Supporting Information

Ru(III)-Catalyzed Cyclization of Arene-Alkene Substrates via Intramolecular Electrophilic Hydroarylation

So Won Youn,[†] Stefan J. Pastine[‡] and Dalibor Sames[‡]*

[†]*Department of Chemistry, Pukyong National University, Busan, Korea*
[‡]*Department of Chemistry, Columbia University, New York, NY 10027*

General

Nuclear Magnetic Resonance spectra were recorded on Bruker 300 or 400 Fourier transform NMR spectrometers. Spectra were recorded in $CDCl_3$ solutions referenced to TMS or the solvent residual peak. IR spectra were taken as neat for liquids on NaCl plates, and as KBR pellet for solids using a Perkin-Elmer 1600 FTIR spectrometer. High Resolution Mass Spectra were obtained on a JOEL JMS_HX110 HF mass spectrometer. Flash chromatography was performed on SILICYCLE silica gel (230-400 mesh). All catalyst were bought from Strem or Aldrich and used as received.

General Procedure for the Preparation of Homoallylic Phenyl Ethers

A solution of the 3-buten-1-ol, the corresponding phenol (3 eq.), and PPh_3 (1.3 eq.) in THF (0.3 M) was treated with DEAD (1.3 eq.) at rt. The resulting homogeneous solution was heated at reflux for 1-3 h, cooled at rt, and concentrated in vacuo. The residue was purified via flash column chromatography (EtOAc:Hexanes=1:30~1:50) to afford the corresponding product. (73-96%)

Spectral data for 1-(4-Methoxyphenoxy)-3-butene (**3**)[1] were consistent with data reported in the literature.

1-(3,5-Dimethylphenoxy)-3-butene (1)

colorless oil, δ_H($CDCl_3$, 300 MHz) 2.33 (s, 6H), 2.57 (q, J = 6.7 Hz, 2H), 4.02 (t, J = 6.7 Hz, 2H), 5.18 (m, 2H), 5.94 (m, 1H), 6.58 (s, 2H), 6.63 (s, 1H). δ_C($CDCl_3$, 75 MHz) 21.4, 33.7, 66.9, 112.3, 116.8, 122.4, 134.6, 139.1, 158.9. ν_{max}(NaCl)/cm^{-1} 2922, 1596, 1468, 1324, 1296, 1169, 1156, 1069, 916, 829, 688. HREIMS *m/z* 176.1201 $(M)^+$, calcd for $C_{12}H_{16}O$ 176.1201.

1-(2-Naphthoxy)-3-butene (5)

colorless oil, δ_H($CDCl_3$, 400 MHz) 2.65 (q, J = 6.7 Hz, 2H), 4.16 (t, J = 6.7 Hz, 2H), 5.23 (m, 2H), 6.01 (m, 1H), 7.18 (d, J = 2.3 Hz, 1H), 7.21 (dd, J = 2.5, 8.9 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.78 (d, J = 8.9 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H). δ_C($CDCl_3$, 100 MHz) 33.7, 67.2, 106.6, 116.8, 118.8, 123.4, 126.1, 126.5, 127.4, 128.8, 129.1, 134.2, 134.4, 156.6. ν_{max}(NaCl)/cm^{-1} 3059, 2926, 1630, 1600, 1511, 1465, 1389, 1258, 1217, 1182, 1120, 1034, 918, 836, 811, 746. HREIMS *m/z* 198.1037 $(M)^+$, calcd for $C_{14}H_{14}O$ 198.1045.

1-(4-Bromo-3,5-dimethylphenoxy)-3-butene (7)

white solid, δ_H($CDCl_3$, 400 MHz) 2.40 (s, 6H), 2.54 (q, J = 6.7 Hz, 2H), 3.97 (t, J = 6.7 Hz, 2H), 5.16 (m, 2H), 5.91 (m, 1H), 6.66 (s, 2H). δ_C($CDCl_3$, 100 MHz) 24.1, 33.7, 67.2, 114.3, 116.8, 118.0, 134.1, 138.7, 157.1. ν_{max}(NaCl)/cm^{-1} 3077, 2924, 1585, 1466, 1322, 1169, 1072, 1018, 917, 855. HRFABMS *m/z* 254.0317 $(M)^+$, calcd for $C_{12}H_{15}BrO$ 254.0306.

(*R*)-2-(4-Methoxyphenoxy)-4-pentene (41)

Following the general procedure, (*S*)-4-penten-2-ol (0.2 ml, 1.89 mmol, 99% ee) and 4-methoxyphenol (709 mg, 5.66 mmol) gave **45** as a colorless oil (348 mg, 96%) in 92% ee as determined by HPLC analysis (Daicel OD, 1% *i*-PrOH in Hexanes, 250 nm, 1.0 ml/min) t_r = 22.1 (*R*), 25.1 (*S*) min. δ_H($CDCl_3$, 400 MHz) 1.28 (d, J = 6.2 Hz, 3H), 2.31 (quintet, J = 7.0 Hz, 1H), 2.47 (quintet, J = 7.1 Hz, 1H), 3.76 (s, 3H), 4.28 (sextet, J = 6.1 Hz, 1H), 5.10 (m, 2H), 5.87 (m, 1H), 6.83 (m, 4H). δ_C($CDCl_3$, 100 MHz) 19.6, 40.7, 55.7, 74.5, 114.5, 117.1, 117.5, 134.2, 151.7, 153.7. ν_{max}(NaCl)/cm^{-1} 3076, 2977, 1507, 1229, 1039, 917, 827, 739. HREIMS *m/z* 192.1159 $(M)^+$, calcd for $C_{12}H_{16}O_2$ 192.1150.

Preparation of 1-(4-*N*-Fmoc-aminophenoxy)-3-butene (9)

To a solution of 4-*N*-Boc-aminophenol[2] (1.5 g, 7.17 mmol) in DMF (7 ml) was added K_2CO_3 (3.0 g, 21.52 mmol), NaI (109 mg, 0.72 mmol), and 4-bromobutene (0.85 ml, 7.89 mmol). After stirring at 80 ^oC for 24 h, the reaction mixture was diluted with ether and washed with water. The aqueous phase was extracted with ether (10 ml x 3), and the organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:8) to give 1-(4-*N*-Boc-aminophenoxy)-3-butene (860 mg, 46%) as a white solid. 1-(4-*N*-Boc-aminophenoxy)-3-butene (788 mg, 3.0 mmol) was treated with TFA (2 ml) in CH_2Cl_2 (8 ml) at rt. After 30 min, the solvent was blown off with Ar, the residue was diluted with CH_2Cl_2, basified with sat. $NaHCO_3$, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:1) to give 1-(4-aminophenoxy)-3-butene (447 mg, 92%) as a yellow oil. To a solution of 1-(4-aminophenoxy)-3-butene (145 mg, 0.89 mmol) in aq. dioxane (2 ml) were added *i*-Pr_2NEt (187 μl, 1.07 mmol) and FmocCl (261 mg, 0.98 mmol) at 0 ^oC. After being stirred at rt for 30 min., the reaction mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:8) to give 1-(4-*N*-Fmoc-

aminophenoxy)-3-butene (**9**) (250 mg, 73%) as a beige solid.
δ_H($CDCl_3$, 300 MHz) 2.53 (q, J = 6.7 Hz, 2H), 3.98 (t, J = 6.7 Hz, 2H), 4.26 (t, J = 6.5 Hz, 1H), 4.51 (d, J = 6.6 Hz, 2H), 5.13 (m, 2H), 5.89 (m, 1H), 6.53 (br s, 1H), 6.83 (d, J = 8.8 Hz, 2H), 7.26 (br s, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.58 (m, 2H), 7.76 (d, J = 7.4 Hz, 2H). δ_C($CDCl_3$, 75 MHz) 33.6, 47.1, 66.7, 67.5, 115.0, 117.0, 120.0, 120.7, 124.9, 127.1, 127.7, 130.7, 134.4, 141.3, 143.7, 153.8, 155.3. ν_{max}(NaCl)/cm^{-1} 3335, 2919, 1694, 1529, 1296, 1225, 1089, 1055, 823, 737, 646. HRFABMS *m/z* 385.1663 $(M)^+$, calcd for $C_{25}H_{23}NO_3$ 385.1678.

Preparation of 4-Methoxyphenyl cinnamate (11)

To a solution of 4-methoxyphenol (300 mg, 2.4 mmol) in CH_2Cl_2 (2 ml) was added cinnamic acid (358 mg, 2.4 mmol), DMAP (30 mg, 0.24 mmol), and the solution of DCC (499 mg, 2.4 mmol) in CH_2Cl_2 (2 ml) at 0 ^oC. After being stirred at rt for 3 h, the precipitate was filtered off and the filtrate was washed with H_2O, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:5) to give **11** (606 mg, 99%) as a white solid. Spectral data were consistent with data reported in the literature.[3]

General Procedure for the Preparation of 5-Phenylpentene (13) and 5-(3-Methoxyphenyl)pentene (21)

To a solution of the corresponding phenethyl bromide in THF was added allylmagnesium chloride (1.5 eq., 2.0 M solution in THF) at 0 ^oC. After being stirred at reflux for 1 h, the reaction mixture was quenched with sat. NH_4Cl solution, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane=1:50 ~ only hexanes) to afford the corresponding product. (95-98%)
Spectral data for 5-Phenylpentene (**13**)[4] and 5-(3-Methoxyphenyl)pentene (**21**)[5] were consistent with data reported in the literature.

