

Supplementary Materials

**Copper-catalyzed S-arylation of carbohydrate-fused  
oxazolidine-2-thiones**

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Arnaud Tatibouët <sup>3,\*</sup>

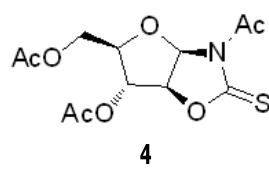
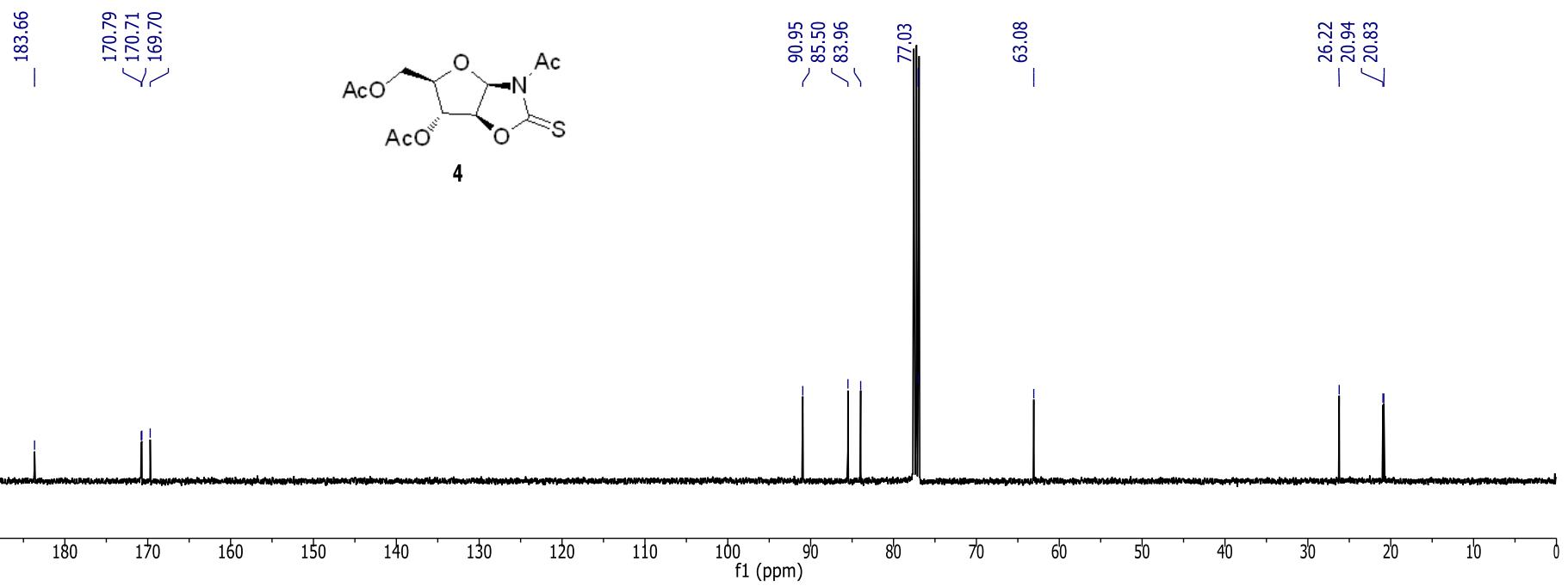
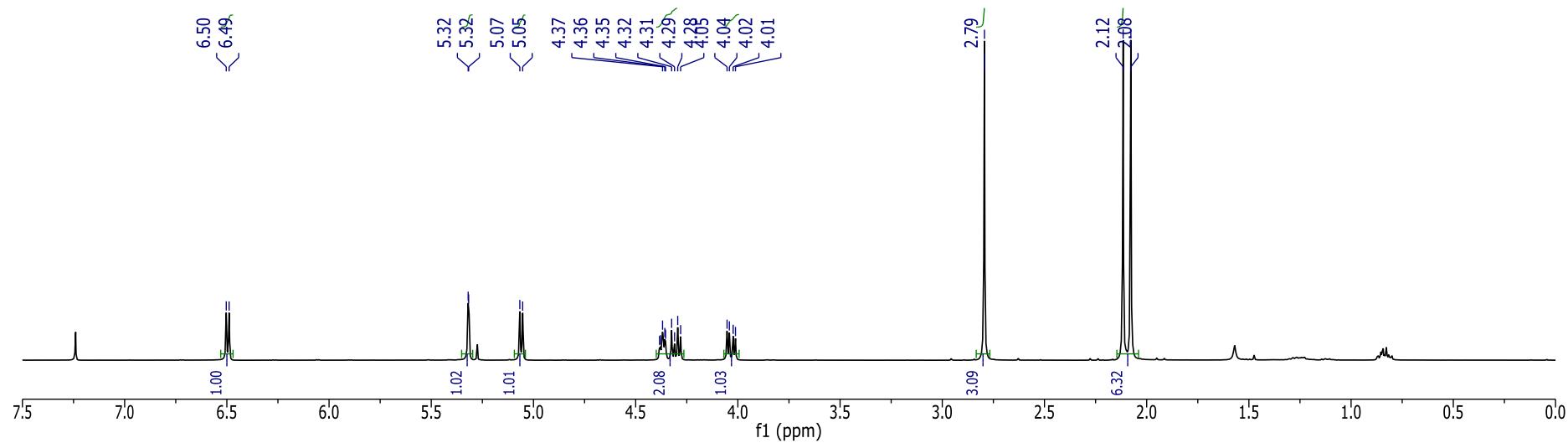
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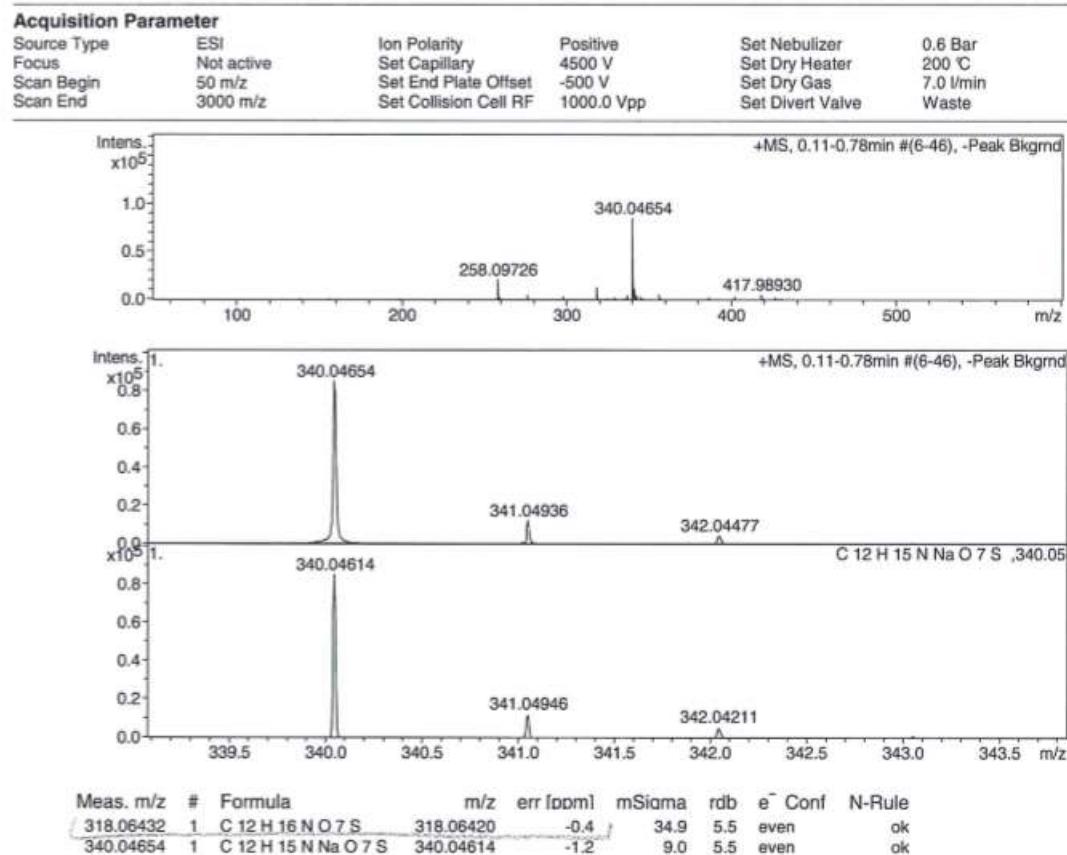
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\* Corresponding authors

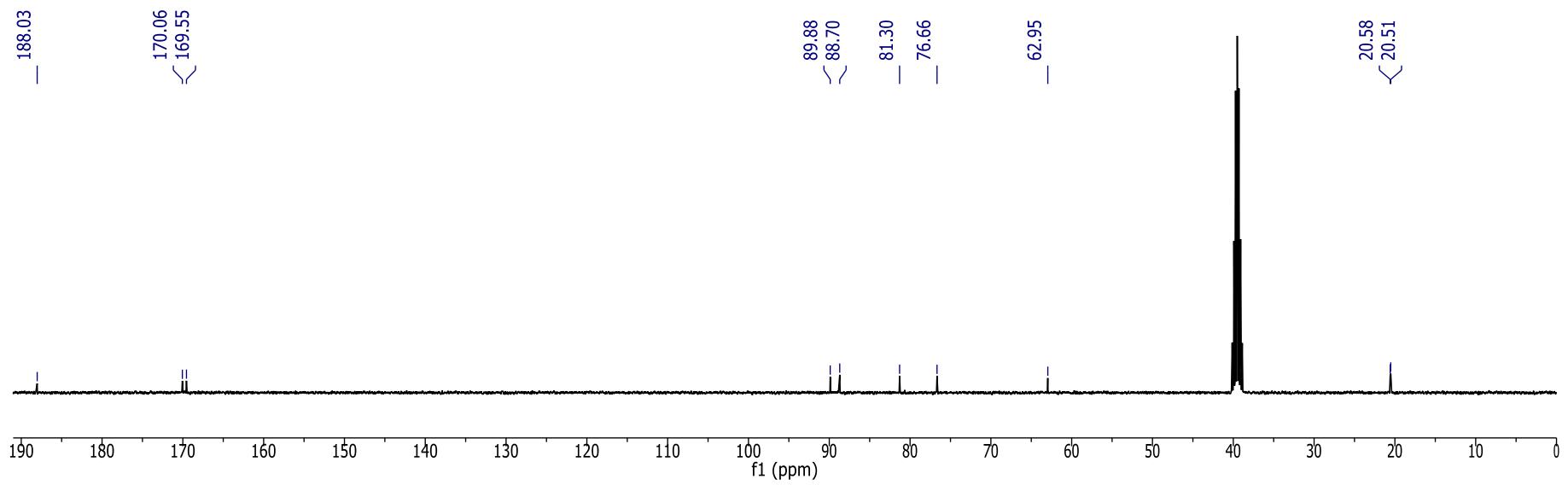
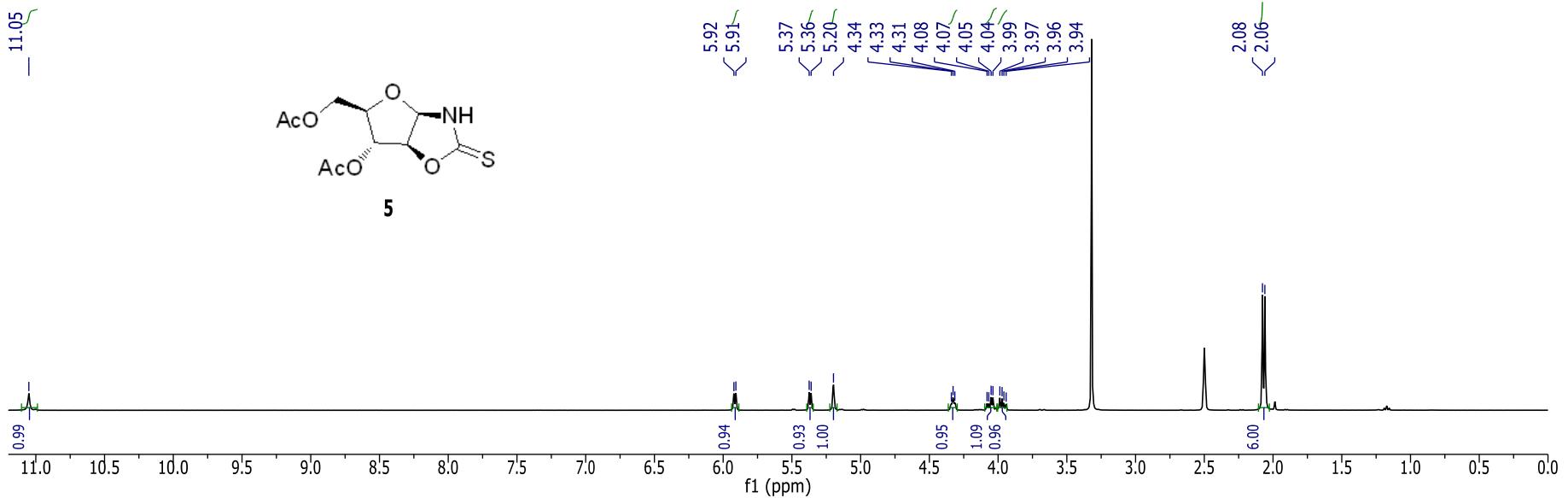
E-mail address: vilija.kederiene@ktu.lt (V. Kederienė); arnaud.tatibouet@univ-orleans.fr (A. Tatibouët)



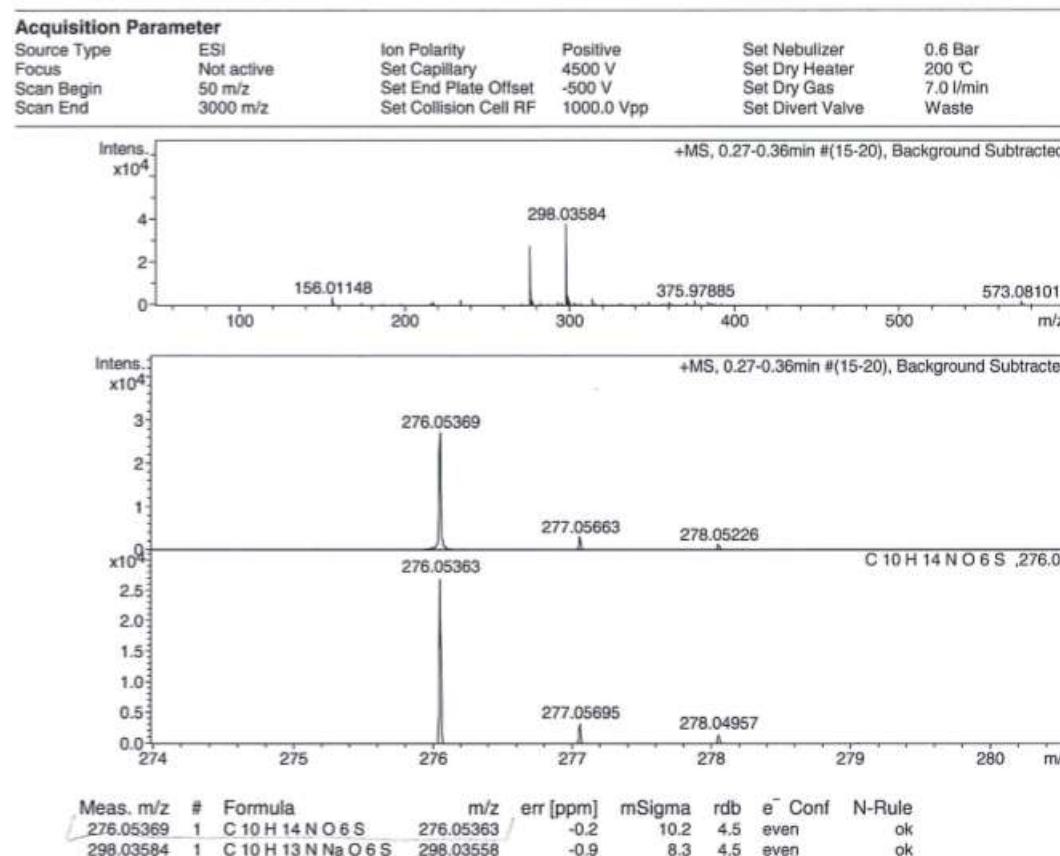
**Figure S1.** *N*-acetyl-4,5-dihydro(3',5'-di-*O*-acetyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazolidine-2-thione (**4**).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



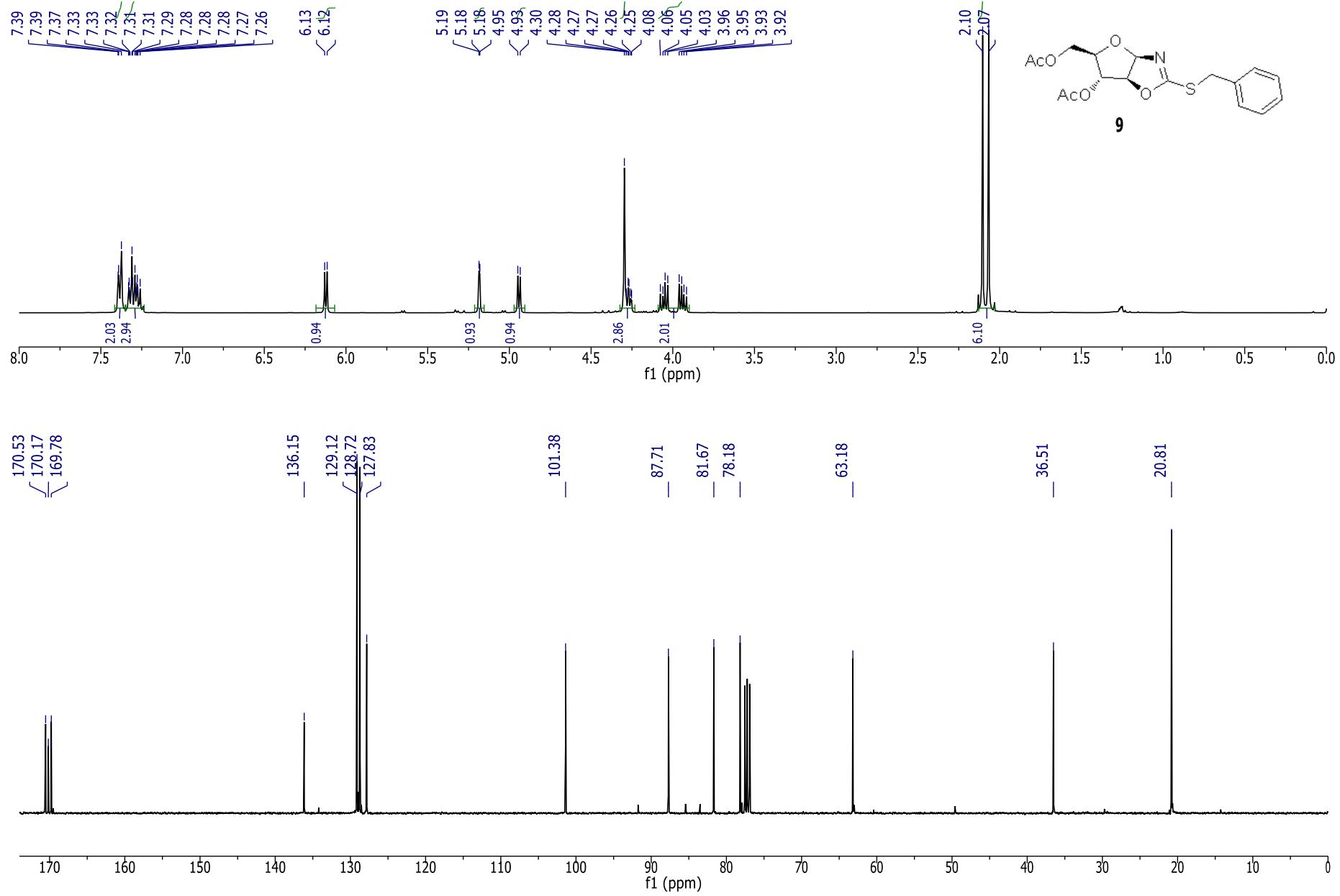
**Figure S2.** *N*-acetyl-4,5-dihydro(3',5'-di-*O*-acetyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazolidine-2-thione (**4**). HRMS (ESI).



