Optimization of Asymmetric Catalysts Using Achiral Ligands: Metal Geometry-Induced Ligand Asymmetry

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Supporting Information

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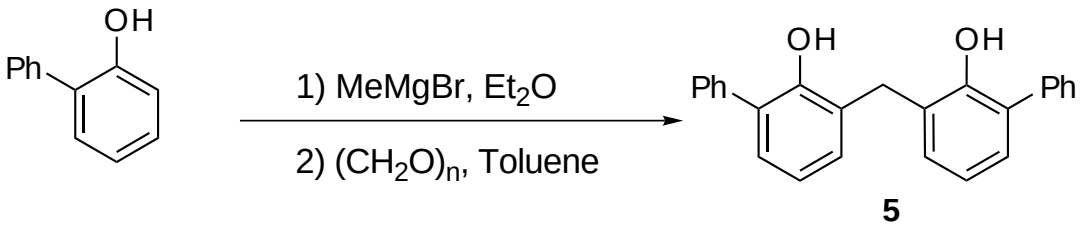
General Experimental Section. All manipulations involving titanium alkoxides and diethylzinc were carried out under an inert atmosphere in a Vacuum Atmospheres drybox with attached MO-40 Dritrain, or by using standard Schlenk or vacuum line techniques. Solutions were degassed as follows: they were cooled to -196 ^{o}C, evacuated under high vacuum and thawed. This sequence was repeated three times in each case. ^{1}H NMR spectra were obtained on either the Bruker 200 MHz or 500 MHz Fourier transform NMR spectrometer at the University of Pennsylvania NMR facility. ^{1}H NMR spectra were recorded relative to residual protiated solvent. ^{13}C{^{1}H} NMR spectra were obtained at either 50 or 125 MHz on the 200 or 500 MHz instruments, respectively, and chemical shifts were recorded relative to the solvent resonance. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane and all coupling constants are reported in Hz. IR spectra were obtained on a Perkin - Elmer 1600 series spectrometer. Unless otherwise specified, all reagents were purchased from Aldrich Chemical Co. and used without further purification. Titanium tetraisopropoxide, benzaldehyde, 4-methylbenzaldehyde, (*S*)-2-phenyl-1-propanol and (*S*)-2-tolyl-1-propanol were distilled under vacuum and stored in glass vessels sealed with Teflon stoppers. Diethylzinc (1M in hexanes) and titanium alkoxide (0.15M in dichloromethane) solutions were prepared in the drybox and stored in glass vessels sealed with Teflon stoppers.

Hexanes (UV grade, alkene free) was distilled from sodium benzophenone ketyl/tetraglyme under nitrogen. Benzene, toluene, diethyl ether and THF were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. Deuterated solvents (purchased form Cambridge Isotopes) for use in NMR experiments were dried in the same manner as their protiated analogs but were vacuum transferred from the drying agent. $CDCl_3$ was dried over calcium hydride and vacuum transferred.

Enantiometic excesses were determined using GC methods. GC analysis were carried on Helwett-Packard 6890 gas chromatograph with a 30-m Supelco β-DEX™ column.

Synthesis and characterization of 1-12

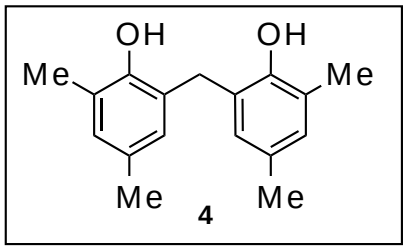
The procedure for the preparation of compounds **4-6** and **8-10** were identical and is described for the synthesis of **5**.[1]



5

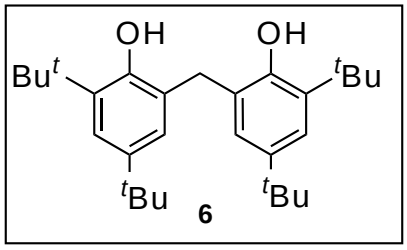
A stirred solution of 2-phenylphenol (5.10 g, 30 mmol) in 50 mL of diethylether under nitrogen was cooled to 0 °C. To this solution was slowly added methylmagnesium bromide (10.0 mL, 3.0M in diethylether). After gas evolution had ceased, the solvent was removed *in vacuo*. The resulting residue was dissolved in 100 mL of toluene. Formaldehyde (450 mg, 15 mmol) was added and the reaction mixture was refluxed for 12 h. After cooling to room temperature the reaction mixture was washed with saturated NH_4Cl. The layers were separated and the aqueous layer was extracted with diethylether. The combined organic extracts were dried with $MgSO_4$ and the volatile materials were removed at reduced pressure. Chromatographic purification on silica gel (hexanes:diethylether, 95:5) yielded 2.20 g (42%) of 2,2'-methylenebis(2-phenylphenol), (**5**). m.p. 111°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.06 (s, 2H), 6.27 (s, 2H), 6.94 (t, J = 7.5 Hz, 2H), 7.12 (dd, J_1 = 1.6 Hz, J_2 = 7.5 Hz, 2H), 7.28 (dd, J_1 = 1.6 Hz, J_2 = 7.5 Hz, 2H), 7.3-7.4 (m, 2H), 7.4-7.5 (m, 8H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 31.0, 121.0, 127.0, 127.6, 128.7, 128.8, 128.9, 129.2, 130.2, 137.5, 149.8 ppm; IR (KBr) 3502, 3462, 1586, 1454, 1431, 1321, 1208, 1182, 1078, 825, 762, 702 cm^{-1}; MS (ES(+), 30 eV) m/z: 727.4 (2M+Na, 100%). Elemental analysis; Calculated for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72; Found: C, 84.78; H, 5.85.

[1] G. Casiraghi, G. Casnati, M. Cornia, A. Pochini, G. Puglia, G. Sartoria, R. Ungaro. *J. Chem. Soc. Perkin Trans. 1*, **1977**, 318-321.



