Supporting Information

Total Synthesis of ($\pm$) Maoecrystal V

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General Information

All reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially, and used without further purification. Anhydrous THF and dioxane were distilled from sodium-benzophenone, and dichloromethane was distilled from calcium hydride. Yields refer to chromatographically, unless otherwise stated.

Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. Tsingdao silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography.

Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. NMR spectra were recorded on either a Bruker Advance 400 (^1H : 400 MHz, ^{13}C : 100 MHz), Bruker Advance 500 (^1H : 500 MHz, ^{13}C 125 MHz). Mass spectrometric data were obtained using Bruker Apex IV RTMS.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

Synthesis of Compound 8:

To a solution of compound **7** (21.2 g, 171.0 mmol) in THF (500 mL) was added NaH (20.6 g, 80% in mineral oil, 686 mmol) over 1 h in portions under N₂. After stirring at 0°C for 10 min dimethyl carbonate (115 mL, 1.37 mol) was added slowly over 30 min. The reaction mixture was then refluxed for 4 h, cooled to 0°C and quenched with 3M HCl until pH= 6~7. The aqueous layer was extracted by EtOAc (3×60 mL); the combined organic layer was finally dried over Na₂SO₄, filtered, and solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1/10) to give compound **8** (28.6 g) as colorless oil in 92 % yield; *R*_f = 0.81 (silica gel, EtOAc/hexanes = 1/20); ¹H NMR (500 MHz, CDCl₃): δ 12.41 (s, 1H), 5.60-5.57 (m, 1H), 5.41-5.38 (m, 1H), 3.77 (2, 3H), 2.90 (dd, *J* = 3.0 Hz, *J* = 2.0 Hz, 1H), 1.25 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 175.8, 172.9, 133.9, 120.8, 93.7, 51.4, 36.7, 25.5; HRMS-ESI Calcd for C₁₀H₁₅O₃ [M + H⁺]: 183.1021; Found: 183.1019.

Synthesis of Compound 10:

The aryllead compound **9** (8.1 g, 15 mmol) was added in portions over 15 min to a stirred mixture of Compound **8** (2.2 g, 12 mmol) and pyridine (4.8 mL, 60 mmol) in chloroform (50 mL) under N₂ at 60°C, the mixture was stirred at 60 °C for 12 h. The mixture was shaken with 3M H₂SO₄ (10 mL), filtered over a silica gel plug and washed with CHCl₃, The aqueous phase was extracted with chloroform (2×150 mL), and then the combined chloroform was dried (Na₂SO₄), filtered, and evaporated. The residue was dissolved in ether (200 mL) and shaken with ice-cold aqueous NaOH (3M, 50 mL), and then with water (100 mL) finally brine (100 mL). The ether solution was dried (Na₂SO₄) and evaporated the solvent. The crude product was purified by flash column chromatography on silica gel (EtOAc/hexane = 1/10) to give compound **10** (3.5 g) as white solid in 88% yield; *R*_f = 0.52 (silica gel, EtOAc/hexanes = 1/6); ¹H NMR (500 MHz, CDCl₃): δ 7.16 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5, Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.90-5.87 (m, 1H), 5.75 (dd, *J* = 10.0 Hz, *J* = 2.5 Hz, 1H), 4.88 (d, *J* = 6.0 Hz, 1H), 4.80 (d, *J* = 6.0 Hz, 1H), 3.76 (s, 3H), 3.53 (s, 3H), 3.20-3.15 (m, 1H), 3.02 (dd, *J* = 11.0 Hz, *J* = 6.0 Hz, 1H), 2.37 (s, 3H), 1.33 (s, 3H), 1.25 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 210.4, 171.4, 154.8, 137.1, 132.4, 131.7, 131.2, 125.5, 123.7, 123.0, 99.7, 62.9, 56.9, 52.3, 46.0, 32.8, 27.9, 27.8, 17.8; HRMS-ESI Calcd for C₁₉H₂₄O₅Na [M + Na⁺]: 335.1521; Found: 335.1527.

Synthesis of Compound 6a and 6b:

To a solution of compound **11a** (800 mg, 2.4 mmol) in THF (20 mL) was added LiAlH_4 (365 mg, 9.6 mmol) at 0 °C. The reaction was stirred for 24h at room temperature, quenched by slow addition of H_2O at 0 °C. The reaction was worked by filtration off the precipitate and dissolved with EtOAc (200 mL), washed with a saturated solution of NaHCO_3 (3×50 mL). The aqueous layer was extracted by EtOAc (300 mL), the combined organic layer was dried over Na_2SO_4 , filtered, and solvent was removed under *vacuum*, and the residue was purified by a flash chromatography on silica gel to give compound **6a** (89 mg) and **6b** (530 mg) in 84 % overall yield;

Compound **6a**, white solid, $R_f = 0.32$ (silica gel, EtOAc/hexanes = 1/2); ^1H NMR (500 MHz, CDCl_3): δ 7.43 (dd, $J = 7.5$ Hz, $J = 1$ Hz, 1H), 7.12 (dd, $J = 7.5$ Hz, $J = 1$ Hz, 1H), 7.04 (t, $J = 7.8$ Hz, 1H), 5.63-5.60 (m, 1H), 5.41-5.39 (m, 1H), 5.09 (dd, $J = 6.5$ Hz, $J = 5$ Hz, 2H), 4.60 (d, $J = 4.5$ Hz, 1H), 4.30 (dd, $J = 12$ Hz, $J = 4.5$ Hz, 1H), 4.20 (dd, $J = 11.5$ Hz, $J = 3$ Hz, 1H), 3.62 (s, 3H), 3.30 (s, 1H), 2.83 (d, $J = 5.5$ Hz, 1H), 2.68-2.63 (m, 1H), 2.39-2.34 (m, 1H), 2.32 (s, 3H), 1.15 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 155.3, 135.9, 135.4, 131.1, 130.9, 128.2, 124.2, 121.9, 99.6, 79.5, 67.8, 57.6, 48.0, 37.9, 32.6, 29.4, 24.3, 18.3; HRMS-ESI Calcd for $\text{C}_{18}\text{H}_{27}\text{O}_4$ [$\text{M} + \text{H}^+$]: 307.1909; Found: 307.1908.

Compound **6b**, white solid, $R_f = 0.28$ (silica gel, EtOAc/hexanes = 1/2); ^1H NMR (500 MHz, CDCl_3): δ 7.16 (d, $J = 8.0$ Hz, 1H), 7.12 (d, $J = 7.0$ Hz, 1H), 7.01 (t, $J = 7.5$ Hz, 1H), 5.68-5.64 (m, 1H), 5.34 (dd, $J = 10.0$ Hz, $J = 2.5$ Hz, 1H), 5.17 (d, $J = 5.0$ Hz, 1H), 5.09 (d, $J = 5.0$ Hz, 1H), 4.67 (d, $J = 8.5$ Hz, 1H), 4.25 (dd, $J = 11$ Hz, $J = 8.5$ Hz, 1H), 4.07 (dd, $J = 11$ Hz, $J = 6$ Hz, 1H), 3.96 (d, $J = 9.0$ Hz, 1H), 3.67 (s, 3H), 2.82 (dd, $J = 17.5$ Hz, $J = 5$ Hz, 1H), 2.59-2.54 (m, 1H), 2.34 (s, 3H), 1.04 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 154.7, 137.4, 132.7, 131.2, 131.0, 130.2, 124.5, 121.5, 100.0, 79.7, 68.3, 58.1, 49.8, 38.4, 35.6, 29.8, 20.0, 18.4; HRMS-ESI Calcd for $\text{C}_{18}\text{H}_{27}\text{O}_4\text{Na}$ [$\text{M} + \text{Na}^+$]: 329.1729; Found: 329.1731.