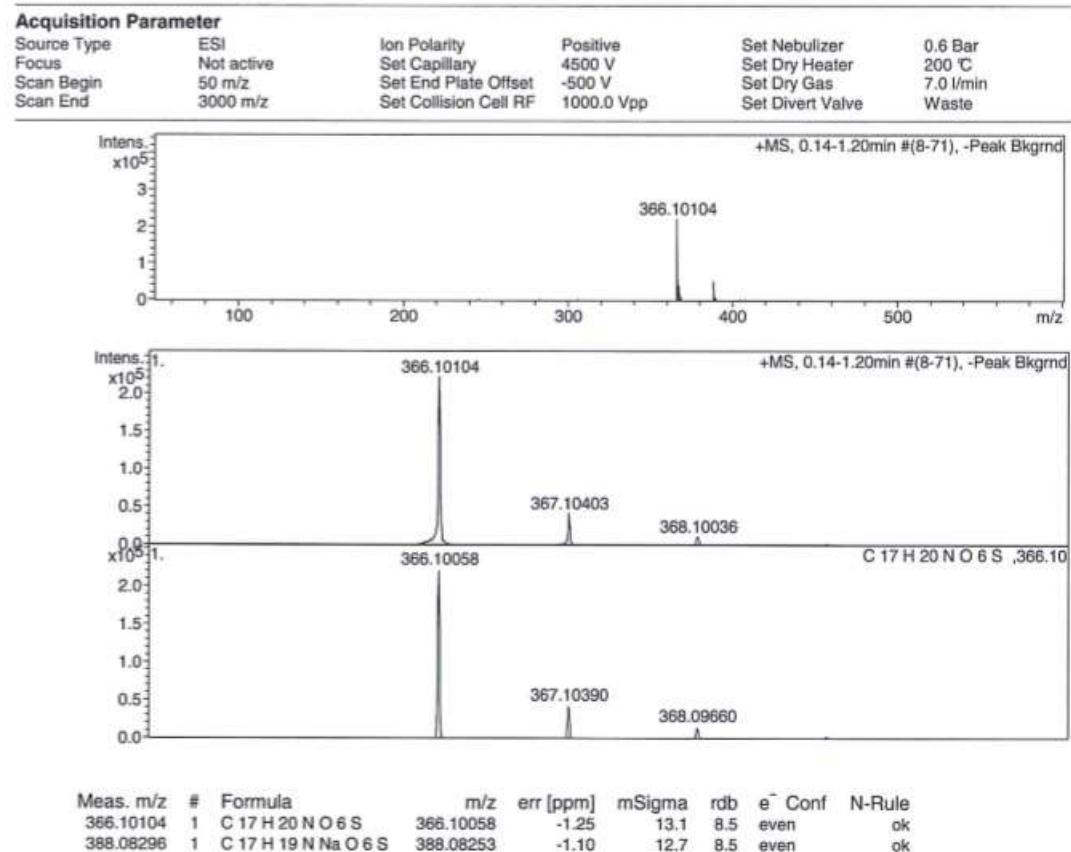
**Figure S3.** 4,5-Dihydro(3',5'-di-O-acetyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-d]-oxazolidine-2-thione (**5**).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) and  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ) spectra.



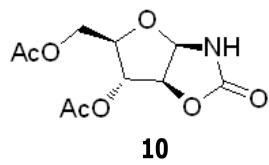
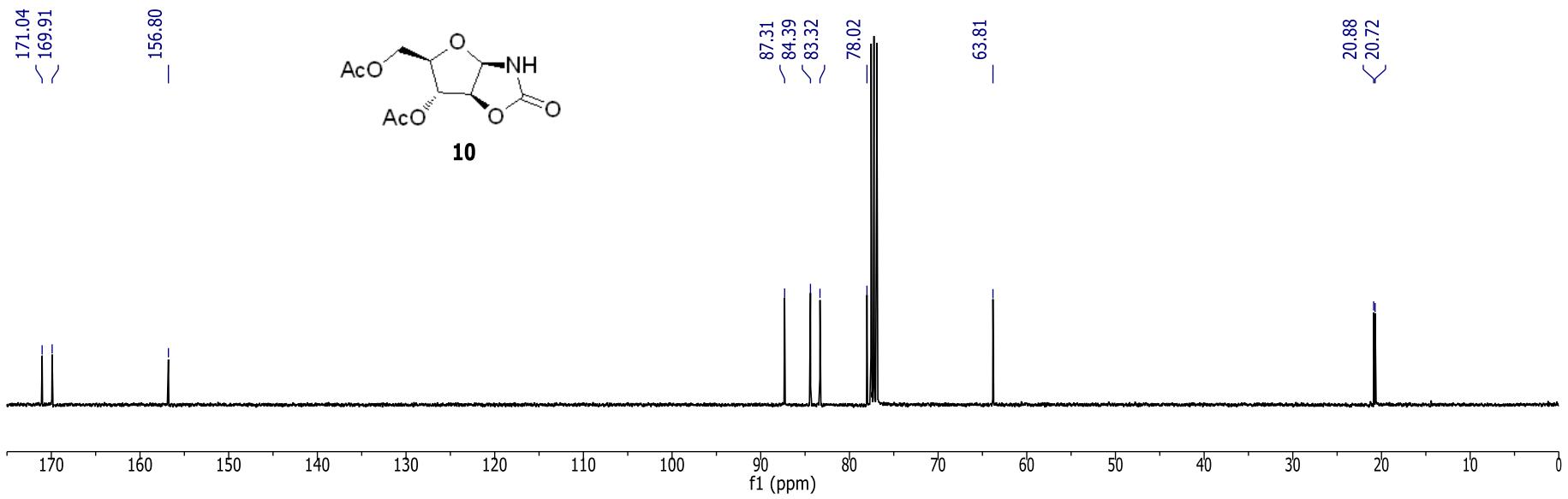
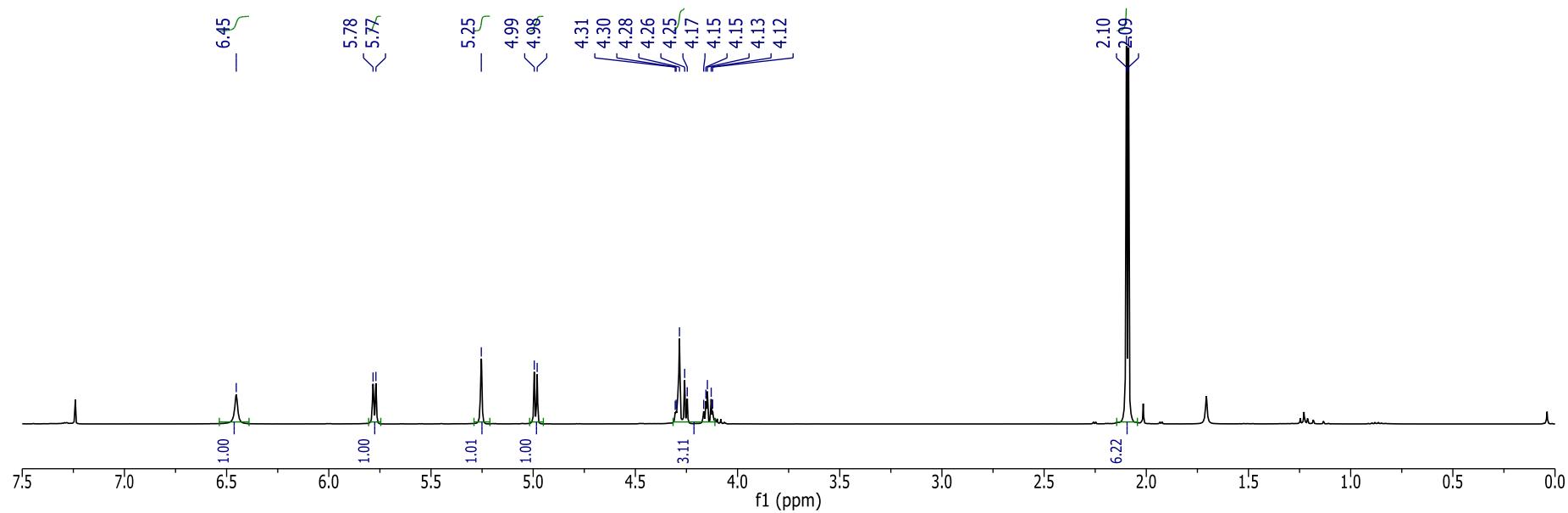
**Figure S4.** 4,5-Dihydro(3',5'-di-O-acetyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-d]-oxazolidine-2-thione (**5**). HRMS (ESI).



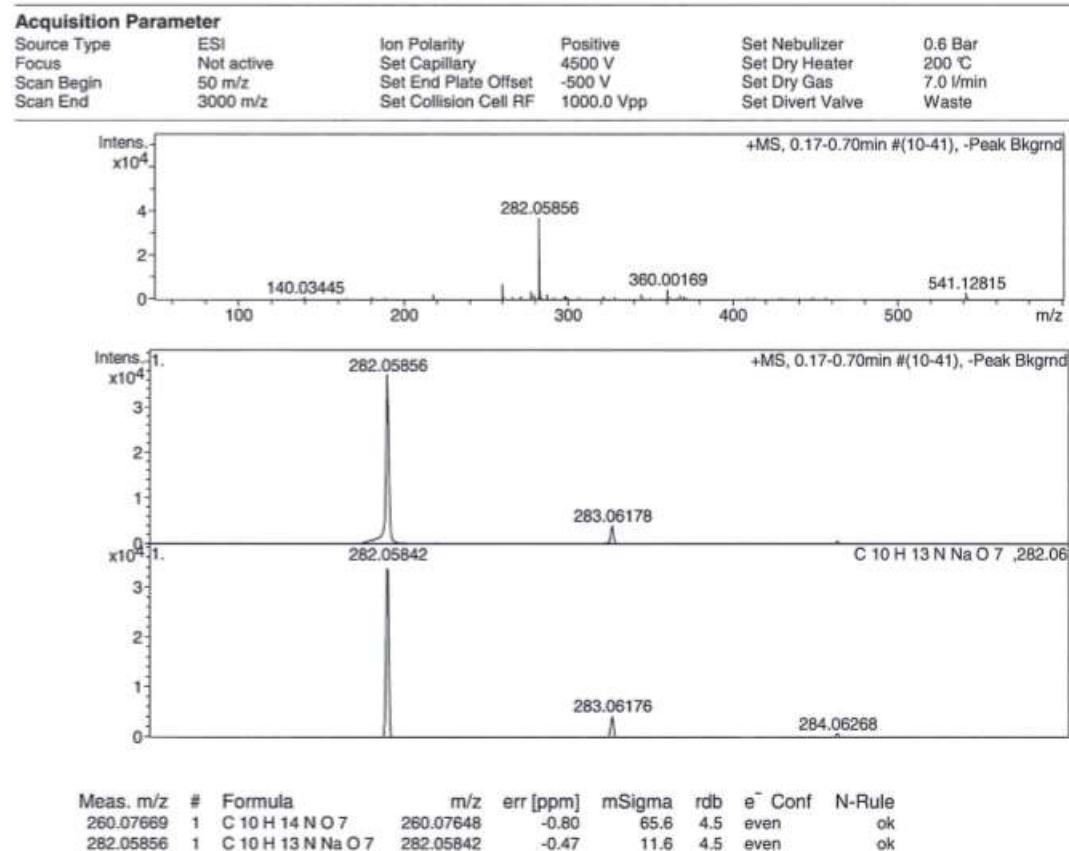
**Figure S5.** 2-Benzylsulfanyl-4,5-dihydro(3',5'-di-O-acetyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-d]-oxazole (9).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



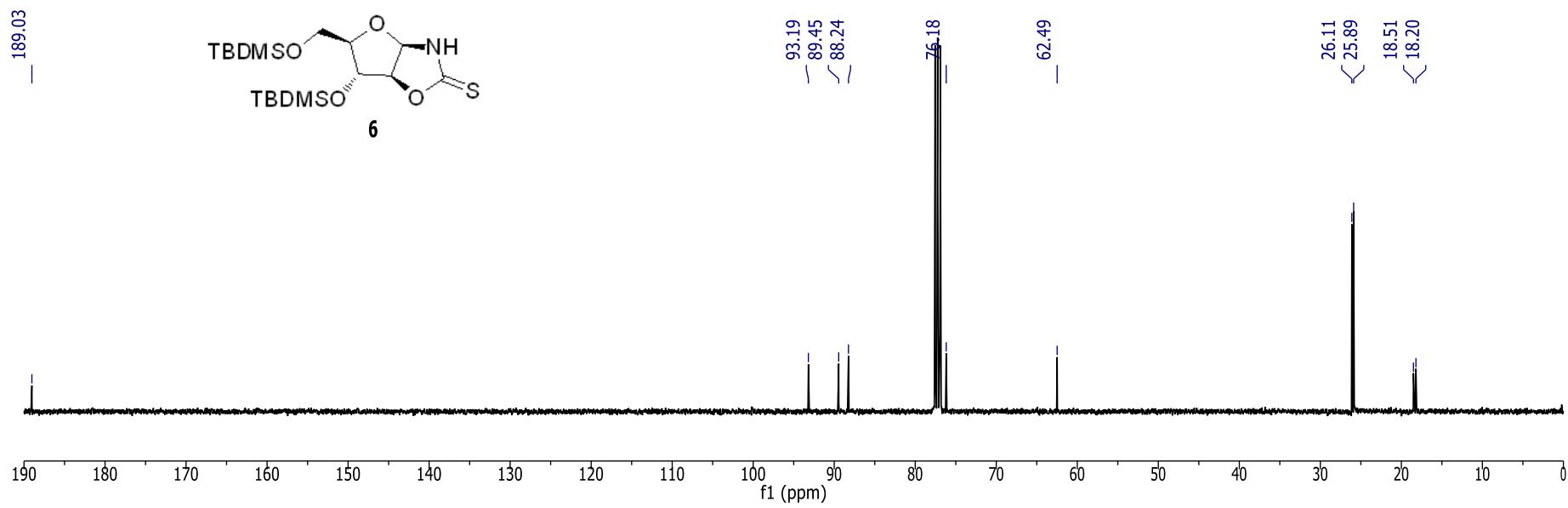
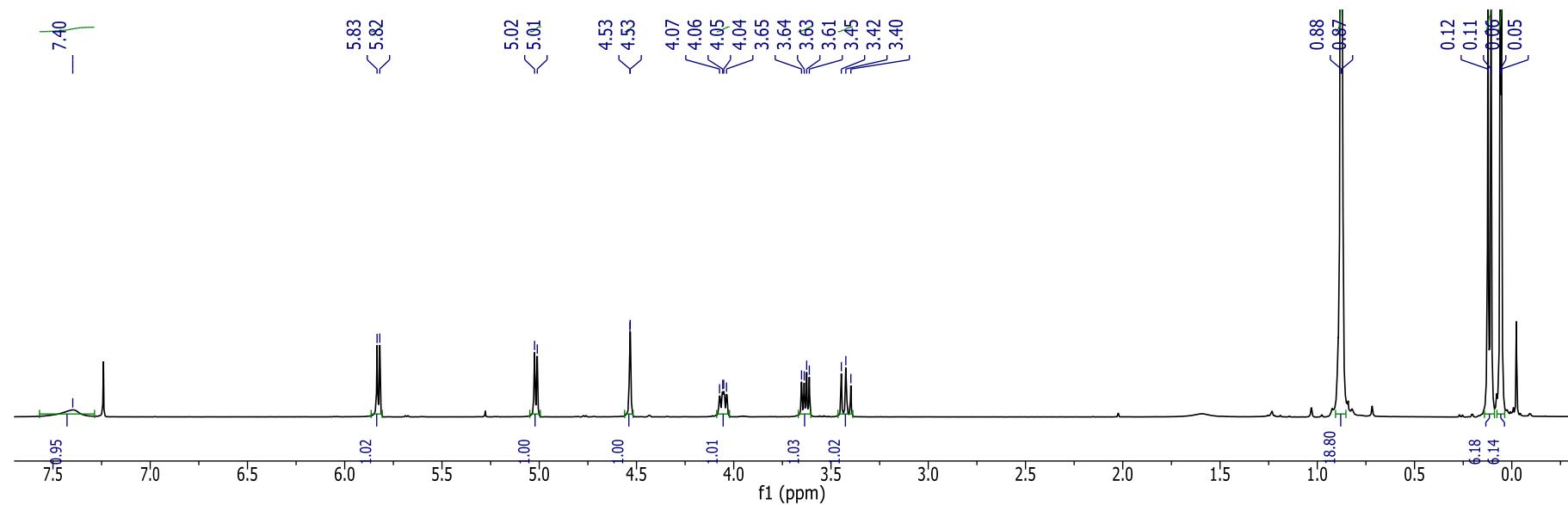
**Figure S6.** 2-Benzylsulfanyl-4,5-dihydro(3',5'-di-O-acetyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-d]-oxazole (9). HRMS (ESI).