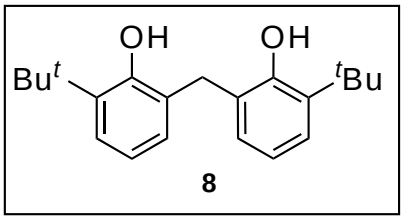
4

Data for **4**: The product was purified by crystallization from ether/hexanes. The yield was 62% (2.38 g, 9.29 mmol). m.p. 144°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.16 (s, 6H), 2.21 (s, 6H), 3.83 (s, 2H), 6.10 (s, 2H), 6.77 (d, J = 1.5 Hz, 2H), 6.91 (d, J = 1.5 Hz, 2H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 15.9, 20.4, 31.2, 123.9, 126.2, 128.8, 129.9, 130.1, 148.8 ppm; IR (KBr) 3470, 3333, 2915, 1484, 1456, 1374, 1284, 1238, 1193, 1151, 1123, 1025, 933, 856, 778, 563 cm^{-1}; MS (ES(-), 30 eV) m/z: 255.2 (M-1, 100%); Elemental analysis; Calculated for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86; Found: C, 80.05; H, 7.85.



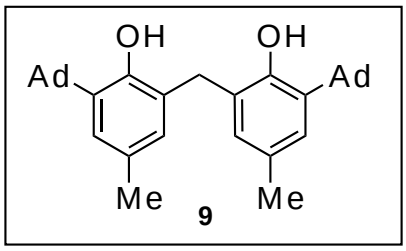
6

Data for **6**: The product was purified by chromatography on silica gel (hexanes:diethylether, 97:3). The yield was 47% (3.0 g, 7.06 mmol). m.p. 141°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.28 (s, 18H), 1.41 (s, 18H), 3.93 (s, 2H), 5.84 (b, 2H), 7.14 (d, J = 2.4 Hz, 2H), 7.19 (d, J = 2.4 Hz, 2H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 30.1, 31.6, 32.5, 34.3, 34.6, 122.5, 125.1, 126.0, 135.5, 143.0, 149.9 ppm; IR (KBr) 3531, 2955, 1478, 1362, 1251, 1214, 1199, 1158, 883, 799 cm^{-1}; MS (ES(-), 30 eV) m/z: 423.5 (M-1, 100%). Elemental analysis; Calculated for $C_{29}H_{44}O_2$: C, 84.02; H, 10.44; Found: C, 84.46; H, 10.79.



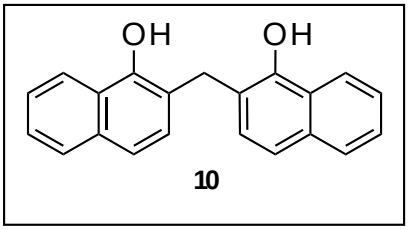
8

Data for **8**: The product was purified by chromatography on silica gel (hexanes). The yield was 21% (1.0 g, 3.20 mmol). m.p. 81°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.49 (s, 18H), 3.95 (s, 2H), 5.95 (s, 2H), 6.84 (t, J = 7.7 Hz, 2H), 7.12 (dd, J_1 = 1.5 Hz, J_2 = 7.7 Hz, 2H), 7.17 (dd, J_1 = 1.5 Hz, J_2 = 7.7 Hz, 2H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 30.0, 31.8, 34.4, 120.8, 125.6, 126.7, 128.5, 136.4, 152.3 ppm; IR (KBr) 3587, 3407, 2954, 1468, 1438, 1369, 1311, 1258, 1229, 1167, 1088, 839, 810, 786, 755 cm^{-1}; MS (ES(+), 30 eV) m/z: 335.2 (M+Na, 50%), 369.3 (55%), 413.4 (100%); Elemental analysis; Calculated for $C_{21}H_{28}O_2$, 80.73; H, 9.03; Found: C, 80.77; H, 9.04..



9

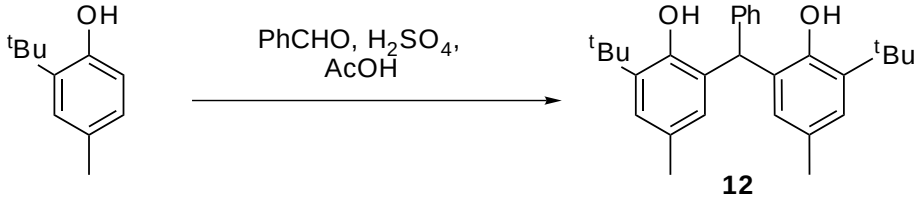
Data for **9**: The product was purified by crystallization from hot dichloromethane. The yield was 69% (1.71 g, 3.44 mmol). m.p. 258°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.77 (s, 12H), 2.08 (s, 12H), 2.25 (s, 6H), 3.85 (s, 2H), 5.75 (s, 2H), 6.92 (s, 2H), 6.93 (s, 2H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 20.9, 29.0, 32.3, 36.6, 37.0, 40.9, 126.4, 126.5, 128.6, 129.8, 136.5, 150.5 ppm; IR (KBr) 3493, 2901, 2850, 1761, 1466, 1368, 1198, 1119, 860 cm^{-1}; MS (ES(-), 30 eV) m/z: 495.4 (M-1, 100%). Elemental analysis; Calculated for $C_{35}H_{44}O_2$: C, 84.63; H, 8.93; Found: C, 84.53; H, 9.07.



10

Data for **10**: The product was purified by crystallization from dichloromethane/hexanes, and recrystallized from chloroform. The yield was 6% (500 mg, 1.66 mmol). m.p.164°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.26 (s, 2H), 6.68 (s, 2H), 7.4 – 7.5 (m, 8H), 7.74 (dd, J_1 = 2.0 Hz, J_2 = 7.4 Hz, 2H), 8.00 (dd, J_1 = 1.4 Hz, J_2 = 8.1 Hz, 2H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 31.4, 120.4, 120.6, 121.3, 124.6, 125.6, 125.8, 127.9, 128.3, 133.6, 147.7 ppm; IR (KBr) 3395, 3047, 2935, 1655, 1598, 1578, 1512, 1379, 1358, 1312, 1276, 1225, 1082, 755 cm^{-1}; MS (ES(-), 30 eV) m/z: 299.2 (M-1, 100%), HRMS for $C_{24}H_{32}O_2$+Na, calculated: 375.2300, found: 375.2302.

