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Synthesis of the first C_2-asymmetric phosphinine and its pyrylium precursor

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ABSTRACT

The synthesis of the first C_2 chiral phosphinine (phosphabenzene) and its pyrylium salt precursor is reported. The chiral phosphinine is derived from (+)-camphor, is a crystalline air-stable solid and is shown to effectively form complexes with metals. A preliminary result using the phosphinine as a ligand for asymmetric catalysis is reported and rationalized structurally.

1. Introduction

Catalytic asymmetric reactions are the most efficient methods for the preparation of high enantiomeric purity organic compounds. The majority of such processes rely on chiral ligands, many of them phosphorus-based. Phosphinines (phosphabenzenes) represent a little-studied class of phosphorus ligands, especially with regard to asymmetric variants.

Achiral phosphinines have been shown to be effective ligands for several catalysts,[1] most notably Breit et al.'s use of triphenyl phosphinine derivatives in hydroformylation.[2] The first report of a chiral phosphinine came in 1996 when Breit synthesized three phosphinines (**1**–**3**, Fig. 1) with bound chiral auxiliaries.[3] However, no enantioselectivity was observed in the hydroformylation reaction. The first successful asymmetric reaction using a phosphinine ligand was reported by Müller et al., where a bidentate phosphinine/phosphite ligand (**4**) achieved asymmetric hydrogenations of dimethylitaconate in as high as 79% ee.[4] Recently this same group reported[5] the first atropisomeric phosphinine (**5**), though its use in asymmetric reactions has yet to be described.

In order to further the development of phosphinines as ligands for asymmetric catalysis, we undertook the development of C_2 chiral phosphinine ligands. It has been recognized[6] that C_2 chiral ligands are generally superior to other types of ligands in asymmetric reactions, probably because the approach of a reactant to either face of a C_2 complex will be equivalent, limiting the number of possible diastereomeric transition states. The best method of preparing highly substituted phosphinines is via the ring transformation reaction of pyrylium salts.[7] Pyrylium salts can be synthesized by a variety of methods that allow various substitution patterns, though in practice aryl substituents are far more common than alkyl groups.[8] Polymerization can compete with pyrylium formation, and tars are a common result, especially from alkyl-substituted substrates. Perhaps not unexpectedly, chiral pyrylium salts are almost entirely unknown, with only one non-racemic example[9] and one racemic case[5] having been reported to date. Yet, by the proper choice of starting materials, we hoped to incorporate C_2 chirality into a pyrylium salt. We chose (+)-camphor as our chiral unit, since ketones are common starting points for building

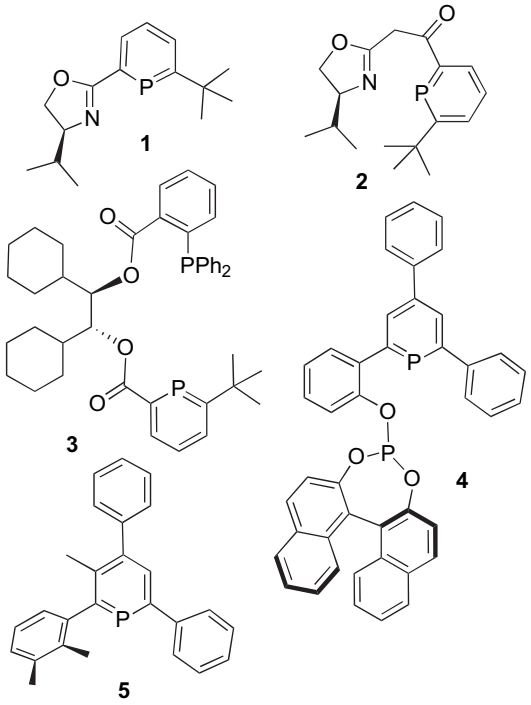

Figure 1. Existing chiral phosphinine ligands.

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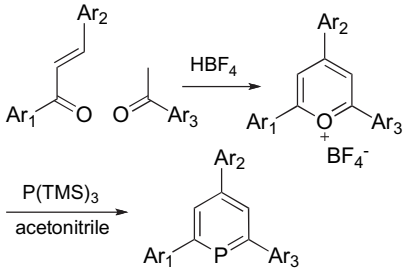
pyrylium rings, and camphor is an inexpensive member of the chiral pool.

