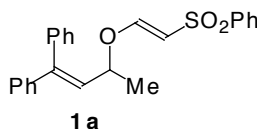


Representative Experimental Procedure for the Asymmetric Palladium Catalyzed Allylic Alkylation of β -Phenylcinnamyl Vinylogous Sulfonate Derivatives: Allyl palladium chloride dimer (4.7 mg, 0.013 mmol) was mixed with the *cis*-phosphino-1,3-oxazine ligand **3**, then THF (1 ml) was added, followed by 30 minutes of stirring at room temperature (20 °C) to give a clear yellow catalyst solution. Dimethylmalonate (0.138 g, 1.03 mmol) was dissolved in THF (3 ml), then NaH (60 % dispersion in mineral oil, 0.039 g, 0.98 mmol) was added portionwise at room temperature, over 5 minutes, under positive nitrogen pressure.

The vinylogous sulfonate **2a** (0.2 g, 0.51 mmol) was dissolved in THF (1 ml), then added to the room temperature solution of sodium salt of dimethylmalonate. The catalyst solution was then added, followed by stirring for 1 hour 10 min. at room temperature. The reaction mixture was partitioned between an aqueous 1N NaOH solution and Et₂O. The combined organic layers were washed with brine, dried (Na₂SO₄) and concentrated *in vacuo* to afford a crude oil. Purification by flash chromatography on silica gel (eluting with a 10-30% diethyl ether/hexane gradient), afforded **4a** (0.164 g, 94 %) as a colorless oil, and the product from hydrolysis **5a** (0.003 g, 3 %).

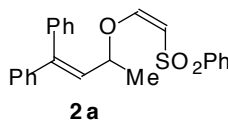


IR (CHCl₃) 3064 (m), 2985 (m), 1731 (w), 1622 (s), 1605 (s) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 7.84-7.79 (m, 2H), 7.58-7.36 (m, 6H), 7.41 (d, *J* = 12.3 Hz, 1H), 7.31-7.25 (m, 3H), 7.23-7.14 (m, 2H), 7.10-7.06 (m, 2H), 5.93 (d, *J* = 9.3 Hz, 1H), 5.44 (d, *J* = 12.1 Hz, 1H), 4.55 (dq, *J* = 9.3 Hz, 6.3 Hz, 1H), 1.48 (d, *J* = 6.3 Hz, 3H).

¹³C-NMR (62.5 MHz, CDCl₃) δ 159.19 (o), 146.17 (e), 142.75 (e), 140.64 (e), 138.43 (e), 132.56 (o), 129.37 (o), 128.99 (o), 128.67 (o), 128.26 (o), 128.19 (o), 127.54 (o), 126.74 (o), 107.56 (o), 76.85 (o), 21.29 (o).

HRMS (EI, M⁺) calcd for C₂₄H₂₂O₃S 390.1289 found 390.1282



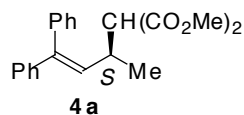
mp 117-119 °C.

IR (CHCl₃) 3060(w), 2984 (w), 1618 (s) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 8.04-8.01 (m, 2H), 7.61-7.47 (m, 3H), 7.41-7.31 (m, 3H), 7.30-7.26 (m, 3H), 7.14-7.10 (m, 2H), 7.04-7.00 (m, 2H), 6.34 (d, *J* = 6.4 Hz, 1H), 5.81 (d, *J* = 9.4 Hz, 1H), 5.55 (d, *J* = 6.4 Hz, 1H), 4.44 (dq, *J* = 9.4 Hz, 6.3 Hz, 1H), 1.39 (d, *J* = 6.3 Hz, 3H).

^{13}C -NMR (62.5 MHz, CDCl_3) δ 154.27 (o), 146.01 (e), 142.81 (e), 140.34 (e), 138.35 (e), 132.72 (o), 129.32 (o), 128.59 (o), 128.43 (o), 128.28 (o), 127.98 (o), 127.86 (o), 127.44 (o), 127.01 (o), 108.27 (o), 79.26 (o), 21.15 (o).

HRMS (EI, M^+) calcd for $\text{C}_{24}\text{H}_{22}\text{O}_3\text{S}$ 390.1289 found 390.1276.



$[\alpha]_{\text{D}}^{18} = -130.3$ ($c = 1.0$, CHCl_3) from **1a**; $\text{Eu}(\text{hfc})_3$ shift, $e.r. = 94.8 : 5.2 = 89.6\%$ *e.e.*

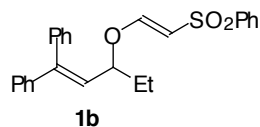
$[\alpha]_{\text{D}}^{18} = -130.6$ ($c = 1.02$, CHCl_3) from **2a**; $\text{Eu}(\text{hfc})_3$ shift, $e.r. = 95.4 : 4.6 = 90.8\%$ *e.e.*

IR (CHCl_3) 2955 (m), 1733 (s) cm^{-1} .

^1H -NMR (250 MHz, CDCl_3) δ 7.40-7.30 (m, 3H), 7.28-7.12 (m, 7H), 5.96 (d, $J = 10.4$ Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 3.35 (d, $J = 8.7$ Hz, 1H), 3.12 (ddq, $J = 10.5, 8.8, 6.5$ Hz, 1H), 1.13 (d, $J = 6.4$ Hz, 3H).

^{13}C -NMR (62.5 MHz, CDCl_3) δ 168.56 (e), 168.51 (e), 142.67 (e), 142.31 (e), 139.51 (e), 130.12 (o), 129.48 (o), 128.26 (o), 128.08 (o), 127.32 (o), 127.22 (o), 57.61 (o), 52.27 (o), 34.22 (o), 19.28 (o).

HRMS (EI, M^+) calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4$ 338.1518 found 338.1514.

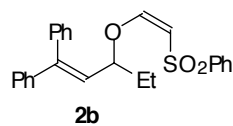


IR (CHCl_3) 3063 (w), 3025 (m), 3013 (m), 2972 (m), 2938 (w), 1710 (w), 1622 (s), 1605 (s) cm^{-1} .

^1H -NMR (250 MHz, CDCl_3) δ 7.80-7.77 (m, 2H), 7.55-7.41 (m, 3H), 7.40 (d, $J = 12.1$ Hz, 1H), 7.40-7.36 (m, 3H), 7.29-7.24 (m, 3H), 7.18-7.13 (m, 2H), 7.08-7.04 (m, 2H), 5.91 (d, $J = 9.6$ Hz, 1H), 5.41 (d, $J = 12.0$ Hz, 1H), 4.32 (dt, $J = 9.6, 6.4$, 1H), 1.90-1.68 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H).

