Tunable Phosphoramidite Ligands for Asymmetric Hydrovinylation: Ligands *par excellence* for Generation of All-Carbon Quaternary Centers

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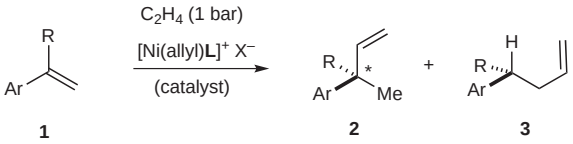
Received 20 April 2009

Abstract: α-Alkylstyrenes undergo efficient hydrovinylation (addition of ethene) in the presence of a nickel catalyst prepared from $[(allyl)NiBr]_2$, $Na^+[BAr_4]^-$ [Ar = 3,5-bis(trifluoromethyl)phenyl], and a phosphoramidite ligand giving products in excellent yields and enantioselectivities. In many cases phosphoramidites derived from achiral 2,2′-biphenol are almost as good as ligands derived from the more expensive enantiopure 1,1′-bi(2-naphthol)s. The hydrovinylation products, which carry two versatile latent functionalities, an aryl and a vinyl group, are potentially useful for the synthesis of several important natural products containing benzylic all-carbon quaternary centers.

Key words: alkenes, asymmetric catalysis, hydrovinylation, phosphoramidite ligands, nickel

Catalytic asymmetric C–C bond-forming reactions continue to attract great interest among synthetic chemists.[1] Among these, a subclass of reactions that depend on the activation and subsequent stereoselective incorporation of small molecules such as CO, CO_2, HCN, acetylene, and ethene into prochiral substrates, are among the most challenging.[2] Ideally, new reactions must accomplish the requisite transformations under nearly ambient conditions with high turnover frequencies, high regio- and stereoselectivities, all the while generating only little or no side products. Further, the newly installed functionality must be amenable to further transformations leading to valuable end products. Research in this area could lead to new breakthroughs in fundamental science, and under the most optimistic scenario, will add to our repertoire of methods for economically viable syntheses of valuable chemical intermediates.

In developing new metal-catalyzed reactions, the ligand is a major factor as efficiency (turnover frequency), selectivity, and catalytic stability are often dependent on the properties of the ligand. In the area of asymmetric catalysis, success often depends on the availability of enantiomerically pure ligands that are amenable to fine tuning for optimum performance. Once the essential features of the catalytic system are identified, systematic modifications in the ligand scaffolding, especially, those affecting the steric and electronic environment around the chelating atoms, are often required to achieve acceptable levels of catalytic efficiency and selectivity. Such a strategy has been employed in the discovery of many new asymmetric catalytic processes that involve the use of carbon feedstocks for selective C–C bond-forming reactions.[2,3] Phosphoramidites, originally introduced by Feringa[4a,b] for the asymmetric copper-catalyzed conjugate addition of dialkylzinc reagents to enones, are among the most versatile and tunable ligands for C–C and C–H bond-forming reactions.[4c–i] Recently we[5] and the Zhou group[6] have described the use of phosphoramidite ligands derived from different sources for the asymmetric hydrovinylation reactions of (1-alkylvinyl)arenes leading to useful intermediates with all-carbon quaternary centers (Equation 1).[7] In this paper we disclose the full details of our efforts, including results of more recent studies aimed at exploring the scope and limitations of this reaction.

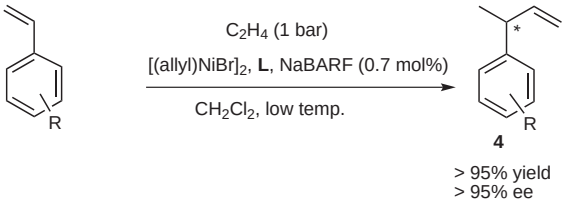


Equation 1

Asymmetric Hydrovinylation

Hydrovinylation,[8] the addition of ethene as a hydrogen and a vinyl group across an activated olefin (Equations 1 and 2), has received much renewed attention[9] since we disclosed new protocols for this prototypical heterodimerization reaction.[10] During the past decade the scope of the reaction has also been considerably broadened.[8b] Since ethene is an inexpensive, abundantly available feedstock carbon source, and the vinyl group in the resulting product readily transformed into a variety of other common functionalities, this reaction has huge potential to be a scalable, environmentally benign method for the preparation of valuable chemical intermediates. Application of old (Figure 1, **5**,[8a] **6**[10]) and new (**7**,[7c,11] **8**,[3f] **9**,[7] **10**[6]) ligands have enabled successful asymmetric hydrovinylation of vinylarenes, 1,3-dienes and strained bicyclic olefins such as norbornene. Asymmetric hydrovinylation of vinylarenes (Equation 2) has been the most developed, and the resulting 3-arylbut-1-enes **4** have been converted into a number of synthetically useful derivatives such alcohols,[3b,12] halides, aldehydes, carboxylic acids, and chiral 1-ethylarylamines.[13]

SYNTHESIS 2009, No. 12, pp 2089–2100
Advanced online publication: 14.05.2009
DOI: 10.1055/s-0029-1216826; Art ID: C01309SS



Equation 2

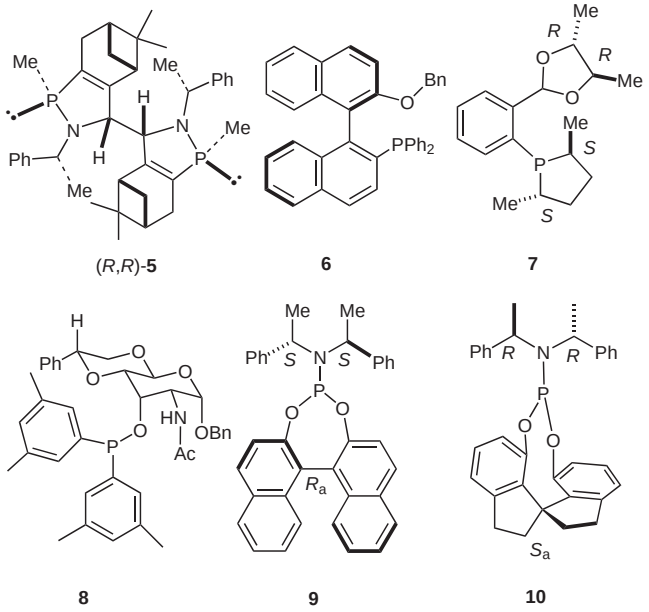
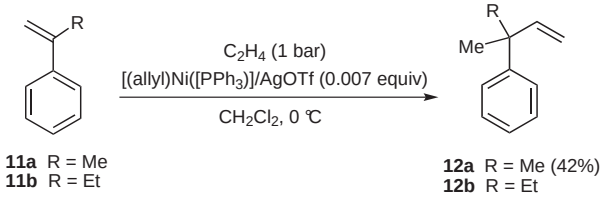


Figure 1 Assorted ligands for asymmetric hydrovinylation

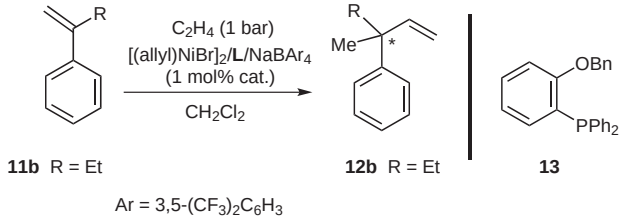
Ligand Tuning for the Generation of All-Carbon Quaternary Centers via Asymmetric Hydrovinylation

The search for new methods for stereoselective generation of all-carbon quaternary centers is a subject of considerable topical interest.[14] Several important pharmaceutically relevant compounds, among them, analgesic (–)-eptazocine,[15] protein kinase C activator lyngbyatoxin and related structures like teleocidin B4,[16] and cognitive enhancing agent (–)-phenserine,[17] contain an all-carbon quaternary center at the benzylic position. The viability of hydrovinylation of α-alkylstyrene as a method for generating an all-carbon quaternary benzylic center was initially discovered during the scouting phase of our studies of hydrovinylation (Equation 3, **11a** → **12a**), even though the conversions were only modest under the highly catalytic reaction conditions.[3e]



Equation 3

We chose α-ethylstyrene (**11b**, Equation 3) as a prototypical substrate for the initial studies. A racemic sample of the expected product **12b** was conveniently prepared by carrying out the reaction under conditions described in Equation 4, using [2-(benzyloxy)phenyl]diphenylphosphine (**13**)[7c] as a ligand. This was followed by studies using **6**–**8**, a set of ligands we had used with varying degree of success in the asymmetric hydrovinylation of monosubstituted vinylarenes and 1,3-dienes. The results of these scouting experiments are listed in Table 1.



