Supporting Information

Synthesis, Resolution, Configurational Stability and Properties of Cationic Functionalized [5]helicenes

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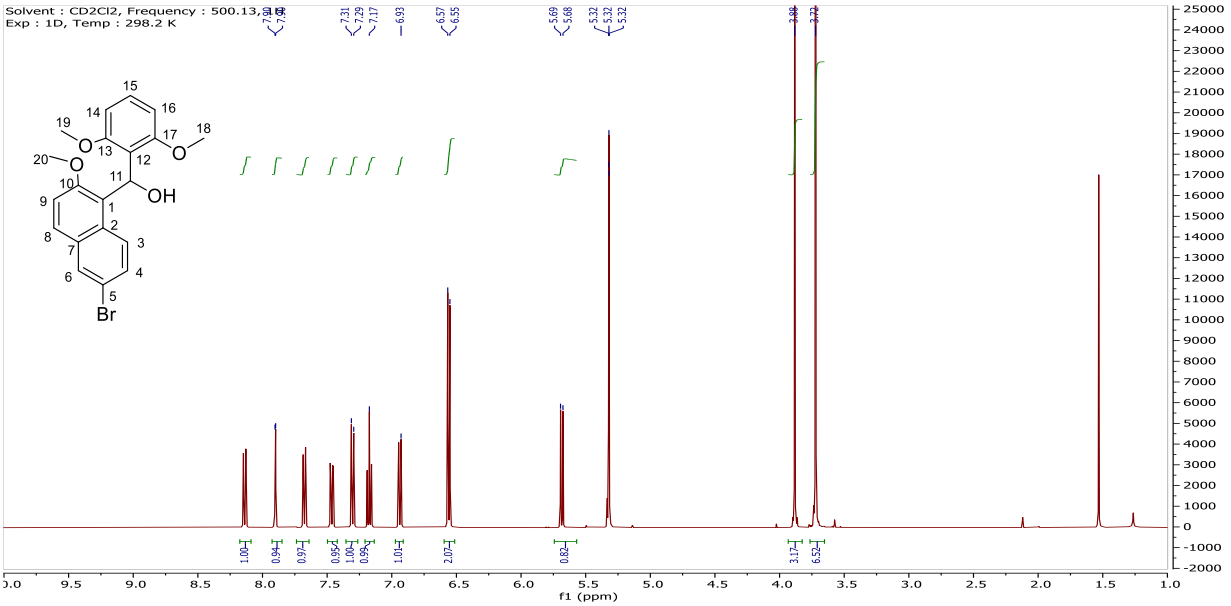
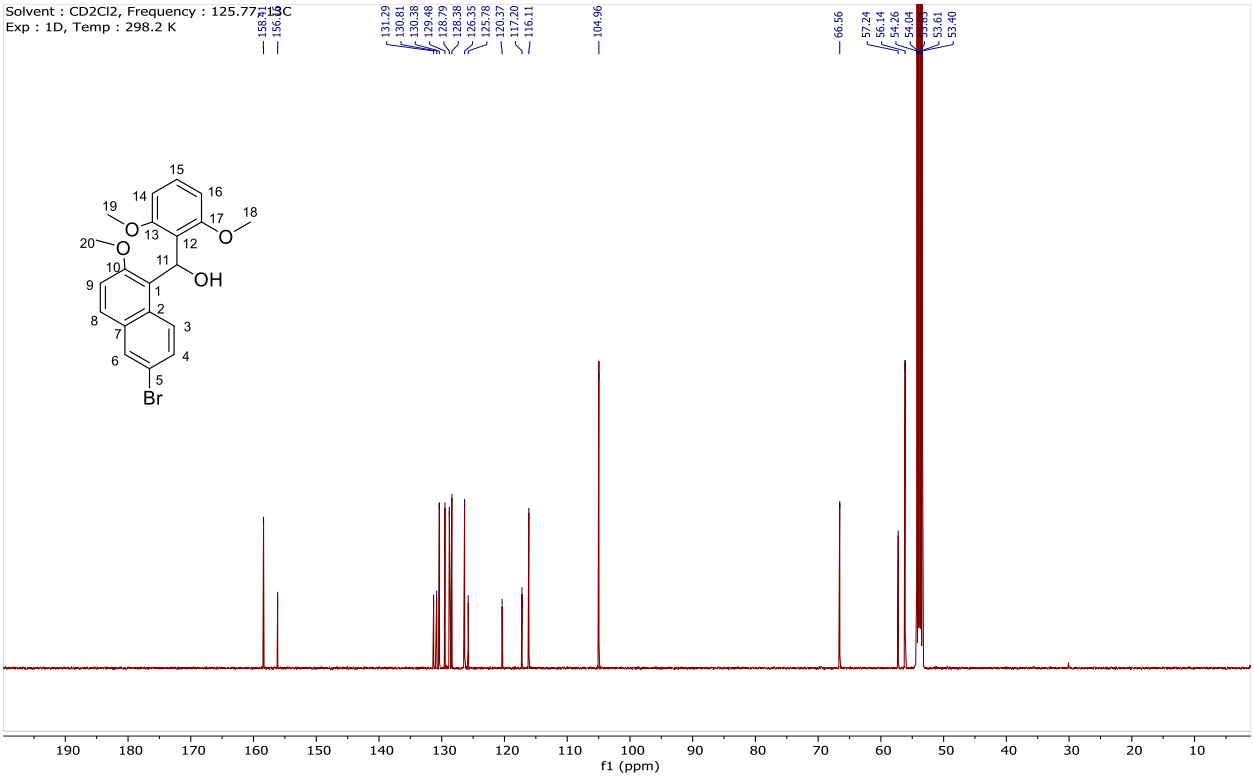
S-I. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, NOESY and HRMS spectra of the compounds

(6-Bromo-2-methoxynaphthalen-1-yl)(2,6-dimethoxyphenyl)methanol (I)





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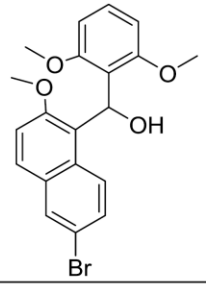
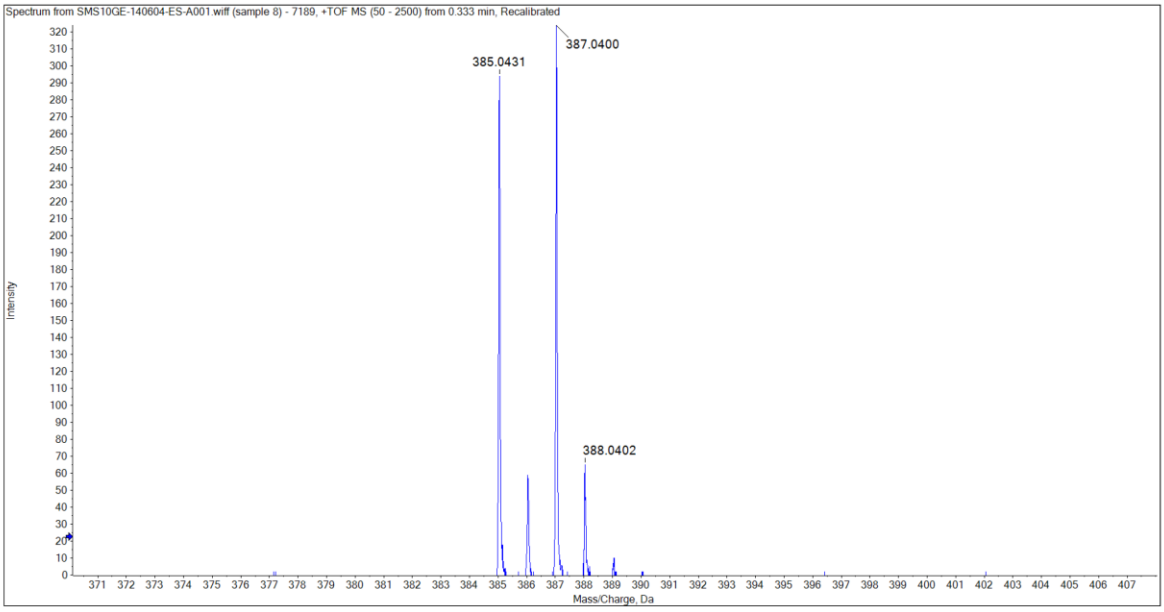
Sciences Mass Spectrometry

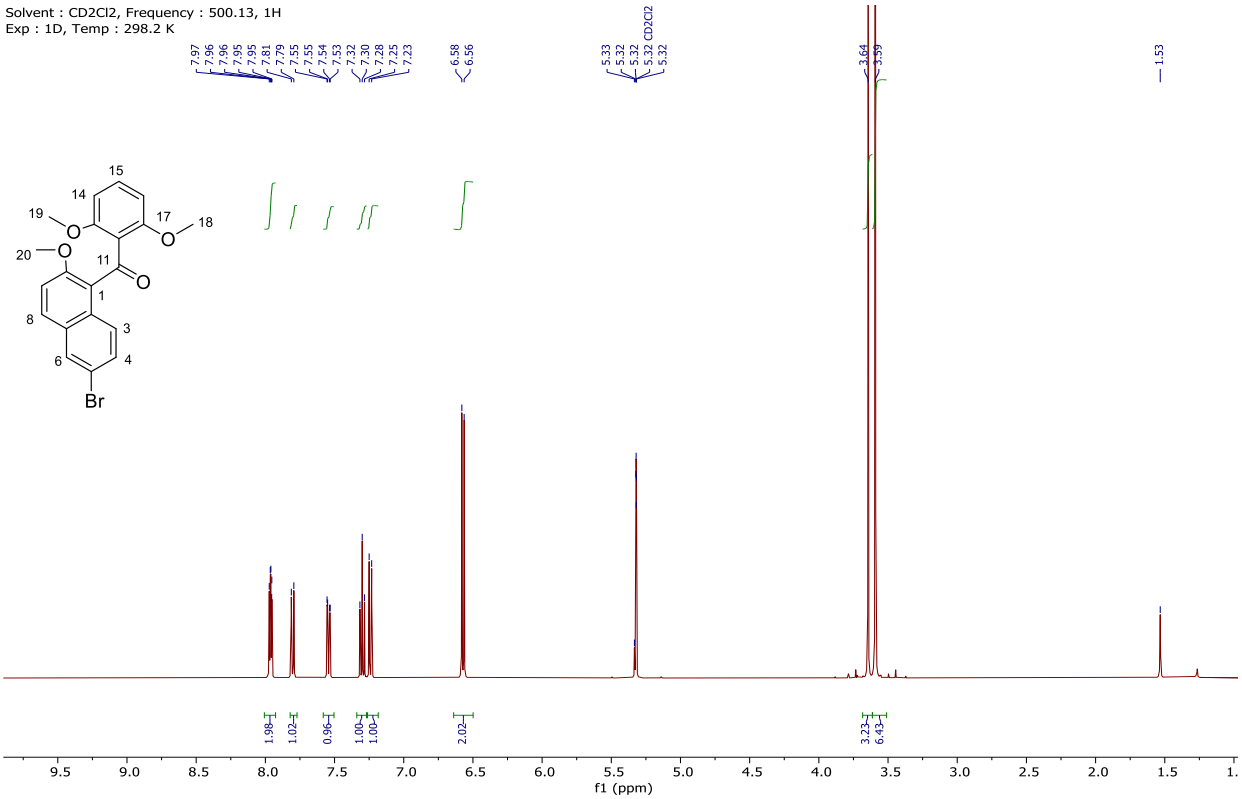
Submitter:	MARINOVA	Date of reception:	03/06/14
Sample name:	MMD0505	Date of certificate:	04/06/14
Sample number:	7189	Data filename:	SMS10GE-140604-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

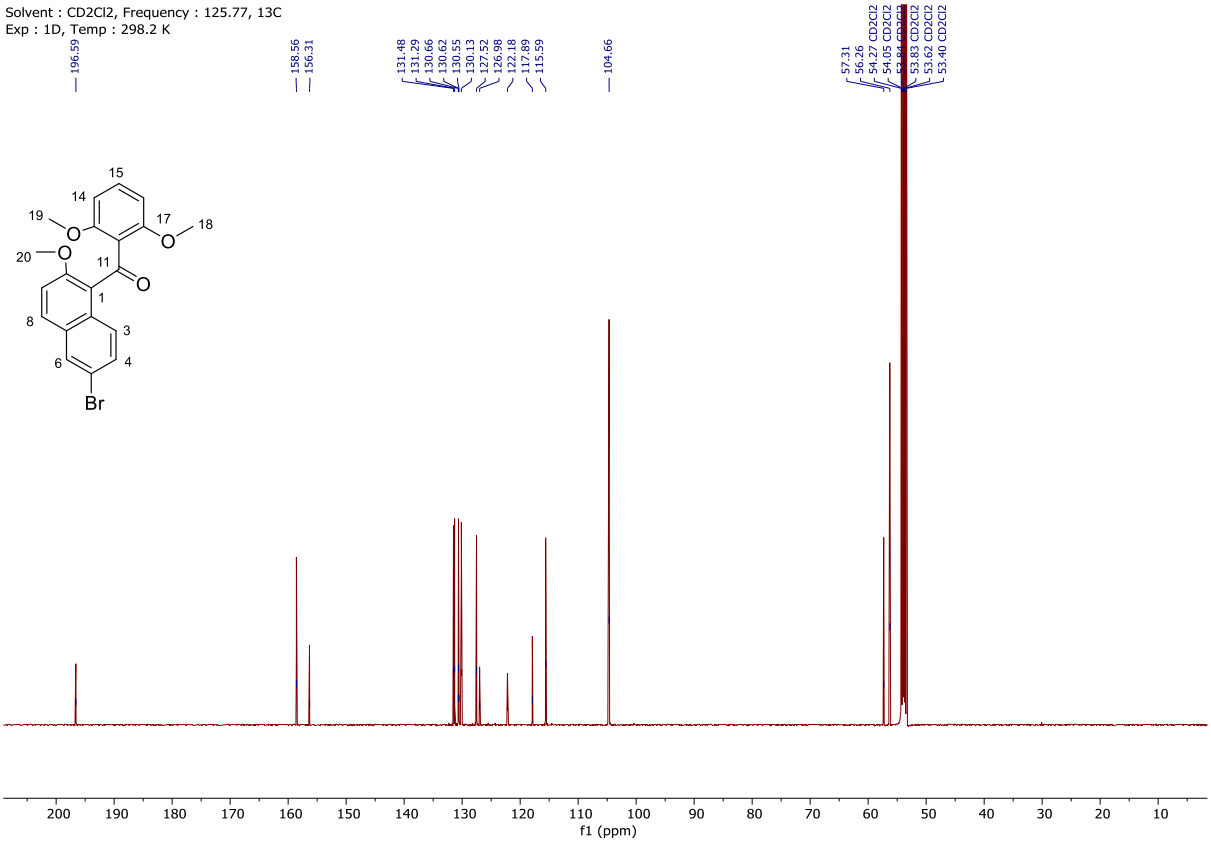
Expected Formula	Observed *m/z* $[M\text{-}OH]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{20}H_{19}BrO_4$	385.0431	385.0434	-0.8





(6-Bromo-2-methoxynaphthalen-1-yl)(2,6-dimethoxyphenyl)methanone (II)





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Sciences Mass Spectrometry

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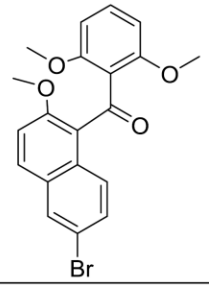
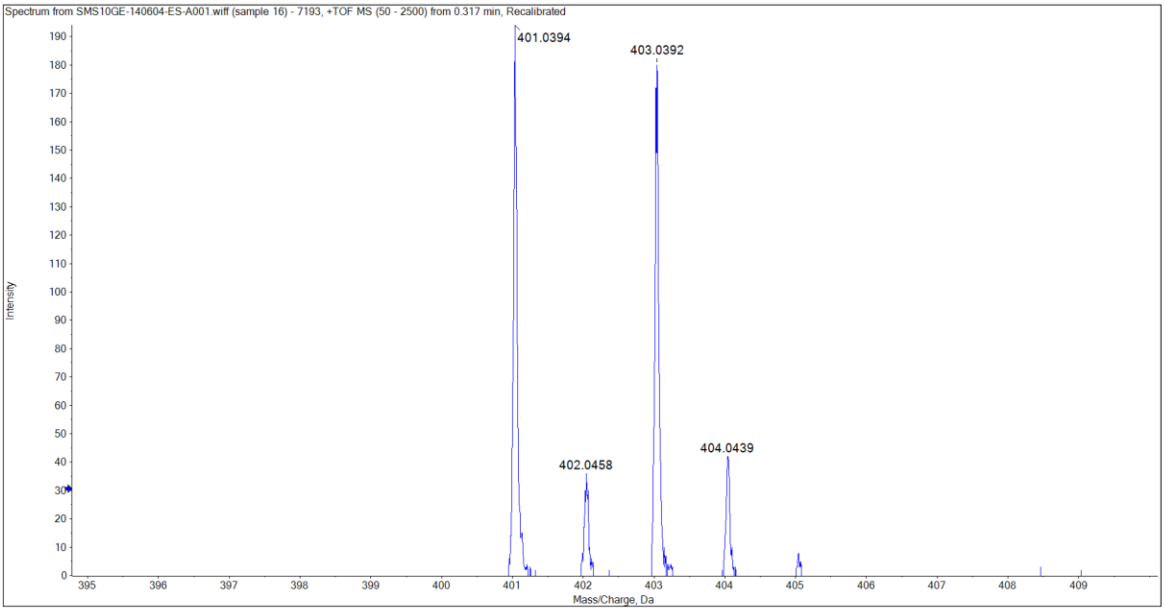
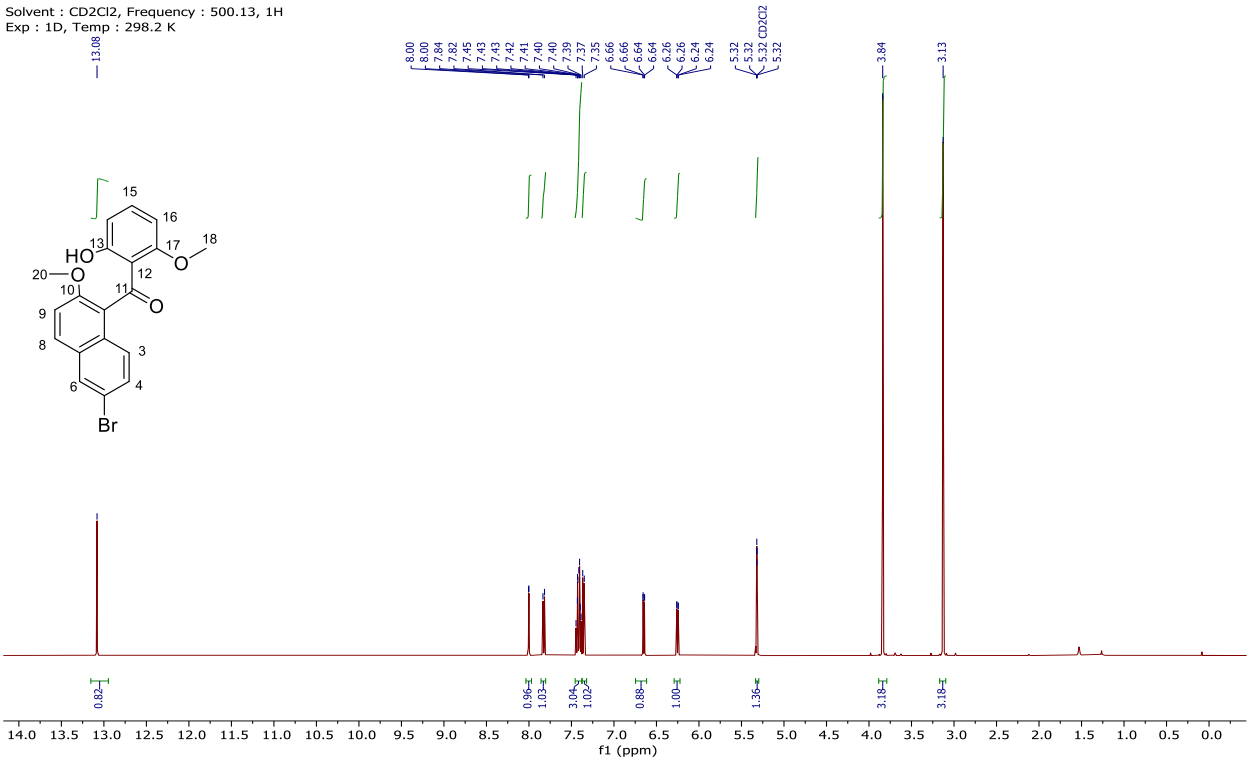
Sample name:	MMD0102	Date of certificate:	04/06/14
Sample number:	7193	Data filename:	SMS10GE-140604-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

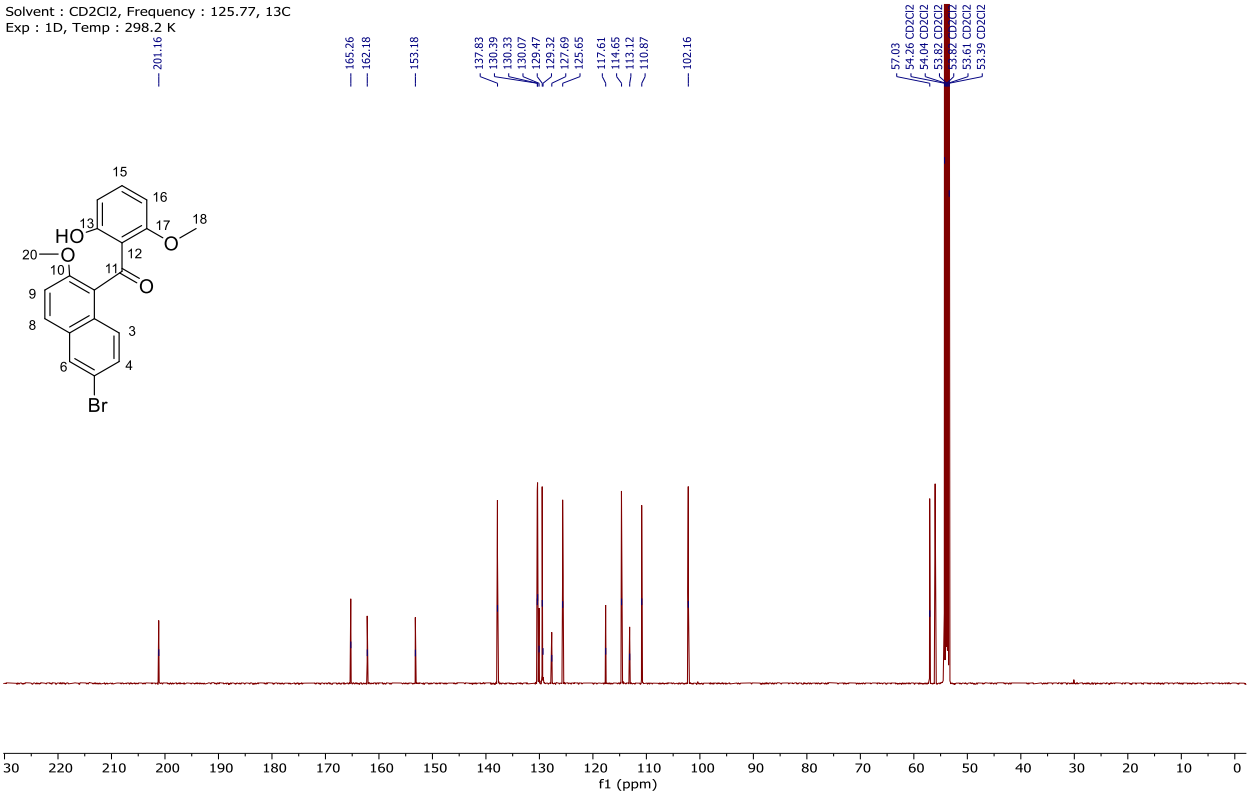
Expected Formula	Observed *m/z* $[M+H]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{20}H_{17}BrO_4$	401.0394	401.0383	2.8





(6-Bromo-2-methoxynaphthalen-1-yl)(2-hydroxy-6-methoxyphenyl)methanone (III)





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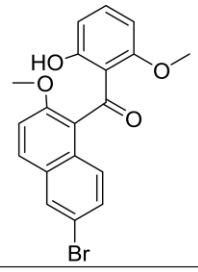
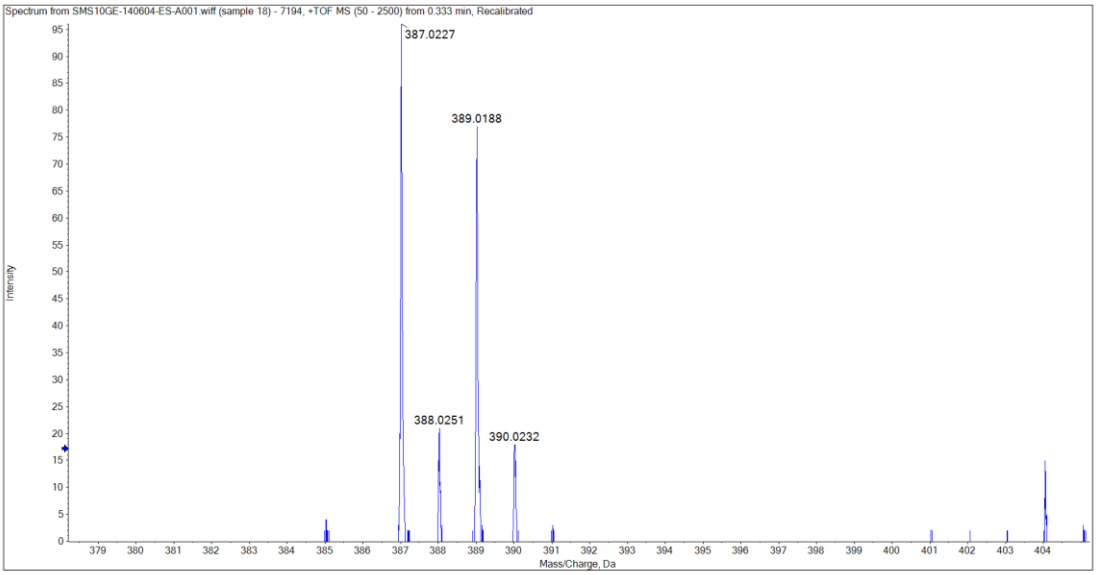
Sample number:	7194	Data filename:	SMS10GE-140604-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

Expected Formula	Observed *m/z* $[M+H]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{19}H_{15}BrO_4$	387.0227	387.0227	0.0





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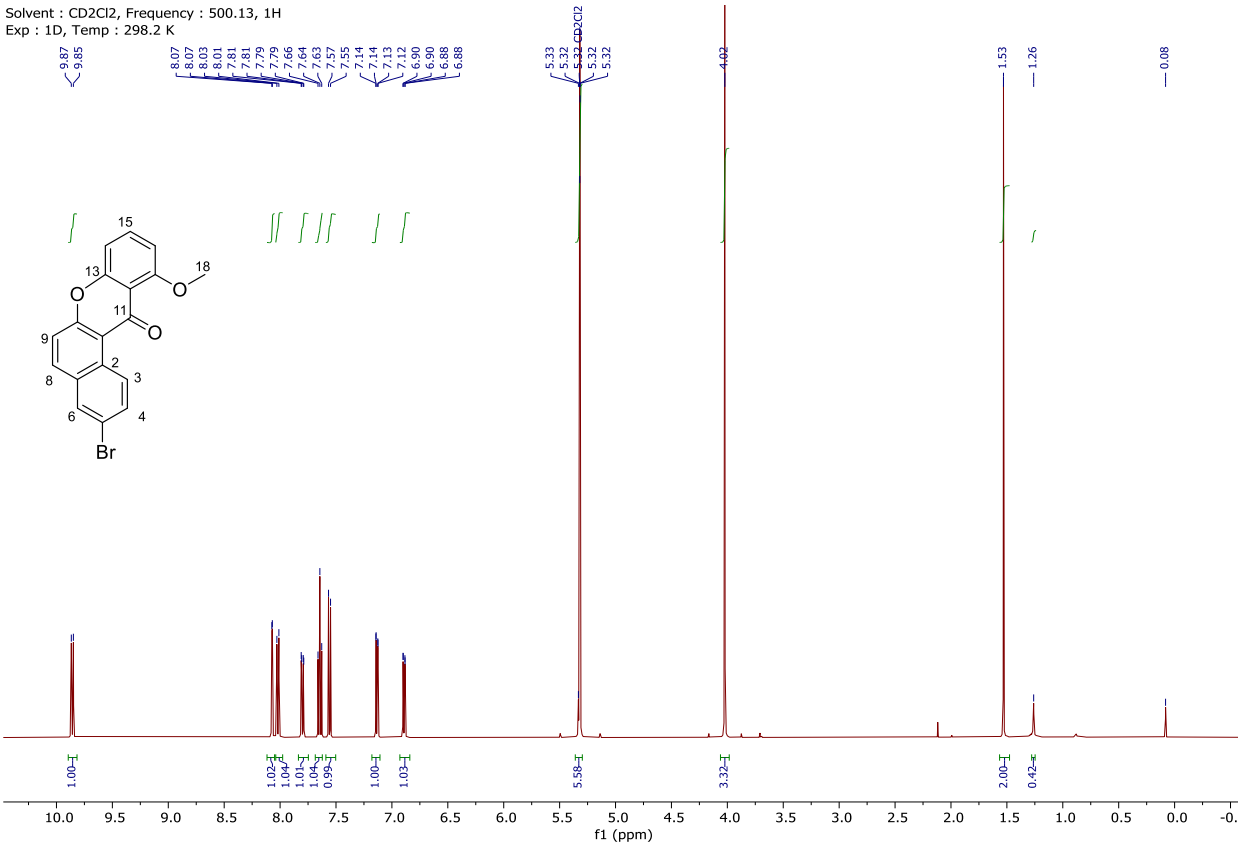
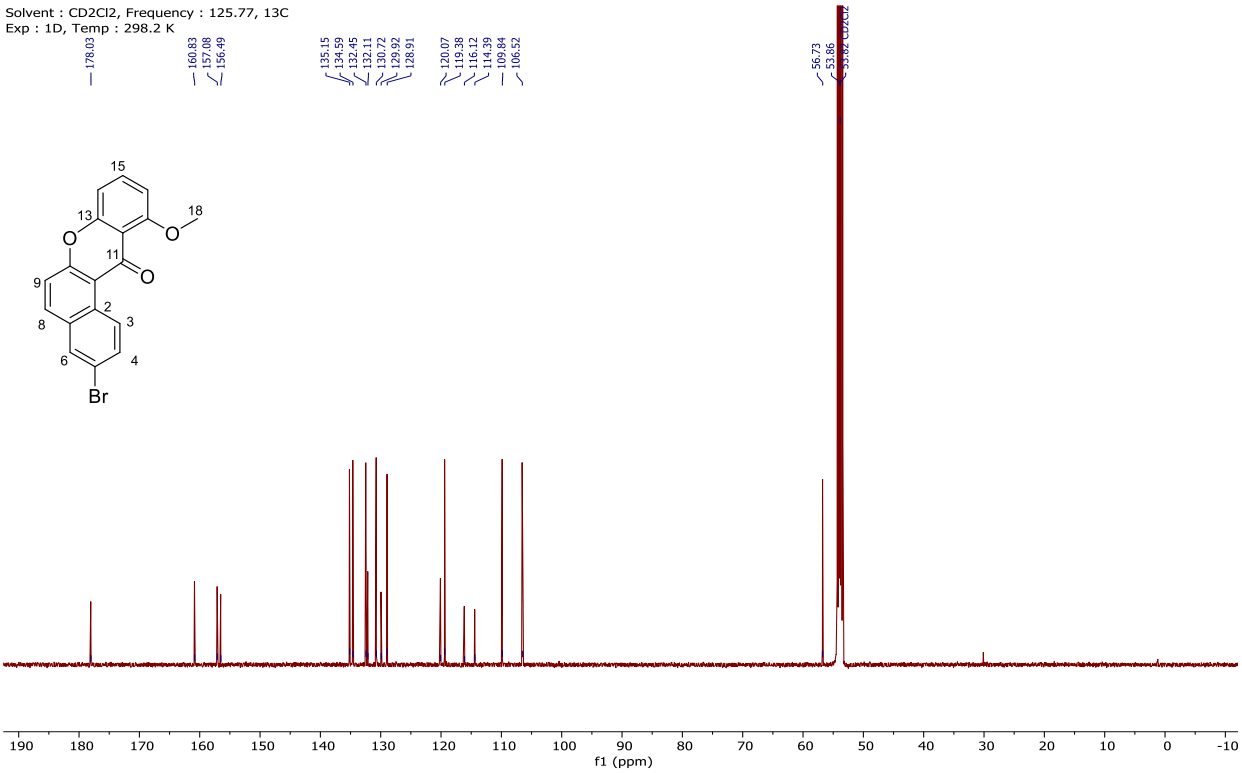
3-Bromo-11-methoxy-12*H*-benzo[*a*]xanthen-12-one (11)





