Supporting Information

General Comments

Benzene, pyridine, diethyl ether, 1,4-dioxane, xylenes, triethylamine, and Hunig's base were distilled from CaH_2 prior to use and stored in Sure Seal® bottles over 4 Å molecular sieves. THF and DME were distilled immediately prior to use from sodium benzophenone ketyl. All reactions were performed under an inert atmosphere of nitrogen or argon gas unless stated otherwise. Melting points and boiling points are uncorrected. NMR spectra were recorded using $CDCl_3$ as solvent unless stated otherwise. ^1H and ^{13}C spectra were internally referenced to residual chloroform (7.27 ppm) and $^{13}CDCl_3$ (77.0 ppm) respectively. ^{31}P-NMR spectra were externally referenced using a 30% H_3PO_4 solution in D_2O (0.0 ppm). In cases were ambiguity exists due ^{13}C-^{31}P coupling, each ^{13}C peak is listed along with its DEPT assignment.

Naphtho[2,1-*b*]furan-3(2H)-one (10).

2-Naphthoxyacetic acid (20.1 g, 99.3 mmol) in dry benzene (1000 mL) was treated with a catalytic amount of pyridine and 2 equiv. $SOCl_2$ (14.4 mL, 198.6 mmol) at reflux under a N_2 atmosphere for 2 h. The cooled solution was then concentrated in vacuo and the resulting residue was taken up into C_6H_6 (500 mL) and cooled to 0 ^oC. To the solution was then added $AlCl_3$ (19.8 g, 148.9 mmol) and the resulting solution stirred for 12 h at ambient temperature. The mixture was then quenched with brine and extracted with benzene (2 x 100 mL). The combined organic extracts were then washed with water (2 x 100 mL) and filtered through neutral alumina. The filtrate was then concentrated under reduced pressure to afford the desired product (17.2 g, 95%) which was clean by ^1H-NMR analysis. mp 133ºC (lit[1] 133ºC); IR (KBr) cm^{-1} 1688; ^1H-NMR (200 MHz, $CDCl_3$) δ 8.75 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.66 (dt, J = 7.6, 0.9 Hz, 1H), 7.47 (dt, J = 7.6, 1.0 Hz, 1H), 7.24 (dd, J = 7.8, 2.4 Hz, 1H), 4.77 (s, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 199.9 (C), 176.6 (C), 139.7 (CH), 129.8 (CH), 129.2 (C), 129.1 (C), 126.4 (CH), 125.4 (CH), 123.1 (CH), 113.9 (CH), 113.5 (C), 75.5 (CH_2); mass spectrum, *m/z* (relative intensity, %) 184 (M^+, 74), 155 (87), 126 (100); Exact mass calcd for $C_{12}H_8O$: 184.0524. Found: 184.0520.

3,3'-binaphtho[2,1-*b*]furan (11).

In a 1 L 3-neck round bottom flask equipped with an addition funnel was weighed out activated zinc dust (29.3 g, 0.448 mol) and DME (300 mL). The mixture was cooled to –78 ^{o}C and to it was carefully added $TiCl_4$ dropwise via syringe over a 30 min period. The resulting blue mixture was warmed to reflux and the starting naphthoketone (10.0 g, 54.4 mmol in 100 mL DME) was added dropwise over a 20 min period. The resulting mixture was heated to reflux under a N_2 atmosphere for 18 h. The cooled mixture was then filtered through a coarse sintered glass funnel and the filtrate was concentrated under reduced pressure. The resulting orange gummy residue was then dissolved in C_6H_6 (300 mL) and treated with DDQ (6.17 g, 27.2 mmol) at reflux under a N_2 atmosphere for 4 h. The cooled mixture was then quenched with saturated $Na_2S_2O_3$ and extracted with ether (3 x 100 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated to afford the crude title compound. The product was readily purified by flash chromatography (100:1 hexanes/ethyl acetate) to afford the analytically pure biaryl (7.13 g, 78%). mp 292-294 ^{o}C; IR (KBr) 2850, 1436 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.86 (s, 1 H), 7.84 (m, 2H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.35 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.09 (dt, *J* = 7.7, 1.3 Hz, 1H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 153.5 (C), 142.8 (CH), 130.8 (C), 128.6 (CH), 128.4 (C), 126.4 (CH), 126.3 (CH), 124.5 (CH), 123.3 (CH), 112.1 (C), 113.9 (C), 112.6 (CH); mass spectrum, *m/z* (relative intensity, %) 334 (M^+, 100), 305 (31), 276 (32), 138 (18); Exact mass calcd for $C_{24}H_{14}O_2$: 334.0994. Found: 334.0970; Anal Calcd. For $C_{24}H_{14}O_2$: C, 86.20; H, 4.22. Found: C, 85.96; H, 4.04.

