Supporting information file

(For Review only)

Synthesis of naturally occurring pyranonaphthoquinones: ($\pm$) 9-Demethoxyeleutherin, ($\pm$) 9-Demethoxyisoeleutherin and Pentalongin via Nef reaction

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General experiments

Preparation of 2-formyl-1,4-dimethoxynaphthalene (7)

Vilsmeier-Haack complex was prepared by standard protocol from dry N,N-dimethyl formamide (10ml, 0.125mol) and phosphorous oxychloride (12ml, 0.049). 1,4-dimethoxynaphthalene (5g, 0.026mmol) was added to the complex at 0°C under vigorous stirring. The resultant viscous mass was heated on a steam bath for 8h, cooled in ice bath and then poured into an ice cold sodium acetate solution (100ml). The reaction mass was then extracted with ether(30 x 3), combined ethereal layer was washed with excess of water, brine and dried over anhydrous Na₂SO₄ (20g). Removal of solvent provided crude product which was purified by column chromatography over silica gel using hexane as eluent which gave 2-Formyl-1,4-dimethoxynaphthalene (**7**) as a bright yellow solid. Yield: 5.4g (94%), MP 124°C (Lit.¹⁴: 124-126°C), IR(KBr) $\nu_{\max}$: 1714, 1605 cm⁻¹ ¹H δ ppm: 3.94 (s, 3H, -OCH₃), 4.08 (s, 3H, -OCH₃), 7.12 (s, 1H, C3 H), 7.55-7.68 (m, 2H, C6-H & C7-H), 8.18 (d, *J*=8Hz, 1H, C5-H), 8.28 (d, *J*=8Hz, 1H, C8-H), 10.56 (s, 1H, -CHO).

¹³C δ ppm: 57.2(2 CH₃), 102 (CH), 108.1 (C), 121 (CH), 123(CH), 126.2(CH), 128.1(C), 130.1(C), 149.3(C), 153.3(C), 192.1 (CHO); **Anal. Calcd for** C₁₃H₁₂O₃: C, 72.21; H, 5.59. Found: C, 72.11, H, 5.67. (Spectral data is in accordance with ref.14).

Preparation of 1,4-Dimethoxy-2-((E)-2-nitroprop-1-enyl)naphthalene (8) & 1,4-Dimethoxy-2-((E)-2-nitrovinyl)naphthalene(11)

A mixture of (**7**, 2.1g, 0.01mol), ammonium acetate (3.8g, 0.05mol) and nitroalkane (2ml, 0.02mol) in acetic acid(20ml) was refluxed for 20min and then cooled to room temperature. Ice (100g) was added to the mixture and the yellow precipitate was filtered. Further purification using column chromatography over silica gel using hexane as eluent provided the products as.

1,4-Dimethoxy-2-(E-2-nitroprop-1-enyl) naphthalene(8): Yield: 2.3g (86%), Yellow Solid; mp: 102⁰C. IR(KBr) $\nu_{\max}$: 1521, 1458 cm⁻¹; ¹H δ ppm : 2.42 (s, 3H, CH₃-C=), 3.85 (s, 3H, -OCH₃), 4.02 (s, 3H, -OCH₃), 6.62 (s, 1H, C3-H), 7.54-7.68 (m, 2H, C6-H & C7-H), 8.14 (d, *J*=8Hz, 1H, C5-H), 8.26 (d, *J*=8Hz, 1H, C8-H), 8.40 (d, *J*=3Hz, 1H, HC=C); ¹³C δ ppm: 14.2 (CH₃), 56.3 (CH₃), 57.1(CH₃), 102.6 (CH), 116.4, 122.1 (2 CH), 125.2 (CH), 125.7 (CH), 126.9 (2 CH), 128.2(C), 141.6(C), 145.4(C), 149.1(C); **Anal. Calcd for C₁₅H₁₅NO₄:** C, 65.92; H, 5.53; N, 5.13. Found: C, 65.83, H: 5.59, N, 5.21.

1,4-Dimethoxy-2-[(E)-2-nitrovinyl]naphthalene(11): Yield: 2.2g (84%); Bright yellow solid; mp: 86⁰C. IR(KBr) $\nu_{\max}$: 1605, 1528, 1458 cm⁻¹; ¹H δ ppm : 3.96 (s, 3H, -OCH₃), 4.05 (s, 3H, -OCH₃), 6.7 (s, 1H, C3-H), 7.26 (d, *J*= 16Hz, 1H, =CH-NO₂), 7.60-7.68 (m, 2H, C6-H & C7-H), 8.12 (d, *J*=8Hz, 1H, C5-H), 8.28 (d, *J*=8Hz, 1H, C8-H), 8.48 (d, 1H, *J*= 16Hz, 1H, HC=); ¹³C δ ppm: 56.3(CH₃), 57.1(CH₃), 102.8(CH), 116.2(C), 121.9(CH), 125.4(CH), 126.0(CH), 126.9(C), 128.4(C), 131.6(CH), 134.4(CH), 145.5(C), 149.1(C); **Anal. Calcd for C₁₄H₁₃NO₄:** C, 64.86; H, 5.05; N, 5.40. Found: C, 64.80; H, 5.12; N, 5.48.