Synthesis of Compound 11a:

To a solution of compound **10** (4.0 g, 12.0 mmol) in methanol (90 mL) and THF (30 mL) was added Tetra-*n*-butylammonium borohydride (9.3 g, 36.0 mmol) in portions over 10 min at 0 °C. The reaction was heated to 40 °C and stirred for 48h. The reaction was quenched with a saturated solution

of NH_4Cl (30 mL). The aqueous layer was extracted with EtOAc (3×100 mL), dried over Na_2SO_4 , filtered, and solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1/30) to give compound **11a** (2.6 g) as white solid in 65% yield together with 950 mg of starting material **10** (89% brsm); R_f = 0.50 (silica gel, EtOAc/hexanes = 1/6); ^1H NMR (500 MHz, CDCl_3): δ 7.39 (d, J = 7.1 Hz, 1H), 7.13 (dd, J = 7.3 Hz, J = 0.6 Hz, 1H), 7.04 (t, J = 7.7 Hz, 1H), 5.63–5.59 (m, 1H), 5.45–5.42 (m, 1H), 4.94 (d, J = 5.4 Hz, 1H), 4.87 (d, J = 5.4 Hz, 1H), 4.42 (d, J = 7.4 Hz, 1H), 3.72 (s, 3H), 3.59 (s, 3H), 2.94–2.90 (m, 1H), 2.33 (s, 3H), 2.24 (d, J = 17.5 Hz, 1H), 0.95 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 176.1, 154.8, 135.7, 135.5, 131.0, 130.8, 125.9, 123.9, 121.1, 99.4, 76.1, 57.2, 51.9, 51.5, 37.5, 29.6, 29.2, 17.9; HRMS-ESI Calcd for $\text{C}_{19}\text{H}_{27}\text{O}_5$ [$\text{M} + \text{H}^+$]: 335.1858; Found: 335.1857.

Synthesis of Compound 6a:

To a solution of compound **11a** (1.20 g, 3.6 mmol) in THF (30 mL) was added LiAlH_4 (550 mg, 14.4 mmol) at 0 °C. The reaction was stirred for 18 h at room temperature, quenched by slow addition of H_2O at 0 °C. The reaction was worked by filtration off the precipitate and dissolved with EtOAc (250 mL), washed with a saturated solution of NaHCO_3 (3×100 mL). The aqueous layer was extracted by EtOAc (350 mL), the combined organic layer was dried over Na_2SO_4 , filtered, and solvent was removed under vacuum, and the residue was purified by a flash chromatography on silica gel to give compound **6a** (970 mg) as white solid in 88 % yield; R_f = 0.32 (silica gel, EtOAc/hexanes = 1/2); ^1H NMR (500 MHz, CDCl_3): δ 7.43 (dd, J = 7.5 Hz, J = 1 Hz, 1H), 7.12 (dd, J = 7.5 Hz, J = 1 Hz, 1H), 7.04 (t, J = 7.8 Hz, 1H), 5.63–5.60 (m, 1H), 5.41–5.39 (m, 1H), 5.09 (dd, J = 6.5 Hz, J = 5 Hz, 2H), 4.60 (d, J = 4.5 Hz, 1H), 4.30 (dd, J = 12 Hz, J = 4.5 Hz, 1H), 4.20 (dd, J = 11.5 Hz, J = 3 Hz, 1H), 3.62 (s, 3H), 3.30 (s, 1H), 2.83 (d, J = 5.5 Hz, 1H), 2.68–2.63 (m, 1H), 2.39–2.34 (m, 1H), 2.32 (s, 3H), 1.15 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 155.3, 135.9, 135.4, 131.1, 130.9, 128.2, 124.2, 121.9, 99.6, 79.5, 67.8, 57.6, 48.0, 37.9, 32.6, 29.4, 24.3, 18.3; HRMS-ESI Calcd for $\text{C}_{18}\text{H}_{27}\text{O}_4$ [$\text{M} + \text{H}^+$]: 307.1909; Found: 307.1908.

Synthesis of Compound 5' and 5:

To a solution of compound **6** (1.50 g, 4.90 mmol), diethyl phosphonoacetic acid (1.92 g, 9.80 mmol) and DMAP (1.79 g, 14.7 mmol) in CH_2Cl_2 (50 mL) was added EDCI (1.88 g, 9.8 mmol) at 0

°C, and the mixture was stirred at room temperature for 18h. The reaction was quenched with a saturated solution of NaHCO₃ (30 mL). The aqueous layer was extracted with CH₂Cl₂ (3×100 mL), washed with a saturated solution of brine (3×10 mL). The combined organic layer was dried over Na₂SO₄, filtered, and solvent was removed under vacuum, and the residue was purified by flash chromatography (EtOAc/hexane = 1/1) to afford compound **5'** (1.95 g) as colorless oil in 82% yield. R_f = 0.21 (silica gel, EtOAc/hexanes = 1/1); ¹H NMR (500 MHz, CDCl₃): δ 7.15 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.95 (t, *J* = 7.7 Hz, 1H), 5.68-5.65 (m, 1H), 5.37 (d, *J* = 10 Hz, 1H), 5.06-5.03 (m, 2H), 4.96 (d, *J* = 11.1 Hz, 1H), 4.80 (d, *J* = 11.2 Hz, 1H), 4.52 (d, *J* = 8 Hz, 1H), 4.25-4.00 (m, 4H), 3.64 (s, 3H), 2.85-2.81 (m, 3H), 2.42-2.38 (m, 1H), 2.30 (s, 3H), 2.22 (d, *J* = 8 Hz, 1H), 1.27-1.23 (m, 6H), 1.05 (s, 3H), 0.55 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 165.72, 165.67, 156.1, 135.5, 134.0, 131.0, 130.9, 127.8, 123.5, 121.6, 99.4, 77.1, 70.9, 62.58, 62.53, 62.48, 57.4, 46.9, 38.0, 34.9, 33.8, 31.0, 28.2, 25.5, 18.4, 16.3, 16.2; HRMS-ESI Calcd for C₂₄H₃₈O₈P [M + H⁺]: 485.2304; Found: 485.2298.

