclo[3.2.1]octane **2***

A mixture of 3-benzyl-8-dimethylamino-3-azabicyclo[3.2.1]octane **1** (1.34 g, 5.5 mmol), ammonium formate (1.39 g, 22 mmol) and 5% Pd/C (contains 50% H_2O, 0.3 g) in MeOH (50 ml) was refluxed with stirring for 4 h, cooled and filtered through celite. The solution was evaporated to the volume of 20 ml, and 10 N NaOH (20 ml) was added. The mixture was refluxed with stirring for 1 h, extracted with $CHCl_3$, washed with brine, dried over Na_2SO_4 and evaporated. The residue was dissolved in $CHCl_3$ (70 ml), ferrocenecarbaldehyde (1.18 g, 5.5 mmol) was added followed by portionwise addition of sodium triacetoxyborohydride (3.5 g, 16.5 mmol). The mixture was stirred at room temperature for 2 h, diluted with water, basified with sodium hydroxide solution to pH 10, extracted with $CHCl_3$, washed with water and brine, dried over Na_2SO_4 and evaporated. The residue was purified by Al_2O_3 column chromatography with AcOEt/petroleum ether (1:250 → 5:250) to afford **2** (1.13 g, 58%) as an orange powder. M.p. 95-96° C. Anal.: C, 68.19; H, 8.07; N, 7.81 %. Calc. for $C_{20}H_{28}FeN_2$: C, 68.19; H, 7.95; N, 8.01 %. IR (KBr, ν, cm^{-1}): 1103, 1002, 809, 488 (FcH). EI-MS, m/z (RI, %): 352 $[M]^+$ (71). ^1H NMR (500 MHz, $CDCl_3$) δ 4.19 (t, *J* = 1.7 Hz, 2H, *o*-C_5H_4), 4.11 (s, 5H, C_5H_5), 4.08 (t, *J* = 1.7 Hz, 2H, *m*-C_5H_4), 3.36 (s, 2H, CH_2Fc), 2.52 (d, *J* = 10.1 Hz, 2H, CH_2N), 2.37 (dd, *J* = 10.3, 3.6 Hz, 2H, CH_2N), 2.22 (s, 6H, NMe_2), 2.06 (br s, 2H, H1,5), 1.85 (t, *J* = 4.2 Hz, 1H, H8), 1.75 – 1.69 (m, 2H, H6,7), 1.63 – 1.57 (m, 2H, H6,7). ^{13}C NMR (126 MHz, $CDCl_3$) δ 85.12 (*ipso*-C_5H_4), 70.41 (C8), 69.98 (C_5H_4, C14,15), 68.47 (C_5H_5), 67.47 (C_5H_4, C13,16), 57.79 (CH_2Ph), 52.78 (CH_2N), 44.50 (NMe_2), 36.52 (C1, C5), 27.16 (C6, C7).

*(8-Dimethylamino-3-azabicyclo[3.2.1]octane-3-ylmethyl)ferrocenyl]-(C,N,N)-palladium chloride **3***

Method A. A mixture of $PdCl_2$ (0.142 g, 0.8 mmol) and lithium chloride (0.068 g, 1.6 mmol) in MeOH (15 ml) was refluxed with stirring for 3 h and cooled. To the obtained solution was added a solution of compound **2** (0.282 g, 0.8 mmol) and sodium acetate trihydrate (0.109 g, 0.8 mmol) in MeOH (5ml). The mixture was stirred for 24 h at room temperature and evaporated. The crude was diluted with water and extracted with CH_2Cl_2. The organic layers were washed with water and brine, dried over Na_2SO_4, filtered and evaporated. The solid residue was washed with ether and small amount of acetone and dried to afford **3** (0.344 g, 87 %).

