

Electronic Supplementary Information for

Diastereoselective route to 2,5-diaryl-3,4-disubstituted tetrahydrofuran lignans: Protection free synthesis of (+)-galbelgin and (+)-galbacin

Sunit Hazra and Saumen Hajra^{*}

Department of Chemistry, IIT Kharagpur, Kharagpur-721302, India

E-mail: shajra@chem.iitkgpnet.in

Content	Page No
General information	2
Experimental procedure and spectral data	2-9
Reference	10
Spectra of compounds	10-29

General Information

All the reactions were carried out using oven dried glassware under an atmosphere of Argon (Ar). All reagents were used as purchased from commercial supplier without further purification. Solvents were dried and distilled following usual protocols. Flash column chromatography was performed in all cases using the indicated solvent system on Rankem silica gel (230-400 mesh) purchased from Rankem India. Analytical thin layer chromatography was performed using Merk 60 F254 precoated silica gel plate (0.2 mm thickness) and compounds were visualized by irradiation of UV light. The ^1H NMR and ^{13}C NMR spectra were measured with 200 MHz in CDCl_3 . ^1H NMR chemical shifts are expressed in parts per million (δ) downfield to CHCl_3 ($\delta = 7.26$); ^{13}C NMR chemical shifts are expressed in parts per million (δ) relative to the central CDCl_3 resonance ($\delta = 77.0$). Coupling constants in ^1H NMR are expressed in Hz. Melting points (mp) of solid compounds are reported without correction. HRMS (ESI) spectra were recorded on a Q-ToF analyzer.

Experimental section:

(*R*)-methyl 4-(4-isopropyl-2-oxooxazolidin-3-yl)-4-oxobutanoate (8)

Title compound was prepared according to the literature procedure^{7a} from *D*-valine derived oxazolidinone in 80% yield as colourless gummy liquid. $[\alpha]_{\text{D}}^{28} -65.2$ (c 2.0, CHCl_3). ^1H NMR (200 MHz, CDCl_3) δ : 0.86 (d, $J = 4.6$ Hz, 3H), 0.90 (d, $J = 4.6$ Hz, 3H), 2.25–2.50 (m, 1H), 2.65 (t, $J = 5.8$ Hz, 2H), 3.23 (t, $J = 5.8$ Hz, 2H), 3.68 (s, 3H), 4.20 (dd, $J = 7.9, 3.4$ Hz, 1H), 4.28 (t, $J = 7.9$ Hz, 1H), 4.35–4.50 (m, 1H) ^{13}C NMR (50 MHz, CDCl_3) δ : 14.4., 17.6, 27.9, 28.2, 30.5, 51.5, 58.2, 63.4, 153.9, 171.6, 172.6.

3-[2-(3,4-Dimethoxy-phenyl)-5-oxo-tetrahydro-furan-3-carbonyl]-4-isopropyl-oxazolidin-2-one (7a)¹; Dibutylboron triflate mediated syn-aldol reaction and lactonization:

To a well-stirred solution of *N*-succinyl oxazolidinone **8** (0.972 g, 4.0 mmol) in dry DCM (30 mL) was dropwise added 4.4 mL of Bu₂BOTf [(1.0 M) solution in DCM, 4.4 mmol] at –78 °C under argon atmosphere and the solution allowed to stir for 30 min. To this solution was added *i*-Pr₂NEt (0.84 mL, 4.8 mmol) and allowed to stir for 45 min. at –78 °C. A solution of veratraldehyde (0.93 g, 1.4 equiv., 5.6 mmol) in 5 mL of DCM was drop wise added to the reaction mixture at –78 °C. After stirring the reaction at this temperature for 2 h, and then was gradually raised to -10 °C. The reaction was monitored by TLC and on completion; quenched with aqueous NH₄Cl, extracted with DCM (2 x 50 mL), washed with brine, dried over Na₂SO₄ and concentrated. The resultant residue was purified immediately by flash chromatography to obtain 1.39 g of lactone **7a** (92%) as a white solid. Mp 123-125 °C; MF: C₁₉H₂₃NO₇. MW: 377.38. $[\alpha]_D^{29}$ –154.04 (c 0.62, CH₃COCH₃). ¹H NMR (200 MHz, CDCl₃) δ: 0.88 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 2.30-2.43 (m, 1H), 2.72 (dd, *J* = 17.2, 9.4 Hz, 1H), 3.24 (dd, *J* = 17.2, 8.9 Hz, 1H), 3.87 (s, 3H), 3.89 (s, 3H), 4.24–4.32 (m, 2H), 4.39-4.51 (m, 2H), 5.83 (d, *J* = 7.6 Hz, 1H), 6.81-6.95 (m, 3H). ¹³C NMR (50 MHz, CDCl₃) δ: 14.9, 18.1, 28.5, 33.7, 48.5, 56.2, 56.2, 58.8, 64.0, 81.8, 109.3, 111.3, 118.9, 129.9, 149.6, 149.8, 153.6, 170.3, 173.8.

(*R*)-3-((2*R*,3*R*)-2-(benzo[d][1,3]dioxol-5-yl)-5-oxotetrahydrofuran-3-carbonyl)-4-

isopropyloxazolidin-2-one (7b): 1.27 g of lactone **7b** (88%) obtained as a gummy liquid from 0.972 g of compound **8** using the procedure as of lactone **7a**. MF: C₁₈H₁₉NO₇. MW: 361.35. $[\alpha]_D^{27}$ –160.35 (c 0.69, CHCl₃). ¹H NMR (CDCl₃, 200 MHz) δ: 0.84 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 2.25-2.41 (m, 1H), 2.66 (dd, *J* = 9.4, 17.2 Hz, 1H) 3.20 (dd, *J* =

9.0, 17.4 Hz, 1H), 4.16-4.29 (m, 2H), 4.34- 4.45 (m, 1H), 5.77 (d, J = 7.4 Hz, 1H), 5.92 (s, 2H), 6.75(s, 1H), 6.79 (s, 1H), 6.82 (d, J = 1.4 Hz, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 14.8, 17.9, 28.4, 33.5, 48.4, 58.6, 64.0, 81.5, 101.5, 106.5, 108.4, 112.0, 131.3, 148.2 (2C), 153.5, 170.1, 173.7. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{19}\text{NNaO}_7$ $[\text{M} + \text{Na}]^+$ 361.1162; found 361.1165

(4*S*,5*R*)-5-(3,4-dimethoxyphenyl)-4-(hydroxymethyl)dihydrofuran-2(3*H*)-one (5a)

To a well stirred solution of lactone **7a** (1.0 g, 2.65 mmol) in THF-MeOH (9:1, 11 mL; 4 mL/mmol) at 0 °C was added NaBH_4 (0.1 g, 1.0 equiv., 2.65 mmol) portion wise. After stirring the reaction at 0 °C for 3 h, reaction was quenched with aq. NH_4Cl solution, solvent was evaporated at room temperature and residue was diluted with EtOAc. Organic layer was separated; aqueous layer was extracted with EtOAc (3 times), washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography and gave 0.625 g of lactone alcohol **5a** as a gummy liquid (93%). MF: $\text{C}_{13}\text{H}_{16}\text{O}_5$, MW: 252.26. $[\alpha]_D^{29}$ -8.04 (c 1.0, CHCl_3). ^1H NMR (CDCl_3 , 200 MHz) δ : 2.47-2.76 (m, 3H), 3.73 (d, J = 5.2 Hz, 2H), 3.86 (s, 6H), 5.30 (d, J = 6.0 Hz, 1H), 6.85 (s, 3H). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 31.7, 46.2, 56.1 (2C), 61.3, 83.3, 109.0, 111.2, 118.6, 131.0, 149.4 (2C), 176.9. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{16}\text{NaO}_5$ $[\text{M} + \text{Na}]^+$ 275.0895; found 275.0895.

(4*S*,5*R*)-5-(benzo[*d*][1,3]dioxol-5-yl)-4-(hydroxymethyl)dihydrofuran-2(3*H*)-one (5b)

Lactone alcohol **5b** (0.59 g) was synthesized from lactone **7b** (1.0 g) according to the procedure compound **5a** in 90 % yield as gummy liquid. MF: $\text{C}_{12}\text{H}_{12}\text{O}_5$, MW: 236.22. $[\alpha]_D^{29}$ -4.41(c 0.78, CHCl_3). ^1H NMR (CDCl_3 , 200 MHz) δ : 2.04 (bs, 1H), 2.55-2.77 (m, 3H), 3.75 (d, J = 4.2 Hz, 2H), 5.29 (d, J = 6.0 Hz, 1H), 5.98 (s, 2H), 6.80 (s, 2H), 6.82 (s, 1H). ^{13}C NMR (CDCl_3 , 50 MHz) δ : 31.6, 46.2, 61.2, 83.3, 101.5, 106.4, 108.4, 119.8, 132.4, 148.0, 148.3, 177.1. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{O}_5$ $[\text{M} + \text{H}]^+$ 237.0763; found 237.0767.

(3*R*,4*S*,5*R*)-5-(3,4-dimethoxyphenyl)-4-(hydroxymethyl)-3-methyldihydrofuran-2(3*H*)-one (12a)

To a cold (−30 °C) solution of LDA (4.2 mmol, 2.1 equiv.) [LDA was prepared by reaction of *n*-BuLi (1.8 mL, 2.5 M in hexane) and diisopropylamine (0.6 mL, 4.2 mmol) in THF (12 mL) at 0 °C for 30 min, then temperature was decreased to −30 °C] in THF (12 mL) under argon atmosphere, lactone alcohol **5a** (0.504 g, 2.0 mmol, 1.0 equiv.) in THF (4 mL) was added drop wise. After stirring at that temperature for 1 h, a solution MeI (0.13 mL, 2.0 mmol, 1.0 equiv.) in THF (4 mL) was added drop wise. The reaction mixture was stirred at this temperature for 2 h, then quenched with saturated aqueous NH₄Cl and extracted with EtOAc, washed with brine, dried over Na₂SO₄, and concentrated. The crude product was purified by flash chromatography and afforded 0.335 g of C-methyl lactone **12a** (63%) along with 0.15 g recovery of **5a** (30%). MF of compound **12a**: C₁₄H₁₈O₅. MW: 266.19. [α]^{30.7}_D +8.3 (c 1.0, CHCl₃). ¹H NMR (CDCl₃, 200 MHz) δ : 1.25 (d, 3H, *J* = 7.0 Hz), 2.04-2.21 (m, 1H), 2.42 (bs, 1H), 2.78-2.95 (m, 1H), 3.68-3.82 (m, 2H), 3.86 (s, 6H), 5.22 (d, 1H, *J* = 9.6 Hz), 6.77-6.96 (m, 3H). ¹³C NMR (CDCl₃, 50 MHz) δ : 13.7, 37.4, 54.3, 55.9, 56.0, 58.7, 81.0, 109.2, 111.1, 119.1, 130.3, 149.3, 149.5, 179.1. HRMS (ESI) calcd for C₁₄H₁₈NaO₅ [*M* + Na]⁺ 289.1052; found 289.1054.

(3*R*,4*S*,5*R*)-5-(benzo[*d*][1,3]dioxol-5-yl)-4-(hydroxymethyl)-3-methyldihydrofuran-2(3*H*)-one (12b)

Lactone **12b** (0.305 g) was synthesized from **5b** (0.472 g) according to the procedure of compound **12a** in 61% yield along with 30% recovery of **5b**. MF: C₁₃H₁₄O₅. MW: 250.25. [α]²⁷_D +12.3 (c 0.88, CHCl₃). ¹H NMR (CDCl₃, 200 MHz) δ : 1.32 (d, *J* = 7.0 Hz, 1H), 1.86 (bs), 2.12-2.26 (m, 1H), 2.79-2.95 (m, 1H), 3.44-3.60 (m, 2H), 5.14 (d, *J* = 9.4 Hz, 1H), 5.99 (s, 2H), 6.81-6.84 (3 Ar-*H*). ¹³C NMR (CDCl₃, 50 MHz) δ : 13.9, 37.5, 54.6, 59.0, 81.1,

101.5, 106.8, 108.5, 120.5, 132.0, 148.3, 148.4, 178.9. HRMS (ESI) calcd for C₁₃H₁₅O₅ [M + H]⁺ 251.0920; found 251.0921.

(3*R*,4*R*,5*R*)-4-(bromomethyl)-5-(3,4-dimethoxyphenyl)-3-methyldihydrofuran-2(3*H*)-one (13a)

To a stirred solution of lactone alcohol **12a** (0.532 g, 2.0 mmol, 1.0 equiv.) in CH₂Cl₂ (10 mL) was added PPh₃ (0.577 g, 2.2 mmol, 1.2 equiv.) and NBS (0.196 g, 2.1 mmol, 1.1 equiv.) under argon at room temperature. After completion of reaction, solvent was evaporated and residue was purified by flash chromatography and gave bromomethyl lactone **13a** (0.605 g, 92%) as a gummy liquid. MF: C₁₄H₁₇BrO₄. MW: 329.03. [α]_D²⁹ −40.2 (c 0.53, CHCl₃). ¹H NMR (CDCl₃, 200 MHz) δ: 1.29 (d, *J* = 7.0 Hz, 3H), 2.12-2.26 (m, 1H), 2.80-2.89 (m, 1H), 3.41-3.57 (m, 2H), 3.85 (s, 6H), 5.14 (d, *J* = 9.4 Hz, 1H), 6.83-6.84 (3 Ar-*H*). ¹³C NMR (CDCl₃, 50 MHz) δ: 13.2, 30.9, 39.1, 53.0, 56.0, 56.1, 81.9, 108.8, 111.1, 119.0, 129.0, 149.5, 149.7, 177.5. HRMS (ESI) calcd for C₁₄H₁₇BrNaO₅ [M + Na]⁺ 351.0208; found 351.0211

(3*R*,4*R*,5*R*)-5-(benzo[*d*][1,3]dioxol-5-yl)-4-(bromomethyl)-3-methyldihydrofuran-2(3*H*)-one (13b)

Bromomethyl lactone **13b** (0.578 g) was synthesized from **12b** (0.50 g) using same procedure as of compound **13a** in 92% yield as a gummy liquid. MF: C₁₃H₁₃BrO₄, MW: 314.0. [α]_D^{30.7} −32.4 (c 0.7, CHCl₃). ¹H NMR (CDCl₃, 200 MHz) δ: 1.32 (dd, *J* = 7.0, 5.0 Hz, 3H), 2.12-2.26 (m, 1H), 2.77-2.94 (m, 1H), 3.44-3.59 (m, 2H), 5.13 (d, *J* = 9.4 Hz, 1H), 5.98 (s, 2H), 6.81 (s, 3H). ¹³C NMR (CDCl₃, 50 MHz) δ: 13.3, 30.8, 39.1, 53.1, 81.8, 101.4, 106.3, 108.4, 120.3, 130.5, 148.3 (2C), 177.3. HRMS (ESI) calcd for C₁₃H₁₄BrO₄ [M + H]⁺ 313.0075; found 313.0079.

