Supporting Information

Palladium-catalyzed [4+3] annulation of 2-bromobiphenyls and epoxides for the assembly of dihydrodibenzo[*b*,*d*]oxepines

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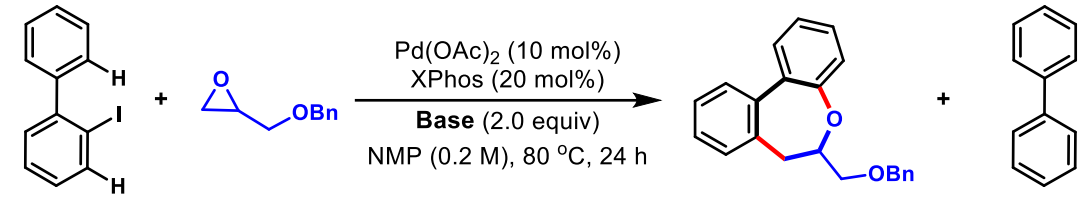
1. General principles

All reactions dealing with air- or moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere or in the argon-filled glove box. Anhydrous DMF, CH_3CN, THF and Toluene were dried by JC Meyer Solvent Drying System. Anhydrous (over molecular sieve) NMP, DMA, DMSO, 1,4-dioxane and DCE were purchased from Energy Chemical and used as received. Most reagents were purchased from commercial sources and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.2 mm commercial silica gel plates, using UV light as the visualizing agent or basic solution of $KMnO_4$ or acidic solution of *p*-anisaldehyde and heat as a developing agent. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), 376 MHz (^{19}F NMR) or Bruker spectrometer at 600MHz (^{1}H NMR), 150 MHz (^{13}C NMR) and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$ @7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR; DMSO-*d*$_6$ @ 2.50 ppm ^{1}H NMR, 39.5 ppm ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, br = broad. High resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer.

2. Optimization of reaction conditions

Table S1. Screening of bases

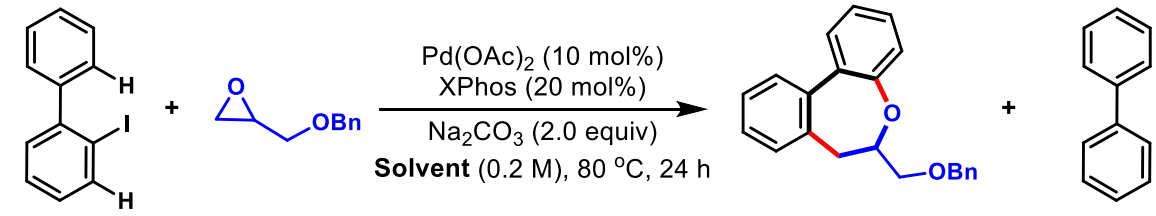


1a, 0.2 mmol **2a,** 0.4 mmol **3a** **BP**

Entry	Base	Conversion of **1a**[a]	Yield of **3a**[a]	Yield of **BP**[a]
1	K_2CO_3	34	17	7
2	**Na_2CO_3**	**60**	**55**	**3**
3	Cs_2CO_3	90	3	74
4	K_3PO_4	50	5	33
5	$KHCO_3$	34	25	2
6	$NaHCO_3$	29	22	5
7	KOAc	42	26	4
8	NaOAc	1	trace	trace
9	CsOAc	39	2	22

[a] GC yield with *n*-tridecane as an internal standard.

Table S2. Screening of solvents

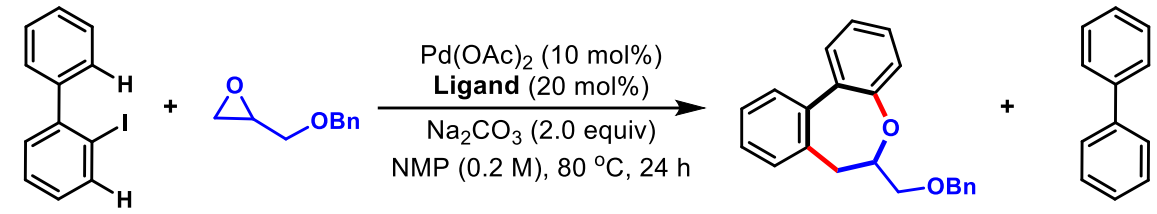


1a, 0.2 mmol **2a,** 0.4 mmol **3a** **BP**

Entry	Solvent	Conversion of **1a**[a]	Yield of **3a**[a]	Yield of **BP**[a]
1	**NMP**	**60**	**55**	**3**
2	DMF	28	12	3
3	DMA	30	22	5
4	CH_3CN	9	trace	2
5	1,4-dioxane	10	trace	9
6	DMSO	16	trace	trace
7	DCE	9	trace	3
8	Toluene	10	trace	9
9	THF	11	trace	8

[a] GC yield with *n*-tridecane as an internal standard.

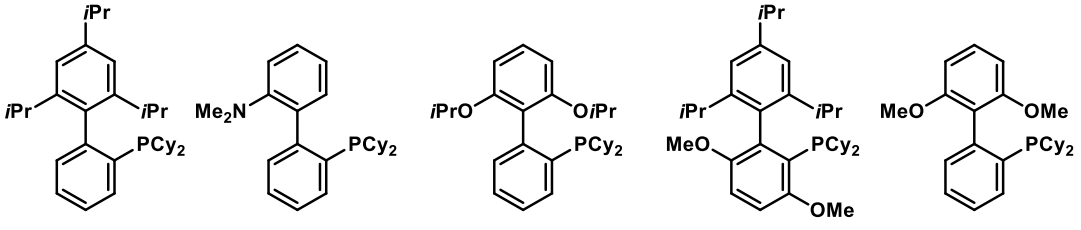
Table S3. Screening of ligands



1a, 0.2 mmol **2a,** 0.4 mmol **3a** **BP**

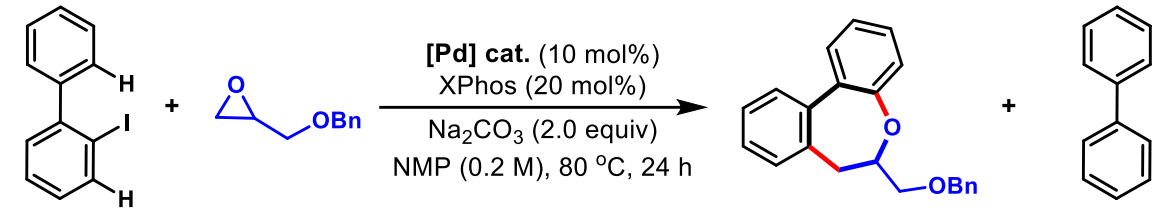
Entry	Ligand	Conversion of **1a**[a]	Yield of **3a**[a]	Yield of **BP**[a]
1	**XPhos**	**60**	**55**	**3**
2	PPh_3	37	trace	7
3	Pcy_3	25	trace	6
4	TFP	65	trace	trace
5	DavePhos	88	19	9
6	RuPhos	21	5	5
7	BrettPhos	76	32	5
8	SPhos	13	3	6
9	dppf	35	trace	3

[a] GC yield with *n*-tridecane as an internal standard.



XPhos **DavePhos** **RuPhos** **BrettPhos** **SPhos**

Table S4. Screening of palladium catalysts

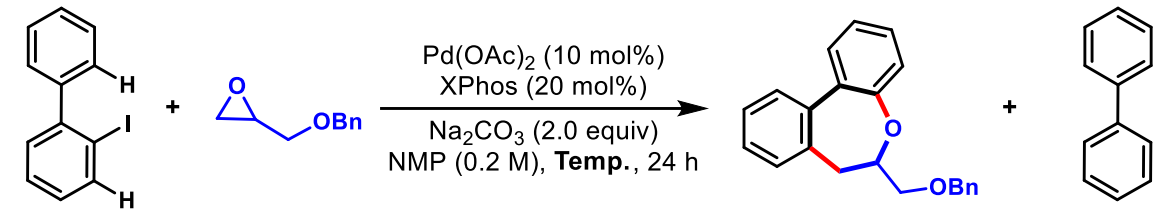


1a, 0.2 mmol **2a,** 0.4 mmol **3a** **BP**

Entry	[Pd] cat.	Conversion of **1a**[a]	Yield of **3a**[a]	Yield of **BP**[a]
1	**$Pd(OAc)_2$**	**60**	**55**	**3**
2	$PdCl_2$	22	2	2
3	$Pd(OOCCF_3)_2$	41	17	8
4	$Pd(CH_3CN)_2Cl_2$	23	1	2
5	$[Pd(C_3H_5)Cl]_2$	35	4	5
6	Pd_2dba_3	25	3	6

[a] GC yield with *n*-tridecane as an internal standard.

Table S5. Screening of reaction temperature

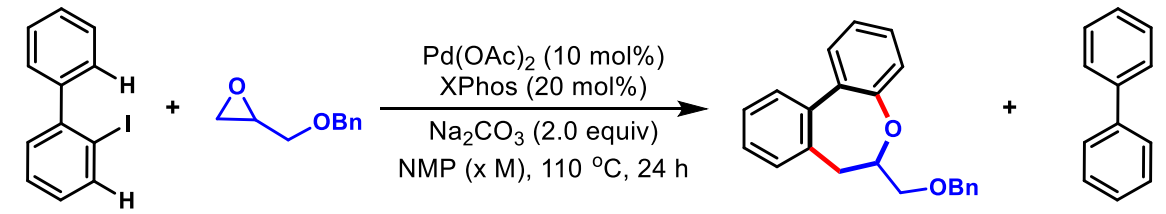


1a, 0.2 mmol **2a,** 0.4 mmol **3a** **BP**

Entry	Temp. [°C]	Conversion of **1a**[a]	Yield of **3a**[a]	Yield of **BP**[a]
1	60	18	5	3
2	70	33	18	trace
3	80	60	55	3
4	90	64	60	3
5	100	81	67	6
6	**110**	**100**	**73**	**7**
7	120	100	59	7
8	130	100	53	6

[a] GC yield with *n*-tridecane as an internal standard.

Table S6. Screening of reaction concentration

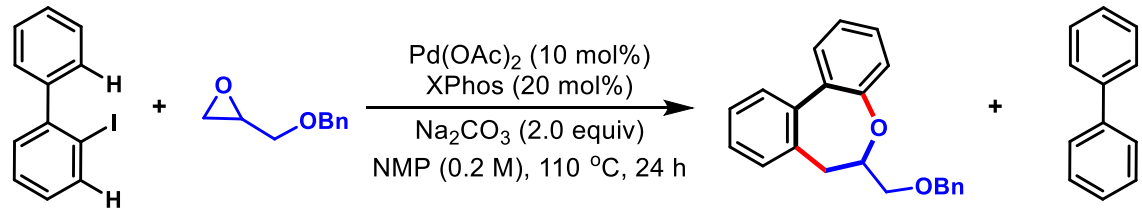


1a, 0.2 mmol **2a,** 0.4 mmol **3a** **BP**

Entry	x	Conversion of **1a**[a]	Yield of **3a**[a]	Yield of **BP**[a]
1	0.1	84	40	5
2	0.15	100	67	4
3	**0.2**	**100**	**73**	**7**
4	0.25	100	71	5
5	0.3	100	61	5
6	0.4	100	54	3

[a] GC yield with *n*-tridecane as an internal standard.

Table S7. Screening of equivalents of **2a**

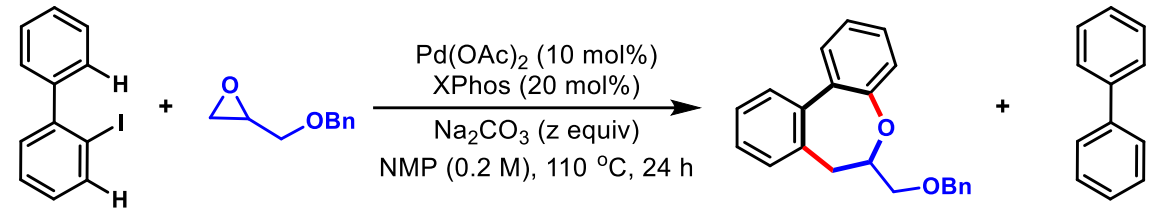


1a, 0.2 mmol (1.0 equiv) | **2a** (y equiv) | **3a** | **BP**

Entry	y	Conversion of **1a**[a]	Yield of **3a**[a]	Yield of **BP**[a]
1	1.2	83	44	7
2	1.5	95	50	7
3	**2.0**	**100**	**73**	**7**
4	2.5	100	73	4
5	3.0	100	72	5
6	3.5	100	65	4
7	4.0	100	63	5

[a] GC yield with *n*-tridecane as an internal standard.

Table S8. Screening of the equivalents of base

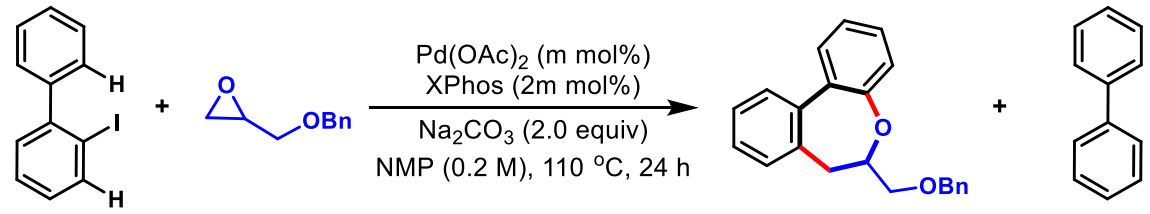


1a, 0.2 mmol **2a,** 0.4 mmol **3a** **BP**

Entry	z	Conversion of **1a**[a]	Yield of **3a**[a]	Yield of **BP**[a]
1	1.2	87	48	5
2	1.6	94	54	7
3	**2.0**	**100**	**73**	**7**
4	2.4	100	71	3
5	2.8	100	46	5

[a] GC yield with *n*-tridecane as an internal standard.

Table S9. Screening of the loading of palladium catalysts

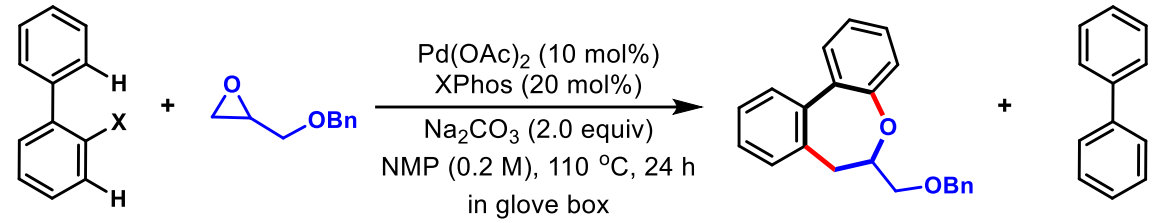


1a, 0.2 mmol **2a,** 0.4 mmol **3a** **BP**

Entry	m	Conversion of **1a**[a]	Yield of **3a**[a]	Yield of **BP**[a]
1	**10.0**	**100**	**73**	**7**
2	5.0	45	30	3
3	2.5	15	8	trace

[a] GC yield with *n*-tridecane as an internal standard.

Table S10. Screening of the substrate **1**



1, 0.2 mmol **2a,** 0.4 mmol **3a** **BP**

Entry	X	Conversion of **1**[a]	Yield of **3a**[a]	Yield of **BP**[a]
1	Cl	23	12 (10)[b]	8
2	Br	99	83 (80)[b]	2
3	I	100	73 (72)[b]	7
4[c]	**Br**	**100**	**85 (84)**[b]	**2**

[a] GC yield with *n*-tridecane as an internal standard. [b] Isolated yield. [c] 28 h.

3. Preparation of substrates

2-bromobiphenyls were known compounds and synthesized according to the reported procedure[1].

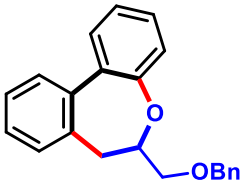
Epoxides **2n** and **2o** were known compounds and synthesized according to the reported procedure[2]. Other epoxides were commercially available and directly used without further purification.

4. General procedure for palladium-catalyzed [4+3] annulation of 2-bromobiphenyls and epoxides

To a 4 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with palladium acetate (4.4 mg, 0.02 mmol, 10 mol%) and XPhos (19.3 mg, 0.04 mmol, 20 mol%) inside a glove box. Dry NMP (0.3 mL) was added and the solution was pre-stirred at room temperature inside the glovebox for 30 minutes. After that, to this mixture was added sodium carbonate (42.4 mg, 0.4 mmol, 2.0 equiv), 2-bromobiphenyls **1** (0.2 mmol, 1.0 equiv), epoxides **2** (0.4 mmol, 2.0 equiv) and dry NMP (0.7 mL). Then the Schlenk tube was sealed and transferred out of the glovebox. The reaction mixture was heated to 110 ℃ and stirred for 28 h. After completion of the reaction, the mixture was cooled to room temperature and quenched with H_2O (10 mL). The mixture was extracted with EtOAc (3 × 10 mL), and the combined organic phase was washed with H_2O (3 × 20 mL), NaCl (sat. aq., 20 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel or purified by PTLC to give the desired products.

5. Characterization data for compounds

6-((benzyloxy)methyl)-6,7-dihydrodibenzo[*b,d*]oxepine (3a)



Physical state: colorless oil;

Yield: 84%;

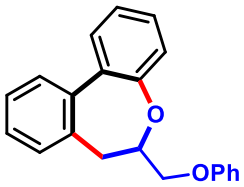
R_f = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.39 (m, 2H), 7.38 – 7.33 (m, 5H), 7.32 – 7.25 (m, 3H), 7.23 – 7.18 (m, 2H), 7.08 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.85 – 4.79 (m, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 3.72 (dd, *J* = 9.7, 5.9 Hz, 1H), 3.53 (dd, *J* = 9.7, 6.3 Hz, 1H), 2.85 (dd, *J* = 14.2, 5.2 Hz, 1H), 2.71 (dd, *J* = 14.2, 6.9 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 138.8, 138.3, 136.0, 135.1, 129.3, 129.1, 129.0, 128.6, 128.1, 128.0, 127.9, 127.7, 127.5, 124.7, 123.4, 86.9, 73.6, 71.2, 35.1;

HRMS (ESI-TOF): calc'd for $C_{20}H_{20}NaO_2^+$ [M+Na^+] 299.1406, found 299.1400.

6-(phenoxymethyl)-6,7-dihydrodibenzo[*b,d*]oxepine (3b)



Physical state: colorless oil;

Yield: 86%;

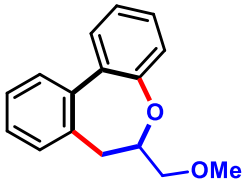
R_f = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.42 (m, 2H), 7.41 – 7.36 (m, 1H), 7.33 – 7.23 (m, 6H), 7.13 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.99 – 6.94 (m, 3H), 5.03 – 4.97 (m, 1H), 4.22 (dd, *J* = 9.5, 5.5 Hz, 1H), 4.02 (dd, *J* = 9.5, 6.4 Hz, 1H), 2.96 (dd, *J* = 14.3, 5.2 Hz, 1H), 2.87 (dd, *J* = 14.3, 6.9 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 153.3, 138.8, 135.7, 135.1, 129.7, 129.4, 129.2, 129.1, 128.2, 127.9, 127.7, 125.0, 123.4, 121.3, 114.9, 86.2, 68.6, 35.0;

HRMS (ESI-TOF): calc'd for $C_{21}H_{18}NaO_2^+$ [M+Na^+] 325.1199, found 325.1194.

6-(methoxymethyl)-6,7-dihydrodibenzo[*b,d*]oxepine (3c)



Physical state: colorless oil;

Yield: 89%;

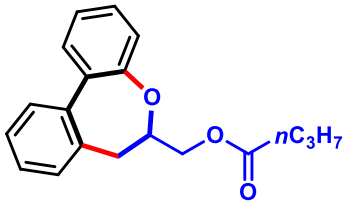
***R**f* = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.36 (m, 3H), 7.34 – 7.29 (m, 2H), 7.27 – 7.21 (m, 2H), 7.13 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.83 – 4.77 (m, 1H), 3.65 (dd, *J* = 9.8, 6.5 Hz, 1H), 3.49 – 3.45 (m, 1H), 3.44 (s, 3H), 2.85 (dd, *J* = 14.2, 5.3 Hz, 1H), 2.68 (dd, *J* = 14.2, 6.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 138.8, 136.0, 135.2, 129.3, 129.0, 128.2, 127.8, 127.6, 124.8, 123.4, 86.7, 73.9, 59.4, 35.1;

HRMS (ESI-TOF): calc'd for $C_{16}H_{16}NaO_2^+$ [M+Na^+] 263.1043, found 263.1039.

(6,7-dihydrodibenzo[*b,d*]oxepin-6-yl)methyl butyrate (3d)



Physical state: colorless oil;

Yield: 73%;

***R**f* = 0.2 (silica gel, PE:EtOAc = 20:1);

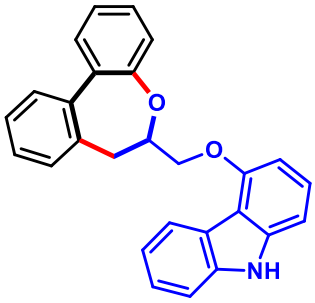
^{1}H NMR (400 MHz, $CDCl_3$): 7.50 – 7.37 (m, 3H), 7.35 – 7.30 (m, 2H), 7.28 – 7.23 (m, 2H), 7.13 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.88 – 4.82 (m, 1H), 4.33 (dd, *J* = 11.5, 6.8 Hz, 1H), 4.23 (dd, *J* = 11.5, 4.7 Hz, 1H), 2.83 (dd, *J* = 14.2, 5.1 Hz, 1H), 2.69 (dd, *J* = 14.2, 8.1 Hz, 1H), 2.36 (t, *J* = 7.4 Hz, 2H), 1.73 – 1.64 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 152.9, 138.7, 135.5, 135.1, 129.4, 129.1, 128.9,

128.2, 127.9, 127.8, 125.0, 123.6, 85.8, 65.0, 36.3, 35.0, 18.6, 13.9;

HRMS (ESI-TOF): calc'd for $C_{19}H_{20}NaO_3^+$ [M+Na$^+$] 319.1305, found 319.1302.

4-((6,7-dihydrodibenzo[*b,d*]oxepin-6-yl)methoxy)-9H-carbazole (3e)



Physical state: colorless oil;

Yield: 45%;

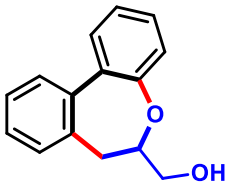
***R*$_f$** = 0.2 (silica gel, PE:EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.9 Hz, 1H), 8.04 (s, 1H), 7.51 – 7.48 (m, 2H), 7.43 – 7.36 (m, 3H), 7.34 – 7.30 (m, 3H), 7.27 – 7.24 (m, 2H), 7.19 – 7.12 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.26 – 5.20 (m, 1H), 4.45 (dd, *J* = 9.6, 5.2 Hz, 1H), 4.37 (dd, *J* = 9.6, 5.8 Hz, 1H), 3.16 (dd, *J* = 14.3, 7.8 Hz, 1H), 3.02 (dd, *J* = 14.3, 5.0 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 153.4, 141.1, 138.9, 135.9, 135.0, 129.4, 129.2, 128.3, 127.9, 127.8, 126.8, 125.2, 125.0, 123.7, 123.4, 122.7, 120.0, 113.0, 110.1, 104.0, 101.3, 86.5, 69.0, 35.2;

HRMS (ESI-TOF): calc'd for $C_{27}H_{21}NaO_2^+$ [M+Na$^+$] 400.1434, found 400.1432.

(6,7-dihydrodibenzo[*b,d*]oxepin-6-yl)methanol (3f)



Physical state: colorless oil;

Yield: 70%;

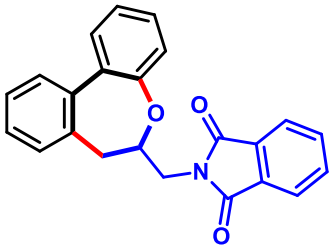
***R*$_f$** = 0.3 (silica gel, PE:EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.43 (m, 2H), 7.41 – 7.37 (m, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.23 (m, 2H), 7.12 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.76 – 4.70 (m, 1H), 3.85 (dd, *J* = 11.4, 8.2 Hz, 1H), 3.68 (dd, *J* = 11.5, 3.8 Hz, 1H), 2.84 (dd, *J* = 14.3, 5.4 Hz, 1H), 2.63 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.04 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 138.6, 135.9, 135.2, 129.5, 129.2, 129.0, 128.2, 127.9, 127.7, 125.0, 123.1, 89.0, 64.7, 34.7;

HRMS (ESI-TOF): calc'd for $C_{15}H_{14}NaO_2^+$ [M+Na$^+$] 249.0886, found 249.0883.

2-((6,7-dihydrodibenzo[*b*,*d*]oxepin-6-yl)methyl)isoindoline-1,3-dione (3g)



Physical state: colorless oil;

Yield: 39%;

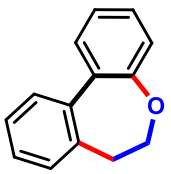
***R*$_f$** = 0.2 (silica gel, PE:EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.87 (m, 2H), 7.76 – 7.74 (m, 2H), 7.47 – 7.31 (m, 7H), 7.28 – 7.24 (m, 1H), 5.04 – 4.97 (m, 1H), 4.14 (dd, *J* = 14.0, 7.9 Hz, 1H), 3.73 (dd, *J* = 14.0, 4.5 Hz, 1H), 2.86 (dd, *J* = 14.2, 4.7 Hz, 1H), 2.72 (dd, *J* = 14.2, 8.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 152.5, 138.8, 135.5, 135.0, 134.3, 132.3, 129.4, 129.3, 129.1, 128.1, 127.9, 127.8, 125.0, 123.9, 123.6, 85.5, 41.3, 35.9;

HRMS (ESI-TOF): calc'd for $C_{23}H_{17}NNaO_3^+$ [M+Na$^+$] 378.1101, found 378.1105.

6,7-dihydrobibenzo[*b*,*d*]oxapine (3h)



Physical state: colorless oil;

Yield: 86%;

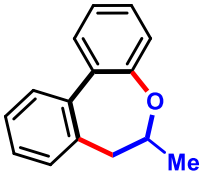
***R*$_f$** = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.36 (m, 3H), 7.34 – 7.21 (m, 4H), 7.14 (d, *J* = 7.9 Hz, 1H), 4.57 (t, *J* = 6.4 Hz, 2H), 2.80 (t, *J* = 6.4 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 139.1, 137.6, 135.4, 129.4, 129.2, 128.3, 128.2, 127.9, 127.5, 124.7, 122.5, 78.6, 33.6;

HRMS (ESI-TOF): calc'd for $C_{14}H_{12}NaO^+$ [M+Na^+] 219.0780, found 219.0766.

6-methyl-6,7-dihydrobibenzo[*b*,*d*]oxapine (3i)



Physical state: colorless oil;

Yield: 76%;

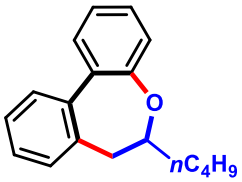
***R*$_f$** = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 2H), 7.39 – 7.36 (m, 1H), 7.33 – 7.29 (m, 2H), 7.27 – 7.21 (m, 2H), 7.10 (d, *J* = 7.8 Hz, 1H), 4.87 – 4.79 (m, 1H), 2.84 (dd, *J* = 14.0, 5.2 Hz, 1H), 2.52 (dd, *J* = 14.0, 6.9 Hz, 1H), 1.38 (d, *J* = 6.3 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 138.9, 136.6, 135.5, 129.2, 129.0, 128.9, 128.1, 127.6, 127.4, 124.6, 123.5, 84.9, 39.8, 20.5;

HRMS (ESI-TOF): calc'd for $C_{15}H_{14}NaO^+$ [M+Na^+] 233.0936, found 233.0930.

6-butyl-6,7-dihydrobibenzo[*b*,*d*]oxapine (3j)



Physical state: colorless oil;

Yield: 76%;

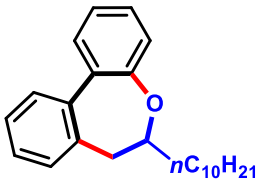
***R*$_f$** = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 2H), 7.40 – 7.36 (m, 1H), 7.34 – 7.29 (m, 2H), 7.25 – 7.21 (m, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 4.65 – 4.59 (m, 1H), 2.81 (dd, *J* = 14.1, 5.1 Hz, 1H), 2.57 (dd, *J* = 14.1, 7.6 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.64 – 1.32 (m, 5H), 0.96 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 138.9, 136.9, 135.6, 129.2, 128.9, 128.9, 128.1, 127.6, 127.4, 124.5, 123.6, 89.2, 38.4, 34.3, 28.4, 22.8, 14.3;

HRMS (ESI-TOF): calc'd for $C_{18}H_{20}NaO^+$ [M+Na^+] 275.1406, found 275.1402.

