

Supplementary Material

A-ring functionalization of cholestane with highly substituted pyrans and 2-aminoisophthalonitriles

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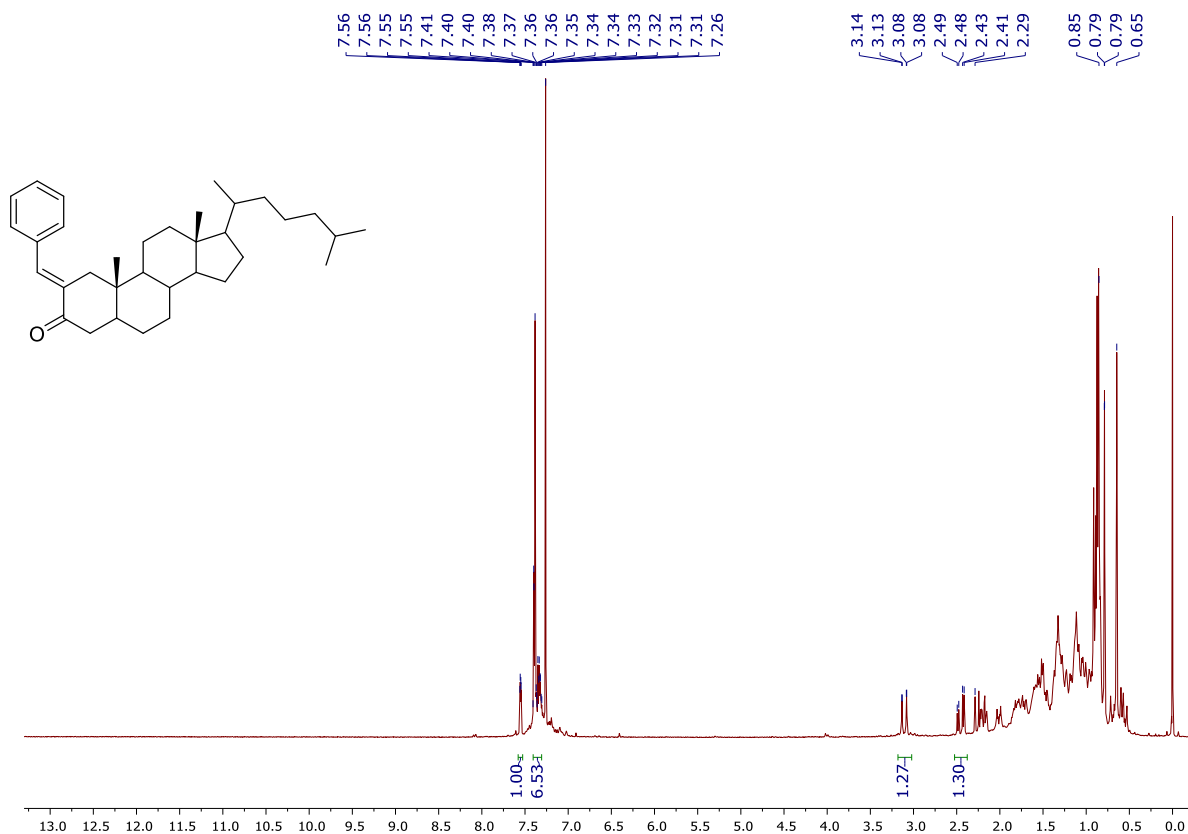


Figure S1: $^1\text{H-NMR}$ (300 MHz, CDCl_3) of compound **3a**.

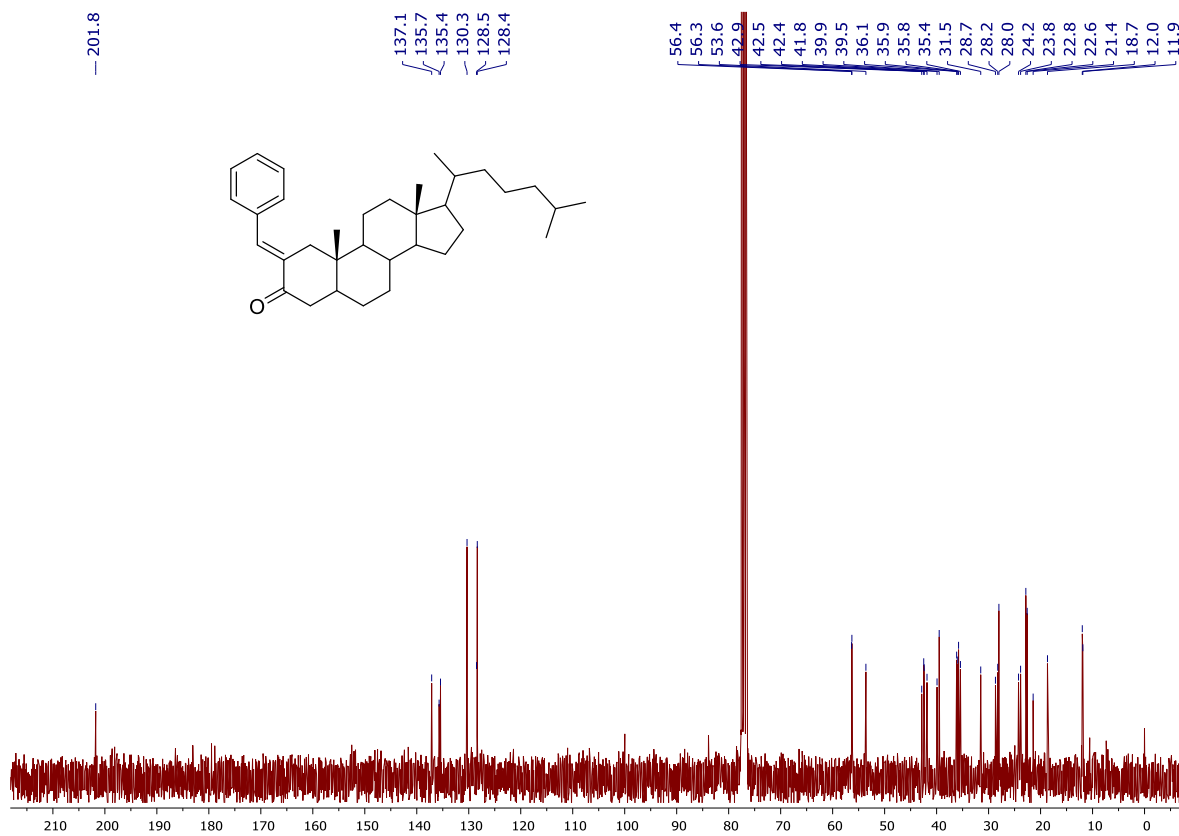
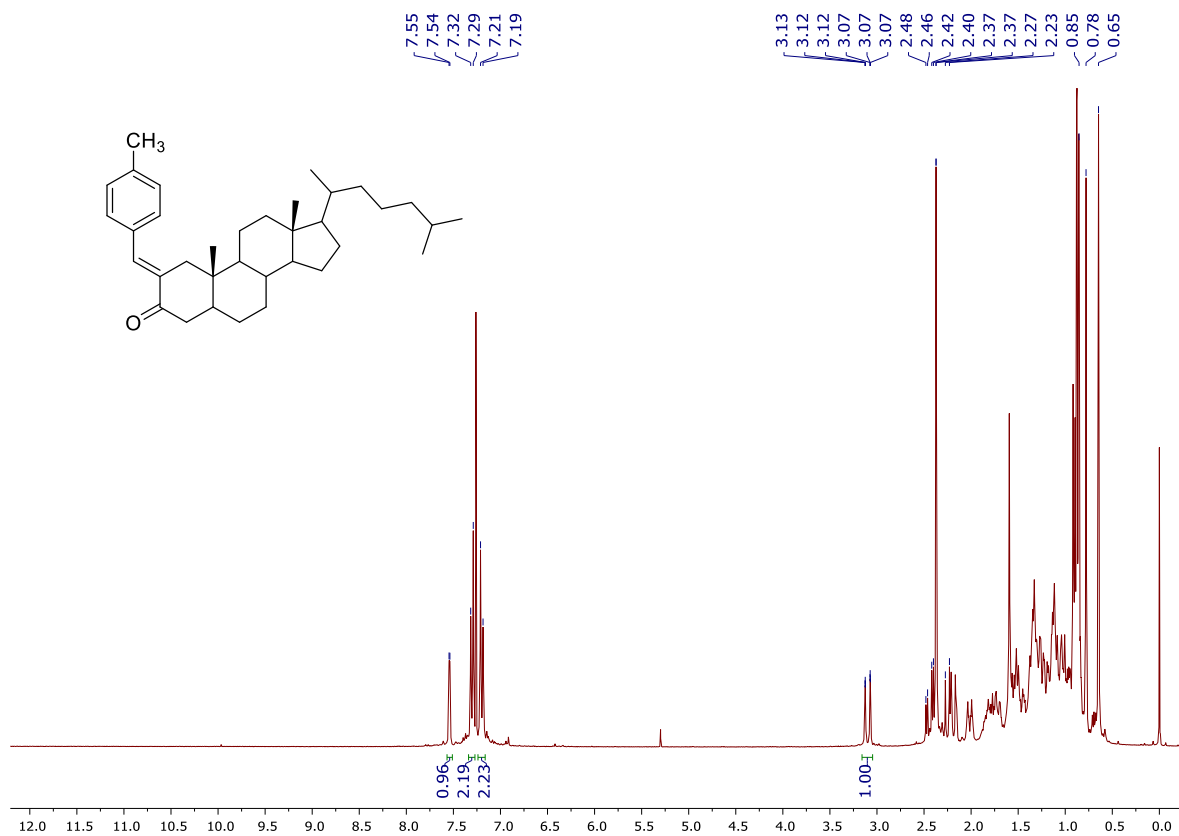
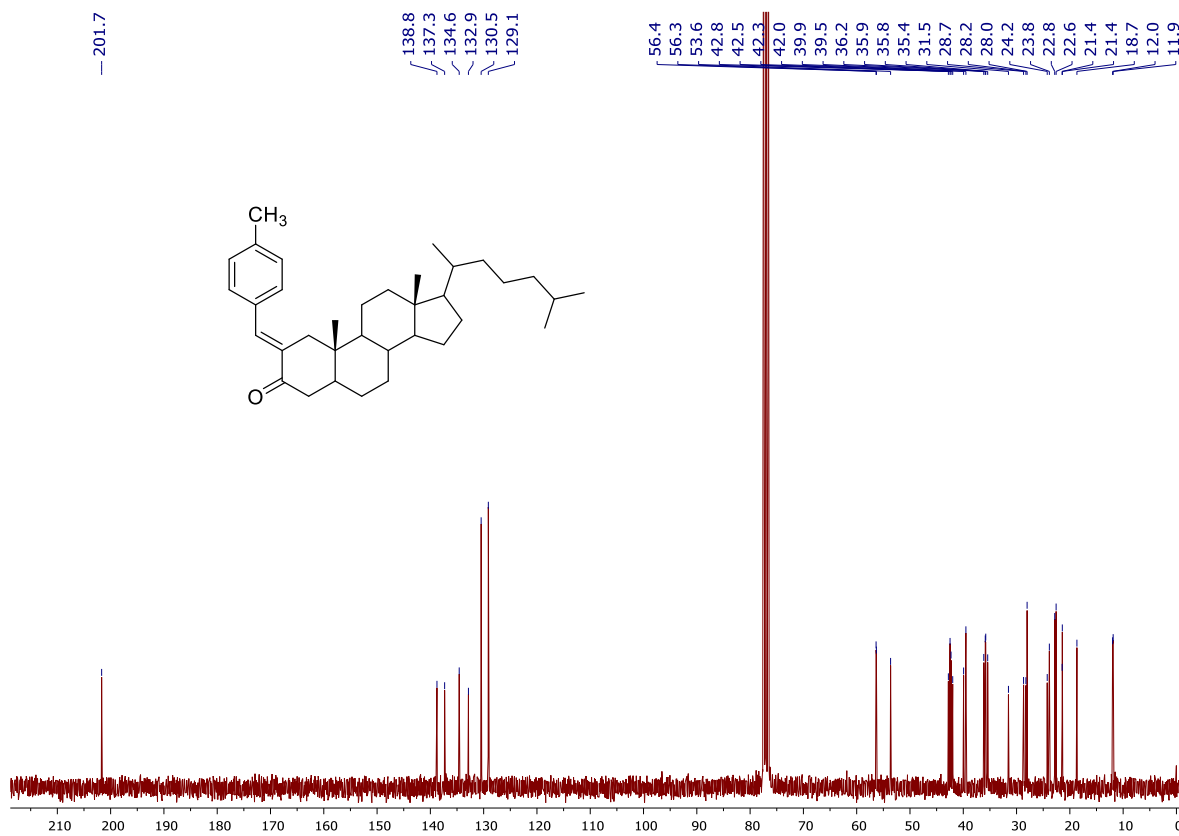
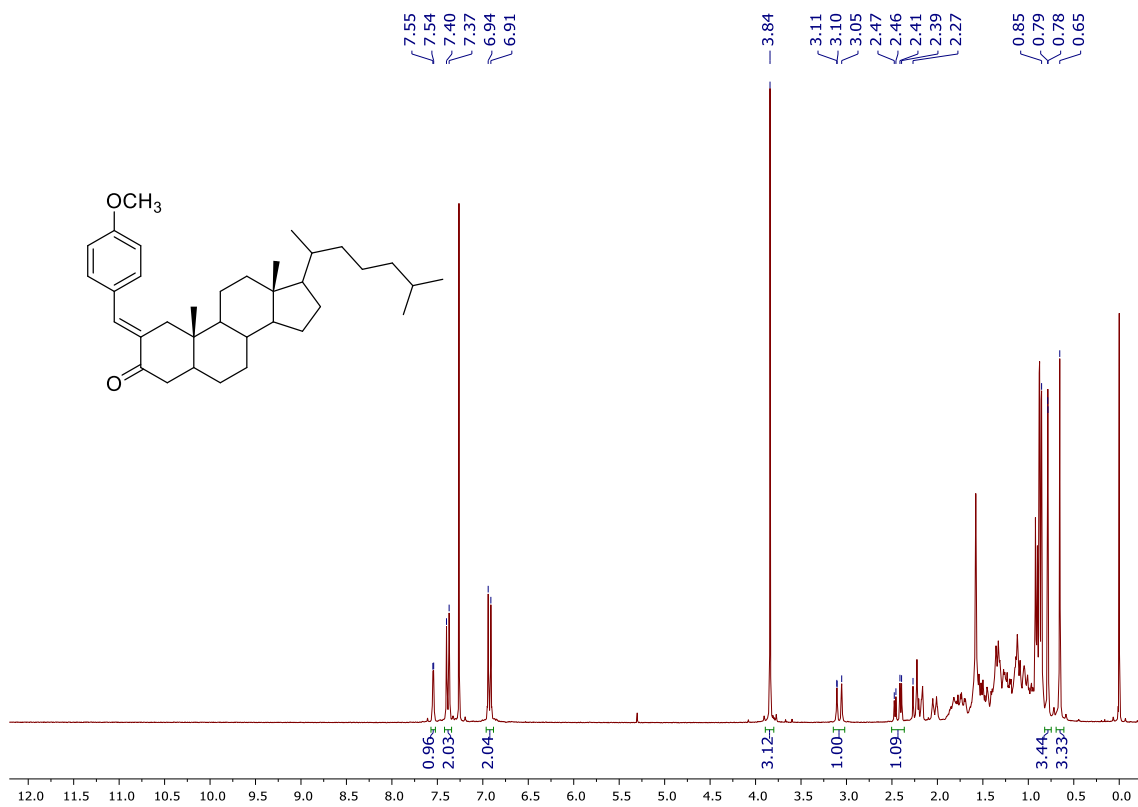
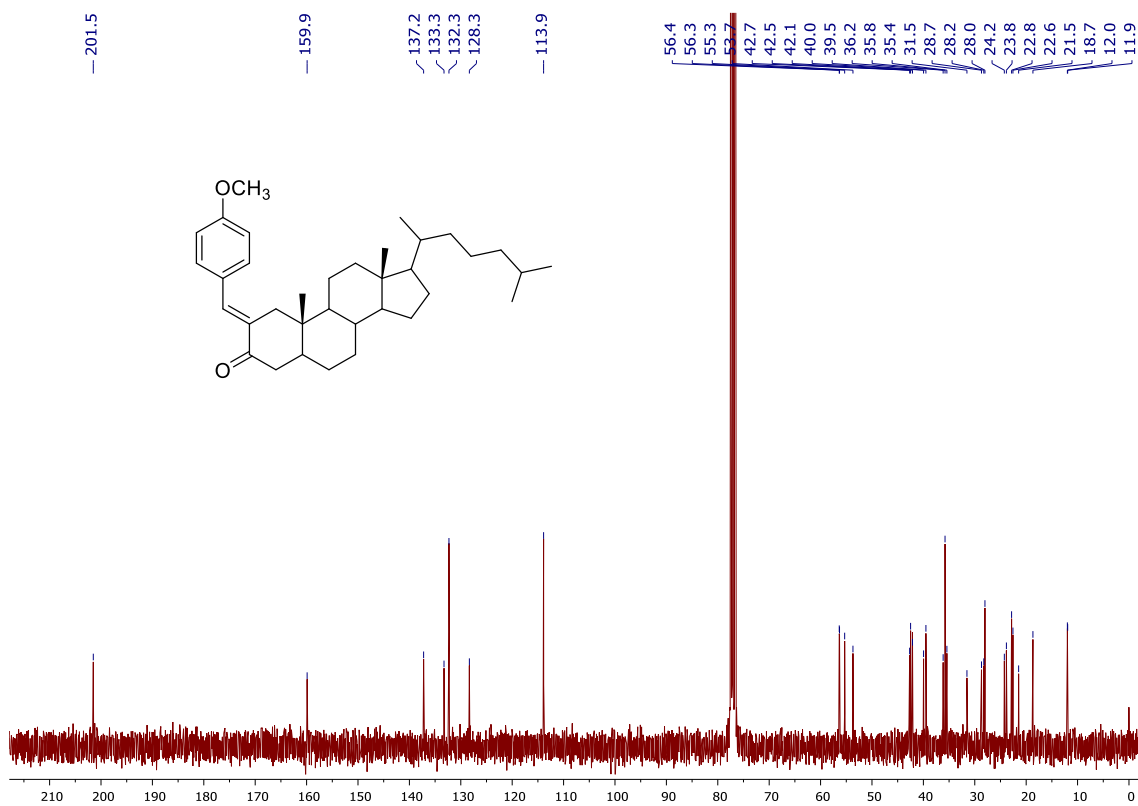
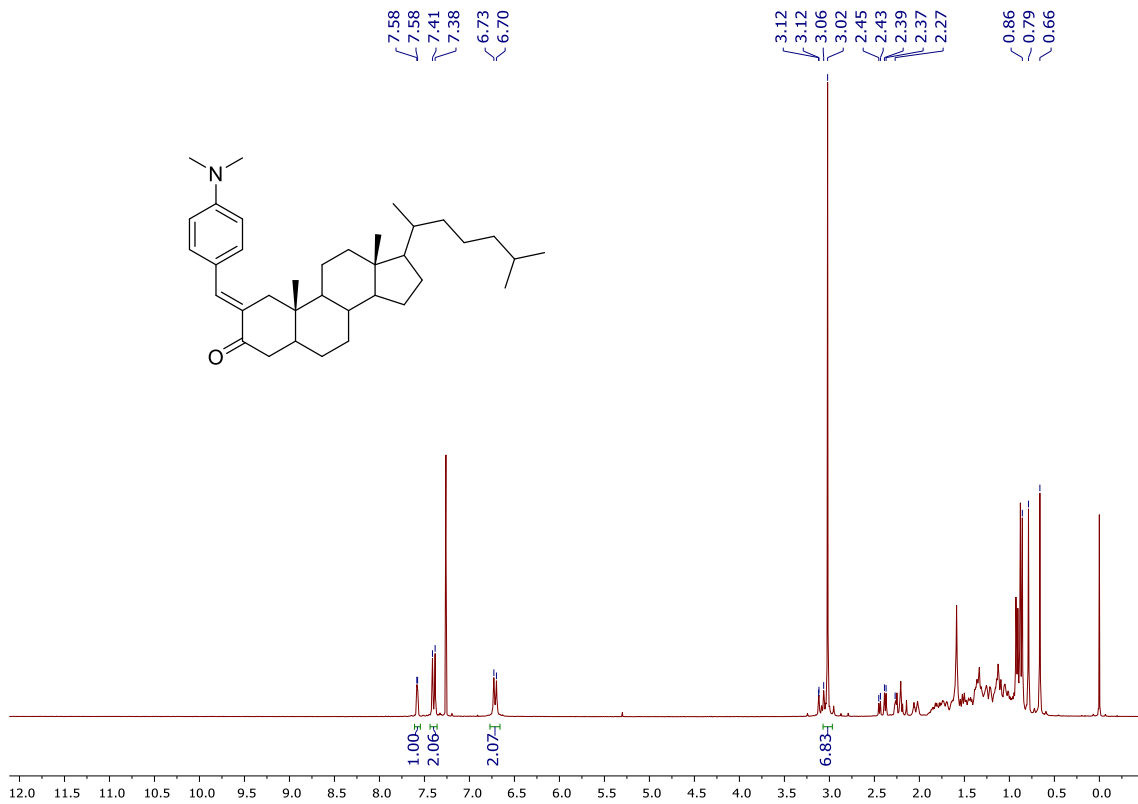
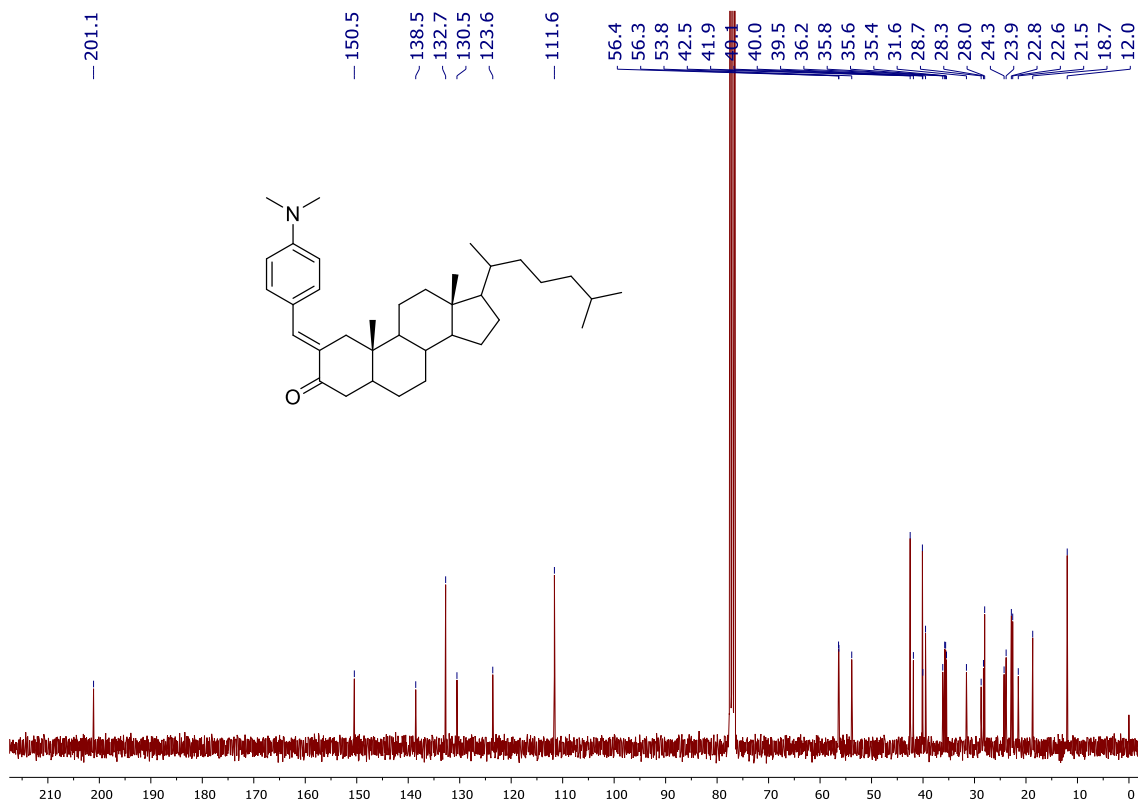
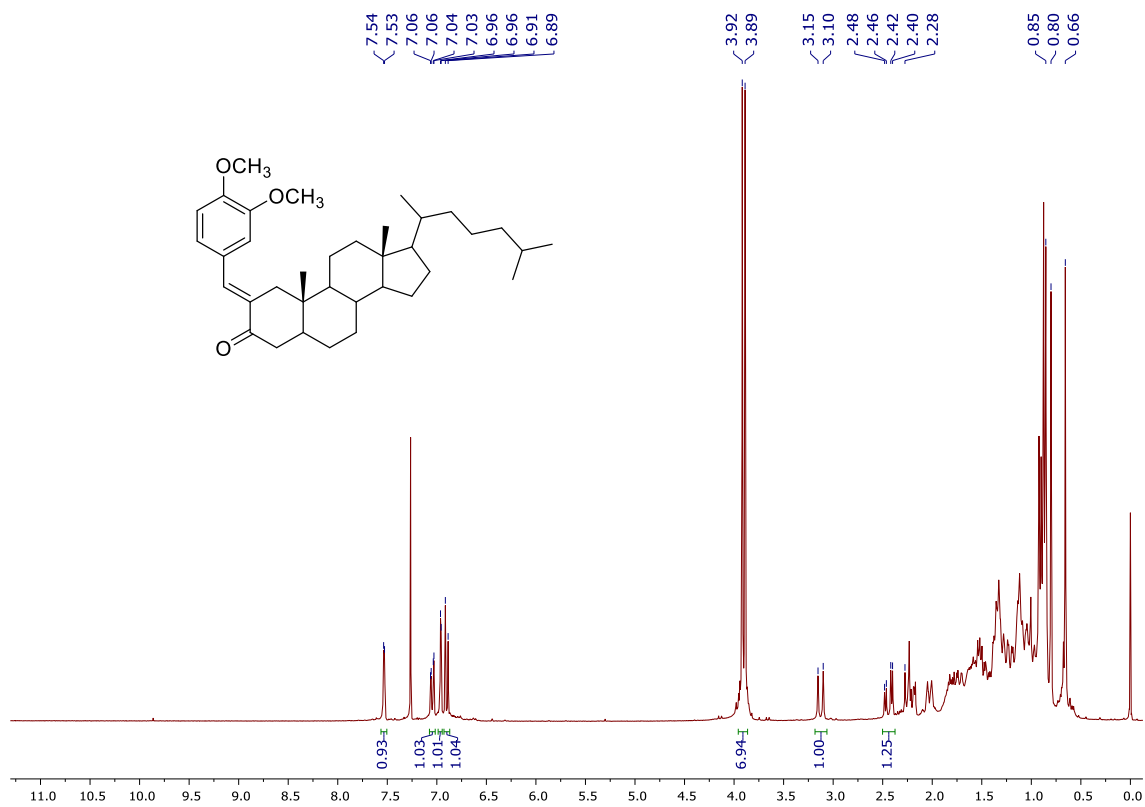
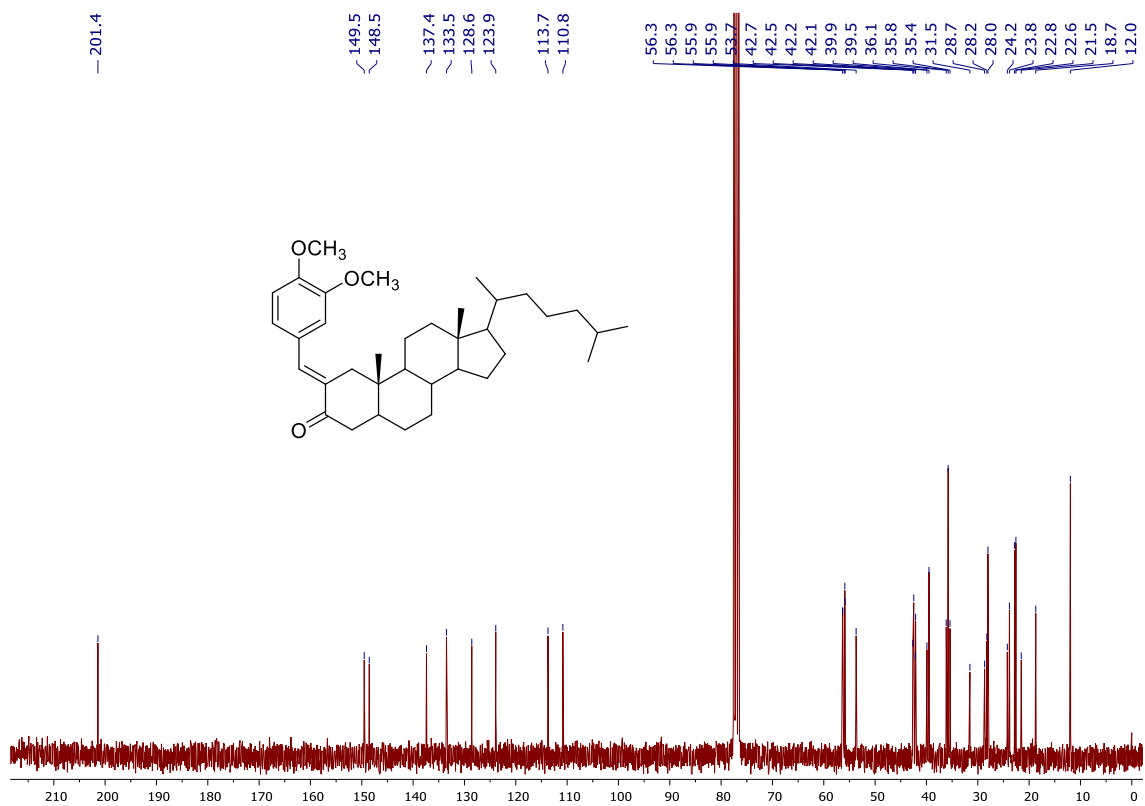


