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

Supplementary Information for

Abietane diterpenoids from *Caryopteris incana* (Thunb.) Miq.

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S1.Detailed isolation procedures

General Experimental procedures

Infrared spectra were measured on a PerkinElmer FT-IR spectrometer. CD spectra were performedusing aJASCO J-815 spectrometer. Melting points were carried out on an BUCHI Melting pointB-540. Bruker AV-400 andBruker AV- 500 were used for 1D and 2D NMR spectra with TMS as internal standard. HRESIMS data were performed on a LCQ DECA XP Plus ESI-MS mass spectrometer. Column chromatography (CC): silica gel (200–300 mesh; Qingdao Marine Chemical Factory, China). TLC was conducted on silica gel GF254 plates (Qingdao Marine Chemical Factory, China) and Sephadex LH-20 (Amersham Pharmacia Biotech) were carried out with column chromatography. Semipreparative HPLC were performed on a Agilent 1260 series instrument equipped with a Shiseido Capcellpak Prep C18 ODS column (250 × 20 mm, 5μm, flow rate: 16mL/min).

Plant Material

The plants of *Caryopteris incana* (Thunb.) Miq. were collected from Hexian County of Anhui Province, People's Republic of China, in September 2012. The identification of plant material was verified by Qingshan Yang. A voucher specimen (No.20120915-1) hasbeen deposited in Shanghai R&D Center for Standardization of Traditional Chinese Medicines,Shanghai, 201203,China.

Extraction and Isolation

The dried and powdered plants of *Caryopteris incana* (Thunb.) Miq. (19.5kg) were extracted with EtOH (70 L × 4) at room temperature, the solvent was evaporated under reduced pressure. The crude extract was dissolved inhot water (10L, 60℃) and partitioned with PE and EtOAc to get the PE and EtOAc phases.

ThePE phase (234g) dissolved in CH_2Cl_2, and subjected to column chromatography over silica gel with PE/EtOAc as eluent (from PE to PE/EtOAc (3/1)) to afford 8 fractions (I−VIII).

Fraction II (16.2 g) was further chromatographed over silica gel with PE/EtOAc(10/1) as eluent to provided Compounds **6** (16.2 mg) and **7**(10.6 mg). Compounds **5** (8.6 mg), **23** (5.3 mg), **24** (7.1 mg)were isolated from Fraction III (17.4g) through silicagel CC with PE/EtOAc (10/1 to 5/1) and were further purified by gel permeation chromatography on Sephadex LH–20 in MeOH/CH_2Cl_2(3/1). Fraction IV(23.6g) was subjected to repeated silica gel CC with PE/EtOAc (10/1 to 3/1) to yield compounds**22** (37.0 mg), **30** (44.5 mg). Fraction V (28.9g) was further chromatographed on a Sephadex LH-20 column using CH_2Cl_2/MeOH eluent (CH_2Cl_2/MeOH(1/3)) to afford V-1~V-8,subfraction V-4(3.7g)was chromatographed on a Sephadex LH-20 column using MeOH eluent to get themixture of compounds **9** and **10**, followed by Pre-HPLC to afford compound **9** (17.9mg) and compound **10**(6.2mg),subfraction V-6(2.3g) was chromatographed on a Sephadex LH-20 column using MeOH eluent, followed by Pre-HPLC toafford compound **1** (12.3mg);Fraction VI (38.5 g) was further subjected to column chromatography over silica gel with PE/EtOAc as eluent (from PE/EtOAc(8/1) to EtOAc) to afford 6 fractions (VI−1~VI-6),subfraction VI-5 (2.2g) chromatographed on a Sephadex LH-20 column using MeOH eluent to get the mixture of compounds **35** and **39**, followed by Pre-HPLC to afford compound**35** (24.0mg) and compound **39**(38.2mg); Subfraction VI-6(6.2g) was chromatographed on a Sephadex LH-20 columnusingMeOH eluent followed by Pre-HPLC to afford compound **2** (42.1mg).

The EtOAc phase (355g) dissolved in CH_2Cl_2, and subjected to column chromatography over silica gel with CH_2Cl_2/MeOH as eluent (from CH_2Cl_2 to MeOH) to afford 16 fractions (I−XVI). Fraction III (25.2 g) was chromatographed on a Sephadex LH-20 column using MeOH to afford V-1~V-5, subfraction V-3(7.5g) was further subjected to column chromatography over silica gel with CH_2Cl_2/MeOH as eluent (from CH_2Cl_2/MeOH (15/1) to CH_2Cl_2/MeOH (8/1)) to provided Compounds **13** (162.7 mg) and **20**(240.5 mg).Fraction IV (15.2 g) was repeated chromatographed on a Sephadex LH-20 column using MeOH, followed by Pre- HPLC to get compound **8** (25.3mg), **36** (8.1mg) and **36** (11.9mg).

Fraction V (12.6 g)was chromatographed on a Sephadex LH-20 column using MeOH to afford V-1~V-8, subfraction V-4(1.5g) subjected by Pre- HPLC to get compound **25** (12.3mg),**26** (13.0mg) and **34** (77.5mg).Fraction VI (19.3 g) was subjected to repeated silica gel CC with CH_2Cl_2/MeOH (10/1 to 5/1) to yield compounds **38** (9.0 mg), **40**(6.7 mg).Fraction VII (26.1 g)was repeated chromatographed on a Sephadex LH-20 column using MeOH to afford V-1~V-10, VI-5 (4.1g) chromatographed on a Sephadex LH-20 column using MeOH eluent to get the mixture of compounds **11**, **12**, **14**, **15**, followed by Pre-HPLC to afford compound **11**(9.0mg), **12**(7.2mg), **14**(12.0mg), **15**(7.7mg).

Fraction VIII (34.5 g)was chromatographed on a Sephadex LH-20 column using MeOH to afford V-1~V-8, subfraction V-2(3.8g)was further subjected to column chromatography over silica gel with CH_2Cl_2/MeOH as eluent (from CH_2Cl_2/MeOH (8/1) to CH_2Cl_2/MeOH (4/1)) to provided Compounds**27**(8.2mg); subfraction V-5(5.6g)was chromatographed on a Sephadex LH-20 column using MeOH eluent, followed by Pre-HPLC to afford compound **16**(12.0mg) and**17**(10.0mg).

Fraction IX (33.2 g) was further chromatographed on a silica gel column using CH_2Cl_2/MeOH eluent (from CH_2Cl_2 to CH_2Cl_2/MeOH (1/5)) to afford IX -1~IX -10, subfraction IX-4 (3.3g) was chromatographed on a Sephadex LH-20 column using MeOH eluent, followed by Pre- HPLC to get compound **18** (8.2mg), **19** (7.0mg)and compound **21** (15.8mg); Subfraction IX-8 (5.3g) was chromatographed on a Sephadex LH-20 column using MeOH eluent, followed by Pre- HPLC to get compound **3** (55.2mg) and compound **4** (65.8mg).

Fraction X (53.2 g) was further chromatographed on a silica gel column using CH_2Cl_2/MeOH eluent (from CH_2Cl_2 to CH_2Cl_2/MeOH (1/3)) to afford IX -1~ IX -6, subfraction IX-2 (5.3g)was chromatographed on a Sephadex LH-20 column using MeOH eluent, followed by Pre- HPLC to get compound **28** (6.6mg), **29** (6.8mg), **31** (5.8mg), **32** (8.5mg),**33** (9.7mg).

S2. X-ray crastal data for caryopincaolide A~C (1~3)

Crystal data and structure refinement for caryopincaolide A (**1**).

Identification code	cu_dm13699_0m	
Empirical formula	C_{20} H_{24} O_3	
Formula weight	312.39	
Temperature	140(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.38710(10) Å	a= 90°.
	b = 10.73400(10) Å	b= 103.68°.
	c = 12.86660(10) Å	g = 90°.
Volume	1662.25(2) Å3	
Z	4	
Density (calculated)	1.248 Mg/m3	
Absorption coefficient	0.656 mm-1	
F(000)	672	
Crystal size	0.230 x 0.080 x 0.050 mm3	
Theta range for data collection	3.672 to 69.722°.	
Index ranges	-14<=h<=14, -10<=k<=12, -15<=l<=15	
Reflections collected	12075	
Independent reflections	4834 [R(int) = 0.0286]	
Data / restraints / parameters	4834 / 1 / 427	
Goodness-of-fit on F2	0.947	
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0991	
R indices (all data)	R1 = 0.0375, wR2 = 0.1004	
Absolute structure parameter	-0.02(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.419 and -0.302 e.Å-3	

Crystal data and structure refinement for caryopincaolide B (**2**)

Identification code	cu_dm13690_0m	
Empirical formula	C19 H26 O4	
Formula weight	318.40	
Temperature	140(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 9.7007(2) Å	= 90°.
	b = 6.22280(10) Å	= 101.8700(10)°.
	c = 13.9225(3) Å	= 90°.
Volume	822.47(3) $Å^3$	
Z	2	
Density (calculated)	1.286 Mg/m^3	
Absorption coefficient	0.715 mm^{-1}	
F(000)	344	
Crystal size	0.300 x 0.080 x 0.020 mm^3	
Theta range for data collection	3.244 to 69.346°.	
Index ranges	-11<=h<=11, -7<=k<=5, -16<=l<=16	
Reflections collected	6186	
Independent reflections	2318 [R(int) = 0.1364]	
Completeness to theta = 67.679°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7532 and 0.6055	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2318 / 1 / 212	
Goodness-of-fit on F^2	1.104	
Final R indices [I>2sigma(I)]	R1 = 0.0836, wR2 = 0.2171	
R indices (all data)	R1 = 0.0851, wR2 = 0.2190	
Absolute structure parameter	0.2(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.404 and -0.496 e.$Å^{-3}$	

Crystal data and structure refinement for caryopincaolide C (**3**)

Identification code	cu_dm14215_0m	
Empirical formula	C20 H26 O5	
Formula weight	346.41	
Temperature	130 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 11.9342(11) Å	= 106.111(5)°.
	b = 12.3874(11) Å	= 92.693(5)°.
	c = 13.3401(13) Å	= 95.261(6)°.
Volume	1881.3(3) $Å^3$	
Z	4	
Density (calculated)	1.223 Mg/m^3	
Absorption coefficient	0.709 mm^{-1}	
F(000)	744	
Crystal size	0.2 x 0.05 x 0.03 mm^3	
Theta range for data collection	3.458 to 67.498°.	
Index ranges	-11<=h<=14, -14<=k<=14, -15<=l<=15	
Reflections collected	15264	
Independent reflections	8863 [R(int) = 0.0521]	
Completeness to theta = 67.679°	93.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.4824	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8863 / 3 / 920	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0662, wR2 = 0.1770	
R indices (all data)	R1 = 0.0838, wR2 = 0.2030	
Absolute structure parameter	-0.1(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.370 and -0.378 $e.Å^{-3}$	

Crystallographic datafor the structure of **1**~**3** have been deposited in the Cambridge Crystallographic Data Centre(deposition numbers CCDC 1401888 for **1**, 1401889 for **2**,1401890 for **3**). Copies of the data can be obtained free of charge onapplication to the director from the CCDC 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44)1223-336-003 or e-mail: deposit@ccdc.cam.ac.uk] or viawww.ccdc.cam.ac.uk/conts/retrieving.html

Figure S1. ^{13}C NMR spectrum of caryopincaolide A (**1**) in $CDCl_3$ (100 MHz)

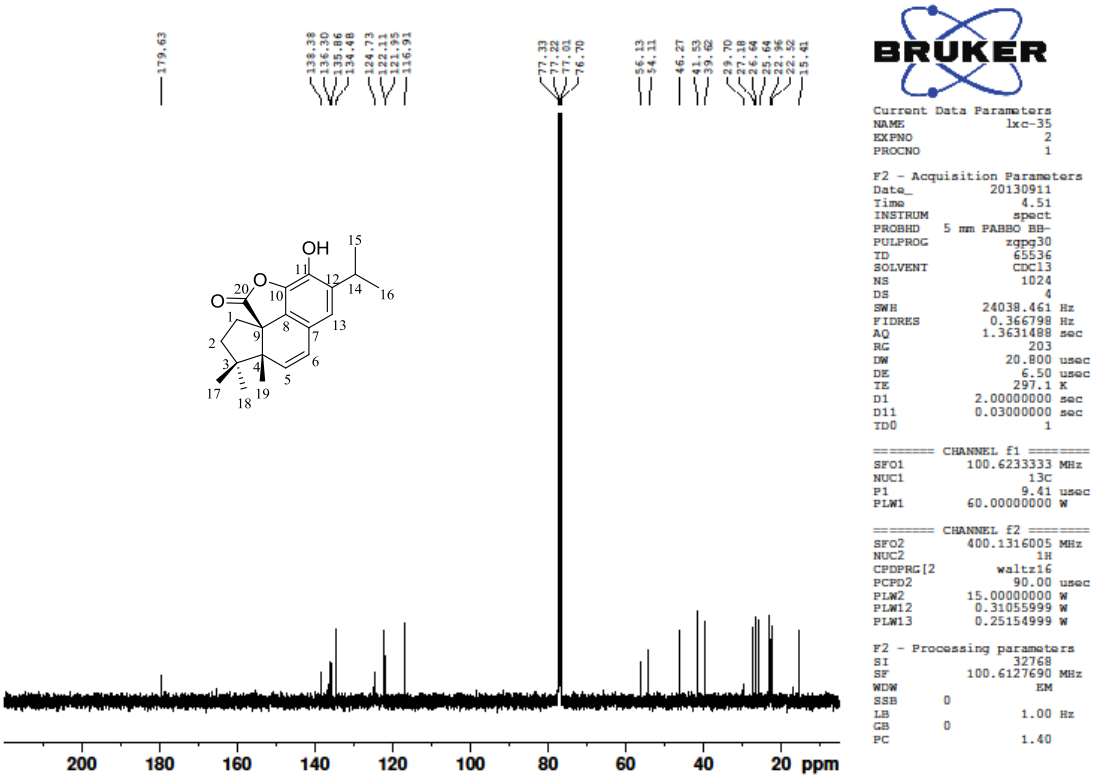


Figure S2. ^{1}H NMR spectrum of caryopincaolide A (**1**) in $CDCl_3$ (400 MHz)

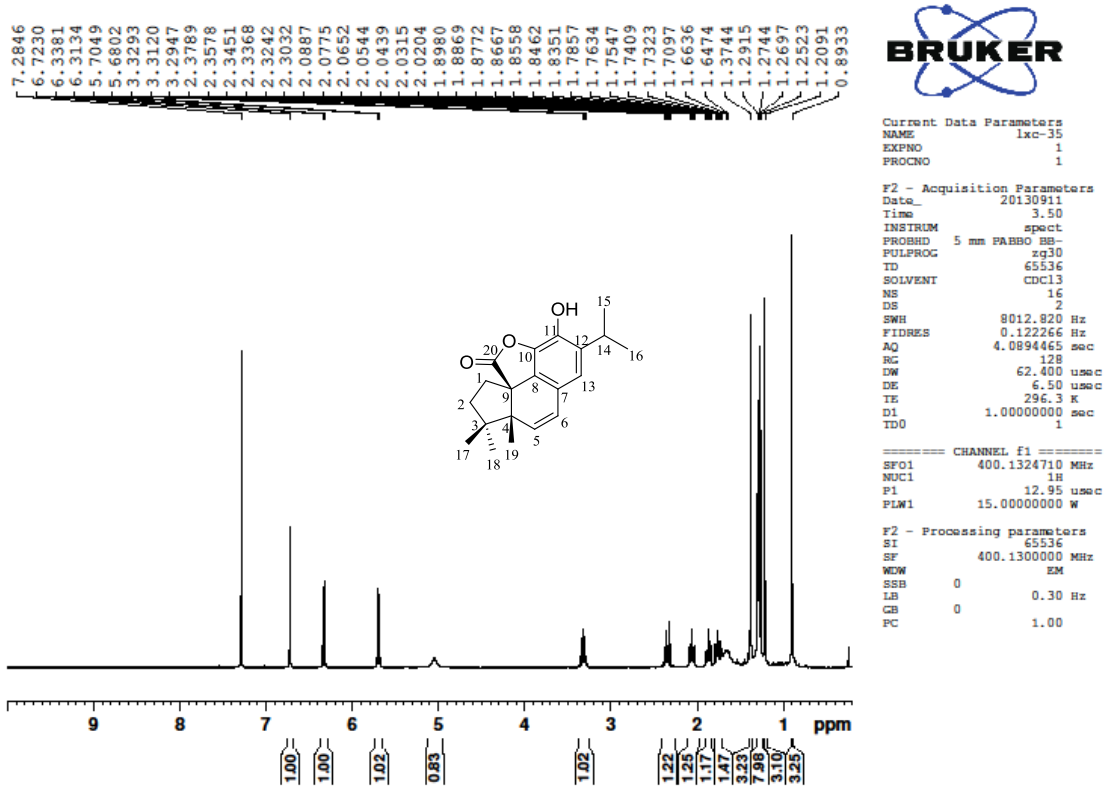


Figure S3. HSQC spectrum of caryopincaolide A (**1**) in $CDCl_3$

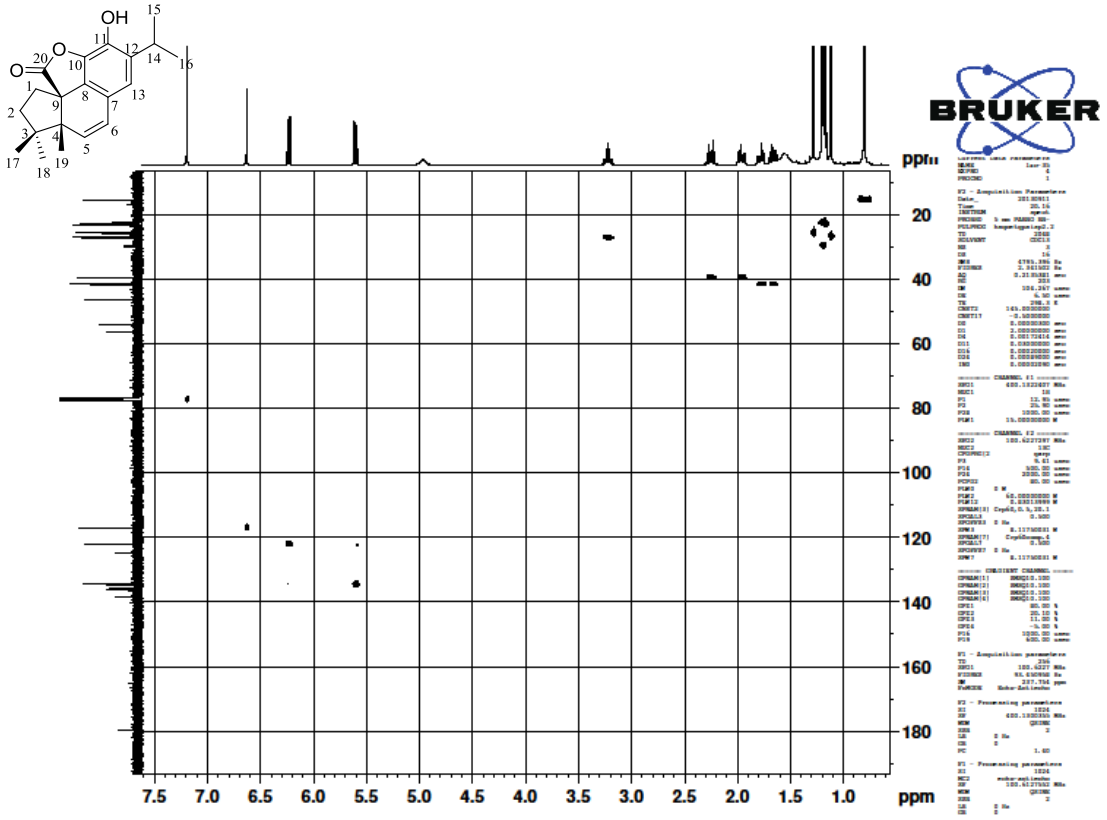


Figure S4. HMBC spectrum of caryopincaolide A (**1**) in $CDCl_3$

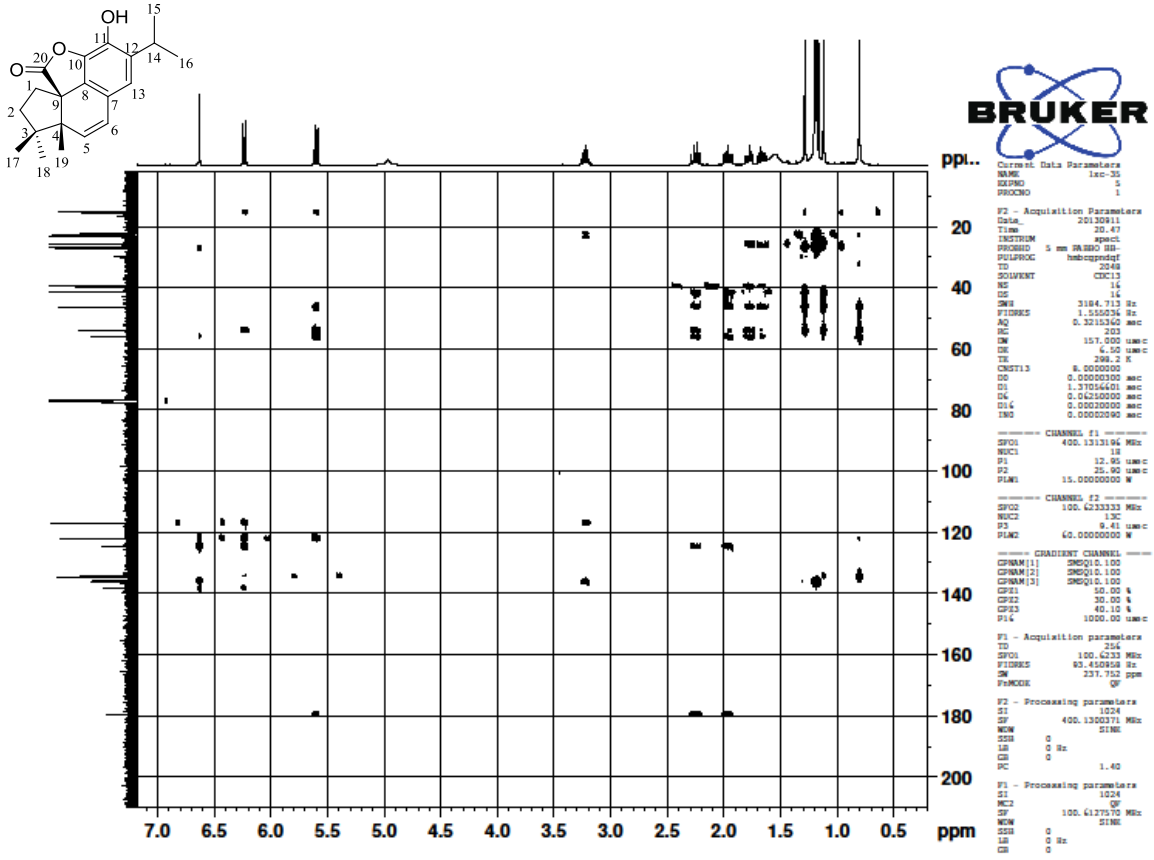


Figure S5. NOESY spectrum of caryopincaolide A (**1**) in $CDCl_3$

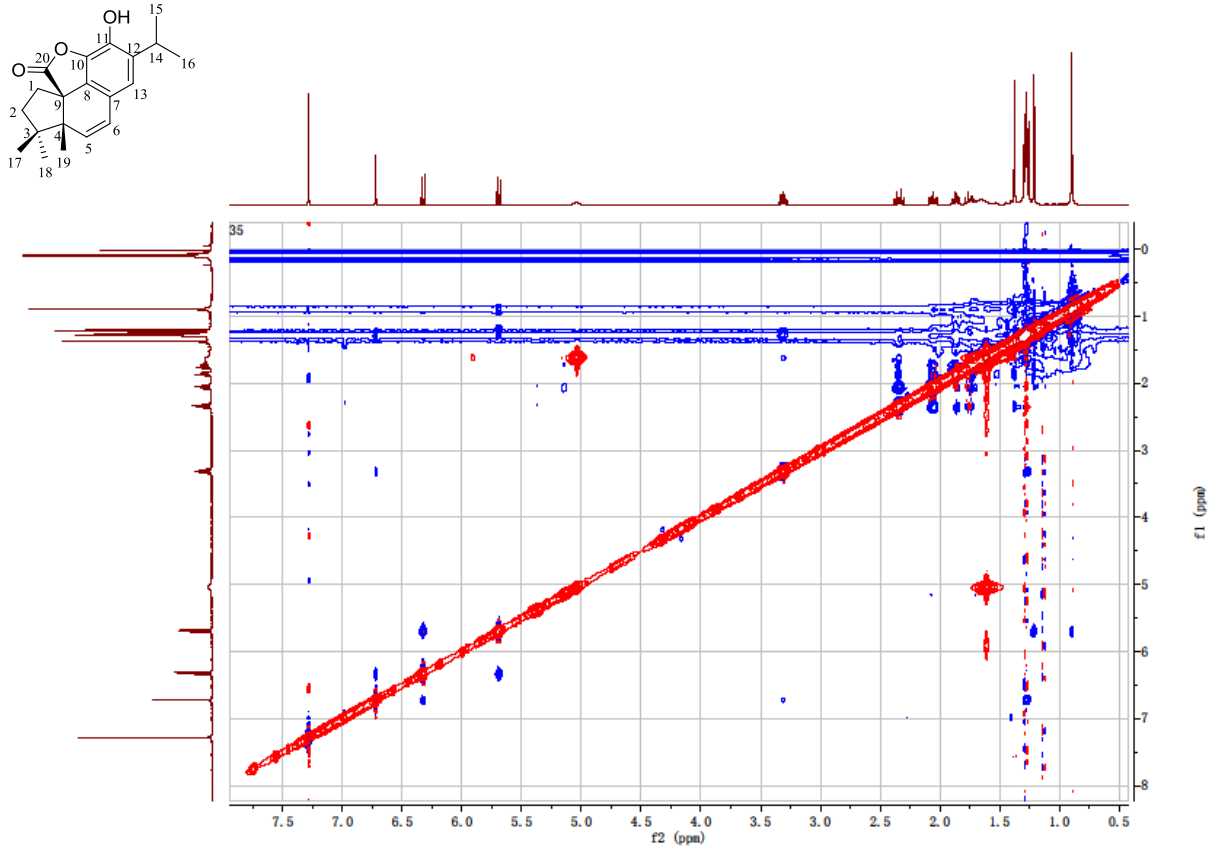


Figure S6. ^{1}H–^{1}H COSYspectrum of caryopincaolide A (**1**) in $CDCl_3$

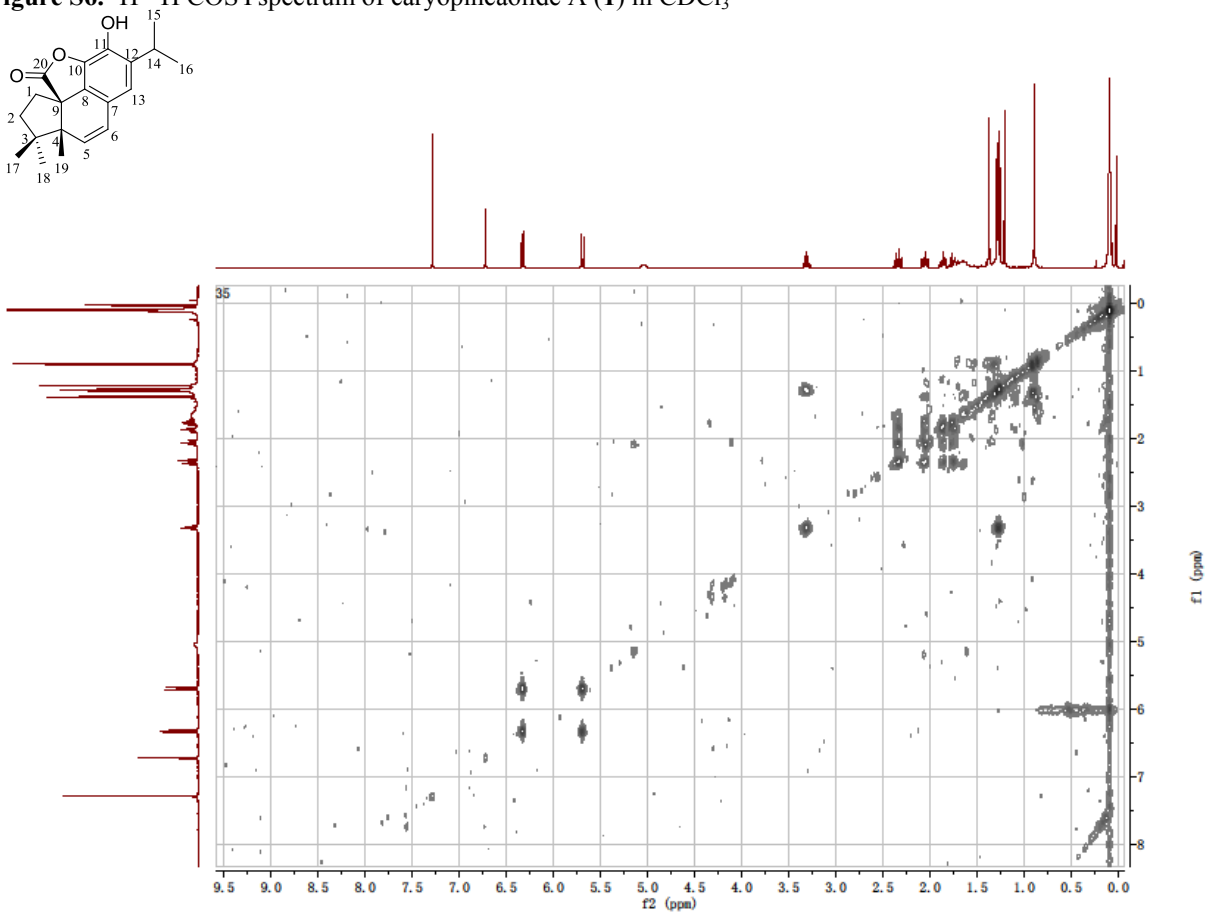
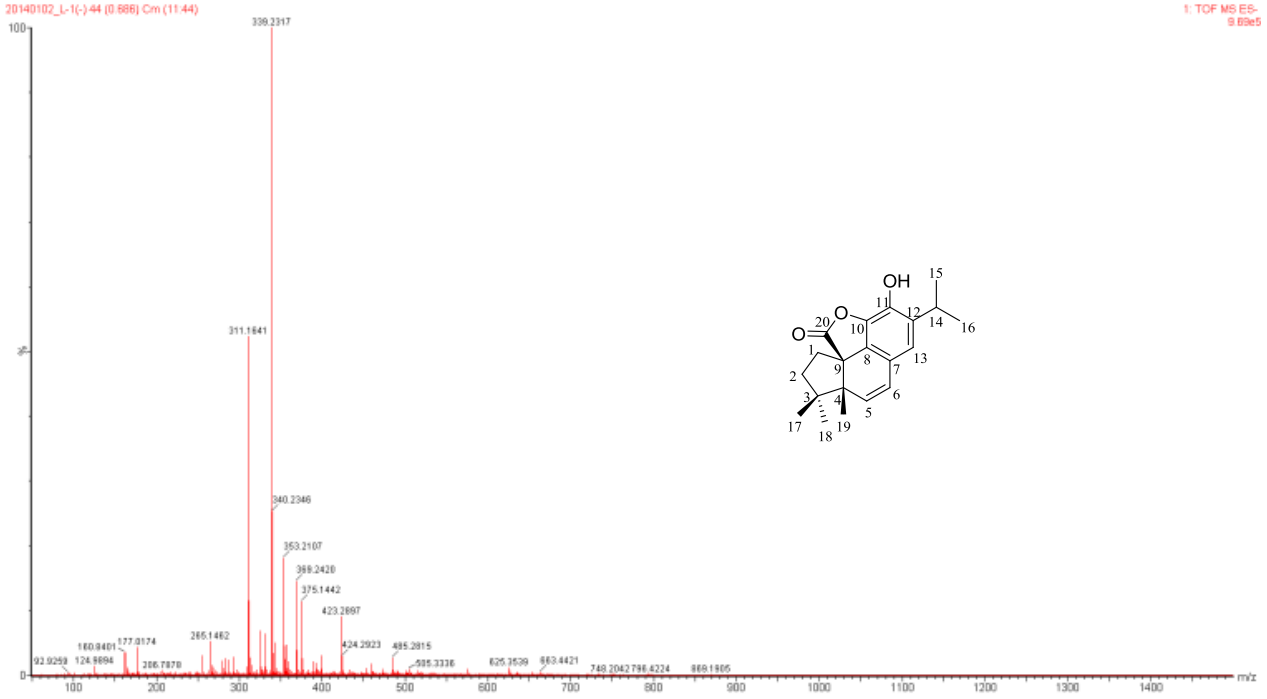


Figure S7. HRESIMS spectrum of caryopincaolide A (**1**)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
311.1641	311.1647	-0.6	-1.9	9.5	524.1	0.357	69.97	C20 H23 O3
	311.1623	1.8	5.8	6.5	524.9	1.203	30.03	C18 H24 O3 Na

Figure S8. IR spectrum of caryopincaolide A (**1**)

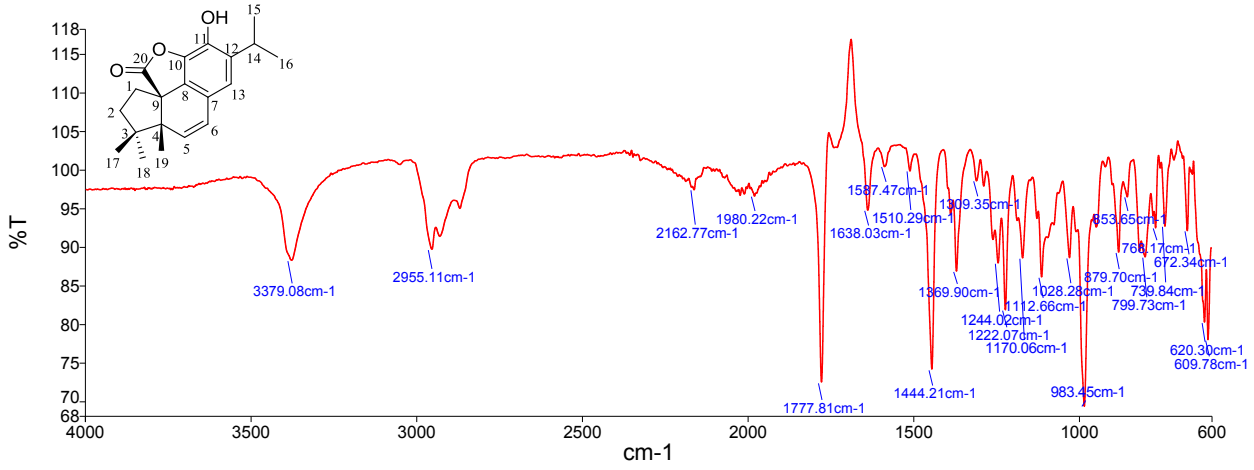


Figure S9. ^{13}C NMR spectrum of caryopincaolide B (**2**) in $CDCl_3$ (100 MHz)

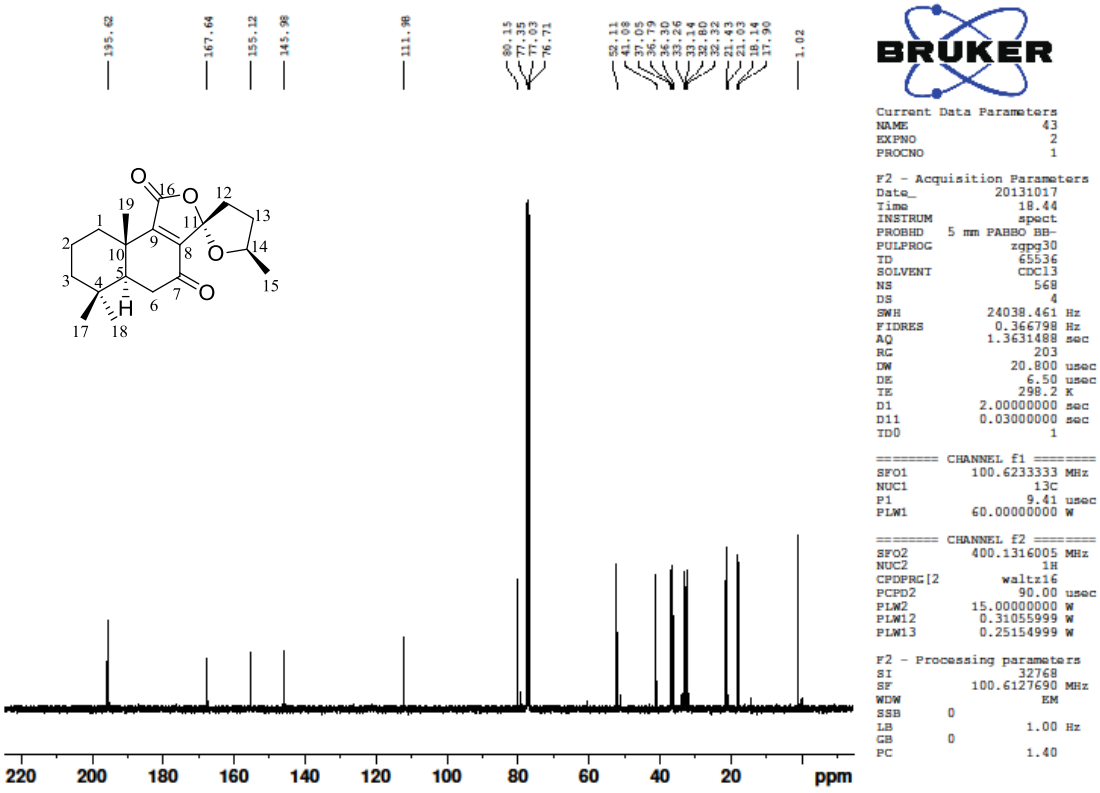


Figure S10. ^{1}H NMR spectrum of caryopincaolide B (**2**) in $CDCl_3$ (400 MHz)

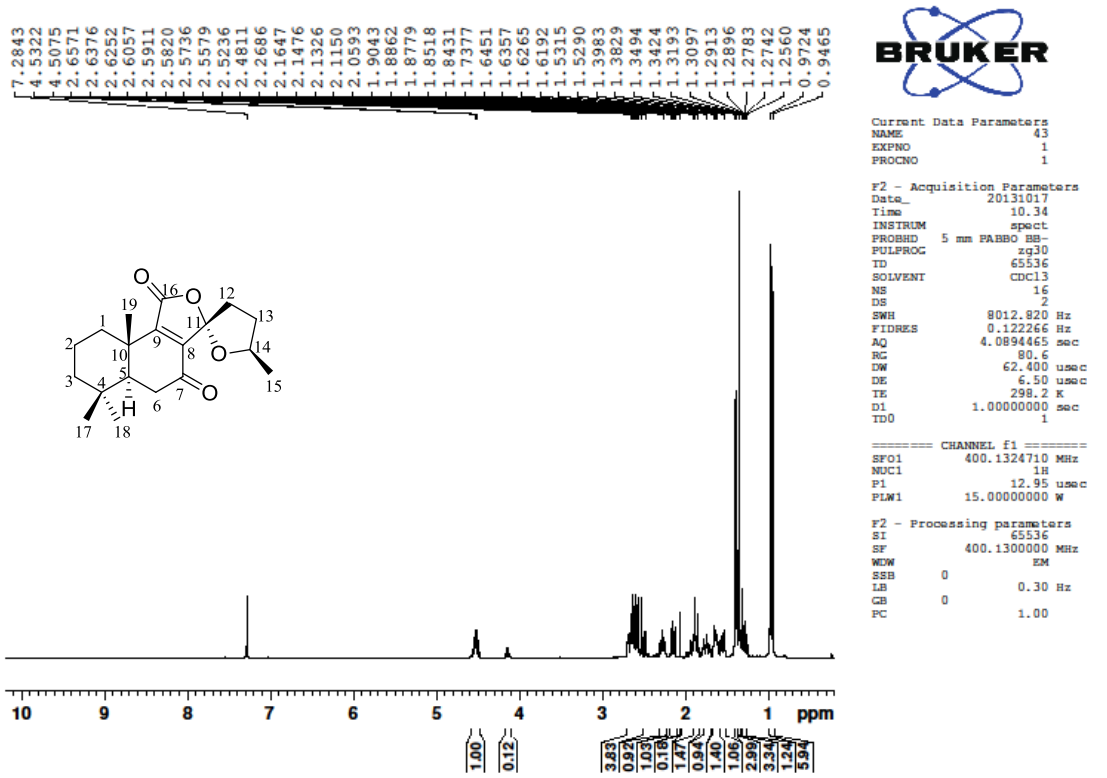


Figure S11. HSQC spectrum of caryopincaolide B (**2**) in $CDCl_3$

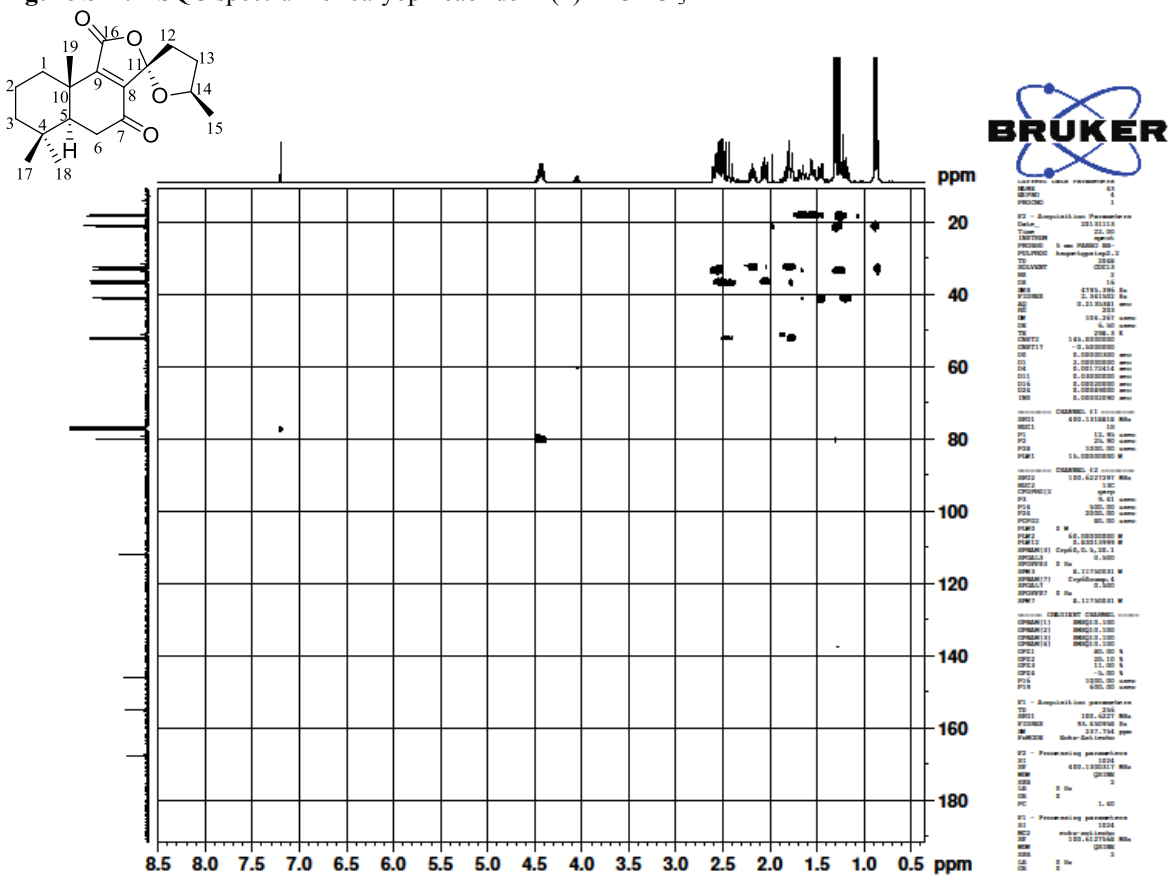


Figure S12. HMBC spectrum of caryopincaolide B (**2**) in $CDCl_3$

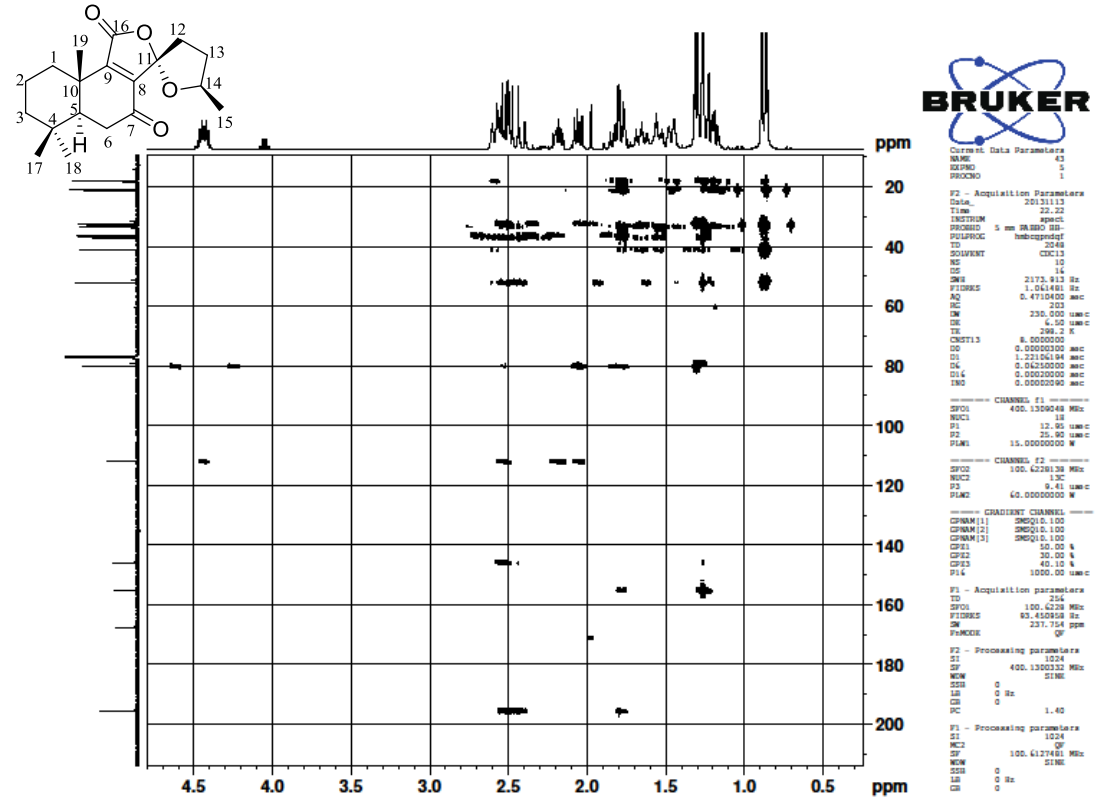


Figure S13. NOESY spectrum of caryopincaolide B (**2**) in $CDCl_3$

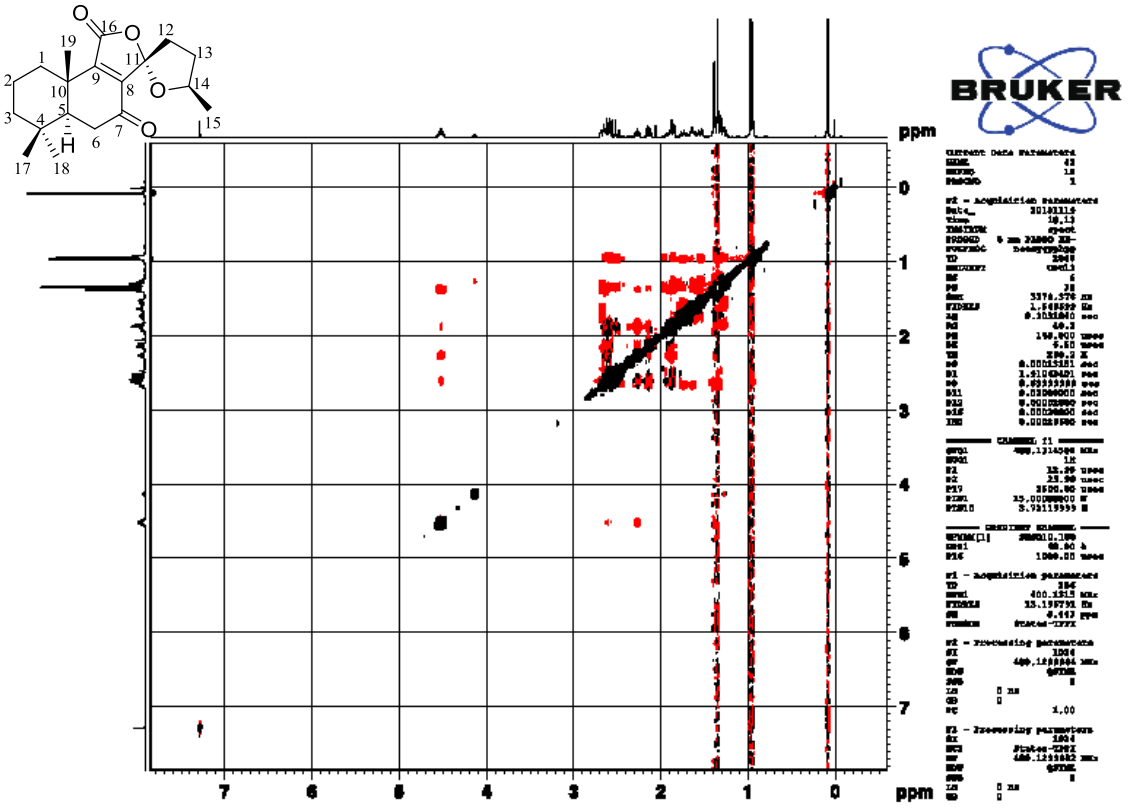
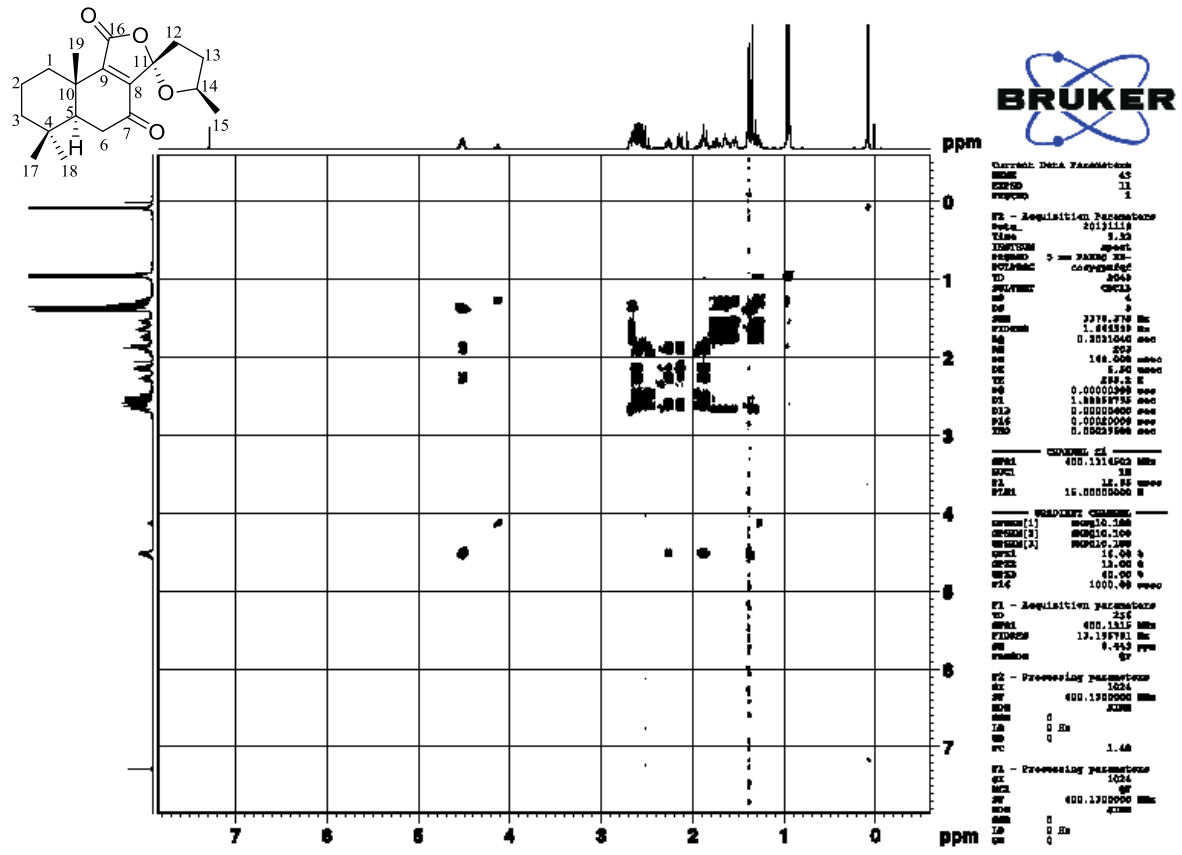
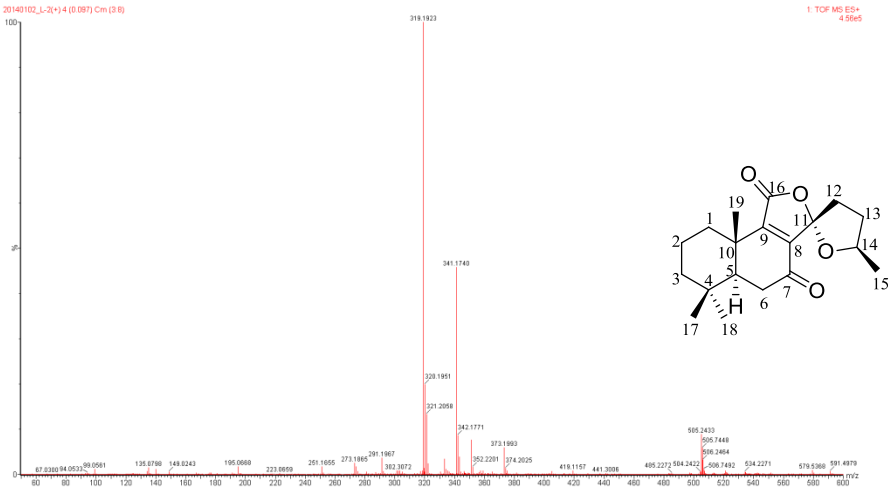


Figure S14. ^{1}H–^{1}H COSYspectrum of caryopincaolide B (**2**) in $CDCl_3$



FigureS15..HRESIMS spectrum of caryopincaolide B (**2**)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
319.1922	319.1923	-0.1	-0.3	11.5	417.0	1.804	16.46	C20 H23 N4
	319.1931	-0.9	-2.8	0.5	418.8	3.580	2.79	C7 H24 N10 O3 Na
	319.1909	1.3	4.1	6.5	416.9	1.624	19.71	C19 H27 O4
	319.1941	-1.9	-6.0	-1.5	418.4	3.163	4.23	C8 H27 N6 O7
	319.1899	2.3	7.2	8.5	417.1	1.919	14.68	C18 H24 N4 Na
	319.1955	-3.3	-10.3	3.5	418.4	3.201	4.07	C9 H23 N10 O3
	319.1957	-3.5	-11.0	-0.5	418.0	2.765	6.30	C11 H28 N4 O5 Na
	319.1885	3.7	11.6	3.5	417.1	1.854	15.66	C17 H28 O4 Na
	319.1882	4.0	12.5	7.5	417.5	2.292	10.10	C15 H23 N6 O2
	319.1971	-4.9	-15.4	4.5	418.0	2.812	6.01	C12 H24 N8 O Na

Figure S16. IR spectrum of caryopincaolide B (**2**)

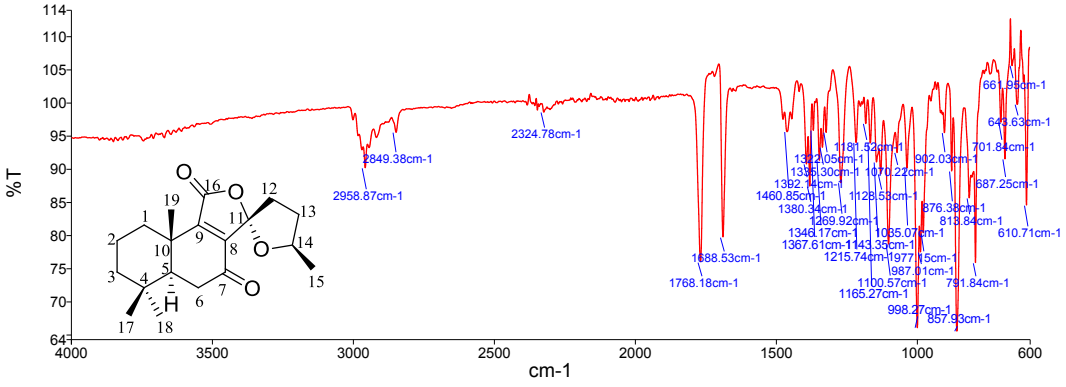


Figure S17. ^{13}C NMR spectrum of caryopincaolide C (**3**) in CD_3OD (150 MHz)

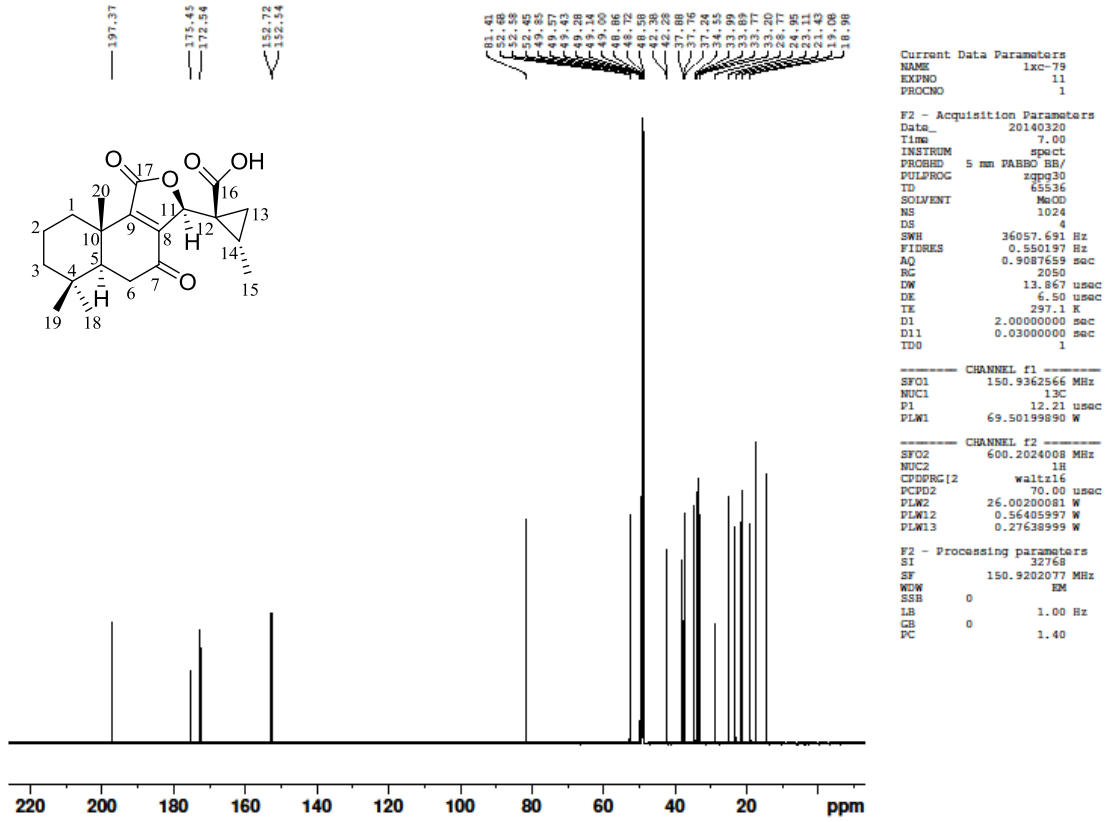


Figure S18. ^{1}H NMR spectrum of caryopincaolide C (**3**) in CD_3OD (600 MHz)

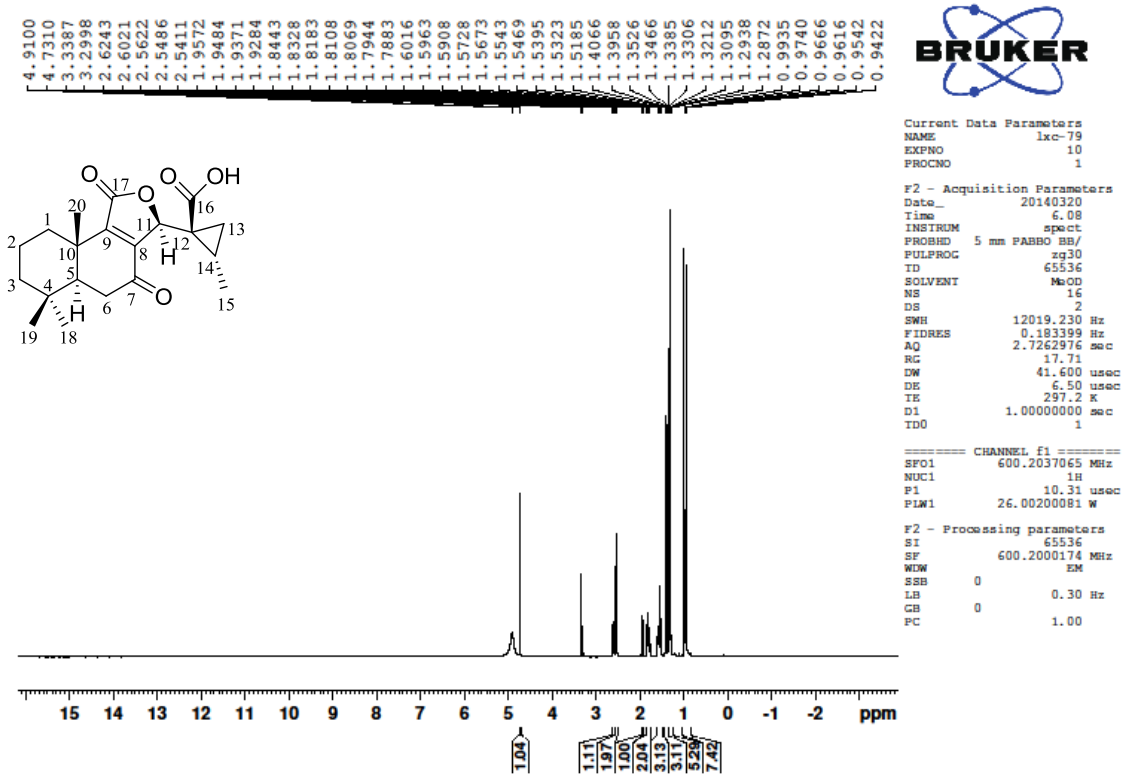


Figure S19. HSQC spectrum of caryopincaolide C (**3**) in CD_3OD

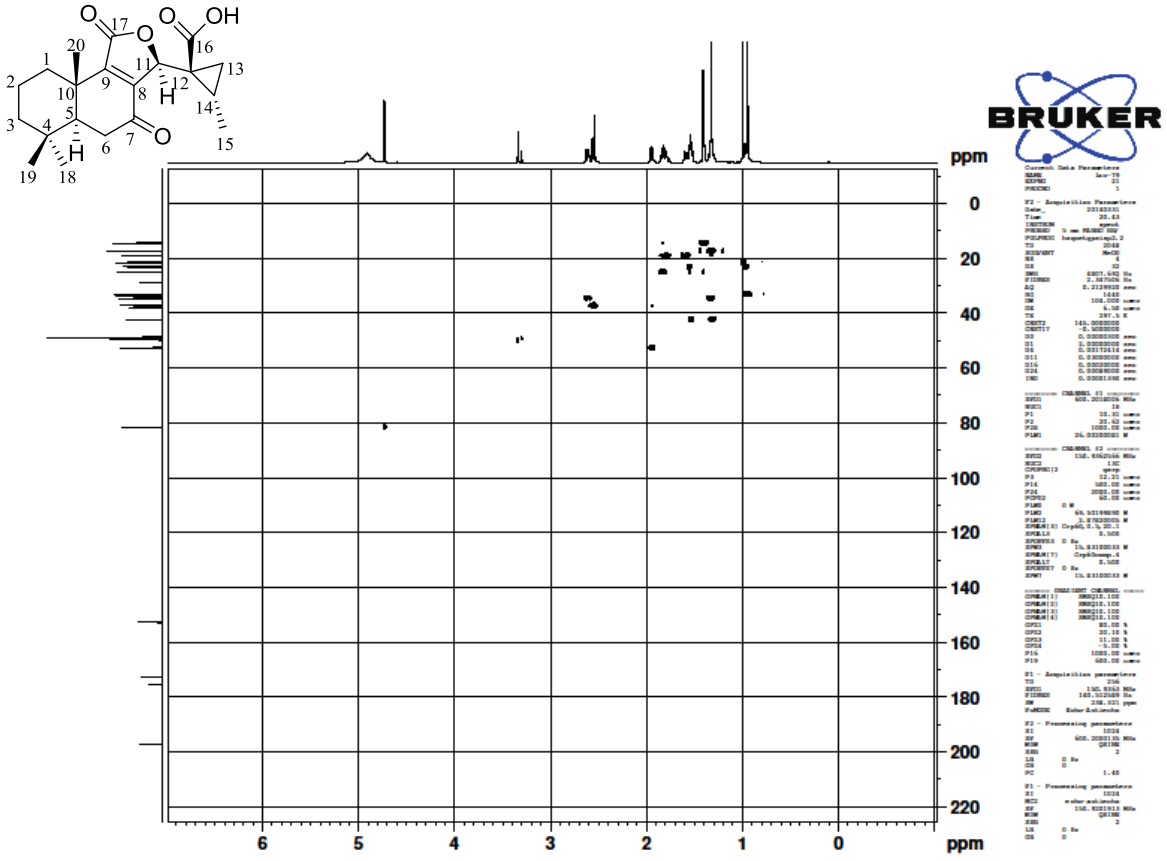


Figure S20. HMBC spectrum of caryopincaolide C (**3**) in CD_3OD

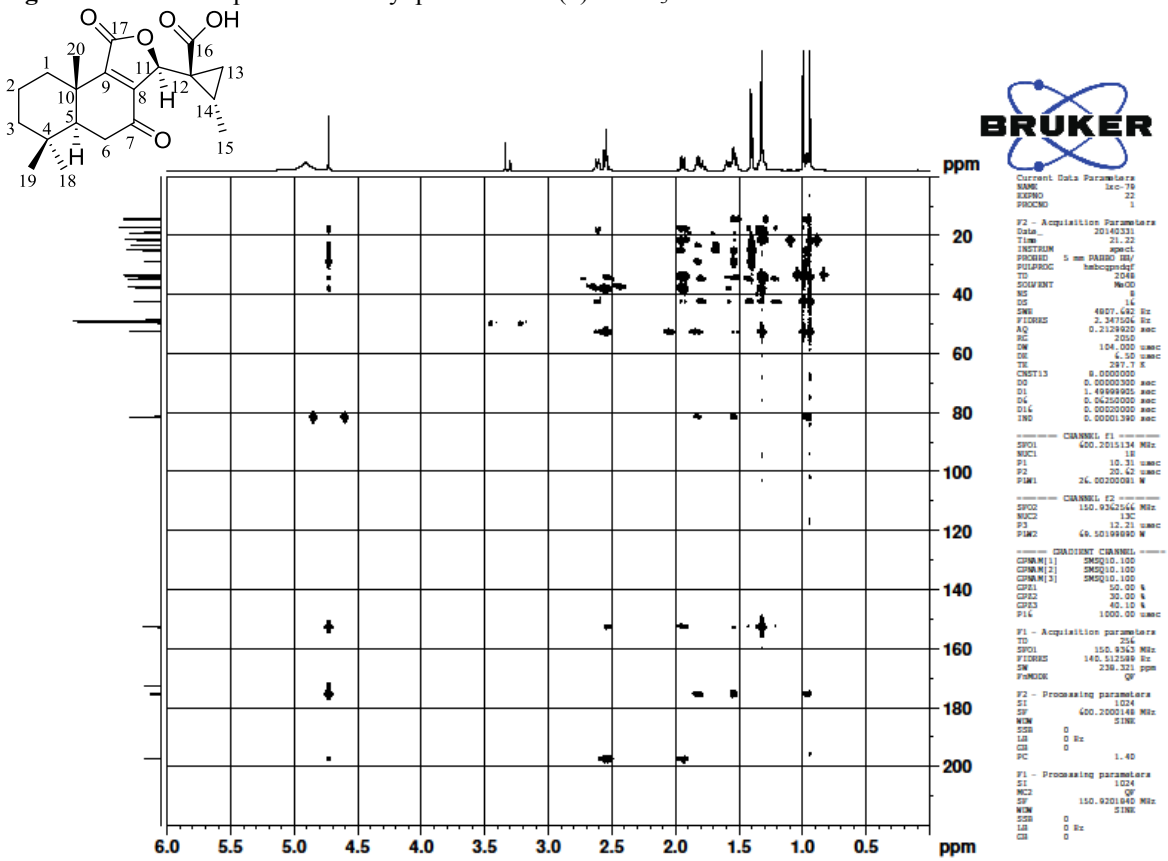


Figure S21. NOESY spectrum of caryopincaolide C (**3**) in CD_3OD

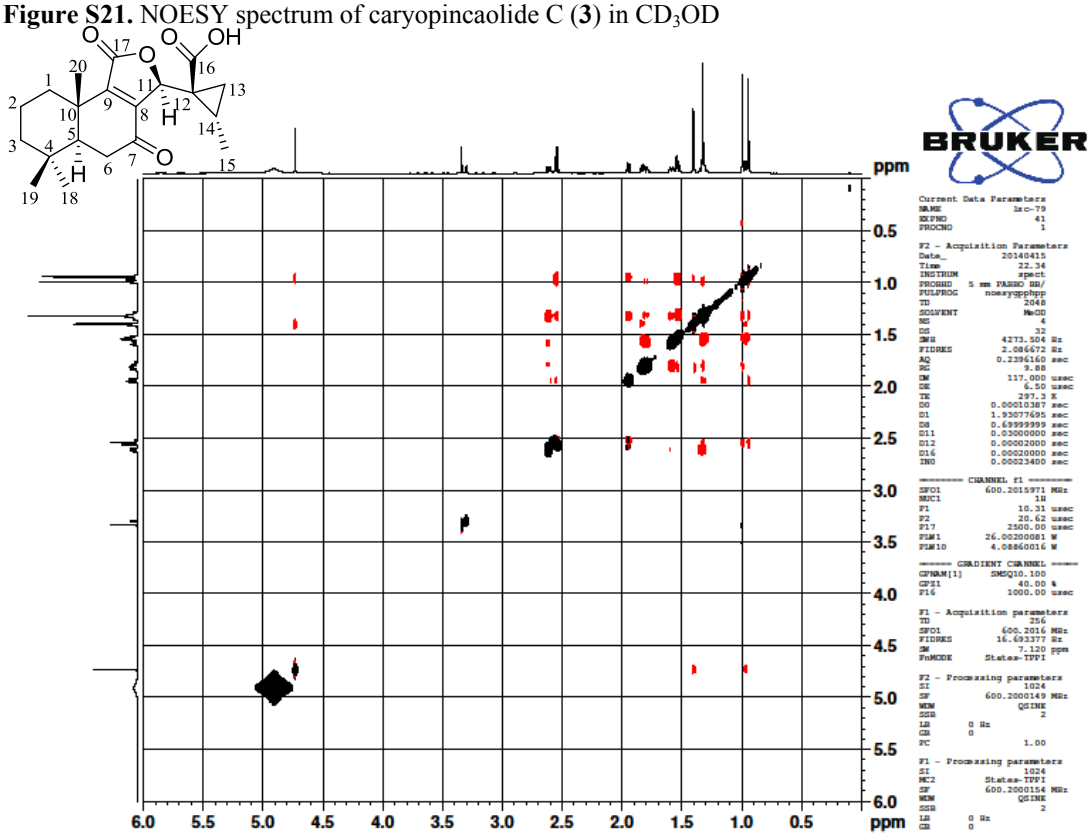


Figure S22. ^{1}H–^{1}H COSYspectrum of caryopincaolide C (**3**) in CD_3OD

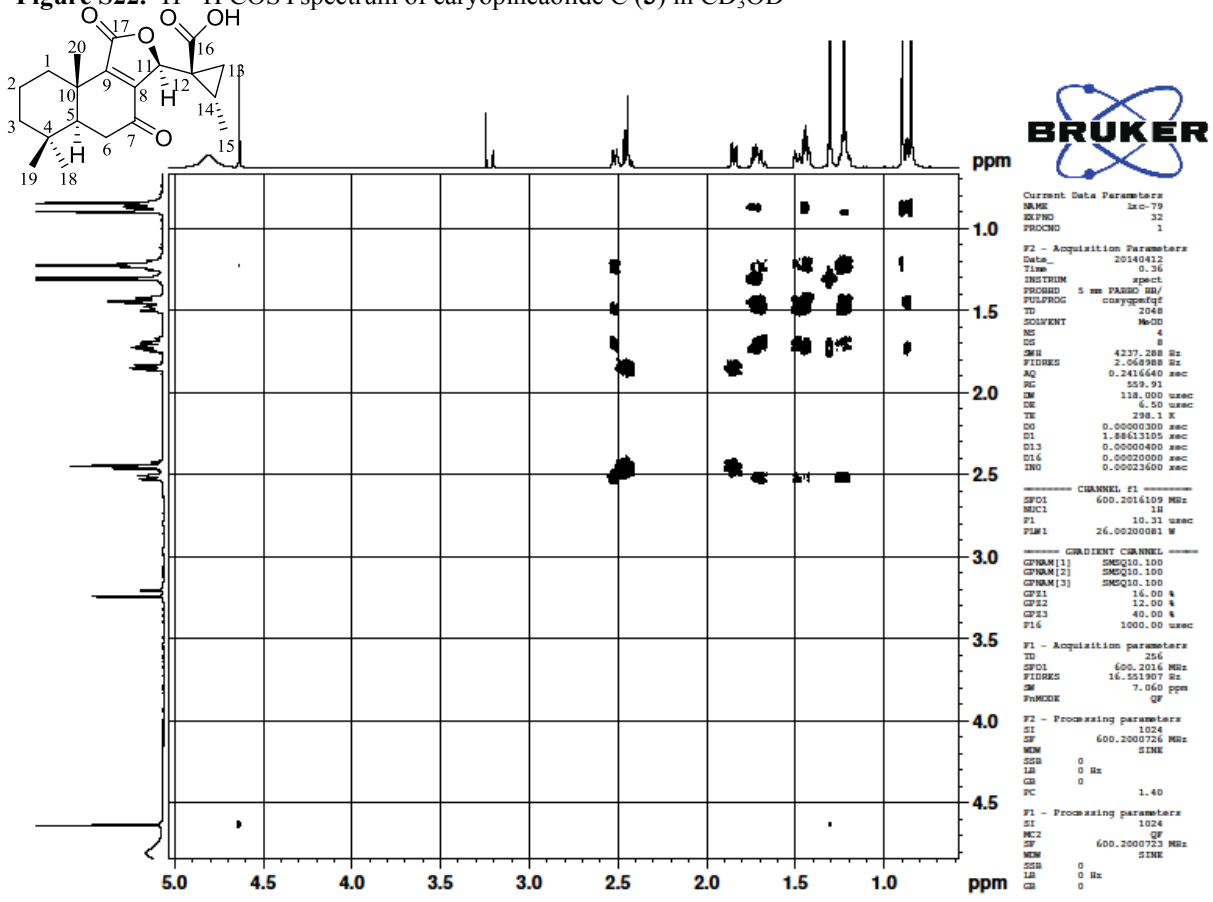
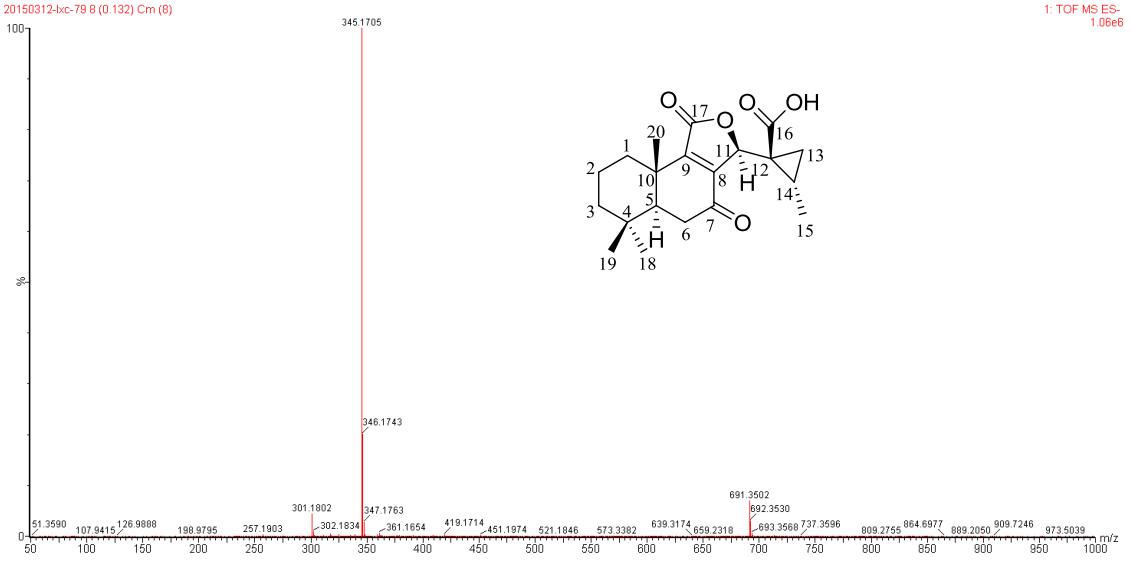