Equation 4

Catalysts derived from the MOP ligand **6** (entry 2)[10] and the phosphinite **8**[3f] (entry 6) showed no reactivity while

Table 1 Hydrovinylation of α-Ethylstyrene (Ligand Scouting)

Entry	Ligand (mol%)	Temp (°C)	Time (h)	Conversion (%)	ee[a] (%)
1	**13** (5)	25	48	74	*rac*
2	**6** (5)	–[b]	–[b]	low	–
3	**7** (5)	–10	16	67	27 (*R*)
4	**7** (5)	0	19	76	27 (*R*)
5	**7** (5)	25	22	72	25 (*R*)
6	**8** (5)	–[b]	–[b]	low	–

[a] Determined by GC analysis on Cyclodex-B column. Configuration assigned by GC retention times of the known compound.[18]
[b] Various.

Table 2 Asymmetric Hydrovinylation of α-Ethylstyrene (**11b**) Using Ligand **9**

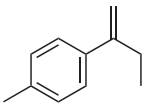
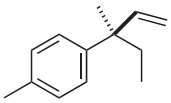
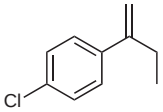
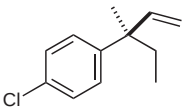
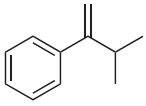
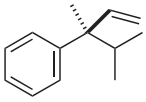
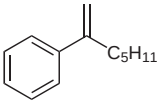
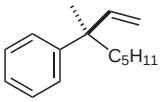
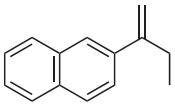
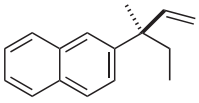
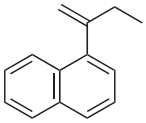
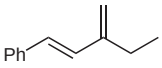
Entry	Ligand (mol%)	Temp (°C)	Time (h)	Conversion (%)	ee[a] (%)
1	**9** (5)	–10	21	>99	79 (*R*)
2	**9** (5)	–30	17	>99	77 (*R*)
3	**9** (5)	–55	19	>99	88 (*R*)
4	**9** (5)	–70	17	>99	93 (*R*)
5	**9** (5)	–70	4	>99	96 (*R*)
6	**9** (1)	–70	4	>99	95 (*R*)
7	**9** (2)	–70 to –65	4	99.7	97.6 (*R*)[b]

[a] Determined by GC analysis on Cyclodex-B column, for authentic product see ref.[18]
[b] Reaction was performed on a 50-mmol scale.

those derived from the phospholane ligand **7**, which gave very high enantiomeric excess and turnover numbers in the hydrovinylation of a number of styrene derivatives,[11] and 1,3-dienes,[7c] showed only moderate reactivity under similar conditions (entries 3–5). At this point we turned our attention to phosphoramidite ligands, starting with one of the 'original' Feringa ligands **9** derived from (*R*)-binaphthol and bis[(*S*)-α-methylbenzyl]amine.[19] The results of these experiments on the asymmetric hydrovinylation of α-ethylstyrene (**11b**) using the ligand **9** are shown in Table 2. In a typical experiment, the phosphoramidite ligand was treated with allylnickel bromide dimer $[(allyl)NiBr]_2$ and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate $\{Na^+[BARF]^-$, BARF = $[3,5\text{-}(CF_3)_2C_6H_3]_4B\}$ in dichloromethane and was subsequently placed under an ethene atmosphere at –70 °C for a few minutes.[20] The ethene line was removed, and the styrene dissolved in dichloromethane was added while maintaining the reaction mixture at –70 °C. After all the starting material had been consumed, the product was isolated after workup by simple filtration through a silica gel column. Optimization of reaction conditions revealed that the enantioselectivity of the reaction depends critically on the temperature at which the reaction is carried out. As little as 10 °C difference can bring about a deterioration of the selectivity (entries 2–4). We also noticed that the hydrovinylation reaction, even at –70 °C, is exothermic and careful control of the reaction conditions (<–70 °C) is essential for obtaining high enantioselectivities. Under these conditions, no isomerization [to (*Z*)- and (*E*)-2-arylbut-2-enes] or oligomerization of starting alkenes was detected, as judged by careful GC analysis and ^1H NMR spectroscopy. The surprisingly high yields and selectivities are highly reproducible and are independent of the catalyst loading (entries 5–7), indicating the total absence of nonselective reactions for this substrate. The reaction can be performed on a 50-mmol scale using 0.02 equivalents of the nickel catalyst (entry 7).

Hydrovinylation of several α-alkylstyrene derivatives were attempted under the optimal conditions and the results are tabulated in Table 3. While the 4-methylstyrene **14** gave excellent selectivity for the formation of the expected product **21** (entry 1), the 4-chloro derivative **15** gave up to 5% isomerization of the starting olefin to a mixture of (*Z*)- and (*E*)-α,β-disubstituted styrenes (entry 2). A similar minor side reaction was also observed for the substrate **17**. An isopropyl group at the α-position of the styrene **16** retards the reaction (entry 3), and it is best ac-

Table 3 Asymmetric Hydrovinylation of α-Alkylstyrenes Using Ligand **9**[a]

Entry	Vinylarene		Product		Temp (°C)	Time (h)	Yield (%)	ee (%)[b]
1	**14**		**21**		–60	12	>90	90
2	**15**		**22**		–70	11	>90[c]	90
3	**16**[d]		**23**		24	20	60[e]	>95
4	**17**		**24**		–70	8	93[c]	>50[f]
5	**18**		**25**		–70	14	>98	93
6	**19**		–		–70	14	0	–
7	**20**		–		–70	14	0	–

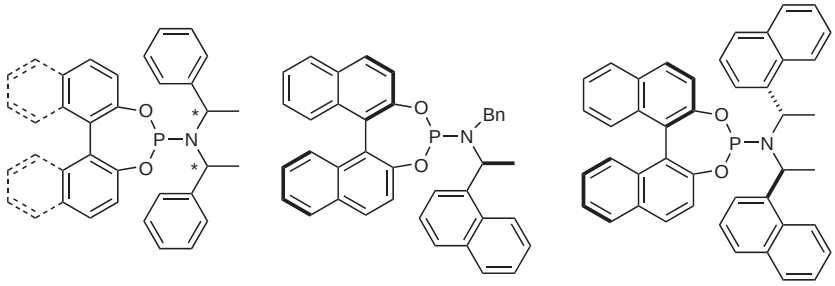
[a] See Equation 4 for details.
[b] Determined by GC, the (*R*)-isomer was assigned by analogy to **12b**.
[c] The remainder was isomerized product from the starting material.
[d] 10 mol% catalyst used.
[e] The remainder was starting material.
[f] Determined via Mosher esters of hydroboration product.

complished at 24 °C with 10 mol% catalyst. Even though the yield of the reaction is only moderate, very high enantiomeric excess (~97%) was observed for the isolated product. The 2-naphthyl derivative **18** gave excellent yield (>98%) and selectivity (93%) for the expected product **25**. 2-(1-Naththyl)but-1-ene (**19**) failed to undergo the reaction (entry 6) and (*E*)-1-phenyl-3-ethylbuta-1,3-diene (**20**) gave a nearly racemic product.

Asymmetric hydrovinylation of functionalized vinylarenes with and without a 1-substituent on the vinyl group of the arene is a key reaction in a number of on-going total synthesis efforts in our group. Some limitations in the use of ligand **9** have been noted in the previous paragraph, and others have become apparent as our studies continued. This applies to asymmetric hydrovinylations of even simple vinylarenes where we had made the most progress. For example, 4-isobutylstyrene and 3-fluoro-4-phenylstyrene, precursors of ibuprofen and flurbiprofen, gave only 90% and 86% ee using **9** as a ligand. In an attempt to improve the selectivity we decided to take advantage of the versatility of the phosphoramidite ligands, especially the ease with which the biaryl and the amine moieties can be modified.[21] Figure 2 shows a selection of the modified phosphoramidites **26**–**28** that were found to be especially useful in early studies for the asymmetric hydrovinylation of simple vinyl arenes. We have since examined the scope of these ligands for the generation of all-carbon benzylic quaternary centers and the results are described in the following paragraphs.

One early application of the modified phosphoramidites has been in our approach to pyrrolidinoindolines like physostigmine and related compounds that carry a methyl-bearing quaternary center at the benzylic position.[22] We reasoned that asymmetric hydrovinylation on a highly functionalized styrene of generic structure **29** would give **30**, from which it should be possible to reach the target molecule(s) (Scheme 1). Asymmetric hydrovinylation of these substrates would also test additional functional group compatibility of this demanding reaction.