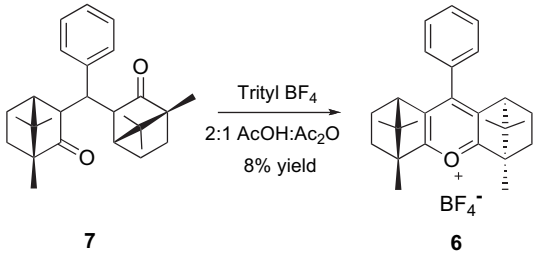
2. Results and discussion

Our initial attempts to create the biscamphorpyrylium **6** (*vide infra*) were based on the 'one pot' methods of creating triphenylpyrylium[10] (Scheme 1), which requires the formal loss of H_2 to furnish the third unit of unsaturation. We first attempted to react 2 equiv of camphor with benzaldehyde under strongly acidic conditions (HBF_4 or BF_3) to form 3-benzylidenecamphor *in situ*, which theoretically could continue to react with camphor, cyclize, and dehydrate to form the pyrylium, to no avail. Alternative approaches starting with either 3-benzylidenecamphor or 3-benzoylcamphor produced only an intractable tar, in which no downfield aromatic peaks indicative of the pyrylium ring could be observed by ^{13}C NMR spectroscopy. In the case of BF_3, the 3-benzoylcamphor route simply produced a crystalline adduct.[11]



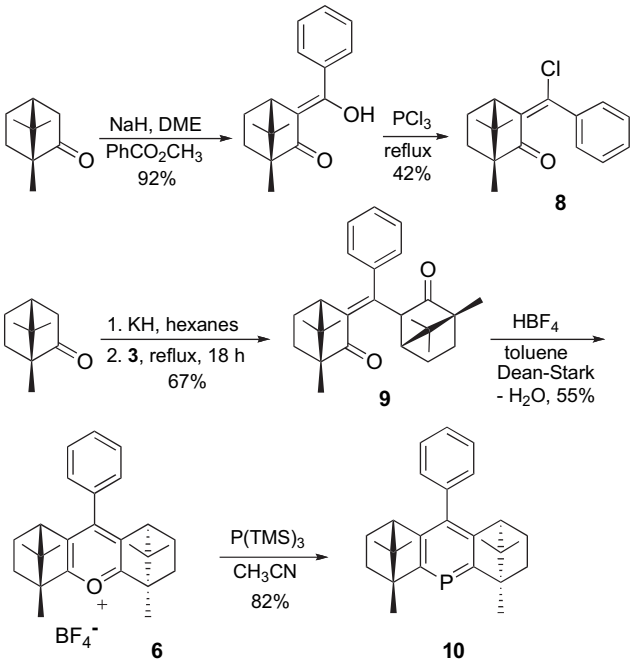
Scheme 1. A typical synthesis of a triarylpyrylium salt and triarylphosphinine.

Our next attempts were patterned after a procedure of Balaban et al., for converting 1,5-diketones to pyryliums, using triphenylcarbenium (trityl) salts as hydride abstraction reagents.[12] Following this lead, the 1,5-diketone **7** (Scheme 2) was synthesized by literature methods.[13] All initial attempts at cyclization using trityl reagents in acetic acid, acetic anhydride, and acetonitrile failed to produce any pyrylium salts, furnishing again only the intractable tars previously experienced. Simalty et al.[9] had experienced similar difficulties in the synthesis of a monocamphorpyrylium, all reactions ending in only tar. However, they found that a mixture of 2:1 acetic acid to acetic anhydride gave their product in ~35% yield. Using this solvent mixture finally produced the desired biscamphorpyrylium **6**, albeit in a miniscule 8% yield. The poor yield and difficult workup made this route less than ideal, so a better method was sought.



Scheme 2. Initial synthesis of biscamphorpyrylium **6**.

