Supporting Information
for DOI: 10.1055/s-0033-1340597
© Georg Thieme Verlag KG Stuttgart · New York 2014
Supporting Information

A Diels-Alder Approach toward the Scaffolds of Polycyclic Sesquiterpenoids with 2-Pyrone

Hai Tong, and Bo Liu*
Table of Contents

General Procedures ........................................................................................................... 4
Experimental Procedures ................................................................................................. 5
  Compound 5 ................................................................................................................. 5
  Compound 7 ............................................................................................................... 5
  Compound 8’ ............................................................................................................... 6
  Compound 8 ............................................................................................................... 7
  Compound 9 ............................................................................................................... 8
  Compound 10 ............................................................................................................. 9
  Compound 3 .............................................................................................................. 9

Representative Procedure of the Diels-Alder Cycloadditions ...................................... 10

References ....................................................................................................................... 18

Spectra for Compounds .................................................................................................. 19

1H NMR (300 MHz, CDCl3) Spectra for Compound 5 .................................................... 19
13C NMR (75 MHz, CDCl3) Spectra for Compound 5 ...................................................... 19
1H NMR (400 MHz, CDCl3+D2O) Spectra for Compound 7 ........................................... 20
13C NMR (100 MHz, CDCl3) Spectra for Compound 7 .................................................... 20
1H NMR (400 MHz, CDCl3) Spectra for Compound 8’ .................................................... 21
13C NMR (100 MHz, CDCl3) Spectra for Compound 8’ .................................................... 21
1H NMR (300 MHz, CDCl3) Spectra for Compound 8 ..................................................... 22
13C NMR (75 MHz, CDCl3) Spectra for Compound 8 ..................................................... 22
1H NMR (300 MHz, CDCl3) Spectra for Compound 9 ..................................................... 23
13C NMR (75 MHz, CDCl3) Spectra for Compound 9 ..................................................... 23
1H NMR (400 MHz, CDCl3) Spectra for Compound 10 ................................................... 24
13C NMR (100 MHz, CDCl3) Spectra for Compound 10 ................................................... 24
1H NMR (400 MHz, CDCl3) Spectra for Compound 3 ..................................................... 25
13C NMR (100 MHz, CDCl3) Spectra for Compound 3 ..................................................... 25
1H NMR (400 MHz, CDCl3) Spectra for Compound 11a and 11b .................................. 26
13C NMR (100 MHz, CDCl3) Spectra for Compound 11a and 11b .................................. 26
1H NMR (400 MHz, CDCl3) Spectra for Compound 12a ................................................ 27
13C NMR (100 MHz, CDCl3) Spectra for Compound 12a ................................................ 27
13C NMR (100 MHz, CDCl3) Spectra for Compound 12b ................................................ 28
1H NMR (400 MHz, CDCl3) Spectra for Compound 13a and 13b ................................. 29
13C NMR (100 MHz, CDCl3) Spectra for Compound 13a and 13b ................................. 29
1H NMR (400 MHz, CDCl3) Spectra for Compound 14a ................................................ 30
13C NMR (100 MHz, CDCl3) Spectra for Compound 14a ................................................ 30
1H NMR (400 MHz, CDCl3) Spectra for Compound 14b ................................................ 31
13C NMR (100 MHz, CDCl3) Spectra for Compound 14b ................................................ 31
1H NMR (400 MHz, CDCl3+D2O) Spectra for Compound 15a ...................................... 32
13C NMR (100 MHz, CDCl3) Spectra for Compound 15a ................................................ 32
1H NMR (400 MHz, CDCl3) Spectra for Compound 16a ................................................ 33
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 16a .................................................. 33
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 16b .................................................. 34
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 16b .................................................. 34
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 17a .................................................. 35
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 17a .................................................. 35
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 17b .................................................. 36
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 17b .................................................. 36
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 18a and 18b ..................................... 37
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 18a and 18b ..................................... 37
$^1$H NMR (300 MHz, CDCl$_3$) Spectra for Compound 19a .................................................. 38
$^{13}$C NMR (75 MHz, DMSO-$d_6$) Spectra for Compound 19a .............................................. 38
$^1$H NMR (300 MHz, CDCl$_3$) Spectra for Compound 19b .................................................. 39
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 19b .................................................. 39
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 20 ....................................................... 40
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 20 ....................................................... 40
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 21a ..................................................... 41
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 21a ..................................................... 41
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 21b ..................................................... 42
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 21b ..................................................... 42
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 22a ..................................................... 43
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 22a ..................................................... 43
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 22b ..................................................... 44
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 22b ..................................................... 44
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 23a ..................................................... 45
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 23a ..................................................... 45
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 24a ..................................................... 46
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 24a ..................................................... 46
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 25a ..................................................... 47
$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 25a ..................................................... 47
$^1$H NMR (400 MHz, DMSO-$d_6$) Spectra for Compound 26a .............................................. 48
$^{13}$C NMR (100 MHz, DMSO-$d_6$) Spectra for Compound 26a .............................................. 48

nOe Spectra for Compound 12b ..................................................................................................... 49
General Procedures

All reactions were carried out using flame-dried round-bottomed flasks under an inert atmosphere of argon with dry solvents, unless otherwise stated. All reagents were obtained from commercial suppliers unless otherwise stated. DCM, DMF, toluene were distilled from calcium hydride under argon; THF was distilled from Na/benzophenone under argon. Methanol was distilled from magnesium turnings. Reactions were monitored by thin layer chromatography (TLC). Visualization was achieved under a UV lamp (254 nm and 365 nm), I₂ and by developing the plates with p-anisaldehyde or phosphomolybdic acid. IR spectra were recorded on a commercial spectrophotometer. ¹H-NMR spectra were recorded on commercial instruments (300 or 400 MHz) with TMS as the internal standard (CDCl₃: ¹H NMR = 7.26, ¹³C NMR = 77.16; DMSO-d₆: ¹H NMR = 2.50, ¹³C NMR =39.52). The following abbreviations were used to explain the multiplicities (s = singlet, d = doublet, t = triplet, q = quart, m = multiplet, br = broad). Coupling constants (J) are reported in Hertz (Hz). High resolution Mass spectra (HRMS) were recorded by using FTMS-7 spectrometers.
Experimental Procedures

