Synthesis, Structures and Properties of Self-Assembling Quaternary Ammonium Dansyl Fluorescent Tags for Porous and Non-Porous Surfaces

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Electronic Supplementary Material (ESI)

A) Includes NMR Spectra (^{1}H, ^{13}C, ^{31}P, ^{29}Si) of all precursor and final compounds
B) Includes MS Spectra of selected precursor and final compounds
C) pH dependent UV-vis and Fluorescence Spectra for Compound **2**
D) Includes X-ray Structure data for Compounds **1** and **7**

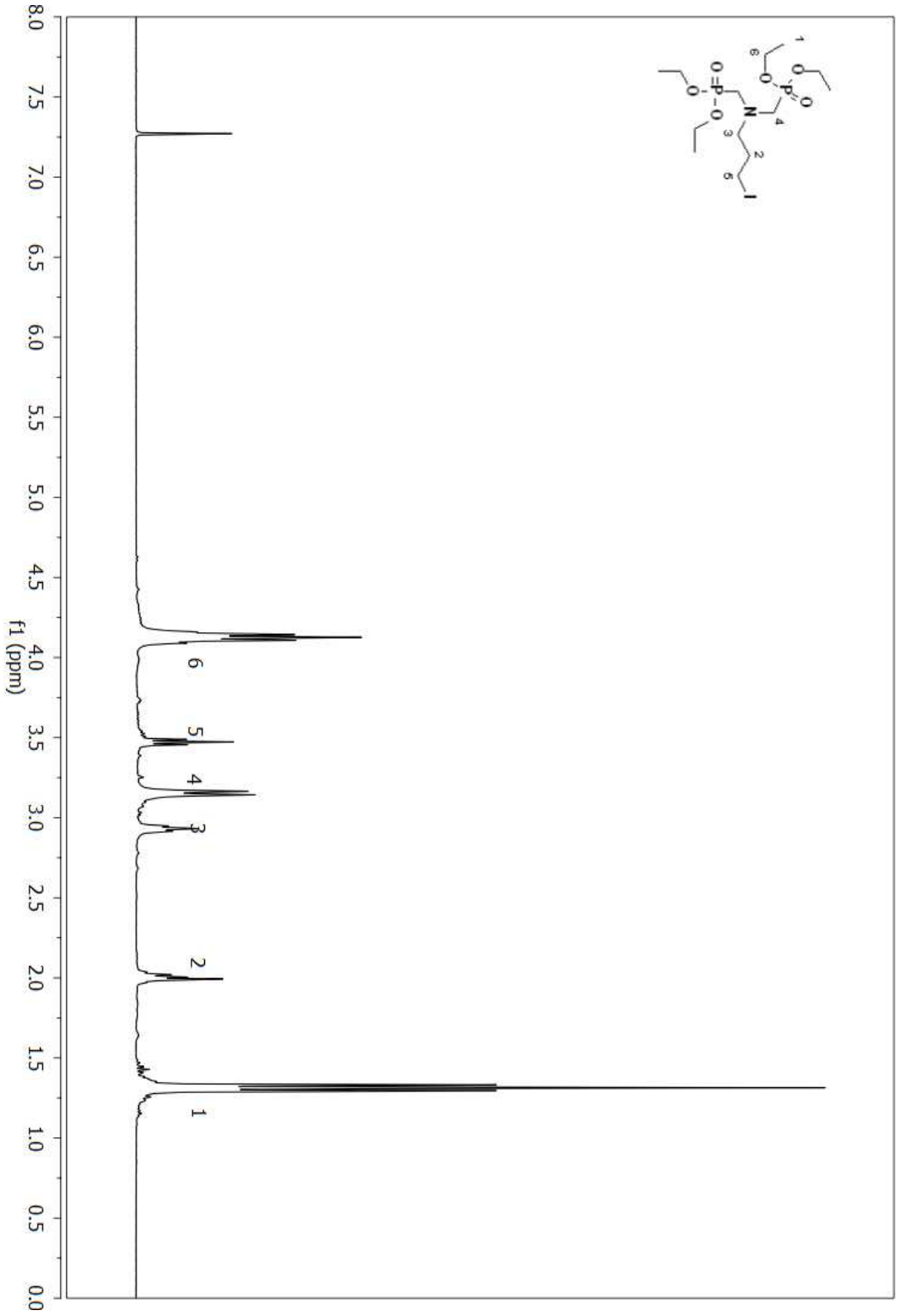

Figure S1. ^{1}H NMR spectrum of **tetraethyl (((3-iodopropyl)azanediyl)bis(methylene)) bis(phosphonate)** in $CDCl_3$.

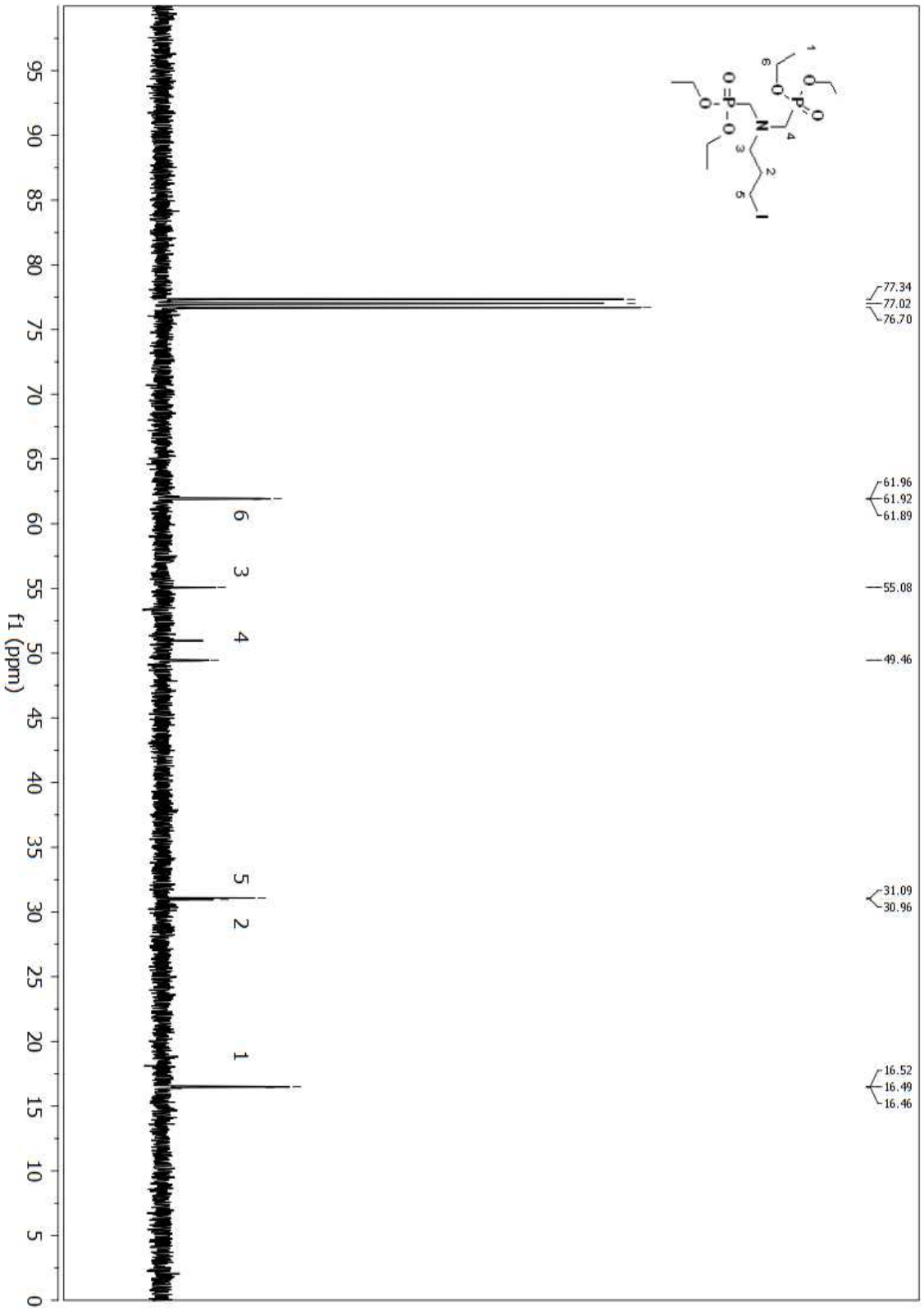

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of compound **tetraethyl (((3-iodopropyl)azanediyl) bis(methylene)) bis(phosphonate)** in $CDCl_3$.

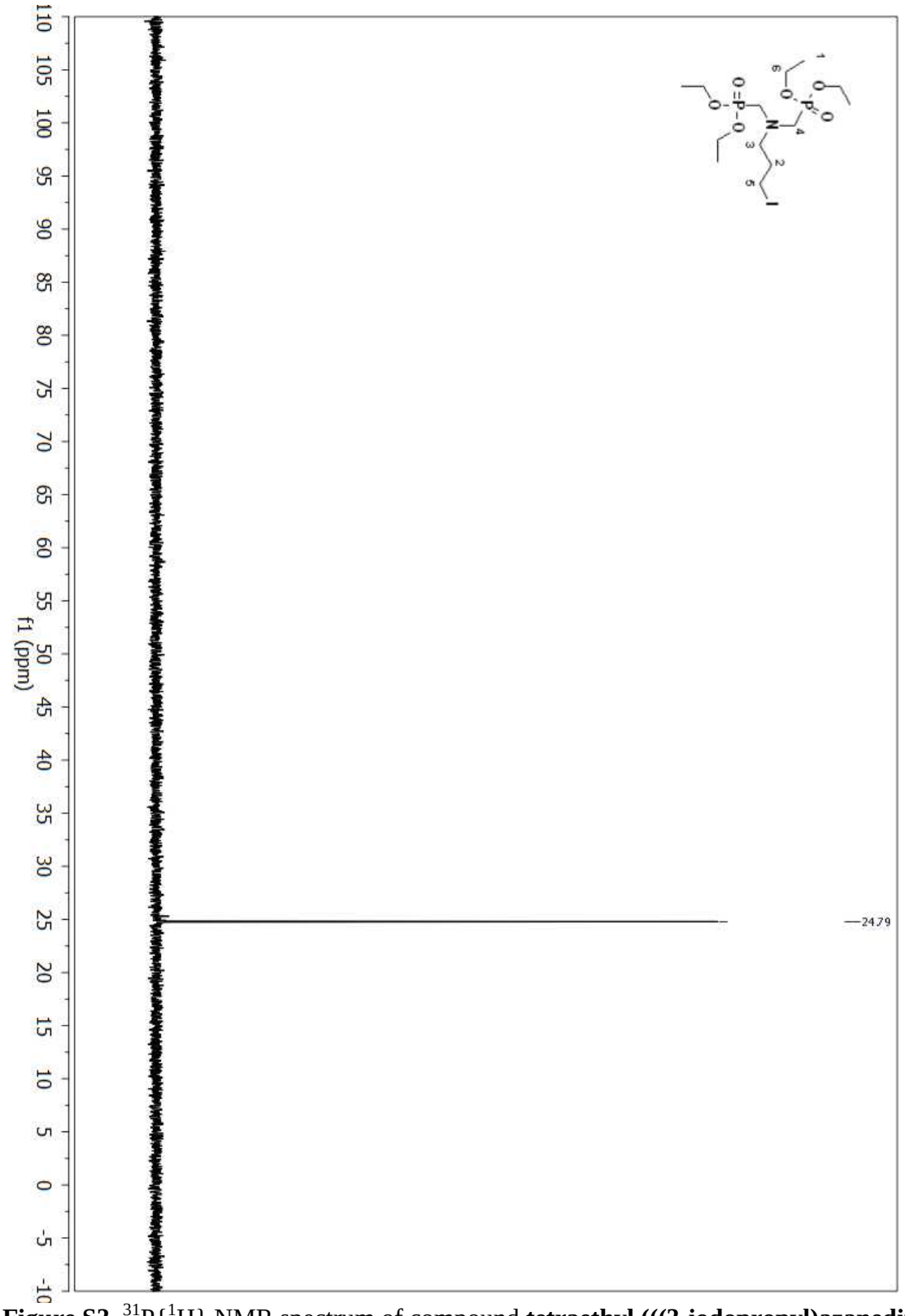

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of compound **tetraethyl (((3-iodopropyl)azanediyl) bis(methylene)) bis(phosphonate)** in $CDCl_3$.

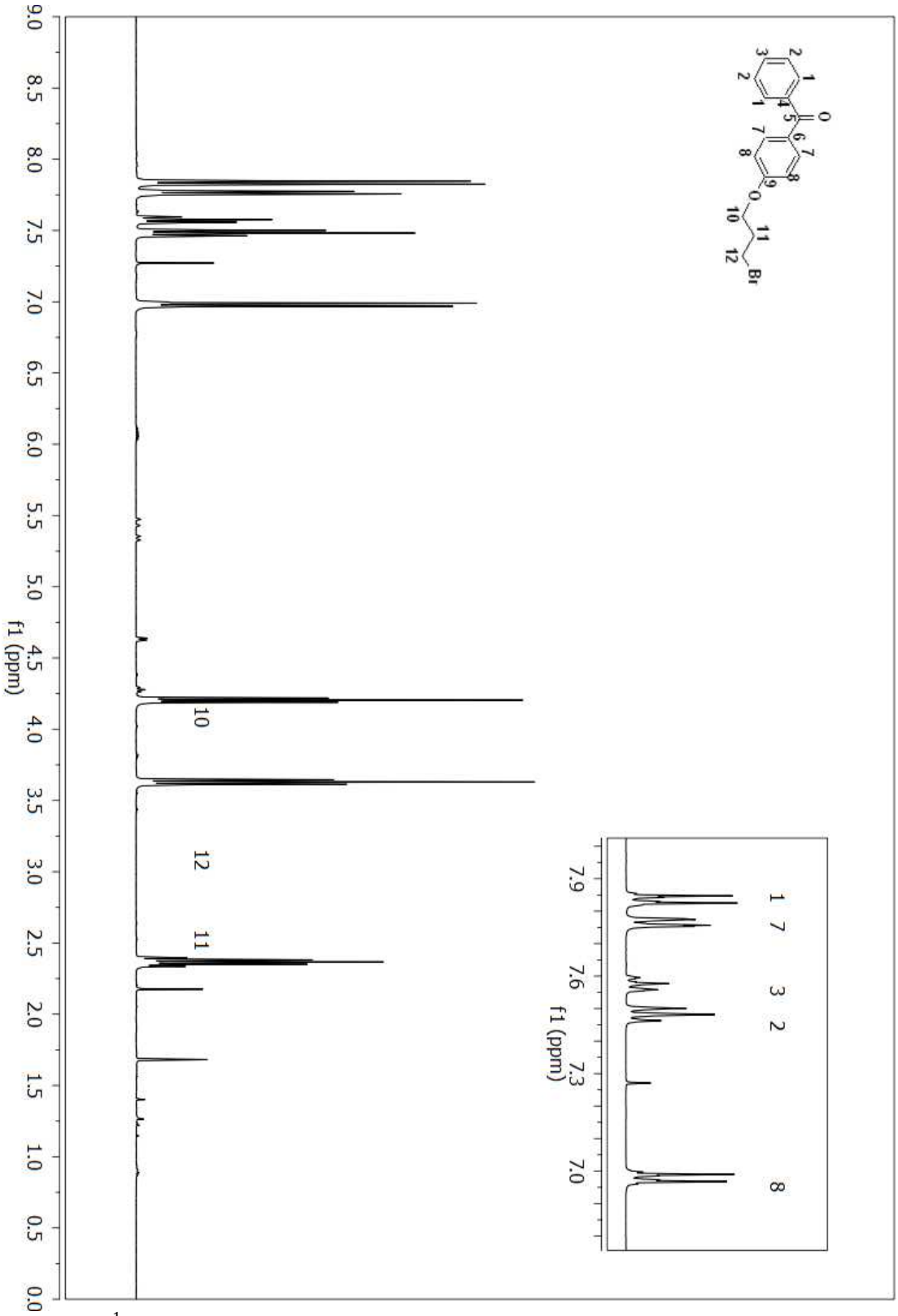

Figure S4. ^{1}H NMR spectrum of **4-(3-bromopropoxy)benzophenone** in $CDCl_3$.

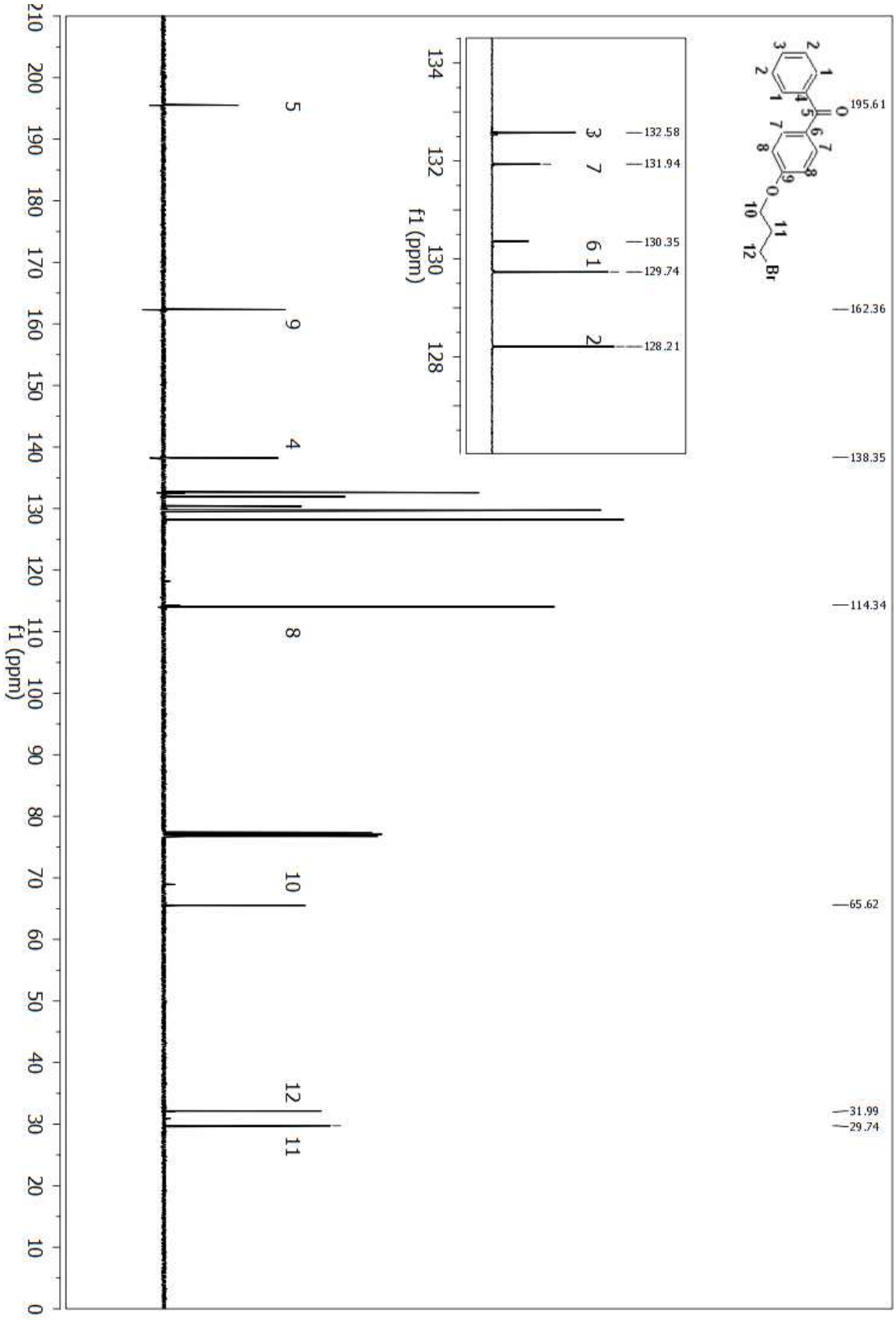

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **4-(3-bromopropoxy)benzophenone** in $CDCl_3$.

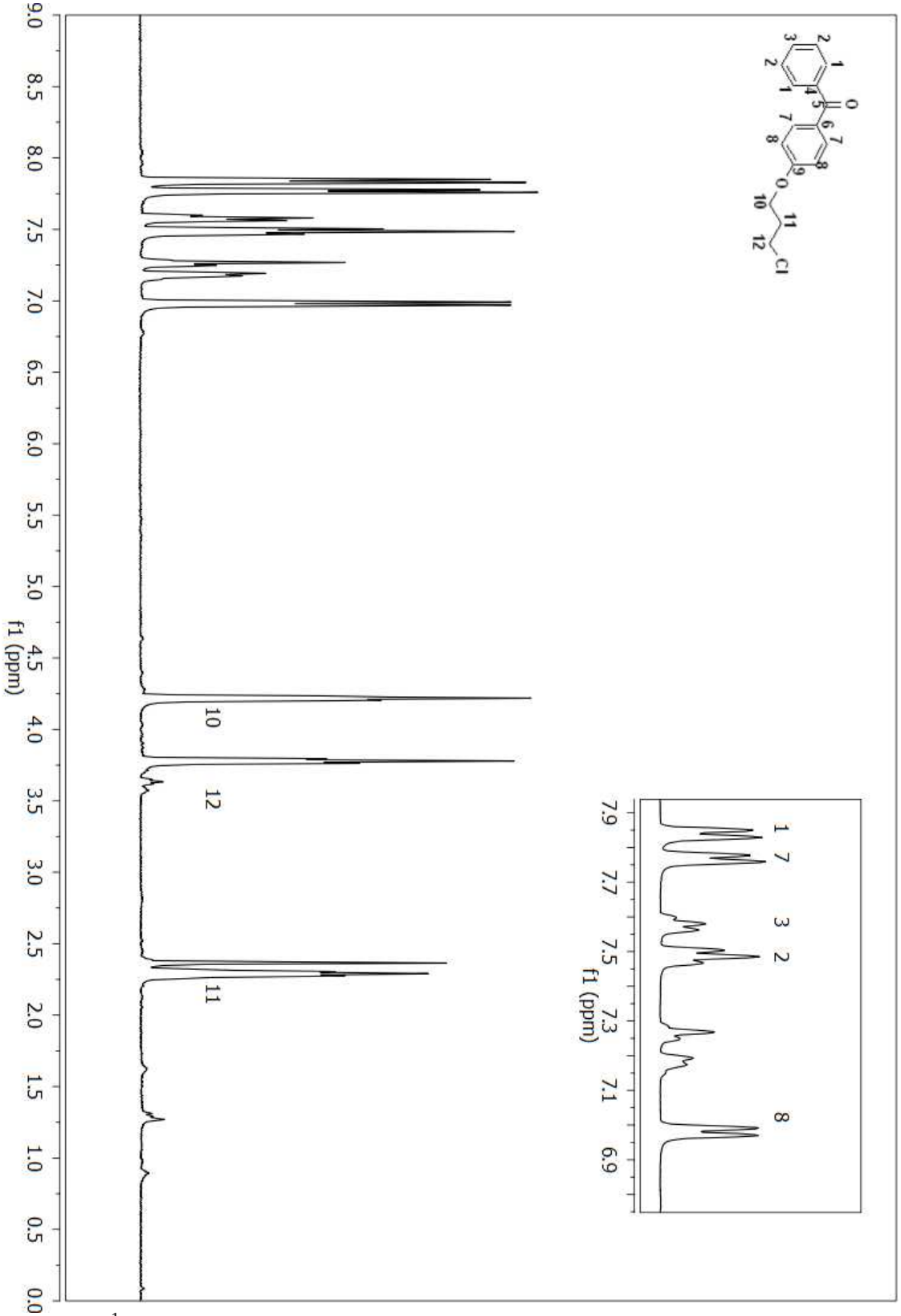

Figure S6. ^{1}H NMR spectrum of **4-(3-chloropropoxy)benzophenone** in $CDCl_3$.

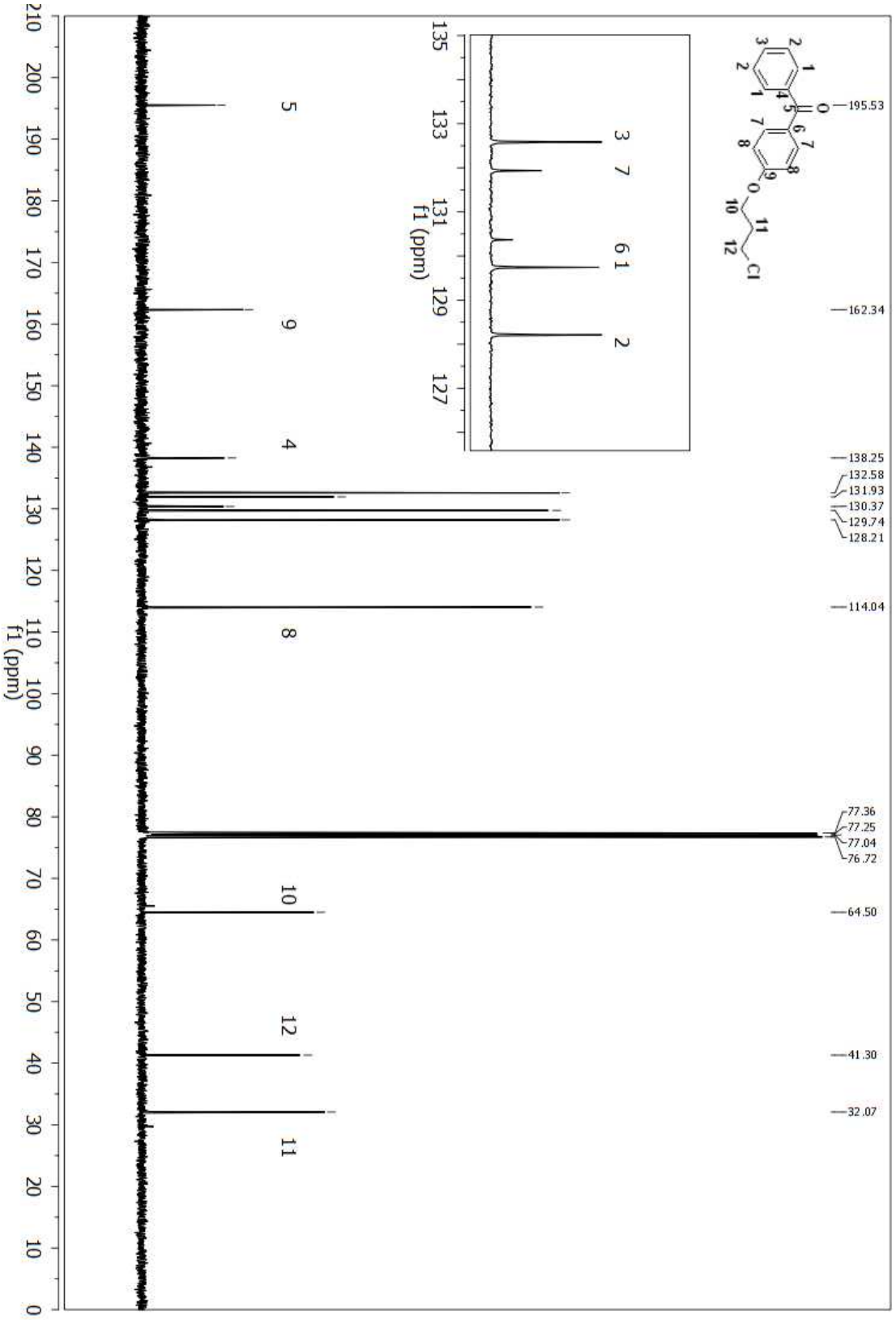

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **4-(3-chloropropoxy)benzophenone** in $CDCl_3$.

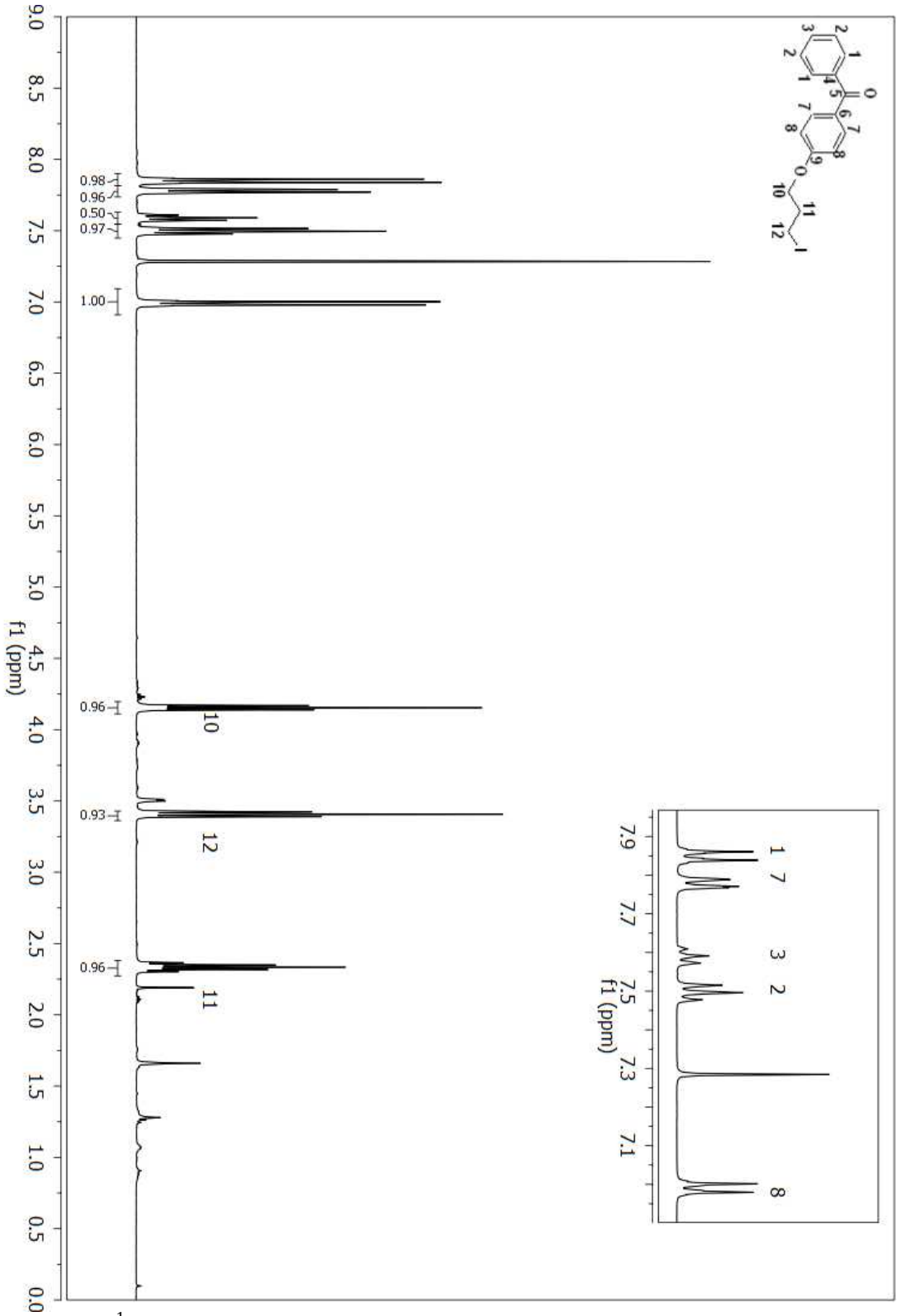

Figure S8. ^{1}H NMR spectrum of **4-(3-iodopropoxy)benzophenone** in $CDCl_3$.

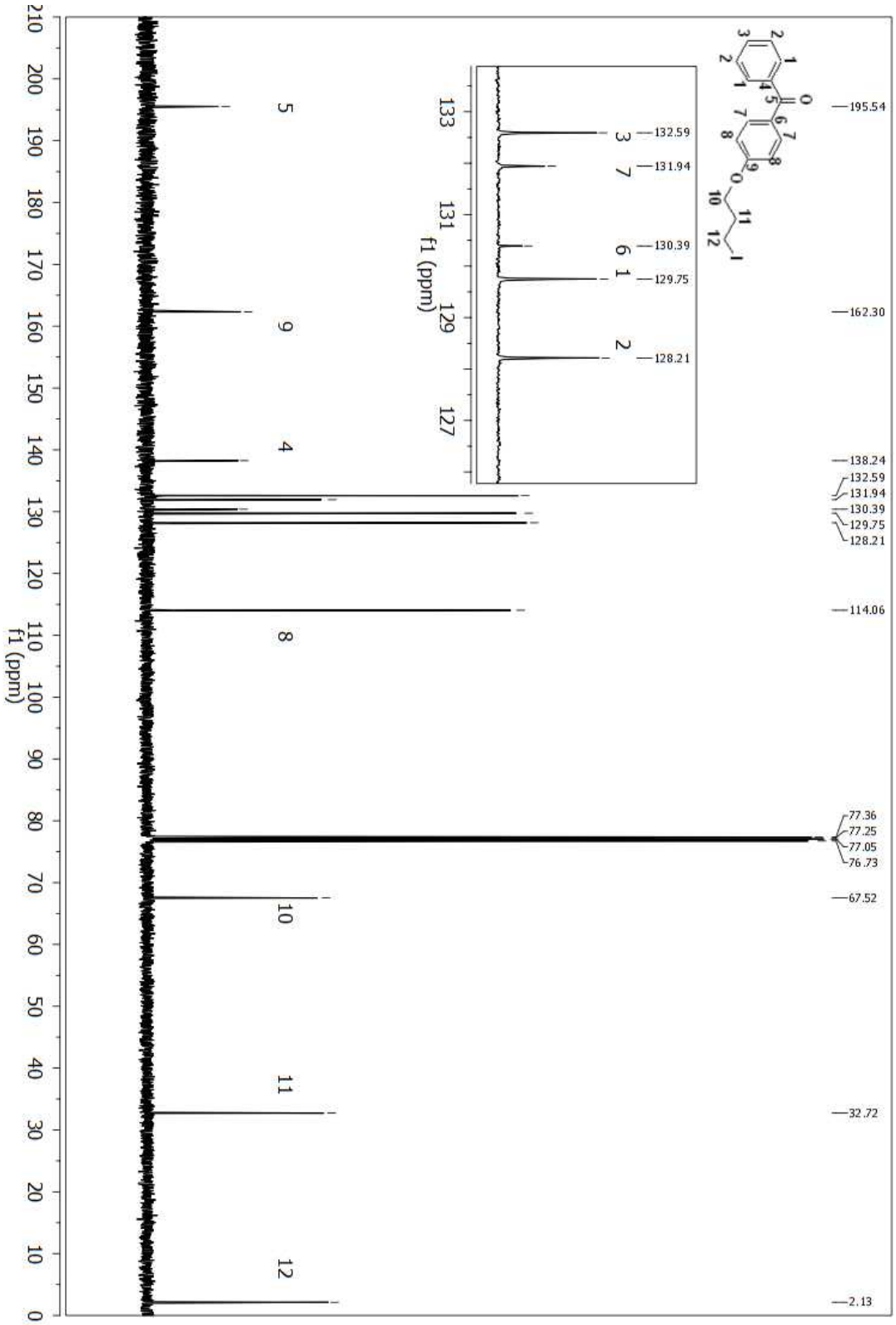

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **4-(3-iodopropoxy)benzophenone** in $CDCl_3$.

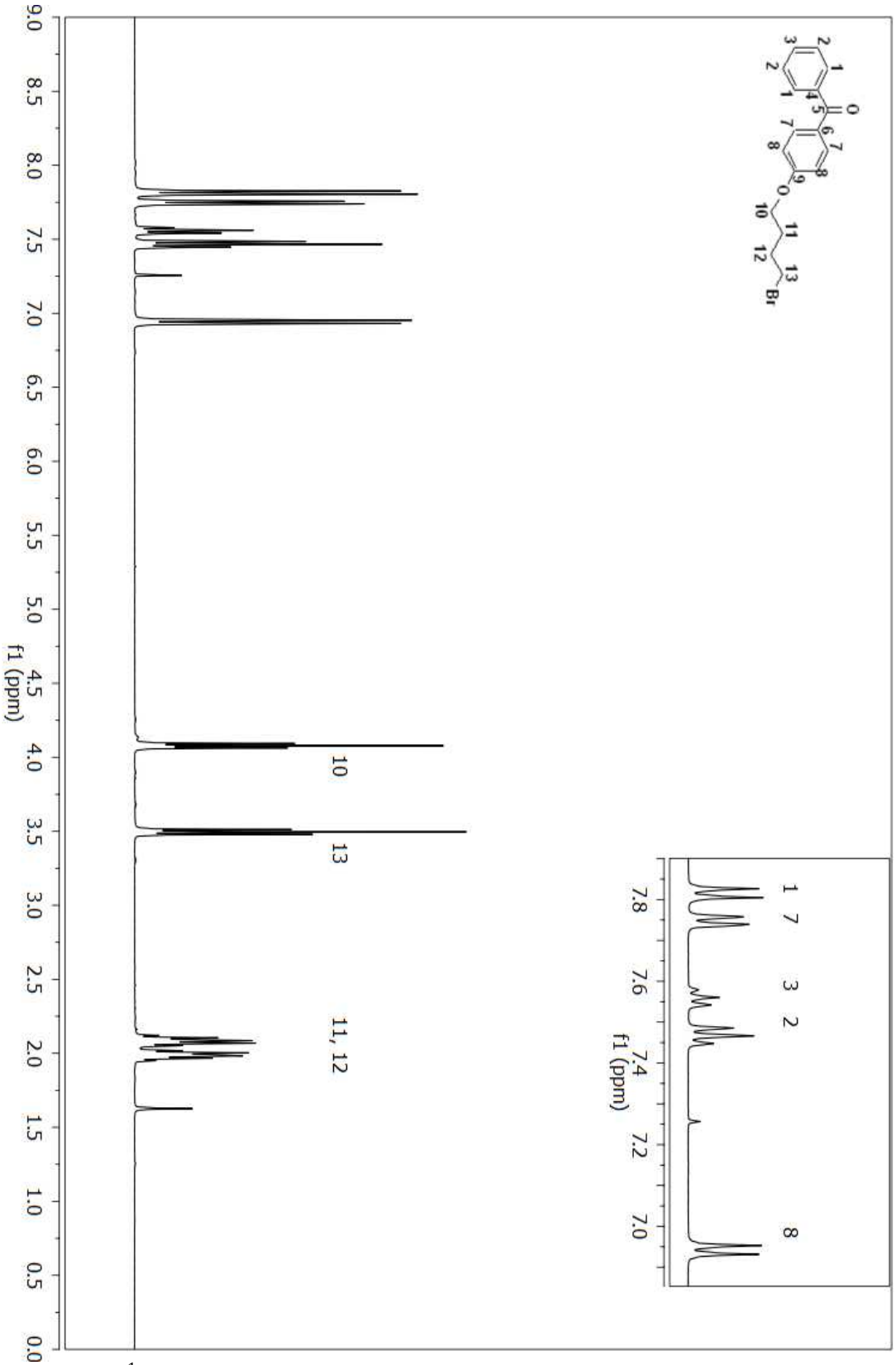

Figure S10. ^{1}H NMR spectrum of **4- (4-bromobutoxy)benzophenone** in $CDCl_3$.

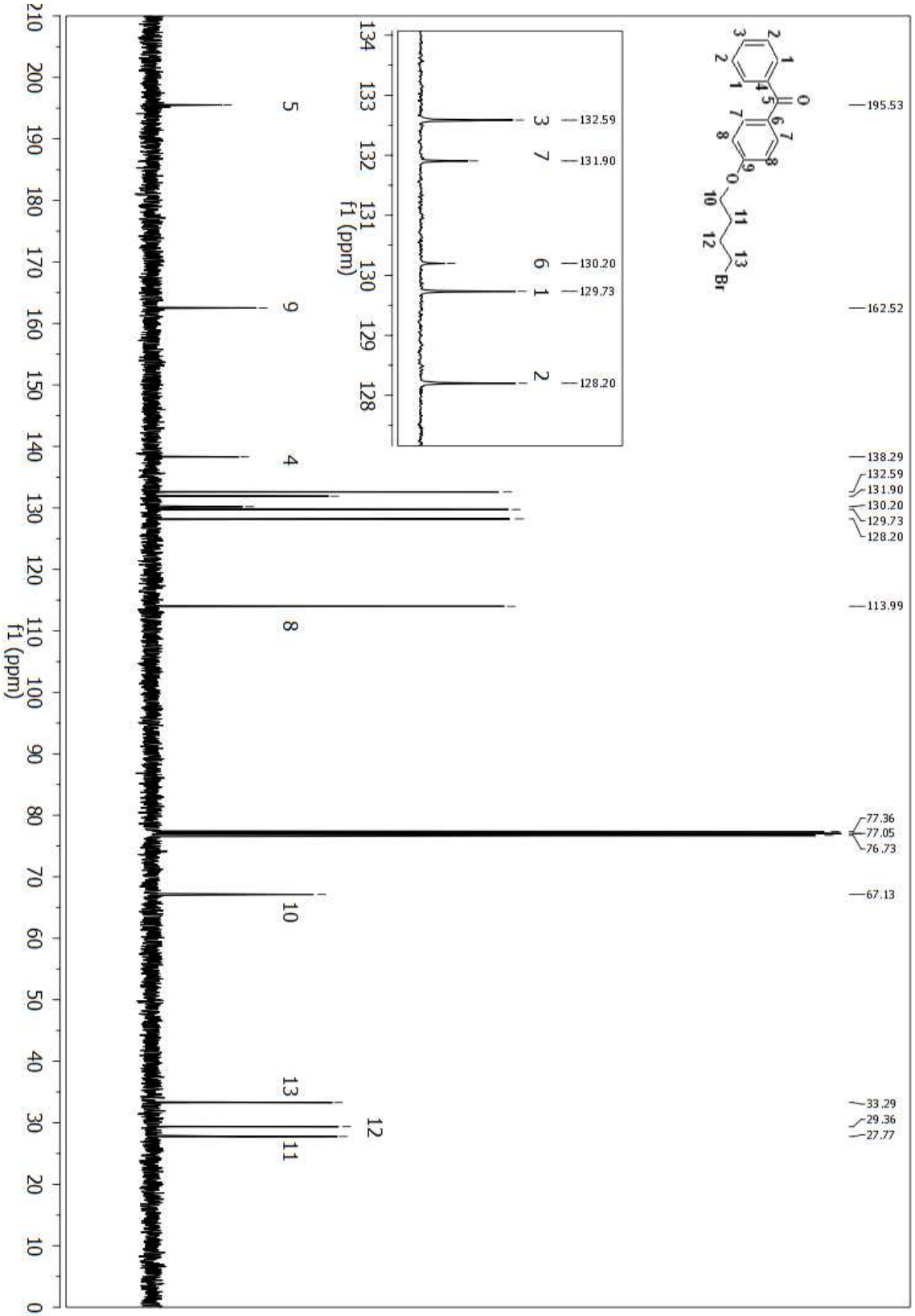

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **4- (4-bromobutoxy)benzophenone** in $CDCl_3$.

