Title: CLICK-BINOL-PHOSPHORIC ACID CATALYSTS IN INTRAMOLECULAR ENANTIOSELECTIVE OXIDATIVE C-H-BOND FUNCTIONALIZATION

Author: Sebastian Stockerl Daniel Gutiérrez Olga García Mancheño

PII: S1381-1169(16)30378-8
DOI: http://dx.doi.org/doi:10.1016/j.molcata.2016.09.006
Reference: MOLCAA 10030

To appear in: *Journal of Molecular Catalysis A: Chemical*

Received date: 6-6-2016
Revised date: 2-9-2016
Accepted date: 3-9-2016

Please cite this article as: Sebastian Stockerl, Daniel Gutiérrez, Olga García Mancheño, CLICK-BINOL-PHOSPHORIC ACID CATALYSTS IN INTRAMOLECULAR ENANTIOSELECTIVE OXIDATIVE C-H-BOND FUNCTIONALIZATION, Journal of Molecular Catalysis A: Chemical http://dx.doi.org/10.1016/j.molcata.2016.09.006

Journal of Molecular Catalysis A: Chemical

CLICK-BINOL-PHOSPHORIC ACID CATALYSTS IN INTRAMOLECULAR ENANTIOSELECTIVE OXIDATIVE C-H-BOND FUNCTIONALIZATION

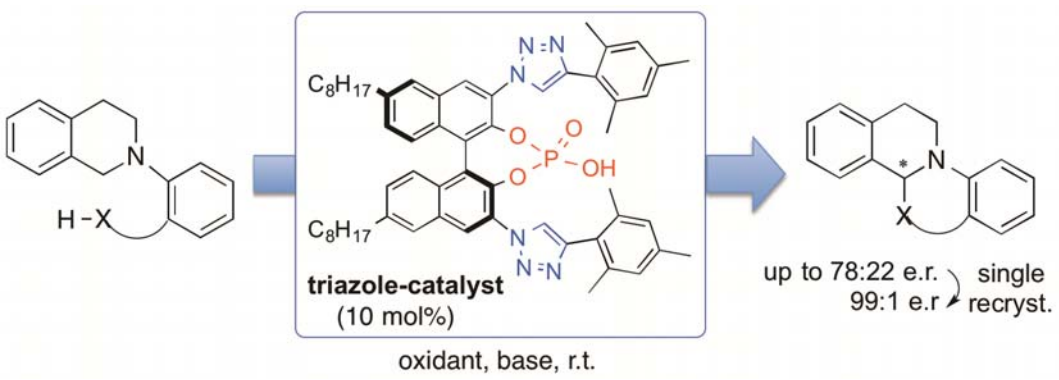
Sebastian Stockerl,[1] Daniel Gutiérrez,[1] Olga García Mancheño*[1,2]

[1] Institute for Organic Chemistry, University of Regensburg, 93053 Regensburg.

[2] Straubing Center of Science for Renewable Resources, 94315 Straubing.

*corresponding author: olga.garcia-mancheno@ur.de

Graphical abstract



Research highlights:

► synthesis of a new family of C2-symmetric triazole-phosphoric acid catalysts.

► intramolecular asymmetric C-H bond functionalization of N-aryl substituted tetrahydroisoquinolines.

► important effects of the triazoles and the regiomeric structures for optimal enantioselectivity.

► π−π vs. cooperative π−π and triazole-substrate interactions.

Abstract:

Counteranion-catalysis represents an appealing but challenging approach for the development of enantioselective oxidative C-H bond functionalization reactions. In this work, a new family of 3,3′-triazolyl BINOL-derived phosphoric acids was synthesized and employed in the intramolecular asymmetric C-H bond functionalization of *N*-aryl substituted tetrahydroisoquinolines. As previously reported with related structures, the presence of the triazole groups on the catalysts was key to attain enantioselectivity. Our study also shows the importance of choosing the appropriate regioisomeric triazole groups at the BINOL backbone to achieve a more efficient chirality transfer. Moderate enantiomeric ratios were obtained with the *N*-benzamide substrates, whereas the change of the nature of the nucleophile fragment was translated to a dramatic loss of the enantioselectivity. Therefore, it can be foreseen that there is a need for designing further superior catalyst structures to develop future counter-anion organocatalyzed asymmetric C-H bond functionalization reactions.

Keywords: C-H functionalization, oxidation, organocatalysis, enantioselective, heterocycles

Introduction

In the last few years, selective C–H bond functionalization has attracted great interest, such as the cross-dehydrogenative coupling (CDC) coined by C.-J. Li,[1] since it offers not only more straightforward approaches but also new possibilities in synthetic chemistry.[2,3] The growing demand on innovative and simple direct C–H bond transformations has led to important breakthroughs in the chemistry of oxidative C(sp^3)–H functionalization.[2-4] Our research group has also contributed to this field by developing novel, mild oxidative reactions for the synthesis of valuable (bioactive)heterocycles.[5] Thus, we have recently introduced the use of TEMPO oxoammonium salts (T^+X^-)[6,7] as alternative mild and efficient oxidants for C–C bond forming reactions of C(sp^3)–H bonds, allowing in some cases to overcome certain substrate or product incompatibilities with the classically used oxidants. Additionally, recent efforts towards the development of enantioselective C(sp^3)–H bond functionalization have been made.[8] Besides the initially explored metal-catalyzed reactions,[9] organocatalysis represents a powerful approach.[10]

Most of the reported examples rely on covalent amino-catalysis, which limit its applicability to carbonyl compounds. Considering that the key intermediate in this type of transformations is an ionic species such as an iminium ion, counteranion organocatalysis has recently been embraced (Scheme 1).[11] The first intramolecular C-H functionalization approach was based on the use of chiral phosphoric acids (PA)[12] to generate *in situ* the active phosphate catalyst responsible for the formation of a chiral close ion-pair and the enantioselectivity control.[13] Shortly after, the combination of metal-photocatalysis and a chiral thiourea as anion-binding catalyst was utilized for the intermolecular functionalization of *N*-aryl tetrahydroisoquinolines (THIQs).[14]

Despite of the tremendous interest that counter**-**anion catalysis is currently evoking in the synthetic scientific community,[11] a still limited number of effective catalyst motifs is available. Aiming at providing alternative novel structures, we recently developed a modular strategy to introduce 1,2,3-triazole moieties into BINOL derivatives (Click-BINOLs), which were employed as ligands in asymmetric Lewis acid metal catalysis (Figure 1, bottom).[15] Later on, the group of Toste[13] reported the performance of phosphoric acids derived from the regioisomeric 3,3'-triazolyl BINOLs (Figure 1, top-right) as superior organocatalysts in the enantioselective C–H bond functionalization of tetrahydroisoquinoline-*N*-benzamides as shown in Scheme 1.[16] As part of our ongoing research program devoted to the development of asymmetric C-H bond functionalization reactions, we herein described our latest results in the area of counteranion-catalysis using a new family of chiral Click-BINOL-based phosphates (Figure 1, top-left).

Experimental

General Information

^{1}H and **^{13}C NMR** spectra were recorded in $CDCl_3$ (reference signals:[17] ^{1}H = 7.26 ppm, ^{13}C = 77.16 ppm, $CDCl_3$) on a *Bruker ARX-300* and a *Varian AV*-300, 400 or 600 MHz. Chemical shifts (δ) are given in ppm and spin-spin coupling constants (J) are given in Hz. Analytical thin layer chromatography was performed using silica gel 60 F_{254} and a solution of $KMnO_4$ or phosphomolybdic acid served as staining agent. Column chromatography was performed on silica gel 60 (0.040-0.063 mm). Exact masses (**HRMS**) were recorded on an *Agilent Q-TOF 6540 UHD* spectrometer (samples in CH_3OH as solvent) using electrospray (ES) or chemical (CI) ionization techniques. Chiral High Pressure Liquid Chromatography (**HPLC**) analyses were performed on an Agilent 1200 series instrument.

Synthesis of PA Catalysts:

Synthesis of alkynes:

2,4,6-Triisopropylbenzaldehyde[18]

A stirring solution of 1-bromo-2,4,6-triisopropylbenzene (5.25 ml, 20.0 mmol, 1.0 eq.) in dry THF (40 ml) was cooled to -78 °C. *n*-BuLi (1.6 M in hexane; 13.8 ml, 22.0 mmol, 1.1 eq.) was added over 20 min. After stirring for additional 20 min, dry DMF (1.8 ml, 22.0 mmol, 1.1 eq.) was added slowly. The reaction mixture was stirred 15 min at -78 °C, allowed to warm to -10 °C and quenched with H_2O (20 ml). The aqueous layer was extracted with ether (3 x 20 ml) and dried over Na_2SO_4. Purification by column chromatography using PE/EtOAc (10:1) as eluent gave the title compound (3.6 g, 15.6 mmol, 78%) as a colorless oil. $\boldsymbol{R_f}$ = 0.66 (10:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 10.66 (s, 1H), 7.11 (s, 2H), 3.60 (sept., *J* = 6.8 Hz, 2H), 2.92 (sept., *J* = 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.26 (d, *J* = 6.9 Hz, 6H). The analytical data are in accordance with the literature.

2,4,6-Triisopropylphenyl acetylene[19]

A stirring, degassed solution of triphenylphosphine (15.9 g, 60.0 mmol, 4.0 eq.) and carbon tetrabromide (10.2 g, 30.0 mmol, 2.0 eq.) in dry dichloromethane (200 ml) was cooled to 0 °C and 2,4,6-triisopropylphenylbenzaldehyde (3.6 g, 15.0 mmol, 1.0 eq.) was added. The reaction mixture was allowed to warm to rt overnight. The solids were filtered off and the solvent was removed under reduced pressure. PE (400 ml) was added and after trituration the solution was filtered over a silica plug using PE as eluent. The solvent was removed under reduced pressure and the crude intermediate was dissolved in dry THF (50 ml). The reaction mixture was cooled to -78 °C, *n*-BuLi (1.6 M in hexane; 11.8 ml, 18.75 mmol, 1.25 eq.) was added dropwise. After 1 h, the reaction mixture was allowed to warm to rt and quenched with sat. aq. NH_4Cl (30 ml). The aqueous layer was extracted with PE (3 x 40 ml). The solvent was removed under reduced pressure and the crude alkyne was filtered over a silica plug using PE as eluent. A small crystal of hydrochinone was added and the solvent was removed to give the title compound (2.5 g, 10.9 mmol, 73%) as a pale purple oil. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 6.98 (s, 2H), 3.54 (sept., *J* = 6.9 Hz, 2H), 3.42 (s, 1H), 2.89 (sept., *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 6.8 Hz, 6H), 1.25 (d, *J* = 6.9 Hz, 6H). The analytical data are in accordance with the literature.

1-((3*r*,5*r*,7*r*)-Adamantan-1-yl)ethan-1-one[20]

A stirring solution of adamantyl carboxylic acid (1.8 g, 10.0 mmol, 1.0 eq.) in thionyl chloride (4.0 ml, 55.1 mmol, 5.51 eq.) was refluxed for 4 h. The excess of thionyl chloride was removed under reduced pressure to give the 1-adamantanecarbonyl chloride. Diethylmalonate (2.5 g, 2.4 ml, 15.5 mmol, 1.55 eq.) in PE (5 ml) was added dropwise to a stirring solution of sodium (0.35 g, 15.5 mmol, 1.55 eq.) in PE (10 ml). After complete consumption of sodium, carbonyl chloride in PE (5 ml) was added slowly and the resulting reaction mixture was stirred overnight at rt. Distilled water

(20 ml) was added, the organic layer was separated and concentrated under vacuum. Acetic acid (8 ml), water (2.4 ml) and sulfuric acid (0.8 ml) were added and the reaction mixture was refluxed for 6 h. The solution was poured into ice water (60 ml) for crystallization. The resulting crystals were filtered off and dried under vacuum to give the title compound (0.8 g, 4.8 mmol, 48%) as white needles. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 2.07 (s, 3H), 2.04 – 2.01 (m, 3-H), 1.78 (d, *J* = 2.8 Hz, 6H), 1.73 - 1.61 (m, 6H). The analytical data are in accordance with the literature.

(3*r*,5*r*,7*r*)-1-Ethynyladamantane[21]

A stirring solution of diisopropyl amine (0.8 ml, 5.7 mmol, 1.19 eq.) in dry THF (7 ml) was cooled to -78 °C followed by dropwise addition of *n*-BuLi (1.6 M in hexane; 3.25 ml, 5.2 mmol, 1.08 mmol) and was stirred for 1 h. Adamantyl methyl ketone (0.85 g, 4.8 mmol, 1.0 eq.) in dry THF (3 ml) was added at -78 °C to the LDA solution. After 1 h, chloro diethyl phosphate (0.86 g, 5.0 mmol, 1.05 eq.) was added dropwise. The resulting reaction mixture was allowed to warm to rt and stirred for 3 h. A second LDA solution was prepared as already described from diisopropyl amine (1.4 ml, 9.5 mmol, 1.98 eq.) in THF (15 ml) and *n*-BuLi (1.6 M in hexane; 6.4 ml, 10.3 ml, 2.15 eq.) at -78 °C. After 3 h the reaction mixture was added to the second LDA solution at -78 °C, allowed to warm to rt and stirred overnight. The reaction mixture was quenched with H_2O (20 ml) and the aqueous layer was extracted with PE (4 x 15 ml). The combined organic layers were washed with ice-cold 1 M HCl (2 x 15 ml), sat. aq. $NaHCO_3$ (2 x 20 ml) (pH should be 9) and dried over Na_2SO_4. The solution was filtered over Celite and the solvent was removed under reduced pressure. Purification by filtration over a silica plug using PE as eluent gave the title compound (0.44 g, 2.8 mmol, 58%) as a colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 2.10 (s, 1H), 1.99 – 1.93 (m, 3H), 1.89 (d, *J* = 2.8 Hz, 6H), 1.69 (t, *J* = 3.1 Hz, 6H)). The analytical data are in accordance with the literature.

4-Bromo-2,6-diisopropylaniline[22]

A solution of Br_2 (2.1 mL, 41.0 mmol, 1.05 eq.) in CH_2Cl_2/MeOH (100 mL, 1:1 v/v) was added to a stirring solution of 2,6-diisopropylaniline (7.4 mL, 39.0 mmol, 1.0 eq.) in CH_2Cl_2/MeOH (200 mL, 1:1 v/v) at r.t. over 2 h. The orange-red solution was stirred for 1 day. The solvents were evaporated and the resultant pink solid was washed with PE and further recristallized from CH_2Cl_2/PE to give the title compound as light orange-red solid (7.8 g, 28.1 mmol, 72%). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 10.08 (s, 2H), 7.36 (s, 2H), 3.80 - 3.62 (m, 2H), 1.29 (d, *J* = 6.7 Hz, 12H). The analytical data are in accordance with the literature.

5-Bromo-2-iodo-1,3-diisopropylbenzene[23]

To a solution of 4-bromo-3,5-dimethylaniline (8.0 g, 40 mmol, 1.0 eq.) in aq. H_2SO_4 (360 mL, 6.0 M) at –15 °C, a solution of $NaNO_2$ (5.6 g, 80 mmol, 2.0 eq.) in H_2O (32 mL) was added dropwise over a period of 20 min. The resulting mixture was stirred at –15 °C for an additional 15 min. Then, a solution of KI (16.6 g, 100.0 mmol, 2.5 eq.) in H_2O (320 mL) was slowly added in portions to the

mixture over a period of 25 min. The reaction mixture was stirred at -10 °C for 30 min, then stirred at 0 °C for 4 h. After the mixture was stirred overnight at room temperature, the resulting mixture was neutralized by adding Na_2CO_3. The mixture was subsequently extracted with Et_2O (2 x 200 mL). The combined organic layers were washed with H_2O (200 mL), aq. Na_2SO_3 (1 M, 2 x 100 mL), aq. NaOH (2.5 M, 2 x 100 mL) and H_2O (100 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography using PE as eluent, providing the title compound (6.4 g, 22.4 mmol, 56%) as colorless oil. The analytical data are in accordance with the literature.