2,2'-Bis(diphenylphosphonyl)-3,3'-binaphtho[2,1-*b*]furan (12).

3,3'-Binaphtho[2,1-*b*]furan (0.593 g, 1.776 mmol) in dry Et_2O (30 mL) was lithiated with *t*-BuLi (2.61 mL, 4.440 mmol, 1.7 M solution in hexanes) at 0 ^{o}C. After 1 h at 0 ^{o}C, the vessel was warmed to rt and stirred for a further 2 h under a N_2 atmosphere. To the mixture was then added freshly distilled diphenylphosphinic chloride (0.85 mL, 4.440 mmol) and the resulting white slurry was stirred overnight at room temperature. The reaction mixture was then quenched with water and extracted with $CHCl_3$ (3 x 50 mL). The combined organic extracts were washed with 10% $NaHCO_3$, water, and brine. The

organic phase was then dried ($MgSO_4$), and concentrated in vacuo to afford a light yellow solid residue. The crude material was purified by column chromatography (3:1 CH_2Cl_2/EtOAc → 19:1 CH_2Cl_2/MeOH) to afford the title compound (1.150 g, 88%). mp 289-290 ºC; IR (KBr) 2924, 1437, 1120 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 9.1 Hz, 1H), 7.72 (m, 2H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.36 (m, 2H), 7.23 (m, 3H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.96 (dt, *J* = 7.7, 3.1 Hz, 2H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 155.5 (d, *J* = 8 Hz, C), 145.8 (d, *J* = 128 Hz, C), 132.1 (CH), 132.1 (d, *J* = 35 Hz, C), 132.0 (CH), 131.9 (d, *J* = 3 Hz, CH), 130.8 (C), 129.9 (d, *J* = 31 Hz, C), 128.7 (CH), 128.1 (d, *J* = 13 Hz, CH), 127.6 (d, *J* = 13 Hz, CH), 126.9 (CH), 124.8 (CH), 124.6 (C), 122.7 (CH), 121.5 (d, *J* = 8 Hz, C), 112.6 (CH); ^{31}P-NMR (81 MHz, $CDCl_3$) δ 16.5; mass spectrum, *m/z* (relative intensity, %) 533 (M^+-P(O)Ph_2, 100), 201 (54); Exact mass calcd for $C_{48}H_{32}P_2O_4$: 734.1778. Found: 734.1731. See appendix A for expanded ^{13}C-NMR spectrum

2,2'-Bis(diphenylphosphino)-3,3'-binaphtho[2,1-*b*]furan (1).

3,3'-binaphtho[2,1-*b*]furan (3.4 g, 10.2 mmol) in dry Et_2O (130 mL) was lithiated with *t*-BuLi (11.2 mL, 22.4 mmol, 2.0 M solution in hexanes) at 0 ºC. After 1 h at 0 ºC, the vessel was warmed to rt and stirred for a further 2 h under a N_2 atmosphere. To the mixture was then added freshly distilled chlorodiphenylphosphine (4.0 mL, 22.4 mmol) and the resulting white slurry was stirred overnight at room temperature. The reaction mixture was quenched with water and extracted with $CHCl_3$ (3 x 125 mL). The combined organic extracts were washed with 10% $NaHCO_3$, water, and brine. The organic phase was dried ($MgSO_4$), and concentrated in vacuo to afford a light brown solid residue. The crude material was purified by crystallization ($CHCl_3$/MeOH) to afford the title compound (6.49 g, 91%). mp 228-229 ºC IR (KBr) 3052, 1433 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 9.1 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.37 (td, *J* = 8.1, 1.5 Hz, 2H), 7.35-7.30 (m, 3H), 7.24-7.14 (m, 4H), 7.04 (td, *J* = 7.4, 1.0 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 156.3 (C), 152.9 (d, *J* = 34 Hz, C), 135.4 (d, *J* = 71 Hz, C), 133.7 (CH), 133.6 (CH), 133.5 (CH), 130.7 (C), 128.6 (d, *J* = 4 Hz, CH), 128.5 (CH), 128.3 (C), 128.1 (d, *J* = 2 Hz, CH),