(3*R*,4*R*,5*R*)-5-(3,4-dimethoxyphenyl)-3,4-dimethyldihydrofuran-2(3*H*)-one (6a)

NaCNBH₃ (0.38 g, 6.0 mmol, 4.0 equiv.) was added to a solution of substrate **13a** (0.493 g, 1.5 mmol, 1.0 equiv.) in HMPA (7.0 mL) under argon and stirred at 70 °C for 12 h. On completion of reaction, the reaction mixture diluted with water, extracted with ether, washed with brine, dried (Na₂SO₄) and concentrated. The crude product was purified by flash chromatography to give 3,4-dimethyl lactone **6a** (0.337 g) in 90% of yield as a gummy liquid. MF: C₁₄H₁₈O₄. MW: 250.29. [α]^{30.7}_D +15.5 (c 0.76, CHCl₃). ¹H NMR (CDCl₃, 200 MHz) δ : 1.13 (d, *J* = 6.6 Hz, 3H), 1.31 (d, *J* = 7.0 Hz, 3H), 1.90-2.10 (m, 1H), 2.28-2.44 (m, 1H), 3.89 (s, 3H), 3.90 (s, 3H), 4.77 (d, *J* = 10.0 Hz, 1H), 6.86-6.87 (3 Ar-*H*). ¹³C NMR (CDCl₃, 50 MHz) δ : 12.9, 14.2, 43.3, 47.6, 55.9, 55.9, 86.3, 109.2, 110.9, 119.2, 129.7, 149.2, 149.4, 178.6. HRMS (ESI) calcd for C₁₄H₁₉O₄ [M + H]⁺ 251.1283; found 251.1281.

(3*R*,4*R*,5*R*)-5-(benzo[d][1,3]dioxol-5-yl)-3,4-dimethyldihydrofuran-2(3*H*)-one (6b)

3,4-Dimethyl lactone **6b** (0.316 g) was synthesized from **13b** (0.471 g) according to the procedure of compound **6a** in 90% yield as a gummy liquid. MF: C₁₃H₁₄O₄. MW: 234.25. [α]²⁹_D +16.5 (c 0.53, CHCl₃). ¹H NMR (CDCl₃, 200 MHz) δ : 1.06 (d, *J* = 6.4 Hz, 3H), 1.23 (d, *J* = 7.0 Hz, 3H), 1.81-2.01 (m, 1H), 2.21-2.37 (m, 1H), 4.67 (d, *J* = 9.8 Hz, 1H), 5.91 (s, 2H), 6.74 (s, 2H), 6.78 (d, *J* = 1.2 Hz, 1H). ¹³C NMR (CDCl₃, 50 MHz) δ : 13.1, 14.4, 43.5, 47.9, 86.4, 101.5, 106.7, 108.3, 120.6, 131.3, 148.2, 148.3, 178.5. HRMS (ESI) calcd for C₁₃H₁₅O₄ [M + H]⁺ 235.0970; found 235.0975.

(2*R*,3*R*,4*R*)-2-(3,4-dimethoxyphenyl)-5-methoxy-3,4-dimethyltetrahydrofuran (14a)

To a solution of lactone **6a** (0.125 g, 0.5 mmol, 1.0 equiv.) in CH₂Cl₂ (10 mL) was added dropwise DIBAL-H (1.0 mL, 1.0 M solution in toluene, 2.0 equiv.) at -78 °C. After being stirred for 1 h, the reaction mixture was quenched with MeOH and allowed to warm to room

temperature. To this mixture, MeOH (4 mL), trimethyl orthoacetate (0.6 mL, 8.0 mmol, 8.0 equiv.), and PTSA (0.043g, 0.25 mmol, 0.5 equiv.) were added. The resulting mixture was stirred for 12 h at rt, quenched with aqueous NaHCO₃, diluted with EtOAc. It was extracted with EtOAc (3 times), washed with brine, dried over anhydrous Na₂SO₄ and concentrated. The crude product was purified by flash chromatography and yielded methyl acetal **14a** (0.125 g, 95%) as a gummy liquid in 1:1 mixture of diastereomers MF: C₁₅H₂₂O₄, MW: 266.33. ¹H NMR (CDCl₃, 200 MHz): δ 0.94 (d, *J* = 6.6 Hz, 6H), 1.02 (d, *J* = 6.2 Hz, 3H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.50-1.64 (m, 2H), 1.76-1.89 (m, 2H), 3.42 (s, 3H), 3.47 (s, 3H), 3.85 (s, 6H), 3.88 (s, 6H), 4.38 (d, *J* = 8.8 Hz, 1H), 4.46 (d, *J* = 9.8 Hz, 1H), 4.77 (d, *J* = 4.0 Hz, 1H), 4.83 (d, *J* = 3.6 Hz, 1H), 6.83 (m, 4H), 6.89 (s, 1H), 6.95 (s, 1H). ¹³C NMR (CDCl₃, 50 MHz): δ 11.2, 14.2, 14.3, 16.2, 46.5, 46.7, 48.9, 50.1, 55.2, 55.9, 56.1 (2C), 86.7, 89.7, 106.7, 109.8, 110.1, 110.8, 111.2, 111.6, 119.5, 133.0, 135.2, 148.7, 149.0, 149.3 (2C). HRMS (ESI) calcd for C₁₅H₂₂NaO₄ [M + Na]⁺ 289.1416; found 289.1419

5-((2*R*,3*R*,4*R*)-5-methoxy-3,4-dimethyltetrahydrofuran-2-yl)benzo[*d*][1,3]dioxole (14b)

Methyl acetal **14b** (0.119 g) was prepared from dimethyl lactone **6b** (0.117 g) in 95% yield as a gummy liquid in 1:1 mixture of diastereomers according to the above procedure of compound **14a**. MF: C₁₄H₁₈O₄. MW: 250.29. ¹H NMR (CDCl₃, 200 MHz) δ: 0.94 (d, *J* = 6.4 Hz, 6H), 1.02 (d, *J* = 6.2 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.52-1.64 (m, 1H), 1.75-1.89 (m, 3H), 3.42 (s, 3H), 3.46 (s, 3H), 4.35 (d, *J* = 9.0 Hz, 1H), 4.44 (d, *J* = 9.6 Hz, 1H), 4.76 (d, *J* = 4.2 Hz, 1H), 4.82 (d, *J* = 4.2 Hz, 1H), 5.92 (s, 4H), 6.76 (m, 4H), 6.88 (s, 2H). ¹³C NMR (CDCl₃, 50 MHz) δ: 11.2, 14.1 (2C), 16.1, 46.4, 46.8, 48.8, 50.2, 55.3, 56.0, 86.7, 89.6, 101.1, 101.1, 106.6, 107.0, 107.4, 107.9, 108.1, 111.5, 120.5, 120.6, 134.5, 136.5, 147.2, 147.4, 148.0 (2C). HRMS (ESI) calcd for C₁₄H₁₈NaO₄ [M + Na]⁺ 273.1103; found 273.1108.

**(2*R*,3*R*,4*R*,5*R*)-2,5-bis(3,4-dimethoxyphenyl)-3,4-dimethyltetrahydrofuran, (+)galbelgin
(1)**

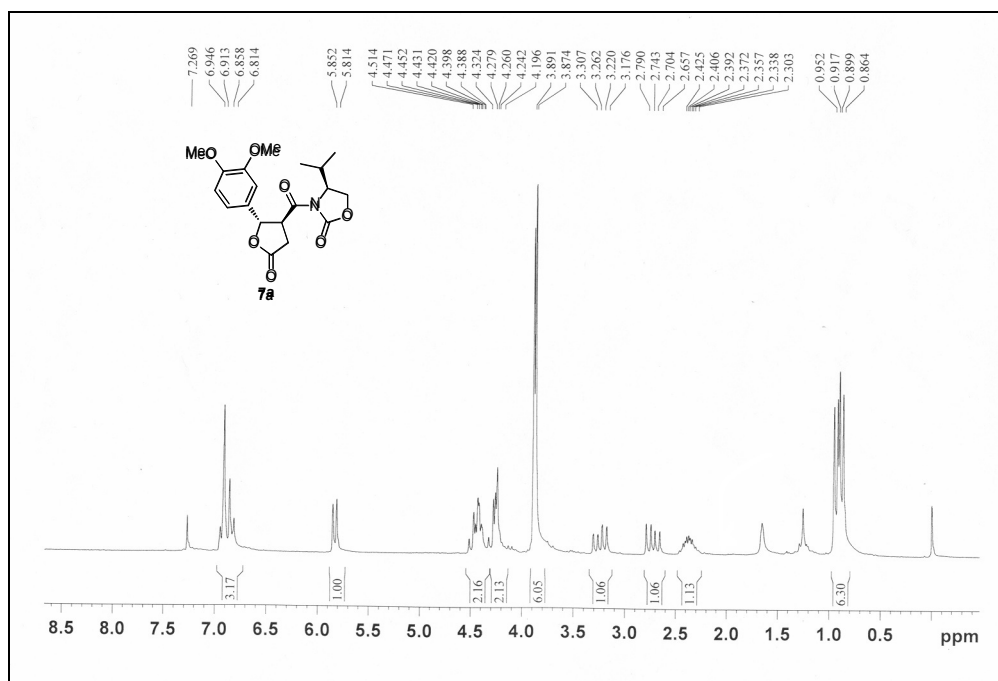
To a stirred solution of methyl acetal **14a** (0.04 g, 0.15 mmol, 1.0 equiv.) and 1,2-dimethoxybenzene (0.105 g, 0.75 mmol, 5.0 equiv.) in CH₂Cl₂ (3.0 mL) was added drop wise BF₃·OEt₂ (0.9 mL, 1.0 M in CH₂Cl₂, 6 equiv.) at –78 °C and stirred for 2 h. Then temperature was raised to –20 °C and stirred for 10 h. The reaction mixture was quenched with aqueous NaHCO₃, extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. The residue was purified by flash chromatography and afforded the desired (+)-galbelgin **1** (0.051 g) in 92% yield. MF: C₂₂H₂₈O₅. MW: 372.45. {[α]_D²⁸ = +80 (c 0.5, CHCl₃), lit.² [α]_D²⁸ = +80.7 (c 0.55, CHCl₃), lit.³ [α]_D²⁸ = +83.4 (c 0.47, CHCl₃)}. ¹H NMR (CDCl₃, 200 MHz) δ: 1.05 (d, *J* = 5.4 Hz, 6H), 1.77-1.82 (m, 2H), 3.88 (s, 6H), 3.91 (s, 6H), 4.66 (d, *J* = 9.0 Hz, 2H), 6.82-6.96 (6 Ar-*H*). ¹³C NMR (CDCl₃, 50 MHz) δ: 14.1 (2C), 51.2 (2C), 56.1 (4C), 88.5 (2C), 109.4 (2C), 111.1 (2C), 118.8 (2C), 135.2 (2C), 148.7 (2C), 149.3 (2C).

5,5'-((2*R*,3*R*,4*R*,5*R*)-3,4-dimethyltetrahydrofuran-2,5-diyl)dibenzo[*d*][1,3]dioxole, (+)-galbacin (2)

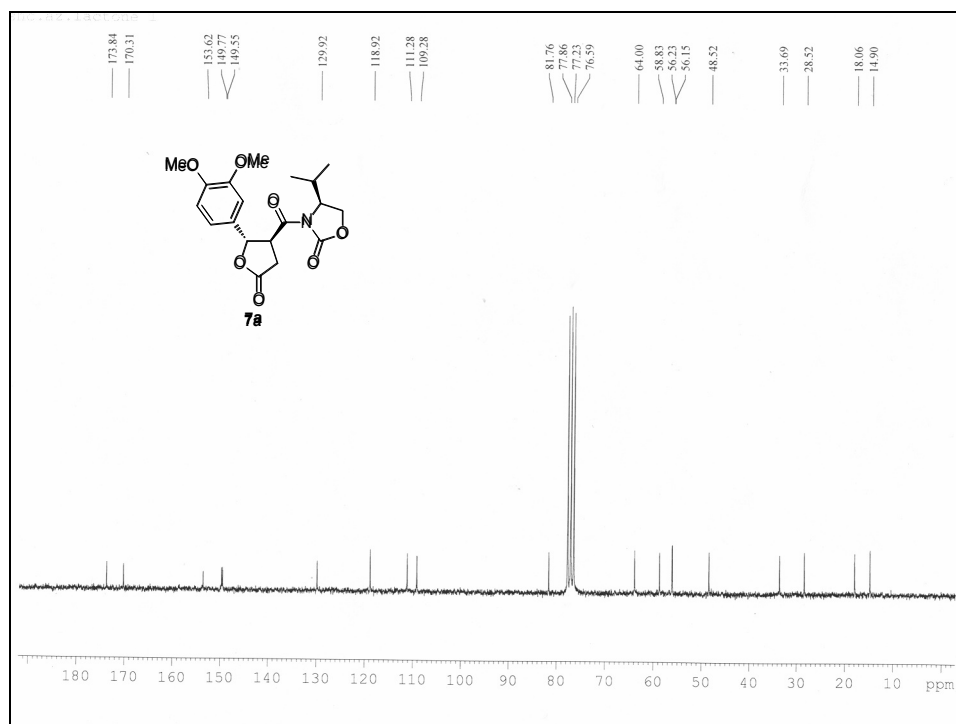
(+)-Galbacin **2** (0.052g) was synthesized from methyl acetal **14b** (0.04 g) and methylenedioxybenzene according to the above procedure in 95% yield MF: C₂₀H₂₀O₅. MW: 340.37. {[α]_D²⁸ = +110 (c 1.0, CHCl₃), lit.⁴ [α]_D²⁸ = +117 (CHCl₃)}. ¹H NMR (CDCl₃, 200 MHz) δ: 1.03 (d, *J* = 6.0 Hz, 6H), 1.71-1.81 (m, 2H), 4.61 (d, *J* = 9.2 Hz, 2H), 5.95 (s, 4H), 6.77 (d, AB type, *J* = 7.8 Hz, 2H), 6.84 (dd, *J* = 8, 1.5 Hz, 2H), 6.93 (d, *J* = 1.5 Hz, 2H). ¹³C NMR (CDCl₃, 50 MHz) δ: 14.0 (2C), 51.2 (2C), 88.5 (2C), 101.1 (2C), 106.8 (2C), 108.1 (2C), 119.9 (2C), 136.5 (2C), 147.1 (2C), 148.0 (2C).

