Electronic Supplementary Information (ESI)

Novel tryptophan metabolites, chromoazepinone A, B and C, produced by a blocked mutant of *Chromobacterium violaceum*, the biosynthetic implications and the biological activity of chromoazepinone A and B

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1. Spectroscopic data of the methyl ester of chromoazepinone A (5)

Fig. S1. EIMS spectrum

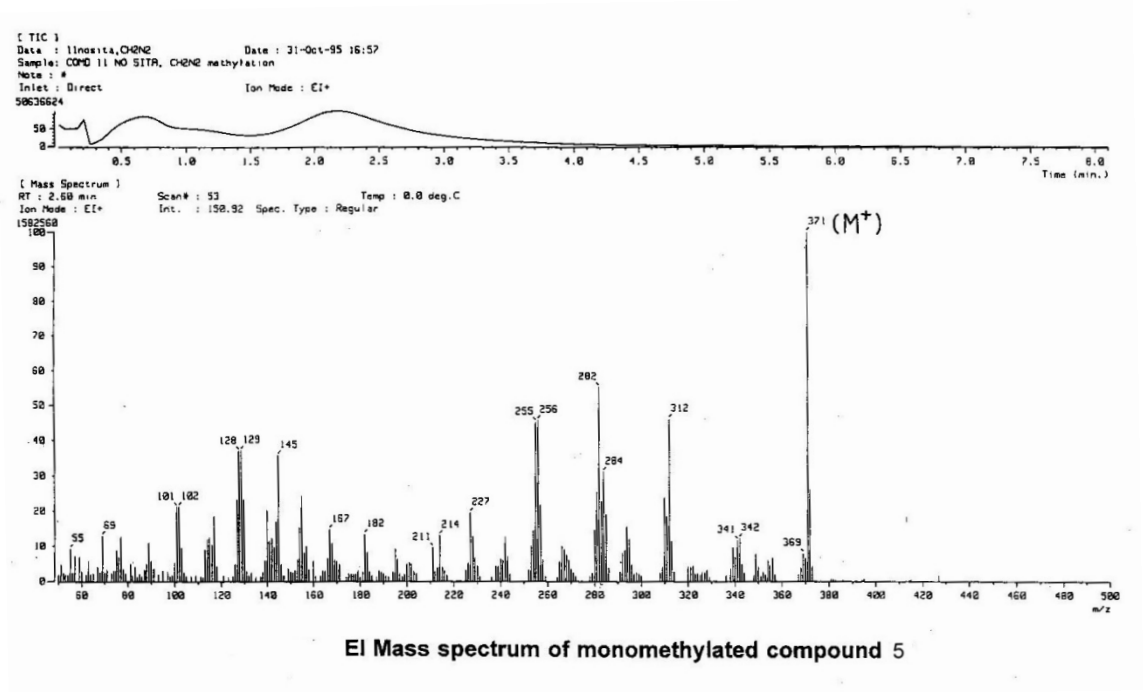


Fig. S2. ^{1}H NMR spectrum of Me ester of **5** inDMSO-d_6

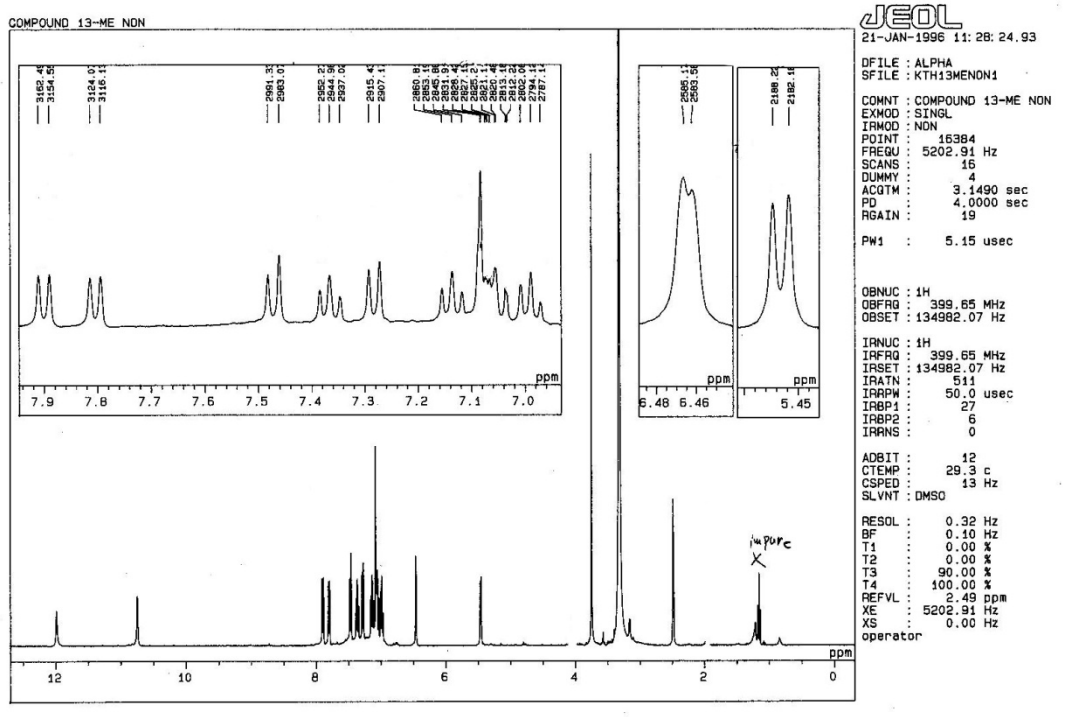


Fig. S3. ^{13}C NMR spectrum of Me ester of **5** inDMSO-d_6

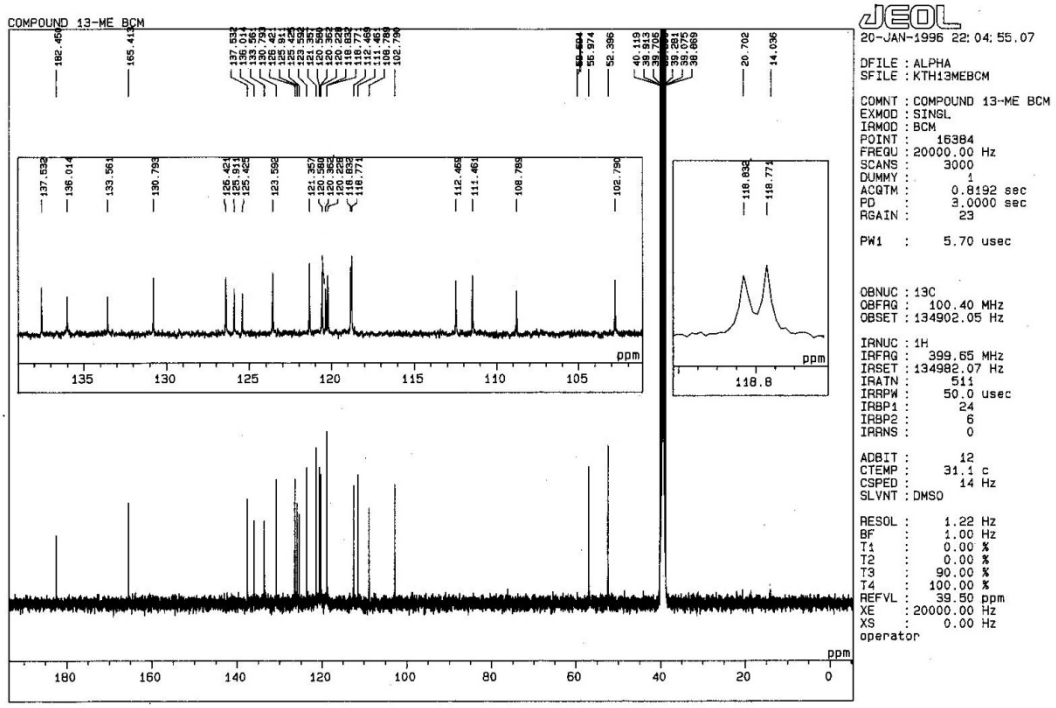


Fig. S4. UV-Visible spectrum of Me ester of **5** in MeOH

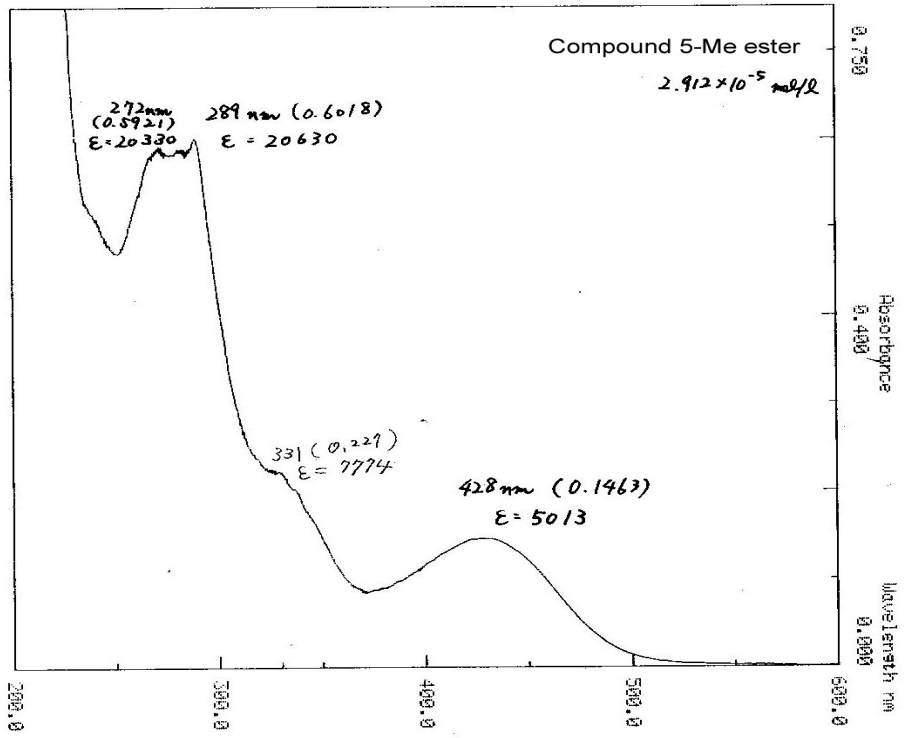
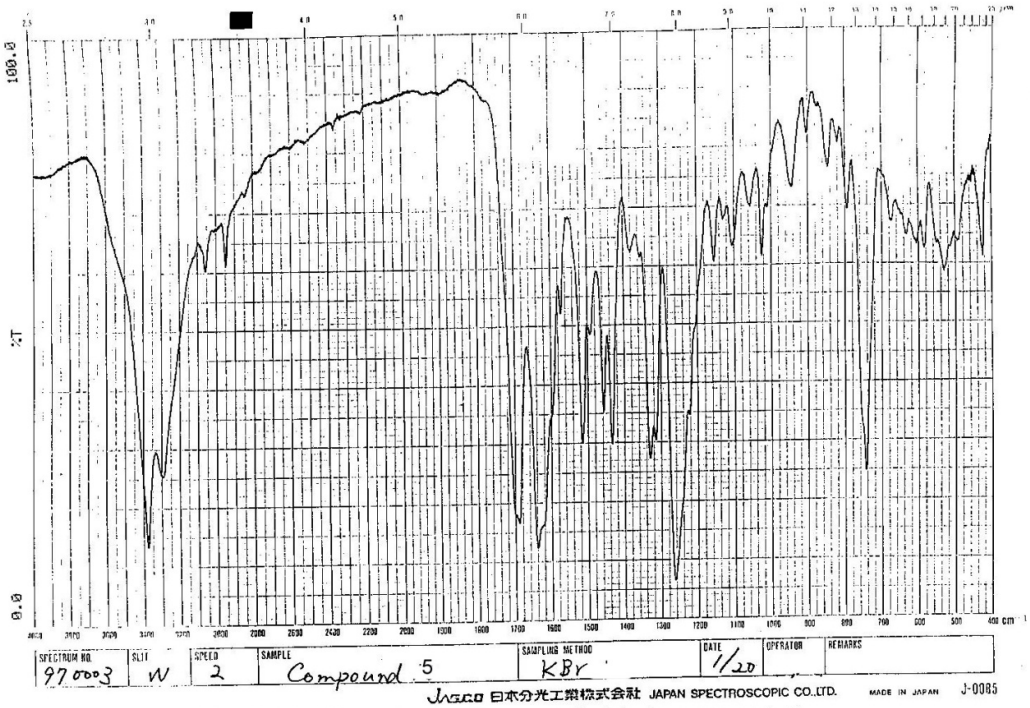
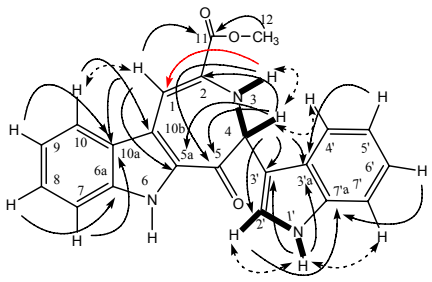


Fig. S5. IR Spectrum of Me ester of **5**



IR spectrum of monomethylated compound 5

Fig. S6. Analyses and assignments of NMR data and its other physical data



Methyl ester of Compound **5**

HMBC
COSY
NOE

Compound **5**
$[\alpha]_D^{20}$ = + 56.0 (*c*=0.16, EtOH);
UV(MeOH) λ_{max} (log ε) 272 (4.30), 289 (4.31), 331shoulder (3.89), 428 (3.70) nm