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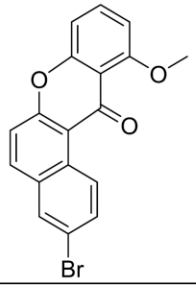
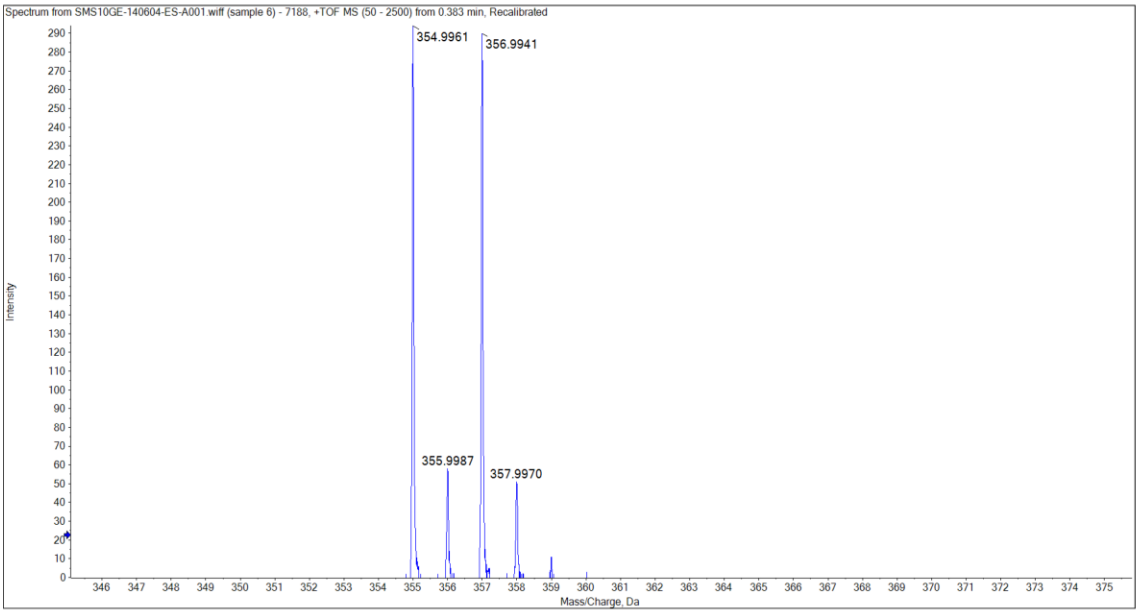
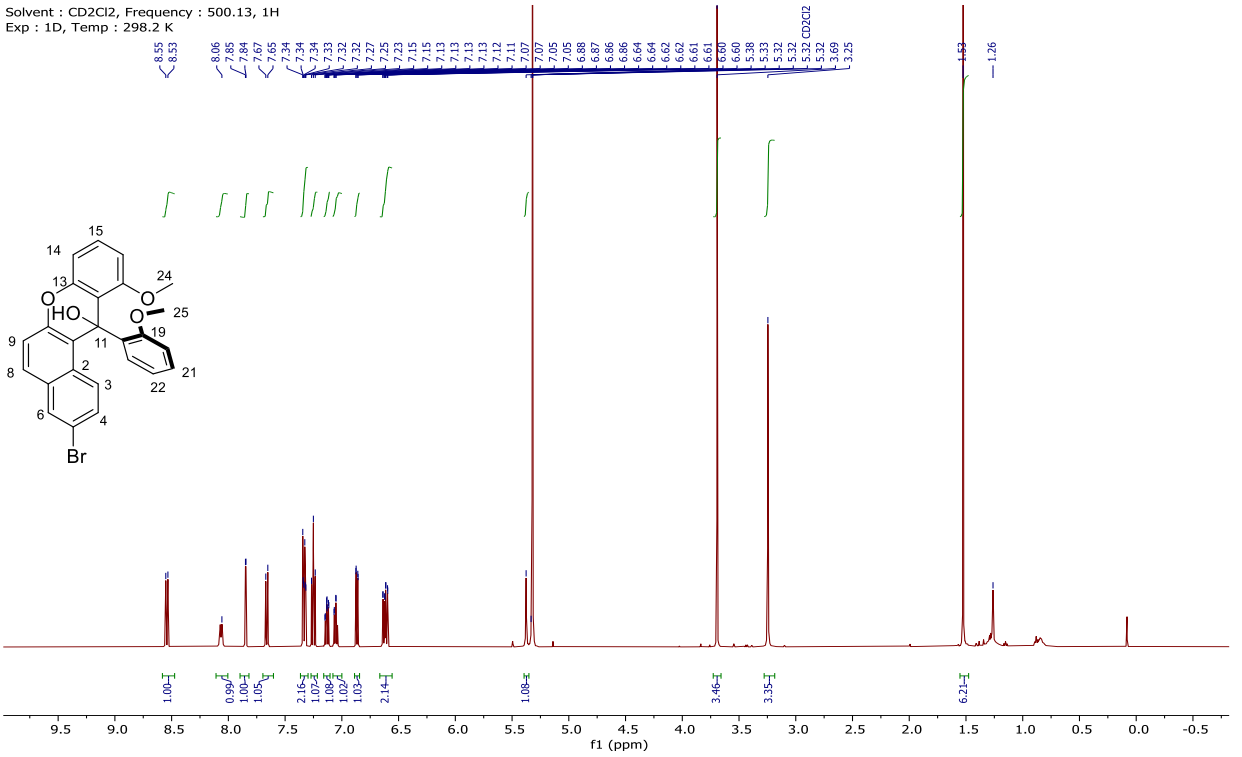
Submitter:	MARINOVA	Date of reception:	03/06/14
Sample name:	MMD0808	Date of certificate:	04/06/14
Sample number:	7188	Data filename:	SMS10GE-140604-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

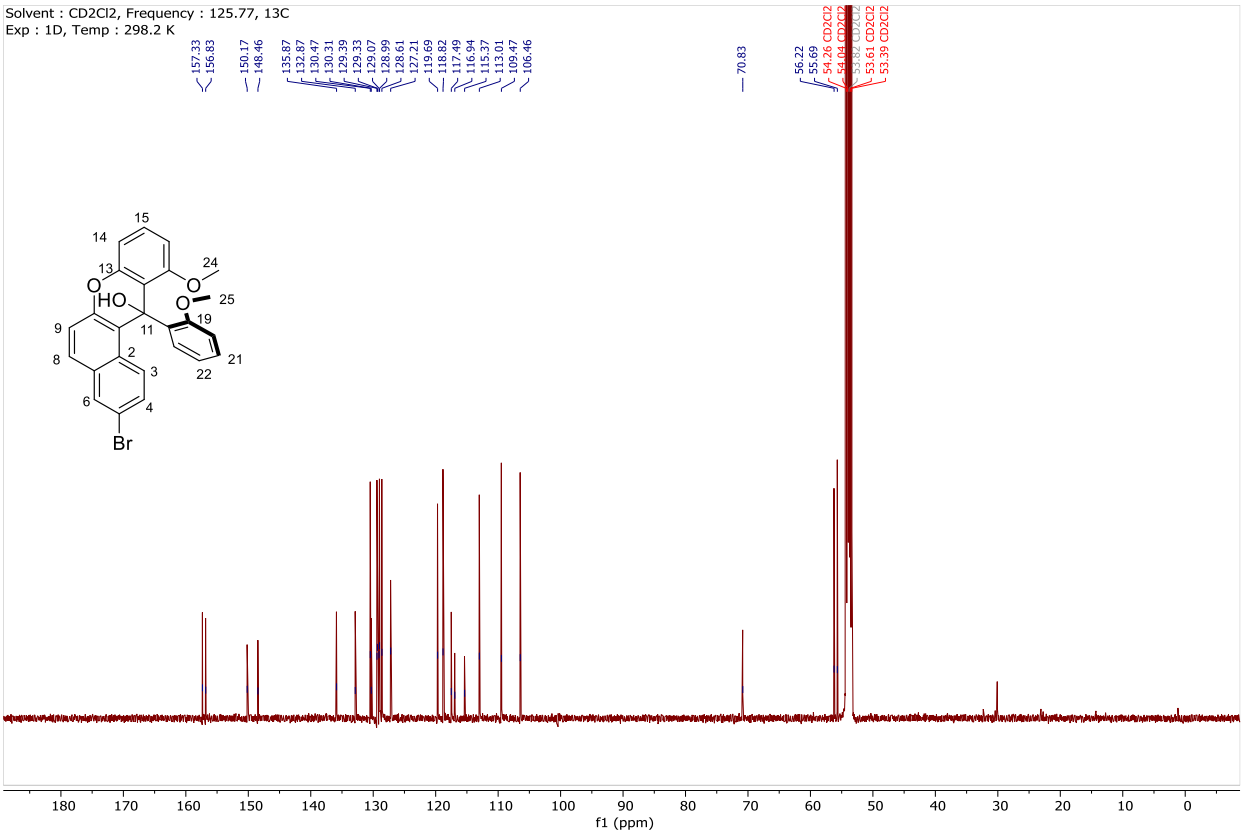
Expected Formula	Observed *m/z* $[M+H]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{18}H_{11}BrO_3$	354.9961	354.9964	-0.8





3-Bromo-11-methoxy-12-(2-methoxyphenyl)-12*H*-benzo[*a*]xanthen-12-ol (12A)





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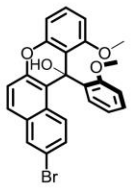
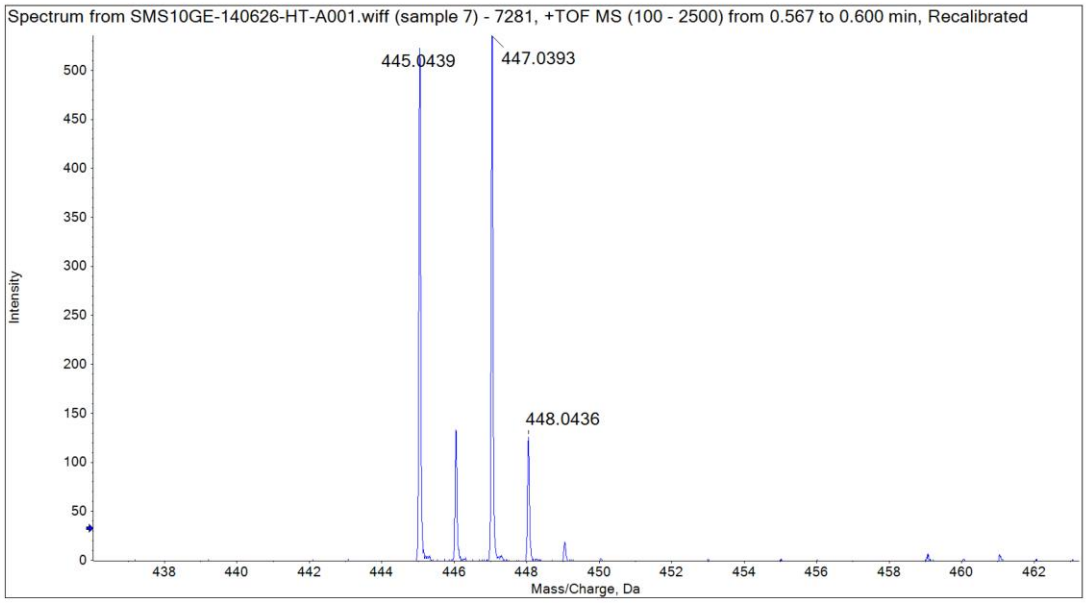
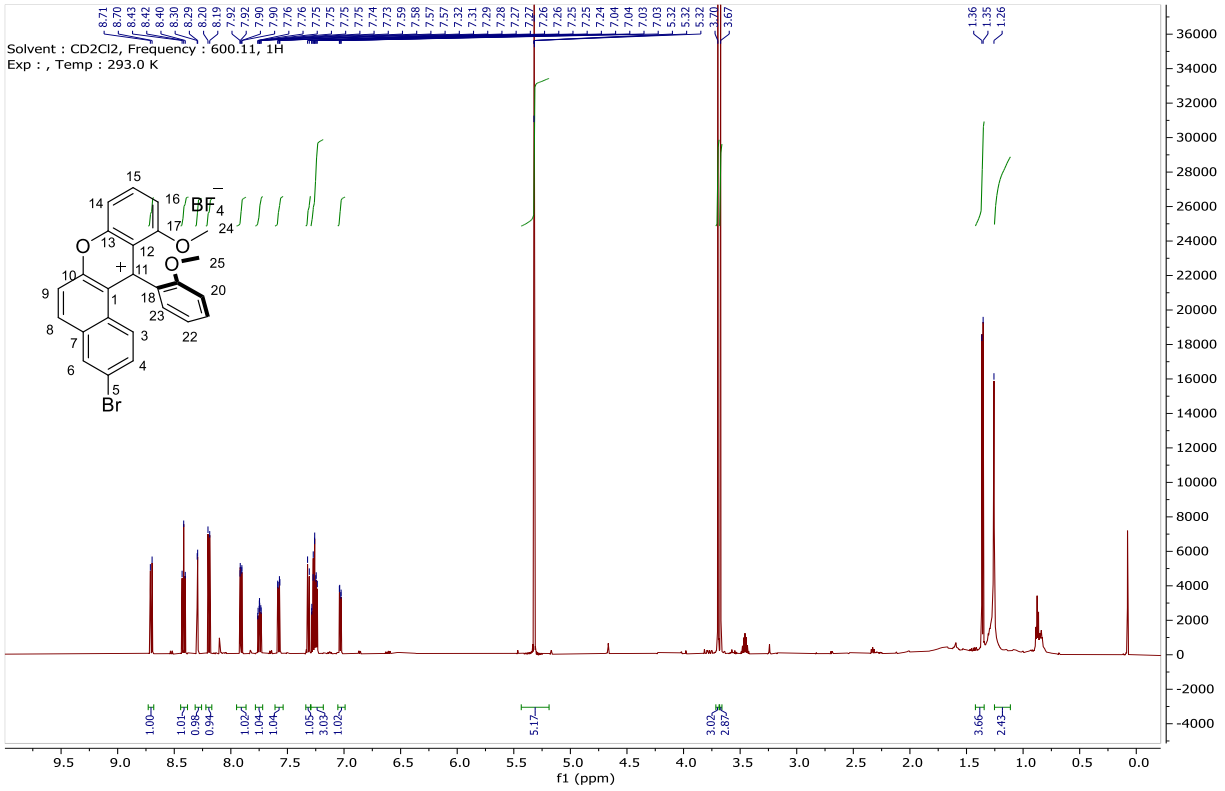
Submitter:	MARINOVA	Date of reception:	25/06/14
Sample name:	?	Date of certificate:	30/06/14
Sample number:	7281	Data filename:	SMS10GE-140626-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

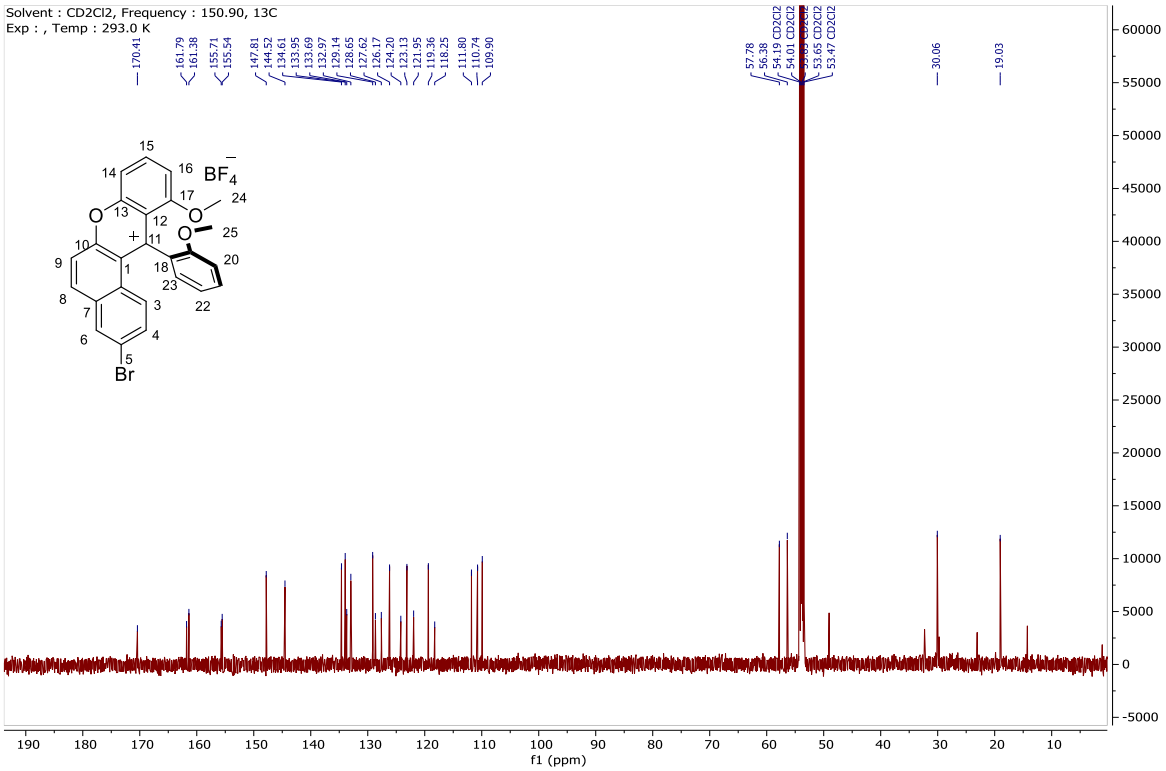
Expected Formula	Observed *m/z* $[M\text{-}OH]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{25}H_{18}BrO_3$	445.0439	445.0434	1.1

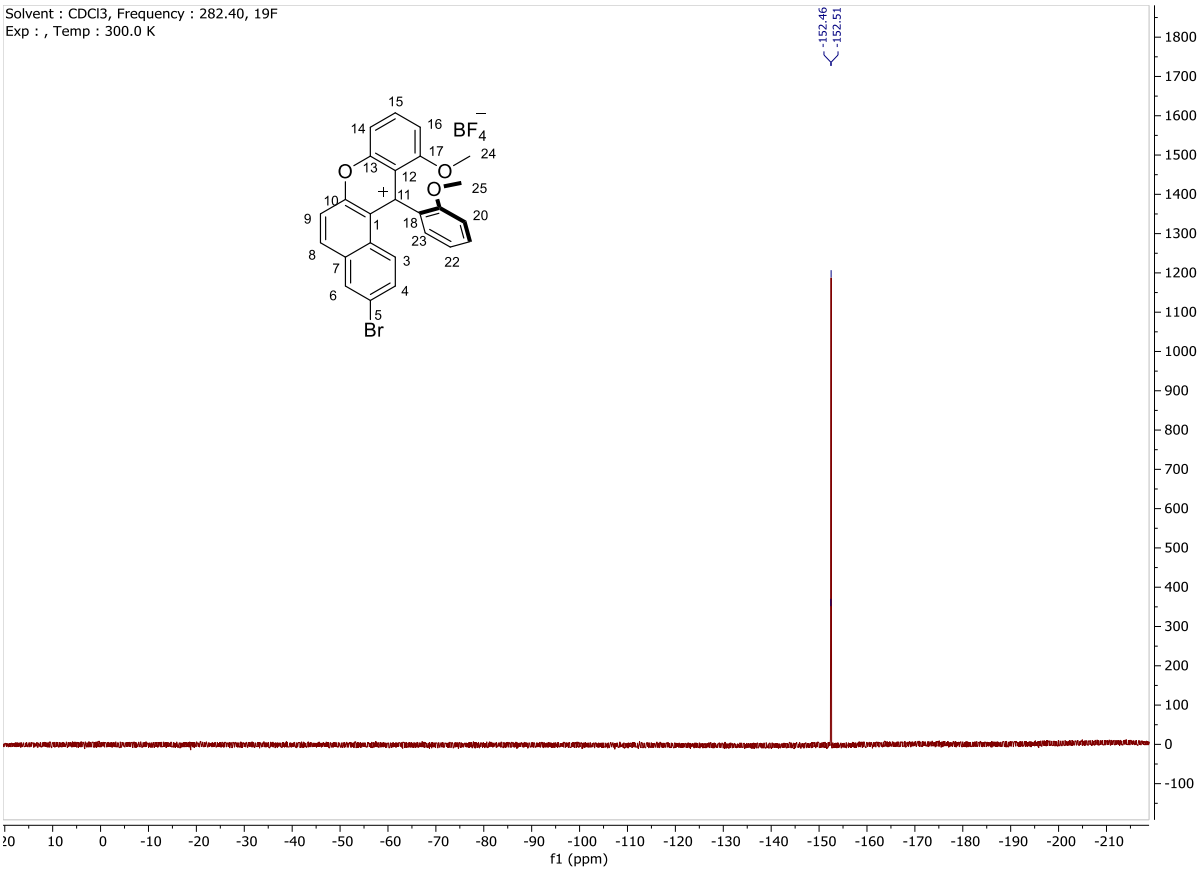




3-Bromo-11-methoxy-12-(2-methoxyphenyl)-12*H*-benzo[*a*]xanthen-12-ylium tetrafluoroborate (13A)






Solvent : CDCl3, Frequency : 282.40, 19F
Exp : , Temp : 300.0 K
-152.46
-152.51
BF4
Br
f1 (ppm)

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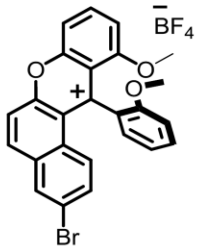
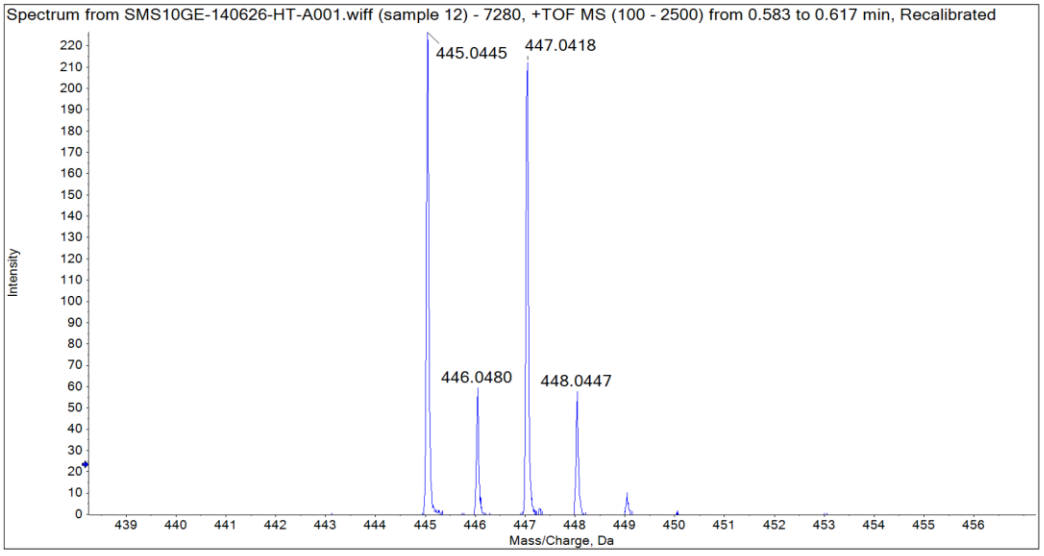
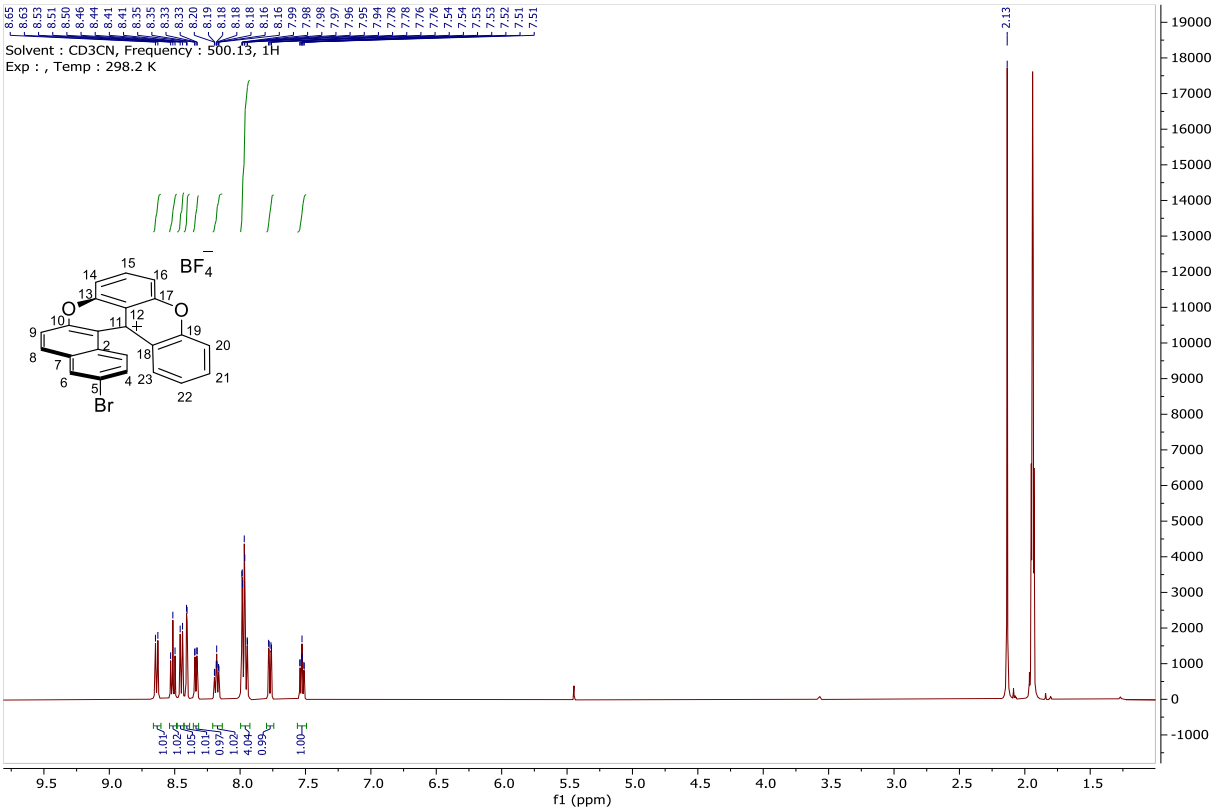
Submitter:	MARINOVA	Date of reception:	25/06/14
Sample name:	MMD7605	Date of certificate:	30/06/14
Sample number:	7280	Data filename:	SMS10GE-140626-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

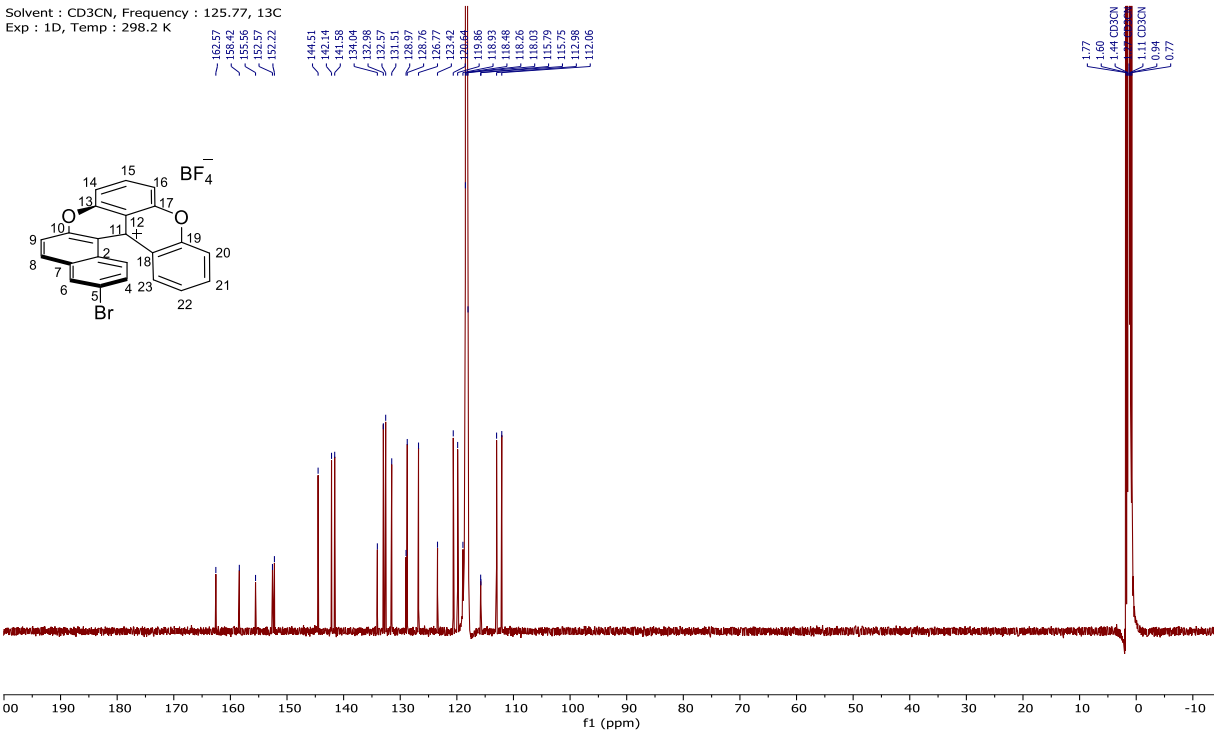
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{25}H_{18}BrO_3$	445.0445	445.0434	2.4