Figure S23.HRESIMS spectrum of caryopincaolide C (**3**)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
345.1698	345.1702	-0.4	-1.2	8.5	248.8	0.000	100.00	C20 H25 O5
	345.1679	1.9	5.5	0.5	265.9	17.080	0.00	C15 H30 O6 K

Figure S24.IR spectrum of caryopincaolide C (**3**)

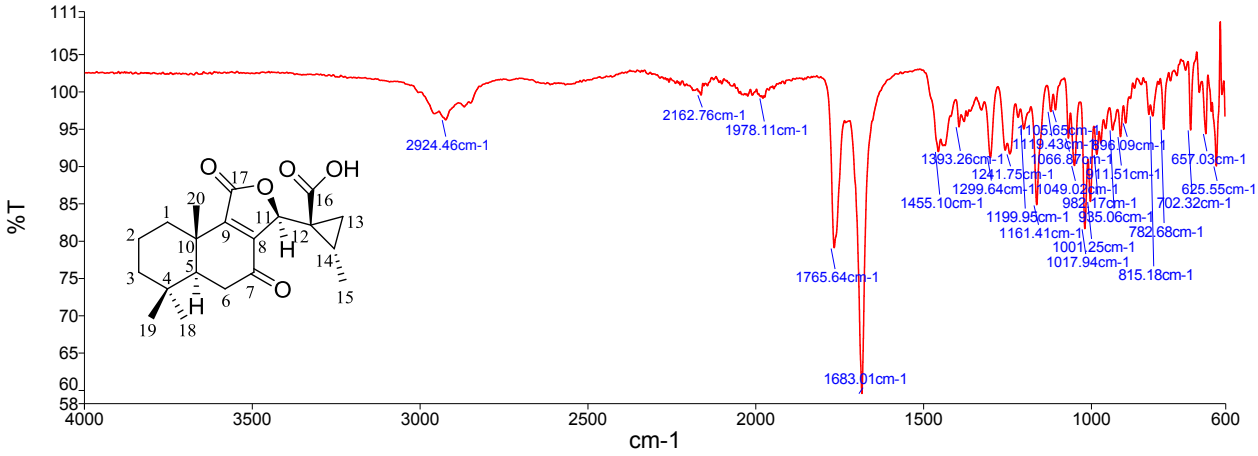


Figure S25. Calculated and Experimental ECD spectrum of caryopincaolide C (**3**)

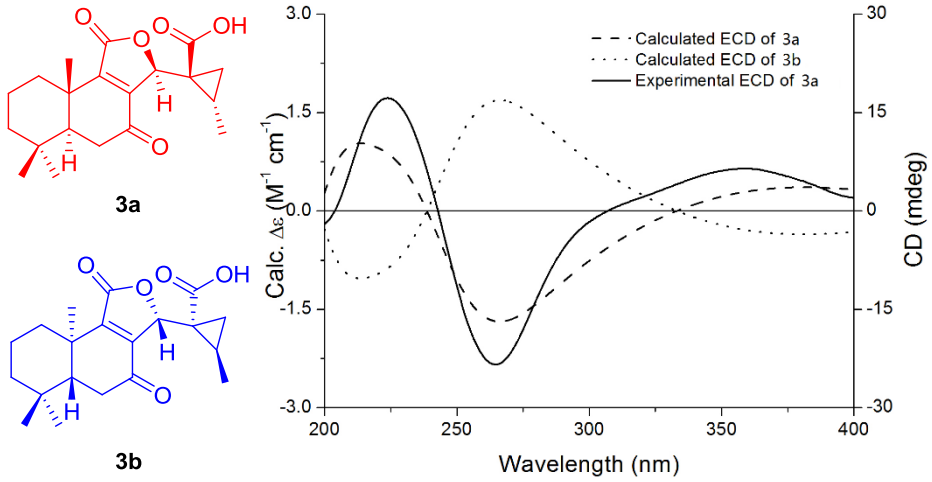


Figure S26. ^{13}C NMR spectrum of caryopincaolide D (**4**) in CD_3OD (150 MHz)

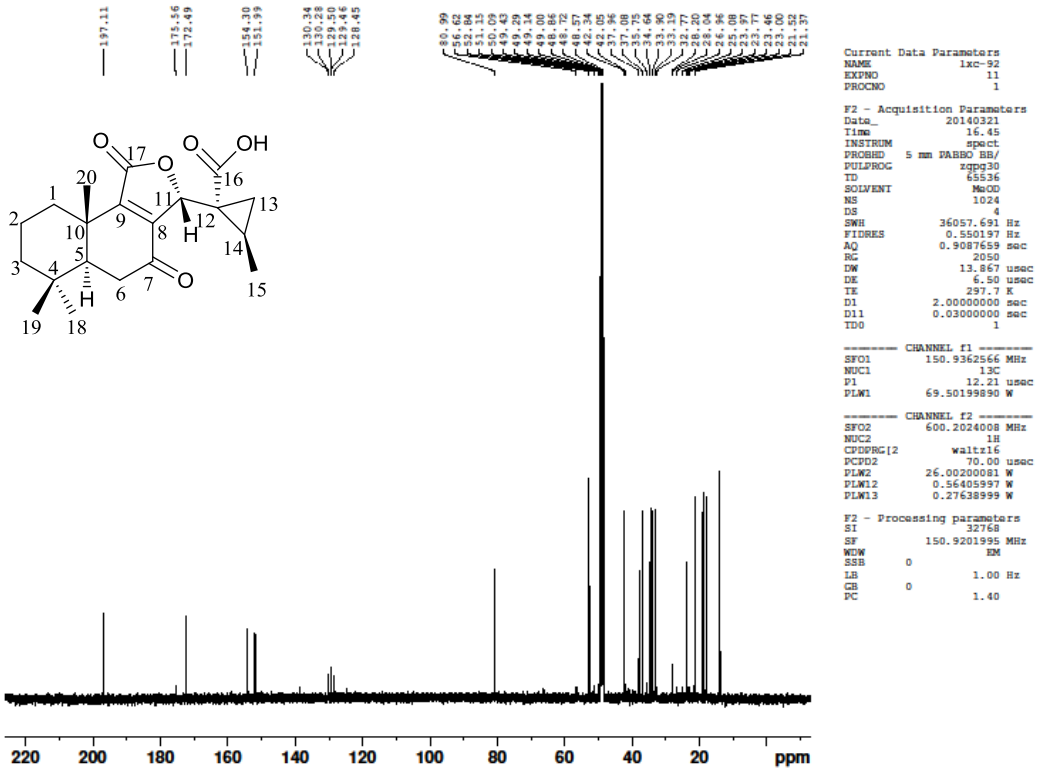


Figure S27. ^{1}H NMR spectrum of caryopincaolide D (**4**) in CD_3OD (150 MHz)

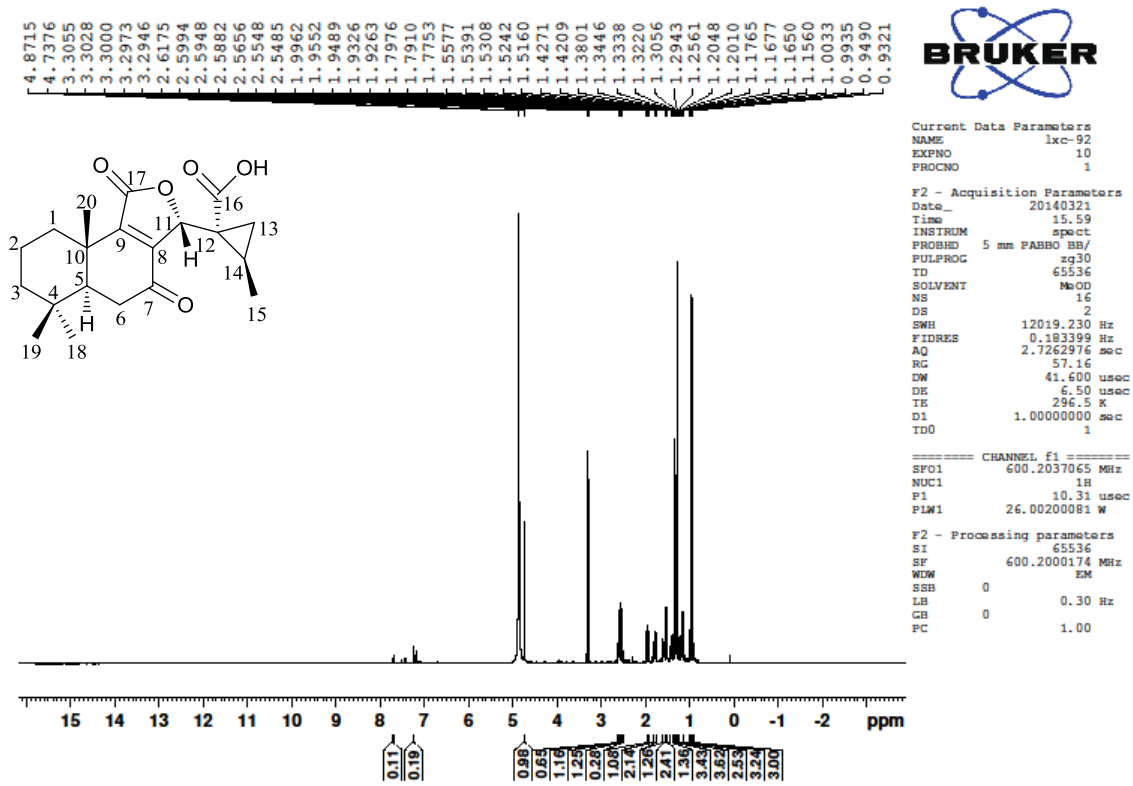


Figure S28. HSQC spectrum of caryopincaolide D (**4**) in CD_3OD

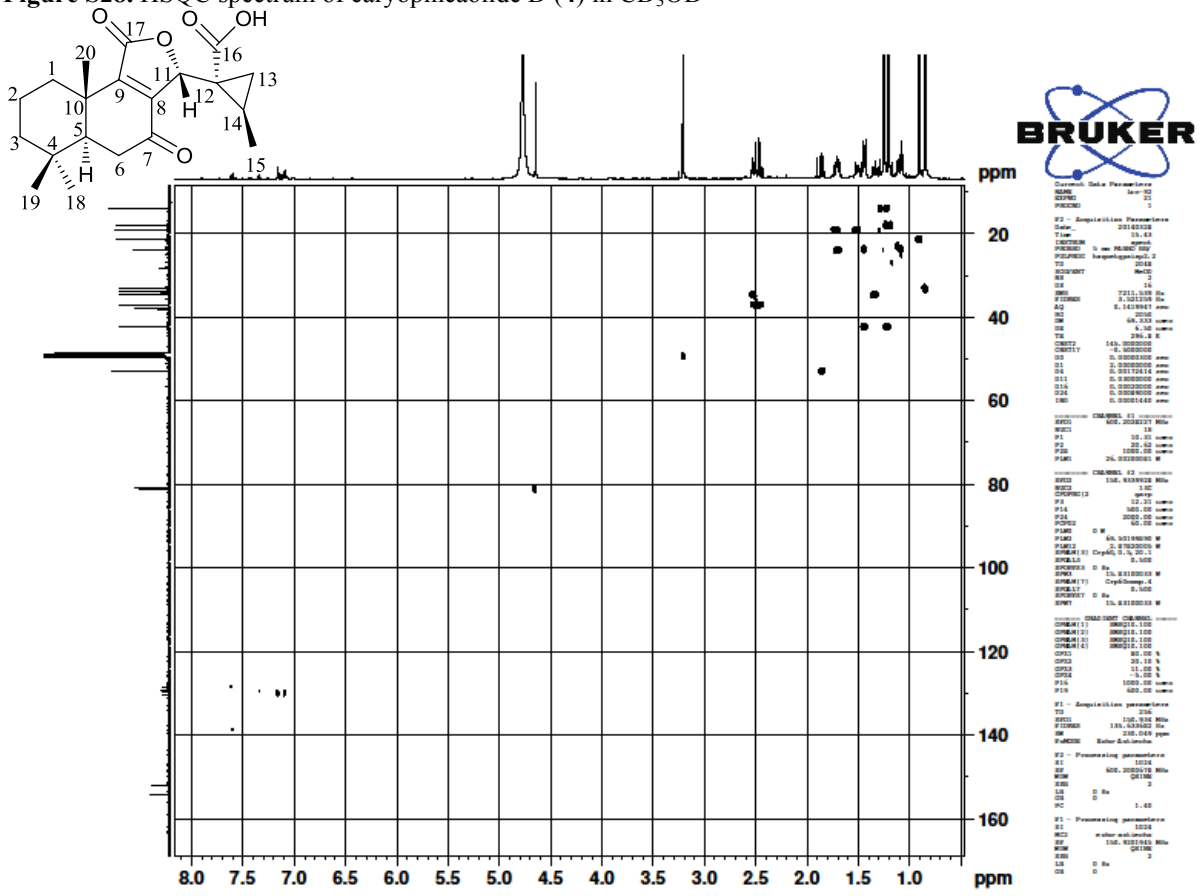


Figure S29. HMBC spectrum of caryopincaolide D (**4**) in CD_3OD

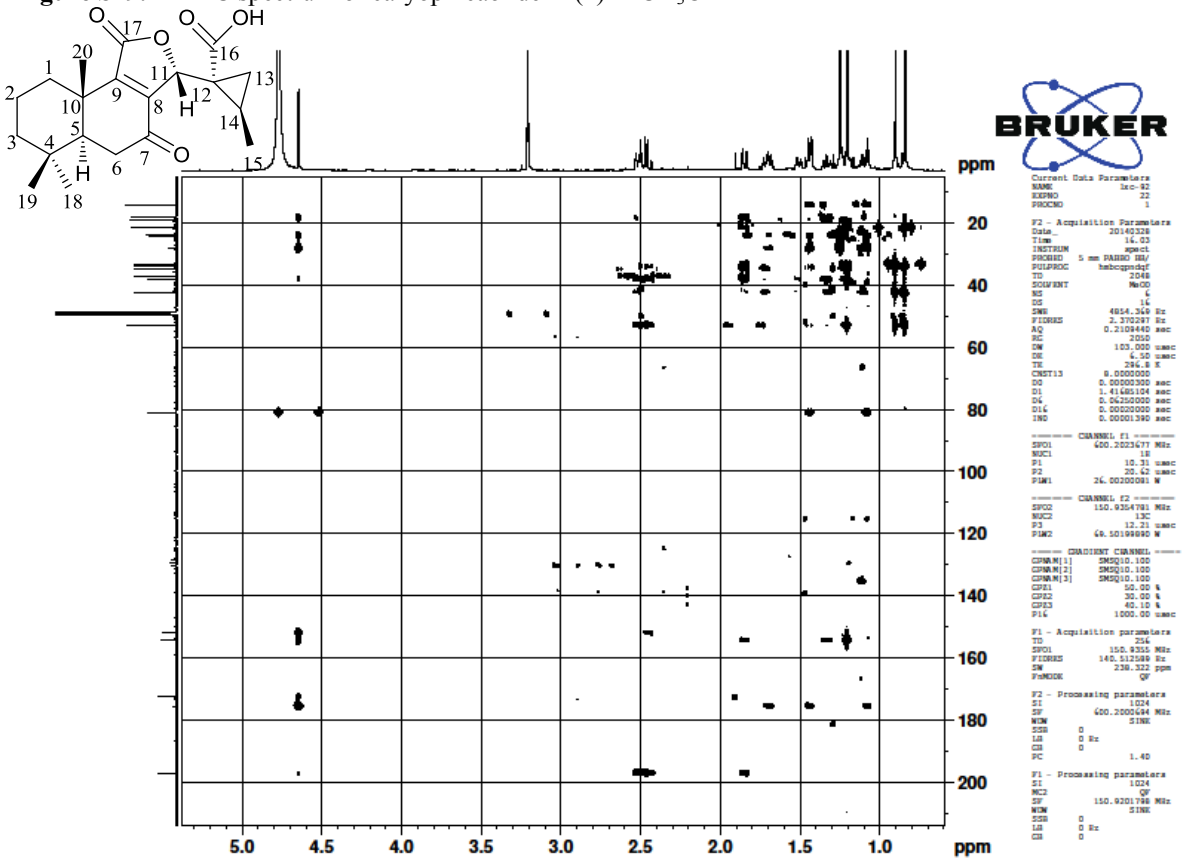


Figure S30. NOESY spectrum of caryopincaolide D (**4**) in CD_3OD

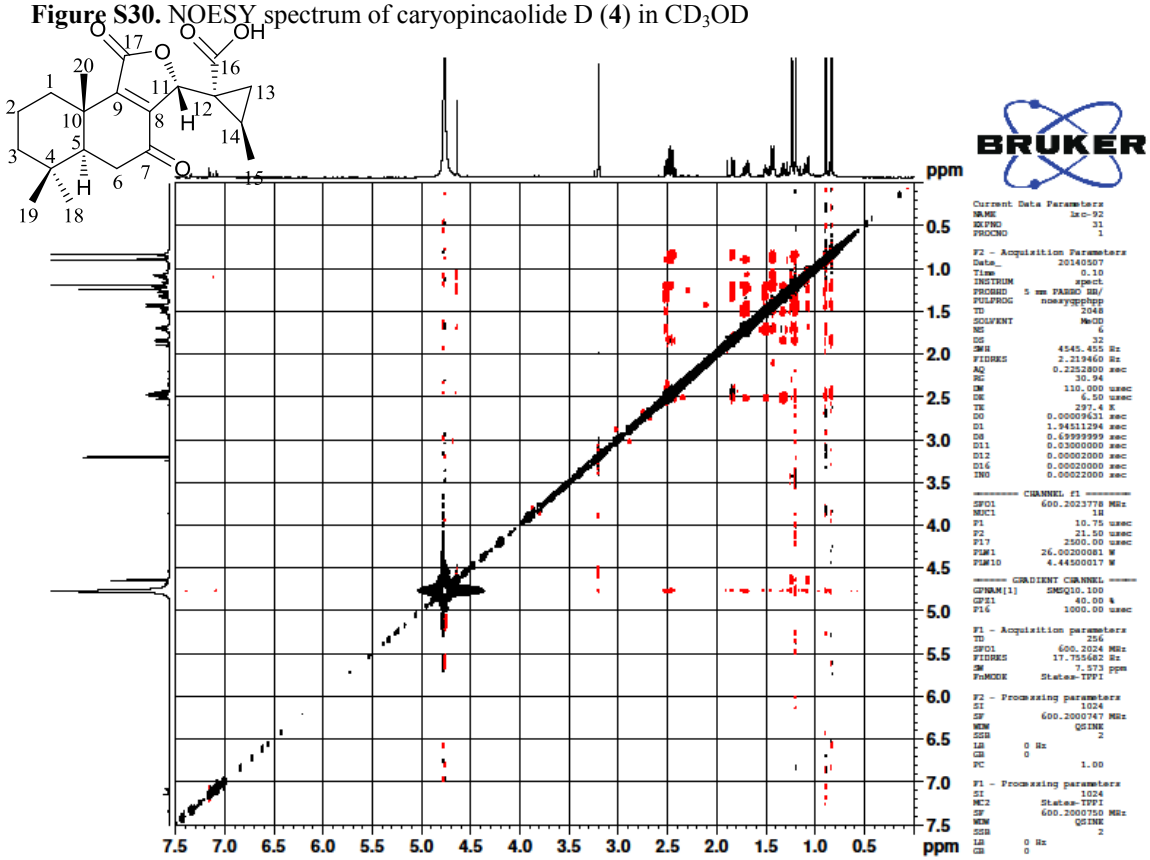


Figure S31. ^1H–^1H COSYspectrum of caryopincaolide D (**4**) in CD_3OD

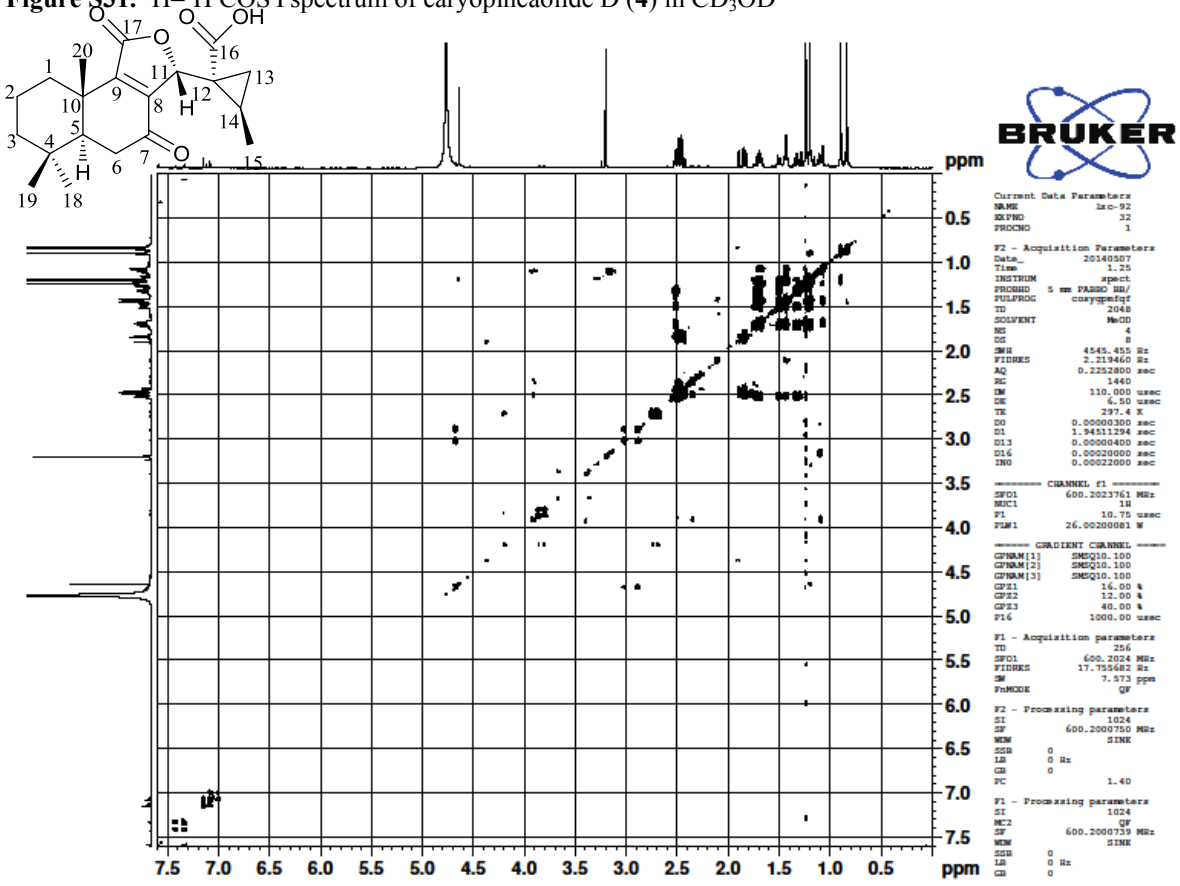
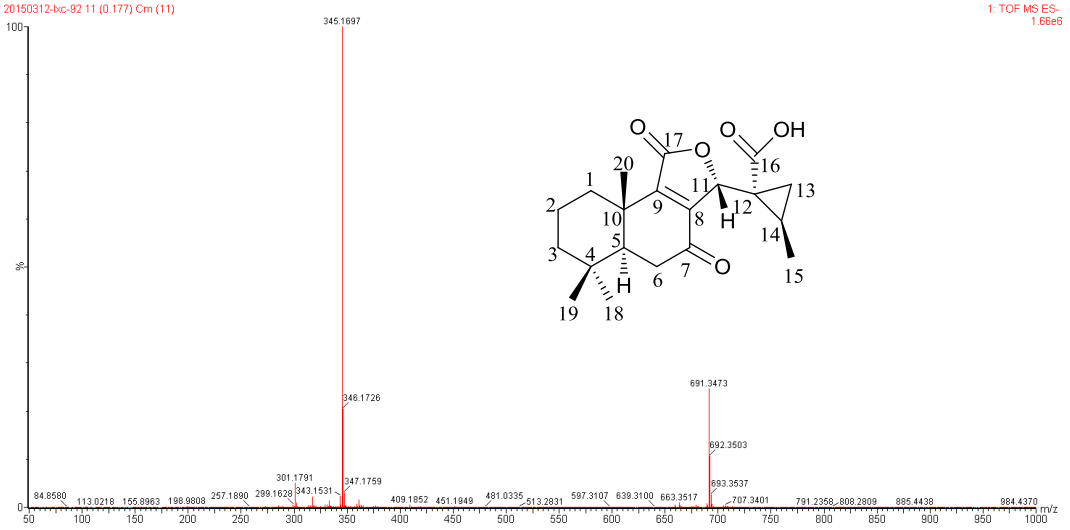


Figure S32. HRESIMS spectrum of caryopincaolide D (**4**)



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
345.1698	345.1702	-0.4	-1.2	8.5	288.2	0.000	100.00	C20 H25 O5
	345.1679	1.9	5.5	0.5	300.2	11.949	0.00	C15 H30 O6 K

Figure S33. IR spectrum of caryopincaolide D (**4**)

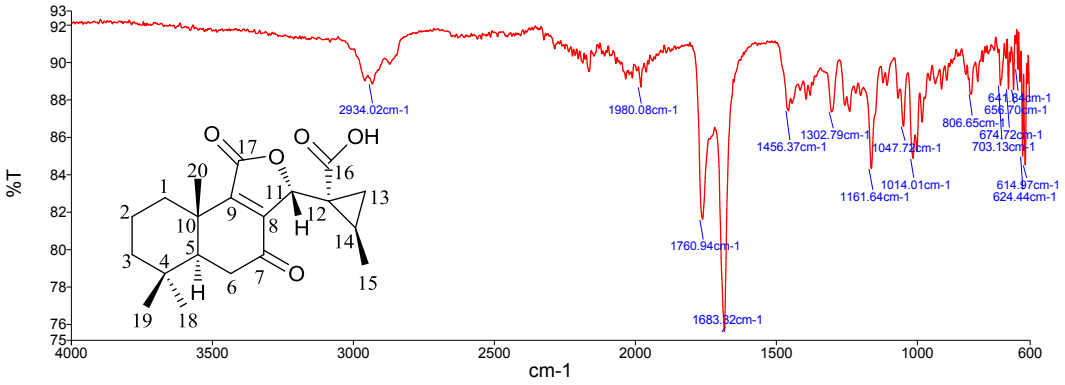


Figure S34.HPLC Date of compound 3 and 4 with different peak time in same HPLC condition (^{18}C MeOH : water = 65 : 35)

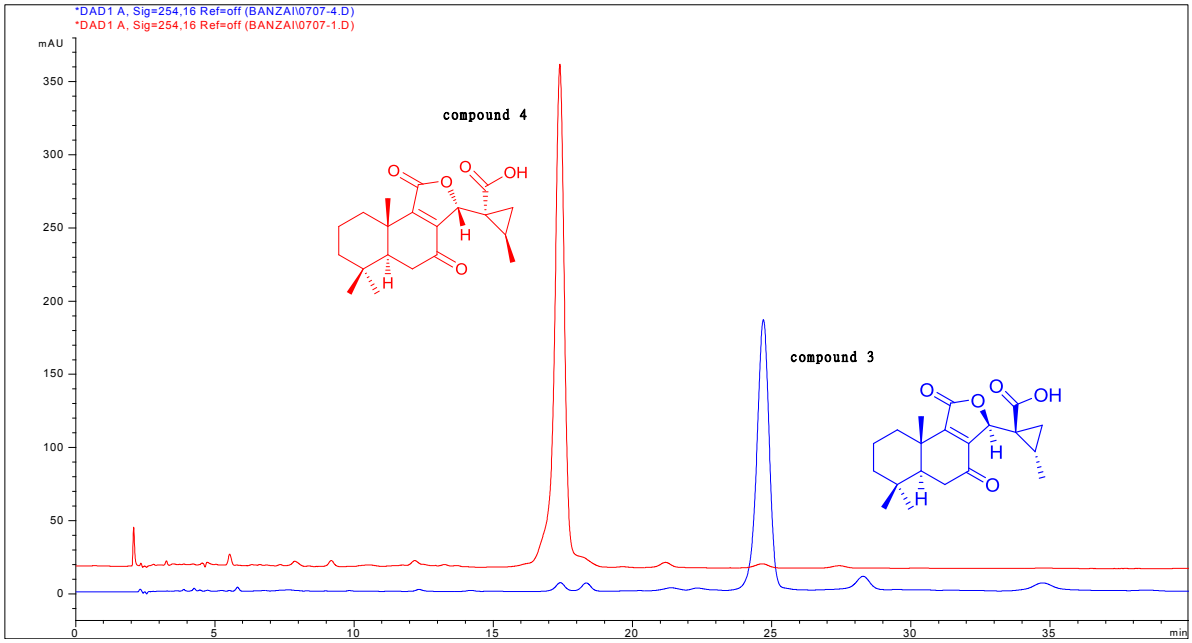


Figure S35. ^{13}C NMR spectrum of caryopincaolide E (**11**) in CD_3OD (150 MHz)

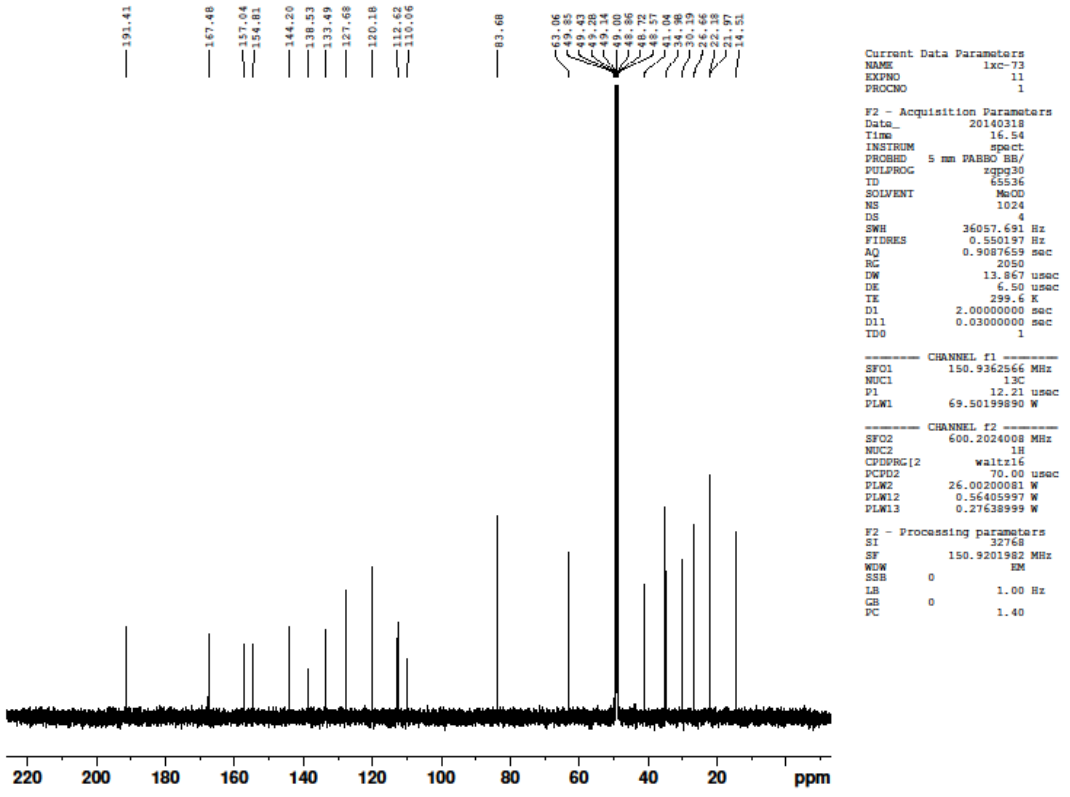


Figure S36. ^{1}H NMR spectrum of caryopincaolide E (**11**) in CD_3OD (600 MHz)

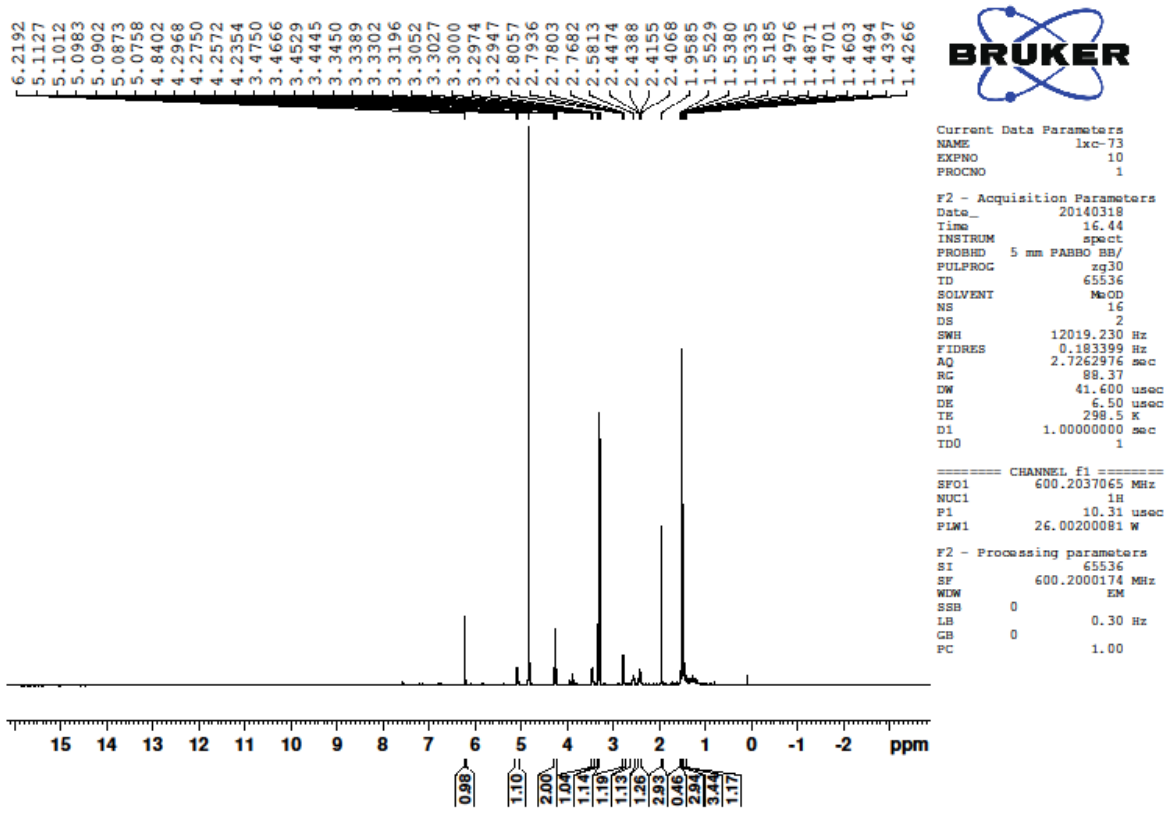


Figure S37. HSQC spectrum of caryopincaolide E (**11**) in CD_3OD

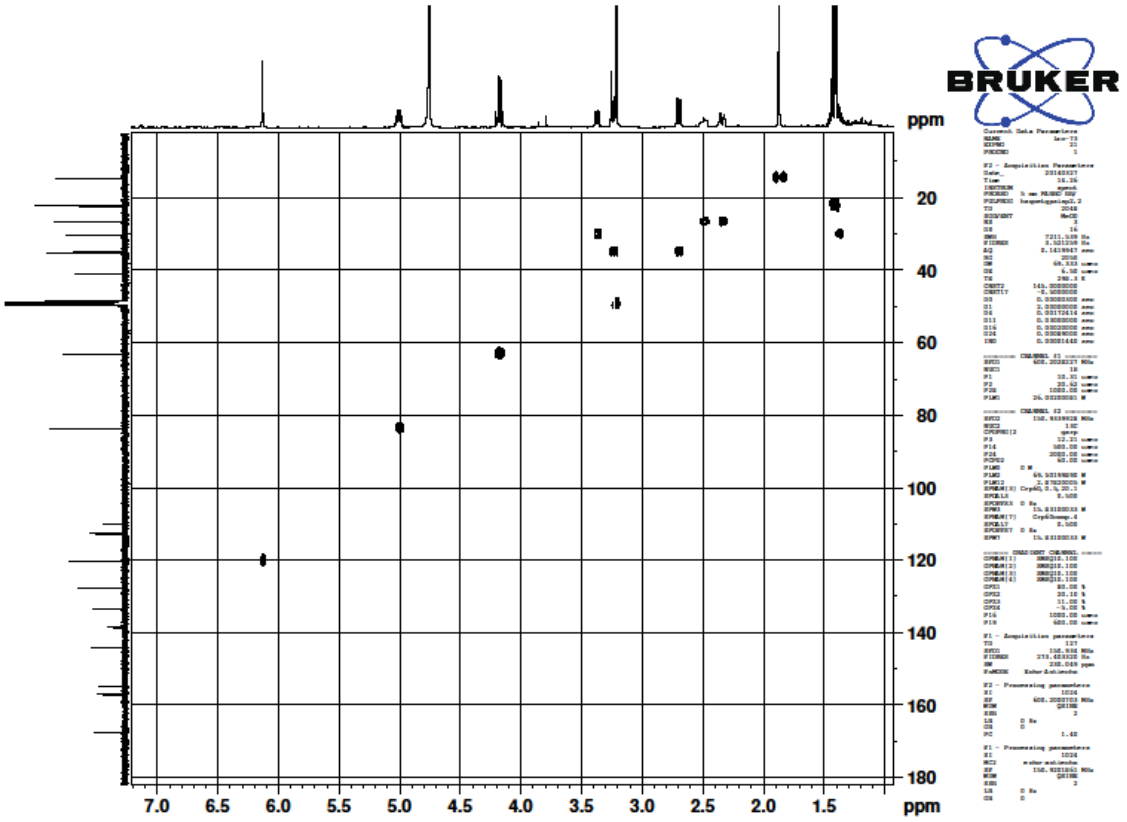


Figure S38. HMBC spectrum of caryopincaolide E (**11**) in CD_3OD

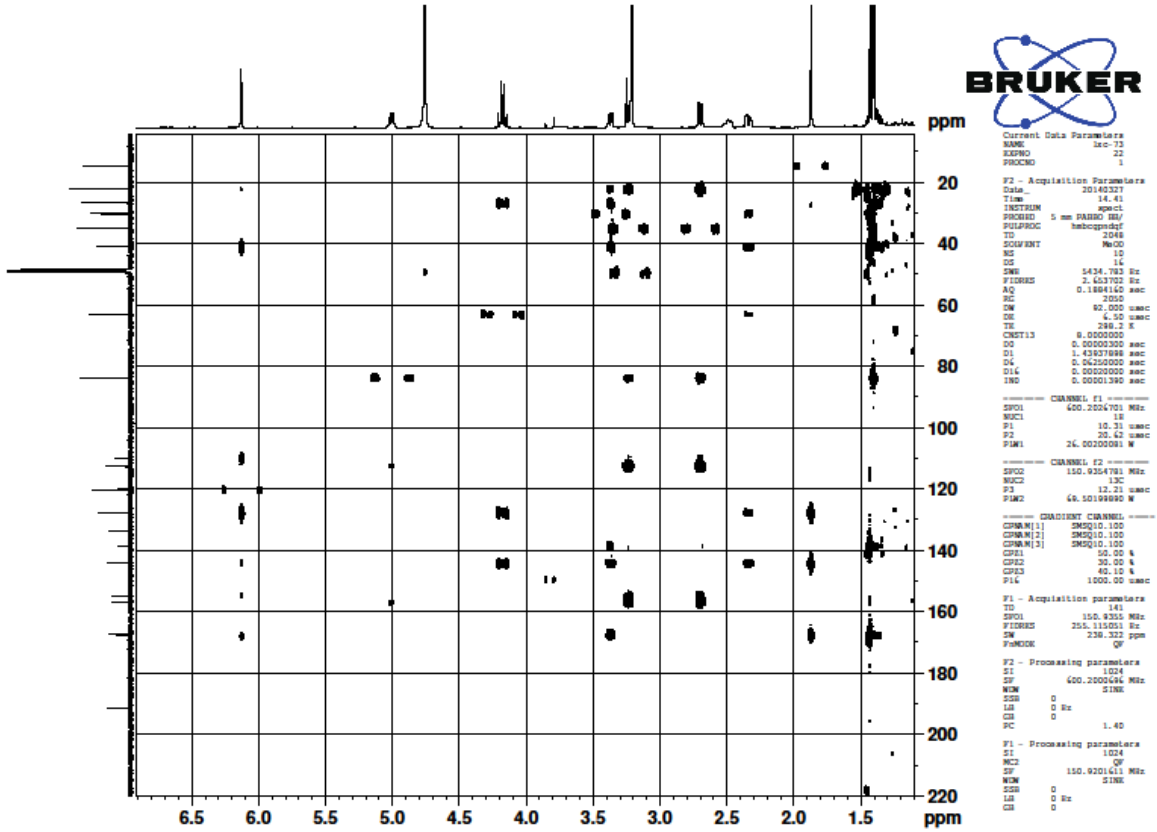


Figure S39. NOESY spectrum of caryopincaolide E (**11**) in CD_3OD

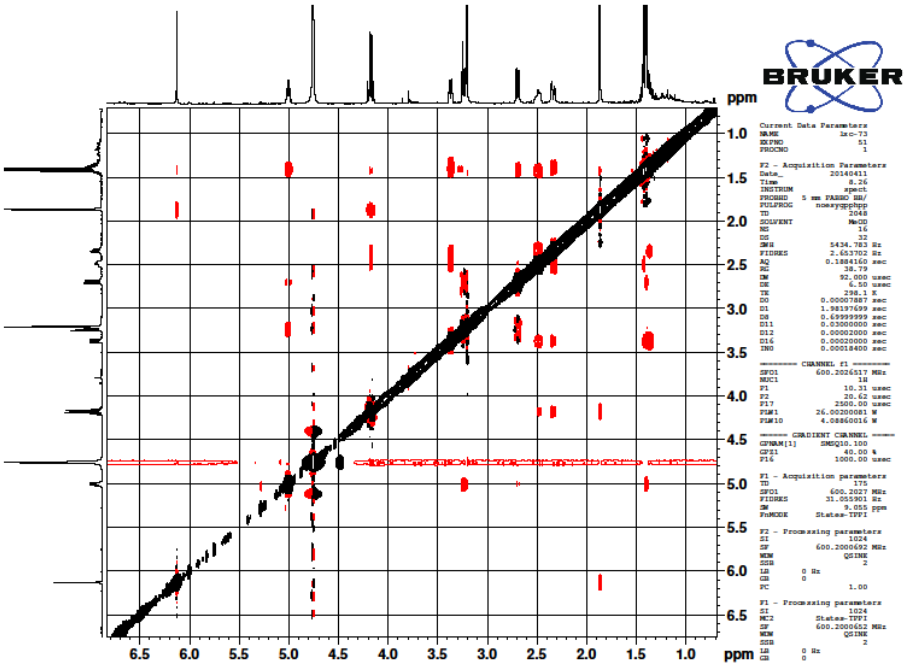
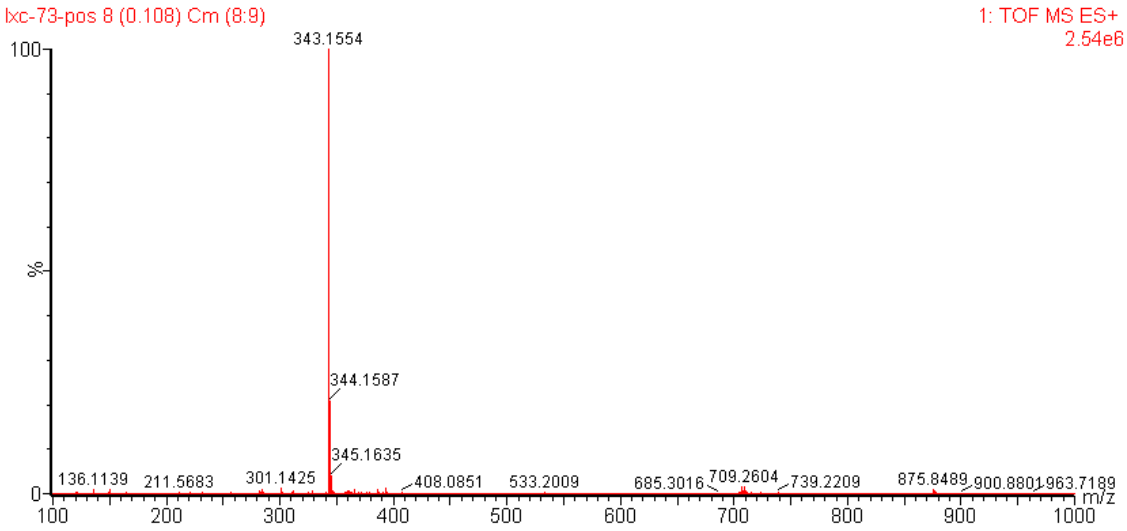


Figure S40. HRESIMS spectrum of caryopincaolide E (**11**) in CD_3OD



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
343.1554	343.1559	-0.5	-1.5	14.5	608.5	2.679	6.87	C21 H19 N4 O
	343.1545	0.9	2.6	9.5	606.0	0.168	84.55	C20 H23 O5
	343.1577	-2.3	-6.7	1.5	613.4	7.557	0.05	C9 H23 N6 O8
	343.1519	3.5	10.2	10.5	609.2	3.388	3.38	C16 H19 N6 O3
	343.1591	-3.7	-10.8	6.5	613.1	7.283	0.07	C10 H19 N10 O4
	343.1505	4.9	14.3	5.5	609.5	3.722	2.42	C15 H23 N2 O7
	343.1604	-5.0	-14.6	0.5	611.6	5.767	0.31	C13 H27 O10
	343.1618	-6.4	-18.7	5.5	610.4	4.573	1.03	C14 H23 N4 O6
	343.1487	6.7	19.5	18.5	610.1	4.324	1.33	C27 H19

Figure S41. ^{13}C NMR spectrum of caryopincaolide F (**12**) in CD_3OD (150 MHz)

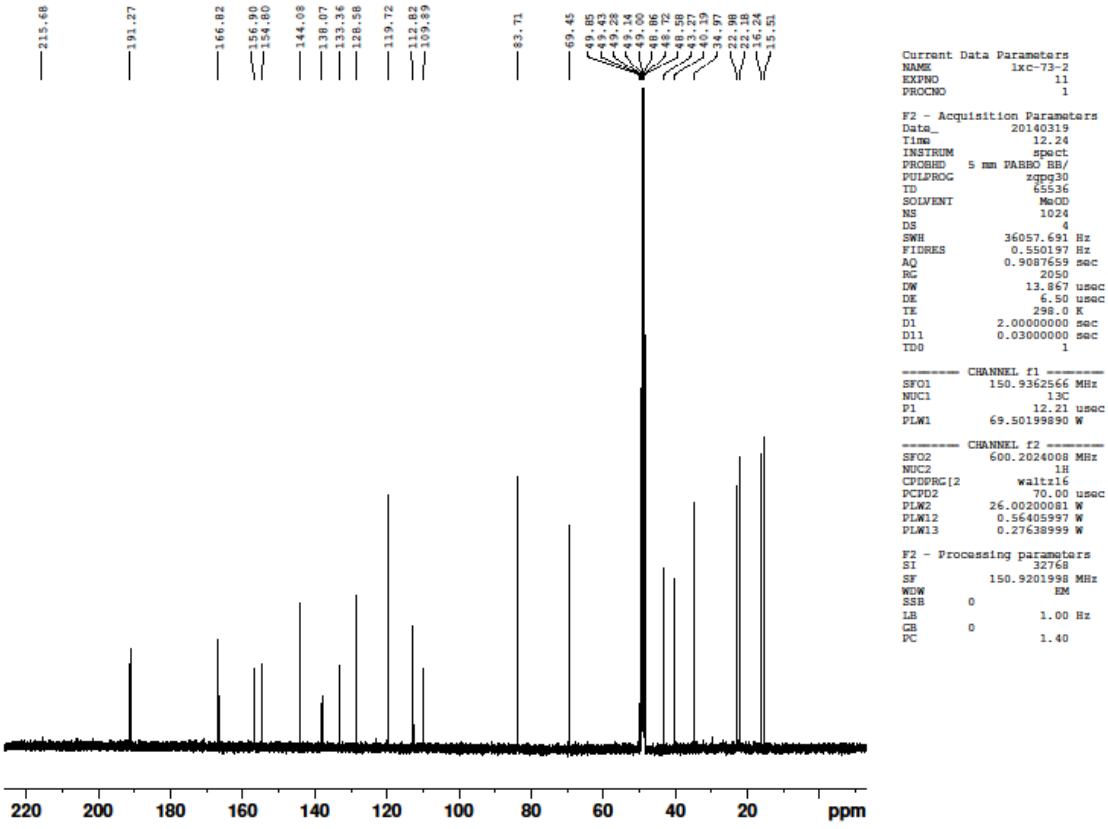


Figure S42. ^{1}H NMR spectrum of caryopincaolide F (**12**) in CD_3OD (600 MHz)

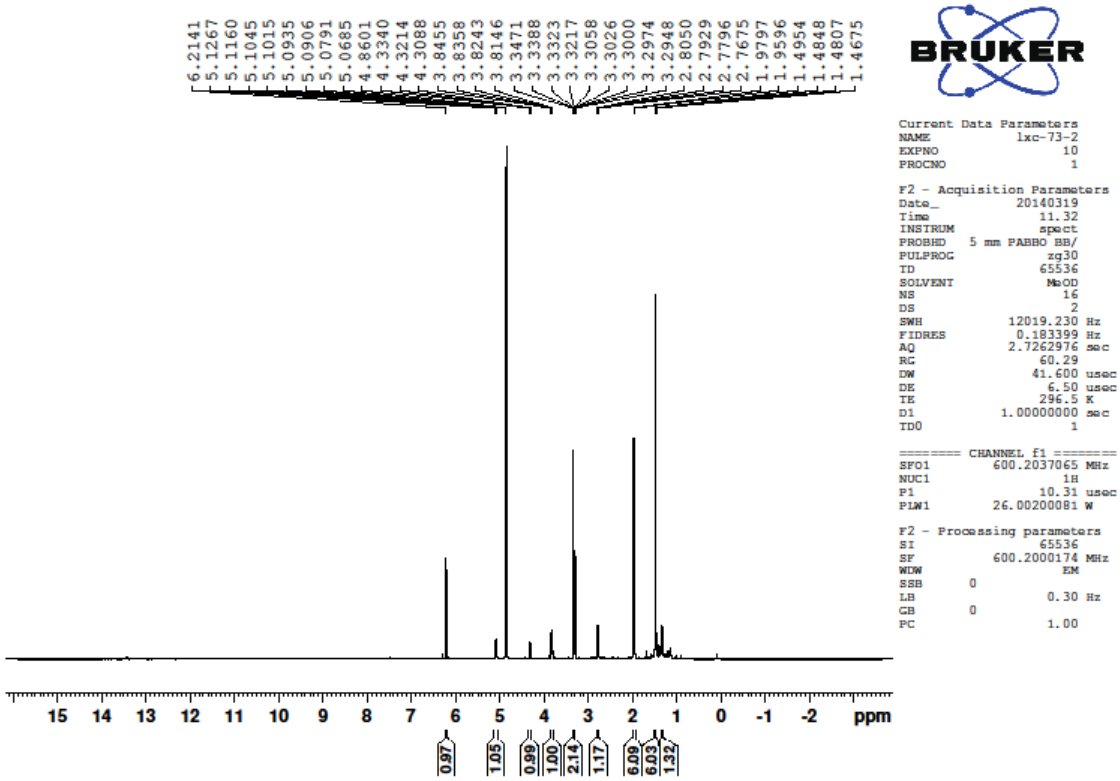


Figure S43. HSQC spectrum of caryopincaolide F (**12**) in CD_3OD

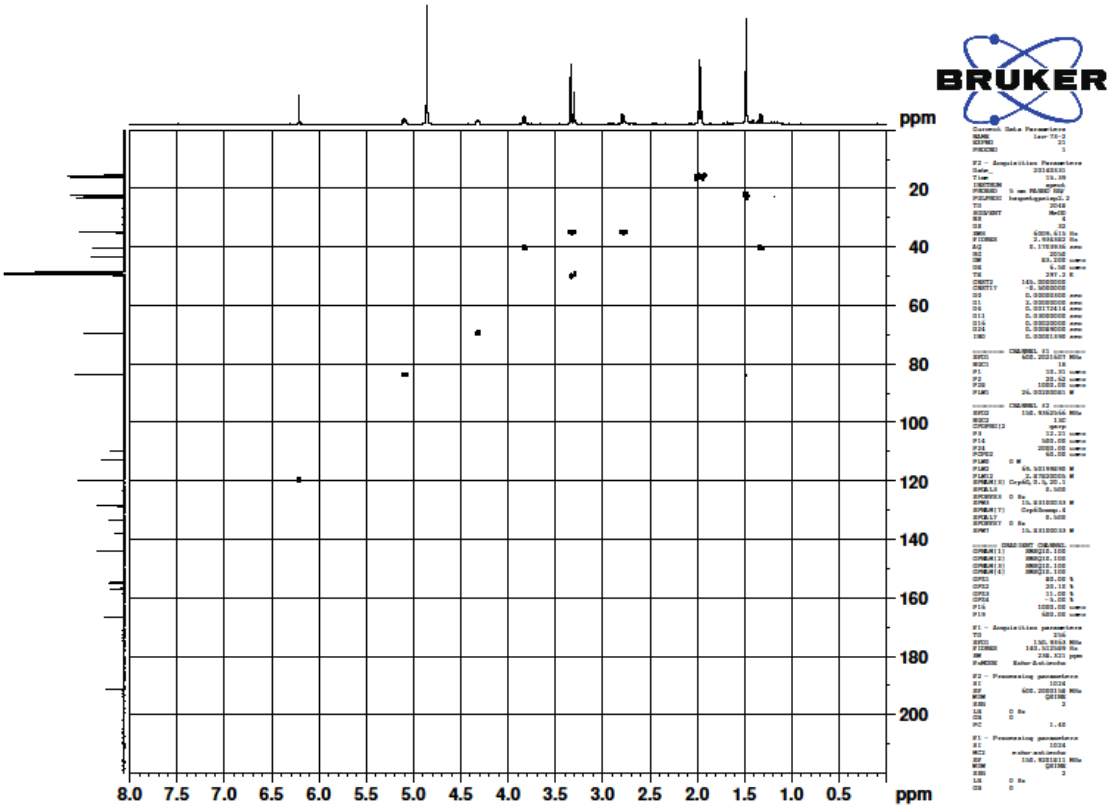


Figure S44. HMBC spectrum of caryopincaolide F (**12**) in CD_3OD

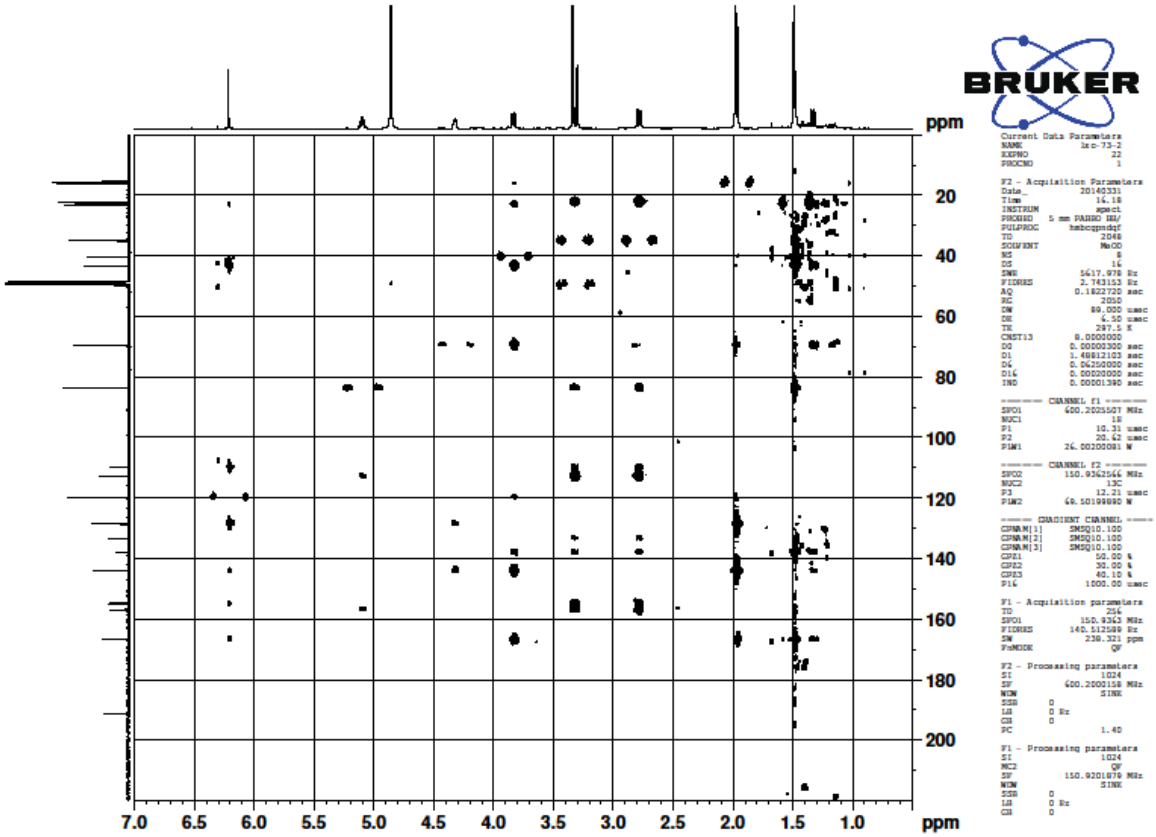


Figure S45. NOESY spectrum of caryopincaolide F (**12**) in CD_3OD

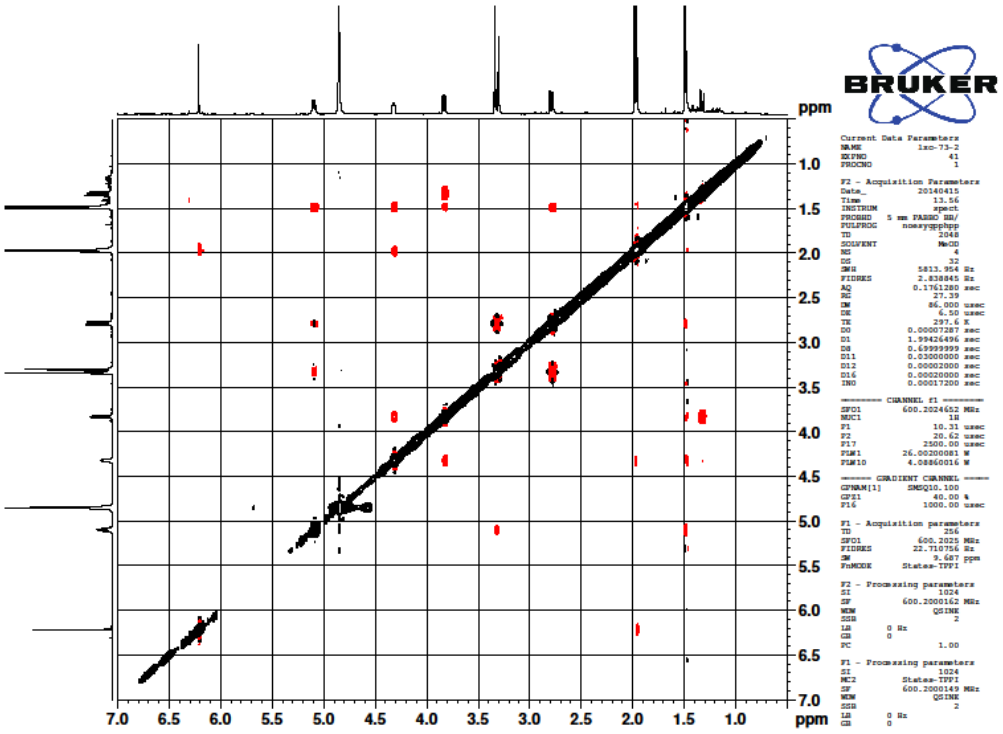
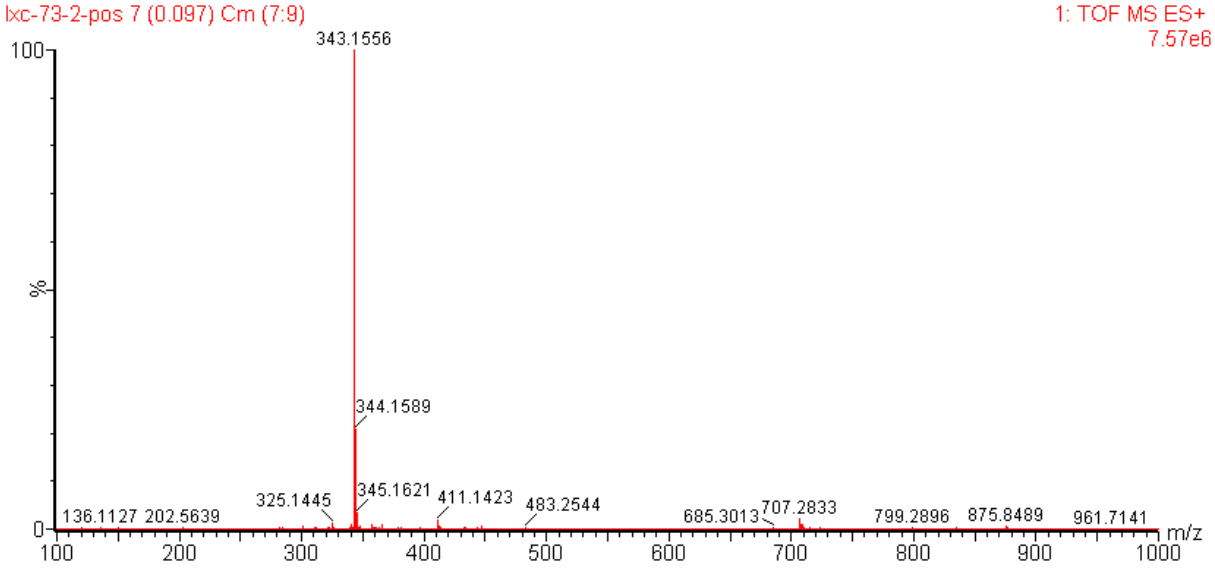


Figure S46. HRESIMS spectrum of caryopincaolide F (**12**) in CD_3OD



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
343.1556	343.1559	-0.3	-0.9	14.5	747.5	3.980	1.87	C21 H19 N4 O
	343.1545	1.1	3.2	9.5	743.6	0.024	97.66	C20 H23 O5
	343.1577	-2.1	-6.1	1.5	755.7	12.160	0.00	C9 H23 N6 O8
	343.1591	-3.5	-10.2	6.5	755.6	12.068	0.00	C10 H19 N10 O4
	343.1519	3.7	10.8	10.5	749.1	5.601	0.37	C16 H19 N6 O3
	343.1604	-4.8	-14.0	0.5	753.7	10.137	0.00	C13 H27 O10
	343.1505	5.1	14.9	5.5	750.8	7.266	0.07	C15 H23 N2 O7
	343.1618	-6.2	-18.1	5.5	751.9	8.402	0.02	C14 H23 N4 O6

Figure S47. ^{13}C NMR spectrum of caryopincaolide G (**16**) in CD_3OD (150 MHz)

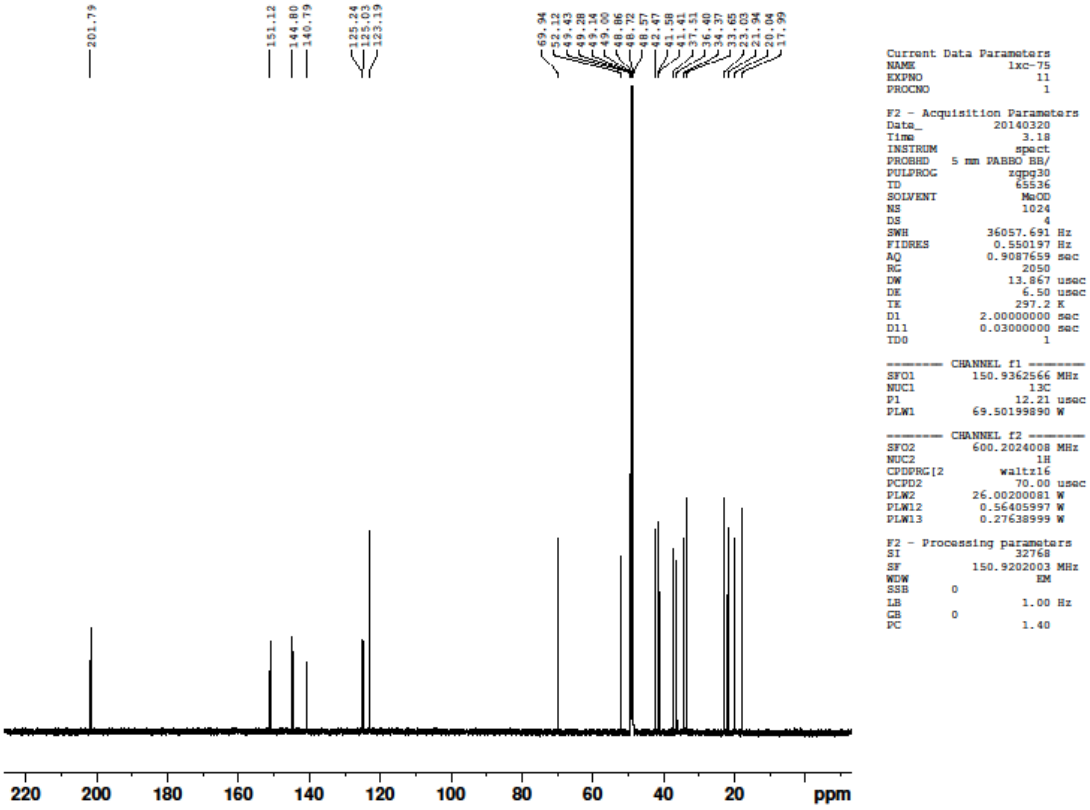


Figure S48. ^{1}H NMR spectrum of caryopincaolide G (**16**) in CD_3OD (600 MHz)