6-decyl-6,7-dihydrobibenzo[*b*,*d*]oxapine (3k)



Physical state: colorless oil;

Yield: 67%;

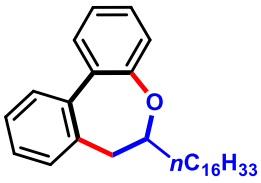
***R*$_f$** = 0.4 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.41 (m, 2H), 7.39 – 7.35 (m, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.18 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 4.64 – 4.58 (m, 1H), 2.79 (dd, *J* = 14.1, 5.1 Hz, 1H), 2.56 (dd, *J* = 14.1, 7.6 Hz, 1H), 1.84 – 1.75 (m, 1H), 1.61 – 1.38 (m, 4H), 1.35 – 1.26 (m, 13H), 0.89 (t, *J* = 6.7 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 138.9, 136.9, 135.6, 129.2, 128.9, 128.9, 128.1, 127.6, 127.4, 124.5, 123.6, 89.2, 38.4, 34.6, 32.1, 29.8, 29.8, 29.5, 26.2, 22.9, 14.3;

HRMS (ESI-TOF): calc'd for $C_{24}H_{32}NaO^+$ [M+Na^+] 359.2345, found 359.2340.

6-hexadecyl-6,7-dihydrobibenzo[*b*,*d*]oxapine (3l)



Phsical state: colorless oil;

Yield: 63%;

***R*$_f$** = 0.5 (silica gel, PE:EtOAc = 20:1);

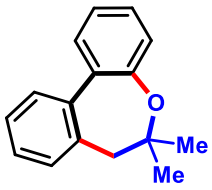
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.41 (m, 2H), 7.38 – 7.34 (m, 1H), 7.33 – 7.27 (m, 2H), 7.25 – 7.19 (m, 2H), 7.09 – 7.06 (m, 1H), 4.64 – 4.58 (m, 1H), 2.79 (dd, *J* = 14.1, 5.1 Hz, 1H), 2.56 (dd, *J* = 14.1, 7.6 Hz, 1H), 1.84 – 1.75 (m, 1H), 1.65 – 1.40 (m,

4H), 1.35 – 1.22 (m, 25H), 0.88 (t, *J* = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 138.9, 136.9, 135.6, 129.2, 128.9, 128.9, 128.1, 127.6, 127.4, 124.5, 123.6, 89.2, 38.4, 34.6, 32.1, 29.9, 29.9, 29.8, 29.8, 29.8, 29.6, 26.2, 22.9, 14.3;

HRMS (ESI-TOF): calc'd for $C_{30}H_{44}NaO^+$ [M+Na^+] 443.3284, found 443.3300.

6,6-dimethyl-6,7-dihydrobibenzo[*b*,*d*]oxapine (3m)



Physical state: colorless oil;

Yield: 25%;

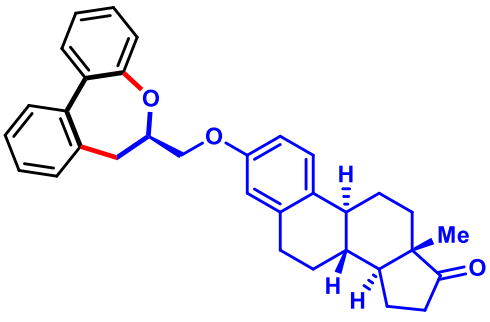
***R*$_f$** = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.44 (m, 2H), 7.40 – 7.36 (m, 1H), 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 2H), 7.06 (dd, *J* = 7.8, 1.1 Hz, 1H), 2.61 (s, 2H), 1.41 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 129.6, 129.2, 128.8, 128.2, 127.5, 127.4, 124.6, 124.3, 89.4, 44.8, 26.9;

HRMS (ESI-TOF): calc'd for $C_{16}H_{16}NaO^+$ [M+Na^+] 247.1093, found 247.1095.

(8*R*,9*S*,13*S*,14*S*)-3-(((*R*)-6,7-dihydrodibenzo[*b*,*d*]oxepin-6-yl)methoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3n)



Physical state: colorless oil;

Yied: 70%;

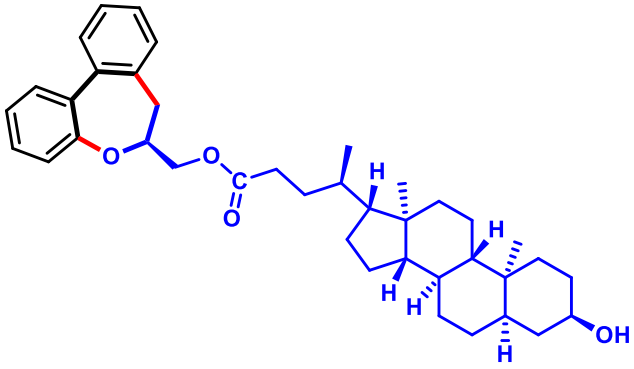
***R**f* = 0.2 (silica gel, PE:EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.36 (m, 3H), 7.33 – 7.19 (m, 5H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.77 – 6.69 (m, 2H), 5.00 – 4.94 (m, 1H), 4.18 (dd, *J* = 9.5, 5.6 Hz, 1H), 3.98 (dd, *J* = 9.5, 6.6 Hz, 1H), 2.96 – 2.82 (m, 4H), 2.49 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.42 – 2.34 (m, 1H), 2.28 – 2.22 (m, 1H), 2.17 – 1.92 (m, 4H), 1.69 – 1.40 (m, 6H), 0.90 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 221.1 156.8, 153.2, 138.8, 138.0, 135.7, 135.1, 132.6, 129.4, 129.2, 129.1, 128.2, 127.8, 127.7, 126.6, 124.9, 123.4, 114.9, 112.4, 86.2, 68.6, 50.6, 48.2, 44.2, 38.5, 36.0, 35.0, 31.7, 29.8, 26.7, 26.1, 21.8, 14.0;

HRMS (ESI-TOF): calc'd for $C_{33}H_{34}NaO_3^+$ [M+Na$^+$] 501.2400, found 501.2406.

((*S*)-6,7-dihydrodibenzo[*b*,*d*]oxepin-6-yl)methyl (*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (3o)



Physical state: colorless oil;

Yield: 33%;

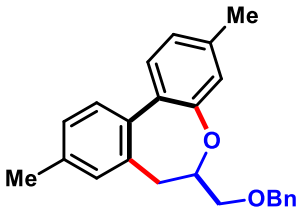
***R**f* = 0.2 (silica gel, PE:EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.37 (m, 3H), 7.35 – 7.30 (m, 2H), 7.25 – 7.23 (m, 2H), 7.12 (d, *J* = 7.2 Hz, 1H), 4.87 – 4.81 (m, 1H), 4.32 (dd, *J* = 11.6, 6.6 Hz, 1H), 4.21 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.66 – 3.59 (m, 1H), 2.83 (dd, *J* = 14.2, 5.1 Hz, 1H), 2.69 (dd, J = 14.2, 8.2 Hz, 1H), 2.45 – 2.37 (m, 1H), 2.32 – 2.24 (m, 1H), 1.97 – 1.93 (m, 1H), 1.88 – 1.67 (m, 6H), 1.49 – 1.31 (m, 10H), 1.27 – 1.21 (m, 4H), 1.17 – 1.00 (m, 6H), 0.92 (d, *J* = 7.5 Hz, 6H), 0.64 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.4, 152.9, 138.7, 135.6, 135.1, 129.4, 129.2, 128.9, 128.2, 127.9, 127.8, 125.0, 123.6, 85.9, 72.1, 65.0, 56.7, 56.1, 42.9, 42.3, 40.6, 40.4, 36.6, 36.0, 35.6, 35.5, 35.0, 34.8, 31.4, 31.2, 30.7, 28.4, 27.4, 26.6, 24.4, 23.6, 21.0, 18.5, 12.2;

HRMS (ESI-TOF): calc'd for $C_{39}H_{52}NaO_4^+$ [M+Na$^+$] 584.3866, found 584.3869.

6-((benzyloxy)methyl)-3,9-dimethyl-6,7-dihydrodibenzo[*b,d*]oxepine (3p)



Physical state: colorless oil;

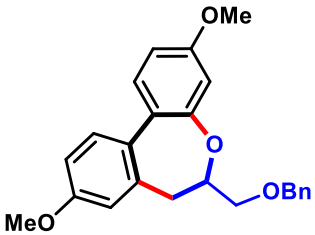
Yield: 72%;

***R**$_f$* = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.40 (m, 4H), 7.38 – 7.35 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 1H),7.21 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 6.6 Hz, 2H), 6.94 (s, 1H), 4.87 – 4.81 (m, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 3.77 (dd, *J* = 9.7, 5.9 Hz, 1H), 3.58 (dd, *J* = 9.7, 6.2 Hz, 1H), 2.85 (dd, *J* = 14.2, 5.2 Hz, 1H), 2.72 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H);**^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.2, 138.9, 138.3, 137.2, 135.9, 135.8, 132.0, 129.8, 128.8, 128.6, 128.2, 128.1, 127.9, 127.8, 125.4, 123.9, 86.7, 73.6, 71.3, 35.2, 21.3, 21.3;

HRMS (ESI-TOF): calc'd for $C_{24}H_{24}NaO_2^+$ [M+Na$^+$] 367.1669, found 367.1672.

6-((benzyloxy)methyl)-3,9-dimethoxy-6,7-dihydrodibenzo[*b,d*]oxepine (3q)



Physical state: colorless oil;

Yield: 73%;

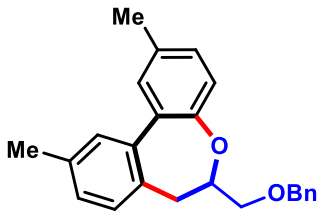
***R*$_f$** = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.37 (m, 4H), 7.35 – 7.29 (m, 3H), 6.92 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.81 – 6.79 (m, 2H), 6.70 (d, *J* = 2.5 Hz, 1H), 4.87 – 4.81 (m, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.76 (dd, *J* = 9.7, 6.0 Hz, 1H), 3.57 (dd, *J* = 9.7, 6.2 Hz, 1H), 2.87 (dd, *J* = 14.2, 5.1 Hz, 1H), 2.73 (dd, *J* = 14.2, 6.9 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 158.9, 154.1, 138.3, 137.1, 131.2, 129.4, 128.8, 128.6, 127.9, 127.9, 127.1, 114.9, 112.6, 110.7, 108.7, 86.5, 73.6, 71.5, 55.6, 55.5, 35.5;

HRMS (ESI-TOF): calc'd for $C_{24}H_{24}NaO_4^+$ [M+Na^+] 399.1567, found 399.1566.

6-((benzyloxy)methyl)-2,10-dimethyl-6,7-dihydrodibenzo[*b,d*]oxepine (3r)



Physical state: colorless oil;

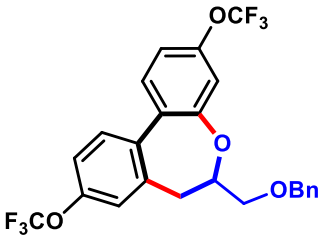
Yield: 82%;

***R*$_f$** = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.28 (m, 5H), 7.25 – 7.19 (m, 2H), 7.09 – 7.06 (m, 3H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.79 – 4.73 (m, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 3.70 (dd, *J* = 9.7, 6.0 Hz, 1H), 3.50 (dd, *J* = 9.7, 6.3 Hz, 1H), 2.80 (dd, *J* = 14.2, 5.3 Hz, 1H), 2.65 (dd, *J* = 14.2, 6.9 Hz, 1H), 2.39 (s, 3H), 2.37 (s, 3H).;**^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.2, 138.8, 138.4, 137.1, 135.0, 134.1, 133.1, 129.8, 129.5, 129.1, 128.8, 128.7, 128.4, 128.1, 128.0, 123.1, 86.7, 73.7, 71.2, 34.8, 21.4, 21.1;

HRMS (ESI-TOF): calc'd for $C_{24}H_{24}NaO_2^+$ [M+Na^+] 367.1669, found 367.1670.

6-((benzyloxy)methyl)-3,9-bis(trifluoromethoxy)-6,7-dihydrodibenzo[*b,d*]oxepine (3s)



Physical state: colorless oil;

Yield: 51%;

R_f = 0.3 (silica gel, PE:EtOAc = 20:1);

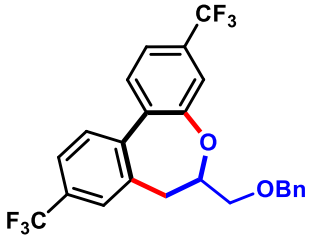
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.21 (m, 7H), 7.24 – 7.21 (m, 1H), 7.13 – 7.07 (m, 2H), 7.03 – 6.98 (m, 1H), 4.90 – 4.80 (m, 1H), 4.66 – 4.54 (m, 2H), 3.73 – 3.66 (m, 1H), 3.59 – 3.50 (m, 1H), 2.90 – 2.74 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 149.7 (q, *J* = 1.8 Hz), 148.8 (q, *J* = 1.9 Hz), 137.9, 136.3, 132.4, 130.0, 129.5, 128.7, 128.1, 128.1, 121.7, 120.7 (q, *J* = 258.6 Hz), 120.6 (q, *J* = 259.6 Hz), 120.0, 117.2, 116.3, 87.2, 73.7, 70.9, 34.9;

^{19}F NMR (376 MHz, $CDCl_3$): δ -57.7, -57.8;

HRMS (ESI-TOF): calc'd for $C_{24}H_{18}F_6NaO_4^+$ [M+Na^+] 507.1001, found 507.0999.

6-((benzyloxy)methyl)-3,9-bis(trifluoromethyl)-6,7-dihydrodibenzo[*b,d*]oxepine (3t)



Physical state: colorless oil;

Yield: 39%;

R_f = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.56 – 7.50 (m, 4H), 7.41 – 7.31 (m, 6H), 4.91 – 4.85 (m, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 3.72 (dd, *J* = 9.8, 5.5 Hz, 1H), 3.58 (dd, *J* = 9.8, 6.0 Hz, 1H), 2.95 – 2.84 (m,

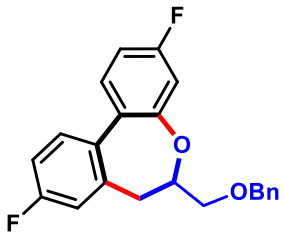
1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 141.1, 137.9, 137.3, 137.1, 132.1 (q, *J* = 32.7 Hz), 130.6 (q, *J* = 32.4 Hz), 129.9, 128.7, 128.2, 128.1, 128.0, 126.1 (q, *J* = 3.8 Hz), 125.4 (q, *J* = 36.0 Hz), 124.7 (q, *J* = 4.0 Hz), 122.7 (q, *J* = 36.0 Hz), 121.6 (q, *J* = 3.9 Hz), 120.9 (q, *J* = 3.7 Hz), 87.6, 73.8, 71.0, 34.8;

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.4, -62.5;

HRMS (ESI-TOF): calc'd for $C_{24}H_{18}F_6NaO_2^+$ [M+Na^+] 475.1103, found 475.1101.

6-((benzyloxy)methyl)-3,9-difluoro-6,7-dihydrodibenzo[*b,d*]oxepine (3u)



Physical state: colorless oil;

Yield: 50%;

***R**$_f$* = 0.3 (silica gel, PE:EtOAc = 20:1);

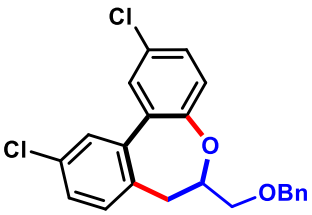
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.30 (m, 7H), 7.06 (td, *J* = 8.5, 2.6 Hz, 1H), 6.97 – 6.91 (m, 2H), 6.83 (dd, *J* = 9.5, 2.6 Hz, 1H), 4.85 – 4.79 (m, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 3.71 (dd, *J* = 9.7, 5.8 Hz, 1H), 3.54 (dd, *J* = 9.7, 6.2 Hz, 1H), 2.83 (dd, *J* = 14.3, 5.1 Hz, 1H), 2.74 (dd, *J* = 14.3, 6.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8 (d, *J* = 69.1 Hz), 161.4 (d, *J* = 68.2 Hz), 154.3 (d, *J* = 11.1 Hz), 138.0, 137.9 (d, *J* = 7.7 Hz), 134.0 (d, *J* = 3.2 Hz), 130.2 (d, *J* = 3.5 Hz), 129.9 (d, *J* = 9.6 Hz), 129.6 (d, *J* = 8.4 Hz), 128.7, 128.1, 116.1 (d, *J* = 21.6 Hz), 114.4 (d, *J* = 21.2 Hz), 111.9 (d, *J* = 21.2 Hz), 110.9 (d, *J* = 22.2 Hz), 86.9, 73.7, 70.9, 35.0;

^{19}F NMR (376 MHz, $CDCl_3$): δ -112.8, -115.0;

HRMS (ESI-TOF): calc'd for $C_{22}H_{18}F_2NaO_2^+$ [M+Na^+] 375.1167, found 375.1162.

6-((benzyloxy)methyl)-2,10-dichloro-6,7-dihydrodibenzo[*b,d*]oxepine (3v)



Physical state: colorless oil;

Yield: 35%;

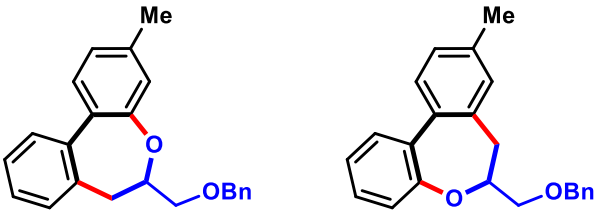
***R*$_f$** = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.30 (m, 7H), 7.28 – 7.25 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 4.81 – 4.75 (m, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 3.68 (dd, *J* = 9.7, 5.8 Hz, 1H), 3.51 (dd, *J* = 9.7, 6.2 Hz, 1H), 2.81 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.71 (dd, *J* = 14.4, 6.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 139.2, 138.0, 135.4, 134.5, 133.4, 130.6, 130.0, 129.4, 128.9, 128.7, 128.1, 128.1, 128.1, 128.0, 124.9, 87.0, 73.7, 70.8, 34.3;

HRMS (ESI-TOF): calc'd for $C_{22}H_{18}Cl_2NaO_2^+$ [M+Na$^+$] 407.0576, found 407.0577.

6-((benzyloxy)methyl)-3-methyl-6,7-dihydrodibenzo[*b,d*]oxepine (3w) and 6-((benzyloxy)methyl)-9-methyl-6,7-dihydrodibenzo[*b,d*]oxepine (3w′)



Physical state: colorless oil;

Yield: 75%, **3w** : **3w′** = 1:1;

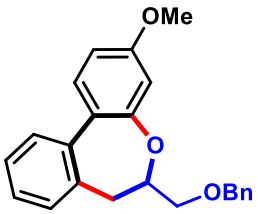
***R*$_f$** = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$) (mixture): δ 7.43 – 7.16 (m, 10H), 7.10 – 7.07 (m, 0.5H), 7.05 – 7.03 (m, 0.5H), 7.02 – 7.01 (m, 0.5H), 6.92 – 6.90 (m, 0.5H), 4.84 – 4.78 (m, 1H), 4.67 – 4.55 (m, 2H), 3.76 – 3.70 (m, 1H), 3.57 – 3.50 (m, 1H), 2.88 – 2.79 (m, 1H), 2.75 – 2.65 (m, 1H), 2.37 (s, 1.5H), 2.35 (s, 1.5H).

^{13}C NMR (100 MHz, $CDCl_3$) (mixture): δ 153.4, 153.2, 139.2, 138.9, 138.3, 137.5, 136.0, 135.9, 135.9, 135.2, 132.0, 129.9, 129.2, 129.1, 129.0, 128.7, 128.6, 128.2, 128.1, 128.0, 128.0, 127.9, 127.5, 127.4, 125.5, 124.7, 124.0, 123.3, 86.8, 86.8, 73.6, 71.2, 71.2, 35.2, 35.1, 21.4, 21.3.

HRMS (ESI-TOF): calc'd for $C_{23}H_{22}NaO_2^+$ [M+Na$^+$] 353.1512, found 353.1504.

6-((benzyloxy)methyl)-3-methoxy-6,7-dihydrodibenzo[*b,d*]oxepine (3x)



Physical state: colorless oil;

Yield: 31%;

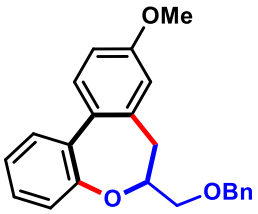
***R**$_f$* = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.38 – 7.28 (m, 7H), 7.25 – 7.19 (m, 2H), 7.08 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.92 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.80 (d, *J* = 2.7 Hz, 1H), 4.85 – 4.79 (m, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 3.84 (s, 3H), 3.74 (dd, *J* = 9.7, 5.9 Hz, 1H), 3.55 (dd, *J* = 9.7, 6.3 Hz, 1H), 2.84 (dd, *J* = 14.2, 5.2 Hz, 1H), 2.70 (dd, *J* = 14.2, 6.9 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 153.2, 138.3, 137.4, 134.9, 131.3, 129.2, 129.1, 128.6, 128.5, 128.0, 127.9, 124.7, 123.3, 114.9, 112.6, 86.5, 73.7, 71.4, 55.5, 35.5;

HRMS (ESI-TOF): calc'd for $C_{23}H_{22}NaO_3^+$ [M+Na$^+$] 369.1461, found 369.1453.

6-((benzyloxy)methyl)-9-methoxy-6,7-dihydrodibenzo[*b,d*]oxepine (3x'')



Physical state: colorless oil;

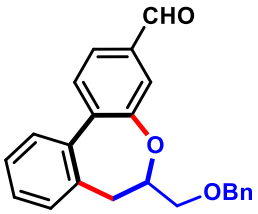
Yield: 43%;

***R*$_f$** = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.41 – 7.29 (m, 8H), 7.27 – 7.23 (m, 1H), 7.19 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.80 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.69 (d, *J* = 2.6 Hz, 1H), 87 – 4.81 (m, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 3.82 (s, 3H), 3.74 (dd, *J* = 9.7, 6.0 Hz, 1H), 3.55 (dd, *J* = 9.7, 6.2 Hz, 1H), 2.88 (dd, *J* = 14.2, 5.2 Hz, 1H), 2.74 (dd, *J* = 14.2, 6.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 154.4, 138.7, 138.3, 135.8, 129.8, 129.1, 128.6, 128.0, 127.9, 127.8, 127.5, 127.4, 127.2, 110.8, 108.7, 87.0, 73.7, 71.4, 55.6, 35.3;
HRMS (ESI-TOF): calc'd for $C_{23}H_{22}NaO_3^+$ [M+Na$^+$] 369.1461, found 369.1448.

6-((benzyloxy)methyl)-6,7-dihydrodibenzo[*b,d*]oxepine-3-carbaldehyde (3y)



Physical state: colorless oil;

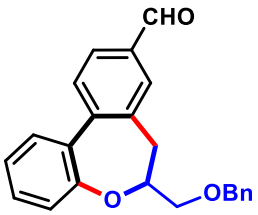
Yield: 34%;

***R*$_f$** = 0.2 (silica gel, PE:EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.75 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.48 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.43 – 7.29 (m, 7H), 7.24 (dd, *J* = 7.3, 1.3 Hz, 1H), 4.91 – 4.85 (m, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 3.74 (dd, *J* = 9.8, 5.7 Hz, 1H), 3.58 (dd, *J* = 9.8, 6.1 Hz, 1H), 2.87 (dd, *J* = 14.4, 5.1 Hz, 1H), 2.78 (dd, *J* = 14.4, 7.2 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 154.1, 141.7, 138.1, 137.6, 137.2, 136.3, 130.1, 129.3, 128.9, 128.7, 128.4, 128.1, 128.0, 127.8, 125.9, 124.5, 87.4, 73.7, 71.1, 35.0;
HRMS (ESI-TOF): calc'd for $C_{23}H_{20}NaO_3^+$ [M+Na$^+$] 367.1304, found 367.1301.

6-((benzyloxy)methyl)-6,7-dihydrodibenzo[b,d]oxepine-9-carbaldehyde (3y′)



Physical state: colorless oil;

Yield: 17%;

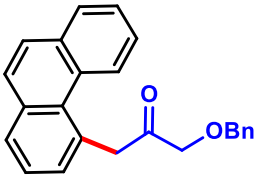
R_f = 0.1 (silica gel, PE:EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H), 7.88 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.71 (d, *J* = 1.7 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.41 – 7.25 (m, 7H), 7.12 (dd, *J* = 8.0, 1.3 Hz, 1H), 4.87 – 4.81 (m, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 3.73 (dd, *J* = 9.8, 5.9 Hz, 1H), 3.55 (dd, *J* = 9.8, 6.2 Hz, 1H), 2.95 (dd, *J* = 14.3, 5.4 Hz, 1H), 2.83 (dd, *J* = 14.3, 6.6 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 153.7, 145.4, 138.1, 137.1, 135.6, 134.0, 130.3, 130.2, 129.5, 129.3, 128.8, 128.7, 128.1, 128.1, 125.0, 123.7, 86.9, 73.7, 71.0, 35.0;

HRMS (ESI-TOF): calc'd for $C_{23}H_{20}NaO_3^+$ [M+Na$^+$] 367.1304, found 367.1308.

1-(benzyloxy)-3-(phenanthren-4-yl)propan-2-one (4)



Physical state: colorless oil;

Yield: 74%;

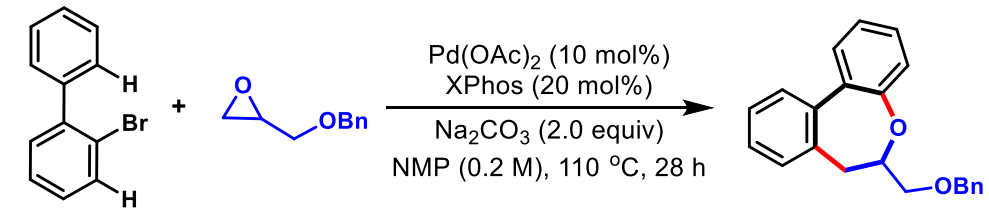
R_f = 0.3 (silica gel, PE:EtOAc = 20:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.81 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.69 (s, 2H), 7.58 – 7.48 (m, 3H), 7.39 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.32 – 7.21 (m, 5H), 4.63 (s, 2H), 4.53 (s, 2H), 4.16 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 207.0, 137.2, 134.2, 133.6, 132.2, 130.8, 130.5, 130.2, 129.1, 129.0, 128.6, 128.1, 128.0, 128.0, 127.5, 126.4, 126.3, 126.2, 126.1, 75.0, 73.5, 49.8;

HRMS (ESI-TOF): calc'd for $C_{24}H_{20}NaO_2^+$ [M+Na^+] 363.1356, found 363.1354.

6. Scale-up experiment



1a', 5.0 mmol **2a,** 10.0 mmol **3a,** 1.15 g, 73%

To a 120 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (110 mg, 0.5 mmol, 10 mol%), XPhos (482.5 mg, 1.0 mmol, 20 mol%) in the glove box. Then, 7.5 mL of dry NMP was added and the solution was pre-stirred for 30 minutes. After that, Na_2CO_3 (1.06 g, 10 mmol, 2.0 equiv), 2-bromobiphenyl **1a′** (1.17 g, 5.0 mmol, 1.0 equiv), benzyl glycidyl ether **2a** (1.64 g, 10.0 mmol, 2.0 equiv), and 17.5 mL of dry NMP were added, then the reaction mixture was heated to 110 ℃ and stirred for 28 h. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature. H_2O (50 mL) was added to quench the reaction and the mixture was extracted with EtOAc (50 mL × 3). The organic layers were collected and the combined organic phase was washed with H_2O (50 mL × 3), NaCl (sat. aq., 50 mL) and dried over anhydrous Na_2SO_4, then filtered. The solvents were evaporated under reduced pressure and the residue was directly purified by column chromatography on silica gel to give the desire product **3a** as a colorless oil (1.15 g, 73%).

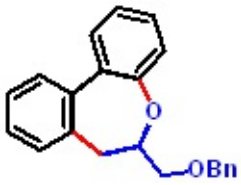
7. References

[1] T. H. Jepsen, M. Larsen, M. Jørgensen, K. A. Solanko, A. D. Bond, A. Kadziola, M. B. Nielsen. *Eur. J. Org. Chem.* **2011**, *1*, 53-57.

[2] H.-G. Cheng, C. Wu, H. Chen, R. Chen, G. Qian, Z. Geng, Q. Wei, Y. Xia, J. Zhang, Y. Zhang, Q. Zhou. *Angew. Chem. Int. Ed*. **2018**, *57*, 3444-3448.

