

Supporting Information

Discovery of novel small-molecule inhibitors of PD-1/PD-L1 interaction via structural simplification strategy

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I. Supplementary Table

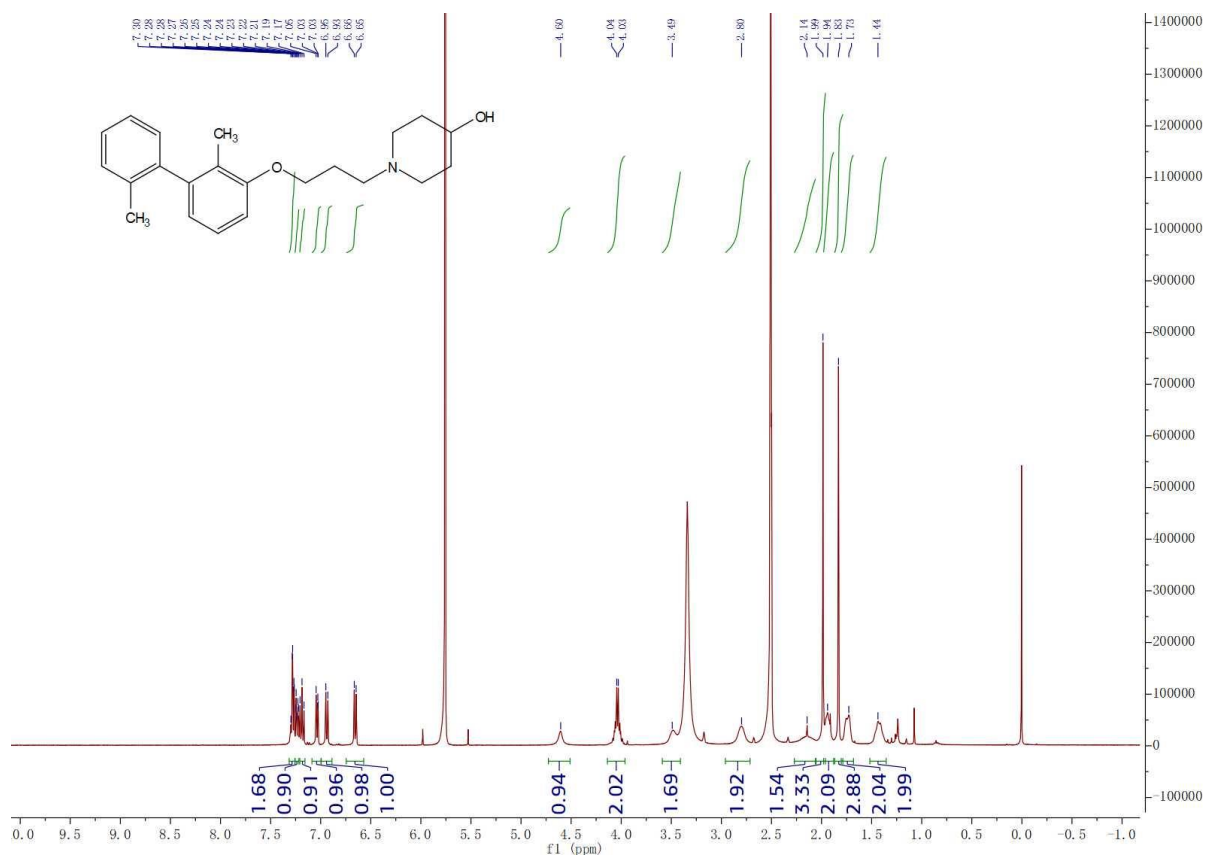
Table S1. The Kinetic Parameters and Binding Affinities of compounds with hPD-L1.

Compound	K_a (M ⁻¹ s ⁻¹)	K_d (s ⁻¹)	K_D (M)	LE ^a
A7	7.89×10 ⁵	6.38×10 ⁻³	8.09×10 ⁻⁹	0.35
A9	5.38×10 ⁵	1.96×10 ⁻³	3.64×10 ⁻⁹	0.40
A11	5.76×10 ⁵	3.68×10 ⁻³	6.39×10 ⁻⁹	0.39
A15	5.05×10 ⁵	1.01×10 ⁻²	1.99×10 ⁻⁸	0.36

^a The result is calculated by the equation: $LE = -1.35 \log K_D / N_{\text{heavy atoms}}$, $N_{\text{heavy atoms}}$ is the number of non-H atoms.

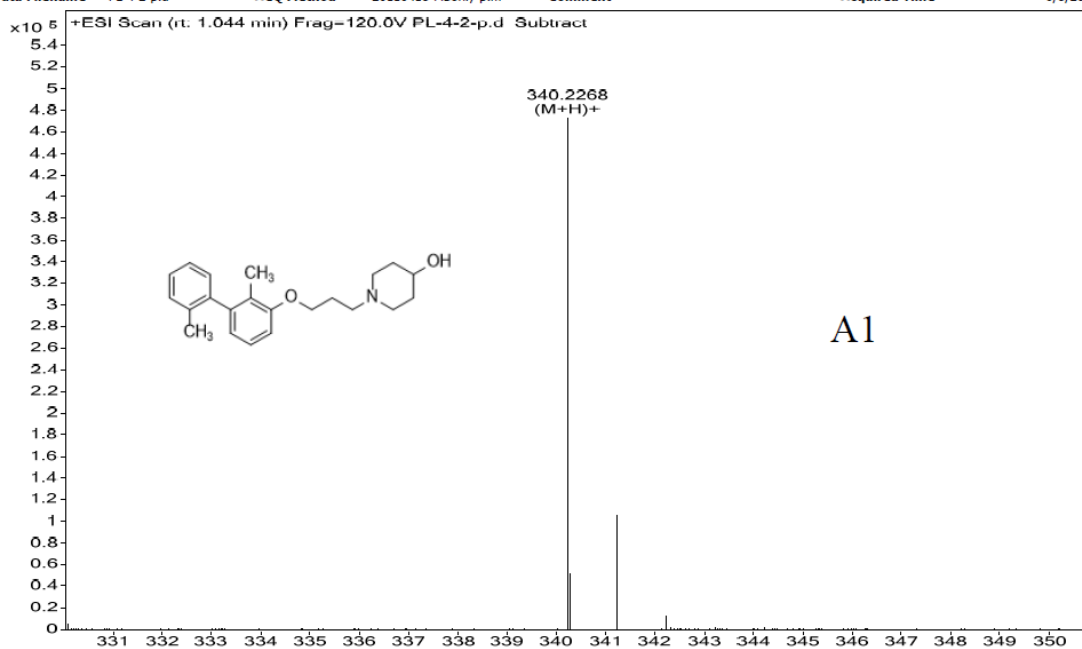
II. Spectroscopic data of compounds A1–18

¹H NMR Spectra for Compound A1

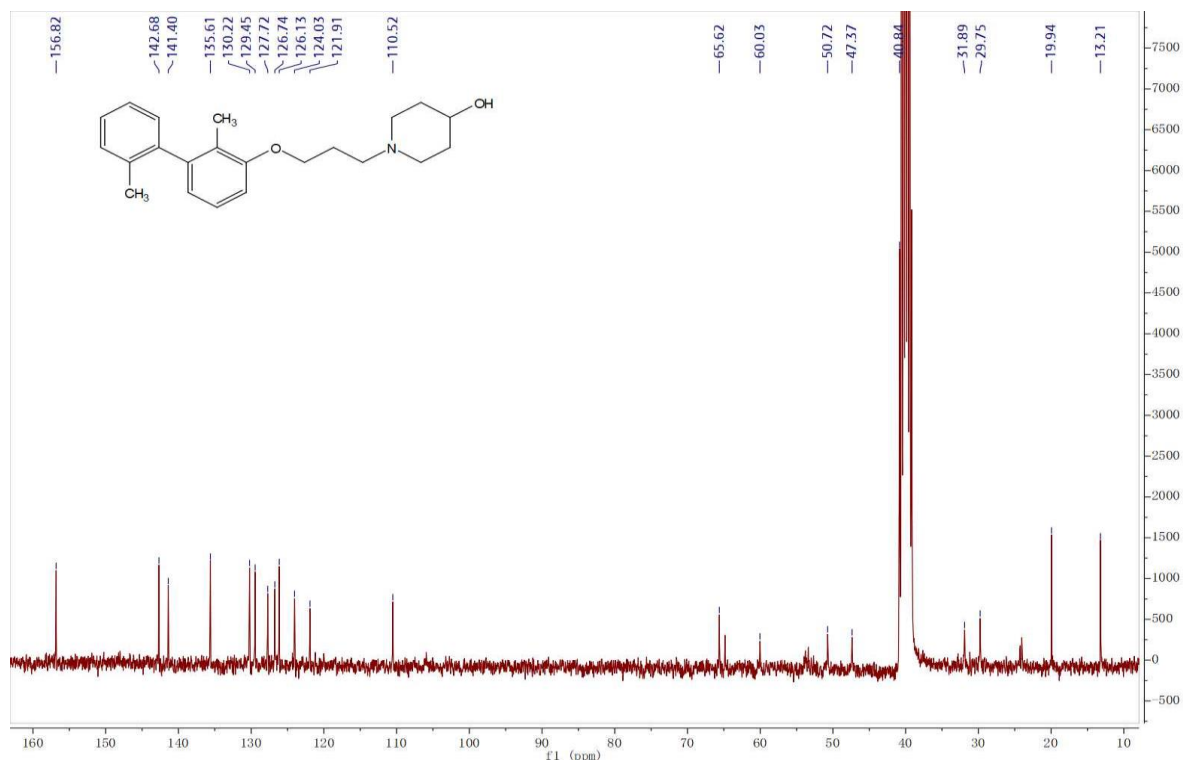


LCMS Spectra for Compound A1

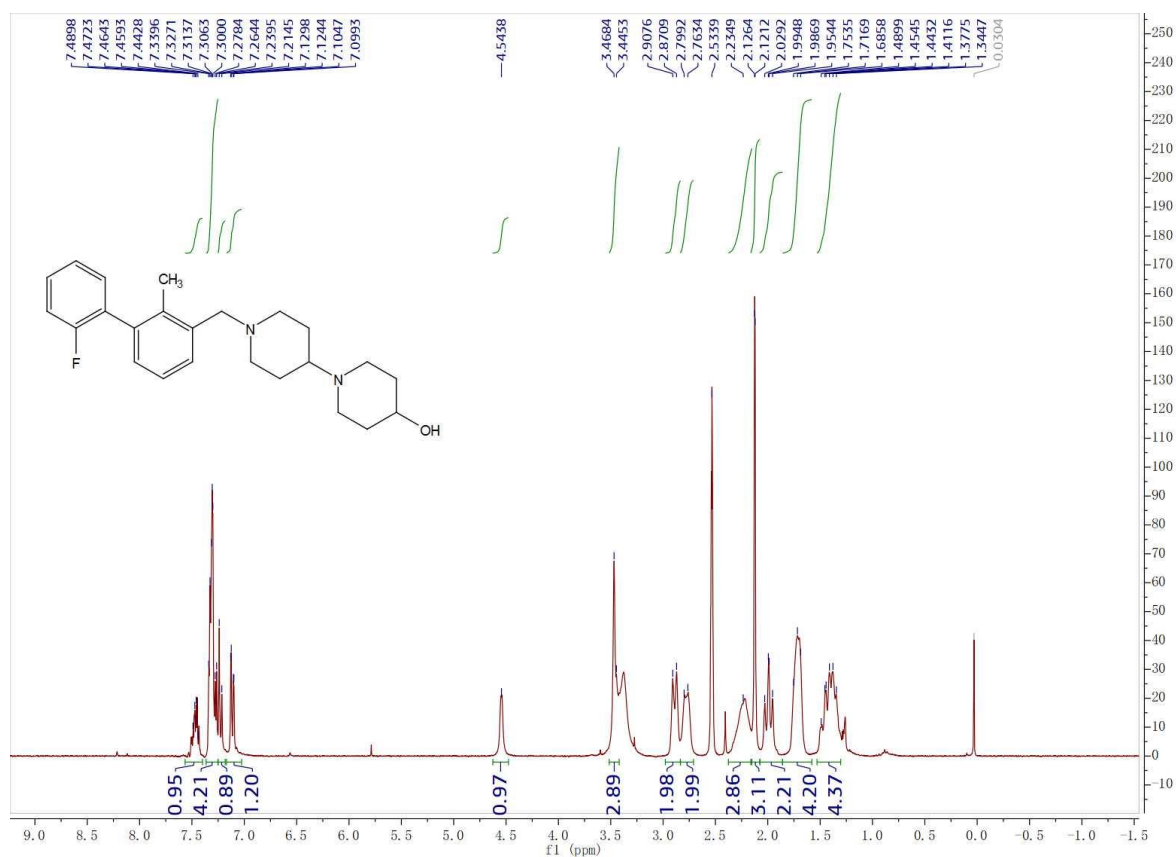
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Data Filename PL-4-2-p.d	ACQ Method 20110418-MSonly-p.m	Comment		Acquired Time	6/8/2020 10:05:29 AM



