New Derivatives of VAPOL and VANOL: Structurally Distinct Vaulted Chiral Ligands and Brønsted Acid Catalysts

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Abstract: Lean and efficient multi-gram scale syntheses of a number of new derivatives of VAPOL and VANOL are described. These are structurally novel chiral ligands and Brønsted acid catalysts, and could provide singular profiles for reactivity and asymmetric inductions in catalysis.

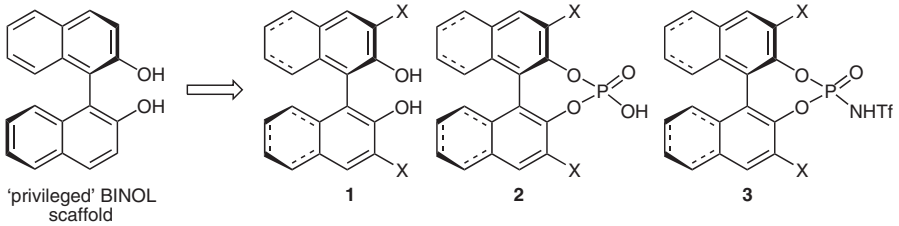
Key words: VAPOL, VANOL, ligand, Brønsted acid, asymmetric catalysis

The field of chiral Brønsted acid catalysis has witnessed an exponential growth in the last decade.[1] Countless efficient asymmetric reaction systems mediated by these organocatalysts have been developed by numerous research groups around the world, and this growth continues unabated till date. The BINOL ligand scaffold has been ubiquitous in the realm of organocatalysis, and is entitled to the label of a 'privileged' ligand.[2]

Shown in Scheme 1 are the three most extensively utilized groups of chiral Brønsted acids derived from the BINOL scaffold. As weakly acidic Brønsted acids, a variety of BINOL derivatives **1** have been prepared and utilized in asymmetric organocatalysis.[3] In 2004, the research groups of Akiyama[4a] and Terada[4b] independently introduced the 3,3′-disubstituted BINOL phosphoric acids **2** for asymmetric Mannich-type reactions. These phosphoric acids have since then proven to be versatile chiral Brønsted acid catalysts, and a multitude of successful catalytic asymmetric systems have been developed under their aegis.[5] Chiral BINOL *N*-triflyl phosphoramide catalysts **3** were subsequently introduced by Yamamoto in 2006 for an asymmetric Diels–Alder reaction.[6] These are stronger Brønsted acids (pK_a of –3 in water)[1c] as compared to the corresponding BINOL phosphoric acids (pK_a of 1 in water);[1c] these *N*-triflyl phosphoramides have also found considerable success in asymmetric organocatalysis in recent years.[7]

The vaulted biaryl diol ligands VAPOL (**4**) and VANOL (**5**) were introduced by our group in 1993 (Figure 1).[8,9] These ligands possess a unique vaulted backbone, and are thus structurally distinct from the BINOL ligands. Since their introduction, VAPOL and VANOL have served as the basis for a number of successful catalytic asymmetric systems from several research groups. Catalysts prepared from VAPOL/VANOL and various boron compounds have been shown to mediate efficient and general asymmetric aziridinations,[10,11] as well as asymmetric hetero-Diels–Alder cycloadditions.[12] VAPOL/VANOL catalysts containing aluminum or zirconium have successfully catalyzed asymmetric Diels–Alder reactions,[8,13] imino-aldol reactions,[14] and Baeyer–Villiger reactions.[15] Phosphoramidite derivatives of VAPOL and VANOL have been shown to be effective ligands in rhodium-catalyzed enantioselective intramolecular hydroarylation of alkenes.[16] VAPOL as a standalone species can mediate asymmetric Petasis reactions, affording chiral α-amino acid esters with high asymmetric inductions.[17] An increasing number of systems in recent years have showcased the use of the chiral phosphoric acid catalysts prepared from VAPOL and VANOL. Imine amidations,[18] imino ester reductions,[19] imine imidations,[20] as well as desymmetrization of *meso*-aziridines to afford vicinal diamines[21] and vicinal amidophenylthioethers[22] have been all shown to proceed with excellent levels of asymmetric inductions under their catalysis.

The utility of VAPOL and VANOL is poised to increase as both antipodes of these ligands are now commercially available.[9,23] Despite the significant use of catalysts derived from VAPOL and VANOL in asymmetric catalysis,



Scheme 1 Chiral Brønsted acid catalysts from the BINOL scaffold

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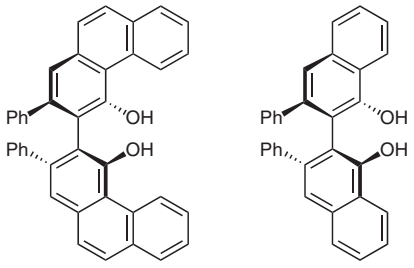


Figure 1 Structurally distinct vaulted biaryl diol ligands

a dearth of information exists in the literature for the preparation of derivatives of these ligands. In the present study, we thus wish to report efficient and reproducible multi-gram scale syntheses of several new derivatives of VAPOL and VANOL. Shown in Figure 2 are the derivatives prepared in the present study, these are structurally novel chiral ligands and Brønsted acid catalysts; the asymmetric active sites created by these derivatives will be electronically and sterically distinct from those created from the corresponding BINOL derivatives, thus resulting in a profile for reactivity and asymmetric inductions that could be quite singular.

We believe that the uniqueness of their structure, and the subsequent promise of radically different reactivity profiles, warrants the inclusion of these derivatives in any screen comprised of chiral Brønsted acid catalysts.

A New Family of Vaulted Ligands – 8,8′-Diaryl VANOL Derivatives

Gaining inspiration from the enormous success associated with the 3,3′-diaryl BINOL derivatives **1** in asymmetric catalysis, we were drawn towards the prospect of creating a new family of structurally distinct vaulted ligands, the 8,8′-diaryl VANOL derivatives **16** (Scheme 2). These would be unique ligands, and could again be completely orthogonal in their reaction profiles as compared to the 3,3′-diaryl BINOL ligands. Not only would they be interesting chiral scaffolds for standalone weak Brønsted acid catalysis, but their phosphoric acid and phosphoramide derivatives would be attractive in the realm of strong Brønsted acid catalysis as well.

We have previously reported the synthesis of one such family member, the 8,8′-Ph_2VANOL **6**.[9b] A linear route was adopted in that study (pathway **a** in Scheme 2), that is, to prepare each new family member **16** with a different aryl group on the 8 and 8′ position of the ligand backbone, one would be required to begin from the very start of the synthetic route, with a different ortho-bromobiaryl **21**, which in turn would have to be prepared from the corresponding aromatic coupling precursors. Such a pathway thus becomes cumbersome and un-amenable for the preparation of an entire family of these ligands.

At the outset of the present study, it was desired to have a general and *nonlinear* route towards these new derivatives, which should make it possible to generate a large number of family members using similar reaction conditions. The ideal retrosynthetic analysis for the preparation of a large family of these ligands is presented by pathway **b** in Scheme 2. The syntheses would start from compound **18**, which is the monomer used for the synthesis of the VANOL ligand. We have already reported an efficient multi-gram scale synthesis for this compound,[9] and this was thus thought to be an attractive starting point for the present work. A transition-metal-catalyzed C–H activation and coupling reaction should then be able to install sterically and electronically different aromatic substituents on the 8-position of the VANOL monomer, thereby providing the requisite monomers **17** for the new ligands. Subsequent dimerization and deracemization, in a similar fashion as done during our previous syntheses of these

