# Organometallic Complexes for Nonlinear Optics. 43. Quadratic optical nonlinearities of dipolar alkynylruthenium complexes with phenyleneethynylene/phenylenevinylene bridges

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**Supporting Information**

**Complete reference 43:**

Baerends, E. J.; Autsbach, J.; Bérces, A.; Bickelhaupt, F. M.; Bo, C.; Boerrigter, P. M.; Cavallo, L.; Chong, D. P.; Deng, L.; Dickson, R. M.; Ellis, D. E.; Faassen, M. v.; Fan, L.; Fischer, T. H.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Groeneveld, J. A.; Gritsenko, O. V.; Gruning, M.; Harris, F. E.; van den Hoek, P.; Jacob, C. R.; Jacobsen, H.; Jensen, L.; van Kessel, G.; Kootstra, F.; van Lenthe, E.; McCormack, D. A.; Michalak, A.; Neugebauer, J.; Osinga, V. P.; Patchkovskii, S.; Philipsen, P. H. T.; Post, D.; Pye, C.; Ravenek, W.; Ros, P.; Schipper, P. R. T.; Schreckenbach, G.; Snijders, J. G.; Sola, M.; Swart, M.; Swerhone, D.; te Velde, G.; Vernooijs, P.; Versluis, L.; Visser, O.; Wang, F.; Wesolowski, T. A.; van Wezenbeek, E.; Wiesenekker, G.; Wolff, S. K.; Woo, T. K.; Yakovlev, A. L.; Ziegler, T.; S.C.M., Theoretical Chemistry, Vrije Universiteit: Amsterdam, the Netherlands, http://www.scm.com, 2006.

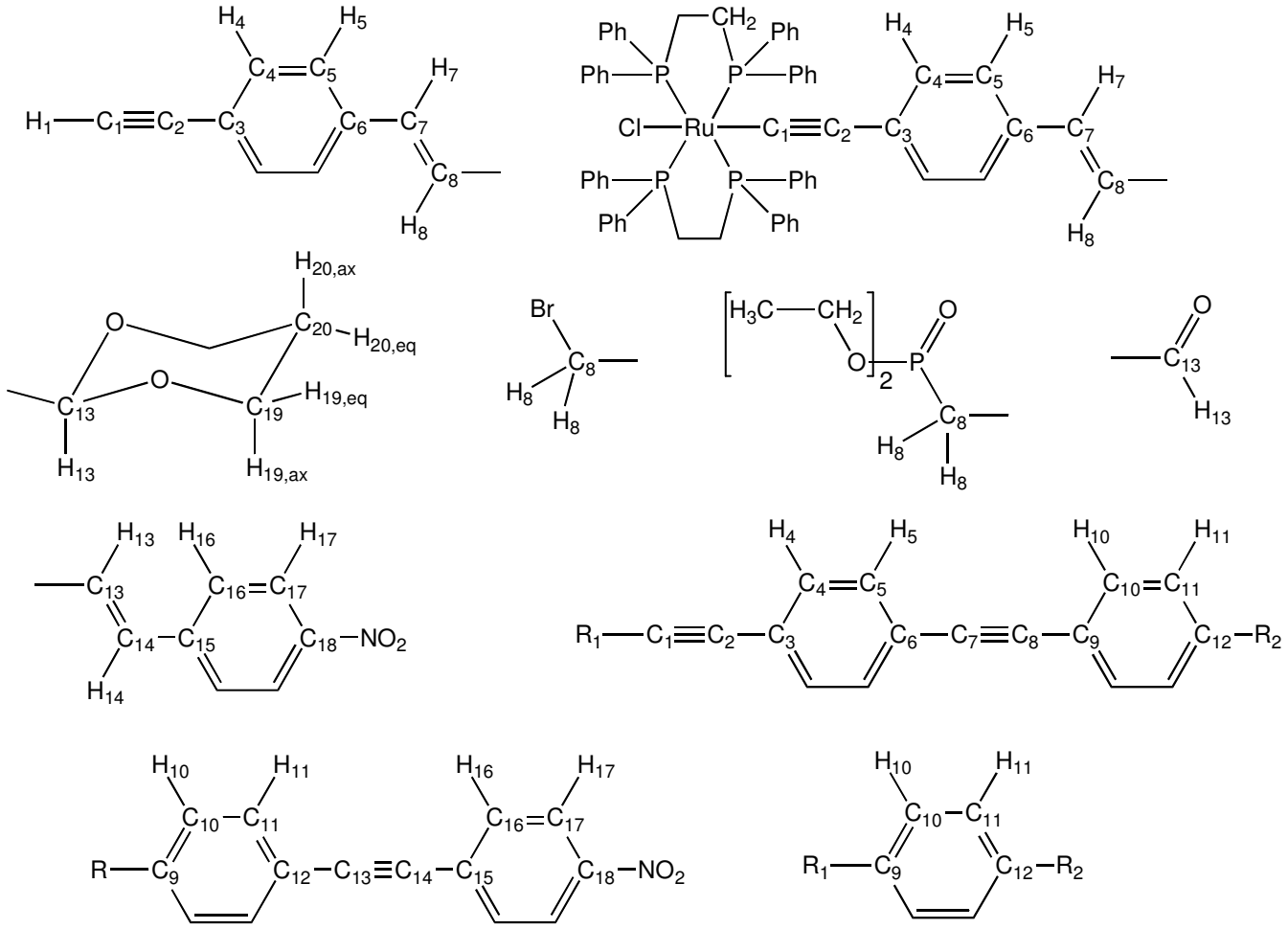

**Chart S1.** Atom labeling for NMR assignments.

**Synthesis of 4,4'-$Me_3SiC\alpha CC_6H_4C\alpha CC_6H_4CHO(CH_2)_3O$** (**1**). $PdCl_2(PPh_3)_2$ (155 mg, 0.22 mmol), CuI (41 mg, 0.22 mmol) and 4-$HC\alpha CC_6H_4CHO(CH_2)_3O$ (820 mg, 4.33 mmol) were added to a solution of 4-$Me_3SiC\alpha CC_6H_4Br$ (1.10 g, 4.33 mmol) in $NEt_3$ (70 mL). The mixture was stirred under reflux for 3 h and at room temperature overnight. The mixture was filtered, the solvent removed from the filtrate, and the resulting orange residue was purified by column chromatography on silica, eluting with $CH_2Cl_2$/petrol (2:1). Reduction in volume of the solvent on a rotary evaporator afforded **1** as a white powder (270 mg, 33%). EI MS: 360 ($[M]^+$, 100). Anal. Calcd for $C_{23}H_{24}O_2Si$: C, 76.62; H, 6.71. Found: C, 76.40; H, 6.61. UV-vis ($CH_2Cl_2$): 30700 [5.4], 31800 sh [4.4], 32700 [5.4], 33700 sh [4.1], 34600 sh [3.8]. IR ($CH_2Cl_2$): 2156 $\nu$(C$\alpha$C). $^1$H NMR: $\delta$ 0.26 (s, 9H, Me), 1.46 (m, 1H, $H_{20,eq}$), 2.23 (m, 1H,