^{13}C -NMR (62.5 MHz, CDCl_3) δ 159.66 (o), 147.08 (e), 142.75 (e), 140.71 (e), 138.48 (e), 132.54 (o), 129.40 (o), 128.98 (o), 128.64 (o), 128.25 (o), 128.20 (o), 128.12 (o), 127.50 (o), 126.74 (o), 125.64 (o), 107.32 (o), 82.04 (o), 28.44 (e), 9.55 (o).

HRMS (EI, M^+) calcd for $\text{C}_{25}\text{H}_{24}\text{O}_3\text{S}$ 404.1446 found 404.1460.

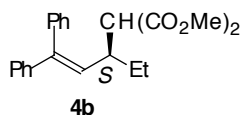


IR (CHCl_3) 3084 (w), 3062 (w), 3020 (m), 2971 (w), 2938 (w), 2880 (w), 1616 (s) cm^{-1} .

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 8.01-7.97 (m, 2H), 7.58-7.44 (m, 3H), 7.37-7.32 (m, 3H), 7.29-7.24 (m, 2H), 7.02-6.99 (m, 2H), 6.33 (d, $J = 6.4$ Hz, 1H), 5.8 (d, $J = 9.6$ Hz, 1H), 5.51 (d, $J = 6.4$ Hz, 1H), 4.21 (dt, $J = 9.6, 6.4$ Hz, 1H), 1.81-1.59 (m, 2H), 0.85 (t, $J = 7.4$ Hz, 3H).

$^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3) δ 154.69 (o), 146.89 (e), 142.87 (e), 140.40 (e), 138.43 (e), 132.66 (o), 129.34 (o), 128.56 (o), 128.45 (o), 128.26 (o), 127.91 (o), 127.71 (o), 127.40 (o), 125.85 (o), 107.80 (o), 84.45 (o), 28.33 (e), 9.44 (o).

HRMS (EI, M^+) calcd for $\text{C}_{25}\text{H}_{24}\text{O}_3\text{S}$ 404.1446 found 404.1445.



$[\alpha]_{\text{D}}^{23} = -51.5$ ($c = 1.0$, CHCl_3), from **1b**; $\text{Eu}(\text{hfc})_3$ shift, $e.r. = 97.1: 2.9 = 94.2\%$ *e.e.*

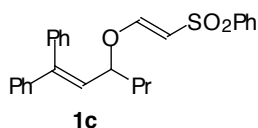
$[\alpha]_{\text{D}}^{23} = -52.9$ ($c = 1.01$, CHCl_3), from **2b**; $\text{Eu}(\text{hfc})_3$ shift, $e.r. = 97.1: 2.9 = 94.2\%$ *e.e.*

IR (CHCl_3) 3028 (m), 3011 (w), 2955 (m), 1732 (s) cm^{-1} .

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.41-7.16 (m, 10H), 5.96 (d, $J=10.8$ Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.46 (d, $J=8.2$ Hz, 1H), 3.06-2.93 (m, 1H), 1.65-1.36 (m, 2H), 0.89 (t, $J=7.4$, 3H).

$^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3) δ 168.65 (e), 144.15 (e), 142.54 (e), 139.57 (e), 129.69 (o), 128.66 (o), 128.12 (o), 128.06 (o), 127.33 (o), 127.19 (o), 127.09 (o), 56.23 (o), 52.27 (o), 52.24 (o), 40.35 (o), 26.50 (e), 11.63 (o).

HRMS (EI, M^+) calcd for $\text{C}_{22}\text{H}_{24}\text{O}_4$ 352.1674 found 352.1660.

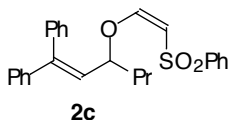


IR (CHCl_3) 3063 (w), 3026 (m), 3015 (w), 2963 (m), 2935 (w), 2875 (w), 1622 (s), 1605 (s) cm^{-1} .

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.81-7.76 (m, 2H), 7.55-7.41 (m, 3H), 7.40 (d, $J = 12.0$ Hz, 1H), 7.39-7.34 (m, 3H), 7.29-7.24 (m, 3H), 7.09-7.03 (m, 2H), 5.90 (d, $J = 9.5$ Hz, 1H), 5.40 (d, $J = 12.0$ Hz, 1H), 4.39 (ddd, $J = 9.5, 7.2, 5.6$ Hz, 1H), 1.88-1.59 (m, 2H), 1.45-1.26 (m, 2H), 0.88 (t, $J = 7.3$, 1H).

$^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3) δ 159.63 (o), 146.80 (e), 142.74 (e), 140.68 (e), 138.44 (e), 132.53 (o), 129.38 (o), 128.97 (o), 128.62 (o), 128.24 (o), 128.17 (o), 127.49 (o), 126.72 (o), 125.90 (o), 107.28 (o), 80.65 (o), 37.39 (e), 18.32 (e), 13.81 (o).

HRMS (EI, M^+) calcd for $\text{C}_{26}\text{H}_{26}\text{O}_3\text{S}$ 418.1602 found 418.1587.



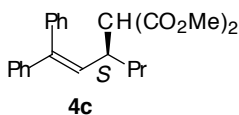
mp = 92-95 °C.

IR (CHCl₃) 3084 (w), 3062 (w), 3021 (m), 3013 (w), 2963 (m), 2935 (w), 1729 (w), 1619 (s) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 8.05-7.90 (m, 2H), 7.61-7.46 (m, 3H), 7.42-7.35 (m, 3H), 7.31-7.22 (m, 3H), 7.16-7.09 (m, 2H), 7.07-7.01 (m, 2H), 6.35 (d, *J* = 6.4 Hz, 1H), 5.82 (d, *J* = 9.6, 1H), 5.54 (d, *J* = 6.4 Hz, 1H), 4.3 (ddd, *J* = 9.6, 7.2, 5.7 Hz, 1H), 1.82-1.52 (m, 2H), 1.35-1.18 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

¹³C-NMR (62.5 MHz, CDCl₃) δ 154.71 (o), 146.60 (e), 142.87 (e), 140.37 (e), 138.39 (e), 132.65 (o), 129.31 (o), 128.55 (o), 128.43 (o), 128.24 (o), 127.92 (o), 127.71 (o), 127.38 (o), 126.12 (o), 107.76 (o), 83.05 (o), 37.29 (e), 18.15 (e), 13.79 (o).

HRMS (EI, M⁺) calcd for C₂₆H₂₆O₃S 418.1602 found 418.1637.



[α]_D²⁵ = -51.7 (c = 1.01, CHCl₃), from **1c**; Eu(hfc)₃ shift, *e.r.* = 97.6 : 2.4 = 95.2% *e.e.*

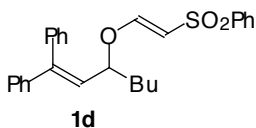
[α]_D²⁵ = -51.2 (c = 1.0, CHCl₃), from **2c**; Eu(hfc)₃ shift, *e.r.* = 97.4 : 2.6 = 94.8% *e.e.*

IR (CHCl₃) 3028 (m), 3020 (w), 2956 (m), 2933 (w), 2874 (w), 1732 (s) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 7.41-7.16 (m, 10H), 5.97 (d, *J* = 10.7 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.45 (d, *J* = 8.0 Hz, 1H), 3.13-3.00 (m, 1H), 2.1-1.16 (m, 4H), 0.80, (t, *J* = 6.9 Hz, 3H).