14-bromo-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (8A)





Solvent : CDCl3, Frequency : 282.38, 19F
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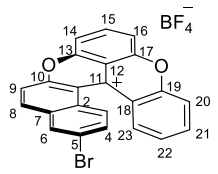

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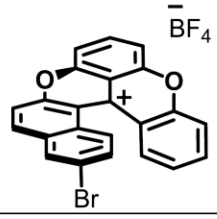
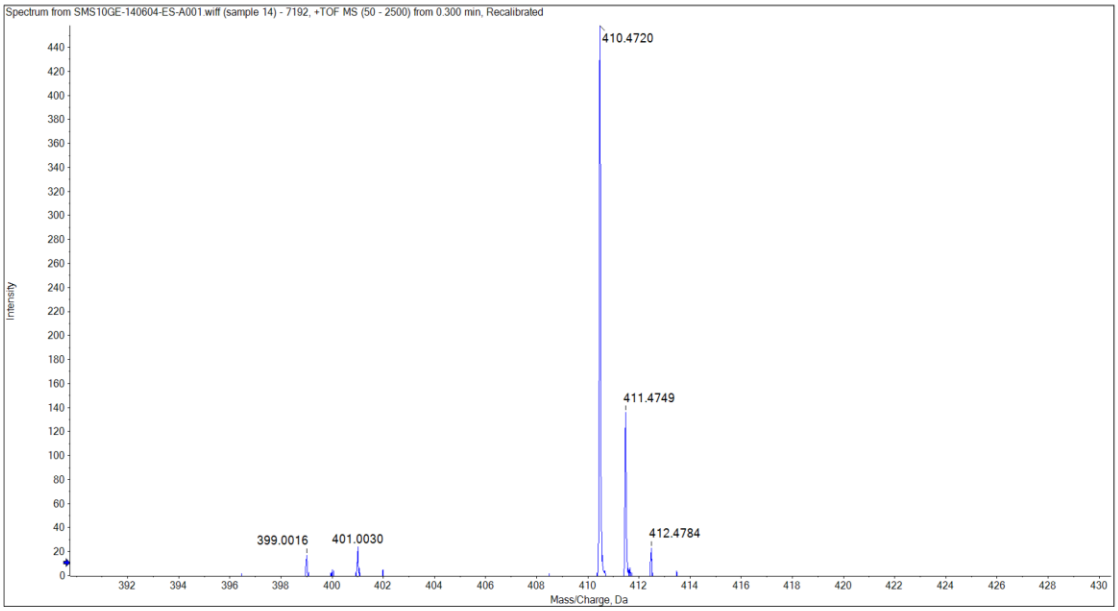
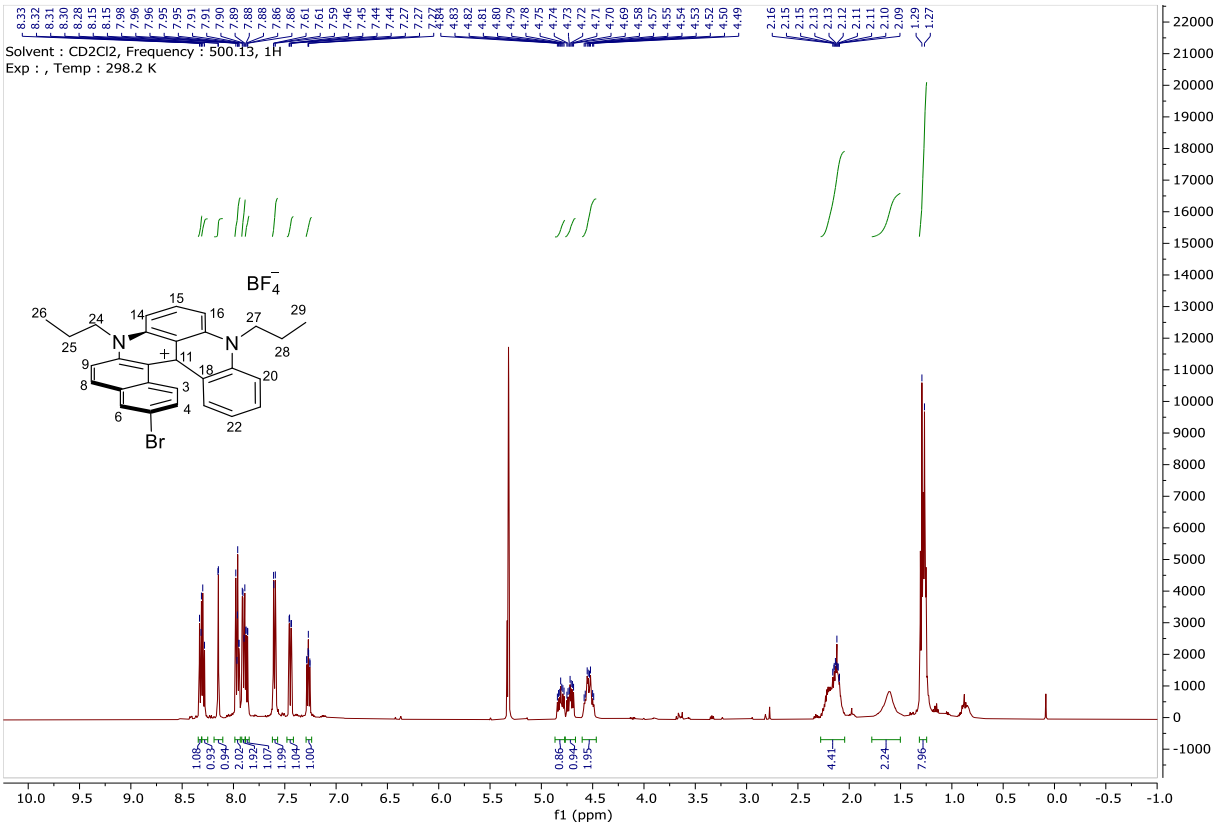
Submitter:	MARINOVA	Date of reception:	03/06/14
Sample name:	MMD6805	Date of certificate:	04/06/14
Sample number:	7192	Data filename:	SMS10GE-140604-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

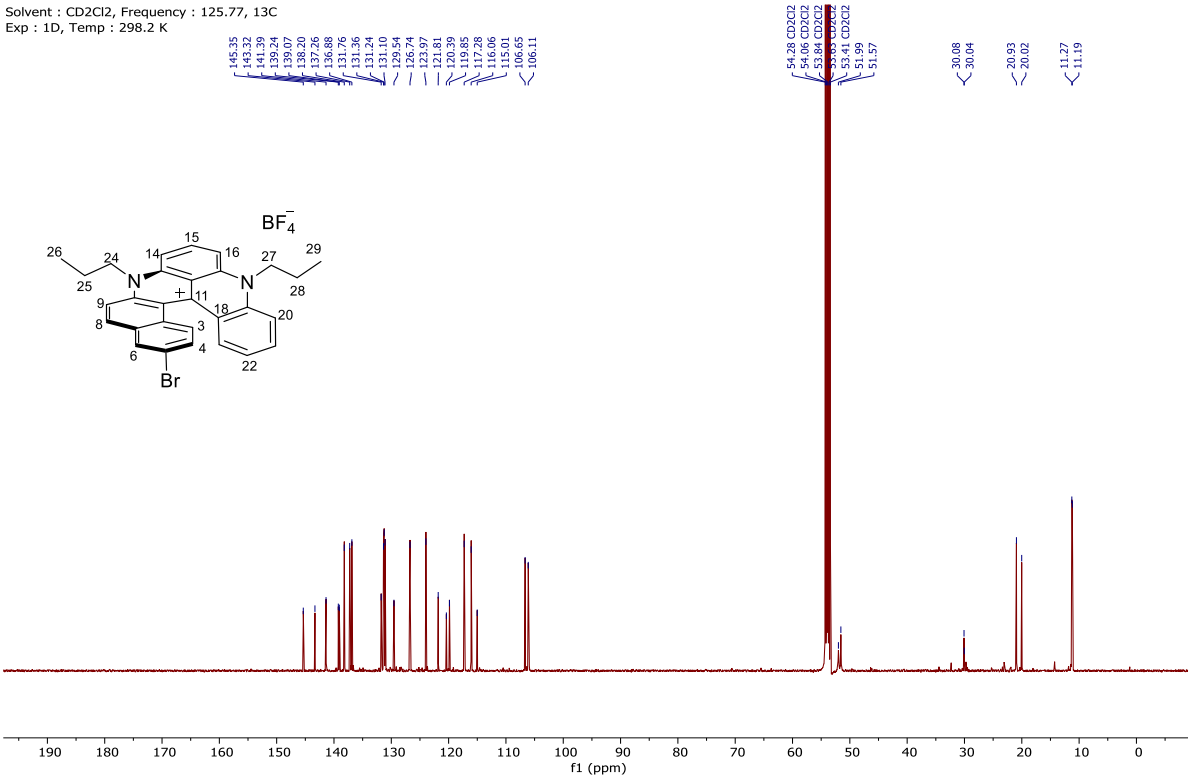
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{23}H_{12}NO_2$	399.0016	399.0015	0.3

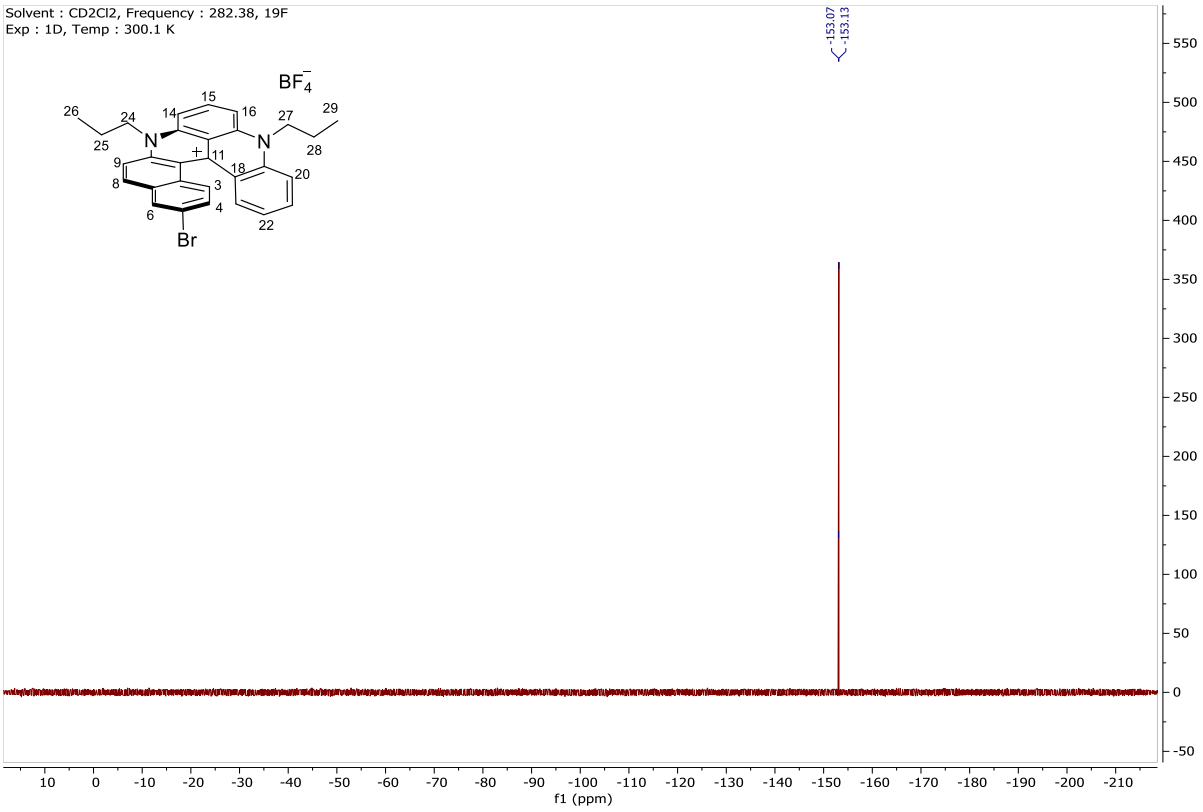


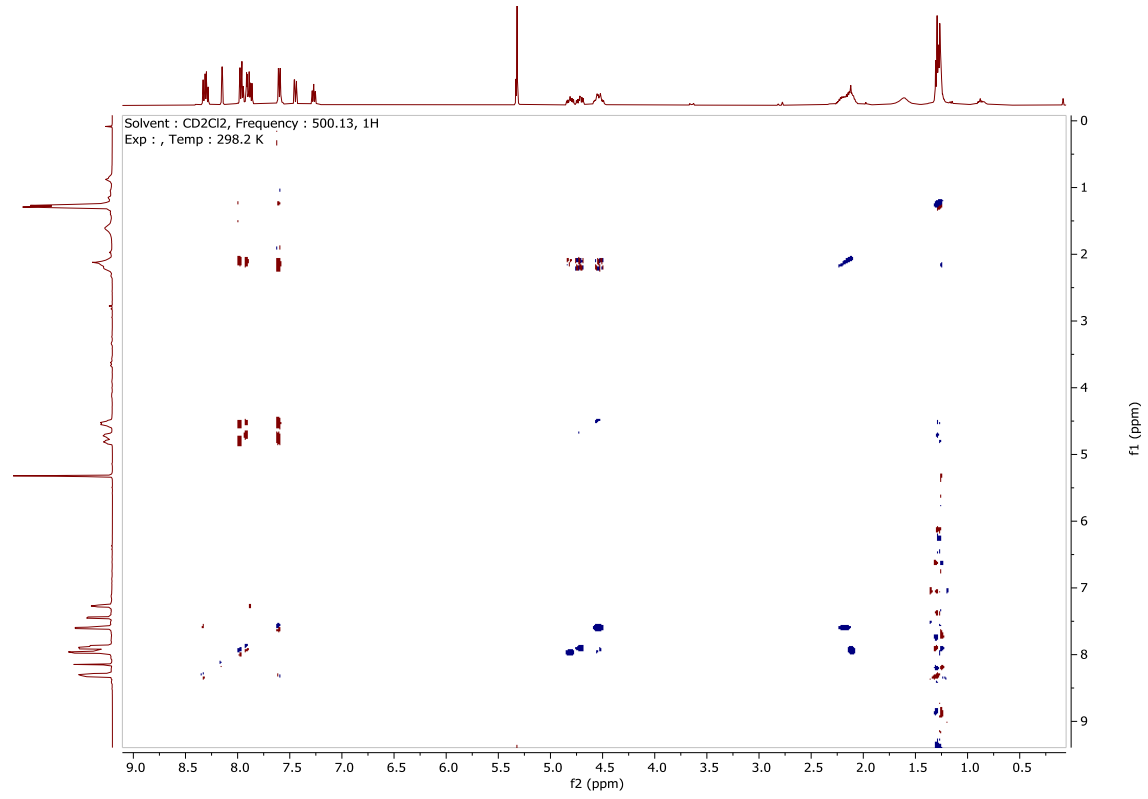


14-bromo-3,7-dipropyl-3,7-dihydro-11b*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridin-11b-ylium tetrafluoroborate (9A)






Solvent : CD2Cl2, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.1 K
-153.07
-153.13
BF4−
Br
f1 (ppm)


Solvent : CD2Cl2, Frequency : 500.13, 1H
Exp : , Temp : 298.2 K
f2 (ppm)
f1 (ppm)

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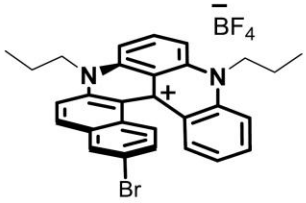
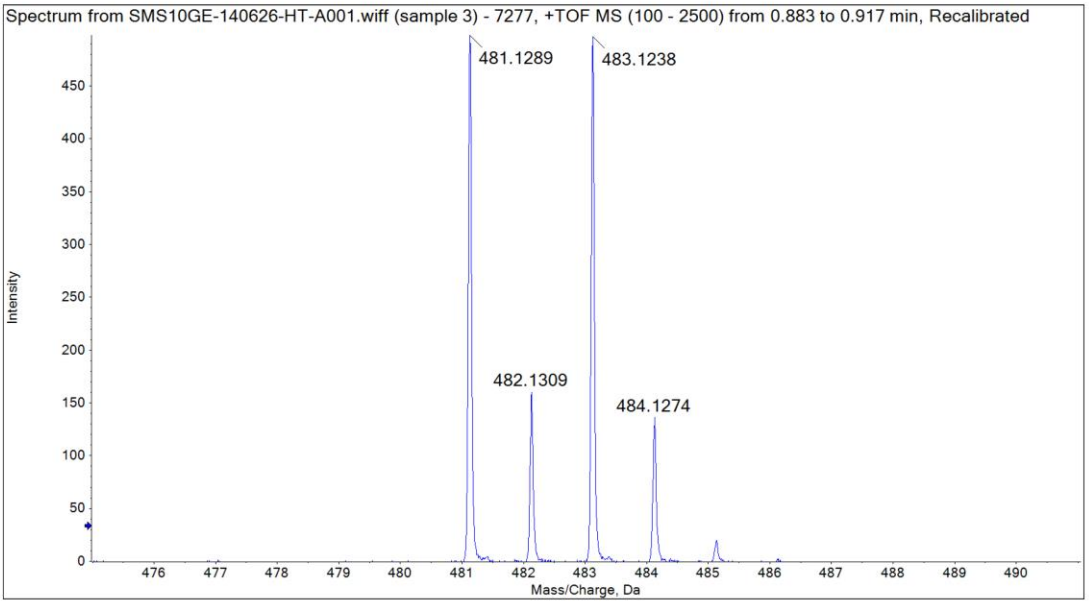
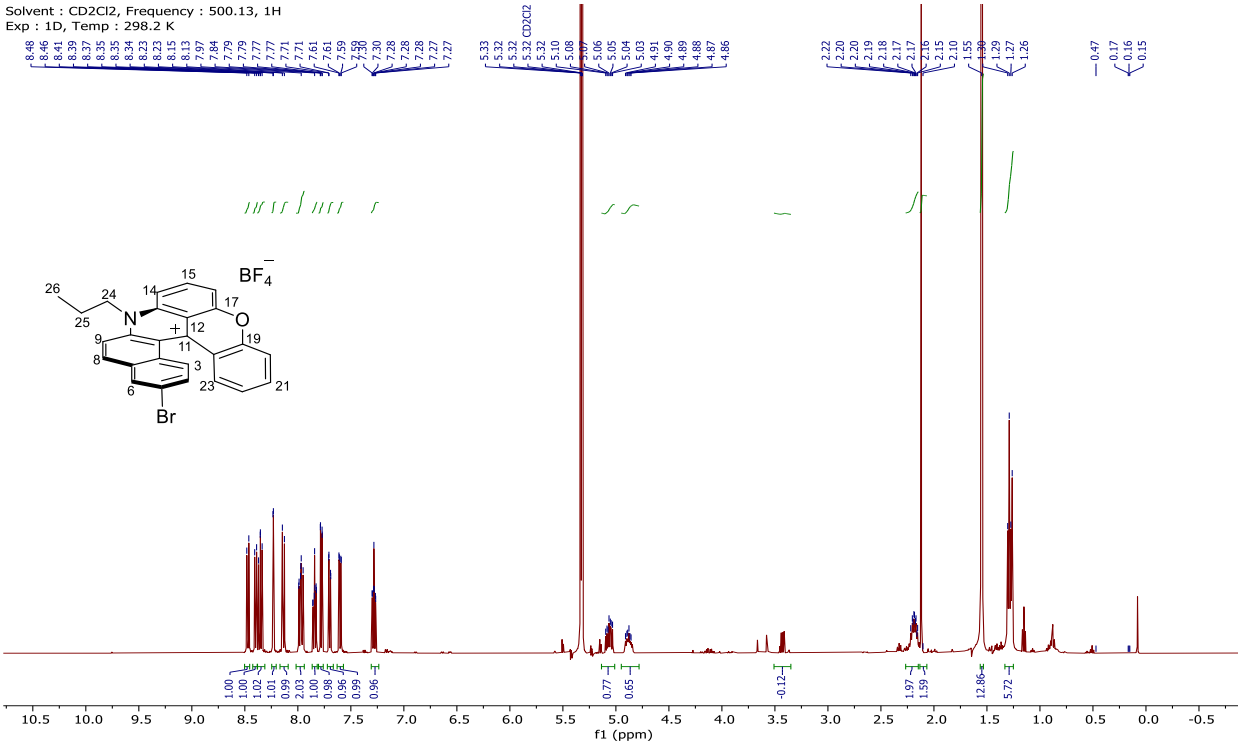
Submitter:	MARINOVA	Date of reception:	25/06/14
Sample name:	MMD8203	Date of certificate:	30/06/14
Sample number:	7277	Data filename:	SMS10GE-140626-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

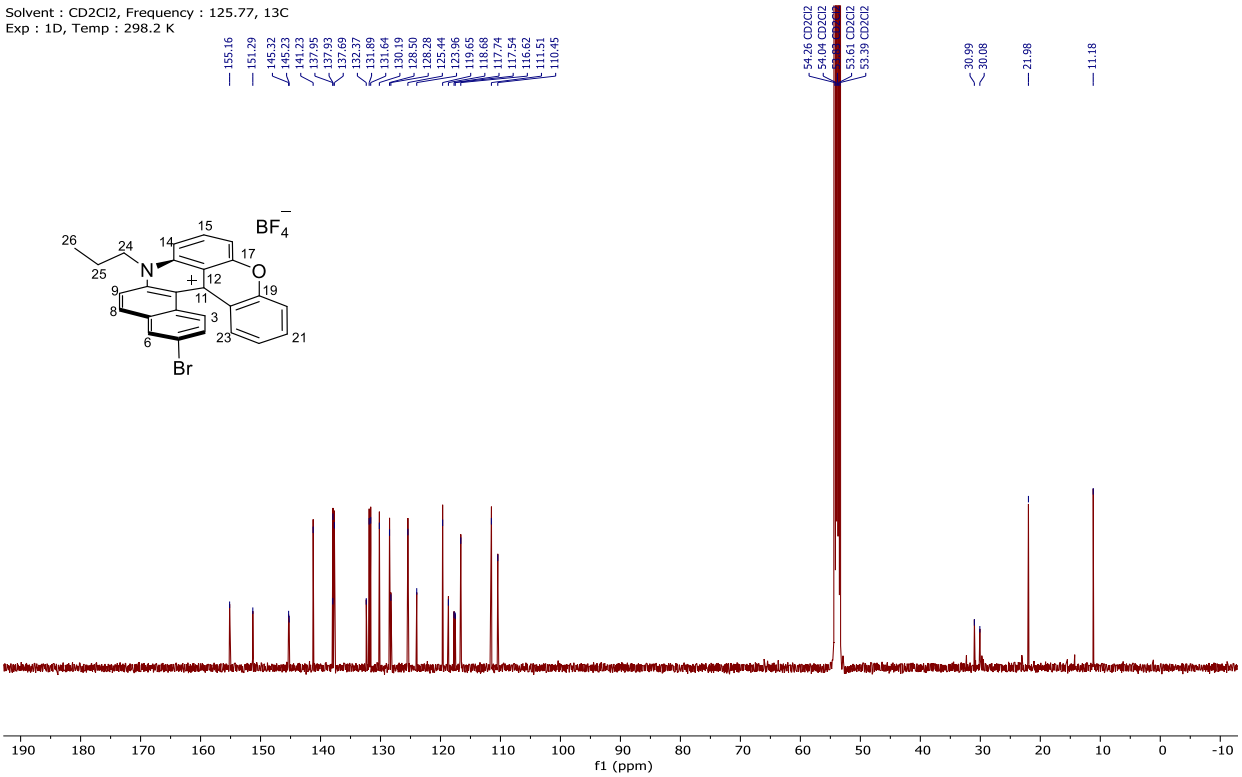
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{29}H_{26}BrN_2$	481.1289	481.1274	3.0

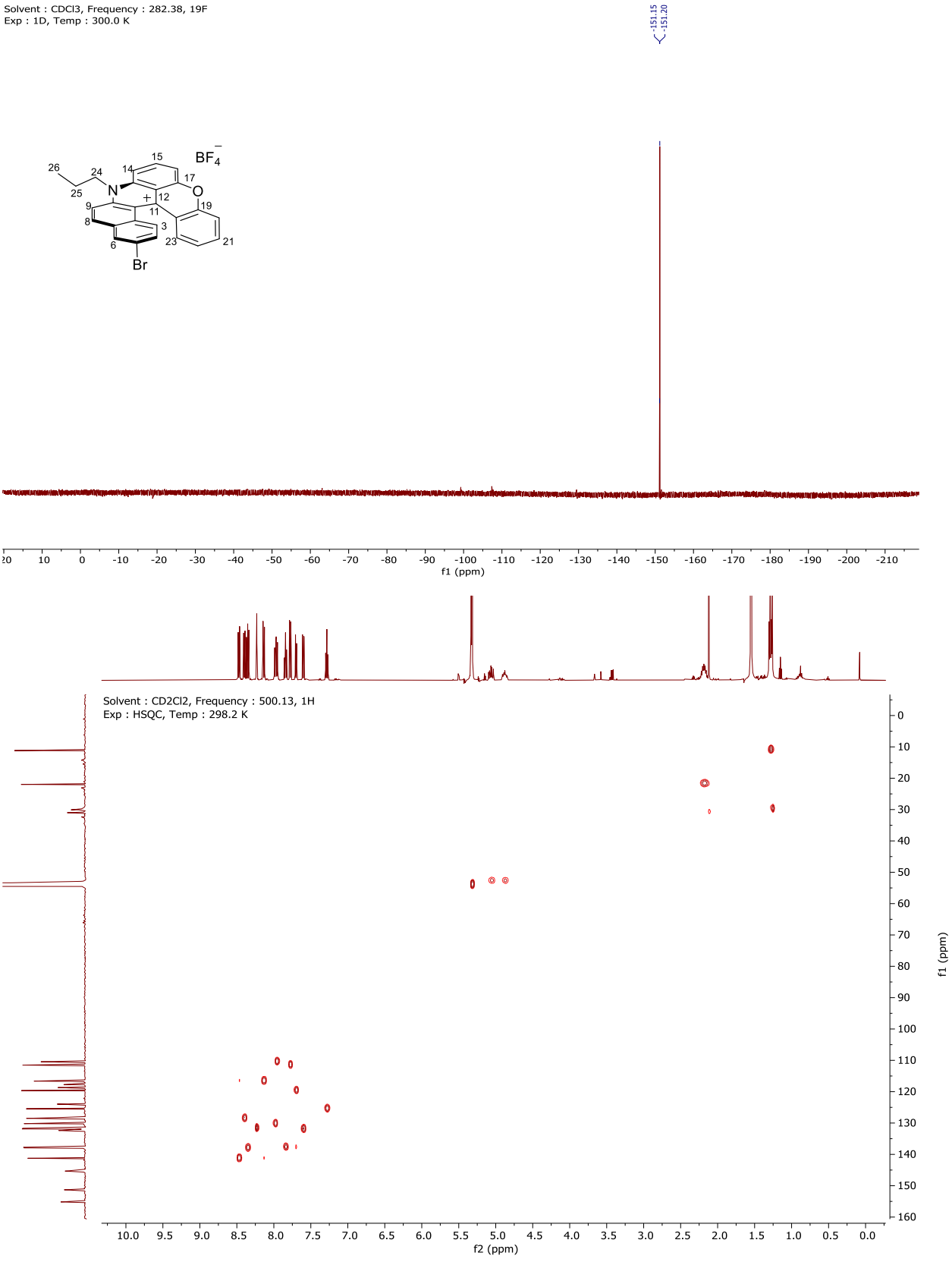




14-Bromo-3-propylbenzo[*a*]chromeno[2,3,4-*kl*]acridin-11b(3*H*)-ylium tetrafluoroborate (10A)



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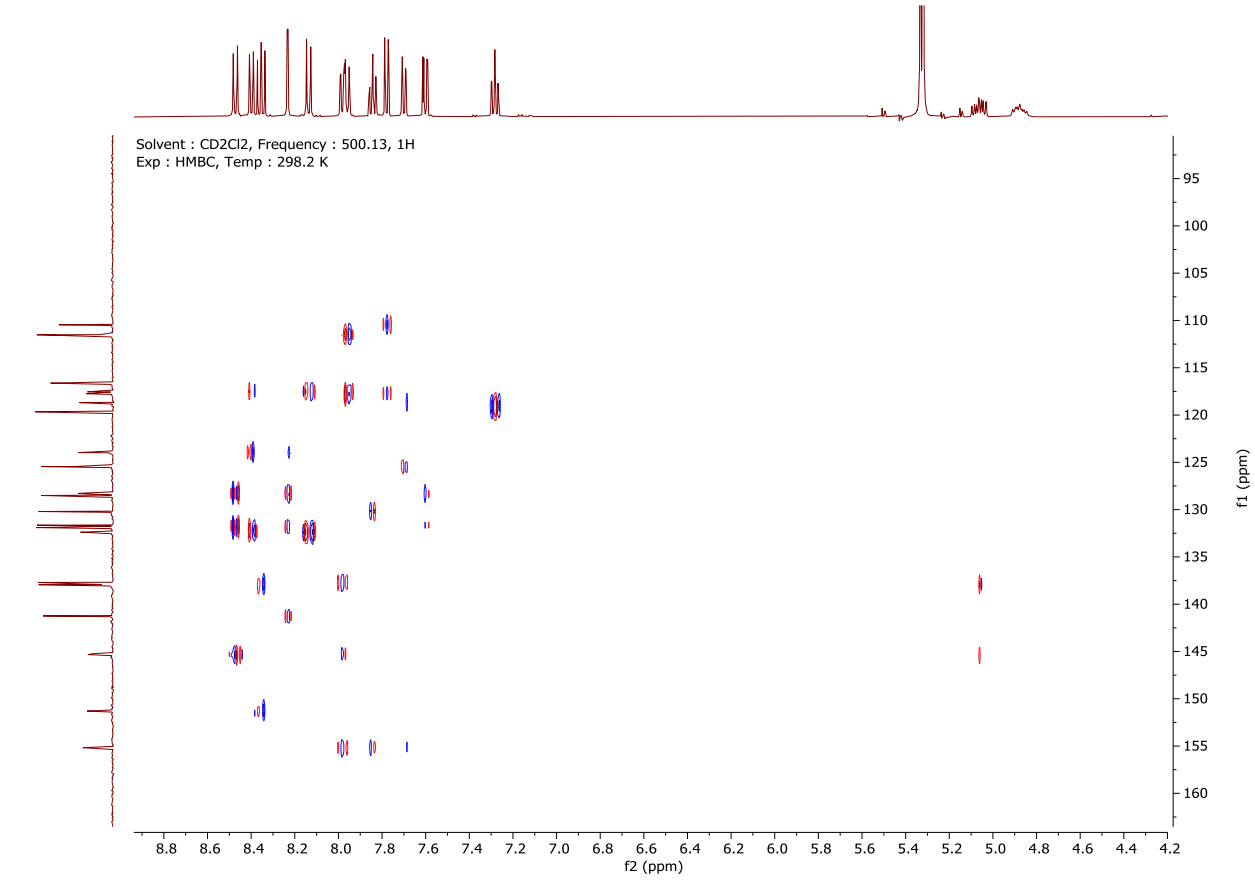
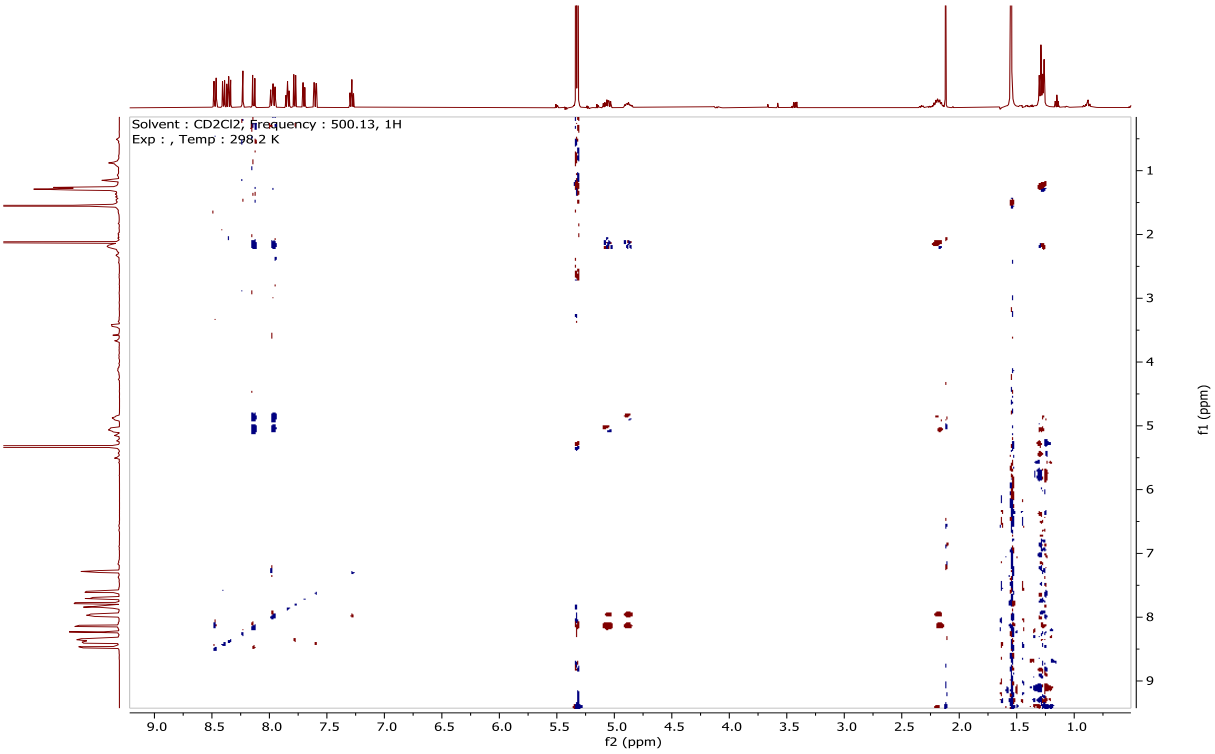
Exp : 1D, Temp : 300.0 K
-151.15
-151.20
BF4−
Br
f1 (ppm)
Solvent : CD2Cl2, Frequency : 500.13, 1H
Exp : HSQC, Temp : 298.2 K
f2 (ppm)
f1 (ppm)