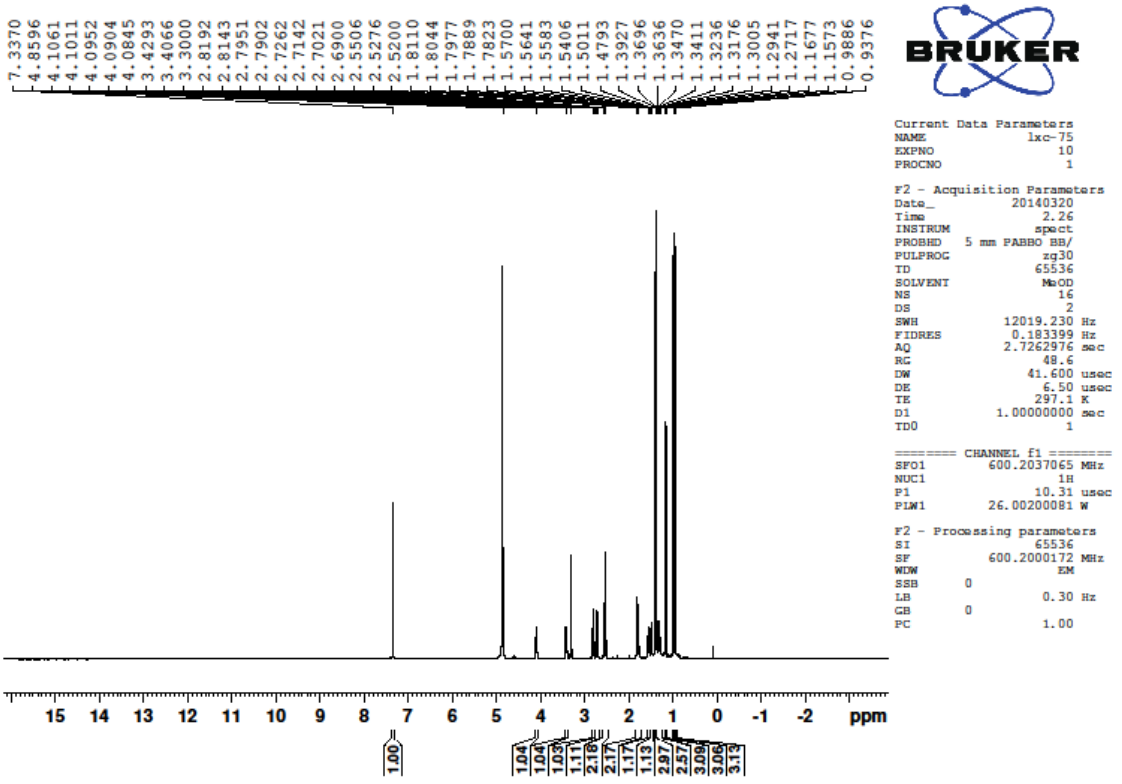


Figure S49. HSQC spectrum of caryopincaolideG (**16**) in CD_3OD

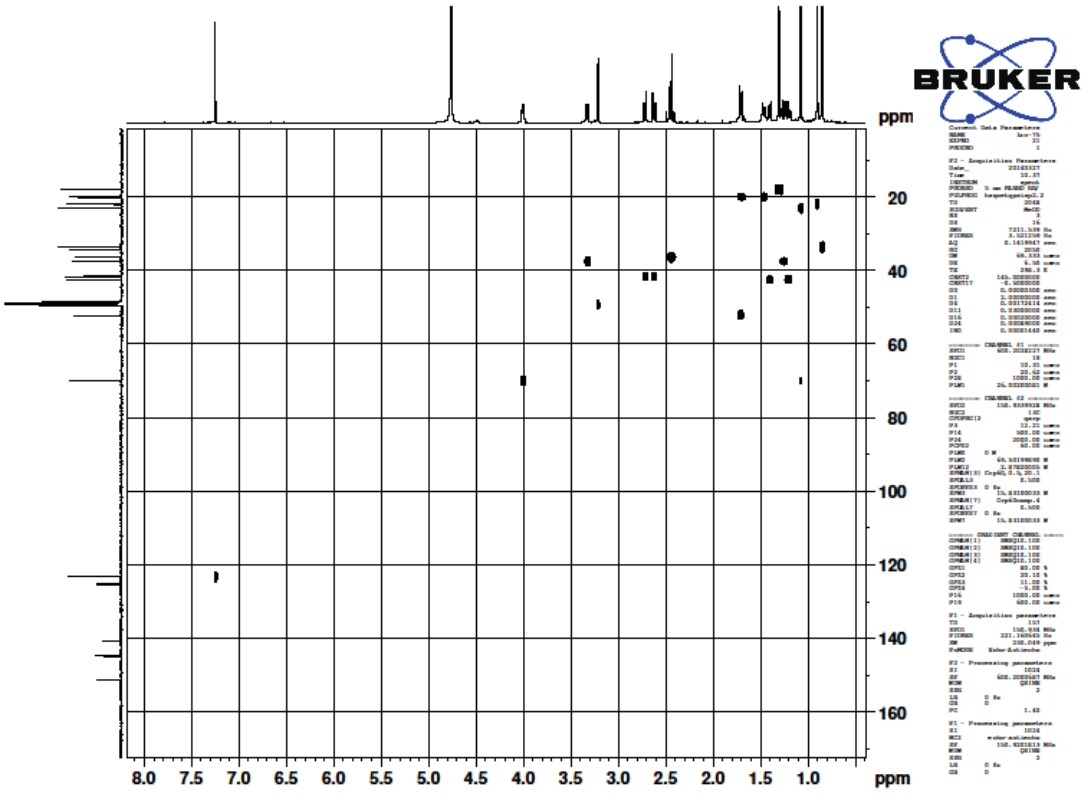


Figure S50. HMBC spectrum of caryopincaolide G (**16**) in CD_3OD

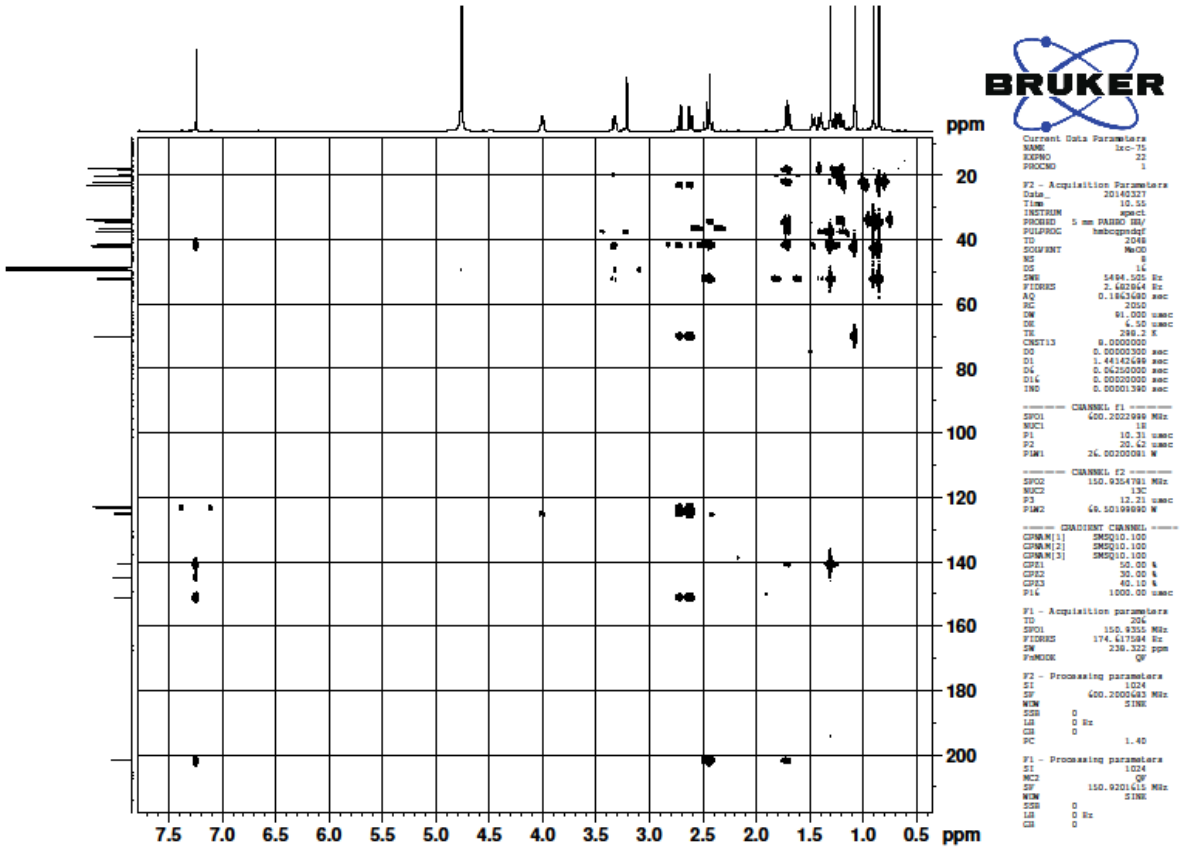


Figure S51. NOESY spectrum of caryopincaolide G (**16**) in CD_3OD

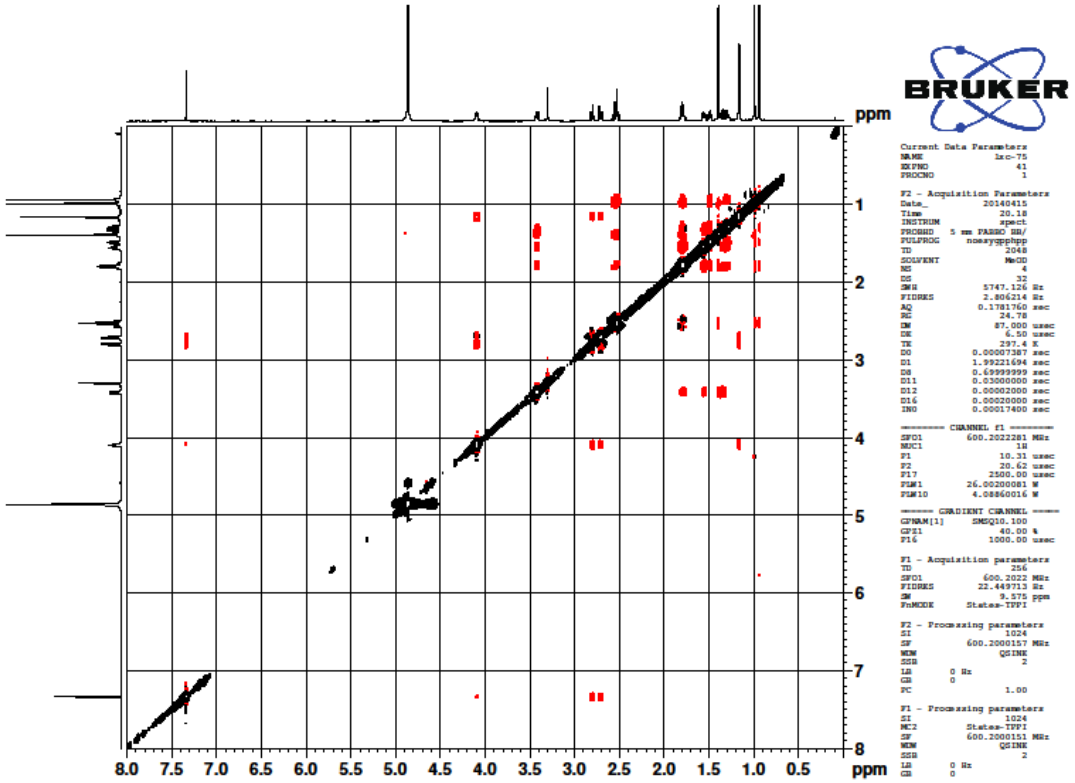
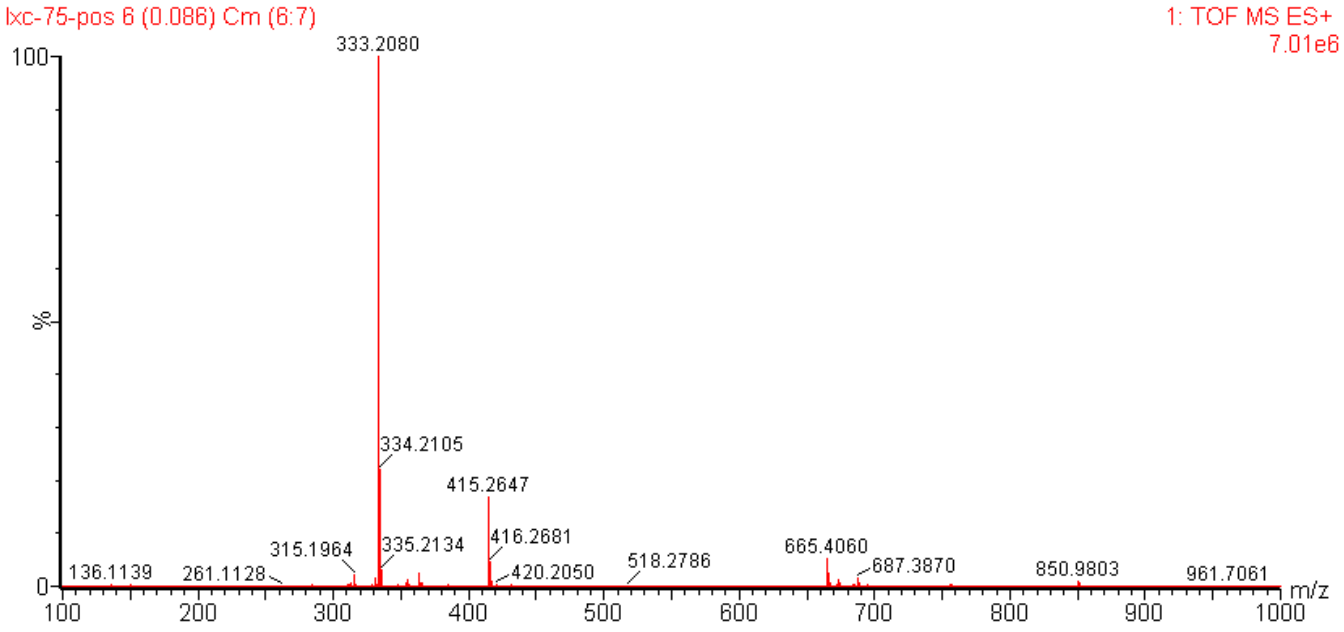


Figure S52. HRESIMS spectrum of caryopincaolide G (**16**) in CD_3OD



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
333.2080	333.2079	0.1	0.3	11.5	745.2	7.040	0.09	C21 H25 N4
	333.2066	1.4	4.2	6.5	738.2	0.001	99.90	C20 H29 O4
	333.2098	-1.8	-5.4	-1.5	752.9	14.685	0.00	C9 H29 N6 O7
	333.2111	-3.1	-9.3	3.5	753.5	15.261	0.00	C10 H25 N10 O3
	333.2039	4.1	12.3	7.5	746.9	8.739	0.02	C16 H25 N6 O2
	333.2026	5.4	16.2	2.5	750.0	11.820	0.00	C15 H29 N2 O6
	333.2138	-5.8	-17.4	2.5	750.6	12.403	0.00	C14 H29 N4 O5

Figure S53. ^{13}C NMR spectrum of caryopincaolide H (**17**) in CD_3OD (150 MHz)

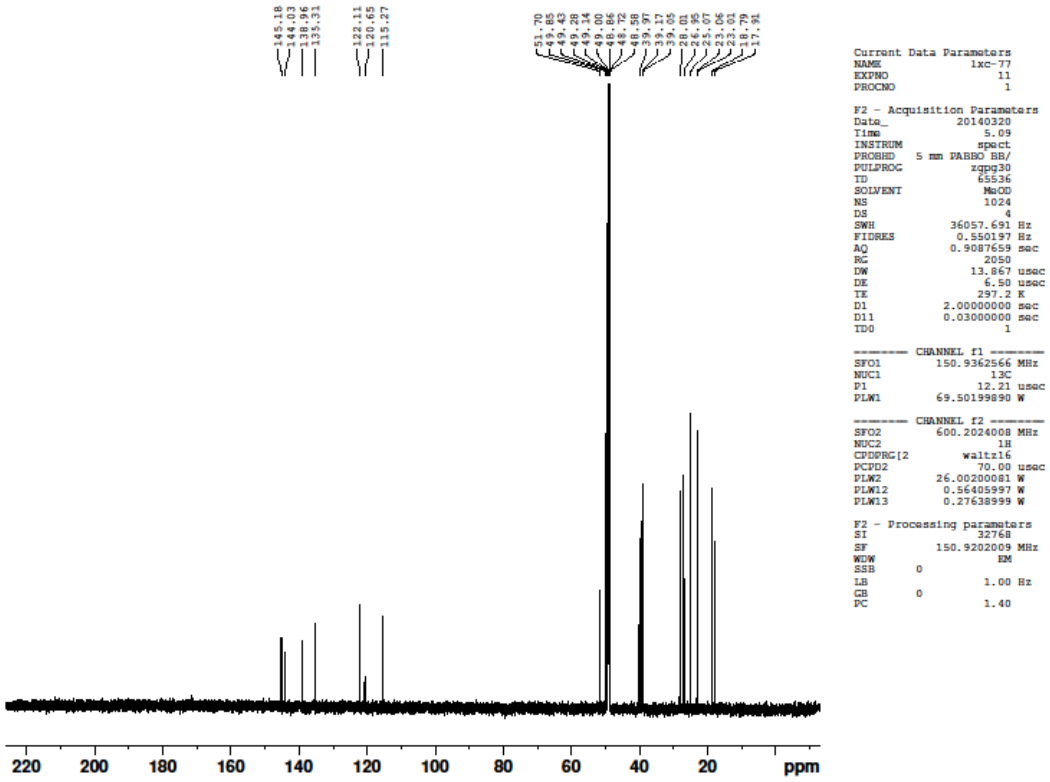


Figure S54. ^{1}H NMR spectrum of caryopincaolide H (**17**) in CD_3OD (600 MHz)

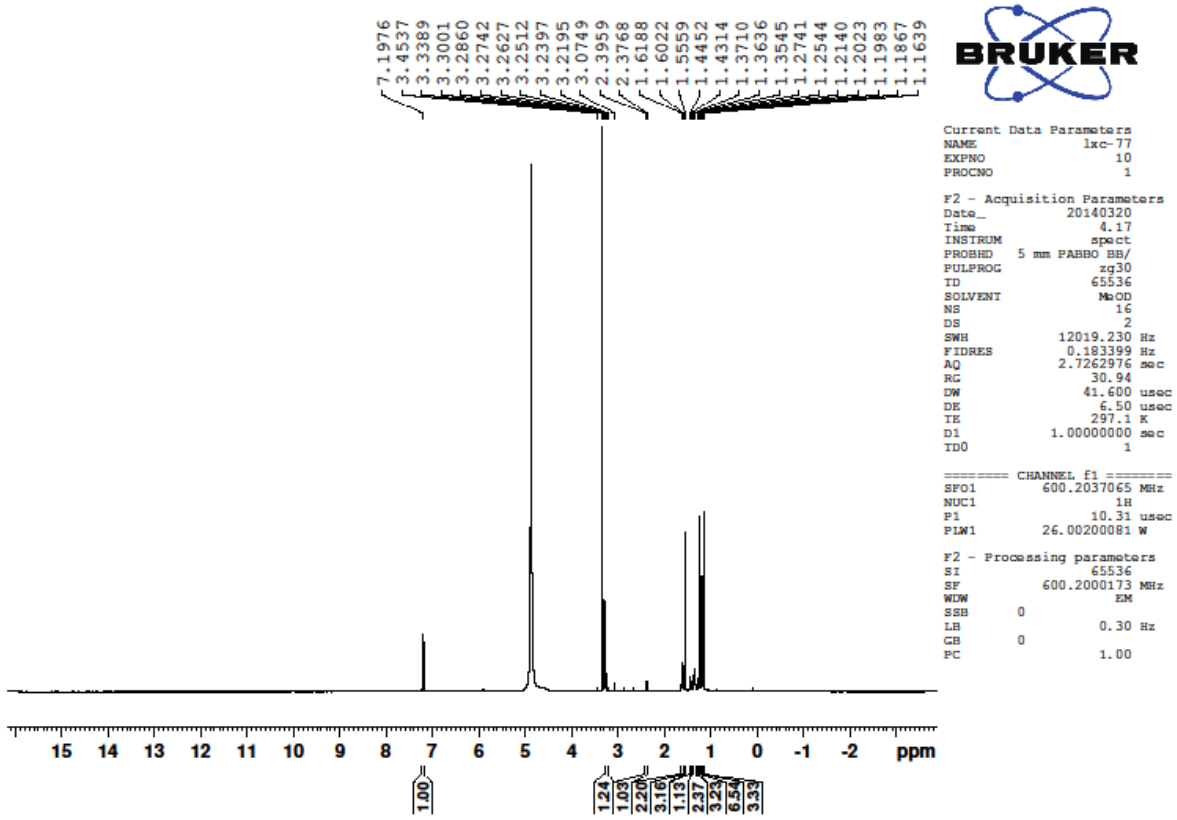


Figure S55. HSQC spectrum of caryopincaolide H (**17**) in CD_3OD

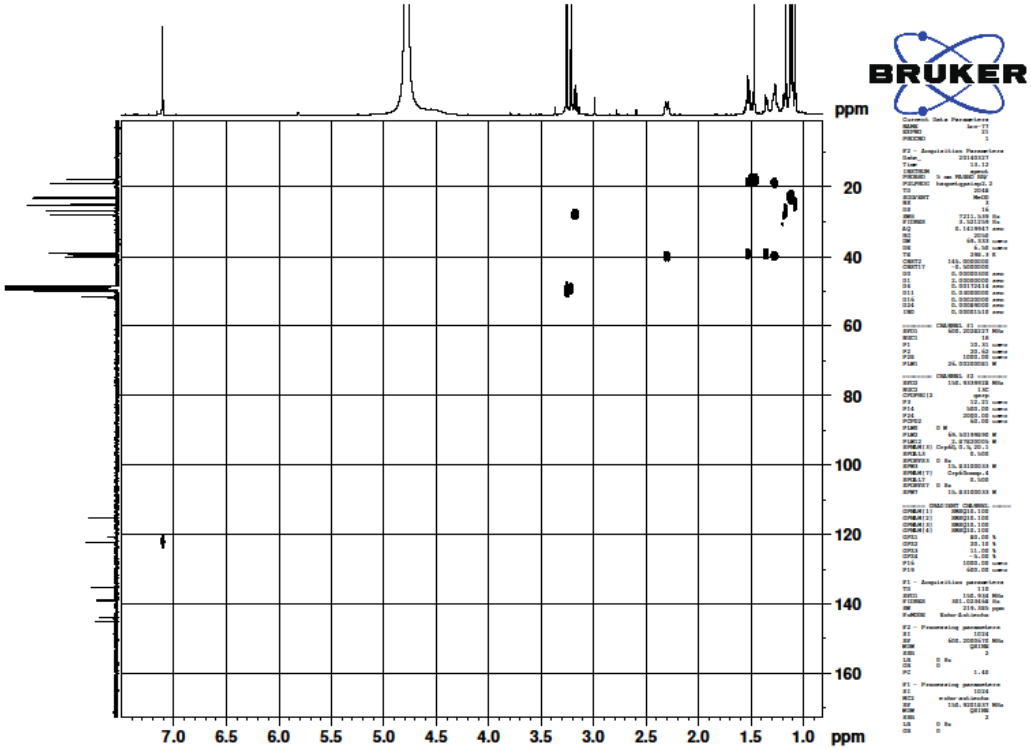


Figure S56. HMBC spectrum of caryopincaolide H (**17**) in CD_3OD

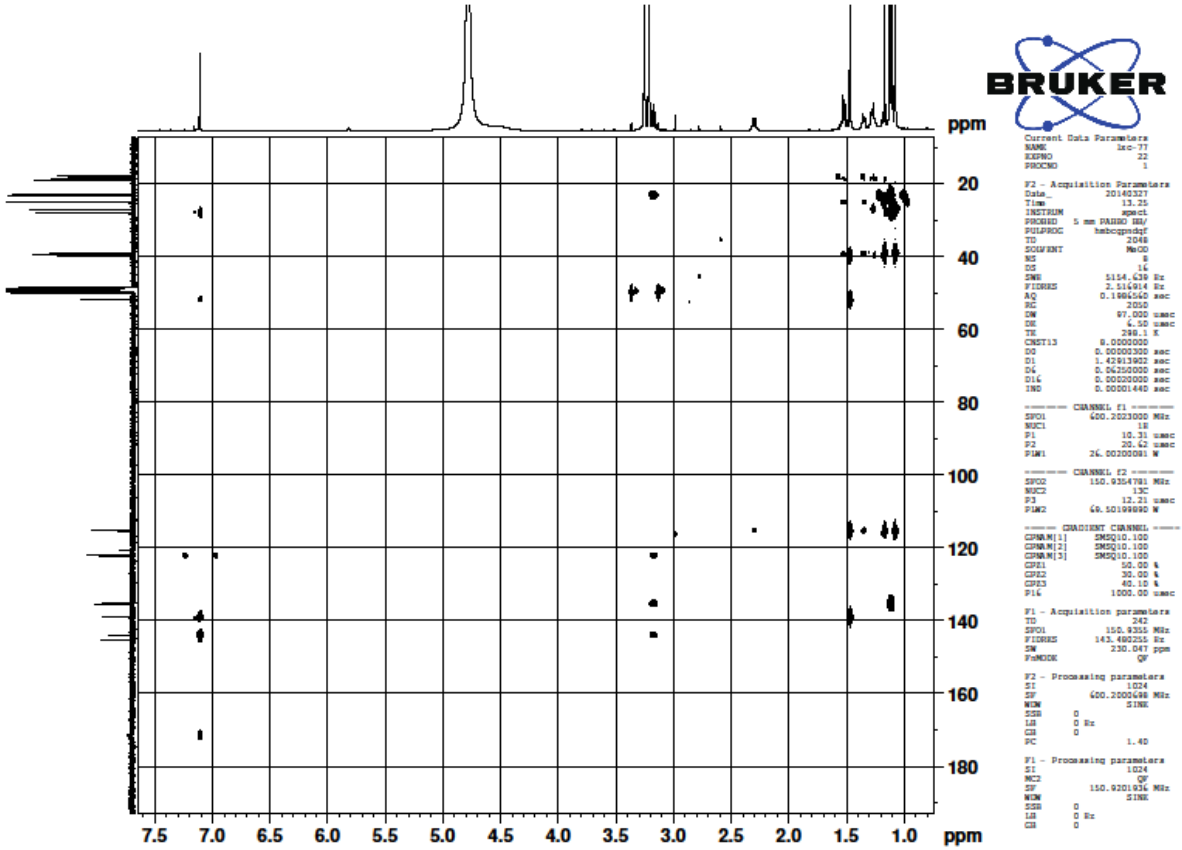


Figure S57. NOESY spectrum of caryopincaolide H (**17**) in CD_3OD

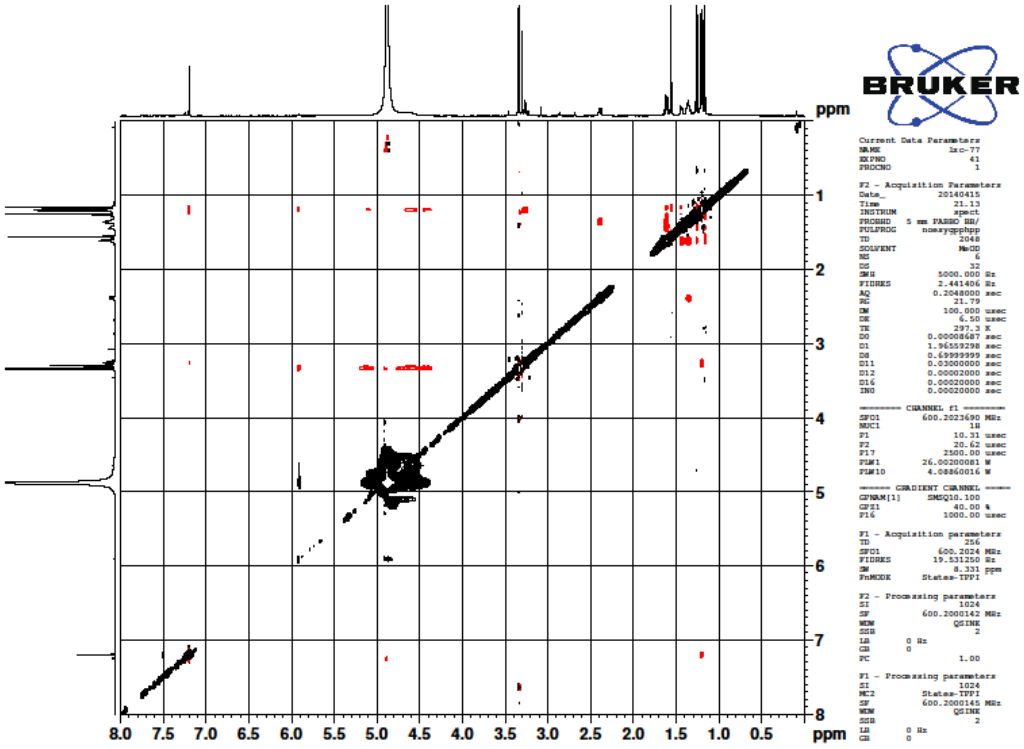
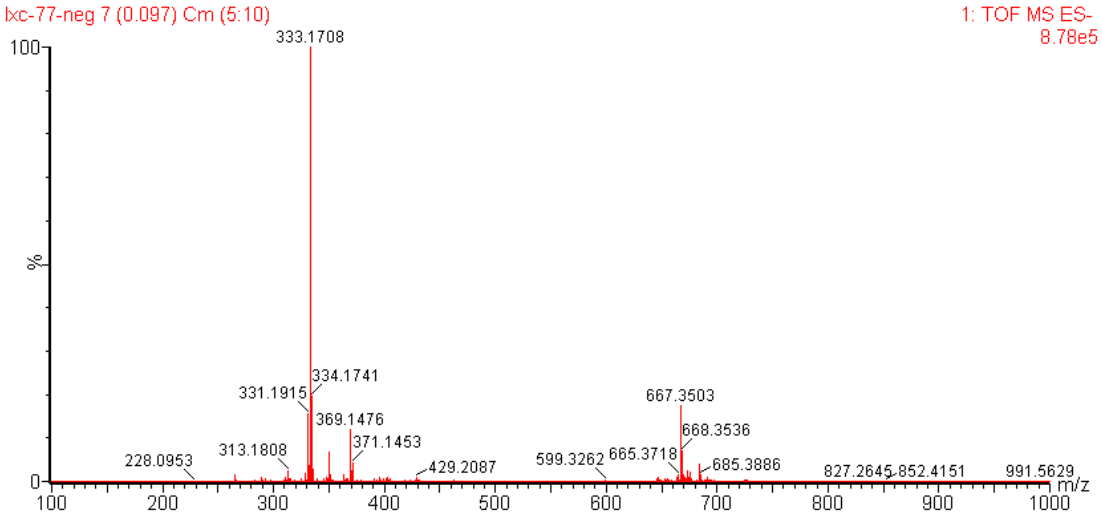


Figure S58. HRESIMS spectrum of caryopincaolide H (**17**) in CD_3OD



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
333.1708	333.1702	0.6	1.8	7.5	435.6	0.037	96.33	C19 H25 O5
	333.1715	-0.7	-2.1	12.5	439.4	3.813	2.21	C20 H21 N4 O
	333.1734	-2.6	-7.8	-0.5	447.5	11.977	0.00	C8 H25 N6 O8
	333.1675	3.3	9.9	8.5	439.9	4.353	1.29	C15 H21 N6 O3
	333.1747	-3.9	-11.7	4.5	447.6	12.029	0.00	C9 H21 N10 O4
	333.1662	4.6	13.8	3.5	442.2	6.626	0.13	C14 H25 N2 O7
	333.1761	-5.3	-15.9	-1.5	445.5	10.007	0.00	C12 H29 O10
	333.1643	6.5	19.5	16.5	446.0	10.480	0.00	C26 H21
	333.1774	-6.6	-19.8	3.5	443.7	8.134	0.03	C13 H25 N4 O6

Figure S59. ^{13}C NMR spectrum of caryopincaolide I (**18**) in CD_3OD (150 MHz)

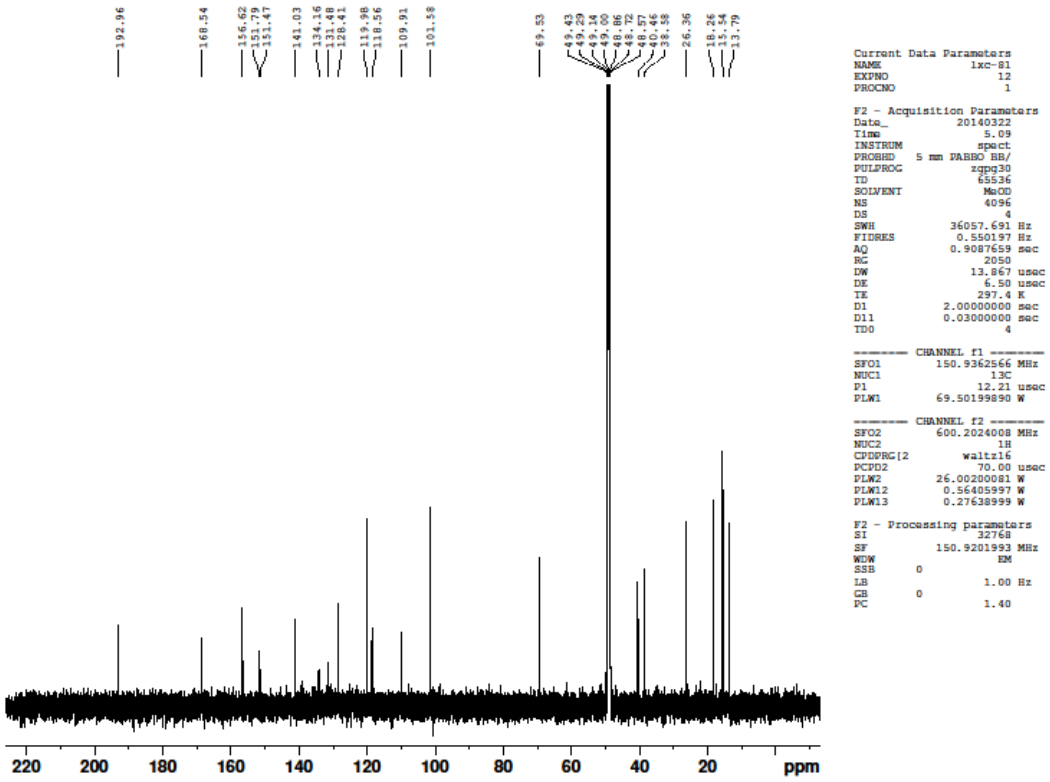


Figure S60. ^{1}H NMR spectrum of caryopincaolide I (**18**) in CD_3OD (600 MHz)

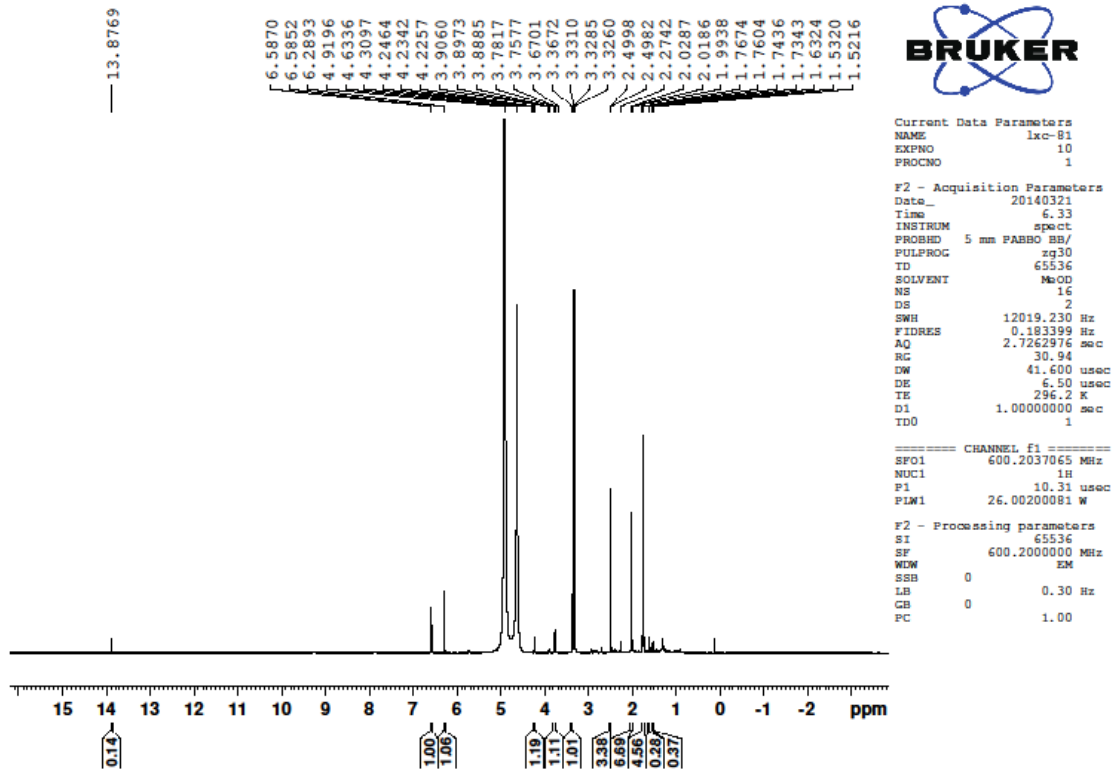


Figure S61. HSQC spectrum of caryopincaolide I (**18**) in CD_3OD

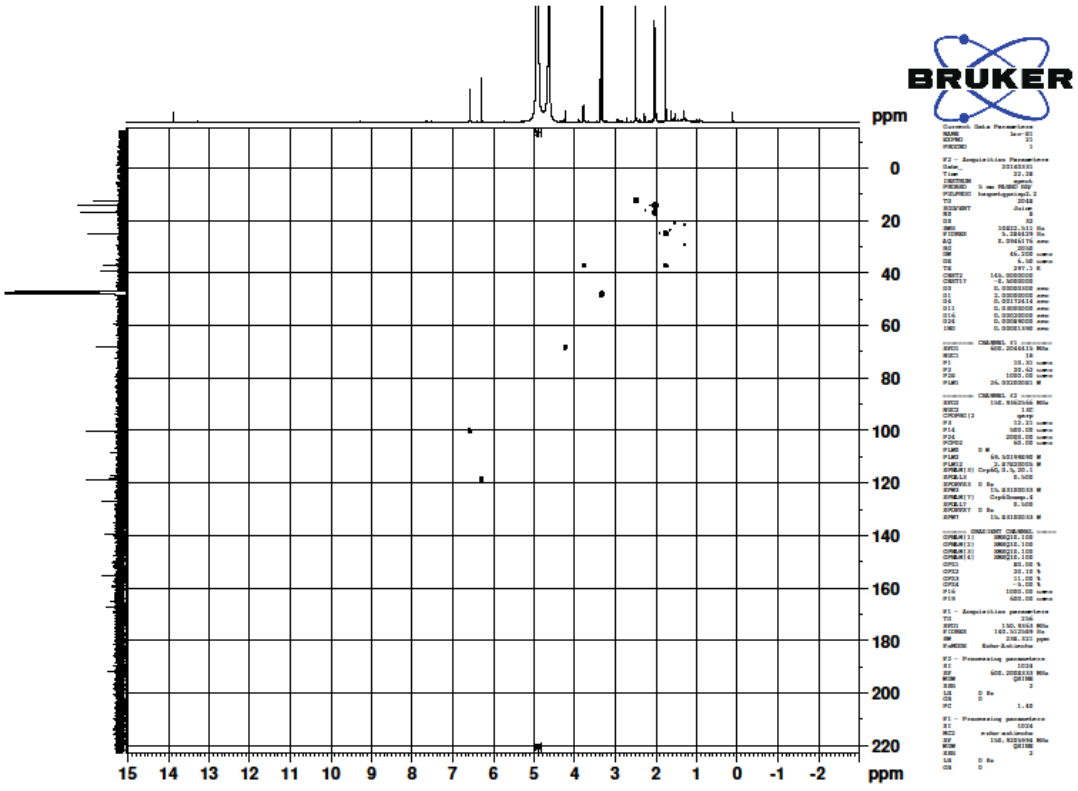


Figure S62. HMBC spectrum of caryopincaolide I (**18**) in CD_3OD

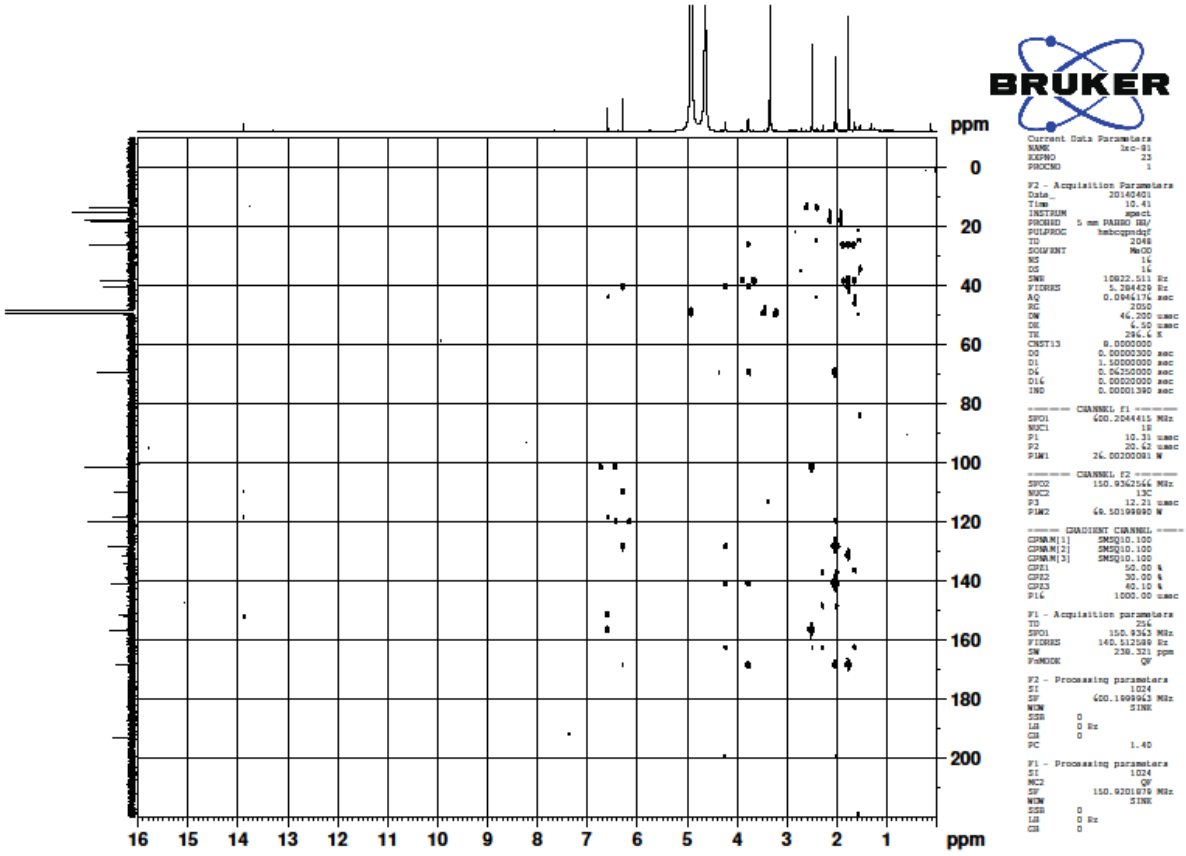


Figure S63. NOESY spectrum of caryopincaolide I (**18**) in CD_3OD

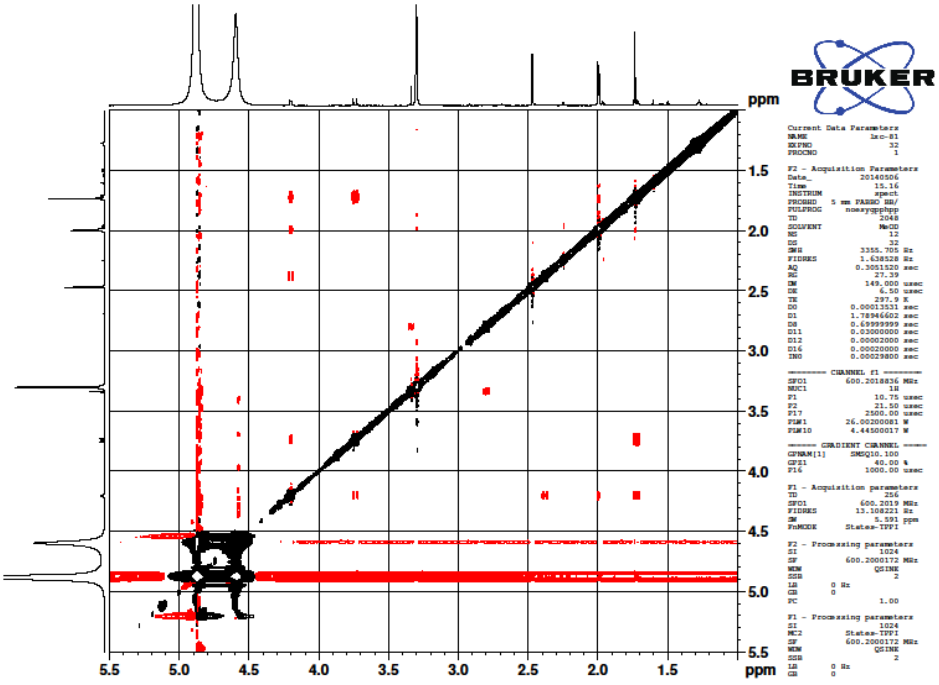
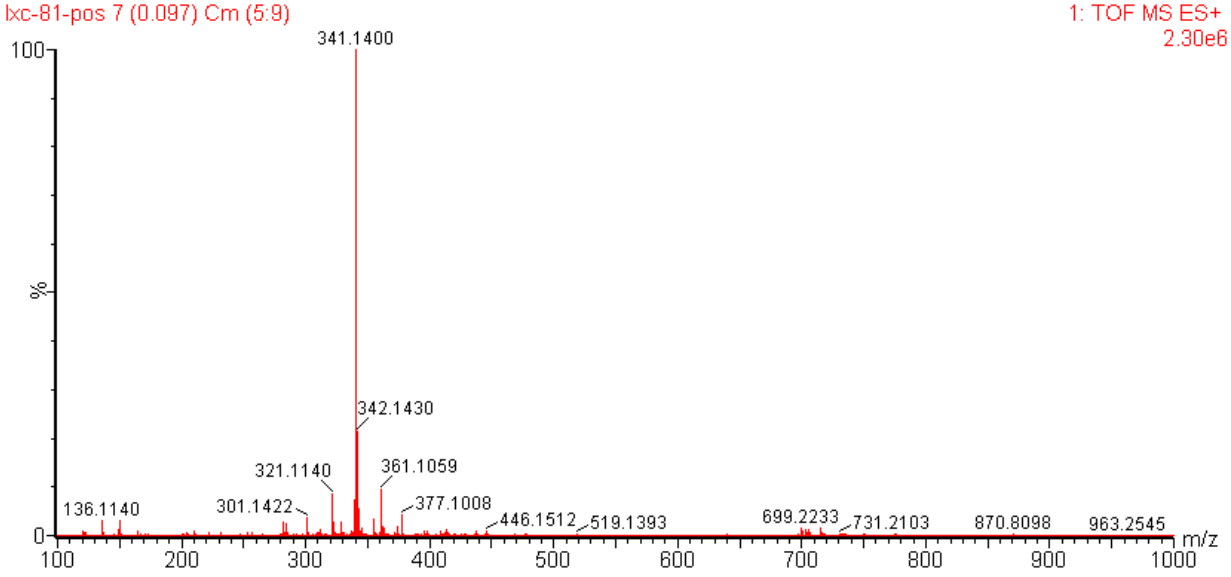


Figure S64. HRESIMS spectrum of caryopincaolide I (**18**) in CD_3OD



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
341.1400	341.1402	-0.2	-0.6	15.5	645.7	1.531	21.63	C21 H17 N4 O
	341.1389	1.1	3.2	10.5	644.7	0.578	56.08	C20 H21 O5
	341.1381	1.9	5.6	-1.5	650.6	6.518	0.15	C4 H21 N8 O10
	341.1421	-2.1	-6.2	2.5	649.3	5.155	0.58	C9 H21 N6 O8
	341.1434	-3.4	-10.0	7.5	649.1	4.973	0.69	C10 H17 N10 O4
	341.1362	3.8	11.1	11.5	646.7	2.554	7.78	C16 H17 N6 O3
	341.1448	-4.8	-14.1	1.5	647.9	3.822	2.19	C13 H25 O10
	341.1349	5.1	14.9	6.5	646.8	2.698	6.73	C15 H21 N2 O7
	341.1461	-6.1	-17.9	6.5	647.3	3.177	4.17	C14 H21 N4 O6

Figure S65. ^{13}C NMR spectrum of caryopincaolide J (**19**) in CD_3OD (150 MHz)

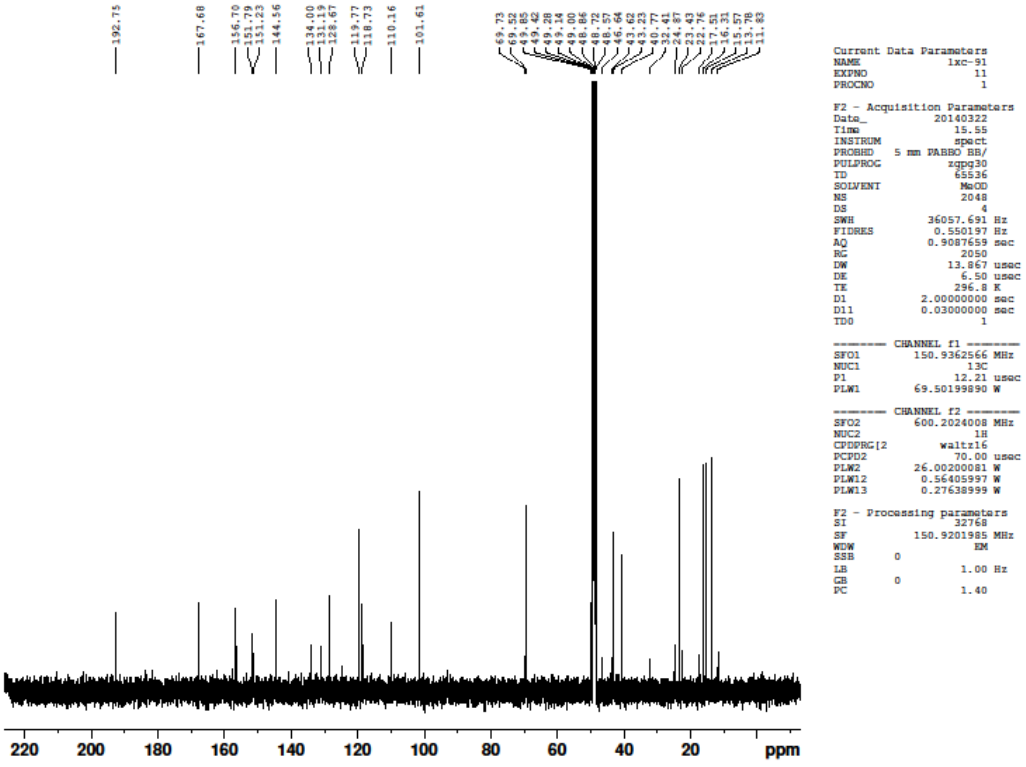


Figure S66. ^{1}H NMR spectrum of caryopincaolide J (**19**) in CD_3OD (600 MHz)

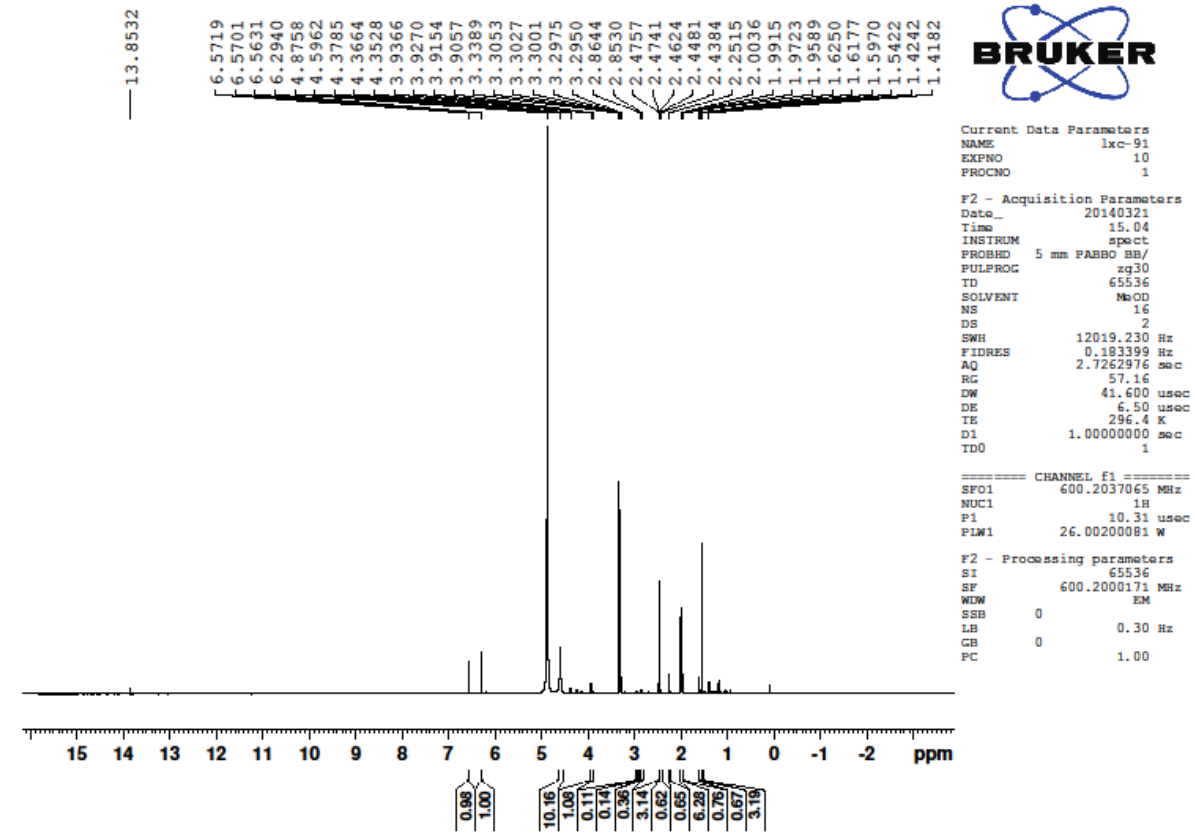


Figure S67. HSQC spectrum of caryopincaolide J (**19**) in CD_3OD

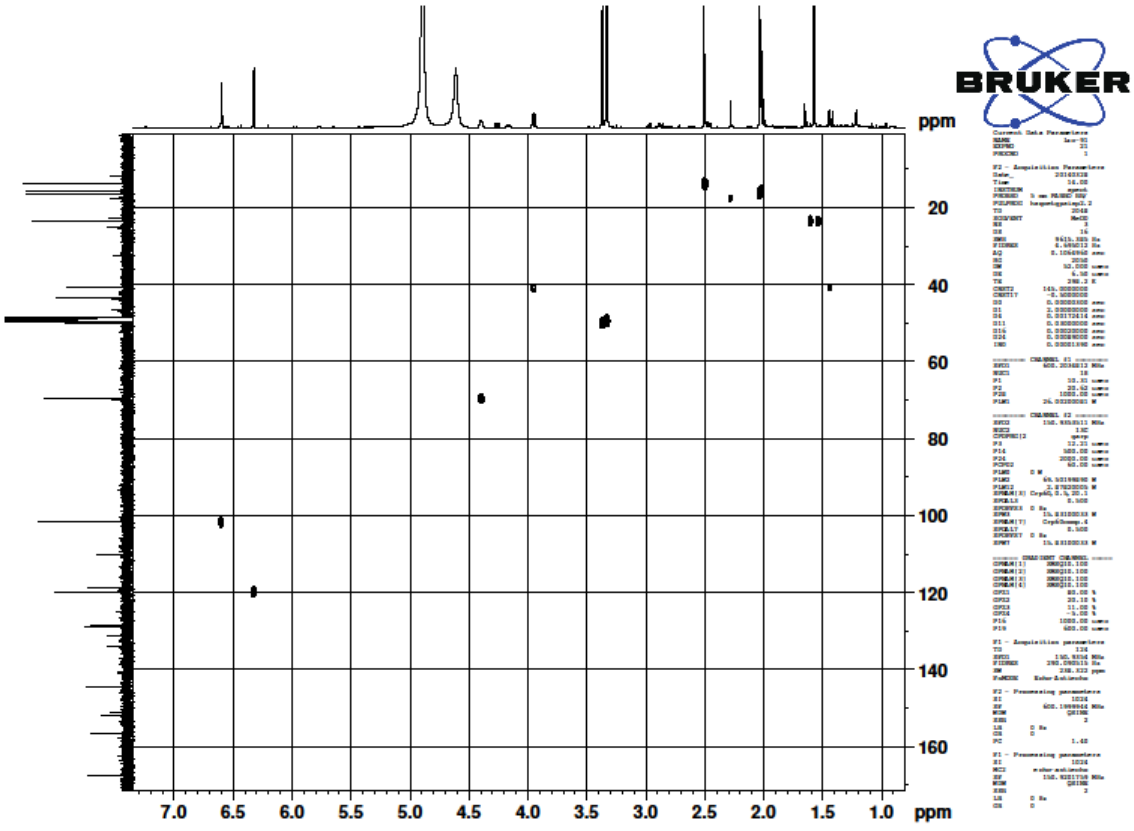


Figure S68. HMBC spectrum of caryopincaolide J (**19**) in CD_3OD

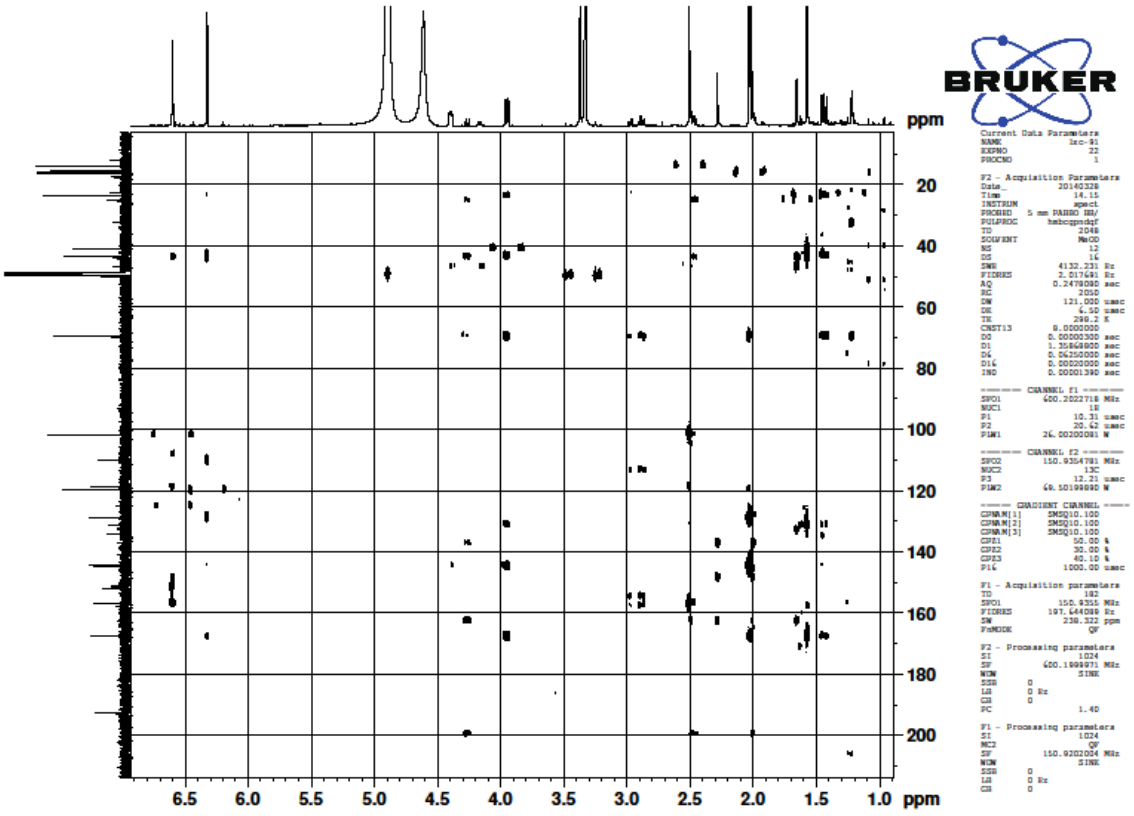


Figure S69. NOESY spectrum of caryopincaolide J (**19**) in CD_3OD

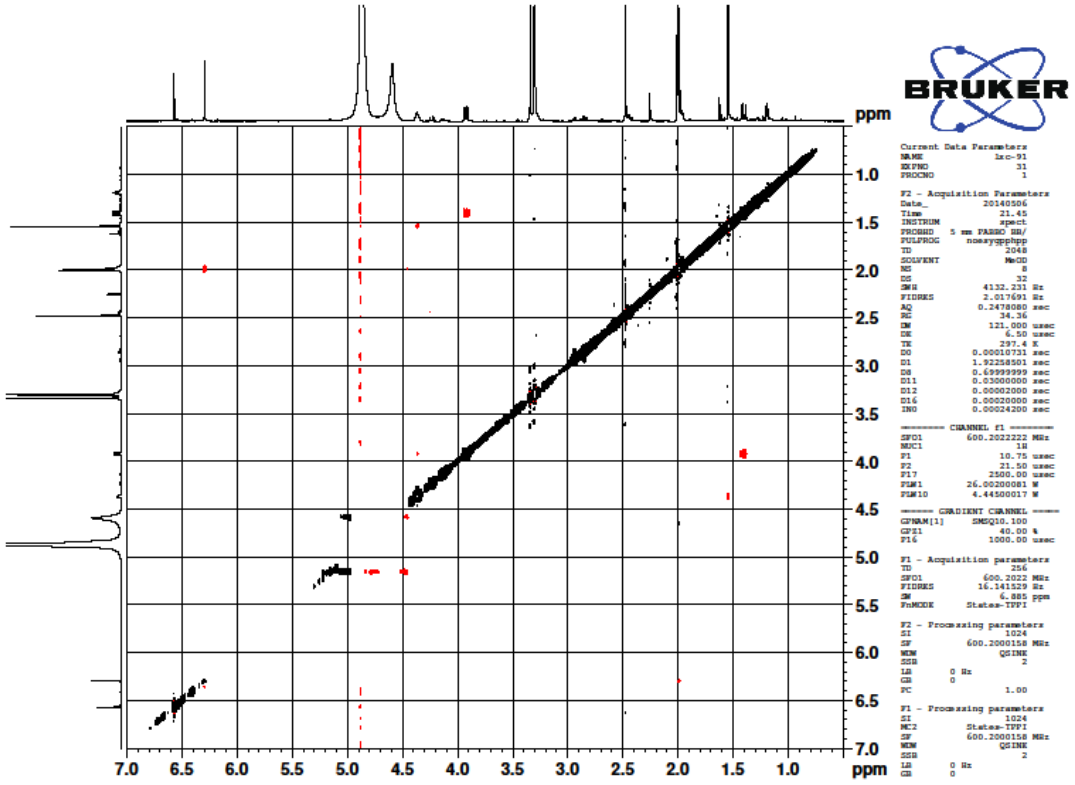
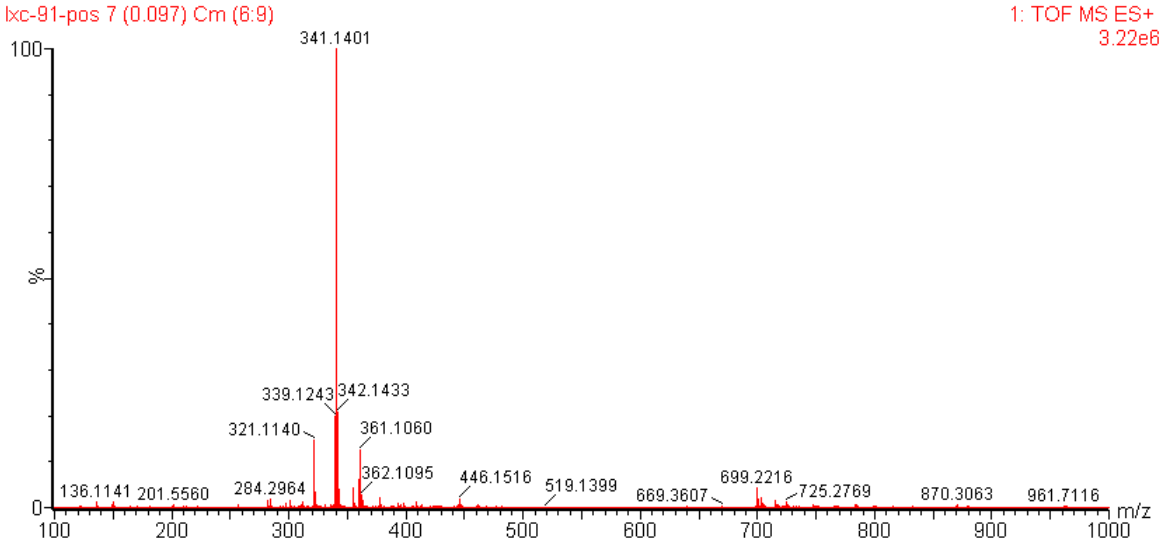


Figure S70. HRESIMS spectrum of caryopincaolide J (**19**) in CD_3OD



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
341.1401	341.1402	-0.1	-0.3	15.5	692.6	2.951	5.23	C21 H17 N4 O
	341.1389	1.2	3.5	10.5	689.7	0.110	89.57	C20 H21 O5
	341.1381	2.0	5.9	-1.5	699.6	10.006	0.00	C4 H21 N8 O10
	341.1421	-2.0	-5.9	2.5	697.7	8.060	0.03	C9 H21 N6 O8
	341.1434	-3.3	-9.7	7.5	697.4	7.766	0.04	C10 H17 N10 O4
	341.1362	3.9	11.4	11.5	693.3	3.634	2.64	C16 H17 N6 O3
	341.1448	-4.7	-13.8	1.5	695.9	6.271	0.19	C13 H25 O10
	341.1349	5.2	15.2	6.5	693.8	4.147	1.58	C15 H21 N2 O7
	341.1461	-6.0	-17.6	6.5	694.6	4.955	0.70	C14 H21 N4 O6

Figure S71. ^{13}C NMR spectrum of caryopincaolide K (**27**) in CD_3OD (150 MHz)

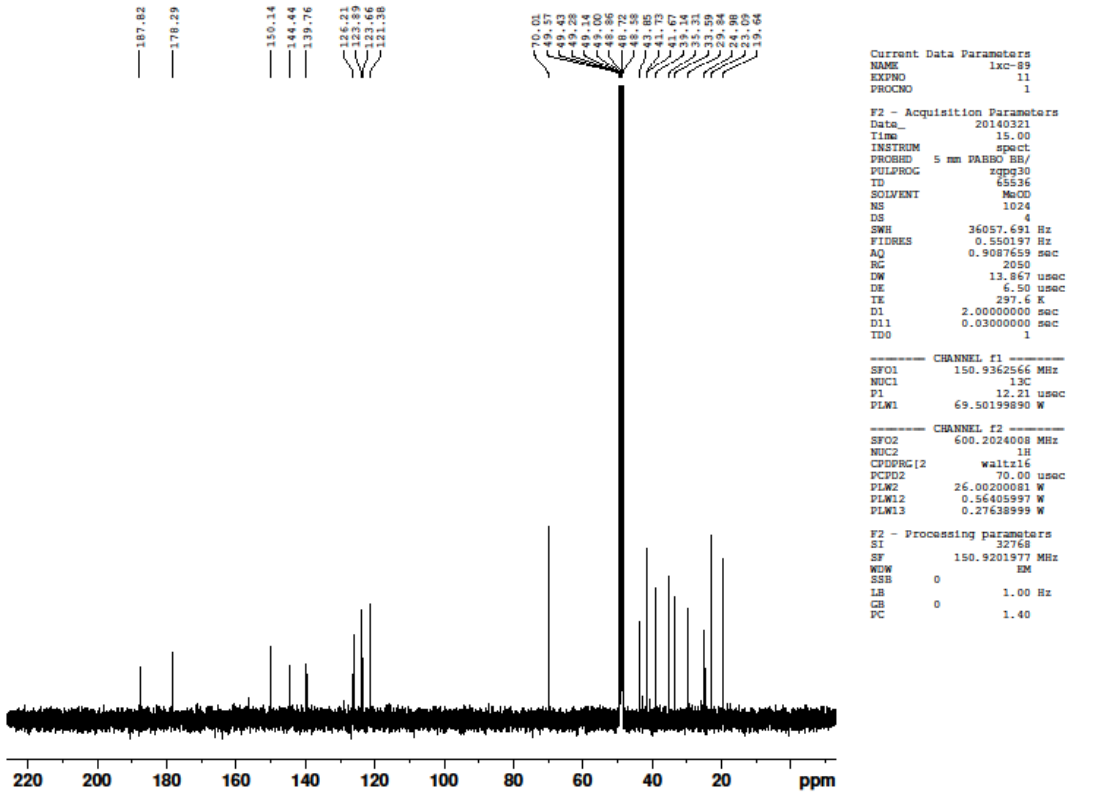


Figure S72. ^{1}H NMR spectrum of caryopincaolide K (**27**) in CD_3OD (600 MHz)