To a solution of compound **5'** (760 mg, 1.57 mmol), 4-methylbenzenesulfonyl azide (466 mg, 2.36 mmol) in CH₂Cl₂ (15 mL) was added DBU (290 μL, 1.88 mmol) slowly at 0 °C, the mixture was stirred at this temperature for 2h, quenched with a saturated solution of NaHCO₃ (10 mL). The aqueous layer was extracted with CH₂Cl₂ (3×100 mL), washed with a saturated solution of brine (3×10 mL). The combined organic layer was dried over Na₂SO₄, filtered, and solvent was removed under vacuum, and the residue was purified by flash chromatography (EtOAc/hexane = 1/4 to 1/1) to afford compound **5** (652 mg) as colorless oil in 81% yield. R_f = 0.32 (silica gel, EtOAc/hexanes = 1/1); ¹H NMR (500 MHz, CDCl₃): δ 7.11 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 5.67-5.65 (m, 1H), 5.37 (d, *J* = 10 Hz, 1H), 5.08-5.03 (m, 3H), 4.79 (d, *J* = 11 Hz, 1H), 4.53 (s, 1H), 4.05-4.00 (m, 2H), 3.95-3.90 (m, 2H), 3.63 (s, 3H), 2.85 (dd, *J* = 18 Hz, *J* = 3.7 Hz, 1H), 2.40 (d, *J* = 18 Hz, 1H), 2.28 (s, 3H), 1.24-1.22 (m, 6H), 1.04 (s, 3H), 0.57 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 163.5, 163.4, 156.1, 135.5, 133.9, 130.9, 130.7, 127.6, 123.5, 121.5, 99.4, 77.0, 71.1, 63.45, 63.40, 63.32, 63.28, 57.4, 47.0, 38.0, 31.3, 28.2, 25.3, 18.4, 16.00, 15.98, 15.95, 15.92; HRMS-ESI Calcd for C₂₄H₃₆N₂O₈P [M + H⁺]: 511.2209; Found: 511.2199.

Synthesis of Compound 4:

To a solution of compound **5** (628 mg, 1.23 mmol) in anhydrous benzene (12 mL) at rt was added rhodium(II) acetate dimer (5.5 mg, 0.0123 mmol). The mixture was immediately immersed in a preheated oil bath (80 °C) and refluxed for 2h. After cooling the solvent was removed under vacuum, and the residue was purified by flash chromatography (EtOAc/hexane = 1/1) to afford compound **4** (360 mg) as white solid in 60% yield. R_f = 0.31 (silica gel, EtOAc/hexanes = 1/1); ¹H NMR (500 MHz, CDCl₃): δ 7.14-7.10 (m, 2H), 6.99 (t, *J* = 7.7 Hz, 1H), 5.75-5.72 (m, 1H), 5.56 (d, *J* = 13.2 Hz, 1H), 5.22 (d, *J* = 10.1 Hz, 1H), 5.13 (d, *J* = 4.8 Hz, 1H), 5.10 (d, *J* = 4.8 Hz, 1H), 4.84 (d, *J* = 18.6 Hz, 1H),

4.75 (s, 1H), 4.36-4.26 (m, 4H), 3.83 (d, $J=13.2$ Hz, 1H), 3.70 (s, 3H), 2.93 (d, $J=18.0$ Hz, 1H), 2.31 (d, $J=6.3$ Hz, 1H), 2.27 (s, 3H), 1.38 (t, $J=7.1$ Hz, 6H), 1.08 (s, 3H), 0.25 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 169.4, 169.3, 155.9, 134.3, 131.9, 131.8, 131.1, 127.4, 124.4, 120.8, 99.7, 90.14, 90.07, 76.6, 75.1, 73.2, 63.43, 63.38, 62.85, 62.80, 57.5, 47.1, 38.2, 27.6, 27.2, 25.6, 18.7, 16.55, 16.50, 16.45; HRMS-ESI Calcd for $\text{C}_{24}\text{H}_{36}\text{O}_8\text{P} [\text{M} + \text{H}^+]$: 483.2148; Found: 483.2136.

Synthesis of Compound 3' and 3:

To a solution of compound **4** (140 mg, 0.29 mmol) in THF (10 mL) was added $t\text{BuOK}$ (1 M solution in THF, 290 μL , 0.29 mmol) at 0 $^\circ\text{C}$, after stirring at this temperature for 0.5h, paraformaldehyde (87 mg, 2.9 mmol) was added quickly as a solid and the mixture was stirred for 0.5h at 0 $^\circ\text{C}$. The reaction was quenched with a saturated solution of NH_4Cl (10 mL). The aqueous layer was extracted with EtOAc (3×10 mL), washed with a saturated solution of brine (2×10 mL). The combined organic layer was dried over Na_2SO_4 , filtered, and solvent was removed under vacuum, and the residue was purified by flash chromatography ($\text{EtOAc}/\text{hexane} = 1/3$) to afford compound **3'** (99 mg) as colorless oil in 95% yield. $R_f = 0.85$ (silica gel, $\text{EtOAc}/\text{hexanes} = 1/1$); ^1H NMR (500 MHz, CDCl_3): δ 7.15-7.11 (m, 2H), 6.97 (t, $J = 7.7$ Hz, 1H), 5.80-5.76 (m, 1H), 5.48 (s, 1H), 5.30 (d, $J = 10$ Hz, 1H), 5.19-5.17 (m, 2H), 5.00 (d, $J = 5.5$ Hz, 1H), 4.87 (d, $J = 12.6$ Hz, 1H), 4.76 (s, 3H), 4.13 (d, $J = 12.6$ Hz, 1H), 3.60 (s, 3H), 2.79 (d, $J = 17.6$ Hz, 1H), 2.59 (dd, $J = 17.6$ Hz, $J = 5.1$ Hz, 1H), 2.30 (s, 3H), 1.12 (s, 3H), 0.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 167.2, 156.3, 153.9, 134.4, 132.7, 131.9, 131.2, 127.2, 123.8, 121.2, 101.2, 99.8, 87.7, 75.8, 57.7, 47.3, 37.4, 27.6, 27.5, 27.0, 18.6; HRMS-ESI Calcd for $\text{C}_{21}\text{H}_{26}\text{O}_5\text{Na} [\text{M} + \text{Na}^+]$: 381.1678; Found: 381.1674.

To a solution of compound **3'** (99 mg, 0.27 mmol) in CH_2Cl_2 (15 mL) was added trifluoroacetic acid (90 μL , 1.20 mmol) at 0 $^\circ\text{C}$, the mixture was stirred for 0.5h at this temperature and quenched with Et_3N (1 mL), filtered, and solvent was removed under vacuum, the residue was purified by flash chromatography ($\text{EtOAc}/\text{hexane} = 1/3$) to afford compound **3** (78 mg) as white solid in 90% yield. $R_f = 0.82$ (silica gel, $\text{EtOAc}/\text{hexanes} = 1/1$); ^1H NMR (500 MHz, CDCl_3): δ 7.07 (d, $J = 7.3$ Hz, 1H), 7.02 (d, $J = 8.1$ Hz, 1H), 6.79 (t, $J = 7.7$ Hz, 1H), 6.28 (s, 1H), 5.80-5.77 (m, 1H), 5.38 (d, $J = 1.4$ Hz, 1H), 5.34 (d, $J = 10.1$ Hz, 1H), 4.72 (s, 1H), 4.63 (d, $J = 12.5$ Hz, 1H), 4.40 (d, $J = 12.5$ Hz, 1H), 2.59 (t, $J = 2.5$ Hz, 2H), 2.23 (s, 3H), 1.10 (s, 3H), 0.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 165.5, 153.5, 152.7, 134.5, 130.5, 126.7, 126.4, 126.3, 120.5, 120.4, 104.8, 83.8, 76.7, 46.7, 37.0, 28.5, 27.0, 26.4, 16.4; HRMS-ESI Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{Na} [\text{M} + \text{Na}^+]$: 337.1416; Found: 337.1412.