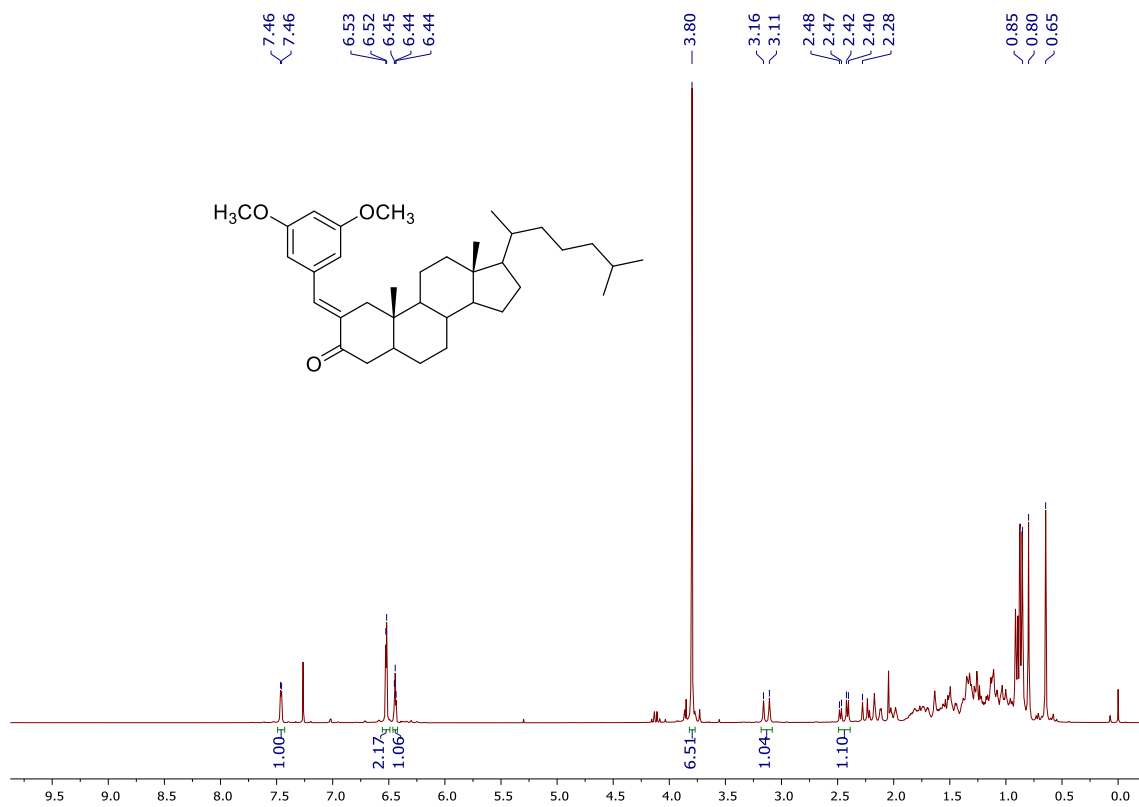
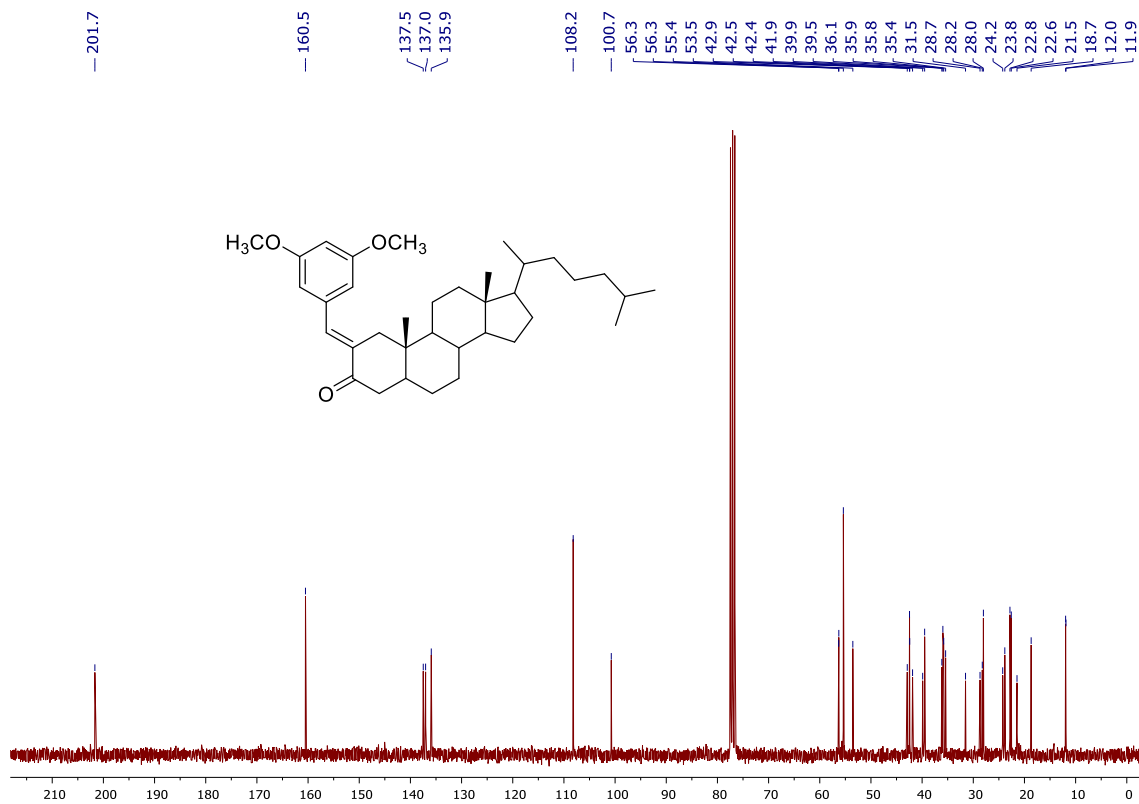
Figure S2: $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) of compound **3a**.