Method B. To a solution of Na_2PdCl_4 (0.086 g, 0.3 mmol) in MeOH (10 ml) was added a solution of **2** (0.103 g, 0.3 mmol) and sodium acetate trihydrate (0.041 g, 0.3 mmol) in MeOH

(10 ml). The mixture was stirred at room temperature for 24 h and evaporated. The crude residue was diluted with water and extracted with CH_2Cl_2. The organic layers were washed with water and brine, dried over Na_2SO_4, filtered and evaporated. The solid residue was washed with ether and small amount of acetone and dried to afford **3** (0.127 g, 86%) as yellow crystals. Decomposes without melting at about 140 °C. Anal.: C, 48.53; H, 5.48; N, 5.70; Cl, 7.13 %. Calc. for $C_{20}H_{27}ClFeN_2Pd$: C, 48.73; H, 5.52; N, 5.68; Cl, 7.19 %. IR (KBr, ν, cm $^{-1}$): 1102, 1005, 814, 485 (FcH); IR (nujol, ν, cm $^{-1}$): 342 (Pd-Cl). EI-MS, m/z (RI, %): 492 $[M]^+$ (9), 352 $[M\text{-}PdCl+H]^+$ (31). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.76 (t, *J* = 10.6 Hz, 1H, CH_2N), 4.43 (br s, 1H, C_5H_3, H14), 4.23 (s, 5H, C_5H_5), 4.11 – 4.07 (m, 1H, CH_2N), 4.05 (br s, 1H, C_5H_3, H15), 3.97 (br s, 1H, C_5H_3, H13), 3.60 (d, *J* = 14.8 Hz, 1H, CH_2Fc), 3.47 (br d, *J* = 15.2 Hz, 1H, CH_2Fc), 2.82 (s, 3H, NMe), 2.74 (br s, 1H, H1,5), 2.71 (s, 3H, NMe), 2.64 (d, *J* = 12.8 Hz, 1H, CH_2N), 2.60 - 2.51 (m, 2H, CH_2N, H 1,5), 2.18 (t, *J* = 3.8 Hz, 1H, H8), 2.08 – 1.99 (m, 2H, H6,7), 1.70 (dq, *J* = 9.3, 6.5 Hz, 2H, H6,7). ^{13}C NMR (126 MHz, $CDCl_3$) δ 95.16 (*ipso*-C_5H_3, C-C), 91.48 (*ipso*-C_5H_3, C-Pd), 70.60 (C_5H_3, C14), 69.75 (C8), 69.08 (C_5H_5), 68.53 (CH_2Fc), 66.03 (CH_2N), 65.42 (C_5H_3, C15 and CH_2N), 60.35 (C_5H_3, C13), 48.79 and 48.35 (NMe_2), 34.02 and 33.92 (C1,5), 31.17 and 31.02 (C6,7).

General procedure for the Suzuki reaction

A mixture of aryl bromide (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol), palladium complex **3** (0.1 mol.%), MeOH (8 ml) and H_2O (4 ml) was heated at 55 °C for 5 h. The reaction mixture was diluted with water and extracted with $CHCl_3$. The combined organic phase was dried over Na_2SO_4, evaporated and purified by chromatography on SiO_2 (petroleum ether/$CHCl_3$ = 8:1). The purified products were identified by ^{1}H NMR spectra.

References

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S2. M. Sato, H. Kono, M. Shiga, I. Motoyama and K. Hata, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 252.

S3. S-J. Liu, Q. Zhao, Q-L. Fan and W. Huang, *Eur. J. Inorg. Chem.*, 2008, **13**, 2177.

