Supporting Information

Ar-BINMOL-derived Salan-Cu(II) Complex Catalyzed Silyl-Reformatsky Reaction of Aromatic Aldehydes

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1. General information:

All reagents and solvents were used directly without purification. Flash column chromatography was performed over silica (200-300 mesh). ^1H -NMR and ^{13}C -NMR spectra were recorded at 400 and 100 MHz, respectively on Advance (Brucker) 400 MHz Nuclear Magnetic Resonance Spectrometer, and were referenced to the internal solvent signals. Thin layer chromatography was performed using silica gel; F254 TLC plates and visualized with ultraviolet light. HPLC was carried out with a Waters 2695 Millennium system equipped with a photodiode array detector. EI and CI mass spectra were performed on a Trace DSQ GC/MS spectrometer. Data are reported in the form of (m/z). The ESI-MS analysis of the samples was operated on an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4). The salan ligand was prepared according to previous report (ref. 11 of Text).

2. General procedure for the Silyl-Reformatsky reaction

All reactions were performed with 5 mol% of Cu salt and 5 mol % of salan ligand (**1**) at a 0.5 M concentration using 1.1 equiv of methyl (trimethylsilyl)acetate in DMSO. All the reactions were run at room temperature in a screw-capped vial for 48 h.

A representative procedure: A flame-dried flask under argon was charged with salan ligand **1** (47.8 mg, 0.05 mmol) and Cu(OAc)₂ (10.0 mg, 0.05 mmol), and DMSO at room temperature. After the mixture was stirred for 1 h, methyl (trimethylsilyl)acetate (1.1 mmol) and aldehyde (1 mmol) were added successively to the solution, and the mixture was stirred at ambient temperature for 48 hours. The reaction mixture was diluted with water and then extracted with DCM. The organic layer were combined, washed with brine, and dried over anhydrous Na₂SO₄, and then concentrated under reduced pressure. The crude residue was purified by column chromatography. All the products are known^[1-20] and confirmed by GC-MS, NMR, IR, HRMS.

Methyl 3-hydroxy-3-phenylpropanoate (**6a**): ¹H NMR (400 MHz, CDCl₃) δ = 7.28-7.35 (m, J = 8.4Hz, 5H, and H_{Ar}), 5.12 (q, J = 9.2Hz, H, and CH-OH), 3.70 (s, 3H, and -OCH₃), 2.72 (m, J = 8.0 Hz, 2H, and -CH₂COOMe); ¹³C NMR (100 MHz, CDCl₃) δ = 172.3 (COOMe), 142.6 (1-C_{Ar}), 128.6 (3-C_{Ar}), 127.8 (4-C_{Ar}), 125.7 (2-C_{Ar}), 70.3 (CHOH), 60.9 (-CH₂COOMe), 43.4 (-OCH₃). IR (neat, cm⁻¹): 3461, 3063, 3031, 2953, 1732, 1454, 1438, 1361, 1269, 1200, 1083, 1061, 1025, 988, 916, 762, 701 cm⁻¹. Exact mass calcd for C₁₀H₁₃O₃[M+H]⁺, 181.0865. Found 181.0850.

Methyl 3-(2-fluorophenyl)-3-hydroxypropanoate (**6b**): ¹H NMR (400 MHz, CDCl₃) δ = 7.54 (t, J = 14.2 Hz, H, and H_{Ar}), 7.28 (t, J = 19.6 Hz, H, and H_{Ar}), 7.17 (t, J = 14.8

Hz, H, and H_{Ar}), 7.03 (t, J = 18.8 Hz, H, and H_{Ar}), 5.42 (q, J = 8.8 Hz, H, and CH-OH), 3.74 (s, 3H, and -OCH₃), 2.81 (q, J = 16.8 Hz, H, and -CH₂COOMe), 2.73 (q, J = 16.4 Hz, H, and -CH₂COOMe); ¹³C NMR (100 MHz, CDCl₃) δ = 172.8 (COOMe), 129.2 (C_{Ar}), 129.1 (C_{Ar}), 127.2 (C_{Ar}), 124.4 (C_{Ar}), 124.3 (C_{Ar}), 115.4 (C_{Ar}), 64.6 (CHOH), 51.9 (-CH₂COOMe), 41.7 (-OCH₃). IR (neat, cm⁻¹): 3469, 2955, 2924, 2853, 1731, 1489, 1456, 1404, 1222, 1177, 1070, 804, 760 cm⁻¹; Exact mass calcd for C₁₀H₁₁NaFO₃ [M+Na]⁺, 221.0590. Found 211.0613.