We theorized that the difficult step in the cyclization/aromatization process was probably the formal loss of hydrogen, so we sought to incorporate the unsaturation into the structure earlier in the synthesis, which proved to be successful (Scheme 3). 3-Benzoylcamphor was refluxed in PCl_3 for 2 h, and then neutralized to furnish the known (*E*)-3-(α-chlorobenzylidene)camphor (**8**) in 42% yield.[14] This compound was then subjected to conjugate addition/



Scheme 3. Synthesis of biscamphorpyrylium **6** and biscamphorphosphinine **10**.

elimination by an excess of camphor enolate in refluxing hexanes to give the corresponding 1,5-enedione (**9**) in 67% yield. When the reaction was performed in polar solvents such as THF, and to some extent in toluene, reduction of the vinyl halide **8** to 3-benzylidenecamphor was observed to occur in high yield. By reducing solvent polarity, this effect was mitigated. A mixture of two isomers of **9** was formed, which was separated by fractional crystallization. The major isomer (93% by GC/MS) was determined by X-ray crystallography to be *E*-(**9**). ^1H and ^{13}C NMR spectroscopy of this compound displayed temperature dependant behavior, at 25 °C giving broadened peaks in the ^1H NMR spectrum and missing peaks in the ^{13}C NMR spectrum. We attributed this to hindered rotation in the molecule, probably around the single bond between the vinyl carbon and the camphor ring. In an attempt to obtain averaged spectra at higher temperature, NMR spectra were obtained in C_6D_6 at 65 °C, but neither the ^1H nor ^{13}C spectra were qualitatively different and there was evidence of *E*/*Z* isomerization occurring. However, at −40 °C, rotation was sufficiently slowed that all expected ^{13}C peaks were observed. Compound **9** then underwent a dehydration/cyclization using HBF_4/diethyl ether in refluxing toluene, using a Dean–Stark trap, to give the pyrylium salt **6** in 55% yield. The ^{13}C NMR spectrum displayed downfield aromatic peaks indicative of the pyrylium cation (184.4, 155.7, and 137.5 ppm).

The pyrylium **6** structure was also verified by X-ray crystallography, as shown in Figure 2. This represents the first C_2 chiral pyrylium salt to be reported. It displays a large optical rotation, $[\alpha]_D^{20}$ +378 (*c* 0.37, CH_2Cl_2), consistent with a highly polarized aromatic ring.

The biscamphorphosphinine **10** was prepared from the pyrylium salt **6** by reaction with tris-(trimethylsilyl)phosphine, $P(TMS)_3$. The yield of this transformation, which is typically only from 15–40%, in this case was remarkably and reproducibly high (82%).[2] This may be due to the *meta* substituents preventing attack on the *para* position, which would lead to byproducts. This compound is easily purified by silica gel chromatography followed by recrystallization, and is obtained as an air-stable crystalline solid. Interestingly, the ^{13}C NMR spectrum of this compound shows carbon–phosphorus coupling as far as five bonds. The X-ray crystal structure of **10** is shown in Figure 3, and represents the first C_2 chiral phosphinine reported to date.

^{31}P NMR spectroscopy showed that this ligand binds strongly to late transition metals, such as palladium(II) and rhodium(I). When

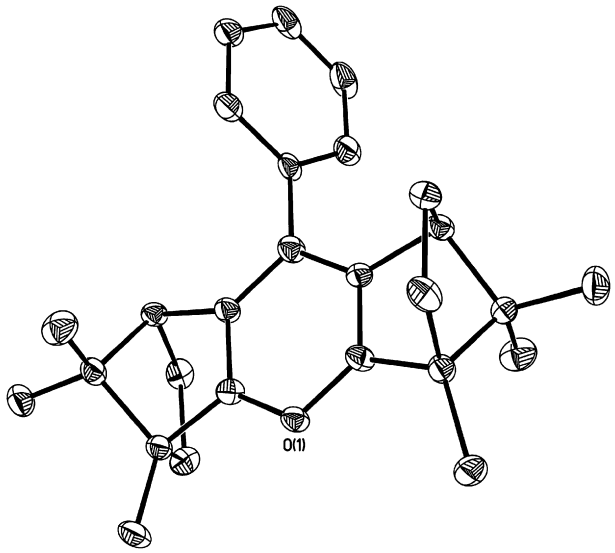


Figure 2. X-ray crystal structure of biscamphorpyrylium tetrafluoroborate **6**. The tetrafluoroborate anion has been omitted for clarity.