Compound 5

To a solution of 4 (4.10 g, 13.66 mmol, 1.0 equiv) in THF (137 mL) was added TBAF (1M in THF, 13.7 mL, 13.7 mmol, 1.0 equiv) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for additional 6 h, then quenched by addition of saturated NH₄Cl solution (50 mL) at 0 °C. The solvent was removed under reduced pressure and the aqueous layer was extracted with EtOAc (8 × 50 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 4:1 to 1:1) to afford alcohol 5 (2.35 g, 12.6 mmol, 93%) as a pale yellow oil.

IR (thin film): 3484, 2988, 2938, 1751 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.76 (d, J = 3.6 Hz, 1 H), 3.74 (d, J = 3.3 Hz, 2 H), 2.70-2.57 (m, 1 H), 2.46 (brs, 1 H), 2.33-2.21 (m, 2 H), 2.08-1.95 (m, 1 H), 1.38 (s, 3 H), 1.36 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 217.4, 111.7, 86.6, 80.1, 60.6, 34.1, 27.3, 26.0, 23.2; HRMS (ES) m/z calcd for C₉H₁₄O₄Na (M + Na)⁺ 209.0790, found 209.0788.

Compound 7

To a solution of alcohol 5 (4.91 g, 26.37 mmol, 1.0 equiv) and 2-(diethoxyphosphoryl)propanoic acid (6.70 g, 31.64 mmol, 1.2 equiv) in DCM (130 mL) were sequentially added DCC (7.10 g, 34.27 mmol, 1.3 equiv) and DMAP (161.0 mg, 1.32 mmol, 0.05 equiv) at 0 °C under argon. The reaction mixture was allowed to warm to room temperature and stirred for additional 16 h before it was diluted with...
Et$_2$O (200 mL). Solid was separated by filtration and the organic layers were washed with brine (4 × 30 mL), the aqueous layer was re-extracted with Et$_2$O (4 × 30 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 15:1 to DCM-MeOH, 20:1) to afford phosphinyl acetate (10.0 g, 26.36 mmol, 100%) as an thick yellow oil.

To a solution of dried LiCl (1.23 g, 28.90 mmol, 3.0 equiv) in freshly distilled DMF (30 mL) was added a solution of phosphinyl acetate (3.65 g, 9.64 mmol, 1.0 equiv) in DMF (40 mL) at room temperature under argon, and stirred for another 0.5 h. After finished the addition of DBU (7.35 g, 48.25 mmol, 5.0 equiv) in DMF (30 mL), the reaction mixture was warmed to 45 ℃ and stirred for additional 4 h. The reaction was quenched by slowly pouring into a mixture of saturated NH$_4$Cl solution (250 mL) and 1.0 N HCl (50 mL) at room temperature. EtOAc (300 mL) was added to the mixture and the organic layers were separated and washed with brine (5 × 40 mL), the combined aqueous layers were re-extracted with EtOAc (5 × 80 mL). The organic layers were combined and dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 1.5:1) to afford 7 (1.69 g, 7.54 mmol, 78%) as a white solid.

IR (thin film): 2990, 2942, 1707 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.60 (d, $J = 12.0$ Hz, A of AB, 1 H), 4.47 (d, $J = 4.8$ Hz, 1 H), 4.27 (d, $J = 12.0$ Hz, B of AB, 1 H), 2.68 (dddd, $J = 20.6$, 13.6, 7.6, 1.6 Hz, A’ of A’B’, 1 H), 2.54 (dd, $J = 15.6$, 6.8 Hz, B’ of A’B’, 1 H), 2.15 (dd, $J = 13.6$, 7.6 Hz, A” of A’’B’’, 1 H), 1.89 (d, $J = 2.0$ Hz, 3 H), 1.67 (dddd, $J = 20.4$, 13.6, 6.8, 1.6 Hz, B” of A’’B’’, 1 H), 1.46 (s, 3 H), 1.39 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.2, 154.7, 121.7, 111.7, 82.5, 81.2, 72.9, 31.3, 27.1, 27.1, 25.6, 13.8; HRMS (ES) $m/z$ calcd for C$_{12}$H$_{16}$O$_4$Na (M + Na)$^+$ 247.0947, found 247.0942.

Compound 8’
To a solution of 7 (3.20 g, 14.26 mmol, 1.0 equiv) in MeOH (145 mL) was added 6 N HCl (9.6 mL, 57.8 mmol, 4.0 equiv) at room temperature. The reaction mixture was refluxed at 65 °C for 6 h before it was quenched by addition of solid NaHCO₃ (5.05 g, 60.0 mmol, 4.0 equiv). The solvent was removed under reduced pressure and the residue was diluted with EtOAc (400 mL) and dried with MgSO₄ directly overnight, then filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (DCM-MeOH, 20:1 to 10:1) to afford diol 8' (2.41 g, 13.08 mmol, 92%) as a white solid.

IR (thin film): 3389, 3317, 2954, 2925, 1690, 1421 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.53 (d, J = 12.0 Hz, A of AB, 1 H), 4.24 (d, J = 12.0 Hz, B of AB, 1 H), 3.98-3.91 (dt, J = 9.2, 9.2 Hz, 1 H), 3.61 (brs, 1 H), 2.83 (d, J = 9.2 Hz, 1 H), 2.70-2.62 (m, 1 H), 2.41-2.32 (m, 1 H), 2.25-2.18 (m, 1 H), 2.03-1.92 (m, 1 H), 1.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 165.9, 156.4, 124.0, 76.2, 75.4, 71.8, 30.8, 24.8, 12.8; HRMS (ES) m/z calcd for C₉H₁₆NO₄ (M + NH₄)⁺ 202.1079, found 202.1073.

