How an Early or Late Transition State Impacts the Stereoselectivity of Tetrahydropyran Formation by Intramolecular oxa-Michael Addition

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Supporting information II: NMR Spectra and crystallographic data

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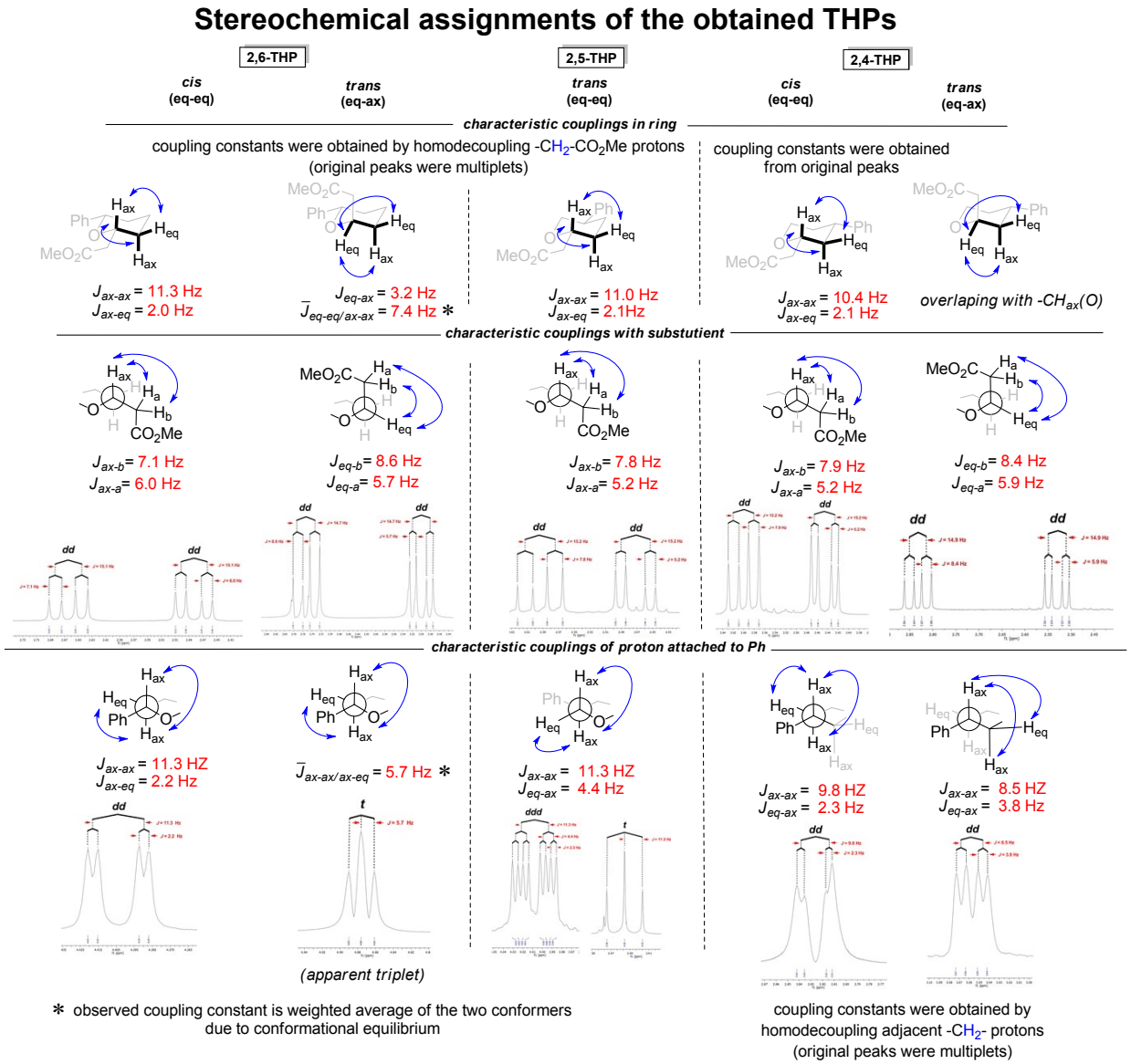
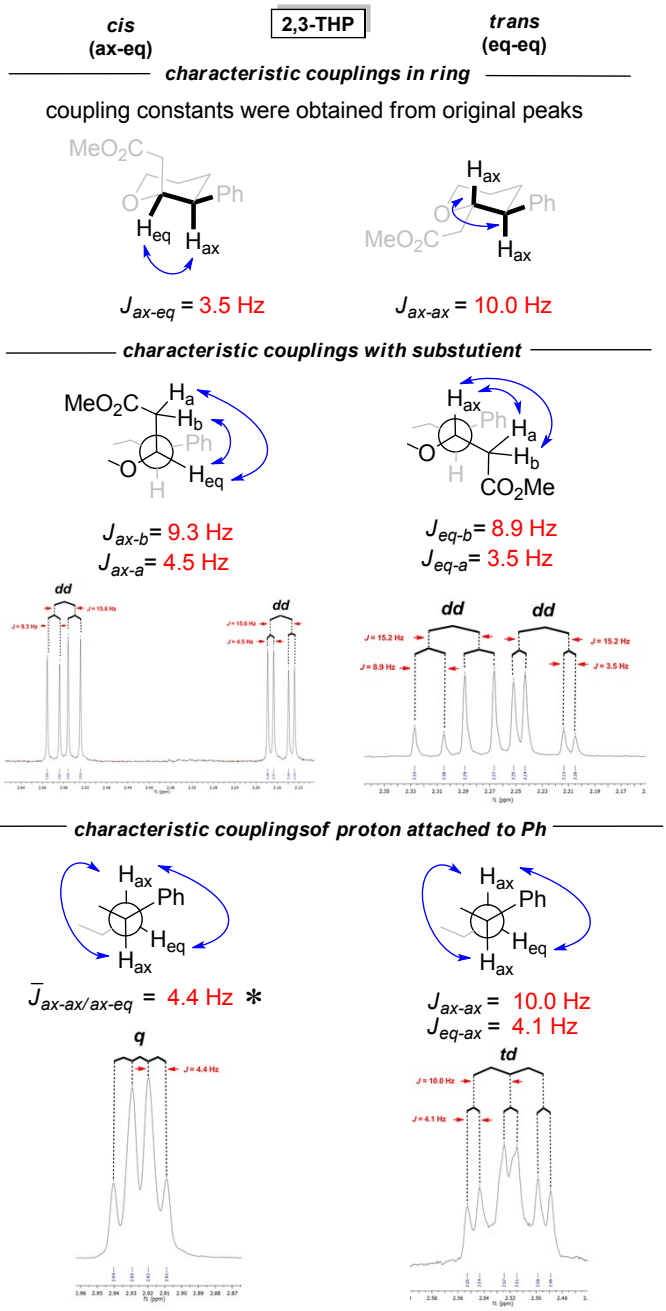


Figure 1 Stereochemical assignment of 2,6-, 2,5-, 2,4-THPs obtained from base-catalysed oxa-Michael cyclisation



* observed coupling constant is weighted average of the two conformers due to conformational equilibrium

Figure 2 Stereochemical assignment of 2,3-THP obtained from base-catalysed oxa-Michael cyclisation

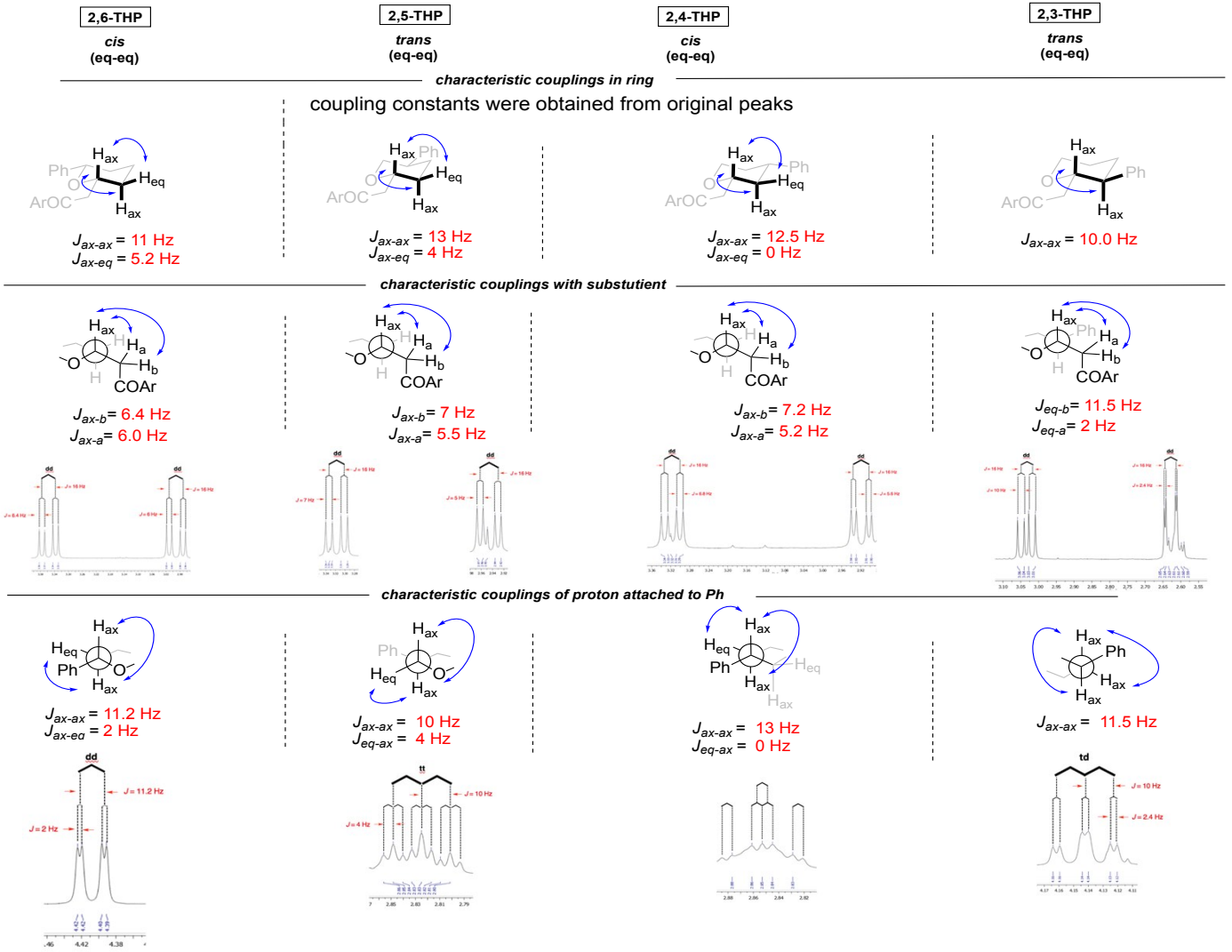


Figure 3 Stereochemical assignment of 2,6-, 2,5-, 2,4, 2,3-THPs obtained from acid-catalysed oxa-Michael cyclisation

NMR Spectra

General information

NMR spectra were recorded on JEOL ECA 400SL (400MHz), JEOL ECA 400 (400MHz) and Bruker AV400 (400 MHz) spectrometers in $CDCl_3$ solutions. Chemical shifts are given in ppm (referenced to the residual chloroform ^{1}H-spectrum 7.26 ppm, ^{13}C-spectrum: 77.16 ppm) and coupling constants in Hz. In the cases of severely overlapping peaks, the integration of individual peaks is assumed to be the expected value.