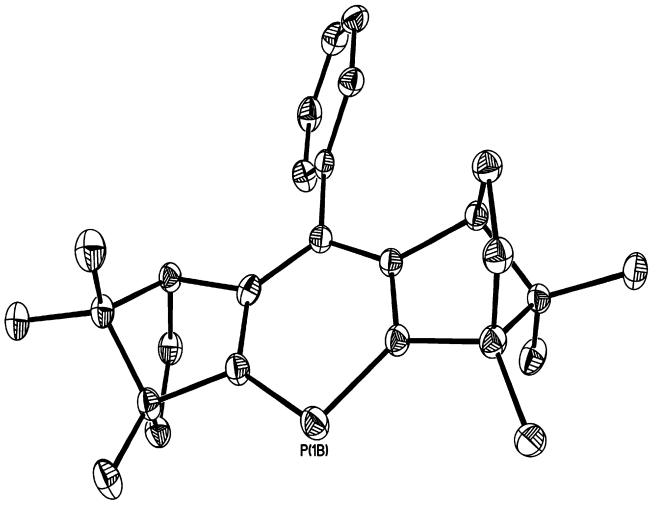
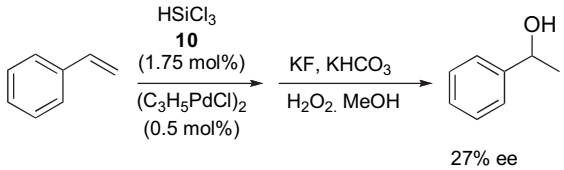


Figure 3. X-ray crystal structure of biscamphorphosphinine **10**.

10 was added to a solution of $Pd(COD)Cl_2$, the ^{31}P NMR signal shifts upfield from 138.9 ppm for the free phosphinine to 119.1 ppm on formation of the di(phosphinine **10**)–dichloropalladium(II) complex. When **10** was reacted with rhodium(dicarbonyl) chloride dimer, the ^{31}P NMR spectrum shows a doublet at 122.5 (J=152 Hz), due to Rh–P coupling, consistent with literature reports for other phosphinines.[4]

Phosphinine **10** was briefly studied in one catalytic asymmetric reaction, a palladium-catalyzed asymmetric hydrosilylation (Scheme 4). Styrene and 1-octene were treated with 0.5 mol% allylpalladium(II) chloride dimer and 1.75 mol% of phosphinine **10**, conditions patterned after those employing other monodentate phosphine ligands.[15] For styrene, the reaction proceeds quantitatively at room temperature in 5 days, or at 40 °C in 24 h to give the trichlorosilane product; however, no reaction occurred for 1-octene. Under either reaction conditions, after isolation of the trichlorosilane product by Kugelrohr distillation, followed by Tamao–Fleming oxidation[16] to the alcohol, the 1-phenylethanol product was found to have 27% ee by chiral GC analysis.[17]



Scheme 4. Hydrosilylation/oxidation of styrene using phosphinine ligand **10**.

The low level of asymmetric induction can be attributed to two features that are evident from the X-ray structure of **10**. The biscamphor ligand influences the metal environment primarily through the bridgehead methyl groups. Unfortunately, these methyl groups cannot extend appreciably into the metal's coordination sphere (Fig. 4), which limits the ligand's ability to enforce an asymmetric environment. In addition, the methyl groups deviate only marginally (~18°) from the plane of the phosphinine ring. If the methyl groups were coplanar with the phosphinine ring, there would be no effective asymmetry at the metal. We believe ligands, which extend further into the metal's environment and with a greater degree of twist (i.e., deviation from the phosphinine plane) will be more effective in asymmetric reactions. Thus, ligands with groups significantly larger than methyl (e.g., phenyl) positioned so as to extend further into the metal's coordination sphere should be superior. In addition, models suggest that bicyclic rings ([2.2.1] or [2.2.2]) fused to the phosphinine cannot provide these extending groups more than the shallow twist angle observed for **10**. We believe a significantly greater angle, perhaps two to three times greater than found in ligand **10**, is necessary for effective asymmetric induction. We are pursuing non-bicyclic C_2 ligands, as well as the utilization of chlorobenzylidene **8** in the rapid preparation of a wide variety of C_1 asymmetric phosphinines.