In the event, a number of new styrene derivatives **29a**–**g** were prepared by Stille coupling of a suitable (tributylstannyl)alkene and the appropriate aryl iodide partner.[23] Results of asymmetric hydrovinylation of these compounds using different phosphoramidite ligands, starting with **9** are shown in Table 4. As seen from entries 1–3, *tert*-butyldimethylsiloxy and azido substituents on the alkyl tether are detrimental to the reaction and no products are formed even when high catalyst loading (10 mol%) is used. Surprisingly, the phthalimido group is tolerated (entries 5–10) and gives products **30d** and **30g** (Table 4) from the respective precursors. However, an *ortho*-substituent (e.g., **29e** and **29f**) prevents the reaction from taking place (entries 11 and 12). Ligand **9** gave marginally better enantioselectivity in the asymmetric hydrovinylation of **29g** (entry 6 vs 9), compared to **26**, prepared from achiral 2,2′-biphenol and (*S*,*S*)-bis(α-methylbenzyl)amine; the latter was found to give a quantitative yield of the product (entry 9), especially under slightly elevated pressure. Ligand **27** gave 68% yield and 50% ee under comparable conditions. We had earlier found that ligand **28** gave low enantioselectivities in the hydrovinylation of even simpler substrates such as α-ethylstyrene. In terms of the overall efficiency (10 mol% catalyst) and selectivity (best: 61% ee) of hydrovinylations, these highly functionalized molecules are among the worst substrates we have examined.

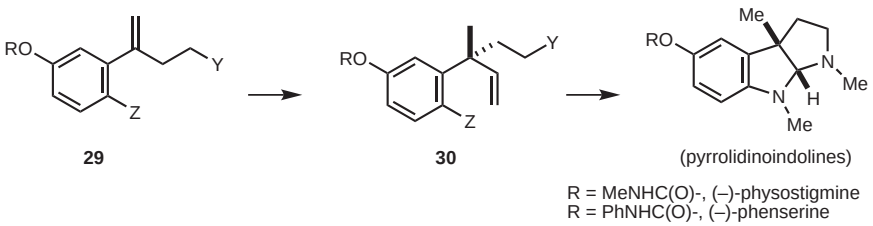


9 R_a,*S*,*S* binaphthyl
ent-**9** S_a,*R*,*R* binaphthyl
26 *S*,*S* biphenyl
ent-**26** *R*,*R* biphenyl
rac-**26** *R*,*R*/*S*,*S* (1:1)

27 (R_a,*S*)

28 (R_a,*S*,*S*)

Figure 2 Selected phosphoramidite ligands

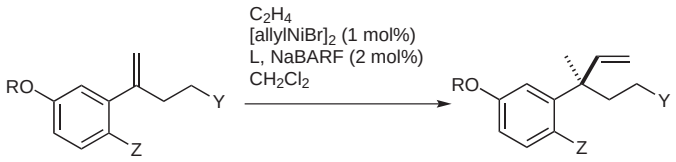


29 **30** (pyrrolidinoindolines)

R = MeNHC(O)-, (–)-physostigmine
R = PhNHC(O)-, (–)-phenserine

Scheme 1 α-Alkylstyrene precursors for pyrrolidinoindolines

Table 4 Asymmetric Hydrovinylation of **29** Using Phosphoramidite Ligands



29 **30**

Entry	Styrene	R	Z	Y	Ligand (mol%)	Conditions	Product	Yield (%)	ee[a] (%)
1	**29a**	Me	H	OTBS	**9** (10)	C_2H_4 (1 bar), r.t., 12 h	–	0	–
2	**29a**	Me	H	OTBS	**9** (10)	C_2H_4 (1 bar), 35 °C, 12 h	–	0	–
3	**29b**	Me	N(Boc)Me	N_3	**9** (10)	C_2H_4 (1 bar), r.t., 12 h	–	0	–
4	**29c**	Me	H	NPhth	**9** (5)	C_2H_4 (1 bar), r.t., 12 h	–	<5	–
5	**29d**	Me	H	NPhth	**9** (10)	C_2H_4 (1 bar), 35 °C, 12 h	**30d**	47	–
6	**29g**	Bn	H	NPhth	**9** (10)	C_2H_4 (1 bar), 35 °C, 48 h	**30g**	69[b]	61
7	**29d**	Me	H	NPhth	**26** (10)	C_2H_4 (1 bar), 35 °C, 12 h	**30d**	81[b]	–
8	**29g**	Bn	H	NPhth	**26** (10)	C_2H_4 (1 bar), 35 °C, 48 h	**30g**	76[b]	53[d]
9	**29g**	Bn	H	NPhth	**26** (10)	C_2H_4 (8.07 bar), 25 °C, 0.5 h[c]	**30g**	>95	55
10	**29g**	Bn	H	NPhth	**27** (10)	C_2H_4 (1 bar), 35 °C, 12 h	**30g**	68[b]	50
11	**29e**	Me	NO_2	NPhth	**26** (10)	C_2H_4 (8.07 bar), 25 °C, 0.5 h[c]	–	0	–
12	**29f**	Me	Br	NPhth	**26** (10)	C_2H_4 (8.07 bar), 25 °C, 0.5 h[c]	–	0	–

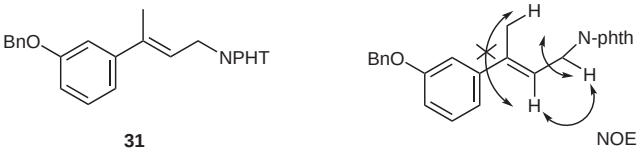
[a] Determined by ^{19}F NMR of the *N*-MTPA derivative of the hydrovinylation product.
[b] Isomerization of the double bond (~15% to **31**, see Figure 3) observed, the configuration of **31** was established by NOE studies.
[c] Carried out in a Fischer–Porter tube.
[d] Analyzed as a γ-lactam after oxidative degradation of the alkene and cyclization.

Notice that the higher pressure of ethene, in addition to having a decidedly beneficial effect on the overall yield of the reaction, also prevents isomerization of the starting alkene to **31** (entries 8 and 9).[24]

The low turnover and enantioselectivity notwithstanding, one notable feature of these ligands is the small difference in the selectivities imparted by the more elaborate (and expensive) (*R*)-1,1′-bi(2-naphthol)-derived phosphoramidite **9** and the simpler (and less expensive) 2,2′-biphenol-derived ligand **26**, and this may have practical consequences in terms of the cost of ligands.[25] Besides, the use of such ligands for the synthesis of racemic intermediates is not without some value since hydrovinylation represents a new method for the generation of quaternary centers.

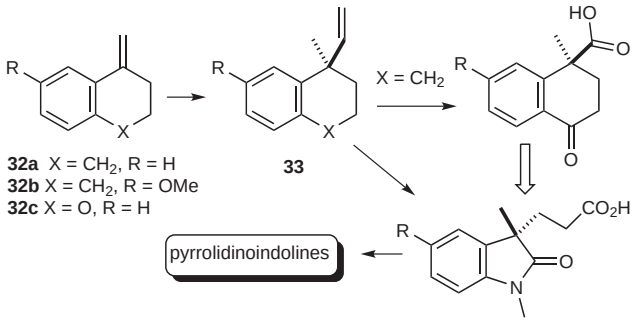
Since the enantioselectivity in the asymmetric hydrovinylation of the alkene precursor **29g** was found to be unacceptable for the planned synthesis of pyrrolidinoindolines, we turned our attention to other substrates that could serve that role. One such class of compounds, more readily accessible compared to **29**, is represented by the 1-methylenetetralin derivatives **32a–c** shown in Scheme 2. We reasoned that these alkenes would be sterically less demanding for the nickel coordination in the hydrovinylation reaction, and, without the phthalimido group, would possibly be less Lewis basic, leading to larger turnovers in the catalyst. After hydrovinylation (to give **33**), the products would still carry either a relatively reactive benzylic position, or a functionalized aromatic carbon suitable for further elaboration into the desired compounds. For example, when X = CH_2, benzylic oxidation followed by some variation of the Beckmann or Schmidt rearrangement would place the nitrogen at the correct position.

