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A Publication
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for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

VINYLATION WITH INEXPENSIVE SILICON-BASED REAGENTS: PREPARATION OF 3-VINYLQUINOLINE AND 4-VINYLBENZOPHENONE
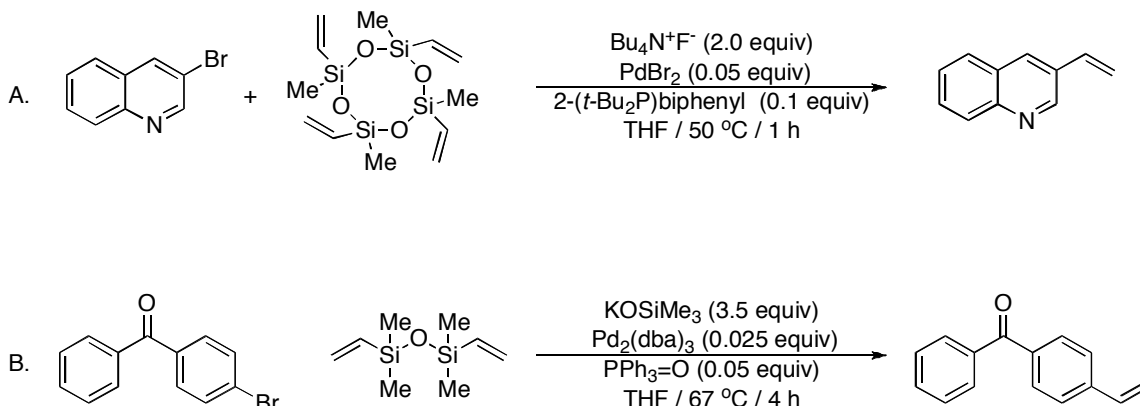
Submitted by Scott E. Denmark and Christopher R. Butler.[1]
Checked by Andreas Pfaltz and David H. Woodmansee.

1. Procedure

A. Preparation of 3-Vinylquinoline. A 250-mL Schlenk flask (Note 1) equipped with a magnetic stir bar and a glass stopper fitted with a PTFE O-ring (Note 2) is flame-dried under vacuum (0.3 mmHg). The flask is then back-filled with an inert atmosphere of argon and allowed to cool to room temperature at which time the flask is charged with palladium bromide (398 mg, 1.49 mmol, 0.05 equiv) (Note 3) and 2-(di-*tert*-butylphosphino)biphenyl (901 mg, 3.02 mmol, 0.10 equiv) (Note 4) under argon purge. The flask is sealed with a septum and the contents of the flask placed under full vacuum (0.3 mmHg) followed by back-filling with argon, and this evacuation/backfill process is repeated three times. 1,3,5,7-Tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4^V) (6.36 mL, 6.34 g, 18.3 mmol, 0.61 equiv) (Note 5) is added neat *via* syringe. A solution of tetrabutylammonium fluoride trihydrate in tetrahydrofuran (60 mL, 1.0 M, 60 mmol, 2 equiv) (Notes 6 and 7) is transferred *via* cannula to the Schlenk flask. The resulting red orange solution is stirred for 15 minutes at room temperature during which time a color change from red to yellow occurs. 3-Bromoquinoline (4.03 mL, 6.24 g, 30.0 mmol, 1 equiv) (Note 8) is added neat *via* syringe, the septum is replaced with a depth adjustable glass

thermometer adapter equipped with a standard laboratory alcohol thermometer and a PTFE faced silicone washer (Note 9) and fitted with a PTFE O-ring (Note 2) ensuring a good seal with the Schlenk flask. The adapted thermometer assembly is secured in place with a metal clamp and the flask is placed in a preheated 50 °C oil bath and is stirred at that temperature. During the first 10 minutes of heating the internal temperature rises past the bath temperature mildly to 62 °C for approximately 10 minutes and gradually returns to 50 °C. The starting material is consumed after 2.5 h (Note 10) and the mixture is allowed to cool to room temperature. Diethyl ether (100 mL) is added and the resulting suspension is then filtered through a short column of silica (Note 11) which is further eluted with an additional 400 mL of diethyl ether. The fractions are combined and concentrated on a rotary evaporator (35 °C, distillation is carried out from 375 mmHg to distill bulk solvent to 10 mmHg to remove final traces of higher boiling volatiles) resulting in 10.4 g of a crude mixture of 3-vinylquinoline contaminated with a siloxane byproduct (Note 12). The crude material is purified by silica gel chromatography (Note 13) eluting with pentane (1000 mL), followed by pentane/ethyl acetate, 9:1 (2000 mL), and final elution with 4:1 pentane/ ethyl acetate (2000 mL). Concentration of the eluate by rotary evaporation (500 mmHg and 40 °C to remove pentane, 10 mmHg and 40 °C to remove ethyl acetate) affords 4.31 g of 3-vinylquinoline which is further purified by Kugelrohr distillation (bp 85-100 °C at 0.6 mmHg) to provide 4.23 g (91%) of 3-vinylquinoline as a colorless liquid (Notes 14, 15, 16).

   B.   Preparation of 4-Vinylbenzophenone. A 250-mL Schlenk flask (Note 1) equipped with a magnetic stir bar and a glass stopper fitted with a PTFE O-ring (Note 2) is flame-dried under vacuum (0.3 mmHg). The flask is then back-filled with an inert atmosphere of argon and allowed to cool to room temperature at which time the flask is charged with potassium trimethylsilanolate (13.5 g, 105 mmol, 3.5 equiv) (Note 17), palladium tris(dibenzylideneacetone) (685 mg, 0.75 mmol, 0.025 equiv) (Note 18), and triphenylphosphine oxide (418 mg, 1.5 mmol, 0.05 equiv) (Note 19) under a very gentle argon purge. The flask is sealed with a septum and the contents of the flask are placed under full vacuum (0.3 mmHg) followed by back-filling with argon, and this evacuation/backfill process is repeated three times. Dry, degassed tetrahydrofuran (60 mL) (Note 7) is added *via* syringe. The stirring is turned off and the septum removed under a gentle argon purge and 4-bromobenzophenone (7.83 g, 30.0 mmol, 1.0 equiv) (Note 20) is added as a solid. The septum is replaced, stirring is restarted and 1,3-