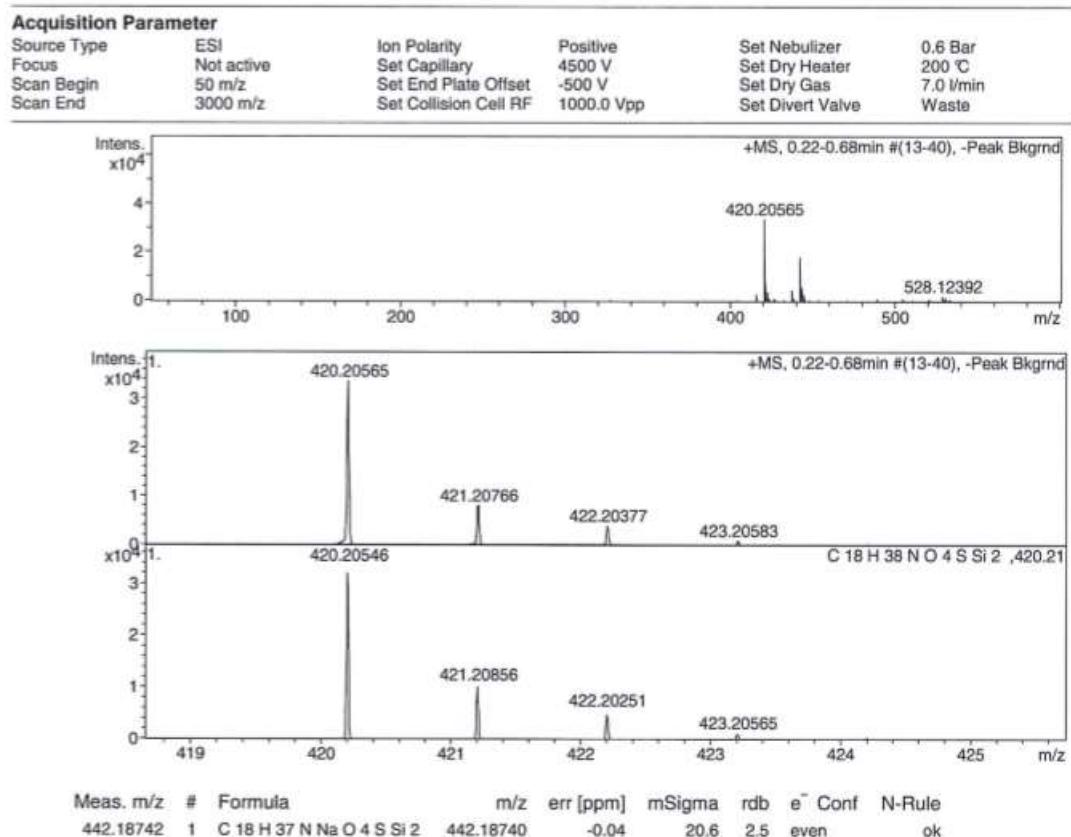
**Figure S7.** 4,5-Dihydro(3',5'-di-O-acetyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-d]-oxazolidine-2-one (10).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectra.



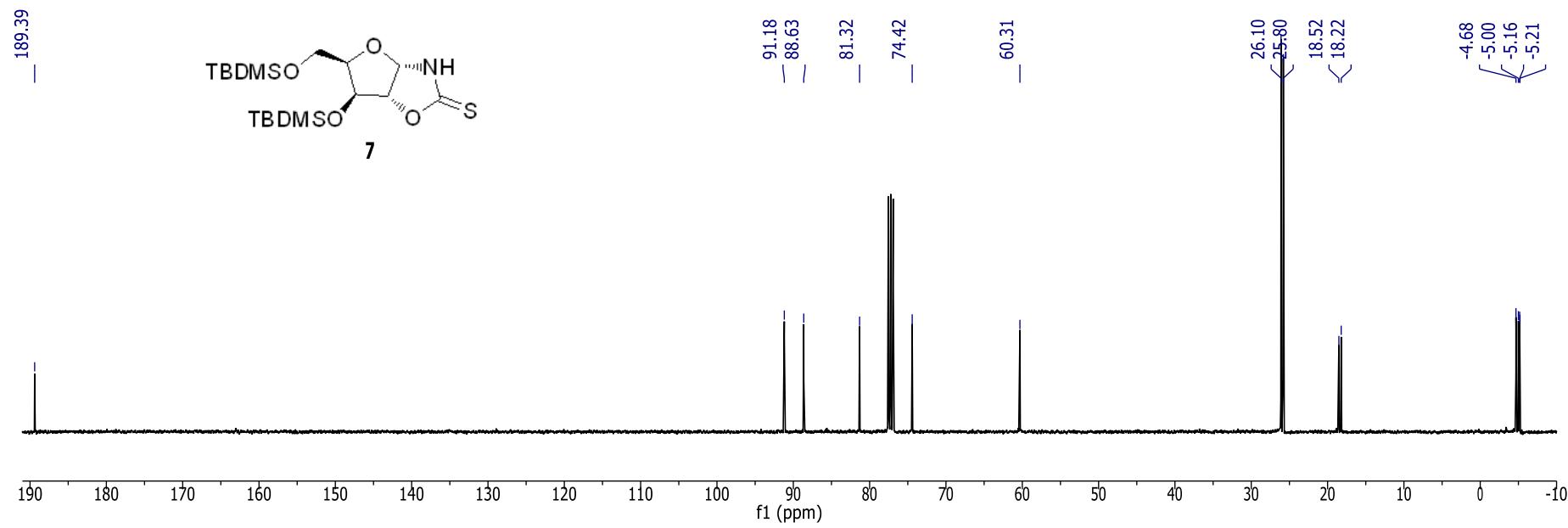
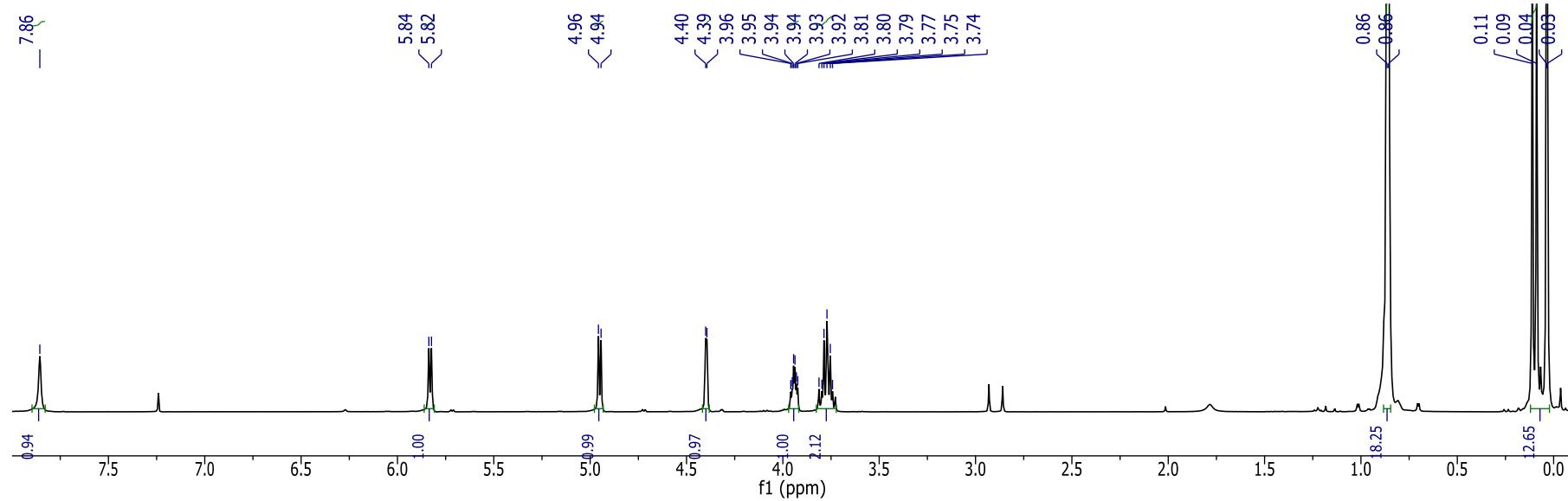
**Figure S8.** 4,5-Dihydro(3',5'-di-O-acetyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-d]-oxazolidine-2-one (10). HRMS (ESI).



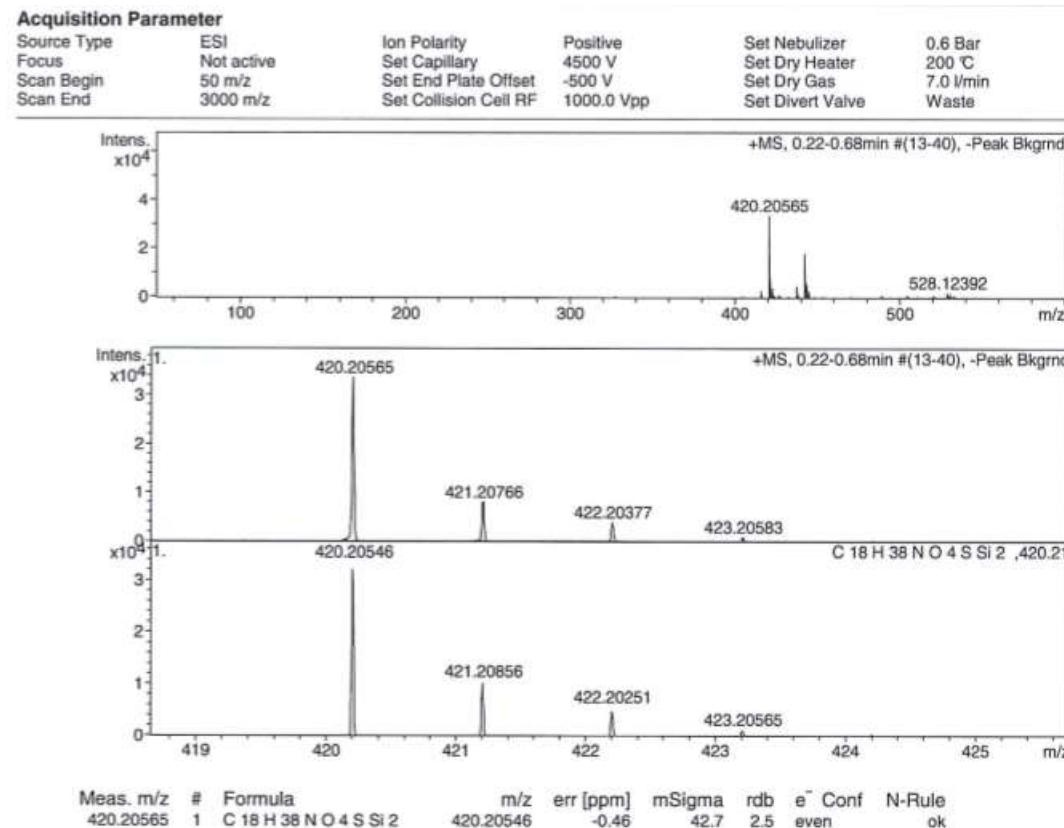
**Figure S9.** 4,5-Dihydro(3',5'-di-O-*tert*-butyldimethylsilyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazolidine-2-thione (**6**).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



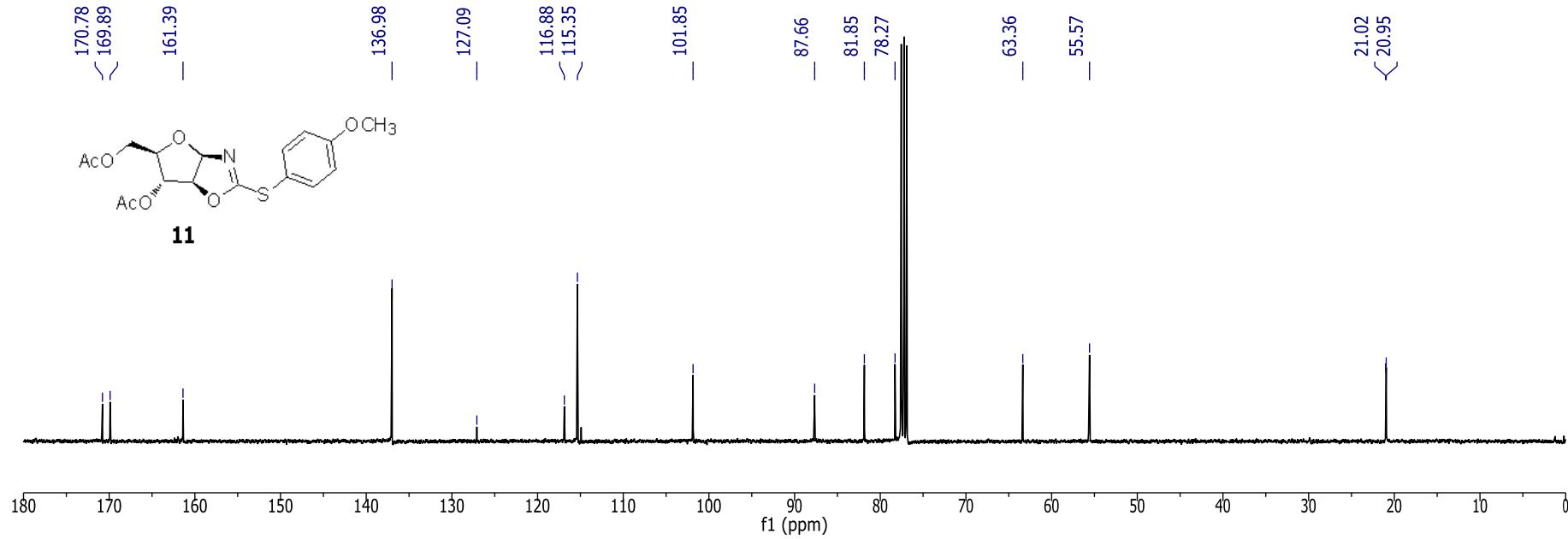
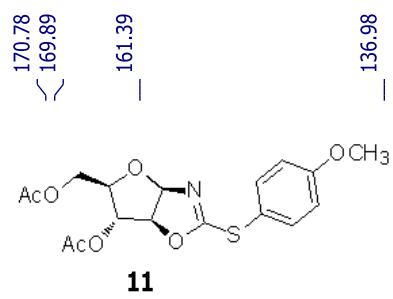
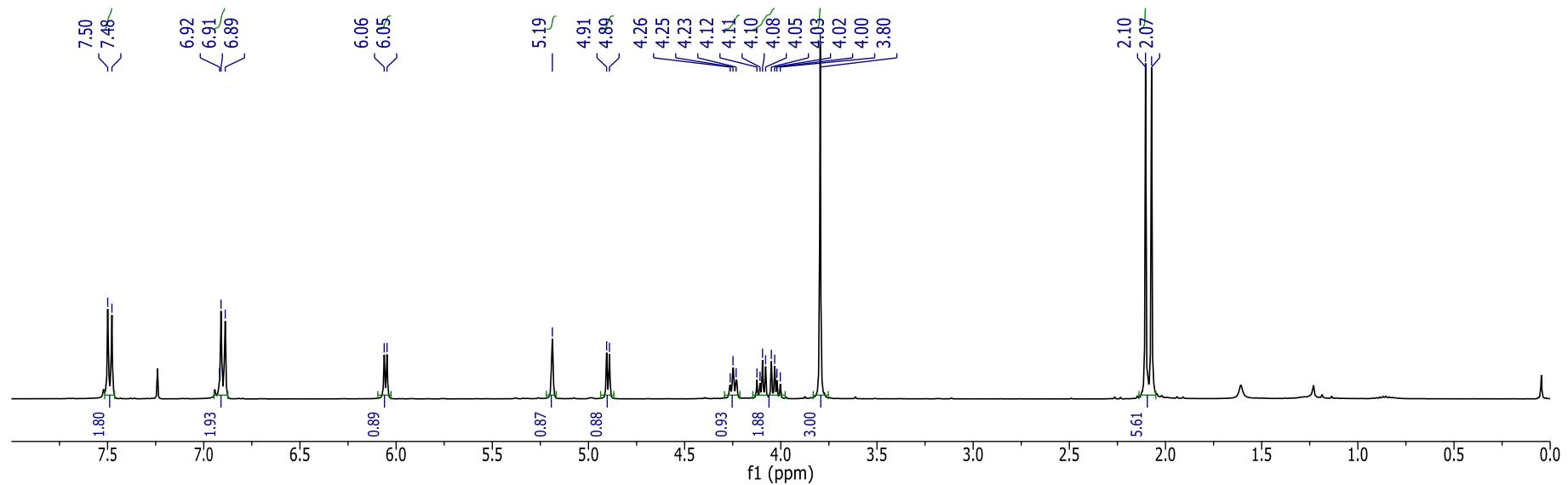
**Figure S10.** 4,5-Dihydro(3',5'-di-O-*tert*-butyldimethylsilyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazolidine-2-thione (**6**). HRMS (ESI).