Nickel-catalyzed asymmetric hydrovinylation of **32a–c** using ligands **9**, **26**, and **27** were carried out under optimized reaction conditions (Equation 5) and the results are shown in Table 5. Most gratifyingly, these substrates undergo efficient (<2 mol% catalyst) hydrovinylation at low temperature, giving excellent enantioselectivities (up to 99% ee) for the expected product. Apart from a minor isomerization of the double bond in the starting materials to give more stable internal alkenes (**34a** or **34b**), this is

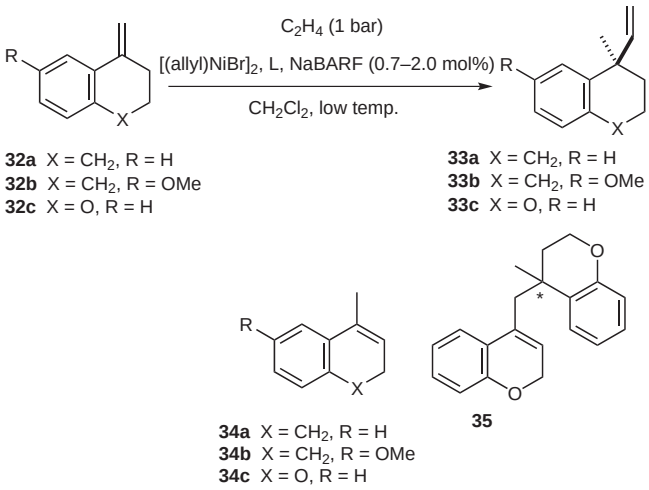


31

Figure 3



Scheme 2 Exomethylene precursors for pyrrolidinoindolines



Equation 5

an exceptionally clean reaction to give the highly valued products. There is very little of this isomerization in the oxygenated substrate **32c**, but it undergoes a competitive dimerization (to give **35** in ~15% yield) in addition to the hydrovinylation product. Compounds like **33a** and **33b** have been used in the syntheses of analgesic (–)-eptazocine, narcotic (–)-aphanorphine and related compounds.[15b,26,27] The minor detraction of the isomerization notwithstanding, the asymmetric hydrovinylation significantly shortens the synthesis of these compounds carrying a benzylic all-carbon quaternary center. For example, **33b** has been previously synthesized via stoichiometic oxazoline directed alkylation (12 steps, 35% overall yield, 99% ee)[26] or an enzyme-catalyzed desymmetrization of a chiral malonate (13 steps, 31% overall yield, 97% ee).[27] A closely related compound has been prepared by using asymmetric intramolecular Heck reaction (~10 steps, 37% overall yield, 93% ee) in a key step.[15b] For comparison, asymmetric hydrovinylation yields the product **33b** in 80% yield and ~99% ee in two steps from 3-methoxytetralone! Attempts to convert these adducts into pyrrolidinoindolines, and intermediates for lyngbyatoxin and teleocidins, are currently underway. Incidentally, we also found that the modified phosphoramidite ligands also give very high yields and selectivities in the asymmetric hydrovinylation of our model substrate, **11b** (entry 4).

We briefly examined the origin of asymmetric induction in the 3,4-dihydro-2*H*-1-benzopyran product **33c** using diastereomeric phosphoramidites. Upon examination of Table 5, entry 3, it is clear that the chirality of the product is determined by the axial chirality of the biaryl moiety of the ligand, not by the chirality of the amine. Thus both (R_a,*S*,*S*)-ligand **9** and a diastereomer with (R_a,*R*,*R*)-configuration gave the (*R*)-product in comparable enantiomeric excess (94% and 89%). The (S_a,*R*,*R*)-ligand (*ent*-**9**) as expected gave the (*S*)-product. Since the phosphoramidite **26** (*S*,*S*), a ligand derived from flexible biphenyl scaffolding, also gives the *R*-configuration in the product, it should be presumed that the chirality of the bis-amine (*S*,*S*) induces *R*-configuration in the biphenyl unit, a behavior that was previously recorded by Alexakis and coworkers.[28] Further support in the present context comes from the solid state structure of a catalytically active (allyl)Ni(**26**)(Br) complex. These results will be reported in due course.

In this study, we have reported the details of a new catalytic method for the generation of all-carbon quaternary centers starting from relatively simple vinylarene derivatives. Fine-tuning of the phosphoramidite ligands suggests that in the construction of these ligands, inexpensive 2,2′-biphenol can effectively replace the more expensive

Table 5 Asymmetric Hydrovinylation of Exomethylene Compounds[a]

Entry	Substrate	Product	Ligand					
			9		**26**		**27**	
			Yield (%)	ee[b] (%)	Yield (%)	ee[b] (%)	Yield (%)	ee[b] (%)
1	**32a**	**33a**	71[c]	99	68[c]	>95	64[c]	99
2	**32b**	**33b**	82[c]	99	–	–	–	–
3	**32c**	**33c**	70[d]	94[e]	66[c]	84	–	–
4	**11b**	**12b**	>97	>97	95	92	92	94

[a] See Equation 5 and experimental section for details.
[b] Determined by GC, (*R*)-isomer of products. Configurations assigned by comparison of $[\alpha]_D^{25}$ to an authentic sample.[26]
[c] The remainder was isomerized product **34** from starting material.
[d] Also contains 15% dimeric product **35** (configuration not established).
[e] A diastereomer of this ligand with (R_a,*R*,*R*)-configuration also gave (*R*)-adduct in ~70% yield and 89% ee.

enantiopure 1,1′-bi(2-naphthol)s. Expansion of the scope of this reaction to dienes and strained bicyclic molecules, and applications in natural product synthesis will be reported in due course.

Reactions requiring air-sensitive manipulations were conducted under an inert atmosphere of N_2 by using Schlenk techniques or a Vacuum Atmospheres glovebox. CH_2Cl_2 was distilled from CaH_2 under N_2 and stored over molecular sieves. THF was distilled under N_2 from Na/benzophenone ketyl. Unless specified other wise, vinylarenes were made via Wittig reaction of the corresponding aldehydes or ketones with methyltriphenylphosphonium bromide using BuLi in hexane soln in THF as a base to generate the ylide. Ligands[4b,21b] **9**, *ent*-**9**, **26**, *ent*-**26**, **27**, and **28**, $Na^+[3,5\text{-}(CF_3)_2C_6H_3]_4B]^-$ (NaBARF),[20,29] and $[(allyl)NiBr]_2$[20,30] were prepared according to the literature. Ethene (99.5%) was purchased from Matheson Inc., and passed through Drierite before use. Analytical TLC was performed on E. Merck precoated (0.25 mm) silica gel 60 F254 plates. Flash column chromatography was carried out on silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). Enantiomeric excesses of chiral compounds **12b**, **21**, **22**, **23**, **25**, and **33a–c** were determined by GC analyses on chiral stationary phase, which were performed on a Hewlett-Packard 5890 equipped with Cyclodex-B (25 m × 0.25 mm, 0.12 μm film thickness) capillary GC column purchased from Chrompack; He was used as the carrier gas. The ee of **24** was determined by ^{19}F NMR using the corresponding Mosher ester of the alcohol derived from hydroboration of **24**. For determining the ee of **30g**, the free amine was liberated from the phthalimide, and was converted into the Mosher amide. ^{19}F NMR analysis of the diastereomeric amides reveals the ee of the original HV product **30g**. Optical rotations were recorded on a Perkin-Elmer Model 241 polarimeter at the Na D line in $CHCl_3$.

The following phosphoramidites were prepared using our recent modifications[21b] of the previously reported methods.[4]

(Biphenyl-2,2′-diyldioxy){bis[(*R*)-1-phenylethyl]amino}phosphine (*ent*-26)

(Biphenyl-2,2′-diyldioxy)chlorophosphine (125 mg, 0.5 mmol) was treated with (–)-bis[(*R*)-1-phenylethyl]amine (102 mg, 0.454 mmol) in THF to afforded *ent*-**26**; yield: 94%; R_f = 0.49 (pentane–CH_2Cl_2, 3:1).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.44 (m, 2 H), 7.36–7.31 (m, 2 H), 7.30–7.27 (m, 2 H), 7.20–7.19 (m, 2 H), 7.14–7.09 (m, 10 H), 4.61–4.56 (m, 2 H), 1.72 (d, *J* = 7.20 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.9, 151.0, 142.9, 131.2, 129.8, 129.0, 127.9, 126.6, 124.3 (d, *J* = 256.0 Hz), 122.2 (d, *J* = 192.0 Hz), 52.6, 22.1.

^{31}P NMR (101 MHz, $CDCl_3$): δ = 146.4 (Lit.[28] 147.0).

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{28}H_{26}NNaO_2P$: 462.1593; found: 462.1591.

{Benzyl[(*S*)-1-(1-naphthyl)ethyl)]amino}[(*R*)-1,1′-binaphthyl-2,2′-diyldioxy]phosphine (27)

The coupling of (–)-[(*R*)-1,1′-binaphth-2,2′-diyldioxy]chlorophosphine (175 mg, 0.5 mmol) with (*S*)-*N*-benzyl-1-(1-naphthyl)ethylamine (119 mg, 0.45 mmol) gave **27**; yield: 90%; R_f = 0.48 (pentane–CH_2Cl_2, 2:1).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.8 Hz, 1 H), 7.86–7.84 (m, 3 H), 7.82 (d, *J* = 8.8 Hz, 1 H), 7.8 (d, *J* = 8.2 Hz, 1 H), 7.66 (d, *J* = 8.8 Hz, 1 H), 7.62 (d, *J* = 7.2 Hz, 1 H), 7.54 (d, *J* = 8.8 Hz, 1 H), 7.48 (t, *J* = 7.4 Hz, 2 H), 7.43–7.37 (m, 2 H), 7.33–7.28 (m, 3 H), 7.25–7.16 (m, 7 H), 6.96 (d, *J* = 8.8 Hz, 1 H), 5.40–5.33 (m, 1 H), 3.95–3.36 (dAB q, ν_A = 4.21, ν_B = 3.11, J_{AB} = 15.3 Hz, $J_{H\text{-}P}$ = 2.1 Hz, 2 H), 1.69 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 150.0, 149.5, 139.3, 136.52, 136.46, 133.9, 123.8, 132.5, 131.5, 131.4, 130.5, 130.2, 129.9, 128.8, 128.7, 128.4, 128.3, 128.1, 128.0, 127.02, 126.96, 126.9, 126.0, 125.6, 125.4, 125.3, 124.9, 124.8, 124.4, 124.1, 124.0, 123.8, 122.3, 122.2, 121.7, 52.0, 47.2, 21.7.

