Asymmetric Additions to Dienes Catalyzed by a Dithiophosphoric Acid

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Supplementary Methods

Preparation of catalysts. The general scheme for synthesis of the dithiophosphoric acid catalysts is illustrated with the preparation of 3h (Supplementary Figure 1).

Supplementary Figure 1. Preparation of catalyst 3h.

S1: A 100 mL flame-dried round-bottom flask was charged with 9-bromoanthracene (3.81 g, 15 mmol, 1.0 equiv), 2,4,6-trimethylphenylboronic acid (3.69 g, 22.5 mmol, 1.5 equiv), Pd(OAc)_2 (101.02 mg, 0.45 mmol, 0.03 equiv), SPhos (369.5 mg, 0.90 mmol, 0.06 equiv), K_3PO_4 (7.96 g, 37.5 mmol, 2.5 equiv), and anhydrous toluene (120 mL). The resulting mixture was subjected to
freeze-pump-thaw cycles (3x) and heated at 105 °C for 18 h. After this time, the reaction mixture was cooled to room temperature and poured over water (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 50 mL). The organic extracts were combined and dried over anhydrous MgSO$_4$, filtered, and concentrated in vacuo. The resulting dark reddish-brown semi-solid was dissolved in minimal amount of CH$_2$Cl$_2$ and triturated with MeOH. The desired product S1 precipitated as a reddish-brown solid, and was filtered and washed with ice-cold MeOH. The solid mass was dried under high vacuum for 2 h until a constant mass of 4.22 g (96% yield) was obtained. $^1$H NMR (300 MHz, CDCl$_3$): δ 8.48 (s, 1H), 8.06 (d, 2H, $J = 8.4$ Hz), 7.50-7.43 (m, 4H), 7.35-7.30 (m, 2H), 7.10 (s, 2H), 2.46 (s, 3H), 1.71 (6H, s). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 137.6, 137.1, 135.7, 134.5, 131.6, 129.7, 128.6, 128.2, 126.0, 126.0, 125.5, 125.1, 21.2, 20.0.

S2: To a flame-dried 250 mL flask was added 9-(2,4,6-trimethylphenyl)-anthracene (S1) (3.20 g, 10.8 mmol, 1.0 equiv) and CCl$_4$ (40 mL). To the resulting solution was added dropwise over 5 minutes Br$_2$ (612 µL, 11.9 mmol, 1.1 equiv). The reaction mixture was allowed to stir for 15 min at room temperature and quenched with saturated Na$_2$SO$_3$ (30 mL). The biphasic mixture was extracted with CH$_2$Cl$_2$ (2 x 50 mL) and the combined organic layers were dried over anhydrous MgSO$_4$, filtered and concentrated in vacuo. The product S2 (3.24 g, 73% yield) was obtained by recrystallization from CH$_2$Cl$_2$/MeOH as a dark green solid. $^1$H NMR (300 MHz, CDCl$_3$): δ 8.63 (d, 2H, $J = 9.0$ Hz), 7.63-7.58 (m, 2H), 7.51 (2H, d, $J = 8.7$ Hz), 7.40-7.35 (m, 2H), 7.11 (s, 2H), 2.47 (s, 3H), 1.71 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 137.4, 137.4, 136.6, 134.1, 130.5, 130.5, 128.3, 128.1, 127.0, 126.4, 125.9, 122.2, 21.2, 20.0.
**S4:** A 100 mL flame-dried round-bottom flask was charged with (R)-3,3'-diiodo-5,5',6,6',7,7',8,8'-octahydro-2,2'-bis(ethoxymethyloxy)-1,1'-binaphthyl\(^{31}\) (818 mg, 1.24 mmol, 1.0 equiv), 9-(2,4,6-trimethylphenyl)10-anthracenylboronic acid (S3, 6.0 equiv, prepared by metallation of the bromide precursor (7.41 mmol) using nBuLi (18.5 mmol, 2.5 equiv), THF 250 mL, B(O-iPr)\(_3\) (22.2 mmol, 3.0 equiv) and used as crude material), Pd(OAc)\(_2\) (27.8 mg, 0.124 mmol, 0.1 equiv), SPhos (101.5 mg, 0.25 mmol, 0.2 equiv), K\(_3\)PO\(_4\) (1.31 g, 6.18 mmol, 2.5 equiv), and anhydrous toluene (25 mL). The resulting mixture was subjected to 3 freeze-pump-thaw cycles and heated at 105 ºC for 18 h. After this time, the reaction mixture was brought to room temperature and poured over water (25 mL). The organic layer was separated and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (2 X 50 mL). The organic extracts were combined and dried over anhydrous MgSO\(_4\), filtered, and concentrated in vacuo and the crude product was purified by flash chromatography (5-40% CH\(_2\)Cl\(_2\)/hexanes) to yield 950.5 mg of S4 in 77% yield as faint yellow solid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.10 (d, 2H, \(J = 8.7\) Hz), 8.00-7.96 (m, 2H), 7.68-7.60 (m, 4H), 7.57-7.52 (m, 2H), 7.46-7.33 (m, 8H), 7.29 (s, 2H), 7.22 (s, 4H), 4.54-4.50 (m, 4H), 2.99 (br, 6H), 2.62-2.45 (m, 12H), 2.01 (m, 8H), 1.90 (s, 6H), 1.87 (s, 6H), 0.70 (t, 6H, \(J = 7.2\) Hz). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 151.2, 137.6, 137.3, 137.1, 137.0, 135.6, 134.8, 133.9, 133.1, 131.6, 130.4, 129.4, 129.3, 129.3, 129.3, 128.2, 127.7, 127.5, 126.0, 125.8, 125.3, 125.1, 96.5, 77.2, 63.8, 29.5, 27.9, 23.4, 23.0, 21.2, 20.1, 20.0, 14.5.

**S5:** Compound S4 (840 mg, 0.84 mmol) was suspended in dioxane (50 mL). To the mixture was added conc. HCl (5 mL) and the mixture was heated to 70 ºC for 2 h. The reaction mixture was cooled to room temperature and concentrated in vacuo. The resulting semi-solid was dissolved in CH\(_2\)Cl\(_2\) (70 mL) and washed with water (25 mL) and saturated NaHCO\(_3\) (25 mL) and dried
over anhydrous MgSO₄, filtered, and concentrated in vacuo. The residue was purified by recrystallization from CH₂Cl₂/hexanes to yield 789 mg (94% yield) of the desired product F as a faint yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, 2H, J = 8.8 Hz), 7.80-7.78 (m, 2H), 7.53-7.46 (m, 6H), 7.40-7.36 (m, 2H), 7.32-7.27 (m, 4H), 7.21 (s, 2H), 7.13 (brs, 4H), 4.70 (s, 2H), 3.72 (s, 2H), 2.90 (m, 4H), 2.80-2.62 (m, 4H), 2.48 (s, 6H), 1.95-1.89 (m, 8H), 1.80 (s, 6H), 1.75 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 149.3, 137.7, 137.6, 137.1, 136.4, 134.7, 133.2, 131.4, 130.6, 130.5, 129.9, 129.6, 128.3, 126.9, 126.4, 126.2, 125.7, 125.5, 125.4, 122.5, 121.0, 67.1, 29.3, 27.5, 23.4, 23.1, 21.3, 20.1, 20.1. HRMS (ESI) calc. for [M+H]+ (C₆₆H₅₉O₂) 883.4510, found 883.4493.

3h: The following procedure is representative for all the dithioacid catalysts used in this study. A flame dried flask was charged with diol S₅ (650 mg, 0.74 mmol, 1.0 equiv), P₂S₅ (81.9 mg, 0.37 mmol, 0.5 equiv), and anhydrous m-xylene (10 mL). The flask was equipped with a condenser and placed in an oil-bath preheated to 150 ºC. The progress of the reaction was monitored by disappearance of the phenolic protons (¹H NMR). After 2 h, the reaction was judged complete and allowed to cool to room temperature. The solution was decanted into a flame-dried 100 mL flask and the solvent was evaporated in vacuo. The crude product was dissolved in anhydrous CH₂Cl₂ (5 mL) and treated with hexanes (50 mL). At this point, a fine precipitate was observed. The solvent was then partially evaporated until about 2 to 3 mL solvent was left. The precipitate was then collected by filtration and washed with ice-cold hexanes. Following this procedure, the product 3h (617 mg) was obtained as a faint-yellow powder in 85% yield. ¹H NMR (300 MHz, CDCl₃): δ 8.09 (d, 2H, J = 8.8 Hz), 7.77 (d, 2H, J = 8.8 Hz), 7.51-6.99 (m, 18H), 3.13-3.05 (m, 6H), 2.77-2.72 (m, 2H), 2.46 (s, 6H), 2.07-2.01 (m,
8H), 1.83 (s, 6H), 1.60 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.3, 137.0, 136.7, 135.7, 134.9, 134.3, 131.0, 130.7, 129.9, 129.6, 129.1, 128.3, 128.1, 128.0, 126.8, 126.1, 126.0, 125.9, 125.6, 125.1, 125.0, 124.5, 29.4, 28.4, 22.8, 22.8, 21.3, 21.2, 20.1, 19.8. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 89.7. HRMS (ESI) calc. for [M+H]$^+$ (C$_{66}$H$_{58}$O$_2$PS$_2$) 977.3610, found 977.3617.

**Characterization data for other catalysts**

3a: NMR analysis of this and related compounds (3c and 3d) is complicated by the presence of multiple conformers due to slow rotation around the 3,3'-biaryl bonds and the unsymmetrical nature of the 1-naphthyl substituent. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.12-7.33 (m, 24H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 93.4, 93.2, 93.1.

3c: Prepared by the method of Cheon and Yamamoto$^{32}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.24-7.31 (m, 24H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 53.4 (br). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ –75.2,
HRMS (ESI, negative mode) calc. for [M−H]− (C_{41}H_{24}O_{4}NF_{3}PS_{2}) 746.0842, found 746.0822.

3d: Prepared by the method of Nakashima and Yamamoto.\textsuperscript{33} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.09-7.31 (m, 24H). \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}): δ 4.2, 3.9, 3.2, 2.9. \textsuperscript{19}F NMR (377 MHz, CDCl\textsubscript{3}): δ −79.6, −79.7, −80.0. HRMS (ESI) calc. for [M+H]\textsuperscript{+} (C_{41}H_{26}O_{5}NF_{3}PS) 732.1216, found 732.1203.

3e: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.47 (s, 2H), 8.04-7.97 (m, 6H), 7.68 (d, 2H, J = 8.8 Hz), 7.49-7.27 (m, 10H), 3.13-2.68 (m, 6H), 2.05-1.78 (m, 10H). \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}): δ 90.9. HRMS (ESI) calc. for [M+H]\textsuperscript{+} (C_{48}H_{38}O_{2}PS_{2}) 741.2045, found 741.2057.
**3f:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.11 (d, 2H, $J = 8.8$ Hz), 7.75 (d, 2H, $J = 8.8$ Hz), 7.71-7.24 (m, 24H), 3.14-2.96 (m, 6H), 2.76-2.69 (m, 2H), 2.11-1.89 (m, 6H), 1.77-1.64 (m, 2H), 1.63-1.47 (m, 2H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 91.2. HRMS (ESI) calc. for [M+H]$^+$ (C$_{60}$H$_{46}$O$_2$PS$_2$) 893.2671, found 893.2684.

**3g:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.11 (d, 2H, $J = 9.2$ Hz), 7.76-7.72 (m, 4H), 7.68 (d, 2H, $J = 8.0$ Hz), 7.56 (s, 2H), 7.46 (s, 2H) 7.37 (t, 2H, $J = 8.8$ Hz), 7.29-7.14 (m, 10H), 3.15-2.96 (m, 6H), 2.78-2.68 (m, 2H), 2.15-1.73 (m, 8H), 1.41 (s, 18H), 1.38 (s, 18H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 91.5. HRMS (ESI) calc. for [M+H]$^+$ (C$_{76}$H$_{78}$O$_2$PS$_2$) 1117.5175, found 1117.5185.
9: $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.41 (s, 2H), 2.89-2.75 (m, 4H), 2.57-2.46 (m, 2H), 2.23-2.12 (m, 2H), 1.85-1.70 (m, 6H), 1.63-1.47 (m, 2H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 92.4.

Characterization of substrates

Substrates were prepared by the methods of Widenhoefer and coworkers$^{34}$ according to the general scheme shown in Supplementary Figure 2. Dienyl bromides were prepared by the method of Ollis and coworkers$^{35}$.

Supplementary Figure 2. Preparation of substrates.
1: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, 2H, \(J = 7.2\) Hz), 7.30 (d, 2H, \(J = 7.2\) Hz), 6.09 (d, 1H, \(J = 15.2\) Hz), 5.53 (dt, 1H, \(J = 15.2, 7.8\) Hz), 5.03 (t, 1H, \(J = 6.8\) Hz), 4.88 (s, 1H), 4.86 (s, 1H), 2.66 (d, 2H, \(J = 6.8\) Hz), 2.00 (d, 2H, \(J = 7.8\) Hz), 1.78 (s, 3H), 0.86 (s, 6H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 162.7, 141.8, 135.9, 131.4, 129.2, 125.8, 115.0, 114.2, 55.6, 52.8, 42.7, 34.6, 25.0, 18.7.

1a: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.50 (s, 2H), 7.17 (s, 1H), 6.09 (d, 1H, \(J = 15.3\) Hz), 5.55 (dt, 1H, \(J = 15.3, 7.8\) Hz), 5.22 (t, 1H, \(J = 6.8\) Hz), 4.87 (s, 1H), 4.85 (s, 1H), 2.67 (d, 2H, \(J = 6.8\) Hz), 2.36 (s, 3H), 2.01 (d, 2H, \(J = 7.8\) Hz), 1.78 (s, 3H), 0.87 (s, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 142.1, 139.9, 139.3, 136.2, 134.5, 126.2, 124.8, 115.3, 53.1, 43.0, 35.0, 25.2, 21.5, 19.0. HRMS (ESI) calc. for \([\text{M+H}]^+ (\text{C}_{18}\text{H}_{28}\text{NO}_2\text{S})\) 322.1835, found 322.1832.

