Supplementary Information







Figure S2. seco-Briarellinone, 13C NMR spectrum. The inset shows the total view of spectrum.



Figure S3. seco-Briarellinone, expanded view of the 13C NMR spectrum (9–80 ppm).



Figure S4. seco-Briarellinone, expanded view of the 13C NMR spectrum (80–225 ppm).

Figure S5. seco-Briarellinone, COSY spectrum.



2 (Millions) 2.0 Filename - JF1_32_18 hegc_shigen - JFL_32_18 hegc_shigem DELTA - multiplicity_heg I1_266_11 - CHLOROFORM-D - 12-SEP-2010 14:15:03 16-JUL-2012 16:09:57 - 16-JUL-2012 16:12:22 Author Experiment Sample_id Solvent Creation_time Revision_time Current_time 10.0 ¢. 200 Multiplicity HSQC 2D COMPLEX COMPLEX 1024, 512 1H 13C Comment 30.0 Data_format Dim_size Dim_title - 46 40.0 Dim_units Dimensions Site - [ppm] [ppm] - X Y - Eclipse+ 400 - DELTA_NMR Spectrometer 800 - 9.389766[T] (400[MHz] - 0.2151424[s] Field_strength X_acq_duration X_domain X_freq X_offset 60.0 - 1H - 1H - 399.78219838[MHz] - 4.97708[ppm] - 1024 X_ottset X_points X_resolution X_sweep Y_domain Y_freq Y_offset Y_points Y_presolution Y_sweep 20.0 - 4 - 4.64808425[Hz] - 4.75963827[kHz] 80.0 - 13C - 100.52530333 [MHz] - 100 [ppm] - 256 - 0 8 - 0 - 98.64267677[Hz] - 25.25252525[kHz] - FALSE 100.0 Y sweep Clipped Mod_return - 1 - 64 - 16384 140.0 130.0 120.0 110.0 Scans Total scans X_acq_time X_pulse Y_acq_time Y_pulse Enhance_temp Enhancement Grad 1 - 0.2151424[s] 20 - 9.05[us] - 10.1376[ms] - 9[us] - 12 - 1/6J - 1[ms] Grad 1 Grad_1 Grad_1_amp Grad_1_value Grad_2 Grad_2_amp Grad_2_value Grad_3 Grad_2_amp - 1[ms] - 4[pnt] - 4[pnt*ms] - 1[ms] - -1[pnt] - -1[pnt*ms] - 1[ms] - 1[ms] 150.0 6 Grad_3_amp Grad_recover Grad_selection Grad_shape - 1[ms] - 1[pnt] - 0.1[ms] - 13C - 4:1 - square - 0 200.0190.0 180.0 170.0 160.0 Y : parts per Million : 13C 5 16 17 С 18 Grad_type Initial wait - 0 - 1[s] - 140[Hz] - 3[us] - 30 - 7 2[s] - 1[us] - 0.5952381[ms] - 20.7[dc] - 2[us] J_constant Phase preset Recvr_gain Relaxation_delay Ti Tau Temp_get Unblank_time . 9.0 8.0 7.0 5.0 2.0 1.0 20.0 40.0 6.0 4.0 3.0 Ó X : parts per Million : 1H (Thousands)

Figure S6. seco-Briarellinone, HSQC spectrum.