**Compound 8**

To a solution of diol 8' (2.40 g, 13.0 mmol, 1.0 equiv) in CH₂Cl₂ (65 mL) were sequentially added TEA (2.7 mL, 19.5 mmol, 1.5 equiv), DMAP (159.0 mg, 1.30 mmol, 0.1 equiv) and Ac₂O (1.36 mL, 14.4 mmol, 1.1 equiv) at 0 °C under argon. After 5 min stirring at 0 °C, the reaction mixture was quenched by addition of saturated NaHCO₃ solution (20 mL). The organic layers were separated and the aqueous layer was extracted with DCM (6 × 30 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum
ether-EtOAc, 1:1 to 1:2) to afford the tertiary alcohol **8** (2.35 g, 10.4 mmol, 80%) as a white solid.

IR (thin film): 3416, 2954, 1712, 1243 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.80 (dd, J = 9.3, 8.7 Hz, 1H), 4.41 (d, J = 12.3 Hz, A of AB, 1 H), 4.28 (d, J = 12.3 Hz, B of AB, 1 H), 3.53 (brs, 1 H), 2.73-2.65 (m, 1 H), 2.46-2.33 (m, 1 H), 2.24-2.19 (m, 2 H), 2.11 (s, 3 H), 1.80 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃) δ 170.9, 165.1, 154.8, 124.2, 76.8, 75.3, 72.2, 27.1, 24.5, 20.9, 12.8; HRMS (ES) m/z calcd for C₁₁H₁₈NO₅ (M + NH₄)⁺ 244.1185, found 244.1182.

**Compound 9**

![Diagram of compounds](image)

To a solution of the tertiary alcohol **8** (2.30 g, 10.16 mmol, 1.0 equiv) in dry toluene (68 mL) was added (Methoxycarbonylsulfamoyl)triethylammonium Hydroxide Inner Salt (Burgess’ reagent) (8.48 g, 35.6 mmol, 3.5 equiv) at room temperature under argon. The reaction mixture was heated to 50 ℃ for 3 h before it was quenched by addition of water (30 mL). The solvent was removed under reduced pressure and the residue was extracted with EtOAc (5 × 30 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 2:1 to 1:1.5) to afford **9** (1.73 g, 8.3 mmol, 82%) as a white solid.

IR (thin film): 3099, 2949, 1712, 1594, 1373, 1239 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.59 (s, 1 H), 5.81 (dd, J = 6.0, 2.4 Hz, 1 H), 2.87 (ddd, J = 17.7, 8.9, 3.5 Hz, A of AB, 1 H), 2.73 (ddd, J = 17.8, 8.1, 3.6 Hz, B of AB, 1 H), 2.33-2.23 (m, 1 H), 2.23-2.18 (m, 1 H), 2.02 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 171.0, 163.4, 157.6, 146.9, 123.1, 118.7, 73.8, 32.3, 28.8, 21.2, 13.2; HRMS (ES) m/z calcd for C₁₁H₁₆NO₄ (M + NH₄)⁺ 226.1079, found 226.1077.
Compound 10

![Chemical Structure](image)

To a solution of 9 (576.0 mg, 2.76 mmol, 1.0 equiv) in absolute MeOH (30 mL) was added sodium methoxide (1.1M in MeOH, 5.0 mL, 5.5 mmol, 2.0 equiv) at 0 °C under argon. After 1 h’ stirring at 0 °C, the reaction mixture was quenched by addition of 6 N HCl to adjust pH to 7. The solvent was removed under reduced pressure and the residue was diluted with EtOAc (200 mL) and dried with MgSO₄ directly overnight, then filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 1:1 to 0:1) to afford 10 (348.4 mg, 2.1 mmol, 76%) as a white solid.

IR (thin film): 3480, 3090, 2918, 1676, 1583, 1378, 1247 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (s, 1 H), 5.08 (dt, J = 4.8, 4.8 Hz, 1 H), 2.93-2.85 (m, 1 H), 2.68-2.60 (m, 1 H), 2.35-2.26 (m, 1 H), 2.20 (d, J = 4.8 Hz, 1H), 2.06-1.98 (m, 1 H), 2.02 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 158.2, 144.3, 126.9, 118.6, 71.7, 35.7, 28.4, 13.0; HRMS (ES) m/z calcd for C₉H₁₀O₃Na (M + Na)+ 189.0528, found 189.0522.

Compound 3

![Chemical Structure](image)

To a solution of 10 (348.4 mg, 2.1 mmol, 1.0equiv) in dry EtOAc (40mL) was added 2-Iodoxybenzoic acid (IBX) (1.76 g, 6.28 mmol, 3.0 equiv) at room temperature and the reaction mixture was heated to reflux at 75 °C for 6 h. After it was cooled to the room temperature, the reaction mixture was diluted with anhydrous ether. Solid was separated by filtration and the organic layers was concentrated under reduced pressure to give crude 2-pyrone 3 as a white solid (345.0 mg, 2.1 mmol, 100%) which was used directly in the next step without further purification.

IR (thin film): 3075, 2926, 1710, 1644, 1251 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ
8.10 (s, 1 H), 2.98-2.94 (m, 2 H), 2.71-2.68 (m, 2 H), 2.08 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.6, 162.2, 157.6, 150.5, 120.0, 119.4, 37.1, 24.2, 12.3; HRMS (ES) m/z calcd for C$_9$H$_9$O$_3$ (M + H)$^+$ 165.0546, found 165.0549.

