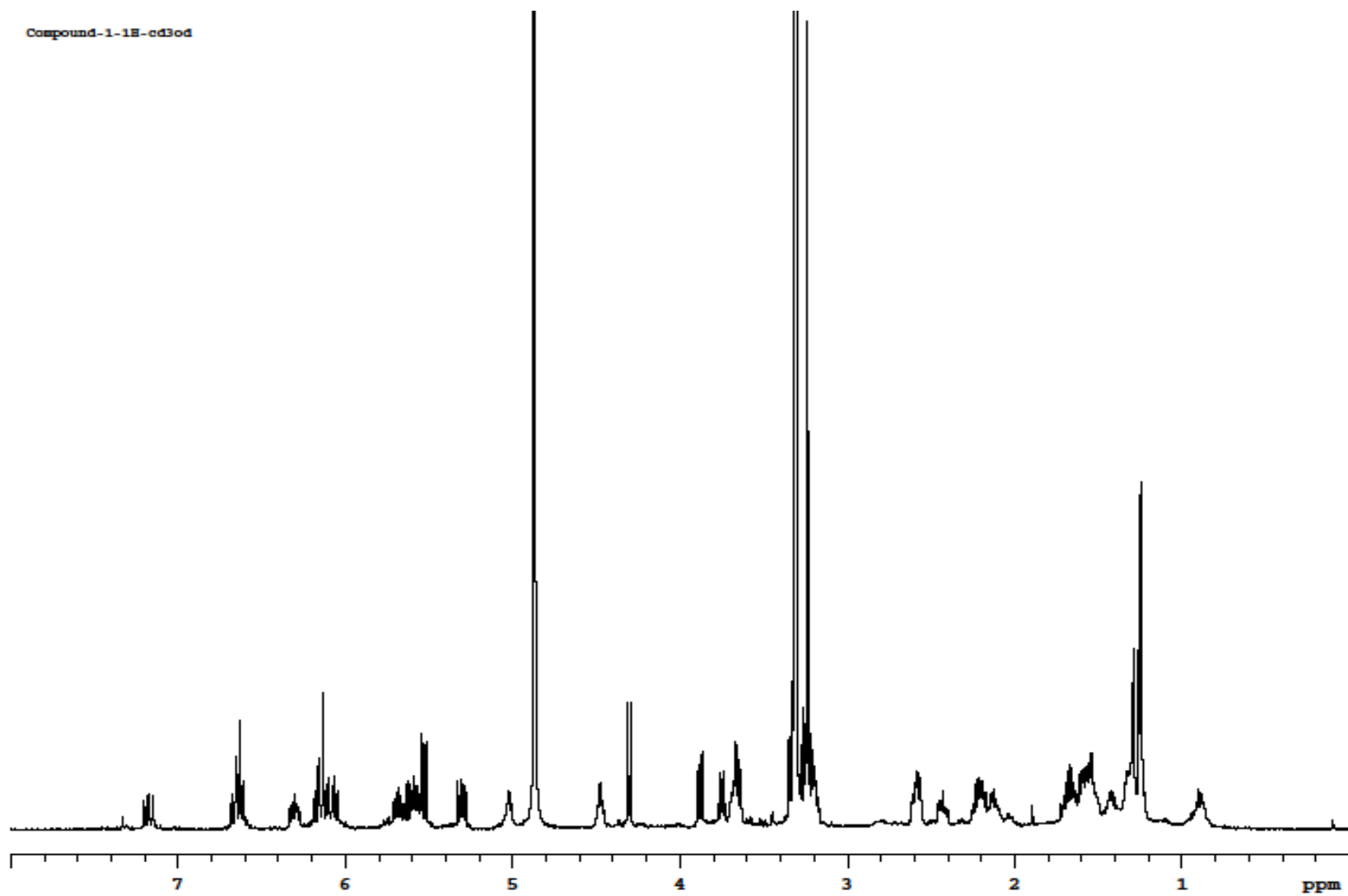


GLYCOSYLATED METHOXY–MACROLACTINS ISOLATED FROM A MARINE SEDIMENT BACTERIUM *BACILLUS SUBTILIS*

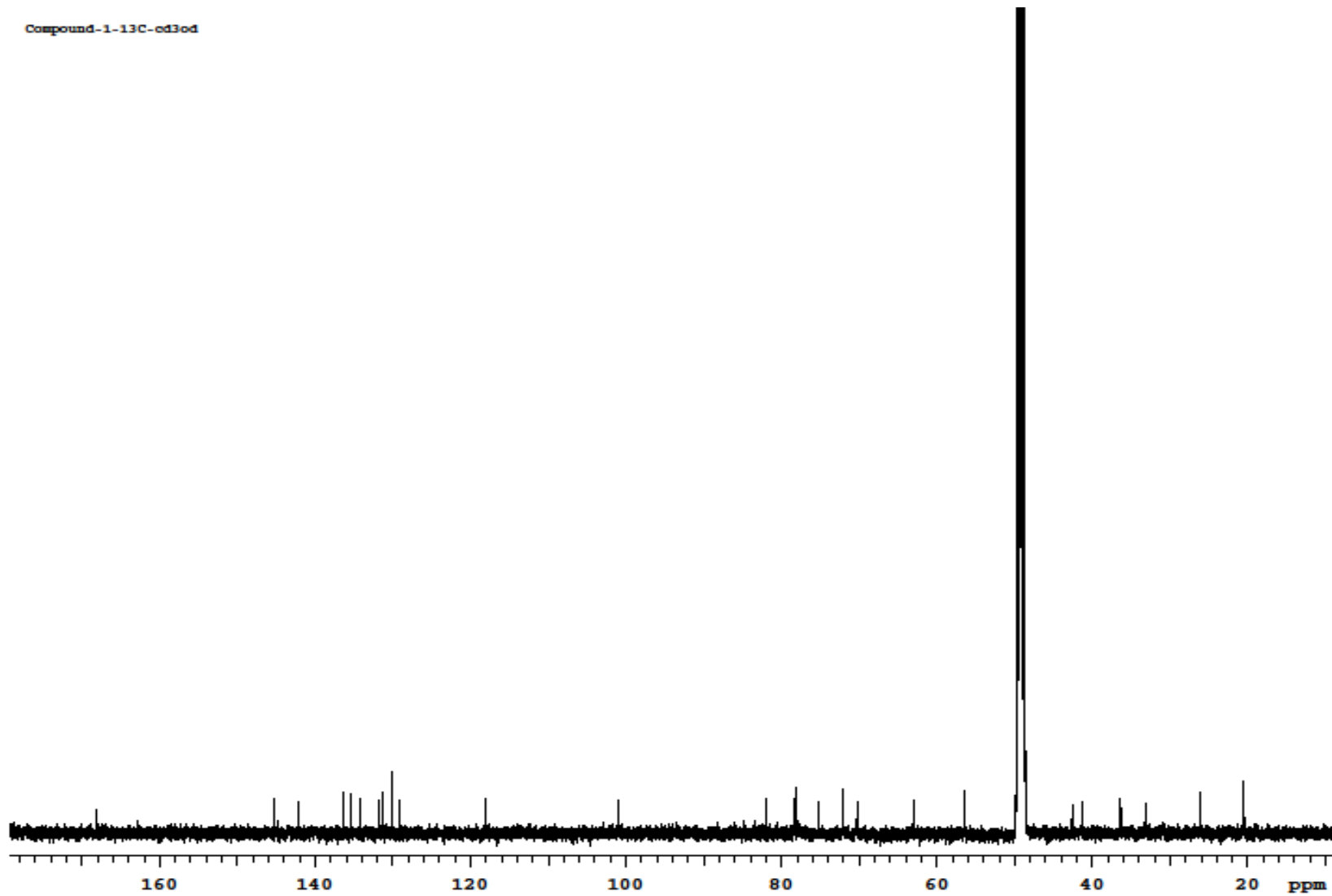
Hee Jae Shin,^{1,2*} Fakir Shahidullah Tareq,^{1,2} Ji Hye Kim,² Min Ah Lee,² Hyi-Seung Lee,² Yeon-Ju Lee,² and Jong-Seok Lee²

^{1,2} University of Science and Technology, 117 Gwahangno, Yuseong-gu, Daejeon, Republic of Korea. ² Marine Natural Products Chemistry Laboratory, Korea Institute of Ocean Science and Technology (KIOST), Ansan, Republic of Korea. E-Mail: shinhj@kiost.ac

