Towards the Rhodium-Catalyzed Bis-Hydroformylation of 1,3-Butadiene to Adipic Aldehyde

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Supporting Information

I. General Experimental Details

General: Unless otherwise noted, all reactions and manipulations were carried out under an Ar atmosphere using standard Schlenk and high-vacuum line techniques, or in a Braun inert atmosphere glovebox (Ar) at ambient temperature. Glassware was dried for a minimum of 8 h at 150 ^{o}C. Unless otherwise noted, all NMR were obtained at ambient temperature using a Bruker DPX-200 MHz spectrometer. All NMR chemical shifts are reported as δ in parts per million (ppm). ^{1}H NMR spectra were referenced to residual protiated solvent, and chemical shifts are reported in parts per million downfield from tetramethylsilane. ^{31}P{^{1}H} NMR spectra are reported relative to trimethyl phosphate as the external standard. ^{13}C{^{1}H} NMR spectra were referenced to the solvent.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Toluene, hexane, THF, and methylene chloride were dried using an MBraun SPS-800 drying machine and degassed by either three freeze-pump-thaw cycles or by sparging with Ar for a minimum of 15 minutes. Silica gel for flash chromatography (particle size 0.035-0.070 mm, 60 A) was supplied by Acros. Celite was dried at 150 ^{o}C in the oven for 1 week, followed by heating to 180 ^{o}C under vacuum for 8 h. Deuterated solvents were purchased from Deutero GmbH or Aldrich. THF-d_8 was vacuum transferred from purple sodium/benzophenone ketyl. CD_2Cl_2 was vacuum transferred from CaH_2 after stirring for at least 8 h at room temperature. THF-d_8, and CD_2Cl_2 were degassed by three freeze-pump-thaw cycles. The compounds adipic aldehyde[1] and 1,8-dihydroxytriptycene[2] were prepared according to literature procedures. The bisphosphine ligands from Table 5 were a generous gift from Dr. Thomas Schnetz (entries 2-4) and the bisphosphite ligands (entries 5-7 and 9-12) were synthesized according to the thesis of Dr. Tobias Rosendahl (*vide infra* the related synthesis of **13**).

II. Synthesis of Hydroformylation Product Manifold

General Method for the Synthesis of Aldehydes. (*E*)-3-Pentenal (3). Dess-Martin periodinane (DMP) (1.29 g, 3.04 mmol) was added to a 50 mL Schlenk flask followed by 15 mL of CH_2Cl_2. (*E*)-Pent-3-en-1-ol[3] (**1**) (204 mg, 2.37 mmol) was diluted with 10 mL CH_2Cl_2 and then added to the stirred DMP slurry. The reaction mixture was stirred for 4 h and then the volatile materials were vacuum transferred to a clean 50 mL flask. The vacuum transferred materials were washed twice with distilled H_2O (25 mL) and then the organic layer was dried over $MgSO_4$, filtered, and concentrated using a rotary evaporator (500 mbar) yielding a clear, nearly colorless oil contaminated primarily with residual CH_2Cl_2. The yield was determined to be 14% using the method described in the "General Method for the Quantification of Aldehydes" section. The NMR spectra match those reported for (*E*)-3-pentenal,[4] (*Z*)- 3-pentenal,[6] and 2-methylbut-3-enal.[7]

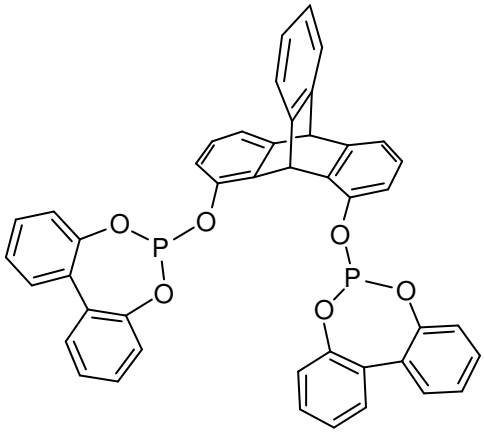
2-Ethylbutanedial (5) and 2-Methylpentanedial (6): A hydroformylation experiment was conducted using the procedure as described in the "Representative Procedure for the Catalytic Hydroformylation of 1,3-Butadiene" section with the amounts: $(CO)_2Rh(acac)$ (10.3 mg, 0.0399 mmol), **13** (38.8 mg, 0.0543 mmol) and 1,3-butadiene (0.94 M, 5.0 mL, 4.7 mmol) at 90 ^oC under 80 bar syngas. After 24 h, the reaction was cooled and the contents removed from the autoclave. The reaction solution was filtered through a silica column and the column was flushed first with CH_2Cl_2 (180 mL), then 10% Et_2O in CH_2Cl_2 (200 mL), and finally 100% Et_2O (350 mL). The 100% Et_2O fraction was collected and concentrated with a rotary evaporator. The product was isolated by Kugelrohr distillation at 85 ^oC under 45 mbar, yielding a colorless oil (46 mg, 8%), which consisted of a mixture of **5**, **6** and **7** in a ratio of 3.2:4.4:1.0. The products **5** and **6** were characterized as this mixture. ^1H NMR (500 MHz, CD_2Cl_2): 0.95 (t, 3H, ^3J = 7.4 Hz, -CH_3, **5**), 1.10 (d, 3H, ^3J = 7.2 Hz, -CH_3, **6**), 1.51-1.61 (m, 1H, -CH_2CH$_3$, **5**), 1.61-1.70 (m, 1H, -CH_2CH$_2$CH(O), **6**), 1.73-1.83 (m, 1H, -CH_2CH$_3$, **5**), 1.95-2.04 (m, 1H, -CH_2CH$_2$CH(O), **6**), 2.33-2.41 (m, 1H, -CH$_2$CH(CH$_3$)CH(O),

6), 2.41-2.47 (m, 1H, **5**), 2.46-2.53 (m, 2H, -CH_2CH_2CH(O), **6**), 2.80-2.88 (m, 2H, **5**), 9.60 (d, 1H, ^3J = 1.6 Hz, CH_3CH(C*H*(O))- , **6**), 9.68 (br s, 1H, -C*H*(O), **5**), 9.74 (t, 1H, ^3J = 1.1 Hz, -CH_2C*H*(O), **6**), 9.76 (br s, 1H, -C*H*(O), **5**). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 11.4 (*C*H_3-, **5**), 13.5 (*C*H_3-, **6**), 21.9 (CH_3CH_2-, **5**), 22.6 (-*C*H_2CH_2CH(O), **6**), 41.4 (-CH_2CH_2CH(O), **6**), 42.2 (-*C*H_2CH(O), **5**), 45.7 (-CH_2*C*H(CH_3)CH(O), **6**), 47.3 (CH_3CH_2*C*H(CH(O))-, **5**), 200.5 (-*C*H(O), **5**), 201.7 (-*C*H(O), **6**), 203.1 (-*C*H(O), **5**), 204.4 (-*C*H(O), **6**). HRMS (EI+): calc for $[M+H]^+$ = m/z, 115.0759, found 115.0758.

1-Formylcyclopentene (12). Cyclopentenylmethanol (89 mg, 0.91 mmol) was added to a 50 mL round bottom flask equipped with a stir bar. To this round bottom flask was added 10 mL of CH_2Cl_2 and DMP (502 mg, 1.18 mmol). The reaction mixture was stirred for ~ 16 h and filtered through a pad of celite. The celite pad was rinsed with ~ 5 mL of CH_2Cl_2 and combined with the filtrate. The CH_2Cl_2 layer was then washed with 2 x 12 mL distilled H_2O, dried with anhydrous $MgSO_4$, filtered and concentrated using a rotary evaporator. The product was purified by silica gel chromatography (100% CH_2Cl_2), yielding a pale yellow oil (59 mg, 67%). The NMR spectra match those previously reported for 1-formylcyclopentene.[8]

Cyclopentenylmethanol. Cyclopent-1-enecarboxylic acid (506.9 mg, 4.52 mmol) was added to a 100 mL round bottom flask. To the round bottom flask was added 50 mL of dry THF and the mixture was cooled to 0 ^oC with an ice bath. To the stirring solution was added BH_3·THF (1 M, 5.0 mL, 5 mmol) dropwise. After stirring for 30 min at 0 ^oC, the reaction flask was removed from the ice bath and allowed to slowly reach room temperature. The reaction mixture was stirred for 10 d at room temperature. After this time, 25 mL of a saturated $NaHCO_3$ solution was added to the stirring reaction mixture, followed by 25 mL of distilled H_2O. The product was extracted with 4 x 50 mL of Et_2O. The organic layer was then dried over $MgSO_4$, filtered and concentrated with a rotary evaporator, yielding a pale yellow oil with a white solid. The product was purified by silica gel chromatography (20:80 Et_2O:CH_2Cl_2), yielding a clear oil (90 mg, 20% yield). This product is contaminated with ~

21% of the fully hydrogenated cyclopentylmethanol. This product was then carried on with this contaminant to the next step. The NMR spectra also match those previously reported for cyclopentylmethanol.[9]

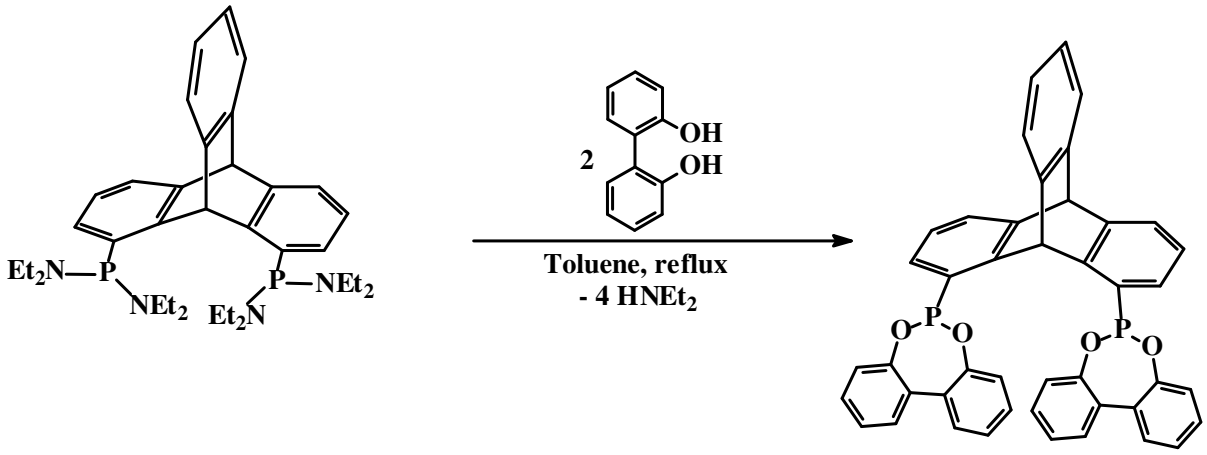


13. (Entry 8 in Tables 5 and S1) THF (~ 27 mL) was added to an oven-dried 100 mL Schlenk flask followed by 1,8-dihydroxytriptycene (794 mg, 2.77 mmol) and the solution was then cooled to –78 ^{o}C with a dry ice/IPA bath. In a separate flask the (1,1'-biphenyl-2,2'-diyl)phosphorochlorodite (1.46 g, 5.83 mmol) was dissolved in ~ 24 mL THF and slowly syringed into the diol/THF solution, followed by slow addition of NEt_3 (1.00 mL, 7.17 mmol). The flask was sealed under Ar with a glass stopper and allowed to slowly warm to RT overnight while stirring. The heterogeneous solution was cannula transferred to a Schlenk frit and filtered. The filtrate was concentrated, yielding an off-white solid. The product was purified by silica gel column chromatography (5:3 hexane:DCM), yielding a white solid (920 mg, 46%). This product was further dried by exposing to vacuum for 2 d with a vial of P_2O_5 as desiccant. ^{1}H NMR (200 MHz, CD_2Cl_2): 5.60 (s, 1H, *bridgehead H*), 6.54 (s, 1H, *bridgehead H*), 6.97-7.16 (m, H, *aryl*), 7.17-7.40 (m, H, *aryl*), 7.44-7.61 (m, H, *aryl*). ^{13}C{^{1}H} NMR: 42.4 (*bridgehead C*), 54.7 (*bridgehead C*), 118.5, 118.6, 118.7, 120.6, 122.7, 122.8, 124.4, 124.8, 126.0, 127.0, 129.8, 129.9, 130.5, 130.6, 131.59, 131.62, 136.06, 136.09, 136.13, 144.6, 146.1, 147.23, 147.28, 147.34, 148.9, 149.49, 149.55, 149.61, 149.67. ^{31}P{^{1}H} NMR (CD_2Cl_2): 143.0 ppm. HRMS (FAB^{+}) calc for $[M+H]^{+}$ = m/z, 715.1440, found 715.1449.

