Catalytic Asymmetric Synthesis of Chiral Allylic Amines. Evaluation of Ferrocenyloxazoline Palladacycle Catalysts and Imidate Motifs

Carolyn E. Anderson, Yariv Donde, Christopher J. Douglas and Larry E. Overman*

Department of Chemistry, 516 Rowland Hall, University of California, Irvine, CA
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Supporting Information

(63 Pages)

Section A contains representative experimental procedures for the preparation of **5c–d**, **6c–d**, **26a–h**, **27a–c**, **27e–f**, **27h**, **29–36**, **43c–d**, **45–47**, **49**, **50**, **53** with tabulated characterization data for these new compounds. Pages S2–S23

Section B contains copies of ^1H and ^{13}C NMR spectra for new compounds described in section A. Pages S24–S57

Section C contains representative HPLC traces for selected reactions. Pages S58–S63

A. Experimental Procedures and Tabulated Characterization Data

General experimental details: The procedure employed to purify THF and CH₂Cl₂ has been described;¹ other general experimental details also have been described.²

(*R*_p)-1-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-2-phenyl ferrocene (26a). Iodide **25**

(300 mg, 0.69 mmol), phenylboronic acid (167 mg, 1.3 mmol), and PdCl₂dppf·CH₂Cl₂ (56 mg, 0.07 mmol) were charged to a sealable reaction flask. The flask was evacuated and backfilled with argon before adding DME (3.5 mL) and aqueous NaOH (3 N, 0.56 mL, 1.73 mmol). The resulting black suspension was sparged with argon

for 15 min. The reaction was heated to 85 °C and maintained for 2 h before cooling to room temperature. The reaction was then diluted with EtOAc (50 mL) and extracted with water (50 mL). The aqueous phase was extracted with EtOAc (50 mL) and the combined organic portions were washed with brine (50 mL), dried (MgSO₄), and concentrated *in vacuo* to afford a red oil. Purification by column chromatography (CH₂Cl₂) provided **26a** (224 mg, 84%) as an orange foam: [α]_D²⁶ = −8.8°, [α]₅₇₇²⁶ = −10.1°, [α]₅₄₆²⁶ = −16.0°, (c = 0.9, CHCl₃); ¹H NMR (500 MHz, C₆D₆) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.25 (m, 1H),²⁰ 5.06 (app s, 1H), 4.47 (app s 1H), 4.19 (s, 5H), 3.80–3.89 (m, 3H), 0.98 (s, 9H); ¹³C NMR (125 MHz, C₆D₆) δ 164.3, 137.8, 130.6, 127.2, 126.7, 89.6, 76.9, 72.8, 71.6, 71.3, 70.5, 69.2, 67.8, 33.9, 26.3; IR (film) 2955, 1659, 1602 cm^{−1}; LRMS (ES) *m/z* 410 (M + Na)⁺, 388 (M + H)⁺; Anal. Calcd for C₂₃H₂₅FeNO: C, 71.33; H, 6.51; N, 3.62. Found: C, 71.19; H, 6.57; N, 3.52.

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, **1996**, 15, 1518.

² Deng, W.; Overman, L. E. *J. Am. Chem. Soc.* **1994**, 116, 11241.

(*R_p*)-1-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-2-(4-methoxyphenyl) ferrocene

(26b). According to the procedure for the preparation of **26a**, 4-methoxyphenylboronic acid (148 mg, 0.92 mmol) and iodide **25** (200 mg, 0.46 mmol) were condensed to afford a red oil which upon purification by column chromatography (1:99, Et₂O/CH₂Cl₂) provided **26b** (169 mg, 88%) as an orange foam: $[\alpha]_D^{26} = -12.4^\circ$, $[\alpha]_{577}^{26} = -14.1^\circ$, $[\alpha]_{546}^{26} = -22.5^\circ$, ($c = 0.9$,

CHCl₃); ¹H NMR (500 MHz, C₆D₆) δ 7.90 (app dt, $J = 8.9, 2.2$ Hz, 2H), 6.96 (app dt, $J = 8.8, 2.6$ Hz, 2H), 5.07 (dd, $J = 2.6, 1.7$ Hz, 1H), 4.48 (dd, $J = 2.4, 1.7$ Hz, 1H), 4.23 (s, 5H), 4.20 (app t, $J = 2.6$ Hz, 1H), 3.90–3.92 (m, 2H), 3.83 (dd, $J = 10.2, 7.8$ Hz, 1H), 3.46 (s, 3H), 1.00 (s, 9H); ¹³C NMR (125 MHz, C₆D₆) δ 164.5, 158.8, 131.6, 129.7, 112.9, 89.7, 76.9, 72.5, 71.3, 71.2, 70.2, 69.0, 67.8, 54.9, 33.9, 26.3; IR (film) 2955, 1660, 1612 cm⁻¹; LRMS (CI, isobutane) m/z 417 (M)⁺, 360 (M – *t*-Bu)⁺, 317 (M – methoxyphenyl)⁺; Anal. Calcd for C₂₄H₂₇FeNO₂: C, 69.07; H, 6.52; N, 3.36. Found: C, 69.28; H, 6.39; N, 3.09.

(*R_p*)-1-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-2-(4-trifluoromethylphenyl) ferrocene (26c).

According to the procedure for the preparation of **26a**, 4-trifluoromethylphenylboronic acid (1.9 g, 10.0 mmol) and iodide **25** (1.09 g, 2.5 mmol) were condensed to afford a red oil which upon purification by column chromatography (5:95, Et₂O/CH₂Cl₂) and recrystallization (*n*-hexane, –20 °C) gave **26c**

(351 mg, 33%) as orange prisms: mp 132–135 °C; $[\alpha]_D^{26} = -14.8^\circ$, $[\alpha]_{577}^{26} = -16.9^\circ$, $[\alpha]_{546}^{26} = -25.2^\circ$, ($c = 2.2$, CHCl₃); ¹H NMR (400 MHz, C₆D₆) δ 7.74 (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 8.1$ Hz, 2H), 4.94 (dd, $J = 2.6, 1.6$ Hz, 1H), 4.24 (dd, $J = 2.5, 1.6$ Hz, 1H), 4.07 (app t, $J = 2.6$ Hz, 1H), 4.02 (s, 5H), 3.74–3.72 (m, 2H), 3.66 (dd, $J = 10.7, 7.0$ Hz, 1H), 0.83 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 164.6, 141.8, 130.3, 128.4 (q, $J = 32.3$ Hz), 124.4 (q, $J = 270.3$ Hz), 124.0 (app q, $J = 3.5$ Hz), 86.8, 76.6, 72.2, 71.7, 71.1, 70.0, 69.4, 67.9, 33.8, 26.0; IR (film) 3054, 2961, 1659, 1616 cm⁻¹; LRMS (ES) m/z 478 (M +

Na)⁺, 456 (M + H)⁺; Anal. Calcd for C₂₄H₂₄F₃FeNO: C, 63.31; H, 5.31; N, 3.08. Found: C, 63.38; H, 5.52; N, 2.95.

(R_p)-1-[(4S)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-2-(2,6-dimethoxyphenyl) ferrocene

(26d). According to the procedure for the preparation of **26a**, 2,6-dimethoxyphenylboronic acid (546 mg, 3.0 mmol) and iodide **25** (658 mg, 1.5 mmol) were condensed to afford a red oil which upon purification by column chromatography (5:95, Et₂O/CH₂Cl₂) and recrystallization (pentane, −20 °C) afforded

26d (134 mg, 20%) as orange needles: mp 147–149 °C; [α]_D²⁶ = +37.3°, [α]₅₇₇²⁶ = +47.4°, [α]₅₄₆²⁶ = +79.1°, [α]₄₃₅²⁶ = −241.7°, [α]₄₀₅²⁶ = −312.8°, (c = 0.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.90 (t, *J* = 8.3 Hz, 1H), 6.55 (d, *J* = 8.3 Hz, 2H), 4.90 (app t, *J* = 2.0 Hz, 1H), 4.43–4.44 (m, 2H), 4.18 (s, 5H), 4.15 (dd, *J* = 8.3, 7.2 Hz, 1H), 3.74–3.83 (m, 8H), 0.94 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 167.1, 158.2 (b), 127.6, 113.9, 103.9, 80.4, 75.9, 73.7, 71.1, 70.8, 68.9, 68.6, 68.4, 55.8, 33.2, 26.4; IR (film) 2953, 1645, 1586 cm^{−1}; LRMS (ES) *m/z* 470 (M + Na)⁺, 448 (M + H)⁺; Anal. Calcd for C₂₅H₂₉FeNO₃: C, 67.12; H, 6.53; N, 3.13. Found: C, 67.34; H, 6.60; N, 3.06.

(R_p)-1-[(4S)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-2-(1-naphthyl) ferrocene (26e).