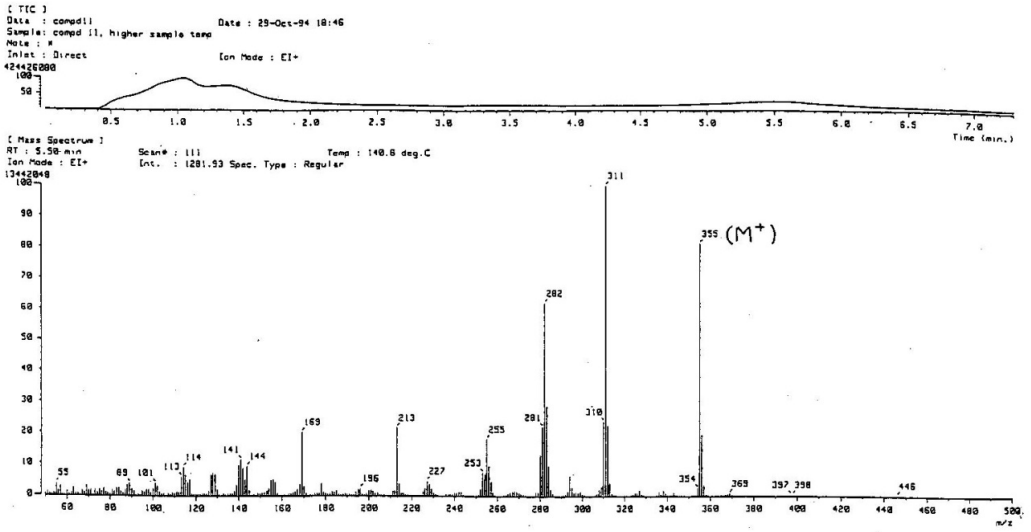
Me ester of Compound **5**
UV (MeOH) λ_{max} (log ε) 270 (4.14), 289 (4.23), 425 (3.66) nm; IR (KBr) ν_{max} 1690, 1640, 1518, 1260, 740 cm^{-1}
HREIMS of Me ester of **5**
m/z M^+ 371.1272 (calcd for $C_{22}H_{17}O_3N_3$, 371.1270)

400 MHz, DMSO-d_6 The solvent peak: δ_H=2.49, δ_C=39.50

Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C
1	7.09 (s)	**102.8 (d)**	**5a**	—	**133.6(s)**	**9**	7.14 (t, J=7.9 Hz)	**120.2(d)**	**2'**	6.46 (d, J=1.5 Hz)	**123.6(d)**	**6'**	7.06 (t, J=8.0 Hz)	**121.4(d)**
2	—	**130.8 (s)**	**6**	11.99 (br s)	—	**10**	7.90 (d, J=7.9 Hz)	**120.6(d)**	**3'**	—	**108.8(s)**	**7'**	7.28 (d, J=8.0 Hz)	**111.5(d)**
3	7.07 (d, J=6.1Hz)	—	**6a**	—	**137.5(s)**	**10a**	—	**125.4(s)**	**3'a**	—	**125.9(s)**	**7'a**	—	**136.0(s)**
4	5.46 (d, J=6.1 Hz)	**56.97 (d)**	**7**	7.47 (d, J=7.9 Hz)	**112.5(d)**	**10b**	—	**120.4(s)**	**4'**	7.81 (d, J=8.0 Hz)	**118.8(d)**	**11**	—	**165.4(s)**
5	—	**182.5 (s)**	**8**	7.37 (t, J=7.9 Hz)	**126.4(d)**	**1'**	10.75 (brs)	—	**5'**	6.99 (t, J=8.0 Hz)	**118.8(d)**	**12**	3.75 (3H, s)	**52.40(q)**