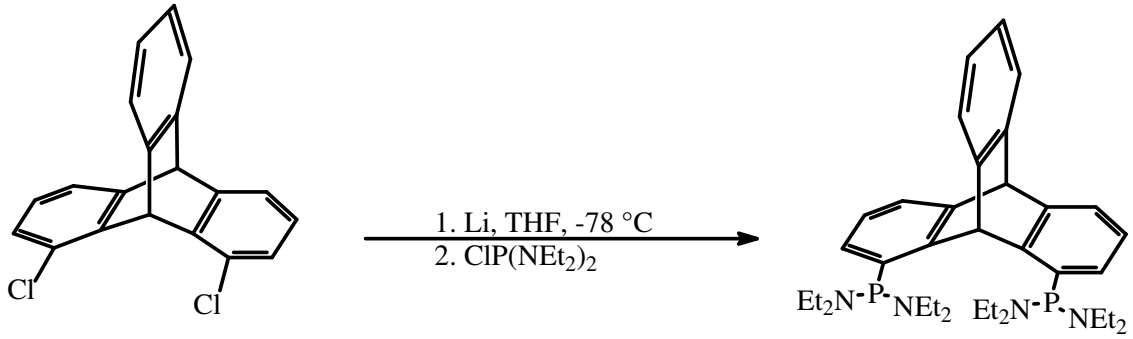
(1,1'-biphenyl-2,2'-diyl)phosphorochlorodite. To a 500 mL Schlenk flask was added ~ 300 mL of THF. The 2,2'-bisphenol (7.48 g, 40.2 mmol) was added to the Schlenk flask under a stream of Ar and the flask was then capped with a rubber septum. The flask was

immersed in a dry ice/^{i}PrOH bath and cooled to –78 ^{o}C. PCl_3 (3.8 mL, 43.6 mmol) was added dropwise to the pre-cooled solution, followed by dropwise addition of NEt_3 (14 mL, 100 mmol). The Schlenk flask was sealed with a glass stopper under a blanket of Ar and allowed to slowly warm to room temperature. The reaction mixture was stirred for 1 day, filtered through a pad of celite using a Schlenk frit, and the solid washed with ~ 250 mL THF. The filtrate was then concentrated, yielding a thick brown oil, which slowly solidifies over time. This solid was used without further purification in the subsequent steps. The NMR spectra match those reported for (1,1'-biphenyl-2,2'-diyl)phosphorochlorodite.[10]

Ligand **13** can also be prepared via the alternative route shown below:



The 1,8-bis[bis(diethylamino)phosphanyl]triptycene precursor for this reaction is easily accessible from 1,8-dichlorotriptycene[11]:



III. Quantification of Aldehydes and Additional Table

General Method for the Quantification of Aldehydes. The isolated sample of the aldehyde was dissolved in CD_2Cl_2 and mesitylene (13.2 mg, 0.110 mmol) was added to the aldehyde solution. The solution was then transferred to a 2.00 mL volumetric flask and diluted with CD_2Cl_2 until 2.00 mL were attained. A ^1H NMR spectrum of this stock solution was then aquired (number of scans = 1, dummy scans = 0, delay = 60 s). The concentration of aldehyde was determined based on the ^1H NMR spectrum and this value was then used to prepare the calibration curve. All calibration curves were prepared using nominee as the internal standard at a concentration of 3.59 mg/mL.

Figure S1. Possible Aldehyde Products from the Hydroformylation of 1,3-Butadiene

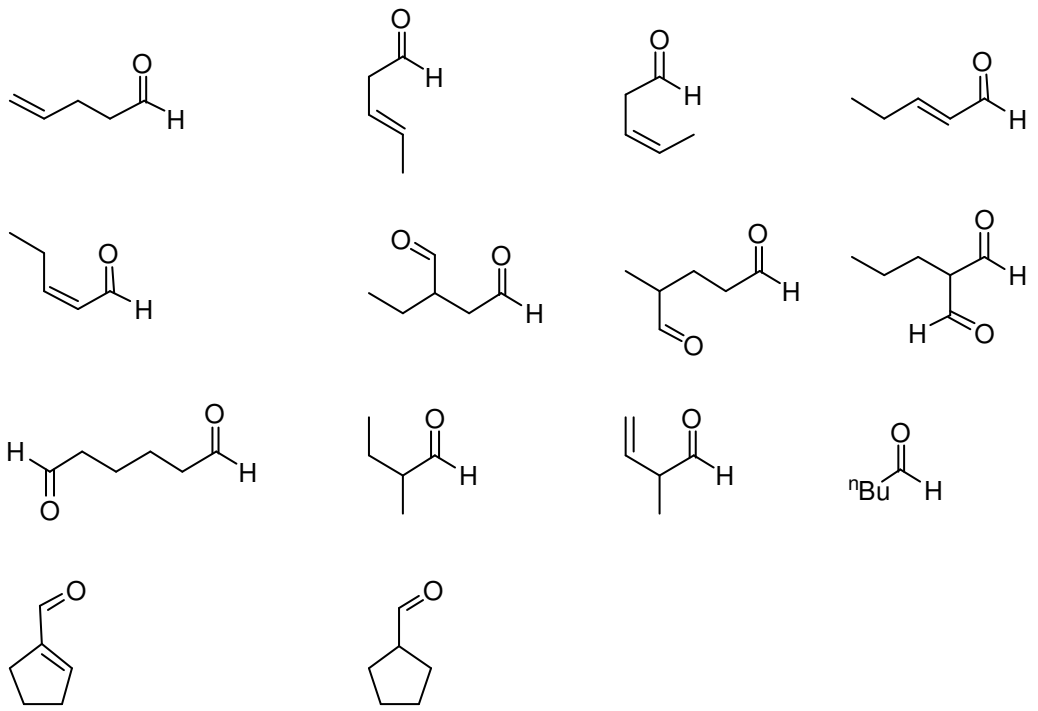
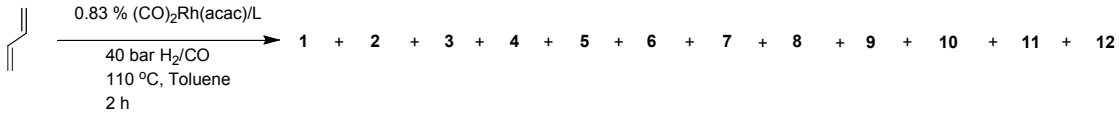
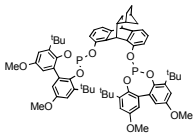
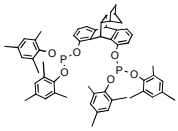
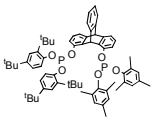
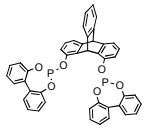
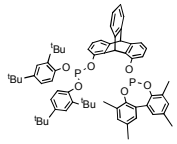
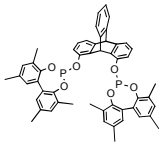
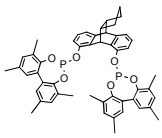
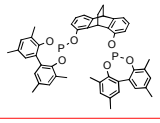


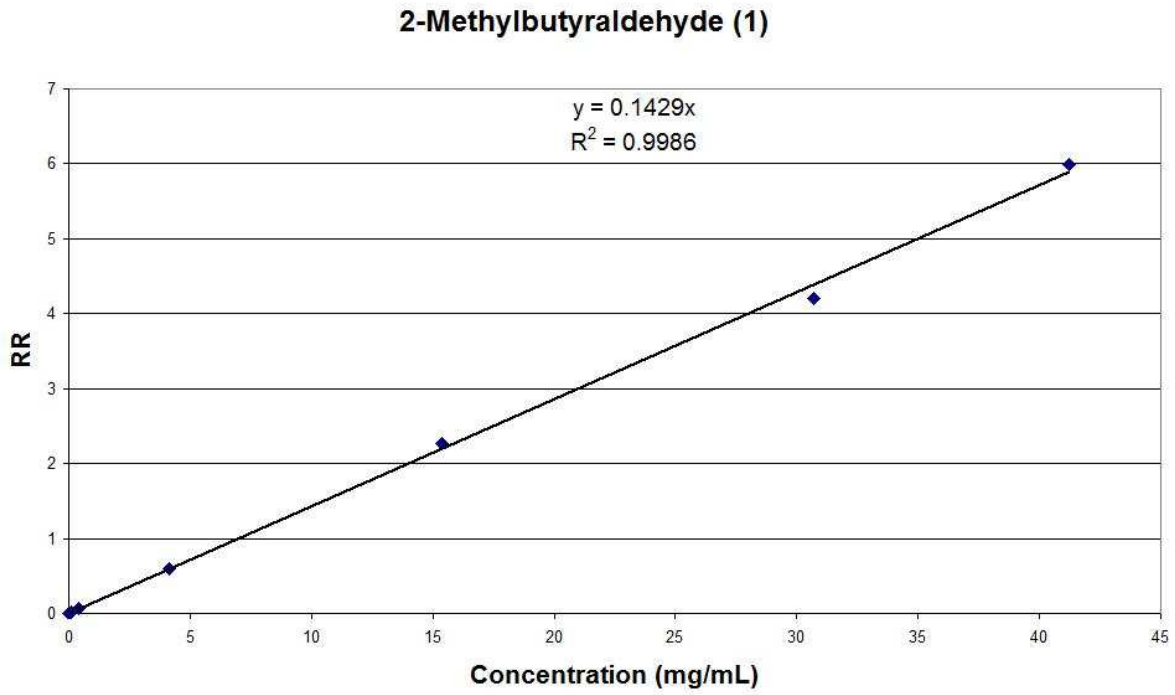
Table S1. Expanded Version of Table 5 Depicted in the Manuscript