Solvent : CD2Cl2, Frequency : 500.13, 1H
Exp : HMBC, Temp : 298.2 K
f2 (ppm)
f1 (ppm)


Solvent : CD2Cl2, Frequency : 500.13, 1H
Exp : , Temp : 298.2 K
f2 (ppm)
f1 (ppm)

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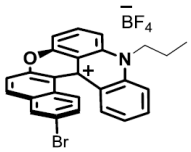
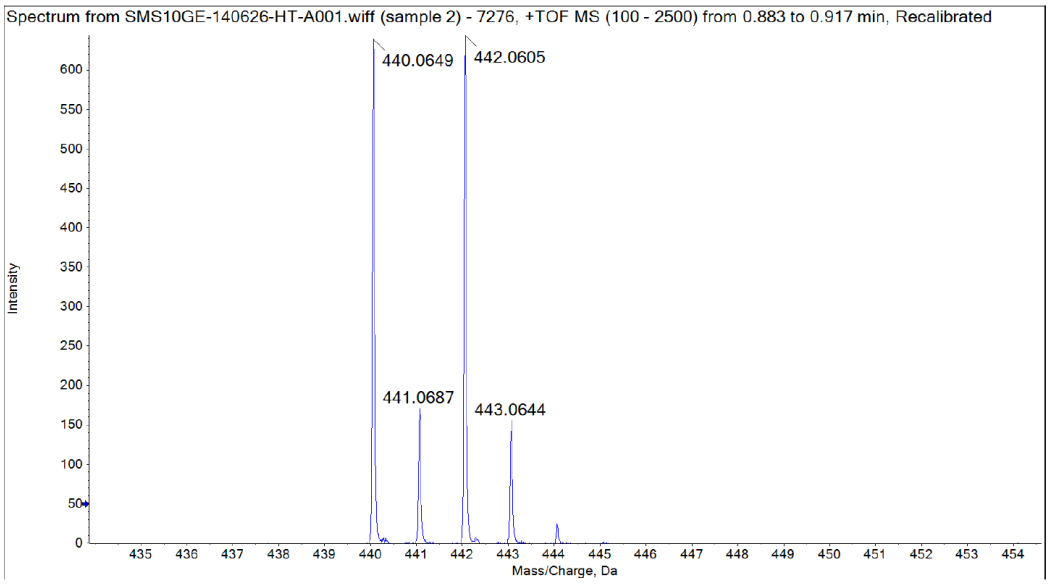
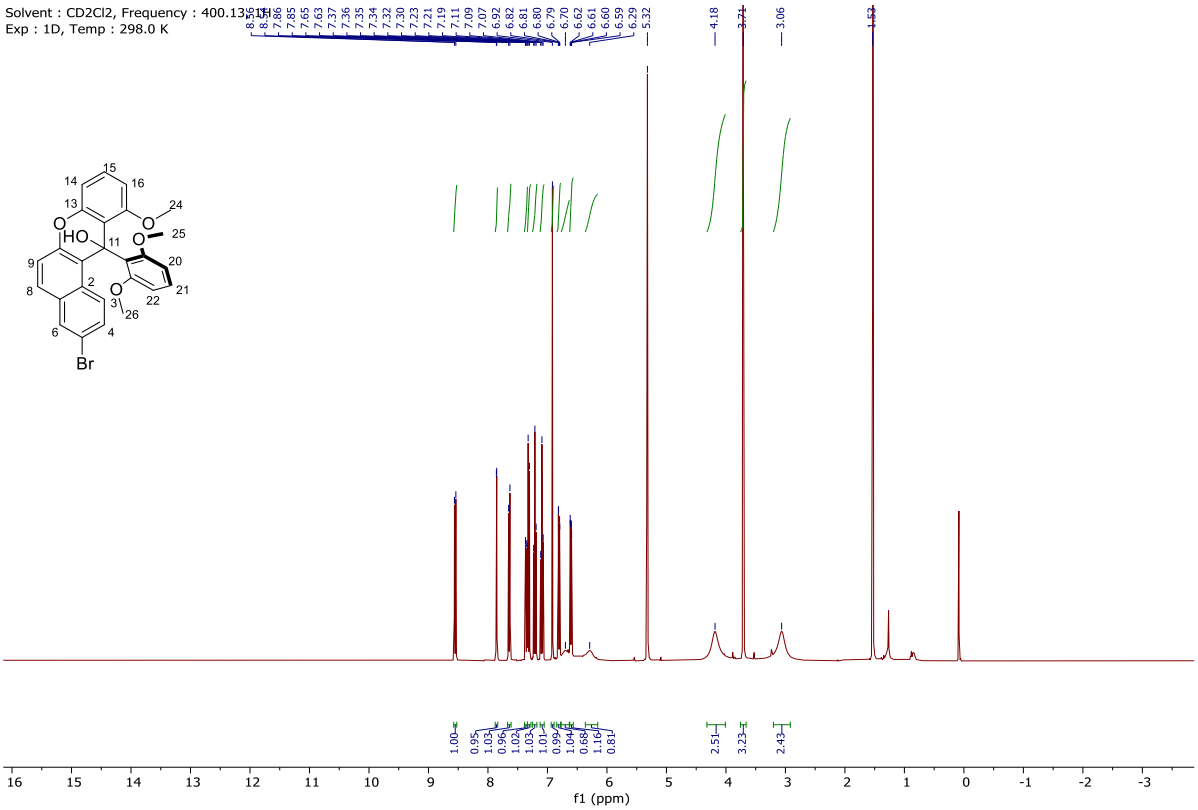
Submitter:	MARINOVA	Date of reception:	25/06/14
Sample name:	MMD7505	Date of certificate:	30/06/14
Sample number:	7276	Data filename:	SMS10GE-140626-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

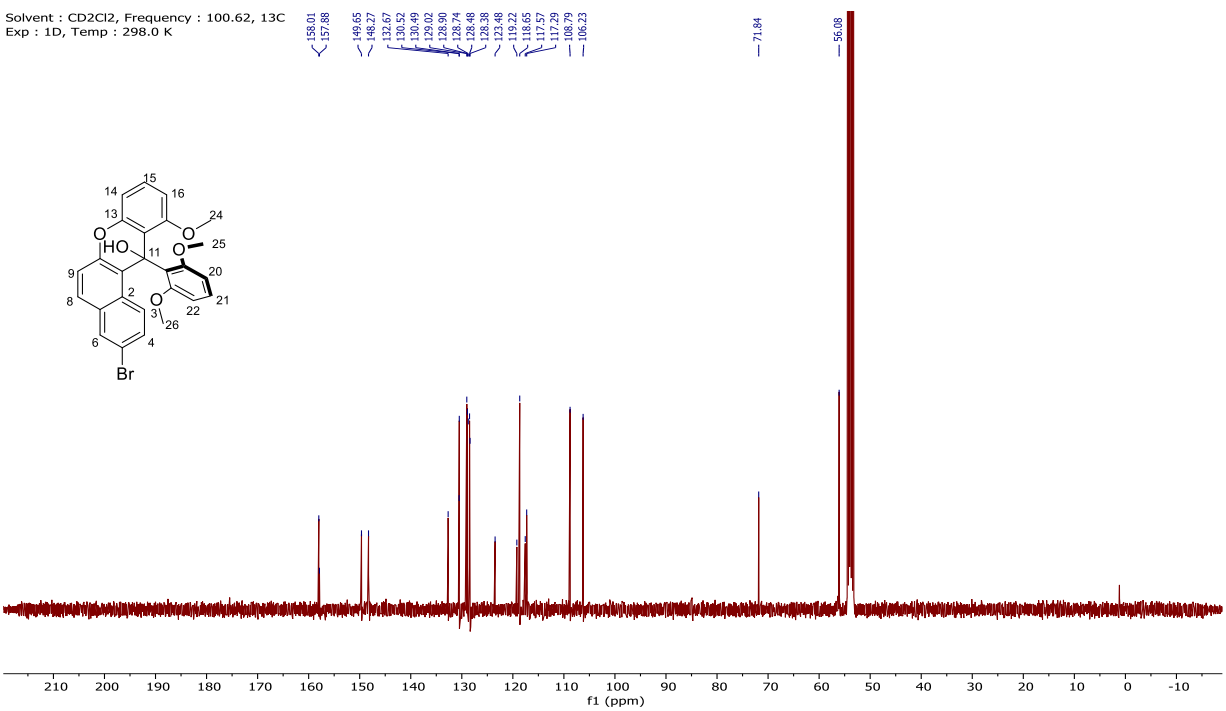
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{35}H_{58}NO_2Si$	440.0649	440.0645	1.1





3-bromo-12-(2,6-dimethoxyphenyl)-11-methoxy-12*H*-benzo[*a*]xanthen-12-ol (12B)





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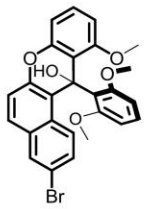
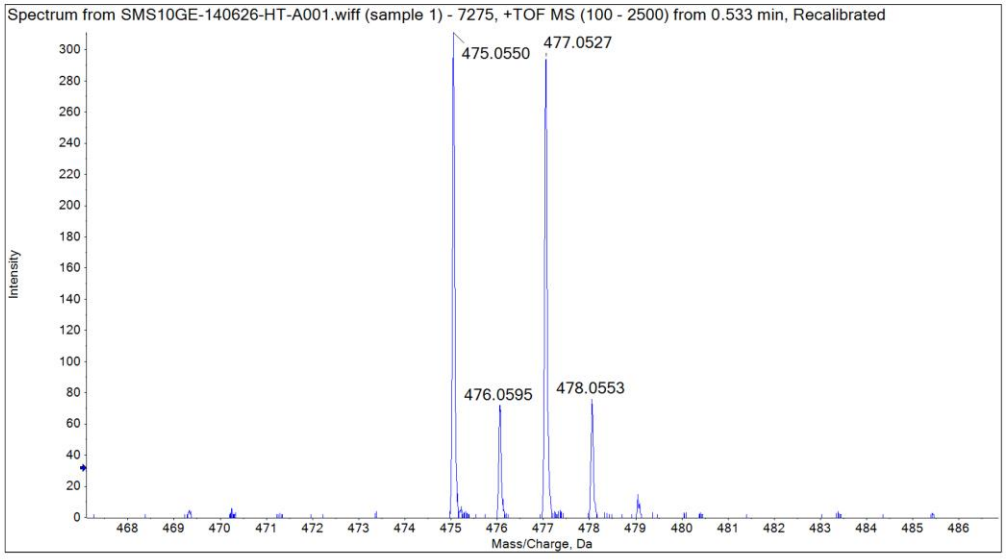
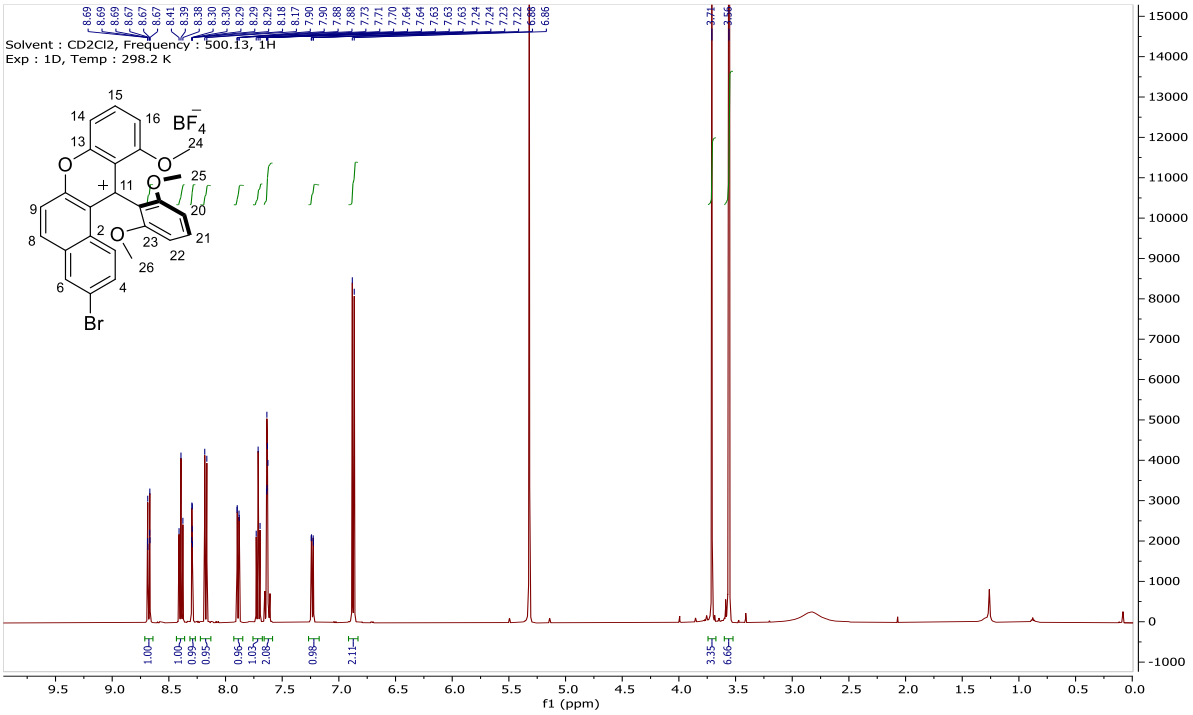
Submitter:	MARINOVA	Date of reception:	25/06/14
Sample name:	MMD5603	Date of certificate:	30/06/14
Sample number:	7275	Data filename:	SMS10GE-140626-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

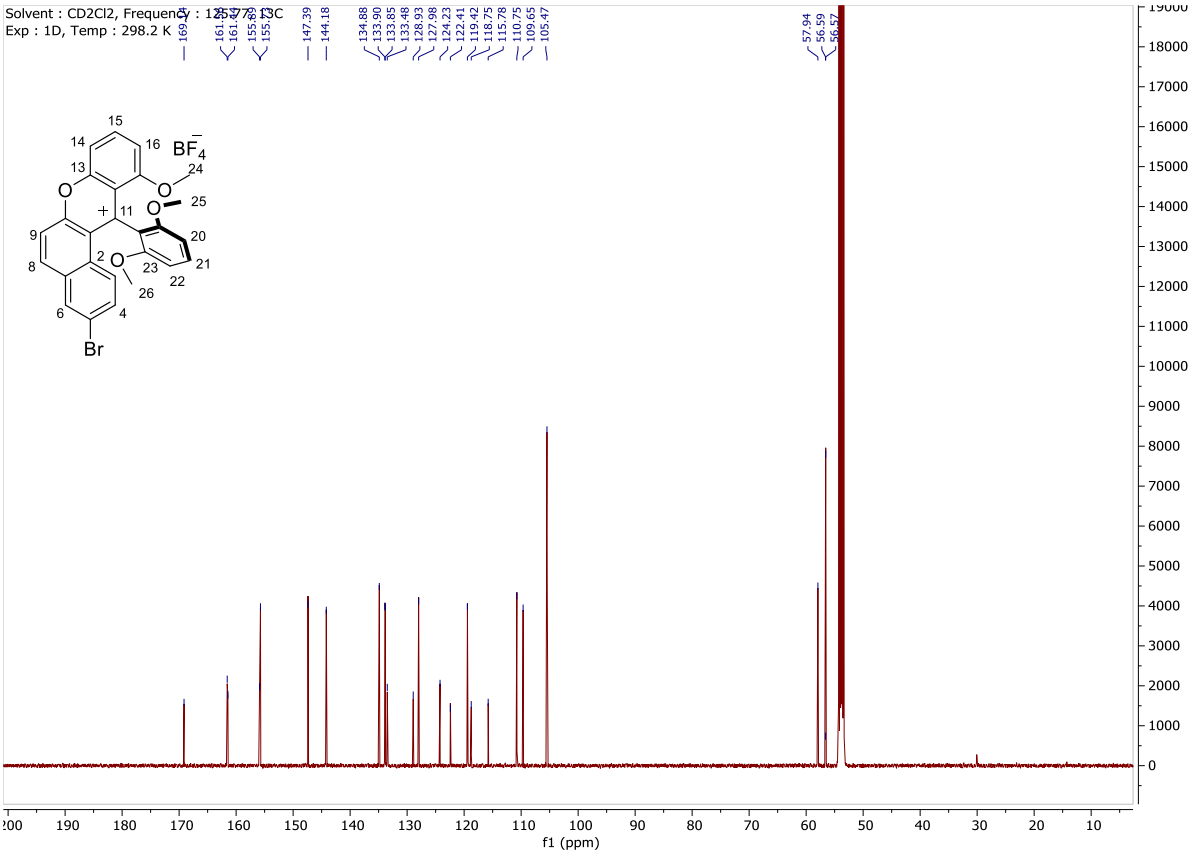
Expected Formula	Observed *m/z* $[M\text{-}OH]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{26}H_{20}BrO_4$	475.0550	475.0540	2.1

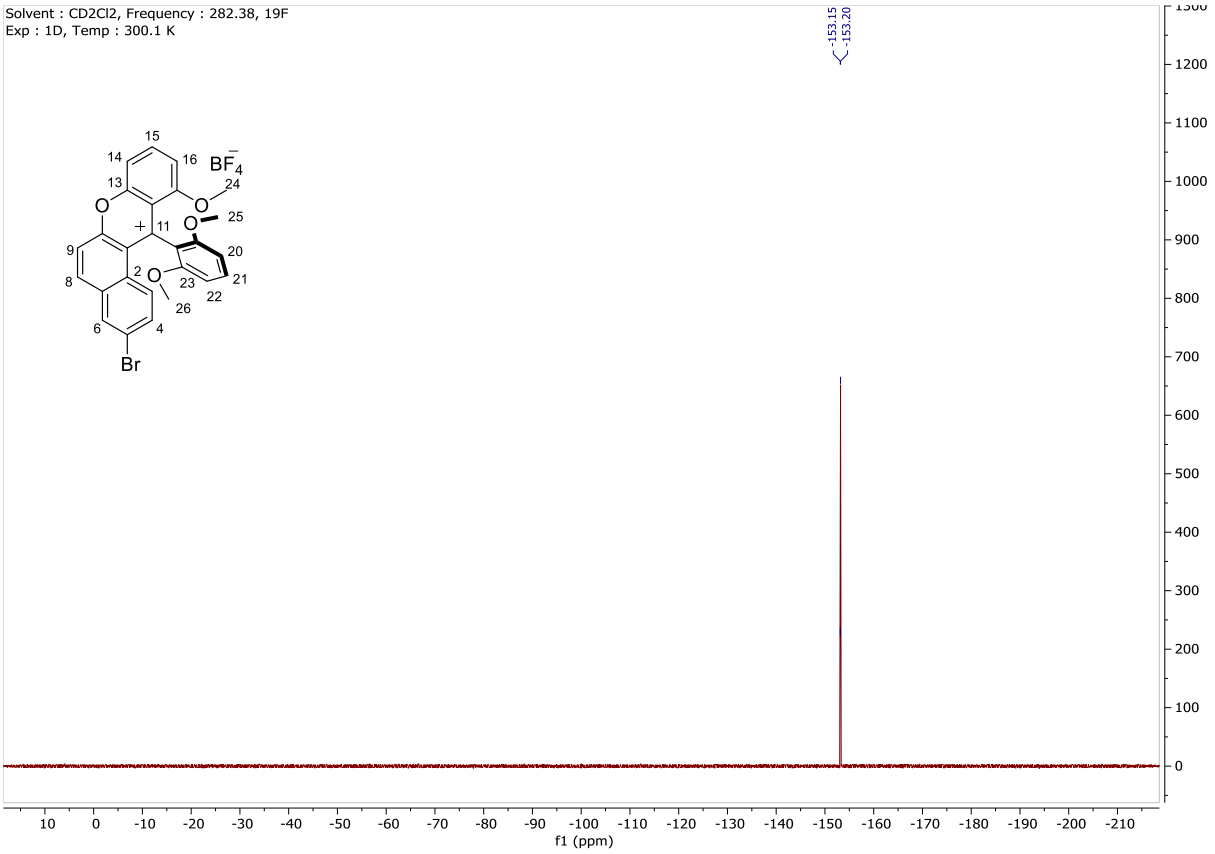




3-bromo-12-(2,6-dimethoxyphenyl)-11-methoxy-12*H*-benzo[*a*]xanthen-12-ylium tetrafluoroborate (13B)






Solvent : CD2Cl2, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.1 K
-153.15
-153.20
BF4
Br
f1 (ppm)

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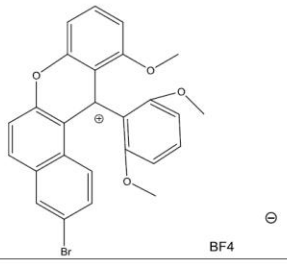
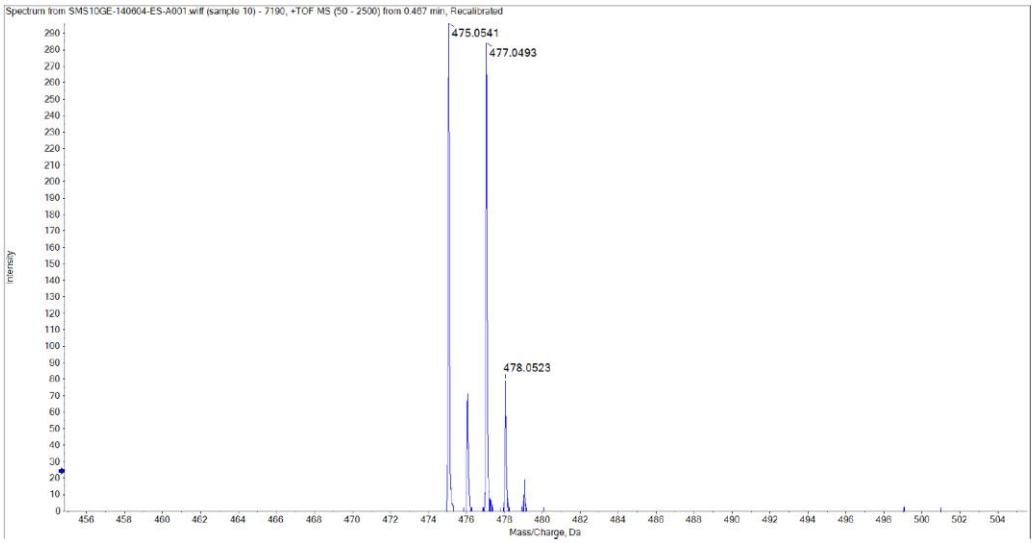
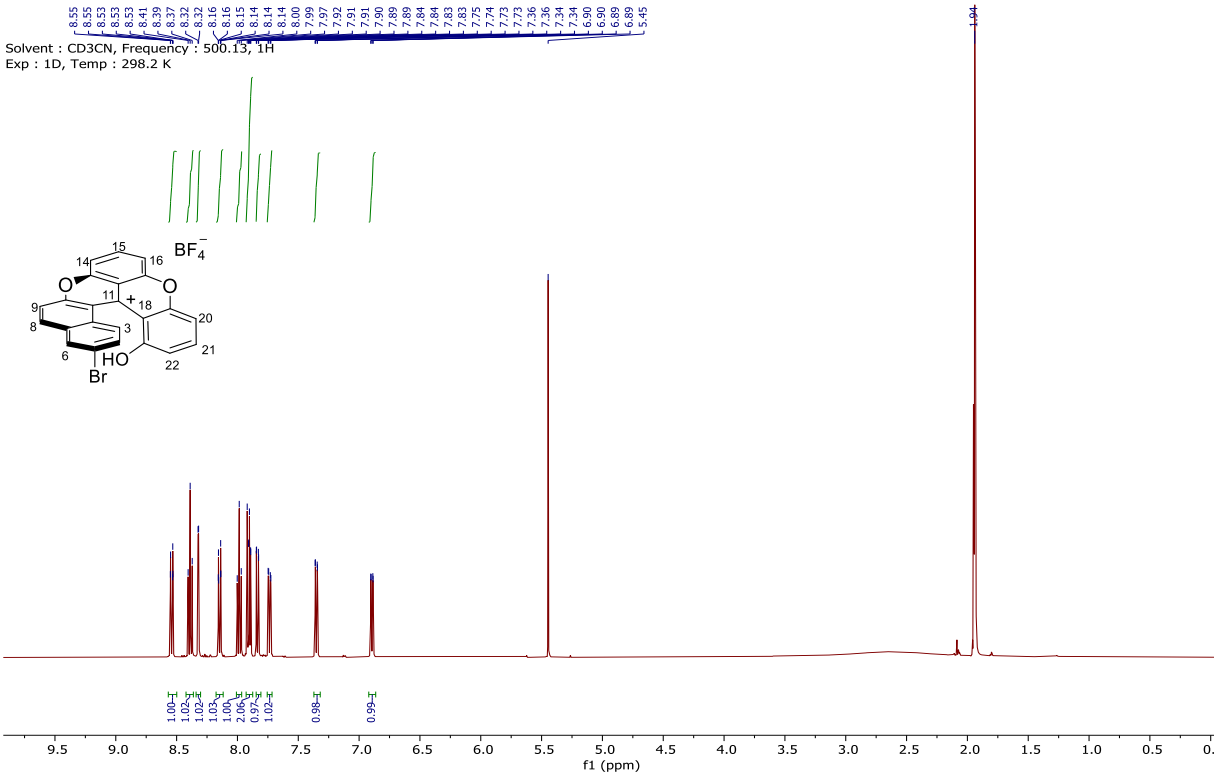
Submitter:	MARINOVA	Date of reception:	03/06/14
Sample name:	MMD69	Date of certificate:	04/06/14
Sample number:	7190	Data filename:	SMS10GE-140604-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

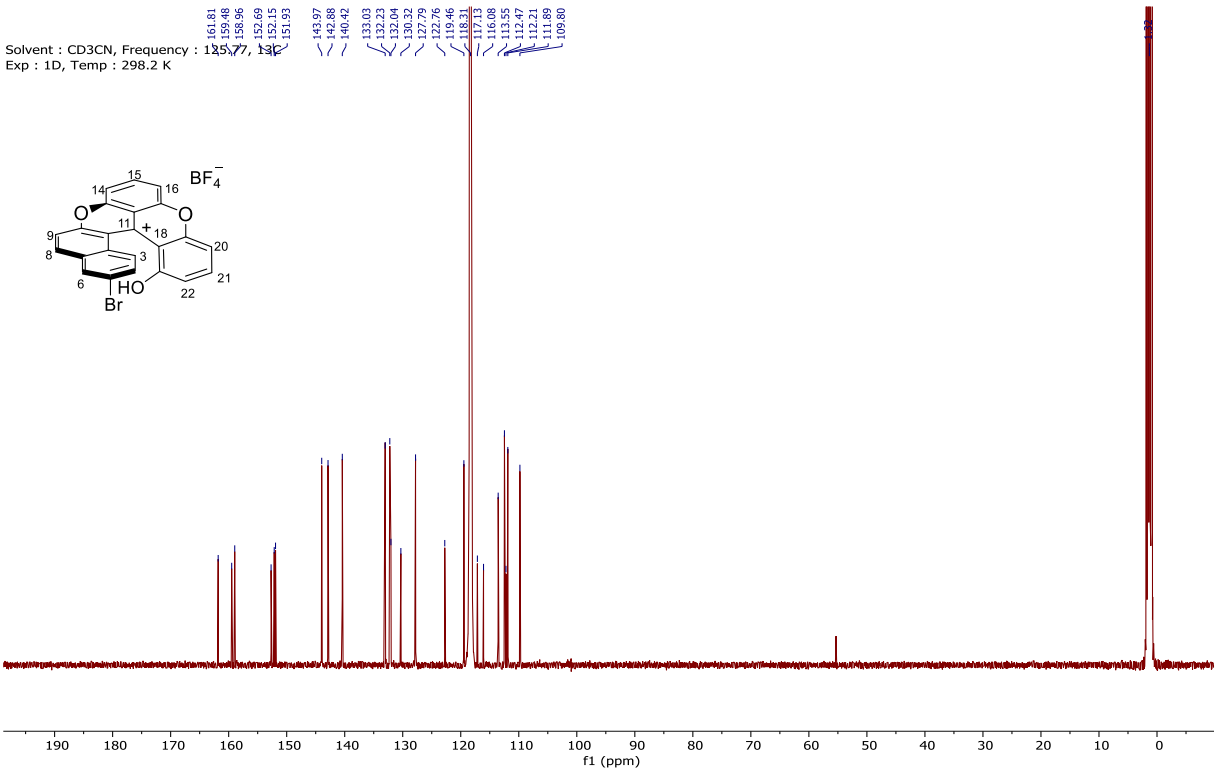
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{26}H_{20}BrO_4$	475.0541	475.0540	0.4