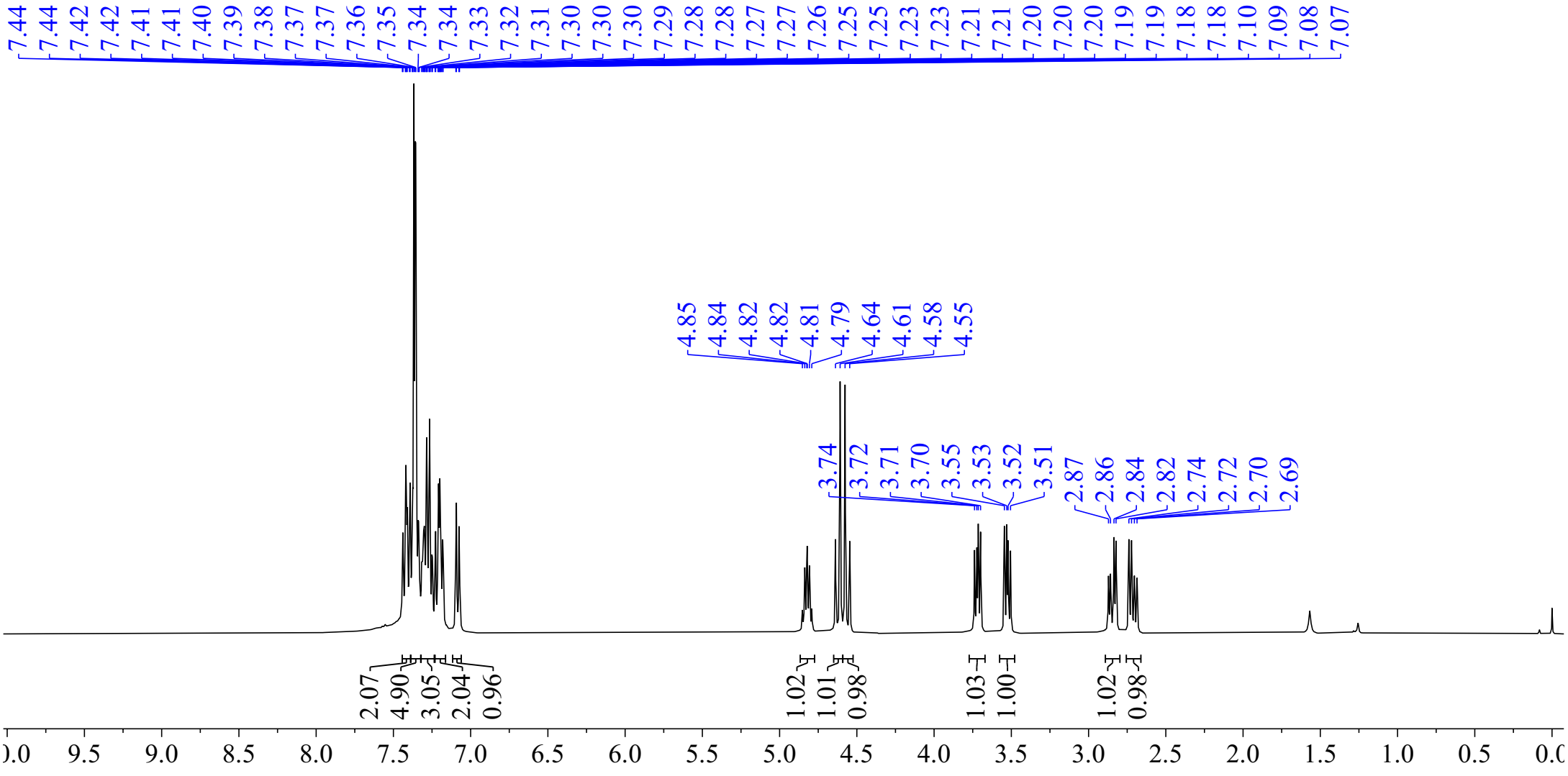
8. Copies of NMR spectra

szp-273-1

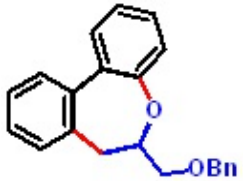


3a

^{1}H NMR, $CDCl_3$

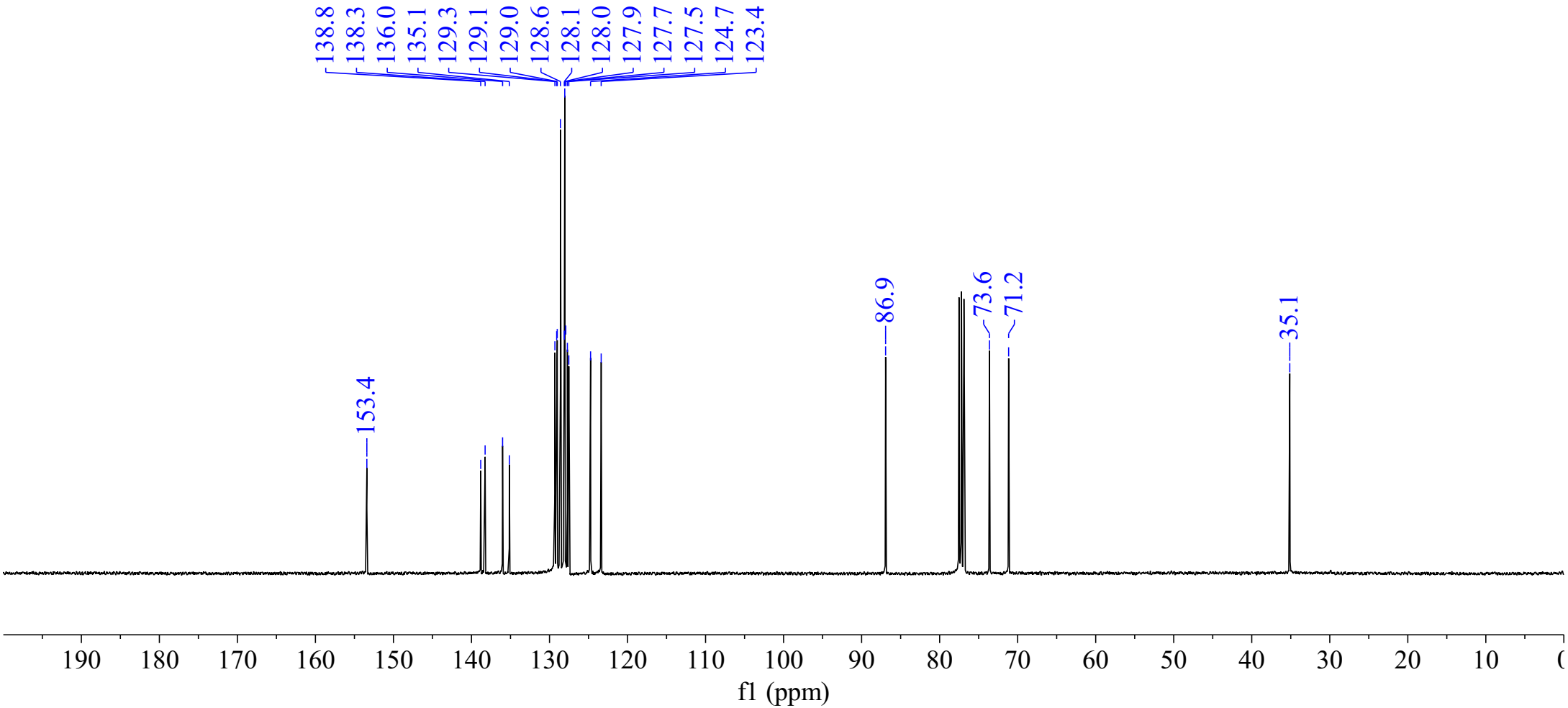


szp-273-1.2.fid

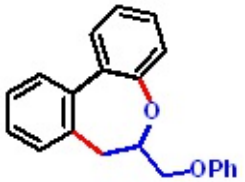


3a

^{13}C NMR, $CDCl_3$

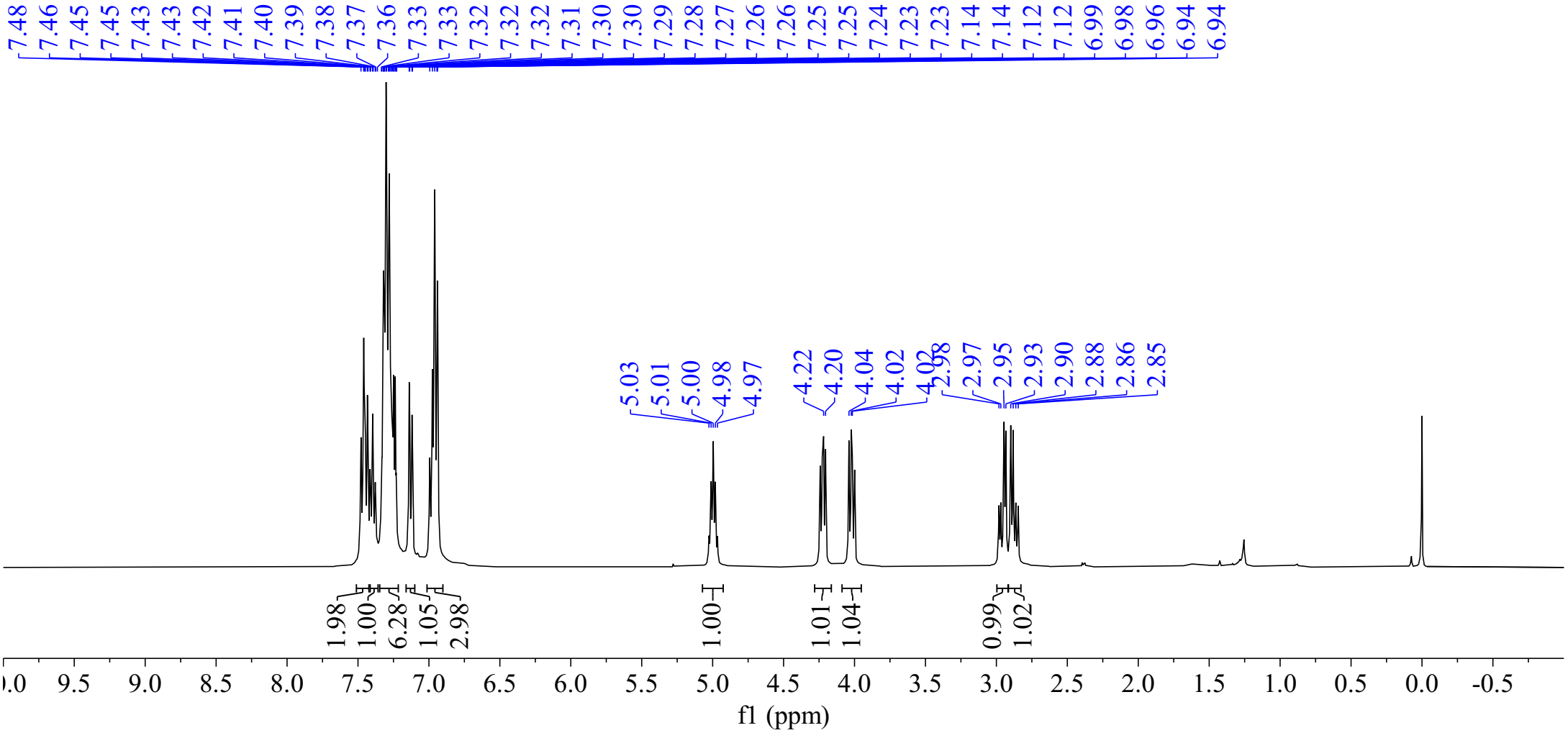


szp-3g1

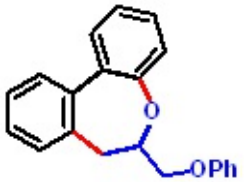


3b

^{1}H NMR, $CDCl_3$

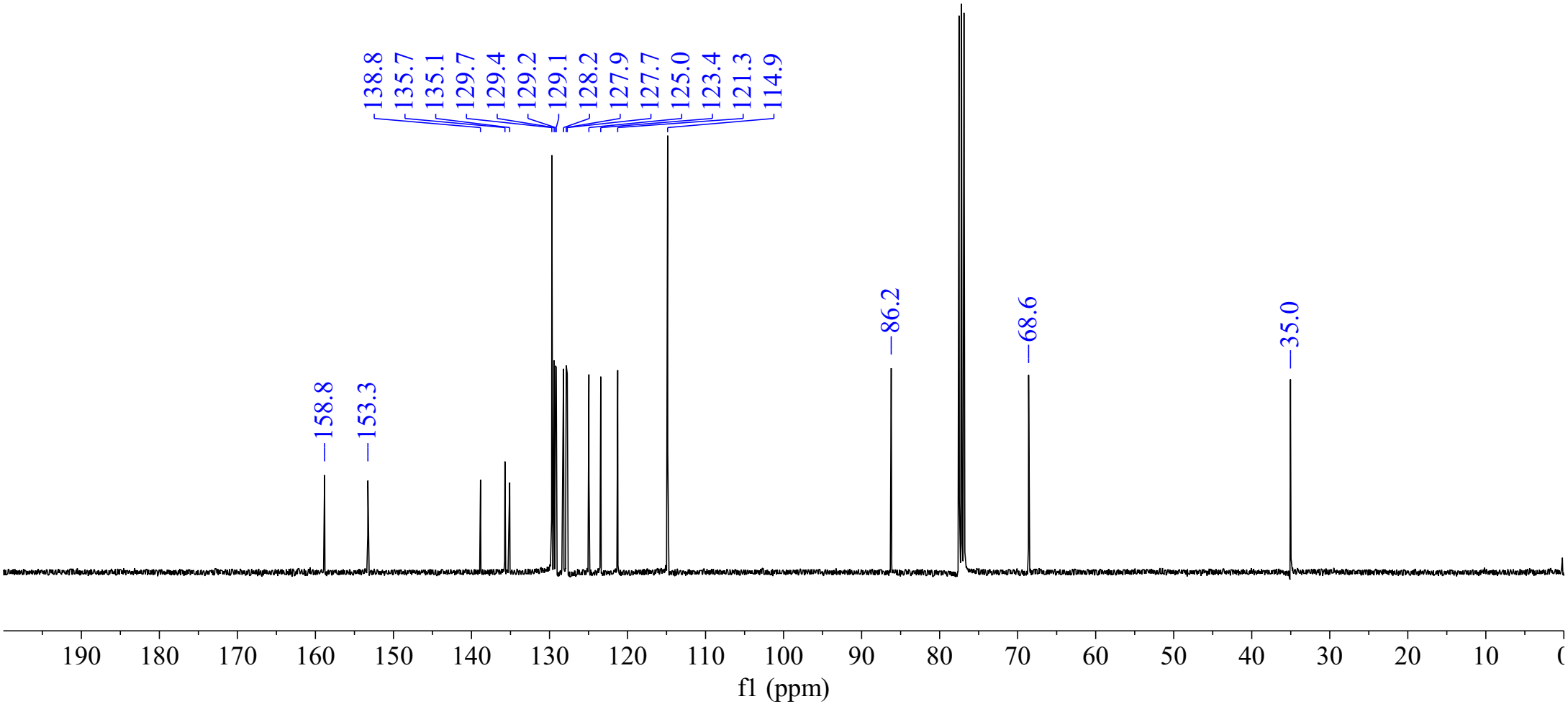


szp-3g1.2.fid



3b

^{13}C NMR, $CDCl_3$



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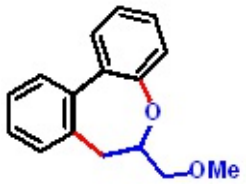
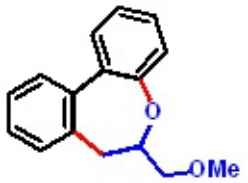


3c

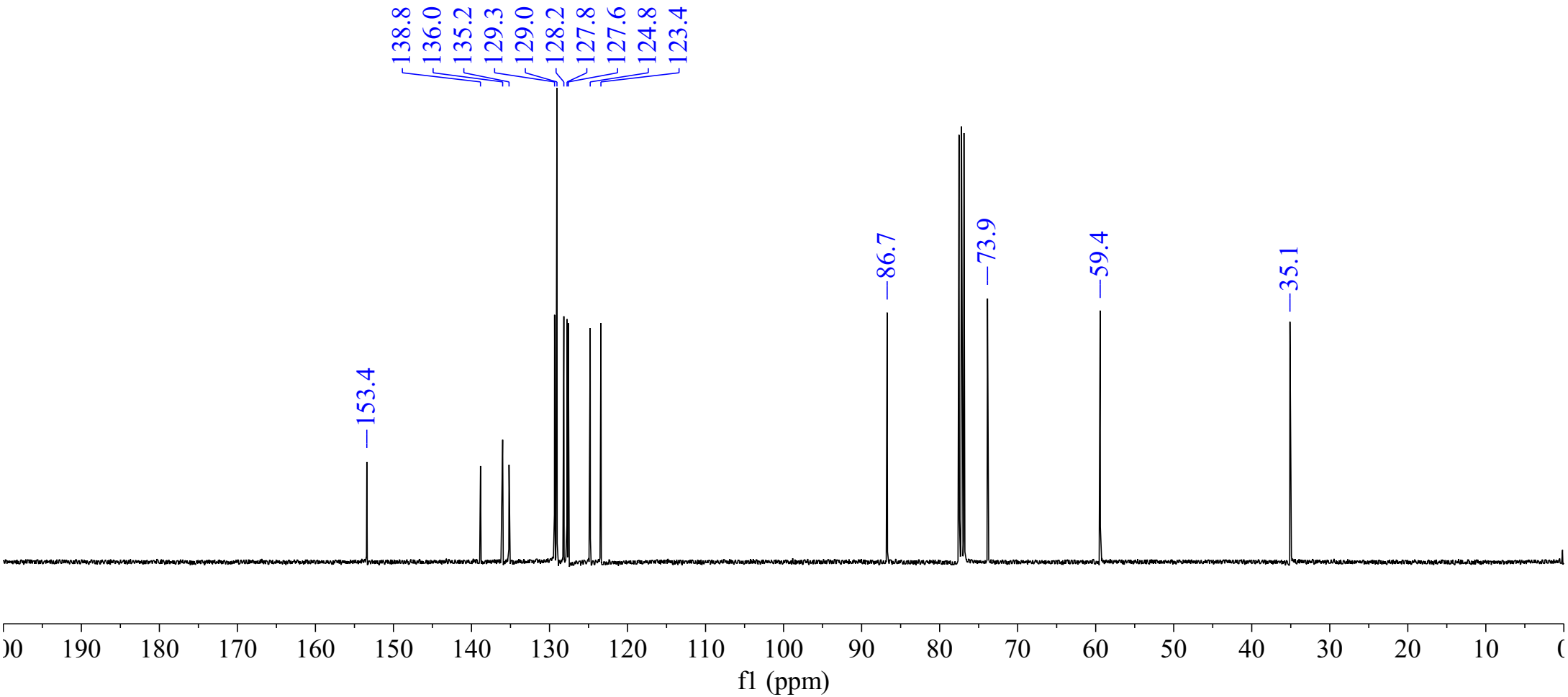
^{1}H NMR, $CDCl_3$

szp-3i1.2.fid

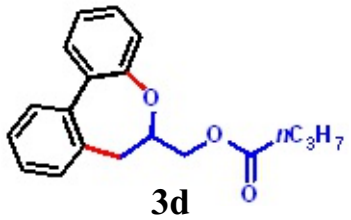


3c

^{13}C NMR, $CDCl_3$

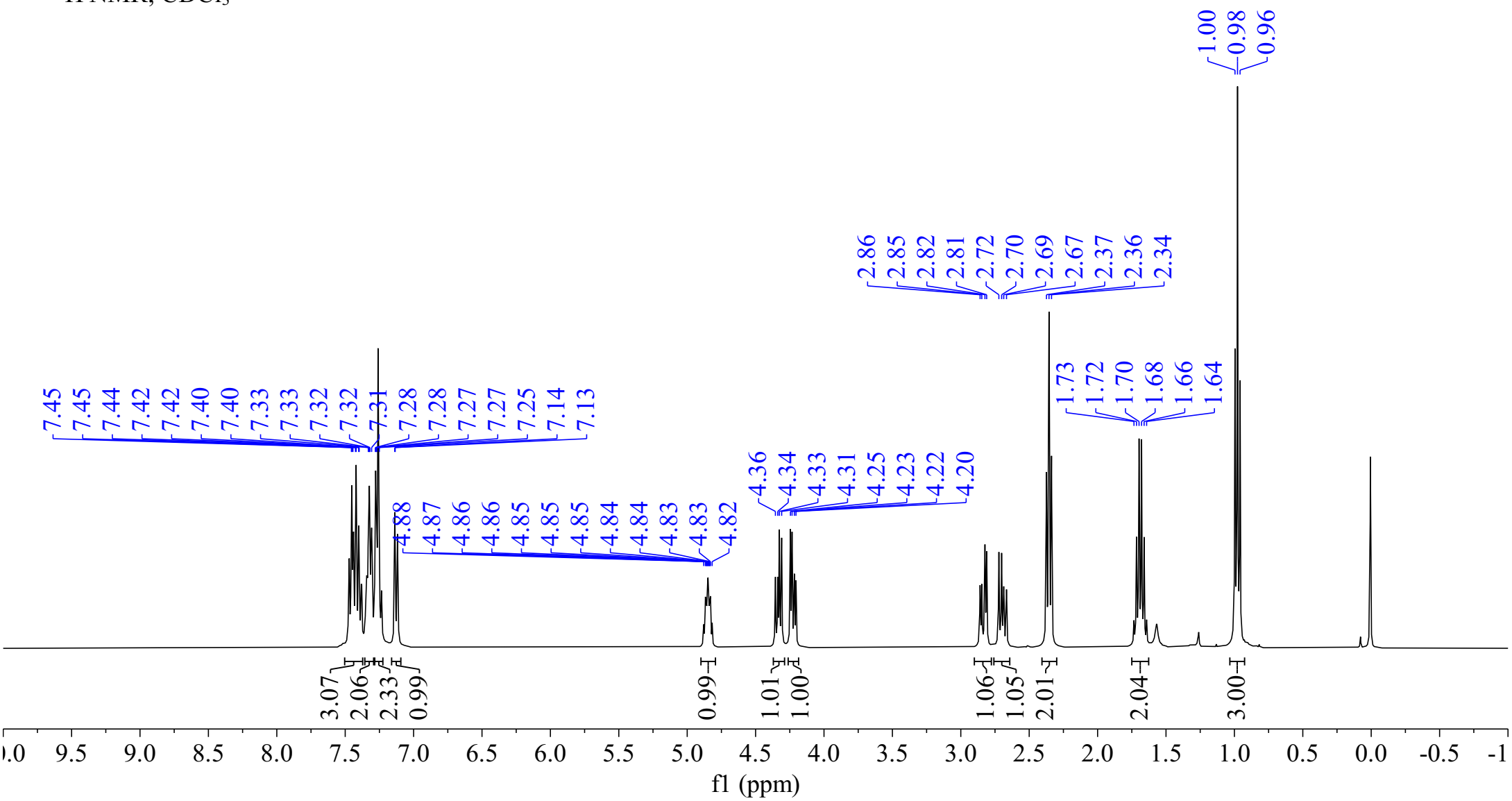


szp-3k1



3d

^{1}H NMR, $CDCl_3$



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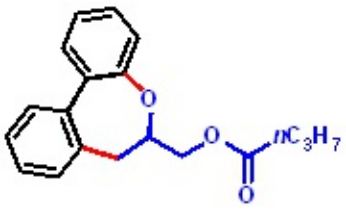


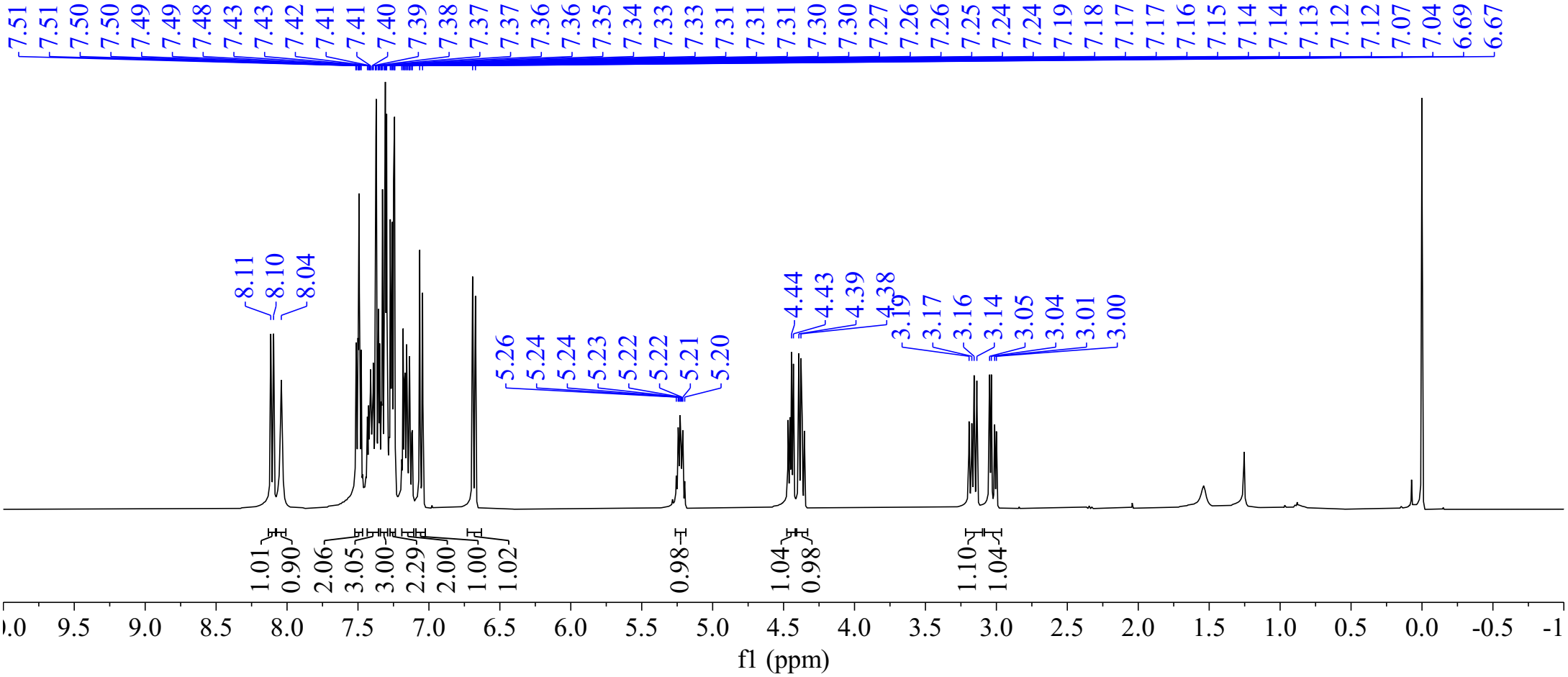
3d

^{13}C NMR, $CDCl_3$

szp-271-33

3e

^{1}H NMR, $CDCl_3$



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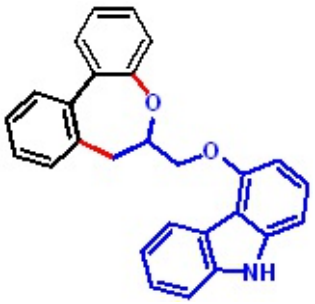
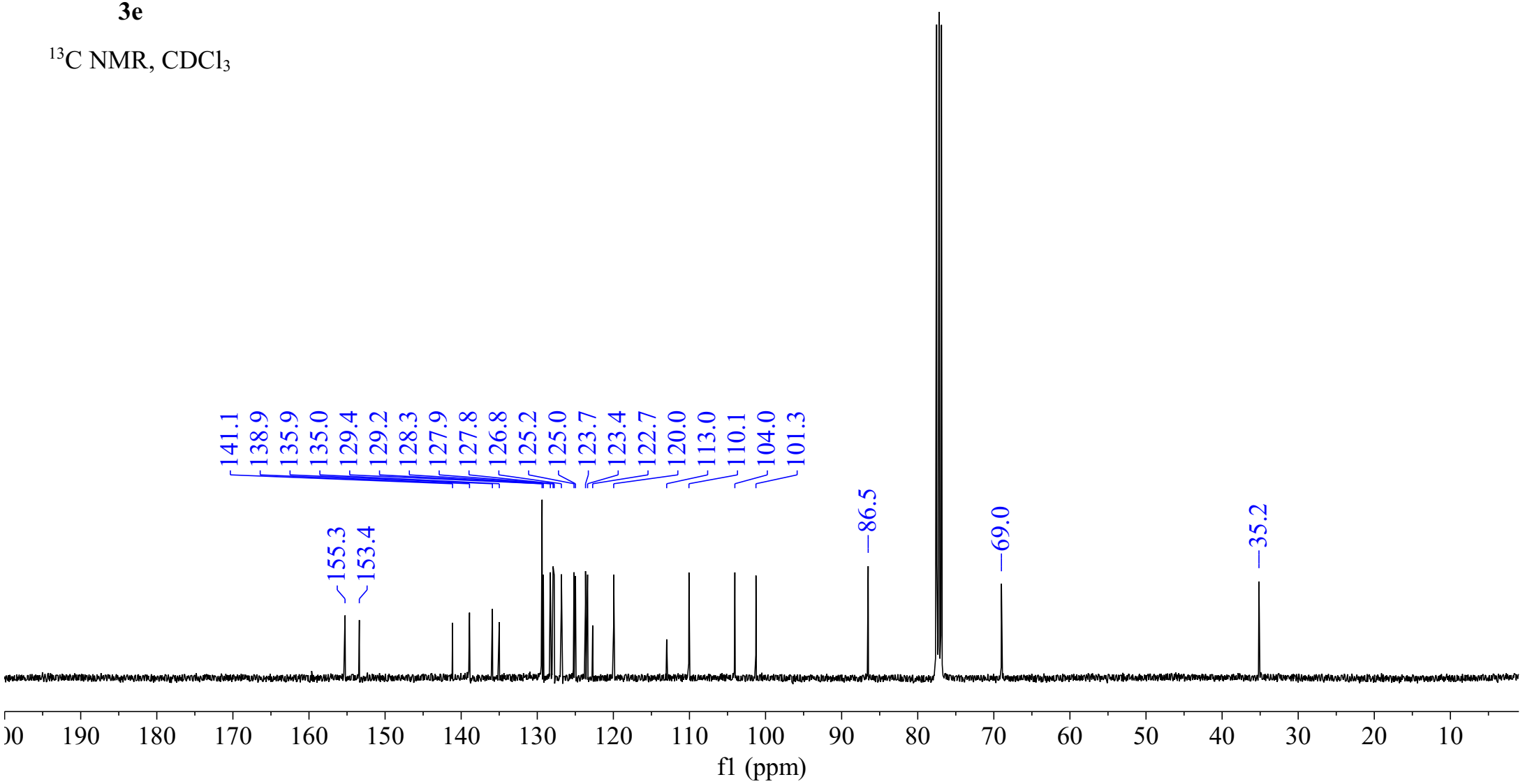
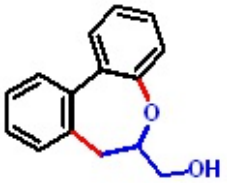