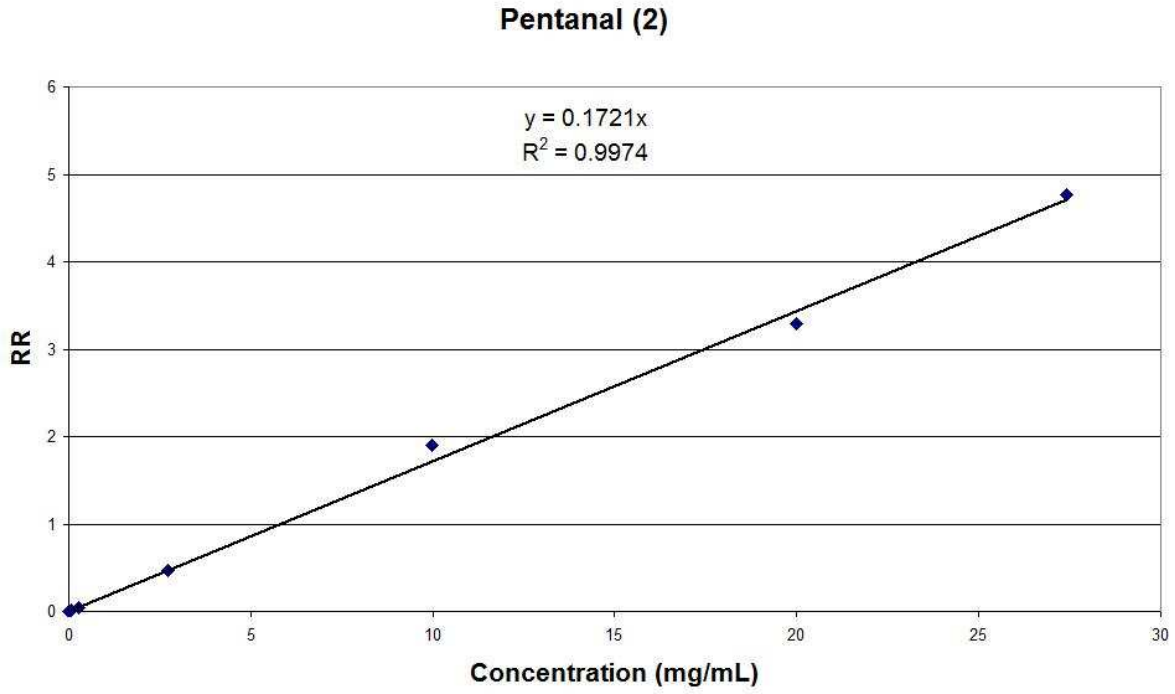


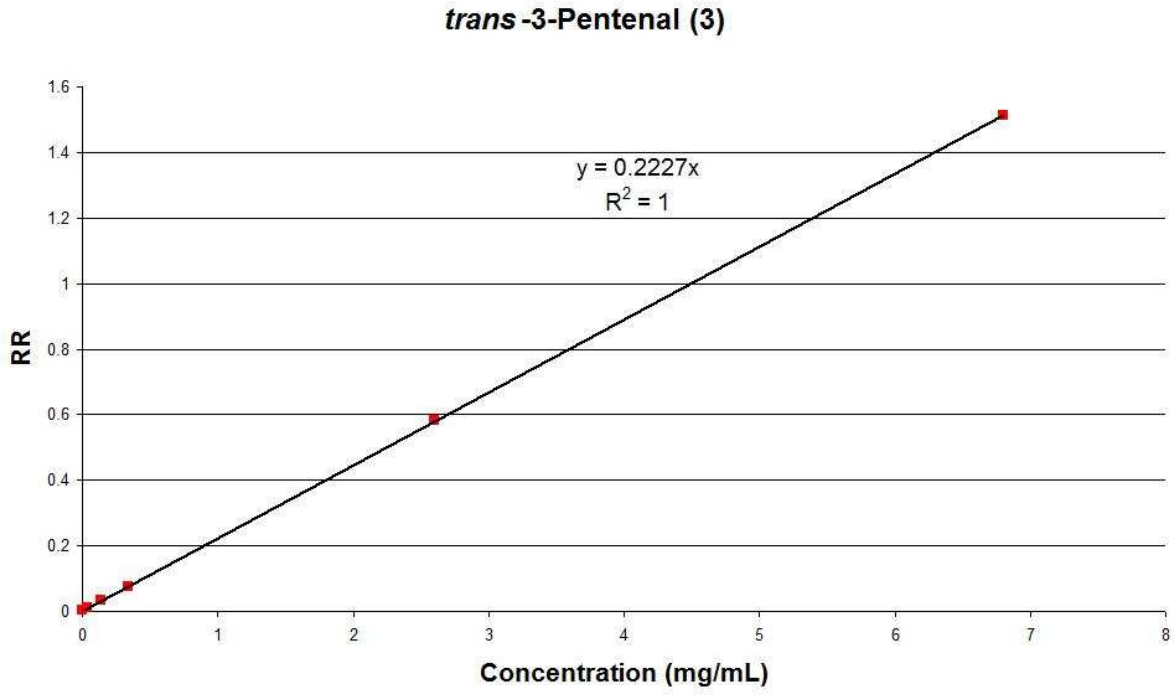
Entry	Ligand	L/M	*i*:*n*	Selec. 7[a]	% Conv.[b]	1[c]	2[c]	3[c]	4[c]	5[c]	6[c]	7[c]	8[c]	9[c]	10[c]	11[c]	12[c]
1		5.1	6.3	11.8	67.0	4.8	4.6	31.1	10.8	0.3	4.6	7.9	0.2	1.2	1.2	0.0	0.1
2		1.6	3.2	0.0	1.1	0.2	0.0	0.1	0.2	0.0	0.0	0.0	0.0	0.3	0.4	0.0	0.0
3		1.5	3.1	0.0	1.6	0.2	0.0	0.5	0.2	0.0	0.0	0.0	0.0	0.4	0.4	0.0	0.0
4		1.5	NA	0.0	0.3	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5		1.5	2.7	0.0	5.0	1.2	0.3	1.4	0.6	0.0	0.0	0.0	0.0	1.3	0.1	0.0	0.0
6		1.5	4.1	1.9	8.7	1.3	0.2	3.6	1.7	0.0	0.0	0.2	0.0	1.5	0.2	0.0	0.0
7		1.5	5.4	7.5	35.1	2.2	1.6	16.7	7.7	0.0	0.4	2.6	0.3	2.8	0.8	0.0	0.0
8		1.5	3.4	22.8	95.7	3.7	38.6	0.0	0.0	6.8	23.0	21.8	0.0	0.0	1.6	0.0	0.2
9		1.5	1.9	34.0	84.0	0.8	1.6	30.0	12.2	0.6	3.2	25.5	0.0	0.3	0.6	9.0	0.2
10		1.5	1.6	37.8	86.0	0.4	1.0	27.5	15.2	0.4	2.4	28.9	0.0	0.2	0.3	9.5	0.1
11		1.5	1.1	47.8	93.0	0.3	1.1	26.2	15.7	0.6	3.7	44.4	0.0	0.2	0.3	0.0	0.3
12		1.5	1.0	49.8	98.0	0.3	1.6	25.1	14.0	1.0	4.8	47.6	0.0	0.2	0.3	2.7	0.5

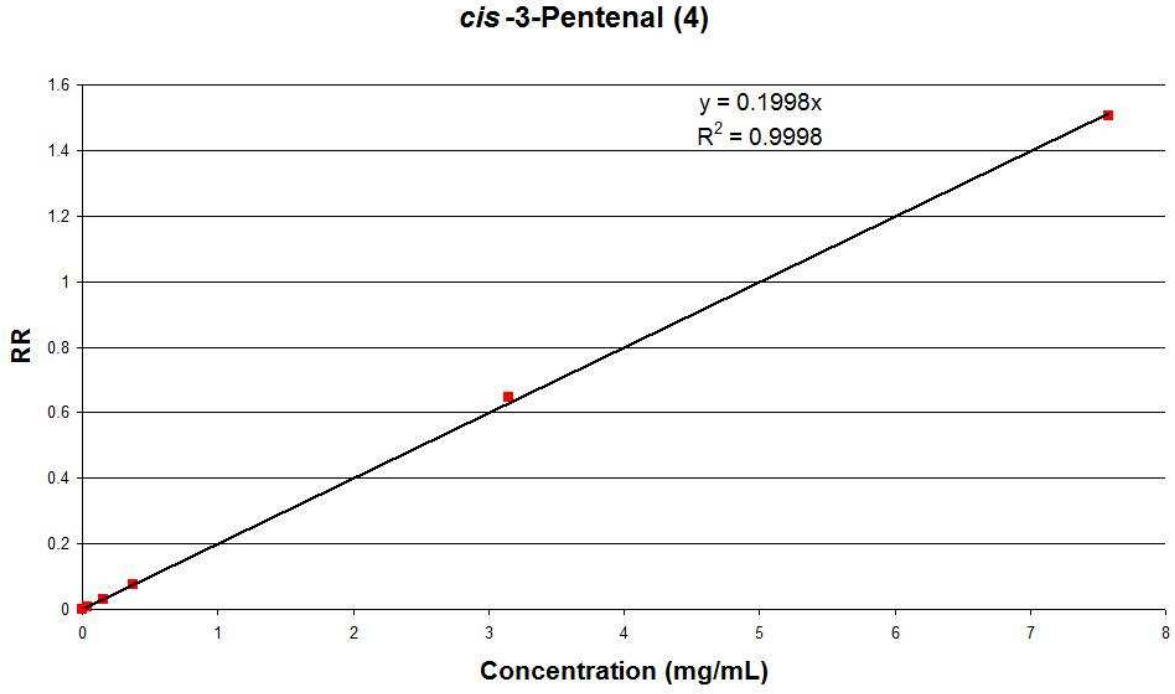
[a] Selec. **7** = Selectivity for **7**, [b] % Conv. = % conversion to the shown products, [c] % of the respective product relative to added 1,3-butadiene, NA = Not Applicable, [1,3-butadiene] = 0.23 M.