((4-Bromo-2,6-diisopropylphenyl)ethynyl)trimethylsilane[23]

$PdCl_2(PPh_3)_2$ (0.13 g, 0.19 mmol, 1.2 mol%), CuI (72 mg, 0.38 mmol, 2.4 mol%) and H_2O (0.5 ml, 27.0 mmol, 1.7 eq.) were added to a solution of 5-bromo-2-iodo-1,3-diisopropylbenzene (5.8 g, 15.8 mmol, 1.0 eq.) and trimethylsilylacetylene (4.1 g, 22.0 mmol, 1.4 eq.) in degassed piperidine (30 mL) at 0 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C for 1 h and for an additional 2 h at r.t. After filtration over Celite, the solvent was removed under reduced pressure. The residue was dissolved in 1 M HCl (30 ml) and Et_2O (30 ml). The organic layer was washed with brine (2 x 20 ml), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography using PE as an eluent to give the title compound (2.5 g, 7.4 mmol, 47%) as colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.23 (s, 2H), 3.47 (sept., *J* = 6.8 Hz, 2H), 1.25 (d, *J* = 6.9 Hz, 12H), 0.28 (s, 9H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 147.9, 127.7, 127.2, 122.1, 104.9, 94.1, 33.5, 22.9, 0.0. **HRMS** (EI): *m/z* $[M]^{+\cdot}$ calcd for $C_{17}H_{25}BrSi^{+\cdot}$: 336.0909; found: 336.0894.

5-Bromo-2-ethynyl-1,3-diisopropylbenzene[23]

K_2CO_3 (3.0 g, 21.0 mmol, 2.8 eq.) was added to a solution of ((4-bromo-2,6-diisopropylphenyl) ethynyl)trimethylsilane (2.5 g, 7.4 mmol, 1.0 eq.) in dry MeOH (25 mL) under an argon atmosphere and the mixture was stirred at 40 °C for 24 h. Sat. aq. NH_4Cl solution (100 mL) and pentane (100 mL) were added to the mixture and the layers were separated. The organic layer was washed with H_2O (2 x 50 ml), dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification by column chromatography using PE as an eluent gave the title compound (1.5 g, 4.7 mmol, 64%) as colorless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.22 (s, 2H), 3.44 (sept., *J* = 6.8 Hz, 2H), 3.07 (s, 1H), 1.21 (d, *J* = 6.8 Hz, 12H)**. ^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 148.1, 127.9, 127.5, 121.1, 83.6, 77.2, 33.5, 22.9. **HRMS** (EI): *m/z* $[M]^{+\cdot}$ calcd for $C_{14}H_{17}Br^{+\cdot}$: 264.0514; found: 264.0510.

Introduction of the side-chain:

(*S*)-6,6'-Dibromo-[1,1'-binaphthalene]-2,2'-diol (**6-Br-BINOL)**[24]

(*S*)-BINOL (7.20 g, 25.0 mmol, 1.0 eq.) was suspended in CH_2Cl_2 (250 mL) at -78 °C. A solution of Br_2 (3.9 mL, 34.0 mmol, 1.4 eq.) in CH_2Cl_2 (40 mL) was added dropwise to the reaction (over 20-30 min) and stirred further 15 min at -78 °C. The mixture was then let to reach r.t. and reacted until full conversion was observed by TLC (aprox. 3 h). A sat. aq. solution of $Na_2S_2O_3$ (50 mL) was added and the aqueous layer extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Recrystallization from CH_2Cl_2/pentane gave the title compound as a white solid (10.34 g, 23.3 mmol, 93%). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.03 (d, *J* = 1.9 Hz, 2H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.45 – 7.35 (m, *m* 4H), 6.94 (d, *J* = 9.0 Hz, 2H), 5.00 (bs, 2H). **^{13}C-NMR** (75MHz, $CDCl_3$) δ[ppm]: 153.0, 131.9, 130.8, 130.7, 130.6, 130.4, 125.9, 119.0, 118.0, 110.7. The analytical data are in accordance with the literature.

(*S*)-6,6'-Dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (7)[25]

A stirring solution of NaH (60 % in mineral oil, 1.5 g, 37.5 mmol, 2.5 eq.) in a mixture of THF-DMF (2:1, 45 ml) was cooled to 0 °C. (*S*)- 6-Br-BINOL (6.7 g, 15.0 mmol, 1.0 eq.) in THF (10 ml) was added dropwise and the resulting solution was stirred at rt for 1 h. Chloro(methoxy)methane (4.2 g, 52.5 mmol, 3.5 eq.) was added and the reaction mixture was stirred at rt for 4 h. The solution was quenched with H_2O (50 ml) and extracted with EtOAc (3 x 50 ml). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Recrystallization from MeOH gave the title compound (7.1 g, 13.3 mmol, 89%) as a yellow solid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ[ppm]: 8.03 (d, *J* = 1.9 Hz, 2H), 7.86 (d, *J* = 9.1 Hz, 2H), 7.59 (d, *J* = 9.1 Hz, 2H), 7.29 (dd, *J* = 9.0, 2.0 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 5.09 (d, *J* = 6.9 Hz, 2H), 4.98 (d, *J* = 6.9 Hz, 2H), 3.16 (bs, 6H). The analytical data are in accordance with the literature.

***General procedure A:* Grignard reaction**

A stirring solution of dibromo-MOM-BINOL **132** (1.0 eq.) and $PdCl_2$(dppf) (5 mol%) in THF (200 ml) was cooled to 0 °C. *n*-Alkyl-MgX (5 eq.) was added dropwise and the reaction mixture was refluxed for 3 h. The solution was allowed to cool to room temperature, was quenched with sat. aq. NH_4Cl (150 ml) and was extracted with EtOAc (3 x 100 ml). The combined organic layers were washed with brine (100 ml), dried over Na_2SO_4 and the solvent was removed under reduced pressure. Purification by column chromatography using PE/EtOAc as eluent gave desired products.

(*S*)-2,2'-Bis(methoxymethoxy)-6,6'-dioctyl-1,1'-binaphthalene (8)[13]

Following the *General Procedure A*, subjection of dibromo-MOM-BINOL **7** (6.9 g, 13.0 mmol, 1.0 eq.) and *n*-Oct-MgBr (2.0 M in Et_2O, 32.5 ml, 65.0 mmol, 5 eq.), provided after purification by column chromatography [PE/EtOAc (5:1)] the title compound (7.6 g, 12.7 mmol, 98%) as a yellow oil. R_f = 0.52 (5:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ[ppm]: 7.86 (d, *J* = 9.0 Hz, 2H),

7.62 (s, 2H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.07 (s, 4H), 5.04 (d, *J* = 6.7 Hz, 2H), 4.94 (d, *J* = 6.7 Hz, 2H), 3.13 (s, 6H), 2.72 - 2.68 (m, 4H), 1.70 - 1.60 (m, 4H), 1.36 - 1.20 (m, 20H), 0.89 - 0.85 (m, 6H). The analytical data are in accordance with the literature.

(*S*)-2,2'-Bis(methoxymethoxy)-6,6'-didodecyl-1,1'-binaphthalene (9)[26]

Following the *General Procedure A*, subjection of dibromo-MOM-BINOL **7** (1.8 g, 3.3 mmol, 1.0 eq.) and *n*-dodecyl-MgBr (1.5 M in Et_2O, 11 ml, 16.5 mmol, 5 eq.), provided after purification by column chromatography [PE/EtOAc (10:1)] the title compound (2.0 g, 2.8 mmol, 85%) as a yellow oil. $\boldsymbol{R_f}$ = 0.53 (10:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.99 (d, *J* = 9.0 Hz, 2H), 7.79 (s, 2H), 7.76 - 7.64 (m, 2H), 7.42 - 7.18 (m, 4H), 5.17 (d, *J* = 6.6 Hz, 2H), 5.08 (d, *J* = 6.5 Hz, 2H), 3.27 (s, 6H), 2.88 (s, 4H), 1.86 (s, 4H), 1.64 – 1.43 (m, 36H), 1.10 (d, *J* = 5.1 Hz, 6H). The analytical data are in accordance with the literature.

(*S*)-2,2'-Bis(methoxymethoxy)-6,6'-dioctadecyl-1,1'-binaphthalene (10)

Following the *General Procedure A*, subjection of dibromo-MOM-BINOL **7** (1.8 g, 3.3 mmol, 1.0 eq.) and *n*-octadecyl-MgCl (0.5 M in Et_2O, 33 ml, 16.5 mmol, 5 eq.), provided after purification by column chromatography [PE/EtOAc (10:1)] the title compound (2.9 g, 3.2 mmol, 99%) as a yellow oil. $\boldsymbol{R_f}$ = 0.44 (10:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.88 (d, *J* = 9.0 Hz, 2H), 7.64 (s, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.09 (s, 4H), 5.07 (d, *J* = 6.4 Hz, 2H), 4.98 (d, *J* = 6.4 Hz, 2H), 3.15 (s, 6H), 2.78 - 2.66 (m, 4H), 1.80 - 1.61 (m, 4H), 1.27 (bs, 60H), 0.89 (t, *J* = 6.7 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 152.1, 138.6, 132.5, 130.1, 128.9, 128.8, 128.0, 126.2, 125.6, 121.6, 117.5, 117.4, 95.5, 55.9, 55.8, 35.9, 32.0, 31.4, 29.8, 29.7, 29.6, 29.5, 29.4, 22.7, 14.2. **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd for $C_{60}H_{94}O_4$ + Na: 901.7044; found: 901.7035.

***General Procedure B:* Synthesis of Diazido-MOM-BINOLs**[15a]

To a magnetically stirred solution of the corresponding MOM-BINOL (4.50 mmol, 1.00 eq.) and TMEDA (2.09 g, 18.00 mmol, 4.00 eq.) in Et_2O (100 ml), *n*-BuLi (1.6 M in pentane, 7.7 ml, 12.38 mmol, 2.75 eq.) was added dropwise at 0 °C. The reaction mixture was allowed to stir at room temperature for 1 h and was cooled to 0 °C again. Then, TsN_3 (2.66 g, 13.50 mmol, 3.00 eq.) was added dropwise and the reaction mixture was kept at 0 °C. After 1 h, the cooling bath was removed and the solution was stirred at room temperature for 18 h. The reaction mixture was diluted with water (20 ml) and aqueous layer was extracted with CH_2Cl_2 (3 x 40 ml). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The products were obtained by column chromatography on silica gel using petroleum ether (PE)/EtOAc/CH_2Cl_2 (30:2:1 → 20:2:1) as eluent.

(*S*)-3,3'-Diazido-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (4)[15a]

Following the *General Procedure B*, subjection of (*S*)-MOM-BINOL (1.66 g, 4.5 mmol, 1.0 eq.) with subsequent purification by column chromatography using PE/EtOAc/CH_2Cl_2 (30:2:1 → 20:2:1) as eluent gave the title compound (1.60 g, 3.5 mmol, 78%) as a brown solid. R_f = 0.42 (30:2:1) (SiO_2, PE/EtOAc/CH_2Cl_2). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ[ppm]: 7.82 (d, *J* = 8.2 Hz, 2H), 7.68 (s, 2H), 7.43 (ddd, *J* = 11.7, 5.8, 2.4 Hz, 2H), 7.25-7.21 (m, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 4.87 (d, *J* = 5.8 Hz, 2H), 4.76 (d, *J* = 5.8 Hz, 2H), 2.65 (bs, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 145.7, 133.1, 131.3, 130.8, 127.2, 126.7, 126.4, 126.0, 126.0, 117.7, 98.9, 56.4. The analytical data are in accordance with the literature.

(*S*)-3,3'-Diazido-2,2'-bis(methoxymethoxy)-6,6'-dioctyl-1,1'-binaphthalene (11)

Following the *General Procedure B*, subjection of dioctyl-MOM-BINOL **8** (7.6 g, 12.7 mmol, 1.0 eq.) with subsequent purification by column chromatography using PE/EtOAc/CH_2Cl_2 (30:2:1) as eluent gave the title compound (8.1 g, 11.9 mmol, 94%) as a brown oil. R_f = 0.63 (20:2:1) (SiO_2, PE/EtOAc/CH_2Cl_2). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.65 (s, 2H), 7.60 (s,2H), 7.12 (s, 4H), 4.89 (dd, *J* = 5.8, 1.0 Hz, 2H), 4.78 (dd, *J* = 5.8, 1.0 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 4H), 2.69 (s, 6H), 1.77 - 1.64 (m, 4H), 1.30 (bs, 20H), 0.95 - 0.85 (m, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 145.1, 145.1, 140.7, 133.0, 131.1, 129.8, 127.6, 127.2, 126.3, 125.1, 117.2, 98.9, 56.4, 35.9, 32.0, 31.9, 31.2, 29.8, 29.7, 29.5, 29.4, 29.3, 22.8, 22.7, 22.7, 14.1, 11.5. **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd for $C_{40}H_{52}N_6O_4$ + Na: 703.3942; found: 703.3940.

3,3'-Diazido-2,2'-bis(methoxymethoxy)-6,6'-didodecyl-1,1'-binaphthalene (12)

Following the *General Procedure B*, subjection of dodecyl-MOM-BINOL **9** (2.0 g, 2.8 mmol, 1.0 eq.) with subsequent purification by column chromatography using PE/EtOAc/CH_2Cl_2 (30:2:1) as eluent gave the title compound (2.1 g, 2.7 mmol, 99%) as a brown oil. R_f = 0.50 (30:2:1) (SiO_2, PE/EtOAc/CH_2Cl_2). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.88- 7.82 (m, 2H), 7.60 (d, *J* = 3.2 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.09 - 7.04 (m, 2H), 5.24 - 4.63 (m, 4H), 2.79 - 2.60 (m, 4H), 2.47 (s, 6H), 1.67 – 1.60 (m, 4H), 1.32 – 1.23 (m, 36H), 0.91 - 0.78 (m, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 152.2, 152.1, 146.2, 144.6, 140.5, 138.7, 138.6, 135.6, 133.3, 133.0, 132.9, 132.4, 131.2, 130.3, 130.1, 129.8, 129.3, 128.7, 128.3, 127.9, 127.6, 127.3, 126.2, 126.0, 125.5, 125.4, 125.1, 121.6, 120.0, 117.5, 117.1, 116.8, 116.5, 98.9, 95.5, 95.1, 70.4, 56.5, 56.4, 55.9, 55.8, 35.8, 31.9, 31.3, 31.2, 31.2, 30.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 22.7, 21.7, 21.6, 18.6, 14.1, 13.4. **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd for $C_{48}H_{68}N_6O_4$ + Na: 815.5194; found: 815.5187.

3,3'-Diazido-2,2'-bis(methoxymethoxy)-6,6'-dioctadecyl-1,1'-binaphthalene (13)

Following the *General Procedure B*, subjection of octadecyl-MOM-BINOL **10** (2.9 g, 3.2 mmol, 1.0 eq.) with subsequent purification by column chromatography using PE/EtOAc/CH_2Cl_2 (30:2:1) as eluent gave the title compound (2.2 g, 2.3 mmol, 70%) as a brown oil. R_f = 0.38 (30:2:1) (SiO_2, PE/EtOAc/CH_2Cl_2). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.89 - 7.83 (m, 2H), 7.62 - 7.55 (m, 2H), 7.41

(d, *J* = 8.0 Hz, 2H), 7.07 (s, 2H), 4.84 (d, *J* = 5.8 Hz, 2H), 4.73 (d, *J* = 5.9 Hz, 2H), 2.77 - 2.67 (m, 4H), 2.65 (s, 6H), 1.66 (s, 4H), 1.25 (bs, 60H), 0.88 (t, *J* = 6.7 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 145.0, 140.8, 132.9, 131.0, 130.3, 129.7, 127.6, 127.1, 126.3, 125.0, 117.1, 98.9, 56.4, 35.9, 32.0, 31.1, 29.7, 29.6, 29.5, 29.4, 22.7, 21.8, 14.2. **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd for $C_{60}H_{92}N_6O_4$ + Na: 983.7072; found: 983.7064.