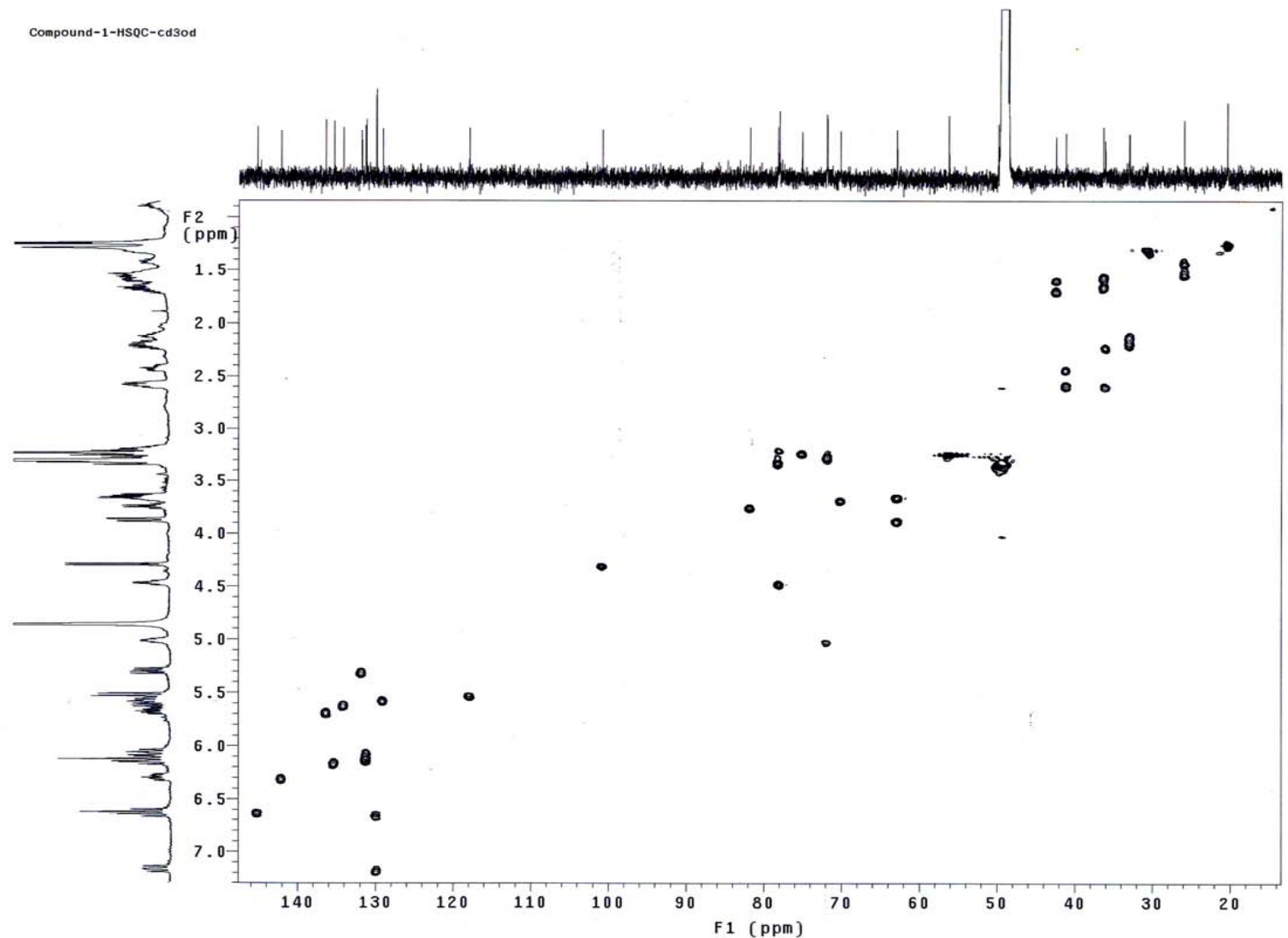
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| SI 2. | ¹³ C NMR spectrum of compound 1 in CD ₃ OD at 125 MHz..... | 4 |
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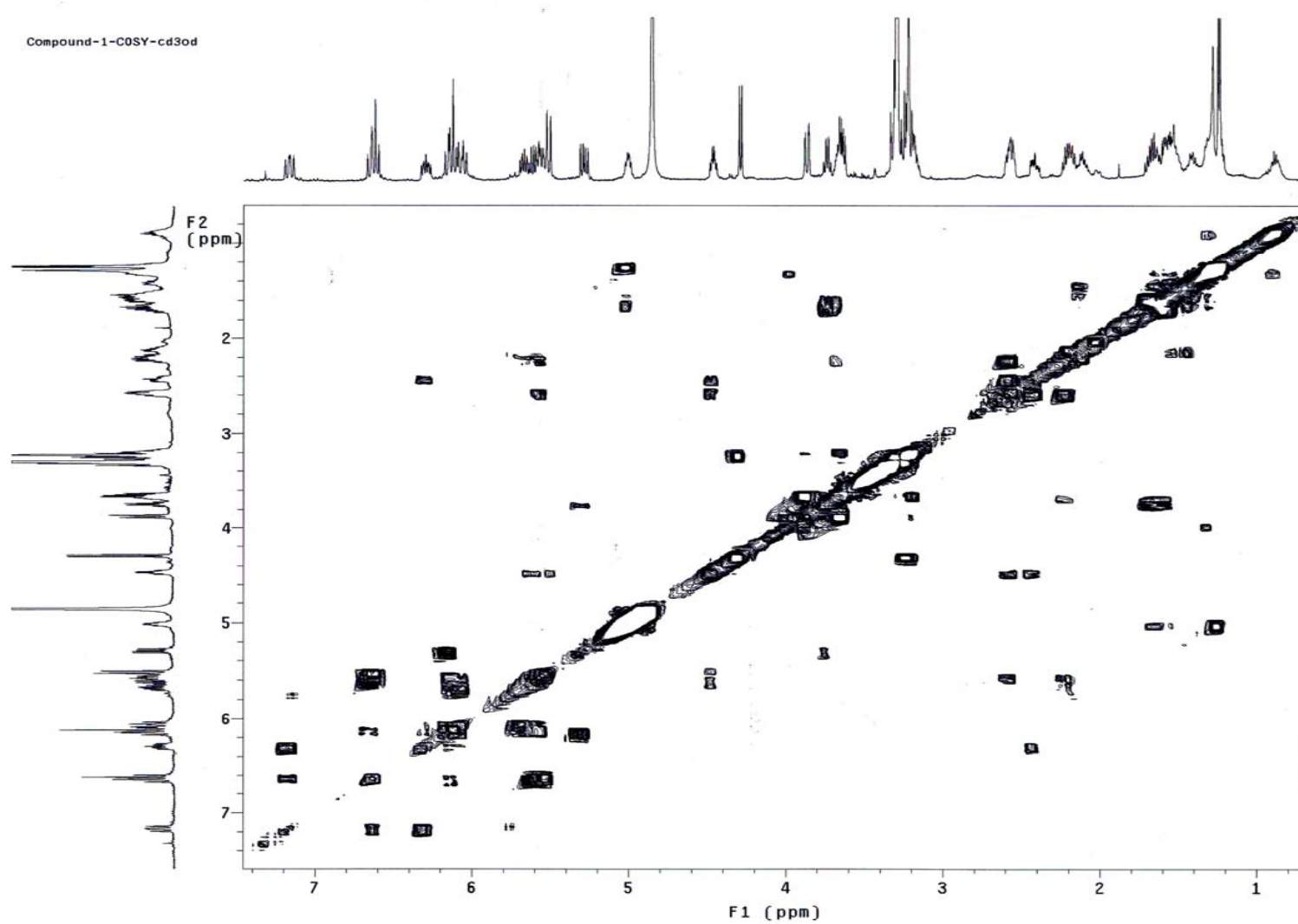


SI. 1. ^1H NMR spectrum of compound **1** in CD_3OD at 500 MHz.

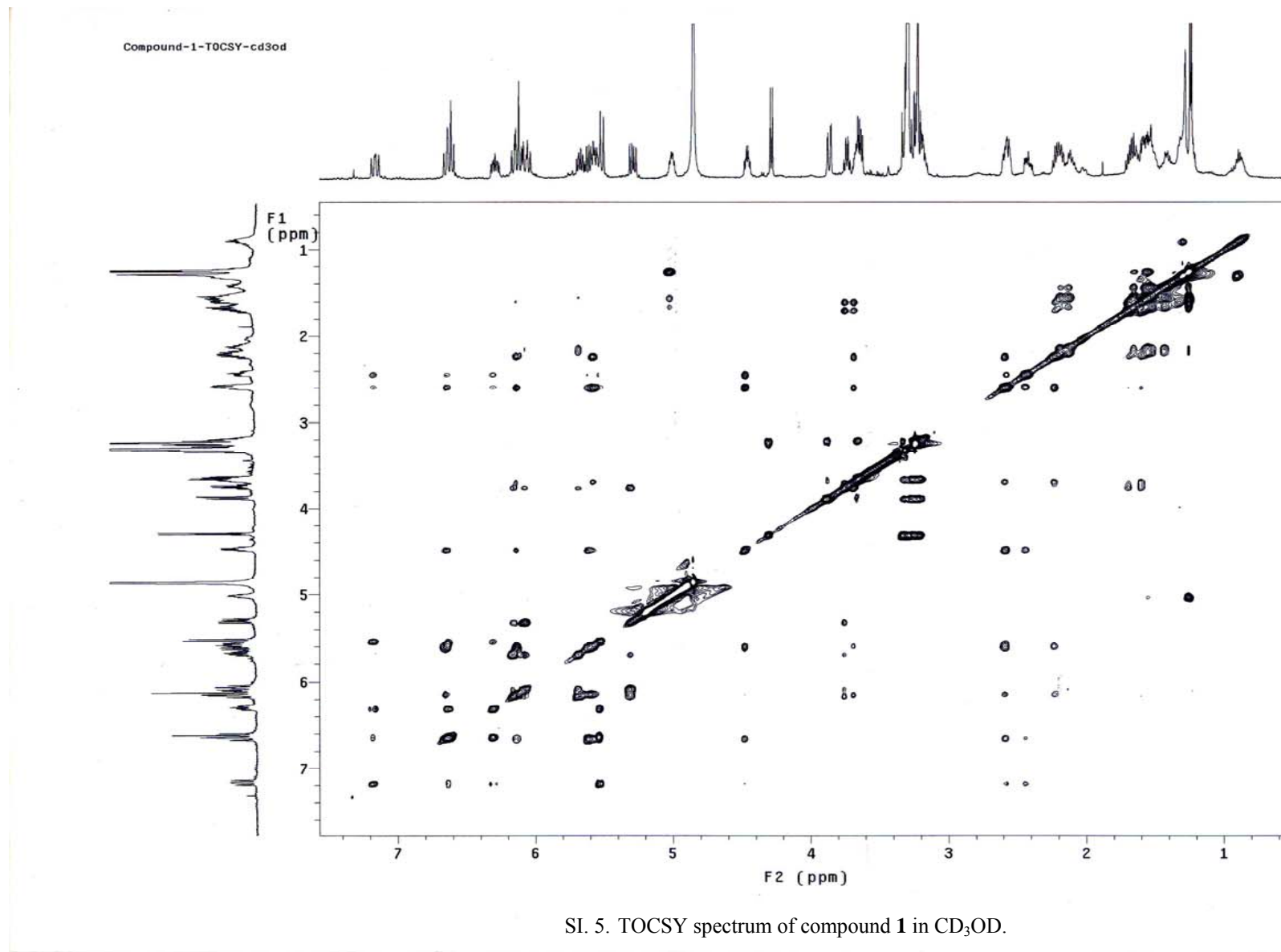


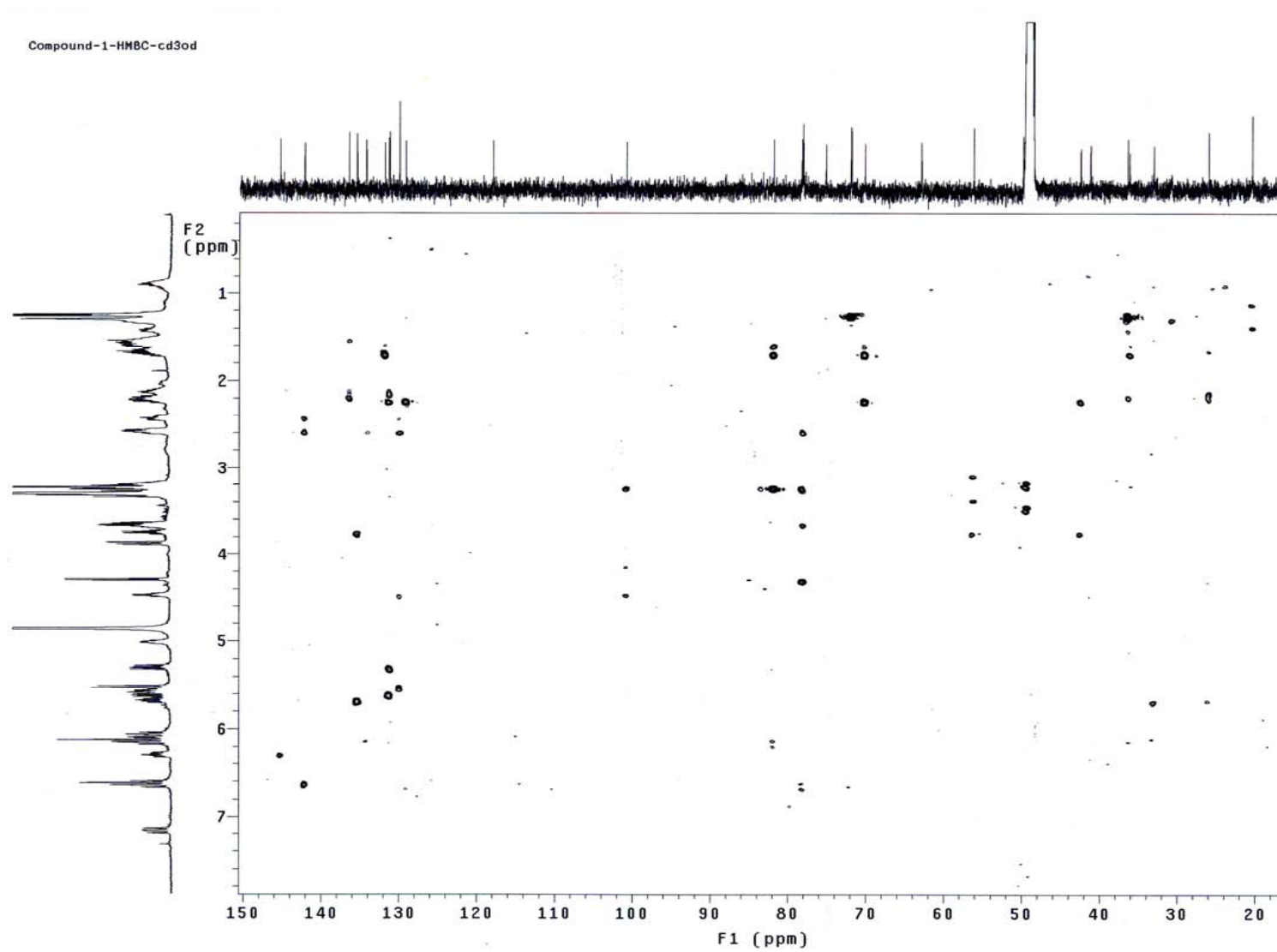
SI. 2. ¹³C NMR spectrum of compound **1** in CD₃OD at 125 MHz.