According to the procedure for the preparation of **26a**, iodide **25** (876 mg, 2.00 mmol) and 1-naphthaleneboronic acid (688 mg, 4.00 mmol) were condensed to afford a red oil. Purification of this oil by column chromatography (CH₂Cl₂) and recrystallization (*n*-hexane, −20 °C) provided **26e** (802 mg,

92%) as yellow needles: mp 107–109 °C; [α]_D²⁶ = +21.1°, [α]₅₇₇²⁶ = +24.3°, [α]₅₄₆²⁶ = +37.8°, [α]₄₃₅²⁶ = −42.7°, [α]₄₀₅²⁶ = −68.8°, (c = 1.0, CHCl₃); ¹H NMR (500 MHz, C₆D₆) δ 8.32 (d, *J* = 7.0 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.87 (t, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.27–7.33 (m, 2H), 5.25 (app t, *J* = 2.0 Hz, 1H), 4.38 (app t, *J* = 1.8 Hz, 1H), 4.32 (s, 5H), 4.21 (app t, *J* = 2.4 Hz, 1H), 3.61–3.68 (m, 2H), 3.36–3.42 (m, 1H), 0.87 (s,

9H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.1, 134.6, 133.3, 133.0, 129.3, 128.0, 127.3, 125.9, 125.5, 125.1, 124.8, 89.9, 76.0, 75.0, 71.5, 70.8, 69.3, 68.7, 68.1, 33.5, 26.0; IR (film) 3054, 2986, 1646, 1598 cm^{-1} ; LRMS (ES) m/z 460 ($\text{M} + \text{Na}$) $^+$, 438 ($\text{M} + \text{H}$) $^+$; Anal. Calcd for $\text{C}_{27}\text{H}_{27}\text{FeNO}$: C, 74.15; H, 6.22; N, 3.20. Found: C, 74.02; H, 6.31; N, 3.32.

(*R_p*)-1-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-2-(2-methylphenyl) ferrocene (26f).

According to the procedure for the preparation of **26a**, *o*-tolylboronic acid (126 mg, 0.92 mmol) and iodide **25** (200 mg, 0.46 mmol) were condensed to afford a red oil which upon purification by column chromatography (CH_2Cl_2) provided **26f** (163 mg, 89%) as an orange foam: $[\alpha]_{\text{D}}^{26} = +9.7^\circ$, $[\alpha]_{577}^{26} = +10.9^\circ$, $[\alpha]_{546}^{26} = +19.5^\circ$, ($c = 0.8$, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.07 (dd, $J = 7.6, 1.4$ Hz, 1H), 7.23 (app dt, $J = 7.5, 1.9$ Hz, 2H), 7.15–7.17 (m, 1H), 7.07 (app d, $J = 7.5$ Hz, 1H), 4.99 (dd, $J = 2.6, 1.6$ Hz, 1H), 4.19 (s, 5H), 4.09 (dd, $J = 2.4, 1.6$ Hz, 1H), 4.04 (app t, $J = 2.5$, 1H), 3.60–3.71 (m, 3H), 2.11 (s, 3H), 0.77 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.7, 138.5, 136.8, 132.9, 129.4, 127.2, 125.1, 92.3, 76.6, 74.1, 71.5, 71.0, 69.9, 68.7, 68.0, 33.7, 26.1, 20.7; IR (film) 1645, 1605 cm^{-1} ; LRMS (CI, isobutane) m/z 401 (M) $^+$, 344 ($\text{M} - t\text{-Bu}$) $^+$; Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{FeNO}$: C, 71.83; H, 6.78; N, 3.49. Found: C, 71.56; H, 6.65; N, 3.29.

(*R_p*)-1-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-2-(2-methoxyphenyl) ferrocene (26g).

According to the procedure for the preparation of **26a**, 2-methoxyphenylboronic acid (148 mg, 0.92 mmol) and iodide **25** (200 mg, 0.46 mmol) were condensed to afford a red oil which upon purification by column chromatography (2:98 acetone/hexanes) provided **26g** (160 mg, 83%) as an orange foam: $[\alpha]_{\text{D}}^{26} = -168.6^\circ$, $[\alpha]_{577}^{26} = -112.8^\circ$, $[\alpha]_{546}^{26} = +28.1^\circ$, ($c = 0.2$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 8.10 (d, $J = 7.4$ Hz, 1H), 7.11–7.14 (m, 1H), 6.69 (d, $J = 8.2$ Hz, 1H), 5.18 (app s, 1H), 4.52 (app s, 1H), 4.28 (s, 1H), 4.21 (dd, $J = 2.5, 2.4$ Hz, 1H), 3.76–3.92

(m, 3H), 3.20 (s, 3H), 1.02 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 166.1, 158.9, 134.0, 128.0, 127.2, 120.5, 111.2, 77.2, 74.9, 71.6, 70.9, 69.3, 68.7, 55.7, 34.1, 26.9; IR (film) 3019, 2959, 1643, 1602 cm^{-1} ; LRMS (ES) m/z 440 ($\text{M} + \text{Na}$) $^+$, 418 ($\text{M} + \text{H}$) $^+$; Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{FeNO}_2$: C, 69.07; H, 6.52; N, 3.36. Found: C, 69.25; H, 6.58; N, 3.36.

(*R_p*)-1-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-2-(4-thiomethylphenyl) ferrocene

(26h). According to the procedure for the preparation of **26a**, 4-(methylthio)phenylboronic acid (672 mg, 4.0 mmol) and iodide **25** (875 mg, 2.0 mmol) were condensed to afford a red oil which upon purification by column chromatography (CH_2Cl_2) provided **26h** (660 mg, 76%) as a red oil which solidified upon standing:

mp 86–87 °C; $[\alpha]_{\text{D}}^{26} = -17.0^\circ$, $[\alpha]_{577}^{26} = -19.4^\circ$, $[\alpha]_{546}^{26} = -32.7^\circ$, ($c = 0.6$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.84 (d, $J = 8.3$ Hz, 1H), 7.29 (d, $J = 8.3$ Hz, 2H), 5.07 (app d, $J = 1.7$ Hz, 1H), 4.45 (app d, $J = 1.7$ Hz, 1H), 4.20–4.21 (overlapping peaks, m, 1H, s, 5H), 3.81–3.90 (m, 3H), 2.15 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.9, 136.3, 134.3, 130.4, 125.6, 88.2, 76.4, 71.9, 71.0, 70.9, 69.4, 69.0, 67.9, 33.8, 26.0, 15.9; IR (film) 2955, 1660, 1599 cm^{-1} ; LRMS (ES) m/z 456 ($\text{M} + \text{Na}$) $^+$, 435 ($\text{M} + \text{H}$) $^+$, 434 (M) $^+$; Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{FeNOS}$: C, 66.51; H, 6.28; N, 3.23. Found: C, 66.45; H, 6.45; N, 3.06.

(*R_p*)-2-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-1-iodo-3-phenyl ferrocene (27a). A

solution of oxazoline **26a** (357 mg, 0.92 mmol) in THF (9.0 mL) was precooled to 0 °C and *tert*-BuLi (1.5 M in pentane, 0.5 mL, 0.83 mmol) was added dropwise. The dark red solution was maintained at 0 °C for 15 min. A solution of diiodoethane (233 mg, 0.83 mmol) in THF (5.0 mL) was added by cannula. The solution

was allowed to warm to room temperature and quenched with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution (10 mL). The mixture was extracted with EtOAc (2 $\times$ 10 mL), the combined EtOAc solution dried (MgSO_4), and concentrated *in vacuo* to provide a red oil.

Purification by column chromatography (5:95 EtOAc/hexanes) provided **27a** (332 mg, 78% based on *tert*-BuLi) as a light sensitive orange foam: ^1H NMR (500 MHz, CDCl_3) δ 7.58–7.60 (m, 2H), 7.27–7.34 (m, 3H), 4.70 (d, $J = 2.5$ Hz, 1H), 4.64 (d, $J = 2.5$ Hz, 1H), 4.31 (dd, $J = 10.1, 8.5$ Hz, 1H), 4.29 (s, 5H), 4.18 (app t, $J = 8.7$ Hz, 1H), 4.08 (dd, $J = 10.1, 8.8$ Hz, 1H), 1.02 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.6, 136.6, 129.1, 127.7, 126.9, 88.4, 77.04, 76.7, 75.6, 74.2, 70.5, 68.7, 43.4, 33.8, 26.2; IR (film) 2955, 1660, 1602 cm^{-1} ; LRMS (ES) m/z 514 ($\text{M} + \text{H}^+$); HRMS (CI, NH_3) m/z 512.0177 (512.0174 calcd for $\text{C}_{23}\text{H}_{23}\text{FeINO}$, ($\text{M} - \text{H}^+$)).

(*R_p*)-2-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-1-iodo-3-(4-methoxyphenyl)

ferrocene (27b). According to the procedure for the preparation of **27a**, oxazoline **26b** (297 mg, 0.71 mmol) in THF (7.0 mL) was treated with *tert*-BuLi (1.40 M in pentane, 0.5 mL, 0.70 mmol) and quenched with a solution of diiodoethane (183 mg, 0.65 mmol) in THF (3.5 mL). Purification by column

chromatography (10:90 EtOAc/hexanes) provided **27b** (259 mg, 73% based on diiodoethane) as a light sensitive orange foam: $[\alpha]_{\text{D}}^{26} = +111.0^\circ$, ($c = 0.2$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.45 (app dt, $J = 8.8, 2.5$ Hz, 2H), 6.80 (app dt, $J = 8.8, 2.5$ Hz, 2H), 4.60 (d, $J = 2.5$ Hz, 1H), 4.52 (d, $J = 2.5$ Hz, 1H), 4.27 (dd, $J = 10.1, 8.6$ Hz, 1H), 4.21 (s, 5H), 4.11 (app t, $J = 8.6$ Hz, 1H), 4.00 (dd, $J = 10.1, 8.8$ Hz, 1H), 3.80 (s, 3H), 0.95 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.7, 158.6, 130.1, 128.6, 113.2, 88.4, 76.9, 76.2, 75.3, 74.0, 70.2, 68.6, 55.2, 43.3, 33.7, 26.2; IR (film) 2956, 1661, 1612 cm^{-1} ; LRMS (ES) m/z 566 ($\text{M} + \text{Na}^+$), 544 ($\text{M} + \text{H}^+$); HRMS (CI, NH_3) m/z 543.0358 (543.0360 calcd for $\text{C}_{24}\text{H}_{26}\text{FeINO}_2$, M^+).

(*R*_p)-2-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-1-iodo-3-(4-trifluoromethylphenyl) ferrocene (27c).