Synthesis of Compound 2a, 2b and 2c:

To a solution of compound **3** (460 mg, 1.46 mmol) in AcOH (10 mL) was added $\text{Pb}(\text{OAc})_4$ (3.90 g, 8.80 mmol) at 0°C . The reaction was stirred for 5 min at 0°C , the reaction was worked by filtration off the precipitate and dissolved with EtOAc (250 mL), washed with a saturated solution of NaHCO_3 (3×100 mL). The aqueous layer was extracted by EtOAc (350 mL), the combined organic layer was dried with Na_2SO_4 , filtered, and solvent was removed under *vacuum* to afford the crude product (480 mg) as yellow solid which was carried onto the next reaction without any further purification.

The crude product was dissolved in toluene (60 mL), and the mixture was heated to 145°C in a sealed tube for 24 h. The solvent was removed under *vacuum*, and the residue was purified by flash chromatography ($\text{EtOAc}/\text{hexane} = 1/10$ to $1/5$) to afford the D-A product **2a** (150 mg), **2b** (65 mg), **2c** (198 mg) in 76% overall yield.

Compound **2a** (28%), white solid, $R_f = 0.85$ (silica gel, $\text{EtOAc}/\text{hexanes} = 1/2$); ^1H NMR (500 MHz, CDCl_3): δ 6.81 (t, $J = 7.1$ Hz, 1H), 6.04 (d, $J = 8.0$ Hz, 1H), 5.55–5.48 (m, 2H), 4.83 (dd, $J = 11.8$ Hz, $J = 1.4$ Hz, 1H), 4.63 (d, $J = 11.2$ Hz, 1H), 3.96 (t, $J = 2.8$ Hz, 1H), 3.90 (s, 1H), 3.00 (dd, $J = 14.6$ Hz, $J = 3.2$ Hz, 1H), 2.50 (d, $J = 17.5$ Hz, 1H), 2.26 (dd, $J = 17.8$ Hz, $J = 4.7$ Hz, 1H), 2.00 (s, 3H), 1.77 (d, $J = 14.6$ Hz, 1H), 1.58 (s, 3H), 1.14 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 197.1, 170.0, 168.0, 140.7, 136.7, 123.6, 120.9, 89.1, 83.9, 80.0, 68.6, 60.7, 41.2, 40.7, 36.3, 31.3, 31.0, 28.1, 21.7, 20.1, 19.9; HRMS-ESI Calcd for $\text{C}_{21}\text{H}_{25}\text{O}_6$ [$\text{M} + \text{H}^+$]: 373.1651; Found: 373.1641.

Compound **2b** (12%), white solid, $R_f = 0.80$ (silica gel, $\text{EtOAc}/\text{hexanes} = 1/2$); ^1H NMR (500 MHz, CDCl_3): δ 6.78 (t, $J = 7.2$ Hz, 1H), 6.06 (d, $J = 8.0$ Hz, 1H), 5.55–5.48 (m, 2H), 4.90 (d, $J = 11.8$ Hz, 1H), 4.64 (d, $J = 11.7$ Hz, 1H), 3.99 (t, $J = 1.7$ Hz, 1H), 3.93 (s, 1H), 3.19 (dd, $J = 15.2$ Hz, $J = 3.2$ Hz, 1H), 2.54 (d, $J = 17.7$ Hz, 1H), 2.25 (dd, $J = 17.8$ Hz, $J = 5.0$ Hz, 1H), 1.99 (s, 3H), 1.90 (d, $J = 15.2$ Hz, $J = 2.7$ Hz, 1H), 1.52 (s, 3H), 1.13 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 201.0, 169.5, 168.8, 139.7, 136.5, 122.4, 120.9, 89.7, 83.7, 81.5, 68.7, 61.3, 41.8, 39.4, 36.4, 31.3, 31.1, 28.0, 21.9, 20.1, 18.8; HRMS-ESI Calcd for $\text{C}_{21}\text{H}_{25}\text{O}_6$ [$\text{M} + \text{H}^+$]: 373.1651; Found: 373.1648.

Compound **2c** (36%), white solid, $R_f = 0.76$ (silica gel, $\text{EtOAc}/\text{hexanes} = 1/2$); ^1H NMR (500 MHz, CDCl_3): δ 6.66 (dd, $J = 8.2$ Hz, $J = 7.0$ Hz, 1H), 6.31 (dd, $J = 8.3$ Hz, $J = 0.8$ Hz, 1H), 5.58–5.55 (m, 1H), 5.48 (dd, $J = 10.0$ Hz, $J = 2.1$ Hz, 1H), 4.72 (d, $J = 12.3$ Hz, 1H), 4.46 (s, 1H), 4.13 (dd, $J = 12.3$ Hz, $J = 1.2$ Hz, 1H), 4.03 (t, $J = 6.0$ Hz, 1H), 3.77–3.73 (m, 1H), 2.98 (dd, $J = 14.5$ Hz, $J = 4.7$ Hz, 1H), 2.13 (s, 3H), 2.09 (d, $J = 15.0$ Hz, 1H), 1.87 (dd, $J = 17.6$ Hz, $J = 5.3$ Hz, 1H), 1.62 (s, 3H), 1.15 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ : 203.9, 169.8, 168.4, 141.7, 135.8, 123.2, 121.8, 89.4, 89.2, 81.2, 69.0, 59.5, 41.6, 40.0, 36.7, 31.4, 26.9, 24.8, 21.8, 20.0; HRMS-ESI Calcd for

C₂₁H₂₅O₆ [M + H⁺]: 373.1651; Found: 373.1650.

Synthesis of Compound 12' and 12:

To a solution of compound **2c** (80 mg, 0.21 mmol) in CCl₄ (10 mL) was added NBS (58 mg, 0.32 mmol) and benzoyl peroxide (5 mg, 0.32 mmol) at room temperature, the mixture was refluxing for 2h, cooled to room temperature, solvent was removed under vacuum, and the residue was purified by flash chromatography (EtOAc/hexane = 1/15) to afford compound **12'** (88 mg) as white solid in 90% yield. *R_f* = 0.55 (silica gel, EtOAc/hexanes = 1/5); ¹H NMR (500 MHz, CDCl₃): δ 6.66 (t, *J* = 8.0 Hz, 1H), 6.50 (s, 1H), 6.48 (d, *J* = 8.1 Hz, 1H), 5.75 (t, *J* = 8.7 Hz, 1H), 5.53 (dd, *J* = 10.1 Hz, *J* = 2.2 Hz, 1H), 4.85 (d, *J* = 12.6 Hz, 1H), 4.70 (d, *J* = 12.6 Hz, 1H), 4.44 (s, 1H), 4.02 (s, 1H), 2.95 (dd, *J* = 14.5 Hz, *J* = 3.9 Hz, 1H), 2.13 (s, 3H), 2.06 (d, *J* = 14.0 Hz, 1H), 1.65 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 204.1, 169.8, 167.5, 141.5, 137.7, 126.7, 123.5, 89.5, 88.6, 81.3, 68.5, 59.2, 46.3, 45.4, 39.9, 37.1, 31.3, 24.6, 22.1, 21.9, 19.9; HRMS-ESI Calcd for C₂₁H₂₄BrO₆ [M + H⁺]: 451.0756; Found: 451.0755.