^{31}P NMR (101 MHz, $CDCl_3$): δ = 145.5.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{39}H_{30}NNaO_2P$: 598.1906; found: 598.1907.

Asymmetric Hydrovinylation, Synthesis of (*R*)-3-Methyl-3-phenylpent-1-ene (12b);[20] Typical Procedure

Precatalyst preparation: In a glovebox, a 100-mL, pear-shaped Schlenk flask with one side-arm fitted with a rubber septum and equipped with a magnetic stirrer bar was evacuated, flame-dried, and purged with argon. The flask was charged with anhyd CH_2Cl_2 (50 mL) and was transferred into a glovebox. To the flask was quickly added $[(allyl)NiBr]_2$ (180 mg, 0.50 mmol, 0.01 equiv), [(*R*)-1,1′-binaphthyl-2,2′-diyldioxy]{bis[(*S*)-(1-phenylethyl)]amino}phosphine (**9**, 539 mg, 1.00 mmol, 0.02 equiv), and NaBARF (886 mg, 1.00 mmol, 0.02 equiv) in the order mentioned. The resulting suspension was stirred at r.t. for 2 h to afford a dark-brown soln containing a small amount of fine particles (NaBr).

Asymmetric hydrovinylation: A 1-L, three-necked, round-bottomed flask equipped with a rubber septum, a Teflon-taped flow-controlled argon inlet, a thermometer, and a magnetic stir bar was flame-dried and purged with argon. The flask was then charged with anhyd CH_2Cl_2 (150 mL). The catalyst soln prepared above, now removed from the dry box, was introduced to the vessel via cannula. The flask containing the catalyst soln was further rinsed with CH_2Cl_2 (10 mL), and this soln was also transferred to the mixture. Upon completion of precatalyst transfer, the system closed at the flow-controlled stopcock and then was cooled to –70 °C in a dry ice/acetone bath, creating a small vacuum. A strong flow of dry ethene was introduced through a needle through the serum stopper to relieve the vacuum and then was adjusted to maintain a pressure of 1 mbar by releasing excess gas through an oil bubbler. The introduction of the ethene caused the internal temperature to rise. Within ca. 5 min, the internal temperature increased by 5 °C and the ethylene line was removed. The soln was cooled back to –70 C with vigorous stirring. A soln of 2-phenylbut-1-ene (**11b**, 6.60 g, 50.0 mmol) in anhyd CH_2Cl_2 (30 mL) was introduced as a weak stream into the soln of precatalyst over a 2-min period via syringe followed by a rinse with CH_2Cl_2 (10 mL). Ethene was introduced again through a needle, first as a strong flow and then regulated to maintain a pressure of 1 atm. Under an ethene atmosphere, the internal temperature of the mixture was then maintained between –65 °C and –70 °C for a period of 4 h. At the end of this period the ethene line was removed and the mixture was slowly poured into an Erlenmeyer flask containing pentane (500 mL) and was combined with a pentane rinse (50 mL) of the reaction vessel. After warming to r.t., the resulting, cloudy soln was filtered through a plug of silica gel [Merck, grade 9385, mesh 230–400, 60 Å, 4 cm × 5 cm, (d × h)], which was eluted with pentane (100 mL). The combined eluates were concentrated by rotary evaporation (20 °C/26.7 mbar) to afford **12b** (7.99 g, 99.7%) as clear liquid; 97.6% ee.

GC (HP methylsilicone column, 25 m × 0.25 mm, conditions: 5 min at 100 °C, 5 °C/min, 5 min at 200 °C): t_R = 10.61 min.

GC (Cyclodex-B, 40 min at 70 °C, 5 °C/min, 10 min at 90 °C): t_R = 53.90 (*R*), 55.65 min (*S*).

$[\alpha]_D^{22}$ –22.3 (*c* 1.05, $CHCl_3$) {Lit.[31] $[\alpha]_D^{20}$ –12.5 (*c* 0.8, $CHCl_3$, 92% ee)}.

IR (neat): 3083, 3058, 2966, 2877, 1636, 1600, 1493, 1446, 1030, 913, 760, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.27 (m, 4 H), 7.19–7.15 (m, 1 H), 6.02 (dd, *J* = 17.6, 10.8 Hz, 1 H), 5.10 (dd, *J* = 10.8, 1.2 Hz, 1 H), 5.03 (dd, *J* = 17.6, 1.2 Hz, 1 H), 1.88–1.70 (ABX_3, ν_A = 1.83, ν_B = 1.75, J_{AB} = 13.8 Hz, J_{AX} = 7.4 Hz, J_{BX} = 7.4 Hz, 2 H), 1.34 (s, 3 H), 0.76 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.4, 146.9, 128.0, 126.7, 125.7, 111.7, 44.5, 33.4, 24.4, 8.9.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{12}H_{16}$: 160.1252; found: 160.1257.

Other compounds in the Tables 3– 5 were prepared by appropriate modifications in the amount of catalyst, reaction temperature, and reaction time as indicated therein.

(*R*)-3-Methyl-3-(4-methylphenyl)pent-1-ene (21)
GC (85 °C isothermal): t_R = 53.69, 55.96 min; 90% ee.

$[\alpha]_D^{20}$ –22.1 (*c* 1.28, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 7.5 Hz, 2 H), 7.11 (d, *J* = 7.5 Hz, 2 H), 6.01 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.09 (d, *J* = 11.0 Hz, 1 H), 5.03 (d, *J* = 17.5 Hz, 1 H), 2.32 (s, 3 H), 1.90–1.70 (m, 2 H), 1.34 (s, 3 H), 0.77 (t, *J* = 6.5 Hz, 3 H).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 147.2, 144.6, 135.2, 128.9, 126.7, 111.7, 44.3, 33.5, 24.5, 21.0, 9.1.

HRMS (LCT ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{18}Na$: 197.1306; found: 197.1302.

3-(4-Chlorophenyl)-3-methylpent-1-ene (22)
GC (105 °C isothermal): t_R = 57.68, 62.15 min; 90% ee.

$[\alpha]_D^{20}$ –21.5 (*c* 1.25, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–7.20 (m, 4 H), 6.00 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.14 (d, *J* = 11.0 Hz, 1 H), 5.05 (d, *J* = 17.5 Hz, 1 H), 1.90–1.70 (m, 2 H), 1.36 (s, 3 H), 0.78 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 146.6, 146.1, 131.6, 128.4, 128.2, 112.4, 44.5, 33.6, 24.6, 9.0.

3,4-Dimethyl-3-phenylpent-1-ene (23)
GC (60 min at 70 °C, 0.5 °C/min, 60 min at 90 °C): t_R = 101.39, 102.99 min; 97% ee.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.25 (m, 3 H), 7.25–7.10 (m, 2 H), 6.19 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.19 (d, *J* = 11.0 Hz, 1 H), 5.06 (d, *J* =17.5 Hz, 1 H), 2.25–2.15 (m, 1 H), 1.35 (s, 3 H), 0.86 (d, *J* = 7.0 Hz, 3 H), 0.78 (d, *J* = 7 Hz, 3 H).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 148.4, 144.9, 128.1, 126.8, 125.7, 113.3, 47.6, 36.3, 20.7, 18.3, 17.9.

3-Methyl-3-phenyloct-1-ene (24)
50–55% ee by Mosher method.

$[\alpha]_D^{20}$ –6.9 (*c* 1.06, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 4 H), 7.25–7.15 (m, 1 H), 6.05 (dd, *J* = 17.5, 10.5 Hz, 1 H), 5.10 (d, *J* = 10.5 Hz, 1 H), 5.04 (d, *J* = 17.5 Hz, 1 H), 1.85–1.65 (m, 2 H), 1.37 (s, 3 H), 1.35–1.10 (m, 6 H), 0.88 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 147.9, 147.4, 128.2, 126.7, 125.8, 111.7, 44.4, 41.3, 32.7, 25.1, 24.3, 22.7, 14.2.