$H_{20,ax}$), 3.99 (m, 2H, $H_{19,ax}$), 4.28 (m, 2H, $H_{19,eq}$), 5.51 (s, 1H, $H_{13}$), 7.44 (s, 4H, $H_4$ and $H_5$), 7.50 (AA'BB', 4H, $H_{10}$ and $H_{11}$). $^{13}$C NMR: $\delta$ 25.8 ($C_{20}$), 67.5 ($C_{19}$), 89.3 ($C_1$), 91.2 ($C_2$), 96.3 ($C_7$), 101.1 ($C_{13}$), 104.7 ($C_8$), 122.9 ($C_3$), 123.2 ($C_6$), 123.4 ($C_9$), 126.1 ($C_{11}$), 131.4, 131.6, 131.9 ($C_4$, $C_5$, $C_{10}$), 138.9 ($C_{12}$).

**Synthesis of 4,4'-$Me_3SiC\alpha CC_6H_4C\alpha CC_6H_4CHO$** (**2**) *Method A.* $PdCl_2(PPh_3)_2$ (60 mg, 0.09 mmol), CuI (14 mg, 0.08 mmol) and 4-$HC\alpha CC_6H_4CHO$ (252 mg, 1.93 mmol) were added to a solution of 4-$Me_3SiC\alpha CC_6H_4I$ (577 mg, 1.92 mmol) in $NEt_3$ (60 mL). The mixture was stirred under reflux overnight. The solvent was removed from the mixture and the resulting residue was extracted with $Et_2O$ (2 × 40 mL), yielding a yellow-orange organic phase that was adsorbed on alumina and purified by column chromatography on alumina, eluting with $CH_2Cl_2$/petrol (1:1). Reduction in volume of the solvent on a rotary evaporator afforded **2** as a white powder (52 mg, 10%).

*Method B.* HCl 9% w/w (1 mL) was added to a solution of **1** (201 mg, 0.56 mmol) in acetone (20 mL). The mixture was stirred under reflux for 1 h. The reaction mixture was treated with distilled water (30 mL) and extracted with $Et_2O$ (2 × 30 mL). The organic phase was washed with aqueous $NaHCO_3$, $H_2O$ and dried with $MgSO_4$. Reduction in volume of the solvent on a rotary evaporator afforded **2** as a white powder (141 mg, 82%). EI MS: 302 ($[M]^+$, 80), 287 ($[M - Me]^+$, 100). HR EI MS $[C_{20}H_{18}SiO]^+$: calcd 302.1127, found 302.1127. Anal. Calcd for $C_{20}H_{18}OSi.0.25CH_2Cl_2$: C, 75.14; H, 5.76. Found: C, 74.95; H, 6.11. UV-vis ($CH_2Cl_2$): 29100 [2.5], 30600 [2.7], 33700 sh [1.0], 34200 sh [1.5]. IR ($CH_2Cl_2$): 2215, 2156 $\nu$(C$\alpha$C); 1702 $\nu$(C=O). $^1$H NMR: $\delta$ 0.26 (s, 9H, Me), 5.28 (s, 0.5H, $CH_2Cl_2$), 7.47 (s, 4H, $H_4$ and $H_5$), 7.66 (d, $J_{HH}$ = 8 Hz, 2H, $H_{10}$), 7.87 (d, $J_{HH}$ = 8 Hz, 2H, $H_{11}$), 10.02 (s, 1H, $H_{13}$). $^{13}$C NMR: $\delta$ -0.1 ($SiMe_3$), 90.3, 93.0, 96.9 ($C_1$, $C_7$, $C_8$), 103.3 ($C_2$), 122.5, 123.7 ($C_3$, $C_6$), 129.3 ($C_9$), 129.6 ($C_{11}$), 131.6, 131.8, 132.1 ($C_4$, $C_5$, $C_{10}$), 135.6 ($C_{12}$), 191.4 ($C_{13}$).

**Synthesis of (*E*)-4,4',4''-$Me_3SiC\alpha CC_6H_4C\alpha CC_6H_4CH{=}CHC_6H_4NO_2$** (**3**). $PdCl_2(PPh_3)_2$ (122 mg, 0.17 mmol), CuI (36 mg, 0.19 mmol) and (*E*)-4,4'-$HC\alpha CC_6H_4CH{=}CHC_6H_4NO_2$ (750 mg, 3.01 mmol) were added to a solution of 4-$Me_3SiC\alpha CC_6H_4I$ (970 mg, 3.24 mmol) in $NEt_3$ (100 mL). The mixture