General Procedure C: **Copper-catalyzed cycloaddition of azides with alkynes (CuAAC)**

A stirring solution of azide (1.0 eq.), the corresponding alkyne (3 eq.), 0.04 M aq. $CuSO_4$ (8 mol%) and 0.12 M aq. sodium ascorbate (24 mol%) in a mixture of CH_2Cl_2/*t*-BuOH/H_2O (1:1:1; 15-30 ml; H_2O from the $CuSO_4$ and sodium ascorbate stock solution) was heated to 50 °C. After complete consumption of the starting material as judged by TLC, the reaction mixture was allowed to cool to room temperature, was diluted with water (8 ml) and the aqueous layer was extracted with CH_2Cl_2 (3 x 8 ml). The combined organic layers were washed with 25% aq. ammonia (3 x 8 ml) and brine (8 ml). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Purification by column chromatography gave the desired products.

(*S*)-1,1'-(2,2'-Bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)bis(4-phenyl-1*H*-1,2,3-triazole) (5a)[15a]

Following the *General Procedure C*, subjection of 3,3'-diazido-MOM-BINOL **4** (0.90 g, 2.0 mmol, 1.0 eq.) and phenylacetylene (0.62 g, 6.0 mmol, 3.0 eq.) with subsequent purification by column chromatography using PE/EtOAc (20:1) as eluent gave the title compound (0.97 g, 1.5 mmol, 75%) as a grey solid. R_f = 0.29 (20:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ[ppm]: 8.52 (s, 2H), 8.45 (s, 2H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.96 (t, *J* = 11.1, 4.0 Hz, 4H), 7.60 - 7.54 (m, 2H), 7.52 - 7.42 (m, 6H), 7.41 - 7.30 (m, 4H), 4.51 (d, *J* = 5.8 Hz, 2H), 4.40 (d, *J* = 5.8 Hz, 2H), 2.57 (s, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 148.1, 146.4, 133.7, 130.4, 130.3, 129.0, 128.7, 128.5, 128.3, 126.8, 126.3, 126.2, 125.9, 122.2, 99.6, 60.4, 56.7, 21.1, 14.2. The analytical data are in accordance with the literature.

(*S*)-1,1'-(2,2'-Bis(methoxymethoxy)-[1,1'-binaphthalene]-3,3'-diyl)bis(4-mesityl-1*H*-1,2,3-triazole) (5b)[15a]

Following the *General Procedure C*, subjection of 3,3'-diazido-MOM-BINOL **4** (0.46 g, 1.0 mmol, 1.0 eq.) and mesitylacetylene (0.44 g, 3.0 mmol, 3.0 eq.) with subsequent purification by column chromatography using PE/EtOAc (20:1) as eluent gave the title compound (0.26 g, 0.35 mmol, 35%) as a grey solid. R_f = 0.38 (20:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ[ppm]: 8.50 (d, *J* = 6.5 Hz, 2H), 8.25 - 8.17 (m, 2H), 7.73 (s, 1H), 7.50 - 7.31 (m, 4H), 7.30 - 7.19 (m, 3H), 6.97 (s, 4H), 4.43 (m, 4H), 2.54 (s, 3H), 2.49 (s, 3H), 2.33 (s, 6H), 2.20 (bs, 12H). The analytical data are in accordance with the literature.

(*S*)-1,1'-(2,2'-Bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(4-mesityl-1*H*-1,2,3-triazole) (5c)

Following the *General Procedure C*, subjection of 3,3'-diazido-MOM-BINOL **11** (1.44 g, 2.11 mmol, 1.0 eq.) and mesitylacetylene (0.91 g, 6.32 mmol, 3.0 eq.) with subsequent purification by column chromatography using PE/EtOAc (4:1) as eluent gave the title compound (0.97 g, 1.01 mmol, 48%) as a brown solid. R_f = 0.55 (4:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ[ppm]: 8.36 (s, 1H), 8.07 (s, 1H), 7.99 (s, 1H), 7.75 (s, 1H), 7.71 (s, 1H), 7.64 (s, 1H), 7.24 - 7.21 (m, 2H), 7.15 (dd, *J* = 8.7, 1.5 Hz, 1H), 6.99 (s, 2H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.79 (d, *J* = 19.1 Hz, 2H), 4.52 (d, *J* = 5.3 Hz, 1H), 4.41 (d, *J* = 5.3 Hz, 1H), 4.04 (d, *J* = 5.9 Hz, 1H), 3.99 (d, *J* = 5.9 Hz, 1H), 2.79 - 2.68 (m, 4H), 2.48 (s, 3H), 2.35 (s, 3H), 2.22 (bs, 7H), 2.19 (s, 3H), 2.16 (s, 3H), 2.03 (s, 3H), 1.75 - 1.64 (m, 6H), 1.41 - 1.18 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 147.7, 145.7, 145.6, 141.3, 141.2, 139.2, 138.8, 138.7, 138.3, 138.1, 137.8, 133.8, 132.5, 131.8, 130.5, 130.1, 130.1, 130.0, 129.9, 129.6, 128.5, 128.4, 128.3, 128.3, 126.9, 126.8, 126.6, 126.4, 126.2, 126.1, 126.0, 125.4, 125.1, 122.8, 99.7, 98.9, 56.3, 56.2, 35.8, 31.9, 31.1, 29.5, 29.4, 29.4, 29.3, 29.3, 29.3, 22.7, 21.7, 21.0, 20.9, 20.5, 20.4, 14.1. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{62}H_{76}N_6O_4P$ + H: 969.6001; found: 969.6003.

(*S*)-1,1'-(2,2'-Bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(4-(2,4,6-triisopropylphenyl)-1*H*-1,2,3-triazole) (5d)

Following the *General Procedure C*, subjection of 3,3'-diazido-MOM-BINOL **11** (1.36 g, 2.0 mmol, 1.0 eq.) and 2,4,6-triisopropylbenzene acetylene (1.37 g, 6.0 mmol, 3.0 eq.) with subsequent purification by column chromatography using PE/EtOAc (10:1) as eluent gave the title compound (1.33 g, 1.16 mmol, 58%) as a brown solid. R_f = 0.22 (10:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.44 (d, *J* = 5.9 Hz, 2H), 8.19 (d, *J* = 1.5 Hz, 2H), 7.78 (s, 2H), 7.27 (d, *J* = 0.7 Hz, 2H), 7.17 (dd, *J* = 10.0, 0.8 Hz, 2H), 7.10 (s, 4H), 4.50 (d, *J* = 5.4 Hz, 2H), 4.38 (d, *J* = 5.2 Hz, 2H), 3.23 (s, 2H), 2.97 – 2.90 (m, 4H), 2.85 - 2.67 (m, 12H), 2.54 (s, 6H), 1.73 – 1.65 (m, 6H), 1.43 - 1.22 (m, 20H), 1.18 – 1.11 (m, 12H), 1.00 - 0.73 (m, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 149.8, 148.7, 148.6, 145.5, 145.3, 141.5, 130.7, 130.6, 130.4, 129.7, 129.5, 128.6, 126.8, 126.7, 125.1, 125.0, 122.1, 120.7, 99.0, 60.4, 56.4, 56.0, 41.4, 36.1, 35.9, 34.5, 34.3, 34.1, 31.9, 31.6, 31.1, 30.6, 29.5, 29.3, 29.1, 27.7, 24.3, 24.2, 24.1, 24.0, 23.9, 23.8, 22.7, 22.6, 20.5, 19.5, 18.8, 14.3, 14.2, 14.1, 11.5. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{74}H_{100}N_6O_4$ + H: 1137.7879; found: 1137.7878.

(*S*)-1,1'-(2,2'-Bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(4-(adamantyl)-1*H*-1,2,3-triazole) (5e)

Following the *General Procedure C*, subjection of 3,3'-diazido-MOM-BINOL **11** (0.64 g, 0.93 mmol, 1.0 eq.) and adamantyl acetylene (0.44 g, 2.79 mmol, 3.0 eq.) with subsequent purification by column chromatography using PE/EtOAc (5:1) as eluent gave the title compound (0.43 g, 0.43 mmol, 46%) as a brown solid. R_f = 0.45 (5:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.82 (d, *J* = 9.0 Hz, 2H), 7.58 (s, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.03 (s, 4H), 5.00 (d, *J* = 6.7 Hz, 2H), 4.90 (d, *J* = 6.7 Hz, 2H), 3.09 (s, 6H), 2.72 - 2.61 (m, 4H), 2.09 – 2.02 (m, 4H), 1.79 – 1.74 (m, 10H), 1.65 – 1.61 (m, 20H), 1.21 (bs, 20H), 0.80 (s, 6H). **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{64}H_{84}N_6O_4$ + H: 1001.6627; found: 1001.6637.

(S)-1,1'-2,2'-Bis(methoxymethoxy)-6,6'-dioctyl-[1,1'-binaphthalene]-3,3'-diyl)bis(4-(4-bromo-2,6-diisopropylphenyl)-1*H*-1,2,3-triazole) (5f)

Following the *General Procedure C*, subjection of 3,3'-diazido-MOM-BINOL **11** (1.01 g, 1.5 mmol, 1.0 eq.) and 1-ethynyl-2-bromo-2,6-diisopropylbenzene (0.98 g, 3.7 mmol, 2.5 eq.) with subsequent purification by column chromatography using PE/EtOAc (10:1) as eluent gave the title compound (1.27 g, 1.05 mmol, 71%) as a brown solid. R_f = 0.51 (10:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.53 (s, 2H), 8.32 (s, 2H), 7.70 (s, 4H), 7.37 - 7.12 (m, 6H), 4.52 (d, *J* = 5.8 Hz, 2H), 4.41 (d, *J* = 5.8 Hz, 2H), 3.61 – 3.51 (m, , 4H), 2.76 (dd, *J* = 15.2, 7.6 Hz, 4H), 2.58 (s, 6H), 1.75 – 1.62 (m, 4H), 1.35 – 1.31 (m, 24H), 1.29 – 1.18 (m, 20H), 0.87 (t, *J* = 6.5 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 148.6, 147.7, 145.7, 141.7, 132.2, 130.6, 130.3, 130.0, 129.5, 126.9, 126.8, 126.6, 126.1, 126.0, 122.1, 121.7, 99.7, 56.7, 35.9, 33.8, 31.9, 31.1, 29.5, 29.4, 29.3, 23.1, 22.7, 14.1. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{68}H_{86}Br_2N_6O_4$ + H: 1209.5150; found: 1209.5138.

(*S*)-1,1'-2,2'-Bis(methoxymethoxy)-(6,6'-didodecyl-[1,1'-binaphthalene]-3,3'-diyl)bis(4-mesityl-1*H*-1,2,3-triazole) (5g)

Following the *General Procedure C*, subjection of 3,3'-diazido-MOM-BINOL **12** (1.72 g, 2.2 mmol, 1.0 eq.) and mesityl acetylene (0.95 g, 6.6 mmol, 3.0 eq.) with subsequent purification by column chromatography using PE/EtOAc (20:1) as eluent gave the title compound (1.76 g, 1.8 mmol, 80%) as a brown solid. R_f = 0.38 (20:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.82 (d, *J* = 9.1 Hz, 2H), 7.58 (s, 2H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.22 (s, 2H), 7.03 (s, 4H), 6.82 (s, 2H), 5.01 (d, *J* = 6.7 Hz, 2H), 4.90 (d, *J* = 6.7 Hz, 2H), 3.09 (s, 6H), 2.74 - 2.61 (m, 4H), 2.37 (s, 9H), 2.24 (s, 9H), 1.66 - 1.57 (m, 4H), 1.20 (bs, 36H), 0.89 - 0.77 (m, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 152.3, 145.9, 145.6, 144.7, 141.0, 138.9, 138.2, 137.9, 137.8, 132.1, 130.7, 130.6, 130.4, 130.3, 129.8, 129.2, 128.8, 128.4, 127.9, 126.8, 126.2, 125.5, 119.4, 117.5, 99.0, 95.5, 56.6, 56.0, 55.8, 35.9, 31.9, 31.3, 31.2, 29.7, 29.7, 29.6, 29.6, 29.4, 22.7, 21.2, 20.8, 14.2. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{70}H_{92}N_6O_4$ + H: 1081.7253; found: 1081.7245.

(*S*)-1,1'-(2,2'-Bis(methoxymethoxy)-6,6'-dioctadecyl-[1,1'-binaphthalene]-3,3'-diyl)bis(4-mesityl-1*H*-1,2,3-triazole) (5h)

Following the *General Procedure C*, subjection of 3,3'-diazido-MOM-BINOL **13** (2.24 g, 2.3 mmol, 1.0 eq.) and mesityl acetylene (1.00 g, 6.9 mmol, 3.0 eq.) with subsequent purification by column chromatography using PE/EtOAc (10:1) as eluent gave the title compound (1.89 g, 1.5 mmol, 66%) as a brown solid. R_f = 0.42 (10:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.41 (s, 2H), 8.19 (s, 2H), 7.78 (s, 2H), 7.27 (s, 4H), 6.97 (s, 4H), 4.49 (d, *J* = 5.5 Hz, 2H), 4.38 (d, *J* = 5.5 Hz, 2H), 2.83 - 2.70 (m, 4H), 2.54 (s, 6H), 2.33 (s, 6H), 2.20 (bs, 12H), 1.76 - 1.65 (m, 4H), 1.26 (bs, 60H), 0.88 (t, *J* = 6.9 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 145.9, 145.4, 141.5, 138.3, 137.8, 132.0, 130.6, 130.3, 129.8, 128.5, 126.9, 126.8, 126.7, 126.2, 125.6, 125.0, 99.1, 56.5, 35.9, 32.0, 31.1, 29.8, 29.7, 29.6, 29.5, 29.4, 22.7, 21.2, 20.9, 14.2. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{82}H_{116}N_6O_4$ + H: 1249.9131; found: 1249.9156.

***General Procedure D:* MOM-deprotection of BINOL derivatives**

A stirring solution of MOM-protected BINOL derivative (1 eq.) in a 1:2 mixture of CH_2Cl_2/MeOH (33 ml) was treated with 12 M aq. HCl (38 eq.). The reaction mixture was stirred for 12 h at 50 °C. The solution was allowed to cool to room temperature, was neutralized with sat. aq. $NaHCO_3$ and extracted with CH_2Cl_2 (3 x 30 ml). The combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The desired products were obtained by precipitation (CH_2Cl_2-cyclohexane) and filtration.

(*S*)-3,3'-Bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)-[1,1'-binaphthalene]-2,2'-diol (6a)[15a]

Following the *General procedure D*, the deprotection of triazolyl-MOM-BINOL **5a** (0.97 g, 1.5 mmol, 1.0 eq.) gave the title compound (0.69 g, 1.2 mmol, 80%) as a brown solid. **^{1}H-NMR** (300 MHz, DMSO-d6) δ[ppm]: 9.58 (s, 2H), 9.05 (s, 2H), 8.46 (s, 2H), 8.11 (d, *J* = 7.4 Hz, 2H), 8.02 - 7.97 (m, 4H), 7.55 - 7.34 (m, 10H), 7.06 (d, *J* = 8.2 Hz, 2H). The analytical data are in accordance with the literature.

(*S*)-3,3'-Bis(4-mesityl-1*H*-1,2,3-triazol-1-yl)-[1,1'-binaphthalene]-2,2'-diol (6b)[15a]

Following the *General procedure D*, the deprotection of triazolyl-MOM-BINOL **5b** (257.3 mg, 0.35 mmol, 1.0 eq.) gave the title compound (211.5 mg, 0.32 mmol, 91%) as a brown solid. **^{1}H-NMR** (300 MHz, DMSO-d6) δ[ppm]: 9.31 (s, 2H), 8.53 - 8.50 (m, 2H), 8.12 -7.99 (m, 2H), 7.79 - 7.73 (m, 2H), 7.34 – 7.25 (m, 4H), 6.97 (s, 4H), 6.85 (s, 2H), 2.21 (s, 6H), 2.14 (bs, 12H). The analytical data are in accordance with the literature.

