Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

# Supporting Information

## Biomimetic Total Syntheses of Chromane Meroterpenoids, Guadials B-C, Guapsidial A and Psiguajadial D

**Dattatraya H. Dethe*, Vijay Kumar B. and Rakesh Maiti**

**Department of Chemistry, Indian Institute of Technology-Kanpur, Kanpur - 208016, India.**

**Tel: + 91-512-2596537, Fax: + 91-512-2597436.**

**Email: ddethe@iitk.ac.in**

## Table of Contents

## 1. General Information

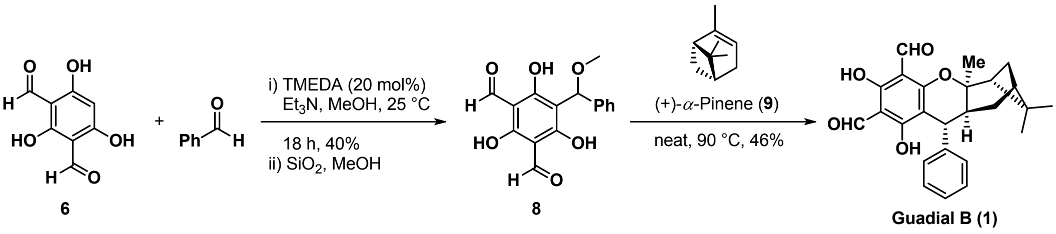
All reactions were carried out under nitrogen atmosphere with dry solvents under anhydrous conditions unless otherwise mentioned. All the chemicals used were purchased commercially, and used without further purification. Anhydrous DMF was prepared by distilling from KOH. Yields refer to chromatographically pure material, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and *p*-anisaldehyde stain as coloring agent, and heat as development agents. Merck silica gel (particle size 100-200 and 230-400 mesh) 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 JEOL ECX 500 ($^1$H: 500/400 MHz, $^{13}$C: 125/100 MHz) in Acetonitrile-$D_3$ or $CDCl_3$ having TMS 0.03% as internal standard. Mass spectrometric data were obtained using WATERS-Q-T of Premier-ESI-MS.

The following abbreviations were used to explain the multiplicities: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *dd* = doublet of doublet, *ddd* = doublet of a doublet of a doublet, *dt* = doublet of a triplet, *td* = triplet of a doublet, *m* = multiplet, *br* = broad.

## Experimental Procedures:

### Guadial B (1):

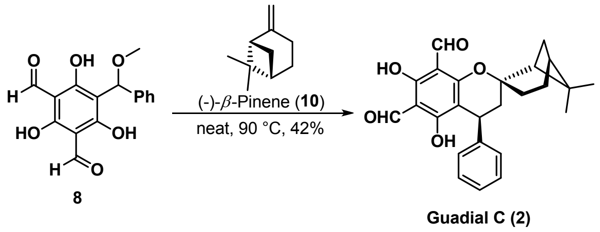


Compound **6** was synthesized from commercially available phloroglucinol following the procedure reported by Liu and co-workers.[1]

To a mixture of dialdehyde **6** (64 mg, 0.35 mmol, 1 equiv.), triethylamine (146 µL, 1.05 mmol, 3 equiv.) and benzaldehyde (0.36 mL, 3.50 mmol, 10 equiv.) in MeOH (0.500 mL) was added, at 25°C, N,N,N′,N′-tetramethylethane-1,2-diamine (TMEDA) (10.5 µl, 0.07 mmol, 0.2 equiv.). And the reaction mixture was stirred for 18 h at the same temperature. The reaction mixture was directly subjected to chromatography on silica gel (DCM/MeOH 20:1) to give a yellow solid which was passed through a bed of silica gel (DCM) to give crude **8** (40.0 mg, 40 % yield) as colourless oil. Compound **8** was readily undergoing decomposition hence the next reaction was performed immediately without proper purification.

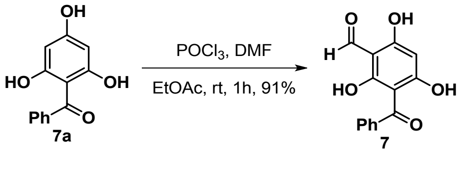
A mixture of ether **8** (40.0 mg, 0.13 mmol, 1 equiv.) and (+)-α-pinene **9** (63.06 µL, 0.39 mmol, 3 equiv.) was stirred for 24 hrs. at 90 °C without adding any solvent. The mixture was purified using column chromatography with 1-2% EtOAc-Hexane to separate excess α-pinene. Then crude fraction obtained was further purified by preparative TLC to isolate desired natural product (**1**) in pure state as a colorless oil; yield = 22.6 mg, 42%. $R_f$ = 0.5 in 90:10 hexane-EtOAc; $[\alpha]_D^{28}$ = +126.0° (*c* 0.025, $CHCl_3$); **IR (neat):** $\nu_{max}/cm^{-1}$ 2921, 1635, 1493, 1444, 1388, 1308, 1250, 1224, 1150, 1112, 1082, 1010, 945, 911, 885, 844, 782, 758, 734, 645, 607, 575, 547, 518; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 13.53 (s, 1H), 13.21 (s, 1H), 10.19 (s, 1H), 10.03 (s, 1H), 7.30 (br s, 1H), 7.28 (br s, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.10 (br s, 1H), 7.08 (br s, 1H), 4.24 (s, 1H), 3.00 (br t, *J* = 8.6 Hz, 1H), 2.53 – 2.41 (m, 1H), 2.15 – 2.06 (m, 2H), 1.93 (dd, *J* = 9.3, 3.9 Hz, 1H), 1.57 – 1.49 (m, 1H), 1.28 (s, 3H), 1.06 (s, 3H), 1.01 (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.23, 191.68, 169.45, 168.90, 166.46, 142.61, 128.73, 127.47, 126.77, 104.10, 103.78, 101.59, 89.01, 56.37, 41.24, 40.69, 40.29, 39.19, 36.61, 29.78, 29.25, 27.97, 27.63, 22.94. **HRMS (ESI)** *m/z* calcd. for $C_{25}H_{27}O_5$ $[M+H]^+$ 407.1853, found 407.1856.

### Guadial C (2):



A mixture of ether **8** (40.0 mg, 0.13 mmol, 1 equiv.) and (-)-*β*-pinene **10** (62.02 µL, 0.39 mmol, 3 equiv.) was stirred for 24 hrs. at 90 °C without adding any solvent. The mixture was purified using column chromatography with 1-2% EtOAc-Hexane to separate excess *β*-pinene. Then crude fraction obtained was further purified by preparative TLC to isolate desired natural product (**2**) in pure state as a colorless oil; yield = 23 mg, 42%. $R_f = 0.5$ in 90:10 hexane-EtOAc; $[\alpha]_D^{28}$ = -75.2° (*c* 0.029, $CHCl_3$); **IR** (neat): $\nu_{max}/cm^{-1}$ 3433, 2923, 1634, 1442, 1385, 1302, 1185, 1161, 1146, 1090, 1014, 978, 855, 766, 701, 609, 533; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 13.51 (s, 1H), 13.13 (s, 1H), 10.11 (s, 2H), 7.28 (t, *J* = 7.2 Hz, 3H), 7.24 – 7.18 (m, 1H), 7.13 (d, *J* = 7.0 Hz, 2H), 3.99 (dd, *J* = 10.2, 6.9 Hz, 1H), 2.43 (dd, *J* = 14.4, 6.9 Hz, 1H), 2.32 – 2.27 (m, 1H), 2.25 – 2.16 (m, 1H), 2.15 – 2.10 (m, 1H), 2.07 (dd, *J* = 14.4, 3.0 Hz, 1H), 2.03 – 1.97 (m, 2H), 1.78 (ddd, *J* = 13.8, 11.4, 2.6 Hz, 2H), 1.50 (d, *J* = 10.2 Hz, 1H), 1.30 (s, 3H), 1.00 (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.28, 191.66, 169.56, 168.70, 164.73, 144.46, 128.64, 126.85, 126.38, 104.53, 104.17, 103.05, 86.27, 47.63, 43.74, 40.62, 38.39, 35.15, 30.01, 29.78, 27.60, 26.42, 24.65, 23.20; **HRMS (ESI)** *m/z* calcd. for $C_{25}H_{27}O_5$ $[M+H]^+$ 407.1853, found 407.1858.