NMR spectra

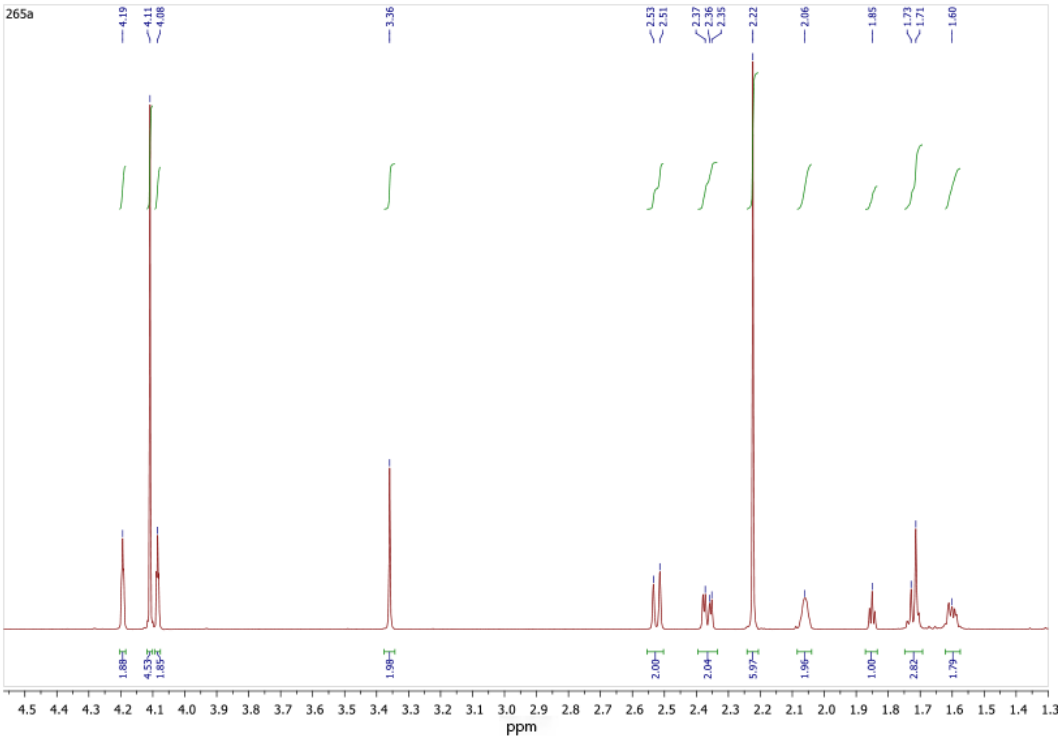

Figure S1. ^{1}H NMR spectrum of **2** ($CDCl_3$).