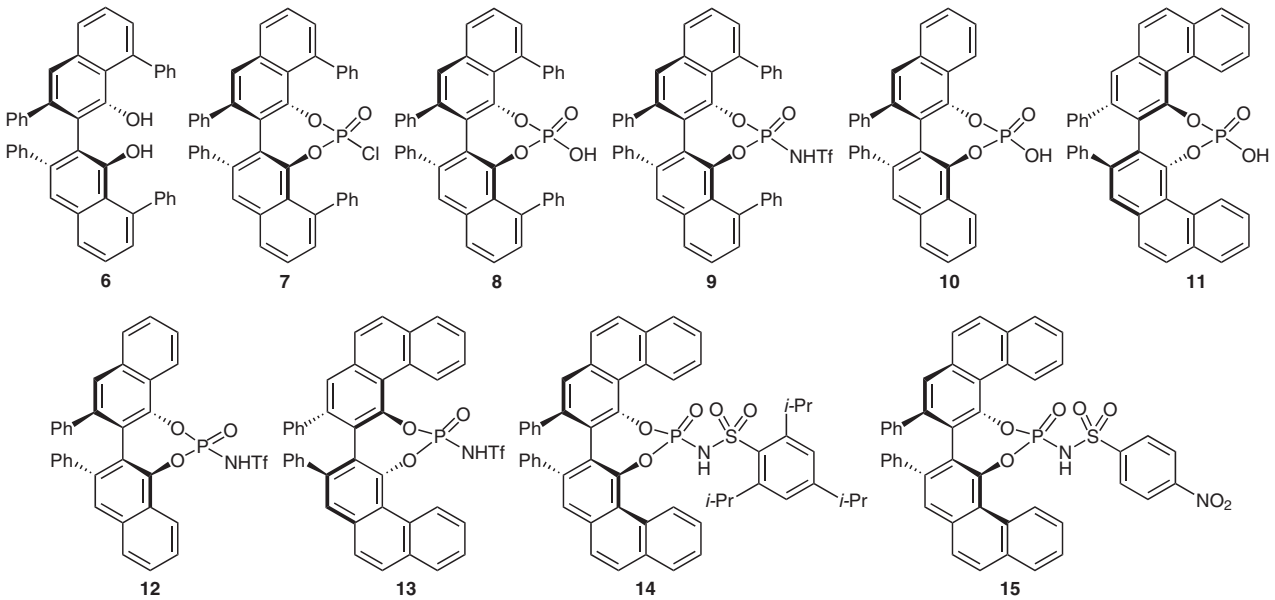


Figure 2 New derivatives of VAPOL and VANOL available from the present study

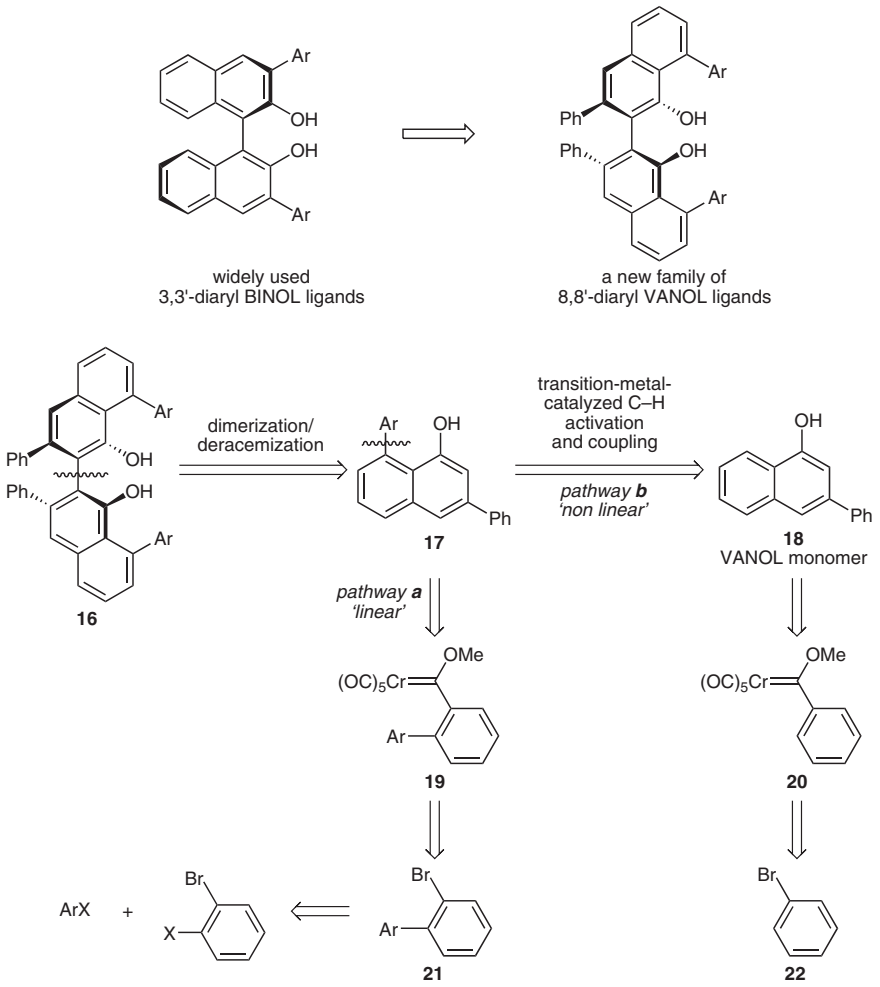
vaulted ligands,[9] should then afford the new family of 8,8′-diaryl VANOL ligands **16**.

The expectations from this retrosynthetic analysis were borne out quite satisfyingly when the multi-gram synthesis of (*S*)-8,8′-Ph_2VANOL **6** was carried out as a proof of principle (Scheme 3). All reactions were optimized on a small scale first, and then demonstrated on larger scales for multiple times. The yields reported are the average of all runs on larger scales. The initial transition-metal-catalyzed C–H activation/coupling step was the key for the synthesis; it was our synthetic handle to be able to rapidly prepare the entire family of these new ligands. To our pleasure, a phenoxy-directed palladium-mediated C–H activation/coupling protocol developed by Miura and coworkers[24] worked smoothly from the VANOL monomer **18** to afford the corresponding new acetylated monomer **23**, in 75% isolated yield over 2 steps at a multi-gram scale. Attempts to isolate the monomer **24** after the initial Pd-coupling reaction by silica gel chromatography failed,[24] thus requiring the subsequent acetylation of the crude material to afford the acetylated monomer **23**. This could then be isolated as a pure compound after silica gel column chromatography, and a simple deacetylation was then optimized to afford the pure monomer **24** in excellent yield, again at a multi-gram scale. The monomer was dimerized in air with acceptable yields; the dimer was then subjected to a deracemization protocol with CuCl and (–)-sparteine to afford the optically pure (*S*)-8,8′-Ph_2VANOL ligand **6** in good yields in multi-gram quantities.

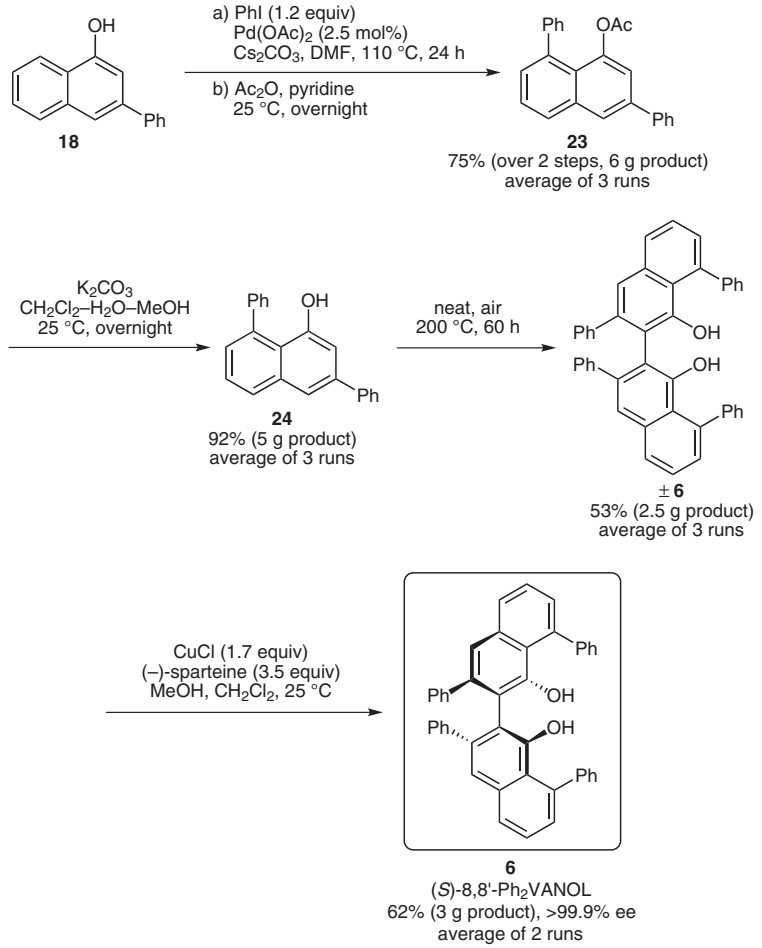
Thus, a lean, efficient and multi-gram scale synthesis of **6** could be developed, and a proof of principle demonstrated for the synthesis of a new family of biaryl diol ligands in the future; this should in principle be easily achieved by simply substituting iodobenzene in the initial Pd-catalyzed C–H activation/coupling reaction in the above synthetic route with a variety of electronically and sterically distinct aryl iodides, and the rest of the synthesis should be identical as for **6**.