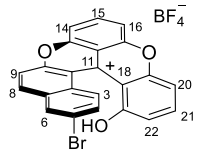


14-bromo-11-hydroxy-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoro-borate (14B)





Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K



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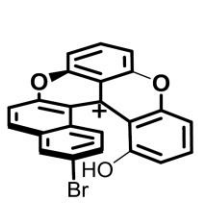
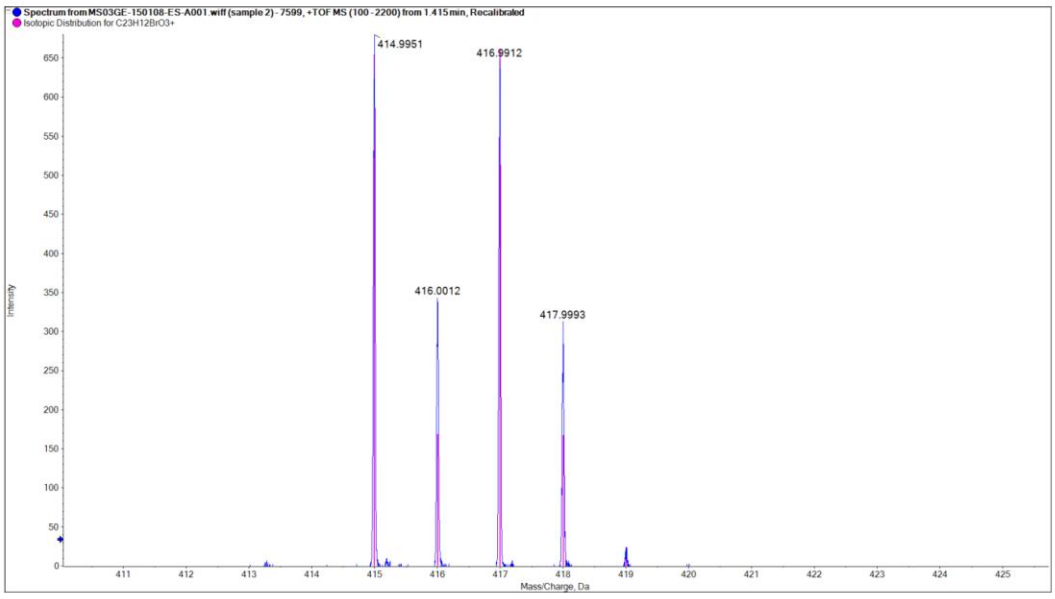
Submitter:	MARINOVA	Date of reception:	15/12/14
Sample name:	MME0210	Date of certificate:	08/01/15
Sample number:	7599	Data filename:	MS03GE-150108-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR XL (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

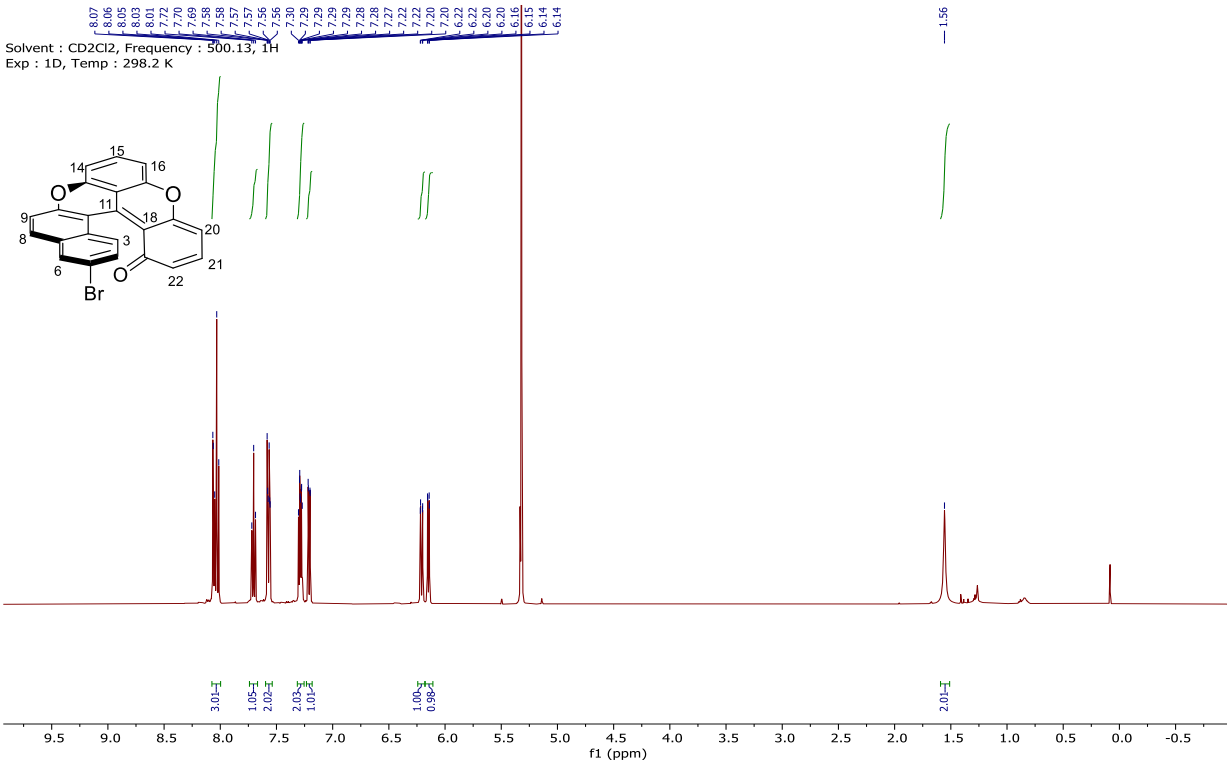
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{23}H_{12}BrO_3$	414.9951	414.9964	-3.1

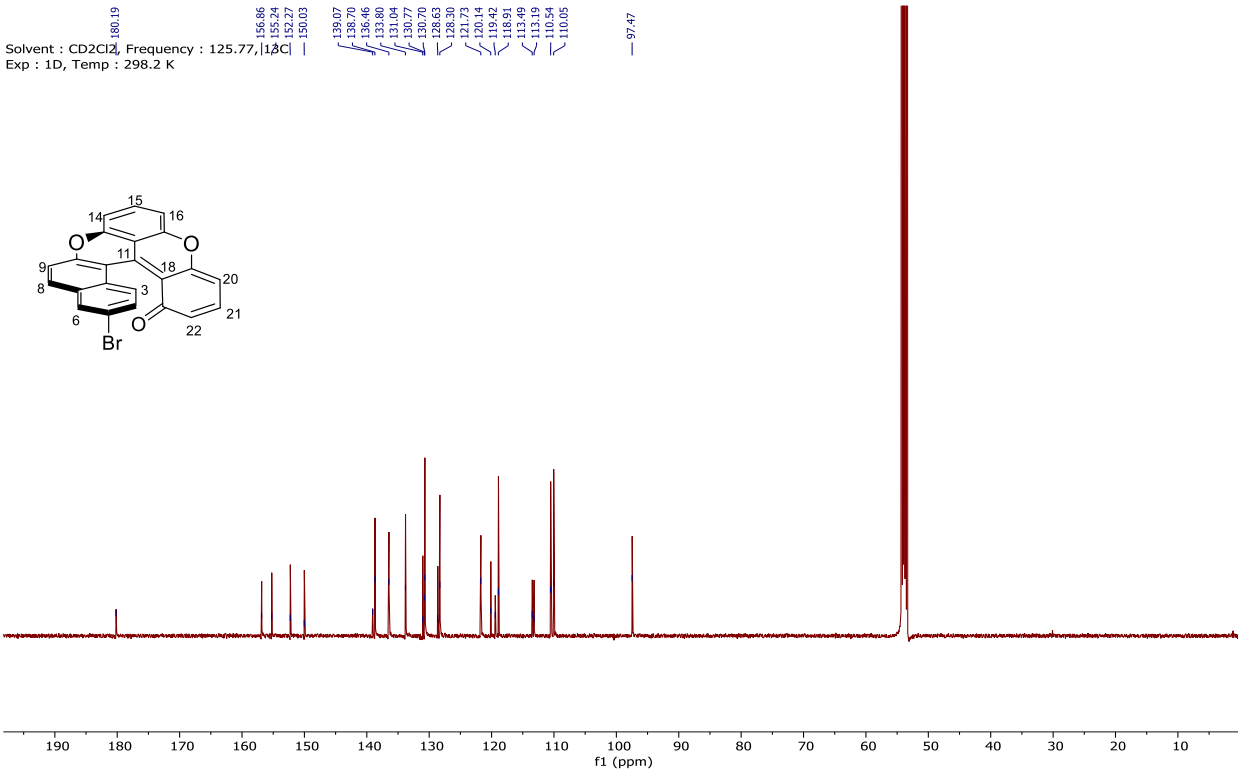


MME0210



14-bromo-11*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11-one (15B)





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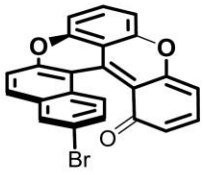
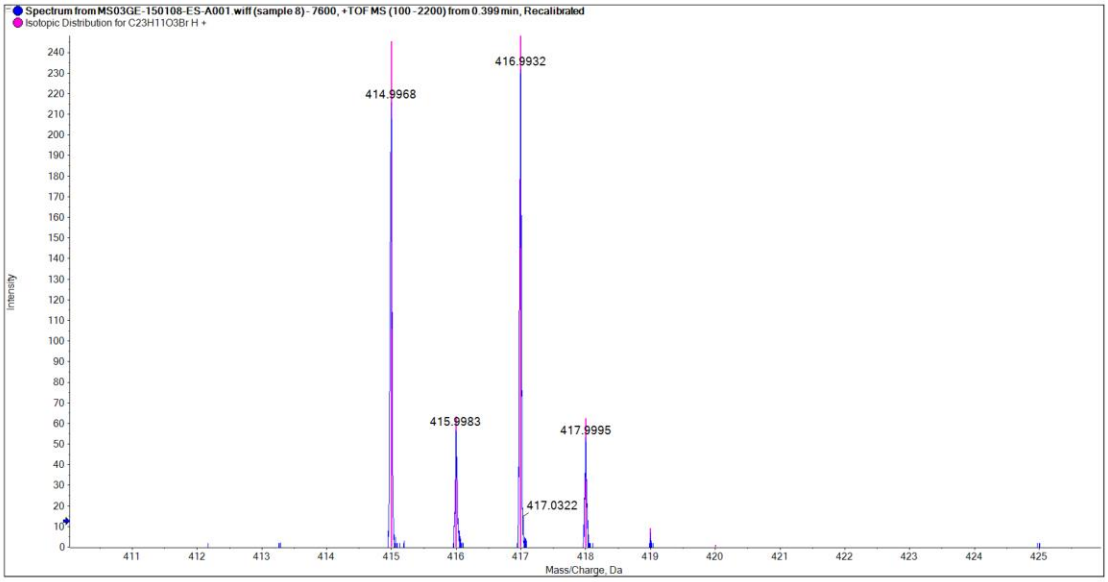
Submitter:	MARINOVA	Date of reception:	15/12/14
Sample name:	MME2305	Date of certificate:	08/01/15
Sample number:	7600	Data filename:	MS03GE-150108-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR XL (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

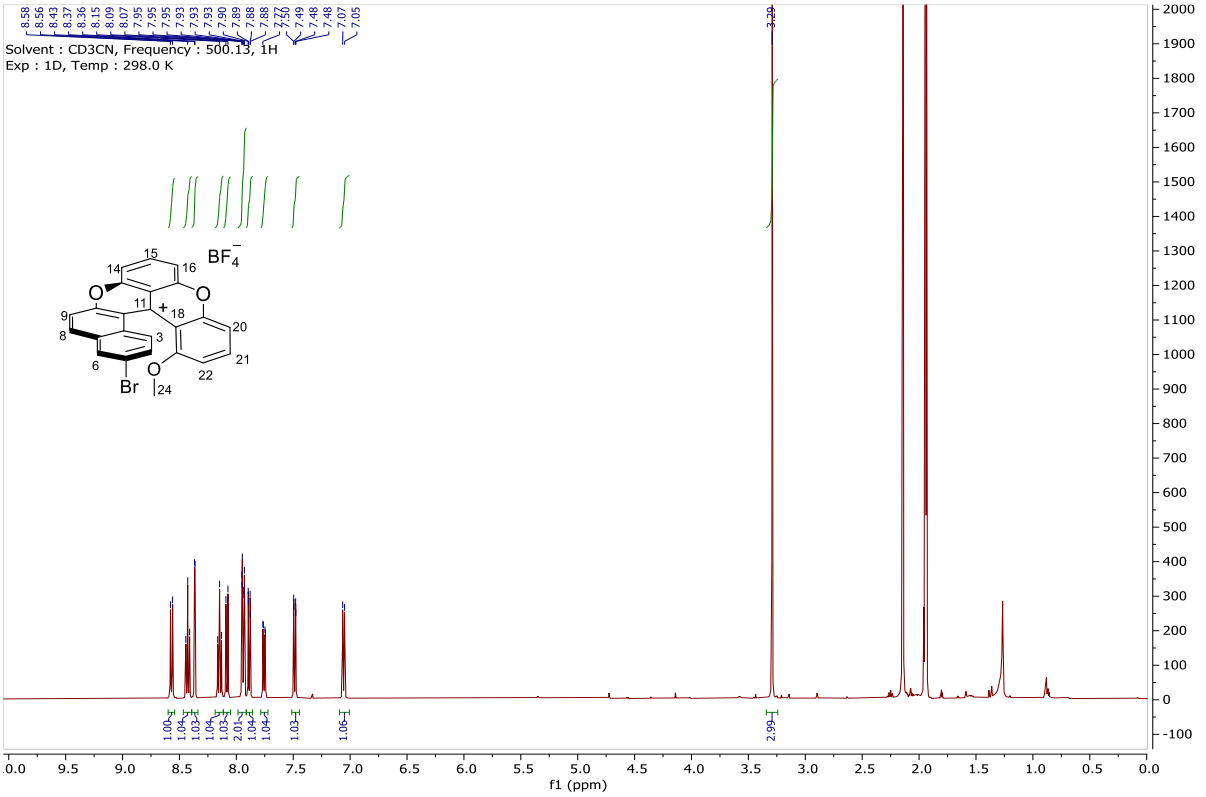
Expected Formula	Observed *m/z* $[M+H]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{23}H_{11}BrO_3$	414.9968	414.9964	0.9

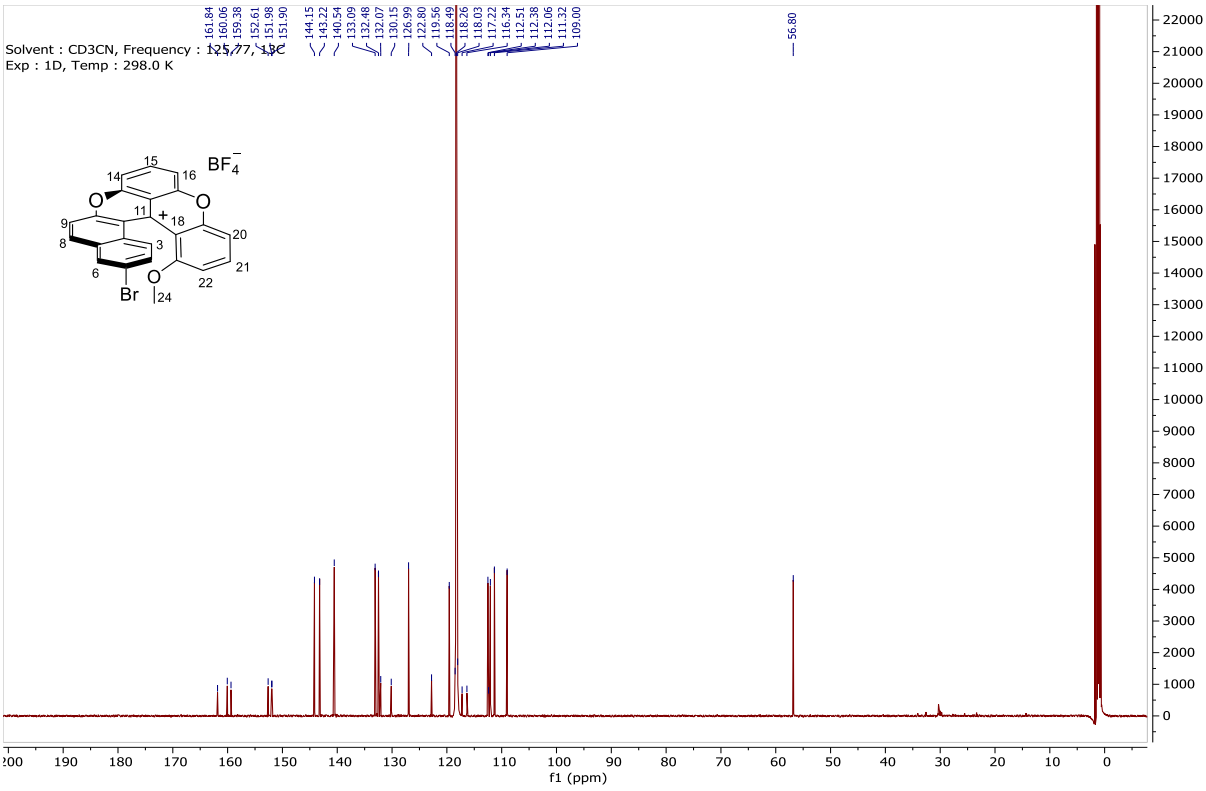


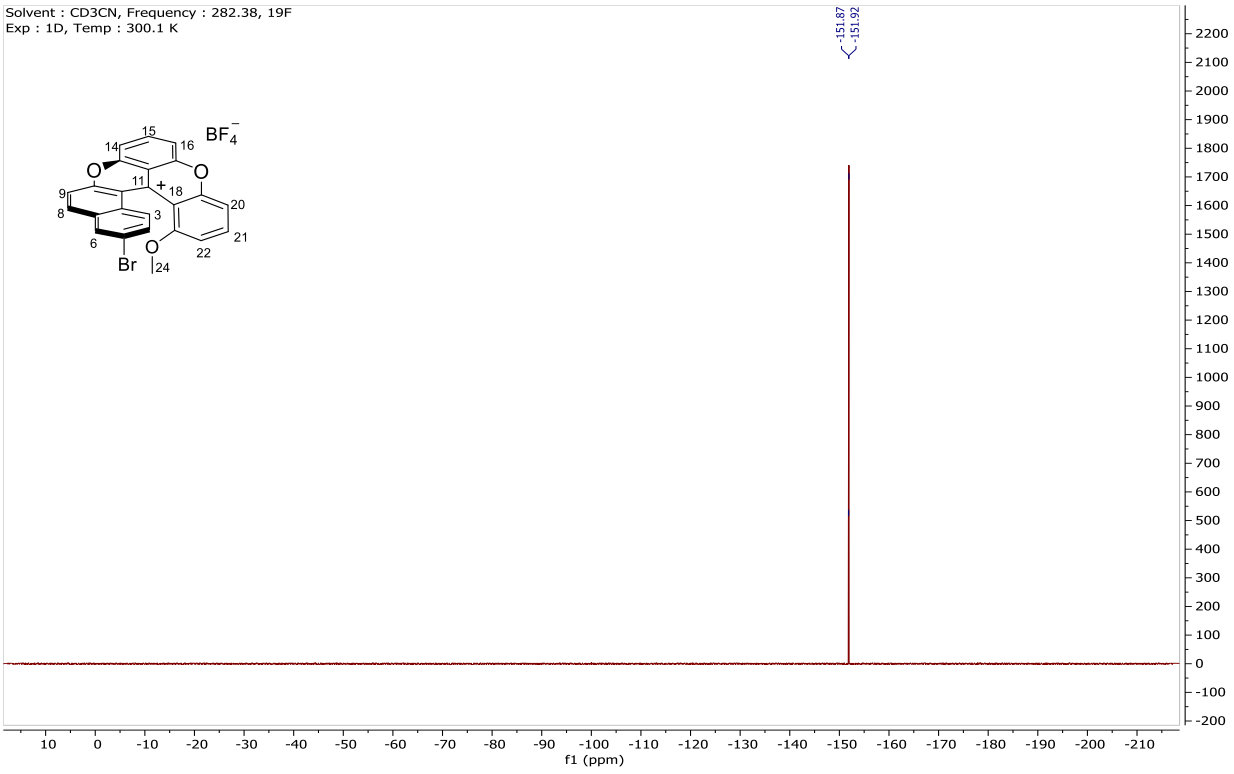
MME2305



14-bromo-11-methoxy-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoro-borate (8B)






Solvent : CD3CN, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.1 K
-151.87
-151.92
BF4
Br
f1 (ppm)

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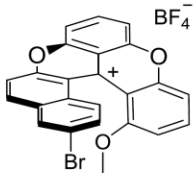
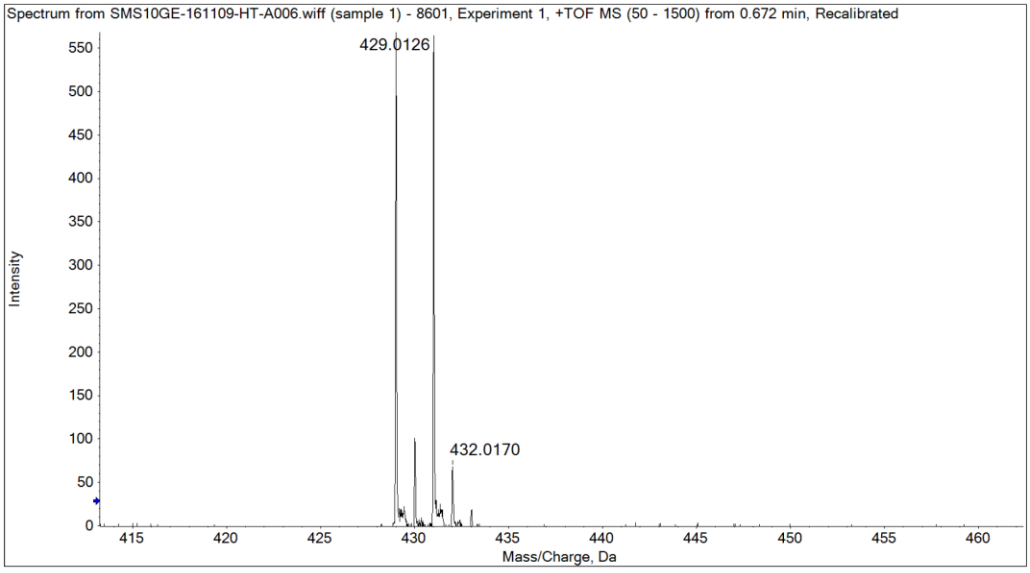
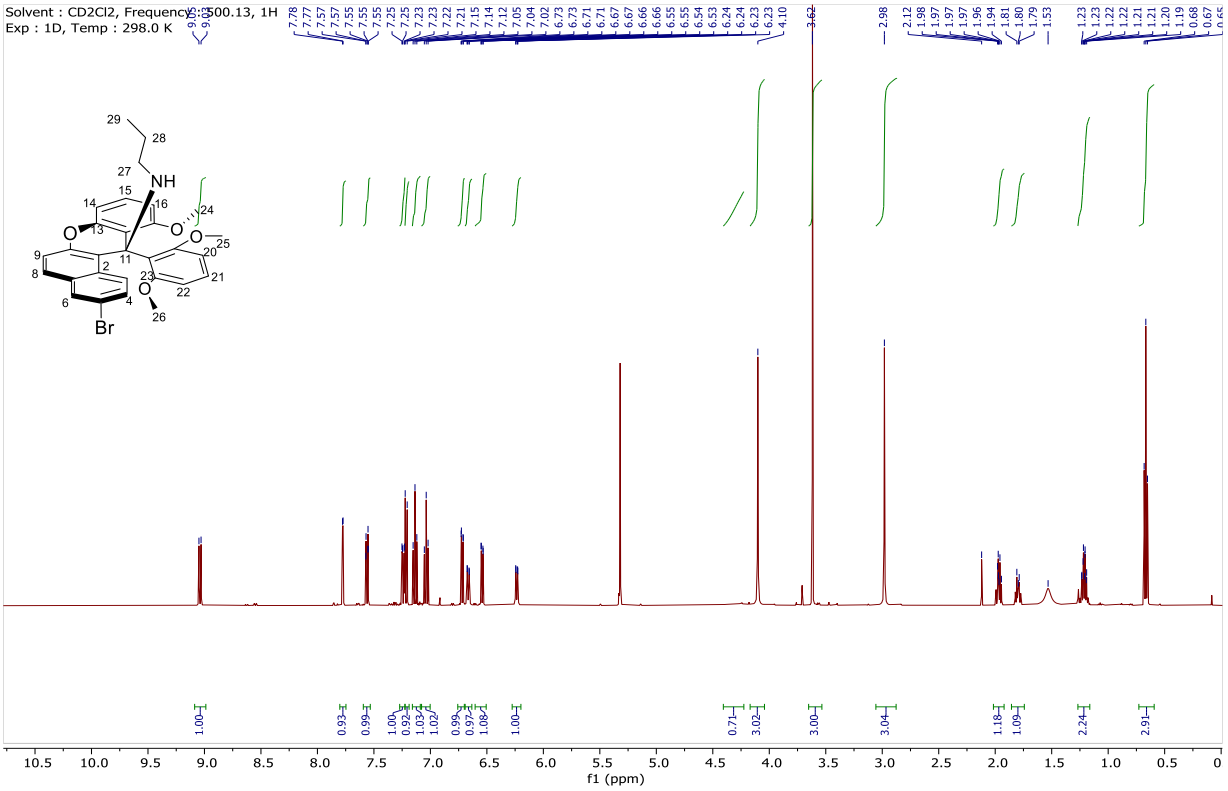
Submitter: MARINOVA	Date of reception: 08/11/2016
Sample name: MME6207	Date of certificate: 10/11/2016
Sample number: 8601	Data filename: SMS10GE-161109-HT-A006
Operator: Harry Théraulaz	Instrument: QSTAR Pulsar (AB/MDS Sciex)
Principal investigator: Dr. Sophie Michalet	Ionisation mode: ESI (positive mode)

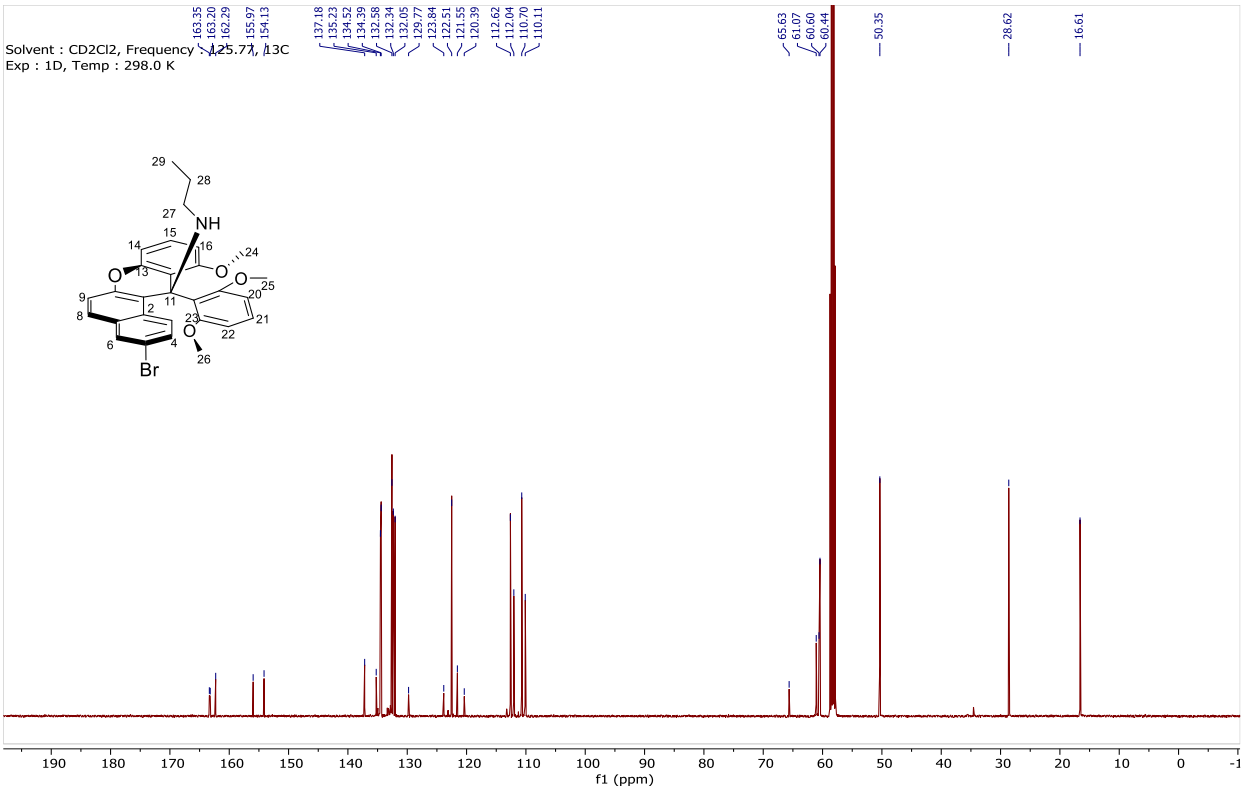
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{24}H_{14}BrO_3$	429.0126	429.0121	1.2





3-bromo-12-(2,6-dimethoxyphenyl)-11-methoxy-N-propyl-12H-benzo[a]xanthen-12-amine (16B)





