Some Chemical Speculation on the Biosynthesis of Corallidictyals A-D

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Supporting Information

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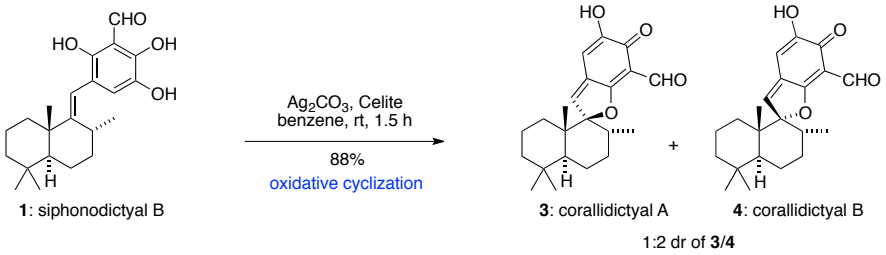
1. General methods

All chemicals used were purchased from commercial suppliers and used as received. All reactions were performed under an inert atmosphere of N_2, unless otherwise stated. All organic extracts were dried over anhydrous magnesium sulfate. Thin layer chromatography was performed using aluminium sheets coated with silica gel. Visualization was aided by viewing under a UV lamp and staining with ceric ammonium molybdate stain followed by heating. All R_f values were measured to the nearest 0.05. Flash chromatography was performed using 40-63 micron grade silica gel. Melting points were recorded on a digital melting point apparatus and are uncorrected. Infrared spectra were recorded using an FT-IR spectrometer as the neat compounds. High field NMR was recorded using a 500 MHz spectrometer (^{1}H at 500 MHz, ^{13}C at 125 MHz). The solvent used for NMR spectra was $CDCl_3$ unless otherwise specified. ^{1}H chemical shifts are reported in ppm on the δ-scale relative to TMS (δ 0.0) and ^{13}C NMR chemical shifts are reported in ppm relative to $CDCl_3$ (δ 77.0). Multiplicities are reported as (br) broad, (s) singlet, (d) doublet, (t) triplet, (q) quartet and (m) multiplet. All *J*-values were rounded to the nearest 0.1 Hz. ESI high resolution mass spectra were recorded on a Q-TOF mass spectrometer.

2. Experimental procedures

Oxidative cyclization of siphonodictyal B to give corallidictyals A and B



1: siphonodictyal B **3**: corallidictyal A **4**: corallidictyal B

1:2 dr of **3**/**4**

To a solution of siphonodictyal B (**1**) (7.0 mg, 0.020 mmol) in benzene (6 mL) at room temperature was added Ag_2CO_3 (21.5 mg, 0.078 mmol) and Celite (50 mg). The resultant reaction mixture was stirred at room temperature for 1.5 h. The mixture was diluted with Et_2O (50 mL), filtered through a pad of Celite, and finally the solvent was removed under reduced pressure to give an inseparable 1:2 mixture of corallidictyal A (**3**) and corallidictyal B (**4**) as a light brown solid (6.1 mg, 88%).

Data for 3 and 4:

R_f = 0.60 (petrol/EtOAc, 1:1)

IR (film): 3322, 2927, 2856, 1692, 1643, 1598, 1566 cm^{-1}

HRMS ($C_{22}H_{28}O_4$, ESI): calculated $[M-H]^-$ 355.1915, found 355.1911.

NMR data for 3:

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.26 (s, 1H), 7.50 (s, 1H), 7.42 (br s, 1H), 6.48 (s, 1H), 2.63 (m, 1H), 2.05 – 1.99 (m, 2H), 1.83 – 1.73 (m, 1H), 1.67 – 0.77 (m, 8H), 1.35 (s, 3H), 0.93 (s, 3H), 0.91 (s, 3H), 0.54 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 186.6, 180.3, 175.8, 150.27, 147.9, 131.7, 113.1, 107.68, 98.5, 52.3, 44.8, 41.7, 35.5, 33.83, 33.6, 33.50, 33.47, 21.86, 21.48, 18.23, 16.4, 15.5.

NMR data for 4:

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.30 (s, 1H), 7.42 (br s, 1H), 7.25 (s, 1H), 6.43 (s, 1H), 2.43 (m, 1H), 1.83 – 1.73 (m, 3H), 1.67 – 0.77 (m, 8H), 1.27 (s, 3H), 0.95 (s, 3H), 0.87 (s, 3H), 0.55 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 186.2, 180.0, 177.1, 150.30, 149.8, 130.8, 111.2, 107.71, 98.2, 47.3, 44.0, 41.2, 34.2, 33.75, 33.31, 32.9 32.0, 21.89, 21.45, 19.4, 18.18 15.6.

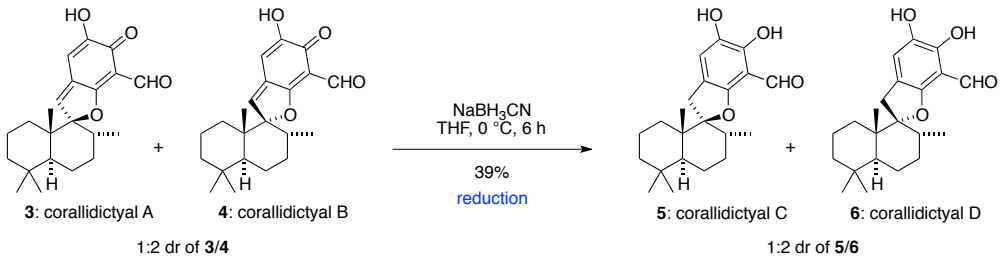
Alternative oxidative cyclization procedure using chloranil as the oxidant

To a solution of siphonodictyal B (**1**) (10.0 mg, 0.028 mmol) in CH_2Cl_2 (6 mL) at room temperature was added chloranil (73 mg, 0.30 mmol). The resultant mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on SiO_2 (petrol/EtOAc, 8:1) to give an inseparable 1:2 mixture of corallidictyal A (**3**) and corallidictyal B (**4**) as a light brown solid (6.2 mg, 62%).

Aerobic oxidation of siphonodictyal B to give corallidictyals A and B

A solution of siphonodictyal B (**1**) (56 mg, 0.16 mmol) in MeOH (30 mL) at room temperature was stirred for 8 days under an O_2 atmosphere. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on SiO_2 (petrol/ethyl acetate, 4:1) to give an inseparable 1:2 mixture of corallidictyal A (**3**) and corallidictyal B (**4**) as a light brown solid (16 mg, 29%).

Reduction of corallidictyals A and B to give corallidictyals C and D



To a solution of corallidictyal A (**3**) and corallidictyal B (**4**) (1:2 dr, 50 mg, 0.14 mmol) in THF (20 mL) at 0 °C, was added sodium cyanoborohydride (49 mg, 0.77 mmol). The resultant mixture was stirred at 0 °C for 6 h. The mixture was quenched with water (20 mL) and extracted with Et_2O (2 x 50 mL). The combined organic extracts were sequentially washed with water (50 mL), brine (25 mL) then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resultant residue was purified by flash column chromatography on SiO_2 (petrol/Et_2O, 3:1) to give an inseparable 1:2 mixture of corallidictyal C (**5**) and corallidictyal D (**6**) as a yellow solid (20 mg, 39%).

Data for 5 and 6:

R_f = 0.75 (petrol/EtOAc, 1:1)

IR (film): 3340, 2922, 2852, 1732, 1651, 1575, 1466 cm^{-1}

HRMS ($C_{22}H_{30}O_4$, ESI): calculated $[M-H]^-$ 357.2071, found 357.2078.

NMR data for 5:

^{1}H NMR (500 MHz, DMSO-d6): δ 10.53 (br s, 1H), 10.08 (s, 1H), 8.66 (br s, 1H), 6.94 (s, 1H), 3.05 (d, *J* = 16.6 Hz, 1H), 2.85 (d, *J* = 16.6 Hz, 1H), 2.18 (m, 1H), 1.63 – 1.06 (m, 10H), 1.12 (s, 3H), 1.04 (dd, *J* = 12.5 Hz, *J* = 3.1 Hz, 1H), 0.85 (s, 3H), 0.82 (s, 3H), 0.68 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d6): δ 191.7, 155.0, 147.0, 137.3, 120.6, 117.2, 106.14, 99.8, 47.1, 43.0, 41.2, 34.6, 33.17, 32.6, 30.5, 30.3, 29.1, 21.5, 20.7, 17.7, 15.0, 14.6.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.10 (br s, 1H), 10.13 (s, 1H), 6.96 (s, 1H), 5.04 (br s, 1H), 3.07 (d, *J* = 16.3 Hz, 1H), 2.88 (d, *J* = 16.3 Hz, 1H), 2.26 (m, 1H), 1.70 – 0.99 (m, 10 H), 1.17 (s, 3H), 1.01 (dd, *J* = 13.0 Hz, *J* = 3.3 Hz, 1H), 0.88 (s, 3H), 0.86 (s, 3H), 0.74 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ, 192.87, 156.5, 146.10, 136.7, 119.3, 117.7, 105.6, 100.9, 48.1, 42.5, 35.1, 33.47, 33.3, 33.0, 31.2, 30.9, 21.6, 21.2, 18.1, 15.3, 14.9.

NMR data for 6:

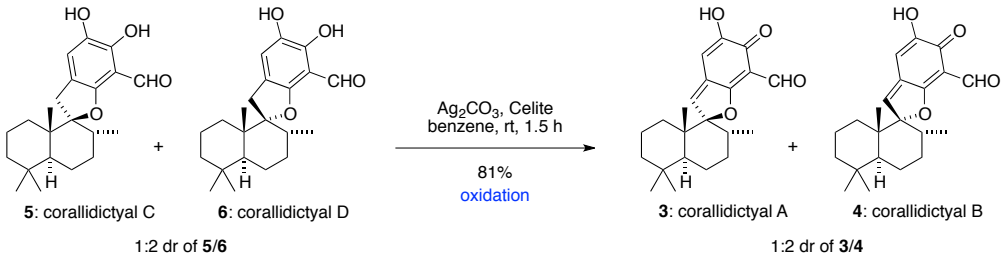
^{1}H NMR (500 MHz, DMSO-d6): δ 10.53 (br s, 1H), 10.14 (s, 1H), 8.66 (br s, 1H), 6.90 (s, 1H), 3.09 (d, *J* = 16.3 Hz, 1H), 2.71 (d, *J* = 16.3 Hz, 1H), 1.77 (m, 1H), 1.63 – 1.06 (m, 11H), 0.92 (s, 3H), 0.88 (s, 3H), 0.82 (s, 3H), 0.66 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d6): δ 192.0, 155.7, 146.9, 137.4, 120.7, 116.8, 106.06, 98.2, 46.1, 42.0, 41.3, 36.4, 33.23, 32.9, 32.8, 30.70, 30.68, 21.7, 20.9, 17.8, 15.7, 15.5.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.09 (br s, 1H), 10.20 (s, 1H), 6.93 (s, 1H), 5.04 (br s, 1H), 3.15 (d, *J* = 16.0 Hz, 1H), 2.73 (d, *J* = 16.0 Hz, 1H), 1.79 (m, 1H), 1.70 – 0.99 (m, 10 H), 1.48 (dd, *J* = 12.9 Hz, *J* = 4.0 Hz, 1H), 0.96 (s, 3H), 0.91 (s, 3H), 0.85 (s, 3H), 0.74 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 192.91, 156.9, 146.1, 136.8, 119.4, 117.4, 105.7, 99.3, 46.8, 41.9, 41.7, 37.1, 33.50, 33.4, 31.3, 31.1, 29.8, 21.9, 21.4, 18.2, 16.2, 15.6.