divinyltetramethyldisiloxane (7.63 mL, 6.17 g, 33.1 mmol, 1.1 equiv) (Note 21) is added neat *via* syringe. The septum is replaced with a depth adjustable glass thermometer adapter equipped with a standard laboratory alcohol thermometer and a PTFE faced silicone washer (Note 9) and fitted with a PTFE O-ring (Note 2) ensuring a good seal with the Schlenk flask. The adapted thermometer assembly is secured in place with a metal clamp and the flask is placed in a preheated 70 °C oil bath and is stirred at that temperature. The internal temperature rises to approximately 66 °C and the resulting dark solution is stirred for 5 h (Note 22). The flask is removed from the oil bath and allowed to cool to room temperature at which time the flask is opened and 50 mL of diethyl ether is added and the mixture stirred for 5 min. The resulting suspension is filtered through a short column of silica gel which is eluted with an additional 200 mL of ether (Note 23). The fractions are combined and concentrated on a rotary evaporator (35 °C, distillation was carried out from 375 mmHg to distill bulk solvent to 10 mmHg to remove final traces of higher boiling volatiles) resulting in 8.5 g of crude material which is purified by column chromatography (Note 24) eluting with pentane (1000 mL), followed by pentane/ dichloromethane, 50:50 (2000 mL), and finishing with dichloromethane (1500 mL). The solvent is removed from clean fractions on a rotary evaporator (35 °C, distillation is carried out from 375 mmHg to distill bulk solvent to 10 mmHg to remove final traces of higher boiling volatiles), resulting in 5.15 g of 4-vinylbenzophenone. Mixed fractions of the product and aryl bromide (0.5 g) are combined and purified by chromatography under proportional conditions (Note 25), the purified fractions are combined with previously isolated material and the solvent removed on the rotavap (35 °C, distillation is carried out from 375 mmHg to distill bulk solvent to 10 mmHg to remove final traces of higher boiling volatiles) to provide a total of 5.62 g (90%) of 4-vinylbenzophenone (Note 26) as a white solid.

2. Notes

1. Schlenk flask (250 mL with 29/32 female joint) can be purchased from Aldrich, part number Z515760-1ea. The submitters used a 250-mL single-necked, round-bottomed flask equipped with a T-shaped side-arm adapter.

2. The Checkers used GLINDEMANN®-sealing rings (PTFE) purchased from AMSI-Glas AG.

3. Checkers and submitters purchased palladium(II) bromide (99%) from Strem Chemicals and used the chemical as received.

4. Checkers purchased 2-(di-*tert*-butylphosphino)biphenyl (99%) from Strem Chemicals and used the chemical as received. Submitters purchased 2-(di-*tert*-butylphosphino)biphenyl (97%) from Aldrich Chemical Company and used the chemical as received.

5. Checkers purchased 1,3,5,7-Tetramethyl-1,3,5,7-tetravinyl-cyclotetrasiloxane (D_4^V) from Aldrich Chemical Company and used the chemical as received. Submitters purchased 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane from Gelest and used the chemical as received.

6. Checkers and submitters purchased tetrabutylammonium fluoride trihydrate (97%) from Fluka Chemical Corporation as a solid. A 1M solution of tetrabutylammonium fluoride was prepared in a glove box with absolute THF (Note 7) and used immediately to avoid contamination with moisture and air.

7. The Checkers purchased HPLC-grade THF from VWR and dried the solvent using a Pure-Solv™ system in accordance with Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520. The submitters purchased HPLC grade THF from Fisher which was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon.

8. Checkers purchased 3-bromoquinoline ($\geq$ 97%) from Fluka Chemical Corporation and used the chemical as received. Submitters purchased 3-bromoquinoline 98% from Alfa-Aesar and used the chemical as received.

9. A thermometer adapter complete with PTFE faced silicone washer can be purchased from Aldrich Chemical Company, part number Z551805-1EA for 29/42 ground glass joint. The submitters used a Teflon-coated digital thermometer inserted through a septum in place of the thermometer adapter, available from Omega Instruments, Digicator Model 400a with K-type thermocouple leads.

10. Checkers followed the progress of the reaction by quickly removing the thermometer adapter assembly under a very gentle purge of argon and removing a drop of reaction solution with the tip of a pipette. The reaction solution was transferred to a micropipette by simple capillary action and the solution was spotted on a TLC plate along with starting material and

a cospot. The TLC plate was run in pentane/ ethyl acetate 9/1 and the R_f for 3-bromoquinoline is 0.7, R_f for 3-vinylquinoline is 0.3.   When no discernable starting material remained a small aliquot of 100 μL was removed and the sample was concentrated under a stream of nitrogen, the remaining amorphous material was taken up in 1 mL of ether and passed through a plug of silica (150 mg of silica loaded into a Pasteur pipette plugged with glass wool). The filtrate was analyzed by GC/MS on an HP6890 gas chromatograph with a HP5970A detector equipped with a Machery and Nagel Optima5 5% polyphenylmethylsiloxane column, 25 m x 0.2 mm id and 35 μM film thickness, flow set to 20 psi of hydrogen carrier gas, a 20/1 split ratio.   The oven was programmed for a starting temperature of 100 °C, a 2 minute holding time at that temperature, a 10 °C/minute ramp with a final temperature of 270 °C and a holding time of 10 minutes at that temperature. Starting material elutes at 10.8 minutes and product elutes at 10.6 minutes.   Submitters monitored the reaction as follows: A 50-μL aliquot was removed *via* syringe and quenched into 4 drops of an aqueous *N,N*-dimethyl-2-aminoethanethiol solution (10% w/w).   The aliquot was extracted with 1 mL of ethyl acetate and the organic layer was passed through a pipette plug of silica gel. GC analysis: product, t_R 4.69 min; 3-bromoquinoline, 4.91 min (HP-1, 100 ° to 250 °C, 15 psi H_2, 20 °C /min).

11. Checkers purchased silica gel from Fluka with a 0.040 – 0.063 mm particle size and 0.1% Ca stabilizer. Checkers used for a rough purification 50 g of silica gel loaded as a pentane slurry into a 60 mm diameter column. Submitters silica gel was purchased from Aldrich Chemical Company, (Merck, grade 9385, 230-400 mesh). For the purification submitters used 50 g of silica gel loaded as a diethyl ether slurry into a 65 mm diameter glass column.

12. A byproduct was found to make up a significant amount of the initial isolated weight. The byproduct distilled with the product and was not detectable on TLC plates under UV light. The byproduct stained poorly with standard stains but a very faint iodine stain was observed to streak just before the product on TLC.   Upon isolation the byproduct showed the following physical properties: ^{1}H-NMR (400.1 MHz, CDCl$_3$, 298 K) δ: 0.47-0.45 (broad m, 2H), 0.93-0.89 (m, 10 H), 1.01-0.98 (m, 3 H), 1.31-1.25 (m, 10 H), 1.42-1.37 (m, 6 H), 1.78-1.71 (m, 13 H), 2.4-2.36 (m, 6 H), 2.78 (t, *J* = 7.4 Hz, 2 H), 3.6-3.49 (m, 1 H); GC/MS elution time of 6.2 min (Note 10); MS (EI) *m/z* 143 (4), 142 (46), 101 (2), 100 (30), 84 (3), 58 (10), 44 (14).

