

Supplementary Material

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

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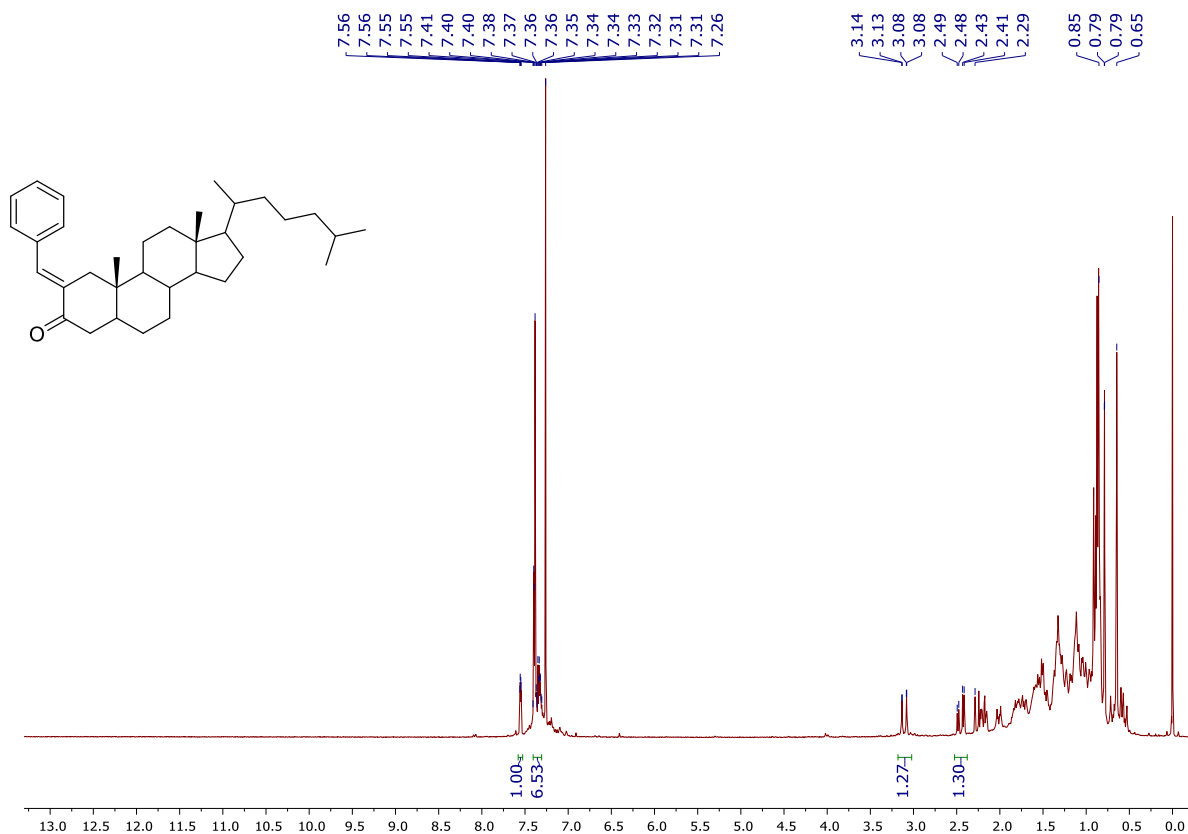
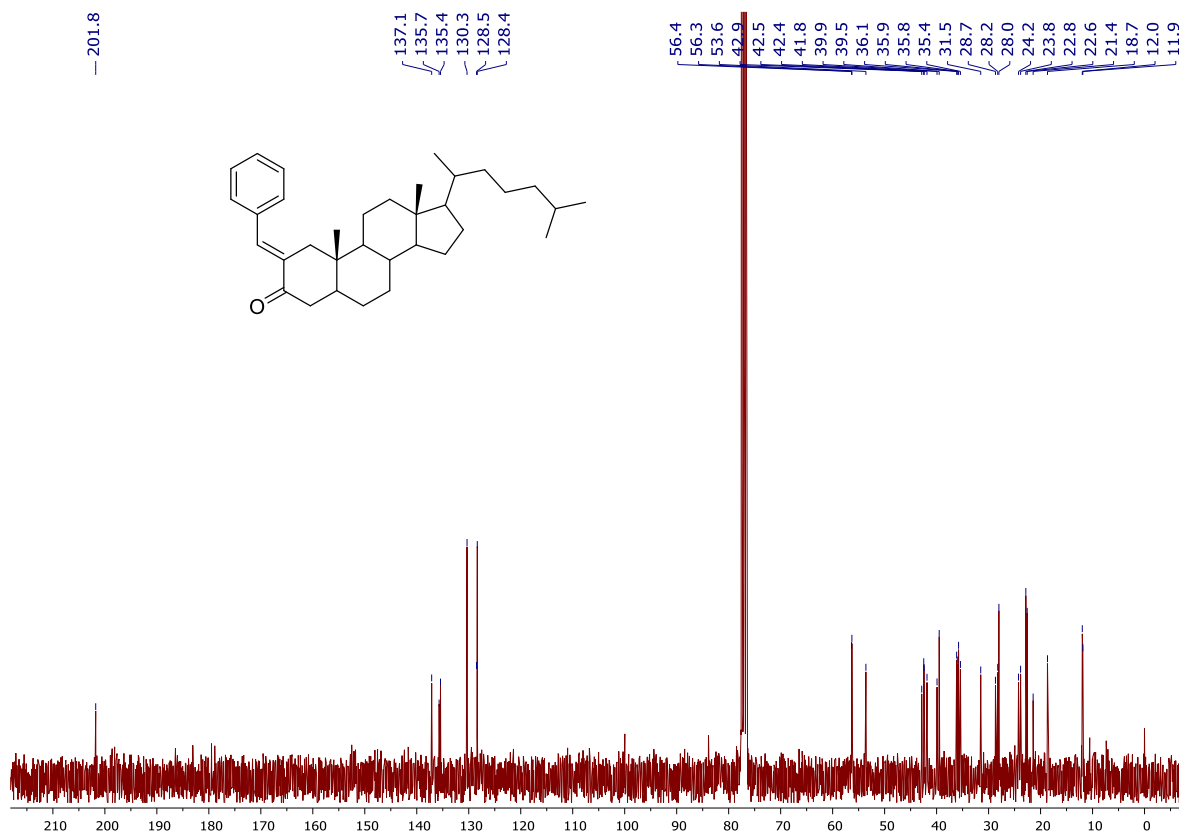
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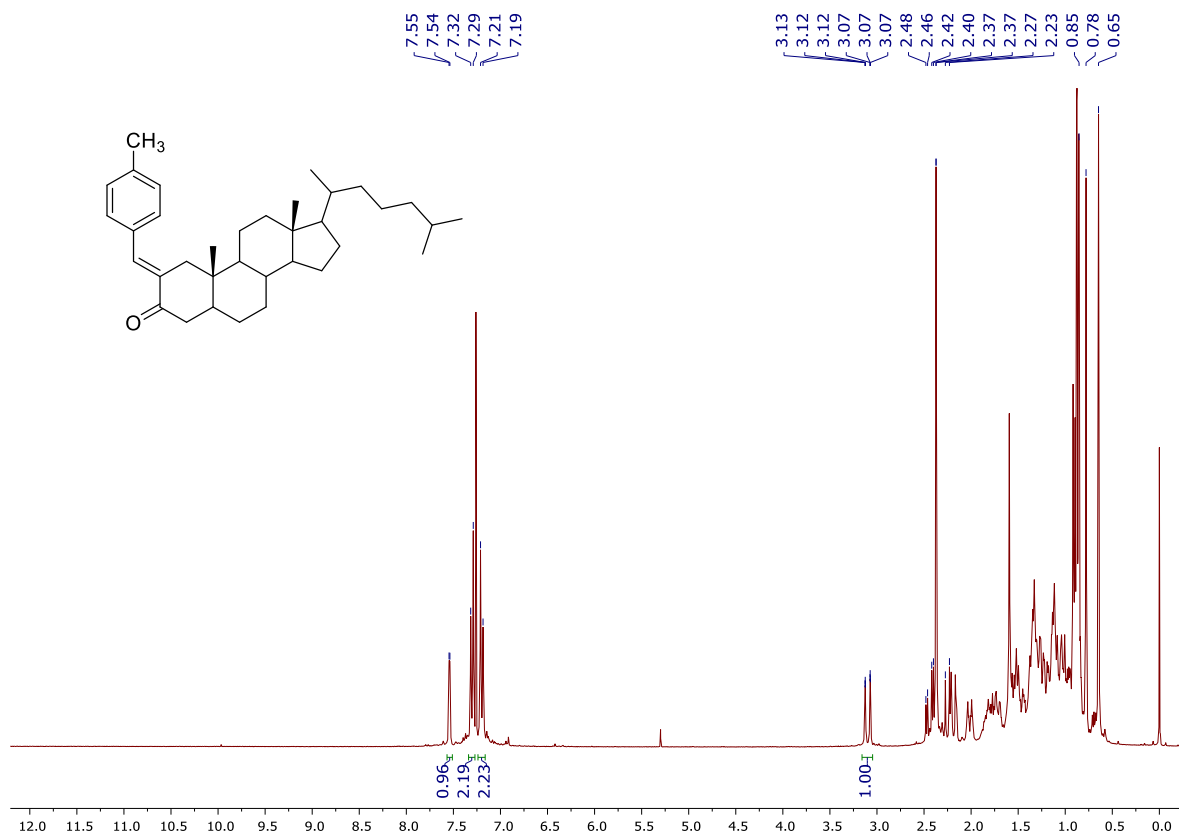
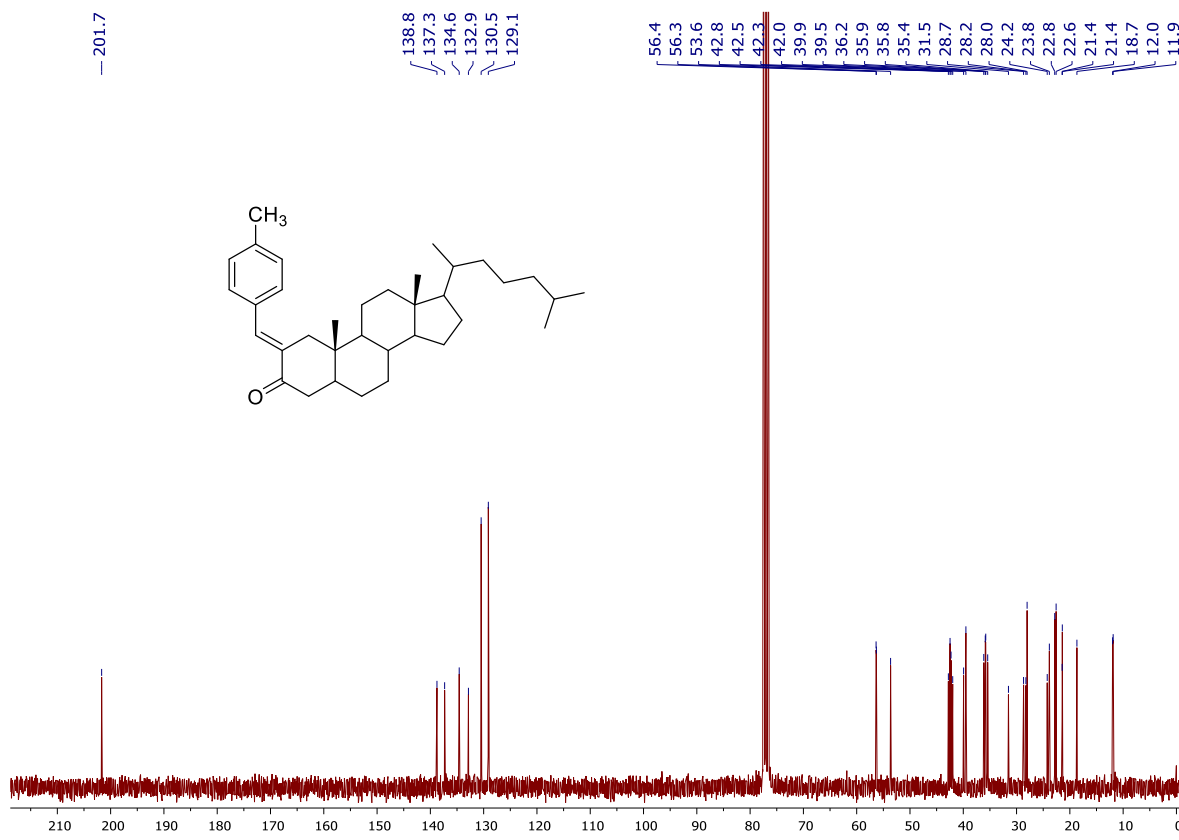
¹H- and ¹³C-NMR of compounds

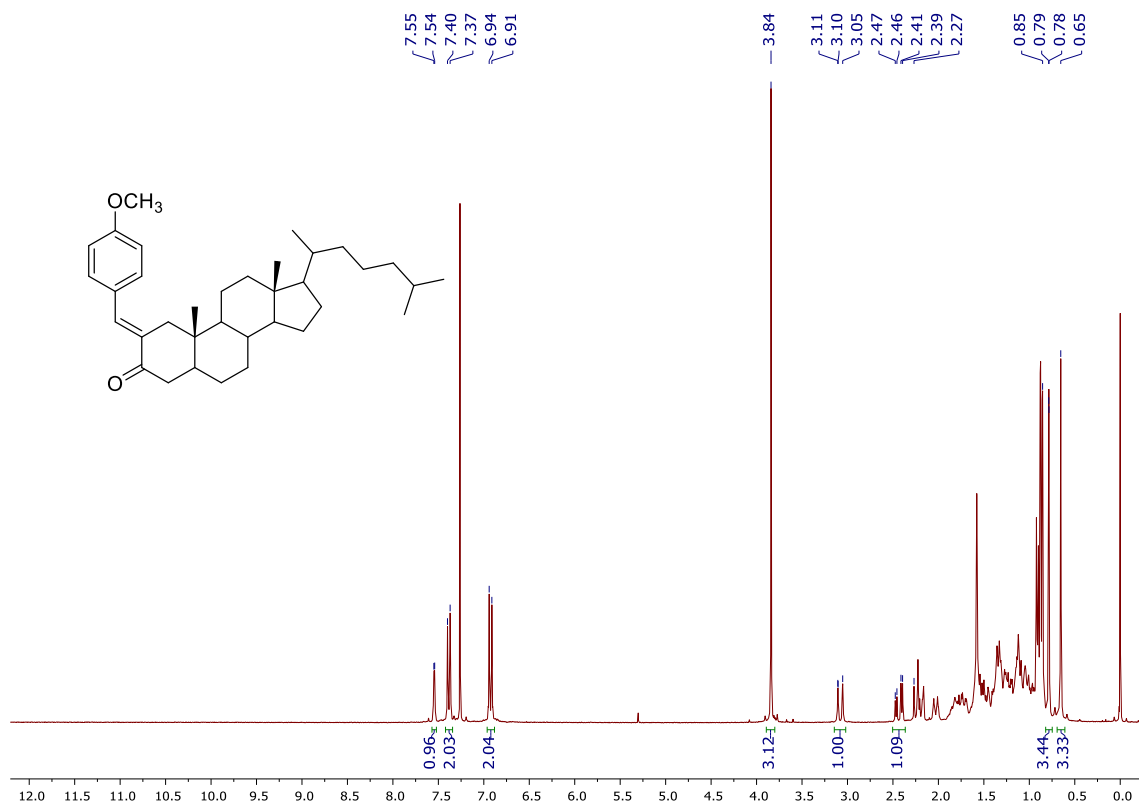
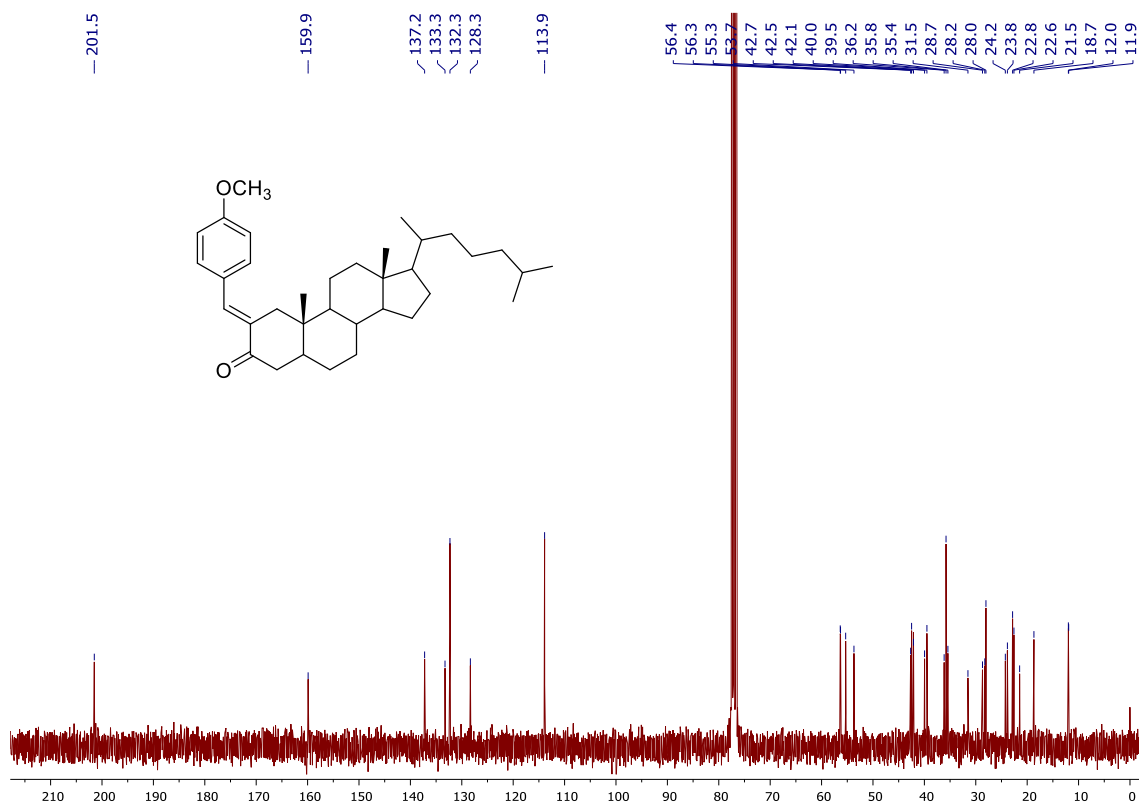
Compound (3a)	S2
Compound (3b)	S3
Compound (3c)	S4
Compound (3d)	S5
Compound (3e)	S6
Compound (3f)	S7
Mixture of diastereomers (4a)	S8
Mixture of diastereomers (4b)	S9
Mixture of diastereomers (4c)	S10
Mixture of diastereomers (4d)	S11
Mixture of diastereomers (4e)	S12
Mixture of diastereomers (4f)	S13
Compound (5b)	S14
Compound (5c)	S15