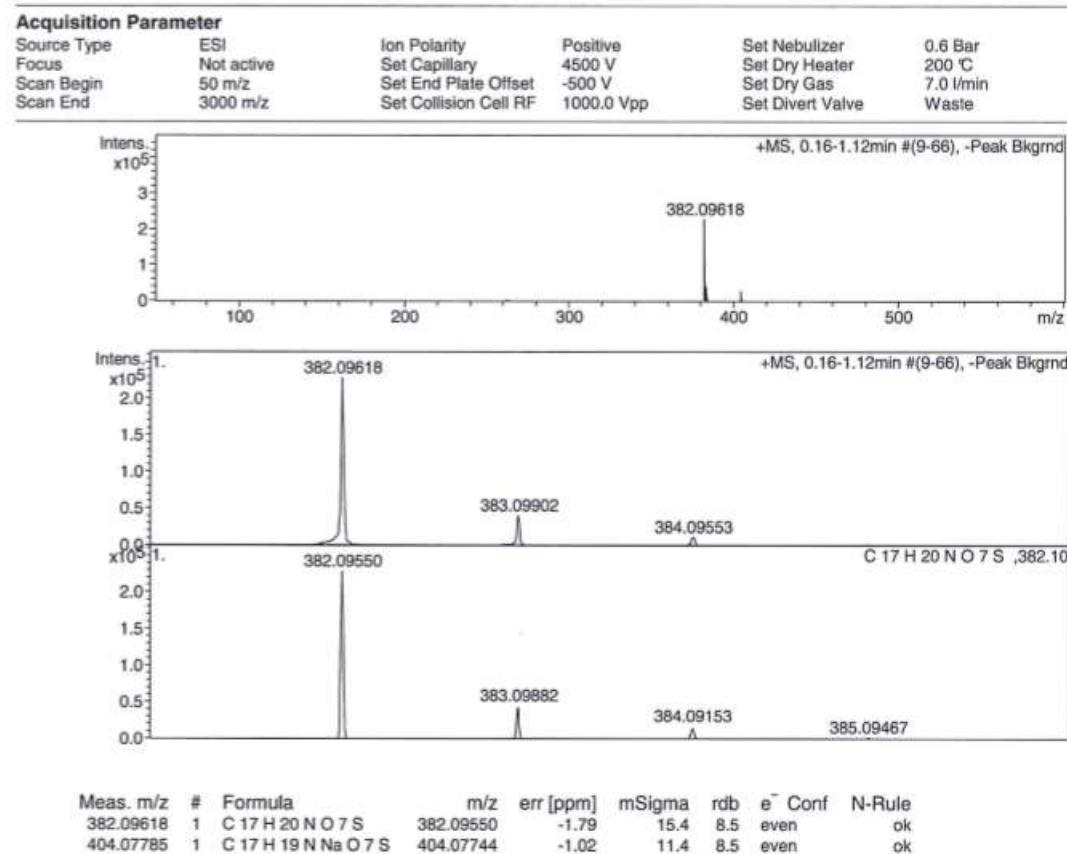
**Figure S11.** 4,5-Dihydro(3',5'-di-O-*tert*-butyldimethylsilyl-1',2'-dideoxy- $\alpha$ -D-xylofuranoso)-[1,2-*d*]-oxazolidine-2-thione (7).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



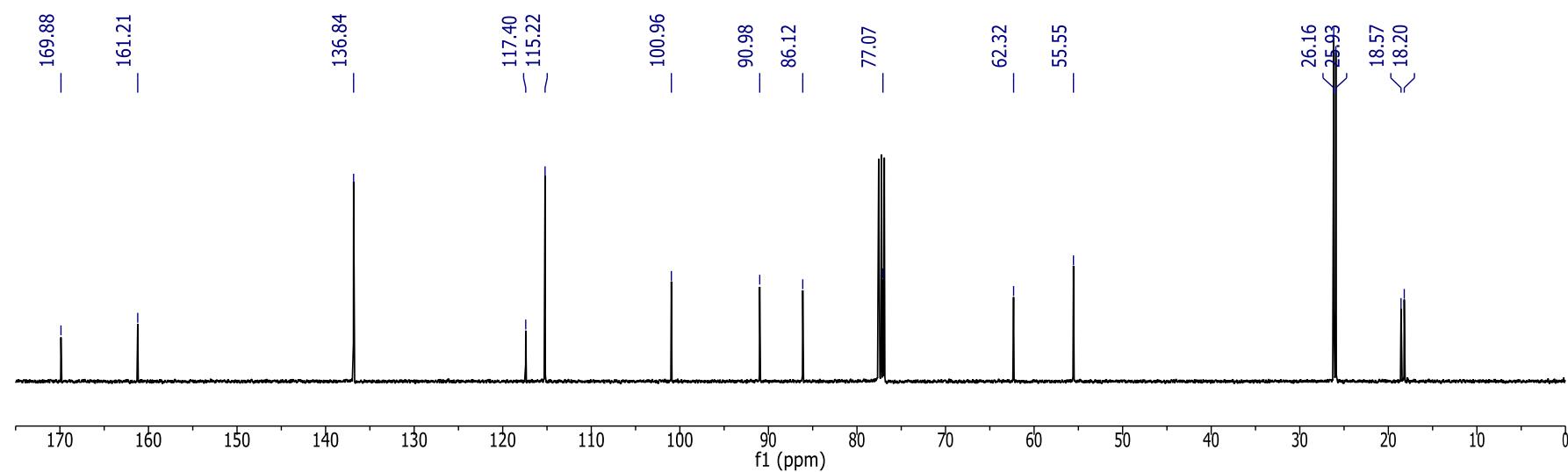
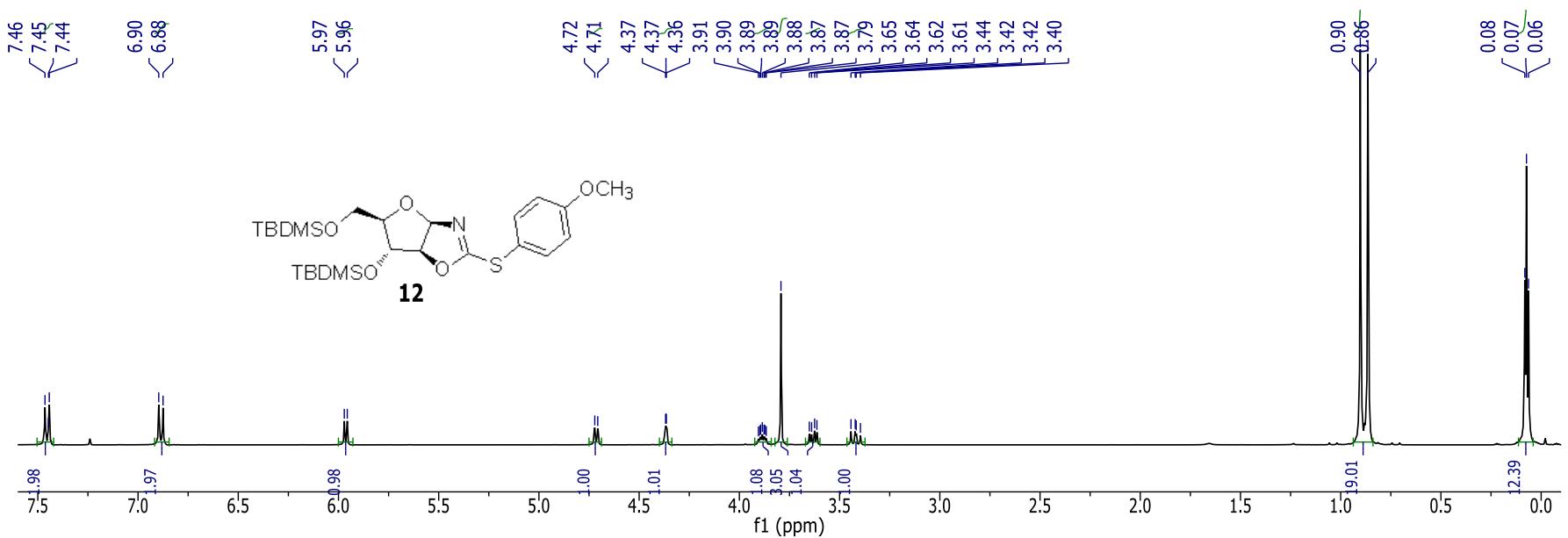
**Figure S12.** 4,5-Dihydro(3',5'-di-O-*tert*-butyldimethylsilyl-1',2'-dideoxy- $\alpha$ -D-xylofuranoso)-[1,2-*d*]-oxazolidine-2-thione (7). HRMS (ESI).



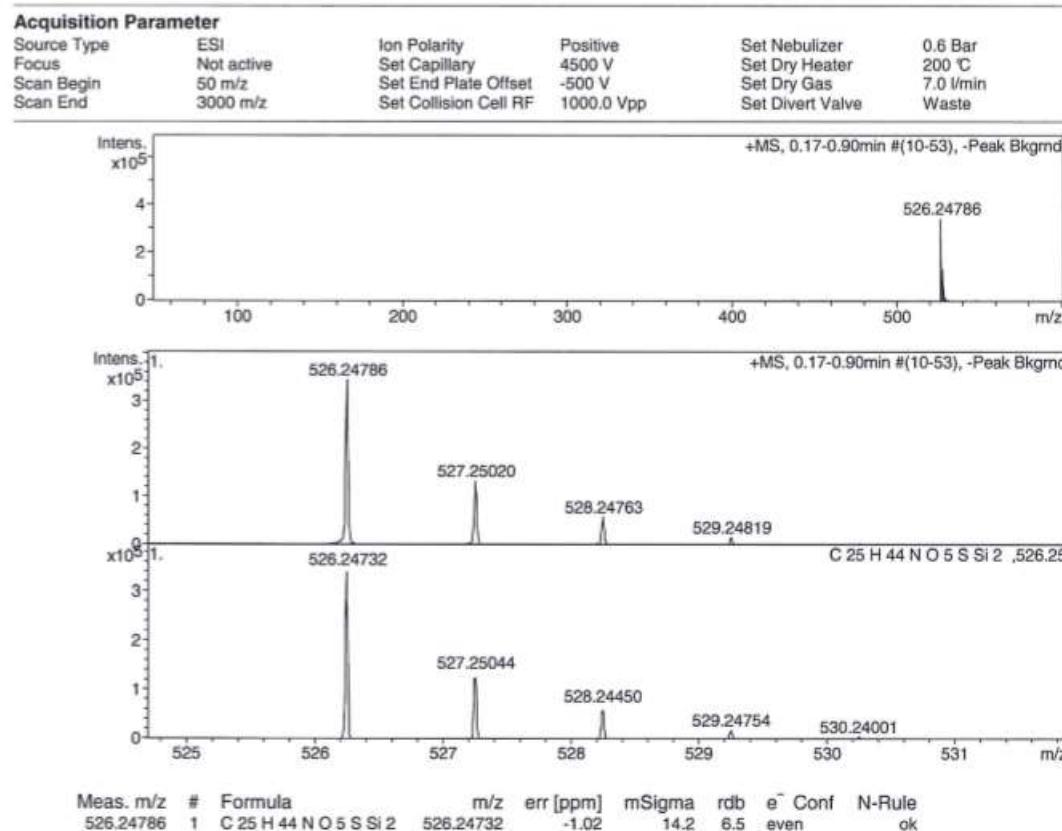
**Figure S13.** 2-[(4-Methoxyphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-acetyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-d]-oxazole (11).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



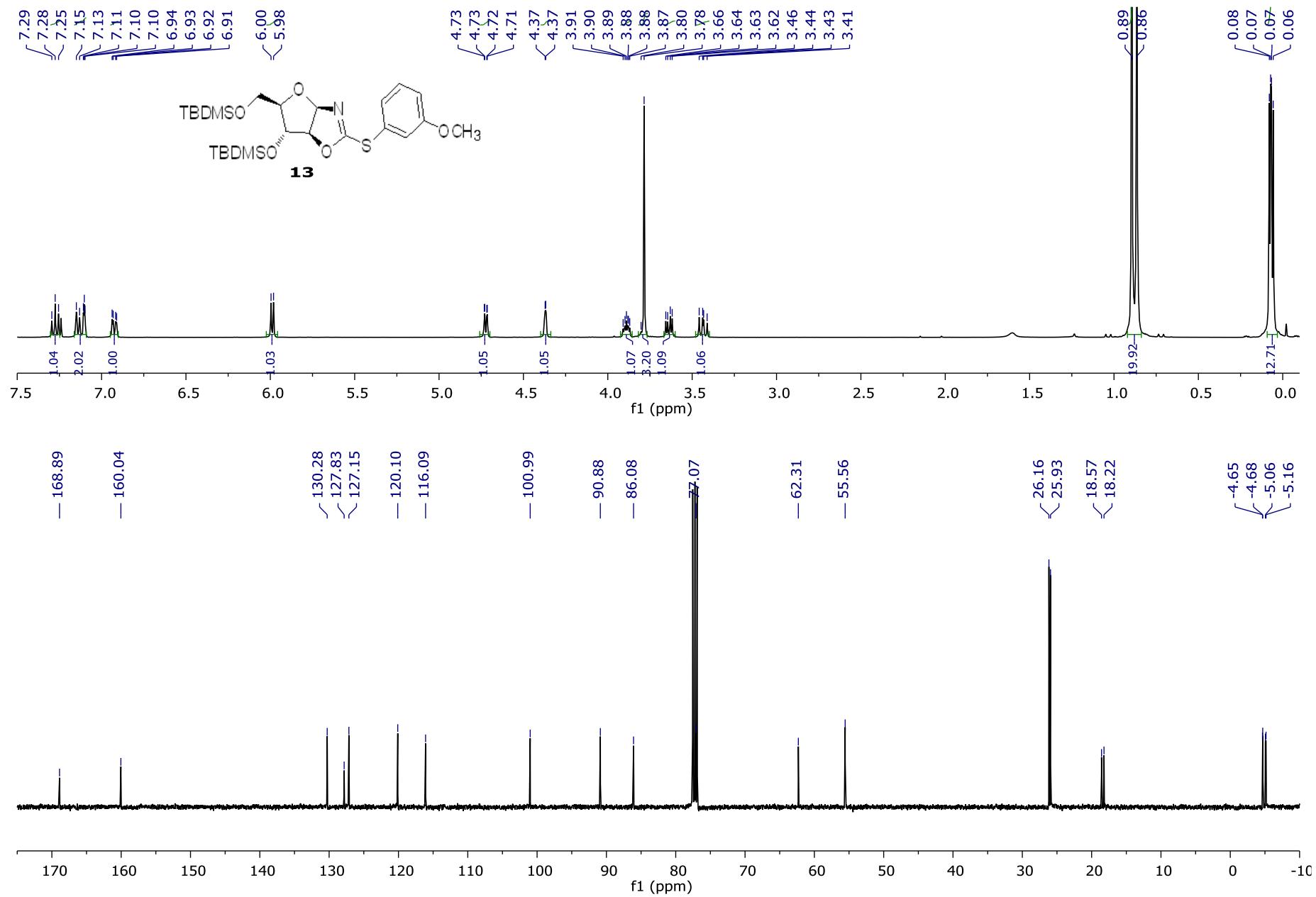
**Figure S14.** 2-[(4-Methoxyphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-acetyl-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-d]-oxazole (11). HRMS (ESI).