was stirred at 35-40°C overnight. The mixture was filtered and washed with $NEt_3$, and the resultant solid residue was extracted with $CH_2Cl_2$ (200 mL) and the solvent removed from the extract on a rotary evaporator. The resulting yellow-brown residue was purified by passing through a small pad of alumina, eluting with $CH_2Cl_2$. Reduction in volume of the solvent on a rotary evaporator afforded **3** as a pale yellow powder (320 mg, 25%). EI MS: 421 ($[M]^+$, 100), 406 ($[M - Me]^+$, 50). HR EI MS $[C_{27}H_{23}NSiO_2]^+$: calcd 421.1498, found 421.1488. Anal. Calcd for $C_{27}H_{23}NO_2Si.0.125CH_2Cl_2$: C, 75.38; H, 5.56; N, 3.24. Found: C, 75.84; H, 5.73; N, 3.15. UV-vis ($CH_2Cl_2$): 26600 [9.2], 30800 sh [5.3]. IR ($CH_2Cl_2$): 2154 $\nu$(CαC); 1592 $\nu$(C=C); 1517, 1343 $\nu(NO_2)$. $^1$H NMR: $\delta$ 0.26 (s, 9H, Me), 5.28 (s, 0.25H, $CH_2Cl_2$), 7.17 (d, $J_{HH}$ = 16 Hz, 1H, $H_{13}$), 7.25 (d, $J_{HH}$ = 16 Hz, 1H, $H_{14}$), 7.46 (s, 4H, $H_4$ and $H_5$), 7.54 (s, 4H, $H_{10}$ and $H_{11}$), 7.65 (d, $J_{HH}$ = 9 Hz, 2H, $H_{16}$), 8.24 (d, $J_{HH}$ = 9 Hz, 2H, $H_{17}$). $^{13}$C NMR: $\delta$ 0.03 ($SiMe_3$), 90.8, 91.2 ($C_7$, $C_8$), 96.5, 104.6 ($C_1$, $C_2$), 123.1, 123.3 ($C_3$, $C_6$), 124.2, 127.0, 127.2 (2C), 131.4, 132.0, 132.1, 132.5 ($C_4$, $C_5$, $C_{10}$, $C_{11}$, $C_{13}$, $C_{14}$, $C_{16}$, $C_{17}$), 136.2 ($C_{12}$), 143.5 ($C_{15}$), 146.9 ($C_{18}$), $C_9$ not observed.

**Synthesis of (*E*)-4,4',4''-HCαCC$_6$H$_4$CαCC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$ (4).** *Method A.* $NBu^n_4F$ (2.5 mL, 1 M solution in THF) was added to a solution of **3** (214 mg, 0.51 mmol) in $CH_2Cl_2$ (20 mL) yielding a suspension. This was stirred at room temperature for 2 h. The mixture was passed through a small pad of alumina, eluting with $CH_2Cl_2$, and the solvent reduced in volume, affording **4** as a yellow powder (143 mg, 80%).

*Method B.* Solid NaOMe (excess) was added to a solution of 4-$(EtO)_2(O)PCH_2C_6H_4NO_2$ (164 mg, 0.60 mmol) in THF (20 mL) and the purple solution was stirred at 0°C for 15 min. **2** (171 mg, 0.57 mmol) was added and the resultant mixture stirred at 0°C for 20 min and then at room temperature for another 20 min. $H_2O$ (30 mL) and MeOH (12 mL) were added to the mixture to afford a yellow precipitate, which was collected, washed ($H_2O$/MeOH mixture), and dried in vacuo to afford **4** as a yellow powder (120 mg, 60%). EI MS: 349 ($[M]^+$, 10), 319 ($[M - NO]^+$, 5). HR EI MS $[C_{24}H_{15}NO_2]^+$: calcd 349.1103, found 349.1103. UV-vis ($CH_2Cl_2$): 26700 [6.0], 31100 sh [3.1]. IR ($CH_2Cl_2$): 2103

$\nu$(CαC); 1512, 1345 $\nu$($NO_2$). $^1$H NMR: $\delta$ 3.19 (s, 1H, $H_1$), 7.17 (d, $J_{HH}$ = 16 Hz, 1H, $H_{13}$), 7.25 (d, $J_{HH}$ = 16 Hz, 1H, $H_{14}$), 7.49 (s, 4H, $H_4$ and $H_5$), 7.55 (s, 4H, $H_{10}$ and $H_{11}$), 7.65 (d, $J_{HH}$ = 9 Hz, 2H, $H_{16}$), 8.24 (d, $J_{HH}$ = 9 Hz, 2H, $H_{17}$).

**Synthesis of 4,4'-$(EtO)_2(O)PCH_2C_6H_4C\alpha CC_6H_4NO_2$** (**5**). $Pd(PPh_3)_4$ (93 mg, 0.08 mmol) and 4-$HC\alpha CC_6H_4NO_2$ (375 mg, 2.55 mmol) were added to a solution of 4-$(EtO)_2(O)PCH_2C_6H_4I$ (900 mg, 2.54 mmol) in $NEt_3$ (30 mL). The orange mixture was stirred under reflux overnight. The dark mixture was filtered, the filtrate taken to dryness and purified by column chromatography on alumina, eluting with a gradient polarity eluent (acetone/petrol 1:3, EtOAc/petrol 1:1, EtOAc). Removal of the solvent on a rotary evaporator afforded **5** as a pale yellow oil (560 mg, 59%). EI MS: 373 ($[M]^+$, 100), 236 ([M – $P(O)(OEt)_2]^+$. HR EI MS $[C_{19}H_{20}NO_5P]^+$: calcd 373.1079, found 373.1081. UV-vis ($CH_2Cl_2$): 29500 [2.0]. IR ($CH_2Cl_2$): 2217 $\nu$(CαC); 1520, 1346 $\nu$($NO_2$)**.** $^1$H NMR: $\delta$ 1.25 (t, $J_{HH}$ = 7 Hz, 6H, $CH_3$), 3.17 (d, $J_{PH}$ = 22 Hz, 2H, $H_8$), 4.04 (q, $J_{HH}$ = 7 Hz, 4H, $CH_2$), 7.32 (dd, $J_{HH}$ = 8 Hz, $J_{PH}$ = 2 Hz, 2H, $H_{10}$), 7.50 (d, $J_{HH}$ = 8 Hz, 2H, $H_{11}$), 7.65 (d, $J_{HH}$ = 9 Hz, 2H, $H_{16}$), 8.21 (d, $J_{HH}$ = 9 Hz, 2H, $H_{17}$). $^{13}$C NMR: $\delta$ 16.4 (d, $J_{CP}$ = 23 Hz, $CH_3$), 34.0 (d, $J_{CP}$ = 548 Hz, $C_8$), 62.3 (d, $J_{CP}$ = 27 Hz, $CH_2$), 87.8 ($C_{14}$), 94.5 ($C_{13}$), 120.7 ($C_{12}$), 123.7 ($C_{17}$), 130.0, 130.3 ($C_{15}$, $C_{10}$), 132.0, 132.3 ($C_{11}$, $C_{16}$), 133.3 ($C_9$), 147.0 ($C_{18}$). $^{31}$P NMR: $\delta$ 26.1.