3e

^{13}C NMR, $CDCl_3$

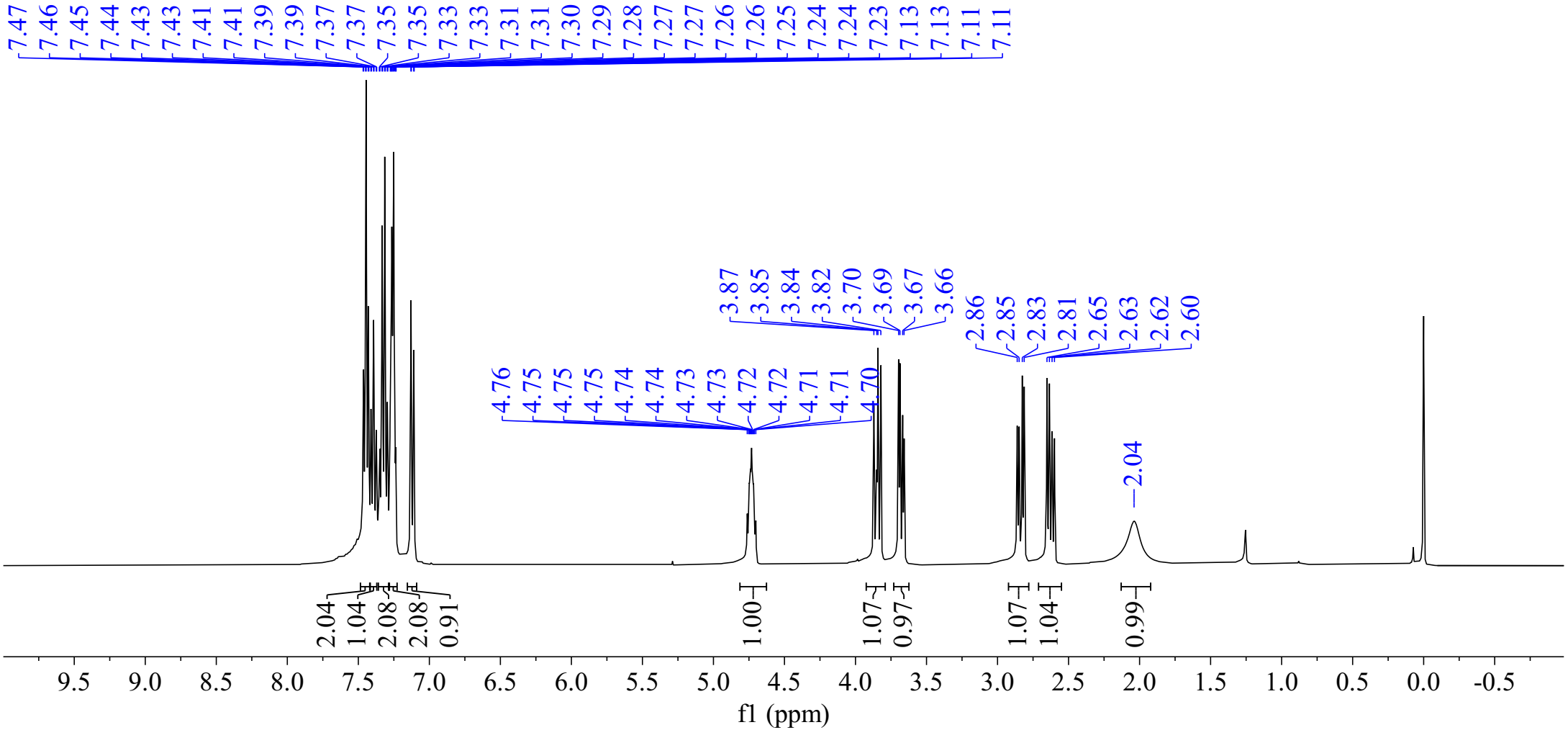


szp-3n1

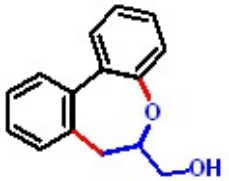


3f

^{1}H NMR, $CDCl_3$

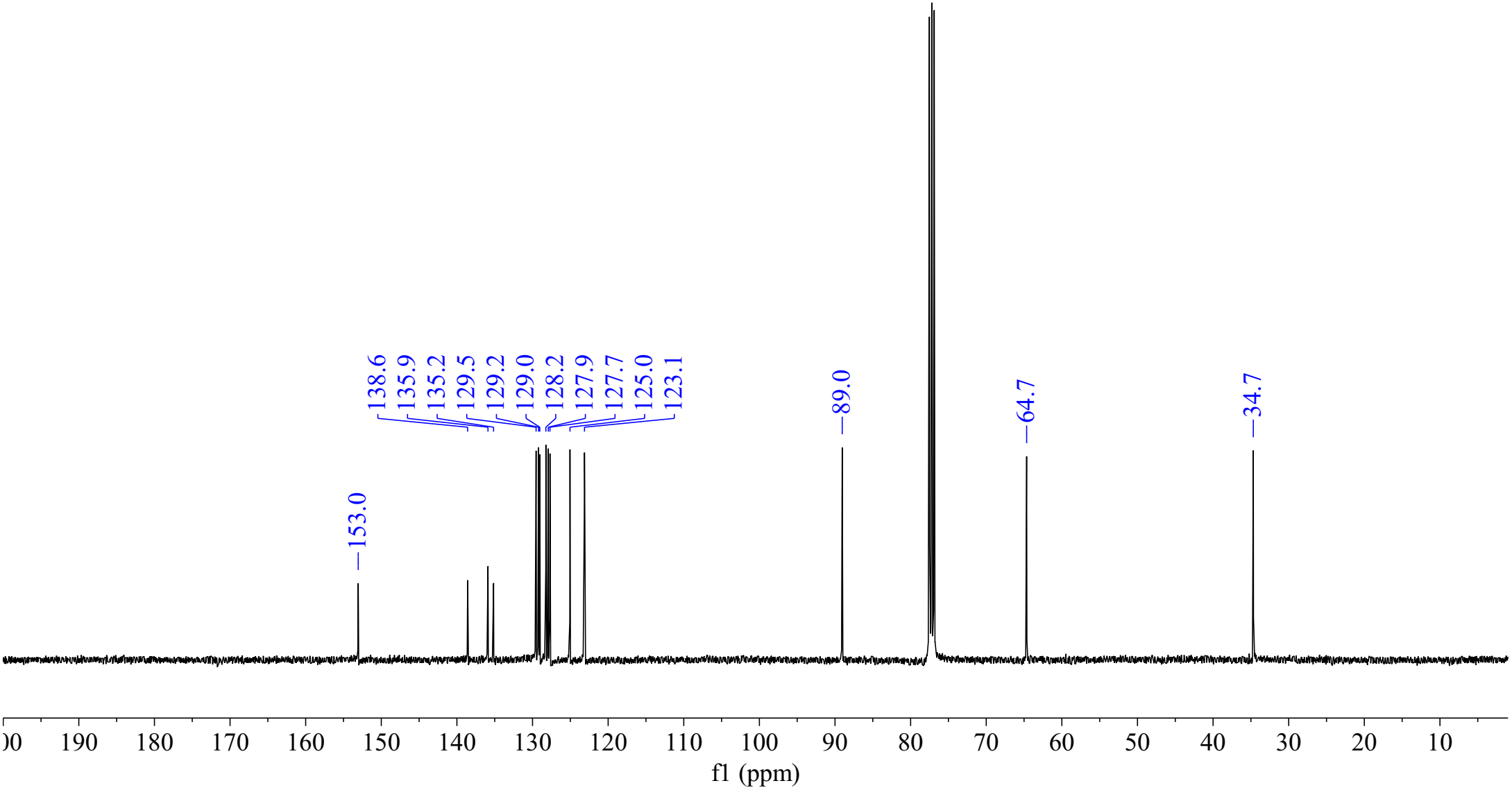


szp-3n1.2.fid

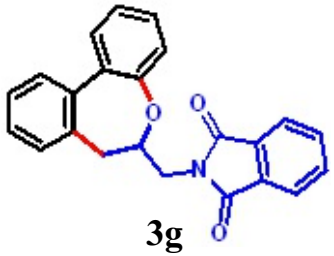


3f

^{13}C NMR, $CDCl_3$

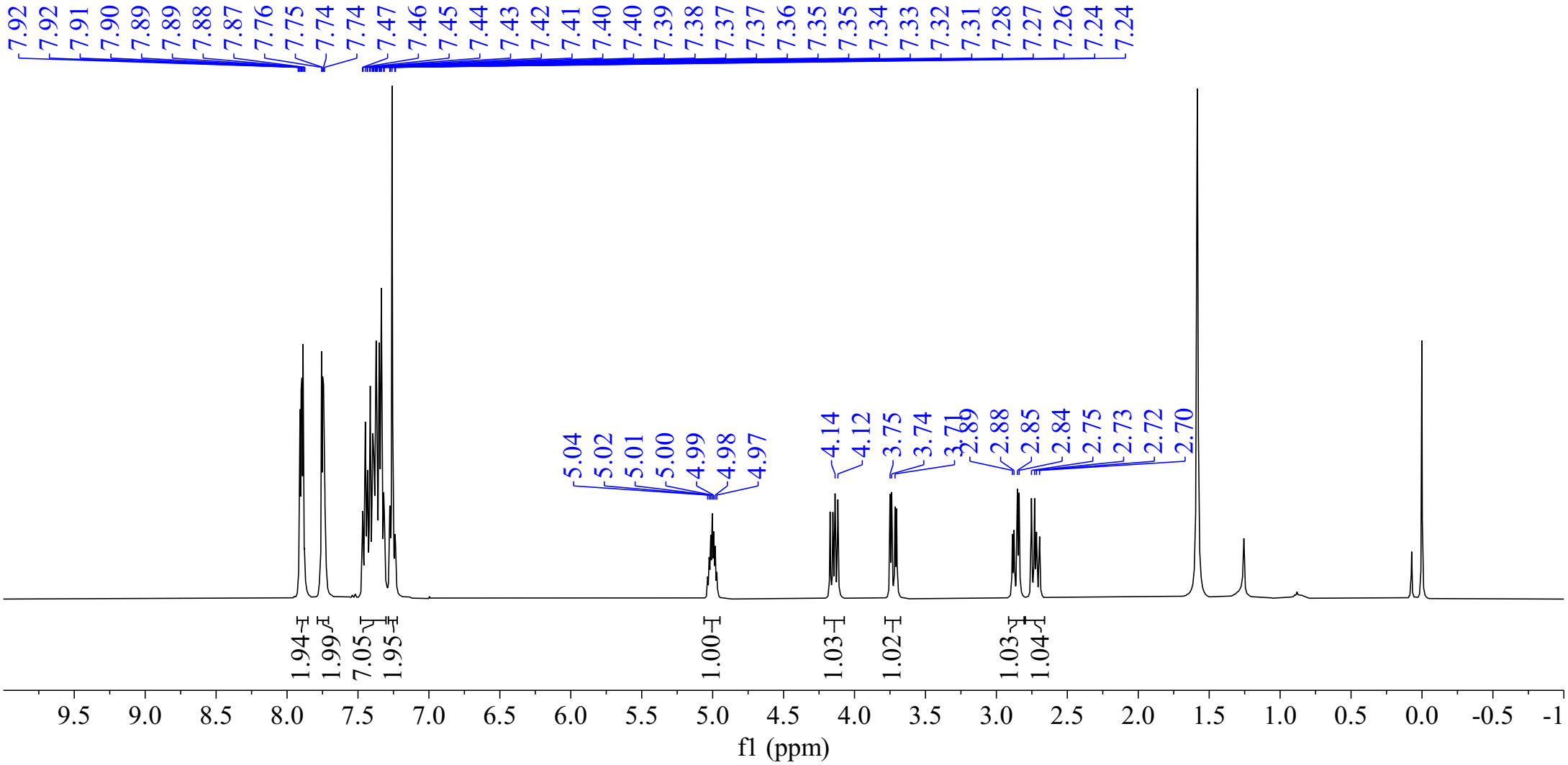


SZP-282-11.1.1.1r

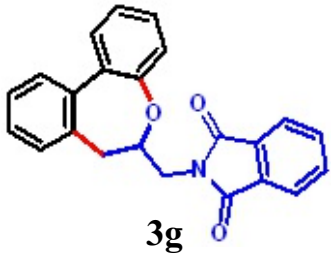


3g

^{1}H NMR, $CDCl_3$



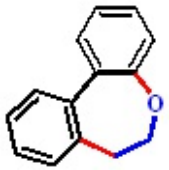
SZP-282-11.2.fid



3g

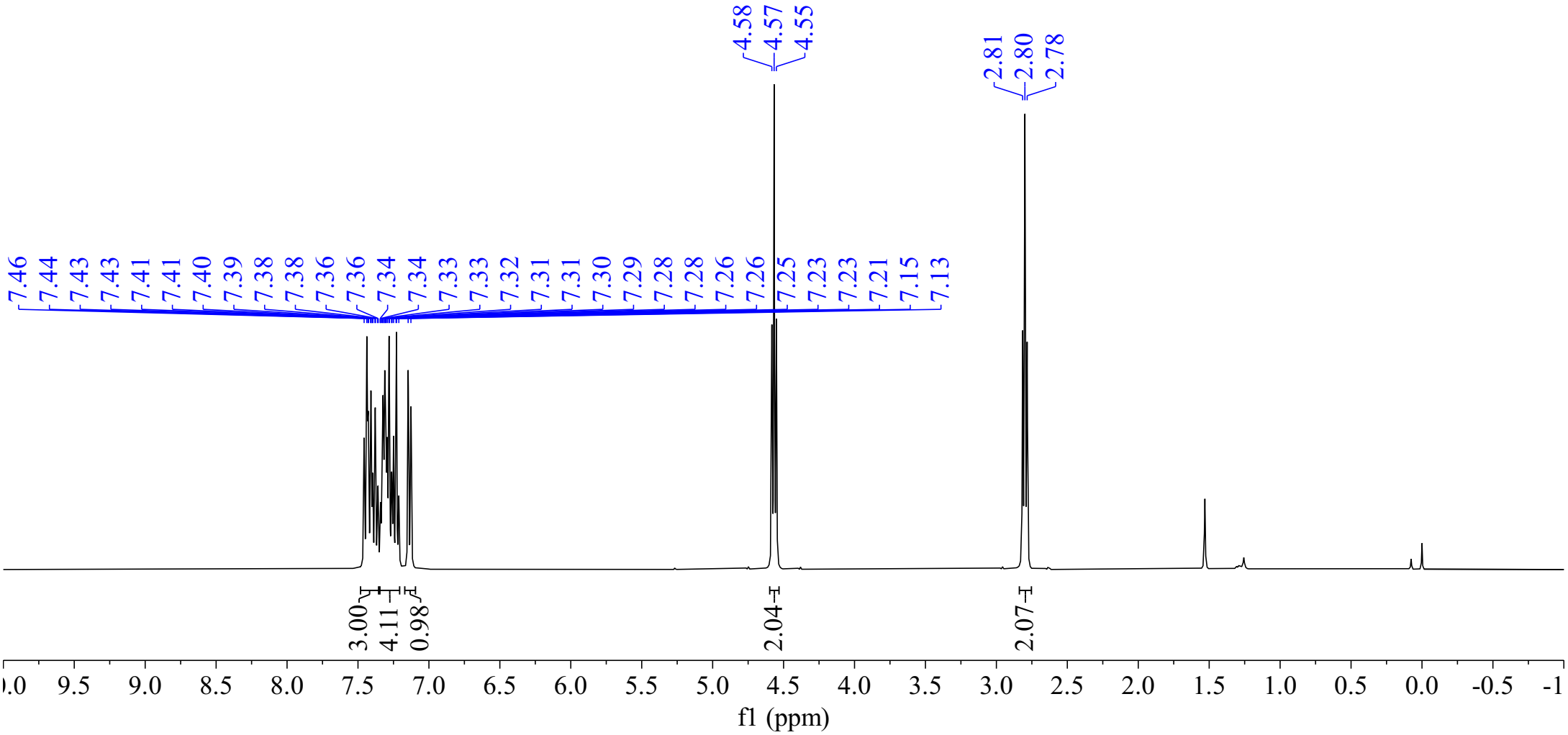
^{13}C NMR, $CDCl_3$

szp-280-1

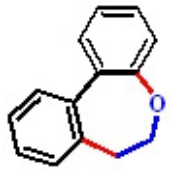


3h

^{1}H NMR, $CDCl_3$

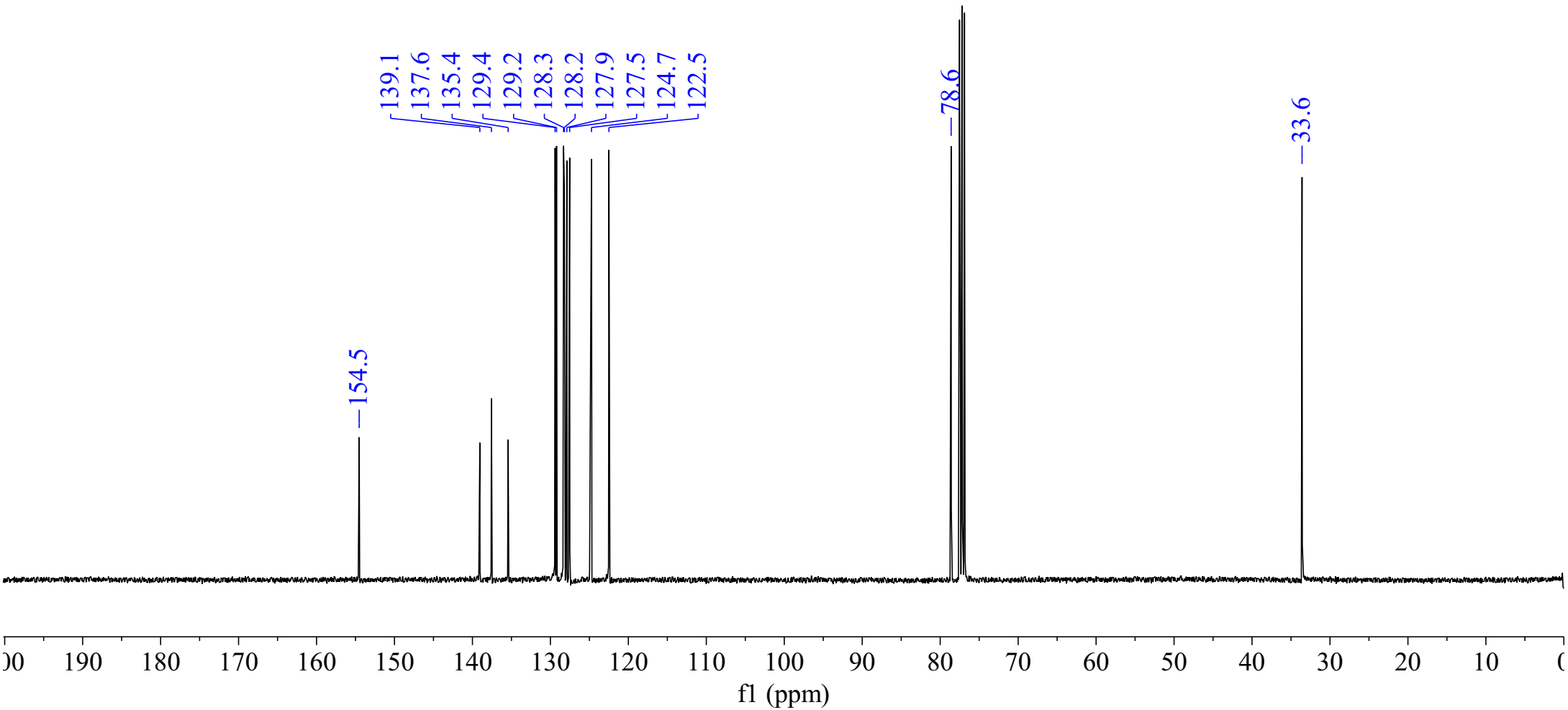


szp-280-1.2.fid



3h

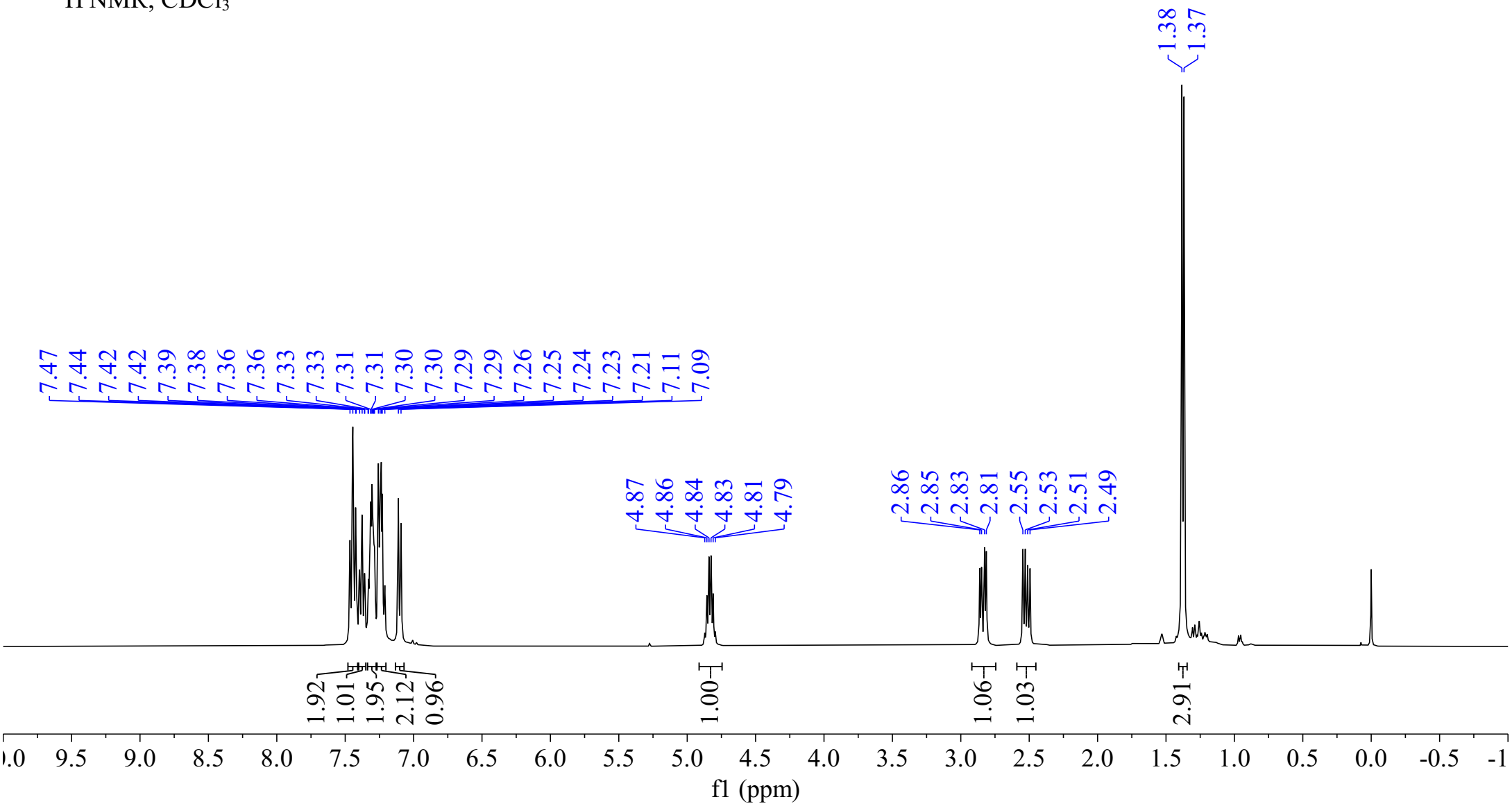
^{13}C NMR, $CDCl_3$



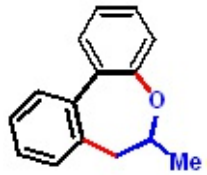
szp-3b1

3i

^{1}H NMR, $CDCl_3$

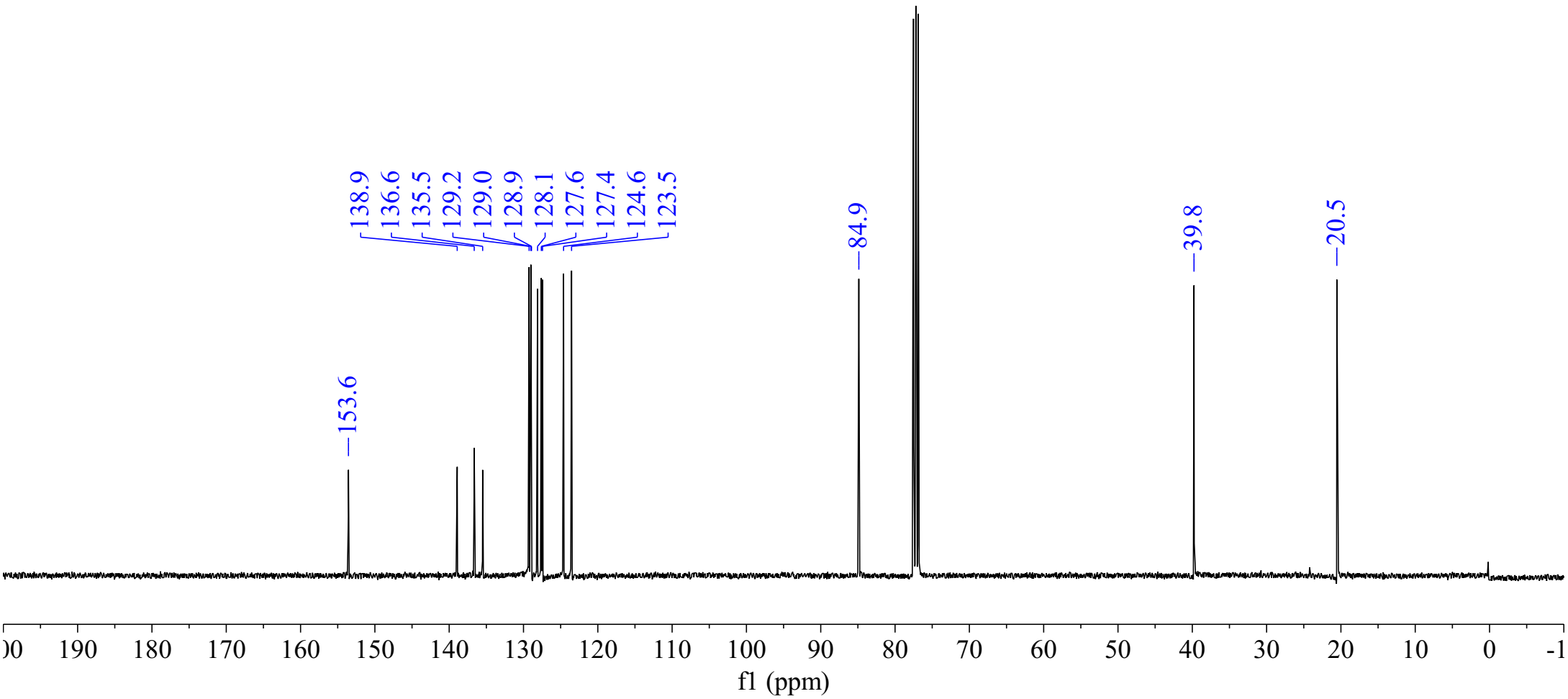


szp-3b1.2.fid



3i

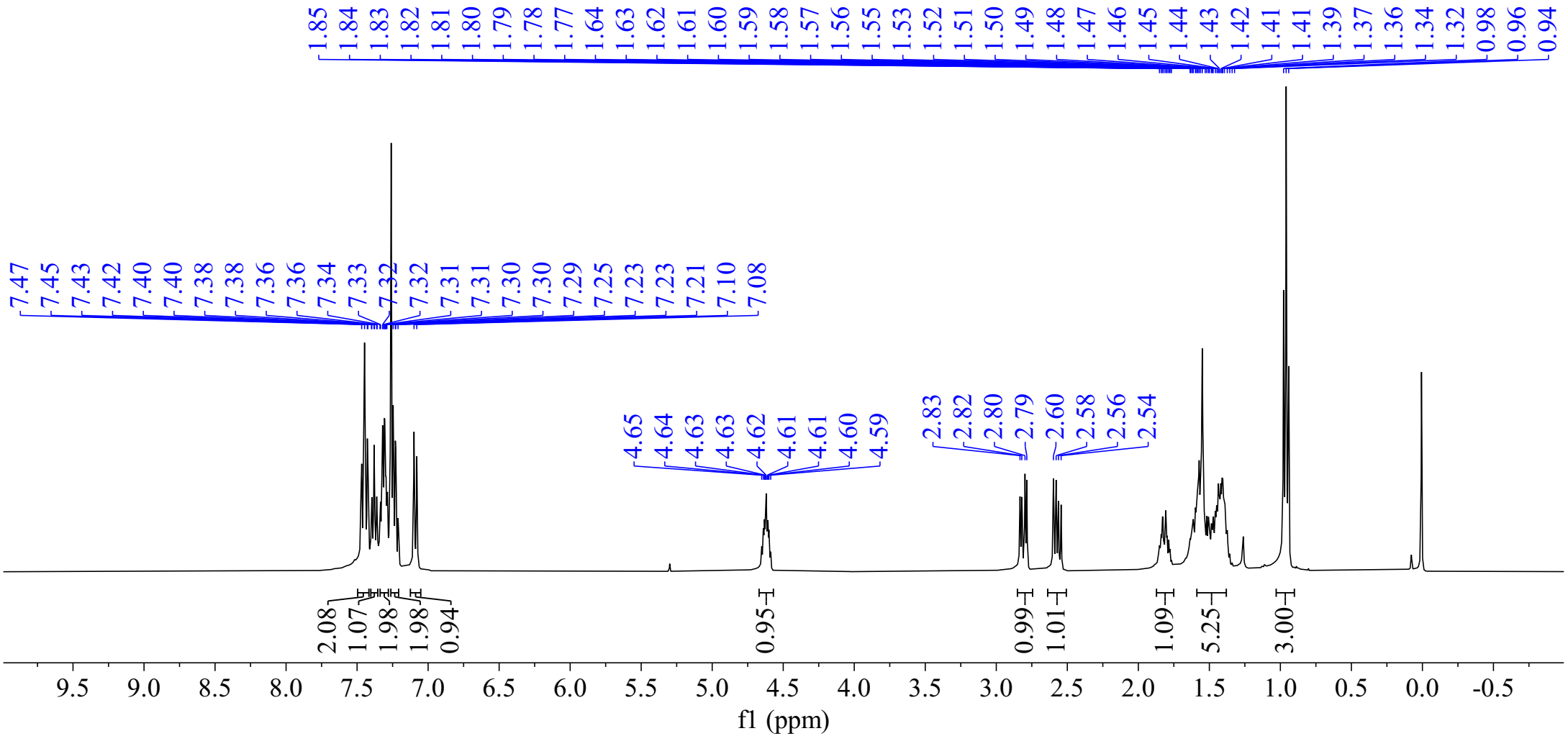
^{13}C NMR, $CDCl_3$



szp-3o

3j

^{1}H NMR, $CDCl_3$

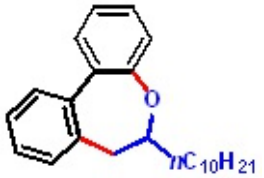


szp-3o.2.fid

3j

^{13}C NMR, $CDCl_3$

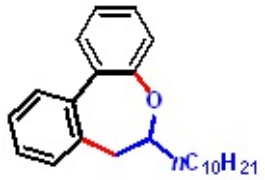
szp-235-4-3



3k

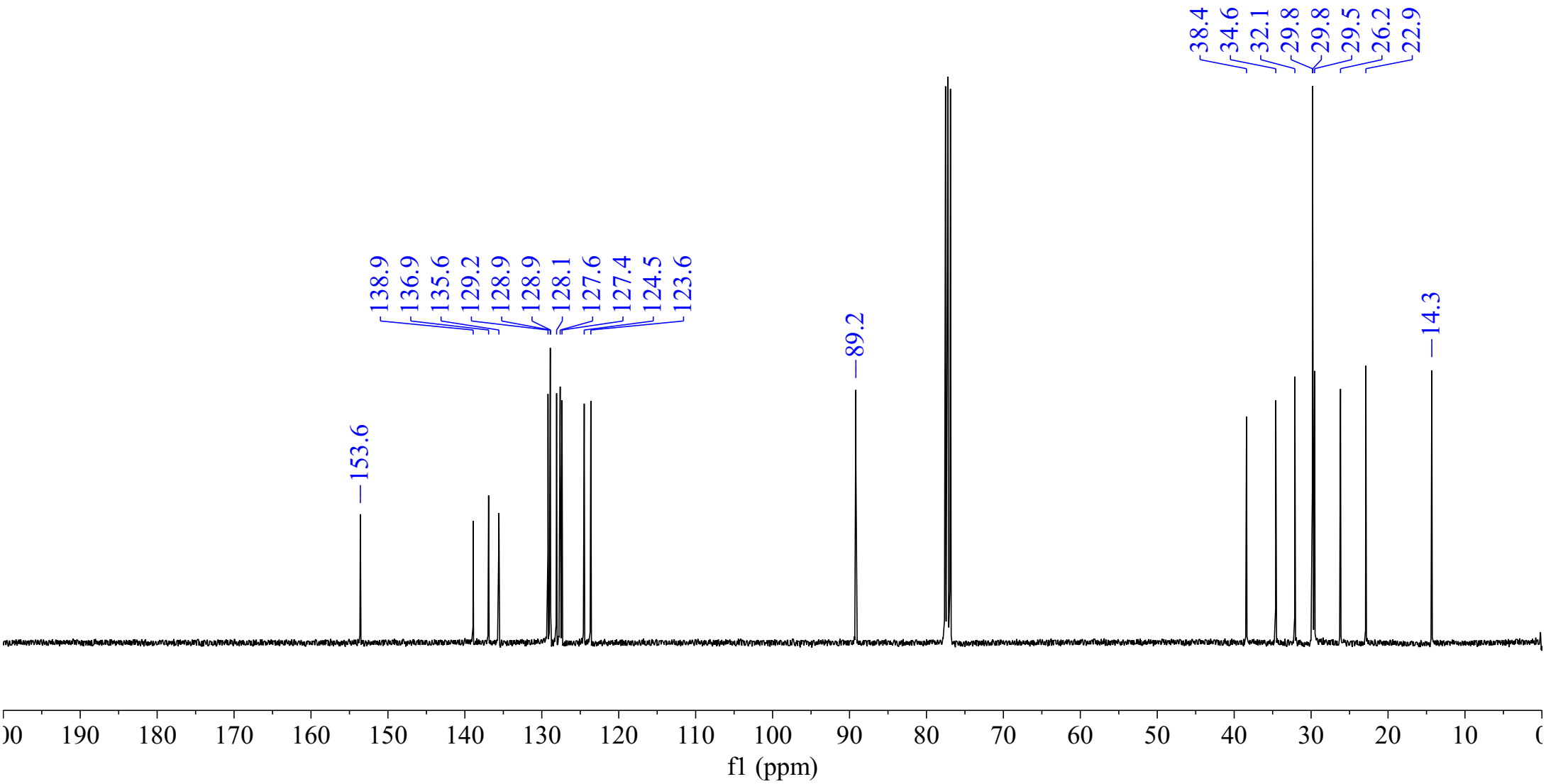
^{1}H NMR, $CDCl_3$

szp-235-4-3.2.fid

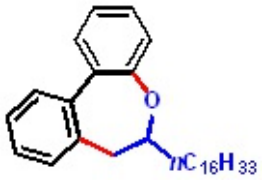


3k

