Organic Syntheses

Iridium-Catalyzed Enantioselective Allylic Vinylation with Potassium Alkenyltrifluoroborates

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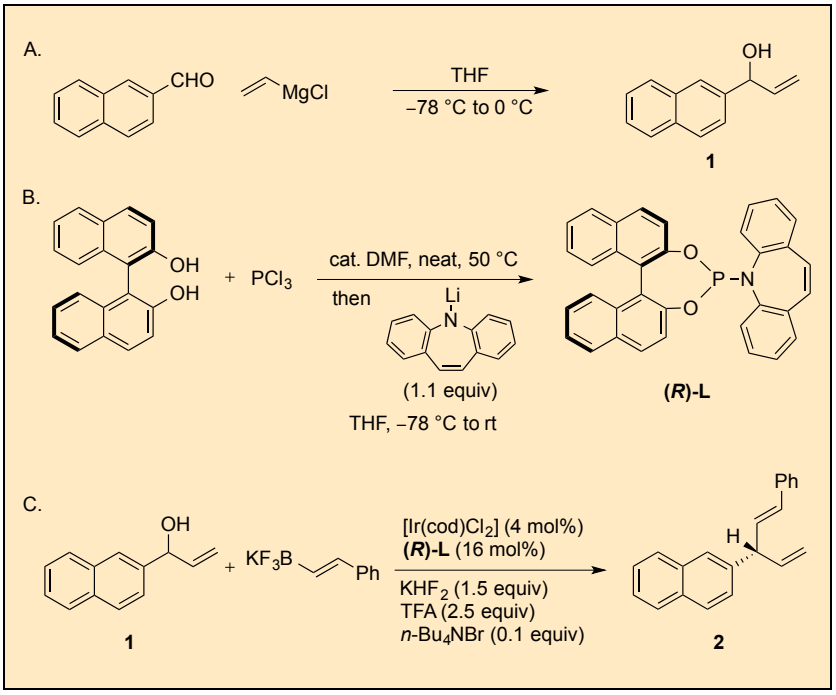


Procedure

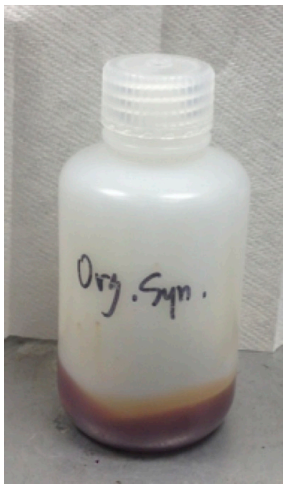
A. *1-(Naphthalen-2-yl)prop-2-en-1-ol* (**1**). An oven-dried 250 mL round-bottomed flask, fitted with a rubber septum, is charged with a 2.5 cm Teflon-coated magnetic oval stir bar and 2-naphthaldehyde (4.69 g,

30.0 mmol, 1.0 equiv) (Note 1). The flask is flushed with nitrogen via a nitrogen line inlet and charged with anhydrous THF (60 mL) via a 60 mL syringe (Note 2). The stirred homogeneous solution (Note 3) is cooled in a dry ice-acetone bath (−78 °C bath temp), and vinylmagnesium chloride solution (20.6 mL, 33.0 mmol, 1.1 equiv) is added dropwise over 20 min via a syringe. The resulting clear yellow solution is stirred at −78 °C for 1 h and then at 0 °C in an ice bath for 30 min (Note 4). The reaction mixture is quenched with saturated aqueous NH_4Cl solution (30 mL) and diluted with H_2O (30 mL). After being warmed up to ambient temperature, the mixture is transferred to a 250 mL separatory funnel. Additional diethyl ether (20 mL) is used to assist transfer. The aqueous layer is separated and further extracted with diethyl ether (2 x 50 mL). The combined organic layers are washed with saturated aqueous NaCl solution (50 mL), dried over sodium sulfate (20 g), filtered through a 150 mL coarse porosity sintered glass funnel, and concentrated using a rotary evaporator (25 °C, 25 mmHg) to afford a yellow oil (Note 5). This crude product is purified by flash chromatography on silica gel to afford **1** (5.23–5.35 g, 95–97%) as a colorless oil (Note 6).

B. *(R)-(−)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a′]dinaphthalen-4-yl)-dibenzo[b,f]-azepine* (**(*R*)-L**). An oven-dried 100 mL Schlenk flask, fitted with a rubber septum, is charged with a 2.5 cm Teflon-coated magnetic oval stir bar and (*R*)-(+)-1,1□-bi(2-naphthol) (2.29 g, 8.0 mmol, 1.0 equiv) (Note 7). The side arm of the flask, fitted with a glass stopcock, is connected to a vacuum/N_2 line. The flask is evacuated and refilled with nitrogen 3 times. Phosphorus trichloride (10.5 mL, 16.5 g, 15 equiv) and anhydrous *N*,*N*-dimethylformamide (19 μL, 18 mg, 0.24 mmol, 0.03 equiv) are added by syringes through the septum. The reaction mixture is stirred (Note 8) at 50 °C in an oil bath for 30 min, during which time it becomes a colorless homogeneous solution. Excess phosphorus trichloride is removed via vacuum distillation (Notes 9 and 10) and azeotropic removal with toluene (2 x 3 mL) under high vacuum (see photograph) (Notes 11 and 12) to afford the phosphochloridite as an oily foam. A separate oven-dried 250 mL round-bottomed flask is charged with a 2.5 cm Teflon-coated magnetic oval stir bar and 5*H*-dibenz[*b*,*f*]azepine (1.70 g, 8.80 mmol, 1.1 equiv). The flask is fitted with a rubber septum with a nitrogen line inlet and flushed with nitrogen. Anhydrous THF (47 mL) is added by syringe, and the stirred orange solution is cooled in a dry ice-acetone bath (−78 °C bath temp) (Note 13). *n*-Butyllithium (5.50 mL, 8.80 mmol, 1.1 equiv) is then added dropwise

over 10 min with a syringe, and the resulting dark blue solution is stirred at −78 °C for 1 h. The phosphochloridite prepared as above is dissolved in anhydrous THF (37 mL) and added to the deprotonated 5*H*-dibenz[*b*,*f*]azepine solution at −78 °C dropwise via a cannula over 20 min. Additional anhydrous THF (10 mL) is used to assist transfer. The dark blue solution is stirred for 12 h while being gradually warmed to ambient temperature (Note 14). Silica gel (20 g) is added to the orange reaction mixture, and the resulting slurry is carefully concentrated by rotary evaporation (35 °C, 25 mmHg). Flash chromatography on silica gel yields **(*R*)-L** (2.96–3.07 g, 73–75%) as a white solid (Note 15).