Preparation of 12.[2]



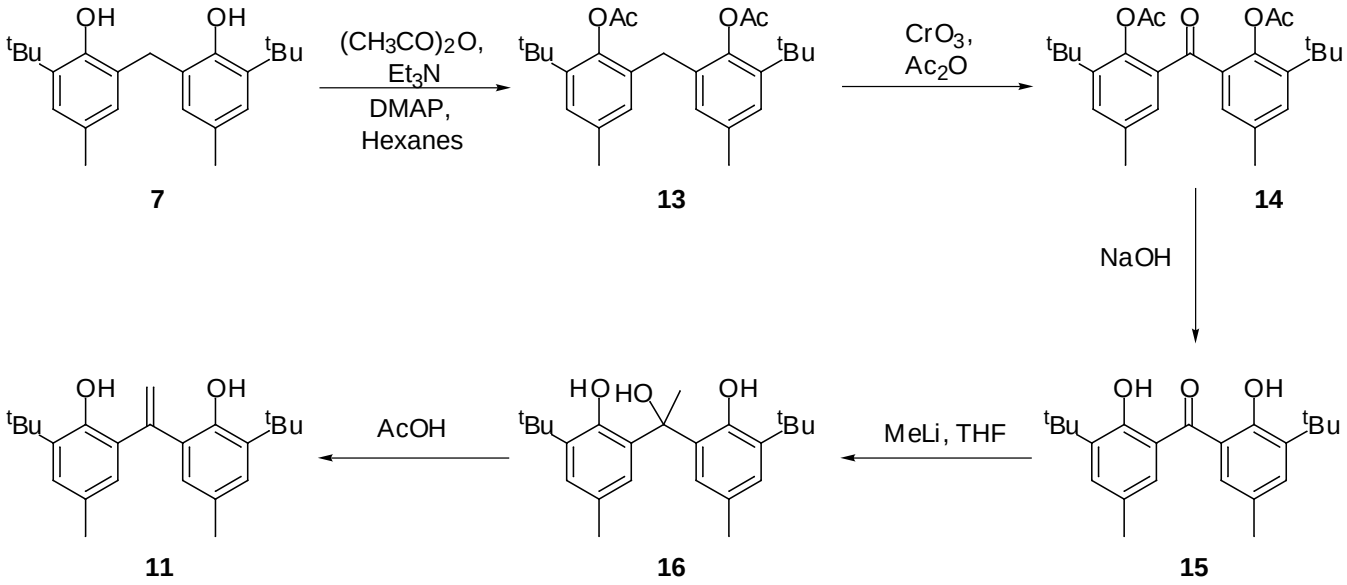
12

To a solution of 2-*tert*-Butyl-4-methylphenol (3.81 g, 23.2 mmol) in 20 mL of acetic acid was added benzaldehyde (1.18 mL, 11.61 mmol) and concentrated sulfuric acid (0.8 mL). The resulting mixture was warmed to 40 °C for 4 hours and then diluted with ice-water. The precipitate obtained was filtered off and

[2] C. Grüttner, V. Böhmer, R. Assmus, S. Scherf. *J. Chem. Soc. Perkin Trans. 1*, **1995**, 93-94.

recrystallized from hexanes to give the bisphenol **12**. The yield was 28% (1.37 g, 3.29 mmol). m.p. 168 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.36 (s, 18H), 2.17 (s, 6H), 4.77 (s, 2H), 5.58 (s, 1H), 6.49 (d, J = 1.9 Hz, 2H), 7.05 (d, J = 1.9 Hz, 2H), 7.19 (d, J = 7.1 Hz, 2H), 7.3 – 7.4 (m, 3H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 21.0, 29.8, 34.6, 47.2, 127.1, 127.3, 127.8, 128.2, 129.0, 129.5, 129.6, 137.5, 140.7, 150.8 ppm; IR (KBr) 3556, 3535, 2950, 1471, 1442, 1363, 1320, 1256, 1177, 869, 754, 702 cm^{-1}; MS (ES(-), 30 eV) m/z: 415.3 (M-1, 100%). Elemental analysis; Calculated for $C_{29}H_{36}O_2$: C, 83.61; H, 8.71; Found: C, 83.77; H, 8.96.

Scheme 1. Synthesis of 11.



Preparation of 13. To a solution of 2,2'-methylenebis(2-*tert*-butyl-4-methylphenol) (12.0 g, 35.2 mmol) in 100 mL of hexanes were added acetic anhydride (10 mL, 106 mmol), triethylamine (10 mL, 71.7 mmol) and DMAP (40 mg, 0.327 mmol). The mixture was stirred for 24 hours or until no starting material was detected by TLC. The resulting solution was diluted with dichloromethane, washed twice with 2N HCl and twice with water. Removal of solvents at reduced pressure yielded diacetate **13** (14.1 g, 33.2 mmol, 94%) as a viscous oil. It was used without further purification. m.p. 58°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.32 (s, 18H), 2.1 – 2.2 (b, 6H), 2.25 (s, 6H), 3.3 – 3.7 (b, 2H), 6.71 (b, 2H),

7.07 (d, J = 1.8 Hz, 2H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 21.2, 30.5, 31.7, 34.5, 126.3, 129.3, 133.0, 135.0, 141.0, 145.8, 169.4 ppm; IR (KBr) 2961, 1761, 1603, 1442, 1368, 1194, 1117, 1009, 912, 857, 646, 597 cm^{-1}; MS (ES(+), 30 eV) m/z: 447.2 (M+Na, 100%), 871.3 (2M+Na, 68%).

Preparation of 14 (Scheme 1). To a warm solution (65 ^{o}C) of diacetate **13** (10.61 g, 25 mmol) in 100 mL of acetic anhydride was added chromium trioxide (7.5 g, 75 mmol) portionwise over 1 hour. After the addition was complete, the mixture was stirred for another 30 minutes at 65 ^{o}C, and then poured over ice-water (500 mL). Stirring was continued until no heat evolution was observed (2 hours). Extraction of the aqueous mixture with dichloromethane and removal of the solvents yielded a dark oil that was purified by chromatography on silica gel (hexanes/diethylether) to obtain **14** as a white solid (1.13 g, 2.57 mmol, 10% yield). m.p. 160°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.37 (s, 18H), 1.97 (s, 6H), 2.33 (s, 6H), 7.26 (d, J = 2.0 Hz, 2H), 7.36 (d, J = 2.0 Hz, 2H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 21.0, 21.1, 30.3, 34.7, 130.2, 131.5, 132.6, 134.6, 141.4, 145.7, 169.9, 194.1 ppm; IR (KBr) 2960, 1757, 1668, 1590, 1438, 1364, 1315, 1253, 1202, 1124, 1005, 909, 871, 802, 702, 646, 593 cm^{-1}; MS (ES(+), 30 eV) m/z: 316.0 (98%), 464.8 (100%), 899.7 (2M+Na, 70%).

