



Supporting Information

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Intermolecular Oxidative Enolate Heterocoupling

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General Procedures. All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), dichloromethane, dimethylformamide (DMF), methanol, toluene, and benzene were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and either an ceric ammonium molybdate in aqueous H_2SO_4 or *p*-anisaldehyde in ethanol/aqueous $\text{H}_2\text{SO}_4/\text{CH}_3\text{CO}_2\text{H}$ and heat as developing agents. NMR spectra were recorded on either Bruker DRX 600, DRX 500, or AMX 400 instruments, and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintuplet, sext = sextet, sep =

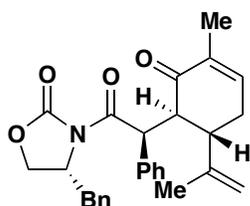
septet, a = apparent, b = broad. IR spectra were recorded on a Perkin-Elmer Spectrum BX spectrometer. High resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). Melting points (m.p.) are uncorrected and were recorded on a Fisher-Johns 12-144 melting point apparatus. Optical rotations were obtained on a Perkin-Elmer 431 Polarimeter. Chiral HPLC was performed on a Shimadzu Sc110A VP using a Chiralpak AS column.

Intermolecular oxidative heterocoupling. General procedures.

Procedure A: Oxazolidinone or oxindole (0.10 mmol, 1.0 equiv) and carbonyl compound (0.10 mmol, 1.0 equiv) were dissolved in benzene (1.0 mL) and the solvent removed *in vacuo*. This process was repeated a second time (azeotropic water removal). The starting materials were then dissolved in THF (340 μ L, 0.3 M), and the solution was cooled to -78 °C. A solution of LDA (0.50 M in THF, 428 μ L, 2.1 equiv) was added dropwise by syringe over 30 sec. The reaction was allowed to stir for 30 minutes at -78 °C, and was then warmed to ambient temperature. After 5 min of stirring 23 °C, a solution of Fe(acac)₃ (0.50 M, 408 μ L, 2.0 equiv) was added all at once (less than 1 sec addition time). The reaction was stirred at ambient temperature for 20 min and was then quenched by the addition of 1 N HCl (1 mL). The aqueous layer was partitioned with EtOAc (2 mL), separated, and then extracted twice with EtOAc (2 mL). The organic portions were combined, washed with brine (5 mL), dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Flash chromatography (silica gel) of the crude reaction afforded pure coupled product. *Note: This procedure can be performed on gram scale (see entry 3).*

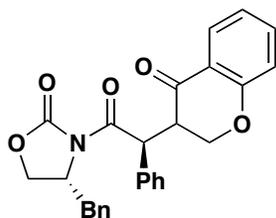
Procedure B: Oxazolidinone (0.33 mmol, 1.0 equiv) and powdered lithium chloride (1.64 mmol, 5.0 equiv) were taken up in benzene (1.0 mL) and the solvent removed *in vacuo*. This process was repeated a second time (azeotropic water removal). To this mixture was added toluene (546 μL , 0.6 *M*), and the resulting solution was cooled to -78 $^{\circ}\text{C}$. A solution of LDA (0.50 *M* in THF, 759 μL , 1.15 equiv) was added by syringe down the sides of the reaction vessel over 10 sec. After stirring at -78 $^{\circ}\text{C}$ for 10 min, the solution was warmed to 0 $^{\circ}\text{C}$ for 10 min (color changes from pale to bright yellow), and then cooled to -78 $^{\circ}\text{C}$ for 5 min. In a separate reaction vessel, the carbonyl compound (0.57 mmol, 1.75 equiv) was dissolved in benzene (1.0 mL) and the solvent removed *in vacuo*. This process was repeated a second time. To this was added toluene (546 μL , 0.6 *M*), and the solution was cooled to -78 $^{\circ}\text{C}$. A solution of LDA (0.50 *M* in THF, 1.2 mL, 1.85 equiv) was added by syringe down the sides of the reaction vessel over 10 sec and the resulting solution was stirred at -78 $^{\circ}\text{C}$ for 25 min. At this time, the carbonyl enolate solution was transferred, *via* canula, into the oxazolidinone enolate solution. The reaction vessel was stirred at -78 $^{\circ}\text{C}$ for an additional 5 min at which time a -78 $^{\circ}\text{C}$ solution of copper(II)-2-ethylhexanoate (0.3 *M* in toluene, 3.0 mL, 2.75 equiv) was transferred into the reaction vessel *via* canula. Immediately following addition, the vessel was quickly removed from the -78 $^{\circ}\text{C}$ bath and placed into a room temperature water bath, where the color changed from light blue to brown. The reaction was stirred for 20 min and was subsequently quenched by the addition of 5% aqueous NH_4OH (5 mL). The aqueous layer was partitioned with EtOAc (5 mL), separated, and then extracted twice with EtOAc (2 mL). The organic portions were combined, washed with brine (5 mL),

dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. Flash chromatography (silica gel) of the crude reaction afforded pure coupled product. *Note: This procedure can be performed on gram scale (see entry 11).*



Entry 1, benzyl oxazolidinone – carvone adduct: Procedure A

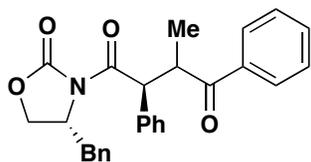
(0.68 mmol scale); yield = 52% (*dr* = 2.7:1, major diastereomer presented); colorless needles; m.p. = 146 – 147 °C; R_f = 0.36 (silica gel, 1:1 hexanes:Et₂O); $[\alpha]_D = -9.6$ (CHCl₃, *c* = 0.40); IR (film) ν_{max} 1774, 1691, 1454, 1366, 1284, 1208, 1108 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.15 – 7.29 (m, 8 H), 6.90 (ad, *J* = 6.0 Hz, 2 H), 6.59 (bs, 1 H), 5.40 (d, *J* = 10.2 Hz, 1 H), 4.78 (s, 1 H), 4.77 (t, *J* = 8.4 Hz, 1 H), 4.68 (s, 1 H), 4.18 (t, *J* = 8.4 Hz, 1 H), 4.06 (dd, *J* = 8.7, 2.6 Hz, 1 H), 3.55 (dd, *J* = 10.1, 4.0 Hz, 1 H), 3.07 (dd, *J* = 13.5, 2.7 Hz, 1 H), 2.63 – 2.65 (m, 2 H), 2.55 (dd, *J* = 8.8, 6.8 Hz, 1 H), 2.42 (bd, *J* = 20.5 Hz, 1 H), 1.72 (s, 3 H), 1.61 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃) δ 199.1, 172.0, 153.1, 144.8, 141.7, 135.0 (2), 134.7, 129.5 (2), 129.4 (2), 128.8 (2), 128.5 (2), 127.9, 127.1, 112.3, 65.8, 55.2, 52.8, 50.0, 44.2, 37.1, 28.0, 21.3, 16.0; HRMS (ESI-TOF) calcd. for C₂₈H₃₀NO₄ [*M* + H⁺] 444.2196, found 444.2187. Structure verified by X-ray crystallography. See CCDC 617245-617247.



Entries 2–3, benzyl oxazolidinone – 4-chromanone adduct:

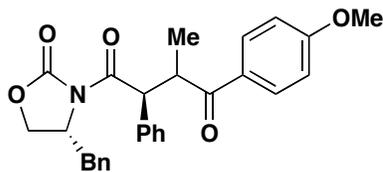
Procedure A (0.51 mmol scale); yield = 59% (*dr* = 2.8:1, major diastereomer presented); white foam; R_f = 0.40 (silica gel, 1:1 hexanes:Et₂O); $[\alpha]_D = +130$ (CHCl₃, *c* = 0.88); IR (film) ν_{max} 1780, 1687, 1605, 1480, 1458, 1388, 1213 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.83 (d, *J* = 7.7 Hz, 1 H), 7.47 (t, *J*

= 8.2 Hz, 1 H), 7.34 – 7.40 (m, 3 H), 7.22 – 7.28 (m, 5 H), 7.05 (t, $J = 3.6$ Hz, 2 H), 7.01 (t, $J = 7.6$ Hz, 1 H), 6.95 (d, $J = 8.4$ Hz, 1 H), 5.8 (d, $J = 6.8$ Hz, 1 H), 5.02 (t, $J = 11.1$ Hz, 1 H), 4.76 – 4.80 (m, 1 H), 4.36 (dd, $J = 11.3, 4.6$ Hz, 1 H), 4.25 (t, $J = 8.4$ Hz, 1 H), 4.08 (dd, $J = 9.0, 2.6$ Hz, 1 H), 3.34 – 3.38 (m, 1 H), 3.23 (dd, $J = 13.4, 3.3$ Hz, 1 H), 2.57 (dd, $J = 13.3, 9.6$ Hz, 1 H); ^{13}C NMR (150 MHz, CDCl_3) δ 192.9, 171.8, 161.8, 152.5, 136.0, 134.9, 134.3, 129.3 (2), 129.0 (4), 128.9 (2), 127.9, 127.3, 127.2, 121.4, 120.8, 117.8, 69.3, 65.9, 54.9, 50.1, 46.3, 37.5; HRMS (ESI-TOF) calcd. for $\text{C}_{27}\text{H}_{23}\text{NO}_5\text{Na}$ [$\text{M} + \text{Na}^+$] 464.1468, found 464.1478. *Note: Entry 3 was performed on larger than one gram scale (3.72 mmol), proceeding in 60% yield, dr = 2.6:1, with no experimental alterations necessary.*