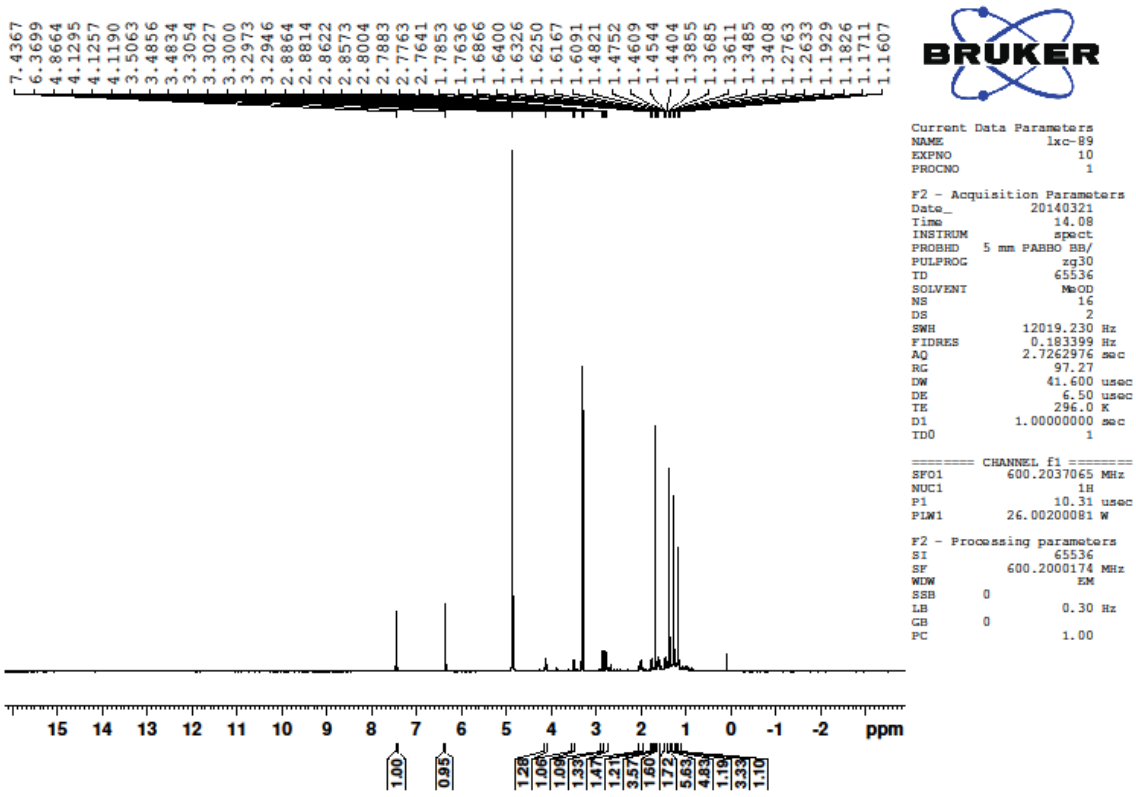


Figure S73. HSQC spectrum of caryopincaolide K (**27**) in CD_3OD

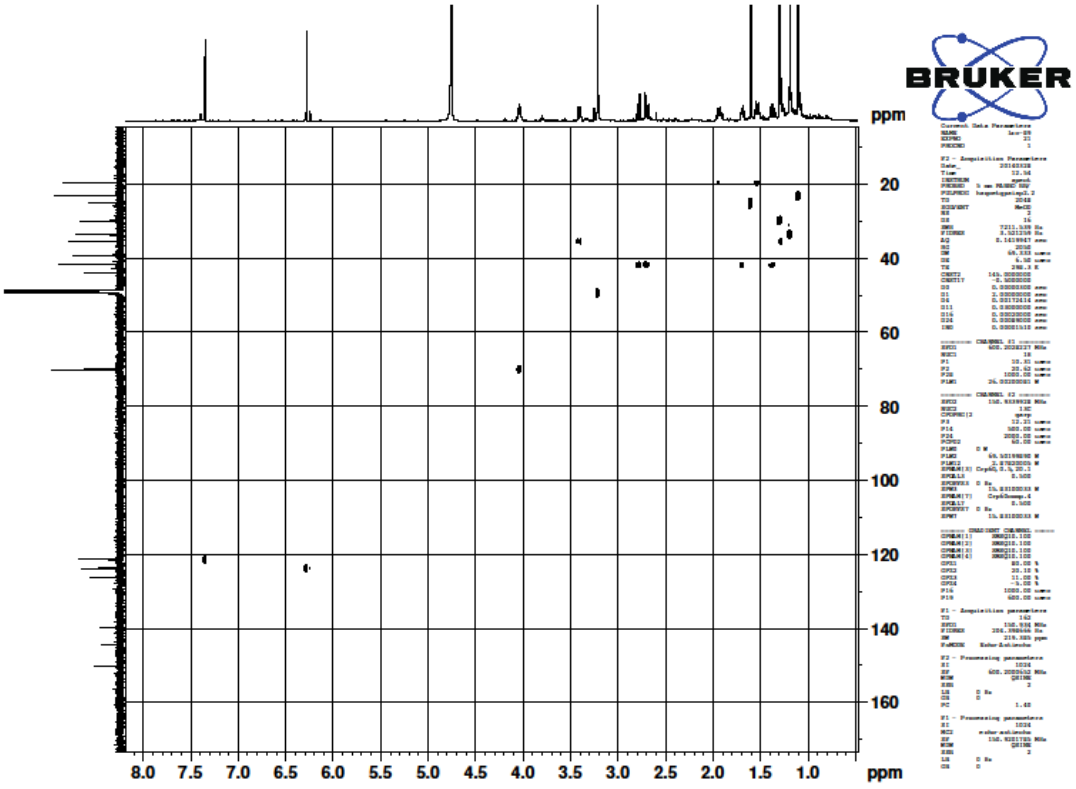


Figure S74. HMBC spectrum of caryopincaolide K (**27**) in CD_3OD

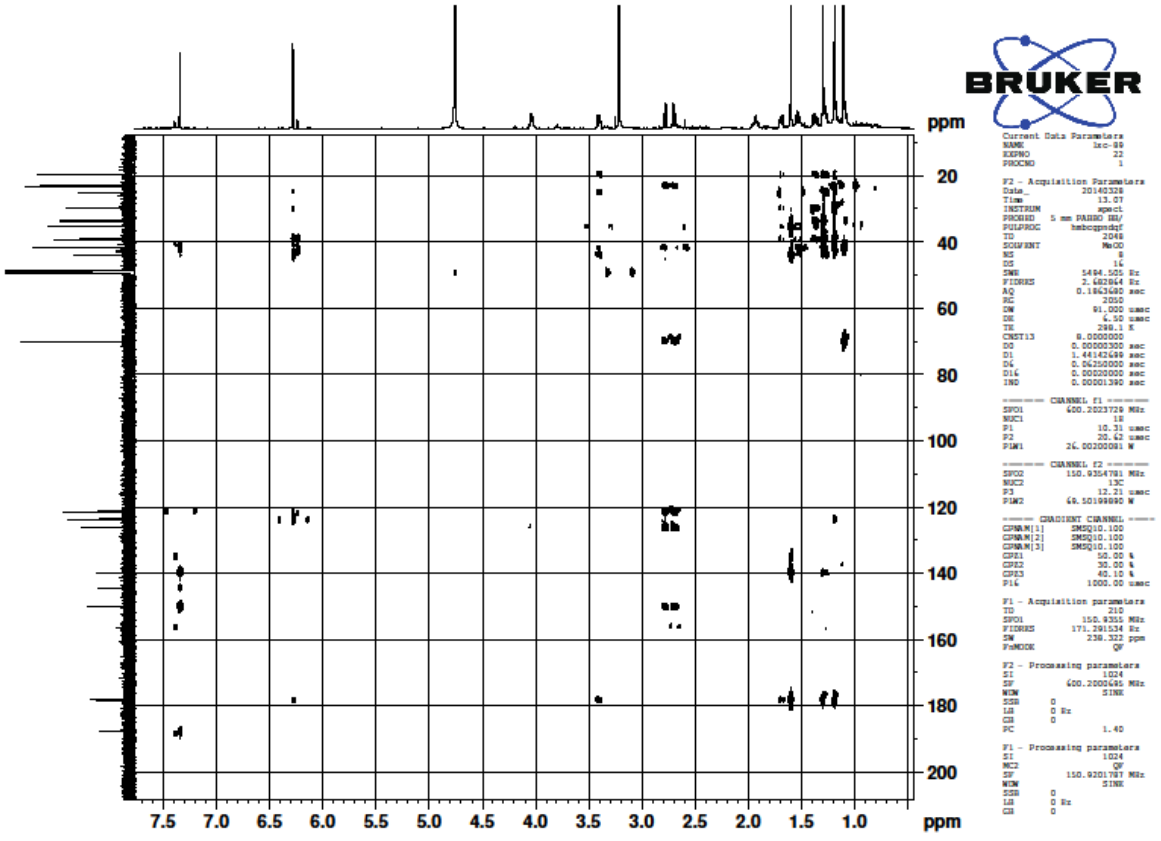


Figure S75. NOESY spectrum of caryopincaolide K (**27**) in CD_3OD

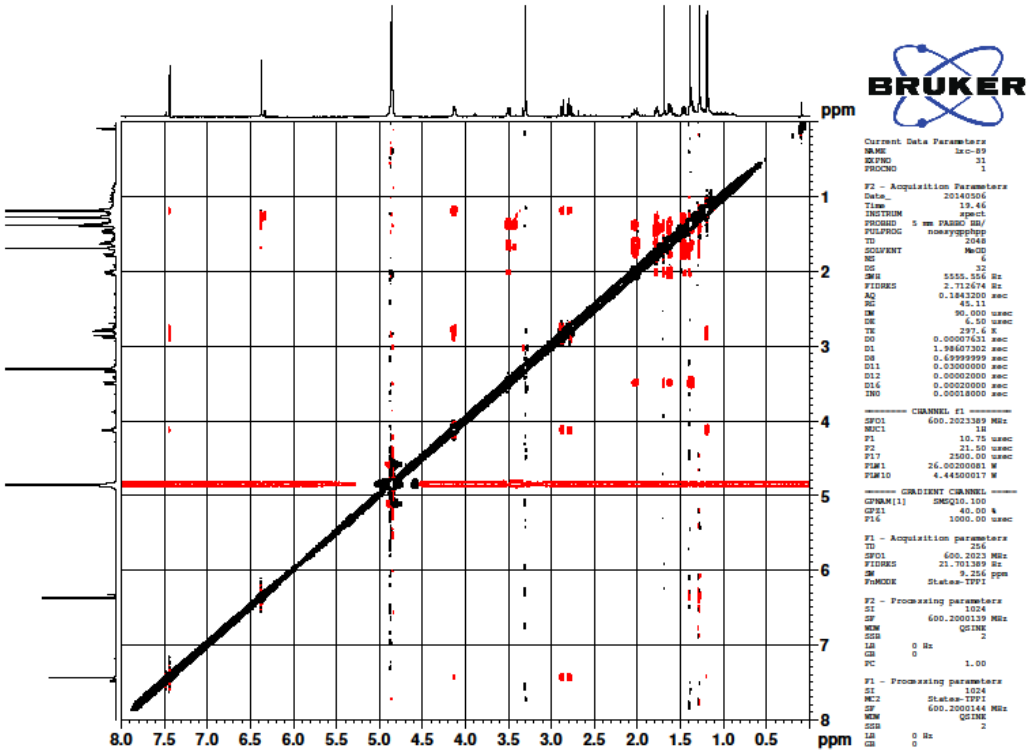
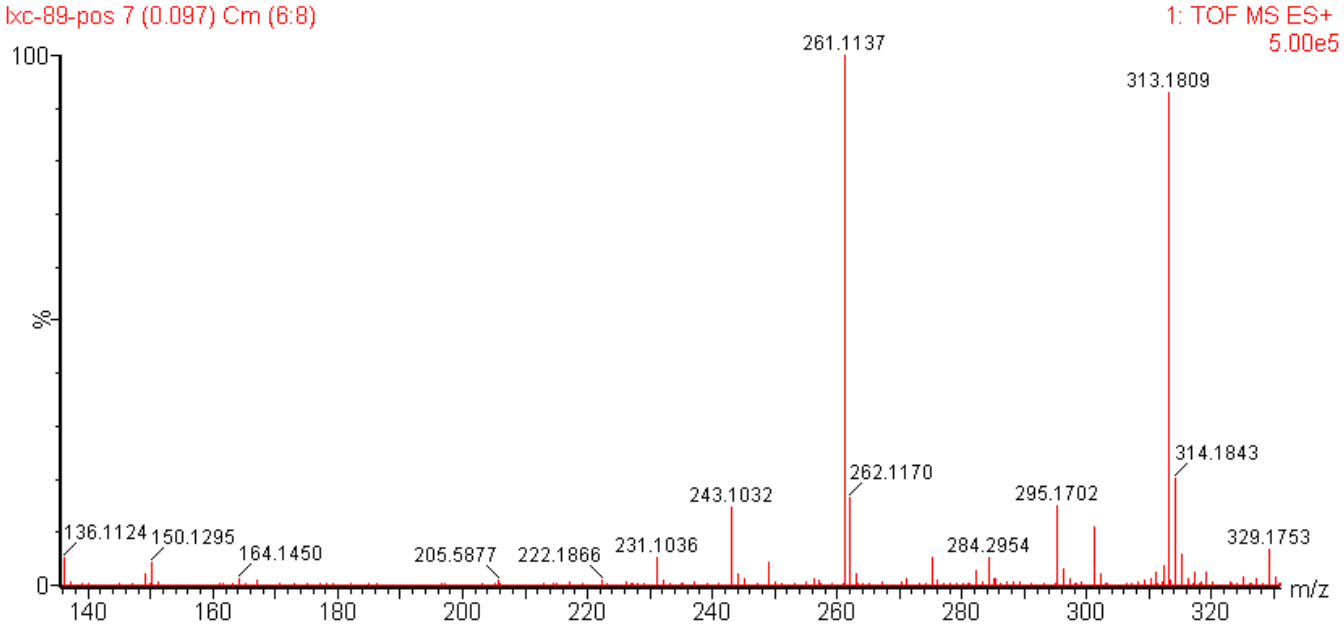


Figure S76. HRESIMS spectrum of caryopincaolide K (**27**) in CD_3OD



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
313.1809	313.1804	0.5	1.6	8.5	631.3	0.422	65.60	C20 H25 O3
	313.1836	-2.7	-8.6	0.5	635.1	4.151	1.57	C9 H25 N6 O6
	313.1777	3.2	10.2	9.5	632.9	2.025	13.20	C16 H21 N6 O
	313.1849	-4.0	-12.8	5.5	635.0	4.127	1.61	C10 H21 N10 O2
	313.1763	4.6	14.7	4.5	633.0	2.081	12.48	C15 H25 N2 O5
	313.1862	-5.3	-16.9	-0.5	633.8	2.895	5.53	C13 H29 O8

Figure S77. ^{13}C NMR spectrum of caryopincaolide L (**28**) in CD_3OD (150 MHz)

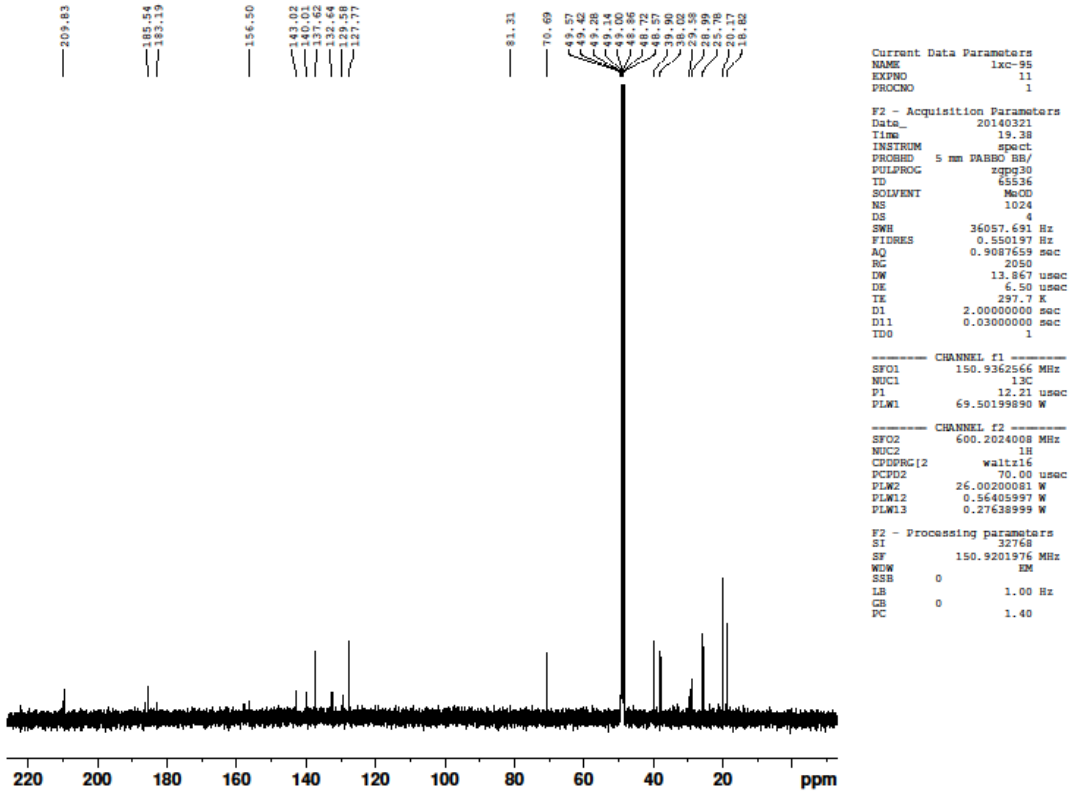


Figure S78. ^{1}H NMR spectrum of caryopincaolide L (**28**) in CD_3OD (600 MHz)

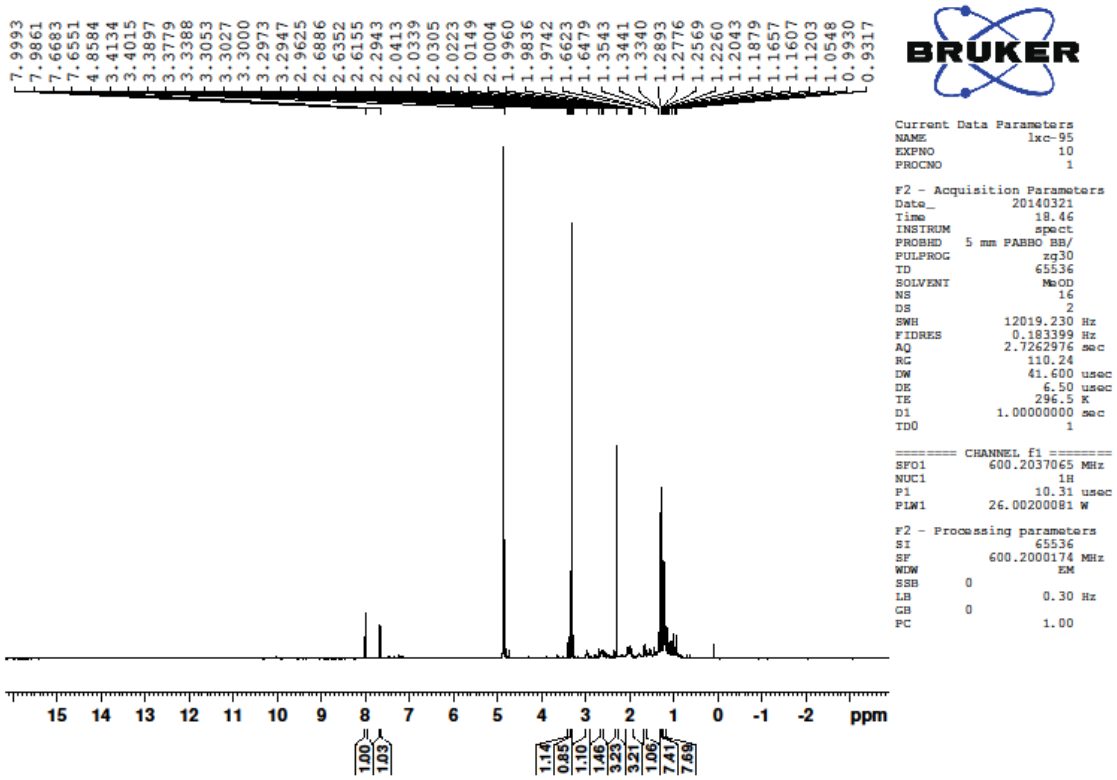


Figure S79. HSQC spectrum of caryopincaolide L (**28**) in CD_3OD

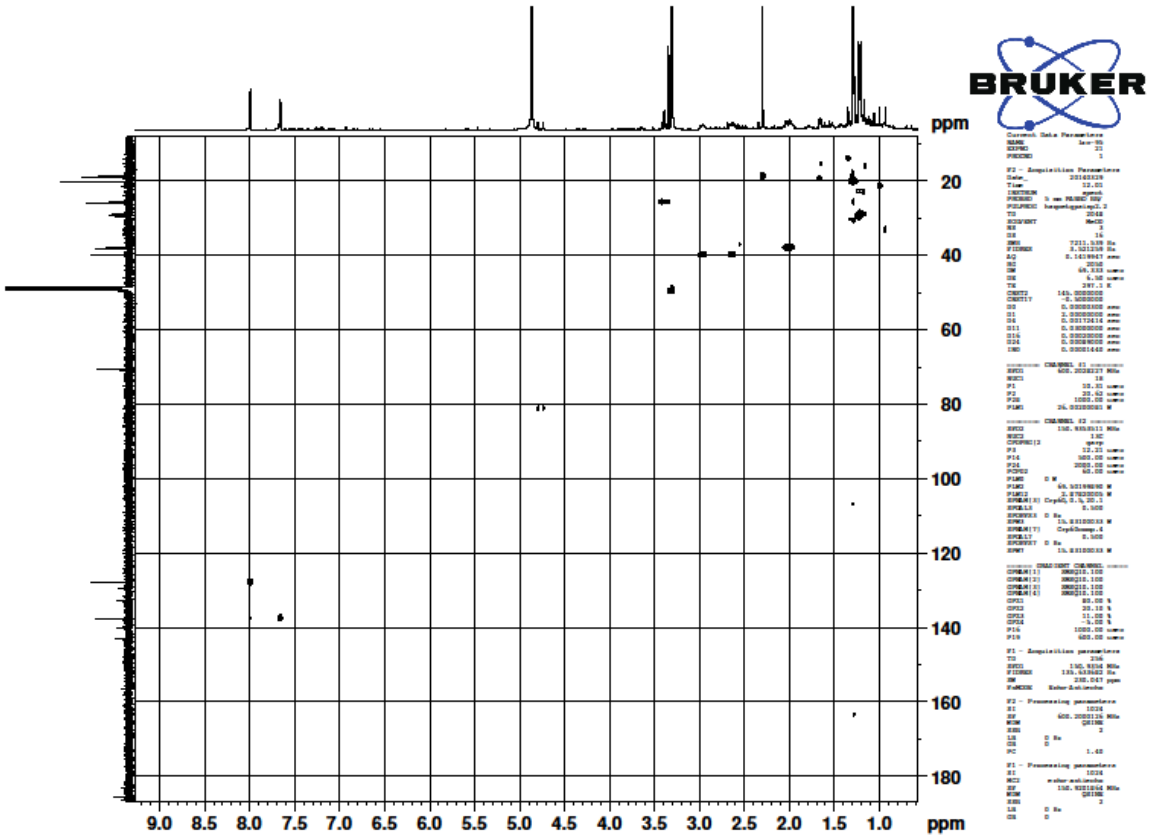


Figure S80. HMBC spectrum of caryopincaolide L (**28**) in CD_3OD

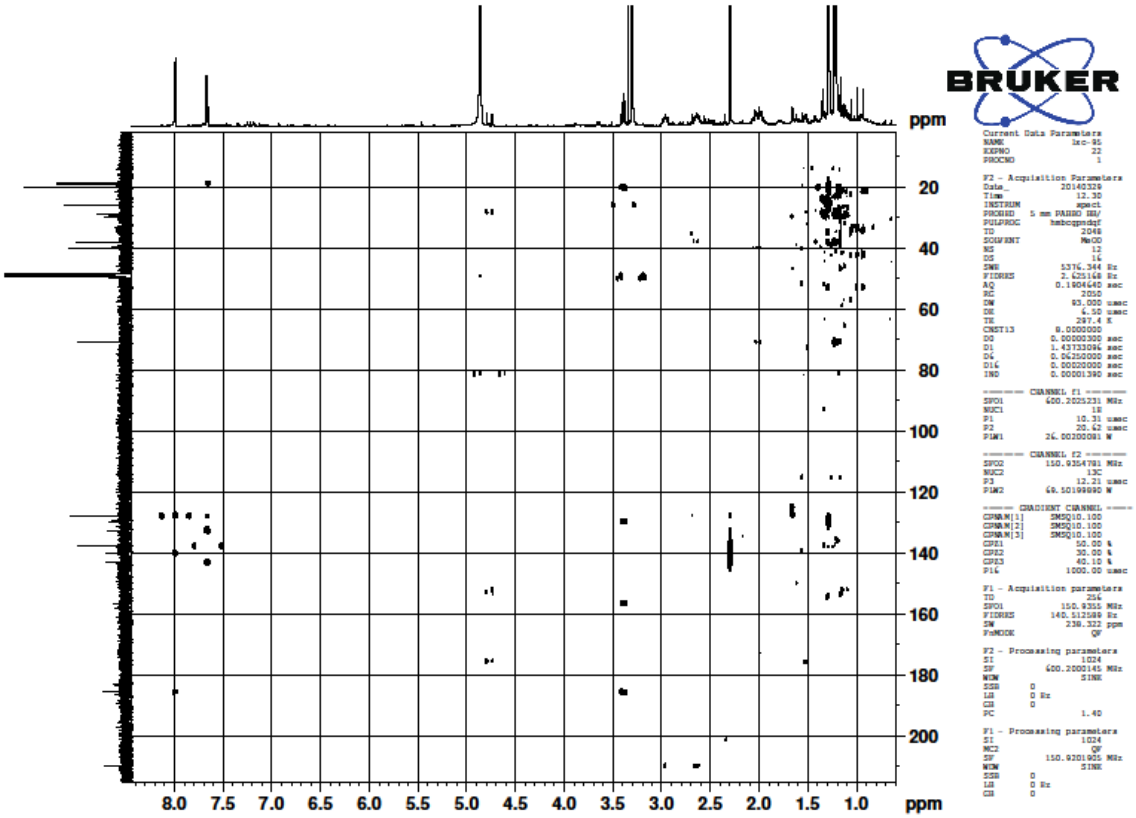
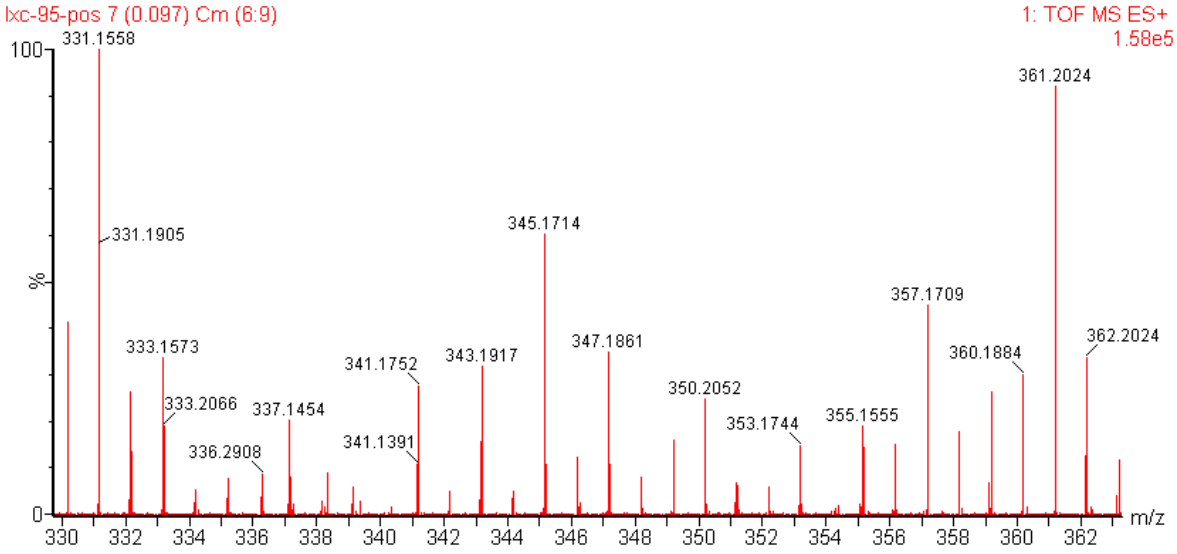


Figure S81. HRESIMS spectrum of caryopincaolide L (**28**) in CD_3OD



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
345.1714	345.1715	-0.1	-0.3	13.5	565.3	1.755	17.29	C21 H21 N4 O
	345.1702	1.2	3.5	8.5	565.3	1.741	17.53	C20 H25 O5
	345.1734	-2.0	-5.8	0.5	565.9	2.415	8.93	C9 H25 N6 O8
	345.1747	-3.3	-9.6	5.5	566.0	2.494	8.25	C10 H21 N10 O4
	345.1675	3.9	11.3	9.5	565.6	2.070	12.61	C16 H21 N6 O3
	345.1761	-4.7	-13.6	-0.5	565.7	2.207	11.01	C13 H29 O10
	345.1662	5.2	15.1	4.5	565.6	2.077	12.54	C15 H25 N2 O7
	345.1774	-6.0	-17.4	4.5	565.7	2.134	11.84	C14 H25 N4 O6

Figure S82. ^{13}C NMR spectrum of compound **5** in $CDCl_3$ (100 MHz)

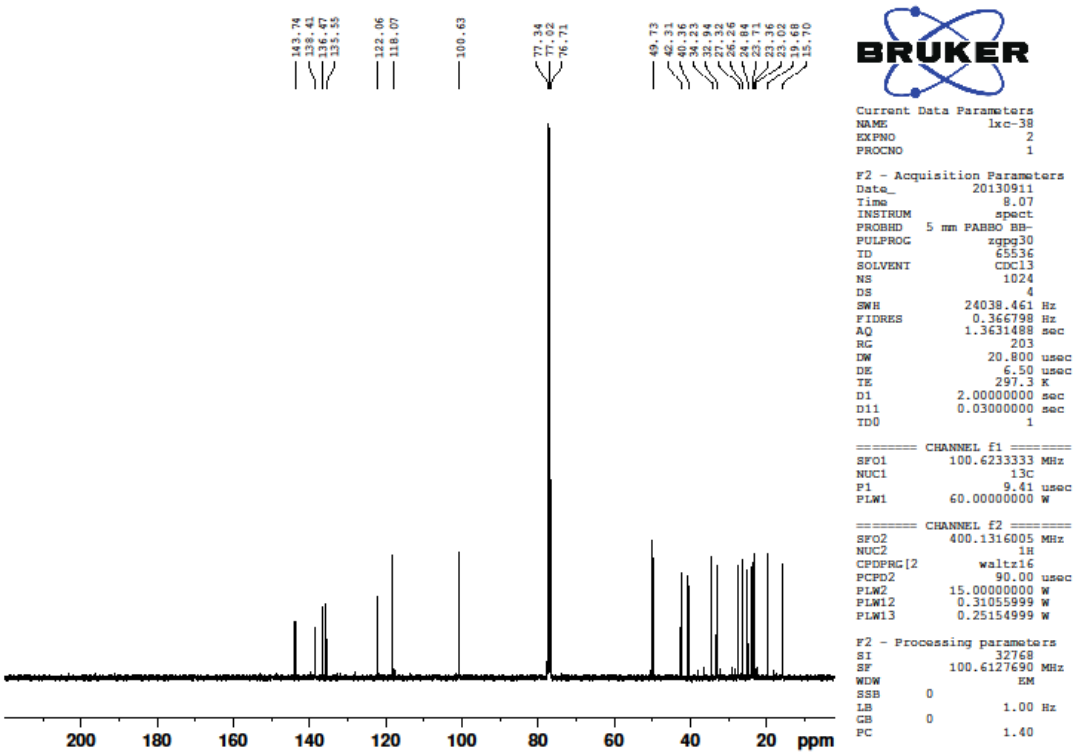


Figure S83. ^{1}H NMR spectrum of compound **5** in $CDCl_3$ (400 MHz)

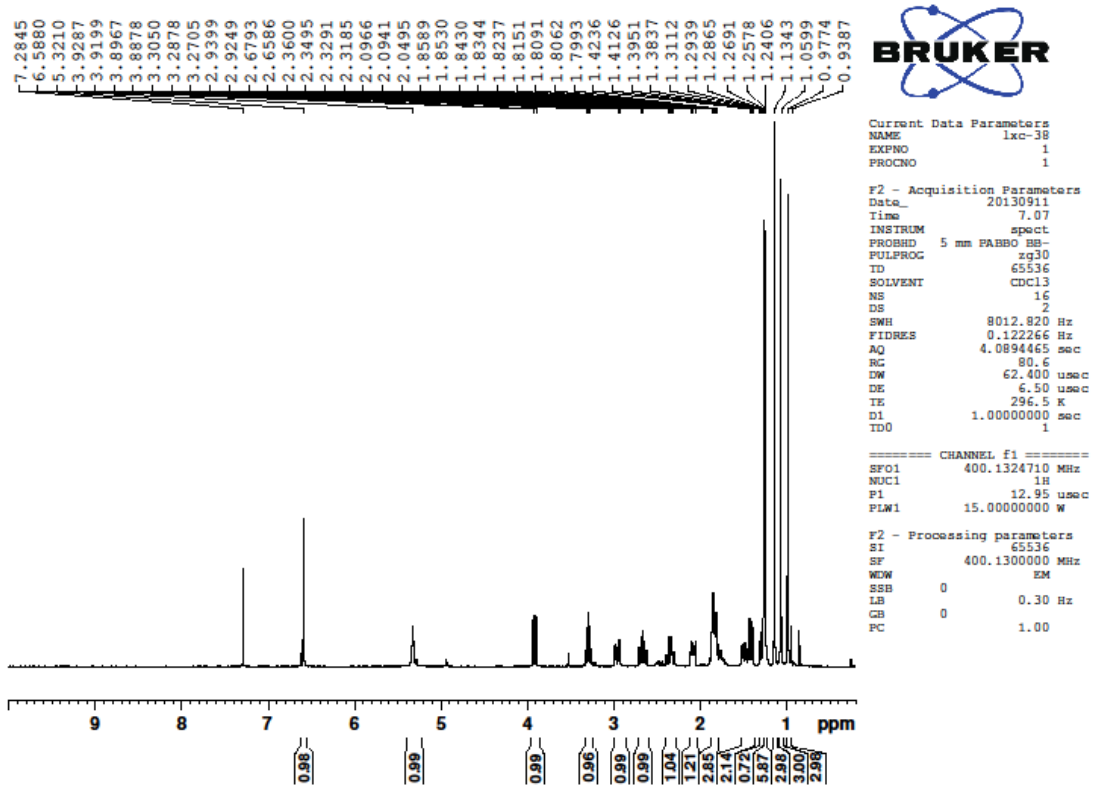


Figure S84. HSQC spectrum of compound **5** in $CDCl_3$

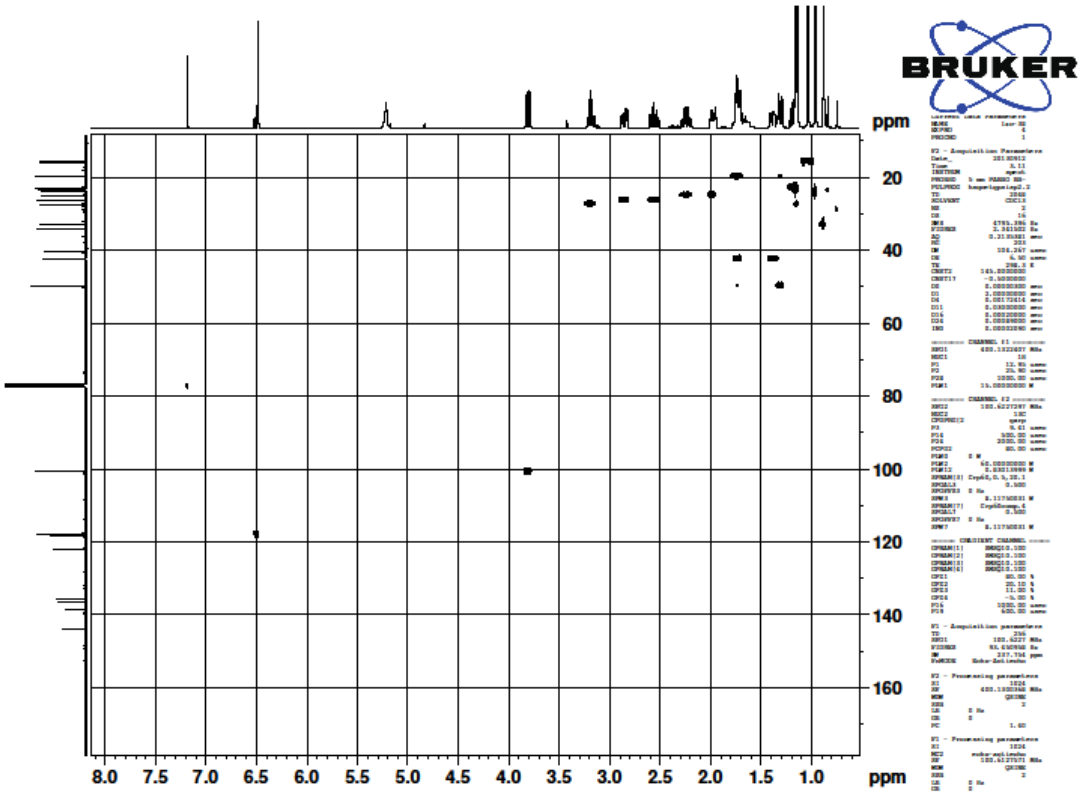


Figure S85. HMBC spectrum of compound **5** in $CDCl_3$

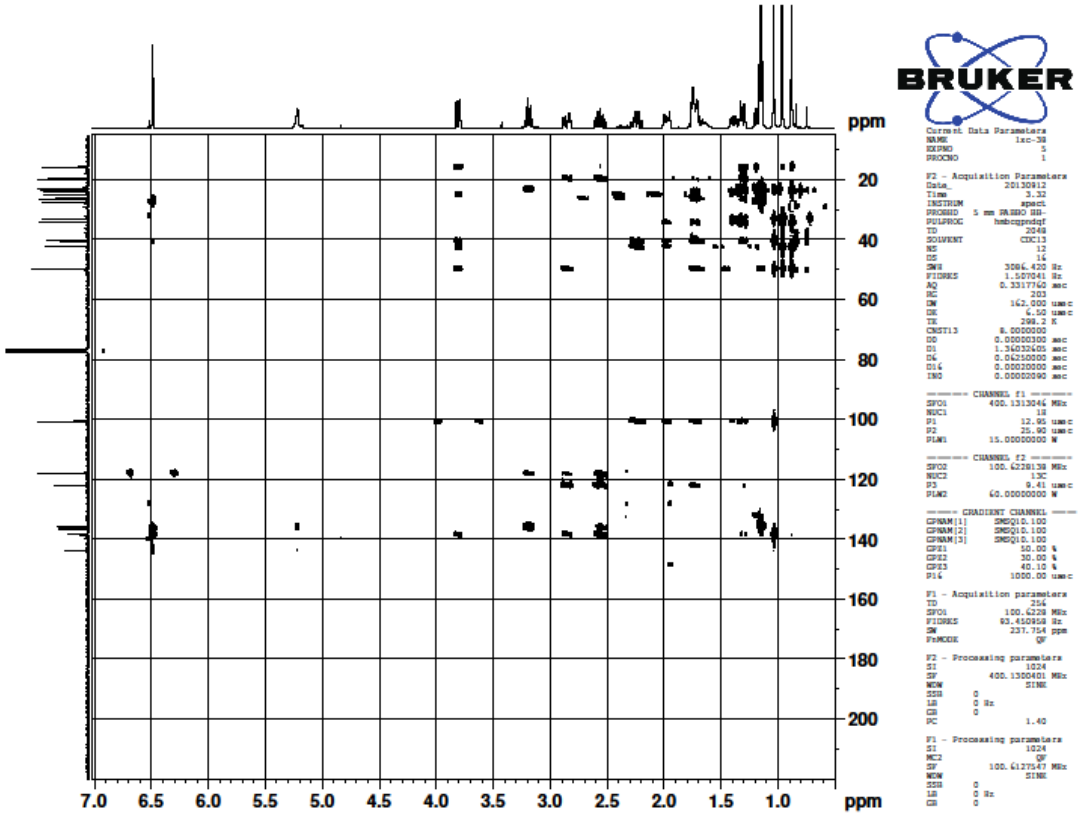


Figure S86. ^{13}C NMR spectrum of compound **6** in $CDCl_3$ (100 MHz)

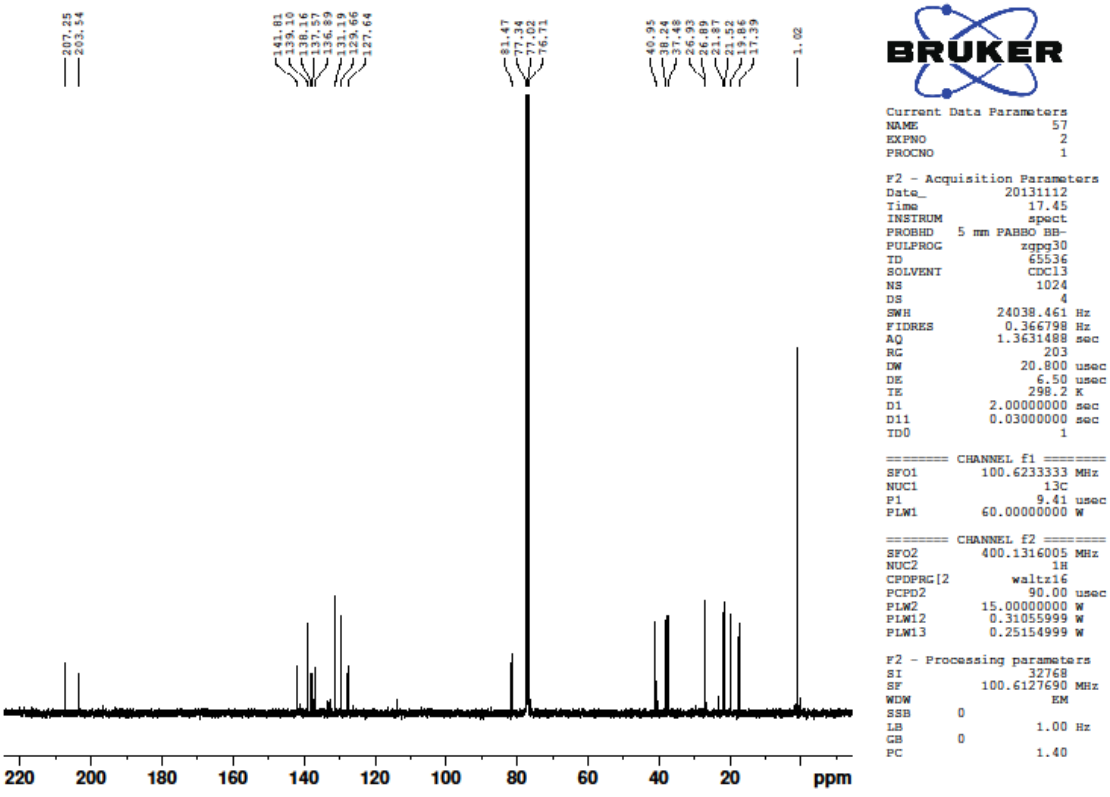


Figure S87. ^{1}H NMR spectrum of compound **6** in $CDCl_3$ (400 MHz)

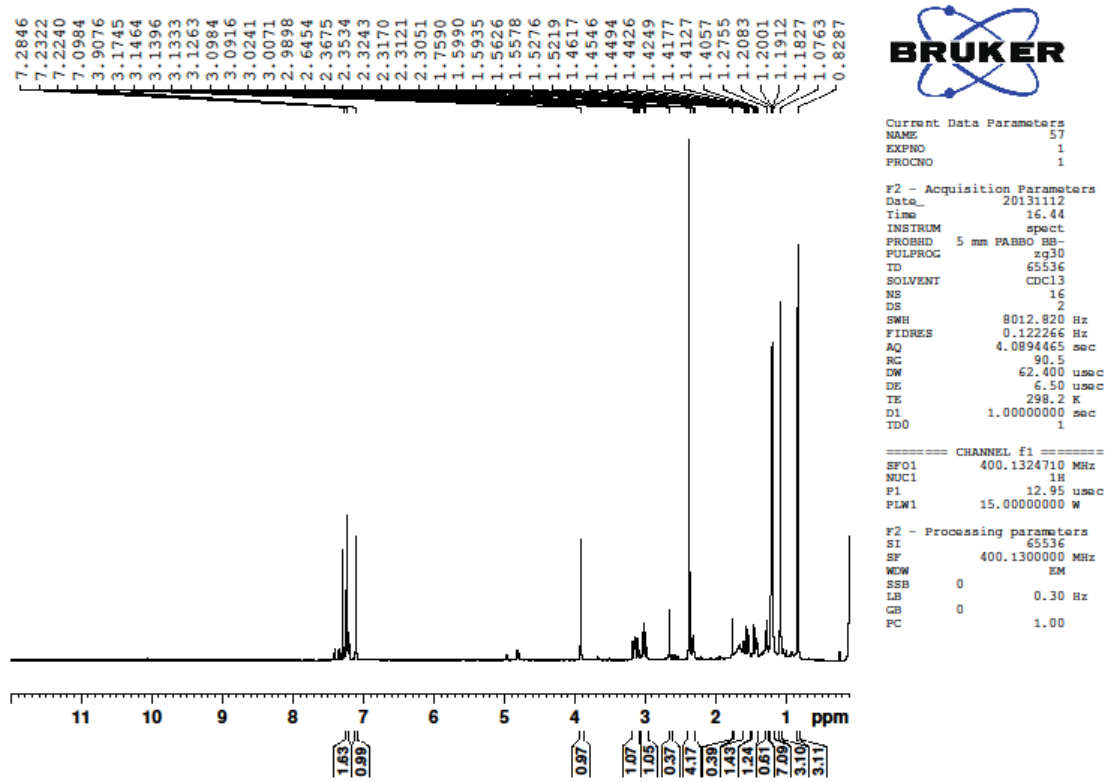


Figure S88. HSQC spectrum of compound **6** in $CDCl_3$

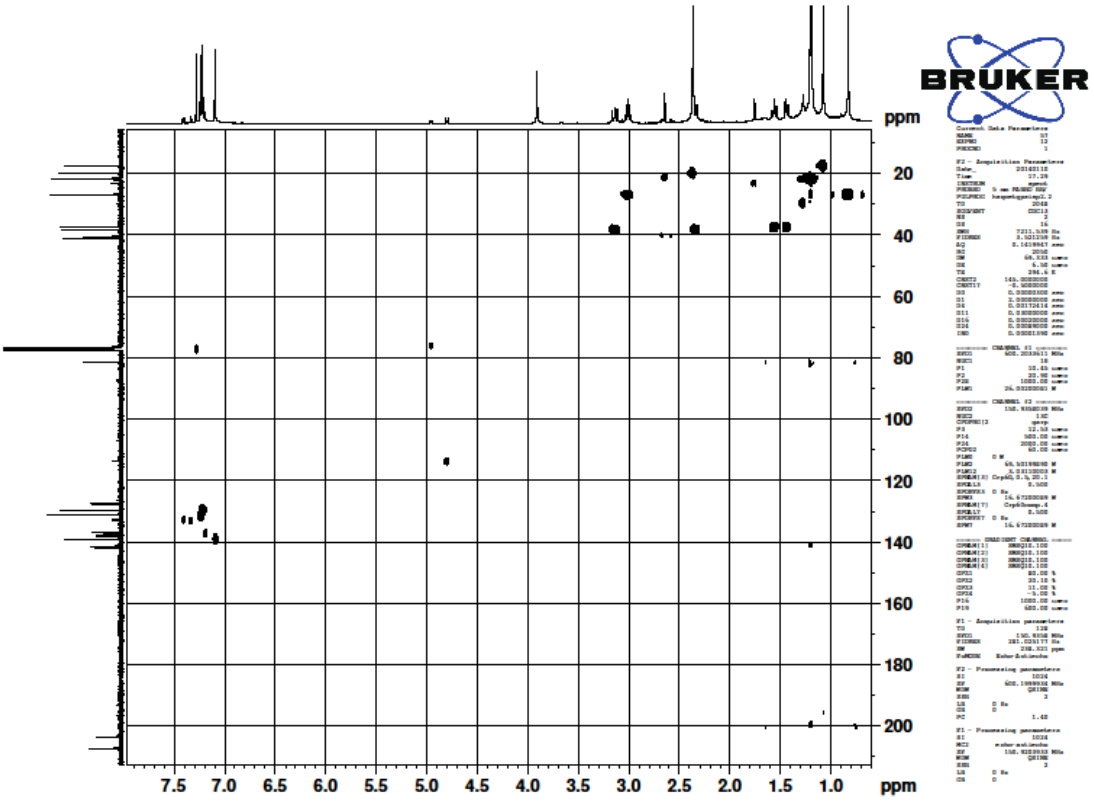


Figure S89. HMBC spectrum of compound **6** in $CDCl_3$

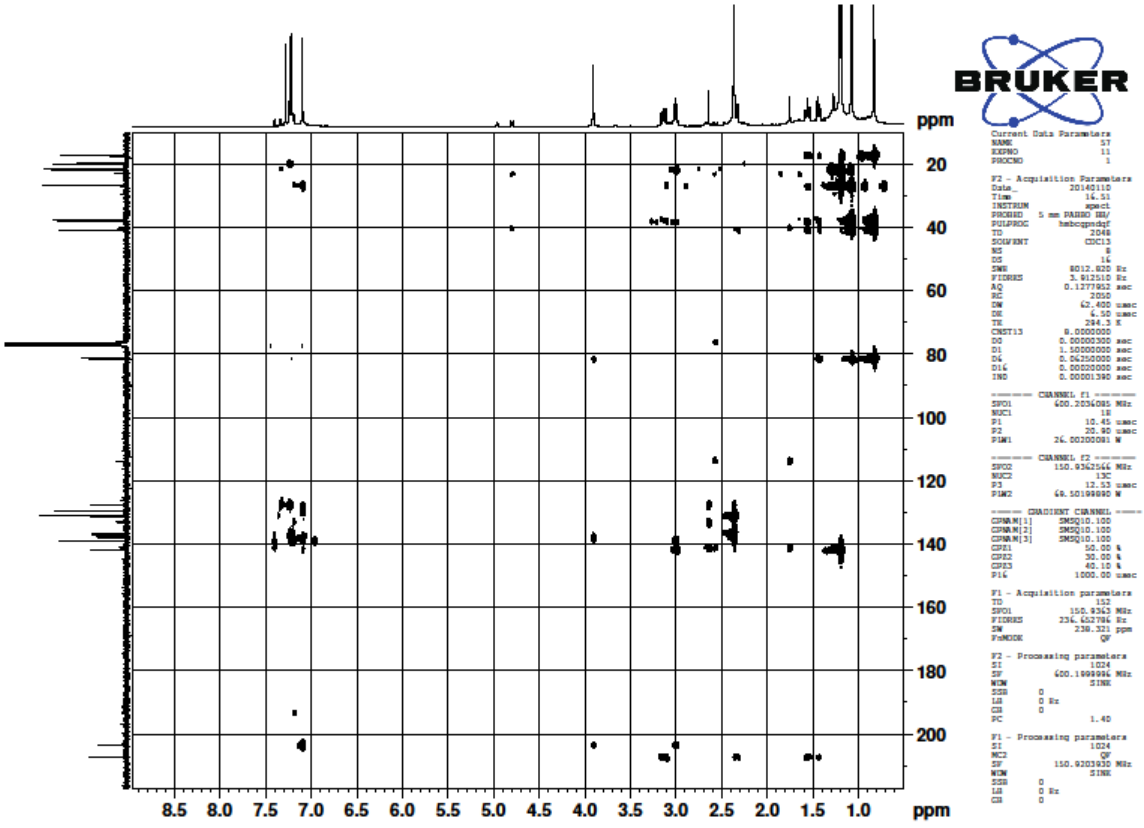


Figure S90. ^{13}C NMR spectrum of compound **7** in $CDCl_3$ (100 MHz)

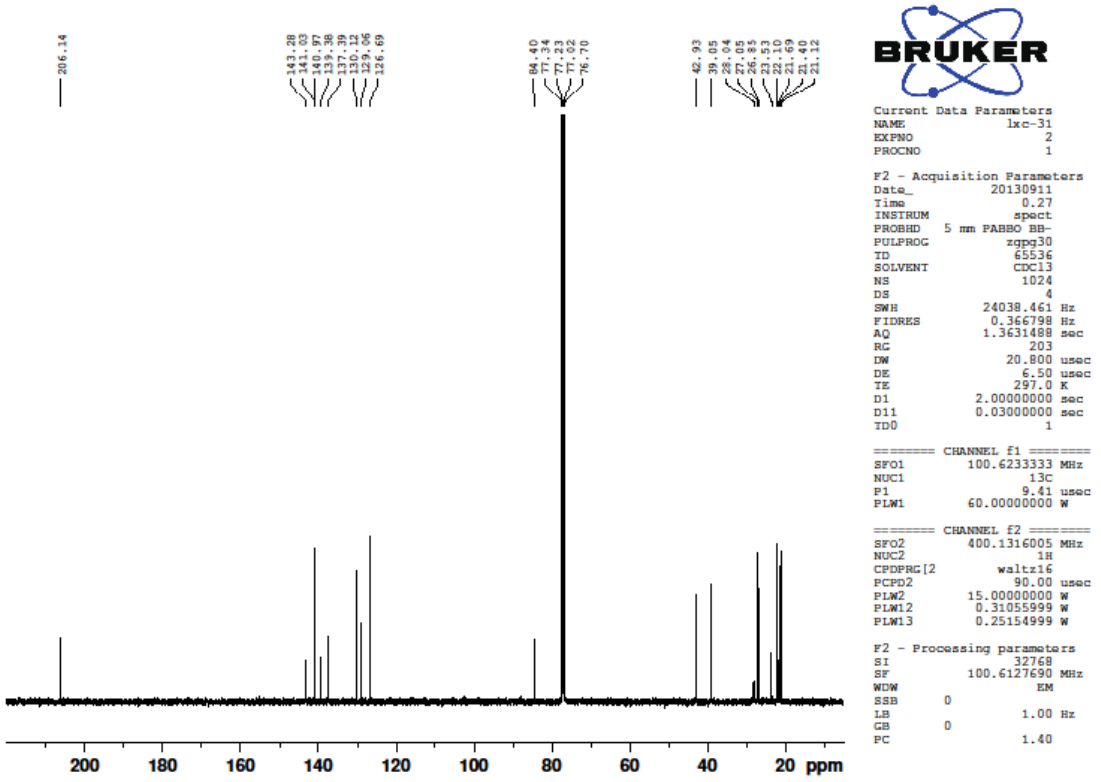


Figure S91. ^{1}H NMR spectrum of compound **7** in $CDCl_3$ (400 MHz)

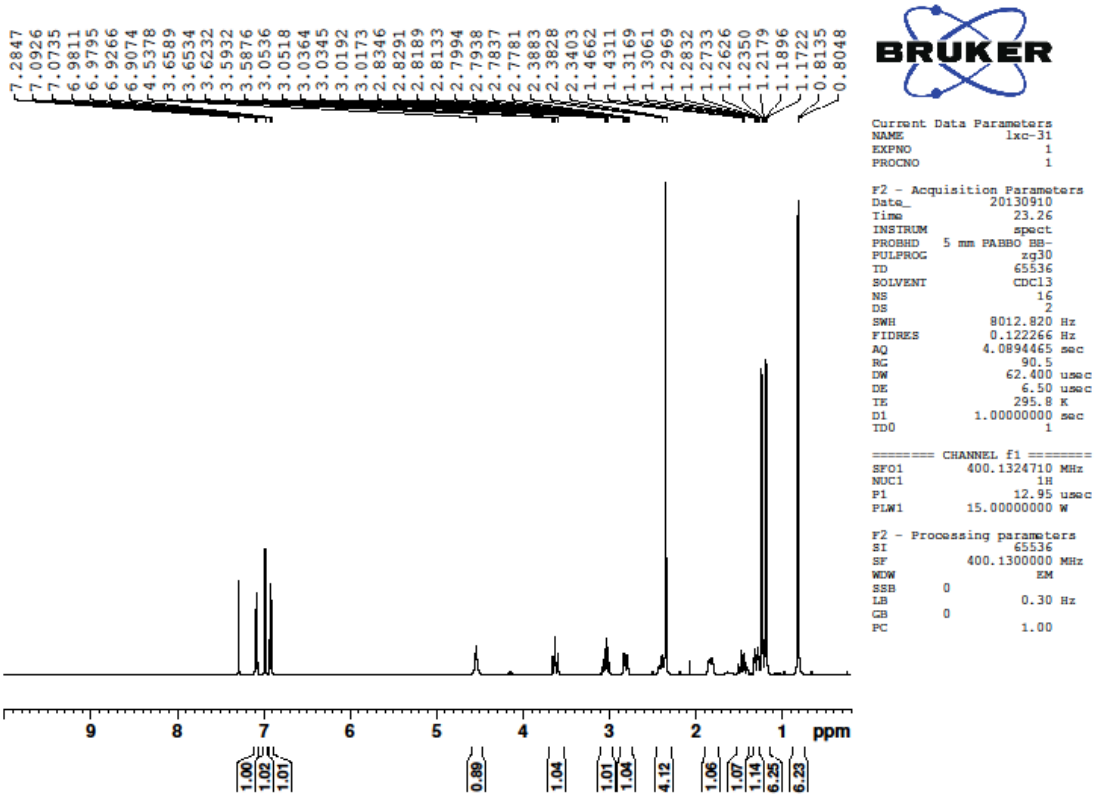


Figure S92. HSQC spectrum of compound **7** in $CDCl_3$

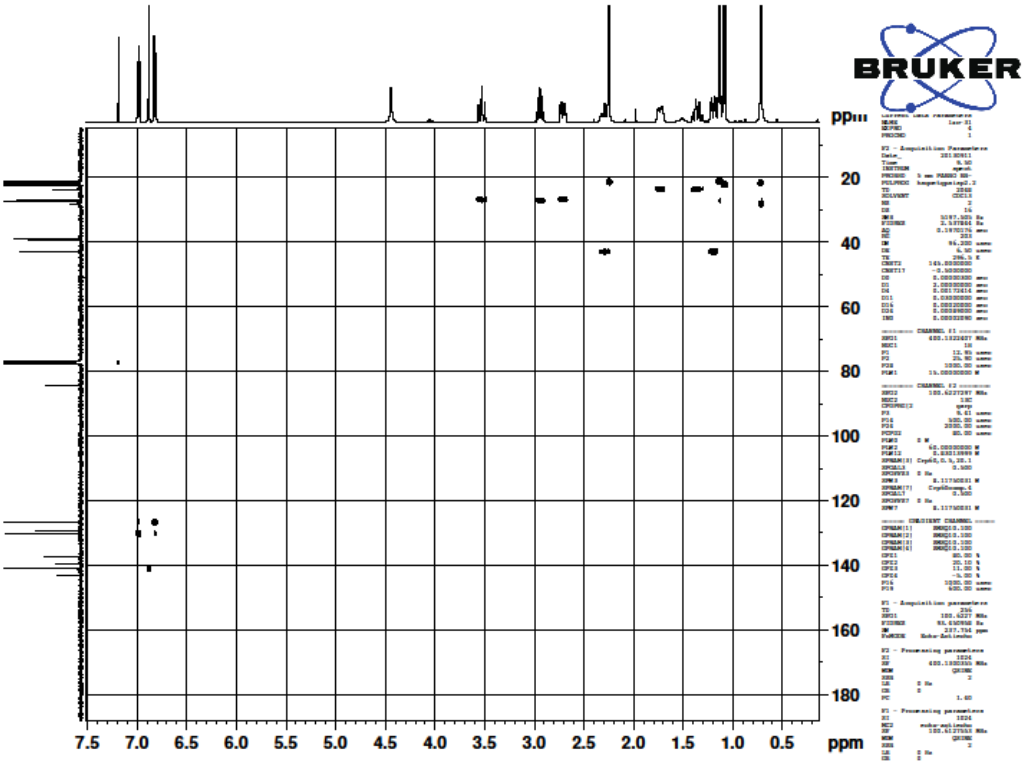


Figure S93. HMBC spectrum of compound **7** in $CDCl_3$

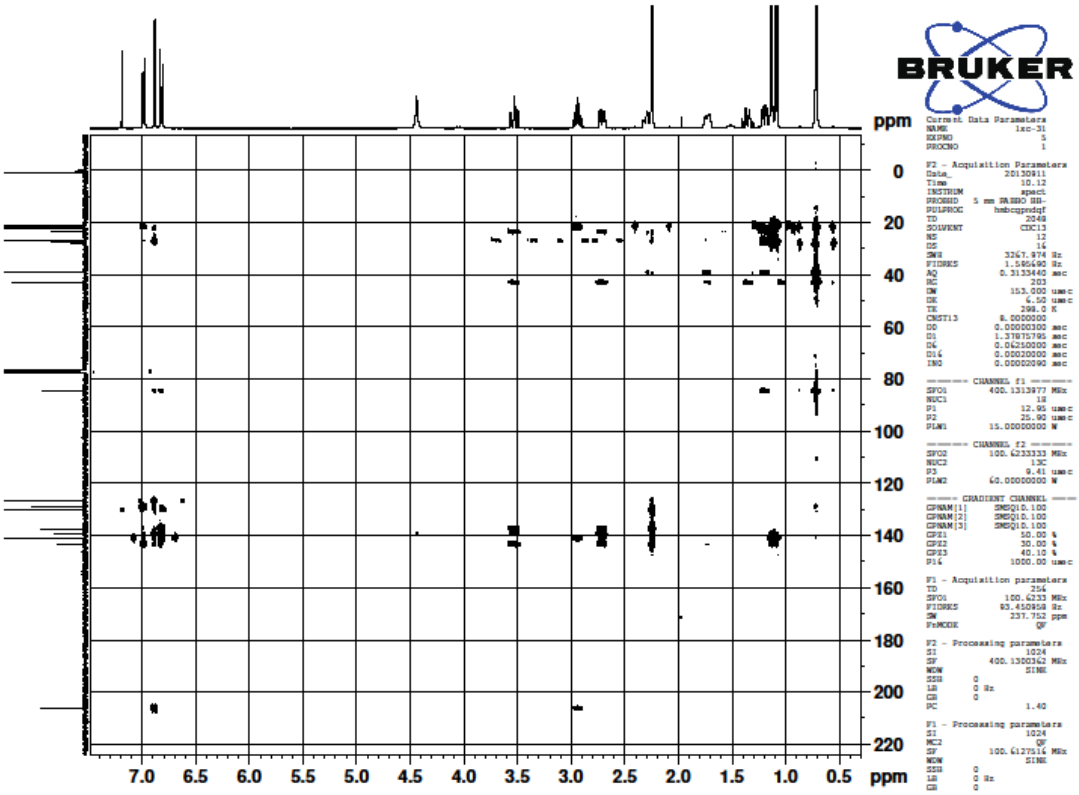


Figure S94. ^{13}C NMR spectrum of compound **8** in $CDCl_3$ (150 MHz)

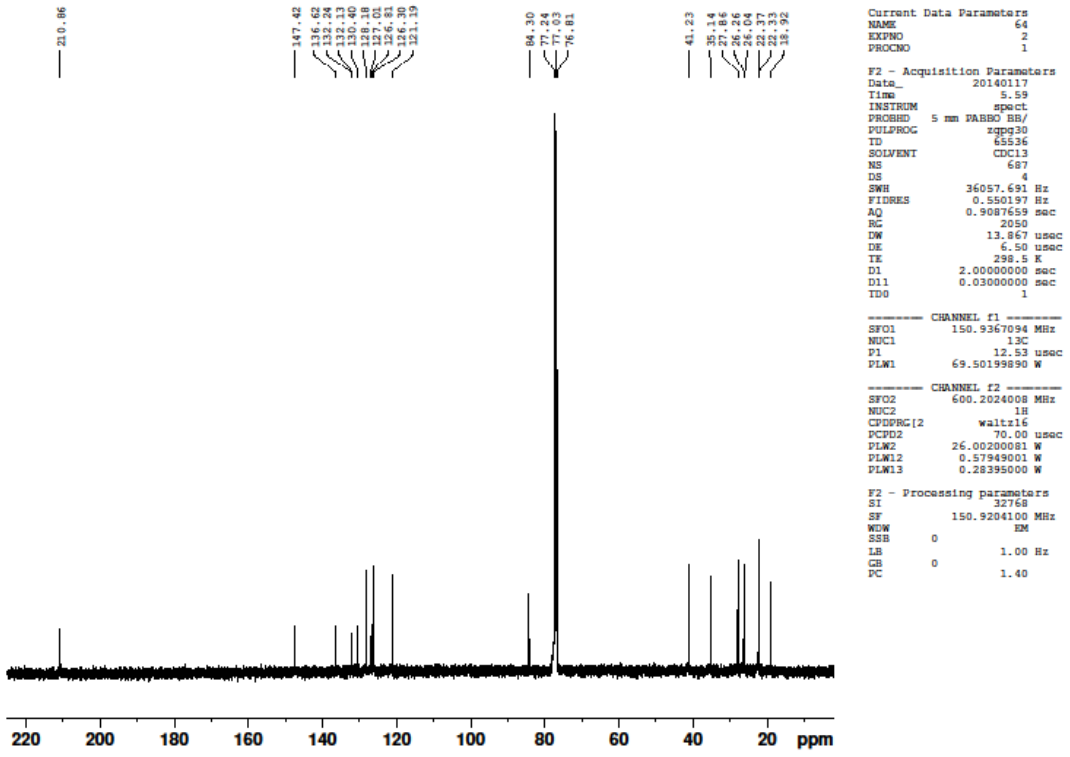


Figure S95. ^{1}H NMR spectrum of compound **8** in $CDCl_3$ (600 MHz)

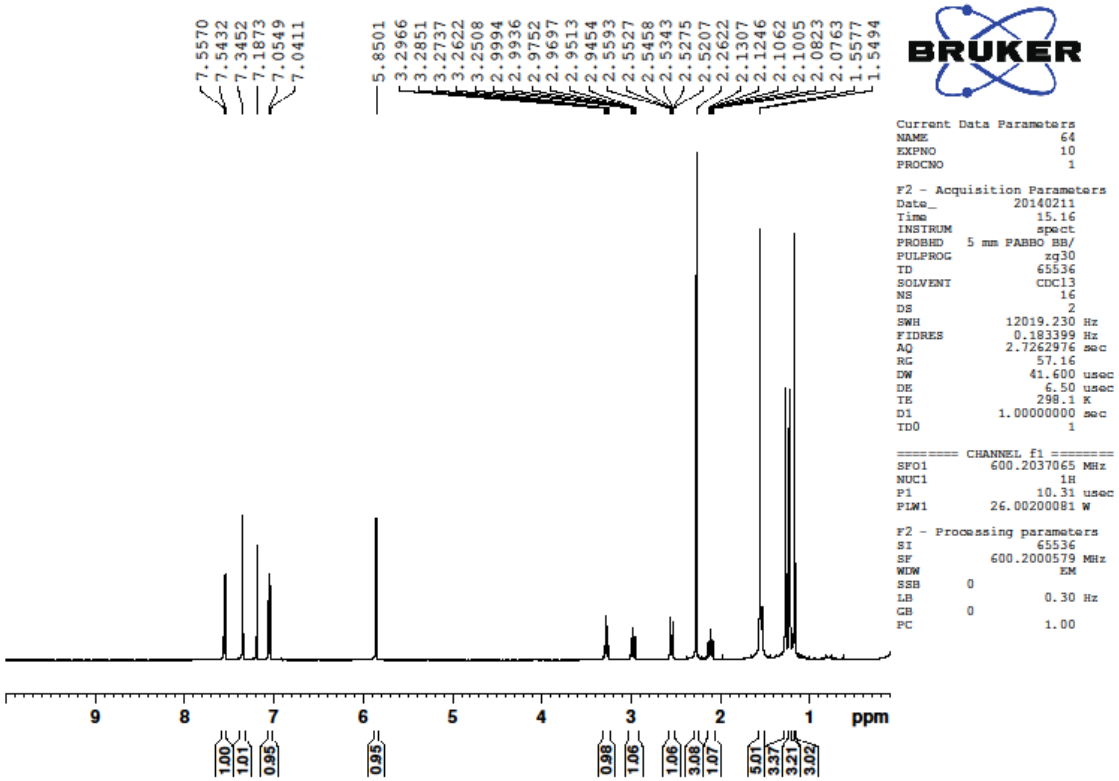


Figure S96. HSQC spectrum of compound **8** in $CDCl_3$

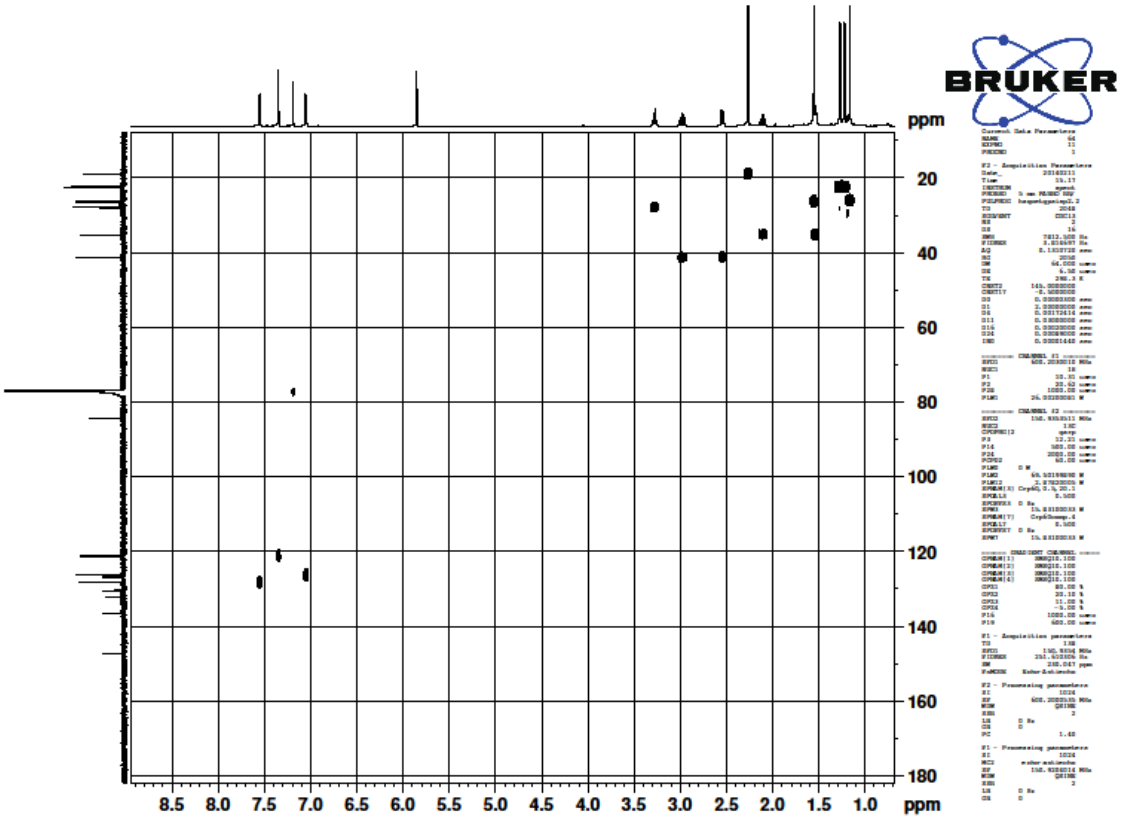


Figure S97. HMBC spectrum of compound **8** in $CDCl_3$

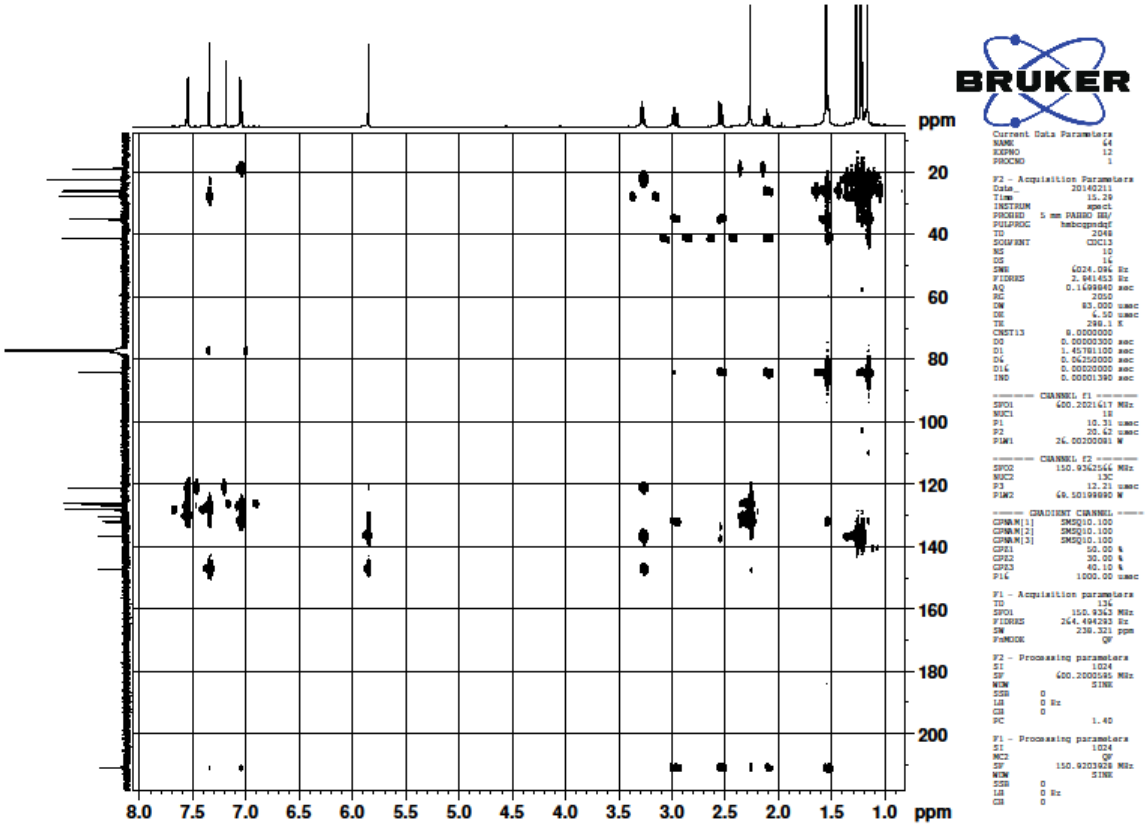


Figure S98. ^{13}C NMR spectrum of compound **9** in $CDCl_3$ (100 MHz)