Oxidation of corallidictyalsf C and D to give corallidictyals A and B



5: corallidictyal C **6**: corallidictyal D

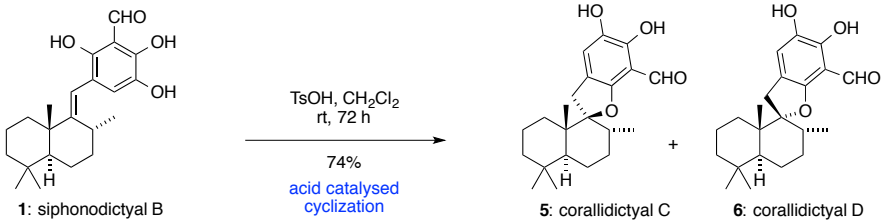
1:2 dr of **5**/**6**

3: corallidictyal A **4**: corallidictyal B

1:2 dr of **3**/**4**

To a solution of corallidictyal C (**5**) and corallidictyal D (**6**) (1:2 dr, 10.0 mg, 0.028 mmol) mmol) in benzene (3 mL) at room temperature was added Ag_2CO_3 (31 mg, 0.11 mmol) and Celite (50 mg). The resultant mixture was stirred at room temperature for 1.5 h. The mixture was then diluted with Et_2O (50 mL), filtered through a pad of Celite, and the solvent was removed under reduced pressure to give an inseparable 1:2 mixture of corallidictyal A (**3**) and corallidictyal B (**4**) as a light brown solid (8.1 mg, 81%). Data for **3** and **4** matched that previously obtained.

Acid catalysed cyclization of siphonodictyal B to give corallidictyals C and D



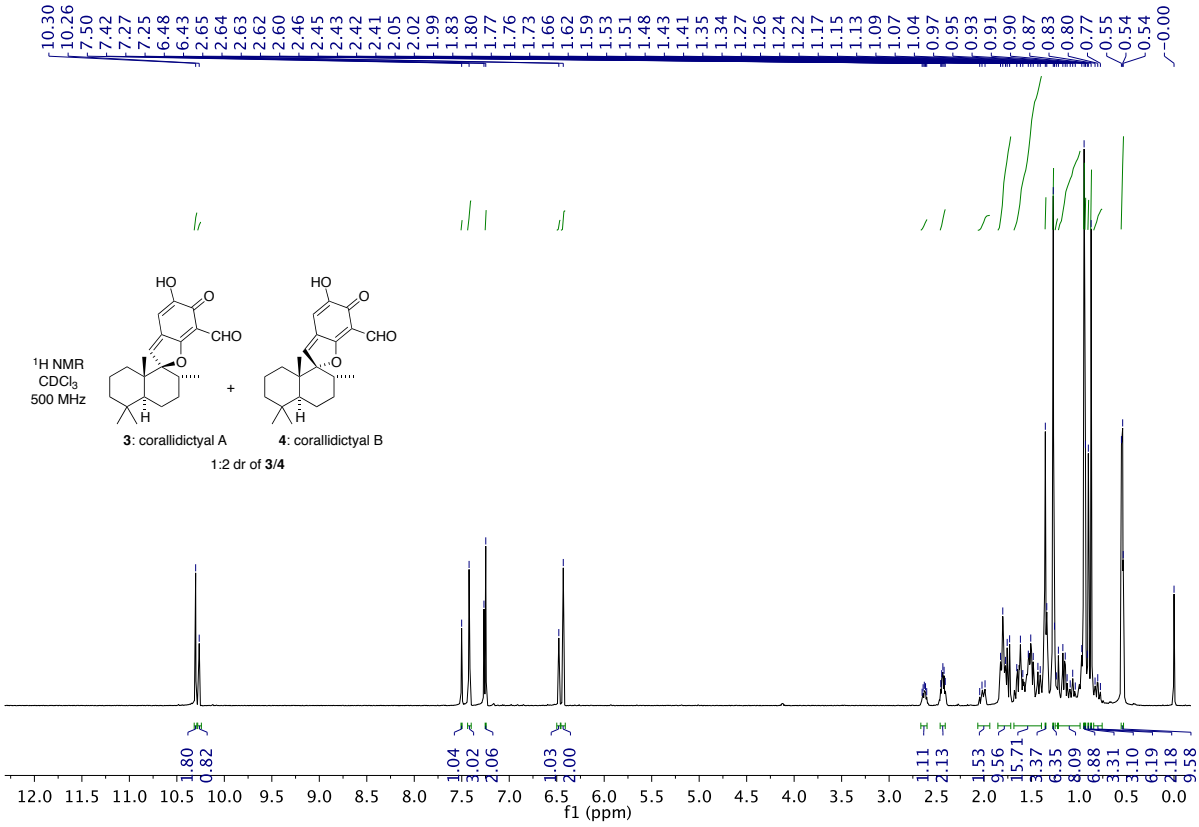
1: siphonodictyal B

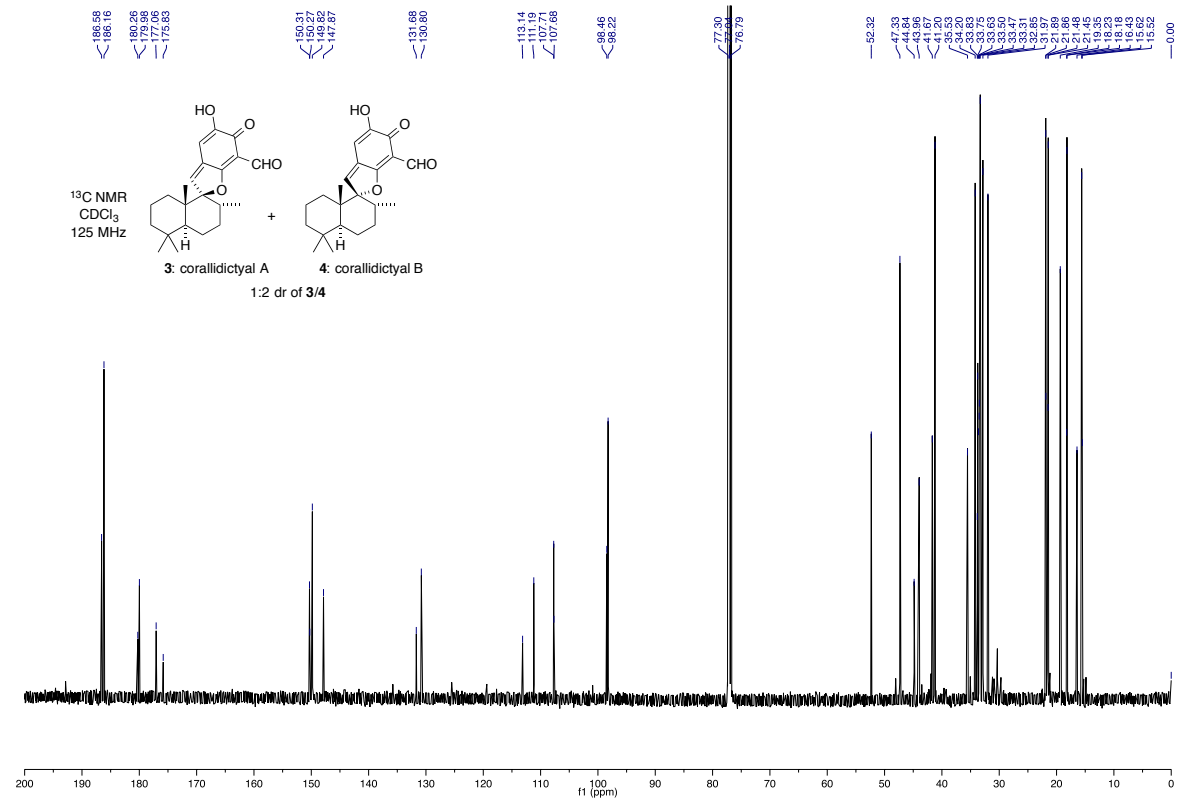
5: corallidictyal C **6**: corallidictyal D

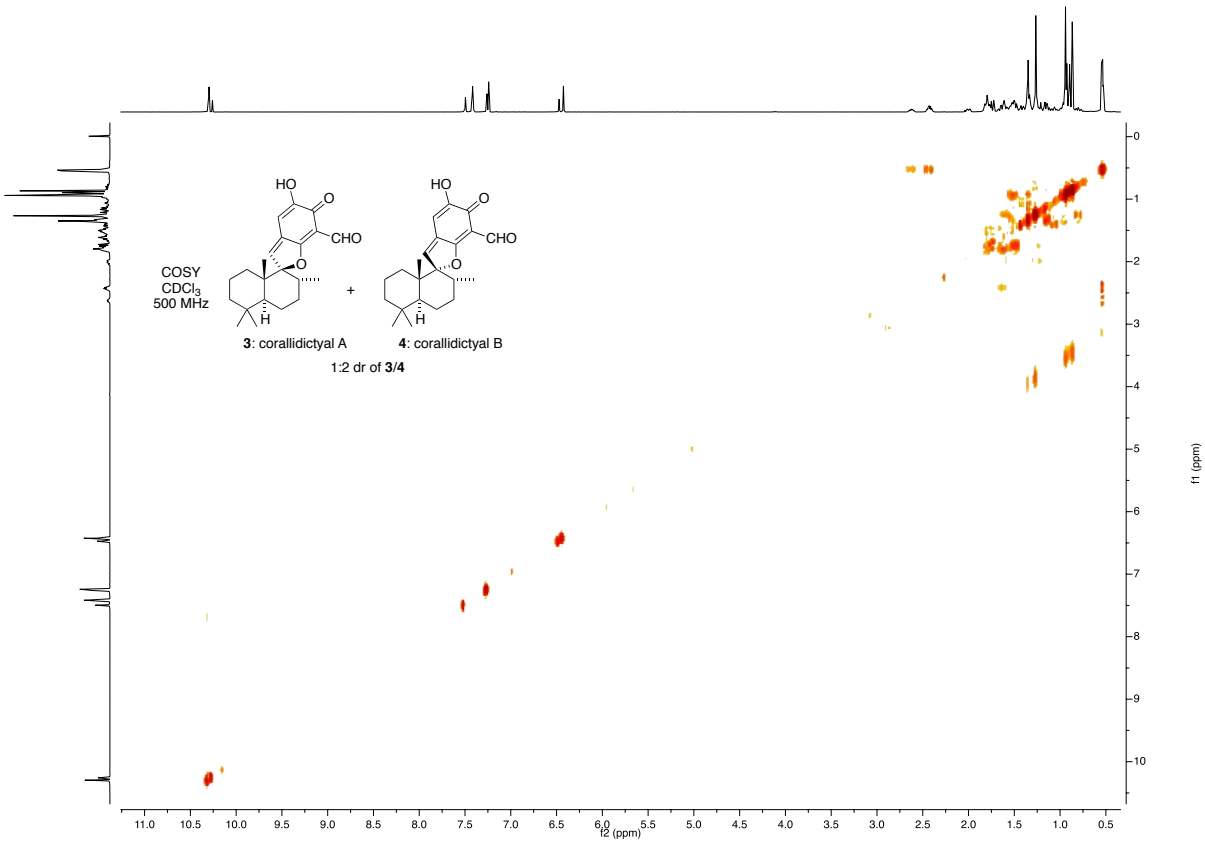
1:1:0.5 mixture of **5**/**6**/unknown isomer

To a solution of siphonodictyal B (**1**) (7.0 mg, 0.020 mmol) in CH_2Cl_2 (10 mL) at room temperature was added *p*-toluenesulfonic acid (5.2 mg, 0.030 mmol). The resultant mixture was stirred at room temperature for 72 h. The mixture was diluted with water (20 mL) and extracted with Et_2O (2 x 25 mL). The combined organic extracts were sequentially washed with saturated $NaHCO_3$ solution (10 mL), water (25 mL) and brine (10 mL), and then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography on SiO_2 (petrol/Et_2O, 3:1) to give an inseparable 1:1:0.5 mixture of corallidictyal C (**5**), corallidictyal D (**6**) and an unknown isomer as a yellow solid (5.2 mg, 74%).