**Representative Procedure of the Diels-Alder Cycloadditions**

A mixture of crude 2-pyrone 3 (32.8 mg, 0.20 mmol), methyl acrylate (69.0 mg, 0.80 mmol) and 2,6-Di-tert-butyl-4-methylphenol (BHT) (8.8 mg, 0.04 mmol) in 1 mL anhydrous DCM was heated at 100 °C in a sealed tube for 10 h. After the reaction, the reaction mixture was concentrated and purified by flash column chromatography on silica gel (petroleum ether-EtOAc, 4:1 to 2:1) to afford chromatographed to give 30.5 mg (0.12 mmol) of 5-endo-12a and 10.2 mg (0.04 mmol) of 6-endo-12b, in yields of 61% and 20% respectively.

White solid, 81%, 12a (5-endo) : 12b (6-endo) = 3.0 : 1, for 12a (5-endo), IR (thin film): 2951, 1750, 1701, 1641 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.55 (dd, $J = 3.9, 1.2$ Hz, 1 H), 3.69 (s, 3 H), 2.95 (dd, $J = 10.0, 4.0$ Hz, A of AB, 1 H), 2.85-2.78 (m, 1 H), 2.77-2.71 (m, 2 H), 2.64-2.61 (m, 2 H), 1.79 (ddd, $J = 13.6, 4.0, 1.2$ Hz, B of AB, 1 H), 1.58 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.8, 179.6, 172.1, 171.9, 142.8, 69.4, 52.3, 49.7, 43.0, 37.0, 32.9, 26.2, 12.7; HRMS (ES) m/z calcd for C$_{13}$H$_{18}$NO$_5$ (M + NH$_4$)$^+$ 268.1179, found 268.1176.

For 12b (6-endo), IR (thin film): 2951, 1705, 1642 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.72 (d, $J = 3.6$ Hz, 1 H), 3.68 (s, 3 H), 3.52 (m, 1 H), 2.73-2.72 (m, 2 H), 2.60-2.57 (m, 2 H), 2.11 (dd, $J = 13.2, 9.2$ Hz, A of A B, 1 H), 2.04 (dd, $J = 13.2, 5.6$ Hz, B of A B, 1 H), 1.58 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.5, 181.0, 173.3, 170.6, 141.9, 70.8, 52.9, 47.5, 44.4, 37.0, 31.6, 25.1, 14.5; HRMS (ES) m/z calcd for C$_{13}$H$_{18}$NO$_5$ (M + NH$_4$)$^+$ 268.1179, found 268.1176.
White solid, 85%, 11a (5-endo) : 11b (6-endo) = 6.6 : 1; IR (thin film): 2940, 1713, 1639 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.75 (d, \(J = 4.0\) Hz, 0.05 H), 5.55 (m, 1 H), 3.62-3.57 (m, 0.05 H), 3.13 (dd, \(J = 10.8, 4.8\) Hz, 1 H), 3.00 (ddd, \(J = 20.8, 6.0, 2.8\) Hz, 1 H), 2.80 (ddd, \(J = 14.0, 10.0, 4.0\) Hz, 1 H), 2.72-2.65 (m, 1 H), 2.62-2.58 (m, 2 H), 2.18 (s, 3 H), 1.60 (ddd, \(J = 13.6, 4.8, 1.2\) Hz, 1 H), 1.56 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 205.3, 200.3, 181.3, 173.0, 142.1, 69.5, 50.5, 50.0, 37.2, 32.4, 30.7, 26.5, 12.9; HRMS (ES) \(m/z\) calcld for C\(_{13}\)H\(_{15}\)O\(_4\) (M + H\(^+\)) 235.0965, found 235.0967.

White solid, 85%, 13a (5-endo) : 13b (6-endo) = 4.3 : 1; IR (thin film) 2979, 2939, 1762, 1706 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.67 (d, \(J = 4.0\) Hz, 0.23 H), 5.54 (d, \(J = 3.6\) Hz, 1 H), 3.42 (m, 0.24 H), 2.84-2.83 (m, 1.26 H), 2.78-2.76 (m, 0.76 H), 2.73-2.65 (m, 2.73 H), 2.64-2.55 (m, 2.39 H), 2.05 (dd, \(J = 13.2, 5.2\) Hz, A of AB, 0.26 H), 2.00 (dd, \(J = 13.2, 8.8\) Hz, B of AB, 0.26 H), 1.75 (ddd, \(J = 13.6, 4.0, 1.2\) Hz, 1 H), 1.59 (s, 3 H), 1.56 (s, 0.81 H), 1.42 (s, 9 H), 1.40 (s, 2.3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) Major: 200.2, 179.9, 172.7, 170.7, 143.0, 82.7, 69.9, 50.2, 44.4, 37.3, 33.1, 28.0, 26.6, 12.9; \(\delta\) Minor: 199.5, 181.2, 173.6, 169.0, 141.8, 83.1, 71.1, 47.4, 45.4, 37.0, 31.1, 27.9, 25.1, 14.5; HRMS (ES) \(m/z\) calcld for C\(_{16}\)H\(_{24}\)NO\(_5\) (M + NH\(_4\))\(^+\) 310.1649, found 310.1653.