Methyl 3-(3-fluorophenyl)-3-hydroxypropanoate (**6c**): ¹H NMR (400 MHz, CDCl₃) δ = 7.32 (q, J = 14.4 Hz, H, and H_{Ar}), 7.13 (q, J = 6.4 Hz, 2H, and H_{Ar}), 6.98 (t, J = 16.8 Hz, H, and H_{Ar}), 5.14 (t, J = 12.8 Hz, H, and CH-OH), 3.73 (s, 3H, and -OCH₃), 2.72 (d, J = 6.8 Hz, H, and -CH₂COOMe), 2.61 (s, H, and -CH₂COOMe); ¹³C NMR (100 MHz, CDCl₃) δ = 172.6 (COOMe), 130.1 (C_{Ar}), 121.2 (C_{Ar}), 114.8 (C_{Ar}), 114.5 (C_{Ar}), 112.8 (C_{Ar}), 112.6 (C_{Ar}), 69.7 (CHOH), 69.6 (-CH₂COOMe), 52.0 (-OCH₃). IR (neat, cm⁻¹): 3466, 2955, 1732, 1616, 1592, 1440, 1403, 1290, 1249, 1169, 1065, 1034, 999, 877, 791, 697 cm⁻¹; Exact mass calcd for C₁₀H₁₂FO₃ [M+H]⁺, 199.0770. Found 199.0774.

Methyl 3-(4-fluorophenyl)-3-hydroxypropanoate (**6d**): ¹H NMR (400 MHz, CDCl₃) δ = 7.35 (t, J = 5.6 Hz, 2H, and H_{Ar}), 7.04 (t, J = 8.4 Hz, 2H, and H_{Ar}), 5.13 (t, J = 8.4 Hz, H, and CH-OH), 3.73 (s, 3H, and -OCH₃), 3.30 (s, H, and -CH₂COOMe), 2.73 (d, J = 8.8 Hz, H, and -CH₂COOMe); ¹³C NMR (100 MHz, CDCl₃) δ = 172.7 (COOMe), 138.2 (C_{Ar}), 127.3 (C_{Ar}), 115.5 (C_{Ar}), 115.3 (C_{Ar}), 69.7 (CHOH), 52.0 (-CH₂COOMe), 43.1 (-OCH₃). IR (neat, cm⁻¹): 3461, 2955, 2922, 2851, 1733, 1605, 1558, 1511, 1439, 1361, 1268, 1222, 1071, 1034, 884, 838, 796 cm⁻¹; Exact mass calcd for C₁₀H₁₂FO₃

$[M+H]^+$, 199.0770. Found 199.0785.

Methyl 3-(2-chlorophenyl)-3-hydroxypropanoate (**6e**): ^1H NMR (400 MHz, CDCl_3) δ = 7.65 (s, H, and H_{Ar}), 7.34 (s, 2H, and H_{Ar}), 7.28 (d, J = 4.4 Hz, H, and H_{Ar}), 5.50 (s, H, and CH-OH), 3.77 (s, 3H, and $-\text{OCH}_3$), 2.89 (d, J = 16.8 Hz, H, and $-\text{CH}_2\text{COOMe}$), 2.62 (d, J = 6.8 Hz, H, and $-\text{CH}_2\text{COOMe}$); ^{13}C NMR (100 MHz, CDCl_3) δ = 172.9 (COOMe), 129.4 (C_{Ar}), 128.8 (C_{Ar}), 127.3 (C_{Ar}), 127.0 (C_{Ar}), 67.1 (CHOH), 52.0 ($-\text{CH}_2\text{COOMe}$), 41.2 ($-\text{OCH}_3$). IR (neat, cm^{-1}): 3479, 2925, 2854, 1732, 1596, 1439, 1403, 1261, 1200, 1166, 1076, 1051, 1031, 989, 757, 736 cm^{-1} ; Exact mass calcd for $\text{C}_{10}\text{H}_{11}\text{ClNaO}_3$ $[M+\text{Na}]^+$ 237.0294. Found 237.0292.