127.4 (CH), 126.5 (d, *J* = 35 Hz, C), 126.7 (CH), 124.5 (CH), 123.0 (CH), 122.5 (C), 112.9; (CH); ^{31}P-NMR (81 MHz, $CDCl_3$) δ -32.3; mass spectrum, *m/z* (relative intensity, %) 625 (M^+- Ph, 1), 517 (37), 408 (79), 183 (100); Exact mass calcd for $C_{48}H_{32}P_2O_2$: 702.1878. Found:702.1841. See appendix B for expanded ^{13}C-NMR spectrum.

Phosphinimine 15a and 15b.

BINAPFu **1** (2.65 g, 3.78 mmol) in THF (60 mL) was treated with (1*S*)-camphor-10-sulfonyl azide[2] (1.95 g, 7.55 mmol) at reflux under a N_2 atmosphere for 12 h. The cooled mixture was then concentrated under reduced pressure to afford a 1:1 mixture of **15a** and **15b** in quantitative yield. The diastereomeric products were separated by flash chromatography (9:1 $CHCl_3/CH_3CN$). The first spot off the column **15a** was determined to be the *S* axial isomer by single crystal X-ray analysis and afforded the following analytical data: mp 175-177 ºC; $[\alpha]_D^{21}$ = -72.1º (c 4.13, $CHCl_3$); IR (KBr) 1745 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.97-7.52 (m, 11H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.17 (t, *J* = 6.6 Hz, 1H), 6.88 (m, 2H), 2.51-2.26 (m, 2H), 2.18 (dt, *J* = 16.0, 3.0 Hz, 1H), 1.94-1.54 (m, 4H), 1.50-1.07 (m, 2H), 0.90 (s, 3H), 0.53 (s, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 214.8 (C), 156.3 (d, *J* = 10 Hz, C), 140.1 (d, *J* = 154 Hz, C), 134.1 (CH), 134.0 (CH), 133.9 (CH), 133.8 (CH), 133.0 (d, *J* = 1 Hz, C), 131.2 (C), 129.9 (CH), 129.5 (CH), 129.4 (CH), 129.3 (CH), 129.0 (C), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.9 (d, *J* = 15 Hz, C), 127.4 (d, *J* = 81 Hz, C), 126.3 (d, *J* = 84 Hz, C), 123.7 (CH), 122.5 (d, *J* = 8 Hz, C), 112.5 (CH), 58.7 (C), 51.7 (d, *J* = 4 Hz, CH_2), 47.8 (C), 42.9 (CH), 27.3 (CH_2), 24.6 (CH_2), 20.4 (CH_3), 20.2 (CH_3); ^{31}P-NMR (81 MHz, $CDCl_3$) δ 5.7. mass spectrum, *m/z* (relative intensity, %) 531 (M^+- $C_{32}H_{40}NO_6PS_2$, 1); FAB MS, *m/z* (relative intensity, %) 1161 (M^+, 31), 531 (68). See appendix C for expanded ^{13}C-NMR spectrum. Compound **15b** gave the following analytical data: mp 229 ºC (dec.); $[\alpha]_D^{21}$ +66.5º (c 1.55, $CHCl_3$); IR (KBr) 1743 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.93 (t, *J* = 9.6, 2H), 7.78 (t, *J* = 8.5, 4H), 7.70-7.29 (m, 7H), 7.11 (t, *J* = 8.0, 1H), 6.89-6.71 (m, 2H), 2.59-2.32 (m, 2H), 2.21 (dt, *J* = 16.0, 3.0, 1H), 1.93-1.60 (m, 4H), 1.49-1.08 (m, 2H), 0.71 (s, 3H), 0.45 (s, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 215.0 (C), 156.5 (d, *J* = 9 Hz, C), 140.0 (d, *J* = 151 Hz, C), 134.1 (CH), 134.0 (CH), 133.7 (CH), 133.6 (CH), 133.5 (CH), 132.9 (d, *J* = 1 Hz, CH), 131.4 (C), 130.5 (CH), 129.6