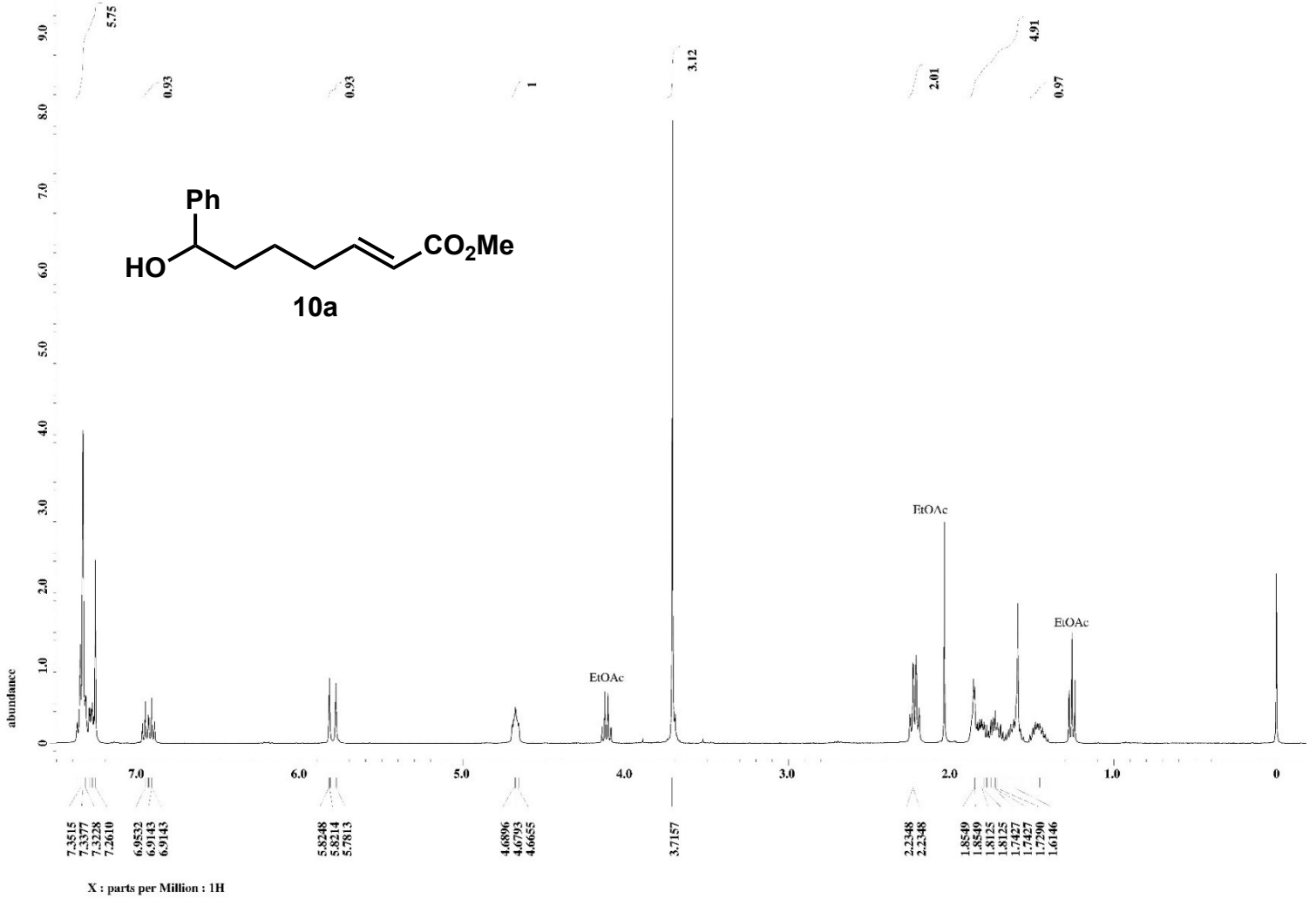


Figure 4 ^{1}H NMR spectrum of 10a

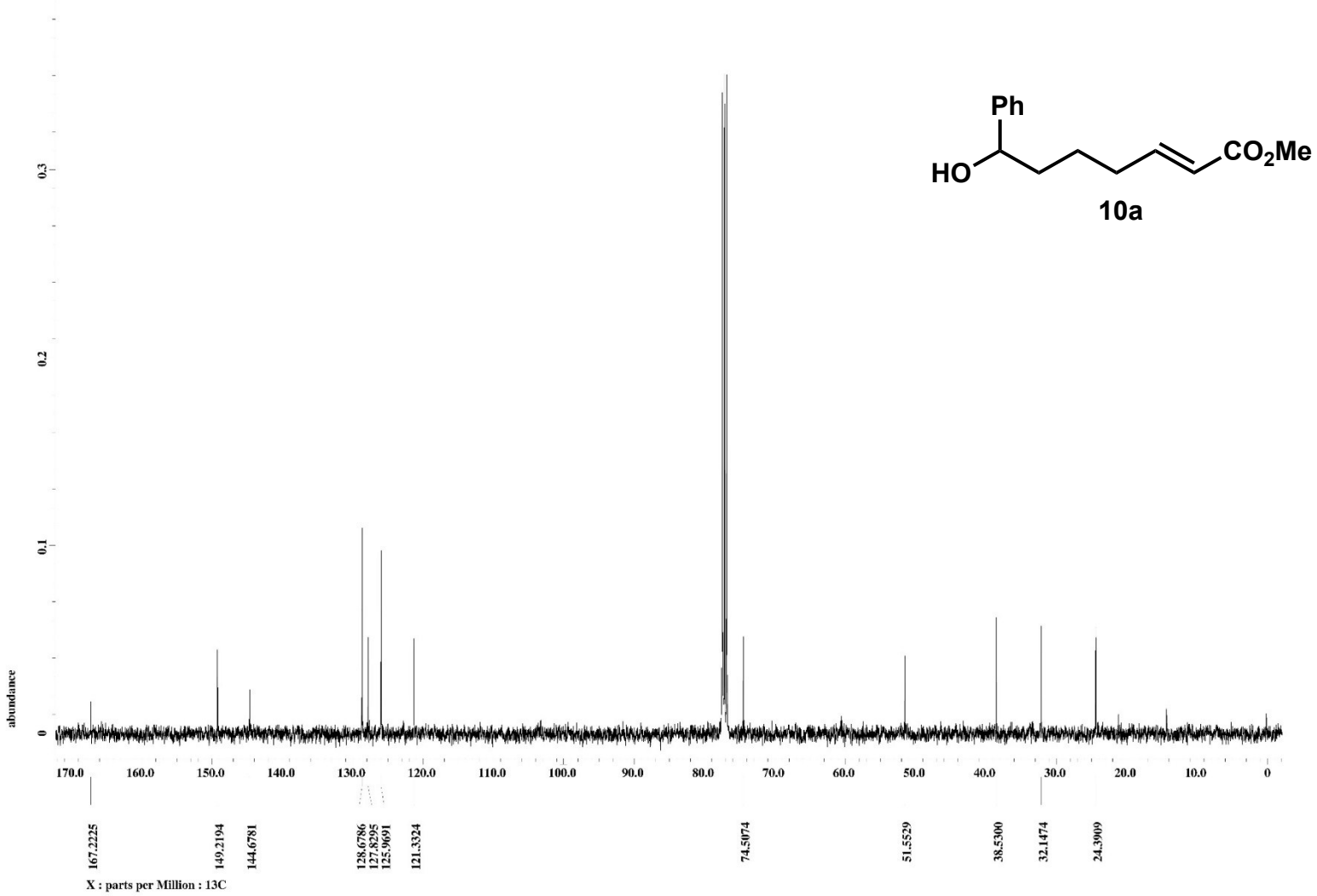


Figure 5 ^{13}C NMR spectrum of 10a

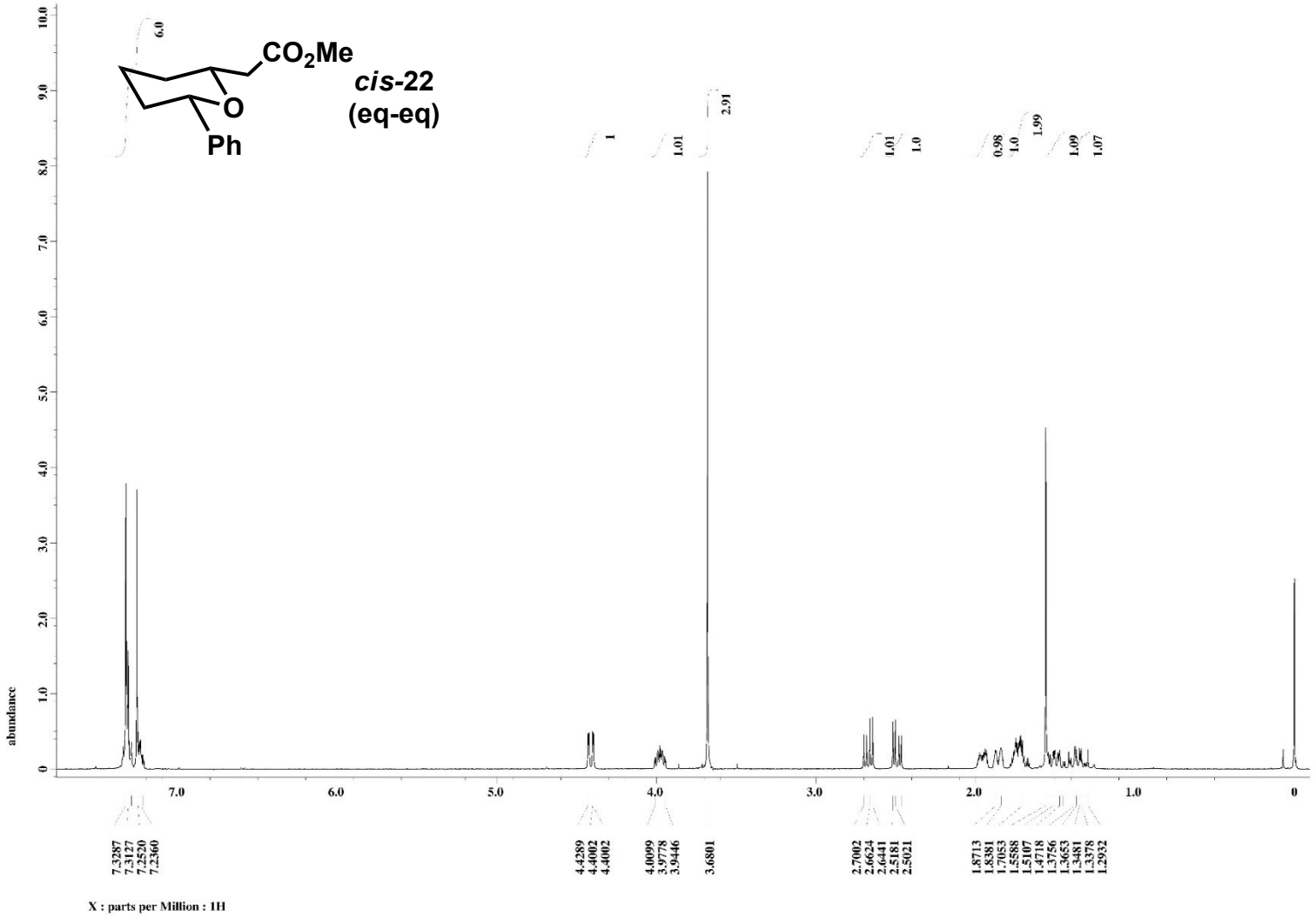


Figure 6 ^{1}H NMR spectrum of cis-22

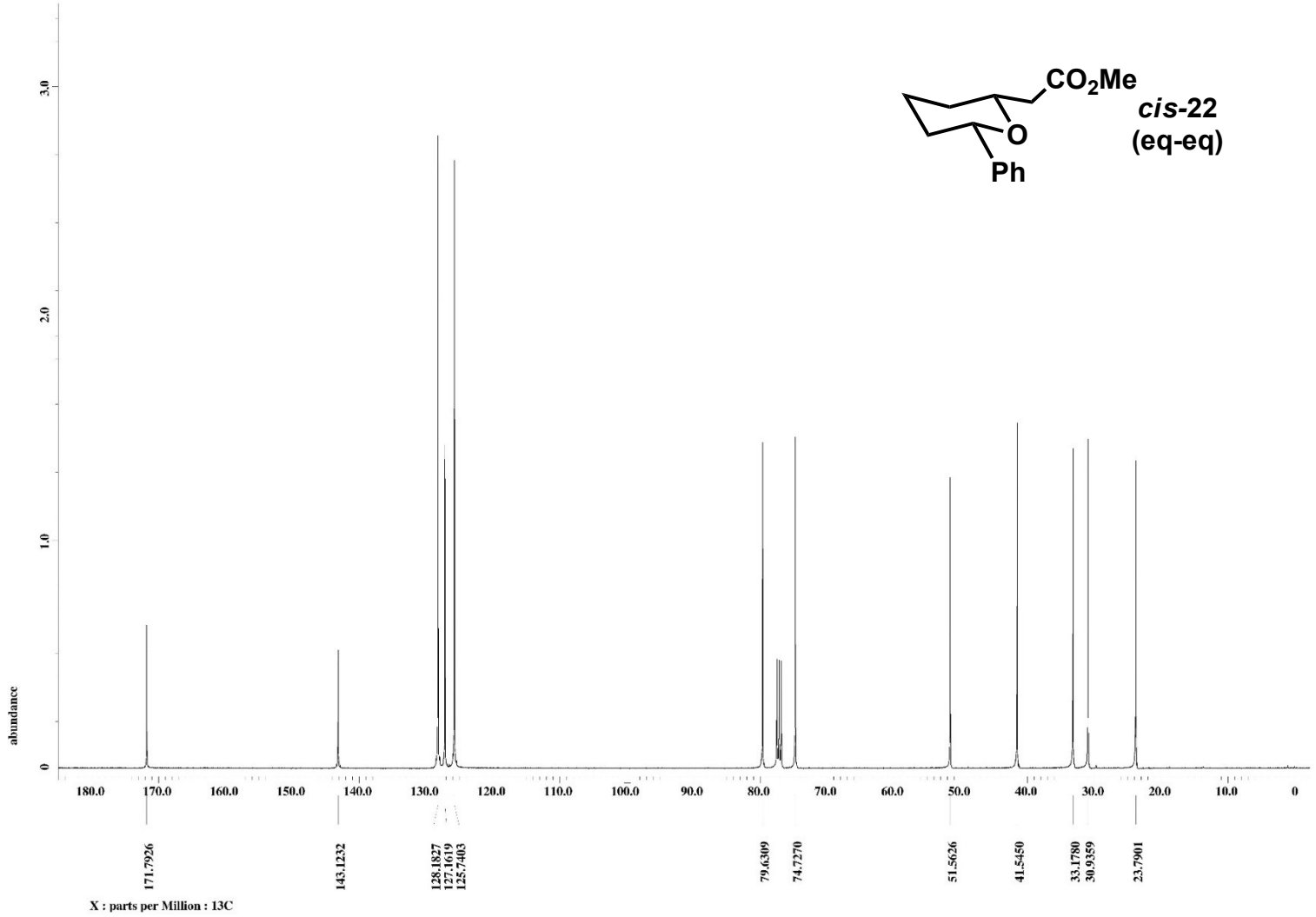


Figure 7 ^{13}C NMR spectrum of cis-22

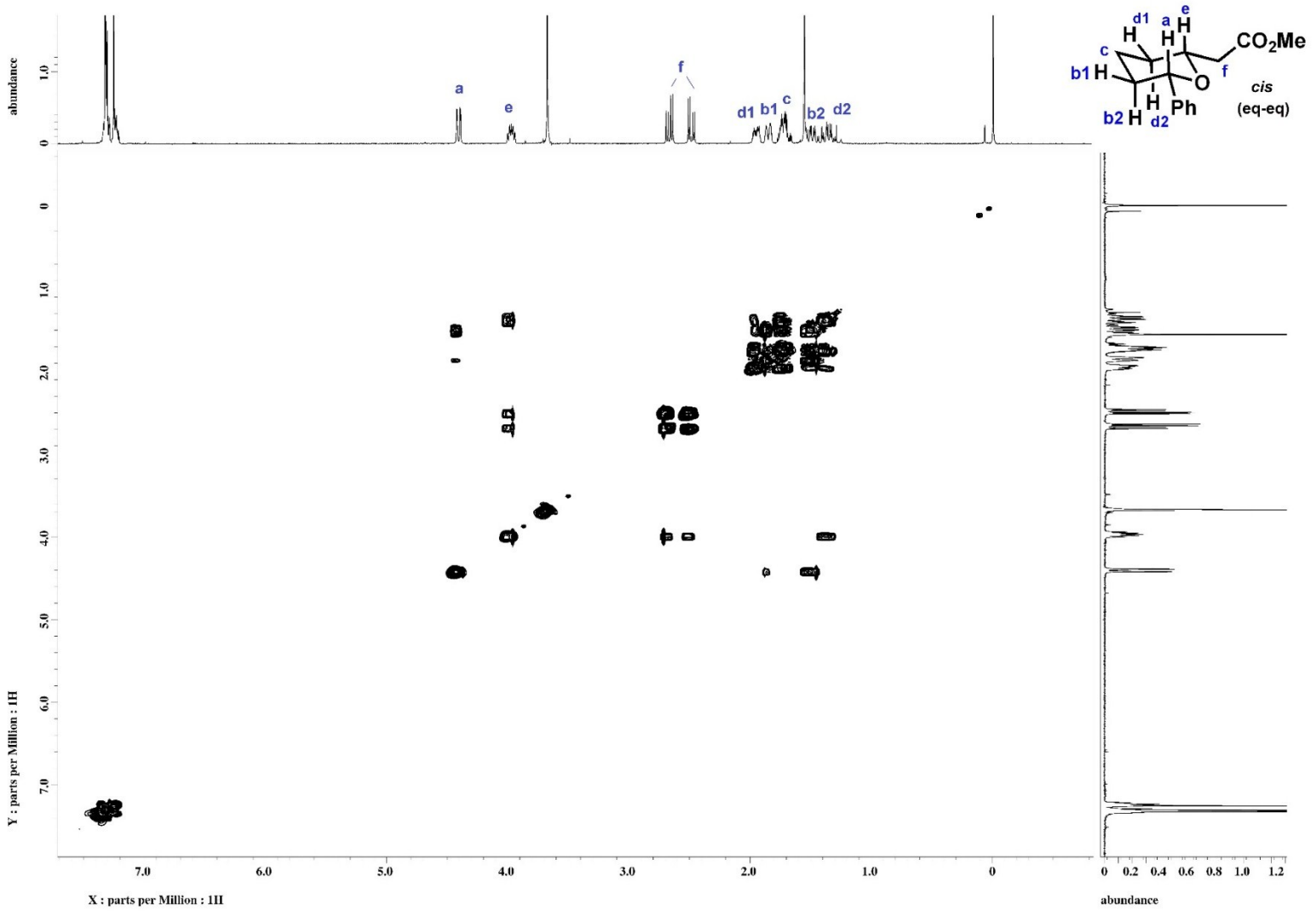


Figure 8 COSY spectrum of cis-22

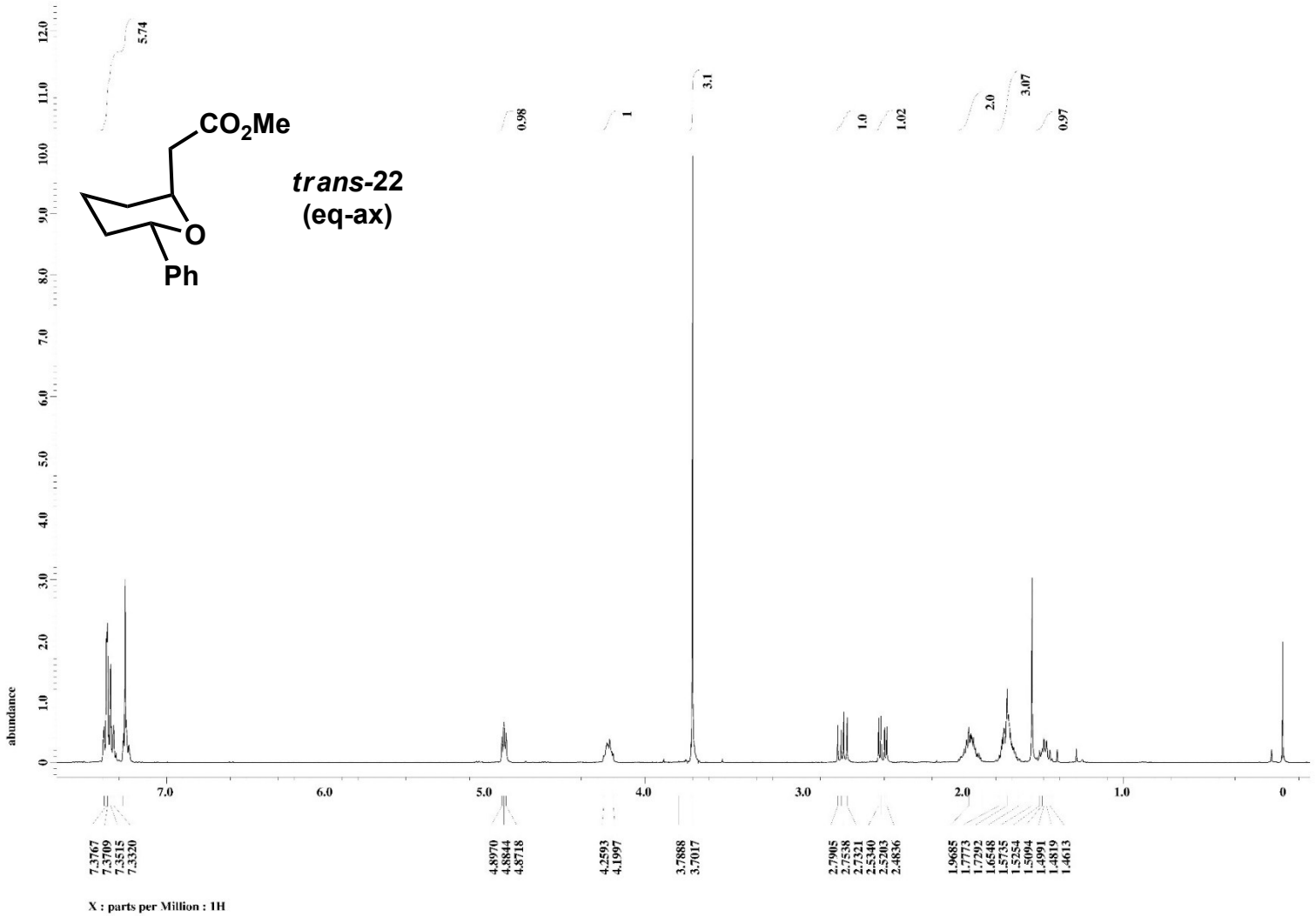


Figure 9 ^{1}H NMR spectrum of trans-22

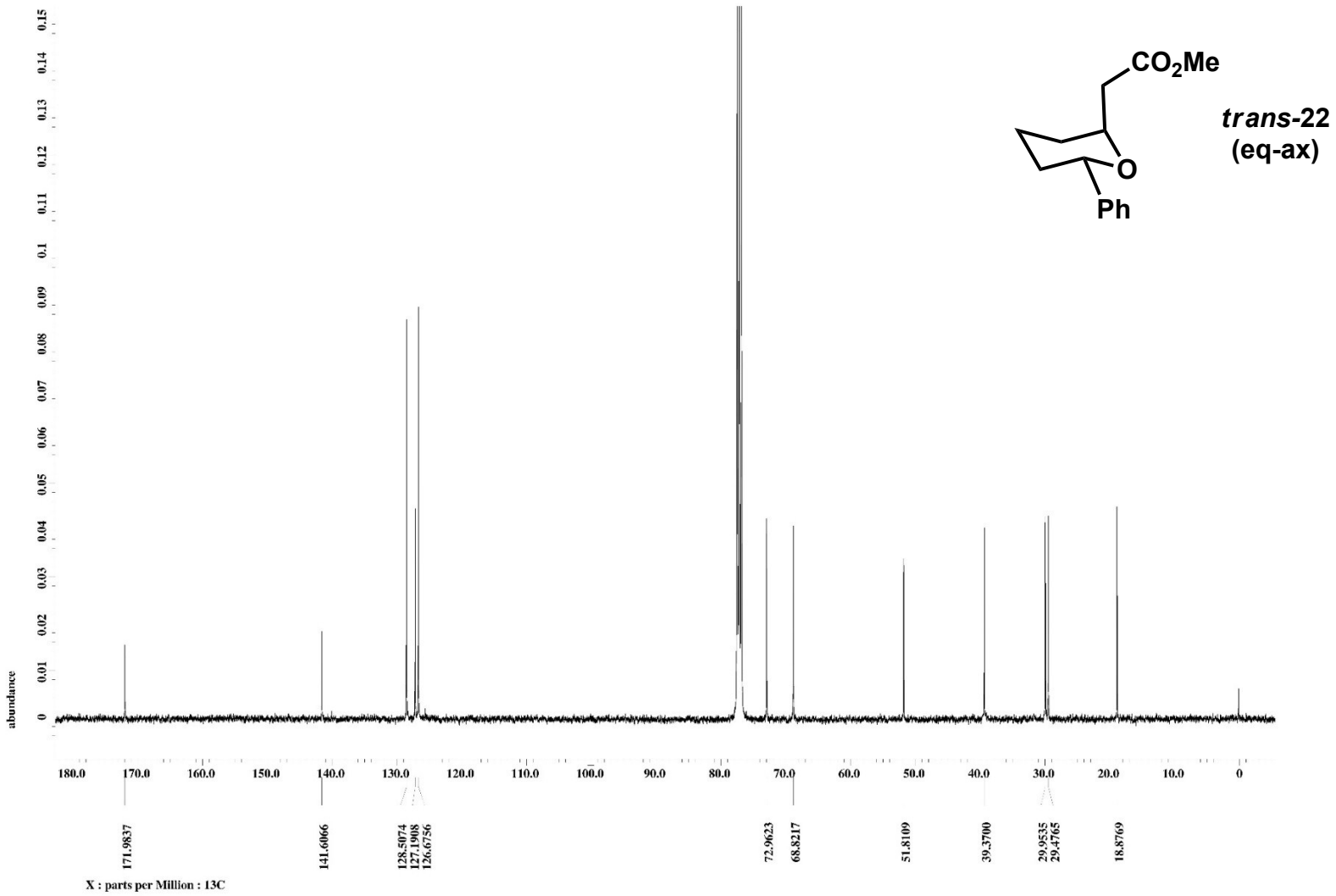


Figure 10 ^{13}C NMR spectrum of trans-22

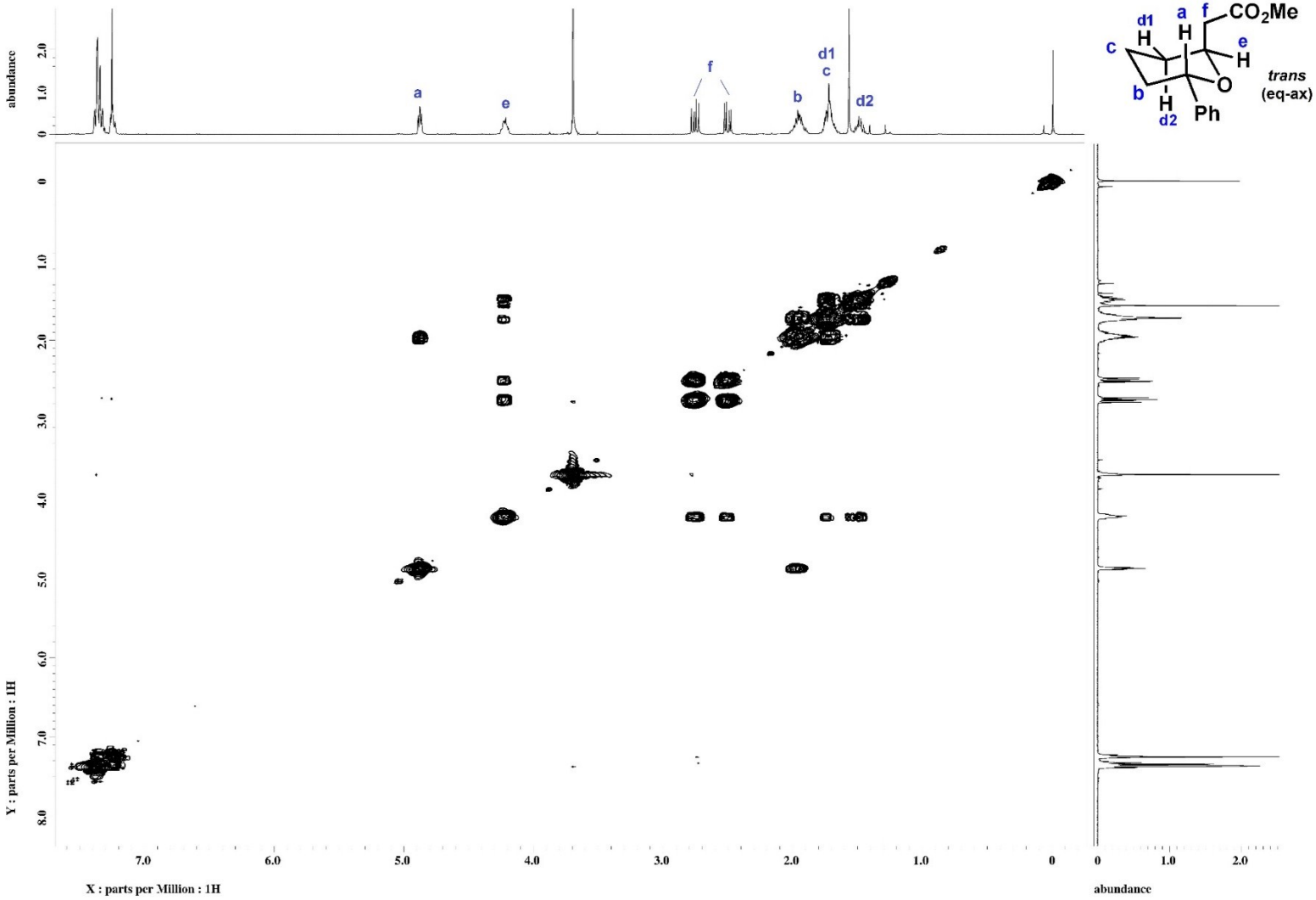


Figure 11 COSY spectrum of trans-22

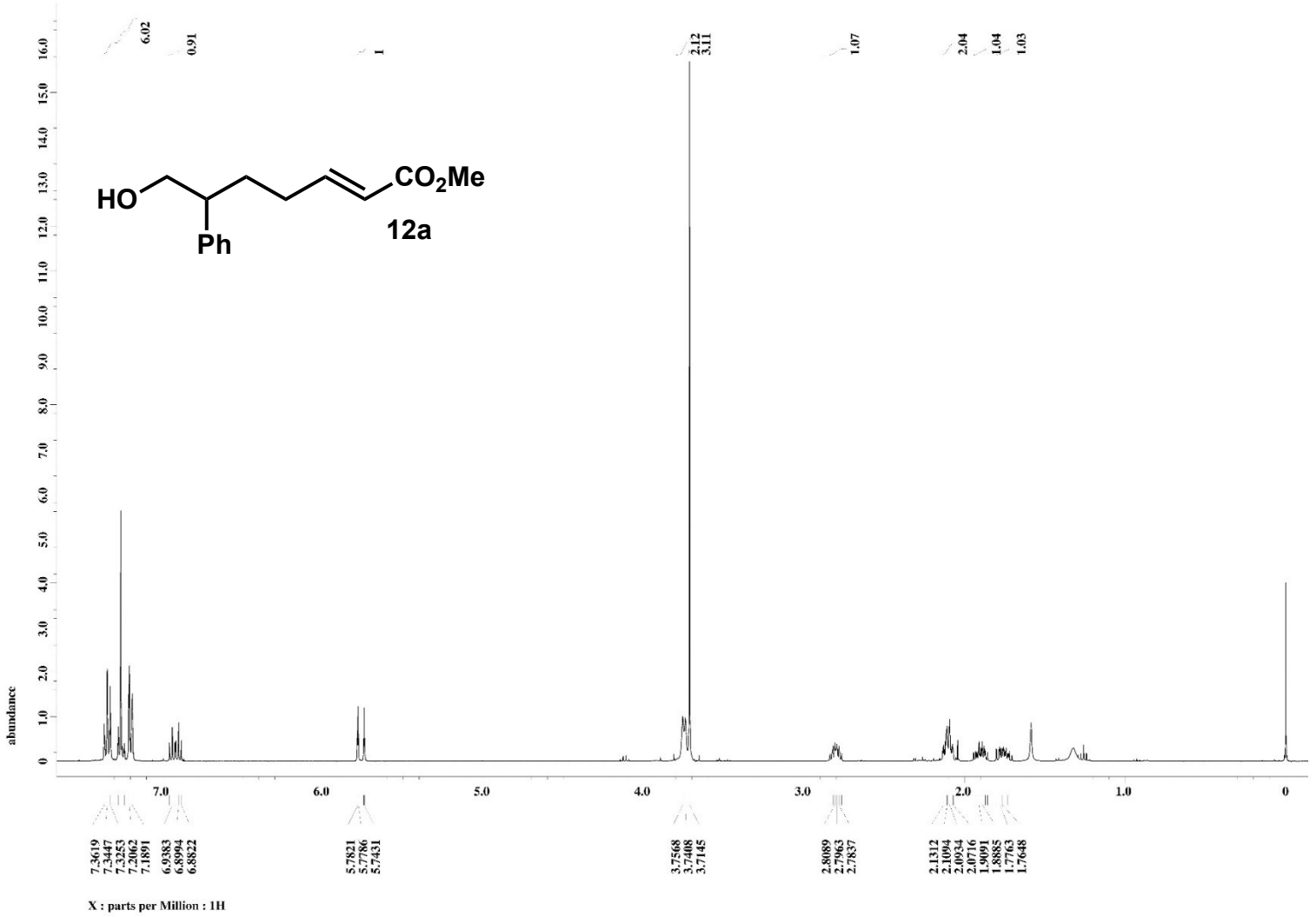


Figure 12 ^{1}H NMR spectrum of 12a

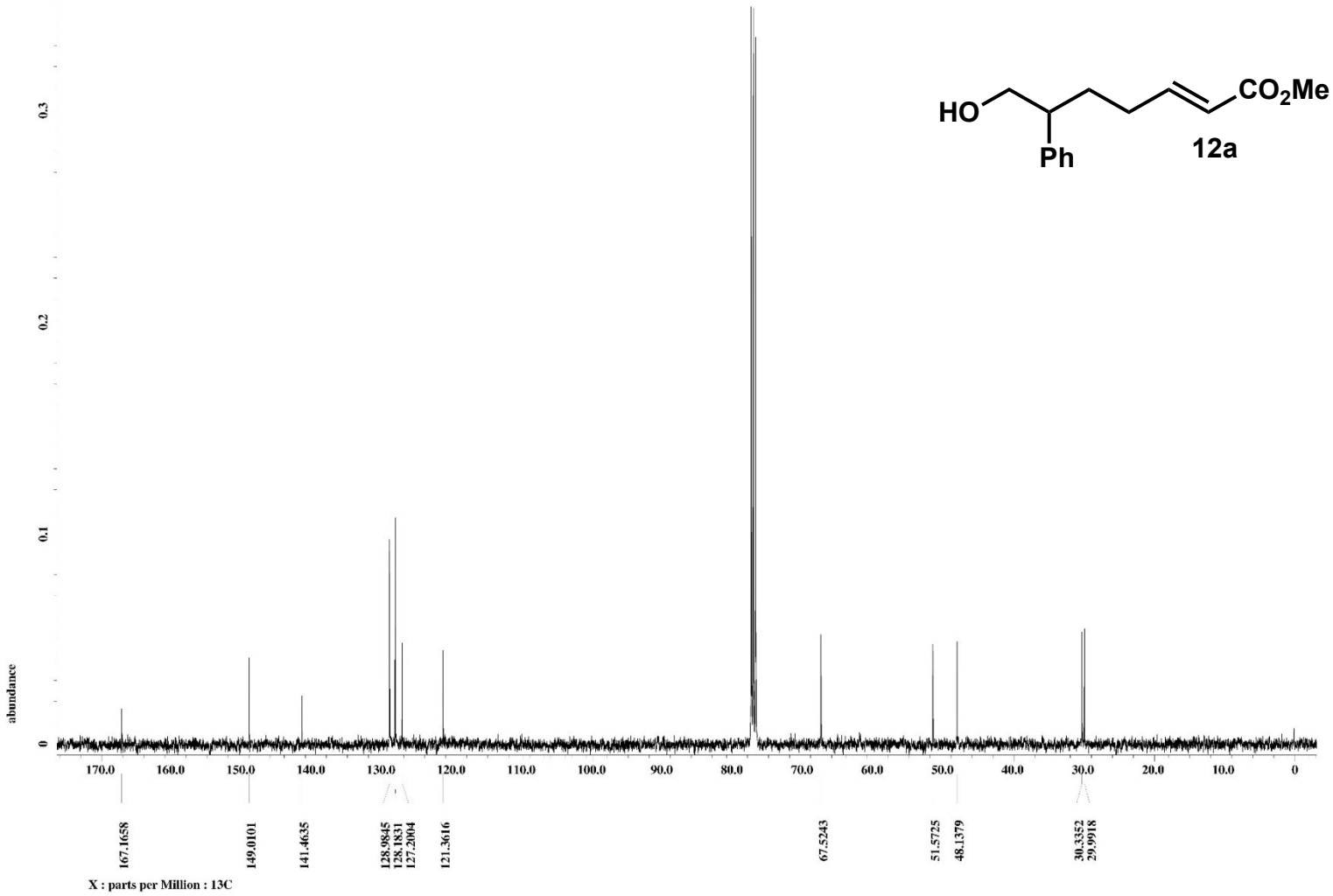


Figure 13 ^{13}C NMR spectrum of 12a

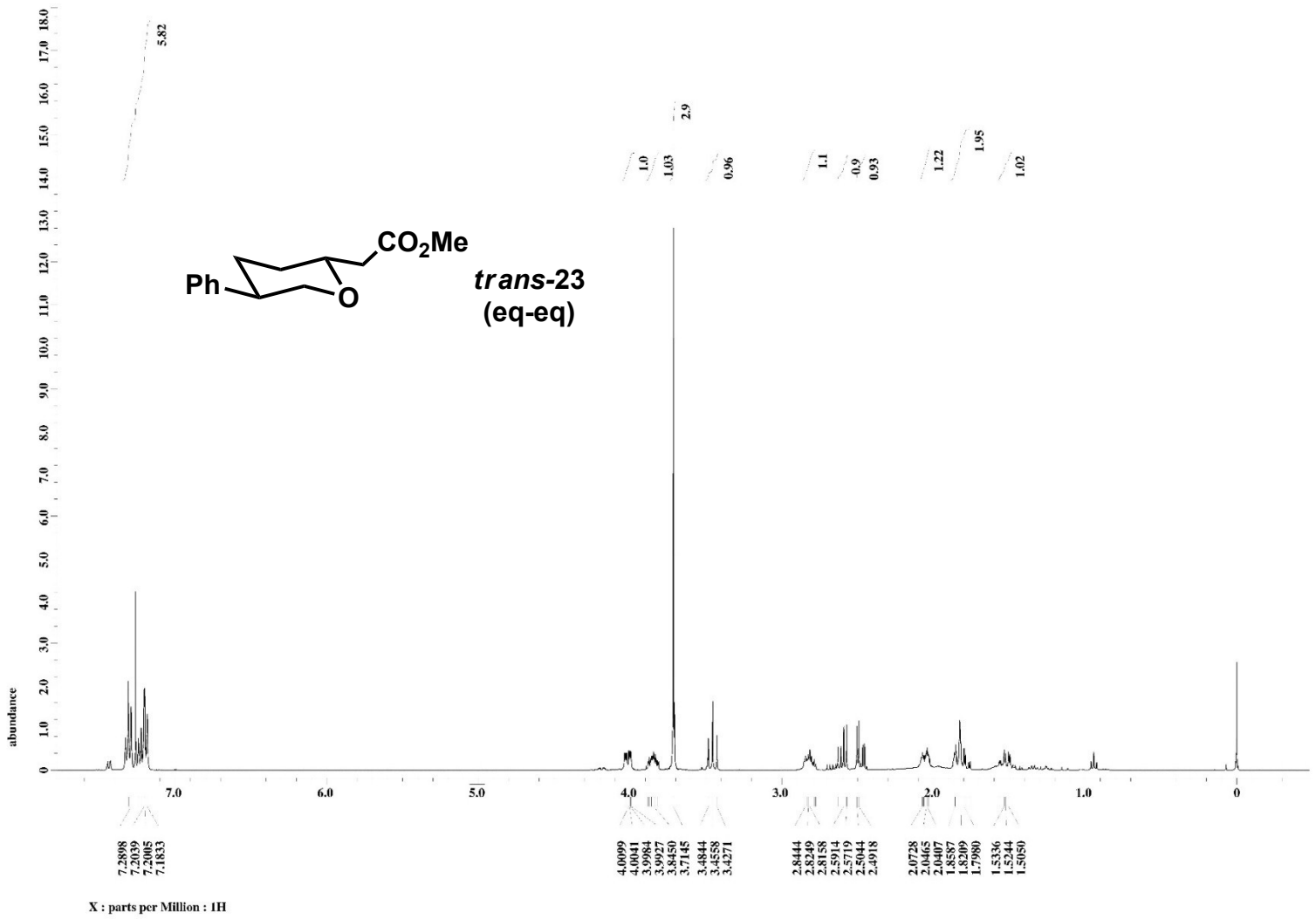


Figure 14 ^{1}H NMR spectrum of trans-23

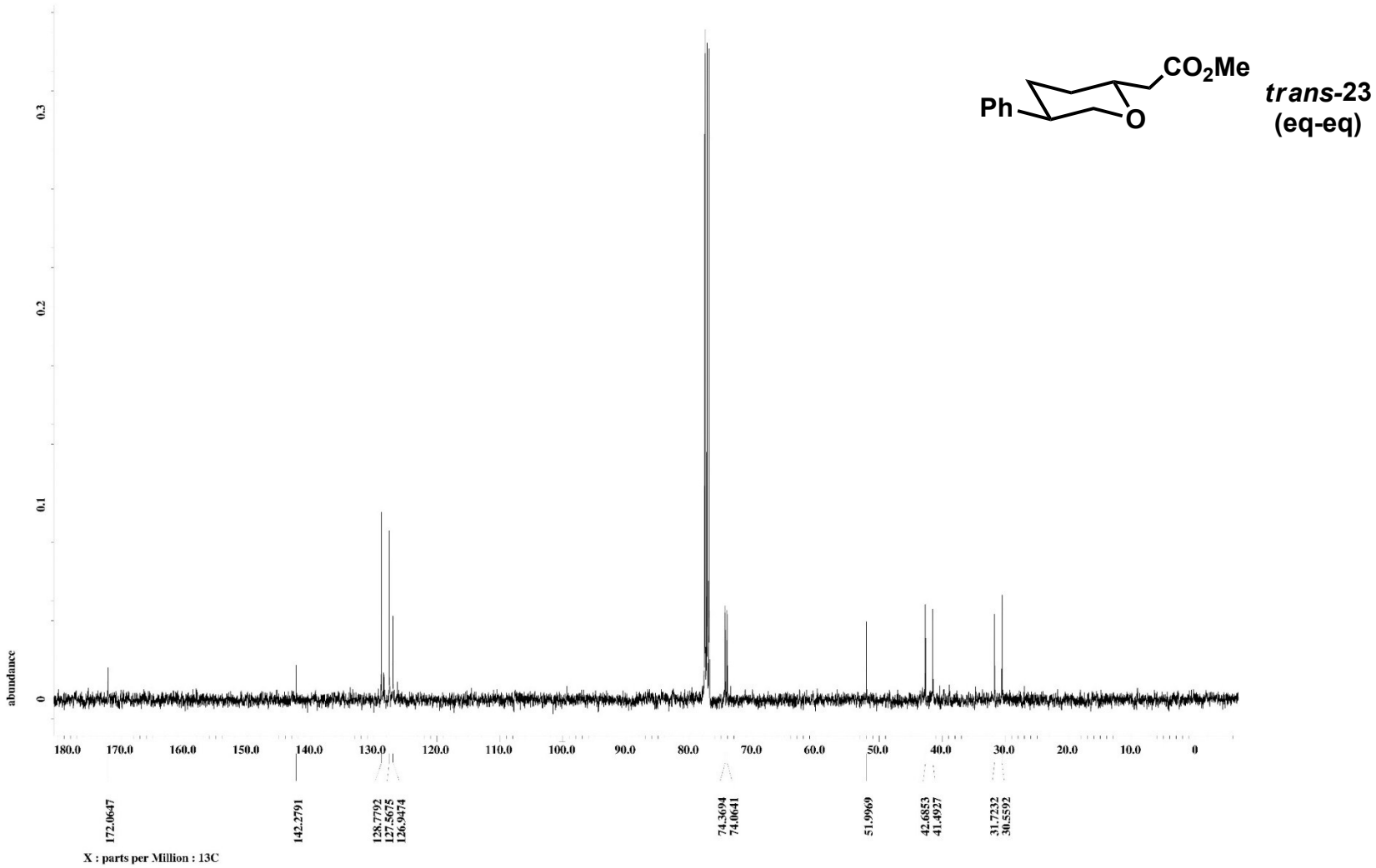


Figure 15 ^{13}C NMR spectrum of trans-23