Reference

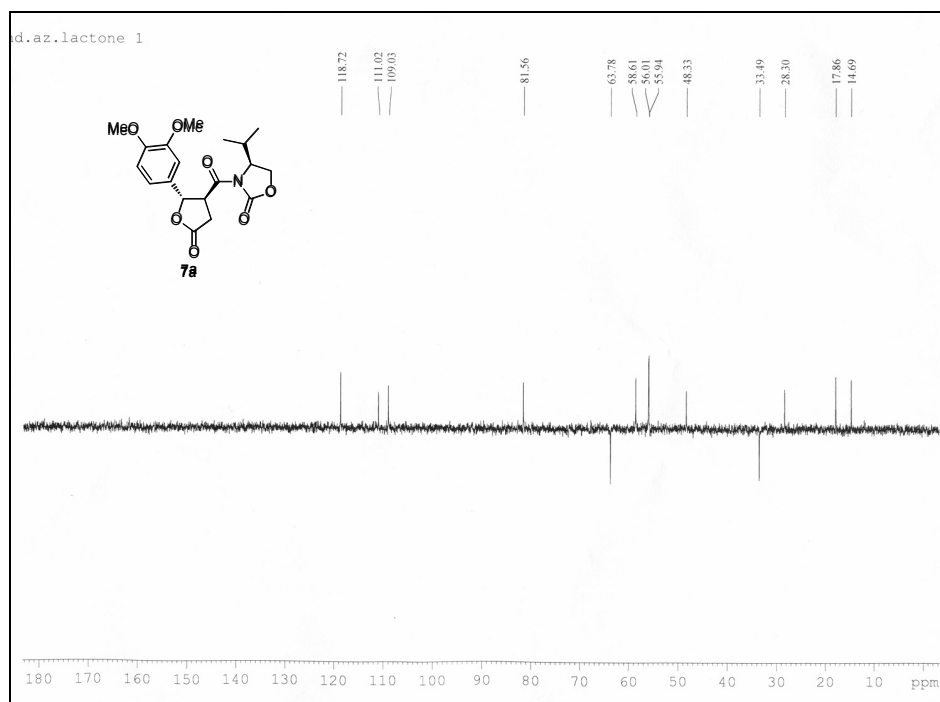
1. S. Hajra, A. K. Giri, A. Karmakar, S. Khatua, *Chem. Commun.* **2007**, 2408–2410.
2. H. Kim, C. M. Wooten, Y. Park, J. Hong, *Org. Lett.* **2007**, 9, 3965–3968.
3. S. Hanessian, G. J. Reddy, *Synlett* **2007**, 3, 475–479.
4. D. Takaoka, K. Watanabe, M. Hiroi, *Bull. Chem. Soc. Jpn.* **1976**, 49, 3564–3566.



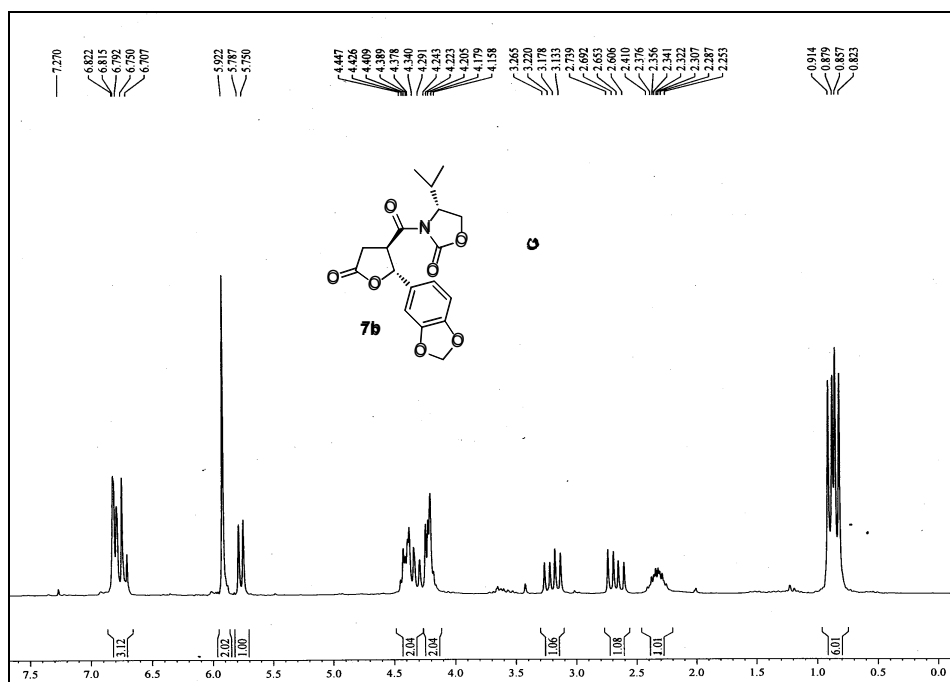
^1H NMR of **7a** (200 MHz)



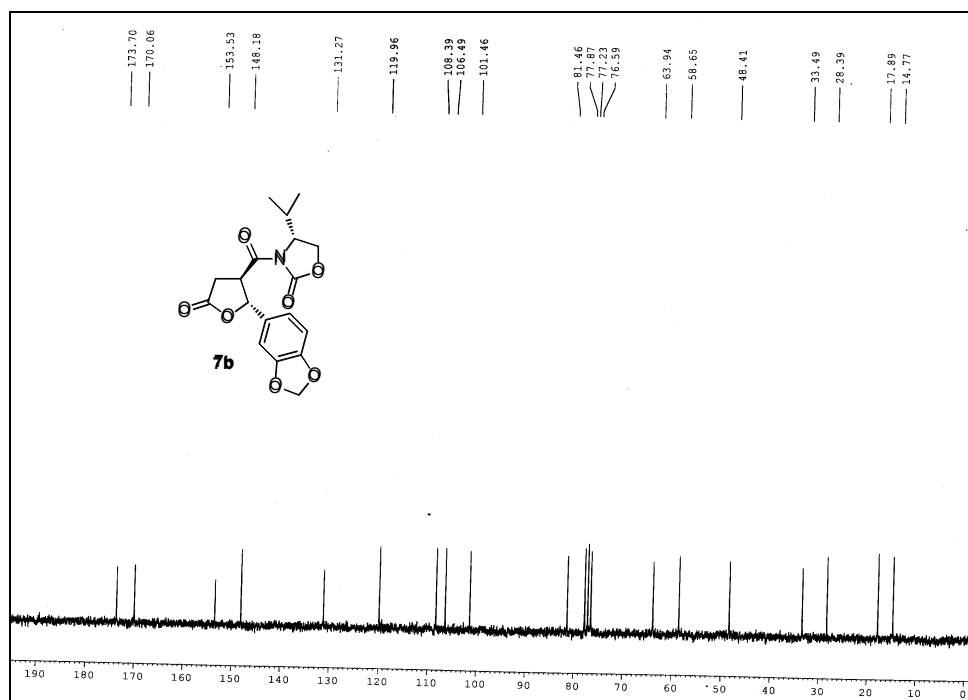
^{13}C NMR of **7a** (50 MHz)



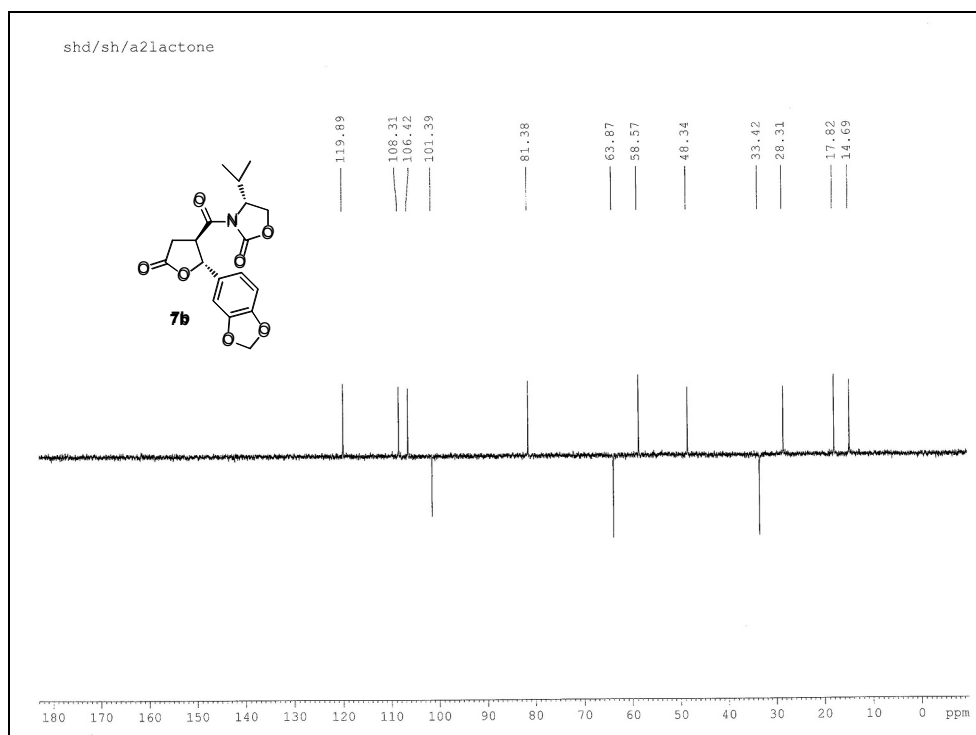
DEPT-135 NMR of **7a** (50 MHz)



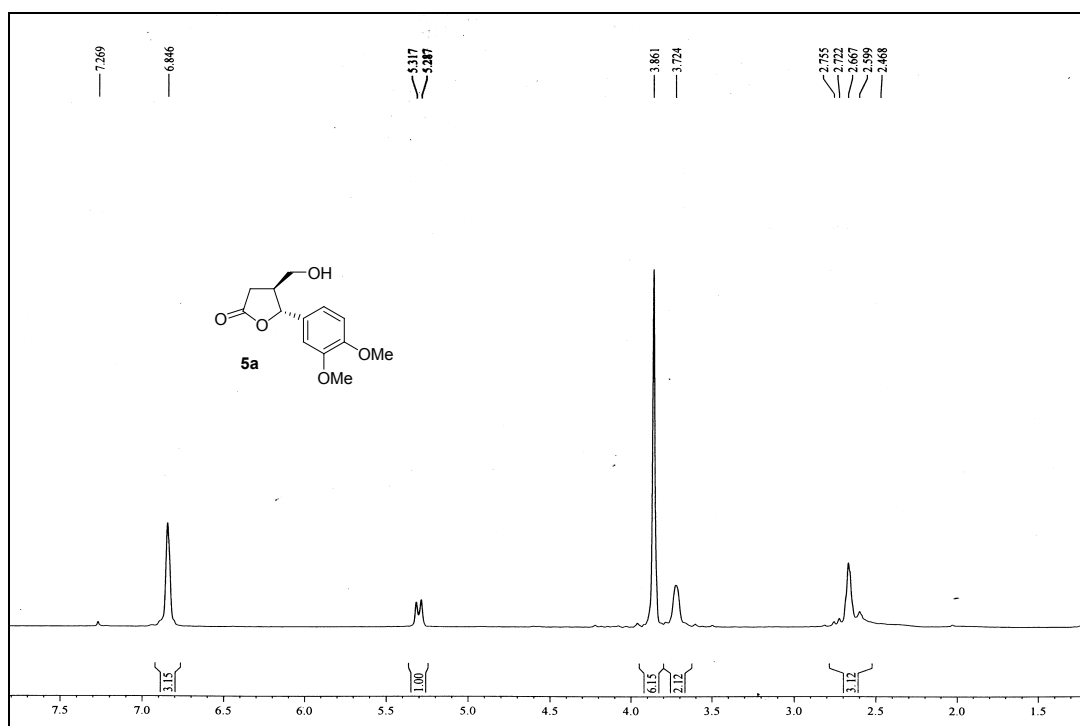
¹H NMR of 7b (200 MHz)



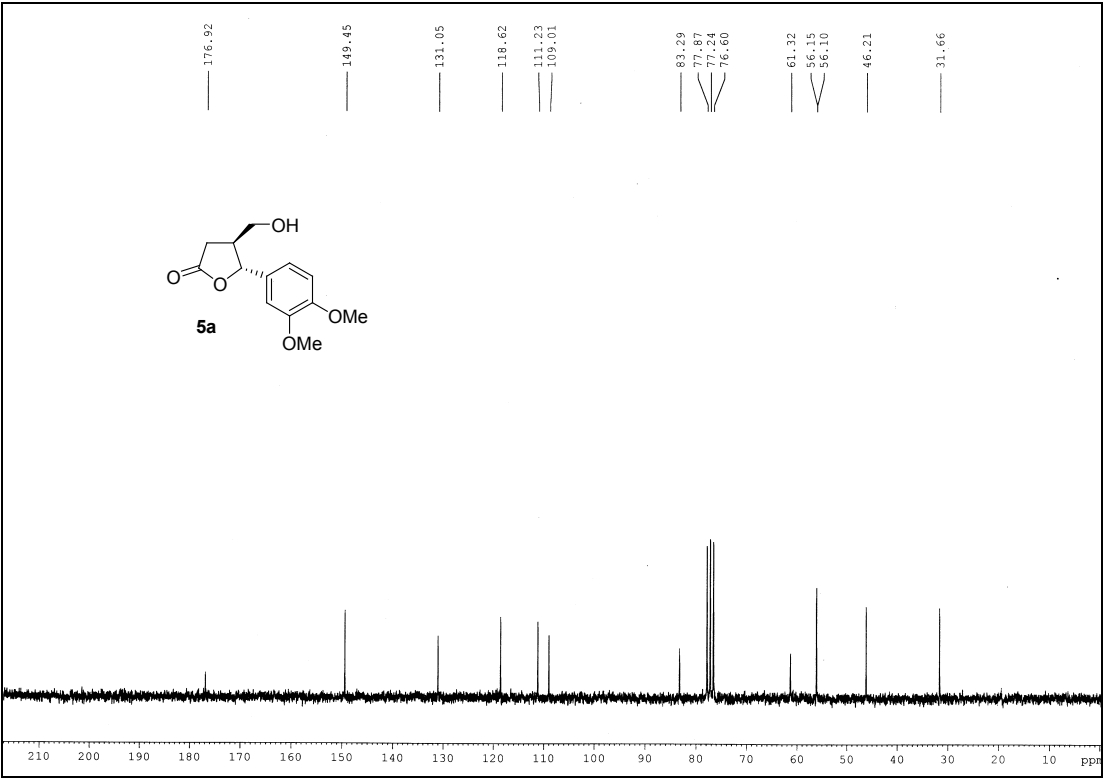
¹³C NMR of 7b (50 MHz)