According to the procedure for the preparation of **27a**, oxazoline **26c** (100 mg, 0.22 mmol) in THF (2.0 mL) was treated with *tert*-BuLi (1.25 M in pentane, 0.16 mL, 0.2 mmol) and quenched with a solution of diiodoethane (60 mg, 0.21 mmol) in THF (1.0 mL). Purification by column chromatography

(CH₂Cl₂) provided **27c** (66 mg, 57% based on *tert*-BuLi) as a light sensitive orange foam: $[\alpha]_D^{26} = -56.0^\circ$, (*c* = 0.1, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 4.69 (d, *J* = 2.5 Hz, 1H), 4.61 (d, *J* = 2.5 Hz, 1H), 4.30 (dd, *J* = 10.0, 8.7 Hz, 1H), 4.23 (s, 5H), 4.12 (app t, *J* = 8.7 Hz, 1H), 4.02 (app t, *J* = 9.5 Hz, 1H), 0.95 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 162.3, 141.1, 129.2, 128.8 (q, *J* = 32.3 Hz), 124.6 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 270.1 Hz), 86.5, 77.04, 76.9, 76.2, 74.3, 70.8, 68.7, 43.3, 33.8, 26.2; IR (film) 2955, 1658, 1617 cm⁻¹; LRMS (ES) *m/z* 604 (*M* + Na)⁺, 582 (*M* + H)⁺; HRMS (EI) *m/z* 581.0117 (581.0127 calcd for C₂₄H₂₃F₃FeINO, *M*⁺).

(*R*_p)-2-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-1-iodo-3-(1-naphthyl) ferrocene (27e).

According to the procedure for the preparation of **27a**, oxazoline **26e** (400 mg, 0.91 mmol) in THF (9.0 mL) was treated with *tert*-BuLi (1.25 M in pentane, 0.7 mL, 0.87 mmol) and quenched with diiodoethane (268 mg, 0.87 mmol) in THF (4.5 mL). Purification by column chromatography (2:98

EtOAc/hexanes) provided **27e** (323 mg, 66% based on *tert*-BuLi) as a light sensitive orange foam: $[\alpha]_D^{26} = +20.0^\circ$, $[\alpha]_{577}^{26} = +23.8^\circ$, $[\alpha]_{546}^{26} = +23.8^\circ$, $[\alpha]_{435}^{26} = +89.2^\circ$, $[\alpha]_{405}^{26} = +22.5^\circ$, (*c* = 0.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 7.0 Hz, 1H), 7.76–7.81 (m, 3H), 7.56 (app t, *J* = 7.9 Hz, 1H), 7.39 (app t, *J* = 7.4 Hz, 1H), 7.34 (app t, *J* = 7.5 Hz, 1H), 4.77 (d, *J* = 2.4 Hz, 1H), 4.78 (d, *J* = 2.6 Hz, 1H), 4.37 (s, 5H), 4.01 (app t, *J* = 12.6 Hz, 1H), 3.73–3.77 (m, 2H), 0.87 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 162.3, 133.3, 133.2, 133.1, 129.3, 128.0, 127.7, 125.9, 125.8, 125.4, 124.7, 90.0, 76.7, 76.5, 75.7, 74.1, 73.8, 68.2, 42.0, 33.5, 25.8; IR (film) 3049, 2954, 1657, 1594 cm⁻¹;

LRMS (ES) m/z 586 ($M + Na$)⁺, 564 ($M + H$)⁺; HRMS (EI) m/z 563.0423 (563.0410 calcd for $C_{27}H_{26}FeINO$, M^+).

(*R*_p)-2-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-1-iodo-3-(2-methylphenyl)

ferrocene (27f). According to the procedure for the preparation of **27a**, oxazoline **26f** (410 mg, 1.02 mmol) in THF (10.0 mL) and *tert*-BuLi (1.5 M in pentane, 0.6 mL, 0.92 mmol) was quenched with a solution of diiodoethane (259 mg, 0.92 mmol) in THF (5.0 mL). Purification by column chromatography (5:95 EtOAc/hexanes)

provided **27f** (361 mg, 74% based on *tert*-BuLi) as a light sensitive orange foam: $[\alpha]_D^{26} = +45.0^\circ$, $[\alpha]_{577}^{26} = +33.2^\circ$, $[\alpha]_{546}^{26} = +23.2^\circ$, ($c = 0.2$, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$) δ 7.79 (app dd, $J = 8.9, 2.7$ Hz, 1H), 7.14–7.24 (m, 2H), 7.09–7.11 (m, 1H), 4.66 (d, $J = 2.4$ Hz, 1H), 4.37 (d, $J = 2.4$ Hz, 1H), 4.33 (s, 5H), 4.12 (dd, $J = 10.0, 8.7$ Hz, 1H), 4.00 (app t, $J = 8.2$ Hz, 1H), 3.82 (dd, $J = 10.1, 7.8$ Hz, 1H), 2.08 (s, 3H), 0.77 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 138.2, 134.7, 132.1, 129.2, 127.1, 124.7, 91.3, 76.5, 76.4, 75.3, 73.9, 72.6, 68.2, 42.2, 33.6, 25.8, 20.6; IR (film) 2952, 1651, 1603 cm^{-1} ; LRMS (ES) m/z 550 ($M + Na$)⁺, 528 ($M + H$)⁺; HRMS (CI, NH_3) m/z 527.0407 (527.0409 calcd for $C_{24}H_{26}FeINO$, M^+).

(*R*_p)-2-[(4*S*)-4,5-dihydro-4-*tert*-butyl-2-oxazolyl]-1-iodo-3-(4-methylthiophenyl)

ferrocene (27h). According to the procedure for the preparation of **27a**, oxazoline **26h** (660 mg, 1.52 mmol) in THF (15.0 mL) and *tert*-BuLi (0.77 M in pentane, 1.9 mL, 1.44 mmol) was quenched with a solution of diiodoethane (406 mg, 1.44 mmol) in THF (7.5 mL). Purification by column chromatography (CH_2Cl_2) provided **27h** (644 mg, 80% based on *tert*-BuLi) as a

light sensitive orange foam: $[\alpha]_D^{26} = +120.0$, ($c = 0.1$, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 7.48 (app dt, $J = 8.6, 2.0$ Hz, 2H), 7.18 (app dt, $J = 8.5, 2.0$ Hz, 2H), 4.67 (d, $J = 2.5$ Hz, 1H), 4.59 (d, $J = 2.5$ Hz, 1H), 4.32 (dd, $J = 10.1, 8.5$ Hz, 1H), 4.25 (s, 5H), 4.12

(app t, $J = 8.6$ Hz, 1H), 4.05 (dd, $J = 10.1, 8.8$ Hz, 1H), 2.52 (s, 3H), 1.00 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 162.5, 136.9, 133.5, 129.4, 126.0, 87.9, 77.3, 76.6, 75.9, 74.4, 70.6, 69.0, 43.8, 34.2, 26.7, 16.3; IR (film) 2953, 1657, 1599 cm^{-1} ; LRMS (ES) m/z 582 ($\text{M} + \text{Na}$) $^+$, 560 ($\text{M} + \text{H}$) $^+$; HRMS (EI) m/z 559.0130 (559.0131 calcd for $\text{C}_{24}\text{H}_{26}\text{FeINOS}$, M^+).

(R_p)-bis-(μ -iodo-{2-[(4S)-2-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)]-3-phenyl-ferrocenyl} dipalladium (29).

To a solution of iodide **27a** (361 mg, 0.69 mmol) in benzene (15.0 mL), $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (427 mg, 0.41 mmol) was added in one portion. The dark red solution was protected from light and maintained for 18 h before filtering through a plug of Florisil (100–200 mesh, benzene), and

concentrating *in vacuo* to provide a red solid. Purification of the residue by column chromatography (1:2 hexanes/benzene) provided **29** (350 mg, 81%) as a mixture of isomers, red prisms.: mp 190–194 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.49–7.52 (m, 4H), 7.21–7.29 (m, 6H) 20 , 5.03–5.07 (m, 2H), 4.75–4.78 (m, 2H), 4.39–4.43 (m, 10H), 3.92–3.95 (m, 5H), 1.03 (s, 9H), 1.02 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 179.9, 179.5, 136.8, 129.1, 128.8, 128.0, 127.9, 126.8, 99.7, 99.2, 86.7, 79.1, 78.5, 74.6, 73.2, 73.1, 73.0, 72.8, 71.8, 71.6, 71.2, 70.1, 70.0, 69.5, 35.8, 35.8, 30.1, 27.2, 27.1, (not all carbon signals for the two isomers are resolved); IR (film) 2961, 1583 cm^{-1} ; MS (FAB, MNBA) m/z 1239, 619, 388; Anal. Calcd for $\text{C}_{46}\text{H}_{48}\text{Fe}_2\text{I}_2\text{N}_2\text{O}_2\text{Pd}_2$: C, 44.58; H, 3.90; N, 2.26. Found: C, 44.39; H, 3.78; N, 2.24.