2. Spectroscopic data of chromoazepinone B (6)

Fig. S7. EIMS spectrum



EI Mass Spectrum of compound 6

Fig. S8. ^{1}H-NMR spectrum in DMSO d_6

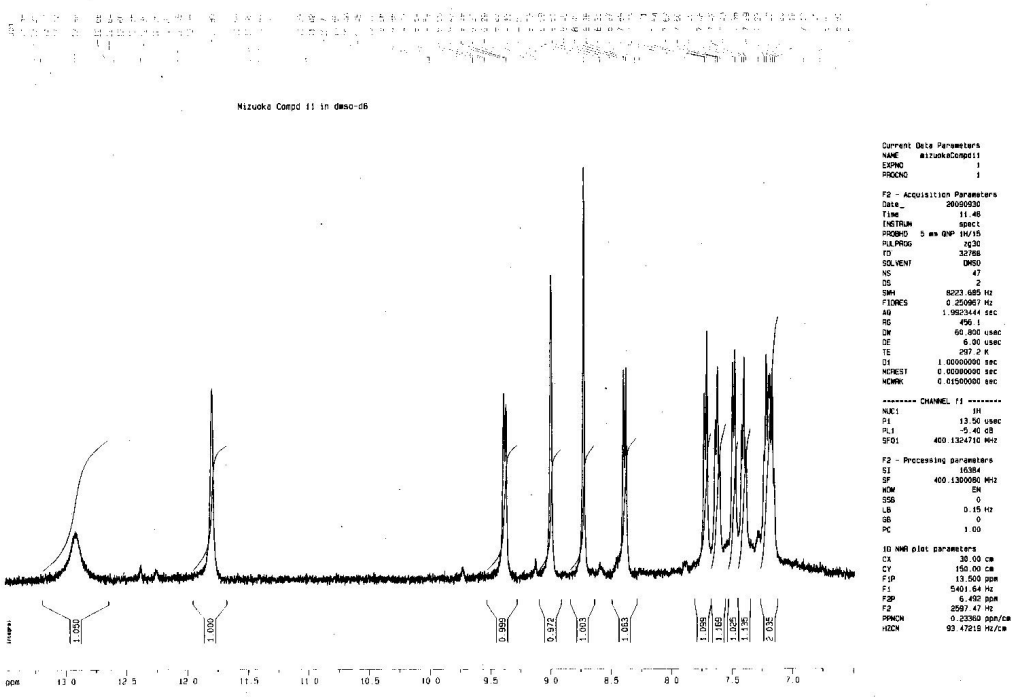


Fig. S9. ^{13}C-NMR spectrum in DMSO d_6

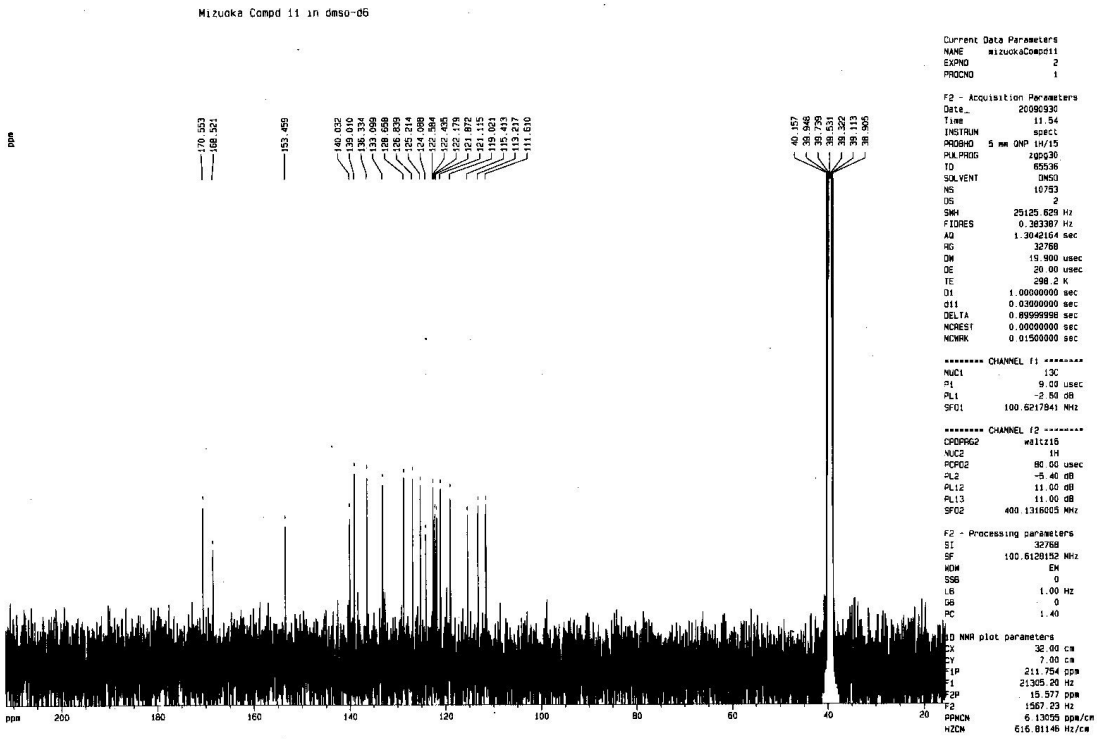


Fig. S10. UV-visible spectrum of **6** and its change as a function of pH.

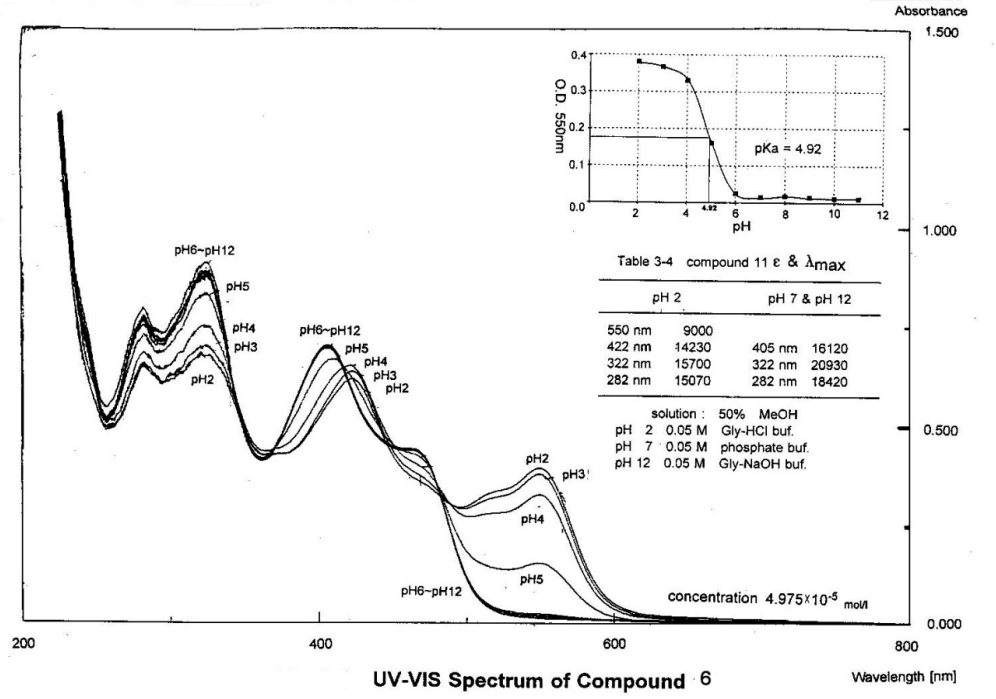
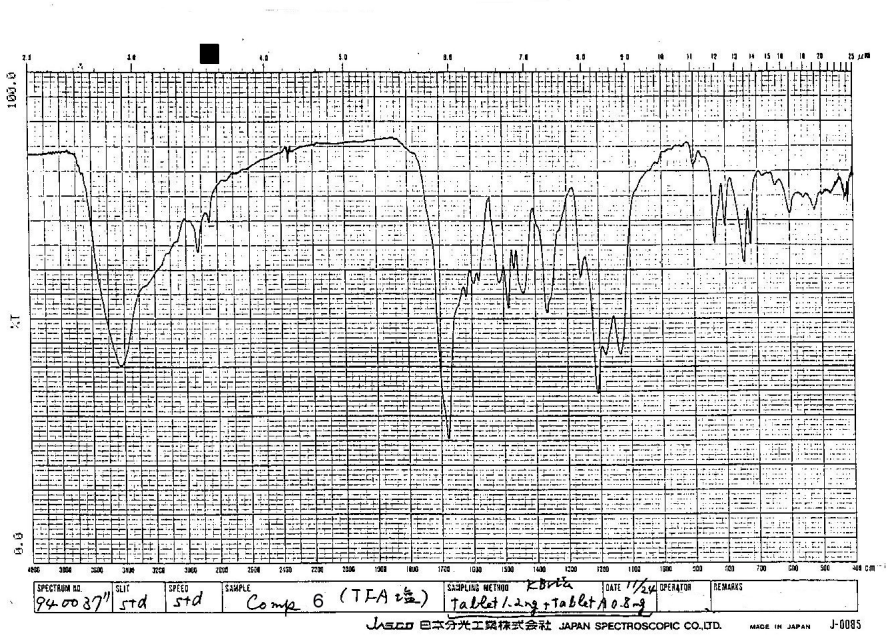
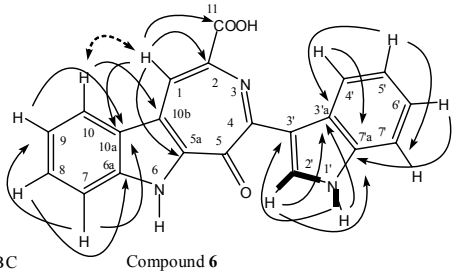


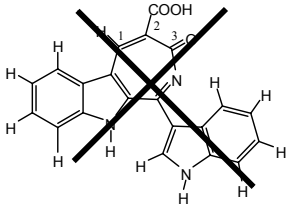
Fig. S11. IR spectrum (KBr tablet) of **6**



IR Spectrum of compound 6 (TFA salt)

Fig. S12. Analyses and assignments of NMR data and its other physical data





No HMBC cross peak between H-1 and C-3 leads to the conclusion that this structure is incorrect.