C. *(S,E)-2-(1-Phenylpenta-1,4-dien-3-yl)naphthalene* (**2**). A screw cap 100 mL cylindrical polyethylene bottle (diameter: 4.5 cm, height: 9.5 cm) with a 4 cm Teflon-coated magnetic cylindrical stir bar is charged with bis(1,5-cyclooctadiene)diiridium dichloride (0.725 g, 1.08 mmol, 0.04 equiv), **(*R*)-L** (2.19 g, 4.32 mmol, 0.16 equiv) and 1,4-dioxane (34 mL) (Note 16). The resulting dark brown solution (see photograph) is stirred for 15 min (Note 17). 1-(Naphthalen-2-yl)prop-2-en-1-ol (**1**) (4.97 g, 27.0 mmol, 1.0 equiv), potassium *trans*-styryltrifluoroborate (8.51 g, 40.5 mmol, 1.5 equiv), tetrabutylammonium bromide (0.87 g, 2.7 mmol, 0.1 equiv) and potassium hydrogen difluoride (3.16 g, 40.5 mmol, 1.5 equiv) are sequentially added,



and additional 1,4-dioxane (2.0 mL) is added to rinse the reaction vessel wall. To the resulting stirred dark-yellow heterogeneous mixture is added trifluoroacetic acid (5.17 mL, 7.70 g, 67.5 mmol, 2.5 equiv) dropwise. The red heterogeneous mixture is vigorously stirred for 6 h, during which time it gradually turns light yellow (Note 18). Upon completion of the reaction, excess trifluoroacetic acid is quenched by addition of triethylamine (5 mL), and the heterogeneous mixture is filtered through a short silica pad (Note 19). The filtrate is concentrated by rotary evaporation (35 °C, 25 mmHg). The concentrate is purified by flash chromatography on silica gel to afford **2** (5.74 g, 79%) as a white solid (Notes 20 and 21).

Notes

1. The following reagents in this section were purchased from commercial sources and used without further purification: 2-naphthaldehyde (98%, Aldrich) and vinylmagnesium chloride solution (1.6 M in THF, Aldrich).
2. Anhydrous THF in all sections was obtained by passage over activated alumina under an atmosphere of argon (H_2O content <30 ppm, *Karl Fischer* titration).
3. The mixture is stirred at 900 rpm throughout the reaction.

4. The reaction is monitored by TLC on Merck silica gel 60 F_{254} TLC glass plates and visualized with UV light and $KMnO_4$ staining solution. R_f (product): 0.23 (9:1 hexanes:EtOAc)
5. Additional diethyl ether (2 x 10 mL) is used during filtration to assist transfer.
6. The crude product is loaded onto a column (diameter: 5 cm, height: 16 cm) packed with silica gel (150 g) slurry in 9:1 hexanes:EtOAc. After 500 mL of initial elution, 100 mL fractions are collected. The desired product is obtained in fractions 3–12, which are concentrated by rotary evaporation (25 °C, 25 mmHg). The product has been characterized as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.04 (br s, 1 H), 5.25 (dt, *J* = 10.3, 1.4 Hz, 1 H), 5.35 (d, *J* = 6.0 Hz, 1 H), 5.41 (dt, *J* = 17.1, 1.5 Hz, 1 H), 6.13 (ddd, *J* = 17.1, 10.3, 6.0 Hz, 1 H), 7.47 – 7.52 (m, 3 H), 7.83 – 7.87 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 75.5, 115.5, 124.6, 125.0, 126.1, 126.3, 127.8, 128.1, 128.4, 133.1, 133.4, 140.0, 140.2; IR (neat): 3358 (br), 3055, 1633, 1601, 1508, 1408, 1361, 1269, 1124, 1018, 988, 926, 819, 745 cm^{-1}; HRMS (EI): *m*/*z* calcd for $C_{13}H_{12}O$ $[M]^+$ 184.0888, found 184.0860; Anal. calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.56; found: C, 84.31, H, 6.57.
7. The following reagents in this section were purchased from commercial sources and used without further purification: (*R*)-(+)-1,1′-bi(2-naphthol) (98%, Combi-Blocks), phosphorus trichloride (99%, Sigma-Aldrich), anhydrous *N*,*N*-dimethylformamide (99.8%, Sigma-Aldrich), 5*H*-dibenz[*b*,*f*]azepine (97%, Aldrich) and *n*-butyllithium (1.6 M in hexane, Aldrich).
8. The mixture is stirred at 300 rpm throughout the reaction.
9. The reaction mixture is maintained at 50 °C throughout distillation and subsequent azeotropic removal of residual phosphorus trichloride with toluene.
10. The Schlenk flask is uncapped and quickly connected to a distillation apparatus (oven-dried and N_2 flushed). The receiving flask is cooled to −78 °C in a dry ice-acetone bath, and the vacuum line from the distillation head is connected to a liquid nitrogen cold trap. Upon reaching 375 mmHg (membrane pump), the pressure of the distillation apparatus is lowered carefully (50 mmHg per minute). Vigorous stirring (800 rpm) is maintained to keep the solution from rapid foaming. Upon reaching 150 mmHg, the distillation is maintained for 30 min.
11. After distillation, the system is refilled with N_2, and the distillation apparatus is quickly exchanged with a three-way stopcock and

connected to high vacuum line (0.9 mmHg) with liquid nitrogen cold trap. Toluene (3 mL) (≥99.7%, Fluka, ACS reagent) is added into the flask with a syringe through the three-way stopcock, followed by swirling of the mixture to completely dissolve the oily foam. Using the three-way stopcock and vigorous stirring (800 rpm), vacuum is applied carefully to avoid rapid foaming. After complete removal of toluene, another 3 mL of toluene is used to repeat the process. After the second azeotropic distillation, the vacuum is further maintained for 30 min.