**Synthesis of (*E*)-4,4',4''-$HC\alpha CC_6H_4CH{=}CHC_6H_4C\alpha CC_6H_4NO_2$** (**6**). Solid NaOMe (excess) was added to a solution of **5** (535 mg, 1.43 mmol) in THF (20 mL) and the dark green solution was stirred at 0°C for 15 min. 4-$Me_3SiC\alpha CC_6H_4CHO$ (287 mg, 1.42 mmol) was added and the mixture stirred at 0°C for 10 min and then at room temperature for a further 15 min. $H_2O$ (30 mL) and MeOH (12 mL) were added to the mixture to afford a yellow precipitate, which was collected, washed ($H_2O$/MeOH mixture) and dried in vacuo to afford **6** as a yellow powder (454 mg, 92%). EI MS: 349 ($[M]^+$, 25), 319 ([M – $NO]^+$. HR EI MS $[C_{24}H_{15}NO_2]^+$: calcd 349.1103, found 349.1103. UV-vis: 27000 [5.4]. IR (KBr): 2212 $\nu$(CαC); 1513, 1345 $\nu$($NO_2$). $^1$H NMR: $\delta$ 3.15 (s, 1H, $H_1$), 7.13 (s, 2H, $H_7$ and $H_8$), 7.49 (s, 4H, $H_4$ and $H_5$), 7.54 (s, 4H, $H_{10}$ and $H_{11}$), 7.66 (d, $J_{HH}$ = 7 Hz, 2H, $H_{16}$), 8.23 (d, $J_{HH}$ = 7 Hz, 2H, $H_{17}$).

**Synthesis of 4-BrCH$_2$C$_6$H$_4$CHO(CH$_2$)$_3$O** (**7**). 1,3-Propandiol (0.5 mL, 6.96 mmol) and 4-MeC$_6$H$_4$SO$_3$H (60 mg, 0.32 mmol) were added to a solution of 4-BrCH$_2$C$_6$H$_4$CHO (473 mg, 2.37 mmol) in toluene (40 mL). The mixture was stirred under reflux for 4 h with the use of a Dean-Stark apparatus, then cooled and washed once with aqueous NaOH, twice with water, and then dried with MgSO$_4$. The organic phase was taken to dryness to afford a yellowish crude product, which was purified by column chromatography on silica, eluting with a gradient polarity eluent (petrol/CH$_2$Cl$_2$ 2:1, petrol/CH$_2$Cl$_2$ 1:1). Reduction in volume of the solvent on a rotary evaporator afforded **7** as a white solid (450 mg, 74%). EI MS: 255 ([M – H]$^+$, 20), 197 ([M – O(CH$_2$)$_3$ – H]$^+$, 15), 177 ([M – Br]$^+$, 100). Anal. Calcd for C$_{11}$H$_{13}$BrO$_2$: C, 51.38; H, 5.10. Found: C, 51.38; H, 5.38. UV-vis (CH$_2$Cl$_2$): 36400 [0.06]. IR (CH$_2$Cl$_2$): 1684 $\nu$(O-C-O); 1607 $\nu$(C=C). $^1$H NMR: $\delta$ 1.45 (m, 1H, H$_{20,eq}$), 2.22 (m, 1H, H$_{20,ax}$), 3.99 (m, 2H, H$_{19,ax}$), 4.27 (m, 2H, H$_{19,eq}$), 4.48 (s, 2H, H$_8$), 5.49 (s, 1H, H$_{13}$), 7.42 (AA'BB', 4H, H$_{10}$ and H$_{11}$). $^{13}$C NMR: $\delta$25.8 (C$_{20}$), 33.2 (C$_8$), 67.4 (C$_{19}$), 101.1 (C$_{13}$), 126.5 (C$_{11}$), 129.0 (C$_{10}$), 138.3 (C$_9$), 138.9 (C$_{12}$).

**Synthesis of 4-(EtO)$_2$(O)PCH$_2$C$_6$H$_4$CHO(CH$_2$)$_3$O** (**8**). P(OEt)$_3$ (1.5 mL, 8.75 mmol) was added to **9** (400 mg, 1.56 mmol) in a Schlenk tube and the mixture was stirred under reflux overnight. The excess of P(OEt)$_3$ was removed affording **8** as a colorless oil (488 mg, 100%). EI MS: 313 ([M]$^+$, 80), 197 ([M – 2Et]$^+$, 60). HR EI MS [C$_{15}$H$_{22}$O$_5$P] ([M – H]$^+$): calcd 313.1205, found 313.1202. UV-vis (CH$_2$Cl$_2$): 35500 [0.9]. IR (CH$_2$Cl$_2$): 1714 $\nu$(O-C-O); 1609 $\nu$(C=C). $^1$H NMR: $\delta$ 1.22 (t, $J_{HH}$ = 7 Hz, 6H, CH$_3$), 1.45 (m, 1H, H$_{20,eq}$), 2.21 (m, 1H, H$_{20,ax}$), 3.14 (d, $J_{PH}$ = 22 Hz, 2H, H$_8$), 3.90-4.10 (m, 6H, CH$_2$ and H$_{19,ax}$), 4.26 (m, 2H, H$_{19,eq}$), 5.48 (s, 1H, H$_{13}$), 7.28 (dd, $J_{HH}$ = 8 Hz, $J_{PH}$ = 2 Hz, 2H, H$_{10}$), 7.41 (d, $J_{HH}$ = 8 Hz, 2H, H$_{11}$). $^{13}$C NMR: $\delta$16.4 (d, $J_{CP}$ = 23 Hz, CH$_3$), 25.8 (C$_{20}$), 33.6 (d, $J_{CP}$ = 548 Hz, C$_8$), 62.1 (d, $J_{CP}$ = 25 Hz, CH$_2$), 67.4 (C$_{19}$), 101.4 (C$_{13}$), 126.2 (d, $J_{CP}$ = 13 Hz, C$_{11}$), 129.7 (d, $J_{CP}$ = 25 Hz, C$_{10}$), 132.3 (d, $J_{CP}$ = 35 Hz, C$_9$), 137.4 (C$_{12}$). $^{31}$P NMR: $\delta$26.7.