HMBC
NOE
COSY

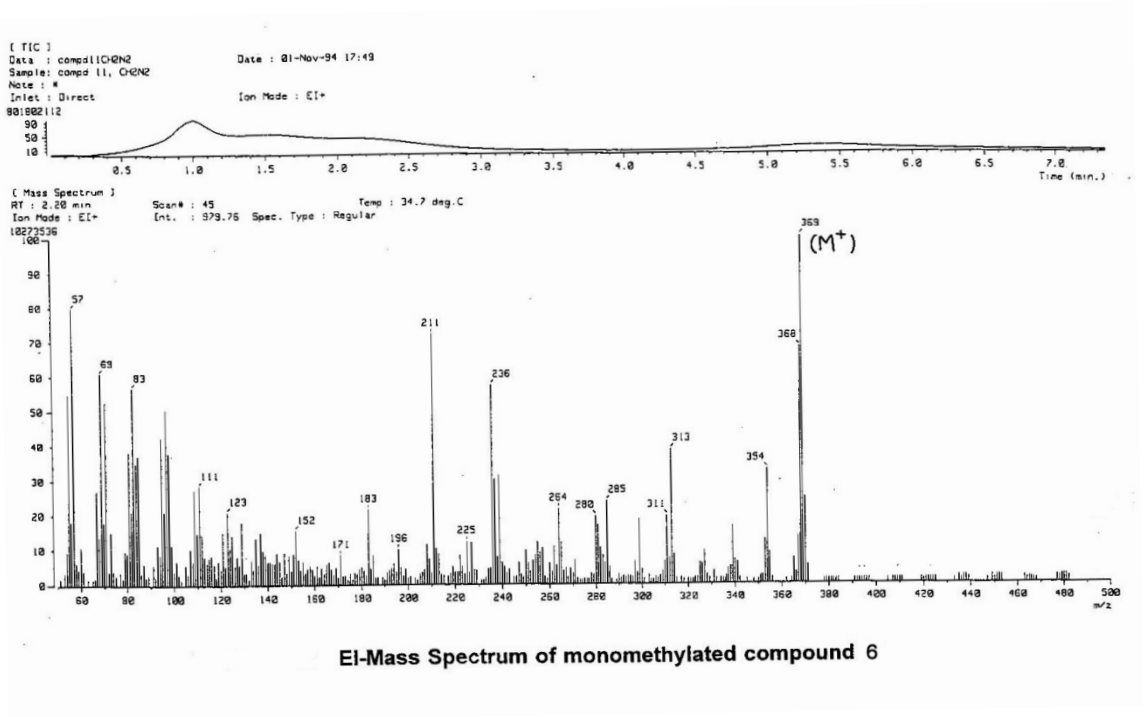
Compound **6**
UV(MeOH): pH 2.0, λ_{max} (log ε) 282 (4.18), 322 (4.20), 422 (4.15), 550 (3.95) nm; pH 7 & 12, λ_{max} (log ε) 282 (4.26), 322 (4.32), 405 (4.21) nm.
HREIMS *m/z* M^+ 355.0930 (calcd for $C_{21}H_{13}O_3N_3$, 355.0957)

400 MHz, DMSO-d_6 The solvent peak: δ_H=2.49, δ_C=39.50

Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C
1	8.73 (s)	**119.0**	**5a**	—	**140.0**	**9**	7.40 (t, J=7.6 Hz)	**122.2**	**2'**	9.00 (s)	**133.1**	**6'**	7.22 (t, J=7.9 Hz)	**122.6**
2	—	**134.8**	**6**	13.17 (very brs)	—	**10**	8.39 (d, J=7.6 Hz)	**121.9**	**3'**	—	**115.4**	**7'**	7.48 (d, J=7.9 Hz)	**111.6**
3	—	—	**6a**	—	**139.0**	**10a**	—	**125.2**	**3'a**	—	**126.8**	**7'a**	—	**136.3**
4	—	**153.4**	**7**	7.71 (d, J=7.6 Hz)	**113.2**	**10b**	—	**122.4**	**4'**	9.38 (d, J=7.9 Hz)	**124.1**	**11**	—	**168.5**
5	—	**170.6**	**8**	7.62 (t, J=7.6 Hz)	**128.6**	**1'**	11.80 (s)	—	**5'**	7.17(t, J=7.9 Hz)	**121.1**			

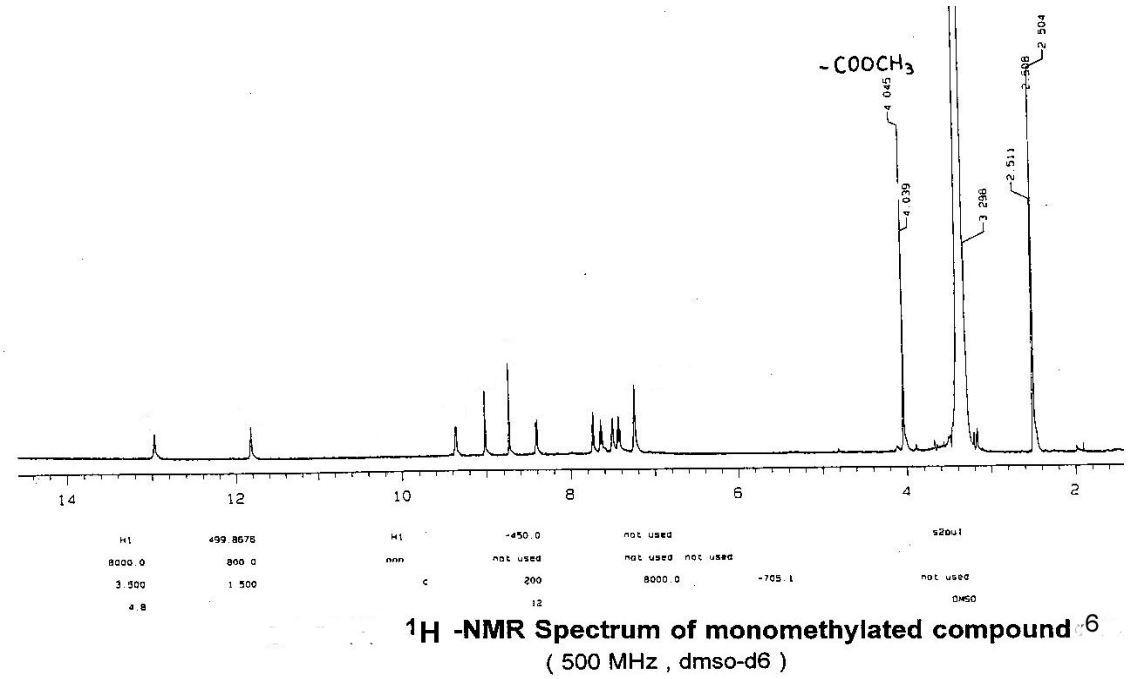
3. Spectroscopic data of methyl ester of chromoazepinone B (6)

Fig. S13. EIMS spectrum



EI-Mass Spectrum of monomethylated compound 6

Fig. S14. ^{1}H NMR spectrum in DMSO d_6



^{1}H -NMR Spectrum of monomethylated compound 6
(500 MHz , dmso-d6)