¹³C NMR Spectra for Compound A1

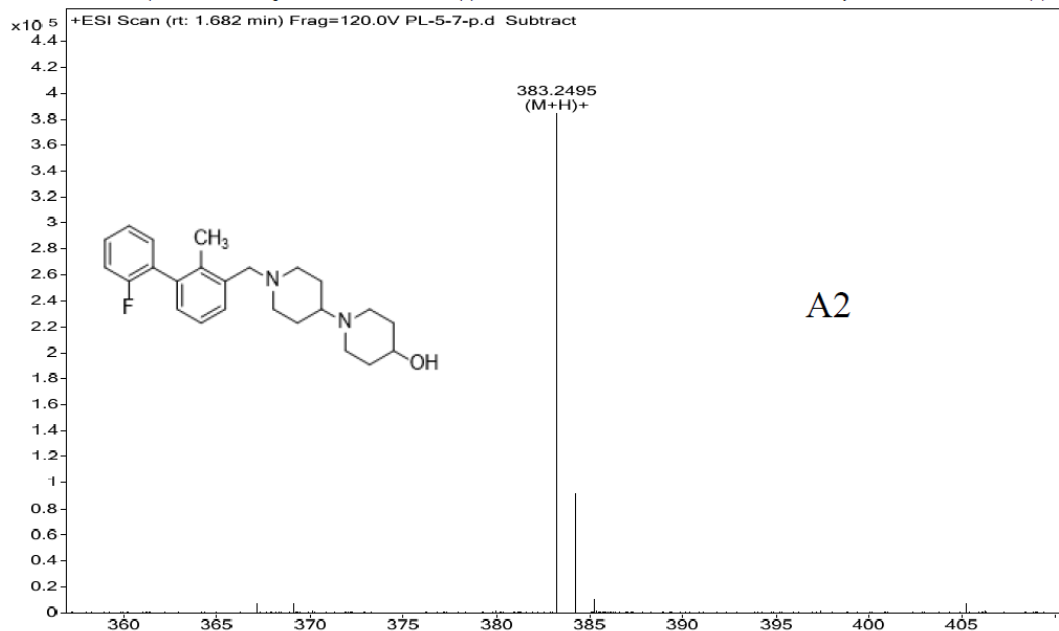


¹H NMR Spectra for Compound A2

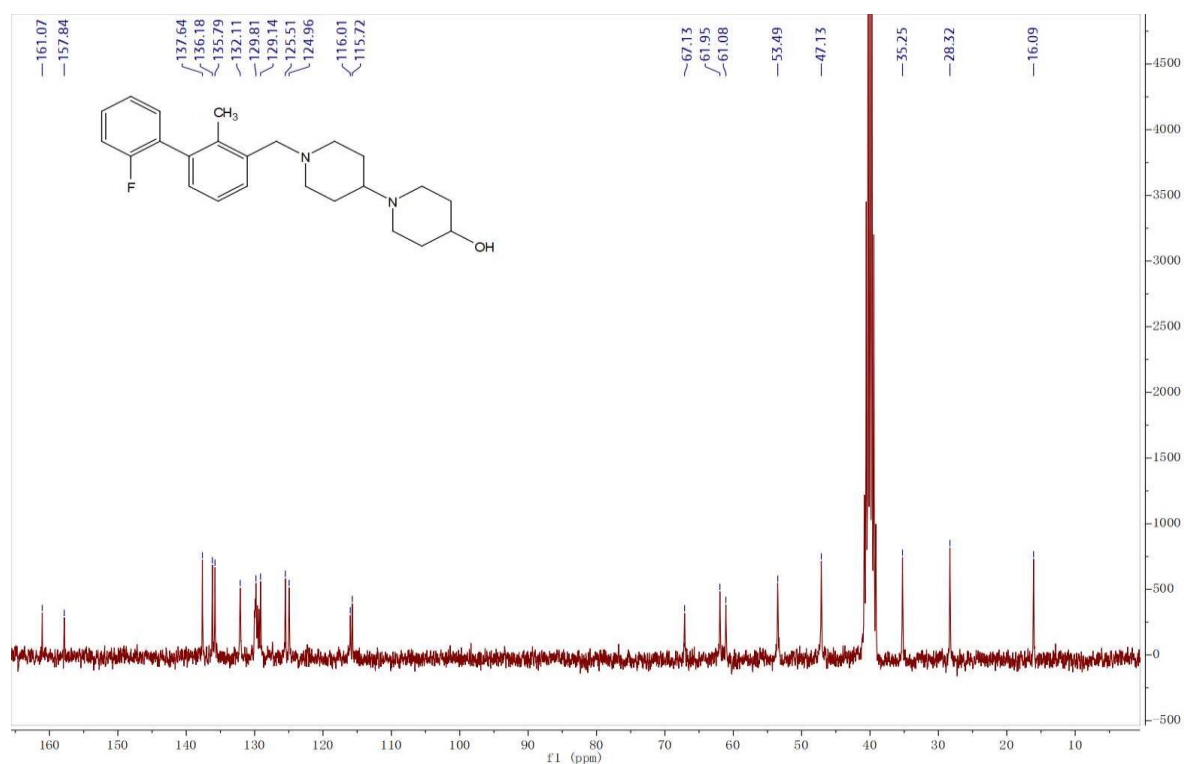


LCMS Spectra for Compound A2

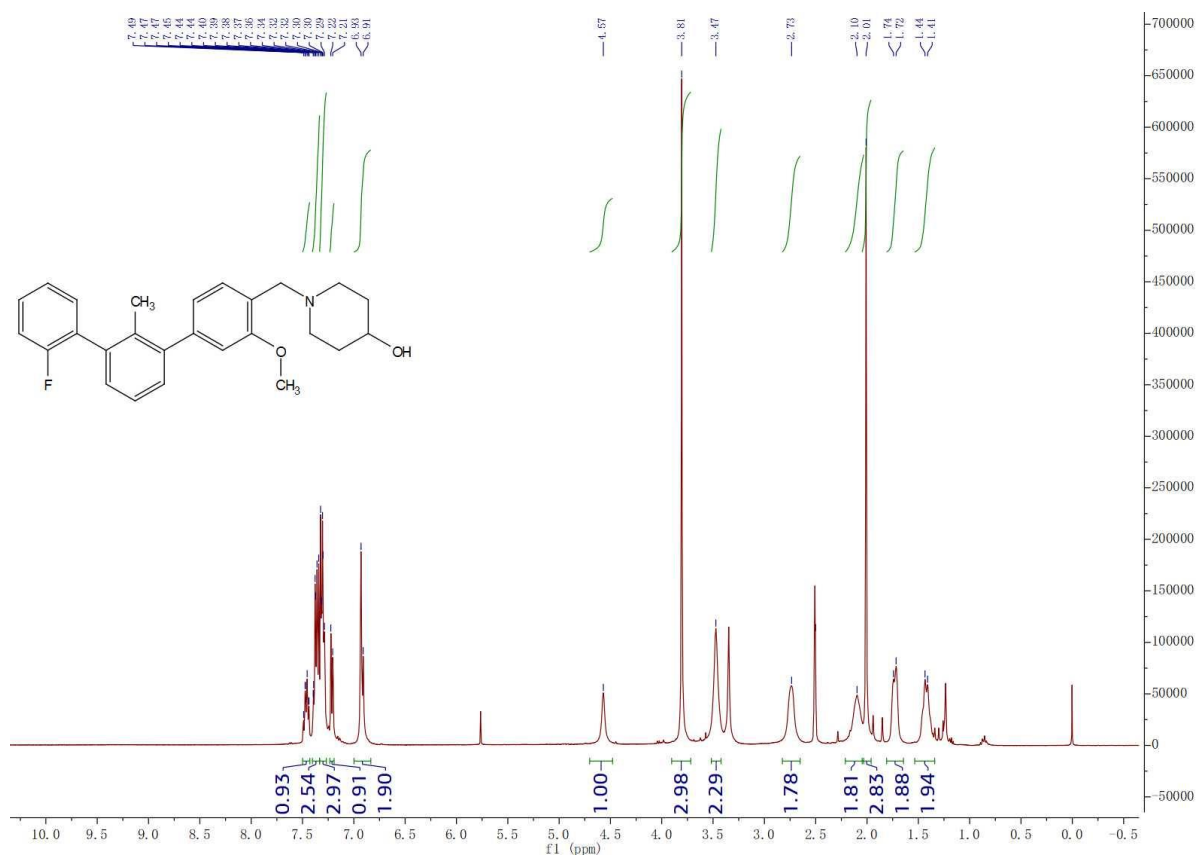
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Inj Vol 0.1	p2B9	SampleType	Sample	IRM Calibration Status	Success
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¹³C NMR Spectra for Compound A2

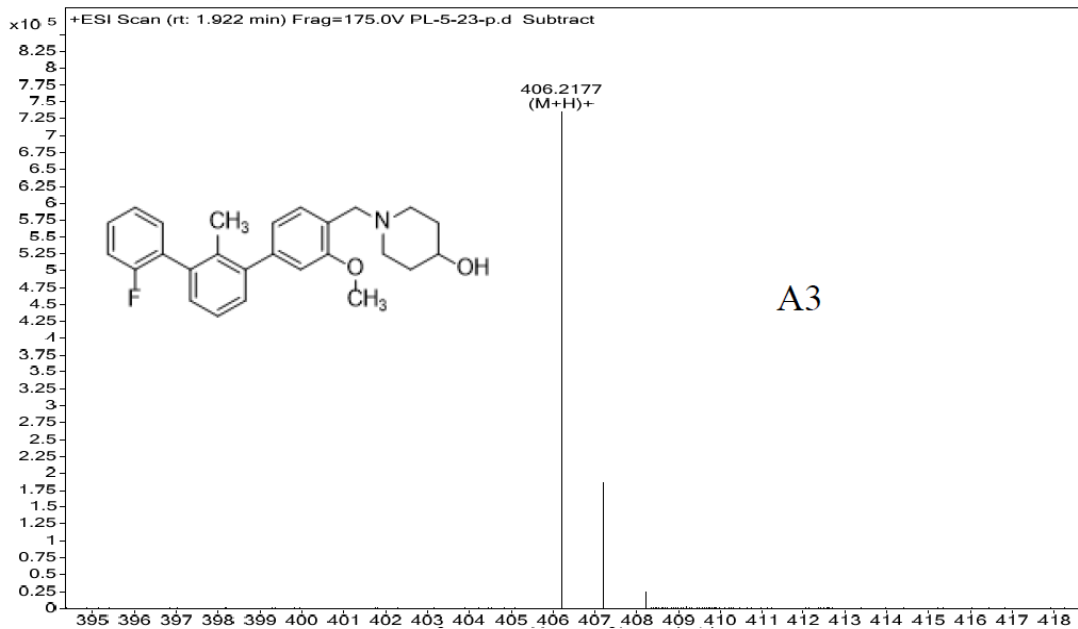


¹H NMR Spectra for Compound A3

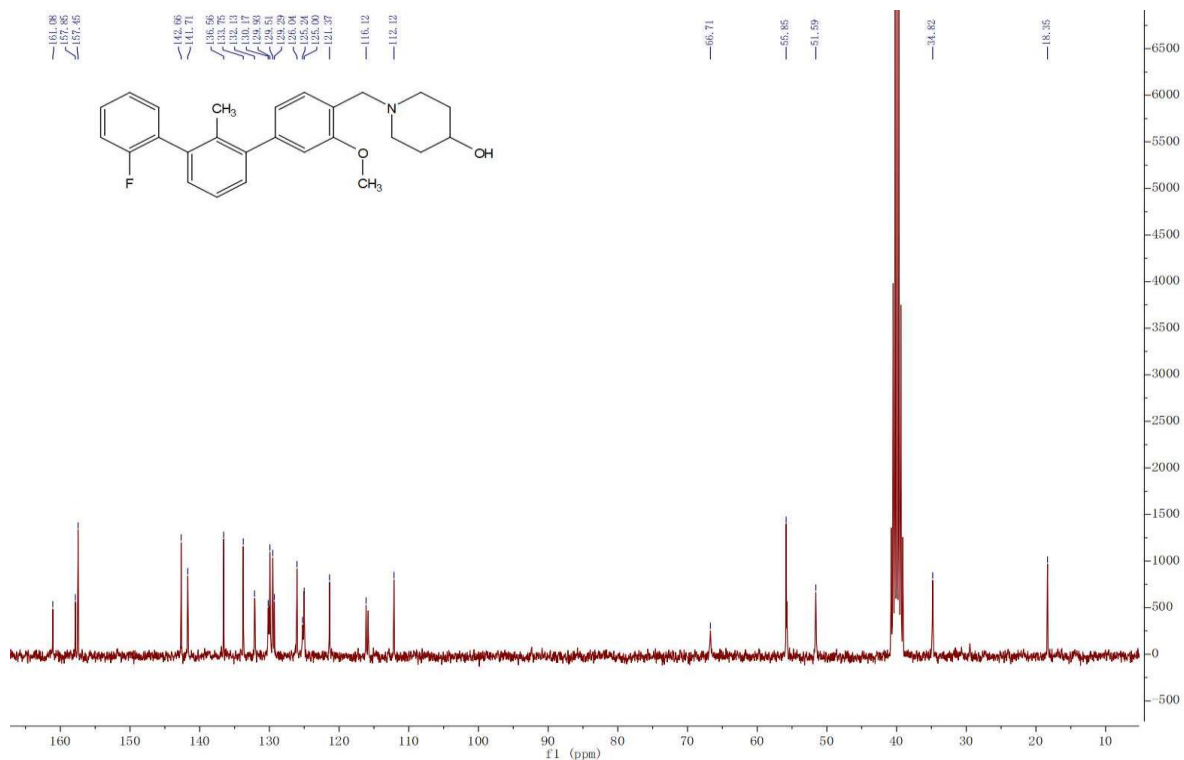


LCMS Spectra for Compound A3

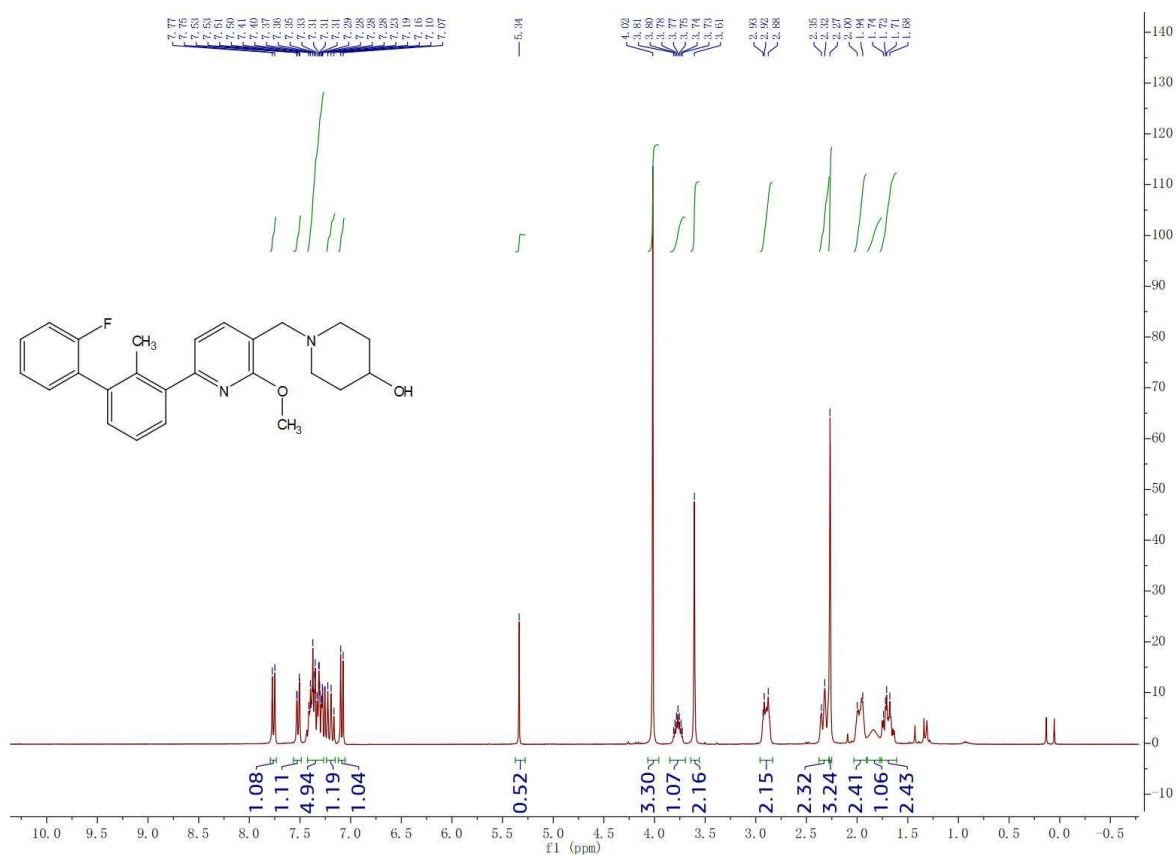
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Data Filename	PL-5-23-p.d	ACQ Method	Comment	Acquired Time	12/25/2020 10:52:43 AM