1b: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.80 (d, 2H, \(J = 8.7\) Hz), 7.46 (d, 2H, \(J = 8.7\) Hz), 6.08 (d, 1H, \(J = 15.6\) Hz), 5.51 (dt, 1H, \(J = 15.6, 7.8\) Hz), 5.21 (t, 1H, \(J = 6.8\) Hz), 4.87 (s, 1H), 4.85 (s, 1H), 2.66 (d, 2H, \(J = 6.8\) Hz), 1.98 (d, 2H, \(J = 7.8\) Hz), 1.76 (s, 3H), 0.85 (s,
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.74 (d, 2H, $J$ = 8.1 Hz), 7.27 (d, 2H, $J$ = 8.1 Hz), 5.94 (d, 1H, $J$ = 15.6 Hz), 5.59 (bs, 1H), 5.37 (dt, 1H, $J$ = 15.6, 7.5 Hz), 5.09 (t, 1H, $J$ = 6.9 Hz), 2.63 (d, 2H, $J$ = 6.9 Hz), 2.40 (s, 3H), 2.12-1.98 (m, 4H), 1.94 (d, 2H, $J$ = 7.5 Hz), 1.68-1.50 (m, 4H), 0.82 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 143.1, 136.8, 136.5, 135.3, 129.5, 127.8, 127.0, 121.3, 52.7, 42.7, 34.5, 25.6, 24.9, 24.5, 22.5, 22.4, 21.4. HRMS (ESI) calc. for [M+H]$^+$ (C$_{18}$H$_{28}$NO$_2$S) 322.1835, found 322.1831.
4e: Isolated as about a 6:1 mixture of \( E \) and \( Z \) olefin isomers. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.75 (d, 2H, \( J = 8.1 \) Hz), 7.30 (d, 2H, \( J = 8.1 \) Hz), 6.03 (d, 1H, \( J = 15.9 \) Hz), 5.63-5.53 (m, 1H), 4.96-4.86 (m, 2H), 2.66 (d, 2H, \( J = 6.9 \) Hz), 2.42 (s, 3H), 2.16 (q, 2H, \( J = 7.5 \) Hz) 1.98 (d, 2H, \( J = 7.5 \) Hz), 1.05 (t, 3H, \( J = 7.5 \) Hz), 0.89 (s, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) 147.4, 143.2, 136.8, 135.2, 129.6, 127.0, 124.8, 112.9, 52.8, 42.8, 34.6, 24.9, 24.8, 21.5, 12.6.

4f: \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.76 (d, 2H, \( J = 8.1 \) Hz), 7.31 (d, 2H, \( J = 8.1 \) Hz), 6.02 (d, 1H, \( J = 15.6 \) Hz), 5.62 (dt, 1H, \( J = 15.6, 7.8 \) Hz), 4.96 (T, 1H, \( J = 6.8 \) Hz), 4.90 (app s, 2H), 3.63 (t, 2H, \( J = 6.3 \) Hz), 2.67 (d, 2H, \( J = 6.8 \) Hz), 2.43 (s, 3H), 2.22 (t, 2H, \( J = 7.7 \) Hz), 2.00 (d, 2H, \( J = 7.8 \) Hz), 1.67 (app quintet, 2H, \( J = 6.9 \) Hz), 0.90 (s, 9H), 0.87 (s, 6H), 0.06 (s, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) 145.9, 143.5, 137.2, 135.4, 130.0, 127.3, 125.5, 114.4, 63.0, 53.7, 53.2, 43.1, 35.0, 31.7, 28.6, 26.2, 25.2, 21.8, 18.6, -5.0. HRMS (ESI) calc. for [M-H]+ (C\(_{25}\)H\(_{42}\)NO\(_3\)SSi) 464.2649, found 464.2650.

4g: \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.74 (d, 2H, \( J = 8.1 \) Hz), 7.27 (d, 2H, \( J = 8.1 \) Hz), 6.09 (d, 1H, \( J = 15.6 \) Hz), 5.46 (dt, 1H, \( J = 15.6, 7.5 \) Hz), 5.06 (t, 1H, \( J = 6.7 \) Hz), 4.85 (s, 1H), 4.83 (s, 1H), 2.70 (d, 2H, \( J = 6.8 \) Hz), 2.39 (s, 3H), 2.09 (d, 2H, \( J = 7.5 \) Hz), 1.72 (s, 3H), 1.60-1.45 (m, 4H), 1.45-1.30 (m, 4H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) 145.5, 142.1, 137.0, 136.0,
130.0, 127.4, 126.7, 115.3, 50.5, 46.3, 40.8, 35.5, 25.1, 21.8, 18.9. HRMS (ESI) calc. for [M+H]+
(C_{19}H_{28}NO_{2}S) 334.1835, found 334.1834.

4h: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.73 (d, 2H, $J = 8.1$ Hz), 7.27 (d, 2H, $J = 8.1$ Hz), 6.09 (d, 1H, $J = 15.6$ Hz), 5.47 (dt, 1H, $J = 15.6, 7.8$ Hz), 5.89-5.78 (m, 3H), 2.70 (d, 2H, $J = 6.9$ Hz), 2.40 (s, 3H), 2.05 (d, 2H, $J = 7.8$ Hz), 1.73 (s, 3H), 1.42-1.20 (m, 10H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 143.5, 142.1, 137.0, 136.1, 129.9, 127.4, 125.7, 115.4, 53.7, 49.5, 39.4, 37.1, 33.7, 26.3, 21.8, 21.6, 18.9. HRMS (ESI) calc. for [M+H]+ (C$_{20}$H$_{30}$NO$_2$S) 348.1992, found 348.1987.

4i: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, 2H, $J = 7.7$ Hz), 7.29 (d, 2H, $J = 7.7$ Hz), 4.81 (m, 1H), 4.60 (t, 1H, $J = 7.1$ Hz), 2.71 (d, 2H, $J = 7.1$ Hz), 2.42 (s, 3H), 1.83 (d, 2H, $J = 8.1$ Hz), 1.61 (s, 3H), 1.60 (s, 3H), 0.86 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 203.3, 143.3, 137.2, 129.7, 127.1, 94.2, 84.2, 52.5, 39.8, 34.5, 24.8, 21.5, 20.5. HRMS (ESI) calc. for [M+H]+
(C$_{17}$H$_{36}$NO$_2$S) 308.1679, found 308.1685.
**4j**: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.13-8.07 (m, 1H), 7.88-7.82 (m, 1H), 7.76-7.71 (m, 2H), 5.31 (t, 1H, $J = 6.9$ Hz), 4.88-4.79 (m, 1H), 2.88 (d, 2H, $J = 6.9$ Hz), 1.88 (d, 2H, $J = 7.8$ Hz), 1.63 (s, 3H), 1.62 (s, 3H), 0.90 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 203.4, 147.9, 133.5, 132.7, 131.0, 125.2, 94.2, 83.7, 52.9, 39.6, 34.6, 24.6, 20.4. HRMS (ESI) calc. for [M+H]$^+$ (C$_{16}$H$_{23}$N$_2$O$_4$S) 339.1373, found 339.1377.

**4k**: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.93-7.86 (m, 4H), 7.52-7.40 (m, 6H), 4.88-4.79 (m, 1H), 2.88 (br, 1H), 2.76 (t, 2H, $J = 6.9$ Hz), 1.88 (d, 2H, $J = 8.1$ Hz), 1.59 (s, 3H), 1.58 (s, 3H), 0.90 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 203.1, 133.4, 132.1, 132.0, 131.7, 128.5, 128.3, 94.0, 84.3, 50.4, 39.9, 34.9, 34.8, 24.7, 20.4. HRMS (ESI) calc. for [M+H]$^+$ (C$_{22}$H$_{29}$NOP) 354.1981, found 354.1988.
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\text{MeO} \quad \text{SO}_2 \quad \text{NH}
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**4l:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.79 (d, 2H, $J = 8.7$ Hz), 6.96 (d, 2H, $J = 8.7$ Hz), 4.90-4.81 (m, 2H), 3.85 (s, 3H), 2.68 (d, 2H, $J = 6.9$ Hz), 2.04-1.98 (m, 4H), 1.84 (d, 2H, $J = 8.1$ Hz), 1.57-1.43 (m, 6H), 0.86 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 199.8, 162.6, 131.6, 129.0, 114.1, 101.3, 83.9, 55.5, 52.3, 40.1, 34.4, 31.4, 27.2, 25.9, 24.6. HRMS (ESI) calc. for [M+H]$^+$ (C$_{20}$H$_{30}$NO$_3$S) 364.1941, found 364.1950.

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\text{O}^+\text{NHTs}
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**4m:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.81 (d, 2H, $J = 8.4$ Hz), 7.33 (d, 2H, $J = 8.4$ Hz), 7.07 (s, 1H), 4.87 (app septet, 1H, $J = 3.0$ Hz), 3.79 (s, 2H), 2.49 (s, 3H), 1.65 (s, 3H), 1.64 (s, 3H), 0.97 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 200.0, 144.7, 133.7, 129.6, 128.6, 97.3, 96.5, 86.1, 35.8, 25.0, 21.6, 20.6. HRMS (ESI) calc. for [M+H]$^+$ (C$_{16}$H$_{24}$NO$_3$S) 310.1471, found 310.1478.

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\text{O}^+\text{NHTs}
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**4n:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.81 (d, 2H, $J = 8.1$ Hz), 7.33 (d, 2H, $J = 8.1$ Hz), 7.03 (s, 1H), 4.92-4.86 (m, 1H), 4.01 (t, 2H, $J = 6.9$ Hz), 2.44 (s, 3H), 2.25 (q, 2H, $J = 6.9$ Hz), 2.08-2.02 (m, 4H), 1.60-1.46 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 199.0, 144.7, 133.5, 129.6, 128.5, 103.0, 84.1, 31.5, 28.2, 27.3, 26.0, 21.6.
**S6**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.14 (d, 1H, $J = 8.8$ Hz), 7.03 (d, 1H, $J = 2.4$ Hz), 6.84 (m, 2H), 4.96 (m, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.66 (s, 3H), 3.44 (s, 2H), 2.65 (d, 2H, $J = 7.6$ Hz), 2.13 (m, 4H), 1.60 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.5, 171.6, 153.8, 132.0, 128.8, 111.7, 109.8, 107.8, 102.4, 100.9, 83.1, 58.8, 55.9, 52.3, 32.8, 32.7, 31.5, 27.4, 27.1, 26.0. HRMS (ESI) calc. for [M+H]$^+$ (C$_{25}$H$_{32}$NO$_5$) 426.2275, found 425.2278.

**S7**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 (s, 1H), 7.25 (d, 1H, $J = 8.4$ Hz), 7.11 (d, 1H, $J = 8.4$ Hz), 6.90 (s, 1H), 4.90 (m, 1H), 3.71 (s, 3H), 3.68 (s, 6H), 3.41 (s, 2H), 2.62 (d, 2H, $J = 7.6$ Hz), 2.15 (m, 4H), 1.60 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.7, 171.3, 135.2, 130.1, 129.5, 124.2, 121.5, 112.4, 110.7, 108.0, 102.5, 82.9, 58.5, 52.4, 32.9, 32.7, 31.6, 27.2, 27.1, 26.0. HRMS (ESI) calc. for [M+H]$^+$ (C$_{24}$H$_{29}$BrNO$_4$) 474.1274, found 474.1284.
**S8**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, 1H, $J = 8.0$ Hz), 7.27 (m, 1H), 7.19 (dt, 1H, $J = 7.2$, 0.8 Hz), 7.09 (dt, 1H, $J = 8.0$, 0.8 Hz), 6.86 (s, 1H), 4.96 (m, 1H), 3.73 (s, 3H), 3.67 (s, 6H), 3.48 (s, 2H), 2.63 (d, 2H, $J = 7.6$ Hz), 1.73 (s, 3H), 1.73 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 203.8, 171.5, 136.6, 128.6, 128.1, 121.4, 118.9, 118.8, 109.1, 108.4, 95.2, 83.4, 58.9, 52.2, 32.6, 32.6, 27.6, 20.6. HRMS (ESI) calc. for [M+H]$^+$ (C$_{21}$H$_{26}$NO$_4$) 356.1856, found 356.1862.

**Characterization of the products**

**2**: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.65 (d, 2H, $J = 8.4$ Hz), 7.26 (d, 2H, $J = 8.4$ Hz), 5.00 (d, 1H, $J = 8.5$ Hz), 4.34 (app q, 1H, $J = 8.5$ Hz), 3.20 (d, 1H, $J = 9.9$ Hz), 3.10 (d, 1H, $J = 9.9$ Hz), 2.40 (s, 3H), 1.74 (dd, 1H, $J = 12.6$, 7.2 Hz), 1.66 (s, 3H), 1.61 (s, 3H), 1.40 (dd, 1H, $J = 12.6$, 8.5 Hz), 1.03 (s, 3H), 0.77 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 143.1, 136.8, 133.1, 129.5, 127.7, 126.8, 61.2, 58.0, 48.1, 37.7, 26.7, 26.3, 26.0, 21.8, 18.2. HRMS (ESI) calc. for [M+H]$^+$ (C$_{17}$H$_{26}$NO$_2$S) 308.1679, found 308.1675. Enantiopurity was determined by HPLC analysis (Chiralpak AD-H column, 98:2 hexanes/ethanol, 1 mL/min) $t_R$ 8.9 min (minor), 11.6 min (major). Absolute configuration was assigned by comparison with a previous report, and the rest of the products were assigned by analogy.$^{36}$
5a: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.38 (s, 2H), 7.15 (s, 1H), 5.01 (d, 1H, $J = 9$ Hz), 4.36 (dd, 1H, $J = 16.2, 9$ Hz), 3.24 (d, 1H, $J = 9.9$ Hz), 3.10 (d, 1H, $J = 9.9$ Hz), 2.36 (s, 6H), 1.75 (dd, 1H, $J = 12.3, 7.2$ Hz), 1.68 (s, 3H), 1.64 (s, 3H), 1.41 (dd, 1H, $J = 12.3, 9$ Hz), 1.04 (s, 3H), 0.81 (s, 3H). NMR (75 MHz, CDCl$_3$) $\delta$ 139.1, 138.4, 133.8, 132.8, 126.4, 124.9, 60.8, 57.7, 47.8, 37.3, 26.4, 25.9, 25.6, 21.2, 17.9. HRMS (ESI) calc. for [M+H]$^+$ (C$_{18}$H$_{28}$NO$_2$S)$_3$ 322.1835, found 322.1830. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99.5:0.5 hexanes/ethanol, 1 mL/min) $t_R$ 11.5 min (minor), 14.5 min (major).