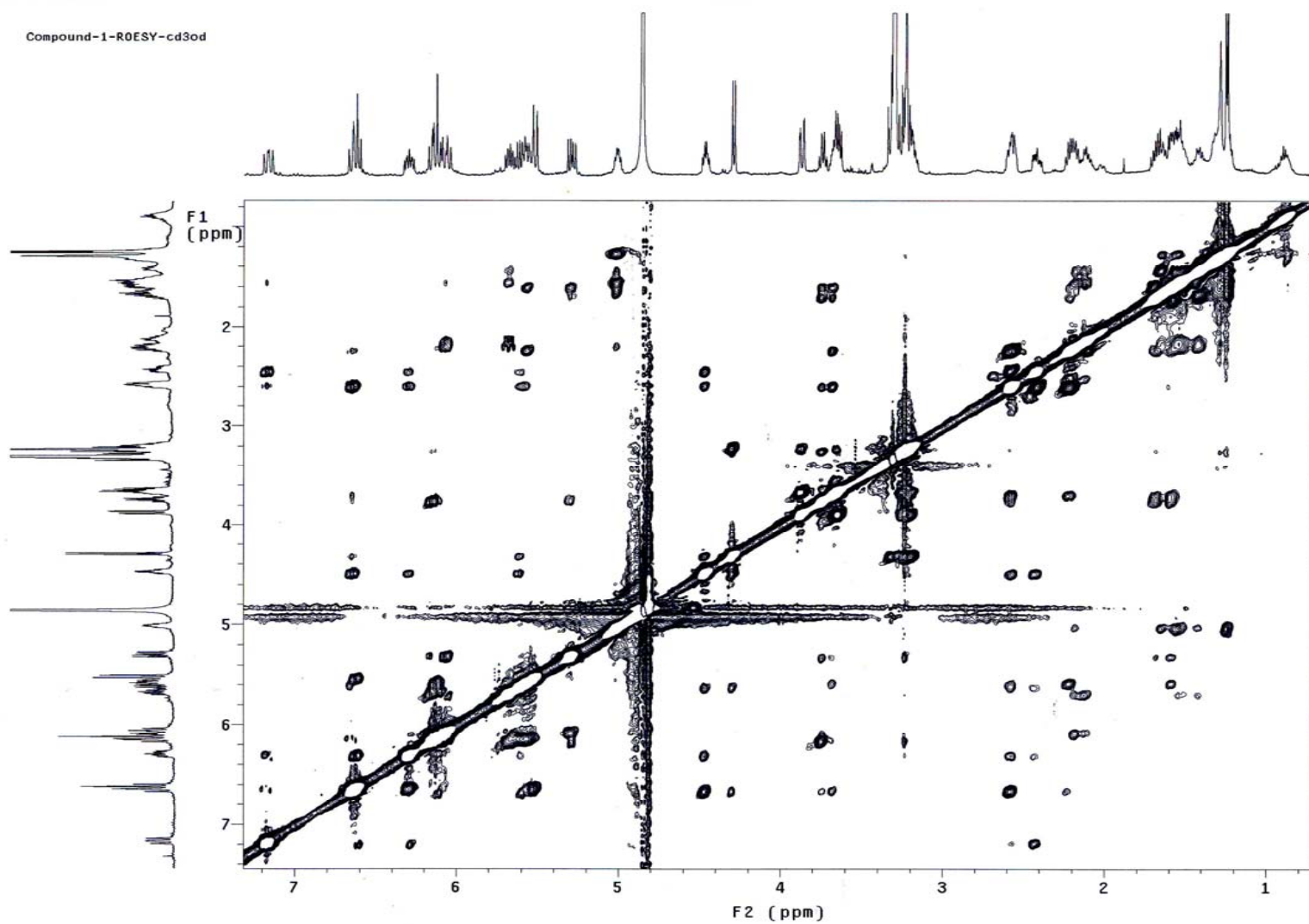
SI. 3. HSQC spectrum of compound **1** in CD_3OD .



SI. 4. COSY spectrum of compound **1** in CD₃OD.



SI. 6. HMBC spectrum of compound **1** in CD₃OD.



SI. 7. ROESY spectrum of compound 1 in CD₃OD.

Formula Predictor Report - 109GGC020_2_60%M_ssf3_rp2.lcd

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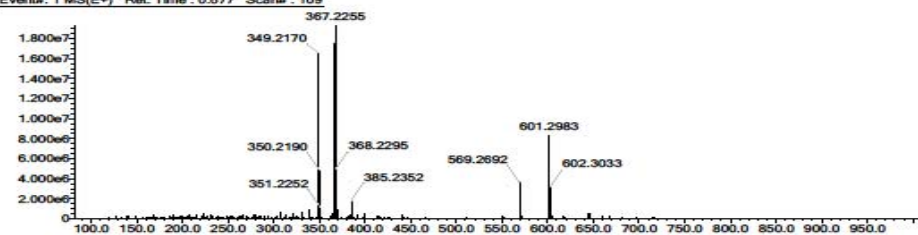
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| C | 4 | 0 | 150 | | | | | |
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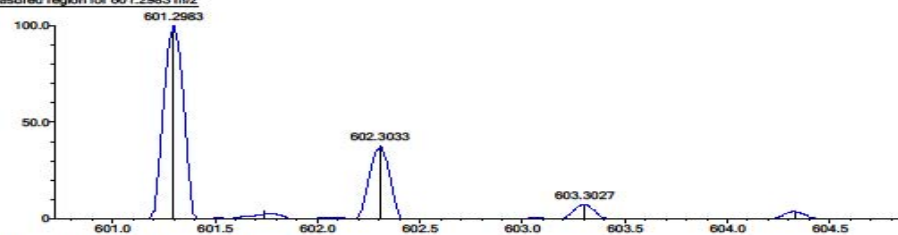
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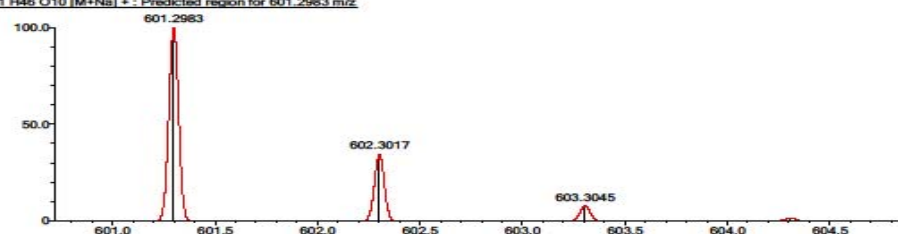
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Measured region for 601.2983 m/z