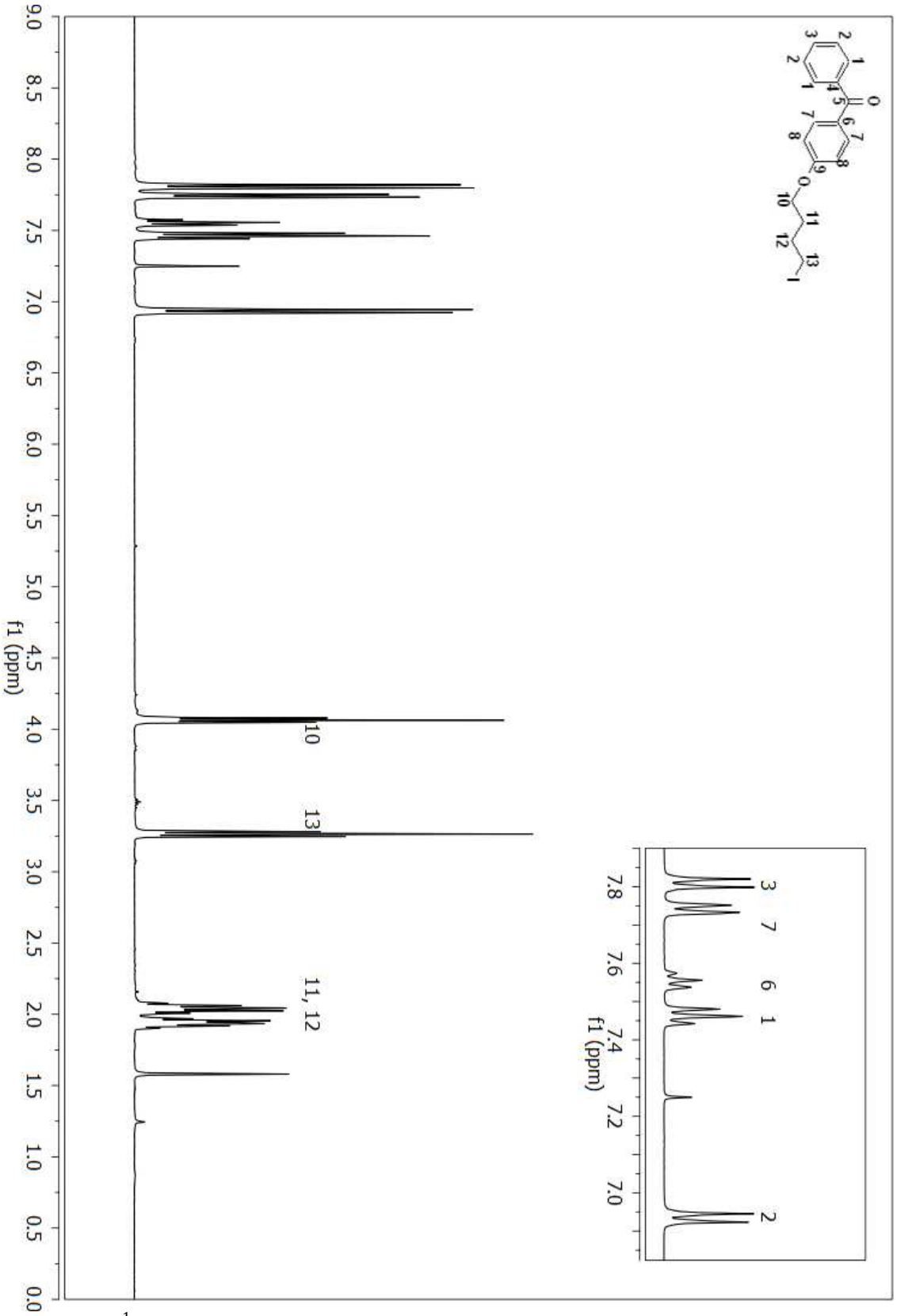

Figure S12. ^{1}H NMR spectrum of **4- (4-iodobutoxy)benzophenone** in $CDCl_3$.

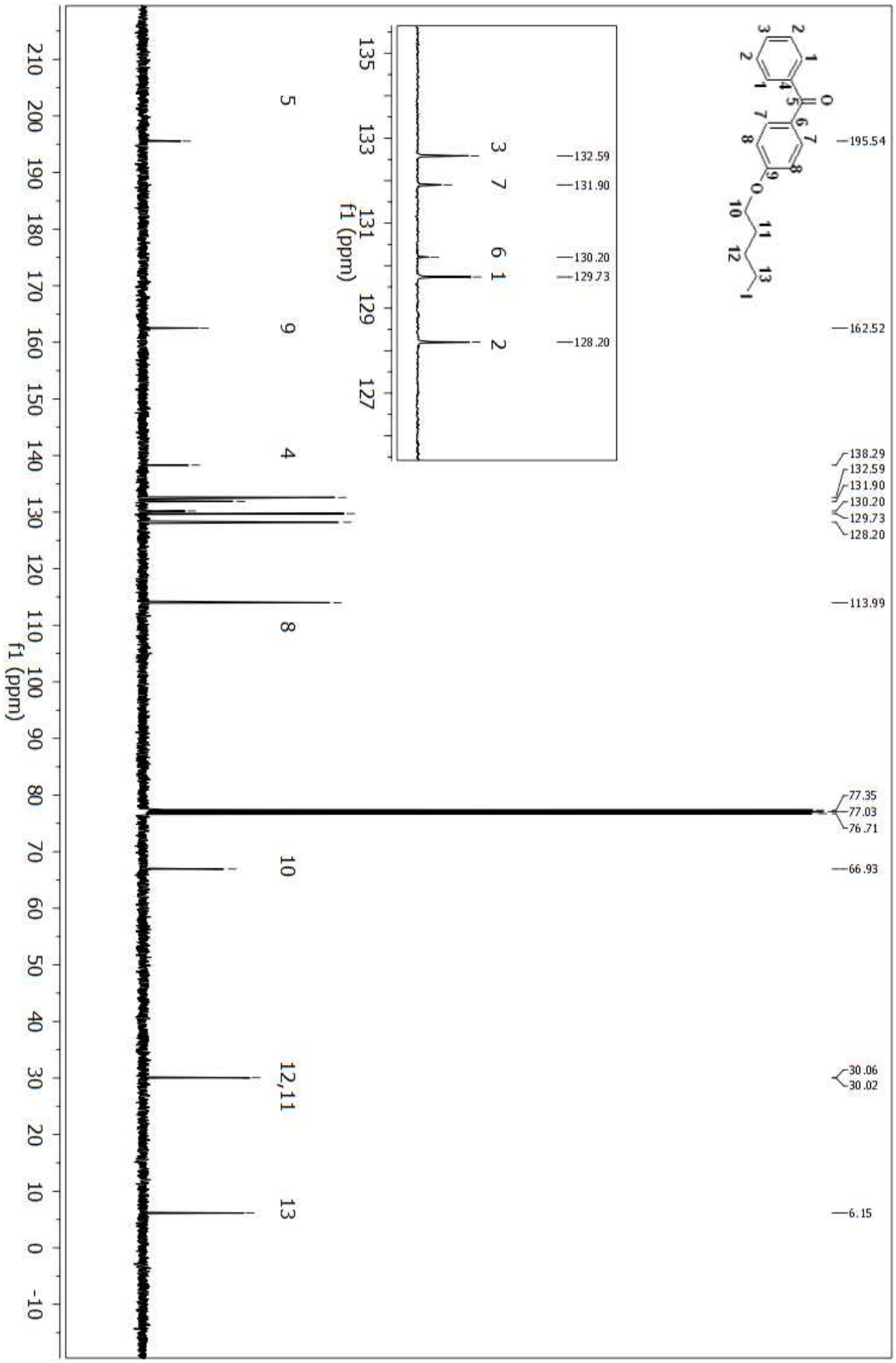

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **4- (4-iodobutoxy)benzophenone** in $CDCl_3$.

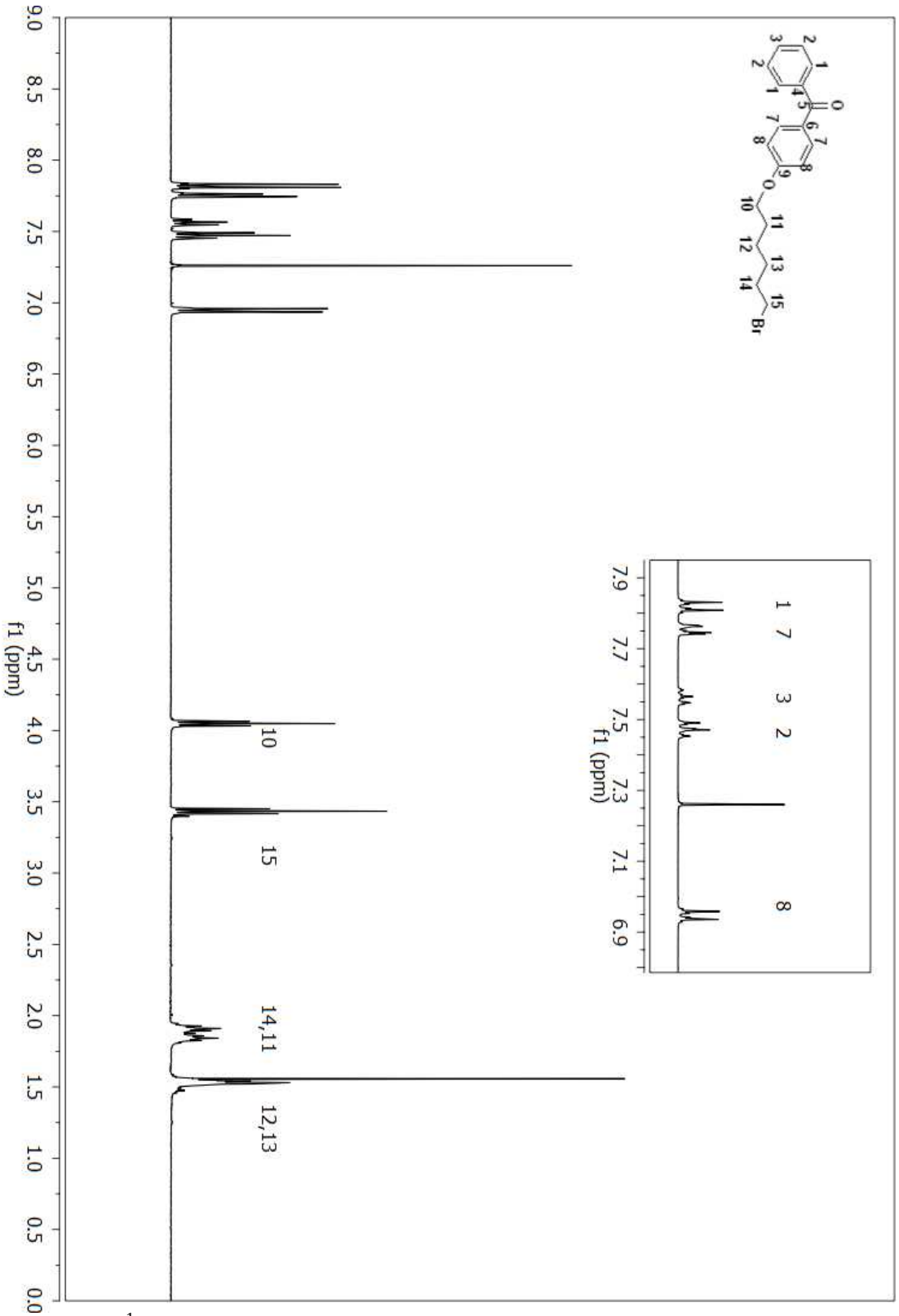

Figure S14. ^{1}H NMR spectrum of **4-(6-bromohexyoxy)benzophenone** in $CDCl_3$.

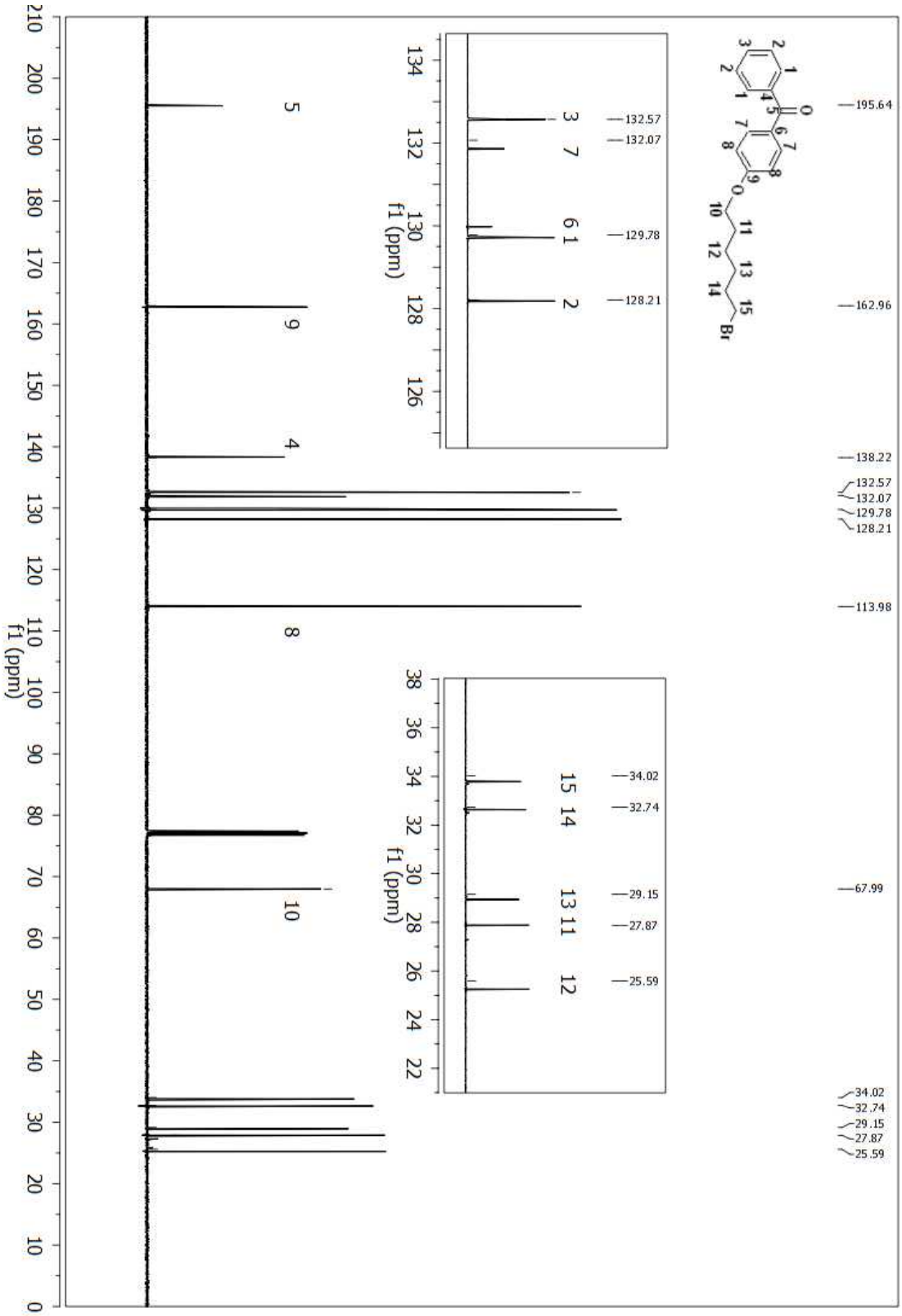

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **4-(6-bromohexyoxy)benzophenone** in $CDCl_3$.

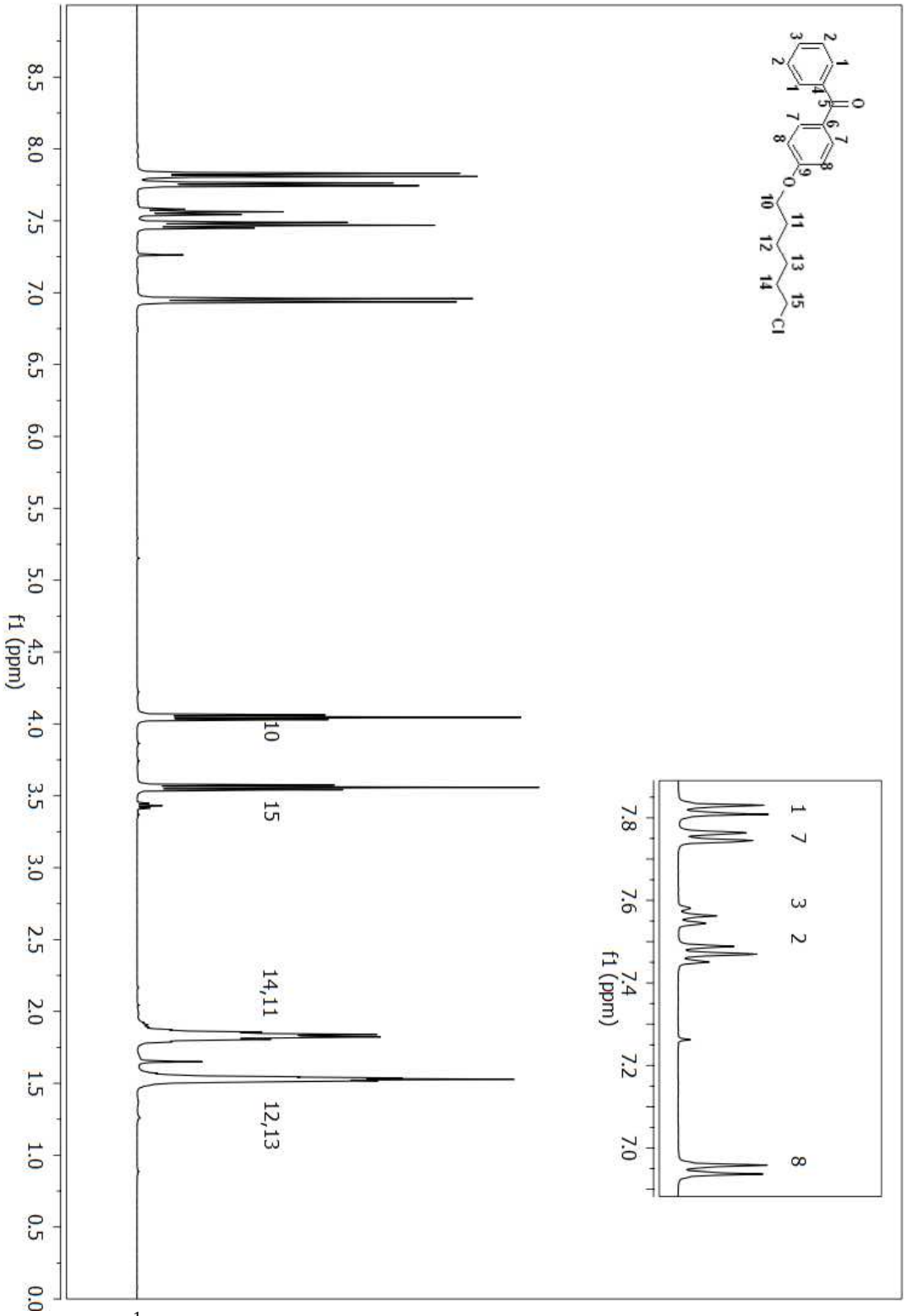

Figure S16. ^{1}H NMR spectrum of **4-(6-chlorohexoxy)benzophenone** in $CDCl_3$.

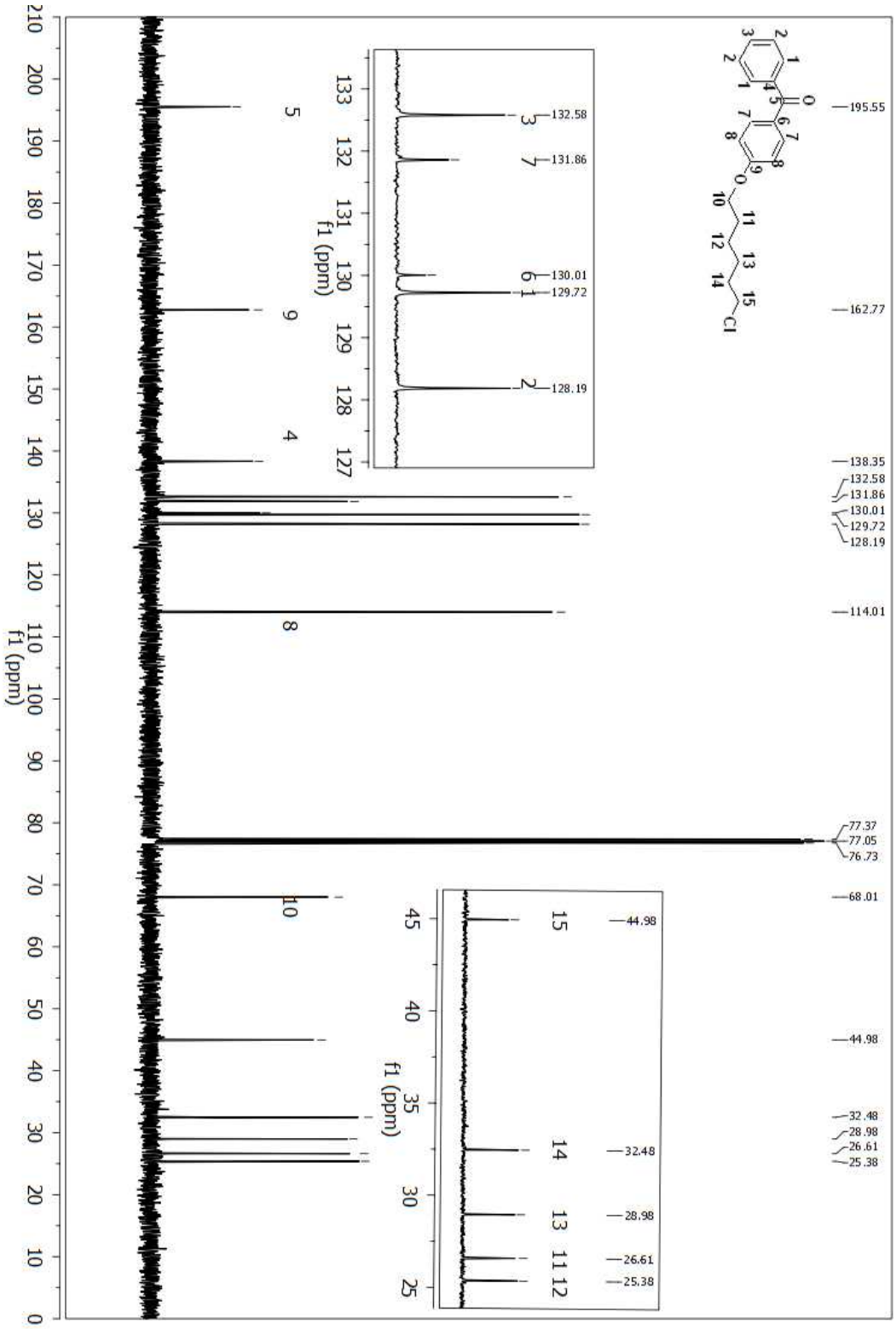

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **4- (6-chlorohexoxy)benzophenone** in $CDCl_3$.

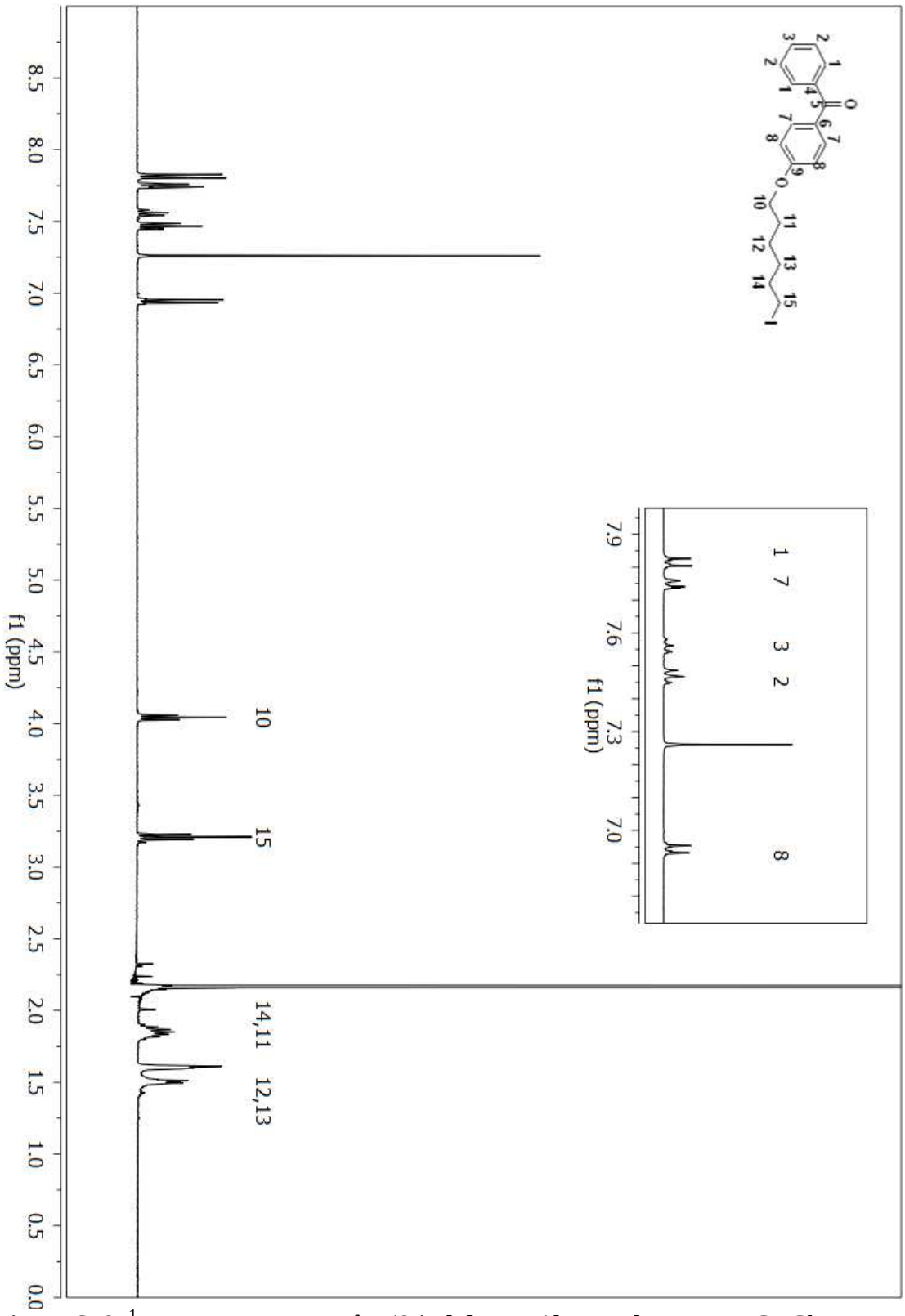

Figure S18. ^{1}H NMR spectrum of **4-(6-iodohexoxy)benzophenone** in $CDCl_3$.

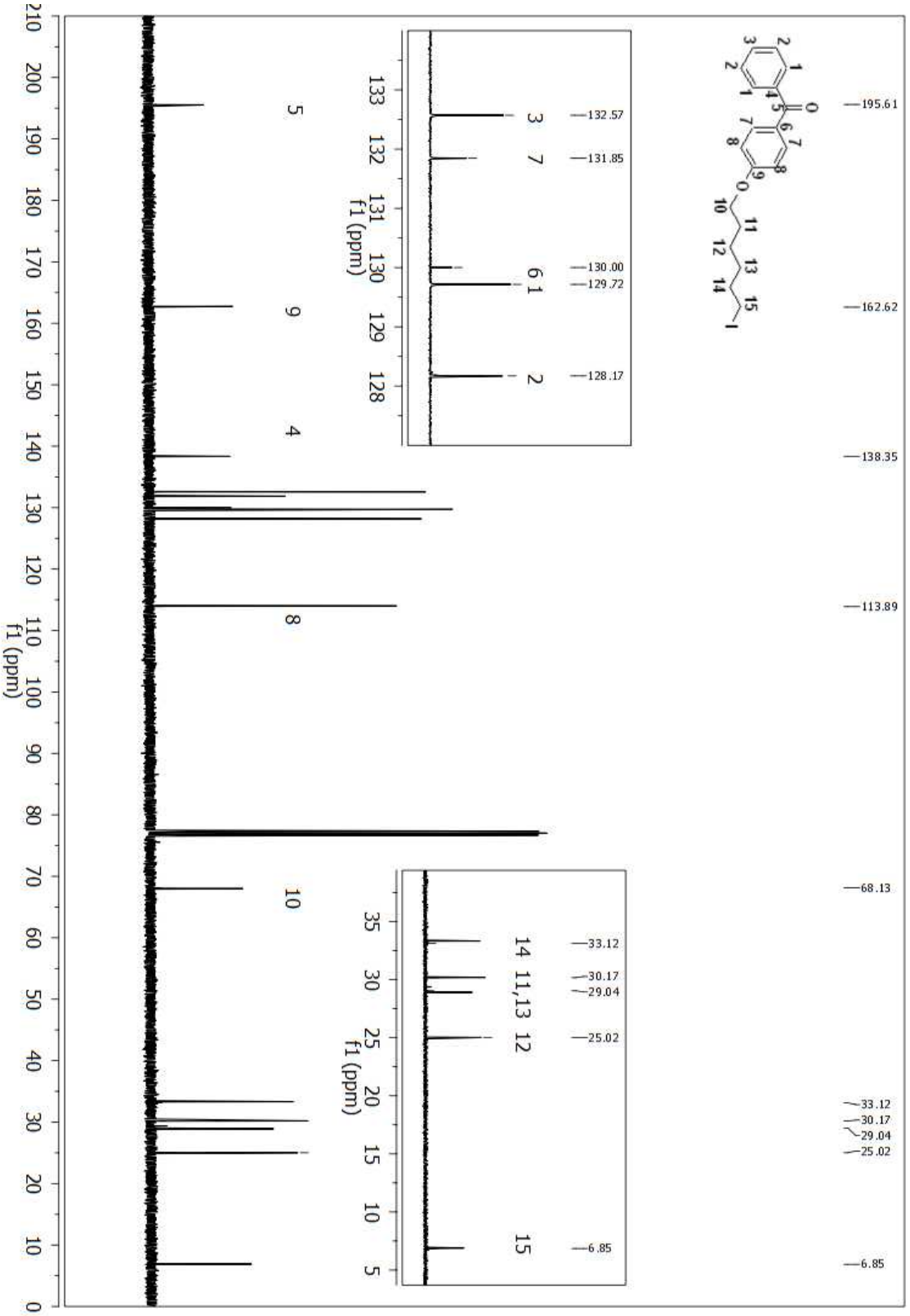

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **4-(6-iodohexyoxy)benzophenone** in $CDCl_3$.

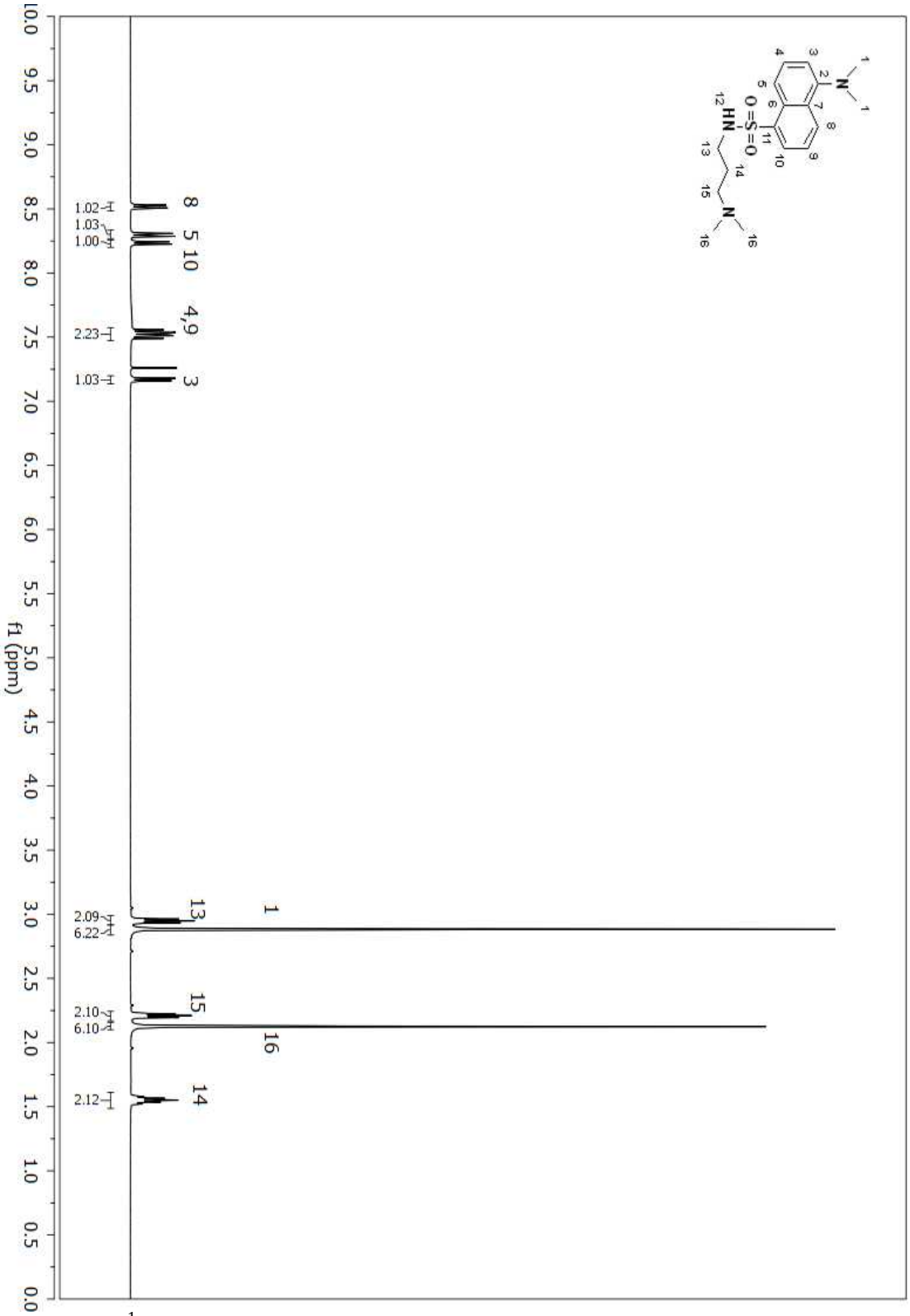

Figure S20. ^{1}H NMR spectrum of precursor dansyl compound **1** in $CDCl_3$.

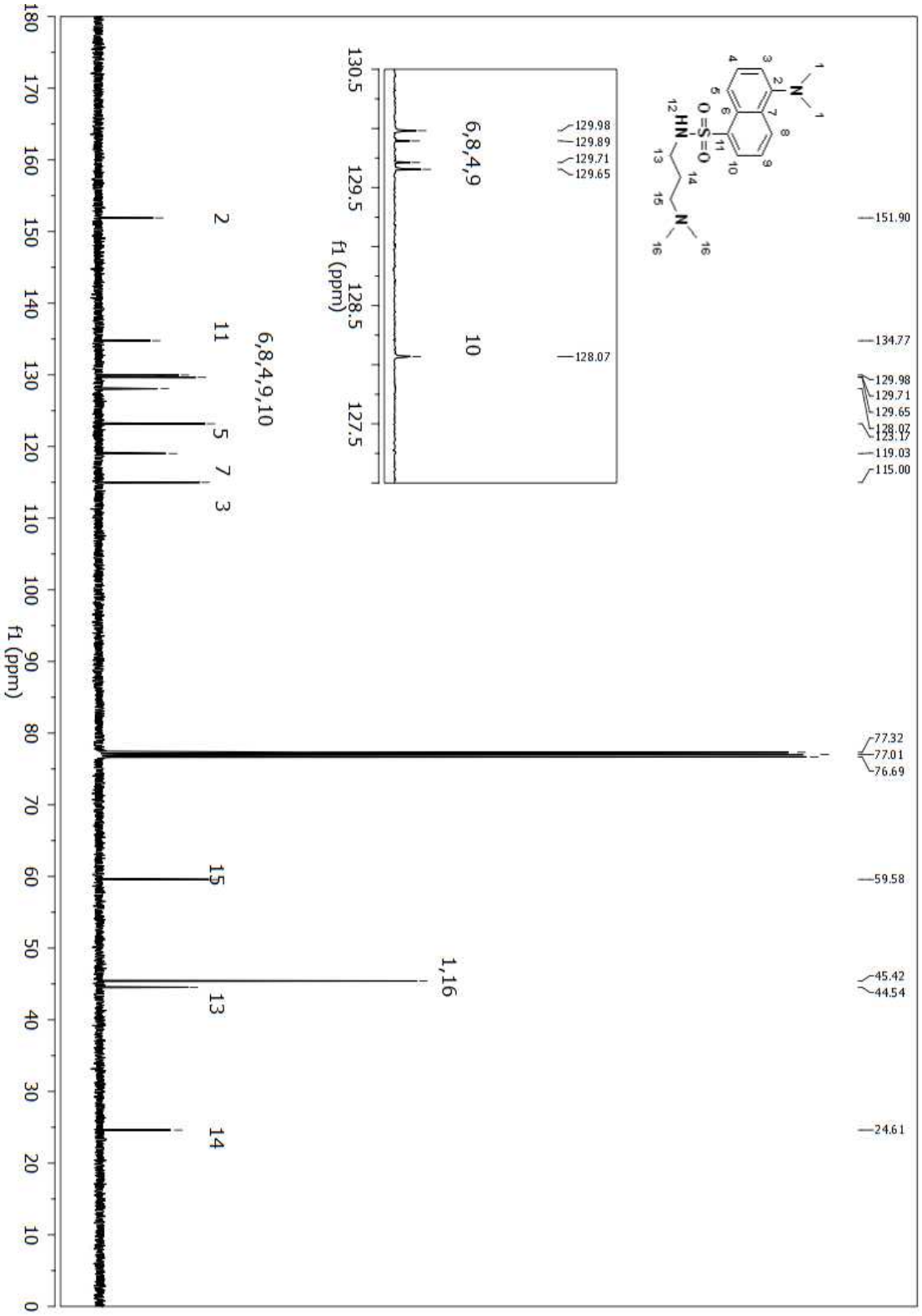

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** in $CDCl_3$.