5b: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.72 (dt, 2H, $J = 8.7, 2.1$ Hz), 7.45 (dt, 2H, $J = 8.7, 2.1$ Hz), 4.91 (doublet of septets, 1H, $J = 9.3, 1.2$ Hz), 4.43 (ddd, 1H, $J = 9.3, 8.7, 7.5$ Hz), 3.29 (dd, 1H, $J = 9.9, 1.2$ Hz), 3.09 (d, 1H, $J = 9.9$ Hz), 1.80 (ddd, 1H, $J = 12.6, 7.5, 1.2$ Hz), 1.68 (d, 3H, $J = 1.2$ Hz), 1.62 (d, 3H, $J = 1.2$ Hz), 1.42 (dd, 1H, $J = 12.6, 8.7$ Hz), 1.06 (s, 3H), 0.88 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.9, 138.8, 133.9, 129.1, 129.0, 126.2, 61.1, 58.1, 48.1, 37.8, 26.5, 26.3, 25.9, 18.2. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/ethanol, 1 mL/min) $t_R$ 14.1 min (minor), 15.5 min (major).
Using 4d as starting material, 5d was isolated as a 4.7:1 mixture of olefin isomers favoring the E isomer. Using 4e as starting material, the product was isolated as a 2:1 mixture of isomers favoring the Z isomer. NMR data are reported for the 4.7:1 mixture. The E and Z isomers were assigned on the basis of a 2D $^1$H-$^1$H NOESY experiment. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.67 (d, 2H, $J = 8.4$ Hz), 7.30-7.25 (m, 2H), 5.02-4.96 (m, 1H), 4.45-4.35 (m, 1H), 3.30-3.20 (m, 1H), 3.17-3.09 (m, 1H), 2.41 (s, 3H), 2.24-2.14 (m, 0.18H), 2.07-1.87 (m, 0.18H), 1.91 (q, 1.48H, $J = 7.4$ Hz), 1.76 (ddd, 0.82H, $J = 12.6, 8.4, 1.2$ Hz), 1.80-1.70 (m, 0.18H), 1.67 (d, 2.46H, $J = 0.9$ Hz), 1.62 (d, 0.54H, $J = 1.2$ Hz), 1.47-1.35 (m, 1H), 1.06 (s, 2.46H), 1.05 (s, 0.54H), 1.01 (t, 0.54H, $J = 7.5$ Hz), 0.91 (t, 2.46H, $J = 7.4$ Hz), 0.82 (s, 2.46H), 0.80 (s, 0.54H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 142.8, 137.9, 136.7, 129.2, 127.3, 124.8, 60.9, 57.6, 47.9, 37.4, 32.0, 26.4, 26.0, 21.5, 16.3, 12.0. HRMS (ESI) calc. for [M+H]$^+$ (C$_{18}$H$_{28}$NO$_2$S) 322.1835, found 322.1832. Enantiopurity was determined by HPLC analysis (Chiralpak AD-H
column, 99.5:0.5 hexanes/ethanol, 1 mL/min) \( t_R \) 15.5 min (Z diastereomer, minor enantiomer), 17.0 min (\( E \) diastereomer, minor enantiomer), 18.5 min (Z diastereomer, major enantiomer), 26.4 min (\( E \) diastereomer, major enantiomer).

5f: Isolated as a 78:22 mixture of olefin isomers. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.68-7.64 (m, 2H), 7.28-7.26 (m, 2H), 5.05-5.02 (m, 1H), 5.04 (m, 0.22H), 4.41-4.35 (m, 1H), 3.60 (t, 0.44H, \( J = 6.3 \) Hz), 3.57 (t, 1.56H, \( J = 6.6 \) Hz), 3.25-3.20 (m, 1H), 3.14-3.10 (m, 1H), 2.41 (s, 3H), 2.32-2.25 (m, 0.22H), 1.97-1.92 (m, 1.77H), 1.78-1.73 (m, 1.23H), 1.67 (d, 2.34H, \( J = 0.6 \) Hz), 1.63 (d, 0.66H, \( J = 0.6 \) Hz), 1.61-1.47 (m, 2H), 1.45-1.39 (m, 1H), 1.05 (s, 2.34H), 1.04 (s, 0.66H), 0.892 (s, 7.02H), 0.888 (s, 1.98H), 0.80 (s, 2.34H), 0.79 (s, 0.66H), 0.06 (s, 4.68H), 0.06 (s, 1.32H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 162.3, 142.8, 136.5, 136.1, 129.2, 127.4, 127.2, 62.9, 60.8, 57.3, 48.2, 37.4, 31.4, 28.3, 26.4, 25.9, 23.2, 21.5, 18.3, -5.3. HRMS (ESI) calc. for \([M+H]^+ \) (C\(_{25}\)H\(_{44}\)NO\(_3\)Si) 466.2806, found 466.2805. Enantiopurity was determined by HPLC analysis after deprotection of the alcohol with tetrabutylammonium fluoride (Regis Technologies Whelk-O1 column, 97:3 hexanes/ethanol, 1 mL/min) \( t_R \) 51.4 min (Z diastereomer, minor enantiomer), 57.1 min (Z diastereomer, major enantiomer), 73.1 min (\( E \) diastereomer, minor enantiomer), 83.3 min (\( E \) diastereomer, major enantiomer).
5g: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.67 (d, 2H, $J = 8.1$ Hz), 7.28 (d, 2H, $J = 8.1$ Hz), 5.06 (d, 1H, $J = 8.3$ Hz), 4.30 (app q, 1H, $J = 8.3$ Hz), 3.26 (d, 1H, $J = 9.9$ Hz), 3.20 (d, 1H, $J = 9.9$ Hz), 2.42 (s, 3H), 1.84 (dd, 1H, $J = 12.3$, 7.2 Hz), 1.68 (s, 3H), 1.64 (s, 3H), 1.63-1.45 (m, 7H), 1.25-1.15 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 143.1, 136.6, 133.0, 129.5, 127.7, 126.9, 59.8, 58.3, 48.9, 46.4, 37.2, 36.7, 26.0, 24.9, 24.8, 21.8, 18.3. HRMS (ESI) calc. for [M+H]$^+$ (C$_{19}$H$_{28}$NO$_2$S) 334.1835, found 334.1832. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/ethanol, 1 mL/min) $t_R$ 20.7 min (minor), 28.1 min (major).

5h: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.67 (d, 2H, $J = 8.4$ Hz), 7.28 (d, 2H, $J = 8.4$ Hz), 5.06 (d, 1H, $J = 8.5$ Hz), 4.30 (app q, 1H, $J = 8.5$ Hz), 3.36 (d, 1H, $J = 10.2$ Hz), 3.10 (d, 1H, $J = 10.2$ Hz), 2.42 (s, 3H), 1.83 (dd, 1H, $J = 12.63$, 7.2 Hz), 1.67 (s, 3H), 1.64 (s, 3H), 1.48-1.22 (m, 9H), 1.10-1.00 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 143.1, 136.4, 132.9, 129.5, 127.7, 126.9, 58.7, 57.3, 46.1, 41.4, 36.8, 34.7, 26.2, 26.0, 24.0, 23.2, 23.2, 21.8, 18.3. HRMS (ESI) calc. for [M+H]$^+$ (C$_{19}$H$_{28}$NO$_2$S) 334.1992, found 334.1990. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/ethanol, 1 mL/min) $t_R$ 22.1 min (minor), 28.5 min (major).
**5j:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.93-7.87 (m, 1H), 7.63-7.55 (m, 3H), 4.72-4.62 (m, 2H), 3.57 (dd, 1H, $J$ = 10.5, 0.6 Hz), 3.16 (d, 1H, $J$ = 10.2 Hz), 1.89-1.82 (m, 1H), 1.64 (s, 3H), 1.48-1.44 (m, 1H), 1.39 (s, 3H), 1.09 (s, 3H), 1.07 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 147.7, 135.4, 135.2, 132.8, 131.0, 130.8, 124.5, 123.7, 61.3, 57.8, 47.8, 44.4, 37.5, 25.5, 25.4, 17.7. HRMS (ESI) calc. for [M+H]$^+$ (C$_{16}$H$_{23}$N$_2$O$_4$S) 339.1373, found 339.1376. Enantiopurity was determined by HPLC analysis (Chiralpak IA column, 98:2 hexanes/isopropanol, 1 mL/min) $t_R$ 11.7 min (major), 12.6 min (minor).

**5k:** $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.95-7.81 (m, 4H), 7.44-7.31 (m, 6H), 5.08 (d, 1H, $J$ = 9.3 Hz), 4.39 (app quintet, 1H, $J$ = 8.4 Hz), 3.05-2.88 (m, 2H), 3.16 (d, 1H, $J$ = 10.2 Hz), 1.82 (dd, 1H, $J$ = 12.3, 7.5 Hz), 1.42 (dd, 1H, $J$ = 12.6, 8.7 Hz), 1.36 (s, 3H), 1.17 (s, 3H), 1.04 (s, 3H), 0.92 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 134.3, 133.6, 132.8, 132.6, 132.3, 131.9, 131.5, 131.1, 131.0, 128.3, 128.2, 127.9, 127.7, 60.1, 56.3, 48.6, 38.8, 26.1, 25.2, 16.7. HRMS (ESI) calc. for [M+H]$^+$ (C$_{22}$H$_{29}$NOP) 354.1981, found 354.1988. Enantiopurity was determined by HPLC analysis (Chiralpak IA column, 98:2 hexanes/isopropanol, 1 mL/min) $t_R$ 34.5 min (major), 42.4 min (minor).
1H NMR (300 MHz, CDCl₃) δ 7.79-7.71 (m, 2H), 7.00-6.92 (m, 2H), 5.00 (d, 9H), 4.39 (dd, 1H, J = 16.2, 9 Hz), 3.87 (s, 3H), 3.23 (d, 1H, J = 9.9 Hz), 3.13 (d, 1H, J = 9.9 Hz), 2.30-1.96 (m, 4H), 1.80-1.33 (m, 8 H), 1.05 (s, 3H), 0.79 (s, 3H). 13C NMR (75 MHz, CDCl₃) δ 162.5, 140.4, 131.3, 129.4, 123.3, 113.7, 61.0, 56.8, 55.5, 48.4, 37.3, 36.9, 29.0, 28.2, 27.5, 26.7, 26.4, 26.0. HRMS (ESI) calc. for [M+H]⁺ (C₂₀H₃₀NO₃S) 364.1941, found 364.1934.

Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 98:2 hexanes/ethanol, 1 mL/min) tᵣ 25.0 min (minor), 30.1 min (major).

5m: 1H NMR (300 MHz, CDCl₃) δ 7.88 (d, 2H, J = 8.1 Hz), 7.37 (d, 2H, J = 8.1 Hz), 5.21 (d, 1H, J = 9.6 Hz), 4.17 (d, 1H, J = 9.6 Hz), 3.57 (d, 1H, J = 8.1 Hz), 3.42 (d, 1H, J = 8.1 Hz), 2.46 (s, 3H), 1.83 (s, 3H), 1.76 (s, 3H), 1.08 (s, 3H), 0.94 (s, 3H). 13C NMR (75 MHz, CDCl₃) δ 144.8, 137.4, 132.3, 129.6, 129.4, 119.2, 80.3, 66.4, 47.7, 26.3, 21.7, 21.1, 18.3. HRMS (ESI) calc. for [M+H]⁺ (C₁₆H₂₄NO₃S) 310.1471, found 310.1468. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/ethanol, 1 mL/min) tᵣ 16.3 min (minor), 19.1 min (major).
5n: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.85 (d, 2H, $J = 8.1$ Hz), 7.34 (d, 2H, $J = 8.1$ Hz), 5.13 (d, 1H, $J = 8.7$ Hz), 5.05-4.97 (m, 1H), 4.08-3.96 (m, 2H), 2.44 (s, 3H), 2.41-1.96 (m, 6H), 1.63-1.55 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 144.9, 144.0, 133.4, 129.7, 129.3, 120.4, 70.1, 56.7, 37.0, 36.7, 29.3, 28.4, 27.7, 26.7, 21.8. Enantiopurity was determined by HPLC analysis (Chiralpak AS-H column, 98:2 hexanes/ethanol, 1 mL/min) $t_R$ 14.2 min (minor), 29.7 min (major).

S9: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.11 (d, 1H, $J = 8.8$ Hz), 6.97 (d, 1H, $J = 2.4$ Hz), 6.83 (dd, 1H, $J = 8.8$, 2.4 Hz), 5.06 (d, 1H, $J = 9.2$ Hz), 4.11 (q, 1H, $J = 8.8$ Hz), 3.86 (s, 3H), 3.78 (s, 3H), 3.65 (s, 3H), 3.55 (s, 3H), 3.45 (d, 1H, $J = 15.6$ Hz), 3.23 (dd, 1H, $J = 15.2$, 1.6 Hz), 2.66 (ddd, 1H, $J = 13.6$, 6.4, 1.6 Hz), 2.35 (m, 2H), 2.14 (m, 2H), 1.98 (dd, 1H, $J = 13.6$, 9.2 Hz), 1.61 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.2, 171.4, 153.7, 141.1, 136.9, 133.0, 126.7, 123.1, 110.8, 109.2, 105.8, 100.3, 56.0, 54.3, 52.7, 52.6, 37.0, 36.8, 30.3, 28.9, 28.5, 27.7, 27.6, 26.8. HRMS (ESI) calc. for [M+H]$^+$ (C$_{25}$H$_{32}$NO$_5$) 426.2275, found 425.2279. Enantiopurity was determined by HPLC analysis (Chiralpak IA column, 98:2 hexanes/isopropanol, 1 mL/min) $t_R$ 19.7 min (minor), 27.2 min (major).
S10: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (d, 1H, $J = 2.0$ Hz), 7.23 (dd, 1H, $J = 8.8$, 2.0 Hz), 7.08 (d, 1H, $J = 8.8$ Hz), 5.04 (d, 1H, $J = 9.2$ Hz), 4.11 (q, 1H, $J = 9.6$ Hz), 3.77 (s, 3H), 3.65 (s, 3H), 3.56 (s, 3H), 3.41 (d, 1H, $J = 15.2$ Hz), 3.19 (dd, 1H, $J = 15.6$, 2.0 Hz), 2.65 (dd, 1H, $J = 11.6$, 4.8 Hz), 2.34 (m, 2H), 2.13 (m, 2H), 1.97 (dd, 1H, $J = 13.6$, 9.2 Hz), 1.61 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.0, 171.2, 141.7, 137.6, 136.3, 128.1, 123.7, 122.5, 120.6, 112.0, 110.0, 106.0, 54.1, 52.8, 52.7, 37.0, 36.8, 30.4, 30.3, 28.9, 28.4, 27.7, 27.4, 26.7. HRMS (ESI) calc. for [M+H]$^+$ ($C_{24}H_{29}BrNO_4$) 474.1274, found 474.1280. Enantiopurity was determined by HPLC analysis (Chiralpak IA column, 98:2 hexanes/isopropanol, 1 mL/min) $t_R$ 11.4 min (minor), 21.5 min (major).