13. Checkers dissolved 10.4 g of crude material in 100 mL of dichloromethane in a 500-mL round-bottomed flask with 35 g of silica gel and removed the solvent at the rotovap (35 °C, distillation is carried out from 375 mmHg to distill bulk solvent to 10 mmHg to remove final traces of low boiling volatiles) resulting in a free flowing powder suitable for dry loading (if the resulting powder is not free flowing after sonication 5 g of silica gel and 100 mL of DCM are added and the process repeated). Silica gel (230 g) is loaded as a pentane slurry into a 60-mm glass column and packed under nitrogen pressure (150 mmHg) until the stationary phase forms a solid column and 10 cm of pentane is left on top of the packed silica gel to cushion the packing of the crude absorbed silica gel. The product on silica gel is gently added to the column with the help of a glass funnel and packed under pressure. Samples are collected in 50 mL test tubes, the first fractions of product are found to contain a byproduct (Note 12) which is not observable by TLC but clear in the ^{1}H NMR and GC/MS. Mixed fractions are combined and chromatographed under proportional conditions and the purified fractions are combined with the rest of the pure material. All attempts to purify the product from the byproduct by Kugelrohr resulted in codistillation.

14. Boiling points (bp) correspond to uncorrected air-bath temperatures in the Buchi GKR-50 Kugelrohr. Submitters used a slightly higher pressure (1.2 mmHg) and found a slightly higher boiling point range (100-120 °C). Checkers recommend using the best vacuum available to avoid excessive heat and the resulting polymerization.

15. The product displayed the following physical properties ^{1}H-NMR (400.1 MHz, CDCl$_3$, 298 K) δ: 5.47 (d, J = 11.0 Hz, 1 H), 6.00 (d, J = 17.7 Hz, 1 H), 6.87 (dd, J = 17.7, 11.0 Hz, 1 H), 7.54 (t, J = 7.9 Hz, 1 H), 7.68 (t, J = 8.3 Hz, 1 H), 7.80 (d, J = 8.1 Hz, 1 H), 8.04–8.13 (m, 2 H), 9.02 (d, J = 2.2 Hz, 1 H). ^{13}C-NMR (100.6 MHz, CDCl$_3$, 298 K) δ: 116.4, 127.0, 127.9, 128.0, 129.1, 129.3, 130.3, 132.6, 133.7, 147.5, 149.0. IR (NaCl) 3063, 3007, 1632, 1618, 1568, 1492, 1461, 1429, 1413, 1369, 1327, 1124, 987, 974, 908, 860, 786, 752, 699, 609 cm^{-1}. MS (EI) m/z: 156.00 (m+1)$/z$ (12.29 %), 155.00 (m)$/z$ (100.0 %), 154.00 (6.59 %), 127.95 (12.45 %), 126.95 (20.20 %), 102.00 (0.90 %), 77.00 (0.96 %), 75.00 (1.07 %), 64.00 (1.17 %), 63.05 (1.20 %), 50.95 (1.58 %), 49.95 (1.21 %). TLC: R_f = 0.30 (SiO$_2$, pentane/EtOAc, 9:1); Anal. Calcd. for C$_{11}$H$_9$N: C, 85.13; H, 5.85; N, 9.03. Found C, 84.64; H, 6.10; N, 9.26. The submitters elemental analysis found C, 84.83; H, 5.93; N, 9.07.

16. A second run made on a half scale yielded 2.04 g (88% yield) of product matching the previously synthesized material perfectly. The product is fairly prone to polymerization with light and heat, so great care should be exercised if absolutely pure sample is required. The product's freezing point is below –20 ˚C and it remains a liquid at most regular freezer temperatures. A 50 mg sample left in a 4 °C refrigerator over a period of two days was found to leave 10 mg of residue after distillation. The samples also turn a light brown fairly quickly, presumably from CO_2 absorption.

17. The checkers purchased potassium trimethylsilanolate, tech. ~90% from Fluka and used the chemical as received. The submitters purchased potassium trimethylsilanolate, tech. ~90% from Aldrich Chemical Company and used the chemical as received. The source of the potassium trimethylsilanolate is critical to the successful outcome of this reaction. Different product distributions were obtained depending upon the supplier. In reactions using potassium trimethylsilanolate purchased from Gelest, Inc. (two distinct lots), the reduction of the aryl bromide to the corresponding arene was observed, whereas reactions using potassium trimethylsilanolate purchased from Aldrich (three distinct lots) provided the desired vinylation product. Therefore, it is highly recommended to purchase the $KOSiMe_3$ from Aldrich Chemical Company for the vinylation of aryl bromides.

18. The checkers purchased tris(benzylideneacetone)dipalladium (0) from Strem Chemicals and used the chemical as received. The submitters purchased tris(benzylideneacetone)dipalladium (0), minimum 21.5 % Pd, from Alfa-Aesar and used the chemical as received.

19. The checkers purchased triphenylphosphine oxide (≥ 98%) from Fluka and used the chemical as received. The submitters purchased triphenylphosphine oxide (98%) from Aldrich Chemical Company and used the chemical as received.

20. The checkers purchased 4-bromobenzophenone (98%) from Aldrich Chemical Company and used the chemical as received. The submitters purchased 4-bromobenzophenone (98%) from Alfa-Aesar and used the chemical as received.

21. The checkers purchased 1,3-divinyltetramethyldisiloxane (97%) from Aldrich Chemical company and used the chemical as received. Submitters purchased 1,3-divinyltetramethyldisiloxane from Gelest and used the chemical as received

22. The checkers monitored the progress of the reaction by the disappearance of starting material on TLC (Note 10). The checkers used a

mobile phase of dichloromethane/pentane in 50:50 ratio and noted a very tight separation, with the 4-vinylbenzophenone exhibiting $R_f = 0.32$ and the 4-bromobenzophenone exhibiting $R_f = 0.44$. After 4 hours a faint spot of the 4-bromobenzophenone remained and an aliquot was removed and treated as in note 10 under identical GC/MS parameters. A trace of 4-bromobenzophenone (t_r 15.6 min) remained with a smaller amount of benzophenone (t_r 12.6 min) and mostly product so the reaction was allowed to proceed for an additional 30 min and a second aliquot was worked up. No visible change in the ratios of 4-bromobenzophenone, benzophenone, or product was observed for the second aliquot so the reaction was stopped to prevent loss from thermal polymerization. The submitters monitored the reaction as follows: A 50-µL aliquot was removed *via* syringe and quenched into 4 drops of an aqueous *N,N*-dimethyl-2-aminoethanethiol solution (10% w/w). The aliquot was extracted with 1 mL of ethyl acetate and the organic layer was passed through a pipette plug of silica gel. GC analysis: 4-vinylbenzophenone, t_R 7.16 min; 4-bromobenzophenone, 7.41 min.