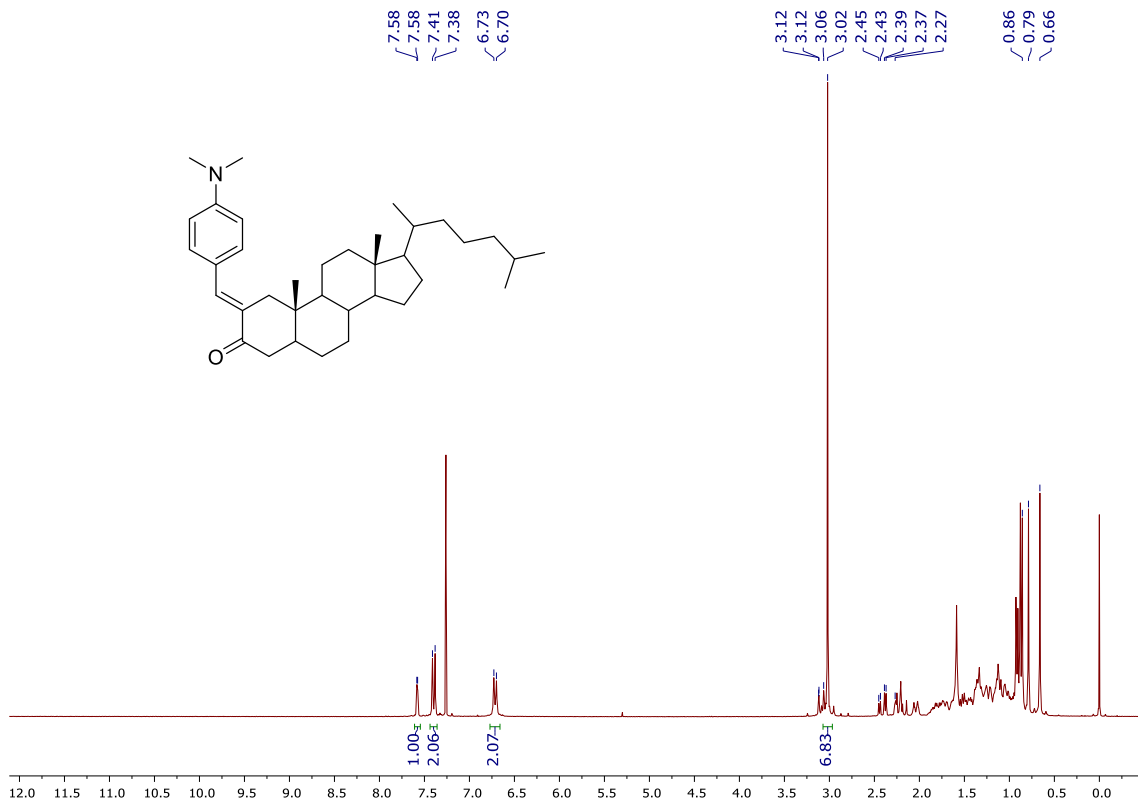
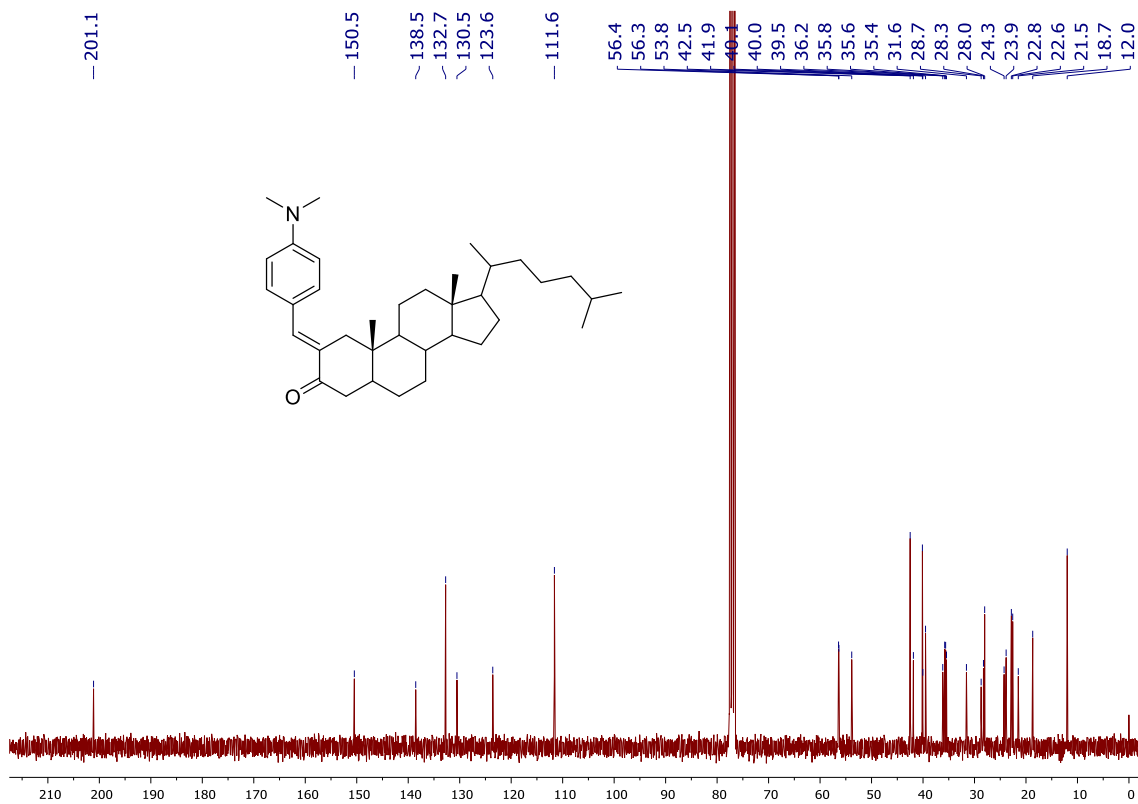
High-resolution mass spectra (HRMS) of compounds

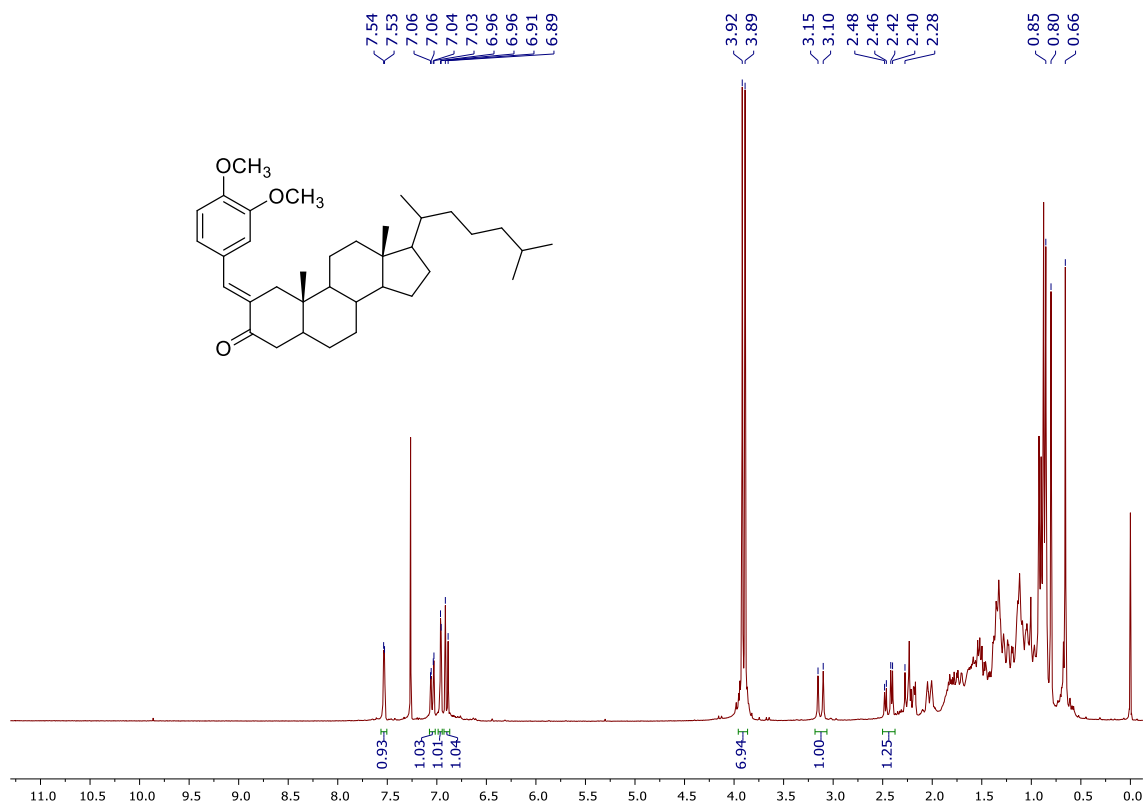
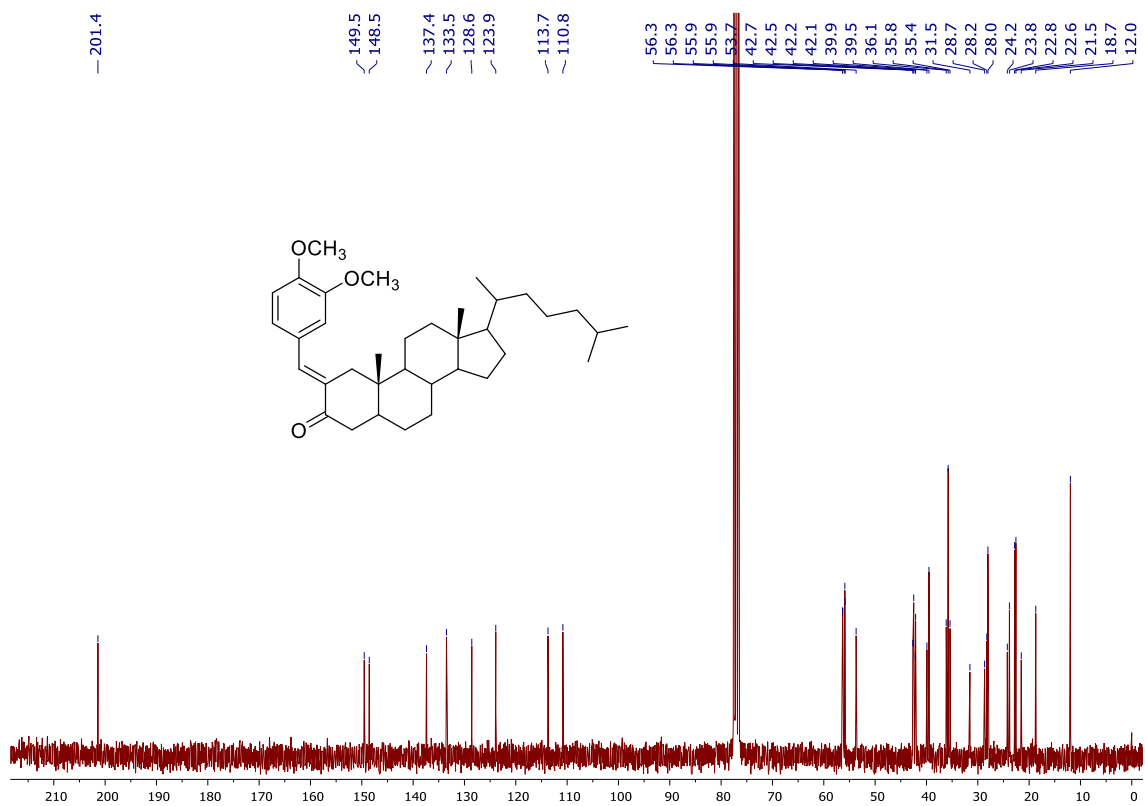
Compound (3a)	S16
Compound (3b)	S17
Compound (3c)	S18
Compound (3d)	S19
Compound (3e)	S20
Compound (3f)	S21
Mixture of diastereomers (4a)	S22
Mixture of diastereomers (4b)	S23
Mixture of diastereomers (4c)	S24
Mixture of diastereomers (4d)	S25
Mixture of diastereomers (4e)	S26
Mixture of diastereomers (4f)	S27
Compound (5b)	S28
Compound (5c)	S29

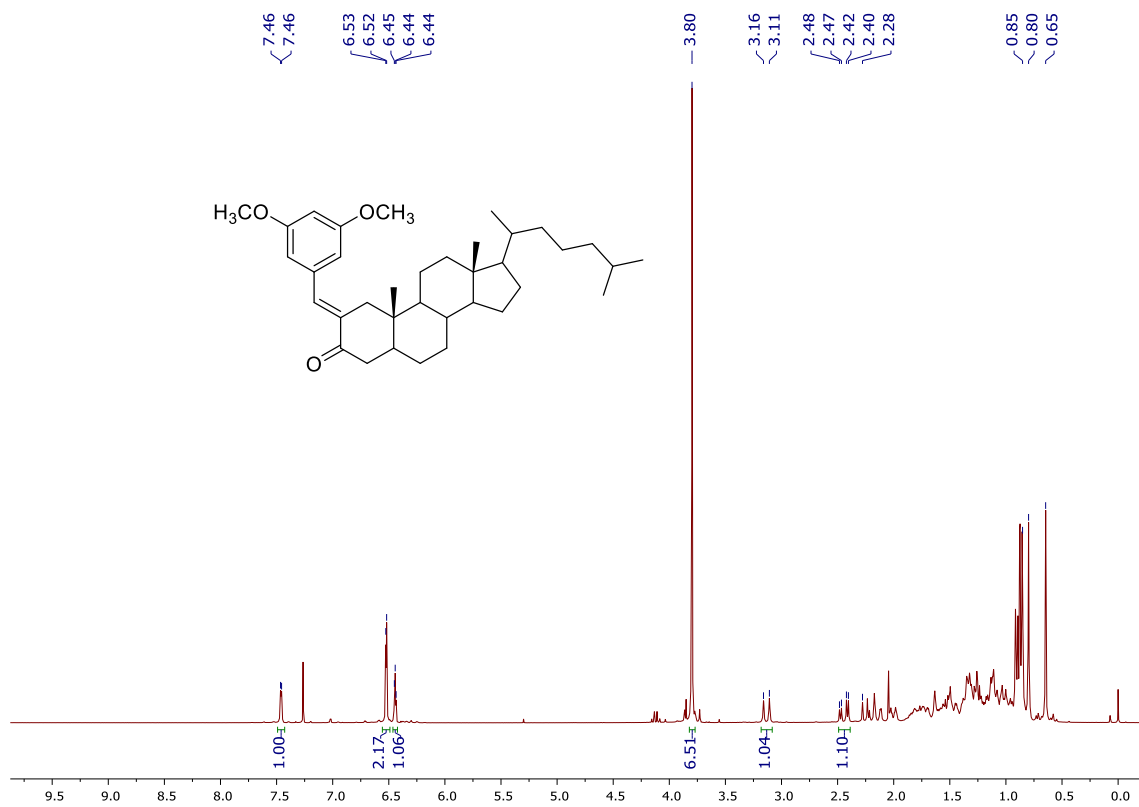
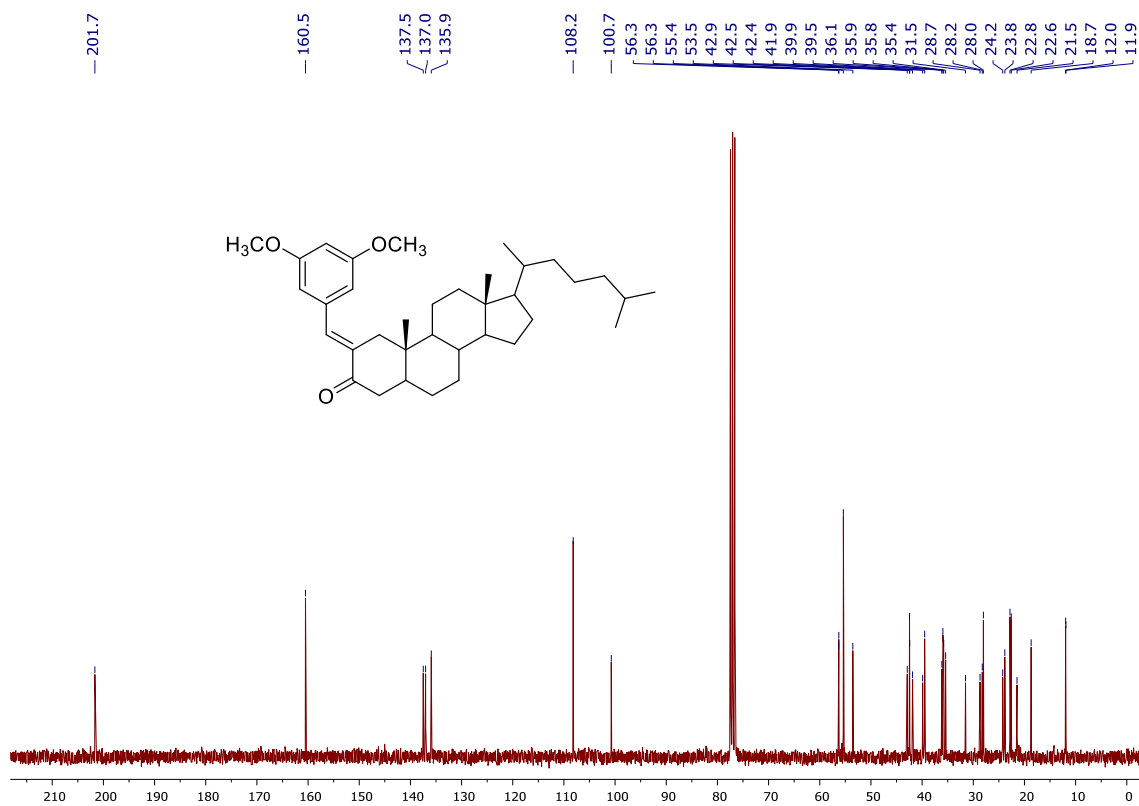
Figure S1: $^1\text{H-NMR}$ (300 MHz, CDCl_3) of compound 3a.Figure S2: $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) of compound 3a.