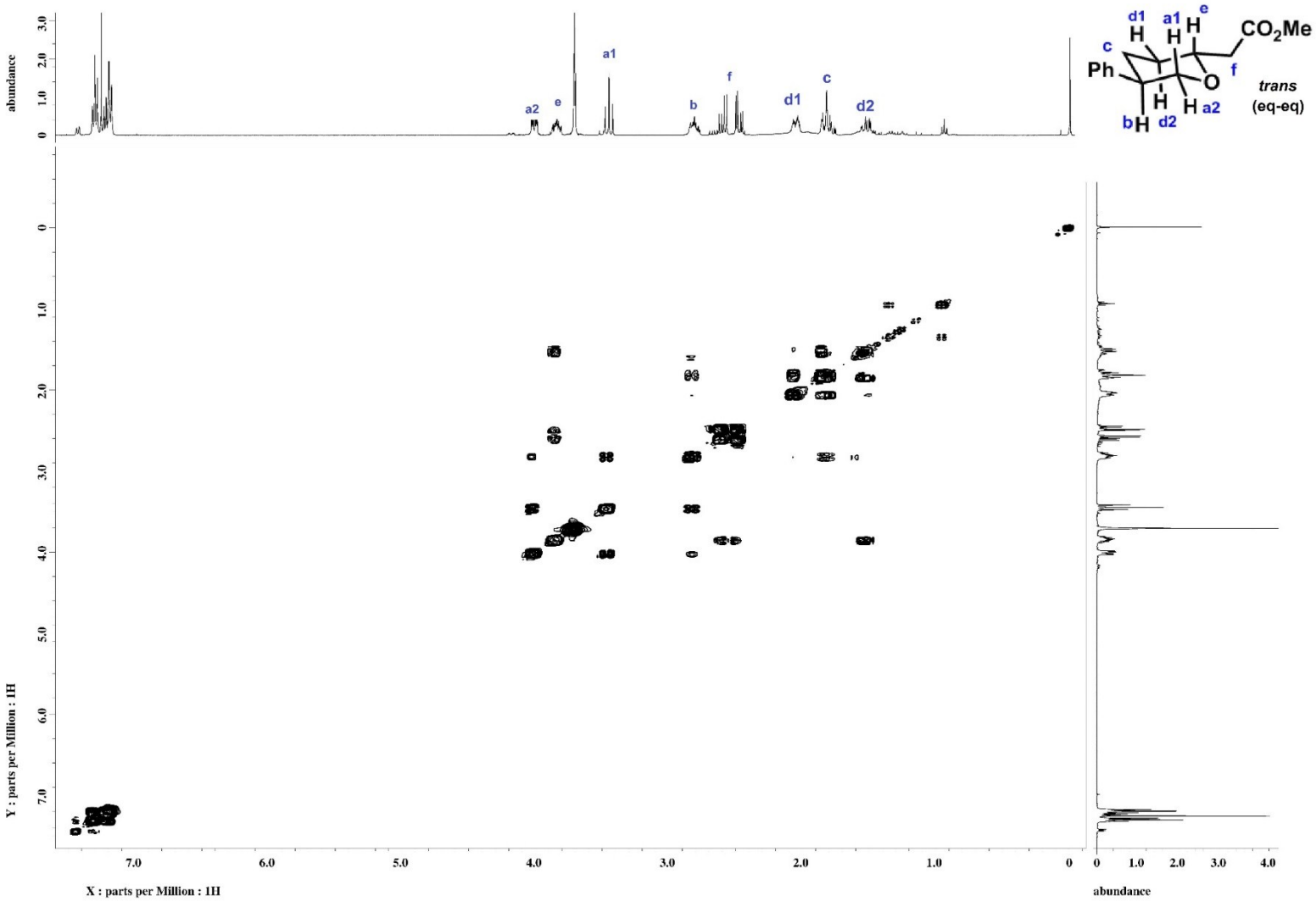


Figure 16 COSY spectrum of trans-23

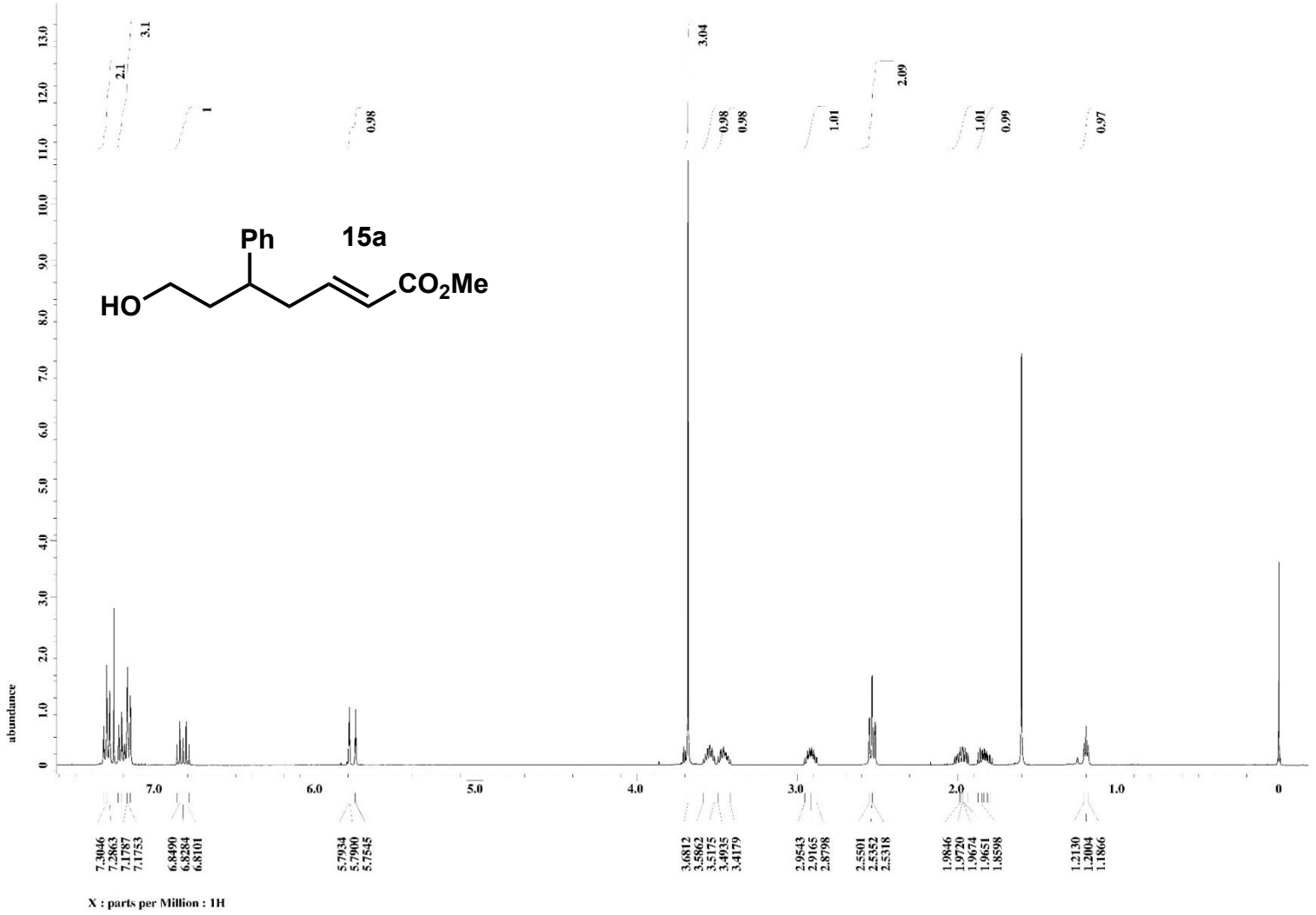


Figure 17 ^{1}H NMR spectrum of 15a

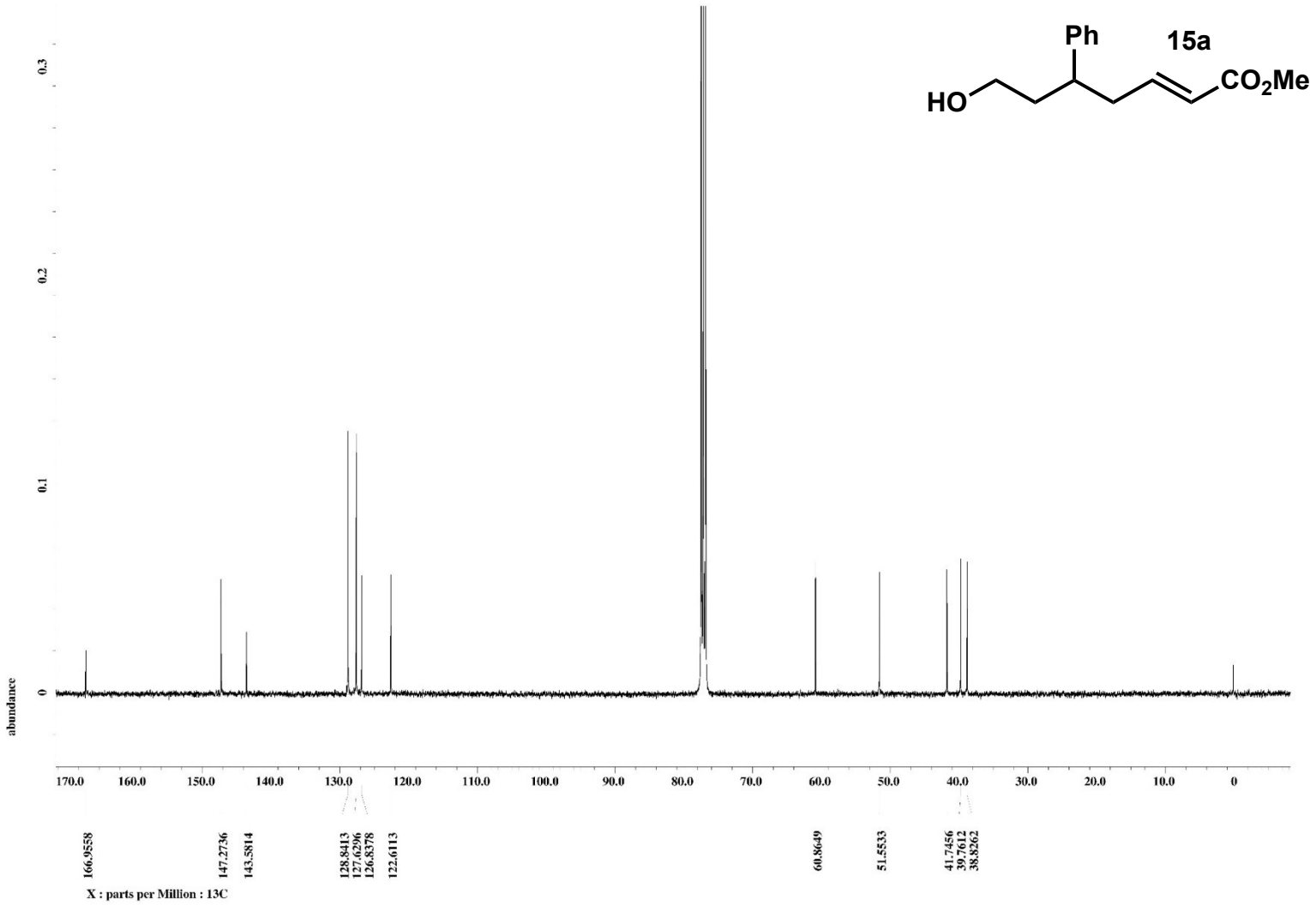


Figure 18 ^{13}C NMR spectrum of 15a

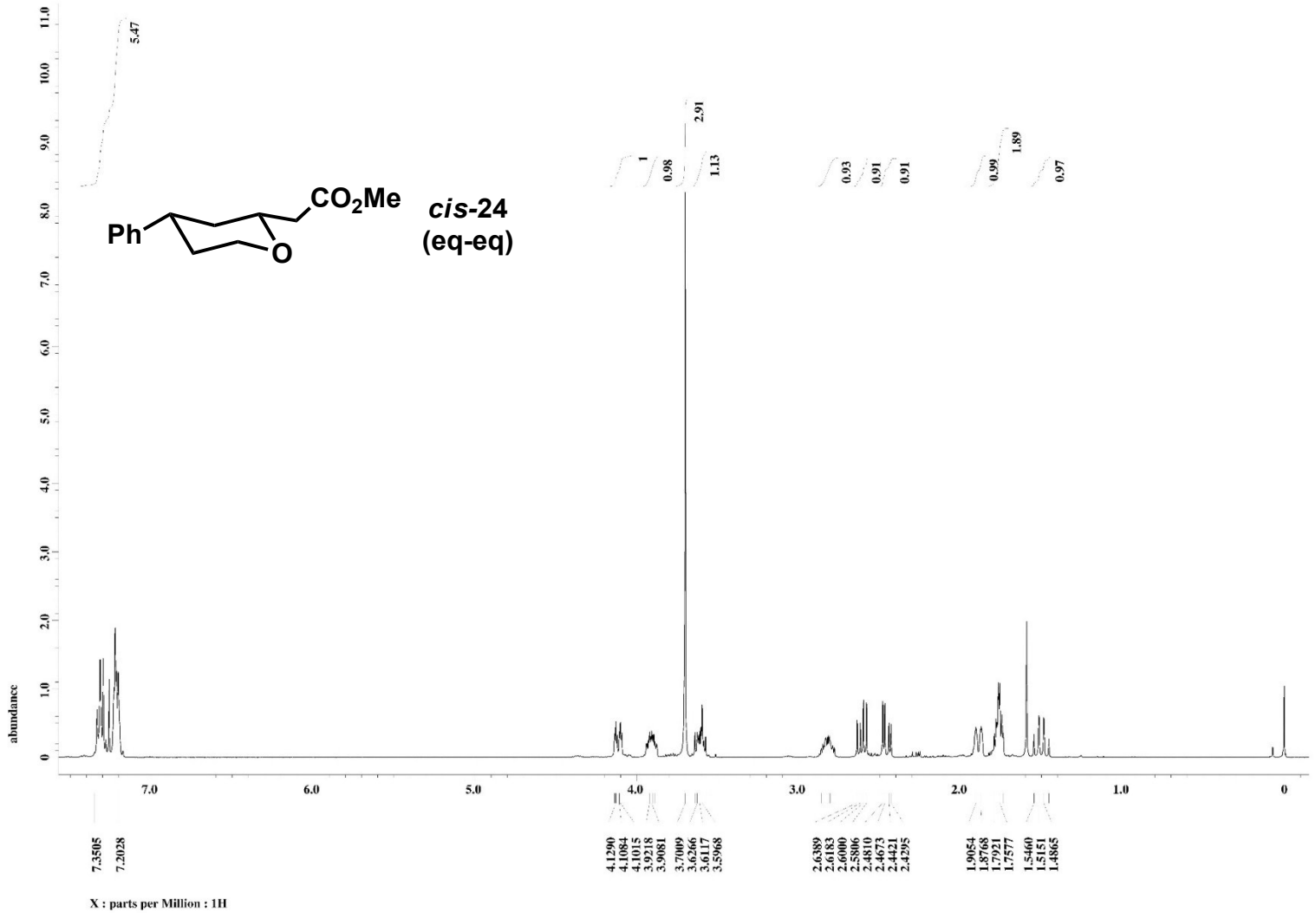


Figure 19 ^{1}H NMR spectrum of cis-24

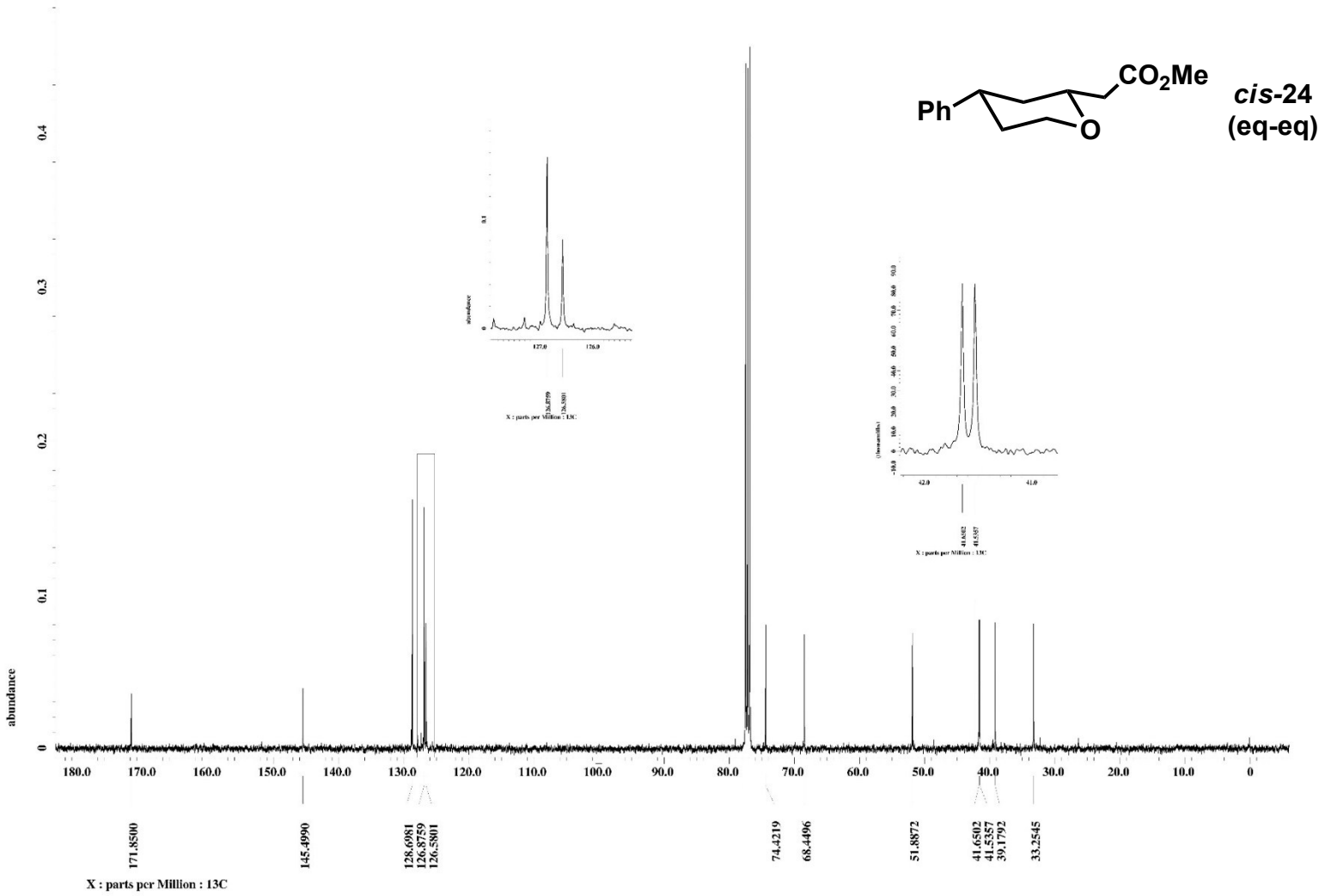


Figure 20 ^{13}C NMR spectrum of cis-24

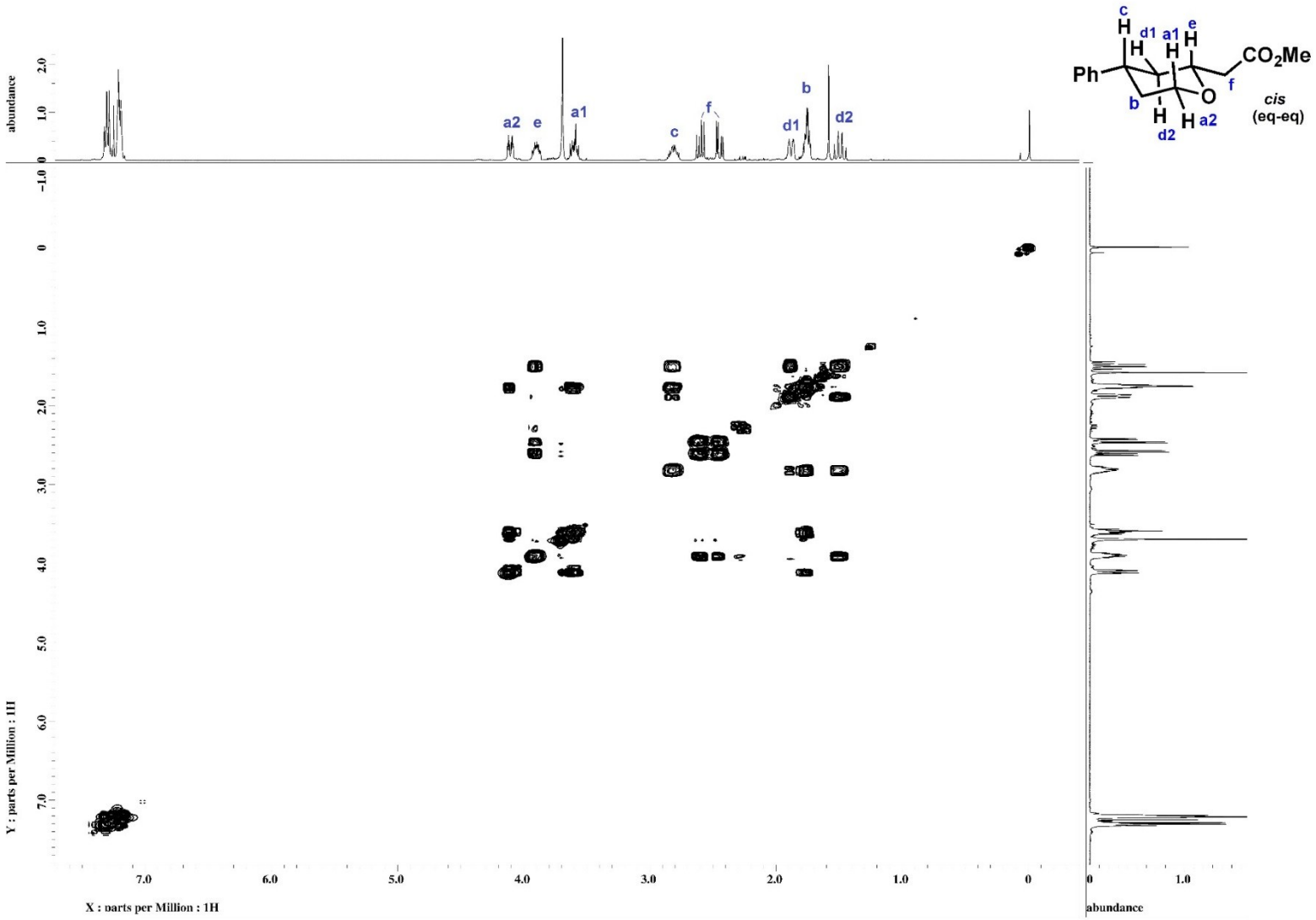


Figure 21 COSY spectrum of cis-24

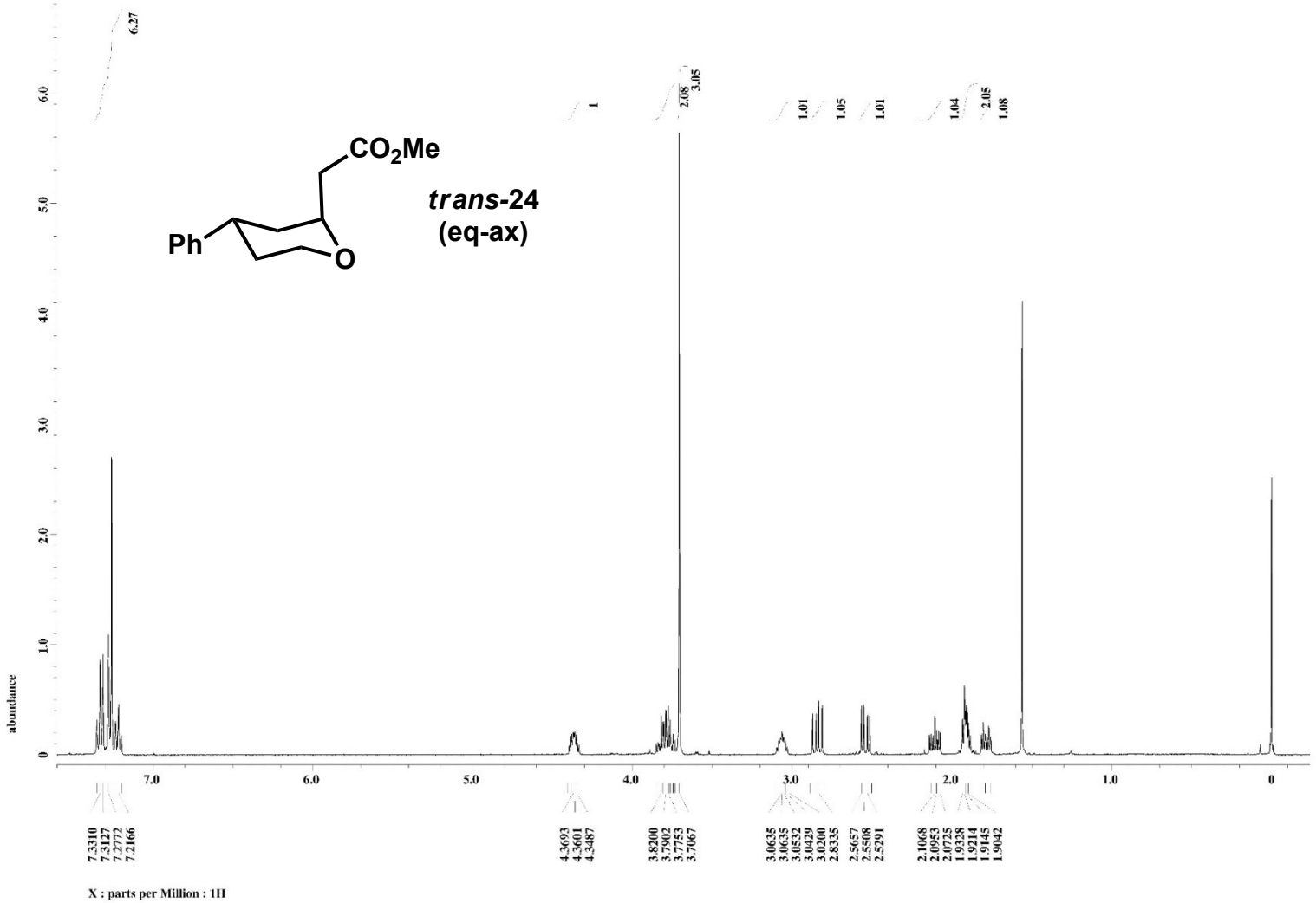


Figure 22 ^{1}H NMR spectrum of trans-24

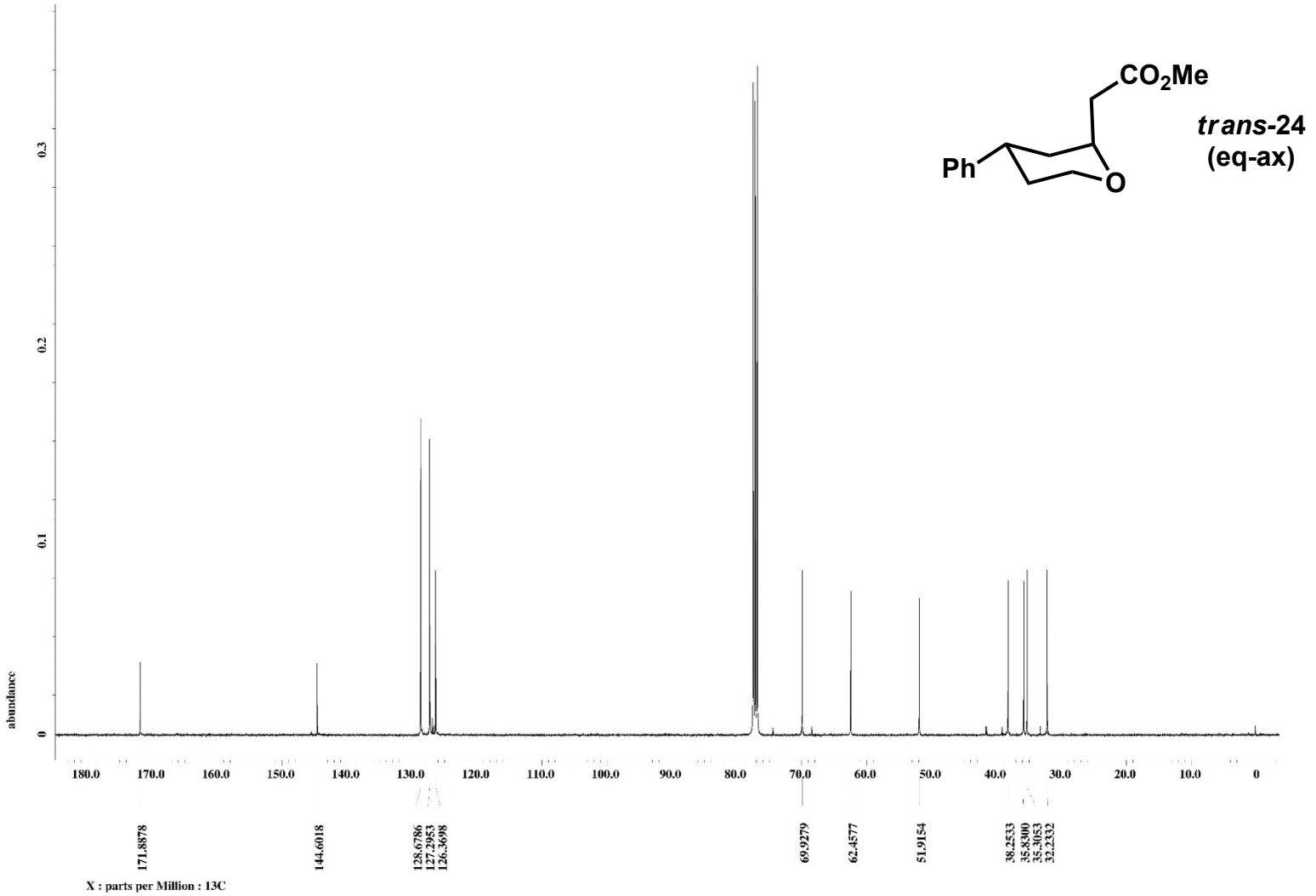


Figure 23 ^{13}C NMR spectrum of trans-24

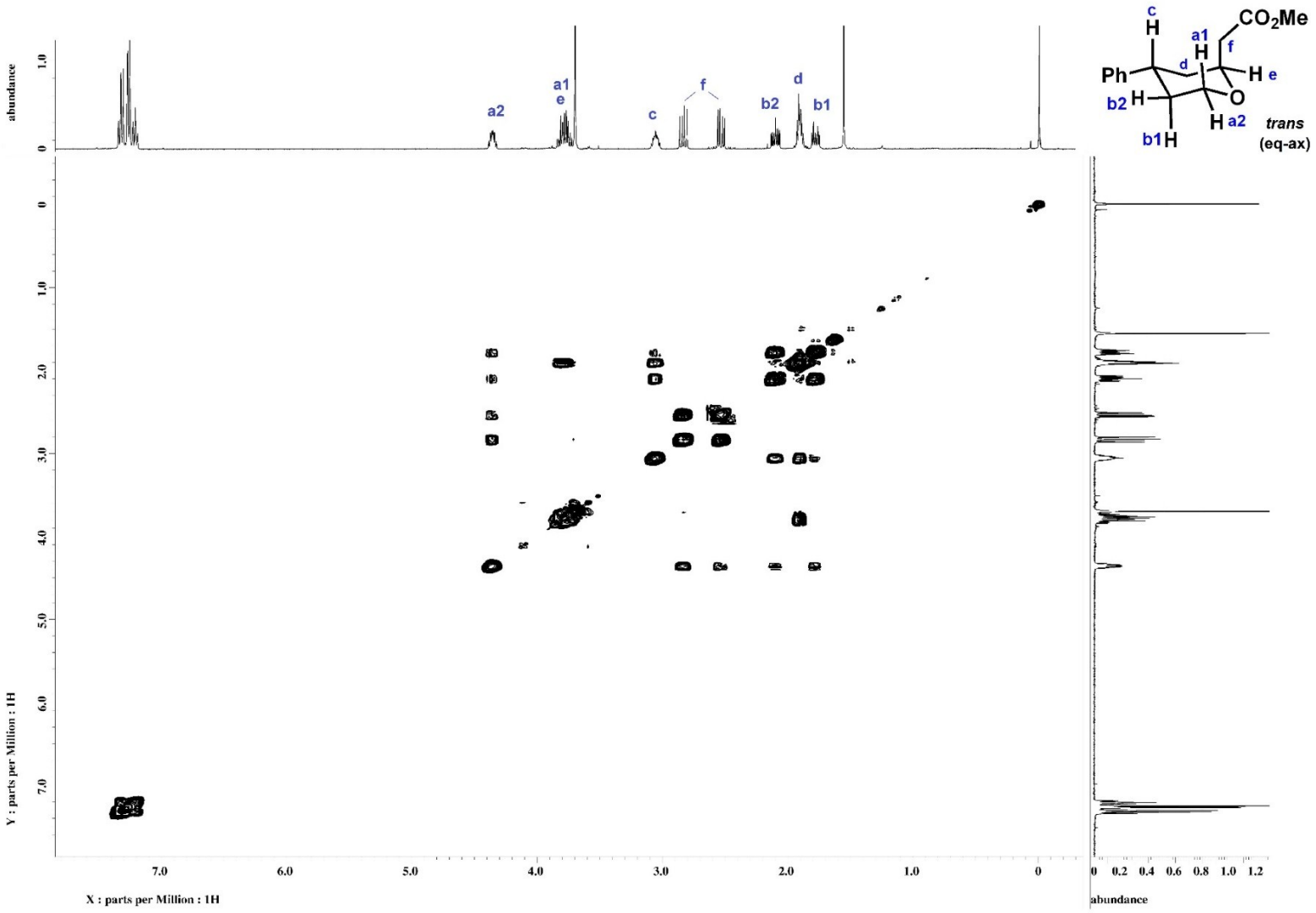


Figure 24 COSY spectrum of trans-24

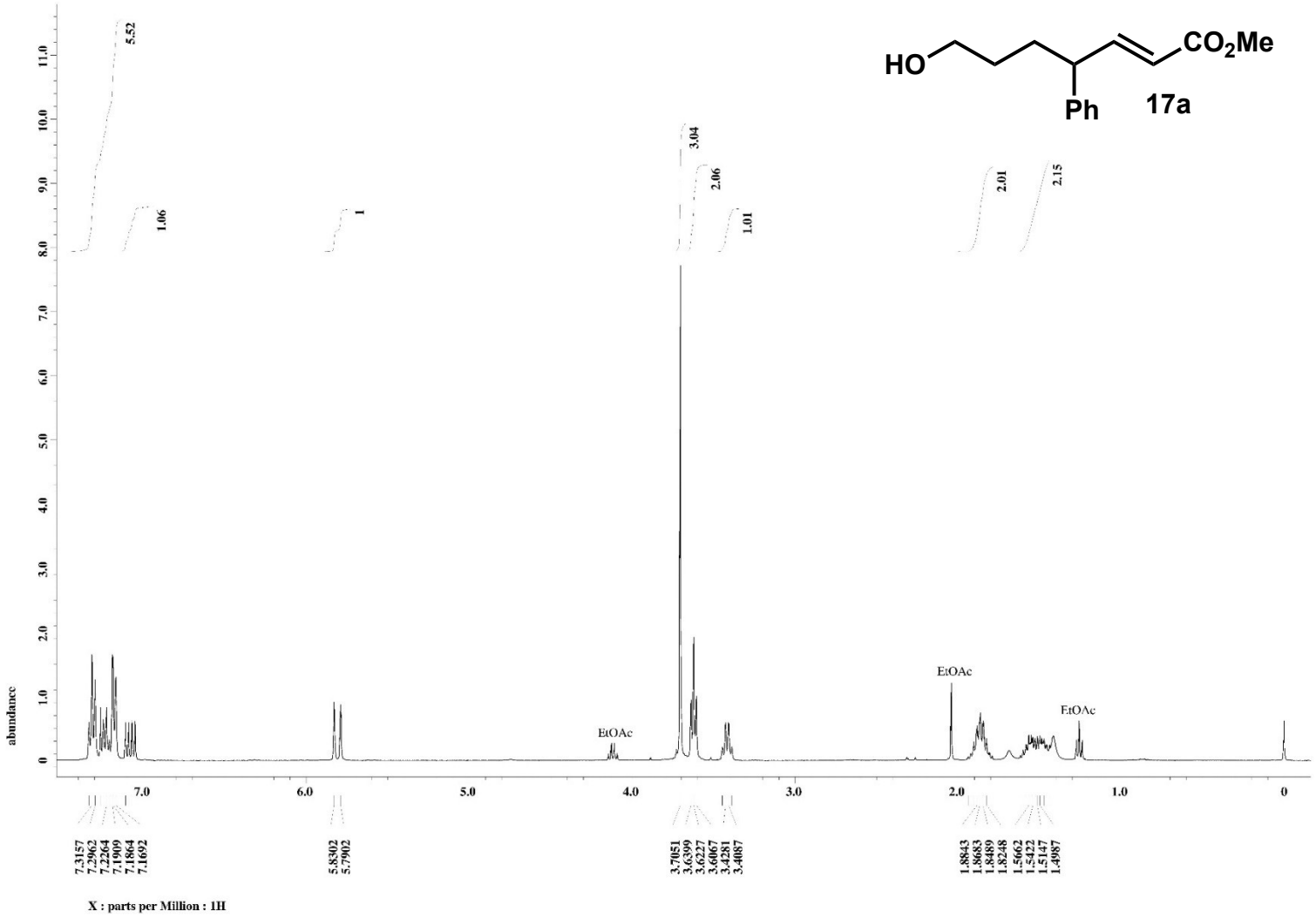


Figure 25 ^{1}H NMR spectrum of 17a

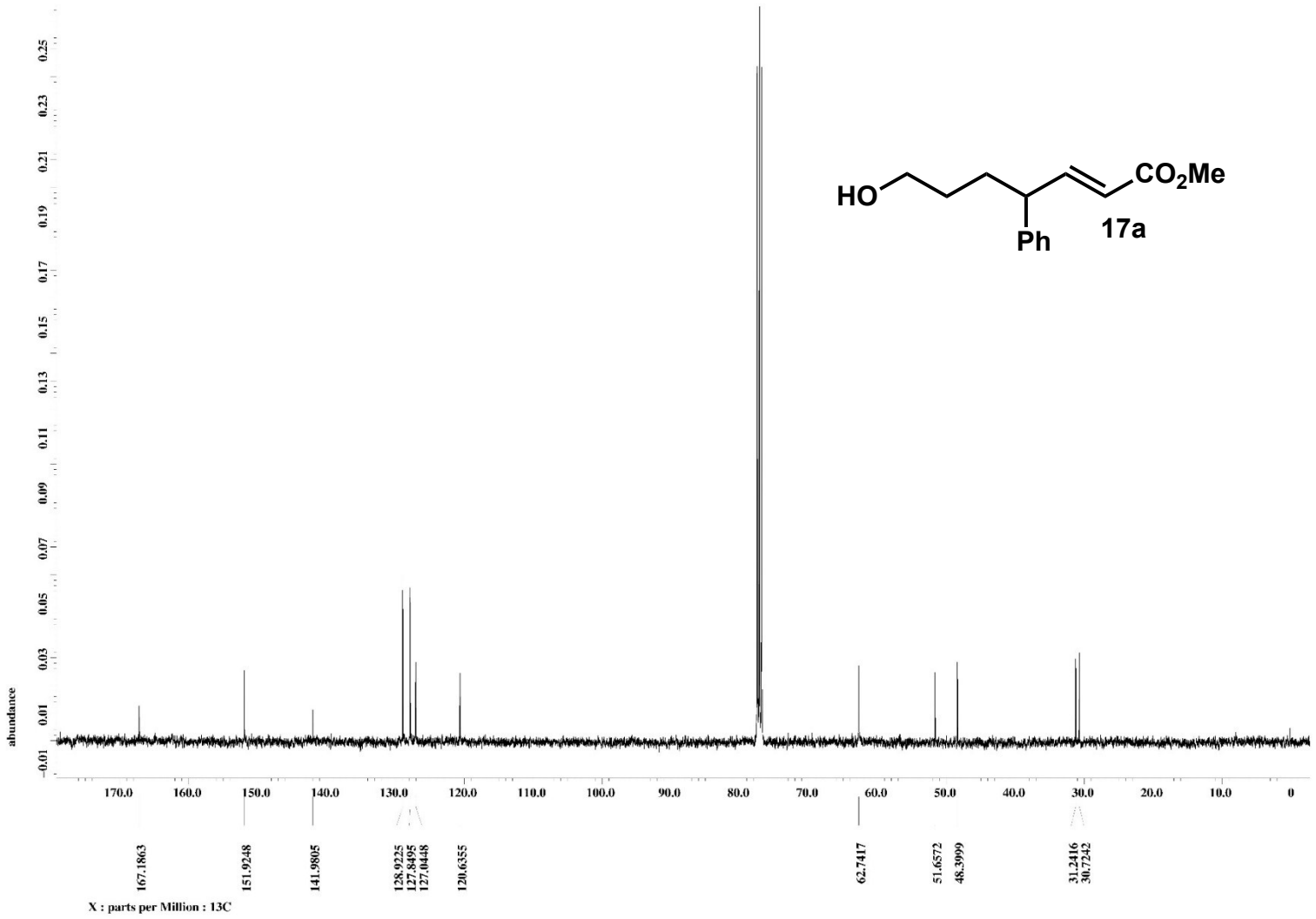


Figure 26 ^{13}C NMR spectrum of 17a

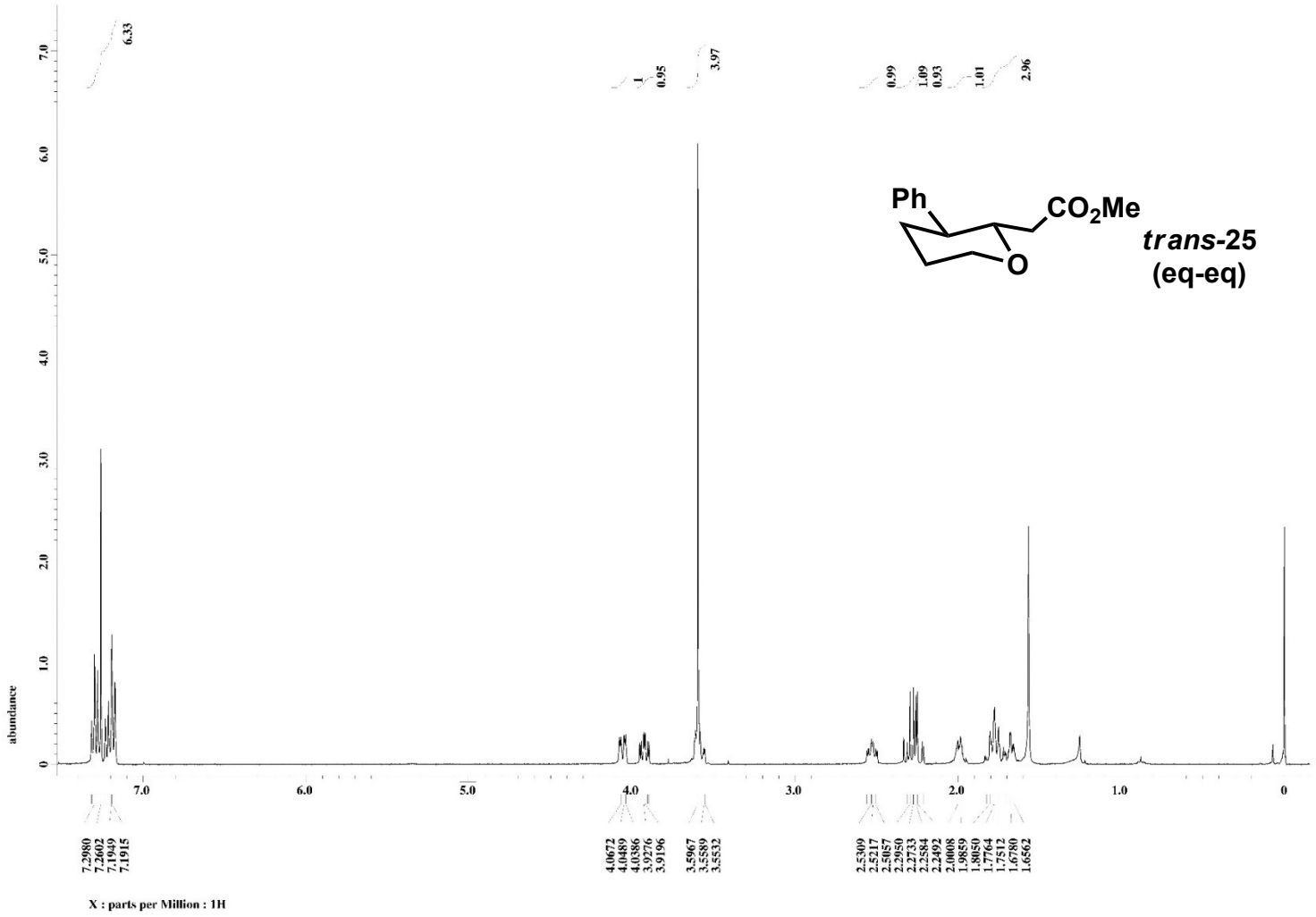