23. The checkers used 100 g of silica gel loaded into a 60-mm diameter column as a pentane slurry. For the purification the submitters used 75 g of silica gel loaded as a diethyl ether slurry into a 65 mm diameter glass column.

24. The checkers dry loaded the 4-vinylbenzophenone crude as in Note 13 except using 40 g of silica gel for absorption which was loaded as in Note 13 onto a 240 gram silica column packed and prepared in a 50-mm diameter glass column. The submitters used for the purification 200 g of silica gel loaded as a hexane slurry into a 50-mm diameter glass column.

25. The 0.5 g of mixed fractions are absorbed onto 3 g of silica gel and loaded onto a 20 gram column packed as a pentane slurry on a 15 mm diameter column.

26. The product exhibited the following physical properties: mp: 47.8-48.5 °C. ^{1}H-NMR (400.1 MHz, CDCl$_3$, 298 K) δ: 5.41 (d, J = 10.8 Hz, 1 H), 5.90 (d, J = 17.6 Hz, 1 H), 6.78 (dd, J = 17.6, 10.8 Hz, 1 H), 7.47–7.52 (m, 4 H), 7.59 (tt, J = 7.5, 1.3 Hz, 1 H), 7.78-7.81 (m, 4 H). ^{13}C-NMR (100.6 MHz, CDCl$_3$, 298 K) δ: 116.6, 126.0, 128.3, 129.9, 130.5, 132.3, 136.0, 136.6, 137.7, 141.5, 196.2. IR (NaCl) 3082, 3060, 3007, 1650, 1603, 1554, 1446, 1402, 1316, 1277, 1176, 1148, 1115.7, 1073, 1027, 1000, 991, 937, 923, 857, 797, 755, 702, 597 cm^{-1}. MS (EI) *m/z*: 209.05 (*m*+1)/z (1.18%), 208.05 (*m*)/z (6.85%), 131.95 (10.22%), 130.95 (100.00%), 105.05 (3.38%), 103.00 (2.35%), 78.00 (0.65%), 77.00 (7.95%), 76.10 (0.59%), 50.95

(3.40%), 49.95 (1.21%). TLC: R_f 0.32 (SiO$_2$, pentane/DCM, 1:1). Anal. Calcd. for C$_{15}$H$_{12}$O: C, 86.51; H, 5.81; Found C, 85.93; H, 5.96. The submitters elemental analysis found C, 86.22; H, 5.85. A second run on half scale provided 2.72 g (87%) matching in excellent agreement to the material made previously.

Waste Disposal Information

All toxic materials were disposed of in accordance with " Prudent Practices in the Laboratory", National Academy Press; Washington, DC, 1995.

3. Discussion

A number of new synthetic methods to prepare styrenes have been developed that involve the installation of the vinyl group by palladium-catalyzed cross-coupling reactions. The most common organometallic donors for this process include, among others, vinyltri-*n*-butyltin,[2] a trivinylboroxane-pyridine complex,[3] substituted vinylboronic esters,[4] potassium vinyltrifluoroborate,[5] and vinyltrimethylsilane.[6]

Recent disclosures from these laboratories have described a range of cost-efficient, non-toxic, widely available polyvinylsiloxanes that can serve as highly efficient vinyl donors in the cross-coupling reaction with aryl iodides.[7] Tetrabutylammonium fluoride (TBAF) serves as an activator for these coupling reactions. Of these, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D$_4$^{V}) was chosen based upon efficiency of vinyl transfer and its low cost. The cross coupling reaction of D$_4$^{V} provides high yields for a variety of aryl iodides.

Extension of this reaction to include aryl bromides as substrates has been accomplished using D$_4$^{V} as the vinyl donor and TBAF as the most effective promoter.[8] The use of a bulky phosphine ligand, 2-(di-*tert*-butylphosphino)biphenyl,[9] was required, likely to facilitate oxidative addition of the aryl bromide onto the palladium center (which is known to be more challenging for a carbon-bromine bond, relative to a carbon-iodine bond). The reaction requires 0.5 equiv of the tetrameric D$_4$^{V}, implying that two of the four vinyl groups on the donor are effectively transferred. The reactions occur under mild conditions (50 °C) and generally take less than 12 hours. The reaction has high tolerance for a range of functional groups

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and substitution patterns, as shown in Scheme 1. The presence of heteroatoms or sterically bulky substituents does not impact the yield significantly, although reaction times are often longer for more hindered substrates.

Scheme 1
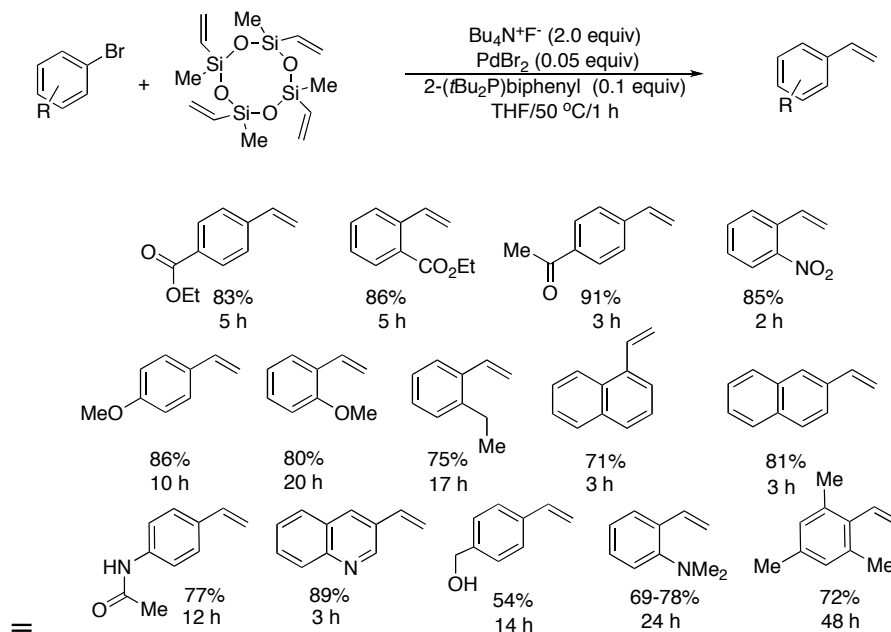
A complementary method for the vinylation of aryl halides using organosilane reagents has been developed which does not require fluoride activation.[10] In this case, two equivalents of potassium vinyldimethylsilanolate are generated in situ by a silanolate exchange between potassium trimethylsilanolate and divinyltetramethyldisiloxane (DVDS). This exchange has been shown to occur readily in both THF and DMF. The vinyldimethylsilanolate generated reacts with aryl iodides and bromides (using a palladium catalyst) to afford the corresponding styrenes in moderate to excellent yield. The reactions with aryl iodides occur under very mild conditions (room temperature, in 30 min to 12 h) and employ Pd(dba)$_2$ as catalyst and DMF as solvent (Scheme 2). These conditions often lead to exothermic reactions.