Brønsted Acid Derivatives of 8,8′-Ph_2VANOL

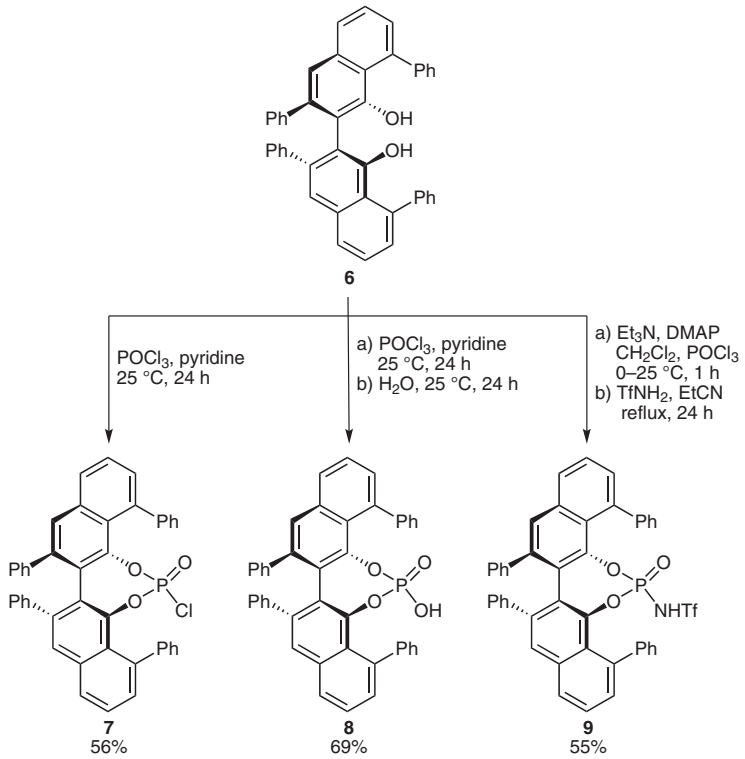
We were subsequently interested in demonstrating the preparation of the phosphoric acid **8** and the *N*-triflyl phosphoramide **9** derivatives of the new 8,8′-Ph_2VANOL ligand **6**. This was done in acceptable yields, and is presented in Scheme 4. An interesting and unexpected outcome during the optimization of these syntheses was that the phosphorous chloride intermediate **7** could be isolated by silica gel chromatography in good yields (Scheme 4).



Scheme 2 A new family of structurally distinct vaulted ligands



Scheme 3 Multi-gram scale synthesis of (*S*)-8,8′-Ph_2VANOL **6**

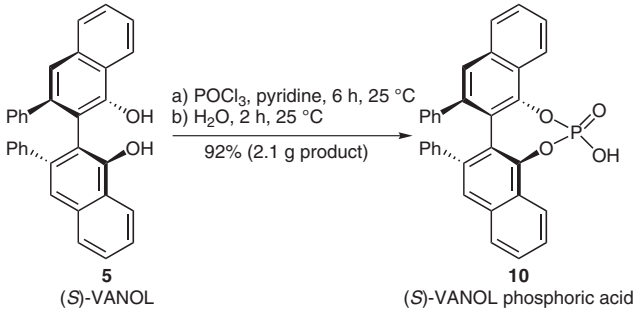


Scheme 4 Brønsted acid derivatives of 8,8′-Ph_2VANOL **6**

Displacement of chloride from this intermediate should be facile, to introduce other functionality such as urea/thiourea groups, thus paving the way towards other novel Brønsted acid catalysts or H-bonding ligands for use in asymmetric catalysis.

Brønsted Acid Derivatives of VANOL

VANOL phosphoric acid **10** was prepared at a multi-gram scale from VANOL (**5**), in an excellent yield and under mild conditions (Scheme 5). Thus, VANOL was reacted with $POCl_3$ at room temperature, followed by the addition of water, which upon workup and purification afforded pure VANOL phosphoric acid **10** in 92% isolated yield (2.1 g product). While the synthesis of optically active **10** has never been reported before, we have previously reported the synthesis of racemic **10**, via a route that involved significantly harsher conditions than those that have been developed for the present study.[9a,25] We find that these milder conditions lead to cleaner reaction mixtures and higher yields.



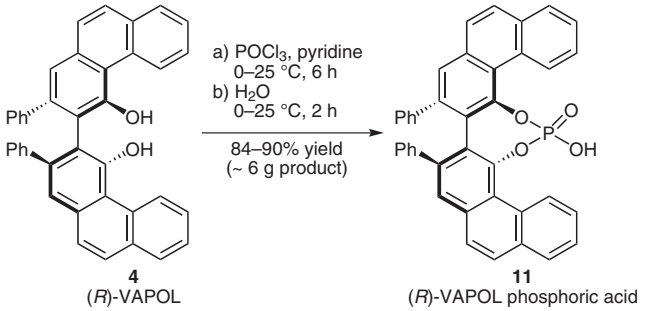
Scheme 5 Multi-gram scale synthesis of VANOL phosphoric acid **10**

The stronger Brønsted acid, *N*-triflyl VANOL phosphoramide **12**, was prepared in 76% isolated yield (2.2 g product) in a one-pot two-step sequence[6] starting from VANOL **5** (Scheme 6).

Brønsted Acid Derivatives of VAPOL

As with VANOL, the phosphoric acid **11**[25] (Scheme 7) and the *N*-triflyl phosphoramide **13** (Scheme 8) Brønsted acid derivatives of VAPOL were also prepared at multi-gram scales, and with excellent yields.

It was realized that the *N*-triflyl phosphoramide derivatives offered yet another handle with which to tune the

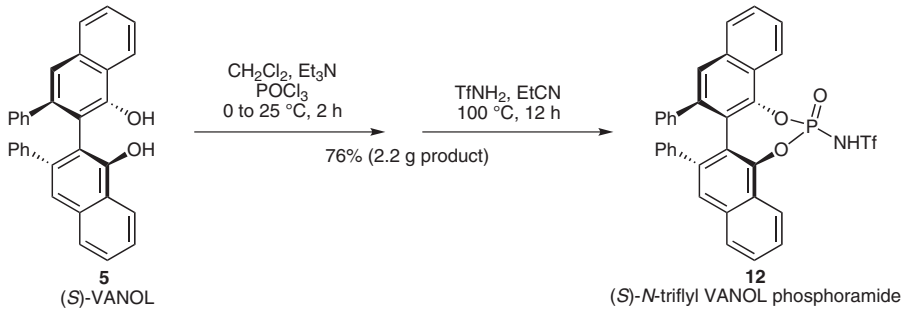


Scheme 7 Multi-gram scale synthesis of VAPOL phosphoric acid **11**

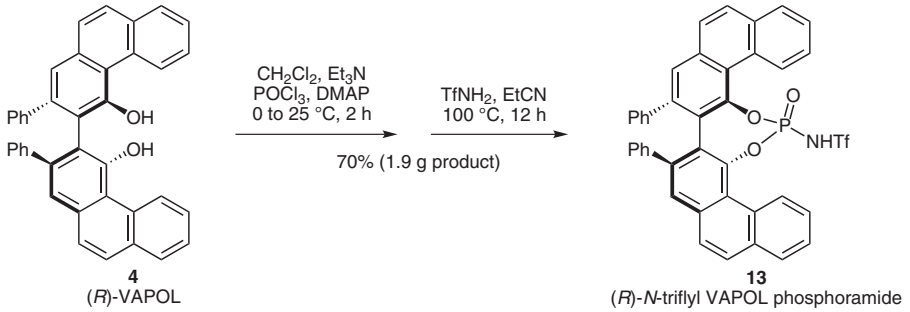
asymmetric active sites of these catalysts – the triflate side chain. If the trifluoromethyl group in these derivatives was to be replaced with a bulky aromatic group, it would add yet another element of steric bulk into the system. Thus, the *N*-TRIP-benzenesulfonyl VAPOL phosphoramide **14** and the *N*-nitrobenzenesulfonyl VAPOL phosphoramide **15** Brønsted acids were also prepared using similar procedures as before (Scheme 9).