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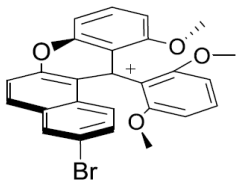
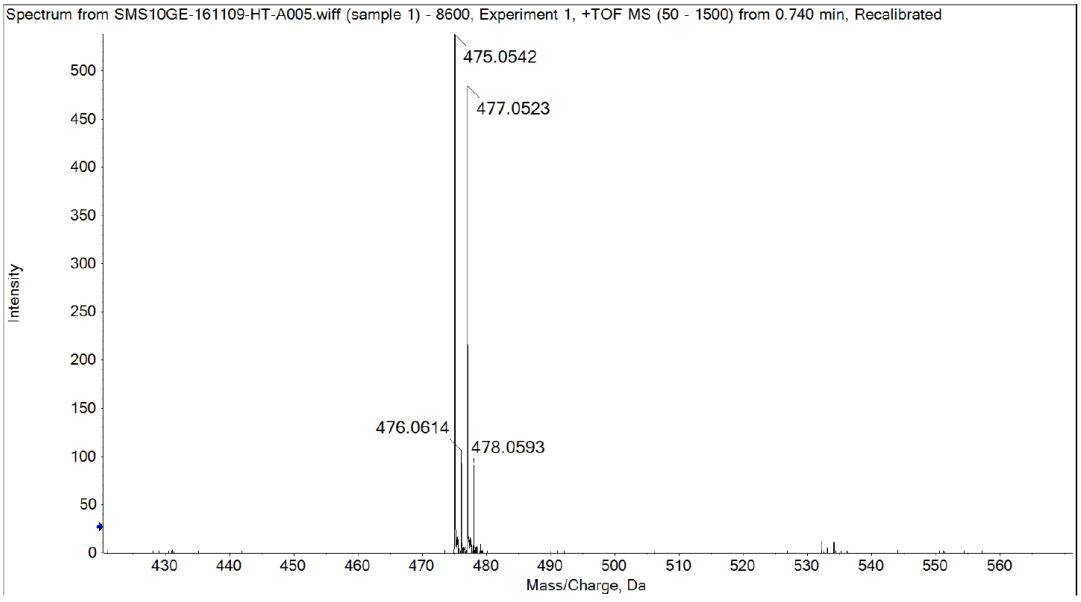
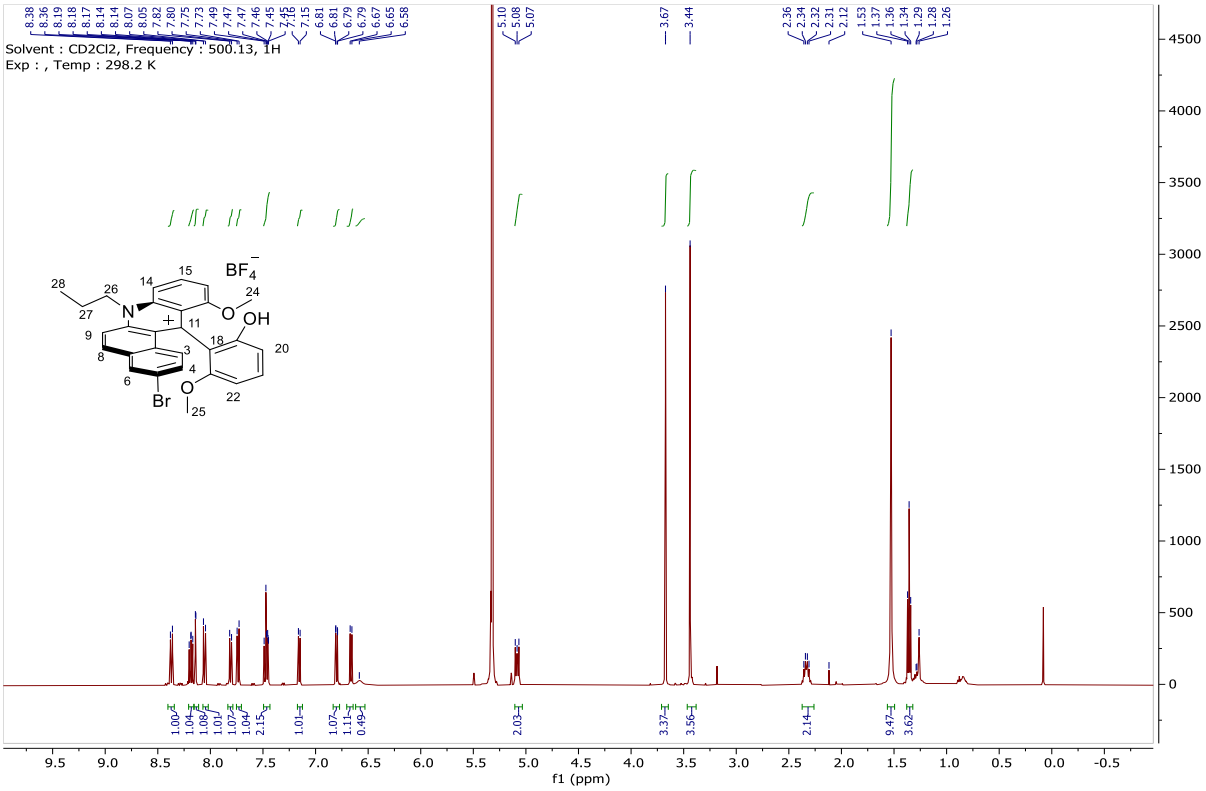
Submitter:	MARINOVA	Date of reception:	08/11/2016
Sample name:	MME0102	Date of certificate:	10/11/2016
Sample number:	8600	Data filename:	SMS10GE-161109-HT-A005
Operator:	Harry Théraulaz	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

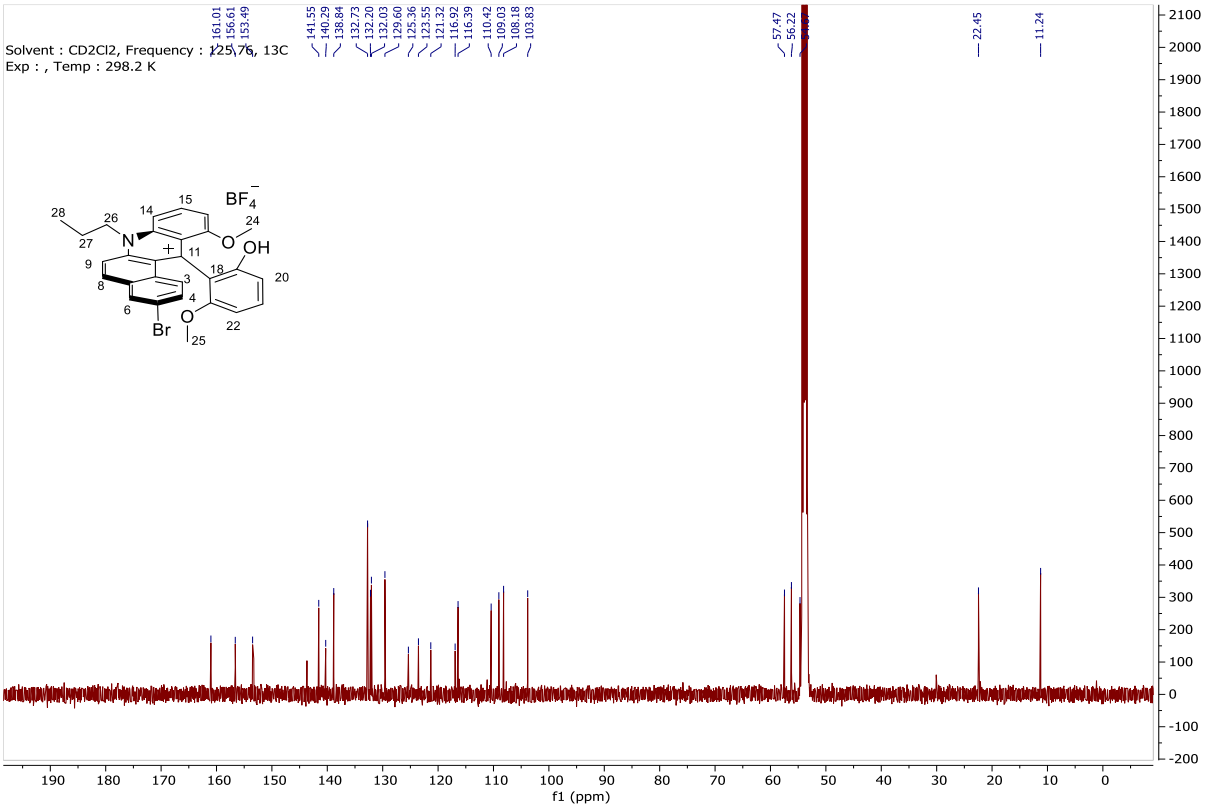
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{26}H_{20}BrO_4$	475.0542	475.0540	0.5

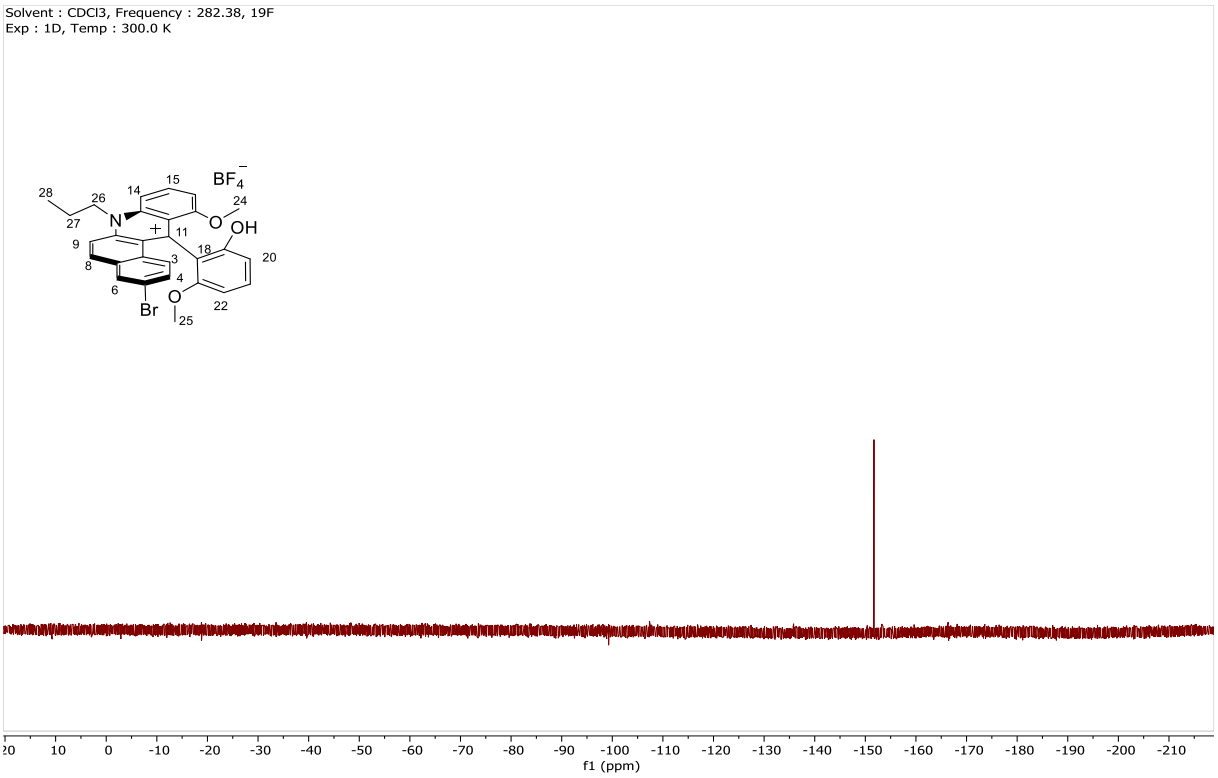


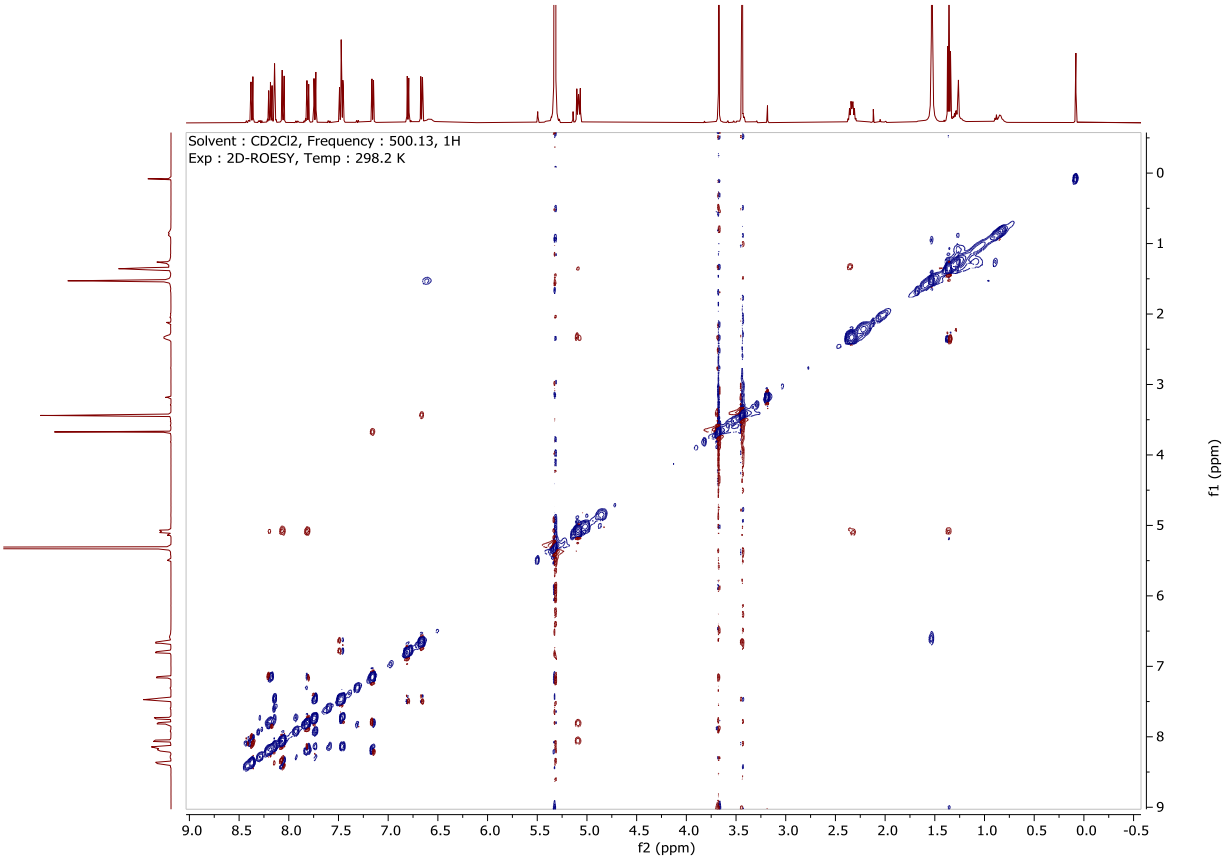


3-bromo-12-(2-hydroxy-6-methoxyphenyl)-11-methoxy-7-propyl-7,12-dihydrobenzo[*a*]-acridin-12-ylium tetrafluoroborate (19B)






Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K
BF4
OH
Br
f1 (ppm)


Solvent : CD2Cl2, Frequency : 500.13, 1H
Exp : 2D-ROESY, Temp : 298.2 K
f2 (ppm)
f1 (ppm)

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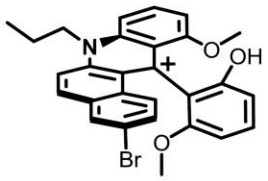
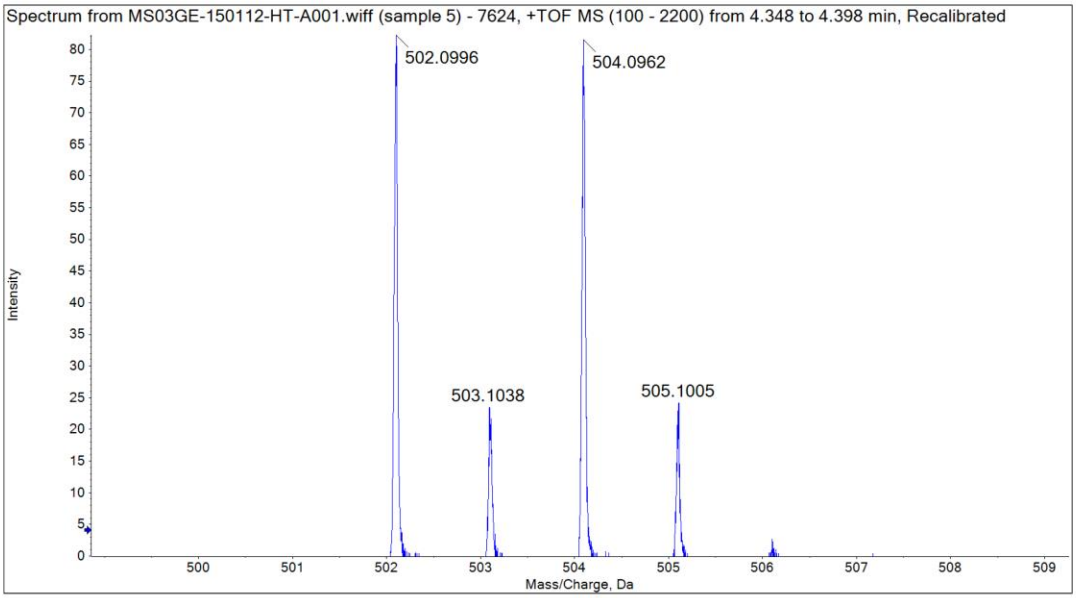
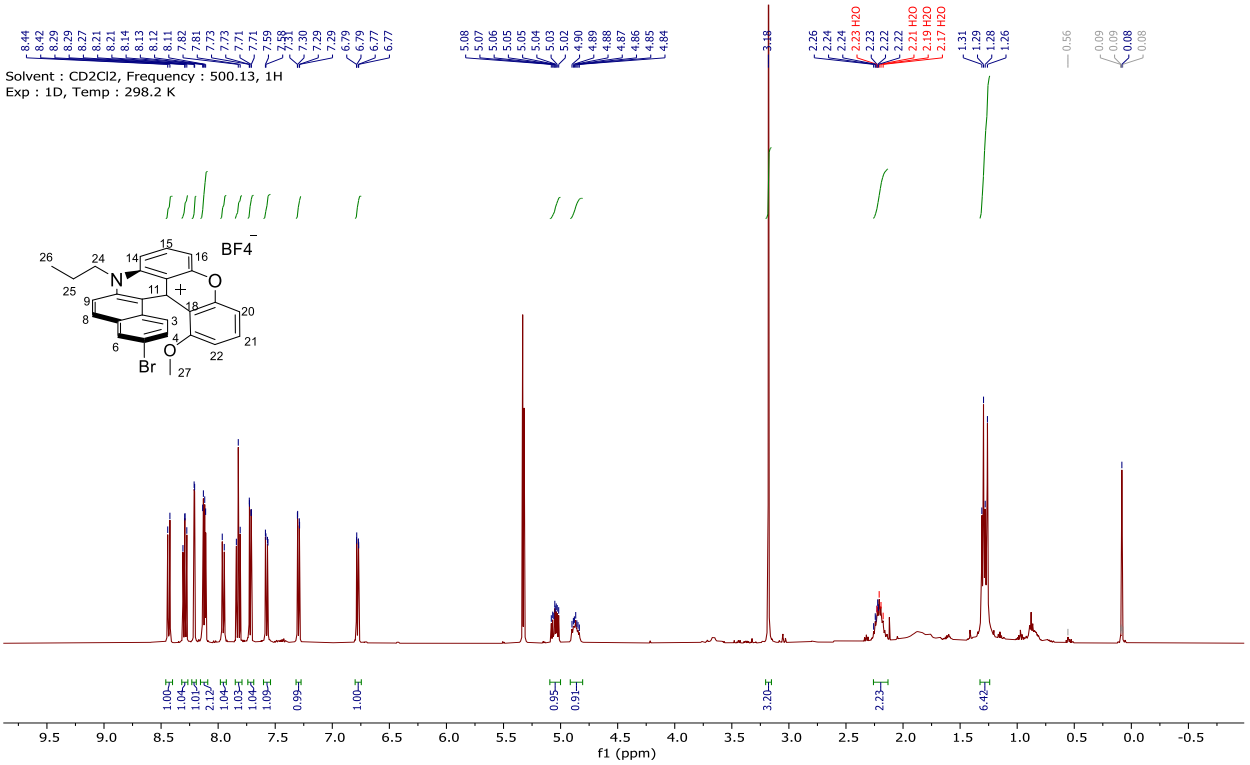
Submitter:	Maya MARINOVA	Date of reception:	05/01/15
Sample name:	MME2009	Date of certificate:	13/01/15
Sample number:	7624	Data filename:	MS03GE-150112-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR XL (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

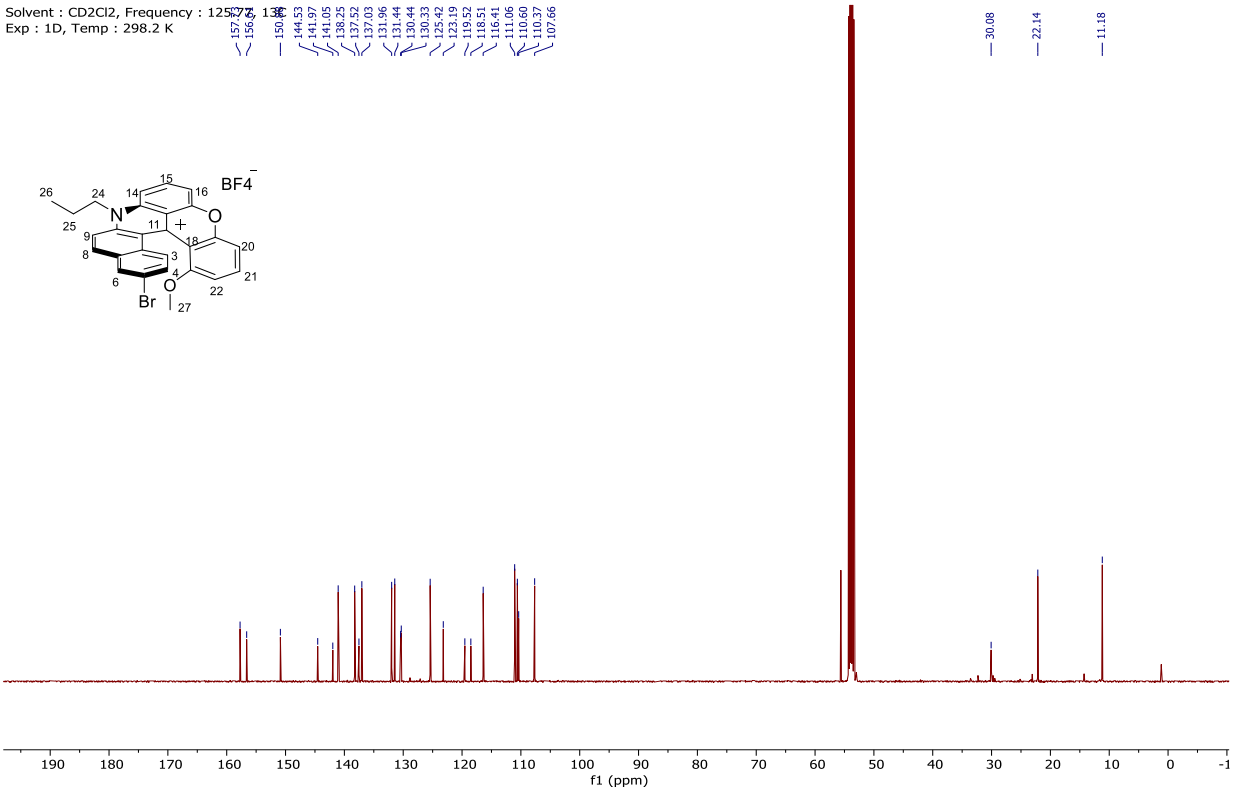
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{28}H_{25}BrNO_3$	502.0996	502.1012	-3.3





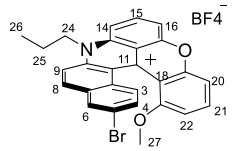
14-bromo-11-methoxy-3-propylbenzo[*a*]chromeno[2,3,4-*kl*]acridin-11b(3*H*)-ylium tetrafluoroborate (10B)

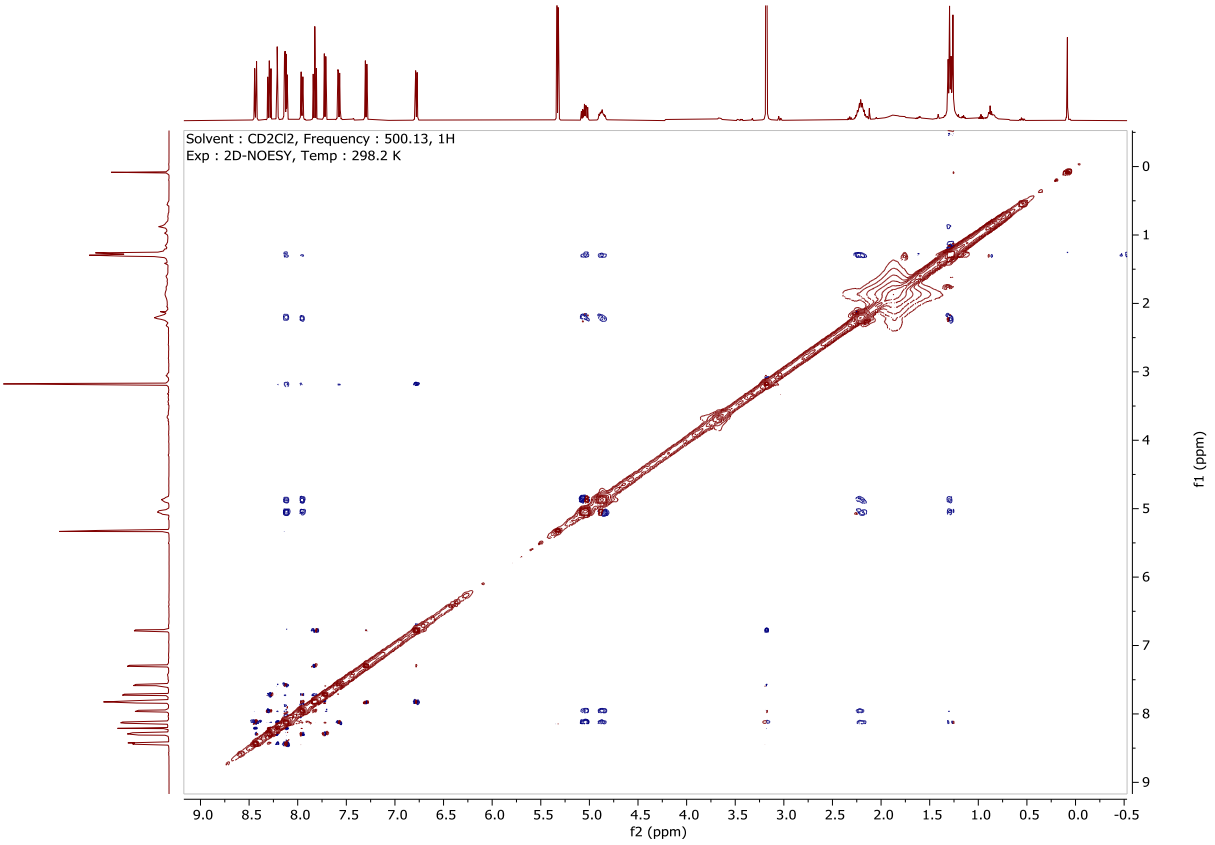




Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K

-152.03
-152.09





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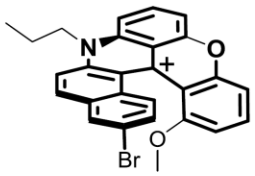
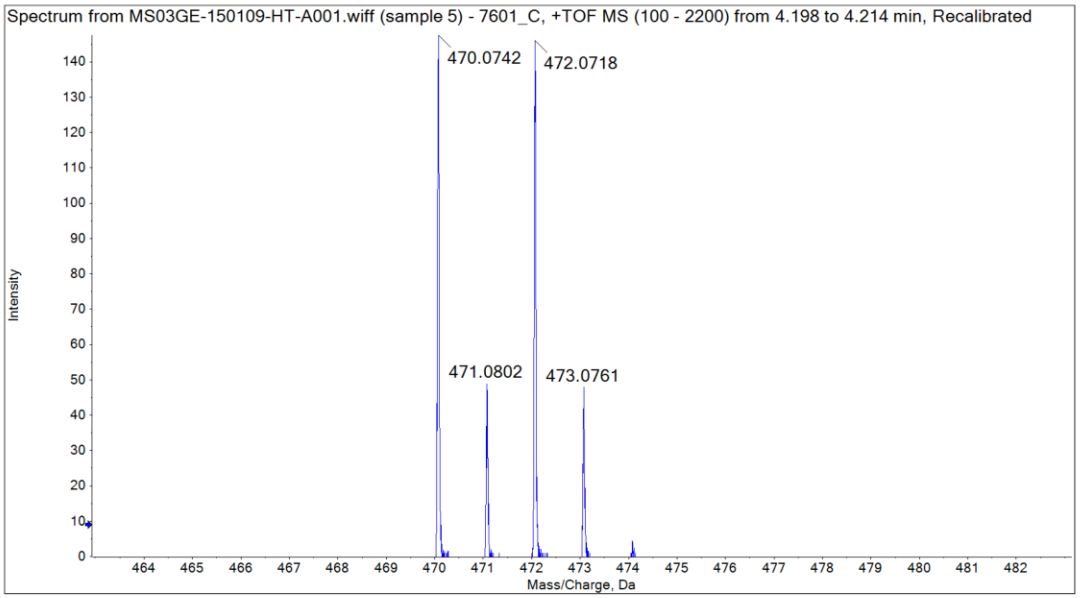
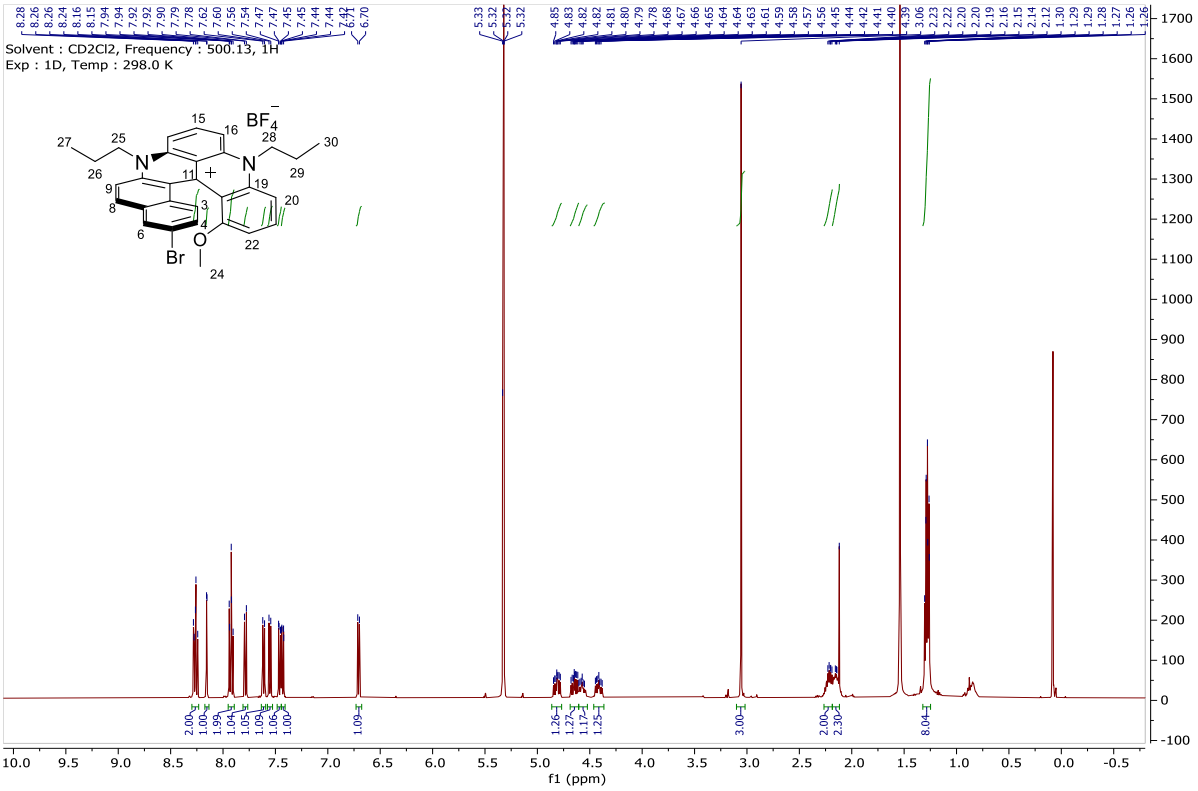
Submitter:	Maya MARINOVA	Date of reception:	15/12/14
Sample name:	MME1507	Date of certificate:	13/01/15
Sample number:	7601	Data filename:	MS03GE-150109-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR XL (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