White solid, 81%, 14a (5-endo) : 14b (5-exo) = 12.4 : 1, for 14a (5-endo), IR (thin film): 2951, 1699 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.47 (dd, \(J = 3.6, 1.6\) Hz, 1 H), 3.66 (s, 3 H), 2.82 (dd, \(J = 18.8, 5.6, 3.2\) Hz, A of AB, 1 H), 2.67 (ddd, \(J = 18.4, 4.8, 3.2\) Hz, B of AB, 1 H), 2.61-2.59 (m, 2 H), 2.31 (dd, \(J = 14.0, 3.6\) Hz, A’ of A’B’, 1 H), 2.25 (dd, \(J = 14.0, 1.6\) Hz, B’ of A’B’, 1 H), 1.55 (s, 3 H), 1.42 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 200.2, 181.8, 173.7, 172.4, 143.0, 69.7, 54.6, 52.7, 47.4, 42.0, 37.3, 26.4, 22.5, 10.4; HRMS
For **14b** (5-exo), IR (thin film): 2952, 1744, 1708, 1641 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.52 (dd, \(J = 3.6, 1.2\) Hz, 1 H), 3.75 (s, 3 H), 2.92 (dd, \(J = 13.6, 3.6\) Hz, A of AB, 1 H), 2.78 (ddd, \(J = 19.2, 5.2, 3.6\) Hz, B' of AB, 1 H), 2.66-2.63 (m, 2 H), 2.58 (ddd, \(J = 20.0, 4.8, 4.0\) Hz, B' of AB, 1 H), 1.58 (dd, \(J = 13.6, 1.2\) Hz, B of AB, 1 H), 1.45 (s, 3 H), 1.13 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.7, 180.2, 173.9, 172.5, 144.2, 68.5, 54.5, 53.0, 48.4, 40.2, 37.4, 26.9, 21.2, 10.4; HRMS (ES) \(m/z\) calcd for C\(_{14}\)H\(_{20}\)NO\(_5\) (M + NH\(_4\))\(^+\) 282.1336, found 282.1333.

For **15a**, white solid, 30%, IR (thin film): 2956, 1762, 1738, 1708, 1646 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.54 (s, 1 H), 3.81 (dd, \(J = 10.0, 6.8\) Hz, 1 H), 3.72 (d, \(J = 9.2\) Hz, 1 H), 3.69 (s, 3 H), 2.83 (ddd, \(J = 20.0, 5.2, 2.8\) Hz, 1 H), 2.71-2.69 (m, 1 H), 2.66-2.62 (m, 2 H), 2.4 (d, \(J = 4.8\) Hz, 1 H), 2.19-2.14 (m, 1 H), 1.54 (s, 3 H), 0.89 (s, 9 H), 0.08 (s, 3 H), 0.07 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 200.1, 180.5, 172.5, 171.9, 143.6, 70.3, 62.7, 52.7, 50.0, 48.7, 47.4, 37.5, 26.5, 25.9, 18.4, 12.9, -5.4, -5.4; HRMS (ES) \(m/z\) calcd for C\(_{20}\)H\(_{31}\)O\(_6\)Si (M + H\(^+\)) 395.1884, found 395.1886.

White solid, 90%, **16a** (5-endo-6-exo) : **16b** (5-exo-6-endo) = 1 : 3, for **16a** (5-endo-6-exo), IR (thin film): 2956, 1768, 1739, 1707, 1646 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 5.85 (d, \(J = 1.2\) Hz, 1 H), 3.83 (s, 3 H), 3.71 (s, 3 H), 3.60 (d, \(J = 4.4\) Hz, 1 H), 2.96 (dd, \(J = 4.4, 1.2\) Hz, 1 H), 2.81 (ddd, \(J = 18.8, 5.6, 2.8\) Hz, 1 H), 2.73-2.70 (m, 1 H), 2.66-2.62 (m, 2 H), 1.61 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.6, 181.1, 171.4, 169.3, 142.7, 71.4, 53.5, 53.0, 50.5, 46.2, 37.4, 26.6, 13.0, one signal is hidden; HRMS (ES) \(m/z\) calcd for C\(_{15}\)H\(_{16}\)O\(_2\)K (M + K\(^+\)) 347.0528, found 347.0531.
For **16b** (5-exo-6-endo), IR (thin film): 2956, 1769, 1737, 1707, 1646 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.73 (d, J = 4.0 Hz, 1 H), 3.79 (s, 3 H), 3.76 (dd, J = 5.2, 4.0 Hz, 1 H), 3.70 (s, 3 H), 3.03 (d, J = 5.2 Hz, 1 H), 2.74-2.71 (m, 2 H), 2.62-2.59 (m, 2 H), 1.54 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 199.0, 179.7, 170.8, 170.6, 169.5, 143.5, 69.8, 53.3, 53.2, 49.8, 49.4, 47.9, 37.1, 25.1, 12.8; HRMS (ES) m/z calcd for C₁₅H₁₆O₇K (M + K)+ 347.0528, found 347.0531.

White solid, 77%, **17a** (5-endo-6-exo) : **17b** (5-exo-6-endo) = 1 : 1, for **17a** (5-endo-6-exo), IR (thin film): 2940, 1713, 1639 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.79 (s, 1 H), 3.36 (d, J = 4.4 Hz, 1 H), 2.82 (d, J = 4.0 Hz, 1 H), 2.76-2.69 (m, 2 H), 2.65-2.62 (m, 2 H), 1.61 (s, 3 H), 1.49 (s, 9 H), 1.43 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 199.8, 181.1, 171.9, 170.1, 168.0, 142.8, 83.3, 83.1, 71.7, 51.3, 50.3, 47.1, 37.4, 28.1, 28.1, 26.6, 13.0; HRMS (ES) m/z calcd for C₂₁H₂₉O₇(M + H)+ 397.1908, found 397.1910.

For **17b** (5-exo-6-endo), IR (thin film): 2940, 1713, 1639 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.65 (d, J = 3.6 Hz, 1 H), 3.58 (dd, J = 4.8, 4.0 Hz, 1 H), 2.81 (d, J = 5.2 Hz, 1 H), 2.76-2.69 (m, 2 H), 2.65-2.50 (m, 2 H), 1.54 (s, 3 H), 1.47 (s, 9 H), 1.40 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ 199.1, 180.1, 171.1, 169.2, 168.0, 143.4, 83.6, 83.6, 70.0, 50.3, 49.8, 49.0, 37.2, 27.9, 25.0, 12.7, one signal is hidden; HRMS (ES) m/z calcd for C₂₁H₂₉O₇(M + H)+ 397.1908, found 397.1910.