IV. Calibration Curves

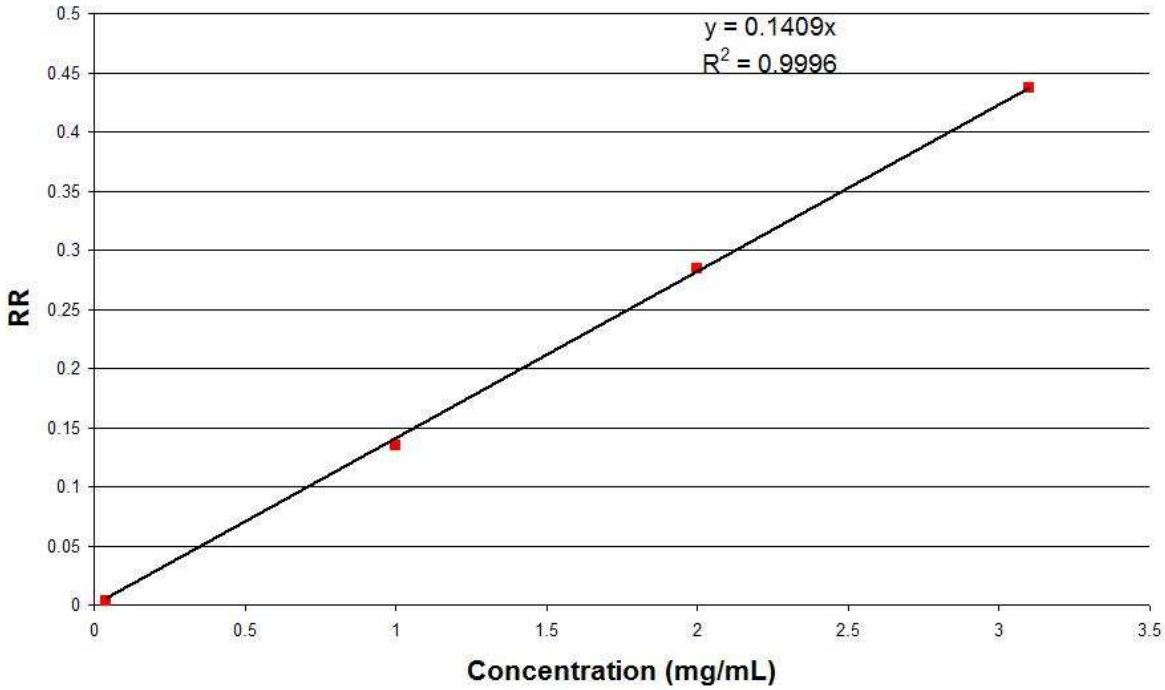




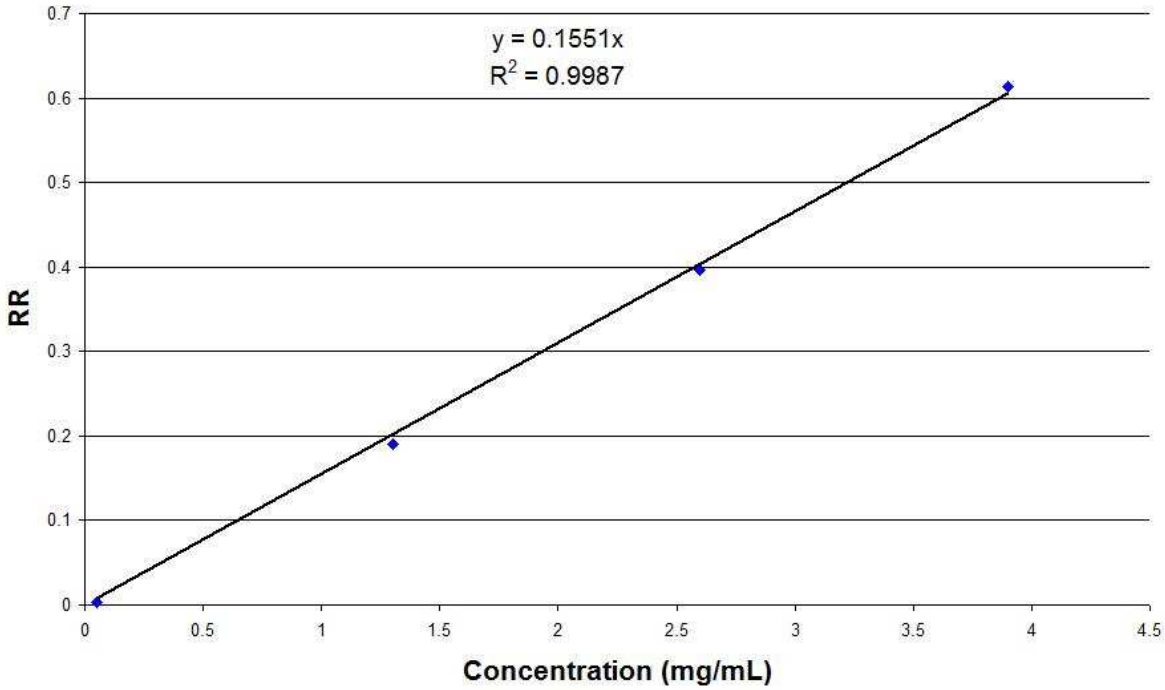

trans -3-Pentenal (3)
y = 0.2227x
R^2 = 1
RR
Concentration (mg/mL)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
1
2
3
4
5
6
7
8

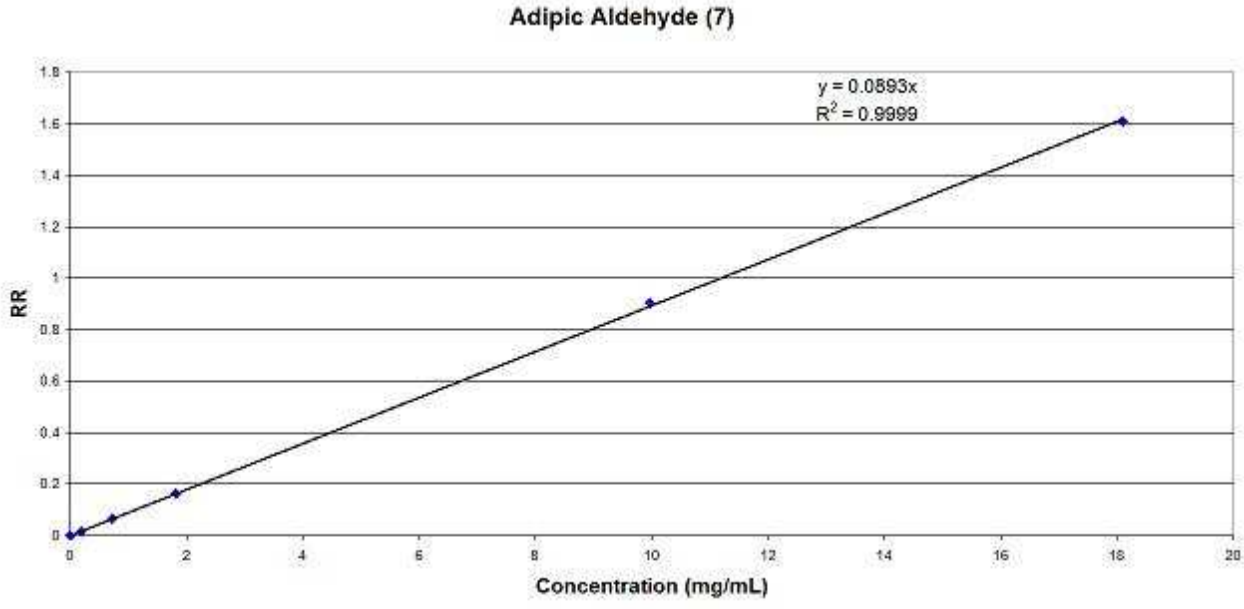

cis -3-Pentenal (4)
y = 0.1998x
R^2 = 0.9998
RR
Concentration (mg/mL)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
1
2
3
4
5
6
7
8

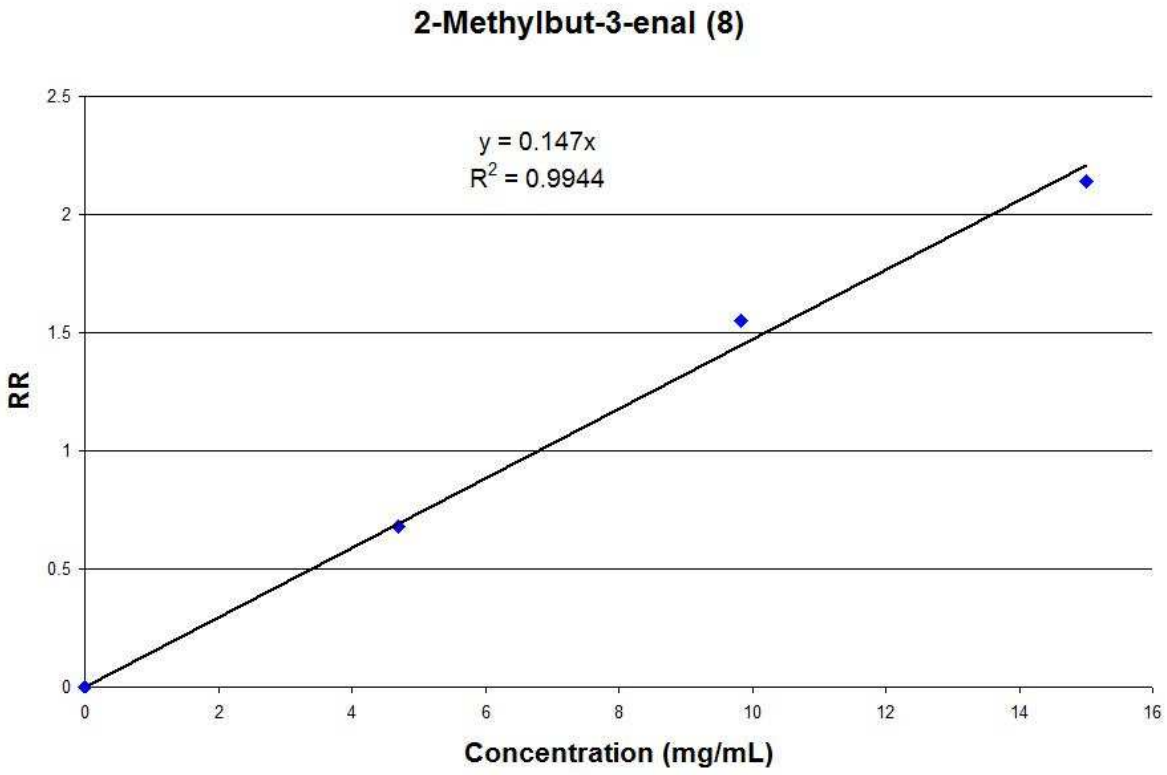
2-Ethylbutanedial (5)



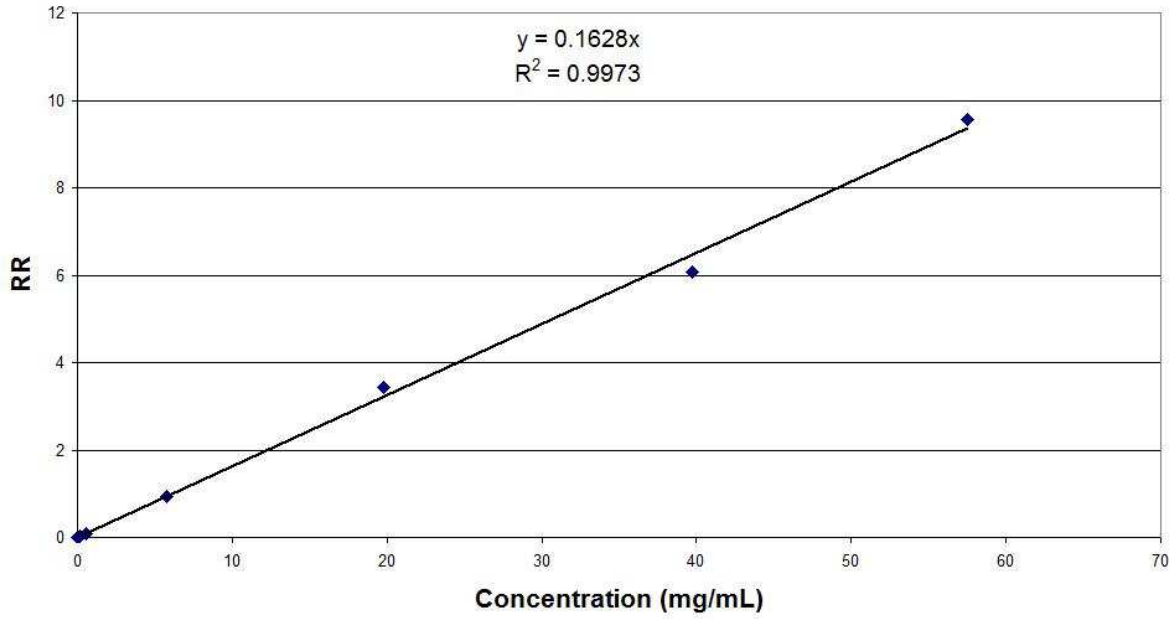
2-Methylpentanedial (6)