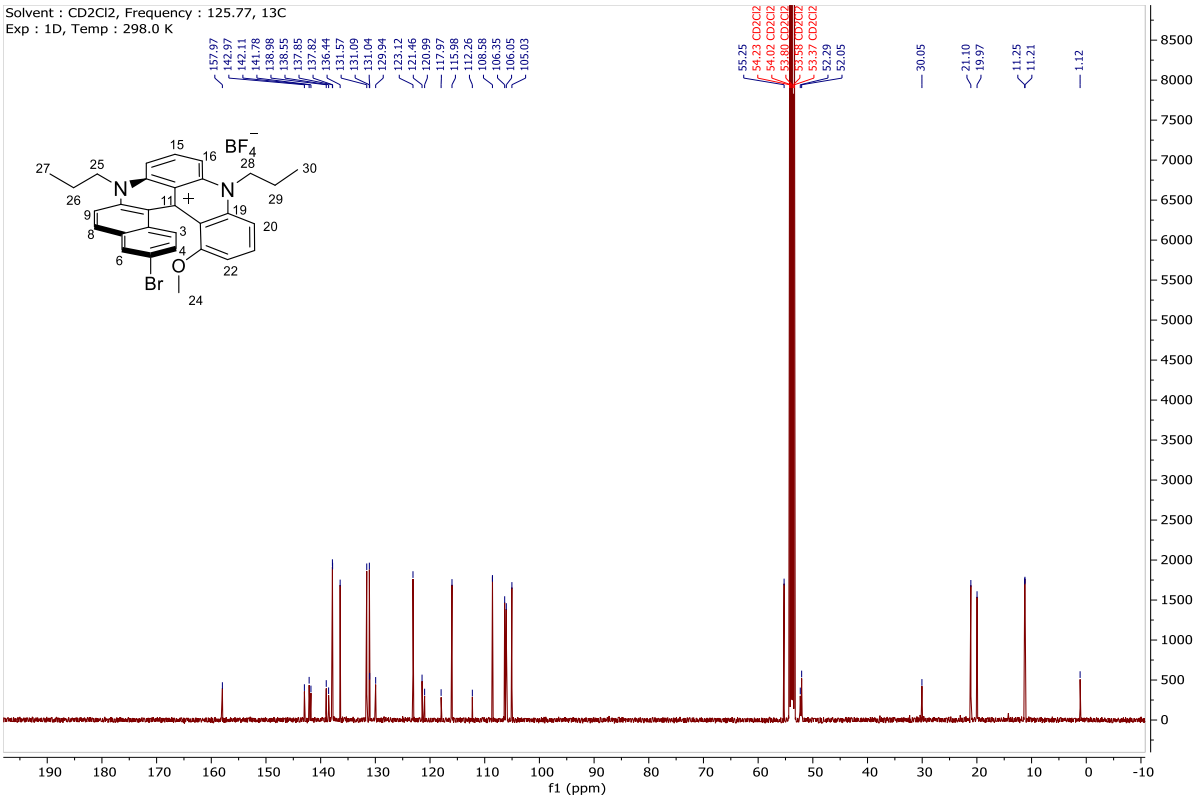
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{27}H_{21}BrNO_2$	470.0742	470.0750	-1.7

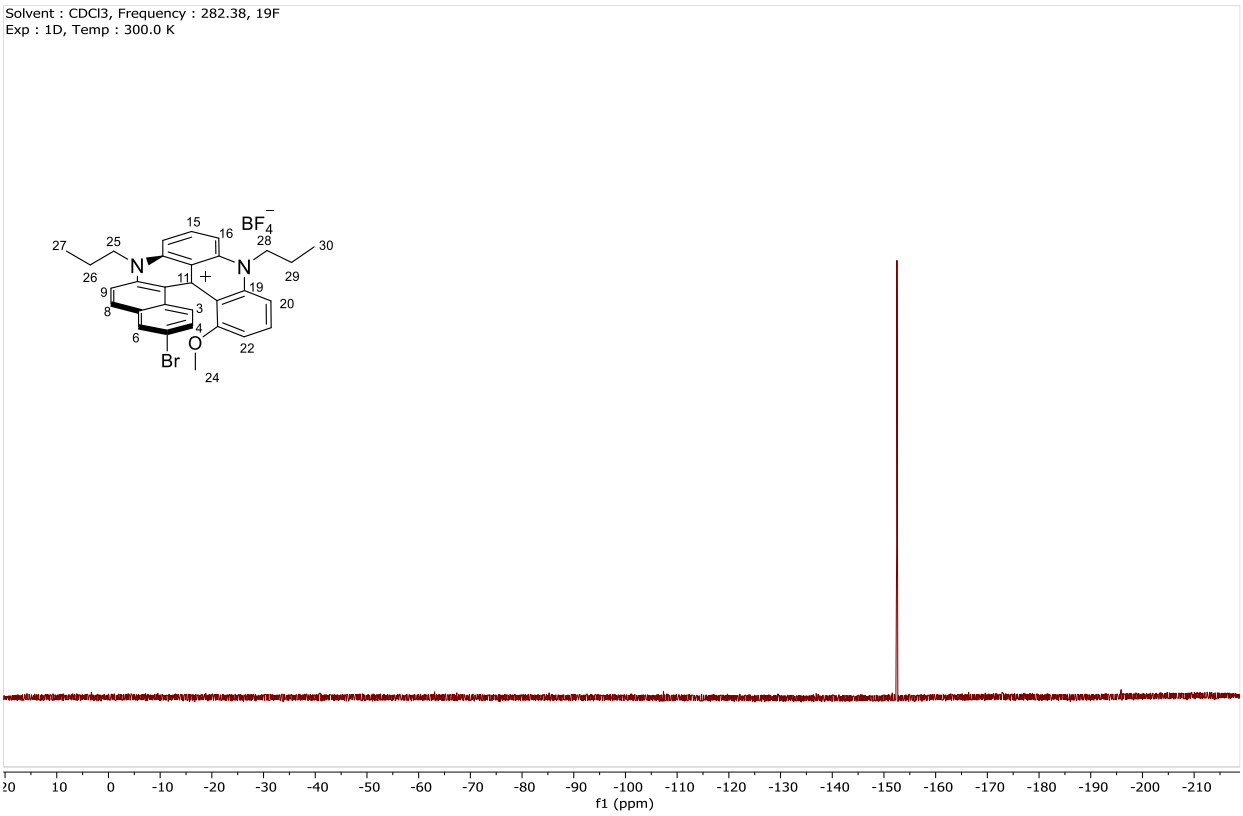


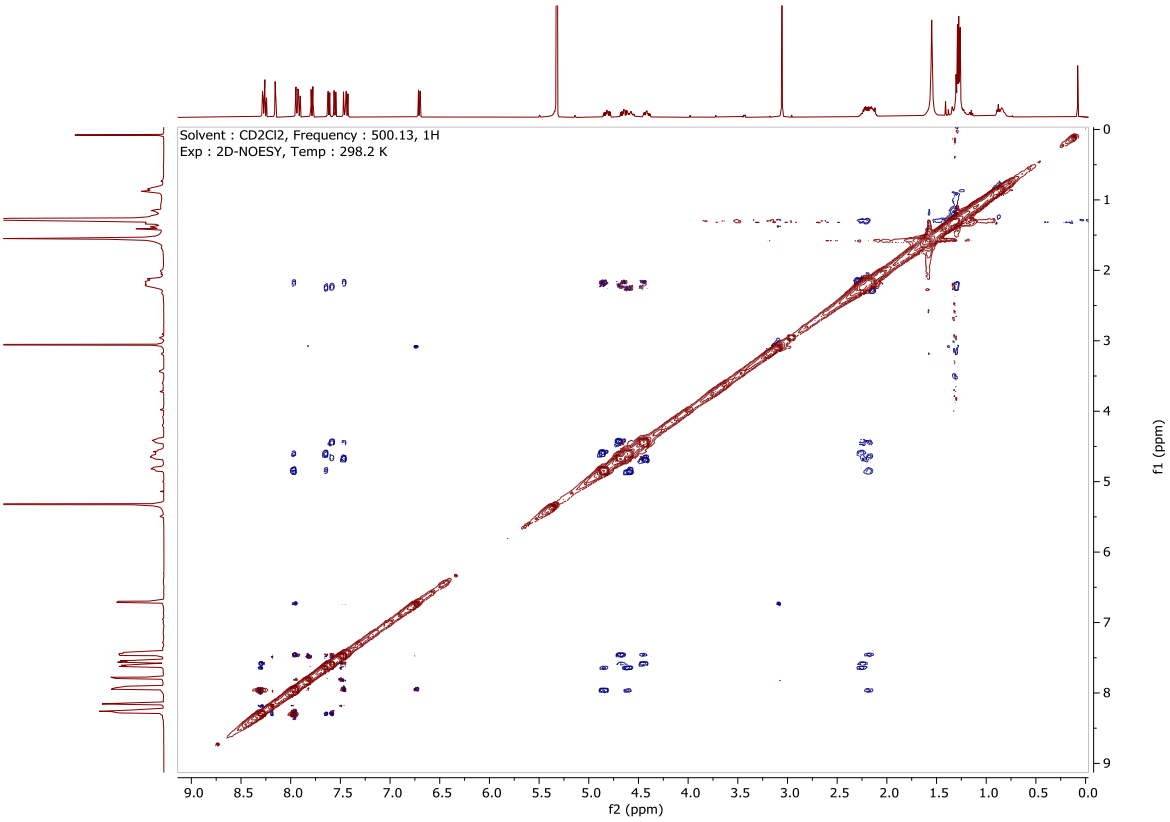


14-bromo-11-methoxy-3,7-dipropyl-3,7-dihydro-11b*H*-benzo[a]quinolino[2,3,4-*kl*]acridin-11b-ylium tetrafluoroborate (9B)






Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K
BF4
Br
f1 (ppm)


Solvent : CD2Cl2, Frequency : 500.13, 1H
Exp : 2D-NOESY, Temp : 298.2 K
f2 (ppm)
f1 (ppm)

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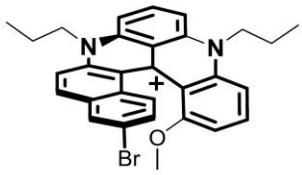
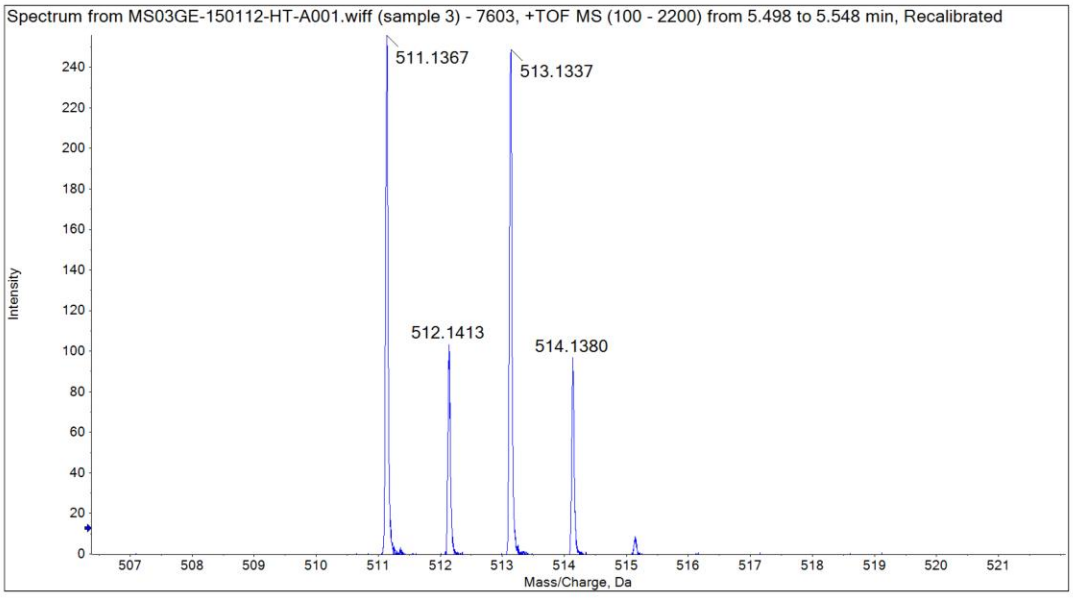
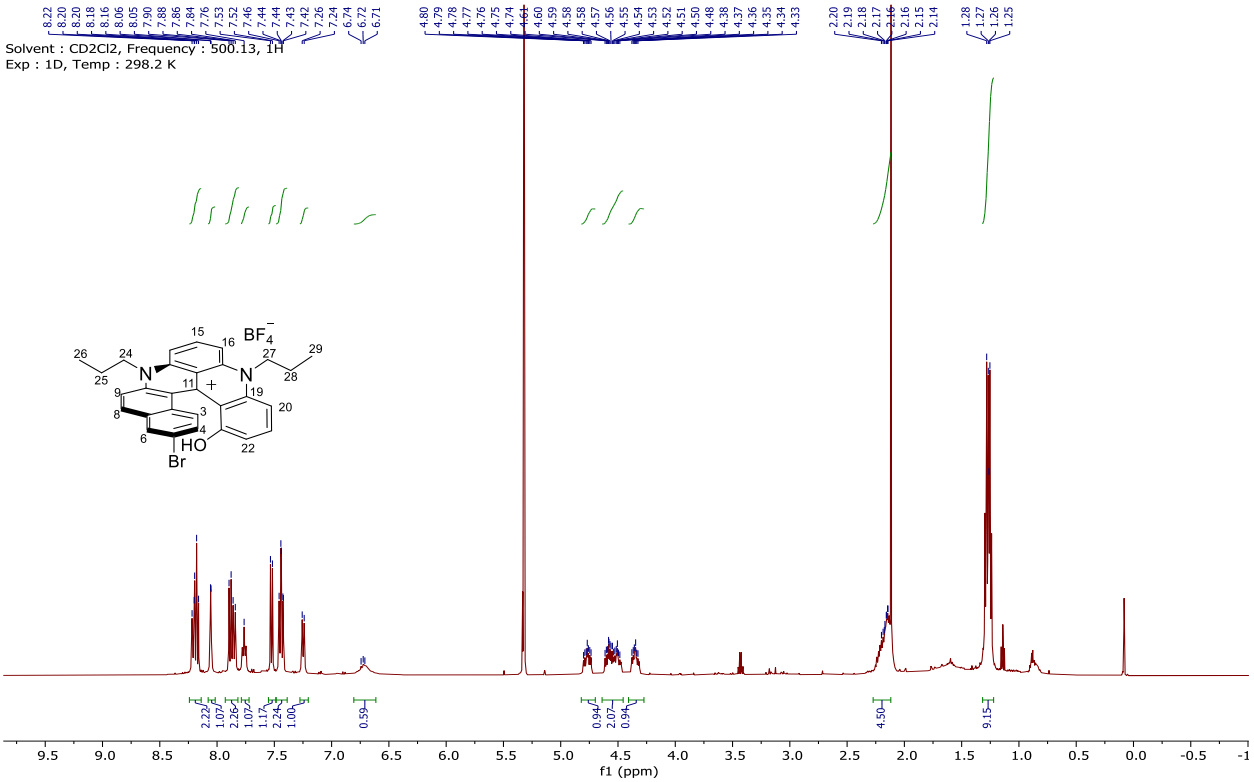
Submitter:	Maya MARINOVA	Date of reception:	15/12/14
Sample name:	MME3904	Date of certificate:	13/01/15
Sample number:	7603	Data filename:	MS03GE-150112-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR XL (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

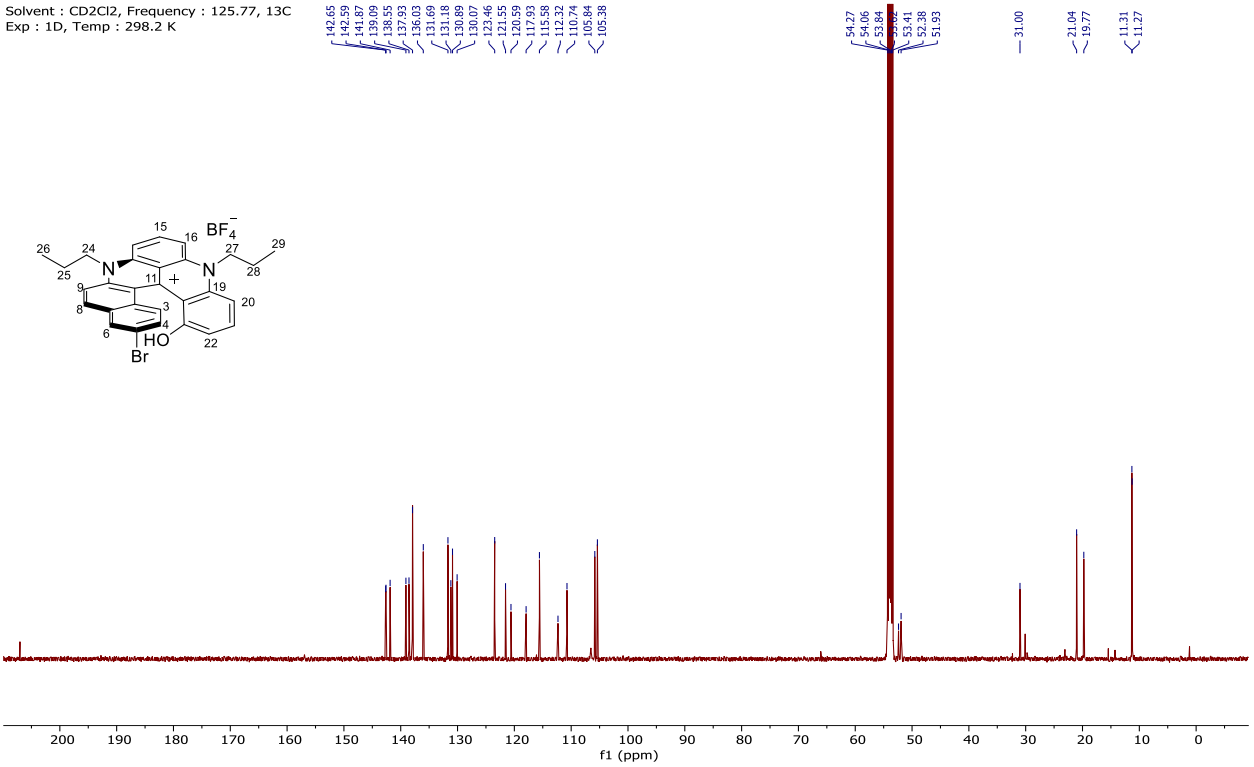
Expected Formula	Observed *m/z* [M]$^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{30}H_{28}BrN_2O$	511.1367	511.1380	-2.4

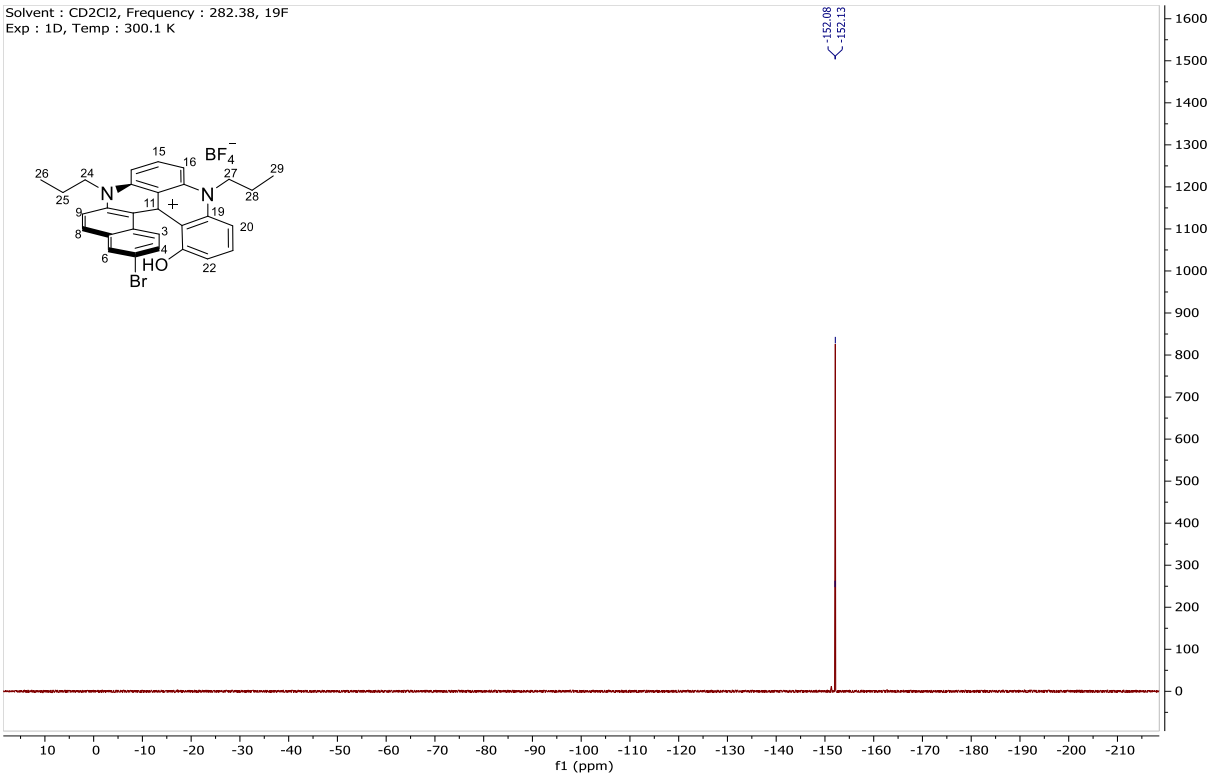


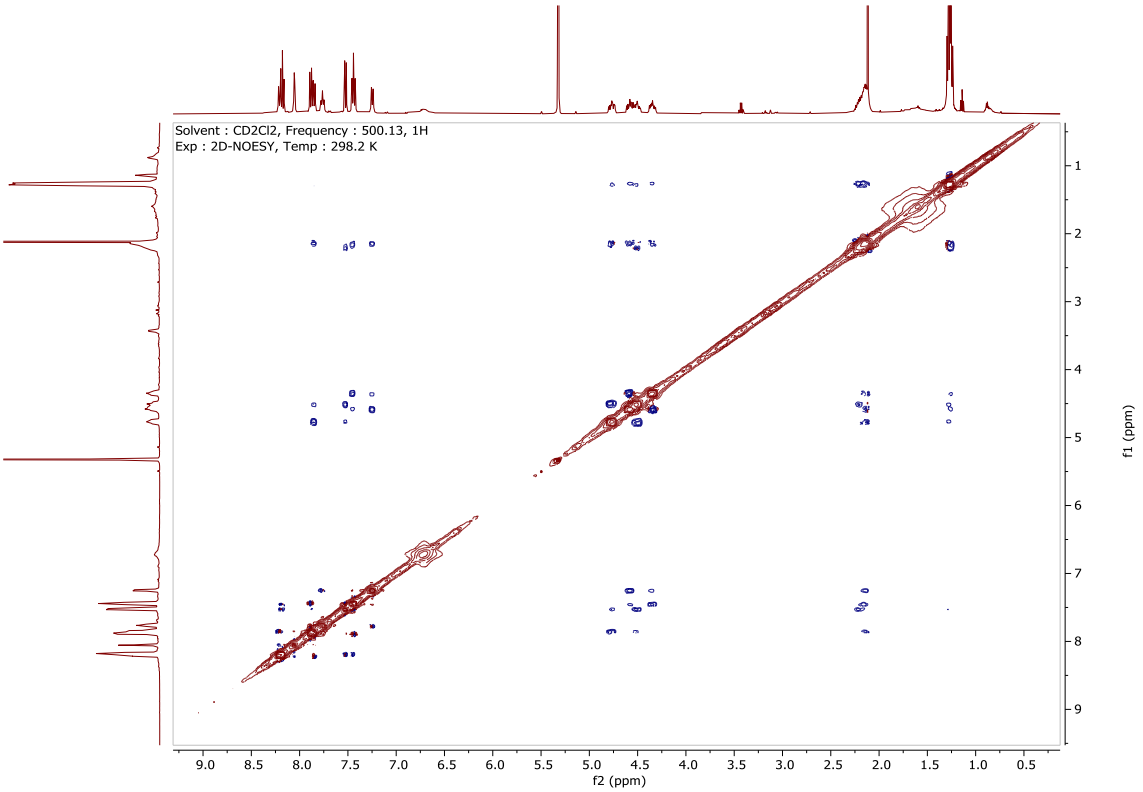


14-bromo-11-hydroxy-3,7-dipropyl-3,7-dihydro-11b*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridin-11b-ylium tetrafluoroborate (17B)






Solvent : CD2Cl2, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.1 K
-152.08
-152.13
BF4
HO
Br
f1 (ppm)


Solvent : CD2Cl2, Frequency : 500.13, 1H
Exp : 2D-NOESY, Temp : 298.2 K
f1 (ppm)
f2 (ppm)

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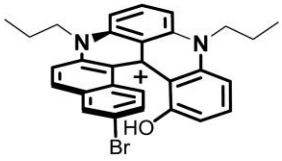
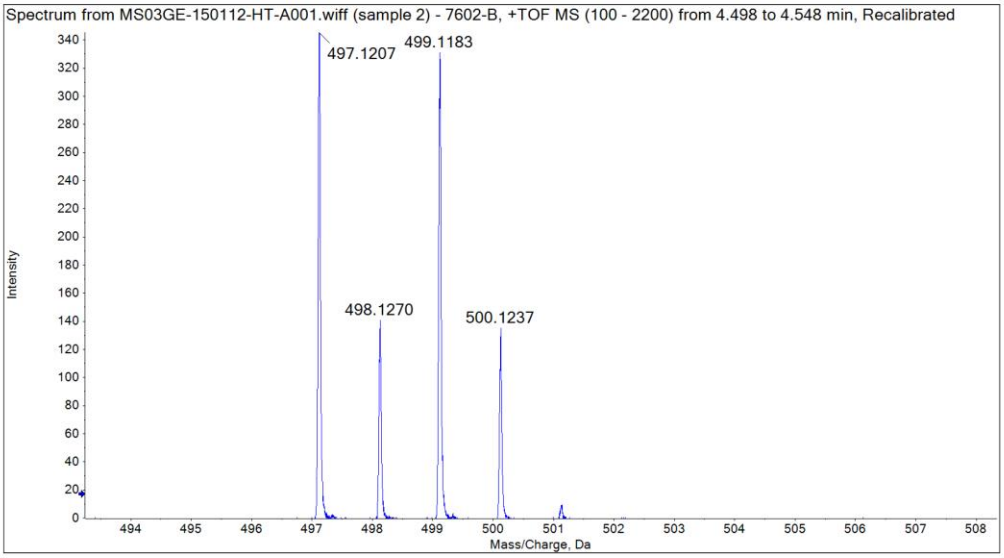
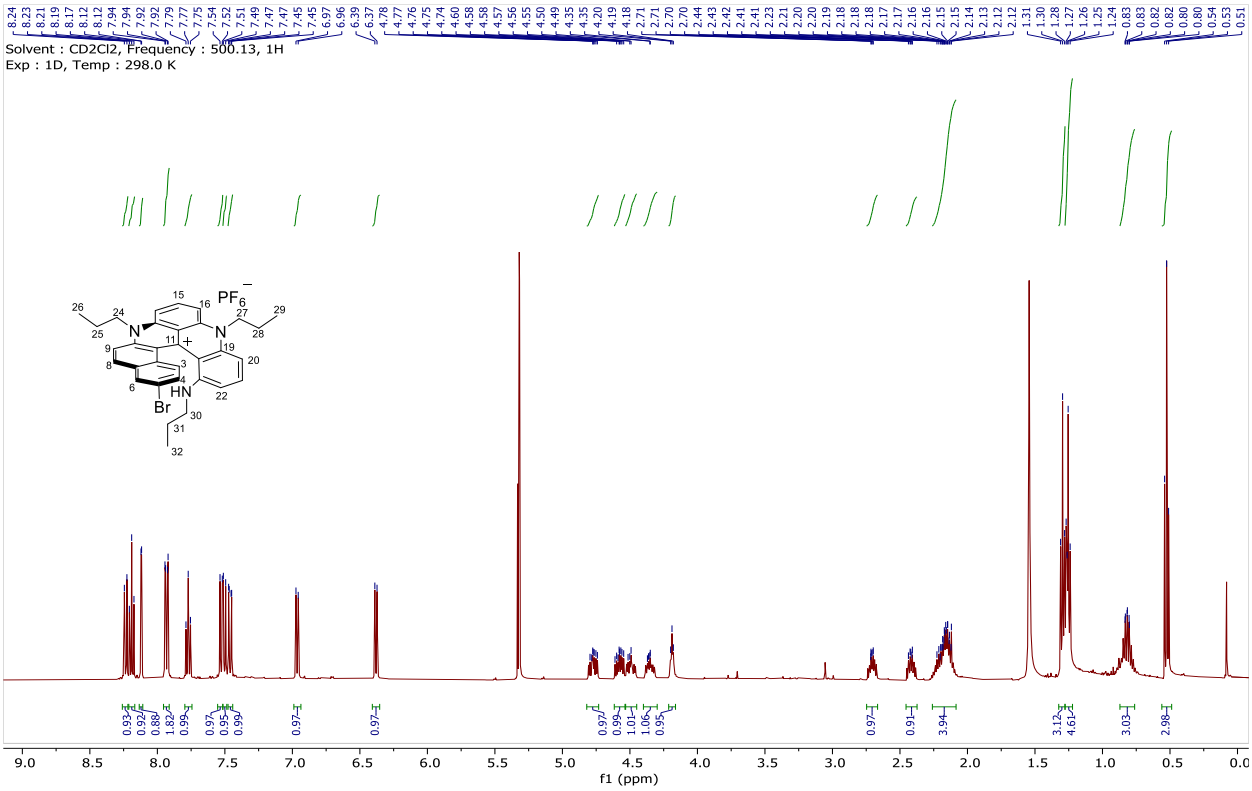
Submitter:	Maya MARINOVA	Date of reception:	15/12/14
Sample name:	MME3901	Date of certificate:	13/01/15
Sample number:	7602	Data filename:	MS03GE-150112-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR XL (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