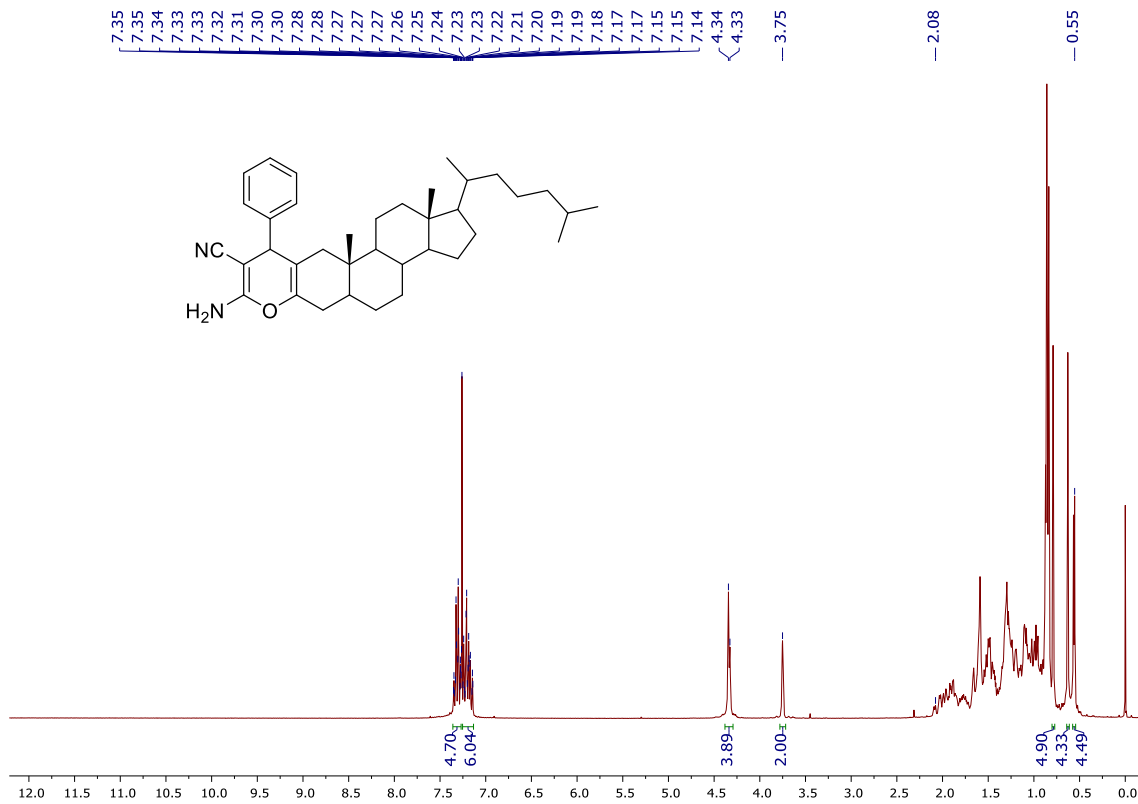
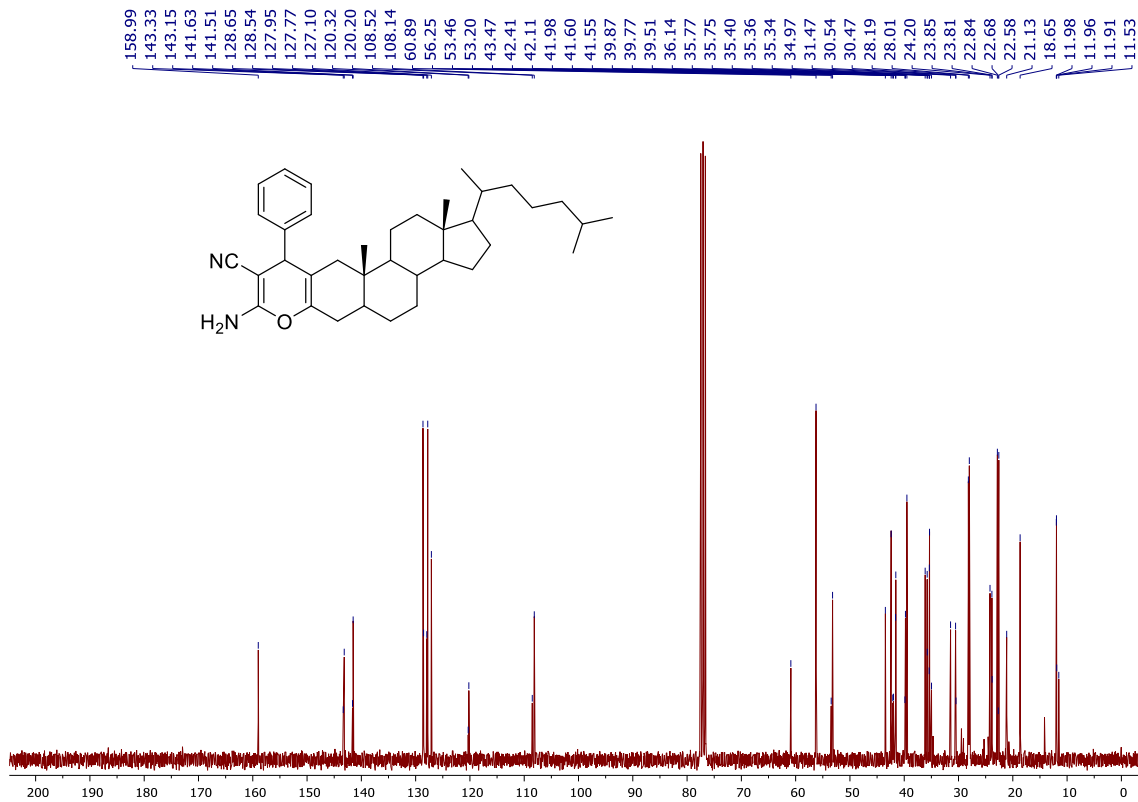
Figure S3: ¹H-NMR (300 MHz, CDCl₃) of compound **3b**.Figure S4: ¹³C-NMR (75 MHz, CDCl₃) of compound **3b**.

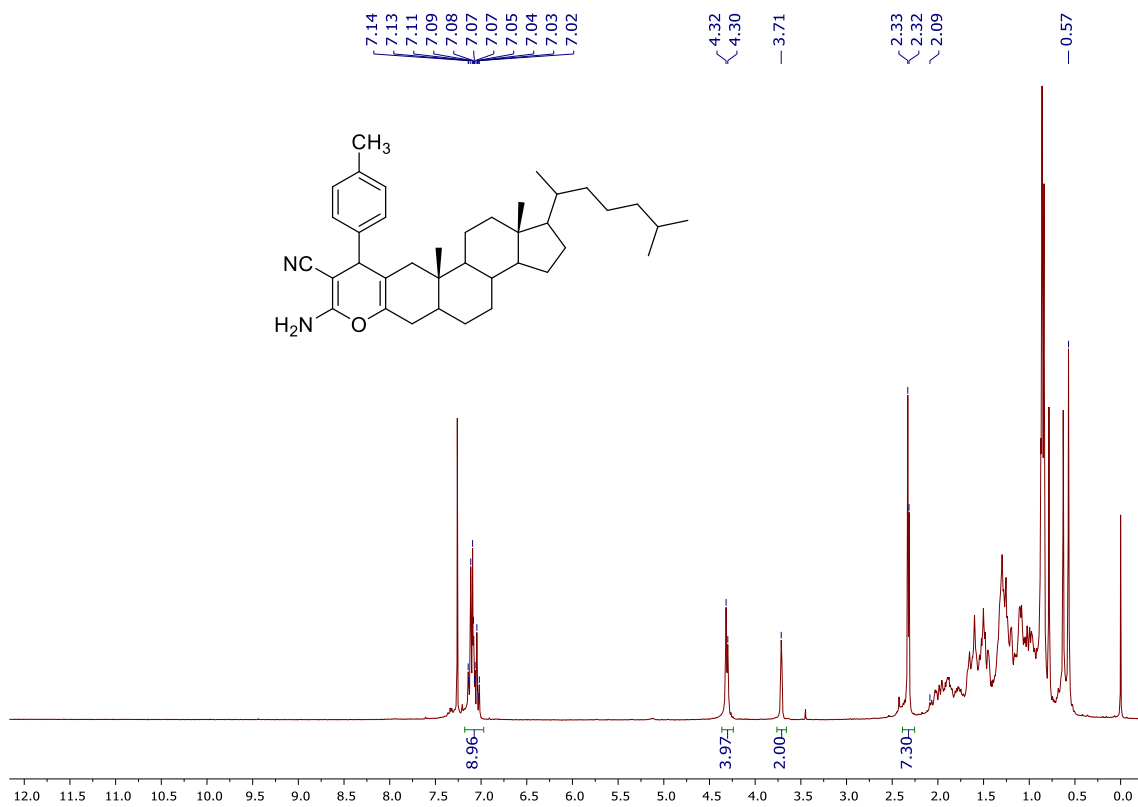
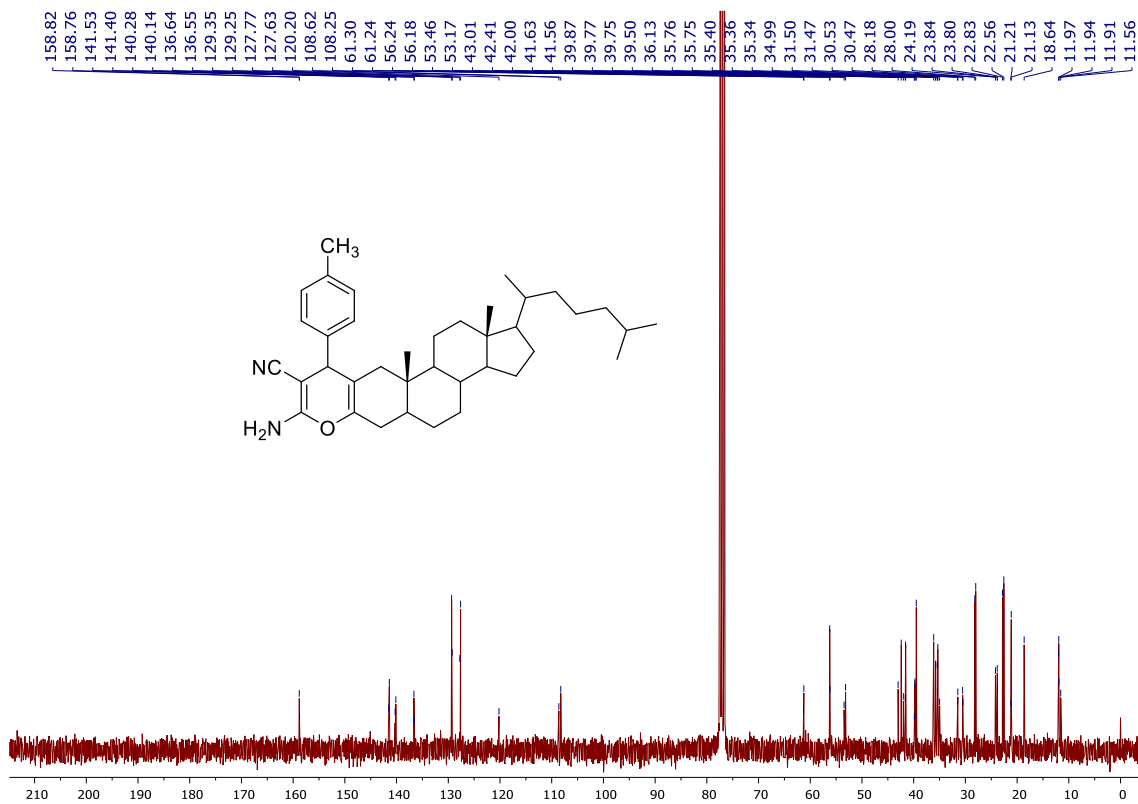
Figure S5: ¹H-NMR (300 MHz, CDCl₃) of compound **3c**.Figure S6: ¹³C-NMR (75 MHz, CDCl₃) of compound **3c**.

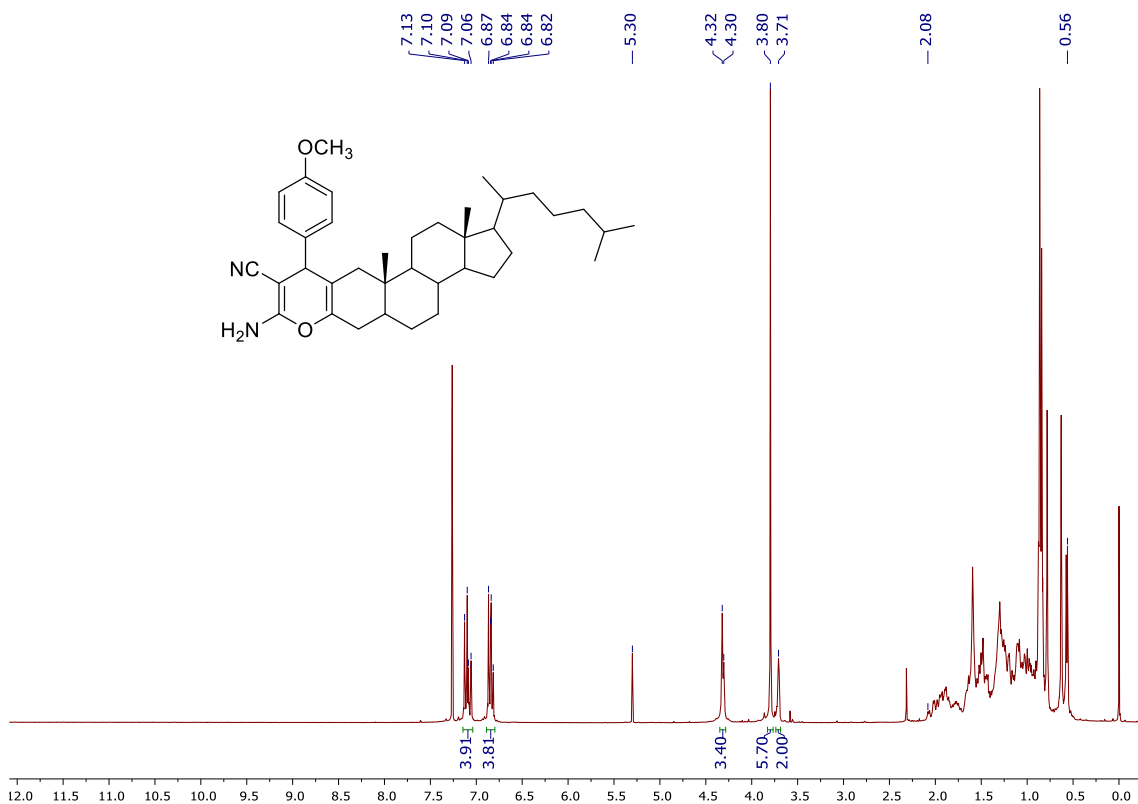
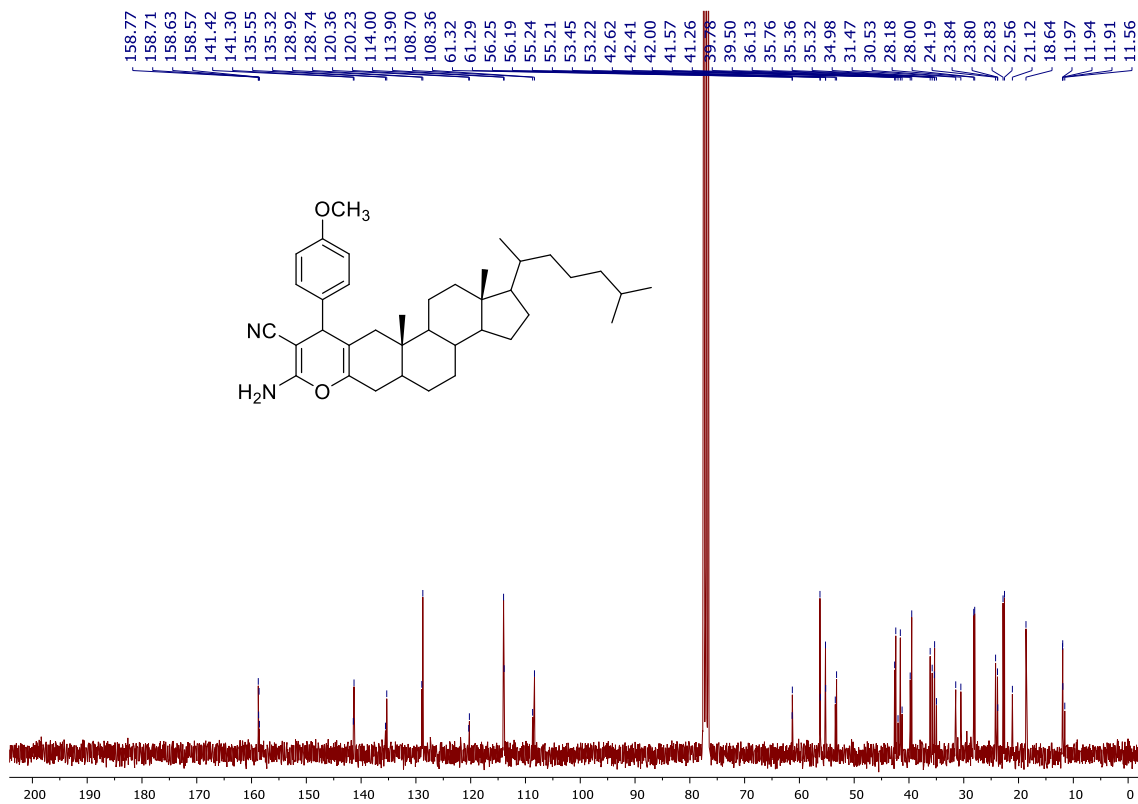
**Figure S7:** ¹H-NMR (300 MHz, CDCl₃) of compound 3d.**Figure S8:** ¹³C-NMR (75 MHz, CDCl₃) of compound 3d.