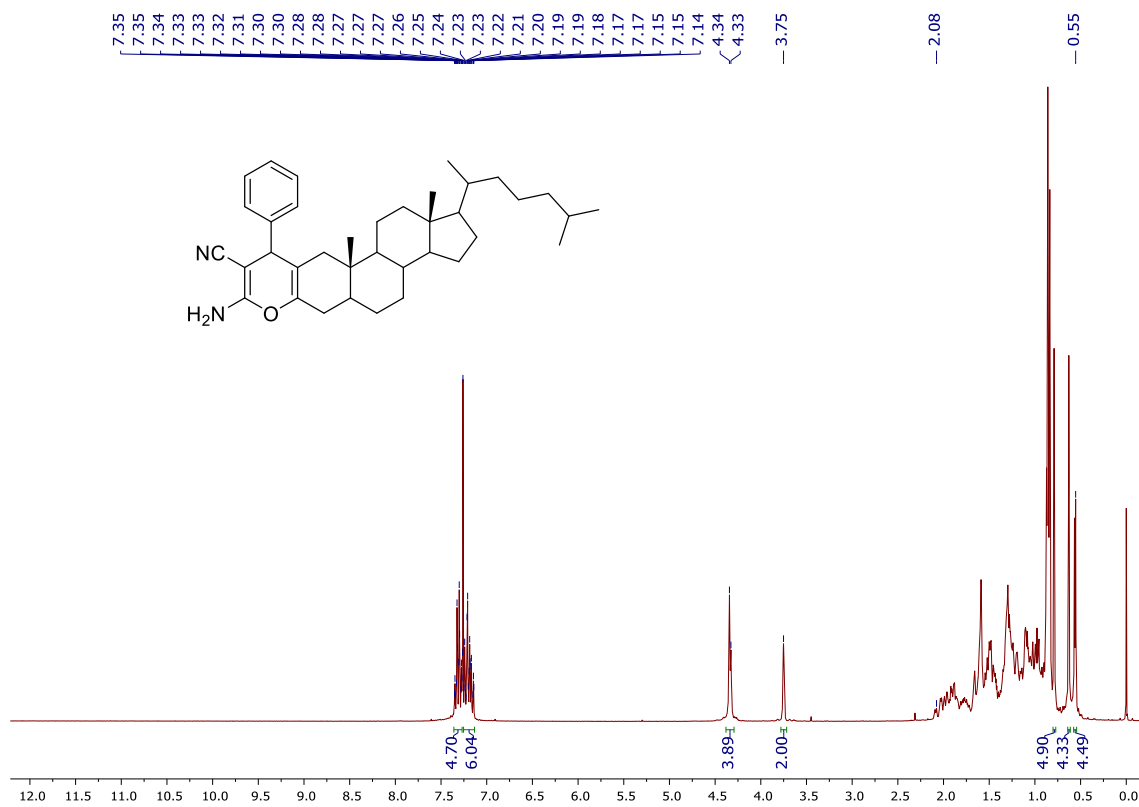
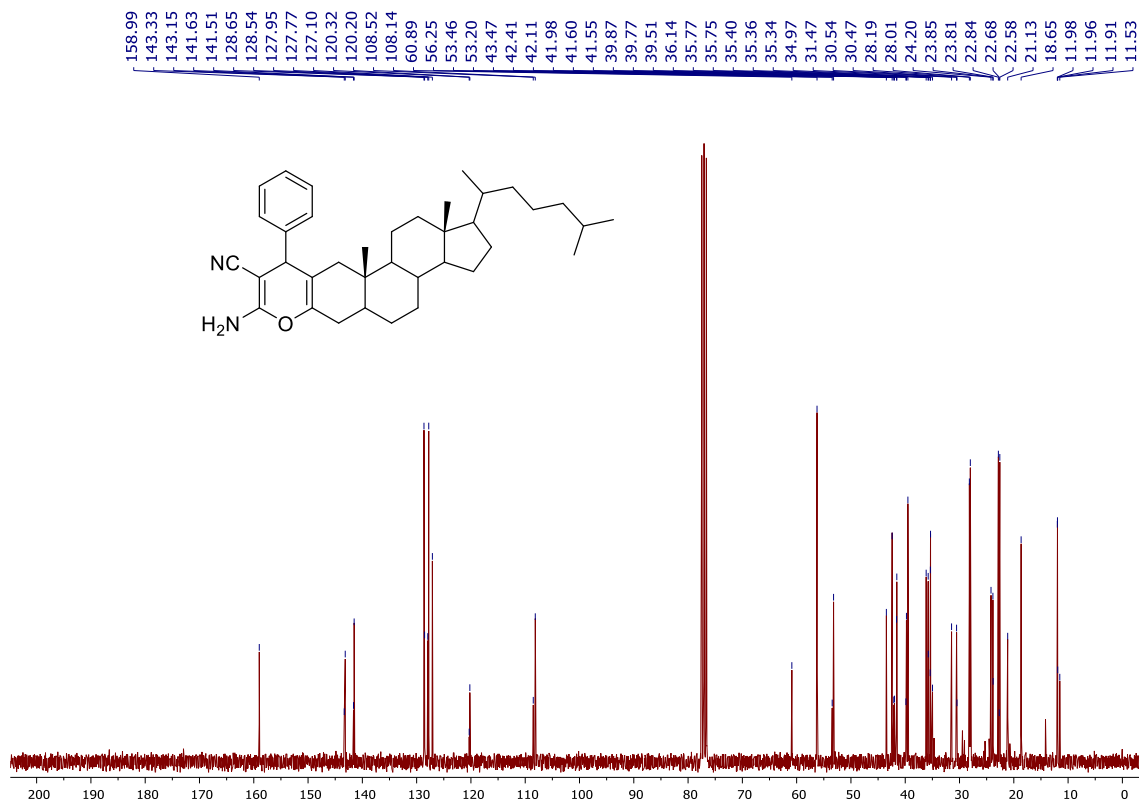
**Figure S3:** ¹H-NMR (300 MHz, CDCl₃) of compound **3b**.**Figure S4:** ¹³C-NMR (75 MHz, CDCl₃) of compound **3b**.

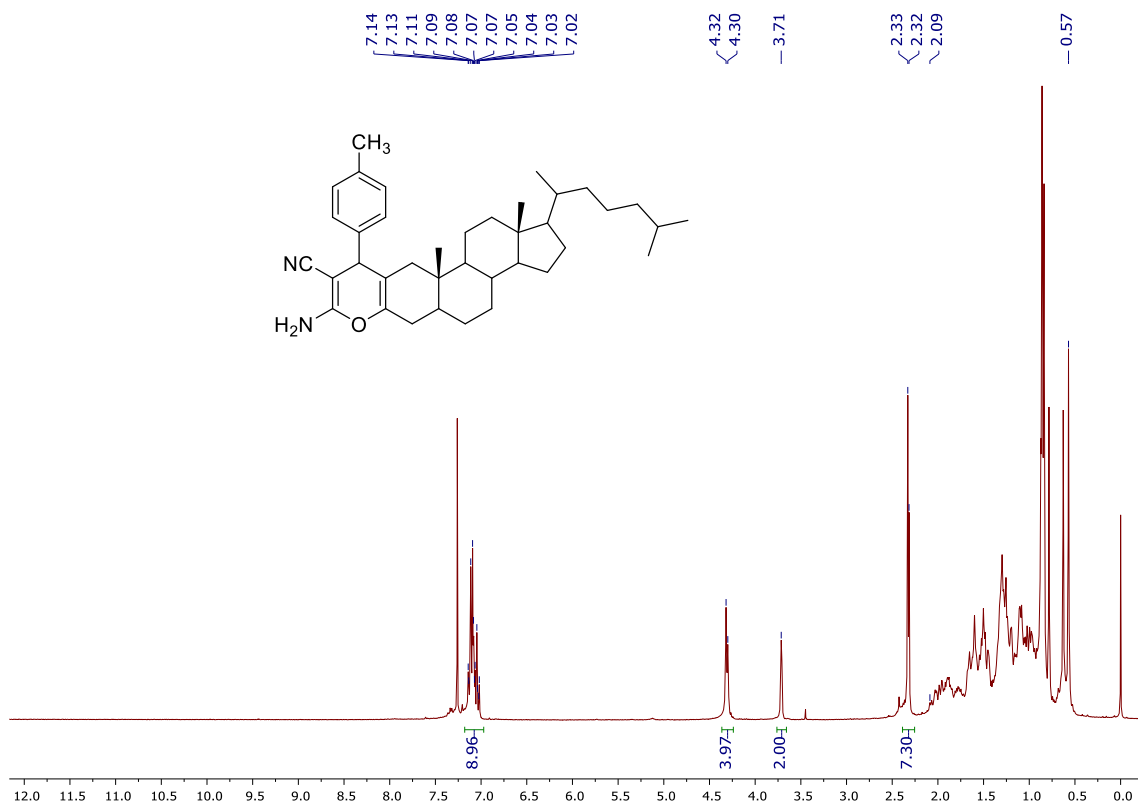
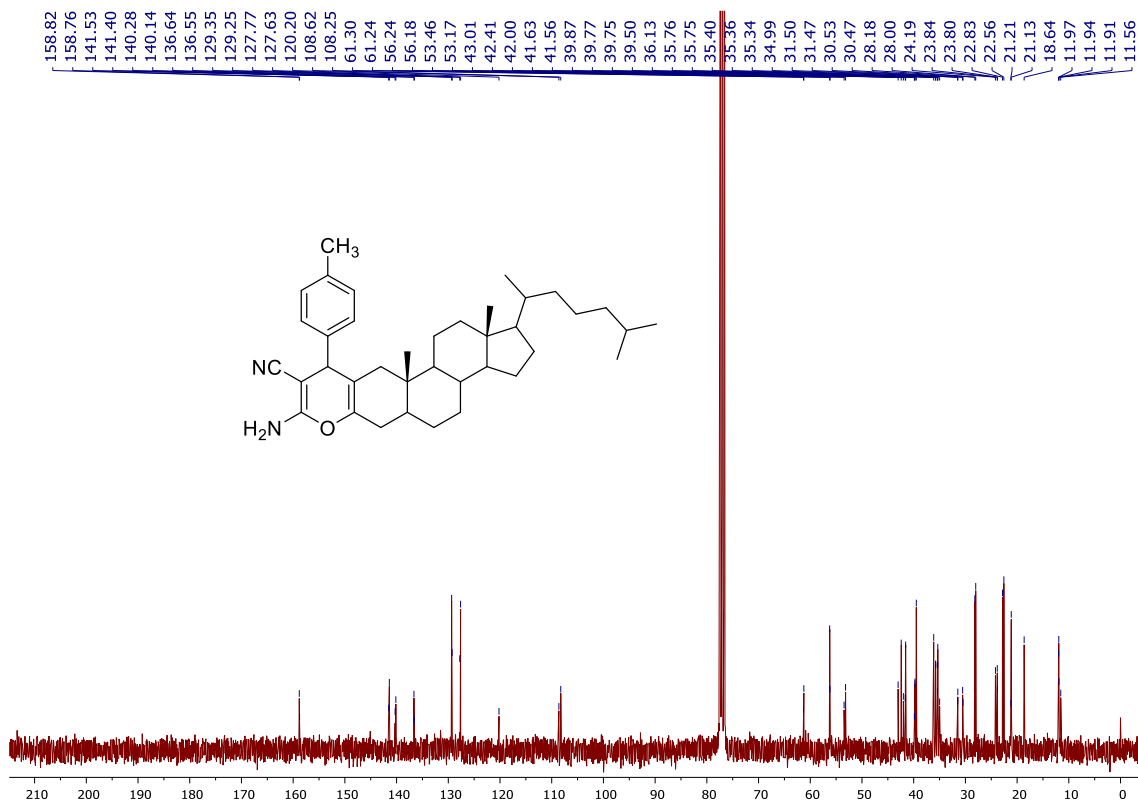
**Figure S5:** ¹H-NMR (300 MHz, CDCl₃) of compound **3c**.**Figure S6:** ¹³C-NMR (75 MHz, CDCl₃) of compound **3c**.

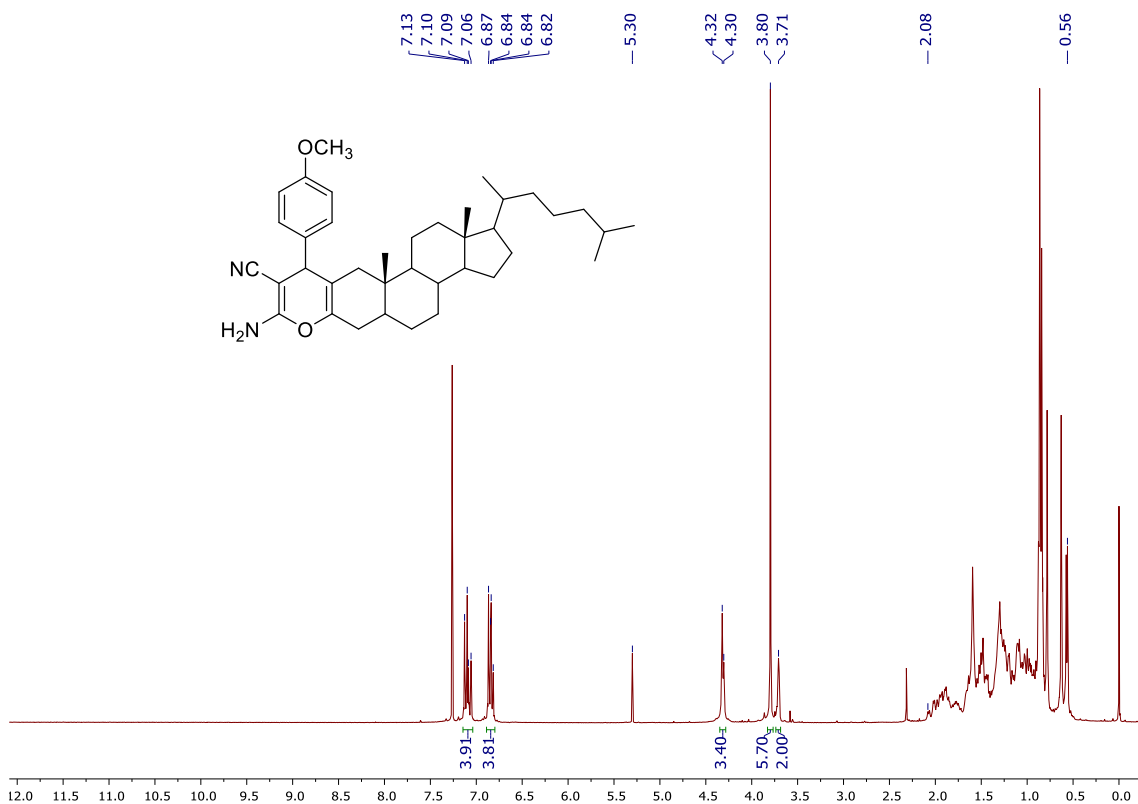
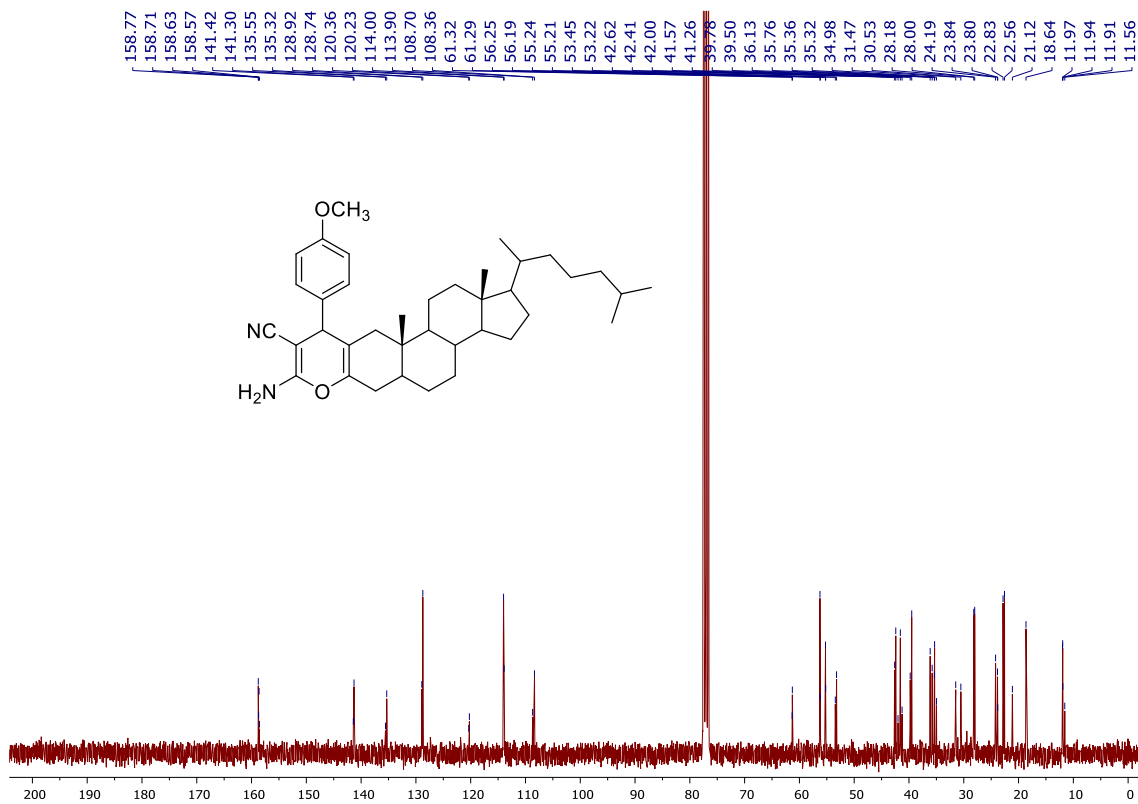
Figure S7: ¹H-NMR (300 MHz, CDCl₃) of compound 3d.Figure S8: ¹³C-NMR (75 MHz, CDCl₃) of compound 3d.