Figure 27 ^{1}H NMR spectrum of trans-25

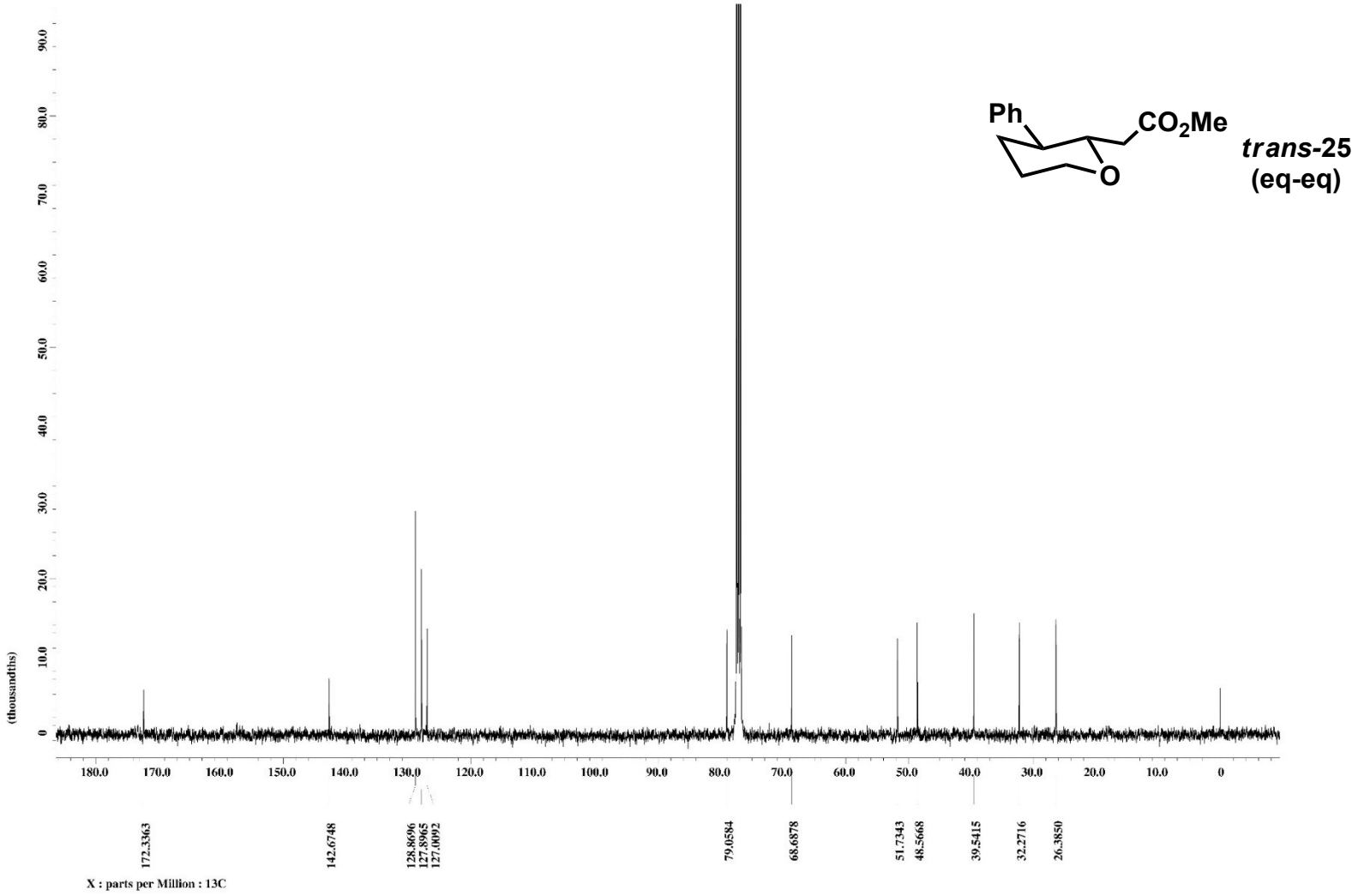


Figure 28 ^{13}C NMR spectrum of trans-25

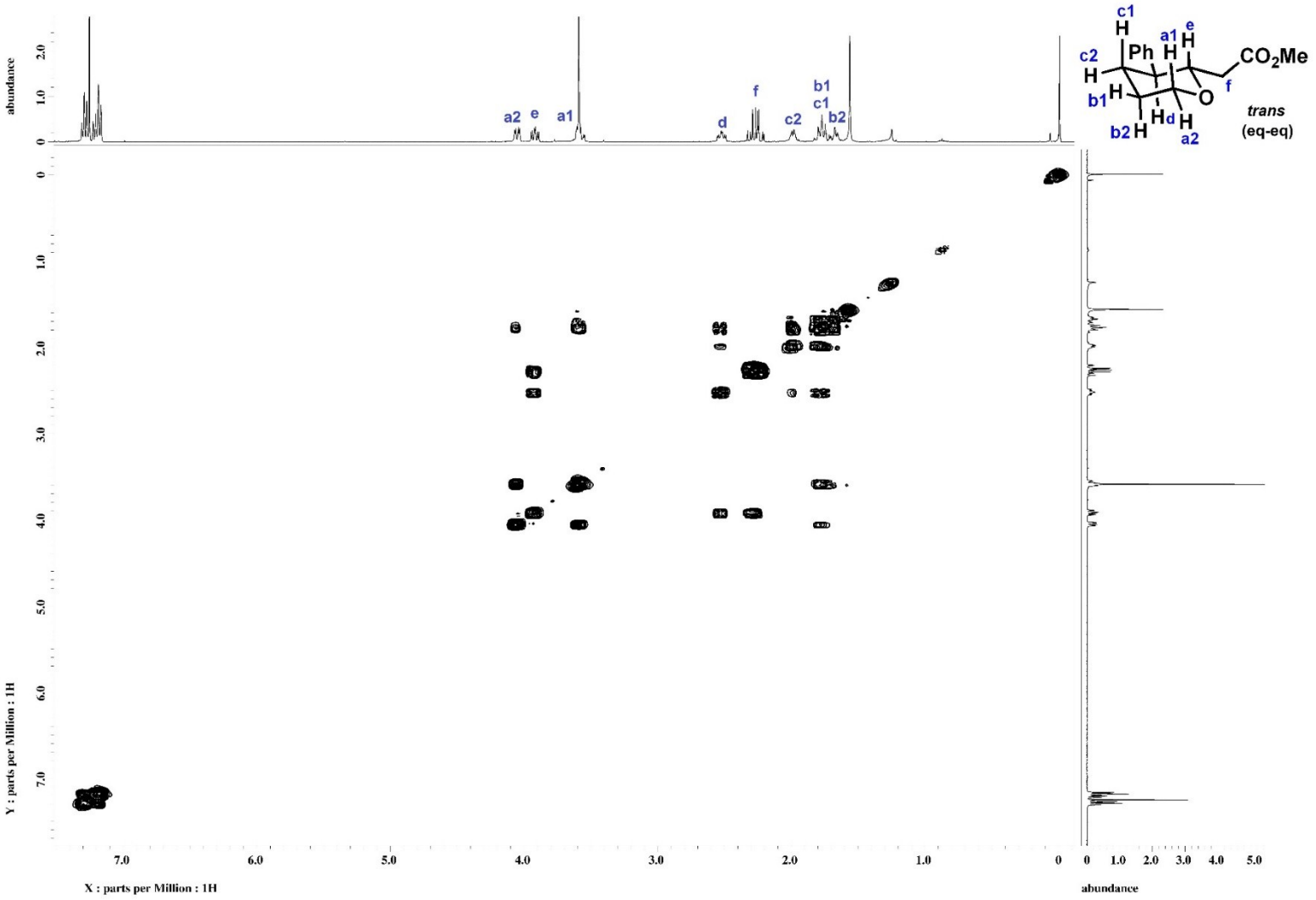


Figure 29 COSY spectrum of trans-25

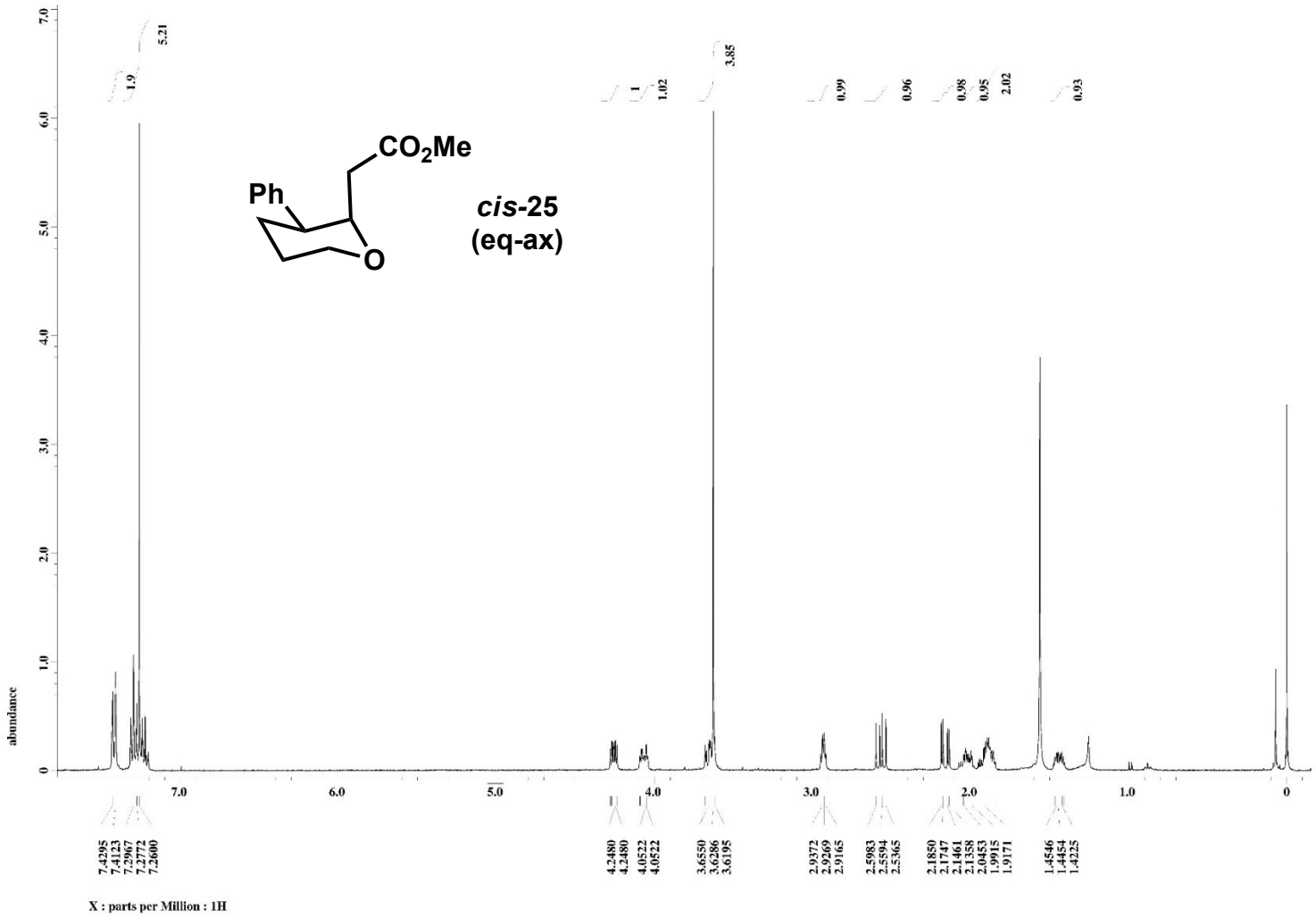


Figure 30 ^{1}H NMR spectrum of cis-25

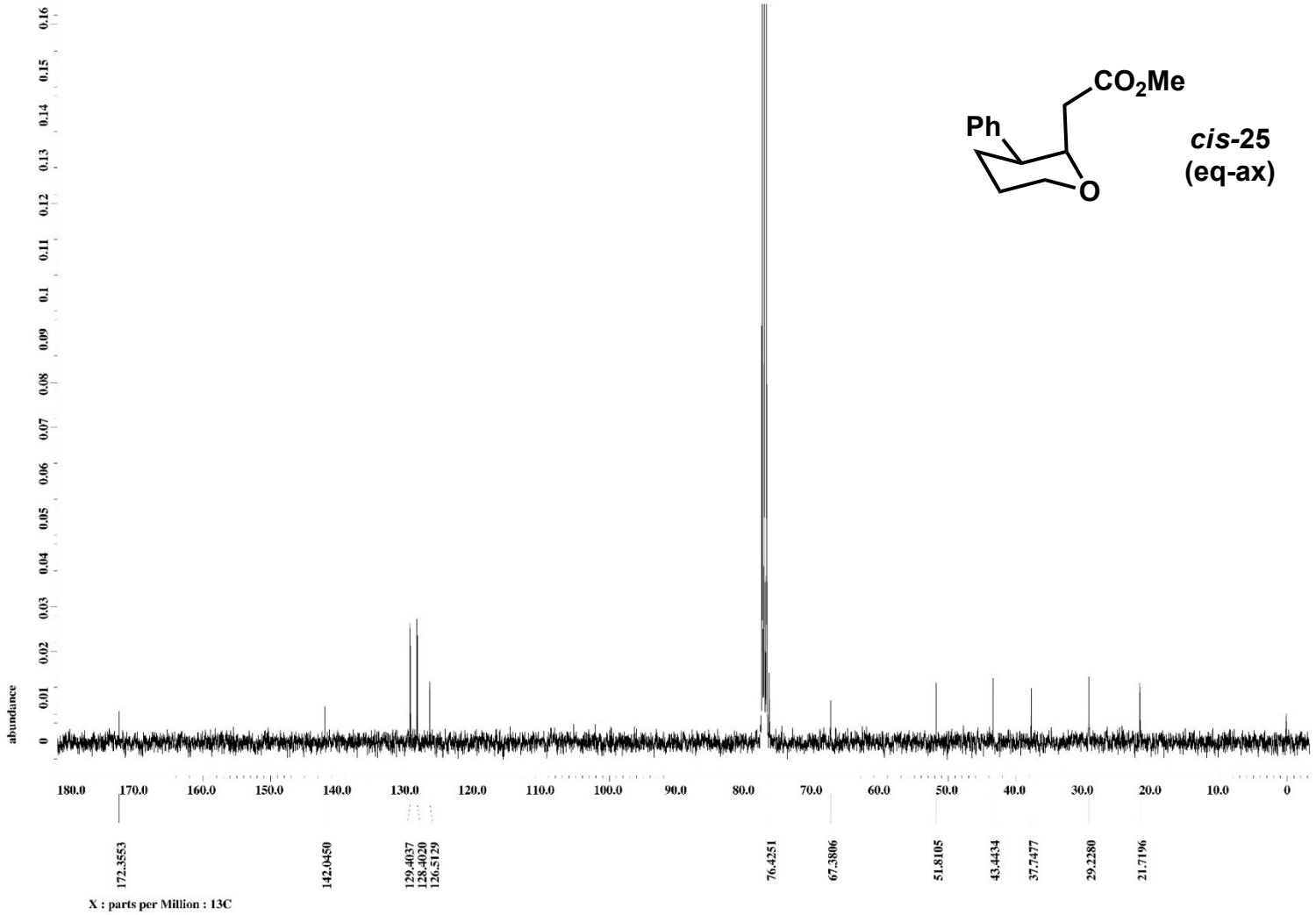


Figure 31 ^{13}C NMR spectrum of cis-25

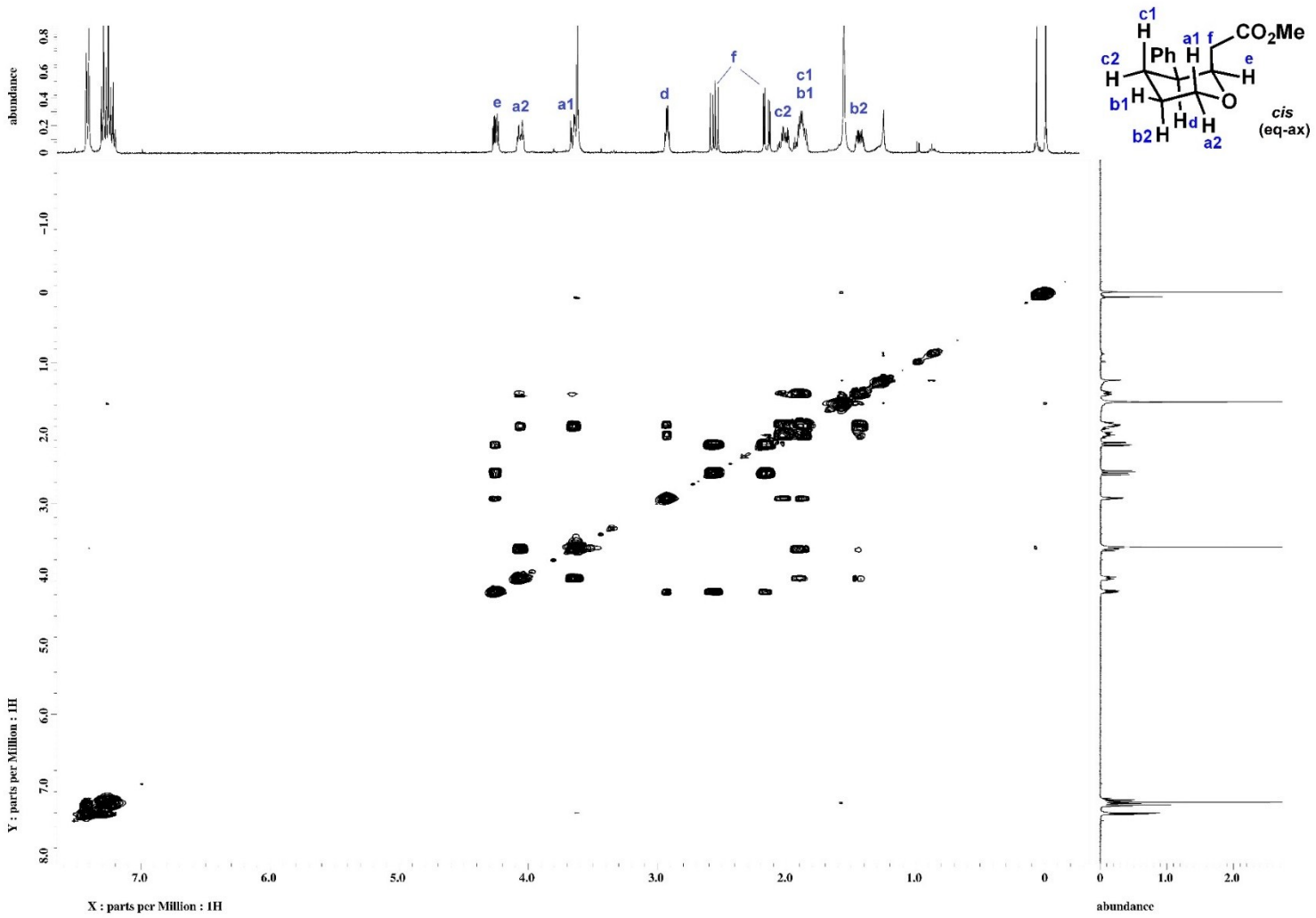


Figure 32 COSY spectrum of cis-25

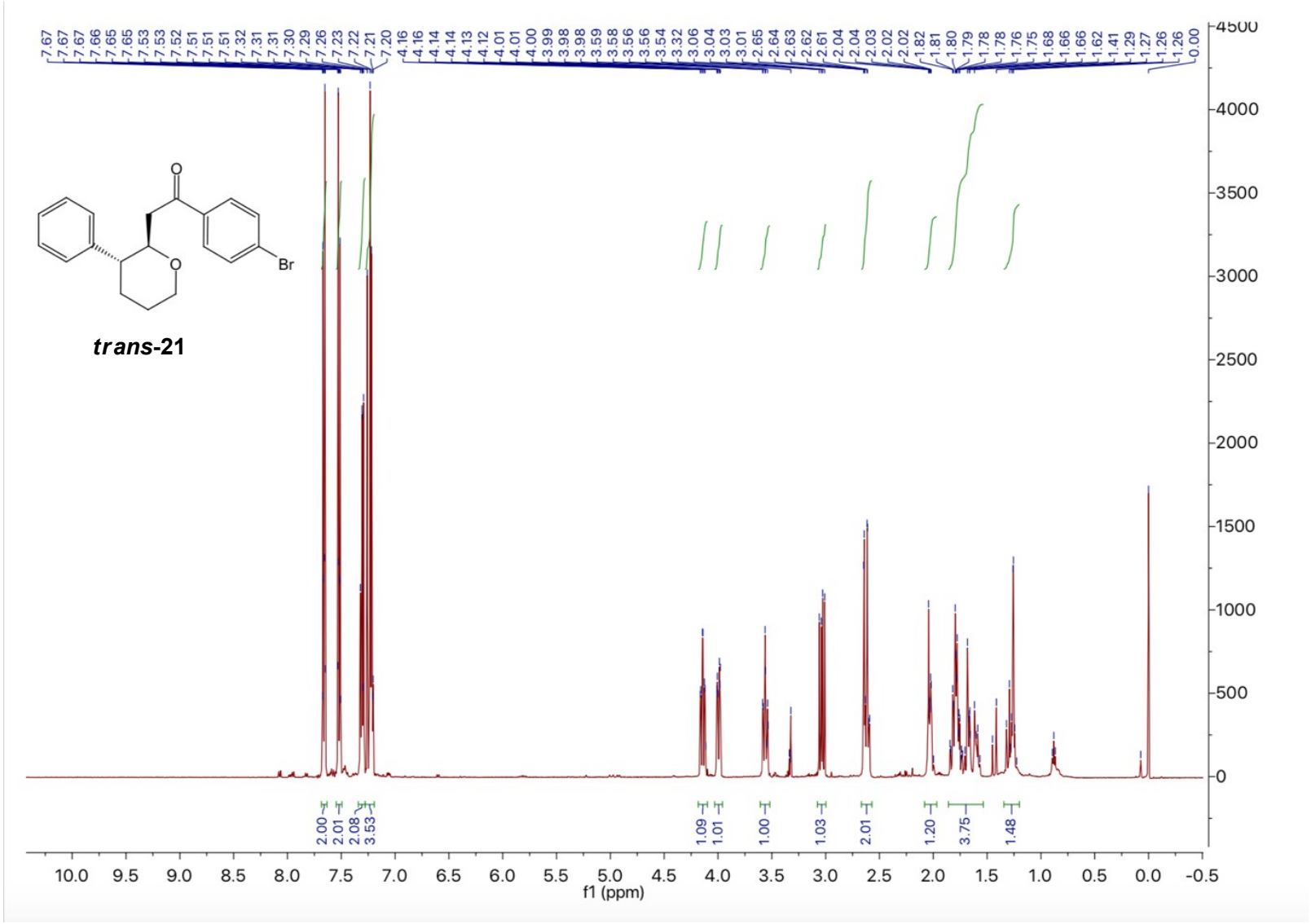


Figure 33 ^{1}H NMR spectrum of trans-21

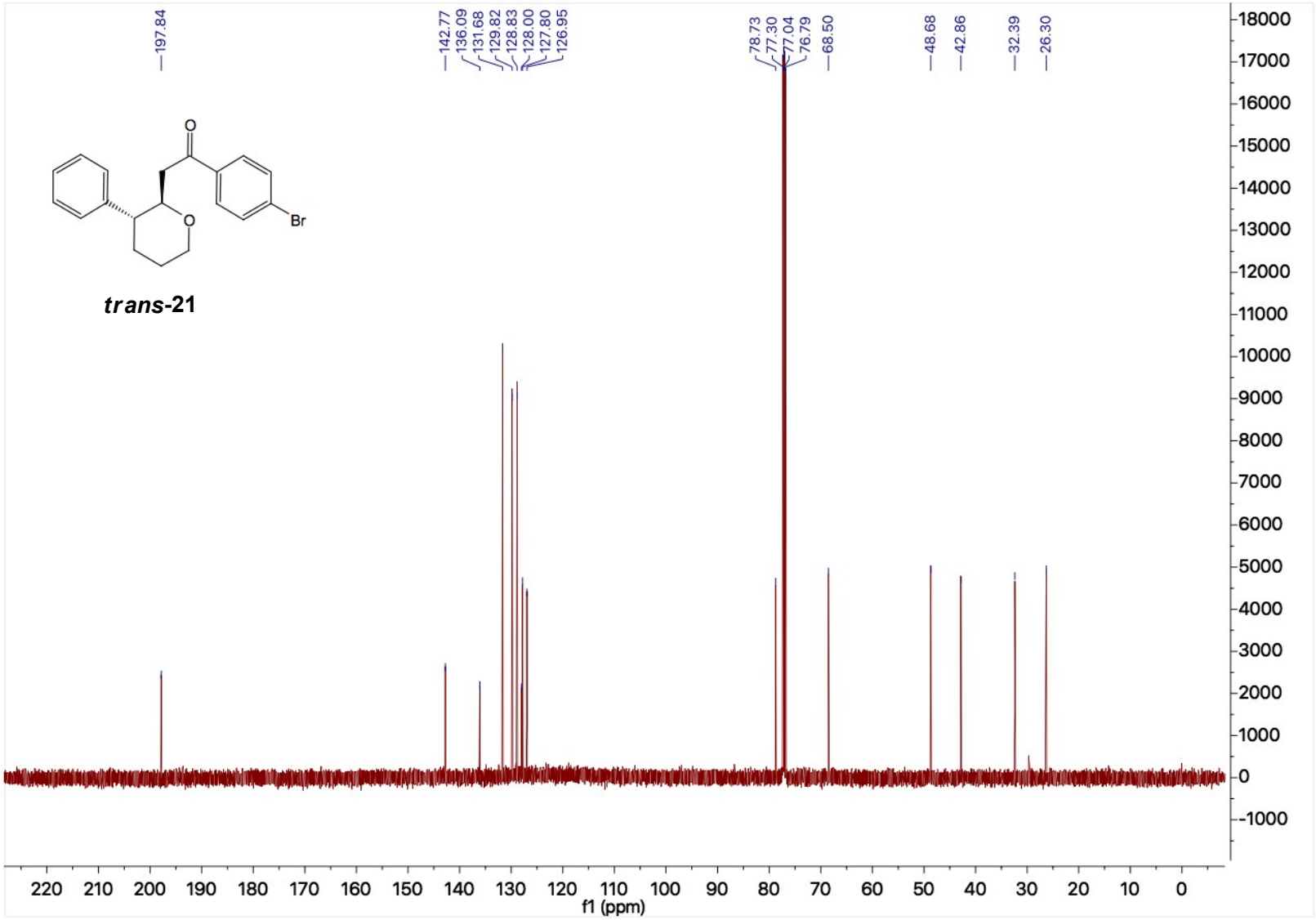


Figure 34 ^{13}C NMR spectrum of trans-21

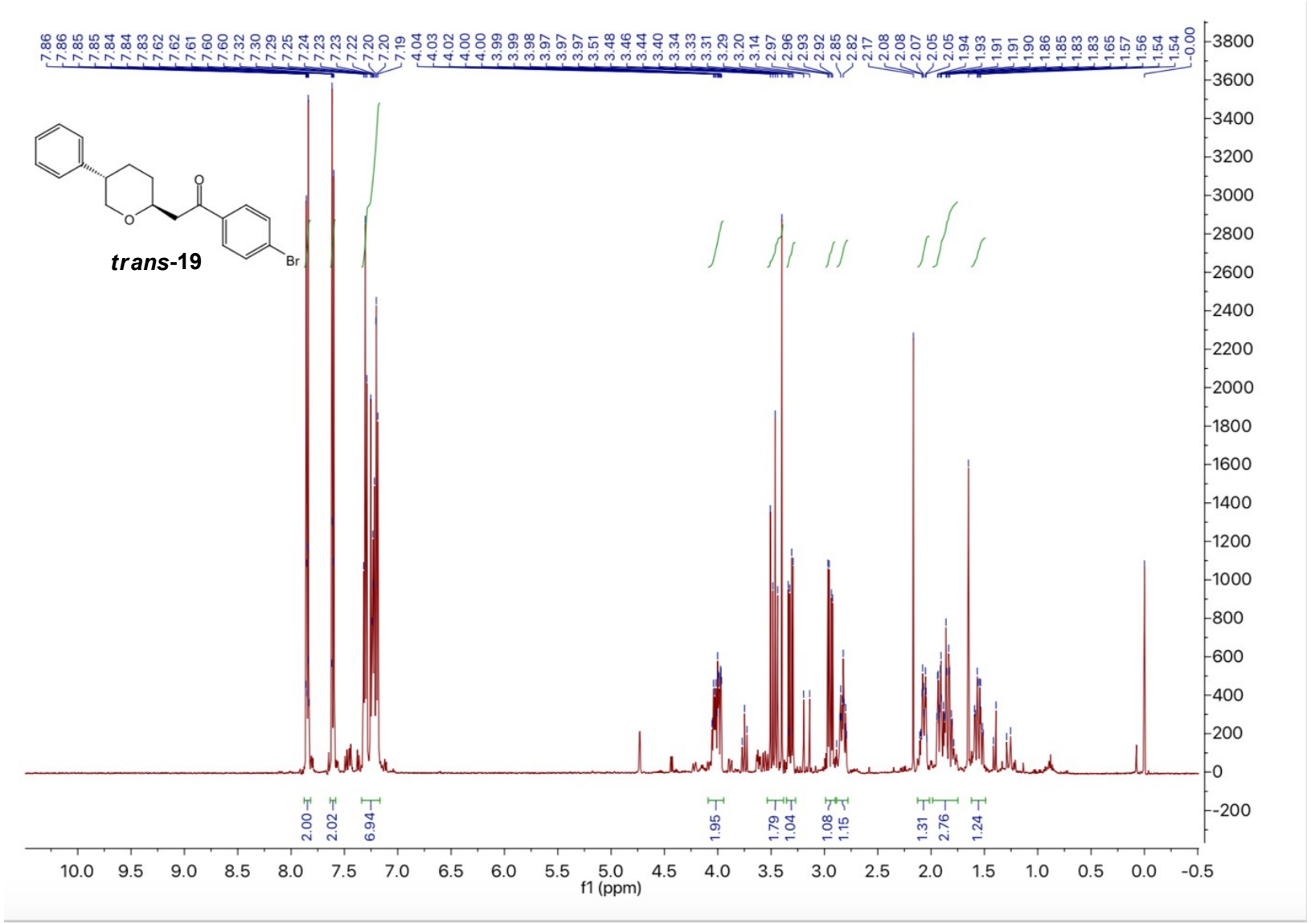


Figure 35 ^{1}H NMR spectrum of trans-19

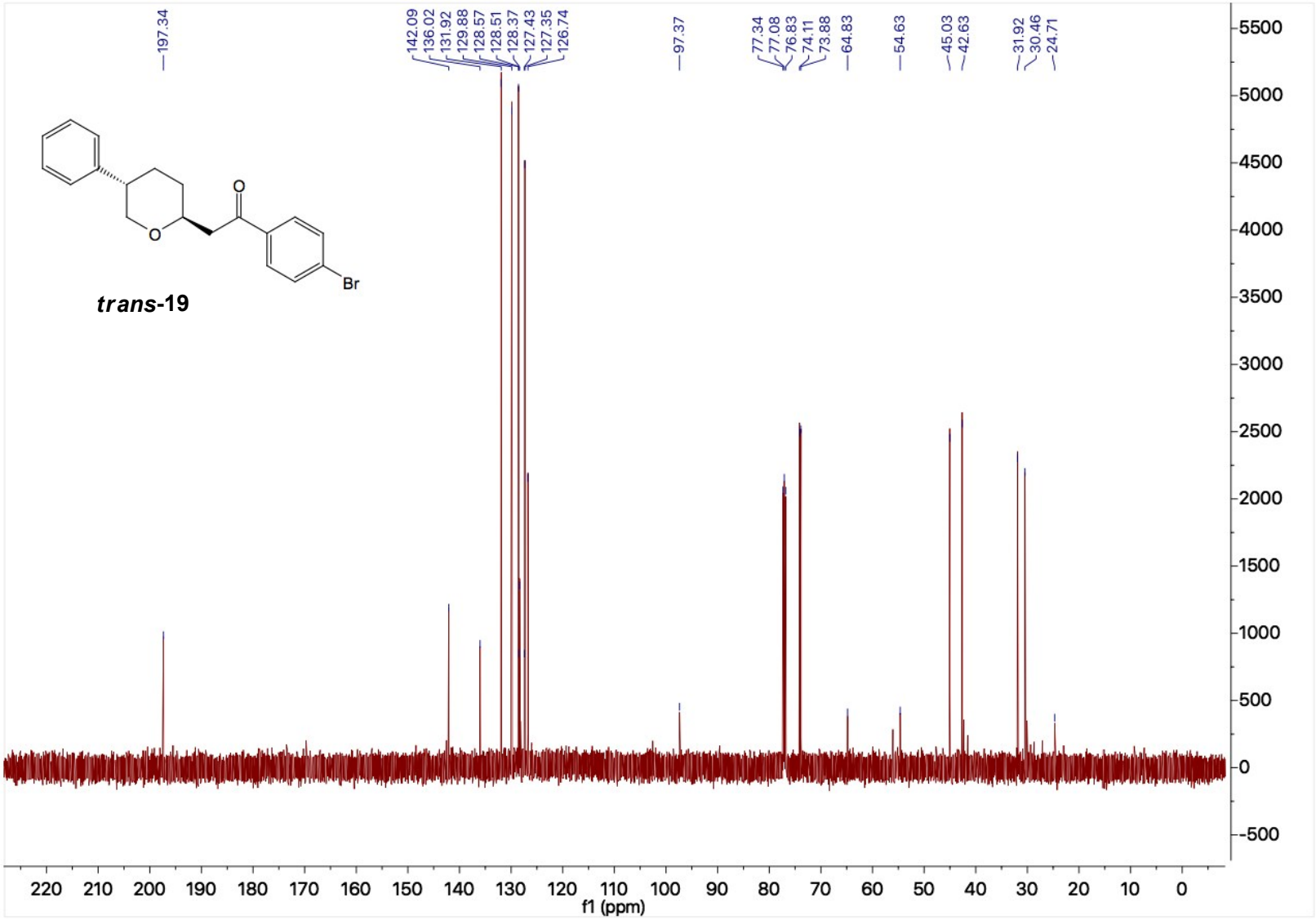


Figure 36 ^{13}C NMR spectrum of trans-19

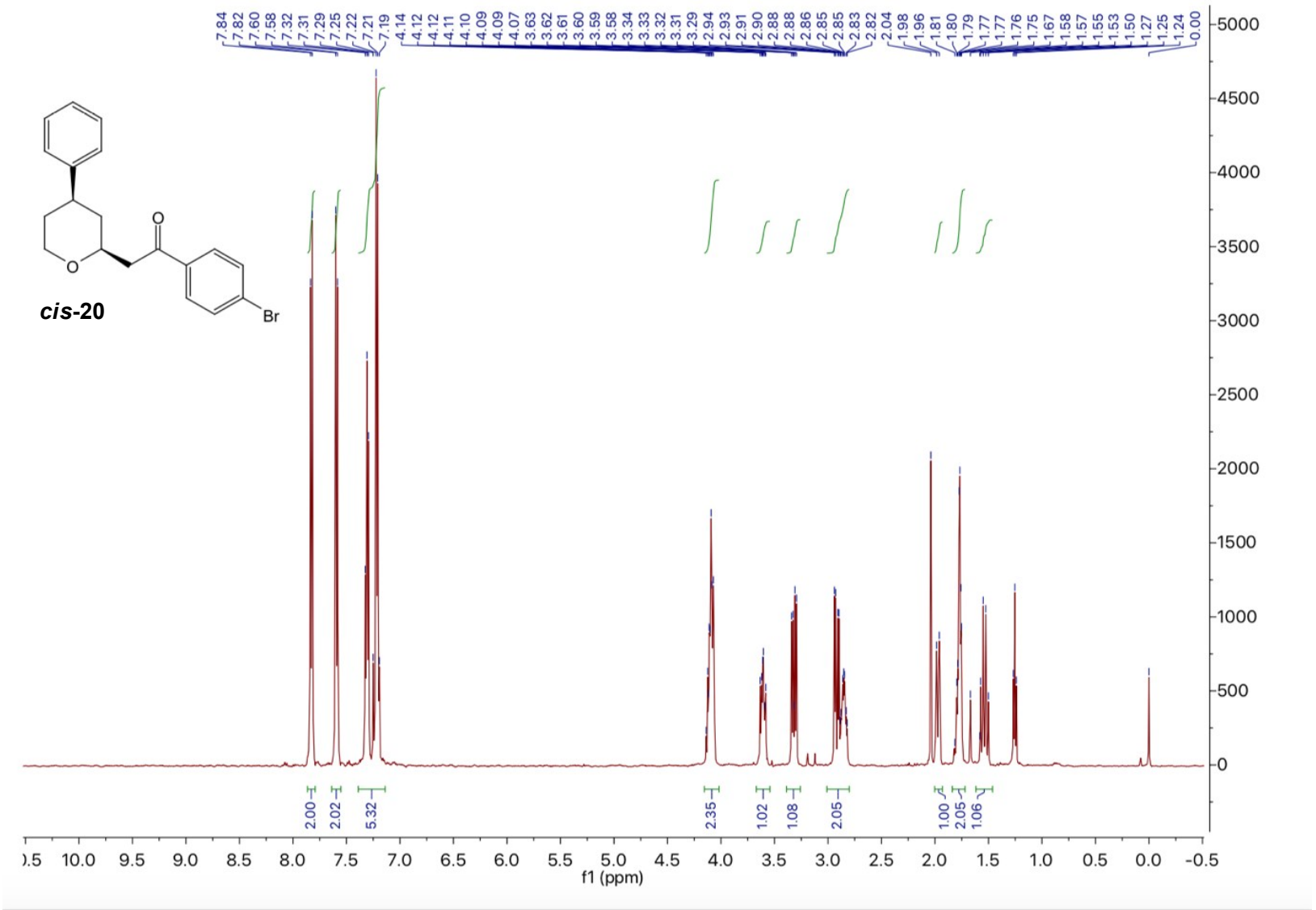


Figure 37 ^{1}H NMR spectrum of cis-20

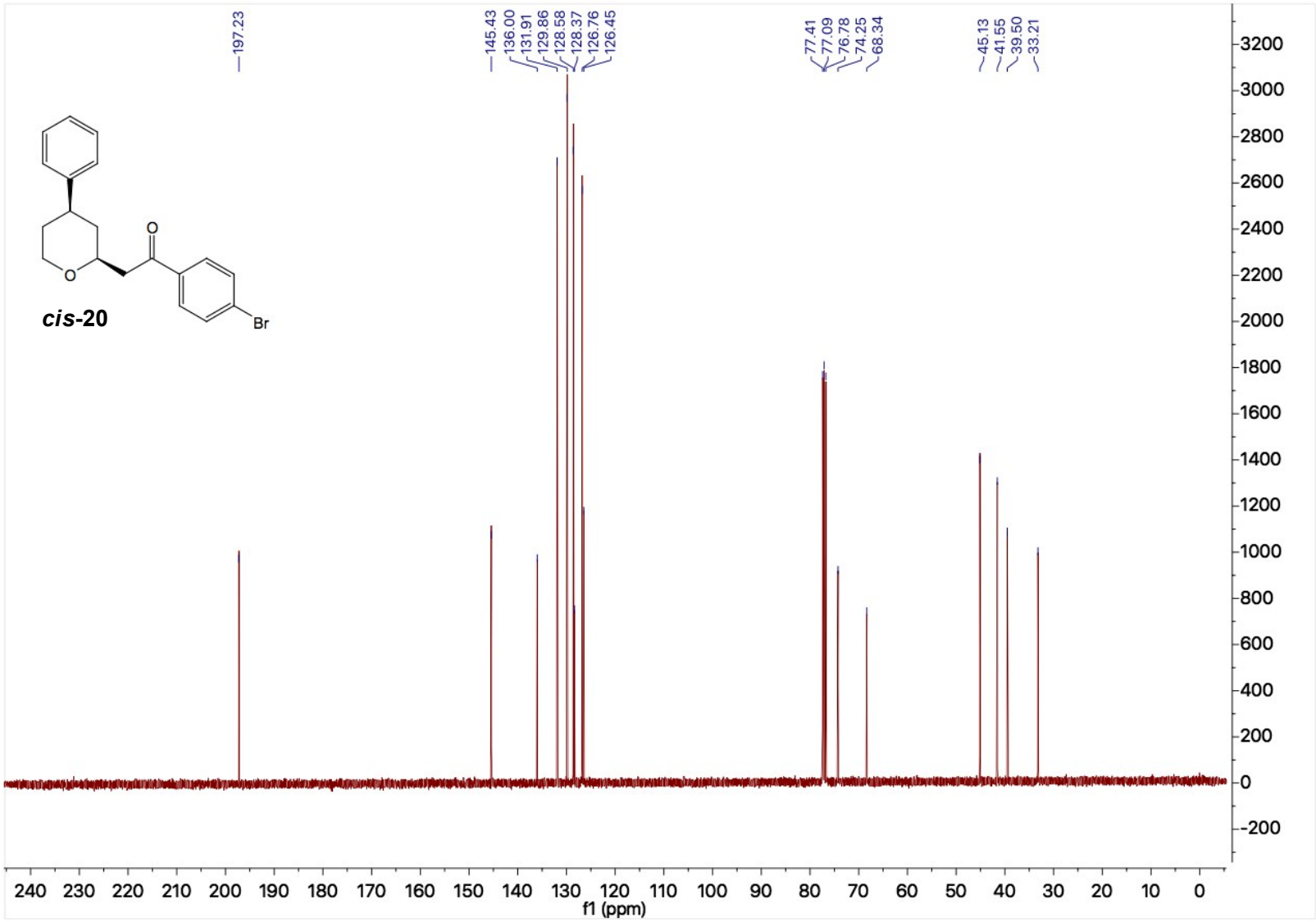


Figure 38 ^{13}C NMR spectrum of cis-20