3. NMR spectra



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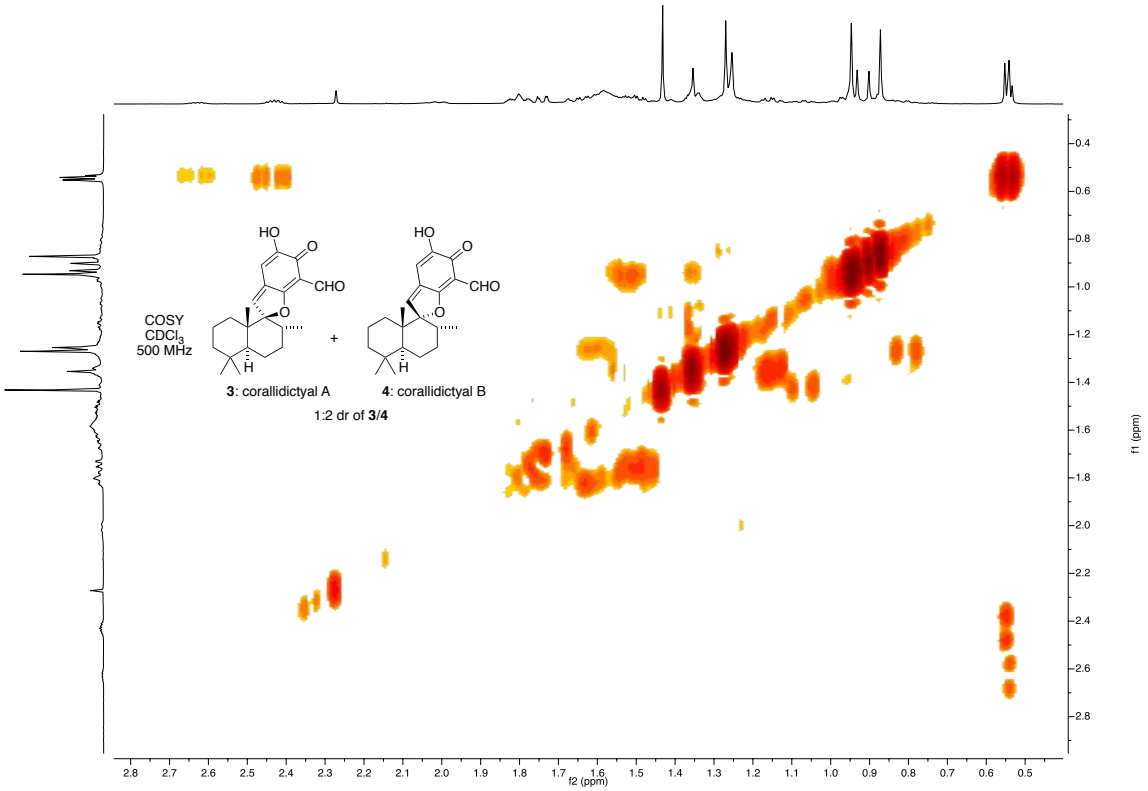
O
CHO
O
H
+
3: corallidictyal A
4: corallidictyal B
1:2 dr of 3/4
f2 (ppm)
f1 (ppm)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+
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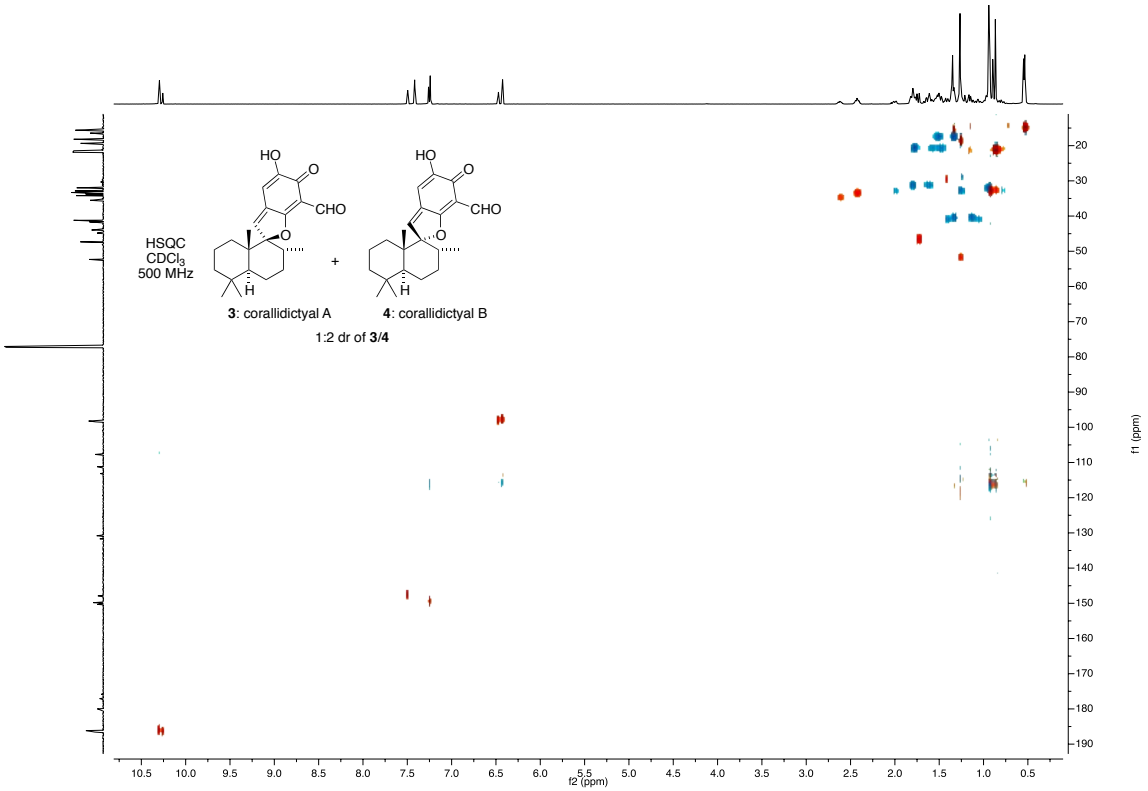
4: corallidictyal B
1:2 dr of 3/4
f2 (ppm)
f1 (ppm)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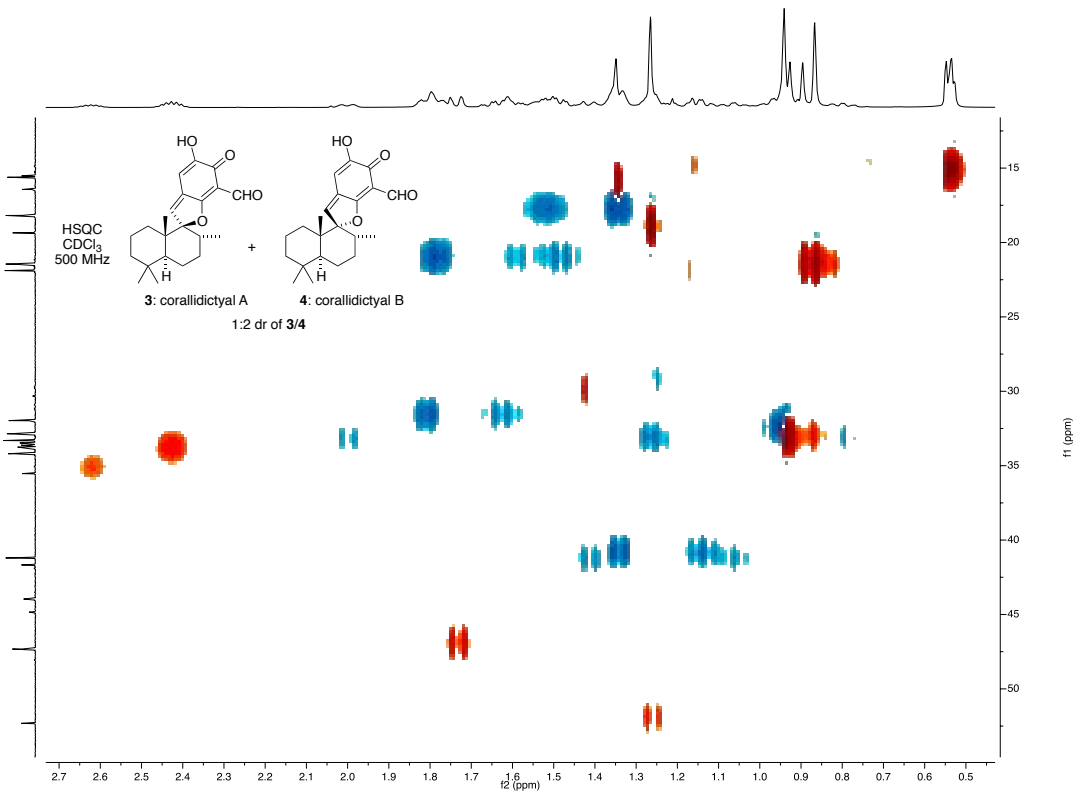