S11: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, 1H, $J = 7.6$ Hz), 7.29 (d, 1H, $J = 8.0$ Hz), 7.22 (t, 1H, $J = 7.2$ Hz), 7.13 (t, 1H, $J = 7.6$ Hz), 5.16 (d, 1H, $J = 9.2$ Hz), 4.11 (q, 1H, $J = 8.8$ Hz), 3.81 (s, 3H), 3.69 (s, 3H), 3.59 (s, 3H), 3.51 (d, 1H, $J = 8.4$ Hz), 3.30 (dd, 1H, $J = 15.6$, 2.0 Hz), 2.73 (ddd, 1H, $J = 13.6$, 6.4, 1.6 Hz), 2.02 (dd, 1H, $J = 13.2$ Hz, 9.2 Hz), 1.88 (s, 3H, 1.81 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.3, 171.3, 137.1, 136.2, 133.3, 126.5, 126.4, 121.0, 118.8, 118.0, 108.6, 106.3, 54.2, 52.7, 52.6, 36.3, 31.2, 30.0, 27.5, 25.6, 17.8. HRMS (ESI) calc. for [M+H]$^+$ ($C_{21}H_{26}NO_4$) 356.1856, found 356.1862. Enantiopurity was determined
by HPLC analysis (Chiralpak AS-H column, 99:1 hexanes/isopropanol, 1 mL/min) tₚ 8.4 min (major), 9.7 min (minor).

Supplementary Figure 3. Reaction analyzed by mass spectrometry.

Studies of reaction intermediate by TOF-MS

A one-dram screw cap vial was charged with catalyst S6 (0.01 mmol), substrate 1 (0.1 mmol), and fluorobenzene (0.2 mL). The mixture was stirred for 14 h. 0.1 mL of the mixture was diluted with 1 mL CH₃CN, and this solution was analyzed by TOFMS⁻ (negative mode). A peak fully consistent with the proposed intermediate was observed at 1198.43. The peak had an isotopic distribution in excellent agreement with the theoretical pattern (Supplementary Figure 4). This species was then subjected to further ionization (TOFMSMS⁻), which revealed a fragment corresponding to the regenerated catalyst as the sole negative ion with mass of 892.26 (Supplementary Figure 5).
Supplementary Figure 4. Comparison of measured and theoretical isotopic mass distributions for the observed intermediate.
Supplementary Figure 5. MS/MS of the intermediate ion yields a fragmentation peak corresponding to reformed catalyst.

Details of deuterium labeling experiments

Supplementary Figure 6. Addition of an achiral dithiophosphinic acid across an olefin proceeds with syn stereoselectivity.
A mixture of acenapthylene (tech. grade, 75%, 30 mg, 0.2 mmol) and diphenyldithiophosphinic acid (25 mg, 0.1 mmol) was dissolved in a 1:1 mixture of CDCl$_3$/D$_2$O (1.5 mL total). The mixture was shaken for about 5 mins then was allowed to stand without stirring at rt for 48 h. The CDCl$_3$ layer was removed and loaded directly onto a silica gel column. The product was eluted with 20:1 hexanes/EtOAc to afford 8 mg of a white solid (20% yield). An experiment without D$_2$O was also performed to obtain a protiated reference compound. Dithiodiphenylphosphinic acid was chosen because it is an achiral dithioacid that avoids complications arising from the generation of diastereomers when using a chiral catalyst; it is also commercially available in high purity (Alfa Aesar). Alternative achiral catalysts such as diphenyl dithiophosphate ((PhO)$_2$PSSH) or diethyl dithiophosphate ((EtO)$_2$PSSH) are much more hydrolytically labile and were not suitable for the D$_2$O conditions.

**Protiated compound 7**: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.10-7.98 (m, 4H), 7.67-7.35 (m, 10H), 7.20 (d, 1H, $J = 6.9$ Hz), 5.42 (ddd, 1H, $J = 12.9$ (H-31P coupling), 7.8 (cis coupling), 3.0 (trans coupling) Hz), 3.82 (dd, 1H, $J = 18.0$ (geminal coupling), 8.1 (cis coupling) Hz, proton trans to dithiophosphinate), 3.40 (dd, 1H, $J = 18.0$, 3.0 (trans coupling) Hz, proton cis to dithiophosphinate).

**Deuterated compound 7**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10-7.98 (m, 4H), 7.67-7.35 (m, 10H), 7.20 (d, 1H, $J = 6.9$ Hz), 5.42 (dd, 1H, $J = 12.8$, 8.0 Hz), 3.82 (d, 1H, $J = 18.0$, 8.4 Hz, trans to dithiophosphinate). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 132.0, 132.0, 131.8, 131.7, 131.6, 131.5, 131.2, 128.8, 128.7, 128.7, 128.6, 128.2, 128.2, 128.1, 77.2, 47.4. $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 63.0. The cis and trans protons were assigned based on the well-established coupling constant ranges of monosubstituted acenaphthenes that arise from the rigidity of the system:
protons in a \textit{cis} relationship have large vicinal coupling constants (6–8 Hz), while \textit{trans} protons have small vicinal coupling constants (2–3 Hz)\textsuperscript{37–39}.

\begin{center}
\includegraphics[width=0.8\textwidth]{reaction_diagram}
\end{center}

**Supplementary Figure 7.** Dithiophosphoric acid-promoted reaction of a cyclic substrate proceeds with predominant \textit{cis}-1,4-stereoselectivity.

Cyclic substrate \textbf{8} (3.2 mg, 0.01 mmol) was reacted with racemic dithiophosphoric acid \textbf{9} (5.5 mg, 0.01 mmol) in 1.5 mL of 1:1 CDCl\textsubscript{3}/D\textsubscript{2}O. The mixture was shaken for about 5 mins then was allowed to stand without stirring at 50 °C for 48 h. The CDCl\textsubscript{3} layer was removed and loaded directly onto a silica gel column. The product was eluted with 20:1 hexanes/EtOAc to afford 2.0 mg of a colorless oil (63% yield). An experiment without D\textsubscript{2}O was also performed to obtain a protiated reference compound.

\begin{center}
\includegraphics[width=0.8\textwidth]{protiated_compound}
\end{center}

**Protiated compound 10:** \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 7.80-7.77 (m, 2H, H\textsubscript{D}), 6.96-6.93 (m, 2H), 5.66-5.63 (m, 1H), 5.53-5.50 (m, 1H), 3.87 (s, 3H), 3.15 (d, 1H, J = 8.5 Hz), 3.04 (d, 1H, J = 9.0 Hz), 2.62-2.57 (m, 1H, H\textsubscript{C}), 2.17-2.08 (m, 1H, H\textsubscript{A}), 1.95-1.89 (m, 1H, H\textsubscript{B}), 1.87-1.73 (m, 4H), 1.57-1.47 (m, 1H), 1.09 (s, 3H), 1.00 (s, 3H). \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) δ 162.6, 133.5,
Specific protons were assigned on the basis of 2D COSY, HMQC, and NOESY experiments. The NOESY spectrum revealed correlations between H_d and H_c and between H_c and H_a, and it lacked correlations between H_d and any other protons on the cyclohexene ring or between H_c and H_b.

**Deuterated compound 10:** ^1^H NMR (500 MHz, CDCl₃) δ 7.80-7.77 (m, 2H, H_D), 6.96-6.93 (m, 2H), 5.66-5.63 (m, 1H), 5.53-5.50 (m, 1H), 3.87 (s, 3H), 3.15 (d, 1H, J = 8.5 Hz), 3.04 (d, 1H, J = 9.0 Hz), 2.62-2.57 (m, 0.93H, H_C), 2.17-2.08 (m, 0.19H, H_A), 1.91-1.70 (m, 5H, H_B was no longer well enough resolved from the rest of the multiplet), 1.57-1.47 (m, 1H), 1.09 (s, 3H), 1.00 (s, 3H). HRMS (ESI) calc. for [M+H]^+ (C₁₈H₂₅²H N O₃ S) 337.1691, found 337.1692.

**Removal of the nosyl group from product 5j**

To a 1-dram screw cap vial equipped with a magnetic stir bar was added sequentially sulfonamide 5j (30.0 mg, 0.088 mmol, 1.0 equiv), thiophenol (25.3 mg, 0.27 mmol, 3.0 equiv), anhydrous K₂CO₃ (49.0 mg, 0.35 mmol, 4.0 equiv), 1,3,5-trimethoxybenzene (internal NMR standard) and CD₃CN (1.0 mL). A t = 0 ^1^H NMR spectrum was recorded for calibration of the internal standard. The mixture was heated to 50 ºC and allowed to stir for 2 h. After the elapsed time, TLC indicated complete consumption of the starting material. ^1^H NMR indicated that the yield of desired product was 86%. The reaction mixture was diluted with Et₂O (10 mL) and washed with water (2 × 20 mL). The organic layer was then extracted with 3N HCl (2 × 20 mL).
The combined acidic aqueous layer was made basic by the addition of 10% NaOH until pH = 11. The product was subsequently extracted with Et₂O (2 × 10 mL) and the combined ethereal extracts was dried over anhydrous MgSO₄, filtered and concentrated in vacuo to give 6.9 mg (51 % isolated yield) of the desired product S7 as a yellow oil (Rf = 0.1 in 5% MeOH/CH₂Cl₂). The product was found to be somewhat volatile.

$^1$H NMR (400 MHz, CDCl₃) δ 5.13 (d, 1H, $J = 8.4$ Hz), 3.92 (q, 1H, $J = 8.4$ Hz), 2.75 (d, 1H, $J = 10.4$ Hz), 2.62 (d, 1H, $J = 10.0$ Hz), 1.70 (s, 3H), 1.67 (s, 3H), 1.08 (s, 3H), 1.08 (s, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ 133.2, 128.6, 60.7, 56.4, 48.4, 39.5, 28.6, 27.8, 25.7, 18.1.

**Supplementary Figure 9.** Mass spectrometry analysis of hydroarylation reaction mixture.
Supplementary Figure 10. Comparison of measured and theoretical isotopic mass distributions for the observed intermediate of hydroarylation reaction.

Supplementary Figure 11. X-ray crystal structure of compound S10.
Experimental details for X-ray structural determination

A colorless plate 0.12 x 0.08 x 0.04 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using phi and omega scans. Crystal-to-detector distance was 60 mm and exposure time was 5 seconds per frame using a scan width of 1.0°. Data collection was 96.8% complete to 67.00° in θ. A total of 17687 reflections were collected covering the indices, -10<=h<=9, -13<=k<=13, -15<=l<=15. 3881 reflections were found to be symmetry independent, with an R_int of 0.0312. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P-1 (No. 2). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-97) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.
| **Supplementary Table 1. Crystal data and structure refinement for compound S10.** |
|----------------------------------|----------------------------------|
| X-ray ID                         | toste34                          |
| Sample/notebook ID               | JW-04-146SC                      |
| Empirical formula                | C24 H28 Br N O4                  |
| Formula weight                   | 474.38                           |
| Temperature                      | 100(2) K                         |
| Wavelength                       | 1.54178 Å                        |
| Crystal system                   | Triclinic                        |
| Space group                      | P-1                              |
| Unit cell dimensions             | $a = 8.5353(7)$ Å, $\alpha = 65.561(4)^\circ$.
|                                 | $b = 11.5050(8)$ Å, $\beta = 78.907(5)^\circ$.
|                                 | $c = 12.9696(10)$ Å, $\gamma = 76.104(5)^\circ$.
| Volume                           | 1119.30(15) Å³                   |
| Z                                | 2                                |
| Density (calculated)             | 1.408 Mg/m³                      |
| Absorption coefficient           | 2.745 mm$^{-1}$                  |
| F(000)                           | 492                              |
| Crystal size                     | 0.12 x 0.08 x 0.04 mm$^3$        |
| Crystal color/habit              | colorless plate                  |
| Theta range for data collection  | 3.76 to 67.57°                   |
| Index ranges                     | $-10 \leq h \leq 9, -13 \leq k \leq 13, -15 \leq l \leq 15$ |
| Reflections collected            | 17687                            |
| Independent reflections          | 3881 [R(int) = 0.0312]            |
| Completeness to theta = 67.00°   | 96.8 %                           |
| Absorption correction            | Semi-empirical from equivalents  |
| Max. and min. transmission       | 0.8981 and 0.7341                |
| Refinement method                | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters   | 3881 / 0 / 274                   |
| Goodness-of-fit on F$^2$         | 1.084                            |
| Final R indices [I>2sigma(I)]    | R1 = 0.0378, wR2 = 0.0953        |
| R indices (all data)             | R1 = 0.0412, wR2 = 0.0980        |
| Largest diff. peak and hole      | 0.918 and -0.266 e.Å$^{-3}$      |
31. Sattely, E. S., Meek, S. J., Malcolmson, S. J., Schrock, R. R. & Hoveyda, A. H. Design and stereoselective preparation of a new class of chiral olefin metathesis catalysts and application to enantioselective synthesis of quebrachamine: catalyst development inspired by natural product synthesis. *J. Am. Chem. Soc.* **131**, 943–953 (2009).

32. Cheon, C. H. & Yamamoto, H. A Brønsted acid catalyst for the enantioselective protonation reaction. *J. Am. Chem. Soc.* **130**, 9246–9247 (2008).

33. Nakashima, D. & Yamamoto, H. Design of chiral N-triflyl phosphoramidate as a strong chiral Brønsted acid and its application to asymmetric Diels–Alder reaction. *J. Am. Chem. Soc.* **128**, 9626–9627 (2006).

34. Zhang, Z., Bender, C. F. & Widenhoefer, R. A. Gold(I)-catalyzed dynamic kinetic enantioselective intramolecular hydroamination of allenes *J. Am. Chem. Soc.* **129**, 14148–14149 (2007).