By virtue of their unique vaulted structure, the biaryl diol ligands VAPOL and VANOL have carved a special niche for themselves in asymmetric catalysis. A multitude of different catalytic asymmetric reactions have been mediated by the catalysts prepared from these ligands, affording excellent selectivities, yields and asymmetric inductions.[8,10–22] The use of these ligands in the future will be further facilitated by that they are now commercially available.[9,23]

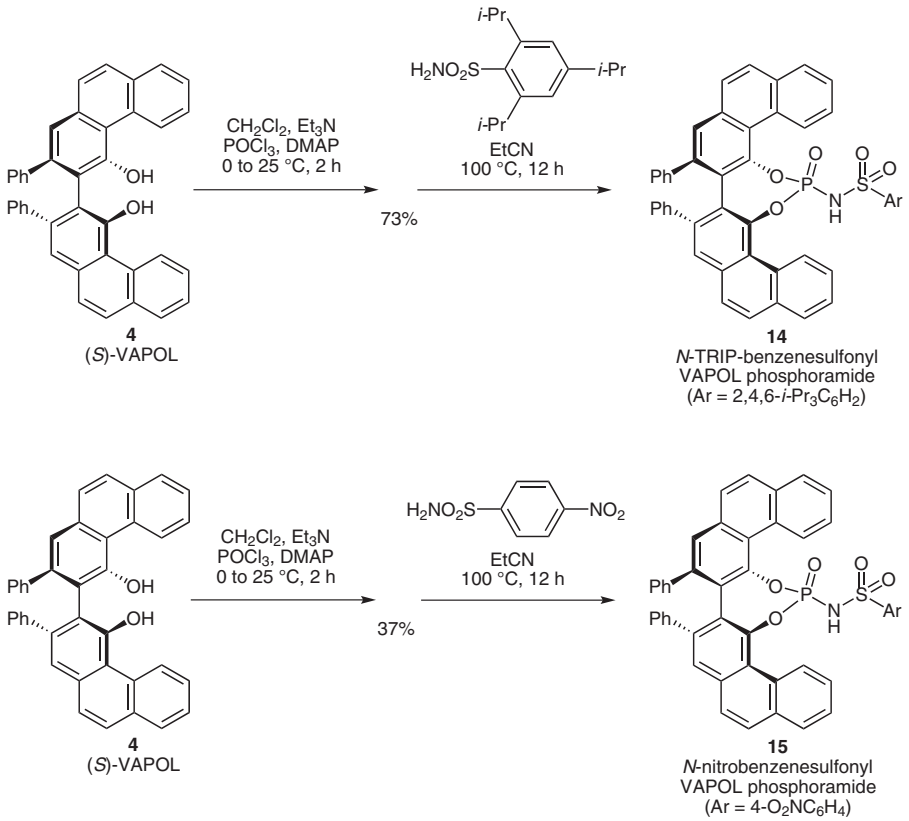
Anticipating an increased use of these ligands in asymmetric catalysis in the near future, we have initiated a program to prepare novel derivatives of these ligands. Herein, we have reported our preliminary results from this study; efficient and reproducible multi-gram scale syntheses of several new chiral ligands and Brønsted acid catalysts based on the framework of VAPOL and VANOL have been presented. These are structurally distinct as compared to the traditional BINOL scaffolds, and should generate singular profiles for reactivity and asymmetric inductions. We hope that this expectation gets borne out in our laboratories in the near future, and in those of others actively engaged in the science of asymmetric catalysis.



Scheme 6 Multi-gram scale synthesis of *N*-triflyl VANOL phosphoramide **12**



Scheme 8 Multi-gram scale synthesis of *N*-triflyl VAPOL phosphoramide **13**



Scheme 9 *N*-Benzenesulfonyl VAPOL phosphoramide Brønsted acid catalysts

Both antipodes of VAPOL and VANOL are commercially available from Aldrich and Strem Chemicals, Inc. Alternatively, they can be prepared according to a procedure described in literature.[9] If desired, they could be purified using column chromatography on regular silica gel using an eluent mixture of 2:1 CH_2Cl_2–hexanes. $POCl_3$ was purchased from Aldrich, and pyridine from Jade Scientific, and both were used as obtained. Other reagents were used as purchased from commercial sources. CH_2Cl_2 and Et_3N were dried from CaH_2 under N_2. Propionitrile and DMF were distilled appropriately before use. The VANOL monomer **18** can be prepared on a multi-gram scale according to a procedure described in literature.[9] For the synthesis of VAPOL phosphoric acid **11**, see reference 25.

The silica gel for column chromatography was purchased from Sorbent Technologies with the following specifications: standard grade, 60 Å porosity, 230 × 400 mesh particle size, 500–600 m^2/g surface area and 0.4 g/mL bulk density. IR spectra were taken on a Nicolet IR/42 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a VXR-500 MHz instrument in DMSO-d_6 or $CDCl_3$ unless otherwise noted, wherein either DMSO-d_5 was used as the internal standard for both ^1H NMR ($\delta = 2.49$) and ^{13}C NMR ($\delta = 39.5$) or $CHCl_3$ was used as the internal standard for both ^1H NMR ($\delta = 7.24$) and ^{13}C NMR ($\delta = 77$), respectively. Low-resolution mass spectra analysis was performed at the Department of Chemistry at Michigan State University. High-resolution mass spectra analysis was performed at the Department of Biochemistry at Michigan State University. Analytical TLC was performed on Silicycle silica gel plates with F-254 indicator. Visualization was by short wave (254 nm) and long wave (365 nm) ultraviolet light, or by staining with phosphomolybdic acid reagent (20% wt in EtOH, Aldrich). HPLC was carried out using a Varian Prostar 210 Solvent Delivery Module with a Prostar 330 PDA Detector and a Prostar Workstation. Optical rotations were obtained on a PerkinElmer 341 polarimeter at a wavelength of 589 nm (sodium D line) using a 1.0 decimeter cell with a total volume of 1.0 mL. Specific rotations are reported in degrees per decimeter at 25 °C and the concentrations are given in grams per 100 mL of the solvent indicated.

3,8-Diphenylnaphthalen-1-yl Acetate (23)

A 250 mL round-bottom flask, equipped with a magnetic stir bar and a water condenser, was flame dried and cooled under argon. To the flask was added Cs_2CO_3 (14.81 g, 45.45 mmol, 2 equiv), and the assembly was then heated at 150 °C for 2 h under high vacuum (0.1 mmHg). This was subsequently cooled to r.t., and the VANOL monomer **18** (5.00 g, 22.73 mmol, 1 equiv) was added, which was followed by the addition of $Pd(OAc)_2$ (127.5 mg, 0.57 mmol, 0.025 equiv), DMF (120 mL), and iodobenzene (3.04 mL, 27.28 mmol, 1.2 equiv). The assembly was then fitted with a rubber septum and an argon balloon, and stirred in an oil bath at 110 °C for 24 h. The reaction mixture was subsequently cooled to r.t., and added to a separatory funnel. Also added to the funnel were EtOAc (200 mL), H_2O (200 mL), and brine (50 mL). The layers were separated, the aqueous layer extracted with EtOAc (4 × 200 mL), the organic layers were combined, and washed with H_2O (2 × 500 mL), aq 0.5 N HCl (2 × 500 mL), and brine. The organic layer was dried (Na_2SO_4), filtered through a pad of Celite, subjected to rotary evaporation till dryness, and finally to high vacuum (0.1 mm Hg) overnight to afford the crude intermediate product. To the flask containing the crude product was then added pyridine (120 mL) to dissolve the crude product. The flask was equipped with a rubber septum and an argon balloon. Ac_2O (11.00 mL, 113.65 mmol, 5 equiv) was then added slowly via a syringe and the reaction mixture stirred at r.t. for 12 h. The mixture was added to a separatory funnel, with CH_2Cl_2 (700 mL). This was then washed with aq 1 N HCl (4 × 700 mL), the organic layers combined, washed with brine, dried (Na_2SO_4), filtered through a pad of Celite, subjected to rotary evaporation till dryness, and finally to high vacuum to afford crude product **23**. Column chromatography with regular silica gel and an eluent system of 1:19 EtOAc–hexanes afforded pure **23** as a light yellow solid in 76% isolated yield (5.86 g, 17.34 mmol); light yellow solid; mp 117–119 °C; R_f = 0.24 (1:19 EtOAc–hexanes).