(*S*)-3,3'-Bis(4-mesityl-1*H*-1,2,3-triazol-1-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (6c)

Following the *General procedure D*, the deprotection of triazolyl-MOM-BINOL **5c** (0.97 g, 1.0 mmol, 1.0 eq.) gave the title compound (0.88 g, 0.99 mmol, 99%) as a brown solid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ[ppm]: 8.38 - 7.95 (m, 4H), 7.74 - 7.56 (m, 2H), 7.29 - 7.08 (m, 4H), 7.01 - 6.79 (m, 4H), 2.88- 2.51 (m, 4H), 2.37 - 2.24 (m, 6H), 2.22 - 1.88 (m, 12H), 1.78 - 1.52 (m, 4H), 1.45 - 1.18 (m,

20H), 0.95 - 0.81 (m, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 145.6, 144.7, 139.6, 138.5, 137.9, 131.9, 129.7, 128.6, 128.4, 128.3, 126.9, 126.3, 125.1, 124.8, 122.6, 120.4, 118.2, 35.9, 32.0, 31.5, 31.3, 29.6, 29.5, 29.4, 22.8, 21.2, 20.8, 20.3, 19.7, 14.2. **HRMS** (ESI): *m/z* $[M - H]^-$ calcd for $C_{58}H_{67}N_6O_2$ - H: 879.5331; found: 879.5333.

(*S*)-6,6'-Dioctyl-3,3'-bis(4-(2,4,6-triisopropylphenyl)-1*H*-1,2,3-triazol-1-yl)-[1,1'-binaphthalene]-2,2'-diol (6d)

Following the *General procedure D*, the deprotection of triazolyl-MOM-BINOL **5d** (1.68 g, 1.5 mmol, 1.0 eq.) gave the title compound (1.43 g, 1.36 mmol, 91%) as a brown solid. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 9.50 (s, 2H), 8.26 (s, 2H), 8.17 (s, 2H), 7.74 (s, 2H), 7.23 (s, 4H), 7.14 (s, 4H), 2.97 (dd, *J* = 13.7, 6.9 Hz, 3H), 2.83 - 2.60 (m, 14H), 1.73 – 1.64 (m, 8H), 1.27 (bs, 20H), 1.21 – 1.15 (m, 34H), 0.88 (t, *J* = 6.4 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 152.2, 150.3, 150.0, 148.8, 147.6, 145.7, 145.4, 144.6, 144.4, 139.8, 138.3, 132.1, 131.8, 130.5, 129.9, 129.5, 129.4, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.0, 126.9, 126.6, 125.4, 125.0, 124.9, 124.8, 124.5, 124.4, 123.6, 122.3, 121.7, 121.6, 120.9, 120.8, 119.7, 118.5, 118.1, 117.1, 112.2, 53.5, 35.9, 34.6, 34.4, 32.0, 31.5, 31.3, 30.8, 30.7, 30.0, 29.6, 29.5, 29.4, 29.3, 24.3, 24.2, 24.1, 23.9, 22.8, 21.7, 14.2. **HRMS** (ESI): *m/z* $[M - H]^+$ calcd for $C_{70}H_{92}N_6O_2$ + H: 1049.7355; found: 1049.7351.

(*S*)-6,6'-Dioctyl-3,3'-bis(4-(adamantyl)-1*H*-1,2,3-triazol-1-yl)-[1,1'-binaphthalene]-2,2'-diol (6e)

Following the *General procedure D*, the deprotection of triazolyl-MOM-BINOL **5e** (0.43 g, 0.43 mmol, 1.0 eq.) gave the title compound (0.37 g, 0.40 mmol, 93%) as a brown solid. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 9.57 (s, 2H), 8.05 (s, 2H), 8.02 (s, 2H), 7.67 (s, 2H), 7.18 - 7.13 (m, 4H), 2.71 (dd, *J* = 14.6, 6.5 Hz, 6H), 2.07 (s, 15H), 1.89 (d, *J* = 2.9 Hz, 2H), 1.82 (bs, 15H), 1.25 (bs, 20H), 0.92 - 0.84 (m, 6H). **HRMS** (ESI): *m/z* $[M - H]^+$ calcd for $C_{60}H_{76}N_6O_2$ + H: 913.6103; found: 913.6105.

(*S*)-3,3'-Bis(4-(4-bromo-2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-1-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (6f)

Following the *General procedure D*, the deprotection of triazolyl-MOM-BINOL **5f** (1.27 g, 1.05 mmol, 1.0 eq.) gave the title compound (0.82 g, 0.73 mmol, 70%) as a brown solid. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.94 (s, 2H), 8.58 (s, 2H), 8.24 (s, 2H), 7.75 - 7.60 (m, 4H), 7.25 - 7.08 (m, 4H), 3.63 – 3.53 (m, 4H), 2.76 – 2.70 (m, , 4H), 1.77 - 1.62 (m, 4H), 1.36 – 1.32 (m, 24H), 1.31 – 1.22 (m, 20H), 0.87 (t, *J* = 5.8 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 148.7, 147.7, 144.4, 139.9, 131.6, 129.9, 128.9, 128.2, 127.1, 126.8, 124.7, 121.9, 121.8, 120.0, 119.2, 118.0, 35.8, 33.7, 31.9, 31.1, 29.5, 29.3, 29.2, 23.0, 22.7, 14.1. **HRMS** (ESI): *m/z* $[M - H]^+$ calcd for $C_{64}H_{78}Br_2N_6O_2$ + H: 1121.4626; found: 1121.4615.

(*S*)-3,3'-Bis(4-mesityl-1*H*-1,2,3-triazol-1-yl)-6,6'-didodecyl-[1,1'-binaphthalene]-2,2'-diol (6g)

Following the *General procedure D*, the deprotection of triazolyl-MOM-BINOL **5g** (1.76 g, 1.8 mmol, 1.0 eq.) gave the title compound (1.26 g, 1.26 mmol, 70%) as a brown solid. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.32 – 8.18 (m, 2H), 7.95 - 7.59 (m, 4H), 7.34 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.25 - 7.06 (m, 4H), 7.00 (d, *J* = 2.1 Hz, 2H), 2.77 – 2.70 (m, 4H), 2.36 (s, 6H), 2.20 (s, 12H), 1.78 - 1.58 (m, 4H), 1.42 - 1.19 (m, 36H), 0.91 - 0.81 (m, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 145.8, 144.7, 144.5, 140.1, 139.8, 138.7, 138.6, 138.5, 138.4, 137.9, 131.7, 131.6, 130.8, 130.6, 130.1, 129.8, 129.6, 129.5, 129.0, 128.8, 128.6, 128.5, 128.2, 127.9, 126.9, 126.3, 126.1, 125.0, 124.7, 124.2, 122.8, 121.3, 118.4, 117.8, 117.6, 116.1, 112.2, 110.9, 35.8, 32.0, 31.5, 31.3, 29.8, 29.7, 29.6, 29.5, 29.4, 22.7, 21.2, 20.8, 14.2. **HRMS** (ESI): *m/z* [M - H]$^+$ calcd for $C_{66}H_{84}N_6O_2$ + H: 993.6729; found: 993.6719.

(*S*)-3,3'-Bis(4-mesityl-1*H*-1,2,3-triazol-1-yl)-6,6'-dioctadecyl-[1,1'-binaphthalene]-2,2'-diol (6h)

Following the *General procedure D*, the deprotection of triazolyl-MOM-BINOL **5h** (1.89 g, 1.5 mmol, 1.0 eq.) gave the title compound (1.48 g, 1.27 mmol, 85%) as a brown solid. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.24 (s, 2H), 8.16 (s, 2H), 7.72 (s, 2H), 7.21 (s, 4H), 7.00 (s, 4H), 2.87 - 2.63 (m, 4H), 2.35 (s, 6H), 2.20 (bs, 12H), 1.76 - 1.57 (m, 4H), 1.25 (bs, 60H), 0.88 (t, *J* = 6.7 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 145.9, 144.5, 139.8, 138.7, 137.9, 131.6, 129.8, 128.6, 128.1, 126.7, 126.1, 124.7, 121.9, 119.5, 118.4, 35.9, 32.0, 31.2, 29.8, 29.7, 29.6, 29.4, 22.7, 21.2, 20.8, 14.2. **HRMS** (ESI): *m/z* [M - H]$^+$ calcd for $C_{78}H_{108}N_6O_2$ + H: 1161.8607; found: 1161.8619.

***General procedure E*: Synthesis of phosphoric acids**[13]

To a stirring solution of triazolyl diol (1 eq.) in pyridine (0.1 M) was added phosphoryl chloride (4 eq.) dropwise under an atmosphere of N_2. The reaction mixture was heated to 95 °C. Upon complete consumption of the starting material, as judged by TLC, the reaction mixture was allowed to cool to room temperature. H_2O (1.0 M) was added dropwise at 0 °C and the mixture was again stirred at 95 °C. Upon complete consumption of the starting material, as judged by TLC, the reaction mixture was allowed to cool to room temperature and the mixture was diluted with CH_2Cl_2 (10 ml) and 1.0 M HCl (5 ml). The aqueous layer was separated with a Whatman© phase separator. The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The desired products were obtained by column chromatography.

(*S*)-4-Hydroxy-2,6-bis(4-phenyl-1*H*-1,2,3-triazol-1-yl)dinaphtho[2,1-d:1',2'-f]-[1,3,2]dioxaphosphepine 4-oxide (1a)

Following the *General Procedure E*, subjection of triazolyl diol **6a** (0.57 g, 1.0 mmol, 1.0 eq.) and phosphorylchloride (0.61 g, 4.0 mmol, 4.0 eq.) with subsequent purification by column chromatography using CH_2Cl_2/MeOH (50:1) as eluent gave the title compound (0.49 g, 0.77 mmol, 77%) as a brown solid. R_f = 0.33 (50:1) (SiO_2, CH_2Cl_2/MeOH). **^{1}H-NMR** (400 MHz, DMSO-d6)

δ[ppm]: 9.74 (s, 2H), 8.69 (s, 2H), 8.15 - 7.99 (m, 2H), 7.95 (d, *J* = 7.3 Hz, 4H), 7.57 - 7.44 (m, 8H), 7.44 - 7.33 (m, 2H), 7.28 (d, *J* = 5.2 Hz, 2H). **^{13}C-NMR** (100 MHz, DMSO-d6) δ[ppm]: 154.0, 147.2, 146.5, 146.4, 141.7, 141.6, 133.8, 131.6, 130.5, 130.5, 129.9, 129.2, 129.1, 129.0, 128.9, 128.9, 128.7, 128.2, 128.1, 127.7, 127.3, 127.2, 126.5, 126.1, 125.4, 125.3, 124.2, 124.2, 124.1, 123.5, 123.3, 123.2, 123.2, 116.6. **^{31}P-NMR** (162 MHz, DMSO-d6) δ[ppm]: 5.19. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{36}H_{23}N_6O_4P$ + H: 635.1591; found: 635.1593.

(*S*)-4-Hydroxy-2,6-bis(4-mesityl-1*H*-1,2,3-triazol-1-yl)dinaphtho[2,1-d:1',2'-f]-[1,3,2]dioxaphosphepine 4-oxide (1b)

Following the *General Procedure E*, subjection of triazolyl diol **6b** (206.8 mg, 0.32 mmol, 1.0 eq.) and phosphorylchloride (196.3 mg, 1.30 mmol, 4.0 eq.) with subsequent purification by column chromatography using CH_2Cl_2/MeOH (20:1) as eluent gave the title compound (63.1 mg, 0.09 mmol, 27%) as a brown solid. R_f = 0.29 (20:1) (SiO_2, CH_2Cl_2/MeOH). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ[ppm]: 8.92 - 6.54 (bm, 28H) (should be 17H), 1.38 - 1.11 (bm, 12H), 0.92 - 0.77 (bm, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: no signals could be recorded after 7000 scans. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ[ppm]: 2.72. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{42}H_{35}N_6O_4P$ + H: 719.2530; found: 719.2536.

(4*R*,11b*S*)-4-Hydroxy-2,6-bis(4-mesityl-1*H*-1,2,3-triazol-1-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*]-[1,3,2]dioxaphosphepine 4-oxide (1c)

Following the *General Procedure E*, subjection of triazolyl diol **6c** (876.0 mg, 0.99 mmol, 1.0 eq.) and phosphorylchloride (607.0 mg, 3.96 mmol, 4.0 eq.) with subsequent purification by column chromatography using CH_2Cl_2/MeOH (20:1) as eluent gave the title compound (788.9 mg, 0.83 mmol, 84%) as a brown solid. R_f = 0.33 (20:1) (SiO_2, CH_2Cl_2/MeOH). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ[ppm]: 8.31 - 7.90 (m, 3H), 7.79 - 7.49 (m, 2H), 7.42 - 7.10 (m, 3H), 7.06 - 6.62 (m, 6H), 2.89 - 2.67 (m, 4H), 2.64 (s, 3H), 2.35 (s, 3H), 2.20 (s, 6H), 1.92 (s, 6H), 1.75 - 1.52 (m, 4H), 1.29 (bs, 20H), 0.89 (t, *J* = 6.4 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 145.9, 144.5, 140.8, 139.7, 138.6, 137.8, 137.7, 131.6, 130.3, 129.7, 128.5, 128.4, 128.1, 126.7, 124.7, 123.4, 121.9, 119.5, 118.4, 35.8, 35.7, 31.9, 31.2, 30.9, 29.5, 29.4, 29.3, 29.3, 29.2, 22.7, 22.6, 21.1, 21.0, 20.8, 20.6, 14.1, 14.1. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ[ppm]: 0.99. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{58}H_{66}N_6O_4P$ + H: 943.5034; found: 943.5029.

(4*R*,11b*S*)-4-hydroxy-9,14-dioctyl-2,6-bis(4-(2,4,6-triisopropylphenyl)-1*H*-1,2,3-triazol-1-yl) dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (1d)

Following the General Procedure E, subjection of triazolyl diol **6d** (876.0 mg, 0.99 mmol, 1.0 eq.) and phosphorylchloride (607.0 mg, 3.96 mmol, 4.0 eq.) with subsequent purification by column chromatography using CH_2Cl_2/MeOH (20:1) as eluent gave the title compound (788.9 mg, 0.83 mmol, 84%) as a brown solid. R_f = 0.33 (20:1) (SiO_2, CH_2Cl_2/MeOH). **^{1}H-NMR** (300 MHz,

$CDCl_3$) δ[ppm]: 8.59 (s, 2H), 8.27 (s, 2H), 7.69 (s, 2H), 7.20 (t, *J* = 7.3 Hz, 4H), 7.03 (s, 4H), 2.92 (dt, *J* = 13.7, 6.9 Hz, 2H), 2.79 – 2.68 (m, 8H), 1.67 (s, 4H), 1.41 – 1.27 (m, 32H), 1.08 – 1.03 (m, 22H), 0.91 – 0.86 (m, 8H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 149.6, 148.8, 145.0, 141.2, 130.5, 129.3, 127.0, 126.7, 120.6, 35.7, 34.5, 31.9, 31.1, 30.5, 29.5, 29.4, 29.3, 24.2, 24.1, 22.7, 14.2. **^{31}P-NMR** (121 MHz, $CDCl_3$) δ[ppm]: 3.11. **HRMS** (ESI): *m/z* $[M - H]^+$ calcd for $C_{70}H_{91}N_6O_4P$ + H: 1111.6912; found: 1111.6916.

(4*R*,11b*S*)-4-hydroxy-9,14-dioctyl-2,6-bis(4-(adamantyl)-1*H*-1,2,3-triazol-1-yl)dinaphtho [2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (1e)

Following the General Procedure E, subjection of triazolyl diol **6e** (366.7 mg, 0.4 mmol, 1.0 eq.) and phosphorylchloride (245.3 mg, 1.6 mmol, 4.0 eq.) with subsequent purification by column chromatography using CH_2Cl_2/MeOH (20:1) as eluent gave the title compound (320.3 mg, 0.33 mmol, 83%) as a brown solid. R_f = 0.5 (20:1) (SiO_2, CH_2Cl_2/MeOH). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.39 - 7.82 (m, 4H), 7.61 – 7.55 (m, 2H), 7.16 - 6.81 (m, 4H), 2.67 (t, *J* = 7.5 Hz, 4H), 2.20 - 1.96 (m, 6H), 1.91 – 1.52 (m, 22H), 1.40 - 1.07 (m, 26H), 0.82 (dd, *J* = 7.7, 5.3 Hz, 6H). **^{13}C-NMR** (100 MHz, $CDCl_3$) δ[ppm]: 158.0, 144.6, 139.4, 131.5, 130.4, 129.5, 129.1, 128.0, 126.6, 124.7, 118.6, 42.7, 42.4, 42.1, 36.6, 36.5, 36.3, 35.8, 32.8, 31.9, 31.2, 29.7, 29.5, 29.4, 29.4, 29.3, 28.4, 28.3, 27.9, 22.7, 14.2. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ[ppm]: 3.34. **HRMS** (ESI): *m/z* $[M - H]^+$ calcd for $C_{60}H_{75}N_6O_4P$ + H: 975.5660; found: 975.5663.