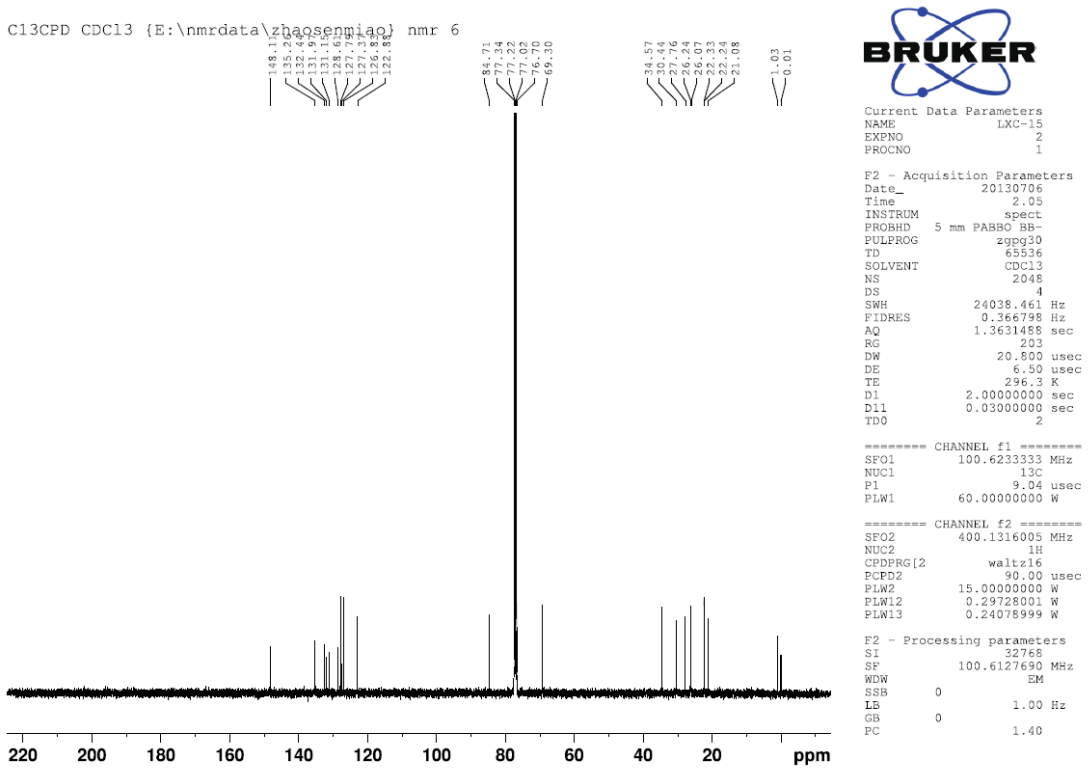


Figure S99. ^{1}H NMR spectrum of compound **9** in $CDCl_3$ (400 MHz)

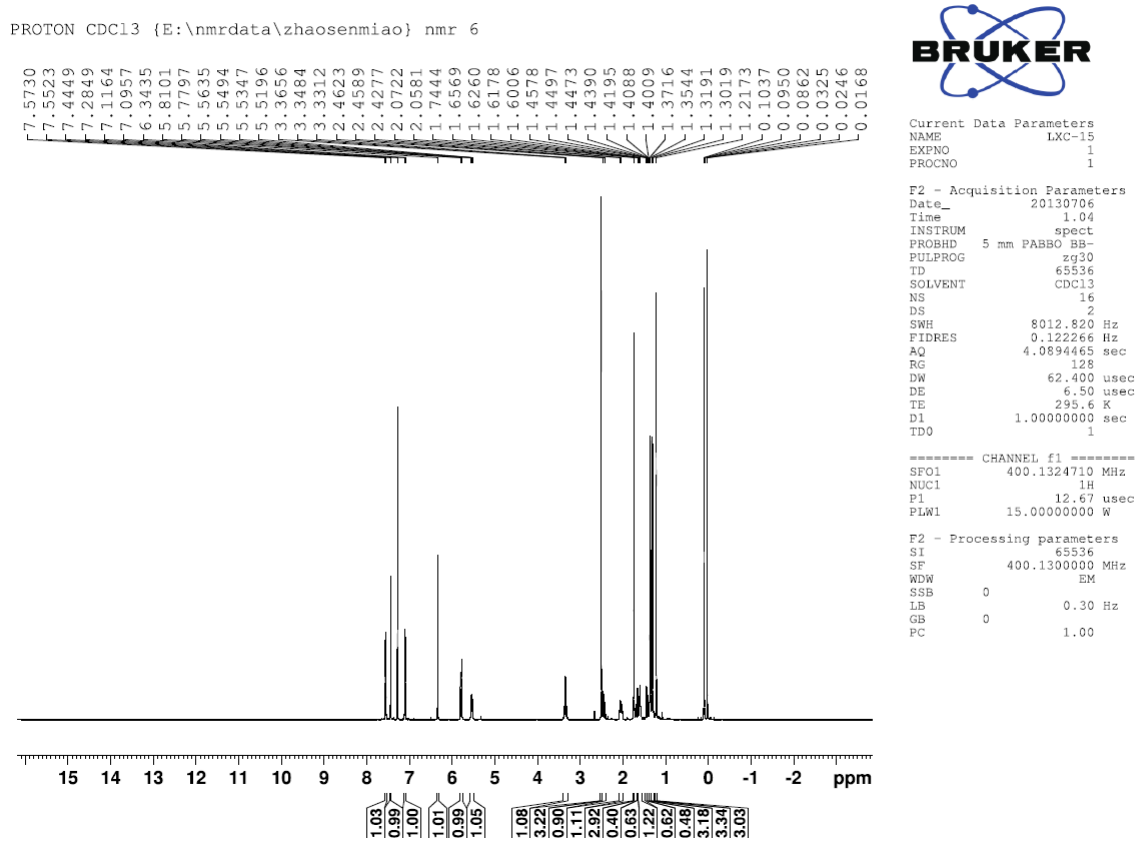


Figure S100. HSQC spectrum of compound **10** in $CDCl_3$

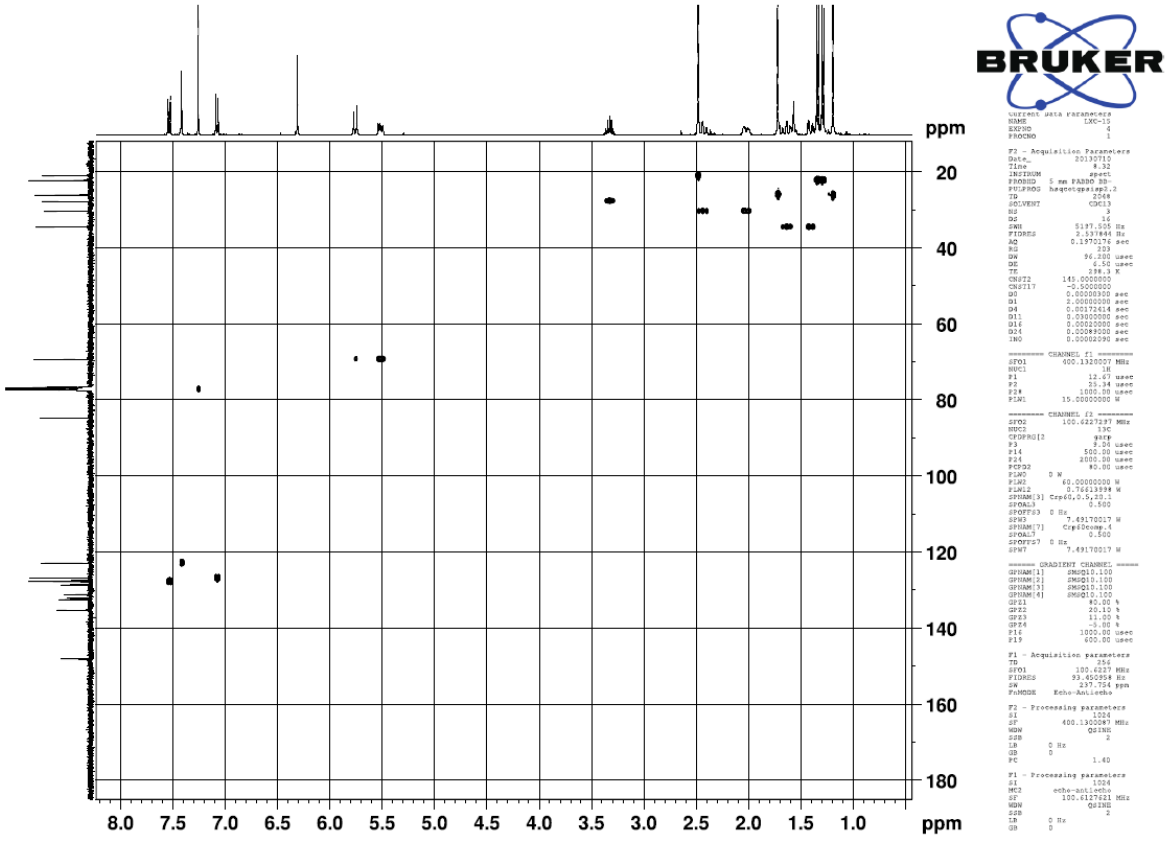


Figure S101. HMBC spectrum of compound **9** in $CDCl_3$

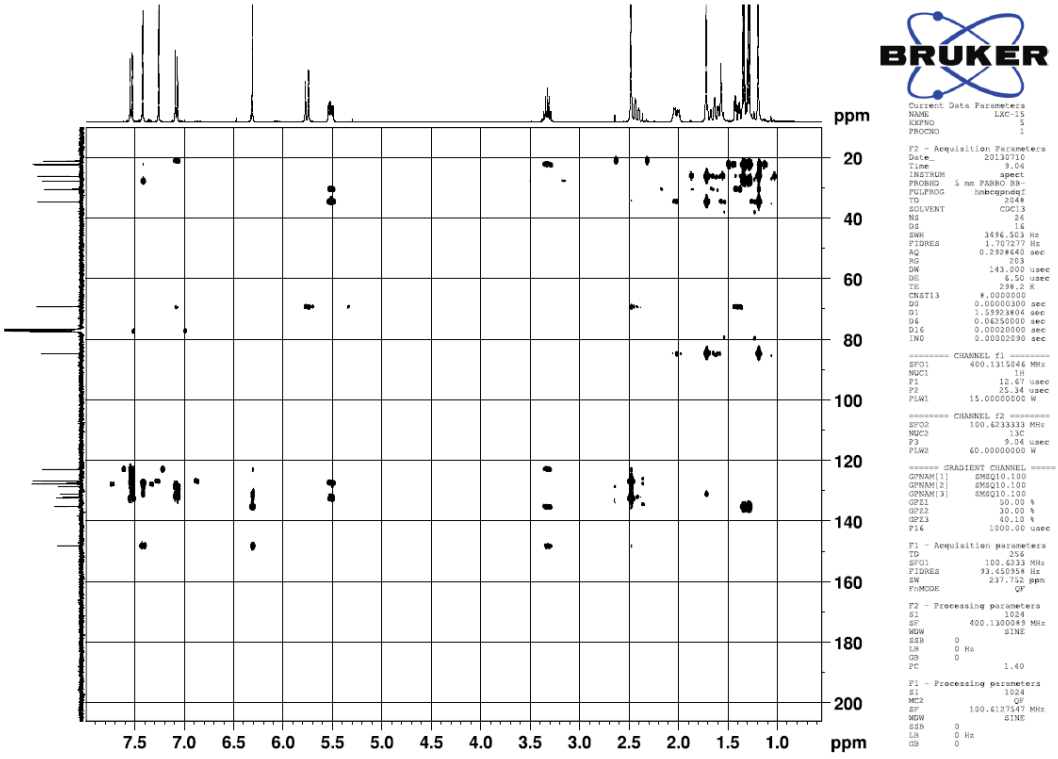


Figure S102. ^{13}C NMR spectrum of compound **10** in $CDCl_3$ (150 MHz)

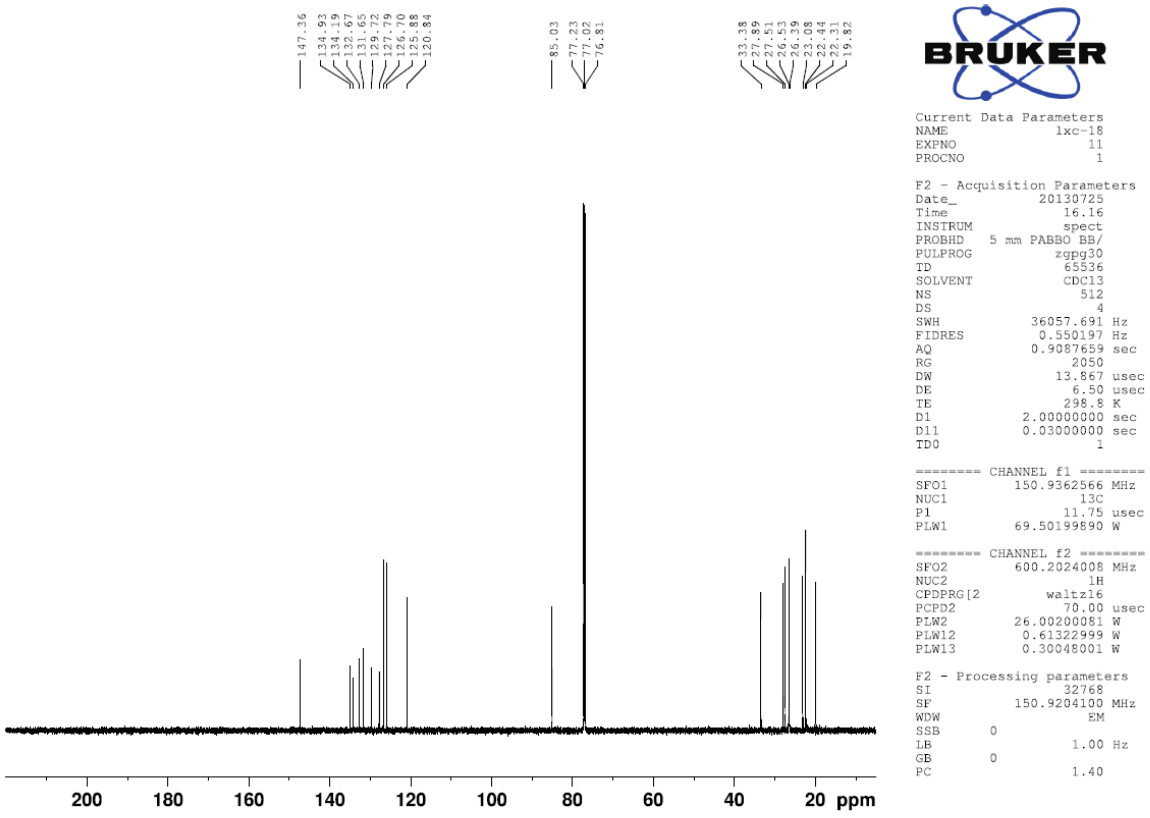


Figure S103. ^{1}H NMR spectrum of compound **10** in $CDCl_3$ (600 MHz)

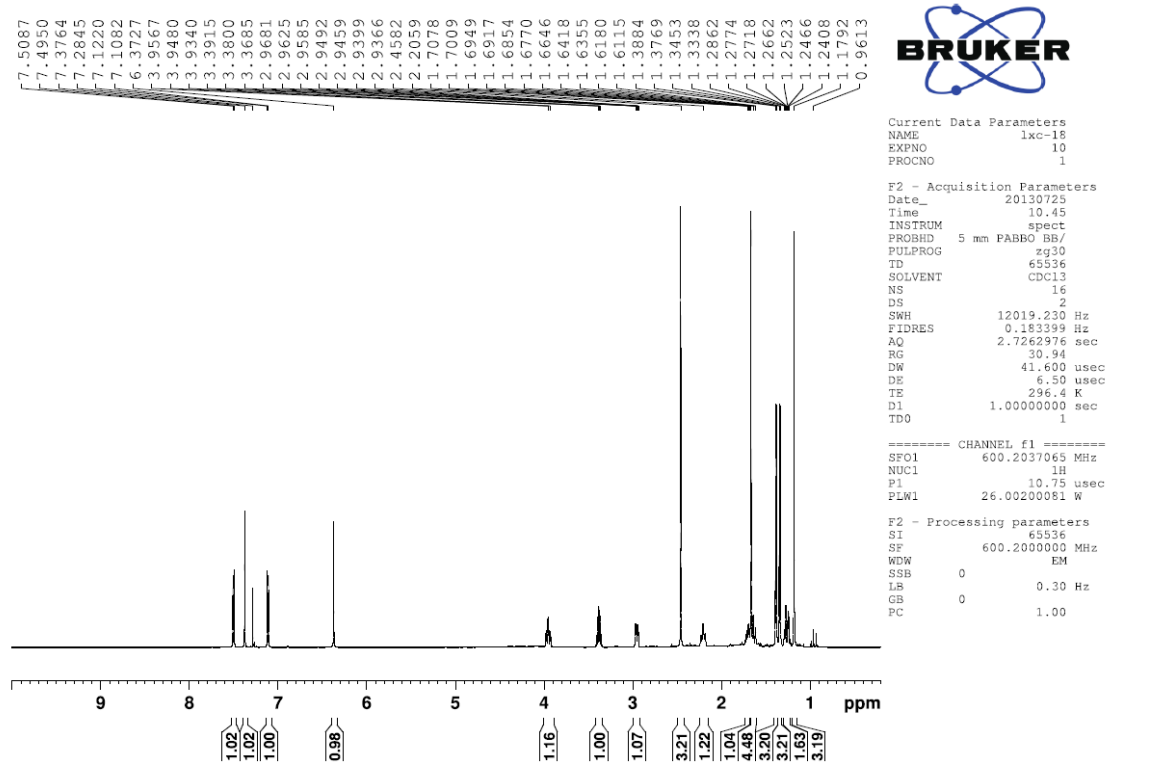


Figure S104. HSQC spectrum of compound **10** in $CDCl_3$

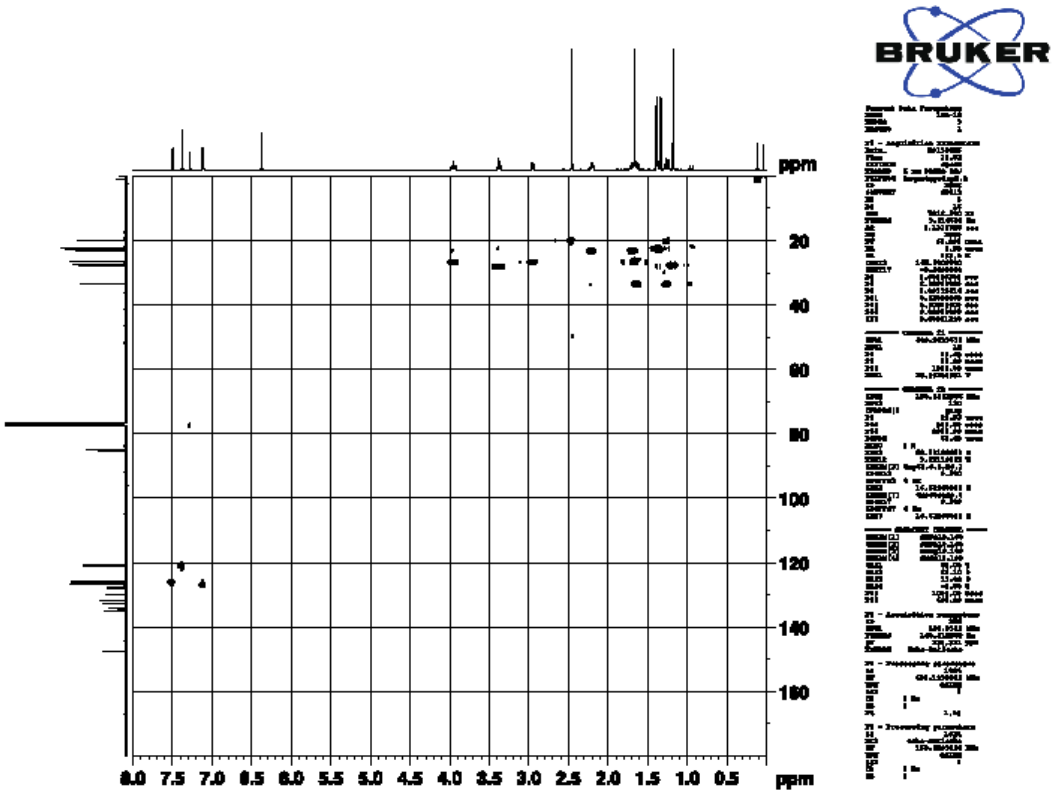


Figure S105. HMBC spectrum of compound **10** in $CDCl_3$

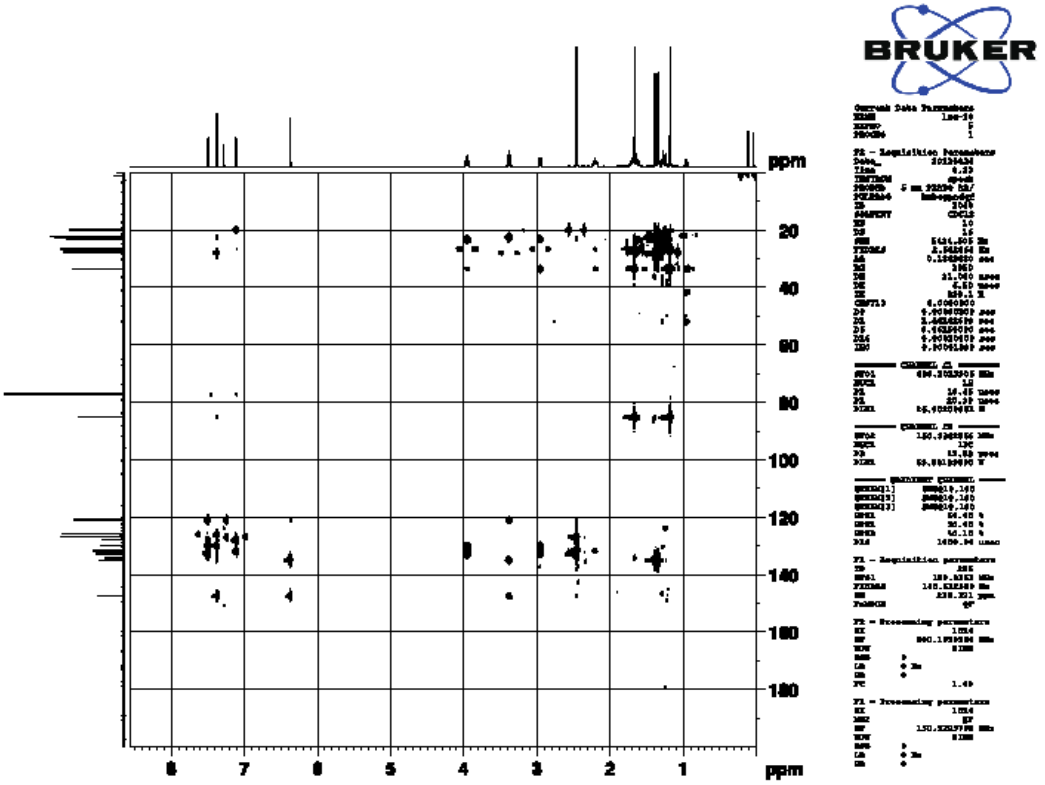


Figure S106. ^{13}C NMR spectrum of compound **13** in DMSO (100 MHz)

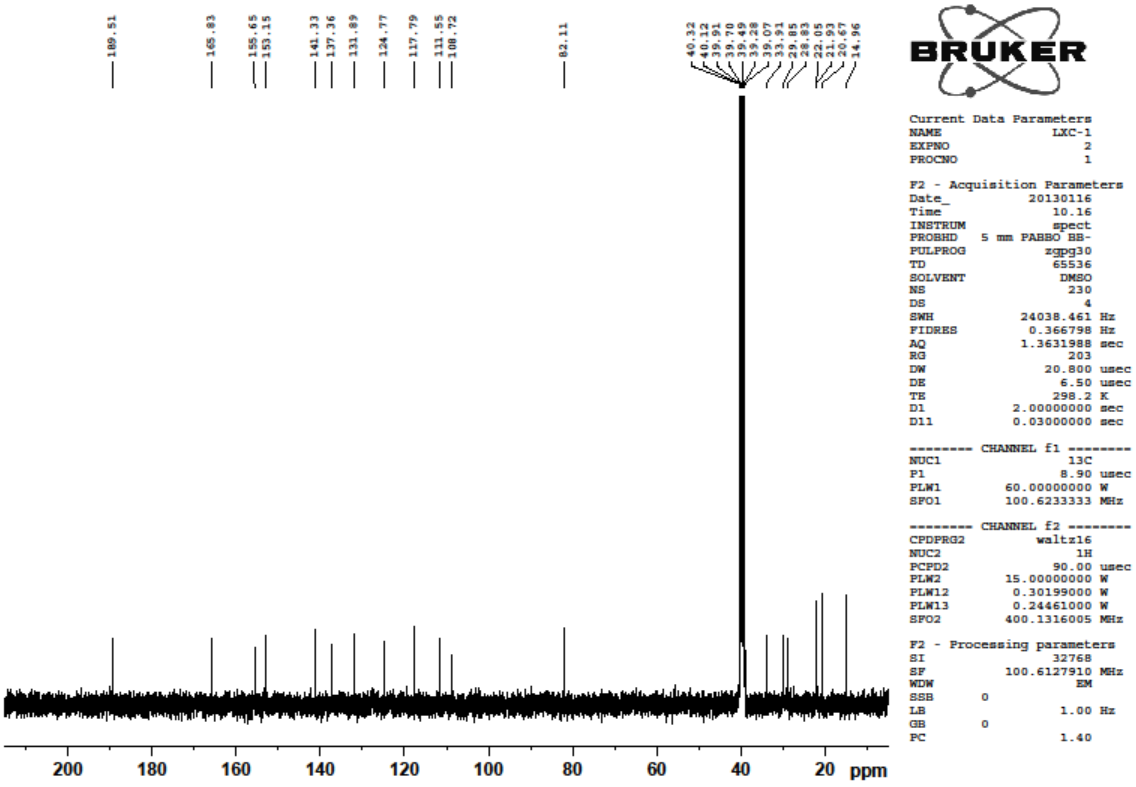


Figure S107. ^{1}H NMR spectrum of compound **13** in DMSO (400 MHz)

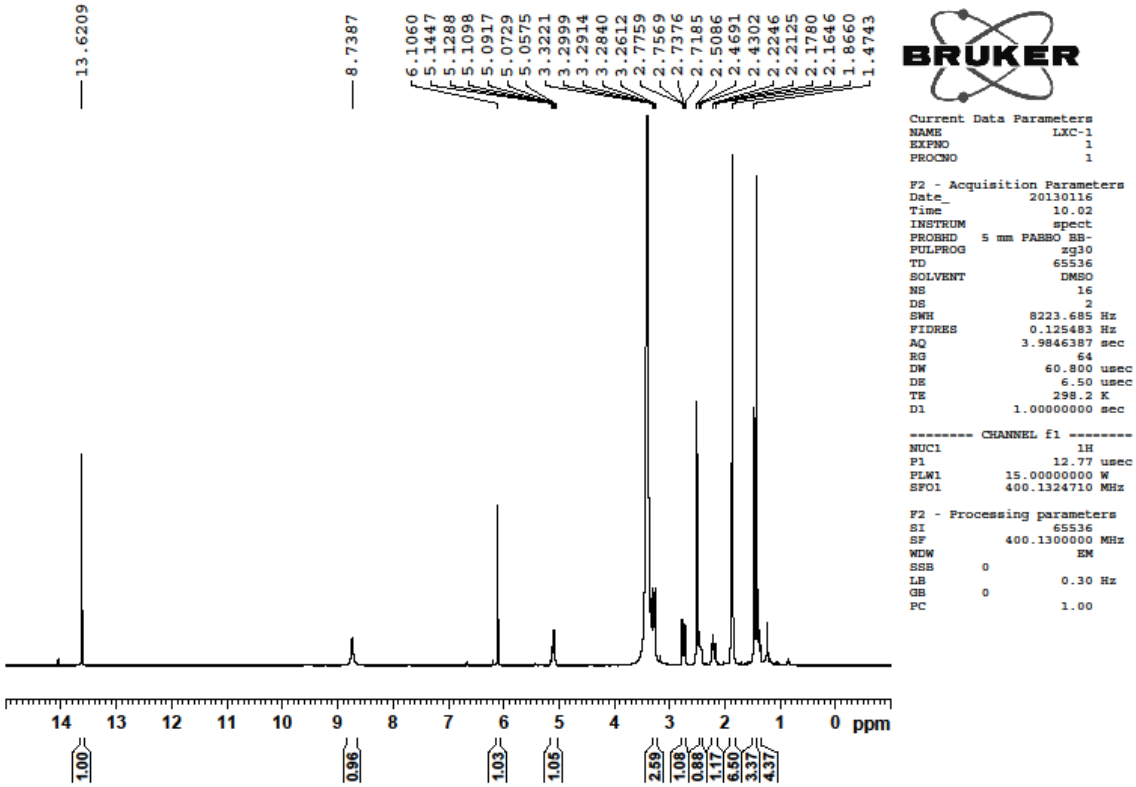


Figure S108. HSQC spectrum of compound **13** in DMSO

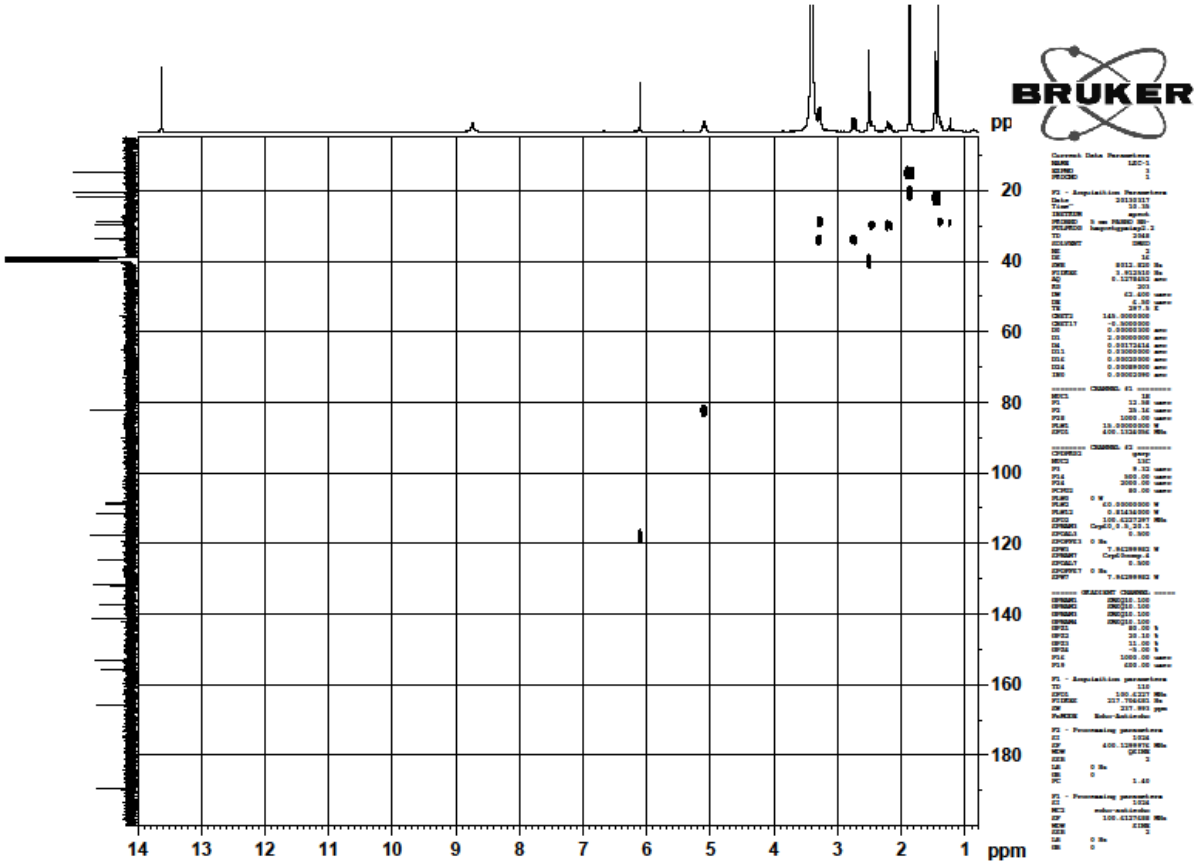


Figure S109. HMBC spectrum of compound **13** in DMSO

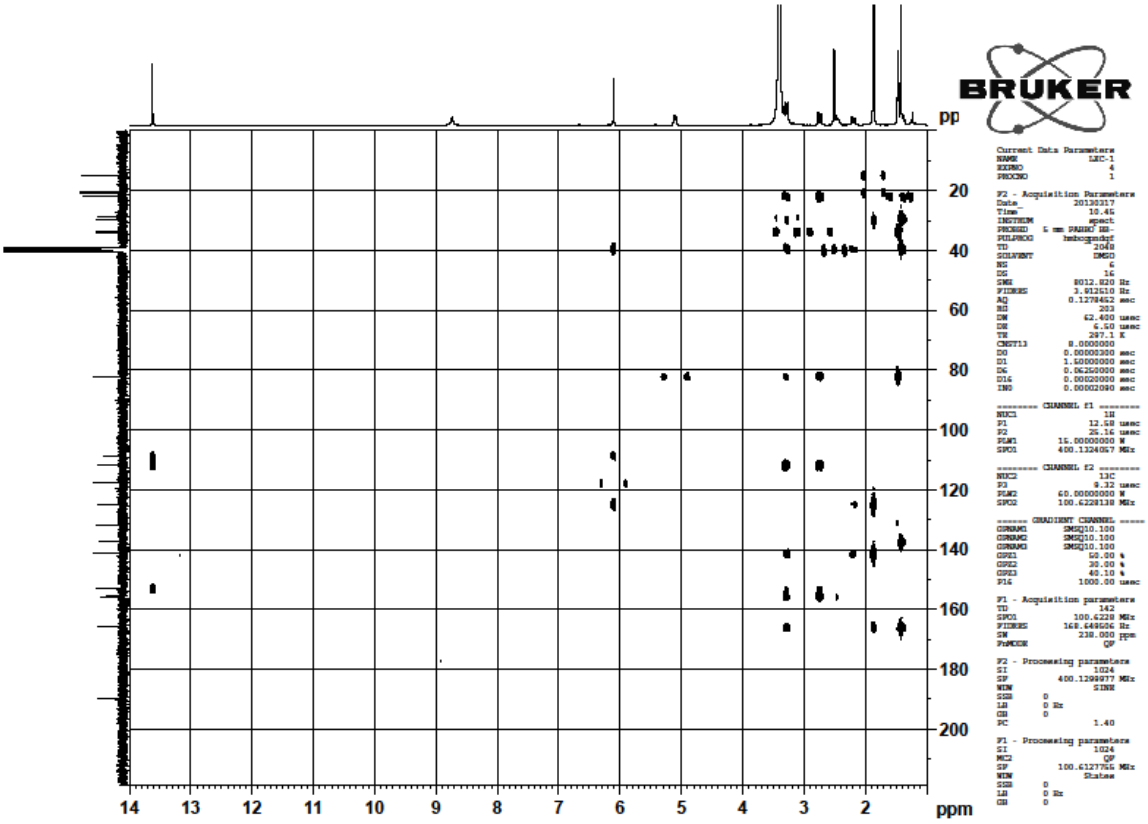


Figure S110. ^{13}C NMR spectrum of compound **14** in $CDCl_3$ (150 MHz)

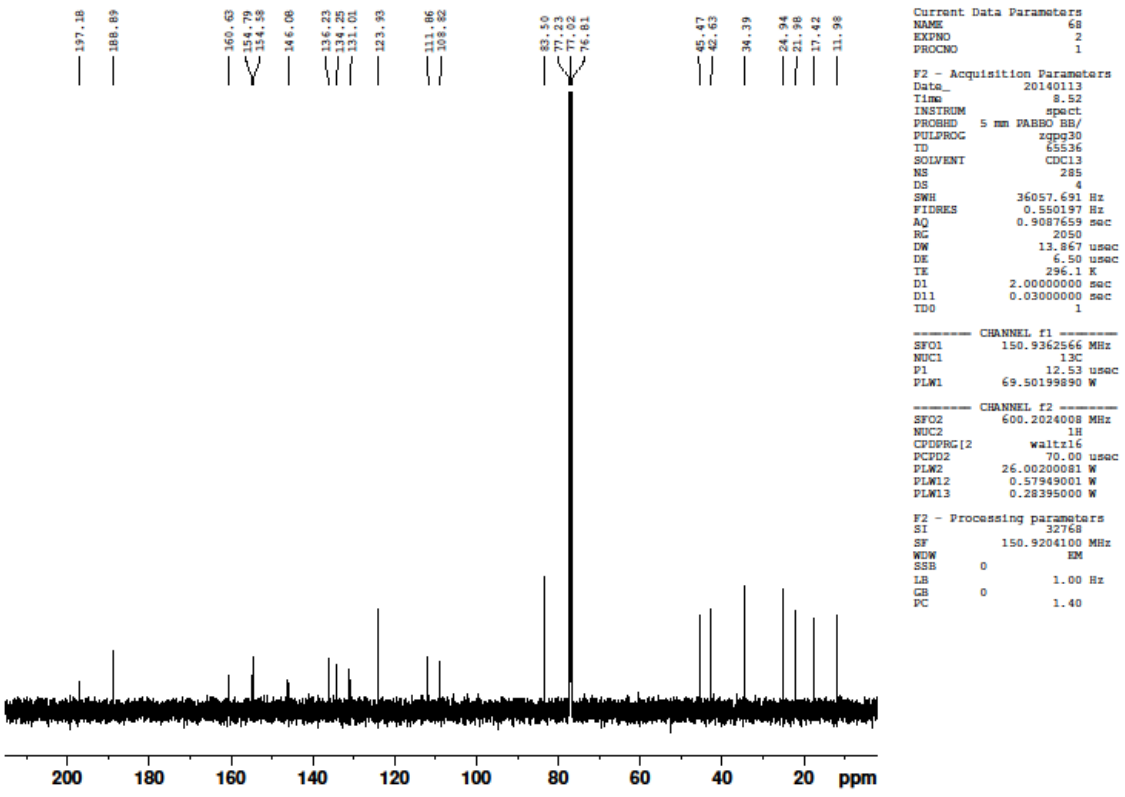


Figure S111. ^{1}H NMR spectrum of compound **14** in $CDCl_3$ (600 MHz)

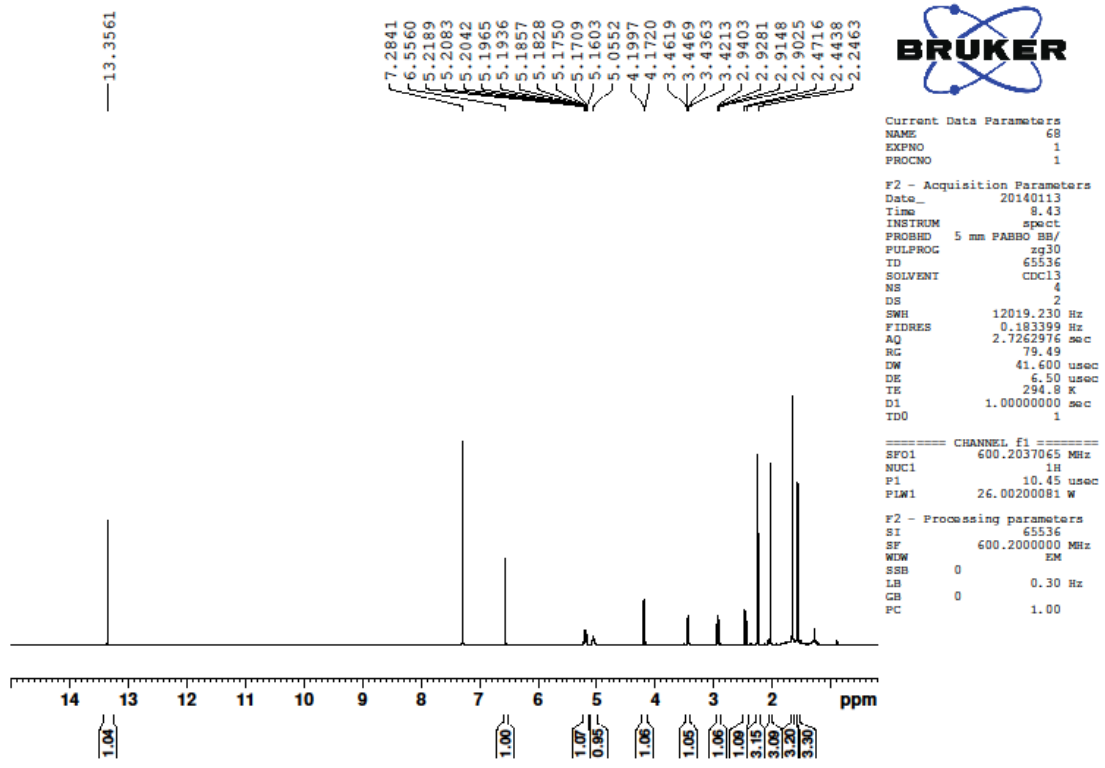


Figure S112. HSQC spectrum of compound **14** in $CDCl_3$

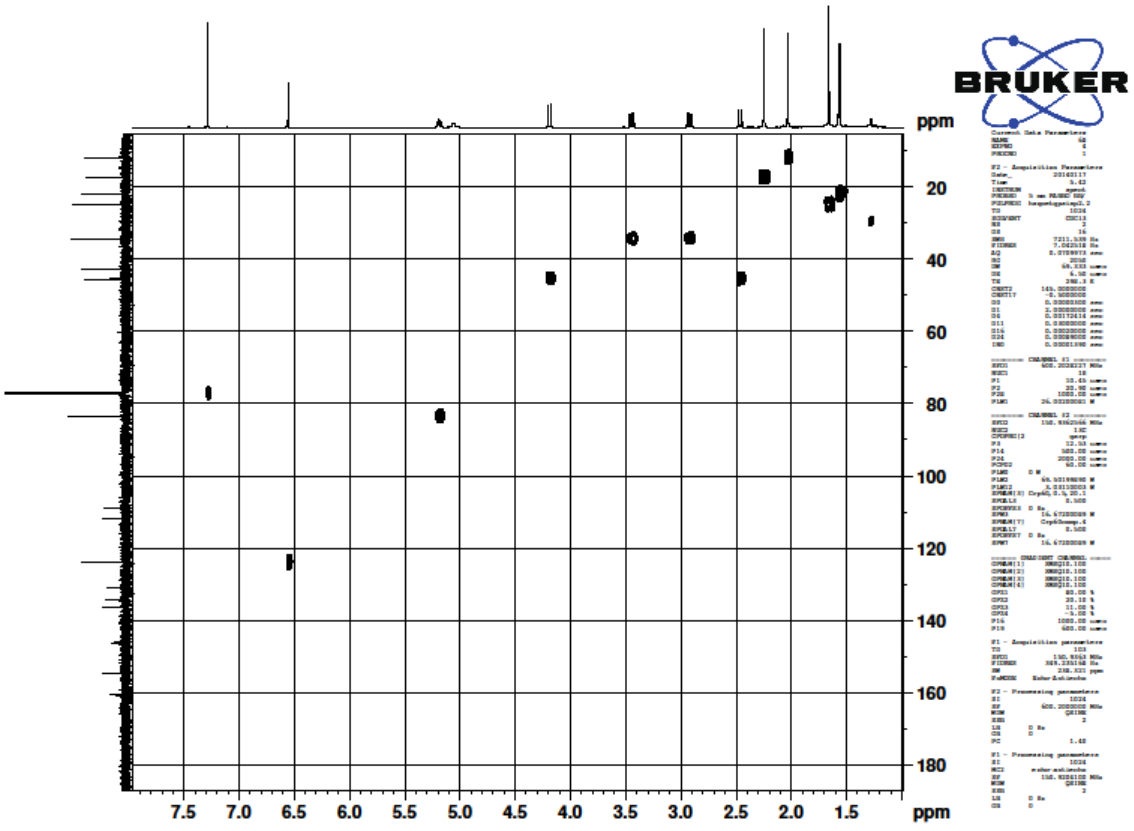


Figure S113. HMBC spectrum of compound **14** in $CDCl_3$

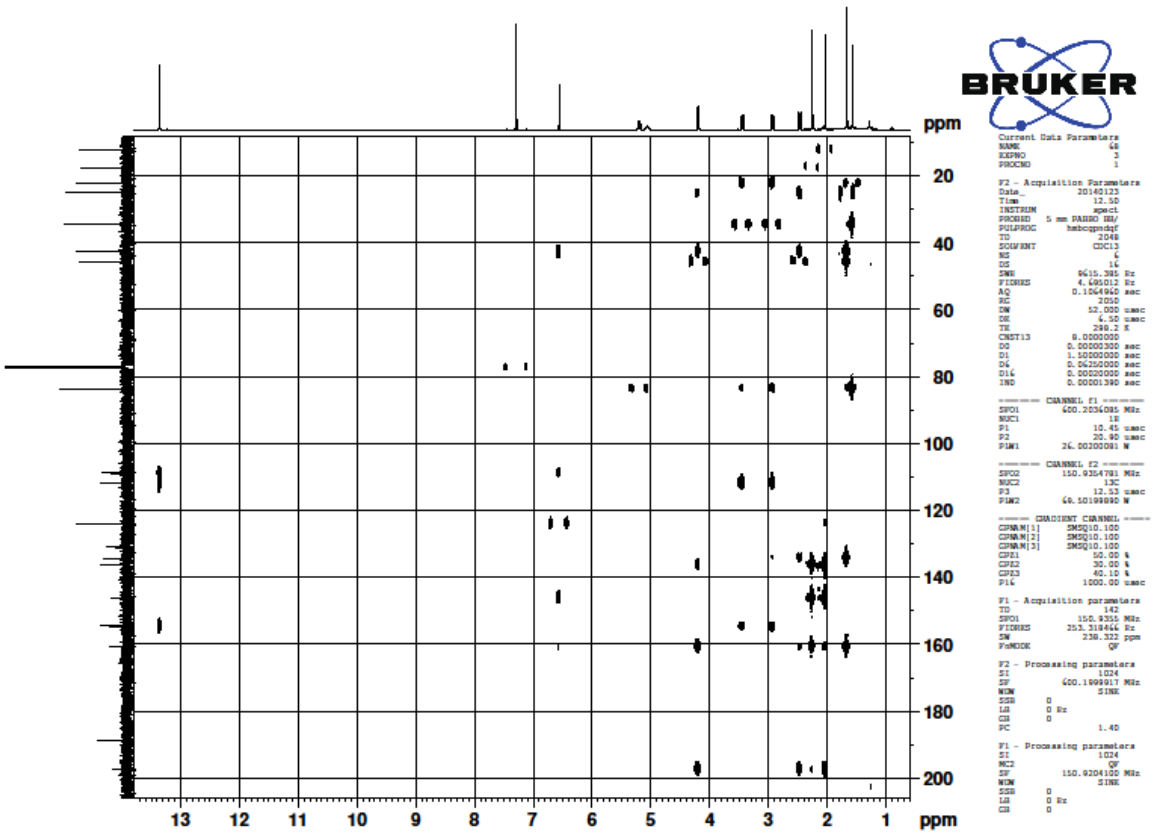


Figure S114. ^{13}C NMR spectrum of compound **15** in CD_3OD (150 MHz)

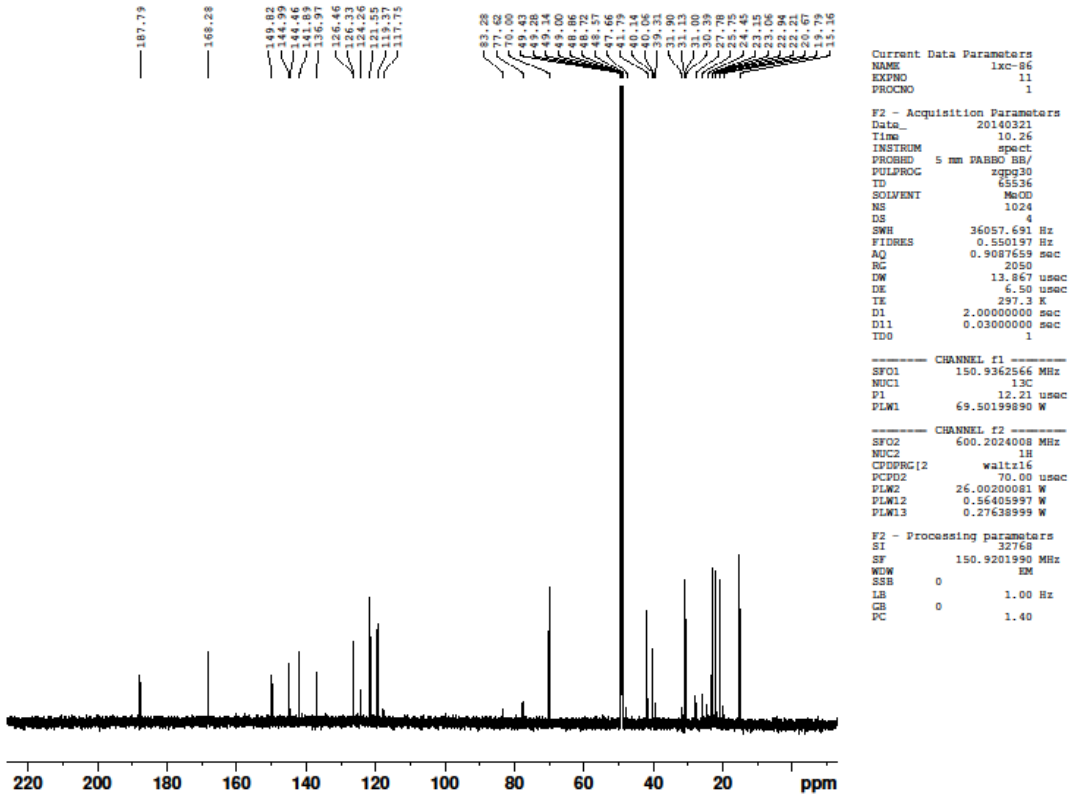


Figure S115. ^{1}H NMR spectrum of compound **15** in CD_3OD (600 MHz)

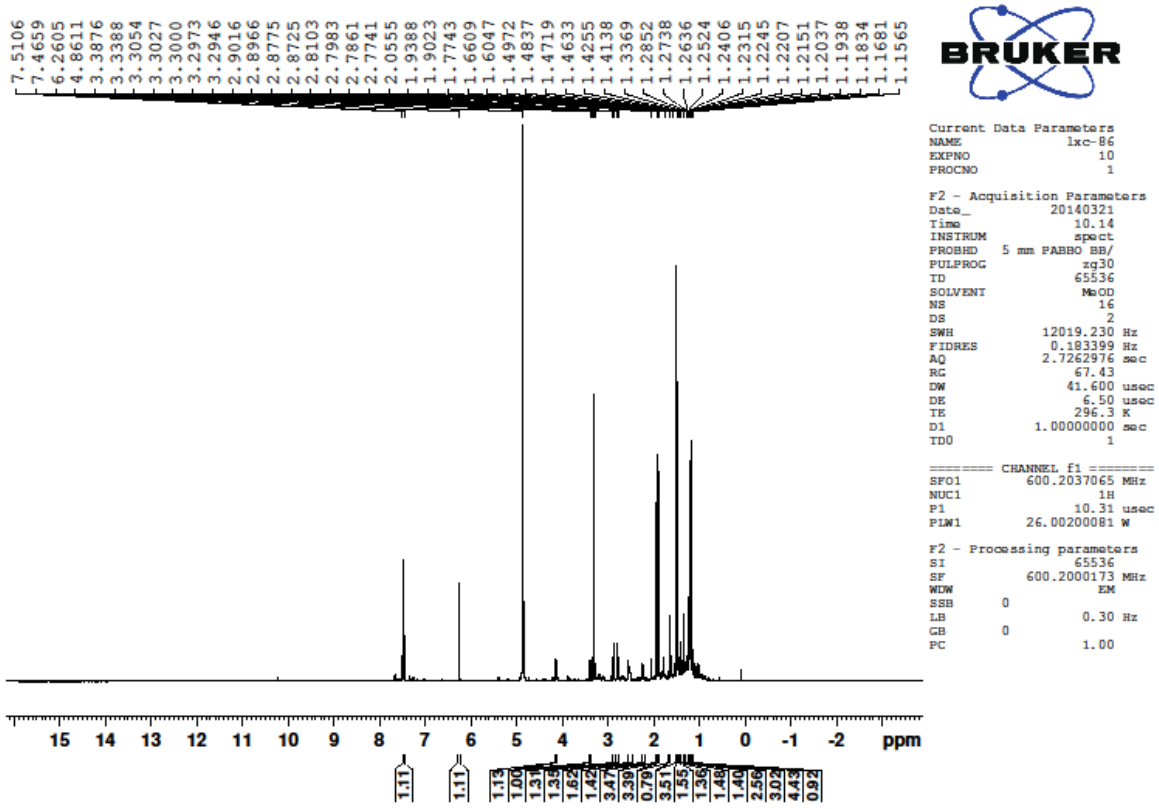


Figure S116. HSQC spectrum of compound **15** in CD_3OD

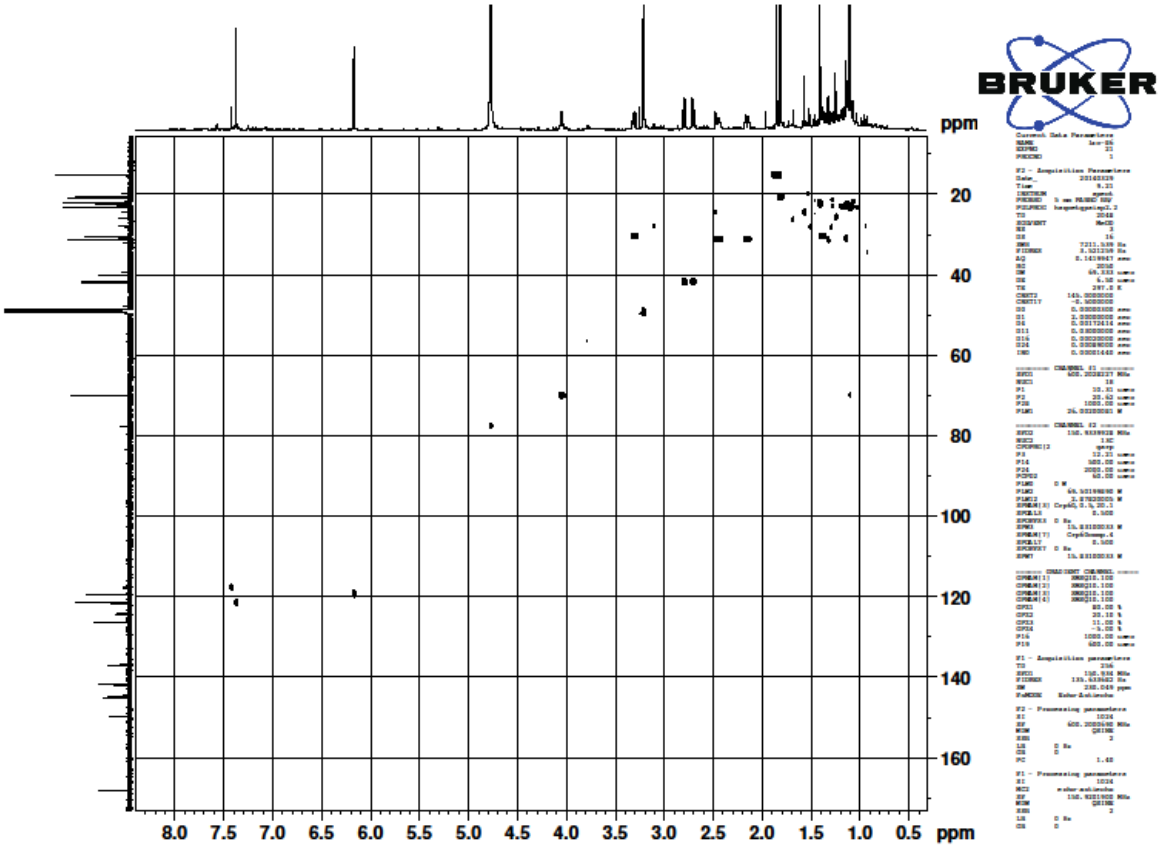


Figure S117. HMBC spectrum of compound **15** in CD_3OD

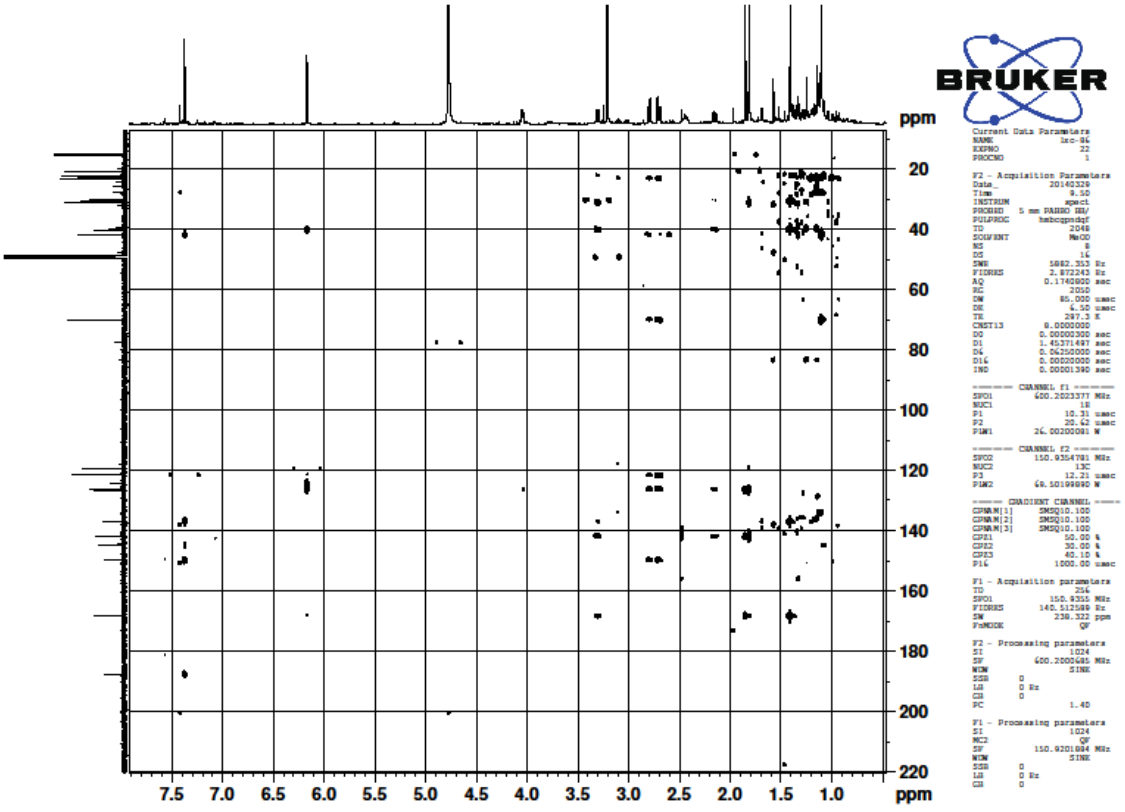


Figure S118. ^{13}C NMR spectrum of compound **20** in DMSO (100 MHz)

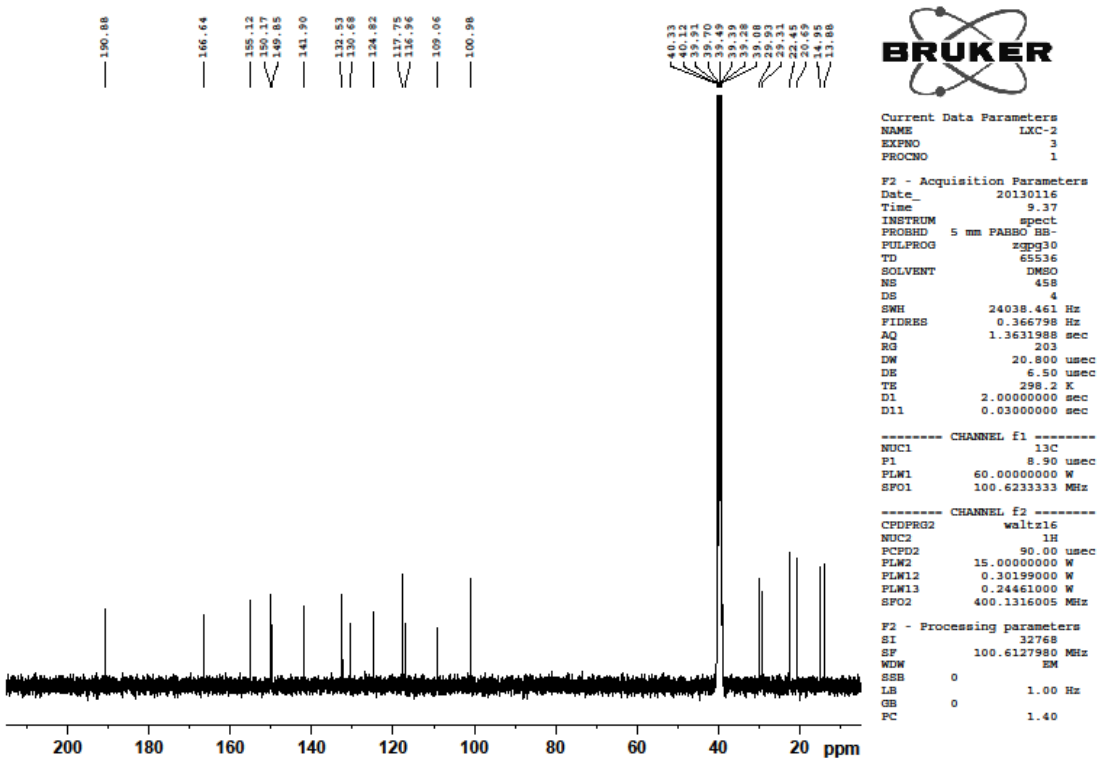


Figure S119. ^{1}H NMR spectrum of compound **20** in DMSO (400 MHz)

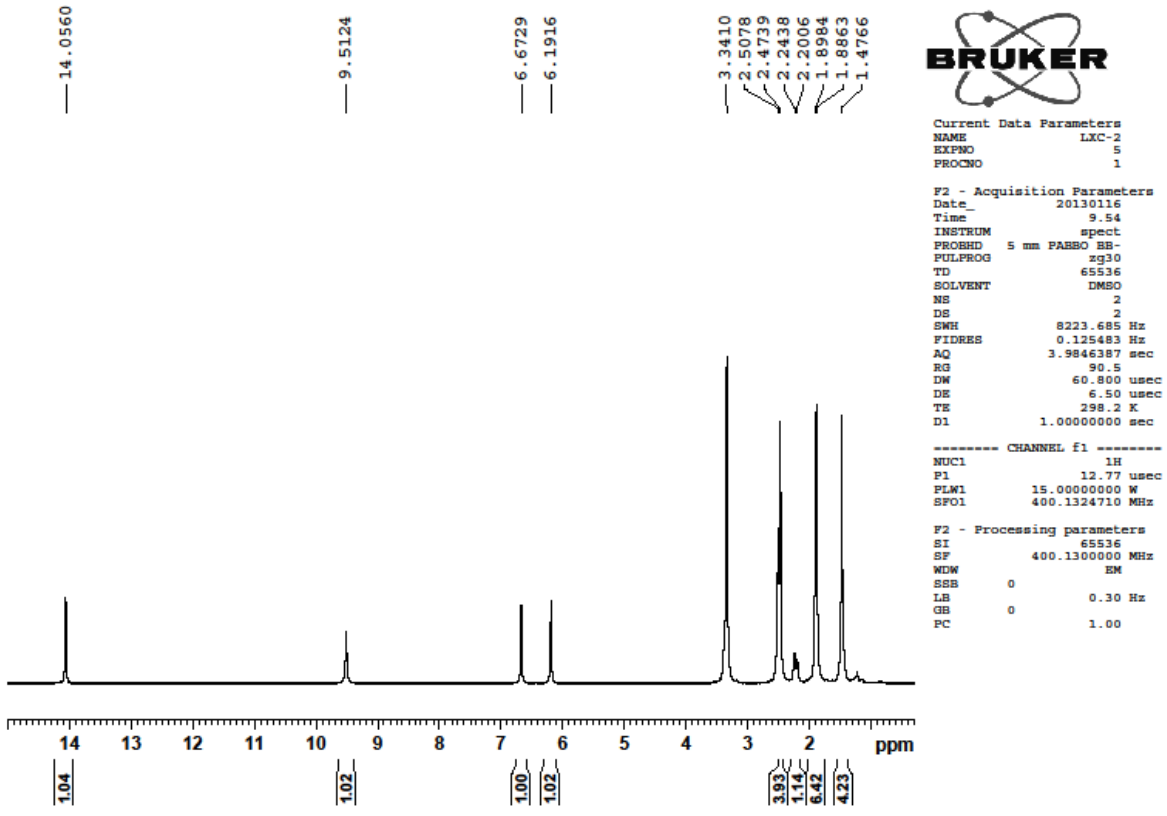


Figure S120. HSQC spectrum of compound **20** in DMSO

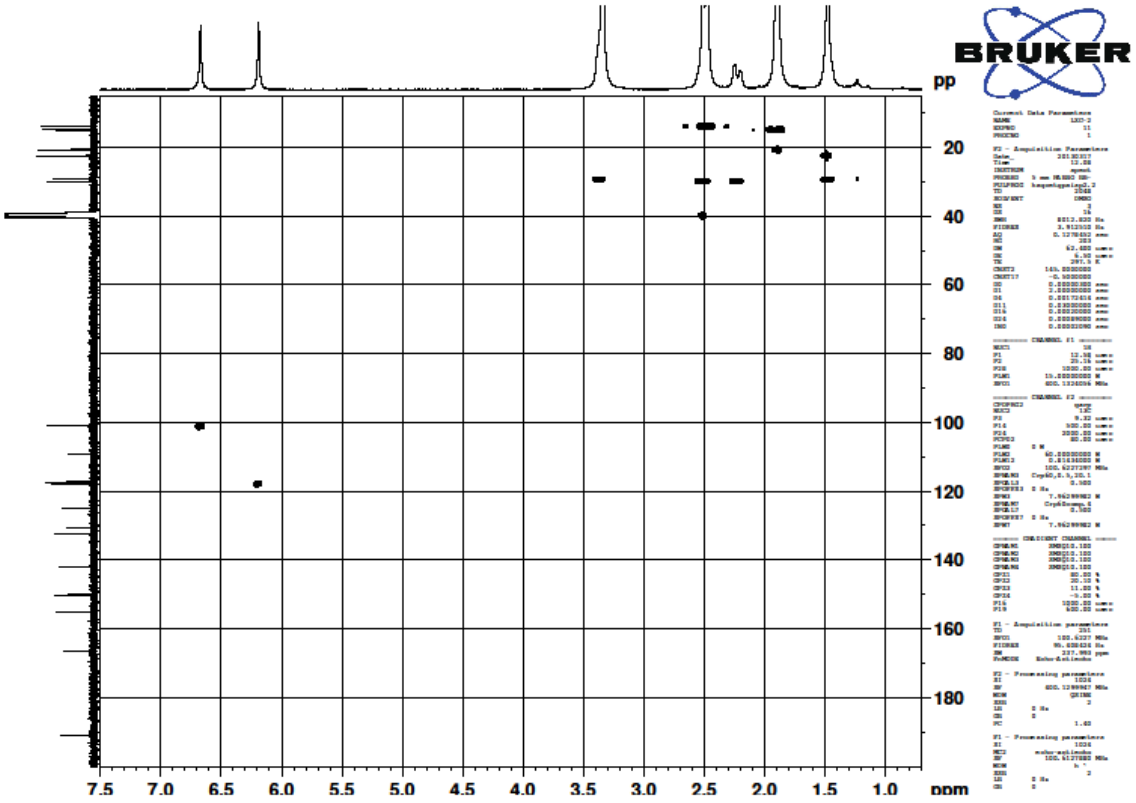


Figure S121. HMBC spectrum of compound **20** in DMSO

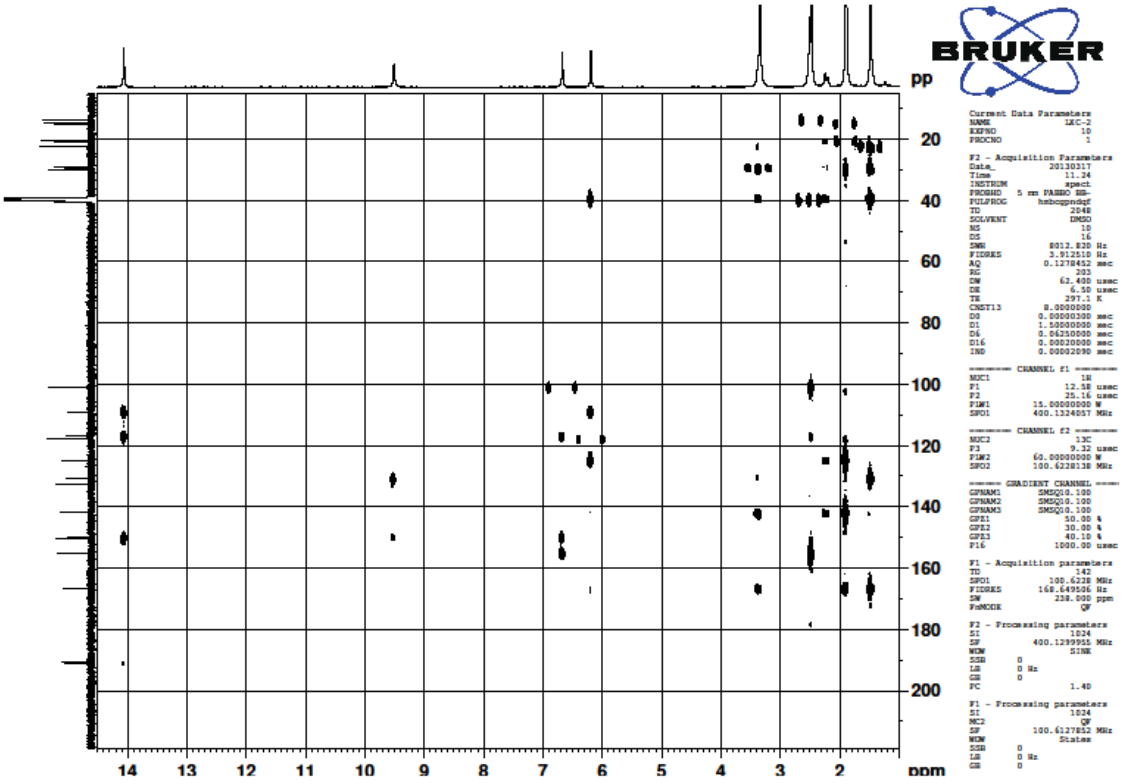


Figure S122. ^{13}C NMR spectrum of compound **21** in CD_3OD (150 MHz)