Preparation of 15 (Scheme 1). To a solution of diacetate **14** (270 mg, 0.615 mmol) in 15 mL of ethanol was added 4N NaOH until the formation of a precipitate was observed. Stirring was continued for 1 hour or until complete dissolution of the solid. The reaction mixture was acidified to pH=5 with 2N HCl, then extracted with dichloromethane. Removal of the solvent yielded bisphenol **15** as a yellow solid (196 mg, 0.553 mmol, 90%). It was used without further purification. m.p. 173°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.45 (s, 18H), 3.27 (s, 6H), 8.21 (d, J = 1.9 Hz, 2H), 8.31 (d, J = 1.9 Hz, 2H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 20.8, 29.4 ($6CH_3$), 35.0, 120.1 (2C), 126.5 (2C), 131.1 (2CH), 133.9 (2CH), 138.4 (2C), 158.8 (2C), 204.2 (2C) ppm; IR (KBr) 2954, 1612, 1579, 1424,

1392, 1351, 1250, 1228, 1209, 1192, 1046, 996, 876, 806, 718 cm^{-1}; MS (ES(-), 30 eV) m/z: 353.2 (M-1, 100%), 419.3 (80%).

Preparation of 16 (Scheme 1). To a solution of bisphenol **15** (200 mg, 0.564 mmol) in 10 mL of THF was slowly added a solution of methyllithium (2.21 mL, 3.10 mmol) in hexanes. Stirring was continued for 2 hours. The reaction was quenched with water and the product extracted with dichloromethane. After removal of the solvents, the residue was purified by chromatography on silica gel (hexanes/diethylether) to obtain **16** as a white solid (140 mg, 0.378 mmol, 67%). m.p. 65°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.40 (s, 18H), 2.03 (s, 3H), 2.20 (s, 6H), 3.75 (s, 1H), 6.58 (d, J = 1.8 Hz, 2H), 7.08 (d, J = 1.8 Hz, 2H), 7.67 (s, 2H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 21.0, 28.4, 29.8, 34.8, 81.6, 124.9, 127.9, 128.1, 129.3, 138.0, 152.3 ppm; IR (KBr) 3383, 2957, 1473, 1438, 1390, 1234, 1207, 1073, 865, 771, 688 cm^{-1}; MS (ES(-), 30 eV) m/z: 369.1 (M-1, 100%).

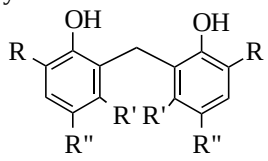
Preparation of 11 (Scheme 1). Alcohol **16** (170 mg, 0.458 mmol) was dissolved in 5 mL of acetic acid and refluxed for 5 minutes. The mixture was diluted with dichloromethane, washed with water and the solvents removed. The resulting crude product was purified by chromatography on silica gel (hexanes/diethylether) to obtain **11** as a white solid (123 mg, 0.348 mmol, 76%). m.p. 94°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.36 (s, 18H), 2.26 (s, 6H), 5.42 (s, 2H), 5.63 (s, 2H), 6.93 (d, J = 2.0 Hz, 2H), 7.09 (d, J = 2.0 Hz, 2H) ppm; ^{13}C {^{1}H}NMR ($CDCl_3$, 125 MHz) δ 20.8, 29.5, 34.8, 120.0, 126.6, 127.6, 128.7, 129.3, 137.0, 143.8, 150.0 ppm; IR (KBr) 3495, 2959, 1596, 1439, 1389, 1360, 1323, 1267, 1237, 1197, 1161, 920, 865, 780.2 cm^{-1}; MS (ES(-), 30 eV) m/z: 351.2 (M-1, 100%).

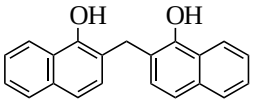
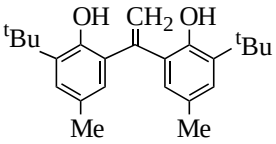
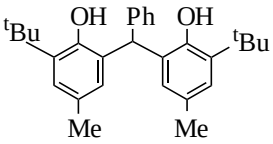
Preparation of titanium tetra((*S*)-2-tolyl-1-propoxide): (*S*)-2-Tolyl-1-propanol (3.71 g, 24.7 mmol, 99.0% ee) was introduced in a Schlenk flask which was then purged with nitrogen. With stirring, titanium isopropoxide (7.29 mL, 24.7 mmol) was added. High vacuum was applied to the system for 4 hours, or until no weight loss was observed. Absence of isopropoxide was confirmed by NMR. The yield was 100%. $[\alpha]_D$ = -125.22 (c 9.67, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.80 (t, J = 7.7 Hz, 12H), 1.63 (m, 8H), 2.32 (s, 12H), 4.97 (t, J = 6.4 Hz, 4H), 7.02 (d, J = 8.0 Hz, 8H), 7.08 (d, J = 8.0 Hz, 8H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz); δ 10.2 ($4CH_3$), 21.1 ($4CH_3$), 33.5 ($4CH_2$), 87.9 (4CH), 125.8 (8CH), 128.6 (8CH), 136.2 (4C), 142.4 (4C) ppm; IR (film) 3060, 3027, 2963, 2931, 2873, 1947, 1882, 1805, 1759, 1682, 1602, 1492, 1353, 1200, 1096, 1053, 1005, 918, 898, 746, 698 cm^{-1}.

General procedure for the asymmetric alkylation of benzaldehyde using achiral $MBPH_2$ ligands and titanium tetra((*S*)-2-tolyl-1-propoxide): The achiral methylenebisphenol (0.06 mmol, 20 mol%) was introduced in a dry Schlenk flask, and the system purged with nitrogen. A solution of titanium tetra((*S*)-2-tolyl-1-propoxide) (2.5 mL, 0.15 M in dichloromethane, 1.2 eq.) was added to the ligand and the resulting red or yellow solution cooled to -20 °C. Diethylzinc (0.92 mL, 1.0 M in hexanes, 3.2 eq.) was added and the mixture stirred for 20 minutes. Finally, benzaldehyde (31 μL, 0.3 mmol, 1.0 eq.) was added to the reaction mixture. Samples from the reaction were taken at different reaction times and quenched by stirring with 2N HCl. The organic layer was diluted with pentane, and the resulting solution stored at -20 °C to produce the precipitation of the ligand. Samples were analyzed by gas chromatography. Supelco SPB™-5, 30m x 0.25mm. 115 °C, 1.3 mL/min. (*S*)-2-phenyl-1-propanol: 16.0 min.; (*R*)-2-phenyl-1-propanol: 16.9 min. The ee values recorded in Table 1 are at low conversion (5-8%) to minimize the effect of incorporation of the product alkoxide into the catalyst. Reactions were quenched after 40 h and the percent conversion determined by GC. Conversions ranged from 45% to 99% as seen in Table S1. In all reactions less than 1.3% of the MPV oxidation product [EtCO(4-C6H4-Me)] was

detected. When the (*R*) enantiomer of the chiral alkoxide was employed, the (*R*) enantiomer of the product alcohol predominated with identical enantioselectivity.