^{13}C NMR, $CDCl_3$



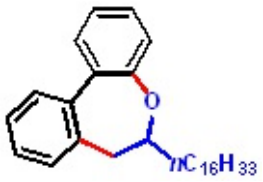
szp-235-5



3l

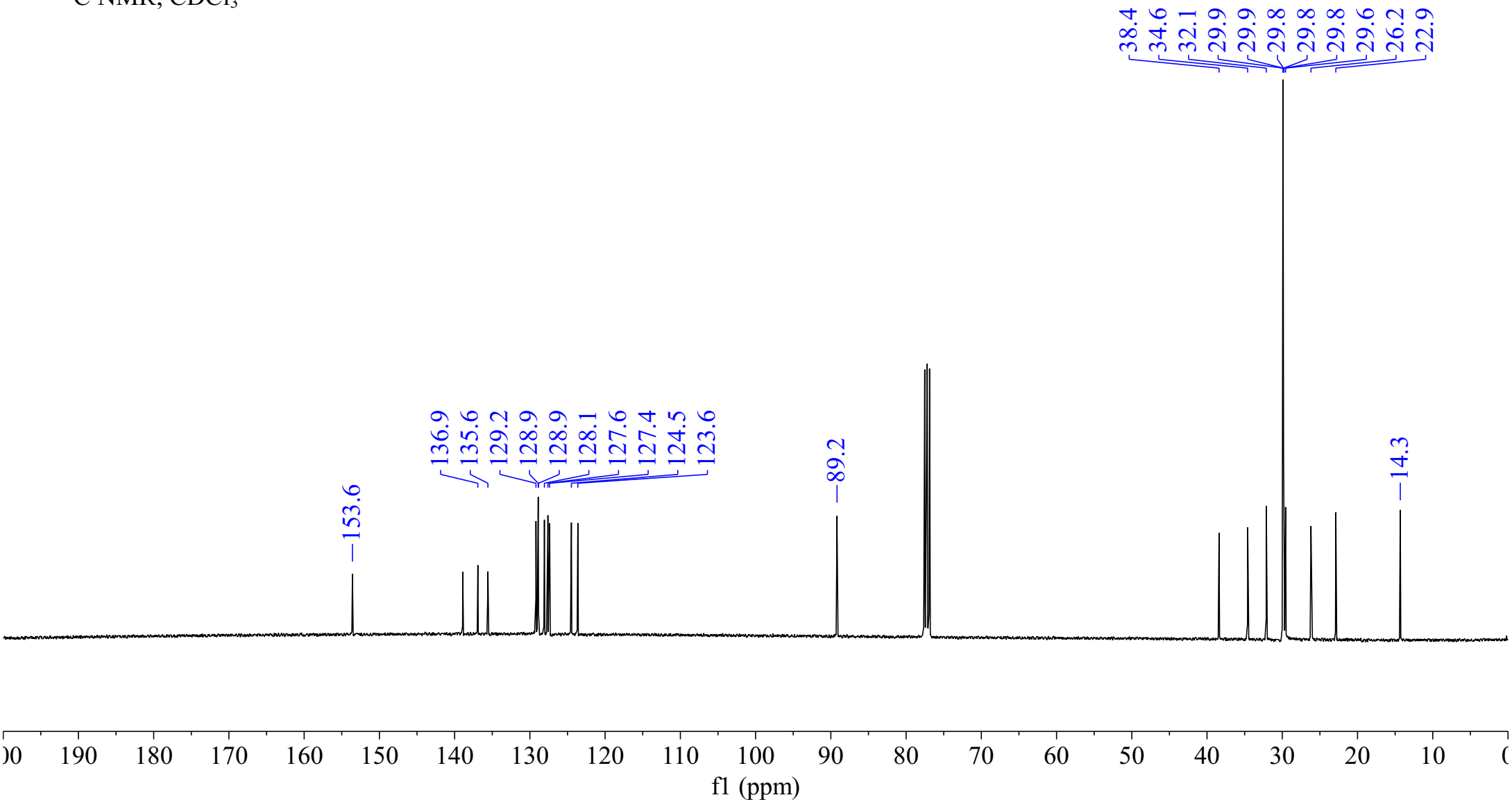
^{1}H NMR, $CDCl_3$

szp-235-5.2.fid

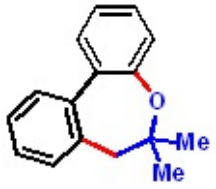


3l

^{13}C NMR, $CDCl_3$

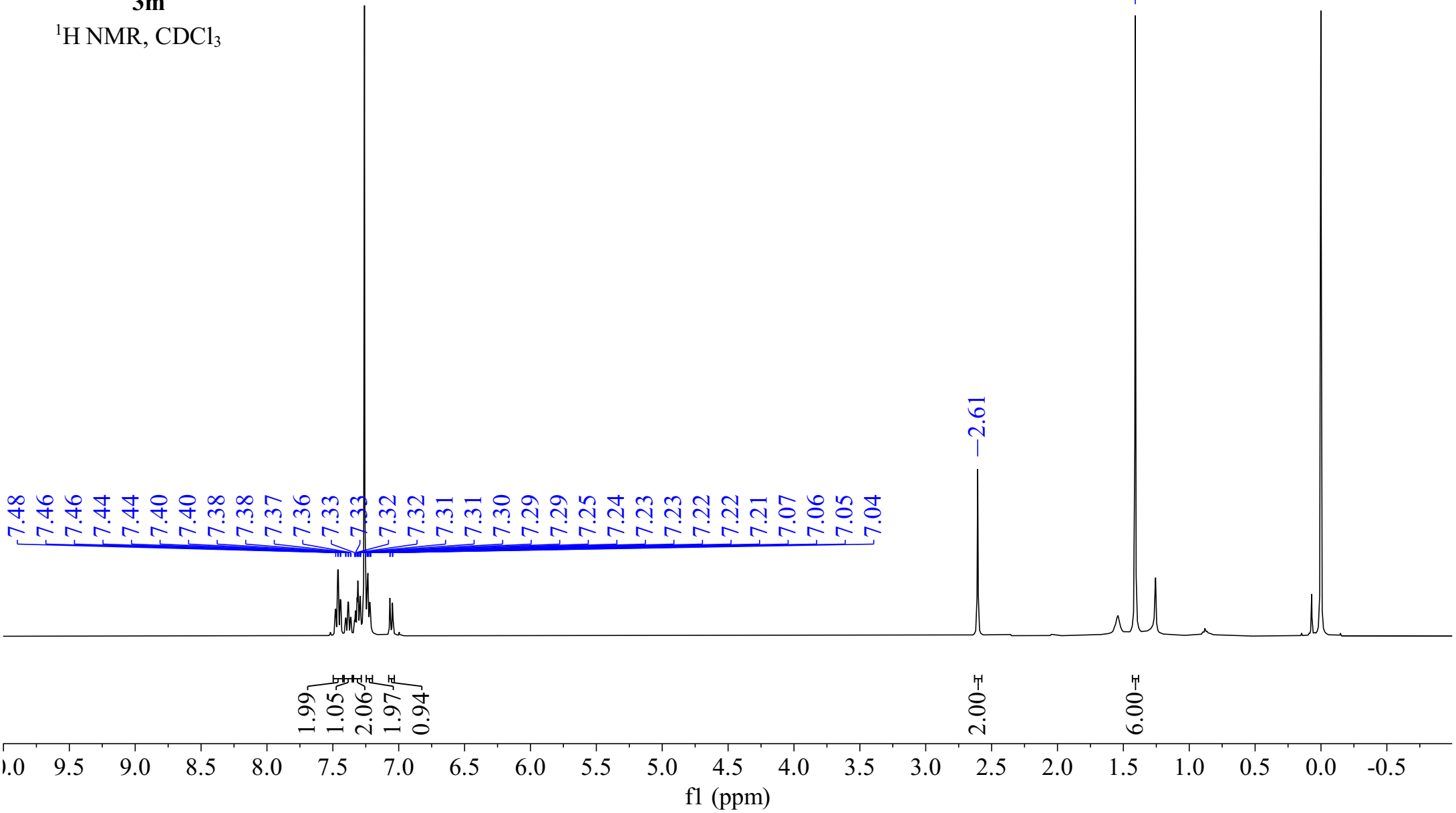


szp-249-1111

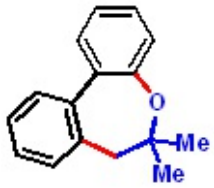


3m

^{1}H NMR, $CDCl_3$



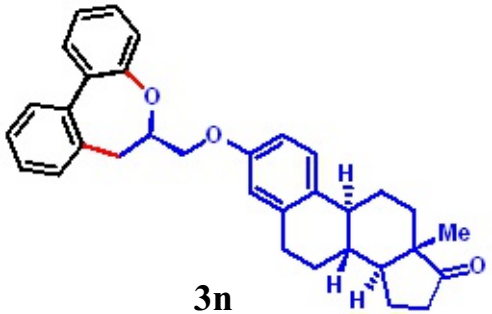
szp-249-1111.2.fid



3m

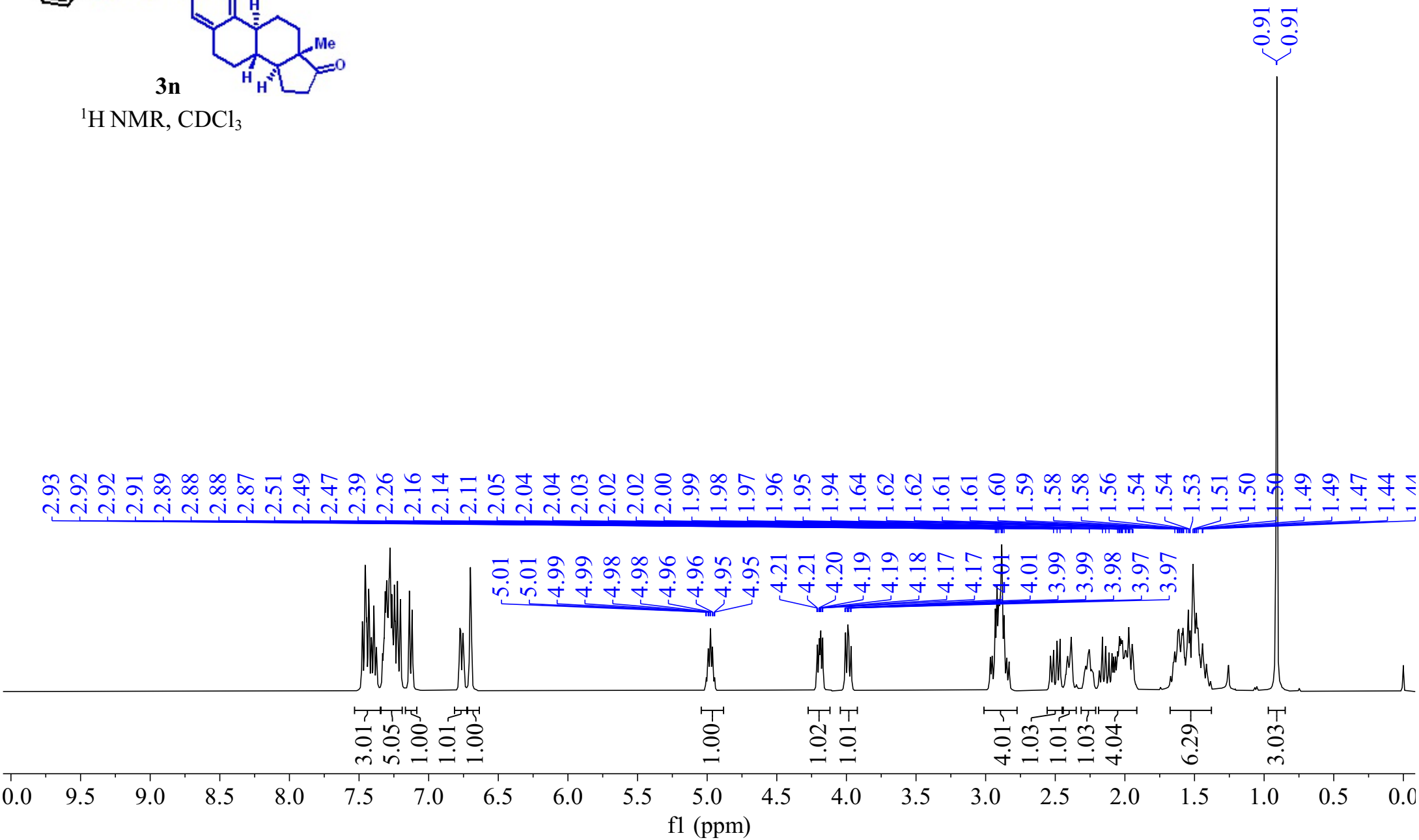
^{13}C NMR, $CDCl_3$

ZN-0470.1.fid

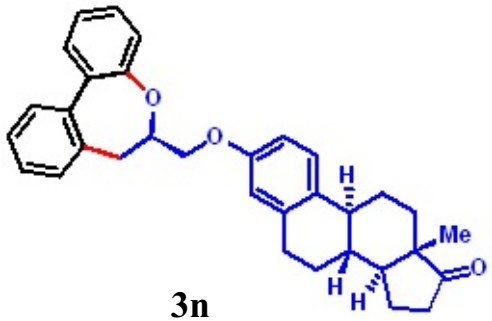


3n

^{1}H NMR, $CDCl_3$

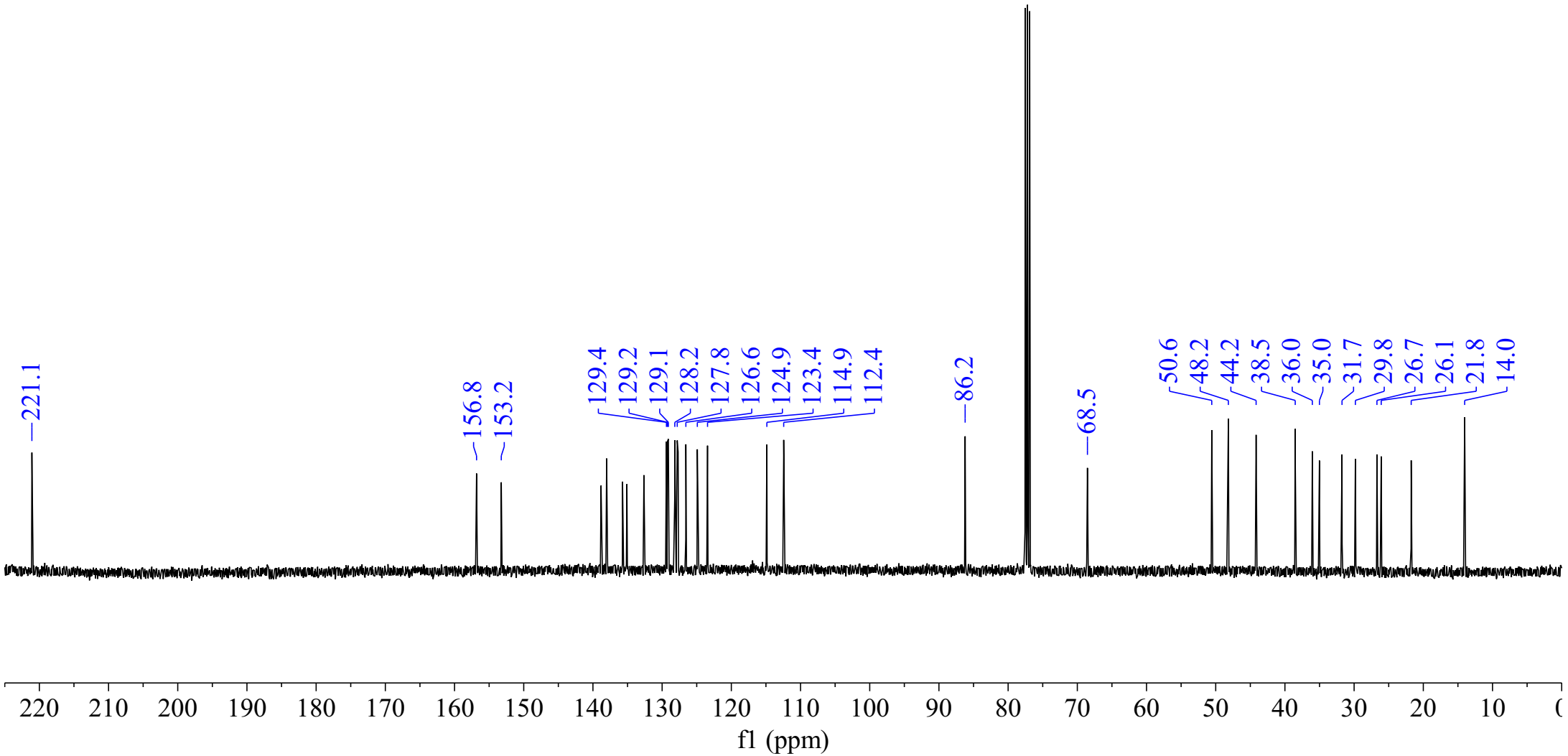


ZN-0470.2.fid

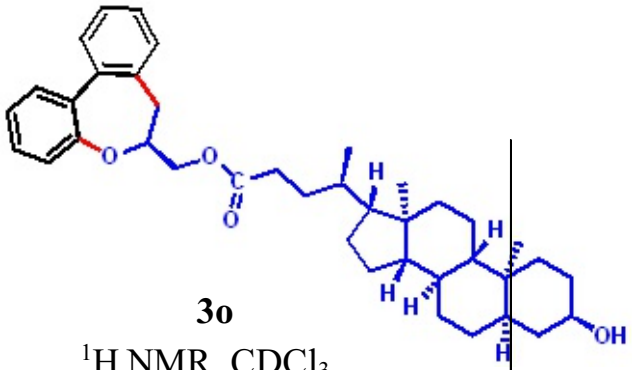


3n

^{13}C NMR, $CDCl_3$

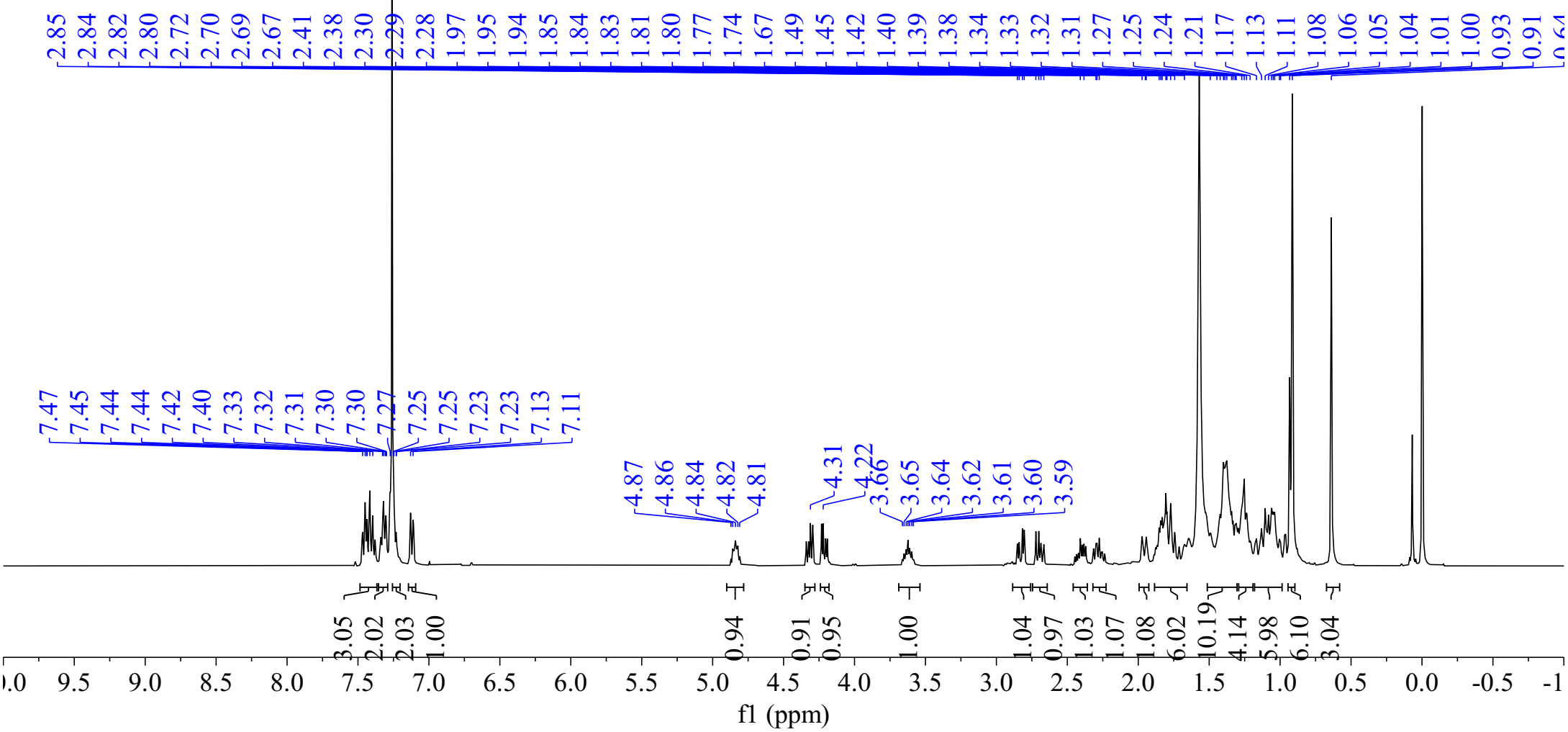


SZP-288-33

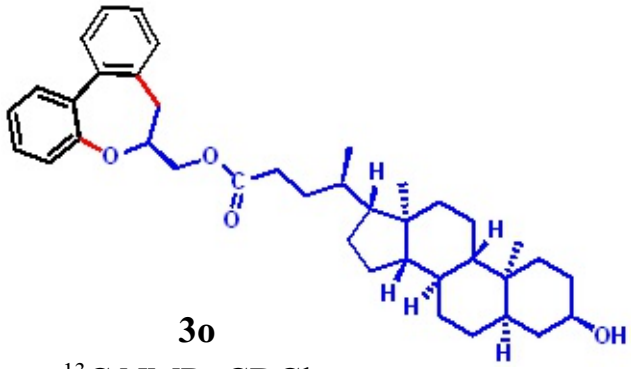


3o

^{1}H NMR, $CDCl_3$



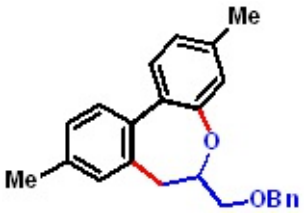
SZP-288-33.2.fid



3o

^{13}C NMR, $CDCl_3$

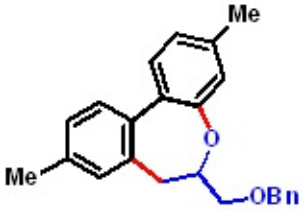
szp-279-3



3p

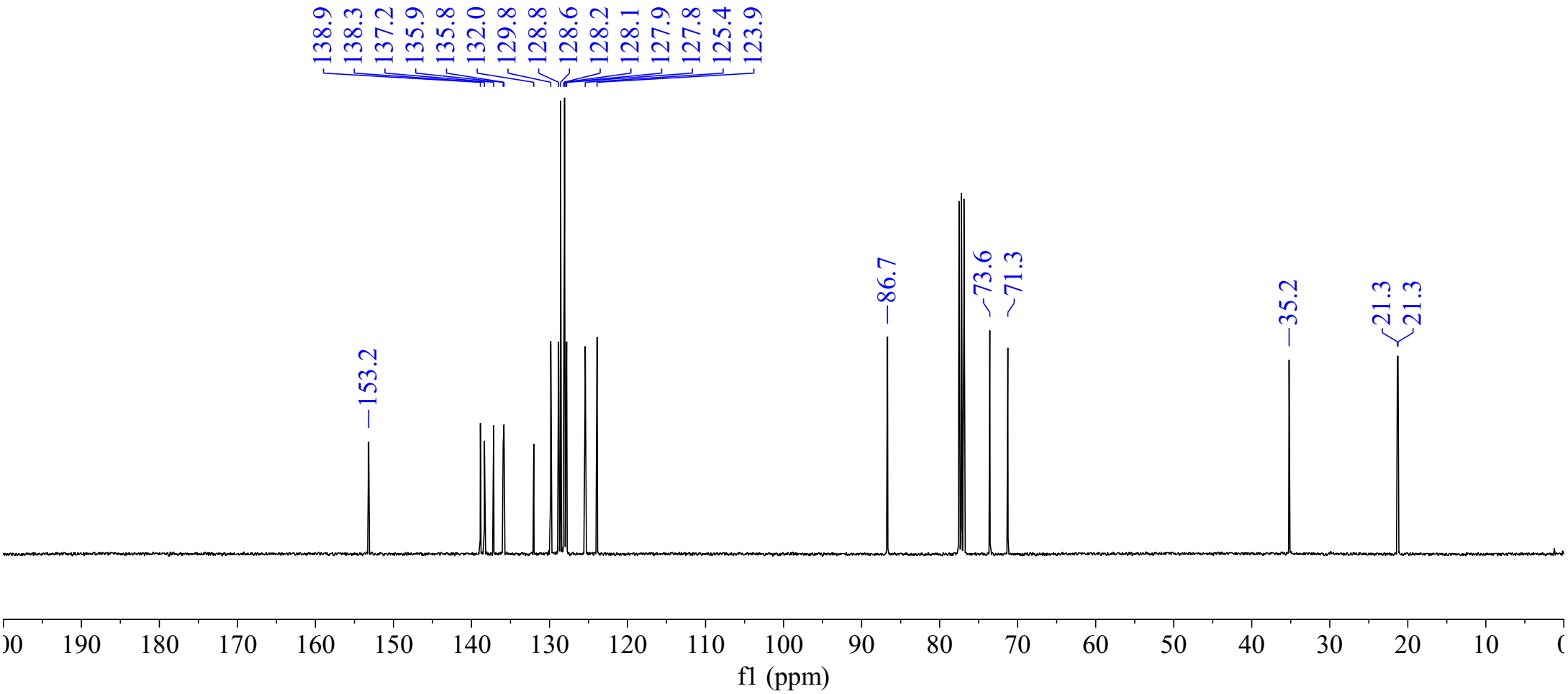
^{1}H NMR, $CDCl_3$

szp-279-3.2.fid

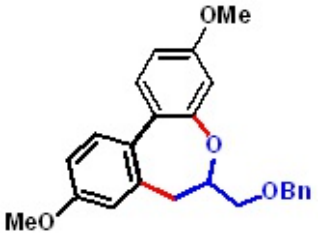


3p

^{13}C NMR, $CDCl_3$

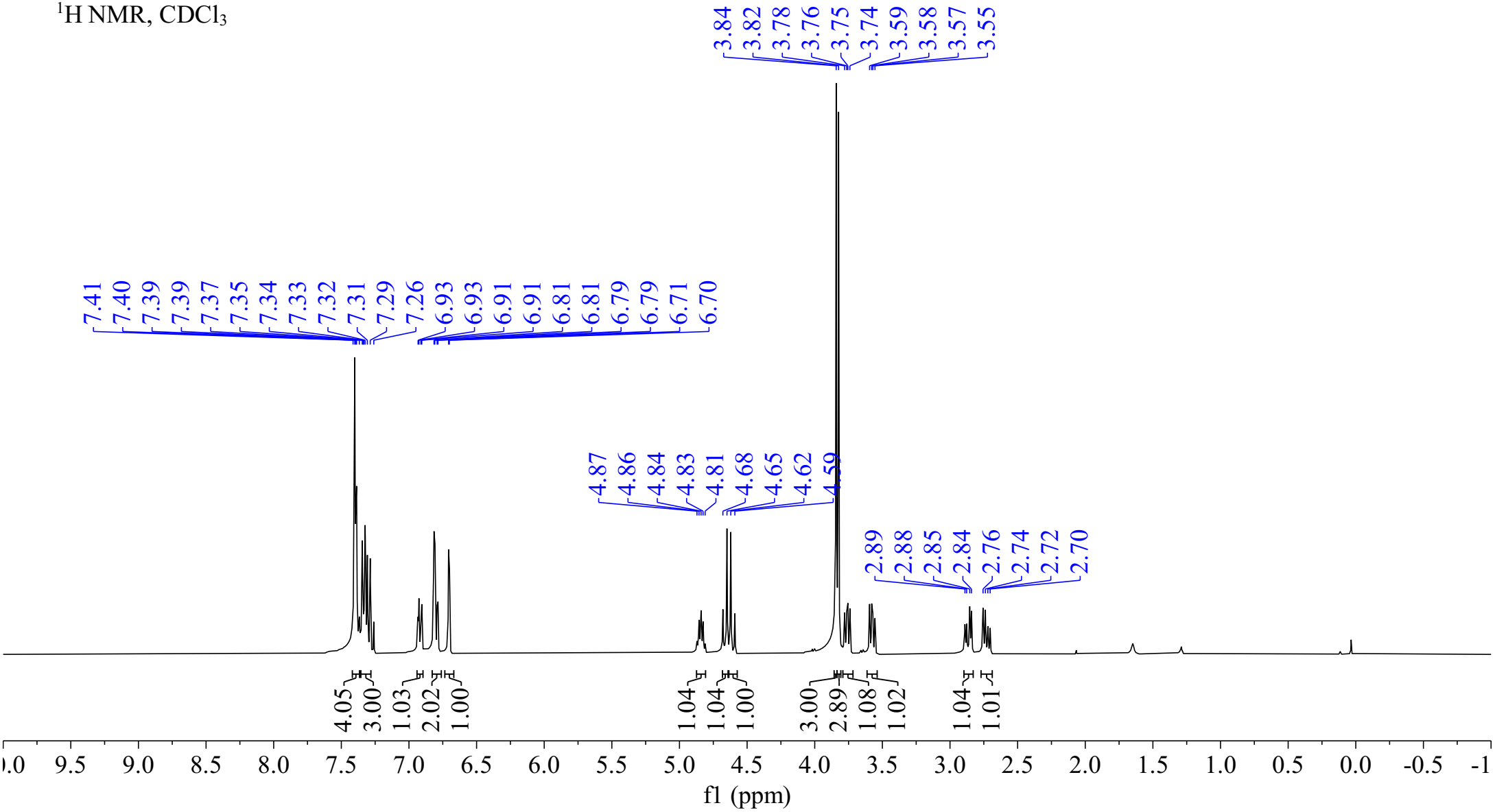


szp-273-3

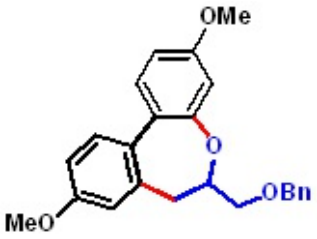


3q

^{1}H NMR, $CDCl_3$

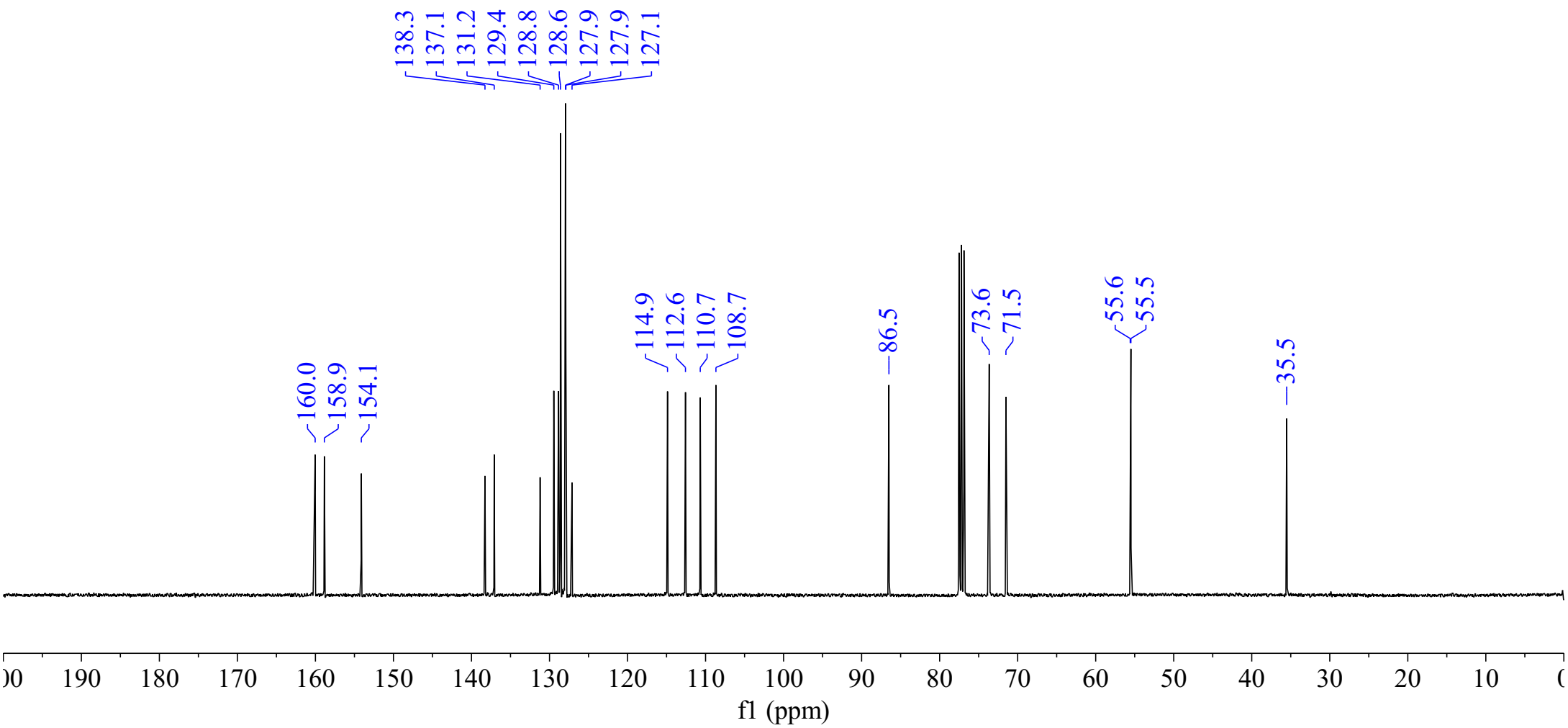