IR (thin film): 3055w, 3028w, 1785s, 1367m, 1203s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.38 (s, 3 H), 7.25 (dd, *J* = 1.2, 7.1 Hz, 1 H), 7.34–7.51 (m, 10 H), 7.68–7.70 (m, 2 H), 7.93 (d, *J* = 8.3 Hz, 1 H), 8.02 (d, *J* = 1.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.7, 119.8, 123.8, 124.7, 125.9, 126.6, 127.3, 127.6, 127.7, 128.6, 128.9, 129.5, 130.2, 136.0, 137.3, 138.4, 139.7, 143.4, 147.2, 169.9.

MS: *m*/*z* (%) = 338 (10, M^+), 297 (28), 296 (100).

HRMS (ESI+): *m*/*z* calcd for $C_{24}H_{19}O_2$ (M + H): 339.1385; found: 339.1393.

3,8-Diphenylnaphthalen-1-ol (24)

To a 500 mL round-bottom flask, fitted with a magnetic stir bar, was added compound **23** (5.76 g, 17.04 mmol, 1 equiv) and anhyd CH_2Cl_2 (25 mL) to obtain a clear yellow solution. To this was added slowly a clear solution of K_2CO_3 (4.71 g, 34.08 mmol, 2 equiv) in H_2O (18 mL). To the reaction flask was then added MeOH (110 mL), and the reaction mixture was stirred at r.t. for 15 h. During the course of the reaction, the color of the solution changed from yellow to an intense green and finally to light brown/orange, and salts precipitated out. For the workup, the reaction mixture was added to a separatory funnel, and H_2O (150 mL) and CH_2Cl_2 (150 mL) were also added. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 150 mL) and Et_2O (2 × 150 mL). The organic layers were combined, washed with brine, dried (Na_2SO_4), filtered through a pad of Celite, subjected to rotary evaporation till dryness, and finally to high vacuum to afford crude product **24**. Column chromatography with regular silica gel and an eluent mixture of 1:19 EtOAc–hexanes afforded pure **24** as a colorless oil in 94% isolated yield (4.80 g, 16.22 mmol); R_f = 0.22 (1:19 EtOAc–hexanes).

IR (thin film): 3490s, 3055w, 1628m, 1496m, 1373m cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 5.47 (s, 1 H), 7.18–7.20 (m, 2 H), 7.36 (tt, *J* = 1.2, 7.4 Hz, 1 H), 7.44–7.48 (m, 3 H), 7.50–7.54 (m, 5 H), 7.70–7.72 (m, 3 H), 7.90 (dd, *J* = 1.0, 8.3 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 111.2, 118.9, 120.5, 125.3, 127.2, 127.5, 128.4, 128.7, 128.8, 129.0, 129.0, 129.5, 135.9, 136.1, 139.6, 140.4, 141.1, 153.3.

MS: *m*/*z* (%) = 296 (100, M^+).

HRMS (ESI+): *m*/*z* calcd for $C_{22}H_{17}O$ (M + H): 297.1279; found: 297.1274.

3,3′,8,8′-Tetraphenyl-2,2′-binaphthyl-1,1′-diol (*rac*-8,8′-Ph_2VANOL, ±6)

The monomer **24** (4.65 g, 15.71 mmol) was dissolved in Et_2O and divided equally into 5 glass test tubes (18 d × 150 h mm). The Et_2O in all test tubes was then evaporated by heating slightly on a water bath in a fume hood. All test tubes were fitted with magnetic stir bars, and subsequently heated in an oil bath at 200 °C with rapid stirring for 60 h. The test tubes were then allowed to cool down to r.t., the crude product in the test tubes dissolved in CH_2Cl_2, combined, and subjected to rotary evaporation till dryness and finally to high vacuum to afford crude product ±**6**. Careful column chromatography with regular silica gel and an eluent mixture of 1:19 EtOAc–hexanes afforded pure ±**6** as a light yellow solid in 54% isolated yield (2.50 g, 4.24 mmol); light yellow solid; mp 222–226 °C; R_f = 0.15 (1:19 EtOAc–hexanes).

IR (thin film): 3524s, 3053w, 1568m, 1493m, 1348s cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 5.46 (s, 2 H), 6.98 (d, *J* = 7.2 Hz, 2 H), 7.00–7.02 (m, 4 H), 7.11 (t, *J* = 7.5 Hz, 4 H), 7.14–7.17 (m, 4 H), 7.30–7.45 (m, 12 H), 7.74 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 117.5, 120.6, 121.2, 125.2, 125.8, 126.3, 126.9, 127.1, 127.6, 128.6, 128.6, 129.4, 135.0, 138.5, 140.9, 141.2, 144.2, 152.2.

MS: *m*/*z* (%) = 590 (100, M^+), 295 (44).

HRMS (ESI+): *m*/*z* calcd for $C_{44}H_{31}O_2$ (M + H): 591.2324; found: 591.2309.

(*S*)-3,3′,8,8′-Tetraphenyl-2,2′-binaphthyl-1,1′-diol 6

A 250 mL round-bottom flask was flame-dried and cooled under argon. After the flask had cooled to r.t., it was opened to air. To the flask were then added CuCl (1.38 g, 13.9 mmol, 1.7 equiv), MeOH (125 mL), and (–)-sparteine (6.64 mL, 28.88 mmol, 3.5 equiv), and this mixture was sonicated open to air in an ultrasound water bath at r.t. for 1 h. A dark green solution was obtained at this stage; the flask was then fitted with a rubber septum, and the solution was deoxygenated by bubbling in argon via a metallic needle (1 h inside the solution and 0.5 h above the solution). A different 1 L round-bottom flask fitted with a magnetic stir bar was flame dried and cooled under argon. To this flask was added the racemic ligand ±**6** (4.9 g, 8.3 mmol, 1 equiv), which was dissolved in anhyd CH_2Cl_2 (400 mL) to obtain a clear yellow solution. The flask was then fitted with a rubber septum, and the solution was deoxygenated with argon in a similar way as above. The copper-sparteine complex prepared above was added to this 1 L reaction flask via a cannula under argon pressure. The cannula was replaced with an argon balloon; the flask was sonicated in an ultrasound water bath for 15 min, covered with aluminum foil, and subsequently stirred at r.t. with a magnetic stirrer for 3 h. The reaction mixture was then quenched with sat. aq $NaHCO_3$ (70 mL), stirred for 10 min, and then added to a separatory funnel, which was followed by the addition of H_2O (200 mL). The layers were separated, the aqueous layer extracted with CH_2Cl_2 (3 × 200 mL), the organic layers combined, dried (Na_2SO_4), filtered through a pad of Celite, subjected to rotary evaporation till dryness and finally to high vacuum to afford a dark green crude product. This was dissolved in a minimum amount of CH_2Cl_2, and subjected

to flash column chromatography with regular silica gel and CH_2Cl_2 as the eluent, to separate the copper salts and other baseline impurities. This afforded again the crude product **6**, which was subjected to careful column chromatography with regular silica gel and an eluent mixture of 1:9 EtOAc–hexanes to afford pure **6** as a light yellow solid in 60% isolated yield (2.92 g, 4.95 mmol); mp 130–134 °C.