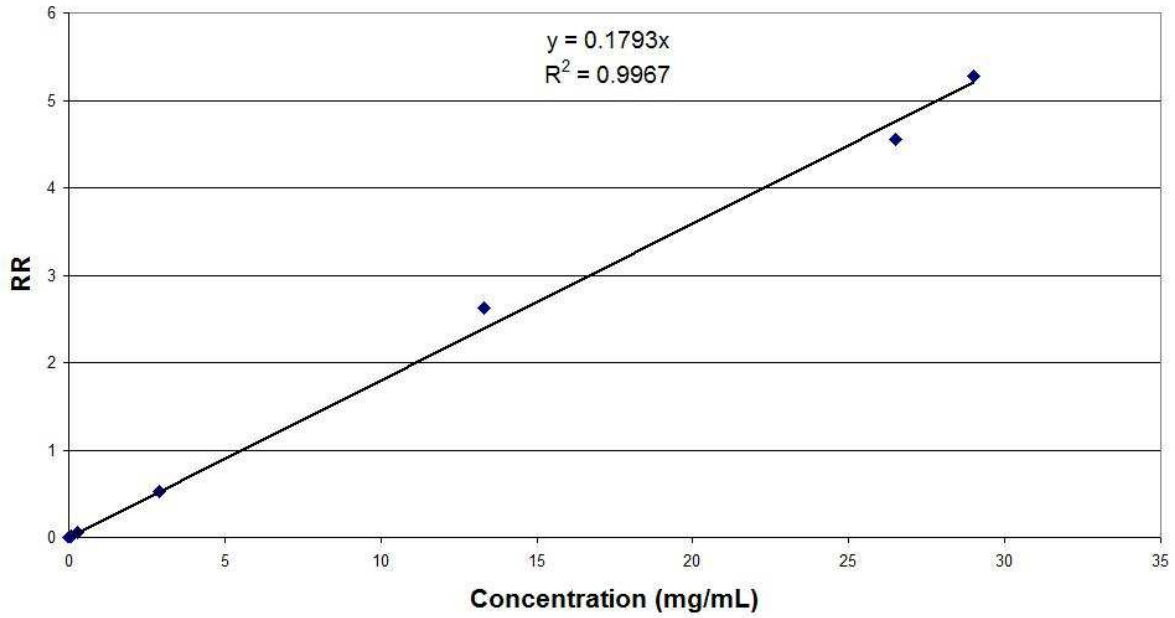

Adipic Aldehyde (7)
y = 0.0893x
R2 = 0.9999
RR
Concentration (mg/mL)

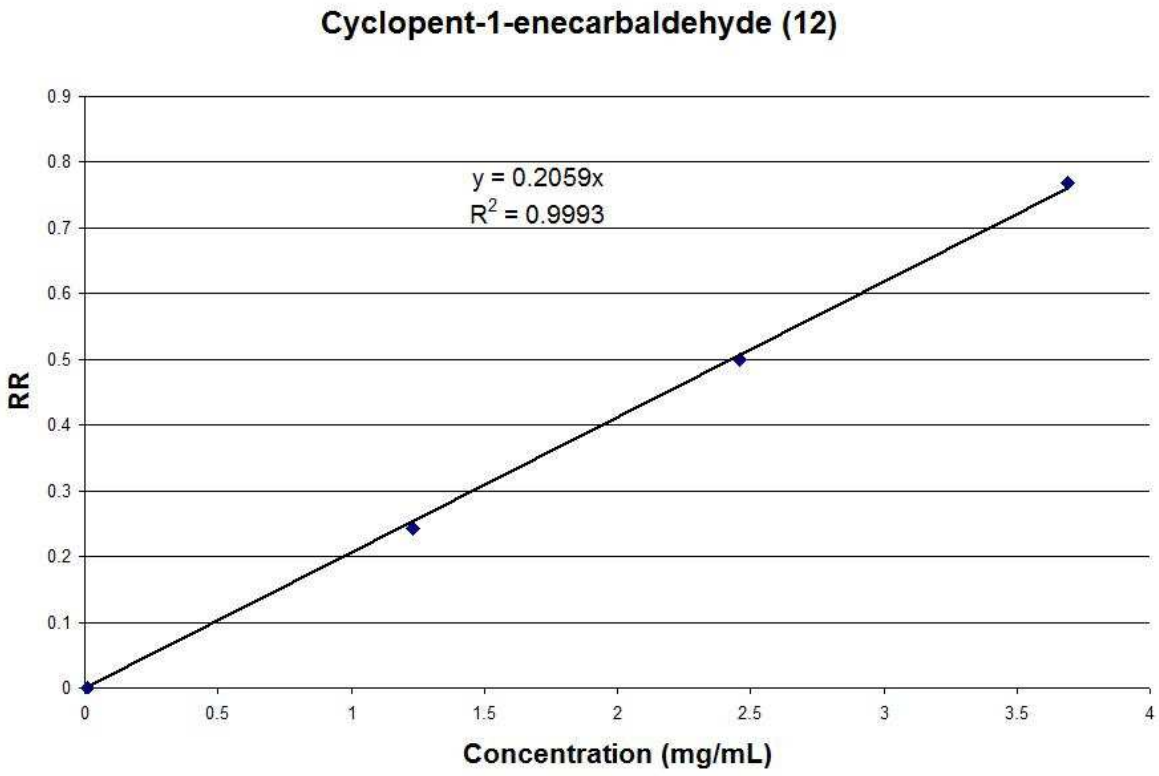

2-Methylbut-3-enal (8)
y = 0.147x
R2 = 0.9944
RR
Concentration (mg/mL)

4-Pentenal (9)



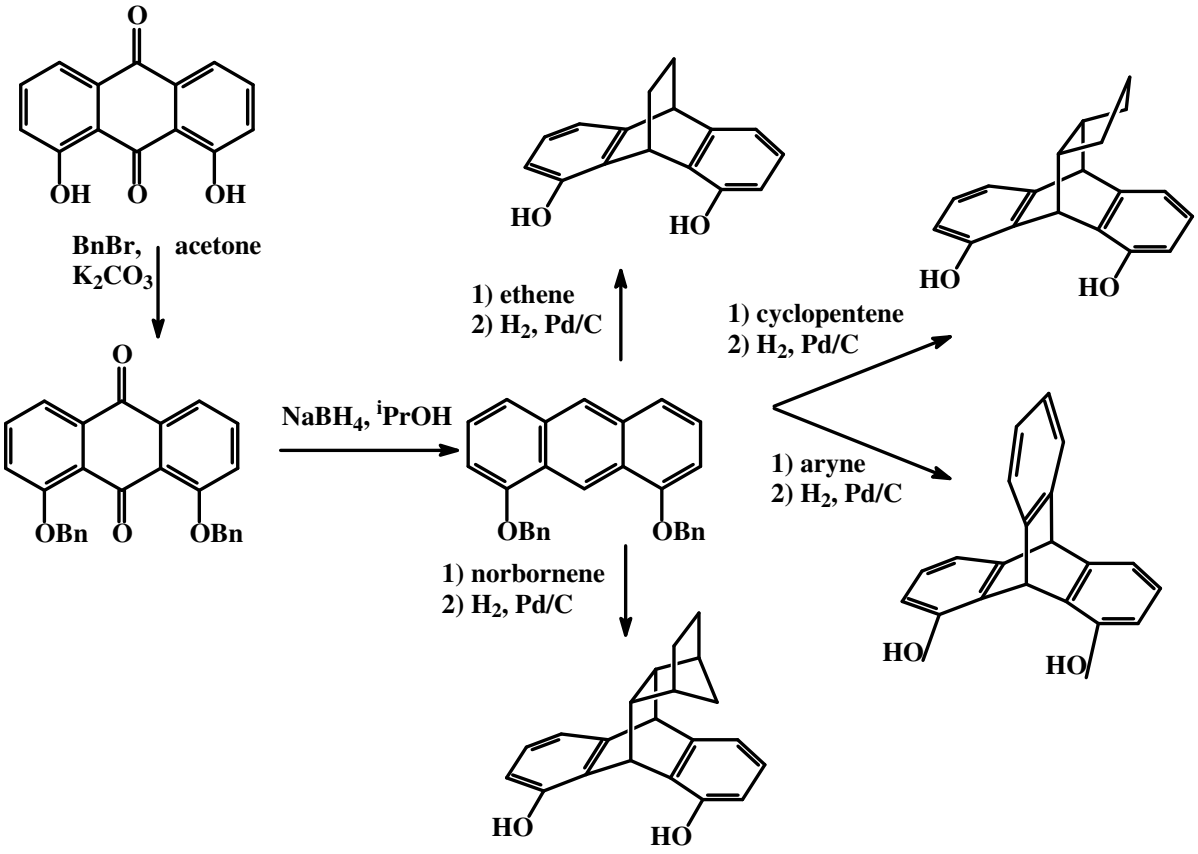
***trans*-2-pentenal (10)**





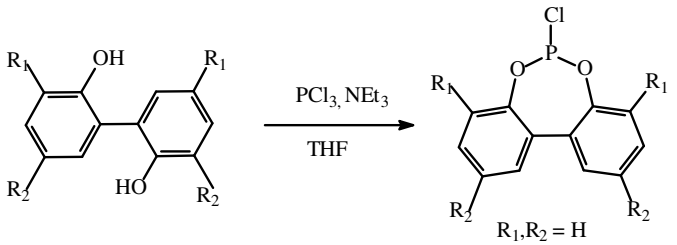
V. Synthesis of Ligands Used in Entries 5-7 and 9-12 of Tables 5 and S1

***General preparative strategy*:** the synthesis of all bisphosphites (entries 5 – 12 of Tables 5 and S1) was based upon commercial 1,8-dihydroxyanthraquinone.



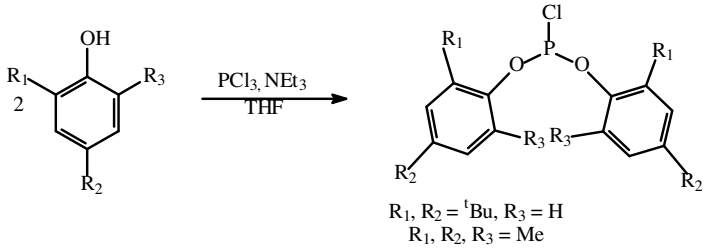
As shown in the Scheme above, 1,8-dihydroxyanthraquinone was protected by bis-benzylation and reduced in a one-pot reaction using $NaBH_4$ in refluxing *i*-propanol to the corresponding anthracene. This compound could be transformed to the various bridged bisphenols by Diels-Alder reactions with appropriate dienophiles in good yields.