35. Laird, T., Ollis, W. D. & Sutherland, I. O. Base catalysed rearrangements involving ylide intermediates. Part 7. The rearrangements of allyl(pentadienyl)- and propynyl(pentadienyl)ammonium cations. The [5,4] sigmatropic rearrangement. *J. Chem. Soc., Perkin Trans. 1*, 2033–2048 (1980).

36. LaLonde, R. L., Sherry, B. D., Kang, E. J. & Toste, F. D. Gold(I)-catalyzed enantioselective intramolecular hydroamination of allenes. *J. Am. Chem. Soc.* **129**, 2452–2453 (2007).

37. Eisch, J. J. & Fichter, K. C. Organometallic compounds of Group III. 40. Kinetic control and locoselectivity in the electrophilic cleavage of allylic aluminum compounds:
reactions of acenaphthenylaluminum reagents with carbonyl substrates. J. Org. Chem. 49, 4631–4639 (1984).

38. Hunter, D. H., Lin, Y. T., McIntyre, A. L., Shearing, D. J. & Zvagulis, M. Elcb reaction of 1-methoxyacenaphthene. I. Nature of the carbanion-forming step. J. Am. Chem. Soc. 95, 8327–8333 (1973).

39. Gironès, J., Duran, J., Polo, A. & Real, J. Enantioselectivity in the catalytic hydroesterification of acenaphthylene: direct evidence of the racemization of Pd\textsuperscript{II}-alkyl species by a degenerate substitution equilibrium with Pd\textsuperscript{0}L\textsubscript{n}. Chem. Commun. 1776 (2003).

Supplementary Data: Copies of NMR and HPLC spectra.
AV-400 QNP 31P Starting parameters. Trimethyl phosphate.
Dual C-H probe proton starting parameters 7/23

![NMR Spectrum]

**NAME:** VHI-1-95-diene-substrate

**PROCNO:** 1

**Date:** 20100223

**Time:** 15:58

**INSTRON:** nvr-500

**PROPHOS:** 9 mm Dual 13C

**PULPROG:** gg10

**TD:** 65336

**SOVVENT:** CDCl3

**NI:** 8

**DS:**

**SNR:** 6172.839 Hz

**FIDRES:** 0.094190 Hz

**AQ:** 5.3986500 sec

**DI:** 81.000 usec

**DE:** 6.80 usec

**TE:** 293.8 K

**GCL:** 0.200000000 sec

**TD0:** 1

**--------- CHANNEL F1 ---------

**MUSIC:** 1H

**F1:** 31.00 usec

**PUL1:** -1.00 dB

**FLW:** 25.9953241 W

**SPW1:** 205.111853 Hz

**SI:** 32768

**SV:** 300.1300003 Hz

**WRW:** 0

**S2B:** 0

**LB:** 0.30 Hz

**GB:** 0

**PC:** 0.00
AV-300 Dual C-H probe proton starting parameters 7/23/03 RN.

NAME: VRT-1-124B
EXPNO: 1
PROCNO: 1
Data: 20100120
Time: 10:02
INSTRUM: av-300
PROBHD: 5 mm Dual 13C/1H
PULPROG: 2030
TD: 65236
SOLVENT: CDCl3
NS: 10
DS: 0
SNR: 6172.839 Hz
FIDRES: 0.094190 Hz
AQ: 5.3084660 sec
AX: 6
DN: 81.000 us
DE: 6.00 us
TB: 294.3 K
D1: 0.2000000 sec
D2D: 4

Channel: 1
NUC1: 1H
PI: 11.00 us
PL1: -3.00 dB
PL1W: 25.55555555 MHz
SP1: 300.13318663 MHz
SI: 12768
SP: 300.13318663 MHz
W1W: 50 MHz
SSB: 0
LB: 0.30 Hz
GR: 0
PC: 4.00

ppm
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME       VRT-1-124B-13C
EXNO       1
PROCNO      1
Date        20100120
Time        10.03
INSTRUM      av-300
PROBHD   5 mm Dual 13C/
FUPROR      sspp30
TD         65536
SOLVENT    CDC33
NS       23
DS       0
SNR       17985.61 Hz
FIDRES      0.294410 Hz
AQ        1.8298908 sec
RG       32.9638
DN        29.800 usec
DE       6.00 usec
TD       294.3 K
DD       1.00000000 sec
DD1      0.03000000 sec
TD0       40

======== CHANNEL f1 ========
NUC1      13C
F1        10.50 usec
PL1       0.00 dB
PL1W    32.65452194 W
SF01      75 4760505 MHz

======== CHANNEL f2 ========
CPDPRG2   waltz
NUC2      1H
FCPD2     120.00 usec
PL2       -3.00 dB
PL12      17.76 dB
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME VRT-1-124C-13C
EXPRC 1
PROCNO 1
Date_ 20100220
Time 10:06
INSTRUM av-300
PROBND 5 mm Dual 13C/
PULPROG zgq30
TD 50.534
SOLVENT CDC13
NS 14
DS 0
GAM 17985.61 Hz
FMRES 0.274438 Hz
AQ 1.8219508 sec
RG 32768
DW 27.800 usec
DE 6.00 usec
TF 294.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 20

======== CHANNEL f1 ========
NUC1 13C
FLJ 10.50 usec
PL1 0.00 dB
PL1W 32.65452194 W
SP01 75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 120.00 usec
PL2 -3.00 dB
PLL2 17.76 dB
AV-300 Dual C-H probe proton starting parameters 7/23/03 RN.
NAME: VRT-1-105C-13C
EXPH0: 1
PROCNO: 1
Date: 20091222
Time: 19:07
INSTRUM: av-300
PROBHD: 5 mm Dual 13C/
PULPROG: zgpg30
TD: 65536
G0: 0
G0: 0
SMH: 17985.611 Hz
FIDRES: 0.276439 Hz
AQ: 1.8219508 sec
BG: 32768
DW: 27.800 usec
DE: 6.00 usec
TZ: 294.3 us
DI: 1.00000000 sec
D1L: 0.03000000 sec
TD0: 10

======== CHANNEL f1 ========
  NUC1: 13C
  FL1: 10.50 usec
  FL1W: 3265452194
  SP01: 75.4760505 MHz

======== CHANNEL f2 ========
  CPDPRG2: waltz16
  NUC2: 1H
  rCPD2: 120.00 usec
  FL2: -3.00 dB
  FL2: 17.76 dB
AV-300 Dual C-H probe proton starting parameters 7/23/03 RN.

NAME: VRT-1-998
EXPMOD: 1
PROCNO: 1
Date: 20091216
Time: 18:14
INSTRUM: av-300
PROBHLD: 5 mm Dual 13C
PULPROG: zg20
TD: 65536
SOLVENT: CDCl3
NS: 1f
DS: 0
SNR: 6372.839 Hz
FIDRES: 0.094190 Hz
AQ: 5.3084660 sec
RG: 75.0
lw: 81.000 usec
DE: 6.00 usec
TE: 29.4 K
DI: 0.20000000 sec
TD0: 4

====== CHANNEL f1 ======
NECl: 1H
Pl: 11.00 usec
PL: -3.00 dB
PLIM: 25.05936241 w
SP1: 300.131853 MHz
SI: 32768
sp: 300.130000 MHz
NWI: 1
USB: 0
LB: 0.30 Hz
GB: 0
PC: 4.00

--- Chart ---
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME  VRT-1-99B-13C
EXPNO  1
PROCNO  1
Date  20051216
Time  18:16
INSTRUM  av-300
PROBID  5 mm Dual 13C/
PULPROG  zgpg10
TD  65536
SOLVENT  CDC13
NS  47
DS  0
SWH  17985.611 Hz
PTDRRS  0.274439 Hz
AQ  1.8219508 sec
RG  32768
DW  27.800 usec
DE  6.00 usec
TE  294.1 K
D1  1.0000000 sec
D11  0.03000000 sec
TDO  40

======== CHANNEL f1 ========
NUC1  13C
F1  10.50 usec
FL1  0.00 dB
FL1W  32.65452194 W
SF01  75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2  wait16
NUC2  1H
ECPD2  120.00 usec
PL2  -3.00 dB
PL12  17.76 dB
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME  VRT-1-103F-Feb-2
EXPNUM  1
PROCNO  1
Date_  20100202
Time  15.25
INSTRUM  av-300
PROBMD  5 mm Dual 13C/
PULPROC  zg30
TD  65516
SOLVENT  CDC13
NS  7
DS  D
S1W  6172.839 Hz
S1FS  0.094130 Hz
AQ  5.306660 sec
RG  45.3
DW  0.000000 sec
DE  0.000000 sec
TR  293.9 K
DI  0.2000000 sec
TDG  4

======== CHANNEL f1 ========
NUCL  1H
FI  21.00 usec
FL1  -2.00 dB
FL1W  25.05936241 W
FPO1  300.1318533 MHz
ST  32766
SF  300.1300000 MHz
WOW  EM
SSB  0
LB  1.50 Hz
GB  0
FC  1.40
**NAME**  VRT-1-105F-Feb-2-13C
**EXPRO**  1
**PROENO**  1
**Date_**  20100202
**Time**  15.28
**INSTRUM**  av-300
**PROINO**  5 mm Dual 13C/
**PULPROM**  zgpg30
**TD**  65536
**SOLVENT**  circl3
**NS**  46
**DS**  0
**SN**  17985.61 Hz
**FIDRES**  0.274439 Hz
**AQ**  1.8219508 sec
**E5**  32768
**DW**  27.800 usec
**DE**  6.00 usec
**TE**  294.1 K
**D1**  1.0000000 sec
**D11**  0.03000000 sec
**TD0**  60

======= CHANNEL f1 =======
**NUC1**  13C
**P1**  10.50 usec
**PL1**  0.00 dB
**PL1W**  32.65452194 W
**SF01**  75.476000 MHz

======= CHANNEL f2 =======
**CPDPRG2**  walter16
**NUC2**  1H
**FCPD2**  120.00 usec
**PL2**  -3.00 dB
**PL12**  17.76 dB
AV-300 Dual C-H probe carbon starting parameters 7/23/03

NAME   VRT-1-122A-cyclopentyl-tosyl

EXPNR   1
PROCNO   1
Date_   20100115
Time    19.4
INSTRUM  av-300
FREQMD   5 mm Dual 13C
PULPROG   smpg30
TD      65536
SOLVENT    CDC13
NS     31
DS      0
SWH    17395.611 Hz
FIDRES  0.274439 Hz
AQ     1.0219508 sec
B1     32768
DW    27.800 ussec
SE      6.00 ussec
TE    294.4 #
D1   1.00000000 sec
D11  0.03000000 sec
TD0   20

======== CHANNEL f1 ========
NUC1    1H
P1     10.50 usec
PL1    0.00 dB
PL1W   32.6552194 W
SFC1   75.4760505 MHz

======== CHANNEL f2 ========
CPUPRD2  waltz16
NUC2    1H
PCTD2  120.00 usec
PL2    -3.00 dB
PL12   17.76 dB

ppm
-300 Dual C-H probe proton starting parameters 7/23/03 RN.

NHTs

4h

NHTs

4h

9 8 7 6 5 4 3 2 1 0 ppm

2.159 2.240 1.000 1.018 3.073 2.149 3.270 2.045 3.232 1.369
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME VRT-1-122B-cyclohexyl-tosyla
EXPNO 1
PROCNO 1
Date_ 20100115
Time 13.42
INSTRUM av-300
PROBND 5 mm Dual 13C/
PULPROG zpg30
TD 62336
SOLVENT CCl3
NS 32
DS 0
SWX 17985.611 Hz
P1DRES 0.274439 Hz
AG 1.8219508 sec
NG 32768
DW 27.890 usec
DE 6.00 usec
TD 294.4 K
T1 1.00000000 sec
TD1 0.03000000 sec
TD0 20

======== CHANNEL f1 ========
NUC1 13C
FL 10.50 usec
PL1 0.00 dB
PL1W 32.65452194 W
SPQ1 75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCP2 120.30 usec
PL2 -3.00 dB
PL2 17.76 dB

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
Dual C-H probe proton starting parameters 7/23

NAME: VRT-15-119
EXPMO: 1
PROCNO: 1
Date: 20100220
Time: 15:54
_INSTRUM_ av-300
PROHBD 5 mm Dual 1H-
PULPROG zg30
TC: 65536
SOLVENT: CDC13
NS: 4
DS: 0
SNH: 6172.839 Hz
PDRES 0.594190 Hz
AQ: 5.3084660sec
RG: 8
DW: 61.000 usec
DR: 6.000 usec
TR: 293.8 K
DI: 0.20000000 sec
TD0: 1

=*=*=*=*= CHANNEL f1 =*=*=*=*==

NUCL: 1H
FI: 11.000 usec
PL: -3.00 dB
PL1W 25.05936241 W
SFOL: 300.1318533 MHz
SI: 32768
SF: 300.1300030 MHz
WAV: EM
S2B: 0
LS: 0.30 Hz
GB: 0
PC: 4.00

[Chemical structure image]
MeO

S

NH

41

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

AV-300 Dual C-H probe Carbon starting parameters 7/23/03
**Dual C-H probe proton starting parameters 7/23**

| NAME   | VRT-15-157        |
|--------|-------------------|
| EXPNO  | 1                 |
| PROCNO | 1                 |
| Date   | 20100220          |
| Time   | 16:00             |
| INSTRUM| AV-520            |
| PROBND | 5 mm Dual 1H/13C |
| PULPROG| zg50              |
| TD     | 65316             |
| SOLVENT| CDCl3            |
| NS     | 4                 |
| DS     | 0                 |
| SWH    | 6172.839 Hz       |
| FIDRES | 0.094150 Hz       |
| AQ     | 5.3084600 sec     |
| TRG    | 8                 |
| DM     | 81.000 usec       |
| TE     | 293.8 K.          |
| D1     | 0.20000000 usec   |
| TDO    | 1                 |

**-------- CHANNEL 'f1' --------**

| NUC1  | 1H                |
| P1    | 11.00 usec        |
| PL1   | -3.00 dB          |
| PLW   | 21.05936241 W     |
| SPFO1 | 300.1319533 MHz   |
| SI    | 32768             |
| SP    | 300.1305032 MHz   |
| NDM   | 0                 |
| SSB   | 0                 |
| LB    | 0.30 Hz           |
| Gp    | 0                 |
| PC    | 4.00              |

![Chemical structure diagram](image)
AV-300 Dual C-H probe proton starting parameters 7/23/03 RN.