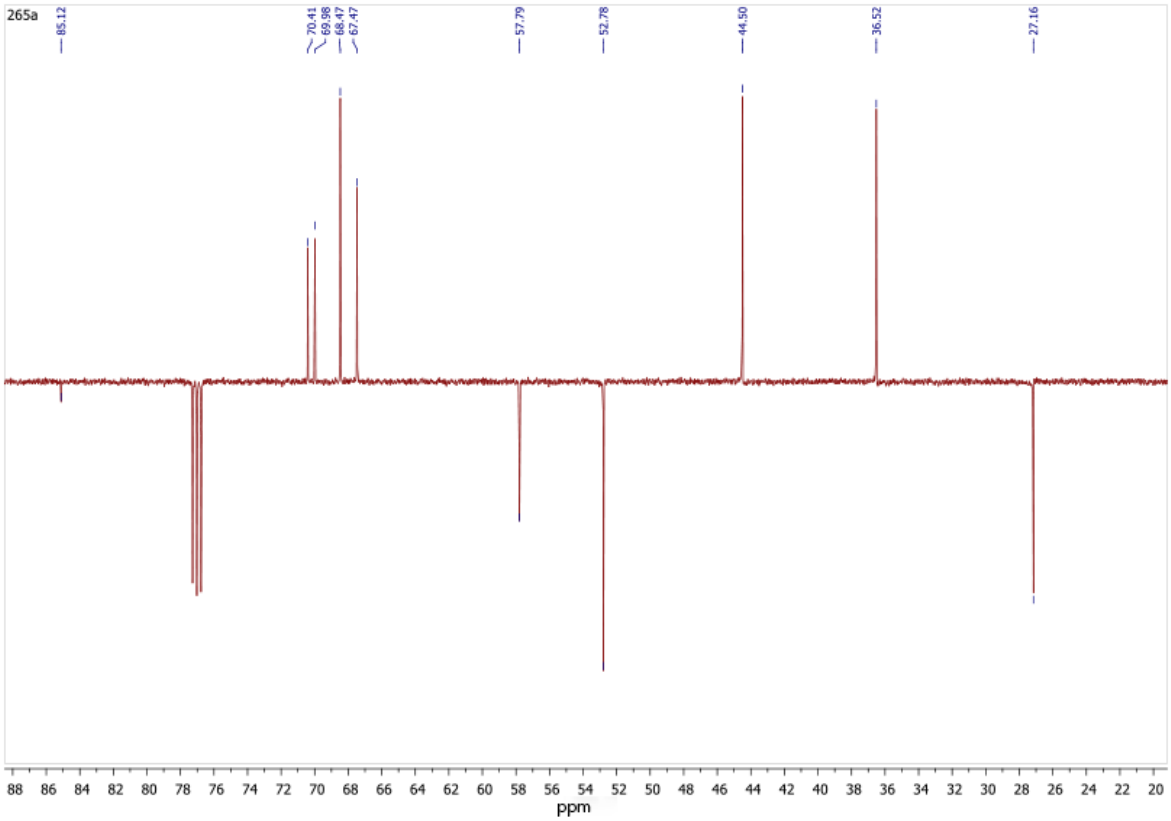

Figure S2. ^{13}C NMR spectrum of **2** ($CDCl_3$).

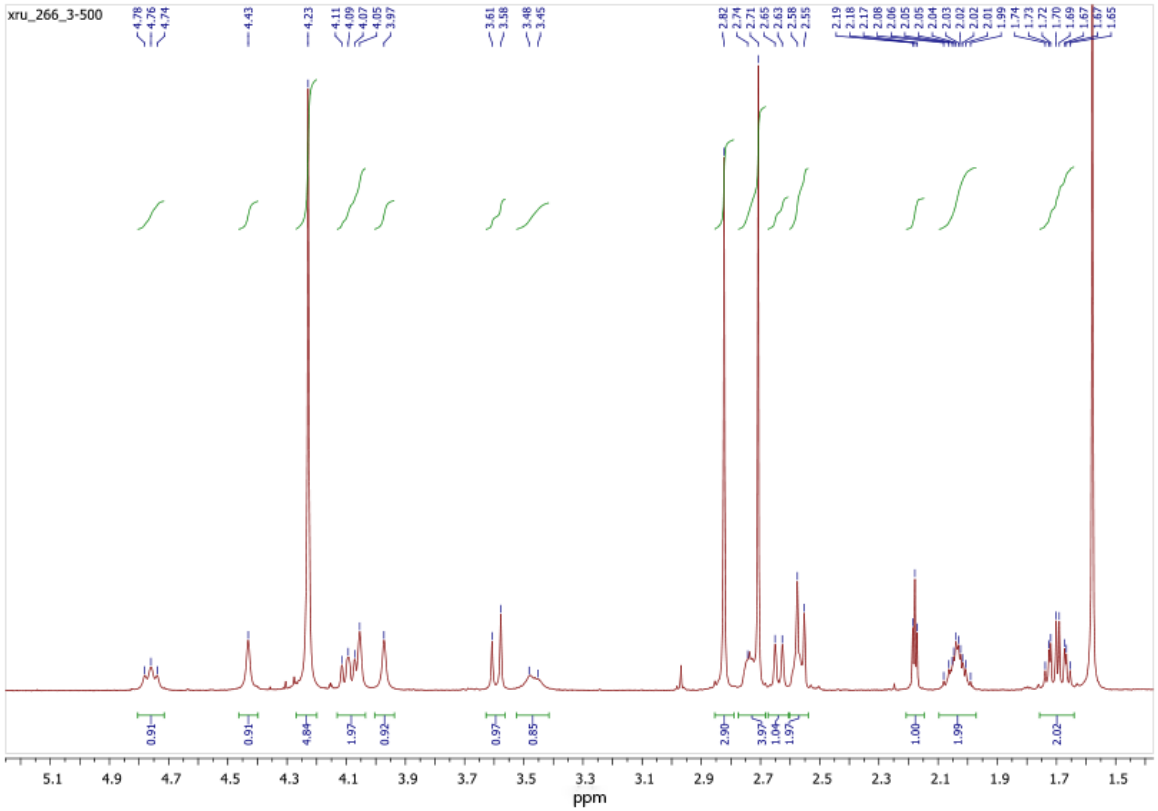

Figure S3. ^{1}H NMR spectrum of **3** ($CDCl_3$)