¹³C NMR Spectra for Compound A3



¹H NMR Spectra for Compound A4

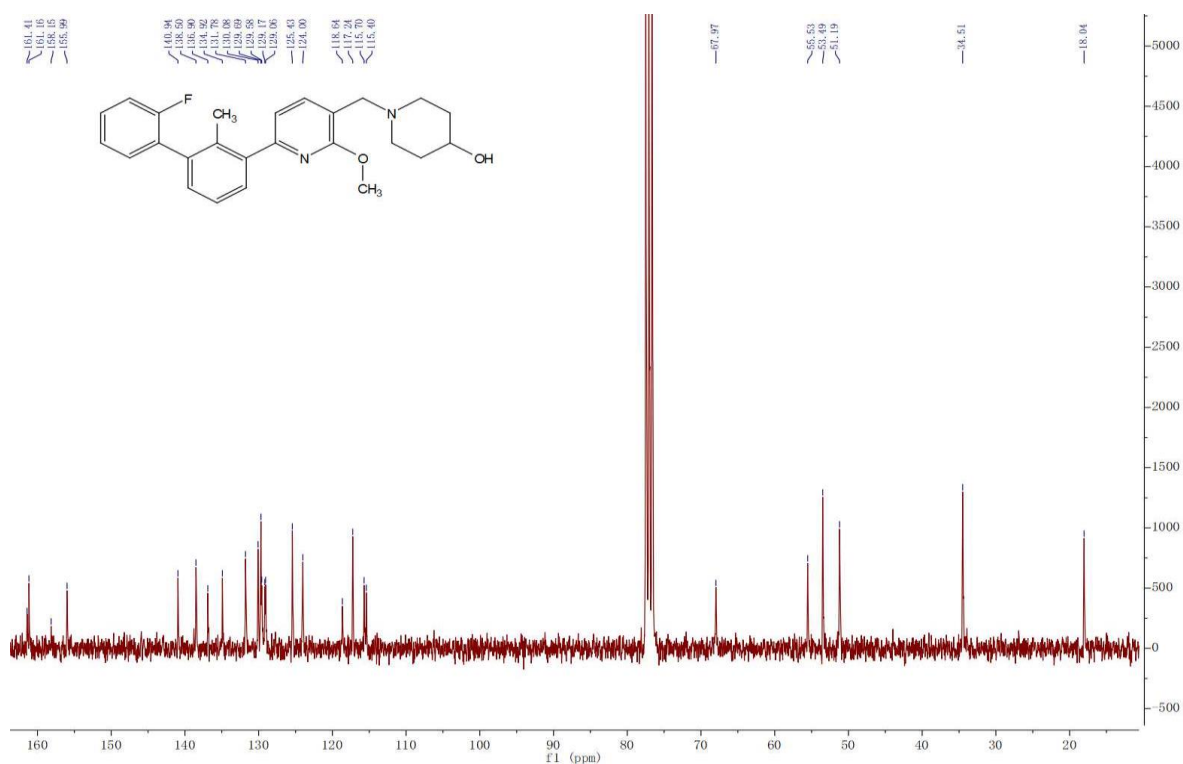


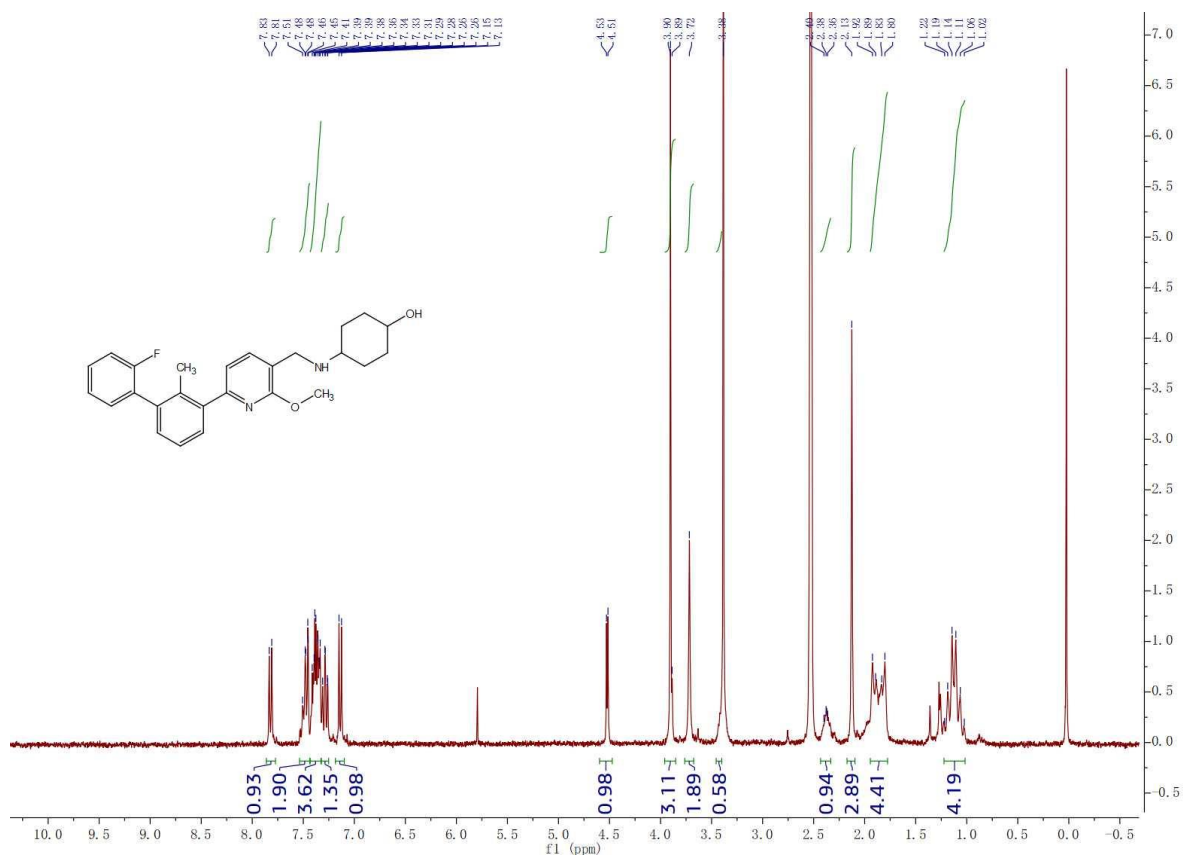
LCMS Spectra for Compound A4

ESI Scan (rt: 1.926 min) Frag=175.0V PL-5-12-p.d

407.2137
(M+H)⁺

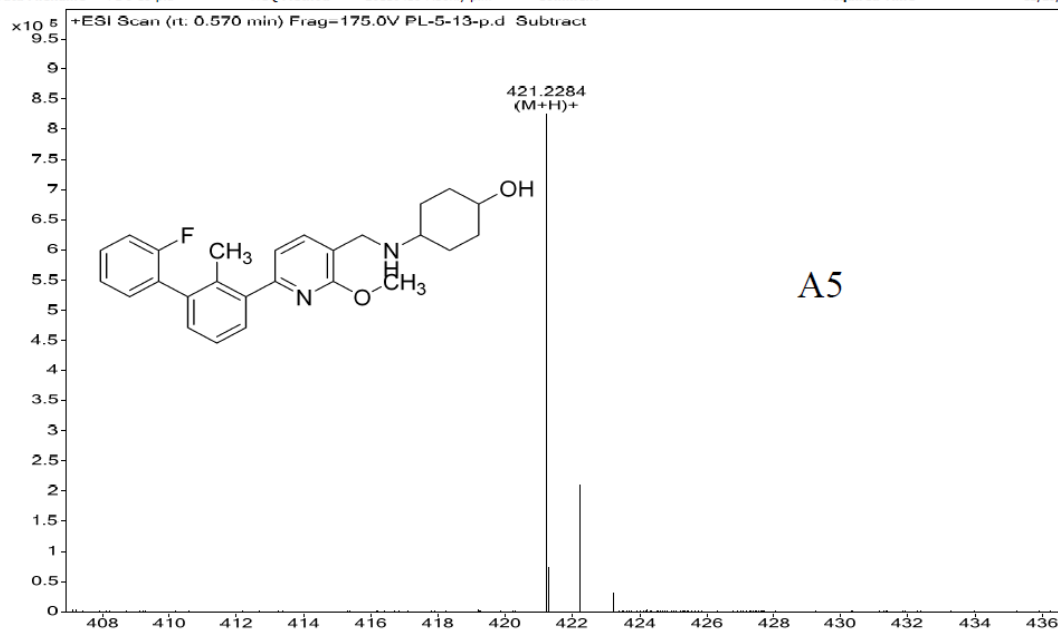
A4

COC1=CC=C(C=C1C2=CC=CC=C2C(F)=C3C=CC(=C3)C=C2C)C4=CC=CC=C4N(CCCO)CC4

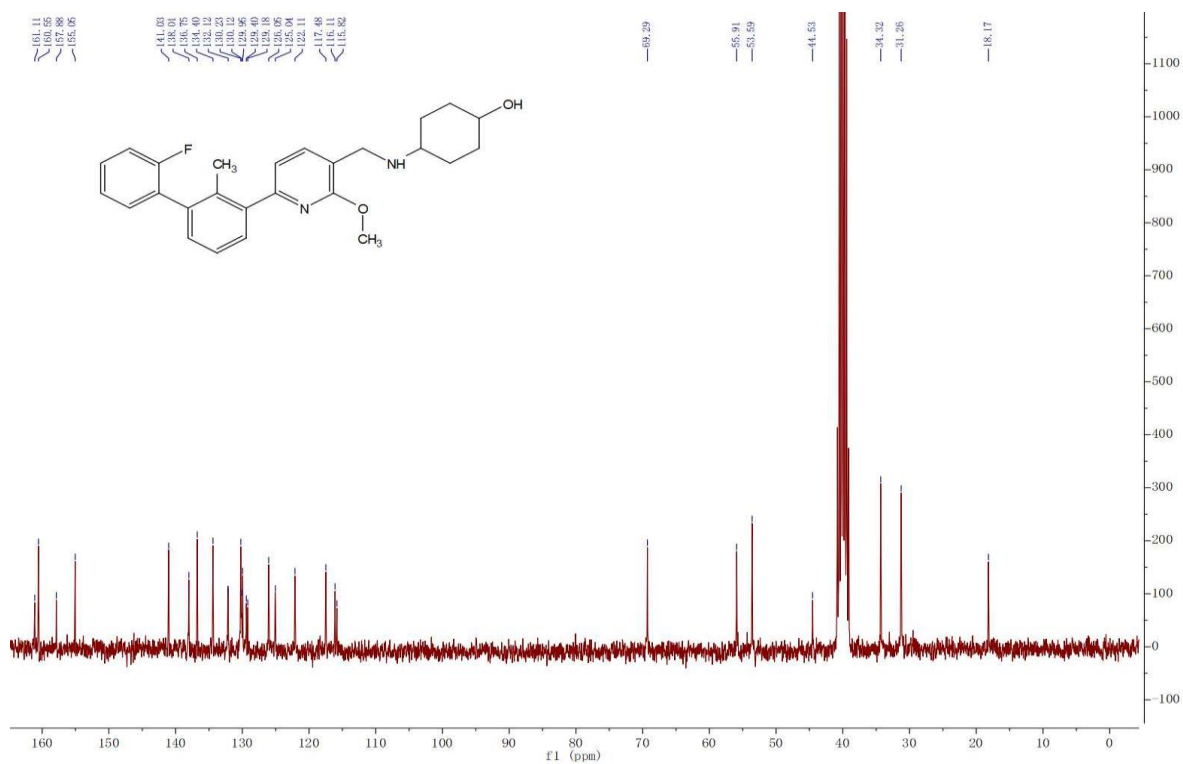


LCMS Spectra for Compound A5

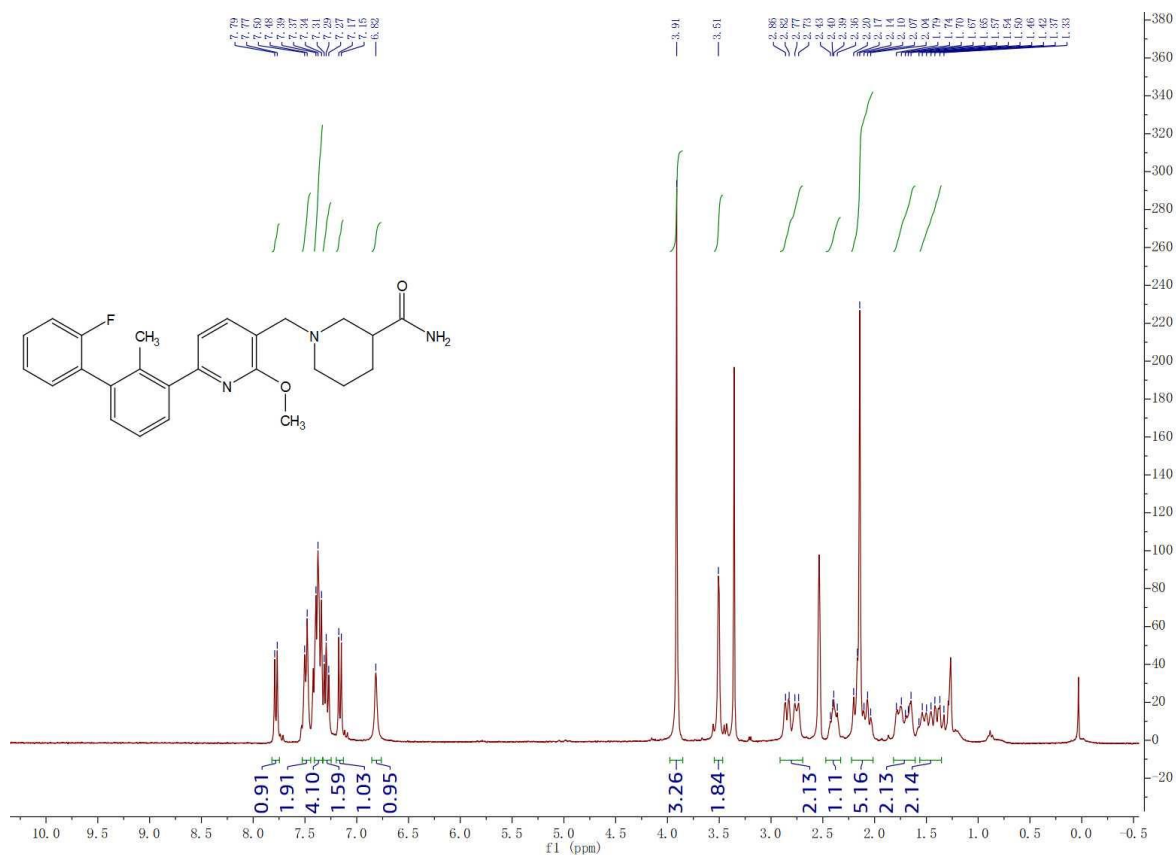
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Data Filename	ACQ Method	Comment		Acquired Time	12/25/2020 10:01:24 AM



¹³C NMR Spectra for Compound A5

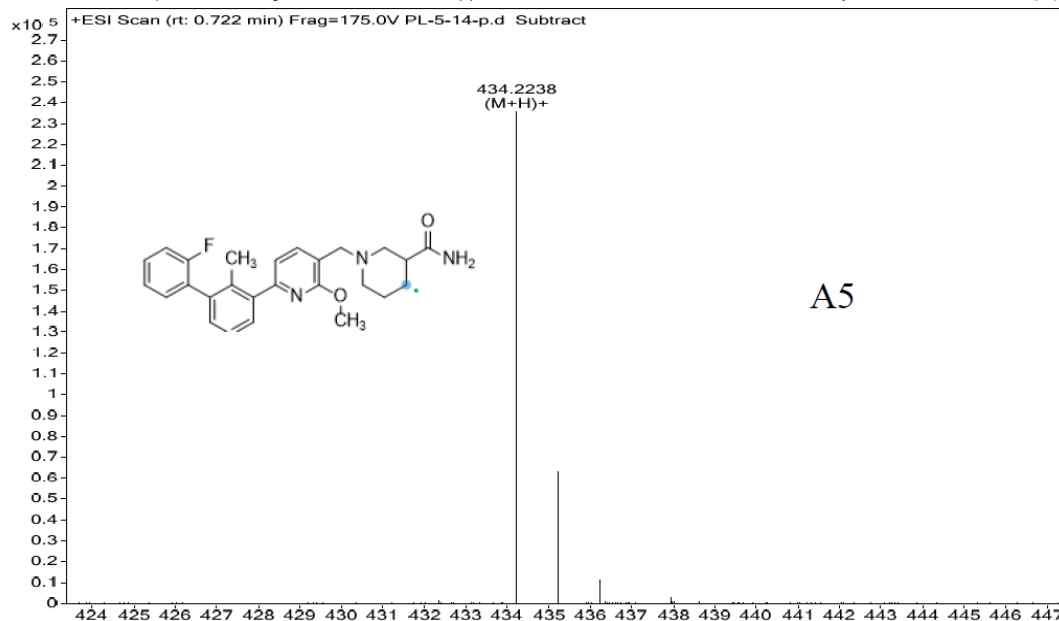


¹H NMR Spectra for Compound A6

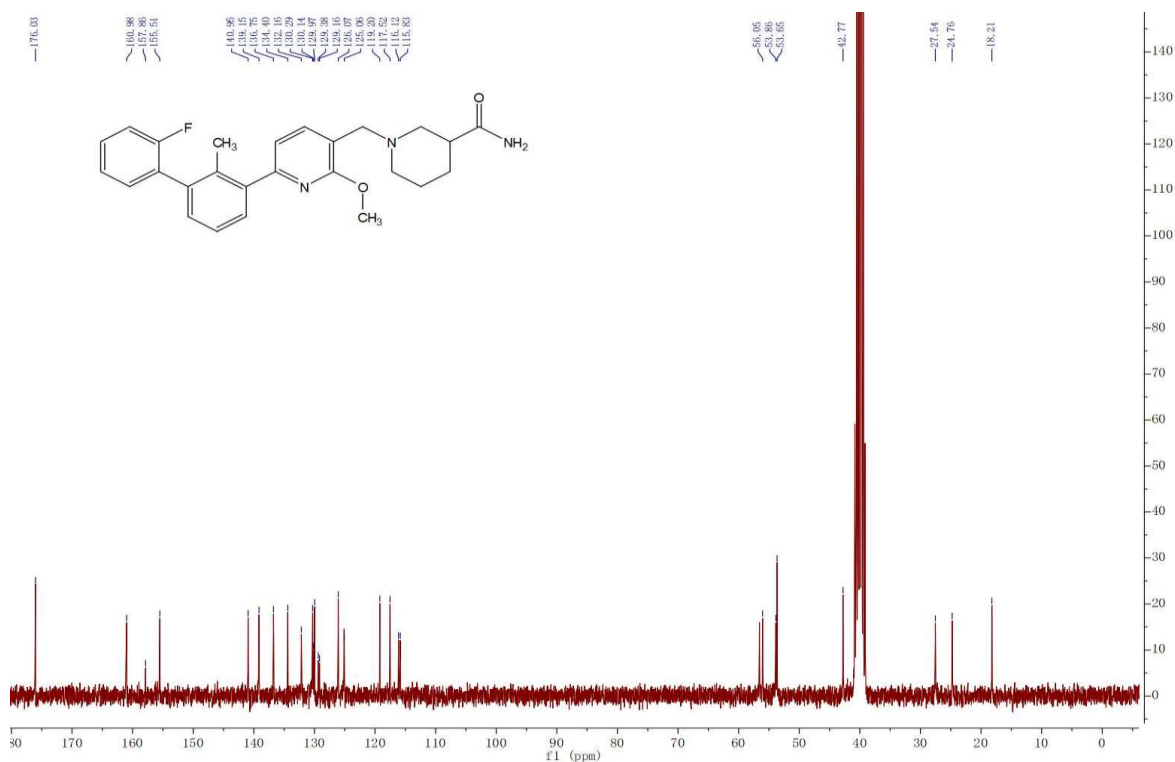


LCMS Spectra for Compound A6

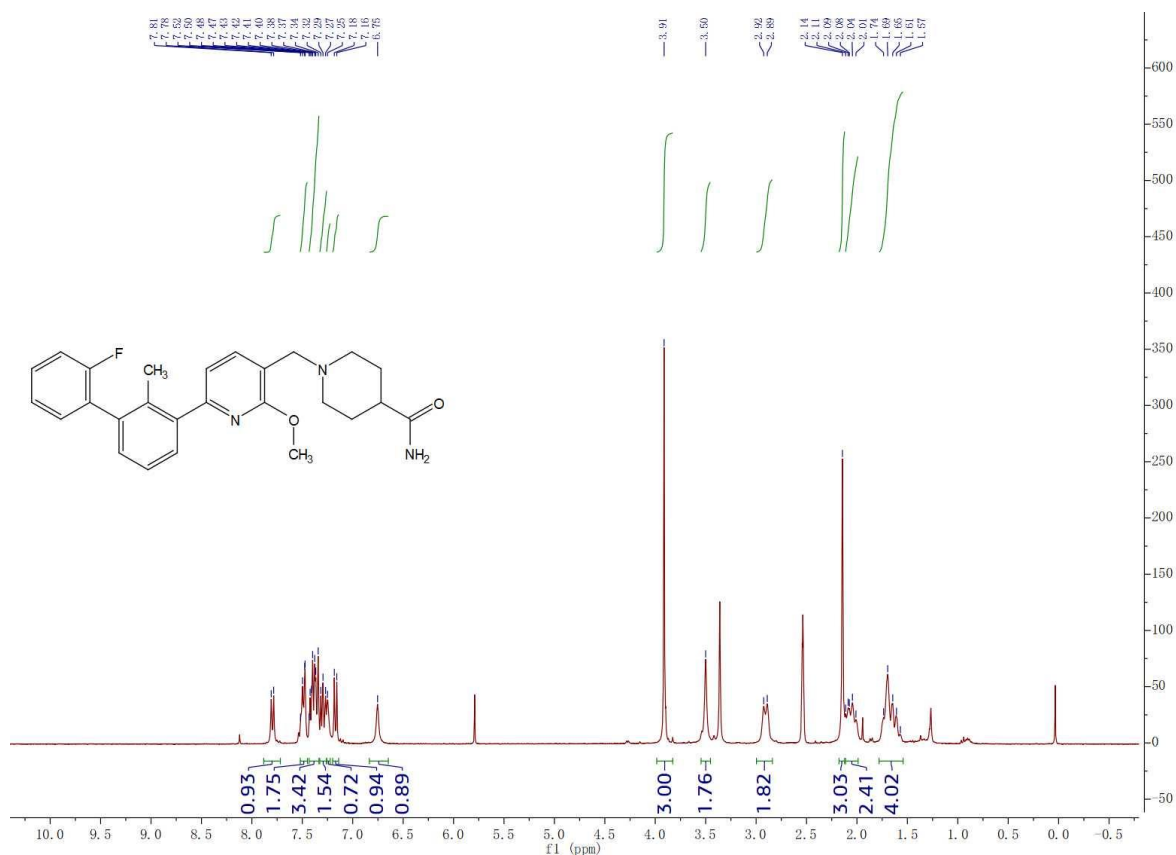
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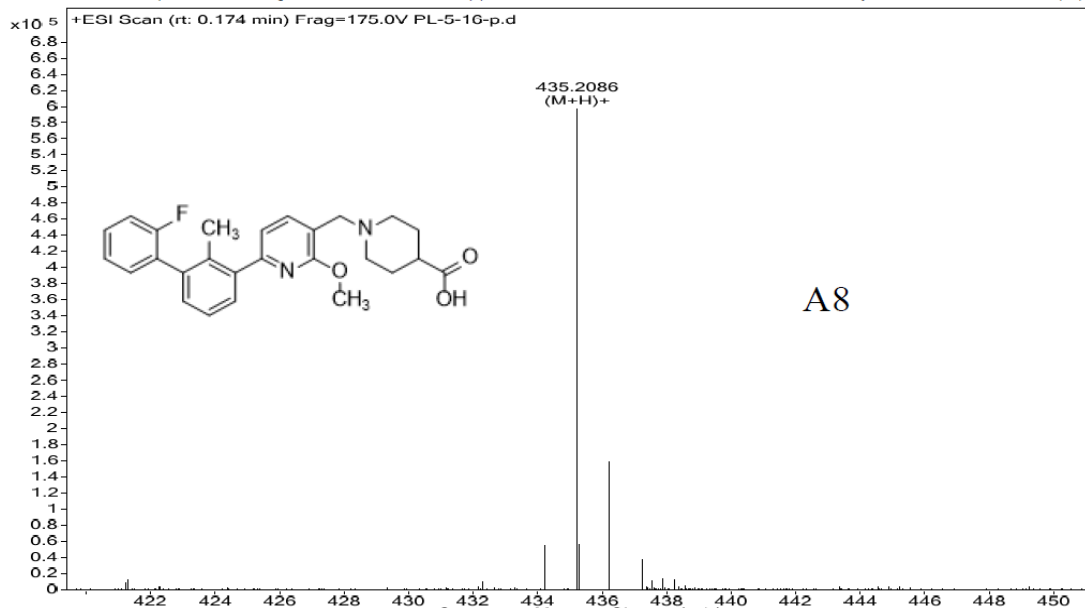
¹³C NMR Spectra for Compound A6