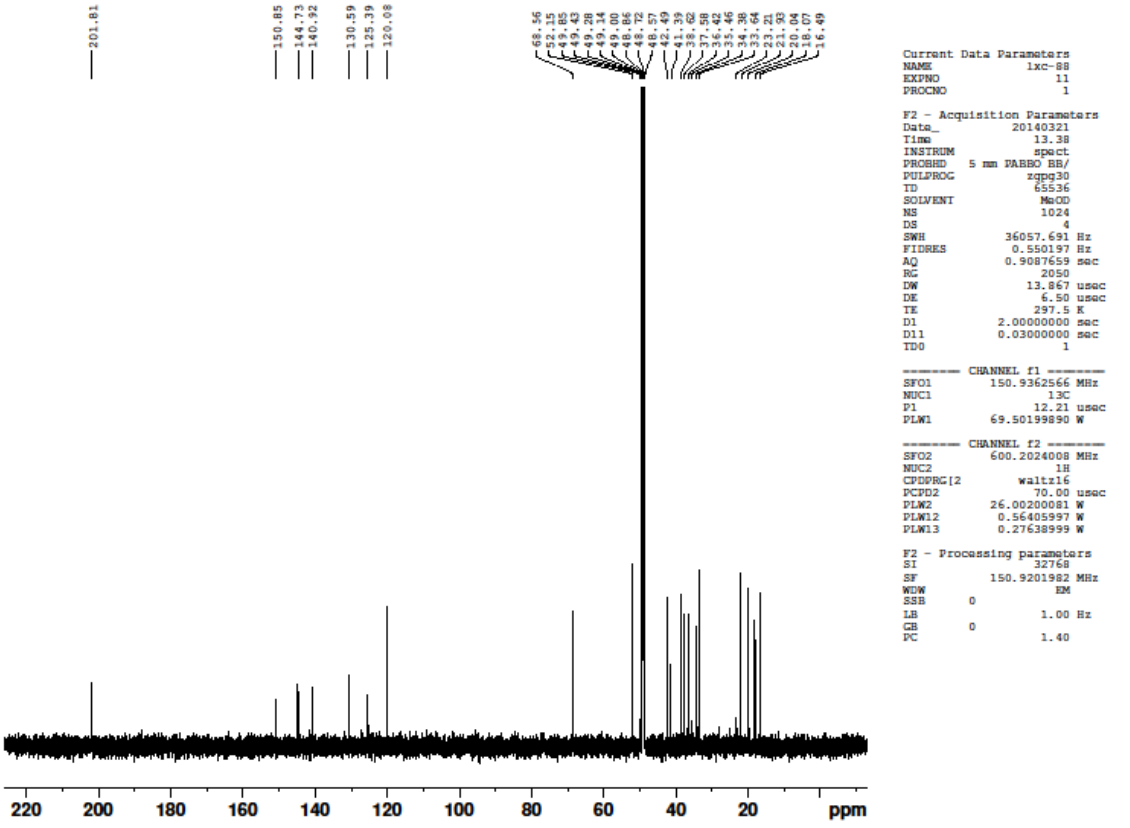


Figure S123. ^{1}H NMR spectrum of compound **21** in CD_3OD (600 MHz)

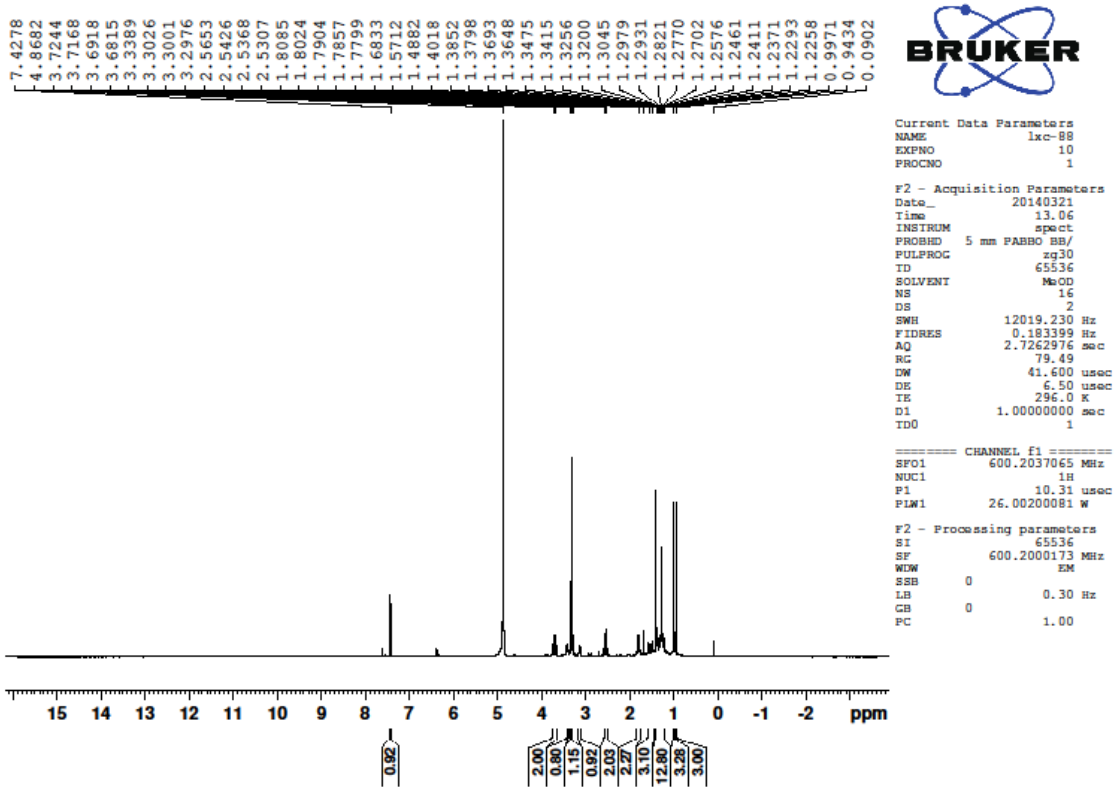


Figure S124. HSQC spectrum of compound **21** in CD_3OD

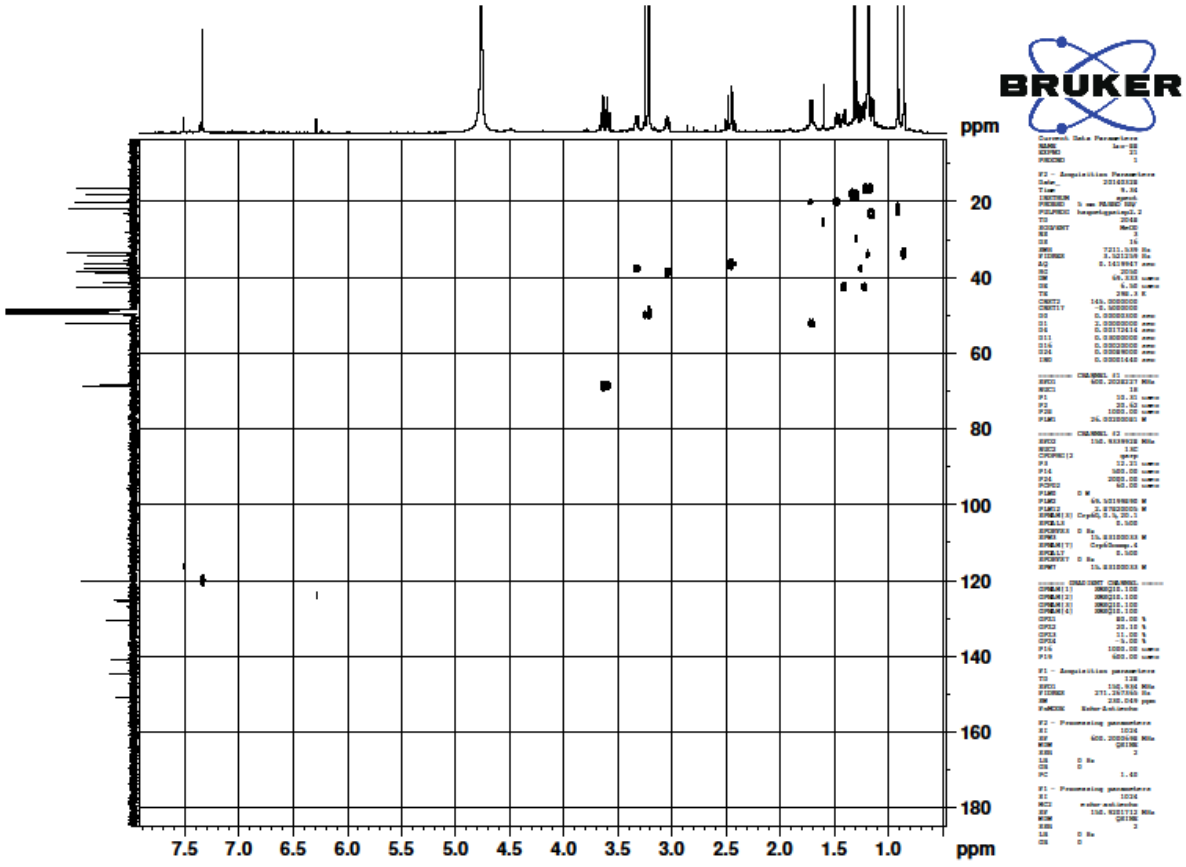


Figure S125. HMBC spectrum of compound **21** in CD_3OD

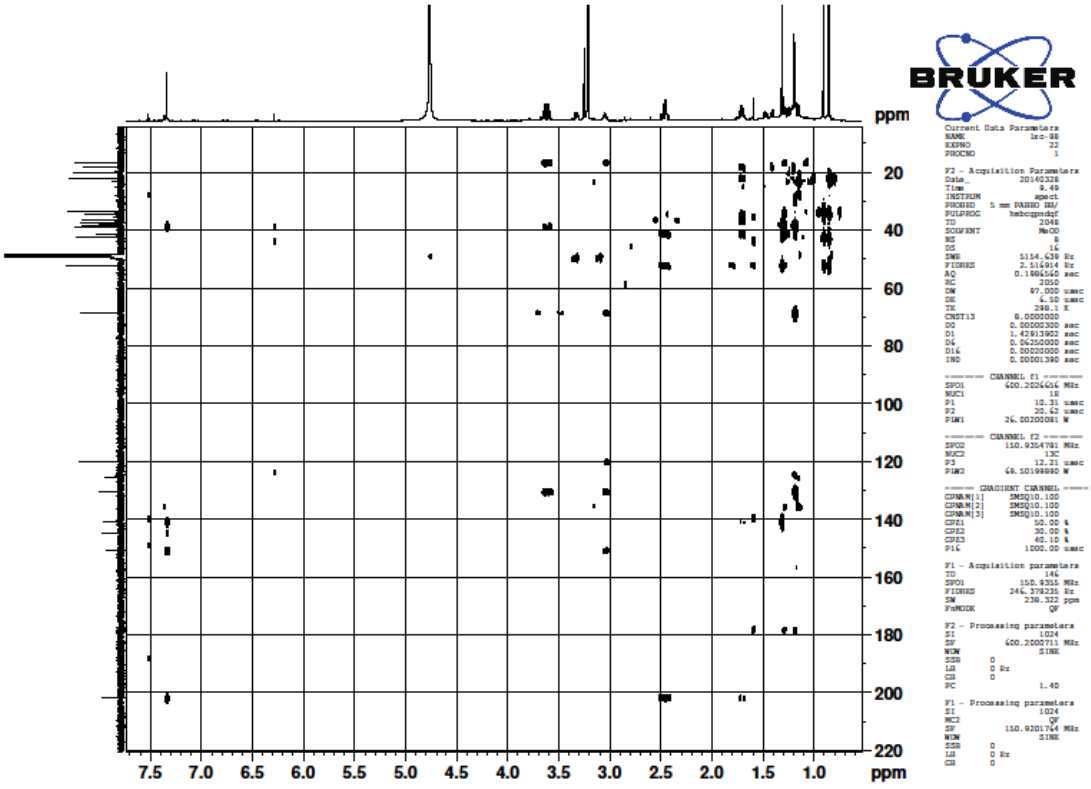


Figure S126. ^{13}C NMR spectrum of compound **22** in DMSO (100 MHz)

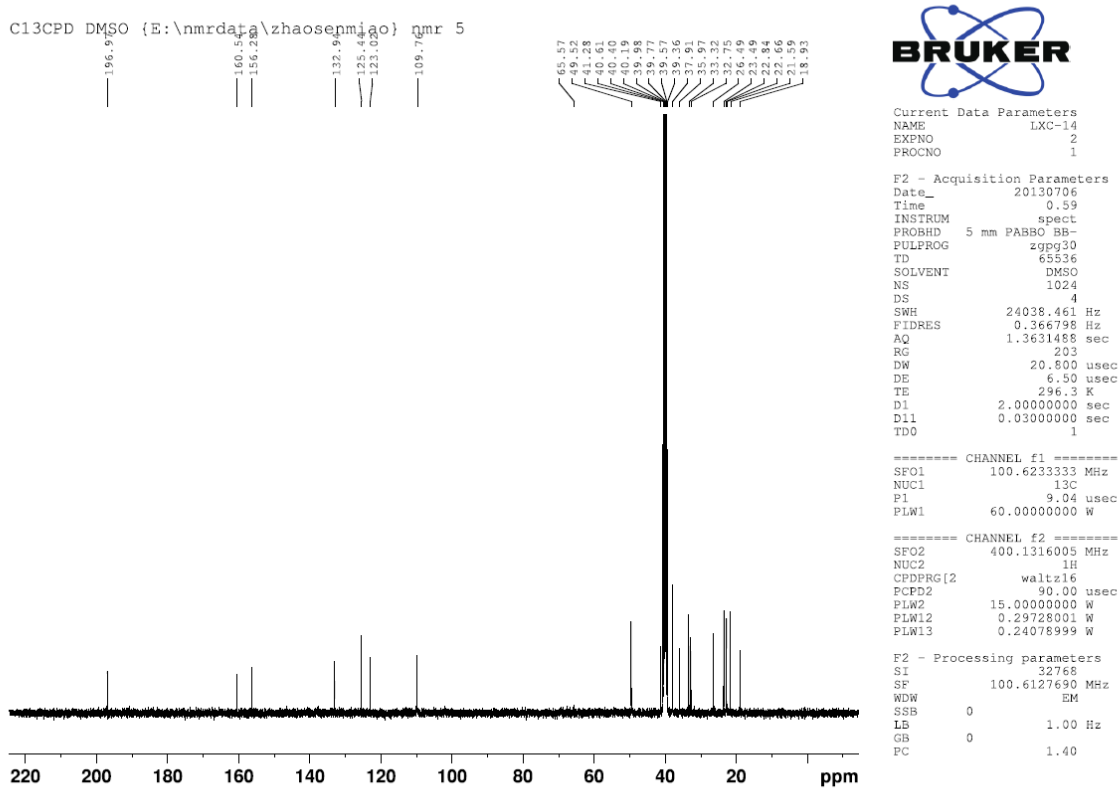


Figure S127. ^{1}H NMR spectrum of compound **22** in DMSO (400 MHz)

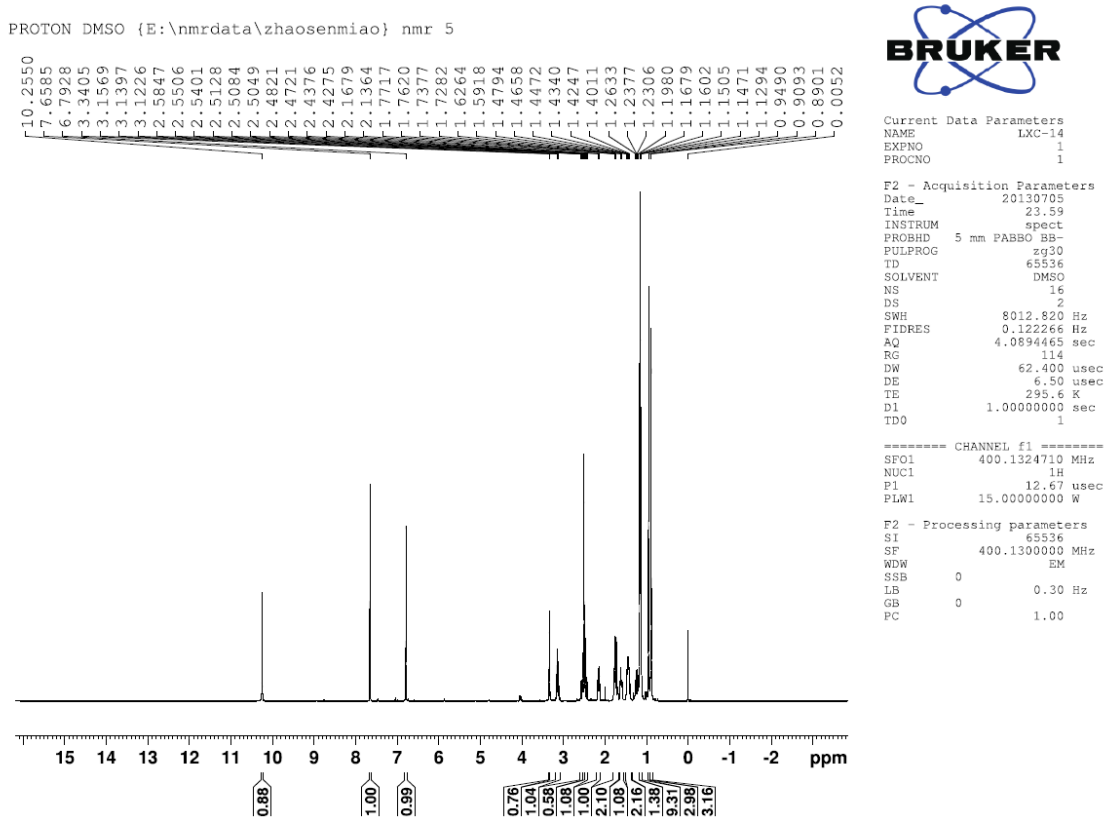


Figure S128. HSQC spectrum of compound **22** inDMSO

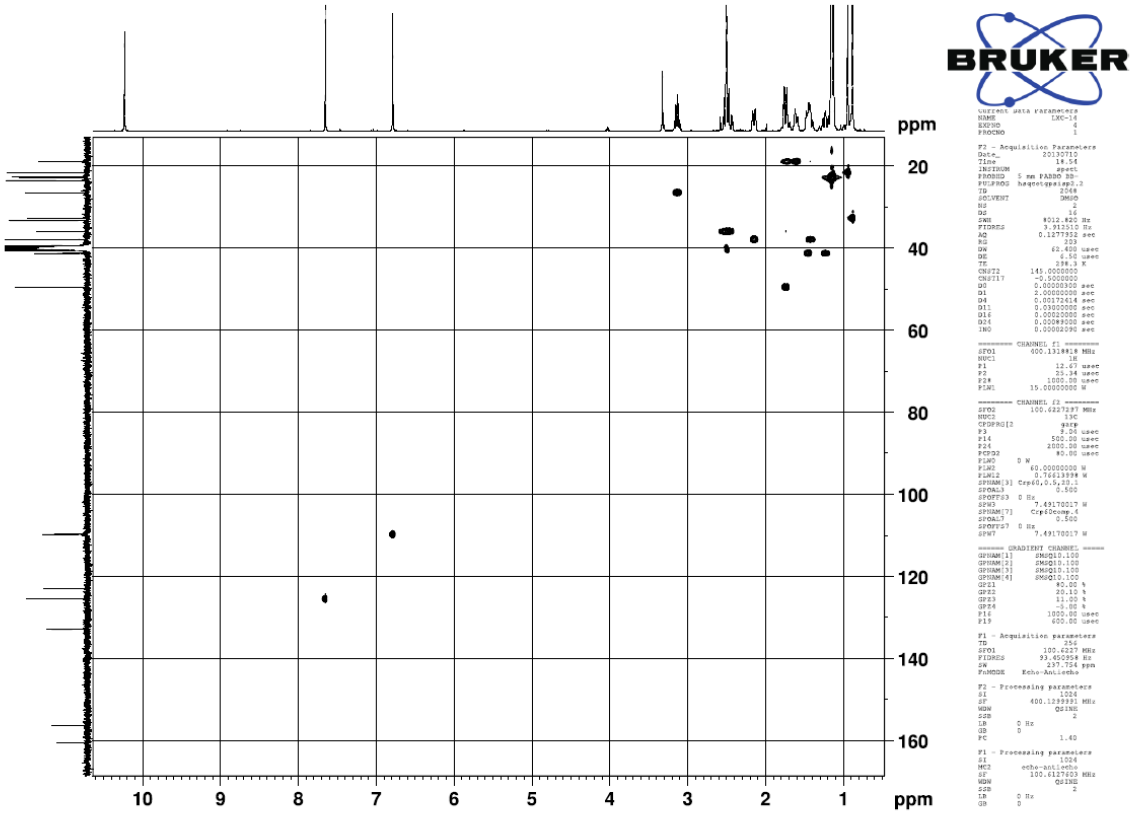


Figure S129. HMBC spectrum of compound **22** in DMSO

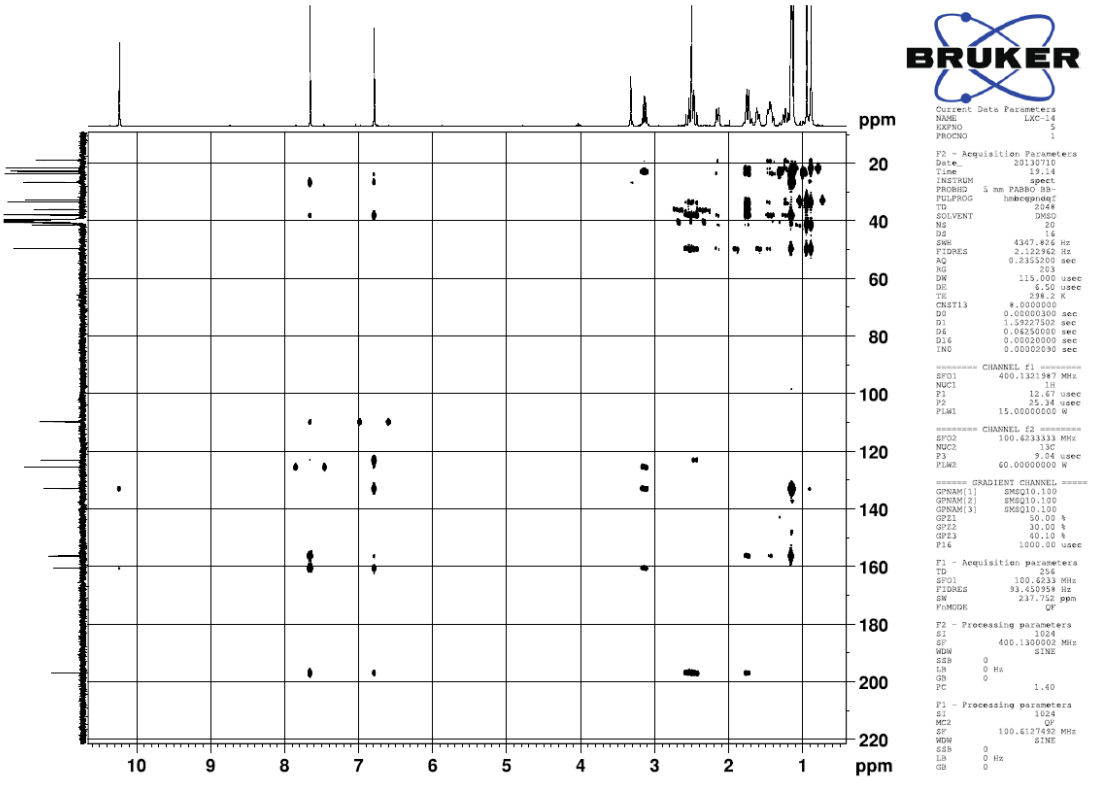


Figure S130. ^{13}C NMR spectrum of compound **23** in $CDCl_3$ (100 MHz)

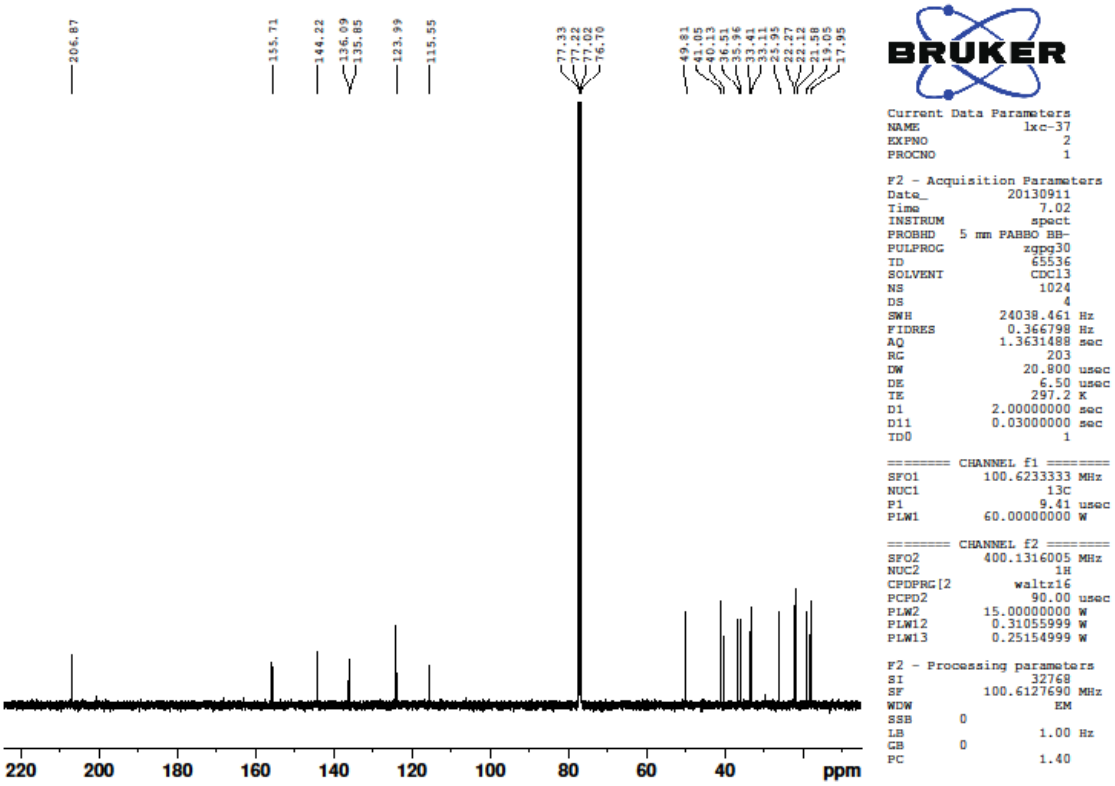


Figure S131. ^{1}H NMR spectrum of compound **23** in $CDCl_3$ (400 MHz)

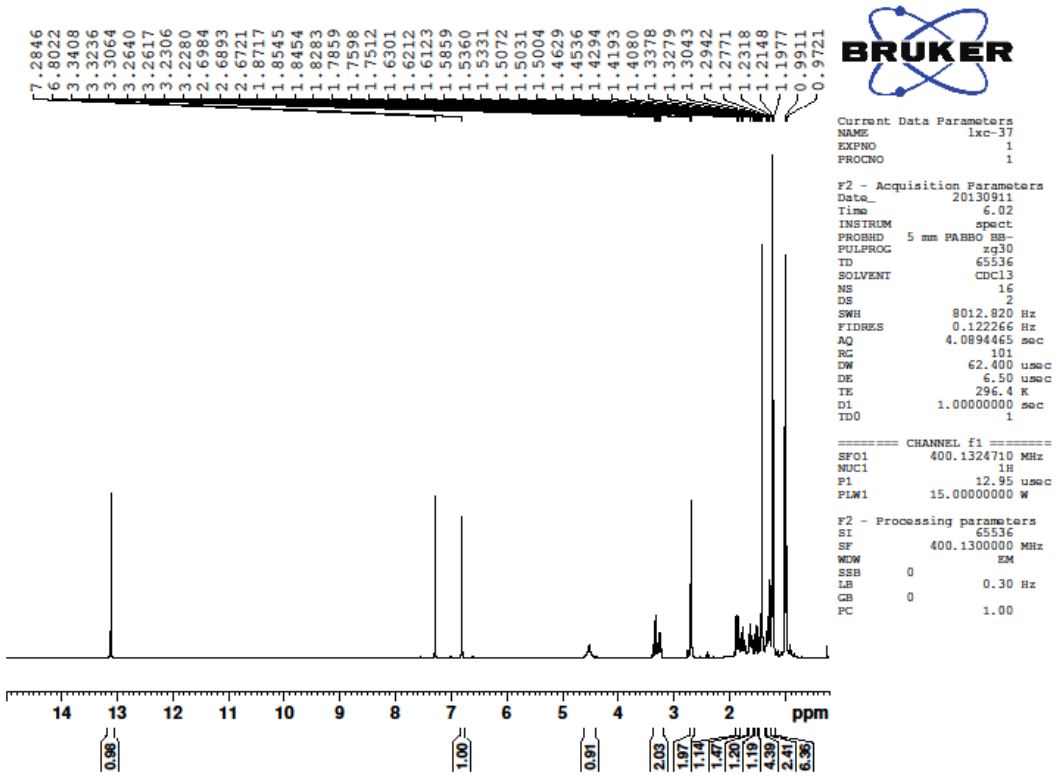


Figure S132. HSQC spectrum of compound **23** in $CDCl_3$

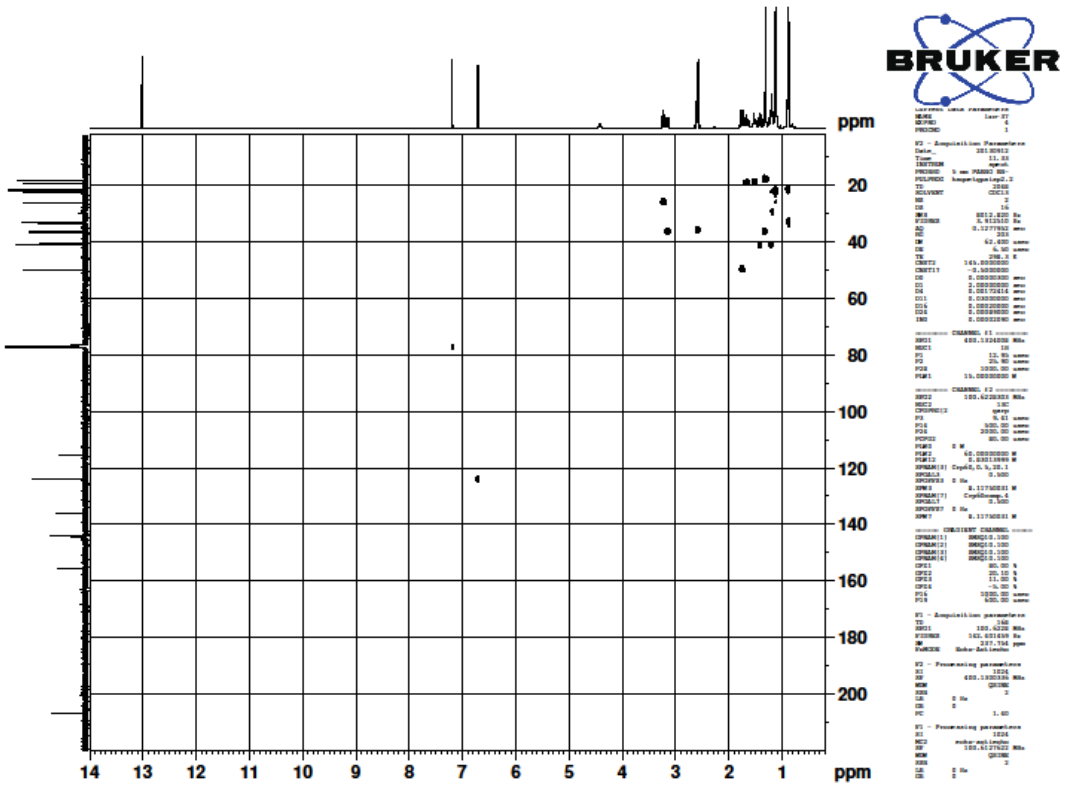


Figure S133. HMBC spectrum of compound **23** in $CDCl_3$

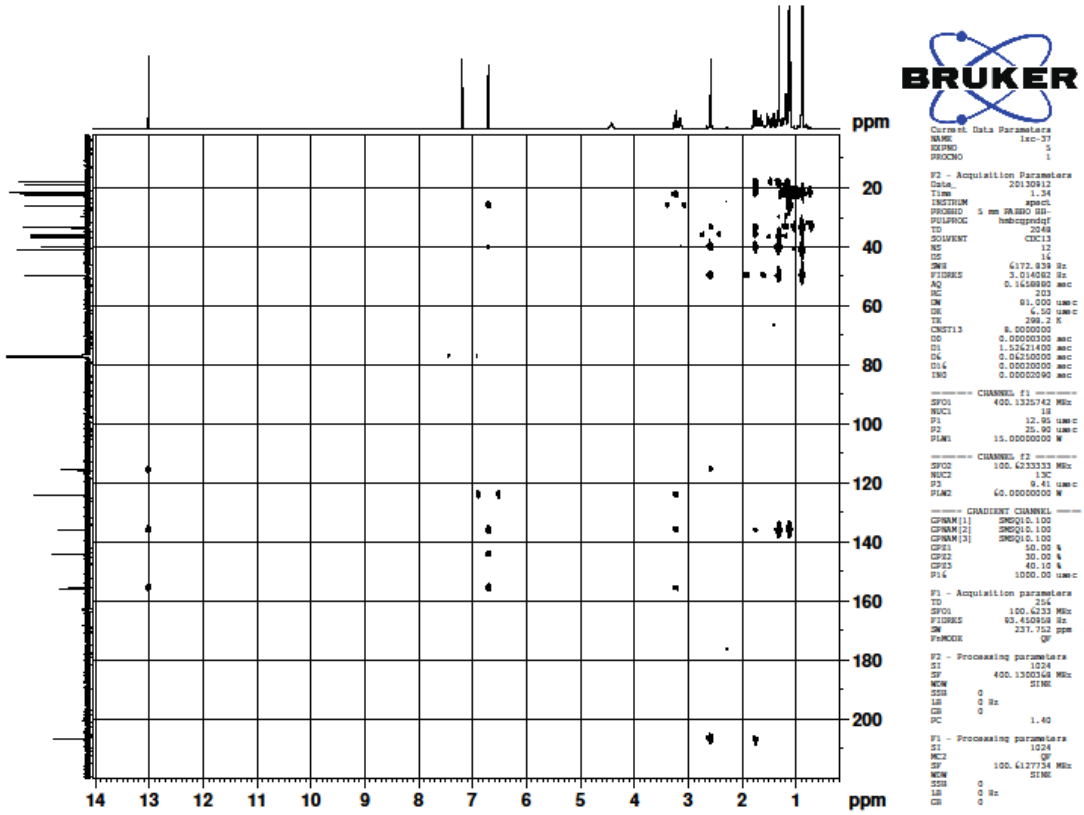


Figure S134. ^{13}C NMR spectrum of compound **24** in $CDCl_3$ (100 MHz)

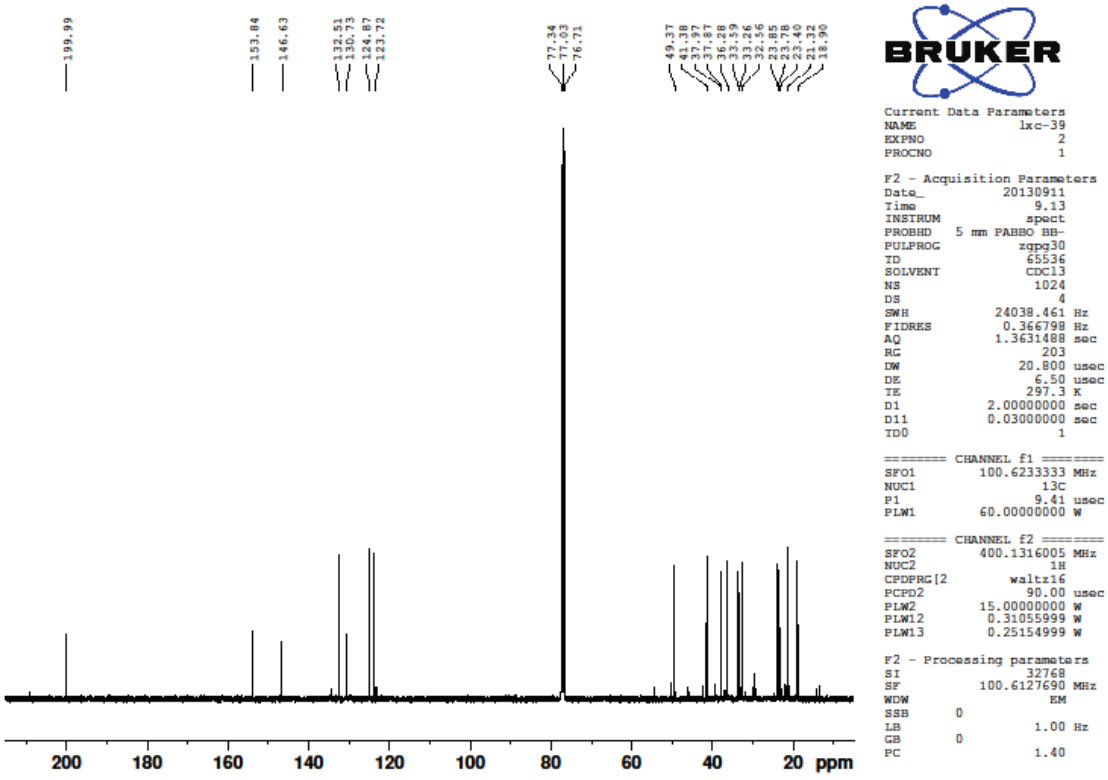


Figure S135. ^{1}H NMR spectrum of compound **24** in $CDCl_3$ (400 MHz)

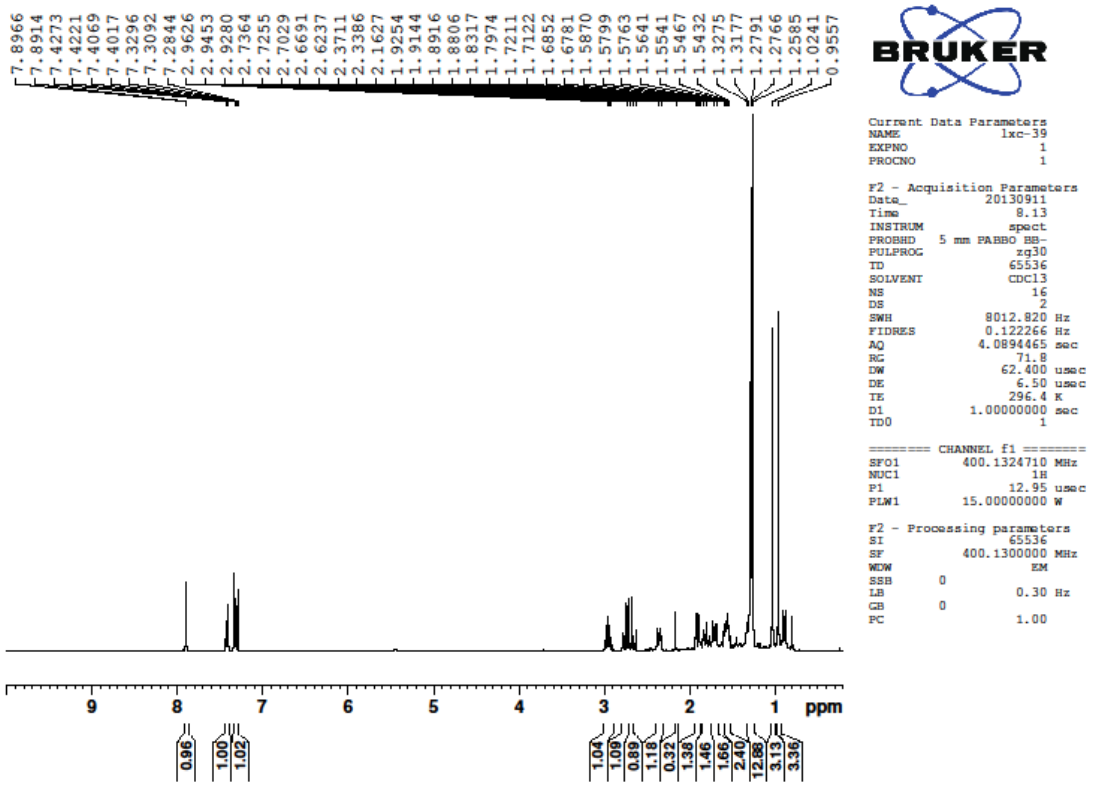


Figure S136. HSQC spectrum of compound **24** in$CDCl_3$

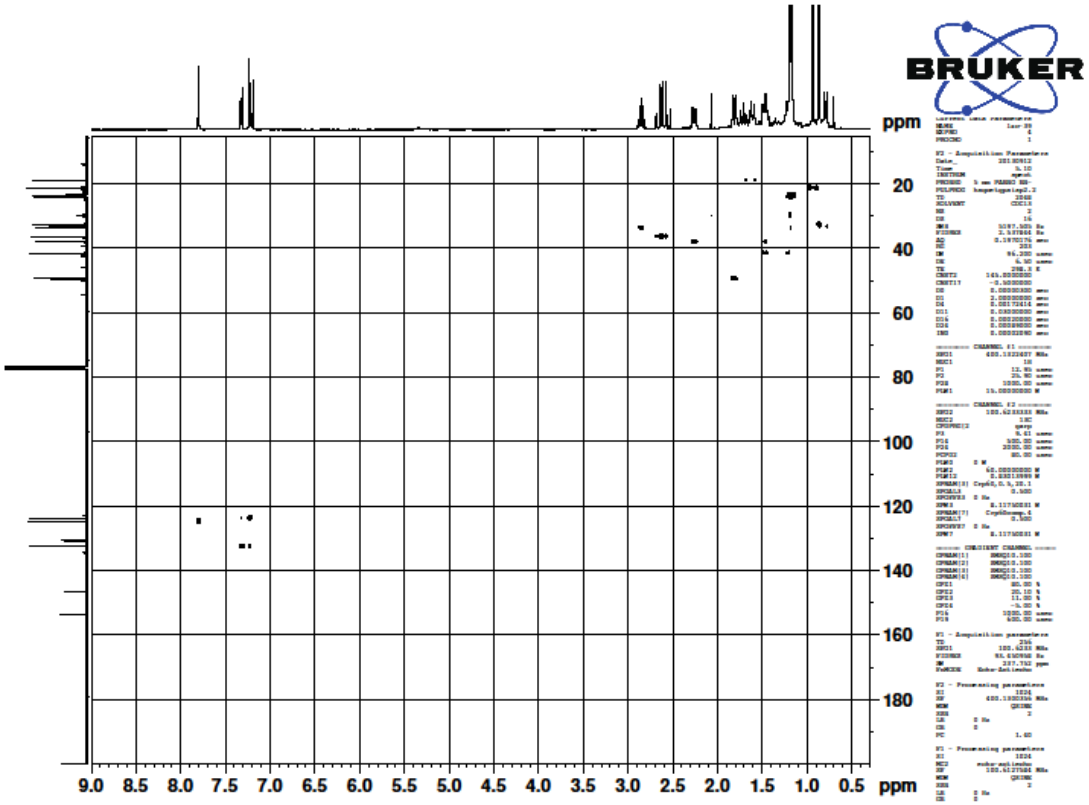


Figure S137. HMBC spectrum of compound **24** in $CDCl_3$

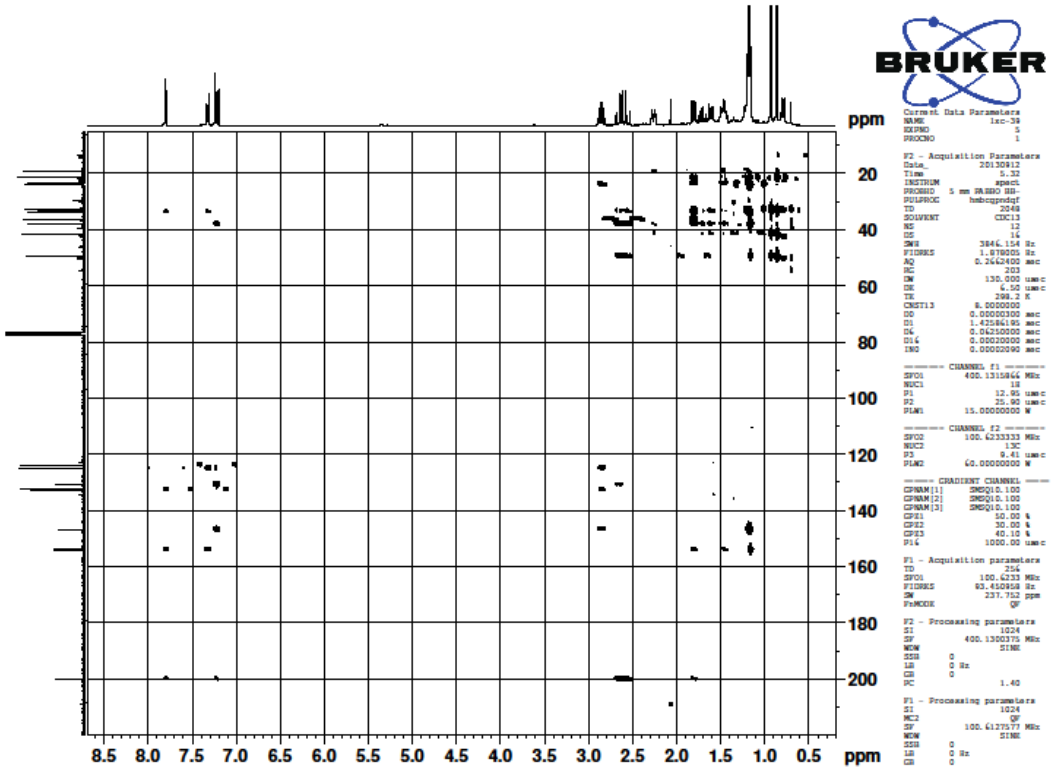


Figure S138. ^{13}C NMR spectrum of compound **25** in $CDCl_3$ (100 MHz)

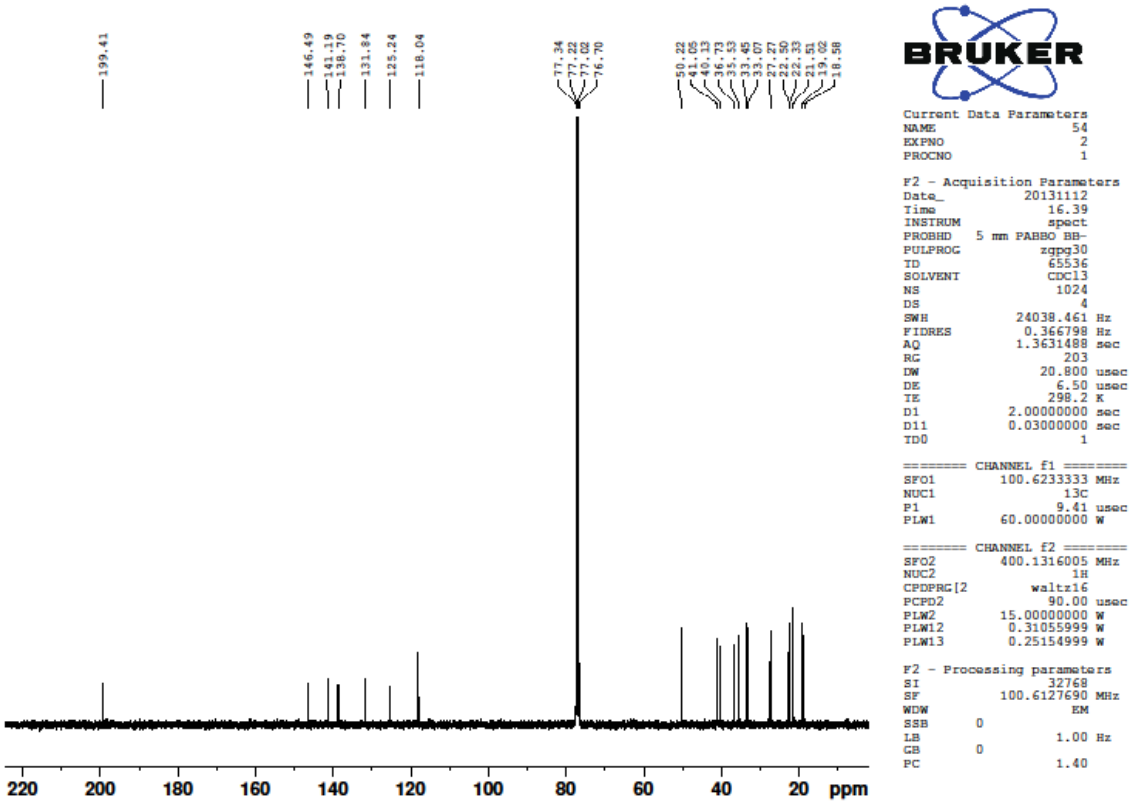


Figure S139. ^{1}H NMR spectrum of compound **25** in $CDCl_3$ (400 MHz)

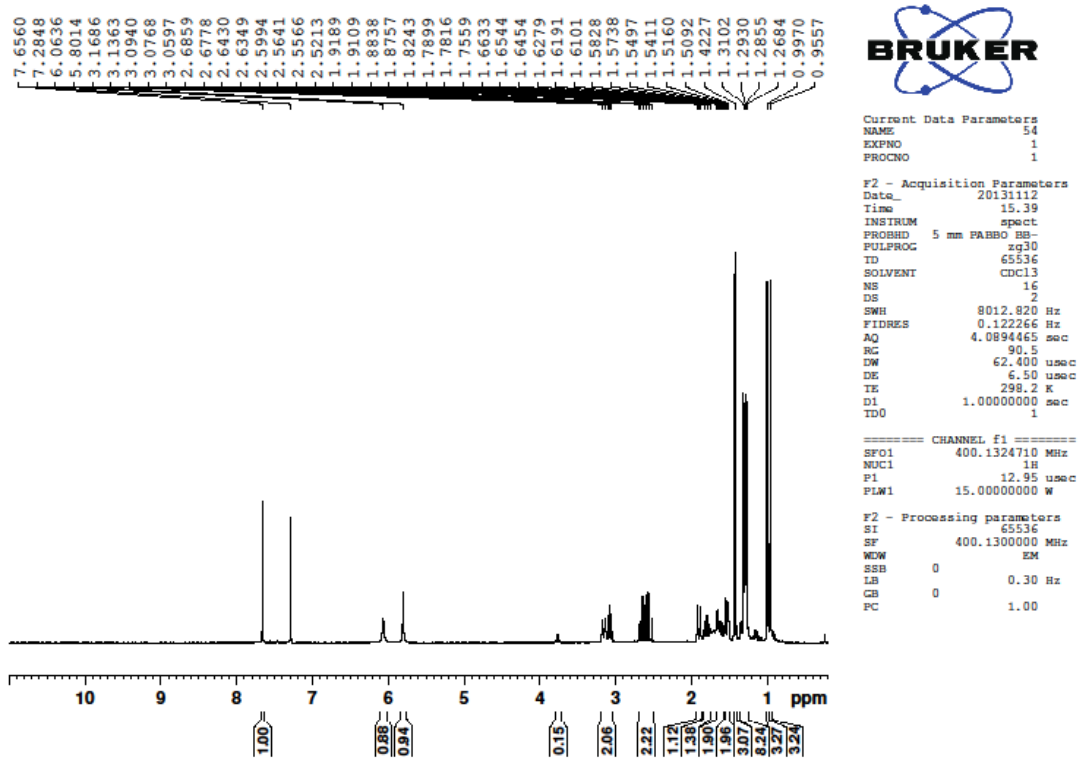


Figure S140. HSQC spectrum of compound **25** in $CDCl_3$

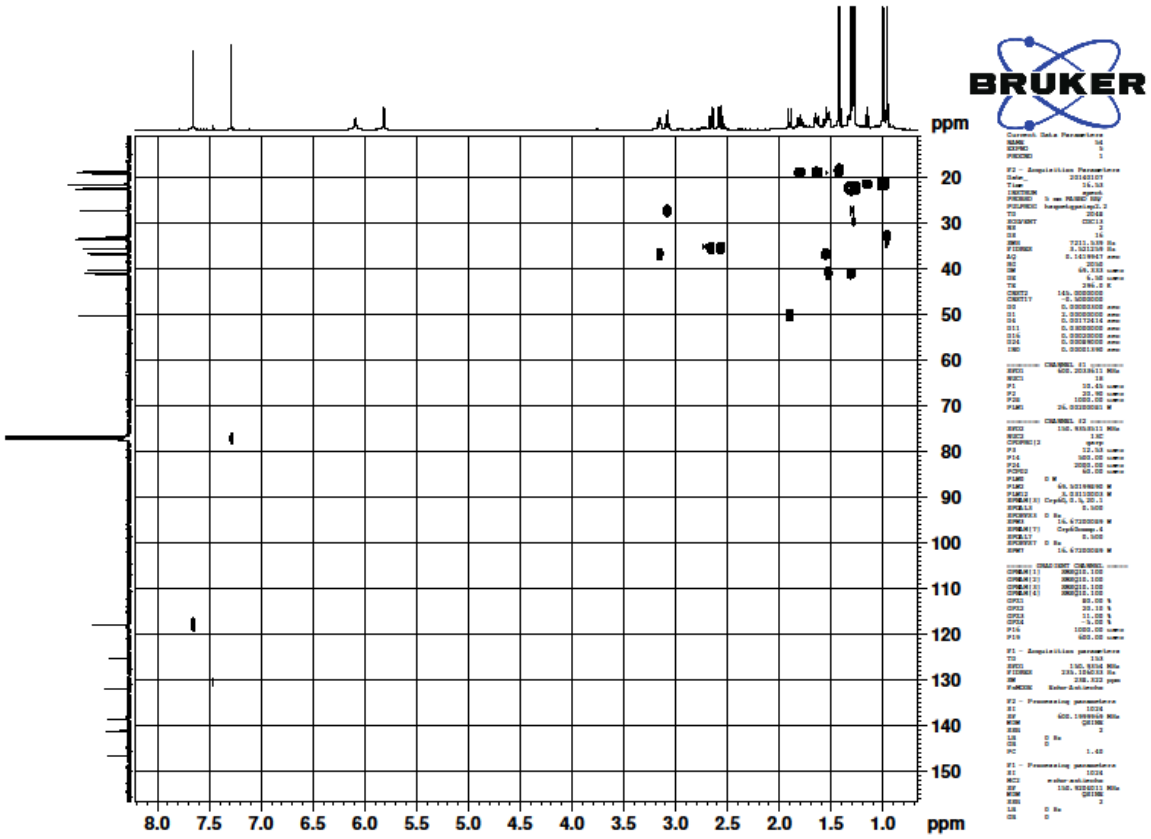


Figure S141. HMBC spectrum of compound **25** in $CDCl_3$

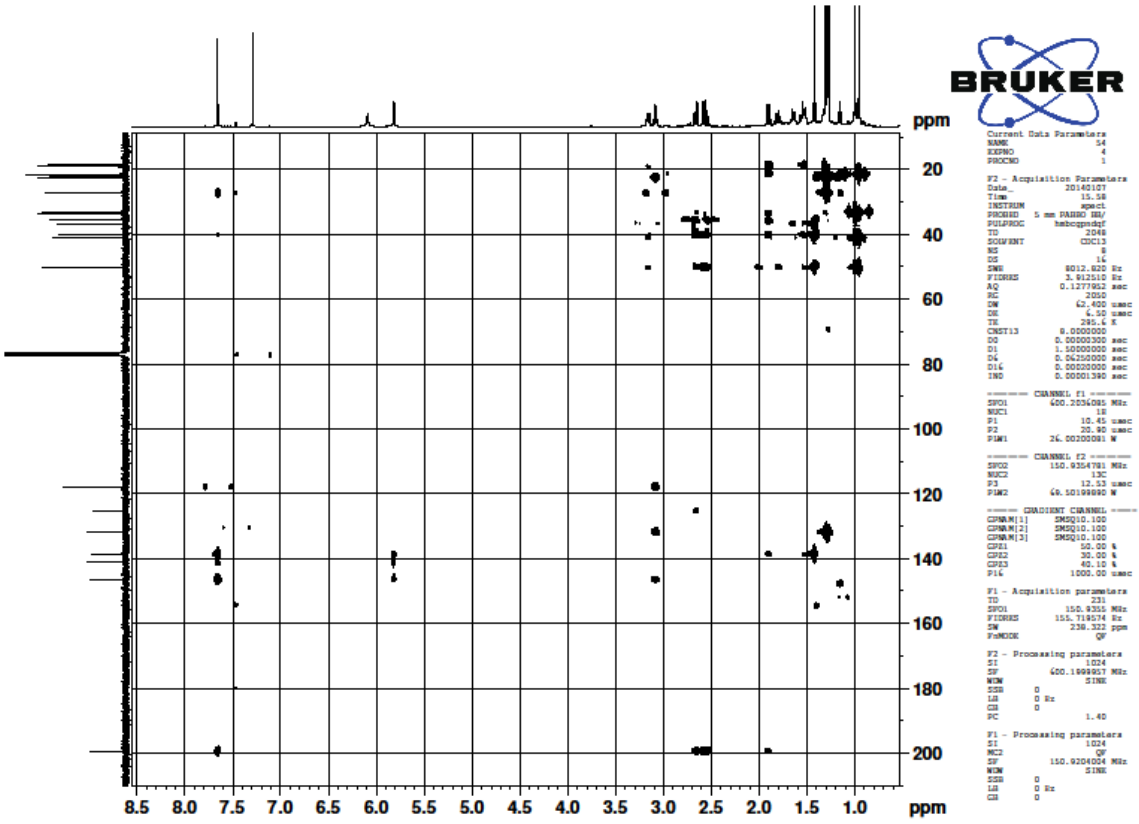


Figure S142. ^{13}C NMR spectrum of compound **26** in $CDCl_3$ (100 MHz)

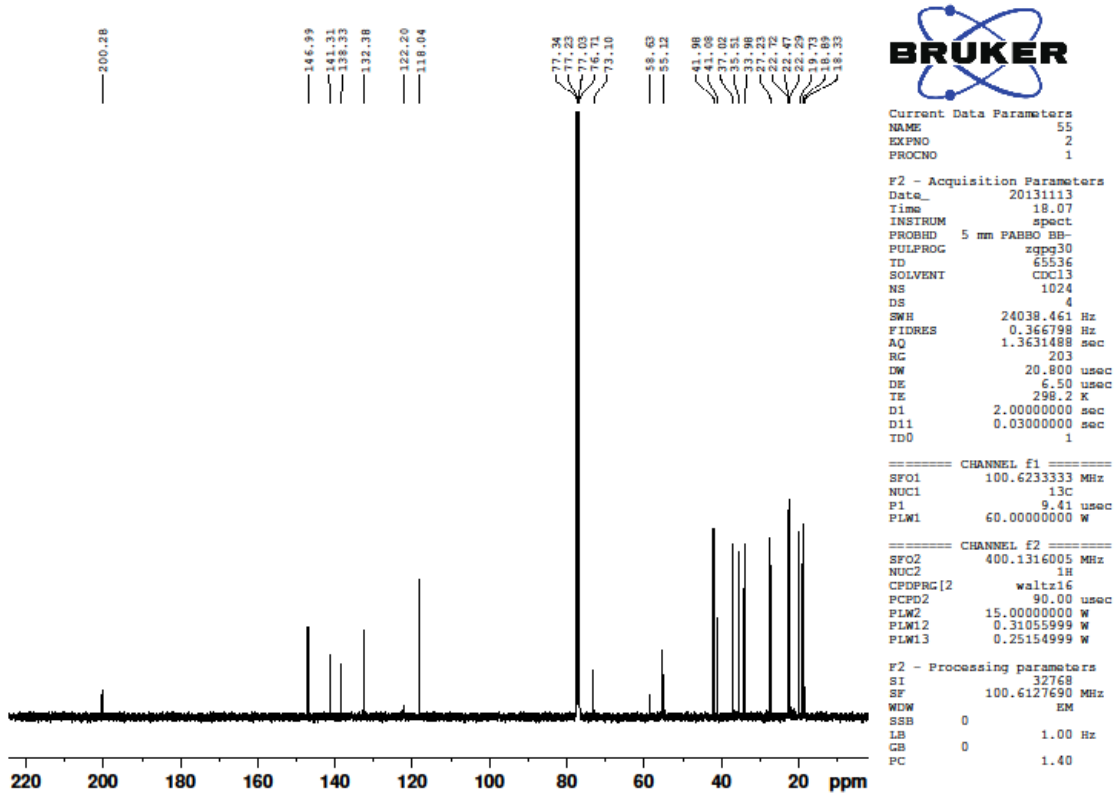


Figure S143. ^{1}H NMR spectrum of compound **26** in $CDCl_3$ (400 MHz)

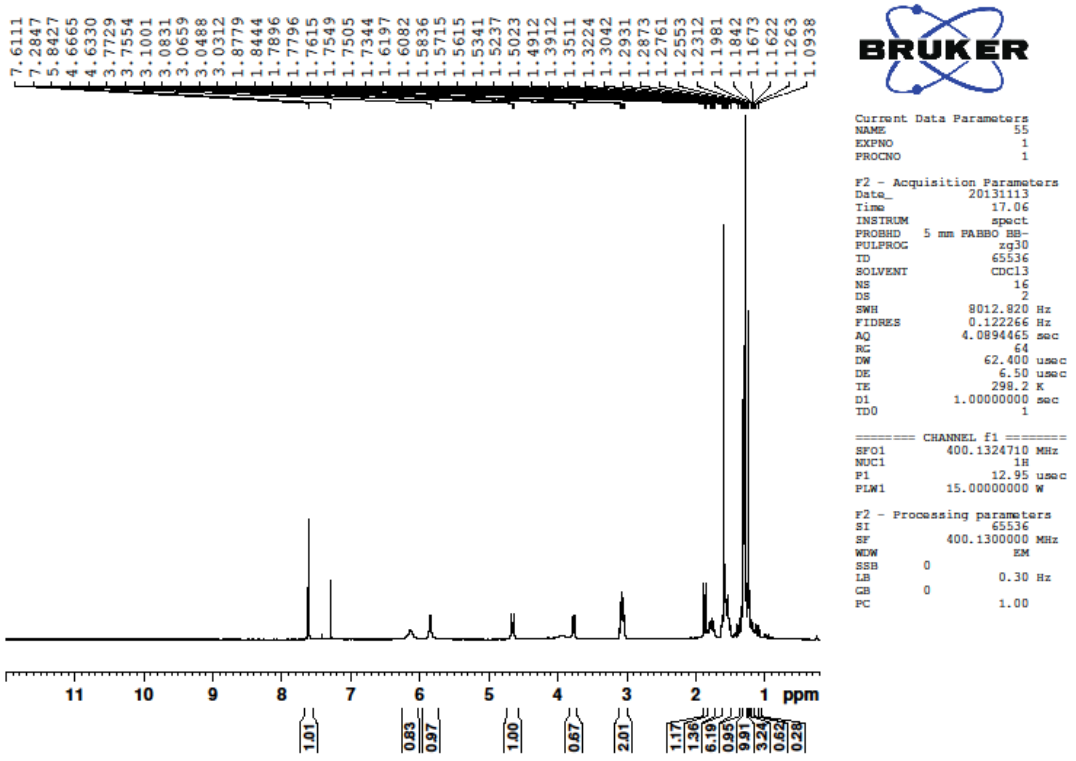


Figure S144. HSQC spectrum of compound **26** in $CDCl_3$

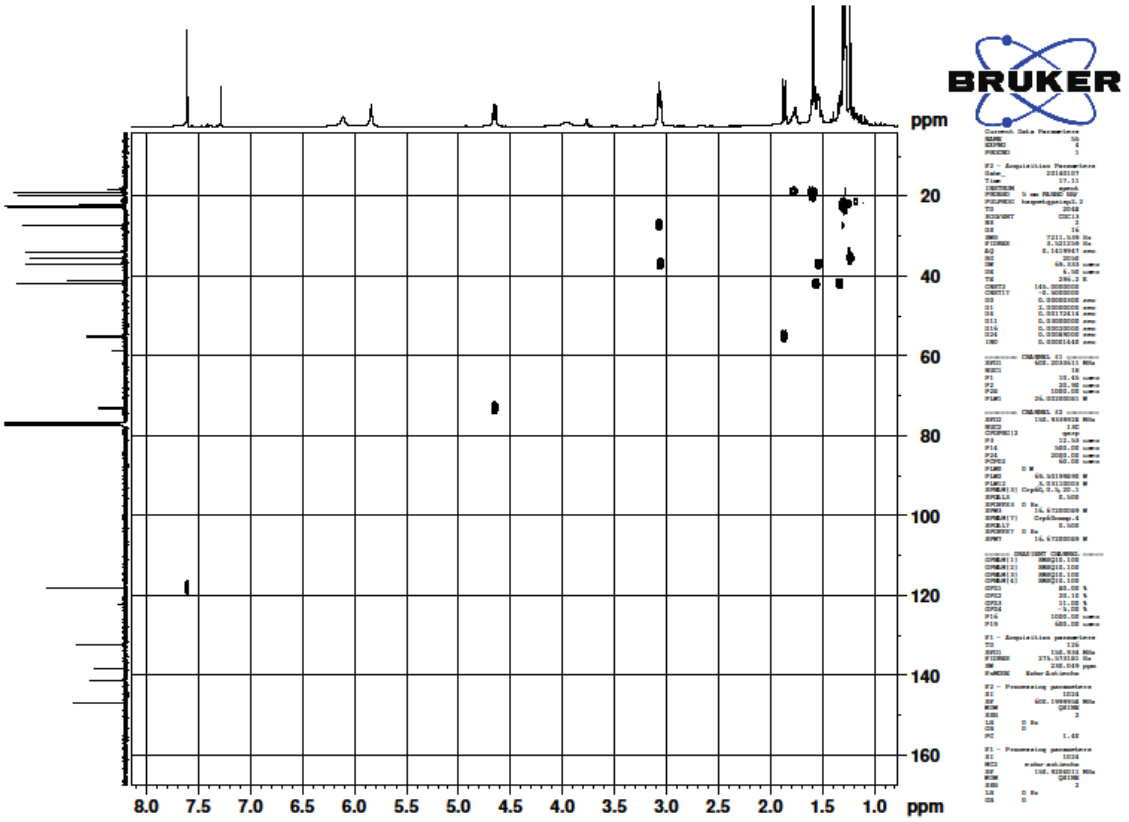


Figure S145. HMBC spectrum of compound **26** in$CDCl_3$

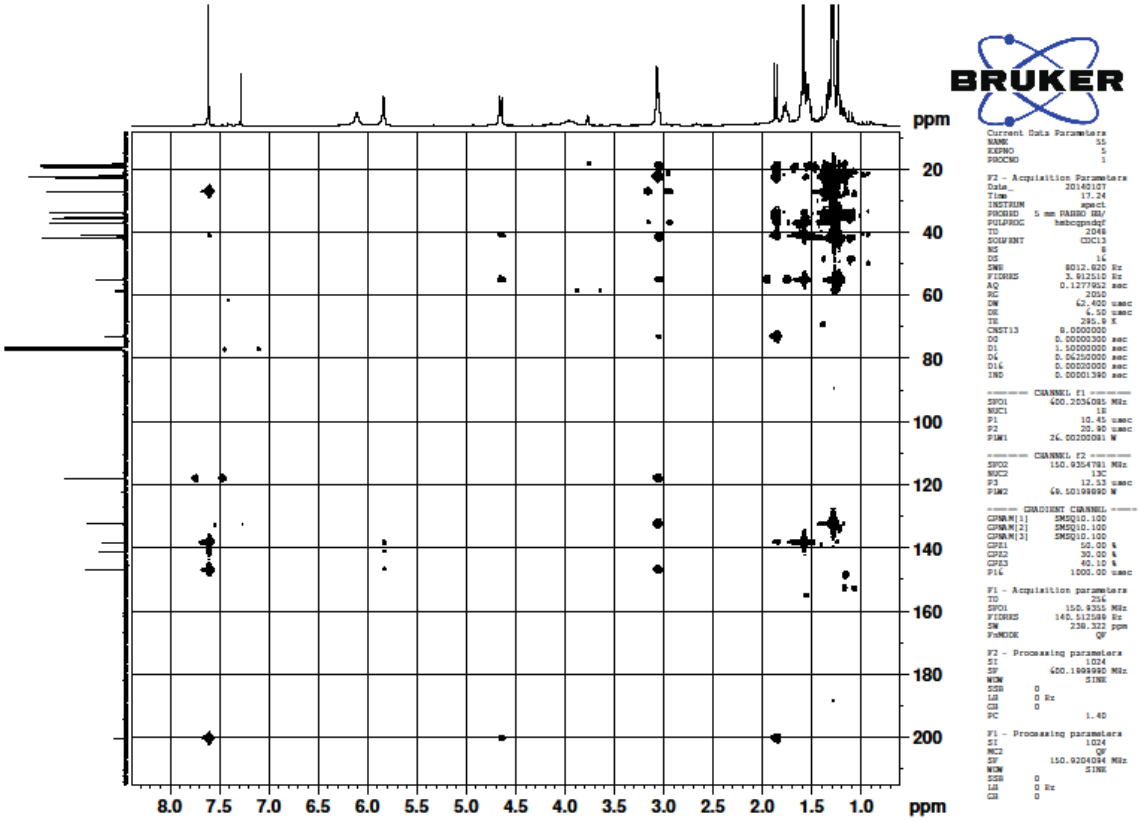


Figure S146. ^{13}C NMR spectrum of compound **29** in CD_3OD (150 MHz)

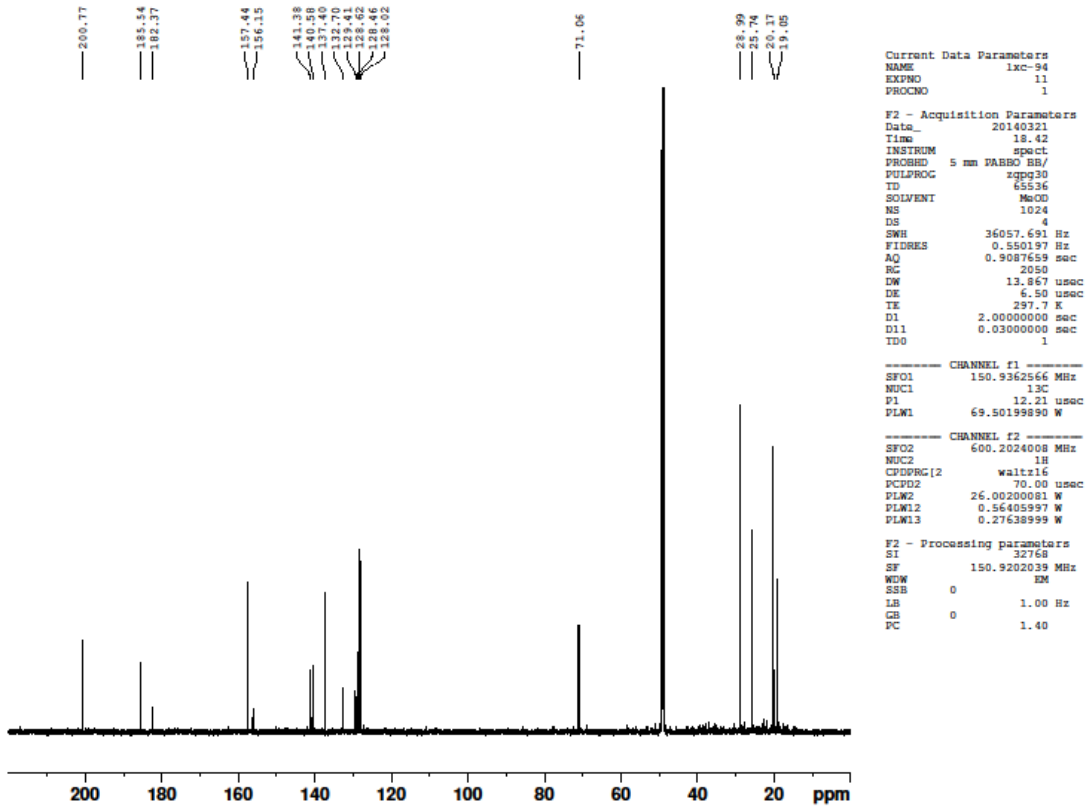


Figure S147. ^{1}H NMR spectrum of compound **29** in CD_3OD (600 MHz)