(4*R*,11b*S*)-2,6-Bis(4-(4-bromo-2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-1-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (1f)

Following the *General Procedure E*, subjection of triazolyl diol **6f** (821.3 mg, 0.73 mmol, 1.0 eq.) and phosphorylchloride (447.7 mg, 2.92 mmol, 4.0 eq.) with subsequent purification by column chromatography using CH_2Cl_2/MeOH (20:1) as eluent gave the title compound (711.3 mg, 0.6 mmol, 82%) as a brown solid. R_f = 0.52 (20:1) (SiO_2, CH_2Cl_2/MeOH). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.61 (s, 2H), 8.19 (s, 2H), 7.74 - 7.28 (m, 6H), 7.22 - 6.97 (m, 4H), 3.78 - 3.44 (m, 4H), 2.79 - 2.49 (m, 4H), 1.63 (s, 4H), 1.44 - 1.14 (m, 44H), 0.90 (t, *J* = 6.5 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 148.5, 148.4, 147.4, 144.6, 139.7, 131.7, 129.9, 128.8, 128.2, 126.9, 126.8, 124.9, 124.5, 121.8, 120.6, 119.7, 117.7, 35.8, 33.7, 32.0, 31.2, 29.5, 29.4, 29.3, 23.0, 22.7, 14.2. **^{31}P-NMR** (121 MHz, $CDCl_3$) δ[ppm]: 3.25. **HRMS** (ESI): *m/z* $[M - H]^+$ calcd for $C_{64}H_{77}Br_2N_6O_4P$ + H: 1183.4183; found: 1183.4168.

(4*R*,11b*S*)-2,6-Bis(4-mesityl-1*H*-1,2,3-triazol-1-yl)-4-hydroxy--9,14-didodecyldinaphtho [2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (1g)

Following the *General Procedure E*, subjection of triazolyl diol **6g** (1.26 g, 1.26 mmol, 1.0 eq.) and phosphorylchloride (0.77 g, 5.04 mmol, 4.0 eq.) with subsequent purification by column

chromatography using CH_2Cl_2/MeOH (20:1) as eluent gave the title compound (185.9 mg, 0.18 mmol, 14%) as a brown solid. R_f = 0.14 (20:1) (SiO_2, CH_2Cl_2/MeOH). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.33 - 8.16 (m, 4H), 7.63 (s, 2H), 7.08 (s, 4H), 6.76 (s, 4H), 2.70 (s, 4H), 2.26 (s, 6H), 2.02 (s, 12H), 1.65 (s, 4H), 1.29 (bs, 36H), 0.90 (t, *J* = 6.6 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 145.1, 141.1, 141.0, 140.8, 137.7, 137.6, 130.4, 130.2, 129.0, 128.8, 128.3, 126.9, 126.6, 126.5, 126.4, 125.8, 123.5, 35.6, 31.9, 30.9, 29.7, 29.6, 29.5, 29.4, 29.3, 22.6, 21.0, 20.7, 14.0. **^{31}P-NMR** (121 MHz, $CDCl_3$) δ[ppm]: 2.37. **HRMS** (ESI): *m/z* $[M - H]^+$ calcd for $C_{66}H_{83}N_6O_4P$ + H: 1055.6286; found: 1055.6273.

(4*R*,11b*S*)-2,6-Bis(4-mesityl-1*H*-1,2,3-triazol-1-yl)-4-hydroxy-9,14-dioctadecyldinaphtho [2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (1h)

Following the *General Procedure E*, subjection of triazolyl diol **6h** (1.48 g, 1.27 mmol, 1.0 eq.) and phosphorylchloride (0.78 g, 5.08 mmol, 4.0 eq.) with subsequent purification by column chromatography using CH_2Cl_2/MeOH (20:1) as eluent gave the title compound (750.6 mg, 0.61 mmol, 48%) as a brown solid. R_f = 0.49 (20:1) (SiO_2, CH_2Cl_2/MeOH). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.11 (s, 4H), 7.58 (s, 2H), 7.05 (s, 4H), 6.71 (s, 4H), 2.69 (s, 4H), 2.27 (s, 6H), 1.96 (s, 12H), 1.65 (s, 4H), 1.31 (bs, 60H), 0.91 (t, *J* = 6.7 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 148.4, 144.9, 140.9, 140.6, 137.5, 137.3, 136.1, 130.3, 130.0, 128.8, 128.5, 128.3, 126.8, 126.4, 126.2, 125.8, 123.2, 35.6, 31.8, 30.8, 29.6, 29.5, 29.4, 29.2, 22.6, 20.9, 20.6, 14.0. **^{31}P-NMR** (121 MHz, $CDCl_3$) δ[ppm]: 1.69. **HRMS** (ESI): *m/z* $[M - H]^+$ calcd for $C_{78}H_{107}N_6O_4P$ + H: 1223.8164; found: 1223.8157.

***N*-((4*S*,11b*S*)-2,6-Bis(4-mesityl-1*H*-1,2,3-triazol-1-yl)-9,14-dioctyl-4-oxidodinaphtho[2,1-*d*:1',2'-*f*] [1,3,2]dioxaphosphepin-4-yl)-1,1,1-trifluoromethanesulfonamide (1c#)**[27]

To a solution of BINOL (1.2 g, 1.4 mmol, 1.0 eq.) in CH_2Cl_2 (7.0 mL) were added Et_3N (1.3 mL, 9.6 mmol, 6.9 eq.), $POCl_3$ (0.16 mL, 1.7 mmol, 1.2 eq.) and DMAP (334 mg, 2.7 mmol, 2.0 eq.) at 0 °C. After being stirred for 1 hour at room temperature, EtCN (7.0 mL) and $TfNH_2$ (0.5 g, 3.4 mmol, 2.4 eq.) were added at room temperature. The reaction mixture was stirred at 100 °C and was allowed to cool to room temperature after 12 hours. The solution was quenched with H_2O (15 ml) and extracted with Et_2O (2 x 15 ml). The combined organic layers were washed with sat. aq. $NaHCO_3$ (10 ml), 4M HCl (2 x 10 ml), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. Purification of the crude product by column chromatography (PE/EA 4:1) gave the title compound (105.3 mg, 0.01 mmol, 7%) as a brown solid [along with the PA **1c** (330.1 mg, 0.35 mmol, 25%)]. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.35 (s, 1H), 8.17 (s, 1H), 7.92 – 7.86 (m, 2H), 7.77 (d, *J* = 5.9 Hz, 2H), 7.30 (t, *J* = 9.3 Hz, 2H), 7.23 (s, 2H), 6.92 (s, 2H), 6.61 (s, 2H), 2.80 – 2.74 (m, 4H), 2.31 (s, 3H), 2.10 (s, 9H), 2.00 (s, 6H), 1.68 (s, 4H), 1.40 - 1.17 (m, 20H), 0.93 - 0.81 (m, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 145.1, 140.9, 137.8, 130.5, 130.3, 129.1, 128.4, 126.9,

126.7, 126.4, 126.3, 123.6, 35.7, 31.9, 31.0, 29.5, 29.3, 22.7, 21.1, 20.7, 14.2. **^{31}P-NMR** (121 MHz, $CDCl_3$) δ[ppm]: 3.55. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{59}H_{68}F_3N_7O_5PS$ + H: 1074.4687; found: 1074.4680.

General Procedure for the Catalytic Reaction:

The PA catalyst **1c** (18.9 mg, 0.02 mmol, 10 mol%) and Na_3PO_4 (50.9 mg, 0.48 mmol, 2.4 eq.) were dissolved in dry Et_2O (8 ml) and stirred for 30 min until the catalyst was completely dissolved. Dihydroisoquinoline benzamide **2** (0.2 mmol, 1.0 eq.) and oxidant $AcNHT^+BF_4^-$ (132.0 mg, 0.44 mmol, 2.2 eq.) were added and the reaction mixture was stirred vigorously for 24 h at room temperature. After this time, the reaction mixture was diluted with sat. aq. Na_2SO_3 (4 ml) and the contents were shaken. The mixture was extracted with EtOAc (3 x 4 ml) and the combined organic layers were dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The desired product was purified by column chromatography with a PE/EtOAc mixture as eluent.

5-Benzyl-4b,5,12,13-tetrahydro-6*H*-isoquinolino[2,1-*a*]quinazolin-6-one (3a)[13,16c]

Following the *General Catalytic Procedure*, the reaction of benzamide **2a** (68.5 mg, 0.20 mmol) provided, after column chromatography (PE/EtOAc, 4:1), the desired product (66.9 mg, 0.19 mmol, 99%, 78:22 e.r.) as a white solid. The scale-up reaction of **2a** (342.5 mg, 1.0 mmol) and **1c** (94.3 mg, 0.1 mmol, 10 mol%) in 40 mL Et_2O provided **3a** (324.9 mg, 95%) with a 70:30 e.r., and the recrystallization from CH_2Cl_2/hexane led to the product in 92:8 e.r (130.0 mg, 40% of recrystallization). R_f = 0.35 (4:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.34 – 7.22 (m, 7H), 7.19 – 7.09 (m, 2H), 7.02 – 6.96 (m, 1H), 6.83 (dd, *J* = 13.6, 7.7 Hz, 2H), 5.70 (bd, *J* = 14.5 Hz, 1H), 5.64 (s, 1H), 4.34 (d, *J* = 15.3 Hz, 1H), 3.97 (dd, *J* = 14.2, 5.1 Hz, 1H), 3.47 (ddd, *J* = 14.2, 11.1, 5.7 Hz, 1H), 3.16 – 2.98 (m, 1H), 2.67 (dd, *J* = 17.0, 3.8 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 163.5, 147.5, 137.3, 134.9, 133.5, 129.6, 129.3, 128.7, 128.3, 127.7, 127.6, 126.3, 126.0, 119.5, 118.6, 113.7, 71.8, 49.8, 44.7, 24.6. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{23}H_{20}N_2$ + H: 341.1648; found: 341.1655. **HPLC** (Chiralpak IC column, 75:25 hexanes/isopropanol, 1 ml/min); t_r = 20.9 (minor), 25.0 (major) min.

5-(4-Chlorobenzyl)-4b,5,12,13-tetrahydro-6*H*-isoquinolino[2,1-*a*]quinazolin-6-one (3b)

Following the *General Catalytic Procedure*, the reaction of benzamide **2b** (40.2 mg, 0.10 mmol, 1.0 eq.) provided, after column chromatography (CH_2Cl_2), the desired product (30.0 mg, 0.08 mmol, 80%, 72:28 e.r.) as a white solid. R_f = 0.49 (SiO_2, CH_2Cl_2). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.96 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.28 – 7.14 (m, 8H), 7.06 – 7.01 (m, 1H), 6.93 – 6.83 (m, 2H), 5.65 (s, 1H), 5.55 (bs, 1H), 4.37 (d, *J* = 15.5 Hz, 1H), 4.04 – 3.90 (m, 1H), 3.50 (ddd, *J* = 14.1, 10.9, 5.7 Hz, 1H), 3.16 – 2.96 (m, 1H), 2.73 (ddd, *J* = 16.9, 5.4, 2.4 Hz, 1H). **^{13}C-NMR** (75MHz, $CDCl_3$) δ[ppm]: 163.7, 147.7, 136.0, 135.0, 133.6, 133.3, 132.4, 129.6, 129.4,

129.1, 128.8, 128.7, 128.5, 126.4, 126.2, 119.7, 114.0, 71.9, 48.9, 44.7, 24.9. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{23}H_{20}ClN_2O$ + H: 375.1259; found: 375.1265. **HPLC** (Chiralpak IC column, 75:25 hexanes/isopropanol, 1 ml/min); t_r = 16.0 (minor), 22.0 (major) min.

5-(3,4-Dimethoxybenzyl)-4b,5,12,13-tetrahydro-6*H*-isoquinolino[2,1-*a*]quinazolin-6-one (3c)[16c]
Following the *General Catalytic Procedure*, the reaction of benzamide **2c** (37.7 mg, 0.100 mmol, 1.0 eq.) provided, after column chromatography (PE/EtOAc, 4:1 → 2:1), the desired product (32.4 mg, 0.081 mmol, 81%, 71:29 e.r.) as a pale yellow solid. R_f = 0.05 (4:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.95 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.33 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.12 (m, 2H), 7.05 – 6.98 (m, 1H), 6.91 – 6.73 (m, 5H), 5.65 (s, 2H), 4.31 (d, *J* = 15.1 Hz, 1H), 4.06 – 3.93 (m, 1H), 3.50 (ddd, *J* = 14.2, 11.0, 5.8 Hz, 1H), 3.19 – 3.03 (m, 1H), 2.71 (dd, *J* = 17.0, 3.5 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 163.4, 149.1, 148.4, 147.4, 134.8, 133.4, 129.7, 129.5, 129.2, 128.2, 126.2, 126.0, 120.2, 119.4, 113.7, 111.0, 111.0, 71.3, 68.0, 55.9, 44.6, 25.6. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{25}H_{25}N_2O_3$ + H: 401.1860; found: 401.1868. **HPLC** (Chiralpak IA column, 80:20 hexanes/isopropanol, 1 ml/min); t_r = 27.8 (major), 32.5 (minor) min.

5-((*S*)-1-Phenylethyl)-4b,5,12,13-tetrahydro-6*H*-isoquinolino[2,1-*a*]quinazolin-6-one (3d)
Following the *General Catalytic Procedure*, the reaction of benzamide **2d** (35.6 mg, 0.100 mmol, 1.0 eq.) provided, after column chromatography (PE/EtOAc, 4:1), the desired product (28.0 mg, 0.079 mmol, 79%, 68:32 d.r.) as a white solid. R_f = 0.42 (4:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.86 (d, *J* = 7.8 Hz, 1H major + 1H minor), 7.57 (d, *J* = 7.4 Hz, 1H major + 1H minor), 7.45 (d, *J* = 7.5 Hz, 1H major + 1H minor), 7.42 – 7.22 (m, 5H major + 5H minor), 7.16 – 7.07 (m, 1H major + 1H minor), 7.05 – 6.66 (m, 3H major + 5H minor), 6.48 (d, *J* = 7.7 Hz, 1H major), 6.17 (s, 1H minor), 6.05 (s, 1H major), 5.73 (s, 1H major), 5.54 (s, 1H minor), 4.21 (dd, *J* = 14.4, 7.3 Hz, 1H major), 4.15 – 4.04 (m, 1H minor), 3.83 – 3.66 (m, 1H major), 3.56 – 3.42 (m, 1H minor), 3.30 – 3.10 (m, 1H major + 1H minor), 2.81 – 2.64 (m, 1H major + 1H minor), 1.81 (d, *J* = 7.1 Hz, 3H major), 1.75 (d, *J* = 7.3 Hz, 3H, minor). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 163.8, 147.3, 142.4, 133.4, 133.3, 129.7, 129.6, 129.2, 128.9, 128.8, 128.6, 128.5, 128.0, 127.5, 127.0, 126.4, 126.0, 125.5, 119.4, 119.0, 113.2, 69.3, 54.4, 53.3, 45.1, 44.7, 23.9, 18.9. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{24}H_{22}N_2O$ + H: 355.1805; found: 355.1810. **HPLC** (Chiralpak IA column, 85:15 hexanes/isopropanol, 1 ml/min); t_r = 11.5 (minor), 16.3 (major) min.

4b,5,12,13-Tetrahydro-6*H*-isoquinolino[2,1-*a*]quinazolin-6-one (3e)[16a,b]
Following the *General Catalytic Procedure*, the reaction of benzamide **2e** (25.2 mg, 0.100 mmol, 1.0 eq.) provided, after column chromatography (PE/EtOAc, 3:1), the desired product (17.1 mg, 0.041 mmol, 41%, 60:40 e.r.) as a white solid. R_f = 0.07 (3:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.04 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.49 (ddd, *J* = 8.4, 7.4, 1.7 Hz, 1H), 7.36 – 7.29 (m,

3H), 7.25 – 7.20 (m, 1H), 7.06 – 7.00 (m, 1H), 6.07 (bs, 1H), 5.73 (s, 1H), 3.92 – 3.84 (m, 1H), 3.29 – 3.19 (m, 1H), 3.17 – 3.11 (m, 1H), 3.04 – 2.94 (m, 1H). The analytical data are in accordance with the literature. **HPLC** (Chiralpak IC column, 75:25 hexanes/isopropanol, 1 ml/min); t_r = 18.0 (major), 20.2 (minor) min.