1-(1,4-Dimethoxynaphthalen-2-yl)propan-2-ol (10): To a solution of 2-(1,4-dimethoxynaphthalen-3-yl)propan-2-one (**15**, 1 g, 0.004 mol) in methanol (10 ml 20 ml), sodium borohydride (0.3 g, 0.008 mol) was added in portions under stirring. Reaction was continued at room temperature for 3h. The reaction mixture was then concentrated, decomposed over a sat.NH₄Cl solution (30ml) and extracted with ether. Combined ethereal layers were washed with cold water and dried over anhydrous Na₂SO₄ (10g). Removal of ether under vacuum provided a viscous mass, which was purified by column chromatography over silica gel using hexane-ethyl acetate as eluent to obtain

1-(1,4-dimethoxynaphthalen-2-yl)propan-2-ol (**10**) as colourless crystals. Yield: 1.9g (94%);, MP: 48⁰C; IR (KBr) $\nu_{\max}$: 3440, 1270, 1100 cm⁻¹ ¹H δ ppm: 1.30 (d, *J*=6Hz, 3H, -CH₃) 2.30-2.45 (bs, 1H, OH), 2.94 (d, *J*=6Hz, 2H, Ar-CH₂), 3.96 (s, 3H, -OCH₃), 4.06 (s, 3H, -OCH₃), 4.18 (sextet *J*=6Hz, 1H, -CHOH), 6.62 (s, 1H, C3-H), 7.40-7.65 (m, 2H, C6-H & C7-H), 8.03(d, *J*=8Hz, 1H, C5-H), 8.24 (d, *J*=8Hz, 1H, C8-H). ¹³C δ ppm:

24.6 (CH₃), 43.8 (CH₂), 56.2 (CH₃), 56.8 (CH₃), 70.1(CH), 107.5 (CH) , 118.1(C), 121(2 CH), 124.5 (2 CH), 126.2 (C),128.5 (C), 144.4 (C),148.7

(C); **Anal. Calcd for** C₁₅H₁₈O₃: C, 73.15; H, 7.37. Found: C,73.02, H, 7.30; H, 6.01%;

1,4-Dimethoxy-2-(2-nitroethyl)naphthalene (12)

To a solution of NaBH₄ (0.5g, 0.014mol) in ethyl acetate-ethanol (20ml, 8:2), 1,4-dimethoxy-2-((E)-2-nitrovinyl) naphthalene (**16**, 2g, 0.007mol) was added portion wise at 15-20⁰C. The contents were stirred at room temperature for 1h and the reaction was monitored by TLC. Usual work up followed by column chromatographic purification over silica gel provided, 1,4-dimethoxy-2-(2-nitroethyl)naphthalene (**13**).

Yield: 1.6g, (80%); faint brown oil. IR (neat) $\nu_{\max}$: 1625, 1536, 1462, 1184 cm⁻¹, **¹H δ ppm** : 3.46 (t, *J*= 7Hz, 2H, Ar-CH₂), 3.90 (s, 3H, -OCH₃), 3.98 (s, 3H, -OCH₃), 4.74 (t, *J*= 7Hz, 2H, CH₂-NO₂), 6.58 (s, 1H, C3 H) , 7.45-7.61 (m, 2H, C6-H & C7-H) ,8.00-8.22 (m, *J*=8Hz, 1H, C5 & C8-H). **¹³C δ ppm**: 28.2(CH₂), 56.3(2CH₃), 78.3(CH₂), 107.7(CH), 117.2(C), 121.6(2CH), 124.4(CH), 125.8(CH), 126.7(C), 128.5(C), 144.9(C), 148.7(C); **Anal. Calcd for** C₁₄H₁₅NO₄: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.40; H, 5.73; N, 5.40.

S1. 2-Formyl-1,4-dimethoxynaphthalene (7)

¹H

¹³C

153.336
149.321
130.158
128.123
126.226
123.008
121.108
108.140
108.242
77.394
77.076
76.758
55.230

S2. 1,4-dimethoxy-2-((E)-2-nitroprop-1-enyl)naphthalene(8)

^1H

^{13}C

152.777
152.406
141.256
137.496
134.283
129.056
128.496
128.108
127.692
123.104
122.834
118.612
99.848
77.387
77.069
76.751
64.049
55.738

S3. 1-(1,4-Dimethoxynaphthalen-2-yl)propan-2-one (9)

¹H

¹³C

189.664
151.797
148.232
130.058
128.923
127.774
127.377
122.983
122.597
120.608
103.336
77.394
77.076
76.758
63.273
55.901
55.730
14.527

S4. 1-(1,4-Dimethoxynaphthalen-2-yl)propan-2-ol (10)

^1H

^{13}C

S5. 9-Demethoxyeleutherin (4)

¹H

¹³C

183.963
183.829
146.686
142.558
133.680
133.512
132.385
131.782
131.746
126.223
126.171
77.375
77.056
76.738
69.950
68.693
30.411
21.250
20.838

S6. 9-Demethoxyisoeleutherin(5)

¹H

¹³C

183.963
183.829
146.686
142.558
133.680
133.512
132.385
131.782
131.746
126.223
126.171
77.375
77.056
76.738
69.950
68.693
30.411
21.250
20.838

S7. 1,4-Dimethoxy-2-((E)-2-nitrovinyl)naphthalene(11)

¹H

¹³C

151.406
149.256
137.496
134.283
129.056
128.496
128.108
127.692
123.104
122.834
118.612
99.848
77.387
77.069
76.751
64.049
57.538

S7. 1,4-Dimethoxy-2-(2-nitroethyl)naphthalene (12)

¹H

¹³C

150.297
147.032
128.523
126.774
125.377
124.436
121.608
107.736
77.394
77.076
76.758
75.109
56.307
28.273

S9. 2-(1,4-Dimethoxynaphthalen-2-yl)acetic acid (13)

^1H

^{13}C