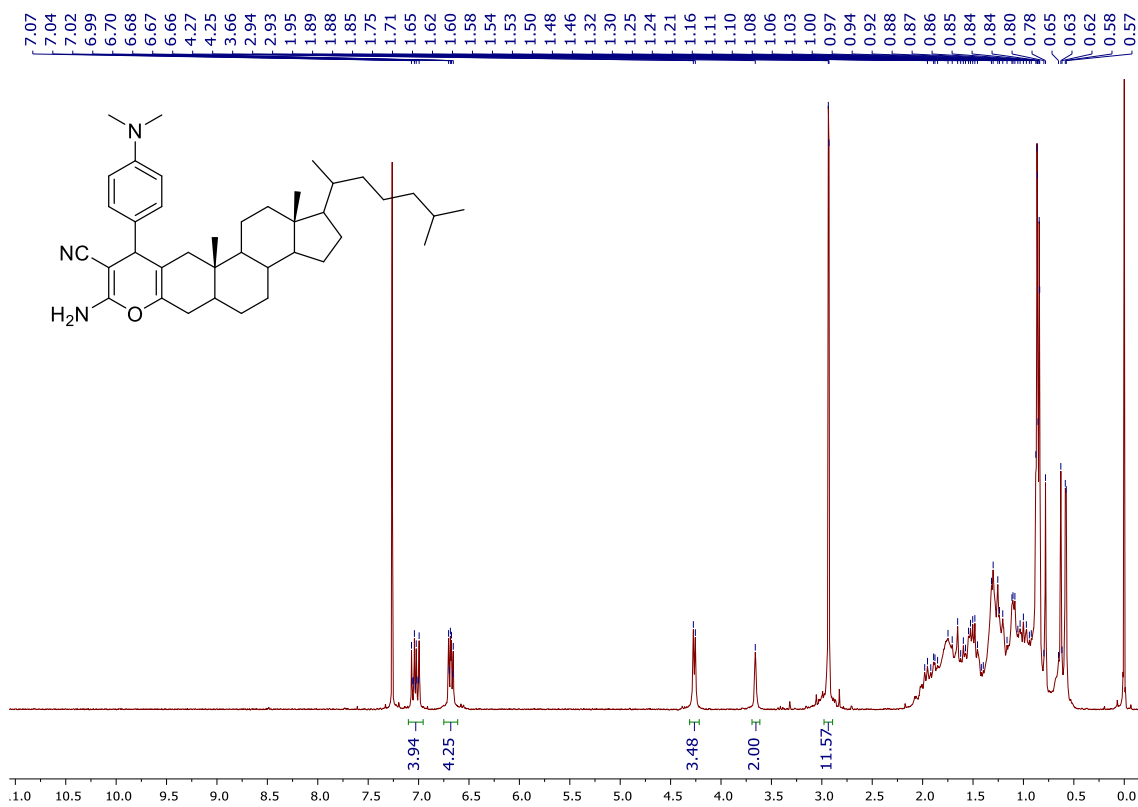
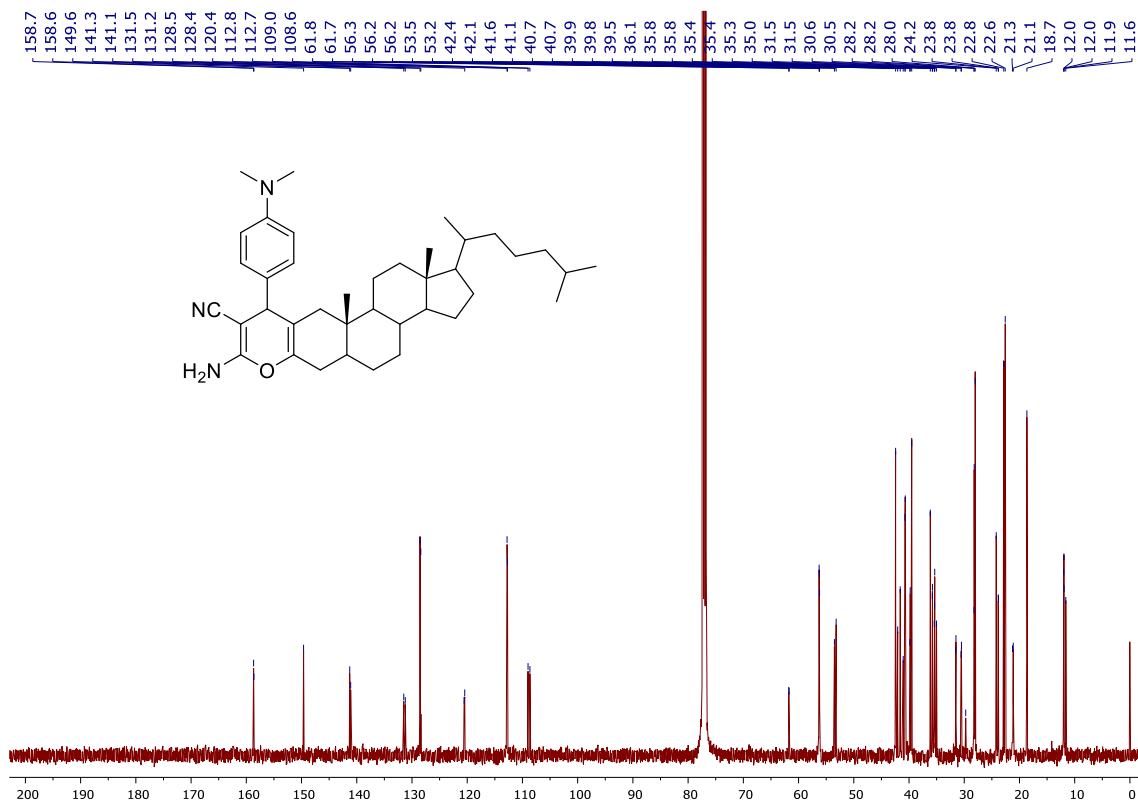
Figure S9: ¹H-NMR (300 MHz, CDCl₃) of compound **3e**.Figure S10: ¹³C-NMR (75 MHz, CDCl₃) of compound **3e**.

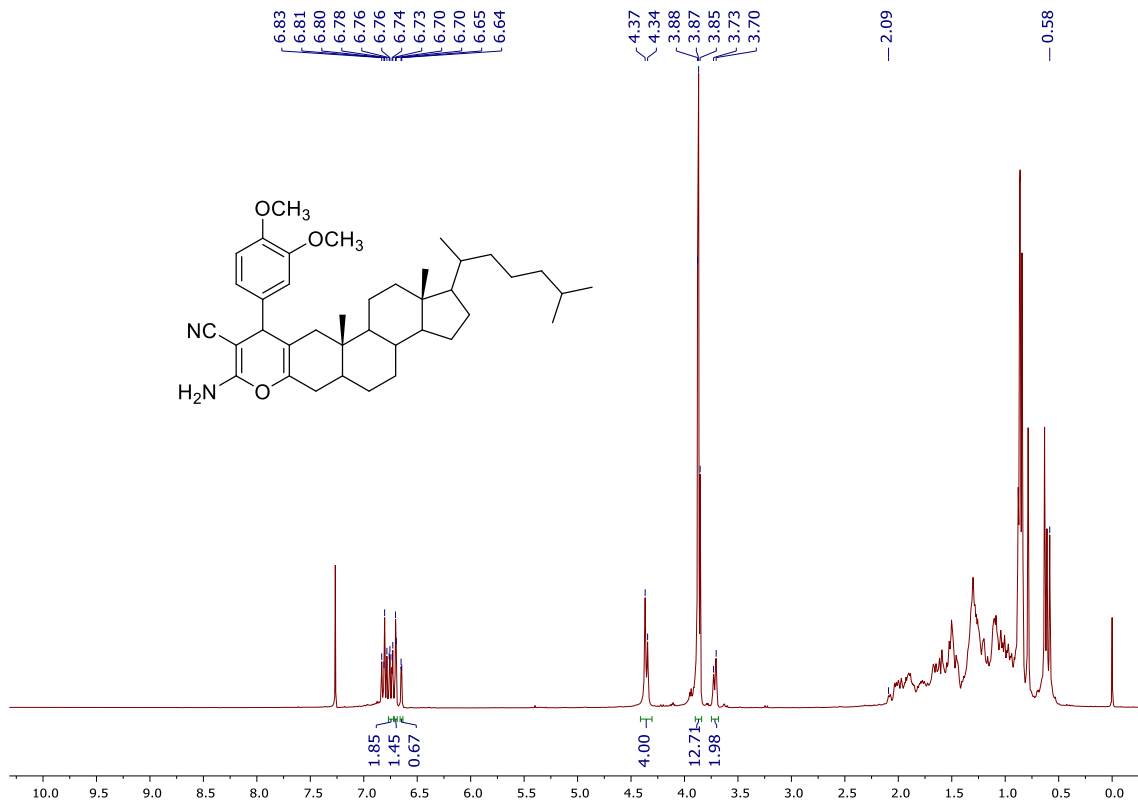
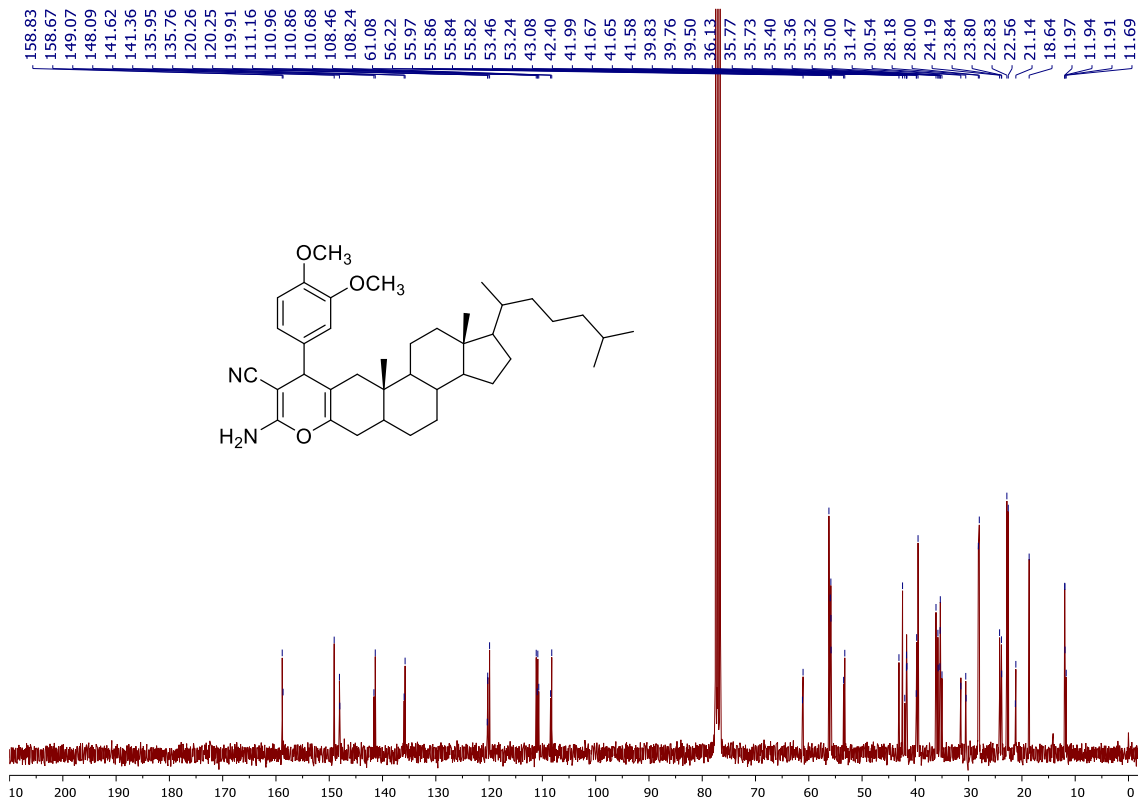
Figure S11: ¹H-NMR (300 MHz, CDCl₃) of compound **3f**.Figure S12: ¹³C-NMR (75 MHz, CDCl₃) of compound **3f**.

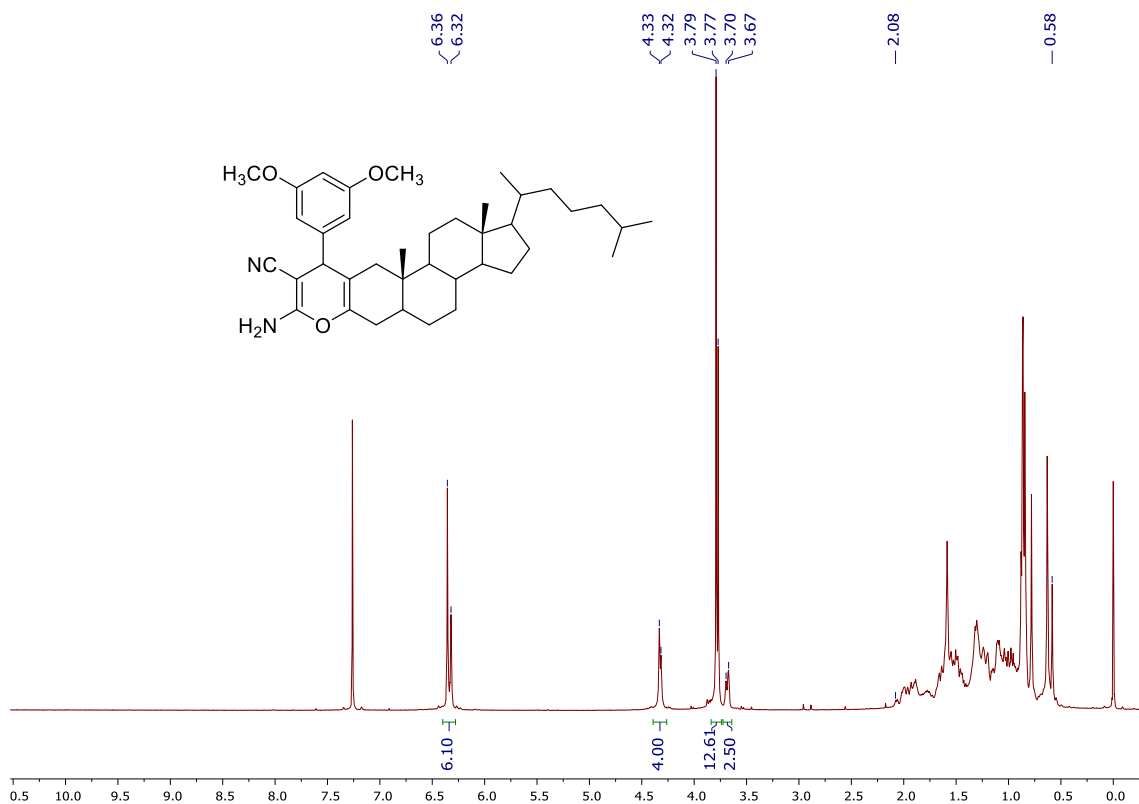
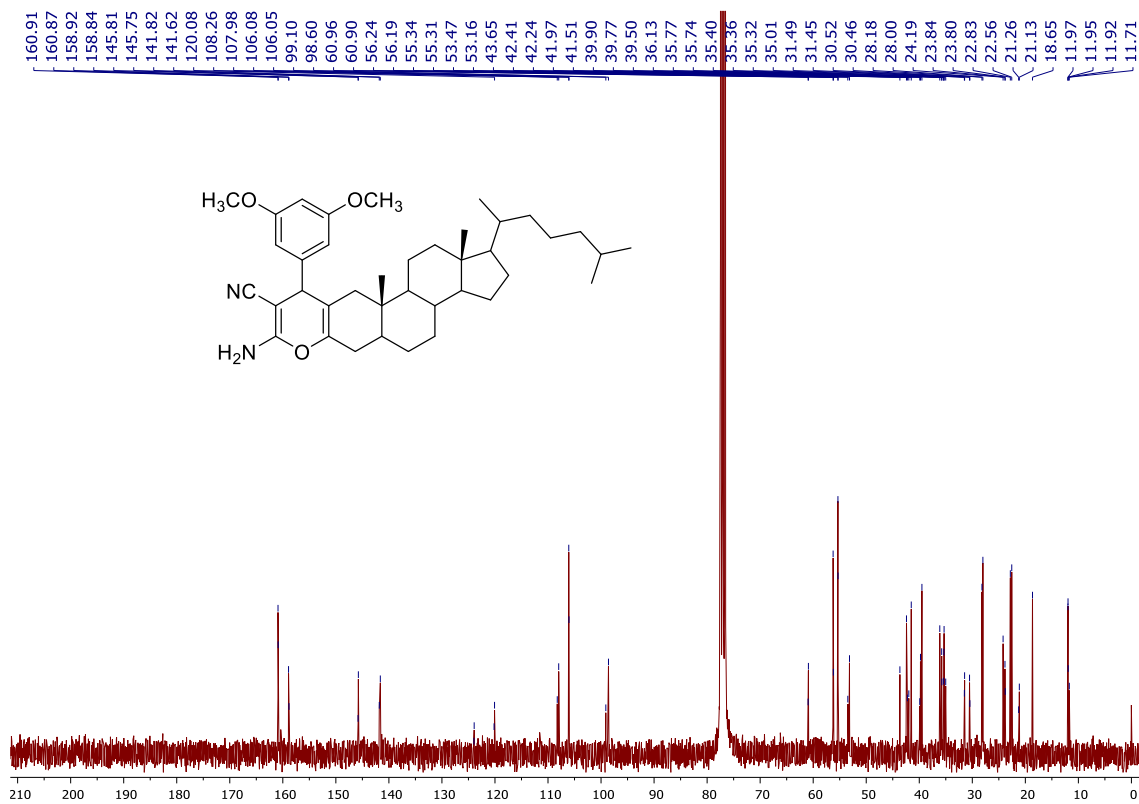
Figure S13: ¹H-NMR (300 MHz, CDCl₃) of compound 4a.Figure S14: ¹³C-NMR (75 MHz, CDCl₃) of compound 4a.