Scheme 2
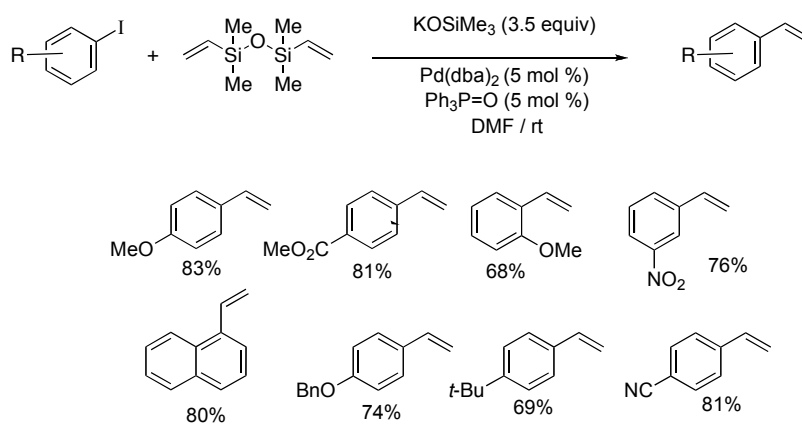
The vinylations using aryl bromides are performed using either of two protocols. The first employs potassium tri*ethyl*silanolate and DVDS, and requires a bulky phosphine ligand, 2-(di-*tert*-butylphosphino)biphenyl, and allylpalladium chloride dimer as the catalyst in DMF. These reactions occur at lower temperatures (ambient to 40 °C) and have a broad substrate scope (Scheme 3).

Scheme 3
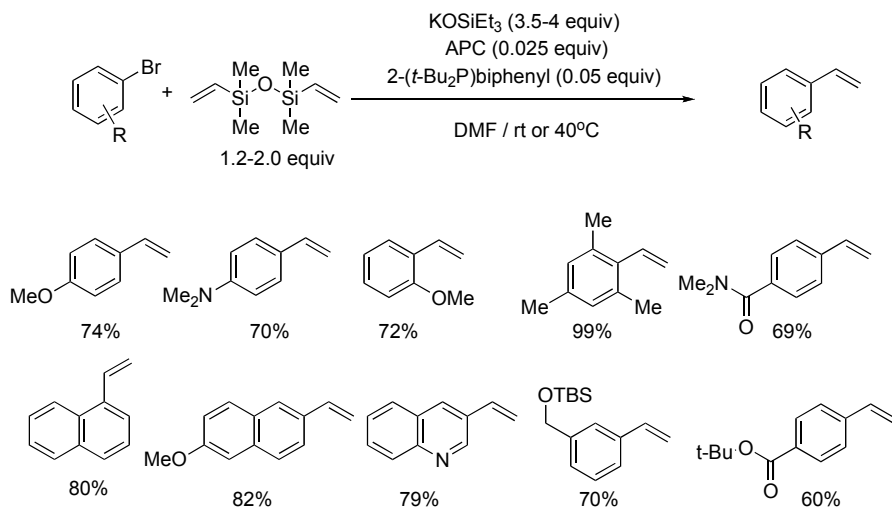
The second protocol employs the commercially available potassium tri*methyl*silanolate and DVDS as the potassium vinyldimethylsilanolate precursors. These reactions are performed using Pd(dba)$_2$ or Pd$_2$(dba)$_3$ as the palladium source, triphenylphosphine oxide as the ligand in THF and require elevated temperatures (67 °C). Successful couplings using this protocol are shown in Scheme 4.

Scheme 4
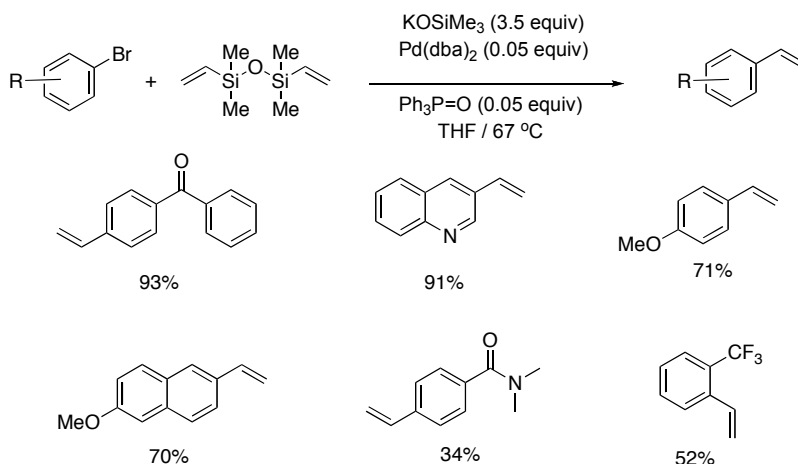
These complementary protocols (fluoride and non-fluoride activation) provide a set of practical, mild, cost-efficient, and high-yielding alternatives to current vinylation methods.

1. Department of Chemistry, Roger Adams Laboratory, University of Illinois at Urbana-Champaign. Urbana, IL, 61801, email: denmark@scs.uiuc.edu.
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4-Vinylbenzophenone: Methanone, (4-ethenylphenyl)phenyl-; **(**3139-85-3)

3-Vinylquinoline: Quinoline, 3-ethenyl-; **(**67752-31-2)

1,3,5,7-Tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane; (2554-06-5)

Palladium tris(dibenzylideneacetone); (48243-18-1)