¹³C-NMR (62.5 MHz, CDCl₃) δ 168.66 (e), 143.85 (e), 142.54 (e), 139.53 (e), 129.69 (o), 129.09 (o), 128.11 (o), 128.05 (o), 127.32 (o), 127.17 (o), 127.09 (o), 56.48 (o), 52.24 (o), 38.81 (o), 35.84 (e), 20.32 (e), 14.04 (o).

HRMS (EI, M⁺) calcd for C₂₃H₂₆O₄ 366.1831 found 366.1837.



mp 78-81 °C

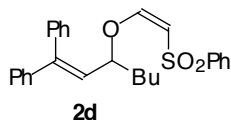
IR (CHCl₃) 2960 (m), 2934 (m), 2863 (w), 1622 (s), 1605 (s) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 7.83-7.79 (m, 2H), 7.58-7.42 (m, 3H), 7.47 (d, *J* = 12.2, 1H), 7.41-7.31 (m, 3H), 7.30-7.26 (m, 3H), 7.24-7.15 (m, 2H), 7.12-7.06 (m, 2H), 5.93 (d, *J* = 9.5 Hz, 1H), 5.44 (d, *J*

= 12.2 Hz, 1H), 4.41 (ddd, $J = 9.5, 7.1, 5.6$ Hz, 1H), 1.88-1.57 (m, 2H), 1.40-1.21 (m, 4H), 0.89 (t, $J = 7.0$ Hz, 3H).

^{13}C -NMR (62.5 MHz, CDCl_3) δ 159.68 (o), 146.81 (e), 142.81 (e), 140.72 (e), 138.48 (e), 132.53 (o), 129.40 (o), 128.98 (o), 128.64 (o), 128.26 (o), 128.20 (o), 128.14 (o), 127.52 (o), 126.75 (o), 125.96 (o), 107.32 (o), 80.93 (o), 35.04 (e), 27.14 (e), 22.40 (e), 13.86 (o).

HRMS (EI, M^+) calcd for $\text{C}_{27}\text{H}_{28}\text{O}_3\text{S}$ 432.1759 found 432.1755



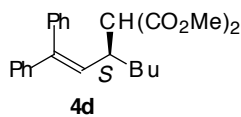
mp 63-66 °C

IR (CHCl_3) 2960 (w), 2934 (w), 2863 (w), 1618 (s) cm^{-1} .

^1H -NMR (250 MHz, CDCl_3) δ 8.04-8.00 (m, 2H), 7.61-7.49 (m, 3H), 7.47-7.33 (m, 3H), 7.31-7.26 (m, 3H), 7.19-7.11 (m, 2H), 7.07-7.01 (m, 2H), 6.34 (d, $J = 6.4$ Hz, 1H), 5.83 (d, $J = 9.5$ Hz, 1H), 5.53 (d, $J = 6.4$ Hz, 1H), 4.28 (ddd, $J = 9.5, 7.1, 5.8$ Hz, 1H), 1.82-1.57 (m, 2H), 1.34-0.94 (m, 4H), 0.87 (t, $J = 6.8$ Hz, 3H).

^{13}C -NMR (62.5 MHz, CDCl_3) δ 154.71 (o), 146.60 (e), 142.93 (e), 140.41 (e), 138.45 (e), 132.66 (o), 129.34 (o), 128.57 (o), 128.45 (o), 128.27 (o), 128.09 (o), 127.93 (o), 127.75 (o), 127.41 (o), 126.19 (o), 107.80 (o), 83.31 (o), 34.92 (e), 26.97 (e), 22.38 (e), 13.83 (o).

HRMS (EI, M^+) calcd for $\text{C}_{27}\text{H}_{28}\text{O}_3\text{S}$ 432.1759 found 432.1742



$[\alpha]_{\text{D}}^{18} = -64.5$ ($c = 1.0$, CHCl_3) from **1d**; $\text{Eu}(\text{hfc})_3$ shift $e.r. = 97.0 : 3.0 = 94.0\%$ *e.e.*

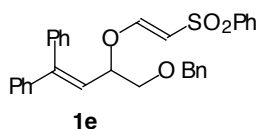
$[\alpha]_{\text{D}}^{18} = -58.5$ ($c = 1.0$, CHCl_3) from **2d**; $\text{Eu}(\text{hfc})_3$ shift $e.r. = 96.3 : 3.6 = 92.7\%$ *e.e.*

IR (CHCl_3) 2956 (s), 2931 (m), 2861 (m), 1732 (s) cm^{-1} .

^1H -NMR (250 MHz, CDCl_3) δ 7.39-7.28 (m, 3H), 7.27-7.14 (m, 7H), 5.95 (d, $J = 10.7$ Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 3.42 (d, $J = 8.0$ Hz, 1H), 3.03 (ddt, $J = 10.7$ Hz, 8.3 Hz, 4.4 Hz, 1H), 1.49-1.14 (m, 6H), 0.81 (t, $J = 6.9$ Hz, 3H).

^{13}C -NMR (62.5 MHz, CDCl_3) δ 168.68 (e), 143.83 (e), 142.57 (e), 139.57 (e), 129.69 (o), 129.14 (o), 128.12 (o), 128.08 (o), 127.36 (o), 127.19 (o), 127.11 (o), 56.47 (o), 52.26 (o), 38.88 (o), 33.29 (e), 29.20 (e), 22.59 (e), 13.90 (o).

HRMS (EI, M^+) calcd for $\text{C}_{24}\text{H}_{28}\text{O}_4$ 380.1987 found 380.1982.

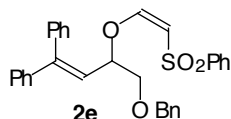


IR (CHCl₃) 3069 (w), 2864 (w), 1731 (w), 1622 (s), 1608 (s) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 7.78-7.74 (m, 2H), 7.57-7.21 (m, 14H), 7.43 (d, *J* = 12.2 Hz, 1 H), 7.17-7.12 (m, 2H), 7.07-7.03 (m, 2H), 5.91 (d, *J* = 9.5 Hz, 1H), 5.47 (d, *J* = 12.2, 1H), 4.65-4.57 (m, 1H), 4.53 (s, 2H), 3.74-3.64 (m, 2H).

¹³C-NMR (62.5 MHz, CDCl₃) δ 159.73 (o), 148.60 (e), 142.68 (e), 140.52 (e), 138.17 (e), 137.47 (e), 132.80 (o), 132.56 (o), 129.37 (o), 129.13 (o), 128.97 (o), 128.90 (o), 128.82 (o), 128.70 (o), 128.45 (o), 128.39 (o), 128.33 (o), 128.28 (o), 127.84 (o), 127.63 (o), 127.60 (o), 126.92 (o), 126.80 (o), 121.77 (o), 107.72 (o), 80.10 (o), 73.74 (e), 73.42 (e), 71.76 (e).