Fig. S15. ^{13}C NMR spectrum in DMSO d_6

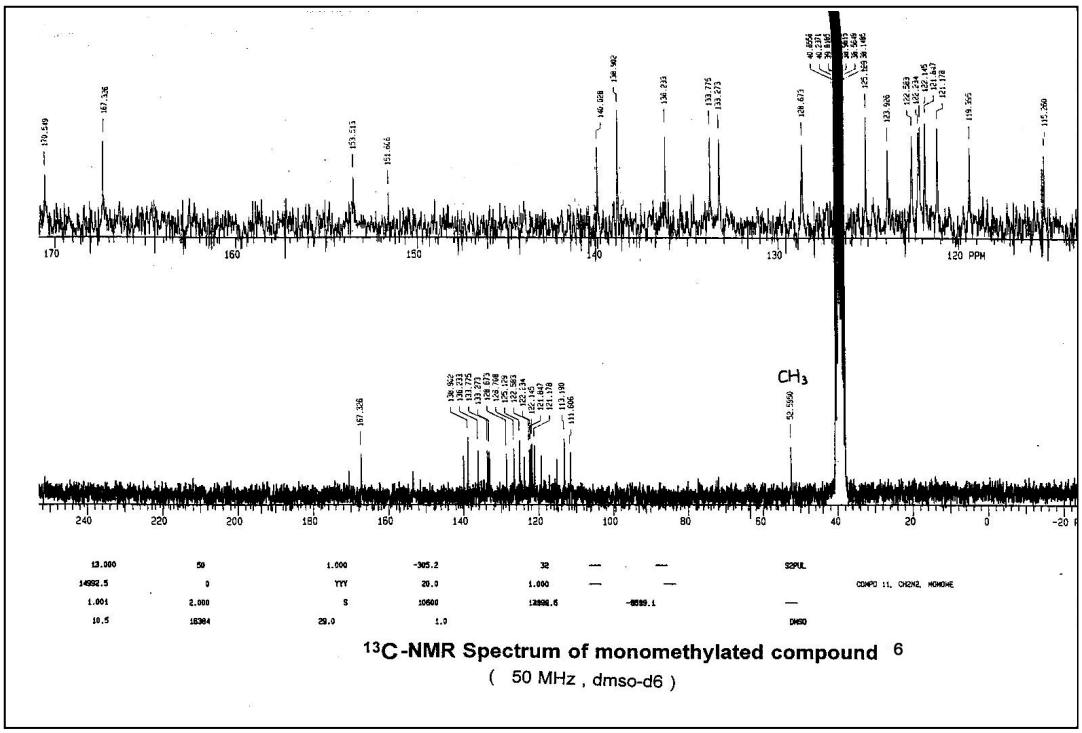
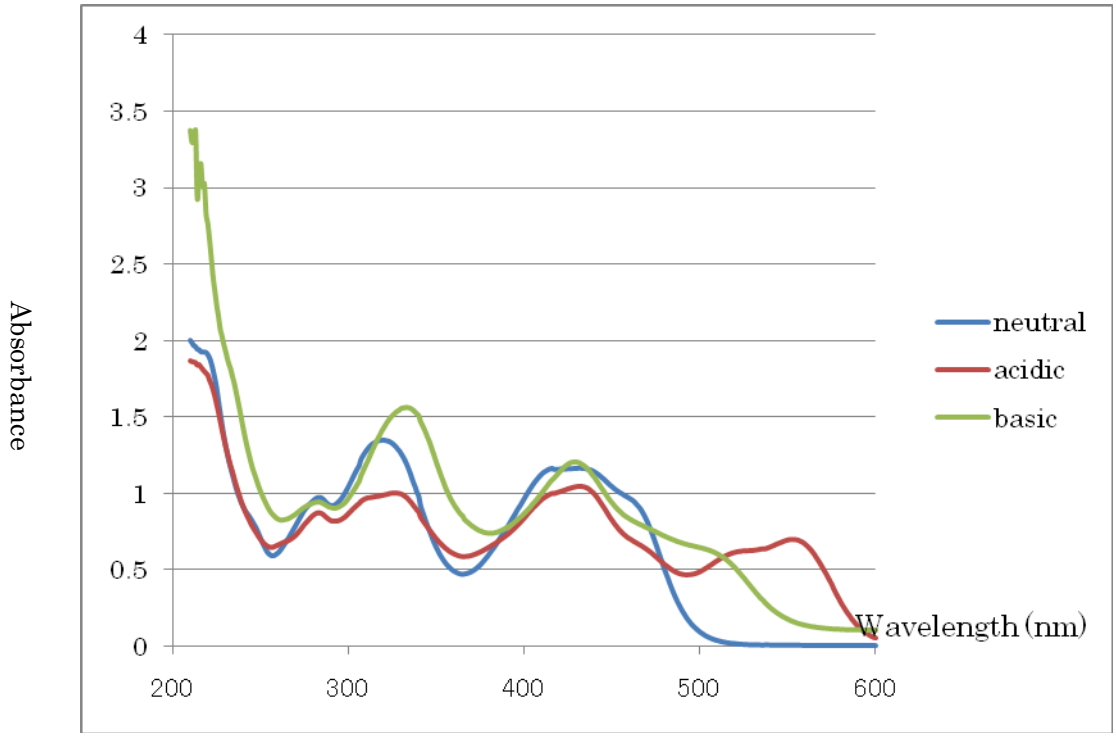
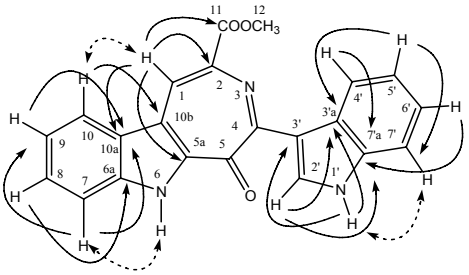


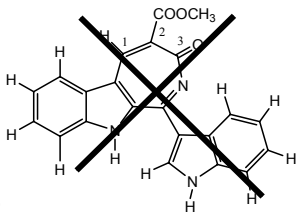
Fig. S16. UV-visible spectrum dissolved in MeOH ($8.67x10^{-5}M$)



IR spectrum of compound **6**-Me ester; Not Measured

Fig. S17. Analyses and assignments of NMR data and its physical data





No HMBC cross peak between H-1 and C-3 leads to the conclusion that this structure is incorrect.

UV (MeOH); acidic: λ_{max} (log ε) 283 (4.00), 326 (4.06), 416 (4.06), 432 (4.08), 536 (3.86), 553 (3.86) nm; neutral: 283 (4.05), 318 (4.19), 416 (4.13), 420 (4.13) nm; basic: 283 (4.04), 333 (4.26), 429 (4.14) 507 shoulder (3.86) nm
HREIMS *m/z* M^+ 369.1111 (calcd for $C_{22}H_{15}N_3O_3$ 369.1113)

400 MHz, DMSO-d_6 The solvent peak: δ_H=2.49, δ_C=39.50

Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C
1	8.73 (s)	**119.3**	**5a**	—	**140.0**	**9**	7.43 (t, J=8.0 Hz)	**122.2**	**2'**	9.02 (d, J=2.5Hz)	**133.1**	**6'**	7.24 (m)	**122.5**
2	—	**133.7**	**6**	12.97 (brs)	—	**10**	8.39 (d, J=8.0 Hz)	**121.8**	**3'**	—	**115.2**	**7'**	7.51 (m)	**111.6**
3	—	—	**6a**	—	**138.9**	**10a**	—	**125.1**	**3'a**	—	**126.7**	**7'a**	—	**136.2**
4	—	**153.5**	**7**	7.73 (d, J=8.0 Hz)	**113.7**	**10b**	—	**122.1**	**4'**	9.36 (m)	**123.9**	**11**	—	**167.3**
5	—	**170.5**	**8**	7.65 (t, J=8.0 Hz)	**128.6**	**1'**	11.81 (s)	—	**5'**	7.24 (m)	**121.1**	**12**	4.04 (3H, s)	**52.59**