Entry 4, benzyl oxazolidinone – propiophenone adduct:

Procedure A (0.34 mmol scale); yield = 57% ($dr = 2.8:1$, major diastereomer presented); white foam; $R_f = 0.28$ (silica gel, 1:1 hexanes: Et_2O); $[\alpha]_D = +10$ (CHCl_3 , $c = 0.46$); IR (film) ν_{max} 1779, 1679, 1454, 1351, 1325, 1200, 1106, 974 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, $J = 7.2$ Hz, 2 H), 7.47 (t, $J = 7.5$ Hz, 3 H), 7.36 (t, $J = 7.8$ Hz, 2 H), 7.15 – 7.24 (m, 6 H), 6.90 (d, $J = 6.6$ Hz, 2 H), 5.58 (d, $J = 10.2$ Hz, 1 H), 4.79 – 4.84 (m, 1 H), 4.48 (dq, $J = 10.2, 6.9$ Hz, 1 H), 4.24 (t, $J = 8.6$ Hz, 1 H), 4.10 (dd, $J = 9.0, 2.9$ Hz, 1 H), 3.02 (dd, $J = 13.6, 3.3$ Hz, 1 H), 2.60 (dd, $J = 13.7, 8.6$ Hz, 1 H), 1.36 (d, $J = 6.9$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.9, 172.7, 152.6, 136.5, 136.2, 134.6, 132.9, 129.5 (2), 129.3 (2), 128.8 (2), 128.4 (4), 128.1 (2), 127.5, 127.2, 65.6, 54.8, 51.3, 44.5, 37.1 17.4; HRMS (ESI-TOF) calcd. for $\text{C}_{27}\text{H}_{26}\text{NO}_4$ [$\text{M} + \text{H}^+$] 428.1856, found 428.1859.



Entry 5, benzyl oxazolidinone - 4'-methoxypropiophenone adduct: Procedure A (0.17

mmol scale); yield = 67% (*dr* = 2.5:1, major

diastereomer presented); white foam; R_f = 0.17 (silica gel, 1:1 hexanes:Et₂O); $[\alpha]_D = +2.8$

(CHCl₃, *c* = 0.94); IR (film) ν_{\max} 1778, 1671, 1599, 1352, 1322, 1261, 1202, 1173, 1105,

975 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.80 (dd, *J* = 11.6, 2.8 Hz, 2 H), 7.48 (d, *J* = 7.3

Hz, 2 H), 7.13 – 7.26 (m, 6 H), 6.90 (d, *J* = 6.7 Hz, 2 H), 6.83 (dd, *J* = 11.7, 2.8 Hz, 2 H),

5.57 (d, *J* = 10.1 Hz, 1 H), 4.79 – 4.84 (m, 1 H), 4.44 (dq, *J* = 10.2, 6.8 Hz, 1 H), 4.24 (t,

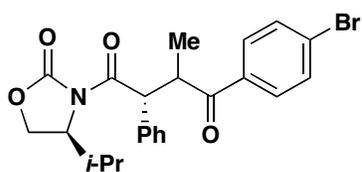
J = 8.3 Hz, 1 H), 4.09 (dd, *J* = 9.0, 2.8 Hz, 1 H), 3.82 (s, 3 H), 3.02 (dd, *J* = 13.6, 3.4 Hz,

1 H), 2.60 (dd, *J* = 13.6, 8.5 Hz, 1 H), 1.34 (d, *J* = 6.8 Hz, 3 H); ¹³C NMR (150 MHz,

CDCl₃) δ 200.2, 172.9, 163.3, 152.3, 136.4 (2), 134.7, 130.5 (2), 129.5 (2), 129.4 (2),

128.8 (2), 128.4 (2), 127.4, 127.2, 113.6 (2), 65.6, 55.4, 54.8, 51.4, 44.0, 37.1, 17.5;

HRMS (ESI-TOF) calcd. for C₂₈H₂₈NO₅ [*M* + H⁺] 458.1962, found 458.1961.



Entry 6, isopropyl oxazolidinone - 4'-bromopropiophenone adduct: Procedure A (0.20 mmol

scale); yield = 55% (*dr* = 2.5:1, major diastereomer

presented); colorless plates; m.p. = 177 – 179 °C; R_f = 0.36 (silica gel, 1:1 hexanes:Et₂O);

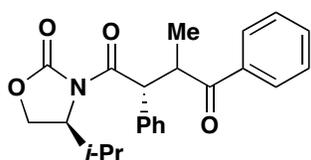
$[\alpha]_D = -3.8$ (CHCl₃, *c* = 0.35); IR (film) ν_{\max} 1779, 1680, 1584, 1386, 1321, 1198, 975

cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.63 (d, *J* = 8.6 Hz, 2 H), 7.48 (t, *J* = 8.7 Hz, 2 H),

7.37 (d, *J* = 8.0 Hz, 2 H), 7.16 (t, *J* = 7.7 Hz, 2 H), 7.09 (t, *J* = 7.3 Hz, 1 H), 5.59 (d, *J* =

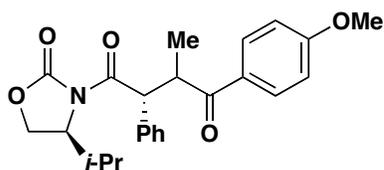
10.3 Hz, 1 H), 4.52 – 4.55 (m, 1 H), 4.38 (dq, *J* = 10.3, 6.8 Hz, 1 H), 4.28 (t, *J* = 8.8 Hz, 1

H), 4.12 (dd, $J = 9.1, 3.2$ Hz, 1 H), 2.11 – 2.19 (m, 1 H), 1.31 (d, $J = 6.8$ Hz, 3 H), 0.79 (d, $J = 7.1$ Hz, 3 H), 0.36 (d, $J = 6.9$ Hz, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 201.1, 172.7, 153.1, 136.4, 135.5, 131.7 (2), 129.7 (2), 129.1 (2), 128.4 (2), 128.0, 127.6, 62.9, 58.1, 51.7, 43.9, 27.8, 17.7, 17.4, 13.9; HRMS (ESI-TOF) calcd. for $\text{C}_{23}\text{H}_{25}\text{BrNO}_4$ [$\text{M} + \text{H}^+$] 458.0961, found 458.0968. Structure verified by X-ray crystallography. See CCDC 617245-617247.



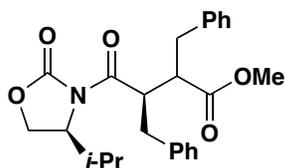
Entry 7, isopropyl oxazolidinone – propiophenone adduct:

Procedure A (0.20 mmol scale); yield = 66% ($dr = 2.1:1$, major diastereomer presented); colorless oil; $R_f = 0.33$ (silica gel, 1:1 hexanes: Et_2O); $[\alpha]_D = -25$ (CHCl_3 , $c = 0.35$); IR (film) ν_{max} 1777, 1681, 1374, 1325, 1199, 1102, 975 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.78 (d, $J = 7.3$ Hz, 2 H), 7.46 (t, $J = 7.4$ Hz, 1 H), 7.40 (d, $J = 7.3$ Hz, 2 H), 7.35 (t, $J = 7.7$ Hz, 2 H), 7.16 (t, $J = 7.8$ Hz, 2 H), 7.08 (t, $J = 7.4$ Hz, 1 H), 5.63 (d, $J = 10.3$ Hz, 1 H), 4.52 – 4.55 (m, 1 H), 4.45 (dq, $J = 10.2, 6.8$ Hz, 1 H), 4.29 (t, $J = 8.8$ Hz, 1 H), 4.11 (dd, $J = 9.1, 3.2$ Hz, 1 H), 2.12 – 2.19 (m, 1 H), 1.33 (d, $J = 6.8$ Hz, 3 H), 0.79 (d, $J = 7.1$ Hz, 3 H), 0.36 (d, $J = 6.9$ Hz, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 201.9, 172.9, 153.2, 136.6 (2), 132.8, 129.2 (2), 128.4 (2), 128.3 (2), 128.1 (2), 127.4, 62.8, 58.0, 51.5, 44.0, 27.8, 17.7, 17.5, 13.9; HRMS (ESI-TOF) calcd. for $\text{C}_{23}\text{H}_{26}\text{NO}_4$ [$\text{M} + \text{H}^+$] 380.1856, found 380.1848.