(CH), 129.3 (CH), 129.2 (CH), 128.9 (C), 128.3 (CH), 128.2 (CH), 127.8 (d, *J* = 15 Hz, C), 127.8 (CH), 127.2 (C), 126.5 (C), 125.7 (CH), 125.5 (C), 123.7 (CH), 122.2 (d, *J* = 8 Hz, C), 112.6 (CH), 58.3 (C), 51.7 (d, *J* = 3 Hz, CH_2), 47.6 (C), 42.6 (CH), 27.2 (CH_2), 24.8 (CH_2), 20.4 (CH_3), 20.2 (CH_3); ^{31}P-NMR (81 MHz, $CDCl_3$) δ 4.9. mass spectrum, *m/z* (relative intensity, %) 531 (M^+- $C_{32}H_{40}NO_6PS_2$, 1); FAB MS, *m/z* (relative intensity, %) 1161 (M^+, 38), 531 (72). Anal Calcd for $C_{68}H_{62}P_2S_2O_8N_2$ + $CHCl_3$: C, 64.61; H, 5.11: N, 2.18. Found: C, 64.75; H, 4.98; N, 2.37. See appendix D for expanded ^{13}C-NMR spectrum.

Hydrolysis of Diastereomerically Pure Phosphinimines 15a and 15b.

Phosphinimine **15a** (1.44 g, 1.24 mmol) in dioxane (50 mL) was treated with 3 M aqueous H_2SO_4 (35 mL) and the resulting mixture was heated to reflux for 12 h. The cooled mixture was then quenched with 10% NaOH and extracted with $CHCl_3$ (3 x 100 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo to afford the crude phosphine oxide. The product was purified by flash chromatography on basic alumina (1:1 hexanes/ethyl acetate $\rightarrow$ 9:1 $CHCl_3$/MeOH) to afford the desired phosphine oxide **12** in quantitative yield. $[\alpha]_D^{19}$ -166.6^o (c 1.01, $CHCl_3$).