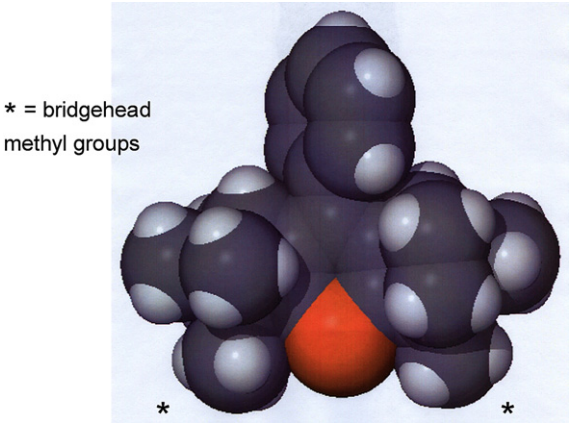


Figure 4. Face-on space-filling view of phosphinine **10**. Phosphorus atom is at bottom center.

3. Experimental section

3.1. General

Reagents and solvents were generally purchased from the Aldrich Chemical Company or from Alfa Aesar, and were used as received unless otherwise noted. Tris-(trimethylsilyl)phosphine was obtained from Strem Chemical. NMR spectra were obtained at 500 MHz for ^1H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P. Spectra obtained in $CDCl_3$ were referenced to TMS (0 ppm) for ^1H and to solvent (77.0 ppm) for ^{13}C. ^{31}P spectra were referenced to an external standard of 85% H_3PO_4 (0 ppm). GC–MS was done on a Hewlett-Packard GCD using a 30 m×0.25 mm HP-5 capillary column with helium carrier and EI ionization. Analysis for enantiomeric purity was by capillary gas chromatography using an HP5890 with a Restek Rt-βDEXsa, 30 m×0.25 mm column. High resolution mass spectra were obtained from the Baylor University mass spectroscopy facility. Elemental

analyses were performed by Atlantic Microlabs, Norcross, GA. Melting points were calibrated against accepted standards.

3.2. Enedione 9

To 1.1 g (27 mmol, 2.5 equiv) of KH in 30 mL of hexanes, 5.42 g (35.7 mmol, 3 equiv) of (+)-camphor was added and refluxed for 2 h. Then 3.00 g (10.9 mmol, 1 equiv) of (+)-(*E*)-3-(α-chlorobenzylidene) camphor[14] in 20 mL of hexanes was slowly added by syringe, and the reaction mixture was refluxed for 18 h. The reaction was quenched by addition of saturated ammonium chloride solution, and brought to neutral pH with 6.0 M HCl. The mixture was extracted with diethyl ether, dried with magnesium sulfate, filtered, and evaporated to a solid. The mixture was dissolved in warm methanol and, after cooling to −20 °C, filtered to give crystalline enedione **9** (2.87 g, 68% yield). Mp 142–144 °C; $[\alpha]_D^{20}$ +82.6 (*c* 0.33, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, −40 °C): δ 7.38–7.32 (m, 4H, ArH), 7.13 (br d, *J*=7.8 Hz, 1H, ArH), 5.32 (br d, *J*=3.6 Hz, 1H), 2.38 (br t, *J*=3.8 Hz, 1H), 2.17 (br d, *J*=4.0 Hz, 1H), 1.99–1.91 (m, 1H), 1.76–1.68 (m, 1H), 1.56–1.39 (m, 4H), 1.23–1.15 (m, 1H), 1.04 (s, 3H), 0.98 (s, 3H), 0.93 (s, 3H), 0.88 (s, 3H), 0.85 (s, 3H), 0.82 (s, 3H), 0.80–0.74 (m, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$, −40 °C): δ 217.9, 209.9, 143.6, 142.9, 140.2, 128.5, 128.0, 127.7, 127.6, 127.1, 59.2, 59.0, 52.6, 50.5, 49.4, 46.4, 46.0, 30.0, 29.0, 26.4, 21.7, 20.3, 19.3, 18.8, 18.1, 9.7, 9.5; IR (KBr) 2960, 1741, 1711, 1622 cm^{-1}; HRMS (EI) calcd for $C_{27}H_{34}O_2$ [M^+] 390.2559, found 390.2560. Elemental analysis calcd (%) for $C_{27}H_{34}O_2$: C, 83.03; H, 8.77. Found: C, 82.86; H, 8.91.