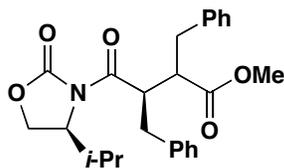
Entry 8, isopropyl oxazolidinone – 4'-methoxypropiophenone adduct: Procedure A (0.20 mmol scale); yield = 65% ($dr = 2.3:1$, major

diastereomer presented); colorless oil; $R_f = 0.23$ (silica gel, 1:1 hexanes:Et₂O); $[\alpha]_D = -5.8$ (CHCl₃, $c = 0.62$); IR (film) ν_{\max} 1778, 1671, 1600, 1374, 1320, 1260, 1201, 1023, 976 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.78 (d, $J = 8.9$ Hz, 2 H), 7.40 (d, $J = 7.4$ Hz, 2 H), 7.15 (t, $J = 7.5$ Hz, 2 H), 7.08 (t, $J = 7.3$ Hz, 1 H), 6.82 (d, $J = 8.9$ Hz, 2 H), 5.61 (d, $J = 10.3$ Hz, 1 H), 4.52 – 4.55 (m, 1 H), 4.39 (dq, $J = 10.3, 6.8$ Hz, 1 H), 4.27 (t, $J = 8.8$ Hz, 1 H), 4.11 (dd, $J = 9.0, 3.2$ Hz, 1 H), 3.81 (s, 3 H), 2.12 – 2.18 (m, 1 H), 1.31 (d, $J = 6.8$ Hz, 3 H), 0.79 (d, $J = 7.0$ Hz, 3 H), 0.36 (d, $J = 6.9$ Hz, 3 H); ¹³C NMR (150 MHz, CDCl₃) δ 200.3, 173.0, 163.3, 153.2, 136.8, 130.5 (2), 129.5, 129.2 (2), 128.3 (2), 127.3, 113.6 (2), 62.8, 58.0, 55.4, 51.5, 43.5, 27.8, 17.7, 17.6, 13.9; HRMS (ESI-TOF) calcd. for C₂₄H₂₇NO₅Na [M + Na⁺] 432.1781, found 432.1763.

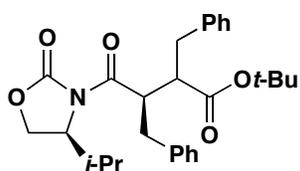


Entry 9, isopropyl oxazolidinone – methyl dihydrocinnamate adduct (upper diastereomer): Procedure B (0.19 mmol scale); yield = 51% ($dr = 1.0:1$, minor diastereomer); colorless oil; $R_f =$

0.48 (silica gel, 1:1 hexanes:Et₂O); $[\alpha]_D = +73$ (CHCl₃, $c = 0.38$); IR (film) ν_{\max} 1778, 1736, 1696, 1386, 1320, 1199 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.25 – 7.28 (m, 4H), 7.16 – 7.21 (m, 6 H), 4.63 (ddd, $J = 10.1, 7.8, 5.7$ Hz, 1 H), 4.05 (ddd, $J = 8.1, 3.9, 2.3$ Hz, 1 H), 3.99 (dd, $J = 8.9, 2.2$ Hz, 1 H), 3.65 (t, $J = 8.5$ Hz, 1 H), 3.54 (s, 3 H), 3.24 (ddd, $J = 11.4, 7.9, 3.8$ Hz, 1 H), 3.09 (dd, $J = 13.3, 11.3$ Hz, 1 H), 2.84 – 2.94 (m, 3 H), 2.24 – 2.30 (m, 1 H), 0.87 (d, $J = 7.1$ Hz, 3 H), 0.84 (d, $J = 6.9$ Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 173.5, 173.3, 153.5, 138.6, 138.1, 129.1 (2), 128.3 (2), 128.4 (2), 128.3 (2), 126.6, 126.5, 63.3, 58.9, 51.5, 59.4, 48.8, 36.8, 36.5, 28.8, 18.0, 14.8; HRMS (ESI-TOF) calcd. for C₂₅H₃₀NO₅ [M + H⁺] 424.2118, found 424.2129.

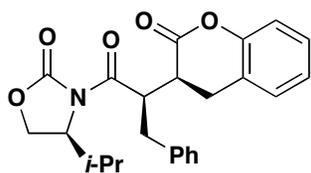
**Entry 9, isopropyl oxazolidinone – methyldihydrocinnamate****adduct (lower diastereomer):** Procedure B (0.19 mmol scale);yield = 51% (*dr* = 1.0:1, major diastereomer); colorless oil; R_f =

0.40 (silica gel, 1:1 hexanes:Et₂O); $[\alpha]_D^{25} = +101$ (CHCl₃, *c* = 0.40); IR (film) ν_{\max} 1780, 1733, 1694, 1385, 1199 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.14 (d, *J* = 7.4 Hz, 4H), 7.18 – 7.28 (m, 6 H), 4.64 (ddd, *J* = 10.0, 7.8, 5.8 Hz, 1 H), 4.02 (ddd, *J* = 8.0, 3.7, 2.3 Hz, 1 H), 3.95 (dd, *J* = 8.9, 2.1 Hz, 1 H), 3.61 (t, *J* = 8.5 Hz, 1 H), 3.54 (s, 3 H), 3.14 – 3.18 (m, 1 H), 3.00 – 3.12 (m, 3 H), 2.84 (dd, *J* = 13.0, 10.2 Hz, 1 H), 2.18 – 2.23 (m, 1 H), 0.83 (d, *J* = 7.1 Hz, 3 H), 0.81 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 174.5, 173.9, 153.2, 138.4, 137.8, 129.2 (2), 128.8 (2), 128.4 (2), 128.3 (2), 126.7, 126.6, 63.0, 58.7, 51.6, 48.9, 45.3, 37.0, 35.4, 28.7, 17.9, 14.8; HRMS (ESI-TOF) calcd. for C₂₅H₃₀NO₅ [M + H⁺] 424.2118, found 424.2126.

**Entries 10–11, Isopropyl oxazolidinone – *t*-butyldihydrocinnamate adduct (mixture of diastereomers):**Procedure B (0.19 mmol scale); yield = 51% (*dr* = 1.6:1);

colorless oil; R_f = 0.54 (silica gel, 1:1 hexanes:Et₂O); IR (film) ν_{\max} 1779, 1723, 1693, 1386, 1365, 1200, 1148 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.16 – 7.29 (m, 20 H), 4.60 – 4.68 (m, 2 H), 3.98 – 4.02 (m, 2 H), 3.93 – 3.96 (m, 2 H), 3.56 – 3.59 (m, 2 H), 2.79 – 3.13 (m, 10 H), 2.18 – 2.30 (m, 2 H), 1.29/1.24 (2s, 18 H), 0.81 – 0.86 (m, 12 H); ¹³C NMR (150 MHz, CDCl₃) δ 174.8, 173.9, 173.1, 172.0, 153.4, 153.1, 138.7 (2), 138.4, 137.9, 129.2 (2), 129.1 (6), 128.3 (2), 128.2 (2), 128.1 (4), 126.6, 126.5, 126.4 (2), 81.0,

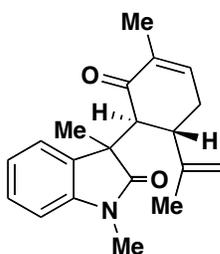
80.7, 63.2, 62.9, 58.9, 58.7, 51.1, 49.9, 47.0, 45.5, 37.2, 37.1, 36.9, 36.0, 28.8 (3), 28.6 (3), 27.9, 27.7, 18.0 (2), 14.9, 14.7; HRMS (ESI-TOF) calcd. for $C_{28}H_{34}NO_5$ [$M + H^+$] 466.2588, found 466.2584. *Note: Entry 11 was performed on larger than one gram scale (4.34 mmol), proceeding in 53% yield, dr = 1.6:1, with no experimental alterations necessary.*



Entry 12, isopropyl oxazolidinone – dihydrocoumarin

adduct: Procedure B (0.19 mmol scale); yield = 54% (*dr* = 2.4:1, major diastereomer presented); colorless pipes; m.p. =