Mosher ester

^{19}F NMR (376.5 MHz, $CDCl_3$): δ = –71.30 (diastereomer 1), –71.31 (diastereomer 2).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.10 (diastereomer 1), 24.04 (diastereomer 2).

HRMS (LCT ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{15}H_{22}Na$: 225.1619; found: 225.1618.

(*R*)-3-Methyl-3-(2-naphthyl)pent-1-ene (25)
GC (120 °C isothermal): t_R = 130.79, 132.86 min; 93% ee.

$[\alpha]_D^{20}$ –22.9 (*c* 1.43, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85–7.75 (m, 3 H), 7.73 (s, 1 H), 7.50–7.40 (m, 3 H), 6.12 (dd, *J* = 17.5, 11 Hz, 1 H), 5.16 (d, *J* = 11.0 Hz, 1 H), 5.09 (d, *J* = 11.0 Hz, 1 H), 2.00–1.90 (m, 1 H), 1.90–1.80 (m, 1 H), 1.46 (s, 3 H), 0.80 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 147.0, 145.0, 133.5, 132.0, 128.1, 127.6, 127.5, 126.0, 125.9, 125.5, 125.0, 112.2, 44.9, 33.4, 24.5, 9.1.

HRMS (LCT ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{18}Na$: 233.1306; found: 233.1310.

Synthesis of Alkenes 29a–f via Stille Coupling; General Procedure
A flask was charged with the aryl iodide (100 mol%, 1–5 mmol scale), vinyltin (120 mol%), $PdCl_2(PPh_3)_2$ (5 mol%), K_2CO_3 (100 mol%), Et_4NCl (100 mol%), and deoxygenated DMF (5 mL), and the resulting mixture was stirred at 110 °C overnight. After the reaction was completed, the mixture was cooled to r.t. and then was filtered through Celite to remove solid impurities. The soln was diluted with H_2O and the crude product was extracted with EtOAc, dried ($MgSO_4$), and purified by column chromatography.

1-[4-(*tert*-Butyldimethylsiloxy)but-1-en-2-yl]-3-methoxybenzene (29a)
Following the general procedure, **29a** was obtained in 70% isolated yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.27 (t, *J* = 7.8 Hz, 1 H, Ar), 7.09–7.02 (m, 2 H, Ar), 6.89–6.86 (m, 1 H, Ar), 5.40 (s, 1 H, =CH_2), 5.17 (s, 1 H, =CH_2), 3.85 (s, 3 H, ArOMe), 3.80–3.77 (t, *J* = 7.2 Hz, 2 H, CH_2OTBS), 2.81–2.78 (m, 2 H, CH_2CH$_2$OTBS), 0.98 (s, 9 H, *t*-Bu), 0.09 [s, 6 H, Si(*t*-Bu)Me_2].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 145.4, 142.8, 129.4, 118.8, 114.2, 112.9, 112.2, 62.6, 55.3, 39.1, 26.1, 18.5, –5.2.

1-[(*tert*-Butoxycarbonyl)(methyl)amino]-2-[4-(*tert*-butyldimethylsiloxy)but-1-en-2-yl]-4-methoxybenzene (29b)
Following the general procedure, **29b** was obtained in 56% isolated yield as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95–6.93 (d, *J* = 7.6 Hz, 1 H, Ar), 6.75–6.69 (m, 2 H, Ar), 5.15 (s, 1 H, vinyl), 5.02 (s, 1 H, vinyl), 3.78 (s, 3 H), 3.60–3.55 (m, 2 H), 3.03 (s, 3 H), 2.52–2.50 (m, 2 H), 1.32 (s, 9 H), 0.84 (s, 9 H), –0.02 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 155.3, 129.3, 114.9, 113.1, 79.7, 61.6, 55.4, 39.4, 28.3, 27.8, 26.8, 25.9, 18.2, –4.5.

1-(4-Azidobut-1-en-2-yl)-3-methoxybenzene (29c)
To a stirred soln of **29a** (50 mg, 0.17 mmol) in EtOH (2 mL) was added 1 M HCl (0.1 mL) and the resulting soln was stirred at r.t. for 1 h. When the deprotection was complete, the mixture was diluted with H_2O (3 mL) and the product was extracted CH_2Cl_2 (3 × 3 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude alcohol was dissolved in CH_2Cl_2 (3 mL) and Et_3N (59 μL, 0.042 mmol), and methanesulfonyl chloride (16 μL, 0.021 mmol) were added in succession at 0 °C. The resulting mixture was stirred at r.t. for 2 h after which the solvent was evaporated. The residue was dissolved in DMF (2 mL) and NaN_3 (23 mg, 0.034 mmol) was added. The mixture was heated to 60 °C for 12 h. The soln was diluted with H_2O (5 mL), and the product was extracted with EtOAc (3 × 5 mL). The crude product was purified by preparative TLC to give **29c** (28 mg, 82%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.29 (t, *J* = 8.0 Hz, 1 H, Ar), 7.03–6.98 (m, 2 H, Ar), 6.90–6.88 (dd, *J* = 4.0, 2.4 Hz, 1 H, Ar),

5.44 (s, 1 H, =CH_2), 5.22 (s, 1 H, =CH_2), 3.86 (s, 3 H, ArOMe), 3.42–3.38 (t, *J* = 7.2 Hz, 2 H, CH_2N_3), 2.85–2.81 (t, *J* = 7.0 Hz, 2 H, C*H*$_2$$CH_2N_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 144.8, 141.8, 129.6, 118.7, 115.1, 113.1, 112.3, 55.4, 49.9, 35.2.

1-Methoxy-3-(4-phthalimidobut-1-en-2-yl)benzene (29d)

Following the general Stille procedure, **29d** was obtained in 63% isolated yield as pale yellow oil.

IR (neat): 3072, 2941, 2835, 1770. 1712, 1598, 1576, 1488, 1466, 1434, 1394, 1359, 1328, 1287, 1231, 1187, 1120, 1087, 1047, 1001 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.78 (dd, *J* = 3.0, 2.4 Hz, 2 H, Ar), 7.69–7.66 (dd, *J* = 3.0, 2.4 Hz, 2 H, Ar), 7.22–7.18 (t, *J* = 8.0 Hz, 1 H, Ar), 7.04–7.02 (d, *J* = 7.6 Hz, 1 H, Ar), 6.99 (s, 1 H, Ar), 6.75–6.73 (dd, *J* = 8.0, 2.4 Hz, 1 H, Ar), 5.37 (s, 1 H, =CH_2), 5.16 (s, 1 H, =CH_2), 3.85–3.79 (m, 5 H, ArOMe, RC*H*$_2$NPhth), 2.91–2.88 (t, *J* = 7.2 Hz, 2 H, C*H*$_2$$CH_2$NPhth).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 159.6, 144.9, 141.6, 133.8, 132.1, 129.3, 123.0, 118.6, 114.7, 113.1, 111.7, 55.2, 37.5, 34.0.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}NO_3$: 308.1287; found 308.1272.

4-Methoxy-1-nitro-2-(4-phthalimidobut-1-en-2-yl)benzene (29e)

Following the general procedure, purification by column chromatography (25% EtOAc–hexane) [R_f = 0.5 (50% EtOAc–hexanes)] gave **29e** (39% yield) as a colorless oil.

IR (neat): 3085, 2943, 2848, 1770, 1722, 1601, 1574, 1514, 1393, 1337, 1249, 1187, 1097, 1065, 1027 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01–7.99 (d, *J* = 9.2 Hz, 1 H, Ar), 7.81–7.79 (m, 2 H, Ar), 7.70–7.66 (m, 2 H, Ar), 6.86–6.80 (m, 2 H, Ar), 5.16 (s, 1 H, =CH_2), 4.99 (s, 1 H, =CH_2), 3.89 (s, 3 H, ArOMe), 3.80–3.77 (t, *J* = 7.0 Hz, 2 H, C*H*$_2$NPhth), 2.80–2.76 (t, *J* = 6.8 Hz, 2 H, C*H*$_2$$CH_2$NPhth).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 168.4, 163.2, 144.9, 140.7, 134.3, 131.9, 127.5, 126.2, 123.4, 118.2, 116.6, 116.3, 113.7, 56.2, 37.0, 35.2.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{17}N_2O_5$: 353.1137; found: 353.1120.