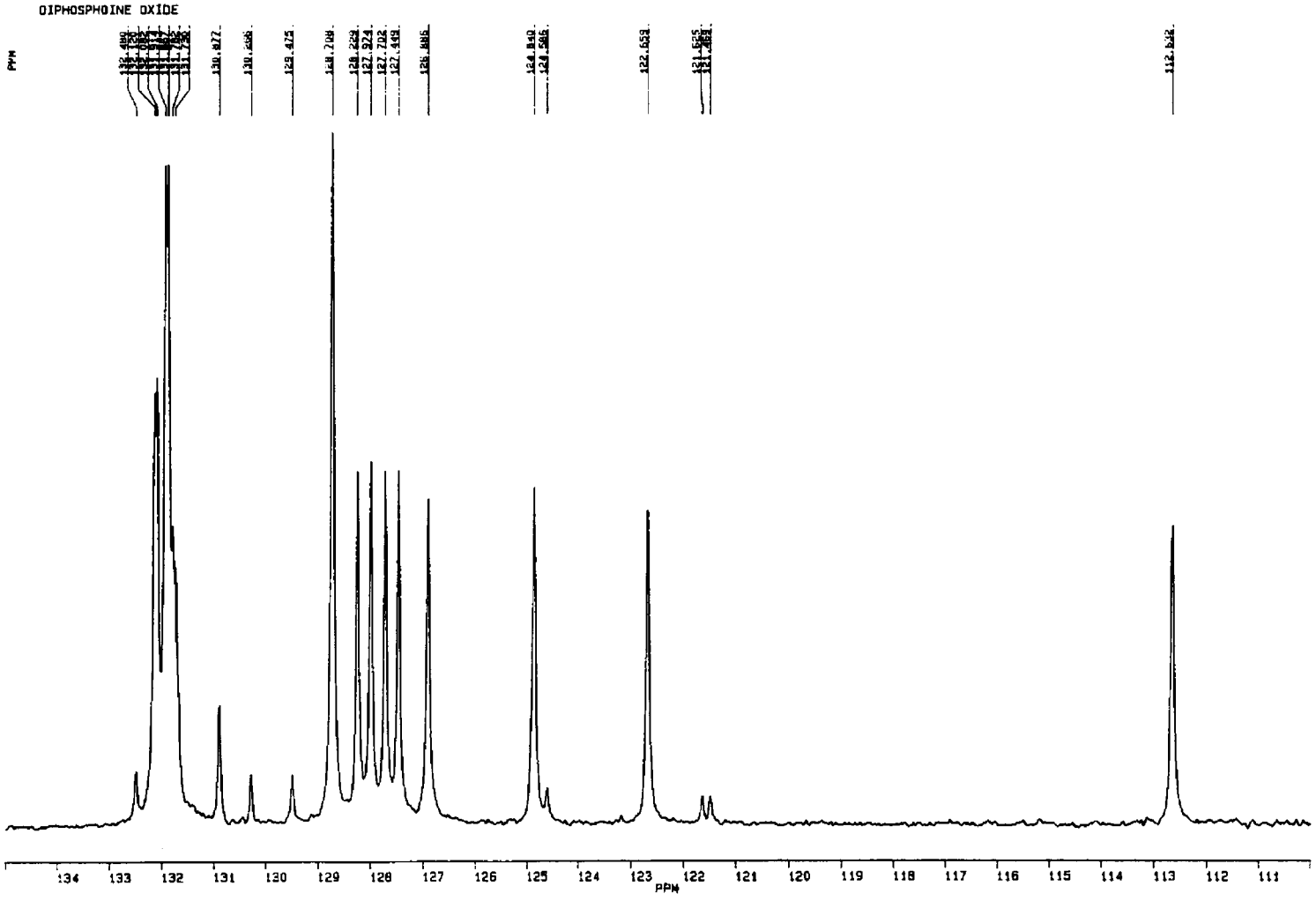
Trichlorosilane Reduction of Phosphine Oxide 12.

Phosphine oxide **12** (821 mg, 1.12 mmol) was dissolved in a mixture of xylenes (25 mL) and Et_3N (3.75 mL, 26.8 mmol). To the solution was added $SiCl_3H$ (2.26 mL, 22.4 mmol) and the resulting mixture was heated to 100 ^{o}C under argon for 1 hr. The mixture was then heated to 150 ^{o}C for 3h and subsequently cooled to 65 ^{o}C. To the vessel was then added dropwise 30% NaOH (60 mL). The resulting mixture was vigorously stirred for 1 h at 65 ^{o}C. The cooled reaction mixture was extracted with $CHCl_3$ (3 x 100 mL) and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The product was purified by flash chromatography (20:1 hexanes/ethyl acetate) to afford the optically pure (*S*)-BINAPFu (785 mg, 100%). $[\alpha]_D^{19}$ -203.0^o (c 1.09, $CHCl_3$). Heating the enantiopure ligand in *p*-xylenes at 150 ^{o}C for 7d did not result in any racemization of the chiral axis as evidenced by optical rotation and HPLC analysis (Chiralcel® OJ, 95/5 MeOH/EtOH, 0.5 mL/min, 270 nm detection).