szp-273-3.2.fid

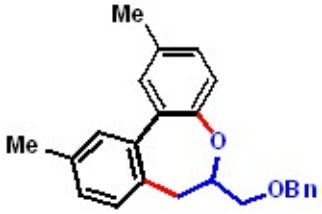


3q

^{13}C NMR, $CDCl_3$

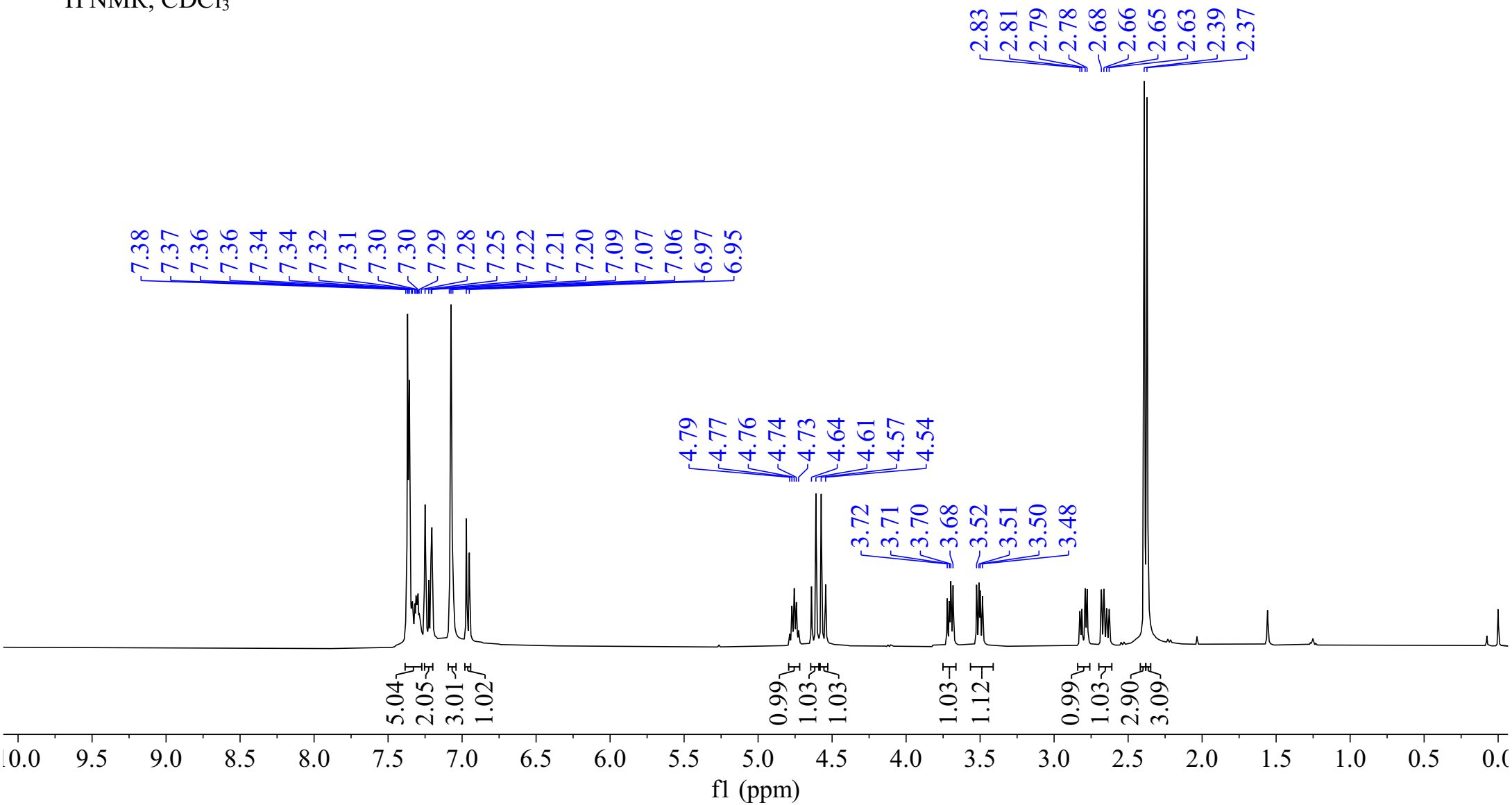


szp-266-11

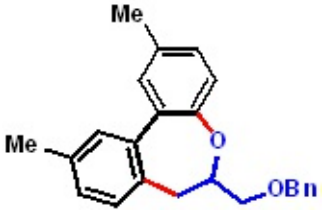


3r

^{1}H NMR, $CDCl_3$

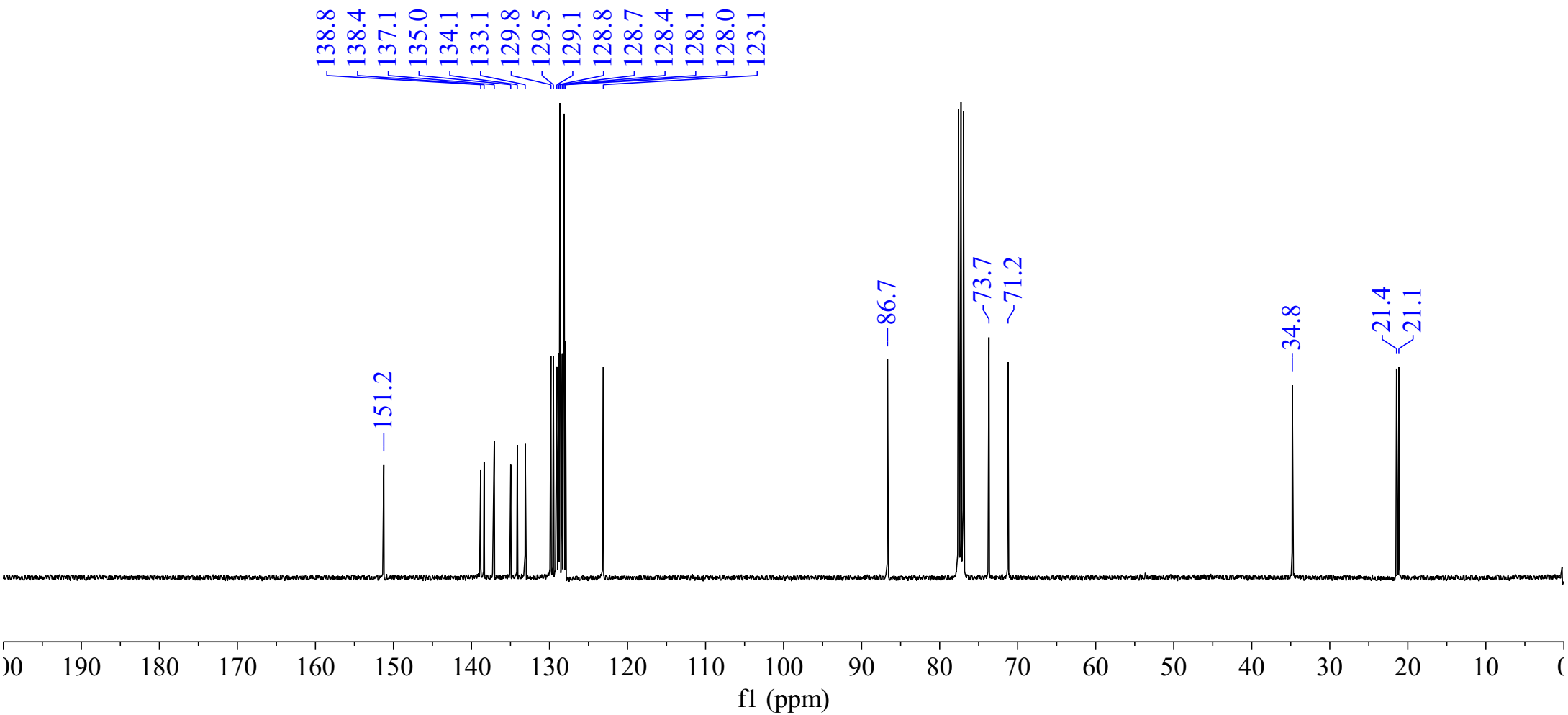


szp-266-111.1.fid

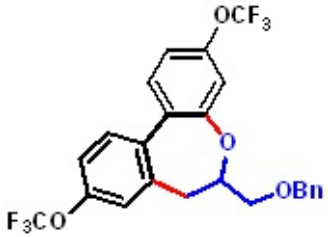


3r

^{13}C NMR, $CDCl_3$

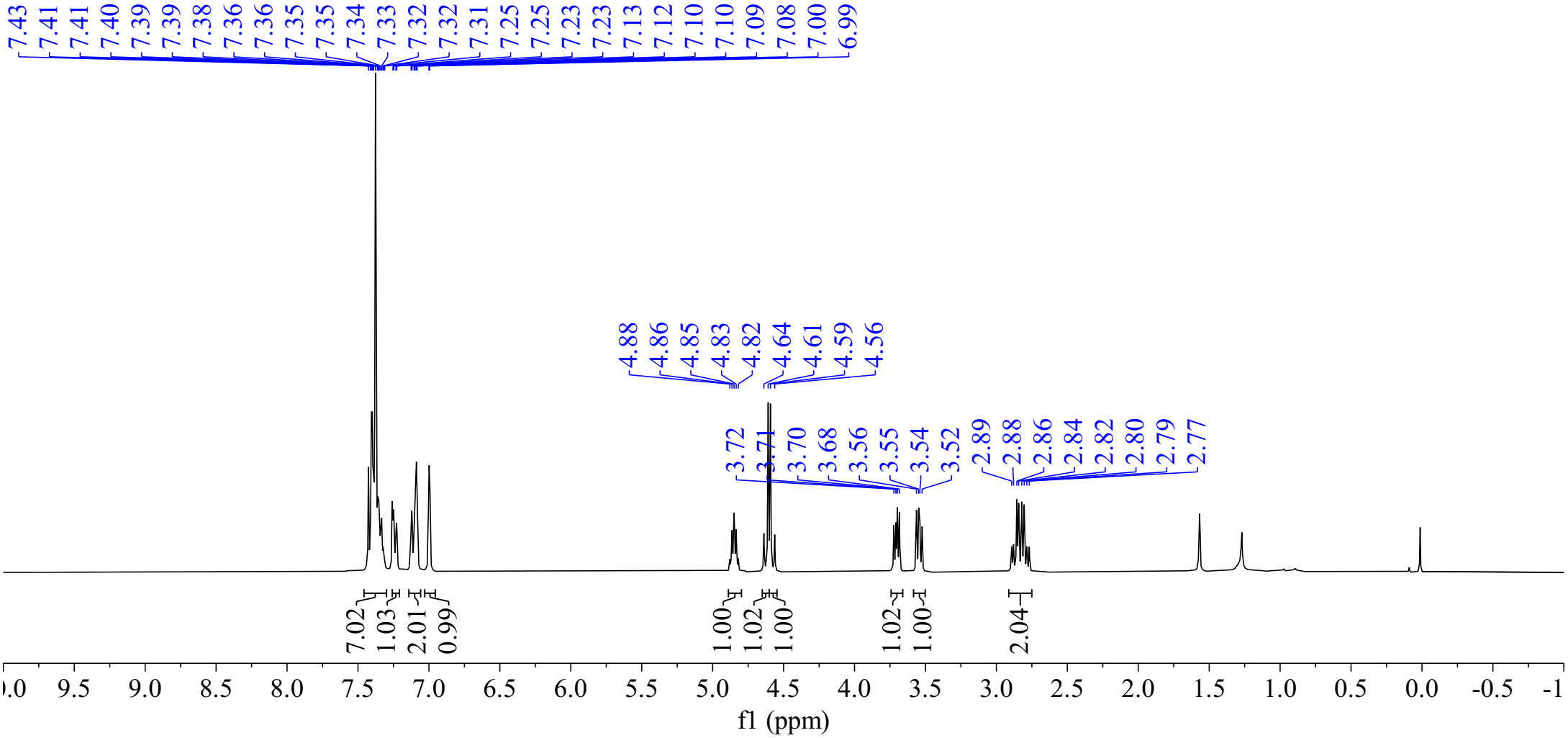


ZN-2022-0905.1.fid

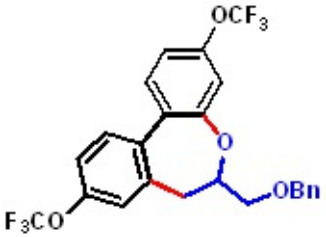


3s

^{1}H NMR, $CDCl_3$

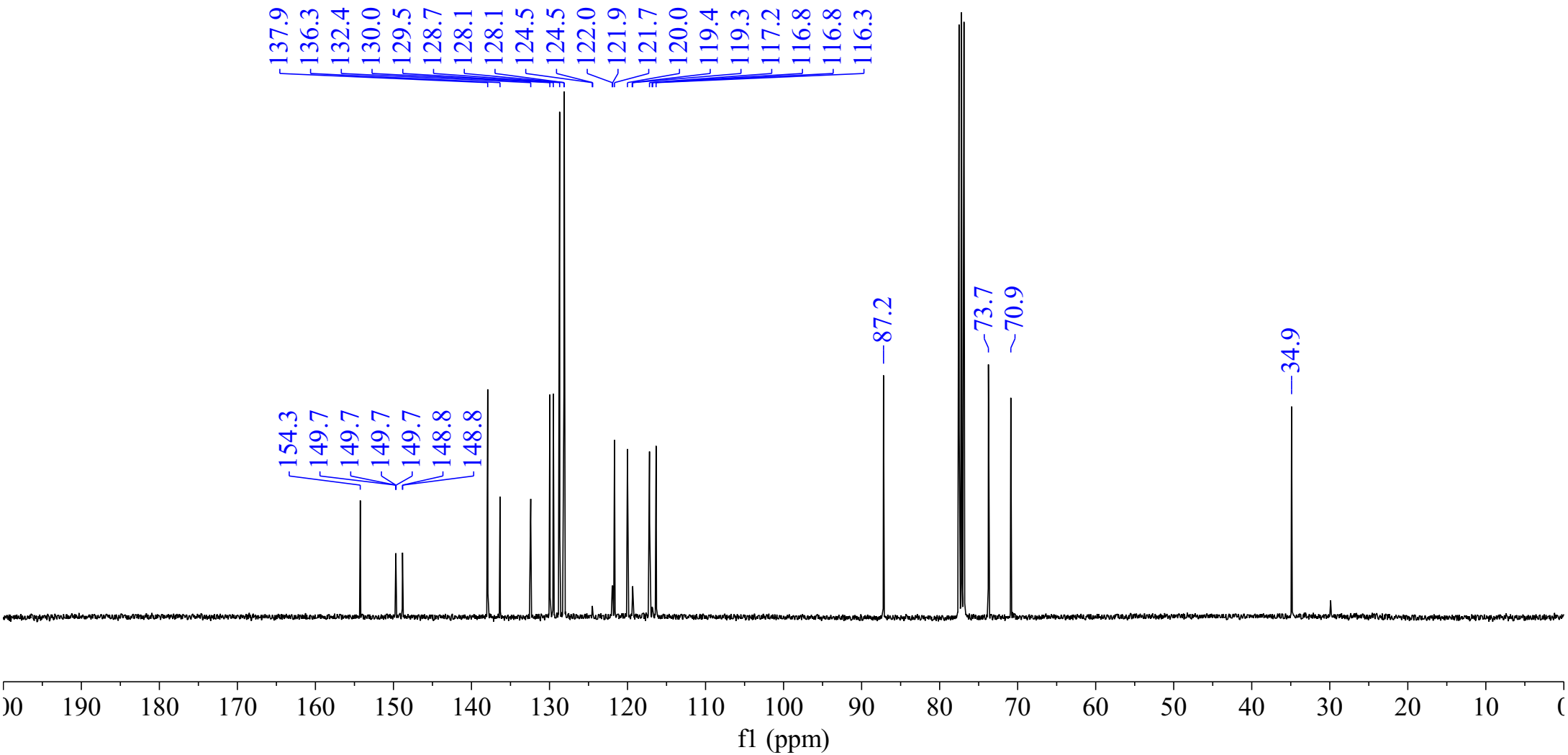


SZP-OCF3.2.fid

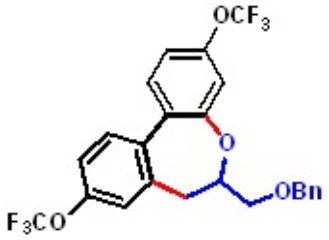


3s

^{13}C NMR, $CDCl_3$

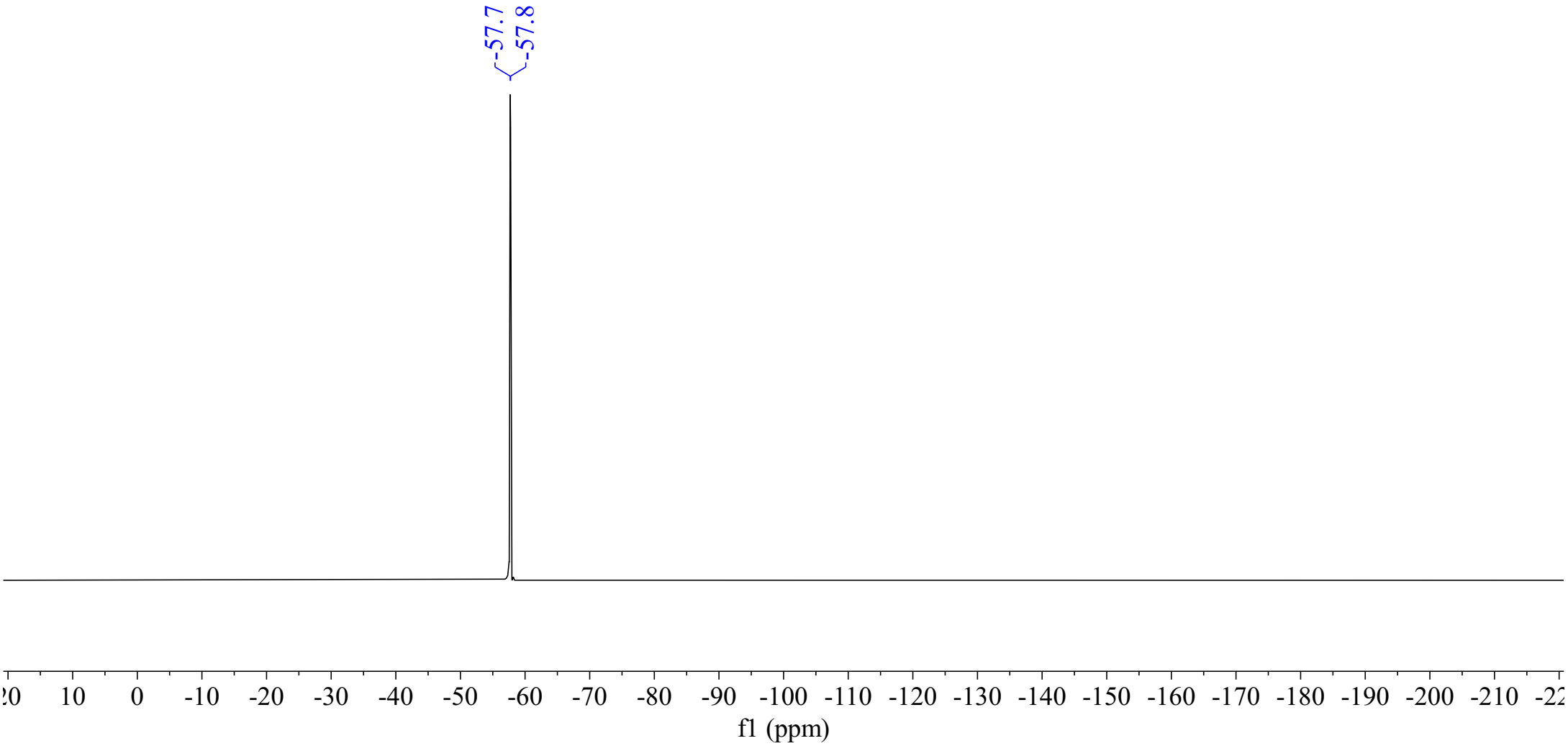


SZP-OCF3.3.fid

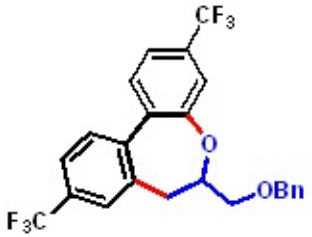


3s

^{19}F NMR, $CDCl_3$

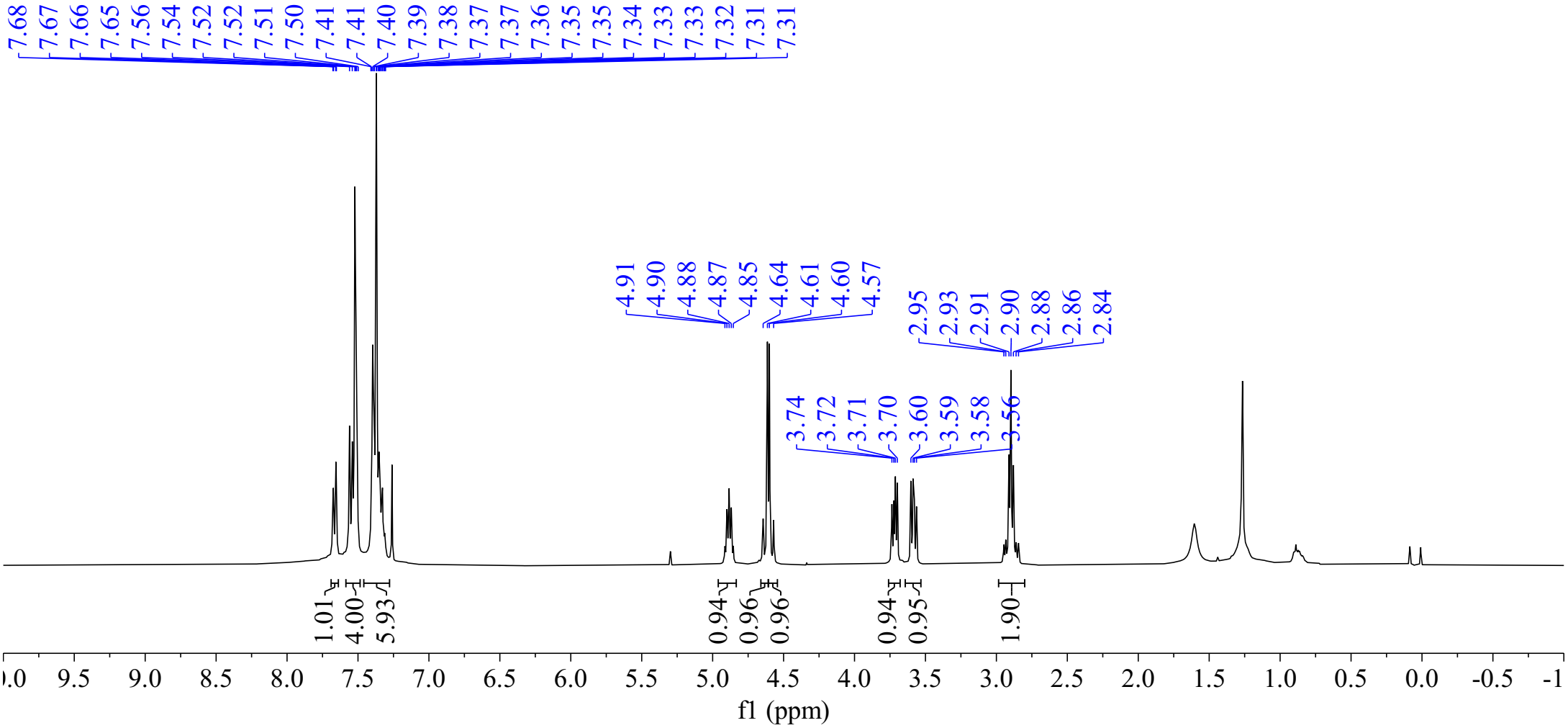


szp-302-CF3

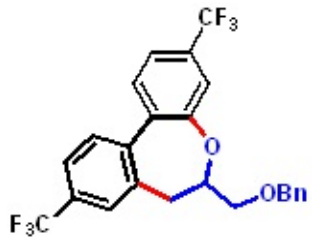


3t

^{1}H NMR, $CDCl_3$



szp-302-CF3.2.fid



3t

^{13}C NMR, $CDCl_3$

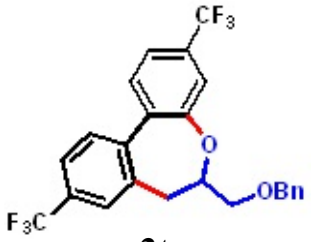
141.1
137.9
137.3
137.1
132.6
132.2
131.9
131.5
131.1
130.7
130.4
129.9
128.7
128.2
128.1
128.0
126.1
126.1
125.5
125.2
124.7
124.6
122.8
122.5
121.6
121.6
120.9
120.9

153.9
87.6
73.8
71.0
34.8

)0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 (

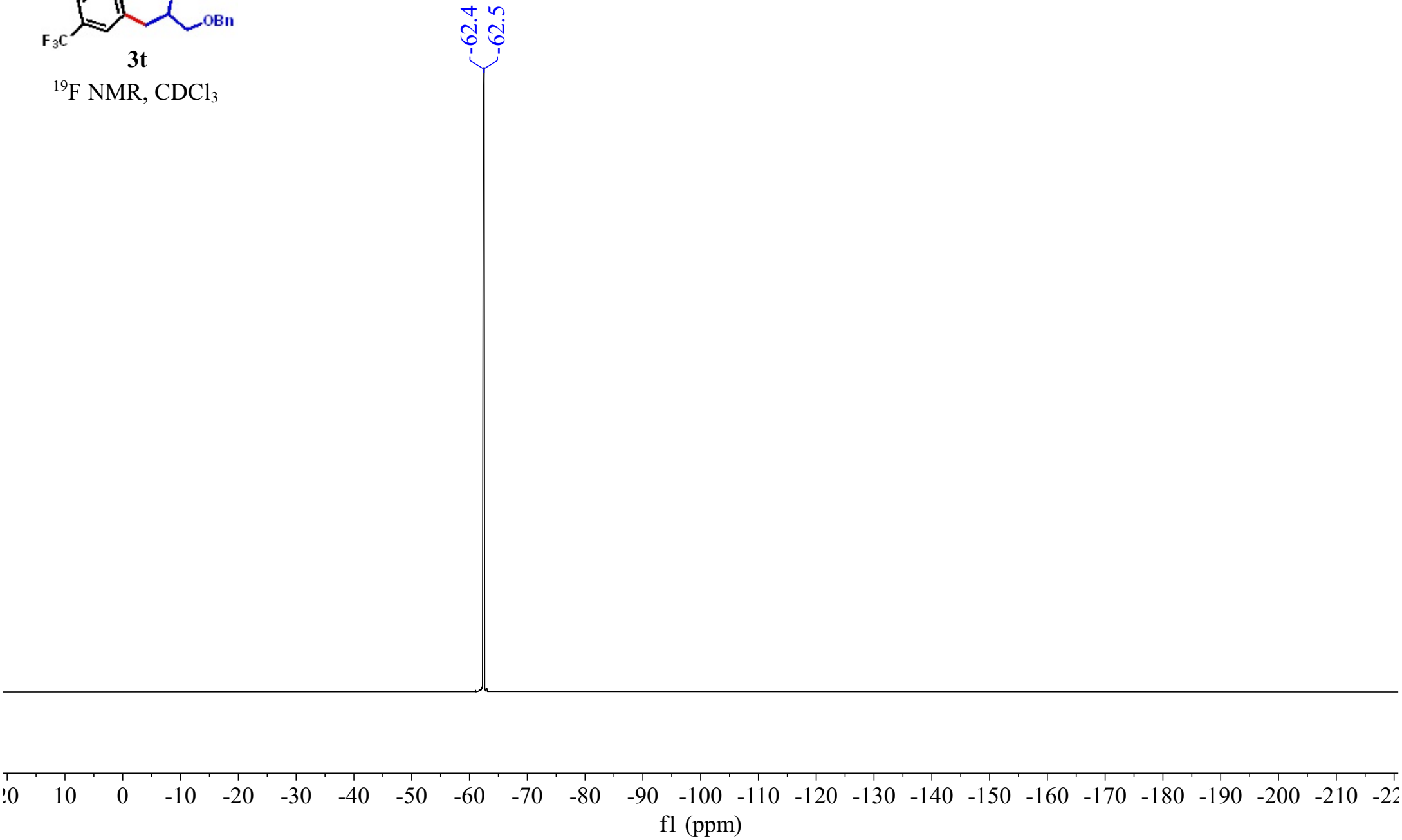
f1 (ppm)