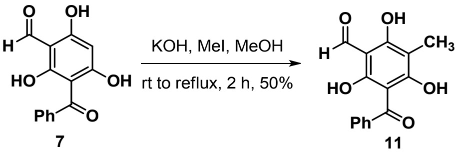
### Compound 7:



Compound 7a was synthesized from commercially available phloroglucinol following the procedure reported by Jonathan and co-workers.[2]

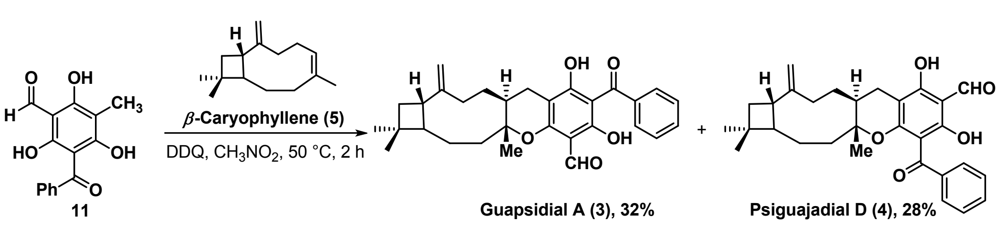
According the procedure reported by Bharate and co-workers[3], To the solution of benzoyl-phloroglucinol **7a** (400 mg, 1.74 mmol, 1 equiv.) in ethyl acetate (12 mL) were added DMF (0.15 mL, 1.91 mmol, 1.1 equiv.) and phosphoryl chloride (0.18 mL, 1.91 mmol, 1.1 equiv.) at room temperature. The reaction mixture was further stirred for 30 min at the same temperature. Water was added to the reaction mixture and extracted with ethyl acetate (2 x 50 mL). The combined ethyl acetate layers were washed with brine and dried over $Na_2SO_4$ and concentrated to afford the crude product. Column chromatography over silica gel using hexane/EtOAc (70:30) as eluent provided **7** as a pale yellow solid. Yield = 408 mg, 91 %. $R_f$ = 0.3 in 70:30 hexane-EtOAc; MP = 170 °C ; **IR** (neat): $v_{max}/cm^{-1}$ 3242, 2925, 2854, 1627, 1599, 1523, 1489, 1434, 1380, 1307, 1274, 1228, 1192, 1130, 1100, 973, 927, 896, 875, 817, 802, 761, 730, 691, 607, 577, 432; **$^{1}$H NMR** (400 MHz, $CD_3CN$) $\delta$ 13.46 (s, 1H), 10.02 (s, 1H), 7.59 – 7.54 (m, 2H), 7.51 (t, $J$ = 7.4 Hz, 1H), 7.39 (t, $J$ = 7.7 Hz, 2H), 5.90 (s, 1H); **$^{13}$C NMR** (100 MHz, $CD_3CN$) $\delta$ 198.96, 192.23, 140.55, 131.79, 128.16, 127.91, 117.41, 104.52, 103.83, 94.69; **HRMS (ESI)** *m/z* calcd. for $C_{14}H_{11}O_5$ $[M+H]^+$ 259.0606, found 259.0609.

### Compound 11:



According the procedure reported by Bharate and co-workers[3], to the solution of formylated benzoyl phloroglucinol **7** (258 mg, 1 mmol, 1 equiv.) in methanol (10 mL), was added potassium hydroxide (112 mg, 2 mmol, 2 equiv.) was added, at room temperature, methyl iodide (0.3 mL, 5 mmol, 5 equiv.). The reaction mixture was refluxed for 2 h. Solvent was evaporated and the crude product was purified by silica gel column chromatography using hexane/EtOAc (80:20) as eluent to afford **11** (136 mg, 50%) as pale yellow solid. $R_f$ = 0.5 in 70:30 hexane-EtOAc. MP =140 °C; **IR** (neat): $v_{max}/cm^{-1}$ 2955, 2925, 2853, 1626, 1492, 1448, 1429, 1377, 1321, 1276, 1226, 1157, 1097, 976, 948, 836, 734, 697, 624, 607, 541, 476, 440; **$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 13.13 (s, 1H), 10.78 (s, 1H), 10.16 (s, 1H), 8.56 (s, 1H), 7.60 (t, $J$ = 19.6 Hz, 5H), 2.00 (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) $\delta$ 192.33, 166.22, 132.90, 129.75, 127.91, 29.78, 6.58; **HRMS (ESI)** *m/z* calcd. for $C_{15}H_{13}O_5$ $[M+H]^+$ 273.0757, found 273.0762.

### Guapsidial A (3) and Psiguajadial D (4):



To a solution of **11** (50 mg, 0.184 mmol, 1 equiv.) and DDQ (41.7 mg, 0.184 mmol, 1 equiv.) in nitromethane (5 mL) was added β-caryophyllene (37.6 mg, 0.184 mmol) and the reaction mixture was stirred at 50 °C for 2 h. The solvent was then evaporated under vacuum and the crude product was purified by silica gel column chromatography (hexane/ EtOAc = 95:5) to get a viscous liquid as a mixture of two isomers. They could not be separated through silica gel column chromatography. However, they were separated by careful preparative thin layer chromatography (hexane/ EtOAc = 98:2) to afford **3** and **4** as colorless oils in 1:1 ratio in 60% combined yield (52 mg); $R_f$ = 0.5 in 95:5 hexane-EtOAc.

**Guapsidial A (3):** Yield = 28mg (32%); $[\alpha]^{28}_{D}$ = -25.4° (*c* 0.032, $CHCl_3$); **IR** (neat): $v_{max}$/cm$^{-1}$ 2924, 2853, 1628, 1447, 1432, 1367, 1294, 1227, 1206, 1170, 1147, 1116, 1057, 1005, 888, 868, 773, 754, 695, 662, 606, 459; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 13.69 (s, 1H), 13.60 (s, 1H), 10.00 (d, *J* = 3.7 Hz, 1H), 7.61 (br d, *J* = 7.0 Hz, 2H), 7.51 (br t, *J* = 7.4 Hz, 1H), 6.4 Hz, 1H), 7.41 (br t, *J* = 7.6 Hz, 2H), 4.92 (br s, 1H), 4.89 (br s, 1H), 2.71 (dd, *J* = 11.2, 10.6 Hz, 1H), 2.53 – 2.39 (m, 2H), 2.20 (m, 2H), 2.12 (br d, 2H), 2.01 – 1.88 (m, 2H), 1.78 (m, 1H), 1.74 (m, 2H), 1.6 (m, 2H), 1.47 (m, 1H), 1.24 (s, 3H), 1.00 (s, 6H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 199.73, 191.80, 169.53, 166.88, 162.08, 152.04, 140.84, 131.58, 128.15, 127.87, 110.61, 104.20, 102.89, 101.36, 84.42, 53.39, 41.90, 38.00, 36.48, 35.36, 33.93, 33.88, 33.68, 30.33, 24.80, 22.59, 22.29, 21.31; **HRMS (ESI)** *m*/*z* calcd. for $C_{30}H_{35}O_5$ $[M+H]^+$ 475.2479, found 475.2484.

**Psiguajadial D (4):** Yield = 24.3mg (32%); $[\alpha]^{28}_{D}$ = -122.4° (*c* 0.046, $CHCl_3$); **IR** (neat): $v_{max}$/cm$^{-1}$ 2924, 2853, 1628, 1447, 1431, 1367, 1226, 1206, 1169, 1147, 1057, 1005, 888, 868, 773, 754, 695, 662, 606, 459; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 13.70 (s, 1H), 13.23 (s, 1H), 10.23 (s, 1H), 7.46 (dd, *J* = 9.0, 4.7 Hz, 1H), 7.39 (m, 4H), 4.82 (d, *J* = 10.9 Hz, 2H), 2.61 (dd, *J* = 16.6, 5.4 Hz, 1H), 2.41 – 2.20 (m, 2H), 2.08 – 1.97 (m, 2H), 1.86 – 1.77 (m, 1H), 1.72 – 1.41 (m, 9H), 1.00 (s, 3H), 0.93 (s, 3H), 0.87 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 200.25, 192.04, 168.76, 167.16, 162.09, 151.90, 142.35, 130.12, 127.63, 126.62, 110.21, 104.08, 103.55, 100.63, 84.49, 53.06, 41.36, 37.36, 36.21, 34.88, 33.54, 33.43, 33.02, 30.09, 24.18, 21.98, 20.32; **HRMS (ESI)** *m*/*z* calcd. for $C_{30}H_{35}O_5$ $[M+H]^+$ 475.2479, found 475.2482.

## REFERENCES:

1) Gao, Y.; Wang, G. Q.; Wei, K.; Hai, P.; Wang, F.; Liu, J. K. *Org. Lett.* **2012**, *14*, 5936–5939.

2) Pepper, H. P.; Tulip, S. J.; Nakano, Y.; George, J. H. *J. Org. Chem.* **2014**, *79*, 2564−2573.
3) Bharate, S. B.; Bhutani, K. K.; Khan, S. I.; Tekwani, B. I.; Jacob, M. R.; Khan, I. A.; Singh, I. P. *Bioorganic Med. Chem.,* **2006***, 14,* 1750–1760.