NMPD  VRT-1-456_SM-1H
PFXNO  1
PROCNO  1
Date...  20100125
Time...  15:00
INSTRUN av-300
PRORNO  5 mM Dual 13C/
PULPROC zg10
TD  65536
SOLVENT CCl4
NS  7
DS  0
SWH  6172.839 Hz
FIDRES  0.094190 Hz
AQ  5.3084660 sec
RG  8
DW  81.000 usec
DE  6.00 usec
TE  283.8 K
EI  0:200000000 sec
TD0  4

= CHANNEL f1 =
Nuc1  1H
Fl  11.00 usec
PLL -3.00 dB
PL1W 25.05936241 w
SP01 300.1318533 MHz
SI  32768
SF  300.000035 MHz
KOW BB
SSB  0
LR  0.30 Hz
GB  0
FC  4.00

---

ppm
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME      VRT-1-145B_SM-13C
EXPRO     1
PROCNO    1
Date_     20100325
Time_     15:01
INSTRUM    av-300
PROBND    5 mm Dual 13C/
PULPROG   zzpg30
TD         55536
SOLVENT   CDC13
NS         17
DS         0
SNR      17985.61 Hz
FIDRES    0.274439 Hz
AQ      1.8219508 sec
RG         38768
DW         27.800 usec
DE         6.00 usec
TS       293.8 K
D1      1.00000000 sec
D11    0.03000000 sec
TD0       444

====== CHANNEL F1 ======
NOC1      13C
P1       10.50 usec
PL1      0.00 dB
PL1W    32.65452194 W
SPD1    75.4760505 MHz

====== CHANNEL F2 ======
CPDPRM2   watt:16
NOC2      1 Hz
PCFD2   120.00 usec
PL2      -3.00 dB
PL22     17.76 dB
AV-300 Dual C-H probe proton starting parameters 7/23/03 kW.

NAME:  VRT-1-134A
EXPN:  1
PROCNO:  1
Date:  20100204
Time:  11:20
INSTRUM:  av-300
PROBID:  5 mm Dual 13C/
PULPROG:  zg30
TD:  65536
SOLEVENT:  CDC13
NS:  9
DS:  0
SMR:  6172.833 Hz
D1RRES:  0.004190 Hz
AQ:  0.3084660 sec
MO:  114
DW:  81,000 usec
DE:  6.00 usec
TE:  293.9 K
DI:  0.0000000 sec
TD0:  4

====== CHANNEL f1 ======
NUC1:  1H
FH:  11.00 usec
FL:  -3.00 dB
FLIN:  25.05932421 kHz
SFO1:  300.1318533 MHz
CI:  32768
SF:  300.1300000 MHz
WD:  0.1 kHz
SSB:  0
LB:  0.30 Hz
GB:  0
PC:  4.00

ppm

2.05  2.50  1.00  1.02  2.06  3.10  7.49  1.18  3.15  3.13
AV-300 Dual C-H probe Carbon starting parameters 7/23/08

NAMES VXT-1-134A-13C
EXPN0 1
PROCNO 1
Date_ 20100204
Time 11.22
INSTRUM av-300
PROBID 5 mm Dual 13C/
PULPROG spg930
TD 695.34
SOLVENT CDCl3
Nq 35
DS 0
SNR 17985.61 Hz
FIDRES 4.276439 Hz
AQ 1.8219508 sec
BG 32768
KW 27.800 usec
DE 6.00 usec
TE 293.9 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1000

============= CHANNEL f1 =============
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
PL1W 32 6545194 W
SF01 75.4760505 MHz

============= CHANNEL f2 =============
CPDPROG waltz16
NUC2 1H
Pc02 120.00 usec
PL2 -3.00 dB
PL12 17.76 dB
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME: VRT-1-139-3
EXPNO: 1
PROCNO: 1
Date: 20100215
Time: 14:29
INSTROM: av-300
PRLID: 5 mm Dual 13C/
PULPROC: zg30
TD: 65516
SOLVENT: CCl4
MS: 7
DS: 0
SNW: 6172.839 Hz
FIDRES: 0.094190 Hz
AQ: 5.3084660 sec
RG: 8
DW: 81.000 usec
ME: 6.000 usec
TE: 293.9 K
TD: 0.20000000 sec
TTD: 4

------------ CHANNEL f1 ------------
NUC1: 1H
P1: 11.70 usec
PL1: -3.00 dH
FLW1: 25.05936241 W
SF1: 300.1318533 MHz
SI: 32768
SF: 300.1300064 MHz
WEDW: 8M
SSB: 0
LB: 1.50 Hz
GB: 0
RC: 1.40

ppm
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME: 13C
EXNO: 1
PROCNO: 1
Date: 20100015
Time: 14.30
INSTRUM: AV-300
PROBE: 1 mm Dual 13C
FULLPRED: zgpe10
TD: 65516
SOLVENT: CDCl3
NS: 45
DS: 0
SNH: 17995.411 Hz
FDMRBS: 0.27443 Hz
AQ: 1.8215905 sec
RG: 32768
DW: 27.800 usec
DE: 6.60 usec
TS: 293.9 K
D1: 1.080000000 sec
D11: 0.030000000 sec
TD0: 4444

======== CHANNEL f1 ========
NUC1: 13C
PL: 10.50 usec
PL1: 0.00 dB
PL1W: 32.65452194 W
SFO1: 75.4760505 MHz

======== CHANNEL f2 ========
CPD2: waltz16
NUC2: 1H
PCPD2: 120.60 usec
PL2: -3.00 dB
PL12: 17.76 dB
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

| Parameter | Value |
|-----------|-------|
| NAME      | VRT-1-132A-13C |
| EXPNO     | 1     |
| PROCNO    | 1     |
| December  | 20100204 |
| Time      | 13.52 |
| INSTRUM    | av-300 |
| PROBED    | 5 mm Dual 13C/ |
| PULPROG   | zgpg30 |
| TD        | 655.34 |
| SOLVENT   | CMC13 |
| NS        | 21    |
| DS        | 0     |
| SWH       | 17985.611 Hz |
| FIDRES    | 0.274439 Hz |
| AQ        | 1.8219088 sec |
| RG        | 32769 |
| DW        | 27.800 usec |
| DS        | 6.00 usec |
| TE        | 294.0 K |
| DI        | 1.00000000 usec |
| D11       | 0.030000000 usec |
| TDO       | 44    |

====== CHANNEL f1 ======

| Parameter | Value |
|-----------|-------|
| NUC1      | 13C   |
| PL        | 10.50 usec |
| PL1       | 0.00 da |
| PL1W      | 32.65452194 M |
| SP01      | 75.4765055 MHz |

====== CHANNEL f2 ======

| Parameter | Value |
|-----------|-------|
| Chympg2   | waltz16 |
| NUC2      | 1H    |
| PCYD2     | 120.60 usec |
| PL2       | -3.60 da |
| PL12      | 17.76 da |

ppm

![NMR spectrum](image)
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME   VRT-1-137E-13C  
EXPNO   1  
PROCNO  1  
Date_   20100218  
Time    15.19  
INSTRUM av-300  
PROBID  5 mm Dual 13C/  
PULPROG zppp30  
TU      65536  
SOLVENT CDCl3  
NS      73  
DS      0  
SW1    17985.611 Hz  
FIDRES  0.278439 Hz  
AQ      1.62192508 sec  
AG      32768  
DW      27.800 usec  
DE      6.00 usec  
TS      293.8 K  
P1      1.00000000 sec  
P1L     0.00000000 sec  
TDO     444  

==== CHANNEL f1 ======
NUC1    13C  
P1       10.50 usec  
PL1      0.00 db  
PL1W     32.65452194 W  
SFQ1     75.4760505 MHz  

==== CHANNEL f2 ======
CPDPRG2 waltz16  
NUC2    1H  
PCPD2   120.00 usec  
PL2     -3.00 db  
PL12    17.76 db
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

**NMR**
- VRT-1-139-10
- EXPRO 1
- PROCNO 1
- Date 20100215
- Time 14:16
- INSTRUM av-300
- PROBID 5 mm Dual 13C/
- PULPROG b250
- TD 65536
- SOLVENT CDCl3
- NS 16
- DS 0
- SNH 6172.829 Hz
- FIDRES 0.994190 Hz
- AQ 5.3084660 sec
- RG 8
- DW 31.000 usec
- DE 5.00 usec
- TE 293.9 K
- DI 0.20000000 sec
- TOO 4

**=CHANNEL f1===**
- NUC1 1H
- P1 11.00 usec
- FL1 -3.00 dB
- FL1W 25.0556241 W
- SPO1 300.1318533 MHz
- SL 32768
- SF 300.1300030 MHz
- WWN 8M
- SSB 0
- LB 1.50 Hz
- CB 0
- FC 1.40

**ppm**
0.22 0.99 1.99 2.03 2.99 3.09 5.86
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME: VRT-1-133B-13C
EXPMNO: 1
PROCNO: 1
DATE: 20100204
TIME: 19:30
INSTRUM: av-300
PROBND: 5 mm Dual 13C/
FURPBD: zpgpq3D
TD: 65536
SOLVENT: CDC13
NS: 44
DS: 0
SNH: 17985.611 Hz
PDRES: 0.274439 Hz
AQ: 1.8319508 sec
BG: 32768
DM: 27.800 usec
DR: 6.00 usec
TE: 294.0 K
DI: 1.0000000 sec
D11: 0.0300000 sec
TD0: 4444

======== CHANNEL f1 ========
NDC1: 13C
F1: 10.50 usec
PL1: 0.00 dB
PL1W: 32.65452194 W
SPOL: 75.4760195 MHz

======== CHANNEL f2 ========
CPEP2Z: wait1e6
NDC2: 1H
CP2D2: 120.00 usec
PL2: 3.00 dB
PLL2: 17.76 dB

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME        VRT-1-133A-13C
EXPNO       1
PROCNO      1
Date         20100204
Time         19.24
INSTRUM      av-300
PROBHD       5 mm Dual 15°/
PULPROG      zpg316
TD           65536
SOLVENT      CDCl3
NS           43
DS           0
SNR          17985.61 Hz
FIDSNR       0.274459 Hz
AQ           1.8219508 sec
PG           30768
DW           27.800 ussec
DE           6.00 usec
TE           296.0 K
DI           1.00000000 sec
D11          0.03000000 sec
TDD          444

---------- CHANNEL f1 ----------
NDEC1        3C
P1           10.50 usec
PL1          0.00 db
PL1W         32.6542194 W
SPOL         75.4760505 MHz

---------- CHANNEL f2 ----------
CPDFO2       wait16
NDC2         1H
PCPD2        120.00 usec
PL2          -3.50 db
PL12         17.76 db

ppm

210  200  190  180  170  160  150  140  130  120  110  100  90  80  70  60  50  40  30  20  10
Dual C-H probe proton starting parameters 7/23

NAME       WRT-1-52H
EXPID      1
PROCNO     1
Date       20180323
Time       11.01
INSTRUM    av-300
PROBID     5 mm Dual 1H/13C/
PULPROD    zg30
TD         65536
SOVIENT    cDCl3
NS         9
DS         0
SNR        6172.839 Hz
FIDRES     0.094190 Hz
AQ         5.3984660 sec
RG         8
DW         81.000 ussec
TE         6.000 ussec
TB         293.9 K
DI         0.20000000 sec
TD0        444

-------- CHANNEL 1 --------
NUC1       1H
DI1        11.00 ussec
PL1        -3.00 ussec
PL1W       23.05936241°
SPG1       300.1318933 MHz
SI         32768
SF         300.1300009 MHz
WDM        EM
SSB        0
LB         0.30 Hz
UM         0
PC         4.00
NAME    VRT-1-152H-13C  
EXPNO    1  
PROCNO   1  
Date_    20100333  
Time     11.02  
INSTROM  av-300  
PROBND   5 mm Dual 13C/ 
PULPROG  zppp30  
TD       65536  
SOLVENT  CDCl3  
NS       44  
DG       0  
SNH      17985.611 Hz  
P1DRES   0.274439 Hz  
AQ       1.8219528 sec  
RG       32768  
DW       27.800 usec  
DE       6.00 usec  
TB       293.9 K  
D1       1.00000000 sec  
D11      0.00000000 sec  
TDO      44  

====== CHANNEL f1 ======
NUC1   13C  
P1      10.50 usec  
PL1     0.00 dB  
PL1W    32.65452194 W  
SP01    75.4762905 MHz  

====== CHANNEL f2 ======
CP2PROG  waltz16  
NUC2   1H  
PCPD2   120.00 usec  
PL2     -1.00 dB  
PL2D    17.76 dB
Dual C-H probe proton starting parameters 7/23

| NAME   | VRT-1-1533 |
|--------|------------|
| EXPCNO | 1          |
| Date   | 20100320   |
| Time   | 14:05      |
| INSTRUM| av-300     |
| PULPROG| 5 mm Dual TC/FG30 |
| TD     | 65516      |
| SOLVENT| CDCl3     |
| NS     | 13         |
| DS     | 0          |
| SW     | 6172.83Hz  |
| FIDRES | 0.094190Hz |
| AQC    | 5.3084660 sec |
| DG     | 88.0000sec |
| DE     | 6.0000sec  |
| TE     | 294.3K     |
| D1     | 0.20000000sec |
| T2D    | 444        |

====== CHANNEL 1 ======
| NUM1  | 11.0000sec |
| P1    | 0.0000utm |
| PL1   | 3.0000ns  |
| PL1W  | 25.05936241w |
| SF01  | 300.1318533MHz |
| SI    | 30768     |
| SF    | 300.1300036MHz |
| WDW   | EM        |
| NEN   | 0         |
| LB    | 0.300Hz   |
| GB    | 0         |
| PC    | 4.00      |

Diagram of chemical structure: 

```
\text{O} \text{Ph}_2
\text{N}
```

Diagram of NMR spectrum with peaks at various ppm values.
AV-300 Dual C-H probe Carbon starting parameters 7/23/03

NAME VR-1-139-13-13C
EXPNO 1
PROCNO 1
Date 20100215
Time 13:33
INSTRUM av-300
PROBHLD 5 mm Dual 13C/
PULPROG zgpg30
TD 65536
SOLVENT CDC13
Rel 37
SNM 4
FIDRES 17995.61 Hz
AQ 0.274439 Hz
BQ 1.8219508 sec
BQ 297.68
DW 27.800 usec
DE 6.00 usec
TE 293.8 K
DI 1.00000000 sec
DL 0.03000000 sec
TD0 10000

======== CHANNEL #1 ========

NUC1 13C
Pl 10.50 usec
PL1 0.00 dB
PL1W 32.65652194 W
SP01 75.4760505 MHz

======== CHANNEL #2 ========

CPDPRG2 waltz16

NUC2 13C
PCPD2 120.00 usec
PL2 -3.00 dB
PL2W 17.76 dB
AVB-400 ZBO Carbon Starting parameters 6/11/03 RN

NAME VRT-2-103-13C
EXENO 1
PROCNO 1
Date  20100928
Time  17.08
INSTRUM AVB-400
PROBHD 5 mm PANBO BB-
FULPROG zggp30
TD  65536
SOLVENT CDC13
NS  35
DS  0
SNH 23980.814 Hz
FIDRES 0.365918 Hz
AQ  1.364756 sec
RG  16384
DW  20.850 usec
DE  6.00 usec
TR  302.5 K
D1  1.50000000 sec
D11 0.03000000 sec
TD0 444

===== CHANNEL f1 =====
NUC1 13C
F1  8.50 usec
FL1 -2.00 dB
F1LW 47.77286148 W
SP1 100.6226298 MHz

===== CHANNEL f2 =====
CP/PRG2 waltz16
NUC2 1H
PCF2 70.00 usec
PL2 -3.00 dB
PL2 16.00 dB
AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN

---

**Diagram:**

A diagram of a molecular structure with labels indicating various chemical shifts and peaks.