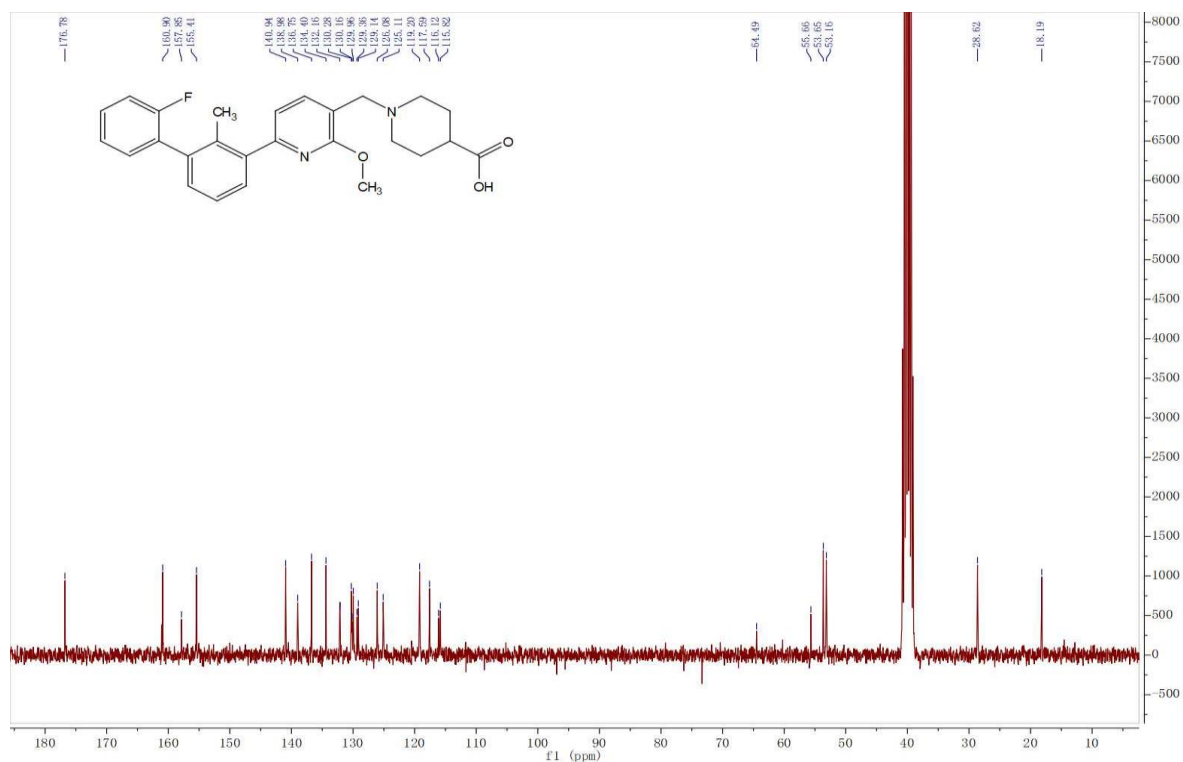
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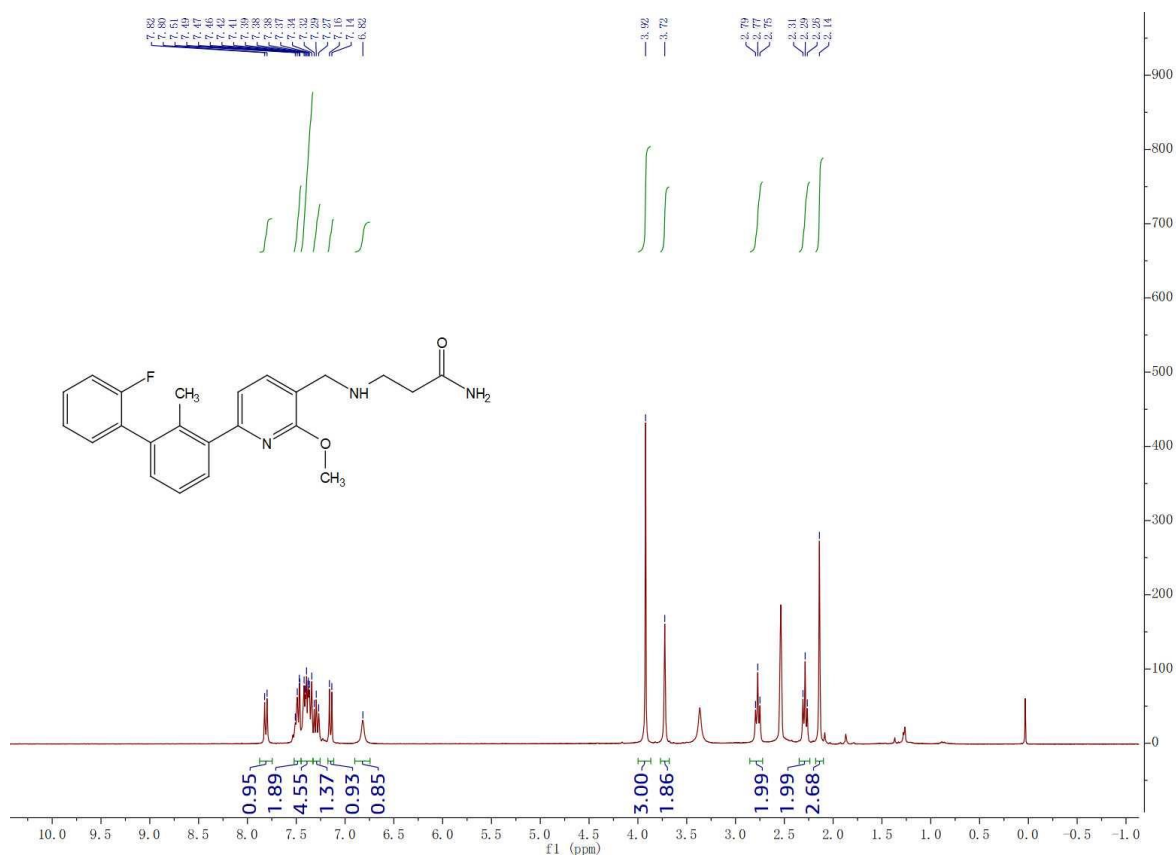
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¹³C NMR Spectra for Compound A8

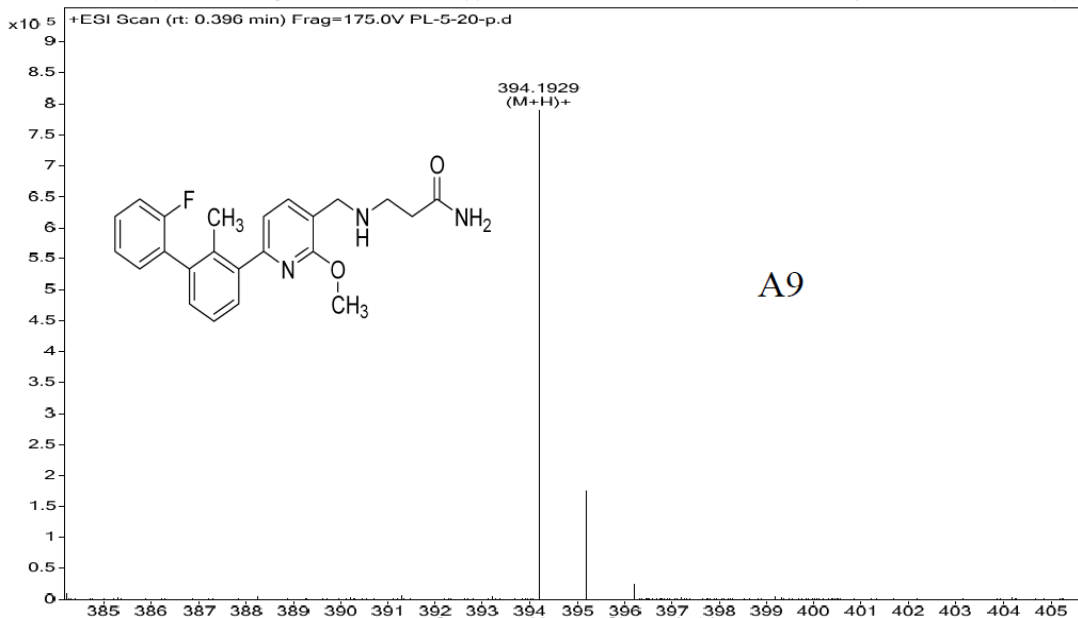


¹H NMR Spectra for Compound A9

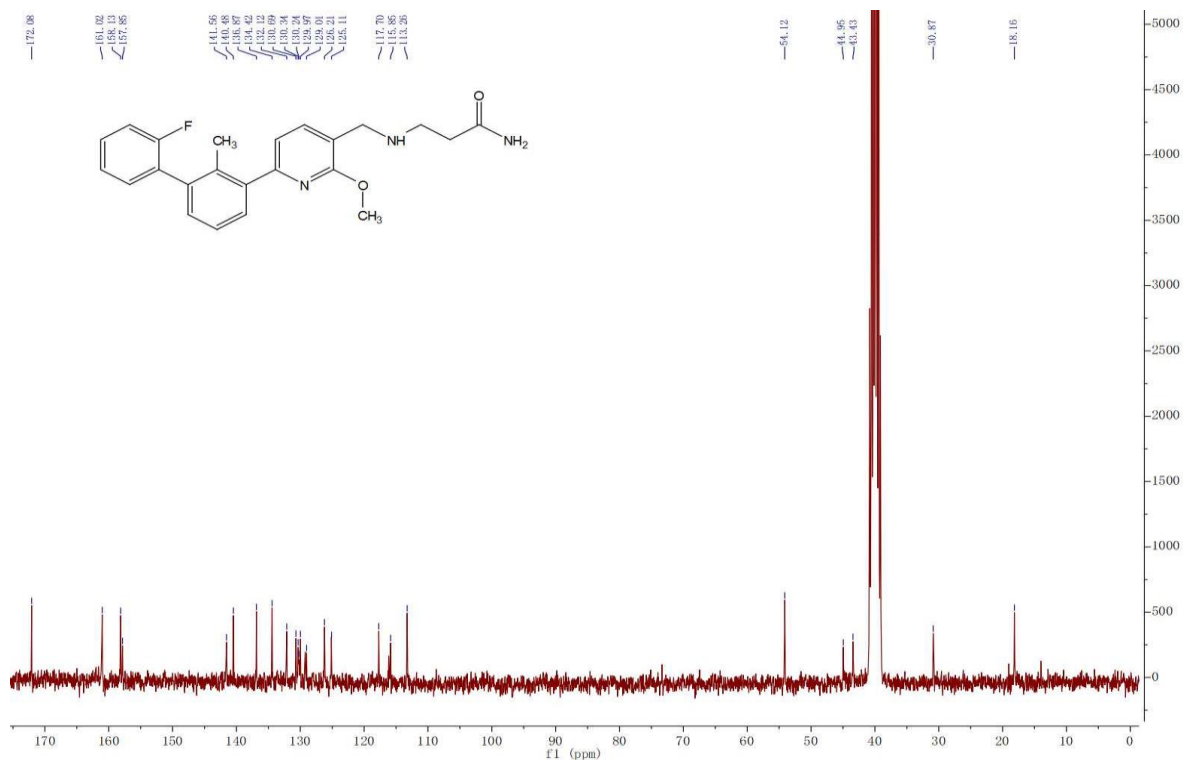


LCMS Spectra for Compound A9

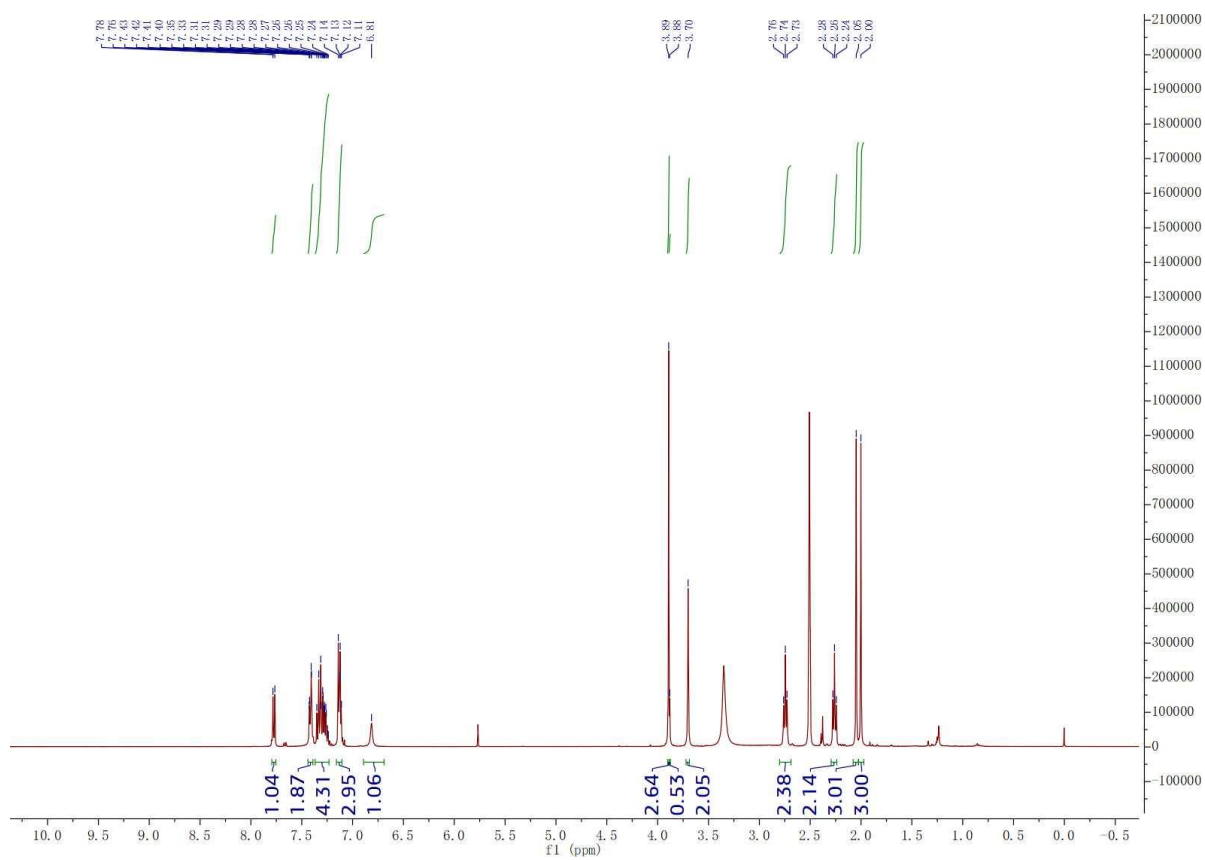
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¹³C NMR Spectra for Compound A9