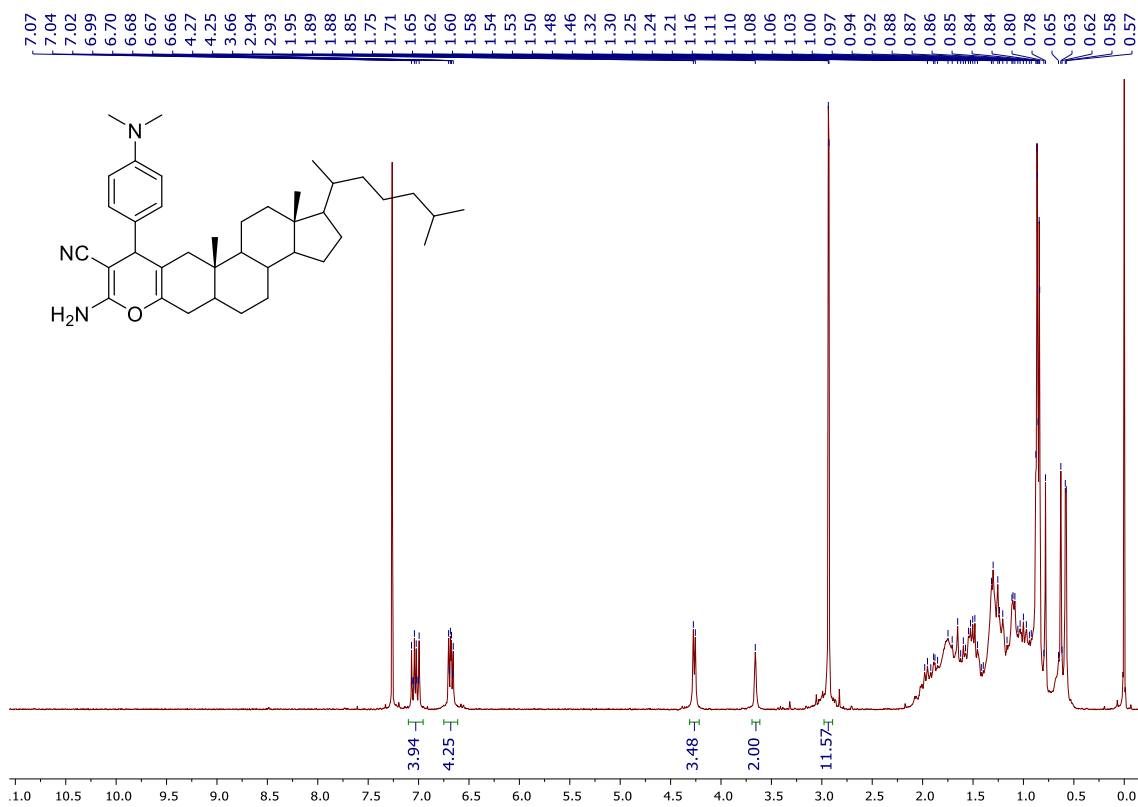
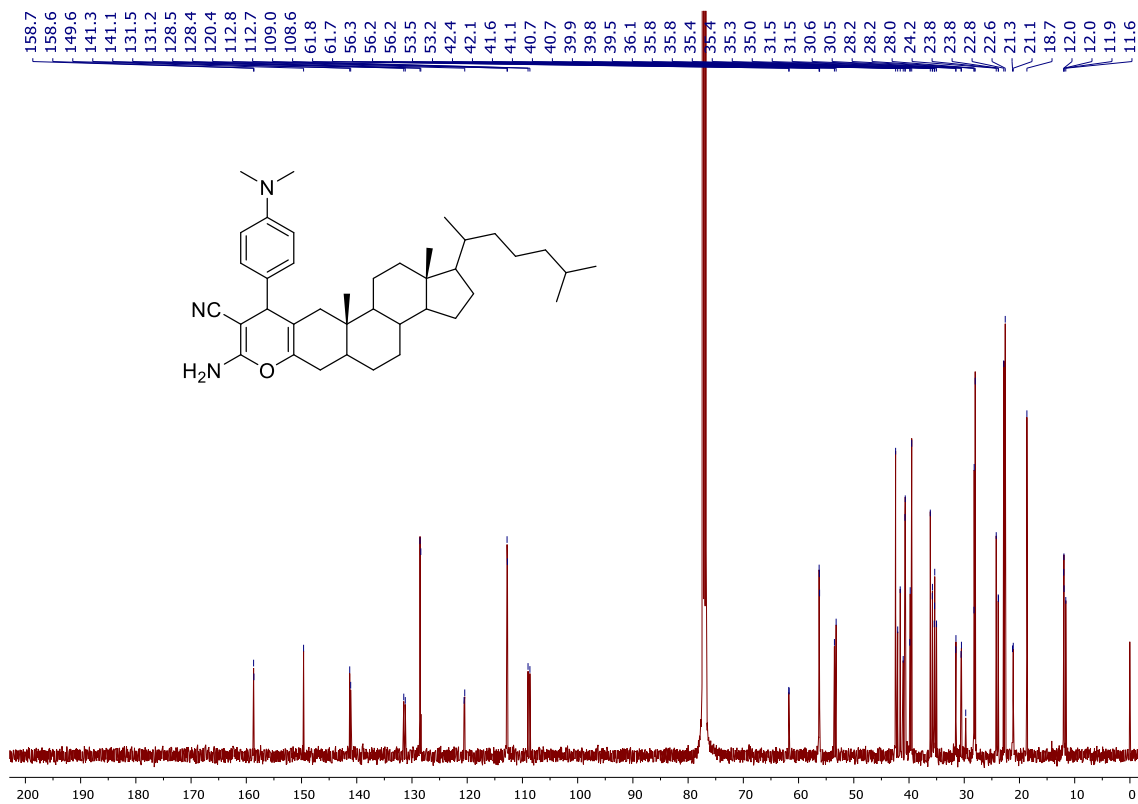
Figure S9: $^1\text{H-NMR}$ (300 MHz, CDCl_3) of compound 3e.Figure S10: $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) of compound 3e.

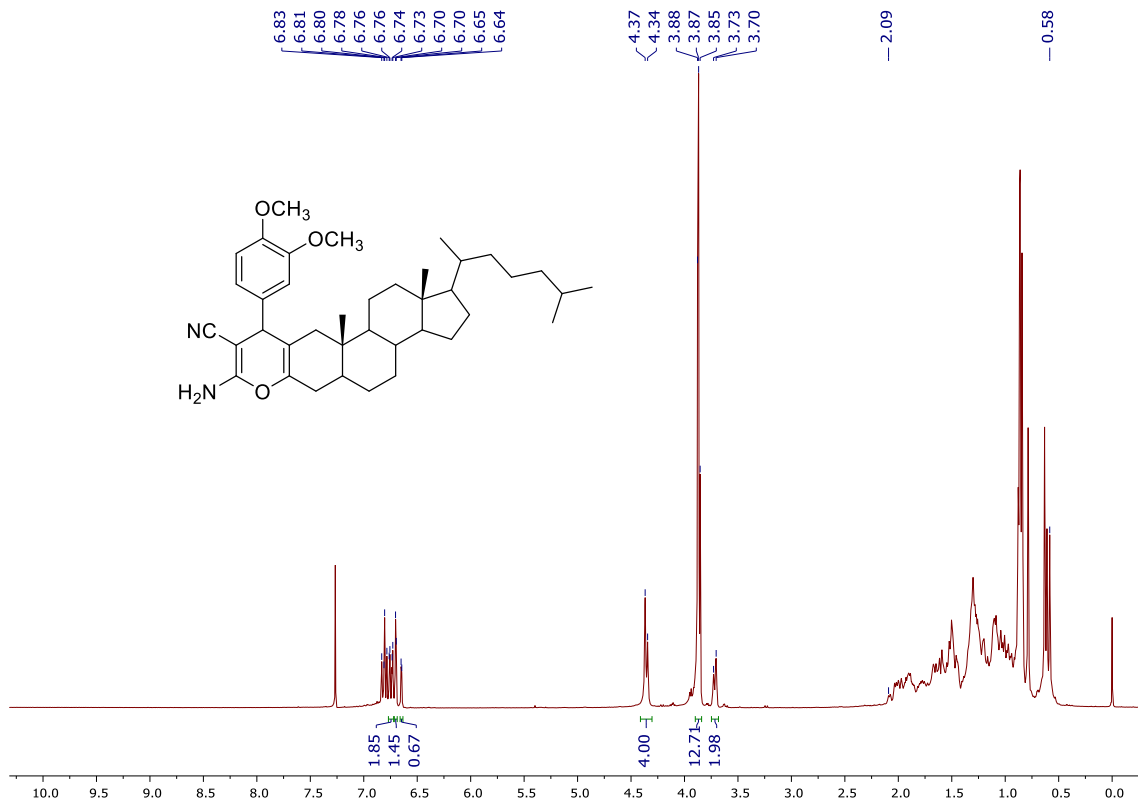
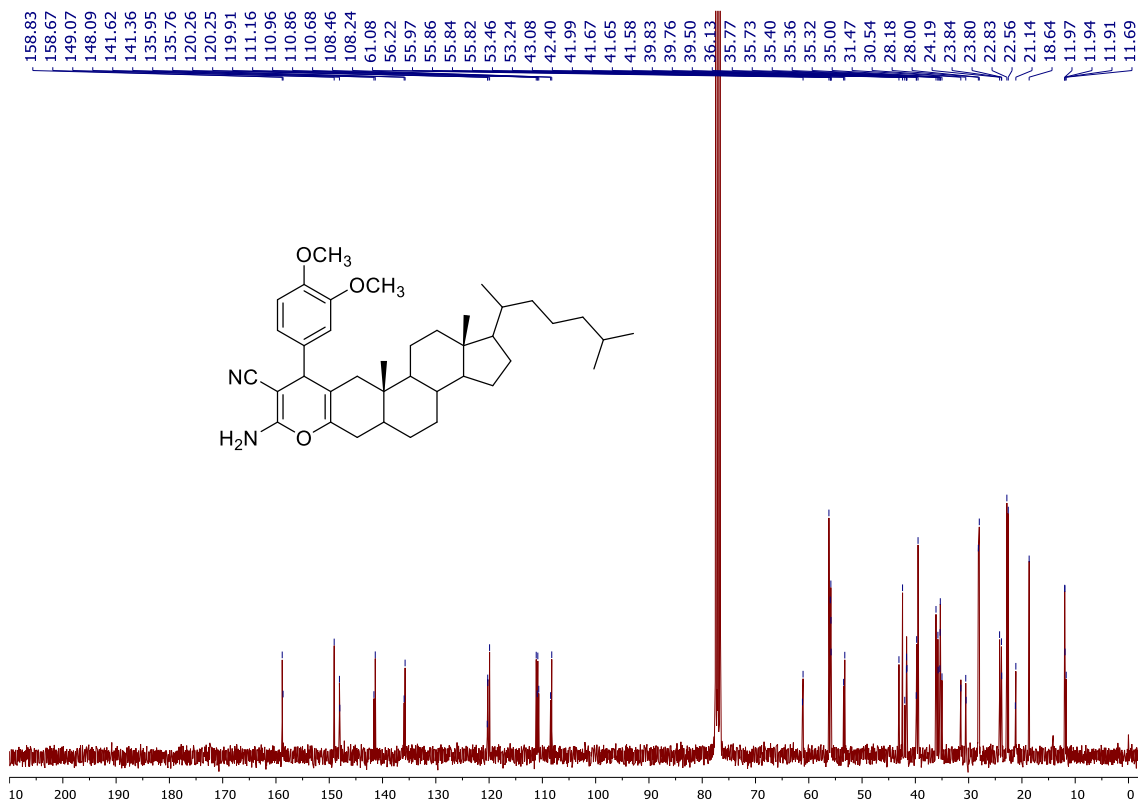
Figure S11: ¹H-NMR (300 MHz, CDCl₃) of compound **3f**.Figure S12: ¹³C-NMR (75 MHz, CDCl₃) of compound **3f**.