X : parts per Million : 1H

2.0 3.0 ... (Millions) ... - JF1_32_18 hmbc_ehigem - DELTA - DELTA - hmbc_pfg_s.exp - 11_265_11 - CHLOROFORM_D - 13-SEF-2010 08:27:08 - 16-JUL_2012 15:44:42 - 16-JUL_2012 15:05:15 2 Filename Author Experiment 61.1 Sample_id Solvent 10.0 Creation time -0 0. Revision_time Current time 20.0 gradient enhanced HMB 2D REAL REAL 1024, 256 Comment 1 Data_format Dim size 40.0 30.0 1 - 1024, 256 - 1H 13C - [ppm] [ppm] - X Y - Eclipse+ 400 Dim_title Dim_units Dimensions Site 50.0 Spectrometer - DELTA_NMR Field_strength X_acq_duration X_domain X_freq X_offset X_points X_prescans X_resolution 1 9.389766[T] (400[MHz] 0.2151424[s] 60.0 1.0 - 1H 399.78219838[MHz] 4.97708[ppm] 1024 20.0 19 - 4 - 4.64808425[Hz] - 4.75963827[kHz] Ð 80.0 20 X_sweep Y_domain Y_freq Y_offset - 4.75963827[kHz] - 13C - 100.52530333[MHz] - 100[ppm] - 128 - 0 - 197.28535354[Hz] - 25.25252525[kHz] - FALSE 220.0 210.0 200.0 190.0 130.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 Y_points Y_prescans Y_resolution Y_resolution Y_sweep Clipped Mod_return С - 1 - 224 - 28672 Scans Total_scans 14 X acq time X_pulse Y_pulse Grad 1 Grad 1_amp Grad 1_value Grad 2 Grad 2_amp Grad 2_value Grad 3_amp Grad 3_value Grad 7_value Grad recover 6 - 0.2151424[s] - 0.2151424[s - 9.05[us] - 5.0688[ms] - 9[us] - 1[ms] - 10[pnt] - 10[pnt] - 10[pnt] 17 \cap 16 - 10 [pnt*ms] 1 [ms] - 10 [pnt] - 10 [pnt*ms] 5 [pnt] - 5 [pnt] - 5 [pnt*ms] - 0.2[ms] - 13C - 2:2:1 - square - 0 - 1[s] Y : parts per Million : 13C Grad_recover Grad_selection Grad_shape Grad_type Initial_wait Grad type 0 Initial wait 1[s] J constant 140[Hz] Long rangej 8[Hz] Phase_preset 3[us] Revr_gdin 30 Relaxiton_delay 2[s] Ti 2[s] Tamp get 9.3[dC] Unblank_time 2[us] 4.0 2.0 40.0 8.0 7.0 6.0 5.0 3.0 20.0 9.0 1.0 10.0

(Thousands)

Figure S7. seco-Briarellinone, HMBC spectrum.



Figure S8. seco-Briarellinone, selective DPFGSE-NOE spectrum by irradiation of H-1.



Figure S9. seco-Briarellinone, selective DPFGSE-NOE spectrum by irradiation of H-2.



Figure S10. seco-Briarellinone, selective DPFGSE-NOE spectrum by irradiation of H-9.



Figure S11. seco-Briarellinone, selective DPFGSE-NOE spectrum by irradiation of H-15.

X : parts per Million : 1H

JEOI \$ (Millions) 2 - 2 seco_briarellin_nee - DELTA - NOESY.exp - 11 264 12 - CHLOROFORM-D - 25-NOV-2010 09:43:16 - 19-JUL-2012 10:42:25 - 19-JUL-2012 10:47:19 Filename Author Author Experiment Sample_id Solvent Creation_time Revision time Current time 20 HO <u>ہ</u> - absolute value noesy - 2D REAL REAL - 1024, 1024 - 1H 1H - [ppm] [ppm] - X Y - X Y - 200 đ Comment Data_format Dim_size С Dim_title Ο Dim_units Dimensions 2 Site - Eclipse+ 400 - DELTA NMR Spectrometer Н' Field_strength X_acq_duration X_dreq X_offeet X_points X_presolution X_resolution X_sweep Y_domain Y_freq = 9.389766[T] (400[MHz] = 0.2176[m] = 1H = 399.78219838[MHz] = 4.88664[ppm] = 1024 1 2 3.0 -- 4.59558824[Hz] - 4.70588235[kHz] - 4.70588235[kHz] - 1H - 399.78219838[MHz] - 4.88664[ppm] - 238 Y_freq Y_offset HO. Y_offset Y_points Y_resolution Y_resolution Y_sweep Clipped Mod_return Scans Total_scans 3-fc \cap - 0 - 19.77261493[Hz] - 4.70588235[kHz] \cap - TRUE - 1 - 96 - 22848 2 X_acq_time X_pulse Y_acq_time Initial_wait Mix_time Phase_preset Recvr_gain Relaxation_delay Ti Temp get - 0.2176[s] - 9.4[us] - 54.4[ms] - 1[s] - 0.6[s] - 3[us] - 21 3 18 8 2.0 - 3[us] - 21 - 1.5[s] - 1[us] - 20.4[dc] - 2[us] đ Temp_get Unblank_time 10.0 9.0 8.0 Y : parts per Million : 1H 4 2.0 1.0 8.0 1.0 3.0 5.0 10.0 9.0 7.0 6.0 5.0 4.0 3.0 0

(Millions)

Figure S12. seco-Briarellinone, NOESY spectrum.



Figure S13. seco-Briarellinone, HRMS-ESI-TOF spectrum.



Figure S14. Briarellin S, 1H NMR spectrum.