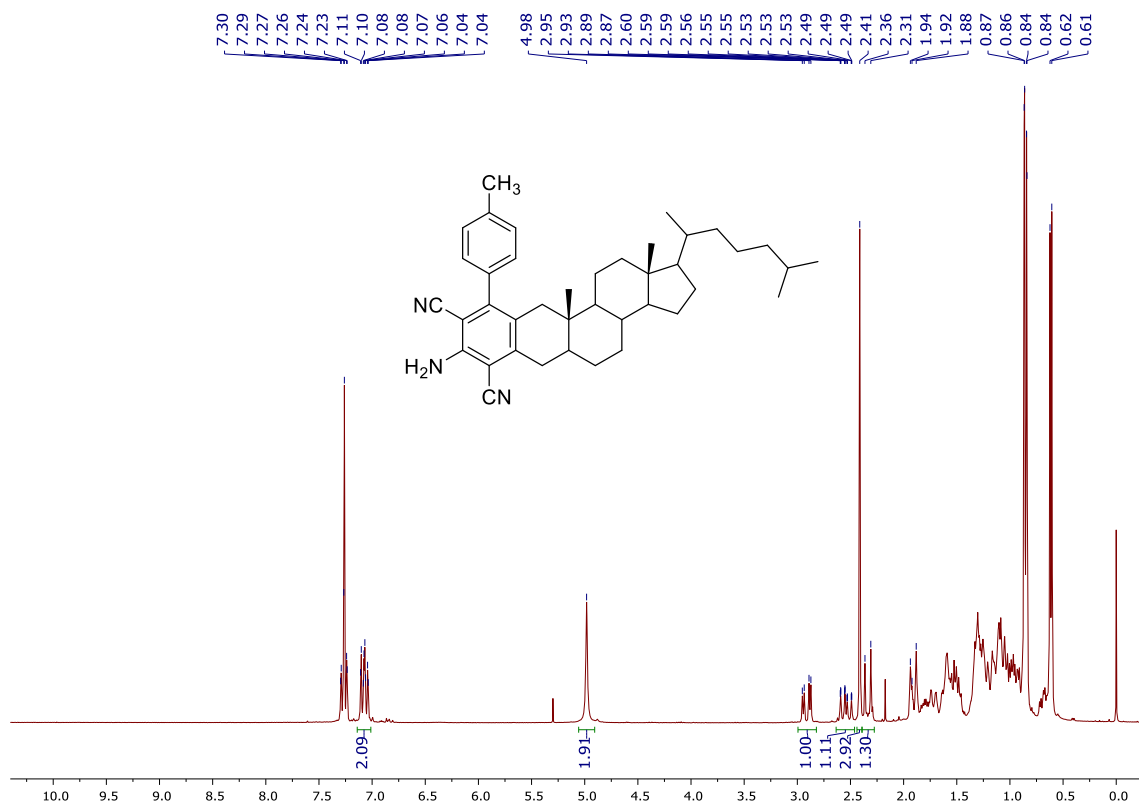
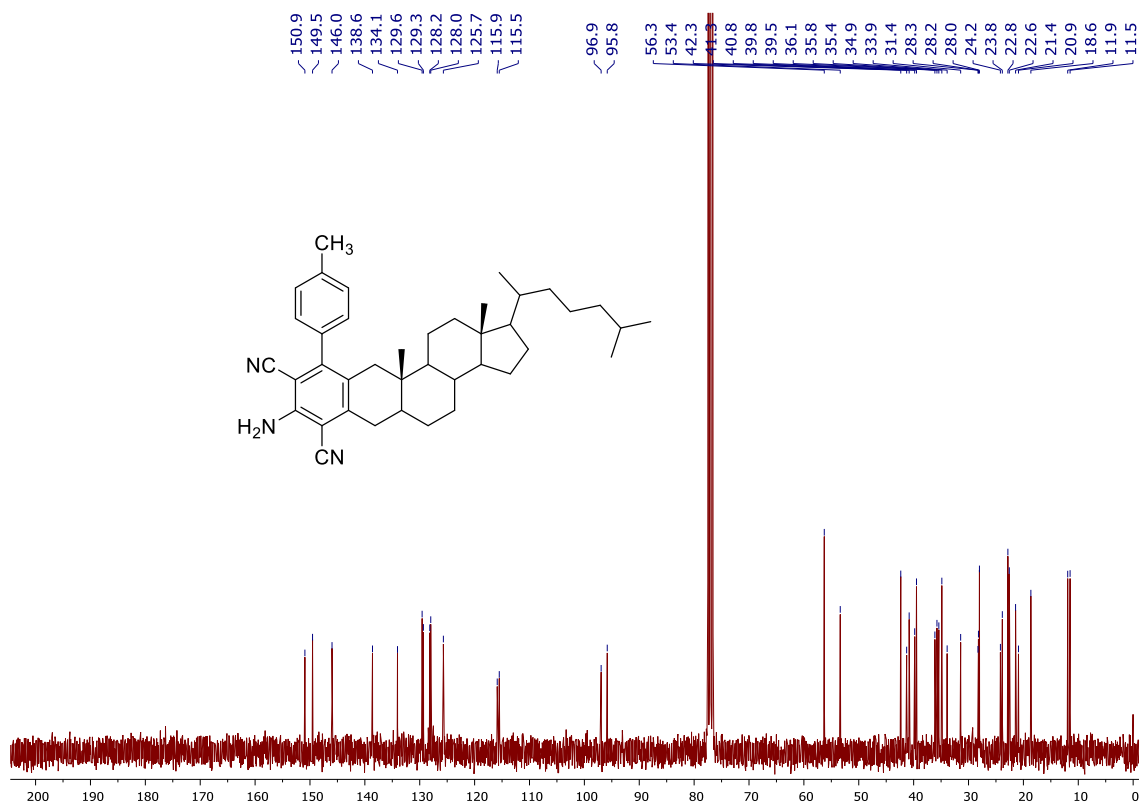
Figure S15: ¹H-NMR (300 MHz, CDCl₃) of compound **4b**.Figure S16: ¹³C-NMR (75 MHz, CDCl₃) of compound **4b**.

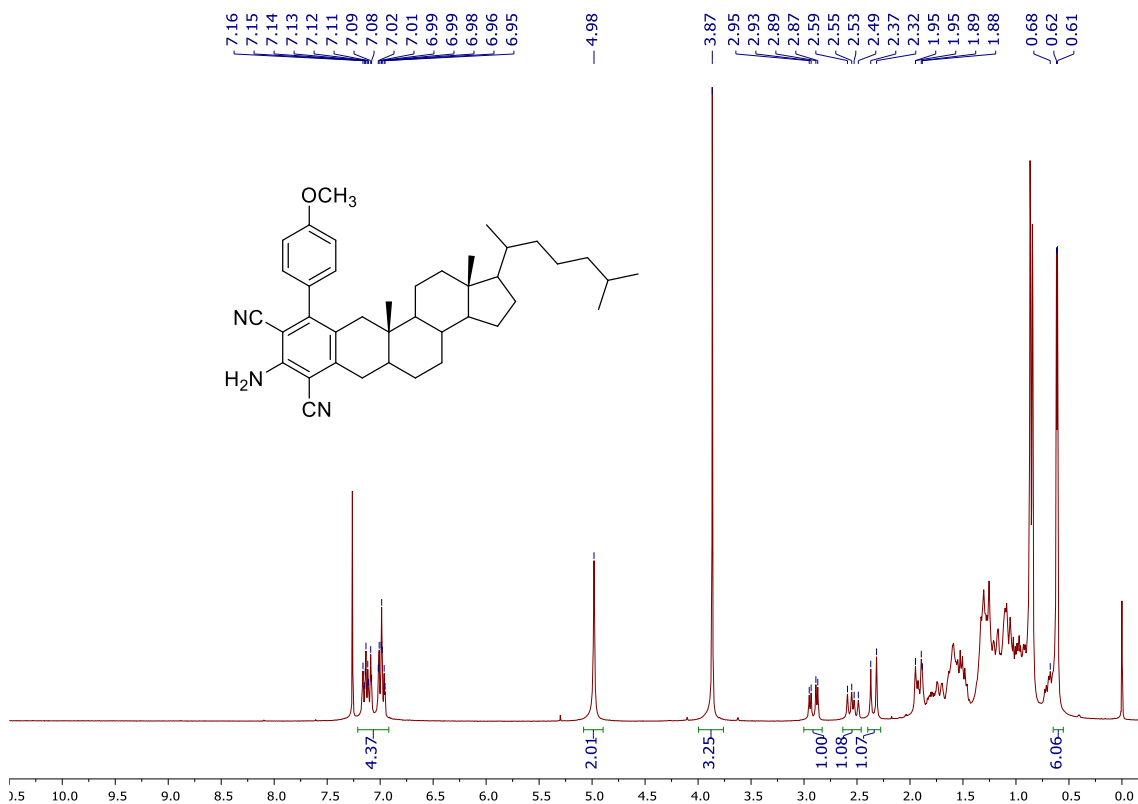
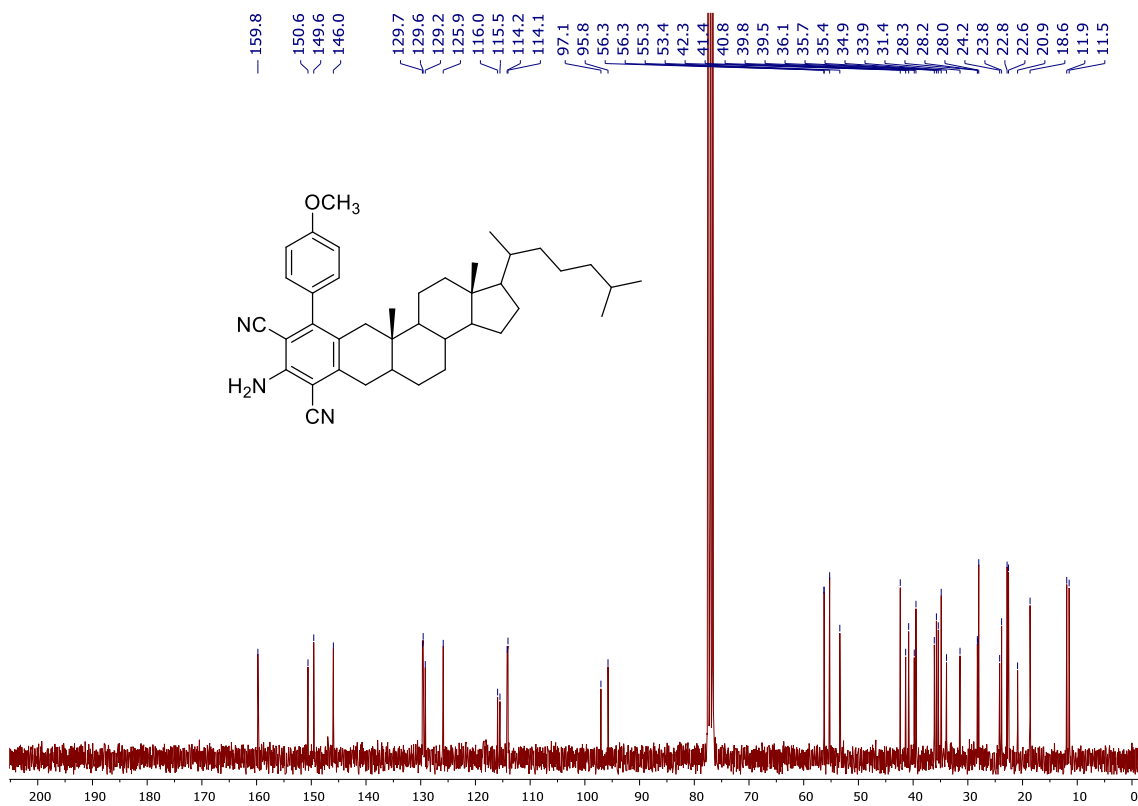
Figure S17: ¹H-NMR (300 MHz, CDCl₃) of compound 4c.Figure S18: ¹³C-NMR (75 MHz, CDCl₃) of compound 4c.

Figure S19: ¹H-NMR (300 MHz, CDCl₃) of compound 4d.Figure S20: ¹³C-NMR (125 MHz, CDCl₃) of compound 4d.

Figure S21: ¹H-NMR (300 MHz, CDCl₃) of compound 4e.Figure S22: ¹³C-NMR (75 MHz, CDCl₃) of compound 4e.

Figure S23: ¹H-NMR (300 MHz, CDCl₃) of compound 4f.Figure S24: ¹³C-NMR (75 MHz, CDCl₃) of compound 4f.

Figure S25: ¹H-NMR (300 MHz, CDCl₃) of compound **5b**.Figure S26: ¹³C-NMR (75 MHz, CDCl₃) of compound **5b**.

Figure S27: ¹H-NMR (300 MHz, CDCl₃) of compound 5c.Figure S28: ¹³C-NMR (75 MHz, CDCl₃) of compound 5c.

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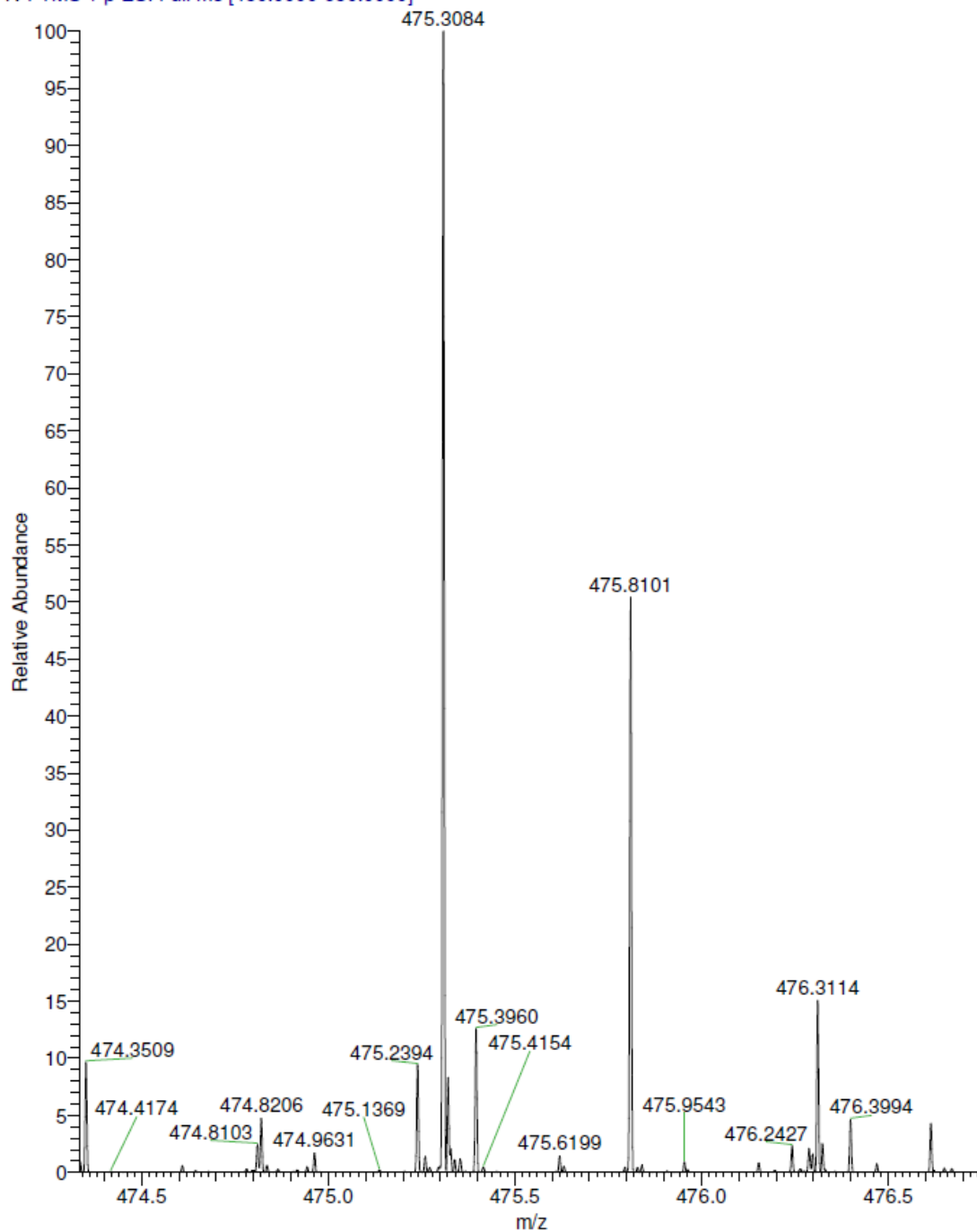
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Figure S29: High-resolution mass spectrum of compound 3a.