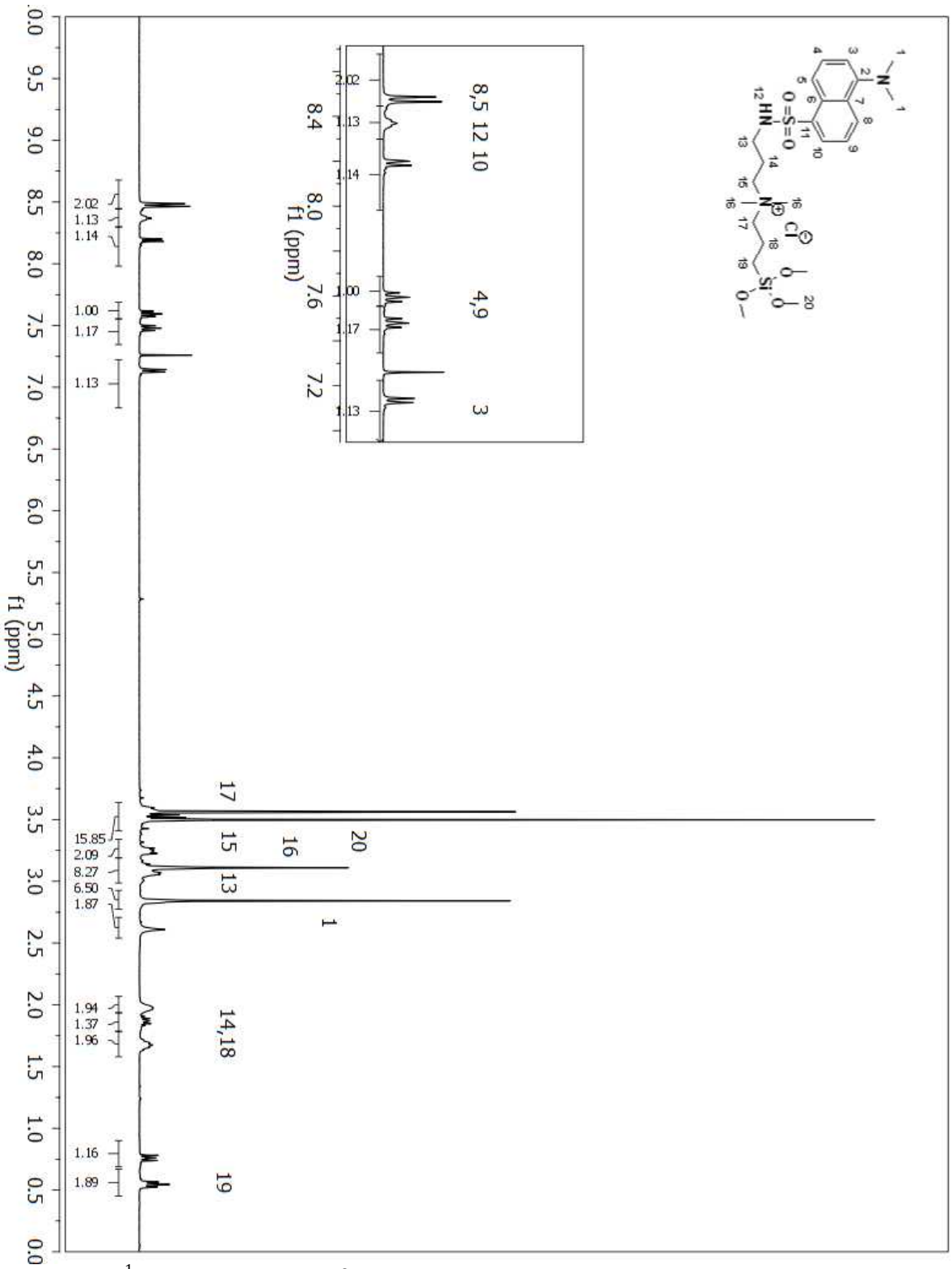

Figure S22. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

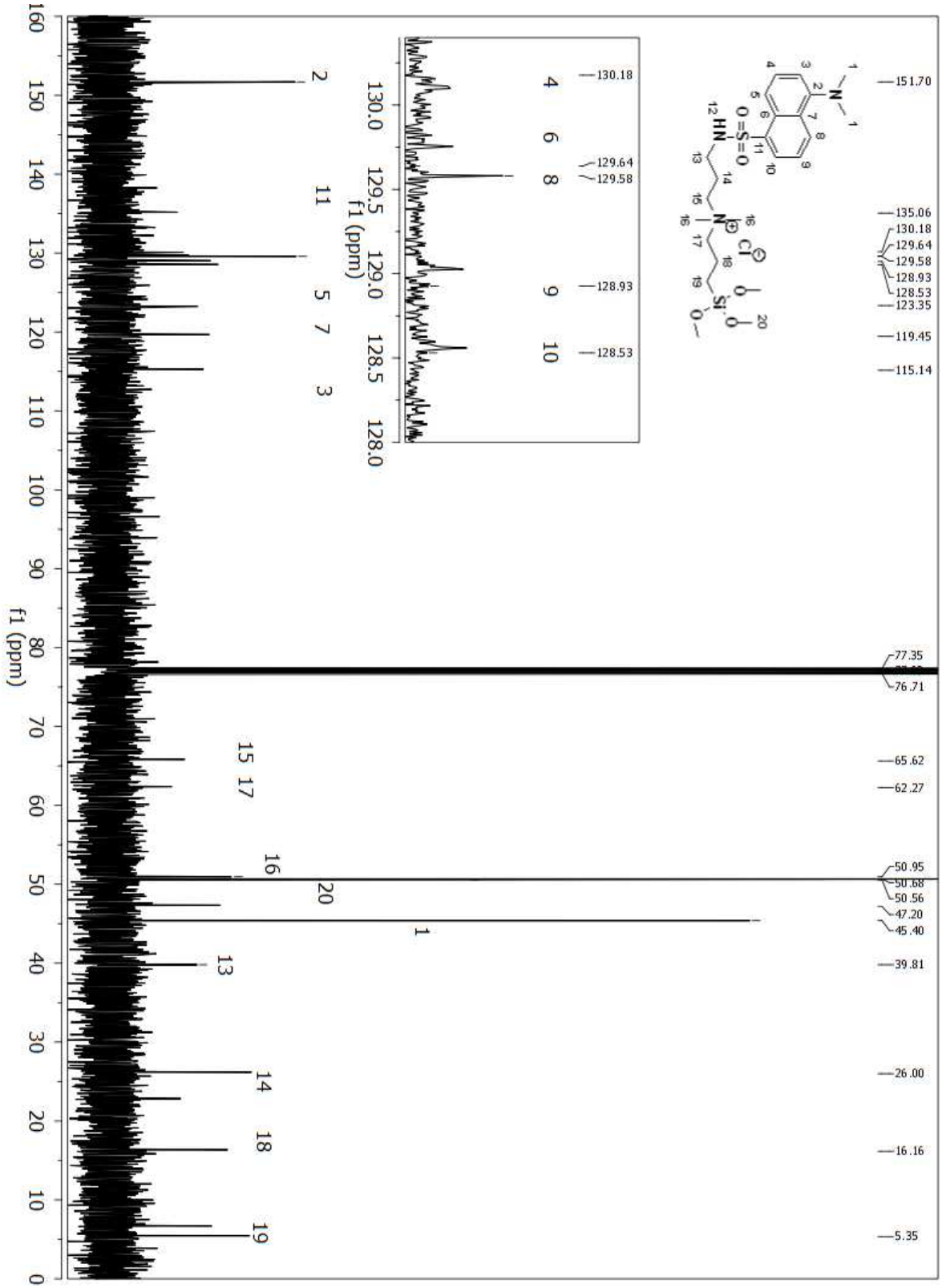

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of precursor dansyl compound **2** in $CDCl_3$.

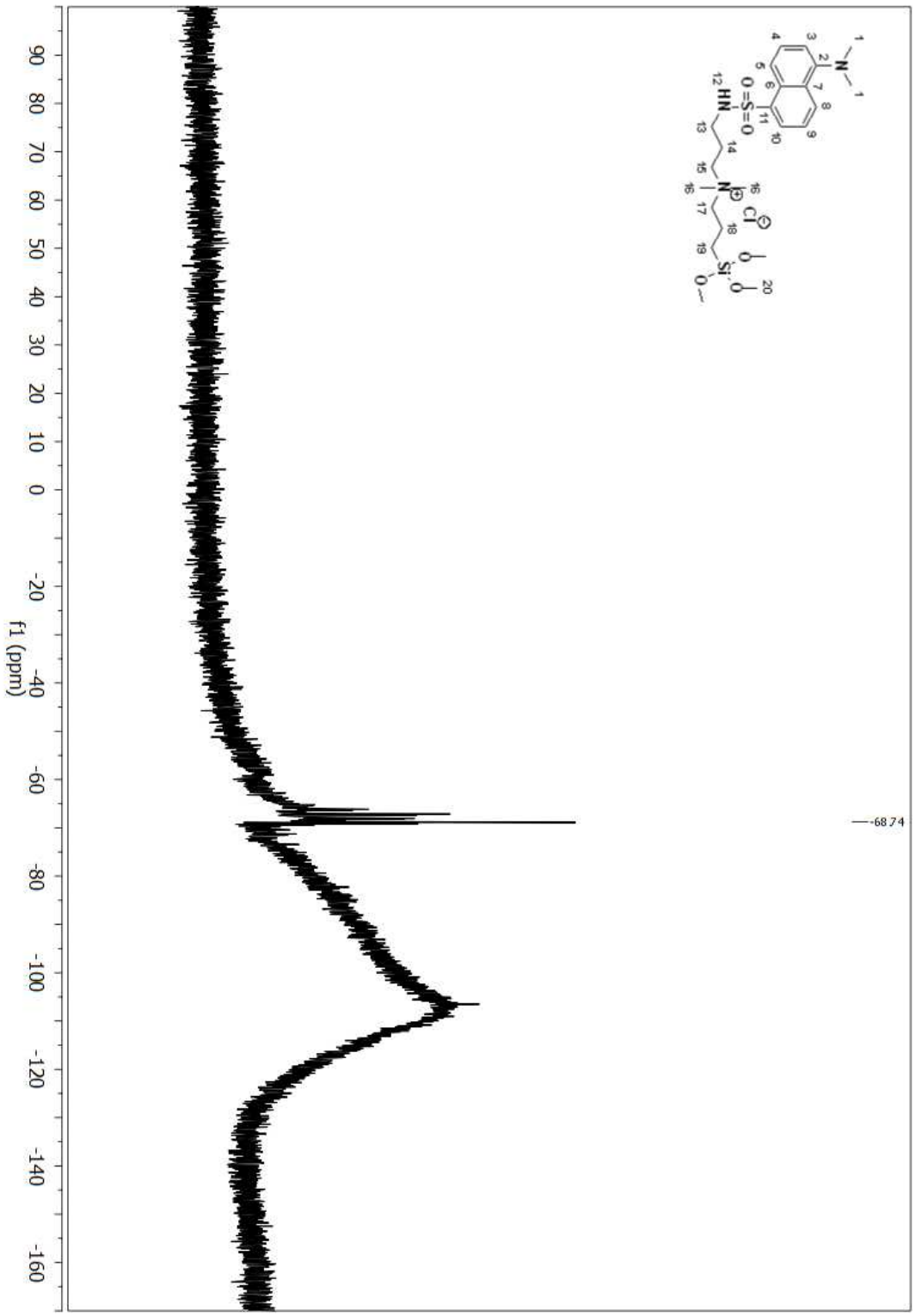

Figure S24. $^{29}Si\{^{1}H\}$ spectrum of precursor dansyl compound **2** in $CDCl_3$.

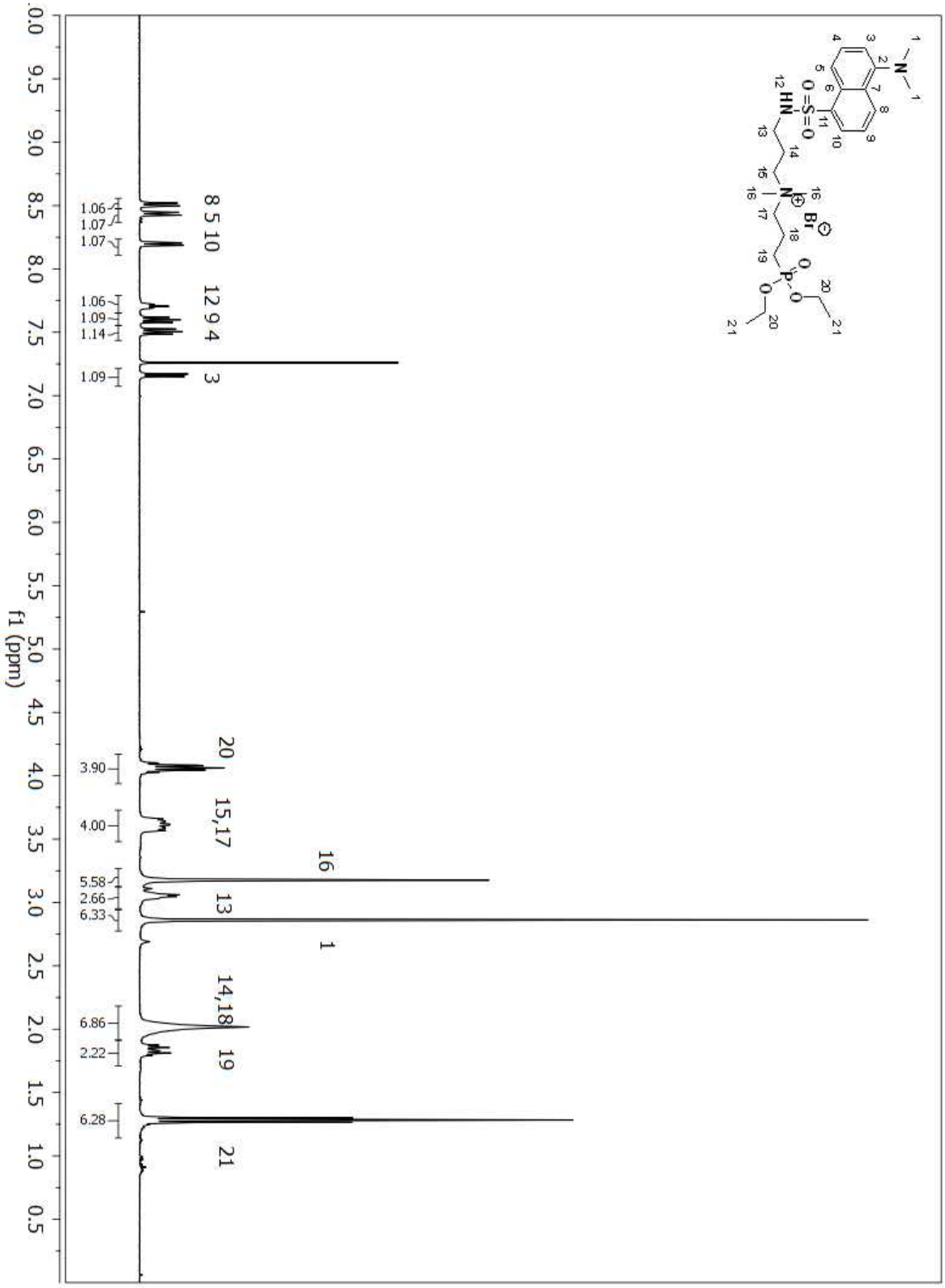

Figure S25. ^{1}H NMR spectrum of precursor dansyl compound **3a** in $CDCl_3$.

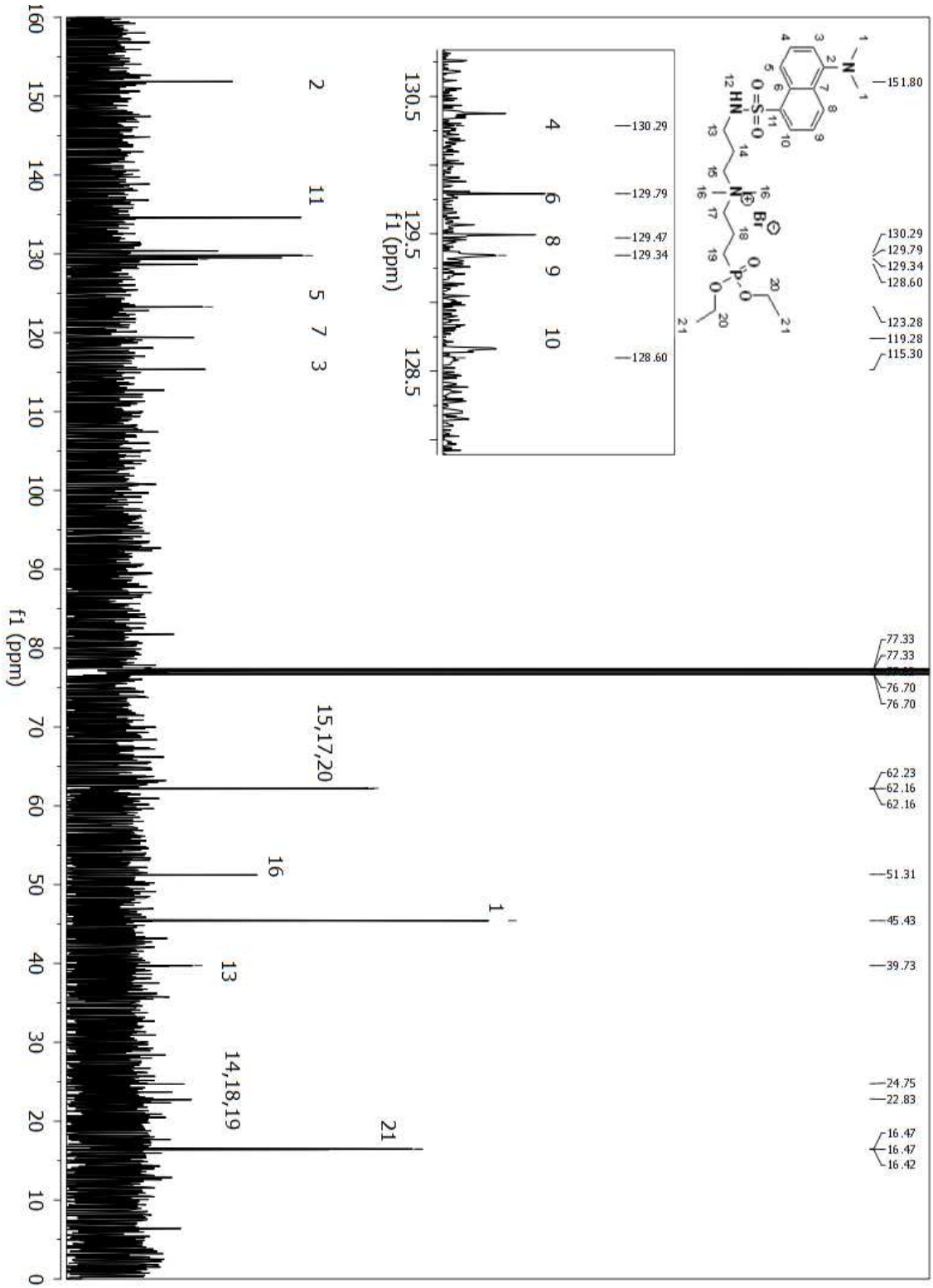

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3a** in $CDCl_3$.

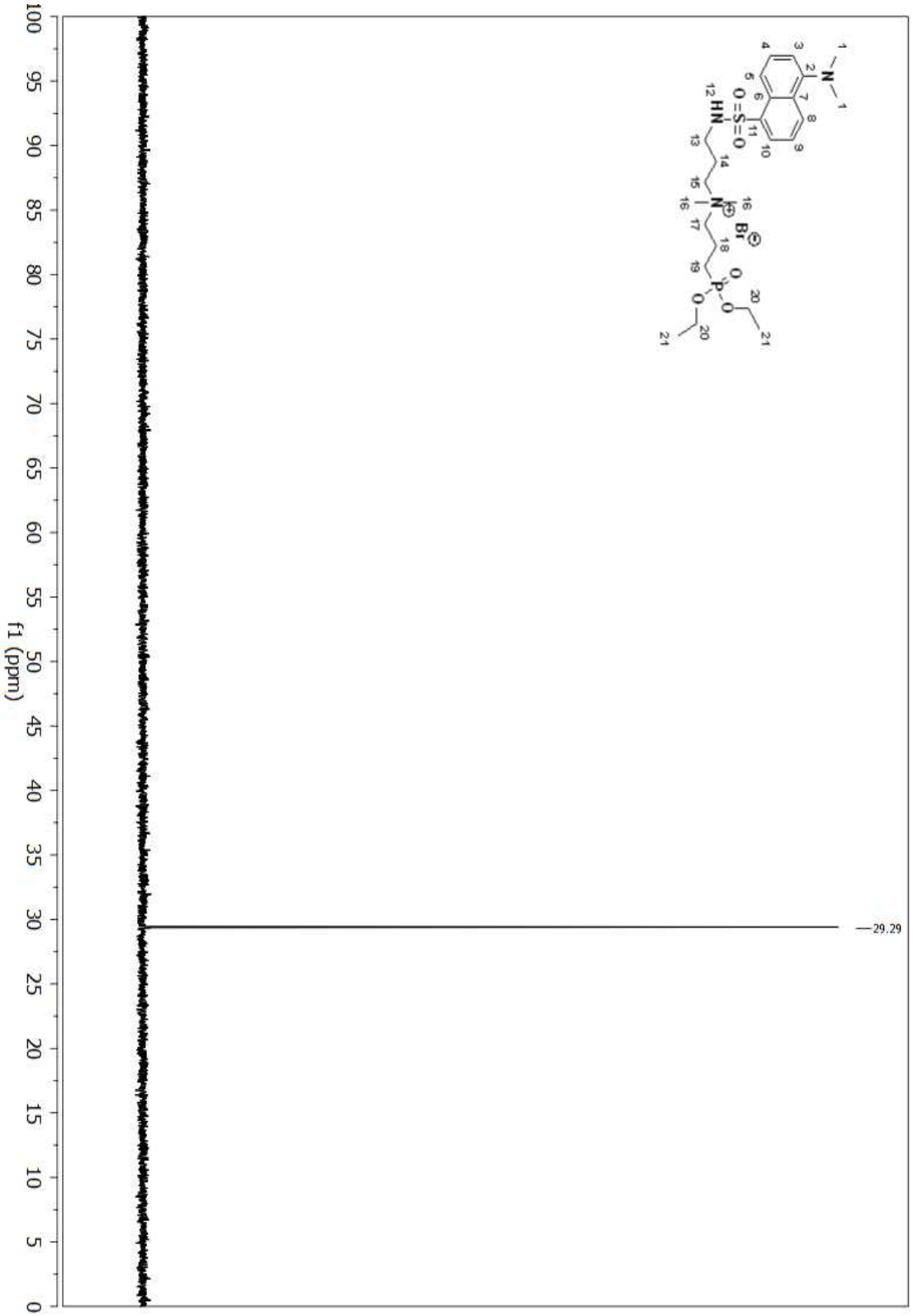

Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum of precursor dansyl compound **3a** in $CDCl_3$.

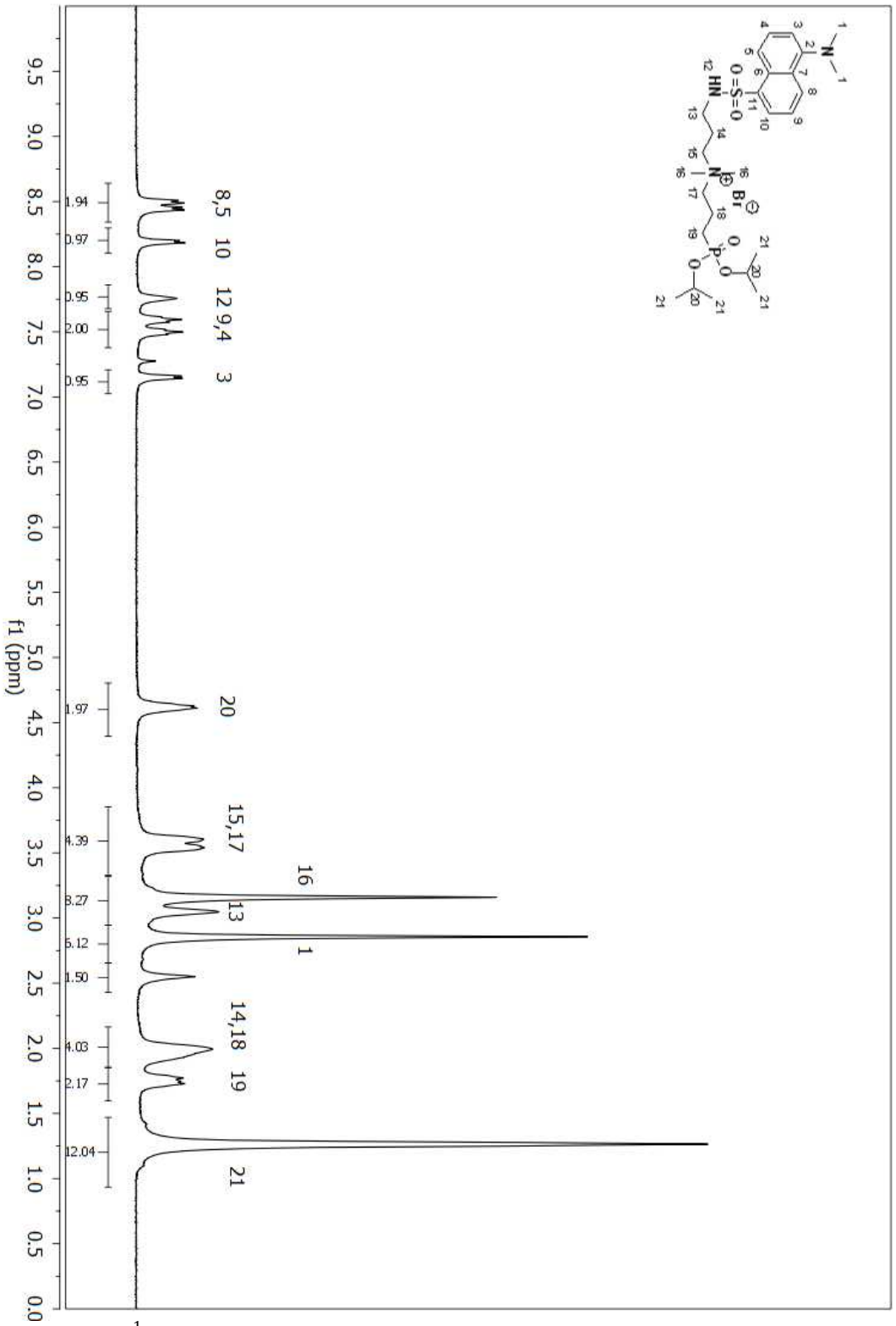

Figure S28. ^{1}H NMR spectrum of precursor dansyl compound **3b** in $CDCl_3$.

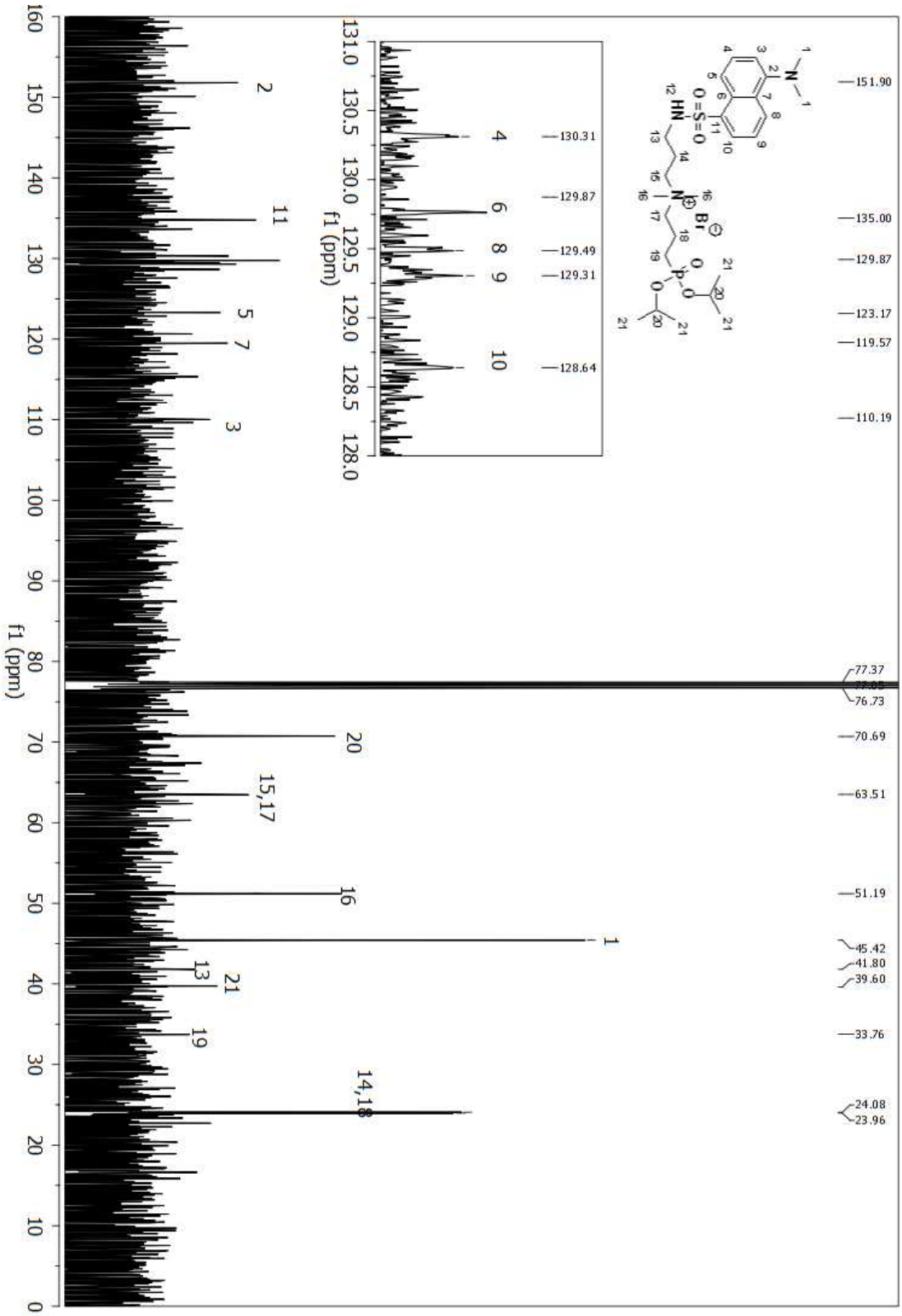

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of precursor dansyl compound **3b** in $CDCl_3$.

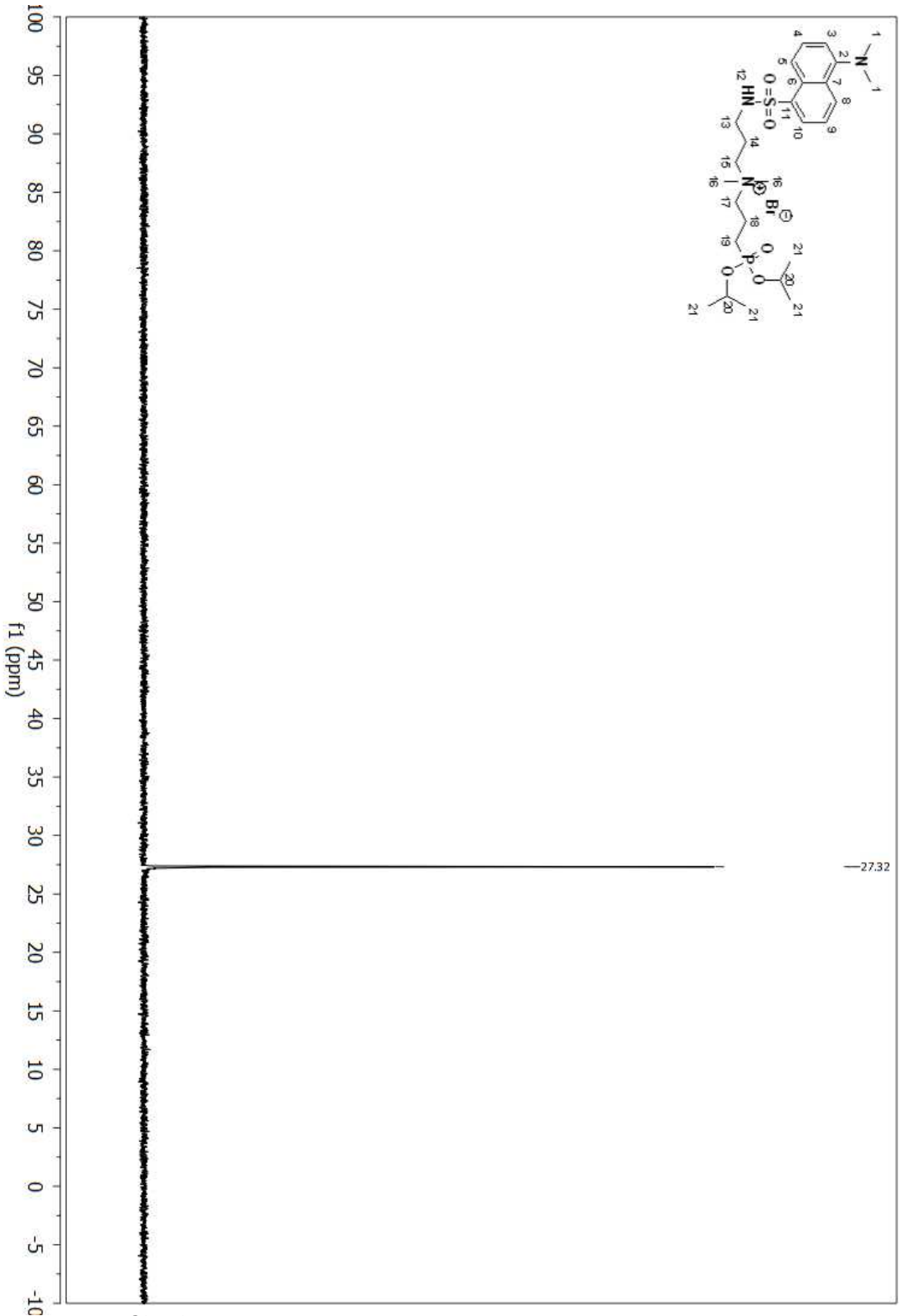

Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum of precursor dansyl compound **3b** in $CDCl_3$.

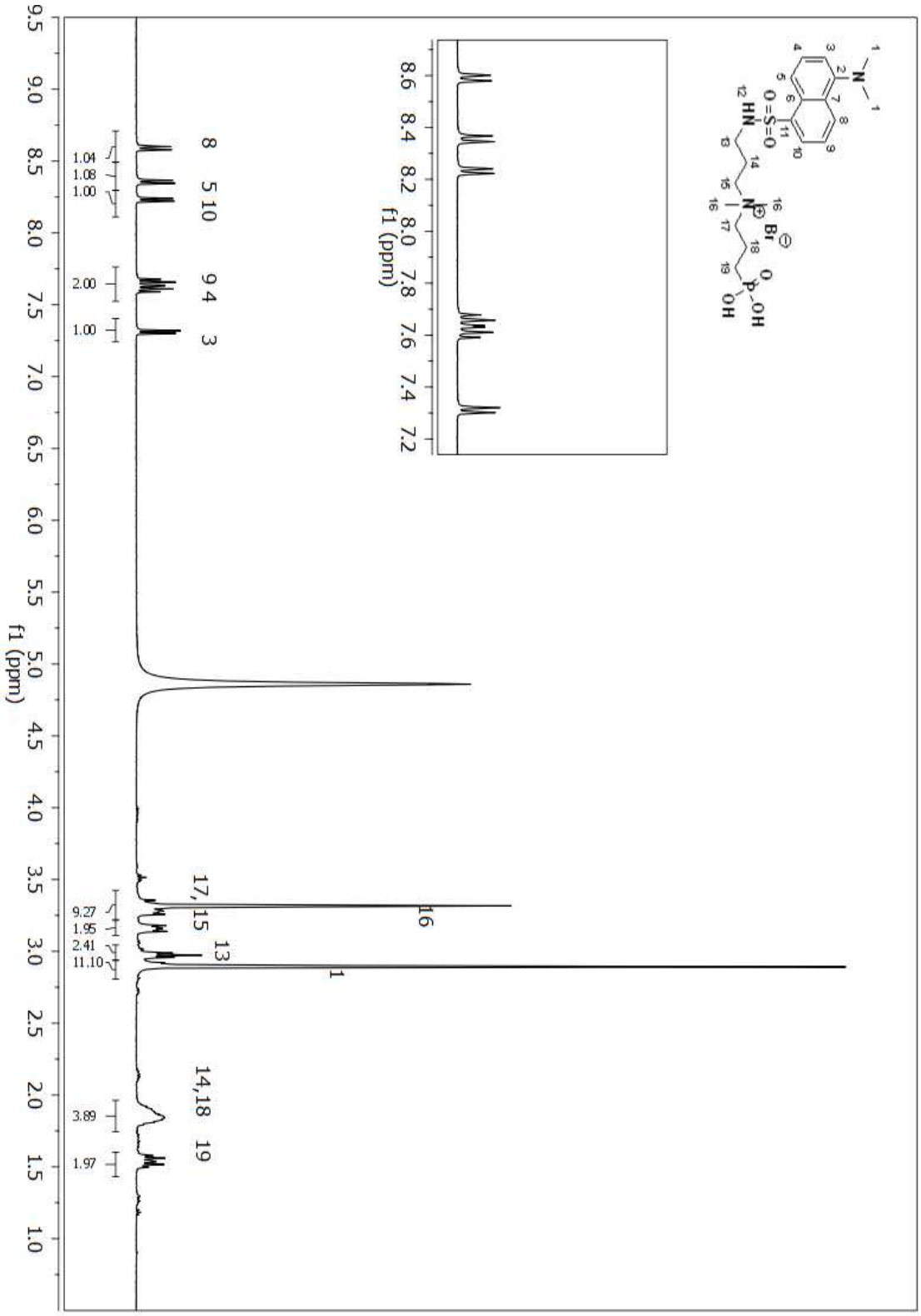

Figure S31. ^{1}H NMR spectrum of precursor dansyl compound **3c** in $CDCl_3$.

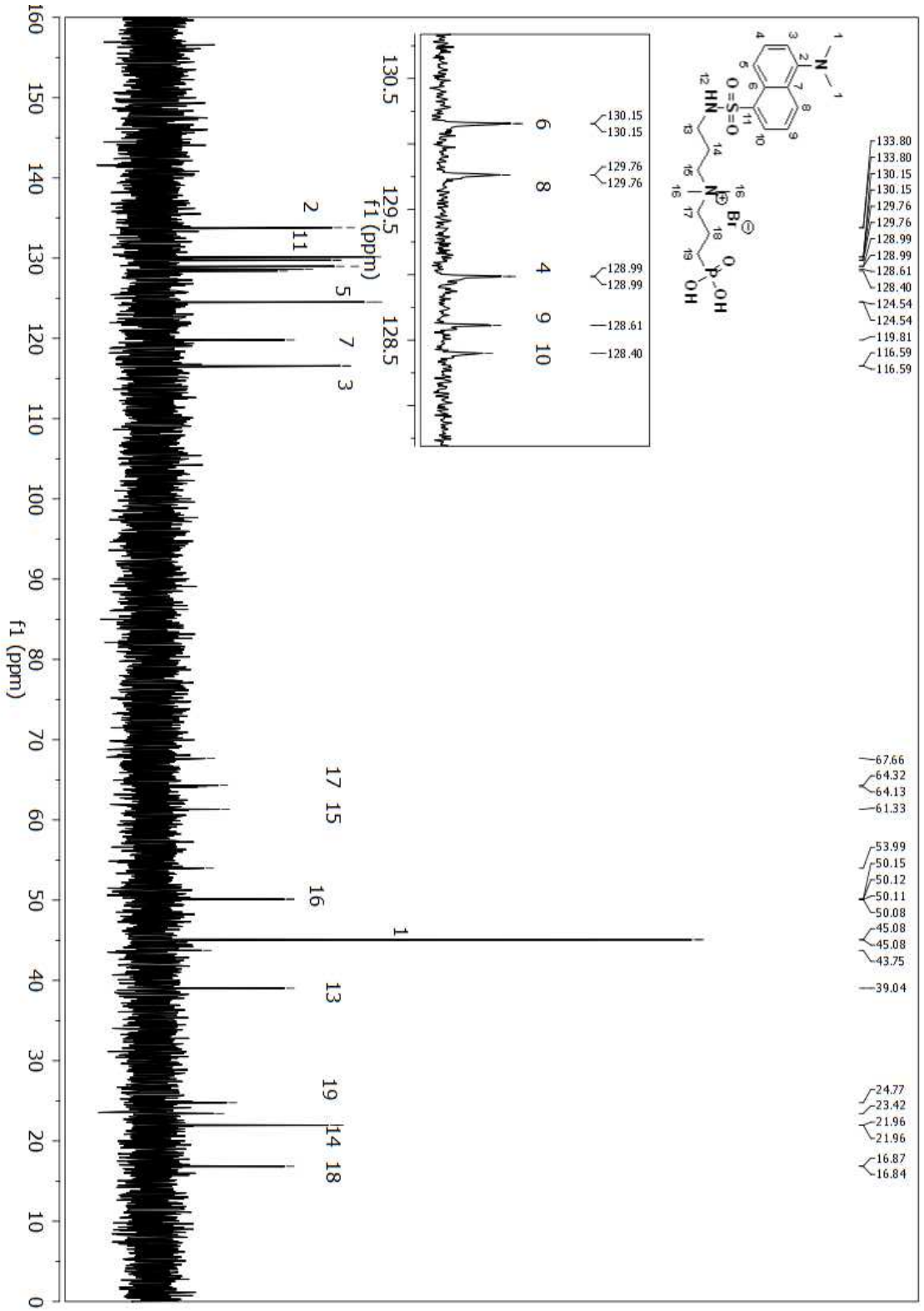

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3c** in $CDCl_3$.