5-Cyclohexyl-4b,5,12,13-tetrahydro-6*H*-isoquinolino[2,1-*a*]quinazolin-6-one (3f)[13,16c]

Following the *General Catalytic Procedure*, the reaction of *N*-alkyl benzamide **2f** (33.4 mg, 0.100 mmol, 1.0 eq.) provided, after column chromatography (CH_2Cl_2), the desired product (7.6 mg, 0.023 mmol, 23%, 59:41 e.r.) as a white solid. $\boldsymbol{R_f}$ = 0.28 (4:1) (SiO_2, CH_2Cl_2). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.83 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.29 – 7.22 (m, 2H), 7.15 – 7.04 (m, 2H), 7.01 – 6.94 (m, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.81 – 6.71 (m, 1H), 5.65 (s, 1H), 4.66 (bs, 1H), 4.22 (dd, *J* = 14.8, 7.1 Hz, 1H), 3.79 (ddd, *J* = 14.8, 11.4, 6.5 Hz, 1H), 3.34 – 3.17 (m, 1H), 2.78 (dd, *J* = 17.3, 6.2 Hz, 1H), 2.17 (d, *J* = 10.3 Hz, 1H), 2.04 (d, *J* = 11.2 Hz, 1H), 1.93 – 1.76 (m, 2H), 1.74 – 1.63 (m, 2H), 1.61 - 1.37 (m, 3H), 1.21 – 1.04 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 163.4, 147.1, 137.6, 134.4, 133.2, 129.5, 129.1, 127.9, 126.6, 125.9, 119.6, 119.2, 113.2, 68.9, 54.6, 45.0, 32.5, 30.9, 26.0, 25.6, 23.8. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{22}H_{24}N_2O$ + H: 333.1961; found: 333.1969. **HPLC** (Chiralpak IC column, 75:25 hexanes/isopropanol, 1 ml/min); t_r = 15.5 (major), 17.4 (minor) min.

5-(2-Chlorophenyl)-4b,5,12,13-tetrahydro-6*H*-isoquinolino[2,1-*a*]quinazolin-6-one (3g)[13]

Following the *General Catalytic Procedure*, the reaction of *N*-aryl benzamide **2g** (36.3 mg, 0.10 mmol, 1.0 eq.) provided, after column chromatography (CH_2Cl_2), the desired product (5.1 mg, 0.14 mmol, 14%, 50:50 e.r.) as a white solid. $\boldsymbol{R_f}$ = 0.26 (4:1) (SiO_2, CH_2Cl_2). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.09 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.42 – 7.36 (m, 1H), 7.11 – 7.02 (m, 5H), 6.99 – 6.89 (m, 2H), 6.87 – 6.70 (m, 2H), 6.17 (s, 1H), 3.94 – 3.83 (m, 1H), 3.47 (dt, *J* = 12.0, 5.9 Hz, 1H), 3.20 – 2.96 (m, 2H). **^{13}C-NMR** (75MHz, $CDCl_3$) δ[ppm]: 164.8, 149.6, 141.3, 136.8, 134.9, 133.7, 130.8, 129.9, 129.6, 129.5, 129.2, 128.8, 128.5, 127.1, 125.9, 121.9, 118.1, 72.4, 45.4, 28.7. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{22}H_{17}ClN_2O$ + H: 361.1102; found: 361.1110. **HPLC** (Chiralpak IC column, 75:25 hexanes/isopropanol, 1 ml/min); t_r = 30.1, 43.5 min.

4b,13-Dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one (3h)[16a,c]

Following the *General Catalytic Procedure*, the reaction of the carboxylic acid **2h** (25.3 mg, 0.100 mmol, 1 eq.) provided, after column chromatography (PE/EtOAc, 4:1), the desired product (15.6 mg, 0.062 mmol, 62%) as a pale yellow solid. $\boldsymbol{R_f}$ = 0.55 (4:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.09 – 8.05 (m, 1H), 7.56 – 7.50 (m, 2H), 7.35 – 7.26 (m, 2H), 7.24 – 7.17 (m, 2H), 7.11 – 7.04 (m, 2H), 6.12 (s, 1H), 3.71 (dt, *J* = 12.0, 6.0 Hz, 1H), 3.50 – 3.38 (m, 2H), 3.07 (t, *J* = 5.9 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 165.2, 150.1, 135.3, 134.8, 131.1, 130.1, 129.5,

128.7, 128.5, 127.1, 122.2, 117.4, 117.1, 85.9, 43.8, 29.1. The analytical data are in accordance with the literature.

6,6-Dimethyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinoline (3i)

Following the *General Catalytic Procedure*, the reaction of the alcohol **2i** (26.7 mg, 0.100 mmol, 1.0 eq.) provided, after column chromatography (PE/EtOAc, 32:1), the desired product (16.8 mg, 0.063 mmol, 63%, 54:46 e.r.) as a white solid. R_f = 0.32 (32:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 7.42 – 7.36 (m, 1H), 7.29 – 7.26 (m, 2H), 7.26 – 7.23 (m, 1H), 7.23 – 7.14 (m, 3H), 7.11 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.04 – 6.96 (m, 1H), 5.50 (s, 1H), 3.59 (td, *J* = 11.2, 3.7 Hz, 1H), 3.41 (ddd, *J* = 11.5, 5.3, 3.6 Hz, 1H), 3.18 (ddd, *J* = 16.1, 11.2, 5.3 Hz, 1H), 2.94 (dt, *J* = 16.0, 3.6 Hz, 1H), 1.76 (s, 3H), 1.57 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ[ppm]: 135.6, 135.4, 133.9, 128.8, 128.5, 128.1, 127.2, 126.5, 126.1, 122.1, 122.0, 116.6, 79.0, 76.0, 46.1, 31.9, 29.9, 29.2. **HRMS** (ESI): *m/z* $[M + H]^+$ calcd for $C_{18}H_{19}NO$ + H: 265.1467; found: 265.1472. **HPLC** (Chiralpak OD-H column, 90:10 hexanes/isopropanol, 1 ml/min); t_r = 4.0 (major), 4.4 (minor) min.

6,7,11b,12-Tetrahydro-13*H*-isoquinolino[2,1-*a*]quinolin-13-one (3j)[16]

Following the *General Catalytic Procedure*, the reaction of the ketone **2j** (25.0 mg, 0.10 mmol, 1.0 eq.) provided, after column chromatography (PE/EtOAc, 9:1), the desired product (13.0 mg, 0.052 mmol, 52%, 58:42 e.r.) as a yellow solid. R_f = 0.14 (9:1) (SiO_2, PE/EtOAc). **^{1}H-NMR** (300 MHz, $CDCl_3$) δ[ppm]: 8.01 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.32 – 7.29 (m, 1H), 7.28 – 7.15 (m, 3H), 7.02 (d, *J* = 8.6 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 4.76 (dd, *J* = 13.7, 2.5 Hz, 1H), 4.19 – 4.05 (m, 1H), 3.29 – 3.05 (m, 3H), 2.99 – 2.90 (m, 1H), 2.84 – 2.75 (m, 1H). The analytical data are in accordance with the literature. **HPLC** (Chiralpak OJ-H column, 85:15 hexanes/isopropanol, 1 ml/min); t_r = 4.8 (major), 5.1 (minor) min.

Results and Discussion

Initially, a small family of Click-BINOL-derived chiral phosphoric acids **1** was synthetized (Scheme 2). Thus, starting from commercially available (*S*)-BINOL, we employed our early procedure for the preparation of the 3,3'-diazido BINOL derivative **4**,[15a] which implies a first MOM protection and an *ortho*-directed lithiation/substitution sequence. Subsequent copper-catalyzed alkyne-azide cycloaddition reaction (CuAAC) and MOM-deprotection led to the corresponding Click-BINOLs **6a** and **6b**. Finally, phosphorylation with phosphoryl trichloride and acid work-up delivered the desired phosphoric acids **1a** and **1b**, bearing a phenyl and a mesityl group at the triazole units, respectively. Similarly, 6,6'-alkyl substituted BINOL-diazides **11-13** were easily prepared in gram scale. The direct bromination of (*S*)-BINOL and reaction with MOM-chloride led to the corresponding dibromo-BINOL **7**, which was subjected to a Kumada cross-coupling with octyl, dodecyl and octadecyl magnesium bromide[13] and subsequent azide formation. CuAAC with various bulky aryl (Mes, mesityl; Trip,

2,4,6-triisopropylphenyl; BDIP, 4-bromo-2,6-diisopropylphenyl) and alkyl (Ad, 1-adamatyl) substituted terminal alkynes followed by MOM-deprotection and phosphorylation, provided the catalysts **1c-h** in moderate to good overall yields. Finally, under non-optimized conditions, the more acidic triflamide derivative **1c#** was also prepared from the corresponding BINOL **6c**.

In order to investigate the importance and effect of the triazole units on the catalytic activity of these new Click-PA catalysts, we next decided to explore them in the intramolecular asymmetric C–H functionalization of tetrahydroisoquinoline-*N*-benzamides, previously studied by Toste and co-workers.[13] Therefore, the reaction with benzamide **2a** in the presence of our catalysts was first optimized (Table 1). It is important to note the strong background reaction with this type of THIQ-*N*-benzamine substrates **2** (entry 1). Consequently, in order to achieve high enantioselectivities a potent catalyst would be required. Therefore, the start point of our study was the screening of the catalysts **1a-e** under analogous reported conditions: Na_3PO_4 as base to form *in situ* the active phosphate catalyst and a TEMPO oxoammonium salt ($AcNHT^+BF_4^-$) as oxidant in toluene (dilution 0.025 M) as apolar solvent to favor the formation of close ion-pairs at room temperature (entries 2-6). Already with the simplest catalysts **1a** and **1b**, the effect of the substitution at the triazole rings could be observed. Thus, an inversion on the enantioselectivity was detected when replacing a phenyl for a bulkier mesityl group (entries 2 and 3). The introduction of a linear C8-alkylic chain in the BINOL-backbone was beneficial, leading to **3a** in an improved enantiomeric ratio (**1c**, 66:34 e.r., entry 4). Similar results were obtained with the catalysts **1d** and **1e** bearing bulkier Trip and Ad groups, respectively (entries 5-6). The screening of solvents was next carried out with **1c**. As expected the solvent had an important effect on the enantioselectivity of the reaction. Whereas *p*-xylene showed a slightly higher enantioinduction (70:30 e.r., entry 7), ethereal solvents such as simple Et_2O provided the best results (78:22 e.r., entry 9). The performance of the triflamide derivative **1c#** and the catalysts **1d-f** was also tested in Et_2O as solvent (entries 10-13). Nevertheless, they were inferior to the mesityl-subtituted catalyst **1c**. Considering the presumable positive effect of the octyl chains by enhancing the catalyst's solubility in the used apolar solvents, other structures with longer alkyl rests such as dodecyl (**1g**) and octadecyl (**1h**) were then investigated (entries 14 and 15). Conversely, the shorter *n*-octyl chain in **1c** remained superior and this PA was further employed as catalyst of choice. Next, various inorganic bases such as phosphates and carbonates, and ionic hydride abstractors or oxidants such as TEMPO and trityl salt derivatives were explored (entries 16-20). However, the initially employed mixture of salts ($AcNHT^+BF_4^-$and Na_3PO_4) gave the higher enantioselectivity. It was also observed that the decrease in the temperature (-20 and -40 °C, entries 21 and 22) was not beneficial, leading to less efficient asymmetric reactions. Lastly, the use of lower catalytic loadings (5 and 2.5 mol%, entries 23 and 24)

was also translated in a gradual decrease of the enantioinduction.

The substitution and nature of the nucleophile was then studied with our identified optimal reaction conditions: 10 mol% of catalyst **1c**, Na_3PO_4 as base, $AcNHT^+BF_4^-$ as oxidant in Et_2O at room temperature (Scheme 3). Differently benzyl-substituted benzamides **2** led to the corresponding quinazolinones **3a-c** in comparable moderate enantioselectivities (71:29 – 78:22 e.r.). Moreover, the reaction with a chiral substrate **2d** provided a similar level of diastereoselectivity (**3d**, 63:27 d.r.), which turned out to be opposite to the one obtained in the uncatalyzed reaction (22:68 d.r.). Unexpectedly, a change in the nature of the nucleophilic unit on the substrate from a *N*-benzyl benzamide to an unsubstituted (NH_2, **2e**), *N*-alkyl (cyclohexyl, **2f**) or *N*-aryl (2-chlorophenyl, **2g**) benzamide proceeded to the expected products **3e-g**, although in inferior yields and low or imperceptible enantioselectivities. Moreover, the formation of C-O or C-C bonds by reaction of the carboxylic acid **2h** and tertiary alcohol **2i** or methyl ketone **2j** also took place, leading to the corresponding products in similar low enantiomeric inductions.

It is important to mention that the reaction could be scaled-up 5 times to a 1.0 mmol scale, leading to only a slightly detriment to the enantioselectivity. Thus, the reaction with **2a** (>340 mg) provided the quinazolinone product **3a** in a good 95% yield and 70:30 e.r. Furthermore, we observed that the racemic compounds **3** possess a high crystallinity, allowing reaching extremely high enantioselectivities (up to 99:1 e.r. for **3a**) by the simple recrystallization (by removal of the racemic crystals from the product of the catalytic reactions). Consequently, in order to avoid getting incorrect

e.r. values, acetonitrile was used to completely dissolve the probes for the HPLC analyses.[28]

Lastly, a comparison of the effectiveness of our developed chiral Click-BINOL-PA catalysts **1** with commercially available derivatives and the previously reported regioisomeric triazole-BINOL-PA **1C'** in the model asymmetric C-H bond functionalization reaction of benzamide **2a** was carried out (Figure 2). The presence of the triazole groups is crucial to achieve enantiomeric induction. Thus, standard chiral phosphoric acids such as **TRIP®** provided the racemic product, while the Click-BINOL-PAs **1c** and **1C'** showed certain levels of enantioselectivity. In this regard, our best Click-BINOL-PA catalysts **1c** afforded a moderate enantioselectivity (78:22 e.r.), while the catalyst **1C'**, which only differ in the rearrangement of the triazole units, led to an enhanced enantiomeric ratio value (89:11 e.r.). The fact that the reaction with *N*-benzylic amides provided the best enantiomeric results might be explained by the already proposed essential $\pi-\pi$ interaction between the triazole ring of the catalyst **1C'** and related structures and the benzylic substituent at the benzylamide.[13b] However, the observation of a match / mismatch effect depending on the regioisomeric triazoles employed suggest an additional positive interaction of the triazole units with the substrate and/or ionic iminium intermediate, which might facilitate the effective formation of the required chiral close ion-pair. Furthermore, the spatial disposition of the substituents on the triazoles in **1C'** permitted a torsion angle of 90° in the transition state, which was proposed to be also key for attaining high enantioinductions.[13b]

A simplified plausible mechanism is shown in Scheme 3, in which the key step to form a close ion-pair **B** and allow chirality transfer is the counter-anion exchange between the active Click-phosphate catalyst **I** and the iminium intermediate **A** (pathway A) and/or ionic oxidant ($AcNHT^+BF_4^-$) (pathway B). Aiming at gaining more information on the counter-anion exchange, a reaction using stoichiometric amounts of the phosphoric acid **1c** was made (Scheme 4). For this purpose, the Click-BINOL-PA **1c**, the base and the oxidant were reacted for 20 min before adding the substrate **2a**. Under these conditions, the same 78:22 enantiomeric ratio was obtained, showing that the anion exchange was as effective in the catalytic as in the stoichiometric reaction.