The optical purity of the product, (*S*)-6, was determined to be >99.9% ee by chiral HPLC analysis [Chiralcel OD-H column, hexanes–*i*-PrOH (99:1), flow rate 0.5 mL/min, 222 nm]; t_R = 12.15 min (major enantiomer); t_R = 19.37 min (minor enantiomer); $[\alpha]_D^{23}$ –43.2 (*c* 1.0, CH_2Cl_2); >99.9% ee.

(*S*)-8,8′-Ph$_2$VANOL Phosphorus Oxychloride 7

A 10 mL round-bottom flask, fitted with a magnetic stir bar, was flame-dried and cooled under argon. To this flask was then added the ligand **6** (100 mg, 0.17 mmol), which was followed by the addition of pyridine (1 mL) and $POCl_3$ (32 μL, 0.34 mmol). The flask was fitted with a rubber septum and an argon balloon, and stirred at r.t. for 24 h, at which the reaction was judged complete by TLC. The reaction mixture was then diluted with CH_2Cl_2, filtered through a pad of Celite, subjected to rotary evaporation till dryness and finally to high vacuum overnight. CH_2Cl_2 was added to the thus obtained solid crude product to get a slurry, which was again filtered through a pad of Celite. The resulting solution was subjected to rotary evaporation till dryness and finally to high vacuum to afford the crude product **7**. This was then subjected to column chromatography with regular silica gel and an eluent mixture of 1:9 EtOAc–hexanes to afford pure product **7** as a white foamy solid in 56% isolated yield (64 mg, 0.095 mmol); white foamy solid; mp 180–200 °C (dec.); R_f = 0.17 (1:9 EtOAc–hexanes); $[\alpha]_D^{23}$ +313.7 (*c* 1.0, CH_2Cl_2).

IR (thin film): 3057w, 1314s, 760s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.54 (dd, 4 H, *J* = 7.3, 11.4 Hz), 7.02 (q, 4 H, *J* = 7.6 Hz), 7.17 (q, 2 H, *J* = 7.5 Hz), 7.27–7.39 (m, 6 H), 7.47–7.54 (m, 5 H), 7.57–7.65 (m, 5 H), 7.84 (t, 2 H, *J* = 7.7 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 122.6 (d, *J* = 3.4 Hz, 1 C), 123.4 (d, *J* = 2.9 Hz, 1 C), 124.5 (d, *J* = 2.9 Hz, 1 C), 124.6 (d, *J* = 3.4 Hz, 1 C), 126.4, 126.6, 126.8, 126.9, 127.2, 127.7, 127.8, 127.9, 127.9, 128.1, 128.2, 128.5, 128.5, 128.5, 129.0, 129.1, 129.3, 129.9, 130.6, 130.9, 131.2, 135.5, 135.5, 135.6, 135.6, 138.1, 138.2, 138.3, 138.3, 139.2, 139.9, 139.9, 140.1, 140.1, 142.0, 142.5, 144.6 (d, *J* = 11.5 Hz, 1 C), 144.9 (d, *J* = 13.2 Hz, 1 C) (2 sp^2 carbons missing).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 7.30 (s).

MS: *m*/*z* (%) = 673 (15, ^{37}Cl, M$^+$), 672 (40, ^{37}Cl), 671 (42, ^{35}Cl, M$^+$), 670 (100, ^{35}Cl).

HRMS (ESI+): *m*/*z* calcd for $C_{44}H_{29}ClO_3P$ (M + H): 671.1543; found: 671.1572.

(*S*)-8,8′-Ph$_2$VANOL Phosphoric Acid 8

A 50 mL round-bottom flask, fitted with a magnetic stir bar, was flame dried and cooled under argon. To this flask was added the ligand **6** (442 mg, 0.75 mmol) and pyridine (3 mL) to obtain a clear solution. The flask was then fitted with a rubber septum and an argon balloon. $POCl_3$ (140 μL, 1.5 mmol) was then added dropwise via a syringe, and the resulting reaction mixture was stirred at r.t. for 24 h. H_2O (3 mL) was then added dropwise via a syringe, and the mixture stirred at r.t. for an additional 24 h. The mixture was then added to a separatory funnel, along with CH_2Cl_2 (75 mL). This was washed with aq 1 N HCl (7 × 75 mL), brine, dried (Na_2SO_4), filtered through a pad of Celite, subjected to rotary evaporation till dryness, and finally to high vacuum to afford crude **8**.

The crude product was subjected to column chromatography with regular silica gel and an eluent mixture of 1:9 MeOH–CH_2Cl_2. The product fractions were collected, subjected to rotary evaporation till dryness and finally to high vacuum to afford product **8**. This was dissolved in a minimum amount of CH_2Cl_2, and precipitated with the addition of excess pentane. Filtration off a Büchner funnel afforded product **8** again. This was again dissolved in CH_2Cl_2, washed with aq 1 N HCl (4 × 100 mL), dried (Na_2SO_4), filtered through a pad of Celite, subjected to rotary evaporation till dryness and finally to high vacuum. The solid **8** thus obtained was again dissolved in a minimum amount of CH_2Cl_2, and precipitated with the addition of excess pentane. Filtration once again off a Büchner funnel afforded the final pure product **8** as a white solid in 69% isolated yield (335 mg, 0.51 mmol); R_f = 0.3 (streak, 1:9 MeOH–CH_2Cl_2); white solid; mp >230 °C (dec.); $[\alpha]_D^{23}$ +362.4 (*c* 1.0, CH_2Cl_2).

IR (thin film): 3446s, 3055w, 1495m, 1334s, 1263s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.50 (d, *J* = 7.2 Hz, 4 H), 6.96 (t, *J* = 7.8 Hz, 4 H), 7.11 (t, *J* = 7.4 Hz, 2 H), 7.19 (t, *J* = 7.2 Hz, 2 H), 7.25–7.30 (m, 6 H), 7.36–7.37 (m, 4 H), 7.43–7.47 (m, 4 H), 7.73 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 123.2, 124.5, 125.7, 125.9, 126.1, 126.5, 127.5, 127.7, 128.1, 128.6, 130.0, 130.2, 135.0, 138.3, 139.4, 139.5, 142.9, 146.5.

^{31}P NMR (121 MHz, DMSO-d_6): δ = 0.91 (s).

MS: *m*/*z* (%) = 652 (100, M$^+$).

HRMS (ESI+): *m*/*z* calcd for $C_{44}H_{30}O_4P$ (M + H): 653.1882; found: 653.1863.

(*S*)-8,8′-Ph$_2$VANOL *N*-Triflyl Phosphoramide 9

A 25 mL round-bottom flask, fitted with a magnetic stir bar, was flame dried and cooled under argon. To the flask was added the ligand **6** (100 mg, 0.17 mmol, 1 equiv) and anhyd CH_2Cl_2 (2 mL) to obtain a clear yellow solution. The flask was fitted with a rubber septum and an argon balloon, and cooled to 0 °C in an ice bath. Et_3N (165 μL, 1.19 mmol, 7 equiv) and $POCl_3$ (19 μL, 0.20 mmol, 1.2 equiv) were added via a syringe, followed by the addition of DMAP (42 mg, 0.34 mmol, 2 equiv). The reaction was then allowed to warm up to r.t., and stirred at r.t. for 1 h; TLC at this stage indicated complete consumption of **6**. EtCN (2 mL) was added to the reaction flask, followed by the addition of $TfNH_2$ (50 mg, 0.34 mmol, 2 equiv). A water condenser, separately flame dried and cooled under argon, was then attached to the reaction flask, and the mixture heated at 100 °C in an oil bath for 24 h. The reaction mixture was allowed to cool to r.t., and stirred at r.t. for an additional 12 h. For the workup, the mixture was diluted with H_2O and CH_2Cl_2, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2, the organic layers were combined, washed with sat. aq $NaHCO_3$, aq 4 N HCl (2 ×), dried (Na_2SO_4), filtered through a pad of Celite, subjected to rotary evaporation till dryness, and finally to high vacuum to afford crude product **9**. This crude product was subjected to column chromatography with regular silica gel and an eluent mixture of 1:9 MeOH–CH_2Cl_2. The product fractions were collected, subjected to rotary evaporation till dryness and finally to high vacuum to afford **9** again, which was subsequently subjected to yet another round of column chromatography with regular silica gel and an eluent mixture of 5:1 EtOAc–hexanes to afford product **9**. The solid product obtained was dissolved in CH_2Cl_2, washed with aq 4 N HCl (2 ×), dried (Na_2SO_4), filtered through a pad of Celite, subjected to rotary evaporation till dryness, and finally to high vacuum to afford solid product **9**. This was finally dissolved in a minimum amount of CH_2Cl_2, and precipitated with excess pentane, which upon filtration off a Büchner funnel afforded the final pure product **9** as a white solid in 55% isolated yield (72 mg, 0.092 mmol); white solid; mp >255 °C (dec.); R_f = 0.3 (streak, 1:9 MeOH–CH_2Cl_2 as well as 5:1 EtOAc–hexanes); $[\alpha]_D^{23}$ +309.5 (*c* 1.0, CH_2Cl_2).