3.3. Biscamphorpyrylium tetrafluoroborate 6

To 0.431 g (1.1 mmol, 1 equiv) of **9** dissolved in 20 mL of toluene in a flask equipped with a Dean–Stark trap was added 1.00 mL (5.9 mmol, 5.4 equiv) of ~52% HBF_4 in diethyl ether (~5.92 M) and the solution refluxed overnight. The toluene solution was diluted with 100 mL of diethyl ether, cooled to 0 °C, and filtered through a Celite pad, trapping a fine precipitate. The pyrylium salt was then washed through the Celite with dichloromethane into a separate flask. The solvent was removed under vacuum, and the compound was recrystallized from acetone/diethyl ether to yield biscamphorpyrylium tetrafluoroborate **6** (0.278 g, 55%). Mp 272–274 °C; $[\alpha]_D^{20}$ +309 (*c* 0.44, CH_3CN), $[\alpha]_D^{20}$ +378 (*c* 0.37, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66–7.63 (m, 3H, ArH), 7.56–7.54 (m, 2H, ArH), 3.25 (d, *J*=4.0 Hz, 2H), 2.39 (ddt, *J*=13.0, 9.8, 4.0 Hz, 2H), 2.22 (ddd, *J*=13.2, 9.8, 4.0 Hz, 2H), 1.79 (ddd, *J*=13.2, 9.3, 3.9 Hz, 2H), 1.60 (ddd, *J*=13.0. 9.3, 3.9 Hz, 2H), 1.50 (s, 6H), 1.05 (s, 6H), 0.77 (s, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 184.4 (2C), 155.7 (1C), 137.5 (2C), 132.5 (1C, CH), 131.1 (1C), 129.65 (2C, CH), 129.64 (2C, CH), 60.6 (2C), 57.0 (2C), 50.4 (2C, CH), 31.3 (2C, CH_2), 25.0 (2C, CH_2), 19.7 (2C, CH_3), 19.0 (2C, CH_3), 8.6 (2C, CH_3); IR (KBr) 2960, 1608, 1415, 1055 cm^{-1}. HRMS (EI) calcd for $C_{27}H_{33}O$ [M^+] 373.2531, found 373.2530. Elemental analysis calcd (%) for $C_{27}H_{33}OBF_4$: C, 70.44; H, 7.23. Found: C, 70.58; H, 7.33.

3.4. Biscamphorphosphinine 10

To 0.913 g (1.98 mmol, 1 equiv) of biscamphorpyrylium tetrafluoroborate (**6**) dissolved in 10 mL of anhydrous acetonitrile placed carefully under nitrogen was added 1.0 g (4.0 mmol, 2 equiv) of $P(TMS)_3$ and the solution was refluxed for 24 h. The solution turned from orange to dark red/black. After cooling to room temperature, the solvent was removed by rotary evaporation and the phosphinine was purified by silica gel column chromatography (5% ethyl acetate in petroleum ether). The resulting yellow solid was recrystallized from methanol to give phosphinine **10** as colorless needles (0.631 g, 82%). Mp 123–124 °C; $[\alpha]_D^{20}$ +51.8 (*c* 0.55, EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (t, *J*=7.4, 2H, ArH), 7.38–7.33 (m, 1H, ArH), 7.24–7.20 (m, 2H, ArH), 2.69 (d, *J*=3.9, 2H), 2.00–1.93 (m, 2H), 1.89 (tdd, *J*=11.2, 3.6, 2.2, 2H), 1.43 (s, 6H), 1.16 (ddd, *J*=11.5, 9.3, 3.2, 2H), 1.07 (ddd, *J*=11.5, 9.1, 3.3, 2H), 0.90 (s, 6H), 0.55 (s, 6H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 176.7 (2C, d, *J*=49.3), 148.9 (1C, d, *J*=12.1), 140.3 (d, *J*=1.9), 132.6 (d, *J*=15.0), 129.4 (2C, d, *J*=1.9, CH), 128.0 (2C, CH), 126.6 (CH), 57.7 (2C, d, *J*=16.7), 56.8 (2C, d, *J*=2.3), 53.1 (2C, d, *J*=1.4, CH), 34.5 (2C, d, *J*=3.3, CH_2), 25.9 (2C, d, *J*=1.8, CH_2), 19.9 (2C, CH_3), 19.3 (2C, d, *J*=1.4, CH_3), 13.6 (2C, d, *J*=11.2, CH_3); ^{31}P NMR (202.3 MHz, $CDCl_3$): δ 138.9; IR (KBr): 3075, 3020, 2964, 1491, 1437, 1385, 1376 cm^{-1}; HRMS (EI) calcd for $C_{27}H_{33}P$ [M^+] 388.2320, found 388.2320. Elemental analysis calcd (%) for $C_{27}H_{33}P$: C, 83.47; H, 8.68. Found: C, 83.65; H, 8.68.