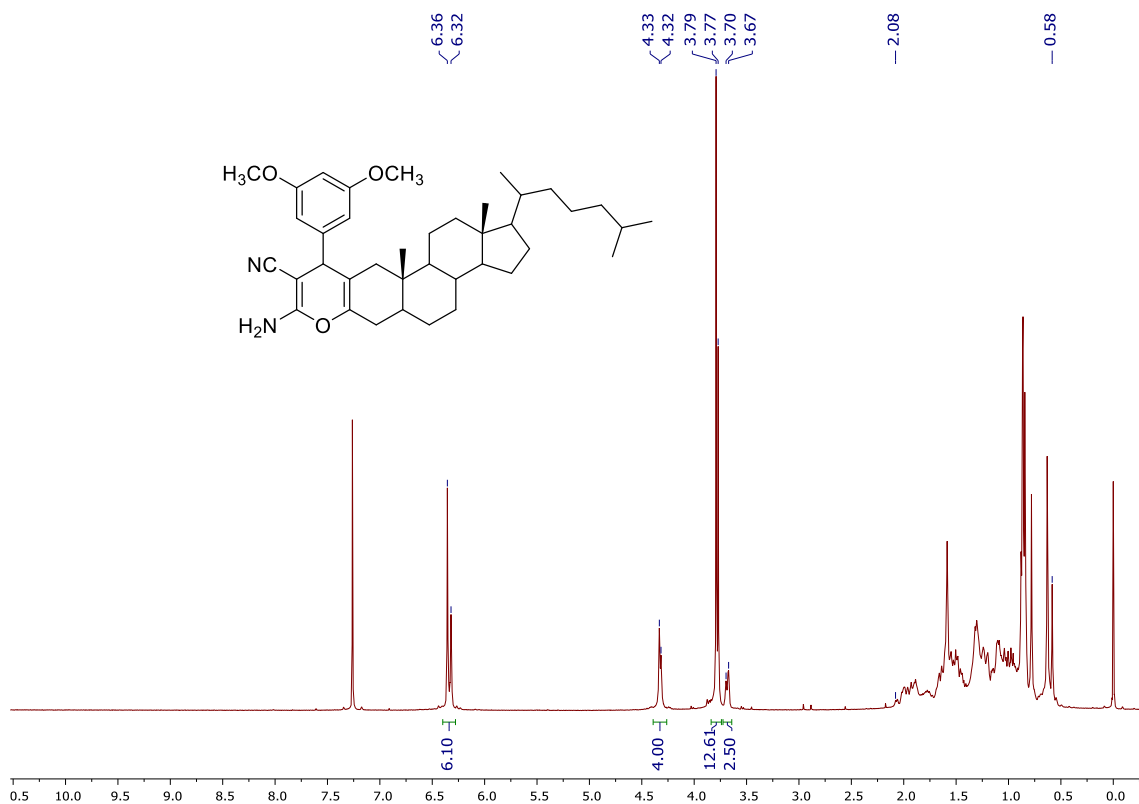
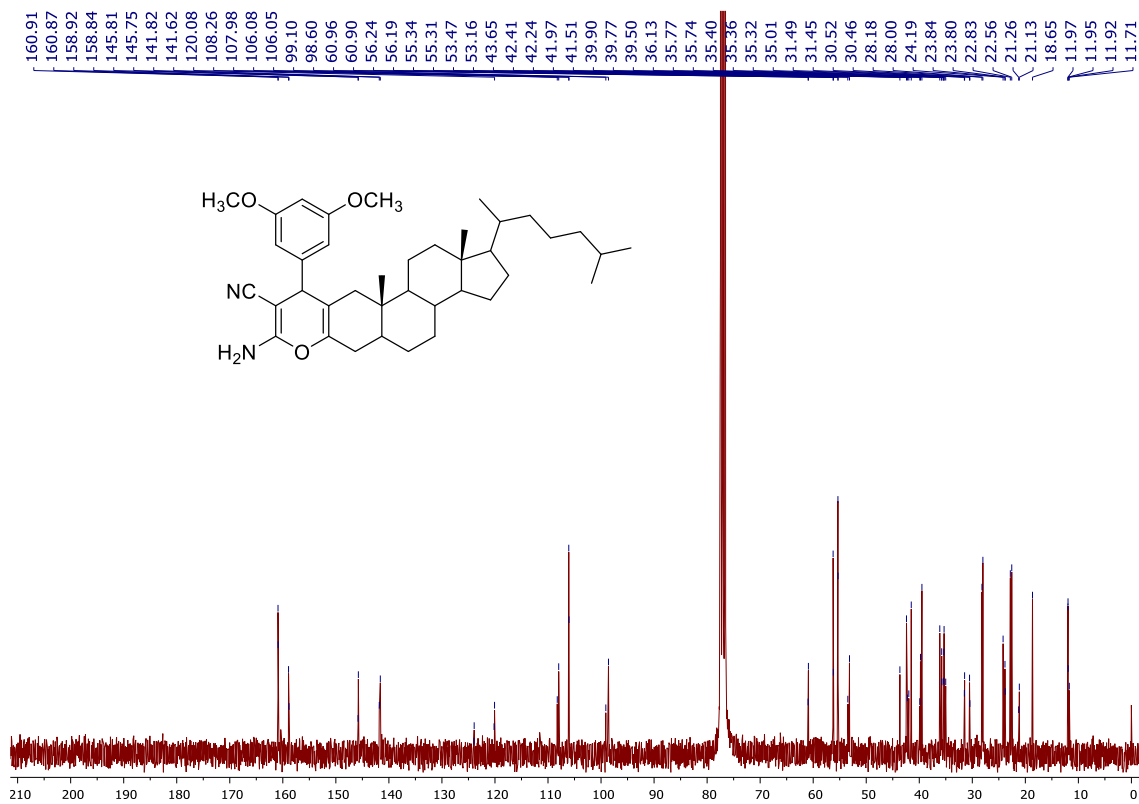
Figure S13: ¹H-NMR (300 MHz, CDCl₃) of compound 4a.Figure S14: ¹³C-NMR (75 MHz, CDCl₃) of compound 4a.

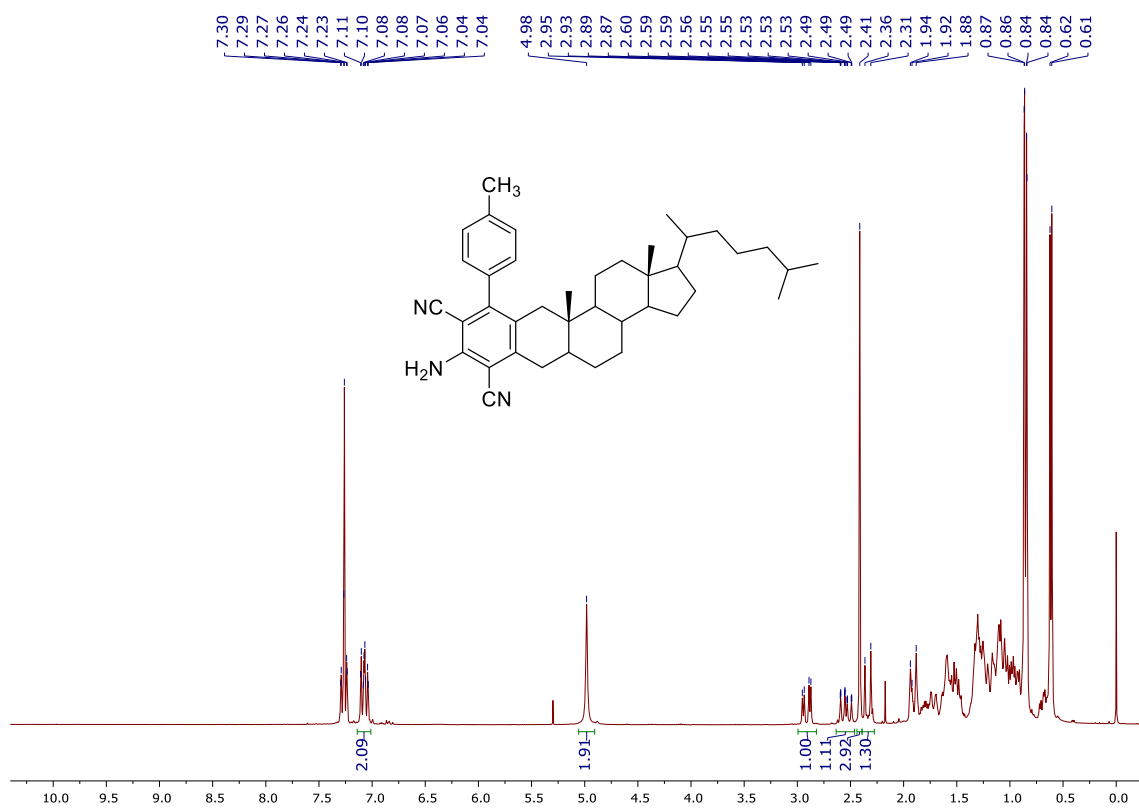
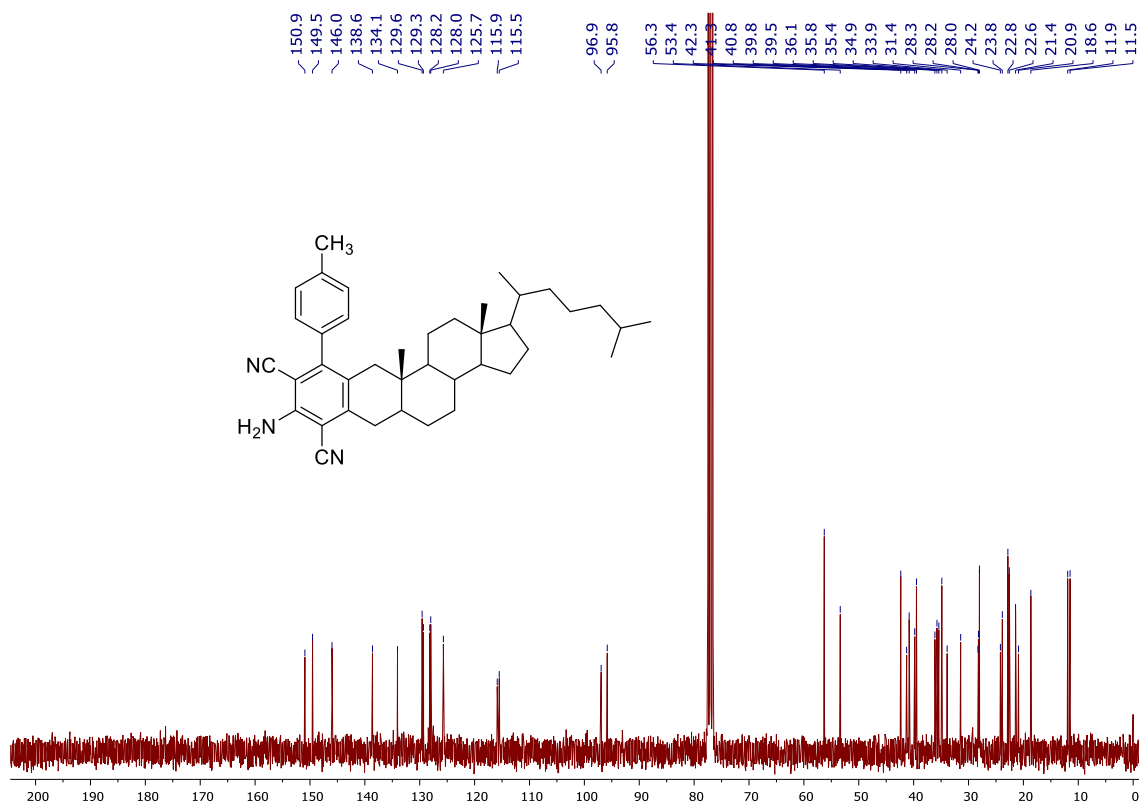
Figure S15: ¹H-NMR (300 MHz, CDCl₃) of compound **4b**.Figure S16: ¹³C-NMR (75 MHz, CDCl₃) of compound **4b**.

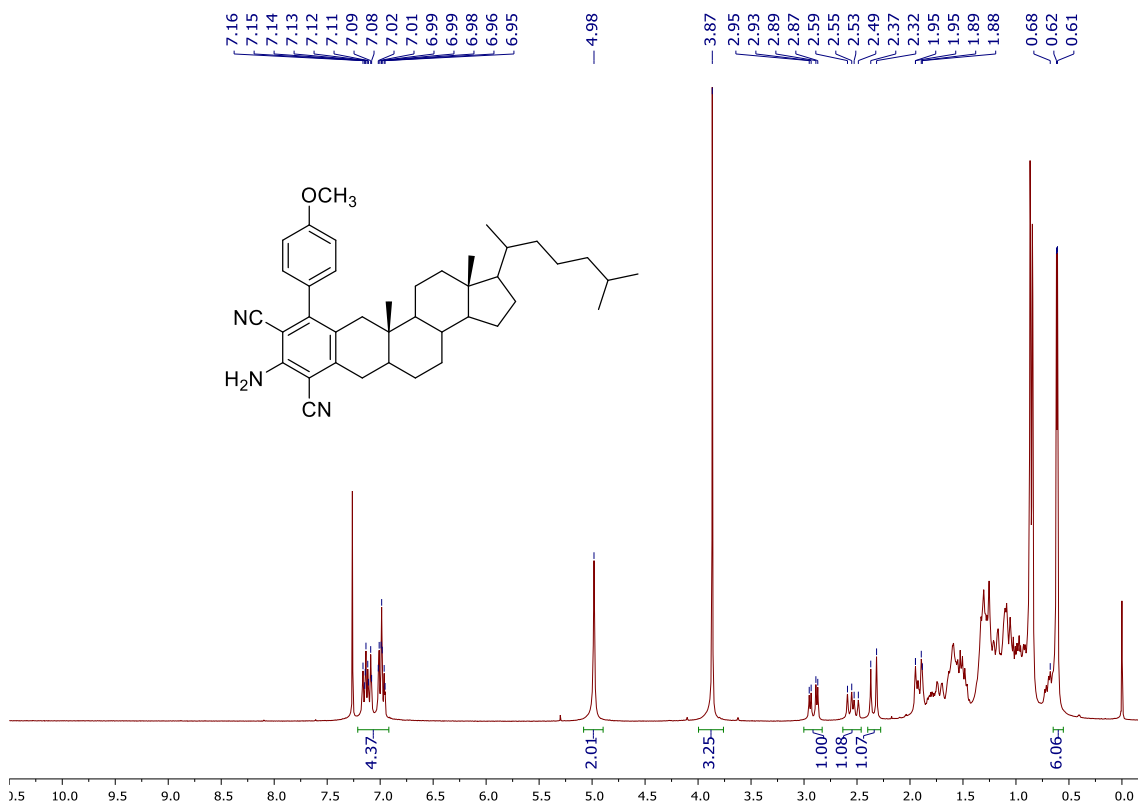
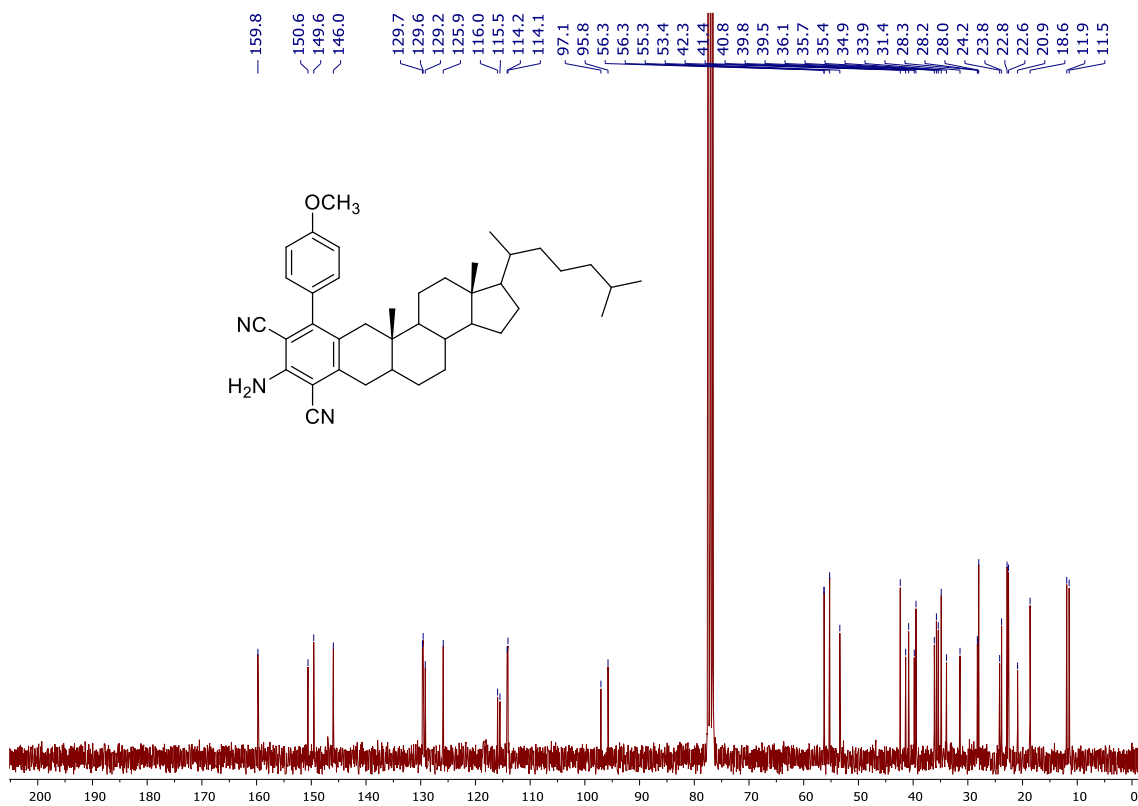
Figure S17: ¹H-NMR (300 MHz, CDCl₃) of compound 4c.Figure S18: ¹³C-NMR (75 MHz, CDCl₃) of compound 4c.

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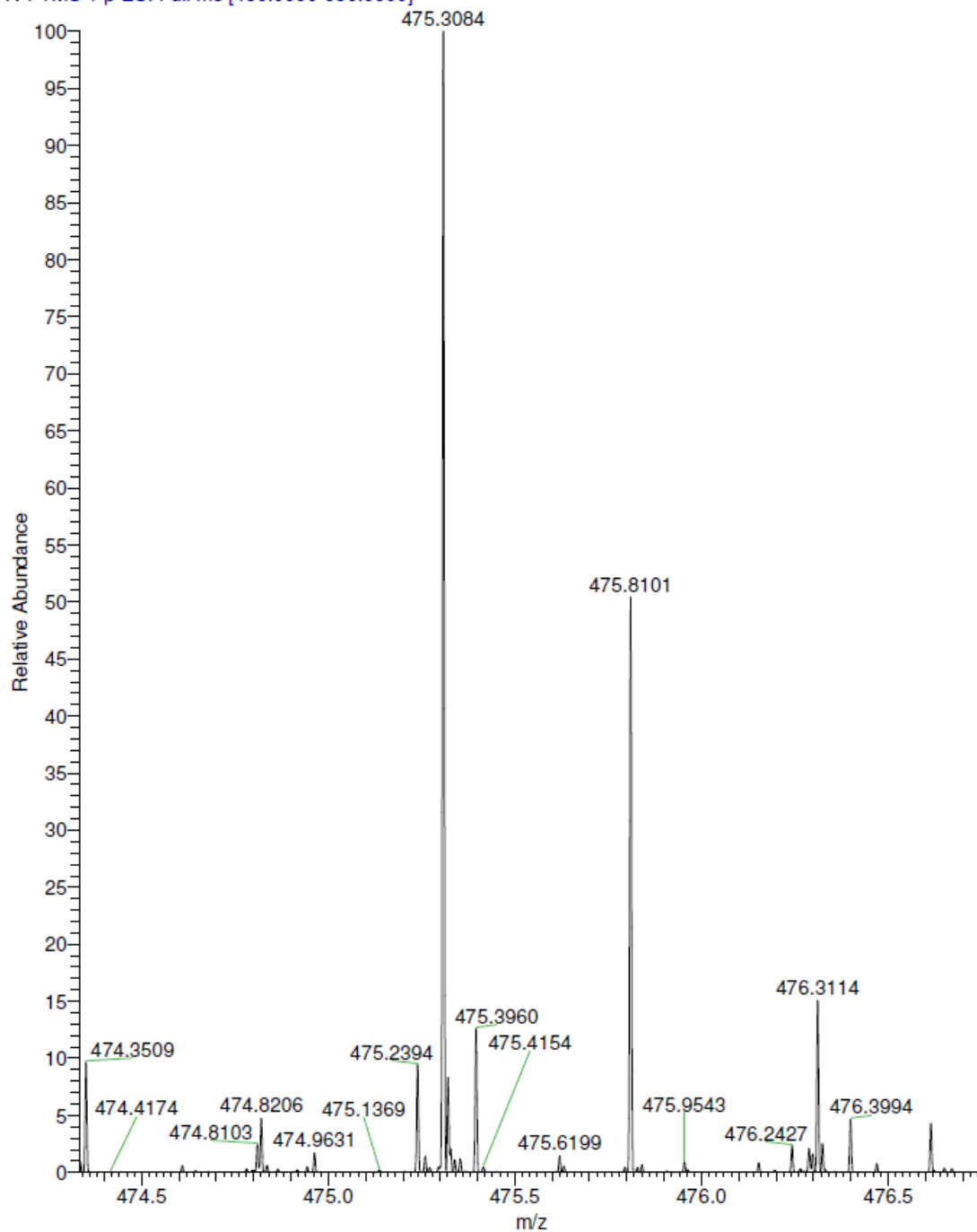
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Figure S29: High-resolution mass spectrum of compound 3a.