To a solution of compound **12'** (88 mg, 0.19 mmol) in benzene (10 mL) was added TEMPO (304 mg, 1.95 mmol) and tri-*n*-butyltin hydride (434 μL, 1.56 mmol) in benzene (10 mL) over 0.5h at 80 °C, the mixture was refluxing for 2h, then cooled to room temperature and filtered through a plug of silica gel, solvent was removed under vacuum, the residue was purified by flash chromatography (EtOAc/hexane = 1/20) to afford compound **12** (77 mg) as white solid in 75% yield. *R_f* = 0.65 (silica gel, EtOAc/hexanes = 1/5); ¹H NMR (500 MHz, CDCl₃): δ 6.67 (t, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 7.7 Hz, 1H), 6.23 (dd, *J* = 10.5 Hz, *J* = 1.2 Hz, 1H), 6.05 (s, 1H), 5.47 (dd, *J* = 10.5 Hz, *J* = 1.9 Hz, 1H), 4.78 (d, *J* = 12.5 Hz, 1H), 4.74 (d, *J* = 12.8 Hz, 1H), 4.32 (s, 1H), 4.03 (t, *J* = 6.0 Hz, 1H), 2.97 (dd, *J* = 14.5 Hz, *J* = 4.7 Hz, 1H), 2.13 (s, 3H), 2.07 (d, *J* = 14.5 Hz, 1H), 1.64 (s, 3H), 1.56 (s, 3H), 1.51-1.26 (m, 8H), 1.17 (s, 3H), 1.13 (s, 6H), 1.06 (s, 6H), 1.04 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 204.5, 169.9, 168.2, 141.1, 134.5, 125.5, 124.7, 89.9, 88.5, 81.7, 76.2, 67.2, 60.6, 59.7, 59.1, 46.2, 40.8, 40.4, 39.9, 37.2, 34.1, 33.8, 31.5, 24.8, 23.6, 21.9, 21.84, 21.83, 20.4, 20.1, 17.1; HRMS-ESI Calcd for C₃₀H₄₂NO₇ [M + H⁺]: 528.2961; Found: 528.2951.

Synthesis of Compound 13' and 13:

To a solution of compound **12** (60 mg, 0.113 mmol) in THF (2 mL) and water (2 mL) was

added acidic acid (6 mL) and Zinc powder (145 mg, 2.26 mmol). The mixture was heated at 70°C for 2h, and then cooled to room temperature. The mixture was diluted with 20 mL CH₂Cl₂ and a solution of NaOH (350 mg) in H₂O (15 mL) was added to neutralize the solution. The mixture was extracted with CH₂Cl₂, and the combined organic layers were washed with brine, dried with Na₂SO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica (EtOAc/hexane = 1/3) to afford compound **13'** (38 mg) as white solid in 85% yield. R_f = 0.45 (silica gel, EtOAc/hexanes = 1/2); ¹H NMR (500 MHz, CDCl₃): δ 6.65 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 8.2 Hz, 1H), 6.03 (s, 1H), 5.56 (dd, *J* = 10.1 Hz, *J* = 1.9 Hz, 1H), 5.49 (d, *J* = 10.2 Hz, 1H), 4.73 (d, *J* = 12.6 Hz, 1H), 4.68 (d, *J* = 12.7 Hz, 1H), 4.28 (s, 1H), 4.02 (t, *J* = 5.3 Hz, 1H), 2.96 (dd, *J* = 14.5 Hz, *J* = 4.7 Hz, 1H), 2.13 (s, 3H), 2.07 (d, *J* = 14.5 Hz, 1H), 1.64 (s, 3H), 1.14 (s, 3H), 1.13 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 204.5, 169.8, 168.2, 141.4, 136.8, 127.8, 124.4, 89.6, 88.0, 81.3, 67.0, 66.9, 59.0, 46.4, 40.0, 36.9, 31.2, 24.8, 22.0, 21.8, 20.0; HRMS-ESI Calcd for C₂₁H₂₅O₇ [M + H]⁺: 389.1600; Found: 389.1592.

Synthesis of Compound 14:

To Lindlar catalyst (5 mg) in dried CH₃OH (2 mL) was added compound **13** (25 mg, 0.080 mmol) in THF (2 mL) at room temperature under H₂ atmosphere. The reaction was stirred at room temperature for 2h and filtered through a plug of silica gel, washed with EtOAc (20 mL). The solvent was removed under vacuum to afford crude product compound **14** (24 mg) as white solid in 92 % yield. R_f = 0.50 (silica gel, EtOAc/hexanes = 1/2); ¹H NMR (500 MHz, CDCl₃): δ 5.92 (s, 1H), 5.50 (d, *J* = 10.1 Hz, 1H), 5.42 (d, *J* = 10.2 Hz, 1H), 4.68 (d, *J* = 12.7 Hz, 1H), 4.55 (d, *J* = 12.7 Hz, 1H), 4.25 (s, 1H), 2.99 (d, *J* = 14.3 Hz, 1H), 2.42 (d, *J* = 6.9 Hz, 1H), 2.14-1.79 (m, 7H), 1.22 (d, *J* = 7.1 Hz, 3H), 1.11 (s, 3H), 1.08 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ: 215.6, 169.8, 136.8, 128.0, 86.4, 85.2, 67.4, 67.0, 60.4, 52.8, 47.4, 6.9, 36.6, 33.1, 31.5, 29.7, 28.2, 23.5, 21.0, 20.1, 18.7, 14.2, 12.5; HRMS-ESI Calcd for C₁₉H₂₃O₅ [M + H⁺]: 333.1702; Found: 333.1690.

To a solution of compound **14** (20 mg, 0.060 mmol) in CH_2Cl_2 (6 ml) at 0 °C was added DMP (51 mg, 0.12 mmol), the mixture was stirred at room temperature for 1h, diluted with CH_2Cl_2 (20 ml), quenched with NaHCO_3 (5 ml) and NaS_2O_3 (5 ml), then filtered through a plug of silica gel, washed with CH_2Cl_2 (20 mL). The solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1/5) to afford the product to afford **C16-epi-Maoecrystal V** (18 mg) as white solid in 88 % yield. R_f = 0.25 (silica gel, EtOAc/hexanes = 1/5); ^1H NMR (500 MHz, CDCl_3): δ 6.67 (d, J = 10.2 Hz, 1H), 5.95 (d, J = 10.1 Hz, 1H), 4.65 (d, J = 12.2 Hz, 1H), 4.53 (s, 1H), 4.14 (d, J = 12.2 Hz, 1H), 2.96 (dd, J = 14.8, 2.8 Hz, 1H), 2.58 – 2.38 (m, 1H), 2.33 – 2.15 (m, 1H), 2.15 – 2.05 (m, 2H), 2.03 (s, 1H), 1.94 – 1.74 (m, 3H), 1.31 (s, 3H), 1.25 (s, 3H), 1.22 (d, J = 7.2 Hz, 3H). ^1H NMR (500 MHz, Pyridine- D_5): δ 6.62 – 6.49 (m, 1H), 5.99 (d, J = 10.1 Hz, 1H), 4.79 (s, 1H), 4.73 (d, J = 12.3 Hz, 1H), 4.31 (d, J = 12.2 Hz, 1H), 3.13 – 2.96 (m, 1H), 2.39 (d, J = 7.1 Hz, 1H), 2.31 – 2.09 (m, 2H), 1.95 (d, J = 14.7 Hz, 1H), 1.86 (s, 1H), 1.64 (m, 2H), 1.22 (s, 3H), 1.07 (s, 5H), 1.05 (s, 1H). ^{13}C NMR (126 MHz, Pyr) δ 211.85, 194.80, 169.41, 156.87, 127.18, 85.90, 85.67, 69.66, 55.83, 52.73, 46.15, 38.52, 33.62, 30.70, 28.26, 23.59, 18.47, 18.42, 12.61. HRMS-ESI Calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5$ [$\text{M} + \text{H}^+$]: 331.1545; Found: 331.1542.