Table S1. 2,2-Methylene bis(phenol) derivatives (MBP-H_2) used in the asymmetric addition of alkyl groups to aldehydes.



Entry	R	R'	R"	T=1h, ee % (config) [% conv]	T=24h, ee % (config) [% conv]
1	H	H	H	1 (*S*) [12]	4 (*S*) [99]
2	H	H	Cl	9 (***R***) [13]	6 (***R***) [95]
3	Cl	Cl	Cl	-	24 (S) [43]
4	Me	H	Me	16 (*S*) [5]	16 (*S*) [45]
5	Ph	H	H	36 (*S*) [4]	24 (*S*) [50]
6	*t*-Bu	H	*t*-Bu	68 (*S*) [7]	67 (*S*) [7]0
7	*t*-Bu	H	Me	79 (*S*) [5]	77 (*S*) [91]
8	*t*-Bu	H	H	73 (*S*) [8]	71 (*S*) [77]
9	Adamantyl	H	Me	83 (*S*) [9]	80 (*S*) [92]
10				28 (*S*) [5]	17 (*S*) [9]
11				45 (*S*) [8]	-
12				-	60 (*S*) [88]
13	NO MBP-H_2 Ligand added			39 (*S*)	

Stoichiometric asymmetric alkylation of benzaldehyde using achiral MBPH_2 ligands and titanium tetra((*S*)-2-tolyl-1-propoxide): The achiral methylene bis(2-adamantylphenol) **9** (122 mg, 0.246 mmol, 1.0 eq.) was introduced in a dry Schlenk flask, and the system purged with nitrogen. A solution of titanium tetra((*S*)-2-tolyl-1-propoxide) (1.64 mL, 0.15 M in dichloromethane, 1.0 eq.) was

added to the ligand and the resulting red solution cooled to -20 °C. Diethylzinc (1.23 mL, 1.0 M in hexanes, 5.0 eq.) was added and the mixture stirred for 20 minutes. Finally, benzaldehyde (25 μL, 0.246 mmol, 1.0 eq.) was added to the reaction mixture. Samples from the reaction were taken at different reaction times and quenched by stirring with 2N HCl. The organic layer was diluted with pentane, and the resulting solution stored at -20 °C to produce the precipitation of the ligand. Samples were analyzed by gas chromatography. Supelco SPB™-5, 30m x 0.25mm. 115 °C, 1.3 mL/min. 87.4% ee (*S*).

The synthesis and characterization of **6g** will be reported in a subsiquent publication.

Table S1. Summary of Structure Determination of Compound 6g.

Formula:	$TiC_{43}H_{57}NO_4Cl_2$
Formula weight:	770.70
Crystal class:	orthorhombic
Space group:	$P2_12_12_1$ (#19)
Z	4
Cell constants:	
a	16.1969(1)Å
b	25.3021(2)Å
c	10.4048(1)Å
V	4264.05(6)$Å^3$
μ	3.65 cm^{-1}
crystal size, mm	0.32 x 0.20 x 0.05
D_{calc}	1.201 g/cm^3
F(000)	1640
Radiation:	Mo-K_α (λ=0.71069Å)
2θ range	5.02 – 50.7 °
hkl collected:	$-19 \leq h \leq 19$; $-30 \leq k \leq 28$; $-11 \leq l \leq 12$
No. reflections measured:	26507
No. unique reflections:	7690 (R_{int}=0.0484)
No. observed reflections	7157 (F>4σ)
No. reflections used in refinement	7690
No. parameters	472
R indices (F>4σ)	R_1=0.0528
	wR_2=0.1089
R indices (all data)	R_1=0.0583
	wR_2=0.1120
GOF:	1.124
Final Difference Peaks, $e/Å^3$	+0.339, -0.476
Flack absolute structure parameter	0.01(3)

Table S2. Refined Positional Parameters for Compound 6g.

Atom	x	y	z	U_{eq}, Å^2
Ti	0.54159(3)	0.68186(2)	0.50485(5)	0.03037(12)
Cl1	0.73745(9)	0.87058(5)	-0.05586(13)	0.0832(4)
Cl2	0.13304(8)	0.53087(7)	0.7072(2)	0.1119(6)
O1	0.50458(14)	0.74383(8)	0.5834(2)	0.0355(5)
O2	0.59961(13)	0.65955(9)	0.6478(2)	0.0357(5)
O3	0.61938(14)	0.69482(9)	0.3877(2)	0.0419(6)
O4	0.48851(13)	0.61926(8)	0.4836(2)	0.0384(5)
N1	0.4418(2)	0.70871(11)	0.3658(3)	0.0401(7)
H1	0.4548(2)	0.74250(11)	0.3437(3)	0.053
C1	0.4987(2)	0.76473(12)	0.7036(3)	0.0322(7)
C2	0.5173(2)	0.81861(13)	0.7247(3)	0.0336(7)
C3	0.5127(2)	0.83655(13)	0.8509(3)	0.0416(8)
H3	0.5270(2)	0.87153(13)	0.8671(3)	0.055
C4	0.4884(2)	0.80575(13)	0.9539(3)	0.0420(8)
C5	0.4668(2)	0.75397(12)	0.9282(3)	0.0400(8)
H5	0.4482(2)	0.73276(12)	0.9952(3)	0.053
C6	0.4719(2)	0.73244(12)	0.8047(3)	0.0345(7)
C7	0.4516(2)	0.67450(12)	0.7889(3)	0.0356(7)
H7a	0.4020(2)	0.66652(12)	0.8374(3)	0.047
H7b	0.4401(2)	0.66741(12)	0.6990(3)	0.047
C8	0.5204(2)	0.63863(12)	0.8334(3)	0.0330(7)
C9	0.5120(2)	0.61051(12)	0.9473(3)	0.0375(7)
H9	0.4634(2)	0.61343(12)	0.9941(3)	0.050
C10	0.5746(2)	0.57826(13)	0.9927(3)	0.0419(7)
C11	0.6470(2)	0.57544(14)	0.9230(3)	0.0427(8)
H11	0.6894(2)	0.55417(14)	0.9541(3)	0.057
C12	0.6600(2)	0.60292(13)	0.8080(3)	0.0369(7)
C13	0.5936(2)	0.63415(12)	0.7631(3)	0.0326(7)
C14	0.5425(2)	0.85493(12)	0.6132(3)	0.0387(7)
C15	0.6256(2)	0.8358(2)	0.5585(4)	0.0543(10)
H15a	0.6675(4)	0.8388(10)	0.6234(9)	0.081
H15b	0.6404(9)	0.8572(7)	0.486(2)	0.081
H15c	0.6208(6)	0.7996(4)	0.532(3)	0.081
C16	0.4759(2)	0.85576(13)	0.5096(4)	0.0529(9)
H16a	0.4928(8)	0.8786(8)	0.4408(12)	0.079
H16b	0.4252(5)	0.8685(10)	0.5457(7)	0.079
H16c	0.4678(12)	0.8206(2)	0.477(2)	0.079
C17	0.5534(2)	0.91243(13)	0.6578(4)	0.0486(9)
H17a	0.5968(11)	0.9142(2)	0.720(2)	0.073