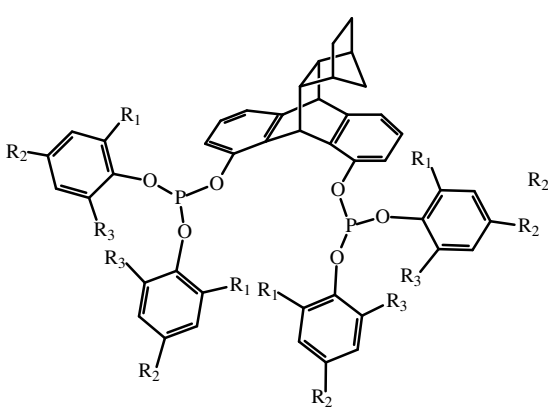
In all bisphosphite cases detailed below and shown in Tables 5 and S1 the bridged bisphenols were reacted with members of a series of dioxachlorophosphepines, which can be obtained from known o,o'-dihydroxybiphenyl derivatives and PCl_3 in the presence of NEt_3 in THF, leading to bisphosphites with their P-donor atoms in biphenyl-derived dioxaphosphepin rings:

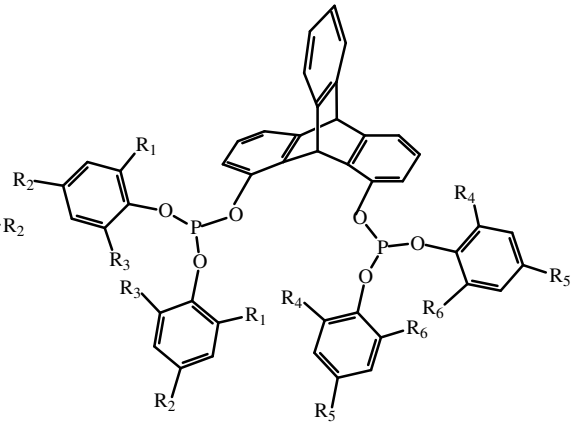


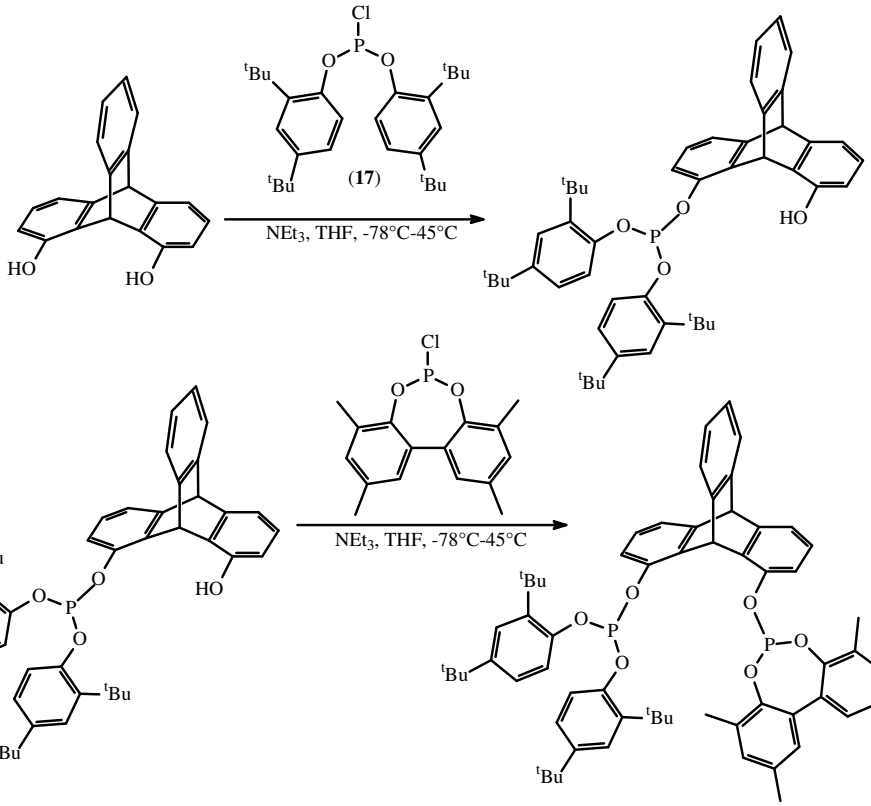
R_1,R_2 = H
R_1,R_2 = Me
R_1,R_2 = ^{t}Bu
R_1 = OMe, R_2 = Me
R_1 = ^{t}Bu, R_2 = OMe

It is also possible to prepare ligands with "open" analogs of dioxaphosphepins by utilizing bis-aryloxyphosphorus chlorides, and left-right unsymmetrical ligands with two different "side wings" attached to the 1,9-dihydro-1,9-bridged anthracene scaffolds can be also made.









The availability of the different bridged bisphenols, of a manifold of dioxachlorophosphepines and of bis-aryloxyphosphorus chlorides opens a simple pathway to

many bisphosphite chelate systems, a fraction of which has been tested in butadiene hydroformylation. It should be noted, that the usually complete conversion to products in P-O bond forming reactions of P-Cl compounds with phenols driven by triethylamine opens a combinatorial approach towards ligand libraries.

Specific bisphosphite ligands (entries 5 – 7, 9 – 12 in Tables 5, S1):

Entries 5 and 10:
1,8-Bis-(2,10-dimethoxy-4,8-di-*tert*-butyldibenzo[d,f]-[1,3,2]dioxaphosphepin-6-yloxy)-9,10-(*exo-cis*-1,2-norbornano)-9,10-dihydroanthracene, and
1,8-bis-(2,4,8,10-tetramethyldibenzo[d,f][1,3,2]dioxaphosphepin-6-yloxy)-triptycene

General procedure. In a Schlenk tube 4.405 mmol of the respective (unsubstituted or substituted) bisphenol is dissolved in 25 ml of THF and cooled down to -78°C. To this solution 0.49 ml (5.6 mmol) of PCl_3 were added and intensely stirred for 10 min. 1.53 ml of NEt_3 (11.0 mmol) was added, warmed to RT and stirred over night. The precipitated salts were filtered off using a frit and the solvent is removed under vacuum. The solid is dissolved again in 10 ml THF and cannula transferred into a -78°C solution of 2.003 mmol of the respective ligand backbone in 20 ml THF. At this temperature 0.78 ml (5.6 mmol) of NEt_3 was added and after warming to RT stirred over night. After this the white suspension is stirred at 45°C for 6.5 h. After cooling to RT, the precipitated salts were filtered off and the solvent is removed under vacuum. The pale yellow solid is purified by column chromatography under argon (SiO_2, 8*2 cm).

For entry 5: Solvent for column chromatography: CH_2Cl_2. Yield: 1.35 g (1.25 mmol, 62.7%) of a white crystalline solid. ^{1}H-NMR 250.1 MHz (CD_2Cl_2, 298 K) δ (ppm) = -0.25 (d, 1H, H17α, $^2J_{H,H}$ = 9.5 Hz), 0.40 (d, 1H, H17β, $^2J_{H,H}$ = 10.5 Hz), 1.05 (br.S, 2H), 1.23 (s, 9H, *t*-Butyl), 1.31 (s, 9H, *t*-Butyl), 1.44 (s, 18H, 2 *t*-Butyl), 1.88 (m, 2H), 2.02 (br S, 1H), 2.22 (br S, 1H), 3.72 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.83 (s, 3H, OMe), 3.85 (s, 3H, OMe), 4.32 (d, 1H, H10, $^3J_{H,H}$ = 2.1 Hz), 5.38 (d, 1H, H9, $^3J_{H,H}$ = 1.9 Hz), 6.72-7.07 (m, 14H, H_{arom}). ^{13}C-

{^{1}H}-NMR 75.5 MHz (CD_2Cl_2, 298 K) [DEPT-135] δ (ppm) = 30.95 ($_{t\text{-Butyl}}CH_3$, [CH_3]), 30.98 ($_{t\text{-Butyl}}CH_3$, [CH_3]), 31.09 ($_{t\text{-Butyl}}CH_3$, [CH_3]), 33.58 (C14, C15, C17, [CH_2]), 35.51 ($C_{t\text{-Butyl}}$, [q]), 35.54 ($C_{t\text{-Butyl}}$, [q]), 35.62 ($C_{t\text{-Butyl}}$, [q]), 35.67 ($C_{t\text{-Butyl}}$, [q]), 35.89 (C9, [CH]), 39.63 (C16, [CH]), 39.69 (C13, [CH]), 40.08 ([CH]), 48.72 (C10, [CH]), 49.14 (C11, [CH]), 49.45 (C12, [CH]), 55.75 (OCH_3, [CH_3]), 55.85 (OCH_3, [CH_3]), 55.91 (OCH_3, [CH_3]), 112.99 (C_{arom}, [CH]), 113.11 (C_{arom}, [CH]), 113.21 (C_{arom}, [CH]), 113.56 (C_{arom}, [CH]), 114.45 (C_{arom}, [CH]), 114.70 (C_{arom}, [CH]), 114.72 (C_{arom}, [CH]), 114.83 (C_{arom}, [CH]), 119.09 (C_{arom}, [CH]), 119.22 (C_{arom}, [CH]), 119.65 (C_{arom}, [CH]), 120.14 (C_{arom}, [CH]), 120.26 (C_{arom}, [CH]), 120.89 (C_{arom}, [CH]), 126.45 (C_{arom}, [CH]), 126.67 (C_{arom}, [CH]), 132.67 (d, C_{arom}, $J_{C,P}$ = 2.9 Hz, [q]), 133.15 (d, C_{arom}, $J_{C,P}$ = 3.5 Hz, [q]), 134.13 (br S, C_{arom}, [q]), 134.67 (d, C_{arom}, $J_{C,P}$ = 4.8 Hz, [q]), 135.41 (d, C_{arom}, $J_{C,P}$ = 2.9 Hz, [q]), 142.72 (C_{arom}, [q]), 143.07 (br S, C_{arom}, [q]), 143.21 (br S, C_{arom}, [q]), 143.25 (br S, C_{arom}, [q]), 144.94 (C_{arom}, [q]), 146.27 (C_{arom}, [q]), 146.91 (C_{arom}, [q]), 147.65 (C_{arom}, [q]), 155.74 (C_{arom}, [q]), 156.09 (C_{arom}, [q]), 156.49 (C_{arom}, [q]). ^{31}P-{^{1}H}-NMR 101.3 MHz (CD_2Cl_2, 298 K) δ (ppm) = 137.3 (br S), 138.7 (s). LT-^{31}P-{^{1}H}-NMR 202.5 MHz (Toluol-d_8, 213 K) δ (ppm) = 136.4 (s), 139.4 (s). MS-FAB$^+$ [NBA-matrix]: m/z 1077.5 [M^+] (20), 982.2 [M^+-C_7H_{10}] (15). MP : 165-172°C. Anal. Calcd for $C_{65}H_{74}O_{10}P_2$ • 0.4 CH_2Cl_2: C 70.69; H 6.78, P 5.57. Found: C 70.72, H 7.02, P 5.47.