2-(Di-*tert*-butylphosphino)biphenyl: Phosphine, [1,1'-biphenyl]-2-ylbis(1,1-dimethylethyl)-; (224311-51-7)
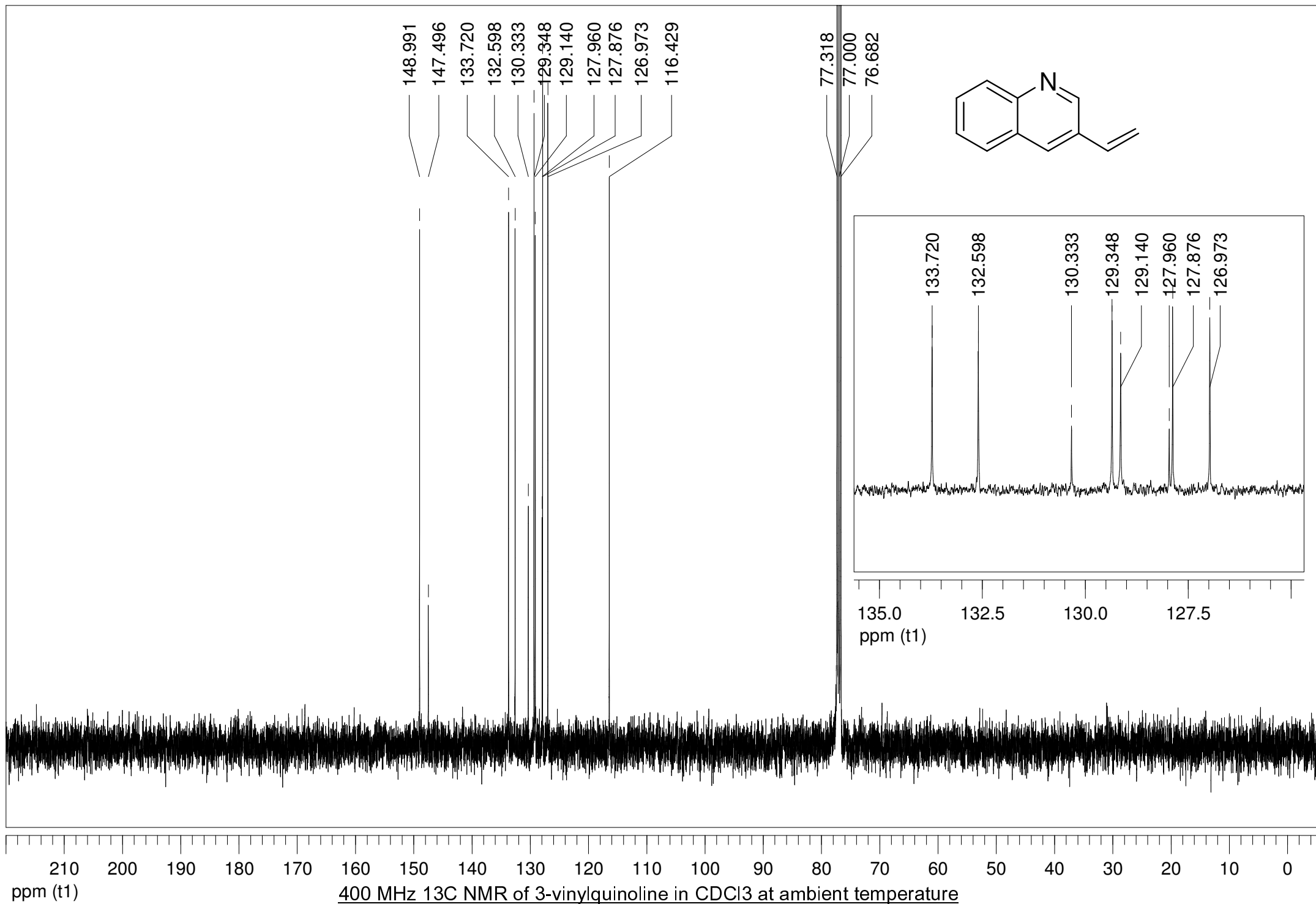
Scott E. Denmark was born in Lynbrook, New York in 1953. He obtained an S.B. degree from MIT in 1975 and his D.Sc.Tech. (with Albert Eschenmoser) from the ETH Zürich in 1980. That same year he began his career at the University of Illinois. He was promoted to associate professor in 1986, to full professor in 1987 and since 1991 he has been the Reynold C. Fuson Professor of Chemistry. He is currently on the Board of Editors of *Organic Syntheses* where he holds the modern record for most procedures checked. As of 2008 he became the Editor in Chief of *Organic Reactions*. He served for six years as an Associate Editor of *Organic Letters* and is co-Editor of *Topics in Stereochemistry*. He counts among his honors the ACS Award for Creative Work in Synthetic Organic Chemistry (2003), the Yamada-Koga Prize (2006), election as a Fellow of the Royal Society (2006), the Prelog Medal (2007) and a crushing victory from pole in the GT-3R class at Road America (2007).
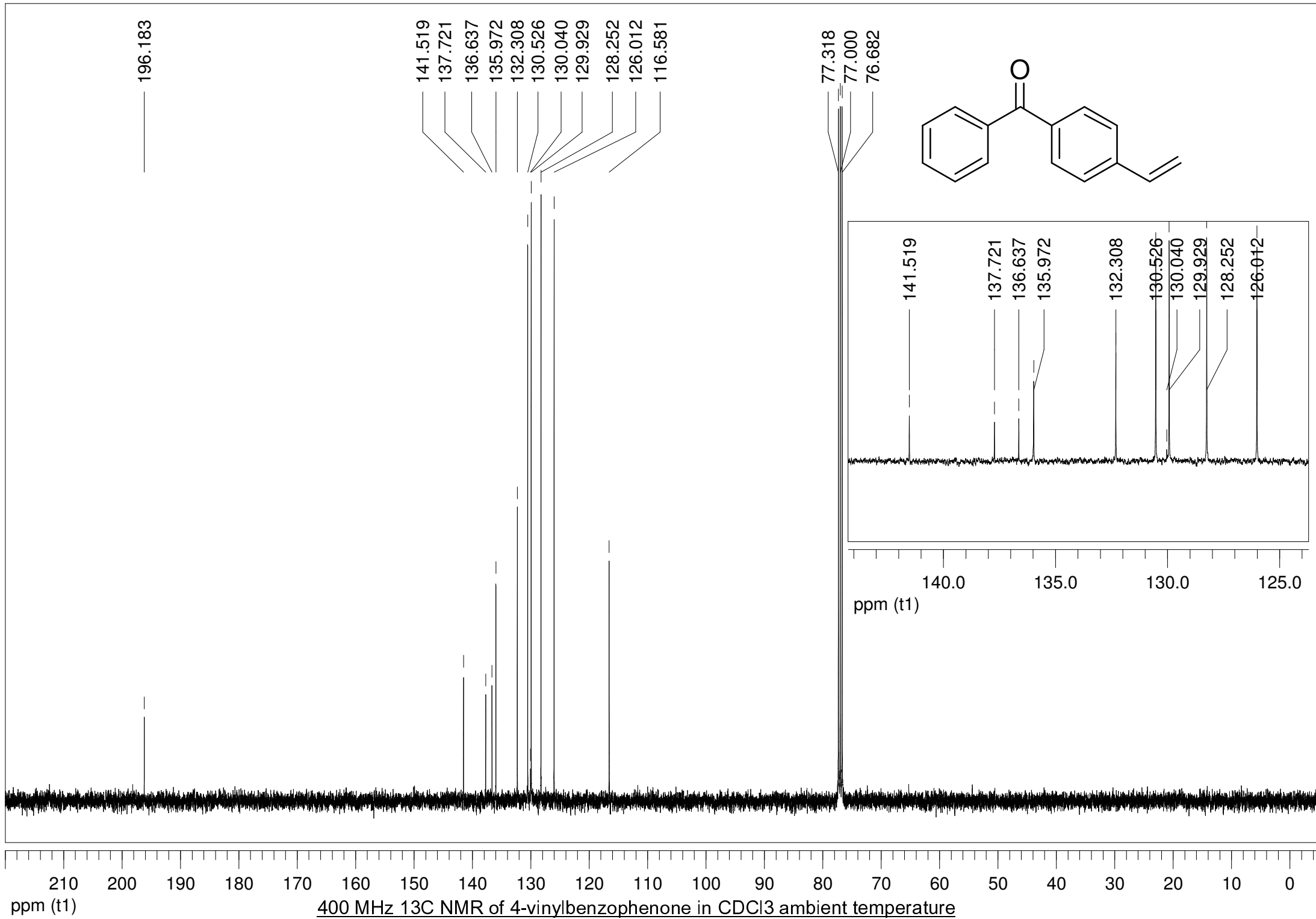