4. Spectroscopic data of the methyl ester of chromoazepinone C (7)

Fig. S18. EIMS spectrum

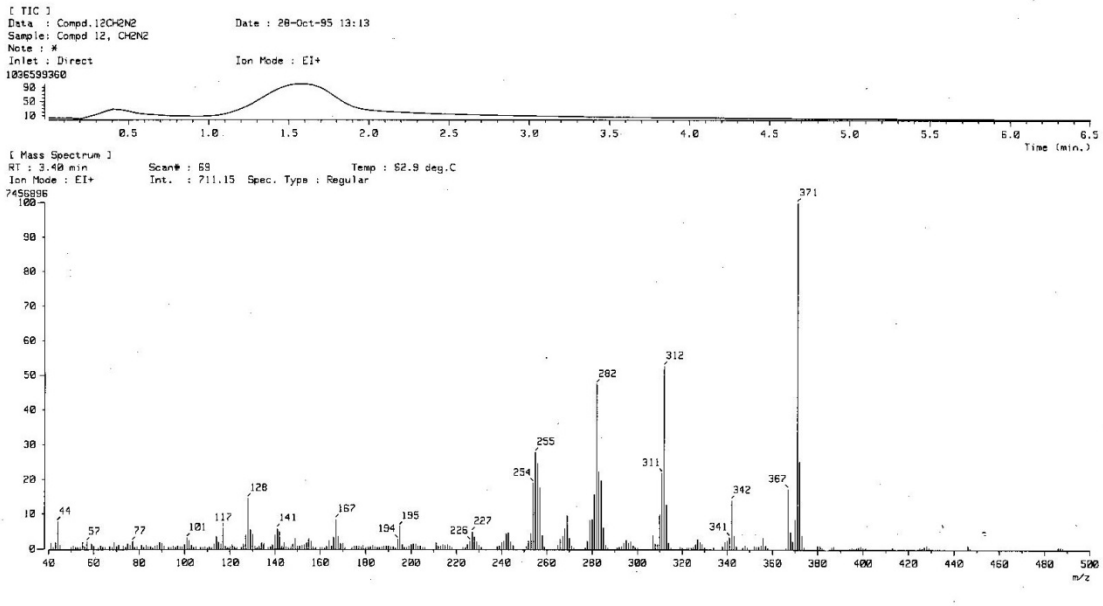


Fig. S19. ^{1}H NMR spectrum of compound **7**-Me ester in DMSO d_6

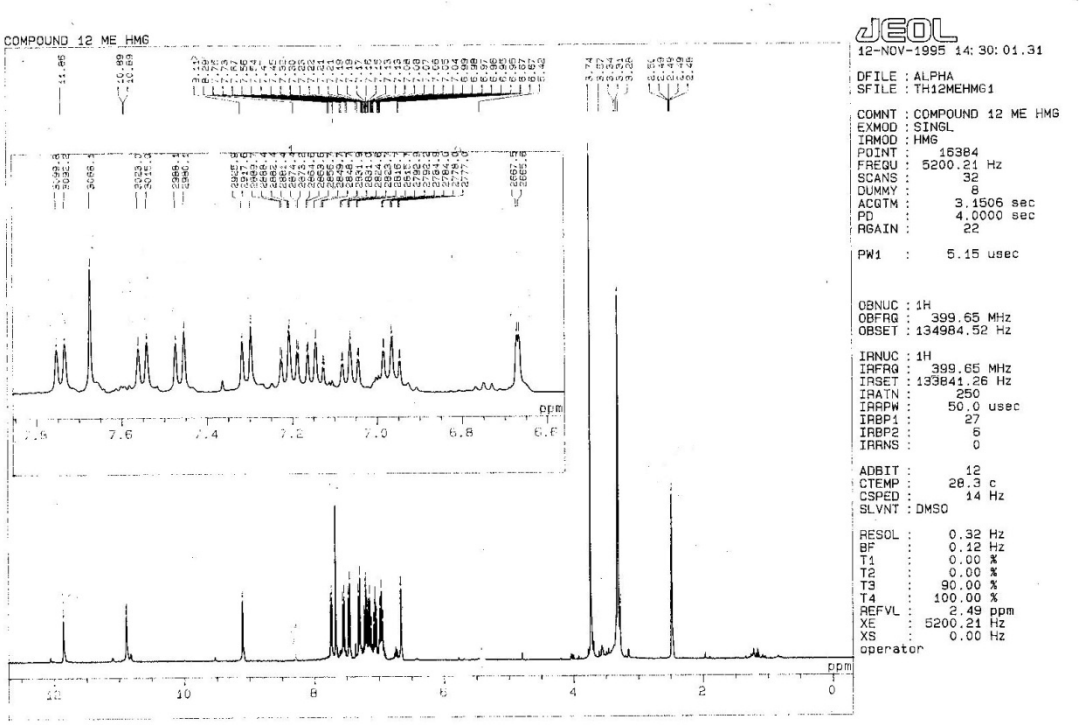


Fig. S20. ^{13}C NMR spectrum of compound **7**-Me ester in DMSO d_6

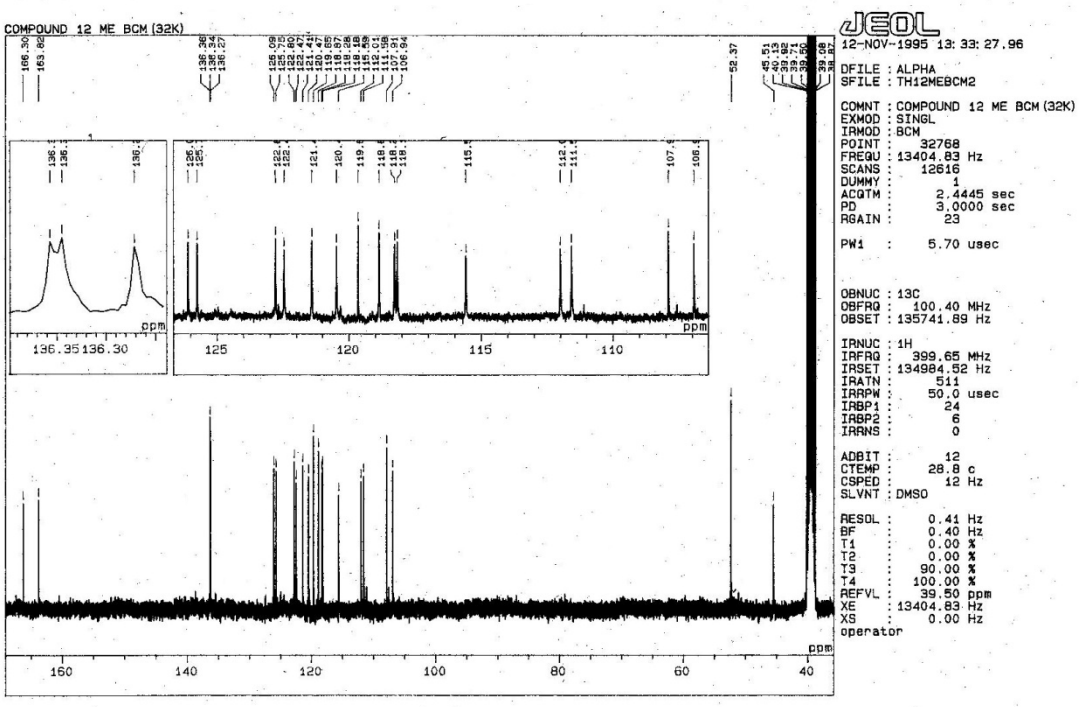


Fig. S21. UV-visible spectrum of compound **7**-Me ester in MeOH

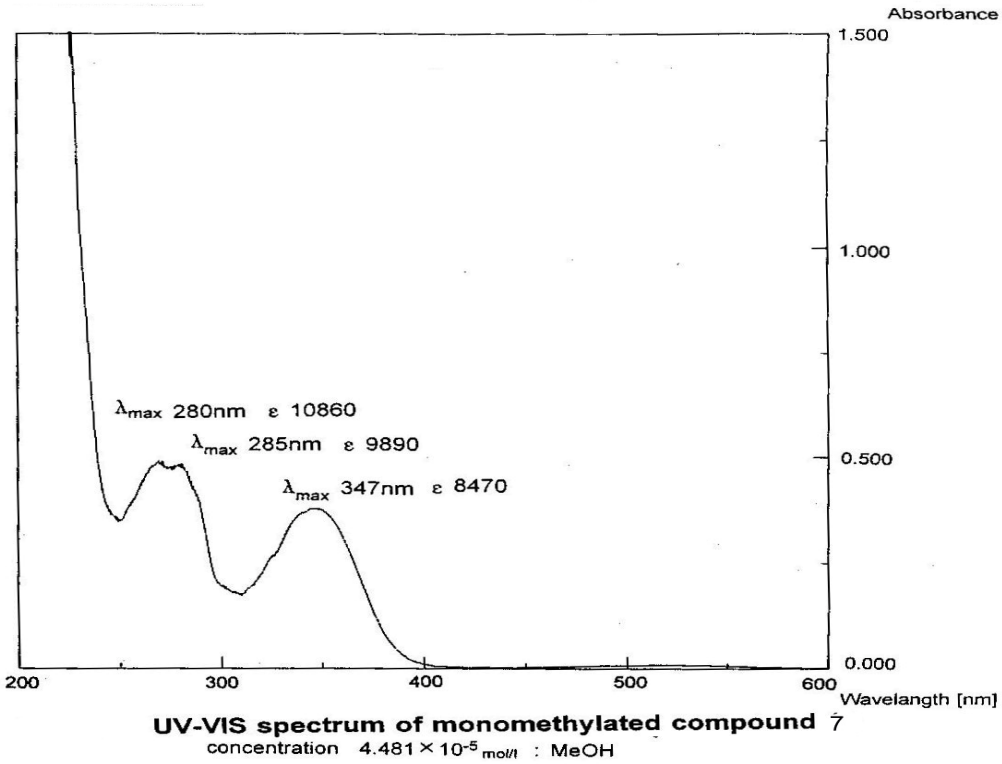


Fig. S22. IR spectrum of compound **7**- Me ester (KBr tablet)