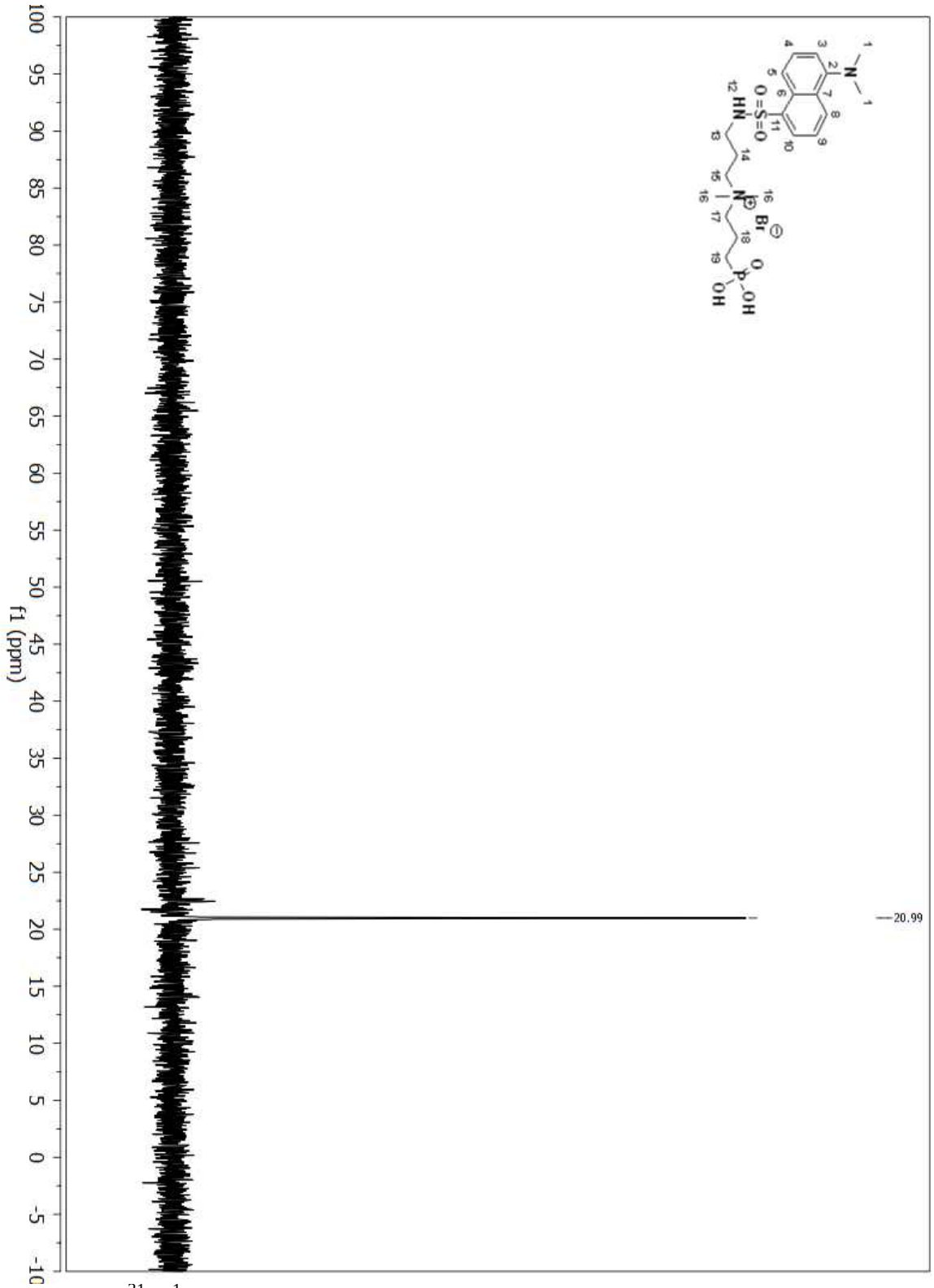

Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum of precursor dansyl compound **3c** in $CDCl_3$.

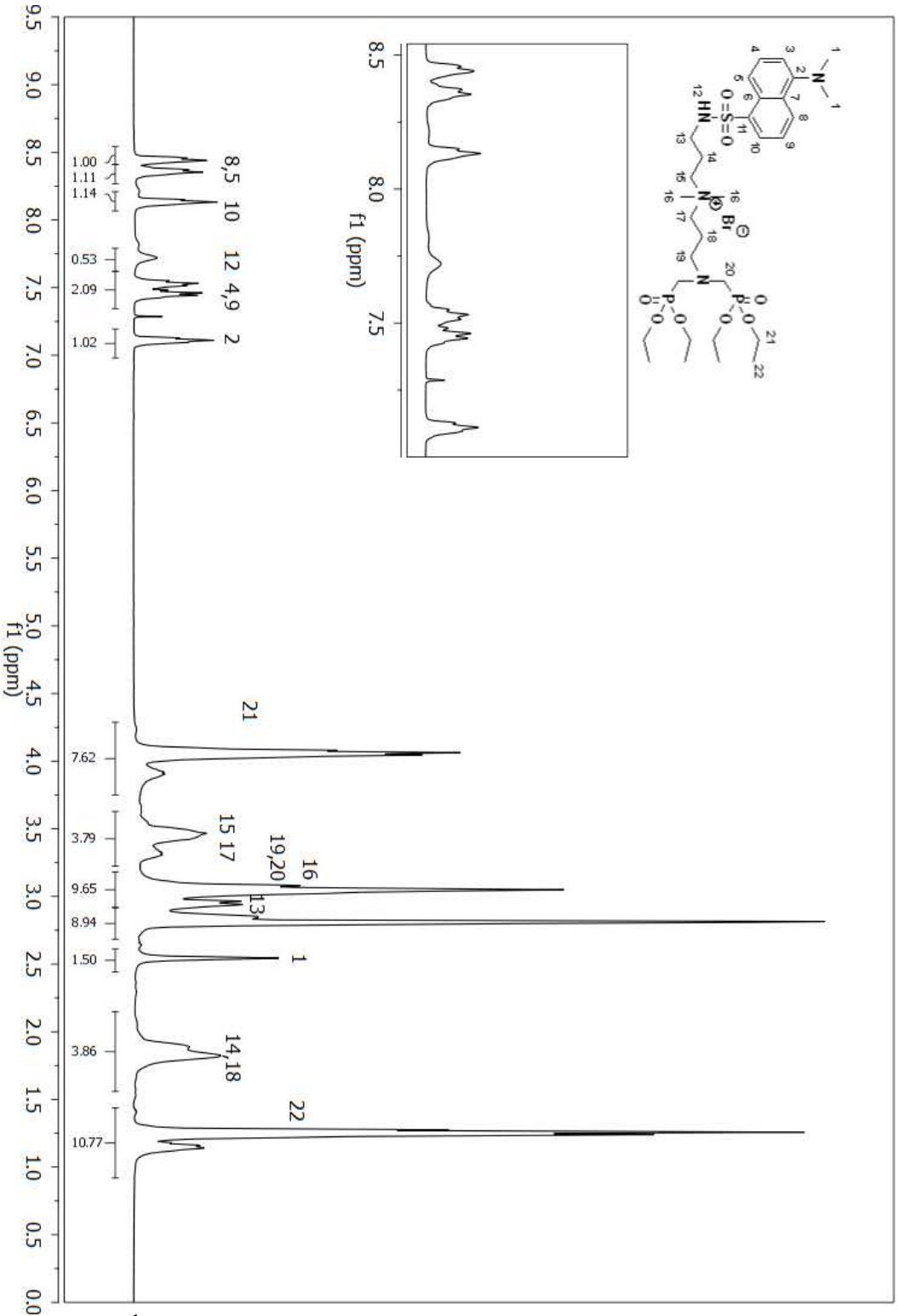

Figure S34. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

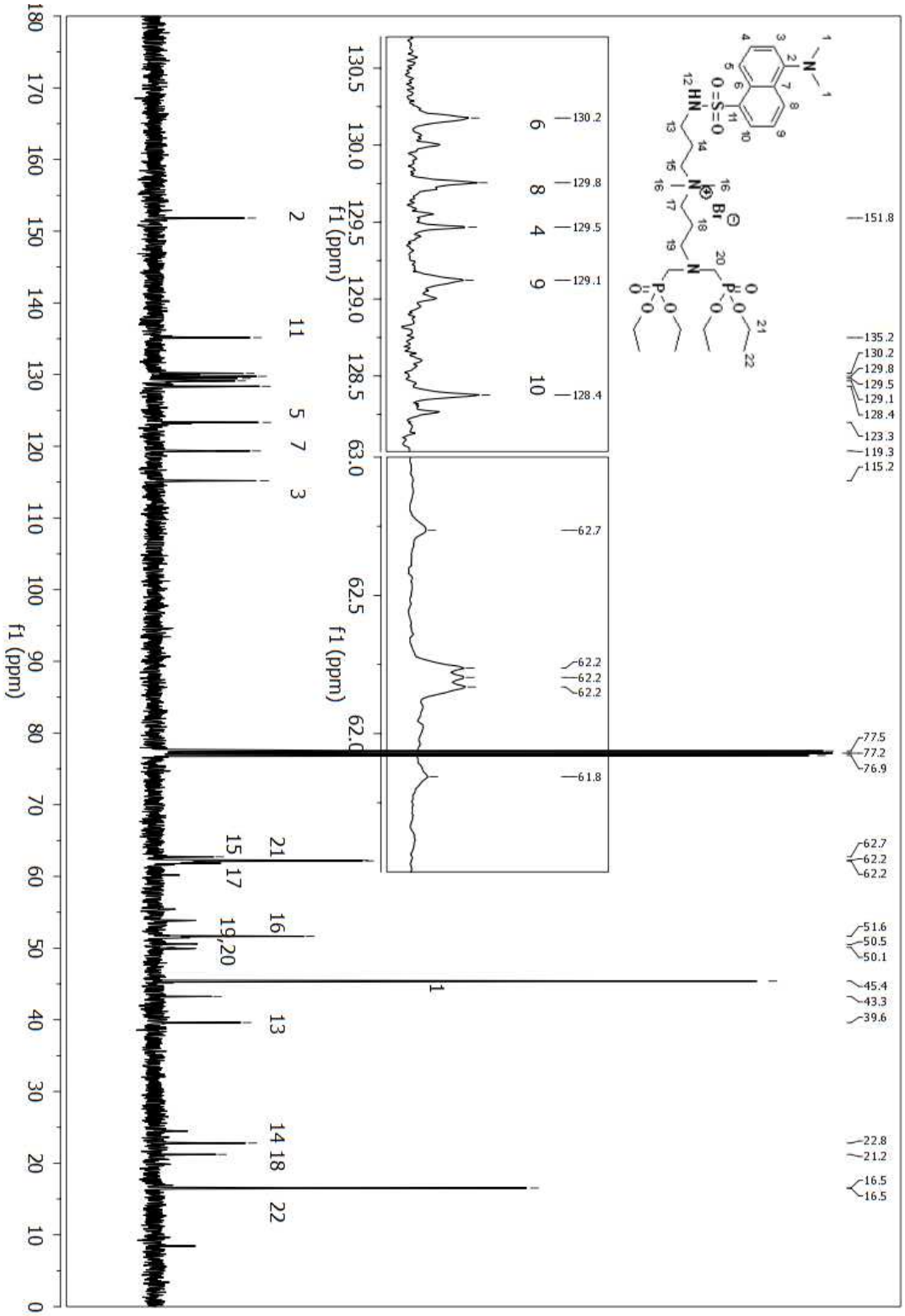

Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of precursor dansyl compound **4** in $CDCl_3$.

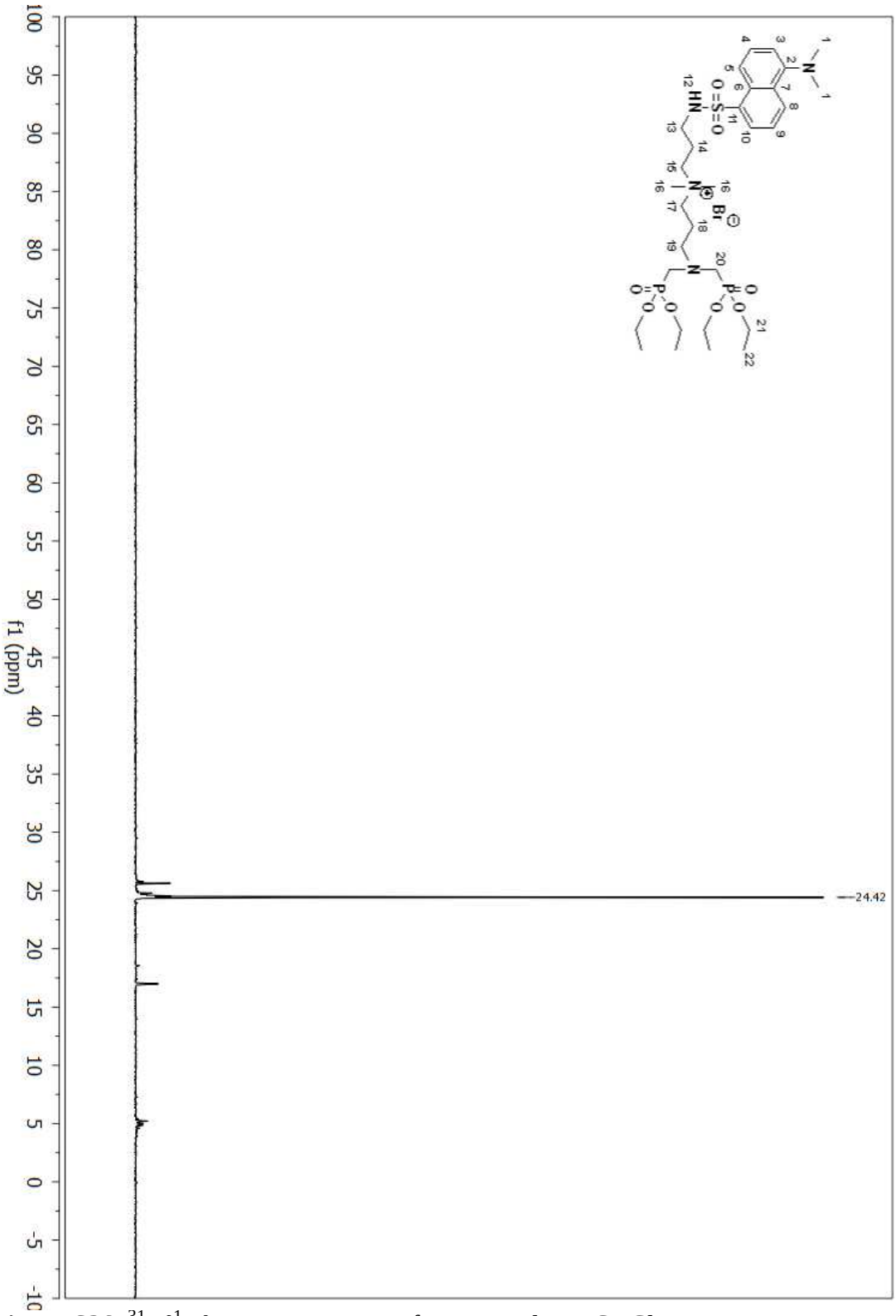

Figure S36. $^{31}P\{^{1}H\}$ NMR spectrum of compound **4** in $CDCl_3$.

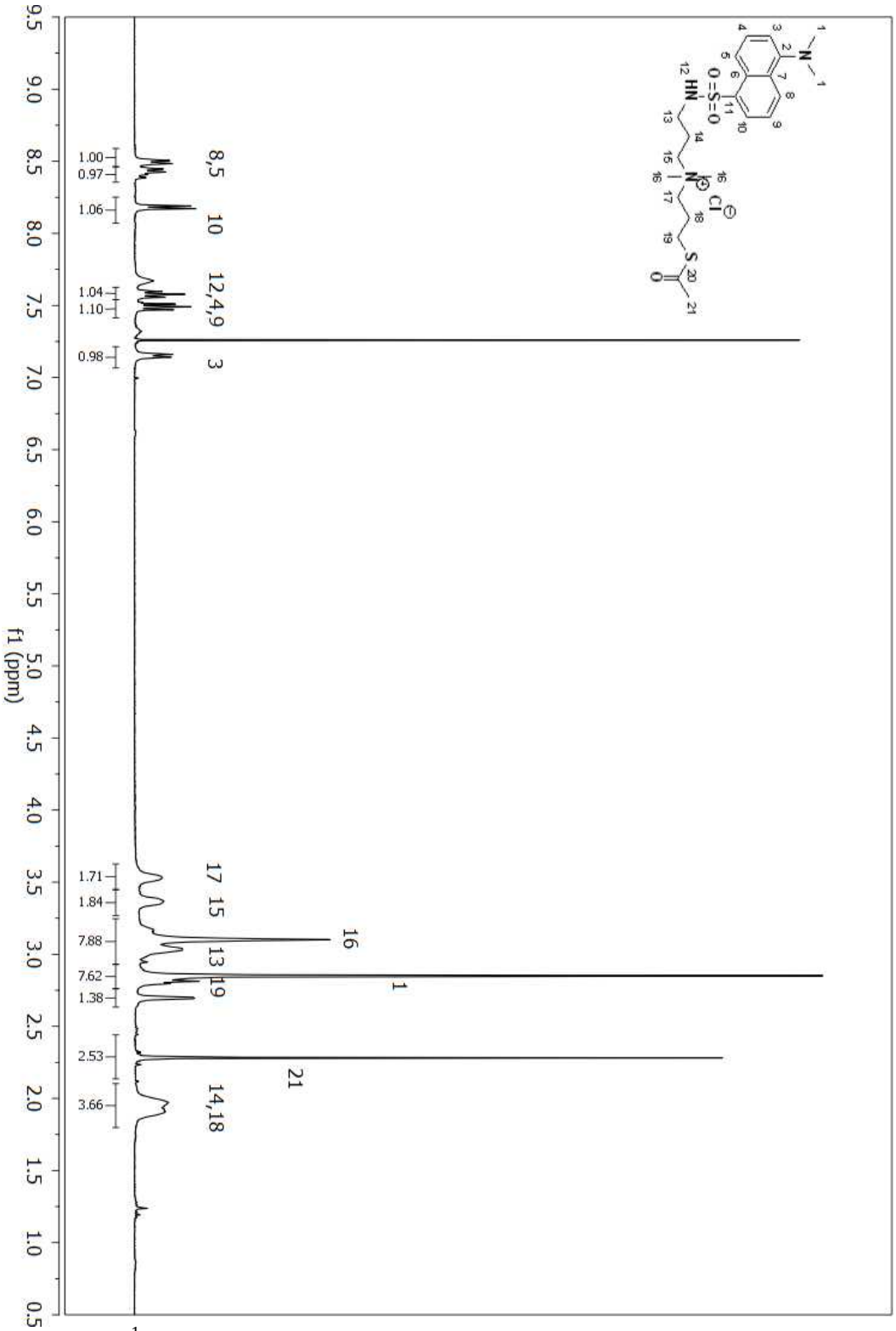

Figure S37. ^{1}H NMR spectrum of precursor dansyl compound **5** in $CDCl_3$.

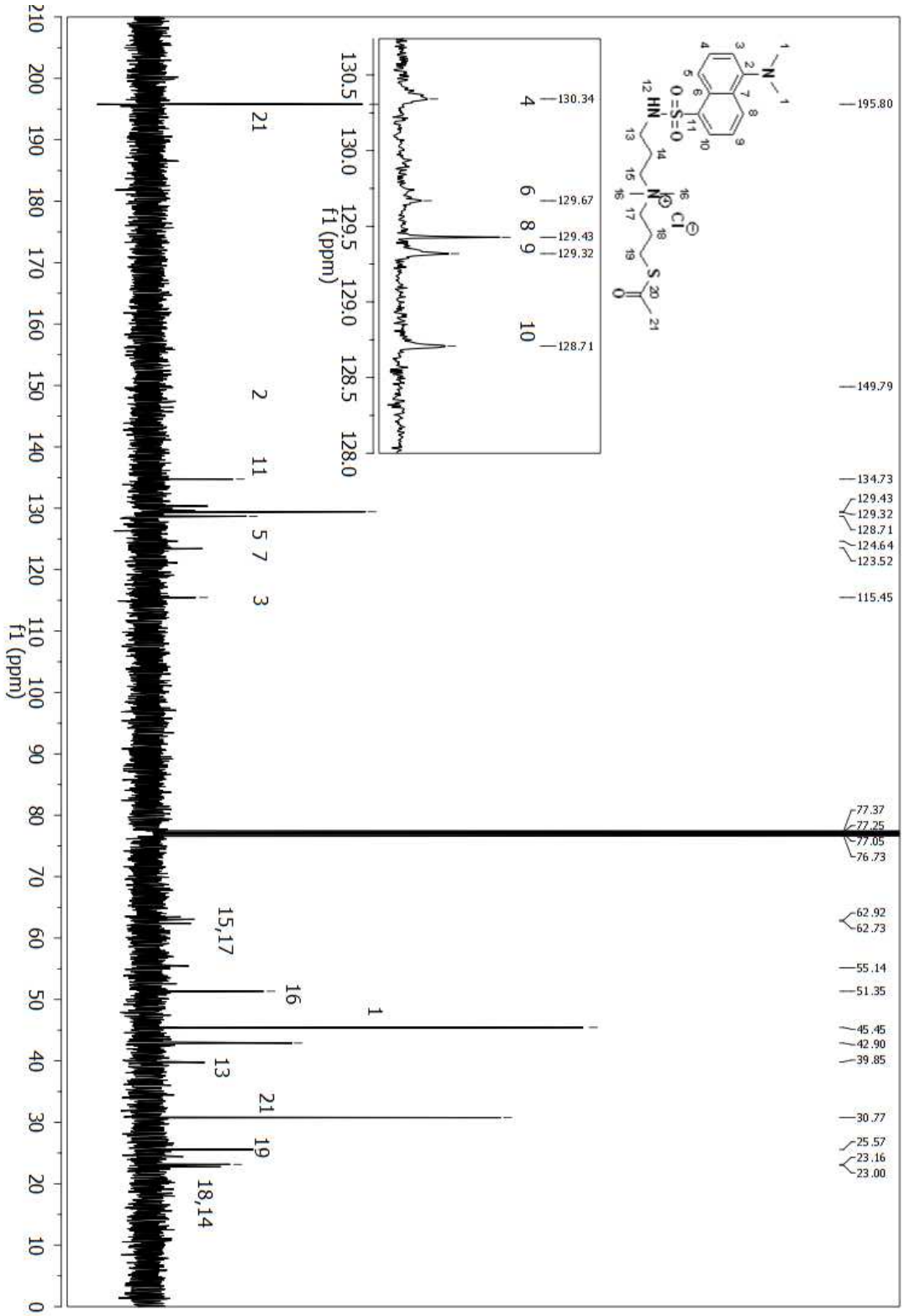

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$.

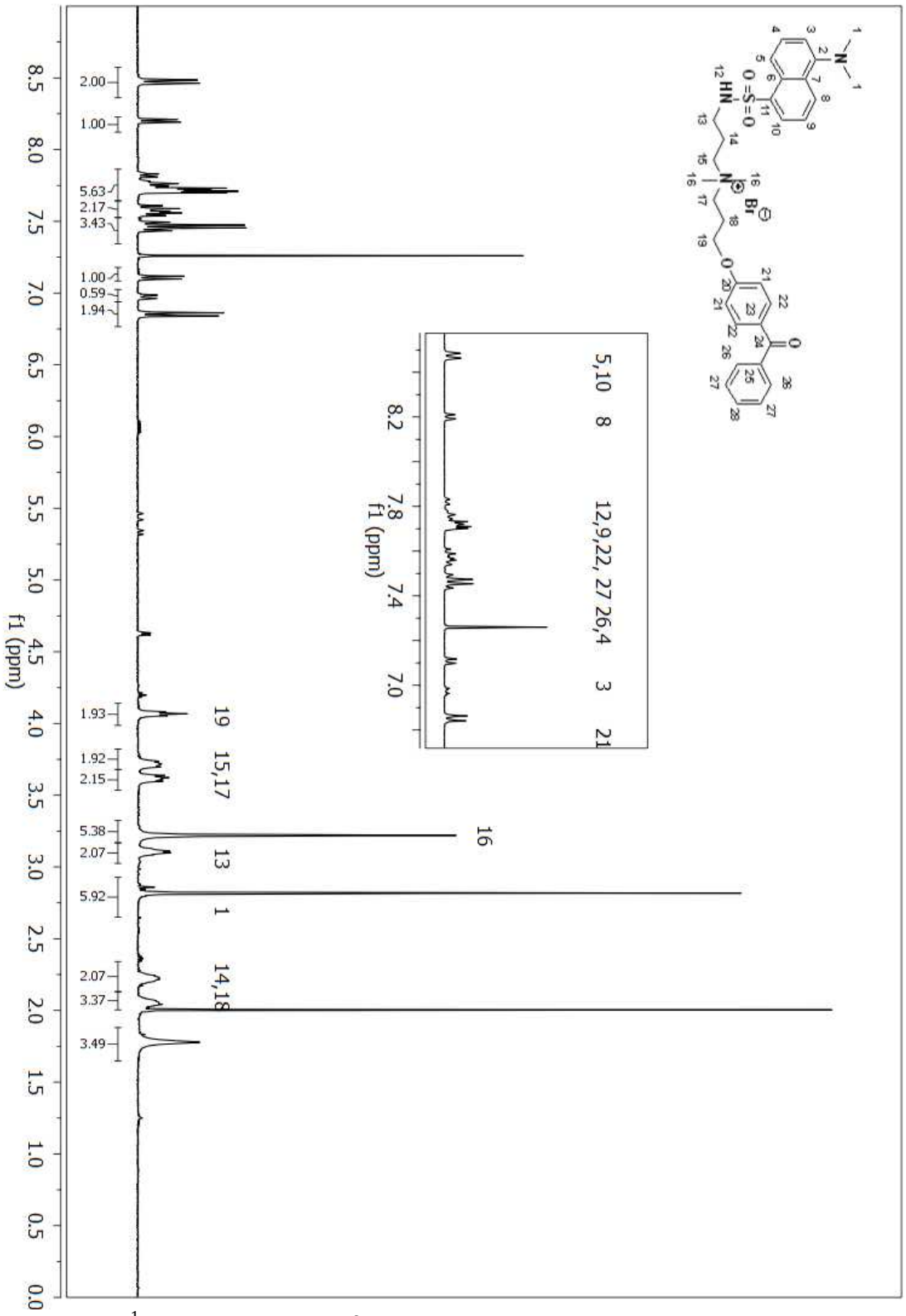

Figure S39. ^{1}H NMR spectrum of precursor dansyl compound **6a** in $CDCl_3$.

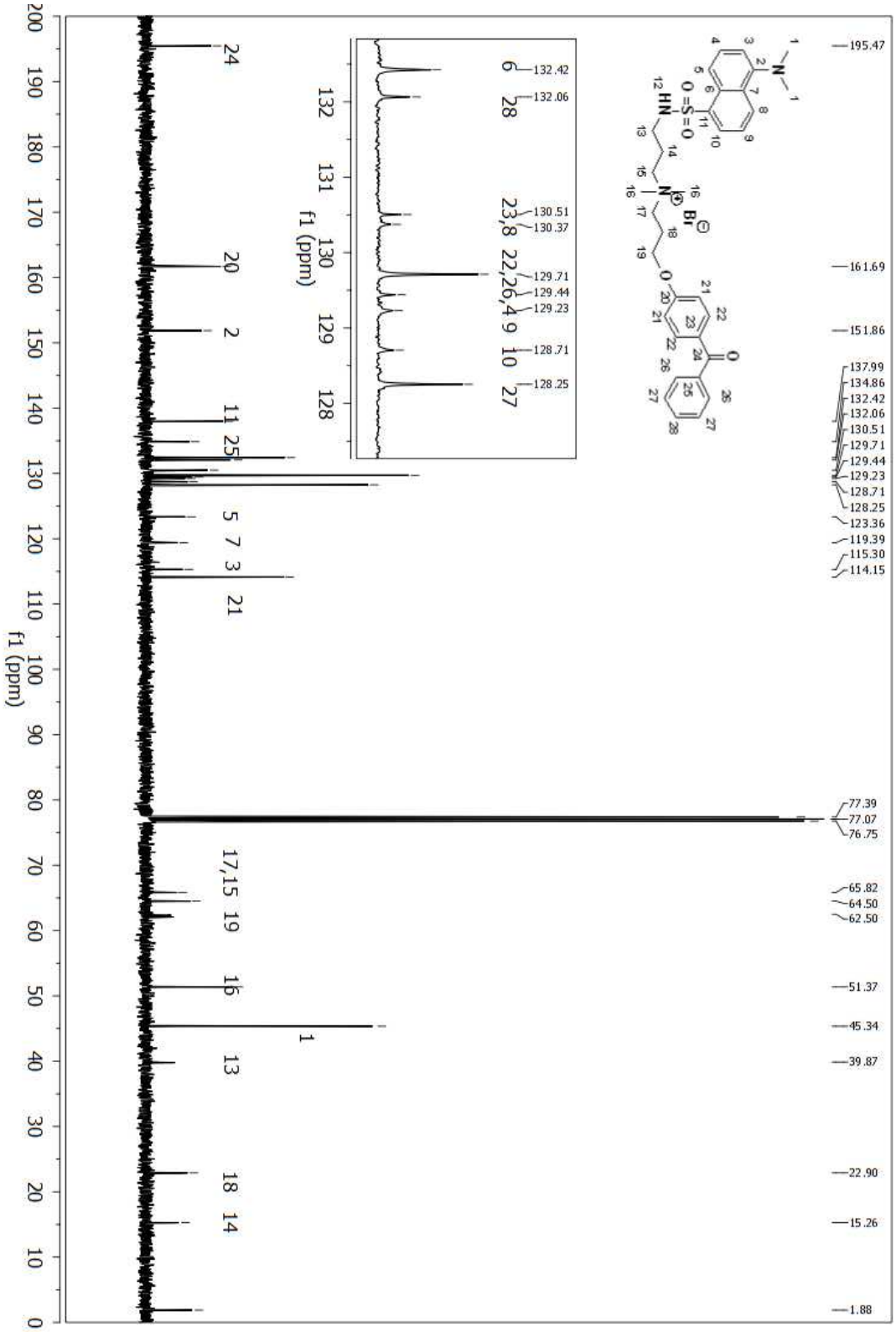

Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6a** in $CDCl_3$.

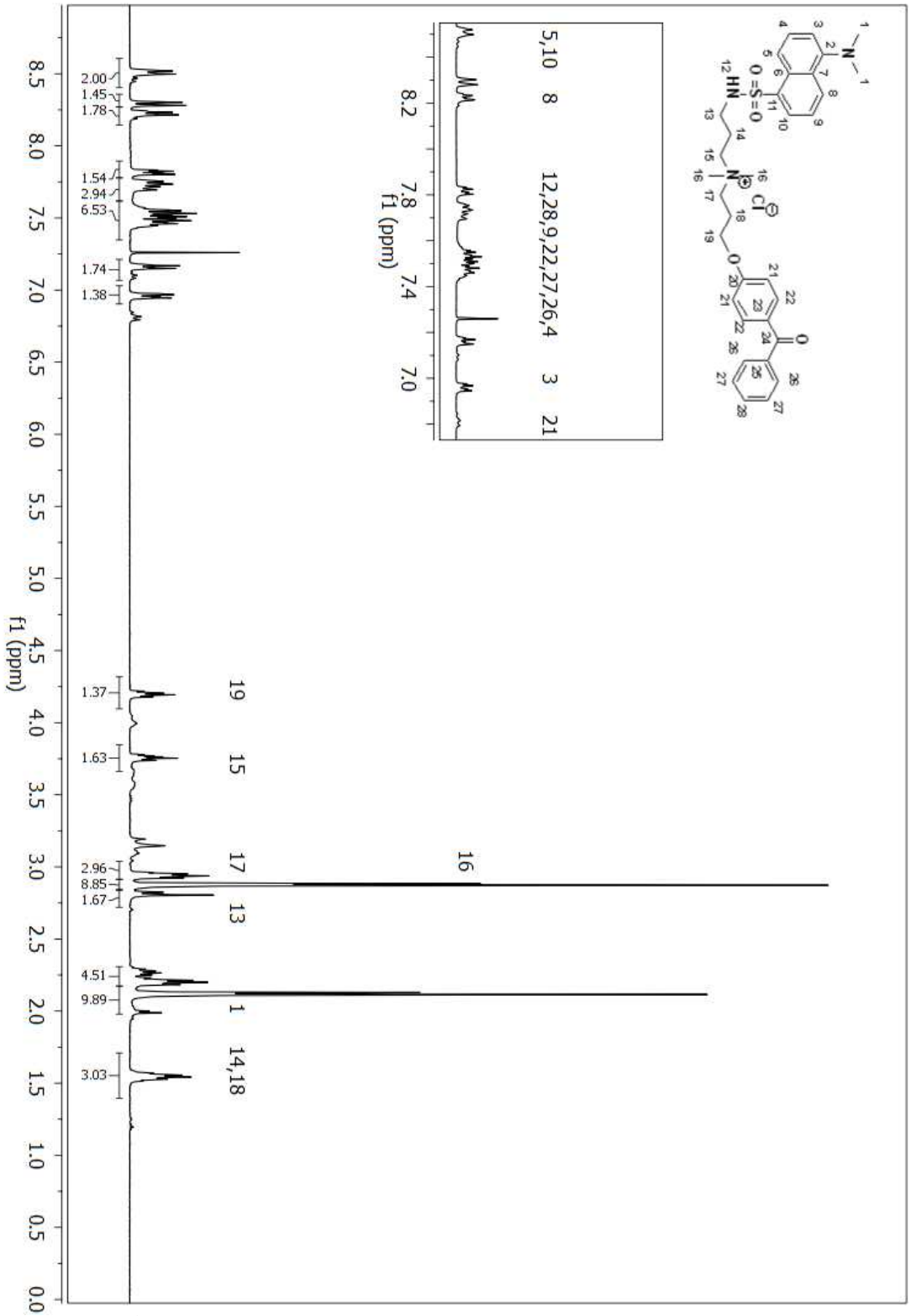

Figure S41. ^{1}H NMR spectrum of precursor dansyl compound **6b** in $CDCl_3$.

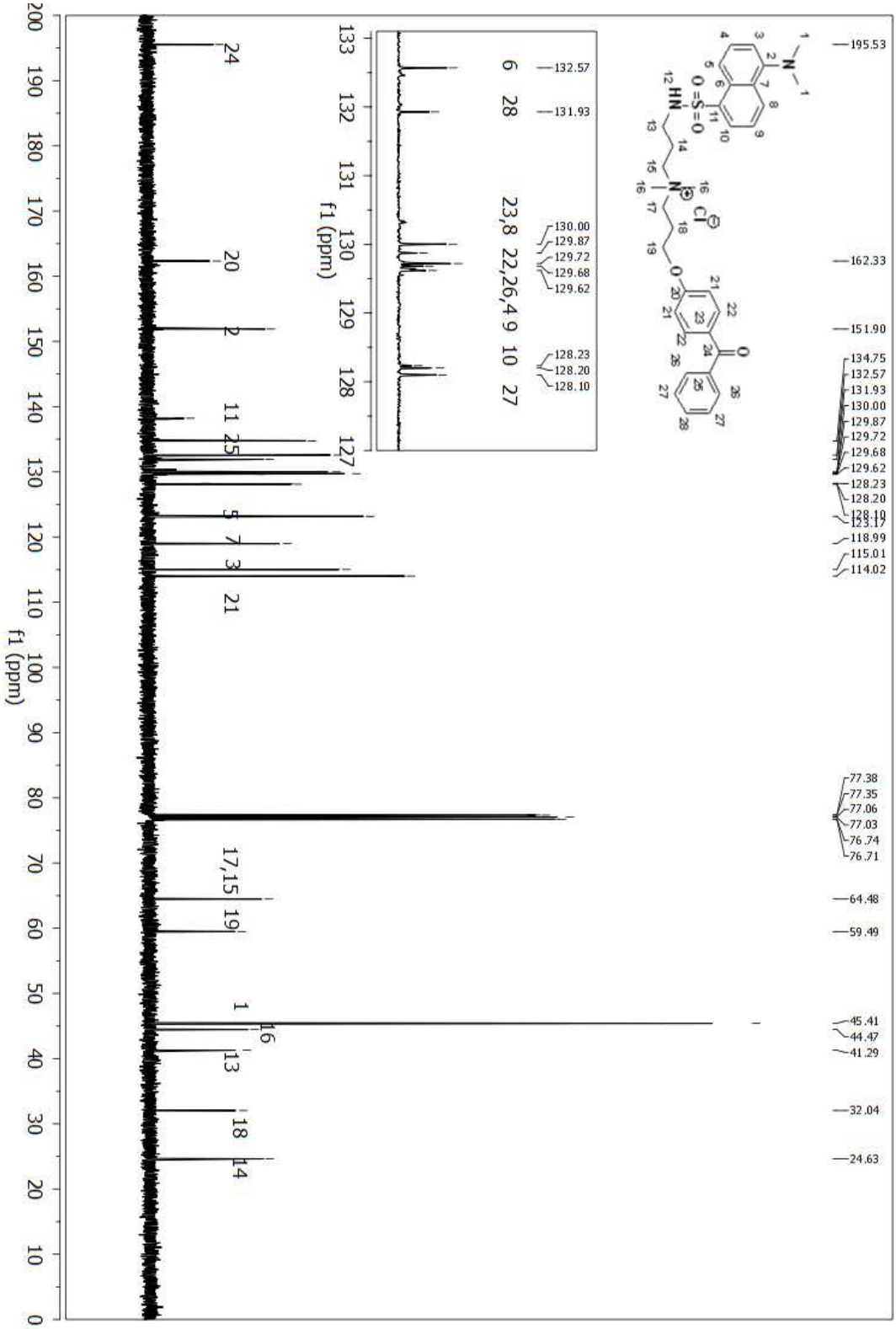

Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6b** in $CDCl_3$

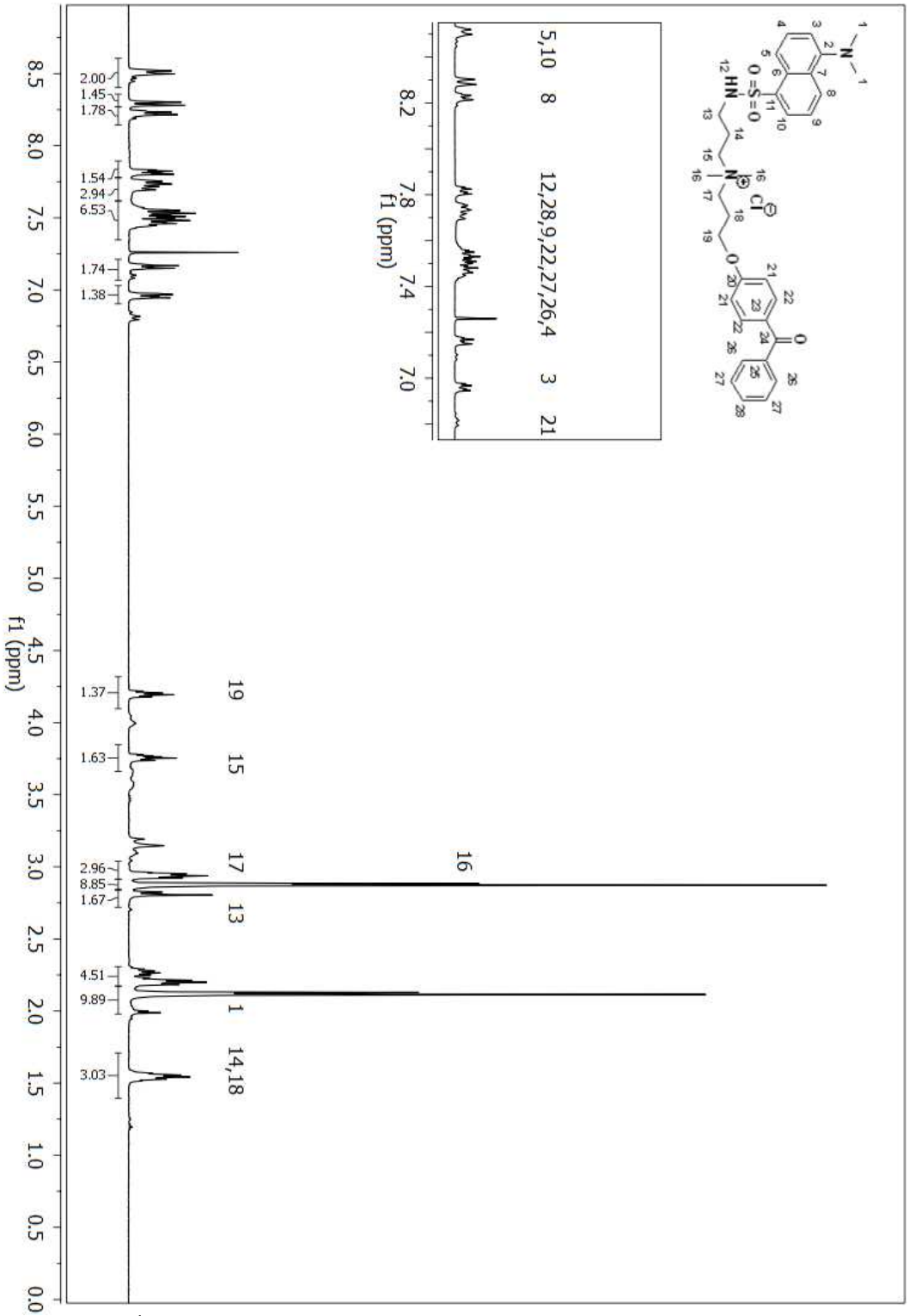

Figure S43. ^{1}H NMR spectrum of precursor dansyl compound **6c** in $CDCl_3$.