Conclusions

To sum up, new chiral triazole-containing phosphoric acids have been developed and employed as catalysts for the intramolecular enantioselective oxidative C–H bond functionalization of tetrahydroisoquinolines. The presence of the triazole groups on the catalysts was key to achieve the transfer of chirality to the products. Moderate enantioselectivities were obtained with the THIQ-*N*-

benzamide substrates, whereas the related regioisomeric catalysts seemed to be more effective for this transformation. The formation of a chiral close ion-pair between the phosphate catalyst and the iminium ion intermediate, which stays in equilibrium with the achiral species, is essential for success. Therefore, the design of further superior catalyst structures is still needed to attain elevated enantioselectivities in further asymmetric C–H bond functionalization reactions that relies on counter-anion organocatalysis.

Supplementary data

Electronic supplementary information (ESI) is available: Procedures and characterization of starting materials; NMR and HPLC collection of new compounds.

Acknowledgements

The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support. D. G. thanks the Deutscher Akademischer Austauschdienst (DAAD) and the University of Regensburg for an iPur PhD-exchangefellowship.

References

[1] Pioneer work on CDC: a) Z.-P. Li, C.-J. Li, *J. Am. Chem. Soc.* 126 (2004) 11810; b) Z.-P. Li, C.-J. Li, *J. Am. Chem. Soc.* 127 (2005) 3672.

[2] Overviews on C–H activation and functionalization: a) F. Kakiuchi, S. Murai, *Activation of Unreactive Bonds and Organic Synthesis* In *Topics in Organometallic Chemistry*, 1999, vol. 3; b) G. Dyker, *Handbook of C–H Transformations*, Wiley-VCH, Weinheim, 2005; c) J.-Q. Yu, Z. J. Shi, *Topics in Current Chemistry*, Springer, vol. 292, 2010.

[3] Selected reviews: a) C. J. Scheuermann, *Chem. Asian J.* 5 (2010) 436; b) M. Klussmann, D. Sureshkumar, *Synthesis* 3 (2011) 353; c) C. S. Yeung, V. M. Dong, *Chem. Rev.* 111 (2011) 1215; d) C. Liu, H. Zhang, W. Shi, A. Lei, *Chem. Rev.* 111 (2011) 1780; e) R. Rohlmann, O. García Mancheño, *Synlett* 24 (2013) 6; f) S. A. Girard, T. Knauber, C. J. Li, *Angew. Chem. Int. Ed.* 53 (2014) 74; g) R. Narayan, K. Matcha, A. P. Antonchick, *Chem. Eur. J.* 21 (2015) 14678; h) H. M. L. Davies, D. Morton, *J. Org. Chem.* 81 (2016) 343; i) J. F. Hartwig, A. A. Larsen, *ACS Cent. Sci.* 2 (2016) 281, and references cited therein.

[4] Recent a review on asymmetric couplings of α–C(sp^3)-H of amines: a) Y. Qin, J. Lv, S. Luo, *Tetrahedron Lett.* 55 (2014) 551. See also: b) W. Liu, S. Liu, R. Jin, H. Guo, J. Zhao, *Org. Chem. Front.* 2 (2015) 288. For a mechanistic study, see: c) E. Boess, C. Schmitz, M. Klussmann, *J. Am. Chem. Soc.* 134 (2012) 5317.

[5] Pioneer work on TEMPO salts as oxidants in C-H functionalization: a) H. Richter, O. García Mancheño, *Eur. J. Org. Chem.* (2010) 4460. See also: b) H. Richter, O. García Mancheño, *Org. Lett.*

13 (2011) 6066; c) H. Richter, R. Rohlmann, O. García Mancheño, *Chem. Eur. J.* 17 (2011) 11622; d) H. Richter, R. Fröhlich, C. G. Daniliuc, O. García Mancheño, *Angew. Chem. Int. Ed.* 51 (2012) 8656; e) R. Rohlmann, T. Stopka, H. Richter, O. García Mancheño, *J. Org. Chem.* 78 (2013) 6050. For oxidative C-H functionalization/ring expansion using benzoylperoxide as oxidant: f) T. Stopka, L. Marzo, M. Zurro, S. Janich, E.-U. Würthwein, C. G. Daniliuc, J. Alemán, O. García Mancheño, *Angew. Chem. Int. Ed.* 54 (2015) 5049.

[6] Reviews on *N*-oxoammonium chemistry: a) J. M. Bobbitt, M. C. L. Flores, *Heterocycles* 27 (1988) 509; b) J. M. Bobbitt, C. Brückner, N. Merbouh, "Oxoammonium- and nitroxide-catalyzed oxidations of alcohols" In Org. Reactions, Ed. S. E. Denmark, Wiley: New York, 2009, 74, pp 103; c) T. Stopka, O. García Mancheño, *Synthesis*, 45 (2013) 1602. See also: d) M. A. Mercadante, C. B. Kelly, J. M. Bobbitt, L. J. Tilley, N. E. Leadbeater, *Nature Protocols* 8 (2013) 666; e) T. A. Hamlin, C. B. Kelly, J. M. Ovian, R. J. Wiles, L. J. Tilley, N. E. Leadbeater, *J. Org. Chem.* 80 (2015) 8150.

[7] For further examples in C-H functionalization, see for example: a) S. Wetz, S. Kodama, A. Studer, *Angew. Chem. Int. Ed.* 50 (2011) 11511; b) C. Yan, Y. Liu, Q. Wang, *RSC Adv.* 4 (2014) 60075; c) S. Sun, C. Li, P. E. Floreancig, H. Lou, L. Liu, *Org. Lett.* 17 (2015) 1684.

[8] Pioneer work: Z. Li, C.-J. Li, *Org. Lett.* 6 (2004) 4997. Recent reviews: a) Y. Qin, J. Lv, S. Luo, *Tetrahedron Lett.* 55 (2014) 551; b) C. Zheng, S.-L. You, *RSC Adv.* 4 (2014) 6173; c) W. Liu, S. Liu, R. Jin, H. Guo, J. Zhao, *Org. Chem. Front.* 2 (2015) 288.

[9] See for example: a) N. Sasamoto, C. Dubs, Y. Hamashima, M. Sodeoka, *J. Am. Chem. Soc.* 128 (2006) 14010; b) O. Basléand, C.-J. Li, *Org. Lett.* 10 (2008) 3661; c) G. Zhang, Y. Zhang, R. Wang, *Angew. Chem. Int. Ed.* 50 (2011) 10429; d) W. Cao, X. Liu, R. Peng, P. He, L. Lin, X. Feng, *Chem. Commun.* 49 (2013) 3470; e) J. Yu, Z. Li, K. Jia, Z. Jiang, M. Liu, W. Su, *Tetrahedron Lett.* 54 (2013) 2006; f) I. Perepichka, S. Kundu, Z. Hearne, C.-J. Li, *Org. Biomol. Chem.* 13 (2015) 447, and references cited herein.

[10] For recent overviews, see: a) Y.-L. Zhao, Y. Wang, Y.-C. Luo, X.-Z. Fu, P.-F. Xu, *Tetrahedron Lett.* 56 (2015) 3703; b) S. Stockerl, O. García Mancheño, *Org. Chem. Front.* 3 (2016) 277. For the initial studies: c) K. C. Nicolaou, R. Reingruber, D. Sarlah, S. Bräse, *J. Am. Chem. Soc.* 131 (2009) 2086; d) J. C. Conrad, J. Kong, B. N. Laforteza, D. W. C. MacMillan, *J. Am. Chem. Soc.* 131 (2009) 11640. See also: e) F. Benfatti, M. G. Capdevila, L. Zoli, E. Benedetto, G. Cozzi, *Chem. Commun.* (2009) 5919; f) X. H. Ho, S. I. Mho, H. Kang, H. Y. Jang, *Eur. J. Org. Chem.* (2010) 4436; g) B. Zhang, S. K. Xiang, L. H. Zhang, Y. X. Cui, N. Jiao, *Org. Lett.* 13 (2011) 5212; h) J. Zhang, B. Tiwari, C. Xing, X. Chen, Y. G. Chi, *Angew. Chem. Int. Ed.* 51 (2012) 3649; i) Z. L. Meng, S. T. Sun, H. Q. Yuan, H. X. Lou, L. Liu, *Angew. Chem. Int. Ed.* 53 (2014) 553; j) Y. Ma, G. Zhang, D. Yang, R. Wang, *Org. Lett.* 16 (2014) 5358; k) X. Liu, S. Sun, Z. Meng, H. Lou, L. Liu, *Org. Lett.* 17 (2015) 2396.

[11] Selected recent reviews: a) M. Mahlau, B. List, *Angew. Chem. Int. Ed.* 52 (2013) 518; b) K.

Brak, E. N. Jacobsen, *Angew. Chem. Int. Ed.* 52 (2013) 534; c) S. Beckendorf, S. Asmus, O. García Mancheño, *ChemCatChem* 4 (2012) 926.

[12] Selected reviews: a) T. Akiyama, *Chem. Rev.* 107 (2007) 5744; (b) M. Terada, *Synthesis* 12 (2010) 1929; c) R. J. Phipps, G. L. Hamilton, D. F. Toste, *Nature Chem.* 4 (2012) 603; d) D. Parmar, E. Sugiono, S. Raja, M. Rueping, *Chem. Rev.* 114 (2014) 9047.

[13] a) A. J. Neel, J. P. Hehn, P. F. Tripet, F. D. Toste, *J. Am. Chem. Soc*. 135 (2013) 14044; b) A. Milo, A. J. Neel, F. D. Toste, *Science* 347 (2015) 737.

[14] G. Bergonzini, C. S. Schindler, C.-J. Wallentin, E. N. Jacobsen, C. R. J. Stephenson, *Chem. Sci.* 5 (2014) 112.

[15] a) S. Beckendorf, O. García Mancheño *Synthesis* 44 (2012) 2162. For just the synthesis of regioisomeric phosphoramidites, see: b) C. Recsei, S. P. McErlean, *Tetrahedron* 68 (2012) 464. For 1,2,4-triazole-BINOLs, see: b) B. Liu, F.-Y. Jiang, H.-B. Song, J.-S. Li, *Tetrahedron: Asymmetry* 17 (2006) 2149.

[16] For related non-asymmetric methods, see: a) W.-P. To, Y. Liu, T.-C. Lau, C.-M. Che, *Chem. Eur. J.* 19 (2013) 5654; b) C. Huo, M. Wu, X. Jia, H. Xie, Y. Yuan, J. Tang, *J. Org. Chem.* 79 (2014) 9860; d) Y. Liu, D. Zhang-Negrerie, K. Zhao, Y. Du, *J. Org. Chem.* 81 (2016) 3372.

[17] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* 62 (1997) 7512.

[18] D. Casarini, L. Lunazzi, A. Mazzanti, *J. Org. Chem.* 73 (2008) 2811.

[19] J. Bouffard, B. K. Keitz, R. Tonner, V. Lavallo, G. Guisado-Barrios, G. Frenking, R. H. Grubbs, G. Bertrand, *Organometallics* 30 (2011) 2617.

[20] Y. Chen, A. Wang, Z. Tao, Y. Deng, X. Hu, *Lett. Org. Chem.* 11 (2014) 627.

[21] M. Busch, M. Schlageter, D. Weingand, T. Gehring, *Chem. Eur. J.* 15 (2009) 8251.

[22] a) M. Basauri-Molina, D. G. A. Verhoeven, A. J. van Schaik, H. Kleijn, R. J. M. Klein Gebbink, *Chem. Eur. J.* 21 (2015) 15676; b) A. L.-F. Chow, M. H. So, W. Lu, N.-Y. Zhu, C.-M. Che, *Chem. Asian J.* 6 (2011) 544.

[23] T. Fujihara, Y. Tomike, T. Ohtake, J. Terao, Y. Tsuni, *Chem. Commun.* 48 (2011) 9699.

[24] C. P. J. Schubert, M. G. Tamba, G. H. Mehl, *Chem. Commun.* 48 (2012) 6851.

[25] H. Ishitani, M. Ueno, S. Kobayashi, *J. Am. Chem. Soc.* 122 (2000) 8180.

[26] D. Ishikawa, T. Mori, Y. Yonamine, W. Nakanishi, D. L. Cheung, J. P. Hill, K. Ariga, *Angew. Chem. Int. Ed.* 54 (2015) 8988.

[27]] D. Nakashima, H. Yamamoto, *J. Am. Chem. Soc.* 128 (2006) 9626.

[28] False positive high enantioselectivities (>90:10 e.r. for **3a**) were obtained at the beginning of the study since the racemic compound was crystallized-out in the HPLC vials when dissolving the probes in a 90:10 hexane/iPrOH mixture, thus enhancing the e.r. in solution.