12. Care should be taken for thorough removal of excess phosphorus trichloride and to avoid exposure of the air sensitive phosphochloridite to ambient atmosphere.
13. The mixture is stirred at 800 rpm throughout the reaction.
14. The reaction flask is kept in a dry ice-acetone bath that is gradually warmed to ambient temperature overnight.
15. Silica gel adsorbed with the crude product is dry-loaded onto a column (diameter: 5.5 cm, height: 22.5 cm) packed with silica gel (200 g) slurry in 2:1 hexanes:toluene (R_f(product): 0.31; visualized with UV light and $KMnO_4$ staining solution). After 500 mL of initial elution, 100 mL fractions are collected. The desired product is obtained in fractions 2–11, which are concentrated by rotary evaporation (35 °C, 25 mmHg). The purified product is stored under an inert atmosphere in the dark for long-term storage. The product has been characterized as follows: ^{1}H NMR (400 MHz, $CDCl_3$ (filtered through basic alumina)) δ: 6.58 (td, *J* = 7.5, 1.4 Hz, 1 H), 6.91 (d, *J* = 8.7 Hz, 1 H), 6.94 – 7.05 (m, 3 H), 7.12 – 7.20 (m, 1 H), 7.21 – 7.36 (m, 9 H), 7.38 – 7.46 (m, 2 H), 7.48 (d, *J* = 8.8 Hz, 1 H), 7.67 (d, *J* = 8.7 Hz, 1 H), 7.80 (dd, *J* = 8.2, 1.2 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 8.03 (d, *J* = 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 121.2 (d, *J* = 2.8 Hz), 121.6, 122.3 (d, *J* = 2.0 Hz), 124.4 (d, *J* = 5.3 Hz), 124.4, 124.9, 125.8, 126.2, 126.3, 126.8 (d, *J* = 1.4 Hz), 126.9, 127.2, 128.0, 128.4, 128.5, 128.7, 129.0, 129.10, 129.12, 129.2 (d, *J* = 2.0 Hz), 129.3, 130.3, 130.5, 131.5, 131.6, 131.7, 132.3 (d, *J* = 1.5 Hz), 133.0 (d, *J* = 1.6 Hz), 135.3, 136.6 (d, *J* = 3.6 Hz), 142.6, 143.0 (d, *J* = 24.0 Hz), 148.8 (d, *J* = 1.2 Hz), 150.0 (d, *J* = 8.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 137.85; IR (neat): 3054, 3020, 1619, 1591, 1485, 1463, 1327, 1283, 1234, 1207, 1155, 1107, 1070, 982, 949, 866, 820, 802, 750 cm^{-1}; HRMS (ESI+): *m*/*z* calcd for $C_{34}H_{23}NO_2P$ $[M+H]^+$ 508.1461, found 508.1464; $[\alpha]^{20}_D$ = –325.4 (c = 1.04, $CHCl_3$); mp 249–250 °C. HPLC: >99% purity, t_R = 5.78 min (column: Eclipse Plus C8 2.1 x 50 mm, 1.8 micron; method: linear gradient of A (H_2O with 0.025% AcOH) and B (MeCN), flow rate of 1.0 mL/min,

254 nm detection, 25 °C column temperature, linear gradient: 40–95% B in 7 min).

16. The following reagents in this section were purchased from commercial sources and used without further purification: bis(1,5-cyclooctadiene)diiridium dichloride (97%, Combi-Blocks), potassium *trans*-styryltrifluoroborate (Sigma-Aldrich, or synthesized by the known procedure: Molander, G. A. *et al*, *J. Org. Chem*. **2002**, *67*, 8424.), tetrabutylammonium bromide (≥99%, Sigma-Aldrich), potassium hydrogen difluoride (≥99%, Sigma-Aldrich) and trifluoroacetic acid (≥99%, Sigma-Aldrich). 1,4-Dioxane (≥99.5%, Acros) was used as received.
17. The mixture is stirred at 400 rpm throughout the reaction. The reaction vessel is capped, and the reaction is performed under ambient atmosphere.
18. The reaction is monitored by TLC and visualized with UV light and $KMnO_4$ staining solution. R_f(SM): 0.42 (4:1 hexanes:EtOAc); R_f(product): 0.32 (19:1 hexane:CH_2Cl_2)
19. The reaction mixture is loaded onto a short silica pad column (diameter: 6.5 cm, height: 4.5 cm) packed with silica gel (70 g) slurry in hexanes. A mixture of 9:1 hexanes:EtOAc (2 L) is used as eluent. The filtrate is concentrated by rotary evaporation (25 °C, 25 mmHg) to yield a dark red oil.
20. The crude product is loaded onto a column (diameter: 5.5 cm, height: 22 cm) packed with silica gel (200 g) slurry in 19:1 hexanes:CH_2Cl_2. After 500 mL of initial elution, 50 mL fractions are collected. The desired product is obtained in fractions 6–41, which are concentrated by rotary evaporation (25 °C, 25 mmHg). The regioisomeric ratio is >50:1, determined by ^{1}H NMR. The product has been characterized as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.40 – 4.44 (m, 1 H), 5.21 (dt, *J* = 17.2, 1.5 Hz, 1 H), 5.26 (dt, *J* = 10.2, 1.4 Hz, 1 H), 6.22 (ddd, *J* = 17.0, 10.2, 6.7 Hz, 1 H), 6.44 – 6.57 (m, 2 H), 7.20 – 7.27 (m, 1 H), 7.28 – 7.35 (m, 2 H), 7.37 – 7.51 (m, 5 H), 7.72 (d, *J* = 1.7 Hz, 1 H), 7.78 – 7.87 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 52.5, 116.1, 125.7, 126.2, 126.42, 126.44, 127.0, 127.4, 127.8, 127.9, 128.3, 128.7, 131.1, 131.8, 132.5, 133.8, 137.5, 140.1, 140.2; IR (neat): 3055, 3023, 1631, 1598, 1494, 1446, 1270, 995, 968, 914, 856, 817, 743 cm^{-1}; HRMS (EI): *m*/*z* calcd. for $C_{21}H_{18}$ $[M]^+$ 270.1408, found 270.1417; $[\alpha]^{24}_D$ = –1.6 (c = 1.1, $CHCl_3$); mp 74–75 °C; SFC: Daicel Chiralcel OJ-H, 10% MeOH, 2.5 mL/min, 40 °C, 254 nm; >99% ee (t_R (minor) = 23.5 min, t_R (major) = 25.1 min). HPLC: >99%

purity, t_R = 7.41 min (column: Eclipse Plus C8 2.1 x 50 mm, 1.8 micron; method: linear gradient of A (H_2O with 0.025% AcOH) and B (MeCN), flow rate of 1.0 mL/min, 254 nm detection, 25 °C column temperature, linear gradient: 20–95% B in 10 min).