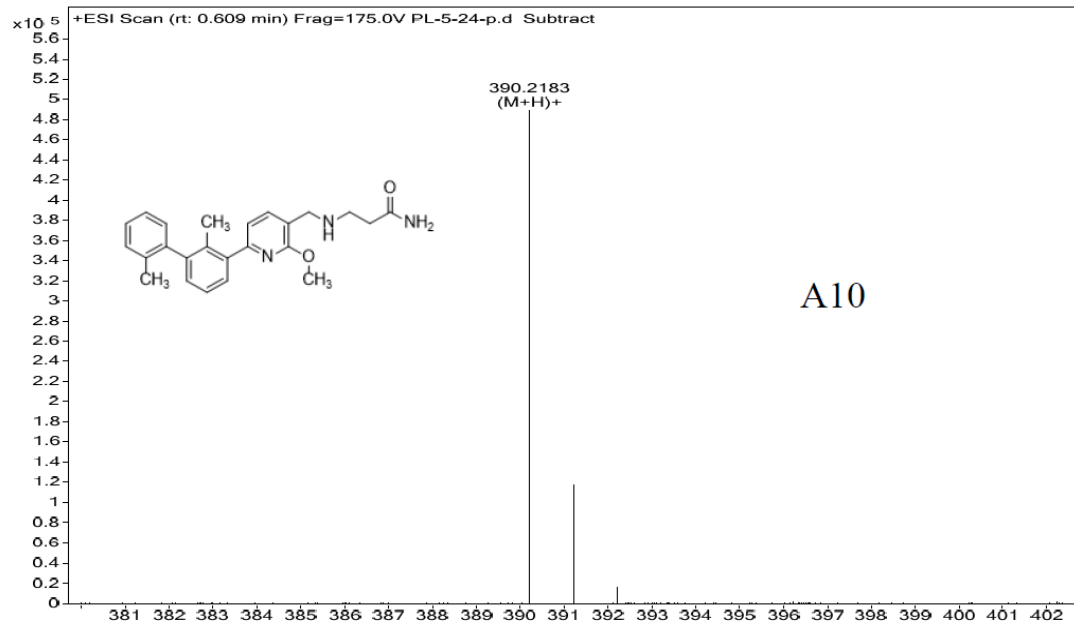


¹H NMR Spectra for Compound A10

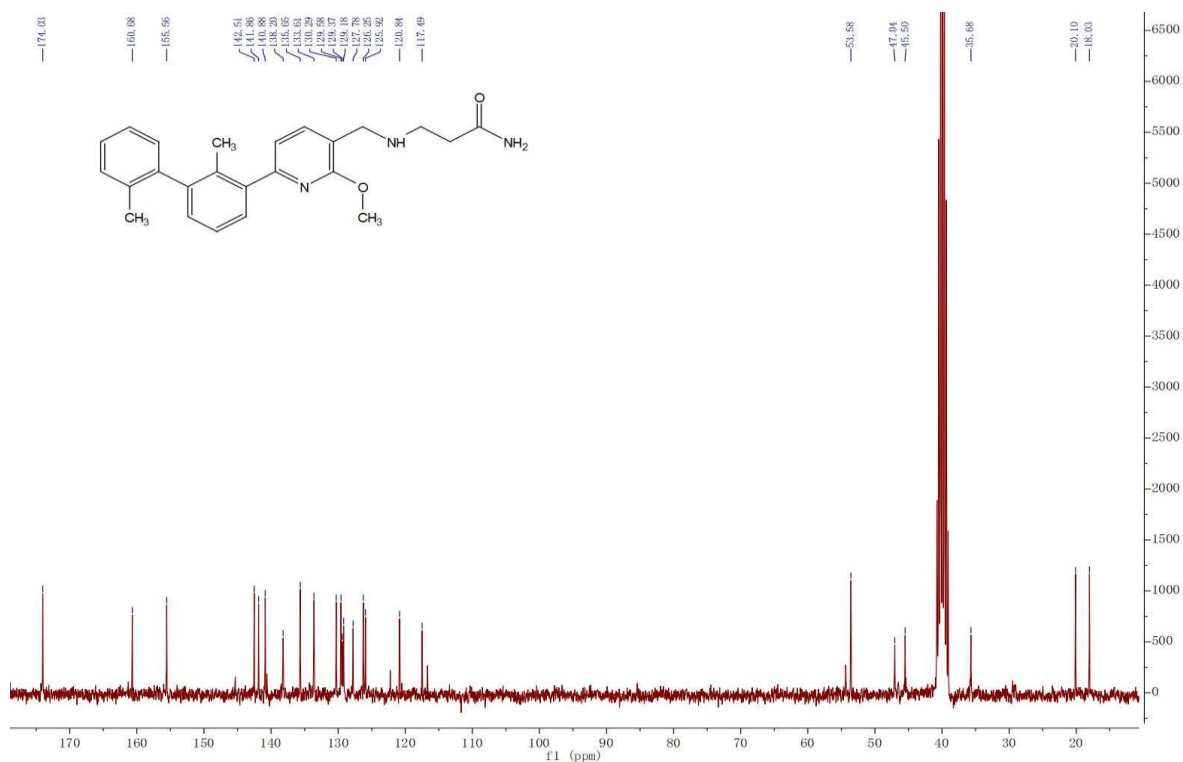


LCMS Spectra for Compound A10

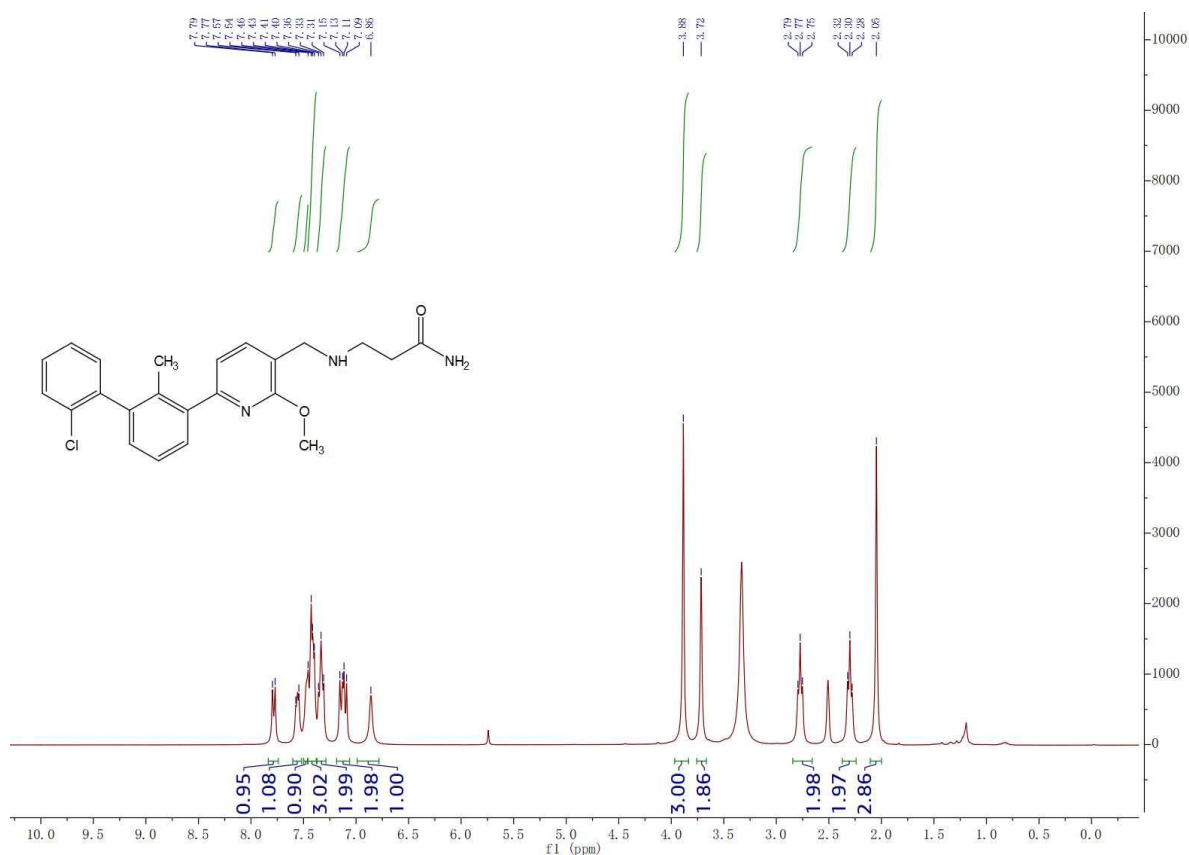
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¹³C NMR Spectra for Compound A10

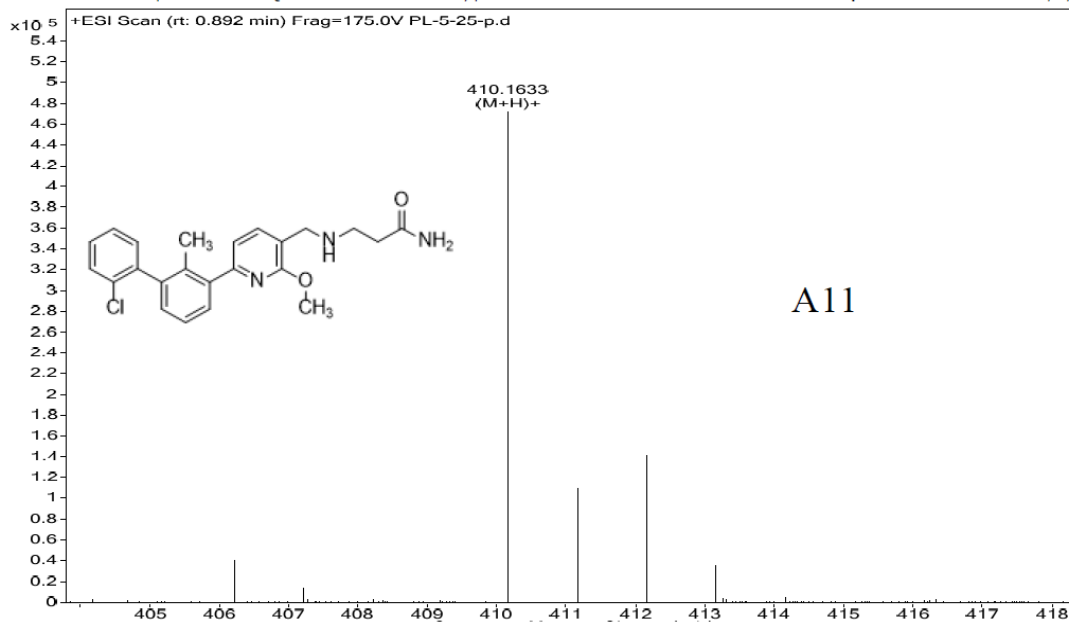


¹H NMR Spectra for Compound A11

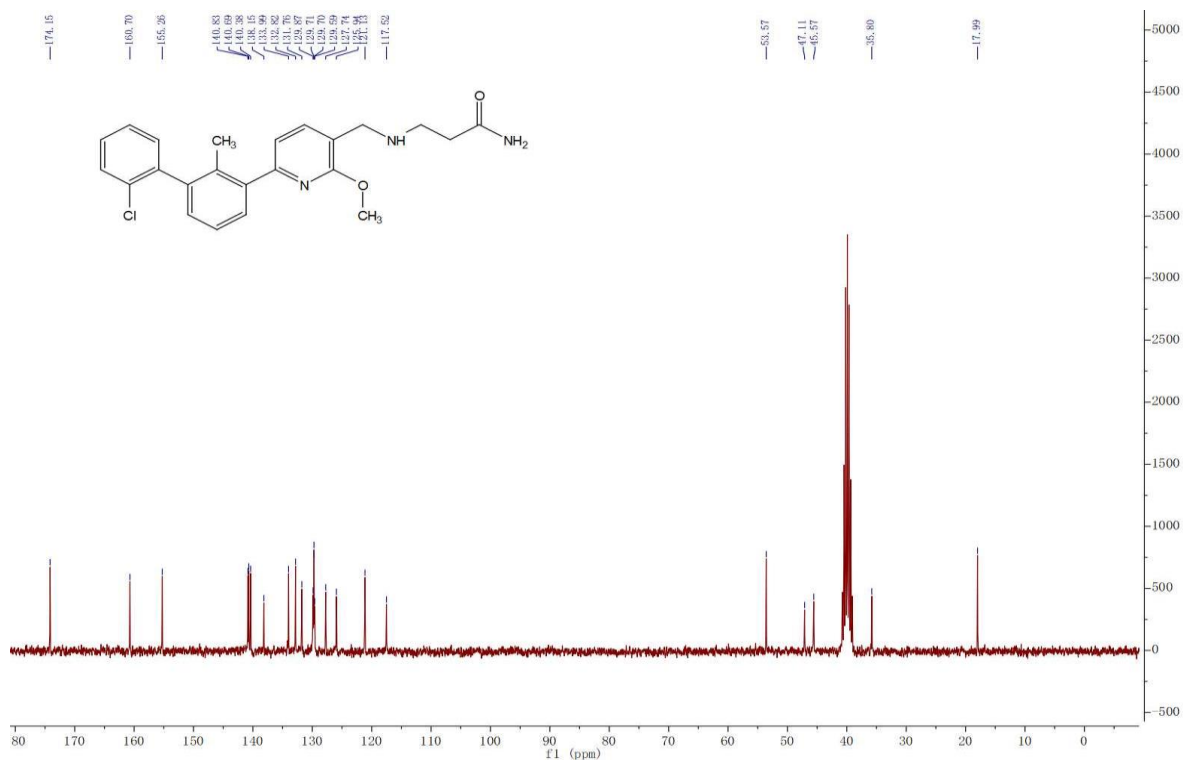


LCMS Spectra for Compound A11

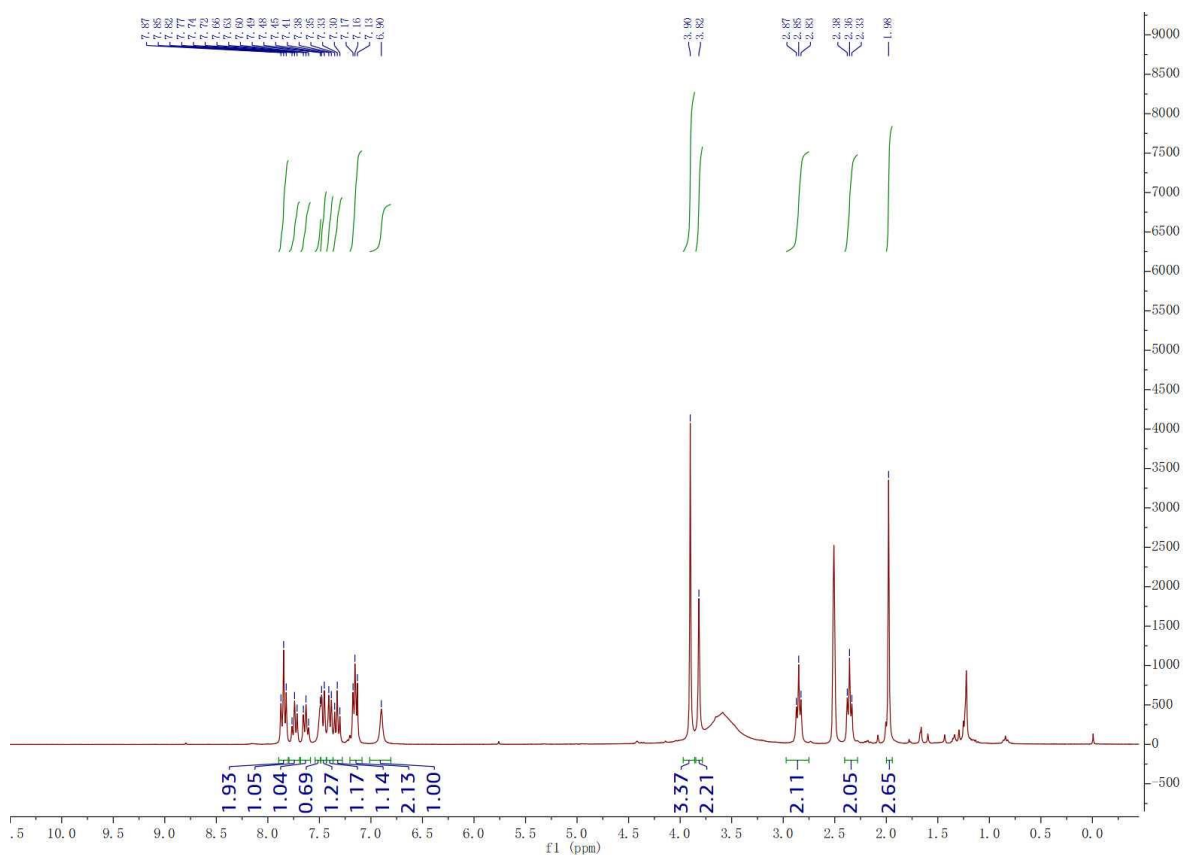
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¹³C NMR Spectra for Compound A11