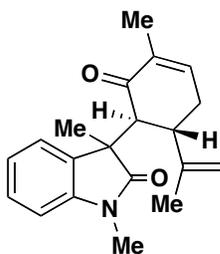
189 – 191 °C; R_f = 0.51 (silica gel, 1:1 hexanes:Et₂O); $[\alpha]_D^{25} = +74$ (CHCl₃, $c = 0.19$); IR (film) ν_{max} 1734, 1696, 1458, 1387, 1234, 1144 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.32 (m, 4H), 7.19 – 7.24 (m, 2 H), 7.16 (d, $J = 8.8$ Hz, 1 H), 7.07 (td, $J = 7.5, 1.0$ Hz, 1H), 7.01 (d, $J = 8.1$ Hz, 1H), 4.90 (dt, $J = 8.3, 6.7$ Hz, 1 H), 4.24 (ddd, $J = 8.3, 3.7, 2.5$ Hz, 1 H), 4.11 (dd, $J = 9.1, 2.4$ Hz, 1 H), 3.92 (t, $J = 8.7$ Hz, 1 H), 3.57 (dd, $J = 15.3, 13.2$ Hz, 1 H), 3.09 – 3.14 (m, 2 H), 3.98 (dd, $J = 13.3, 8.9$ Hz, 1 H), 2.89 (dt, $J = 12.9, 6.2$ Hz, 1 H), 2.33 – 2.39 (m, 1 H), 0.95 (d, $J = 6.8$ Hz, 3 H), 0.90 (d, $J = 8.5$ Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 174.5, 170.1, 153.4, 151.2, 137.4, 128.2 (2), 128.6 (2), 128.2, 128.0, 126.9, 124.4, 122.7, 116.6, 63.1, 58.8, 43.0, 40.7, 35.7, 28.4, 26.6, 18.0, 14.5; HRMS (ESI-TOF) calcd. for $C_{24}H_{25}NO_5Na$ [$M + Na^+$] 430.1625, found 430.1633. Structure verified by X-ray crystallography. See CCDC 617245-617247.



Entries 13–14, 1,3-dimethyloxindole – carvone adduct (upper

diastereomer): Procedure A (0.54 mmol scale); yield = 60% (*dr* =

1.2:1, major diastereomer); white needles; m.p. = 99 – 102 °C; R_f = 0.28 (silica gel, 1:1 hexanes:Et₂O); $[\alpha]_D = -79$ (CHCl₃, $c = 0.31$); IR (film) ν_{\max} 1711, 1657, 1611, 1492, 1471, 1376, 1112, 894 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.27 (td, $J = 7.6, 1.3$ Hz, 1H), 6.82 – 6.95 (m, 3 H), 6.34 (bs, 1 H), 4.67 (s, 1 H), 4.45 (s, 1 H), 3.23 (s, 3 H), 3.05 (d, $J = 2.4$ Hz, 1 H), 2.34 (d, $J = 6.2$ Hz, 1 H), 1.96 – 2.03 (m, 1 H), 1.83 (bs, 3 H), 1.71 – 1.78 (m, 1 H), 1.65 (s, 3 H), 1.43 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 198.4, 179.1, 146.5, 143.7, 143.1, 135.9, 131.5, 128.3, 123.9, 121.7, 111.7, 107.8, 54.1, 51.0, 42.8, 27.8, 26.3, 23.7, 21.5, 16.2; HRMS (ESI-TOF) calcd. for C₂₀H₂₄NO₂ [M + H⁺] 310.1801, found 310.1792. *Note: For entry 13, 2 equivalents of carvone were used resulting in 91% yield, dr = 1.2:1).*



Entries 13–14, 1,3-dimethyloxindole – carvone adduct (lower

diastereomer): Procedure A (0.54 mmol scale); yield = 60% ($dr =$

1.2:1, minor diastereomer); colorless oil; R_f = 0.12 (silica gel, 1:1

hexanes:Et₂O); $[\alpha]_D = +82$ (CHCl₃, $c = 0.84$); IR (film) ν_{\max} 1712,

1661, 1611, 1493, 1471, 1378, 1125, 896 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.26 (t, $J =$

7.7 Hz, 1H), 7.21 (d, $J = 7.2$ Hz, 1 H), 7.03 (t, $J = 7.34$ Hz, 1 H), 6.85 (d, $J = 7.7$ Hz, 1

H), 6.54 (bs, 1 H), 4.76 (s, 1 H), 4.73 (s, 1 H), 3.23 (s, 3 H), 3.07 (d, $J = 5.6$ Hz, 1 H),

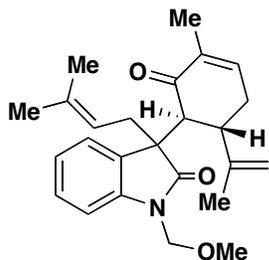
2.62 (dd, $J = 10.9, 5.4$ Hz, 1 H), 2.25 – 2.26 (m, 2 H), 1.70 (s, 3 H), 1.68 (s, 3 H), 1.41 (s,

3 H); ¹³C NMR (125 MHz, CDCl₃) δ 197.9, 179.6, 147.3, 143.6, 142.0, 136.1, 133.2,

127.9, 122.7, 122.3, 112.4, 108.2, 55.4, 52.1, 43.5, 29.4, 26.3, 23.6, 20.6, 16.1; HRMS

(ESI-TOF) calcd. for C₂₀H₂₂NO₂ [M – H]⁻ 308.1656, found 308.1653. *Note: For entry*

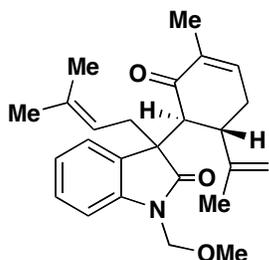
13, 2 equivalents of carvone were used resulting in 91% yield, dr = 1.2:1).

**Entry 15, 1-methoxymethyl-3-prenyloxindole – carvone****adduct (upper diastereomer):** Procedure A (0.10 mmol scale);yield = 48% (*dr* = 1.0:1); colorless oil; R_f = 0.44 (silica gel, 1:1hexanes:Et₂O); $[\alpha]_D = -41$ (CHCl₃, *c* = 0.28); IR (film) ν_{\max} 1718,1654, 1611, 1488, 1466, 1347, 1092, 755 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.26 (t, *J* =7.7 Hz, 1 H), 6.99 (d, *J* = 4.0 Hz, 1 H), 6.95 (t, *J* = 7.5 Hz, 1 H), 6.88 (d, *J* = 7.4 Hz, 1 H),6.34 (bs, 1 H), 5.16 (d, *J* = 10.9 Hz, 1 H), 5.09 (d, *J* = 10.9 Hz, 1 H), 4.70 (s, 1 H), 4.52(s, 1 H), 4.44 (t, *J* = 7.4 Hz, 1 H), 3.30 (s, 3 H), 3.12 (s, 1 H), 2.86 (dd, *J* = 14.3, 8.6 Hz, 1H), 2.62 (dd, *J* = 14.3, 6.3 Hz, 1 H), 2.42 (d, *J* = 6.2 Hz, 1 H), 1.98 (dd, *J* = 19.7, 5.5 Hz,1 H), 1.85 (d, *J* = 1.1 Hz, 3 H), 1.65 (s, 3 H), 1.48 (s, 3 H), 1.40 (s, 3 H), 1.36 – 1.40 (m,1 H); ¹³C NMR (150 MHz, CDCl₃) δ 198.4, 178.7, 146.6, 143.9, 142.3, 136.1, 135.5,

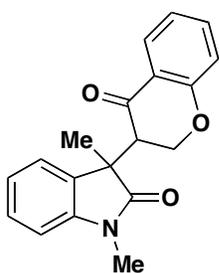
129.1, 128.5, 124.4, 122.0, 117.3, 111.7, 109.0, 71.5, 56.2, 56.0, 54.2, 42.7, 35.7, 27.7,

25.8, 21.6, 18.1, 18.2; HRMS (ESI-TOF) calcd. for C₂₅H₃₁NO₃Na [M + Na]⁺ 416.2196,

found 416.2196.

**Entry 15, 1-methoxymethyl-3-prenyloxindole – carvone****adduct (lower diastereomer):** Procedure A (0.10 mmol scale);yield = 48% (*dr* = 1.0:1); colorless oil; R_f = 0.31 (silica gel, 1:1hexanes:Et₂O); $[\alpha]_D = +63$ (CHCl₃, *c* = 0.43); IR (film) ν_{\max} 1723,1662, 1611, 1488, 1467, 1348, 1091, 755 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.26 (t, *J* =7.8 Hz, 1 H), 7.19 (d, *J* = 7.3 Hz, 1 H), 7.07 (t, *J* = 7.4 Hz, 1 H), 7.02 (d, *J* = 7.8 Hz, 1 H),6.50 (bs, 1 H), 5.13 (d, *J* = 10.9 Hz, 1 H), 5.03 (d, *J* = 10.9 Hz, 1 H), 4.74 (s, 1 H), 4.66

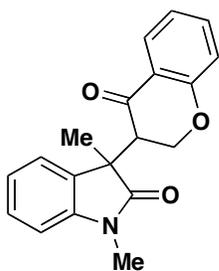
(s, 1 H), 4.61 (t, $J = 7.4$ Hz, 1 H), 3.31 (s, 3 H), 3.09 (d, $J = 3.6$ Hz, 1 H), 2.74 (dd, $J = 13.8, 8.6$ Hz, 1 H), 2.66 (dd, $J = 13.8, 6.3$ Hz, 1 H), 2.51 (d, $J = 4.2$ Hz, 1 H), 2.17 – 2.26 (m, 2 H), 1.75 (s, 3 H), 1.64 (s, 3 H), 1.44 (s, 3 H), 1.39 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 198.1, 178.7, 147.2, 142.8, 141.4, 136.6, 135.8, 130.3, 128.2, 123.4, 122.8, 117.4, 112.2, 109.3, 99.6, 71.5, 56.2, 55.7, 54.9, 42.7, 35.4, 28.7, 25.8, 18.0, 16.3; HRMS (ESI-TOF) calcd. for $\text{C}_{25}\text{H}_{31}\text{NO}_3$ $[\text{M} + \text{Na}]^+$ 416.2196, found 416.2197.