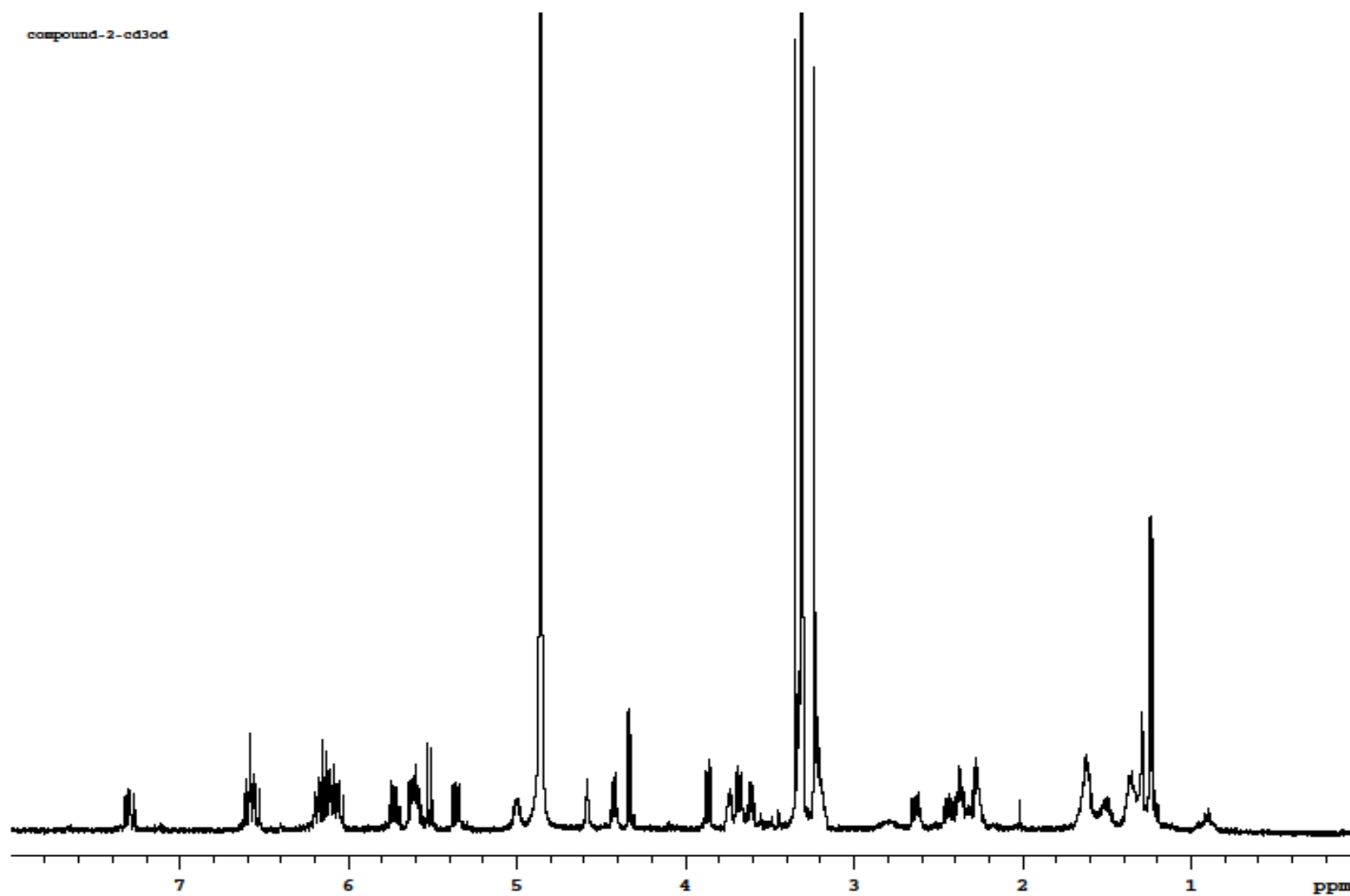


C31 H46 O10 [M+Na]+ : Predicted region for 601.2983 m/z



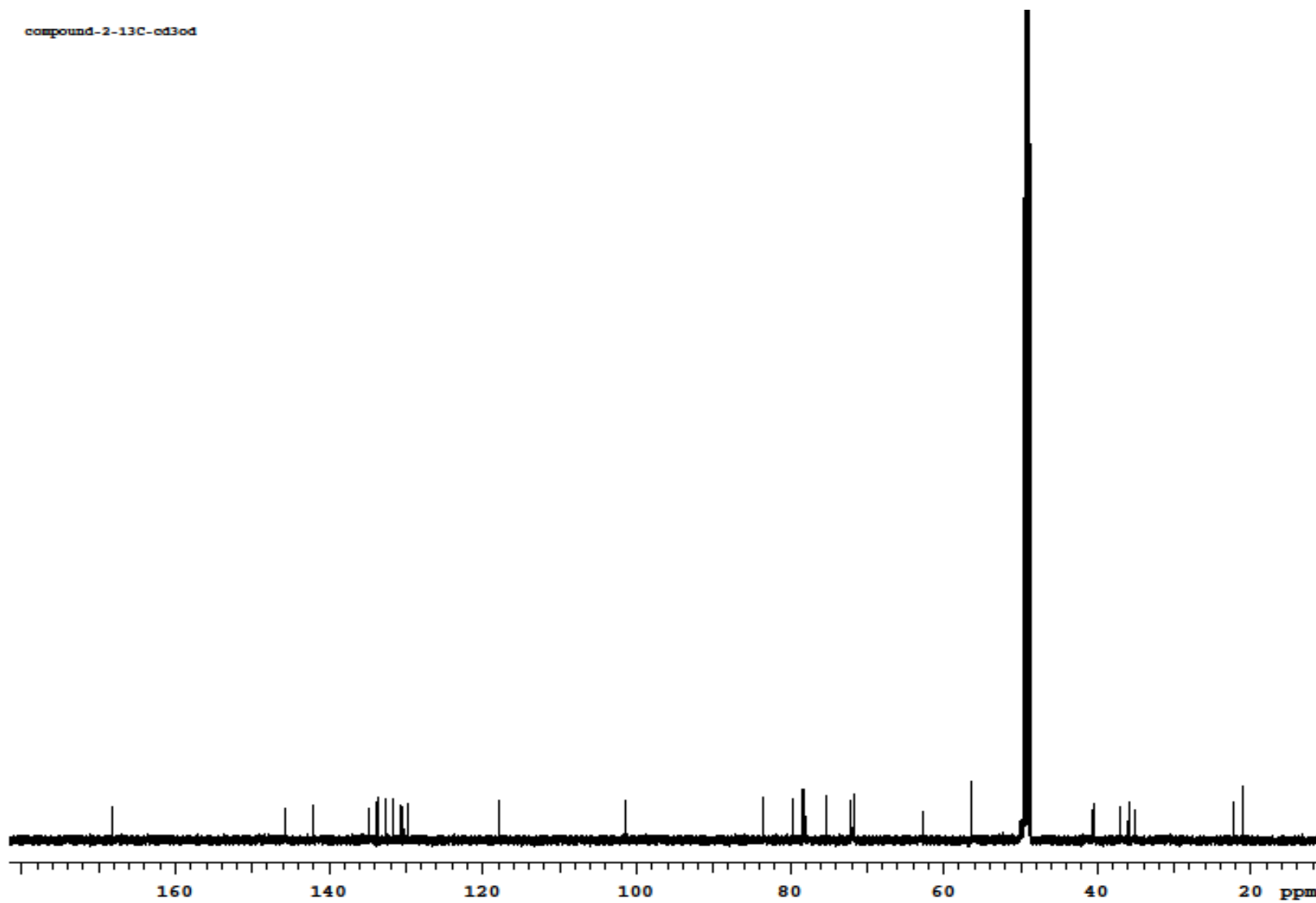
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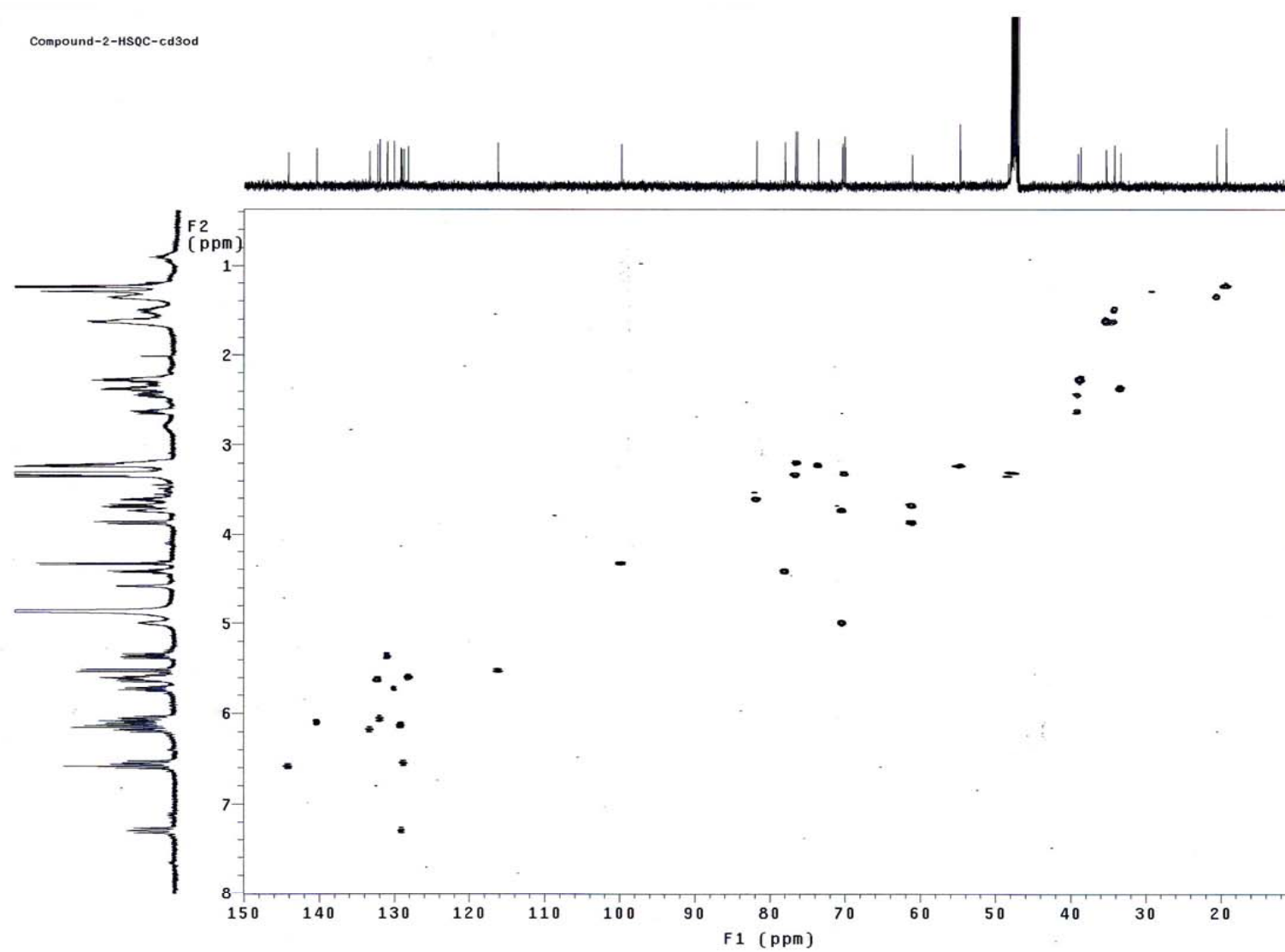
SI. 8. HRESIMS spectrum of compound 1 in CD₃OD.