White solid, 58%, **18a** (5-endo-6-endo) : **18b** (5-exo-6-endo) = 6 : 1, IR (thin film): 2956, 1768, 1739, 1707, 1646 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ Major: 5.67 (d, J = 2.8 Hz, 1 H), 3.81 (dd, J = 10.8 Hz, 1 H), 3.66 (s, 3 H), 3.60 (s, 3 H), 3.30 (d, J = 10.8 Hz, 1 H), 2.80-2.56 (m, 4 H), 1.54 (s, 3 H); δ Minor: 5.71 (d, J =
3.6 Hz, 0.16 H), 3.76 (s, 0.48 H), 3.74 (dd, \( J = 4.8, 4.8 \) Hz, 0.15 H), 3.68 (s, 0.52 H), 3.01 (d, \( J = 5.2 \) Hz, 0.16 H), 2.80-2.56 (m, 1 H), 1.51 (s, 0.49 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) Major: 199.8, 178.7, 171.8, 170.2, 168.6, 142.4, 69.8, 52.7, 52.7, 50.0, 49.1, 48.2, 37.2, 26.5, 13.0; \( \delta \) Minor: 199.0, 179.7, 170.8, 170.6, 169.4, 143.4, 53.2, 53.1, 49.7, 49.3, 47.9, 37.1, 25.0, 12.7, one signal is hidden; HRMS (ES) \( m/z \) calcd for C\(_{13}\)H\(_{16}\)O\(_7\)K (M + K\(^+\)) 347.0528, found 347.0531.

White solid, 90%, \( 19a \) (5-endo-6-endo) : \( 19b \) (5-exo-6-exo) = 4.9 : 1, for \( 19a \) (5-endo-6-endo), IR (thin film): 2947, 1764, 1717, 1387, 1190 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.47-7.40 (m, 3 H), 7.01-6.99 (m, 2 H), 5.93 (d, \( J = 4.5 \) Hz, 1 H), 3.97 (dd, \( J = 8.1, 4.8 \) Hz, 1 H), 3.33 (d, \( J = 7.8 \) Hz, 1 H), 2.86-2.76 (m, 1 H), 2.76-2.64 (m, 1 H), 2.59-2.49 (m, 2 H), 1.94 (s, 3 H); \(^{13}\)C NMR (75 MHz, \( d_6 \)-DMSO) \( \delta \) 199.3, 180.1, 173.3, 172.1, 171.0, 140.5, 131.3, 129.3, 128.9, 126.7, 69.0, 49.8, 46.6, 43.2, 36.8, 25.8, 12.3; HRMS (ES) \( m/z \) calcd for C\(_{19}\)H\(_{19}\)N\(_2\)O\(_5\) (M + NH\(_4\))\(^+\) 355.1288, found 355.1290.

For \( 19b \) (5-exo-6-exo), IR (thin film): 2921, 1754, 1714, 1384, 1191 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.50-7.43 (m, 3 H), 7.23-7.20 (m, 2 H), 5.98 (d, \( J = 1.8 \) Hz, 1 H), 3.36 (d, \( J = 8.7 \) Hz, B of AB, 1 H), 2.82-2.80 (m, 2 H), 2.71-2.68 (m, 2 H), 1.87 (s, 3 H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 198.5, 180.7, 171.7, 171.6, 170.1, 144.6, 131.1, 129.5, 126.6, 70.4, 50.5, 48.3, 45.3, 37.4, 25.6, 12.5, one signal is hidden; HRMS (ES) \( m/z \) calcd for C\(_{19}\)H\(_{19}\)N\(_2\)O\(_5\) (M + NH\(_4\))\(^+\) 355.1288, found 355.1290.

For \( 20 \), pale yellow solid, 98%, IR (thin film): 3035, 2952, 1724, \( cm^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.22 (s, 1 H), 3.97 (s, 3 H), 3.89
(s, 3 H), 3.10-3.07 (m, 2 H), 2.78-2.75 (m, 2 H), 2.31 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 205.7, 169.2, 165.5, 158.8, 140.2, 137.1, 133.9, 127.6, 123.4, 52.8, 52.7, 36.4, 25.4, 14.9; HRMS (ES) m/z calcd for C$_{14}$H$_{14}$O$_5$Na (M + Na)$^+$ 285.0733, found 285.0734.

White solid, 94%, **21a** (5-endo) : **21b** (5-exo) = 12.5 : 1, for **21a** (5-endo), IR (thin film): 2978, 2938, 2879, 1760, 1706 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 5.49 (dd, $J = 3.6$, 1.2 Hz, 1 H), 3.71 (dd, $J = 6.8$, 1.2 Hz, 1 H), 3.50 (dq, $J = 9.2$, 7.2 Hz, A of AB, 1 H), 3.36 (dq, $J = 9.2$, 7.2 Hz, B of AB, 1 H), 2.61-2.57 (m, 1 H), 2.19 (ddd, $J = 13.6$, 3.2, 3.2 Hz, A’ of A’B’, 1 H), 2.08 (ddd, $J = 13.6$, 8.4, 1.2 Hz, B’ of A’B’, 1 H), 1.58 (s, 3 H), 1.20 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 215.7, 183.0, 171.7, 145.4, 76.7, 70.0, 66.2, 54.0, 37.4, 35.1, 25.4, 15.2, 11.5; HRMS (ES) m/z calcd for C$_{13}$H$_{16}$O$_4$Na (M + Na)$^+$ 259.0941, found 259.0942.