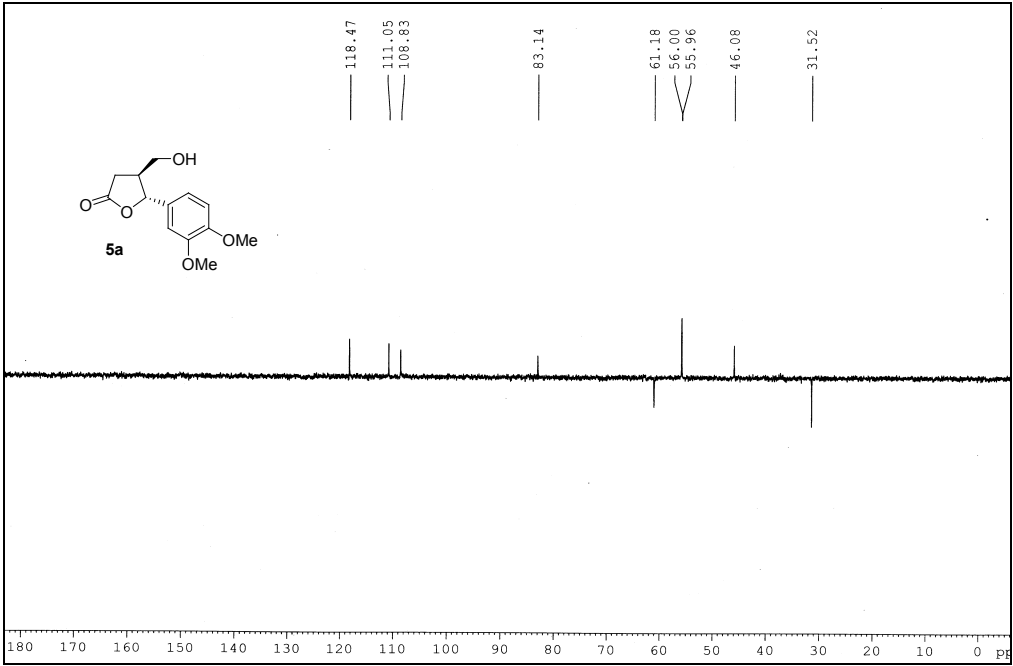
DEPT-135 NMR of **7b** (50 MHz)



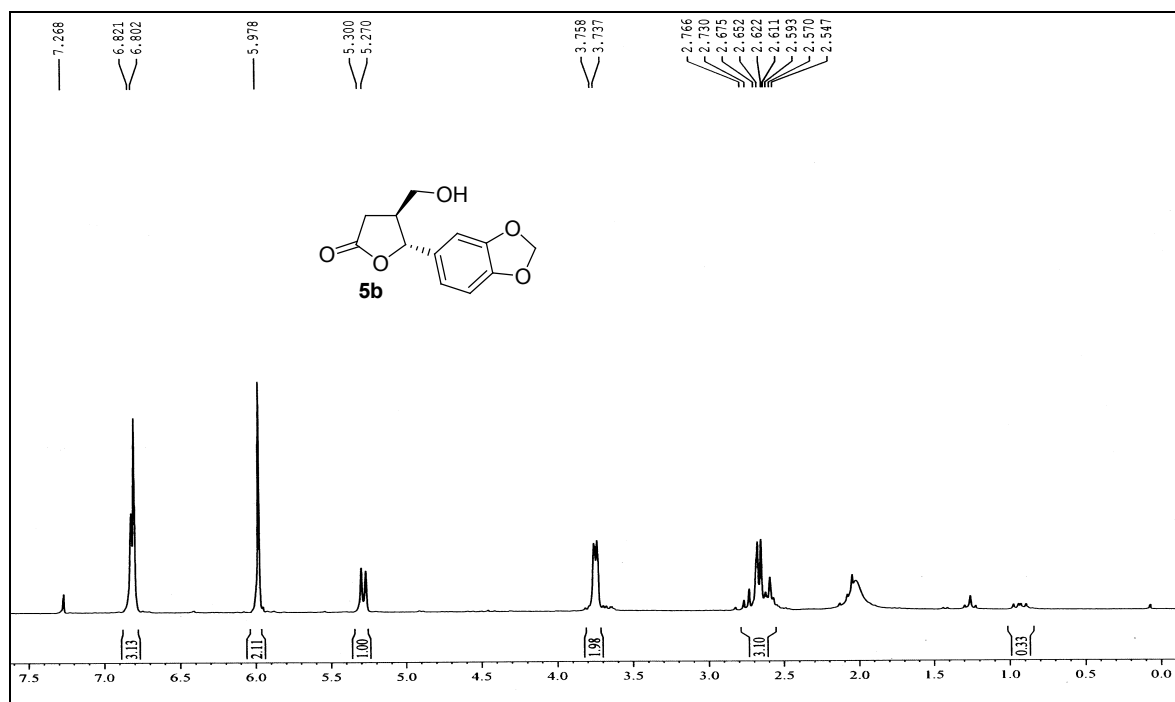
^1H NMR of **5a** (200 MHz)



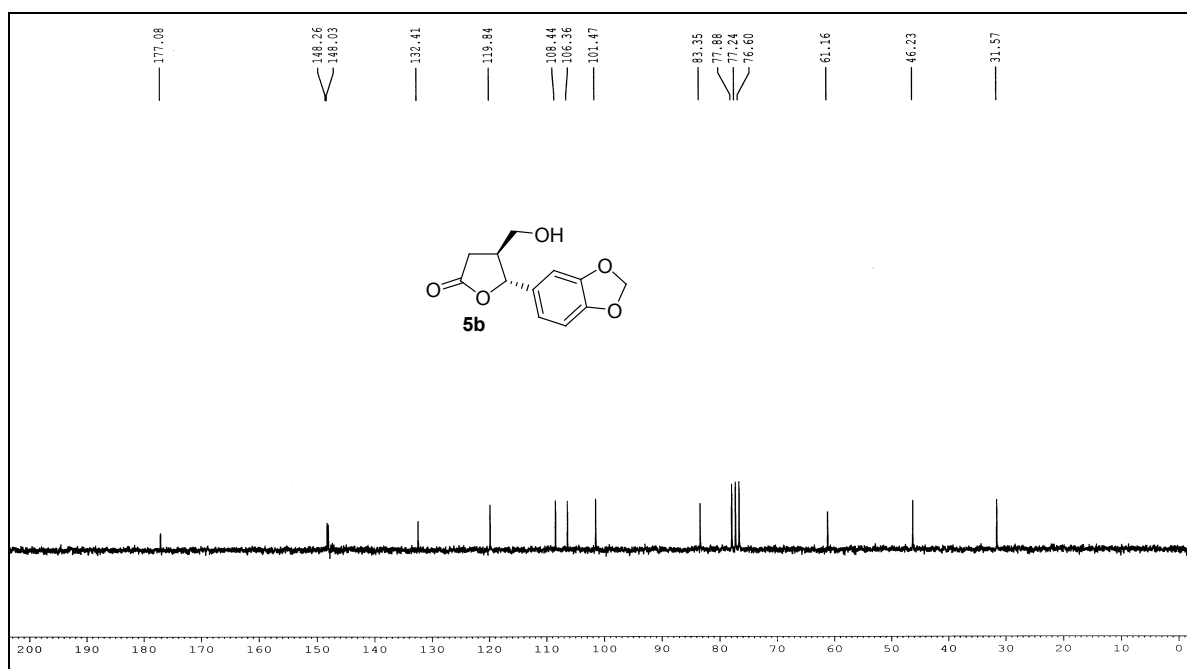
¹³C NMR of **5a** (50 MHz)



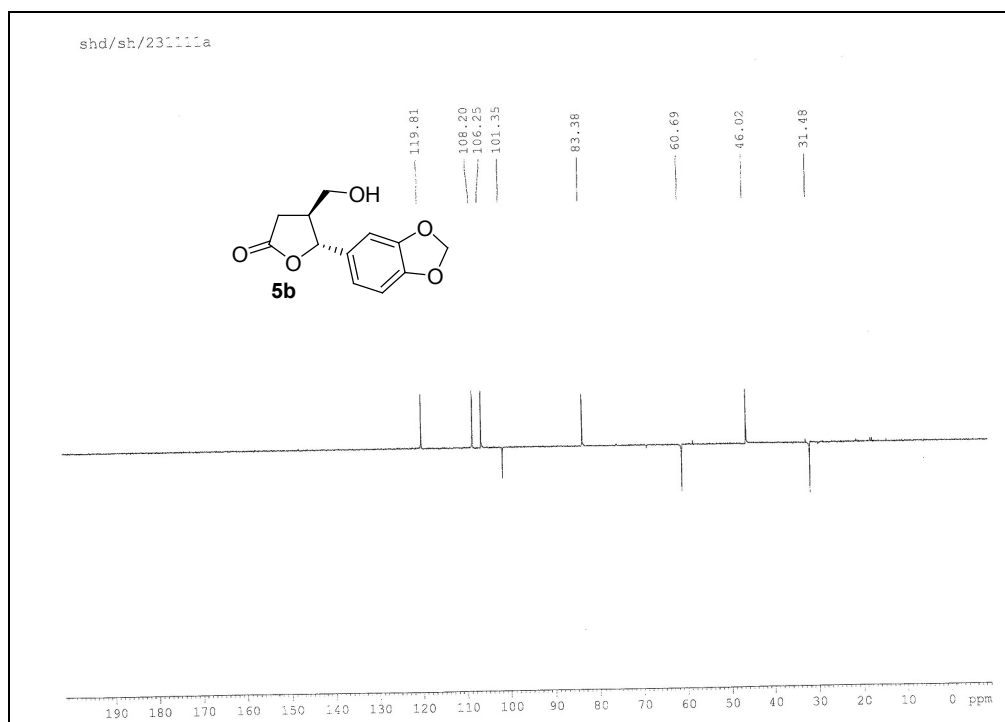
DEPT-135 NMR of **5a** (50 MHz)



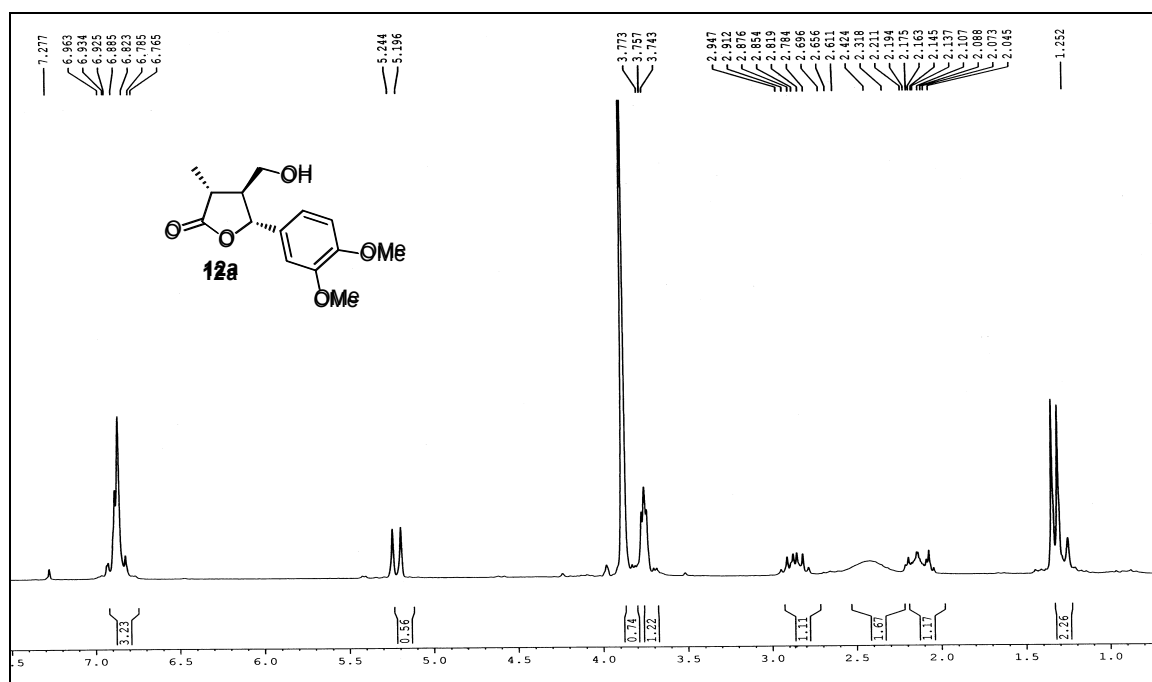
¹H NMR of **5b** (200 MHz)