For Entry 10:

Solvent mixture for column chromatography: CH_2Cl_2:pentane 1:2. Yield: 1.38 g (1.66 mmol, 83.4%) of a white crystalline solid. ^{1}H-NMR 500.1 MHz (CD_2Cl_2, 298 K) δ (ppm) = 2.19 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.30 (s, 6H, CH_3), 2.34 (s, 6H, CH_3), 5.51 (s, 1H, H10), 6.40 (s, 1H, H9), 6.95-7.11 (m, 14H, H_{arom}), 7.24 (d, 2H, H2, H7, $^3J_{H,H}$ = 6.8 Hz), 7.32 (m, 1H, H_{arom}), 7.43 (m, 1H, H_{arom}). ^{13}C-{^{1}H}-NMR 75.5 MHz (CD_2Cl_2, 298 K) [DEPT-135] δ (ppm) = 17.01 (2 [CH_3]), 17.13 (2 [CH_3]), 21.09 (2 [CH_3]), 21.14 (2 [CH_3]), 41.85 (C9, [CH]), 54.55 (C10, [CH]), 117.76 (C_{arom}, [CH]), 117.95 (C_{arom}, [CH]), 120.19 (C_{arom}, [CH]), 124.35 (C_{arom}, [CH]), 124.63 (C_{arom}, [CH]), 125.84 (C_{arom}, [CH]), 125.90 (C_{arom}, [CH]), 126.86 (C_{arom}, [CH]), 128.45

(C_{arom}, [CH]), 130.87 (C_{arom}, [CH]), 130.96 (C_{arom}, [CH]), 131.52 (C_{arom}, [CH]), 131.69 (C_{arom}, [CH]), 134.90 (C_{arom}, [q]), 135.87 (C_{arom}, [q]), 144.85 (C_{arom}, [q]), 145.81 (C_{arom}, [q]), 145.88 (C_{arom}, [q]), 145.97 (C_{arom}, [q]), 146.05 (C_{arom}, [q]), 146.25 (C_{arom}, [q]), 147.68 (C_{arom}, [q]), 147.78 (C_{arom}, [q]), 148.92 (C_{arom}, [q]). ^{31}P-{^{1}H}-NMR 202.5 MHz (CD_2Cl_2, 298 K) δ (ppm) = 140.9 (s). MS-FAB$^+$ [NBA-matrix]: m/z 827.1 [M^+] (80). Anal. Calcd for $C_{52}H_{44}O_6P_2$: C 75.54; H 5.36, P 7.49. Found: C 75.78, H 5.65, P 7.26.

Entry 6:

1,8-Bis-((bis-(2,4,6-trimethylphenyl))phosphito)-9,10-(*exo-cis*-1,2-norbornano)-9,10-dihydroanthracene

In a Schlenk tube 500 mg (1.64 mmol) of the bisphenol is dissolved in 10 ml THF and cooled to -78°C. In another Schlenk tube, 3.298 mmol of the chlorphosphite is dissolved in 20 ml THF and cooled to -78°C. This solution is then cannula transferred into the cool solution of the bisphenol backbone and 0.64 ml (4.6 mmol) NEt_3 is directly added. This suspension is stirred for 72 h at RT and then for 6.5 h at 45°C. The precipitated salts were filtered off using a frit and the solvent is removed under vacuum. The white solid is purified by column chromatography under argon (SiO_2, 10*2 cm).

Solvent mixture for column chromatography: CH_2Cl_2:pentane 1:4. Yield: 772 mg (0.853 mmol, 51.8%) of a white crystalline solid. ^{1}H-NMR 300.1 MHz (CD_2Cl_2, 298 K) δ (ppm) = -0.36 (d, 1H, H17α, $^{2}J_{H,H}$ = 10.5 Hz), 0.28 (d, 1H, H17β, $^{2}J_{H,H}$ = 10.5 Hz), 0.87 (m, 2H), 1.28 (m, 2H), 1.48 (m, 1H), 1.70 (m, 2H), 1.92 (s, 1H), 2.20 (s, 12H, 4CH_3), 2.23 (s, 24H, 8CH_3), 4.21 (d, 1H, H10, $^{3}J_{H,H}$ = 2.8 Hz), 5.07 (d, 1H, H9, $^{3}J_{H,H}$ = 2.9 Hz), 6.81 (d, 8H, H_{arom}, $^{3}J_{H,H}$ = 5.8 Hz), 6.85 (br S, 1H, H_{arom}), 6.90-7.01 (m, 4H, $H_{arom.}$), 7.08 (m, 1H, H_{arom}). ^{13}C-{^{1}H}-NMR 75.5 MHz (CD_2Cl_2, 298 K) [DEPT-135] δ (ppm) = 17.78 ([CH_3]), 17.83 ([CH_3]), 17.91 ([CH_3]), 17.99 ([CH_3]), 20.64 ([CH_3]), 31.02 (C14, [CH_2]), 31.10 (C15, [CH_2]), 33.16 (C17, [CH_2]), 35.22 (C9, [CH]), 39.54 (C16, [CH]), 40.07 (C13, [CH]), 48.61 (C12, [CH]), 49.13 (C11, [CH]), 49.23 (C10, [CH]), 117.62 ($C_{arom,}$ [CH]), 117.80 (C_{arom},

[CH]), 118.14 ($C_{arom,}$ [CH]), 118.32 ($C_{arom,}$ [CH]), 118.99 (C_{arom}, [CH]), 120.16 ($C_{arom,}$ [CH]), 126.09 ($C_{arom,}$ [CH]), 126.38 ($C_{arom,}$ [CH]), 129.73 (C_{arom}, [CH]), 130.47 ($C_{arom,}$ [q]), 130.56 ($C_{arom,}$ [q]), 132.25 (C_{arom}, [q]), 133.92 (C_{arom}, [q]), 134.79 (C_{arom}, [q]), 145.12 ($C_{arom,}$ [q]), 146.73 (C_{arom}, [q]), 147.74 (C_{arom}, [q]), 148.23 (C_{arom}, [q]). ^{31}P-{^{1}H}-NMR 121.5 MHz (CD_2Cl_2, 298 K) δ (ppm) = 138.2 (s), 138,4 (s). MS-FAB$^+$ [NBA-matrix]: m/z 905.4 [M^+] (30), 769.4 [M^+- $C_9H_{11}O$] (83), 633.3 [M^+-2($C_9H_{11}O$)] (20). MP : 155-156°C. Anal. Calcd for $C_{57}H_{62}O_6P_2$: C 75.64; H 6.90, P 6.84. Found: C 75.53, H 6.94, P 6.97.

Entries 7 and 9:

1-(Bis-(2,4-di-*tert*-butylphenyl)phosphito)-8-(bis-(2,4,6-trimethyl-phenyl)phosphito)-triptycene and

1-(2,4,8,10-tetramethyldibenzo[d,f][1,3,2]dioxaphosphepin-6-yloxy)-8-(bis-(2,4-di-*tert*-butylphenyl)phosphito)-triptycene

General procedure. 720 mg (2.51 mmol) 1,8-dihydroxytriptycene is dissolved in 10 ml THF and cooled to -78°C. In another Schlenk tube (2.51 mmol) of the tetra-^{t}Bu-chlorophosphite is dissolved in 10 ml THF and also cooled down to -78°C. This solution is cannula transferred to the cold solution of the bisphenol. After adding 0.97 ml (7.0 mmol) NEt_3, the solution is stirred for 12 h at rt and afterwards for 6.5 h at 45°C oil bath temperature. The precipitated salts were filtered off using a frit and the solvent is removed under vacuum. After drying 1.56 g (2.15 mmol, 85.3%) of a white solid were isolated. It is not necessary to purify the isolated monophosphite. For the synthesis of the respective ligand (entries 7, 9) 750 mg (1.03 mmol) of the monophosphite were dissolved in 10 ml THF and cooled down to -78°C. In another Schlenk tube 1.042 mmol of either the bis-mesitylchlorophosphite or the tetramethyl chlorophosphepin are dissolved in 10 ml THF and also cooled down to -78°C. The solution of the respective P-Cl compound is cannulated to the solution of the previously prepared triptycene monophosphite, and 0.19 ml (1.32 mmol) of NEt_3 were directly added. The white suspension is stirred over night and afterwards for 6.5 h at 45°C. The precipitated salts were

filtered off using a frit and the solvent is removed under vacuum. The solids can be purified using column chromatography under argon. (SiO_2, 8*2 cm).

For entry 7:

Solvent mixture for column chromatography: CH_2Cl_2:pentane 1:3. Yield: 611 mg (0.59 mmol, 57.7%) of a white crystalline solid. ^{1}H-NMR 500.1 MHz (CD_2Cl_2, 298 K) δ (ppm) = 1.16 (s, 9H, *t*-Butyl), 1.28 (s, 9H, *t*-Butyl), 1.29 (s, 9H, *t*-Butyl), 1.37 (s, 9H, *t*-Butyl), 2.17 (s, 9H, 3 CH_3), 2.22 (s, 9H, 3 CH_3), 5.41 (s, 1H, H10), 6.31 (s, 1H, H9), 6.56 (d, 1H, H_{arom}, $^3J_{H,H}$ = 6.8 Hz), 6.74 (dd, 1H, H_{arom}, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,H}$ = 8.3 Hz), 6.79-6.92 (m, 8H, H_{arom}), 7.00-7.08 (m, 4H, H_{arom}), 7.14-7.16 (m, 2H, H_{arom}), 7.21-7.26 (m, 2H, H_{arom}), 7.32 (br S, 2H, H_{arom}), 7.41 (d, 1H, H_{arom}, $^3J_{H,H}$ = 2.1 Hz). ^{13}C-{^{1}H}-NMR 75.5 MHz (CD_2Cl_2, 298 K) [DEPT-135] δ (ppm) = 17.33 ([CH_3]), 17.87 ([CH_3]), 17.94 ([CH_3]), 17.99 ([CH_3]), 18.06 ([CH_3]), 20.75 ([CH_3]), 30.02 ($_{t\text{-Butyl}}CH_3$, [CH_3]), 30.28 ($_{t\text{-Butyl}}CH_3$, [CH_3]), 31.62 (2 $_{t\text{-Butyl}}CH_3$, [CH_3]), 34.72 ($_{t\text{-Butyl}}CH_3$, [CH_3]), 34.77 ($C_{t\text{-Butyl}}$, [q]), 35.12 ($C_{t\text{-Butyl}}$, [q]), 35.30 ($C_{t\text{-Butyl}}$, [q]), 41.85 (C9, [CH]), 54.59 (C10, [CH]), 118.03 (C_{arom}, [CH]), 118.19 (C_{arom}, [CH]), 118.24 (C_{arom}, [CH]), 118.31 (C_{arom}, [CH]), 118.37 (C_{arom}, [CH]), 118.58 (C_{arom}, [CH]), 119.36 (C_{arom}, [CH]), 119.57 (C_{arom}, [CH]), 119.68 (C_{arom}, [CH]), 119.71 (C_{arom}, [CH]), 123.73 (C_{arom}, [CH]), 124.05 (C_{arom}, [CH]), 124.24 (C_{arom}, [CH]), 124.58 (C_{arom}, [CH]), 124.91 (C_{arom}, [CH]), 125.03 (C_{arom}, [CH]), 125.20 (C_{arom}, [CH]), 125.34 (C_{arom}, [CH]), 126.27 (C_{arom}, [CH]), 129.81 (C_{arom}, [CH]), 129.91 (C_{arom}, [CH]), 130.03 (C_{arom}, [CH]), 130.50 (d, $C_{arom,}$ $J_{C,P}$ = 2.8 Hz, [q]), 130.63 (d, $C_{arom,}$ $J_{C,P}$ = 3.3 Hz, [q]), 134.01 (d, $C_{arom,}$ $J_{C,P}$ = 1.7 Hz, [q]), 134.10 (d, $C_{arom,}$ $J_{C,P}$ = 2.1 Hz, [q]), 135.65 (d, $C_{arom,}$ $J_{C,P}$ = 2.2 Hz, [q]), 136.06 (d, $C_{arom,}$ $J_{C,P}$ = 2.8 Hz, [q]), 139.20 ($C_{arom,}$ [q]), 139.24 ($C_{arom,}$ [q]), 139.60 ($C_{arom,}$ [q]), 139.65 ($C_{arom,}$ [q]), 144.49 ($C_{arom,}$ [q]), 145.93 ($C_{arom,}$ [q]), 145.98 ($C_{arom,}$ [q]), 146.36 ($C_{arom,}$ [q]), 146.76 (C_{arom}, [q]), 146.80 (C_{arom}, [q]), 147.40 (C_{arom}, [q]), 147.46 (C_{arom}, [q]), 148.58 (C_{arom}, [q]), 148.76 (C_{arom}, [q]), 149.21 (C_{arom}, [q]), 149.29 (C_{arom}, [q]), 149.40 ($C_{arom,}$ [q]), 149.49 ($C_{arom,}$ [q]). ^{31}P-{^{1}H}-NMR 202.5 MHz (CD_2Cl_2, 298 K) δ (ppm) = 127.6 (s), 139.2 (s). MS-FAB$^+$ [NBA-matrix]: m/z 1027.6 [M^+] (40), 891.5 [M^+-