f2 (ppm)
f1 (ppm)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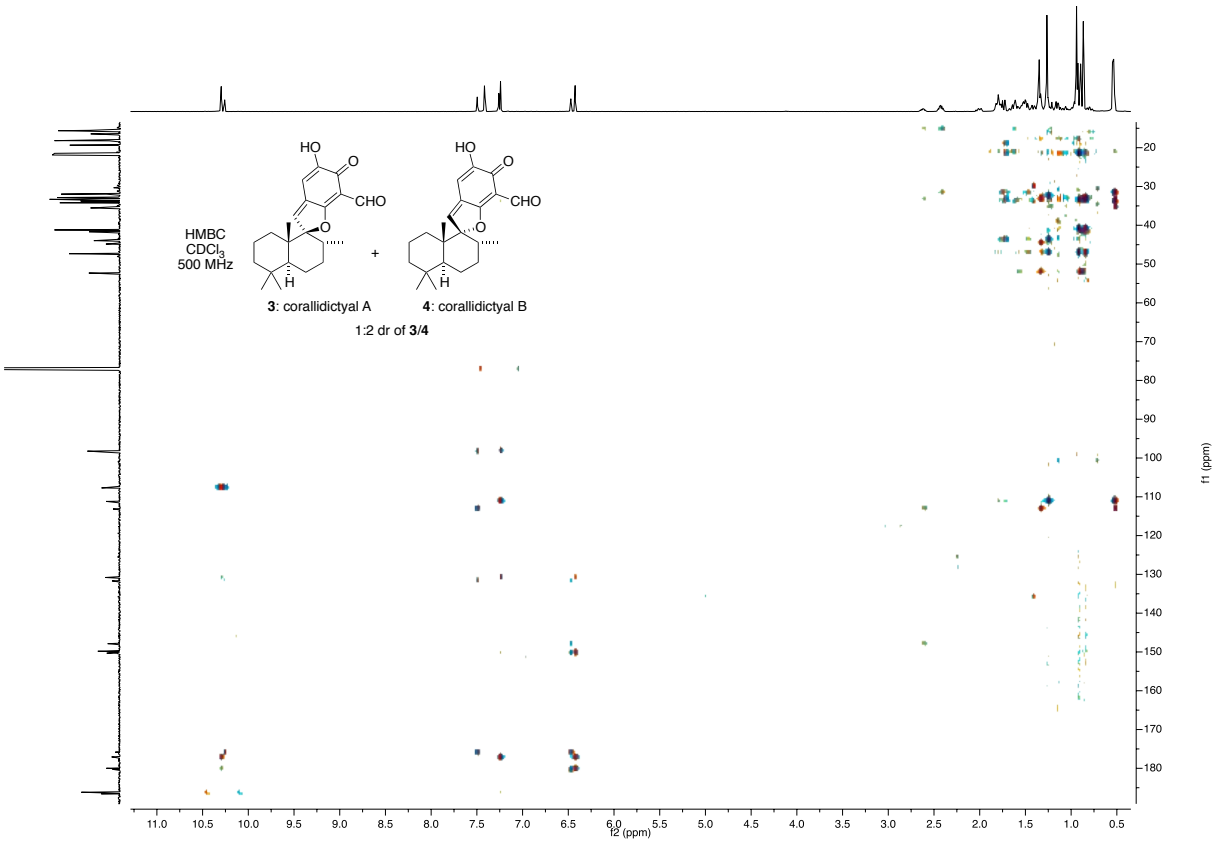
f2 (ppm)
f1 (ppm)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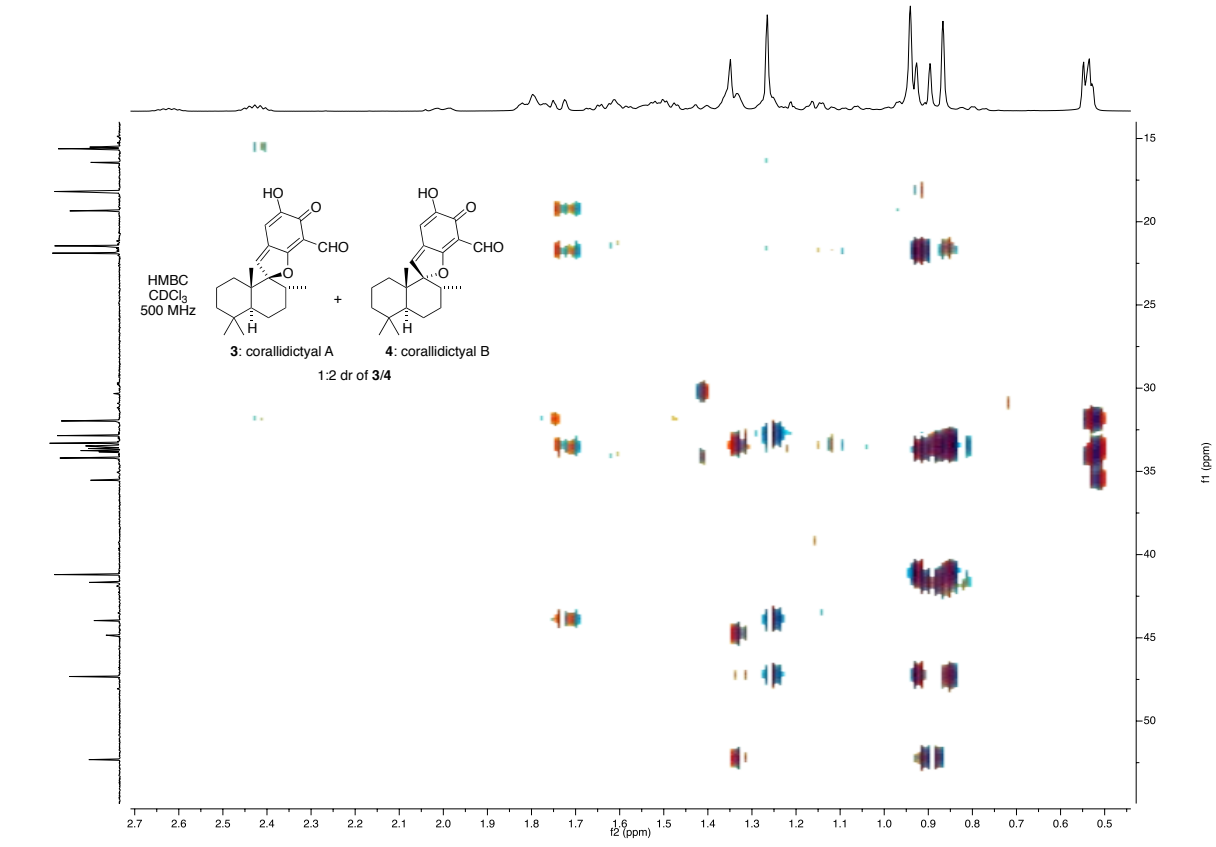
1:2 dr of 3/4
f2 (ppm)
f1 (ppm)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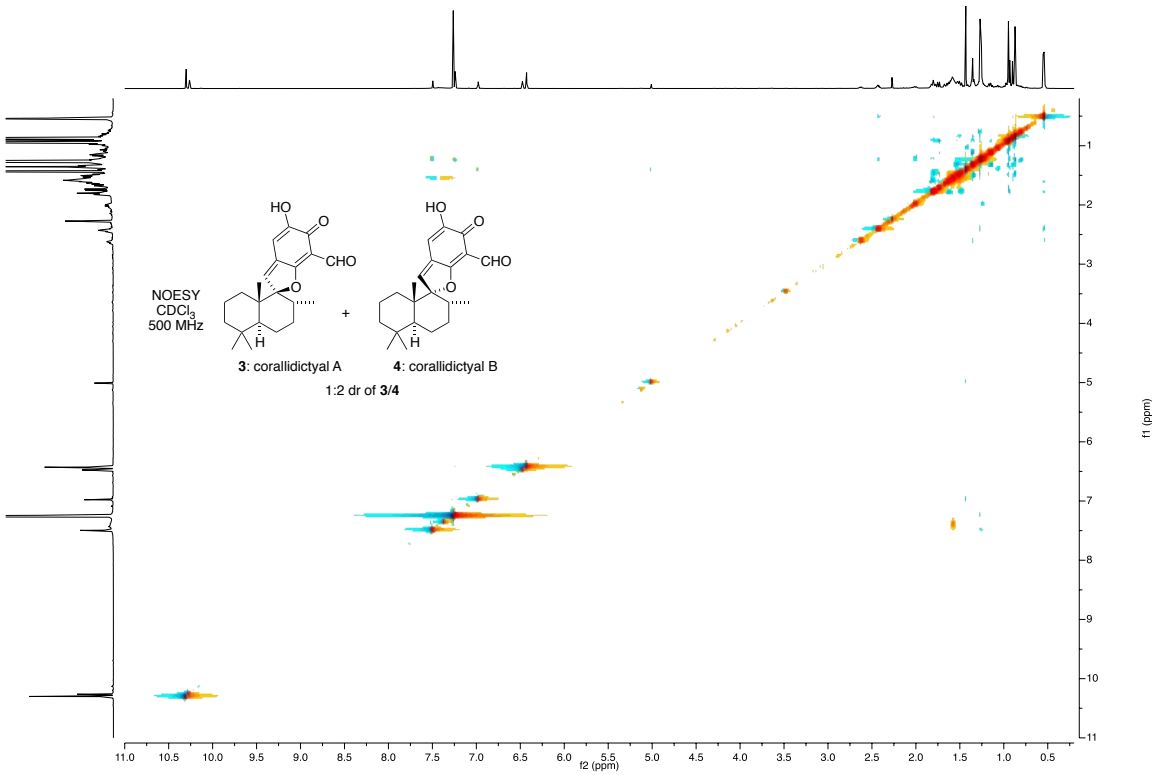
f2 (ppm)
f1 (ppm)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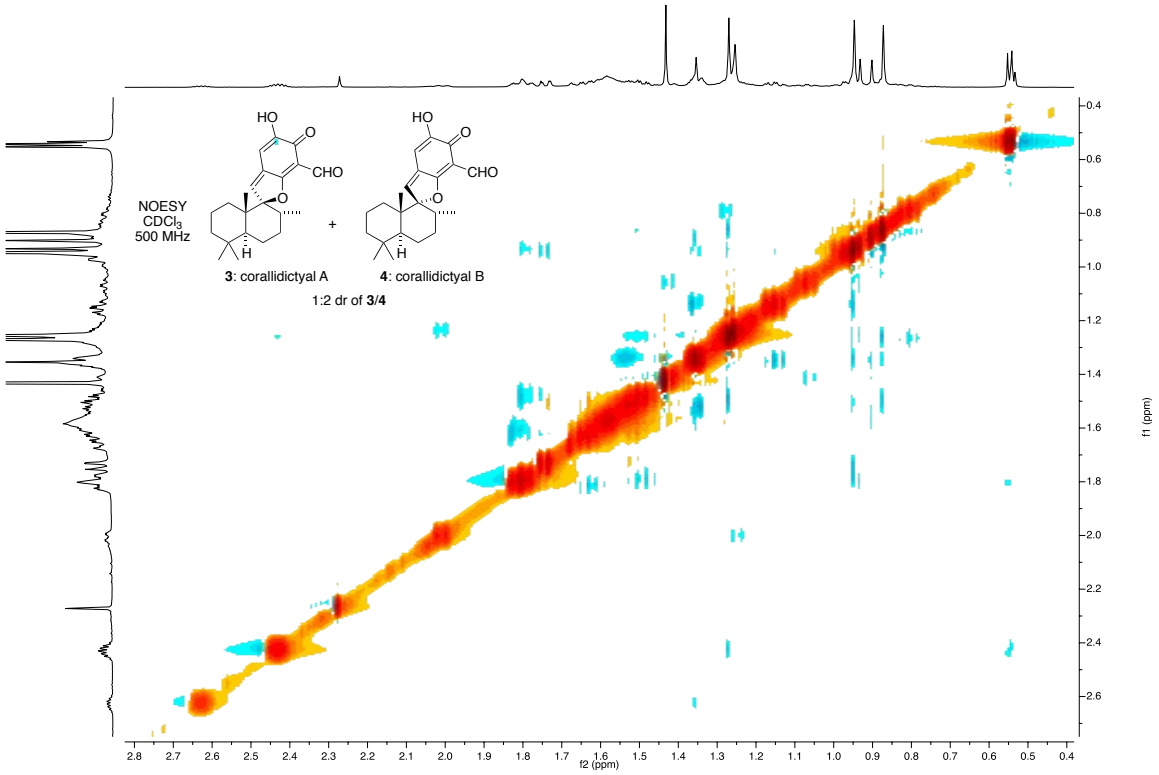
f2 (ppm)