General Procedure for the Preparation of 2-Methyl-5-phenylpentene (15) and (2-Cyclohex-2-enylethyl)benzene (17)

To a suspension of Mg turning (1.6 eq.) in dry THF was added a solution of phenethyl bromide (1.5 eq.) in THF dropwise at rt. After stirred at rt for 30 min and then reflux for 10 min, this Grignard reagent was added to a solution of the corresponding allyl bromide dropwise at rt. After the reaction was completed, the reaction mixture was quenched with sat. NH_4Cl solution and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (only hexanes) to afford the corresponding product. (70-100%)
Spectral data for 2-methyl-5-phenylpentene (**15**)[6] and (2-cyclohex-2-enylethyl)benzene (**17**)[7] were

consistent with data reported in the literature.

Preparation of 3-Methyl-5-phenyl-2-pentene (19)

To a suspension of *t*-BuOK (965.6 mg, 8.17 mmol) in toluene (33 ml) at 0 ^{o}C was added $EtPPh_3Br$ (3.07 g, 8.17 mmol). After being stirred vigorously for 10 min at 0 ^{o}C and 1 h at rt, the reaction mixture was cooled to 0 ^{o}C. 4-Phenyl-2-butanone (0.5 ml, 3.27 mmol) was added and the solution was heated to 75 ^{o}C. After 4 h, the mixture was cooled to 0 ^{o}C, quenched with sat. NH_4Cl/water (1:1, 33 ml), and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting only hexanes to give 3-methyl-5-phenyl-2-pentene (**19**) (524.0 mg, quant. olefin isomer mixture 42:58) as a colorless oil.
Spectral data for 3-methyl-5-phenyl-2-pentene (**19**)[8] were consistent with data reported in the literature.

Preparation of 5-(3-Hydroxyphenyl)pentene (23)

To a solution of **21** (306.6 mg, 1.74 mmol) in xylene (4 ml) was added MeMgI (5.8 ml, 17.4 mmol, 3.0 M solution in Et_2O). After being stirred at 165 ^{o}C for 24 h, the reaction mixture was diluted with EtOAc and quenched with sat. NH_4Cl. The organic phase was separated and the aqueous phase was extracted with EtOAc twice. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:10) to give 5-(3-hydroxyphenyl)pentene (**23**) (222.9 mg, 79%) as a colorless oil.
Spectral data for 5-(3-hydroxyphenyl)pentene (**23**)[9] were consistent with data reported in the literature.

Preparation of ethyl 6-(3-Methoxyphenyl)-3-methylhex-2-enoate (25)

To a solution of 3-allylanisole (814 mg, 5.5 mmol) in dry THF (2.5 ml) was added 9-BBN (5.5 mmol, 0.5 M solution in THF) at 0 ^{o}C. The reaction mixture was warmed up slowly to rt and then stirred for 6 h to give a solution of *B*-alkyl-9-BBN. To the resulting borane solution were added DMF (25 ml), $PdCl_2$(dppf) (122.5 mg, 0.15 mmol), (*Z*)-β-iodo-β-methyl ethyl acrylate (1.2 g, 5 mmol), and powdered K_2CO_3 (1.4 g, 10 mmol). The reaction mixture was stirred for 8 h at 50 ^{o}C and then poured into water. The product was extracted with benzene, washed with water 4 times, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:10) to give ethyl 6-(3-Methoxyphenyl)-3-methylhex-2-enoate **(25)** (620mg, 47%,) as a colorless oil.
δ_H($CDCl_3$, 400 MHz) 1.25 (t, J = 7.1 Hz, 3H), 1.77 (m, 2H), 1.85 (d, J = 1.4 Hz, 3H), 2.63 (t, J = 7.9 Hz, 2H), 2.67 (t, J = 7.9 Hz, 2H), 3.78 (s, 3H), 4.12 (q, J = 7.1 Hz, 2H), 5.66 (s, 1H), 6.72 (m, 2H), 6.77 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H). δ_C($CDCl_3$, 100 MHz) 14.5, 25.2, 30.0, 33.3, 36.2, 55.2, 59.5, 111.0, 114.0, 116.3, 120.7, 129.0, 143.7, 159.3, 159.6, 166.1. ν_{max}(NaCl)/cm^{-1} 2939, 1713,

1648, 1602, 1489, 1453, 1377, 1261, 1236, 1155, 1042, 859, 781, 696. HRFABMS *m/z* 262.1563 $(M)^+$, calcd for $C_{16}H_{22}O_3$ 262.1569.

Preparation of *N*-(Trifluoromethanesulfonyl)-*N*-phenylaminobut-3-ene (27)

To a solution of aniline (1 ml, 11.04 mmol) in EtOH were added NaOAc (1.0 g, 12.14 mmol) and 4-bromobutene (1.2 ml, 11.04 mmol) at rt. After being stirred at reflux for 5 h, the reaction mixture was diluted with CH_2Cl_2 and washed with water. The aqueous phase was extracted with CH_2Cl_2 twice and the collected organic layer was dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:10) to give of *N*-phenylaminobut-3-ene (785.5 mg, 48%) as a yellow oil. To a solution of *N*-phenylaminobut-3-ene (199.8 mg, 1.36 mmol) and NEt_3 (208 μl, 1.49 mmol) in CH_2Cl_2 (3 ml) was added Tf_2O (254 μl, 1.49 mmol) at –78 ^oC. After 1 h, the reaction mixture was quenched with sat. $NaHCO_3$. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 twice and the collected organic layer was dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:30) to give **27** (360.2 mg, 95%) as a white solid.
δ_H($CDCl_3$, 300 MHz) 2.25 (q, *J* = 8.9 Hz, 2H), 3.85 (t, *J* = 9.5 Hz, 2H), 5.06 (m, 2H), 5.69 (m, 1H), 7.31 (m, 2H), 7.41 (m, 3H). δ_C($CDCl_3$, 75 MHz) 32.6, 52.5, 112.9, 118.1, 118.2, 124.3, 129.1, 129.2, 129.6, 130.3, 133.3, 136.6. ν_{max}(NaCl)/cm^{-1} 3063, 2915, 1492, 1380, 1191, 1182, 1128, 1080, 914. HRFABMS *m/z* 279.0545 $(M)^+$, calcd for $C_{11}H_{12}F_3NO_2S$ 279.0541.

Preparation of 3-(4-Penten)indole (31)

To a solution of MeMgI (1.7 ml, 5.24 mmol, 3.0 M solution in Et_2O) in benzene (5 ml) was added a solution of indole (581.3 mg, 4.91 mmol) at rt. After 10 min, 5-bromopentene (0.4 ml, 3.28 mmol) was added and the reaction mixture was allowed to reflux. After 27 h, the reaction mixture was cooled and quenched with sat. NH_4Cl. The organic phase was separated and the aqueous phase was extracted with EtOAc twice. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:10) to give of 3-(4-penten)indole (**31**) (395.9 mg, 65%) as a colorless oil.
δ_H($CDCl_3$, 400 MHz) 1.83 (quintet, *J* = 7.5 Hz, 2H), 2.17 (q, *J* = 7.4 Hz, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 5.03 (m, 2H), 5.88 (m, 1H), 6.96 (s,1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.85 (br s, 1H). δ_C($CDCl_3$, 100 MHz) 24.7, 29.4, 33.7, 110.9, 114.4, 116.4, 118.8, 118.9, 121.0, 121.6, 127.3, 136.0, 138.6. ν_{max}(NaCl)/cm^{-1} 3417, 3058, 2929, 1456, 1418, 1336, 1225, 1091, 1010, 910, 741. HRFABMS *m/z* 185.1206 $(M)^+$, calcd for $C_{13}H_{15}N$ 185.1204.

Preparation of *N*-Methyl-3-(4-penten)indole (29)

To a solution of **31** (138 mg, 0.75 mmol) in THF (3 ml) was added NaH (59.7 mg, 1.49 mmol, 60%

dispersion in mineral oil) at 0 °C. After being stirred at 0 °C for 15 min and then at rt for 1 h, the reaction mixture was cooled to 0 °C, treated with MeI (70 μl, 1.12 mmol), and then allowed to warm to rt. After 1.5 h, the reaction mixture was cooled to 0 °C, quenched with sat. NH_4Cl, and extracted with EtOAc. The organic phase was separated and the aqueous phase was extracted with EtOAc twice. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:50) to give of *N*-methyl-3-(4-penten)indole (**29**) (126 mg, 85%) as a colorless oil.

δ_H($CDCl_3$, 300 MHz) 1.83 (quintet, J = 7.7 Hz, 2H), 2.18 (q, J = 7.7 Hz, 2H), 2.79 (t, J = 7.7 Hz, 2H), 3.75 (s, 3H), 5.04 (m, 2H), 5.89 (m, 1H), 6.83 (s,1H), 7.11 (t, J = 7.5 Hz, 1H), 7.22 (t, J = 8.1 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H). δ_C($CDCl_3$, 75 MHz) 24.5, 29.6, 32.5, 33.6, 109.0, 114.5, 115.1, 118.4, 119.0, 121.4, 126.0, 127.9, 137.0, 138.9. ν_{max}(NaCl)/cm^{-1} 3056, 2929, 1472, 1377, 1325, 1246, 1130, 1012, 910, 738. HRFABMS *m/z* 199.1353 $(M)^+$, calcd for $C_{14}H_{17}N$ 199.1361.