szp-302-CF3.3.fid

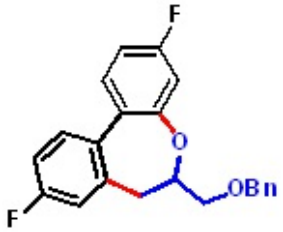


3t

^{19}F NMR, $CDCl_3$

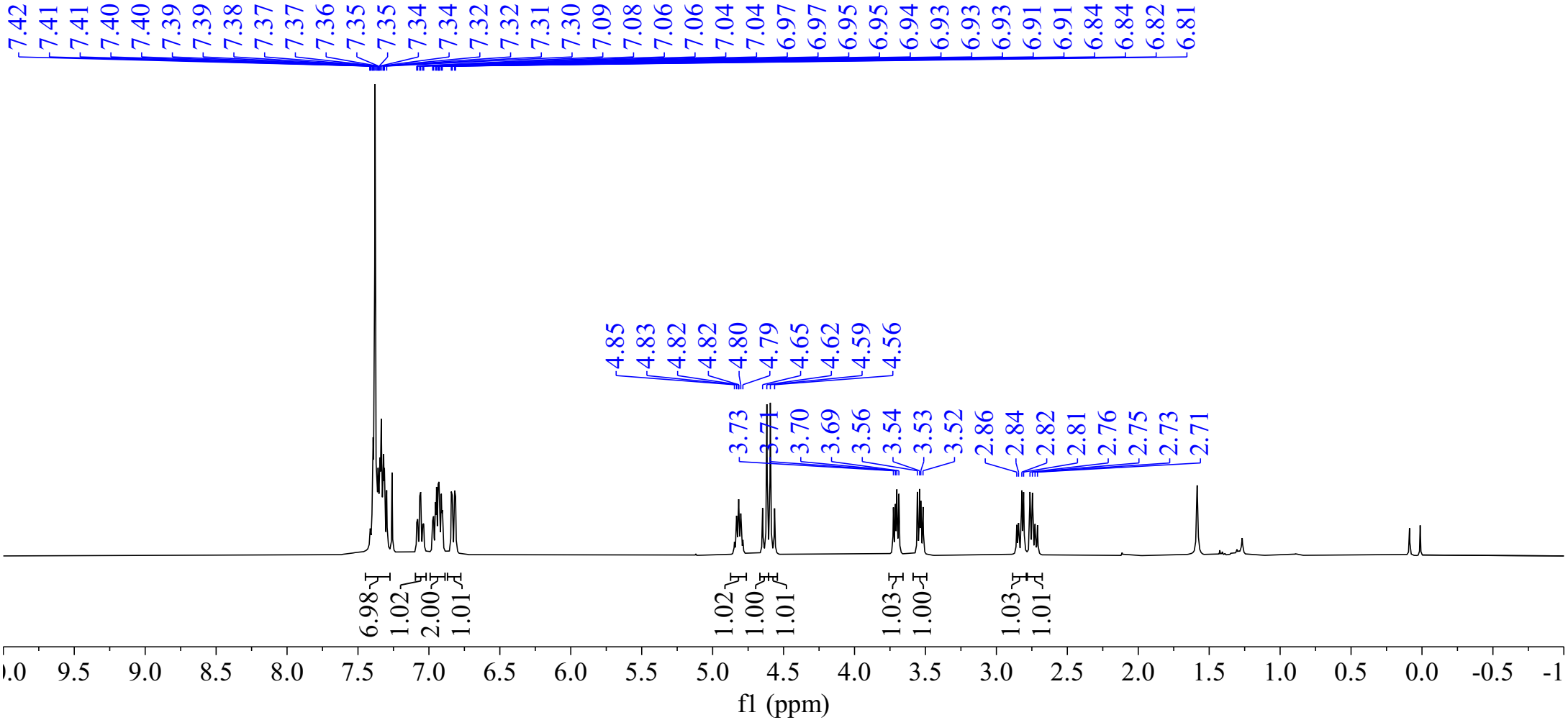


szp-279-1

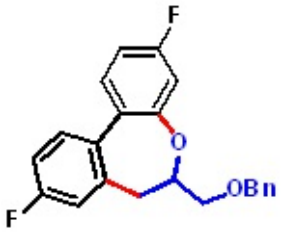


3u

^{1}H NMR, $CDCl_3$

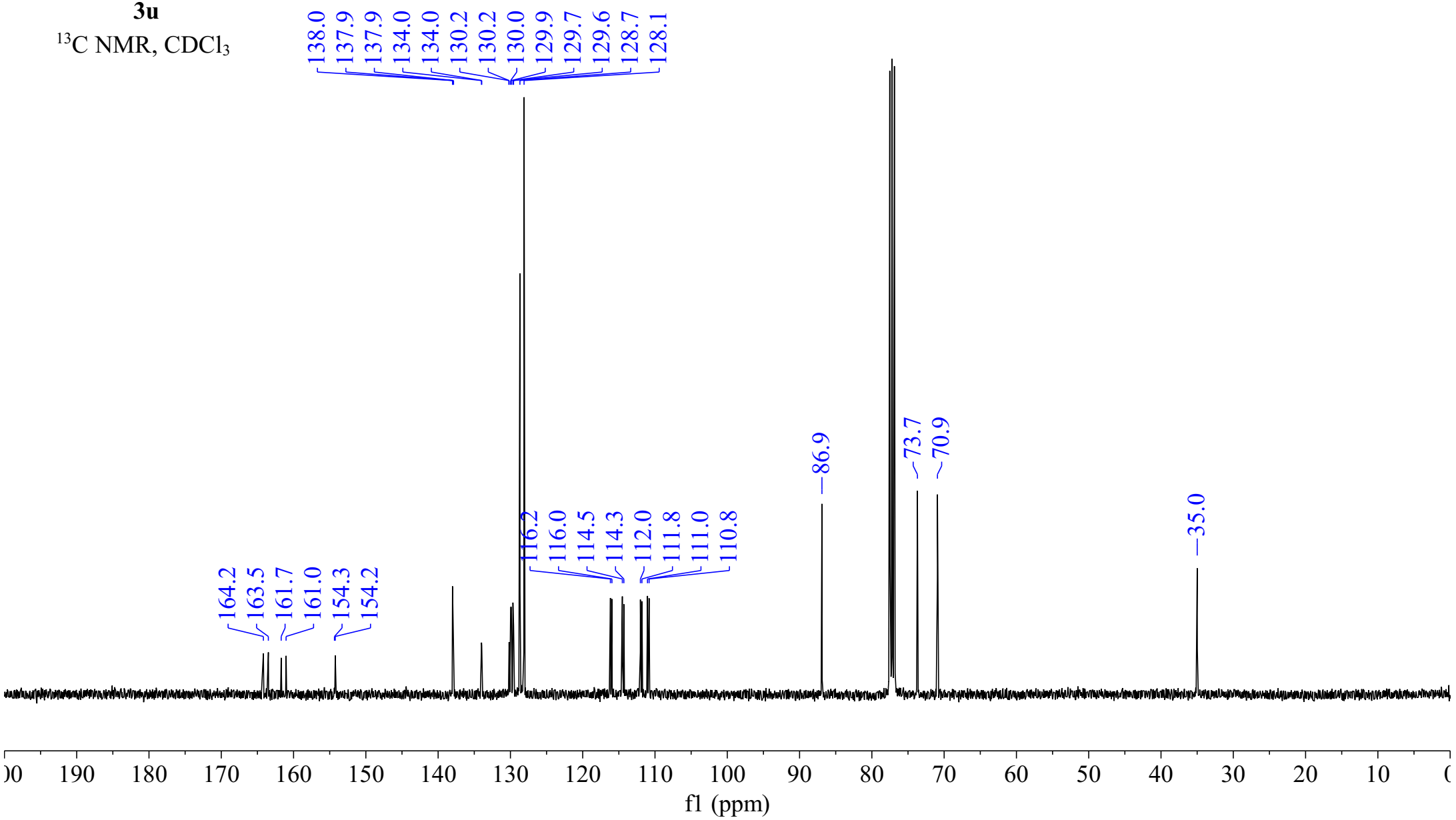


szp-279-1.2.fid

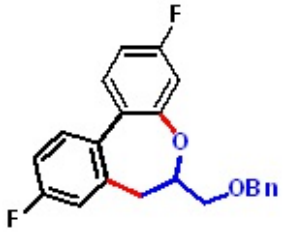


3u

^{13}C NMR, $CDCl_3$

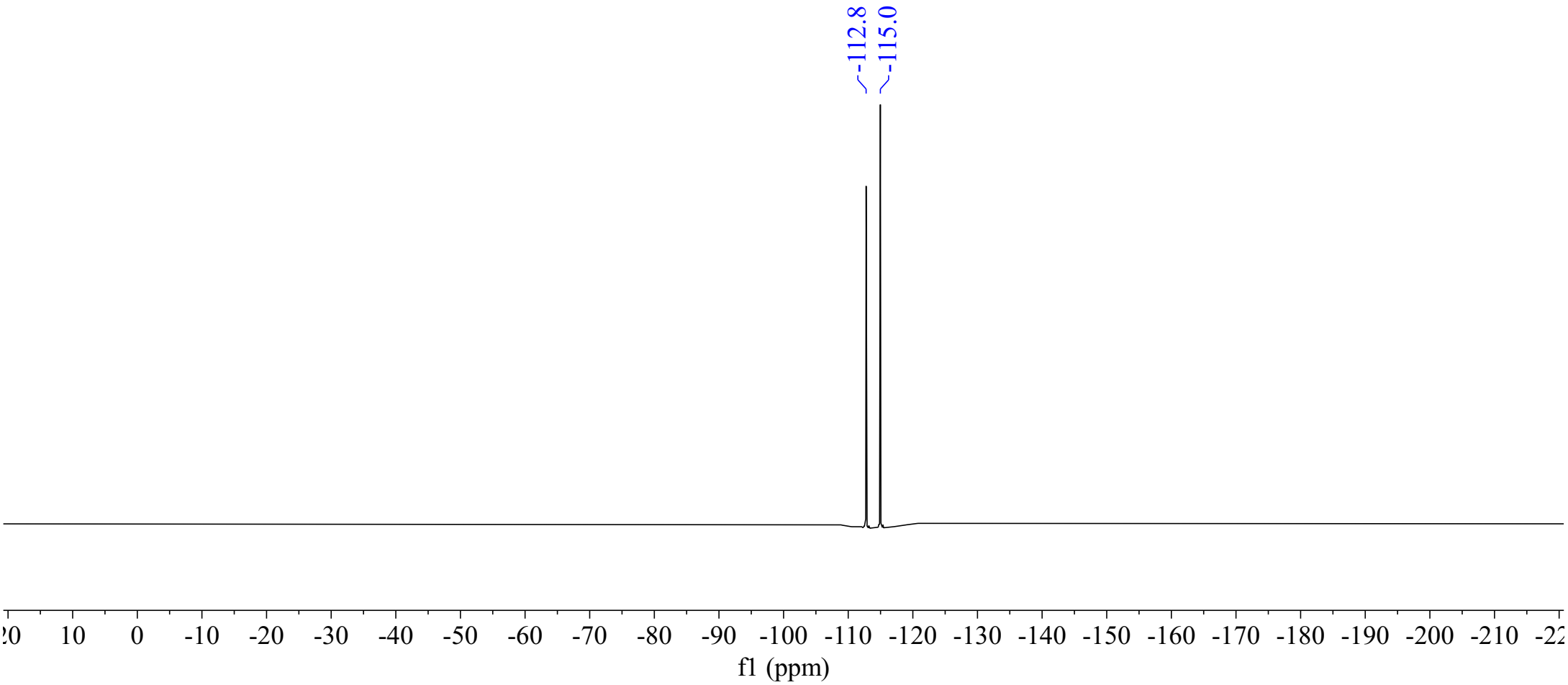


szp-279-1.3.fid

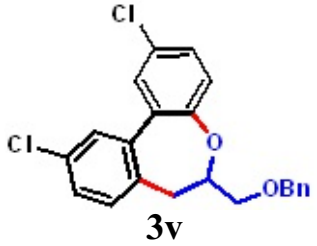


3u

^{19}F NMR, $CDCl_3$

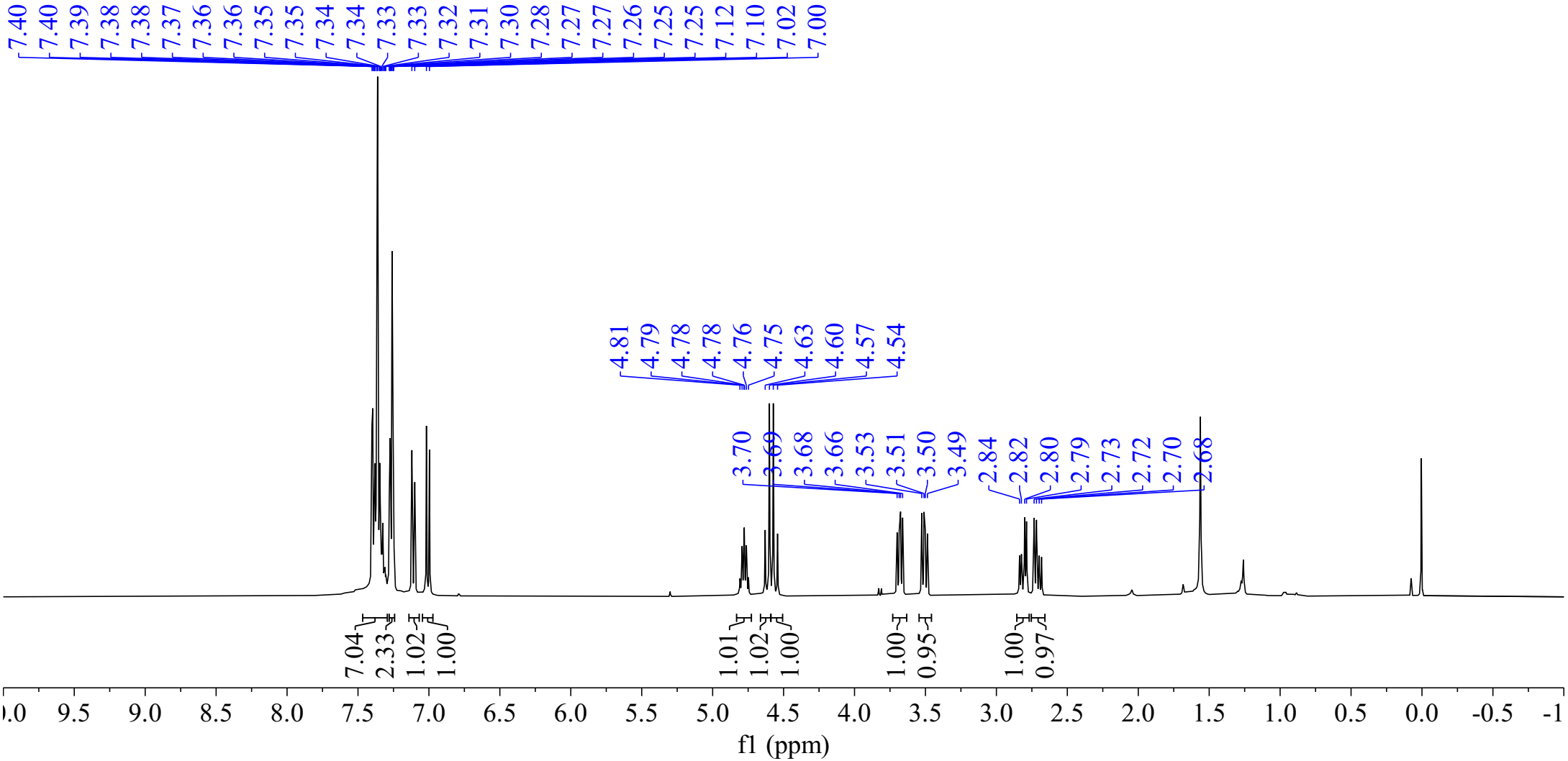


szp-273-2

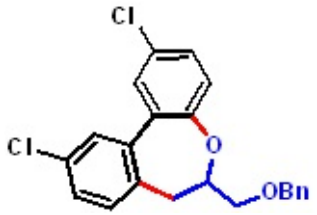


3v

^{1}H NMR, $CDCl_3$

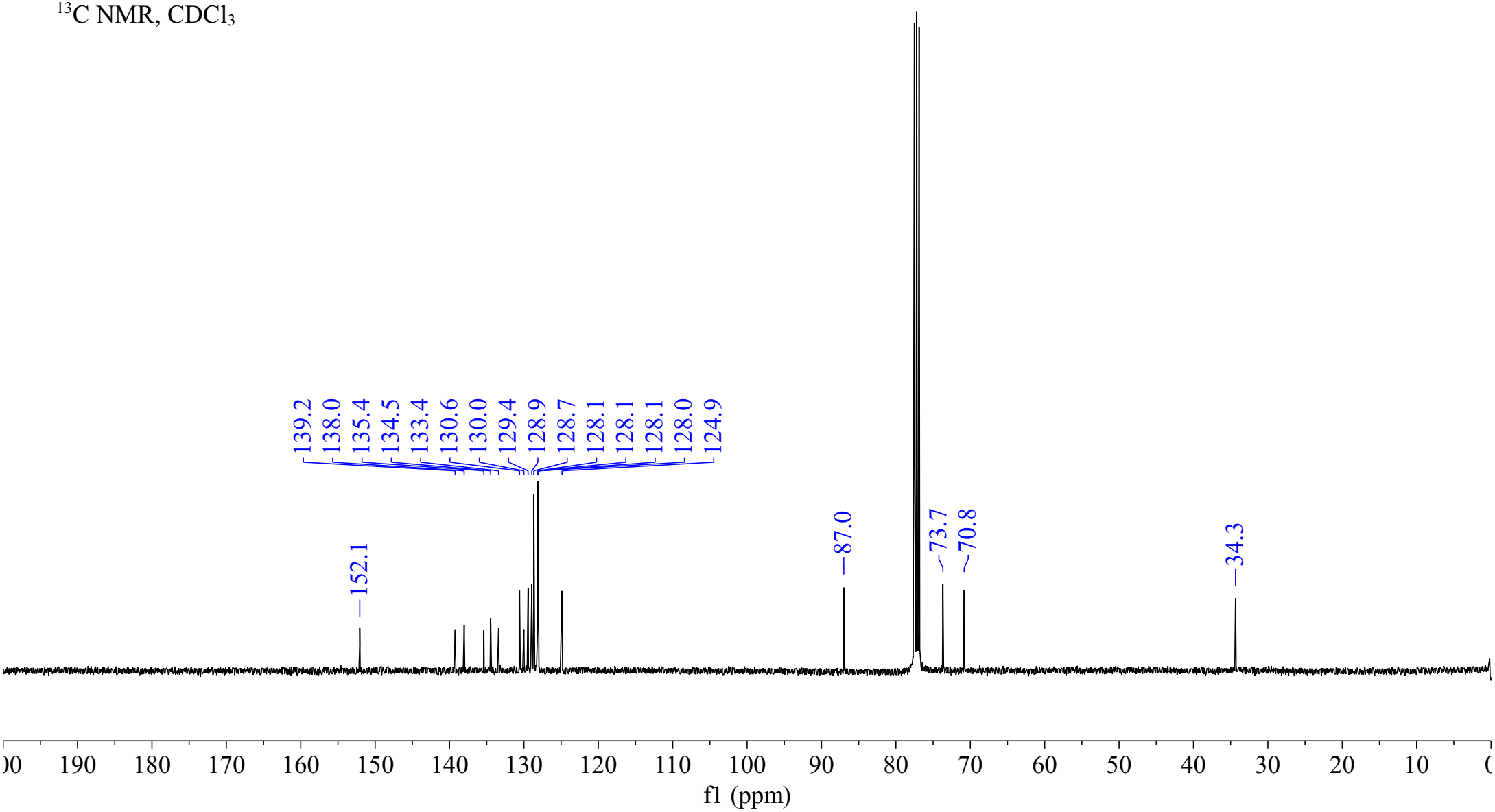


szp-273-2.2.fid

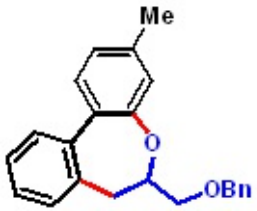


3v

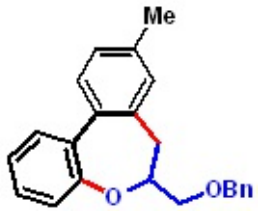
^{13}C NMR, $CDCl_3$



szp-242-11.1.fid

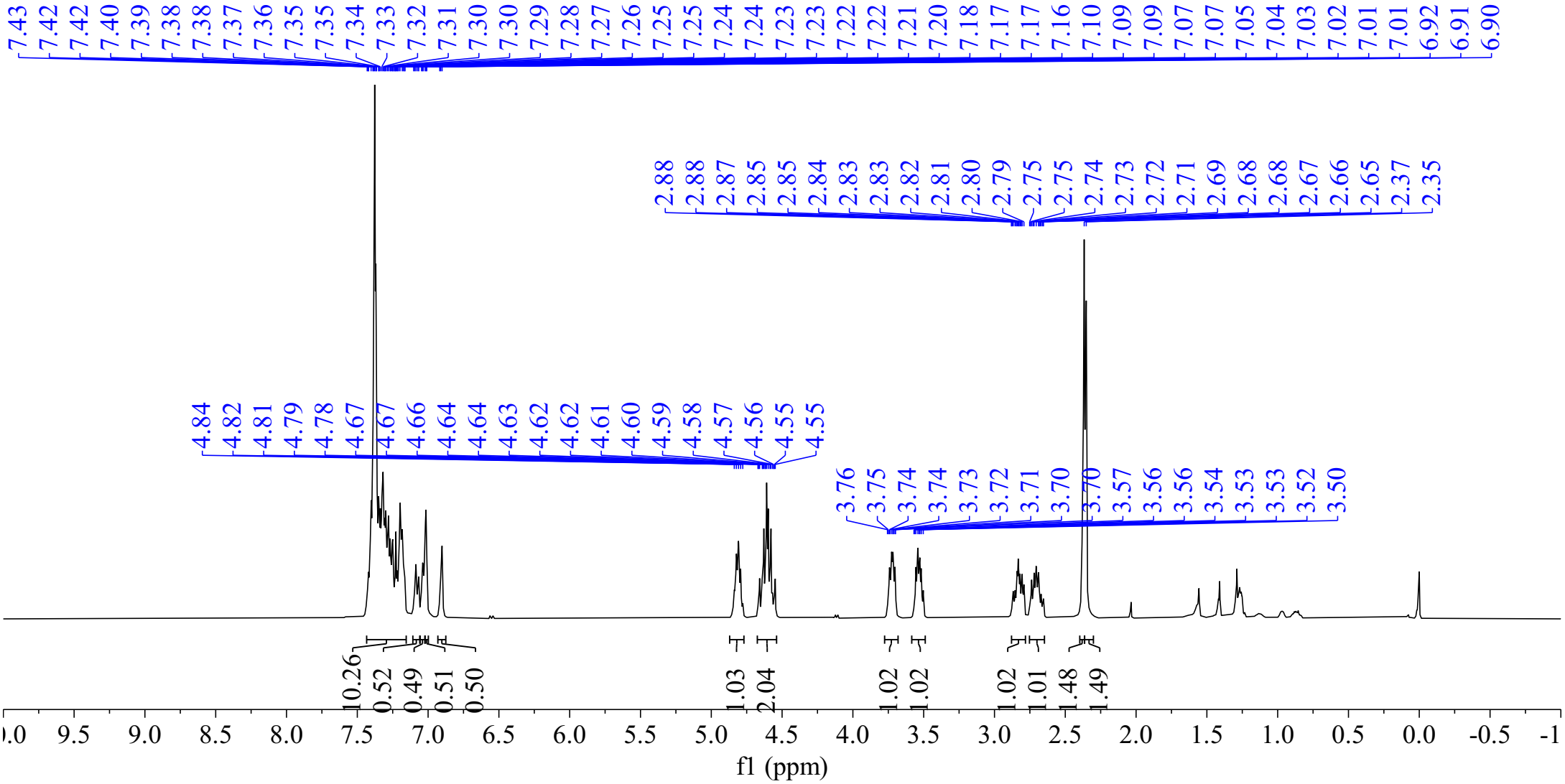


3w

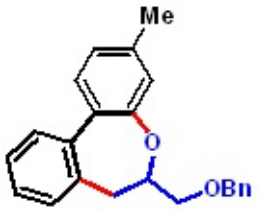


3w'

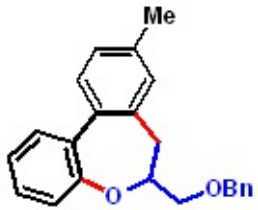
^{1}H NMR, $CDCl_3$



szp-242-11.2.fid

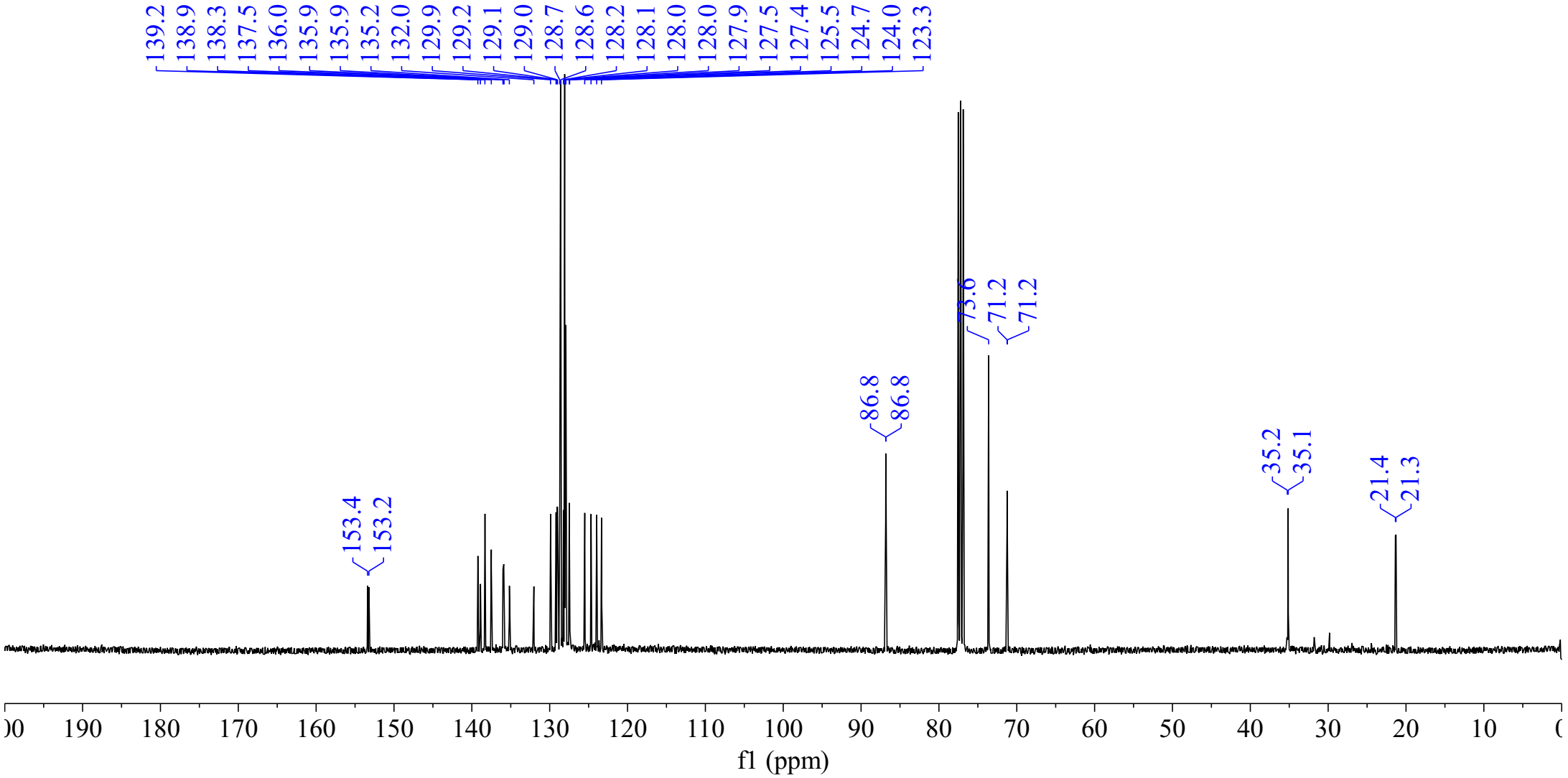


3w

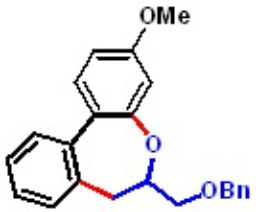