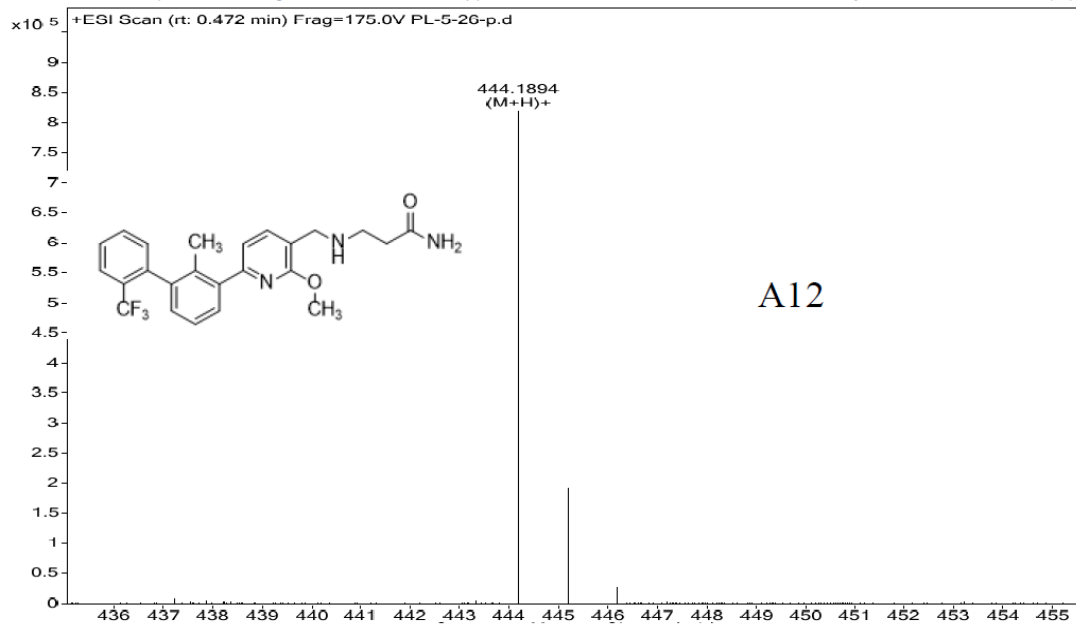


¹H NMR Spectra for Compound A12

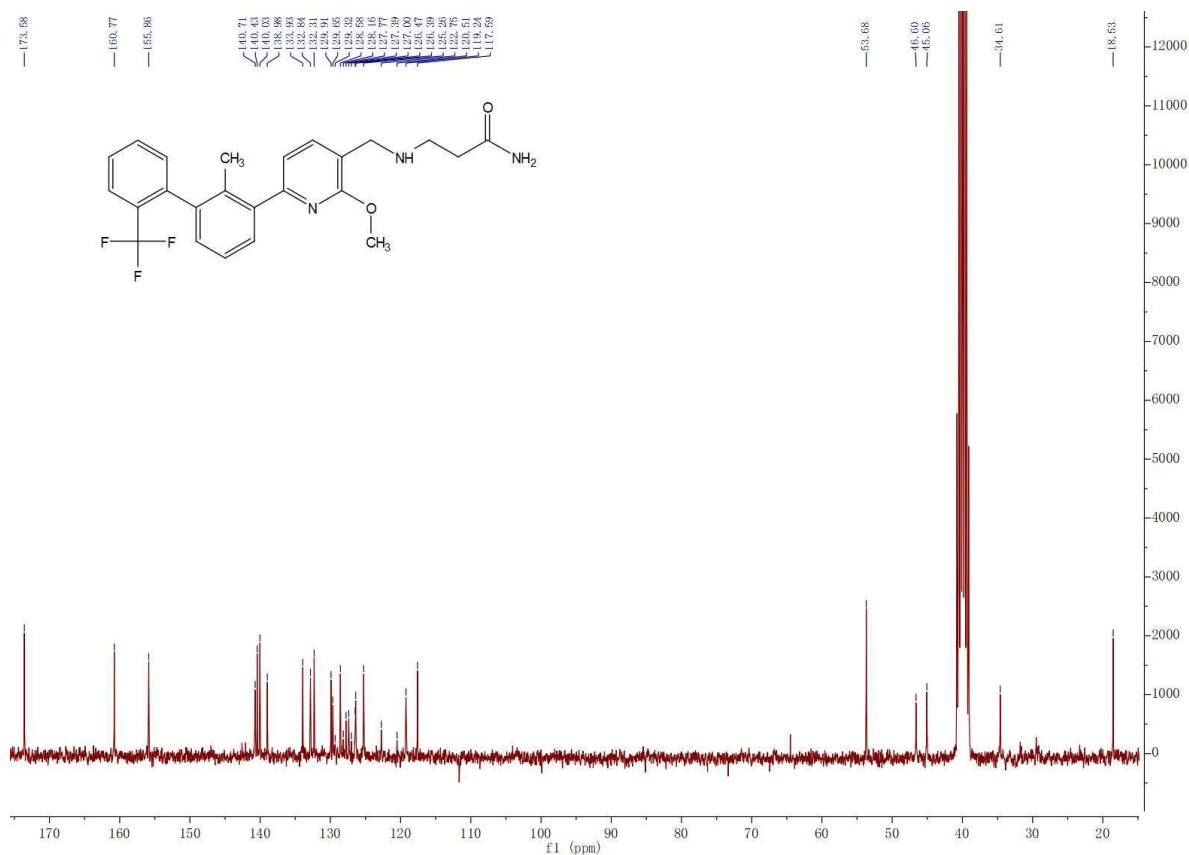


LCMS Spectra for Compound A12

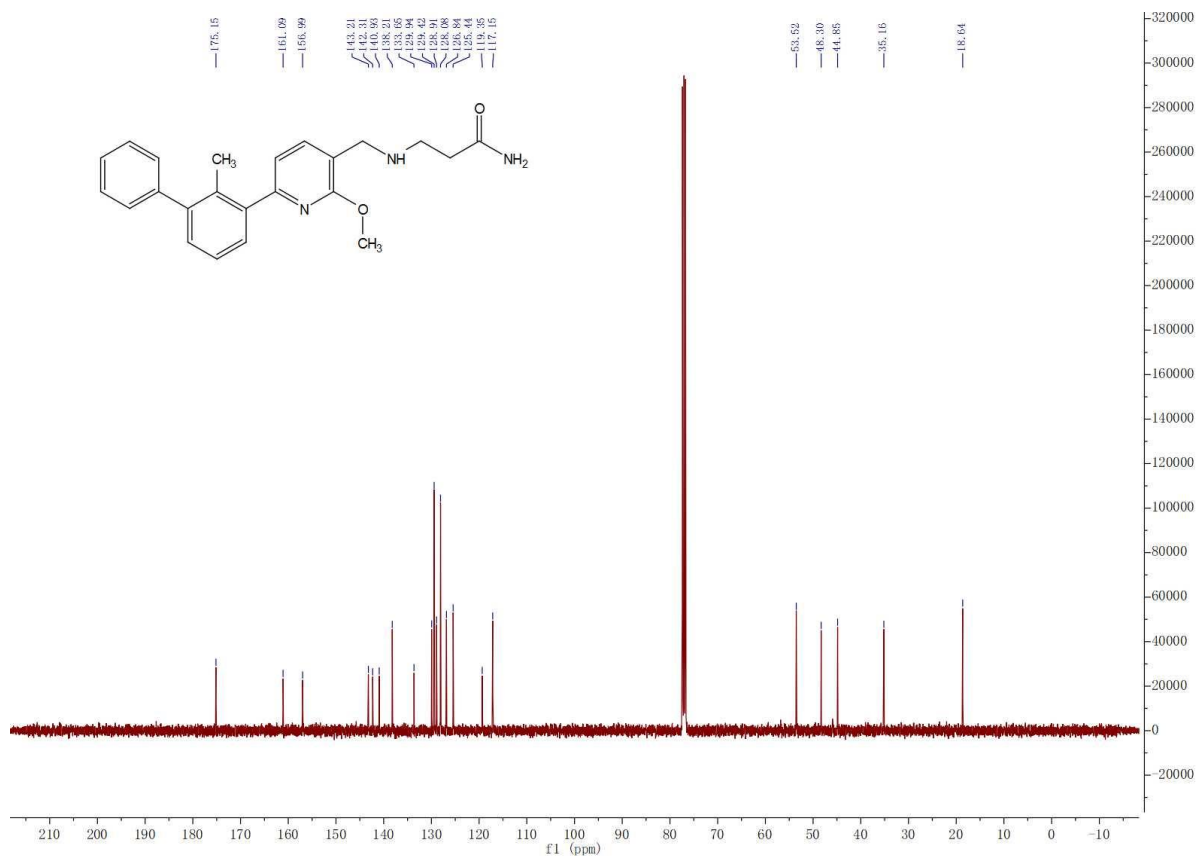
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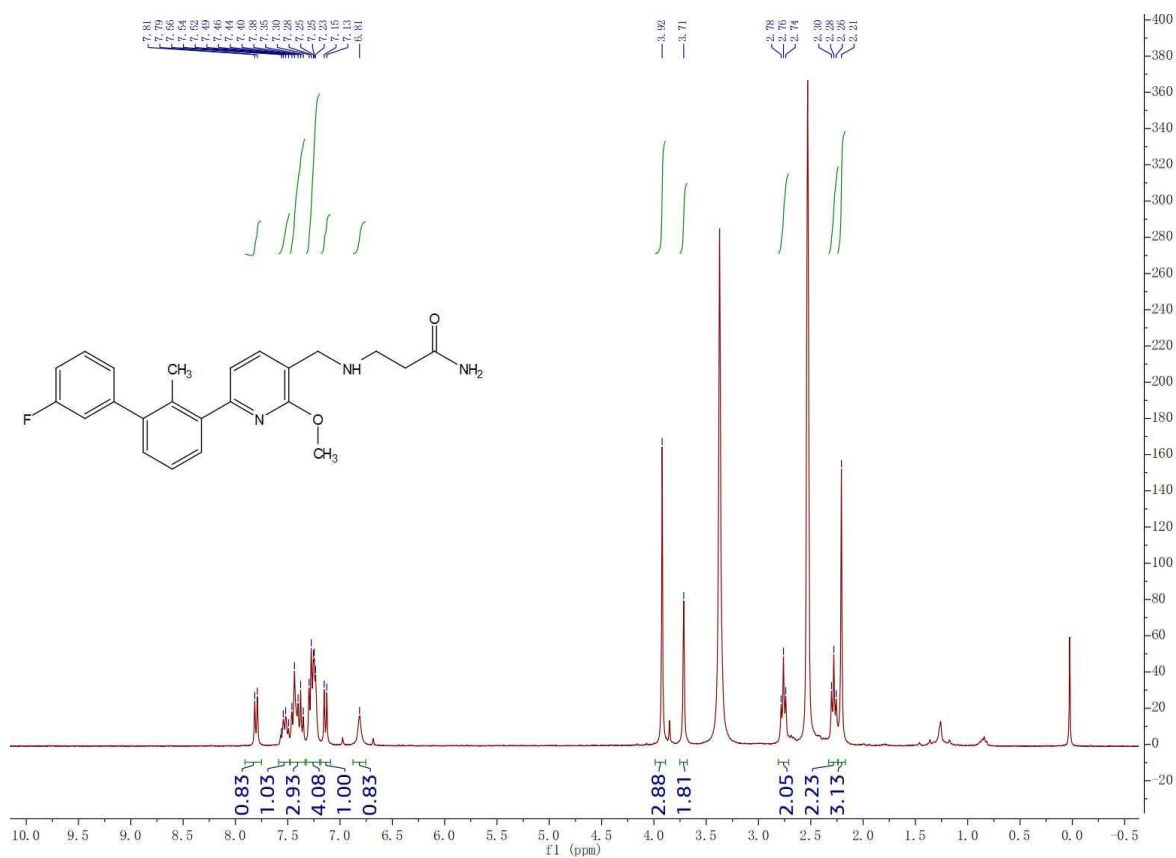
¹³C NMR Spectra for Compound A12



¹H NMR Spectra for Compound A13

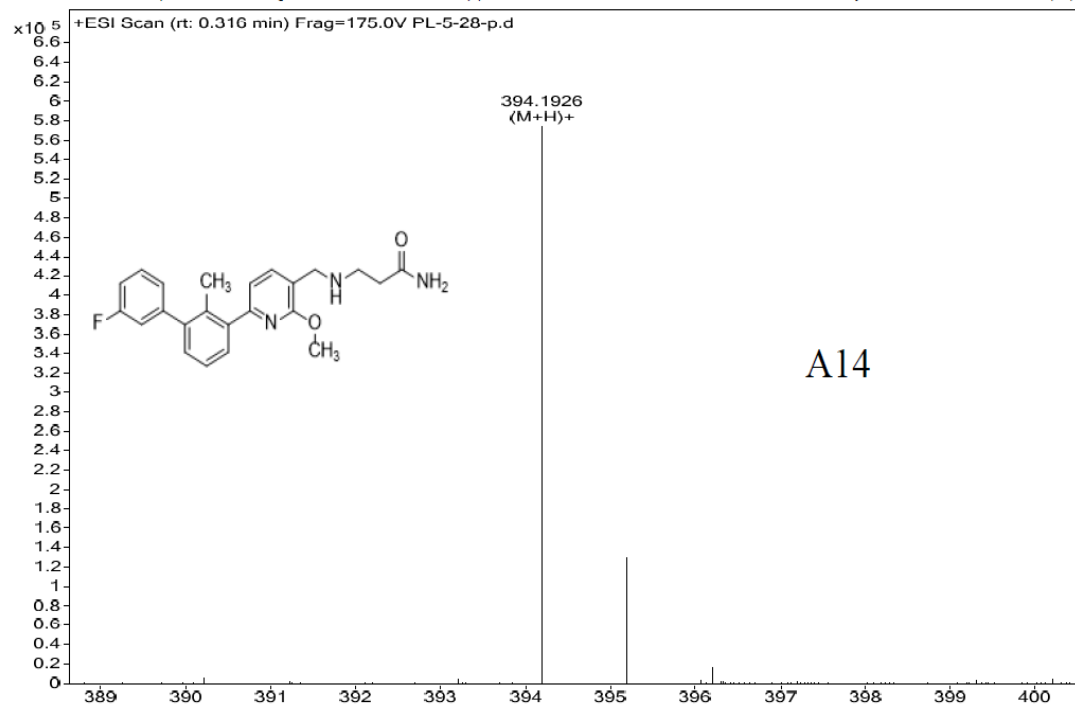


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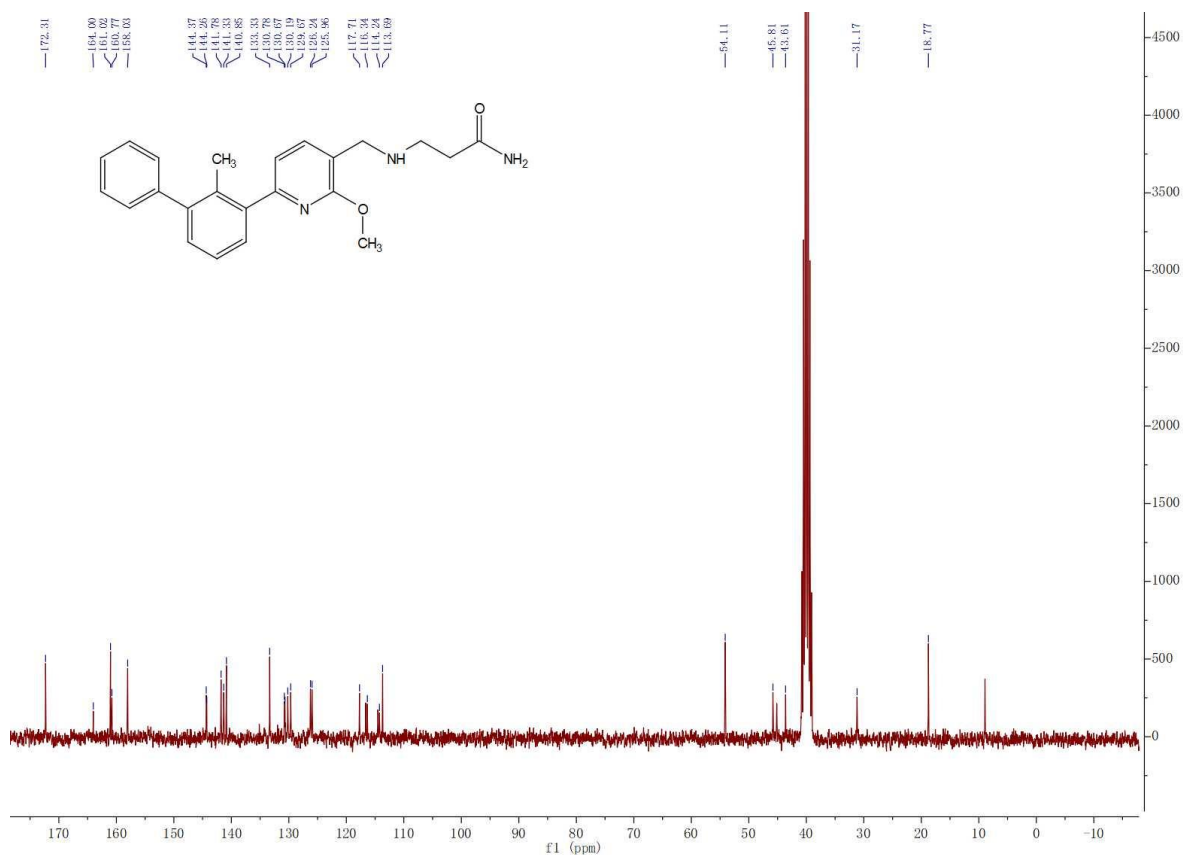


LCMS Spectra for Compound A14

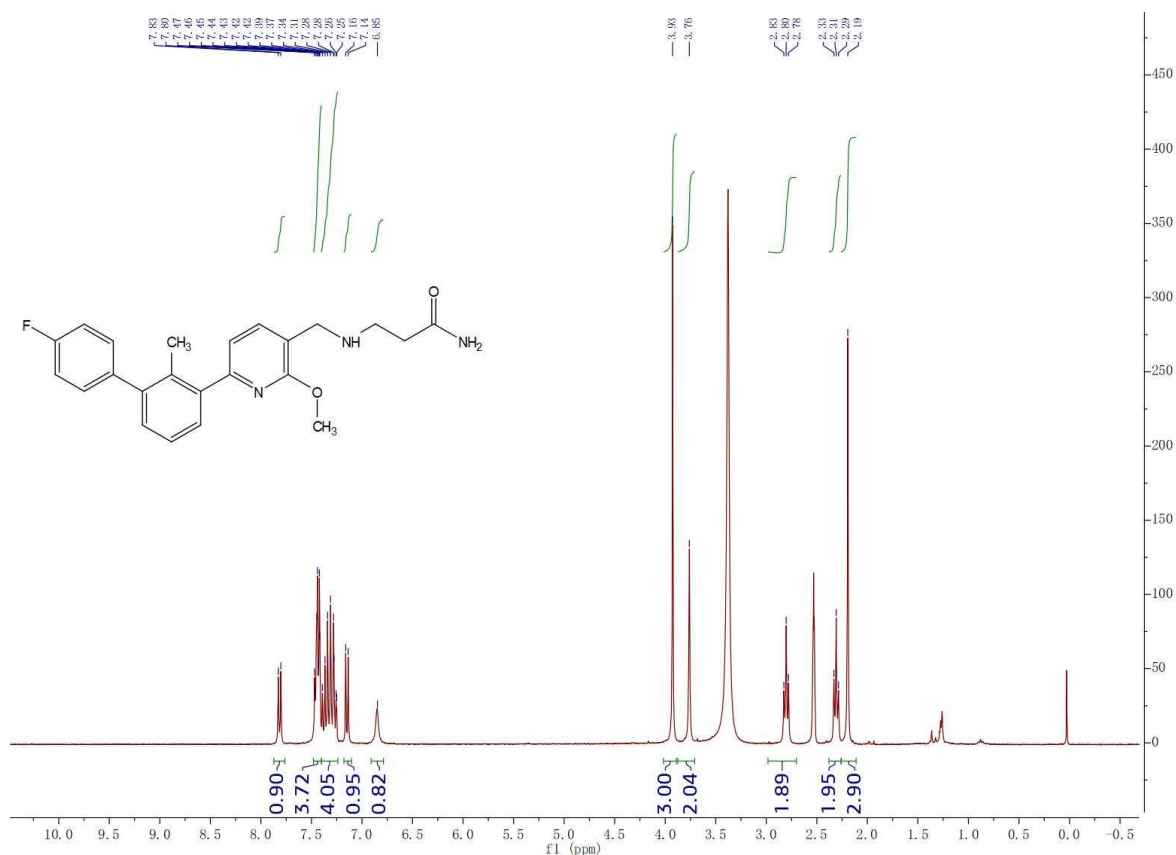
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			12/25/2020 11:05:50 AM