**Specific rotation comparison of reported and synthesized natural products:**

| **Natural product** | **Specific rotation ($[\alpha]^{28}_{D}$) of the natural products isolated** | **Specific rotation ($[\alpha]^{28}_{D}$) of the synthesized natural products (Current manuscript)** |
|---|---|---|
| **Guadial B (1)**<br>**(***Chem. Eur. J.*, 2015, **21**, 9022-9027**)** | + 122.5° (*c* 0.56, $CHCl_3$) | +126.0° (*c* 0.025, $CHCl_3$) |
| **Guadial C (2)**<br>**(***Chem. Eur. J.*, 2015, **21**, 9022-9027**)** | - 75.1° (*c* 0.64, $CHCl_3$) | -75.2° (*c* 0.029, $CHCl_3$) |
| **Guapsidial A (3)**<br>**(***Chem. Eur. J.*, 2015, **21**, 9022-9027**)** | - 32.7° (*c* 0.95, $CHCl_3$) | -25.4° (*c* 0.032, $CHCl_3$) |
| **Psiguajadial D (4)**<br>**(***Sci. Rep.*, 2017, **7**, 1-15.**)** | −149.0° (*c* 0.2, $CHCl_3$) | -122.4° (*c* 0.046, $CHCl_3$) |

**$^{1}$H and $^{13}$C NMR comparison of reported and synthesized Guadial B (1):**

| S.N. | $^{1}$H-NMR data of **1** (500 MHz, $CDCl_3$) from natural source (*Chem. Eur. J.* **2015**, *21*, 9022 – 9027) | $^{1}$H-NMR data of **1** (400 MHz, $CDCl_3$) synthesized by us (current manuscript) | $^{13}$C-NMR data of **1** (125 MHz, $CDCl_3$) from natural source (*Chem. Eur. J.* **2015**, *21*, 9022 – 9027) | $^{13}$C-NMR data of **1** (100 MHz, $CDCl_3$) synthesized by us (current manuscript) |
|---|---|---|---|---|
| 1 | 13.52 (s, 1H) | 13.53 (s, 1H) | 192.3 | 192.23 |
| 2 | 13.21 (s, 1H) | 13.21 (s, 1H) | 191.7 | 191.68 |
| 3 | 10.19 (s, 1H) | 10.19 (s, 1H) | 169.5 | 169.45 |
| 4 | 10.03 (s, 1H) | 10.03 (s, 1H) | 169.0 | 168.90 |
| 5 | 7.28 (t, 7.4, 1H) | 7.28 (br s, 1H) | 166.5 | 166.46 |
| 6 | 7.28 (t, 7.4, 1H) | 7.30 (br s, 1H) | 142.7 | 142.61 |
| 7 | 7.20 (t, 7.4, 1H) | 7.20 (t, *J* = 7.3 Hz, 1H) | 128.8 | 128.73 |
| 8 | 7.09 (d, 7.4, 1H) | 7.10 (br s, 1H) | 126.8 | 126.77 |
| 9 | 7.09 (d, 7.4, 1H) | 7.08 (br s, 1H) | 127.5 | 127.47 |
| 10 | 4.24 (br s, 1H) | 4.24 (s, 1H) | 104.2 | 104.10 |
| 11 | 3.00 (ddd, 9.5, 9.0, 1.0, 1H) | 3.00 (br t, *J* = 8.6 Hz, 1H) | 103.9 | 103.78 |

| | | | | |
|---|---|---|---|---|
| 12 | 2.47 (ddd, 13.5, 9.5, 3.5, 1H) | 2.53 – 2.41 (m, 1H) | 101.7 | 101.59 |
| 13 | 2.11, 2.13 (2H) | 2.15 – 2.06 (m, 2H) | 89.1 | 89.01 |
| 14 | 1.93 (m, 1H) | 1.93 (dd, *J* = 9.3, 3.9 Hz, 1H) | 56.5 | 56.37 |
| 15 | 1.53 (ddd, 13.5, 9.0, 1.6, 1H) | 1.57 – 1.49 (m, 1H) | 41.3 | 41.24 |
| 16 | 1.28 (s, 3H) | 1.28 (s, 3H) | 40.8 | 40.69 |
| 17 | 1.06 (s, 3H) | 1.06 (s, 3H) | 40.4 | 40.29 |
| 18 | 1.01 (s, 3H) | 1.01 (s, 3H) | 39.3 | 39.19 |
| 19 | -- | -- | 36.7 | 36.61 |
| 20 | -- | -- | 29.3 | 29.25 |
| 21 | -- | -- | 28.1 | 27.97 |
| 22 | -- | -- | 27.7 | 27.63 |
| 23 | -- | -- | 23.0 | 22.94 |

## $^{1}$H and $^{13}$C comparison of reported and synthesized Guadial C (2):

| S.N. | $^{1}$H-NMR data of **2** (500 MHz, CDCl$_3$) from natural source (*Chem. Eur. J.* **2015**, *21*, 9022 – 9027) | $^{1}$H-NMR data of **2** (400 MHz, CDCl$_3$) synthesized by us (current manuscript) | $^{13}$C-NMR data of **2** (125 MHz, CDCl$_3$) from natural source (*Chem. Eur. J.* **2015**, *21*, 9022 – 9027) | $^{13}$C-NMR data of **2** (100 MHz, CDCl$_3$) synthesized by us (current manuscript) |
|---|---|---|---|---|
| 1 | 13.51 | 13.51 (s, 1H) | 192.3 | 192.28 |
| 2 | 13.13 | 13.13 (s, 1H) | 191.7 | 191.66 |
| 3 | 10.12 | 10.11 (s, 2H) | 169.6 | 169.56 |
| 4 | 7.28 (t, 7.4, 1H) | 7.28 (t, *J* = 7.2 Hz, 3H) | 168.8 | 168.70 |
| 5 | 7.28 (t, 7.4, 1H) | 7.24 – 7.18 (m, 1H) | 164.8 | 164.73 |
| 6 | 7.13 (d, 7.4, 1H) | 7.13 (d, *J* = 7.0 Hz, 2H) | 144.5 | 144.46 |
| 7 | 3.99 (dd, 10.2, 7.0 Hz, 1H) | 3.99 (dd, *J* = 10.2, 6.9 Hz, 1H) | 128.7 | 128.64 |
| 8 | 2.43 (dd, 14.5, 7.0 Hz, 1H) | 2.43 (dd, *J* = 14.4, 6.9 Hz, 1H) | 126.9 | 126.85 |
| 9 | 2.30 (dd, 5.0, 4.8 Hz, 1H) | 2.32 – 2.27 (m, 1H) | 126.4 | 126.38 |
| 10 | 2.20 (m, 1H) | 2.25 – 2.16 (m, 1H) | 104.6 | 104.53 |
| 11 | 2.12 (dd, 14.5, 10.2, 1H) | 2.15 – 2.10 (m, 1H) | 104.2 | 104.17 |
| 12 | 2.08 (m, 1H) | 2.07 (dd, *J* = 14.4, 3.0 Hz, 1H) | 103.1 | 103.05 |
| 13 | 2.00, 1.98 | 2.03 – 1.97 (m, 2H) | 86.3 | 86.27 |

| | | | | |
|---|---|---|---|---|
| 14 | 1.80 (m, 1H) | 1.78 (ddd, $J$ = 13.8, 11.4, 2.6 Hz, 2H) | 47.7 | 47.63 |
| 15 | 1.50 (d, 10.0, 1H) | 1.50 (d, $J$ = 10.2 Hz, 1H) | 43.8 | 43.74 |
| 16 | 1.30 (s, 3H) | 1.30 (s, 3H) | 40.7 | 40.62 |
| 17 | 1.00 (s, 3H) | 1.00 (s, 3H) | 38.5 | 38.39 |
| 18 | -- | -- | 35.2 | 35.15 |
| 19 | -- | -- | 30.1 | 30.01 |
| 21 | -- | -- | 27.7 | 27.60 |
| 22 | -- | -- | 26.5 | 26.42 |
| 23 | -- | -- | 24.7 | 24.65 |
| 24 | -- | -- | 23.3 | 23.20 |