(R_p)-bis-(μ -iodo-{2-[(4S)-2-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)]-3-(4-

methoxyphenyl)-ferrocenyl} dipalladium (30). A solution of iodide **27b** (241 mg, 0.44 mmol) in benzene (17.0 mL) was allowed to react with $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (280 mg, 0.27 mmol) as described for the preparation of **29**. Purification of the crude product by column chromatography (1:2 hexanes/benzene)

provided **30** (272 mg, 95%). Filtration through a plug of SiO₂ (CH₂Cl₂) provided analytically pure **30** as a mixture of isomers, red prisms (257 mg, 90%): mp 201 °C; $[\alpha]_D^{26} = +20.5^\circ$, $[\alpha]_{577}^{26} = +23.8^\circ$, $[\alpha]_{546}^{26} = +33.2^\circ$, (*c* = 0.2, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.43–7.45 (m, 4H), 6.80–6.83 (m, 4H), 5.01–5.04 (m, 2H), 4.72–4.77 (m, 2H), 4.54–4.58 (m, 2H), 4.42 (s, 5H), 4.38 (s, 5H), 3.91–3.95 (m, 2H), 3.80 (m, 6H), 1.02 (s, 18H); ¹³C NMR (125 MHz, CDCl₃) δ 179.7, 179.3, 158.2, 129.6, 128.5, 129.6, 128.5, 113.3, 113.2, 99.4, 98.9, 86.5, 78.6, 77.9, 74.3, 72.8, 72.7, 70.9, 70.8, 69.7, 69.1, 55.3, 35.5, 26.9, 26.8, (not all carbon signals for the isomers are resolved); IR (film) 2961, 1586 cm⁻¹; MS (MALDI) *m/z* 1340, 1152, 978, 857, 669; Anal. Calcd for C₄₈H₅₂Fe₂I₂N₂O₄Pd₂: C, 44.37; H, 4.03; N, 2.16. Found: C, 44.59; H, 4.18; N, 2.10.

(*R_p*)-bis- μ -iodo-{2-[(4*S*)-2-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)]-3-(4-

trifluoromethylphenyl)-ferrocenyl} dipalladium (31**). A solution of iodide **27c** (113 mg, 0.19 mmol) in benzene (4.0 mL) was allowed to react with Pd₂dba₃·CHCl₃ (118 mg, 0.11 mmol) as described for the preparation of **29**. Purification of the crude product by column chromatography (1:1 hexanes/benzene) provided **31a** (116 mg, 89%) as a mixture of isomers, red prisms:**

mp 220 °C; $[\alpha]_D^{26} = +172.9^\circ$, $[\alpha]_{577}^{26} = +137.7^\circ$, $[\alpha]_{546}^{26} = +43.2^\circ$, (*c* = 0.4, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.61–7.63 (m, 4H), 7.49–7.52 (m, 4H), 5.12 (d, *J* = 2.3 Hz, 1H), 5.09 (d, *J* = 2.2 Hz, 1H), 4.78 (app td, *J* = 9.4, 2.3 Hz, 2H), 4.68–4.67 (m, 2H), 4.55–4.61 (m, 2H), 4.43 (s, 5H), 4.40 (s, 5H), 3.93–3.97 (m, 2H), 0.994 (s, 9H), 0.991 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 179.8, 179.4, 141.3, 128.9, 128.5 (q, *J* = 32.3 Hz), 124.8 (q, *J* = 3.5 Hz), 124.3 (q, *J* = 270.3), 99.6, 99.1, 84.3, 79.5, 78.8, 74.42, 74.38, 73.1, 72.9, 71.8, 71.6, 71.0, 70.1, 69.9, 69.5, 35.4, 26.7, 26.6 (not all carbon signals for the two isomers are resolved); IR (film) 2961, 1617, 1583 cm⁻¹; MS (FAB, MNBA) *m/z* 1376, 1247, 793, 687, 560, 154.

(*R_p*)-bis- λ -iodo-{2-[(4*S*)-2-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)]-3-(2,6-

dimethoxyphenyl)-ferrocenyl} dipalladium (32). According to the procedure for the preparation of iodide **27a**, oxazoline **26d** (250 mg, 0.56 mmol) in THF (7.0 mL) was treated with *tert*-BuLi (1.25 M in pentane, 0.42 mL, 0.53 mmol) and quenched with a solution of diiodoethane (150 mg, 0.53 mmol)

in THF (7.0 mL). Purification by column chromatography (CH_2Cl_2) provided crude **27d** (173 mg, 61% based on *tert*-BuLi) as a light sensitive orange foam which was carried on directly: LRMS (ES) m/z 534 ($M + H$)⁺.

A solution of crude iodide **27d** (190 mg, 0.33 mmol) in benzene (10.0 mL) was allowed to react with $Pd_2dba_3 \cdot CHCl_3$ (207 mg, 0.20 mmol) as described for the preparation of **29**. Purification of the crude product by column chromatography (1:2 hexanes/benzene) provided **32** (212 mg, 95%). Filtration through a plug of SiO_2 (CH_2Cl_2) provided analytically pure **32** as a mixture of isomers, red prisms (202 mg, 90%): mp 223 °C; $[\alpha]_D^{26} = +119.9^\circ$, $[\alpha]_{577}^{26} = +127.5^\circ$, $[\alpha]_{546}^{26} = +126.9^\circ$, $[\alpha]_{435}^{26} = -108.3^\circ$, $[\alpha]_{405}^{26} = -207.3^\circ$, ($c = 0.3$, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 7.20 (m, 2H), 6.57–6.61 (m, 2H), 6.48 (d, $J = 8.3$ Hz, 2H), 5.15 (app t, $J = 2.5$ Hz, 2H), 4.59–4.16 (m, 2H), 4.44–4.49 (m, 14H), 3.86–3.91 (m, 6H), 3.51 (br s, 6H), 1.05 (s, 9H), 1.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 180.4, 158.5, 157.5, 128.0, 112.2, 112.1, 103.7, 103.5, 98.3, 97.9, 78.0, 77.6, 77.24, 77.20, 77.16, 74.0, 73.2, 72.7, 72.6, 71.9, 71.7, 70.6, 69.4, 56.0, 55.8, 55.3, 35.1, 35.0, 26.93, 26.90 (not all carbon signals for the two isomers are resolved); IR (film) 2832, 1585 cm^{-1} ; MS (MALDI) m/z 1360, 1172, 893, 679; Anal. Calcd for $C_{50}H_{58}Fe_2I_2N_2O_6Pd_2$: C, 44.18; H, 4.15; N, 2.06. Found: C, 44.08; H, 4.16; N, 2.05.

(*R_p*)-bis- λ -iodo-{2-[(4*S*)-2-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)]-3-(1-naphthyl)-

ferrocenyl} dipalladium (33). According to the procedure for the preparation of palladacycle **29**, iodide **27e** (260 mg, 0.46 mmol) in benzene (17.0 mL) was reacted with $Pd_2dba_3 \cdot CHCl_3$ (287 mg, 0.28 mmol). Purification of the residue by column

chromatography (1:2 hexanes/benzene) provided **33** (305 mg, 99%). Filtration through a plug of silica (CH_2Cl_2) provided analytically pure **33** as a mixture of isomers, red prisms (298 mg, 98%): mp 210 °C; $[\alpha]_{\text{D}}^{26} = +20.0^\circ$, $[\alpha]_{577}^{26} = +23.8^\circ$, $[\alpha]_{546}^{26} = +23.8^\circ$, $[\alpha]_{435}^{26} = +89.2^\circ$, $[\alpha]_{405}^{26} = +22.5^\circ$, ($c = 0.2$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.96 (app t, $J = 6.8$ Hz, 2H), 7.77–7.85 (overlapping m, 6H), 7.45–7.50 (m, 2H), 7.40 (app t, $J = 7.5$ Hz, 2H), 7.27 (app t, $J = 7.4$, 2H), 5.13–5.15 (m, 2H), 4.58–4.61 (overlapping m, 12H), 4.46 (app d, $J = 9.0$ Hz, 2H), 4.37 (app t, $J = 8.9$ Hz, 2H), 3.87–3.89 (m, 2H), 0.994 (s, 9H), 0.991 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 179.5, 179.1, 132.99, 132.96, 132.91, 129.0, 128.9, 127.9, 127.4, 125.8, 125.41, 125.39, 124.8, 124.7, 98.0, 97.5, 86.7, 86.6, 77.8, 77.1, 74.4, 74.3, 74.2, 74.1, 72.9, 72.8, 71.8, 70.8, 69.6, 35.40, 35.35, 26.92, 26.87 (not all carbon signals for the two isomers are resolved); IR (film) 2961, 1586 cm^{-1} ; MS (MALDI) m/z 1340, 1152, 978, 857, 669; Anal. Calcd for $\text{C}_{54}\text{H}_{52}\text{Fe}_2\text{I}_2\text{N}_2\text{O}_2\text{Pd}_2$: C, 48.43; H, 3.91; N, 2.16. Found: C, 48.59; H, 4.08; N, 2.10.

(R_p)-bis- μ -iodo-{2-[(4S)-2-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)]-3-(2-methylphenyl)-ferrocenyl} dipalladium (34**).**

A solution of iodide **27f** (361 mg, 0.69 mmol) in benzene (15.0 mL) was allowed to react with $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (427 mg, 0.41 mmol) as described for the preparation of **29**. Purification of the crude product by column chromatography (1:2 hexanes/benzene) provided **34** (350 mg, 81%) as a mixture of isomers, red prisms: mp 180–181 °C; $[\alpha]_{\text{D}}^{26} = +160.9^\circ$, $[\alpha]_{577}^{26} = +147.7^\circ$, $[\alpha]_{546}^{26} = +113.2^\circ$, ($c = 0.4$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.67–7.71 (m, 2H), 7.06–7.13 (m, 4H), 6.98–6.99 (m, 2H), 4.93–4.95 (m, 2H), 4.50–4.52 (m, 2H), 4.47 (s, 5H), 4.43 (s, 5H), 4.35 (app t, $J = 9.0$ Hz, 2H), 4.42–4.26 (m, 2H), 3.77–3.81 (m, 2H), 1.95 (s, 6H), 0.91 (s, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ 180.0, 137.7, 135.2, 132.6, 132.5, 130.0, 128.8, 127.5, 125.5, 125.4, 98.6, 98.1, 88.7, 88.6, 78.0, 74.7, 74.6, 73.8, 73.7, 73.2, 73.1, 71.7, 71.2, 70.0, 35.7, 35.6, 27.24, 27.18, 20.7 (not all carbon signals for the two isomers are resolved); IR (film) 2961, 1617, 1583 cm^{-1} ; MS (FAB,

MNBA) m/z 1268, 154; Anal. Calcd for $C_{48}H_{52}Fe_2I_2N_2O_2Pd_2$: C, 45.49; H, 4.14; N, 2.21. Found: C, 45.39; H, 4.10; N, 1.90.