**Synthesis of (*E*)-4,4'-HC$\alpha$CC$_6$H$_4$CH=CHC$_6$H$_4$CHO(CH$_2$)$_3$O** (**9**). Solid NaOMe (excess) was added to a solution of **8** (301 mg, 0.96 mmol) in THF (20 mL) and the mixture was stirred at 0°C for 30 min. 4-Me$_3$SiC$\alpha$CC$_6$H$_4$CHO (195 mg, 0.96 mmol) was added and the mixture was stirred at 0°C for 30 min

and at room temperature for a further 30 min. $H_2O$ (30 mL) and MeOH (12 mL) were added to the mixture to afford a yellow precipitate, which was collected, washed ($H_2O$/MeOH mixture) and dried in vacuo to afford **9** as a pale yellow powder (150 mg, 54%). EI MS: 290 ($[M]^+$, 100), 232 ($[M - O(CH_2)_3]^+$, 75). HR EI MS $C_{20}H_{18}O_2$ ($[M]^+$): calcd 290.1307, found 290.1307. Anal. Calcd for $C_{20}H_{18}O_2.0.2CH_2Cl_2$: C, 78.82; H, 6.48. Found: C, 78.75; H, 6.35. UV-vis (thf): 29200 sh [2.8], 30600 [4.3], 32000 sh [3.7], 34800 sh [2.0]. IR ($CH_2Cl_2$): 2106 $\nu$(CαC); 1602 $\nu$(C=C). $^1$H NMR: $\delta$ 1.45 (m, 1H, $H_{20,eq}$), 2.24 (m, 1H, $H_{20,ax}$), 3.13 (s, 1H, $H_1$), 4.00 (m, 2H, $H_{19,ax}$), 4.28 (m, 2H, $H_{19,eq}$), 5.28 (s, 0.4H, $CH_2Cl_2$), 5.51 (s, 1H, $H_{13}$), 7.07 (d, $J_{HH}$ = 16 Hz, 1H, $H_8$), 7.13 (d, $J_{HH}$ = 16 Hz, 1H, $H_7$), 7.47 (s, 4H, $H_4$ and $H_5$), 7.49 (AA'BB', 4H, $H_{10}$ and $H_{11}$). $^{13}$C NMR: $\delta$ 25.8 ($C_{20}$), 67.5 ($C_{19}$), 78.0 ($C_2$), 83.8 ($C_1$), 101.4 ($C_{13}$), 121.1 ($C_3$), 126.4, 126.5, 126.6 ($C_5$, $C_{10}$, $C_{11}$), 128.1, 129.6 ($C_7$, $C_8$), 132.5 ($C_4$), 137.5, 137.8, 138.4 ($C_6$, $C_9$, $C_{12}$).

**Synthesis of (*E*)-4,4'-HCαCC$_6$H$_4$CH=CHC$_6$H$_4$CHO** (**10**). HCl (9% w/w) (1 mL) was added to a solution of **9** (130 mg, 0.45 mmol) in acetone (20 mL). The mixture was stirred at room temperature for 24 h. The reaction mixture was treated with distilled water (30 mL) and extracted with $Et_2O$ (2 × 30 mL). The organic phase was washed with aqueous $NaHCO_3$, $H_2O$ and dried with $MgSO_4$. Reduction in volume of the solvent on a rotary evaporator afforded **10** as a yellow solid (101 mg, 94%). EI MS: 232 ($[M]^+$, 100), 202 ($[M - CH_2O]^+$, 70). HR EI MS $C_{17}H_{12}O$ ($[M]^+$): calcd 232.0888, found 232.0892. UV-vis ($CH_2Cl_2$): 30600 [1.4]. IR ($CH_2Cl_2$): 2106 $\nu$(CαC); 1698 $\nu$(C=O); 1599 $\nu$(C=C). $^1$H NMR: $\delta$ 3.16 (s, 1H, $H_1$), 7.20 (AB, 2H, $H_7$ and $H_8$), 7.51 (s, 4H, $H_4$ and $H_5$), 7.66 (d, $J_{HH}$ = 8 Hz, 2H, $H_{10}$), 7.88 (d, $J_{HH}$ = 8 Hz, 2H, $H_{11}$). $^{13}$C NMR: $\delta$ 78.5 ($C_1$), 83.5 ($C_2$), 122.0 ($C_3$), 126.8, 127.1 ($C_5$, $C_{10}$), 128.5, 131.3 ($C_7$, $C_8$), 130.3 ($C_{11}$), 132.6 ($C_4$), 135.6 ($C_6$), 137.0 ($C_{12}$), 143.0 ($C_9$), 191.6 ($C_{13}$).

**Synthesis of (*E,E*)-4,4',4''-HCαCC$_6$H$_4$CH=CHC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$** (**11**). Solid NaOMe (excess) was added to a solution of 4-$(EtO)_2(O)PCH_2C_6H_4NO_2$ (110 mg, 0.40 mmol) in THF (30 mL) and the purple solution was stirred at 0°C for 15 min. **10** (95 mg, 0.40 mmol) was added and the mixture stirred at 0°C for 20 min and then at room temperature for a further 20 min. $H_2O$ (30 mL) and MeOH

(12 mL) were added to the mixture to afford a yellow precipitate. This was collected, washed ($H_2O$/MeOH mixture) and dried in vacuo to afford **11** as a yellow solid, which was recrystallized from $CH_2Cl_2$/MeOH mixtures (115 mg, 83%). EI MS: 351 ($[M]^+$, 20). HR EI MS $[C_{24}H_{17}NO_2]^+$ ($[M]^+$): calcd 351.1259, found 351.1255. Anal. Calcd for $C_{24}H_{17}NO_2.0.33CH_2Cl_2$: C, 76.97; H, 4.69; N, 3.69. Found: C, 76.62; H, 4.81; N, 3.50. UV-vis ($CH_2Cl_2$): 25600 [3.9]. IR ($CH_2Cl_2$): 2106 $\nu$(CαC); 1604, 1592 $\nu$(C=C); 1519, 1344 $\nu(NO_2)$. $^1$H NMR: $\delta$ 3.15 (s, 1H, $H_1$), 5.28 (s, 0.67H, $CH_2Cl_2$), 7.13 (s, 2H, $H_7$ and $H_8$), 7.20 (AB, 2H, $H_{13}$ and $H_{14}$), 7.49 (s, 4H, $H_4$ and $H_5$), 7.55 (s, 4H, $H_{10}$ and $H_{11}$), 7.65 (d, $J_{HH}$ = 9 Hz, 2H, $H_{16}$), 8.23 (d, $J_{HH}$ = 9 Hz, 2H, $H_{17}$).