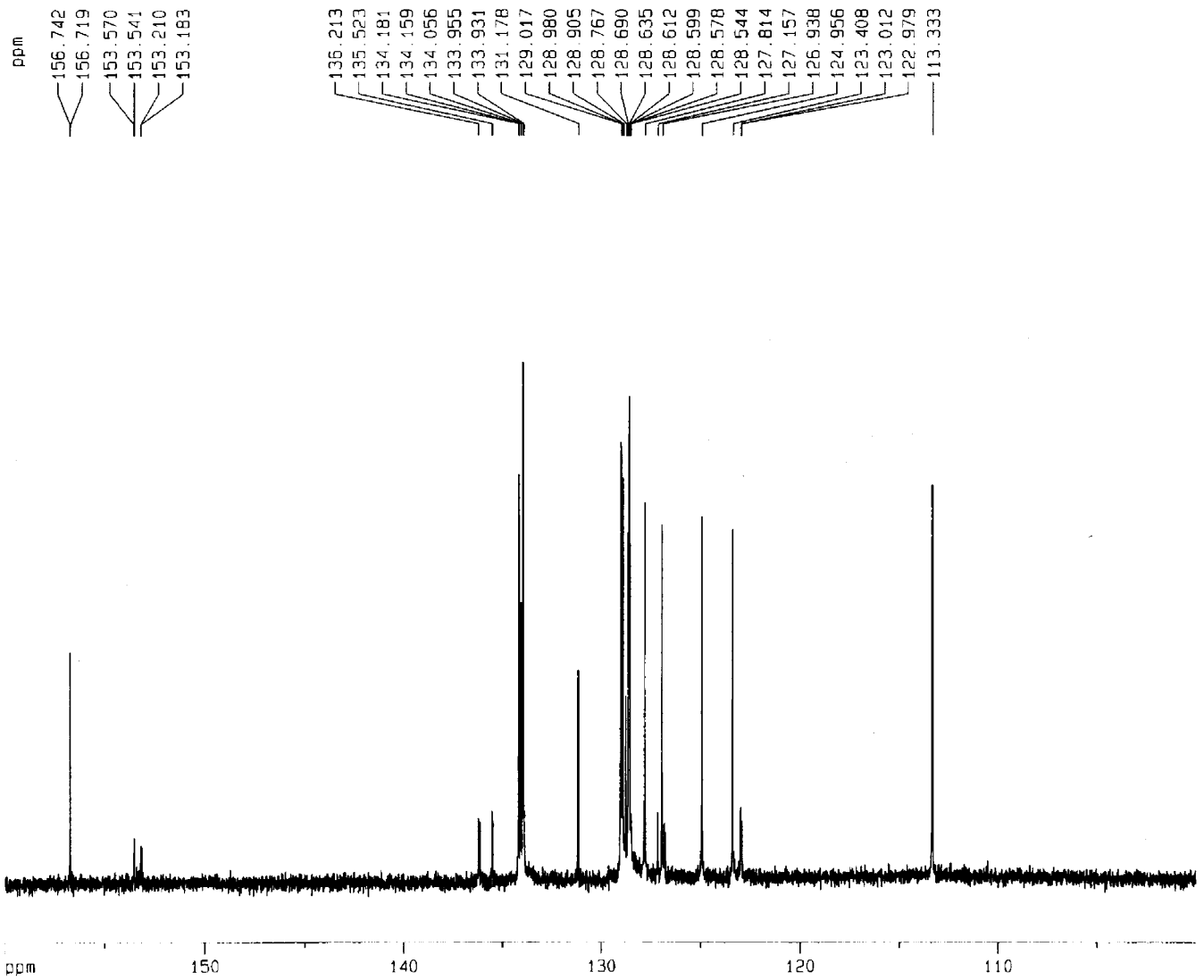
General Procedure for the Heck Arylation of 2,3-Dihydrofuran.

In a 2 dram screw cap vial was measured out $Pd(OAc)_2$ (2.2 mg, 9.97 μmol), (*S*)-BINAPFu (21.0 mg, 29.9 μmol), Hunig's base (255 μL, 1.46 mmol), and 1,4-dioxane (2.5 mL). The resulting mixture was heated to 60 ^{o}C under an argon atmosphere for 30 min. To the vessel was then added 2,3-dihydrofuran (189 μL, 2.50 mmol), and phenyl triflate (79 μL, 0.488 mmol). The mixture was thermostatically heated to 100 ^{o}C for a 7 d period. The crude mixture was filtered through a pad of celite and analyzed by chiral GC (Cyclodex B column, 80 ^{o}C start temperature, 2 min initial hold time, 1 ^{o}C/min ramp rate, 220 ^{o}C final temperature). The reaction products eluted in the following order: (*S*)-2-phenyl-2,3-dihydrofuran T_r=26.1 min; (*R*)-5-phenyl-2,3-dihydrofuran T_r=26.7 min; 2-phenyl-4,5-dihydrofuran T_r=28.9 min; (*R*)-2-phenyl-2,5-dihydrofuran T_r=31.2 min; (*S*)-2-phenyl-2,5-dihydrofuran T_r=31.6 min.