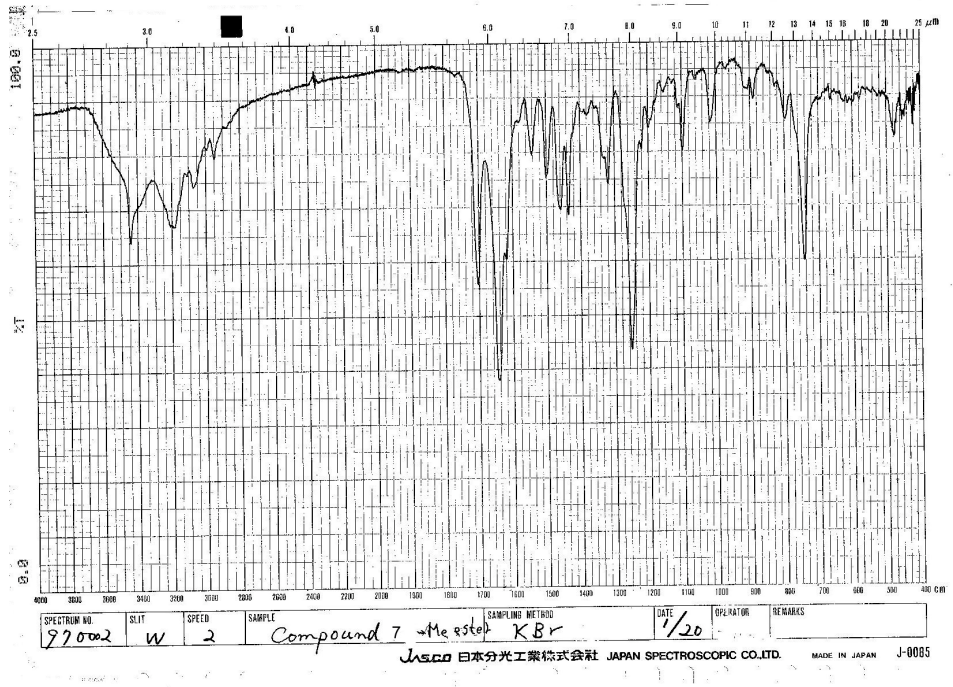
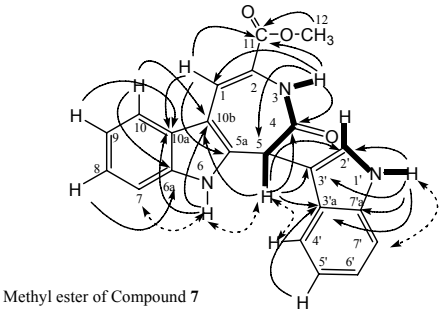


Fig. S23. Analyses and assignments of NMR data of -Me ester of 7 and its physical data



Methyl ester of Compound **7**

HMBC
COSY
NOE

Compound **7**
$[\alpha]_D^{20}$ = + 26.6 (*c*=0.15, EtOH);
Me ester of Compound **7**
UV (MeOH) λ_{max} (log ε) 280 (4.04), 285 (3.99), 347 (3.93) nm; IR (KBr) ν_{max} 1702, 1640, 1620, 1258, 740 cm^{-1}

HREIMS of Me ester of **7**
m/z M^+ 371.1275 (calcd for $C_{22}H_{17}O_3N_3$, 371.1270)

400 MHz, DMSO-d_6 The solvent peak: δ_H=2.49, δ_C=39.50

Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C
1	7.67 (s)	**115.5**	**5a**	—	**136.3**[a]	**9**	7.15 (t, J=8.0 Hz)	**120.4**	**2'**	6.67 (d, J=1.9 Hz)	**122.8**	**6'**	7.06(t, J=8.0 Hz)	121.4
2	—	**119.6**	**6**	11.86 (brs)	—	**10**	7.75 (d, J=8.0 Hz)	**118.1**	**3'**	—	**106.9**	**7'**	7.31 (d, J=8.0 Hz)	**111.5**
3	9.11 (s)	—	**6a**	—	**136.3**[a]	**10a**	—	**126.0**	**3'a**	—	**125.7**	**7'a**	—	**136.2**[a]
4	—	**166.3**	**7**	7.47 (d, J=8.0 Hz)	**112.0**	**10b**	—	**107.9**	**4'**	7.55 (d, J=8.0 Hz)	**118.2**	**11**	—	**163.8**
5	5.42 (d)	**45.51**	**8**	7.21 (t, J=8.0 Hz)	**122.4**	**1'**	10.89 (brs)	—	**5'**	6.97 (t, J=8.0 Hz)	**118.7**	**12**	3.74 (3H, s)	**52.37**

The chemical shifts of C-5a, C-6a and C-7'a are interchangeable due to the very close values.