IR (thin film): 3435s, 3055w, 1215s cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.46 (br s, 1 H), 5.71 (br s, 1 H), 6.47 (d, *J* = 7.3 Hz, 2 H), 6.62 (d, *J* = 7.3 Hz, 2 H), 6.84 (br s, 1 H), 6.96 (t, *J* = 7.9 Hz, 2 H), 7.02 (t, *J* = 7.9 Hz, 3 H), 7.10–7.16 (m, 2 H), 7.19 (d, *J* = 6.9 Hz, 1 H), 7.31–7.53 (m, 8 H), 7.61 (s, 1 H), 7.65–7.70 (m, 2 H), 7.77 (d, *J* = 8.4 Hz, 1 H), 7.87 (d, *J* = 7.4 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 117.9, 118.0, 120.4, 120.5, 123.0, 124.3, 124.3, 124.7, 125.2, 126.2, 126.5, 126.8, 126.8, 126.9, 127.2, 127.7, 127.8, 127.8, 127.9, 128.0, 128.3, 128.8, 129.4, 129.6, 130.5, 131.5, 132.7, 135.5, 135.6, 136.4, 138.6, 139.3, 139.6, 140.1, 142.8, 145.1, 145.3, 145.4, 145.6, 145.6 (4 sp^2 carbons and CF_3 missing).

^{19}F NMR (283 MHz, $CDCl_3$): δ = –79.18 (s).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 2.82 (s).

MS: *m*/*z* (%) = 783 (<1, M^+), 572 (90), 246 (33), 39 (100).

HRMS (ESI–): *m*/*z* calcd for $C_{45}H_{28}F_3NO_5PS$ (M – H): 782.1378; found: 782.1374.

(*S*)-VANOL Phosphoric Acid 10

To a 50 mL round-bottom flask, flame-dried and cooled under argon, was added (*S*)-VANOL (2 g, 4.57 mmol, 1 equiv) and pyridine (8 mL) to obtain a clear yellow solution. The round-bottom flask was fitted with a rubber septum and an argon balloon. Thereafter, $POCl_3$ (0.85 mL, 9.13 mmol, 2 equiv) was added slowly via a syringe. The reaction mixture was then stirred at r.t. for 6 h, in which time salts started precipitating out. Thereafter, H_2O (8 mL) was added via a syringe, and the mixture was stirred at r.t. for 2 h. For the workup, the mixture was taken in a separatory funnel and CH_2Cl_2 (350 mL) was added. This was then washed with aq 1 N HCl (4 × 350 mL). The organic layer was collected, dried (Na_2SO_4), filtered through a pad of Celite, subjected to rotary evaporation, and finally high vacuum to afford the crude product **10** as a white solid. The purification was a simple precipitation. The crude solid was dissolved in a minimum amount of CH_2Cl_2 to obtain a clear yellow solution, which was followed by the addition of excess pentane to precipitate the product as a white solid in the solution. Filtration off a Buchner funnel then provided the pure (*S*)-VANOL phosphoric acid product **10**, which was subjected to high vacuum to completely remove all organic volatiles. Thus, (*S*)-VANOL phosphoric acid **10** was obtained as a white solid in 92% yield (2.1 g, 4.2 mmol); mp >250 °C (dec.); $[\alpha]_D^{23}$ +43.0 (*c* 1.0, CH_2Cl_2).

It was found that (*S*)-VANOL phosphoric acid **10** decomposed on regular silica gel column chromatography.

IR (thin film): 3435s, 3057w, 1634m, 1489m, 1026m cm^{-1}.

^{1}H NMR (500 MHz, THF-d_8): δ = 6.50 (d, *J* = 8.2 Hz, 4 H), 6.92 (t, *J* = 7.7 Hz, 4 H), 7.07 (t, *J* = 7.4 Hz, 2 H), 7.53 (s, 2 H), 7.54–7.61 (m, 4 H), 7.86 (d, *J* = 7.6 Hz, 2 H), 8.46 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (125 MHz, THF-d_8): δ = 123.7, 123.8 (d, *J* = 2.0 Hz, 1 C), 127.0 (d, *J* = 2.6 Hz, 1 C), 127.1, 127.2, 127.3, 128.1, 128.4, 128.4, 129.8, 135.3, 141.1, 141.2, 147.4 (d, *J* = 9.8 Hz, 1 C).

^{31}P NMR ($CDCl_3$, 121 MHz): δ = 7.03 (s).

MS: *m*/*z* (%) = 500 (13, M^+), 83 (14), 73 (20), 57 (22), 44 (100), 41 (25).

HRMS (ESI–): *m*/*z* calcd for $C_{32}H_{20}O_4P$ (M – H): 499.1099; found: 499.1118.

(*S*)-*N*-Triflyl VANOL Phosphoramide 12

This was prepared in the same manner as for the (*R*)-*N*-triflyl VAPOL phosphoramide **13** described below. The entire process was similar, except that DMAP was not utilized in the synthesis of **12**. Thus, (*S*)-VANOL (2 g, 4.57 mmol) was reacted accordingly to afford crude **12**. This was also purified and precipitated accordingly to afford the pure product **12** as a white solid in 76% isolated yield (2.2 g, 3.49 mmol); mp >250 °C (dec.); $[\alpha]_D^{23}$ +137.3 (*c* 1.0, CH_2Cl_2).

IR (thin film): 3430s, 3055w, 1284m, 1217s, 1084s, 760m cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.38–6.40 (m, 4 H), 6.96 (dt, *J* = 2.6, 5.6 Hz, 4 H), 7.12 (t, *J* = 7.4 Hz, 2 H), 7.56 (d, *J* = 8.3 Hz, 2 H), 7.60–7.70 (m, 4 H), 7.95–7.99 (m, 2 H), 8.27 (d, *J* = 8.3 Hz, 1 H), 8.35–8.37 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 120.1 (q, *J* = 318.2 Hz, CF_3), 122.1, 122.5, 122.9, 123.2, 125.6, 125.7, 125.7, 126.2, 126.5, 126.5, 126.7, 126.8, 127.1, 127.3, 127.4, 127.6, 127.7, 127.6, 128.8, 128.9, 133.8, 134.2, 139.8, 139.9, 140.0, 140.1, 145.3 (d, *J* = 8.7 Hz, 1 C), 146.3 (d, *J* = 9.7 Hz, 1 C).

^{19}F NMR (283 MHz, $CDCl_3$): δ = –78.69 (s).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 0.75 (s).

MS: *m*/*z* (%) = 631 (11, M^+), 420 (14), 170 (17), 80 (81), 79 (48), 44 (100).

HRMS (ESI–): *m*/*z* calcd for $C_{33}H_{20}F_3NO_5PS$ (M – H): 630.0752; found: 630.0785.

