Supporting Information for

Asymmetric Catalytic Friedel-Crafts Reaction of Silyl Enol Ethers with Fluoral: A Possible Mechanism of the Mukaiyama-Aldol Reactions

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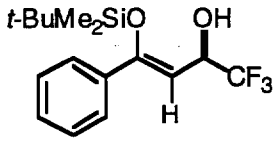
General: ^{1}H NMR and ^{13}C NMR were measured on a Varian Gemini 300 (300 MHz) spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard (0 ppm) in $CDCl_3$. Significant ^{1}H NMR data were tabulated in the following order: multiplicity (s: singlet; d: doublet; t: triplet; q: quartet; quin: quintet; sex: sextet; sep: septet, m: multiplet). Chemical shifts of ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard (77.1 ppm). IR spectra were measured on a JASCO FT/IR-5000 spectrometer. Mass spectra were measured on a JEOL AUTO FAB. Optical rotations were measured on a JASCO DIP-140. Liquid chromatographic analyses were conducted on a JASCO PU-980 instrument equipped with model UV-975 spectrometers as an ultra violet light (254 nm) and chiral column (Daicel CHIRALCEL OD-H or AS). Peak area was calculated by a Shimadzu model C-R6A as an automatic integrator. Analytical thin layer chromatography (TLC) were performed on a glass plates pre-coated with silica gel (Merck Kieselgel 60 F_{254}, layer thickness 0.25 mm). Visualization was accomplished by UV light (254 nm) and phosphomolybdic acid. Column chromatography was performed on Silica Gel 60 (70-230 mesh) purchased from Kanto Chemical Co., Inc. Molecular sieves (MS) 4Å (activated powder) was purchased from Aldrich Chemical Co., Inc. Dehydrated dichloromethane was purchased from Kanto Chemical Co., Inc. Fluoral was generated by the addition of fluoral hydrate to conc. H_2SO_4 at 100 °C.

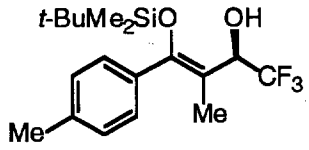
General Procedure for the Asymmetric Friedel-Crafts Reactions of Silyl Enol Ethers with Fluoral Catalyzed by BINOL-Ti Complex.

To a solution of (*R*)-BINOL-Ti complex (**1**), which was prepared from (*R*)-BINOL and $Cl_2Ti(OPr^i)_2$ in the presence of MS 4Å, then filtered and solidified, in dehydrated dichloromethane was added silyl enol ether (**2**) in dehydrated dichloromethane at 0 °C under an argon atmosphere, and then an excess amount of freshly dehydrated and distilled fluoral was introduced into this solution. After stirring for 15 minutes at the same temperature, dichloromethane and sat. $NaHCO_3$ were added to the reaction mixture. Insoluble material was filtered off through a pad of Celite and the aqueous phase was extracted three times with dichloromethane. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. Chromatographic separation by silica gel (dichloromethane : *n*-hexane = 3 : 2) gave the product (**3**).

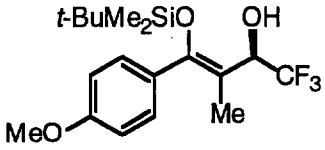


(*Z*)-**3a** pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 3H), 0.10 (s, 3H), 0.92 (s, 9H), 2.03 (d, J = 6.0 Hz, 1H), 4.46 (dquin, J = 10.2, 6.0 Hz, 1H), 5.08 (d, J = 10.2 Hz, 1H), 7.32-7.48 (m, 5H). ^{13}C NMR ($CDCl_3$) δ -4.7, -4.4, 18.2, 25.6, 69.0 (q, J = 33 Hz), 102.0, 124.9 (q, J = 282 Hz), 128.4, 128.4, 129.4, 136.2, 159.6. IR (neat) 3400, 2962, 2936, 2864, 1653, 1475, 1350, 1265, 1174, 1135, 1093, 1029, 874, 837, 781, 700 cm^{-1}. FAB-MS m/z = 333 ([M+H]$^+$). HRMS (FAB$^+$) calcd for $C_{16}H_{24}F_3O_2Si$ 333.1498, found 333.1494 ([M+H]$^+$). $[\alpha]^{26}_D$ +10.0 ° (c 1.22, $CHCl_3$) (98% ee of *R* isomer). Rf (Merck Kieselgel 60 F_{254} / dichloromethane : *n*-hexane = 3 : 2) 0.32.