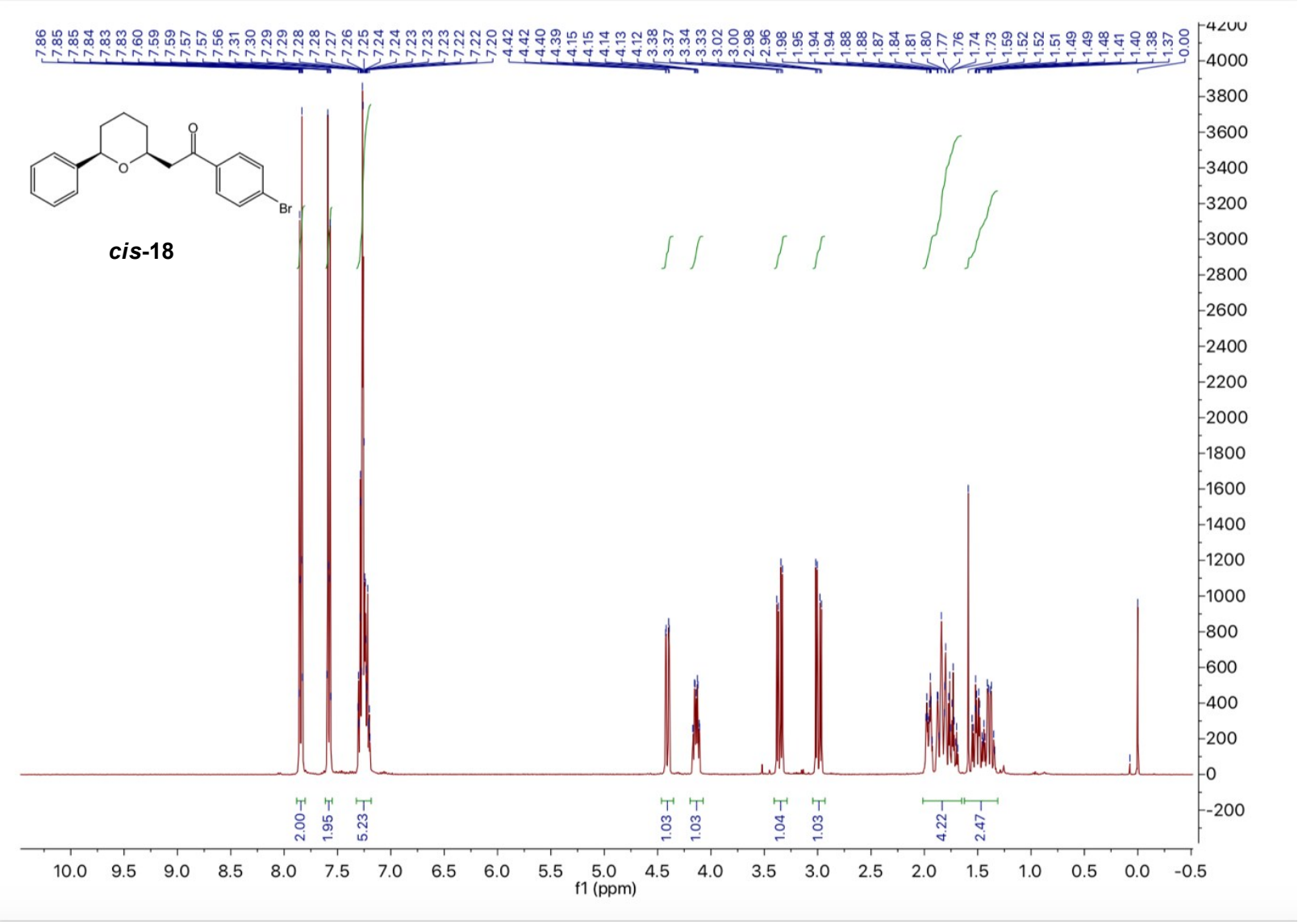


Figure 39 ^{1}H NMR spectrum of cis-18

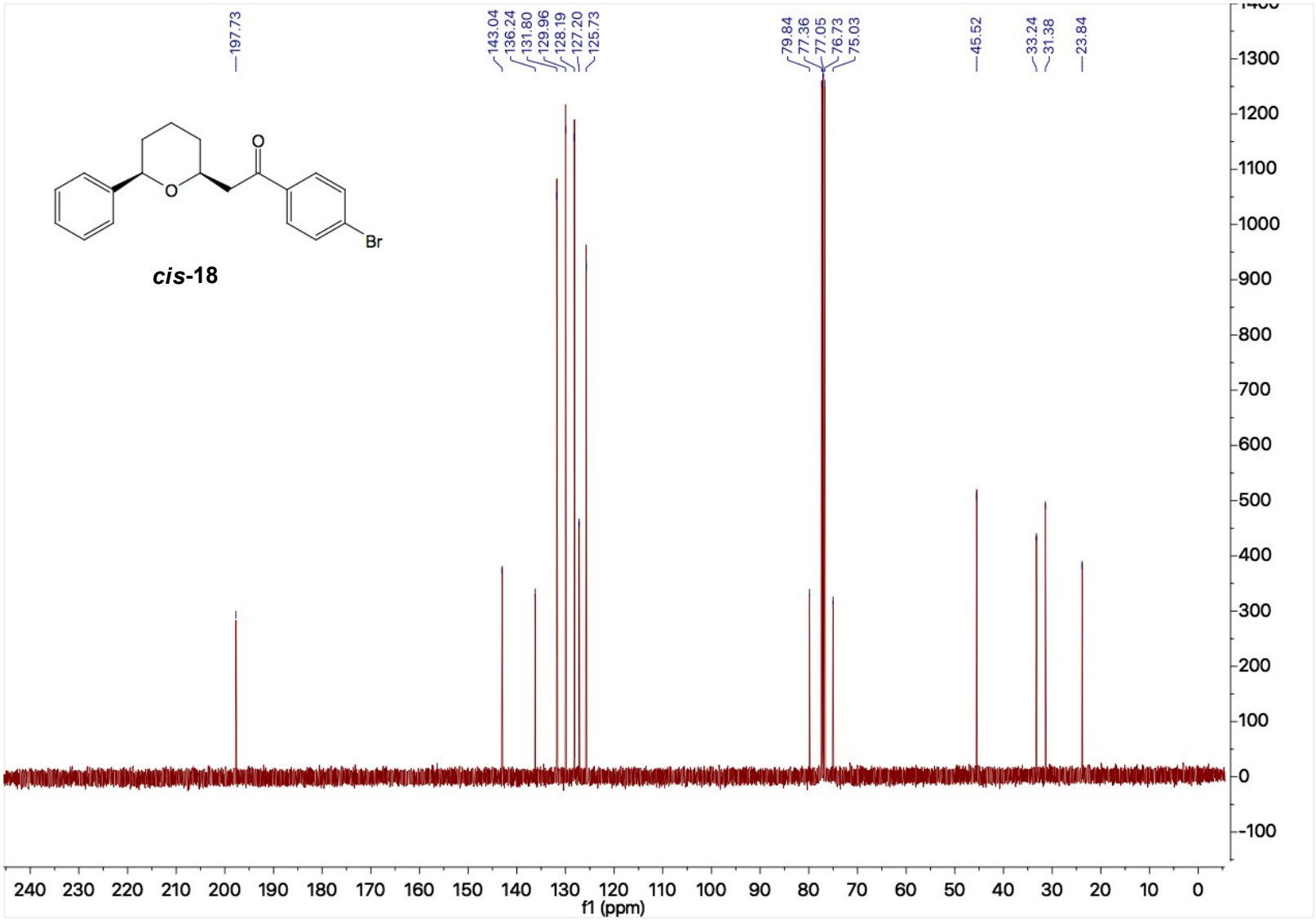


Figure 40 ^{13}C NMR spectrum of cis-18

X-ray crystallographic data

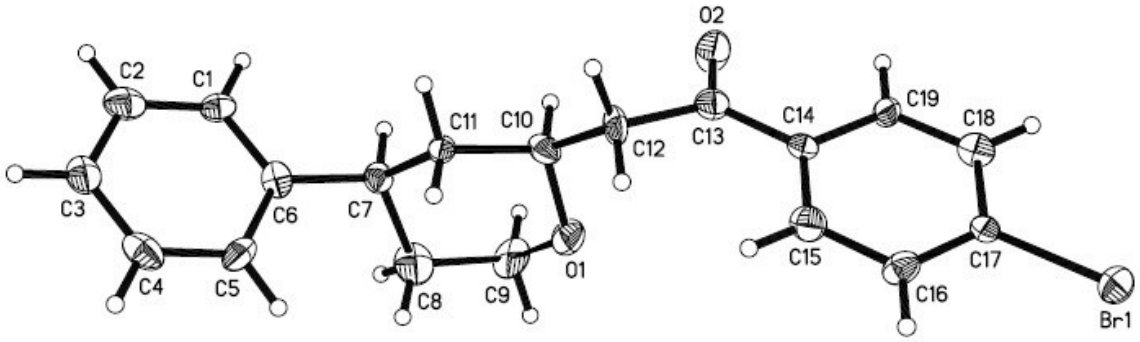


Figure 41 ORTEP diagram of *cis*-20 with 50% probability

Table 1. Sample and crystal data for *cis*-20.

Chemical formula	$C_{19}H_{19}BrO_2$	
Formula weight	359.25 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.120 x 0.320 mm	
Crystal habit	colorless plate	
Crystal system	orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 19.185(2) Å	α = 90°
	b = 5.7454(7) Å	β = 90°
	c = 29.323(3) Å	γ = 90°
Volume	3232.1(7) $Å^3$	
Z	8	
Density (calculated)	1.477 g/cm^3	
Absorption coefficient	2.548 mm^{-1}	
F(000)	1472	

Table 2. Data collection and structure refinement for *cis*-20.

Theta range for data collection	2.23 to 27.94°
Index ranges	-25<=h<=24, -7<=k<=6, -38<=l<=38
Reflections collected	18414