For **21b** (5-exo), IR (thin film): 2978, 2938, 2879, 1760, 1706 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 5.48 (d, $J = 2.8$ Hz, 1 H), 3.61 (dq, $J = 9.2$, 7.2 Hz, A of AB, 1 H), 3.53 (dd, $J = 8.4$, 3.2 Hz, 1 H), 3.41 (dq, $J = 9.2$, 7.2 Hz, B of AB, 1 H), 2.76-2.69 (m, 1 H), 2.67-2.65 (m, 1 H), 2.60-2.58 (m, 2 H), 2.19 (ddd, $J = 13.6$, 3.2, 3.2 Hz, A’ of A’B’, 1 H), 2.08 (ddd, $J = 13.6$, 8.4, 1.2 Hz, B’ of A’B’, 1 H), 1.58 (s, 3 H), 1.20 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 215.7, 183.0, 171.7, 145.4, 76.7, 70.0, 66.2, 54.0, 37.4, 35.1, 25.4, 15.2, 11.5; HRMS (ES) m/z calcd for C$_{13}$H$_{16}$O$_4$Na (M + Na)$^+$ 259.0941, found 259.0942.

White solid, 89%, **22a** (5-endo) : **22b** (5-exo) = 16.6 : 1, for **22a** (5-endo), IR (thin film): 2960, 2874, 1762, 1709 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 5.51 (dd, $J = 3.6$, 1.2 Hz, 1 H), 3.71 (dd, $J = 6.8$, 1.2 Hz, 1 H), 3.20 (dd, $J = 8.8$, 6.4 Hz, A of AB, 1 H), 3.05 (dd, $J = 8.8$, 6.4 Hz, B of AB, 1 H), 2.75-2.68 (m, 1 H), 2.62-2.59 (m, 3 H), 2.58-2.55 (m, 1 H), 1.79-1.69 (m, 1 H), 1.64 (s, 3 H), 1.62 (ddd, $J = 14.4$, 1.2, 1.2 Hz, 1 H), 0.84
(d, J = 6.8 Hz, 3 H), 0.82 (d, J = 6.4 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 200.3, 180.1, 172.5, 141.9, 77.0, 76.8, 69.5, 54.6, 37.4, 35.4, 28.7, 27.0, 19.30, 19.26, 11.8; HRMS (ES) m/z calcd for C$_{13}$H$_{20}$O$_4$Na (M + Na)$^+$ 287.1254, found 287.1255.

For 22b (5-exo): IR (thin film): 2960, 2874, 1762, 1709 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 5.48 (d, J = 2.8, 1 H), 3.51 (dd, J = 8.4, 3.2 Hz, 1 H), 3.31 (dd, J = 8.8, 6.4 Hz, A of AB, 1 H), 3.08 (dd, J = 8.8, 6.8 Hz, B of AB, 1 H), 2.76-2.69 (m, 1 H), 2.67-2.64 (m, 1 H), 2.60-2.58 (m, 2 H), 2.18 (ddd, J = 14.0, 3.2, 3.2 Hz, A’ of A’B’, 1 H), 2.06 (ddd, J = 13.6, 8.4, 1.2 Hz, B’ of A’B’, 1 H), 1.90-1.80 (m, 1 H), 1.59 (s, 3 H), 0.90 (t, J = 6.8 Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.8, 179.1, 170.5, 145.8, 77.6, 76.8, 70.0, 54.2, 37.4, 34.8, 28.8, 25.4, 19.47, 19.45, 11.6; HRMS (ES) m/z calcd for C$_{13}$H$_{20}$O$_4$Na (M + Na)$^+$ 287.1254, found 287.1255.

For 23a (5-endo), white solid, 85%, IR (thin film): 3051, 2987, 1752, 1707 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.81-6.76 (m, 4 H), 5.65 (dd, J = 4.0, 1.2 Hz, 1 H), 3.78 (s, 3 H), 3.16 (dd, J = 9.2, 4.0 Hz, A of AB, 1 H), 2.92 (ddd, J = 13.6, 9.2, 4.0 Hz, B of AB, A’ of A’B’, 1 H), 2.57-2.65 (m, 3 H), 2.23-2.15 (m, 1 H), 1.92 (ddd, J = 14.0, 4.0, 1.2 Hz, B’ of A’B’, 1 H), 1.27 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 200.0, 180.0, 173.7, 159.2, 143.8, 131.0, 128.9, 114.1, 70.0, 55.2, 52.9, 43.5, 37.2, 36.3, 27.0, 13.0; HRMS (ES) m/z calcd for C$_{13}$H$_{22}$NO$_4$ (M + NH$_4$)$^+$ 316.1543, found 316.1544.

For 24a (5-endo), white solid, 92%, IR (thin film): 3043, 2991, 1750, 1710 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.08 (d, J = 8.0, A of AB, 2 H), 6.74 (d, J = 8.0, B of AB, 2 H), 5.67 (d, J = 2.8 Hz, 1 H), 3.16 (dd, J = 9.2, 4.0 Hz, A’ of A’B’, 1 H), 2.93 (ddd, J = 13.6, 9.2, 4.0 Hz, B’ of A’B’, A’’ of A’’B’’, 1 H), 2.66-2.57 (m, 3 H), 2.32 (s, 3 H), 2.23-2.16 (m, 1 H), 1.94 (ddd, J = 14.0, 4.0, 1.2 Hz, B’’ of A’’B’’, 1 H), 1.27 (s, 3 H); $^{13}$C NMR (100 MHz,
CDCl\textsubscript{3} \(\delta\) 200.2, 180.1, 173.9, 144.1, 138.0, 136.2, 129.6, 127.9, 70.3, 53.0, 44.1, 37.3, 36.5, 27.2, 21.1, 13.2; HRMS (ES) \(m/z\) calcd for C\textsubscript{13}H\textsubscript{19}O\textsubscript{3} (M + H\textsuperscript{+}) 283.1329, found 283.1330.