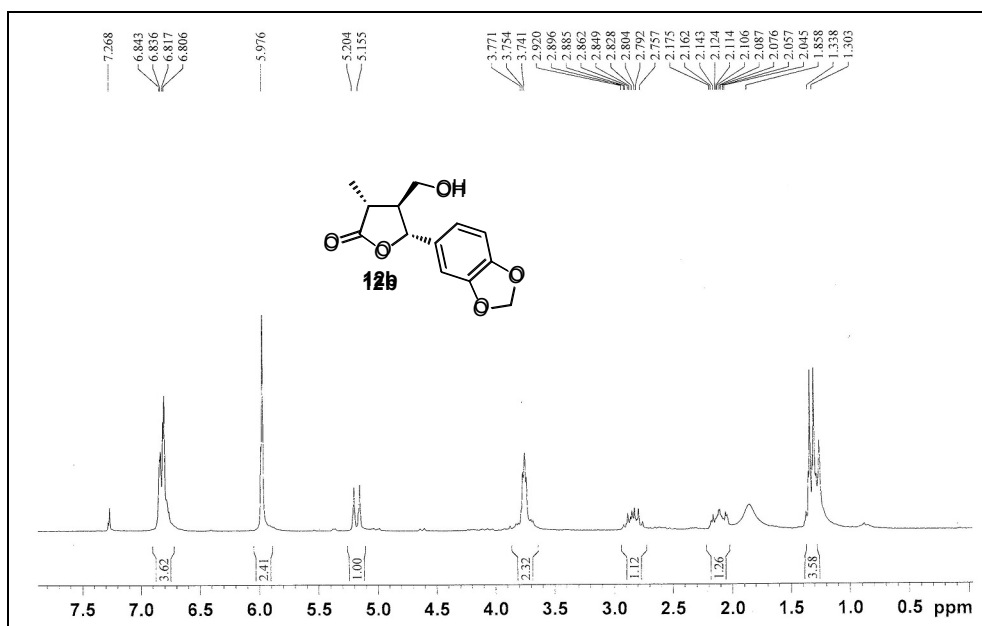
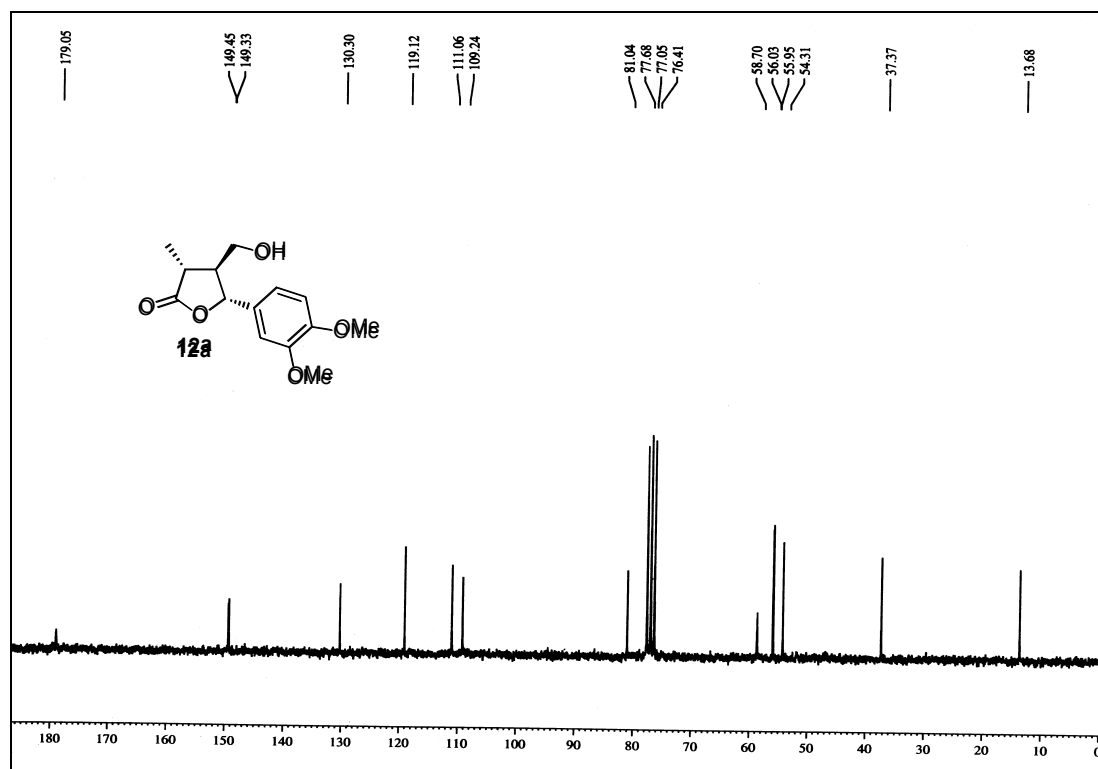
¹³C NMR of **5b** (50 MHz)

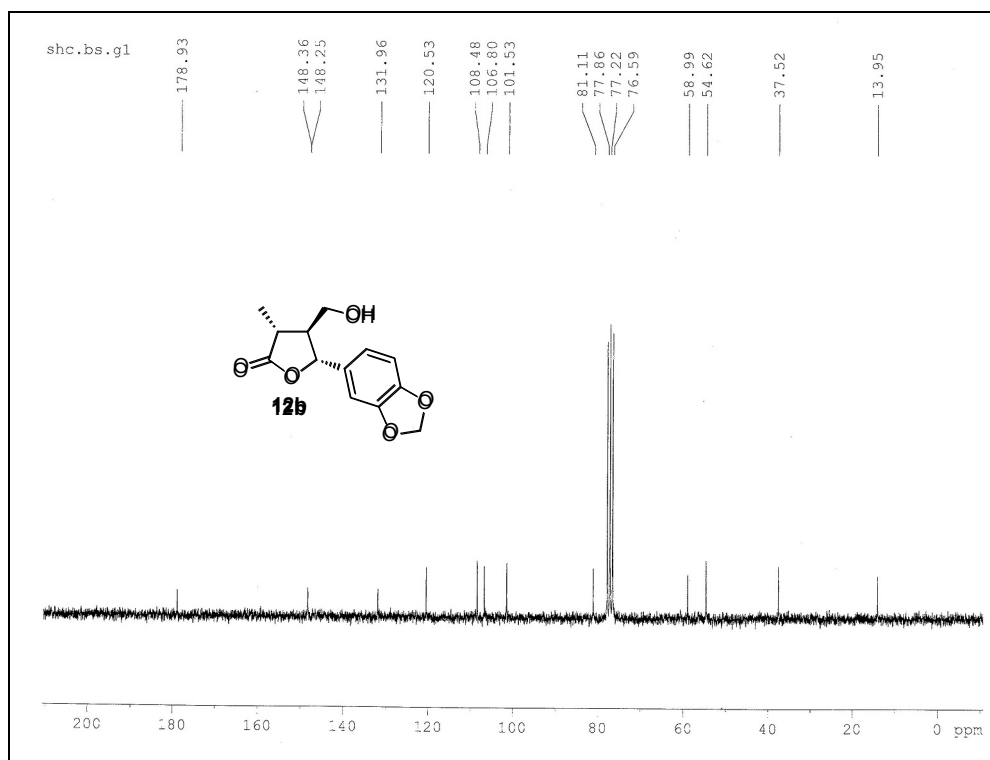


DEPT-135 NMR of **5b** (50 MHz)

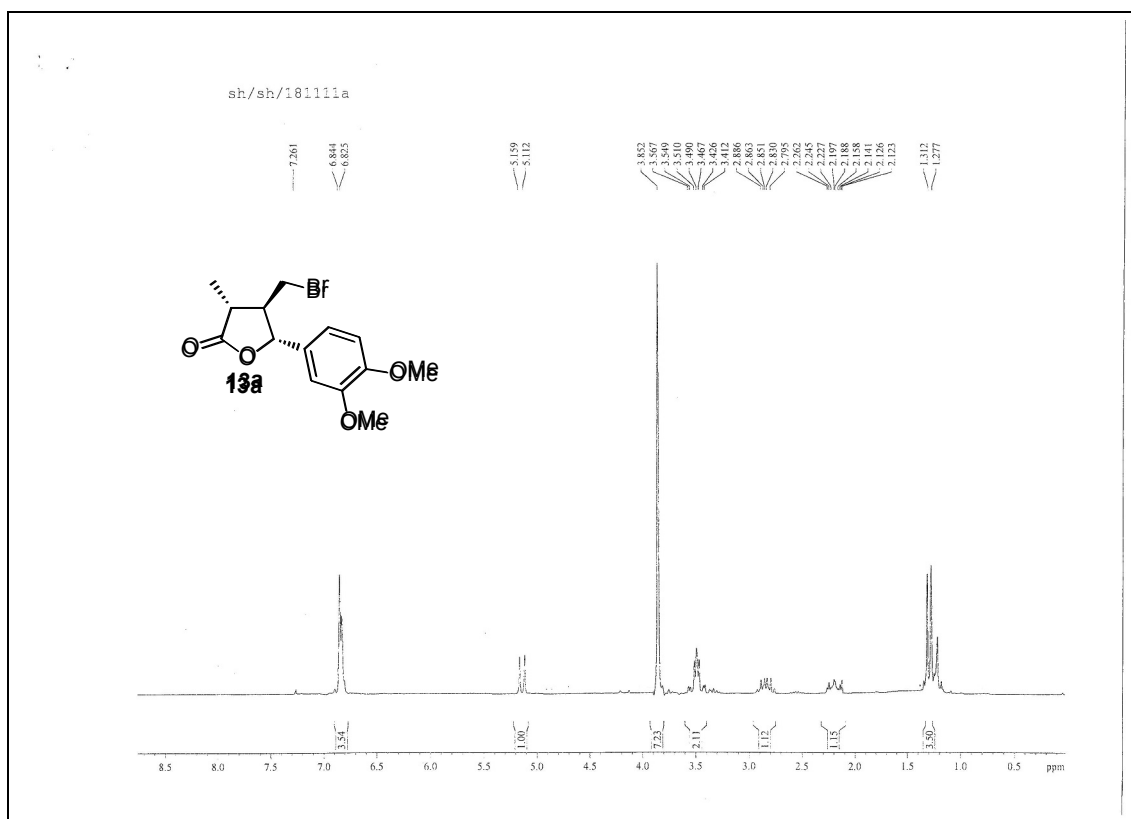


^1H NMR of **12a** (200 MHz)

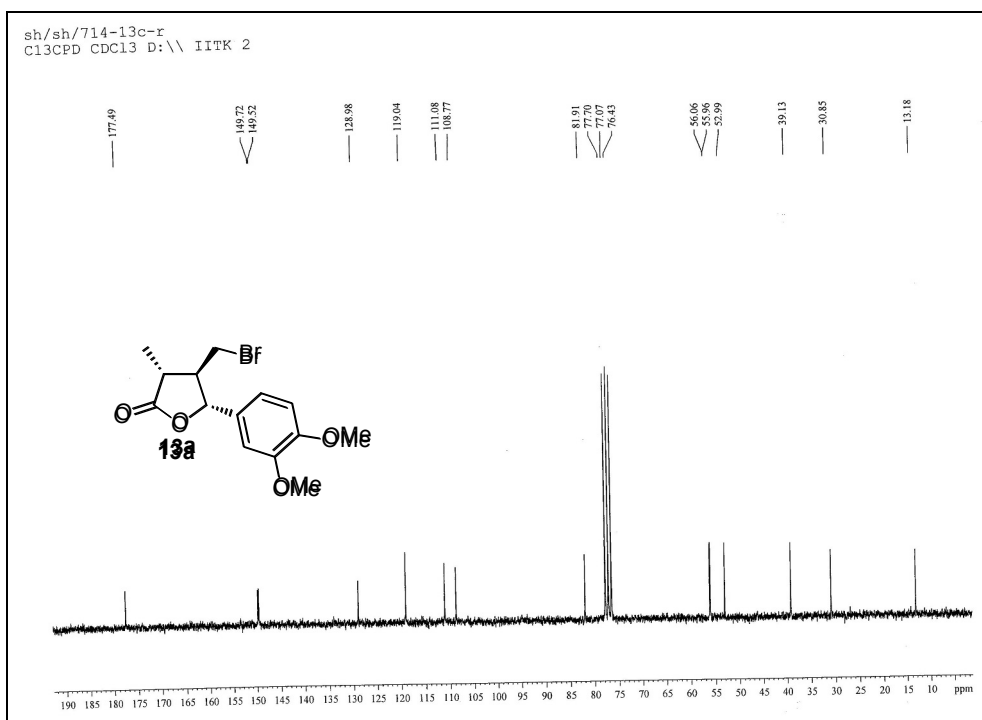




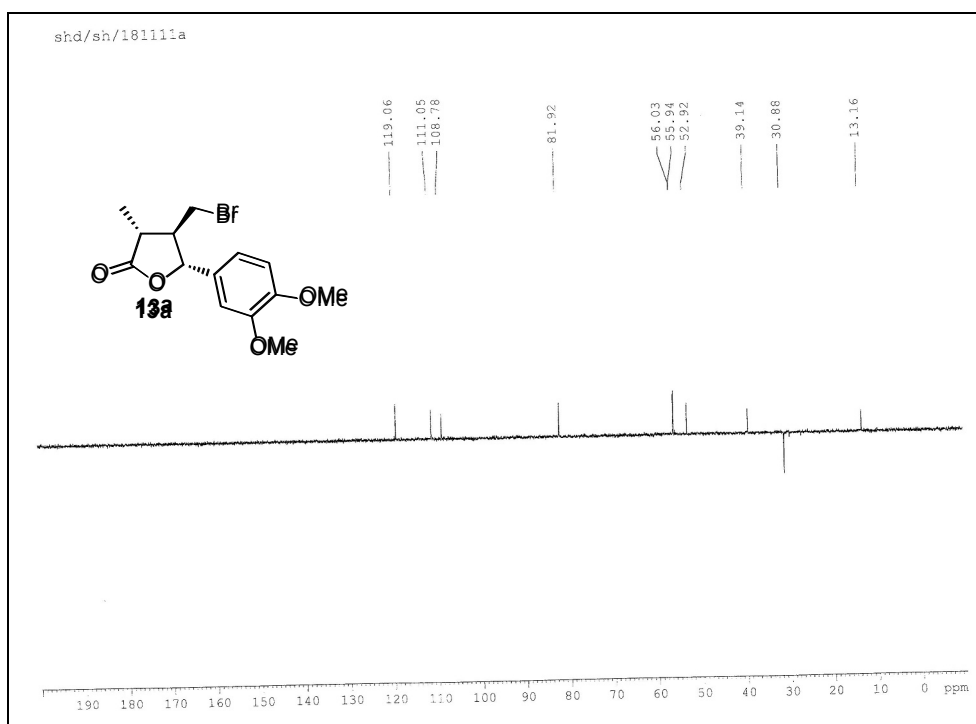
^{13}C NMR of **12b** (50 MHz)