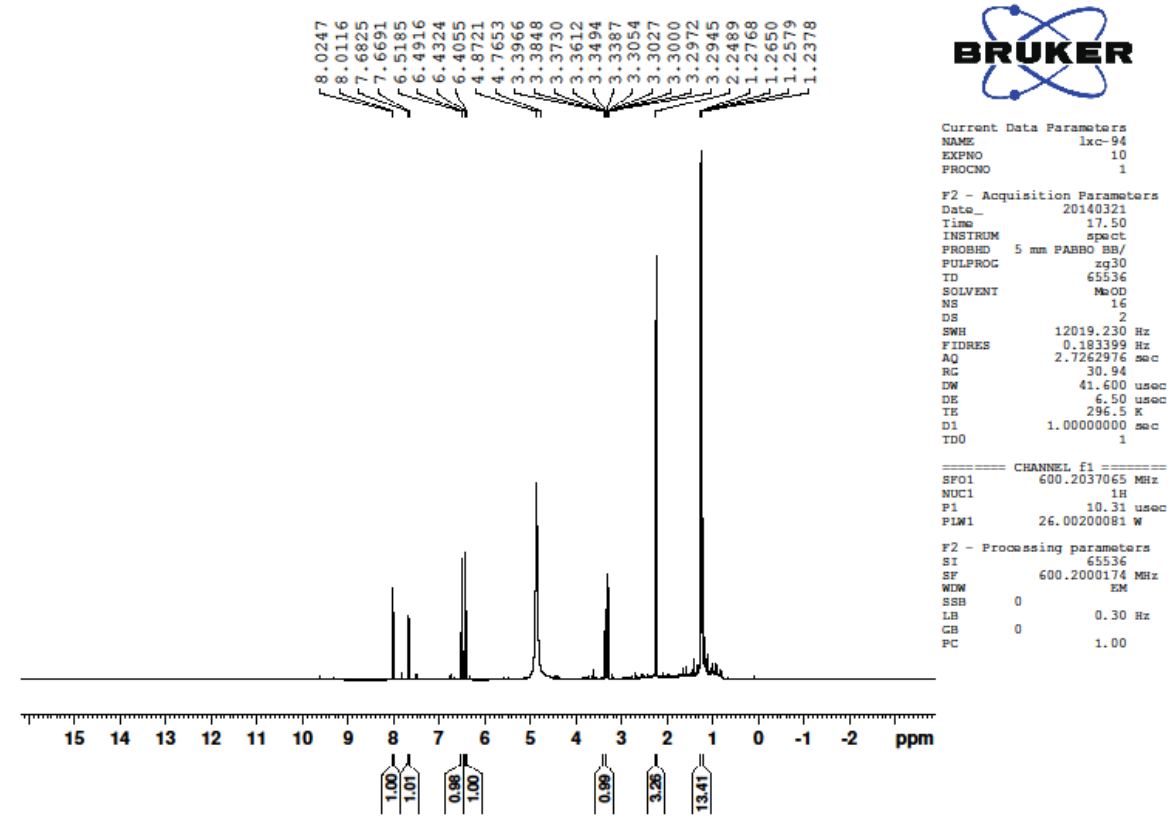


Figure S148. HSQC spectrum of compound **29** in CD_3OD

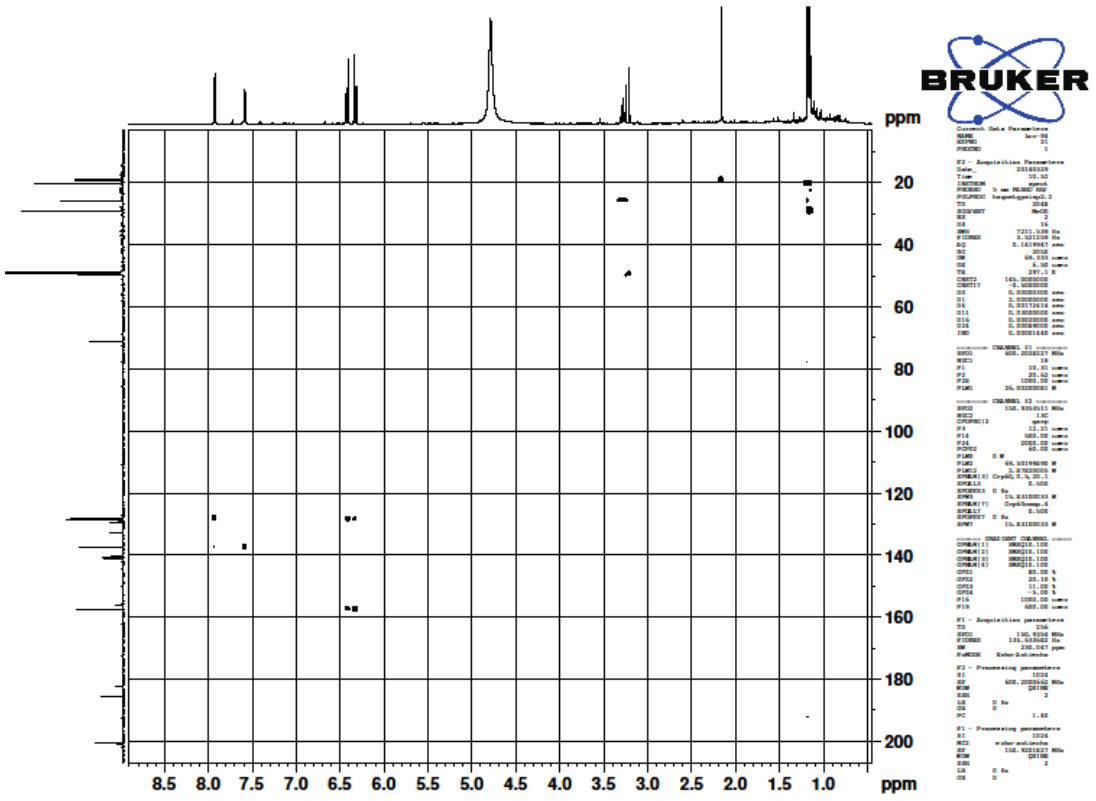


Figure S149. HMBC spectrum of compound **29** in CD_3OD

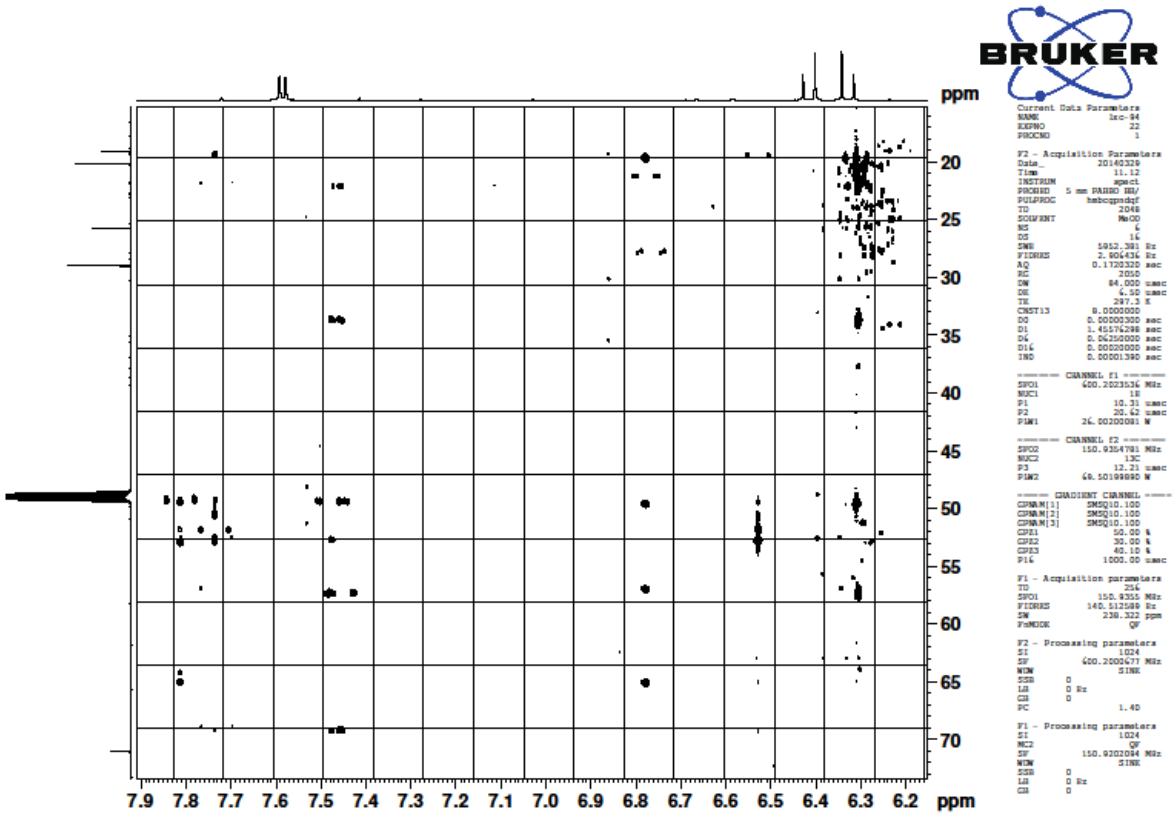


Figure S150. ^{13}C NMR spectrum of compound **30** in $CDCl_3$ (100 MHz)

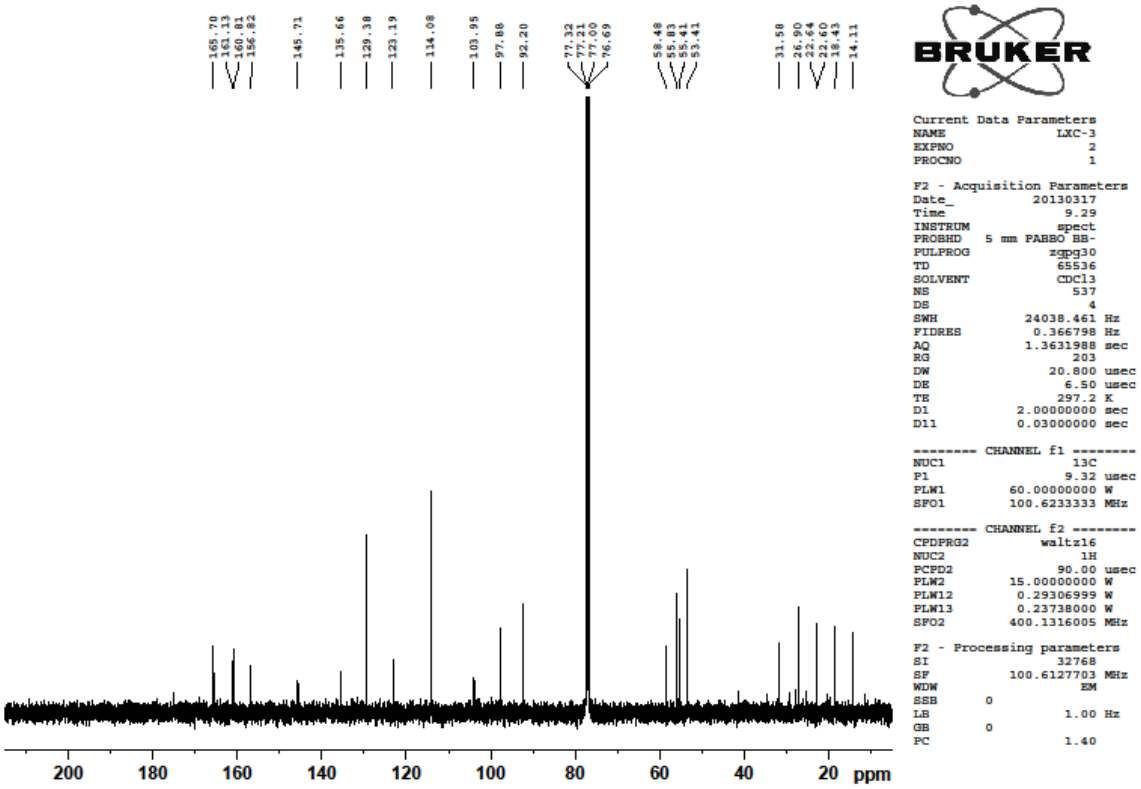


Figure S151. ^{1}H NMR spectrum of compound **30** in $CDCl_3$ (400 MHz)

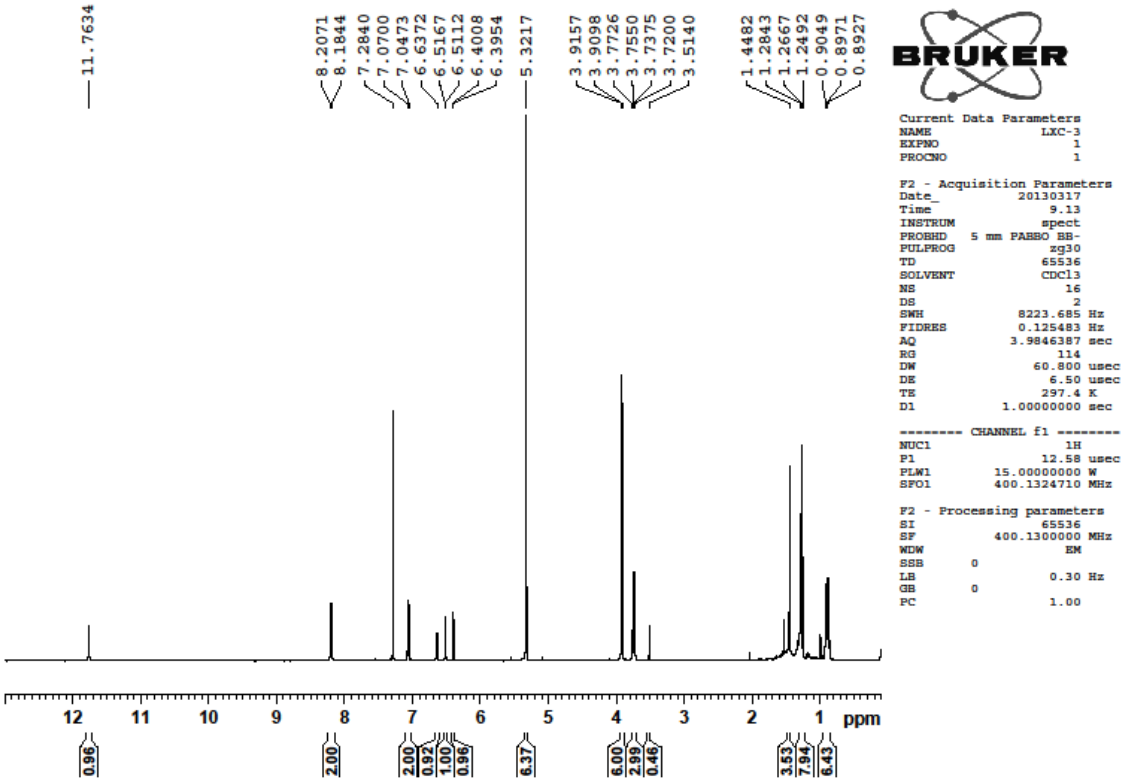


Figure S152. HSQC spectrum of compound **30** in $CDCl_3$

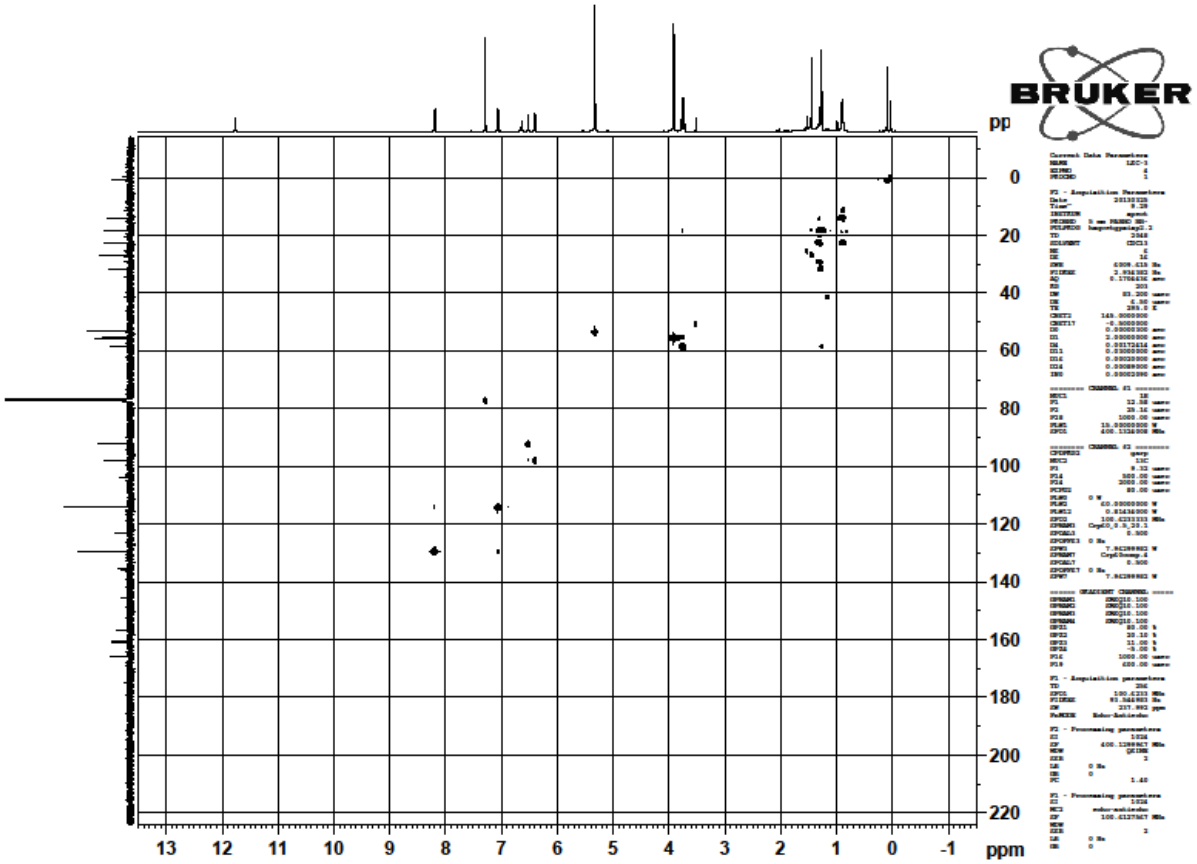


Figure S153. HMBC spectrum of compound **30** in $CDCl_3$

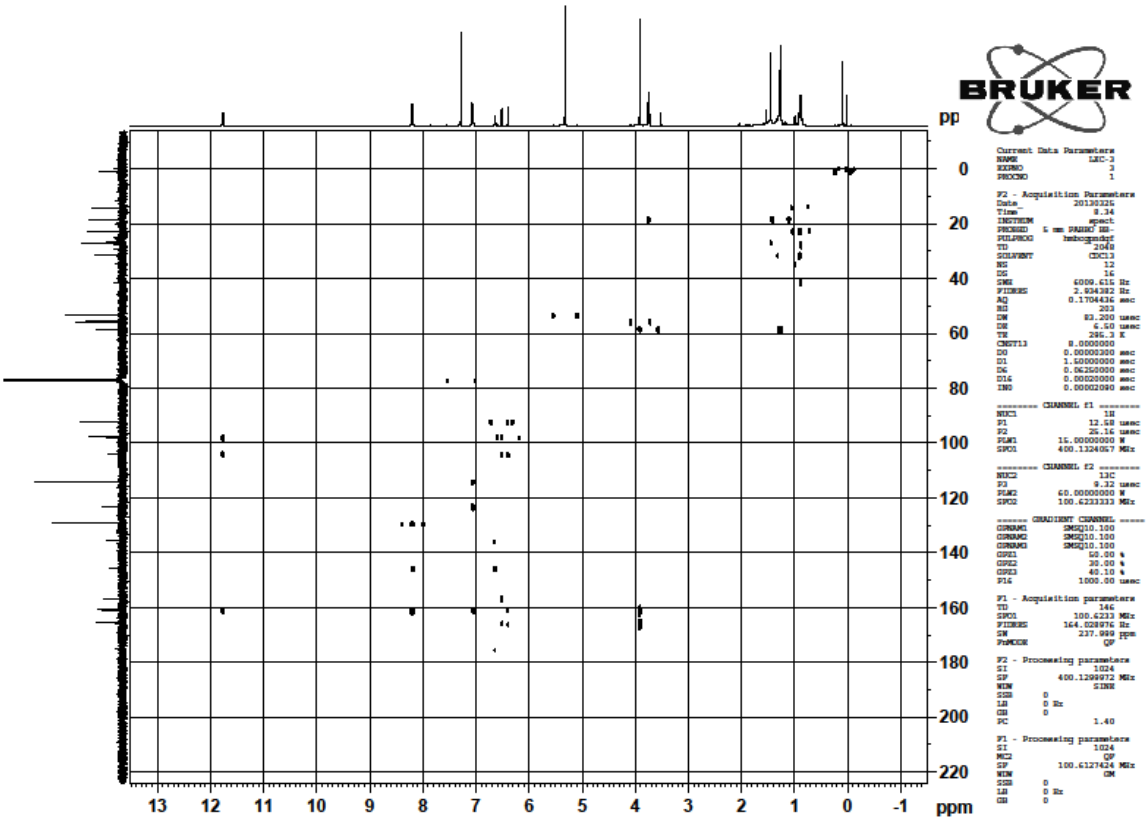


Figure S154. ^{13}C NMR spectrum of compound **31** in$CDCl_3$ (100 MHz)

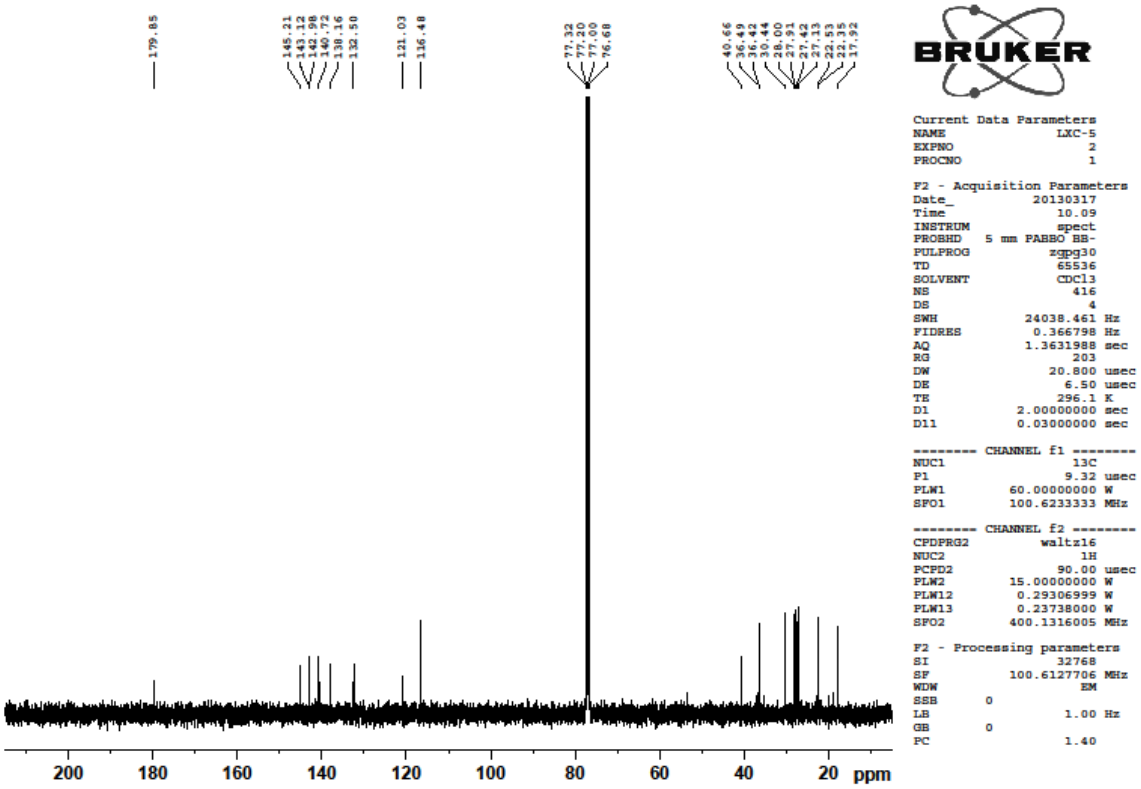


Figure S155. ^{1}H NMR spectrum of compound **31** in $CDCl_3$ (400 MHz)

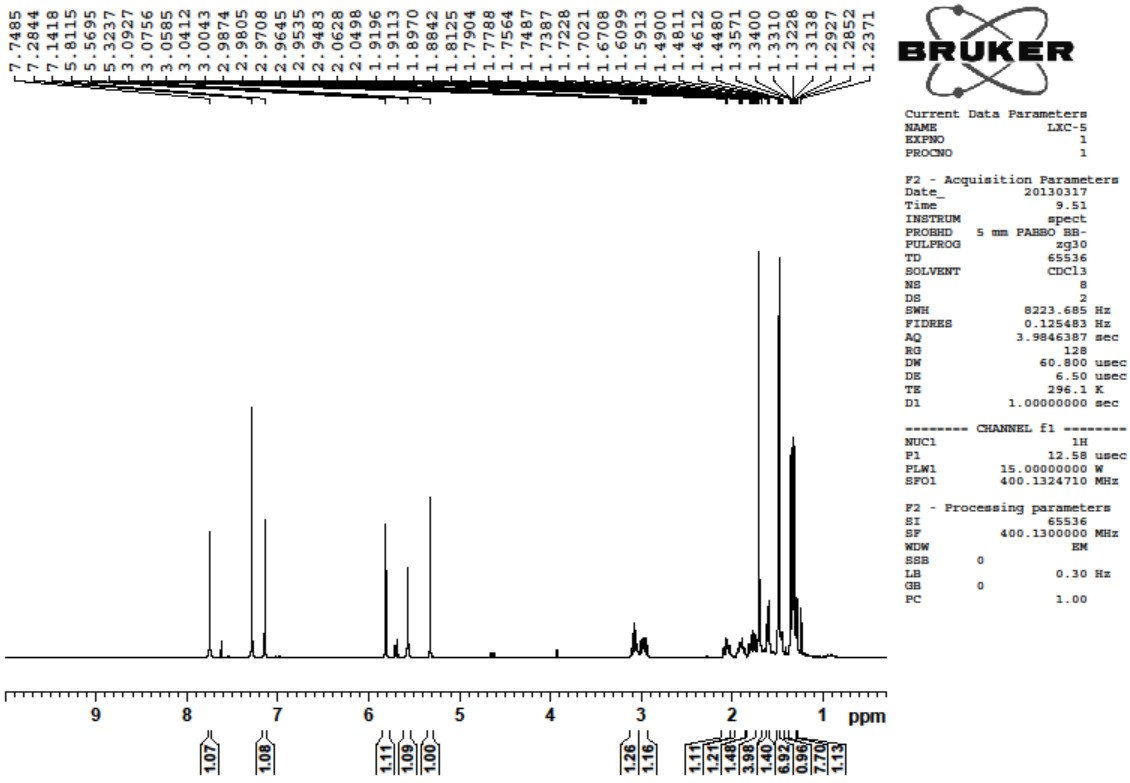


Figure S156. HSQC spectrum of compound **31** in $CDCl_3$

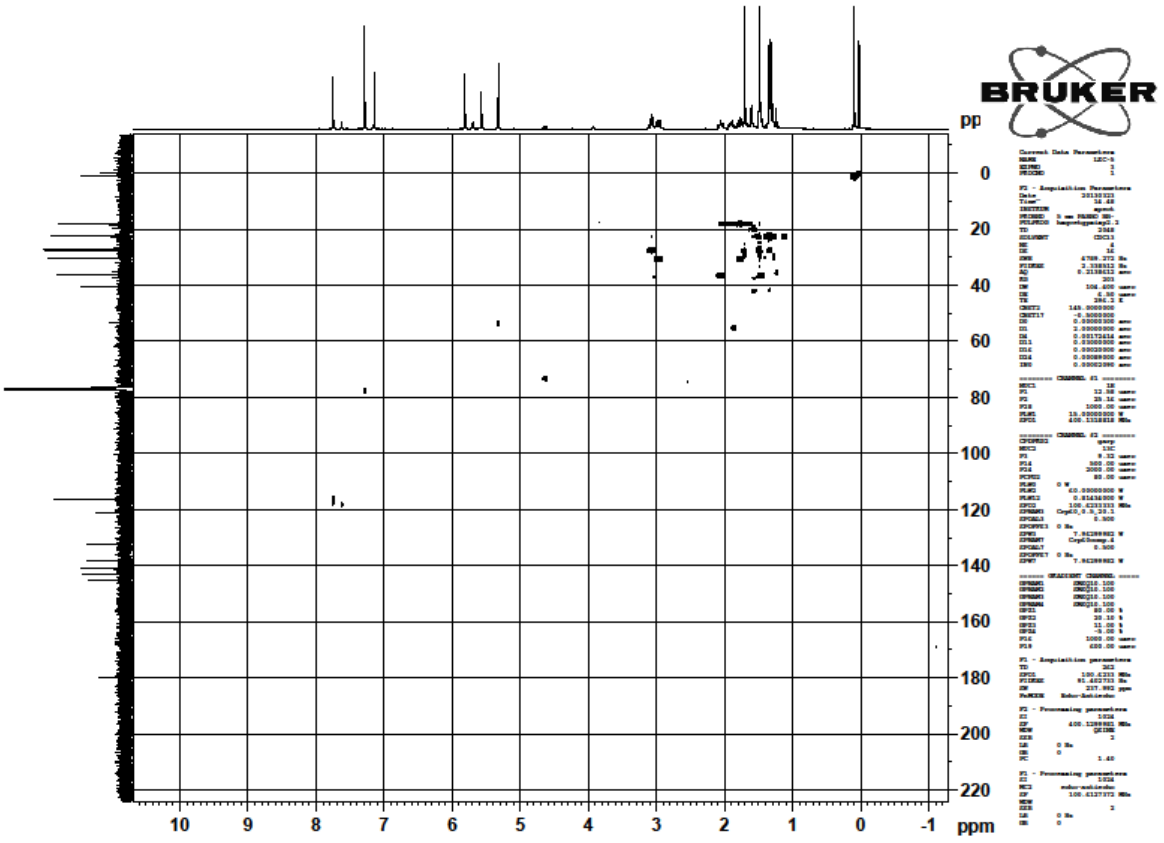


Figure S157. HMBC spectrum of compound **31** in $CDCl_3$

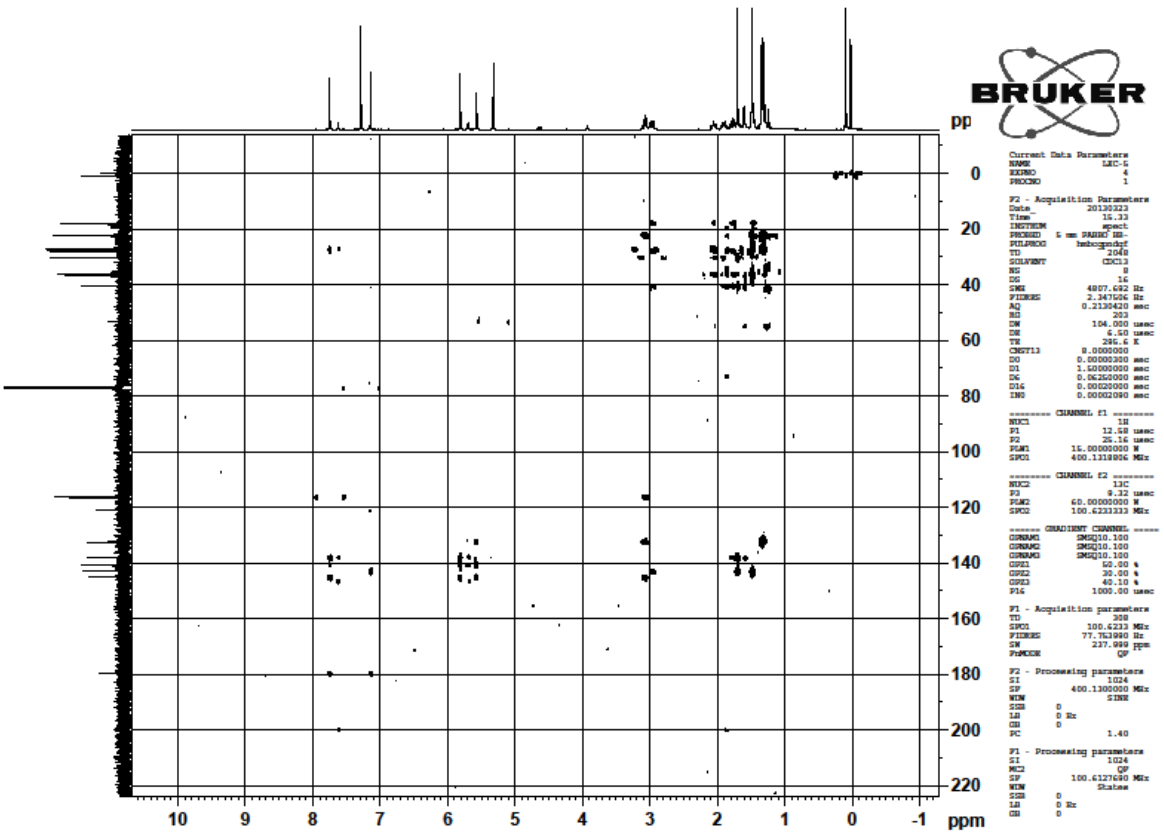


Figure S158. ^{13}C NMR spectrum of compound **32** in $CDCl_3$ (100 MHz)

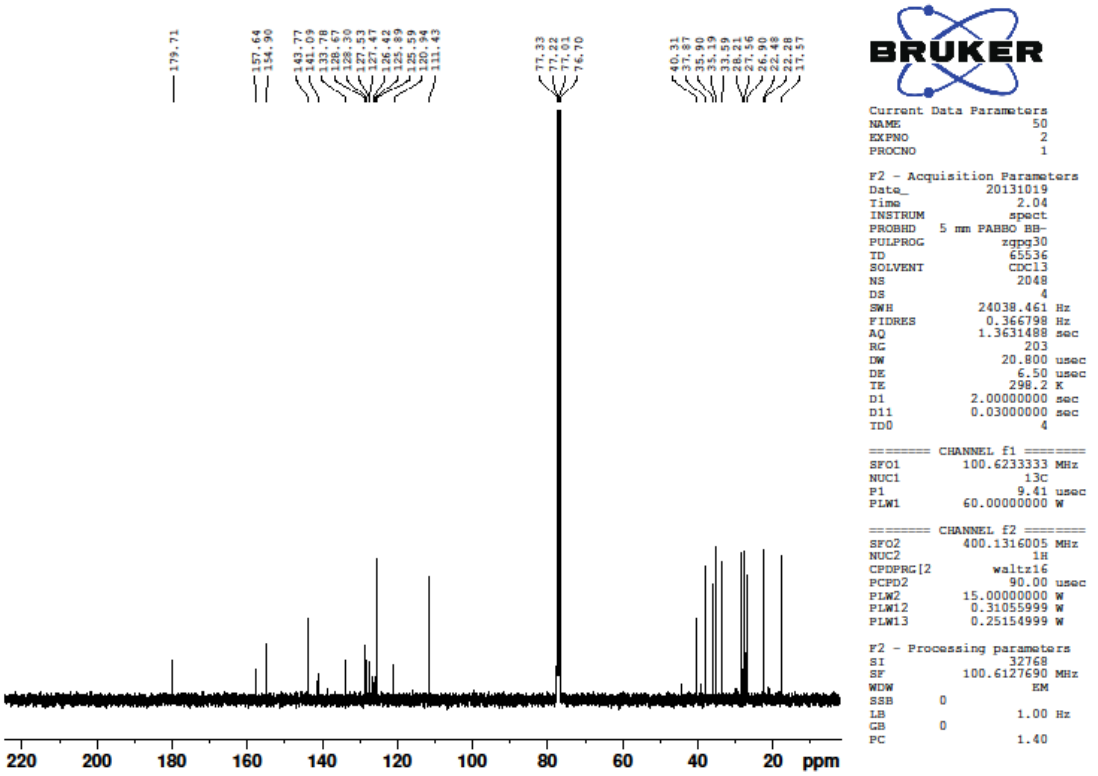


Figure S159. ^{1}H NMR spectrum of compound **32** in $CDCl_3$ (400 MHz)

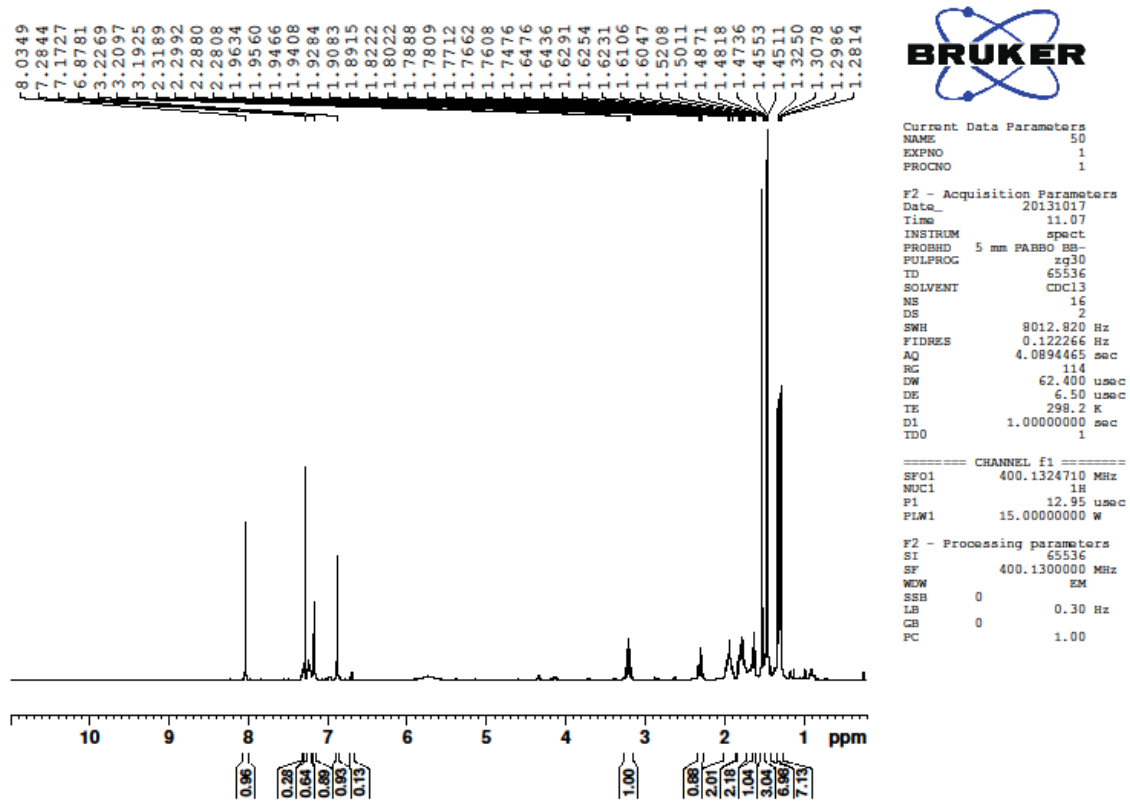


Figure S160. HSQC spectrum of compound **32** in $CDCl_3$

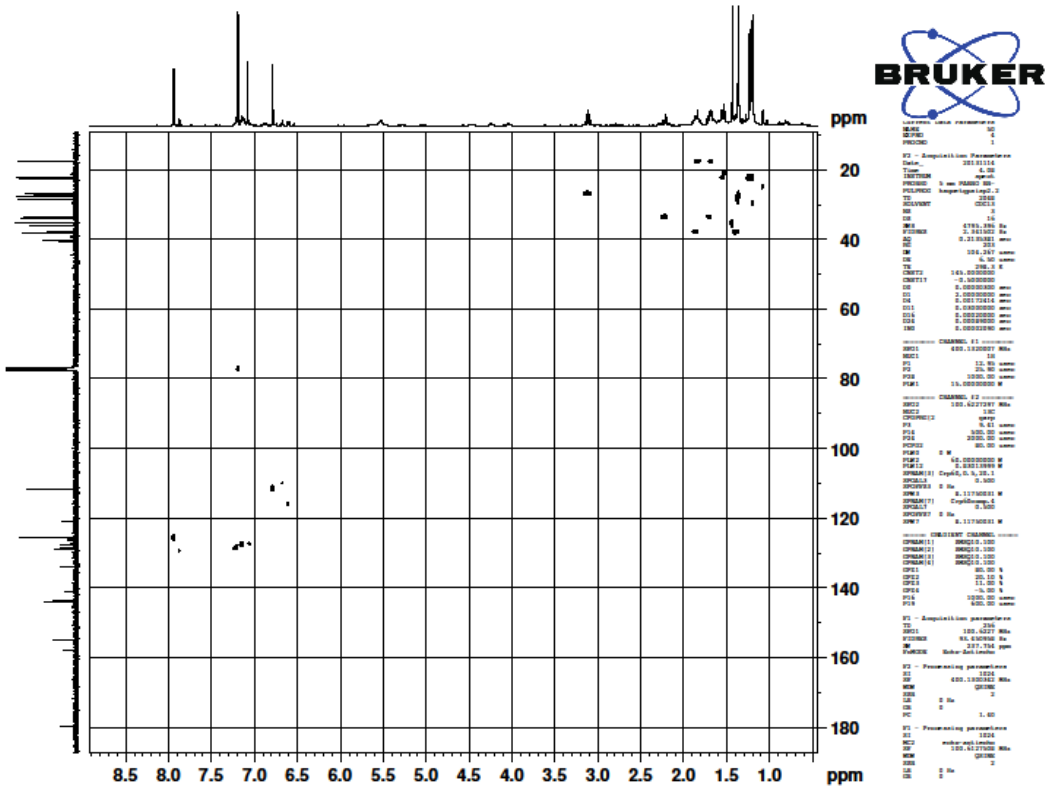


Figure S161. HMBC spectrum of compound **32** in $CDCl_3$

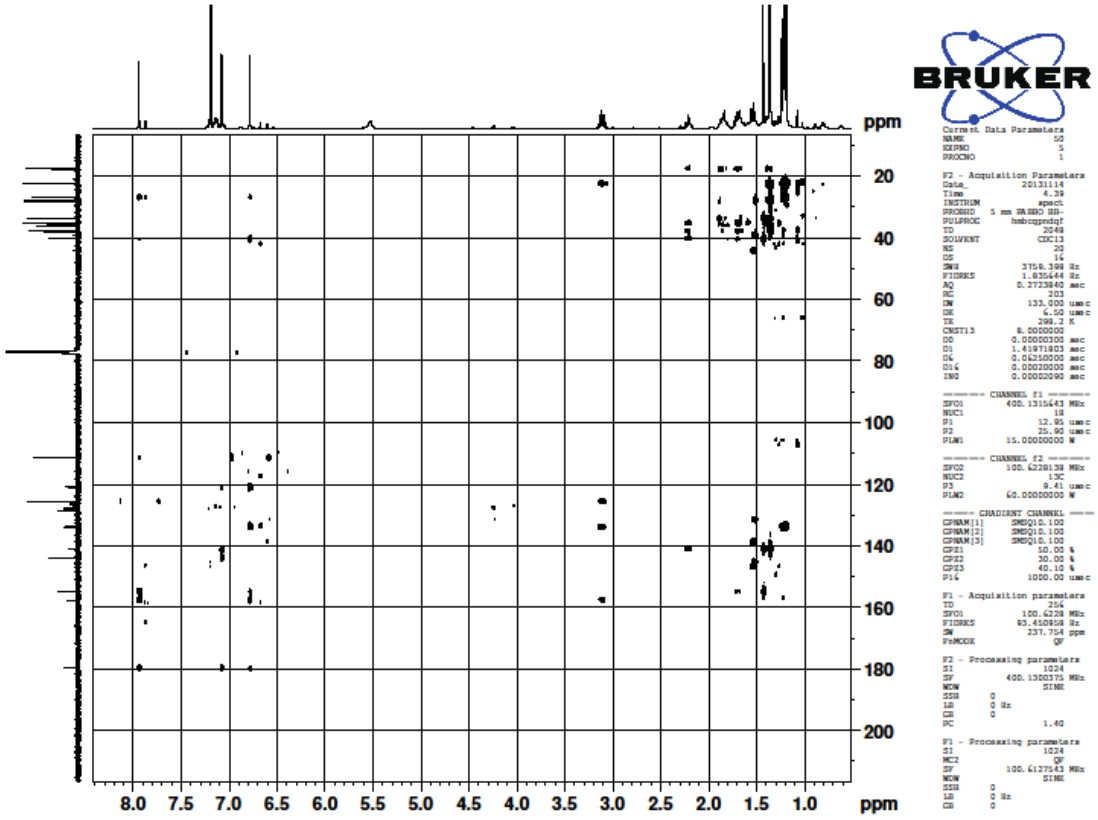


Figure S162. ^{13}C NMR spectrum of compound **33** in CD_3OD (150 MHz)

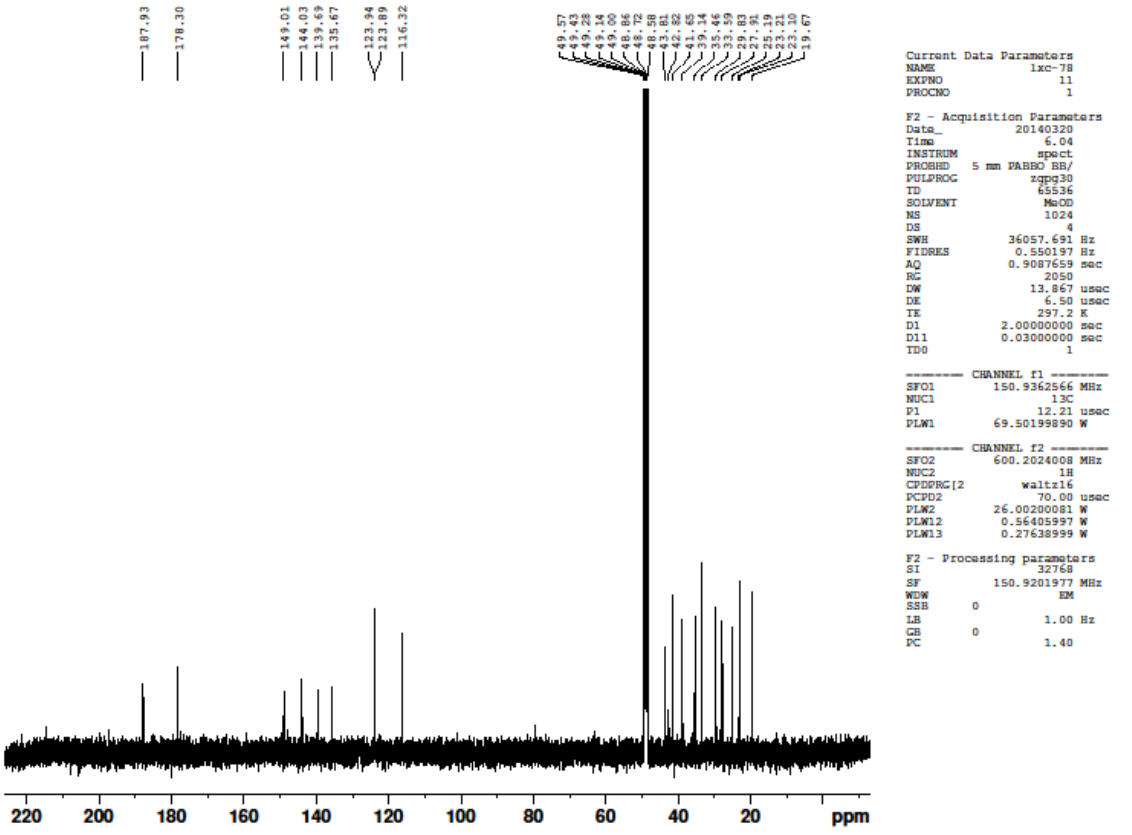


Figure S163. ^{1}H NMR spectrum of compound **33** in CD_3OD(150 MHz)

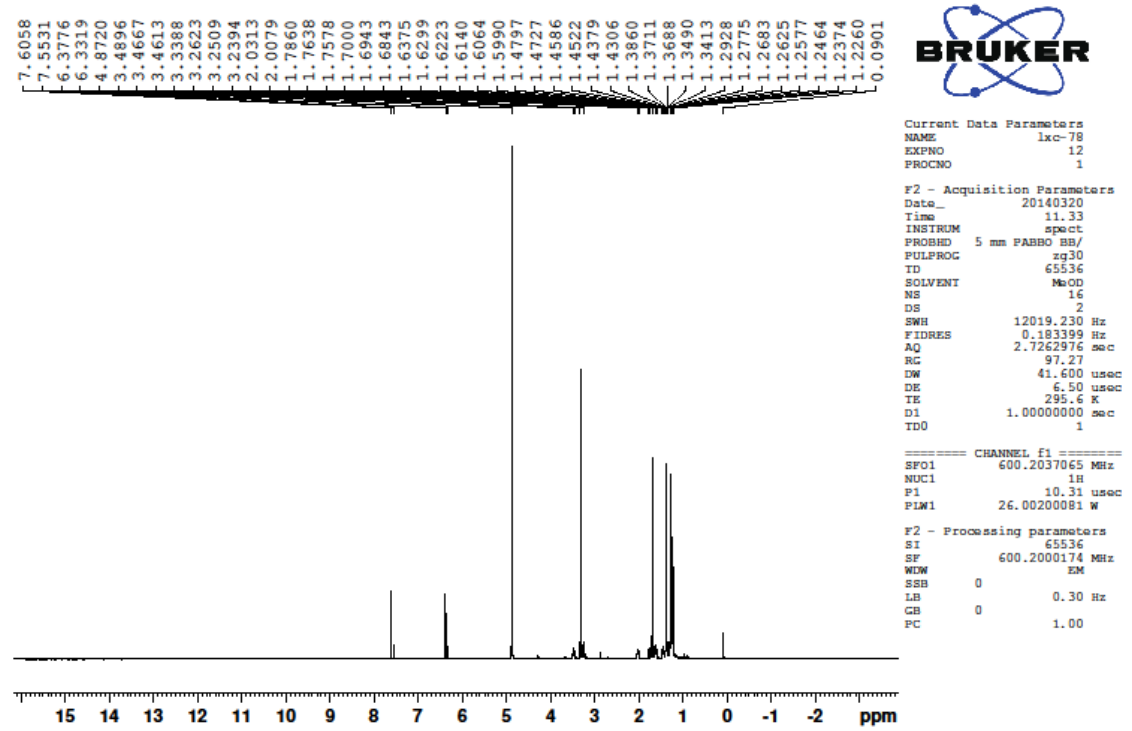


Figure S164. HSQC spectrum of compound **33** in CD_3OD

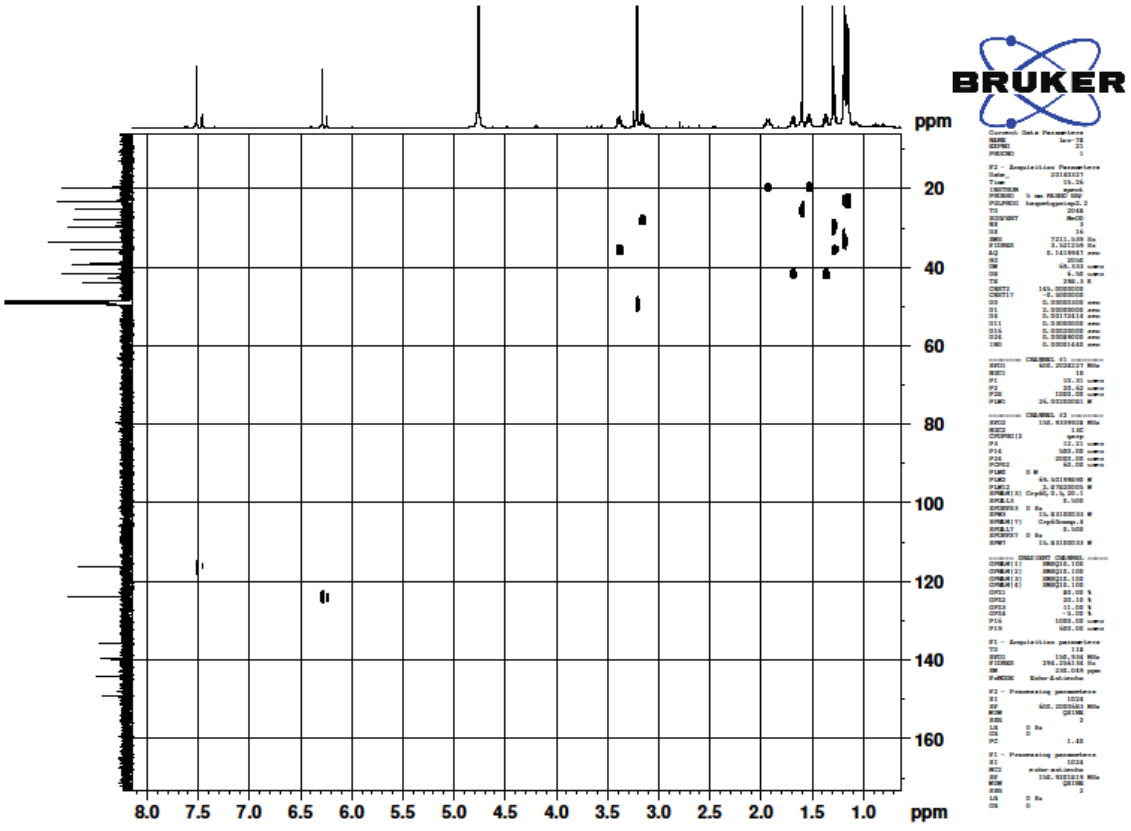


Figure S165. HMBC spectrum of compound **33** in CD_3OD

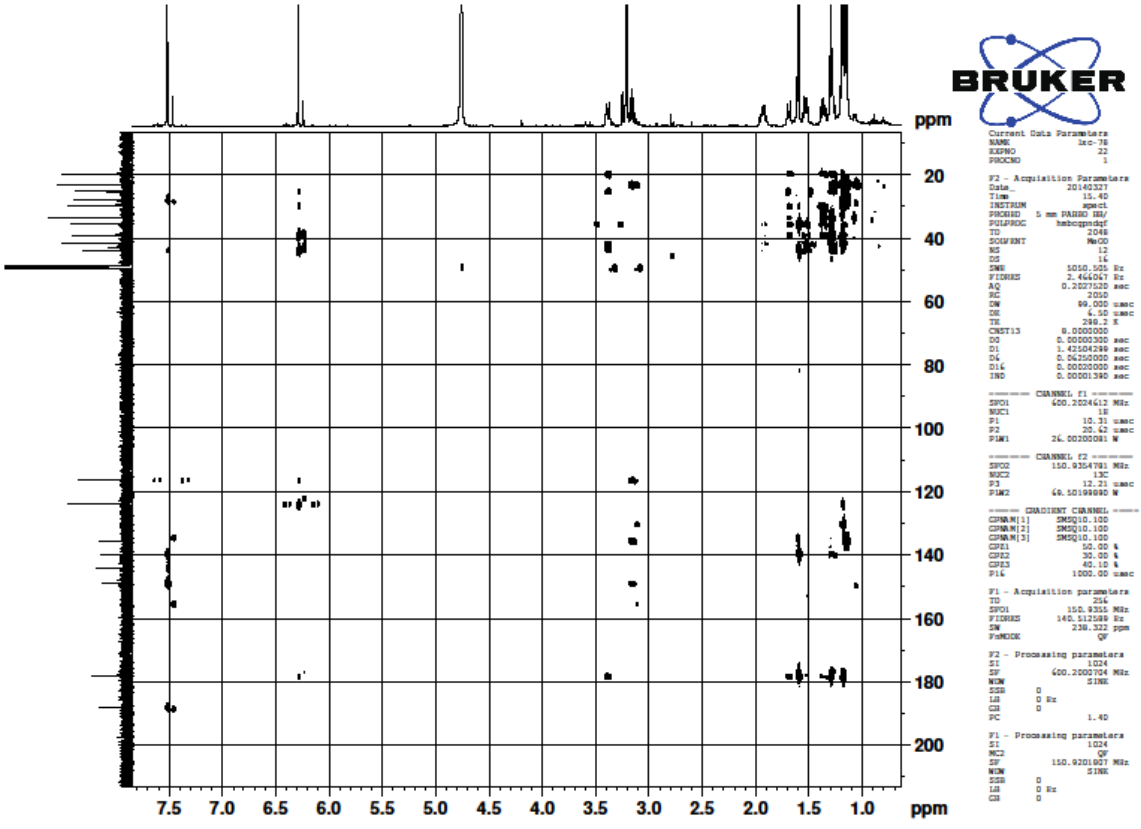


Figure S166. ^{13}C NMR spectrum of compound **34** in $CDCl_3$ (100 MHz)

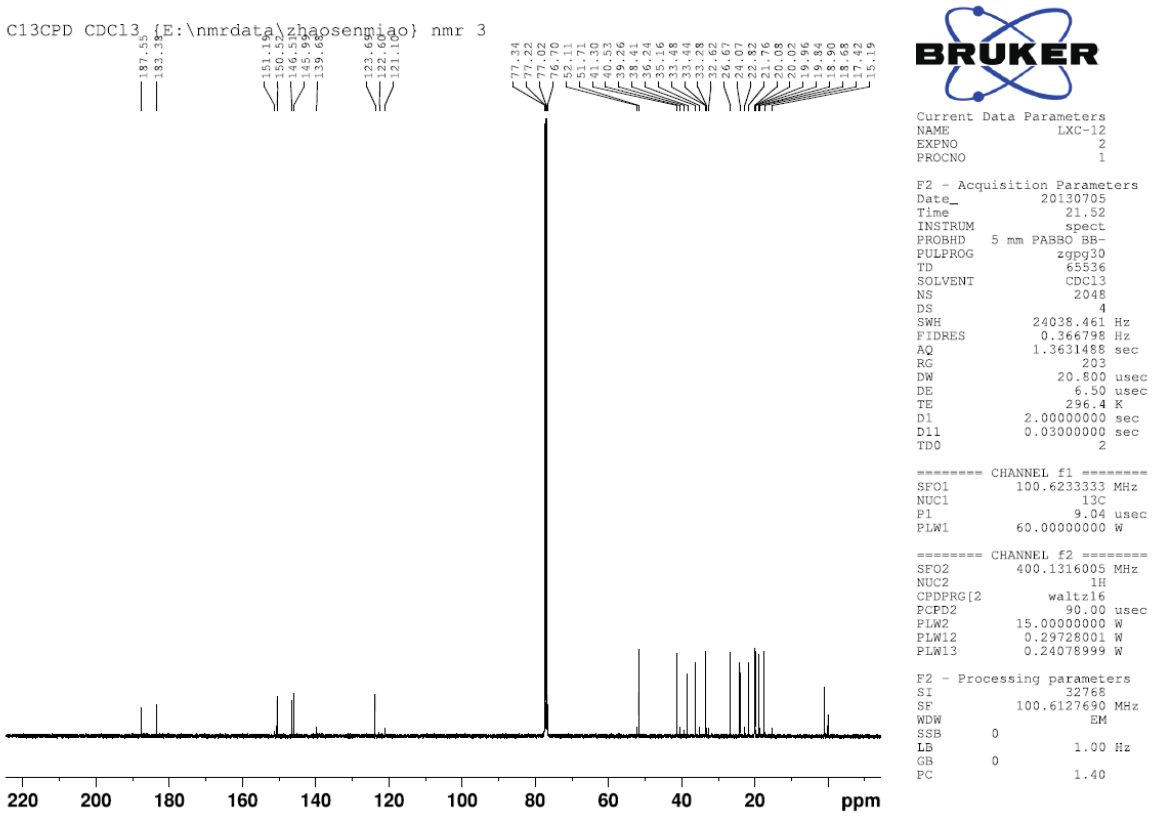


Figure S167. ^{1}H NMR spectrum of compound **34** in $CDCl_3$ (400 MHz)

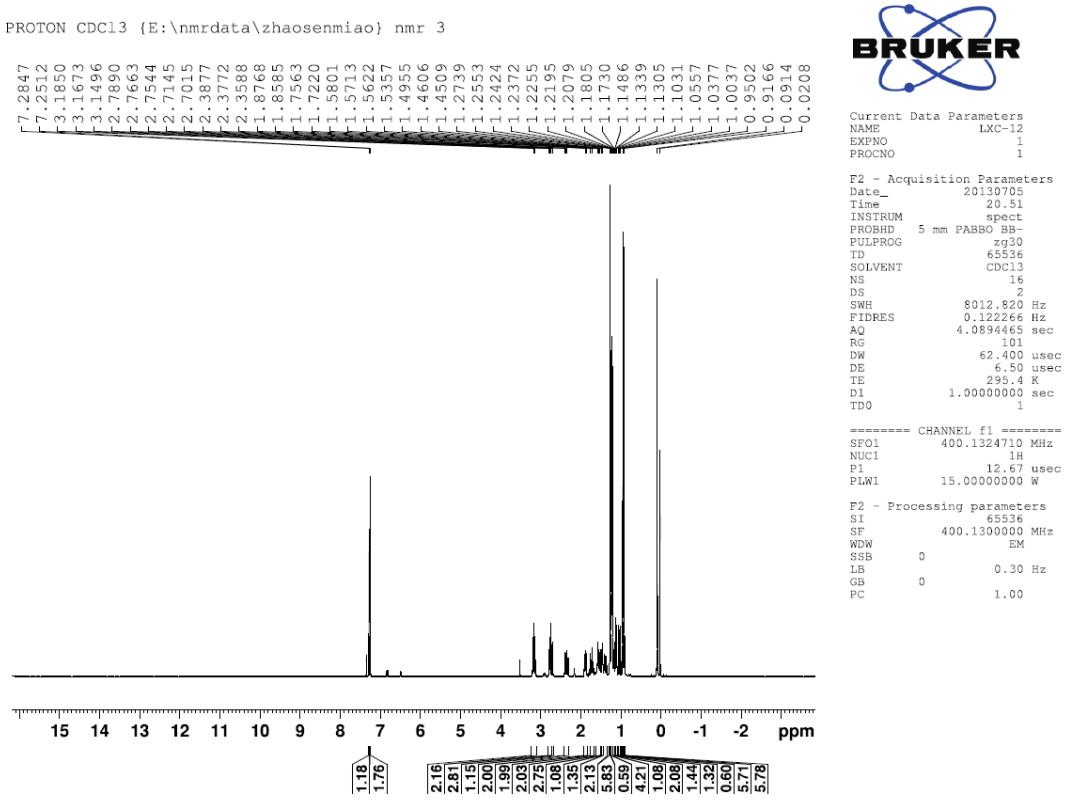


Figure S168. HSQC spectrum of compound **34** in$CDCl_3$

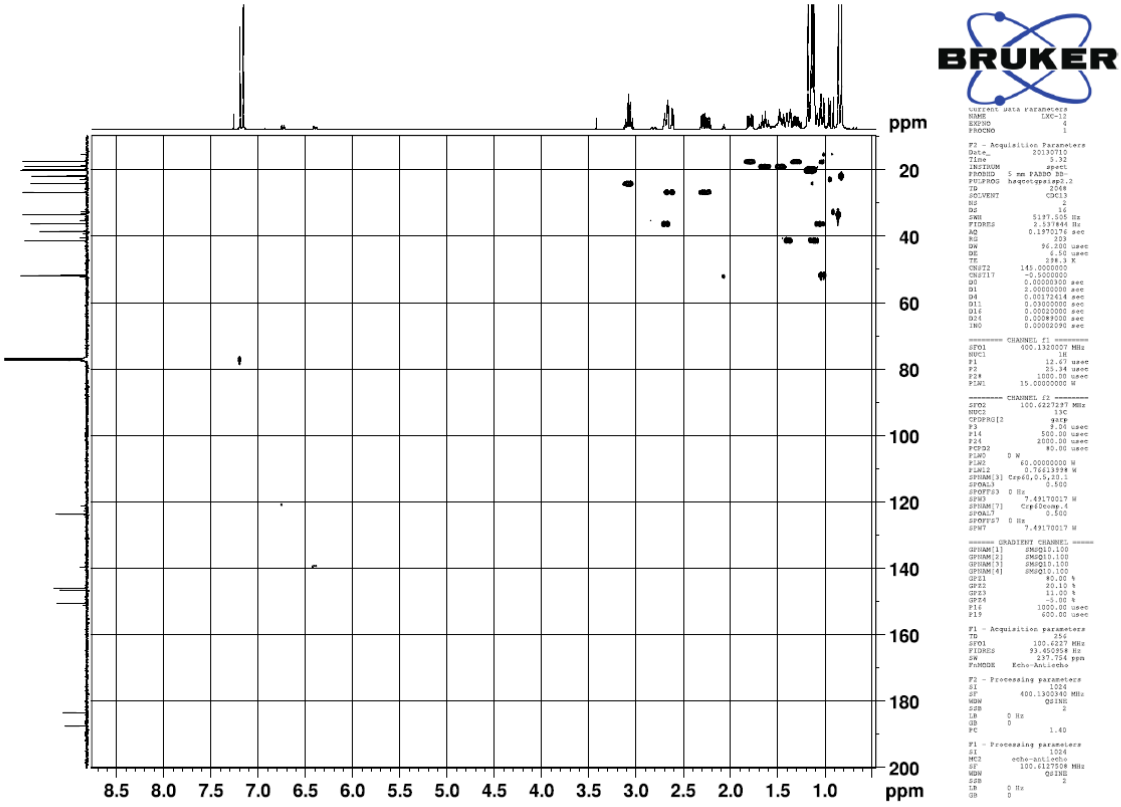


Figure S169. HMBC spectrum of compound **34** in $CDCl_3$

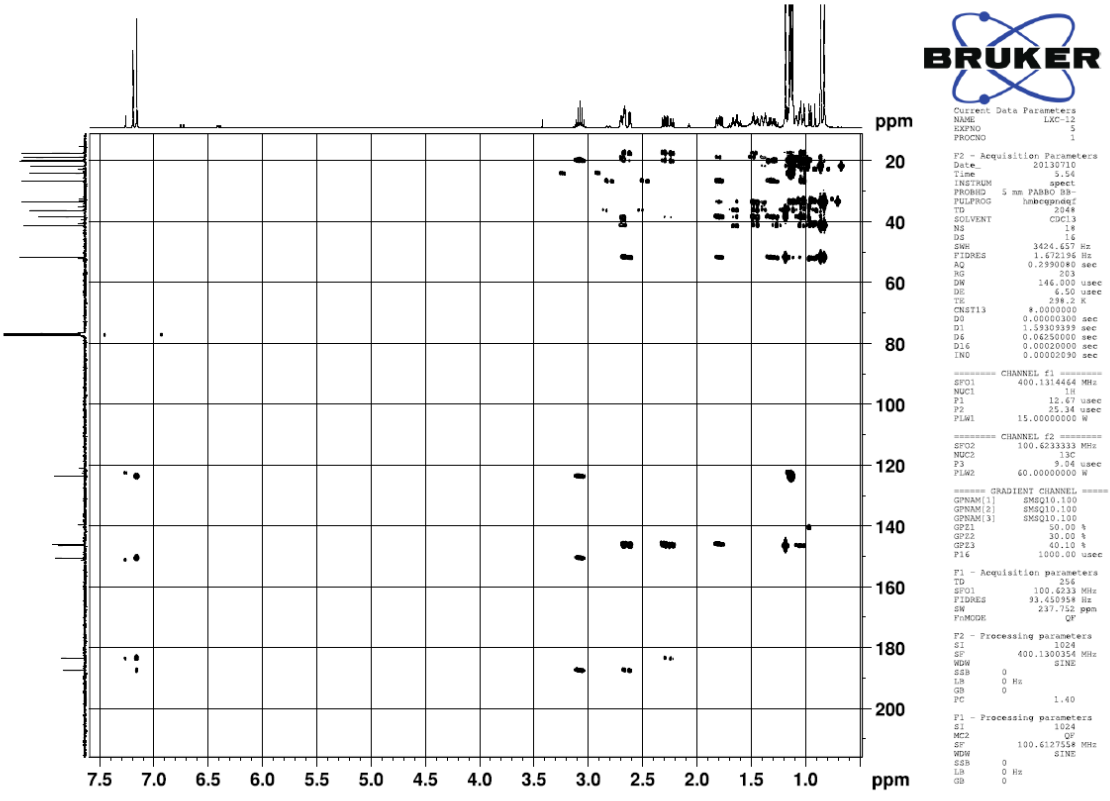


Figure S170. ^{13}C NMR spectrum of compound **35** in $CDCl_3$ (150 MHz)

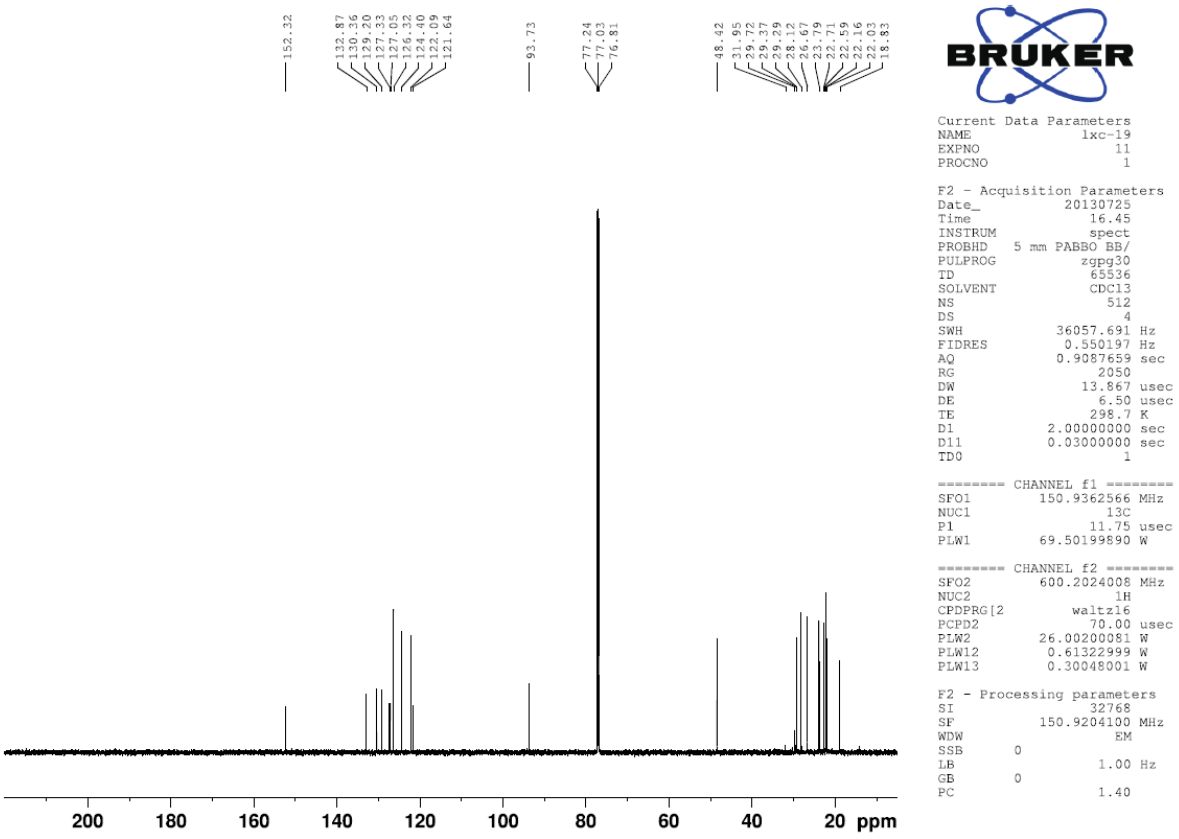


Figure S171. ^{1}H NMR spectrum of compound **35** in $CDCl_3$ (600 MHz)