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10/06/20 14:31:30

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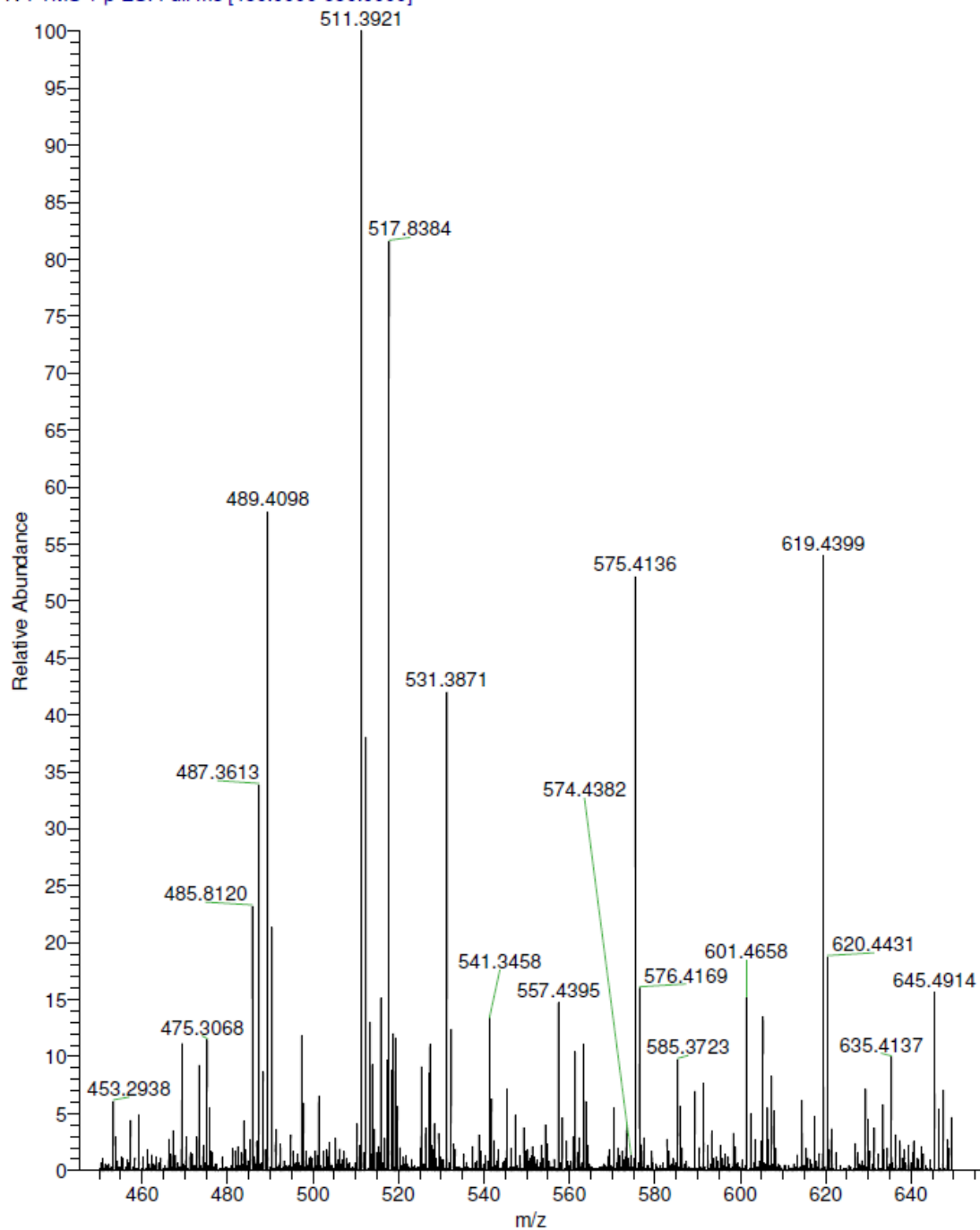


Figure S30: High-resolution mass spectrum of compound 3b.

C:\Xcalibur\...HA-866

10/27/20 14:45:38

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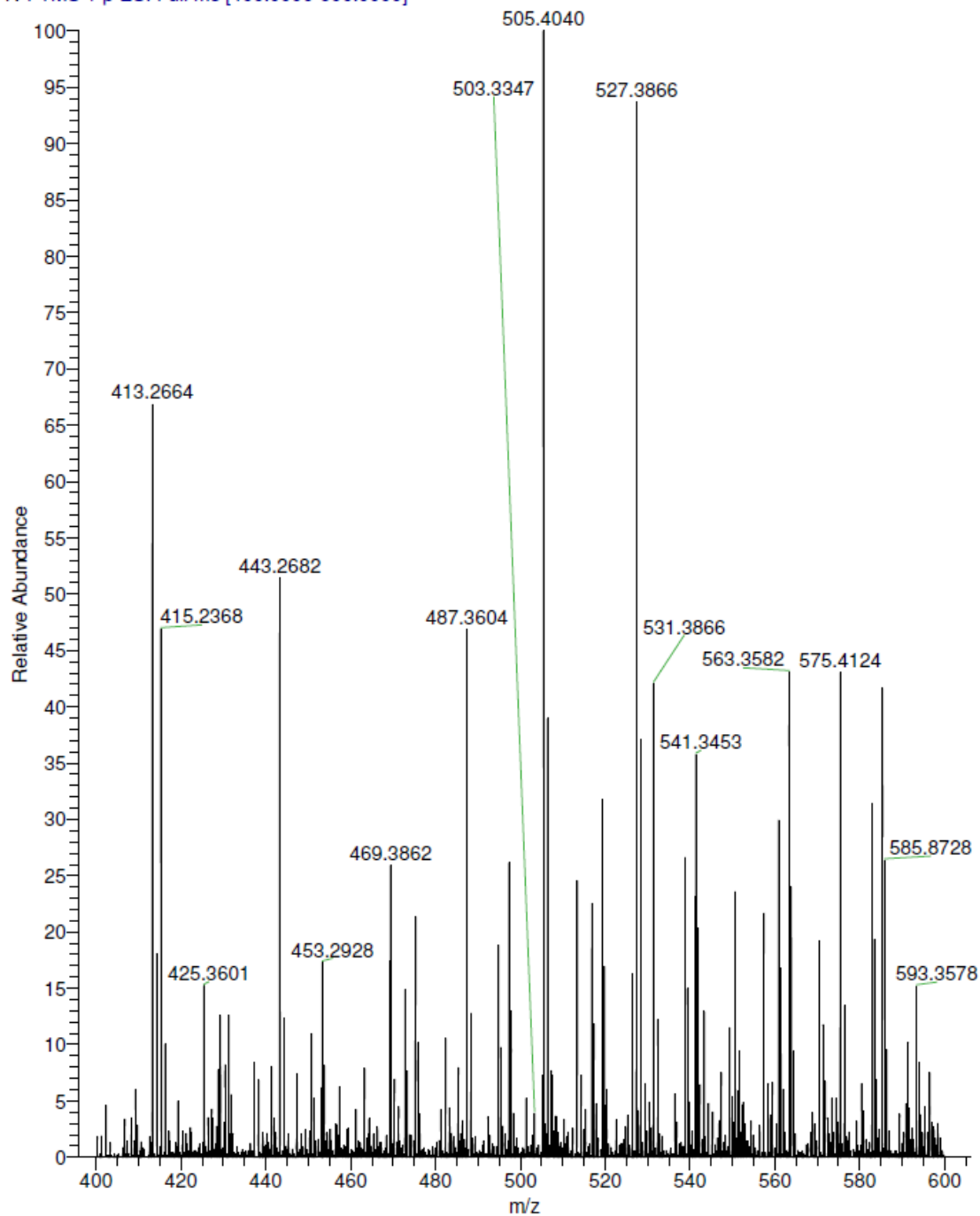


Figure S31: High-resolution mass spectrum of compound 3c.

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10/06/20 14:24:15

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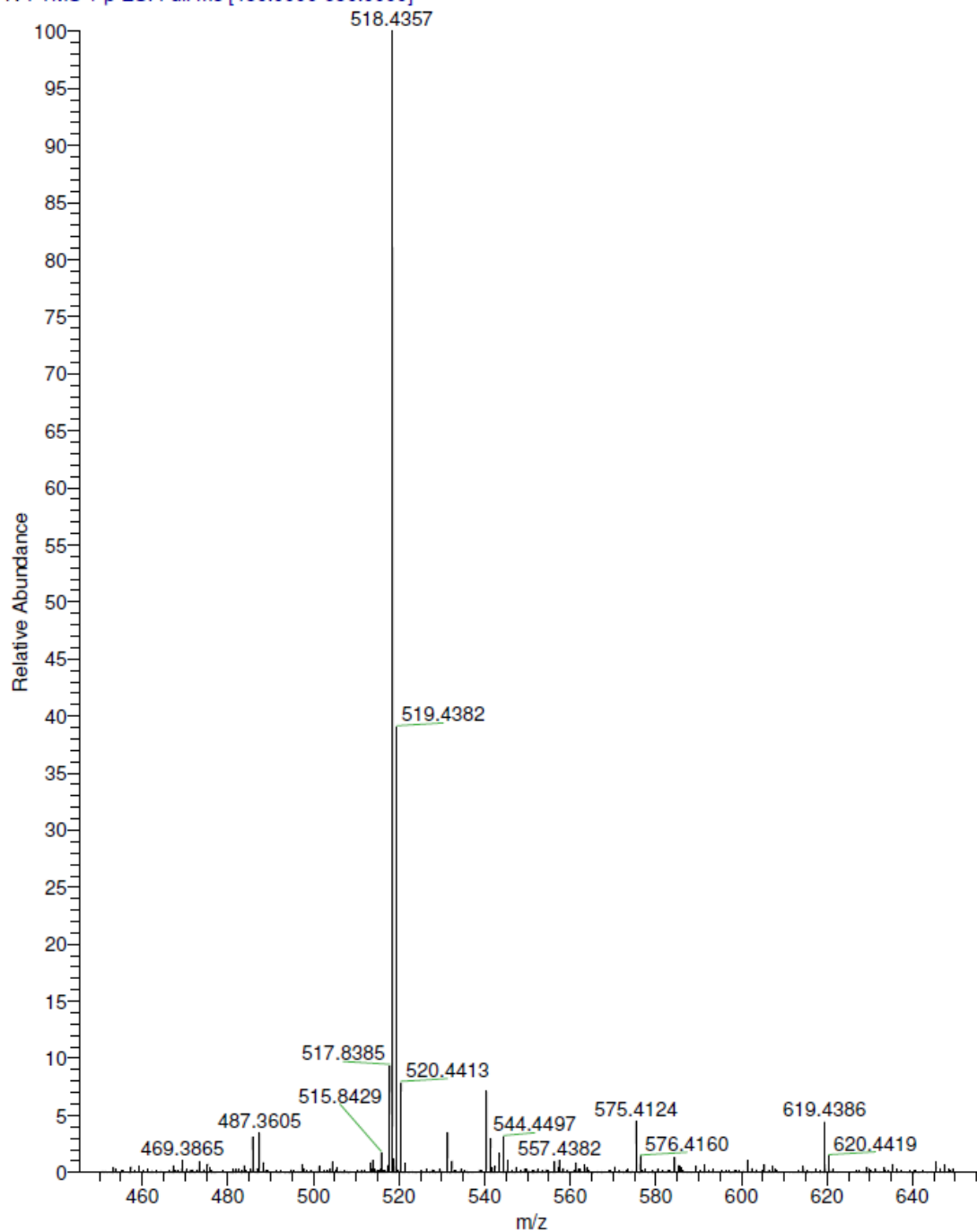


Figure S32: High-resolution mass spectrum of compound 3d.

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10/06/20 11:45:08

HA-862 #23-38 RT: 0.74-1.20 AV: 16 NL: 6.06E6

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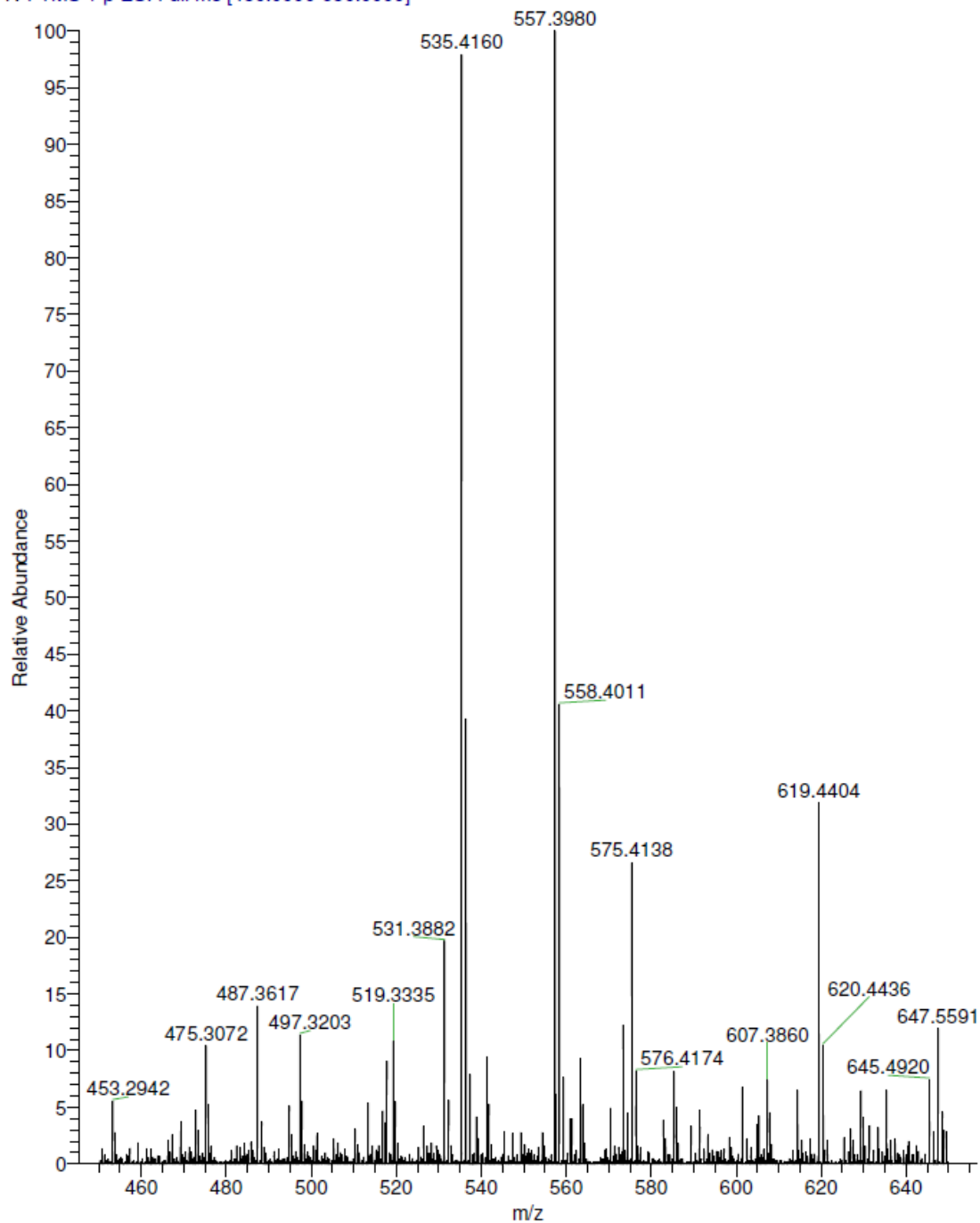


Figure S33: High-resolution mass spectrum of compound 3e.