Synthesis of Maoecrystal V:

To a solution of **C16-epi-Maoecrystal V** (4 mg, 0.012 mmol) in toluene (1 mL) at was added DBU (4 μL , 0.028 mmol), the mixture was stirred at 100 °C for 1h, cooled to room temperature and purified by flash chromatography on silica gel (EtOAc/hexane = 1/5) to afford a 1 : 1.1 mixture of **C16-epi-Maoecrystal V** and **Maoecrystal V** (3.8 mg) as white solid, the mixture was taken up with 5 mL of hot hexane, cooled to room temperature and **Maoecrystal V** (0.7 mg) was crystallized after 0.5h. Repeated the sequential crystallization for five times provided **Maoecrystal V** (1.9 mg) as white solid in 48% yield together with 1.8 mg of starting material (90% brsm). R_f = 0.25 (silica gel, EtOAc/hexanes = 1/5); ^1H NMR (500 MHz, CDCl_3) δ 6.66 (d, J = 10.2 Hz, 1H), 5.96 (d, J = 10.1 Hz, 1H), 4.64 (d, J = 12.2 Hz, 1H), 4.45 (s, 1H), 4.14 (d, J = 12.2 Hz, 1H), 3.20 (dd, J = 14.6, 4.7 Hz, 1H), 2.41 – 2.29 (m, 1H), 2.26 – 2.19 (m, 1H), 2.19 – 1.92 (m, 3H), 1.71 (d, J = 14.7 Hz, 1H), 1.68 – 1.60 (m, 1H), 1.32 (s, 3H), 1.27 (d, J = 7.4 Hz, 3H), 1.24 (s, 3H). ^1H NMR (500 MHz, Pyridine- D_5): δ 6.54 (d, J = 10.1 Hz, 1H), 5.99 (d, J = 10.1 Hz, 1H), 4.73 (d, J = 12.3 Hz, 1H), 4.66 (s, 1H), 4.31 (d, J = 12.3 Hz, 1H), 3.29 (dd, J = 14.4, 4.7 Hz, 1H), 2.36 – 2.25 (m, 1H), 2.25 – 2.02 (m, 3H), 1.89 (s, 1H),

1.77 (d, $J = 14.1$ Hz, 2H), 1.49 (dd, $J = 23.3, 9.7$ Hz, 1H), 1.22 (s, 3H), 1.09 (d, $J = 7.4$ Hz, 3H), 1.06 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (126 MHz, Pyridine- D_5) δ 211.67, 194.70, 169.50, 156.68, 127.30, 85.60, 84.73, 69.57, 57.07, 52.51, 48.47, 38.38, 34.98, 33.07, 30.52, 30.03, 18.80, 18.44, 18.34, 15.02. HRMS-ESI Calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5$ [$\text{M} + \text{H}^+$]: 331.1545; Found: 331.1541.

NMR Spectra for the Synthesized Compounds

NAME GJX-ASC-141
EXPNO 1
PROCNO 1
Date_ 20091031
Time 20.15
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 57
DM 48.400 usec
DE 6.00 usec
TE 304.5 K
D1 1.00000000 sec
D11 1
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300079 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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6.9983
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5.8747
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5.8623
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3.1911
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1.2527

NAME GJX-ASC-141
EXPNO 1
PROCNO 1
Date_ 20091031
Time 20.20
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 31446.540 Hz
FIDRES 0.3059672 Hz
AQ 0.3210771 sec
RG 14384
DM 15.9500 usec
DE 6.50 usec
TE 305.7 K
D1 2.00000000 sec
D11 0.93000000 sec
TDO 1

===== CHANNEL f1 =====
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P1 10.00 usec
PL1 3.50 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
MPC2 80.00 usec
PL2 -0.79 dB
PL2W 25.30924988 W
SFO2 500.1330885 MHz
SI 32768
SF 125.7709936 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

210.405
171.445
154.814
137.095
132.380
131.653
131.243
125.540
123.683
123.023
99.695
77.250
76.596
76.741
62.914
56.923
52.263
45.966
32.824
27.894
27.763
17.752

NAME GJX-ASC-191-up
EXPNO 1
PROCNO 1
Date_ 20091208
Time 20.37
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 114
DM 48.400 usec
DE 6.00 usec
TE 302.7 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300082 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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7.2698
7.1288
7.1276
7.1141
7.1127
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7.0356
7.0202
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5.6140
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5.6020
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2.9350
2.9320
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0.8640

11a

NAME GJX-ASC-189-up
EXPNO 2
PROCNO 1
Date_ 20091207
Time 21.34
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDC13
NS 152
DS 0
SWH 31444.541 Hz
FIDRES 0.938672 Hz
AQ 0.5210771 sec
RG 14384
DM 39.800 usec
DE 6.00 usec
TE 302.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.00 dB
PL1W 58.41413879 W
SFO1 125.7579936 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 13C
PCPD2 80.00 usec
PL2 0.00 dB
PL2W 17.27 dB
PL2W 25.30924988 W
PL2W 0.39562091 W
SFO2 500.1330885 MHz
SI 32768
SF 125.7579936 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

176.182
154.814
135.761
135.476
131.004
130.779
129.855
129.877
121.085
99.490
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76.753
76.114
57.211
51.901
51.453
37.477
29.648
29.213
17.877

11a

NAME GLX-ASC-338
EXPNO 1
PROCNO 1
Date_ 20100818
Time 14:14
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.313264 Hz
AQ 1.5862696 sec
RG 181
SW 48.400 usec
DE 6.00 usec
TE 301.4 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 10.00 usec
PL1 -0.19 dB
PL1W 25.30924988 W
SFO1 500.130005 MHz
SI 32768
SF 500.130005 MHz
WDW DE
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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7.147
7.130
7.094
7.075
6.957
6.942
6.926
5.681
5.676
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5.347
5.061
5.057
5.043
5.032
4.963
4.941
4.798
4.775
4.517
4.501
4.051
4.037
4.021
4.007
3.993
3.990
3.638
2.853
2.805
2.817
2.381
2.380
2.295
2.220
2.207
1.270
1.260
1.255
1.250
1.241
1.236
1.049
0.550

0.999
1.007
1.000
0.962
1.044
2.051
1.013
0.901
1.022
0.660
3.976
2.983
3.025
1.017
3.052
1.092
6.508
2.917
2.909

NAME GLX-ASC-338-13C
EXPNO 2
PROCNO 1
Date_ 20100917
Time 18:53
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 278
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5310771 sec
RG 8192
SW 15.900 usec
DE 6.00 usec
TE 306.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.770936 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 13C
PCPD2 80.00 usec
PL2 -0.19 dB
PL12 17.27 dB
PL1W 25.30924988 W
PL1W 0.3962090 W
SFO2 500.132005 MHz
SI 32768
SF 125.7577925 MHz
WDW DE
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

NAME GTX-ASC-340-en
EXPNO 1
PROCNO 1
Date_ 20100820
Time 13.04
INSTRUM APT00
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.586056 sec
RG 90.5
DM 48.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.79 dB
PL1W 25.30924888 W
SFO1 500.1320885 MHz
SI 32768
SF 500.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