21. The reaction was also checked with half scale (13.5 mmol), and 2.44 g (67% yield) of (*S*,*E*)-2-(1-phenylpenta-1,4-dien-3-yl)naphthalene) was obtained with >99% ee.

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Discussion

Transition metal-catalyzed asymmetric allylic substitution is one of the most powerful methods for enantioselective formation of carbon–heteroatom and carbon–carbon bonds.[2] Despite significant advances in this field, there are only a limited number of methods that offer high stereoselectivity and allow direct substitution of allylic alcohols without prior activation.[3]

Iridium-catalyzed allylic vinylation described above affords highly enantioenriched 1,4-dienes directly from allylic alcohols and potassium alkenyltrifluoroborates.[4] The reaction displays high regioselectivity under conditions that circumvent hazardous handling of hydrofluoric acid.[5] Furthermore, this catalytic enantioselective transformation can be conveniently performed without exclusion of air or moisture, using technical grade solvents. Alternatively, similar structural motifs can be accessed by Cu-catalyzed processes for allylic substitution of allylic phosphates with vinylaluminum and vinylboronic acid ester reagents, reported by Hoveyda and Hayashi, respectively.[6]

The described method is applicable to a range of aryl and heteroaryl allylic alcohols. Potassium alkenyltrifluoroborates as well as potassium alkynyltrifluoroborates of various substitution patterns can be successfully used under the described reaction conditions.[4,5]

References

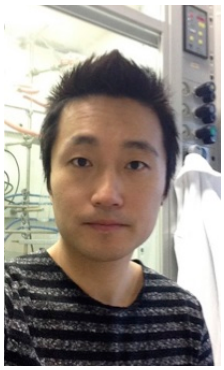
1. Laboratorium für Organische Chemie, Eidgenössische Technische Hochschule Zürich, HCI H335, Wolfgang-Pauli-Strasse 10, CH-8093, Zürich (Switzerland). E-mail: carreira@org.chem.ethz.ch. We are grateful to the ETH Zürich and the Swiss National Science Foundation for financial support.
2. "Transition Metal Catalyzed Enantioselective Allylic Substitution in Organic Synthesis": *Topics in Organometallic Chemistry*, *Vol. 38* (Ed.: U. Kazmaier), Springer, Heidelberg, **2012**.
3. Sundararaju, B.; Achard, M.; Bruneau, C. *Chem. Soc. Rev.* **2012**, *41*, 4467–4483 and references therein.
4. Hamilton, J. Y.; Sarlah, D.; Carreira, E. M. *J. Am. Chem. Soc.* **2013**, *135*, 994–997.

5. Hamilton, J. Y.; Sarlah, D.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2013**, *52*, 7532–7535.
6. (a) Akiyama, K.; Gao, F.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 419–423. (b) Gao, F.; McGrath, K. P.; Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 14315–14320. (c) Gao, F.; Carr, J. L.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2012**, *51*, 6613–6617. (d) Shintani, R.; Takatsu, K.; Takeda, M.; Hayashi, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 8656–8659.

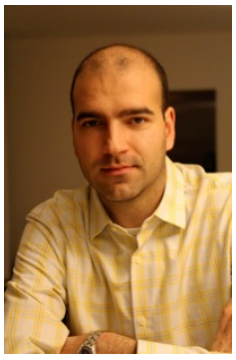
Appendix
Chemical Abstracts Nomenclature (Registry Number)

1-(Naphthalen-2-yl)prop-2-en-1-ol: 2-Naphthalenemethanol, α-ethenyl-; (76635-88-6)
(*R*)-(−)-(3,5-Dioxa-4-phospha-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)-dibenzo[b,f]-azepine (**(*R*)-L**): 5*H*-Dibenz[*b*,*f*]azepine, 5-(11b*R*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl-; (1265884-98-7)
(*S*,*E*)-2-(1-Phenylpenta-1,4-dien-3-yl)naphthalene: Naphthalene, 2-[(1*S*,2*E*)-1-ethenyl-3-phenyl-2-propen-1-yl]-;
2-Naphthaldehyde: 2-Naphthalenecarboxaldehyde; (66-99-9)
Vinylmagnesium chloride: Magnesium, chloroethenyl-; (3536-96-7)
(*R*)-(+)-1,1'-Bi(2-naphthol): [1,1'-Binaphthalene]-2,2'-diol, (1*R*)-; (18531-94-7)
Phosphorous trichloride; (7719-12-2)
5*H*-Dibenz[*b*,*f*]azepine; (256-96-2)
n-Butyllithium: Lithium, butyl-; (109-72-8)
Bis(1,5-cyclooctadiene)diiridium dichloride: Iridium, di-μ-chlorobis[(1,2,5,6-η)-1,5-cyclooctadiene]di-; (12112-67-3)
Potassium *trans*-styryltrifluoroborate: Borate(1-), trifluoro[(1*E*)-2-phenylethenyl]-, potassium (1:1), (*T*-4)-; (201852-49-5)
Tetrabutylammonium bromide: 1-Butanaminium, *N*,*N*,*N*-tributyl-, bromide (1:1); (1643-19-2)
Potassium hydrogen difluoride: Potassium fluoride ($K(HF_2)$); (7789-29-9)
Trifluoroacetic acid: Acetic acid, 2,2,2-trifluoro-; (76-05-1)

Prof. Erick M. Carreira obtained a B.S. degree from the University of Illinois at Urbana-Champaign (1984) and a Ph.D. degree from Harvard University (1990). After carrying out postdoctoral work at the California Institute of Technology through late 1992, he joined the faculty at the same institution as an assistant professor of chemistry and was subsequently promoted to the rank of full professor. Since September 1998, he has been professor of chemistry at ETH Zürich. His research program focuses on asymmetric synthesis of complex natural products, the development of catalytic along with stoichiometric reactions for asymmetric stereocontrol, chemical biology, and medicinal chemistry.