f1 (ppm)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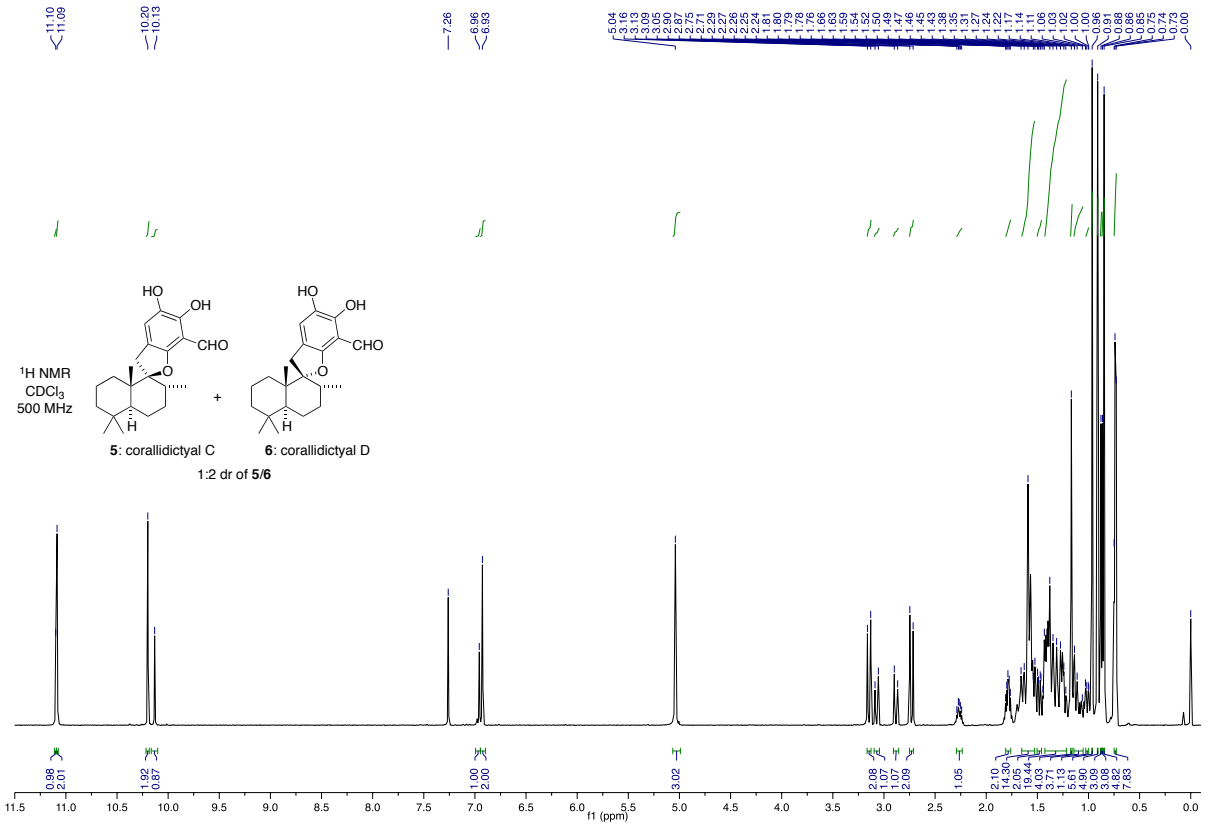
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6: corallidictyal D
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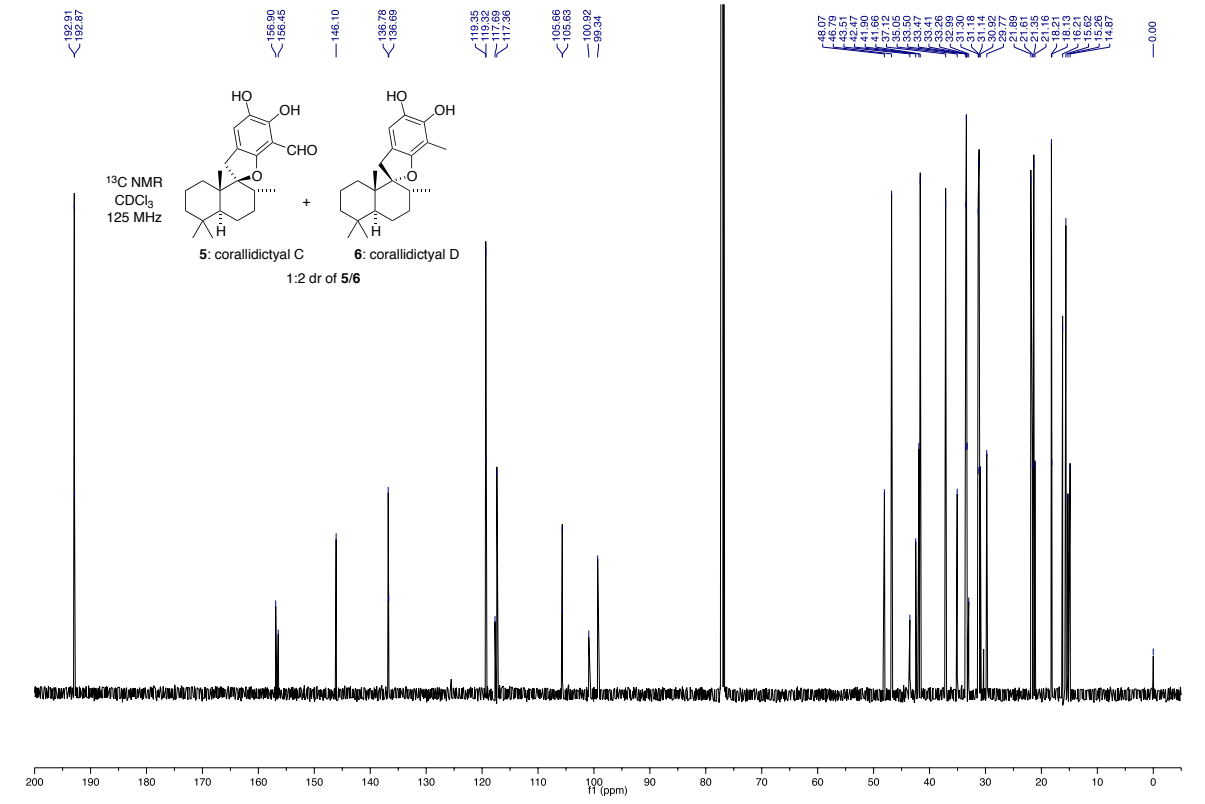
f1 (ppm)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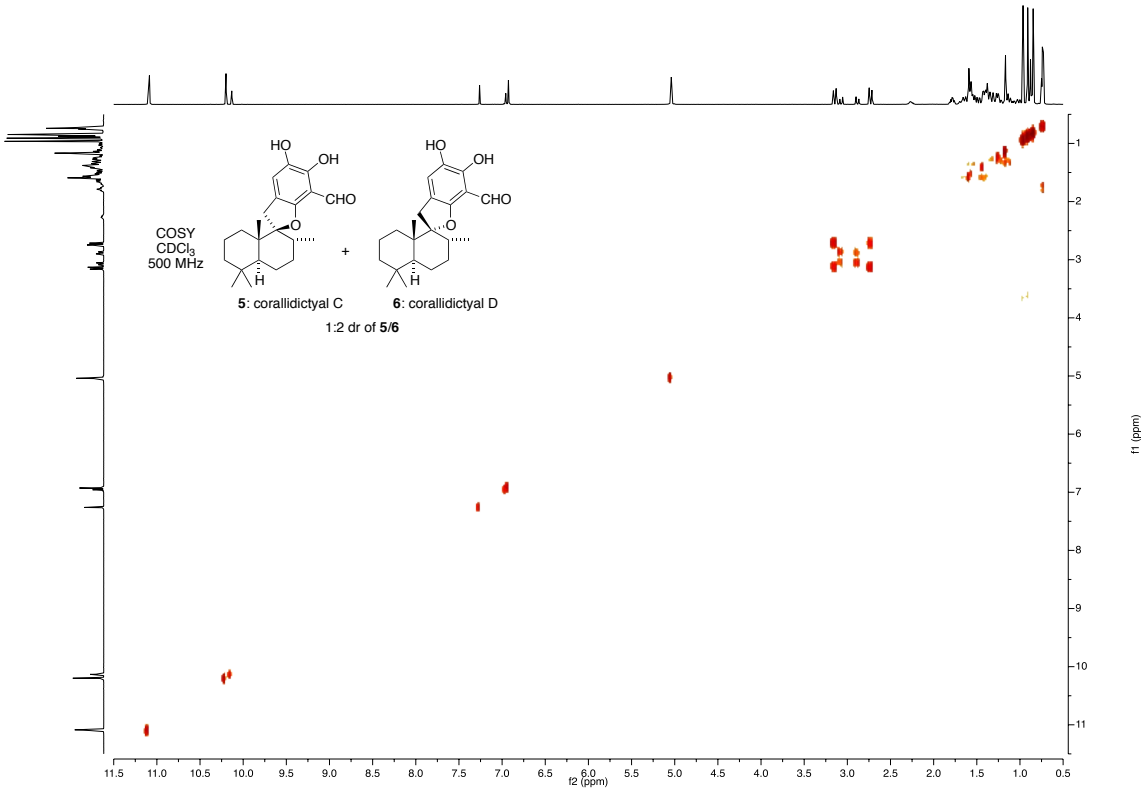
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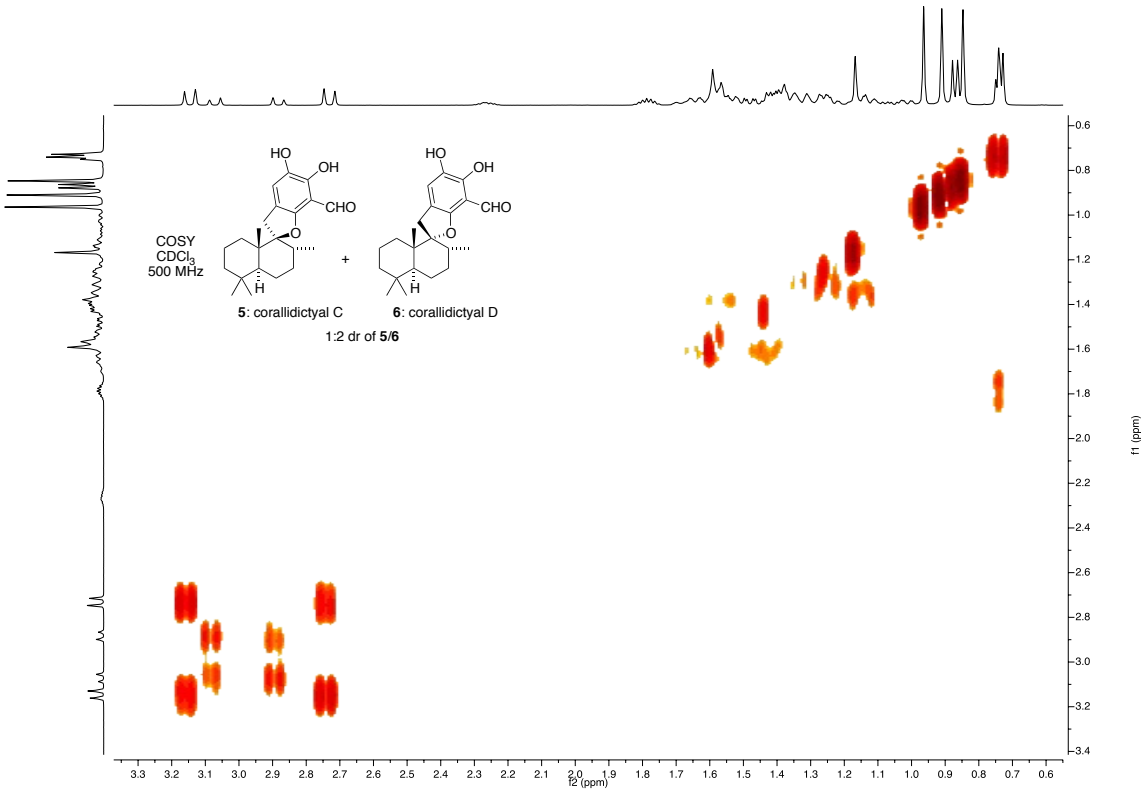