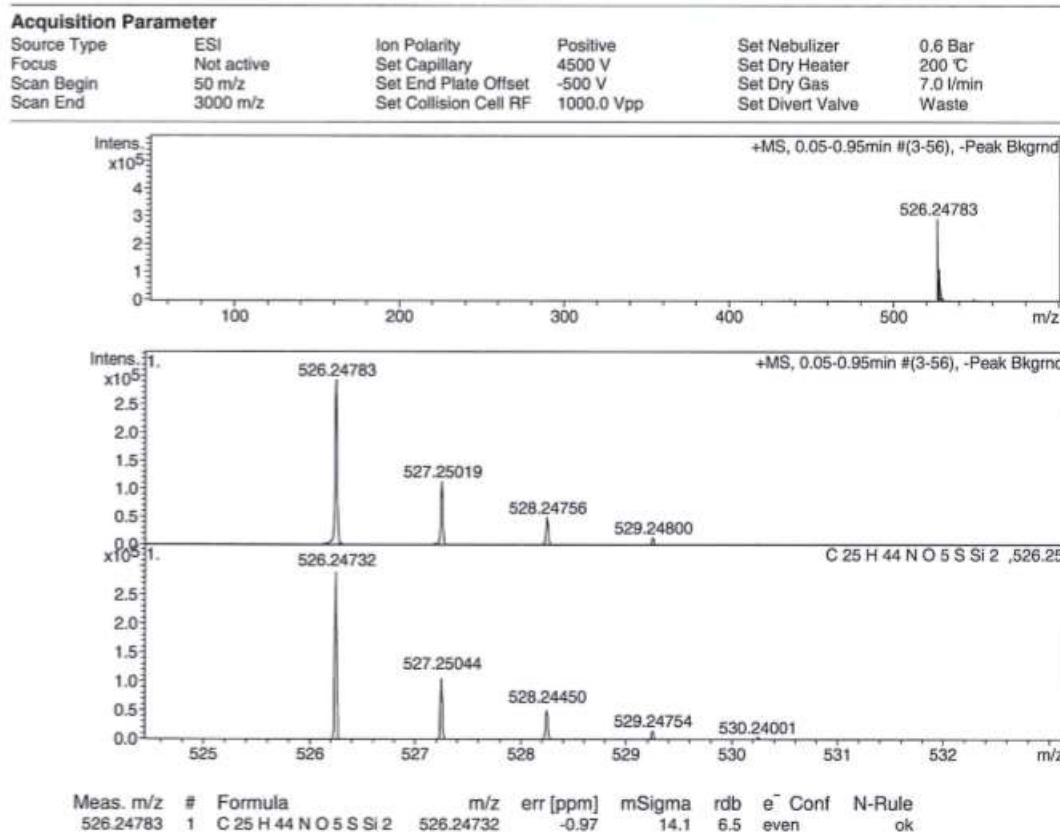
**Figure S15.** 2-[(4-Methoxyphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (12).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



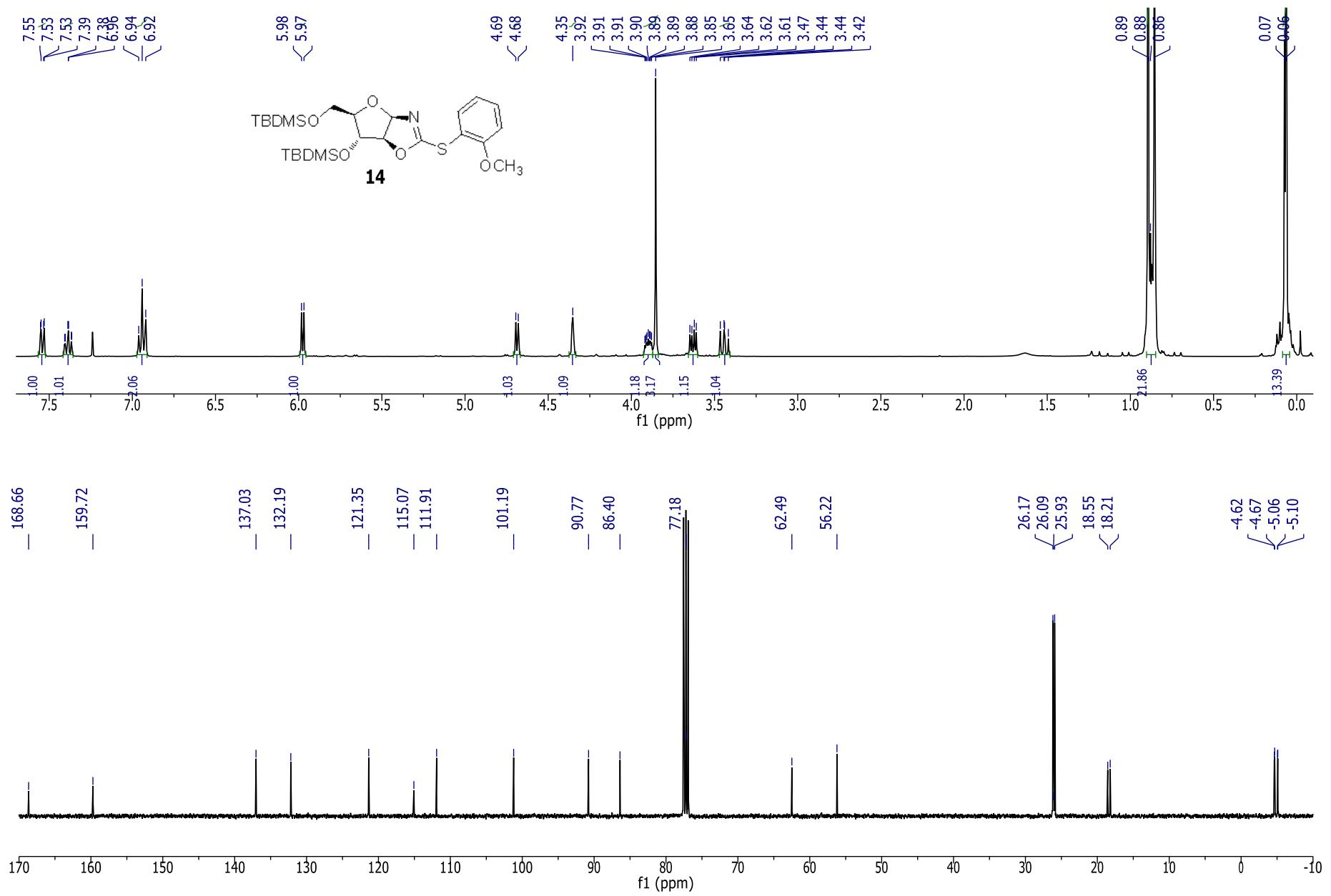
**Figure S16.** 2-[(4-Methoxyphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (12). HRMS (ESI).



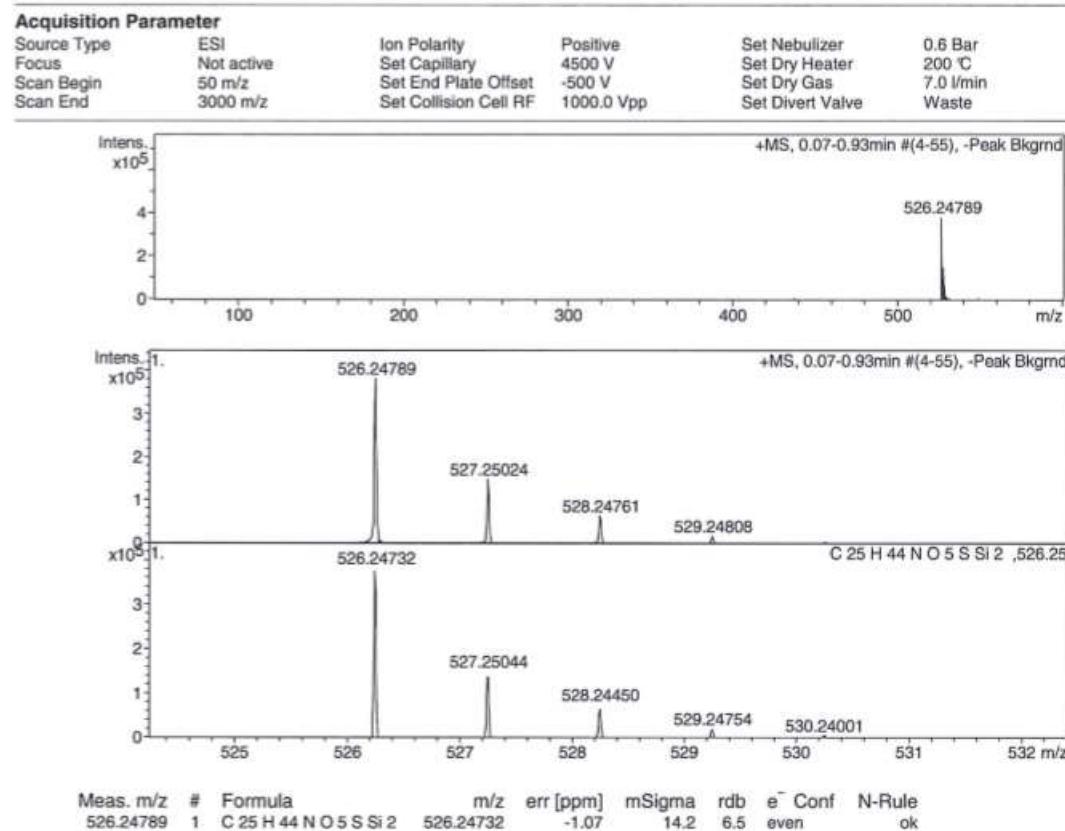
**Figure S17.** 2-[(3-Methoxyphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (13).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



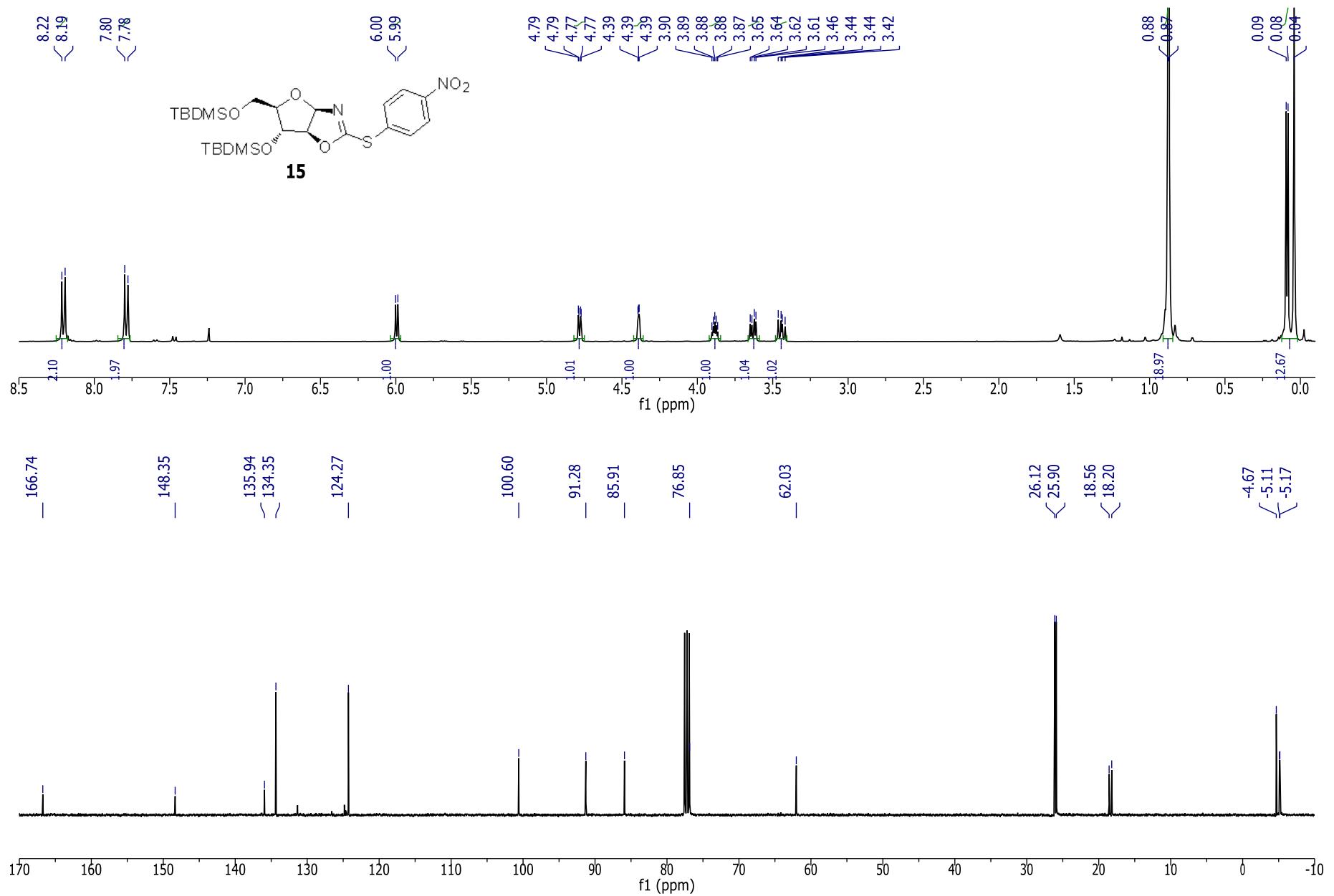
**Figure S18.** 2-[(3-Methoxyphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (13). HRMS (ESI).



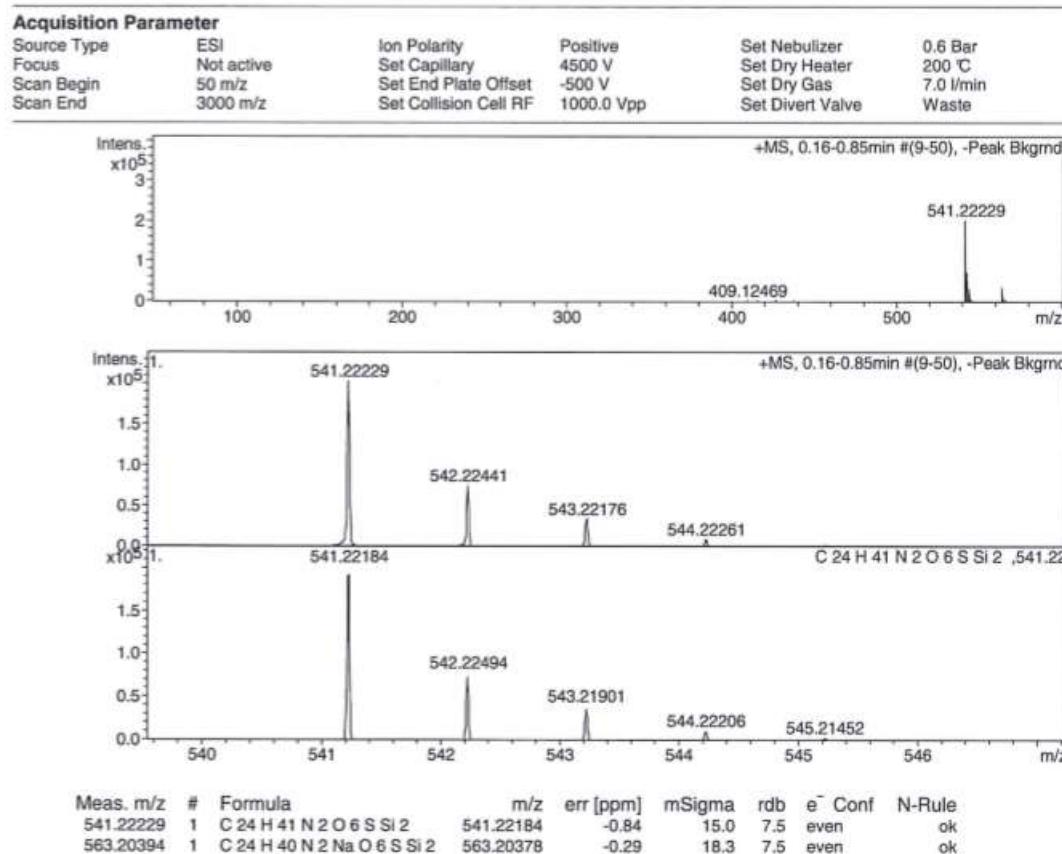
**Figure S19.** 2-[(2-Methoxyphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (14).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



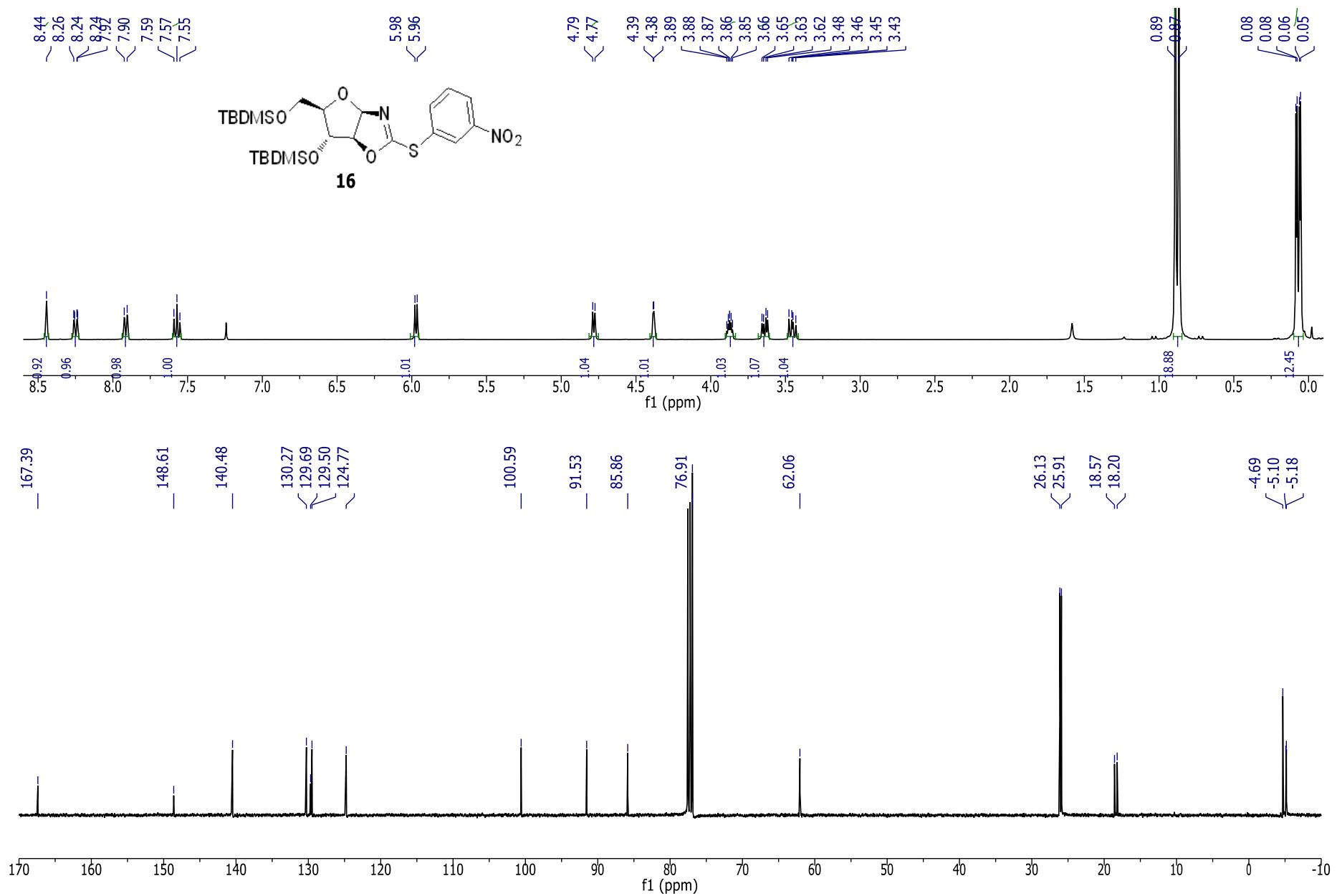
**Figure S20.** 2-[(2-Methoxyphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (14). HRMS (ESI).