## $^1$H and $^{13}$C comparison of reported and synthesized Guapsidial A (3):

| S.N. | $^1$H-NMR data of **3** (400 MHz, CDCl$_3$) from natural source (*Chem. Eur. J.* **2015**, *21*, 9022 – 9027) | $^1$H-NMR data of **3** (400 MHz, CDCl$_3$) synthesized (current manuscript) | $^{13}$C-NMR data of **3** (100 MHz, CDCl$_3$) from natural source (*Chem. Eur. J.* **2015**, *21*, 9022 – 9027) | $^{13}$C-NMR data of **3** (100 MHz, CDCl$_3$) synthesized (current manuscript) |
|---|---|---|---|---|
| 1 | 13.69 (s, 1H) | 13.69 (s, 1H) | 199.8 | 199.73 |
| 2 | 13.60 (s, 1H) | 13.60 (s, 1H) | 191.9 | 191.80 |
| 3 | 10.00 (s, 1H) | 10.00 (d, $J$ = 3.7 Hz, 1H) | 169.6 | 169.53 |
| 4 | 7.61 (d, 7.5, 1H)<br>7.61 (d, 7.5, 1H) | 7.61 (br d, $J$ = 7.0 Hz, 2H) | 167.0 | 166.88 |
| 5 | 7.51 (t, 7.5, 1H) | 7.51 (br t, $J$ = 7.4 Hz, 1H) | 162.2 | 162.08 |
| 6 | 7.41 (t, 7.5, 1H)<br>7.41 (t, 7.5, 1H) | 7.41 (br t, $J$ = 7.6 Hz, 2H) | 152.1 | 152.04 |
| 7 | 4.92 (br s, 1H) | 4.92 (br s, 1H) | 140.9 | 140.84 |
| 8 | 4.89 (br s, 1H) | 4.89 (br s, 1H) | 131.6 | 131.58 |
| 9 | 2.70 (dd, 11.0, 10.6, 1H) | 2.71 (dd, $J$ = 11.2, 10.6 Hz, 1H) | 128.2 | 128.15 |
| 10 | 2.48 (m, 1H)<br>2.45 (m, 1H) | 2.53 – 2.39 (m, 2H) | 127.9 | 127.87 |
| 11 | 2.20 (m, 2H) | 2.20 (m, 2H) | 110.7 | 110.61 |
| 12 | 2.17 (2H) | 2.12 (br d, 2H) | 104.3 | 104.20 |
| 13 | 1.97 (m, 1H)<br>1.92 (m, 1H) | 2.01 – 1.88 (m, 2H) | 103.0 | 102.89 |
| 14 | 1.78 (m, 1H)<br>1.74 (m, 2H)<br>1.71 (m, 2H)<br>1.47 (m, 1H) | 1.78 (m, 1H)<br>1.74 (m, 2H)<br>1.6 (m, 2H)<br>1.47 (m, 1H) | 101.4 | 101.36 |
| 15 | 1.24 (s, 3H) | 1.24 (s, 3H) | 84.5 | 84.42 |
| 16 | 0.99 (s, 6H) | 1.0 (s, 6H) | 53.5 | 53.39 |
| 17 | -- | -- | 42.0 | 41.90 |

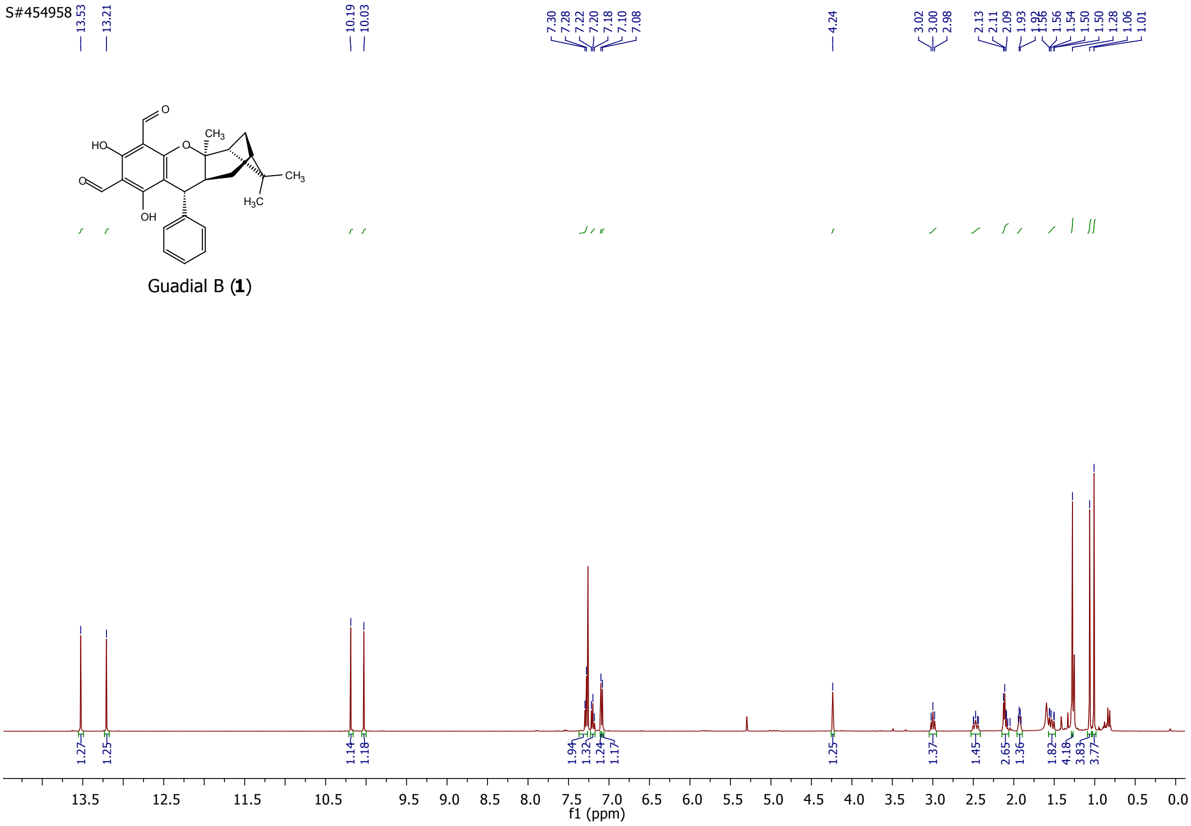
|  |  |  |  |  |
|---|---|---|---|---|
| 18 | -- | -- | 38.1 | 38.00 |
| 19 | -- | -- | 36.6 | 36.48 |
| 20 | -- | -- | 35.4 | 35.36 |
| 21 | -- | -- | 34.0 | 33.93 |
| 22 | -- | -- | 34.0 | 33.88 |
| 23 | -- | -- | 33.8 | 33.68 |
| 24 | -- | -- | 30.4 | 30.33 |
| 25 | -- | -- | 24.9 | 24.80 |
| 26 | -- | -- | 22.7 | 22.59 |
| 27 | -- | -- | 22.3 | 22.29 |
| 28 | -- | -- | 21.4 | 21.31 |

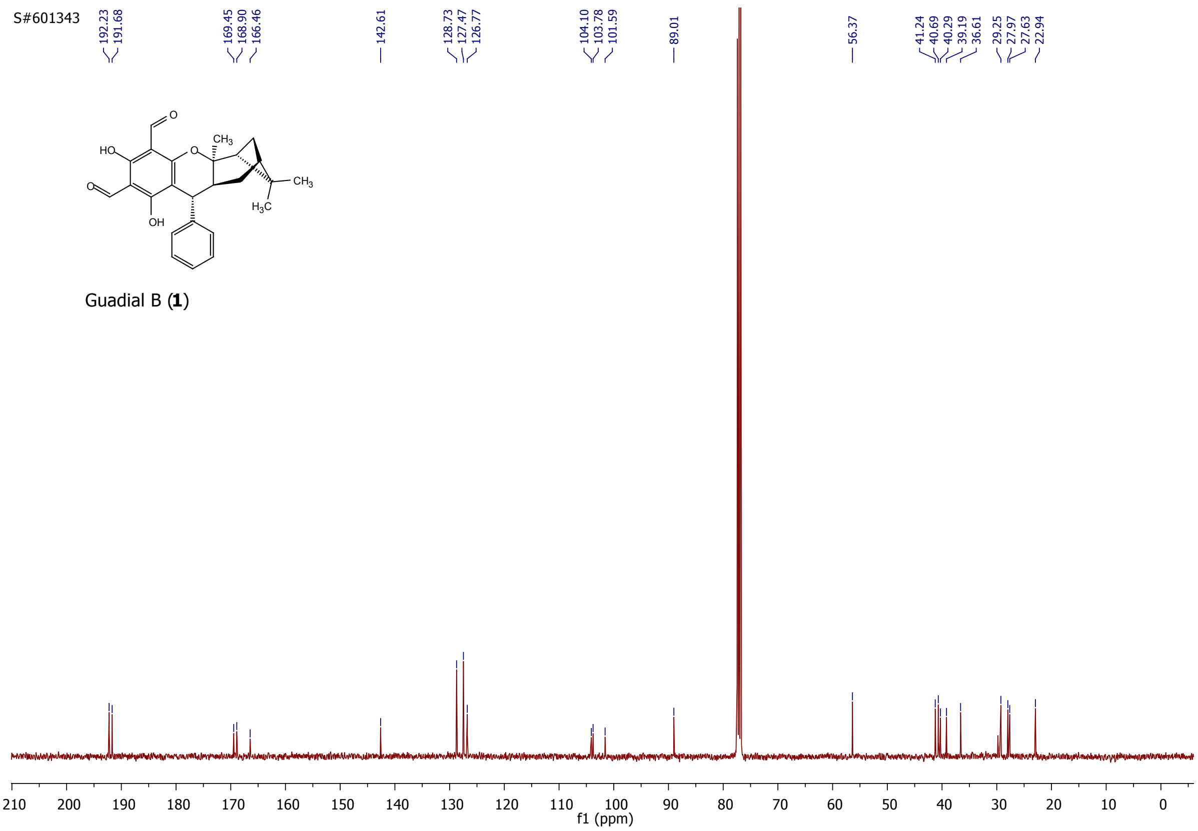
## $^1$H and $^{13}$C comparison of reported and synthesized Psiguajadial D (4):