HRMS (EI, M⁺) calcd for C₃₁H₂₈O₄S 496.1708 found 496.1727.

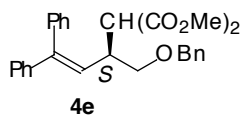


IR (CHCl₃) 3064 (w), 2864 (w), 1621 (s), 1496 (w), 1447 (m) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 8.03-7.99 (m, 2H), 7.53-7.33 (m, 4H), 7.33-7.22 (m, 10H), 7.17-7.10 (m, 2H), 7.01 (m, 2H), 6.40 (d, *J* = 6.4 Hz, 1H), 5.87 (d, *J* = 9.5 Hz, 1H), 5.51 (d, *J* = 6.4 Hz, 1H), 4.53-4.44 (m, 1H), 4.45 (d, *J* = 2.2 Hz, 2H), 3.60-3.57 (m, 2H).

¹³C-NMR (62.5 MHz, CDCl₃) δ 155.24 (o), 148.45 (e), 142.93 (e), 140.35 (e), 138.15 (e), 137.55 (e), 132.65 (o), 130.06 (o), 129.33 (o), 128.55 (o), 128.45 (o), 128.27 (o), 128.07 (o), 127.81 (o), 127.75 (o), 127.65 (o), 127.53 (o), 121.75 (o), 107.55 (o), 82.51 (o), 73.49 (e), 72.09 (e), 60.35 (e), 14.17 (o).

HRMS (EI, M⁺) calcd for C₃₁H₂₈O₄S 496.1708 found 496.1728.



[α]_D¹⁸ = -119.3 (c = 1.0, CHCl₃) from **1c**; Eu(hfc)₃ shift *e.r.* = 97.6 : 2.4 = 95.2% *e.e.*

[α]_D¹⁸ = -119.2 (c = 1.0, CHCl₃) from **2c**; Eu(hfc)₃ shift *e.r.* = 97.5 : 2.5 = 95.0% *e.e.*

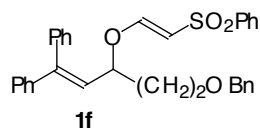
IR (CHCl₃) 2954 (w), 2863 (w), 1732 (s) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 7.44-7.10 (m, 15H), 6.17 (d, *J* = 10.4 Hz, 1H), 4.44 (s, 2H), 3.79 (d, *J* = 8.0 Hz, 1H), 3.69 (s, 3H), 3.62 (s, 3H), 3.62-3.55 (m, 2H), 3.46-3.32 (m, 1H).

¹³C-NMR (62.5 MHz, CDCl₃) δ 168.75 (e), 168.67 (e), 144.99 (e), 142.17 (e), 139.32 (e), 138.07 (e), 129.56 (o), 128.28 (o), 128.08 (o), 127.61 (o), 127.55 (o), 127.40 (o), 127.33 (o), 125.48 (o), 72.98 (e),

71.33 (e), 53.01 (o), 52.31 (o), 39.69 (o).

HRMS (CI, M⁺) calcd for C₂₈H₂₉O₅ 445.2014 found 445.2017.

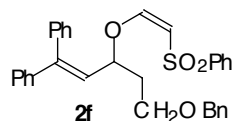


IR (CHCl₃) 3066 (w), 3028 (m), 3016 (m), 2926 (w), 2865 (w), 1622 (s), 1606 (s) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 7.81-7.73 (m, 2H), 7.54-7.37 (m, 4H), 7.37 (d, *J* = 12.2 Hz, 1H), 7.36-7.12 (m, 12 H), 7.08-7.04 (m, 2H), 5.90 (d, *J* = 9.7 Hz, 1H), 5.37 (d, *J* = 12.1 Hz, 1H), 4.70 (ddd, *J* = 9.6, 7.6, 5.2 Hz, 1H), 4.41 (d, *J* = 3.5 Hz, 2H), 3.57-3.50 (m, 2H), 2.16-1.98 (m, 2H).

¹³C-NMR (62.5 MHz, CDCl₃) δ 159.44 (o), 147.32 (e), 142.73 (e), 140.82 (e), 138.24 (e), 138.02 (e), 132.53 (o), 129.51 (o), 128.97 (o), 128.78 (o), 128.61 (o), 128.33 (o), 128.25 (o), 128.18 (o), 127.94 (o), 127.65 (o), 127.60 (o), 127.49 (o), 126.76 (o), 125.38 (o), 107.55 (o), 76.49 (e), 72.94 (e), 65.64 (e), 35.62 (e).

HRMS (FAB, M⁺) calcd for C₃₂H₃₀O₄NaS 533.1762 found 533.1772.

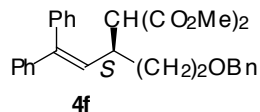


IR (CHCl₃) 3087 (w), 3065 (w), 3020 (m), 2926 (w), 2867 (w), 1620 (s) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 8.00-7.95 (m, 2H), 7.89-7.37 (m, 4H), 7.32-7.09 (m, 12H), 7.05-6.99 (m, 2H), 6.19 (d, *J* = 6.4 Hz, 1H), 5.83 (d, *J* = 9.7 Hz, 1H), 5.45 (d, *J* = 6.4 Hz, 1H), 4.57 (ddd, *J* = 9.7, 7.8, 5.2 Hz, 1H), 4.40 (d, *J* = 11.9 Hz, 1H), 4.31 (d, *J* = 11.9 Hz, 1H), 3.51-3.32 (m, 2H), 2.06-1.91 (m, 2H).

¹³C-NMR (62.5 MHz, CDCl₃) δ 154.93 (o), 146.92 (e), 142.90 (e), 140.48 (e), 138.23 (e), 138.07 (e), 132.67 (o), 129.44 (o), 128.53 (o), 128.47 (o), 128.29 (o), 128.26 (o), 128.05 (o), 127.94 (o), 127.67 (o), 127.53 (o), 127.45 (o), 125.65 (o), 107.72 (o), 80.47 (o), 72.77 (e), 65.43 (e), 35.52 (e).

HRMS (FAB, M⁺) calcd for C₃₂H₃₀O₄NaS 533.1762 found 533.1782.



[α]_D¹⁸ = -39.6 (c = 1.0, CHCl₃), from **1f**; Eu(hfc)₃ shift, *e.r.* = 98.5: 1.5, 97.0 % *e.e.*

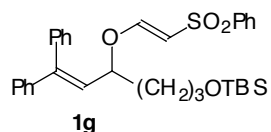
[α]_D¹⁸ = -39.8 (c = 1.0, CHCl₃), from **2f**; Eu(hfc)₃ shift, *e.r.* = 98.8: 1.2, 97.6 % *e.e.*

IR (CHCl₃) 3030 (m), 3012 (m), 2954 (m), 2863 (w), 1733 (s) cm⁻¹.