Methyl 3-(4-chlorophenyl)-3-hydroxypropanoate (**6f**): ^1H NMR (400 MHz, CDCl_3) δ = 7.31 (m, 4H, and H_{Ar}), 5.11 (q, J = 8.0 Hz, H, and CH-OH), 3.72 (s, 3H, and $-\text{OCH}_3$), 2.71 (q, J = 8.4 Hz, 2H, and $-\text{CH}_2\text{COOMe}$); ^{13}C NMR (100 MHz, CDCl_3) δ = 172.6 (COOMe), 141.0 (C_{Ar}), 133.6 (C_{Ar}), 128.7 (C_{Ar}), 127.1 (C_{Ar}), 69.6 (CHOH), 52.0 ($-\text{CH}_2\text{COOMe}$), 43.0 ($-\text{OCH}_3$). IR (neat, cm^{-1}): 3465, 2953, 2924, 2852, 1735, 1493, 1438, 1359, 1284, 1199, 1165, 1073, 1034, 1014, 989, 911, 832, 734 cm^{-1} ; Exact mass calcd for $\text{C}_{10}\text{H}_{11}\text{ClNaO}_3$ $[M+\text{Na}]^+$, 237.0294. Found 237.0306.

Methyl 3-(2-bromophenyl)-3-hydroxypropanoate (**6g**): ^1H NMR (400 MHz, CDCl_3) δ = 7.63 (d, J = 8.0 Hz, H, and H_{Ar}), 7.52 (d, J = 8.0 Hz, H, and H_{Ar}), 7.36 (t, J = 14.8

Hz, H, and H_{Ar}), 7.15 (t, J = 15.2 Hz, H, and H_{Ar}), 5.45 (d, J = 10.0 Hz, H, and CH-OH), 3.75 (s, 3H, and -OCH₃), 2.89 (q, J = 16.8 Hz, H, and -CH₂COOMe), 2.58 (q, J = 16.8 Hz, H, and -CH₂COOMe); ¹³C NMR (100 MHz, CDCl₃) δ = 172.8 (COOMe), 141.4 (C_{Ar}), 132.7 (C_{Ar}), 129.1 (C_{Ar}), 127.9 (C_{Ar}), 127.3 (C_{Ar}), 121.4 (C_{Ar}), 69.3 (CHOH), 52.0 (-CH₂COOMe), 41.4 (-OCH₃). IR (neat, cm⁻¹): 3473, 2953, 2924, 1732, 1468, 1437, 1360, 1291, 1198, 1166, 1074, 1021, 757 cm⁻¹; Exact mass calcd for C₁₀H₁₁BrNaO₃ [M+Na]⁺, 280.9789. Found 280.9800.

Methyl 3-(3-bromophenyl)-3-hydroxypropanoate (**6h**): ¹H NMR (400 MHz, CDCl₃) δ = 7.55 (s, H, and H_{Ar}), 7.42 (d, J = 7.6 Hz, H, and H_{Ar}), 7.29 (d, J = 7.6 Hz, H, and H_{Ar}), 7.22 (t, J = 15.2 Hz, H, and H_{Ar}), 5.11 (t, J = 12.4 Hz, H, and CH-OH), 3.73 (s, 3H, and -OCH₃), 2.72 (d, J = 7.6 Hz, 2H, and -CH₂COOMe); ¹³C NMR (100 MHz, CDCl₃) δ = 172.6 (COOMe), 144.8 (C_{Ar}), 130.9 (C_{Ar}), 130.2 (C_{Ar}), 128.9 (C_{Ar}), 124.3 (C_{Ar}), 122.7 (C_{Ar}), 69.6 (CHOH), 52.0 (-CH₂COOMe), 43.0 (-OCH₃). IR (neat, cm⁻¹): 3454, 2954, 2924, 1731, 1488, 1438, 1402, 1359, 1263, 1199, 1104, 1034, 1011, 988, 826, 727 cm⁻¹; Exact mass calcd for C₁₀H₁₁BrNaO₃ [M+Na]⁺, 280.9789. Found 280.9801.

Methyl 3-(4-bromophenyl)-3-hydroxypropanoate (**6i**): ¹H NMR (400 MHz, CDCl₃) δ = 7.48 (d, J = 8.0 Hz, 2H, and H_{Ar}), 7.38 (s, 2H, and H_{Ar}), 5.10 (t, J = 12.4 Hz, H, and CH-OH), 3.73 (s, 3H, and -OCH₃), 2.71 (t, J = 7.6 Hz, H, and -CH₂COOMe), 2.24 (s, H, and -CH₂COOMe); ¹³C NMR (100 MHz, CDCl₃) δ = 172.6 (COOMe), 144.8 (C_{Ar}), 130.9 (C_{Ar}), 130.1 (C_{Ar}), 128.9 (C_{Ar}), 124.3 (C_{Ar}), 122.7 (C_{Ar}), 69.6 (CHOH), 52.0 (-CH₂COOMe), 43.0 (-OCH₃). IR (neat, cm⁻¹): 3469, 2953, 2925, 2953, 1731, 1595,

1570, 1475, 1438, 1359, 1265, 1197, 1096, 1071, 1034, 997, 889, 786, 697, 666 cm^{-1} ;
 Exact mass calcd for $\text{C}_{10}\text{H}_{11}\text{BrNaO}_3$ $[\text{M}+\text{Na}]^+$, 280.9789. Found 280.9787.