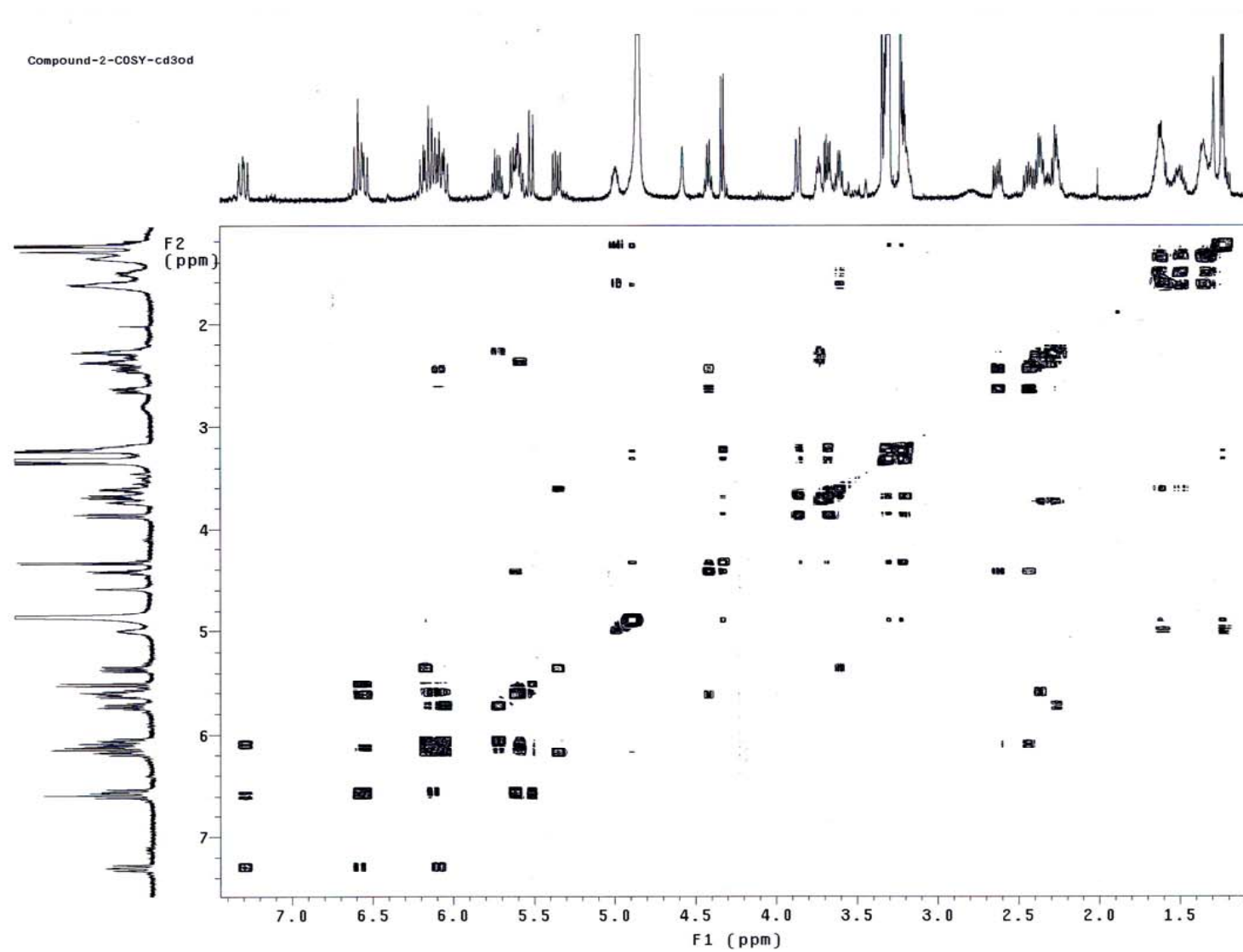


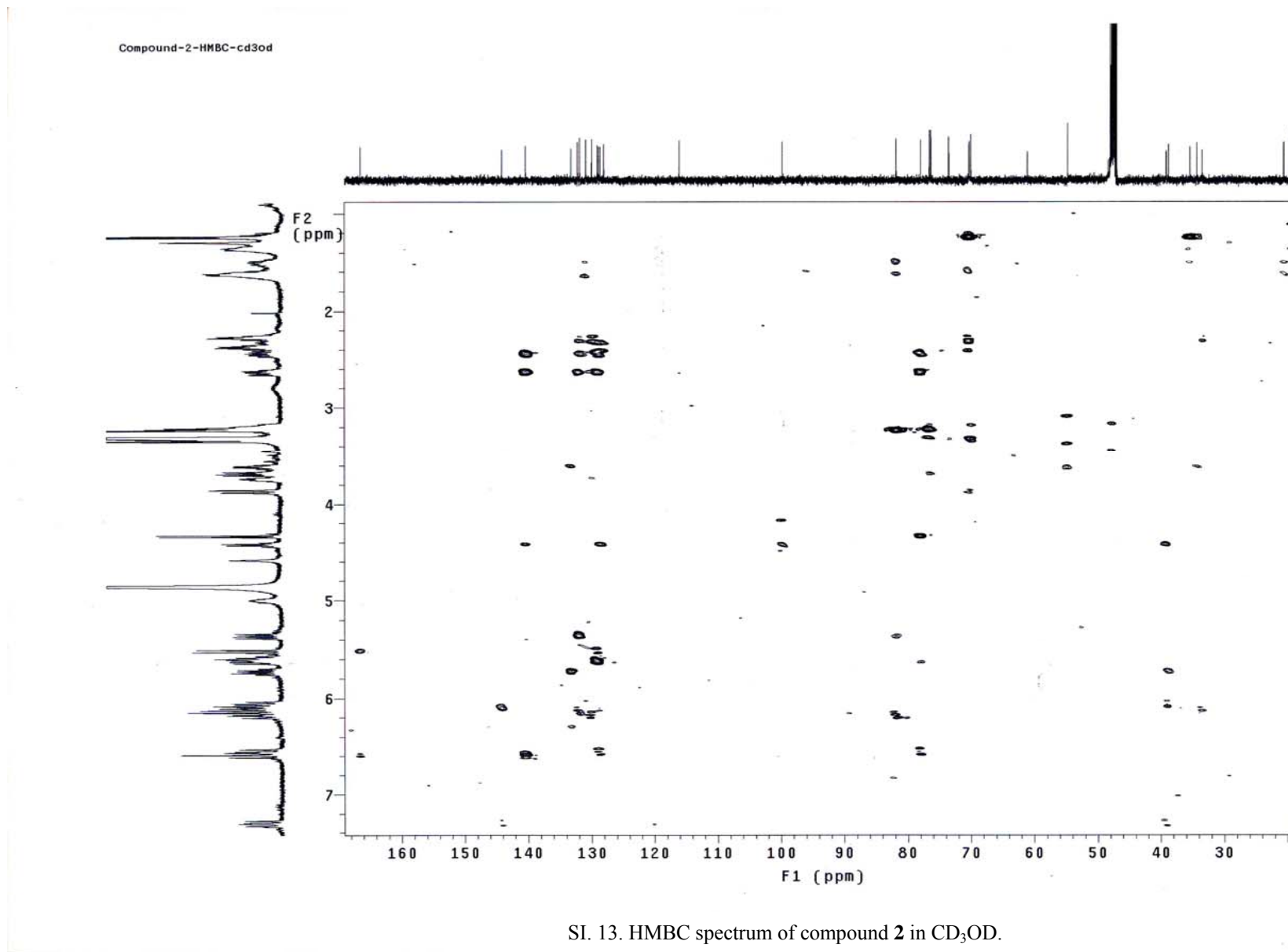
SI. 9. ^1H NMR spectrum of compound 2 in CD_3OD at 500 MHz.

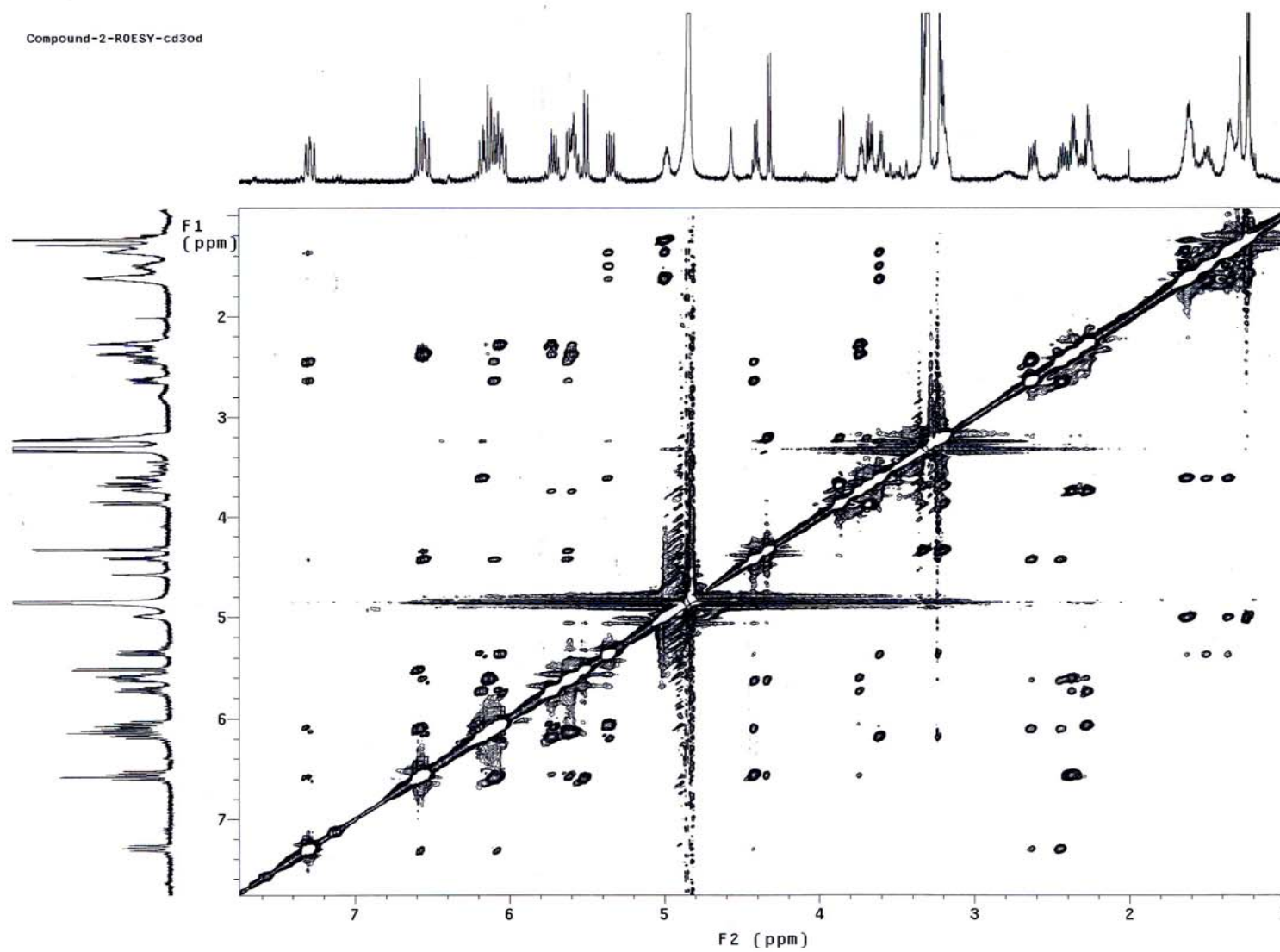
compound-2-13C-cd3od

SI. 10. ^{13}C NMR spectrum of compound 2 in CD_3OD at 125 MHz.

SI. 11.HSQC spectrum of compound **2** in CD₃OD.

SI. 12. COSY spectrum of compound **2** in CD₃OD.



SI. 14. ROESY spectrum of compound 2 in CD₃OD.