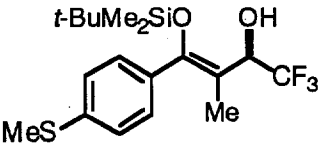
(*Z*)-**3c** colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.07 (d, J = 4.0 Hz, 9H), 1.08 (d, J = 4.0 Hz, 9H), 1.15-1.24 (m, 3H), 2.04 (d, J = 4.0 Hz, 1H), 4.48 (m, 1H), 5.06 (d, J = 8.0 Hz, 1H), 7.36-7.41 (m, 3H), 7.45-7.51 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 12.7, 17.9, 18.0, 69.1 (q, J = 32 Hz), 100.8, 125.0 (q, J = 281 Hz), 128.3, 129.3, 136.3, 159.8. IR (neat) 3393, 2947, 2869, 1650, 1464, 1348, 1273, 1172, 1134, 1097, 1028, 882, 805, 700, 690 cm^{-1}. FAB-MS m/z = 374 ([M]$^+$). HRMS (FAB$^+$) calcd for $C_{19}H_{29}F_3O_2Si$ 374.1889, found 374.1914 ([M]$^+$). $[\alpha]^{27}_D$ +2.2 ° (c 0.93, $CHCl_3$) (96% ee of *R* isomer). Rf (Merck Kieselgel 60 F_{254} / dichloromethane : *n*-hexane = 3 : 2) 0.58.



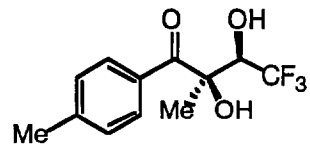
(*Z*)-**3d** colorless oil. ^{1}H NMR ($CDCl_3$) δ -0.24 (s, 3H), -0.16 (s, 3H), 0.90 (s, 9H), 1.84 (q, J = 1.2 Hz, 3H), 2.02 (d, J = 5.7 Hz, 1H), 2.36 (s, 3H), 4.57 (dq, J = 5.7, 7.2 Hz, 1H), 7.15 (m, 4H). ^{13}C NMR ($CDCl_3$) δ -4.2, -4.1, 9.6, 18.3, 21.4, 25.8, 70.8 (q, J = 32 Hz), 109.9, 125.2 (q, J = 283 Hz), 129.0, 129.2, 134.2, 138.6, 153.0. IR (neat) 3400, 2962, 2934, 2864, 1659, 1475, 1294, 1261, 1154, 1116, 1046, 874, 833, 781 cm^{-1}. FAB-MS m/z = 359 ([M-H]$^+$). HRMS (FAB$^+$) calcd for $C_{18}H_{27}F_3NaO_2Si$ 383.1631, found 383.1620 ([M+Na]$^+$). $[\alpha]^{26}_D$ -17.2 ° (c 0.43, $CHCl_3$) (94% ee of *R* isomer). Rf (Merck Kieselgel 60 F_{254} / dichloromethane : *n*-hexane = 3 : 2) 0.35.



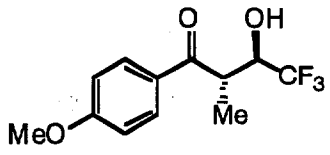
(*Z*)-**3e** colorless oil. ^{1}H NMR ($CDCl_3$) δ -0.23 (s, 3H), -0.15 (s, 3H), 0.90 (s, 9H), 1.84 (q, J = 0.9 Hz, 3H), 2.05 (d, J = 5.4 Hz, 1H), 3.83 (s, 3H), 4.57 (quin, J = 5.4 Hz, 1H), 6.87 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ -4.2, -4.1, 9.6, 18.3, 25.8, 55.3, 70.9 (q, J = 32 Hz), 109.8, 113.7, 125.2 (q, J = 283 Hz), 129.4, 130.6, 152.7, 159.8. IR (neat) 3450, 2960, 2936, 2864, 1659, 1609, 1512, 1464, 1251, 1156, 1114, 1042, 872, 839, 781 cm^{-1}. FAB-MS m/z = 376 ([M]$^+$). HRMS (FAB$^+$) calcd for $C_{18}H_{27}F_3NaO_3Si$ 399.1580, found 399.1577 ([M+Na]$^+$). $[\alpha]^{27}_D$ -16.6 ° (c 0.98, $CHCl_3$) (96% ee of *R* isomer). Rf (Merck Kieselgel 60 F_{254} / dichloromethane : *n*-hexane = 3 : 2) 0.21.