X : parts per Million : 13C

ØJEO 25 2.6 27 - c13_fig_2-3.jdf - DELTA = single_pulse_dec = 11_266_03 - CHLOROFORM-D = 9-SEF-2010_11.09.19 = 17-JUL-2012_16:32:38 = 17-JUL-2012_16:34:25 HO = Filename Author Experiment 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 utimitariantinationalisettentinationalisettentinationalisettentinationalisettentinationalisettentinationalisette Sample_id Solvent \cap 8 Creation_time Revision_time Current_time 9 12 OH 10Ô 13 Single Pulse with Bro 1D COMPLEX 32768 Comment Data_format Н 0 Dim_size Dim_title Dim_units - 32768 - 13C - [ppm] - X - Eclipse+ 400 - DELTA_NMR 15 <u>اً</u> 18 · ′0 <u>16</u>0 Dimensions 17 21 Site Spectrometer Pield_strength X_acq_duration X_domain X_freq X_offset X_points 9.389766[T] (400[MHH] 1.3008896[s] 13C 100.52530333[MH] 100[ppm] 32768 28 - 32/68 - 4 - 0.76870474[Hz] - 25.18891688[kHz] - 1H - 399.78219838[MHz] X_prescans X_resolution X_sweep Irr_domain Irr_freq Irr_offset - 399.78 - 5[ppm] - FALSE - 1 - 2711 - 2711 Clipped Mod_return Scans Total_scans - 11.25[us] - 1.3008896[s] - 30[deg] - 3.75[us] - 1[s] - 3[us] - 25 x_90_width X_90_width 11.25[us] X_acq_time 1.300896 X_angla 30[deg] X_pulse 3.75[us] Jnitial_wait 1[s] Phase_presse 3[us] Balaxation_delay 1[s] Tamp get 23.3[dc] Unblank_time 2[us] (Millions) 0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 92.9132 77.3212 77.0000 76.6788 76.5718 75.6618 73.8036 73.8036 49.1042 214.5520 115,8385 175,1706

Figure S15. Briarellin S, 13C NMR spectrum.



Figure S16. Briarellin S, expanded view of the 13C NMR spectrum (10–40 ppm).



Figure S17. Briarellin S, expanded view of the 13C NMR spectrum (40–80 ppm).



Figure S18. Briarellin S, expanded view of the 13C NMR spectrum (78–220 ppm).

4 (Millions) 20 - JF1_32_08_cosy shigem - DELTA - DELTA - Cosy pfg s.exp - 11_266_03 - CHLOROFORM-D - 14-SEF-2010 00:28:26 - 15-JUL-2012 18:50:00 - 15-JUL-2012 18:51:37 Filename Author Experiment Sample_id Solvent Creation_time Revision_time Current_time 11 2-- gradient absolute val - 2D REAL REAL - 2048. 2048 - 1H 1H - [ppm] - X Y - Eclipset 400 - DELTA_NME Comment Data_format Dim_size Dim_title мÎ ≈ii Dim_units Dimensions Site Spectrometer 50 9.389766[T] (400[MHz] 0.5060608[s] Field strength ŝ X_acq_duration X_domain X_freq X_offset - 0.5060606[0] - 1H - 399.78219838[MHz] - 3.997.044[ppm] - 2048 - 4 - 1.97604715[Hz] - 4.04694456[kHz] - 57 X_offset X_prescans X_resolution X_sweep Y_domain Y_freq Y_offset Y_points Y_prescans Y_resolution Y_secons 20 10 2 HΟ - 1.04054456[KHz] - 1H - 399.78219838[MHz] - 3.87044[ppm] - 512 - 0 0. 12 OH റ - 7.90418859[Hz] - 4.04694456[kHz] - FALSE œ Y sweep Clipped Mod_return Scans Total_scans - 1 - 32 - 16384 Ю 21, - 9.05[us] - 0.5060608[s] - 9.05[us] - 0.1265152[s] ď X_90_width O. <u>x</u> 90 width <u>x</u> acg time <u>x</u> pulse <u>y</u> acg time <u>drad 1</u> drad 1 amp <u>drad 1</u> drad 2 drad 1 drad 1 drad 1 drad 2 drad 2 drad 2 drad 2 drad 2 drad 2 drad 1 drad 1 drad 1 drad 2 drad 1 drad 1 drad 1 drad 1 drad 1 drad 1 drad 2 drad 1 drad 2 d 18 X_pulse - 9.05(us) Y_acq_time - 0.1265152[Grad 1_amp - 5[pnt] Grad 1_value - 5[pnt*ma] Grad 2_amp - 5[pnt] Grad 2_amp - 5[pnt] Grad 2_value - 5[pnt*ma] Grad recover - 1[ms] False recover - 1[ms] Fulse_angle_ - 90[deg] Fulse_angle_ - 16[ms] Tamp_gat - 15.1[dc] Unblank_time - 2[us] 2 28 Y : parts per Million : 1H 3-2 2.0 1.0 7.0 6.0 5.0 4.0 3.0 2.0 4.0 X : parts per Million : 1H (Millions)

Figure S19. Briarellin S, COSY spectrum.