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.34 (m, 15H), 6.02 (d, $J = 10.7$ Hz, 1H), 4.39 (s, 2H), 3.63 (s, 6H), 3.59-3.36 (m, 2H), 3.52 (d, $J = 7.7$ Hz, 1H), 3.25 (ddt, $J = 10.7, 7.7, 4.6$ Hz, 1H), 1.97-1.71 (m, 2H).

$^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3) δ 168.58 (e), 144.16 (e), 142.54 (e), 139.35 (e), 138.29 (e), 129.63 (o), 128.37 (o), 128.26 (o), 128.20 (o), 128.08 (o), 127.59 (o), 127.47 (o), 127.28 (o), 127.21 (o), 72.77 (e), 68.00 (e), 56.17 (o), 52.33 (o), 52.29 (o), 36.37 (o), 33.16 (e).

HRMS (EI, M^+) calcd for $\text{C}_{29}\text{H}_{30}\text{O}_5$ 458.2093 found 458.2084.

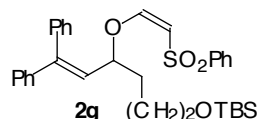


IR (CHCl_3) 2956 (m), 2930 (m), 28.57 (w), 1622 (s), 1605 (s) cm^{-1} .

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.81-7.77 (m, 2H), 7.55-7.39 (m, 3H), 7.41 (d, $J = 12.2$, 1H), 7.38-7.33 (m, 3H), 7.32-7.21 (m, 3H), 7.19-7.13 (m, 2H), 7.08-7.04 (m, 2H), 5.90 (d, $J = 9.5$ Hz, 1H), 5.41 (d, $J = 12.2$ Hz, 1H), 4.41 (dt, $J = 9.5, 6.4$ Hz, 1H), 3.57 (ddd, $J = 12.4, 6.3, 3.9$ Hz, 2H), 1.90-1.78 (m, 2H), 1.65-1.49 (m, 2H), 0.86 (s, 9H), 0.01 (s, 6H).

$^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3) δ 159.45 (o), 146.84 (e), 142.68 (e), 140.62 (e), 138.37 (e), 132.49 (o), 129.32 (o), 128.92 (o), 128.60 (o), 128.19 (o), 127.47 (o), 126.68 (o), 125.75 (o), 107.39 (o), 80.63 (o), 62.27 (e), 31.74 (e), 28.28 (e), 25.85 (o), 18.20 (e), -5.39 (o).

HRMS (FAB, M^+) calcd for $\text{C}_{32}\text{H}_{40}\text{O}_4\text{SiNa}$ 571.2314 found 571.2351.

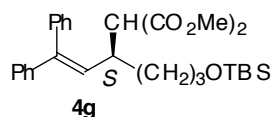


IR (CHCl_3) 2955 (m), 2930 (m), 2856 (w), 1731 (w), 1619 (s) cm^{-1} .

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 8.01-7.97 (m, 2H), 7.58-7.47 (m, 3H), 7.45-7.30 (m, 3H), 7.29-7.24 (m, 3H), 7.22-7.08 (m, 2H), 7.02-6.98 (m, 2H), 6.32 (d, $J = 6.4$, 1H), 5.80 (d, $J = 9.6$, 1H), 5.52 (d, $J = 6.4$ Hz, 1H), 4.30 (dt, $J = 9.6, 6.5$ Hz, 1H), 3.53 (dt, $J = 6.0, 2.9$ Hz, 2H), 1.81-1.69 (m, 2H), 1.51-1.40 (m, 2H), 0.87 (s, 9H), 0.01 (s, 6H).

$^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3) δ 154.61 (o), 146.67 (e), 142.84 (e), 140.35 (e), 138.36 (e), 132.64 (o), 129.30 (o), 128.56 (o), 128.43 (o), 128.23 (o), 127.92 (o), 127.71 (o), 127.40 (o), 126.04 (o), 107.88 (o), 83.13 (o), 62.32 (e), 31.75 (e), 28.13 (e), 25.89 (o), 18.24 (e), -5.37 (o).

HRMS (FAB, M^+) calcd for $\text{C}_{32}\text{H}_{40}\text{O}_4\text{SiNa}$ 571.2314 found 571.2286.



$[\alpha]_D^{18} = -36.6$ ($c = 1.0$, CHCl_3) from **1g**; $\text{Eu}(\text{hfc})_3$ shift $e.r. = 98.0 : 2.0 = 96.0\% e.e.$

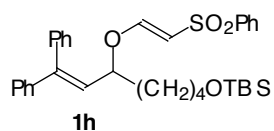
$[\alpha]_D^{18} = -36.6$ ($c = 1.0$, CHCl_3) from **2g**; $\text{Eu}(\text{hfc})_3$ shift $e.r. = 97.4 : 2.6 = 94.8\% e.e.$

IR (CHCl_3) 2954 (s), 2930 (m), 2857 (m), 1733 (s) cm^{-1} .

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.42-7.31 (m, 3H), 7.30-7.16 (m, 7H), 6.00 (d, $J = 10.7$ Hz, 1H), 3.69 (s, 6H), 3.54-3.46 (m, 2H), 3.49 (d, $J = 7.9$ Hz, 1H), 3.14-3.03 (m, 1H), 1.67-1.38 (m, 4H), 0.89 (s, 9H), 0.02 (s, 6H).

$^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3) δ 168.58 (e), 144.02 (e), 142.47 (e), 139.50 (e), 129.65 (o), 128.78 (o), 128.16 (o), 128.04 (o), 127.34 (o), 127.21 (o), 127.13 (o), 62.81 (e), 56.45 (o), 52.26 (o), 38.80 (o), 30.33 (e), 29.84 (e), 25.89 (o), 18.25 (e), -5.35 (o).

HRMS (CI, M^+) calcd for $\text{C}_{29}\text{H}_{41}\text{O}_5\text{Si}$ 497.2723 found 497.2721.

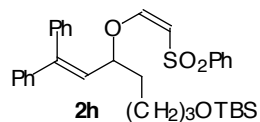


IR (CHCl_3) 3082 (w), 3023 (m), 2953 (s), 2931 (s), 2858 (m), 1622 (s), 1605 (s) cm^{-1} .

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.81-7.76 (m, 2H), 7.56-7.39 (m, 3H), 7.39 (d, $J = 12.0$ Hz, 1H), 7.38-7.35 (m, 3H), 7.29-7.21 (m, 3H), 7.18-7.12 (m, 2H), 7.08-7.02 (m, 2H), 5.90 (d, $J = 9.6$ Hz, 1H), 5.40 (d, $J = 12.2$ Hz, 1H), 4.39 (ddd, $J = 9.5, 7.0, 5.8$ Hz, 1H), 3.57 (t, $J = 5.9$ Hz, 2H), 1.87-1.66 (m, 2H), 1.56-1.24 (m, 4H), 0.86 (s, 9H), 0.01 (s, 6H).