Entry 16, 1,3-dimethyloxindole – 4-chromanone adduct (upper

diastereomer): Procedure A (0.16 mmol scale); yield = 72% ($dr = 2.6:1$, major diastereomer); white needles; m.p. = 141 – 144 °C; $R_f = 0.40$ (silica gel, 1:1 hexanes:Et₂O); IR (film) ν_{max} 1696, 1606, 1479,

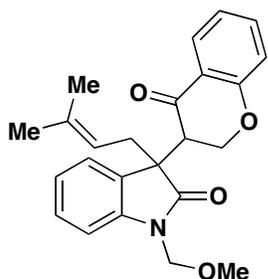
1467, 1326, 1125, 1021, 929, 753 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.83 (dd, $J = 7.9, 1.7$ Hz, 1 H), 7.39 (t, $J = 7.7$ Hz, 1 H), 7.23 (td, $J = 7.7, 1.1$ Hz, 1 H), 7.02 (dd, $J = 7.7, 1.0$ Hz, 1 H), 6.97 (t, $J = 7.9$ Hz, 1 H), 6.88 (t, $J = 7.2$ Hz, 2 H), 6.78 (d, $J = 8.2$ Hz, 1 H), 4.48 (dd, $J = 11.6, 4.7$ Hz, 1 H), 4.35 (dd, $J = 11.5, 10.3$ Hz, 1 H), 3.39 (dd, $J = 10.3, 4.8$ Hz, 1 H), 3.23 (s, 3 H), 1.59 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 192.1, 179.1, 161.3, 143.1, 135.9, 132.6, 128.0, 127.1, 123.0, 122.4, 121.5, 121.3, 117.4, 108.2, 68.4, 51.1, 47.9, 26.3, 23.0; HRMS (ESI-TOF) calcd. for $\text{C}_{19}\text{H}_{18}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 308.1281, found 308.1282.



Entry 16, 1,3-dimethyloxindole – 4-chromanone adduct (lower

diastereomer): Procedure A (0.16 mmol scale); yield = 72% ($dr = 2.6:1$, minor diastereomer); white powder; $R_f = 0.26$ (silica gel, 1:1

hexanes:Et₂O); IR (film) ν_{\max} 1714, 1607, 1479, 1379, 1291, 1216, 1025, 928, 754 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.68 (dd, $J = 7.9, 1.6$ Hz, 1 H), 7.39 (t, $J = 7.8$ Hz, 1 H), 7.26 (t, $J = 8.3$ Hz, 1 H), 7.10 (d, $J = 7.4$ Hz, 1 H), 6.89 – 6.95 (m, 4 H), 4.86 (dd, $J = 11.2, 4.9$, Hz, 1 H), 4.65 (t, $J = 11.2$ Hz, 1 H), 3.51 (dd, $J = 11.2, 4.9$ Hz, 1 H), 3.31 (s, 3 H), 1.45 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃) δ 190.8, 179.6, 161.4, 144.2, 135.8, 131.2, 128.4, 127.3, 123.0, 122.0, 121.5, 121.2, 117.5, 108.4, 67.9, 52.3, 46.8, 42.1, 26.6; HRMS (ESI-TOF) calcd. for C₁₉H₁₈NO₃ [M + H]⁺ 308.1281, found 308.1283.



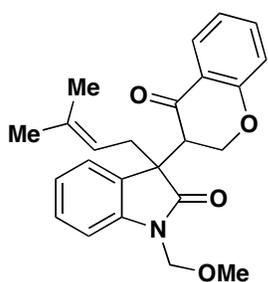
Entry 17, 1-methoxymethyl-3-prenyloxindole – 4-chromanone

adduct (upper diastereomer): Procedure A (0.10 mmol scale);

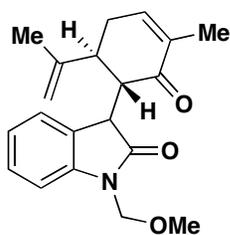
yield = 73% ($dr = 2.0:1$, major diastereomer); yellow oil; $R_f =$

0.45 (silica gel, 1:1 hexanes:Et₂O); IR (film) ν_{\max} 1718, 1606,

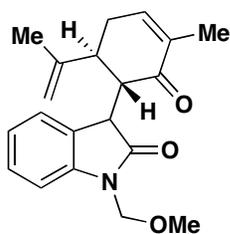
1480, 1466, 1349, 1327, 1093, 755 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.81 (dd, $J = 7.9, 1.4$ Hz, 1 H), 7.40 (t, $J = 7.8$ Hz, 1 H), 7.23 (t, $J = 7.7$ Hz, 1 H), 7.05 (t, $J = 9.3$ Hz, 2 H), 6.98 (t, $J = 7.5$ Hz, 1 H), 6.90 (t, $J = 7.6$ Hz, 1 H), 6.80 (d, $J = 8.3$ Hz, 1 H), 5.16 (d, $J = 10.9$ Hz, 1 H), 5.14 (d, $J = 10.9$ Hz, 1 H), 4.78 – 4.81 (m, 1 H), 4.55 (dd, $J = 11.5, 4.8$ Hz, 1 H), 4.45 (t, $J = 11.5$ Hz, 1 H), 3.50 (dd, $J = 10.7, 4.7$ Hz, 1 H), 3.36 (s, 3 H), 2.99 (dd, $J = 14.1, 6.1$ Hz, 1 H), 2.65 (dd, $J = 14.1, 8.1$ Hz, 1 H), 1.54 (s, 3 H), 1.48 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃) δ 192.1, 179.1, 161.2, 142.1, 136.4, 135.9, 130.3, 128.1, 127.2, 123.5, 122.7, 121.6, 121.3, 117.4, 116.7, 109.3, 71.5, 68.4, 56.2, 52.4, 50.5, 34.8, 25.9, 18.1; HRMS (ESI-TOF) calcd. for C₂₄H₂₅NO₄Na [M + Na]⁺ 414.1676, found 414.1678.

**Entry 17, 1-methoxymethyl-3-prenyloxindole – 4-chromanone****adduct (lower diastereomer):** Procedure A (0.10 mmol scale);yield = 73% (*dr* = 2.0:1, minor diastereomer); colorless oil; R_f =0.33 (silica gel, 1:1 hexanes:Et₂O); IR (film) ν_{\max} 1721, 1607,1480, 1466, 1350, 1088, 756 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.72 (dd, *J* = 7.9, 1.6Hz, 1 H), 7.42 (t, *J* = 8.6 Hz, 1 H), 7.26 (t, *J* = 7.7 Hz, 1 H), 7.12 (d, *J* = 7.4 Hz, 1 H),7.07 (d, *J* = 7.8 Hz, 1 H), 6.98 (t, *J* = 7.5 Hz, 1 H), 6.94 (t, *J* = 7.5 Hz, 1 H), 6.91 (d, *J* =8.3 Hz, 1 H), 5.19 (d, *J* = 11.0 Hz, 1 H), 5.14 (d, *J* = 11.0 Hz, 1 H), 4.77 – 4.82 (m, 2 H),4.61 (t, *J* = 10.8 Hz, 1 H), 3.54 (dd, *J* = 10.2, 4.7 Hz, 1 H), 3.40 (s, 3 H), 2.71 (dd, *J* =13.8, 8.5 Hz, 1 H), 2.55 (dd, *J* = 13.8, 6.2 Hz, 1 H), 1.52 (s, 3 H), 1.48 (s, 3 H); ¹³C NMR(150 MHz, CDCl₃) δ 190.8, 178.9, 161.3, 143.4, 136.3, 135.8, 129.1, 128.5, 127.4, 123.2,

122.5, 121.6, 121.4, 117.4, 116.3, 109.5, 71.9, 68.0, 56.2, 52.0, 51.7, 34.6, 25.9, 18.0;