(*Z*)-**3f** pale yellow oil. ^{1}H NMR ($CDCl_3$) δ -0.22 (s, 3H), -0.14 (s, 3H), 0.90 (s, 9H), 1.84 (s, 3H), 1.98 (d, J = 5.7 Hz, 1H), 2.50 (s, 3H), 4.55 (quin, J = 5.7 Hz, 1H), 7.20 (m, 4H). ^{13}C NMR ($CDCl_3$) δ -4.2, -4.1, 9.6, 15.5, 18.3, 25.7, 70.8 (q, J = 32 Hz), 110.3, 125.1 (q, J = 284 Hz), 125.9, 129.7, 133.6, 139.6, 152.4. IR (neat) 3450, 2960, 2934, 2864, 1657, 1597, 1473, 1290, 1261, 1156, 1116, 1050, 870, 835, 781 cm^{-1}. FAB-MS m/z = 393 ([M+H]$^+$). HRMS (FAB$^+$) calcd for $C_{18}H_{28}F_3O_2SSi$ 393.1532, found 393.1519 ([M+H]$^+$). $[\alpha]^{24}_D$ -12.3 ° (c 0.99, $CHCl_3$) (95% ee of *R* isomer).



syn-**5** colorless needle. ^{1}H NMR ($CDCl_3$) δ 1.74 (q, J = 1.8 Hz, 3H), 2.44 (s, 3H), 3.21 (d, J = 10.5 Hz, 1H), 4.53 (s, 1H), 4.57 (dq, J = 10.5, 6.9 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.95 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 21.8, 23.4, 72.8 (q, J = 29 Hz), 78.8, 124.5 (q, J = 284 Hz), 129.6, 130.0, 145.1, 200.9. IR (neat) 3400, 1667, 1607, 1375, 1270, 1154, 1116, 1073, 959, 911, 833, 824, 748 cm^{-1}. $[\alpha]^{24}_D$ -20.2 ° (c 1.25, $CHCl_3$) (66% ee of 2*R*, 3*R* isomer). Chiral HPLC (Daicel, CHIRALPAK AS, *n*-hexane : *i*-PrOH = 95 : 5, 0.8 ml/min, 254 nm, t_R = 15 min (2*R*, 3*R*), 23 min (2*S*, 3*S*)). Rf (Merck Kieselgel 60 F_{254} / AcOEt : *n*-hexane = 1 : 3) 0.39.



anti-**4e** colorless oil. ^{1}H NMR ($CDCl_3$) δ 1.43 (d, J = 7.2 Hz, 3H), 3.82 (dq, J = 3.6, 7.2 Hz, 1H), 3.89 (s, 3H), 4.15 (dquin, J = 3.6, 9.0 Hz, 1H), 4.97 (d, J = 9.0 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 7.94 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 16.5, 37.1, 55.7, 74.2 (q, J = 30 Hz), 114.3, 125.1 (q, J = 283 Hz), 128.4, 131.0, 164.6, 203.2. IR (neat) 3450, 2982, 2944, 1663, 1603, 1574, 1514, 1462, 1423, 1383, 1363, 1315, 1270, 1220, 1174, 1133, 1031, 977, 843 cm^{-1}. $[\alpha]^{24}_D$ +27.4 ° (c 0.90, $CHCl_3$) (96% ee of 2*S*, 3*R* isomer). Rf (Merck Kieselgel 60 F_{254} / AcOEt : *n*-hexane = 1 : 5) 0.20.