For 25a (5-endo), white solid, 88%, IR (thin film): 2929, 1754, 1704 cm\textsuperscript{-1}; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.42 (d, \(J = 8.4\text{ Hz}, A\text{ of AB}, 2\text{ H}), 6.75 (d, \(J = 8.4\text{ Hz}, B\text{ of AB}, 2\text{ H}), 5.68 (d, \(J = 3.2\text{ Hz}, 1\text{ H}), 3.17 (dd, \(J = 9.6, 4.0\text{ Hz}, A'\text{ of A'B'}, 1\text{ H}), 2.96 (ddd, \(J = 13.6, 10.0, 3.6\text{ Hz}, B'\text{ of A'B'}, A''\text{ of A''B''}, 1\text{ H}, 2.65-2.61 (m, 3\text{ H}), 2.22-2.17 (m, 1\text{ H}), 1.91 (ddd, \(J = 14.0, 4.0, 1.2\text{ Hz}, B''\text{ of A''B''}, 1\text{ H}), 1.28 (s, 3\text{ H}); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 199.9, 178.5, 173.4, 144.4, 138.4, 132.1, 129.6, 122.3, 70.1, 52.7, 43.9, 37.3, 36.4, 27.2, 13.2; HRMS (ES) \(m/z\) calcd for C\textsubscript{17}H\textsubscript{19}BrNO\textsubscript{3} (M + NH\textsubscript{4}\textsuperscript{+}) 364.0548, found 364.0541.

For 26a (5-endo), white solid, 84%, IR (thin film): 2925, 1748, 1705 cm\textsuperscript{-1}; \(^1\)H NMR (400 MHz, \(d_6\)-DMSO) \(\delta\) 8.15 (d, \(J = 8.4\text{ Hz}, A\text{ of AB}, 2\text{ H}), 7.31 (d, \(J = 8.4\text{ Hz}, B\text{ of AB}, 2\text{ H}), 5.69 (d, \(J = 3.2\text{ Hz}, 1\text{ H}), 3.58 (dd, \(J = 9.2, 4.4\text{ Hz}, A'\text{ of A'B'}, 1\text{ H}), 2.90 (ddd, \(J = 13.6, 9.2, 4.0\text{ Hz}, B'\text{ of A'B'}, A''\text{ of A''B''}, 1\text{ H), 2.72-2.70 (m, 1\text{ H), 2.68-2.65 (m, 1\text{ H), 2.56-2.55 (m, 1\text{ H), 2.10 (dd, \(J = 19.2, 6.0\text{ Hz, 1\text{ H}, 1.91 (dd, \(J = 14.0, 4.0\text{ Hz, B'' of A''B''}, 1\text{ H), 1.33 (s, 3\text{ H); \(^{13}\)C NMR (100 MHz, \(d_6\)-DMSO) \(\delta\) 199.8, 178.9, 172.8, 147.6, 146.9, 143.6, 129.6, 123.6, 69.7, 51.8, 42.2, 37.0, 35.6, 26.7, 12.6; HRMS (ES) \(m/z\) calcd for C\textsubscript{17}H\textsubscript{16}NO\textsubscript{5} (M + H\textsuperscript{+}) 314.1023, found 314.1032.
References

Spectra for Compounds

$^1$H NMR (300 MHz, CDCl$_3$) Spectra for Compound 5

$^{13}$C NMR (75 MHz, CDCl$_3$) Spectra for Compound 5
$^1$H NMR (400 MHz, CDCl$_3$+D$_2$O) Spectra for Compound 7

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 7
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 8'

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 8'
$^1$H NMR (300 MHz, CDCl$_3$) Spectra for Compound 8

$^{13}$C NMR (75 MHz, CDCl$_3$) Spectra for Compound 8
$^1$H NMR (300 MHz, CDCl$_3$) Spectra for Compound 9

$^{13}$C NMR (75 MHz, CDCl$_3$) Spectra for Compound 9
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 10

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 10
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 3

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 3
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 11a and 11b

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 11a and 11b
$^{1}H$ NMR (400 MHz, CDCl$_3$) Spectra for Compound 12a

$^{13}C$ NMR (100 MHz, CDCl$_3$) Spectra for Compound 12a
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 12b

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 12b
$^1$H NMR (400 MHz, CDCl₃) Spectra for Compound 13a and 13b

$^{13}$C NMR (100 MHz, CDCl₃) Spectra for Compound 13a and 13b
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 14a

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 14a
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 14b

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 14b
$^1$H NMR (400 MHz, CDCl$_3$+D$_2$O) Spectra for Compound 15a

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 15a
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 16a

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 16a
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 16b

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 16b
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound **17a**

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound **17a**
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 17b

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 17b
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound **18a** and **18b**

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound **18a** and **18b**
$^1$H NMR (300 MHz, CDCl$_3$) Spectra for Compound 19a

$^{13}$C NMR (75 MHz, DMSO-$d_6$) Spectra for Compound 19a
$^1$H NMR (300 MHz, CDCl$_3$) Spectra for Compound **19b**

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound **19b**
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 20

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 20
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 21a

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 21a
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 21b

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 21b
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 22a

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 22a
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound **22b**

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound **22b**
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 23a

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 23a
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 24a

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 24a
$^1$H NMR (400 MHz, CDCl$_3$) Spectra for Compound 25a

$^{13}$C NMR (100 MHz, CDCl$_3$) Spectra for Compound 25a
$^1$H NMR (400 MHz, DMSO-$d_6$) Spectra for Compound 26a

$^{13}$C NMR (100 MHz, DMSO-$d_6$) Spectra for Compound 26a
nOe Spectra for Compound 12b