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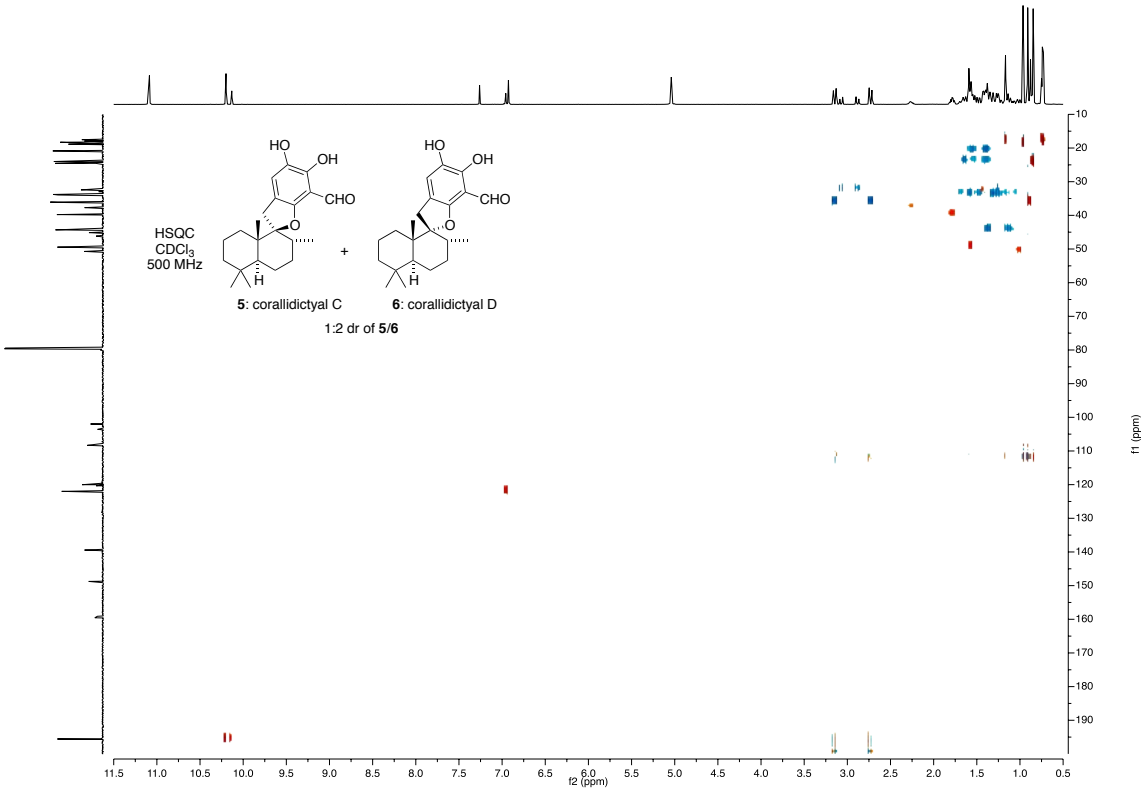
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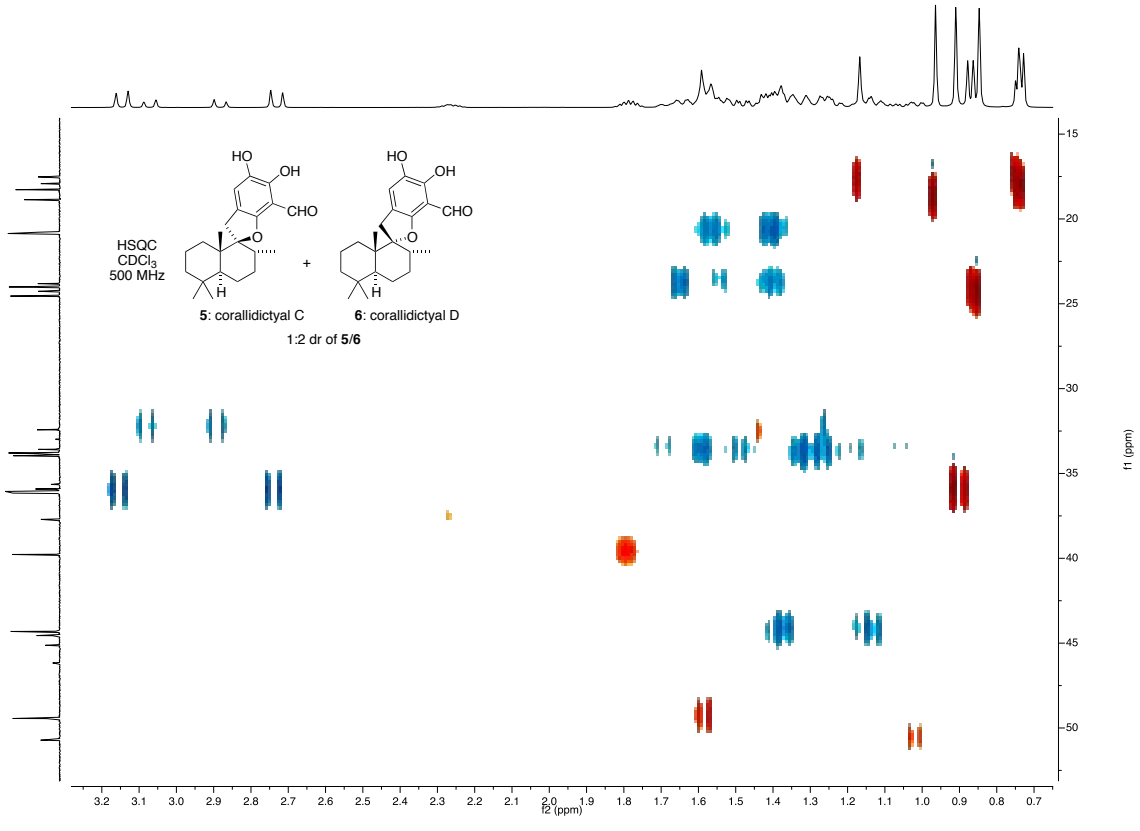
1:2 dr of 5/6
f2 (ppm)
f1 (ppm)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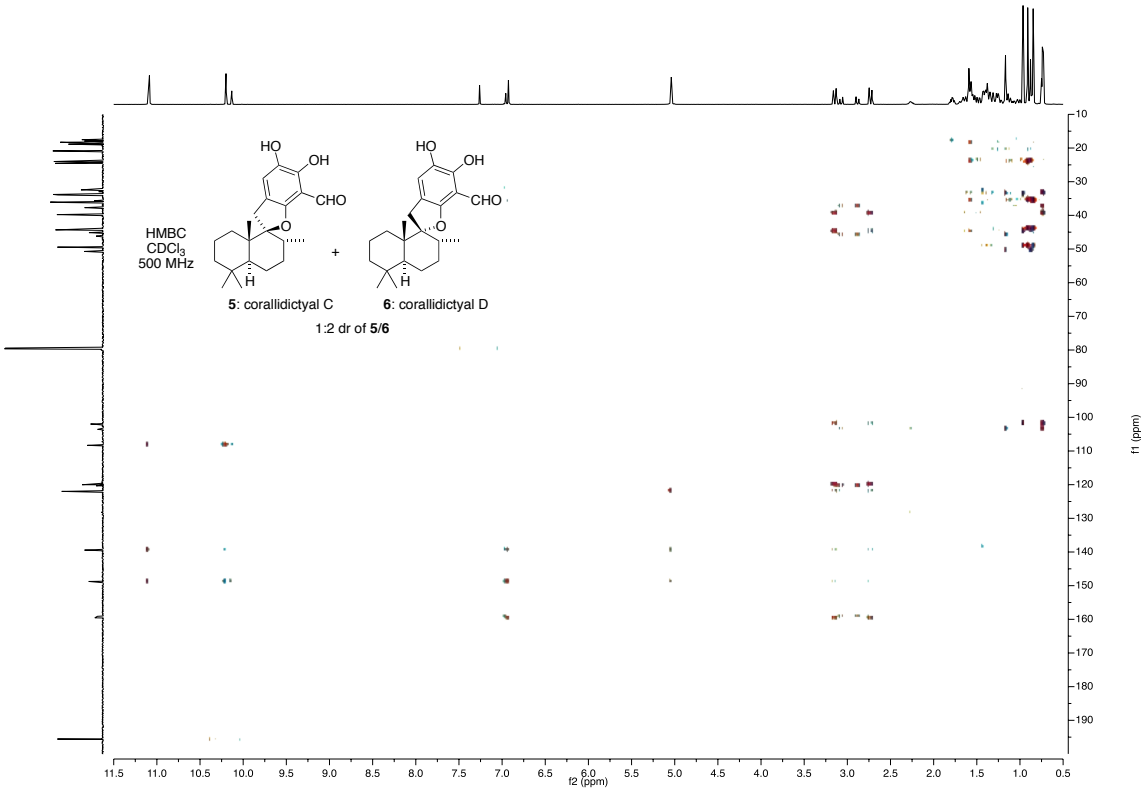
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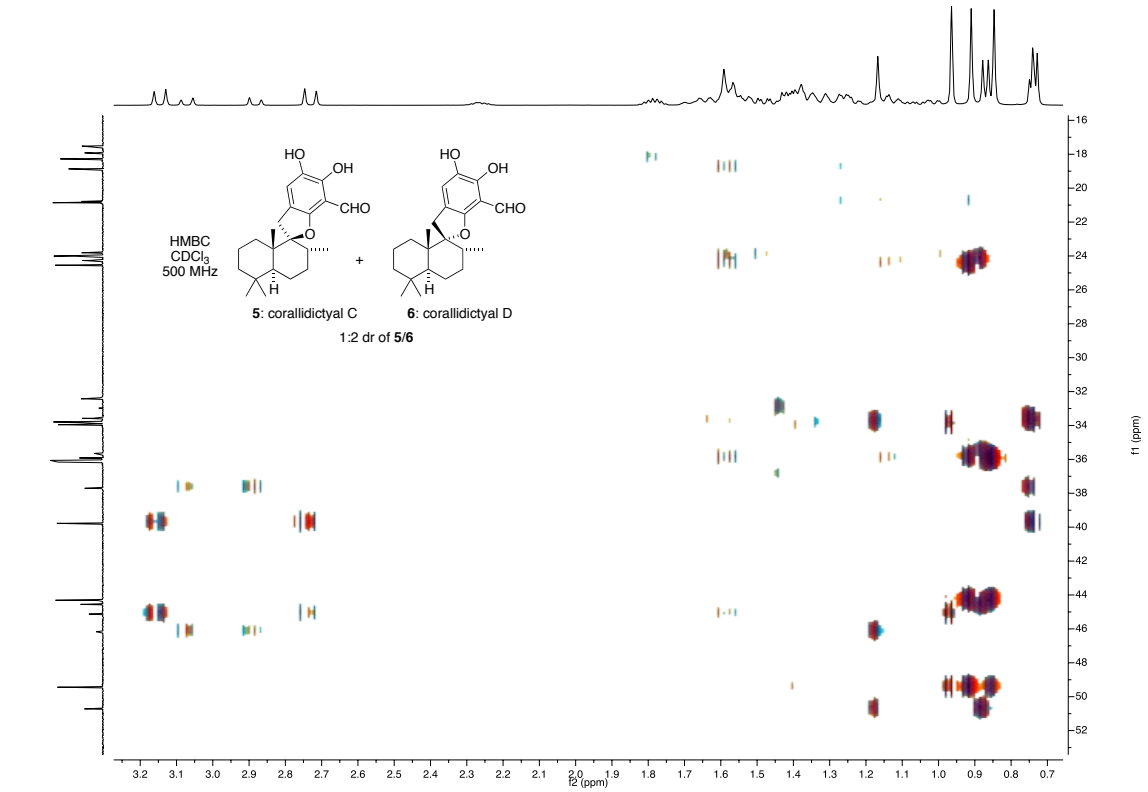
1:2 dr of 5/6
f2 (ppm)
f1 (ppm)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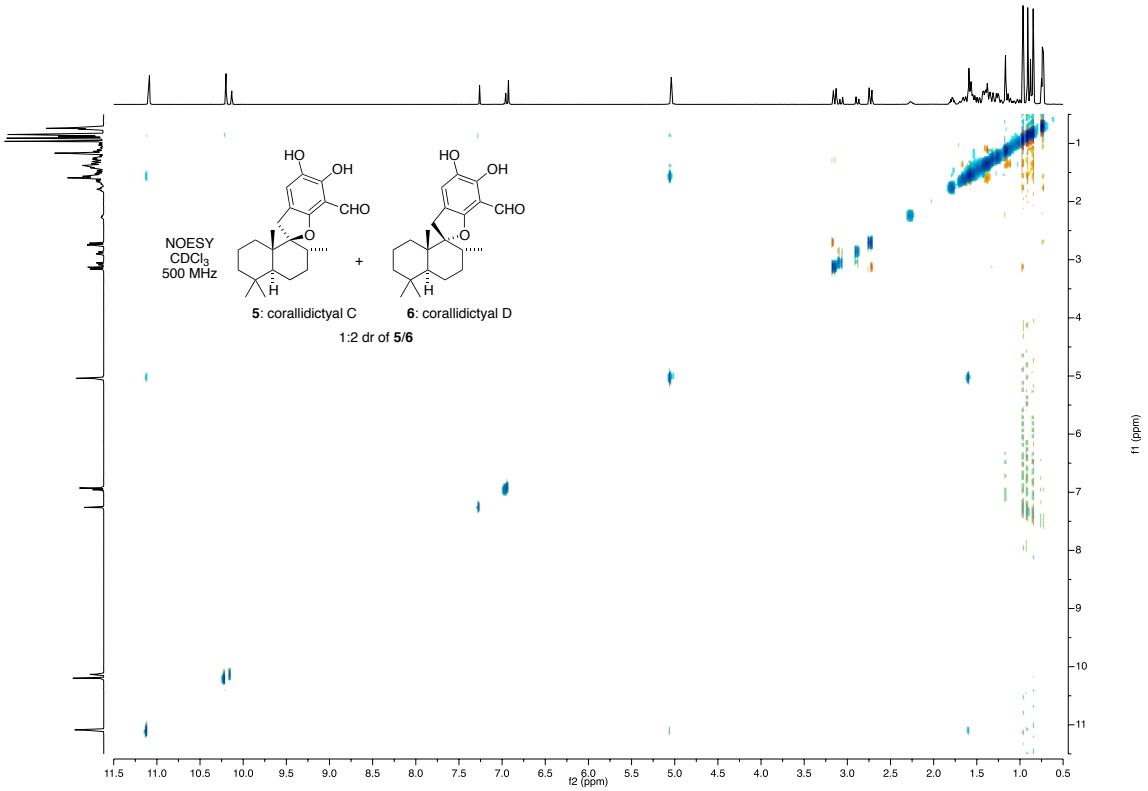