¹³C NMR Spectra for Compound A14

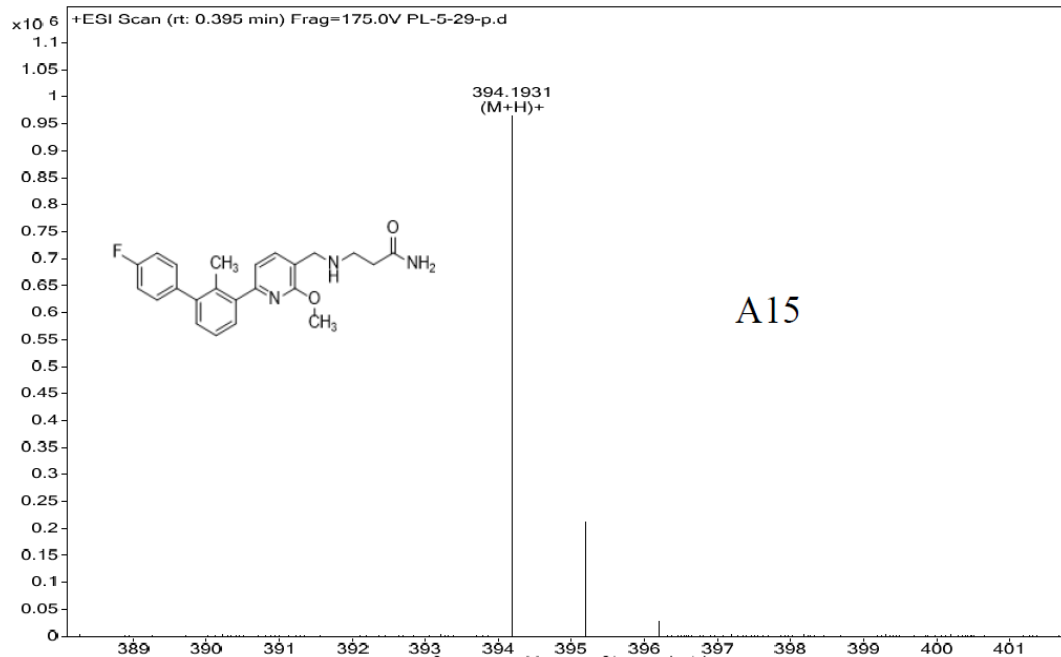


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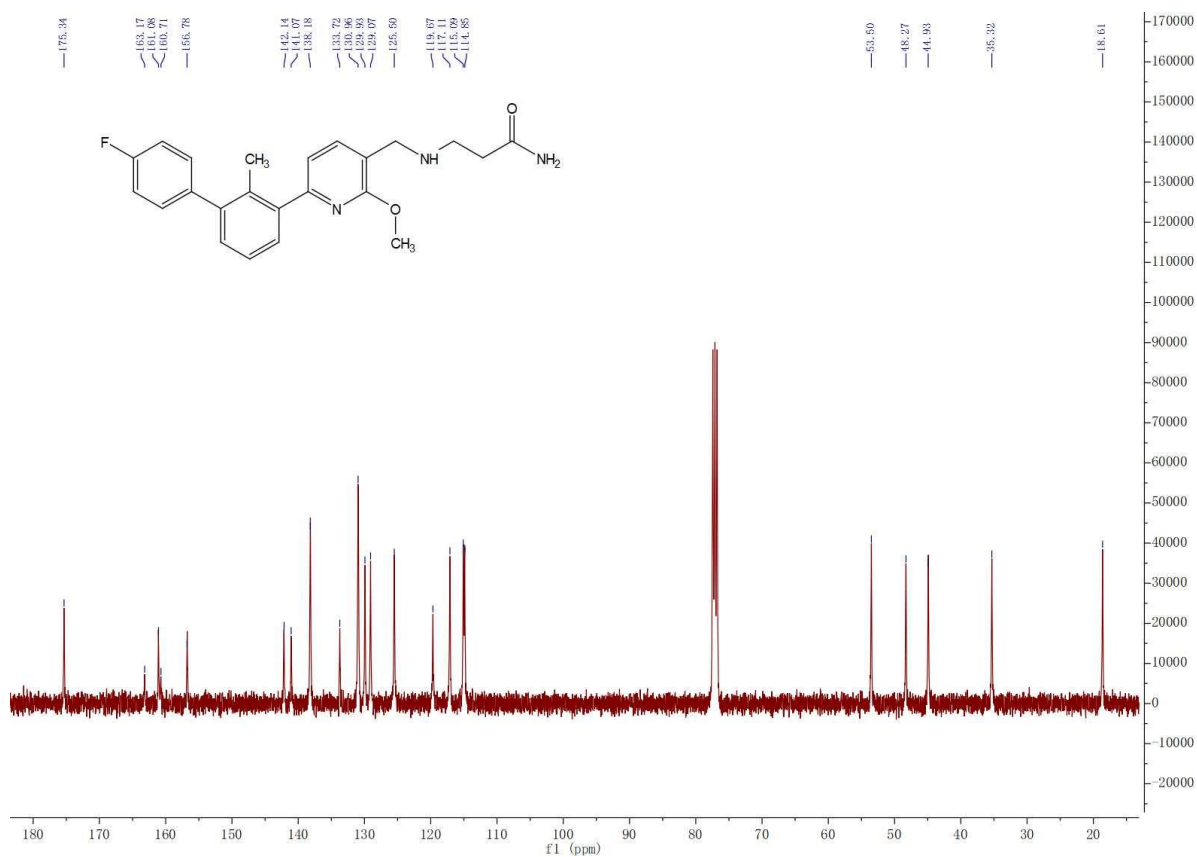


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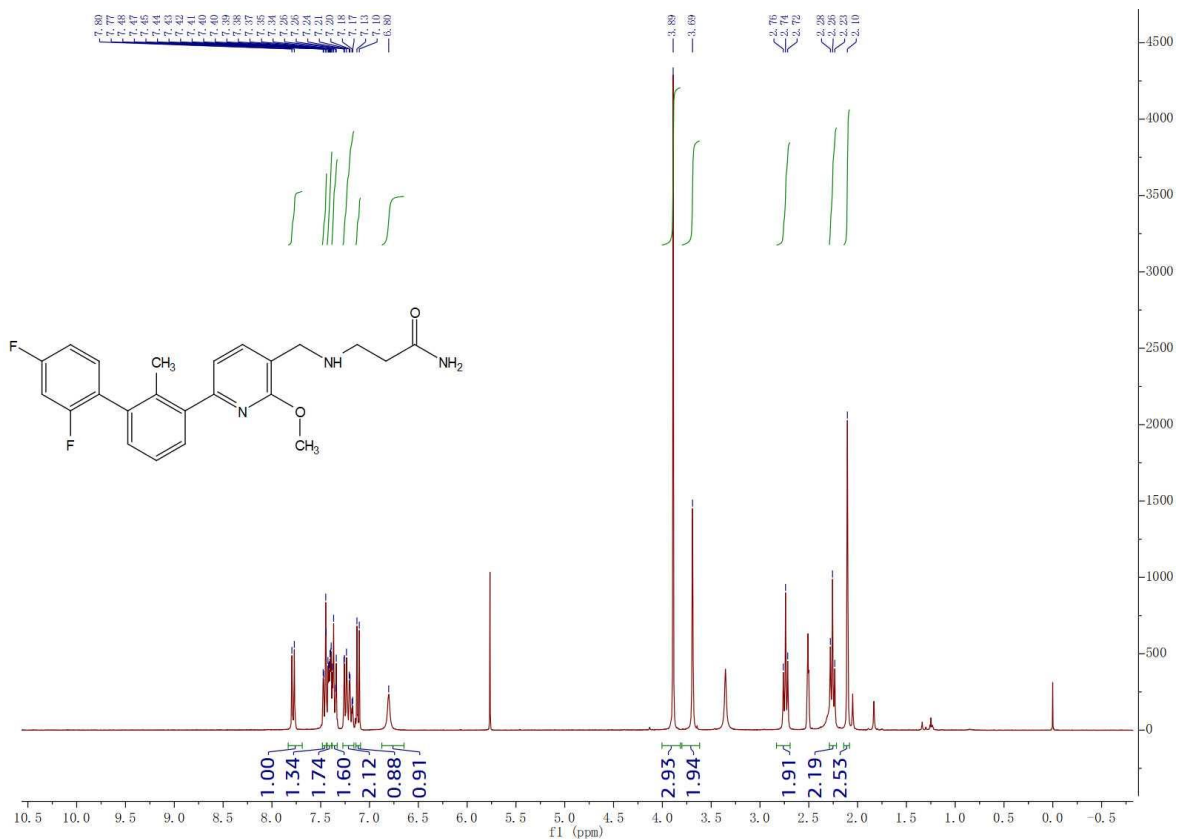
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	ACQ Method	Comment	Acquired Time
	20110418-MSonly-p.m		12/25/2020 11:10:01 AM



¹³C NMR Spectra for Compound A15

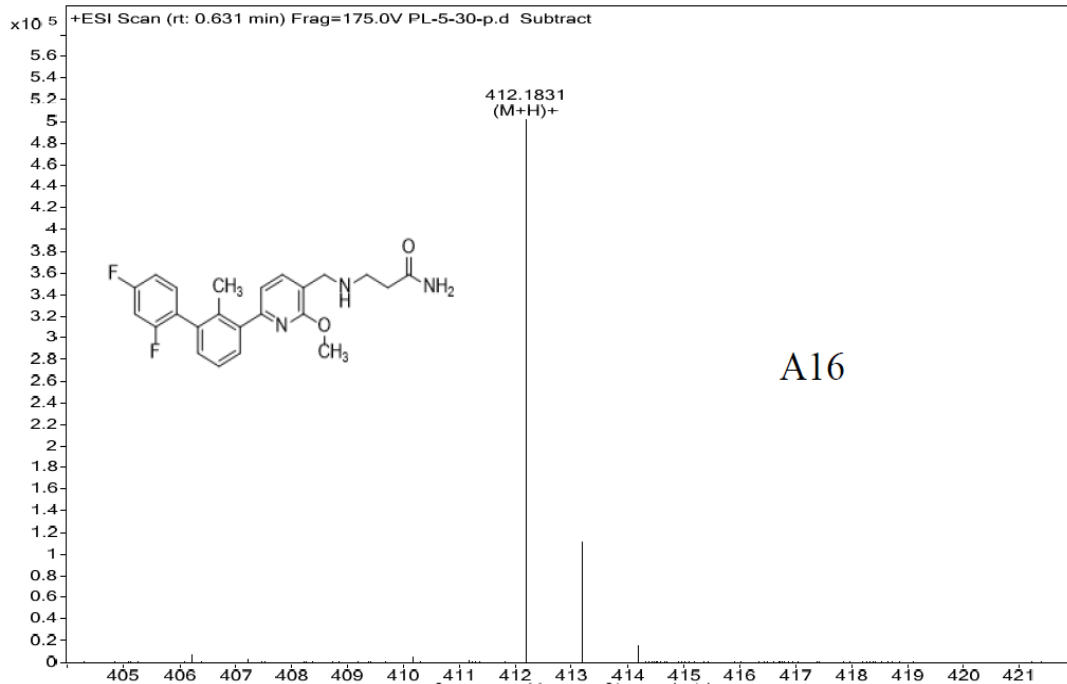


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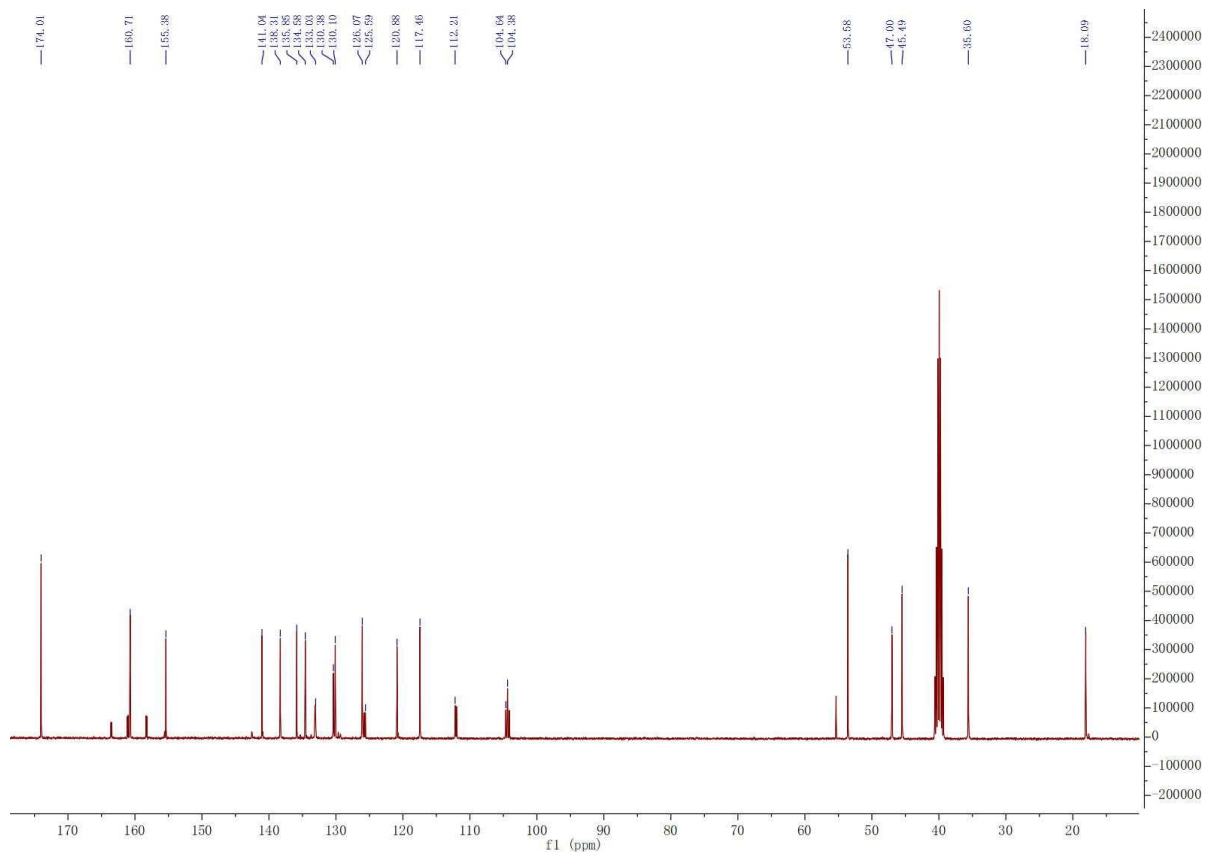


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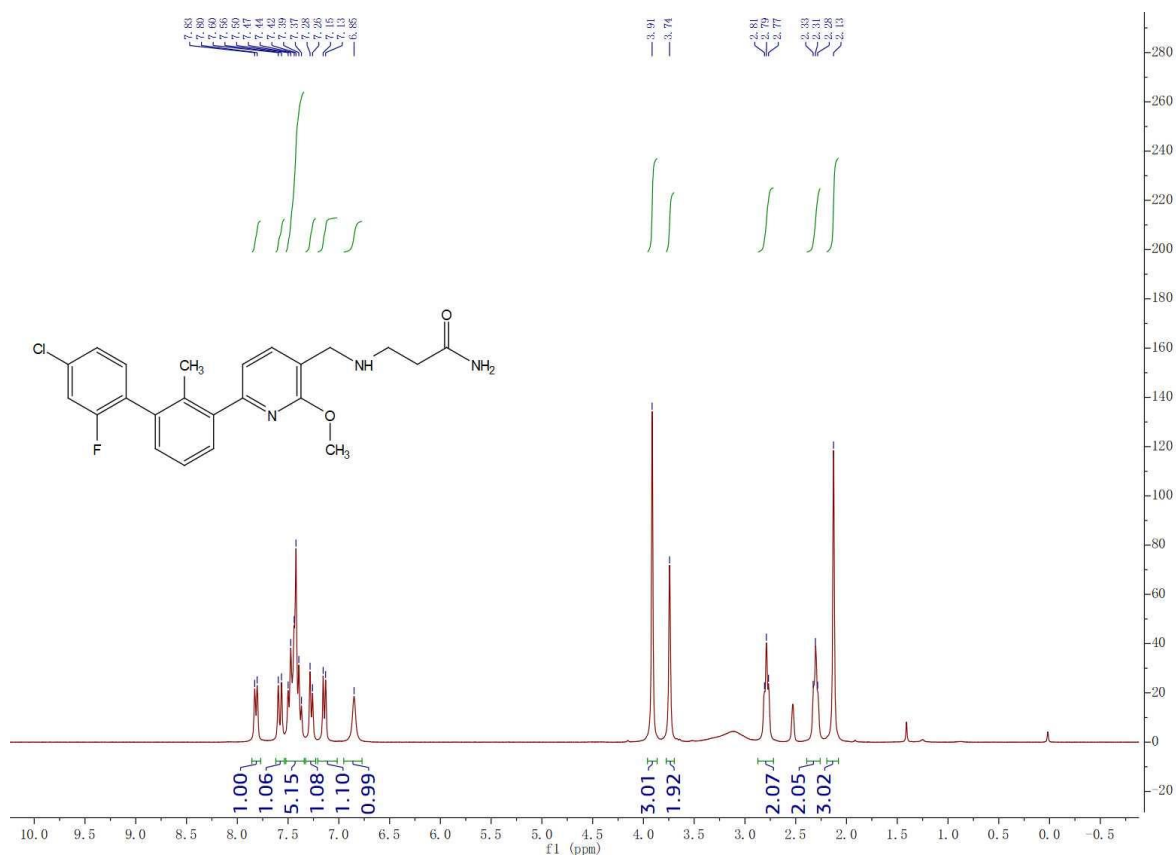
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¹³C NMR Spectra for Compound A16