Preparation of 3-(3-Methyl-3-penten)indole (35)

To a solution of indole (500 mg, 4.23 mmol) in CH_2Cl_2 (8 ml) were added methyl vinyl ketone (355 μl, 4.23 mmol) and $InCl_3$ (93.5 mg, 0.42 mmol) at rt. After 1.5 h, the reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic layer was combined, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting EtOAc-hexane (1:3) to give of 4-(1*H*-indol-3-yl)butan-2-one (633.6 mg, 80%). **35** was prepared in the same manner described above for **19**. 4-(1*H*-Indol-3-yl)butan-2-one (633.6 mg, 3.38 mmol), *t*-BuOK (999.3 mg, 8.46 mmol), and $EtPPh_3Br$ (3.17 g, 8.46 mmol) gave 3-(3-methyl-3-penten)indole (**35**) in 80% (539.5 mg, olefin isomer mixture 43:57) as a colorless oil (SiO_2, EtOAc : hexane = 1:8).

δ_H($CDCl_3$, 400 MHz) 1.56 (d, J = 6.6 Hz, 3H), 1.61 (d, J = 6.6 Hz, 3H), 1.72 (s, 3H), 1.79 (s, 3H), 2.41 (t, J = 7.5 Hz, 2H), 2.45 (t, J = 8.2 Hz, 2H), 2.84 (m, 2H), 2.87 (m, 2H), 5.27 (q, J = 6.6 Hz, 1H), 5.31 (q, J = 6.7 Hz, 1H), 6.96 (s, 1H), 6.98 (s, 1H), 7.13 (m, 1H), 7.14 (m, 1H), 7.20 (m, 1H), 7.20 (m, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.64 (t, J = 8.2 Hz, 1H), 7.64 (t, J = 8.2 Hz, 1H), 7.86 (br s, 1H), 7.86 (br s, 1H). δ_C($CDCl_3$, 100 MHz) 13.6, 14.3, 16.0, 23.6, 24.2, 32.4, 40.3, 110.89, 116.69, 118.38, 118.43, 118.59, 118.62, 118.88, 119.18, 119.21, 120.68, 120.87, 121.66, 127.37, 135.68, 135.79, 136.07 (5 carbons are missing due to overlapping). ν_{max}(NaCl)/cm^{-1} 3418, 2919, 1456, 1351, 1225, 1091, 1010, 803, 741. HRFABMS *m/z* 199.1360 $(M)^+$, calcd for $C_{14}H_{17}N$ 199.1361.

Preparation of *N*-Methyl-3-(3-methyl-3-penten)indole (33)

33 was prepared in the same manner described above for **29**. 3-(3-methyl-3-penten)indole (**35**) (116.2 mg, 0.583 mmol), NaH (46.6 mg, 1.17 mmol, 60% dispersion in mineral oil), and MeI (55 μl, 0.875 mmol) gave *N*-methyl-3-(3-methyl-3-penten)indole (**33**) in 91% (112.6 mg, olefin isomer mixture 43:57) as a colorless oil (SiO_2, EtOAc : hexane = 1:50).

δ_H($CDCl_3$, 400 MHz) 1.57 (d, J = 6.7 Hz, 3H), 1.62 (d, J = 6.7 Hz, 3H), 1.72 (s, 3H), 1.79 (s, 3H), 2.39 (t, J = 7.7 Hz, 2H), 2.44 (t, J = 8.3 Hz, 2H), 2.82 (m, 2H), 2.85 (m, 2H), 3.74 (s, 3H), 3.75 (s, 3H), 5.27 (q, J = 6.8 Hz, 1H), 5.32 (q, J = 6.8 Hz, 1H), 6.84 (s, 1H), 6.86 (s, 1H), 7.09-7.14 (m, 1H), 7.09-7.14 (m, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 7.28-7.31 (m, 1H), 7.28-7.31 (m, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H). δ_C($CDCl_3$, 100 MHz) 13.5, 13.6, 14.4, 16.0, 23.6, 23.7, 24.1, 32.7, 40.6, 108.95, 108.97, 115.13, 118.28, 118.31, 118.34, 118.77, 118.83, 119.10, 121.20, 121.23, 125.68, 127.66, 135.76, 135.89, 136.70, 136.73 (4 carbons are missing due to overlapping). ν_{max}(NaCl)/cm^{-1} 2916, 1473, 737. HRFABMS m/z 213.1515 $(M)^+$, calcd for $C_{15}H_{19}N$ 213.1517.

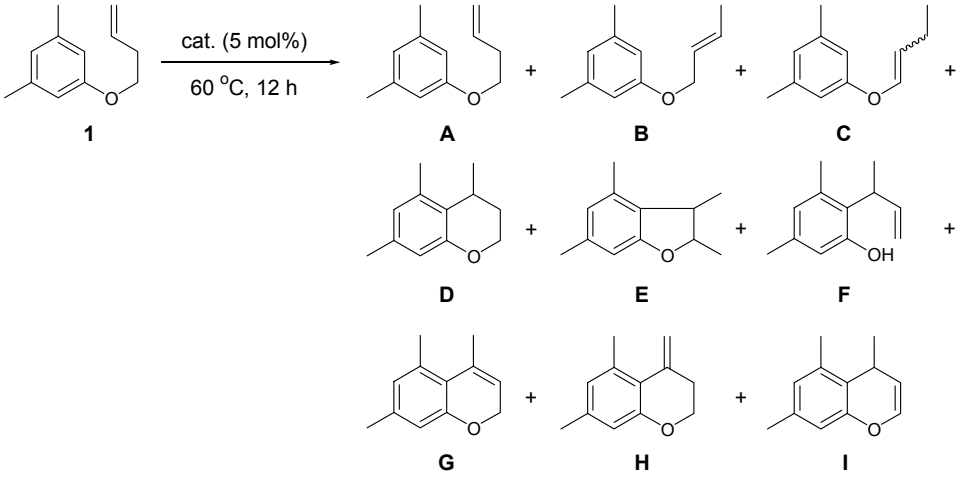
General Procedure for the Preparation of Homogeranylbenzene Derivatives (37 and 39)

To a suspension of Mg turning (2 eq.) in dry THF was added a solution of the corresponding benzyl chloride in THF dropwise at 0 ^oC. After being stirred for 2 h at 0 ^oC, a solution of geranyl diethyl phosphate (1 eq.) in THF was added dropwise to the resulting Grignard solution at rt. The reaction mixture was left overnight at rt, quenched with sat. NH_4Cl solution, and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (CH_2Cl_2:hexane=1:5 ~ only hexanes) to afford the corresponding product. (80-85%)

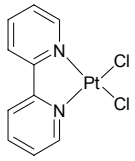
Spectral data for homogeranylbenzene (**37**)[10] and 4-homogeranylanisole (**39**)[11] were consistent with data reported in the literature.

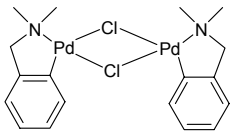
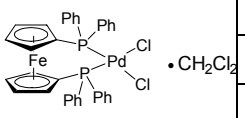
Systematic Screen

Without Additives: Reactions were conducted at 0.2 M concentration with 5 mol% catalyst at 60 ^oC in sealed vials under argon unless otherwise noted. After 12 h, the solvent was evaporated and trichloroethylene was added as an internal standard. Yields were determined via ^1H NMR. Anhydrous grade dichloroethane, and dioxane were purchased from Aldrich and stored over activated 4 angstorm molecular sieves. Methanol and toluene were purified by passage through activated alumina columns.



Cat.	Solvent	Yields (%)[a]								
		A	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
$PtCl_4$	$ClCH_2CH_2Cl$	12	12	-	15	2	-	3	-	-
	1,4-Dioxane	93	7	-	-	-	-	-	-	-
	Toluene	64	6	-	-	-	-	6	-	-
	MeOH	88	12	-	-	-	-	-	-	-
$PtCl_2$	$ClCH_2CH_2Cl$	25	18	-	-	-	-	-	-	-
	1,4-Dioxane	30	70	-	-	-	-	-	-	-
	Toluene	74	15	-	-	-	-	-	-	-
	MeOH	23	14	-	-	-	-	-	8	-
$Na_2PtCl_6{\cdot}6H_2O$	$ClCH_2CH_2Cl$	95	11	-	-	-	-	-	-	-
	1,4-Dioxane	87	-	-	-	-	-	-	-	-
	Toluene	95	5	-	-	-	-	-	-	-
	MeOH	92	8	-	-	-	-	-	-	-
$Na_2PtCl_4{\cdot}xH_2O$	$ClCH_2CH_2Cl$	50	26	-	-	-	-	-	-	-
	1,4-Dioxane	88	12	-	-	-	-	-	-	-
	Toluene	94	6	-	-	-	-	-	-	-
	MeOH	60	13	-	-	-	-	-	10	-
K_2PtCl_4	$ClCH_2CH_2Cl$	100	-	-	-	-	-	-	-	-
	1,4-Dioxane	100	-	-	-	-	-	-	-	-
	Toluene	96	4	-	-	-	-	-	-	-
	MeOH	90	11	-	-	-	-	4	4	-
K_2PtBr_4	$ClCH_2CH_2Cl$	85	14	-	-	-	-	-	-	-
	1,4-Dioxane	100	-	-	-	-	-	-	-	-
	Toluene	96	4	-	-	-	-	-	-	-