Methyl 3-(2,6-dichlorophenyl)-3-hydroxypropanoate (**6j**): ^1H NMR (400 MHz, CDCl_3) δ = 7.29 (t, J = 8.4 Hz, 2H, and H_{Ar}), 7.16 (t, J = 7.2 Hz, H, and H_{Ar}), 5.95 (d, J = 9.6 Hz, H, and CH-OH), 3.74 (s, 3H, and $-\text{OCH}_3$), 3.29 (q, J = 16.0 Hz, H, and $-\text{CH}_2\text{COOMe}$), 2.74 (q, J = 15.6 Hz, H, and $-\text{CH}_2\text{COOMe}$); ^{13}C NMR (100 MHz, CDCl_3) δ = 171.6 (COOMe), 135.9 (C_{Ar}), 134.5 (C_{Ar}), 129.5 (C_{Ar}), 129.4 (C_{Ar}), 68.1 (CHOH), 52.0 ($-\text{CH}_2\text{COOMe}$), 39.5 ($-\text{OCH}_3$). IR (neat, cm^{-1}): 3464, 3088, 2955, 2920, 2850, 1704, 1581, 1562, 1441, 1342, 1251, 1239, 1196, 1085, 1067, 982, 917, 842, 778, 767, 737 cm^{-1} ; Exact mass calcd for $\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{NaO}_3$ $[\text{M}+\text{Na}]^+$, 270.9905. Found 270.9904.

Methyl 3-(2,4-dichlorophenyl)-3-hydroxypropanoate (**6k**): ^1H NMR (400 MHz, CDCl_3) δ = 7.60 (d, J = 8.4 Hz, H, and H_{Ar}), 7.37 (d, J = 16.8 Hz, H, and H_{Ar}), 7.30 (t, J = 8.4 Hz, H, and H_{Ar}), 5.45 (d, J = 9.6 Hz, H, and CH-OH), 3.77 (s, 3H, and $-\text{OCH}_3$), 2.87 (q, J = 16.4 Hz, H, and $-\text{CH}_2\text{COOMe}$), 2.57 (q, J = 16.4 Hz, H, and $-\text{CH}_2\text{COOMe}$); ^{13}C NMR (100 MHz, CDCl_3) δ = 171.6 (COOMe), 135.9 (C_{Ar}), 134.5 (C_{Ar}), 129.5 (C_{Ar}), 129.4 (C_{Ar}), 68.1 (CHOH), 52.0 ($-\text{CH}_2\text{COOMe}$), 39.5 ($-\text{OCH}_3$). IR (neat, cm^{-1}): 3481, 2957, 2925, 2854, 1731, 1591, 1438, 1379, 1361, 1263, 1199, 1167, 1103, 1076, 1050, 822, 773, 743 cm^{-1} ; Exact mass calcd for $\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{NaO}_3$ $[\text{M}+\text{Na}]^+$, 270.9905. Found 270.9904.

Methyl 3-hydroxy-3-(naphthalen-2-yl)propanoate (**6l**): ^1H NMR (400 MHz, CDCl_3) δ = 7.86 (d, J = 15.2 Hz, 4H, and H_{Ar}), 7.50 (t, J = 4.4 Hz, H, and H_{Ar}), 5.33 (q, J = 8.8 Hz, H, and CH-OH), 3.75 (s, 3H, and $-\text{OCH}_3$), 2.85 (t, J = 13.2 Hz, 2H, and $-\text{CH}_2\text{COOMe}$); ^{13}C NMR (100 MHz, CDCl_3) δ = 172.8 (COOMe), 139.9 (C_{Ar}), 133.3 (C_{Ar}), 133.1 (C_{Ar}), 128.4 (C_{Ar}), 128.0 (C_{Ar}), 127.7 (C_{Ar}), 126.3 (C_{Ar}), 126.0 (C_{Ar}), 124.5 (C_{Ar}), 123.7 (C_{Ar}), 70.5 (CHOH), 52.0 ($-\text{CH}_2\text{COOMe}$), 43.2 ($-\text{OCH}_3$). IR (neat, cm^{-1}): 3465, 3055, 2953, 2924, 2853, 1732, 1633, 1493, 1437, 1359, 1273, 1204, 1170, 1071, 1035, 859, 821, 748 cm^{-1} ; Exact mass calcd for $\text{C}_{14}\text{H}_{14}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$, 253.0841. Found 253.0843.