3w'

^{13}C NMR, $CDCl_3$



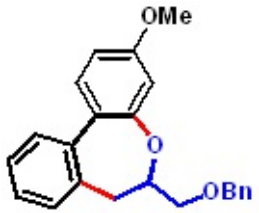
szp-262-113.1.fid



3x

^{1}H NMR, $CDCl_3$

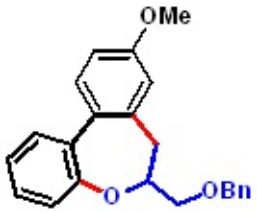
szp-262-113.2.fid



3x

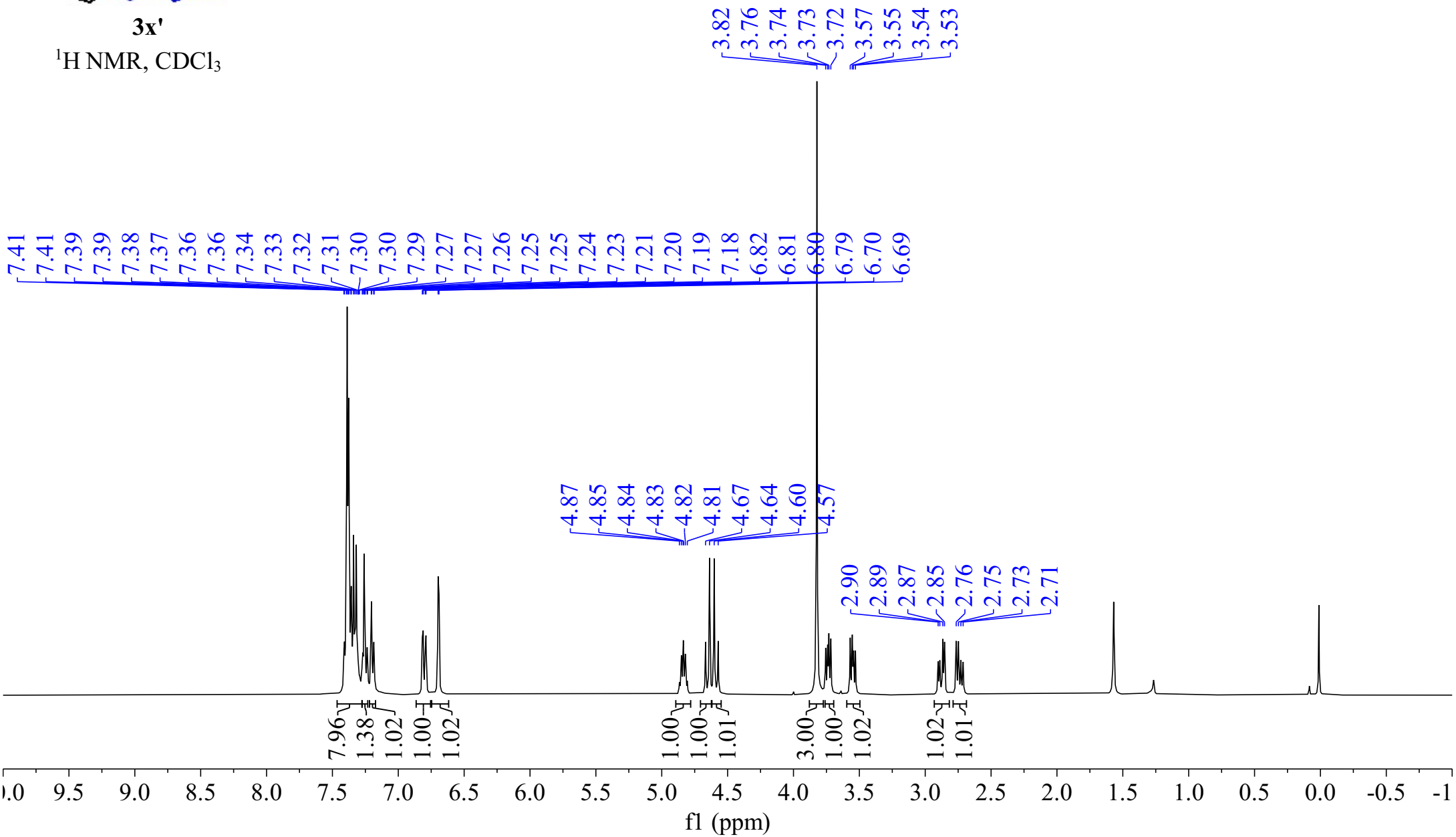
^{13}C NMR, $CDCl_3$

szp-262-111.1.fid

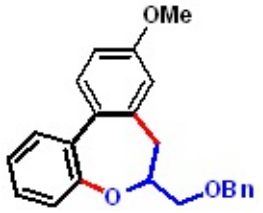


3x'

^{1}H NMR, $CDCl_3$



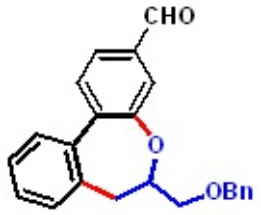
szp-262-111.2.fid



3x'

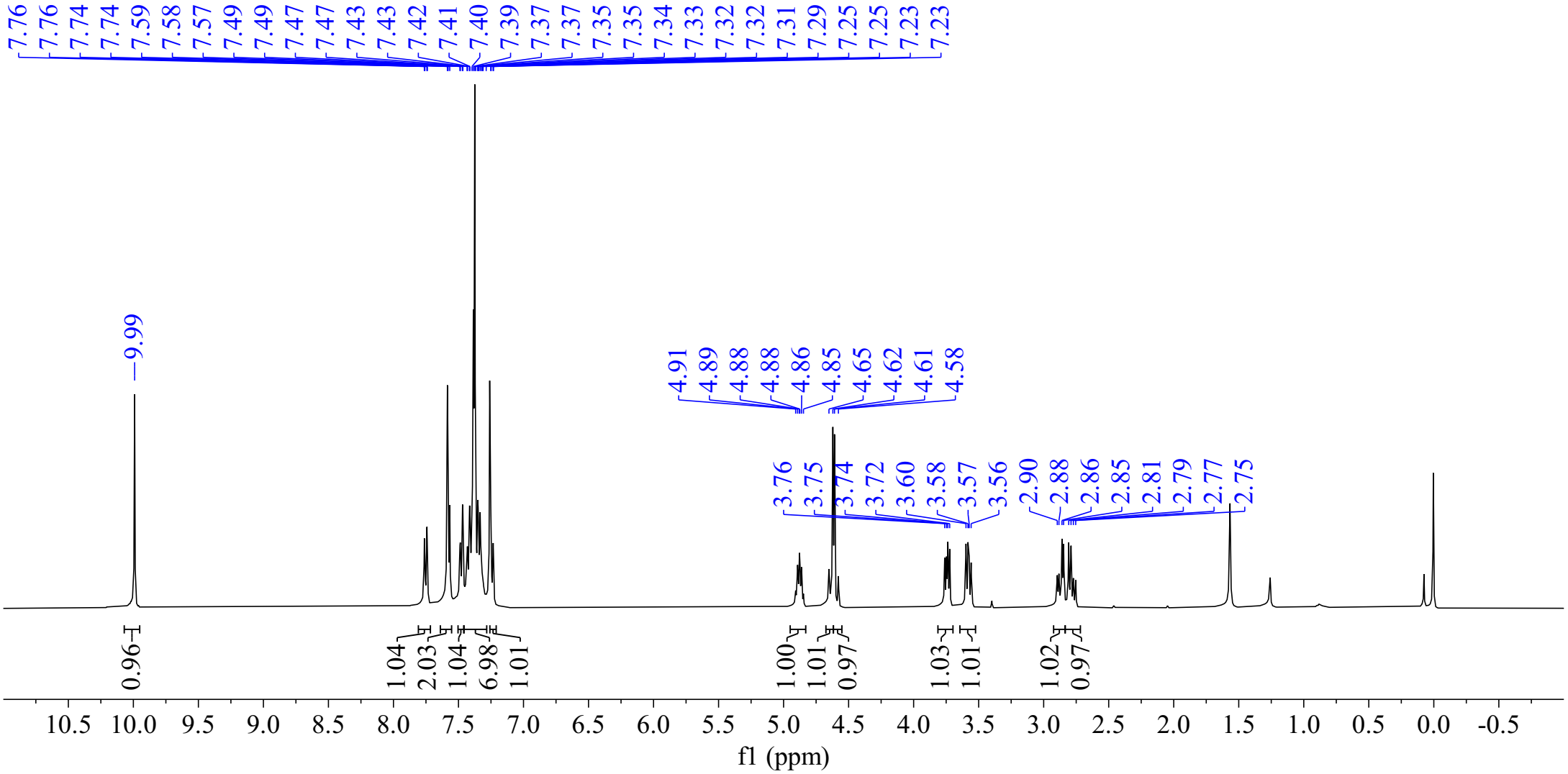
^{13}C NMR, $CDCl_3$

szp-257-4-1.1.fid

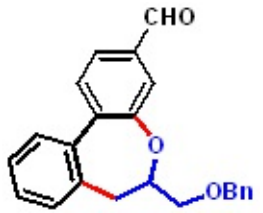


3y

^{1}H NMR, $CDCl_3$

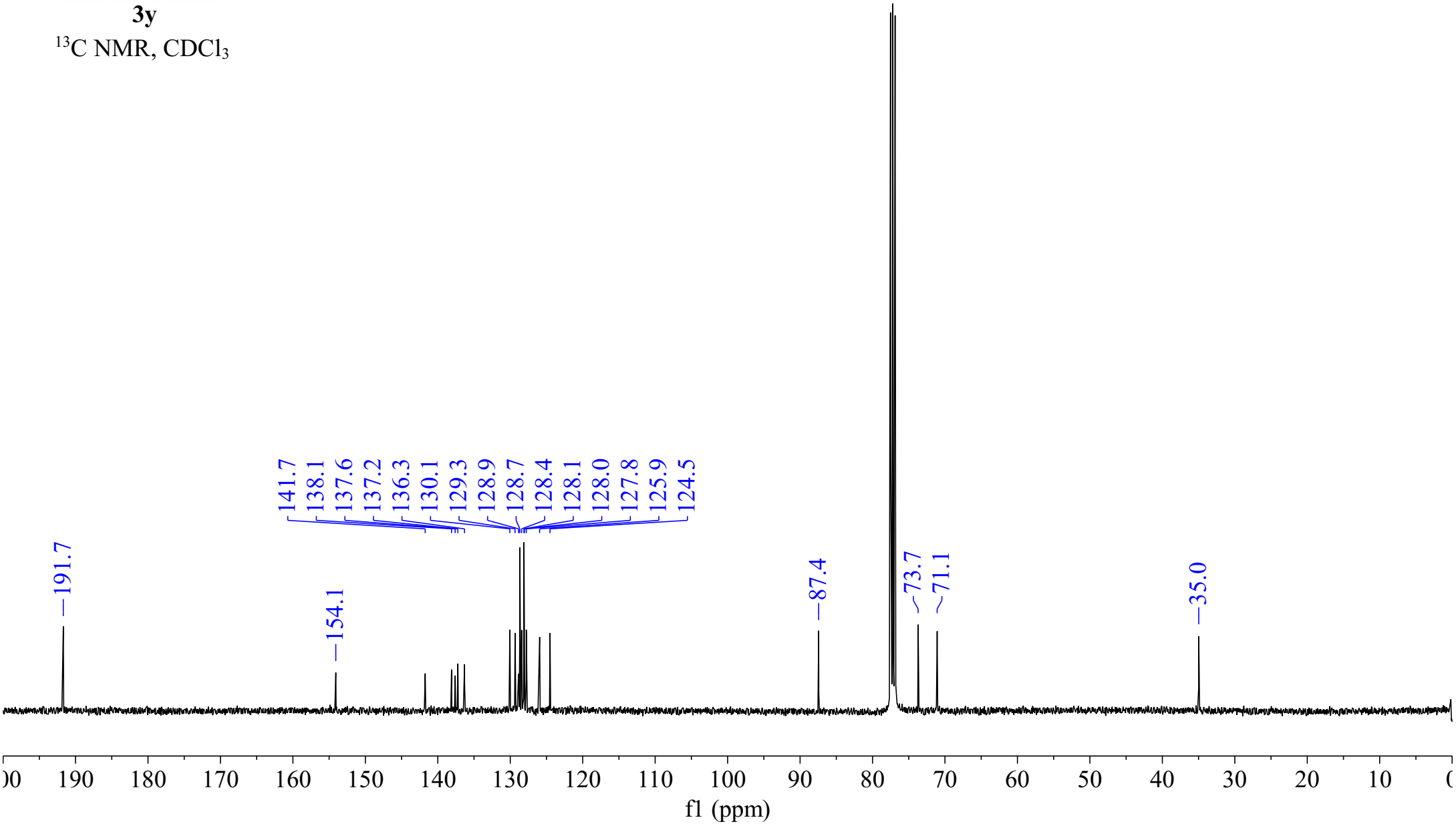


szp-257-4-1.2.fid

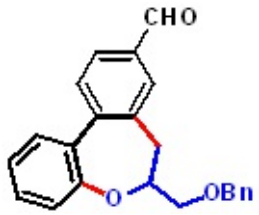


3y

^{13}C NMR, $CDCl_3$



szp-257-4-2-1.1.fid

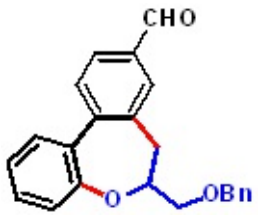


3y'

^{1}H NMR, $CDCl_3$

f1 (ppm)

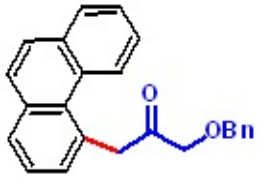
szp-257-4-2-1.2.fid



3y'

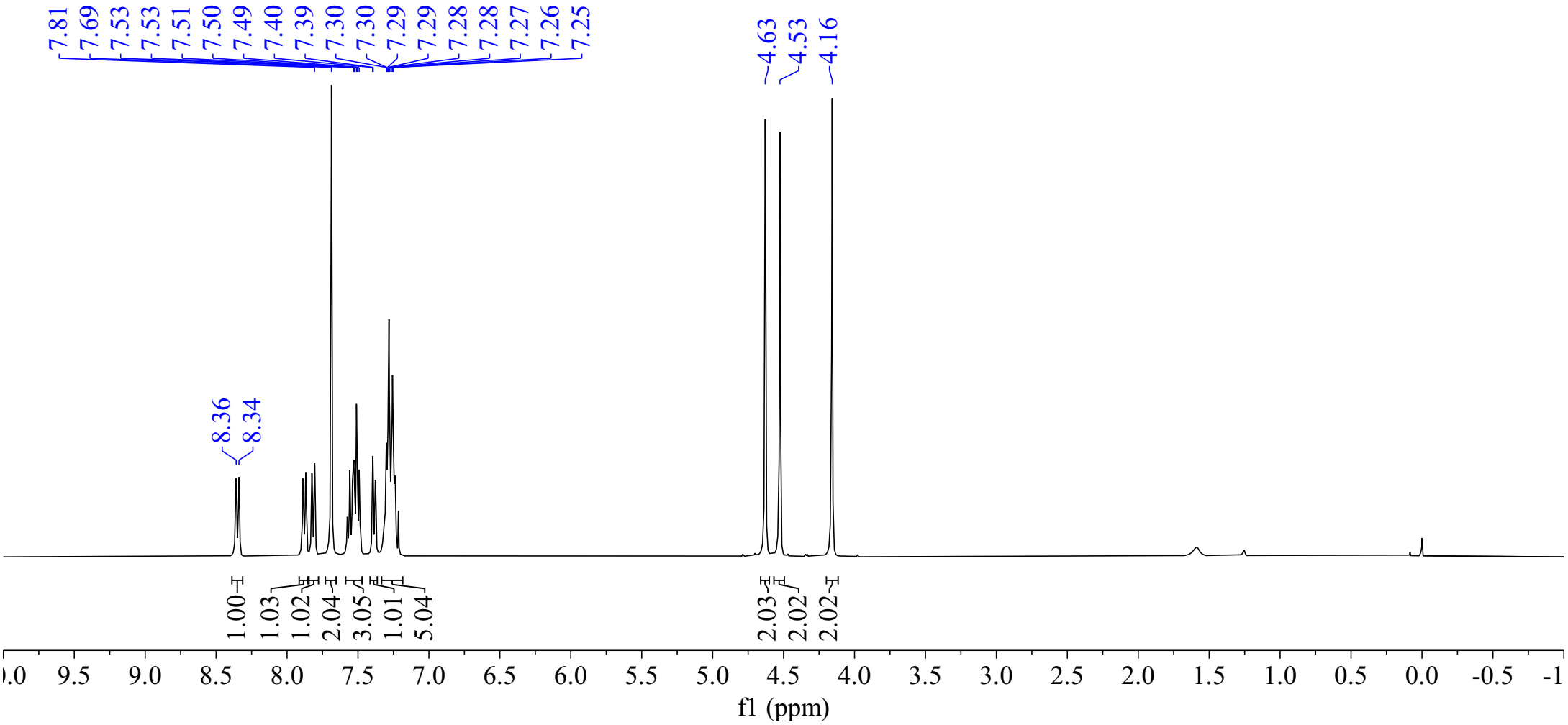
^{13}C NMR, $CDCl_3$

SZP-288-44

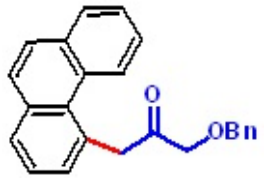


4

^{1}H NMR, $CDCl_3$



SZP-288-44.2.fid



4

^{13}C NMR, $CDCl_3$