Formula Predictor Report - 109GGC020_2_60%M_np1.kcd

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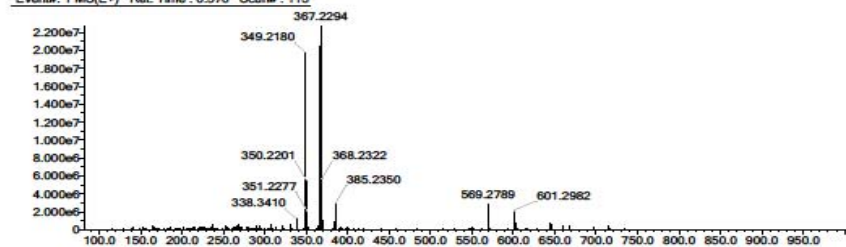
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| C | 4 | 0 | 150 | | | | | |
| N | 3 | 0 | 0 | | | | | |

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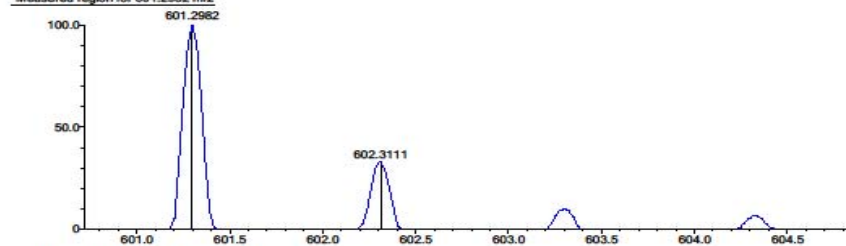
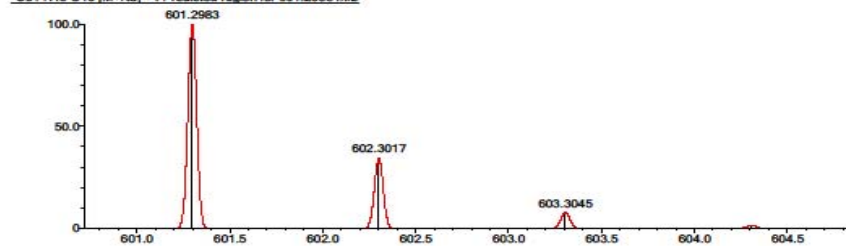
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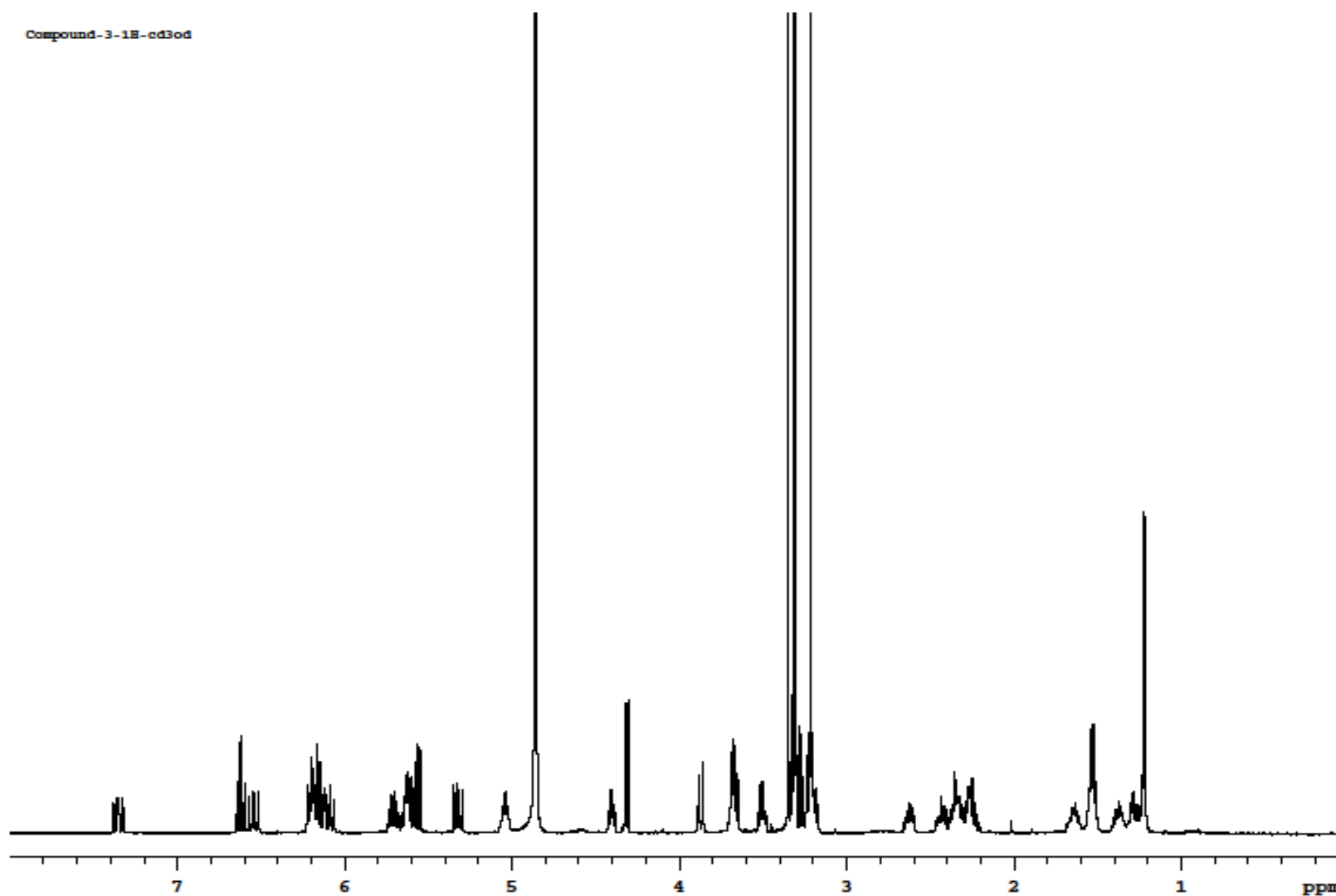


Measured region for 601.2982 m/z

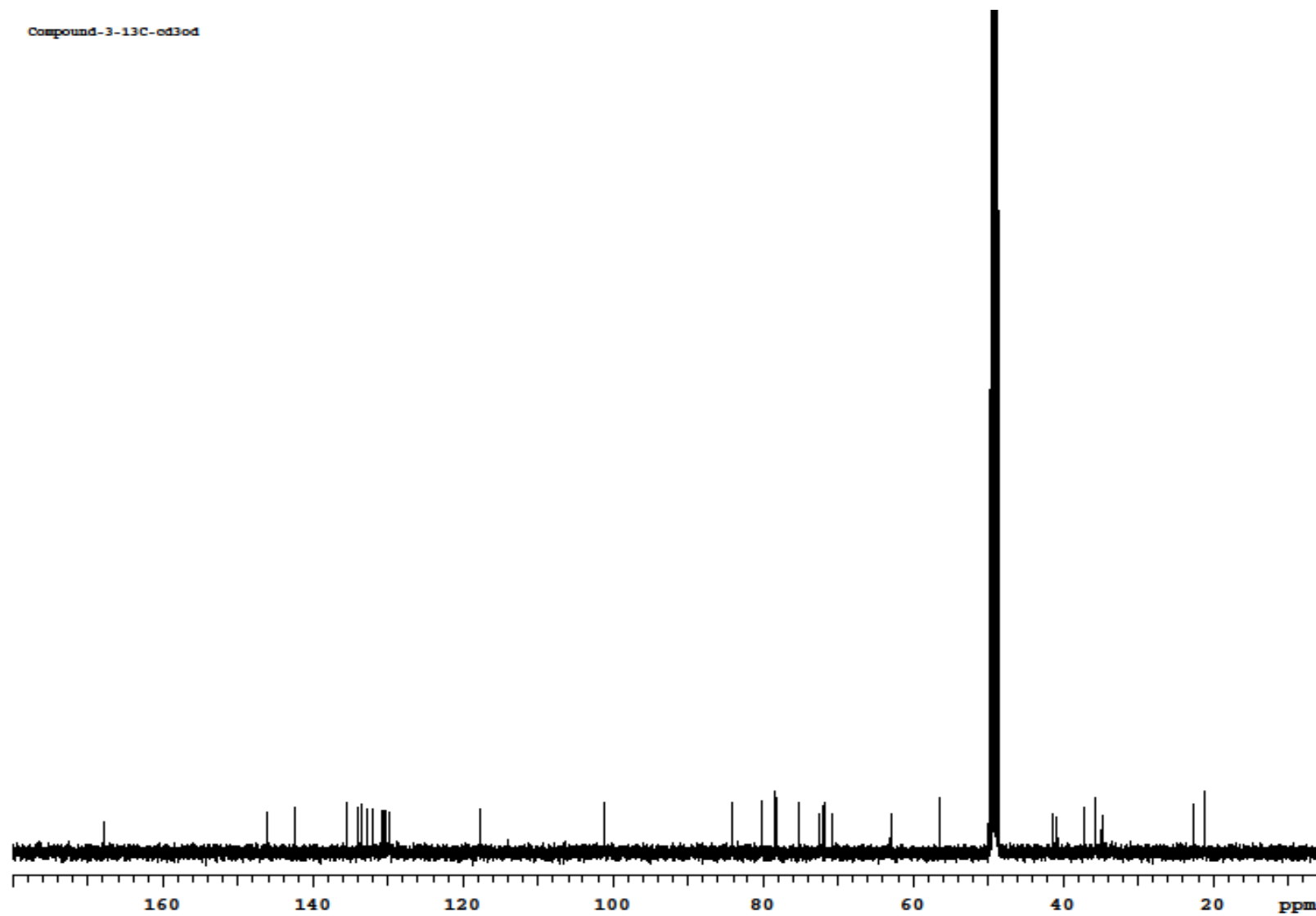
C31 H46 O10 [M+Na]⁺ : Predicted region for 601.2983 m/z

| Rank | Score | Formula (M) | Ion | Mass. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|------|-------|-------------|---------------------|-----------|-----------|-----------|-----------|-------|-----|
| 1 | 65.20 | C31 H46 O10 | [M+Na] ⁺ | 601.2982 | 601.2983 | -0.1 | -0.17 | 65.20 | 9.0 |