James Y. Hamilton was born in South Korea. He received his Bachelor's degree in chemistry and biology from the University of Wyoming (2006) and Master's degree from the University of California, Berkeley (2008) under the supervision of Prof. Dirk Trauner. Since May 2011, he has been a doctoral student in the group of Prof. Erick M. Carreira, working on design and development of transition metal-catalyzed asymmetric reactions.



David Sarlah was born and raised in Slovenia, where he obtained his Bachelor's Degree in Chemistry (University of Ljubljana). He obtained his Ph.D. in chemistry in 2011 for research conducted under Professor K. C. Nicolaou involving the total synthesis of complex natural products. In the fall of 2011, he joined Professor Erick M. Carreira's group as a postdoctoral researcher where he is currently developing new stereoselective methods involving allylic substitution. His research interests encompass chemical synthesis, reaction design and their application to complex natural product synthesis and chemical biology.

Wen-Bo Liu was born in China and he received his Bachelor's Degree in Chemistry from the Nankai University in 2006. He obtained his Ph.D. in organic chemistry (2011) from the Shanghai Institute of Organic Chemistry (SIOC) under the supervision of Professor Li-Xin Dai and Professor Shu-Li You. Then He joined the Professor Brian M. Stoltz laboratory at Caltech as a postdoctoral scholar, working on asymmetric catalysis and sustainable chemistry.

Seo-Jung Han graduated with a B.S. in chemistry from Sogang University in 2008. She received her M.S. degree in 2010 from Sogang University under the direction of Professor Duck-Hyung Lee. She then moved to the California Institute of Technology and began her doctoral studies under the guidance of Professor Brian M. Stoltz. Her graduate research focuses on total synthesis of complex polycyclic natural products.

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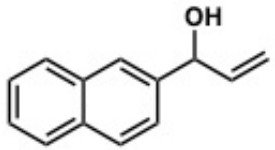
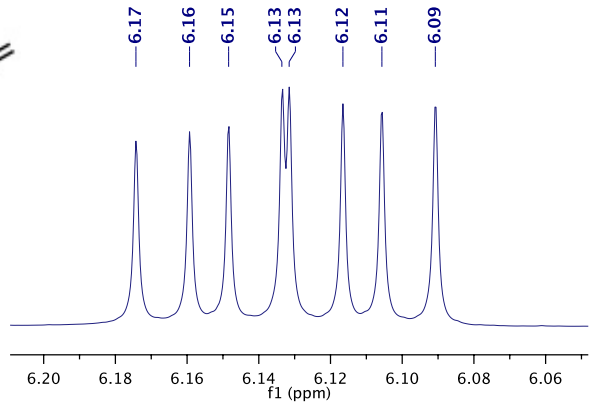
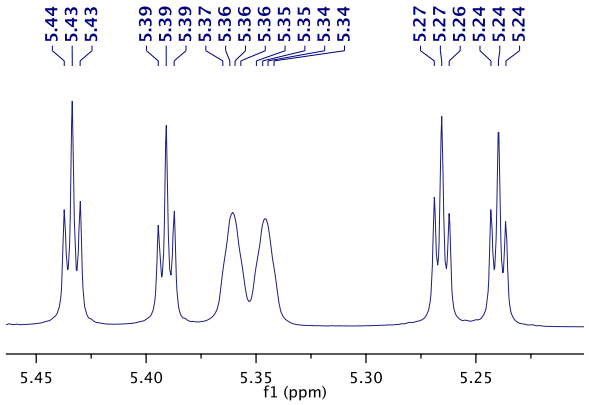
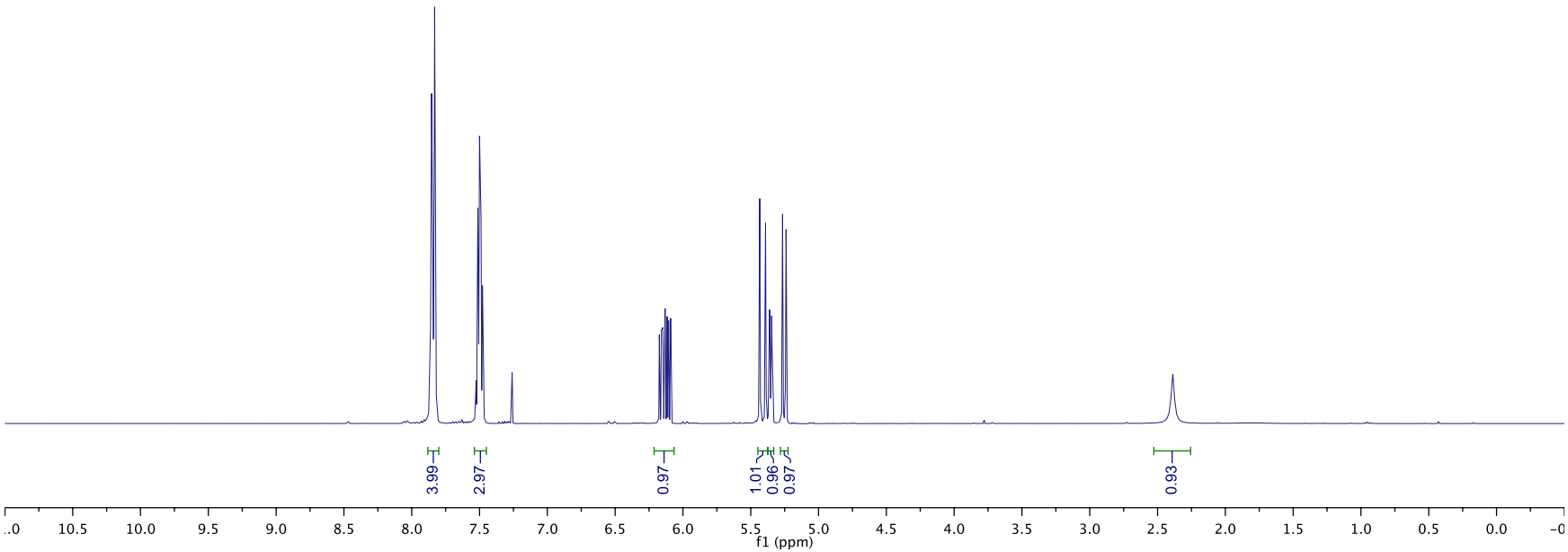