| S.N. | $^1$H-NMR data of **4** (400 MHz, $CDCl_3$) from natural source (*Sci. Rep.* **2017**, *7*, 1-15) | $^1$H-NMR data of **4** (400 MHz, $CDCl_3$) synthesized by us (current manuscript) | $^{13}$C-NMR data of **4** (100 MHz, $CDCl_3$) from natural source (*Sci. Rep.* **2017**, *7*, 1-15) | $^{13}$C-NMR data of **4** (100 MHz, $CDCl_3$) synthesized by us (current manuscript) |
|---|---|---|---|---|
| 1 | 13.71 (s, 1H) | 13.70 (s, 1H) | 200.3 | 200.25 |
| 2 | 13.23 (s, 1H) | 13.23 (s, 1H) | 192.1 | 192.04 |
| 3 | 10.23 (s, 1H) | 10.23 (s, 1H) | 168.9 | 168.76 |
| 4 | 7.47 (m, 1H) | 7.46 (dd, *J* = 9.0, 4.7 Hz, 1H) | 167.3 | 167.16 |
| 5 | 7.40 (m, 2H)<br>7.39 (m, 2H) | 7.39 (m, 4H) | 162.2 | 162.09 |
| 6 | 4.83 (br s, 1H) | 4.83 (br s, 1H) | 152.0 | 151.90 |
| 7 | 4.80 (br s, 1H) | 4.80 (br s, 1H) | 142.5 | 142.35 |
| 8 | 2.61 (dd, *J* = 16.6, 5.4 Hz, 1H) | 2.61 (dd, *J* = 16.6, 5.4 Hz, 1H) | 130.2 | 130.12 |
| 9 | 2.26 (m, 2H) | 2.41 – 2.20 (m, 2H) | 127.7 | 127.63 |
| 10 | 2.03 (m, 1H) | 2.08 – 1.97 (m, 2H) | 126.7 | 126.62 |
| 11 | 1.82 (m, 1H) | 1.86 – 1.77 (m, 1H) | 110.3 | 110.21 |
| 12 | 1.66 (m, 2H)<br>1.61 (m, 2H)<br>1.60 (m, 2H)<br>1.57 (m, 2H)<br>1.49 (m, 1H) | 1.72 – 1.41 (m, 9H) | 104.2 | 104.08 |
| 13 | 1.00 (s, 3H) | 1.00 (s, 3H) | 103.7 | 103.55 |
| 14 | 0.93 (s, 3H) | 0.93 (s, 3H) | 100.9 | 100.63 |
| 15 | 0.87 (s, 3H) | 0.87 (s, 3H) | 84.6 | 84.49 |
| 16 | -- | -- | 53.2 | 53.06 |

|  |  |  |  |  |
|---|---|---|---|---|
| 17 | -- | -- | 41.5 | 41.36 |
| 18 | -- | -- | 37.5 | 37.36 |
| 19 | -- | -- | 36.4 | 36.21 |
| 20 | -- | -- | 35.0 | 34.88 |
| 21 | -- | -- | 33.7 | 33.54 |
| 22 | -- | -- | 33.5 | 33.43 |
| 23 | -- | -- | 33.2 | 33.02 |
| 24 | -- | -- | 30.2 | 30.09 |
| 26 | -- | -- | 24.3 | 24.18 |
| 27 | -- | -- | 22.1 | 21.98 |
| 28 | -- | -- | 20.4 | 20.32 |

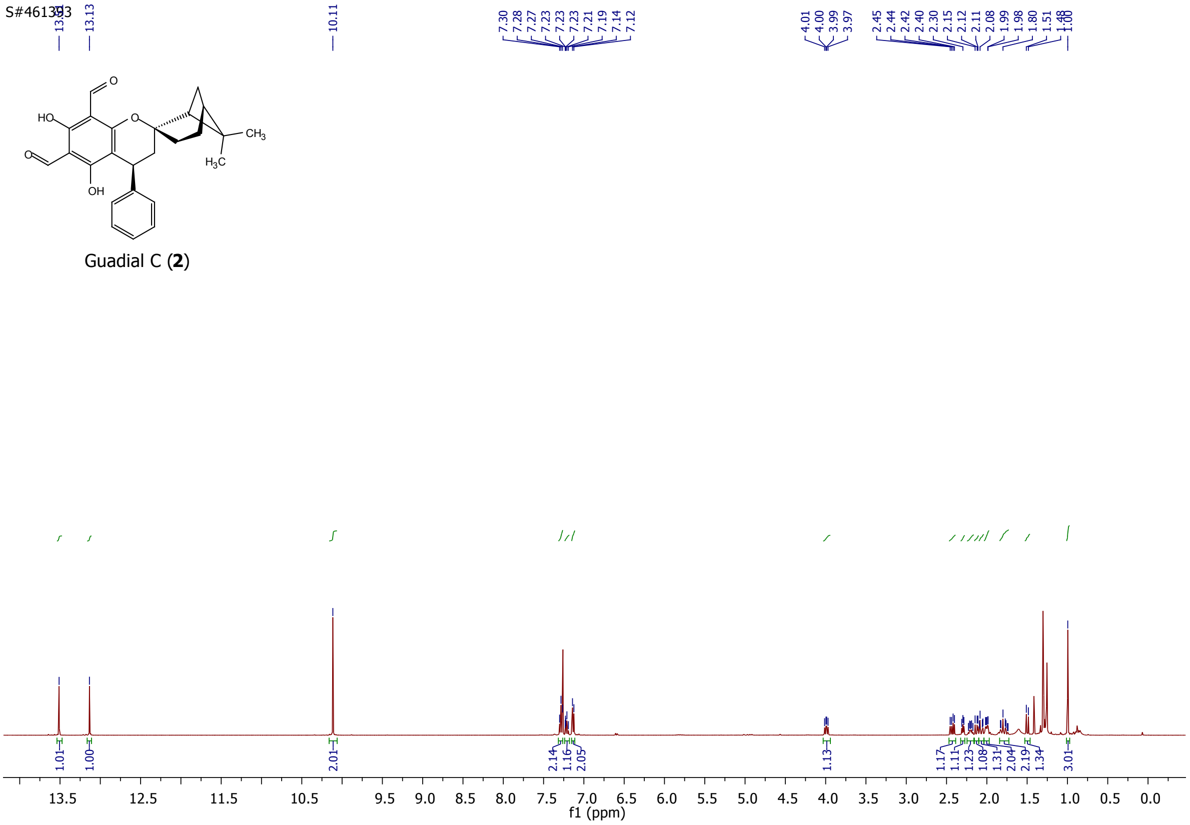
## $^{1}$H and $^{13}$C NMR Spectra of Guadial B (1):


Guadial B (**1**)

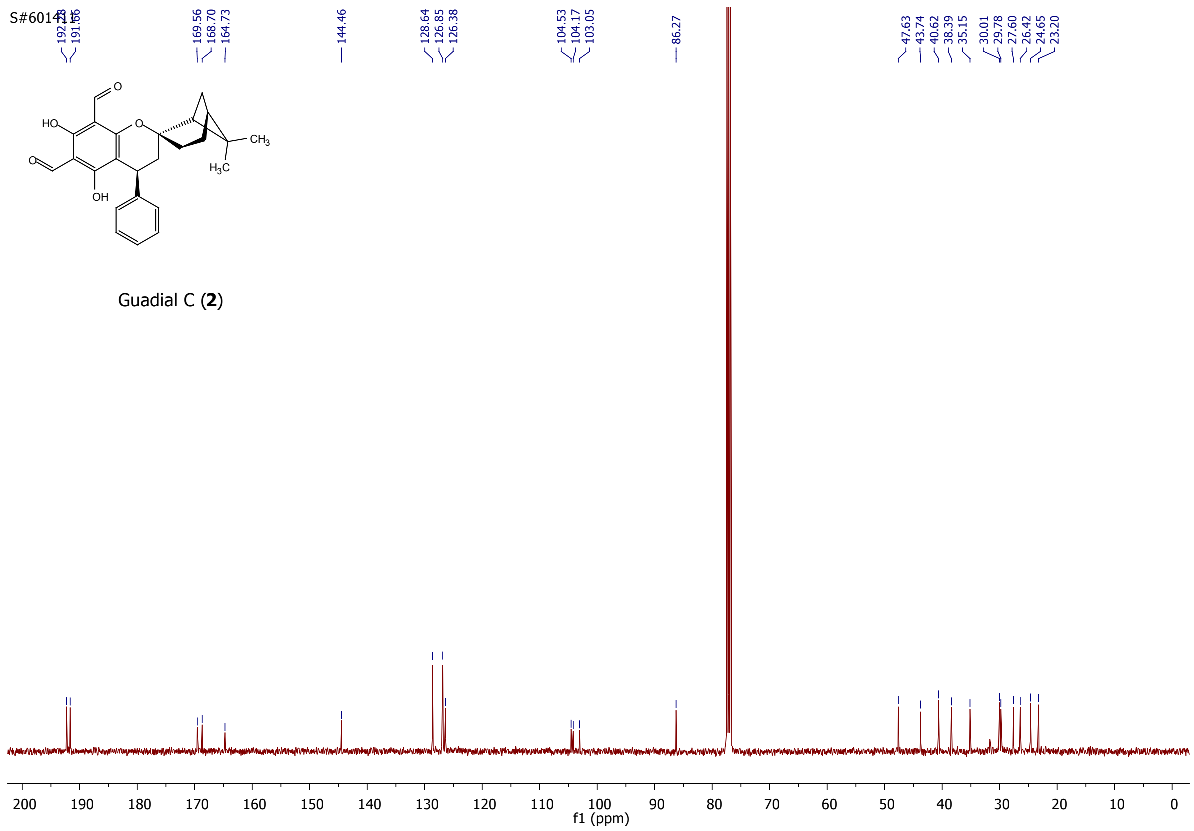


Guadial B (**1**)