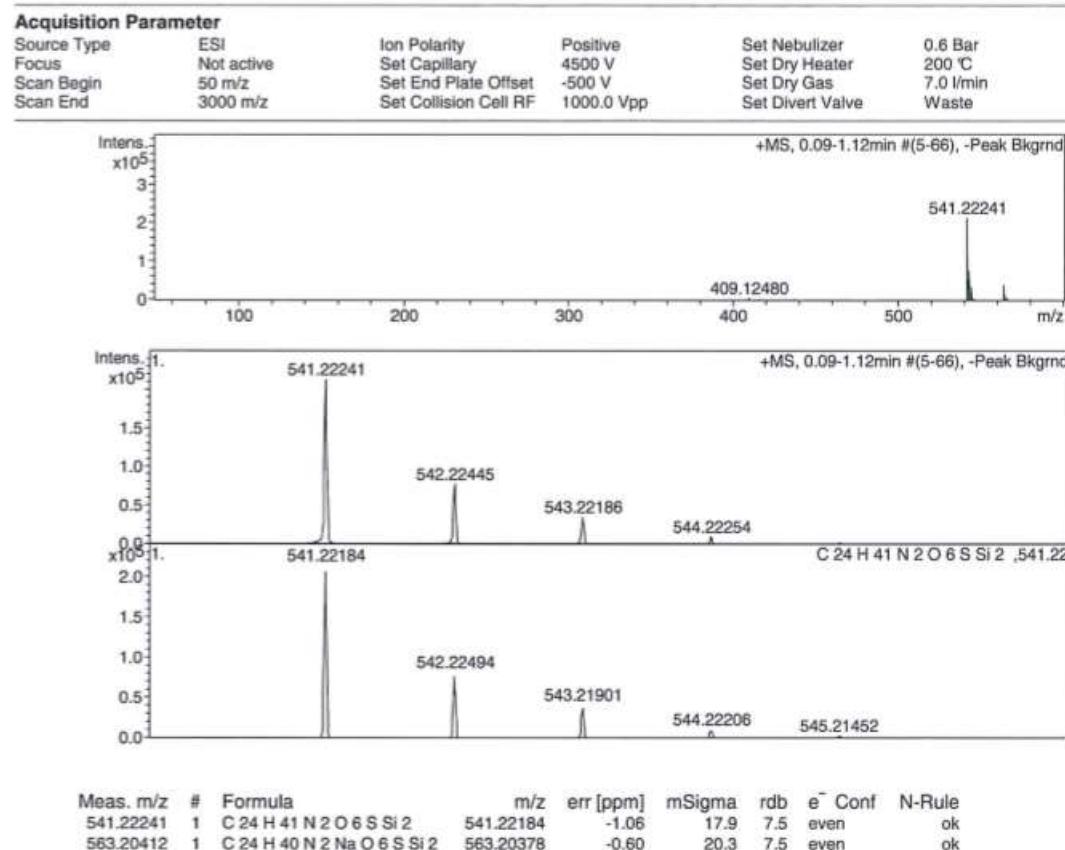
**Figure S21.** 2-[(4-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (**15**).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



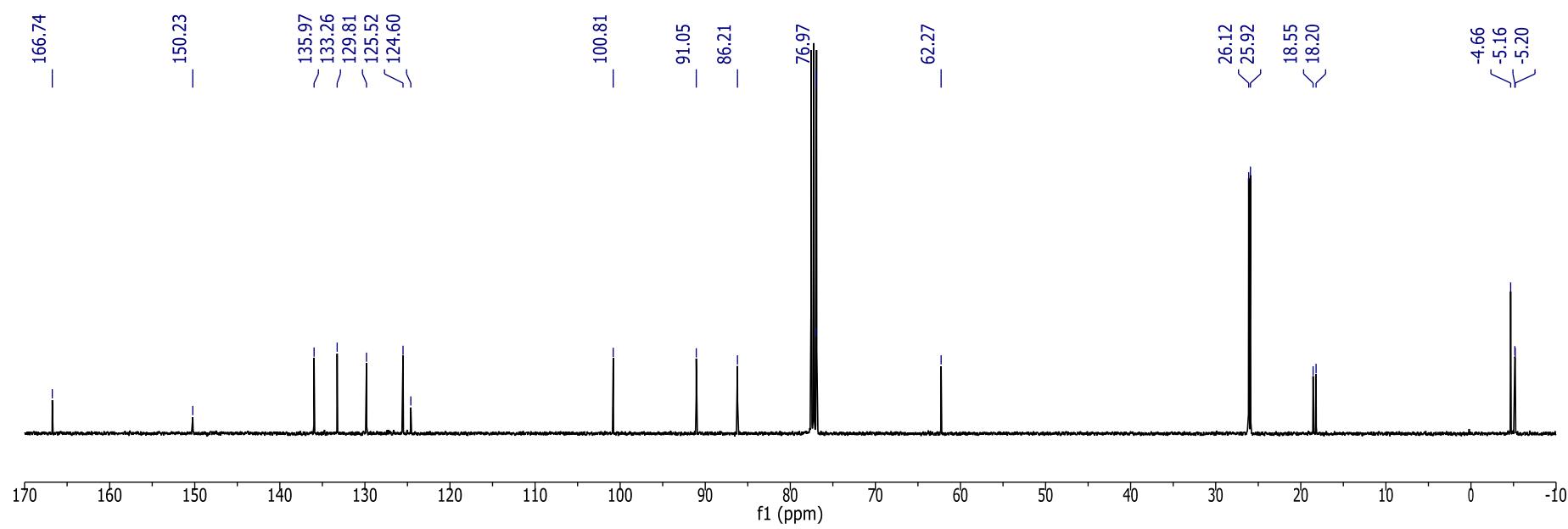
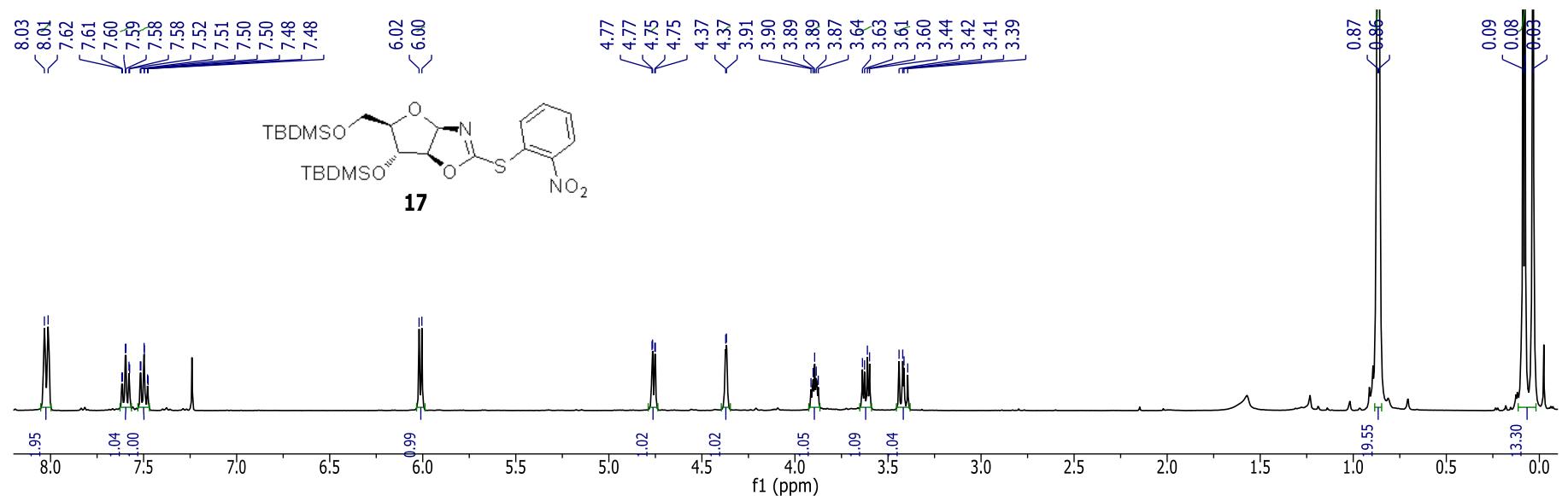
**Figure S22.** 2-[(4-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (**15**). HRMS (ESI).



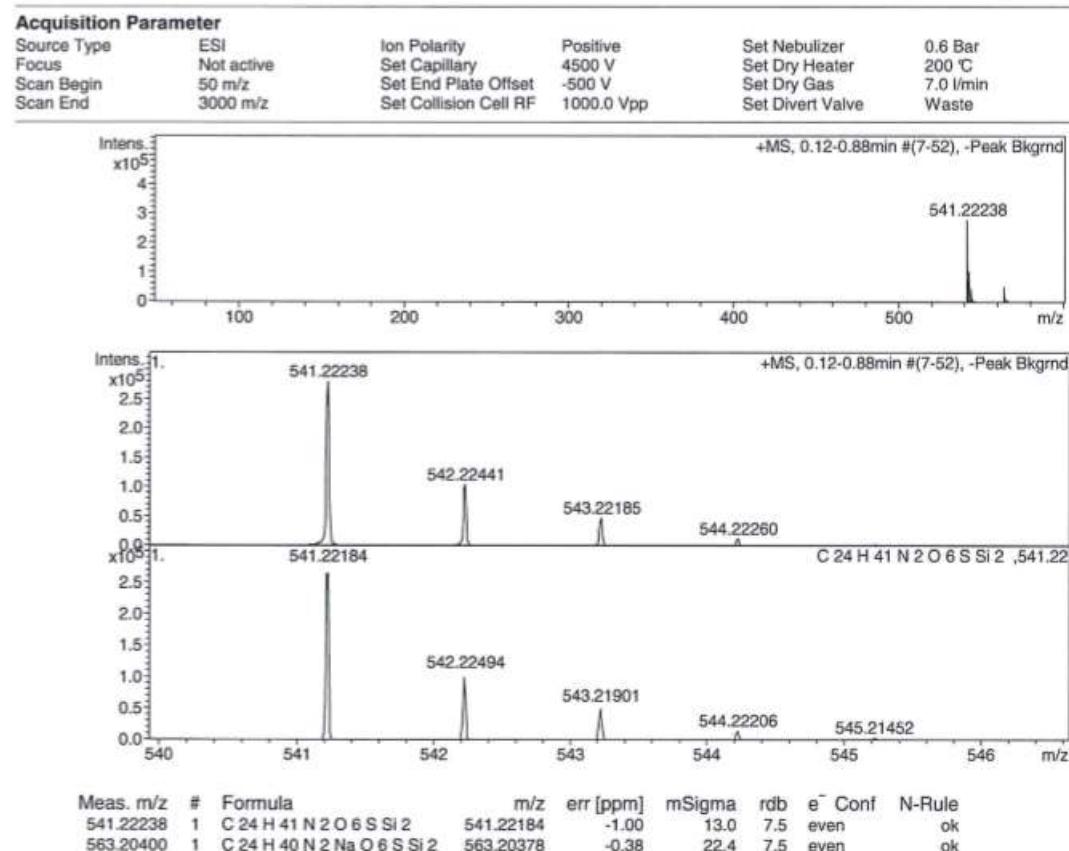
**Figure S23.** 2-[(3-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (16).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



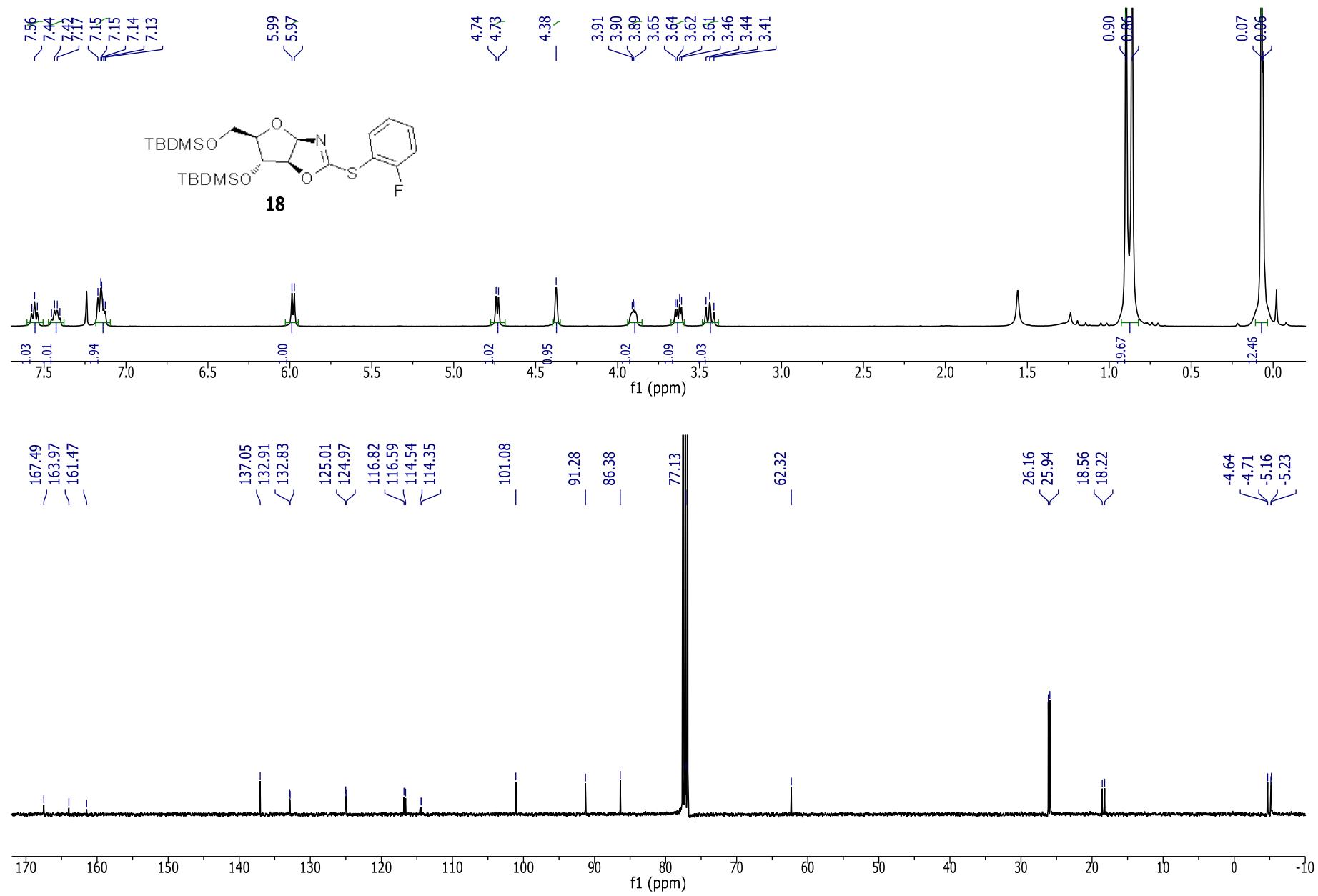
**Figure S24.** 2-[(3-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (16). HRMS (ESI).