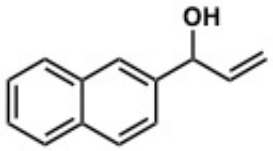


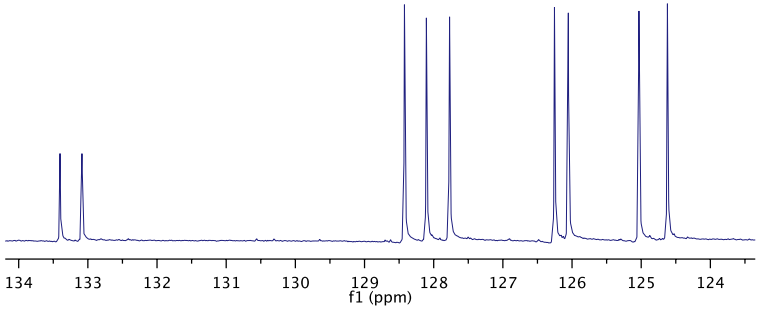


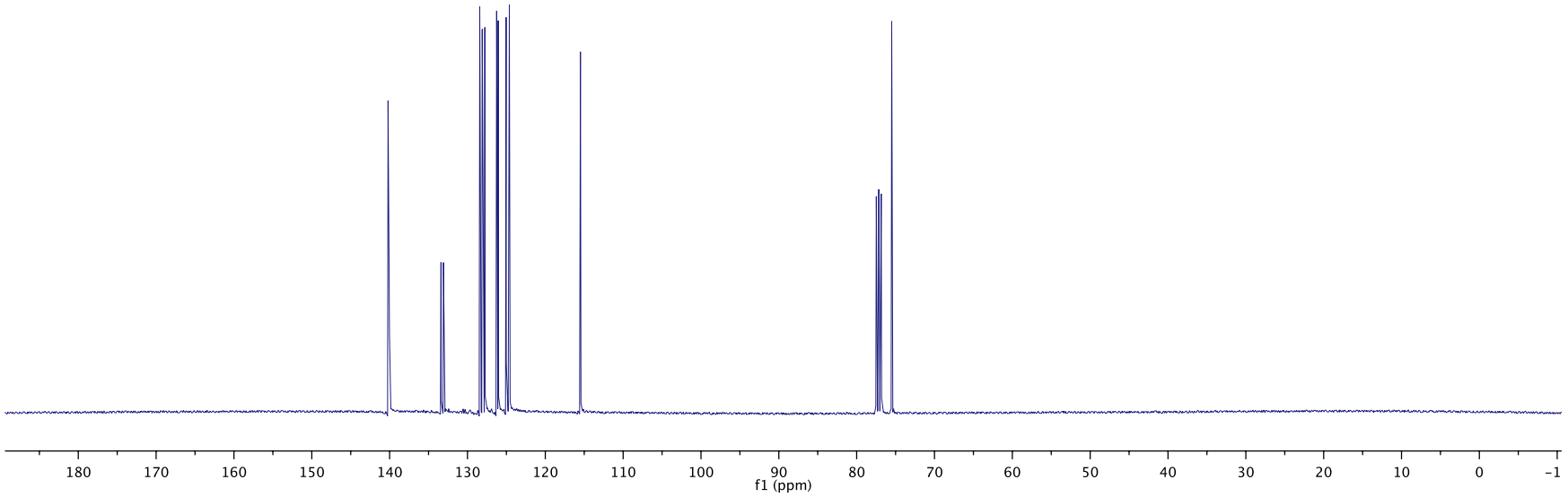
wbl-X-005C+H.2.fid
wbl-X-005C+H

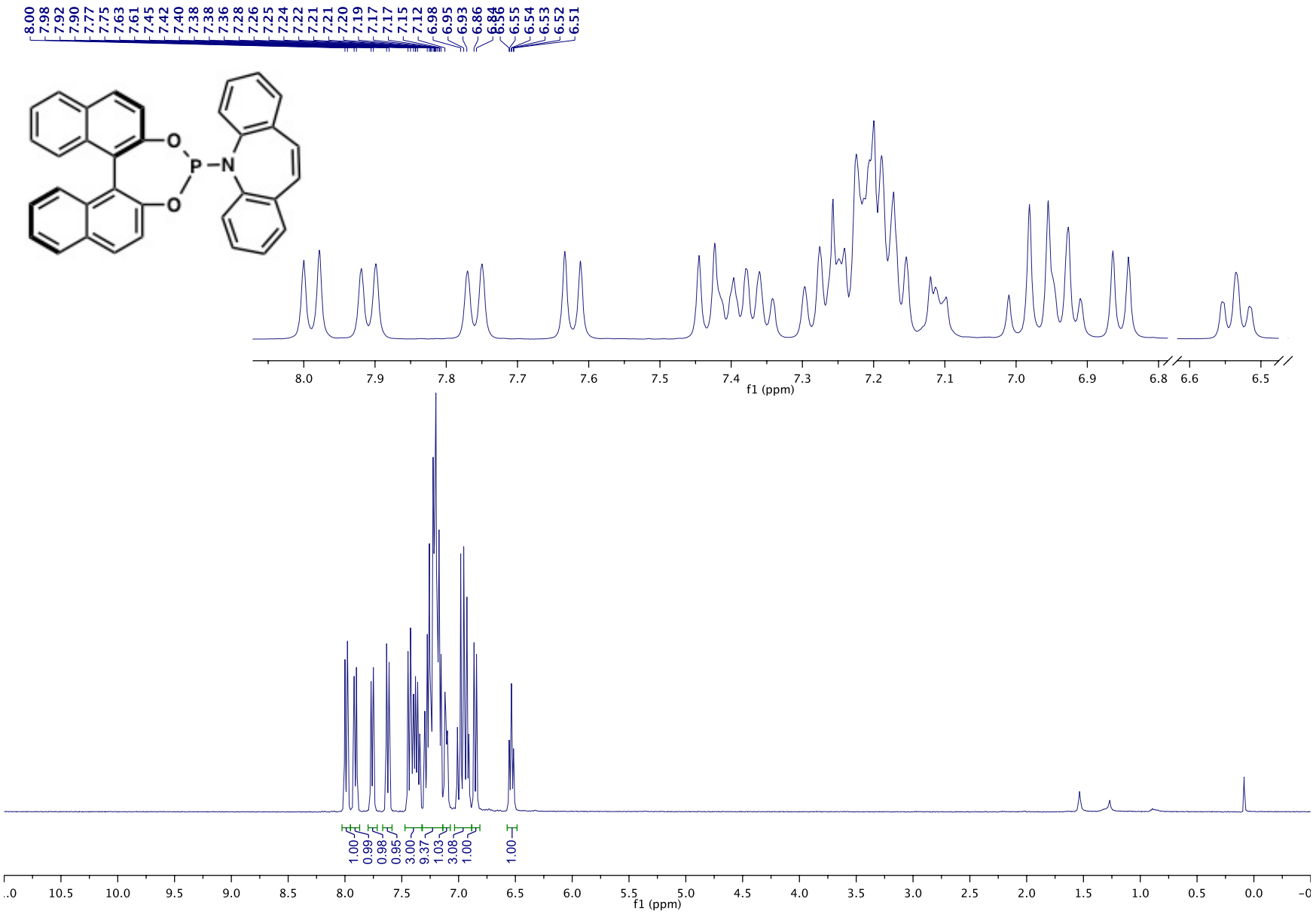
140.20
140.03
133.40
133.08
128.42
128.10
127.77
126.25
126.05
125.03
124.62
115.48