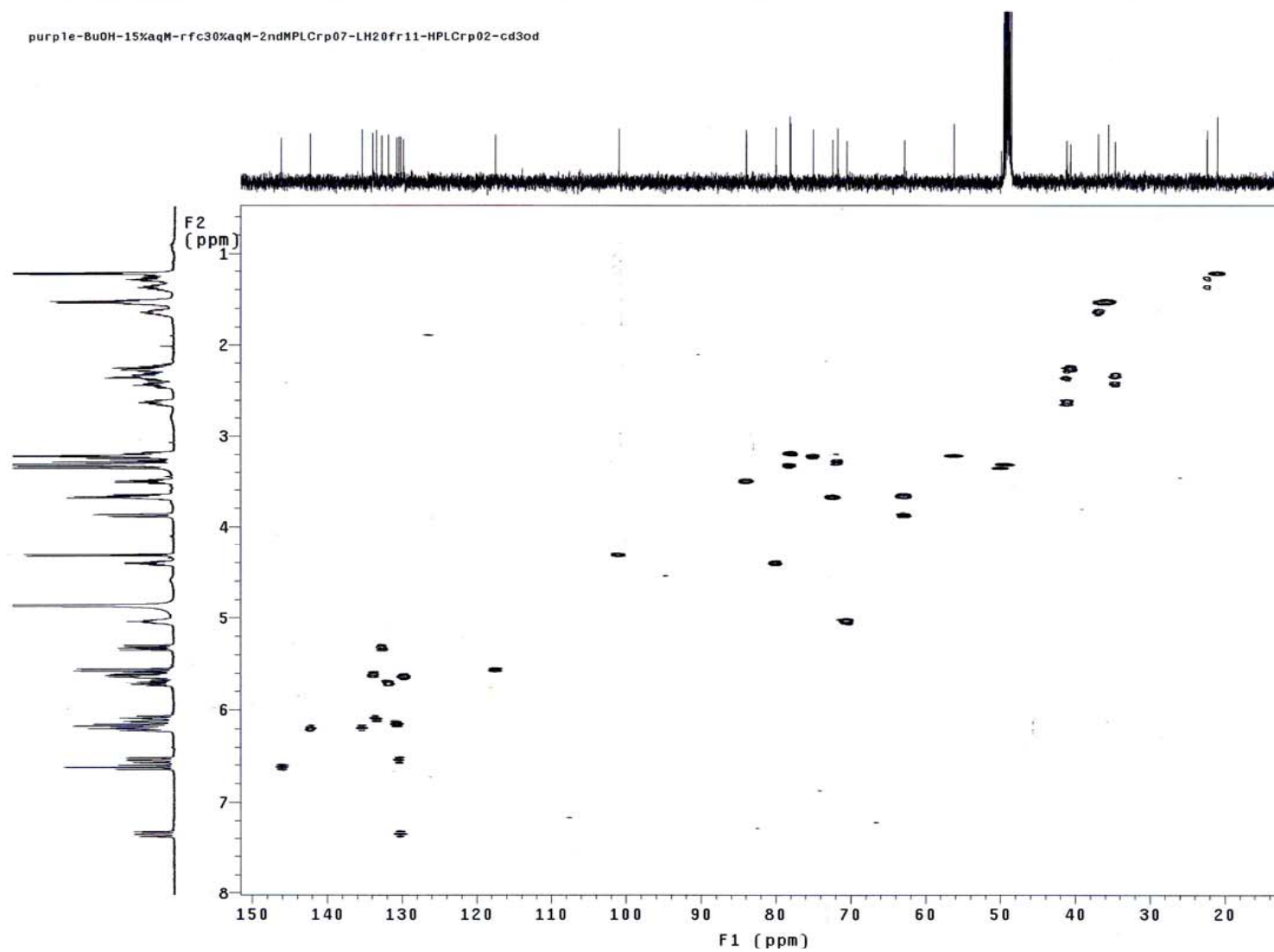
SI. 15. HRESIMS spectrum of compound 2.



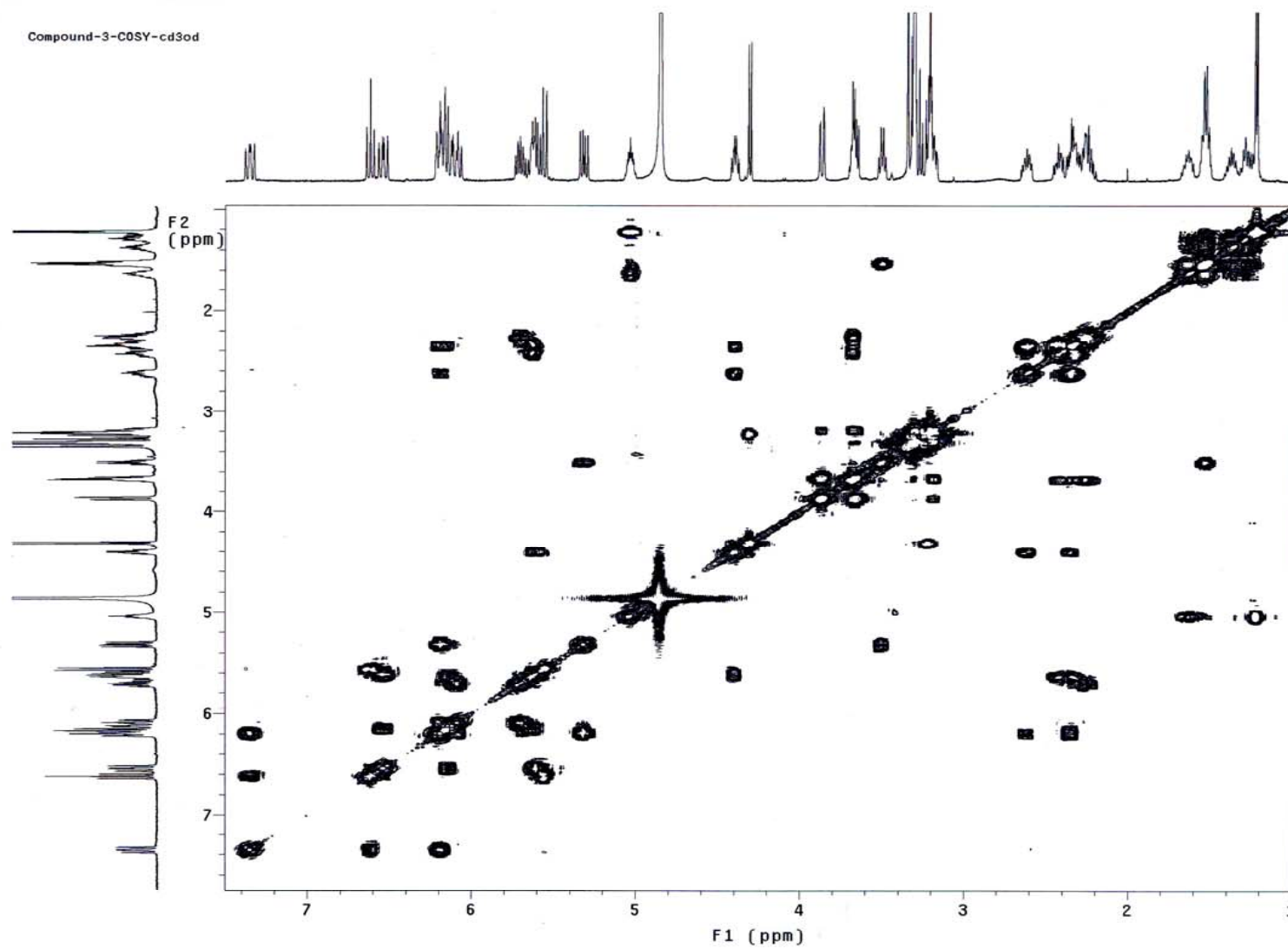
SI. 16. ^1H NMR spectrum of compound **3** in CD_3OD at 500 MHz.

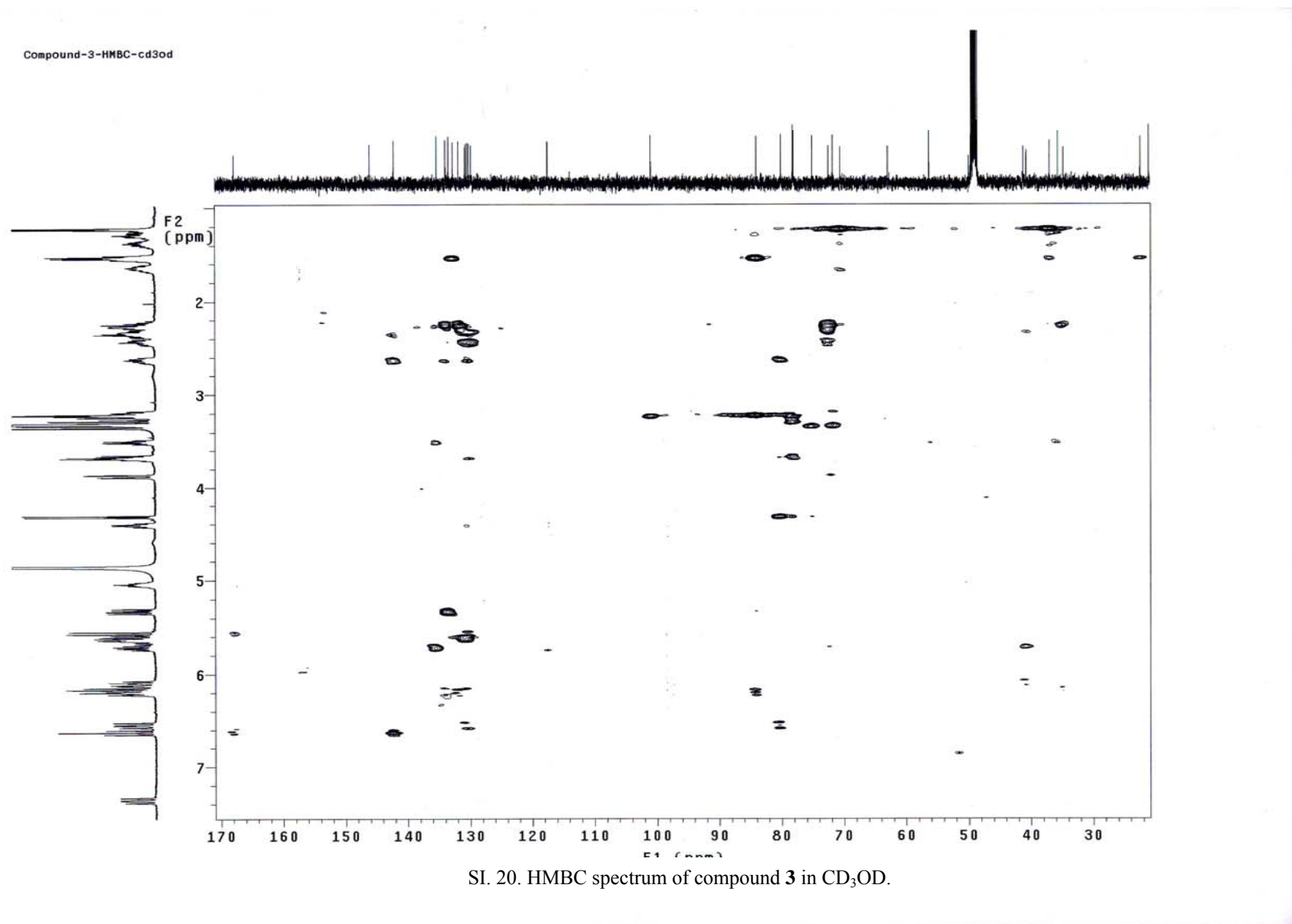
Compound-3-¹³C-ed3odSI. 17. ¹³C NMR spectrum of compound 3 in CD₃OD at 125 MHz.