7.2700
7.1386
7.1224
7.1135
7.0987
6.9929
6.9776
6.9622
5.7482
5.7369
5.7281
5.7169
5.5626
5.5362
5.2202
5.2000
5.1333
5.1238
5.1037
5.0942
4.8422
4.8050
4.7546
4.3555
4.3495
4.3405
4.3352
4.3208
4.3056
4.2989
4.2915
4.2851
4.2777
4.2709
4.2657
4.2639
4.2551
3.8316
3.8052
3.6950
2.9341
2.8980
2.3131
2.3015
2.2698
1.3787
1.3646
1.3505
1.0833
0.2530

NAME GTX-ASC-340-en
EXPNO 1
PROCNO 1
Date_ 20100820
Time 14.17
INSTRUM APT00
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 31446.947 Hz
FIDRES 0.358672 Hz
AQ 0.321771 sec
RG 182
DM 19.800 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.33000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 0.00 dB
PL1W 0.00000000 W
SFO1 125.7597936 MHz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 13C
PCPD2 80.00 usec
PL2 -5.79 dB
PL12 17.27 dB
PL1W 25.30924888 W
PL12W 0.39542091 W
SFO2 100.6261155 MHz
SI 32768
SF 125.7577048 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

169.392
169.321
155.937
134.284
131.889
131.794
131.110
127.397
124.391
120.770
99.686
90.141
90.066
77.257
77.002
76.748
76.573
75.142
73.219
63.432
63.378
62.879
57.789
57.673
47.126
38.194
27.566
27.230
25.565
18.667
16.545
16.497
16.448

NAME GTX-ASC-341
EXPNO 2
PROCNO 1
Date_ 20100820
Time 19.58
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1243
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 8192
DW 15.900 usec
DE 6.00 usec
TE 300.1 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.3094988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577858 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

167.198
156.333
153.874
134.357
132.676
131.854
131.232
127.235
123.751
121.218
106.216
99.775
87.674
77.258
77.003
76.749
75.832
57.671
47.285
37.379
27.637
27.459
26.962
18.561

NAME GTX-ASC-441
EXPNO 4
PROCNO 1
Date_ 20100820
Time 19.58
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1243
DS 0
SWH 30036.029 Hz
FIDRES 0.916444 Hz
AQ 0.5454519 sec
RG 8192
DW 14.450 usec
DE 6.00 usec
TE 300.1 K
D1 2.0000000 sec
D11 0.0300000 sec
D12 0.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.3094988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577858 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

134.32
131.86
127.20
123.75
121.20
106.41
99.75
87.70
75.77
57.71
27.56
27.46
26.93
18.60

NAME GZX-ASC-345-tm
EXPNO 1
PROCNO 1
Date_ 20100902
Time 19.27
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 35.2
RW 48.400 usec
DE 6.00 usec
TE 301.2 K
D1 1.00000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 1H
P1 10.00 usec
PL1 -5.70 dB
PL1W 25.30924988 W
SFO1 500.1330005 MHz
SI 32768
SF 500.1330005 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

NAME GZX-ASC-345-tm
EXPNO 2
PROCNO 1
Date_ 20100902
Time 19.38
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 183
DS 0
SWH 31446.54 Hz
FIDRES 0.999672 Hz
AQ 0.521071 sec
RG 8192
RW 15.900 usec
DE 6.00 usec
TE 303.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7577964 MHz

----- CHANNEL f2 -----
CPOPG2 waltz16
NUC2 1H
PCPG2 80.00 usec
PL2 -0.79 dB
PL12 11.27 dB
PL1W 25.30924988 W
SFO2 500.1330005 MHz
SI 32768
SF 125.7577964 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

NAME GZX-ASC-345-tm
EXPNO 4
PROCNO 1
Date_ 20100902
Time 19.33
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 84
DS 4
SWE 30030.039 Hz
FIDRES 0.516444 Hz
AQ 0.5456539 sec
RG 16384
DM 16.450 usec
DE 6.50 usec
TE 302.2 K
CHET2 145.0000000
D1 2.000000000 sec
D2 0.00344828 sec
D12 0.000000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 13C
P1 10.00 usec
P2 20.00 usec
PL1 3.00 dB
PL1W 58.41413879 M
SFO1 125.7573643 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
P3 10.00 usec
P4 20.00 usec
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 M
SFO2 500.1320002 MHz
SFO12 500.1320002 MHz
SI 32768
SF 125.7573643 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

134.56
130.83
126.81
120.43
120.47
104.81
83.83
77.66

28.45
27.00
26.43
16.51

NAME GZX-ASC-373-a
EXPNO 1
PROCNO 1
Date_ 20100902
Time 16.53
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWE 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860496 sec
RG 128
DM 48.400 usec
DE 6.50 usec
TE 303.1 K
D1 1.000000000 sec
TD0 1

----- CHANNEL f1 -----
NUC1 1H
P1 10.00 usec
PL1 3.00 dB
PL1W 25.30924988 M
SFO1 500.1320002 MHz
SI 32768
SF 500.1320002 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

7.2702
6.8173
6.8032
6.7877
6.0456
5.5295
5.5212
5.5483
5.5411
5.5322
5.5293
5.5211
5.5075
5.5050
5.4873
5.4828
4.8361
4.8344
4.8126
4.8009
4.8009
4.0025
3.0045
3.0044
3.0578
3.0511
3.0989
3.0065
2.9996
2.9774
2.9705
2.5046
2.4690
2.2632
2.2535
2.2279
2.2178
2.0168
1.7739
1.7695
1.7448
1.7404
1.5838
1.1353
1.1207

NAME GJX-ASC-373-04-B
EXPNO 1
PROCNO 1
DATA_ 20100929
TIME 13.42
INSTRUM APT20
PROBHD 5 mm PABBO 80-
PULPROG zgpg30
TD 32768
SOLVENT CDCl₃
NS 0
DS 0
SWH 10330.578 Hz
FIDRES 0.215264 Hz
AQ 1.5860494 sec
RG 181
DM 48.400 usec
DE 6.00 usec
TE 300.4 K
SI 1.00000000 sec
TDO 0

----- CHANNEL f1 -----
NUC1 13C
P1 10.00 usec
PL1 -0.79 dB
PL1W 20.9094988 M
SFO1 500.130585 MHz
SI 32768
SF 500.130584 MHz
WDW EM
GB 0
LB 0.30 Hz
GB 0
PC 1.00

7.2701
6.7830
6.7592
6.7546
6.0568
6.0409
5.5532
5.5342
5.5253
5.5056
5.4851
4.9015
4.8782
4.6470
4.6236
3.9929
3.9317
3.1961
3.1658
2.5417
2.5061
2.2522
2.2428
2.2168
2.2071
2.0213
1.9932
1.9058
1.8756
1.5244
1.1337
1.1222

7.2701
6.6630
6.6490
6.6467
6.6431
6.6305
6.3089
6.2940
6.2924
5.5794
5.5758
5.5687
5.5656
5.5596
5.5559
5.5513
5.5453
5.4848
5.4807
5.4648
5.4606
4.6986
4.4577
4.4345
4.1132
4.1104
4.1074
4.0366
4.0244
4.0141
3.7707
3.7665
3.7621
3.7355
3.7312
3.7267
3.6760
2.9676
2.9386
2.1305
2.0850
2.0549
1.8707
1.8602
1.8355
1.8249
1.6153
1.6123
1.1593