	MeOH	40	10	-	-	-	-	6	5	-
trans-$(NH_3)_2PtCl_2$	$ClCH_2CH_2Cl$	100	-	-	-	-	-	-	-	-
	1,4-Dioxane	100	-	-	-	-	-	-	-	-
	Toluene	97	3	-	-	-	-	-	-	-
	MeOH	95	5	-	-	-	-	-	-	-
	$ClCH_2CH_2Cl$	100	-	-	-	-	-	-	-	-
	1,4-Dioxane	92	-	-	-	-	-	-	-	-
	Toluene	96	4	-	-	-	-	-	-	-
	MeOH	96	4	-	-	-	-	-	-	-
$[PtCl_2(C_2H_4)]_2$[b]	$ClCH_2CH_2Cl$	-	13	13	4	7	-	4	-	8
	1,4-Dioxane	-	12	-	-	-	-	8	-	-
	Toluene	13	3	-	-	-	-	4	-	1
	MeOH	7	11	-	-	-	-	7	10	-
$Pt(PhCN)_2Cl_2$	$ClCH_2CH_2Cl$	-	22	15	-	-	-	3	-	4
	1,4-Dioxane	41	-	13	-	-	-	3	-	5
	Toluene	45	24	5	-	-	-	-	-	-
	MeOH	25	13	-	-	-	-	-	6	-
$PtCl_2(COD)$	$ClCH_2CH_2Cl$	88	4	-	-	-	-	-	-	-
$Pd(OAc)_2$	$ClCH_2CH_2Cl$	85	5	-	-	-	-	-	-	-
	1,4-Dioxane	70	7	-	-	-	-	-	5	-
	Toluene	72	5	-	-	-	-	-	-	-
	MeOH	89	10	-	-	-	-	-	1	-
$PdCl_2$	$ClCH_2CH_2Cl$	1.5	20	60	-	-	-	-	-	3
	1,4-Dioxane	-	7	9	-	-	-	-	-	5
	Toluene	2	30	82	-	-	-	-	-	-
	MeOH	20	43	-	-	-	-	-	3	-
$PdCl_2(PPh_3)_2$	$ClCH_2CH_2Cl$	85	3.5	-	-	-	-	-	-	-
	1,4-Dioxane	86	11	-	-	-	-	-	-	-
	Toluene	85	4	-	-	-	-	-	-	-
	MeOH	95	5	-	-	-	-	-	-	-
$PdCl_2(MeCN)_2$	$ClCH_2CH_2Cl$	1.5	20	13	-	-	-	-	-	5
	1,4-Dioxane	3	7	-	-	-	-	-	-	8
	Toluene	0.5	7	33	-	-	-	-	-	-
	MeOH	34	49	-	-	-	-	-	3	-
$PdCl_2(PhCN)_2$	$ClCH_2CH_2Cl$	1.5	14	40	-	-	-	-	-	6

	1,4-Dioxane	-	3	-	-	-	-	-	-	4
	Toluene	-	8	33	-	-	-	-	-	6
	MeOH	52	40	-	-	-	-	-	2	-
Na_2PdCl_4	$ClCH_2CH_2Cl$	1	18	57	-	-	-	-	-	-
	1,4-Dioxane	-	24	46	-	-	-	-	-	-
	Toluene	2	25	64	-	-	-	-	-	3
	MeOH	34	29	-	-	-	-	-	-	-
Herrmann's Cat.[b]	$ClCH_2CH_2Cl$	84	3	-	-	-	-	-	-	-
	1,4-Dioxane	78	5	-	-	-	-	-	3.5-	-
	Toluene	96	4	-	-	-	-	-	-	-
	MeOH	95	5	-	-	-	-	-	-	-
$Pd(O_2CCF_3)_2$	$ClCH_2CH_2Cl$	94	9	-	-	-	-	-	-	-
	1,4-Dioxane	64	6	-	-	-	-	-	2	-
	Toluene	88	12	-	-	-	-	-	-	-
	MeOH	19	37	8	-	-	-	-	6	-
 b	$ClCH_2CH_2Cl$	90	21	7	-	-	-	-	-	-
	1,4-Dioxane	68	6	-	-	-	-	-	-	-
	Toluene	91	9	-	-	-	-	-	-	-
	MeOH	53	8	-	-	-	-	-	-	-
$PdCl_2(COD)_2$	$ClCH_2CH_2Cl$	25	60	16	-	-	-	-	-	-
	1,4-Dioxane	19	35	31	-	-	-	-	-	-
	Toluene	85	6	-	-	-	-	-	-	-
	MeOH	42	37	-	-	-	-	-	4	-
	$ClCH_2CH_2Cl$	87	24	-	-	-	-	-	-	-
	1,4-Dioxane	66	27	-	-	-	-	-	-	-
	Toluene	75	25	-	-	-	-	-	-	-
	MeOH	3	13	86	-	-	-	-	-	-
$Pd(acac)_2$	$ClCH_2CH_2Cl$	5	67	33	-	-	-	-	-	-
	1,4-Dioxane	56	19	-	-	-	-	-	-	-
	Toluene	76	24	-	-	-	-	-	-	-
	MeOH	78	19	-	-	-	-	-	-	-
$[RuCl_2Ph]_2$ [b]	$ClCH_2CH_2Cl$	88	12	-	-	-	-	-	-	-
	1,4-Dioxane	61	36	17	-	-	-	-	-	-
$RuCl_2(COD)$	$ClCH_2CH_2Cl$	88	9	-	-	-	-	-	-	-
	1,4-Dioxane	90	8	-	-	-	-	-	-	-

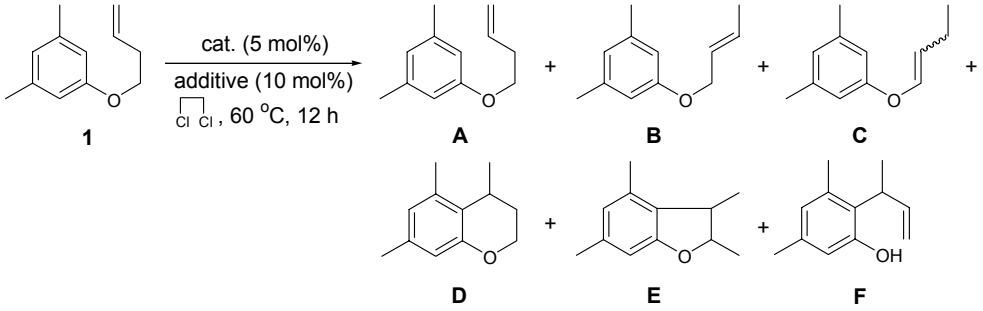
$RuCl_2(PPh_3)_3$	$ClCH_2CH_2Cl$	91	9	-	-	-	-	-	-	-
	1,4-Dioxane	85	15	-	-	-	-	-	-	-
$CpRu(PPh_3)_2Cl$	$ClCH_2CH_2Cl$	99	5	-	-	-	-	-	-	-
	1,4-Dioxane	91	8	-	-	-	-	-	-	-
$[Ru(CO)_2(OAc)]_n$	$ClCH_2CH_2Cl$	87	17	-	-	-	-	-	-	-
	1,4-Dioxane	75	8	-	-	-	-	-	-	-
$RuCl_3 \cdot xH_2O$	$ClCH_2CH_2Cl$	70	4	-	-	-	-	-	-	-
	1,4-Dioxane	50	35	6	-	-	-	-	-	-
$RuCl_3$	$ClCH_2CH_2Cl$	77	15	-	-	-	-	-	-	-
$Ru_3(CO)_{12}$ [c]	$ClCH_2CH_2Cl$	20	66	14	-	-	-	-	-	-
	1,4-Dioxane	32	60	-	-	-	-	-	-	-
$[RuCl_2(CO)_3]_2$ [b]	$ClCH_2CH_2Cl$	96	4	-	-	-	-	-	-	-
	1,4-Dioxane	87	9	-	-	-	-	-	-	-
$CpRu(MeCN)_3^+ PF_6^-$	$ClCH_2CH_2Cl$	93	7	-	-	-	-	-	-	-
	1,4-Dioxane	82	7	-	-	-	-	-	-	-
$Rh(acac)_3$	$ClCH_2CH_2Cl$	25	87	-	-	-	-	-	-	-
	1,4-Dioxane	94	6	1	-	-	-	-	-	-
$[RhCl(COD)]_2$ [b]	$ClCH_2CH_2Cl$	67	33	-	-	-	-	-	-	-
	1,4-Dioxane	57	38	5	-	-	-	-	-	-
$[Rh(O_2CCF_3)_2]_2$ [b]	$ClCH_2CH_2Cl$	98	17	-	-	-	-	-	-	-
	1,4-Dioxane	92	8	-	-	-	-	-	-	-
$RhCl_3 \cdot xH_2O$	$ClCH_2CH_2Cl$	8	63	5	-	-	-	-	-	-
	1,4-Dioxane	25	21	-	-	-	-	-	-	-
$RhCl(PPh_3)_3$	$ClCH_2CH_2Cl$	80	17	-	-	-	-	-	4	-
	1,4-Dioxane	68	29	2	-	-	-	-	-	-
$[Rh(OAc)_2]_2$ [b]	$ClCH_2CH_2Cl$	92	8	-	-	-	-	-	trace	-
	1,4-Dioxane	87	13	-	-	-	-	-	-	-
$[IrCl(COD)]_2$ [b]	$ClCH_2CH_2Cl$	70	10	-	-	-	-	-	-	-
	Toluene	106	11		-	-	-	-	-	-
$Ir(acac)(CO)_2$	$ClCH_2CH_2Cl$	80	11	-	-	-	-	-	-	-
	Toluene	92	8	-	-	-	-	-	-	-
$IrCl_4 \cdot xH_2O$	$ClCH_2CH_2Cl$	80	-	-	-	-	-	-	-	-
	Toluene	100	4	-	-	4	-	-	-	-
$NiCl_2 \cdot 6H_2O$	$ClCH_2CH_2Cl$	82	10	-	-	-	-	-	-	-
	Toluene	75	25	-	-	-	-	-	-	-