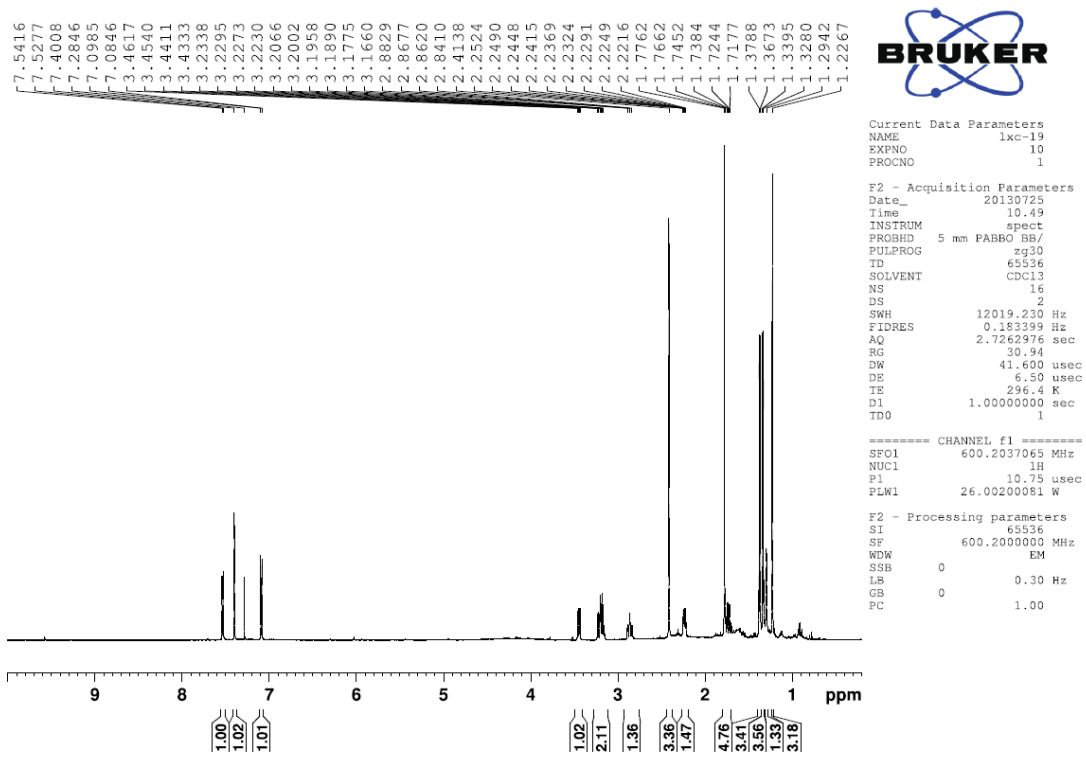


Figure S172. HSQC spectrum of compound **35** in $CDCl_3$

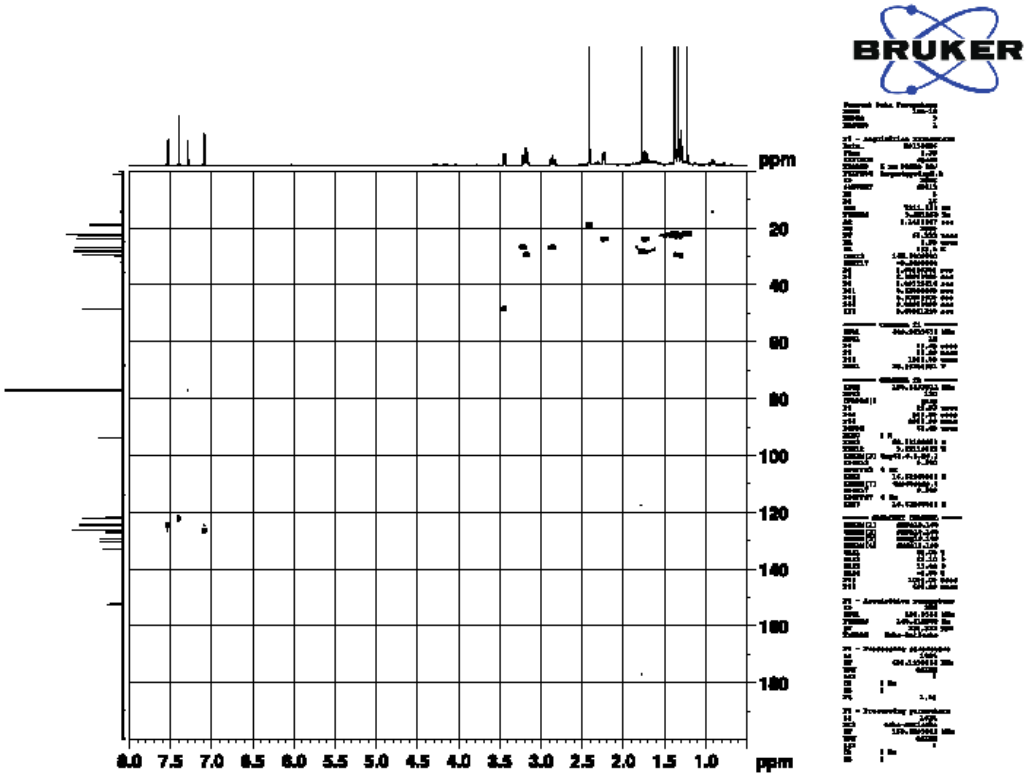


Figure S173. HMBC spectrum of compound **35** in CD_3OD

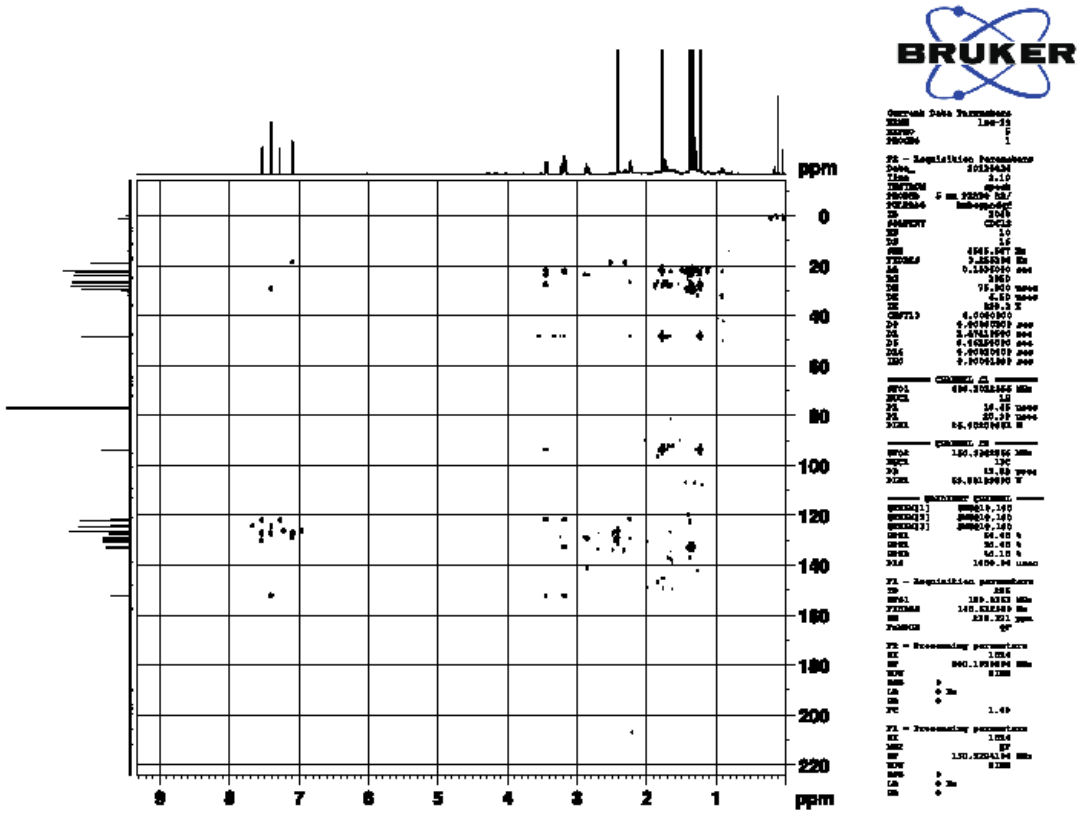


Figure S174. ^{13}C NMR spectrum of compound **36** in $CDCl_3$ (100 MHz)

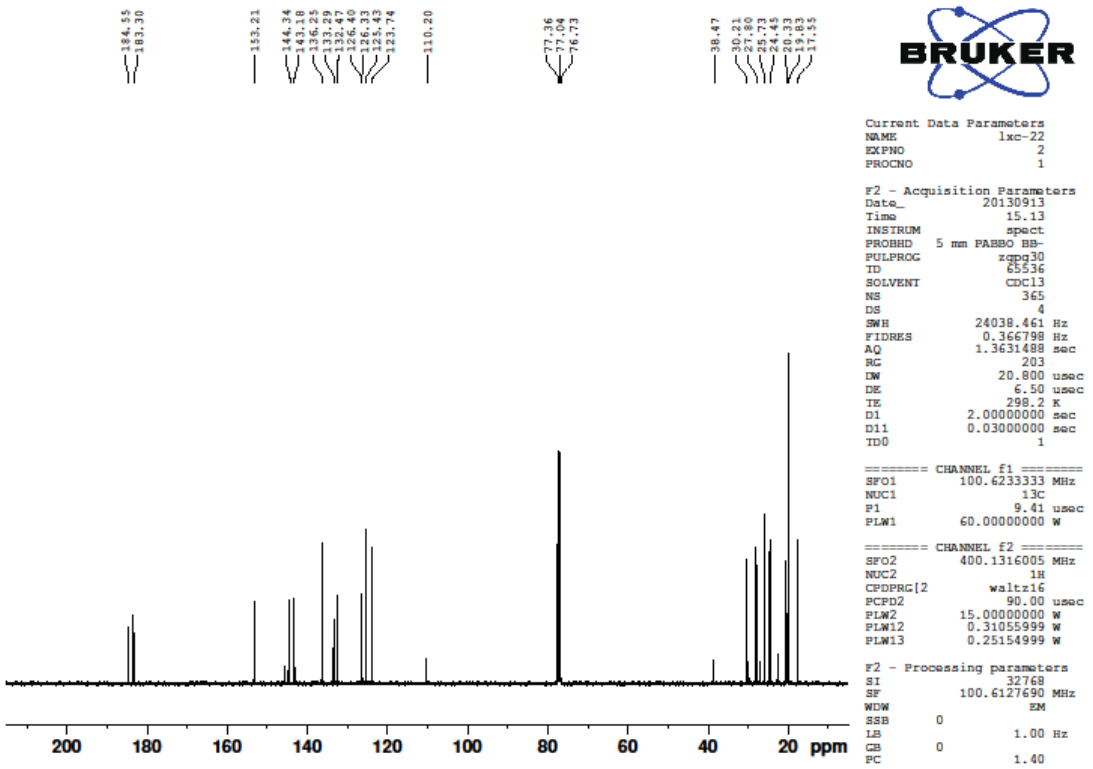


Figure S175. ^{1}H NMR spectrum of compound **36** in $CDCl_3$ (400 MHz)

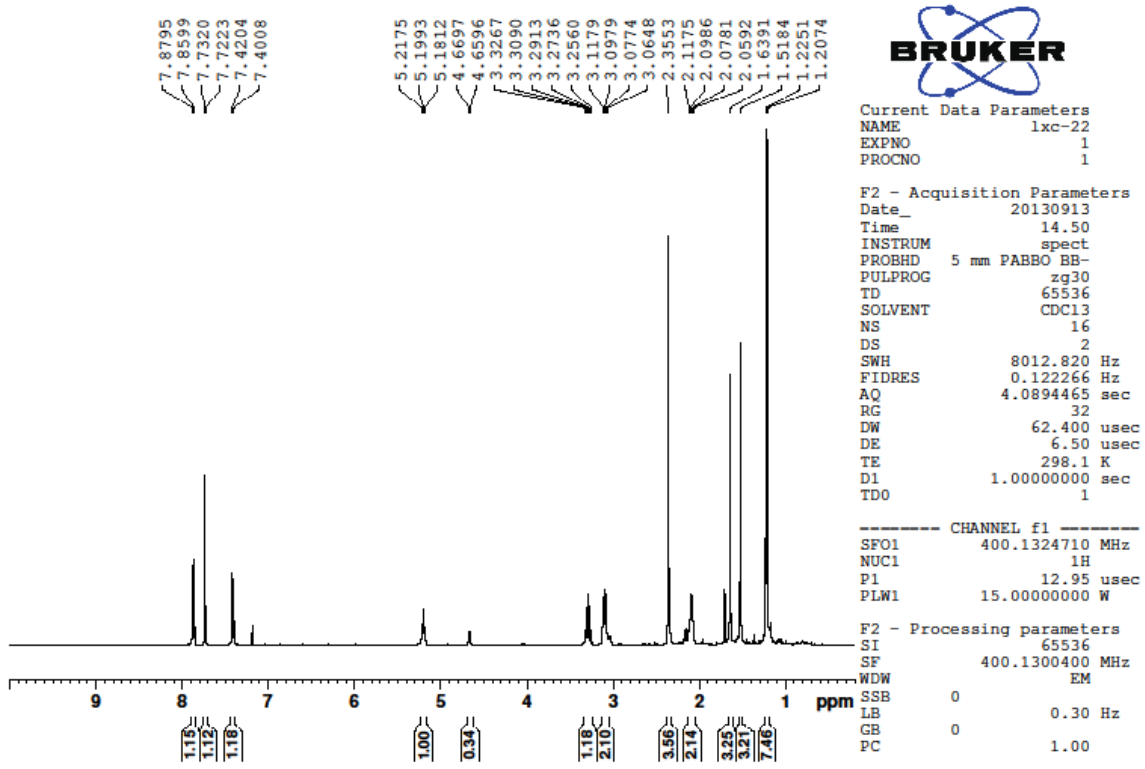


Figure S176. HSQC spectrum of compound **36** in $CDCl_3$

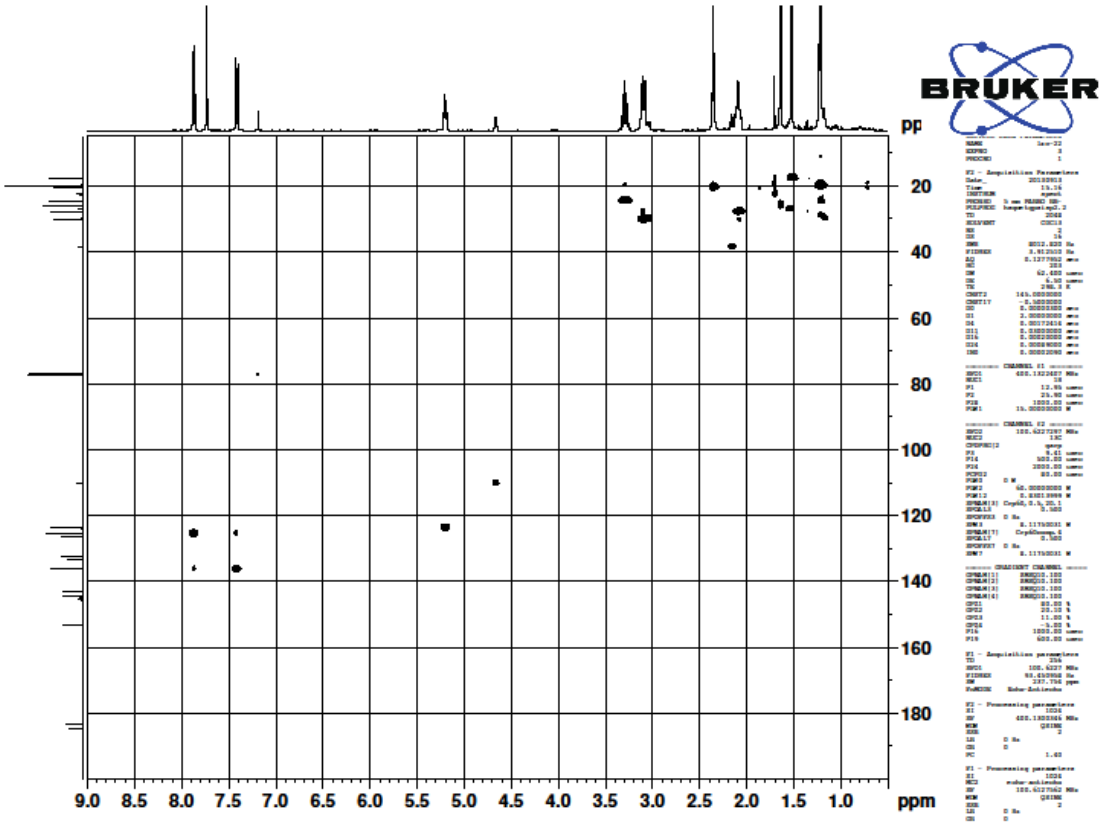


Figure S177. HMBC spectrum of compound **36** in$CDCl_3$

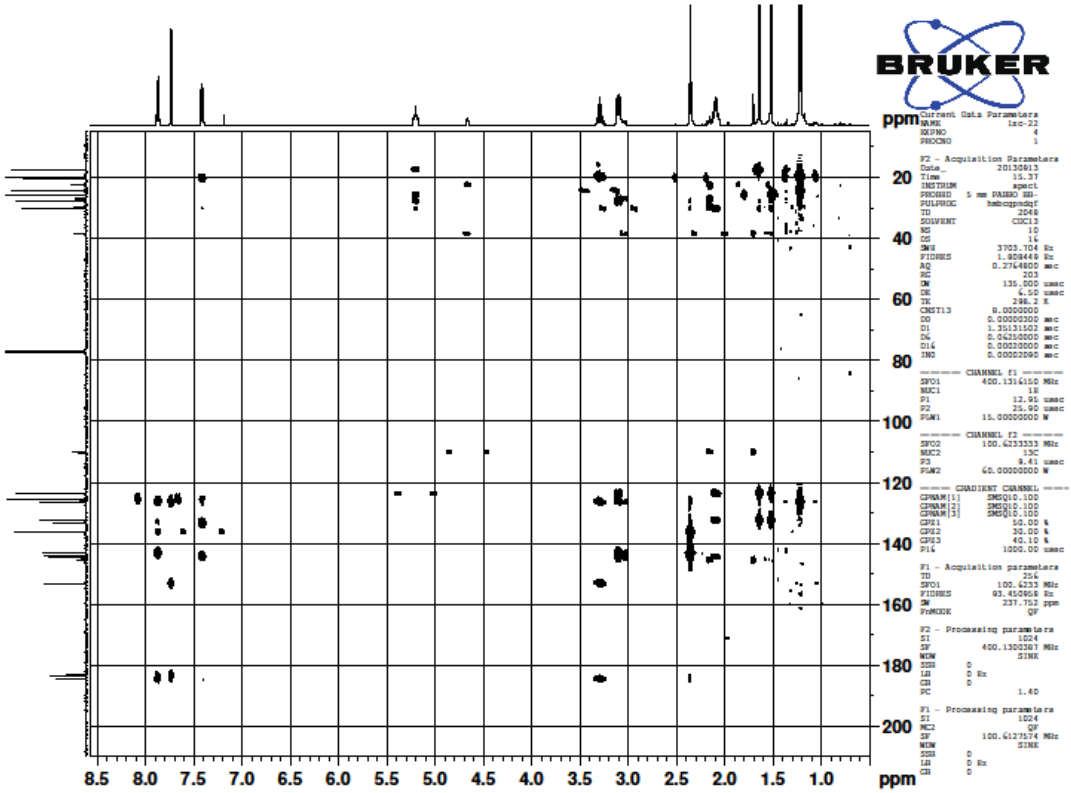


Figure S178. ^{13}C NMR spectrum of compound **38** in $CDCl_3$ (100 MHz)

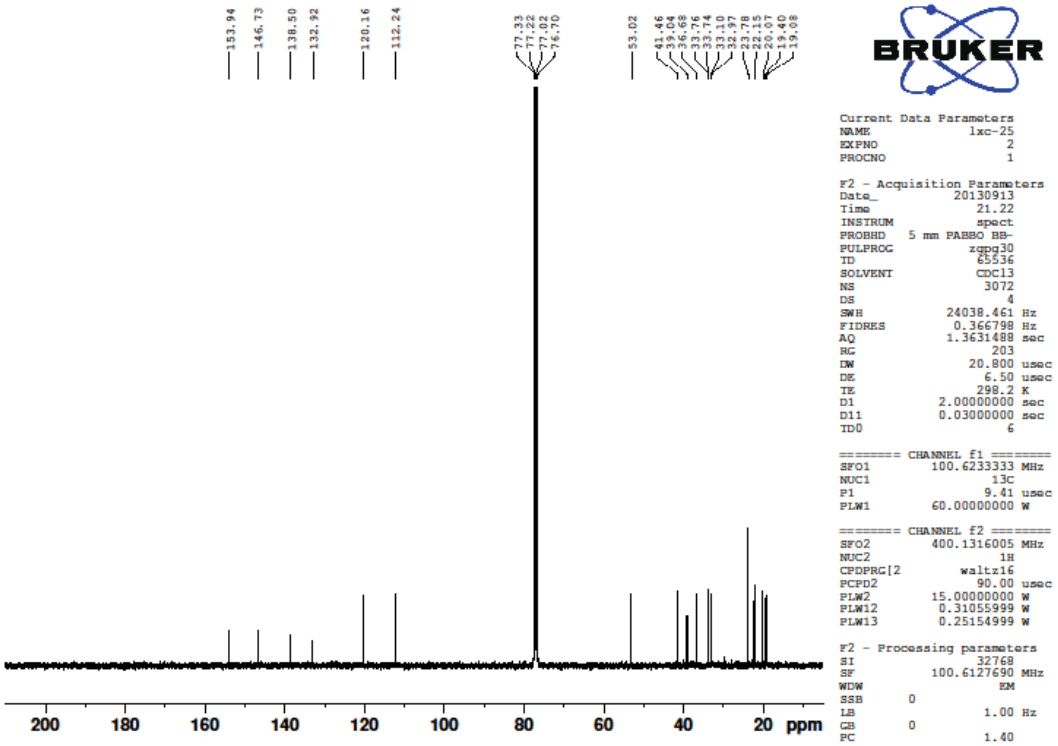


Figure S179. ^{1}H NMR spectrum of compound **38** in $CDCl_3$ (400 MHz)

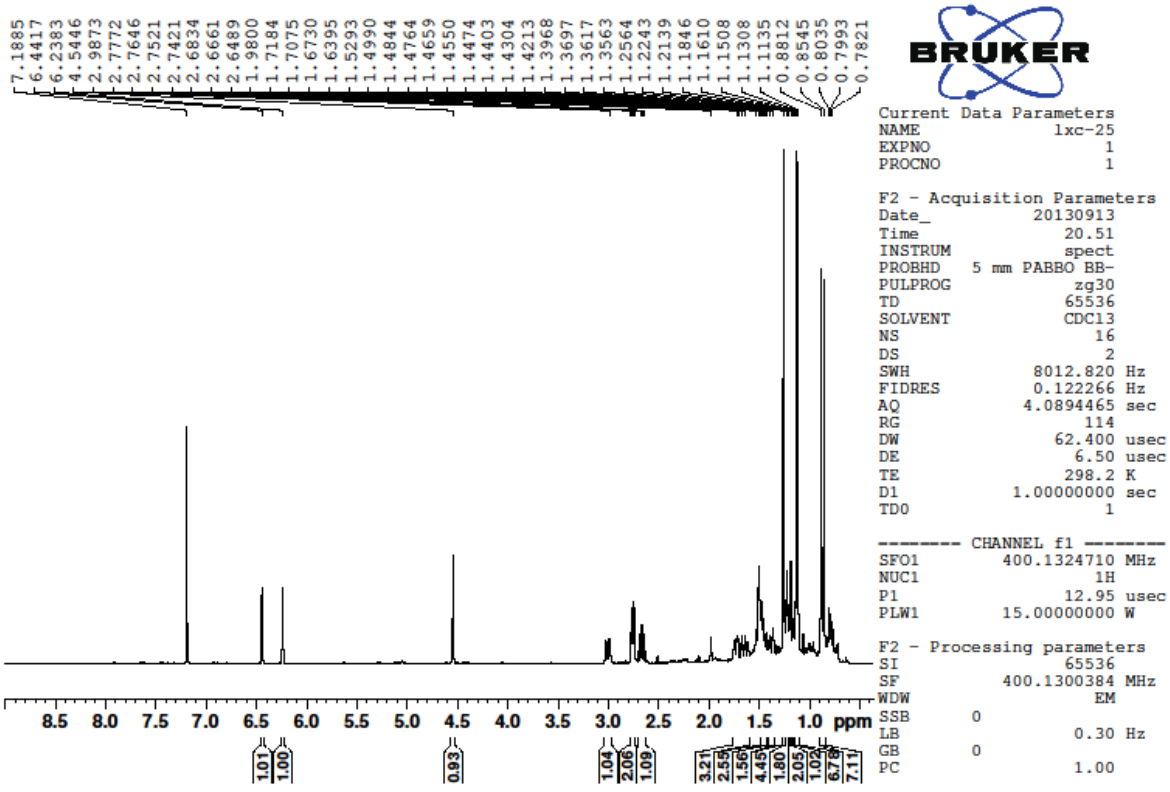


Figure S180. HSQC spectrum of compound **38** in $CDCl_3$

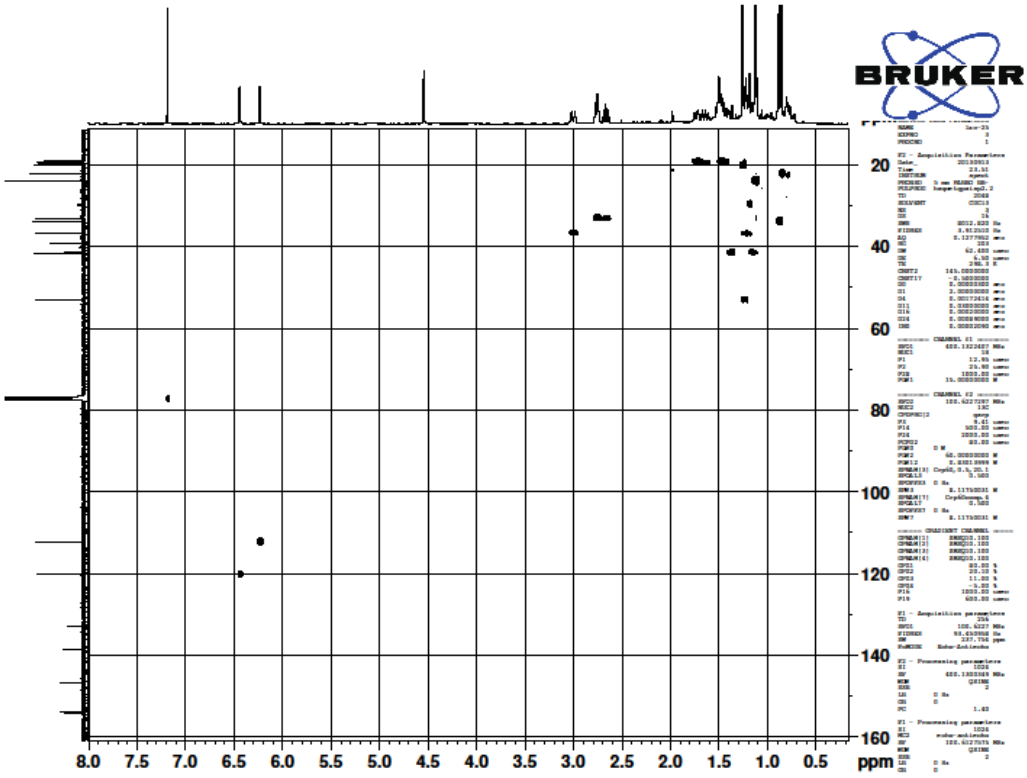


Figure S181. HMBC spectrum of compound **38** in $CDCl_3$

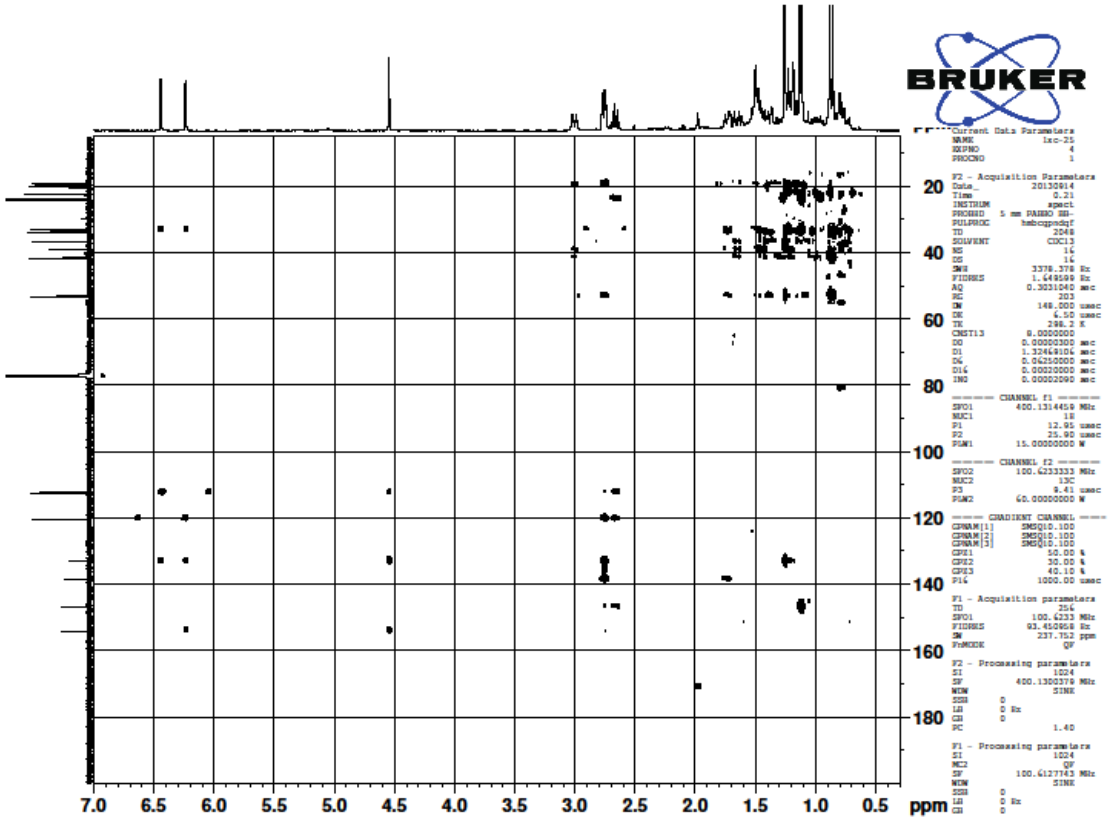


Figure S182. ^{13}C NMR spectrum of compound **39** in $CDCl_3$ (100 MHz)

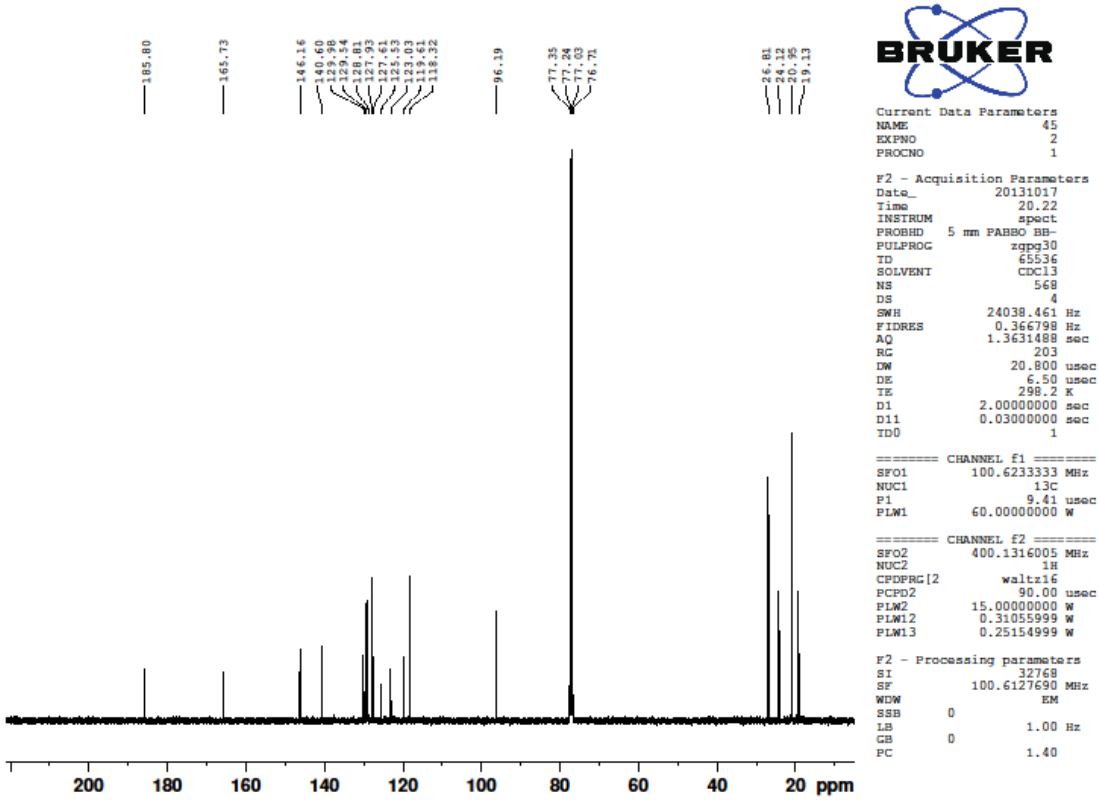


Figure S183. ^{1}H NMR spectrum of compound **39** in $CDCl_3$(400 MHz)

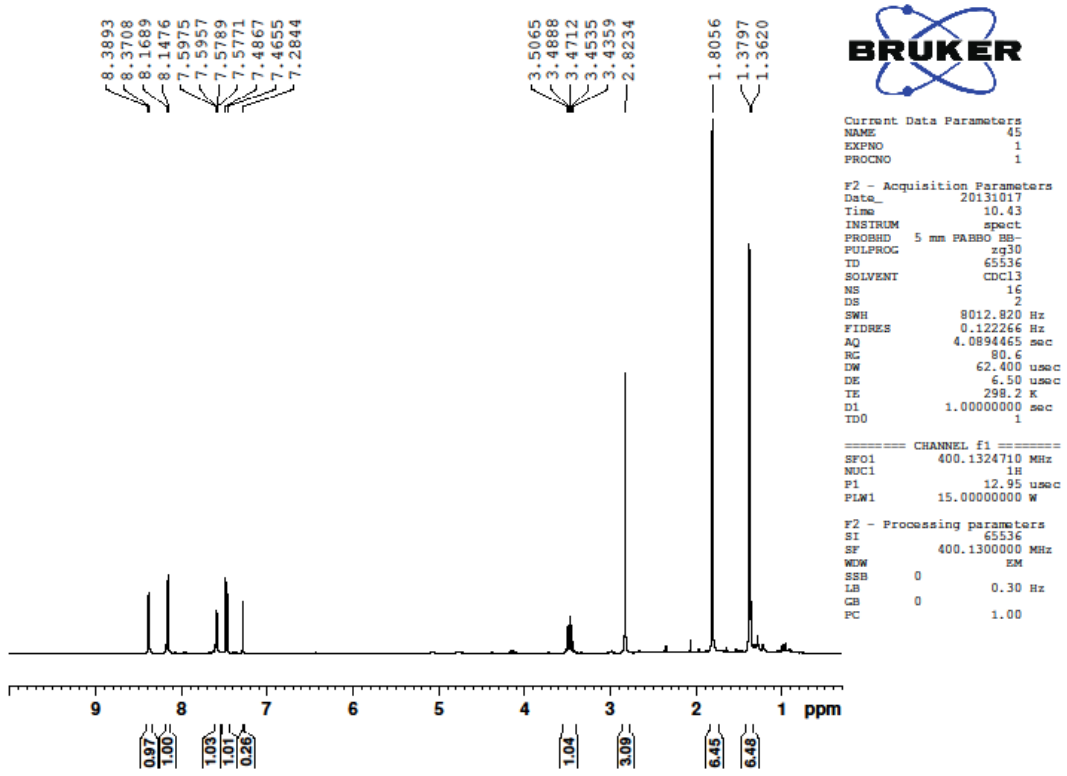


Figure S184. HSQC spectrum of compound **39** in $CDCl_3$

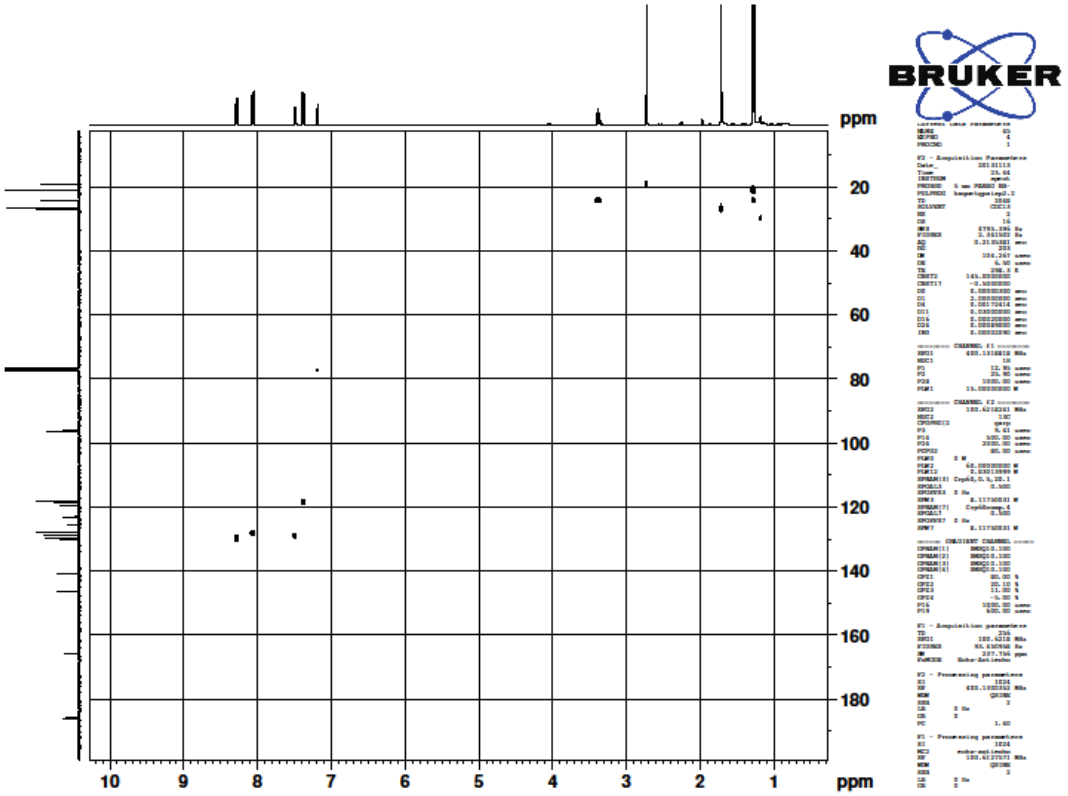


Figure S185. HMBC spectrum of compound **39** in $CDCl_3$

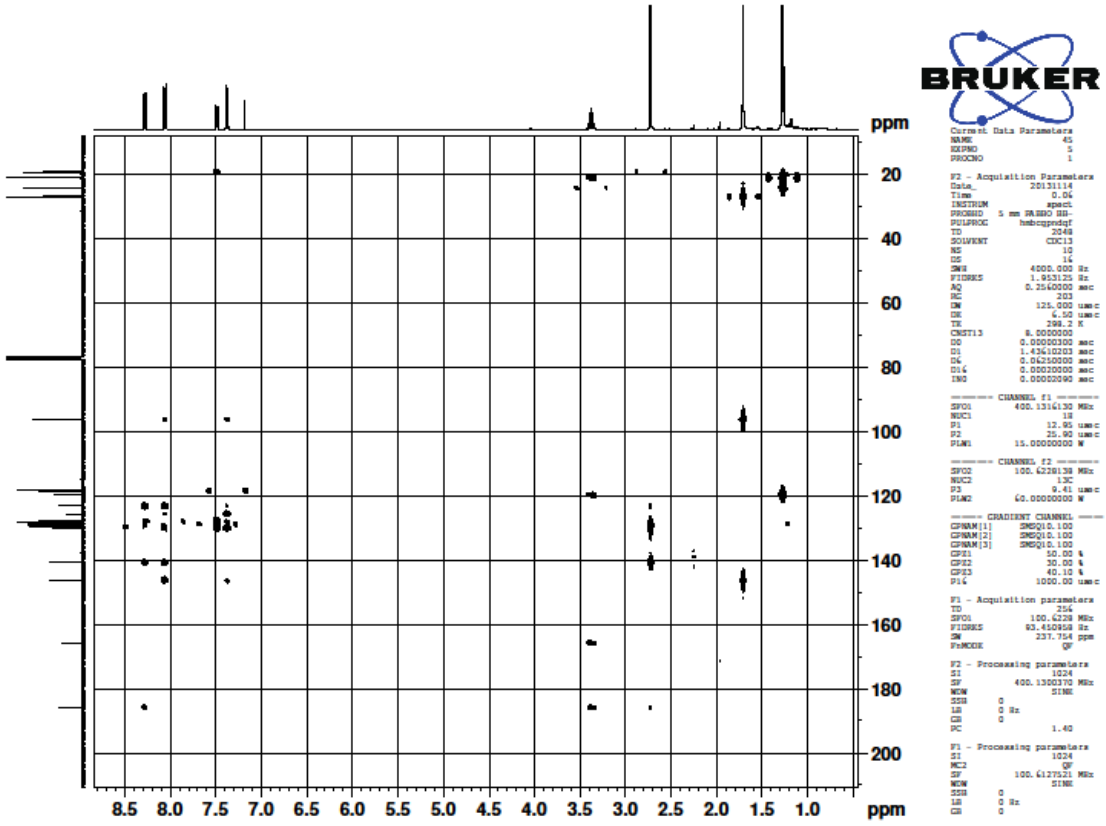


Figure S186. ^{13}C NMR spectrum of compound **40** in $CDCl_3$ (150 MHz)

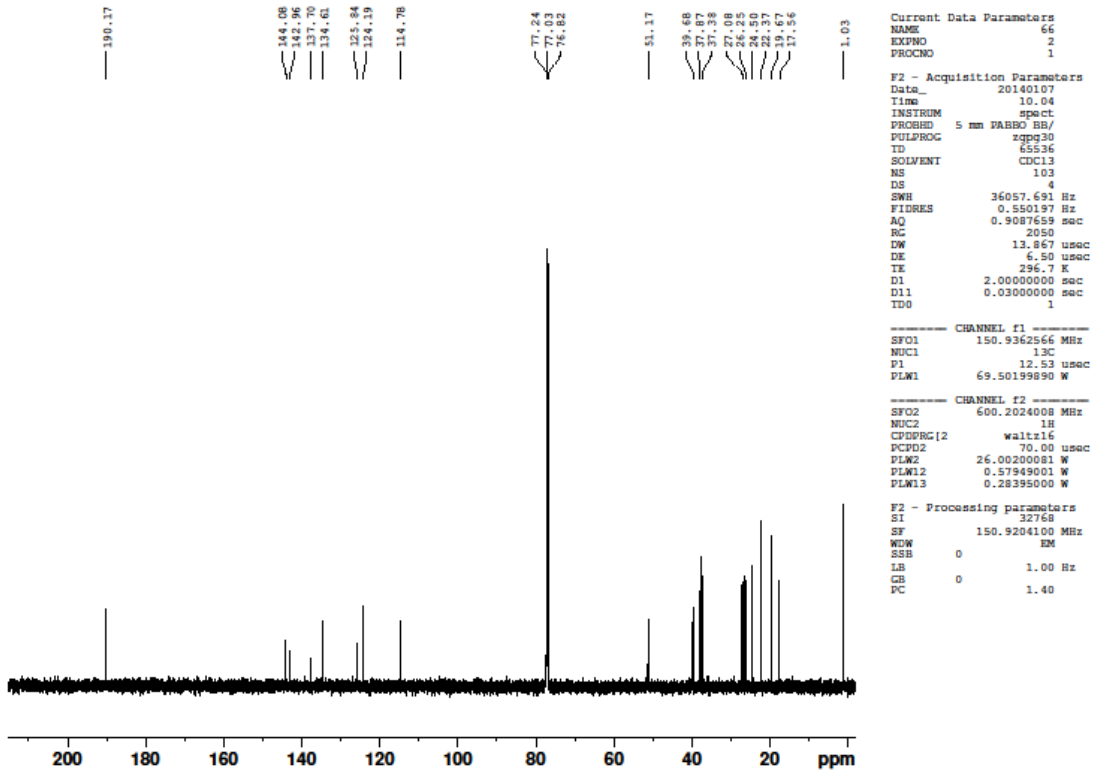


Figure S187. ^{1}H NMR spectrum of compound **40** in $CDCl_3$ (600 MHz)

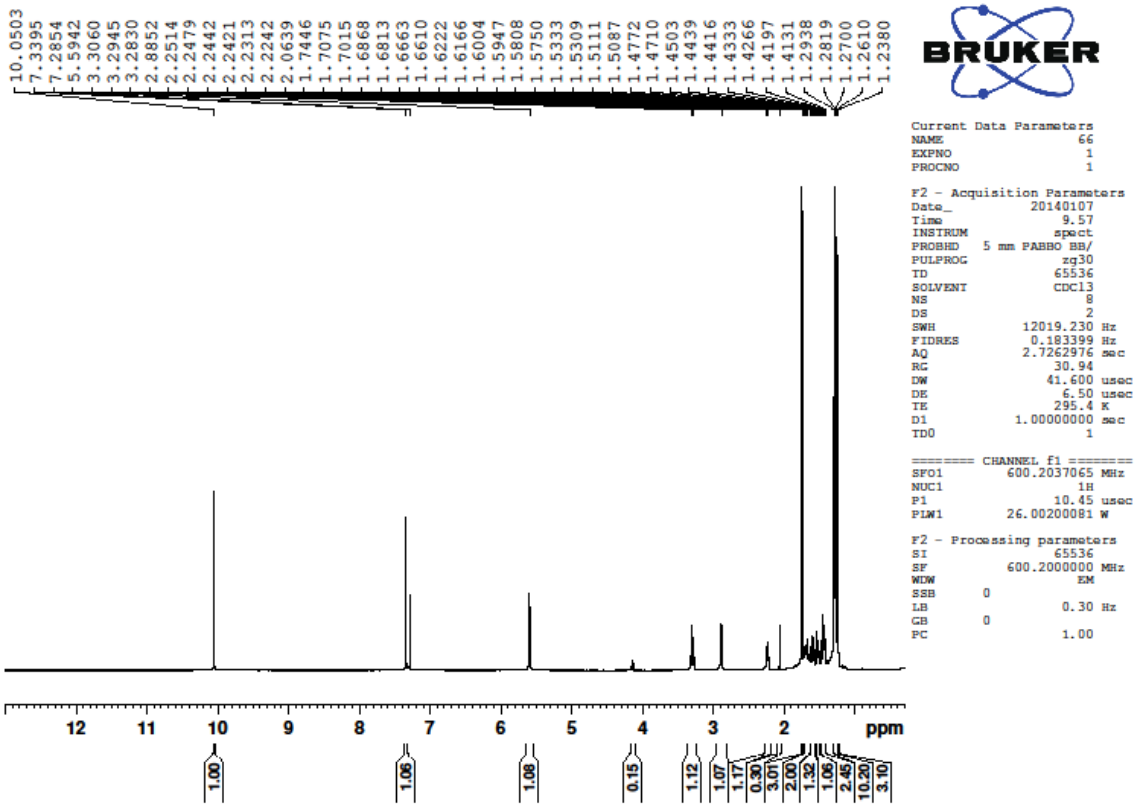


Figure S188. HSQC spectrum of compound **40** in $CDCl_3$

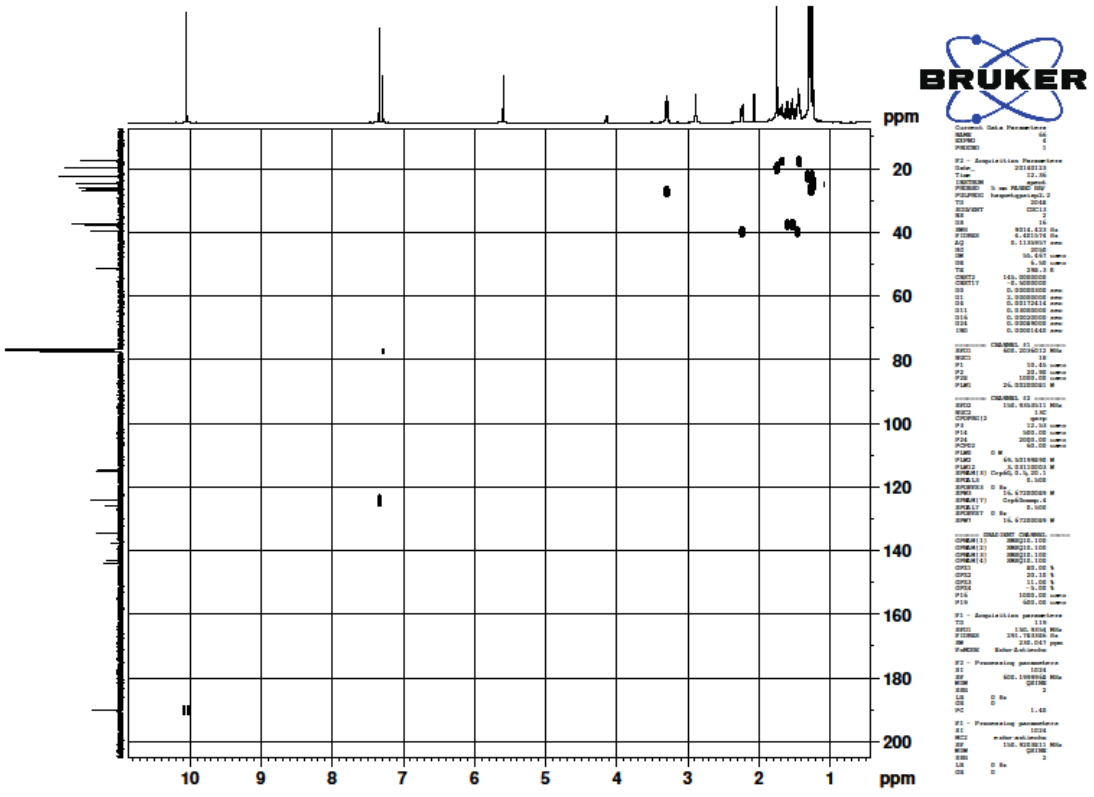
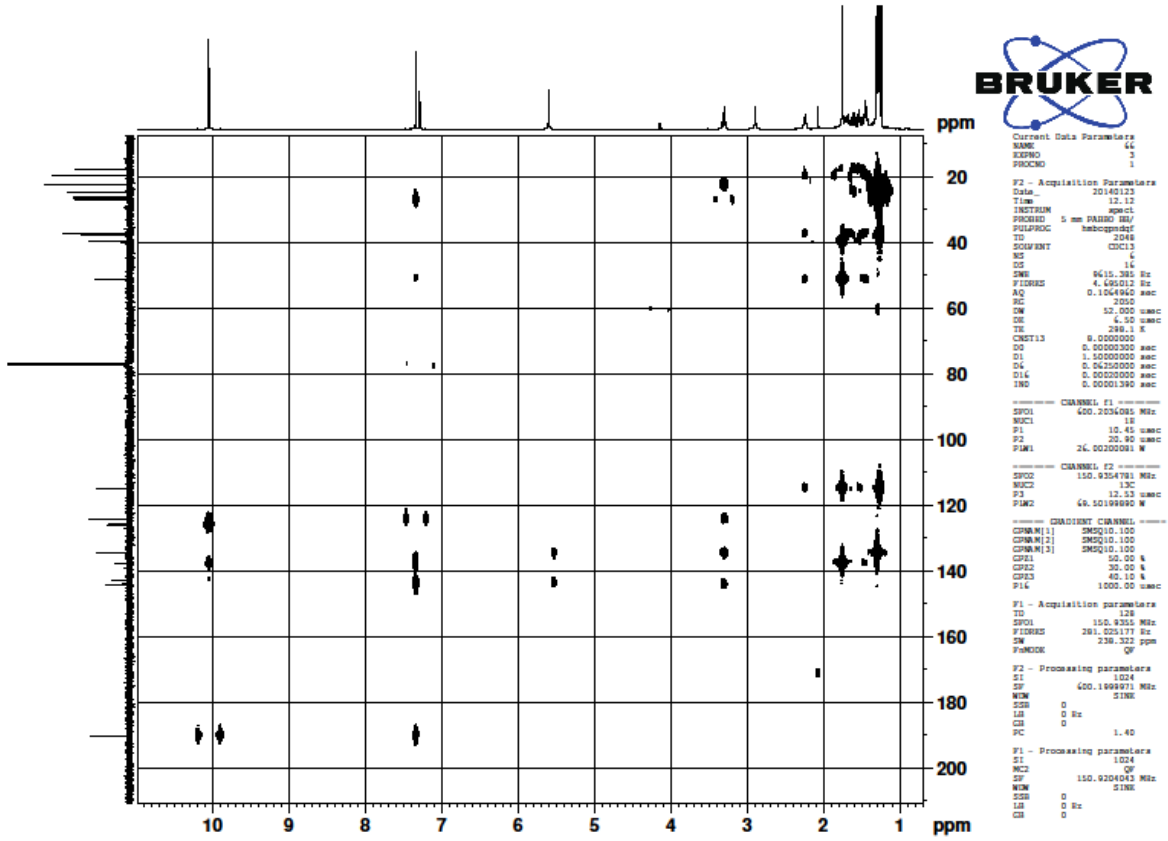


Figure S189. HMBC spectrum of compound **40** in $CDCl_3$



S3. Bioassay

S3.1 DPP-IV inhibitory assay

Dipeptidyl peptidase IV(DPP-IV, Lot: SLBP1407V), Substrate (Gly-Pro-p-nitroaniline hydrochloride, Gly-Pro-pNA, Lot: 12BN6311V),Tris-(hydroxymethyl) aminomethaneand sodium nitrite (Lot: 20130502) were from Shanghai Major Bio Technologies Co.,Ltd. (Shanghai, China),DPP IV inhibitors standards: diprotin A (IIe-Pro-IIe, Lot: 065K1584V), Sitagliptin phosphate(Lot: 2-MIC-14-1), were purchased from Sigma–Aldrich (Deisen-hofen, Germany).DMSO and hydrochloric acid were analytical grade purchased from SinopharmChemical Reagent Co., Ltd. (Shanghai, China). Ultra-pure water waspreparedby a Synergy system (Millipore, Schwalbach, Germany).water bath (SC-15, Shanghai Bilon Instruments Co.,Ltd.), electronic analytical balance (BP211D, METTLER TOLEDO,Germany), microplate reader (ELx800, Bio-Tek Instruments,USA).

Compounds **1**~**40** were prepared from the chemical study of*Caryopteris incana* (Thunb.) Miq.

Diprotin A and sitagliptin phosphate was diluted to various concentrations (20.0, 50.0, 100.0, 200.0, 500.0 μM) using Tris–HCl(1 U/L,70 mM, pH 8.2).

Each sample was diluted to various concentrations (1.0, 5.0, 10.0, 20.0, 50.0mM) using DMSO.

50μL of DPP-IV enzyme diluted with Tris–HCl buffer (1 U/L,70 mM, pH 8.2) was pipetted 50 μL into clear microplate wells.Subsequently, 2μLTris–HCl buffer or Standard and sample solutions wereadded and incubated at 37◦C for 10 min,then 100 μL of chromogenic substrate Gly-Pro-pNA (456 μM) was added into each welland incubated at 37◦C for 30 min. The absorbance was measuredat 405 nm using a microplate reader.

Each sample was analysed in triplicate, and the absorbance values were normalized to sample blanks in which DPPIV was replaced with Tris–HCl buffer (1 U/L,70 mM, pH 8.2) The negative control (no DPP-IV activity) and positive control (DPP-IV activity with no inhibitor) were prepared by using Tris–HCl instead of the sample and DPP-IV solution and instead of the sample, respectively. The DPP-IV inhibitory result showed in Table S1

Table S1*in vitro* DPP-IV inhibitionassay of compounds **1**–**40**

No	IC_{50}(μM)	No	IC_{50}(μM)	No	IC_{50}(μM)
1	-	15	-	29	115.9
2	-	16	-	30	228.9
3	54.2	17	>300	31	-
4	222.9	18	>300	32	-
5	>300	19	>300	33	>300
6	-	20	-	34	-
7	-	21	>300	35	-
8	-	22	-	36	>300
9	-	23	>300	37	-
10	-	24	-	38	>300
11	>300	25	-	39	-
12	>300	26	>300	40	178.3
13	>300	27	-	Diprotin A	2.3
14	-	28	168.7	sitagliptin	5.4

S3.2 Cell viability assay and flow cytometry analysis

Cells

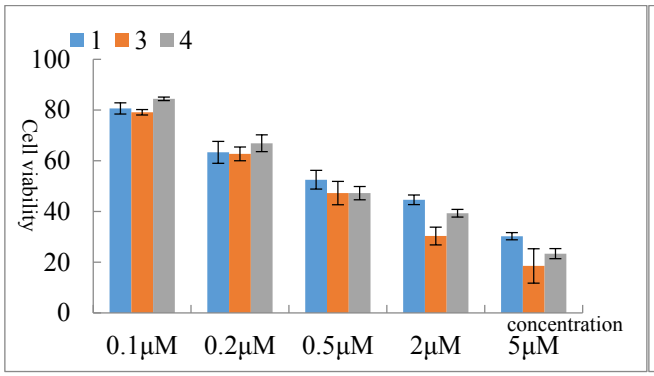
All cells were maintained in Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% fetal bovine serum, 4 mM L-glutamine, 100 IU penicillin, and 100 mg/ml streptomycin at 37℃ in a humidified incubator containing 5% CO_2.

Cell Viability Assay

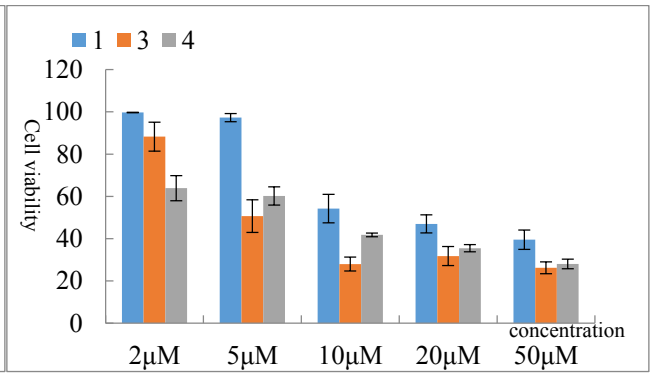
Cell viability was assessed by MTT.Cells were seeded on 24-well plates at a density of 5 × 103 cells per well. A549 cells were treated by DMEM plus 2% fetal bovine serum with fractions obtained by column chromatography over silica gel (2, 5, 10, 20, 50, 100, 200μg/mL); All cells were treated by DMEM plus 2% fetal bovine serum with compound **1**, **3** and **4** (0.1, 0.2, 0.5, 2.0, 5.0 μmol/L for A549 cells, 2, 5, 10, 20, 50 μmol/L for the others) and Compound **2**(10, 20, 50, 100, 200μmol/L) for 24h, Then, cells were incubated with MTT (1 mg/mL) for 4 h. The cells viability was assessed at 490 nm absorbance using a 24-well plate reader (Biotek, VT, USA). The viability was calculated as viability (%) = (A490, sample− A490, blank) / (A490, control − A490, blank) × 100

The percentage of cell growth rate was calculated as follows (**Figure S190**):

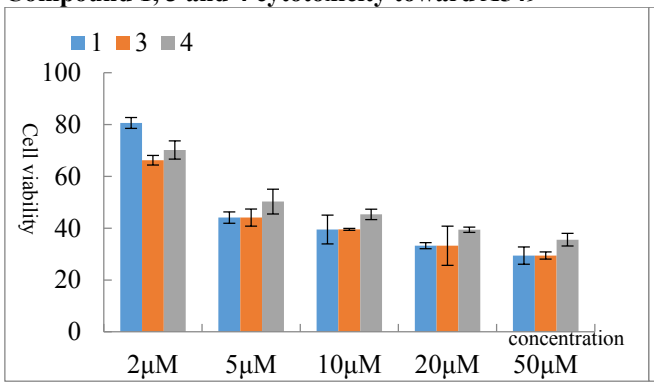
Figure S190. Percentage of cell growth rate



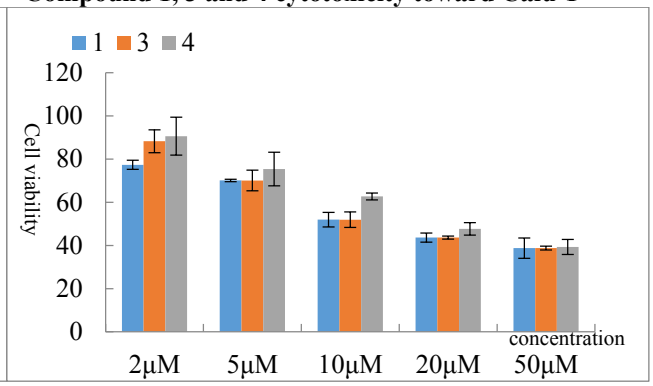
Compound 1, 3 and 4 cytotoxicity toward A549



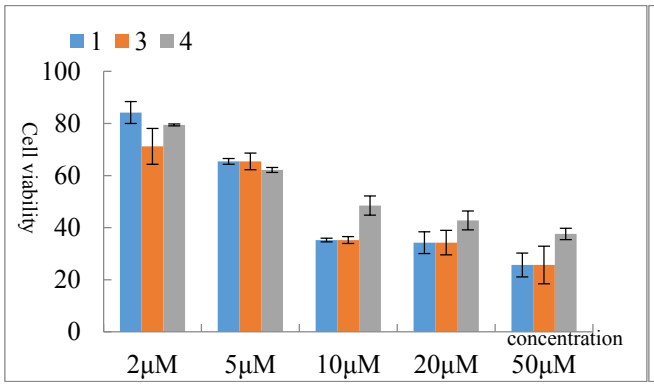
Compound 1, 3 and 4 cytotoxicity toward Calu-1



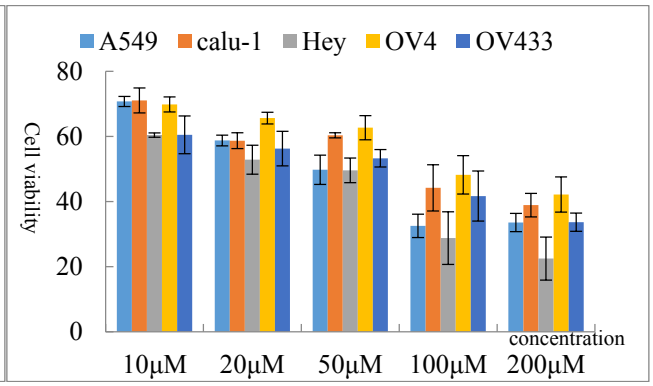
Compound 1, 3 and 4 cytotoxicity toward Hey



Compound 1, 3 and 4 cytotoxicity toward OV4



Compound 1, 3 and 4 cytotoxicity toward OV433



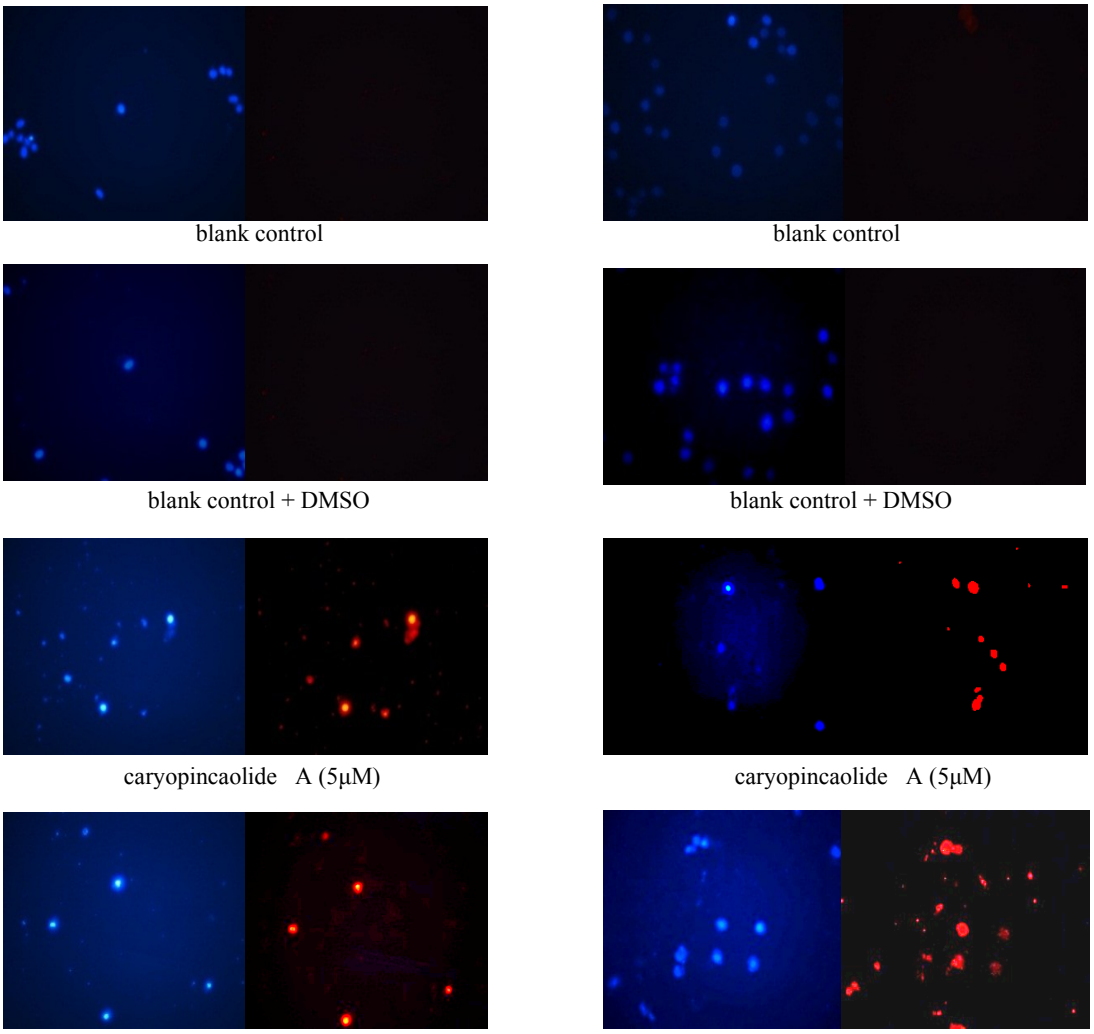
Compound 2 cytotoxicity toward A549, Calu-1, Hey, OV4, OV433

Hoechst 33258/PI Staining.

Cells (5 × 104/well) were seeded in 6-well plates with DMEM plus 2% fetal bovine serum with compound **1** (0,5,10 μmol/L) for 24h. After incubation for 24 h, the cells were fixed with 1mL of 4% paraformaldehyde for 20 min. Then, the cells were incubated in 1mLPBS containing 10 μ mol/L Hoechst 33258 at 37℃ for 30min and observed using fluorescence microscopy (Olympus, Tokyo, Japan) at×400 magnification. Using appropriate filters to examine and compare Hoechst 33342 and PI fluorescence staining in the same cells.

The apoptosis of A549 and Hey under Hoechst 33342 / PI double staining showed as **Figure S191**

Figure S191. Apoptosis of Hey and A549 determined by Hoechst33342 Hoechst 33342/PI staining with **1**



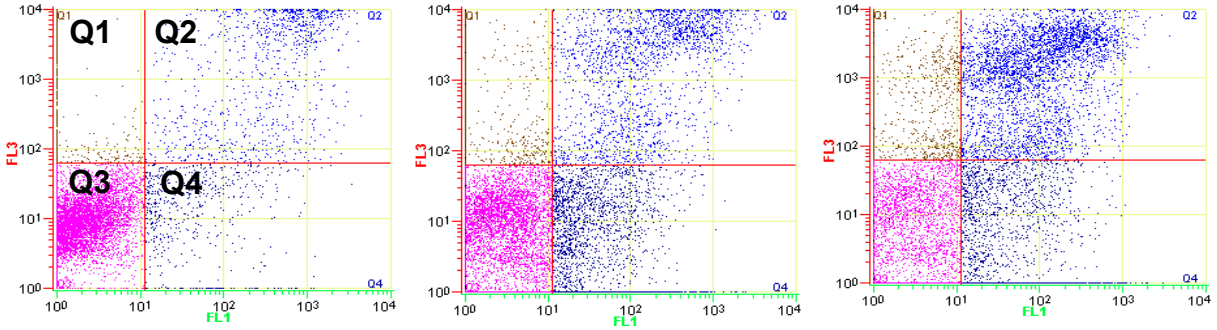
Apoptosis of Hey by Hoechst 33342/PI staining with compound 1

Apoptosis of A549 by Hoechst 33342/PI staining with compound 1

Flow Cytometry Analysis

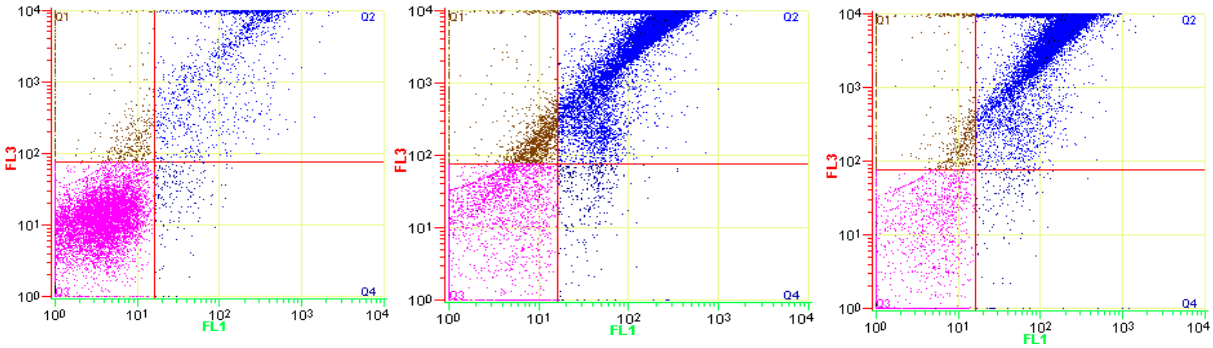
A549 and Hey cells were treated by DMEM plus 2% fetal bovine serum with compound **1** (0, 5, 10 μmol/L) for 24h. Cells were collected after 48 h. The first stained with Alexa Fluro 488 annexin V and propidium iodide (PI) in room temperature for 15 minutes, and analyzed by FACScan (Beckman Coulter, FL, USA). The stainings were carried out using Alexa fluor 488 annexin V/dead cell apoptosis Kit (Invitrogen) according to the manufacture. Detection and quantification of apoptotic cells were obtained by flow cytometry analysis software (Cell Lab Quanta Analysis, Beckman Coulter). The result of Flow Cytometry Analysis showed asFigure S37 (Q1: mechanical injury cells; Q2: death or non-viable apoptotic cells; Q3: living cells; Q4 viable apoptotic cell. The Stimulation of compound 1 to A549 and Hey increased the proportion of cells in Q2 and Q4, which showed compound **1** induced apoptosis in Hey and A-549 cells.)

Figure S192. Flow Cytometry Analysis of compound **1**induced apoptosis in A549 and Hey



blank control caryopincaolide A (5μM) caryopincaolide A (10μM)

Flow Cytometry Analysis of compound 1 induced apoptosis in A549



blank control caryopincaolide A (5μM) caryopincaolide A (10μM)

Flow Cytometry Analysis of compound 1 induced apoptosis in Hey

Scheme S1. Plausible biogenetic pathways for 1-4