—203.894

Chemical structure of compound **2c**, a complex polycyclic molecule. The structure features a central ring system with several stereocenters marked by red asterisks (*). A red number 16 is present near one of the stereocenters. The molecule includes a methyl group (Me) and an acetoxy group (AcO).

```

***** CHANNEL f1 *****
MUC1      13C
P1         10.00 usec
PL1        3.00 dB
PL1W       58.4143879 W
SFO1       125.7709936 MHz

***** CHANNEL f2 *****
CPDPGR2   wait16
MUC2      1H
PCPD2     80.00 usec
PL2       -0.79 dB
PL12      17.27 dB
PL2W      25.3092498 W
PL12W     0.3956209 W
SFO2      500.1320005 MHz
SI         32768
SF         125.7577935 MHz
MDW        RM
SSB        0
GB         1.00 H2
LB         0
PC         1.40

```

NAME G7X-A5C-379-tm
EXPNO 1
PROCNO 1
Date_ 20100928
Time 18:19
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
RG 16
DS 0
DMS 10930.578 Hz
FIDRES 0.315244 Hz
AQ 1.5842694 sec
RG 258.1
DM 48.400 usec
DE 6.00 usec
TE 301.1 K
SI 1.00000000 sec
TDO 1

----- CHANNEL f1 -----
NUC1 1H
P1 10.00 usec
PL1 25.30924988 W
SFO1 500.135085 MHz
SI 32768
SF 500.135085 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

7.2701
6.6711
6.6551
6.6413
6.4937
6.4844
6.2337
6.2313
6.2128
6.2103
6.0517
5.4731
5.4693
5.4521
5.4483
4.7811
4.7561
4.7370
4.7114
4.3185
4.0333
4.0229
4.0109
2.9680
2.9587
2.9391
2.9298
2.1270
2.0685
2.0395
1.6385
1.5633
1.5068
1.4954
1.4675
1.4300
1.4056
1.3504
1.3410
1.3201
1.2761
1.2620
1.1899
1.1276
1.0619
1.0428

NAME LCC5889-2010-9-27-2n-Hol
EXPNO 1
PROCNO 1
Date_ 20100927
Time 15.37
INSTRUM AV500
PROBHD 5 mm F4BBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
DS 16
SSB 0
SWH 10330.379 Hz
FIDRES 0.315264 Hz
AQ 1.5860094 sec
RG 362
DM 48.480 usec
DE 6.00 usec
TE 300.7 K
D1 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.130085 MHz
SI 32768
SF 500.130085 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

NAME GDX-ASC-L1-Zn-AcOH
EXPNO 2
PROCNO 1
Date_ 20100927
Time 12.19
INSTRUM AV500
PROBHD 5 mm F4BBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
DS 16
SSB 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.3210771 sec
RG 3231
DM 15.900 usec
DE 6.00 usec
TE 304.8 K
D1 2.00000000 sec
D11 0.23000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 125.757858 MHz
SI 32768
SF 125.757858 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

NAME LCC993-2010-9-28-Sm12
EXPNO 1
PROCNO 1
Date_ 20100928
Time 17:37
INSTRUM spect
PROBHD 5 mm PABBO 50-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 16
DS 4
SWH 10330.578 Hz
F2RES 9.132644 Hz
AQ 1.5860016 sec
RG 90.5
DM 48.400 usec
DE 6.00 usec
TE 300.1 K
SI 1.00000000 sec
DOS 1

===== CHANNEL f1 =====
NUC1 13
P1 10.00 usec
PL1 -0.70 dB
PL1W 25.30924889 W
SFO1 500.1300005 MHz
SF 500.1300005 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

NAME LCC993-2010-9-28-Sm12
EXPNO 1
PROCNO 1
Date_ 20100928
Time 17:47
INSTRUM spect
PROBHD 5 mm PABBO 50-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 16
DS 4
SWH 10144.541 Hz
F2RES 9.201412 Hz
AQ 1.521071 sec
RG 90.5
DM 48.400 usec
DE 6.00 usec
TE 300.1 K
SI 1.00000000 sec
DOS 1

===== CHANNEL f1 =====
NUC1 13
P1 10.00 usec
PL1 -0.70 dB
PL1W 25.30924889 W
SFO1 500.1300005 MHz
SF 500.1300005 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

```

NAME      GJX-maoecrystal v-methyl nci
EXPNO     1
PROCNO    1
DATA_1    20100919
TIME      18.52
INSTRUM    spect
PROBHD     5 mm PABBO BBI
PULPROG    zgpg30
TD         32768
SOLVENT    py
NS         16
DS         0
SWH         10330.578 Hz
FIDRES     0.515344 Hz
AQ         1.5860096 sec
RG         181
DM         48.400 usec
DE         6.00 usec
TE         302.0 K
SI         1.00000000 sec
TDO        1
===== CHANNEL F1 =====
NUC1       1H
P1         10.00 usec
PL1        -0.19 dB
PL1W       20.90924988 W
SFO1       500.1350885 MHz
SF         500.1339972 MHz
WDW         EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00

```

7.2701
6.6780
6.6577
5.9633
5.9430
4.6637
4.6394
4.5320
4.1520
4.1277
2.9765
2.9730
2.9674
2.9467
2.9433
2.9378
2.5031
2.4885
2.4743
2.4601
2.2549
2.2380
2.2331
2.2254
2.2162
2.2085
2.2040
2.1870
2.1137
2.0965
2.0917
2.0655
1.9035
1.8739
1.8581
1.8285
1.8071
1.7864
1.7792
1.7629
1.3141
1.2510

C16-epi-Maoecrystal V (15)
500 MHz, CDCl₃

```

NAME      GJX-maoecrystal v
EXPNO     1
PROCNO    1
DATA_1    20100919
TIME      18.52
INSTRUM    spect
PROBHD     5 mm PABBO BBI
PULPROG    zgpg30
TD         32768
SOLVENT    py
NS         16
DS         0
SWH         10330.578 Hz
FIDRES     0.515344 Hz
AQ         1.5860096 sec
RG         181
DM         48.400 usec
DE         6.00 usec
TE         302.0 K
SI         1.00000000 sec
TDO        1
===== CHANNEL F1 =====
NUC1       1H
P1         10.00 usec
PL1        -0.19 dB
PL1W       20.90924988 W
SFO1       500.1350885 MHz
SF         500.1339972 MHz
WDW         EM
SSB         0
LB         0.30 Hz
GB         0
PC         1.00

```

7.5593
7.1919
6.5664
6.5462
6.0016
5.9814
4.8480
4.7920
4.7464
4.7218
4.3220
4.2976
3.0709
3.0650
3.0415
3.0358
2.3944
2.3803
2.3668
2.2450
2.2262
2.2153
2.2066
2.1965
2.1771
2.1709
2.1575
2.1446
2.1280
2.1154
1.9624
1.9330
1.8612
1.6492
1.6374
1.6205
1.0701
1.0509

C16-epi-Maoecrystal V (15)
500 MHz, pyridine-D₅

C16-*epi*-Maoecrystal V (**15**)
500 MHz, pyridine-D₅, HMQC

C16-*epi*-Maoecrystal V (**15**)
500 MHz, pyridine-D₅, HMBC

C16-*epi*-Maoecrystal V (**15**)
500 MHz, pyridine-D₅, COSY

C16-*epi*-Maoecrystal V (**15**)
500 MHz, pyridine-D₅, REOSY