HRMS (ESI-TOF) calcd. for C₂₄H₂₅NO₄Na [M + Na]⁺ 414.1676, found 414.1677.**1-methoxymethyl-3-prenyloxindole – 4-chromanone adduct (5, upper****diastereomer):** Procedure A (using Fe(*t*-butylCOCHCF₃)₃ instead ofFe(acac)₃, 0.06 mmol scale); yield = 83% (*dr* = 1.0:1); colorless oil; R_f = 0.36 (silica gel, 1:1 hexanes:Et₂O); [α]_D = + 120 (CHCl₃, *c* =0.31); IR (film) ν_{\max} 1721, 1607, 1480, 1466, 1350, 1088, 756 cm⁻¹; ¹H NMR (600 MHz,CDCl₃) δ 7.24 (t, *J* = 7.8 Hz, 1 H), 6.98 – 7.02 (m, 3 H), 6.75 (d, *J* = 5.8 Hz, 1 H), 5.12(d, *J* = 10.9 Hz, 1 H), 5.00 (d, *J* = 10.9 Hz, 1 H), 4.62 (bs, 1 H), 4.42 (bs, 1 H), 4.24 (bs, 1H), 3.39 (s, 3 H), 3.33 (dd, *J* = 13.5, 1.6 Hz, 1 H), 3.11 (bs, 1 H), 2.49 – 2.55 (m, 1 H),2.28 (dt, *J* = 18.6, 4.6 Hz, 1 H), 1.79 (s, 3 H), 1.67 (s, 3 H); ¹³C NMR (150 MHz, CDCl₃)

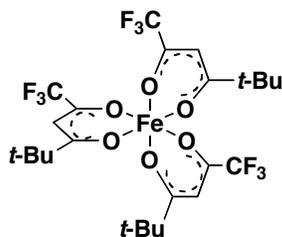
δ 198.3, 178.2, 144.4, 144.0, 143.2, 134.9, 127.7, 123.2, 122.2, 114.8, 109.3, 71.7, 56.4, 51.0, 46.4, 44.1, 31.5, 18.5, 16.1 (1 carbon missing); HRMS (ESI-TOF) calcd. for $C_{20}H_{23}NO_3Na$ $[M + Na]^+$ 348.1570, found 348.1565.



1-methoxymethylindole – 4-chromanone adduct (5, lower diastereomer): Procedure A (using $Fe(t\text{-butylCOCHCF}_3)_3$ instead of

$Fe(acac)_3$, 0.06 mmol scale); yield = 83% ($dr = 1.0:1$); colorless needles; m.p. = 115 – 118 °C; $R_f = 0.30$ (silica gel, 1:1

hexanes: Et_2O); $[\alpha]_D = -237$ ($CHCl_3$, $c = 0.31$); IR (film) ν_{max} 1717, 1670, 1540, 1488, 1351, 1090, 752 cm^{-1} ; 1H NMR (600 MHz, $CDCl_3$) δ 7.25 (t, $J = 7.7$ Hz, 1 H), 7.19 (d, $J = 7.4$ Hz, 1 H), 7.13 (d, $J = 7.8$ Hz, 1 H), 6.98 (t, $J = 7.5$ Hz, 1 H), 6.71 (d, $J = 5.9$ Hz, 1 H), 5.21 (s, 2 H), 5.11 (s, 1 H), 4.98 (s, 1 H), 3.53 (s, 1 H), 5.50 (dd, $J = 13.9, 2.7$ Hz, 1 H), 3.44 (s, 3 H), 3.29 (ddd, $J = 13.9, 11.3, 4.5$ Hz, 1 H), 2.56 – 2.63 (m, 1 H), 2.42 (dt, $J = 18.4, 5.0$ Hz, 1 H), 1.86 (s, 3 H), 1.62 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 178.3, 144.9, 143.7, 143.6, 135.3, 127.8, 127.1, 123.3, 122.3, 115.0, 109.5, 71.7, 56.4, 52.5, 47.5, 44.1, 31.7, 18.2, 15.7; HRMS (ESI-TOF) calcd. for $C_{20}H_{23}NO_3Na$ $[M + Na]^+$ 348.1570, found 348.1566.

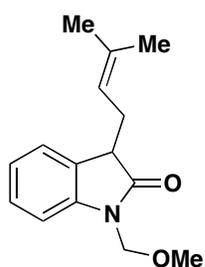


Tris(1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato)iron(III):

To a solution $FeCl_3 \cdot 6H_2O$ (1.3 g, 5 mmol, 1 equiv) in H_2O (9.7 mL, 0.5 M) was added a vigorously stirring solution of 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (2.9 g, 15 mmol, 3 equiv)

in methanol (37.5 mL, 0.4 M) *via* addition funnel over 15 min. A solution of sodium

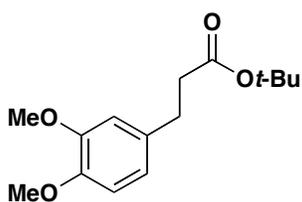
acetate (2.0 g, 24.6 mmol, 5.1 equiv) in H₂O (6.2 mL, 4.0 M) *via* addition funnel over 5 min. Upon completion of addition, the reaction was heated to 80 °C for 15 min. The reaction was cooled to ambient temperature (during which time the title compound began to crash of solution) and was then stirred at 4 °C for 12 hr. The red solid was filtered and collected furnishing 2.8 g (87%) of the title compound as a red solid, which was used in oxidative coupling reactions with no further purification. *Note: This is a representative procedure; all of the iron oxidants (excluding Fe(acac)₃) were made using this protocol.*



1-methoxymethyl-3-(3-methyl-2-butenyl)oxindole (Used in entries

15, 17): 1-methoxymethyloxindole (50 mg, 0.28 mmol) was dissolved in THF (941 μ L, 0.30 M) and cooled to -78 °C. After 5 min at -78 °C, *n*-butyl lithium (113 μ L from a 2.5 M solution in THF, 0.28 mmol, 1 equiv) was added dropwise by syringe. The solution was stirred 1 hr before 3,3-dimethylallyl bromide (63 μ L, 0.42 mmol, 1.5 equiv) was added dropwise by syringe. The solution was stirred for 1 hr at which time it was warmed to room temperature. After 10 min of stirring, the reaction was quenched with saturated aqueous NH₄Cl (2 mL). The solution was diluted with EtOAc (2 mL), the resulting mixture was poured into a separatory funnel, and the layers were separated. The aqueous portion was extracted twice with EtOAc (2 mL). The organic portions were combined, washed with brine (5 mL), dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (silica gel, 1:9 Et₂O:hexanes), furnishing 26 mg (38%) of the title compound as a colorless oil; R_f = 0.58 (silica gel, 1:1 hexanes:Et₂O); IR (film) ν_{\max} 1720, 1613, 1488, 1466, 1346, 1089, 1073 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ

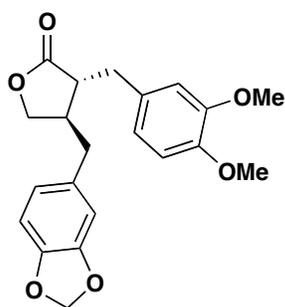
7.24 – 7.28 (m, 2 H), 7.05 (t, $J = 7.5$ Hz, 1 H), 7.00 (d, $J = 7.8$ Hz, 1 H), 5.16 (d, $J = 10.9$ Hz, 1 H), 5.07 (d, $J = 10.8$ Hz, 2 H), 3.54 (t, $J = 5.9$ Hz, 1 H), 3.29 (s, 3 H), 2.64 – 2.73 (m, 2 H), 1.64 (s, 3 H), 1.58 (s, 3 H); ^{13}C NMR (150 MHz, CDCl_3) δ 177.9, 142.4, 134.7, 128.3, 127.7, 123.9, 122.5, 119.2, 109.1, 70.9, 55.7, 45.7, 29.1, 25.6, 17.9; HRMS (ESI-TOF) calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 268.1308, found 268.1305.