$^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3) δ 159.59 (o), 146.98 (e), 142.77 (e), 140.70 (e), 138.45 (e), 132.54 (o), 129.40 (o), 128.99 (o), 128.65 (o), 128.25 (o), 128.16 (o), 127.52 (o), 126.76 (o), 125.85 (o), 107.37 (o), 80.83 (o), 62.65 (e), 35.12 (e), 32.41 (e), 25.92 (o), 21.45 (e), 18.30 (e), -5.31 (o).

HRMS (FAB, M^+) calcd for $\text{C}_{33}\text{H}_{42}\text{O}_4\text{NaSiS}$ 585.2470 found 585.2463.

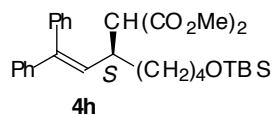


IR (CHCl_3) 3085 (w), 3062 (w), 3023 (m), 3012 (w), 2953 (m), 2931 (m), 2858 (m), 1619 (s) cm^{-1} .

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 8.02-7.97 (m, 2H), 7.58-7.43 (m, 3H), 7.38-7.30 (m, 3H), 7.29-7.21 (m, 3H), 7.13-7.07 (m, 2H), 7.04-6.97 (m, 2H), 6.32 (d, $J = 6.4$ Hz, 1H), 5.79 (d, $J = 9.6$ Hz, 1H), 5.51 (d, $J = 6.4$ Hz, 1H), 4.26 (dt, $J = 6.5, 9.6$ Hz, 1H), 3.54 (t, $J = 6.3$ Hz, 3H), 1.82-1.60 (m, 2H), 1.54-1.40 (m, 2H), 1.38-1.19 (m, 2H), 0.86 (s, 9H), 0.02 (s, 6H).

^{13}C -NMR (62.5 MHz, CDCl_3) δ 154.63 (o), 146.83 (e), 142.91 (e), 140.39 (e), 138.42 (e), 132.66 (o), 129.34 (o), 128.57 (o), 128.45 (o), 128.26 (o), 127.95 (o), 127.75 (o), 127.42 (o), 126.06 (o), 107.88 (o), 83.23 (o), 62.68 (e), 35.00 (e), 32.42 (e), 25.93 (o), 21.29 (e), 18.31 (e), -5.30 (o).

HRMS (EI, M^+) calcd for $\text{C}_{33}\text{H}_{42}\text{O}_4\text{SiS}$ 562.2573 found 562.2540.



$[\alpha]_{\text{D}}^{18} = -46.4$ ($c = 1.0$, CHCl_3), from **1h**; $\text{Eu}(\text{hfc})_3$ shift, *e.r.* = 96.7: 3.3, 93.4 *e.e.*

$[\alpha]_{\text{D}}^{18} = -45.1$ ($c = 1.02$, CHCl_3), from **2h**; $\text{Eu}(\text{hfc})_3$ shift, *e.r.* = 96.1: 3.9, 92.2 % *e.e.*

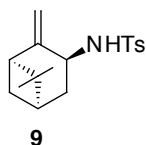
IR (CHCl_3) 3018 (w), 2954 (m), 2931 (m), 2858 (m), 1732 (s) cm^{-1} .

^1H -NMR (250 MHz, CDCl_3) δ 7.38-7.13 (m, 10H), 5.94 (d, $J = 10.8$ Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 3.52 (t, $J = 6.0$ Hz, 2H), 3.42 (d, $J = 7.9$ Hz, 1H), 3.10-2.98 (m, 1H), 1.54-1.31 (m, 5H), 1.25-1.17 (m, 1H), 0.85 (s, 9H), 0.00 (s, 6H).

^{13}C -NMR (62.5 MHz, CDCl_3) δ 168.65 (e), 144.00 (e), 142.58 (e), 139.53 (e), 129.68 (o), 129.01 (o), 128.14 (o), 128.06 (o), 127.39 (o), 127.19 (o), 127.13 (o), 62.86 (e), 56.50 (o), 52.30 (o), 38.98 (o), 33.43 (e), 32.74 (e), 25.93 (o), 23.51 (e), 18.30 (e), -5.31 (o).

HRMS (FAB, M^+) calcd for $\text{C}_{30}\text{H}_{42}\text{O}_5\text{NaSi}$ 533.2699 found 533.2702.

Synthesis of the *cis*-Phosphino(1,3-oxazine) **3**:

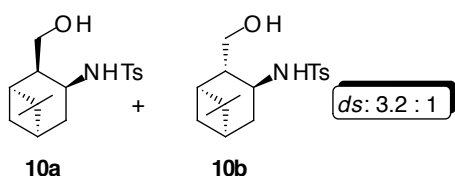


Anhydrous chloramine-T (29.62 g, 127.5 mmol; dried over a 24 hour period in a Kugelröhr oven drying pistol *ca.* 1 mm Hg at 65-70 °C oven temperature) was suspended in anhydrous dichloromethane (210 ml) and mechanically stirred at ambient temperature under an atmosphere of dry argon. Selenium powder (5.08 g, 63.7 mmol) was then added in one portion from a dry flask and the resulting dark gray slurry stirred vigorously for 24 hours. This resulted in a bluish-white slurry which was cooled to 0 °C (NB: If the reagent does not turn this color the reaction will not work). (1*S*)-(-)- β -Pinene (16.2 ml, 101.2 mmol) was then added dropwise *via* syringe, followed after 10 minutes by anhydrous triethylamine (5.6 ml, 40.5 mmol). The resulting greenish-yellow slurry was stirred for *ca.* 2 hours at 0 °C, then a further 12 hours at ambient temperature. The reaction was quenched by the addition of a saturated aqueous solution of sodium bicarbonate (250 ml) and stirred for *ca.* 1 hour. The resulting rusty-brown mixture was filtered through Celite. The organic phase was separated, washed with 1N NaOH (2 x 100 ml), saturated aqueous ammonium chloride (200 ml), brine (200 ml),

dried (Na_2SO_4) and concentrated *in vacuo* to afford a crude brown solid. Hexanes (2 x 100 ml) was added and the mixture was filtered to afford a tannish solid (hexanes washes out much of the organo-selenium residues). The semi-crude solid was purified *via* repeated recrystallizations from toluene to afford **9**¹ (19.19 g, 62%) as a white crystalline solid: $R_f = 0.38$ (3 : 7 ethyl acetate/hexanes). mp 190-192 °C.

IR (CDCl_3) 3373 (m), 3052 (m), 2977 (m), 2934 (m), 1643 (w), cm^{-1} .