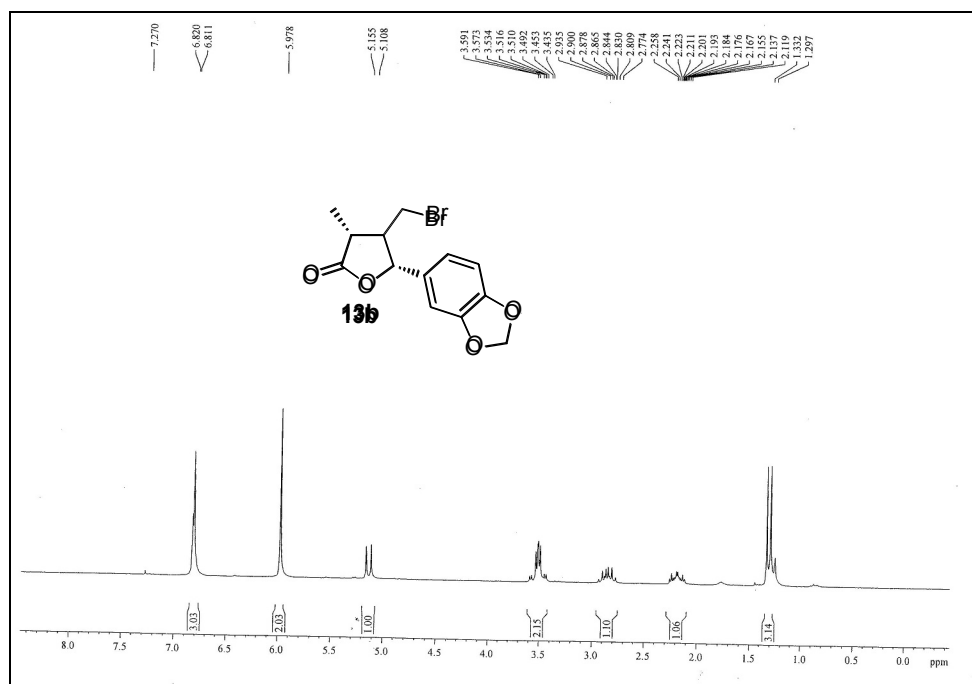
^1H NMR of **13a** (200 MHz)



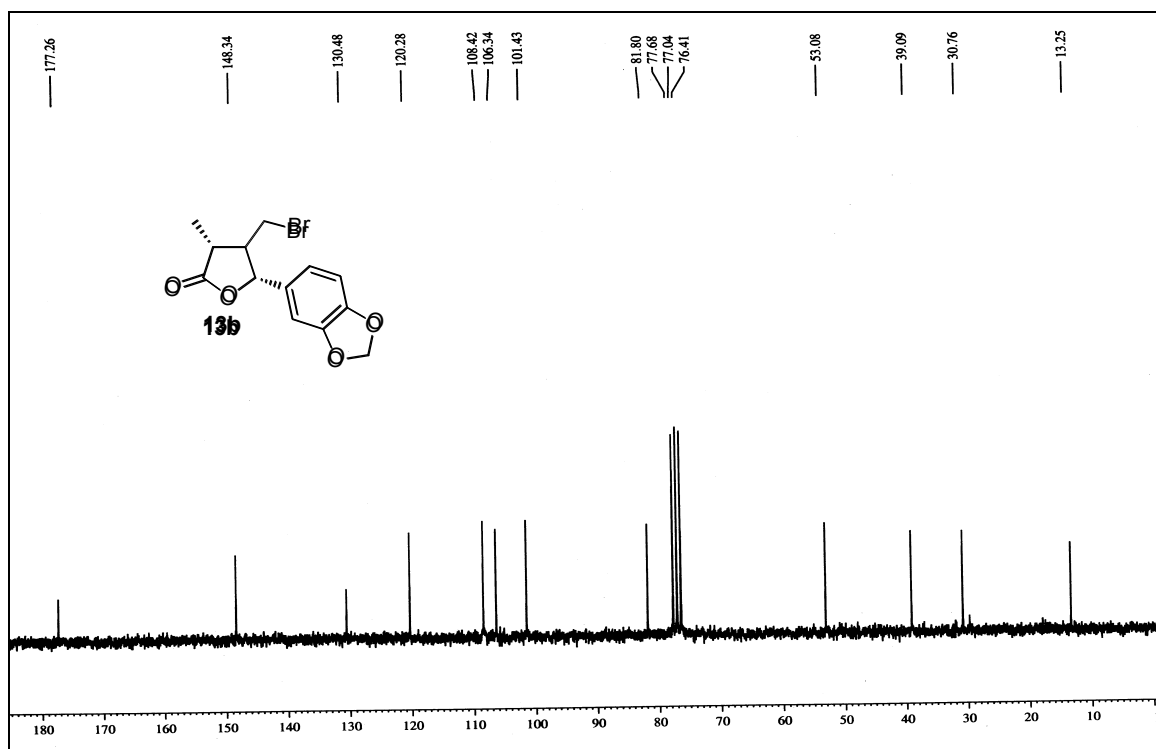
^{13}C NMR of **13a** (50 MHz)



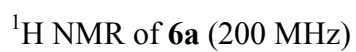
DEPT-135 NMR of **13a** (50 MHz)

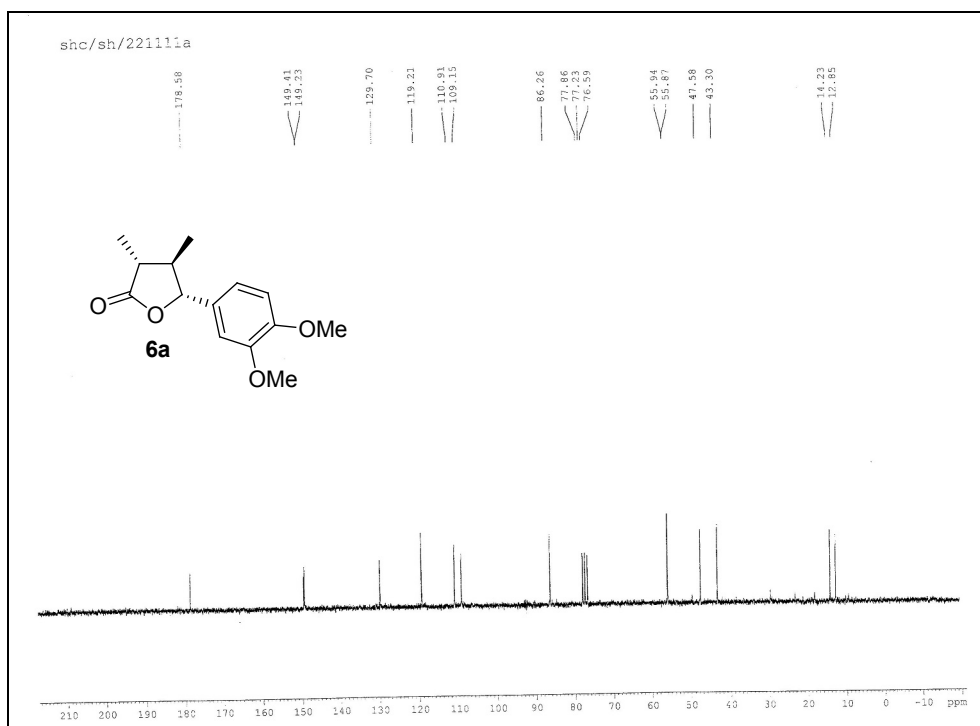


¹H NMR of **13b** (200 MHz)

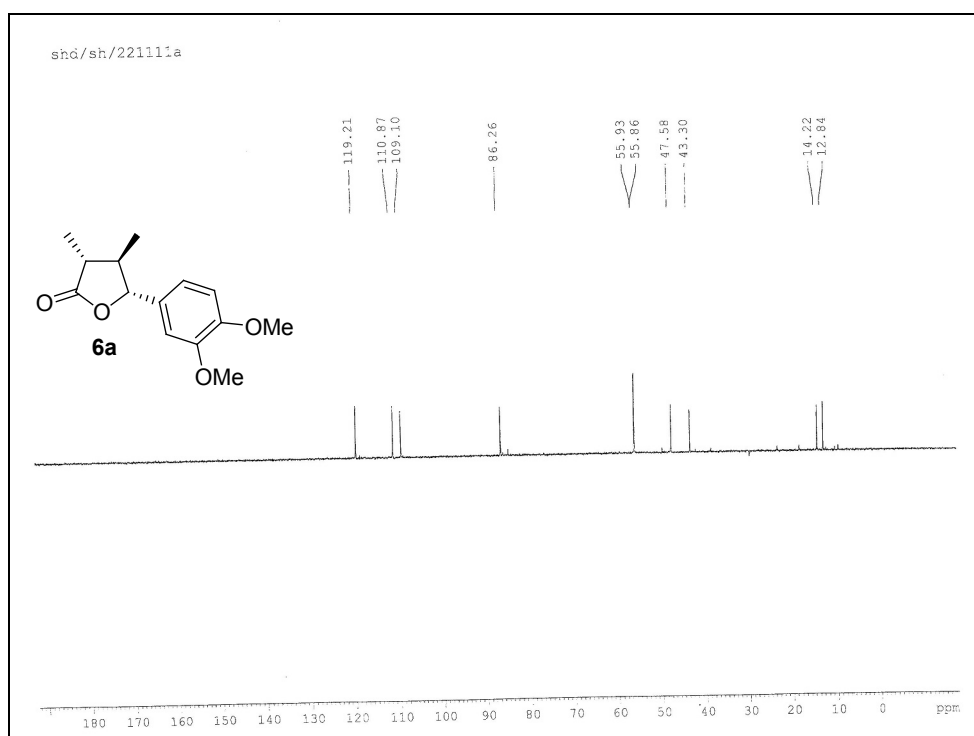


¹³C NMR of **13b** (50 MHz)

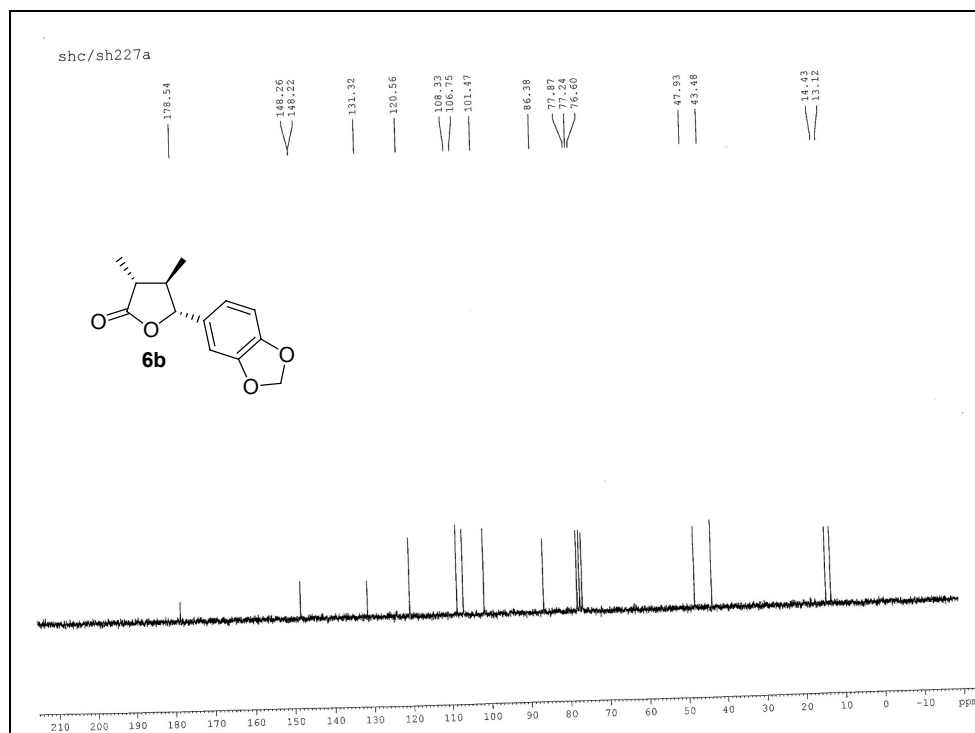
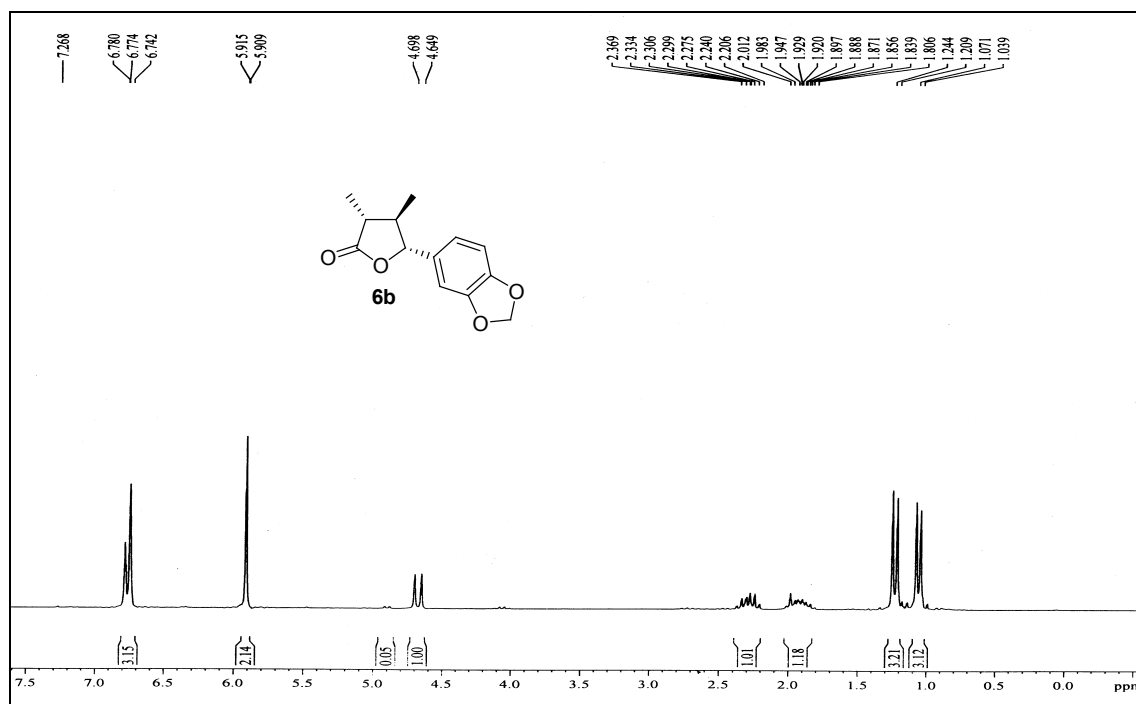