1-Bromo-4-methoxy-2-(4-phthalimidobut-1-en-2-yl)benzene (29f)

Following the general procedure, **29f** was obtained in 40% isolated yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.77 (m, 2 H, Ar), 7.68–7.65 (m, 2 H, Ar), 7.35–7.33 (d, *J* = 8.8 Hz, 1 H, Ar), 6.81–6.80 (d, *J* = 2.8 Hz, 1 H, Ar), 6.63–6.60 (dd, *J* = 8.8, 3.2 Hz, 1 H, Ar), 5.21 (s, 1 H, =CH_2), 5.00 (s, 1 H, =CH_2), 3.76–3.73 (m, 5 H, ArOMe, C*H*$_2$NPhth), 2.85–2.82 (t, *J* = 7.0 Hz, 2 H, C*H*$_2$$CH_2$NPhth).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 158.8, 146.6, 143.7, 134.0, 133.5, 132.2, 123.3, 117.8, 116.2, 114.9, 112.3, 55.6, 36.9, 34.9.

1-(Benzyloxy)-3-(4-phthalimidobut-1-en-2-yl)benzene (29g)

Following the general procedure, **29g** was obtained and further purified by column chromatography [10% EtOAc–hexane, R_f = 0.3 (15% EtOAc–hexane)] to give **29g** (63% isolated yield) as a pale yellow oil.

IR (neat): 3062, 3031, 2945, 2869, 1771, 1713, 1597, 1574, 1488, 1435, 1395, 1360, 1288, 1224, 1121, 1087, 1026, 1001 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.77 (dd, *J* = 5.4, 3.2 Hz, 2 H, Ar), 7.67–7.65 (dd, *J* = 5.4, 3.2 Hz, 2 H, Ar), 7.45–7.31 (m, 5 H, Ar), 7.20–7.18 (t, *J* = 8.0 Hz, 1 H, Ar), 7.05–7.01 (m, 2 H, Ar), 6.81–6.78 (m, 1 H, Ar), 5.33 (s, 1 H, =CH_2), 5.12 (s, 1 H, =CH_2), 5.06 (s, 2 H, OC*H*$_2$Ph), 3.83–3.79 (t, *J* = 7.4 Hz, 2 H, C*H*$_2$NPhth), 2.88–2.85 (t, *J* = 7.2 Hz, 2 H, C*H*$_2$$CH_2$NPhth).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 168.2, 158.8, 144.8, 141.6, 137.1, 133.8, 132.1, 129.4, 128.6, 128.0, 127.6, 123.2, 118.9, 114.9, 114.0, 112.7, 70.0, 37.4, 34.0.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{22}NO_3$: 384.1600; found: 384.1583.

Asymmetric Hydrovinylation of Substrates 29a–g; General Procedure

In a N_2-charged drybox, a two-necked Schlenk tube was charged with [(allyl)NiBr]$_2$ (1 mol%), ligand (2 mol%), and NaBARF (2 mol%), and the mixture was dissolved in anhyd CH_2Cl_2 (5–7 mL/mmol of olefin). This precatalyst was stirred at r.t. for 10 min, and then taken out of the drybox. After the ethene line was connected to the reaction vessel, the line was evacuated 3 times to remove oxygen in the line, and then ethene was introduced to the vessel. Into the activated catalyst, starting olefin in anhyd CH_2Cl_2 (1–2 mL/mmol of olefin) was added, and the resulting mixture was stirred at r.t. under the atmospheric pressure of ethene. After the reaction, the solvent was evaporated, and the crude product was purified by column chromatography.

(*R*)-3-(3-Methoxyphenyl)-3-methyl-5-phthalimidopent-1-ene (30d)

Following the general procedure using (allyl)Ni(**26**)(BARF) (10 mol%) at 35 °C for 12 h gave **30d** (81% isolated yield) as a pale yellow oil.

IR (neat): 3072, 2930, 2837, 1772, 1707, 1601, 1484, 1396, 1366, 1284, 1249, 1173, 1049 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.72 (m, 2 H, Ar), 7.67–7.63 (m, 2 H, Ar), 7.15–7.11 (t, *J* = 8.0 Hz, 1 H, Ar), 6.92–6.87 (m, 2 H, Ar), 6.59–6.56 (dd, *J* = 8.0, 2.4 Hz, 1 H, Ar), 6.09–6.02 (dd, *J* = 11.2, 6.0 Hz, 1 H, C*H*=CH_2), 5.15 (s, 1 H, CH=C*H*$_2$), 5.12–5.10 (d, *J* = 8.0 Hz, 1 H, CH=C*H*$_2$), 3.76 (s, 3 H, OMe), 3.64–3.60 (t, *J* = 8.0 Hz, 2 H, C*H*$_2$NPhth), 2.24–2.18 (m, 1 H, C*H*$_2$$CH_2$NPhth), 2.10–2.05 (m, 1 H, C*H*$_2$$CH_2$NPhth), 1.46 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 159.6, 147.9, 145.9, 133.9, 132.4, 129.4, 123.2, 119.1, 112.9, 112.7, 111.2, 55.3, 43.5, 38.6, 34.8, 25.2.

(*R*)-3-[3-(Benzyloxy)phenyl]-3-methyl-5-phthalimidopent-1-ene (30g)

Following the general procedure using (allyl)Ni(**26**)(BARF) (10 mol%) under 35 °C for 48 h gave **30g** (76%, isolated yield) as a pale yellow oil.

$[\alpha]_D^{22}$ +1.87 (*c* 1.03, $CHCl_3$, 53% ee).

IR (neat): 3084, 3025, 2942, 2872, 1772, 1707, 1601, 1437, 1390, 1360, 1243, 1084, 1026 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.74 (m, 2 H, Ar), 7.66–7.63 (m, 2 H, Ar), 7.44–7.30 (m, 5 H, Ar), 7.16–7.12 (t, *J* = 8.0 Hz, 1 H, Ar), 6.96–6.92 (m, 2 H, Ar), 6.67–6.65 (m, 1 H, Ar), 6.08–6.01 (dd, *J* = 10.8, 6.0 Hz, 1 H, C*H*=CH_2), 5.15 (s, 1 H, CH=C*H*$_2$), 5.12–5.10 (d, *J* = 8.0 Hz, 1 H, CH=C*H*$_2$), 5.01 (s, 2 H, OC*H*$_2$Ph), 3.63–3.59 (t, *J* = 8.0 Hz, 2 H, C*H*$_2$NPhth), 2.25–2.18 (m, 1 H, C*H*$_2$$CH_2$NPhth), 2.13–2.04 (m, 1 H, C*H*$_2$$CH_2$NPhth), 1.46 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 158.9, 148.1, 145.8, 137.4, 133.9, 132.4, 129.4, 128.7, 128.4, 128.1, 127.8, 126.6, 123.2, 119.3, 113.9, 112.7, 112.2, 70.1, 43.5, 38.6, 34.8, 25.2, 21.3.

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{26}NO_3$: 412.1913; found: 412.1916.

3-[3-(Benzyloxy)phenyl]-1-phthalimidobut-2-ene (31)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.69 (m, 4 H, phthalimido), 7.49–7.29 (m, 5 H, Ar), 7.19 (t, *J* = 6.4 Hz, 1 H, Ar), 7.05–6.85 (m, 2 H, Ar), 6.84–6.79 (m, 1 H, Ar), 5.85 [t, *J* = 7.0 Hz, 1 H, Ar(CH_3)C=C*H*CH_2NPhth], 5.03 (s, 2 H, OCH_2Ph), 4.50 [d, *J* = 7.5 Hz, 2 H, Ar(CH_3)C=CHCH_2NPhth, *E*], 4.22 [d, *J* = 6.5 Hz, 2 H, Ar(CH_3)C=CHCH_2NPhth, *Z*], 2.23 [s, 3 H, Ar(CH_3)C=CHCH_2NPhth, *E*], 2.01 [s, 3 H, Ar(CH_3)C=CHCH_2NPhth, *Z*]; the configuration of the major product was established by NOE studies (Figure 3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 144.5, 139.4, 137.3, 134.1, 132.5, 129.6, 128.1, 127.8, 123.4, 121.6, 119.1, 113.7, 113.1, 70.2, 36.5, 16.4.

HRMS: *m*/*z* [M + Na^+] calcd for $C_{25}H_{21}NNaO_3$: 406.1419; found: 406.1400.

(*R*)-3-[3-(Benzyloxy)phenyl]-3-methyl-5-phthalimidopent-1-ene (30g)

Under Elevated Pressure of Ethene (Table 4, entry 9): In an N_2-charged drybox, (allyl)Ni(**26**)(BARF) precatalyst (10 mol%) in CH_2Cl_2 (1.5 mL) was prepared, and then the soln was added to a Fisher–Porter tube. After 10 min of stirring at r.t., starting material **29g** (20 mg, 0.0487 mmol) in CH_2Cl_2 (1.5 mL) was added to the precatalyst soln. The tube was tightly closed, and then taken out from a drybox. After the tube was connected to an ethene line, the line was evacuated (3 ×), and then ethene gas was introduced to the tube, and pressurized to 17 psi. During the reaction, internal pressure decreased, so the system was recharged (3 ×). The soln was stirred for 30 min and then concentrated. The crude product was purified by preparative TLC to give ~20 mg (>95%) of the product **30g** identified in the previous experiment.