Independent reflections	7547 [R(int) = 0.0670]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9050 and 0.4960
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$

Data / restraints / parameters	7547 / 1 / 398
Goodness-of-fit on F^2	1.034
Final R indices	5514 data; I>2σ(I) R1 = 0.0645, wR2 = 0.1480
	all data R1 = 0.0960, wR2 = 0.1637
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0817P)^2+2.4536P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.39(2)
Largest diff. peak and hole	2.354 and -0.874 eÅ^{-3}
R.M.S. deviation from mean	0.125 eÅ^{-3}

Table 3. Bond lengths (Å) for *cis*-20.

Br1-C17	1.889(9)	Br2-C36	1.903(9)
C1-C2	1.368(15)	C1-C6	1.388(14)
C1-H1	0.95	C2-C3	1.384(16)
C2-H2	0.95	C3-C4	1.390(16)
C3-H3	0.95	C4-C5	1.367(15)
C4-H4	0.95	C5-C6	1.401(14)
C5-H5	0.95	C6-C7	1.529(13)
C7-C8	1.509(14)	C7-C11	1.534(13)
C7-H7	1.0	C8-C9	1.496(16)
C8-H8A	0.99	C8-H8B	0.99
C9-O1	1.422(13)	C9-H9A	0.99
C9-H9B	0.99	C10-O1	1.423(11)
C10-C12	1.520(13)	C10-C11	1.541(13)
C10-H10	1.0	C11-H11A	0.99