tert-butyl 3,4-dimethoxydihydrocinnamate, 3: 3,4-

dimethoxydihydrocinnamic acid (5 g, 23.8 mmol) was dissolved in CH_2Cl_2 (23.8 mL, 1 M) and was cooled to 0 °C. After 5 min at 0 °C, oxalyl chloride (5.1 mL, 59.5 mmol, 2.5 equiv) was added dropwise by syringe. The clear solution immediately turned bright orange. DMF (4 drops) was added and, after 10 min at 0 °C, the reaction warmed to room temperature. After 2 hr of stirring, the volatiles were removed *in vacuo* and the resultant orange oil was dissolved in THF (10 mL, 2.4 M). This solution was added to a 0 °C solution of pyridine (1.94 mL, 23.8 mmol, 1 equiv) and *tert*-butanol (4.5 mL, 47.6 mL, 2 equiv) in THF (60 mL, 0.4 M) dropwise by syringe. Upon complete addition, the solution was allowed to warm to room temperature and was stirred for 24 hr. During this time the orange color slowly faded into a pale yellow color as a white precipitate (pyridinium–hydrochloride) crashed out of solution. After 24 hr of stirring, the reaction was quenched with 1 N HCl (50 mL). The solution was diluted with EtOAc (50 mL), the mixture was poured into a separatory funnel, and the layers were separated. The aqueous portion was extracted twice with EtOAc (25 mL). The organic portions were combined, washed with saturated aqueous NaHCO_3 (50 mL), then brine (50 mL), and were dried over anhydrous MgSO_4 , filtered,

and concentrated *in vacuo*. The resulting yellow oil was purified by flash chromatography (silica gel, 1:9 Et₂O:hexanes), furnishing 3.99 g (63%) of the title compound: colorless oil; R_f = 0.51 (silica gel, 1:1 hexanes:Et₂O); IR (film) ν_{max} 1725, 1516, 1366, 1260, 1238, 1145, 1029 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 6.78 (d, *J* = 8.6 Hz, 1 H), 6.73 – 6.79 (m, 2 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 2.85 (t, *J* = 7.8 Hz, 2 H), 2.52 (t, *J* = 7.8 Hz, 2 H), 1.42 (s, 9 H); ¹³C NMR (150 MHz, CDCl₃) δ 172.3, 148.8, 147.3, 133.4, 120.1, 111.6, 111.2, 80.3, 55.9, 55.8, 37.3, 30.7, 28.1 (3); HRMS (ESI-TOF) calcd. for C₁₅H₂₂NO₄Na [M + Na]⁺ 289.1410, found 289.1406.



(-)-bursehernin, 1: Procedure A was followed exactly for the oxidative coupling (1.8 mmol scale) of oxazolidinone **2** and *tert*-butyl ester **3**. The crude reaction was dissolved in THF (22 mL, 0.2 M). Methanol (327 μL, 9.2 mmol, 5.0 equiv) was added and the reaction was cooled to -78 °C. After 5 min at -78 °C, lithium borohydride (9.2 mL from a 2.0 M solution in THF, 18.4 mmol, 10 equiv) was added dropwise by syringe. After stirring for 5 min at -78 °C, the reaction was warmed to -10 °C for 1.5 hr, was quenched with saturated aqueous sodium potassium tartrate (30 mL), and then stirred at ambient temperature for 1 hr. The aqueous layer was partitioned with EtOAc (20 mL), separated, and then extracted twice with EtOAc (20 mL). The organic portions were combined, washed with brine (30 mL), dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The crude oil was dissolved in toluene (37 mL, 0.05 M). 1,8-diazabicyclo[5.4.0]undec-7-ene (2.77 mL, 18.4 mmol, 10 equiv) was added and the reaction was heated to 110 °C in a capped round-bottom flask for 24 hr. After

cooling to ambient temperature, the reaction was quenched with 5% aqueous citric acid (50 mL). The aqueous layer was partitioned with EtOAc (20 mL), separated, and then extracted twice with EtOAc (20 mL). The organic portions were combined, washed with brine (30 mL), dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (silica gel, 1:9 EtOAc:hexanes), furnishing 273 mg (41%) of (-)-bursehernin as a colorless oil. (-)-Bursehernin, **1**: R_f = 0.50 (silica gel, 1:1 hexanes:EtOAc); [α]_D = -13 (CHCl₃, c = 0.46); IR (film) ν_{max} 1767, 1516, 1490, 1443, 1241, 1145, 1028 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 6.78 (d, J = 8.1 Hz, 1 H), 6.66 – 6.68 (m, 3 H), 6.43 – 6.45 (m, 2 H), 5.92 (s, 1 H), 5.91 (s, 1 H), 4.11 (dd, J = 8.9, 7.0 Hz, 1 H), 3.85 (s, 3 H), 3.84 – 3.88 (m, 1 H), 3.83 (s, 3 H), 2.96 (dd, J = 14.0, 5.0 Hz, 1 H), 2.88 (dd, J = 14.1, 7.1 Hz, 1 H), 2.57 – 2.60 (m, 1 H), 2.53 – 2.56 (m, 1 H), 2.46 – 2.48 (m, 1 H), 2.44 – 2.46 (m, 1 H); ¹³C NMR (150 MHz, CDCl₃) δ 178.6, 149.0, 147.9, 147.9, 146.3, 131.6, 130.1, 121.5, 121.3, 112.1, 111.1, 108.7, 108.3, 101.0, 71.2, 55.8, 55.8, 46.5, 41.0, 38.3, 34.6; HRMS (ESI-TOF) calcd. for C₂₁H₂₂O₆Na [M + Na]⁺ 371.1489, found 371.1506.

There are conflicting literature values for the optical rotations of the natural product ((-)-**1**: -45,¹ -46,² -29;³ (+)-**1**: +36⁴). The observed optical rotations for synthetic **1** were consistently different than any of the reported values. This prompted us to employ chiral HPLC in order to *unambiguously* determine the enantiomeric excess of **1**. Procurement of racemic **1** (through synthesis with (*rac*)-**2**, Table S1/Figure S1: 40% 2-propanol/hexanes at 1 mL/min) and subsequent analysis of all samples using chiral HPLC facilitated understanding of our data with regards to the inconsistent literature reports. Our hypothesis is that there must be a small leakage to the β-epimer (α to the oxazolidinone)

in the oxidative coupling step. This would produce a third diastereomer (undetected in the crude ^1H NMR; diagnostic peaks are buried), which would ultimately lead to a small amount of the opposite enantiomer of the natural product (Table S1/Figure S2). This was confirmed by exhaustive purification of the desired set of oxidative coupling product diastereomers (PTLC: 1% EtOAc/DCM, 4 elutions) and subjection of the purified diastereomers to the remainder of the reaction conditions above yielding synthetic **1** in 99% *ee* (Table S1/Figure S3). This exact sample yielded an optical rotation of $[\alpha]_{\text{D}} = -15$ ($c = 0.2$) on our instrument. While this is not in agreement with what the literature reports, we are certain that our material is a single enantiomer. This experiment suggests that the issues of low *ee* and inconsistent optical rotation do not appear to be directly related. While the presence of ~5% of the undesired enantiomer should decrease the absolute value of the optical rotation, it should *not* lower it by ~50-75%. Through use of the synthetic scheme above, the natural product was obtained in 91% *ee*, and can be obtained in 99% *ee* if a purification step is added after the first synthetic operation. For further confirmation of structure, see Table S2 and Figure S4.

		<i>Retention Time (min)</i>	<i>Area Percent (%)</i>	<i>ee (%)</i>
Figure S1	(+)-bursehernin	16.98	47.37	5.26
	(-)-bursehernin	19.55	52.63	
Figure S2	(+)-bursehernin	16.85	95.59	91.18
	(-)-bursehernin	19.13	4.41	
Figure S3	(+)-bursehernin	16.5	0.59	98.82
	(-)-bursehernin	18.13	99.41	

Table S1: Chiral HPLC data for **1**.

Figure S1: Chiral HPLC trace of racemic **1**.

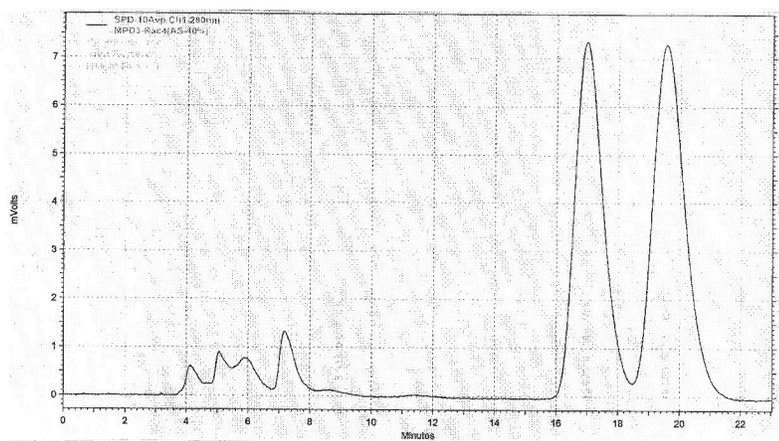


Figure S2: Chiral HPLC trace of **1** (procedure above).