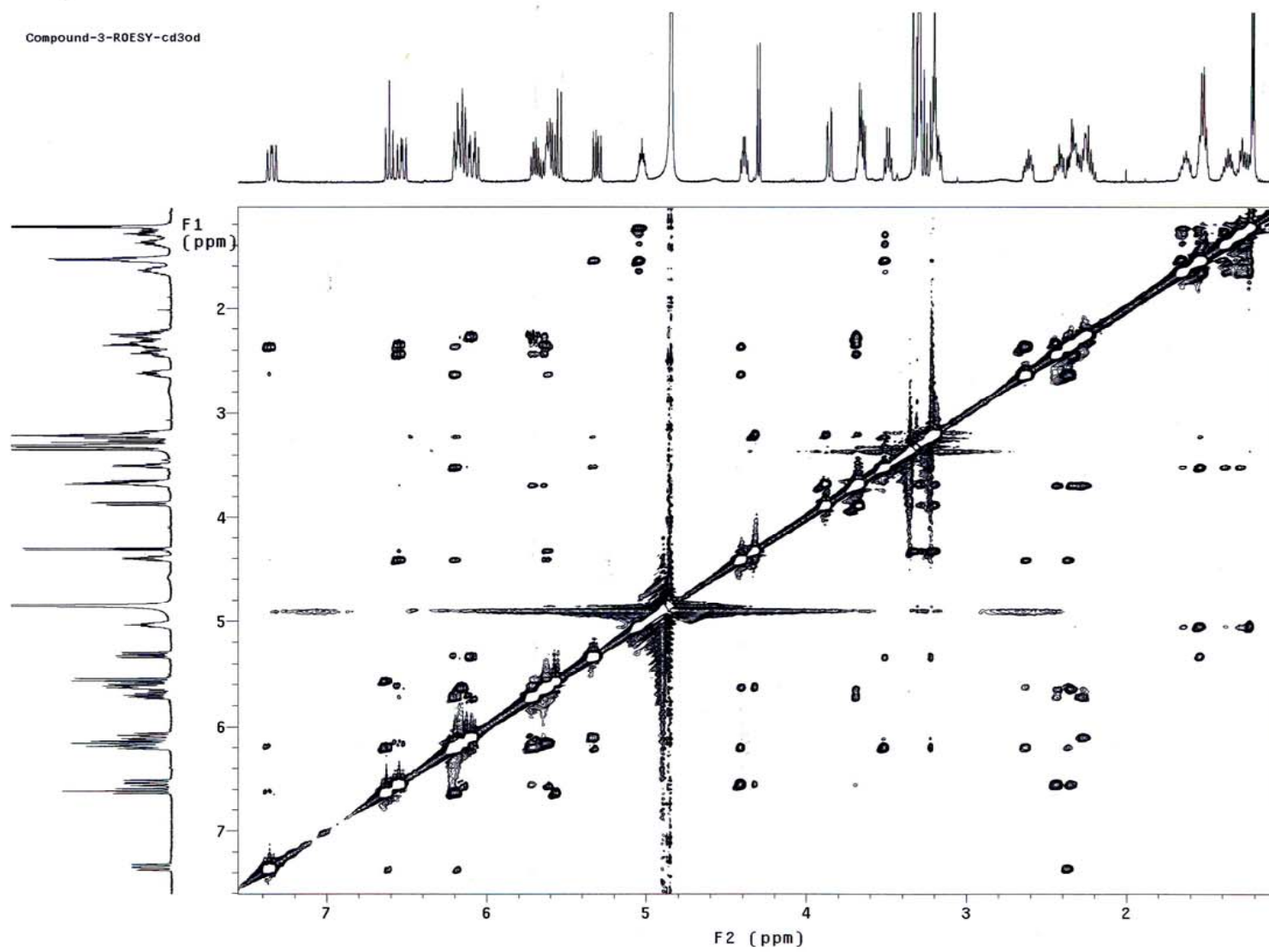
purple-BuOH-15%aqM-rfc30%aqM-2ndMPLCrp07-LH20fr11-HPLCrp02-cd3od



SI. 18. HSQC spectrum of compound 3 in CD_3OD .

SI. 19. COSY spectrum of compound **3** in CD₃OD.



SI. 21. ROESY spectrum of compound 3 in CD₃OD.

Formula Predictor Report - 109GGC020_2_60%M_np2.lcd

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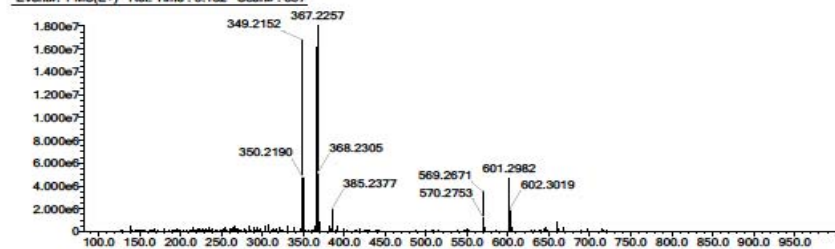
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|------|-----|-----|-----|------|-----|-----|-----|------------|
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| C | 4 | 0 | 150 | | | | | |
| N | 3 | 0 | 0 | | | | | |

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 Max Isotopes: all
 MSn Iso RI (%): 75.00

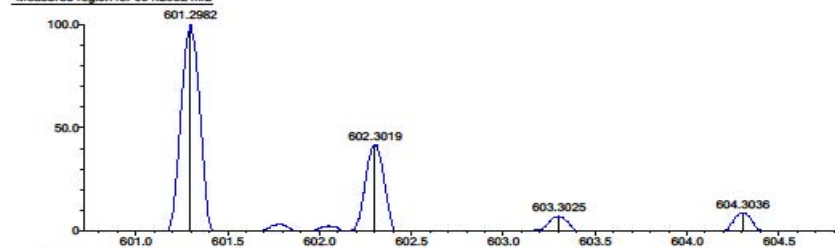
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Electron Ions: both
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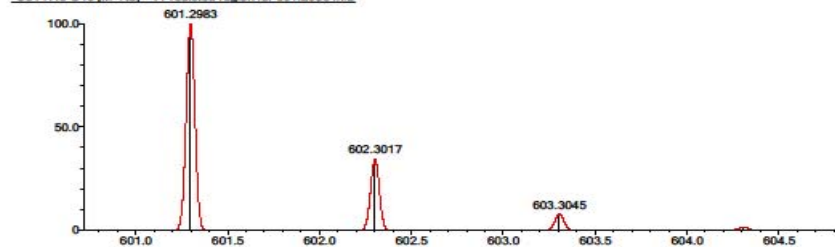
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Measured region for 601.2982 m/z



C31 H46 O10 [M+Na] + - Predicted region for 601.2983 m/z



| Rank | Score | Formula (M) | Ion | Meas. m/z | Pred. m/z | Df. (mDa) | Df. (ppm) | Iso | DBE |
|------|-------|-------------|----------|-----------|-----------|-----------|-----------|-------|-----|
| 1 | 67.46 | C31 H46 O10 | [M+Na] + | 601.2982 | 601.2983 | -0.1 | -0.17 | 67.46 | 9.0 |

SI. 22. HRESIMS spectrum of compound 3.

SI. 23. 2.8.1a. Spectroscopic data of (*S*)-MTPA esters (**1a**) of **1**

1a (0.5 mg): White, amorphous solid; $^1\text{H NMR}$ (CD_3OD): δ_{H} 5.350 (d, $J = 11.2$, H-2), 6.521 (t, $J = 11.3$, H-3), 7.162 (dd, $J = 15.0, 11.3$, H-4), 6.581 (m, H-5), 2.25 (m, H-6a), 2.42 (m, H-6b), 5.52 (m, H-7), 5.723 (m, H-8), 6.481 (m, H-9), 6.367 (m, H-10), 6.215 (m, H-11), 2.125 (m, H-12a), 2.235 (m, H-12a), 5.185 (m, H-13), 1.56 (m, H-14a), 1.45 (m, H-14b), 5.197 (m, H-15), 5.987 (m, H-16), 6.092 (dd, $J = 10.0, 15.0$, H-17), 6.565 (m, H-18), 5.014 (m), H-19), 3.36 (OCH_3 , s), 3.45 (OCH_3 , s), 3.50 (OCH_3 , s), 7.32–7.62 (m); ESIMS m/z 871.42 [$\text{M} + \text{Na}$] $^+$.

2.8.1b. Spectroscopic data of (*R*)-MTPA esters (**1b**) of **1**

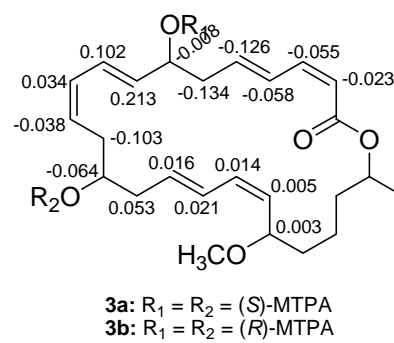
1b (0.4 mg): Amorphous solid; $^1\text{H NMR}$ (CD_3OD) δ_{H} 5.375 (d, $J = 11.0$, H-2), 6.585 (t, $J = 11.0$, H-3), 7.240 (dd, $J = 15.5, 11.0$, H-4), 6.677 (m, H-5), 2.374 (m, H-6a), 2.565 (m, H-6b), 5.512 (m, H-7), 5.609 (m, H-8), 6.36 6.419 (m, H-9), 6.333 (m, H-10), 6.247 (m, H-11), 2.212 (m, H-12a), 2.368 (m, H-12b), 5.269 (m, H-13), 1.549 (m, H-14), 5.191 (m, H-15), 5.956 (m, H-16), 6.078 (m, H-17), 6.559 (m, H-18), 5.012 (m, H-19), 3.37 (OCH_3 , s), 3.47 (OCH_3 , s), 3.52 (OCH_3 , s), 7.35–7.60 (m); ESIMS m/z 871.32 [$\text{M} + \text{Na}$] $^+$.

2.8.2a Spectroscopic data of (*R*)-MTPA esters (**3a**) of **3**

3a (0.6 mg): Amorphous solid; $^1\text{H NMR}$ (CD_3OD) δ_{H} 5.250 (d, $J = 11.5$, H-2), 6.423 (t, $J = 11.0$, H-3), 7.062 (m, H-4), 6.631 (m, H-5), 2.151 (m, H-6), 5.621 (m, H-7), 5.422 (m, H-8), 6.271 (m, H-9), 6.167 (m, H-10), 6.016 (m, H-11), 2.434 (m, H-12), 4.585 (m, H-13), 1.533 (m, H-14), 5.857 (m, H-15), 6.073 (m, H-16), 6.112 (dd, $J = 15.0, 10.0$, H-17), 6.345 (m, H-18), 3.273 (s, H-19), 3.45 (OCH_3 , s), 3.26 (OCH_3 , s), 7.25–7.08 (m), ESIMS m/z 871.25 [$\text{M} + \text{Na}$] $^+$.

2.8.2b Spectroscopic data of (*R*)-MTPA esters (**3b**) of **3**

3b (0.7 mg): Amorphous solid; $^1\text{H NMR}$ (CD_3OD) δ_{H} 5.273 (d, $J = 11.0$, H-2), 6.478 (t, $J = 11.0$, H-3), 7.12 (dd, $J = 15.5, 11.0$, H-4), 6.757 (m, H-5), 2.285 (m, H-6) 5.629 (m, H-7), 5.209 (m, H-8), 6.169 (m, H-9), 6.133 (m, H-10), 6.054 (m, H-11), 2.537 (m, H-12), 4.649 (m, H-13), 1.48 (m, H-14), 5.841 (m, H-15), 6.052 (m, H-16), 6.089 (m, H-17), 6.34 (m, H-18), 3.27 (s, H-19), 3.48 (OCH_3 , s), 3.31 (OCH_3 , s), 7.24–7.09 (m), ESIMS m/z 871.37 [$\text{M} + \text{Na}$] $^+$.



SI. 24. Figure. $\Delta\delta_{\text{H}}$ values ($\Delta\delta_{\text{H}} = \delta_{\text{S}} - \delta_{\text{R}}$) obtained for (*S*) – and (*R*) –MTPA esters of **3**.