$Ni(OAc)_2·4H_2O$	$ClCH_2CH_2Cl$	83	10	-	-	-	-	-	-	-
	Toluene	100	6	-	-	-	-	-	-	-
$NiCl_2$(dppe)	$ClCH_2CH_2Cl$	85	9	-	-	-	-	-	-	-
	Toluene	103	7	-	-	-	-	-	-	-
$CoCl_2·xH_2O$	$ClCH_2CH_2Cl$	50	19	-	-	-	-	-	-	-
	1,4-Dioxane	81	7	-	-	-	-	-	-	-
$Co(OAc)_2·4H_2O$	$ClCH_2CH_2Cl$	58	6	-	-	-	-	-	-	-
	1,4-Dioxane	73	6	-	-	-	-	-	-	-
$Co(acac)_3$	$ClCH_2CH_2Cl$	68	5	-	-	-	-	-	-	-
	1,4-Dioxane	78	5	-	-	-	-	-	-	-
$CoCl_2(PPh_3)_2$	$ClCH_2CH_2Cl$	68	5	-	-	-	-	-	-	-
	1,4-Dioxane	22	4	-	-	-	-	-	-	-
$CpCo(CO)_2$	$ClCH_2CH_2Cl$	43	3	-	-	-	-	-	-	-
	1,4-Dioxane	75	5	-	-	-	-	-	-	-
$FeCl_3·6H_2O$	$ClCH_2CH_2Cl$	2	-	-	-	-	-	-	-	-
	1,4-Dioxane	35	13	-	-	-	-	-	-	-
CuCl	$ClCH_2CH_2Cl$	118	7	-	-	-	-	-	-	-
	Toluene	95	5	-	-	-	-	-	-	-
$CuCl_2$	$ClCH_2CH_2Cl$	78	12	-	-	-	-	-	-	-
	1,4-Dioxane	88	5	-	-	-	-	-	-	-
$Cu(OTf)_2$	$ClCH_2CH_2Cl$	24	-	-	40	24	-	-	-	-
	1,4-Dioxane	77	4	-	-	-	-	-	-	-
	Toluene	89	6	-	-	-	-	-	-	-
$Cu(OAc)_2$	$ClCH_2CH_2Cl$	87	3	-	-	-	-	-	-	-
	1,4-Dioxane	84	5	-	-	-	-	-	-	-
$Cu(CF_3COCH=C(O-)CF_3)_2·xH_2O$	$ClCH_2CH_2Cl$	100	6	-	-	-	-	-	-	-
	Toluene	95	5	-	-	-	-	-	-	-
$AlCl_3$	$ClCH_2CH_2Cl$	76	5	-	-	-	-	-	-	-
$GaCl_3$	$ClCH_2CH_2Cl$	28	-	-	15	10	-	-	-	-
$ZnCl_2$	$ClCH_2CH_2Cl$	77	5	-	-	-	-	-	-	-
$AuCl_3$	$ClCH_2CH_2Cl$	70	12	-	-	-	-	-	-	-
$Zn(OTf)_2$	$ClCH_2CH_2Cl$	65	6	-	-	-	-	-	-	-
	1,4-Dioxane	74	22	-	-	-	-	-	-	-
$Sc(OTf)_3$	$ClCH_2CH_2Cl$	21	-	-	56	10	-	-	-	-
	1,4-Dioxane	71	3	-	-	-	-	-	-	-

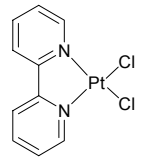
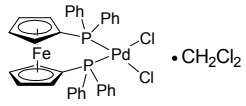
$Yb(OTf)_3$	$ClCH_2CH_2Cl$	97	4	-	-	-	-	-	-	-
	1,4-Dioxane	65	6	-	-	-	-	-	-	-
$HfCl_4$	$ClCH_2CH_2Cl$	33	-	-	18	2	-	-	-	-
	1,4-Dioxane	77	10	-	-	-	-	-	-	-
$AgSbF_6$	$ClCH_2CH_2Cl$	41	-	-	-	-	-	-	-	-
$AgBF_4$	$ClCH_2CH_2Cl$	93	5	-	-	-	-	-	-	-
AgOTf	$ClCH_2CH_2Cl$	84	-	-	-	9	-	-	-	-
$Mo(CO)_6$	$ClCH_2CH_2Cl$	106	5	-	-	-	-	-	-	-
	Toluene	106	5	-	-	-	-	-	-	-

a. Determined by ^1H NMR using trichloroethylene as internal standard. b. Using 2.5 mol% of the dimeric complex. c. Using 5/3 mol% of the trimeric complex.

With Additives: Reactions were conducted at 0.2 M with 5 mol% metal and 10 mol% additive at 60 °C in sealed vials under argon unless otherwise noted. The mixture of metal and additive in dry $ClCH_2CH_2Cl$ was stirred vigorously for 1 h. To a resulting solution was added **1** in $ClCH_2CH_2Cl$. After 12 h, the solvent was evaporated and trichloroethylene was added as an internal standard.



Cat.	Additive	Yields (%)[a]					
		A	**B**	**C**	**D**	**E**	**F**
$PtCl_4$	$AgSbF_6$	-	-	-	5	6	-
	AgOTf	-	-	-	20	23	2.5
	$AgBF_4$	-	-	-	-	-	10
	$AgPF_6$	17	5	-	-	-	-
	AgOAc	7	30	-	-	-	-
	NH_4BF_4	75	12	-	-	-	-
	$GaCl_3$ [b]	-	-	-	7	4	-
$PtCl_2$	$AgSbF_6$	-	-	-	-	3	-
	AgOTf	-	-	-	4	6	2

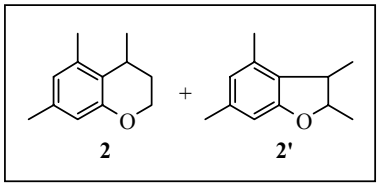
$Pt(PhCN)_2Cl_2$	$AgSbF_6$	-	-	-	10	-	-
	AgOTf	-	-	-	6	5	2
$[PtCl_2(C_2H_4)]_2$ [c]	$AgSbF_6$	-	-	-	2.5	4	-
	AgOTf	-	-	-	9	13	2
	$AgSbF_6$	9	-	-	-	-	-
	AgOTf	-	-	-	23	11	6
$PtCl_2(COD)$	$AgSbF_6$	-	-	-	7	3	-
	AgOTf	-	-	-	3	1	-
K_2PtCl_4	AgOTf	34	4	-	-	-	-
$Na_2PtCl_4 \cdot xH_2O$	AgOTf	8	8	-	-	-	-
$PdCl_2$	$AgSbF_6$	-	-	-	-	18	-
	AgOTf	-	-	-	2	40	3
$Pd(MeCN)_2Cl_2$	$AgSbF_6$	-	-	-	4	32	-
	AgOTf	-	-	-	5	32	10
Na_2PdCl_4	AgOTf	-	-	-	3	45	3
	AgOTf	-	-	-	-	-	4
$CuCl_2$	$AgSbF_6$	6	-	-	7	30	-
	AgOTf	7	-	-	52	9	-
$HfCl_4$	AgOTf	25	-	-	25	7	-
$RuCl_2(COD)$	AgOTf	38	-	-	6	19	-
	$AgPF_6$	75	24	-	-	-	-
	$AgPF_6$ [d]	93	7	-	-	-	-
$RuCl_3 \cdot xH_2O$	$AgSbF_6$	9	-	-	20	19	-
	AgOTf	-	-	-	83	26	-
	AgOTf [e]	10	-	-	50	30	-
	AgOTf [f]	-	-	-	40	30	-
	$AgBF_4$	68	4	-	-	-	-
	$AgPF_6$	75	6	-	-	-	-
	AgOAc	82	4	-	-	-	-
	$AgClO_4$	4	38	18	-	3	-
	NH_4BF_4	85	24	-	-	-	-