**Synthesis of *trans*-[Ru{(*E*)-4,4',4''-CαCC$_6$H$_4$CαCC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$}Cl(dppm)$_2$]** (**13**). *cis*-$[RuCl_2(dppm)_2]$ (162 mg, 0.17 mmol) and $NaPF_6$ (29 mg, 0.17 mmol) were added to a suspension of **4** (60 mg, 0.27 mmol) in $CH_2Cl_2$ (35 mL). The orange mixture was stirred at room temperature overnight. $NEt_3$ (1 mL) was added and the red mixture stirred at room temperature for 24 h. The reaction mixture was purified by passing through a short pad of alumina, eluting with $CH_2Cl_2$/petrol/$NEt_3$ (10:10:1). Reduction in volume of the solvent on a rotary evaporator afforded **13** as a purple powder (95 mg, 44%). ESI MS: 1255 ($[M + H]^+$, 60), 1219 ($[M - Cl]^+$, 100), 905 ($[RuCl(dppm)_2]^+$, 50)$^+$. Anal. Calcd for $C_{74}H_{58}ClNO_2P_4Ru.0.67CH_2Cl_2$: C, 68.45; H, 4.56; N, 1.07. Found: C, 68.44; H, 4.88; N, 1.11. UV-vis ($CH_2Cl_2$): 22700 sh [1.1], 26700 [2.6]. IR (KBr): 3050 $\nu$(H-C=C); 2067 $\nu$(RuCαC). $^1$H NMR: $\delta$ 4.91 (m, 4H, $PCH_2$), 5.28 (s, 1.3H, $CH_2Cl_2$), 6.00 (d, $J_{HH}$ = 8 Hz, 2H, $H_4$), 7.05-7.51 (m, 48H, $H_5$, $H_{10}$, $H_{11}$, $H_{13}$, $H_{14}$ and Ph), 7.66 (d, $J_{HH}$ = 9 Hz, 2H, $H_{16}$), 8.25 (d, $J_{HH}$ = 9 Hz, 2H, $H_{17}$). $^{13}$C NMR: $\delta$ 50.5 ($CH_2$), 89.4 ($C_1$, $C_2$), 93.0 ($C_7$, $C_8$), 124.5 ($C_{17}$), 124.6 ($C_9$), 126.9 ($C_3$, $C_6$), 127.2 ($C_{11}$), 127.8, 132.0, 133.9 (PPh), 132.9 ($C_{10}$), 133.6 ($C_4$, $C_5$), 143.9 ($C_{15}$), 147.0 ($C_{18}$), 135.6 ($C_{12}$). $^{31}$P NMR: $\delta$ -5.94.

**Synthesis of *trans*-[Ru{(*E*)-4,4',4''-CαCC$_6$H$_4$CH=CHC$_6$H$_4$CαCC$_6$H$_4$NO$_2$}Cl(dppe)$_2$]** (**14**). *cis*-$[RuCl_2(dppe)_2]$ (461 mg, 0.48 mmol) and $NaPF_6$ (80 mg, 0.48 mmol) were added to a suspension of **6** (166 mg, 0.48 mmol) in $CH_2Cl_2$ (50 mL). The orange mixture was stirred at room temperature overnight. $NEt_3$ (1 mL) was added and the red mixture stirred at room temperature for 2 h. The reaction

mixture was purified by passing through a short pad of alumina, eluting with $CH_2Cl_2$/petrol/$NEt_3$ (10:10:1). Reduction in volume of the solvent on a rotary evaporator afforded **14** as a purple powder (530 mg, 87%). ESI MS: 1247 ($[M - Cl]^+$, 80), 898 ($[Ru(dppe)_2]^+$, 10). Anal. Calcd for $C_{76}H_{62}ClNO_2P_4Ru.0.67CH_2Cl_2$: C, 68.80; H, 4.77; N, 1.05. Found: C, 68.97; H, 5.30; N, 1.09. UV-vis ($CH_2Cl_2$): 22000 [3.0], 26700 [3.2], 35300 sh [5.5], 36200 [5.9]. IR ($CH_2Cl_2$): 2062 $\nu$(RuC$\alpha$C); 1587 $\nu$(C=C). $^1$H NMR: $\delta$ 2.69 (m, 8H, $PCH_2$), 5.28 (s, 1.3H, $CH_2Cl_2$), 6.64 (d, $J_{HH}$ = 8 Hz, 2H, $H_4$), 6.90-7.60 (m, 48H, $H_5$, $H_7$, $H_8$, $H_{10}$, $H_{11}$ and Ph), 7.68 (d, $J_{HH}$ = 9 Hz, 2H, $H_{16}$), 8.24 (d, $J_{HH}$ = 9 Hz, 2H, $H_{17}$). $^{13}$C NMR: $\delta$ 30.7 ($PCH_2$), 88.4, 95.4 ($C_{13}$, $C_{14}$), 114.9 ($C_2$), 120.2 ($C_1$), 127.1 (d, $J_{CP}$ = 20 Hz), 128.9, 134.4 (d, $J_{CP}$ = 8 Hz), 136.0 (m) (PPh), 123.7, 125.2, 126.1, 126.3, 130.4, 130.7, 132.2, 132.3 ($C_4$, $C_5$, $C_7$, $C_8$, $C_{10}$, $C_{11}$, $C_{16}$, $C_{17}$), 128.7, 130.5, 131.1 ($C_3$, $C_6$, $C_{12}$), 139.1 ($C_{15}$), 146.9 ($C_{18}$), $C_9$ not observed. $^{31}$P NMR: $\delta$ 50.0.