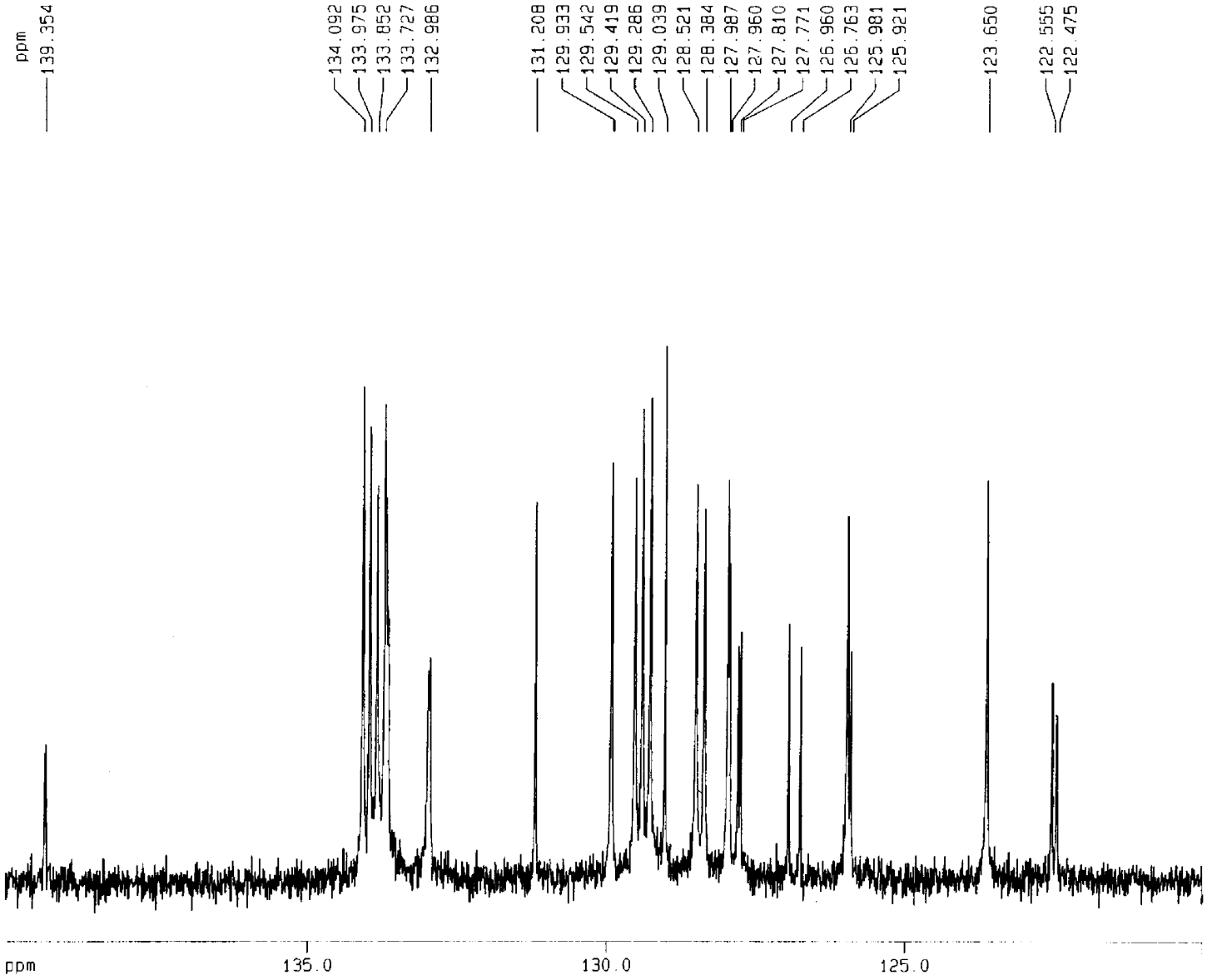
Appendix A: Expanded ^{13}C-NMR spectrum of 2,2'-Bis(diphenylphosphonyl)-3,3'-binaphtho[2,1-*b*]furan (**12**).