(*R*_p)-bis-(4-iodo-2-[(4*S*)-2-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)]-3-(2-methoxyphenyl)-ferrocenyl} dipalladium (35). According to the procedure for the

preparation of iodide **27a**, oxazoline **26g** (290 mg, 0.69 mmol) in THF (2.5 mL) was treated with *tert*-BuLi (1.40 M in pentane, 0.48 mL, 0.67 mmol) and quenched with a solution of diiodoethane (184 mg, 0.67 mmol) in THF (2.0 mL). Purification by column chromatography (CH_2Cl_2) provided crude **27g** (321 mg, 80% based on *tert*-BuLi) as a light sensitive orange foam: LRMS (ES) m/z 566 ($M + Na$)⁺, 544 ($M + H$)⁺.

A solution of iodide **27g** (241 mg, 0.44 mmol) in benzene (17.0 mL) was allowed to react with $Pd_2dba_3 \cdot CHCl_3$ (321 mg, 0.59 mmol) as described for the preparation of **29**. Purification of the crude product by column chromatography (1:2 hexanes/benzene) provided **35** (364 mg, 94%). Filtration through a plug of SiO_2 (CH_2Cl_2) provided analytically pure **35** as a mixture of isomers, red flakes (345 mg, 90%): mp 191 °C; $[\alpha]_D^{26} = +20.0^\circ$, $[\alpha]_{577}^{26} = +111.8^\circ$, $[\alpha]_{546}^{26} = +138.8^\circ$, $[\alpha]_{435}^{26} = +189.2^\circ$, ($c = 0.2$, $CHCl_3$); 1H NMR (500 MHz, $CDCl_3$) δ 7.58–7.61 (m, 2H), 7.22–7.26 (m, 2H), 6.90–6.95 (m, 2H), 6.81–6.84 (m, 2H), 5.04–5.06 (m, 2H), 4.64–4.67 (m, 2H), 4.55–4.57 (m, 2H), 4.45–4.50 (m, 10H), 3.90–3.92 (m, 2H), 3.68 (s, 6H), 1.04 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2, 179.8, 157.0, 132.2, 132.1, 128.2, 124.7, 120.0, 119.9, 110.43, 110.37, 98.7, 98.3, 83.6, 83.5, 78.2, 77.5, 74.5, 73.5, 73.0, 72.9, 71.5, 71.0, 69.8, 55.6, 55.5, 35.70, 35.66, 27.3, 27.1 (not all carbon signals for the isomers are resolved); IR (film) 2961, 1583 cm^{-1} ; MS (FAB, MNBA) m/z 1300, 649, 154; Anal. Calcd for $C_{48}H_{52}Fe_2I_2N_2O_4Pd_2$: C, 44.37; H, 4.03; N, 2.16. Found: C, 44.10; H, 3.87; N, 2.15.

(*R*_p)-bis- λ -iodo-{2-[(4*S*)-2-(4,5-dihydro-4-*tert*-butyl-2-oxazolyl)]-3-(4-methylsulfonyl-phenyl)-ferrocenyl} dipalladium (36).

A solution of iodide **27h** (465 mg, 0.83 mmol) in CH_2Cl_2 (8.0 mL) was cooled to 0 °C and *m*-CPBA (450 mg, 1.83 mmol) was added in one portion. The solution was maintained at 0 °C for 30 min and quenched by addition of 10% aqueous $Na_2S_2O_3$ solution (8 mL).

The biphasic mixture, while protected from light, was allowed to warm to room temperature and stirred for 1 h. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (10 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (10 mL), dried ($MgSO_4$) and concentrated *in vacuo* to give a black tar. Purification by column chromatography (1:1 Et_2O /hexanes) provided sulfone **28** (228 mg, 46%) as an unstable orange foam which was carried on directly: 1H NMR (400 MHz, $CDCl_3$) δ 7.81 (app dt, J = 8.6, 1.9 Hz, 2H), 7.73 (app dt, J = 8.6, 1.9 Hz, 2H), 4.73 (d, J = 2.6 Hz, 1H), 4.64 (d, J = 2.6 Hz, 1H), 4.03 (dd, J = 10.2, 8.6 Hz, 1H), 4.23 (s, 5H), 4.13 (app t, J = 8.7 Hz, 1H), 4.01 (dd, J = 10.2, 8.8 Hz, 1H), 3.05 (s, 3H), 0.96 (s, 9H); IR (film) 2961, 1656, 1598, 1312, 1154 cm^{-1} ; LRMS (ES) m/z 614 ($M + Na$)⁺, 592 ($M + H$)⁺.

The above sulfone **28** was combined with $Pd_2dba_3 \cdot CHCl_3$ (269 mg, 0.26 mmol) in benzene (17 mL) as described for the preparation of **29**. Purification of the crude product by column chromatography (CH_2Cl_2 , then 5:95 Et_2O/CH_2Cl_2) provided **36** (250 mg, 83%). Recrystallization (benzene, room temperature) provided analytically pure **36** as a mixture of isomers, dark red prisms (237 mg, 79%): mp 240 °C; $[\alpha]_D^{26} = +100.5^\circ$, $[\alpha]_{577}^{26} = +109.0^\circ$, $[\alpha]_{546}^{26} = +121.4^\circ$, $[\alpha]_{435}^{26} = -100.6^\circ$, $[\alpha]_{405}^{26} = -189.5^\circ$, (c = 0.30, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 7.80 (app t, J = 7.3 Hz, 4H), 7.68–7.70 (m, 4H), 5.11–5.15 (m, 2H), 4.77–4.81 (m, 2H), 4.54–4.62 (m, 2H), 4.43 (s, 5H), 4.39 (s, 5H), 3.93–3.97 (m, 2H), 3.05 (m, 6H), 1.02 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 179.0, 144.1, 144.0, 138.0, 129.2, 129.1, 127.1, 127.0, 99.7, 99.4, 83.6, 80.1, 79.4, 74.8, 74.7, 73.5, 73.3, 72.4, 72.2, 71.3, 70.6, 70.2, 70.0, 44.9, 35.8, 35.5, 27.1, 27.0, (not all carbon signals for the two isomers are resolved); IR (film) 2961, 1586 cm^{-1} ; MS (FAB, MNBA) m/z

1395, 697, 154; Anal. Calcd for $C_{48}H_{52}Fe_2I_2N_2O_6Pd_2S_2$: C, 41.32; H, 3.76; N, 2.01. Found: C, 41.18; H, 3.83; N, 2.03.

***N*-(2-Methoxyphenyl)benzimidoyl chloride (43c).** *N*-(2-methoxyphenyl)-benzamide

(**42c**) (5.7 g, 25 mmol) and PCl_5 (5.2 g, 25 mmol) were combined in a 25 mL round bottom flask connected in line to an empty trap and a trap containing saturated aqueous $NaHCO_3$. The heterogeneous reaction was warmed to $80^\circ C$ and became a homogenous solution. After 16 hours, the reaction was cooled to room temperature and $POCl_3$ was removed *in vacuo*. The residue was purified by Kugelrohr distillation (10 torr, $225^\circ C$) to give 4.97 g (81%) of **42c** as a viscous yellow oil: 1H NMR (500 MHz, $CDCl_3$) δ 8.19–8.23 (m, 2H), 7.55 (tt, $J = 7.2, 1.3$ Hz, 1H), 7.46–7.52 (m, 2H), 7.16–7.23 (m, 1H), 6.97–7.03 (m, 2H), 6.91–6.96 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 145.2, 137.5, 135.7, 132.3, 129.8, 128.7, 126.2, 121.1, 120.9, 112.0, 56.1; IR (neat) 3005, 2960, 2836, 1657, 1591, 1494, 1257, 1169, 1114, 1026 cm^{-1} .

***N*-(2,4-Dimethoxyphenyl)benzimidoyl chloride (43d).** Benzoic acid (4.9 g, 40 mmol),

PPh_3 (31.5 g, 120 mmol), Et_3N (6.7 mL, 48 mmol) and CCl_4 (20 mL) were cooled to $0^\circ C$ for 10 minutes. 2,4-Dimethoxyaniline (7.4 g, 48 mmol) in CCl_4 (15 mL) was added to the reaction. The mixture was warmed to reflux and maintained for 18 hours. After cooling to room temperature, the volatiles were removed *in vacuo*, and the residue slurried in hexanes (250 mL). The slurry was stirred vigorously for 3 hours and filtered. Concentration of the mother liquor *in vacuo* afforded 4.22 g (38%) of imidoyl chloride **43d** as a yellow oil: 1H NMR (500 MHz, $CDCl_3$) δ 8.17–8.21 (m, 2H), 7.50–7.56 (m, 1H), 7.44–7.50 (m, 2H), 6.94 (d, $J = 8.5$ Hz, 1H), 6.57 (d, $J = 2.5$ Hz, 1H), 6.54 (dd, $J = 8.6, 2.5$ Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 151.2, 135.5, 131.9, 129.5, 128.7, 128.4, 127.0, 121.5, 104.0, 99.6, 55.8, 55.5; IR (neat) 3064, 3002, 2939, 2837, 1659, 1605, 1582, 1526, 1416, 1282, 1207, 1173, 1126, 1033 cm^{-1} .