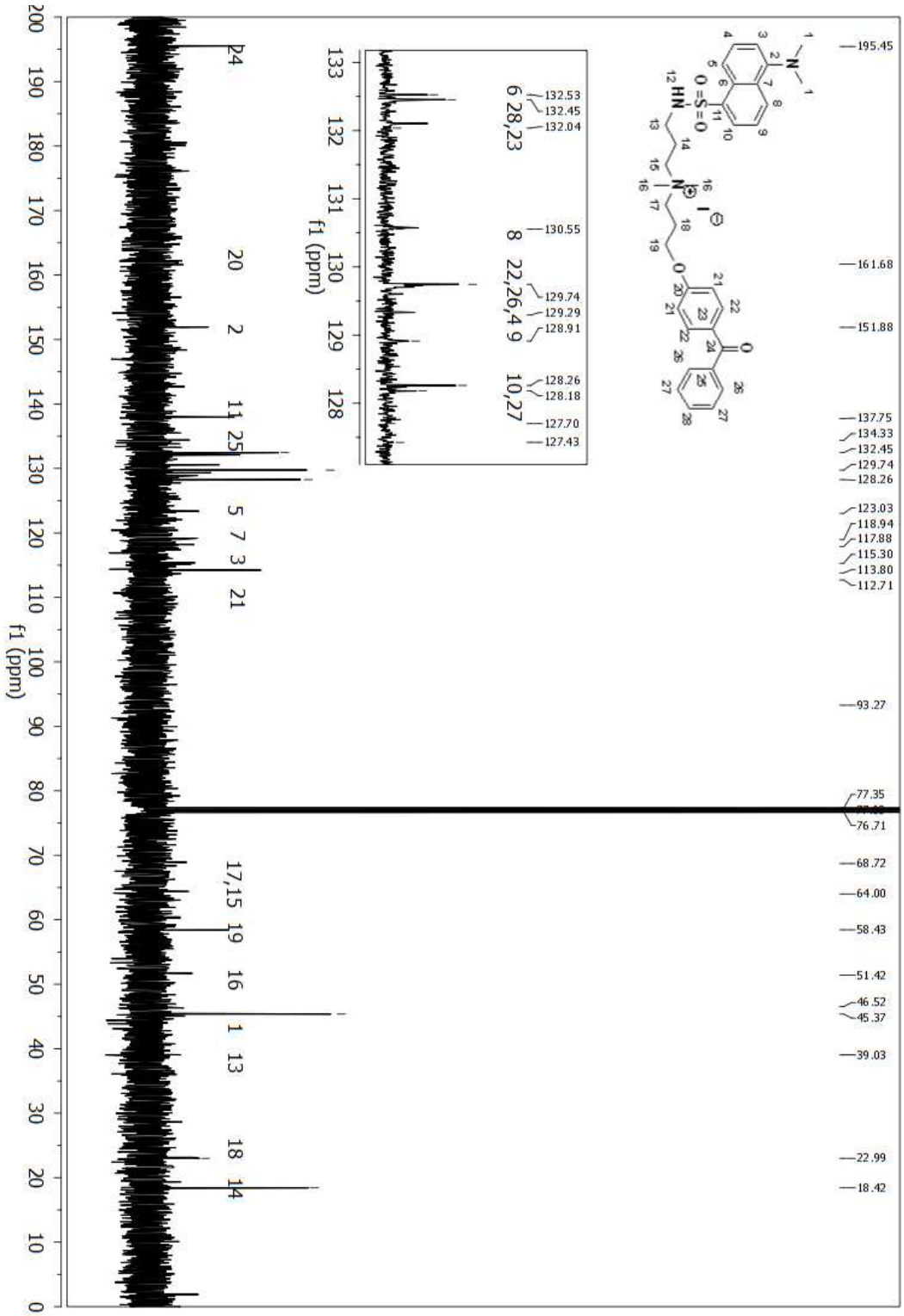

Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6c** in $CDCl_3$

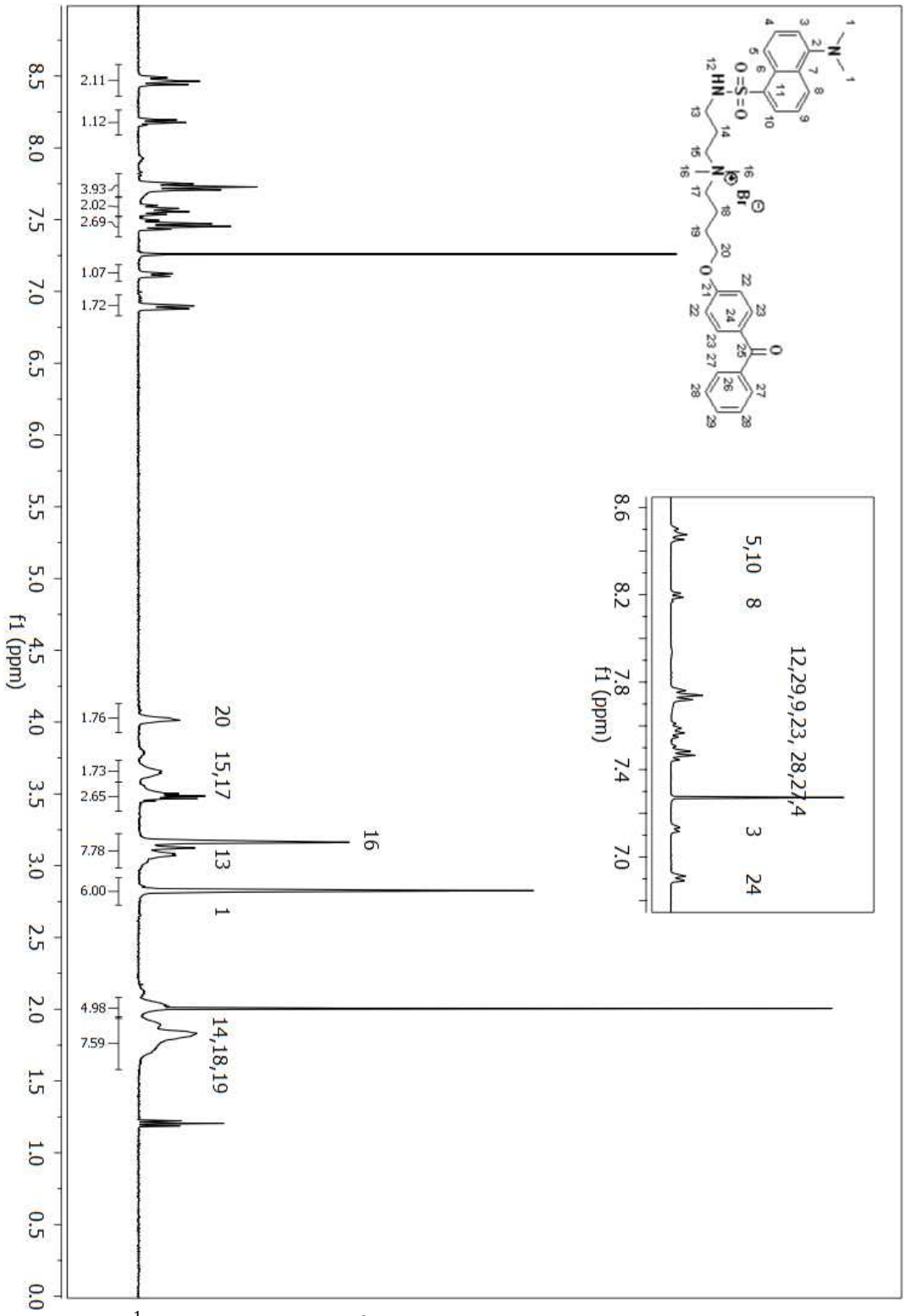

Figure S45. ^{1}H NMR spectrum of compound **6d** in $CDCl_3$.

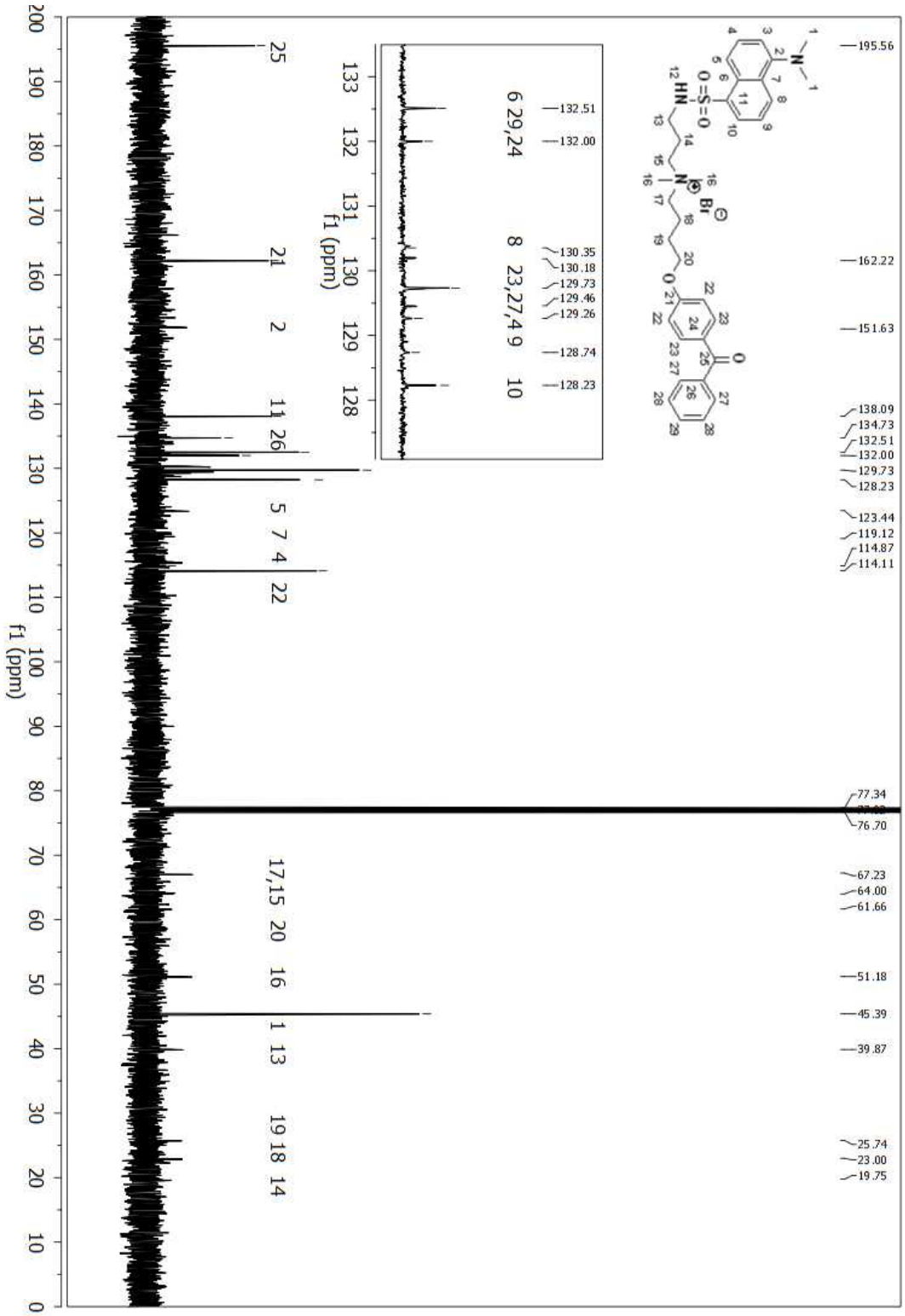

Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6d** in $CDCl_3$.

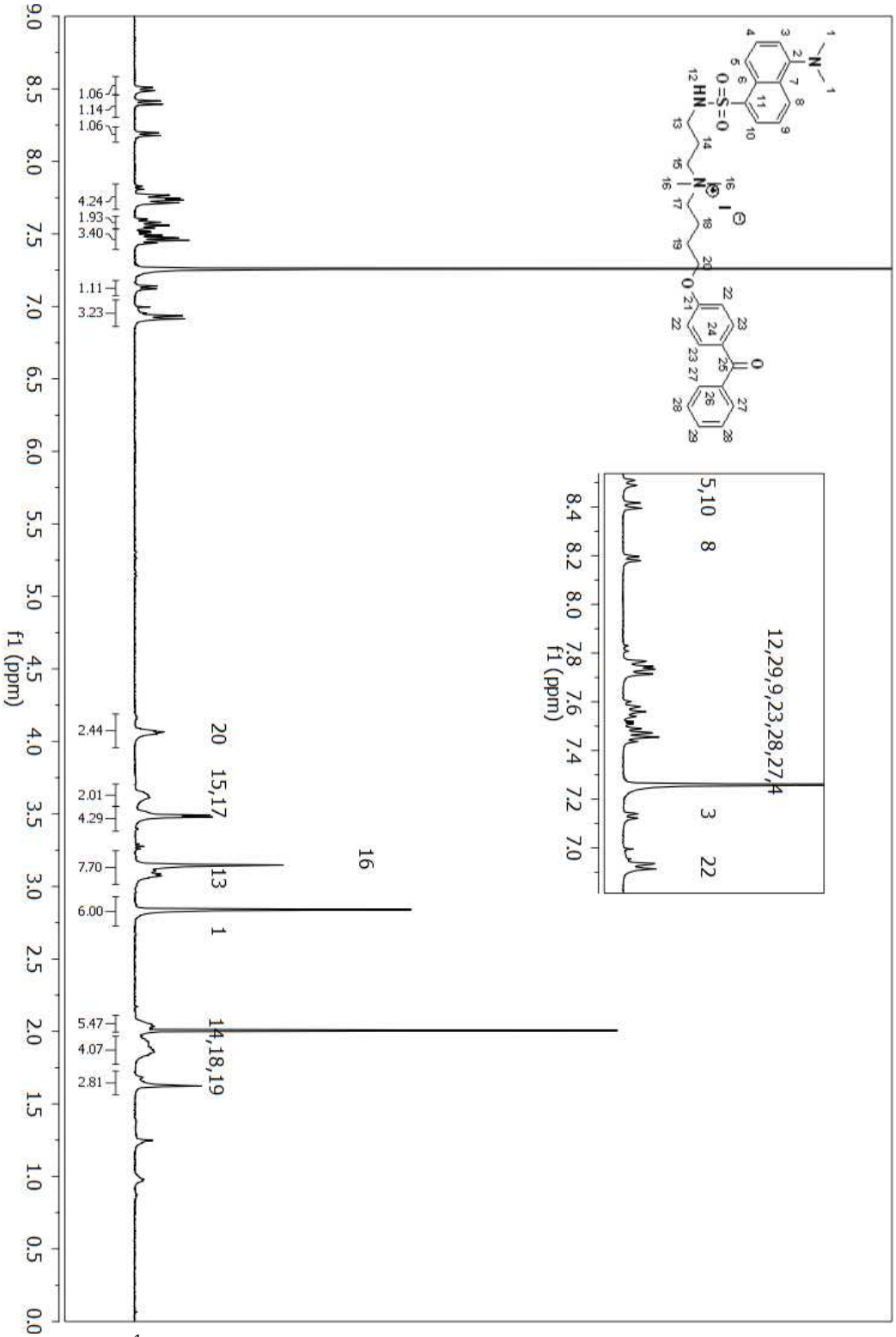

Figure S47. ^{1}H NMR spectrum of compound **6e** in $CDCl_3$.

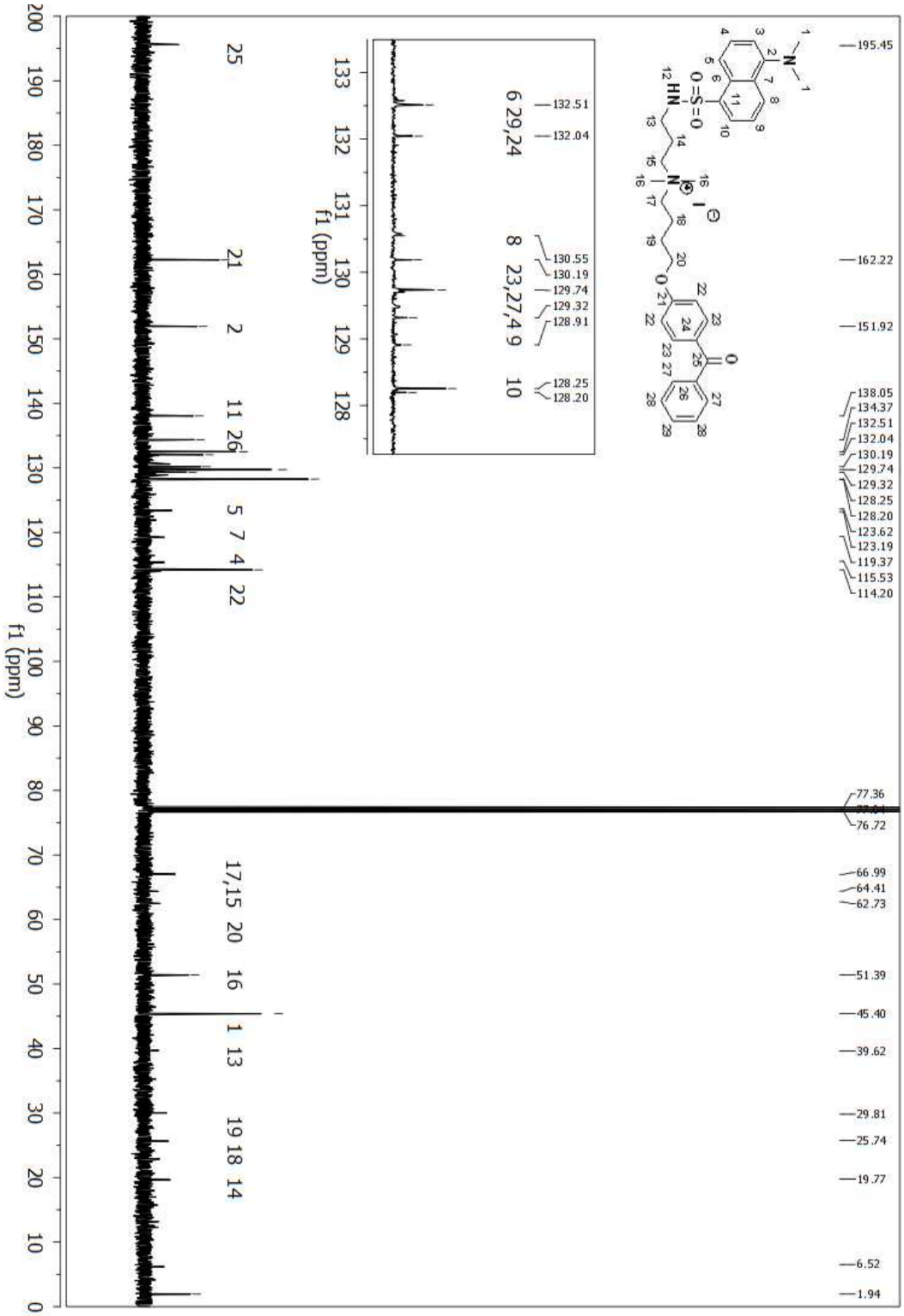

Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6e** in $CDCl_3$.

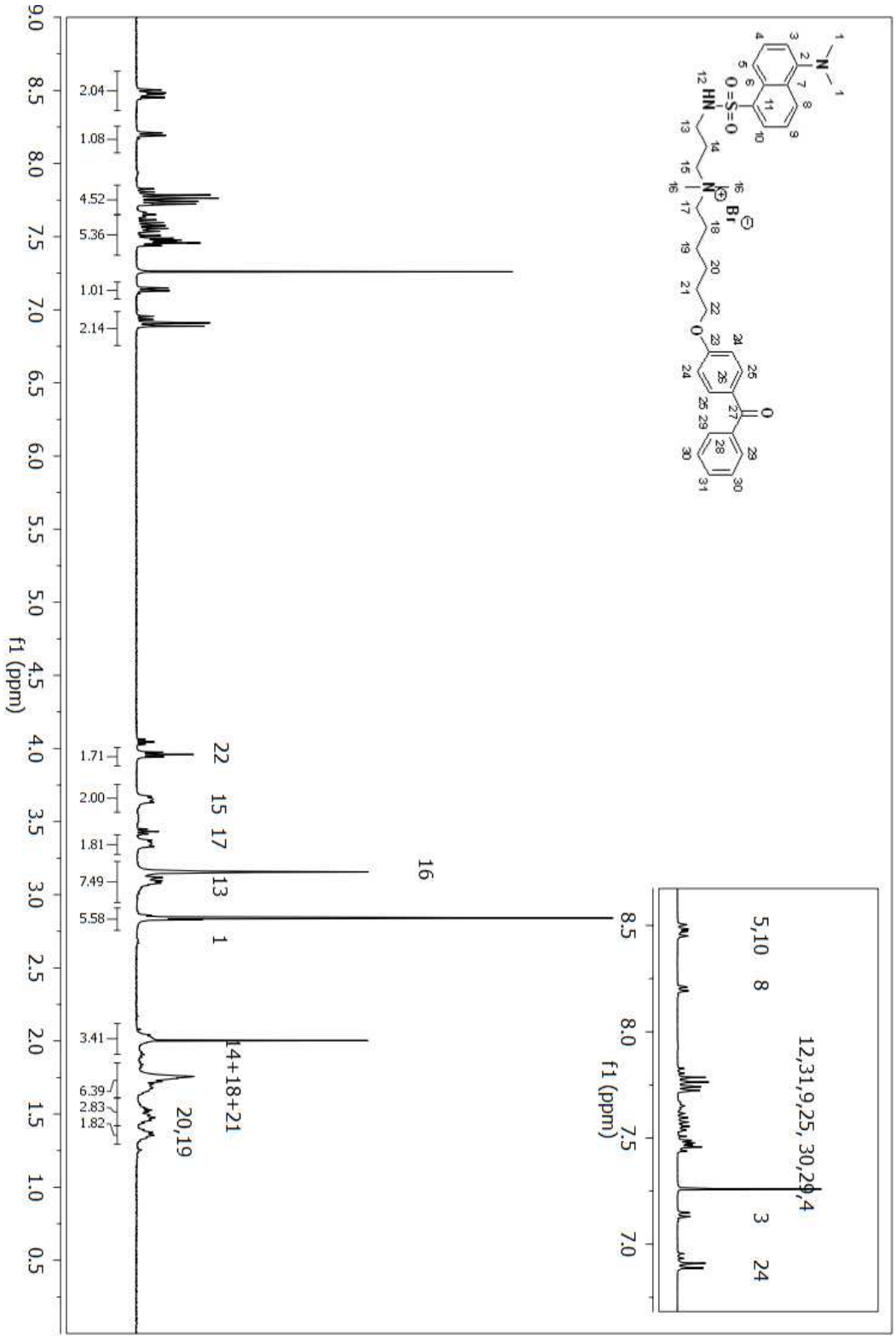

Figure S49. ^{1}H NMR spectrum of compound **6f** in $CDCl_3$.

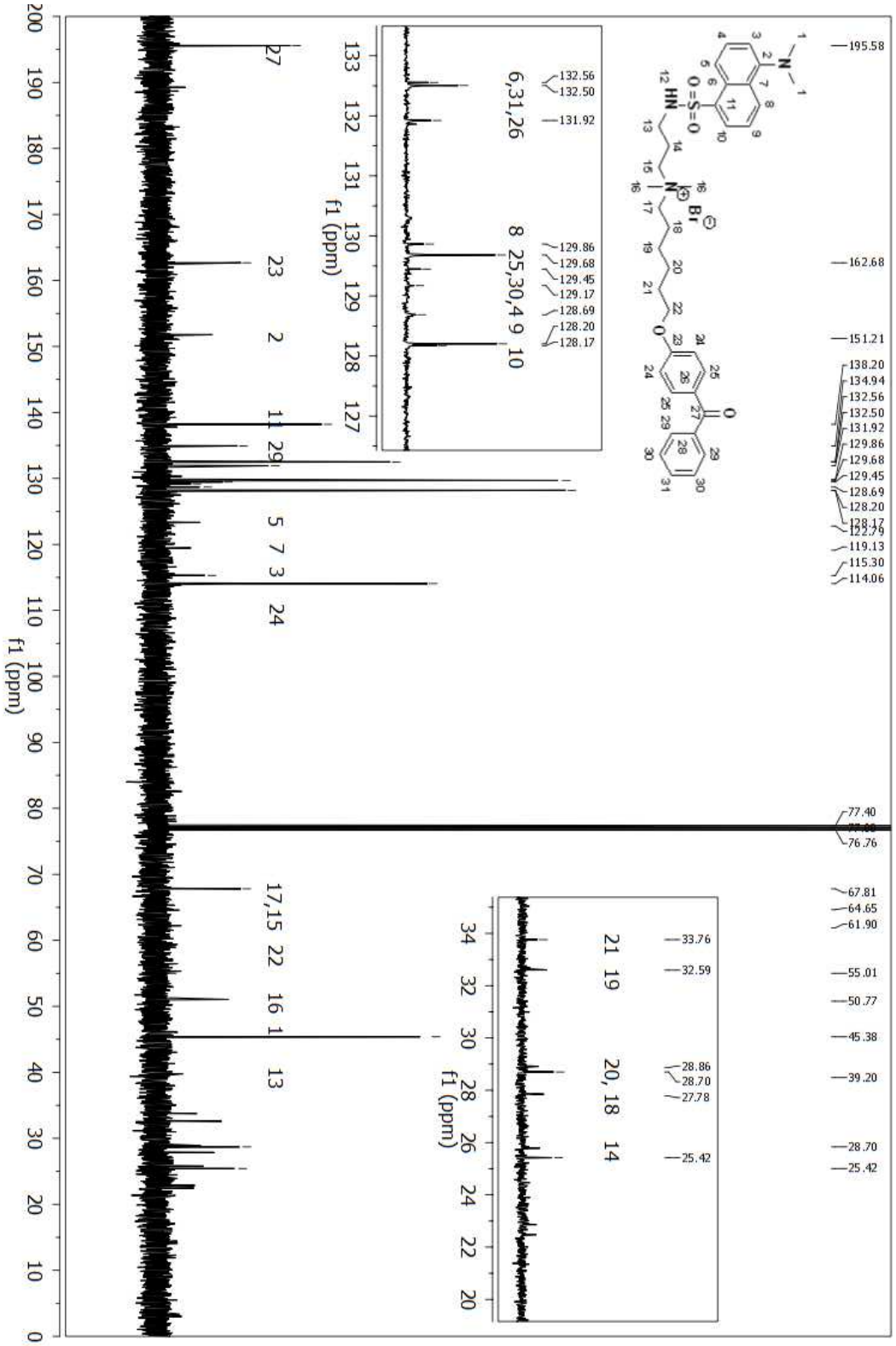

Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6f** in $CDCl_3$.

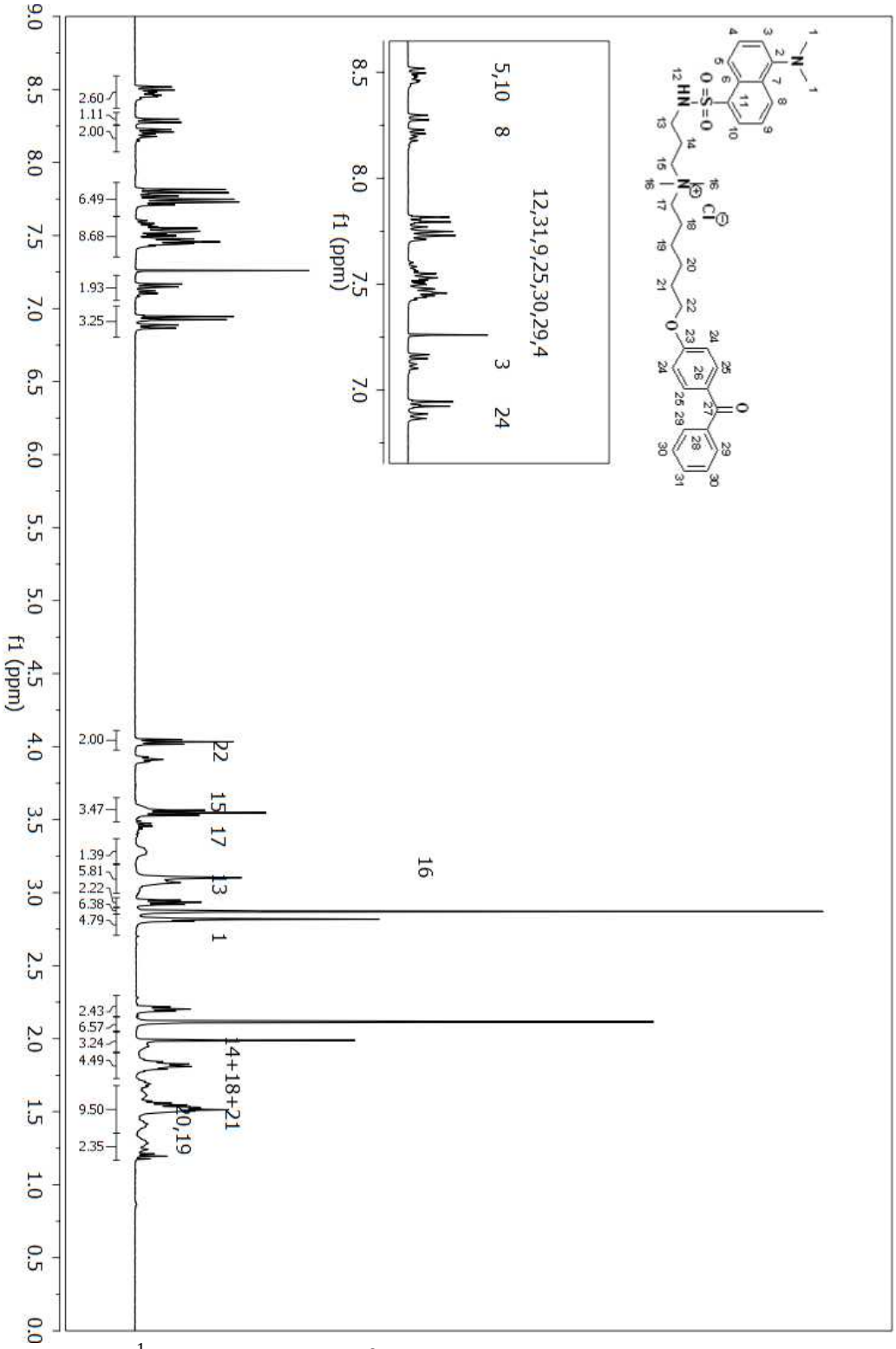

Figure S51. ^{1}H NMR spectrum of compound **6g** in $CDCl_3$.

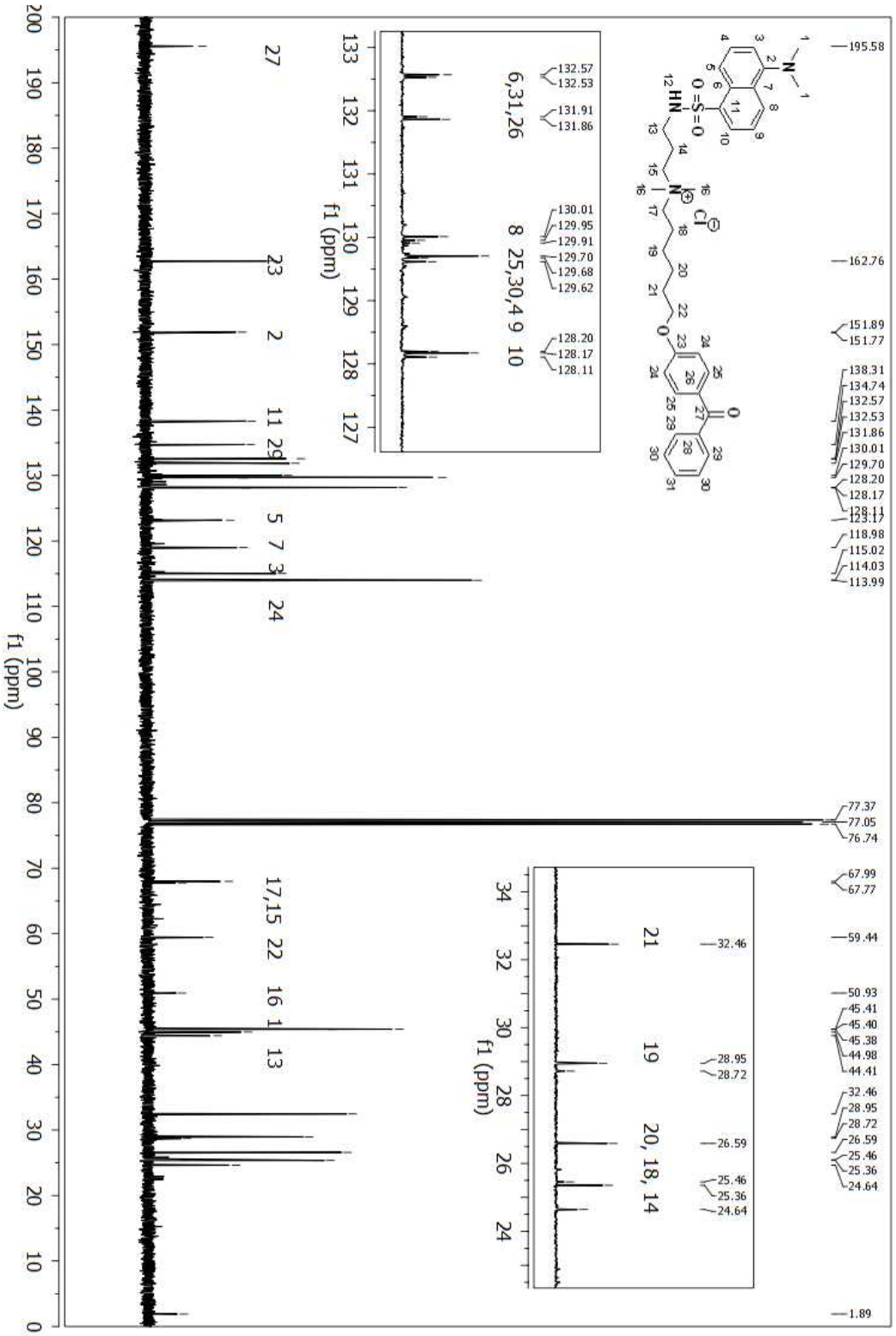

Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6g** in $CDCl_3$.

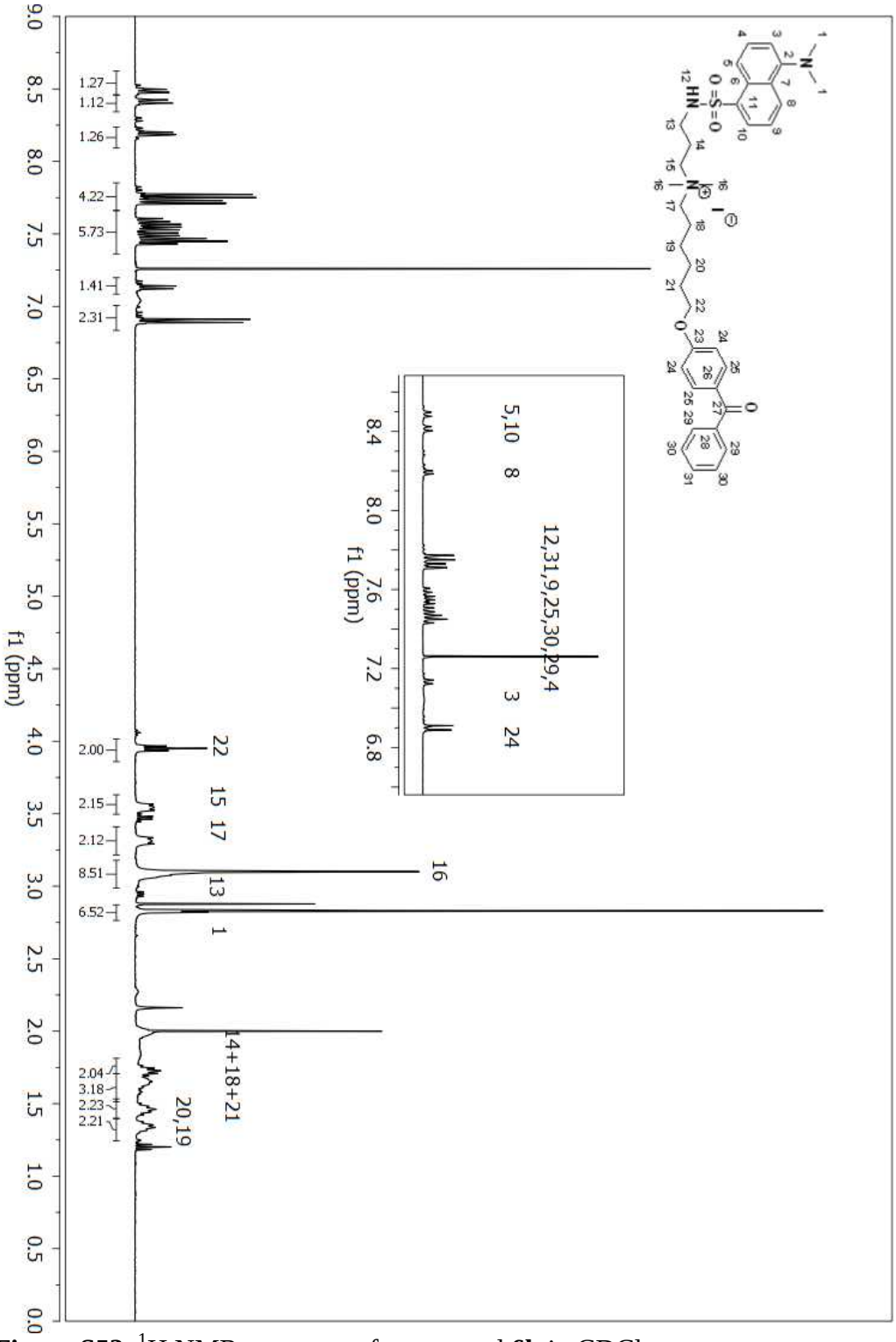

Figure S53. ^{1}H NMR spectrum of compound **6h** in $CDCl_3$.

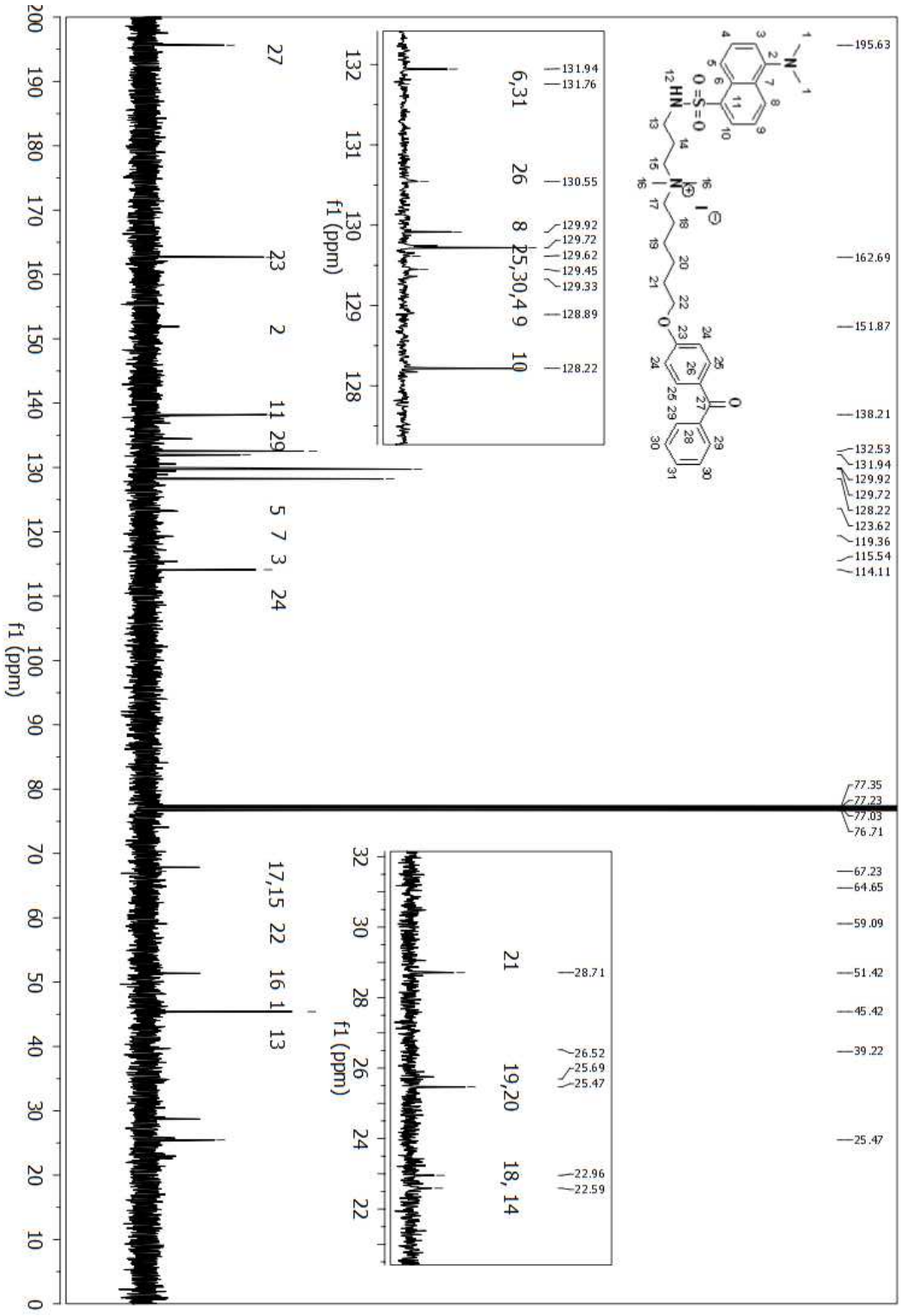

Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6h** in $CDCl_3$.