C11-H11B	0.99	C12-C13	1.538(13)
C12-H12A	0.99	C12-H12B	0.99
C13-O2	1.218(12)	C13-C14	1.482(14)
C14-C15	1.394(13)	C14-C19	1.395(12)
C15-C16	1.402(14)	C15-H15	0.95
C16-C17	1.370(14)	C16-H16	0.95
C17-C18	1.405(14)	C18-C19	1.370(13)
C18-H18	0.95	C19-H19	0.95
C20-C21	1.383(15)	C20-C25	1.393(14)
C20-H20	0.95	C21-C22	1.382(17)
C21-H21	0.95	C22-C23	1.353(16)
C22-H22	0.95	C23-C24	1.396(15)
C23-H23	0.95	C24-C25	1.418(14)
C24-H24	0.95	C25-C26	1.512(14)
C26-C30	1.518(14)	C26-C27	1.528(15)
C26-H26	1.0	C27-C28	1.501(15)
C27-H27A	0.99	C27-H27B	0.99
C28-O3	1.450(13)	C28-H28A	0.99
C28-H28B	0.99	C29-O3	1.425(11)
C29-C30	1.509(13)	C29-C31	1.523(13)
C29-H29	1.0	C30-H30A	0.99
C30-H30B	0.99	C31-C32	1.495(13)
C31-H31A	0.99	C31-H31B	0.99
C32-O4	1.217(12)	C32-C33	1.510(13)

C33-C34	1.378(13)	C33-C38	1.393(13)
C34-C35	1.383(13)	C34-H34	0.95
C35-C36	1.396(13)	C35-H35	0.95
C36-C37	1.378(13)	C37-C38	1.376(13)
C37-H37	0.95	C38-H38	0.95

Table 4. Bond angles (°) for *cis*-20.