---

**Textual Information:**

- **NAME:** 91b-7-102-1
- **RTNO** 1
- **PROCNO** 1
- **Date:** 20100207
- **Time:** 16:56
- **INSTDRUMM:** AVQ-400
- **PROBDN:** 5 mm QNP In/13
- **PULPROG:** zg50
- **TD:** 65336
- **SOLVENT:** CDC13
- **NS:** 8
- **DS:** 0
- **SNR:** 8012.820 Hz
- **FIDRES:** 0.122166 Hz
- **AQ:** 4.0895586 sec
- **RG:** 512
- **CW:** 62.400 use
- **OE:** 6.00 use
- **TE:** 292.7 K
- **D1:** 1.0000000 sec
- **TD0:** 1

---

**CHANNEL f1 =====**

- **MNU1:** 1M
- **P1:** 12.80 use
- **PL1:** 0.20 db
- **PL1W:** 9.545158888 W
- **SP01:** 400.1324700 MHz
- **SL:** 65576
- **SP:** 400.1300142 MHz
- **WCM:** 0
- **SGB:** 0
- **LB:** 0.30 Hz
- **GB:** 0
- **FC:** 4.00

---

**Chemical Shifts:**

- 9.99 ppm
- 8.99 ppm
- 8.10 ppm
- 7.99 ppm
- 7.69 ppm
- 7.65 ppm
- 7.61 ppm
- 7.57 ppm
- 7.53 ppm
- 7.49 ppm
- 7.45 ppm
- 7.41 ppm
- 7.37 ppm
- 7.33 ppm
- 7.29 ppm
- 7.25 ppm
- 7.21 ppm
- 7.17 ppm
- 7.13 ppm
- 7.09 ppm
- 7.05 ppm
- 7.01 ppm
- 6.97 ppm
- 6.93 ppm
- 6.89 ppm
- 6.85 ppm
- 6.81 ppm
- 6.77 ppm
- 6.73 ppm
- 6.69 ppm
- 6.65 ppm
- 6.61 ppm
- 6.57 ppm
- 6.53 ppm
- 6.49 ppm
- 6.45 ppm
- 6.41 ppm
- 6.37 ppm
- 6.33 ppm
- 6.29 ppm
- 6.25 ppm
- 6.21 ppm
- 6.17 ppm
- 6.13 ppm
- 6.09 ppm
- 6.05 ppm
- 6.01 ppm
- 5.97 ppm
- 5.93 ppm
- 5.89 ppm
- 5.85 ppm
- 5.81 ppm
- 5.77 ppm
- 5.73 ppm
- 5.69 ppm
- 5.65 ppm
- 5.61 ppm
- 5.57 ppm
- 5.53 ppm
- 5.49 ppm
- 5.45 ppm
- 5.41 ppm
- 5.37 ppm
- 5.33 ppm
- 5.29 ppm
- 5.25 ppm
- 5.21 ppm
- 5.17 ppm
- 5.13 ppm
- 5.09 ppm
- 5.05 ppm
- 5.01 ppm
- 4.97 ppm
- 4.93 ppm
- 4.89 ppm
- 4.85 ppm
- 4.81 ppm
- 4.77 ppm
- 4.73 ppm
- 4.69 ppm
- 4.65 ppm
- 4.61 ppm
- 4.57 ppm
- 4.53 ppm
- 4.49 ppm
- 4.45 ppm
- 4.41 ppm
- 4.37 ppm
- 4.33 ppm
- 4.29 ppm
- 4.25 ppm
- 4.21 ppm
- 4.17 ppm
- 4.13 ppm
- 4.09 ppm
- 4.05 ppm
- 4.01 ppm
- 3.97 ppm
- 3.93 ppm
- 3.89 ppm
- 3.85 ppm
- 3.81 ppm
- 3.77 ppm
- 3.73 ppm
- 3.69 ppm
- 3.65 ppm
- 3.61 ppm
- 3.57 ppm
- 3.53 ppm
- 3.49 ppm
- 3.45 ppm
- 3.41 ppm
- 3.37 ppm
- 3.33 ppm
- 3.29 ppm
- 3.25 ppm
- 3.21 ppm
- 3.17 ppm
- 3.13 ppm
- 3.09 ppm
- 3.05 ppm
- 3.01 ppm
- 2.97 ppm
- 2.93 ppm
- 2.89 ppm
- 2.85 ppm
- 2.81 ppm
- 2.77 ppm
- 2.73 ppm
- 2.69 ppm
- 2.65 ppm
- 2.61 ppm
- 2.57 ppm
- 2.53 ppm
- 2.49 ppm
- 2.45 ppm
- 2.41 ppm
- 2.37 ppm
- 2.33 ppm
- 2.29 ppm
- 2.25 ppm
- 2.21 ppm
- 2.17 ppm
- 2.13 ppm
- 2.09 ppm
- 2.05 ppm
- 2.01 ppm
- 1.97 ppm
- 1.93 ppm
- 1.89 ppm
- 1.85 ppm
- 1.81 ppm
- 1.77 ppm
- 1.73 ppm
- 1.69 ppm
- 1.65 ppm
- 1.61 ppm
- 1.57 ppm
- 1.53 ppm
- 1.49 ppm
- 1.45 ppm
- 1.41 ppm
- 1.37 ppm
- 1.33 ppm
- 1.29 ppm
- 1.25 ppm
- 1.21 ppm
- 1.17 ppm
- 1.13 ppm
- 1.09 ppm
- 1.05 ppm
- 1.01 ppm
- 0.97 ppm
- 0.93 ppm
- 0.89 ppm
- 0.85 ppm
- 0.81 ppm
- 0.77 ppm
- 0.73 ppm
- 0.69 ppm
- 0.65 ppm
- 0.61 ppm
- 0.57 ppm
- 0.53 ppm
- 0.49 ppm
- 0.45 ppm
- 0.41 ppm
- 0.37 ppm
- 0.33 ppm
- 0.29 ppm
- 0.25 ppm
- 0.21 ppm
- 0.17 ppm
- 0.13 ppm
- 0.09 ppm
- 0.05 ppm
- 0.01 ppm

---
Dual C-H probe proton starting parameters 7/23

NAME    g1h-7-127-2
EXPNO    1
PROCNO   0
Date     20100503
Time     11.54
INSTRUM  ESE-300
PROBMD   5 mm Dual 13C/
FULTRIG  zg30
TD       65336
SOLVENT  CDCl3
NS       32
DS       0
SNH      6172.839 Hz
FIDRES   0.0794190 Hz
AQ       5.3084666 sec
RG       362
DW       61.000 usec
DE       6.000 usec
TE       294.2 K
DI       0.20000000 sec
TDO      0

======== CHANNEL f1 ========
NUCL     1H
P1       11.000 usec
PLL      -2.000 dB
FLW      22.05936241 MHz
SPQ      300.133863 MHz
SI       32768
ST       300.130689 MHz
MDW      EM
SSB      0
LB       0.30 Hz
GB       0
FC       4.00
noesy; δS = 1.2; NS = 2
Sample ID: JW-03-107B
Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-03-107B_AS9901ET_40min.met3-15-2010
11-20-55 PM.dat
Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume: 5 µL

Description: [Data Description]

![Graph with retention times and areas for peaks]

2: 254 nm, 4 nm Results

| Retention Time | Area    | Area Percent |
|----------------|---------|--------------|
| 19.035         | 948215  | 51.478       |
| 22.624         | 893783  | 48.522       |

![Graph with retention times and areas for another set of peaks]

| Retention Time | Area    | Area Percent |
|----------------|---------|--------------|
| 19.035         | 948215  | 51.478       |
| 22.624         | 893783  | 48.522       |
Sample ID: JW-03-107Bchiral
Filename:
C:\EZStart\Projects\Default\Data\JWu\JW-03-107Bchiral_AS9901BT_30min.meet3-16-2010 12-16-41 PM.dat
Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901Et-30min.meet
Injection volume: 5 uL

Description: {Data Description}

![Graph 1]

| Retention Time | Area   | Area Percent |
|----------------|--------|--------------|
| 19.483         | 591399 | 2.547        |
| 22.757         | 2262378| 97.453       |

![Graph 2]

| Retention Time | Area   | Area Percent |
|----------------|--------|--------------|
| 19.477         | 573395 | 2.642        |
| 22.757         | 21131911| 97.358      |
Sample ID: VRT-1-152D-Rac
Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-152D_Rac-AS99505-30min.met?
Method: C:\EZStart\Projects\Default\Method\Vivek\AS99505ET-30min.met
Injection volume: 1 uL

Description: {Data Description}

1: 230 nm, 4 nm Results

| Retention Time | Area       | Area Percent |
|----------------|------------|--------------|
| 11.829         | 2417646    | 49.976       |
| 14.400         | 2419995    | 50.024       |

Page 1 of 2
3/19/2010 4:17:24 PM
Sample ID: VRT-1-152D

File names:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-152DAS99505-30min.met
Method:
C:\EZStart\Projects\Default\Method\Vivek\AS99505ET-30min.met
Injection volume: 2 uL

Description: {Data Description}

4: 220 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 11.541         | 408348   | 4.370        |
| 14.512         | 8936979  | 95.630       |

Retention Time | Area | Area Percent

Page 1 of 2

3/19/2010 4:38:14 PM
Sample ID: JW-03-107D
Filename: C:\EZStart\Projects\Default\Data\JWu\JW-03-107D_AS9901ET_40min.met3-16-2010 12-34-05 AM.dat
Method: C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume: 5 uL

Description: (Data Description)

1: 210 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 13.883         | 4987608  | 50.023       |
| 15.504         | 4982970  | 49.977       |

2: 230 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 13.877         | 5376123  | 50.035       |
| 15.504         | 5368638  | 49.965       |
Sample ID: JW-03-107Dchiral
Filename: C:\EZStart\Projects\Default\Data\JWu\JW-03-107Dchiral_A9901ET_30min.met3-16-2010 1-19-42 PM.dat
Method: C:\EZStart\Projects\Default\Method\Vivek\A9901ET-30min.met
Injection volume: 5 uL

Description: {Data Description}

1: 210 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 14.059         | 454706   | 2.420        |
| 15.552         | 18335038 | 97.580       |

\[95.2\]

2: 230 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 14.064         | 490737   | 2.420        |
| 15.552         | 19789677 | 97.580       |
Sample ID: VRT-1-139-7-rac
Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-139-7-racAS9901E t-30min.met2-15-2010 7-40-36 PM.dat Method: C:\EZStart\Projects\Default\Method\Vivek\AS9901Et-30min.met Injection volume: 5 uL

Description: {Data Description}

![Graph](Image)

1: 230 nm, 4 nm Results

| Retention Time | Area    | Area Percent |
|----------------|---------|--------------|
| 17.584         | 7213123 | 55.650       |
| 19.691         | 5748433 | 44.350       |

![Graph](Image)

| Retention Time | Area    | Area Percent |
|----------------|---------|--------------|
Sample ID: VRT-1-139-7
Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-139-7AS9901Et-30 min_met2-15-2010 8-12-29 PM.dat
Method: C:\EZStart\Projects\Default\Method\Vivek\AS9901Et-30min_met
Injection volume: 5 uL

Description: {Data Description}

![Graph with peaks and data points]

### 1: 230 nm, 4 nm Results

| Retention Time | Area      | Area Percent |
|----------------|-----------|--------------|
| 17.184         | 724444    | 2.884        |
| 18.997         | 24397158  | 97.116       |

![Graph with retention time and area]
Sample ID: 15-174A
Filename: C:\EZStart\Projects\Default\Data\Nathan\ns15-174A-12-19-2009 1-19-37
PM-AD995005ET.met.dat  Method: C:\EZStart\Projects\Default\Method\Nathan\AD995005ET 45min.met
Injection Volume: 4 μL

Description: {Data Description}

1: 230 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 14.821         | 443995   | 8.802        |
| 15.808         | 206784   | 40.980       |
| 16.885         | 494466   | 9.803        |
| 22.096         | 2638556  | 40.415       |

2: 254 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 14.805         | 98102    | 8.817        |
| 15.819         | 454600   | 40.356       |
| 16.880         | 112536   | 10.114       |
| 22.107         | 447454   | 40.214       |
Sample ID: VRT-1-137E

Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-137EVRT-1-136D.met2-11-2010 7:29:21 AM.dat Method: C:\EZStart\Projects\Default\Method\Vivek\VRT-1-136D.met
Injection volume: 2 µL

Description: [Data Description]

1: 230 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 15.579         | 39375    | 0.781        |
| 17.077         | 107920   | 2.139        |
| 18.437         | 803826   | 15.935       |
| 26.421         | 4093302  | 81.145       |