f2 (ppm)
f1 (ppm)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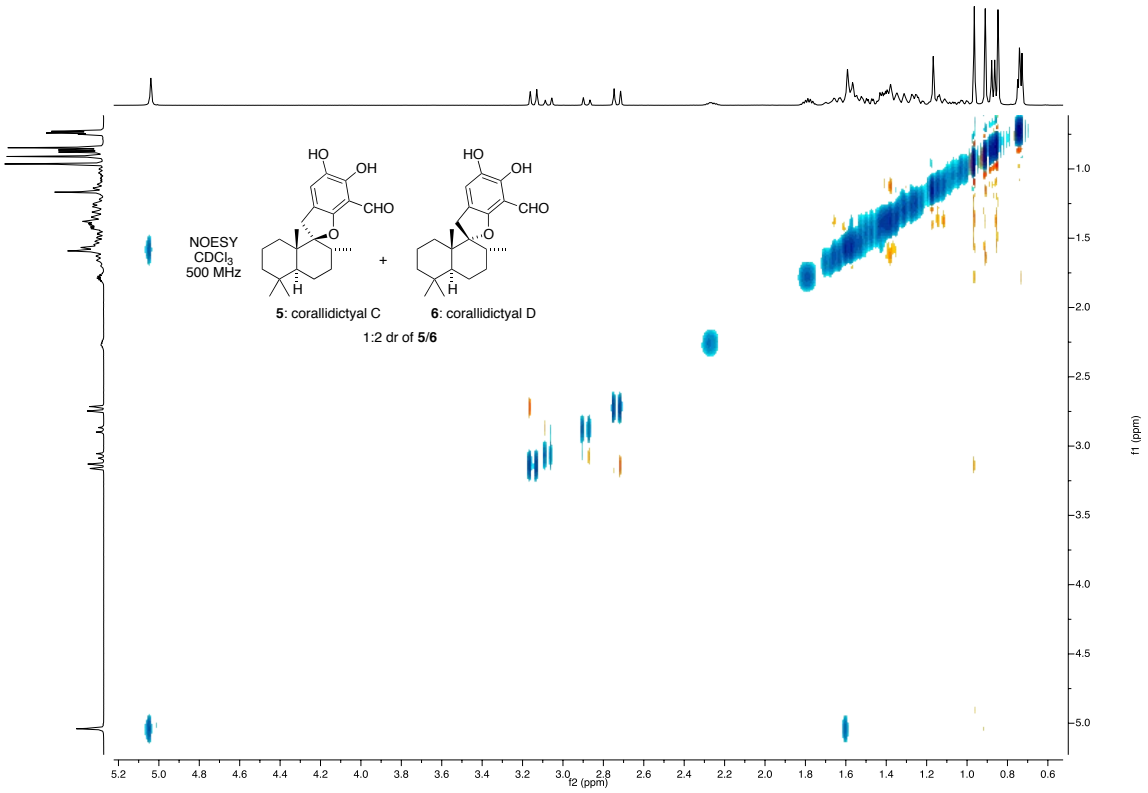
1:2 dr of 5/6
f2 (ppm)
f1 (ppm)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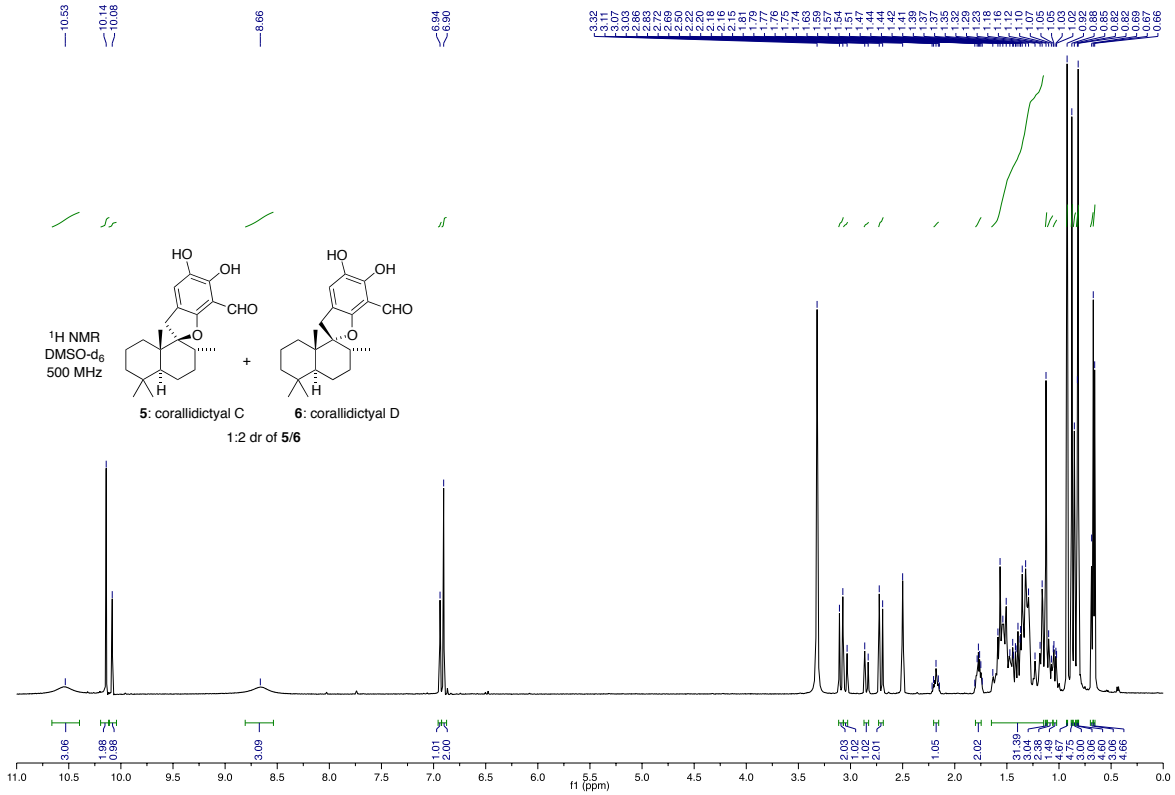
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500 MHz
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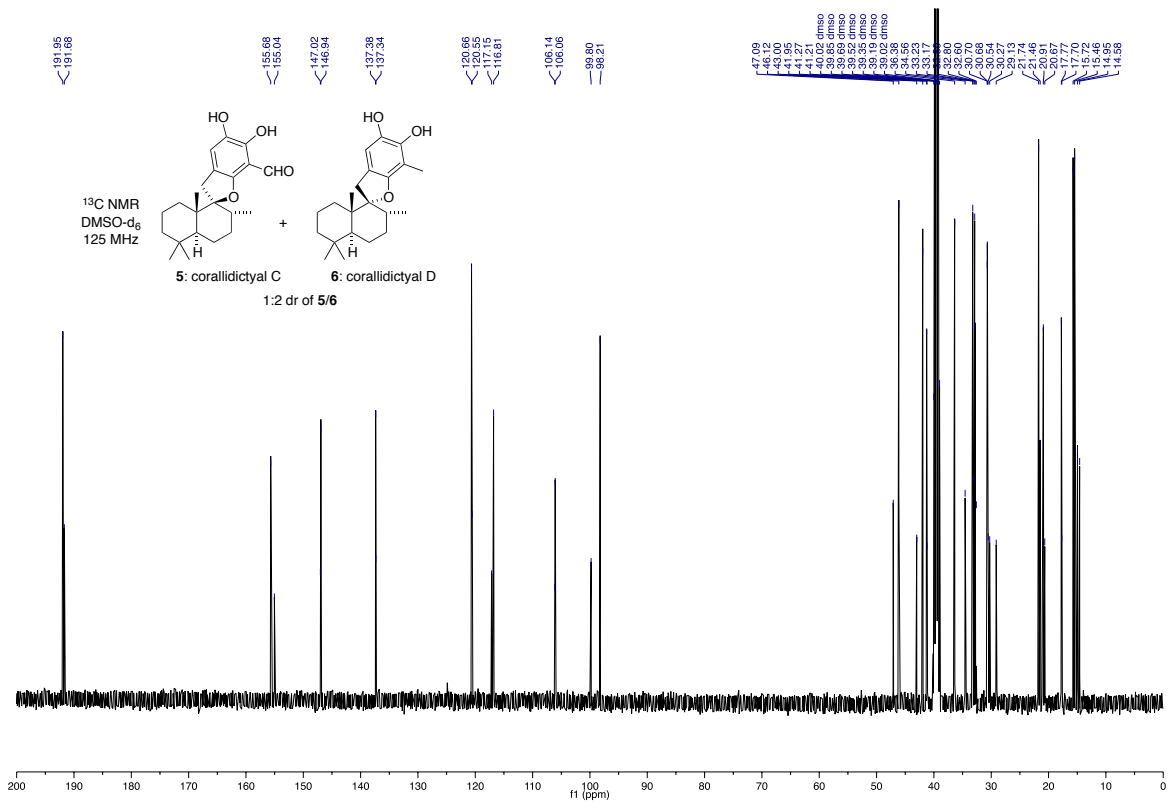
6: corallidictyal D
1:2 dr of 5/6
f1 (ppm)