H17b	0.5028(5)	0.9248(4)	0.695(2)	0.073
H17c	0.567(2)	0.9342(2)	0.5854(6)	0.073
C18	0.4883(3)	0.8265(2)	1.0909(3)	0.0608(11)
H18a	0.4330(4)	0.8256(11)	1.1243(10)	0.091
H18b	0.508(2)	0.8622(4)	1.0917(5)	0.091
H18c	0.523(2)	0.8048(7)	1.1432(7)	0.091
C19	0.7414(2)	0.59801(14)	0.7334(3)	0.0434(8)
C20	0.7765(2)	0.6531(2)	0.7043(4)	0.0549(10)
H20a	0.8288(8)	0.6496(2)	0.662(2)	0.082
H20b	0.784(2)	0.6722(4)	0.7832(5)	0.082
H20c	0.7389(8)	0.6720(4)	0.650(2)	0.082
C21	0.7253(2)	0.5674(2)	0.6085(3)	0.0532(10)
H21a	0.7752(5)	0.5657(10)	0.5590(13)	0.080
H21b	0.6833(12)	0.5851(6)	0.5596(13)	0.080
H21c	0.707(2)	0.5322(4)	0.6287(3)	0.080
C22	0.8074(2)	0.5682(2)	0.8102(4)	0.0644(12)
H22a	0.8574(6)	0.5664(11)	0.7608(13)	0.097
H22b	0.7883(8)	0.5331(5)	0.828(3)	0.097
H22c	0.8179(14)	0.5865(7)	0.889(2)	0.097
C23	0.5642(3)	0.5462(2)	1.1151(4)	0.0610(11)
H23a	0.6130(8)	0.5495(9)	1.1668(13)	0.091
H23b	0.556(2)	0.5098(3)	1.0936(4)	0.091
H23c	0.5175(11)	0.5592(8)	1.1623(14)	0.091
C24	0.6636(2)	0.68092(14)	0.2735(3)	0.0385(7)
H24	0.6301(2)	0.65583(14)	0.2242(3)	0.051
C25	0.6786(2)	0.72901(14)	0.1914(3)	0.0377(7)
C26	0.6690(2)	0.7262(2)	0.0591(3)	0.0451(8)
H26	0.6499(2)	0.6952(2)	0.0214(3)	0.060
C27	0.6879(2)	0.7698(2)	-0.0174(4)	0.0561(10)
H27	0.6824(2)	0.7678(2)	-0.1062(4)	0.075
C28	0.7147(2)	0.8158(2)	0.0391(4)	0.0525(9)
C29	0.7236(2)	0.8195(2)	0.1712(4)	0.0516(9)
H29	0.7410(2)	0.8508(2)	0.2091(4)	0.069
C30	0.7061(2)	0.77582(14)	0.2457(3)	0.0435(8)
H30	0.7128(2)	0.77784(14)	0.3343(3)	0.058
C31	0.7446(2)	0.6538(2)	0.3109(4)	0.0521(10)
H31a	0.7789(2)	0.6788(2)	0.3568(4)	0.068
H31b	0.7324(2)	0.6248(2)	0.3689(4)	0.068
C32	0.7924(3)	0.6326(2)	0.1973(4)	0.0694(13)
H32a	0.8404(11)	0.6142(11)	0.2274(4)	0.104
H32b	0.809(2)	0.6614(2)	0.143(2)	0.104
H32c	0.7581(7)	0.6088(10)	0.149(2)	0.104
C33	0.4840(2)	0.56833(11)	0.5440(3)	0.0342(7)

H33	0.5194(2)	0.56849(11)	0.6205(3)	0.045
C34	0.3965(2)	0.55785(12)	0.5848(3)	0.0332(7)
C35	0.3777(2)	0.54651(13)	0.7112(3)	0.0428(8)
H35	0.4199(2)	0.54471(13)	0.7716(3)	0.057
C36	0.2963(3)	0.5377(2)	0.7499(4)	0.0594(11)
H36	0.2838(3)	0.5306(2)	0.8354(4)	0.079
C37	0.2357(2)	0.5398(2)	0.6595(5)	0.0595(11)
C38	0.2516(2)	0.55050(14)	0.5320(4)	0.0521(10)
H38	0.2090(2)	0.55154(14)	0.4721(4)	0.069
C39	0.3325(2)	0.55969(12)	0.4953(4)	0.0442(8)
H39	0.3444(2)	0.56718(12)	0.4097(4)	0.059
C40	0.5161(2)	0.52689(12)	0.4505(3)	0.0418(8)
H40a	0.4814(2)	0.52647(12)	0.3745(3)	0.056
H40b	0.5717(2)	0.53621(12)	0.4241(3)	0.056
C41	0.5169(3)	0.47217(13)	0.5107(5)	0.0677(12)
H41a	0.542(2)	0.4476(3)	0.452(2)	0.102
H41b	0.4613(3)	0.4612(6)	0.528(3)	0.102
H41c	0.548(2)	0.4731(3)	0.590(2)	0.102
C42	0.4379(3)	0.6788(2)	0.2444(3)	0.0548(10)
H42a	0.4889(7)	0.6830(9)	0.1985(13)	0.082
H42b	0.3932(11)	0.6919(8)	0.1929(12)	0.082
H42c	0.429(2)	0.6421(2)	0.2627(4)	0.082
C43	0.3586(2)	0.7111(2)	0.4250(4)	0.0542(10)
H43a	0.3603(4)	0.7336(9)	0.499(2)	0.081
H43b	0.3417(7)	0.6763(2)	0.450(2)	0.081
H43c	0.3199(4)	0.7252(10)	0.3640(9)	0.081