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

10/06/20 14:39:51

HA-767 #23-39 RT: 0.70-1.17 AV: 17 NL: 8.36E6

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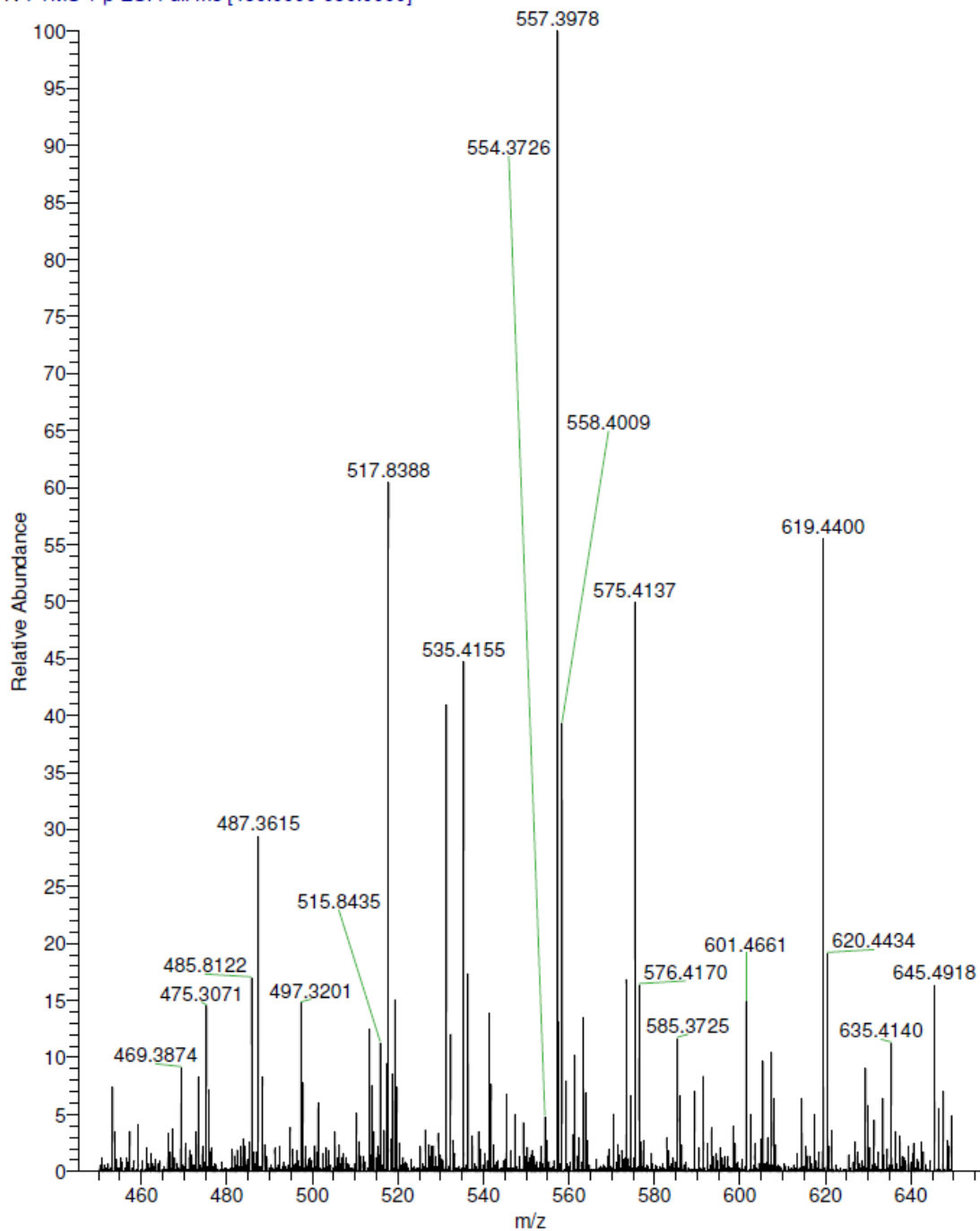


Figure S34: High-resolution mass spectrum of compound 3f.

C:\Xcalibur\1\HA-863

10/27/20 14:53:36

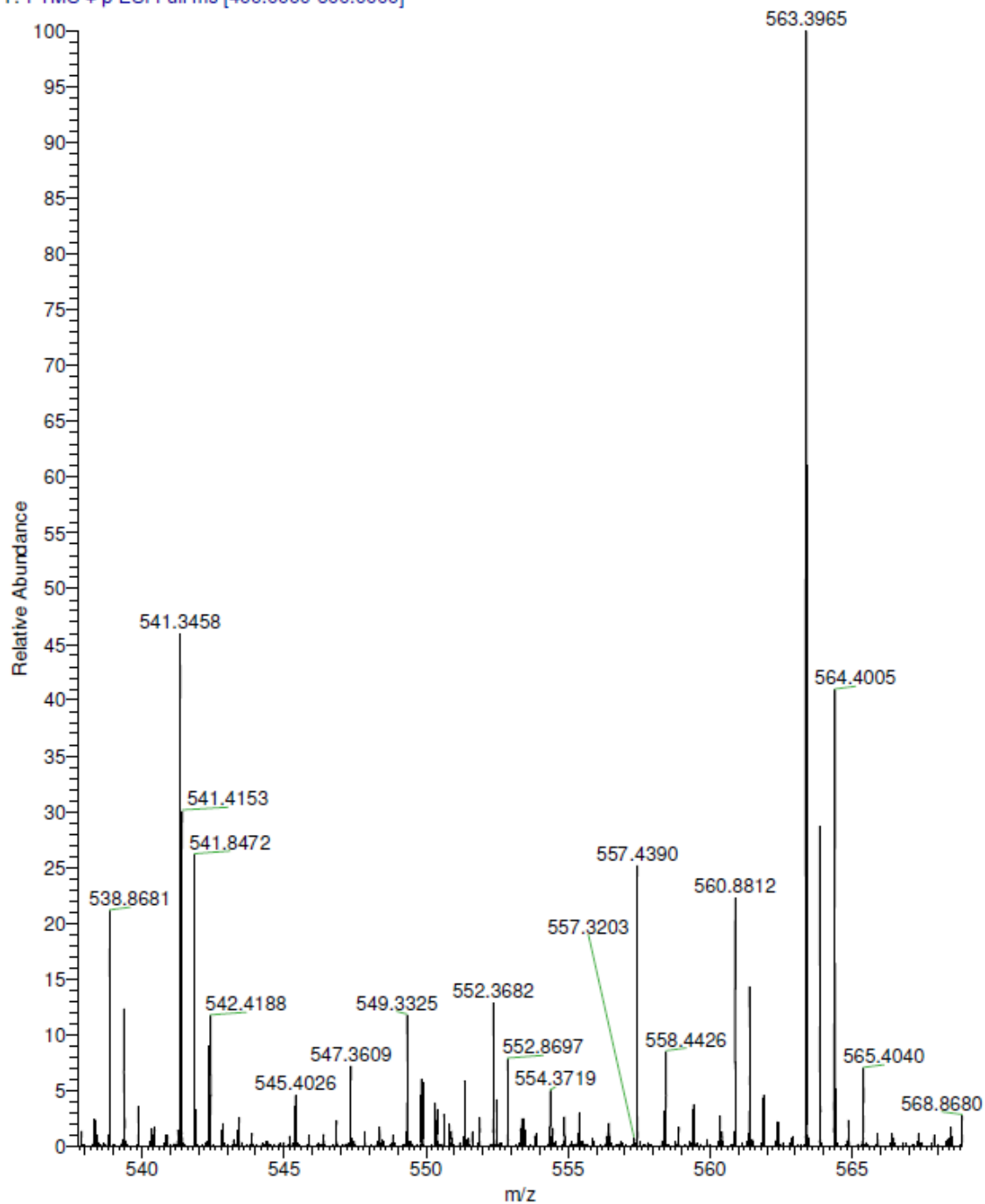
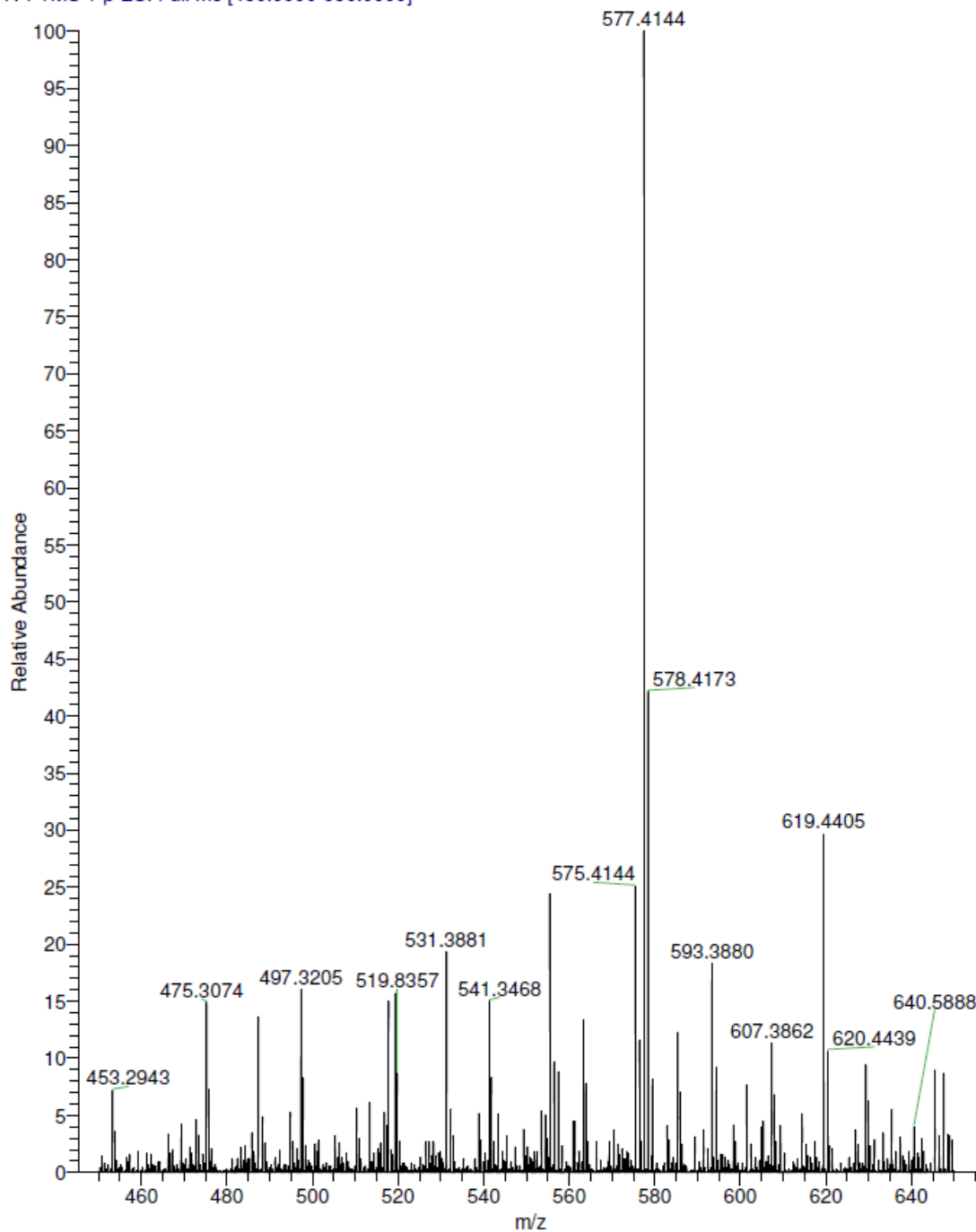
HA-863 #24 RT: 0.74 AV: 1 NL: 4.67E6
T: FTMS + p ESI Full ms [400.0000-600.0000]

Figure S35: High-resolution mass spectrum of compound 4a.

HA-758 #23-35 RT: 0.74-1.12 AV: 13 NL: 4.71E6

T: FTMS + p ESI Full ms [450.0000-650.0000]

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

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

10/06/20 12:04:30

HA-750 #21-36 RT: 0.69-1.17 AV: 16 NL: 1.93E6

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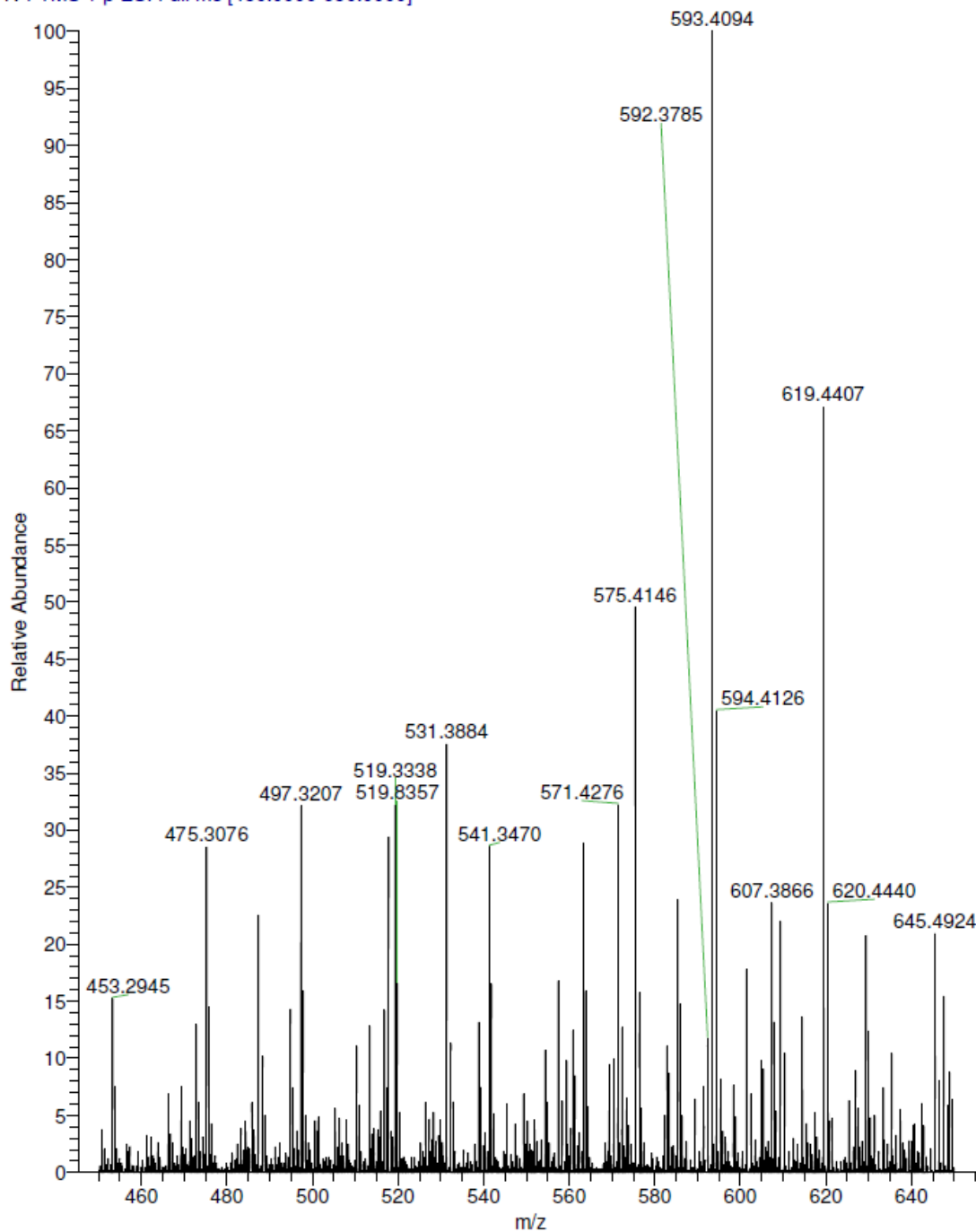


Figure S37: High-resolution mass spectrum of compound 4c.