***trans*-2-Hexenyl-*N*-(2-methoxyphenyl)benzimidate (5c).** Sodium hydride (41 mg, 1.0

mmol) and THF (1 mL) were cooled to 0 °C and *trans*-2-hexen-1-ol (0.12 mL, 1.0 mmol) was added dropwise. The reaction was warmed to room temperature over 4 hours before adding *N*-(2-methoxybenzyl)benzimidoyl chloride (**43c**, 250 mg, 1.0 mmol) in

THF (1 mL). The reaction was maintained for 12 hours before adding EtOAc (10 mL) and H₂O (5 mL). The phases were separated and the aqueous phase was extracted with EtOAc (2 x 5 mL). The combined organic phase was dried (MgSO₄) and concentrated *in vacuo*. Purification by chromatography (95:5 hexanes/EtOAc) yielded 220 mg (70%) of imide **5c** as a pale yellow oil: ¹H NMR (500 MHz, CDCl₃) δ 7.31 (d, *J* = 10.4 Hz, 2H), 7.25 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.19 (app t, *J* = 7.4 Hz, 2H), 6.90–6.95 Hz, 2H), 3.64 (s, 3H), 2.08 (app q, *J* = 7.2 Hz, 2H), 1.45 (sextet, *J* = 7.4 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.0, 150.7, 138.5, 135.8, 132.8, 130.1, 128.9, 128.1, 125.3, 123.8, 122.9, 121.4, 112.1, 67.9, 55.9, 34.9, 22.6, 14.1; IR (neat) 3062, 2958, 2874, 1660, 1593, 1495, 1447, 1266, 1109, 1028 cm⁻¹; LRMS (ES) *m/z* 332.26 (M + Na)⁺. Anal. Calcd for C₂₀H₂₂NO₂: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.82; H, 7.48; N, 4.68.

***trans*-2-Hexenyl-*N*-(2,4-dimethoxyphenyl)benzimidate (5d).** *trans*-2-Hexen-1-ol (0.11

mL, 0.91 mmol) in THF (1.7 mL) was cooled to 0 °C and *n*-BuLi (2.5 M, 0.35 mL, 0.88 mmol) was added dropwise. The reaction was stirred at 0 °C for 15 minutes and then at room temperature for 30 minutes before adding *N*-(2,4-dimethoxyphenyl)benzimidoyl chloride (**43d**, 200 mg, 0.73 mmol) in THF (2.0 mL). The reaction

was maintained for 12 hours before adding EtOAc (10 mL) and H₂O (5 mL). The phases were separated and the aqueous phase was extracted with EtOAc (2 x 10 mL). The combined organic phases were dried (Na₂SO₄) and concentrated *in vacuo*. Purification by column chromatography (19:1 hexanes/EtOAc) yielded 67 mg (27%) of imide **5d** as a

yellow oil: $R_f = 0.29$ (4:1 hexanes/EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 7.24–7.33 (m, 3H), 7.20 (t, $J = 7.4$ Hz, 2H), 6.54 (app d, $J = 8.3$ Hz, 1H), 6.38 (d, $J = 2.4$ Hz, 1H), 6.31 (dd, $J = 8.5, 2.5$ Hz, 1H), 5.75–5.90 (m, 2H), 4.84 (d, $J = 4.6$ Hz, 2H), 3.74 (s, 3H), 3.60 (s, 3H), 2.08 (q, $J = 7.0$ Hz, 2H), 1.44 (sextet, $J = 7.4$ Hz, 2H), 0.93 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.9, 156.3, 151.0, 135.3, 132.5, 131.5, 129.5, 128.4, 127.7, 125.0, 122.5, 104.2, 99.7, 67.3, 55.43, 55.40, 34.5, 22.2, 13.7; IR (neat) 2961, 2934, 2837, 1660, 1606, 1505, 1463, 1270, 1208, 1158, 1112, 1042 cm^{-1} ; LRMS (ES) m/z 362.28 ($\text{M} + \text{Na}$) $^+$. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_2$: C, 74.31; H, 7.42; N, 4.13. Found: C, 74.41; H, 7.60; N, 4.00.

Methyl-*N*-(benzyloxycarbonyl)benzimidate (45). A biphasic mixture of saturated

aqueous NaHCO_3 (20 mL) and pentane (20 mL) was cooled to 0 $^\circ\text{C}$ in a separatory funnel. *O*-Methylbenzimidate hydrochloride³ (**44**) (400 mg, 2.34 mmol) was added and shaken vigorously for 2 minutes. The layers were separated and the organic phase was

dried (Na_2SO_4), and concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2 (2 mL) and K_2CO_3 (311 mg, 2.26 mmol) was added. Benzyl chloroformate (0.39 mL, 2.71 mmol) was added dropwise (caution; *gas evolution*) and the reaction was maintained at 23 $^\circ\text{C}$ for 16 hours before concentrating *in vacuo*. Purification by flash column chromatography (19:1 hexanes/EtOAc) gave 280 mg (46%) of **45** as a pale yellow oil: $R_f = 0.48$ (4:1 hexanes/EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 7.43 (td, $J = 7.2, 1.3$ Hz, 2H), 7.32 (td, $J = 7.5, 1.2$ Hz, 1H), 7.12–7.27 (7H, m), 5.04 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 163.5, 160.7, 135.4, 131.6, 130.7, 128.6, 128.4 (2 overlapping signals), 128.2, 127.8, 68.2, 55.1; IR (film) 3064, 2949, 1715, 1667, 1450, 1263, 1178, 1121, 1024 cm^{-1} ; LRMS (ES) m/z 292.10 ($\text{M} + \text{Na}$) $^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.43; H, 5.77; N, 5.20.

³ Casy, G.; Patterson, J. W.; Taylor, R. J. K. *Org. Synth.* **1988**, 67, 193–197.

***trans*-2-Hexenyl-*N*-(benzyloxycarbonyl)benzimidate (46).** A 100 mL round bottom

flask equipped with a 7 cm vigreux column and a short path distillation head was charged with imidate **45** (120 mg, 0.45 mmol) and benzene (60 mL). *Trans*-2-hexen-1-ol (80 μ L, 0.68 mmol) and potassium *tert*-butoxide (1.5 mg, 0.014 mmol) were added. The reaction was warmed to 87 °C and was distilled to a

volume of 3 mL. The reaction was monitored by TLC and additional portions of benzene (60 mL) were added and distilled to a minimal volume until no starting material remained. The residue was concentrated *in vacuo* and purified by column chromatography (19:1 hexanes/EtOAc) to afford 64 mg (42%) of **46** as a pale yellow oil. An analytical sample of **46** was prepared by column chromatography (2:1 benzene/hexanes): R_f = 0.58 (4:1 hexanes/EtOAc); 1H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.3, 0.8 Hz, 2H), 7.43 (qt, J = 7.5, 0.7 Hz, 1H), 7.20–7.32 (m, 7H), 5.81–5.88 (m, 1H), 5.66–5.74 (m, 1H), 5.13 (s, 2H), 4.73 (d, J = 6.5 Hz, 2H), 2.06 (q, J = 7.1 Hz, 2H), 1.43 (sextet, J = 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 160.5, 136.9, 135.4, 131.4, 131.0, 128.5, 128.35, 128.34, 128.1, 127.8, 123.4, 68.8, 68.0, 34.3, 22.0, 13.5; IR (film) 3063, 2958, 2872, 1716, 1660, 1450, 1253, 1119 cm^{-1} ; LRMS (ES) m/z 360.09 ($M + Na$) $^+$. Anal. Calcd for $C_{16}H_{15}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.88; H, 6.95; N, 4.10.

***Trans*-2-Hexenyl-*N*-(2-hexenyloxycarbonyl)benzimidate (47) formed during the**

conversion of **45 to **46**.** R_f = 0.68 (4:1 hexanes/EtOAc); 1H NMR (500 MHz, $CDCl_3$) δ 7.61–7.64 (m, 2H), 7.47 (tt, J = 6.2, 1.3 Hz, 1H), 7.36–7.41 (m, 2H), 5.80–5.89 (m, 1H), 5.67–5.75 (m, 2H), 5.50 (dddd, J = 14.3, 6.6, 6.6, 1.5 Hz, 1H), 4.73 (dd, J = 6.4, 0.9 Hz, 2H), 4.54 (dd, J = 6.6, 0.9 Hz, 2H),

2.06 (q, J = 6.8 Hz, 2H), 1.98 (q, J = 6.8 Hz, 2H), 1.42 (sextet, J = 7.4 Hz, 2H), 1.37 (sextet, J = 7.3 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, acetone- d_6) δ 161.8, 160.3, 136.7, 136.3, 132.0, 131.8, 129.0, 128.2, 124.6, 124.4,

68.5, 66.7, 34.5, 34.4, 22.32, 22.25, 13.4; IR (film) 2959, 2931, 2873, 1720, 1665 1252, 1119 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_3$ (M)⁺ 329.1991, found 329.1983.

Methyl-*N*-(*tert*-butylsulfonyl)benzimidate (49). *Tert*-butylsulfonamide (**48**) (800 mg,

5.8 mmol) was dissolved in trimethyl orthobenzoate (10 mL, 58 mmol) and a crystal of *p*-toluenesulfonic acid was added. The reaction was warmed to 160°C for 16 hours before cooling to room temperature and removing excess trimethyl orthobenzoate by Kugelrohr distillation.