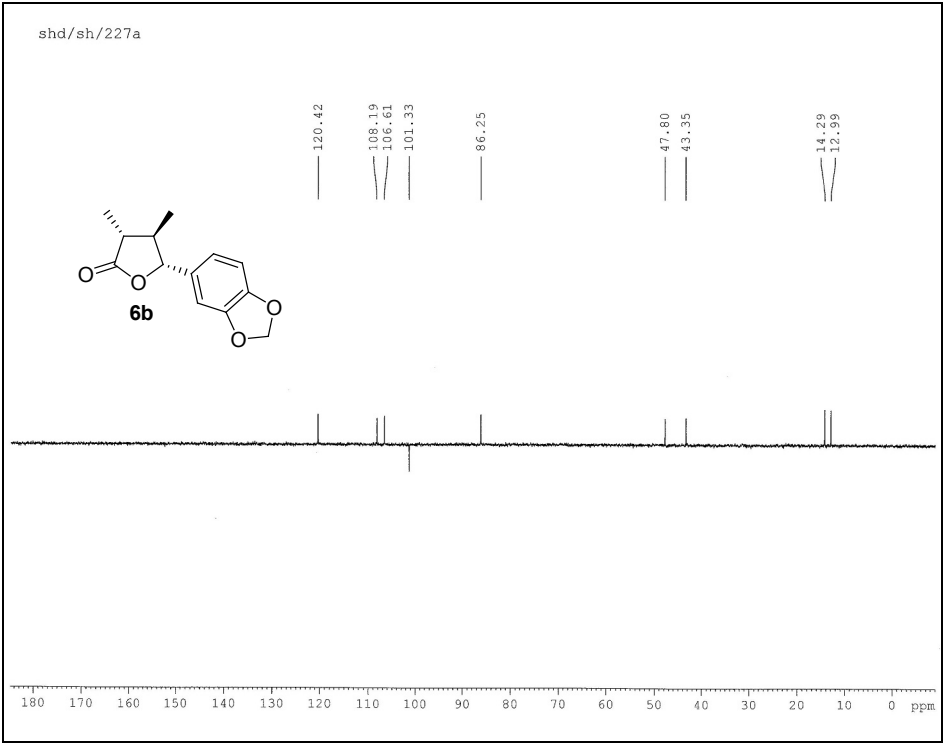


^{13}C NMR of **6a** (50 MHz)

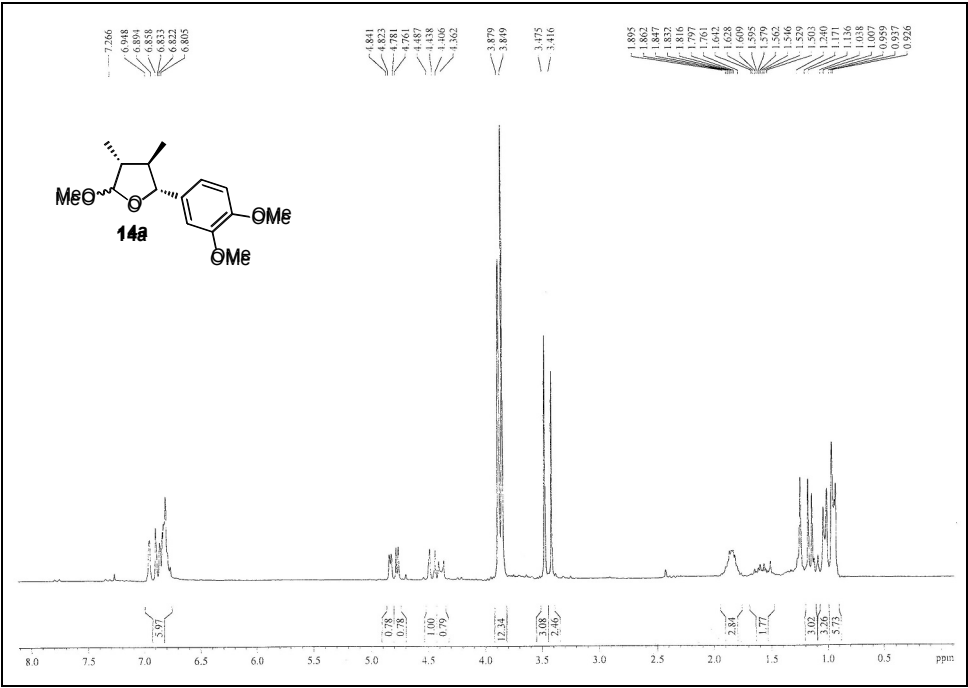


DEPT-135 NMR of **6a** (50 MHz)

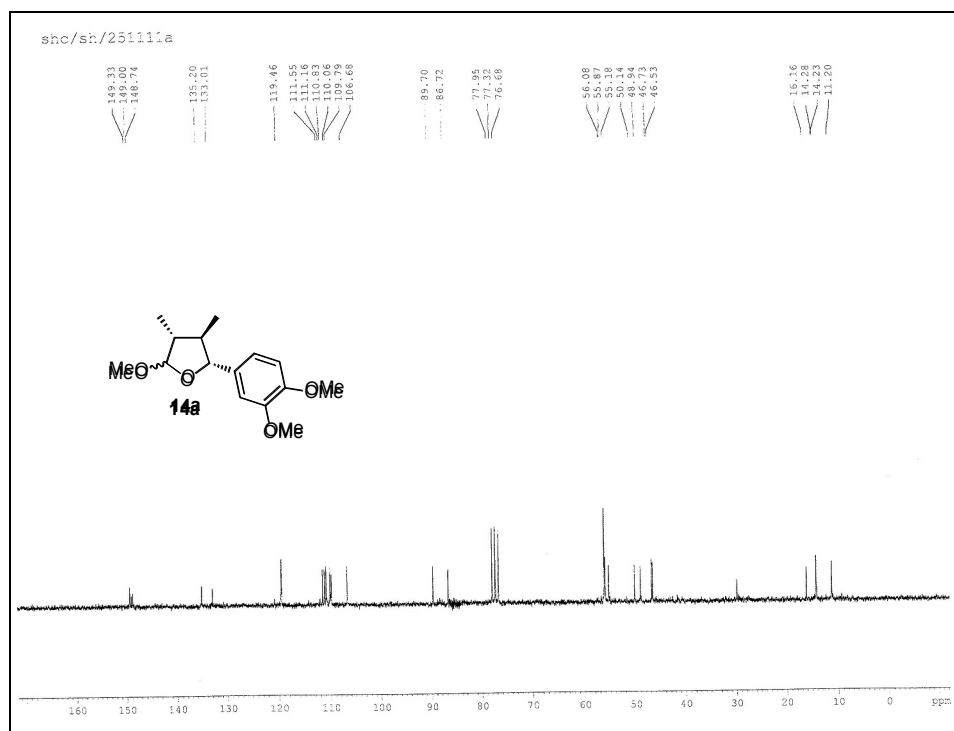




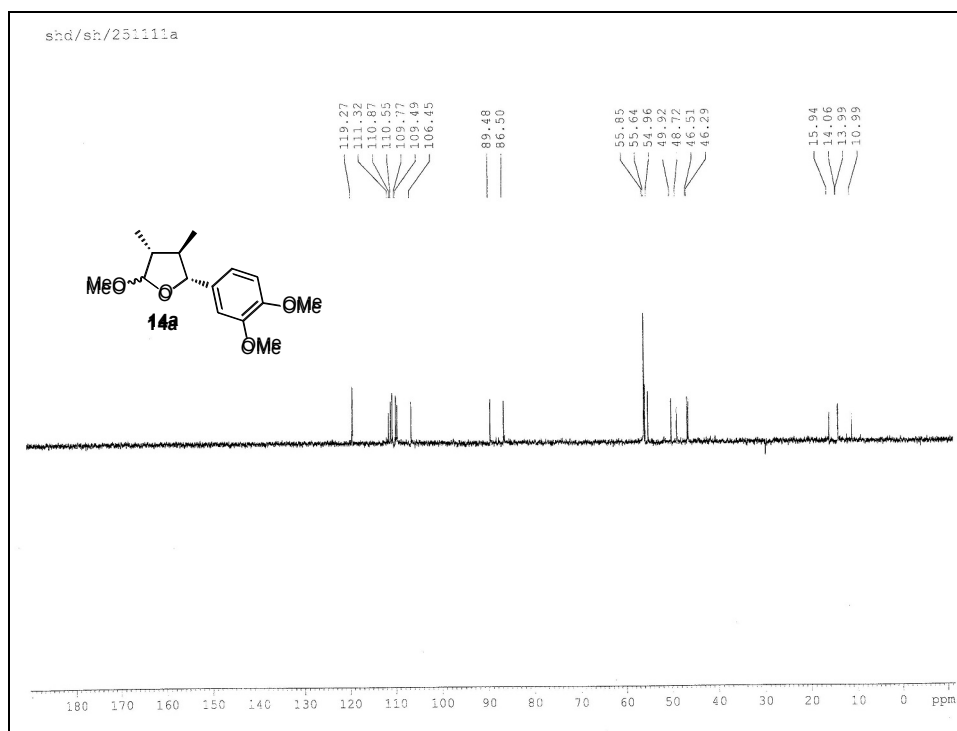
DEPT-135 NMR of **6b** (50 MHz)



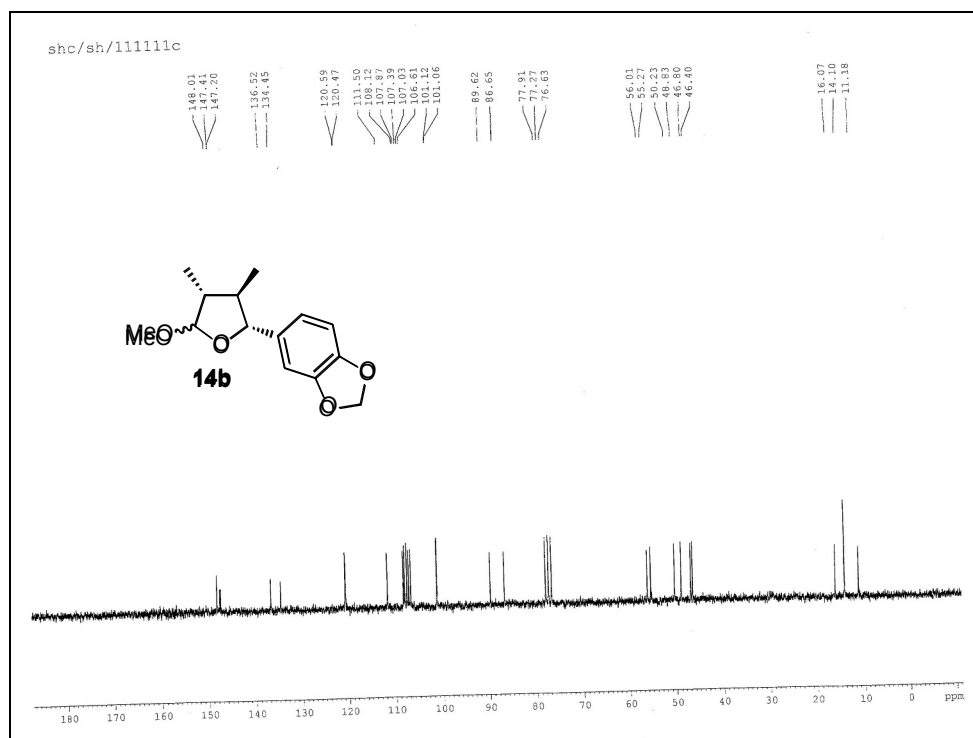
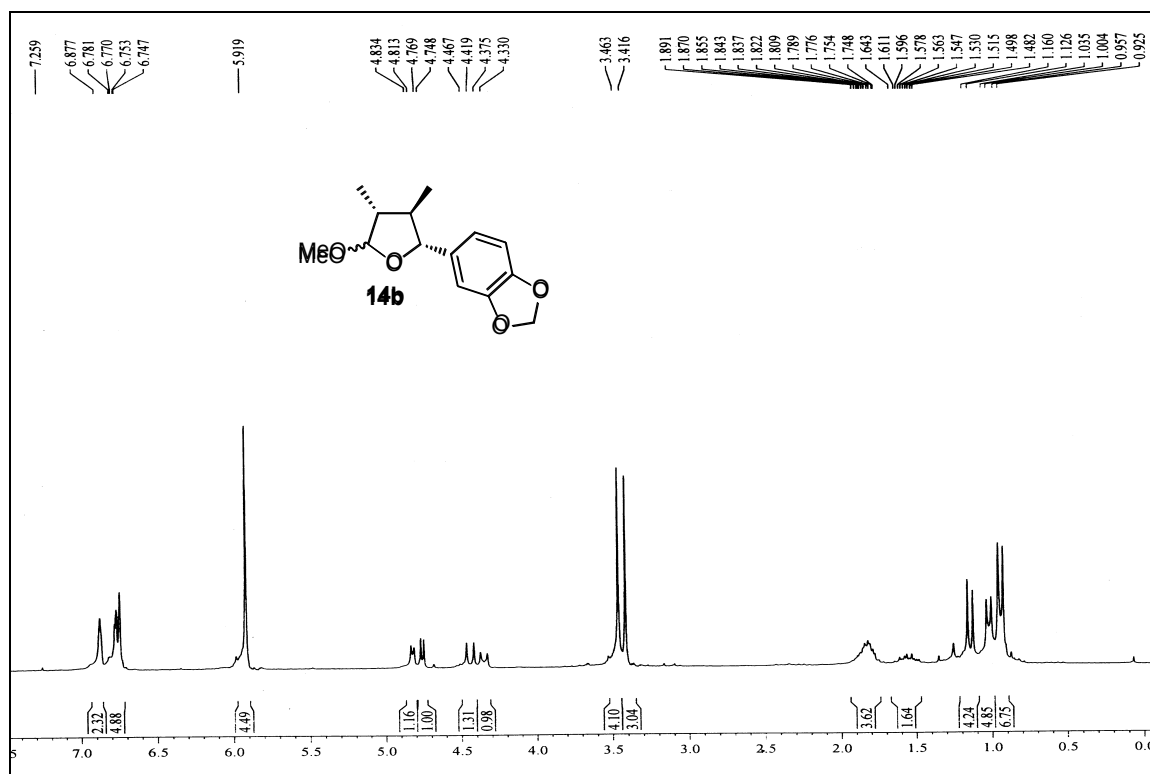
^1H NMR of **14a** (200 MHz)