	NaBARF[g]	77	-	-	-	-	-
$RuCl_3$	AgOTf	2	-	-	80	18	-
RuI_3	AgOTf	15	-	-	25	30	-
$[RuCl_2Ph]_2$ [c]	AgOTf	59	-	-	2	6	-
$RuCl_2(PPh_3)_3$	AgOTf	12	12	-	-	-	-
$CpRu(PPh_3)_2Cl$	AgOTf	75	8	-	-	-	-
$[RuCl_2(CO)_3]_2$ [c]	AgOTf	-	-	-	-	46	5
$RhCl_3 \cdot xH_2O$	AgOTf	-	-	-	40	50	-
$[RhCl(COD)]_2$ [c]	AgOTf	77	6	-	-	-	-
	$AgSbF_6$ [h]	90	10	12	-	-	-
	$AgSbF_6$ [d, h]	71	29	-	-	-	-
$IrCl_4 \cdot xH_2O$	AgOTf	-	-	-	45	30	-
$[IrCl(COD)]_2$ [c]	AgOTf	47	6	-	-	-	-
	$AgSbF_6$ [h]	26	10	10	-	-	-
	$AgSbF_6$ [b, h]	71	10	4	-	-	-
$Na_3IrCl_6 \cdot xH_2O$	AgOTf	87	37	-	-	-	-
$NiCl_2 \cdot 6H_2O$	AgOTf	28	48	-	-	-	-
$FeCl_3 \cdot 6H_2O$	AgOTf	19	5	-	-	-	-
$CoCl_2 \cdot xH_2O$	AgOTf	62	21	-	-	-	-
$HgCl_2$	$GaCl_3$ [b]	-	-	-	70	-	-
$Sc(OTf)_3$	$LiClO_4$	86	-	-	4	23	-

a. Determined by ^1H NMR using trichloroethylene as internal standard. b. In toluene. c. Using 2.5 mol% of the dimeric complex. d. In 1,4-dioxane. e. 5 mol% AgOTf. f. 15 mol% AgOTf. g. NaBARF = $Na^+B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$. h. 5 mol % $AgSbF_6$ and 5 mol% (*R*)-BINAP

General Procedure for the Intramolecular Hydroarylations Using Ru Catalyst

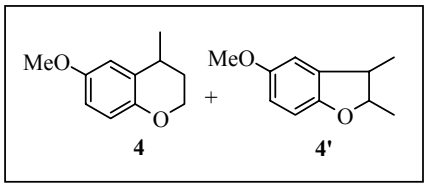
The mixture of $RuCl_3 \cdot xH_2O$ and AgOTf in $ClCH_2CH_2Cl$ was stirred vigorously for 1 h. To a resulting solution was added the substrate in $ClCH_2CH_2Cl$ (0.2 M). After full conversion, the solvent was evaporated and the residue was purified by column chromatography on silica gel to give the corresponding product.



5 mol% $RuCl_3 \cdot xH_2O$ and 10 mol% AgOTf at 60 ^oC for 13 h

The mixture of **2** and **2'** was obtained as a colorless oil (SiO_2, CH_2Cl_2 : Hexanes = 3 : 7).

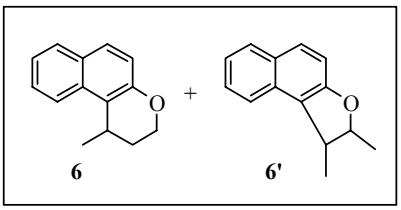
δ_H($CDCl_3$, 400 MHz) 1.08 (d, J = 7.1 Hz, 3H, **2'**), 1.25 (d, J = 7.0 Hz, 3H), 1.46 (d, J = 6.6 Hz, 3H, **2'**), 1.69 (dq, J = 2.1, 13.7 Hz, 1H), 2.09 (tt, J = 4.9, 13.2 Hz, 1H), 2.24 (s, 3H), 2.27 (s, 3H), 2.99 (quintet, J = 6.5 Hz, 1H), 3.20 (quintet, J = 7.1 Hz, 1H, **2'**), 4.20 (m, 2H), 4.74 (quintet, J = 6.7 Hz, 1H, **2'**), 6.45 (s, 1H, **2'**), 6.49 (s, 1H, **2'**), 6.51 (s, 1H), 6.57 (s, 1H). δ_C($CDCl_3$, 100 MHz) 13.9 (**2'**), 15.3 (**2'**), 18.2 (**2'**), 18.6, 21.1, 21.2, 21.6 (**2'**), 25.4, 29.3, 38.4 (**2'**), 61.2, 82.5 (**2'**), 107.5 (**2'**), 114.9, 122.5, 123.0, 136.4, 136.7, 153.5 (5 carbons of **2'** are missing due to overlapping). ν_{max}(NaCl)/cm^{-1} 2923, 1620, 1576, 1452, 1300, 1145, 1124, 1105, 1078, 838. HREIMS *m/z* 176.1192 $(M)^+$, calcd for $C_{12}H_{16}O$ 176.1201.



5 mol% $RuCl_3 \cdot xH_2O$ and 10 mol% AgOTf at 60 ^oC for 11 h

The mixture of **4** and **4'** was obtained as a colorless oil (SiO_2, CH_2Cl_2 : Hexanes = 1 : 1).

δ_H($CDCl_3$, 400 MHz) 1.17 (d, J = 7.1 Hz, 3H, **4'**), 1.31 (d, J = 6.8 Hz, 3H), 1.47 (d, J = 6.2 Hz, 3H, **4'**), 1.68 (m, 1H), 2.05 (m, 1H), 2.91 (sextet, J = 6.6 Hz, 1H), 3.37 (quintet, J = 7.1 Hz, 1H, **4'**), 3.74 (s, 3H), 4.12 (m, 2H), 4.86 (quintet, J = 6.2 Hz, 1H, **4'**), 6.65 (dd, J = 2.9, 8.8 Hz, 1H), 6.69 (d, J = 2.9 Hz, 1H), 6.71 (d, J = 8.8 Hz, 1H). δ_C($CDCl_3$, 100 MHz) 22.4, 28.9 30.5, 55.8, 63.8, 112.8, 113.4, 117.0, 128.1, 148.1, 153.0. ν_{max}(NaCl)/cm^{-1} 2960, 1497, 1425, 1266, 1213, 1056, 812. HREIMS *m/z* 178.0988 $(M)^+$, calcd for $C_{11}H_{14}O_2$ 178.0994.

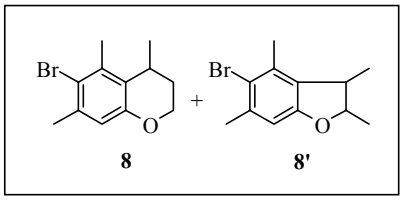


5 mol% $RuCl_3 \cdot xH_2O$ and 10 mol% AgOTf at 60 ^oC for 15 h

The mixture of **6** and **6'** was obtained as a white solid (SiO_2, CH_2Cl_2 : Hexanes = 1 : 4).

δ_H($CDCl_3$, 400 MHz) 1.25 (d, J = 7.1 Hz, 3H, **6'**), 1.47 (d, J = 7.0 Hz, 3H), 1.57 (d, J = 6.5 Hz, 3H, **6'**), 1.85 (dq, J = 2.1, 13.8 Hz, 1H), 2.26 (m, 1H), 3.54 (quintet, J = 6.8 Hz, 1H), 3.68 (quintet, J = 7.2 Hz,

1H, **6'**), 4.33 (m, 2H), 4.99 (quintet, J = 6.7 Hz, 1H, **6'**), 7.04 (d, J = 8.9 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.61 (d, J = 8.9 Hz, 1H), 7.76 (d, J = 7.7 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H). δ_C($CDCl_3$, 100 MHz) 22.2, 24.6, 28.9, 61.6, 118.6, 119.0, 121.8, 122.7, 126.0, 127.7, 128.5, 129.0, 132.4, 151.1. ν_{max}(NaCl)/cm^{-1} 3062, 2965, 1621, 1599, 1514, 1465, 1433, 1403, 1373, 1306, 1265, 1236, 1214, 1095, 1027, 812, 748. HREIMS *m/z* 198.1047 $(M)^+$, calcd for $C_{14}H_{14}O$ 198.1045.

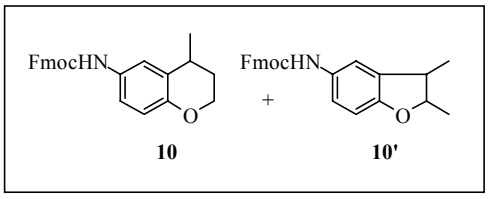


8 **8'**

5 mol% $RuCl_3 \cdot xH_2O$ and 10 mol% AgOTf at 60 °C for 36 h

The mixture of **8** and **8'** was obtained as a colorless oil (SiO_2, CH_2Cl_2 : Hexanes = 1 : 4).

δ_H($CDCl_3$, 400 MHz) 1.06 (d, J = 7.1 Hz, 3H, **8'**), 1.24 (d, J = 7.0 Hz, 3H), 1.45 (d, J = 6.6 Hz, 3H, **8'**), 1.71 (dq, J = 2.1, 13.8 Hz, 1H), 2.07 (tt, J = 4.9, 13.3 Hz, 1H), 2.33 (s, 3H), 2.38 (s, 3H), 3.06 (quintet, J = 6.3 Hz, 1H), 3.21 (quintet, J = 7.1 Hz, 1H, **8'**), 4.11 (ddd, J = 2.1, 10.9, 12.9 Hz, 1H), 4.25 (m, 1H), 4.73 (quintet, J = 6.8 Hz, 1H, **8'**), 6.55 (s, 1H, **8'**), 6.62 (s, 1H). δ_C($CDCl_3$, 100 MHz) 14.1 (**8'**), 15.2 (**8'**), 18.4 (**8'**), 19.4, 21.1 (**8'**), 21.4, 24.0, 26.7, 29.1, 39.7 (**8'**), 61.1, 82.8 (**8'**), 109.3 (**8'**), 116.6, 118.9, 123.8 (**8'**), 124.5, 136.1, 136.6, 137.3 (**8'**), 152.5 (3 carbons of **8'** are missing due to overlapping). ν_{max}(NaCl)/cm^{-1} 2968, 1602, 1563, 1451, 1399, 1300, 1165, 1126, 1108, 853, 674. HRFABMS *m/z* 254.0314 $(M)^+$, calcd for $C_{12}H_{15}BrO$ 254.0306.