Purification by column chromatography (9:1 $\rightarrow$ 4:1 $\rightarrow$ 1:1 hexanes/EtOAc) gave 713 mg (48%) of **49** as a white solid: R_f = 0.26 (4:1 hexanes/EtOAc); mp: 67-69 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.90 (tt, J = 7.2, 1.3 Hz, 2H), 7.53 (tt, J = 7.5, 1.2 Hz, 1H), 7.44 (tt, J = 7.5, 1.6 Hz, 2H), 3.98 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.9, 132.4, 131.2, 129.3, 129.0, 59.1, 55.7, 24.2; IR (film) 3068, 2986, 1614, 1437, 1298, 1121 cm^{-1} ; LRMS (ES) m/z 278.09 ($\text{M} + \text{Na}$)⁺. Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.66; H, 6.73; N, 5.39.

***trans*-2-Hexenyl-*N*-(*tert*-butylsulfonyl)benzimidate (50).** A 100 mL round bottom flask

equipped with a 7 cm vigreux column and a short path distillation head was charged with imidate **49** (263 mg, 1.03 mmol) and benzene (60 mL). *Trans*-2-hexen-1-ol (0.36 mL, 3.09 mmol) and potassium *tert*-butoxide (23 mg, 0.21 mmol) were added. The reaction was warmed to 100°C and distilled to a volume of 3 mL.

Concentration of the residue *in vacuo* and purification by column chromatography (19:1 hexanes/EtOAc) afforded 225 mg (68%) of **50** as a white solid: R_f = 0.42 (4:1 hexanes/EtOAc); mp: 37-39 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.90 (td, J = 7.2, 1.3 Hz, 2H), 7.52 (tt, J = 7.5, 1.0 Hz, 1H), 7.44 (tt, J = 7.9, 1.7 Hz, 2H), 5.85-5.92 (m, 1H), 5.66-5.73 (m, 1H), 4.78 (dd, J = 6.5, 0.9 Hz, 2H), 2.07 (q, J = 7.0 Hz, 2H), 1.49 (s, 9H), 1.42 (sextet, J = 7.4 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ

170.4, 137.7, 132.3, 131.5, 129.3, 128.0, 122.8, 69.5, 59.0, 34.3, 24.2, 21.9, 13.6; IR (film) 2958, 1598, 1579, 1299, 1273, 1122 cm^{-1} ; LRMS (ES) m/z 346.09 ($\text{M} + \text{Na}$)⁺. Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: C, 63.13; H, 7.79; N, 4.33. Found: C, 63.40; H, 7.95; N, 4.25.

(S)-N-(2-Methoxyphenyl)-N-(1-ethenylbutyl)benzamide (6c). Palladium iodide

catalyst **9a** (14 mg, 0.011 mmol) and AgOCOCF_3 (10 mg, 0.044 mmol) were dissolved in CH_2Cl_2 (0.5 mL) under argon and protected from light.

After 3 hours, the solution containing the activated catalyst was filtered through Celite and rinsed with CH_2Cl_2 (0.5 mL) while under argon and

added directly to a solution of imidate **5c** (67 mg, 0.22 mmol) and CH_2Cl_2 (0.5 mL).

Purification by column chromatography (19:1 hexanes/EtOAc) afforded 44 mg (66%) of

6c as a white solid. Separation of enantiomers by chiral HPLC (Chiracel OD-H, 98:2 n-hexanes/IPA, 1 mL/min) showed that **6c** had been formed in 77% ee: mp: 52–54 °C;

$[\alpha]_{\text{D}}^{25} = +16.1$, $[\alpha]_{577}^{25} = +17.9$, $[\alpha]_{546}^{25} = +20.2$, $[\alpha]_{435}^{25} = +38.9$, $[\alpha]_{405}^{25} = +49.0$ (c 0.8,

CHCl_3); ^1H NMR (500 MHz, CDCl_3 , 1:1 mixture of rotamers) δ 7.25–7.30 (m, 4H),

7.05–7.20 (m, 10H), 6.78–6.85 (m, 2H), 6.63 (app t, $J = 6.8$ Hz, 2H), 5.95 (ddd, $J = 17.9$,

10.1, 7.9 Hz, 1H), 5.76 (ddd, $J = 17.5$, 10.1, 7.8 Hz, 1H), 5.32 (d, $J = 17.2$ Hz, 1H), 5.21

(d, $J = 10.2$ Hz, 1H), 5.04–5.16 (m, 3H), 5.00 (d, $J = 10.3$ Hz, 1H), 3.59 (s, 3H), 3.55 (s,

3H), 1.85–1.95 (m, 1H), 1.66–1.82 (m, 2H), 1.46–1.56 (m, 2H), 1.33–1.45 (m, 3H), 1.00

(t, $J = 7.3$ Hz, 3H), 0.85–0.92 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3 , 1:1 mixture of

rotamers) δ 171.7, 171.4, 155.5, 155.4, 138.1, 137.4 (broad), 136.6, 130.8, 130.42,

130.37, 130.2, 128.9, 128.8 (broad), 128.7, 127.8, 127.7, 127.0, 126.9, 120.1, 120.0,

117.1, 116.7, 111.5, 111.4, 60.0, 59.9, 55.0, 54.9, 35.1, 33.3, 19.8, 19.6, 14.01, 13.96; IR

(neat) 3067, 2960, 2873, 1646, 1596, 1498, 1464, 1377, 1327, 1278, 1161, 1027 cm^{-1} ;

HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_2$ (M)⁺ 309.1729, found 309.1722.

(S)-N-(2,4-Dimethoxyphenyl)-N-(1-ethenylbutyl)benzamide (6d). Following the

general procedure for palladium iodide precatalyst activation, **9a** (3.1 mg, 0.0025 mmol) was activated with AgOCOCF₃ (3 mg, 0.014 mmol) to provide a solution containing the active catalyst. Imidate **5d** (17 mg, 0.05 mmol) was treated the solution containing the active

catalyst to afford, after chromatography (19:1 hexanes/EtOAc), 15 mg (88%) of a 3:1 mixture of **6d** and **5d**. Separation of enantiomers by chiral HPLC (Chiracel OD-H, 98:2 n-hexanes/IPA, 1 mL/min) showed that **6d** had been formed in 83% ee: R_f = 0.26 (4:1 hexanes/EtOAc); ¹H NMR (500 MHz, CDCl₃, 1:1 mixture of rotamers) δ 7.24–7.29 (m, 4H), 7.06–7.17 (m, 6H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.29–6.35 (m, 2H), 6.16–6.21 (m, 2H), 5.89 (ddd, *J* = 17.5, 10.1, 7.9 Hz, 1H), 5.72 (ddd, *J* = 17.6, 10.2, 7.9 Hz, 1H), 5.30 (d, *J* = 17.1 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 5.04–5.16 (m, 3H), 5.00 (d, *J* = 10.4 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.57 (s, 3H), 3.55 (s, 3H), 1.80–1.89 (m, 1H), 1.64–1.77 (m, 2H), 1.45–1.54 (m, 2H), 1.32–1.42 (m, 3H), 0.99 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃, 1:1 mixture of rotamers) δ 171.6, 160.0, 159.9, 156.4, 138.2, 137.6, 136.7, 131.5, 131.4, 130.8, 128.8, 128.7, 127.7, 127.6, 127.1, 127.04, 126.97, 117.7, 116.6, 103.8, 103.7, 98.9, 98.8, 98.7, 59.7, 59.6, 55.30, 55.29, 55.0, 54.9, 35.0, 33.3, 19.8, 19.6, 14.1, 14.0; IR (neat) 3080, 2961, 2934, 2872, 1644, 1509, 1309, 1212, 1162, 1034 cm⁻¹; HRMS (CI) *m/z* calcd for C₂₁H₂₅NO (M)⁺ 339.1834, found 339.1834.

N-(benzyloxycarbonyl)-N-(1-ethenylbutyl)benzamide (53). Following the general

procedure for palladium iodide precatalyst activation, **9a** (9.2 mg, 0.0075 mmol) was activated with AgOCOCF₃ (6.6 mg, 0.03 mmol) to provide a solution containing the activated catalyst. Imidate **46** (50 mg, 0.15 mmol) was treated with the solution containing the activated catalyst to afford, after

purification by flash column chromatography (19:1 hexanes/EtOAc), 34 mg (68%) of **53**: R_f = 0.62 (4:1 hexanes/EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.58 (td, *J* = 7.1, 1.1 Hz,

2H), 7.48 (tt, $J = 7.4, 1.3$ Hz, 1H), 7.37 (tt, $J = 7.5, 1.6$ Hz, 2H), 7.28 (tt, $J = 7.3, 1.4$ Hz, 1H), 7.23 (tt, $J = 7.0, 1.3$ Hz, 2H), 6.85 (tt, $J = 7.2, 1.5$ Hz, 2H), 6.19 (ddd, $J = 17.4, 10.3, 7.3$ Hz, 1H), 5.28 (td, $J = 17.3, 1.3$ Hz, 1H), 5.19 (td, $J = 10.3, 1.2$ Hz, 1H), 4.94–4.99 (m, 1H), 4.94 (s, 2H), 1.98–2.08 (m, 1H), 1.81–1.89 (m, 1H), 1.37–1.44 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.0, 155.2, 137.6, 137.5, 134.6, 131.8, 128.6, 128.54 (2 overlapping signals), 128.47, 127.9, 117.6, 68.7, 60.3, 34.7, 20.0, 14.0; IR (film) 2958, 1736, 1677, 1383, 1326, 1221 cm^{-1} ; LRMS (ES) m/z 360.09 ($\text{M} + \text{Na}$) $^+$. Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.93; H, 6.99; N, 4.11.