5. Spectroscopic data of arcyriarubin A (9)

Fig. S24. EIMS spectrum of compound **10**

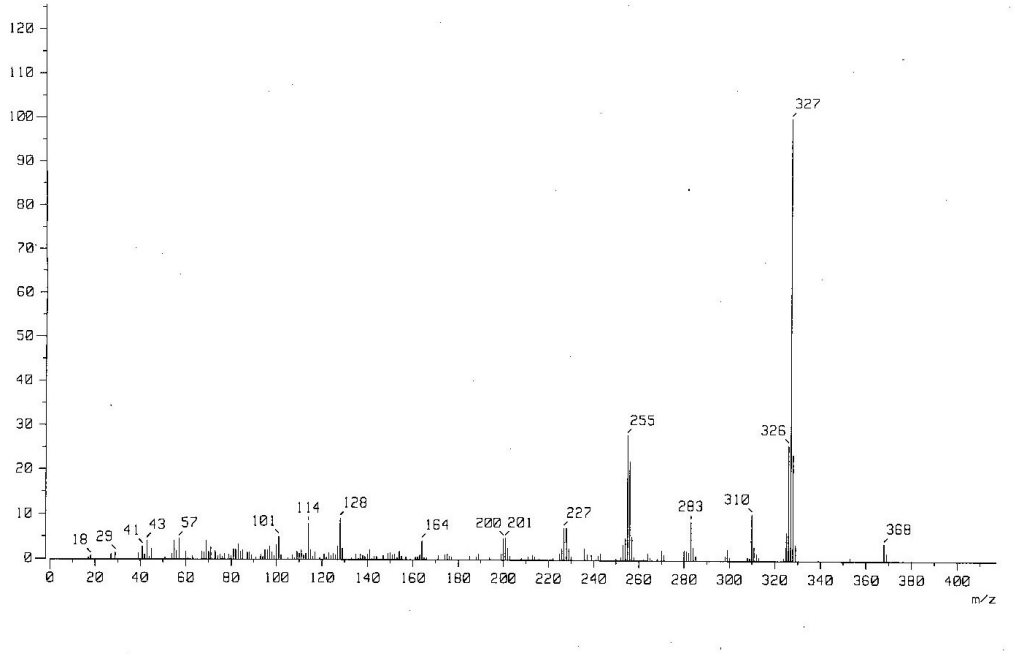


Fig. S25. ^{1}H-NMR spectrum of compound **9** dissolved in DMSO-d_6

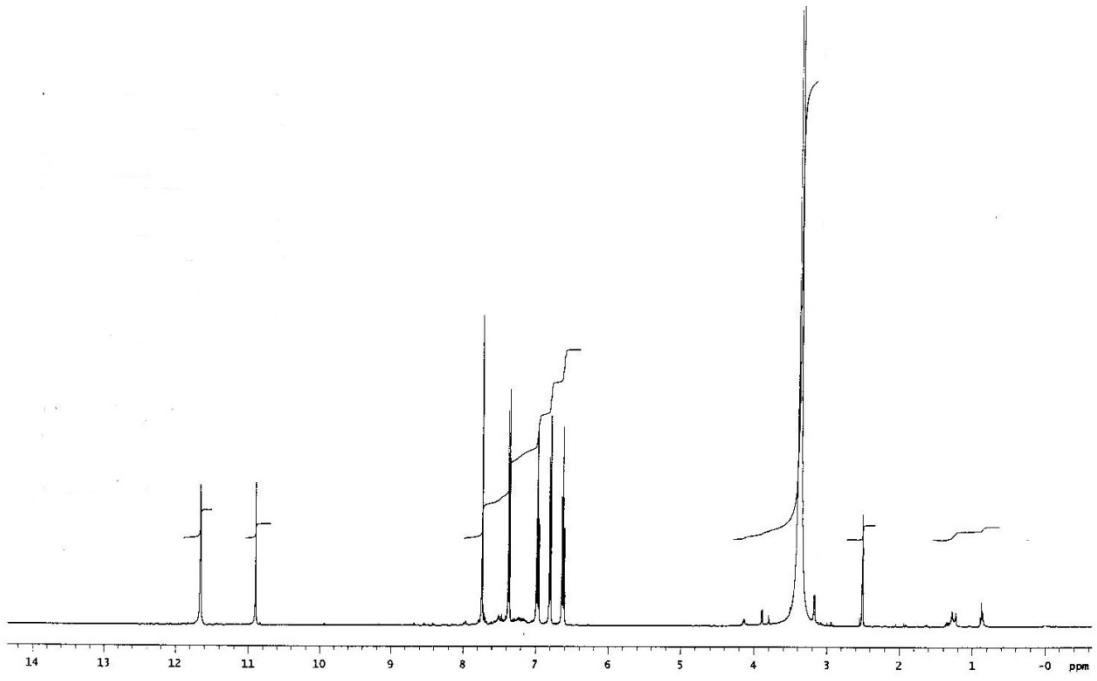


Fig. S26. ^{13}C-NMR spectrum of compound **9** dissolved in DMSO-d_6

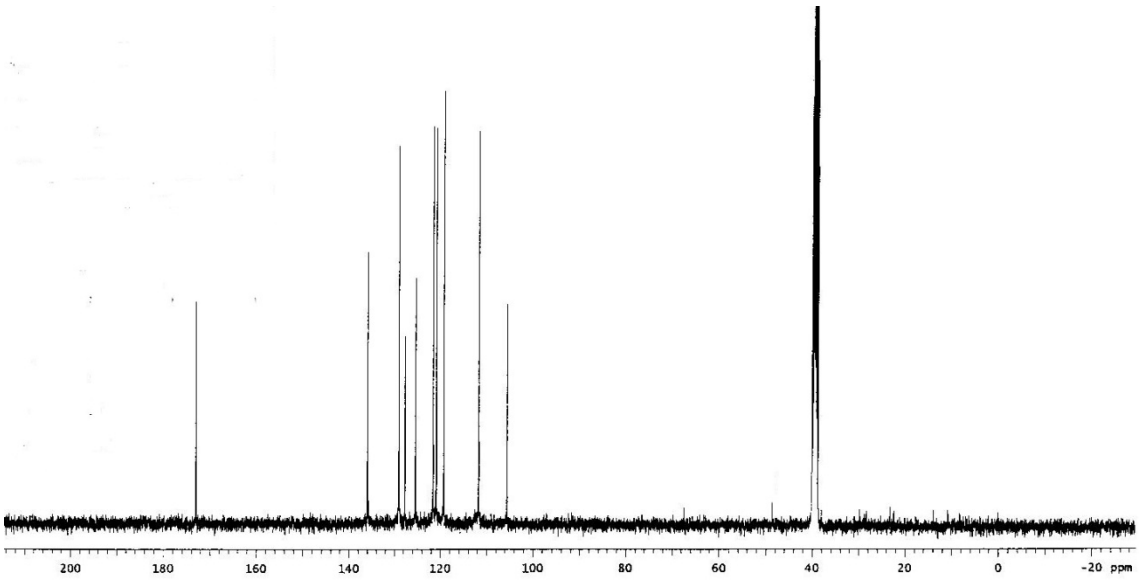


Fig. S27. UV-visible spectrum of compound **9** dissolved in MeOH.

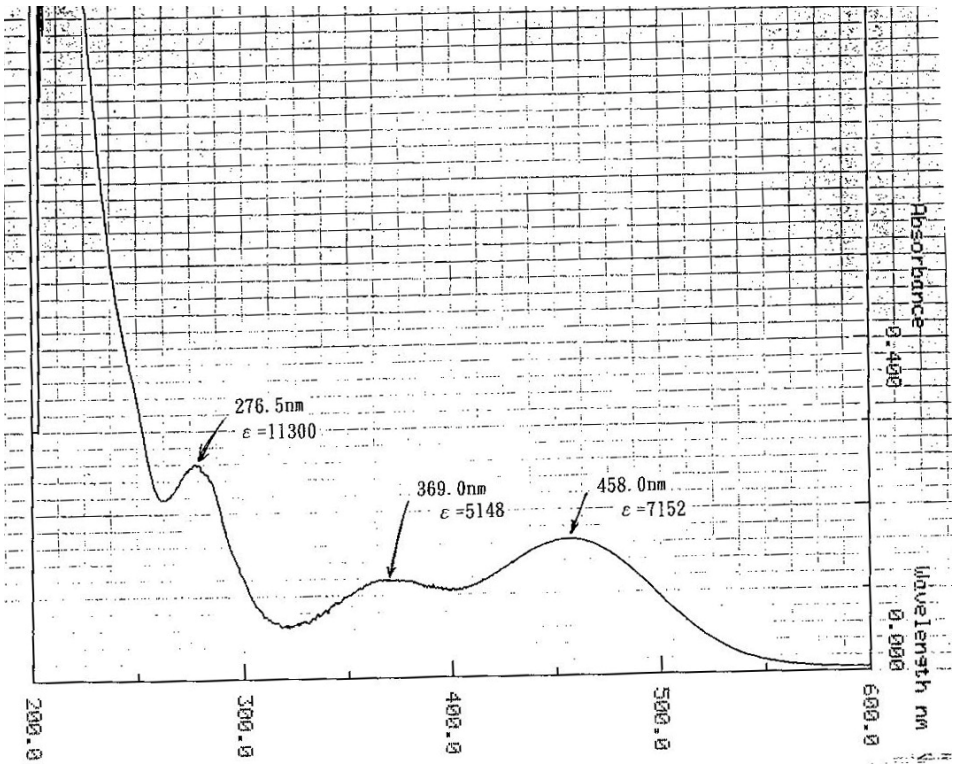


Fig. S28. IR spectrum of compound **9** (KBr)

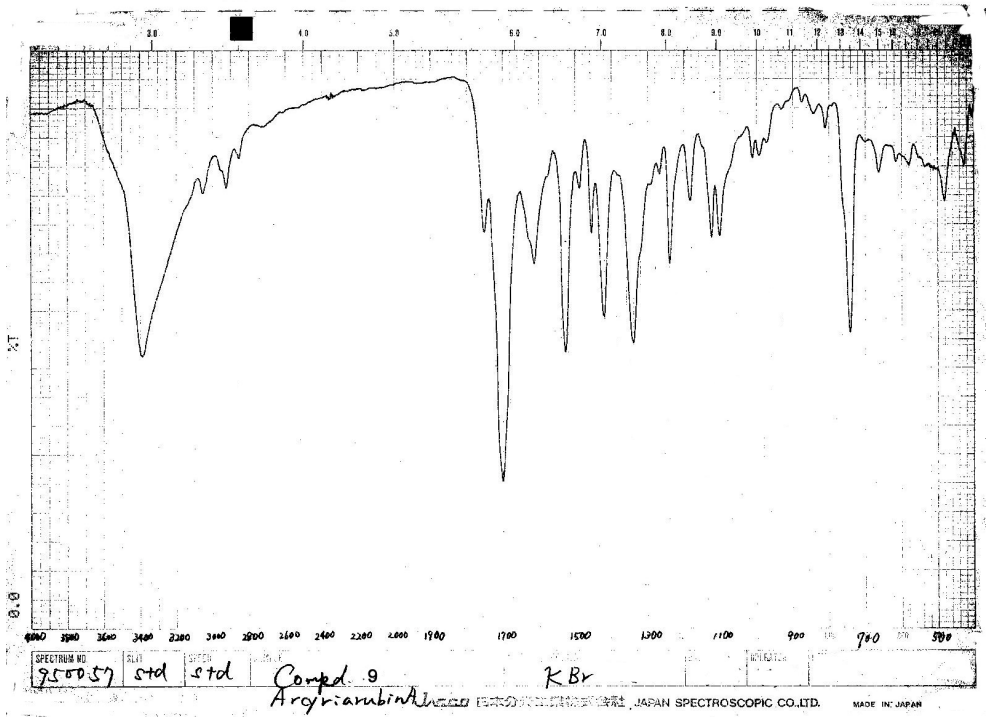
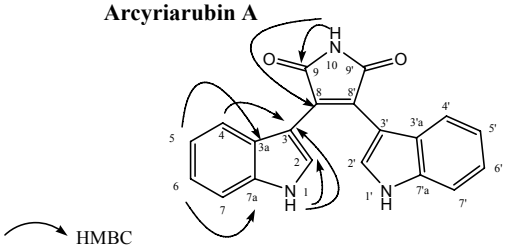


Fig. S29. Analyses and assignments of NMR data of compound **9** and its physical data

Arcyriarubin A



UV (MeOH) λ_{max} (log ε) 276.5 (4.05), 369.0 (3.71), 458.0 (3.85) nm; IR (KBr) ν_{max} 3390, 1750, 1700, 1530, 1340, 740 cm^{-1}
HREIMS *m/z* M^+ 327.1020 (calcd for $C_{20}H_{13}N_3O_2$, 327.1008)

400 MHz, DMSO-d_6 The solvent peak: δ_H=2.49, δ_C=39.50

Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C	Position	^{1}H	^{13}C
1 & 1'	11.65 (s)	—	**3a & 3'a**	—	**126.0 (s)**	**6 & 6'**	6.99 (t, 8.0 Hz)	**122.2 (d)**	**8 & 8'**	—	**128.3 (s)**
2 & 2'	7.73 (d, 2.5 Hz)	129.7 (d)	**4 & 4'**	6.80 (d, 8.0 Hz)	**121.5 (d)**	**7 & 7'**	7.36 (d, 8.0 Hz)	**112.3 (d)**	**9 & 9'**	—	**173.6 (s)**
3 & 3'	—	106.2 (s)	**5 & 5'**	6.64 (t, 8.0 Hz)	**119.9 (d)**	**7a & 7'a**	—	**136.57 (s)**	**10**	10.89 (s)	—