Methyl 3-(2-bromo-5-methoxyphenyl)-3-hydroxypropanoate (**6m**): ^1H NMR (400 MHz, CDCl_3) δ = 7.40 (d, J = 8.8 Hz, H, and H_{Ar}), 7.21 (t, J = 14.4 Hz, H, and H_{Ar}), 6.72 (q, J = 8.8 Hz, H, and H_{Ar}), 5.39 (q, J = 9.6 Hz, H, and CH-OH), 3.82 (s, 3H, and $-\text{OCH}_3$), 3.77 (s, 3H), 2.89 (q, J = 16.4 Hz, H, and $-\text{CH}_2\text{COOMe}$), 2.55 (q, J = 16.8 Hz, H, and $-\text{CH}_2\text{COOMe}$); ^{13}C NMR (100 MHz, CDCl_3) δ = 172.9 (COOMe), 159.4 (C_{Ar}), 142.4 (C_{Ar}), 133.3 (C_{Ar}), 115.3 (C_{Ar}), 112.5 (C_{Ar}), 111.5 (C_{Ar}), 69.3 (CHOH), 55.5 ($-\text{CH}_2\text{COOMe}$), 52.0 ($-\text{OCH}_3$), 41.3 ($-\text{OCH}_3$). IR (neat, cm^{-1}): 3493, 3003, 2954, 2851, 1732, 1595, 1573, 1470, 1438, 1419, 1296, 1236, 1164, 1131, 1056, 1035, 1014, 910, 869, 813, 735, 648 cm^{-1} ; Exact mass calcd for $\text{C}_{11}\text{H}_{13}\text{BrNaO}_4$ $[\text{M}+\text{Na}]^+$, 310.9895. Found 310.9908.

Methyl 3-(2-bromo-4-fluorophenyl)-3-hydroxypropanoate (**6n**): ^1H NMR (400 MHz, CDCl_3) δ = 7.62 (q, J = 8.4 Hz, 2H, and H_{Ar}), 7.16 (t, J = 7.2 Hz, H, and H_{Ar}), 7.09 (t, J = 16.4 Hz, H, and H_{Ar}), 5.41 (d, J = 9.6 Hz, H, and CH-OH), 3.76 (s, 3H, and $-\text{OCH}_3$), 2.87 (q, J = 16.8 Hz, H, and $-\text{CH}_2\text{COOMe}$), 2.56 (q, J = 16.8 Hz, H, and $-\text{CH}_2\text{COOMe}$); ^{13}C NMR (100 MHz, CDCl_3) δ = 172.8 (COOMe), 128.5 (C_{Ar}), 128.4 (C_{Ar}), 119.9 (C_{Ar}), 119.7 (C_{Ar}), 115.1 (C_{Ar}), 114.9 (C_{Ar}), 68.7 (CHOH), 52.1 ($-\text{CH}_2\text{COOMe}$), 41.4 ($-\text{OCH}_3$). IR (neat, cm^{-1}): 3473, 2954, 2927, 1732, 1600, 1485, 1438, 1391, 1361, 1291, 1260, 1216, 1166, 1076, 1028, 912, 860, 825, 673 cm^{-1} ; Exact mass calcd for $\text{C}_{10}\text{H}_9\text{BrFNaO}_3$ [$\text{M}+\text{Na}$] $^+$, 298.9695. Found 298.9703.

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Scheme S1. Catalytic silyl-Reformatsky reaction of various aromatic aldehydes promoted by Salan-Cu complex derived from cyclohexane-1,2-diamine and 2-hydroxybenzaldehyde: the number after Δ is the decreased yield in comparison to that of salan(**1**)-copper catalyst under the same reaction conditions.

4. NMR spectra of products 6

TM 6a: ^1H NMR

^{13}C NMR

TM 6b: ^1H NMR

^{13}C NMR

TM 6c: ^1H NMR

^{13}C NMR

TM 6d: ^1H NMR

^{13}C NMR

TM 6e: ^1H NMR

^{13}C NMR

TM 6f: ^1H NMR

^{13}C NMR

TM 6g: ^1H NMR

^{13}C NMR

TM 6h: ^1H NMR

^{13}C NMR

TM 6i: ^1H NMR

^{13}C NMR

TM 6j: ^1H NMR

^{13}C NMR

TM 6k: ^1H NMR

^{13}C NMR

TM 61: ^1H NMR

^{13}C NMR

TM 6m: ^1H NMR

^{13}C NMR

TM 6n: ^1H NMR

^{13}C NMR