Christopher Butler received a bachelor's degree in Chemistry from Illinois Wesleyan University in 2000. He then worked for three years in drug discovery at Johnson & Johnson Pharmaceutical Research & Development in San Diego CA, before beginning graduate school at the University of Illinois working with Professor Scott E. Denmark in 2003. His thesis work focuses on the development of palladium-catalyzed vinylation of aryl and heteroaryl bromides using inexpensive polyvinylsiloxanes.
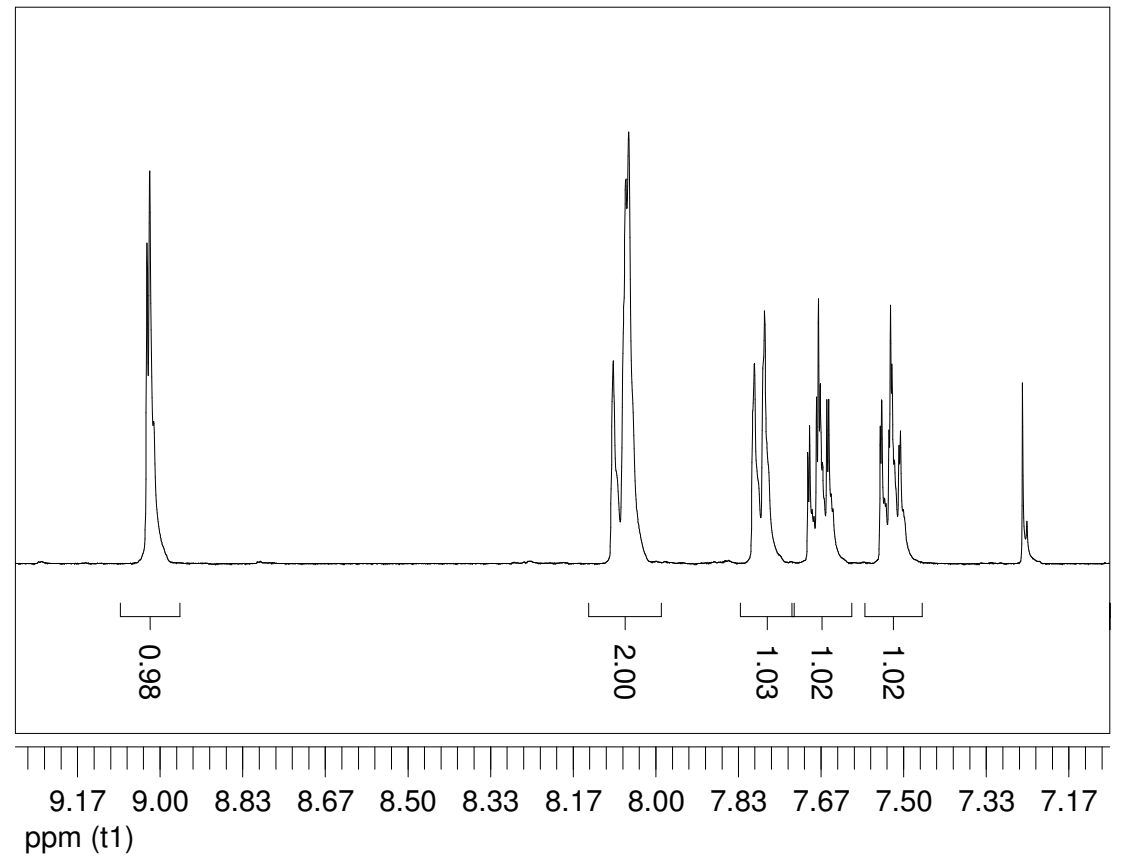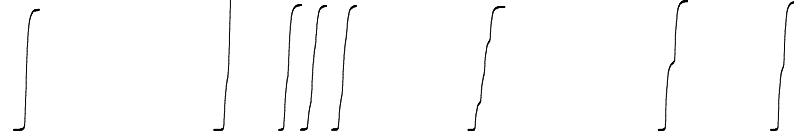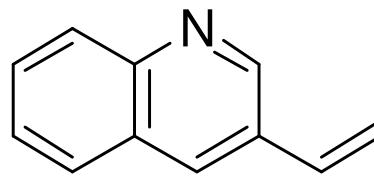
David H. Woodmansee was born in San Diego, California in 1973. He received his bachelors in 1997 and masters in 2000 under the tutelage of Patrick J. Walsh. After working a few years in the San Diego biotech industry as a medicinal chemist including a three-year stay at the Genomics Institute for the Novartis Research Foundation David returned to graduate school and is currently working in the group of Professor Andreas Pfaltz. David's thesis topic is in the area of catalyst design and the elucidation of structure activity relationships in asymmetric catalysis.