(*R*)-*N*-Triflyl VAPOL Phosphoramide 13

To a 100 mL round-bottom flask, flame-dried and cooled under argon, was added (*R*)-VAPOL (2 g, 3.72 mmol) and anhyd CH_2Cl_2 (20 mL) to obtain a clear solution. The round-bottom flask was fitted with a rubber septum and an argon balloon. It was then cooled to 0 °C in an ice-bath. Thereafter, anhyd Et_3N (3.62 mL, 26 mmol) and $POCl_3$ (0.42 mL, 4.46 mmol) were added sequentially via a syringe, which was followed by the addition of DMAP (0.91 g, 7.44 mmol), all at 0 °C. The reaction flask was then warmed up to r.t., and the mixture stirred for 2 h. Thereafter, $TfNH_2$ (1.11 g, 7.44 mmol) and distilled EtCN (20 mL) were added, and a water condenser (flame-dried and cooled under argon separately) was attached. The reaction mixture was then heated at 100 °C for 12 h and cooled down to r.t. thereafter. For the workup, H_2O (100 mL) and Et_2O (150 mL) were then added, stirred, and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 100 mL), the organic layers combined and washed with sat. aq $NaHCO_3$ (300 mL) and aq 4 N HCl (2 × 300 mL), dried (Na_2SO_4), filtered through a pad of Celite and subjected to rotary evaporation and high vacuum (0.1 mmHg) to afford the crude product **13** as a light brown solid. Crude TLC (EtOAc) showed a long product streak in the middle of the TLC plate and a baseline impurity spot. For purification, the crude product was dissolved in EtOAc, flushed through a glass frit packed with 1:1 Celite/silica gel and rinsed with EtOAc. Different fractions were collected and analyzed by TLC. All product fractions showed absence of the baseline impurity. This process was repeated if the fractions were not pure and contained the baseline impurity. All fractions were collected, subjected to rotary evaporation and high vacuum. The pure product was then subjected to precipitation. It was dissolved in a minimum amount of CH_2Cl_2 and an excess of pentane was added to precipitate the product. It was then filtered off a Büchner funnel; the solid product was collected and subjected to high vacuum. This precipitation cycle was repeated until ^{1}H NMR analysis indicated complete (or almost complete) removal of all residual solvent peaks. This process thus afforded the pure product **13** as a white solid in 70% isolated yield (1.9 g, 2.60 mmol); mp >250 °C (dec.); $[\alpha]_D^{23}$ –476.1 (*c* 1.0, CH_2Cl_2).

IR (thin film): 3424s, 1653m, 1635m, 1213w cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.43 (t, *J* = 7.8 Hz, 4 H), 6.96 (t, *J* = 7.6 Hz, 4 H), 7.11 (t, *J* = 7.5 Hz, 2 H), 7.62–7.73 (m, 6 H), 7.88–7.96 (m, 4 H), 8.03–8.06 (m, 2 H), 9.67–9.69 (m, 1 H), 9.91 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 120.2 (q, *J* = 323.6 Hz, CF_3), 121.4, 121.1, 121.4, 121.4, 125.9, 125.9, 126.4, 126.4, 126.5, 126.5,

126.6, 126.6, 126.7, 126.7, 126.9, 126.9, 126.9, 127.5, 127.5, 128.2, 128.3, 128.4, 128.6, 128.7, 128.8, 128.9, 128.9, 132.7, 133.9, 134.0, 139.1, 139.3, 140.5, 140.5, 147.9 (d, J = 8.7 Hz, 1 C), 148.9 (d, J = 11 Hz, 1 C).

^{19}F NMR (283 MHz, $CDCl_3$): δ = –79.69 (s).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 1.07 (s).

MS: m/z (%) = 730 [100, $(M - 1)^-$], 630 (3).

HRMS (ESI–): m/z calcd for $C_{41}H_{24}F_3NO_5PS$ (M – H): 730.1065; found: 730.1080.

(*S*)-*N*-(2,4,6-Triisopropylbenzenesulfonyl) VAPOL Phosphoramide 14

This was prepared in the same manner as for the (*R*)-*N*-triflyl VAPOL phosphoramide **13** described above. The reaction and workup were identical, but the purification was different. Thus, (*S*)-VAPOL (0.30 g, 0.56 mmol) was reacted and worked up accordingly to afford crude **14**. After workup, crude TLC showed the presence of 2,4,6-triisopropylbenzenesulfonamide. Thus, the crude solid product **14** was subjected to column chromatography with an eluent system of 1:3 EtOAc–hexanes to elute the sulfonamide first (R_f = 0.3). Once the sulfonamide was completely eluted from the column (as judged by TLC), the column was flushed with EtOAc to elute the product **14**. This afforded the pure product **14** as a light brown solid in 73% isolated yield (0.35 g, 0.41 mmol); mp >250 °C (dec.); $[\alpha]_D^{23}$ +270.5 (*c* 1.0, CH_2Cl_2).

IR (thin film): 3414s, 3057w, 2961m, 1626s, 1599s, 1226s, 1126s cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 0.91 (t, J = 7.1 Hz, 12 H), 1.20 (t, J = 6.8 Hz, 6 H), 2.81–2.87 (m, 1 H), 4.42–4.50 (m, 2 H), 6.37 (d, J = 7.1 Hz, 2 H), 6.44 (d, J = 7.1 Hz, 2 H), 7.52 (t, J = 7.1 Hz, 1 H), 7.56 (d, J = 3.4 Hz, 2 H), 7.64–7.68 (m, 2 H), 6.93 (t, J = 7.3 Hz, 4 H), 6.97–7.02 (m, 3 H), 7.06–7.10 (m, 2 H), 7.81–7.87 (m, 3 H), 7.89–7.94 (m, 2 H), 8.00–8.02 (m, 1 H), 9.55 (d, J = 8.8 Hz, 1 H), 9.90–9.92 (m, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 23.7, 23.7, 24.5, 24.8, 28.0, 33.3, 121.4, 121.5, 121.6, 121.6, 122.2, 125.6, 125.9, 126.0, 126.1, 126.4, 126.6, 126.6, 126.8, 126.9, 127.0, 127.0, 127.3, 127.4, 127.9, 128.1, 128.3, 128.8, 128.9, 129.0, 129.3, 132.5, 132.7, 133.7, 133.7, 139.5, 139.6, 140.5, 140.5, 142.1, 142.2, 147.6, 148.3, 148.9, 148.9, 148.9 (d, J = 9.2 Hz, 1 C), 150.0 (d, J = 10.9 Hz, 1 C) (1 sp^2 carbon missing).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 0.78 (s).

MS: m/z (%) = 866 [100, $(M + 1)^+$], 301 (60).

HRMS (ESI–): m/z calcd for $C_{55}H_{47}NO_5PS$ (M – H): 864.2913; found: 864.2951.

(*S*)-*N*-(4-Nitrobenenesulfonyl) VAPOL Phosphoramide 15

This was prepared in the same manner as for the (*R*)-*N*-triflyl VAPOL phosphoramide **13** described above. The entire process was similar, except that the precipitation was not done. Thus, (*S*)-VAPOL (0.30 g, 0.56 mmol) was reacted and purified accordingly to afford the pure product **15** as a yellow solid in 37% isolated yield (0.16 g, 0.21 mmol); mp >250 °C (dec.); $[\alpha]_D^{23}$ +257.4 (*c* 1.0, MeOH).

^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.29 (d, J = 7.3 Hz, 2 H), 6.36 (d, J = 7.3 Hz, 2 H), 6.91 (q, J = 7.9 Hz, 4 H), 7.06–7.09 (m, 2 H), 7.48 (d, J = 8.8 Hz, 2 H), 7.54 (s, 1 H), 7.58 (s, 1 H), 7.61–7.72 (m, 4 H), 7.84–7.94 (m, 6 H), 8.02–8.06 (m, 2 H), 9.67 (d, J = 8.1 Hz, 1 H), 10.05 (d, J = 8.5 Hz, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 121.2, 121.4, 122.9, 124.4, 126.0, 126.0, 126.1, 126.3, 126.5, 126.5, 126.6, 126.6, 126.7, 126.7, 126.8, 127.0, 127.1, 127.3, 127.4, 128.1, 128.4, 128.5, 128.5, 128.8, 128.8, 128.9, 129.0, 129.3, 132.6, 132.7, 133.7, 133.8, 139.1, 139.2, 140.4, 140.4, 147.3, 148.3 (d, J = 9.9 Hz, 1 C), 149.1 (d, J = 10.8 Hz, 1 C), 153.1.

^{31}P NMR ($CDCl_3$, 121 MHz): δ = –0.11 (s).

MS: m/z (%) = 783 [100, $(M - 1)^-$], 771 (7).

HRMS (ESI–): m/z calcd for $C_{46}H_{28}N_2O_7PS$ (M – H): 783.1355; found: 783.1342.

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