C2-C1-C6	122.0(9)	C2-C1-H1	119.0
C6-C1-H1	119.0	C1-C2-C3	119.9(10)
C1-C2-H2	120.1	C3-C2-H2	120.1
C2-C3-C4	118.4(10)	C2-C3-H3	120.8
C4-C3-H3	120.8	C5-C4-C3	122.2(11)
C5-C4-H4	118.9	C3-C4-H4	118.9
C4-C5-C6	119.2(10)	C4-C5-H5	120.4
C6-C5-H5	120.4	C1-C6-C5	118.3(9)
C1-C6-C7	120.3(9)	C5-C6-C7	121.3(9)
C8-C7-C6	115.9(9)	C8-C7-C11	109.2(8)
C6-C7-C11	109.1(8)	C8-C7-H7	107.4
C6-C7-H7	107.4	C11-C7-H7	107.4
C9-C8-C7	112.1(9)	C9-C8-H8A	109.2
C7-C8-H8A	109.2	C9-C8-H8B	109.2
C7-C8-H8B	109.2	H8A-C8-H8B	107.9
O1-C9-C8	112.6(9)	O1-C9-H9A	109.1
C8-C9-H9A	109.1	O1-C9-H9B	109.1
C8-C9-H9B	109.1	H9A-C9-H9B	107.8
O1-C10-C12	107.6(8)	O1-C10-C11	110.5(8)
C12-C10-C11	111.5(8)	O1-C10-H10	109.1
C12-C10-H10	109.1	C11-C10-H10	109.1
C7-C11-C10	110.6(8)	C7-C11-H11A	109.5
C10-C11-H11A	109.5	C7-C11-H11B	109.5
C10-C11-H11B	109.5	H11A-C11-H11B	108.1
C10-C12-C13	110.1(8)	C10-C12-H12A	109.6
C13-C12-H12A	109.6	C10-C12-H12B	109.6
C13-C12-H12B	109.6	H12A-C12-H12B	108.1
O2-C13-C14	120.6(9)	O2-C13-C12	118.8(9)
C14-C13-C12	120.5(9)	C15-C14-C19	118.9(9)
C15-C14-C13	123.4(9)	C19-C14-C13	117.6(8)
C14-C15-C16	120.3(9)	C14-C15-H15	119.8
C16-C15-H15	119.8	C17-C16-C15	119.4(9)
C17-C16-H16	120.3	C15-C16-H16	120.3
C16-C17-C18	120.8(9)	C16-C17-Br1	120.5(7)
C18-C17-Br1	118.8(7)	C19-C18-C17	119.3(9)
C19-C18-H18	120.4	C17-C18-H18	120.4
C18-C19-C14	121.2(9)	C18-C19-H19	119.4
C14-C19-H19	119.4	C21-C20-C25	121.4(10)
C21-C20-H20	119.3	C25-C20-H20	119.3
C22-C21-C20	119.9(10)	C22-C21-H21	120.0
C20-C21-H21	120.0	C23-C22-C21	120.5(10)

C23-C22-H22	119.7	C21-C22-H22	119.7
C22-C23-C24	120.5(11)	C22-C23-H23	119.7
C24-C23-H23	119.7	C23-C24-C25	120.2(10)
C23-C24-H24	119.9	C25-C24-H24	119.9
C20-C25-C24	117.3(10)	C20-C25-C26	121.0(9)
C24-C25-C26	121.7(9)	C25-C26-C30	111.0(9)
C25-C26-C27	114.8(9)	C30-C26-C27	108.6(8)
C25-C26-H26	107.4	C30-C26-H26	107.4
C27-C26-H26	107.4	C28-C27-C26	111.7(9)
C28-C27-H27A	109.3	C26-C27-H27A	109.3
C28-C27-H27B	109.3	C26-C27-H27B	109.3
H27A-C27-H27B	107.9	O3-C28-C27	110.7(10)
O3-C28-H28A	109.5	C27-C28-H28A	109.5
O3-C28-H28B	109.5	C27-C28-H28B	109.5
H28A-C28-H28B	108.1	O3-C29-C30	110.9(8)
O3-C29-C31	106.7(8)	C30-C29-C31	114.0(8)
O3-C29-H29	108.4	C30-C29-H29	108.4
C31-C29-H29	108.4	C29-C30-C26	111.7(8)
C29-C30-H30A	109.3	C26-C30-H30A	109.3
C29-C30-H30B	109.3	C26-C30-H30B	109.3
H30A-C30-H30B	107.9	C32-C31-C29	112.2(8)
C32-C31-H31A	109.2	C29-C31-H31A	109.2
C32-C31-H31B	109.2	C29-C31-H31B	109.2
H31A-C31-H31B	107.9	O4-C32-C31	119.9(9)
O4-C32-C33	119.5(8)	C31-C32-C33	120.6(8)
C34-C33-C38	118.1(9)	C34-C33-C32	124.2(9)
C38-C33-C32	117.7(8)	C33-C34-C35	121.5(9)
C33-C34-H34	119.2	C35-C34-H34	119.2
C34-C35-C36	117.8(9)	C34-C35-H35	121.1
C36-C35-H35	121.1	C37-C36-C35	122.8(9)
C37-C36-Br2	118.1(7)	C35-C36-Br2	119.1(7)
C38-C37-C36	116.9(9)	C38-C37-H37	121.5
C36-C37-H37	121.5	C37-C38-C33	122.8(9)
C37-C38-H38	118.6	C33-C38-H38	118.6
C9-O1-C10	111.2(8)	C29-O3-C28	110.0(8)

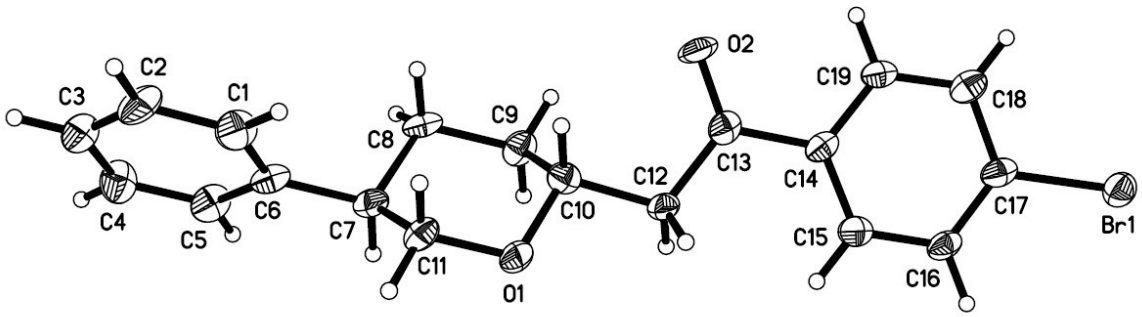


Figure 42 ORTEP diagram of *trans*-19 with 50% probability

Table 5. Sample and crystal data for *trans*-19.

Chemical formula	$C_{19}H_{19}BrO_2$	
Formula weight	359.25 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.040 x 0.220 x 0.240 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 9.6819(10) Å	α = 90°
	b = 9.8937(10) Å	β = 97.704(3)°
	c = 25.250(3) Å	γ = 90°
Volume	2396.9(4) $Å^3$	
Z	6	
Density (calculated)	1.493 g/cm^3	
Absorption coefficient	2.577 mm^{-1}	
F(000)	1104	

Table 6. Data collection and structure refinement for *trans*-19.

Theta range for data collection	2.37 to 27.14°	
Index ranges	-12<=h<=12, -12<=k<=12, -32<=l<=31	
Reflections collected	32466	
Independent reflections	10573 [R(int) = 0.1292]	
Coverage of independent reflections	99.7%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9040 and 0.5770	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	10573 / 1 / 595	
Goodness-of-fit on F^2	1.021	
Δ/σ_{max}	0.001	
Final R indices	7111 data; I>2σ(I)	R1 = 0.0635, wR2 = 0.1258
	all data	R1 = 0.1161, wR2 = 0.1496
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0450P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.093(11)	
Largest diff. peak and hole	0.546 and -1.380 $eÅ^{-3}$	
R.M.S. deviation from mean	0.116 $eÅ^{-3}$	

Table 7. Bond lengths (Å) for *trans*-19.

Br1-C17	1.898(10)	Br2-C36	1.903(9)
Br3-C55	1.889(11)	C1-C6	1.381(15)
C1-C2	1.388(15)	C1-H1	0.95
C2-C3	1.399(15)	C2-H2	0.95

C3-C4	1.374(15)	C3-H3	0.95
C4-C5	1.397(15)	C4-H4	0.95
C5-C6	1.372(14)	C5-H5	0.95
C6-C7	1.521(13)	C7-C11	1.513(13)
C7-C8	1.551(14)	C7-H7	1.0
C8-C9	1.523(13)	C8-H8A	0.99
C8-H8B	0.99	C9-C10	1.506(13)
C9-H9A	0.99	C9-H9B	0.99
C10-O1	1.442(11)	C10-C12	1.534(12)
C10-H10	1.0	C11-O1	1.434(10)
C11-H11A	0.99	C11-H11B	0.99
C12-C13	1.501(14)	C12-H12A	0.99
C12-H12B	0.99	C13-O2	1.223(11)
C13-C14	1.507(13)	C14-C15	1.374(13)
C14-C19	1.400(14)	C15-C16	1.390(14)
C15-H15	0.95	C16-C17	1.382(14)
C16-H16	0.95	C17-C18	1.383(14)
C18-C19	1.395(14)	C18-H18	0.95
C19-H19	0.95	C20-C21	1.390(15)
C20-C25	1.408(14)	C20-H20	0.95
C21-C22	1.374(14)	C21-H21	0.95
C22-C23	1.378(15)	C22-H22	0.95
C23-C24	1.390(15)	C23-H23	0.95
C24-C25	1.382(13)	C24-H24	0.95
C25-C26	1.516(13)	C26-C30	1.515(13)
C26-C27	1.535(14)	C26-H26	1.0
C27-C28	1.523(13)	C27-H27A	0.99
C27-H27B	0.99	C28-C29	1.508(13)
C28-H28A	0.99	C28-H28B	0.99
C29-O3	1.431(11)	C29-C31	1.515(12)
C29-H29	1.0	C30-O3	1.430(10)
C30-H30A	0.99	C30-H30B	0.99
C31-C32	1.504(13)	C31-H31A	0.99
C31-H31B	0.99	C32-O4	1.218(11)
C32-C33	1.496(14)	C33-C38	1.392(13)
C33-C34	1.408(14)	C34-C35	1.369(14)
C34-H34	0.95	C35-C36	1.379(13)
C35-H35	0.95	C36-C37	1.400(13)
C37-C38	1.403(14)	C37-H37	0.95
C38-H38	0.95	C39-C40	1.406(15)
C39-C44	1.416(14)	C39-H39	0.95
C40-C41	1.364(15)	C40-H40	0.95
C41-C42	1.408(16)	C41-H41	0.95
C42-C43	1.387(15)	C42-H42	0.95
C43-C44	1.408(14)	C43-H43	0.95
C44-C45	1.503(14)	C45-C49	1.509(12)
C45-C46	1.528(13)	C45-H45	1.0
C46-C47	1.517(14)	C46-H46A	0.99
C46-H46B	0.99	C47-C48	1.522(13)

C47-H47A	0.99	C47-H47B	0.99
C48-O5	1.449(11)	C48-C50	1.497(14)
C48-H48	1.0	C49-O5	1.435(11)
C49-H49A	0.99	C49-H49B	0.99
C50-C51	1.511(14)	C50-H50A	0.99
C50-H50B	0.99	C51-O6	1.234(11)
C51-C52	1.511(15)	C52-C57	1.380(14)
C52-C53	1.392(14)	C53-C54	1.385(14)
C53-H53	0.95	C54-C55	1.380(15)
C54-H54	0.95	C55-C56	1.385(15)
C56-C57	1.378(15)	C56-H56	0.95
C57-H57	0.95		

Table 8. Bond angles (°) for *trans*-19.

C6-C1-C2	121.1(10)	C6-C1-H1	119.5
C2-C1-H1	119.5	C1-C2-C3	120.3(9)
C1-C2-H2	119.9	C3-C2-H2	119.9
C4-C3-C2	118.6(10)	C4-C3-H3	120.7
C2-C3-H3	120.7	C3-C4-C5	120.3(10)
C3-C4-H4	119.9	C5-C4-H4	119.9
C6-C5-C4	121.6(10)	C6-C5-H5	119.2
C4-C5-H5	119.2	C5-C6-C1	118.2(10)
C5-C6-C7	120.0(9)	C1-C6-C7	121.8(9)
C11-C7-C6	114.6(8)	C11-C7-C8	109.4(8)
C6-C7-C8	111.0(8)	C11-C7-H7	107.1
C6-C7-H7	107.1	C8-C7-H7	107.1
C9-C8-C7	110.5(8)	C9-C8-H8A	109.5
C7-C8-H8A	109.5	C9-C8-H8B	109.5
C7-C8-H8B	109.5	H8A-C8-H8B	108.1
C10-C9-C8	110.6(8)	C10-C9-H9A	109.5
C8-C9-H9A	109.5	C10-C9-H9B	109.5
C8-C9-H9B	109.5	H9A-C9-H9B	108.1
O1-C10-C9	110.2(8)	O1-C10-C12	106.3(7)
C9-C10-C12	114.6(8)	O1-C10-H10	108.5
C9-C10-H10	108.5	C12-C10-H10	108.5
O1-C11-C7	112.1(8)	O1-C11-H11A	109.2
C7-C11-H11A	109.2	O1-C11-H11B	109.2
C7-C11-H11B	109.2	H11A-C11-H11B	107.9
C13-C12-C10	112.7(8)	C13-C12-H12A	109.0
C10-C12-H12A	109.0	C13-C12-H12B	109.0
C10-C12-H12B	109.0	H12A-C12-H12B	107.8
O2-C13-C12	121.3(9)	O2-C13-C14	120.4(9)
C12-C13-C14	118.2(8)	C15-C14-C19	118.5(9)
C15-C14-C13	123.3(9)	C19-C14-C13	118.2(8)
C14-C15-C16	121.5(9)	C14-C15-H15	119.2
C16-C15-H15	119.2	C17-C16-C15	118.5(9)
C17-C16-H16	120.7	C15-C16-H16	120.7
C16-C17-C18	122.2(10)	C16-C17-Br1	119.7(7)
C18-C17-Br1	118.1(8)	C17-C18-C19	117.7(10)

C17-C18-H18	121.1	C19-C18-H18	121.1
C18-C19-C14	121.4(9)	C18-C19-H19	119.3
C14-C19-H19	119.3	C21-C20-C25	119.6(9)
C21-C20-H20	120.2	C25-C20-H20	120.2
C22-C21-C20	121.9(10)	C22-C21-H21	119.0
C20-C21-H21	119.0	C21-C22-C23	118.1(10)
C21-C22-H22	121.0	C23-C22-H22	121.0
C22-C23-C24	121.5(10)	C22-C23-H23	119.2
C24-C23-H23	119.2	C25-C24-C23	120.5(10)
C25-C24-H24	119.7	C23-C24-H24	119.7
C24-C25-C20	118.4(9)	C24-C25-C26	120.8(9)
C20-C25-C26	120.9(9)	C30-C26-C25	113.1(8)
C30-C26-C27	109.9(8)	C25-C26-C27	112.0(8)
C30-C26-H26	107.2	C25-C26-H26	107.2
C27-C26-H26	107.2	C28-C27-C26	109.3(8)
C28-C27-H27A	109.8	C26-C27-H27A	109.8
C28-C27-H27B	109.8	C26-C27-H27B	109.8
H27A-C27-H27B	108.3	C29-C28-C27	111.6(8)
C29-C28-H28A	109.3	C27-C28-H28A	109.3
C29-C28-H28B	109.3	C27-C28-H28B	109.3
H28A-C28-H28B	108.0	O3-C29-C28	109.5(8)
O3-C29-C31	106.0(7)	C28-C29-C31	114.6(8)
O3-C29-H29	108.8	C28-C29-H29	108.8
C31-C29-H29	108.8	O3-C30-C26	111.9(8)
O3-C30-H30A	109.2	C26-C30-H30A	109.2
O3-C30-H30B	109.2	C26-C30-H30B	109.2
H30A-C30-H30B	107.9	C32-C31-C29	113.1(8)
C32-C31-H31A	109.0	C29-C31-H31A	109.0
C32-C31-H31B	109.0	C29-C31-H31B	109.0
H31A-C31-H31B	107.8	O4-C32-C33	120.7(9)
O4-C32-C31	120.8(9)	C33-C32-C31	118.5(8)
C38-C33-C34	119.1(9)	C38-C33-C32	123.1(9)
C34-C33-C32	117.8(9)	C35-C34-C33	120.9(9)
C35-C34-H34	119.5	C33-C34-H34	119.5
C34-C35-C36	119.4(10)	C34-C35-H35	120.3
C36-C35-H35	120.3	C35-C36-C37	121.9(9)
C35-C36-Br2	119.1(8)	C37-C36-Br2	118.9(7)
C36-C37-C38	118.0(9)	C36-C37-H37	121.0
C38-C37-H37	121.0	C33-C38-C37	120.5(10)
C33-C38-H38	119.7	C37-C38-H38	119.7
C40-C39-C44	119.7(10)	C40-C39-H39	120.2
C44-C39-H39	120.2	C41-C40-C39	122.4(10)
C41-C40-H40	118.8	C39-C40-H40	118.8
C40-C41-C42	118.4(11)	C40-C41-H41	120.8
C42-C41-H41	120.8	C43-C42-C41	120.7(10)
C43-C42-H42	119.7	C41-C42-H42	119.7
C42-C43-C44	121.4(10)	C42-C43-H43	119.3
C44-C43-H43	119.3	C43-C44-C39	117.5(10)
C43-C44-C45	120.9(9)	C39-C44-C45	121.3(9)

C44-C45-C49	109.7(8)	C44-C45-C46	116.1(8)
C49-C45-C46	107.8(8)	C44-C45-H45	107.6
C49-C45-H45	107.6	C46-C45-H45	107.6
C47-C46-C45	110.1(8)	C47-C46-H46A	109.6
C45-C46-H46A	109.6	C47-C46-H46B	109.6
C45-C46-H46B	109.6	H46A-C46-H46B	108.2
C46-C47-C48	112.3(8)	C46-C47-H47A	109.2
C48-C47-H47A	109.2	C46-C47-H47B	109.2
C48-C47-H47B	109.2	H47A-C47-H47B	107.9
O5-C48-C50	104.2(7)	O5-C48-C47	110.0(7)
C50-C48-C47	113.8(9)	O5-C48-H48	109.5
C50-C48-H48	109.5	C47-C48-H48	109.5
O5-C49-C45	113.4(8)	O5-C49-H49A	108.9
C45-C49-H49A	108.9	O5-C49-H49B	108.9
C45-C49-H49B	108.9	H49A-C49-H49B	107.7
C48-C50-C51	115.5(8)	C48-C50-H50A	108.4
C51-C50-H50A	108.4	C48-C50-H50B	108.4
C51-C50-H50B	108.4	H50A-C50-H50B	107.5
O6-C51-C50	121.4(10)	O6-C51-C52	119.3(9)
C50-C51-C52	119.2(8)	C57-C52-C53	119.5(10)
C57-C52-C51	120.3(10)	C53-C52-C51	120.2(9)
C54-C53-C52	119.9(9)	C54-C53-H53	120.0
C52-C53-H53	120.0	C55-C54-C53	119.6(10)
C55-C54-H54	120.2	C53-C54-H54	120.2
C54-C55-C56	120.8(11)	C54-C55-Br3	119.9(8)
C56-C55-Br3	119.3(9)	C57-C56-C55	119.1(10)
C57-C56-H56	120.4	C55-C56-H56	120.4
C56-C57-C52	120.9(10)	C56-C57-H57	119.5
C52-C57-H57	119.5	C11-O1-C10	111.2(7)
C30-O3-C29	111.3(7)	C49-O5-C48	113.0(7)

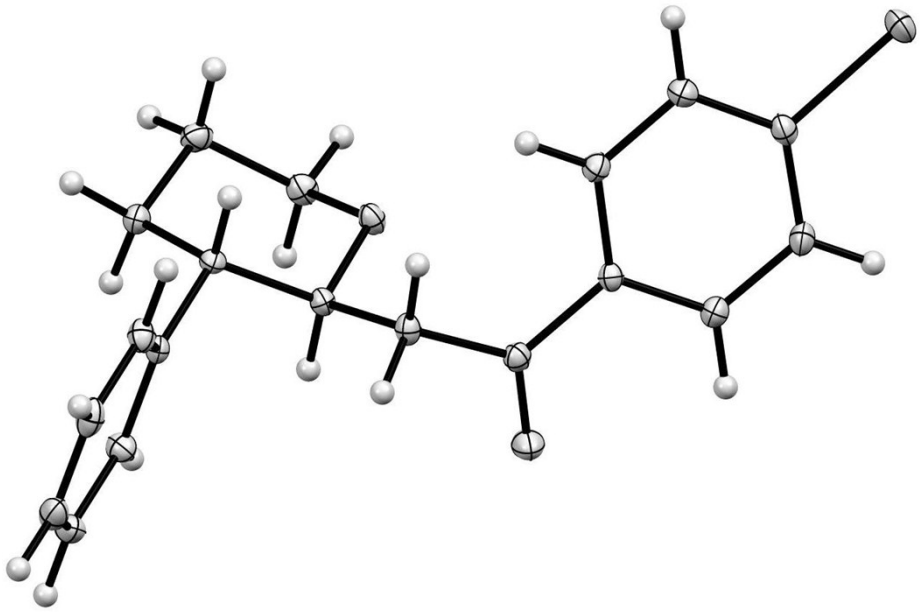


Figure 43 ORTEP diagram of *trans*-21 with 50% probability

Table 9. Sample and crystal data for *trans*-21.

Chemical formula	$C_{19}H_{19}BrO_2$	
Formula weight	359.25 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.120 x 0.320 mm	
Crystal habit	colorless needle	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 15.9582(5) Å	α = 90°
	b = 9.1314(3) Å	β = 91.0981(11)°
	c = 10.7679(3) Å	γ = 90°
Volume	1568.82(8) $Å^3$	
Z	4	
Density (calculated)	1.521 g/cm^3	
Absorption coefficient	2.625 mm^{-1}	
F(000)	736	

Table 10. Data collection and structure refinement for *trans*-21.

Theta range for data collection	2.55 to 36.35°
Index ranges	-26<=h<=26, -15<=k<=15, -13<=l<=17
Reflections collected	27317
Independent reflections	7552 [R(int) = 0.0455]
Coverage of independent reflections	99.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8580 and 0.4870
Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F^2

Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7552 / 0 / 199
Goodness-of-fit on F^2	1.027
Δ/σ_{max}	0.002
Final R indices	5423 data; I>2σ(I) R1 = 0.0380, wR2 = 0.0760
	all data R1 = 0.0677, wR2 = 0.0847
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0316P)^2+0.5508P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.564 and -0.715 eÅ^{-3}
R.M.S. deviation from mean	0.092 eÅ^{-3}

Table 11. Bond lengths (Å) for *trans*-21.

Br1-C11	1.8976(13)	C1-C7	1.5150(18)
C1-C2	1.5282(18)	C2-O1	1.4342(15)
C2-C3	1.5397(17)	C3-C14	1.5142(18)
C3-C4	1.5367(18)	C4-C5	1.5255(19)
C5-C6	1.517(2)	C6-O1	1.4279(16)
C7-O2	1.2215(16)	C7-C8	1.4947(18)
C8-C13	1.3956(18)	C8-C9	1.3984(18)
C9-C10	1.3841(19)	C10-C11	1.3879(19)
C11-C12	1.3837(19)	C12-C13	1.3899(19)
C14-C19	1.3908(18)	C14-C15	1.4000(18)
C15-C16	1.3881(19)	C16-C17	1.396(2)
C17-C18	1.384(2)	C18-C19	1.396(2)

Table 12. Bond angles (°) for *trans*-21.

C7-C1-C2	109.94(10)	O1-C2-C1	105.92(10)
O1-C2-C3	111.25(10)	C1-C2-C3	112.53(10)
C14-C3-C4	111.75(10)	C14-C3-C2	111.72(10)
C4-C3-C2	110.05(10)	C5-C4-C3	111.07(11)
C6-C5-C4	109.06(11)	O1-C6-C5	110.48(11)
O2-C7-C8	120.02(12)	O2-C7-C1	119.62(12)
C8-C7-C1	120.33(11)	C13-C8-C9	119.23(12)
C13-C8-C7	122.17(11)	C9-C8-C7	118.49(11)
C10-C9-C8	120.86(12)	C9-C10-C11	118.51(12)
C12-C11-C10	122.09(12)	C12-C11-Br1	118.63(10)
C10-C11-Br1	119.26(10)	C11-C12-C13	118.76(12)
C12-C13-C8	120.50(12)	C19-C14-C15	118.28(12)
C19-C14-C3	121.24(11)	C15-C14-C3	120.48(11)
C16-C15-C14	121.05(13)	C15-C16-C17	120.13(13)
C18-C17-C16	119.21(13)	C17-C18-C19	120.56(13)
C14-C19-C18	120.77(13)	C6-O1-C2	111.86(10)