$U_{eq}={}^{1}/_{3}[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*cos\gamma+2U_{13}aa^*cc^*cos\beta+2U_{23}bb^*cc^*c$

Table S3. Bond Distances in Compound 6g, Å

Ti-O3	1.784(2)	Ti-O4	1.816(2)	Ti-O2	1.848(2)
Ti-O1	1.867(2)	Ti-N1	2.273(3)	Cl1-C28	1.741(4)
Cl2-C37	1.750(4)	O1-C1	1.361(4)	O2-C13	1.365(4)
O3-C24	1.432(4)	O4-C33	1.435(3)	N1-C42	1.474(4)
N1-C43	1.483(5)	C1-C6	1.400(4)	C1-C2	1.413(4)
C2-C3	1.391(4)	C2-C14	1.536(4)	C3-C4	1.382(5)
C4-C5	1.383(5)	C4-C18	1.518(5)	C5-C6	1.399(4)
C6-C7	1.512(4)	C7-C8	1.510(4)	C8-C9	1.389(4)
C8-C13	1.399(4)	C9-C10	1.383(5)	C10-C11	1.381(5)
C10-C23	1.518(5)	C11-C12	1.399(5)	C12-C13	1.413(4)
C12-C19	1.535(5)	C14-C16	1.525(5)	C14-C17	1.537(4)
C14-C15	1.539(5)	C19-C22	1.533(5)	C19-C21	1.535(5)
C19-C20	1.536(5)	C24-C25	1.506(5)	C24-C31	1.530(5)
C25-C30	1.385(5)	C25-C26	1.387(5)	C26-C27	1.394(5)
C27-C28	1.375(6)	C28-C29	1.385(5)	C29-C30	1.379(5)
C31-C32	1.510(5)	C33-C34	1.503(5)	C33-C40	1.522(4)
C34-C35	1.381(5)	C34-C39	1.394(5)	C35-C36	1.397(5)
C36-C37	1.361(6)	C37-C38	1.378(6)	C38-C39	1.385(5)
C40-C41	1.519(5)				

Table S4. Bond Angles in Compound 6g, °

O3-Ti-O4	114.32(11)	O3-Ti-O2	104.30(10)	O4-Ti-O2	94.14(10)
O3-Ti-O1	111.82(10)	O4-Ti-O1	129.33(10)	O2-Ti-O1	93.87(10)
O3-Ti-N1	90.71(11)	O4-Ti-N1	81.18(10)	O2-Ti-N1	164.86(10)
O1-Ti-N1	78.43(10)	C1-O1-Ti	138.7(2)	C13-O2-Ti	144.7(2)
C24-O3-Ti	151.1(2)	C33-O4-Ti	138.9(2)	C42-N1-C43	109.8(3)
C42-N1-Ti	115.0(2)	C43-N1-Ti	113.2(2)	O1-C1-C6	119.0(3)
O1-C1-C2	120.2(3)	C6-C1-C2	120.8(3)	C3-C2-C1	116.7(3)
C3-C2-C14	122.1(3)	C1-C2-C14	121.1(3)	C4-C3-C2	124.3(3)
C3-C4-C5	117.1(3)	C3-C4-C18	122.2(3)	C5-C4-C18	120.6(3)
C4-C5-C6	122.1(3)	C5-C6-C1	118.8(3)	C5-C6-C7	117.7(3)
C1-C6-C7	123.5(3)	C8-C7-C6	112.9(3)	C9-C8-C13	119.1(3)
C9-C8-C7	119.9(3)	C13-C8-C7	121.0(3)	C10-C9-C8	121.5(3)
C11-C10-C9	118.2(3)	C11-C10-C23	120.4(3)	C9-C10-C23	121.3(3)
C10-C11-C12	123.4(3)	C11-C12-C13	116.5(3)	C11-C12-C19	121.4(3)
C13-C12-C19	122.1(3)	O2-C13-C8	118.8(3)	O2-C13-C12	120.0(3)
C8-C13-C12	121.2(3)	C16-C14-C2	110.8(3)	C16-C14-C17	106.4(3)
C2-C14-C17	111.6(3)	C16-C14-C15	111.2(3)	C2-C14-C15	108.9(3)
C17-C14-C15	108.0(3)	C22-C19-C21	108.2(3)	C22-C19-C12	112.1(3)
C21-C19-C12	108.8(3)	C22-C19-C20	106.9(3)	C21-C19-C20	110.7(3)
C12-C19-C20	110.2(3)	O3-C24-C25	110.7(3)	O3-C24-C31	109.1(3)
C25-C24-C31	111.6(3)	C30-C25-C26	118.9(3)	C30-C25-C24	120.8(3)
C26-C25-C24	120.2(3)	C25-C26-C27	120.1(3)	C28-C27-C26	119.7(3)
C27-C28-C29	120.9(4)	C27-C28-Cl1	119.9(3)	C29-C28-Cl1	119.2(3)
C30-C29-C28	118.9(4)	C29-C30-C25	121.5(3)	C32-C31-C24	113.5(3)
O4-C33-C34	109.2(2)	O4-C33-C40	108.8(2)	C34-C33-C40	112.4(3)
C35-C34-C39	118.6(3)	C35-C34-C33	120.9(3)	C39-C34-C33	120.4(3)
C34-C35-C36	121.1(4)	C37-C36-C35	118.3(4)	C36-C37-C38	122.6(4)
C36-C37-Cl2	118.9(3)	C38-C37-Cl2	118.4(3)	C37-C38-C39	118.3(4)
C38-C39-C34	120.9(4)	C41-C40-C33	111.6(3)		