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HA-760 #22-33 RT: 0.73-1.05 AV: 12 NL: 6.01E7

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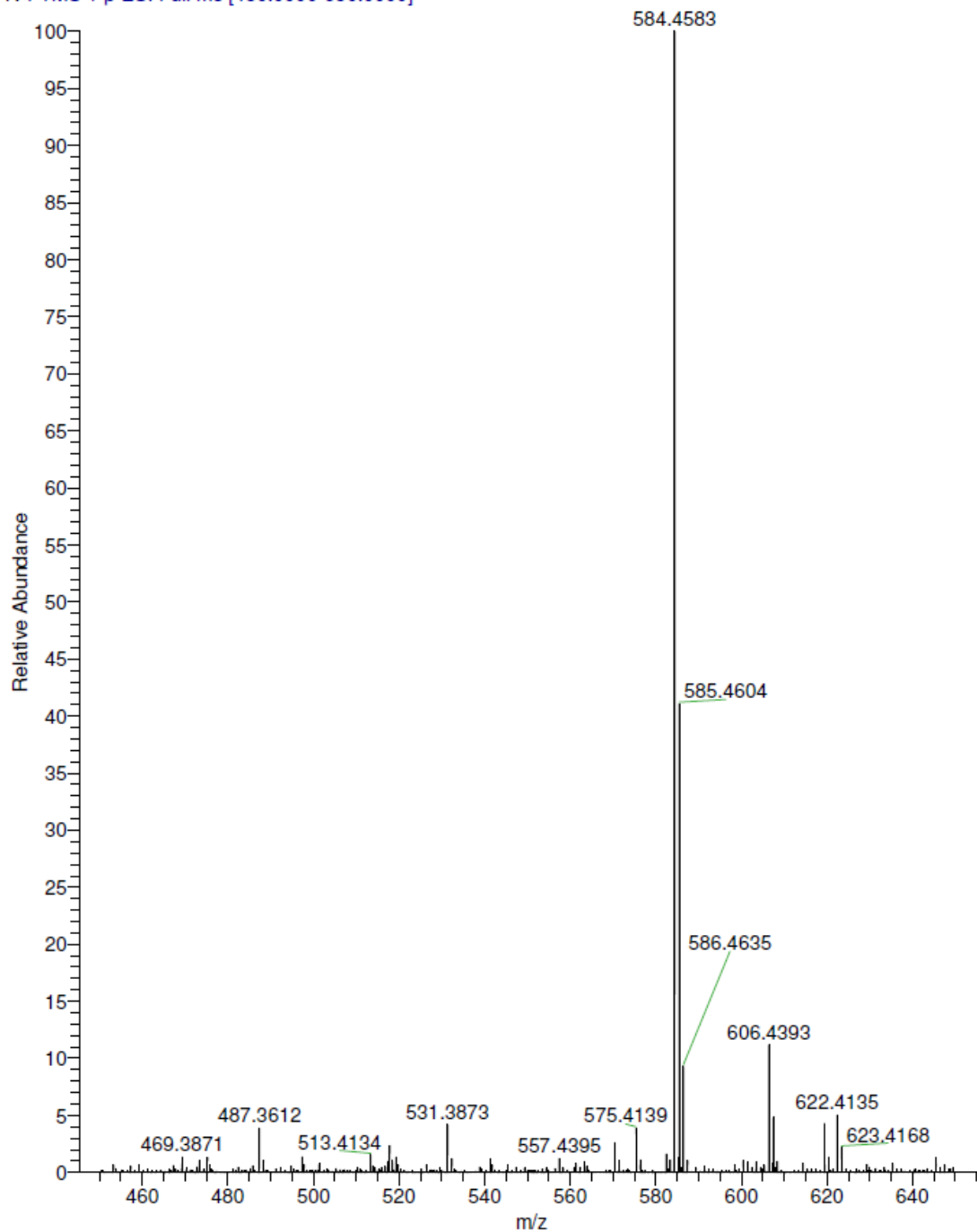


Figure S38: High-resolution mass spectrum of compound 4d.

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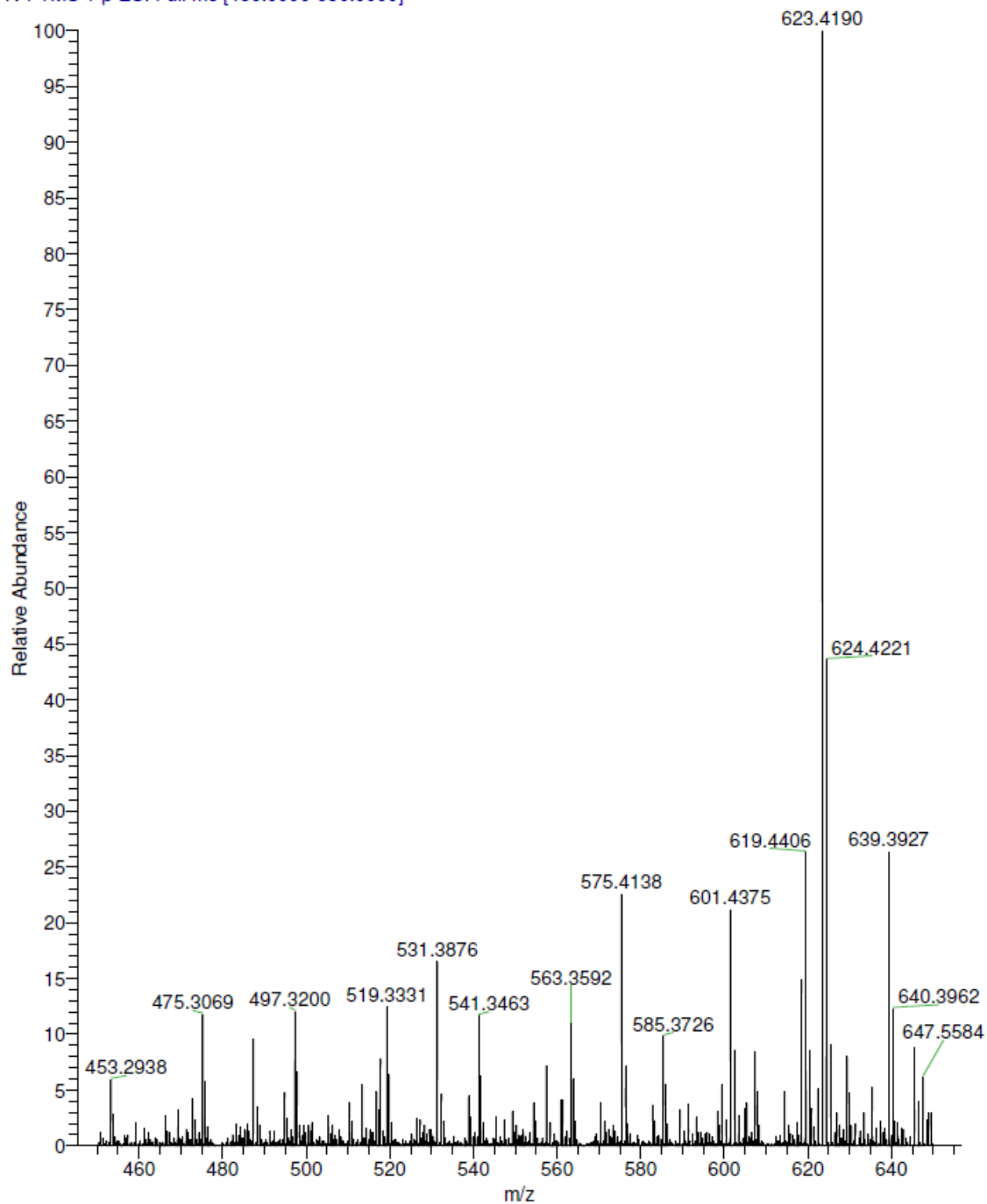


Figure S39: High-resolution mass spectrum of compound 4e.

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10/06/20 11:52:40

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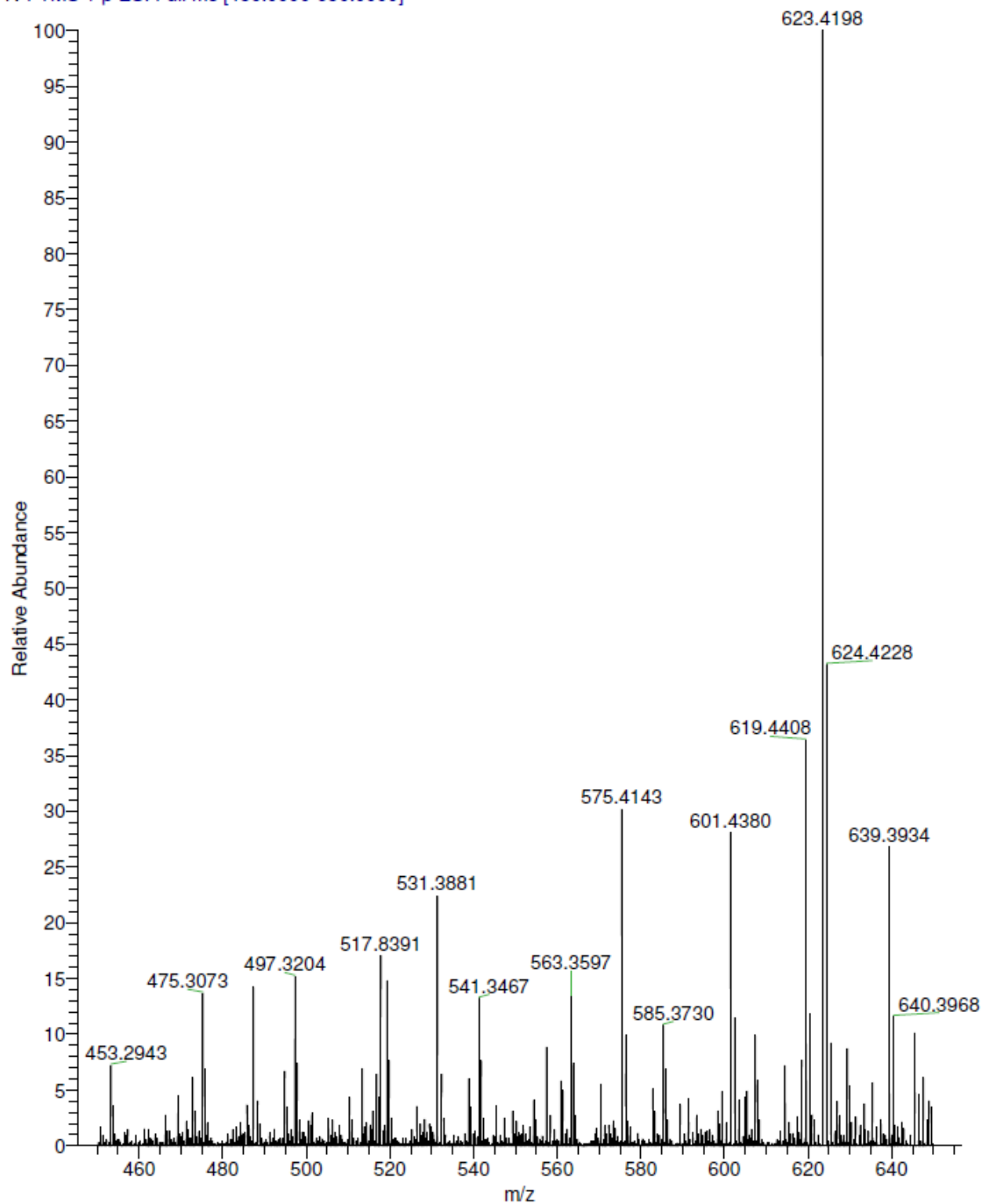


Figure S40: High-resolution mass spectrum of compound 4f.

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10/06/20 12:29:26

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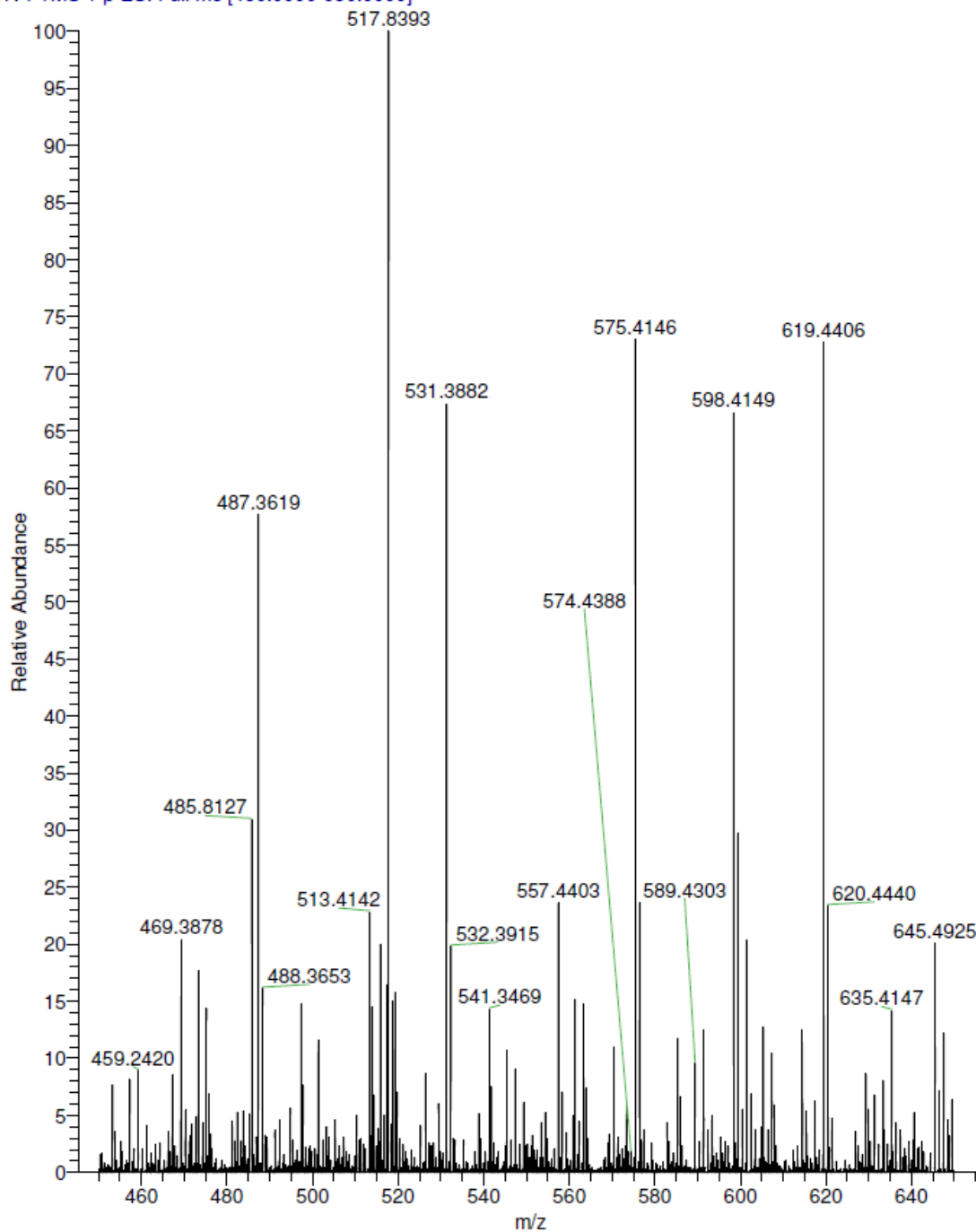


Figure S41: High-resolution mass spectrum of compound 5b.

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10/06/20 12:13:23

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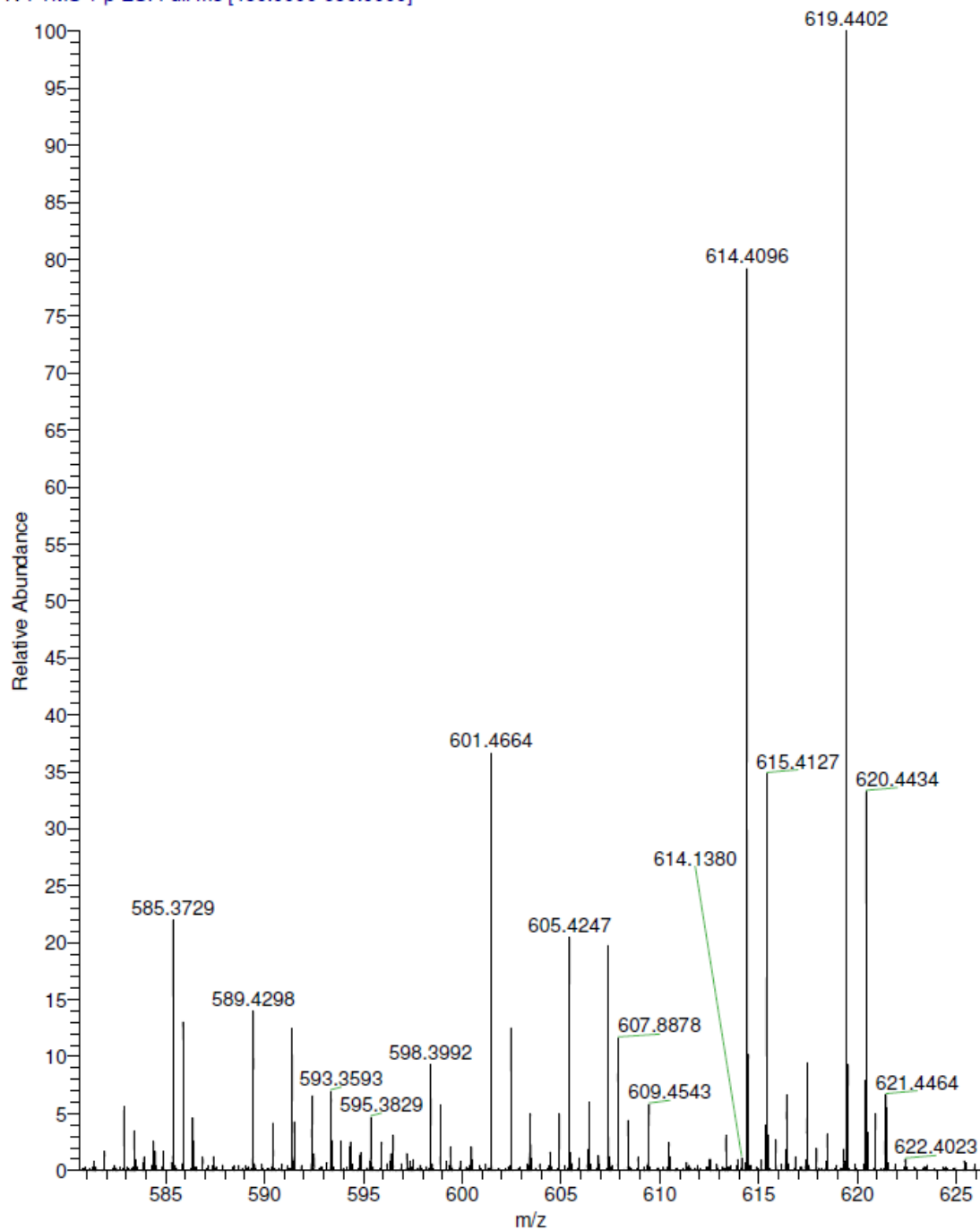


Figure S42: High-resolution mass spectrum of compound 5c.