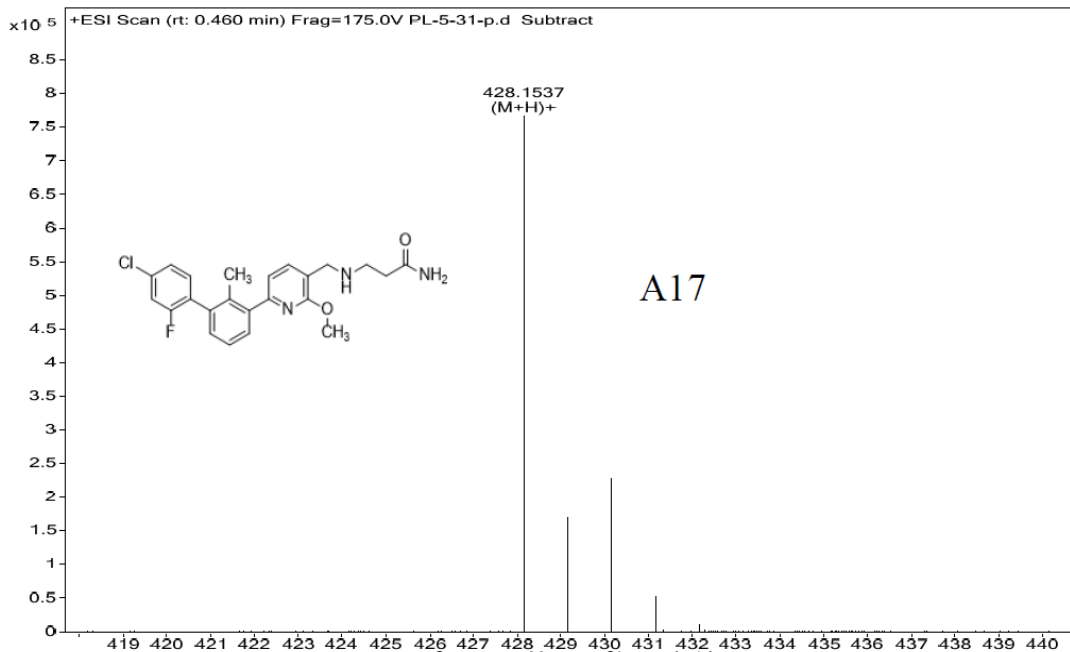


¹H NMR Spectra for Compound A17

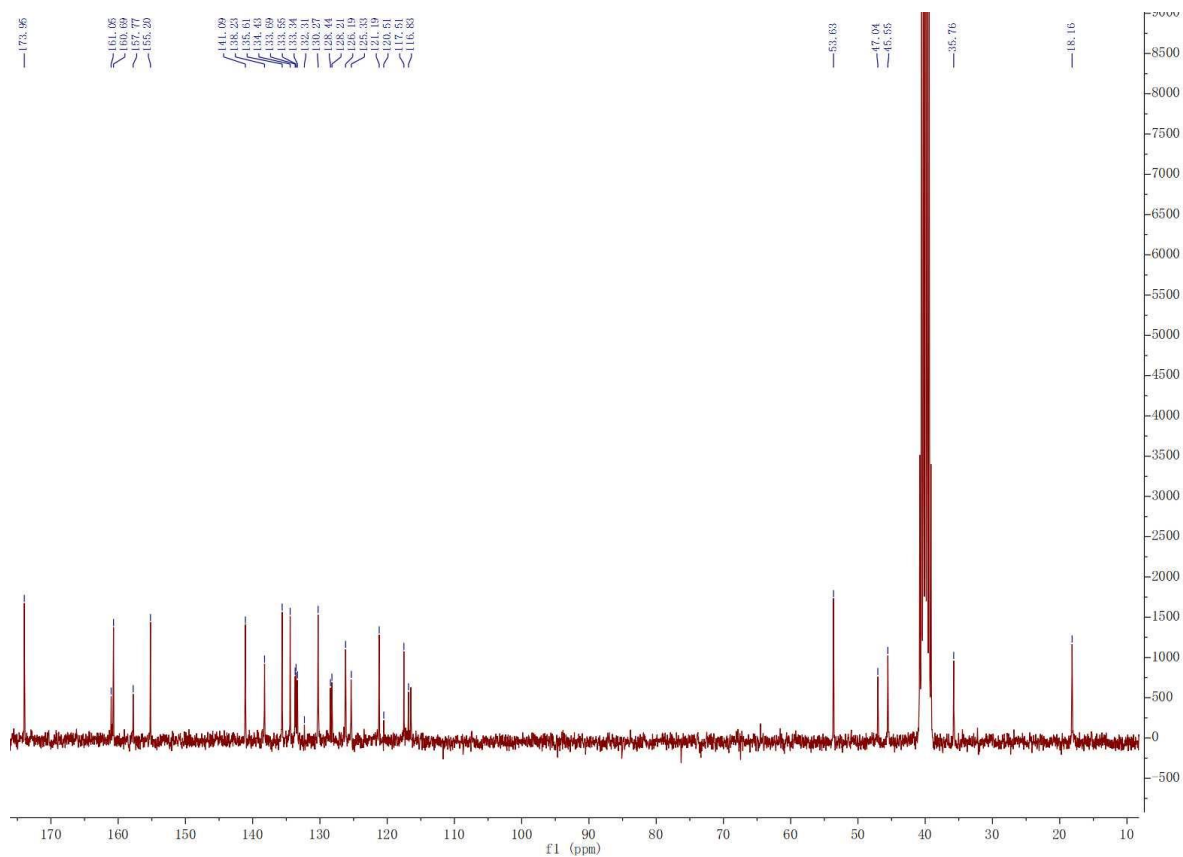


LCMS Spectra for Compound A17

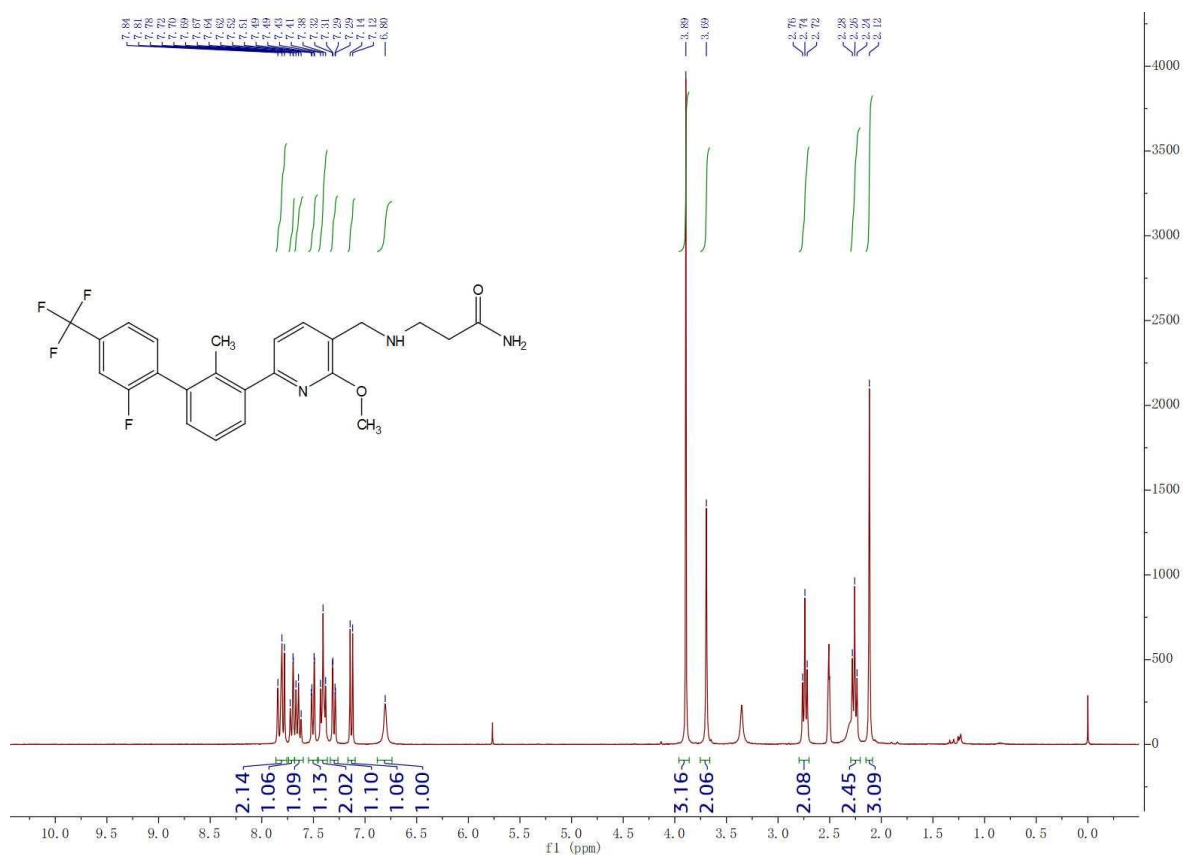
Sample Name	Position	Instrument Name	Instrument 1	User Name	G6520B-PC\Admin
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¹³C NMR Spectra for Compound A17

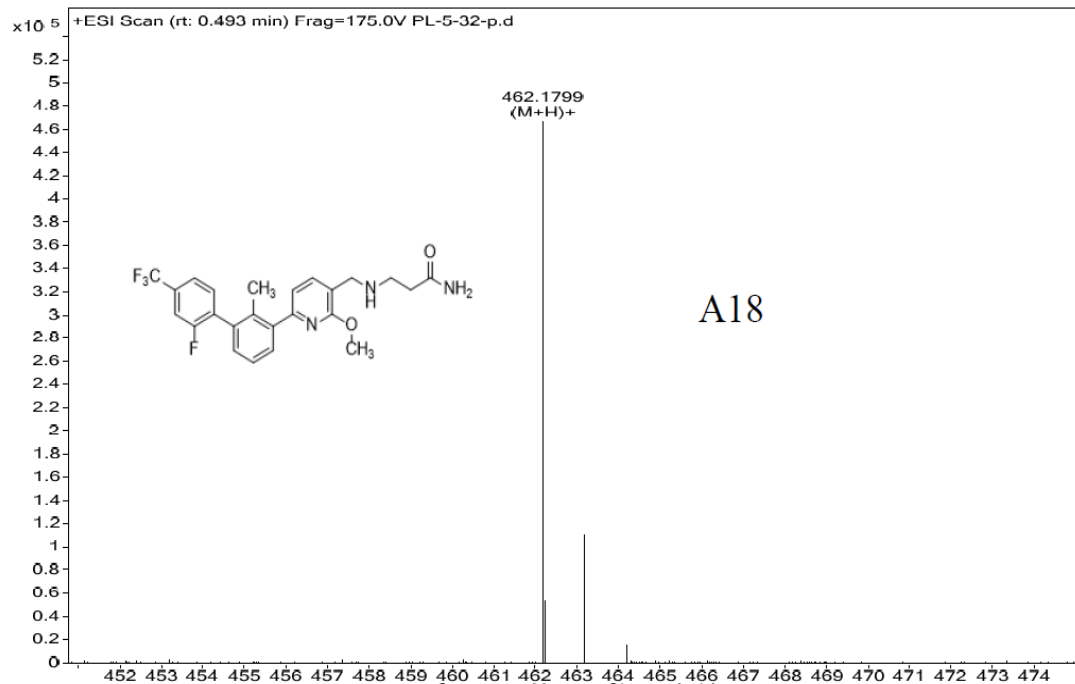


¹H NMR Spectra for Compound A18

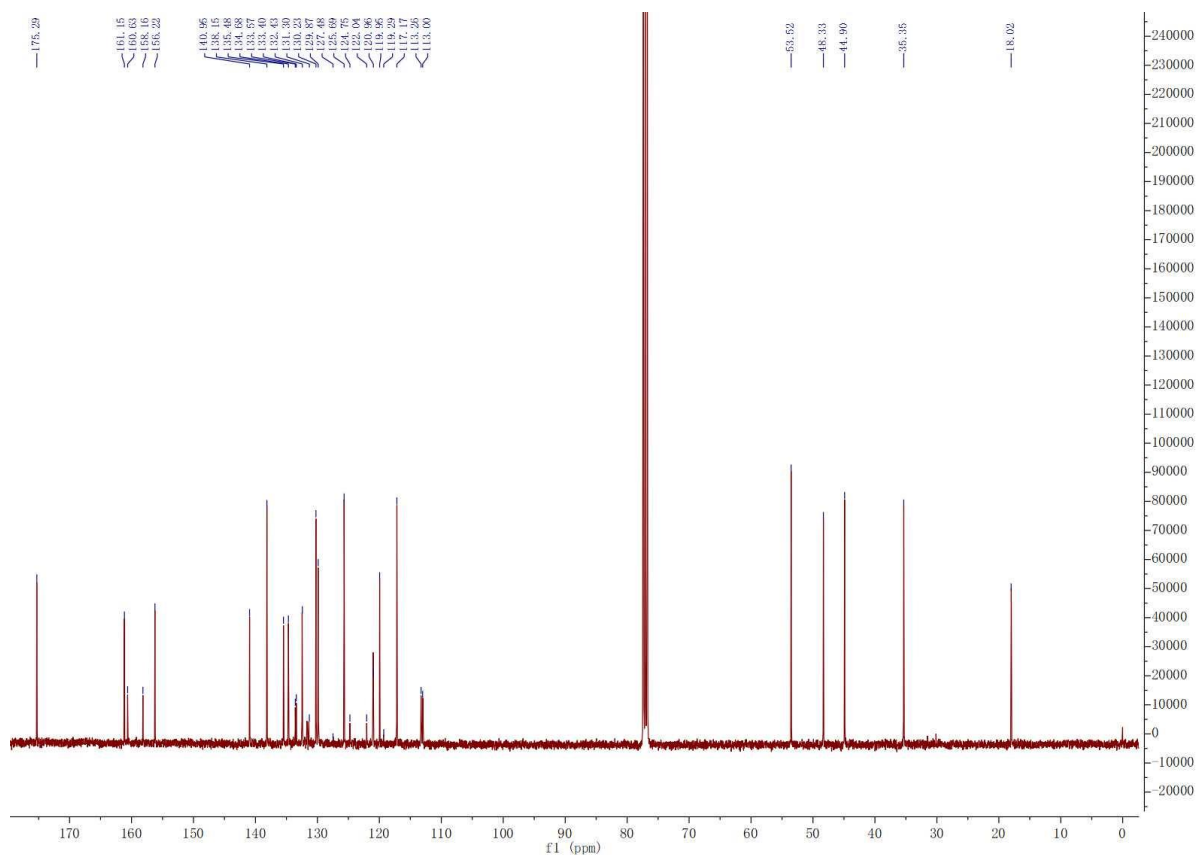


LCMS Spectra for Compound A18

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¹³C NMR Spectra for Compound A18



III. HPLC Spectroscopic data for A9

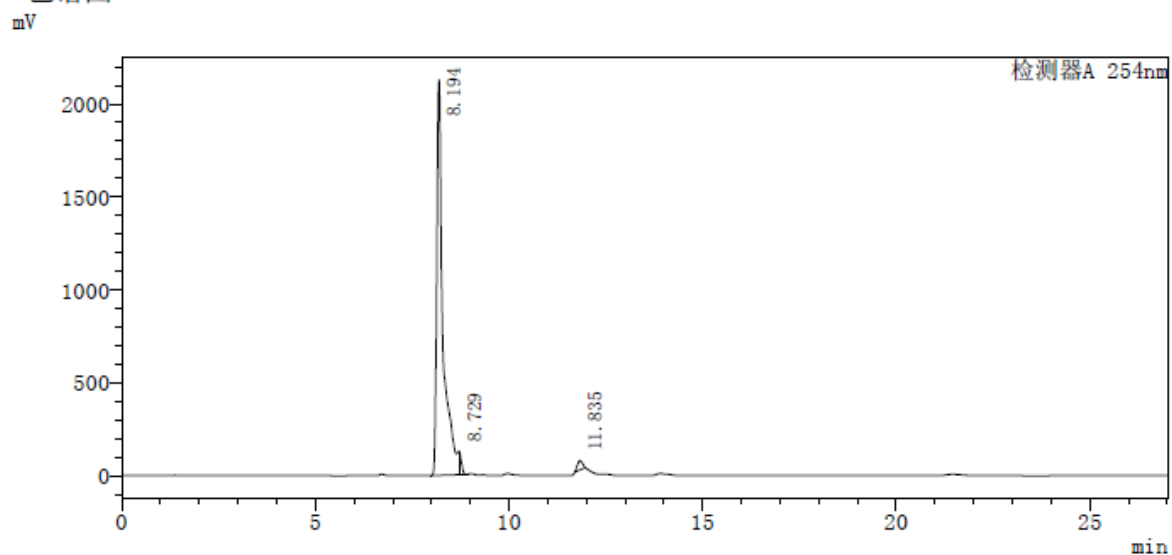
SHIMADZU LabSolutions 分析报告

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 进样体积 : 10 μ L
 分析日期 : 2021/1/14 15:34:51
 处理日期 : 2021/1/14 16:01:59

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 分析者 : System Administrator
 处理者 : System Administrator

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<峰表>

检测器A 254nm

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