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10/06/20 14:31:30

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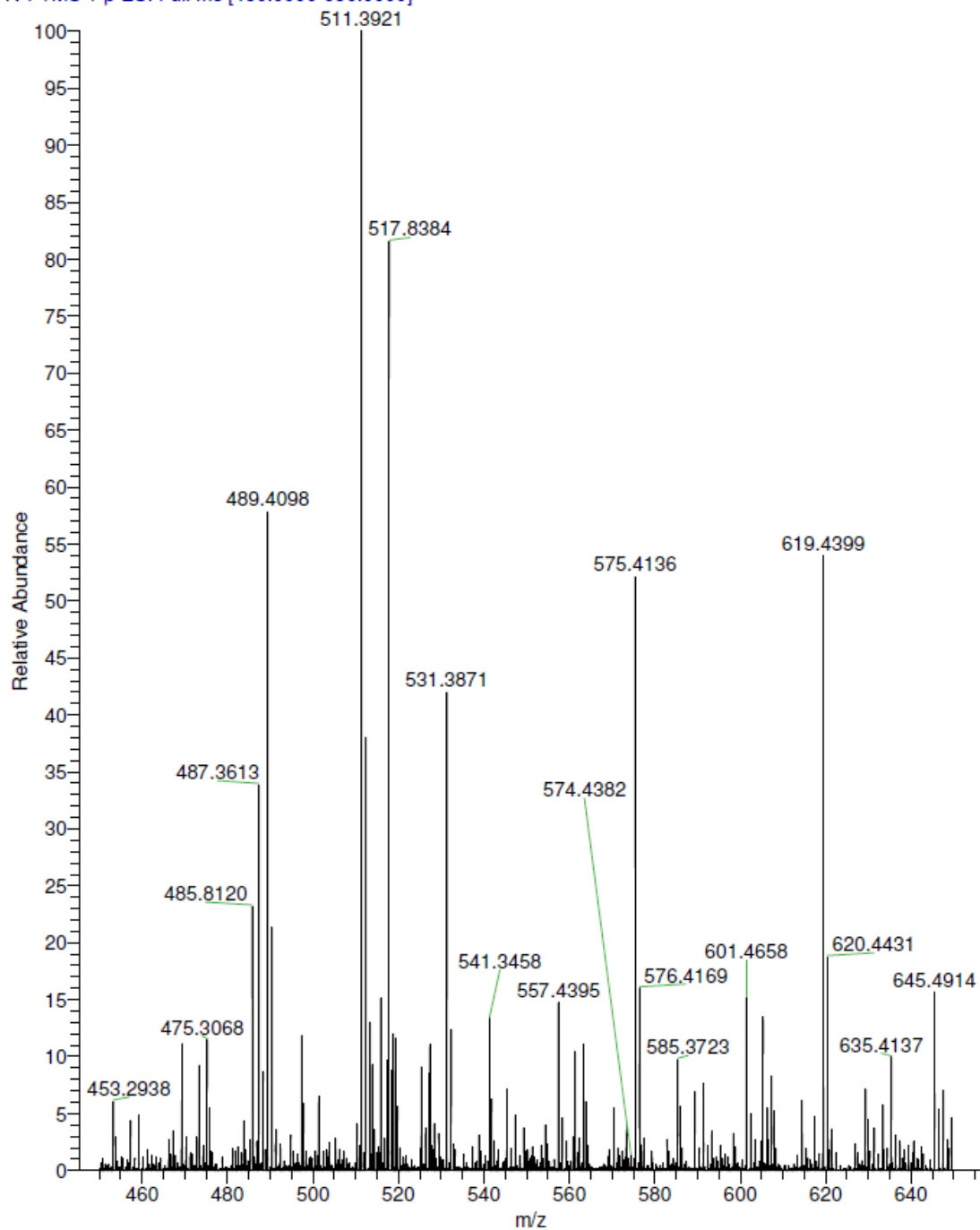


Figure S30: High-resolution mass spectrum of compound 3b.

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10/27/20 14:45:38

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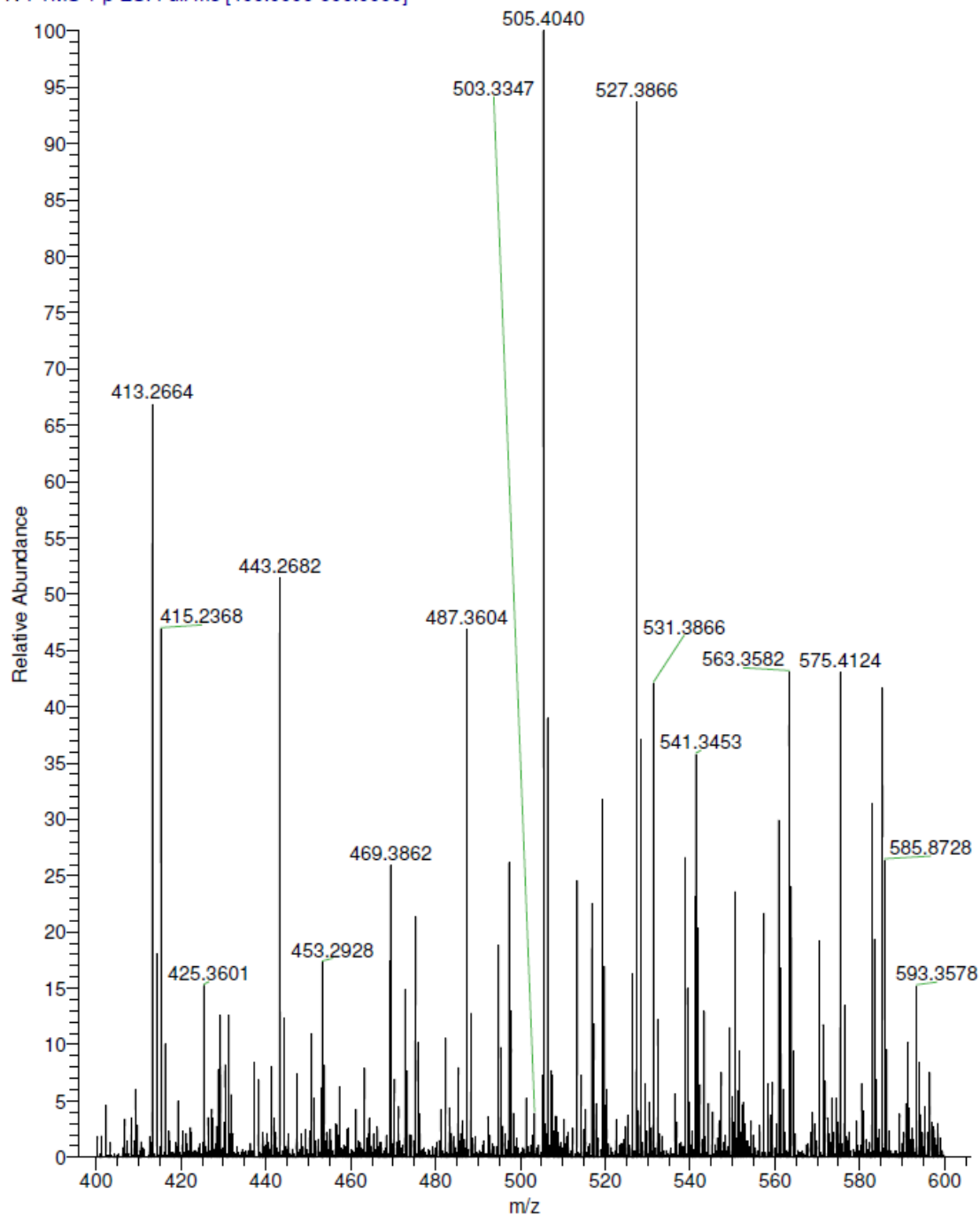


Figure S31: High-resolution mass spectrum of compound 3c.

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10/06/20 14:24:15

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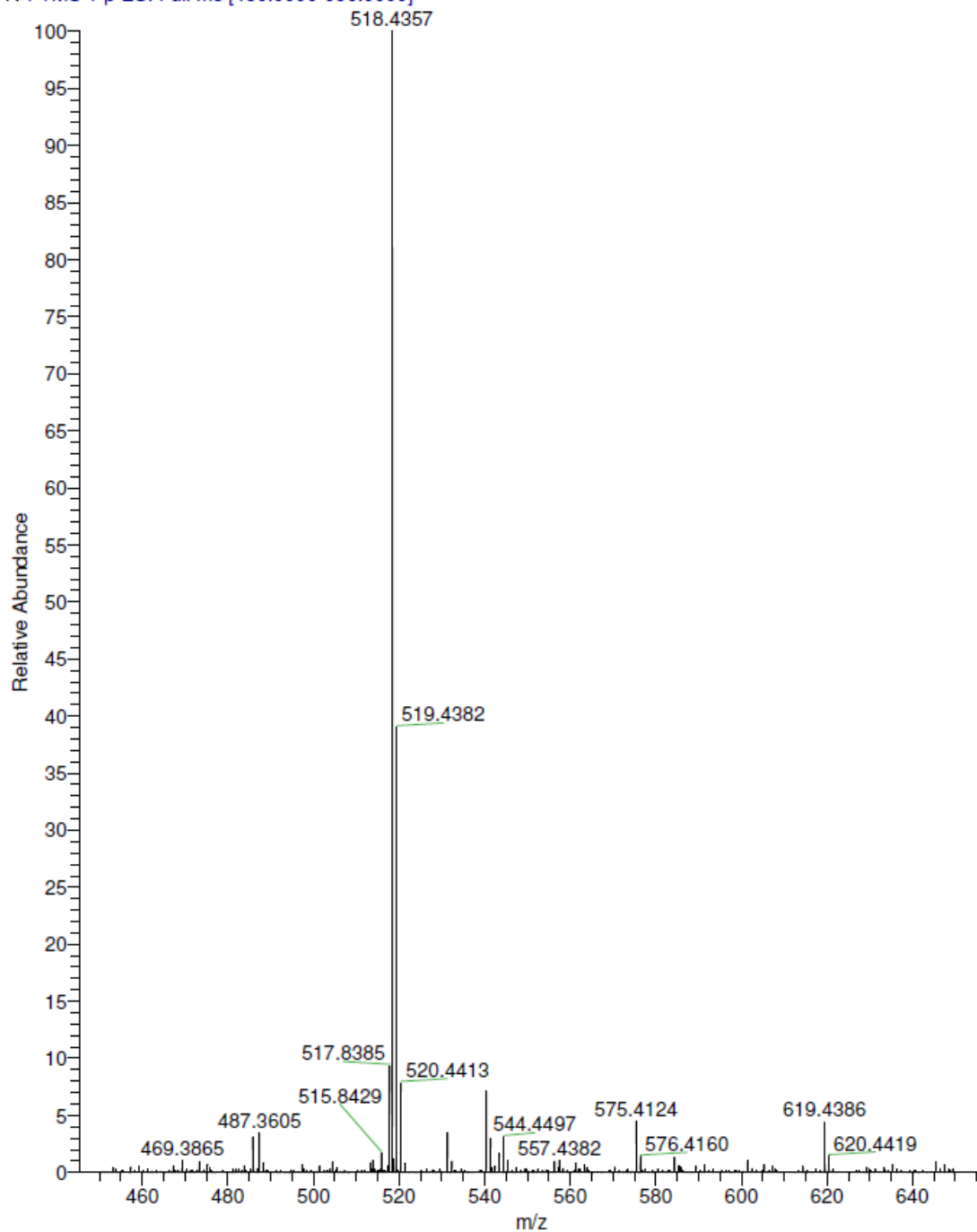


Figure S32: High-resolution mass spectrum of compound 3d.

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10/06/20 11:45:08

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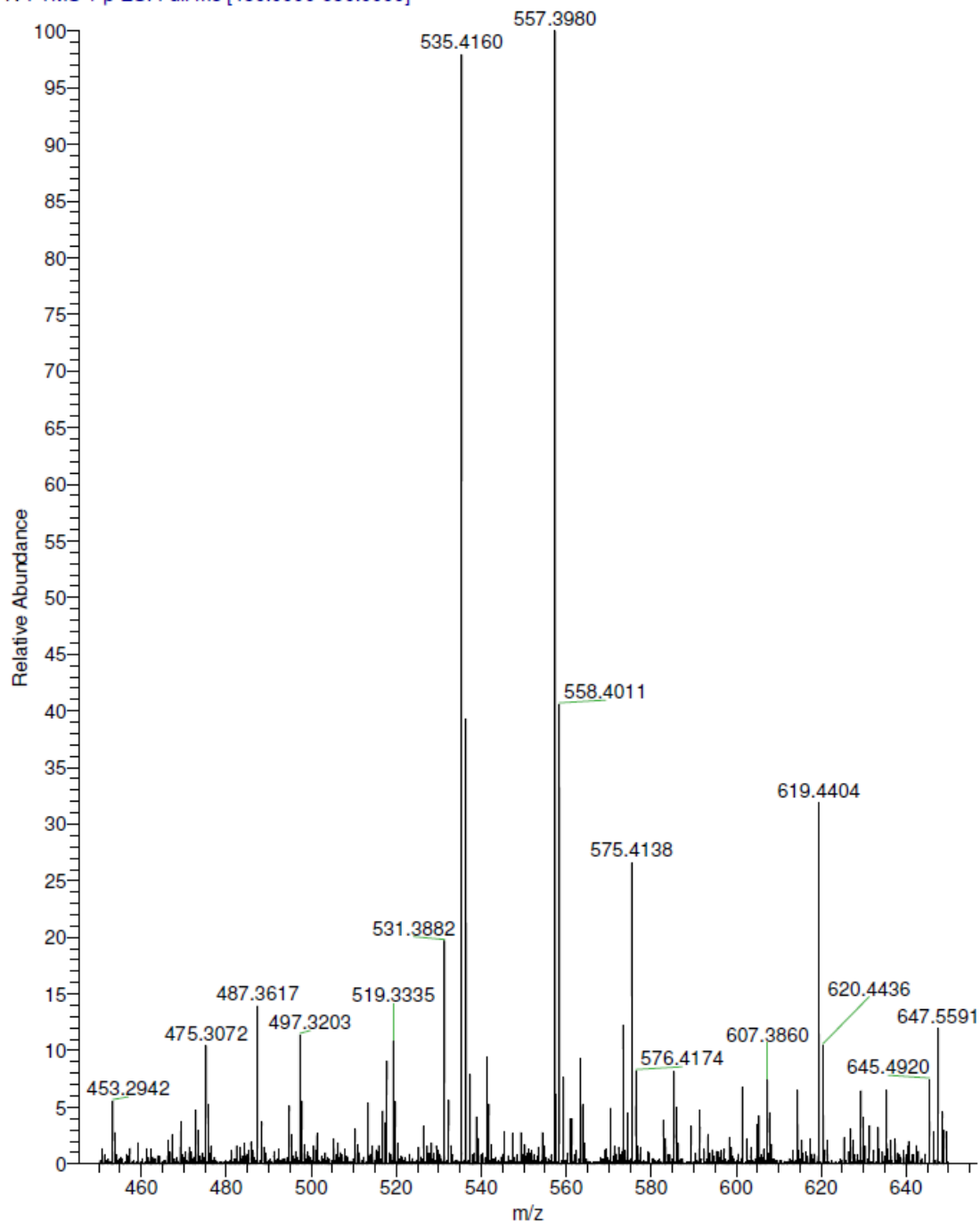


Figure S33: High-resolution mass spectrum of compound 3e.