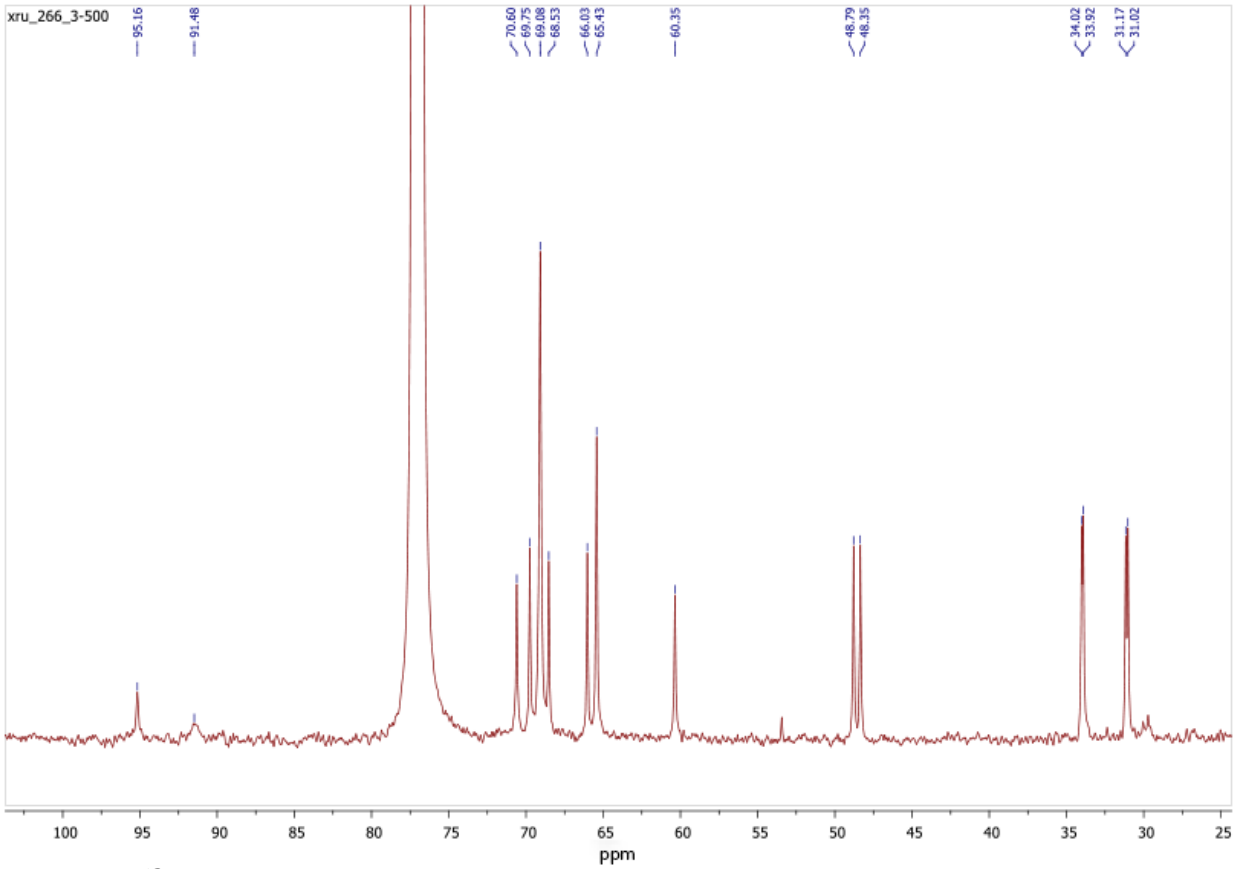

Figure S4. ^{13}C NMR spectrum of **3** ($CDCl_3$).