$C_9H_{11}O$] (37), 821.4 [M^+-$C_{14}H_{21}O$] (15). MP: 103-108°C. Anal. Calcd for $C_{66}H_{76}O_6P_2$ ▪ 0.3 CH_2Cl_2: C 75.64; H 7.33, P 5.88. Found: C 75.40, H 7.35, P 5.83.

For entry 9:

Solvent mixture for column chromatography: CH_2Cl_2:pentane 1:2. Yield: 460 mg (0.461 mmol, 44.7%) of a white crystalline solid. ^{1}H-NMR 500.1 MHz (CD_2Cl_2, 298 K) δ (ppm) = 1.14 (s, 9H, *t*-Butyl), 1.24 (s, 9H, *t*-Butyl), 1.26 (s, 9H, *t*-Butyl), 1.31 (s, 9H, *t*-Butyl), 2.33 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 5.44 (s, 1H, H10), 6.38 (s, 1H, H9), 6.78-7.00 (m, 8H, H_{arom}), 7.06-7.25 (m, 9H, H_{arom}), 7.30 (s, 1H, H_{arom}), 7.35 (m, 2H, H_{arom}). ^{13}C-{^{1}H}-NMR 75.5 MHz (CD_2Cl_2, 298 K) [DEPT-135] δ (ppm) = 17.09 ([CH_3]), 17.14 ([CH_3]), 20.93 ([CH_3]), 29.93 ($_{t\text{-Butyl}}CH_3$, [CH_3]), 30.17 ($_{t\text{-Butyl}}CH_3$, [CH_3]), 31.50 ($_{t\text{-Butyl}}CH_3$, [CH_3]), 31.55 ($_{t\text{-Butyl}}CH_3$, [CH_3]), 34.64 ($C_{t\text{-Butyl}}$, [q]), 35.04 ($C_{t\text{-Butyl}}$, [q]), 35.17 ($C_{t\text{-Butyl}}$, [q]), 41.80 (C9, [CH]), 54.53 (C10, [CH]), 117.76 (C_{arom}, [CH]), 117.91 (C_{arom}, [CH]), 118.22 (C_{arom}, [CH]), 118.35 (C_{arom}, [CH]), 118.45 (C_{arom}, [CH]), 118.72 (C_{arom}, [CH]), 119.02 (C_{arom}, [CH]), 119.24 (C_{arom}, [CH]), 119.66 (C_{arom}, [CH]), 120.05 (C_{arom}, [CH]), 123.81 (C_{arom}, [CH]), 124.00 (C_{arom}, [CH]), 124.26 (C_{arom}, [CH]), 124.47 (C_{arom}, [CH]), 124.69 (C_{arom}, [CH]), 124.91 (C_{arom}, [CH]), 125.32 (C_{arom}, [CH]), 125.42 (C_{arom}, [CH]), 126.23 (C_{arom}, [CH]), 126.49 (C_{arom}, [CH]), 128.42 (C_{arom}, [CH]), 130.55 (d, C_{arom}, $J_{C,P}$ = 1.3 Hz, [q]), 130.70 (d, C_{arom}, $J_{C,P}$ = 1.3 Hz, [q]), 131.38 (d, C_{arom}, $J_{C,P}$ = 3.4 Hz, [q]), 131.50 (C_{arom}, [CH]), 131.60 (C_{arom}, [CH]), 134.82 (C_{arom}, [q]), 135.48 (d, C_{arom}, $J_{C,P}$ = 2.6 Hz, [q]), 136.18 (d, C_{arom}, $J_{C,P}$ = 2.9 Hz, [q]), 139.14 (d, C_{arom}, $J_{C,P}$ = 2.6 Hz, [q]), 139.33 (d, C_{arom}, $J_{C,P}$ = 2.9 Hz, [q]), 144.39 (C_{arom}, [q]), 145.86 (C_{arom}, [q]), 145.98 (C_{arom}, [q]), 146.17 (C_{arom}, [q]), 146.99 (C_{arom}, [q]), 147.07 (C_{arom}, [q]), 147.34 (C_{arom}, [q]), 147.40 (C_{arom}, [q]), 148.40 (C_{arom}, [q]), 148.88 (C_{arom}, [q]), 149.07 (C_{arom}, [q]), 149.17 (C_{arom}, [q]), 149.32 (C_{arom}, [q]), 149.41 (C_{arom}, [q]). ^{31}P-{^{1}H}-NMR 202.5 MHz (CD_2Cl_2, 298 K) δ (ppm) = 126.6 (s), 141.2 (s). MS-FAB$^+$ [NBA-matrix]: m/z 97.5 [M^+] (20), 791.3 [M^+-$C_{14}H_{21}O$] (50), 585.2 [M^+-2($C_{14}H_{21}O$)] (8), 441.3 [$(C_{14}H_{21}O)_2P$] (35).

MP: 142-149°C. Anal. Calcd for $C_{64}H_{70}O_6P_2$: C 77.09; H 7.08, P 6.21. Found: C 76.90, H 7.35, P 6.10.

Entry 12:

1,8-Bis-(2,4,8,10-tetramethyldibenzo[d,f][1,3,2]dioxaphosphepin-6-yloxy)-9,10-ethano-9,10-dihydroanthracene

In a Schlenk tube 776 mg (3.26 mmol) of the ethano-bridged bisphenol is dissolved in 10 ml THF and cooled to -78°C. In another Schlenk tube 2.048 g (6.686 mmol) of the tetramethyl chlorophosphepin are dissolved in 20 ml THF and also cooled down to -78°C. This solution is cannulated into the cool bisphenol solution and 1.27 ml (9.13 mmol) NEt_3 are directly added. The suspension is stirred for 72 h at rt and subsequently for 7 h at 45°C oil bath temperature. The precipitated salts were filtered off using a frit and the solvent is removed under vacuum. The pale yellow solid is purified by column chromatography under argon (SiO_2, 8*2 cm, CH_2Cl_2:pentane 1:2). Yield: 1.32 g (1.62 mmol, 52.0%) of a white crystalline solid. ^{1}H-NMR 250.1 MHz (CD_2Cl_2, 298 K) δ (ppm) = 1.70 (s, 4H, ethano-bridge), 2.23 (s, 12H, CH_3), 2.32 (s, 12H, CH_3), 4.40 (s, 1H, H10), 5.38 (s, 1H, H9), 6.94-7.10 (m, 14H, H_{arom}). ^{13}C-{^{1}H}-NMR 125.8 MHz (CD_2Cl_2, 298 K) [DEPT-135] δ (ppm) = 17.03 (2 [CH_3]), 17.06 (2 [CH_3]), 21.11 (4 [CH_3]), 26.15 (C11, [CH_2]), 26.72 (C12, [CH_2]), 31.79 (C9, [CH]), 44.86 (C10, [CH]), 118.20 (C_{arom}, [CH]), 118.30 (C_{arom}, [CH]), 120.00 (C_{arom}, [CH]), 126.94 (C_{arom}, [CH]), 128.43 (C_{arom}, [CH]), 130.92 (C_{arom}, [CH]), 131.61 (C_{arom}, [CH]), 131.65 (C_{arom}, [CH]), 134.33 (br S, $C_{arom,}$ [q]), 134.79 (br S, $C_{arom,}$ [q]), 145.96 (br S, $C_{arom,}$ [q]), 147.12 ($C_{arom,}$ [q]), 147.17 ($C_{arom,}$ [q]). ^{31}P-{^{1}H}-NMR 101.2 MHz (CD_2Cl_2, 298 K) δ (ppm) = 142.4 (s). MS-FAB$^+$ [NBA-matrix]: m/z 778.5 [M^+] (30), 750.5 [M^+-C_2H_4] (15). MP : 239-242°C. Anal. Calcd for $C_{48}H_{44}O_6P_2$ • 0.2 CH_2Cl_2: C 72.75; H 5.62, P 7.78. Found: C 72.87, H 5.92, P 7.59.

Entry 11:

1,8-Bis-(2,4,8,10-tetramethyldibenzo[d,f][1,3,2]dioxaphosphepin-6-yloxy)-9,10-cyclopentano-9,10-dihydroanthracene

The crude chloro-phosphite in 10ml THF was added dropwise to a solution of 1,8-dihydroxy-9,10-cyclopentano-9,10-dihydroanthracene (556mg, 2mmol) in 10ml THF at –40ºC, and Et_3N (0.7ml, 5.1mmol) was added subsequently. The resulting white suspension was stirred at room temperature overnight. After filtration and evaporation of all the volatiles, the residue was extracted with toluene and filtered through a short column of Al_2O_3. The product was obtained by chromatography (3×30ml, Al_2O_3), eluted with PE/ether as white foam-type solid. Yield: 1.2 g, 73%. ^{1}H-NMR (300HMz, $CDCl_3$): δ 6.89-7.28 (m, 14H, Ar), 5.23 (s, 2H), 4.14 (s, 2H), 2.29 (m, 2H), 2.21 (m, 4H), 1.53 (s, 12H, CH_3), 1.43 (m, 12H, CH_3); ^{31}P {^{1}H}NMR ($CDCl_3$,): δ 140.8, 140.7. ^{13}C{^{1}H}NMR ($CDCl_3$): δ 117.4-148.7 (Ar), 78.4-76.6 (CH), 49.5, 45.2 (-$(CH_2)_3$-CH), 36.0, 30.2, 27.5 (CH_2), 20.8 (CH_3),16.7 (CH_3). IR (KBr, cm^{-1}): 1587 (m), 1468 (s), 1237 (m), 1207 (s), 1184 (s), 1116 (s), 1151 (s), 1079 (s), 1021 (m), 872 (s), 802 (s), 786 (s), 765 (m). Mp: 189-190 ºC. FAB-MS (m/z): 819.2 [M^+]; Anal. Calcd for $C_{51}H_{48}O_6P_2$: C 74.84, H 5.91, P 7.57. Found: C 75.38, H 6.19, P 6.78.

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