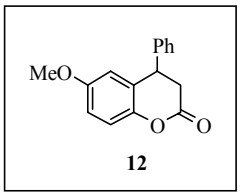


10 **10'**

20 mol% $RuCl_3$ and 40 mol% AgOTf at 80 °C for 72 h

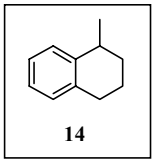
The mixture of **10** and **10'** was obtained as a white solid (SiO_2, EtOAc : Hexanes = 1 : 5).

δ_H($CDCl_3$, 400 MHz) 1.17 (d, J = 7.1 Hz, 3H, **10'**), 1.30 (d, J = 7.0 Hz, 3H), 1.46 (d, J = 6.2 Hz, 3H, **10'**), 1.69 (m, 1H), 2.06 (m, 1H), 2.91 (sextet, J = 6.6 Hz, 1H), 3.36 (quintet, J = 7.1 Hz, 1H, **8'**), 4.15 (m, 2H), 4.25 (t, J = 6.7 Hz, 1H), 4.49 (d, J = 6.8 Hz, 2H), 4.78 (quintet, J = 6.2 Hz, 1H, **10'**), 6.52 (br s, 1H), 6.72 (d, J = 8.7 Hz, 1H), 6.99 (br s, 1H), 7.24 (br s, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.59 (br s, 2H), 7.76 (d, J = 7.5 Hz, 2H). δ_C($CDCl_3$, 100 MHz) 22.3, 28.8, 30.4, 47.3, 63.9, 66.8, 109.1, 116.8, 118.8, 119.8, 124.8, 126.9, 127.5, 127.8, 130.0, 141.1, 143.6, 150.7, 153.6. ν_{max}(NaCl)/cm^{-1} 3309, 3064, 2960, 1700, 1536, 1502, 1450, 1217, 1054, 740. HRFABMS *m/z* 385.1663 $(M)^+$, calcd for $C_{25}H_{23}NO_3$ 385.1678.



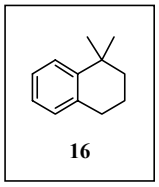
12

20 mol% $RuCl_3$ and 40 mol% AgOTf at 80 ^oC for 32 h
a colorless oil (SiO_2, EtOAc : Hexanes = 1 : 8)
Spectral data were consistent with data reported in the literature.[3]



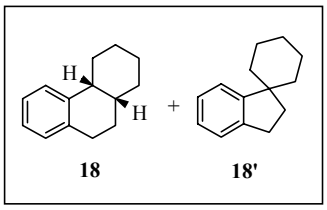
14

1 mol% $RuCl_3 \cdot xH_2O$ and 2 mol% AgOTf at 60 ^oC for 2.5 h
a colorless oil (SiO_2, only Hexanes)
Spectral data were consistent with data reported in the literature.[6]



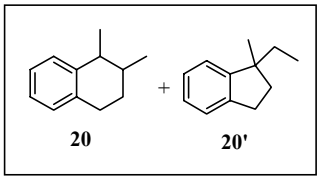
16

1 mol% $RuCl_3 \cdot xH_2O$ and 2 mol% AgOTf at 60 ^oC for 1 h
a colorless oil (SiO_2, only Hexanes)
Spectral data were consistent with data reported in the literature.[6]



18 **18'**

1 mol% $RuCl_3 \cdot xH_2O$ and 2 mol% AgOTf at 60 ^oC for 7 h
The mixture of **18** and **18'** was obtained as a colorless oil (SiO_2, only Hexanes).
Spectral data were consistent with data reported in the literature.[12]

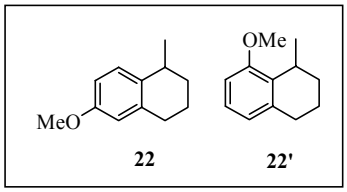


20 **20'**

5 mol% $RuCl_3 \cdot xH_2O$ and 10 mol% AgOTf at 60 °C for 8 h

The mixture of **20** and **20'** was obtained as a colorless oil (SiO_2, only Hexanes).

Spectral data for **20**[13] and **20'**[14] were consistent with data reported in the literature.

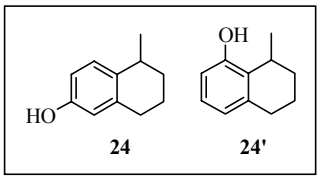


2 mol% $RuCl_3 \cdot xH_2O$ and 4 mol% AgOTf at 60 °C for 5 h

22: a colorless oil (SiO_2, CH_2Cl_2 : Hexanes = 3 : 7)

22': a colorless oil (SiO_2, CH_2Cl_2 : Hexanes = 1 : 4)

Spectral data for **22**[15] and **22'**[5] were consistent with data reported in the literature.

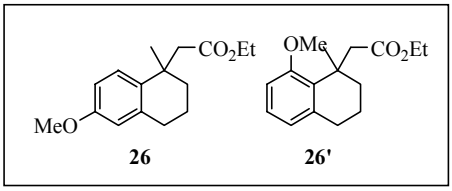


2 mol% $RuCl_3 \cdot xH_2O$ and 4 mol% AgOTf at 60 °C for 11 h

24: a white solid (SiO_2, CH_2Cl_2 : Hexanes = 9 : 1)

24': a colorless oil (SiO_2, CH_2Cl_2 : Hexanes = 7 : 3)

Spectral data for **24**[9] and **24'**[9] were consistent with data reported in the literature.



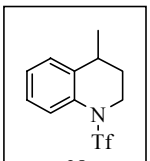
5 mol% $RuCl_3 \cdot xH_2O$ and 10 mol% AgOTf at 60 °C for 27 h

26: a colorless oil (SiO_2, EtOAc : Hexanes = 1 : 50)

δ_H($CDCl_3$, 400 MHz) 1.16 (t, J = 7.1 Hz, 3H), 1.36 (s, 3H), 1.61 (ddd, J = 3.3, 8.4, 13.3 Hz, 1H), 1.80 (m, 2H), 2.05 (ddd, J = 3.4, 8.7, 13.0 Hz, 1H), 2.57 (dd, J = 13.7, 33.1 Hz, 2H), 2.73 (dt, J = 3.1, 6.3 Hz, 2H), 3.75 (s, 3H), 4.04 (dq, J = 1.5, 7.1 Hz, 2H), 6.56 (d, J = 2.8 Hz, 1H), 6.69 (dd, J = 2.8, 8.7 Hz, 1H), 7.17 (d, J = 8.7 Hz, 1H). δ_C($CDCl_3$, 100 MHz) 14.4, 19.6, 29.9, 30.9, 36.0, 36.2, 47.6, 55.2, 60.0, 112.1, 113.3, 127.5, 135.7, 137.6, 157.0, 171.4. ν_{max}(NaCl)/cm^{-1} 2934, 1730, 1609, 1501, 1464, 1241, 1159, 1036, 840. HRFABMS m/z 262.1581 $(M)^+$, calcd for $C_{16}H_{22}O_3$ 262.1569.

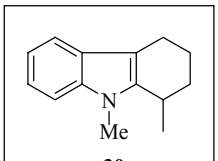
26': a colorless oil (SiO_2, EtOAc : Hexanes = 1 : 50)

δ_H($CDCl_3$, 400 MHz) 1.06 (t, J = 7.1 Hz, 3H), 1.43 (s, 3H), 1.60 (m, 1H), 1.73 (m, 2H), 2.10 (ddd, J = 3.8, 10.1, 13.6 Hz, 1H), 2.71 (d, J = 14.0 Hz, 1H), 2.72 (m, 2H), 3.09 (d, J = 14.0 Hz, 1H), 3.80 (s, 3H), 3.95 (dq, J = 2.6, 7.1 Hz, 2H), 6.66 (dd, J = 0.5, 7.9 Hz, 2H), 7.04 (t, J = 7.9 Hz, 1H). δ_C($CDCl_3$, 100 MHz) 14.3, 19.7, 27.0, 31.8, 36.7, 38.8, 44.8, 55.0, 59.6, 108.7, 121.9, 126.2, 130.9, 138.9, 158.3, 172.3. ν_{max}(NaCl)/cm^{-1} 2936, 1727, 1578, 1468, 1440, 1252, 1159, 1080, 1036, 782, 745. HRFABMS *m/z* 262.1554 $(M)^+$, calcd for $C_{16}H_{22}O_3$ 262.1569.