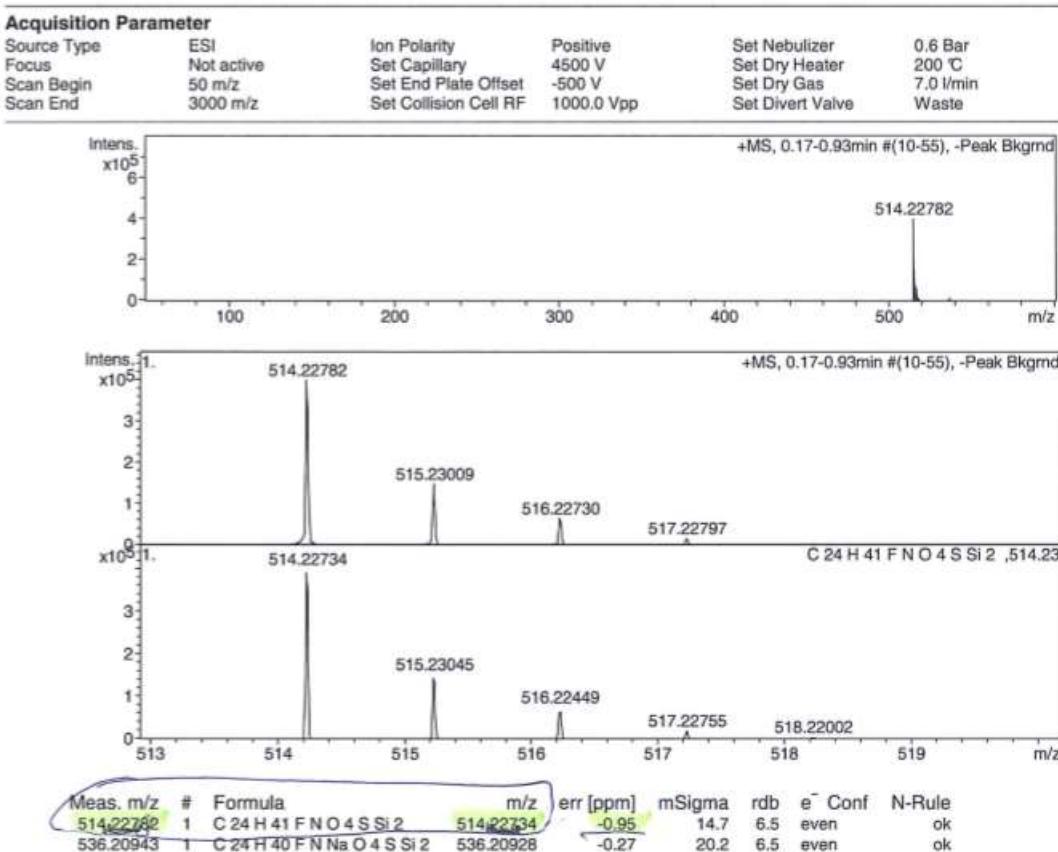
**Figure S25.** 2-[(2-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (17).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



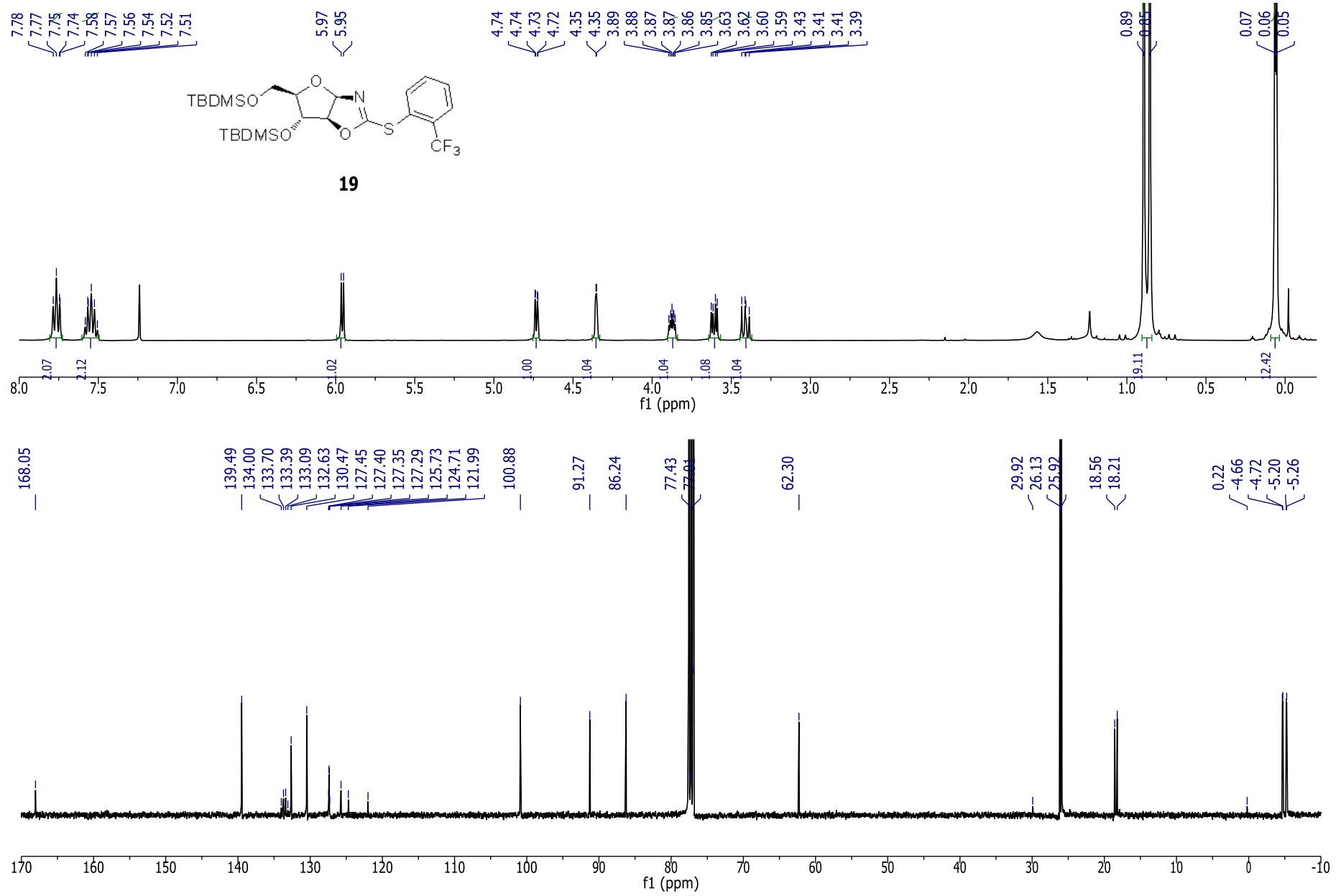
**Figure S26.** 2-[(2-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (17). HRMS (ESI).



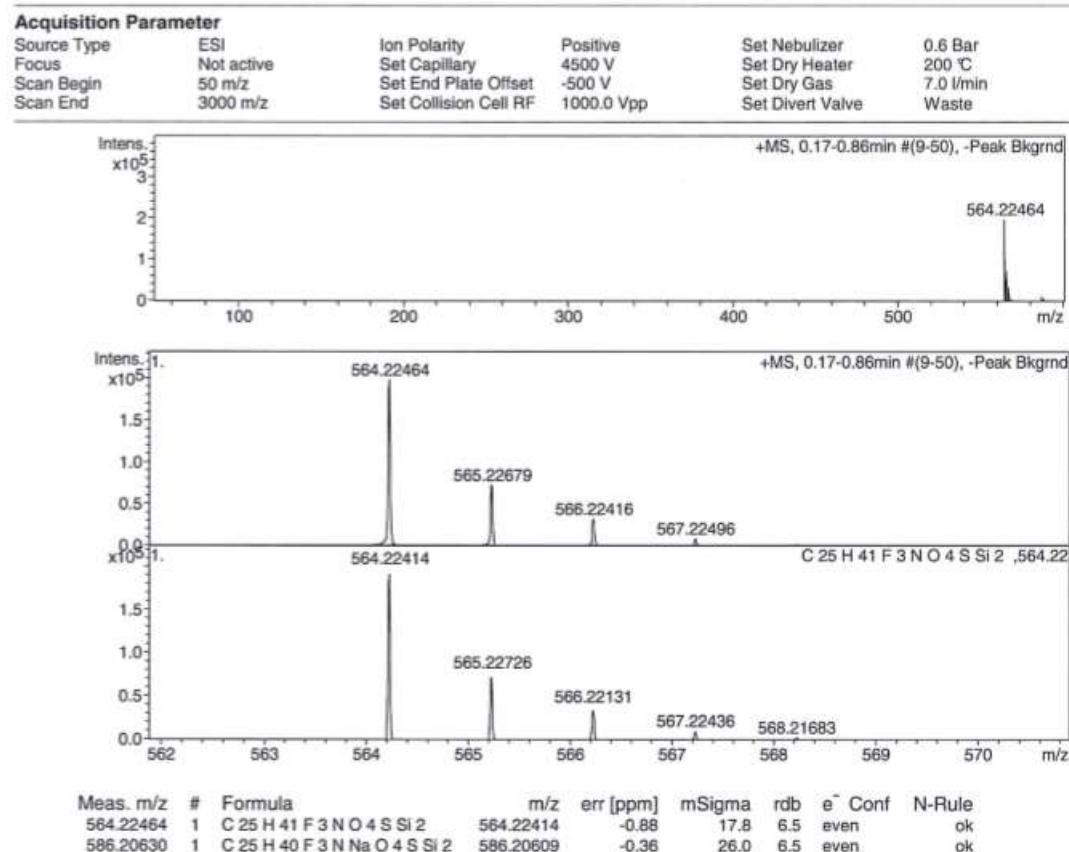
**Figure S27.** 2-[(2-Fluorophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (18).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



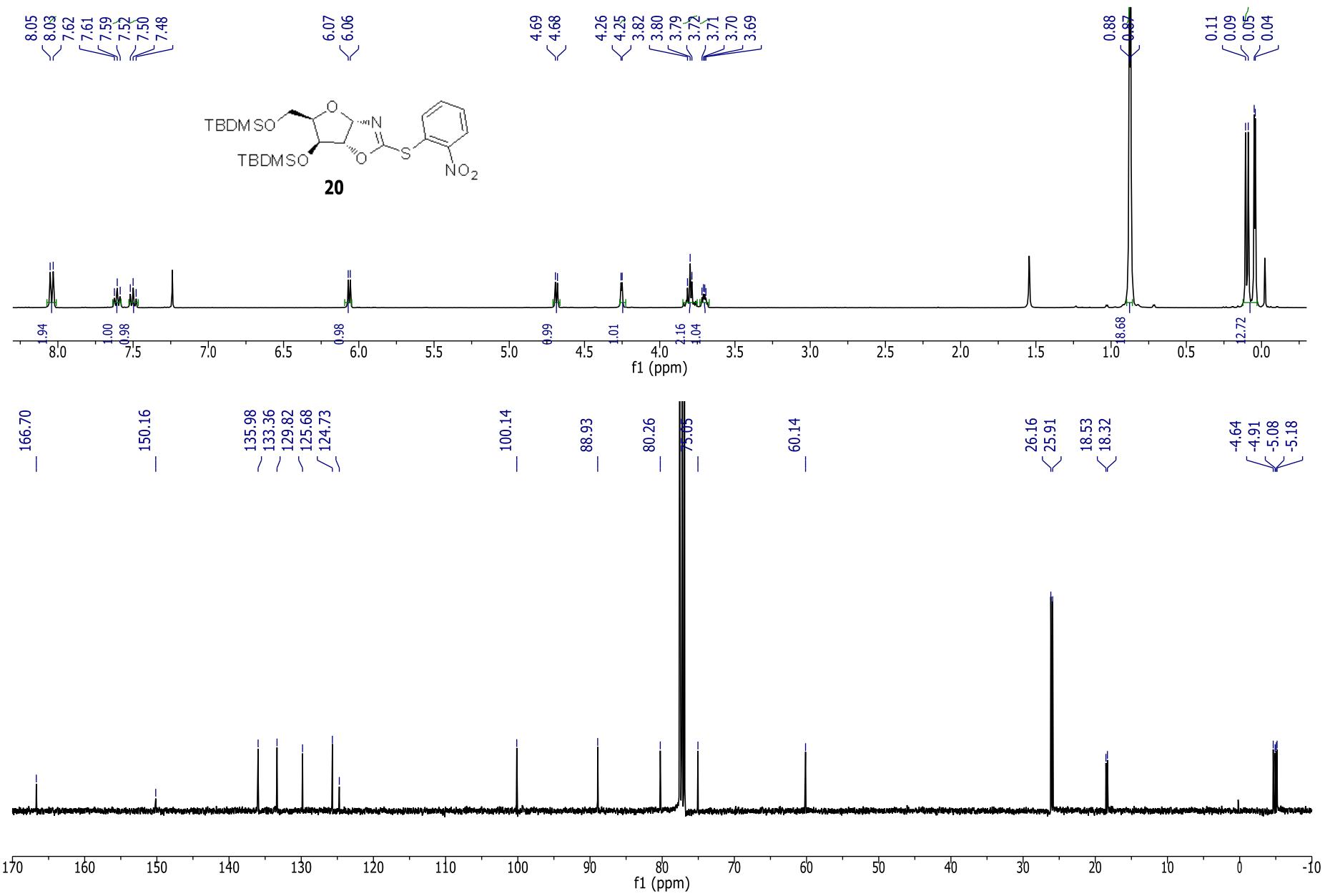
**Figure S28.** 2-[(2-Fluorophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (18). HRMS (ESI).



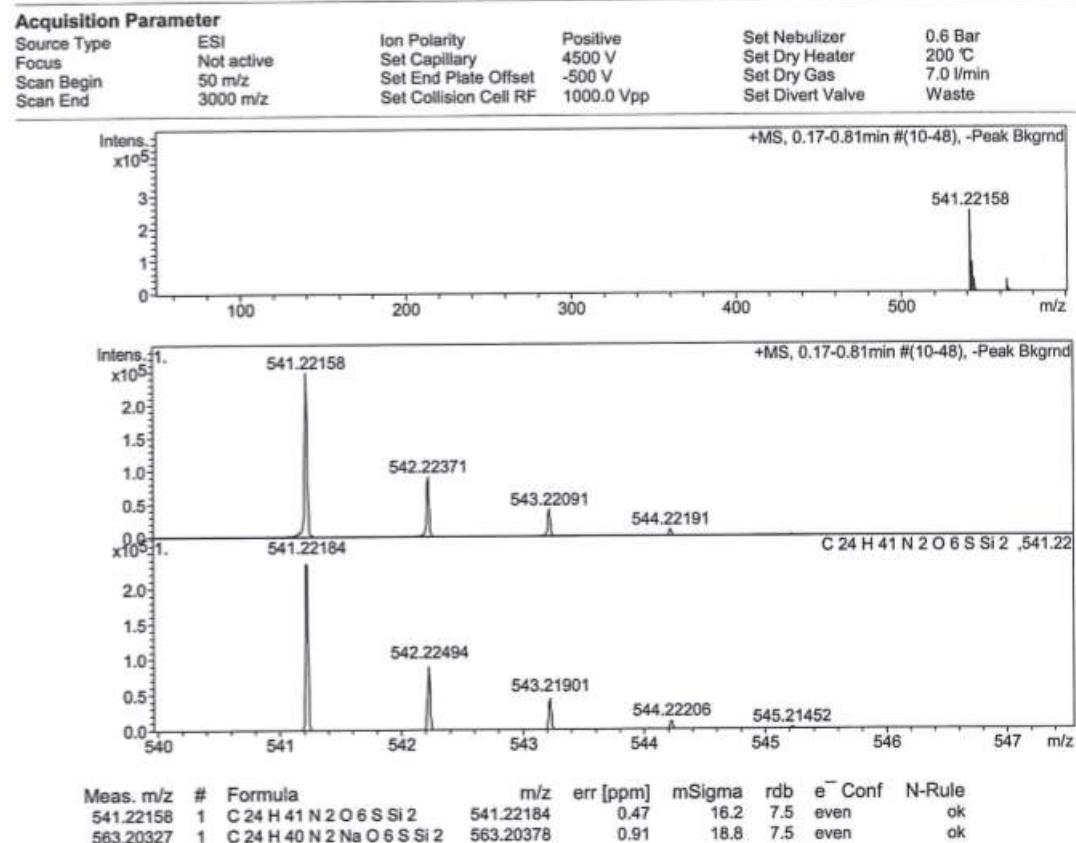
**Figure S29.** 2-[(2-Trifluoromethylphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (**19**).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



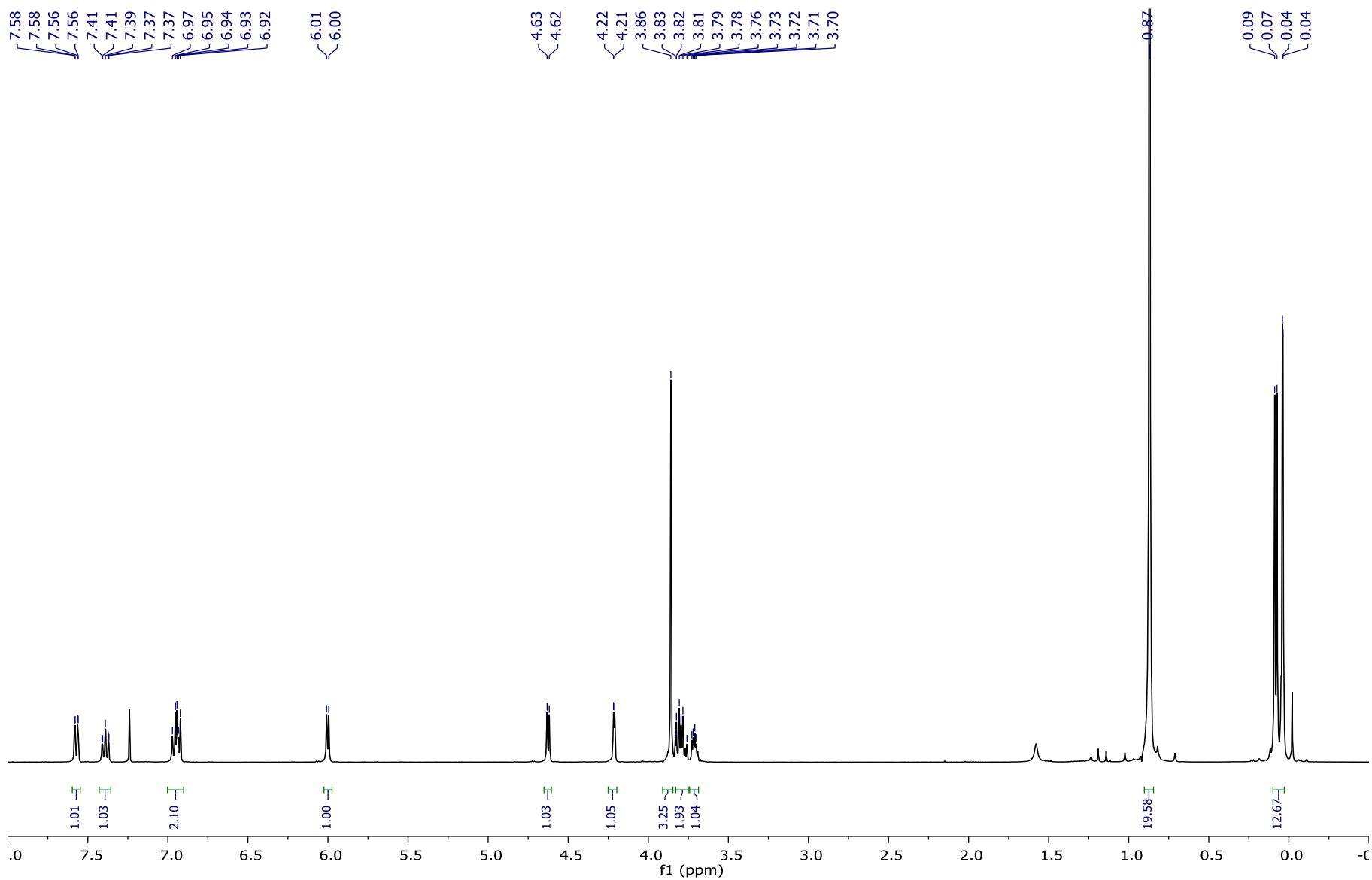
**Figure S30.** 2-[(2-Trifluoromethylphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-arabinofuranoso)-[1,2-*d*]-oxazole (**19**). HRMS (ESI).