Page 1 of 2 2/11/2010 7:30:57 AM
Sample ID: VRT-1-133C-Racemic

Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-133C-RacemicWH9703ET-90min.met 20-2010 3-50-04 PM.dat

Method: C:\EZStart\Projects\Default\Method\Vivek\WH9703ET-90min.met

Injection volume: 1 μL

Description: [Data Description]

![Graph](image)

1: 230 nm, 4 nm Results

| Retention Time | Area   | Area Percent |
|----------------|--------|--------------|
| 51.648         | 475163 | 12.333       |
| 57.611         | 487115 | 12.644       |
| 73.504         | 1420619| 36.874       |
| 83.488         | 1469762| 38.149       |

![Graph](image)

| Retention Time | Area   | Area Percent |
|----------------|--------|--------------|

Page 1 of 2

J/20/2010 3:51:44 PM
Sample ID: VRT-1-152F
Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-152F\WH9703ET-90min.met
Method: C:\EZStart\Projects\Default\Method\Vivek\WH9703ET-90min.met
Injection volume: 1 μL

Description: (Data Description)

1: 230 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 51.429         | 35226    | 0.505        |
| 57.104         | 5525286  | 79.170       |
| 73.056         | 1279889  | 18.339       |
| 83.264         | 138592   | 1.986        |

2: 220 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 51.536         | 31969    | 0.516        |
| 57.099         | 4876875  | 78.795       |
| 73.008         | 1152092  | 18.614       |
| 83.264         | 128446   | 2.075        |
Sample ID: JW-03-108A
Filename: C:\EZStart\Projects\Default\Data\JWu\JW-03-108A_AS9901ET_40min.met3-16-2010
7-57-01 PM.dat
Method: C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume: 5 uL

Description: {Data Description}

1: 210 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 20.219         | 5234845  | 48.972       |
| 27.984         | 5454555  | 51.028       |

2: 230 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 20.219         | 5102514  | 48.828       |
| 27.984         | 5347560  | 51.172       |
Sample ID: VRT-1-152B
Filename:
C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-152BAS901ET-40m
in.met 3-20-2010 10:10:04 PM.dat  Method:
C:\EZStart\Projects\Default\Method\Vivek\AS901ET-40min.met
Injection volume: 5 μL

Description: {Data Description}

1: 230 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 20.677         | 314407   | 2.202        |
| 28.091         | 13964418 | 97.798       |
Sample ID: JW-03-1088
Filename:
C:\EZStart\Projects\Default\Data\JW\JW-03-107B_AS9901ET_40min.met3-16-2010
9-10-05 PM.dat  Method:
C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume: 5 uL

Description: {Data Description}

1: 210 nm, 4 nm Results

| Retention Time | Area   | Area Percent |
|----------------|--------|--------------|
| 21.392         | 5735548| 50.661       |
| 28.197         | 5585924| 49.339       |

2: 230 nm, 4 nm Results

| Retention Time | Area | Area Percent |
|----------------|------|--------------|
| 0.288          | 712  | 0.006        |
| 0.848          | 2899 | 0.024        |
| 1.461          | 39   | 0.000        |
| 2.139          | 68   | 0.001        |
| 2.224          | 72   | 0.001        |
| 2.299          | 93   | 0.001        |
| 2.469          | 115  | 0.001        |
| 2.512          | 48   | 0.000        |
| 2.560          | 105  | 0.001        |
| 2.656          | 97   | 0.001        |
| 3.269          | 21   | 0.000        |
| 3.755          | 297966| 2.476       |
| 4.528          | 89069| 0.740        |
Sample ID: VRT-1-152A
Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-152AAS9901ET-40m in.met 3-10-2010 9-28-10 PM.dat
Method: C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume: 5 μL

Description: {Data Description}

Retention Time | Area | Area Percent
--- | --- | ---
22.123 | 250463 | 1.455
28.528 | 16363043 | 98.545
Results

| Pk # | Retention Time | Area Percent | Lambda Max |
|------|----------------|--------------|------------|
| 1    | 11.868         | 48.997       | 200        |
| 2    | 12.648         | 51.003       | 201        |
1: 255 nm, 4 nm

Results

| Pk # | Retention Time | Area Percent | Lambda Max |
|------|----------------|--------------|------------|
| 1    | 11.732         | 94.922       | 202        |
| 2    | 12.520         | 5.078        | 205        |

Pk # | Retention Time | Area Percent |
|-----|----------------|--------------|
|     |                |              |

P1
1: 195 nm, 4 nm Results

| Retention Time | Area   | Area Percent | Lambda Max |
|----------------|--------|--------------|------------|
| 35.224         | 4058715| 52.359       | 206        |
| 42.404         | 3692945| 47.641       | 205        |

2: 205 nm, 4 nm Results

| Retention Time | Area   | Area Percent | Lambda Max |
|----------------|--------|--------------|------------|
| 0.432          | 115    | 0.001        | 395        |
| 0.680          | 3670   | 0.023        | 198        |
| 0.760          | 3751   | 0.024        | 462        |
| 0.904          | 1655   | 0.011        | 319        |
| 1.240          | 19575  | 0.125        | 491        |
| 1.436          | 20984  | 0.134        | 669        |
| 2.136          | 187    | 0.001        | 416        |
| 2.996          | 192734 | 1.234        | 205        |
| 3.216          | 97385  | 0.623        | 205        |
| 3.412          | 1162283| 7.439        | 205        |
| 4.184          | 2430752| 15.558       | 205        |
| 5.120          | 101369 | 0.649        | 213        |
| 5.296          | 23850  | 0.153        | 210        |
| 5.436          | 49458  | 0.317        | 211        |
| 5.836          | 33462  | 0.214        | 238        |
| 5.984          | 20728  | 0.133        | 226        |
| 6.208          | 13053  | 0.084        | 796        |
| 6.436          | 33632  | 0.215        | 253        |
JW-03-107Chiral
C: \EZStart\Projects\Default\Method\wataru\IC 100%D 1ml min 60min.met
3/17/2010 2:59:32 PM
C: \EZStart\Projects\Default\Data\Jeff\JW-03-107Chiral.dat

1: 195 nm, 4 nm Results
Retention Time   Area      Area Percent  Lambda Max
34.896           5426707   91.713        206
42.360           490326    8.287         205

2: 205 nm, 4 nm Results
Retention Time   Area      Area Percent  Lambda Max
34.888           7742417   91.596        206
42.380           710341    8.404         205

3: 225 nm, 4 nm Results
Sample ID: VRT-1-154C-Racemic
Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-154C-RacemicAS98 02-40min.met3-19-2010 1-35-31 FM.dat
Method: C:\EZStart\Projects\Default\Method\Vivek\AS9802-40min.met
Injection volume: 2 µL

Description: {Data Description}

![Graph showing retention times](image)

1: 230 nm, 4 nm Results

| Retention Time | Area       | Area Percent |
|----------------|------------|--------------|
| 24.875         | 20418087   | 50.126       |
| 30.736         | 20315717   | 49.874       |

![Graph showing retention times](image)

| Retention Time | Area       | Area Percent |
|----------------|------------|--------------|

Page 1 of 2
Sample ID: VRT-1-154C
Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-154C-AS9802-40min.met3-19-2010 2-17-34 PM.dat
Method: C:\EZStart\Projects\Default\Method\Vivek\AS9802-40min.met
Injection volume: 2 µL

Description: [Data Description]

1: 230 nm, 4 nm Results

| Retention Time | Area    | Area Percent |
|----------------|---------|--------------|
| 25.003         | 759114  | 1.467        |
| 30.112         | 5096378 | 98.533       |

Page 1 of 2

3/19/2010 2:19:16 PM
Sample ID: JW-03-108C
Filename: C:\EZStart\Projects\Default\Data\JWu\JW-03-108c_AS9901ET_40min.met3-16-2010 10-23-08 PM.dat
Method: C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume: 5 uL

Description: {Data Description}

1: 210 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 15.947         | 14518430 | 50.435       |
| 19.237         | 14268032 | 49.565       |

2: 230 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 15.947         | 11244006 | 50.367       |
| 19.237         | 11080327 | 49.633       |
Sample ID: JW-03-108Cchiral
Filename: C:\EZStart\Projects\Default\Data\JWu\JW-03-108cChiral_AS9901ET_40min.met3-16-2010 11:36-11 PM.dat
Method: C:\EZStart\Projects\Default\Method\Vivek\AS9901ET-40min.met
Injection volume: 5 uL

Description: {Data Description}

![Graph](image_url)

1: 210 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 16.315         | 2249590  | 4.827        |
| 19.104         | 44353893 | 95.173       |

2: 230 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 16.309         | 1694672  | 4.751        |
| 19.109         | 33976702 | 95.249       |

Page 1 of 2

3/16/2010 11:37:48 PM
Sample ID: VRT-1-145B-Rac
Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-1-145B-Rac\9802-30min.met
Method: C:\EZStart\Projects\Default\Method\Vivek\9802-30min.met
Injection volume: 5 uL

Description: {Data Description}

4: 210 nm, 4 nm Results

| Retention Time | Area     | Area Percent |
|----------------|----------|--------------|
| 14.053         | 4325748  | 50.024       |
| 28.469         | 4321597  | 49.976       |

Retention Time  Area  Area Percent

Page 1 of 2  2/25/2010 2:56:50 PM
Sample ID: JW-03-102
Filename: C:\EZStart\Projects\Default\Data\JWu\JW-03-102_9802ET_35min.met 3-8-2010 6:41-09 PM.dat
Method: C:\EZStart\Projects\Default\Method\Vivek\AS9802ET-35min.met
Injection volume: 5 μL

Description: {Data Description}

![Graph 1: 210 nm, 4 nm Results](image1)

| Retention Time | Area       | Area Percent |
|----------------|------------|--------------|
| 14.325         | 685817     | 4.008        |
| 29.744         | 16425704   | 95.992       |

![Graph 2: 220 nm, 4 nm Results](image2)

| Retention Time | Area       | Area Percent |
|----------------|------------|--------------|
| 14.325         | 750475     | 4.006        |
| 29.744         | 18222910   | 95.994       |

Page 1 of 2  3/8/2010 6:42:45 PM
### 3: 309 nm, 4 nm Results

| Retention Time | Area   | Area Percent | Lambda Max |
|----------------|--------|--------------|------------|
| 19.268         | 695041 | 49.344       | 206        |
| 27.312         | 713517 | 50.656       | 230        |

### 4: 296 nm, 4 nm Results

| Retention Time | Area   | Area Percent | Lambda Max |
|----------------|--------|--------------|------------|
| 19.268         | 1058948| 49.902       | 206        |
| 27.324         | 1063118| 50.098       | 230        |

### 5: 241 nm, 4 nm Results

| Retention Time | Area   | Area Percent | Lambda Max |
|----------------|--------|--------------|------------|
| 19.268         | 2129011| 49.601       | 206        |
| 27.320         | 2163247| 50.399       | 230        |
### 3: 309 nm, 4 nm Results

| Retention Time | Area  | Area Percent | Lambda Max |
|----------------|-------|--------------|------------|
| 19.664         | 24025 | 4.328        | 205        |
| 27.180         | 531135| 95.672       | 205        |

### 4: 296 nm, 4 nm Results

| Retention Time | Area  | Area Percent | Lambda Max |
|----------------|-------|--------------|------------|
| 19.648         | 43303 | 5.108        | 205        |
| 27.176         | 804492| 94.892       | 205        |

### 5: 241 nm, 4 nm Results

| Retention Time | Area  | Area Percent | Lambda Max |
|----------------|-------|--------------|------------|
| 19.656         | 80809 | 4.724        | 205        |
| 27.180         | 1629788| 95.276       | 205        |
### 1: 225 nm, 4

| Retention Time | Area    | Area Percent | Lambda Max |
|----------------|---------|--------------|------------|
| 12.448         | 5127896 | 49.906       | 234        |
| 21.200         | 5147158 | 50.094       | 234        |

### 2: 300 nm, 4

| Retention Time | Area    | Area Percent | Lambda Max |
|----------------|---------|--------------|------------|
| 12.448         | 1221545 | 49.602       | 234        |
| 21.204         | 1241156 | 50.398       | 234        |
### 4: 207 nm, 4 nm Results

| Retention Time | Area   | Area Percent | Lambda Max |
|----------------|--------|--------------|------------|
| 11.448         | 573334 | 6.490        | 235        |
| 21.520         | 8260898| 93.510       | 235        |

### 5: 228 nm, 4 nm Results

| Retention Time | Area    | Area Percent | Lambda Max |
|----------------|---------|--------------|------------|
| 11.452         | 747593  | 6.568        | 235        |
| 21.516         | 10634883| 93.432       | 235        |
Sample ID: VRT-2-109-Rac
Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-2-109-Rac-AS9901IP.met 9-24-2010 10-40-59 AM.dat
Method: C:\EZStart\Projects\Default\Method\AS\AS9901IP.met
Injection volume: 1 µL

Description: [Data Description]

3: 277 nm, 4 nm Results

| Retention Time | Area      | Area Percent |
|----------------|-----------|--------------|
| 8.368          | 1580236   | 50.323       |
| 9.771          | 1559957   | 49.677       |

Page 1 of 2

9/24/2010 10:42:36 AM
Sample ID: VRT-2-109
Filename: C:\EZStart\Projects\Default\Data\Vivek\Hydroamination\VRT-2-109-AS9901IP.met
9-24-2010 10:27-39 AM.dat
Method: C:\EZStart\Projects\Default\Method\AS\AS9901IP.met
Injection volume: 1 uL

3: 277 nm, 4 nm Results

| Retention Time | Area      | Area Percent |
|----------------|-----------|--------------|
| 8.368          | 1534917   | 90.022       |
| 9.701          | 170135    | 9.978        |

S11

MeO₂C

CO₂Me

Me

Me

Me
Reaction mixture

QT16298 3 (0.050) Sb (80,70.00 ); Sm (SG, 3x3.00); Cm (3:178)

Chemical Formula: C_{23}H_{29}NO_{4}
Exact Mass: 383.21

15-Sep-2010
TOF MSMS 1360.00ES+
2.10e3
Reaction mixture, high m/z ions
QT16295  (0.017) Is (0.08,0.05) C89H85NO6PS2

15-Sep-2010
TOF MS ES+
3.29e12

Calculated

QT16295  11 (0.185) Sb (80,70.00 ); Sm (SG, 3x3.00); Cm (1:297)

TOF MS ES+
4.03e3

Measured