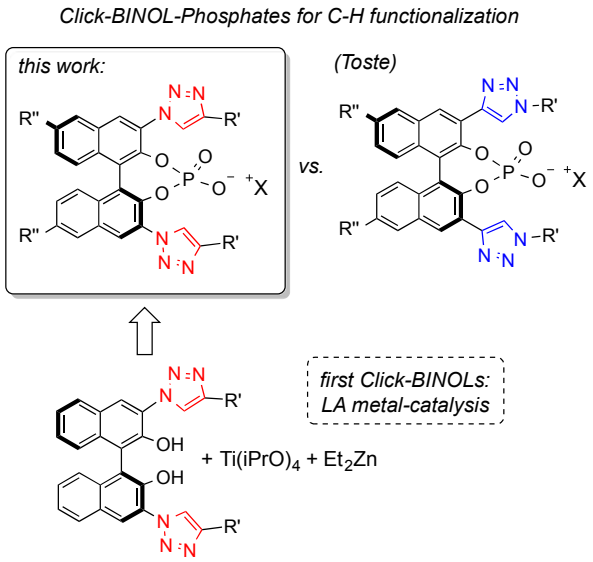


Figure 1. Click-BINOL derivatives in asymmetric catalysis

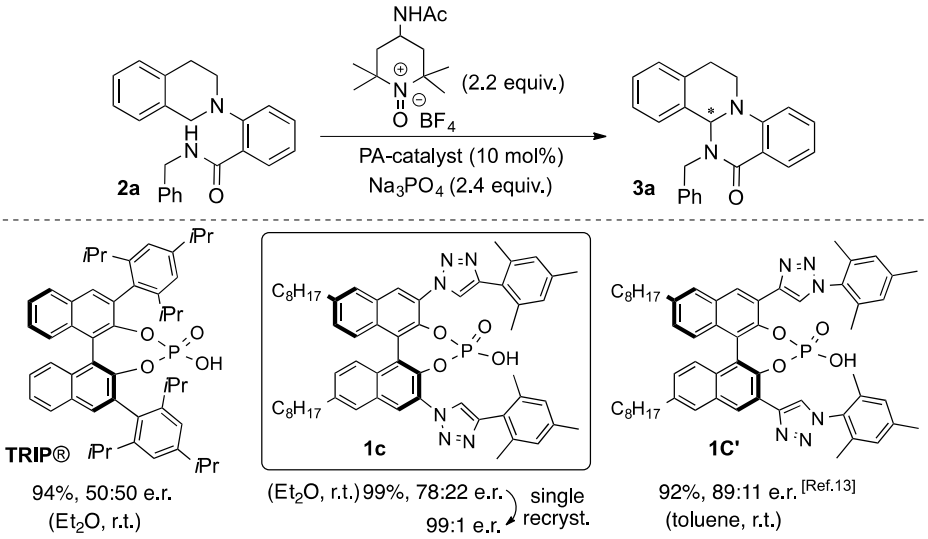
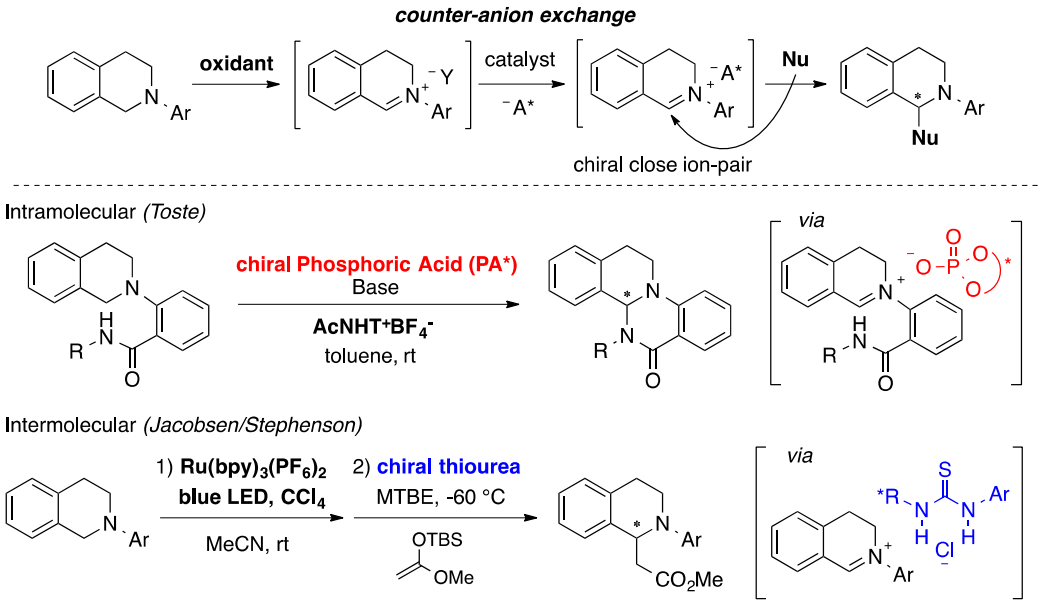
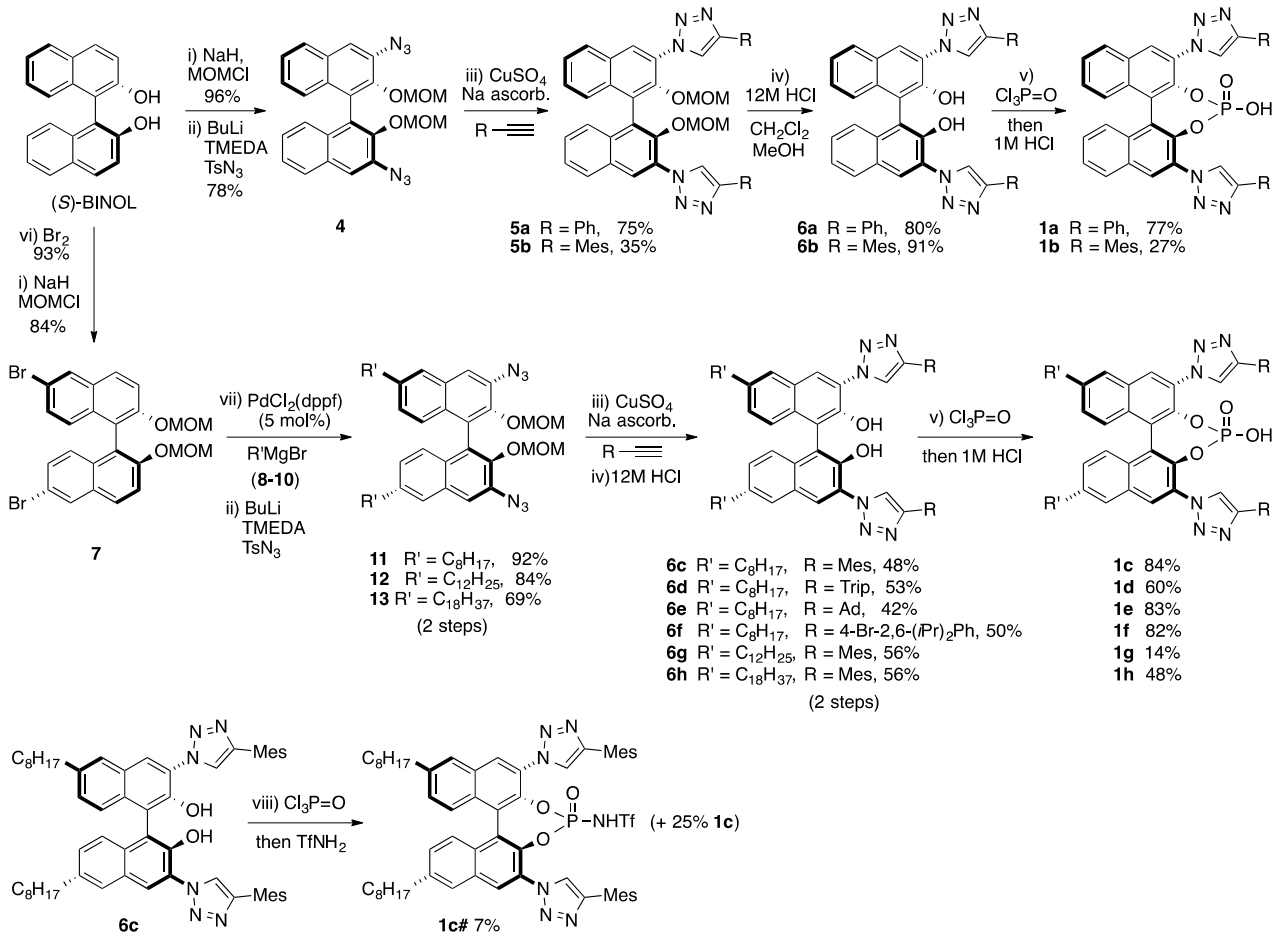


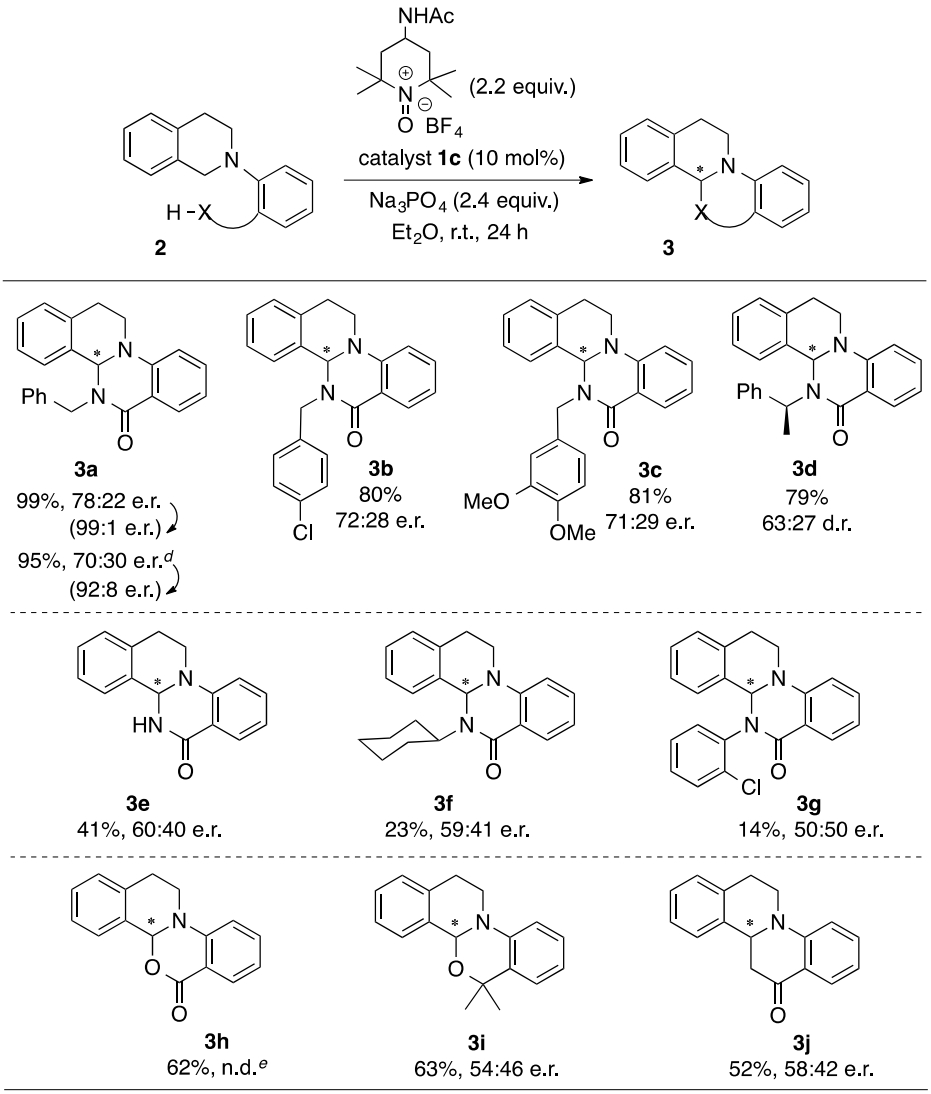
Figure 2. Comparison of PA-catalysts in the model intramolecular C-H functionalization reaction



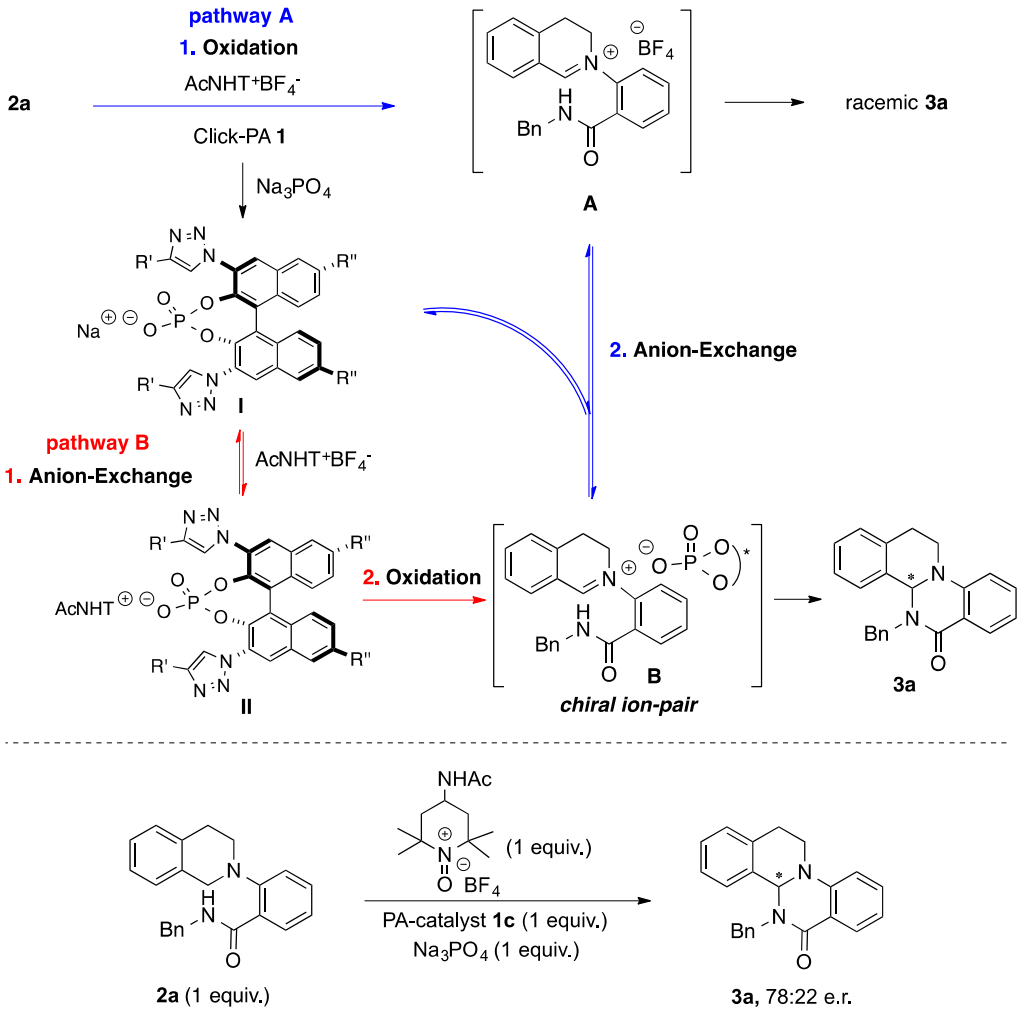
Scheme 1. Concept and examples of asymmetric counter-anion organocatalysis in C-H bond functionalization



Scheme 2. Synthesis of the new triazole-based PA-catalysts

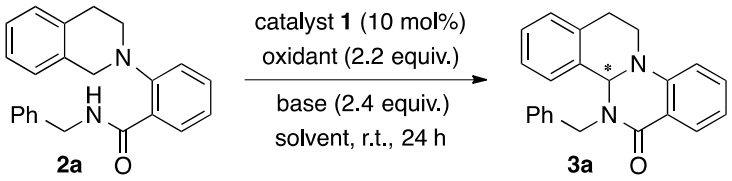


Scheme 3. Reaction with substituted THIQ **2**. [a] Conditions: i) **2** (1 equiv.), $AcNHT^{+}BF_4^{-}$ (2.2 equiv.), **1c** (10 mol%) and Na_3PO_4 (2.4 equiv.) were stirred in dry Et_2O at r.t. for 24 h. [b] Isolated yield. [c] Enantiomeric ratios determined by chiral HPLC (e.r. values after a single recrystallization from CH_2Cl_2/hexane in brackets). [d] 1.0 mmol reaction scale. [e] The enantiomers could not be separated by chiral HPLC using hexanes/iPrOH mixtures as eluent.



Scheme 4. Plausible mechanism and stoichiometric anion-exchange study

Table 1. Optimization of the reaction with **2a**[a]



entry	oxidant	catalyst	base	solvent	yield (%)[b]	e.r.[c]
1	$AcNHT^+BF_4^-$	--	Na_3PO_4	toluene	66	--
2	$AcNHT^+BF_4^-$	**1a**	Na_3PO_4	toluene	65	41:59
3	$AcNHT^+BF_4^-$	**1b**	Na_3PO_4	toluene	89	60:40
4	$AcNHT^+BF_4^-$	**1c**	Na_3PO_4	toluene	99	66:34
5	$AcNHT^+BF_4^-$	**1d**	Na_3PO_4	toluene	99	66:34
6	$AcNHT^+BF_4^-$	**1e**	Na_3PO_4	toluene	99	64:36
7	$AcNHT^+BF_4^-$	**1c**	Na_3PO_4	*p*-xylene	74	70:30
8	$AcNHT^+BF_4^-$	**1c**	Na_3PO_4	MTBE	99	74:26
9	*$AcNHT^+BF_4^-$*	***1c***	Na_3PO_4	*Et_2O*	*99*	*78:22*
10	$AcNHT^+BF_4^-$	**1c#**	Na_3PO_4	Et_2O	73	67:33
11	$AcNHT^+BF_4^-$	**1d**	Na_3PO_4	Et_2O	95	70:30
12	$AcNHT^+BF_4^-$	**1e**	Na_3PO_4	Et_2O	93	74:26
13	$AcNHT^+BF_4^-$	**1f**	Na_3PO_4	Et_2O	84	46:54
14	$AcNHT^+BF_4^-$	**1g**	Na_3PO_4	Et_2O	80	68:32
15	$AcNHT^+BF_4^-$	**1h**	Na_3PO_4	Et_2O	87	74:26
16	$AcNHT^+BF_4^-$	**1c**	K_3PO_4	Et_2O	77	66:34
17	$AcNHT^+BF_4^-$	**1c**	K_2CO_3	Et_2O	60	75:25
18	$AcNHT^+ClO_4^-$	**1c**	Na_3PO_4	Et_2O	99	63:37
19	$T^+BF_4^-$	**1c**	Na_3PO_4	Et_2O	88	66:34
20	$Ph_3C^+BF_4^-$	**1c**	Na_3PO_4	Et_2O	86	54:46
21	$AcNHT^+BF_4^-$	**1c**	Na_3PO_4	Et_2O[d]	78	77:23
22	$AcNHT^+BF_4^-$	**1c**	Na_3PO_4	Et_2O[e]	92	56:44
23	$AcNHT^+BF_4^-$	**1c**[f]	Na_3PO_4	Et_2O	80	75:25
24	$AcNHT^+BF_4^-$	**1c**[g]	Na_3PO_4	Et_2O	83	73:27

[a] Conditions: i) **2a** (1 equiv.), oxidant (2.2 equiv.), PA-catalyst **1** (10 mol%) and base (2.4 equiv.) were stirred in the appropriate dry solvent at r.t. for 24 h. [b] Isolated yield. [c] Enantiomeric ratios determined by chiral HPLC. [d] Reaction at -20 °C. [e] Reaction at -40 °C. [f] 5 mol% of catalyst was used. [g] 2.5 mol% of catalyst was used.