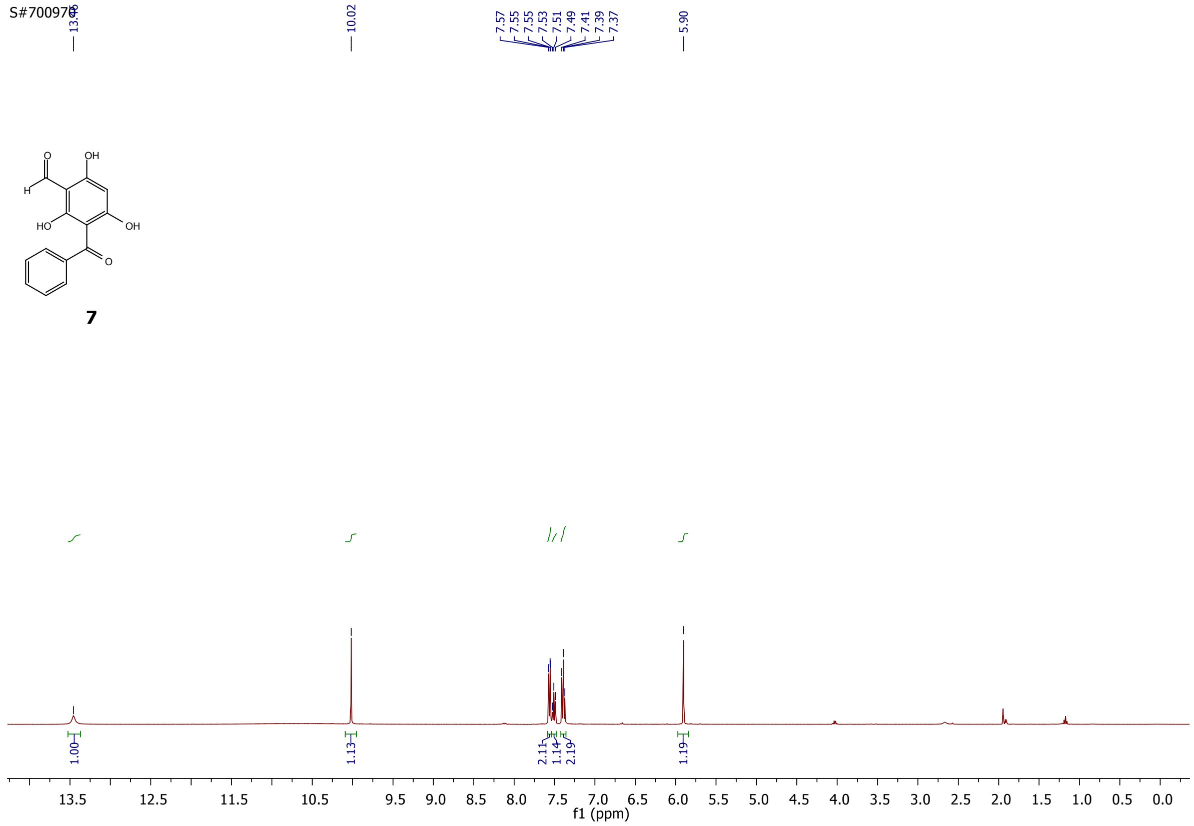
## $^{1}$H and $^{13}$C NMR Spectra of Guadial C (2):

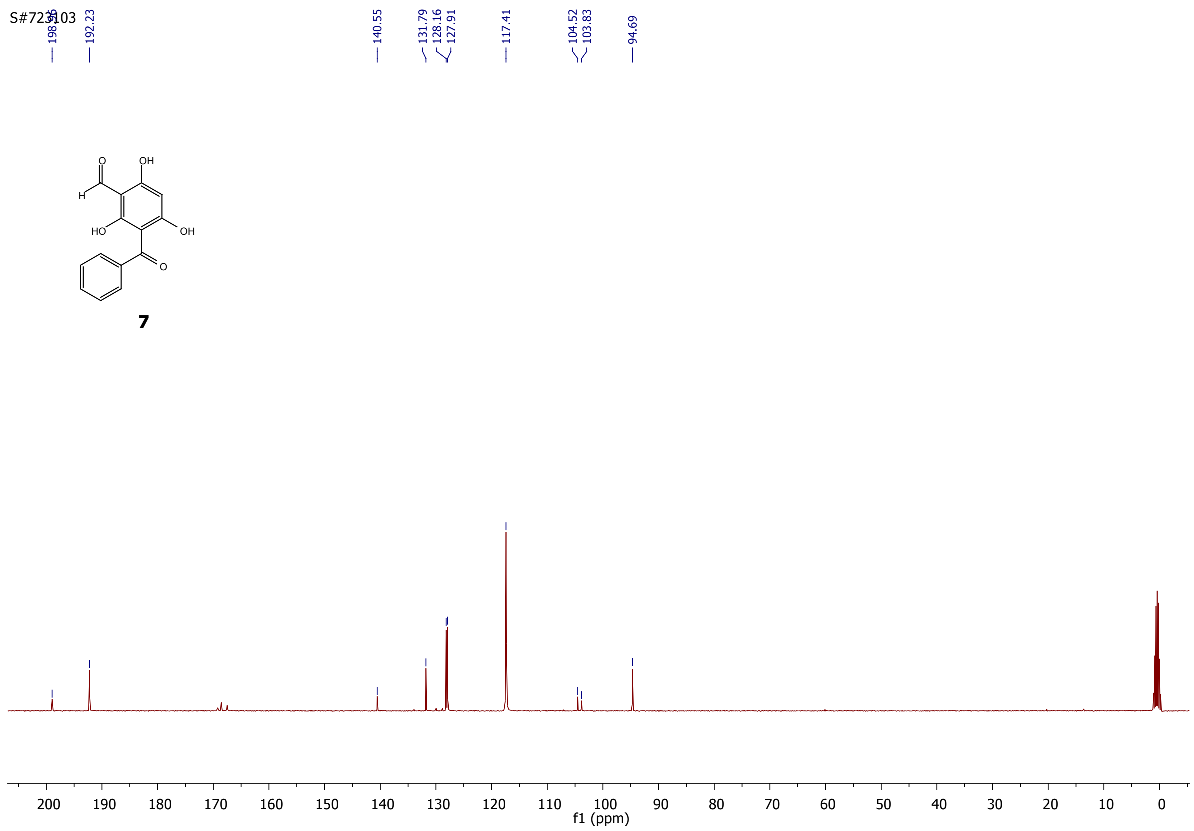


Guadial C (**2**)