Determination of the Enantiomeric Excess of 30g by Mosher's Method

The phthalimide protecting group in hydrovinylation product **30g** (15 mg, 0.036 mmol) was removed by refluxing this material with hydrazine hydrate (500 mol%), and EtOH (3 mL) for 12 h. The crude amine was purified by acid–base workup, and subsequent extraction with CH_2Cl_2. A soln of the amine in CH_2Cl_2 (2 mL) was treated with Et_3N (300 mol%), followed by MTPA-Cl (110 mol%). The enantiomeric excess was determined by the integration of ^{19}F NMR peaks in the diastereomers [^{19}F NMR δ (C_6D_6): Mosher amides from the racemic product: 68.61, and 68.57]. The diastereomeric ratio using ligand **26** was 1.0:3.5 corresponding to an ee of ~55% in the asymmetric catalyzed reaction. For both reactions performed under 1 atmosphere of ethene at 35 °C for 48 h (Table 4, entry 8), and under 17 psi of ethene at 25 °C for 0.5 h (Table 4, entry 9), the selectivity was approximately same, within experimental error. The enantioselectivities for reactions using other ligands were estimated the same way.

Ligand **9** (Table 4, entry 6): d.r. 1.0:4.1, ~61% ee.

Ligand **27** (Table 4, entry 10): d.r. 1.0:3.0 (~50% ee).

(*R*)-1-Methyl-1-vinyl-1,2,3,4-tetrahydronaphthalene (33a)

Yield of **33a**: 71% contaminated with ~28% 1-methyl-3,4-dihydronaphthalene (**34a**).

GC (HP methylsilicone, 5 min at 100 °C, 5 °C/min, 5 min at 200 °C): t_R = 13.10 min.

GC (Cyclodex-B, 75 min at 90 °C): t_R = 62.85 (*S*), 63.69 min (*R*); >99% ee.

$[\alpha]_D^{20}$ –35.4 (*c* 1.15 $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.13 (m, 4 H), 6.01 (dd, *J* = 17.60, 10.40 Hz, 1 H), 5.10 (dd, *J* = 10.40, 1.20 Hz, 1 H), 4.89 (dd, *J* = 17.60, 1.20 Hz, 1 H), 2.84 (d, *J* = 7.6 Hz, 2 H), 1.90–1.83 (m, 3 H), 1.76–1.71 (m, 1 H), 1.46 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 142.3, 135.8, 129.1, 128.5, 125.7, 125.6, 112.0, 40.9, 37.6, 34.1, 28.3, 22.4.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}$: 172.1247; found: 172.1245.

1-Methyl-3,4-dihydronaphthalene (34a)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.17 (m, 2 H), 7.15–7.10 (m, 2 H), 5.85–5.83 (m, 1 H), 2.75 (t, *J* = 8.0 Hz, 2 H), 2.26–2.20 (m, 2 H), 2.04 (dd, J_1 = 3.2 Hz, J_2 = 1.6 Hz, 3 H).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 136.3, 135.9, 132.3, 127.3, 126.7, 126.3, 125.4, 122.8, 28.3, 23.2, 19.3.

(*R*)-7-Methoxy-1-methyl-1-vinyl-1,2,3,4-tetrahydronaphthalene (33b)

Following the general procedure, using 4 mol% of (allyl)Ni(**9**)(BARF) as the catalyst, 7-methoxy-1-methylene-1,2,3,4-tetrahydronaphthalene (**32b**, 0.30 g, 1.72 mmol) was reacted at –70 °C for 6 h. Purification by column chromatography gave the product (0.30 g, >99%) as a mixture of the hydrovinylation product **33b** (82%, >99% ee by chiral GC), isomerized starting material **34b** (15%), and unconverted starting material **32b** (3%). The ratios of these compounds were determined by integration of the diagnostic peaks in the ^{1}H NMR spectrum.

GC (Cyclodex-B, isothermal, 120 °C): t_R = 56.09 (*R*-isomer), 57.10 min (*S*-isomer, obtained using *ent*-**9**); 99% ee.

$[\alpha]_D^{22}$ –14.5 (*c* 0.142, $CHCl_3$) {Lit.[26] $[\alpha]_D^{20}$ –21.1 (*c* 3.8, $CHCl_3$)}.

IR (neat): 2958, 2829, 1722, 1637, 1606, 1580, 1488, 1443, 1368, 1322, 1223, 1190, 1121, 1064 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.01–6.96 (m, 2 H, Ar), 6.68–6.65 (m, 1 H, Ar), 5.95–5.88 (dd, *J* = 17.2, 10.4 Hz, 1 H, C*H*=CH_2), 5.85 (br s, 1 H, isomerized product's vinyl-H), 5.02–4.99 (dd, *J* = 10.4, 1.2 Hz, 1 H, CH=CH_2), 4.87–4.82 (dd, *J* = 17.6, 1.2 Hz, 1 H, CH=CH_2), 3.75 (s, 3 H, OMe), 2.71–2.68 (t, *J* = 6.2 Hz, 2 H, ArCH_2R), 1.85–1.73 (m, 4 H, $ArCH_2CH_2CH_2$, $ArCH_2CH_2CH_2$), 1.36 (s, 3 H, C_qCH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 157.7, 148.8, 143.7, 130.0, 129.0, 113.8, 112.2, 111.9, 55.4, 41.4, 37.7, 29.6, 28.4, 19.6.

(*R*)-4-Methyl-4-vinyl-3,4-dihydro-2*H*-1-benzopyran (33c)

Following the general procedure using 10 mol% of (allyl)Ni(**9**)(BARF) and **32c** (0.2 g, 1.37 mmol) at 35 °C for 12 h, the desired product **33c** (0.167 g, 70%) was obtained as a pale yellow oil after purification. In addition to the expected product, a head-to-tail dimer **35** was also obtained.

GC (Cyclodex-B, isothermal 100 °C): t_R = 47.03 (*S*-isomer, obtained from ligand *ent*-**9**), 48.76 min (*R*-isomer); 94% ee;

IR (neat): 2959, 2830, 1722, 1637, 1605, 1579, 1487, 1443, 1368, 1321, 1223, 1190, 1121, 1064 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.07 (m, 2 H, Ar), 6.88–6.84 (m, 1 H, Ar), 6.81–6.79 (dd, *J* = 8.2, 1.2 Hz, 1 H, Ar), 5.92–5.87 (dd, *J* = 17.5, 10.5 Hz, 1 H, C*H*=CH_2), 5.12–5.10 (dd, *J* = 10.5, 1.5 Hz, 1 H, CH=CH_2), 4.87–4.82 (dd, *J* = 12.2, 1.2 Hz, 1 H, CH=CH_2), 4.18–4.13 (m, 2 H, OCH_2), 1.89–1.86 (m, 2 H, OCH_2CH_2), 1.43 (s, 3 H, CH_3).

^{3}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 147.5, 128.9, 127.9, 127.7, 120.4, 117.1, 114.2, 62.9, 37.9, 36.1, 27.9.

4-[(3,4-Dihydro-2*H*-1-benzopyran-4-yl)methyl]-4-methyl-1,2,3,4-dihydro-2*H*-1-benzopyran (35)

Isolated yields of dimer **35** as a pale yellow oil, from HV using ligand **9** and **26**, were ~15%.

IR (neat): 3058, 2927, 2856, 1725, 1590, 1578, 1487, 1450, 1347, 1266, 1221, 1165, 1090 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.02 (m, 4 H, Ar), 6.84–6.76 (m, 4 H, Ar), 5.42–5.40 (t, *J* = 3.8 Hz, 1 H, vinyl), 4.63–4.62 (d, *J* = 3.6 Hz, 2 H), 4.21–4.18 (m, 1 H, OCH_2CH_2), 4.14–4.11 (m, 1 H, OCH_2CH_2), 2.89–2.86 (d, *J* = 14.0 Hz, 1 H, CH_2C), 2.71–2.67 (d, *J* = 14.0 Hz, 1 H, CH_2C), 2.00–1.97 (m, 1 H, OCH_2CH_2), 1.75–1.69 (m, 1 H, OCH_2CH_2), 1.29 (s, 3 H, CH_3). The assignments were further confirmed by COSY and NOESY experiments.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.1, 128.9, 127.7, 127.5, 124.1, 122.8, 121.2, 120.5, 117.2, 116.4, 65.3, 63.0, 42.4, 34.9, 34.5, 29.7.

Acknowledgment

Financial assistance for this research by NSF (CHE-0610349) and NIH (General Medical Sciences, R01 GM075107) is gratefully acknowledged. We also thank the ACS Organic Division for a graduate fellowship sponsored by The Schering Plough Corporation to Craig Smith.

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