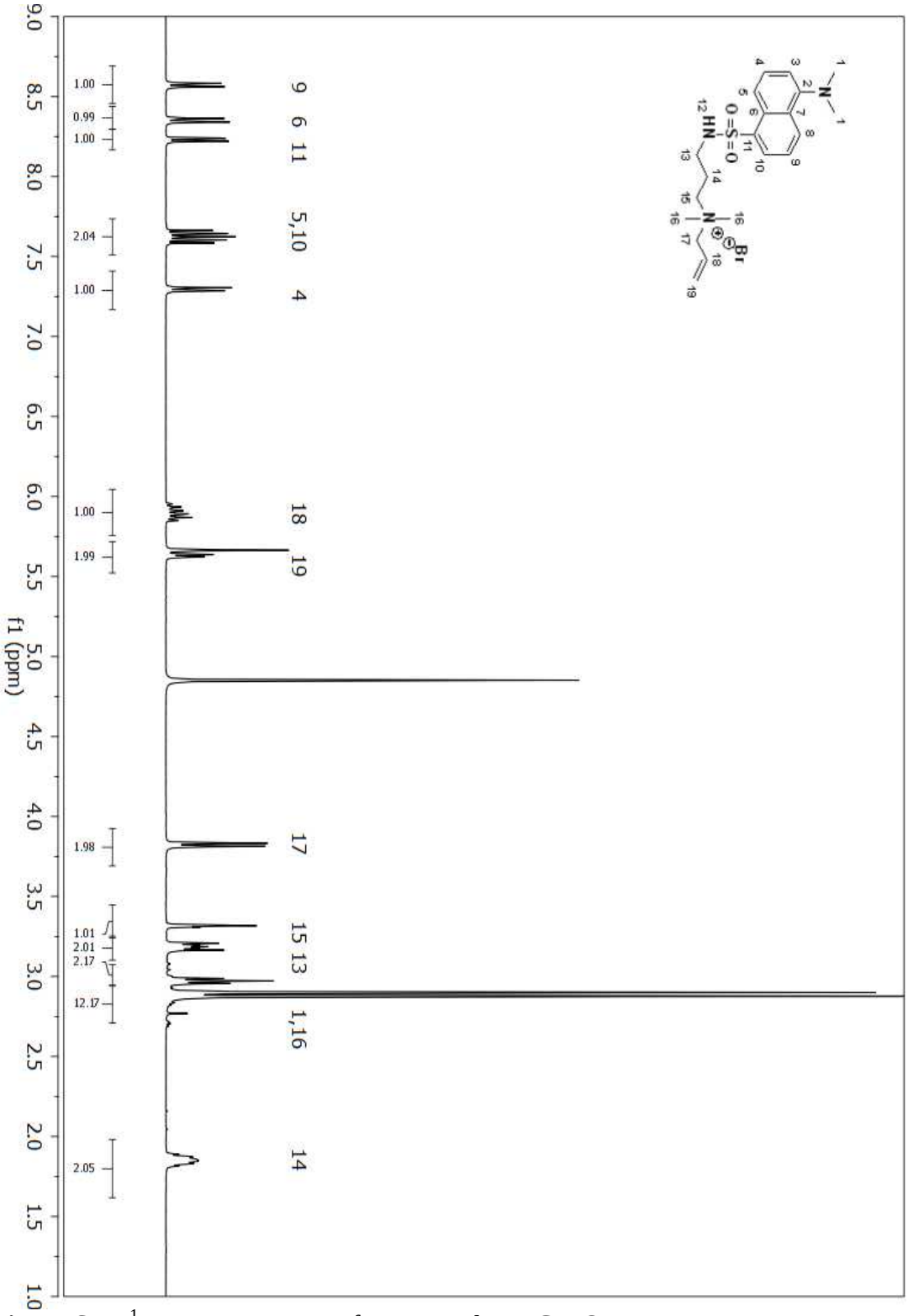

Figure S55. ^{1}H NMR spectrum of compound **7** in CD_3OD.

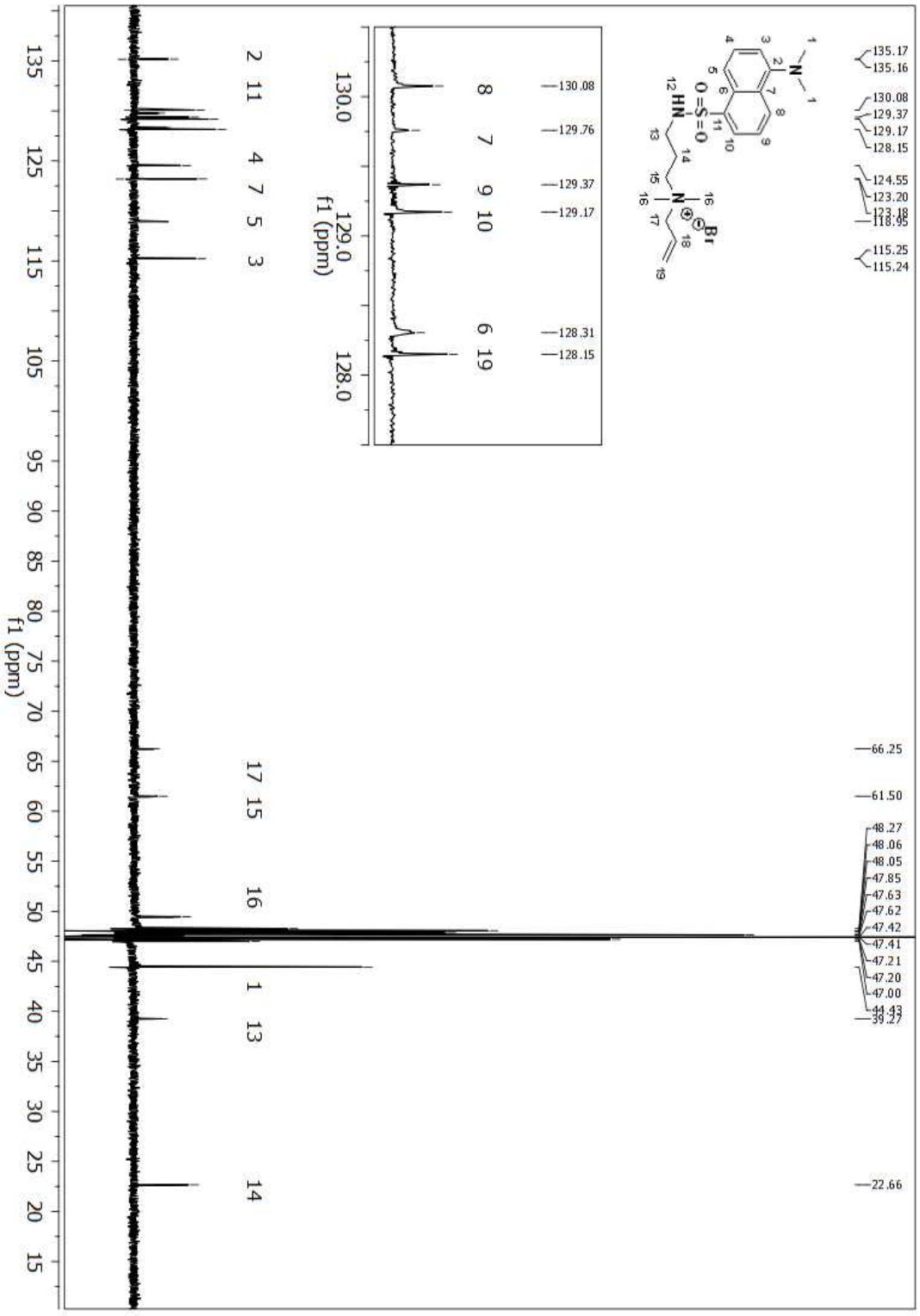

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7** in CD_3OD.

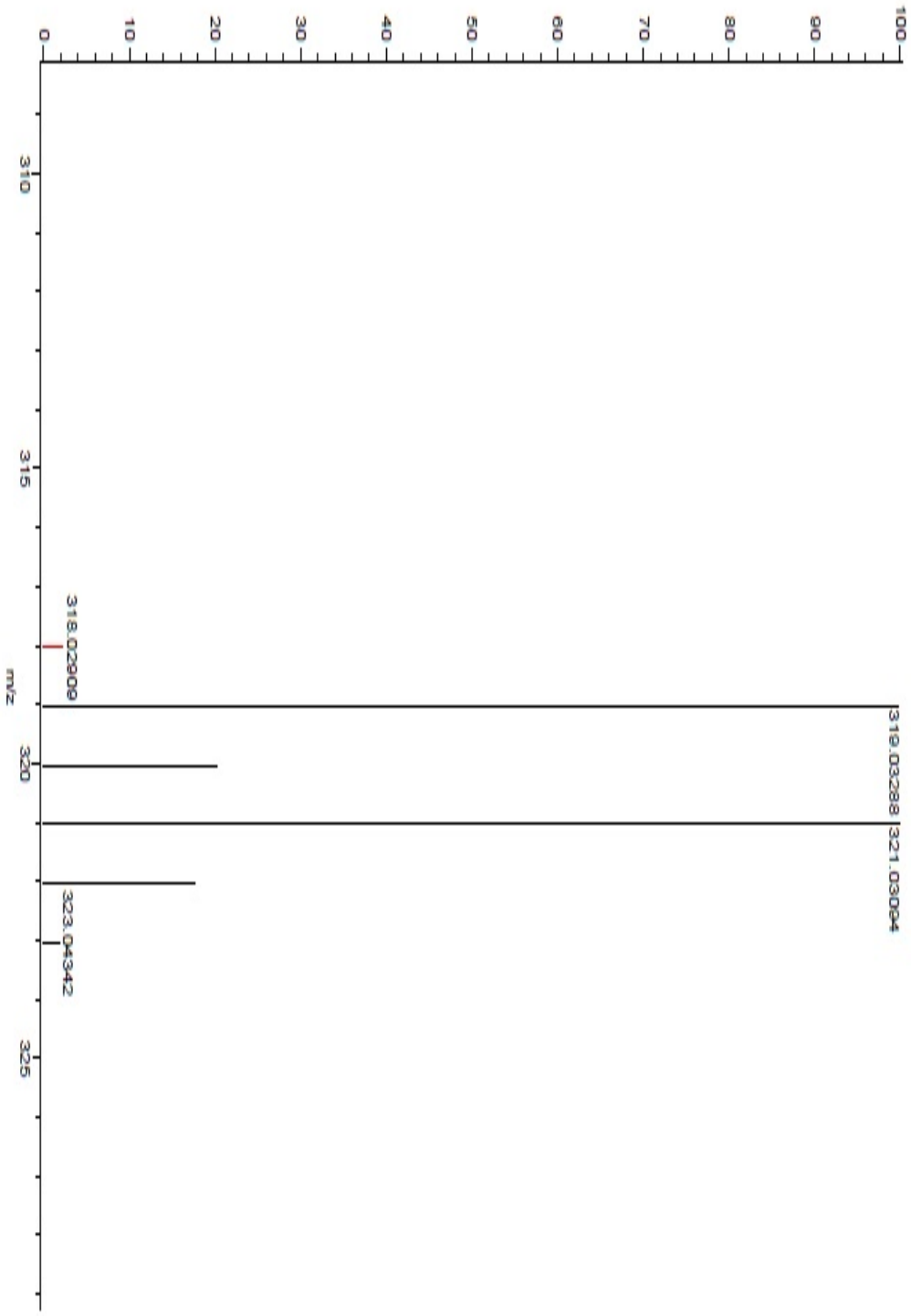

Figure S57. HRMS-DART spectrum of **4-(3-bromopropoxy)benzophenone**.

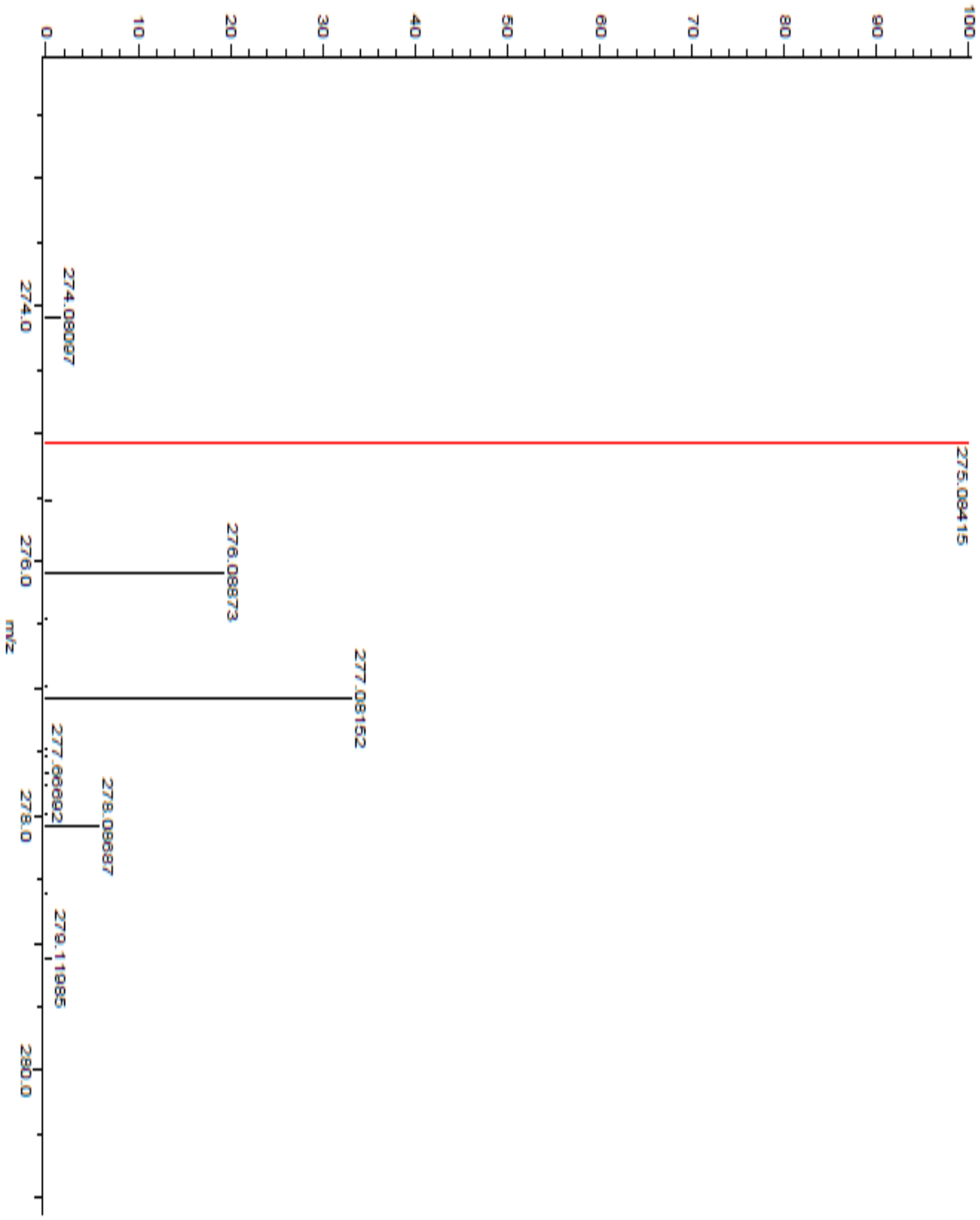

Figure S58. HRMS-DART spectrum of **4-(3-chloropropoxy)benzophenone**.

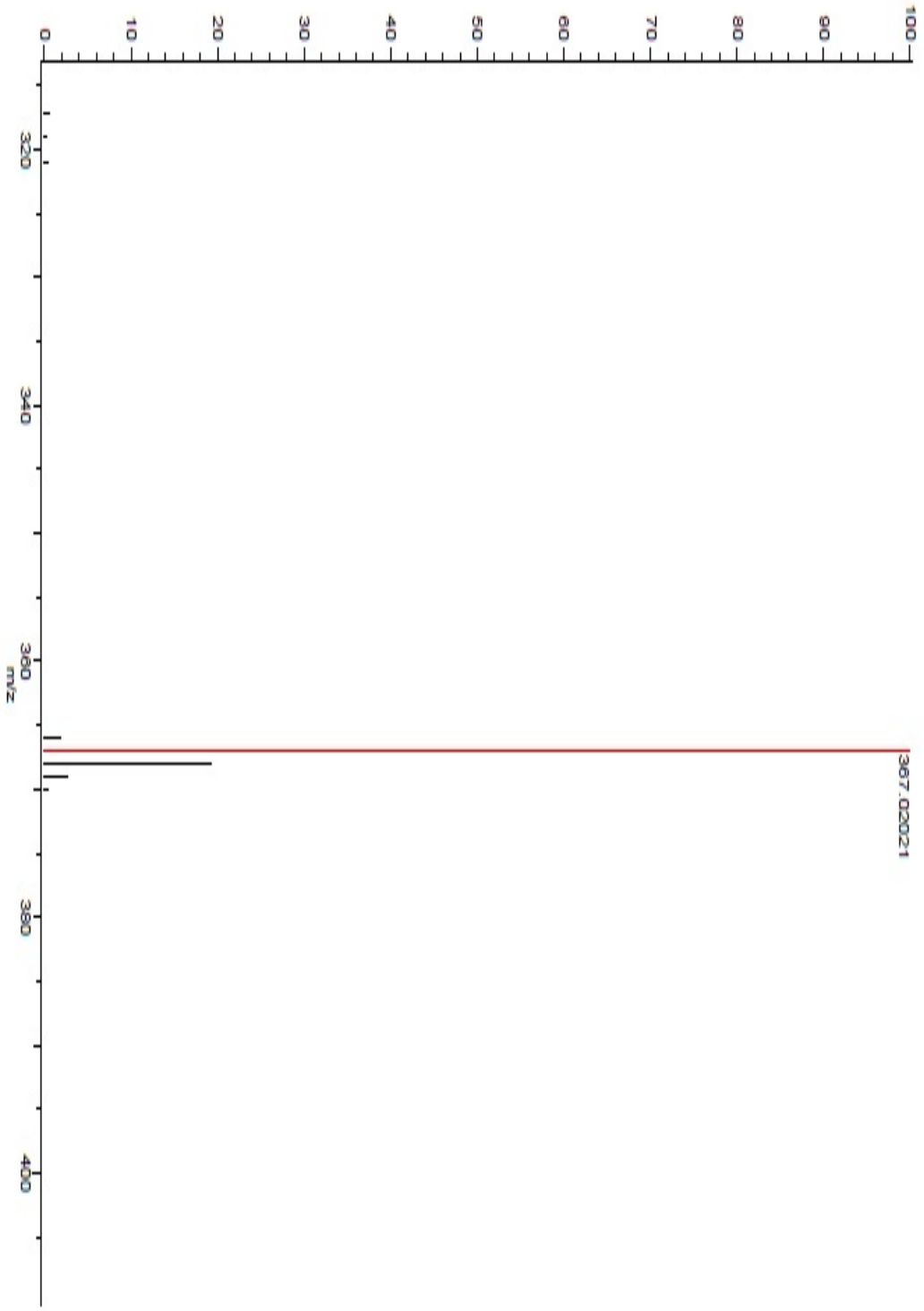

Figure S59. HRMS-DART spectrum of **4-(3-iodopropoxy)benzophenone**.

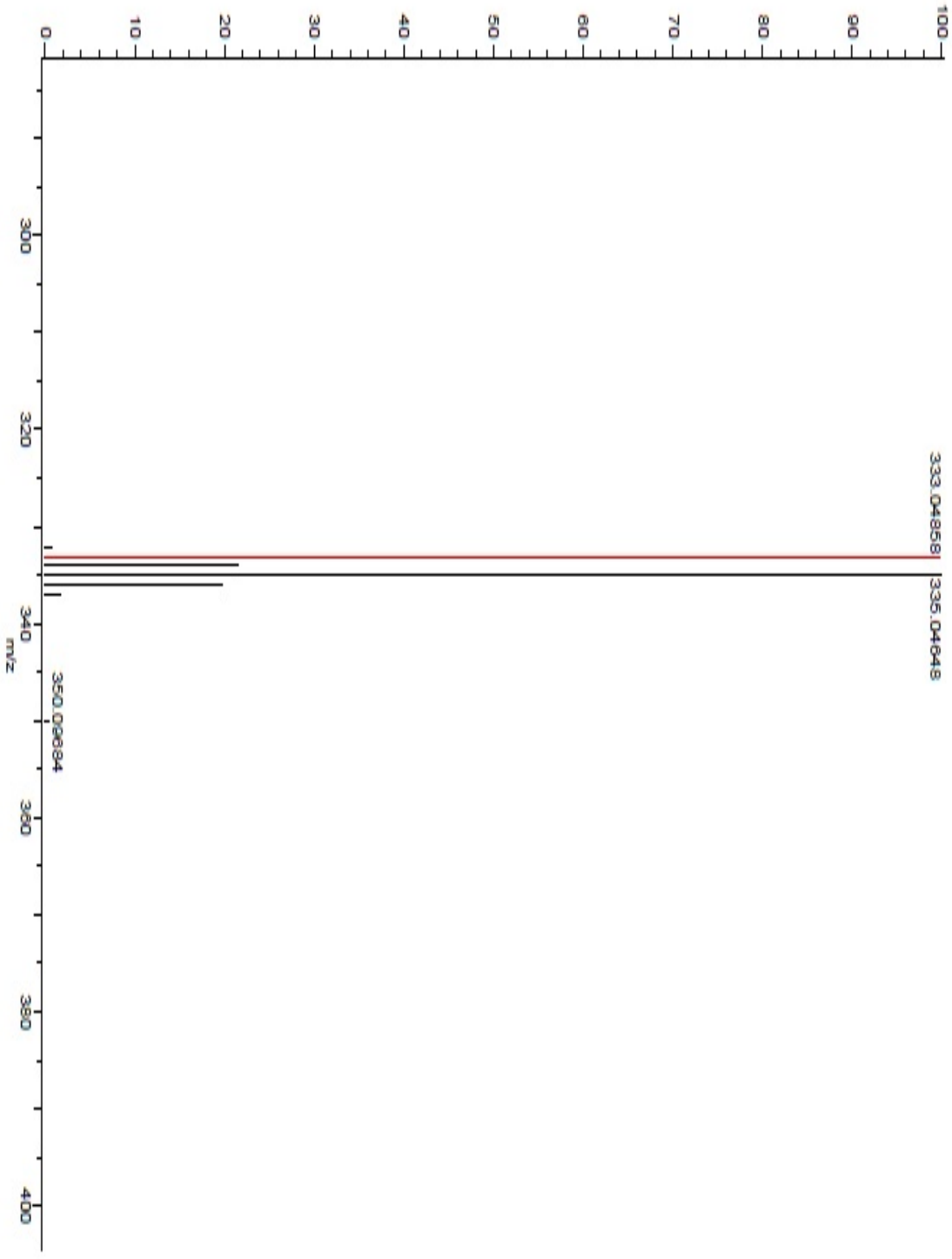

Figure S60. HRMS-DART spectrum of **4-(4-bromobutoxy)benzophenone**.

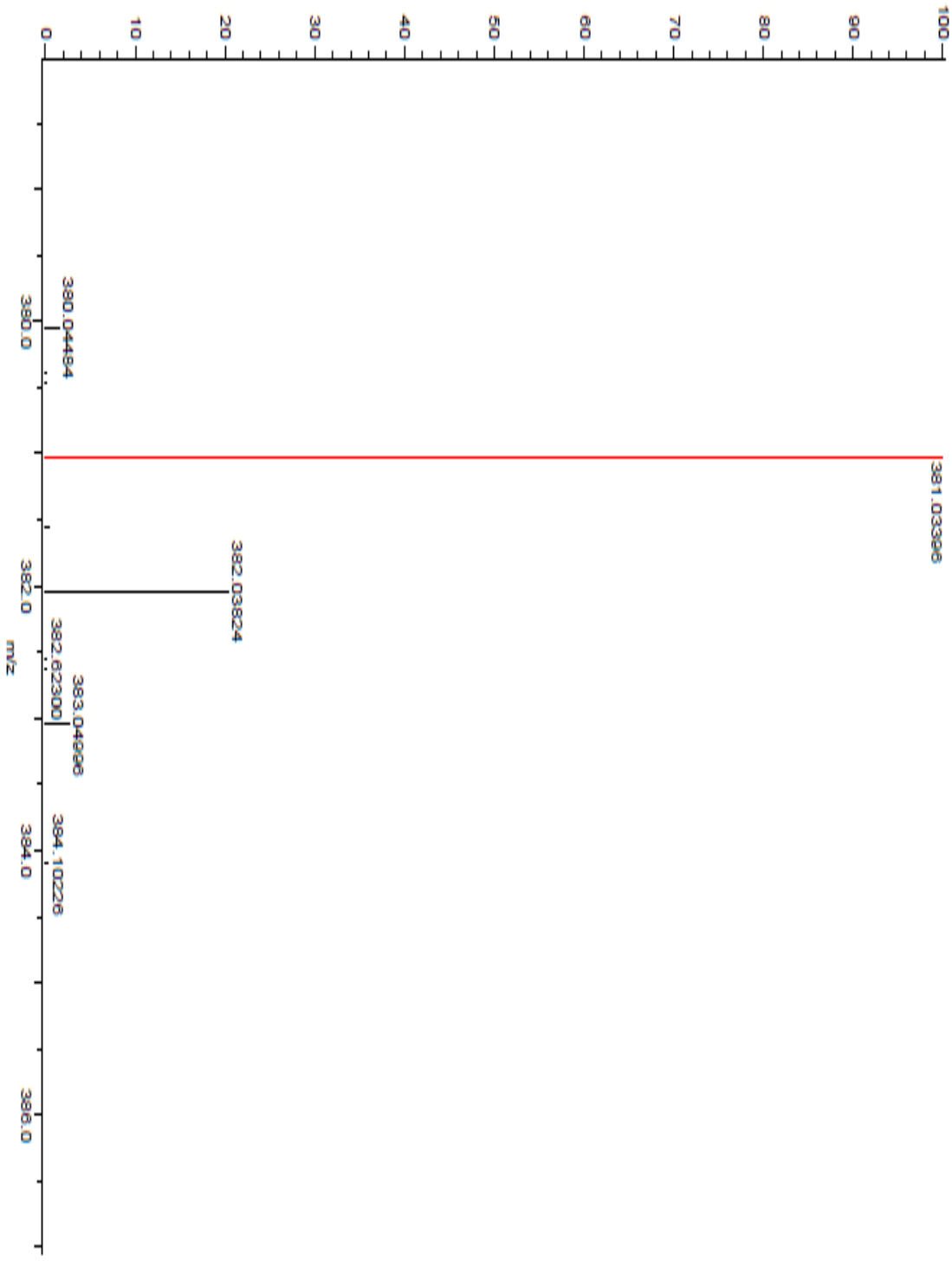

Figure S61. HRMS-DART spectrum of **4-(4-iodobutoxy)benzophenone**.

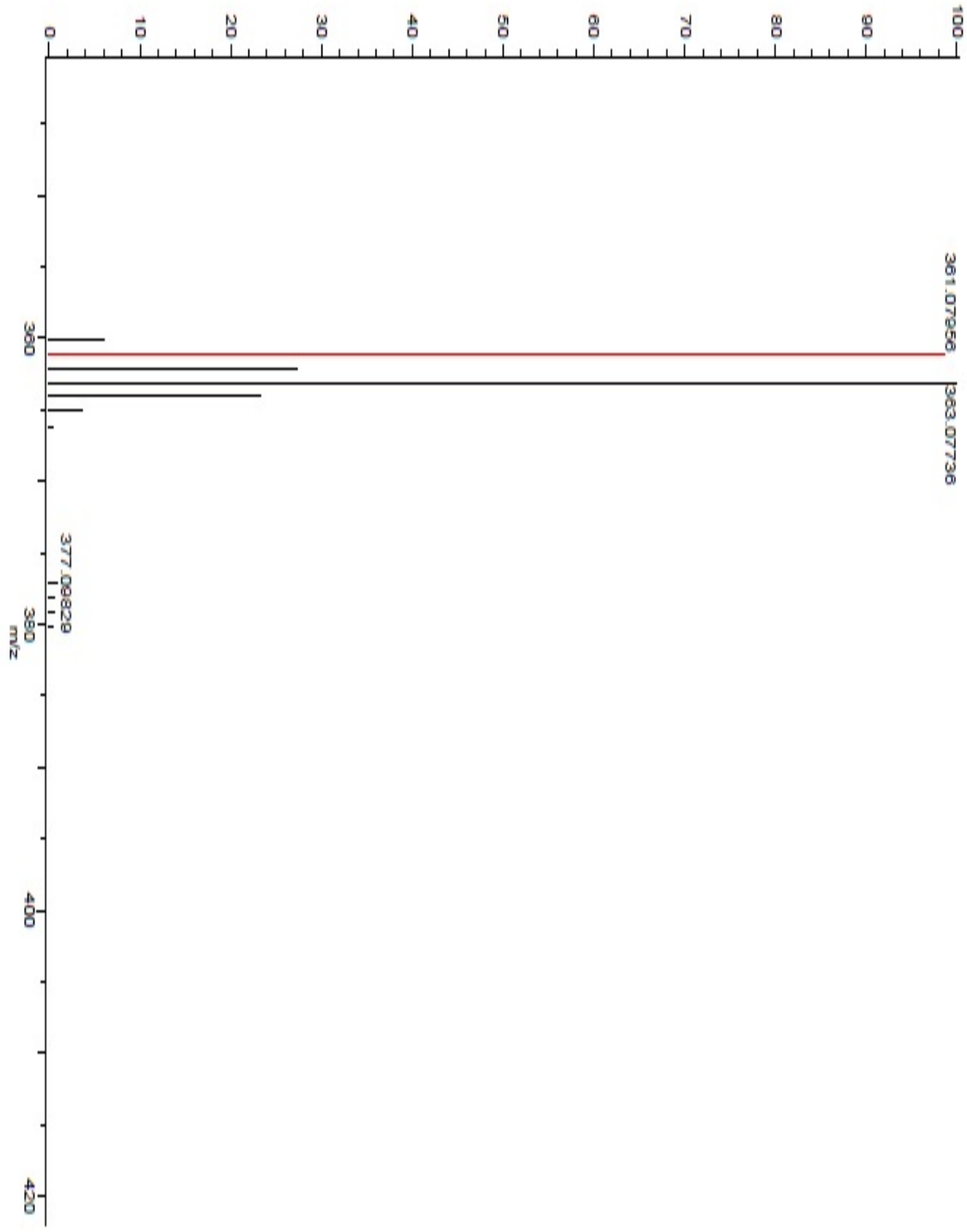

Figure S62. HRMS-DART spectrum of **4-(6-bromobutoxy)benzophenone**.

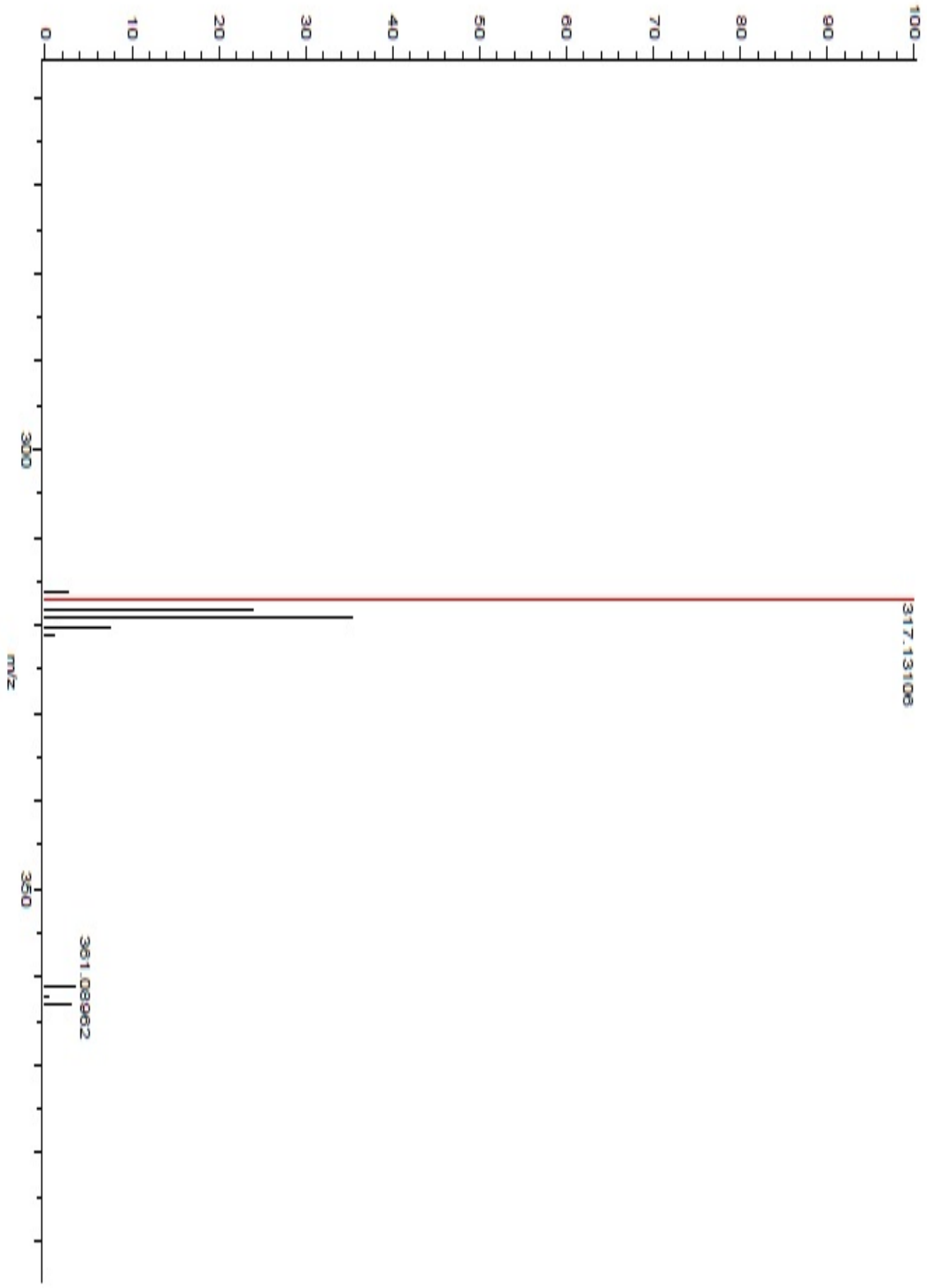

Figure S63. HRMS-DART spectrum of **4-(6-chlorobutoxy)benzophenone**.

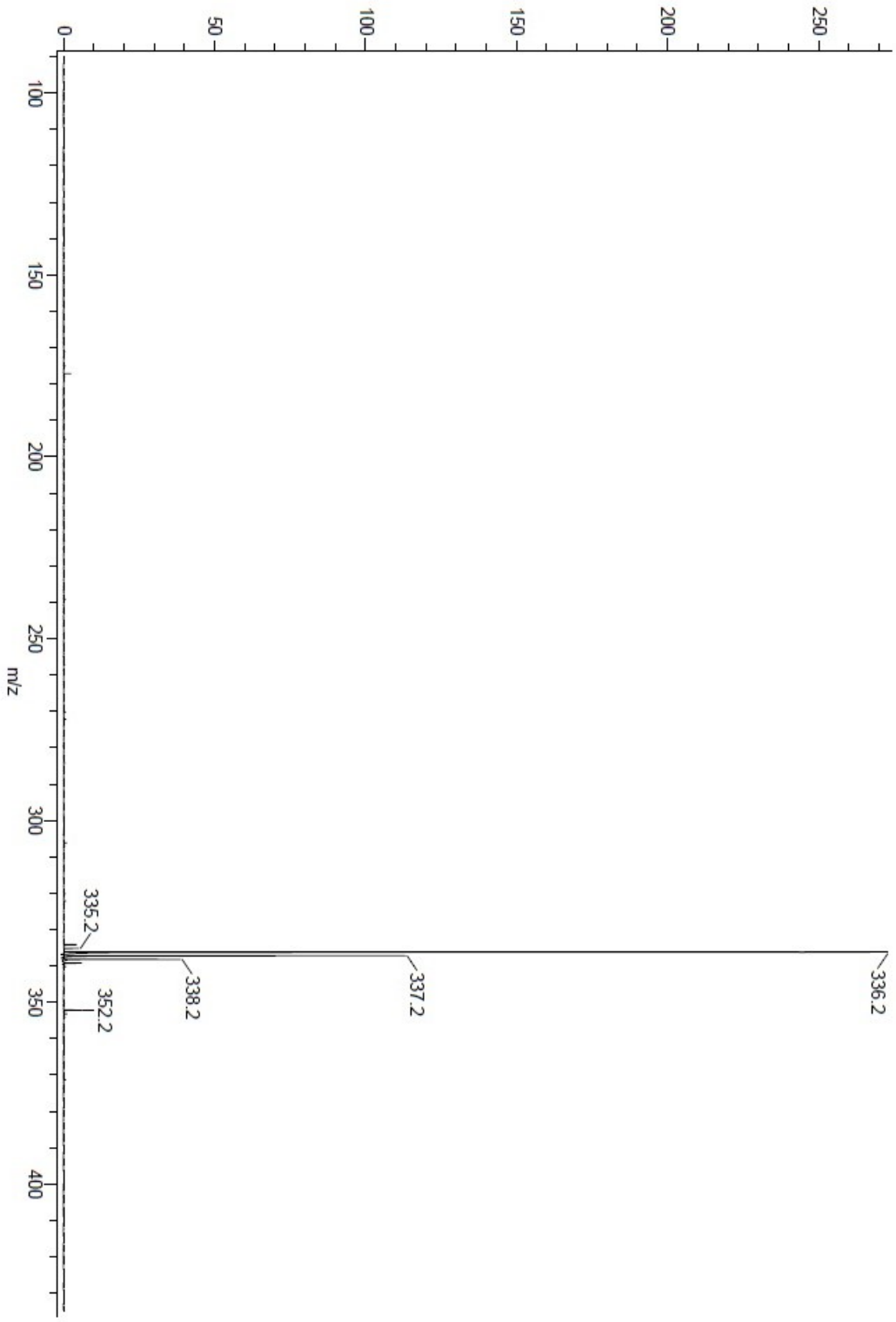

Figure S64. DART spectrum of compound **1**.

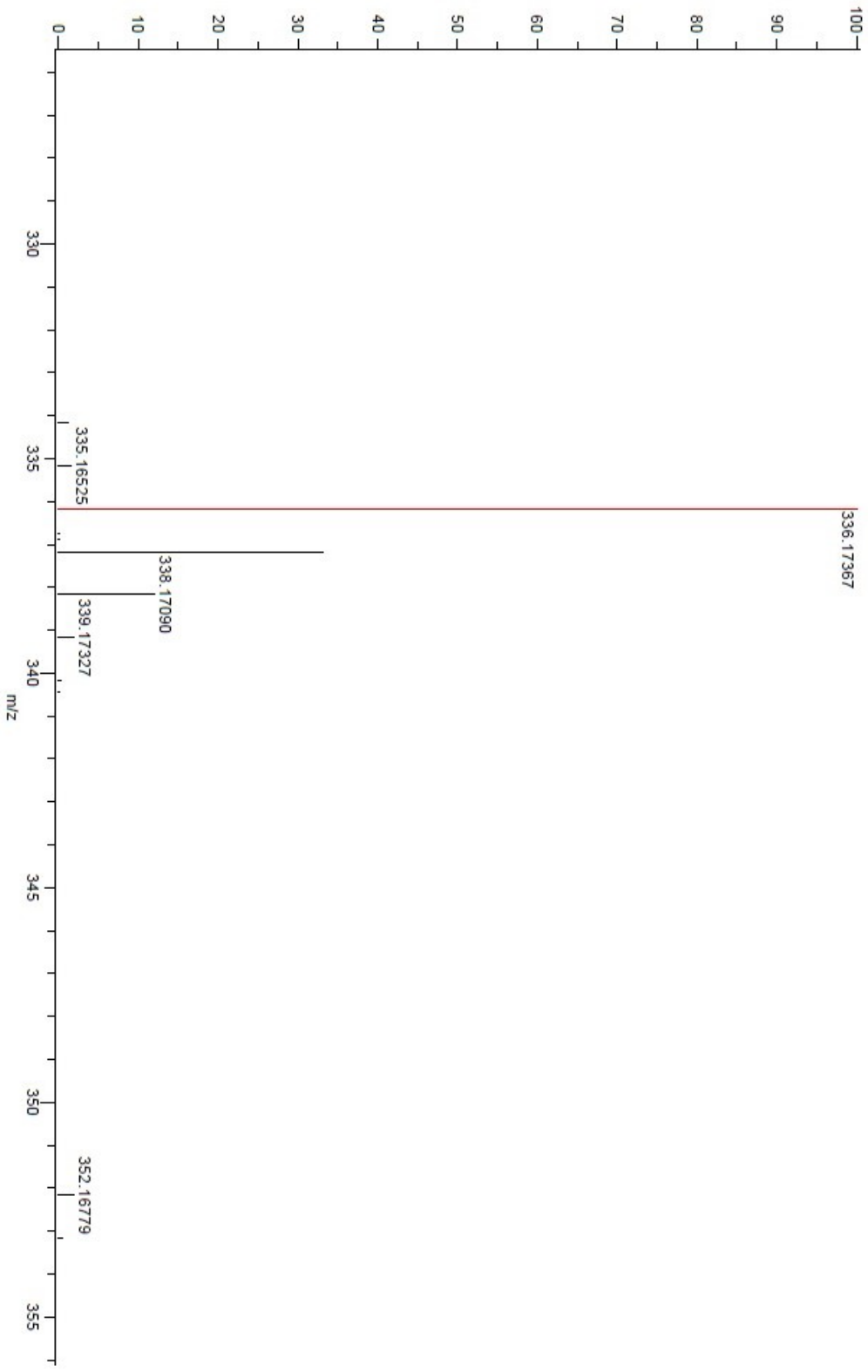

Figure S65. HRMS-DART spectrum of compound **1**.