400 MHz 13C NMR of 3-vinylquinoline in CDCl3 at ambient temperature

Peak labels (main spectrum): 148.991, 147.496, 133.720, 132.598, 130.333, 129.348, 129.140, 127.960, 127.876, 126.973, 116.429, 77.318, 77.000, 76.682

Inset peak labels: 133.720, 132.598, 130.333, 129.348, 129.140, 127.960, 127.876, 126.973

ppm (t1)

400 MHz 13C NMR of 4-vinylbenzophenone in CDCl3 ambient temperature

196.183

141.519
137.721
136.637
135.972
132.308
130.526
130.040
129.929
128.252
126.012
116.581

77.318
77.000
76.682

ppm (t1)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

400 MHz 1H NMR of 3-vinylquinoline in CDCl3 at ambient temperature

ppm (t1)

9.17 9.00 8.83 8.67 8.50 8.33 8.17 8.00 7.83 7.67 7.50 7.33 7.17
ppm (t1)

0.98   2.00   1.03 1.02 1.02

0.98   2.00 1.03 1.02 1.02   1.01   1.06   1.05

9.0   8.0   7.0   6.0   5.0   4.0   3.0   2.0   1.0
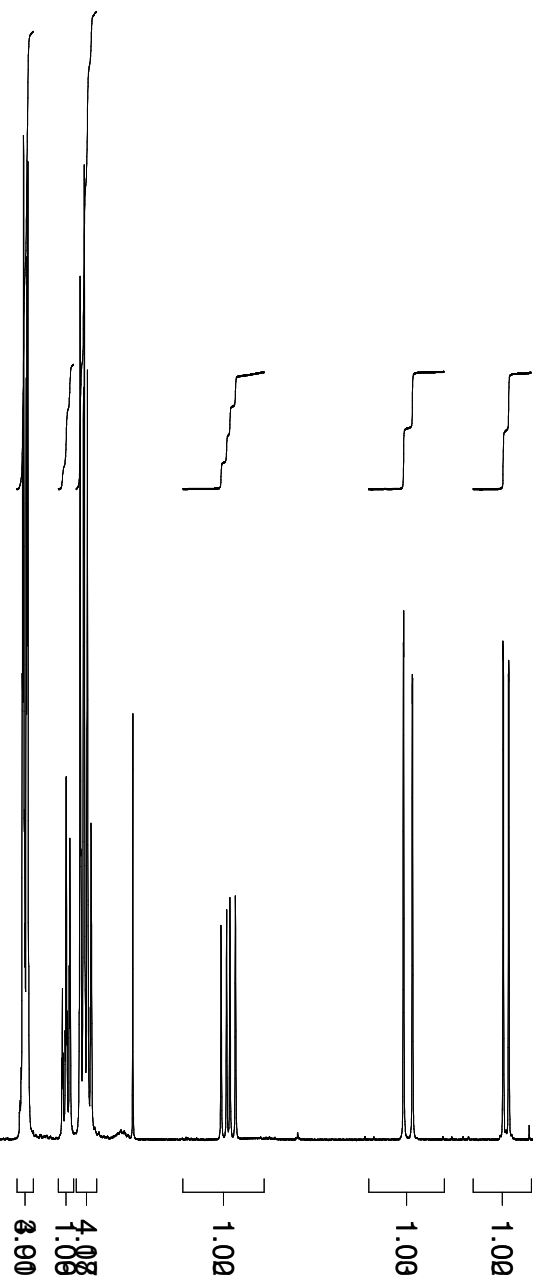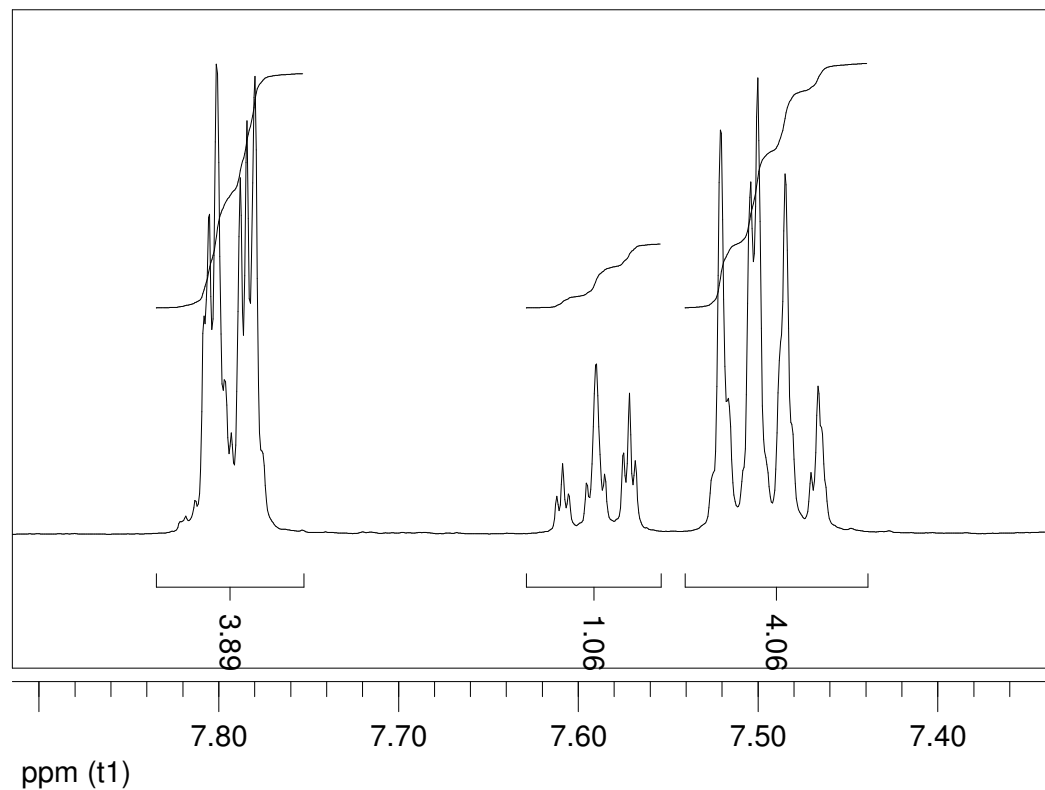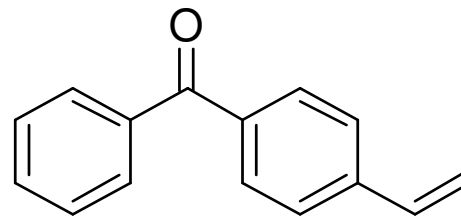
400 MHz 1H NMR of 4-vinylbenzophenone in CDCl3 ambient temperature

ppm (t1)

7.80   7.70   7.60   7.50   7.40

ppm (t1)

3.89   1.06   4.06

9.0   8.0   7.0   6.0   5.0   4.0   3.0   2.0   1.0   0.0

ppm (t1)

3.90   4.08   1.02   1.00   1.02