C:\Xcalibur...\Helder-061020\HA-767

10/06/20 14:39:51

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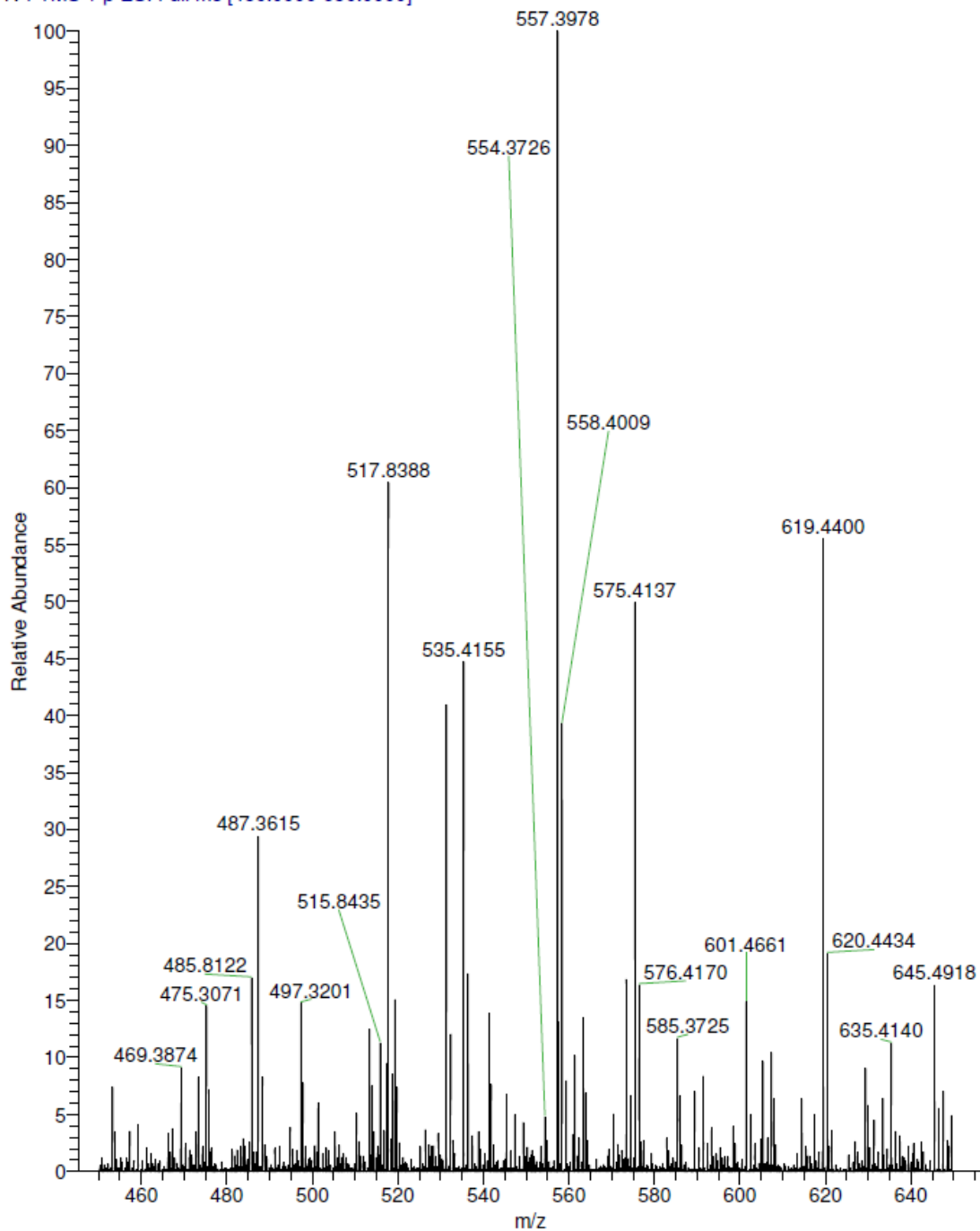


Figure S34: High-resolution mass spectrum of compound 3f.

C:\Xcalibur\1\HA-863

10/27/20 14:53:36

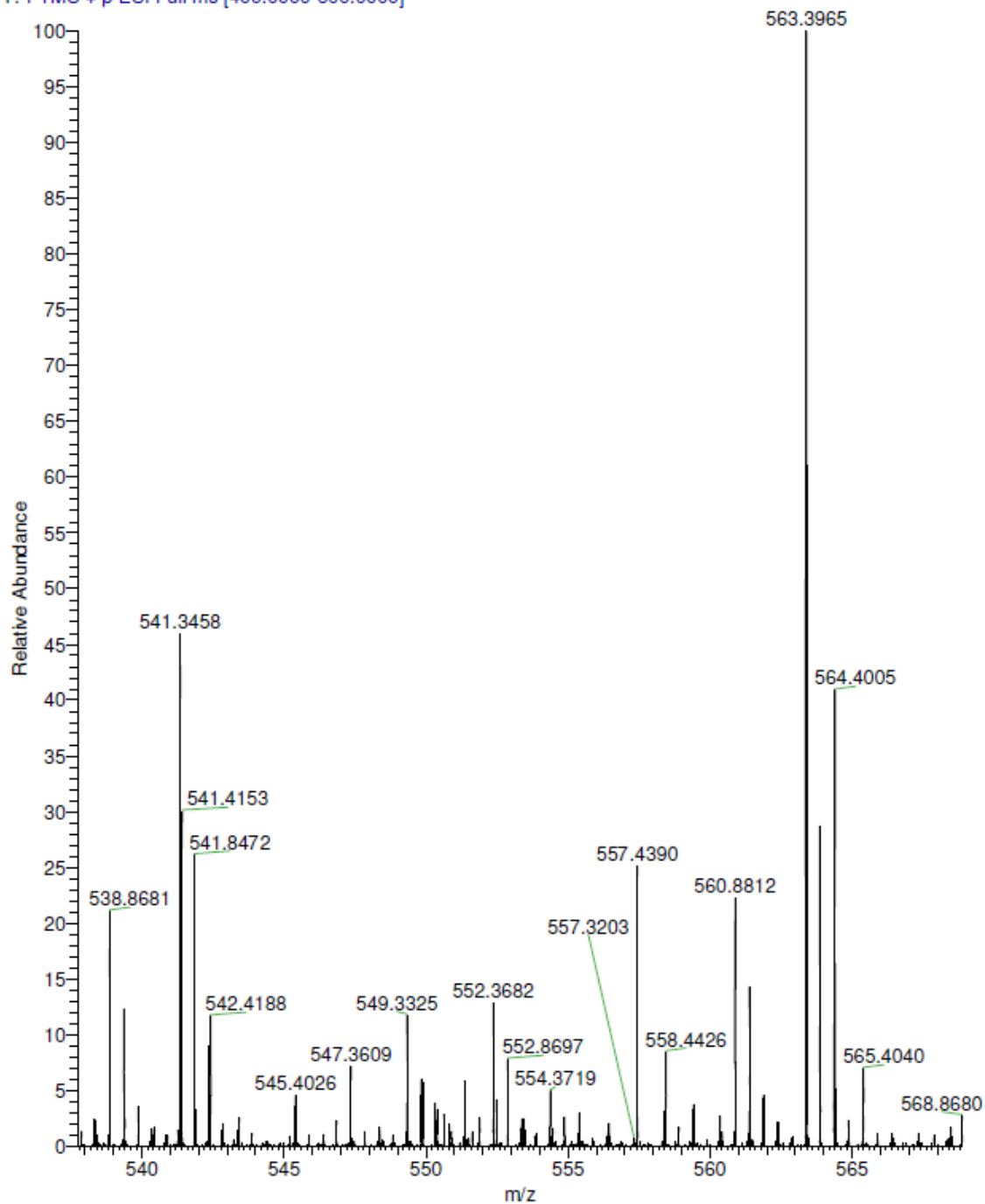
HA-863 #24 RT: 0.74 AV: 1 NL: 4.67E6
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Figure S35: High-resolution mass spectrum of compound 4a.

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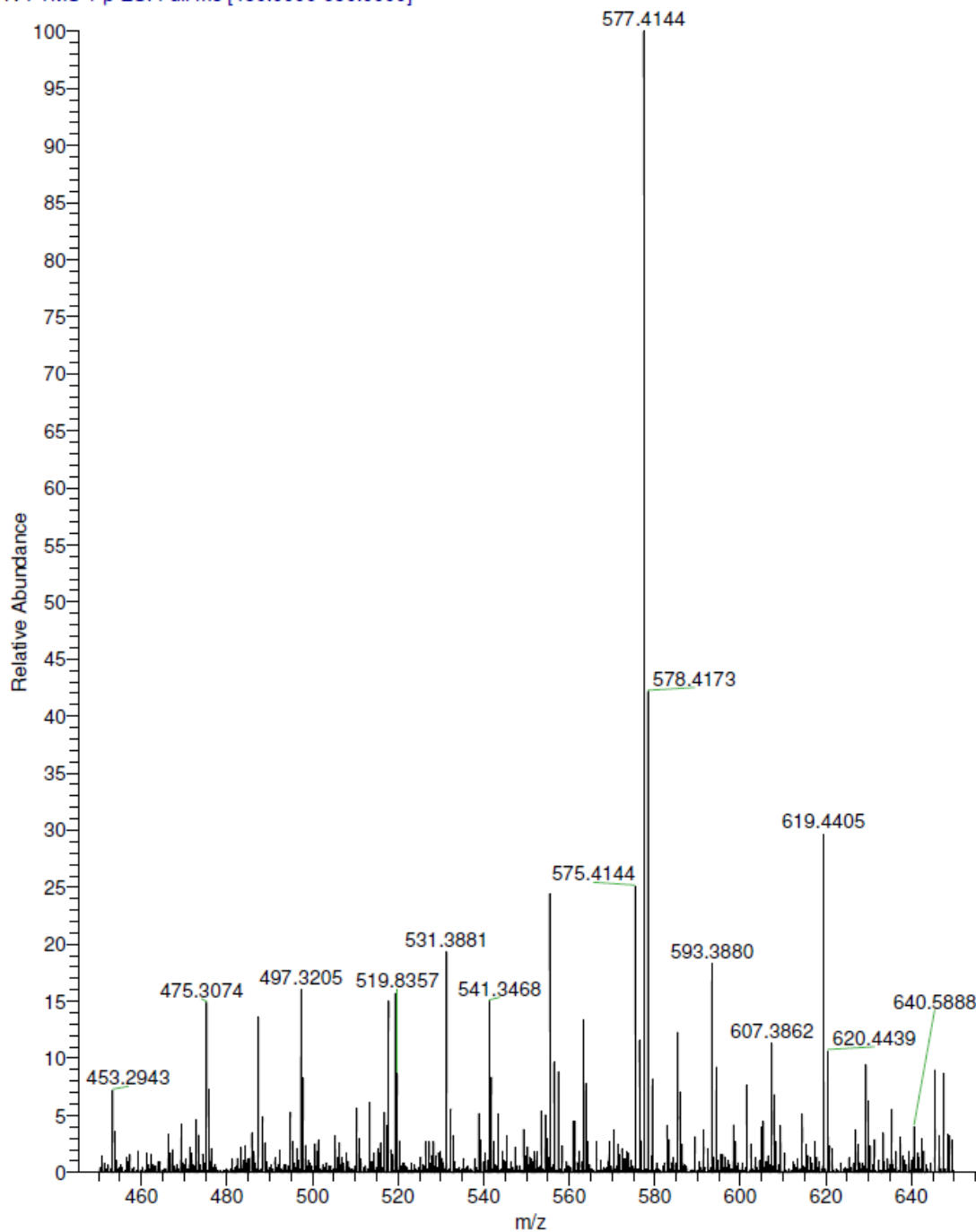


Figure S36: High-resolution mass spectrum of compound 4b.

C:\Xcalibur...\Holder-061020\HA-750

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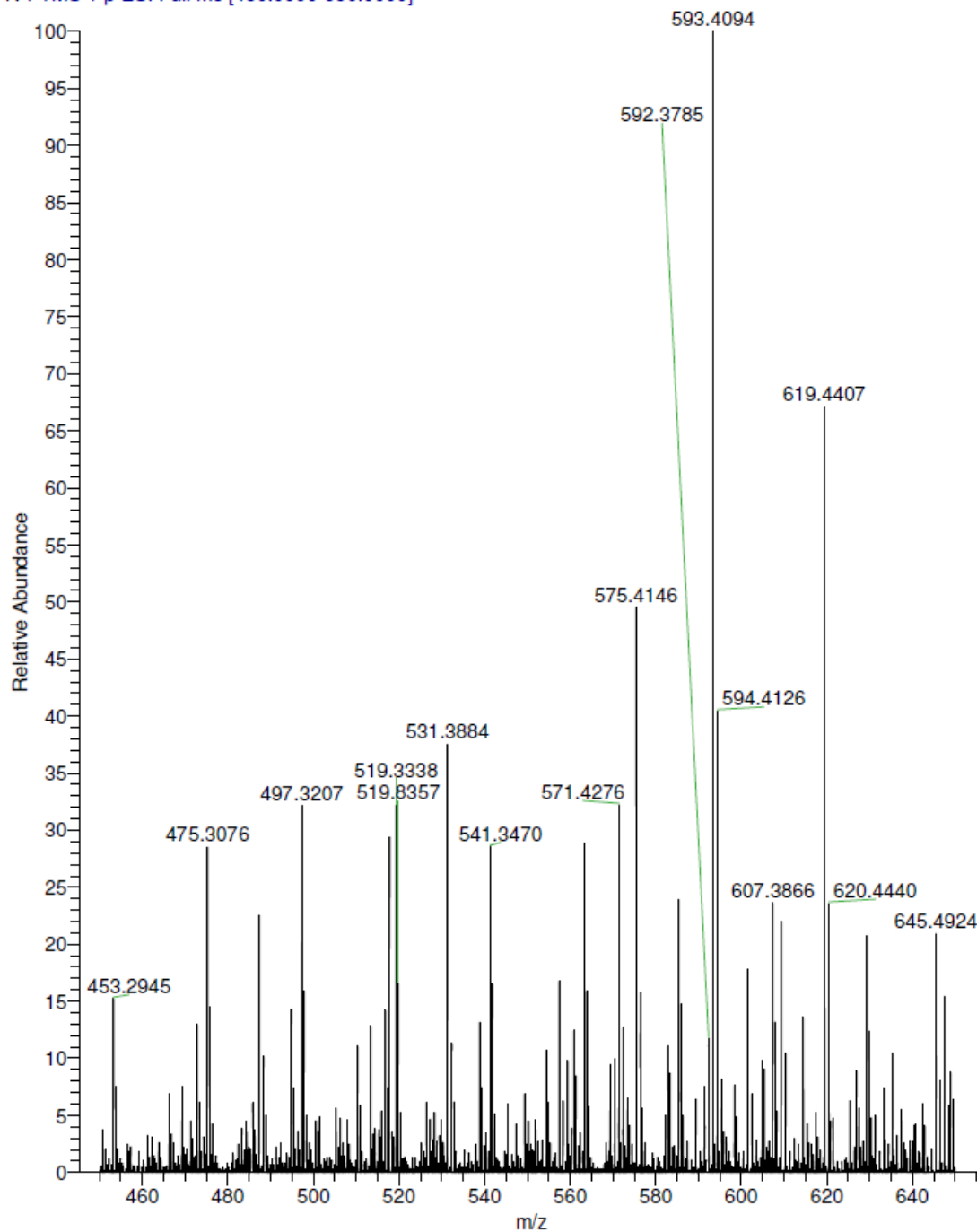


Figure S37: High-resolution mass spectrum of compound 4c.

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10/06/20 14:48:54

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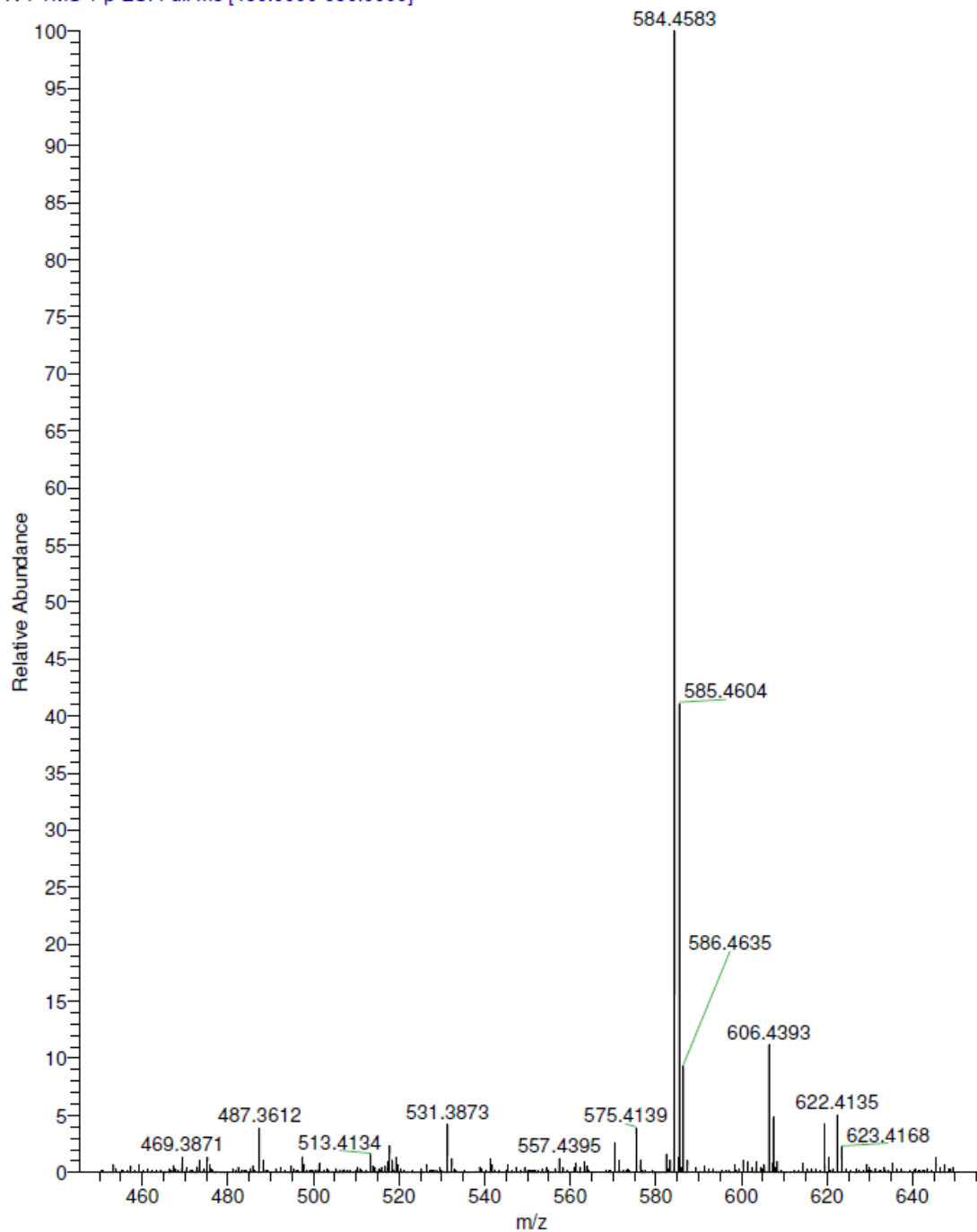


Figure S38: High-resolution mass spectrum of compound 4d.