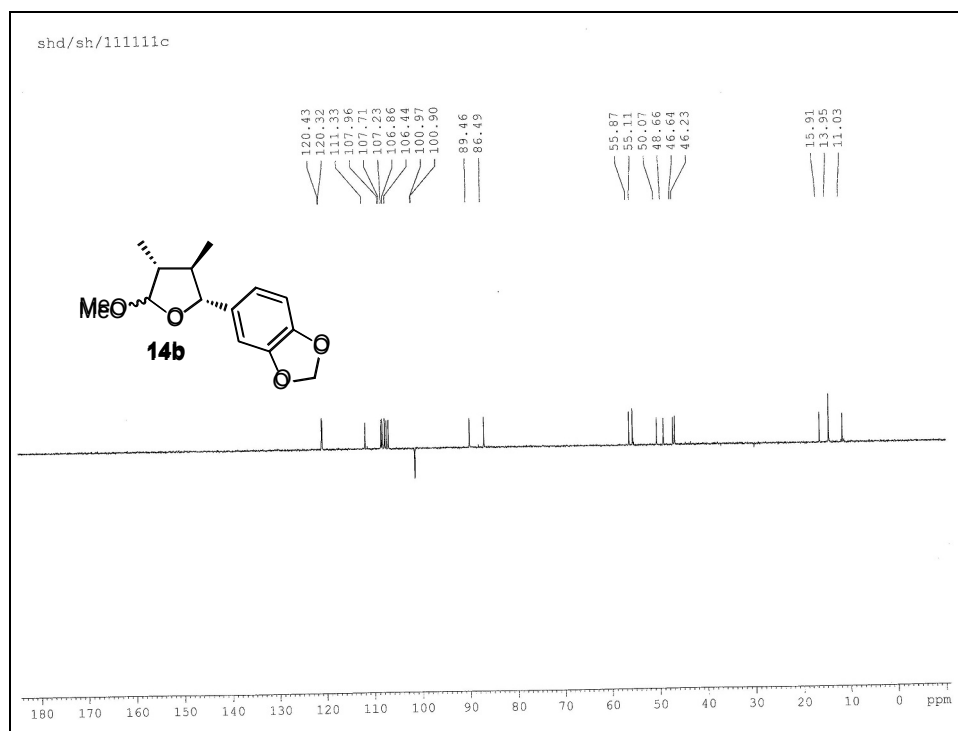


^{13}C NMR of **14a** (50 MHz)

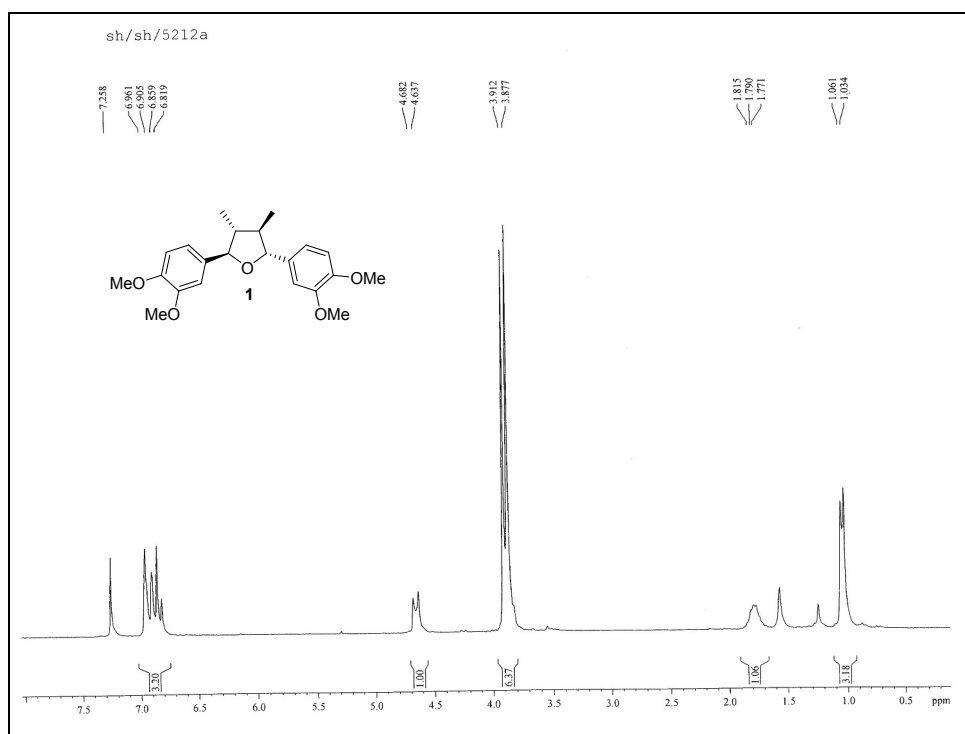


DEPT-135 NMR of **14a** (50 MHz)

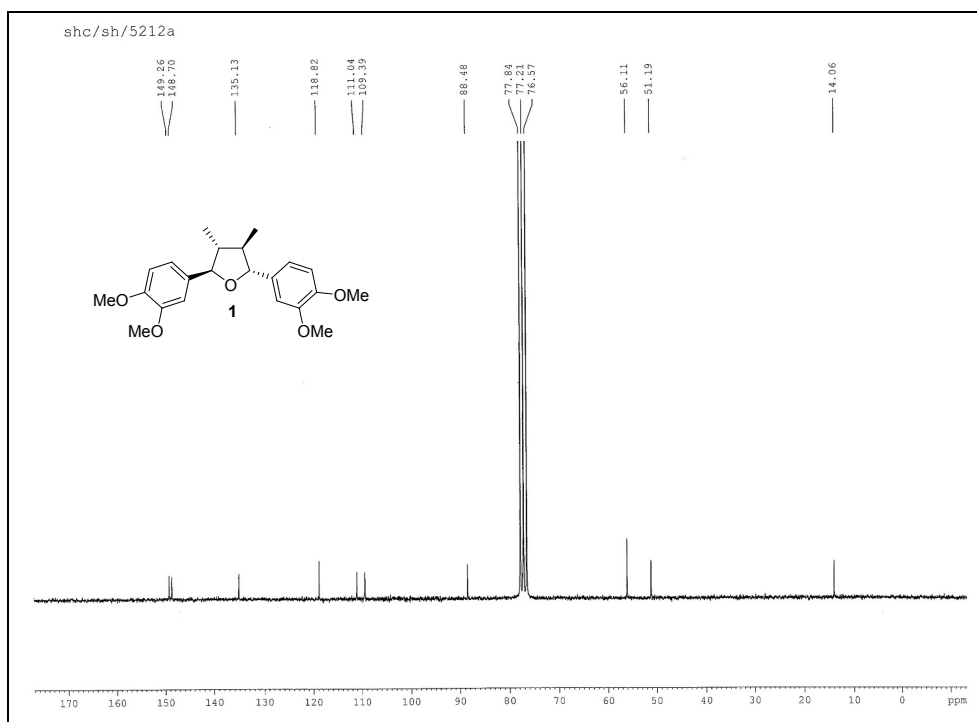




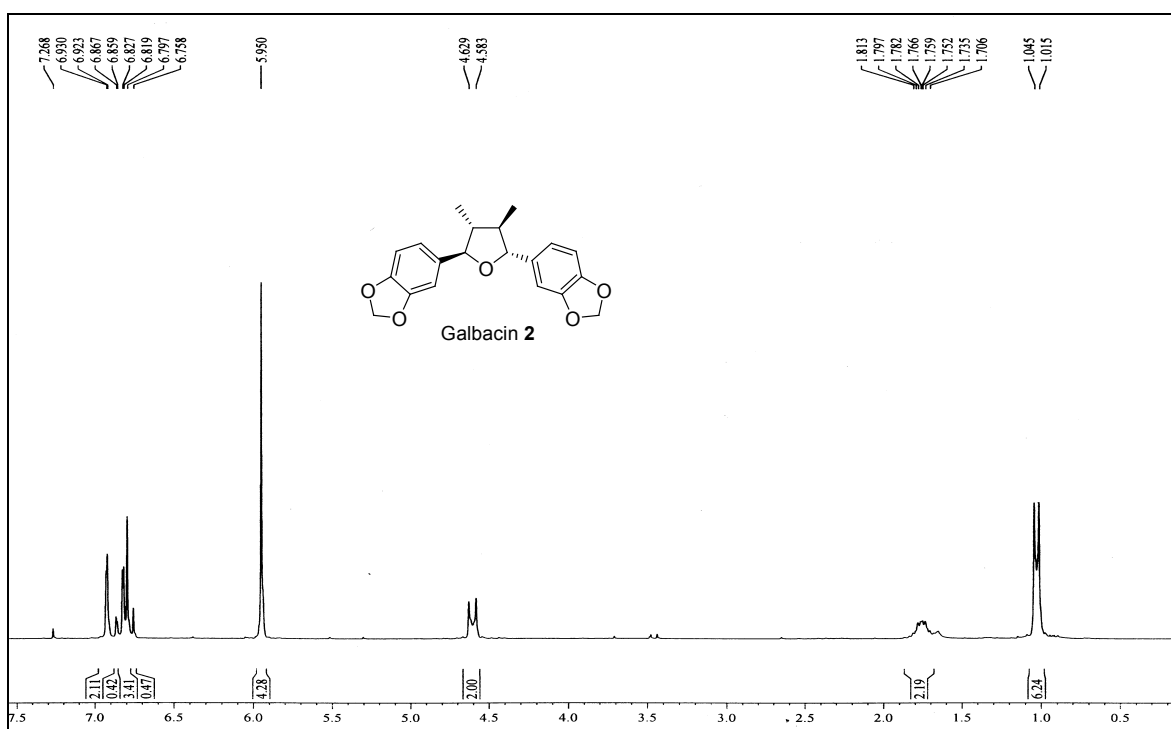
DEPT-135 NMR of **14b** (50 MHz)



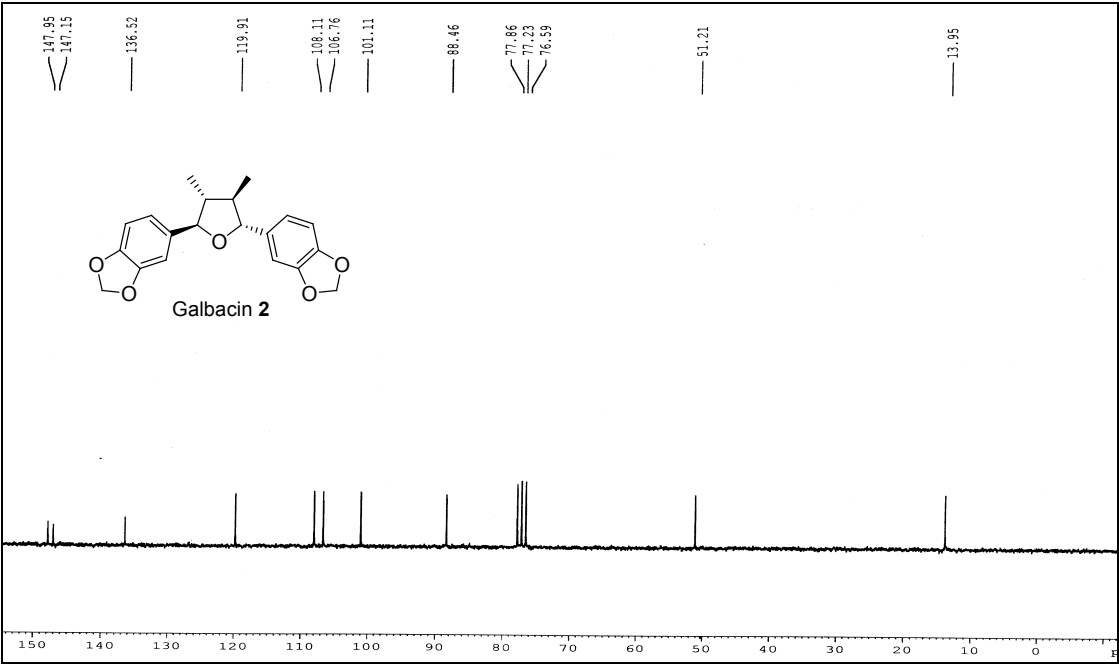
^1H NMR of galbelgin **1** (200 MHz)



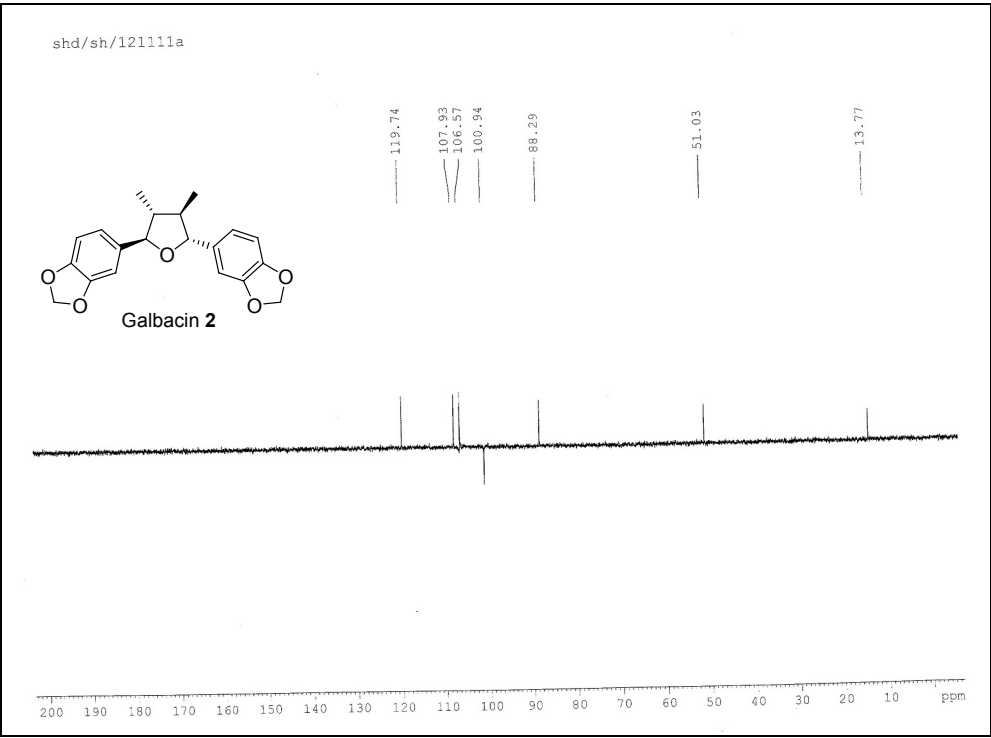
^{13}C NMR of galbelgin 1 (50 MHz)



^1H NMR of galbacin 2 (200 MHz)



¹³C NMR of galbacin 2 (50 MHz)



DEPT-135 NMR of galbacin 2 (50 MHz)