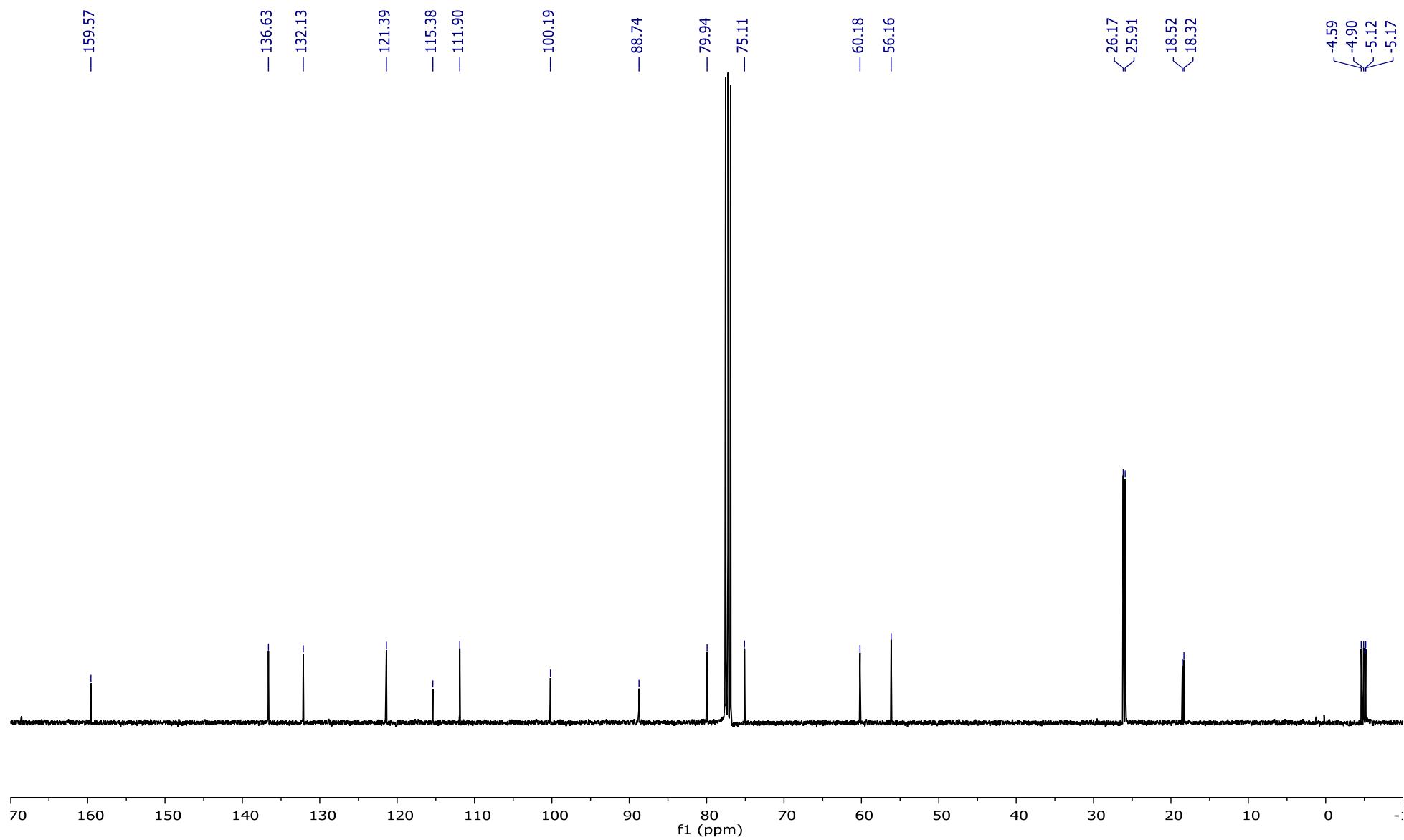
**Figure S31.** 2-[(2-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D- xylofuranoso)-[1,2-*d*]-oxazole (20).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrums.



**Figure S32.** 2-[(2-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D- xylofuranoso)-[1,2-*d*]-oxazole (20). HRMS (ESI).



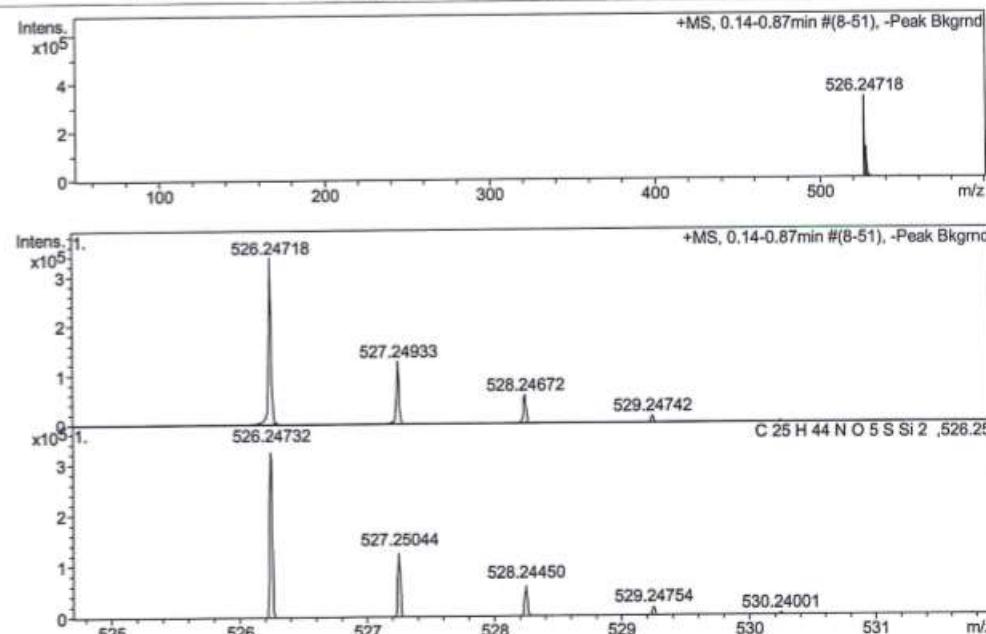
**Figure S33.** 2-[*(2-Methoxyphenyl)sulfanyl*]-4,5-dihydro(3',5'-di-*O-tert*-1',2'-dideoxy- $\beta$ -D- xylofuranoso)-[1,2-*d*]-oxazole (**21**).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum.



**Figure S34.** 2-[(2-Methoxyphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D- xylofuranoso)-[1,2-*d*]-oxazole (21).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum.

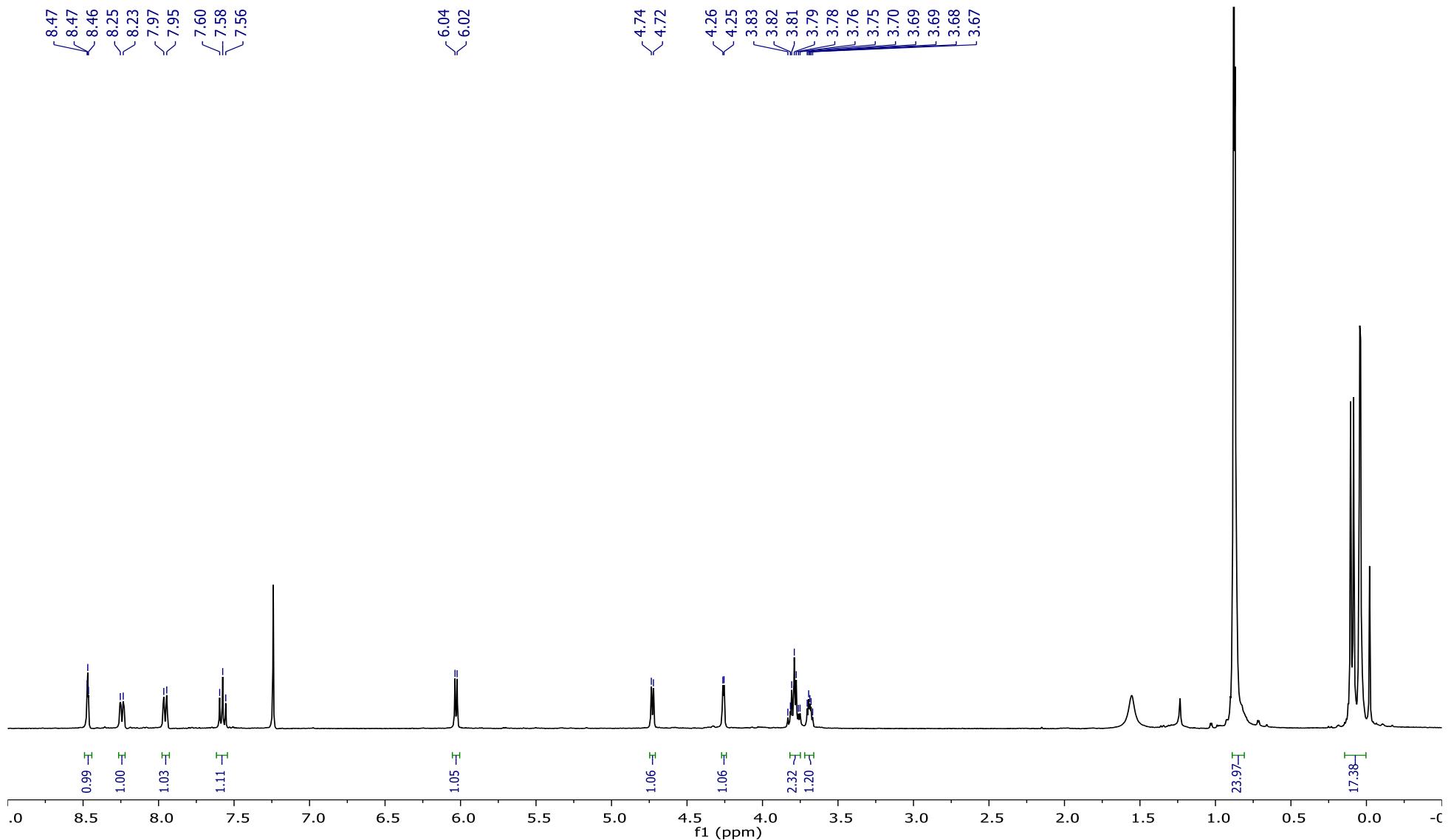
**Acquisition Parameter**

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Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	1000.0 Vpp	Set Divert Valve	Waste

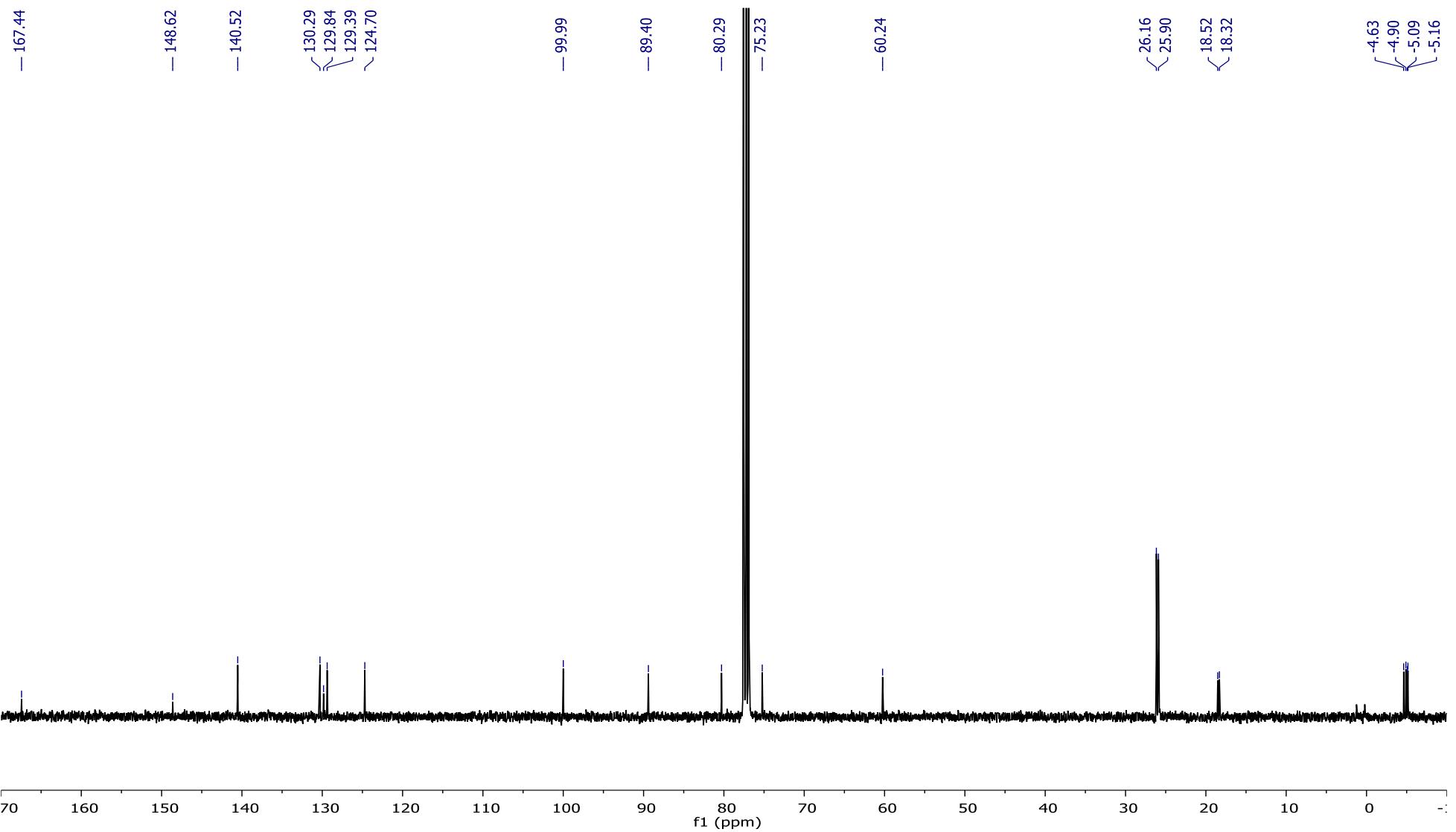


Meas. m/z	#	Formula	m/z	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
526.24718	1	C <sub>25</sub> H <sub>44</sub> N <sub>0</sub> 5S <sub>2</sub> Si <sub>2</sub>	526.24732	0.27	13.0	6.5	even	ok

**Figure S35. 2-[(2-Methoxyphenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-xylofuranoso)-[1,2-*d*]-oxazole (21). HRMS (ESI).**



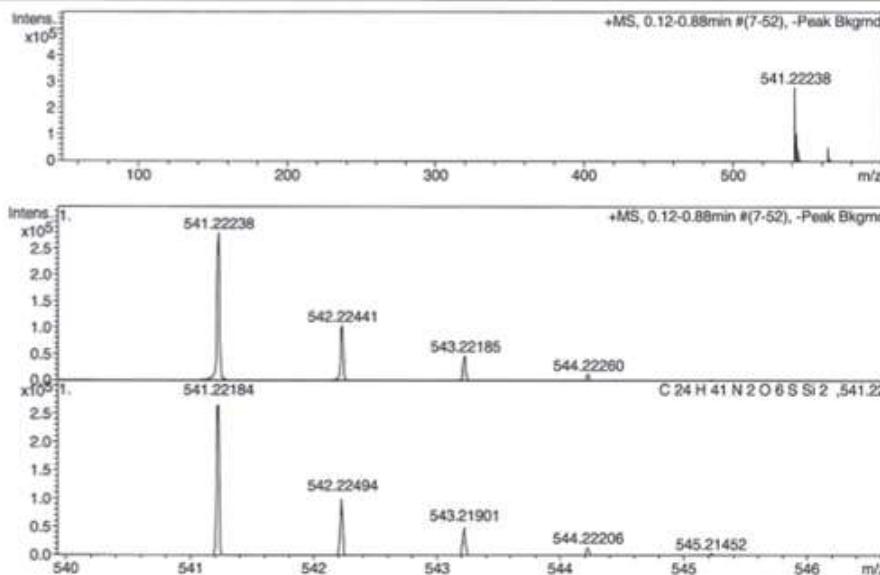
**Figure S36.** 2-[(2-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-ribofuranoso)-[1,2-*d*]-oxazole (22).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum.



**Figure S37.** 2-[(2-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-*O*-*tert*-1',2'-dideoxy- $\beta$ -*D*-ribofuranoso)-[1,2-*d*]-oxazole (22).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum.

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	1000.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
541.22238	1	C <sub>24</sub> H <sub>41</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub> Si <sub>2</sub>	541.22184	-1.00	13.0	7.5	even	ok

**Figure S38. 2-[(2-Nitrophenyl)sulfanyl]-4,5-dihydro(3',5'-di-O-*tert*-1',2'-dideoxy- $\beta$ -D-ribofuranoso)-[1,2-*d*]-oxazole (22). HRMS (ESI).**