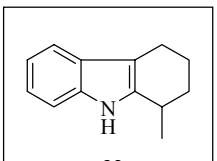
28

20 mol% $RuCl_3$ and 40 mol% AgOTf at 80 °C for 24 h
a colorless oil (SiO_2, EtOAc : Hexanes = 1 : 10)
Spectral data were consistent with data reported in the literature.[16]



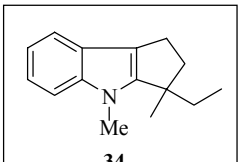
30

10 mol% $RuCl_3 \cdot xH_2O$ and 20 mol% AgOTf at 70 °C for 24 h
a white solid (SiO_2, acetones : Hexanes = 1 : 50)
Spectral data were consistent with data reported in the literature.[17]



32

20 mol% $RuCl_3 \cdot xH_2O$ and 40 mol% AgOTf at 70 °C for 38 h
a white solid (SiO_2, EtOAc : Hexanes = 1 : 10)
Spectral data were consistent with data reported in the literature.[17]

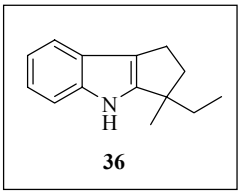


34

10 mol% $RuCl_3 \cdot xH_2O$ and 20 mol% AgOTf at 70 °C for 12 h

a yellow oil (SiO_2, CH_2Cl_2 : Hexanes = 1 : 5)

δ_H($CDCl_3$, 300 MHz) 0.85 (t, J = 7.4 Hz, 3H), 1.40 (s, 3H), 1.76 (q, J = 7.4 Hz, 2H), 2.23 (ddd, J = 5.7, 8.5, 12.9 Hz, 1H), 2.48 (ddd, J = 5.6, 7.8, 13.0 Hz, 1H), 2.78 (m, 2H), 3.70 (s, 3H), 7.06 (t, J = 7.2 Hz, 1H), 7.13, (t, J = 8.0 Hz, 1H), 7.24 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 7.1 Hz, 1H). δ_C($CDCl_3$, 75 MHz) 9.6, 22.7, 26.5, 30.2, 33.3, 37.3, 43.1, 109.1, 117.3, 118.6, 118.8, 119.9, 125.8, 141.7, 150.0. ν_{max}(NaCl)/cm^{-1} 2959, 1466, 1374, 736. HRFABMS *m/z* 213.1511 $(M)^+$, calcd for $C_{15}H_{19}N$ 213.1517.

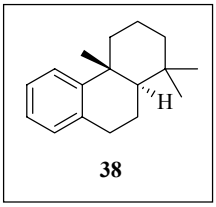


36

20 mol% $RuCl_3 \cdot xH_2O$ and 40 mol% AgOTf at 70 °C for 22 h

a yellow oil (SiO_2, EtOAc : Hexanes = 1 : 20)

δ_H($CDCl_3$, 300 MHz) 0.89 (t, J = 7.4 Hz, 3H), 1.31 (s, 3H), 1.66 (q, J = 7.5 Hz, 2H), 2.26 (m, 1H), 2.42 (m, 1H), 2.80 (t, J = 7.5 Hz, 2H), 7.06 (m, 2H), 7.28 (m, 1H), 7.42 (m, 1H), 7.67 (br s, 1H). ν_{max}(NaCl)/cm^{-1} 3400, 2920, 1462, 740. HRFABMS *m/z* 199.1358 $(M)^+$, calcd for $C_{14}H_{17}N$ 199.1361.

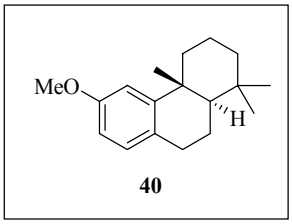


38

1 mol% $RuCl_3 \cdot xH_2O$ and 2 mol% AgOTf at 60 °C for 4 h

a colorless oil (SiO_2, only Hexanes)

Spectral data were consistent with data reported in the literature.[18]

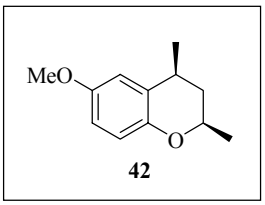


40

1 mol% $RuCl_3 \cdot xH_2O$ and 2 mol% AgOTf at 60 °C for 4 h

a colorless oil (SiO_2, acetones : Hexanes = 1 : 50)

Spectral data were consistent with data reported in the literature.[19]



42

5 mol% $RuCl_3 \cdot xH_2O$ and 10 mol% AgOTf at 60 ^oC for 16 h

a colorless oil (SiO_2, CH_2Cl_2 : Hexanes = 1 : 1)

The structures of *trans*- and *cis*-isomer were confirmed by NOE experiments and related data in the literature.[20]

92% ee as determined by HPLC analysis (Daicel OD, 1% *i*-PrOH in Hexanes, 250 nm, 1.0 ml/min)

t_r = 22.2 (*trans*, 2*S*, 4*S*), 24.7 (*cis*, 2*R*, 4*S*), 27.3 (*trans*, 2*R*, 4*R*), 35.8 (*cis*, 2*S*, 4*R*) min.

δ_H($CDCl_3$, 400 MHz) 1.30 (d, *J* = 6.8 Hz, 3H, *cis*), 1.31 (d, *J* = 7.1 Hz, 3H, *trans*), 1.36 (d, *J* = 6.2 Hz, 3H, *cis*), 1.37 (d, *J* = 6.1 Hz, 3H, *trans*), 1.44 (dd, *J* = 11.6, 24.9 Hz, 1H, *cis*), 1.66 (dt, *J* = 2.3, 13.7 Hz, 1H, *trans*), 1.82 (ddd, *J* = 5.9, 10.5, 13.7 Hz, 1H, *trans*), 1.96 (ddd, *J* = 1.4, 6.0, 13.4 Hz, 1H, *cis*), 2.91 (m, 1H, *trans*), 2.98 (sextet, *J* = 6.6 Hz, 1H, *cis*), 3.75 (s, 3H), 4.08 (sextet, *J* = 6.2 Hz, 1H, *cis*), 4.16 (m, 1H, *trans*), 6.74 (m, 3H). δ_C($CDCl_3$, 100 MHz) 20.6, 21.6, 21.9, 24.4, 28.9, 30.0, 36.6, 39.5, 55.7, 67.5, 72.0, 112.4, 112.5, 113.0, 113.9, 116.8, 117.1, 127.6, 127.8, 148.2, 148.7, 152.9, 153.0 (1 carbon is missing due to overlapping). ν_{max}(NaCl)/cm^{-1} 2933, 1496, 1383, 1266, 1216, 1153, 1071, 1042, 955, 867, 813. HREIMS *m/z* 192.1153 $(M)^+$, calcd for $C_{12}H_{16}O_2$ 192.1150.

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1 Corey, E. J.; Guzman-Perez, A.; Noe, M. C. *J. Am. Chem. Soc.* **1995**, *117*, 10805.

2 Nishikawa, T.; Isobe, M. *Tetrahedron*, **1994**, *50*, 5621.

3 Krajniak, E. R.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.* **1973**, *26*, 899.

4 Alexander, H.; Oonstance, L.; Wagner, R.; Meh, D.; Bowman, R. P. *J. Organomet. Chem.* **1986**, *302*, 5.

5 Ando, T.; Yamawaki, J.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 219.

6 Kropp, P. J.; Breton, G. W.; Craig, S. L.; Crawford, S. D.; Durland, W. F.; Jones, J. E.; Raleigh, J. S. *J. Org. Chem.* **1995**, *60*, 4146.

7 Julia, M.; Labia, R. *Bull. Soc. Chim. Fr.* **1972**, 4151.

8 Markó, I. E.; Murphy, F.; Kumps, L.; Ates, A.; Touillaux, R.; Craig, D.; Carballares, S.; Dolan, S. *Tetrahedron*, **2001**, *57*, 2609.

9 Moreau, C.; Rouessac, F. *Bull. Soc. Chim. Fr.* **1973**, 3427.

10 Julia, M.; Mansuy, J. *Bull. Soc. Chim. Fr.* **1972**, 2689.

11 Nasipuri, D.; Samaddar, A. K.; Das, G. *Indian J. Chem. Sect. B* **1980**, 19, 727.

12 Bright, S. T.; Coxon, J. M.; Steel, P. J. *J. Org. Chem.* **1990**, *55*, 1338.

[13] (a) Khalaf, A. A.; Roberts, R. M. *J. Org. Chem.* **1972**, *37*, 4227. (b) Morin, F. G.; Horton, W. J.; Grant, D. M.; Dalling, D. K.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 3992.

[14] Sakhabutdinov, A. G.; Usmanova, A. G.; Proidakov, A. G.; Bazhenov, B. A.; Schmidt, F. K. *J. Org. Chem. USSR* **1988**, *24*, 1525.

[15] Harrowven, D. C.; Dainty, R. F. *Tetrahedron*, **1997**, *53*, 15771.

[16] Togo, H.; Hoshina, Y.; Muraki, T.; Nakayama, H.; Yokoyama, M. *J. Org. Chem.* **1998**, *63*, 5193.

[17] Naruse, Y.; Ito, Y.; Inagaki, S. *J. Org. Chem.* **1991**, *56*, 2256.

[18] Evans, G. B.; Furneaux, R. H.; Gravestock, M. B.; Lynch, G. P.; Scott, G. K. *Bioorg. Med. Chem.* **1999**, *7*, 1953.

[19] Axon, B. W.; Davis, B. R.; Woodgate, P. D. *J. Chem. Soc. Perkin Trans 1* **1981**, 2956.

[20] Chen, Y.-Y.; Oshima, R.; Kumanotani, J. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2533.