^1H NMR (250 MHz, CDCl_3) δ 7.77 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 7.8$ Hz, 2H), 4.69 (s, 1H), 4.59 (d, $J = 5.4$ Hz, 1H), 4.50 (d, $J = 1.1$ Hz, 1H), 2.45-2.33 (m, 2H), 2.42 (s, 3H), 2.25-2.14 (m, 1H), 1.99-1.89 (m, 2H), 1.29 (d, $J = 9.6$ Hz, 1H), 1.19 (s, 3H), 0.61 (s, 3H).



The alkene **9** (320.5 mg, 1.05 mmol) was dissolved in anhydrous THF (10.5 ml) and cooled with stirring to *ca.* -5 °C under an atmosphere of nitrogen. Borane-methyl sulfide complex (10.0-10.2 M in BH_3 , 0.336 ml, 3.4 mmol) was added dropwise *via* syringe, and the colorless reaction was stirred at this temperature for *ca.* 36 hours. The reaction was then quenched by the slow addition of ethanol (3.0 ml), followed by the dropwise addition of 3N NaOH solution (1.0 ml) both of which resulted in the exothermic evolution of hydrogen. A 30% aqueous solution of H_2O_2 (1.3 ml) was then added (fairly rapid addition, not exothermic), and the cloudy white reaction mixture was then allowed to warm to ambient temperature with vigorous stirring and stirred for *ca.* 3 hours. The reaction mixture was partitioned between saturated aqueous sodium bicarbonate and diethyl ether. The combined organic phases were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo* to afford a white crystalline solid. Purification by flash chromatography on silica gel (eluting with a 30-50% ethyl acetate/hexanes gradient) afforded the *cis*-alcohol **10a** (231.2 mg, 68%) and the *trans*-alcohol **10b** (72.2 mg, 21%) as white crystalline solids: $R_{f-cis} = 0.32$; $R_{f-trans} = 0.21$ (1:1 ethyl acetate/hexane).

mp 149-152 °C

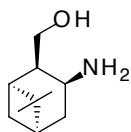
$[\alpha]_D^{18} = -8.7$ ($c = 1.01$, CHCl_3)

IR (CHCl_3) 3514 (s, broad), 3373(m), 3276 (s, broad), 2975 (w), 2928 (s), 1599(m) cm^{-1} .

^1H -NMR (250 MHz, CDCl_3) δ 7.76 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H), 5.17 (d, $J = 8.8$ Hz, 1H), 3.88 (ddd, $J = 11.3, 7.7, 3.5$ Hz, 1H), 3.77-3.67 (m, 1H), 3.43 (ddd, $J = 11.3, 8.8, 4.2$ Hz, 1H), 2.44-2.35 (m, 2H), 2.42 (s, 3H), 2.26-2.17 (m, 1H), 2.08 (dd, $J = 15.0, 8.7$ Hz, 1H), 1.80-1.73 (m, 2H), 1.45 (dd, $J = 14.9, 4.1$ Hz, 1H), 1.17 (s, 3H), 1.08 (d, $J = 10.8$ Hz, 1H), 0.71 (s, 3H).

^{13}C -NMR (62.5 MHz, CDCl_3) δ 143.55 (e), 137.05 (e), 129.81 (o), 127.24 (o), 64.37 (e), 46.42 (o), 43.16 (o), 42.24 (o), 39.87 (o), 39.55 (e), 35.59 (e), 26.28 (e), 26.02 (o), 21.53 (o), 20.26 (o).

HRMS (EI, M⁺) calcd for C₁₇H₂₆NO₃S 324.1633 found 324.1645.



11

Freshly cut sodium metal (1.62 g, 70.5 mmol) was added to a solution of naphthalene (7.04 g, 54.9 mmol; freshly recrystallized) in anhydrous DME (135 ml) at 0 °C under an atmosphere of argon. This mixture was sonicated for 5 minutes to afford a dark green solution that was then stirred for an hour at room temperature. The *N*-tosyl amino alcohol **10a** (2.98 g, 9.21 mmol) was dissolved in anhydrous DME (92 ml) and cooled with stirring to 0 °C. The sodium naphthalenide solution was then added dropwise over *ca.* 30 minutes, and the dark green reaction mixture stirred at 0 °C for a further 3 hours. The reaction was then quenched with saturated aqueous NH₄Cl (20 ml) and allowed to warm to room temperature. The reaction mixture was then diluted with diethyl ether (250 ml) and extracted with 1N HCl solution (3 x 100 ml). The combined aqueous phases were washed with diethyl ether (100 ml), then the pH brought to *ca.* 9 with concentrated NaOH solution and extracted with dichloromethane (6 x 75 ml). The combined organic phases were dried (Na₂SO₄) and concentrated *in vacuo* to furnish the *1,3-amino alcohol 11* (1.468 g, 94%) as an white waxy solid.

mp = 74-77 °C.

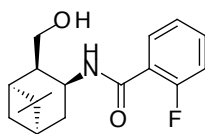
[α]_D¹⁸ = +77.8 (c = 1.0, CHCl₃)

IR (CHCl₃) 3382 (s, broad), 2980 (s), 2922 (s), 2870 (w), 2474 (w), 1582 (m) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 3.75 (t, *J* = 11.0 Hz, 1H), 3.52-3.38 (m, 2H), 2.56-2.38 (m, 5H), 2.22 (ddt, *J* = 6.0, 6.0 4.3 Hz, 1H), 1.93-1.86 (m, 1H), 1.66-1.64 (m, 1H), 1.56 (dt, *J* = 14.4, 2.3 Hz, 1H), 1.19 (s, 3H), 1.17 (d, *J* = 9.1 Hz, 1H), 0.79 (s, 3H).

¹³C-NMR (62.5 MHz, C₆D₆) δ 64.94 (e), 44.38 (o), 44.03 (o), 42.73 (o), 41.63 (o), 40.36 (e), 39.55 (e), 27.13 (e), 26.82 (o), 20.98 (o).

HRMS (CI, M⁺) calcd for C₁₀H₂₀NO 170.1544 found 170.1546.



12

The *1,3-amino alcohol 11* (1.069 g, 6.32 mmol) was dissolved in anhydrous dichloromethane (25 ml) and triethylamine (1.76 ml, 12.62 mmol, 2 eq.) added. The reaction mixture was then cooled with stirring to 0 °C and 2-fluorobenzoyl chloride (800 μL, 6.50 mmol, 1.03 eq.) added neat, and the

reaction stirred for 20 minutes at 0 °C. The reaction was then partitioned between aqueous NaHCO₃ solution and dichloromethane. The combined organic phases were then washed with saturated aqueous NaCl solution, dried (Na₂SO₄) and concentrated *in vacuo* to furnish the crude product. Purification by flash chromatography on silica gel (eluting with a 30-50% ethyl acetate/hexanes gradient) afforded the *amide* **12** (1.26 g, 68%) as a white crystalline solid. Saponification of crude diacylated product (0.539 g, approx. 1.3 mmol) with LiOH.H₂O (0.107 g, 2.55 mmol, 2.0 eq.) in (5 : 1) MeOH/THF (6 ml) at room temperature for *ca.* 9 hours. The reaction was then worked-up and chromatographed as described above to furnish the mono-acylated product (0.183 g, 10 %). Overall yield of *N*-acylated product **12** = 1.443 g, 78%.

mp 112-115 °C.