77.48
77.16
76.84
75.50



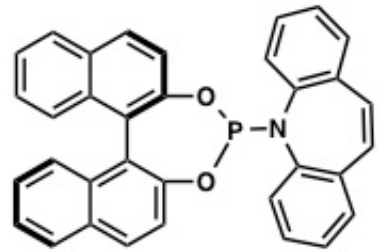


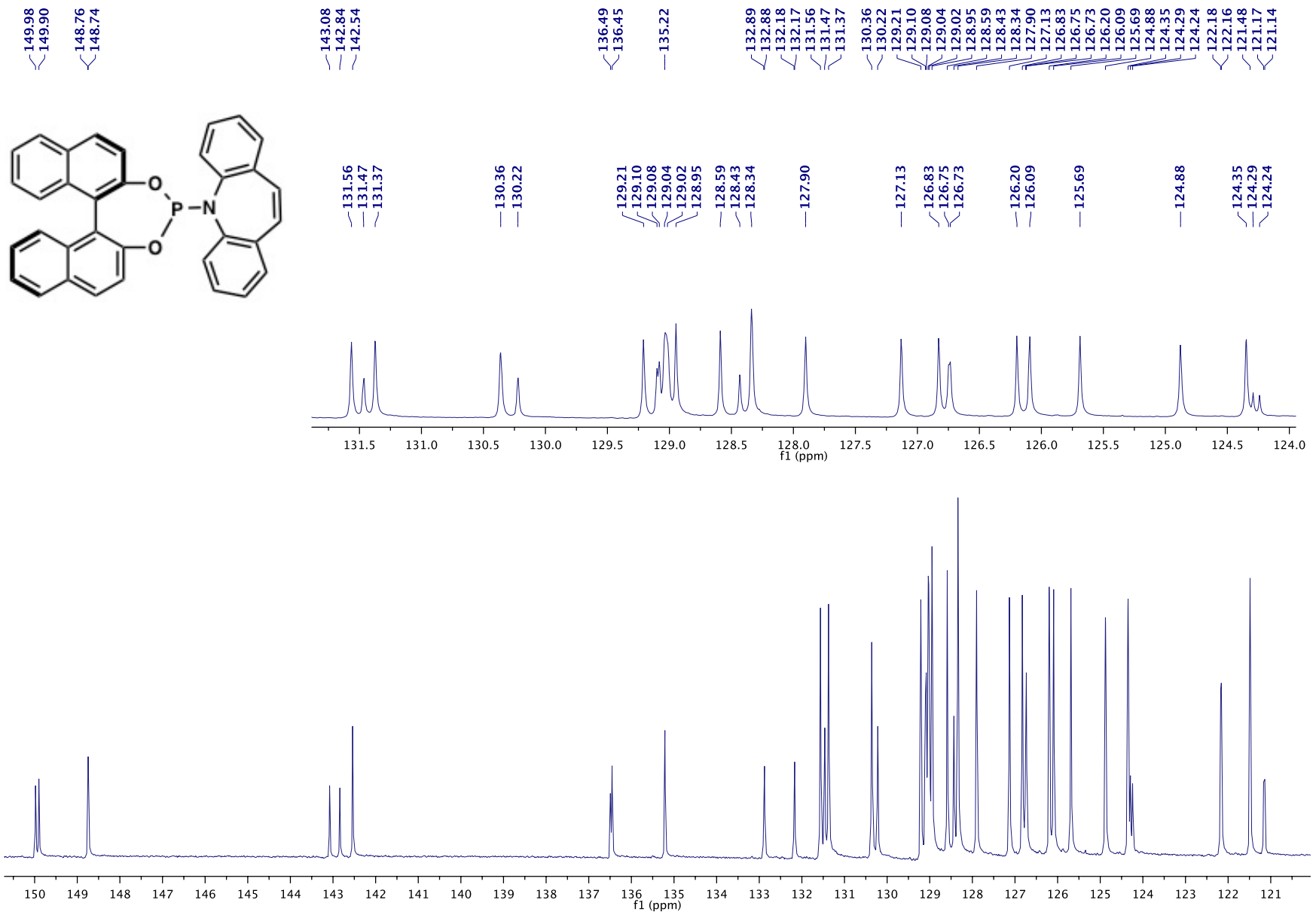



8.00
7.98
7.92
7.90
7.77
7.75
7.63
7.61
7.45
7.42
7.40
7.38
7.38
7.36
7.28
7.26
7.25
7.24
7.22
7.21
7.21
7.20
7.19
7.17
7.17
7.15
7.12
6.98
6.95
6.93
6.86
6.84
6.56
6.55
6.54
6.53
6.52
6.51
O
P
N
O
f1 (ppm)
1.00
0.99
0.98
0.95
3.00
9.37
1.03
3.08
1.00
1.00
f1 (ppm)

wbl-X-007.3.fid
wbl-X-007C

149.98
149.90
148.76
148.74
143.08
142.84
142.54
136.49
136.45
135.22
132.89
132.88
132.18
132.17
131.56
131.47
131.37
130.36
130.22
129.21
129.10
129.08
129.04
129.02
128.95
128.59
128.43
128.34
127.90
127.13
126.83
126.75
126.73
126.20
126.09
125.69
124.88
124.35
124.29
124.24
122.18
122.16
121.48
121.17
121.14