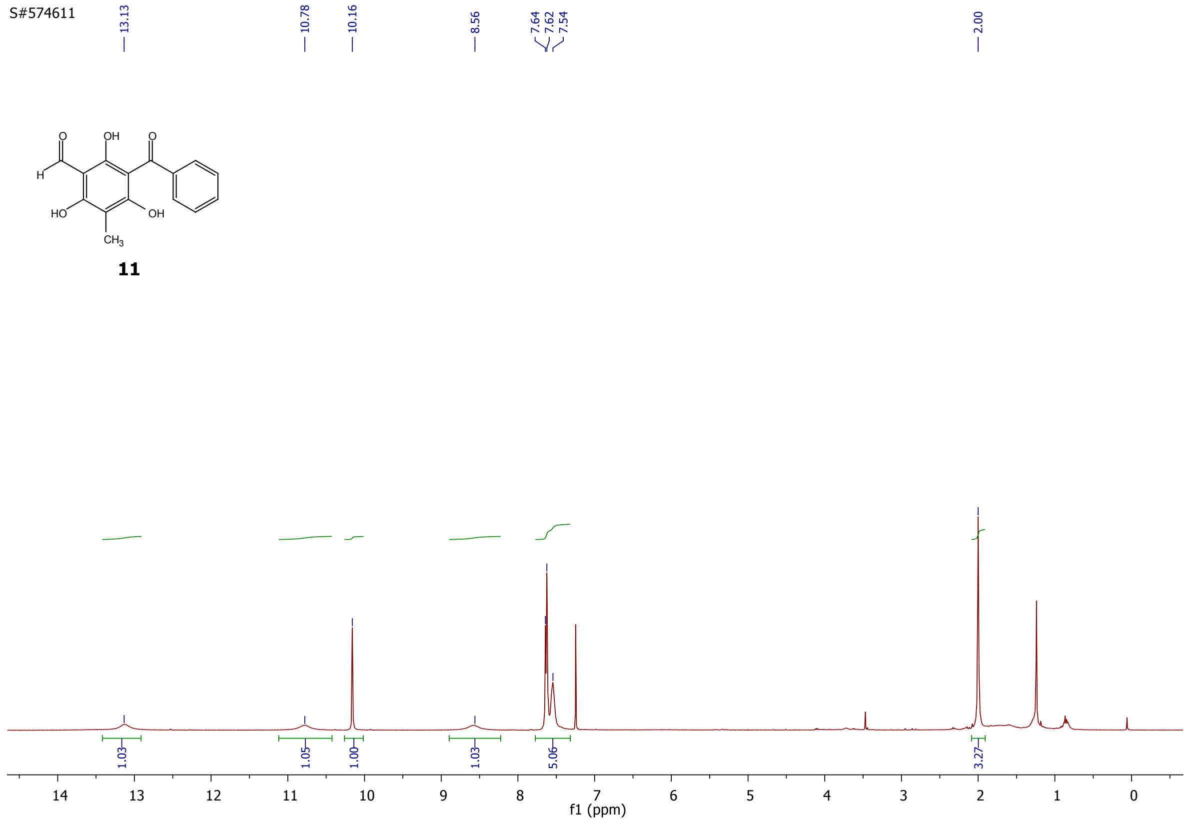

Guadial C (**2**)

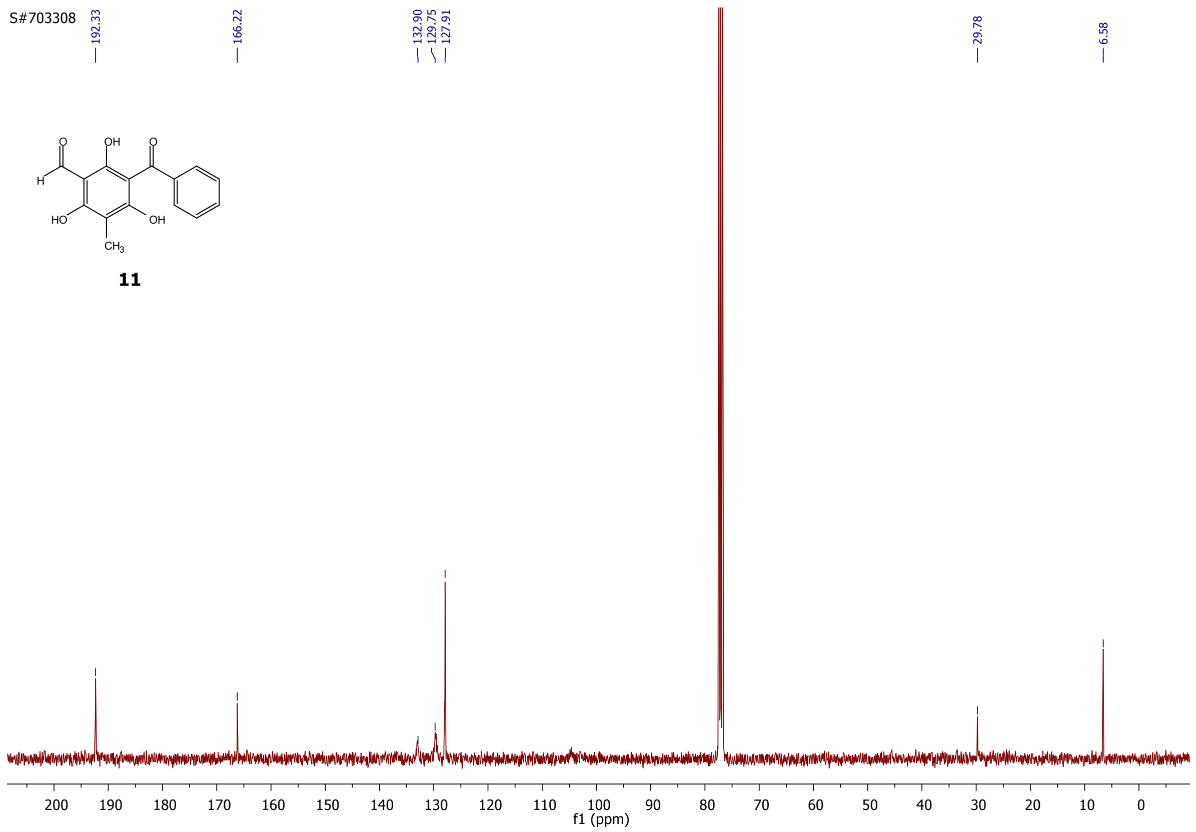
## $^{1}H$ and $^{13}C$ NMR Spectra of Compound 7:


**7**

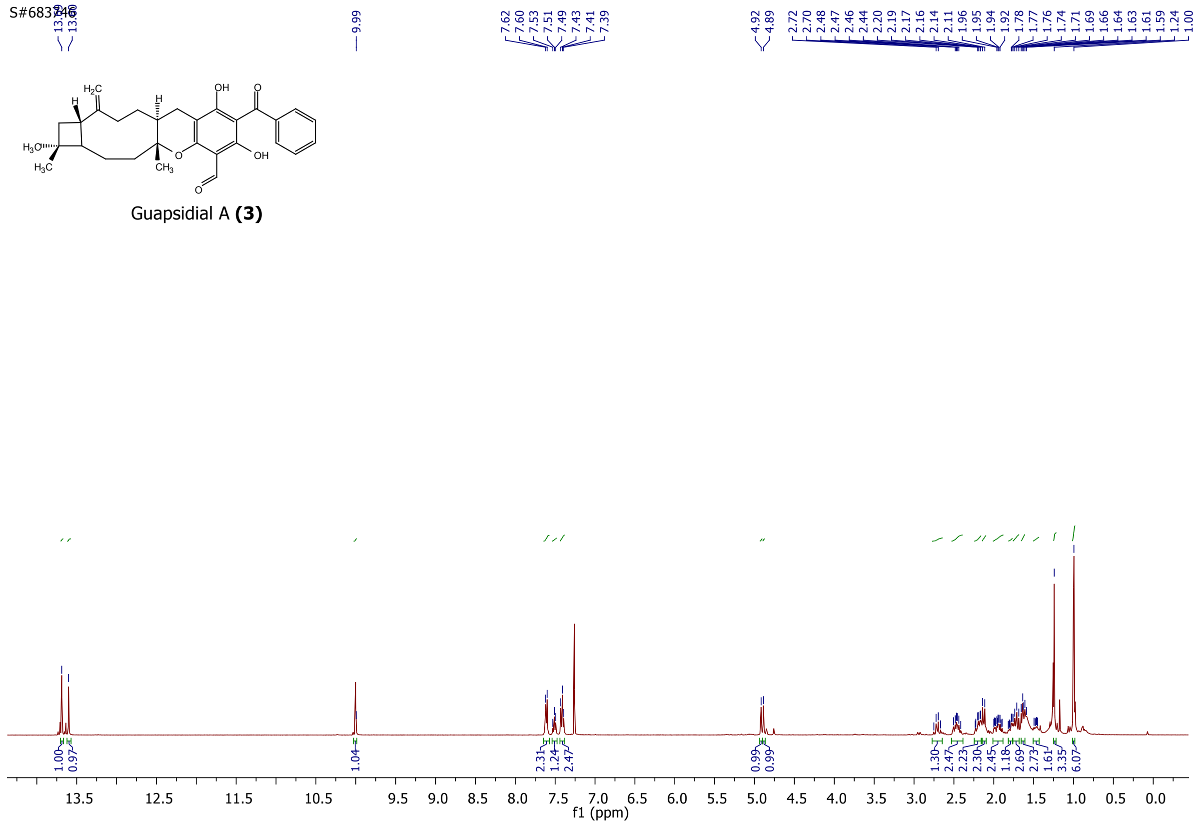


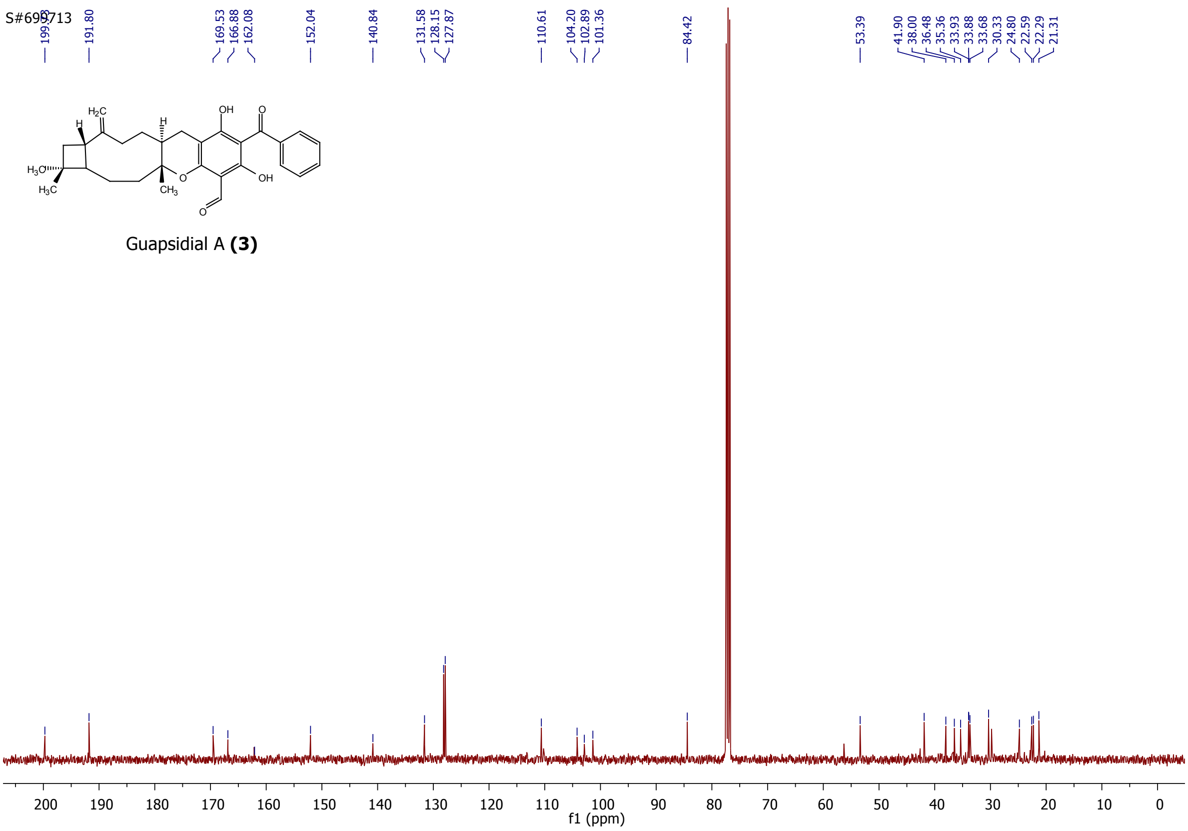
# $^1$H and $^{13}$C NMR Spectra of Compound 11:



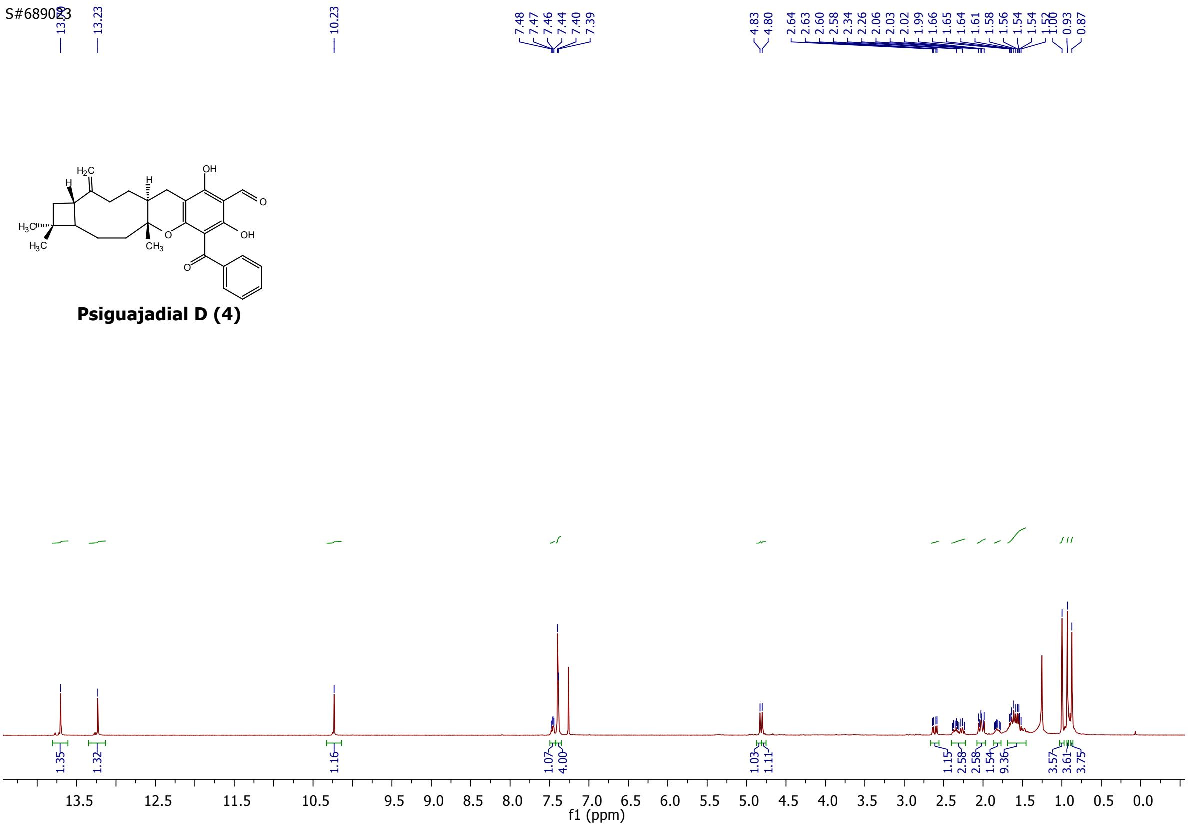


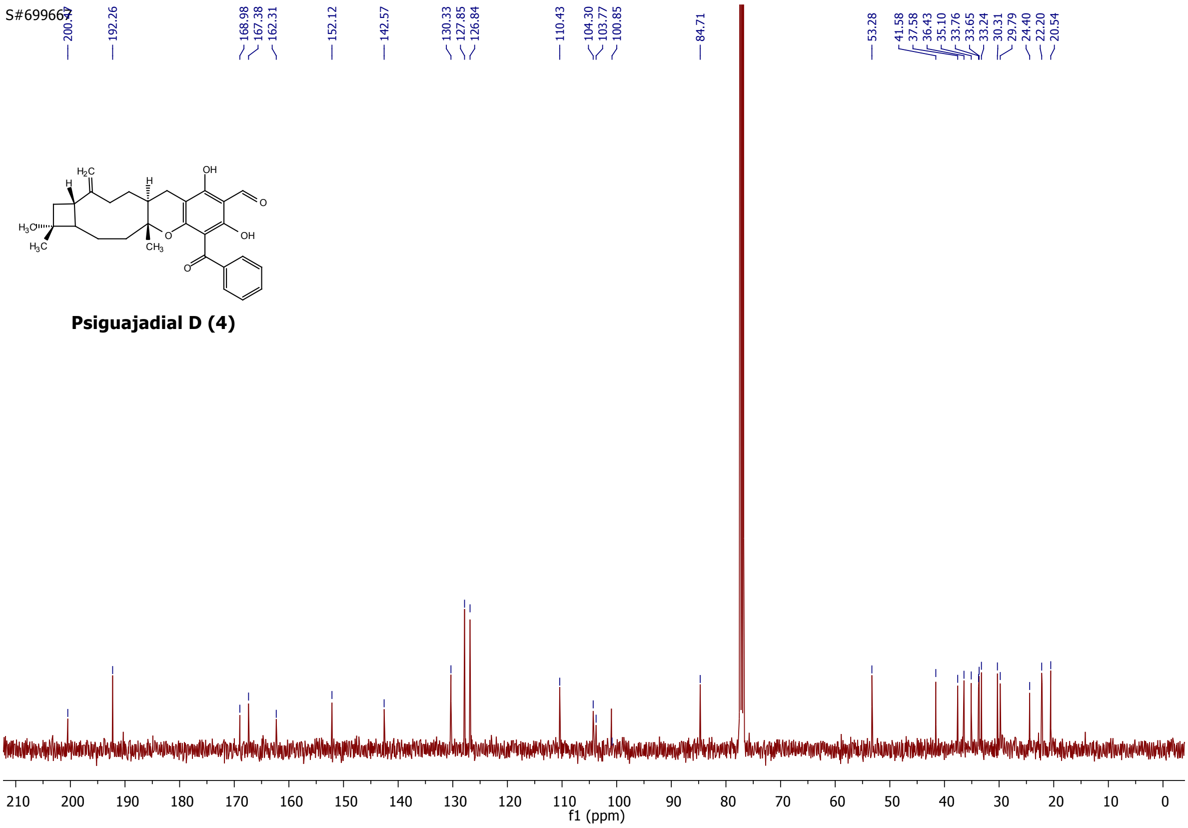
## $^{1}$H and $^{13}$C NMR Spectra of Guapsidial A (3):




Guapsidial A **(3)**

# $^1$H and $^{13}$C NMR Spectra of Psiguajadial D (4):


**Psiguajadial D (4)**



**Psiguajadial D (4)**