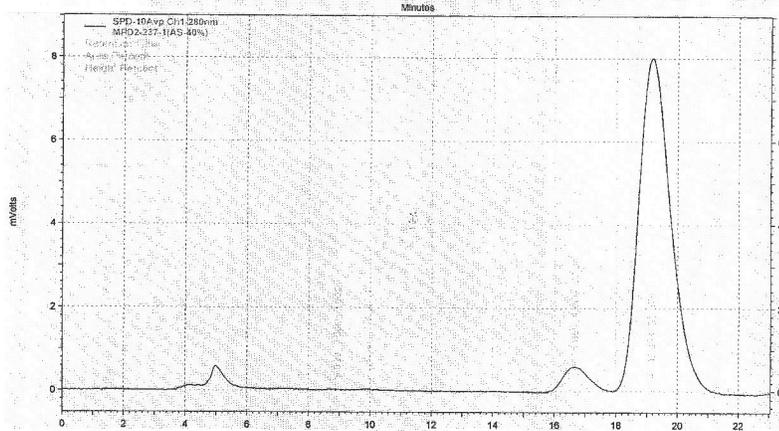
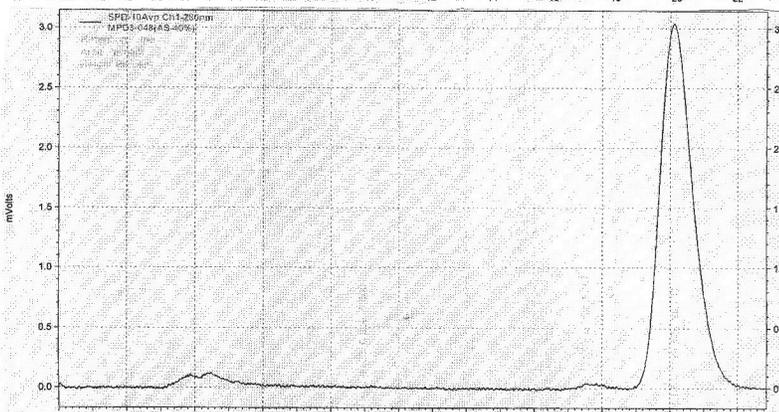
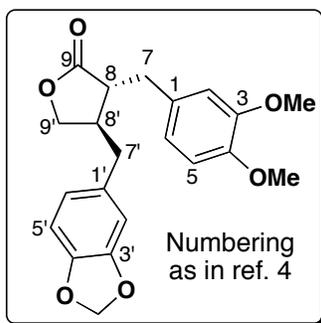


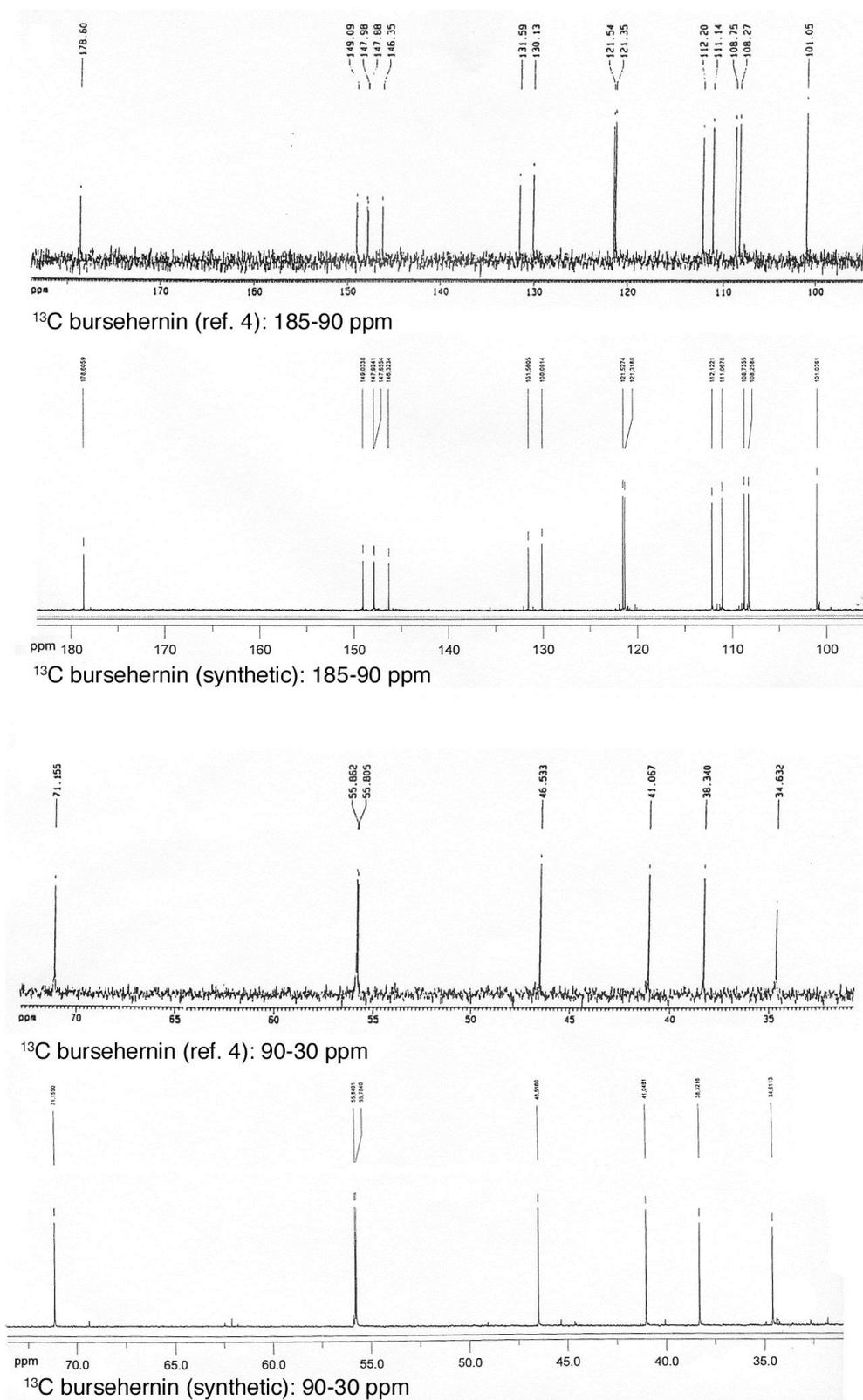
Figure S3: Chiral HPLC trace of **1** (with added purification step).





Carbon Position	Spectral Data: Chemical Shift (ppm)			
	¹ H (ref. 4)	¹ H (synthetic)	¹³ C (Ref 4)	¹³ C (synthetic)
1	–	–	130.1, <i>s</i>	130.1, <i>s</i>
2	6.64, <i>d</i> (1.8)	6.67, <i>m</i>	112.2, <i>d</i>	112.1, <i>d</i>
3	–	–	149.1, <i>s</i>	149.0, <i>s</i>
4	–	–	147.9, <i>s</i>	147.9, <i>s</i>
5	6.77, <i>d</i> (8.0)	6.78, <i>d</i> (8.1)	111.1, <i>d</i>	111.1, <i>d</i>
6	6.66, <i>dd</i> (8.0, 1.8)	6.67, <i>m</i>	121.4, <i>d</i>	121.3, <i>d</i>
7	2.87, <i>dd</i> (14.1, 6.9)	2.88, <i>dd</i> (14.1, 7.1)	34.6, <i>t</i>	34.6, <i>t</i>
	2.94, <i>dd</i> (14.1, 5.1)	2.96, <i>dd</i> (14.0, 5.0)	–	–
8	2.53, <i>dd</i> (13.1, 7.9)	2.56, <i>m</i>	46.5, <i>d</i>	46.5, <i>d</i>
9	–	–	178.6, <i>s</i>	178.6, <i>s</i>
1'	–	–	131.6, <i>s</i>	131.6, <i>s</i>
2'	6.41, <i>d</i> (1.5)	6.44, <i>m</i>	108.3, <i>d</i>	108.3, <i>d</i>
3'	–	–	148.0, <i>s</i>	147.9, <i>s</i>
4'	–	–	146.4, <i>s</i>	146.3, <i>s</i>
5'	6.66, <i>d</i> (7.8)	6.67, <i>m</i>	108.8, <i>d</i>	108.7, <i>d</i>
6'	6.43, <i>dd</i> (7.8, 1.5)	6.44, <i>m</i>	121.5, <i>d</i>	121.5, <i>d</i>
7'	2.44, <i>m</i>	2.45, <i>m</i>	38.3, <i>t</i>	38.3, <i>t</i>
	2.57, <i>dd</i> (17.0, 9.8)	2.58, <i>m</i>	–	–
8'	2.46, <i>m</i>	2.47, <i>m</i>	41.1, <i>d</i>	41.0, <i>d</i>
9'	3.83, <i>m</i>	3.84–3.88, <i>m</i>	71.2, <i>t</i>	71.2, <i>t</i>
	4.09, <i>dd</i> (9.2, 7.0)	4.11, <i>dd</i> (8.9, 7.0)	–	–
3-OMe	3.81, <i>s</i>	3.83, <i>s</i>	55.8, <i>q</i>	55.8, <i>q</i>
4-OMe	3.84, <i>s</i>	3.85, <i>s</i>	55.9, <i>q</i>	55.8, <i>q</i>
3',4'-OCH₂O	5.90, <i>br s</i>	5.91, <i>br s</i>	101.1, <i>t</i>	101.0, <i>t</i>
	5.91, <i>br s</i>	5.92, <i>br s</i>	–	–

Table S2: Proton and carbon NMR spectral data comparison.

**Figure S4:** Spectral comparison for **1**.

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