***N*-(4-Methoxyphenyl)-*N*-(1-ethenylbutyl)trifluoroacetamide (55a).** Following the

general procedure for palladium iodide precatalyst activation, **9a** (15 mg, 0.012 mmol) was treated with AgOCOCF_3 (11 mg, 0.048 mmol) to provide a solution containing the activated catalyst (0.03 M) in CH_2Cl_2 . Imide **52a** (25 mg, 0.08 mmol) was diluted in CH_2Cl_2 (0.2 mL) and the solution containing the activated catalyst (0.03 M, 0.13 mL, 0.006 mmol) was added followed by proton sponge[®] (3 mg, 0.016 mmol). The reaction was sealed, protected from light and maintained for 24 hours before concentrating *in vacuo*. Purification by column chromatography (99.5:0.5 hexanes/EtOAc) afforded 22 mg (88%) of amide **55a** as a pale yellow oil: $[\alpha]_D^{25} = -1.6$, $[\alpha]_{577}^{25} = -2.4$, $[\alpha]_{546}^{25} = -1.4$, $[\alpha]_{435}^{25} = -1.9$, $[\alpha]_{405}^{25} = -3.0$ (c 0.4, CHCl_3); $R_f = 0.52$ (4:1 hexanes-EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 7.06 (app dd, $J = 18.7, 8.6$ Hz, 2H), 6.88 (app t, $J = 7.0$ Hz, 2H), 5.55 (ddd, $J = 17.9, 10.1, 8.3$ Hz, 1H), 5.26 (d, $J = 17.2$ Hz, 1H), 5.19 (dd, $J = 10.2, 0.6$ Hz, 1H), 5.02 (q, $J = 7.6$ Hz, 1H), 3.82 (s, 3H), 1.54–1.64 (m, 1H), 1.39–1.48 (m, 1H), 1.37 (sextet, $J = 7.3$ Hz, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.5, 156.5 (q, $J_{\text{C-CF}_3} = 34$ Hz), 135.2, 131.6, 130.8, 127.7, 119.0, 116.3 (q, $J_{\text{C-F}} = 286$ Hz), 113.6, 113.5, 60.6, 55.4, 33.8, 19.6, 13.9; IR (neat) 3083, 2964, 2877, 1690, 1511, 1299, 1250, 1202, 1187, 1148, 1034 cm^{-1} ; LRMS (ES) m/z 324.10 ($\text{M} + \text{Na}$) $^+$. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{NO}_2$: C, 59.79; H, 6.02; N, 4.65. Found: C, 60.05; H, 6.10; N, 4.69.

B. ¹H and ¹³C NMR Spectra of New Compounds

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Current Data Parameters
USER          jdliao
NAME          csp-1-253-10
CSPNO        1
PROCNO       10

F2 - Acquisition Parameters
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PROBHD        p5000
PULPROG       5 mhz bragg
ALPHA0        20.0
PULPROG       zgpg30
ZD0_VENT      0.000
MSDC0         MS
MSDC1         MS
MSDC2         MS
FREQ0         300.015 MHz
NUC1          9.460000000
AQ           1.0000159 SEC
SI            0.01
DE            16.904 uSec
DE2           30.0 uSec
DE3           30.0 uSec
DE4           0.0000000 SEC
DE5           0.0000000 SEC
D11           0.2300000 SEC

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P2            7.00 uSec
P3            7.00 uSec
SFO1         125.7117924 MHz

----- CHANNEL f2 -----
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P2            7.00 uSec
P3            7.00 uSec
SFO2         125.7117924 MHz
MPC2         0
MPC3         0
MPC4         0
MPC5         0
MPC6         0
MPC7         0
MPC8         0
MPC9         0
MPC10        0
MPC11        0
MPC12        0
MPC13        0
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MPC35        0
MPC36        0
MPC37        0
MPC38        0
MPC39        0
MPC40        0
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MPC46        0
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MPC50        0
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MPC95        0
MPC96        0
MPC97        0
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MPC99        0
MPC100       0
MPC101       0
MPC102       0
MPC103       0
MPC104       0
MPC105       0
MPC106       0
MPC107       0
MPC108       0
MPC109       0
MPC110       0
MPC111       0
MPC112       0
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MPC416       0
MPC417       0
MPC418       0
MPC419       0
MPC420       0
MPC421       0
MPC422       0
MPC423       0
MPC424       0
MPC425       0
MPC426       0
```

¹³C spectrum with ¹H decoupling

C. Representative HPLC traces

Data File D:\HPCHEM\1\DATA\CDOUG\060-0201.D Sample Name: cjd-II-17-1

```
=====
Injection Date   : 8/17/00 3:17:47 PM      Seq. Line :    2
Sample Name      : cjd-II-17-1             Vial       :   60
Acq. Operator    : alec lebsack             Inj        :    1
                                           Inj Volume : 2 ul
Sequence File    : D:\HPCHEM\1\SEQUENCE\CDOUG1.S
Method           : D:\HPCHEM\1\METHODS\CDOUG1.M
Last changed     : 6/2/00 1:38:18 PM by douglas
=====
```

```
=====
                          Area Percent Report
=====
```

```
Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000
```

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.862	BB	0.1496	9.34314	9.43217e-1	0.3055
2	13.157	BB	0.3379	87.80434	3.91124	2.8708
3	14.391	BB	0.3848	2924.17529	117.29665	95.6073
4	18.912	PP	0.4437	37.20314	1.04403	1.2164

Totals : 3058.52591 123.19513

Results obtained with enhanced integrator!

```
=====
*** End of Report ***
```

Data File D:\HPCHEM\1\DATA\CDOUG\043-0601.D

Sample Name: cjd-I-224-1

```

=====
Injection Date   : 5/13/00 3:19:45 PM      Seq. Line :    6
Sample Name     : cjd-I-224-1             Vial      :   43
Acq. Operator   : douglas                  Inj       :    1
                                           Inj Volume: 2 ul

Acq. Method     : D:\HPCHEM\1\METHODS\CDOUG3.M
Last changed    : 5/13/00 12:12:02 PM by douglas
Analysis Method : D:\HPCHEM\1\METHODS\CDOUG1.M
Last changed    : 5/10/00 9:53:40 PM by douglas
=====

```

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=====
                        Area Percent Report
=====

```

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000

```

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.683	BB	0.7099	1305.41296	26.53867	93.8899
2	13.048	PB	0.8041	84.95343	1.24806	6.1101

Totals : 1390.36639 27.78673

Results obtained with enhanced integrator!

```

=====
*** End of Report ***
=====

```

Data File D:\HPCHEM\1\DATA\CDOUG\032-0301.D

Sample Name: cjd-I-239-1

Injection Date : 6/22/00 4:14:55 PM

Seq. Line : 3

Sample Name : cjd-I-239-1

Vial : 32

Acq. Operator : CDOUG

Inj : 1

Inj Volume : 2 ul

Sequence File : D:\HPCHEM\1\SEQUENCE\CDOUG1.S

Method : D:\HPCHEM\1\METHODS\CDOUG3.M

Last changed : 5/13/00 12:12:02 PM by douglas

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.476	BB	0.5642	44.14556	9.36113e-1	2.9690
2	14.880	BB	1.3205	1442.71265	15.35027	97.0310

Totals : 1486.85820 16.28638

Results obtained with enhanced integrator!

*** End of Report ***

Data File D:\HPCHEM\1\DATA\CDOUG\CJD-I227.D

Sample Name: cjd-I-227-2

Injection Date : 5/14/00 12:14:23 PM

Sample Name : cjd-I-227-2

Vial : 51

Acq. Operator : douglas

Inj Volume : 2 ul

Method : D:\HPCHEM\1\METHODS\CDOUG3.M

Last changed : 5/14/00 12:23:11 PM by douglas
(modified after loading)

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.771	PB	0.2307	6.03377	3.47254e-1	0.2775
2	8.929	BB	0.4968	77.34119	2.12420	3.5575
3	13.431	BB	1.0091	2090.67749	30.37284	96.1650

Totals : 2174.05246 32.84429

Results obtained with enhanced integrator!

*** End of Report ***

Data File D:\HPCHEM\1\DATA\CDOUG\022-0101.D

Sample Name: cjd-I-210-1

Injection Date : 5/9/00 9:37:25 PM

Seq. Line : 1

Sample Name : cjd-I-210-1

Vial : 22

Acq. Operator : douglas

Inj : 1

Inj Volume : 2 ul

Acq. Method : D:\HPCHEM\1\METHODS\CDOUG1.M

Last changed : 5/9/00 9:25:40 PM by douglas

Analysis Method : D:\HPCHEM\1\METHODS\CDOUG1.M

Last changed : 5/10/00 9:53:40 PM by douglas

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.495	BB	0.3392	266.18753	12.07376	93.5701
2	14.927	BB	0.3434	18.29179	7.80630e-1	6.4299

Totals : 284.47932 12.85438

Results obtained with enhanced integrator!

*** End of Report ***

Data File D:\HPCHEM\1\DATA\CDOUG\074-0201.D

Sample Name: cjd-I-28-1

```

=====
Injection Date   : 8/26/00 12:53:36 PM      Seq. Line :    2
Sample Name     : cjd-I-28-1              Vial :    74
Acq. Operator   : Chris Douglas            Inj :    1
                                           Inj Volume : 2 ul

Sequence File    : D:\HPCHEM\1\SEQUENCE\CDOUG1.S
Method          : D:\HPCHEM\1\METHODS\CDOUG1.M
Last changed    : 8/17/00 4:06:00 PM by Chris Douglas
=====

```

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=====
Area Percent Report
=====

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```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000

```

Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.262	BB	0.3737	48.77203	1.99130	2.4394
2	15.728	BB	0.4176	1909.21521	70.57770	95.4919
3	20.659	PV	0.4599	41.36152	1.08214	2.0687

Totals : 1999.34876 73.65113

Results obtained with enhanced integrator!

```

=====
*** End of Report ***
=====

```