149.98
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148.76
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142.54
136.49
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132.89
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132.18
132.17
131.56
131.47
131.37
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130.22
129.21
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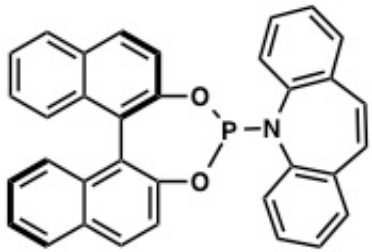
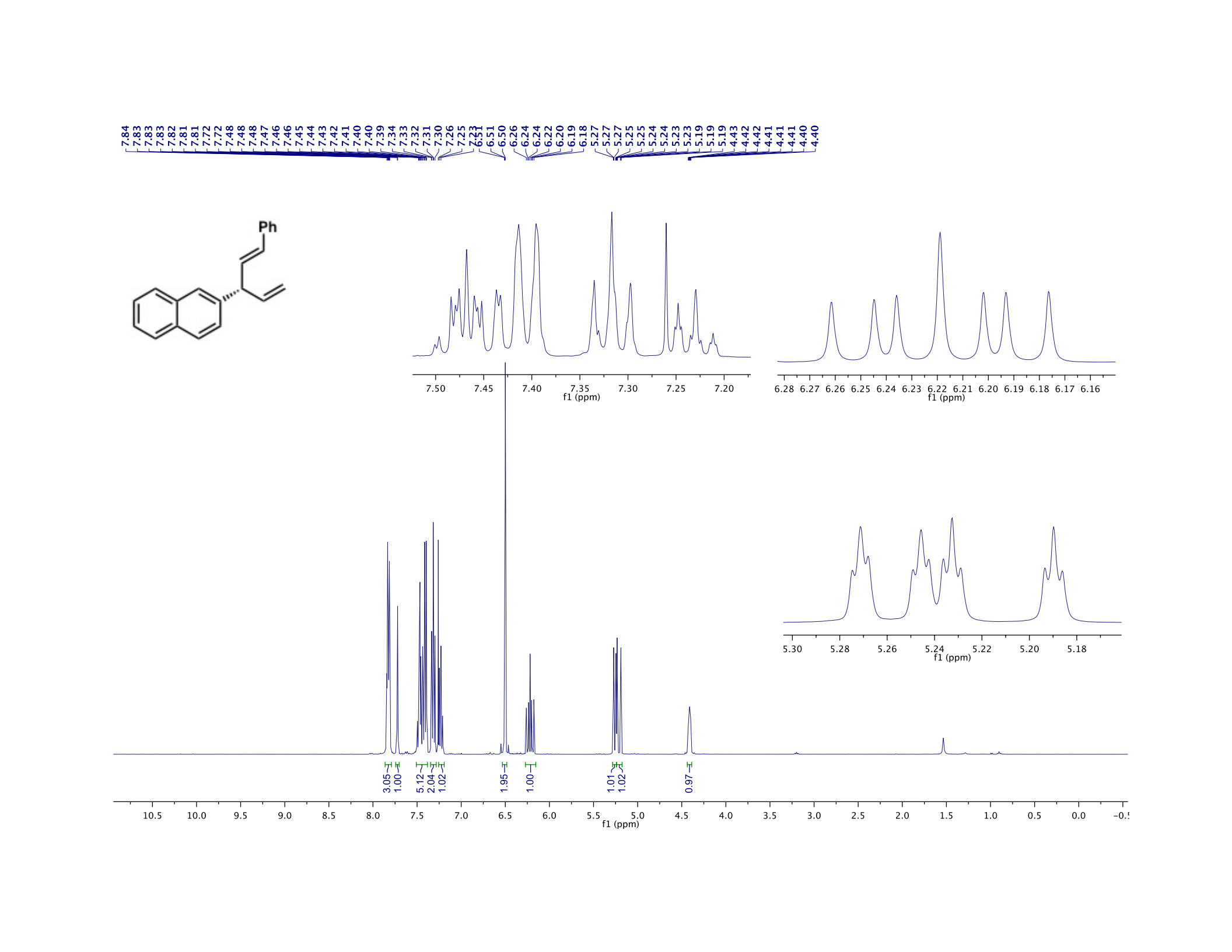
129.08
129.04
129.02
128.95
128.59
128.43
128.34
127.90
127.13
126.83
126.75
126.73
126.20
126.09
125.69
124.88
124.35
124.29
124.24
122.18
122.16
121.48
121.17
121.14
O
P
N
O
131.5
131.0
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
125.5
125.0
124.5
124.0
f1 (ppm)
150
149
148
147
146
145
144
143
142
141
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
f1 (ppm)

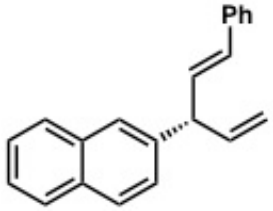
wbl-X-007P
STANDARD PHOSPHORUS PARAMETERS

137.85




7.84 7.83 7.83 7.83 7.82 7.81 7.81 7.72 7.72 7.48 7.48 7.48 7.47 7.46 7.46 7.45 7.44 7.43 7.42 7.41 7.40 7.40 7.39 7.34 7.33 7.32 7.31 7.30 7.26 7.25 7.23 6.51 6.51 6.50 6.26 6.24 6.24 6.22 6.20 6.19 6.18 5.27 5.27 5.25 5.25 5.24 5.24 5.23 5.23 5.19 5.19 4.43 4.42 4.42 4.41 4.41 4.41 4.40 4.40
Ph
7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
6.28 6.27 6.26 6.25 6.24 6.23 6.22 6.21 6.20 6.19 6.18 6.17 6.16
f1 (ppm)
5.30 5.28 5.26 5.24 5.22 5.20 5.18
f1 (ppm)
3.05 1.00 5.12 2.04 1.02 1.95 1.00 1.01 1.02 0.97
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

WBL-IX-011C.1.fid



140.16
140.07
137.46
133.76
132.50
131.75
131.06
128.67
128.28
127.87
127.75
127.44
126.96
126.44
126.42
126.16
125.70
116.11

77.48
77.16
76.84

52.54