Figure S20. Briarellin S, TOCSY spectrum.



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VJEOL . 40 (Millions) 3 - hsqc fig-4.jdf - DELTX - multiplicity_hsq - I1 26\$ 03 - CHLOROFORM-D - 9-SEP-2010 23:24:16 - 15-JUL-2012 18:22:11 - 15-JUL-2012 18:24:48 Filename Author Experiment Sample id Solvent 3 Creation time Revision time Current time Multiplicity HSQC 2D COMPLEX COMPLEX 1024, 512 1H 13C [ppm] [ppm] X Y Relieve 400 Comment Data format Dim size Dim title 2 н Dim units 8 Dimensions - Eclipse+ 400 - DELTA NMR Site ć 12 Spectrometer - 9.389766[T] (400[MHz] - 0.2709504[m] - 1H - 399.78219838[MHz] - 3.80629[ppm] - 1024 Field strength X acq_duration X domain X freq X offset e н 5 X points X prescans X resolution [∰] () <u>16</u>0 = 17 - 1 - 3.6907124[Hz] - 3.77928949[kHz] - 13C - 4 21 18 X sweep Y domain Y freq Y offset Y points Y prescans Y resolution - 13C - 100.52530333 [MHz] - 62.51967 [ppm] - 256 ċ. 8 28 - 256 - 0 - 47.63719512[Hz] - 12.19512195[kHz] - FALSE Y sweep Clipped Mod return Scans Total_scans Q 000 - 1 - 16 - 4096 :0 X acq time X pulse Y pulse Enhance_temp Enhance_temp Grad 1 amp Grad 1 amp Grad 2 amp Grad 2 value Grad 2 value Grad 3 mp Grad 7 value Grad 3 amp Grad recover Grad a sup Grad recover Grad shape Grad shape Grad shape Initial wait - 0.2709504[s] - 9.05[us] - 20.992[ms] - 9[us] - 12 - 1/6J - 1[ms] - 4[pnt] - 4[pnt] - 1[ms] - 1[ms] - 1[ms] 盘台 2 -0 80.0 - 1[ms] - 1[pnt] - 1[pnt*ms] - 1[pnt] - 0.1[ms] - 13C - 4:1 10 90.0 Y : parts per Million : 13C - square - 0 Initial wait 0 J constant 140 [Hz] Phase proset 3[us] Rever gain 30 Relaxition_delay 2[s] Ti 1[us] Tau 0.5552381[ms] Tamp get 19.9[dC] Unblank_time 2[us] 100.0 110.0 200.0 3.0 2.0 1.0 7.0 6.0 5.0 4.0 X : parts per Million : 1H (Thousands)

Figure S21. Briarellin S, HSQC spectrum.



Figure S22. Briarellin S, HMBC spectrum.



Figure S23. Briarellin S, selective DPFGSE-NOE spectrum by irradiation of H-4 and H-19a.



Figure S24. Briarellin S, selective DPFGSE-NOE spectrum by irradiation of H-6.



Figure S25. Briarellin S, selective DPFGSE-NOE spectrum by irradiation of H-17 and H-28.



Figure S26. Briarellin S, selective DPFGSE-NOE spectrum by irradiation of H-18.



Figure S27. Briarellin S, selective DPFGSE-NOE spectrum by irradiation of H-20.



Figure S28. Briarellin S, HRMS-ESI-TOF spectrum. HSQC and HMBC correlations of the olefinic protons at C-19.



Figure S29. Briarellin S, HSQC correlation of H-19 (HSQC spectrum with a low peak threshold level).



Figure S30. Briarellin S, HMBC correlations of H-19 (HMBC spectrum with a low peak threshold level).



Figure S31. Briarellin S, HMBC correlations of H-19 (slice at X = 5.16).



Figure S32. Briarellin S, HMBC correlations of H-19 (slices at Y = 39.90, Y = 74.49 and Y = 153.23).