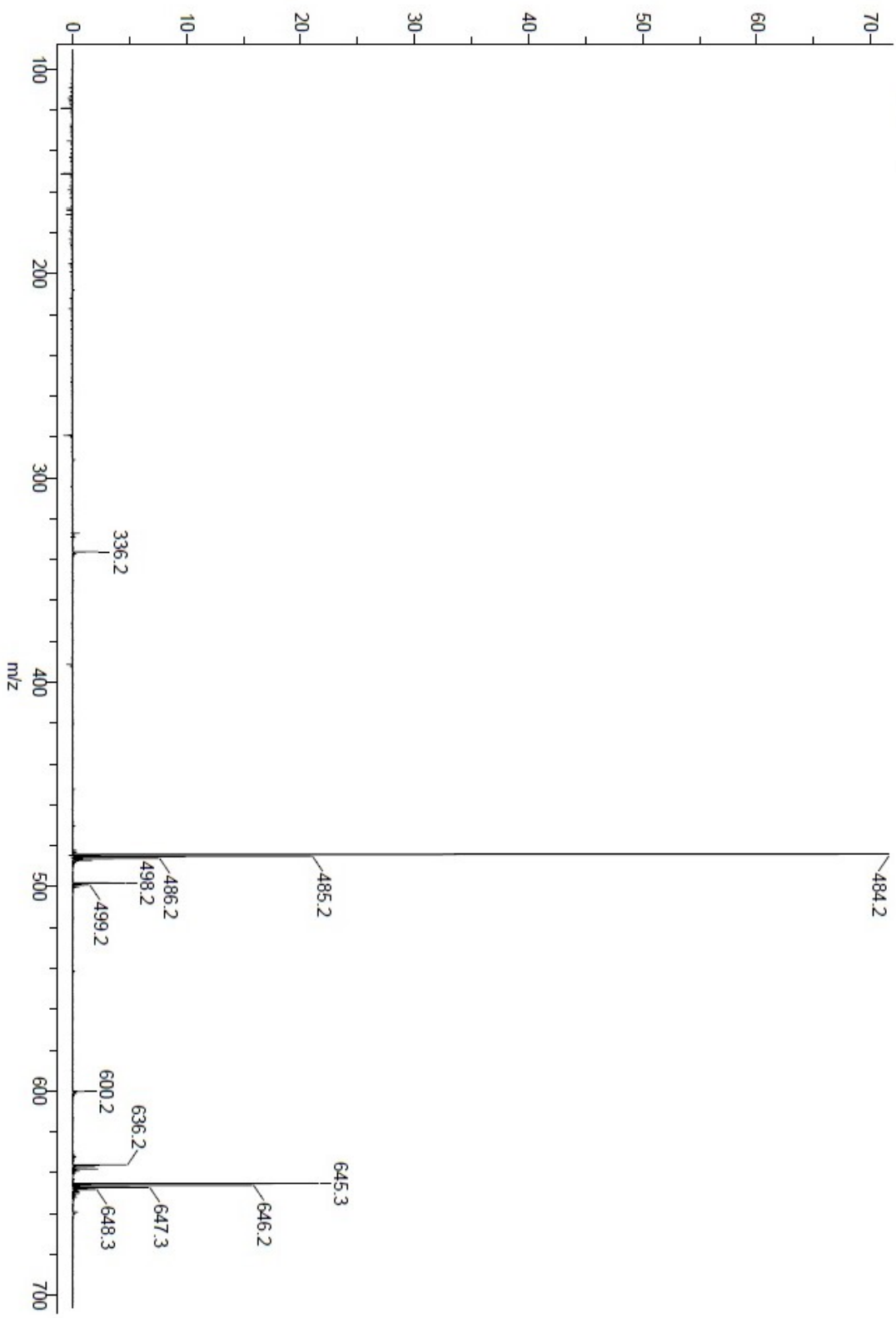

Figure S66. HRMS-DART spectrum of compound **2**.

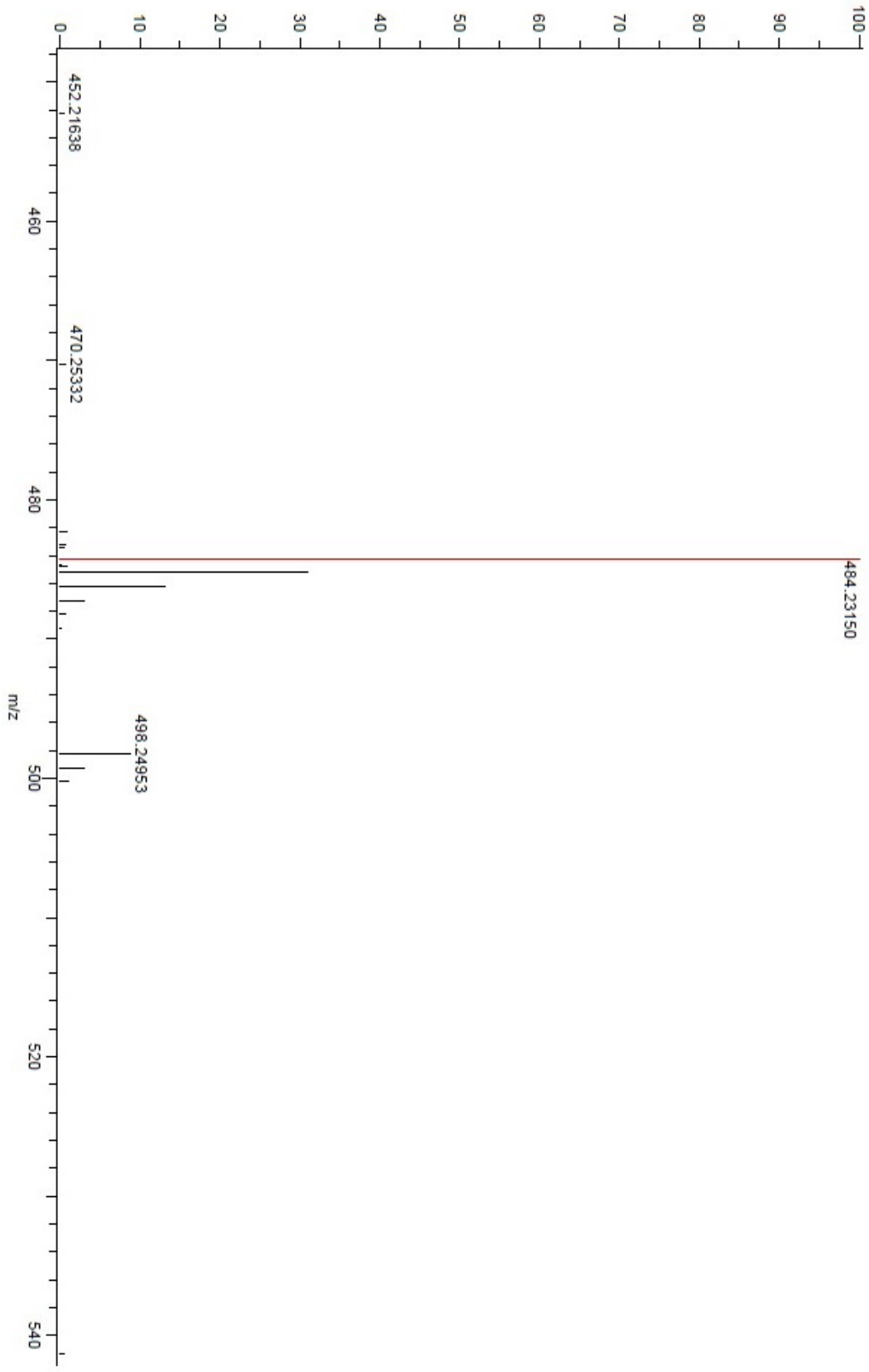

Figure S67. HRMS-DART spectrum of compound **2**.

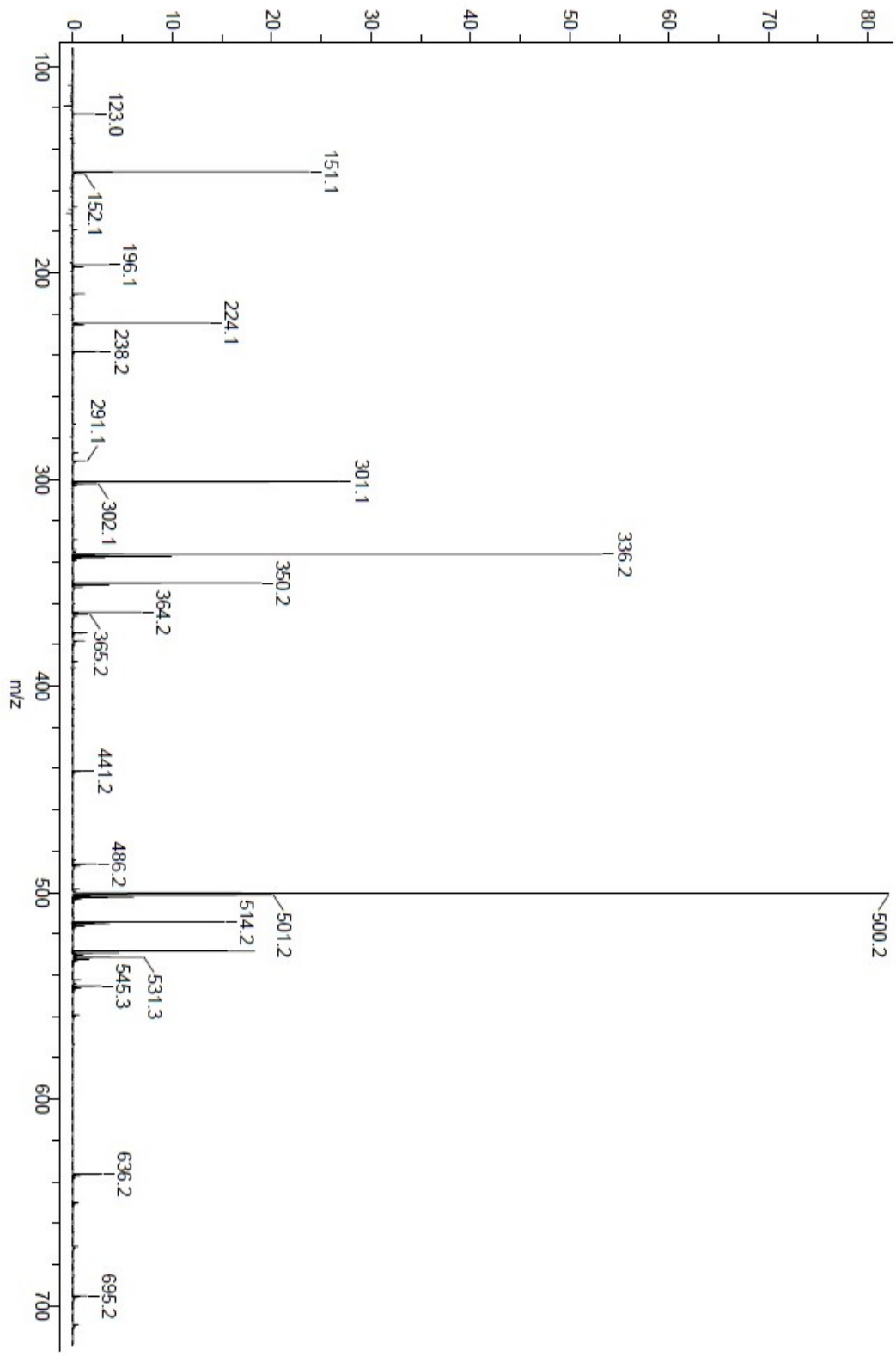

Figure S68. HRMS- DART spectrum of compound **3a**.

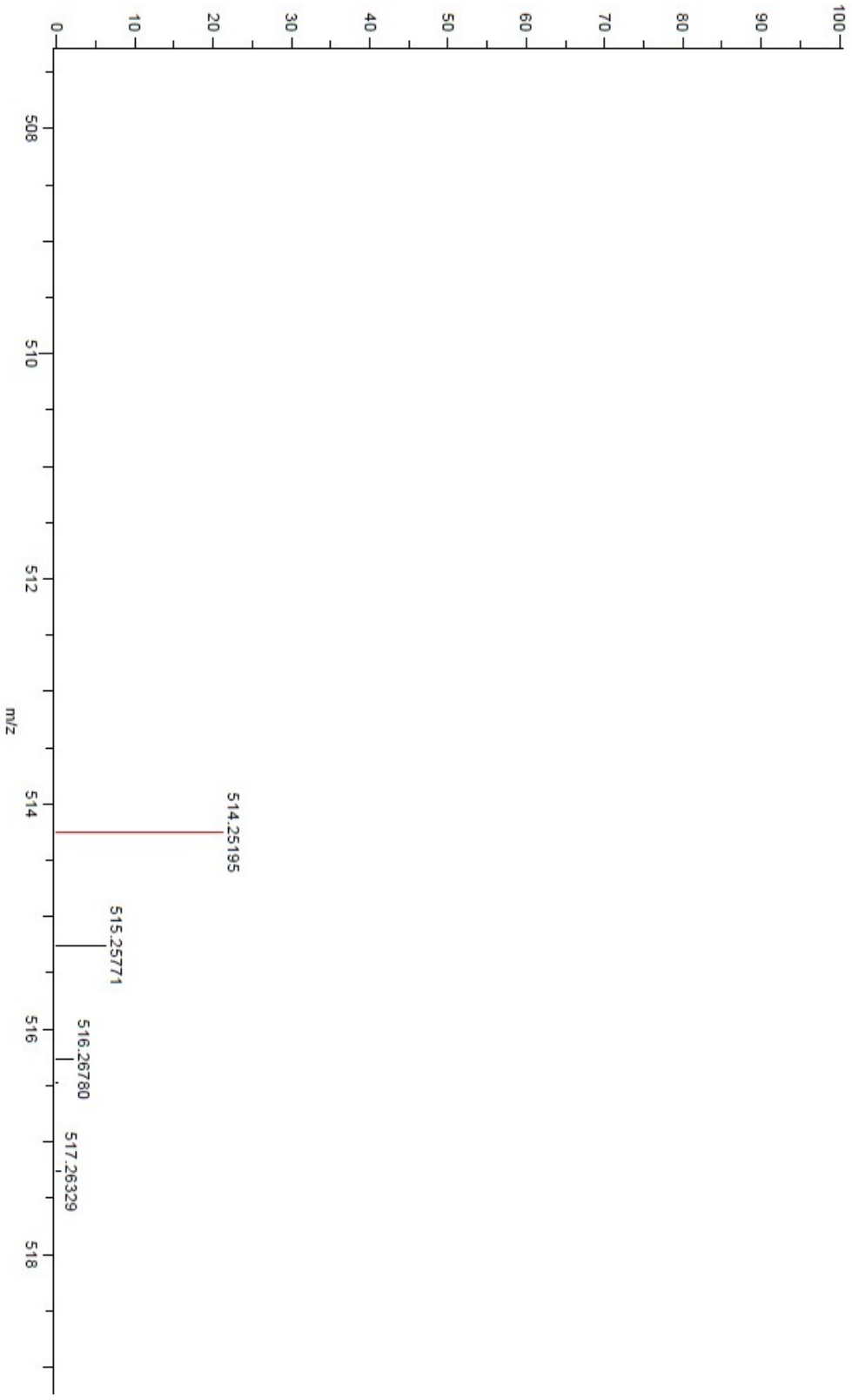

Figure S69. HRMS-DART spectrum of compound **3a**.

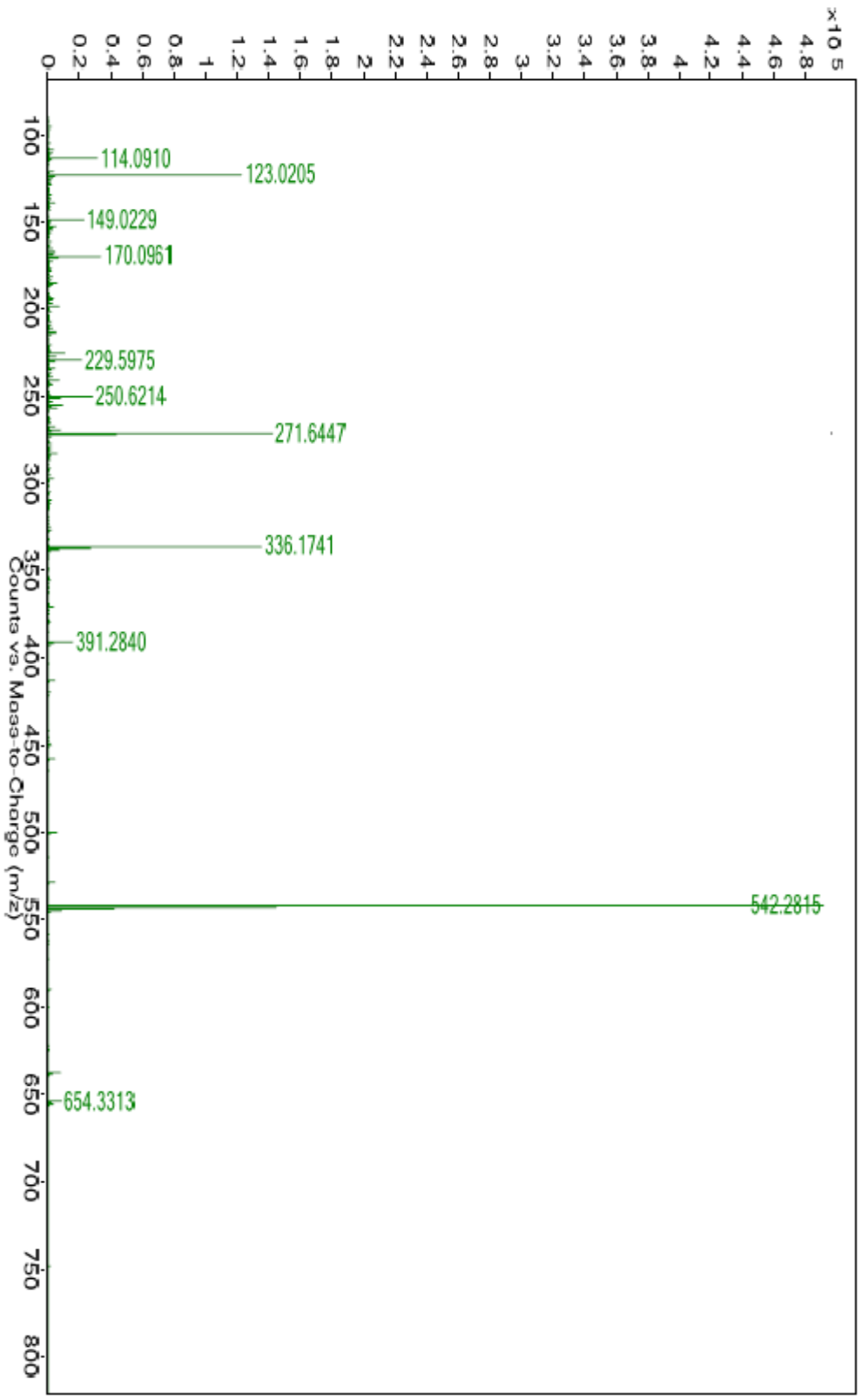

Figure S70. HRMS-ESI-TOF spectrum of compound **3b**.

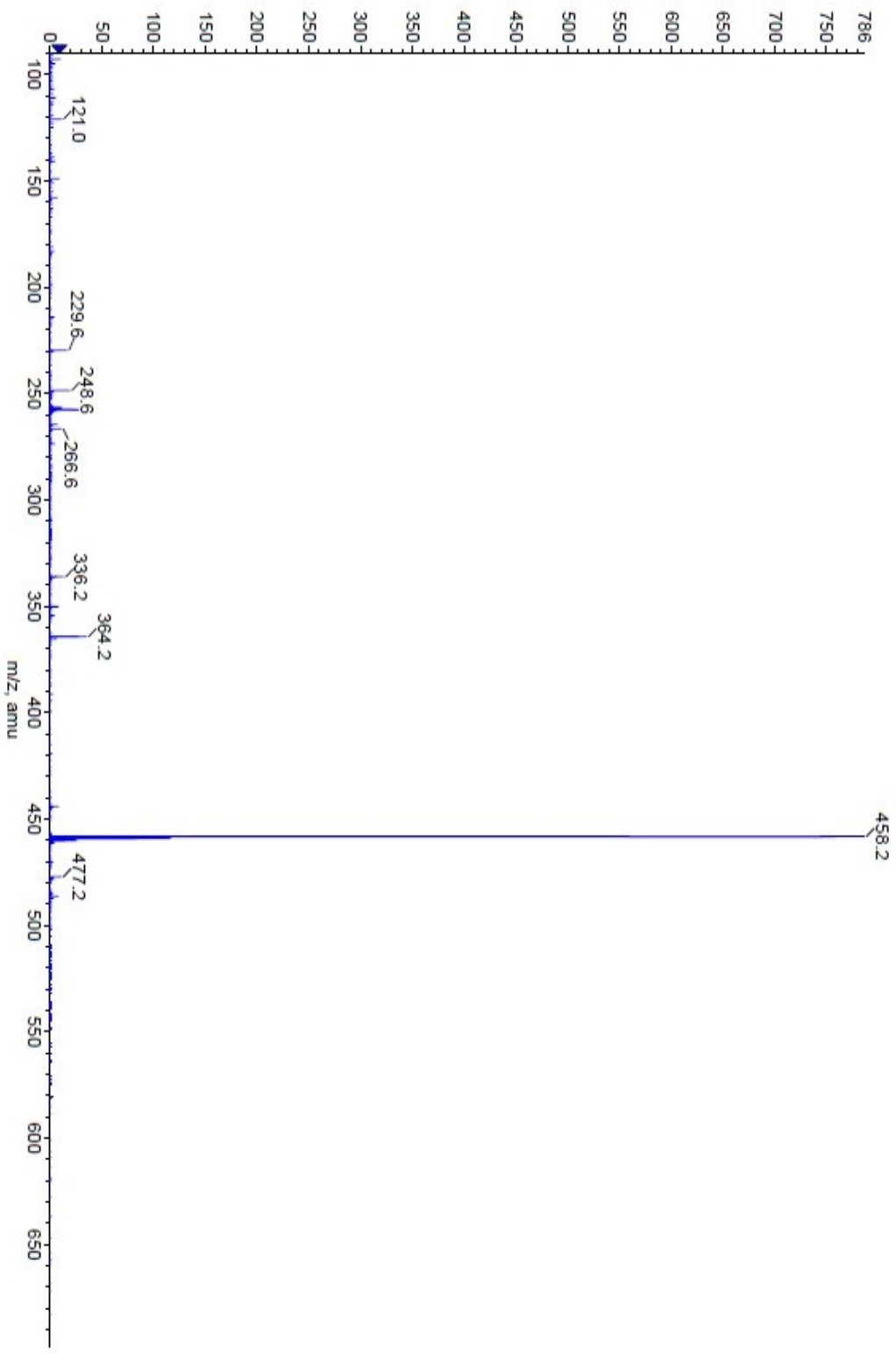

Figure S71. HRMS-ESI-TOF spectrum of compound **3c**.

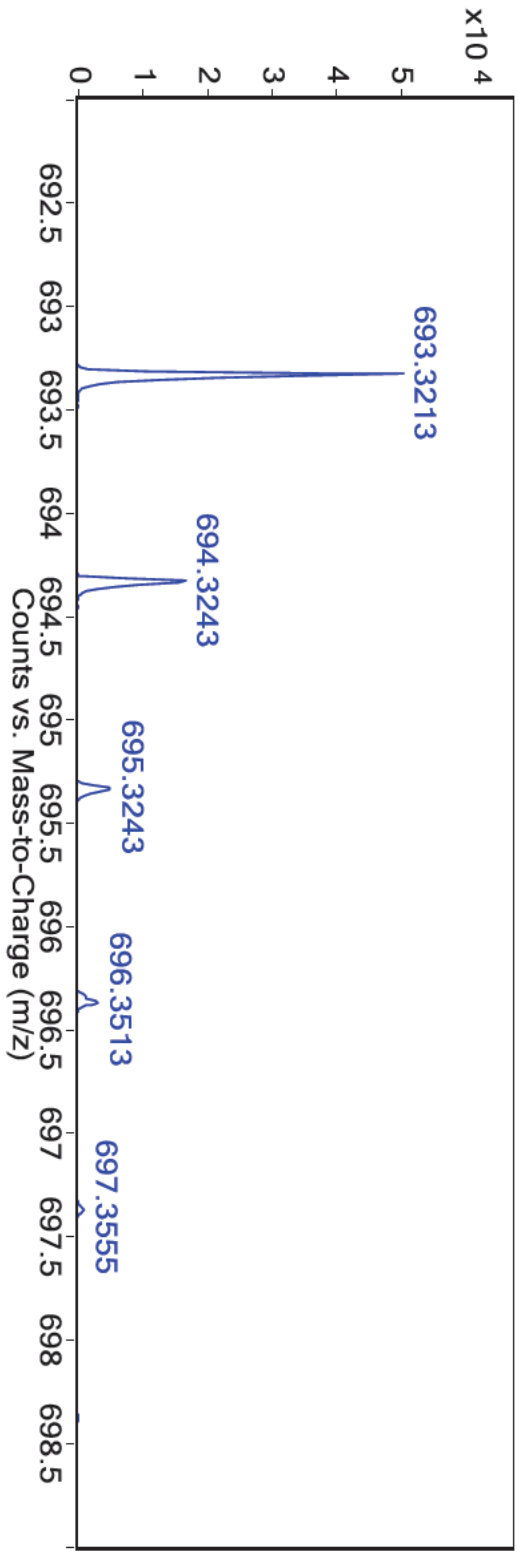

Figure S72. ESI-TOF spectrum of compound **4**.

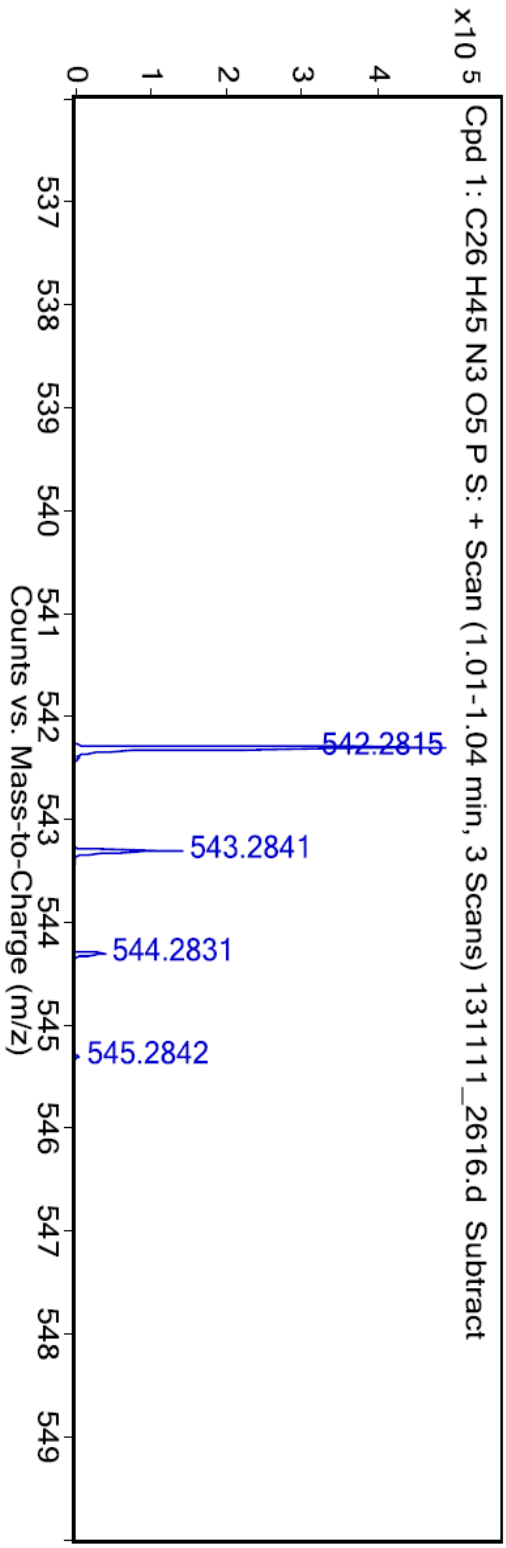

Figure S73. HRMS-ESI-TOF spectrum of compound **5**.

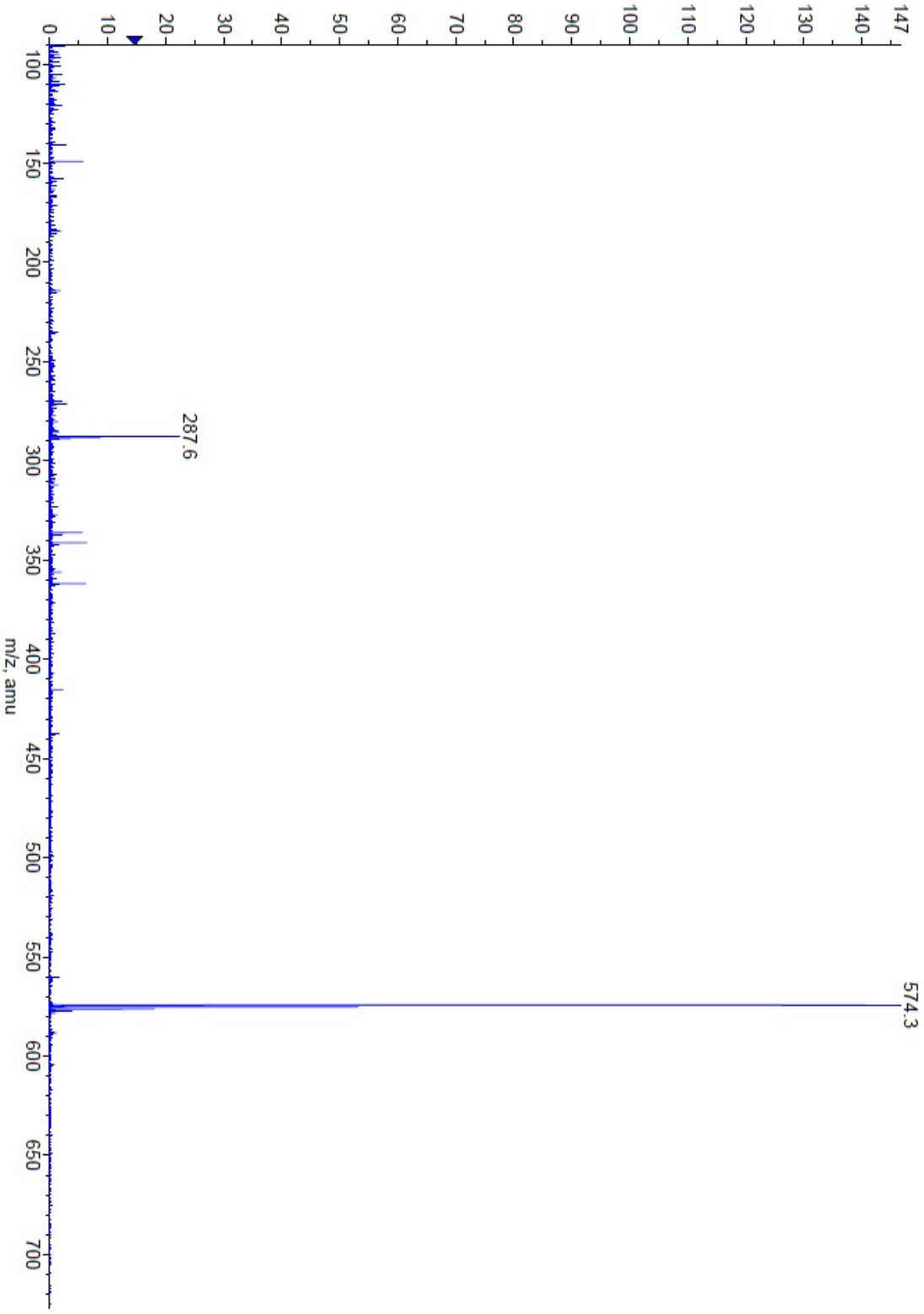

Figure S74. HRMS-ESI-TOF spectrum of compound **6a**.

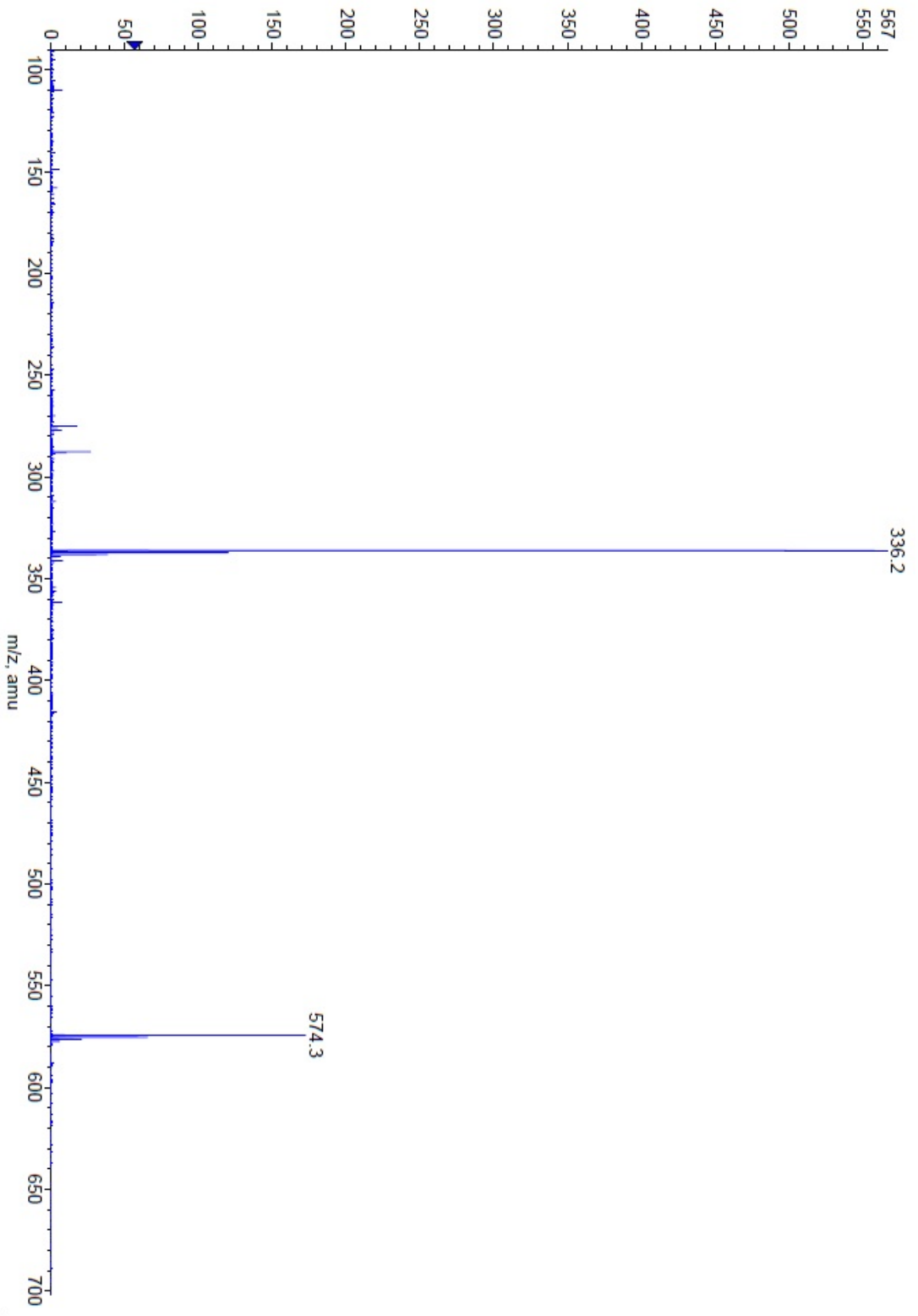

Figure S75. HRMS-ESI-TOF spectrum of compound **6b**.

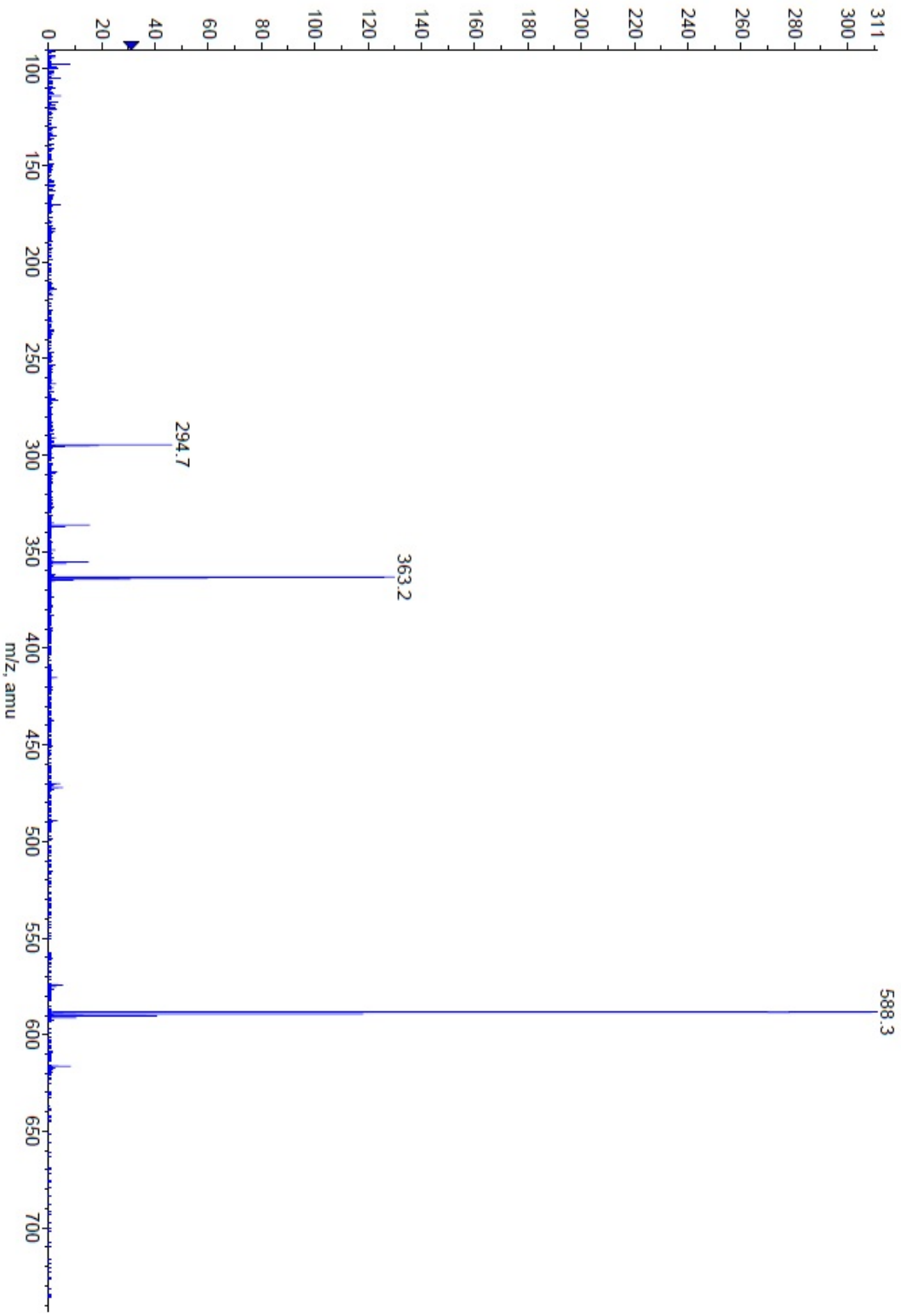

Figure S76. HRMS-ESI-TOF spectrum of compound **6c**.

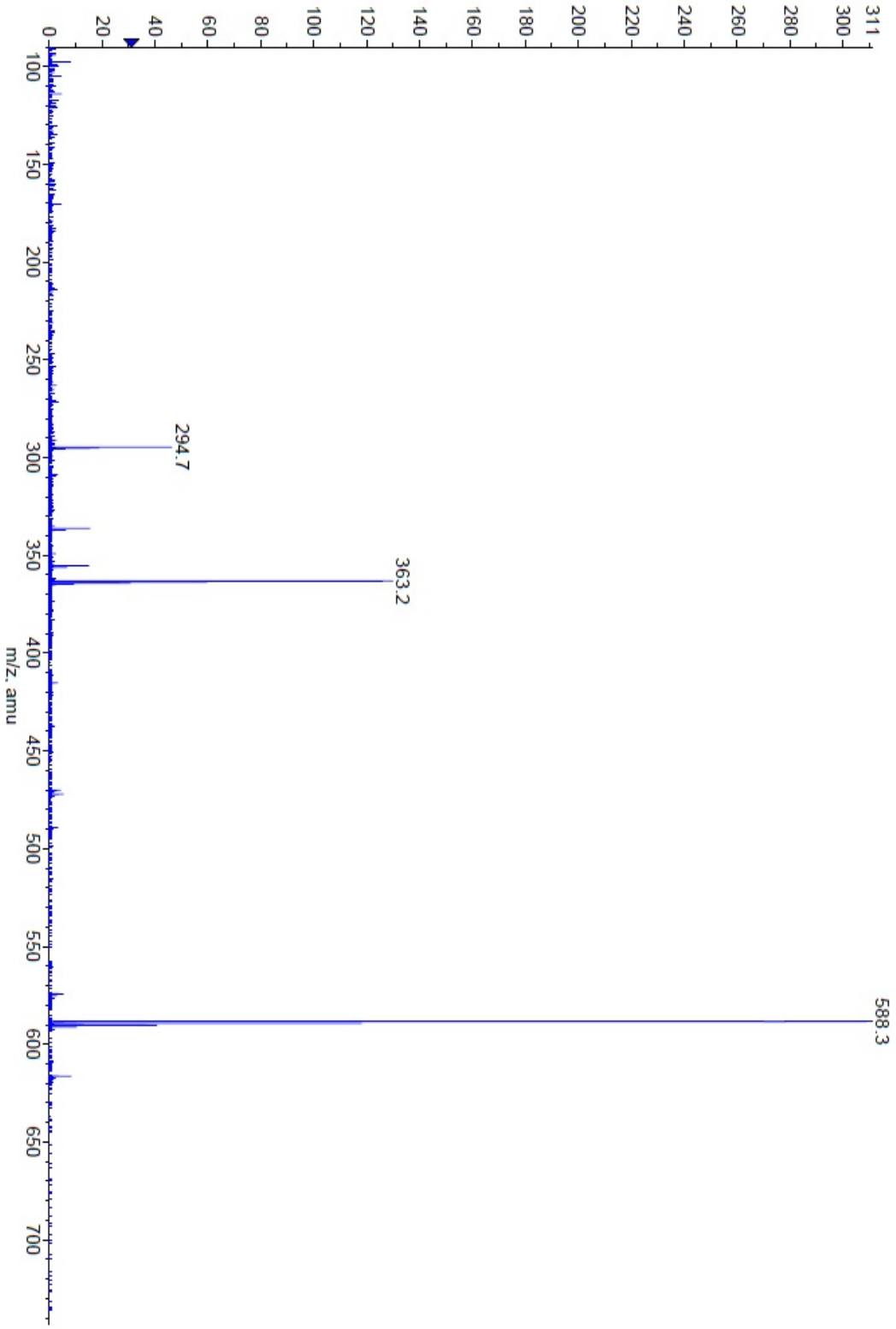

Figure S77. HRMS-ESI-TOF spectrum of compound **6d**.