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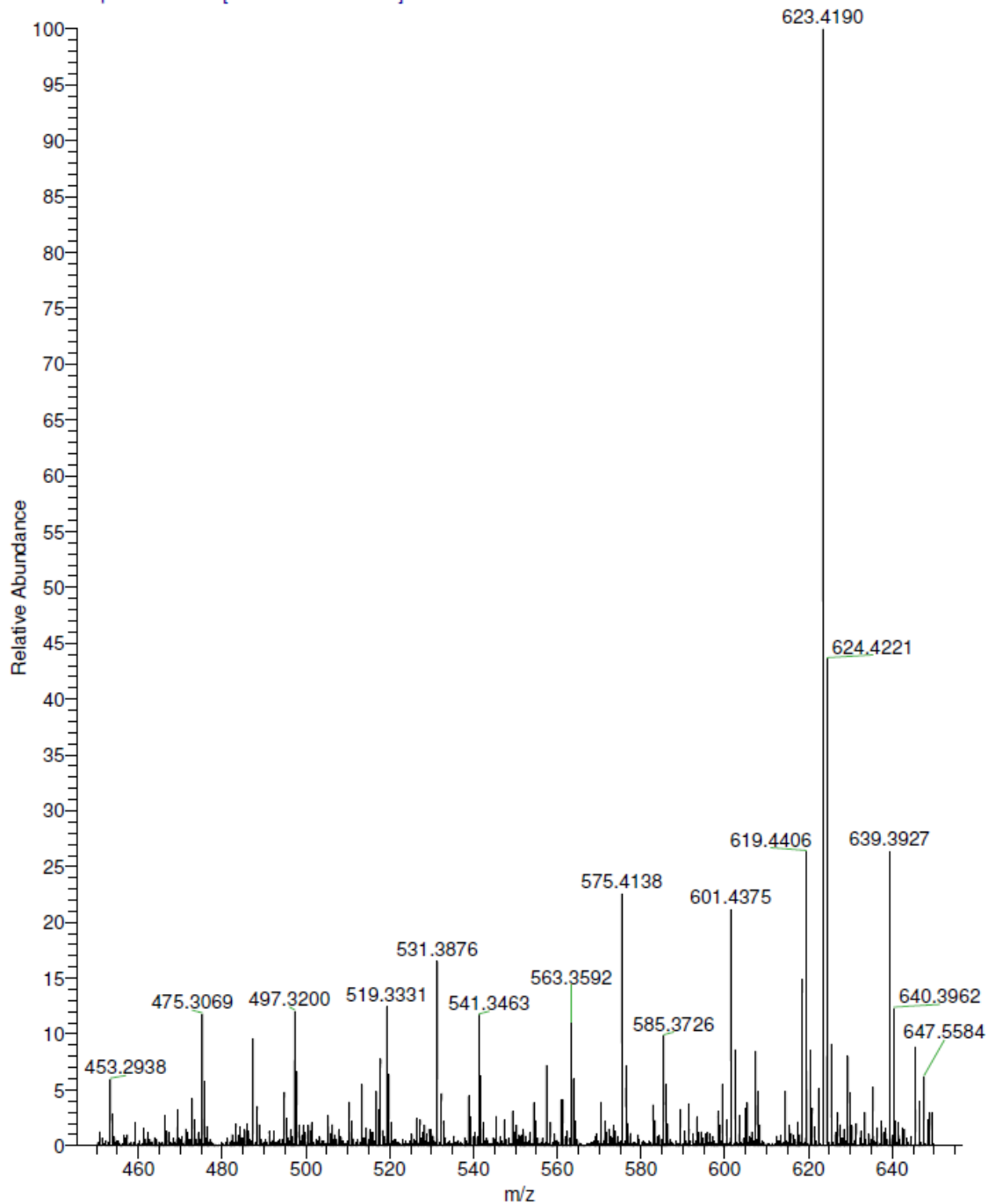


Figure S39: High-resolution mass spectrum of compound 4e.

C:\Xcalibur...\Helder-061020\HA-769

10/06/20 11:52:40

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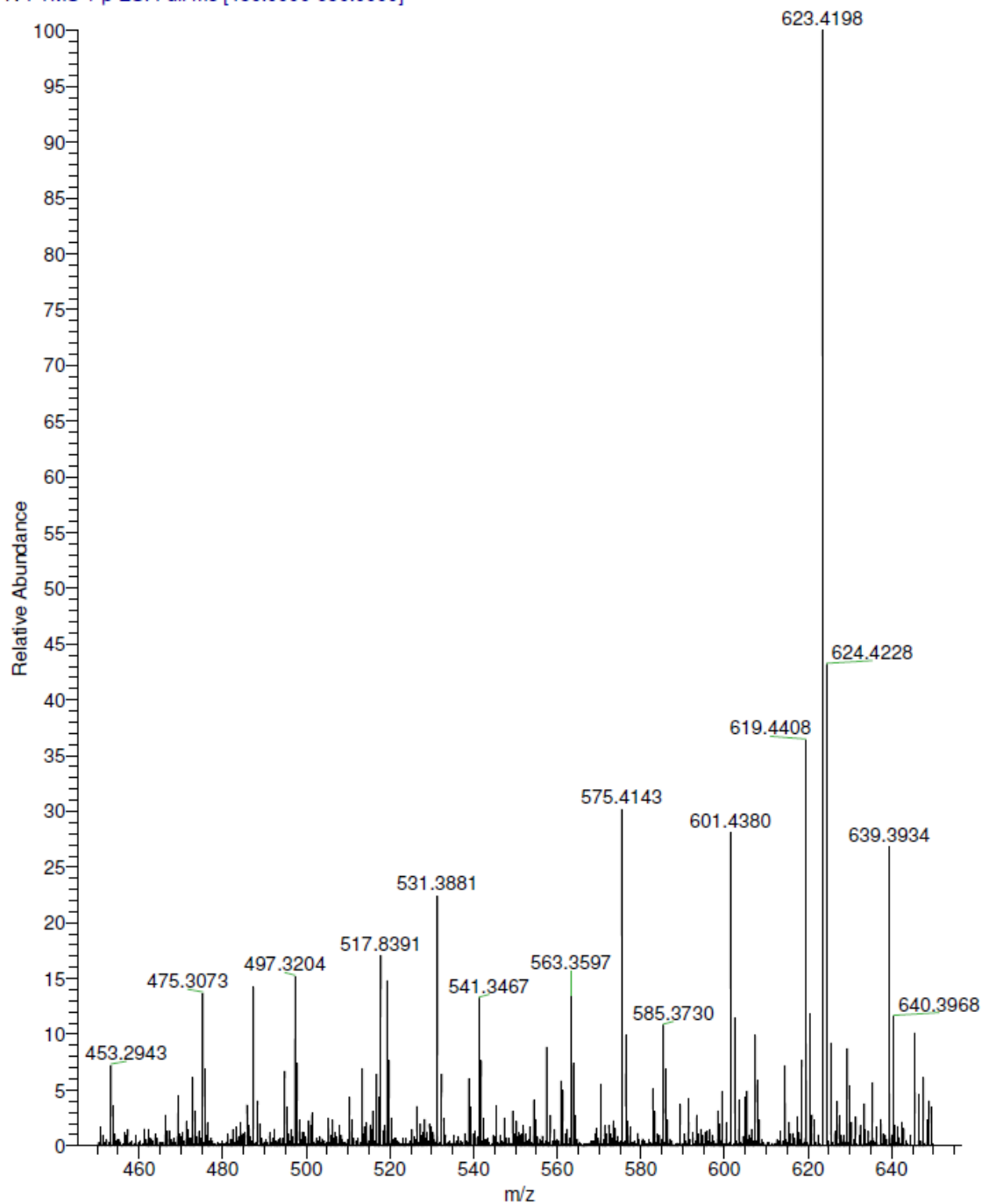


Figure S40: High-resolution mass spectrum of compound 4f.

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10/06/20 12:29:26

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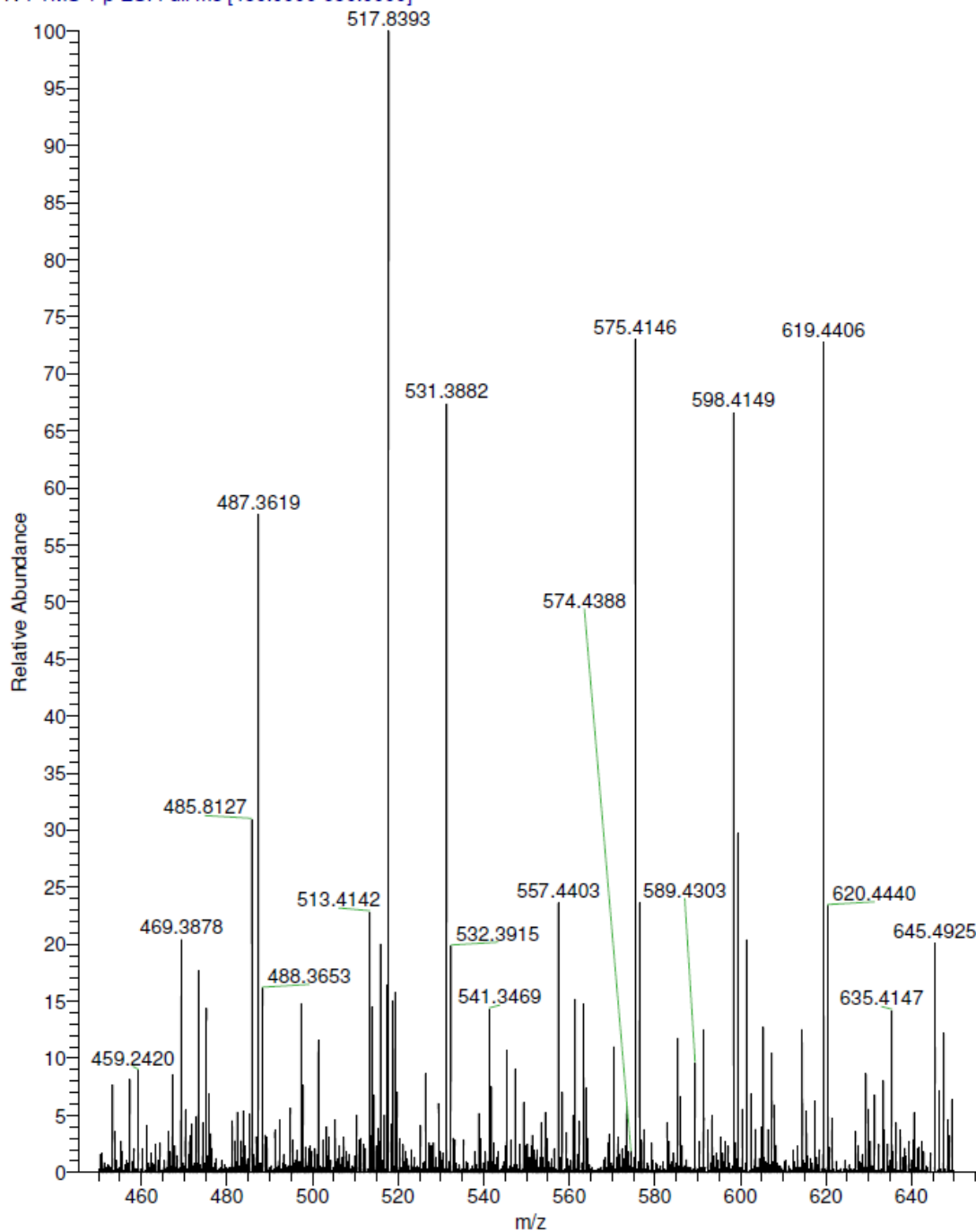


Figure S41: High-resolution mass spectrum of compound 5b.

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10/06/20 12:13:23

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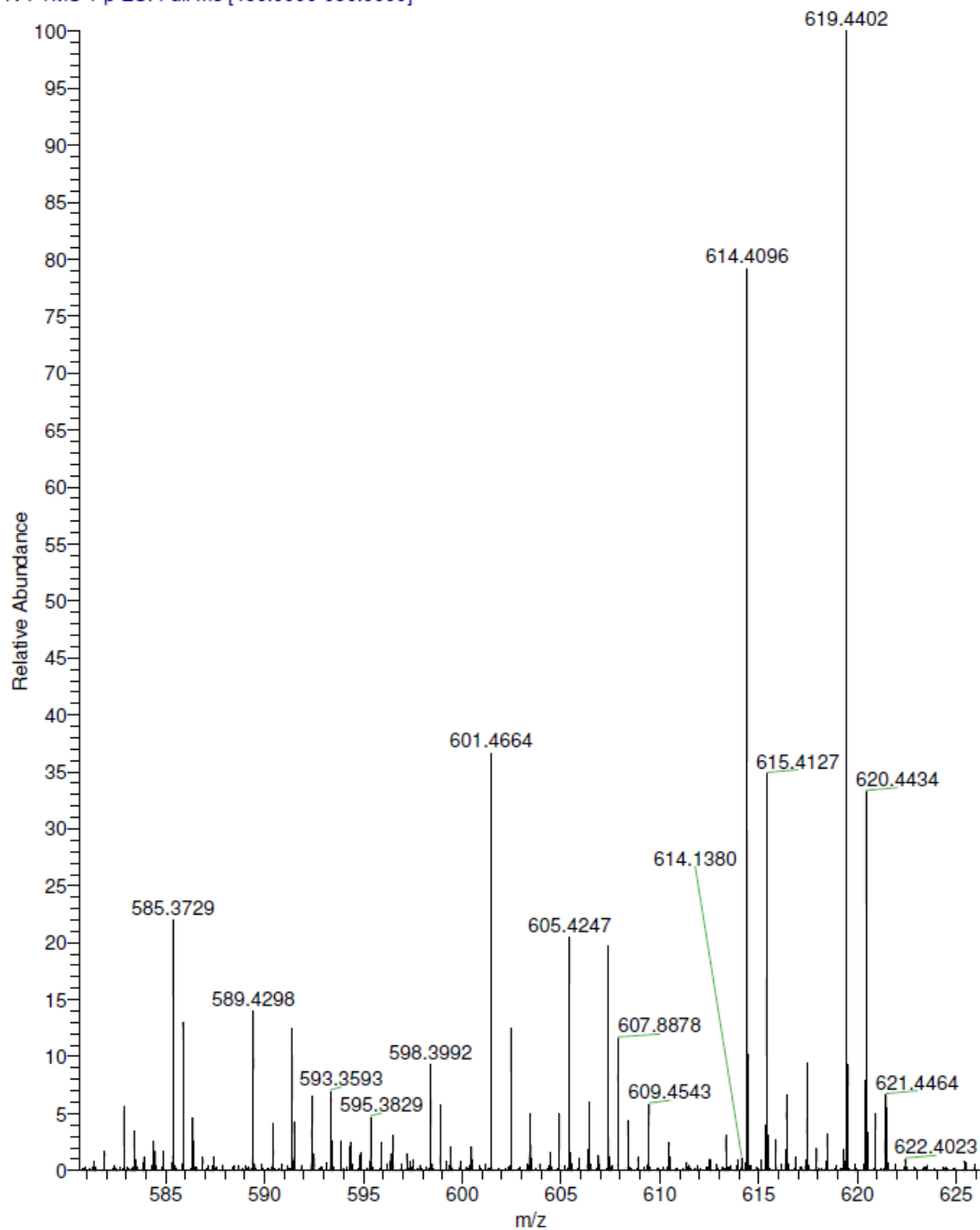


Figure S42: High-resolution mass spectrum of compound 5c.