**Synthesis of *trans*-[Ru{(*E*)-4,4',4''-C$\alpha$CC$_6$H$_4$CH=CHC$_6$H$_4$C$\alpha$CC$_6$H$_4$NO$_2$}Cl(dppm)$_2$]** (**15**). *cis*-$[RuCl_2(dppm)_2]$ (162 mg, 0.17 mmol) and $NaPF_6$ (29 mg, 0.17 mmol) were added to a suspension of **6** (60 mg, 0.17 mmol) in $CH_2Cl_2$ (50 mL). The orange mixture was stirred at room temperature overnight. $NEt_3$ (1 mL) was added and the red mixture stirred at room temperature for 2 h. The reaction mixture was purified by passing through a short pad of alumina, eluting with $CH_2Cl_2$/petrol/$NEt_3$ (10:10:1). Reduction in volume of the solvent on a rotary evaporator afforded **15** as a purple powder (123 mg, 57%). ESI MS: 1255 ($[M + H]^+$, 100), 1219 ($[M - Cl]^+$, 50), 905 ($[RuCl(dppm)_2]^+$, 100)$^+$. Anal. Calcd for $C_{74}H_{58}ClNO_2P_4Ru.0.33CH_2Cl_2$: C, 69.65; H, 4.61; N, 1.09. Found: C, 69.52; H, 4.82; N, 1.24. UV-vis ($CH_2Cl_2$): 22300 [4.9], 26500 [4.9]. IR (KBr): 3051 $\nu$(H-C=C), 2059 $\nu$(RuC$\alpha$C). $^1$H NMR: $\delta$ 4.92 (m, 4H, $PCH_2$), 5.28 (s, 0.67H, $CH_2Cl_2$), 6.07 (d, $J_{HH}$ = 8 Hz, 2H, $H_4$), 6.90-7.54 (m, 48H, $H_5$, $H_7$, $H_8$, $H_{10}$, $H_{11}$, and Ph), 7.67 (d, $J_{HH}$ = 9 Hz, 2H, $H_{16}$), 8.24 (d, $J_{HH}$ = 9 Hz, 2H, $H_{17}$). $^{13}$C NMR: $\delta$ 53.0 ($CH_2$), 88.5 ($C_1$, $C_2$), 95.6 ($C_7$, $C_8$), 120.3 ($C_9$), 123.9 ($C_{17}$), 124.9 ($C_3$, $C_6$), 125.7 ($C_{11}$), 126.4 ($C_{10}$), 127.8, 129.5, 133.9 (PPh), 132.4 ($C_4$, $C_5$), 134.4 ($C_{12}$), 139.4 ($C_{15}$), 147.1 ($C_{18}$). $^{31}$P NMR: $\delta$ -5.90.

**Synthesis of *trans*-[Ru{(*E,E*)-4,4',4''-C$\alpha$CC$_6$H$_4$CH=CHC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$}Cl(dppe)$_2$] (16).** *cis*-[RuCl$_2$(dppe)$_2$] (263 mg, 0.27 mmol) and $NaPF_6$ (46 mg, 0.27 mmol) were added to a suspension of **11** (96 mg, 0.27 mmol) in $CH_2Cl_2$ (35 mL). The dark orange mixture was stirred at room temperature overnight. $NEt_3$ (1 mL) was added and the red mixture stirred at room temperature for 24 h. The reaction mixture was purified by passing through a short pad of alumina, eluting with $CH_2Cl_2$/petrol/$NEt_3$ (10:10:1). Reduction in volume of the solvent on a rotary evaporator afforded **16** as a purple powder (125 mg, 36%). ESI MS: 1247 ([M – Cl]$^+$, 30), 898 ([Ru(dppe)$_2$]$^+$, 10). Anal. Calcd for $C_{76}H_{64}ClNO_2P_4Ru.2CH_2Cl_2$: C, 64.44; H, 4.71; N, 0.96. Found: C, 64.29; H, 5.17; N, 0.99. UV-vis ($CH_2Cl_2$): 21800 [1.6], 26100 [2.2], 35300 sh [6.2], 36200 [6.6]. IR ($CH_2Cl_2$): 2066 $\nu$(RuC$\alpha$C); 1598, 1587 $\nu$(C=C). $^1$H NMR: $\delta$2.69 (m, 8H, $CH_2$), 5.28 (s, 4H, $CH_2Cl_2$), 6.64 (d, $J_{HH}$ = 8 Hz, 2H, $H_4$), 6.95-7.54 (m, 50H, $H_5$, $H_7$, $H_8$, $H_{10}$, $H_{11}$, $H_{13}$, $H_{14}$ and Ph), 7.65 (d, $J_{HH}$ = 9 Hz, 2H, $H_{16}$), 8.23 (d, $J_{HH}$ = 9 Hz, 2H, $H_{17}$). $^{13}$C NMR: $\delta$30.7 ($CH_2$), 114.9 ($C_1$), 124.2 ($C_{17}$), 125.5, 125.7 ($C_7$, $C_8$), 126.0, 126.7, 126.8, 127.5 ($C_5$, $C_{10}$, $C_{11}$, $C_{16}$), 127.1 (d, $J_{CP}$ = 20 Hz), 129.0, 134.4 (d, $J_{CP}$ = 9 Hz), 136.0 (m) (PPh), 129.9, 133.1 ($C_{13}$, $C_{14}$), 130.5 ($C_4$), 134.9 ($C_6$), 131.37 (2C, $C_9$, $C_{12}$), 138.7 ($C_3$), 144.1 ($C_{15}$), 146.7 ($C_{18}$), $C_2$ not observed. $^{31}$P NMR: $\delta$50.0.

**Synthesis of *trans*-[Ru{(*E,E*)-4,4',4''-C$\alpha$CC$_6$H$_4$CH=CHC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)Cl(dppm)$_2$] (17).** *cis*-[RuCl$_2$(dppm)$_2$] (263 mg, 0.27 mmol) and $NaPF_6$ (46 mg, 0.27 mmol) were added to a suspension of **11** (96 mg, 0.27 mmol) in $CH_2Cl_2$ (35 mL). The dark orange mixture was stirred at room temperature overnight. $NEt_3$ (1 mL) was added and the red mixture stirred at room temperature for 24 h. The reaction mixture was purified by passing through a short pad of alumina, eluting with $CH_2Cl_2$/petrol/$NEt_3$ (10:10:1). Reduction in volume of the solvent on a rotary evaporator afforded **17** as a purple powder (90 mg, 46%). ESI MS: 1256 ([M]$^+$, 50), 905 ([RuCl(dppm)$_2$]$^+$, 100). Anal. Calcd for $C_{74}H_{60}ClNO_2P_4Ru.CH_2Cl_2$: C, 67.19; H, 4.66; N, 1.04. Found: C, 66.93; H, 5.31; N, 1.17. UV-vis ($CH_2Cl_2$): 21700 [1.5], 25800 [1.7]. IR (KBr): 3048 $\nu$(H-C=C); 2066 $\nu$(RuC$\alpha$C). $^1$H NMR: $\delta$4.91 (m, 4H, $PCH_2$), 5.28 (s, 2H, $CH_2Cl_2$), 6.06 (d, $J_{HH}$ = 8 Hz, 2H, $H_4$), 6.96-7.50 (m, 50H, $H_5$, $H_7$, $H_8$, $H_{10}$, $H_{11}$,

$H_{13}$, $H_{14}$ and Ph), 7.64 (d, $J_{HH}$ = 9 Hz, 2H, $H_{16}$), 8.24 (d, $J_{HH}$ = 9 Hz, 2H, $H_{17}$). $^{13}$C NMR: $\delta$ 53.2 ($CH_2$), 94.3 ($C_7$, $C_8$), 124.4 ($C_9$), 125.7 ($C_3$, $C_6$), 126.8 ($C_{17}$), 131.2 ($C_{11}$), 127.8, 129.5, 133.9 (PPh), 127.8 ($C_4$, $C_5$), 130.4 ($C_{10}$), 133.6 ($C_{12}$), 139.0 ($C_{15}$), 147.0 ($C_{18}$). $^{31}$P NMR: $\delta$ -5.41.