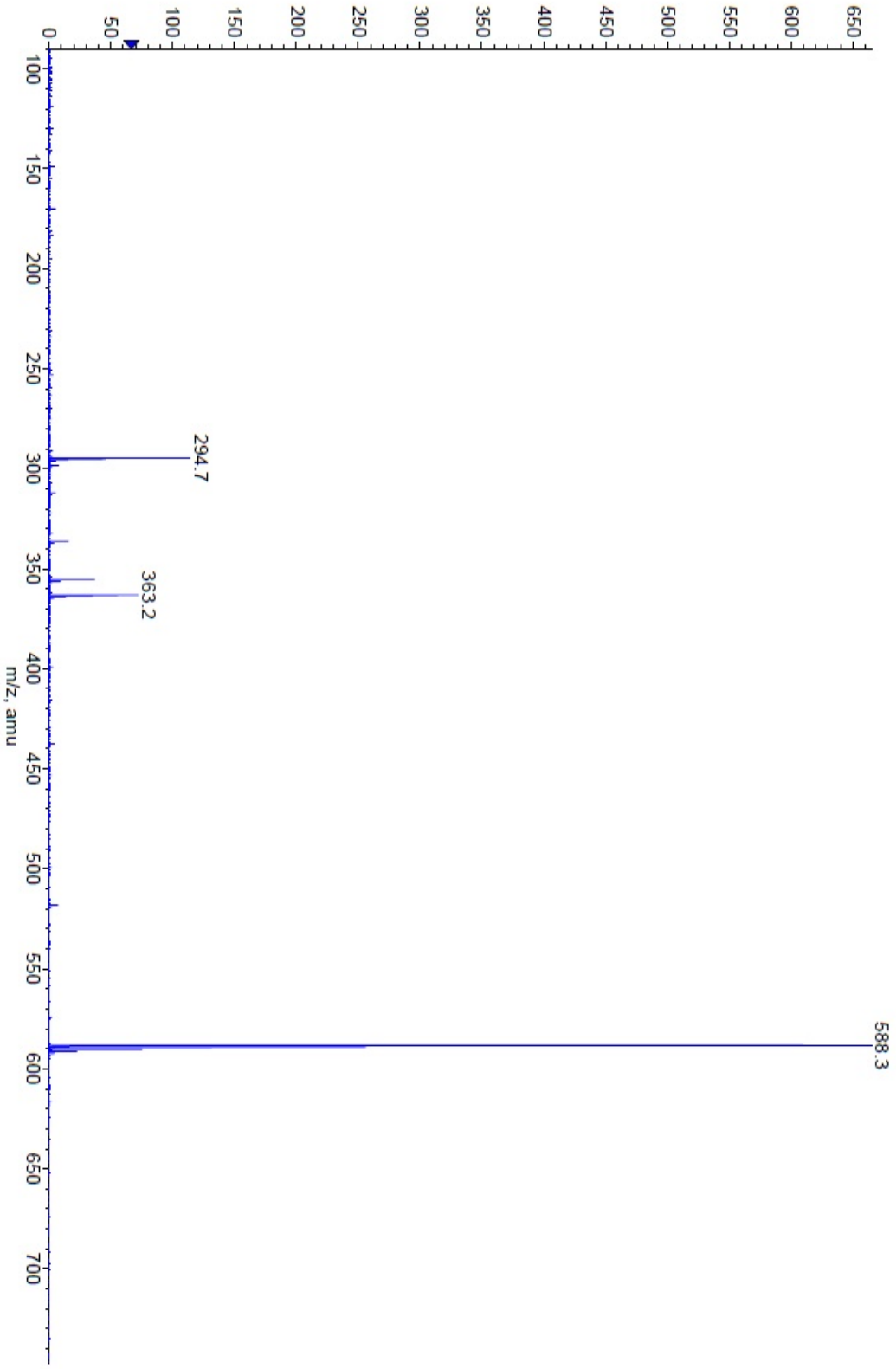

Figure S78**.** HRMS-ESI-TOF spectrum of compound **6e**.

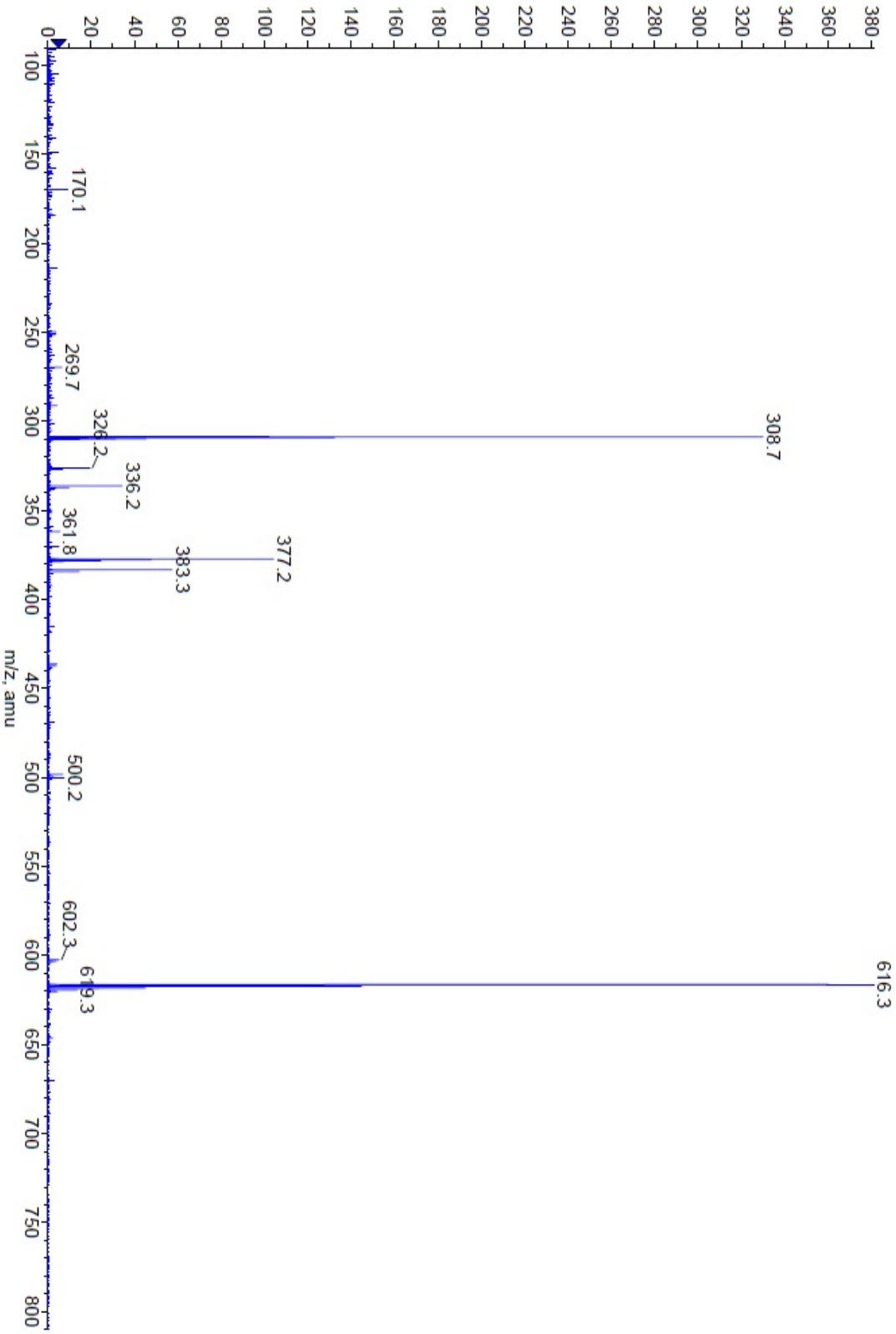

Figure S79. HRMS-ESI-TOF spectrum of compound **6f**.

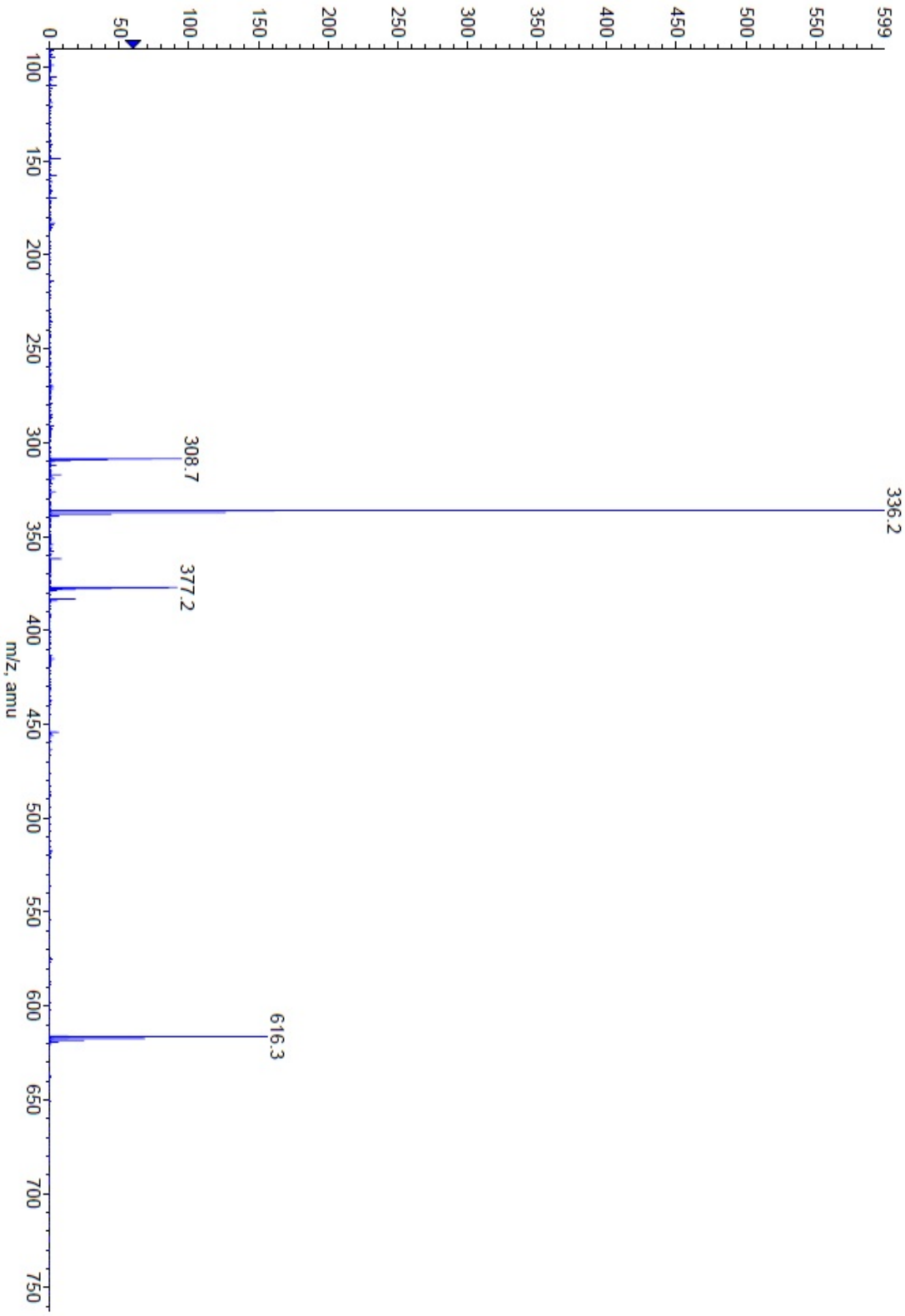

Figure S80. HRMS-ESI-TOF spectrum of compound **6g**.

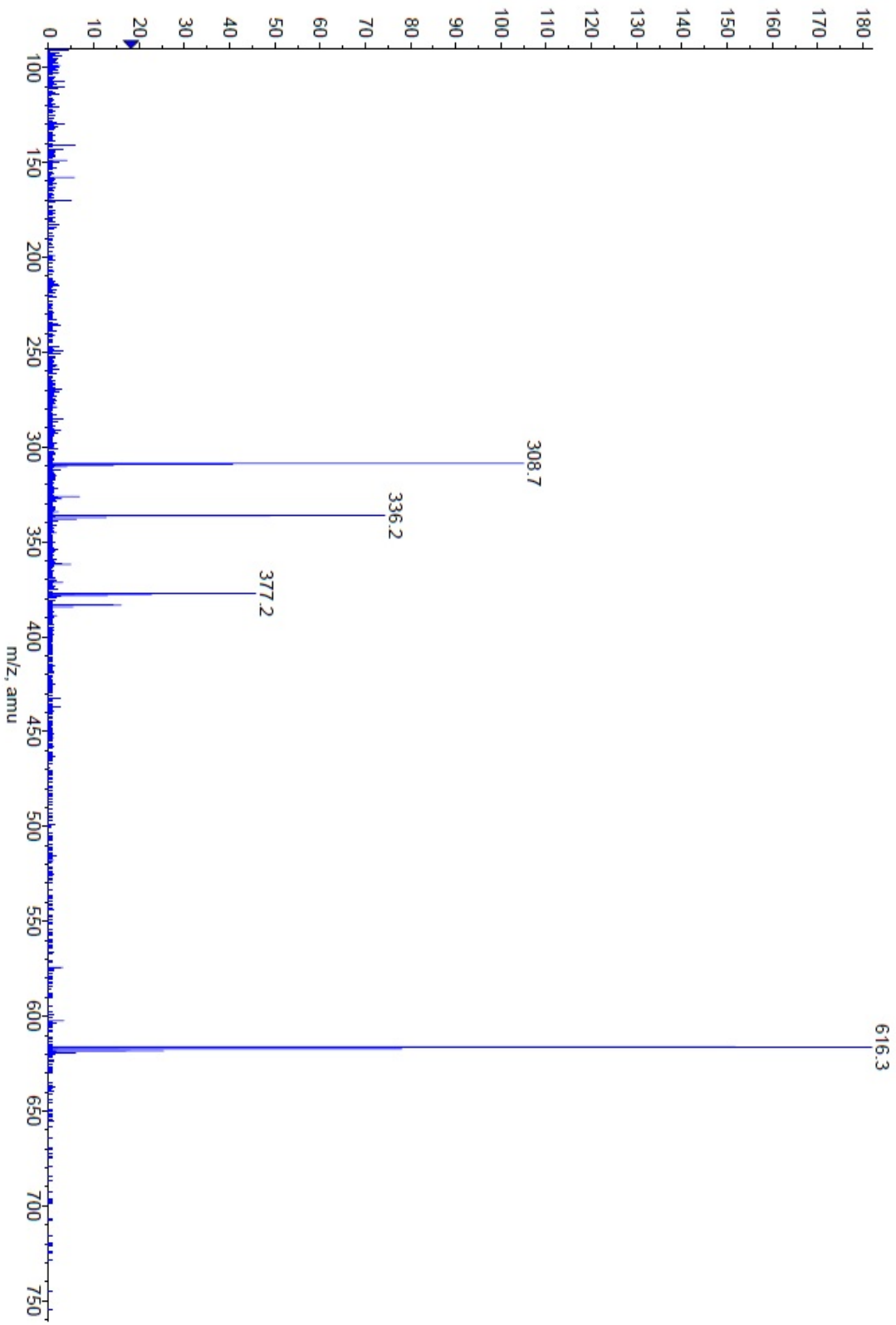

Figure S81. HRMS-ESI-TOF spectrum of compound **6h**.

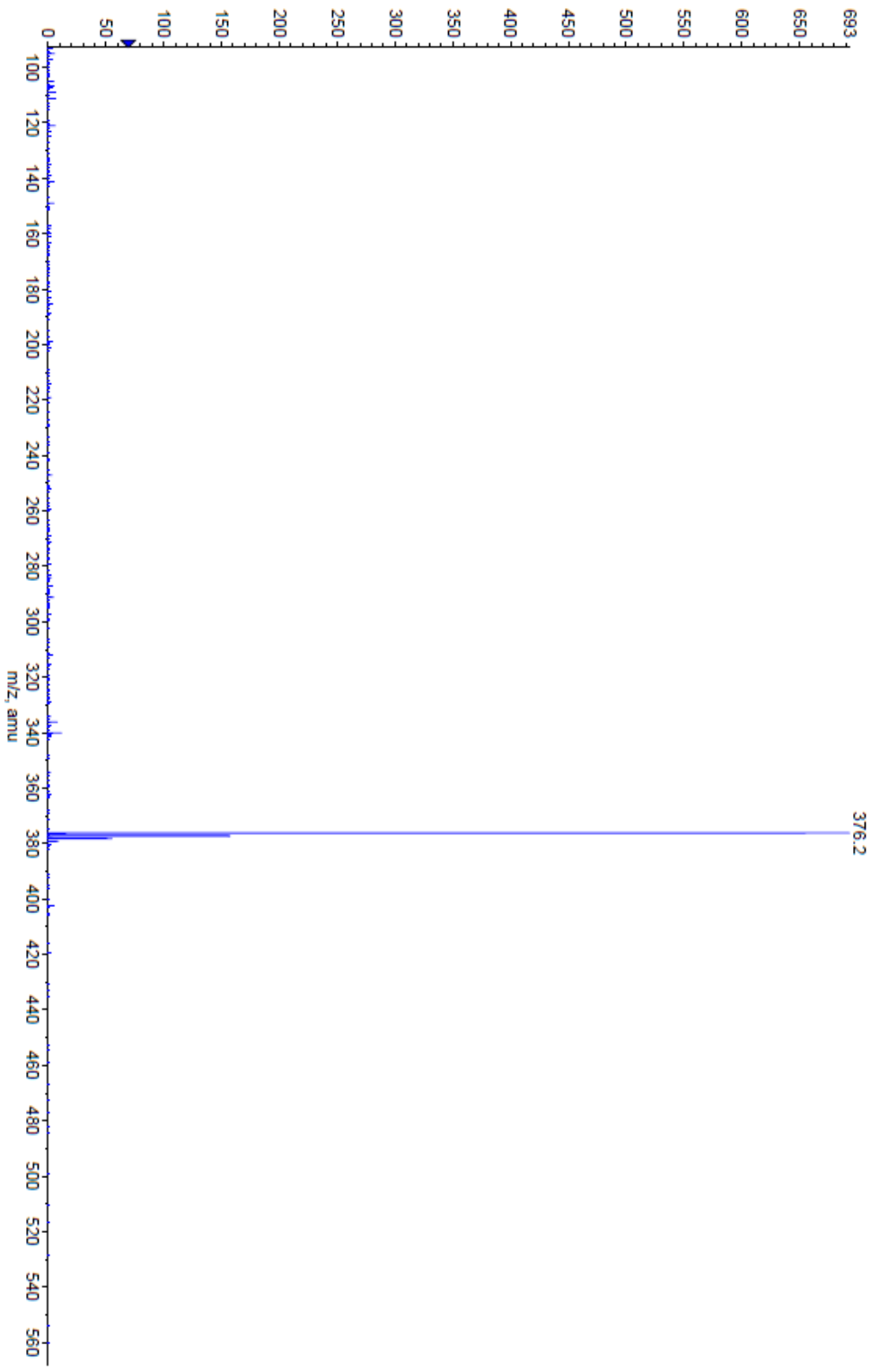

Figure S82. HRMS-ESI-TOF spectrum of compound **7**.

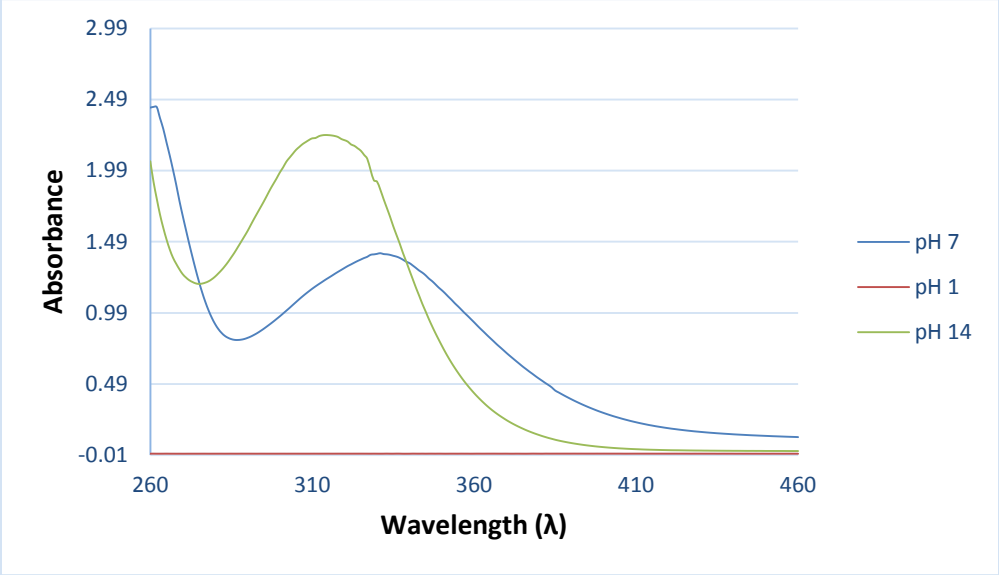

Figure S83. Effect of compound **2** absorption at different pH levels.

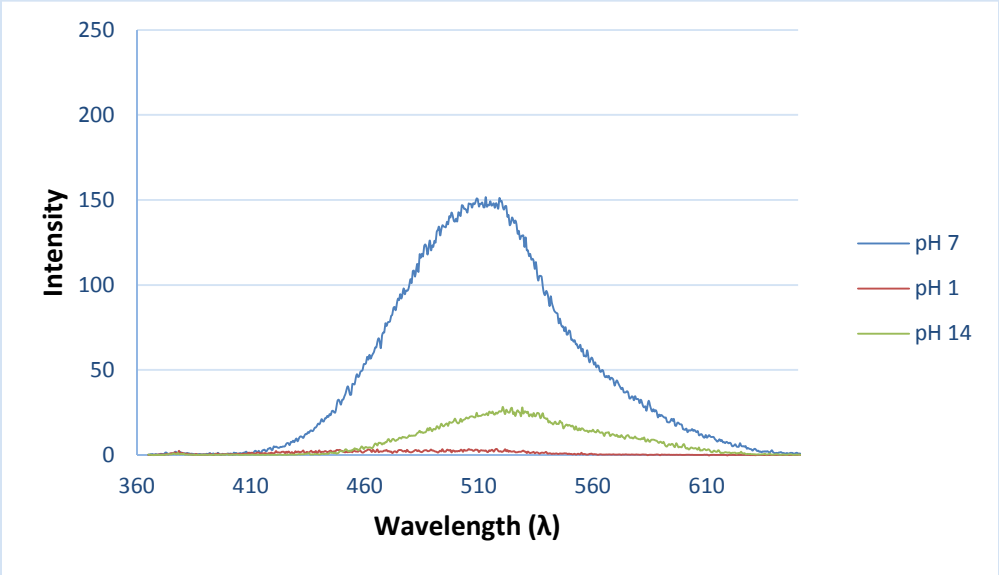

Figure S84. Compound **2** fluorescence quenching at different pH levels.

Table S1. Crystal data and structure refinement for **1**.

Identification code	k1177	
Empirical formula	C_{17} H_{25} N_3 O_2 S	
Formula weight	335.46	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.5518(3) Å	α= 90°.
	b = 12.7906(3) Å	β= 101.5820(13)°.
	c = 13.4228(4) Å	γ = 90°.
Volume	1774.71(8) $Å^3$	
Z	4	
Density (calculated)	1.256 Mg/m^3	
Absorption coefficient	0.195 mm^{-1}	
F(000)	720	
Crystal size	0.35 x 0.30 x 0.05 mm^3	
Theta range for data collection	2.76 to 27.49°.	
Index ranges	-13<=h<=13, -13<=k<=16, -17<=l<=17	
Reflections collected	15607	
Independent reflections	4028 [R(int) = 0.0778]	
Completeness to theta = 27.49°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.005 and 0.658	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4028 / 0 / 216	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1321	
R indices (all data)	R1 = 0.0938, wR2 = 0.1567	
Largest diff. peak and hole	0.380 and -0.394 e.$Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **1**.

S(1)-O(1)	1.4283(16)
S(1)-O(2)	1.4379(15)
S(1)-N(2)	1.5904(19)
S(1)-C(1)	1.785(2)
N(1)-C(6)	1.435(3)
N(1)-C(11)	1.464(3)
N(1)-C(12)	1.464(3)
N(2)-C(13)	1.464(3)
N(3)-C(17)	1.463(3)
N(3)-C(16)	1.471(3)
N(3)-C(15)	1.474(3)
C(1)-C(2)	1.367(3)
C(1)-C(10)	1.435(3)
C(2)-C(3)	1.410(3)
C(3)-C(4)	1.361(3)
C(4)-C(5)	1.418(3)
C(5)-C(6)	1.427(3)
C(5)-C(10)	1.437(3)
C(6)-C(7)	1.367(3)
C(7)-C(8)	1.405(3)
C(8)-C(9)	1.372(3)
C(9)-C(10)	1.414(3)
C(13)-C(14)	1.519(3)
C(14)-C(15)	1.513(3)

O(1)-S(1)-O(2)	118.10(9)
O(1)-S(1)-N(2)	107.36(10)
O(2)-S(1)-N(2)	110.16(10)
O(1)-S(1)-C(1)	109.83(10)
O(2)-S(1)-C(1)	105.58(9)
N(2)-S(1)-C(1)	105.07(10)
C(6)-N(1)-C(11)	114.7(2)
C(6)-N(1)-C(12)	113.57(19)

C(11)-N(1)-C(12)	111.0(2)
C(13)-N(2)-S(1)	122.15(15)
C(17)-N(3)-C(16)	110.23(19)
C(17)-N(3)-C(15)	109.88(18)
C(16)-N(3)-C(15)	111.69(19)
C(2)-C(1)-C(10)	121.7(2)
C(2)-C(1)-S(1)	116.60(17)
C(10)-C(1)-S(1)	121.70(16)
C(1)-C(2)-C(3)	120.2(2)
C(4)-C(3)-C(2)	120.2(2)
C(3)-C(4)-C(5)	121.7(2)
C(4)-C(5)-C(6)	121.7(2)
C(4)-C(5)-C(10)	118.9(2)
C(6)-C(5)-C(10)	119.4(2)
C(7)-C(6)-C(5)	119.6(2)
C(7)-C(6)-N(1)	122.8(2)
C(5)-C(6)-N(1)	117.6(2)
C(6)-C(7)-C(8)	121.1(2)
C(9)-C(8)-C(7)	120.9(2)
C(8)-C(9)-C(10)	120.4(2)
C(9)-C(10)-C(1)	124.0(2)
C(9)-C(10)-C(5)	118.7(2)
C(1)-C(10)-C(5)	117.32(19)
N(2)-C(13)-C(14)	111.49(18)
C(15)-C(14)-C(13)	112.27(18)
N(3)-C(15)-C(14)	114.03(18)

Symmetry transformations used to generate equivalent atoms:

Table S3. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	31(1)	32(1)	34(1)	1(1)	-1(1)	-2(1)
O(1)	32(1)	50(1)	36(1)	4(1)	6(1)	-6(1)
O(2)	40(1)	32(1)	52(1)	-7(1)	-8(1)	-5(1)
N(1)	31(1)	59(1)	40(1)	1(1)	-4(1)	-8(1)
N(2)	44(1)	32(1)	30(1)	2(1)	9(1)	9(1)
N(3)	40(1)	40(1)	43(1)	6(1)	18(1)	7(1)
C(1)	31(1)	29(1)	31(1)	6(1)	2(1)	-4(1)
C(2)	37(1)	32(1)	37(1)	0(1)	-1(1)	-1(1)
C(3)	40(1)	33(1)	46(2)	0(1)	3(1)	7(1)
C(4)	30(1)	41(1)	45(1)	6(1)	2(1)	5(1)
C(5)	33(1)	34(1)	29(1)	7(1)	3(1)	-3(1)
C(6)	33(1)	40(1)	32(1)	7(1)	2(1)	-7(1)
C(7)	46(1)	40(1)	33(1)	-5(1)	1(1)	-13(1)
C(8)	42(1)	36(1)	34(1)	-1(1)	9(1)	-3(1)
C(9)	33(1)	33(1)	30(1)	4(1)	5(1)	-2(1)
C(10)	33(1)	28(1)	27(1)	6(1)	5(1)	-4(1)
C(11)	47(2)	81(2)	45(2)	-3(1)	-11(1)	-7(1)
C(12)	39(2)	76(2)	63(2)	1(2)	6(1)	-13(1)
C(13)	47(1)	43(1)	31(1)	-1(1)	8(1)	10(1)
C(14)	51(1)	39(1)	30(1)	4(1)	17(1)	11(1)
C(15)	42(1)	35(1)	44(1)	8(1)	16(1)	10(1)
C(16)	56(2)	58(2)	65(2)	5(1)	39(2)	8(1)
C(17)	43(1)	56(2)	62(2)	10(1)	9(1)	5(1)

Table S4. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2× 10^3) for **1**.

	x	y	z	U(eq)
H(1N)	6320(20)	6340(20)	4920(20)	58(8)
H(2A)	4197	9367	4591	44
H(3A)	2008	9720	3886	48
H(4A)	859	8634	2668	47
H(7A)	1751	5652	969	49
H(8A)	3925	5283	1649	44
H(9A)	5111	6326	2907	39
H(11A)	379	7030	-52	91
H(11B)	-1070	7109	132	91
H(11C)	-272	6045	384	91
H(12A)	-287	7190	2772	90
H(12B)	-622	6122	2155	90
H(12C)	-1467	7148	1814	90
H(13A)	4906	7554	5984	48
H(13B)	6128	6917	6588	48
H(14A)	5048	5317	6005	47
H(14B)	4292	5971	6719	47
H(15A)	2776	6539	5346	47
H(15B)	3608	6114	4559	47
H(16A)	2609	4804	6619	84
H(16B)	1486	4162	5893	84
H(16C)	1363	5402	6003	84
H(17A)	2134	5038	3596	81
H(17B)	1060	5526	4149	81
H(17C)	1223	4284	4094	81

Table S5. Hydrogen bonds for **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(1N)...N(3)#1	0.82(3)	2.03(3)	2.833(3)	168(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table S6. Crystal data and structure refinement for **7**.

Empirical formula	C_{20} H_{30} Br N_3 O_2 S	
Formula weight	456.44	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.7757(5) Å	α= 90°.
	b = 11.5358(5) Å	β= 94.112(2)°.
	c = 16.1129(7) Å	γ = 90°.
Volume	2183.18(16) $Å^3$	
Z	4	
Density (calculated)	1.389 Mg/m^3	
Absorption coefficient	3.612 mm^{-1}	
F(000)	952	
Crystal size	0.11 × 0.08 × 0.01 mm^3	
Theta range for data collection	4.72 to 66.49°.	
Index ranges	-14<=h<=13, -12<=k<=13, -7<=l<=19	
Reflections collected	13673	
Independent reflections	3752 [R(int) = 0.0313]	
Completeness to theta = 66.49°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6384	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3752 / 0 / 252	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0248, wR2 = 0.0632	
R indices (all data)	R1 = 0.0282, wR2 = 0.0652	
Largest diff. peak and hole	0.252 and -0.304 $e.Å^{-3}$	

Table S7. Bond lengths [Å] and angles [°] for **7**.

S(1)-O(2)	1.4325(13)
S(1)-O(1)	1.4350(13)
S(1)-N(2)	1.6060(16)
S(1)-C(1)	1.7818(18)
N(1)-C(6)	1.412(3)
N(1)-C(12)	1.456(3)
N(1)-C(11)	1.458(3)
N(2)-C(13)	1.459(2)
N(2)-H(2N)	0.84(2)
N(3)-C(19)	1.500(2)
N(3)-C(20)	1.501(2)
N(3)-C(15)	1.516(2)
N(3)-C(16)	1.521(2)
C(1)-C(2)	1.369(3)
C(1)-C(10)	1.433(3)
C(2)-C(3)	1.407(3)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.366(3)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.415(3)
C(4)-H(4A)	0.9500
C(5)-C(10)	1.426(3)
C(5)-C(6)	1.440(3)
C(6)-C(7)	1.375(3)
C(7)-C(8)	1.406(3)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.363(3)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.420(3)
C(9)-H(9A)	0.9500
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800

C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.527(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.519(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.490(3)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.297(3)
C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9500
C(18)-H(18B)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
O(2)-S(1)-O(1)	119.75(8)
O(2)-S(1)-N(2)	107.86(9)
O(1)-S(1)-N(2)	105.94(8)
O(2)-S(1)-C(1)	105.99(8)
O(1)-S(1)-C(1)	108.13(8)
N(2)-S(1)-C(1)	108.85(8)
C(6)-N(1)-C(12)	115.87(17)
C(6)-N(1)-C(11)	115.12(18)
C(12)-N(1)-C(11)	110.99(17)
C(13)-N(2)-S(1)	122.29(14)
C(13)-N(2)-H(2N)	122.8(16)

S(1)-N(2)-H(2N)	113.5(16)
C(19)-N(3)-C(20)	109.57(15)
C(19)-N(3)-C(15)	110.81(15)
C(20)-N(3)-C(15)	110.95(14)
C(19)-N(3)-C(16)	106.94(14)
C(20)-N(3)-C(16)	109.85(15)
C(15)-N(3)-C(16)	108.64(13)
C(2)-C(1)-C(10)	121.53(17)
C(2)-C(1)-S(1)	117.40(14)
C(10)-C(1)-S(1)	121.01(14)
C(1)-C(2)-C(3)	120.10(18)
C(1)-C(2)-H(2A)	120.0
C(3)-C(2)-H(2A)	120.0
C(4)-C(3)-C(2)	120.28(18)
C(4)-C(3)-H(3A)	119.9
C(2)-C(3)-H(3A)	119.9
C(3)-C(4)-C(5)	121.14(18)
C(3)-C(4)-H(4A)	119.4
C(5)-C(4)-H(4A)	119.4
C(4)-C(5)-C(10)	119.39(16)
C(4)-C(5)-C(6)	120.98(17)
C(10)-C(5)-C(6)	119.53(17)
C(7)-C(6)-N(1)	123.19(17)
C(7)-C(6)-C(5)	119.16(17)
N(1)-C(6)-C(5)	117.59(17)
C(6)-C(7)-C(8)	120.59(17)
C(6)-C(7)-H(7A)	119.7
C(8)-C(7)-H(7A)	119.7
C(9)-C(8)-C(7)	121.74(18)
C(9)-C(8)-H(8A)	119.1
C(7)-C(8)-H(8A)	119.1
C(8)-C(9)-C(10)	120.01(18)
C(8)-C(9)-H(9A)	120.0
C(10)-C(9)-H(9A)	120.0
C(9)-C(10)-C(5)	118.94(16)

C(9)-C(10)-C(1)	123.61(17)
C(5)-C(10)-C(1)	117.43(16)
N(1)-C(11)-H(11A)	109.5
N(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
N(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(1)-C(12)-H(12A)	109.5
N(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
N(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(2)-C(13)-C(14)	114.73(16)
N(2)-C(13)-H(13A)	108.6
C(14)-C(13)-H(13A)	108.6
N(2)-C(13)-H(13B)	108.6
C(14)-C(13)-H(13B)	108.6
H(13A)-C(13)-H(13B)	107.6
C(15)-C(14)-C(13)	109.77(15)
C(15)-C(14)-H(14A)	109.7
C(13)-C(14)-H(14A)	109.7
C(15)-C(14)-H(14B)	109.7
C(13)-C(14)-H(14B)	109.7
H(14A)-C(14)-H(14B)	108.2
N(3)-C(15)-C(14)	114.88(15)
N(3)-C(15)-H(15A)	108.5
C(14)-C(15)-H(15A)	108.5
N(3)-C(15)-H(15B)	108.5
C(14)-C(15)-H(15B)	108.5
H(15A)-C(15)-H(15B)	107.5
C(17)-C(16)-N(3)	114.08(15)
C(17)-C(16)-H(16A)	108.7
N(3)-C(16)-H(16A)	108.7

C(17)-C(16)-H(16B)	108.7
N(3)-C(16)-H(16B)	108.7
H(16A)-C(16)-H(16B)	107.6
C(18)-C(17)-C(16)	122.2(2)
C(18)-C(17)-H(17A)	118.9
C(16)-C(17)-H(17A)	118.9
C(17)-C(18)-H(18A)	120.0
C(17)-C(18)-H(18B)	120.0
H(18A)-C(18)-H(18B)	120.0
N(3)-C(19)-H(19A)	109.5
N(3)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
N(3)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(3)-C(20)-H(20A)	109.5
N(3)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
N(3)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S8. Torsion angles [°] for **7**.

O(2)-S(1)-N(2)-C(13)	40.40(16)
O(1)-S(1)-N(2)-C(13)	169.75(14)
C(1)-S(1)-N(2)-C(13)	-74.18(16)
O(2)-S(1)-C(1)-C(2)	5.80(16)
O(1)-S(1)-C(1)-C(2)	-123.77(14)
N(2)-S(1)-C(1)-C(2)	121.58(15)
O(2)-S(1)-C(1)-C(10)	-177.12(14)
O(1)-S(1)-C(1)-C(10)	53.31(16)
N(2)-S(1)-C(1)-C(10)	-61.34(16)
C(10)-C(1)-C(2)-C(3)	-2.1(3)
S(1)-C(1)-C(2)-C(3)	174.97(14)
C(1)-C(2)-C(3)-C(4)	1.3(3)
C(2)-C(3)-C(4)-C(5)	1.8(3)
C(3)-C(4)-C(5)-C(10)	-4.1(3)
C(3)-C(4)-C(5)-C(6)	179.67(17)
C(12)-N(1)-C(6)-C(7)	-21.6(3)
C(11)-N(1)-C(6)-C(7)	110.2(2)
C(12)-N(1)-C(6)-C(5)	155.43(17)
C(11)-N(1)-C(6)-C(5)	-72.7(2)
C(4)-C(5)-C(6)-C(7)	174.11(17)
C(10)-C(5)-C(6)-C(7)	-2.1(3)
C(4)-C(5)-C(6)-N(1)	-3.1(2)
C(10)-C(5)-C(6)-N(1)	-179.30(16)
N(1)-C(6)-C(7)-C(8)	179.04(17)
C(5)-C(6)-C(7)-C(8)	2.0(3)
C(6)-C(7)-C(8)-C(9)	-0.8(3)
C(7)-C(8)-C(9)-C(10)	-0.4(3)
C(8)-C(9)-C(10)-C(5)	0.3(3)
C(8)-C(9)-C(10)-C(1)	-178.15(17)
C(4)-C(5)-C(10)-C(9)	-175.34(16)
C(6)-C(5)-C(10)-C(9)	0.9(2)

C(4)-C(5)-C(10)-C(1)	3.2(2)
C(6)-C(5)-C(10)-C(1)	179.51(15)
C(2)-C(1)-C(10)-C(9)	178.29(17)
S(1)-C(1)-C(10)-C(9)	1.3(2)
C(2)-C(1)-C(10)-C(5)	-0.2(3)
S(1)-C(1)-C(10)-C(5)	-177.16(13)
S(1)-N(2)-C(13)-C(14)	91.22(18)
N(2)-C(13)-C(14)-C(15)	69.6(2)
C(19)-N(3)-C(15)-C(14)	-52.7(2)
C(20)-N(3)-C(15)-C(14)	69.2(2)
C(16)-N(3)-C(15)-C(14)	-169.91(15)
C(13)-C(14)-C(15)-N(3)	-171.87(15)
C(19)-N(3)-C(16)-C(17)	-177.71(17)
C(20)-N(3)-C(16)-C(17)	63.5(2)
C(15)-N(3)-C(16)-C(17)	-58.1(2)
N(3)-C(16)-C(17)-C(18)	-115.5(3)

Symmetry transformations used to generate equivalent atoms:

Table S9. Hydrogen bonds for **7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)...Br(1)	0.84(2)	2.58(3)	3.4037(17)	168(2)

Symmetry transformations used to generate equivalent atoms:

Crystal structures of compound **1** and **7** have been deposited in the Cambridge Structural Database (CSD) with the following deposition numbers: CCDC 971464 and CCDC 971465.