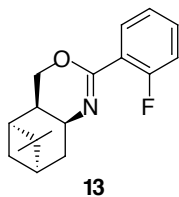
$[\alpha]_D^{18} = -1.1$ (c = 1.01, CHCl₃).

IR (CHCl₃) 3464 (m), 3393 (s, broad), 3007 (s), 2926 (s), 1643 (s), 1616 (m), 1530 (s) cm⁻¹.

¹H-NMR (250 MHz, CDCl₃) δ 8.07 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.50-7.41 (m, 1H), 7.28-7.22 (m, 1H), 7.10 (ddd, *J* = 12.2, 8.2, 1.0 Hz, 1H), 4.73-4.62 (m, 1H), 3.80-3.72 (m, 1H), 3.51 (ddd, *J* = 11.2, 9.3, 4.1 Hz, 1H), 2.75 (dd, *J* = 2.8, 9.3 Hz, 1H), 2.62-2.53 (m, 2H), 2.34-2.26 (m, 1H), 1.99 (dt, *J* = 10.1, 4.5 Hz, 1H), 1.87 (t, *J* = 5.4 Hz, 1H), 1.80-1.73 (m, 1H), 1.26 (s, 3H), 1.22 (d, *J* = 10.9 Hz, 1H), 0.89 (s, 3H).

¹³C-NMR (62.5 MHz, CDCl₃) δ 163.52 (e), 160.59 (e, d, *J* = 247 Hz), 133.32 (o), 133.17 (o), 132.04 (o), 124.84 (o), 124.80 (o), 121.21 (e), 121.02 (e), 116.17 (o), 115.77 (o), 64.79 (e), 43.61 (o), 42.79 (o), 42.32 (o), 40.07 (o), 39.94 (e), 35.07 (e), 26.22 (o), 26.13 (e), 20.30 (o).

HRMS (EI, M⁺) calcd for C₁₇H₂₂NOF 291.1634 found 291.1636.



The hydroxyamide **12** (0.397 g, 1.36 mmol) was dissolved in anhydrous chlorobenzene (6 ml) with heating and added *via* Teflon[®] cannula to a flask containing freshly pyrolyzed zinc chloride (0.042 g, 20 mol%). The reaction mixture was then heated under Dean-Stark conditions for *ca.* 5 hours. The reaction mixture was then concentrated and the crude reaction mixture partitioned between saturated aqueous NaHCO₃ solution and diethyl ether. The combined organic phases were dried (Na₂SO₄) and *in vacuo* to afford the crude product. Purification by flash chromatography on silica gel (eluting with a 10-25% ethyl acetate/hexanes gradient) furnished the *1,3-oxazine* (0.331 g, 89%) as a clear pale yellow oil.

mp 32-34 °C.

$[\alpha]_D^{18} = +77.3$ ($c = 0.99$, CHCl_3).

IR (CHCl_3) 2976 (s), 2939 (s), 2912 (s), 1658 (s) 1615 (m), 1583 (w) cm^{-1} .

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.65 (dt, $J = 7.6, 1.8$ Hz, 1H), 7.38-7.29 (m, 1H), 7.14-7.00 (m, 2H), 4.36 (dd, $J = 11.1, 4.5$ Hz, 1H), 4.07 (dd, $J = 11.1, 2.7$ Hz, 1H), 3.96 (t, $J = 9.5$ Hz, 1H), 2.52-2.39 (m, 2H), 2.22-2.13 (m, 1H), 2.10-2.03 (m, 1H), 1.98-1.89 (m, 2H), 1.39 (d, $J = 10.4$ Hz, 1H), 1.26 (s, 3H), 0.88 (s, 3H).

$^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3) δ 162.83 (e), 156.37 (e, d, $J = 304$ Hz), 131.59 (o), 131.46 (o), 130.48 (o), 123.78 (o), 123.72 (o), 122.81 (e), 122.64 (e), 116.55 (o), 116.20 (o), 69.34 (e), 45.89 (o), 40.64 (e), 40.10 (o), 34.72 (o), 34.37 (e), 26.20 (o), 25.70 (e), 20.23 (o).

HRMS (EI, M^+) calcd for $\text{C}_{17}\text{H}_{20}\text{NOF}$ 273.1528 found 273.1531.

The fluoro-1,3-oxazine **13** (0.331 g, 1.21 mmol) was dissolved in anhydrous THF (10 ml) and heated to reflux. Potassium diphenylphosphide (2.7 ml, 1.35 mmol, 1.1 eq.; 0.5 M solution in THF) was quickly added and the reaction maintained at reflux for an additional 15 minutes. The reaction was then quenched by the addition of water, and partitioned between a saturated aqueous NaHCO_3 solution and diethyl ether. The combined organic layers were washed with brine, dried (Na_2SO_4) and *in vacuo* to afford the crude product. Purification by flash chromatography on silica gel (eluting with a 7-10% ethyl acetate/hexanes gradient) furnished the *phosphino-1,3-oxazine 3* (0.358 g, 67%) as a clear glue-like oil. The product was redissolved in dichloromethane, concentrated under reduced pressure and then dried under high vacuum to furnish the product as a white foam.

mp 109-111 °C.

$[\alpha]_D^{18} = -17.6$ ($c = 1.01$, CHCl_3).

IR (CHCl_3) 3058 (m), 2975 (s), 2937 (s), 1661 (s) cm^{-1} .

$^1\text{H-NMR}$ (250 MHz, CDCl_3) δ 7.76 (m, 1H), 7.27 (m, 12H), 6.84 (m, 1H), 3.86 (m, 1H), 3.74 (m, 2H), 2.27 (m, 1H), 2.02 (m, 2H), 1.82 (m, 3H), 2.43 (d, $J = 10.5$ Hz, 1H), 1.19 (s, 3H), 0.80 (s, 3H).

$^{13}\text{C-NMR}$ (62.5 MHz, CDCl_3) δ 138.78 (e), 138.58 (e), 137.56 (e), 137.22 (e), 134.33 (o), 134.08 (o), 133.99 (o), 133.74 (o), 133.42 (o), 129.78 (o), 129.89 (o), 128.42 (o), 128.38 (o), 128.32 (o), 128.28 (o), 128.22 (o), 68.47 (e), 45.66 (o), 45.43 (o), 40.45 (e), 40.15 (o), 34.63 (o), 33.76 (e), 26.25 (o), 25.78 (e), 20.25 (o).

HRMS (EI, M^+) calcd for $\text{C}_{29}\text{H}_{30}\text{NOP}$ 439.2065 found 439.2067.

References

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