**Synthesis of *trans*-[Ru(4,4',4''-CαCC$_6$H$_4$CαCC$_6$H$_4$CαCC$_6$H$_4$NO$_2$)Cl(dppe)$_2$]** (**18**). *cis*-[$RuCl_2$(dppe)$_2$] (160 mg, 0.16 mmol) and $NaPF_6$ (28.4 mg, 0.17 mmol) were added to a suspension of 4,4',4"-HCαCC$_6$H$_4$CαCC$_6$H$_4$CαCC$_6$H$_4$NO$_2$ (55 mg, 0.16 mmol) in $CH_2Cl_2$ (40 mL). The orange mixture was stirred at room temperature overnight. $NEt_3$ (1 mL) was added and the red mixture obtained was stirred at room temperature for 2 h. The reaction mixture was concentrated and purified by column chromatography on alumina, eluting with $CH_2Cl_2$/petrol/$NEt_3$ (10:10:1). Reduction in volume of the solvent afforded **18** as a red powder (170 mg, 84%). ESI MS: 1245 ([M – Cl]$^+$, 60), 898 ([Ru(dppe)$_2$], 10). Anal. Calcd for $C_{76}H_{60}ClNO_2P_4Ru.0.25CH_2Cl_2$: C, 70.40; H, 4.69; N, 1.08. Found: C, 70.21; H, 5.05; N, 1.40. UV-vis ($CH_2Cl_2$): 23100 sh [2.3], 27300 [3.8]. IR ($CH_2Cl_2$): 2059 cm$^{-1}$ ν(RuCαC). $^1$H NMR: δ 2.68 (m, 8H, $CH_2$), 5.28 (s, 0.5H, $CH_2Cl_2$), 6.53 (d, $J_{HH}$ = 7 Hz, 2H, $H_4$), 6.92-7.49 (m, 46H, $H_5$, $H_{10}$, $H_{11}$, Ph), 7.68 (d, $J_{HH}$ = 9 Hz, 2H, $H_{16}$), 8.24 (d, $J_{HH}$ = 9 Hz, 2H, $H_{17}$). $^{13}$C NMR: $\delta$ 30.6 ($CH_2$), 89.1 ($C_2$), 92.9 ($C_7$, $C_8$, $C_{13}$, $C_{14}$), 123.7 ($C_{17}$), 124.8 ($C_3$, $C_6$), 127.1 (d, $J_{CP}$ = 17 Hz), 128.8, 134.3 (d, $J_{CP}$ = 17 Hz), 136.0 (m) (PPh), 130.5 ($C_4$), 130.9 ($C_{15}$), 131.4 ($C_4$, $C_5$), 131.8 ($C_{10}$, $C_{11}$), 132.3 ($C_{16}$), 147.0 ($C_{18}$), $C_1$, $C_9$, $C_{12}$ not observed. $^{31}$P NMR: δ 49.7.

**Synthesis of *trans*-[Ru(4,4'-CαCC$_6$H$_4$CαCC$_6$H$_4$NO$_2$)Cl(dppe)$_2$]** (**19**). *cis*-[$RuCl_2$(dppe)$_2$] (360 mg, 0.37 mmol) and $NaPF_6$ (68.5 mg, 0.41 mmol) were added to a solution of 4,4'-HCαCC$_6$H$_4$CαCC$_6$H$_4$NO$_2$ (91.7 mg, 0.37 mmol) in $CH_2Cl_2$ (35 mL). The red solution was stirred at room temperature overnight. $NEt_3$ (1 mL) was added and the deep red mixture stirred at room temperature for 1 h. The reaction mixture was purified by passing through a short pad of alumina, eluting with $CH_2Cl_2$/petrol/$NEt_3$ (10:10:1). Reduction in volume of the solvent on a rotary evaporator afforded **16** as a purple powder (400 mg, 92%). ESI MS: 1145 ([M – Cl]$^+$, 60), 898 ([Ru(dppe)$_2$], 20). Anal. Calcd for $C_{68}H_{56}NO_2P_4RuCl.0.25CH_2Cl_2$: C, 68.26; H, 4.47; N, 1.17. Found: C, 68.28; H, 4.96;

N, 1.30. UV-vis ($CH_2Cl_2$): 21400 [1.8], 28600 [2.6]. IR ($CH_2Cl_2$): 2056 $cm^{-1}$ ν(RuCαC). $^1H$ NMR: δ 2.69 (m, 8H, $CH_2$), 5.28 (s, 0.5H, $CH_2Cl_2$), 6.55 (d, $J_{HH}$ = 7 Hz, 2H, $H_4$), 6.92-7.59 (m, 42H, $H_5$, Ph), 7.68 (d, $J_{HH}$ = 8 Hz, 2H, $H_{16}$), 8.24 (d, $J_{HH}$ = 8 Hz, 2H, $H_{17}$). $^{13}C$ NMR: δ 30.6 ($CH_2$), 88.1 ($C_1$), 96.7 ($C_2$), 105.9 ($C_{13}$, $C_{14}$), 123.6 ($C_{17}$), 127.1 (d, $J_{CP}$ = 17 Hz), 128.8, 134.3 (d, $J_{CP}$ = 17 Hz) (PPh), 130.0 ($C_3$), 130.9 ($C_{15}$), 131.2 ($C_4$, $C_5$), 131.8 ($C_{16}$), 146.5 ($C_{18}$). $^{31}P$ NMR: δ 49.7.