Table S5. Refined Thermal Parameters (U's) for Compound 6g.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.0328(3)	0.0303(2)	0.0279(2)	0.0030(3)	0.0004(3)	-0.0018(2)
Cl1	0.0905(9)	0.0752(8)	0.0840(8)	0.0356(7)	0.0163(7)	-0.0108(7)
Cl2	0.0451(6)	0.1405(13)	0.150(2)	0.0695(12)	0.0226(8)	-0.0045(8)
O1	0.0439(13)	0.0323(11)	0.0304(11)	0.0015(9)	-0.0004(10)	-0.0024(10)
O2	0.0326(12)	0.0419(12)	0.0328(11)	0.0051(10)	0.0017(9)	-0.0004(10)
O3	0.0447(14)	0.0473(14)	0.0338(12)	0.0015(11)	0.0091(10)	-0.0043(11)
O4	0.0449(12)	0.0317(10)	0.0386(12)	0.0058(10)	-0.0043(10)	-0.0025(9)
N1	0.047(2)	0.0349(14)	0.038(2)	0.0060(12)	-0.0100(13)	-0.0023(13)
C1	0.031(2)	0.034(2)	0.031(2)	-0.0004(14)	-0.0003(14)	0.0006(13)
C2	0.031(2)	0.032(2)	0.037(2)	-0.0025(14)	0.0024(12)	0.0042(13)
C3	0.049(2)	0.035(2)	0.041(2)	-0.002(2)	0.001(2)	0.007(2)
C4	0.050(2)	0.040(2)	0.036(2)	-0.0012(14)	0.003(2)	0.014(2)
C5	0.047(2)	0.037(2)	0.036(2)	0.0066(14)	0.008(2)	0.007(2)
C6	0.030(2)	0.035(2)	0.038(2)	0.0011(14)	0.0011(13)	0.0046(13)
C7	0.032(2)	0.038(2)	0.037(2)	0.0052(14)	0.0050(14)	0.000(2)
C8	0.036(2)	0.029(2)	0.035(2)	0.0014(13)	-0.0016(13)	-0.0028(13)
C9	0.043(2)	0.034(2)	0.035(2)	0.0020(14)	0.0045(14)	-0.0027(14)
C10	0.051(2)	0.042(2)	0.033(2)	0.008(2)	-0.001(2)	0.0002(14)
C11	0.048(2)	0.043(2)	0.037(2)	0.004(2)	-0.005(2)	0.011(2)
C12	0.038(2)	0.040(2)	0.033(2)	0.000(2)	-0.0027(14)	0.0035(14)
C13	0.036(2)	0.036(2)	0.026(2)	0.0029(13)	-0.0008(13)	-0.0024(14)
C14	0.045(2)	0.033(2)	0.039(2)	0.0031(14)	0.006(2)	-0.001(2)
C15	0.056(2)	0.042(2)	0.065(2)	-0.005(2)	0.021(2)	-0.004(2)
C16	0.069(3)	0.042(2)	0.048(2)	0.007(2)	-0.006(2)	-0.003(2)
C17	0.056(2)	0.035(2)	0.056(2)	0.001(2)	0.011(2)	-0.003(2)
C18	0.093(3)	0.051(2)	0.038(2)	-0.005(2)	0.009(2)	0.017(2)
C19	0.037(2)	0.057(2)	0.037(2)	0.000(2)	-0.001(2)	0.009(2)
C20	0.036(2)	0.066(3)	0.062(2)	-0.001(2)	0.003(2)	-0.002(2)
C21	0.051(2)	0.066(3)	0.043(2)	-0.004(2)	-0.002(2)	0.013(2)
C22	0.044(2)	0.094(3)	0.055(2)	0.003(2)	-0.008(2)	0.020(2)
C23	0.075(3)	0.061(3)	0.047(2)	0.023(2)	0.006(2)	0.003(2)
C24	0.039(2)	0.045(2)	0.031(2)	-0.001(2)	0.0089(13)	-0.005(2)
C25	0.030(2)	0.049(2)	0.033(2)	0.001(2)	0.0042(14)	-0.0038(14)
C26	0.048(2)	0.049(2)	0.038(2)	0.000(2)	0.000(2)	-0.005(2)
C27	0.054(2)	0.076(3)	0.038(2)	0.013(2)	0.000(2)	0.001(2)
C28	0.048(2)	0.058(2)	0.052(2)	0.017(2)	0.008(2)	-0.002(2)
C29	0.048(2)	0.048(2)	0.059(2)	0.005(2)	0.009(2)	-0.008(2)
C30	0.040(2)	0.052(2)	0.039(2)	-0.002(2)	0.003(2)	-0.007(2)
C31	0.050(2)	0.063(2)	0.043(2)	0.007(2)	0.003(2)	0.011(2)

C32	0.051(2)	0.097(3)	0.060(3)	-0.007(3)	0.006(2)	0.021(2)
C33	0.039(2)	0.029(2)	0.035(2)	0.0042(13)	-0.0029(13)	-0.0029(13)
C34	0.037(2)	0.0234(14)	0.039(2)	0.0003(13)	0.0009(14)	0.0008(13)
C35	0.047(2)	0.040(2)	0.041(2)	0.009(2)	0.003(2)	0.000(2)
C36	0.058(3)	0.061(2)	0.060(2)	0.019(2)	0.017(2)	-0.002(2)
C37	0.043(2)	0.052(2)	0.084(3)	0.022(2)	0.010(2)	0.000(2)
C38	0.042(2)	0.045(2)	0.069(3)	0.005(2)	-0.006(2)	0.000(2)
C39	0.043(2)	0.044(2)	0.045(2)	0.000(2)	0.000(2)	0.0030(14)
C40	0.043(2)	0.033(2)	0.050(2)	-0.001(2)	0.013(2)	0.0001(14)
C41	0.072(3)	0.036(2)	0.095(3)	0.002(2)	0.034(3)	0.007(2)
C42	0.063(3)	0.065(2)	0.036(2)	0.001(2)	-0.014(2)	-0.004(2)
C43	0.041(2)	0.058(2)	0.063(2)	0.000(2)	-0.009(2)	0.007(2)

The form of the anisotropic displacement parameter is:
$\exp[-2\pi^2(a^{*2}U\_h^2+b^{*2}U\_k^2+c^{*2}U\_l^2+ 2b^*c^*U\_kl+2a^*c^*U\_hl+2a^*b^*U\_hk)]$.

ORTEP of 6g with full atom labeling