3.5. General method for asymmetric hydrosilylation

To 0.5 mg (1.3 μmol) of $[(allyl)Pd(II)Cl]_2$ in a 10 mL flask fitted with a reflux condenser under nitrogen was added 3.7 mg (9.5 μmole) of biscamphorphosphinine **10**, followed by 25 mmol of neat olefin (styrene or 1-octene). After stirring at room temperature for 10 min, 3 mL (30 mmol) of trichlorosilane was syringed into the flask, and the mixture was brought to reflux overnight. The alkyltrichlorosilane product was isolated by Kugelrohr distillation (100 °C at ~0.5 Torr). The isolated product was subjected to Tamao–Fleming oxidation conditions. The resulting alcohol was analyzed by GC/FID for enantiomeric purity using a Restek Rt-βDEXsa column using hydrogen carrier gas. The enantiomers were well-resolved (12.18 min vs 12.48 min, resolution=3.18, temperature program 80–180 °C at 4 °C per min).

3.6. X-ray crystallography

Crystallographic data (excluding structure factors) for the structures **6**, **8**, **9**, and **10** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 745389, 745390, 745391, and 745392, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk). Abbreviated crystallographic data are given below.

*3.6.1. Pyrylium **6**.* $C_{27}H_{33}BF_4O$, MW=460.34, orthorhombic, $P2_12_12_1$, *a*=14.931(3) Å, *b*=7.4327(19) Å, *c*=10.861(3) Å, α=90.00°, β=90.00°, γ=90.00°, *V*=1205.3(5), *Z*=2, *T*=110 K, μ=0.096, ρ_{calcd}=1.268 Mg m^{-3}, GOF on F^2=1.042, *R*=0.0495, R_w=0.1089 [$I>2\sigma(I)$].

*3.6.2. Chlorobenzylidene **8**.* $C_{17}H_{19}ClO$, MW=274.77, monoclinic, $P2_1$, *a*=6.9230(9) Å, *b*=12.4494(15) Å, *c*=16.783(2) Å, α=90.00°, β=93.181(5)°, γ=90.00°, *V*=1444.2(3), *Z*=4, *T*=110 K, μ=0.0.254, ρ_{calcd}=1.264 Mg m^{-3}, GOF on F^2=1.035, *R*=0.0271, R_w=0.0608 [$I>2\sigma(I)$].

*3.6.3. Enedione **9**.* $C_{27}H_{34}O_2$, MW=390.54, orthorhombic, $P2_12_12_1$, *a*=6.6892(14) Å, *b*=15.409(3) Å, *c*=21.528(4) Å, α=90.00°, β=90.00°, γ=90.00°, *V*=2219.0(7), *Z*=4, *T*=110 K, μ=0.072, ρ_{calcd}=1.169 Mg m^{-3}, GOF on F^2=1.033, *R*=0.0407, R_w=0.0828 [$I>2\sigma(I)$].

*3.6.4. Phosphinine **10**.* $C_{27}H_{33}P$, MW=388.50, triclinic, *P*1, *a*=6.866(2) Å, *b*=12.056(4) Å, *c*=14.084(6) Å, α=78.525(12)°, β=82.284(14)°, γ=74.282(12)°, *V*=1095.7(7), *Z*=2, *T*=110 K, μ=0.135, ρ_{calcd}=1.178 Mg m^{-3}, GOF on F^2=1.024, *R*=0.00405, R_w=0.0908 [$I>2\sigma(I)$].

Acknowledgements

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for partial support of this work, the National Science Foundation (Award #CHE-0420802) for funding the purchase of our 500 MHz NMR, and Dr. Gary Stidsen of Restek Corporation for the gift of a chiral GC column (Rt-βDEXsa).

Supplementary data

Procedures for the synthesis of pyrylium **6** from dione **7** and for the preparation of chlorobenzylidene **8**, X-ray structures of chlorobenzylidene **8** and enedione **9**, a table of X-ray data for compounds **6**, **8**, **9**, and **10** and NMR spectra for compounds **6**, **8**, **9**, and **10** are provided. Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.08.085.

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