^{13}C NMR
DMSO-d$_6$
125 MHz
5: corallidictyal C
6: corallidictyal D
1:2 dr of 5/6
f1 (ppm)

4. Tables of ^{1}H and ^{13}C NMR data for corallidictyals A-D

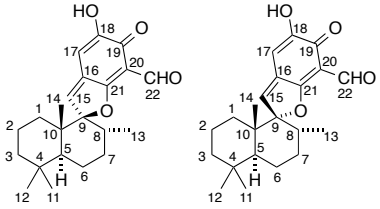
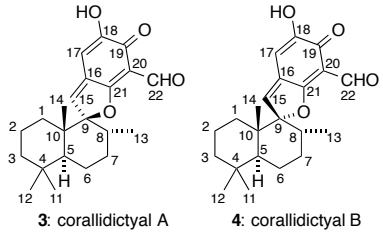


Table 1. Comparison of the ^{1}H NMR spectra of natural and synthetic corallidictyals A (**3**) and B (**4**).[1]

Assignment	Natural **3**, ^{1}H spectrum, $CDCl_3$, 400 MHz	Synthetic **3**, ^{1}H spectrum, $CDCl_3$, 500 MHz	Natural **4**, ^{1}H spectrum, $CDCl_3$, 400 MHz	Synthetic **4**, ^{1}H spectrum, $CDCl_3$, 500 MHz
H-1a, H-1b	2.00-0.80 (m)	2.05 – 1.99 (overlapped m, 1H), 1.67 – 0.77 (overlapped m, 1H)	2.00-0.80 (m)	1.67 – 0.77 (overlapped m, 2H)
H-2a, H-2b	2.00-0.80 (m)	1.67 – 0.77 (overlapped m, 2H)	2.00-0.80 (m)	1.67 – 0.77 (overlapped m, 2H)
H-3a, H-3b	2.00-0.80 (m)	1.67 – 0.77 (overlapped m, 2H)	2.00-0.80 (m)	1.67 – 0.77 (overlapped m, 2H)
H-5	1.24 (dd, *J* = 12.0, 2.9)	1.67 – 0.77 (overlapped m, 1H)	1.75 (dd, *J* = 12.2, 2.7)	1.83 – 1.73 (overlapped m, 1H)
H-6a, H-6b	2.00-0.80 (m)	1.83 – 1.73 (overlapped m, 2H)	2.00-0.80 (m)	1.83 – 1.73 (overlapped m, 1H), 1.67 – 0.77 (overlapped m, 1H)
H-7a, H-7b	2.00-0.80 (m)	2.05 – 1.99 (overlapped m, 1H), 1.67 – 0.77 (overlapped m, 1H)	2.00-0.80 (m)	1.83 – 1.73 (overlapped m, 1H), 1.67 – 0.77 (overlapped m, 1H)
H-8	2.61 (m)	2.63 (m, 1H)	2.42 (m)	2.43 (m, 1H)
Me-11	0.94 (s)	0.93 (s, 3H)	0.95 (s)	0.95 (s, 3H)
Me-12	0.91 (s)	0.91 (s, 3H)	0.88 (s)	0.87 (s, 3H)
Me-13	0.55 (d, *J* = 6.6)	0.54 (d, *J* = 6.6 Hz, 3H)	0.56 (d, *J* = 6.6)	0.54 (d, *J* = 6.5 Hz, 3H)
Me-14	1.35 (s)	1.35 (s, 3H)	1.28 (s)	1.27 (s, 3H)
H-15	7.50 (s)	7.50 (s, 1H)	7.25 (s)	7.25 (s, 1H)
H-17	6.48 (s)	6.48 (s, 1H)	6.43 (s)	6.43 (s, 1H)
OH-18	7.40 (br s)	7.42 (br s, 1H)	7.40 (br s)	7.42 (br s, 1H)
H-22	10.27 (s)	10.26 (s, 1H)	10.31 (s)	10.30 (s, 1H)

[1] J. A. Chan, A. J. Freyer, B. K. Carte, M. E. Hemling, G. A. Hofmann, M. R. Mattern, M. A. Mentzer and J. W. Westley, *J. Nat. Prod.*, 1994, **57**, 1543.



3: corallidictyal A **4**: corallidictyal B

Table 2. Comparison of the ^{13}C NMR spectra of natural and synthetic corallidictyals A (**3**) and B (**4**).[1]

Assignment	Natural **3**, ^{13}C spectrum, $CDCl_3$, 100 MHz	Synthetic **3**, ^{13}C spectrum, $CDCl_3$, 125 MHz	Natural **4**, ^{13}C spectrum, $CDCl_3$, 100 MHz	Synthetic **4**, ^{13}C spectrum, $CDCl_3$, 125 MHz
C-1	41.7-18.2	33.6*	41.2-18.2	32.9
C-2	41.7-18.2	18.23	41.2-18.2	18.18
C-3	41.7-18.2	41.7	41.2-18.2	41.2
C-4	41.7-18.2	33.83*	41.2-18.2	33.75
C-5	52.3	52.3	47.3	47.3
C-6	41.7-18.2	21.48	41.2-18.2	21.45
C-7	41.7-18.2	33.50*	41.2-18.2	32.0
C-8	35.5	35.5	34.2	34.2
C-9	113.1	113.1	111.1	111.2
C-10	44.8	44.8	44.0	44.0
C-11	33.5	33.47*	33.3	33.31
C-12	21.8	21.86	21.9	21.89
C-13	15.5	15.5	15.6	15.6
C-14	16.4	16.4	19.3	19.4
C-15	147.8	147.9	149.7	149.8
C-16	131.7	131.7	130.8	130.8
C-17	98.4	98.5	98.1	98.2
C-18	150.3	150.27	150.3	150.31
C-19	180.3	180.3	180.0	180.0
C-20	107.7	107.68	107.7	107.71
C-21	175.7	175.8	177.0	177.1
C-22	186.6	186.6	186.1	186.2

* These chemical shift assignments are interchangeable due to overlap

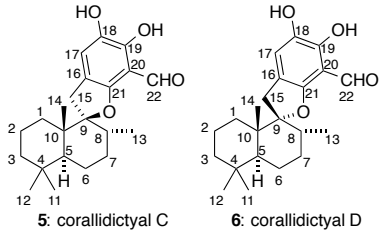


Table 3. Comparison of the ^{1}H NMR spectra of natural and synthetic corallidictyals C (**5**) and D (**6**).[2,3]

Assignment	Natural **5**, ^{1}H spectrum, DMSO-d_6	Synthetic **5**, ^{1}H spectrum, DMSO-d_6, 500 MHz	Natural **6**, ^{1}H spectrum, DMSO-d_6	Synthetic **6**, ^{1}H spectrum, DMSO-d6, 500 MHz	Synthetic **6**, ^{1}H spectrum, Alvarez-Manzaneda DMSO-d6 D, 500 MHz,
H-1a, H-1b	1.44, 1.16	1.63 – 1.06 (overlapped m, 1H)	1.52, 1.30	1.63 – 1.23 (overlapped m, 2H)	1.60 − 1.05 (m, 2H)
H-2a, H-2b	1.52, 1.34	1.63 – 1.06 (overlapped m, 2H)	1.52, 1.34*	1.63 – 1.06 (overlapped m, 2H)	1.60 − 1.05 (m, 2H)
H-3a, H-3b	1.32, 1.11	1.63 – 1.06 (overlapped m, 2H)	1.32, 1.11	1.63 – 1.06 (overlapped m, 2H)	1.60−1.05 (m, 2H)
H-5	1.05	1.04 (dd, J = 3.1 Hz, J = 12.5 Hz, 1H)	1.59	1.63 – 1.23 (overlapped m, 1H)	1.60 − 1.05 (m, 1H)
H-6a, H-6b	1.48, 1.37	1.63 – 1.06 (overlapped m, 2H)	1.57, 1.37	1.63 – 1.06 (overlapped m, 2H)	1.60 − 1.05 (m, 2H)
H-7a, H-7b	1.63, 1.05	1.63 – 1.06 (overlapped m, 2H)	1.52, 1.30*	1.63 – 1.23 (overlapped m, 2H)	1.60 − 1.05 (m, 2H)
H-8	2.18	2.18 (m, 1H)	1.77	1.77 (m, 1H)	1.77 (m, 1H),
Me-11	0.83	0.82 (s, 3H)	0.82	0.82 (s, 3H)	0.88 (s, 3H)
Me-12	0.86	0.85 (s, 3H)	0.88	0.88 (s, 3H)	0.82 (s, 3H)
Me-13	0.69	0.68 (d, J = 6.7 Hz, 3H)	0.67	0.66 (d, J = 6.7 Hz, 3H)	0.67 (d, J = 6.5 Hz, 3H)
Me-14	1.13	1.12 (s, 3H)	0.93	0.92 (s, 3H)	0.93 (s, 3H)
H-15a, H-15b	3.06, 2.85	3.05 (d, J = 16.6 Hz, 1H), 2.85 (d, J = 16.6 Hz, 1H)	3.10/2.71	3.09 (d, J = 16.3 Hz, 1H), 2.71 (d, J = 16.3 Hz, 1H)	3.10 (d, J = 16.2 Hz, 1H), 2.71 (d, J = 16.2 Hz, 1H)
H-17	6.94	6.94 (s, 1H)	6.91	6.90 (s, 1H)	6.90 (s, 1H)
OH-18	8.66	8.66 (br s, 1H)	8.65	8.66 (br s, 1H)	-
OH-19	10.53	10.53 (br s, 1H)	10.55	10.53 (br s, 1H)	-
H-22	10.09	10.08 (s, 1H)	10.15	10.14 (s, 1H)	10.14 (s, 1H)

* These chemical shift assignments are interchangeable due to overlap

[2] A. Grube, M. Assmann, E. Lichte, F. Sasse, J. R. Pawlik and M. Köck, *J. Nat. Prod.*, 2007, **70**, 504.

[3] M. J. Cano, H. Bouanou, R. Tapia, E. Alvarez, R. Alvarez-Manzaneda, R. Chahboun and E. Alvarez-Manzaneda, *J. Org. Chem.* 2013, **78**, 9196.

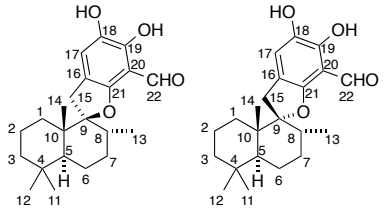


Table 4. Comparison of the ^{13}C NMR spectra of natural and synthetic corallidictyals C (**5**) and D (**6**).[2,3]

Assignment	Natural **5**, ^{13}C spectrum, DMSO-d_6	Synthetic **5**, ^{13}C spectrum, George, DMSO-d_6, 125 MHz	Natural **6**, ^{13}C spectrum, DMSO-d_6	Synthetic **6**, ^{13}C spectrum, George, DMSO-d_6, 125 MHz	Synthetic **6**, ^{13}C spectrum, Alvarez-Manzaneda DMSO-d_6, 125 MHz
C-1	30.5	30.5	30.7	30.70*	30.7
C-2	17.7	17.7	17.7	17.8	17.8
C-3	41.2	41.2	41.2	41.3	41.3
C-4	32.6	32.6	32.9	32.9	32.9
C-5	47.1	47.1	46.1	46.1	46.1
C-6	20.6	20.7	20.9	20.9	20.9
C-7	30.2	30.3	30.7	30.68*	30.7
C-8	34.5	34.6	36.4	36.4	36.4
C-9	99.8	99.8	98.2	98.2	98.2
C-10	43.0	43.0	41.9	42.0	42.0
C-11	21.4	21.5	21.7	21.7	21.7
C-12	33.1	33.17	33.2	33.23	33.2
C-13	14.6	14.6	15.4	15.5	15.5
C-14	14.9	15.0	15.7	15.7	15.7
C-15	29.1	29.1	32.8	32.8	32.8
C-16	117.1	117.2	116.8	116.8	116.8
C-17	120.5	120.6	120.6	120.7	120.6
C-18	137.3	137.3	137.4	137.4	137.4
C-19	147.0	147.0	146.9	146.9	146.9
C-20	106.1	106.14	106.1	106.06	106.1
C-21	155.0	155.0	155.7	155.7	155.7
C-22	191.7	191.7	191.9	192.0	191.9

* These chemical shift assignments are interchangeable due to overlap