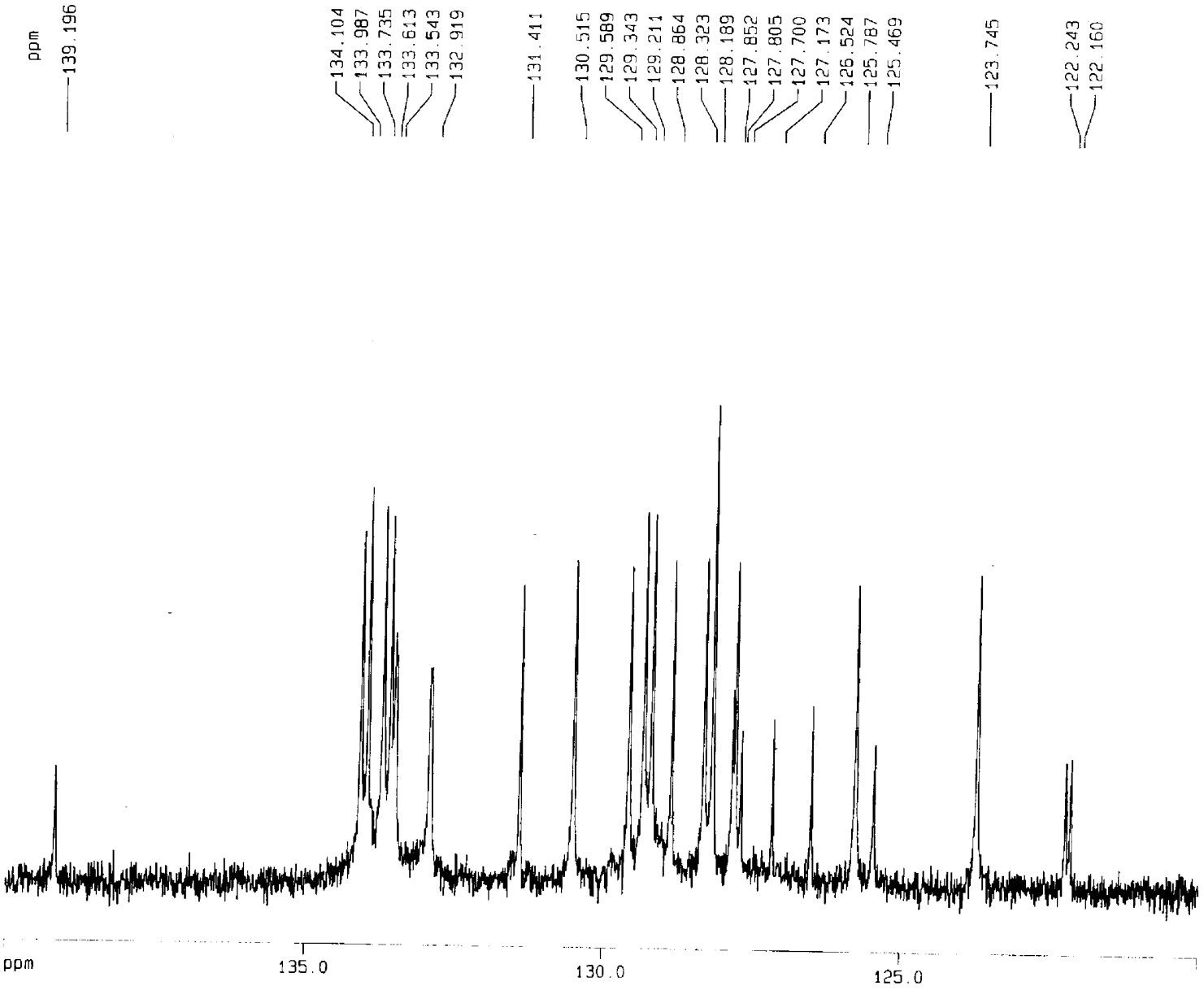
Appendix B: Expanded ^{13}C-NMR spectrum of 2,2'-Bis(diphenylphosphino)-3,3'-binaphtho[2,1-*b*]furan (**1**).



Appendix C: Expanded ^{13}C-NMR spectrum of Phosphinimine **15a**.



Appendix D: Expanded ^{13}C-NMR spectrum of Phosphinimine **15b**.



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