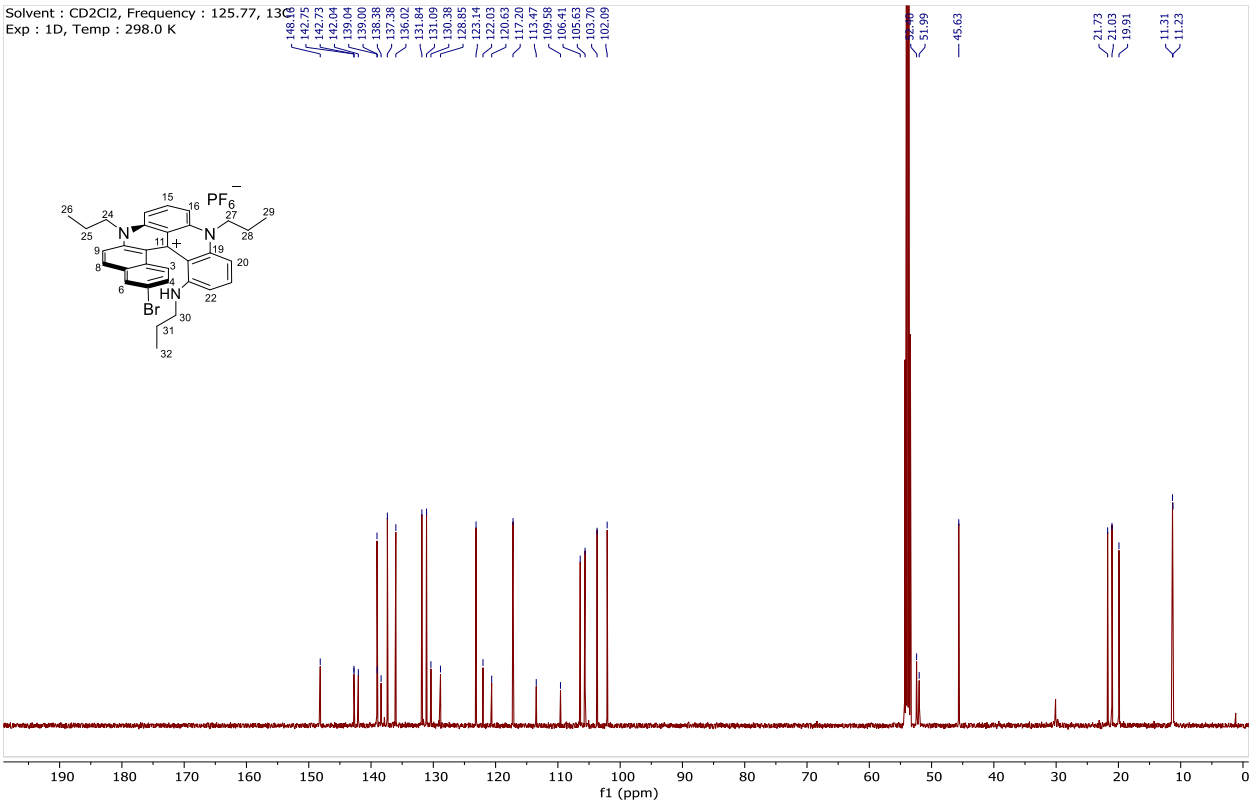
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{29}H_{26}BrN_2O$	497.1207	497.1223	-3.3

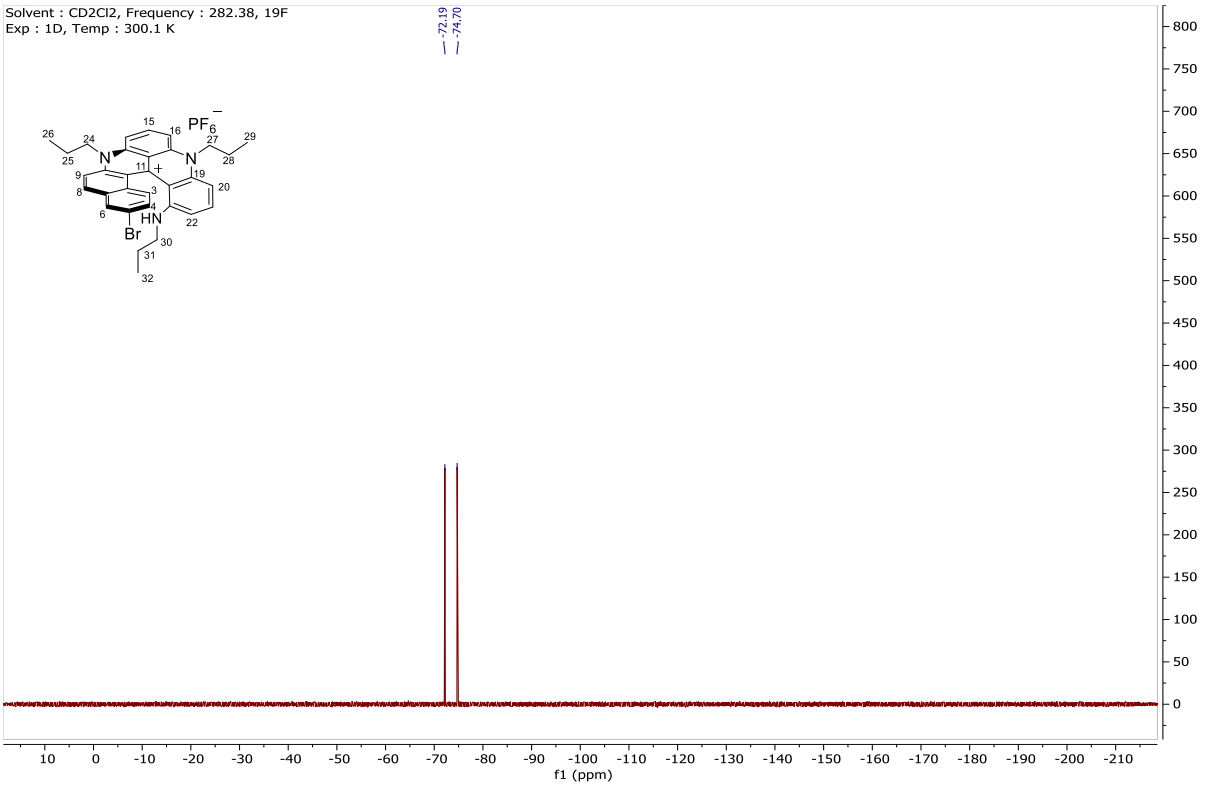


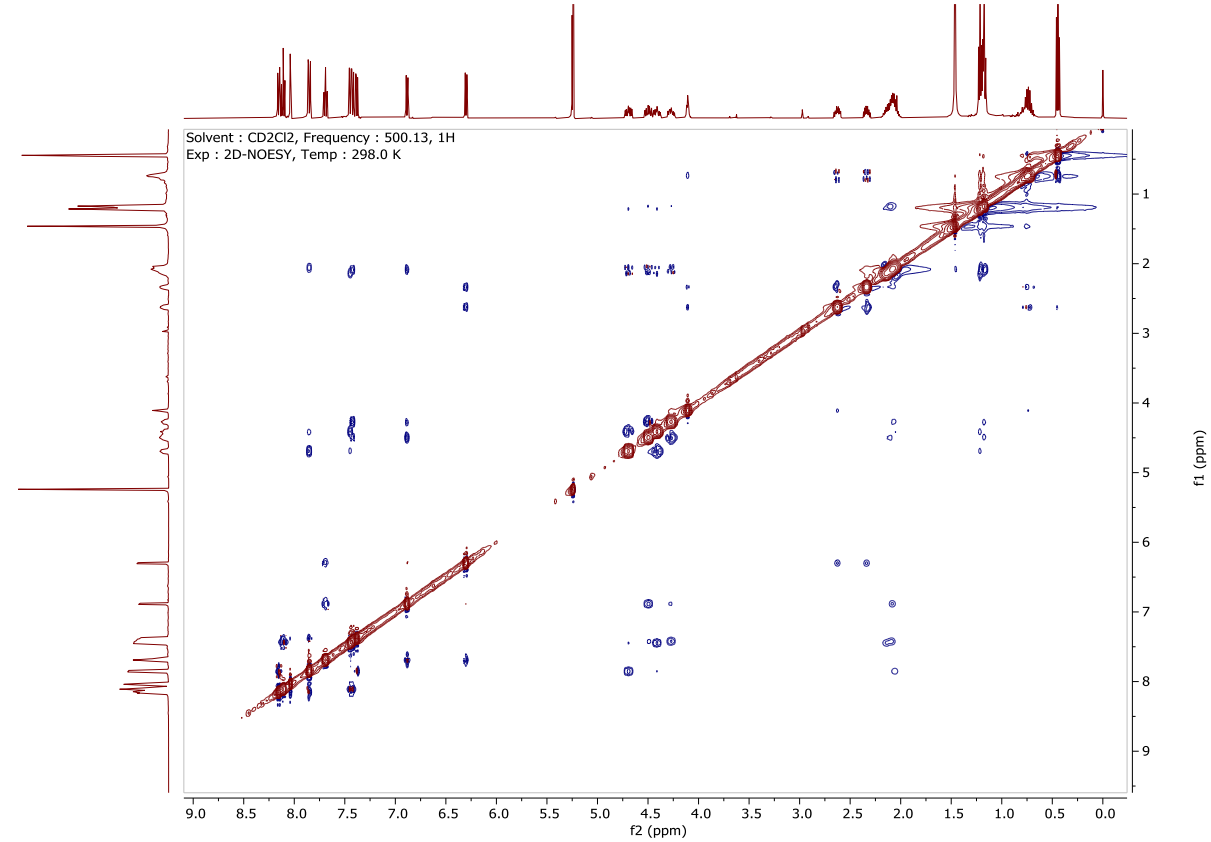


14-bromo-3,7-dipropyl-11-(propylamino)-3,7-dihydro-11b*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridin-11b-ylium tetrafluoroborate (18B)






Solvent : CD2Cl2, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.1 K
-72.19
-74.70
PF6
Br
HN
f1 (ppm)


Solvent : CD2Cl2, Frequency : 500.13, 1H
Exp : 2D-NOESY, Temp : 298.0 K
f2 (ppm)
f1 (ppm)

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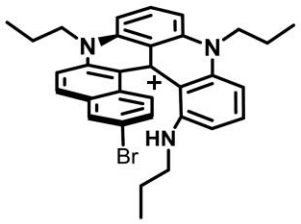
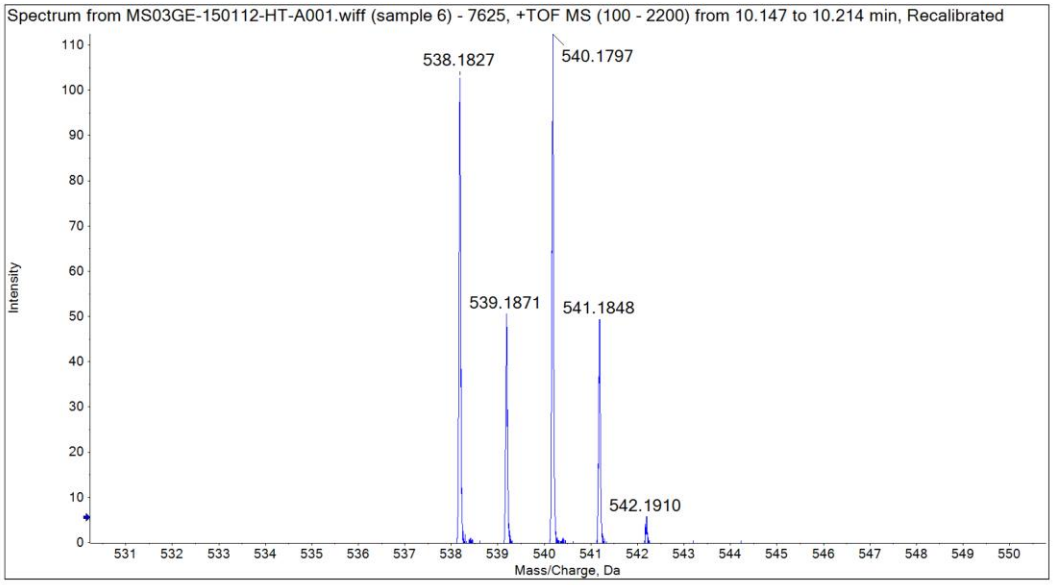
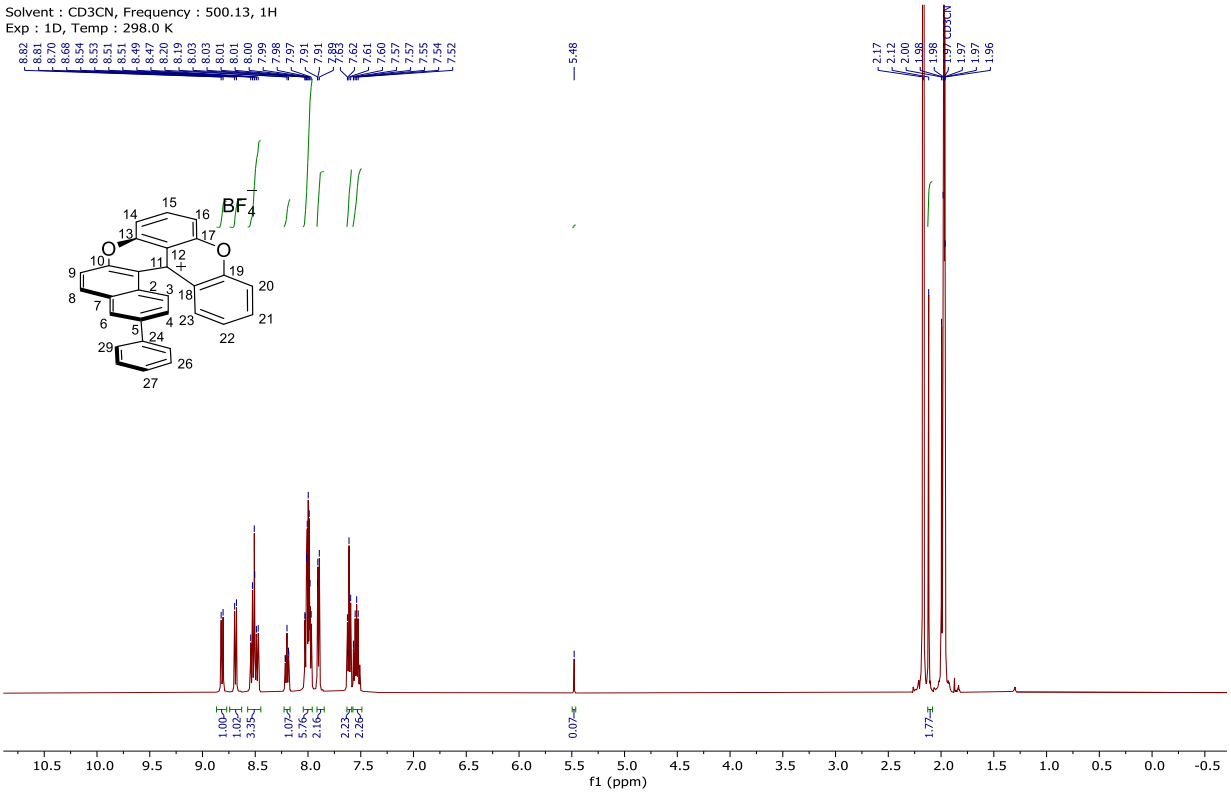
Submitter:	Maya MARINOVA	Date of reception:	05/01/15
Sample name:	MME2009	Date of certificate:	13/01/15
Sample number:	7625	Data filename:	MS03GE-150112-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR XL (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

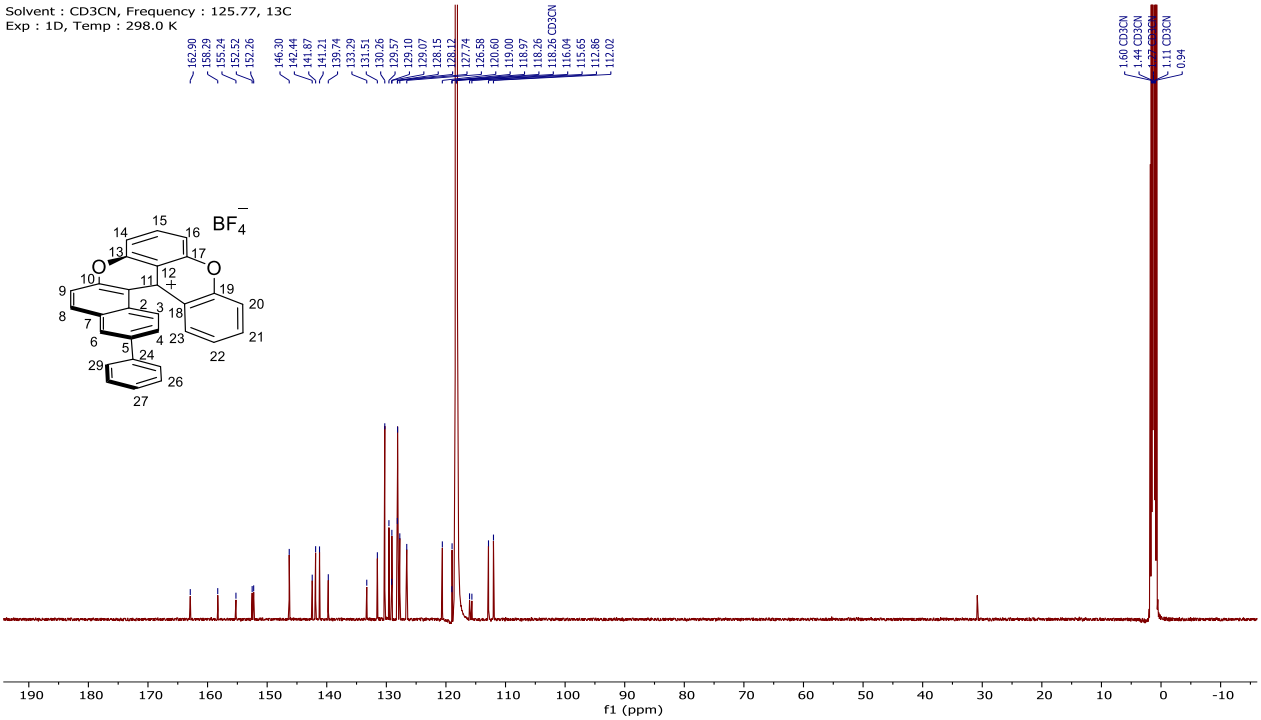
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{32}H_{33}BrN_3$	538.1827	538.1852	-4.7



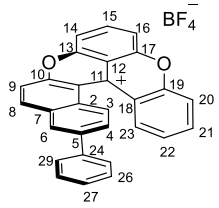


14-Phenyl-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (20a)





Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K



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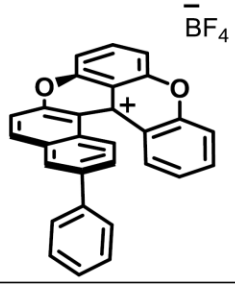
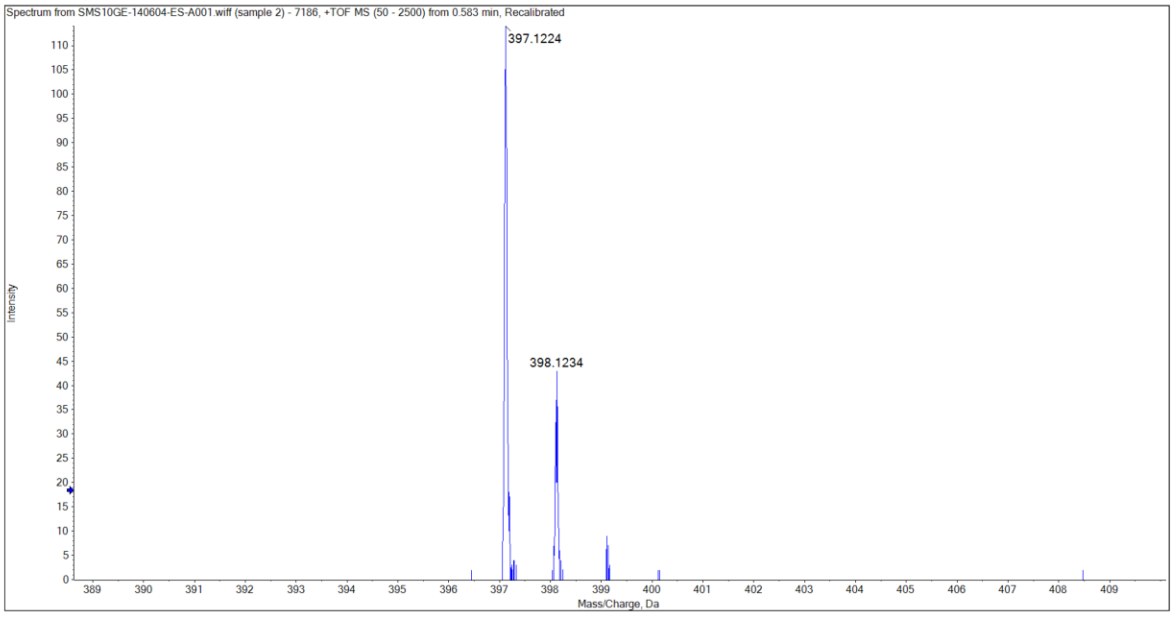
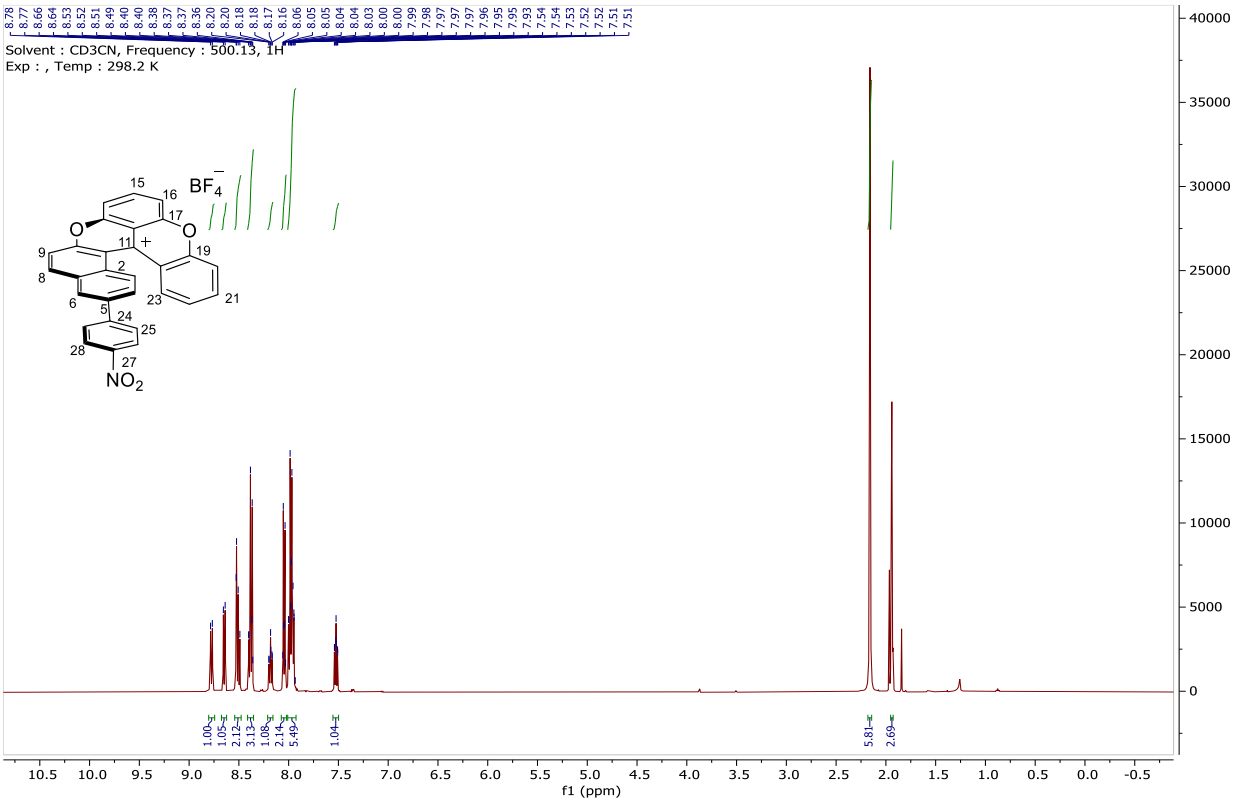
Submitter:	MARINOVA	Date of reception:	03/06/14
Sample name:	MMD4808	Date of certificate:	04/06/14
Sample number:	7186	Data filename:	SMS10GE-140604-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

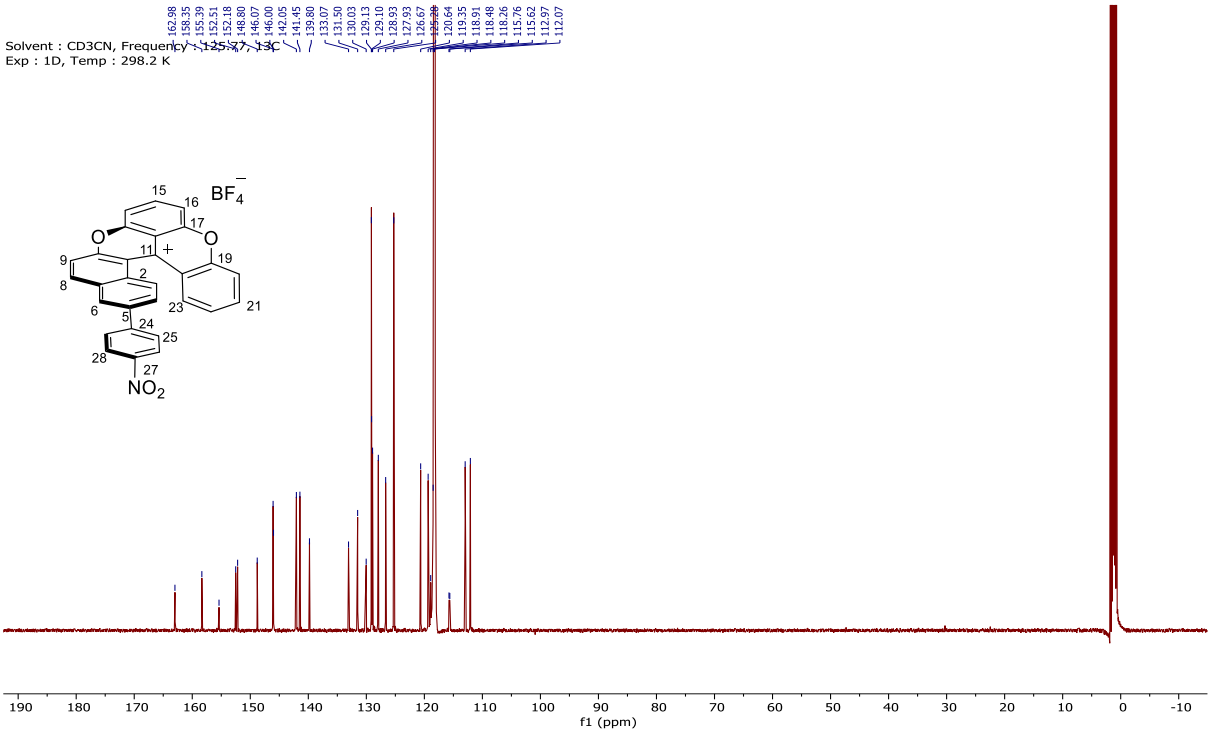
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{29}H_{17}O_2$	397.1224	397.1223	0.1





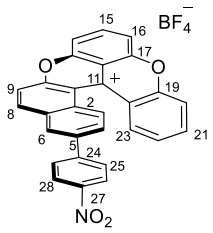
14-(4-Nitrophenyl)-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (20b)

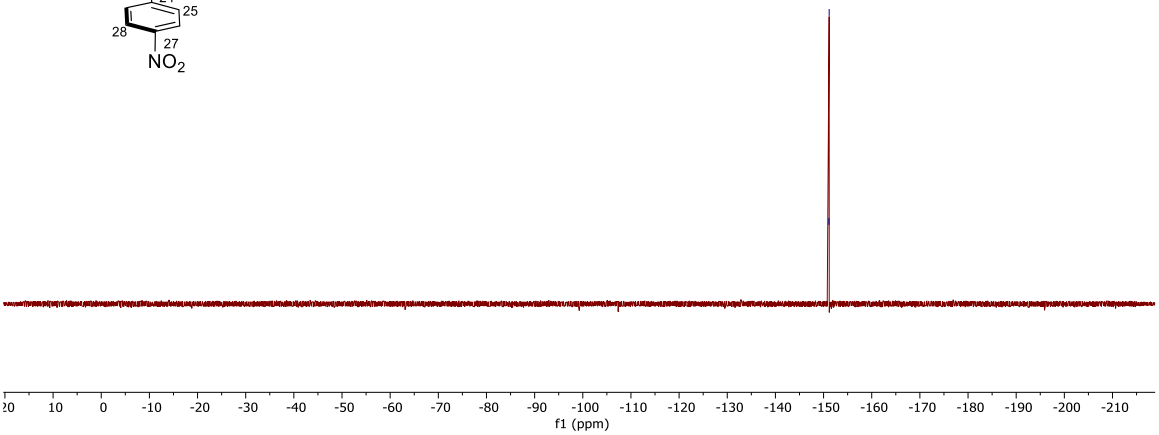




Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K

-151.11
-151.16





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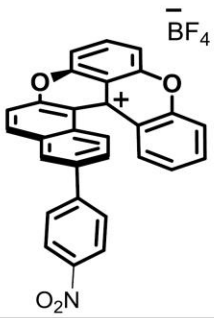
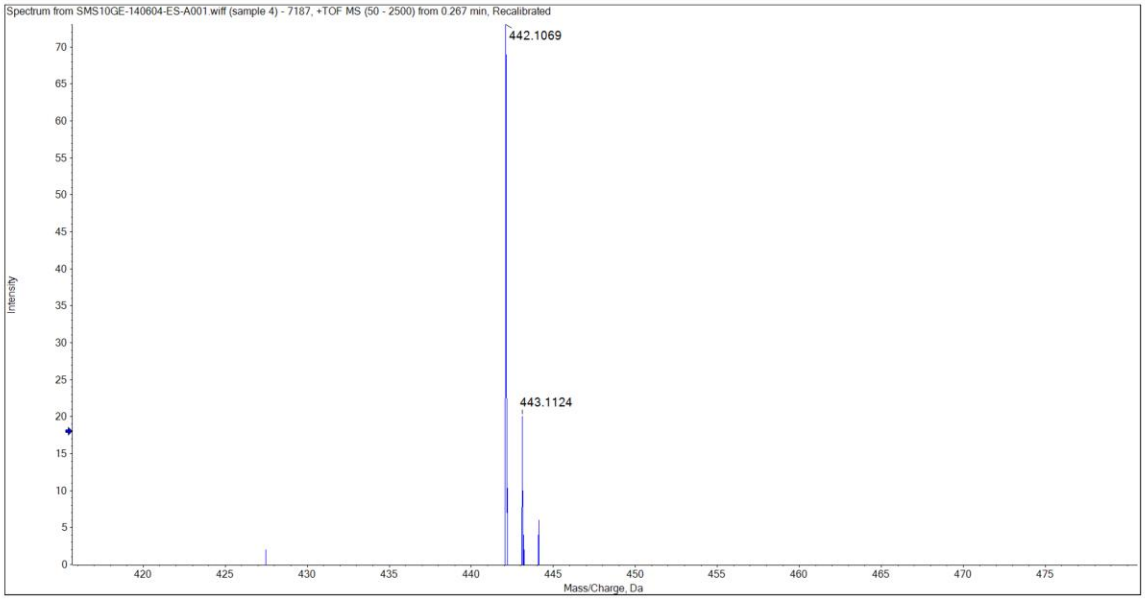
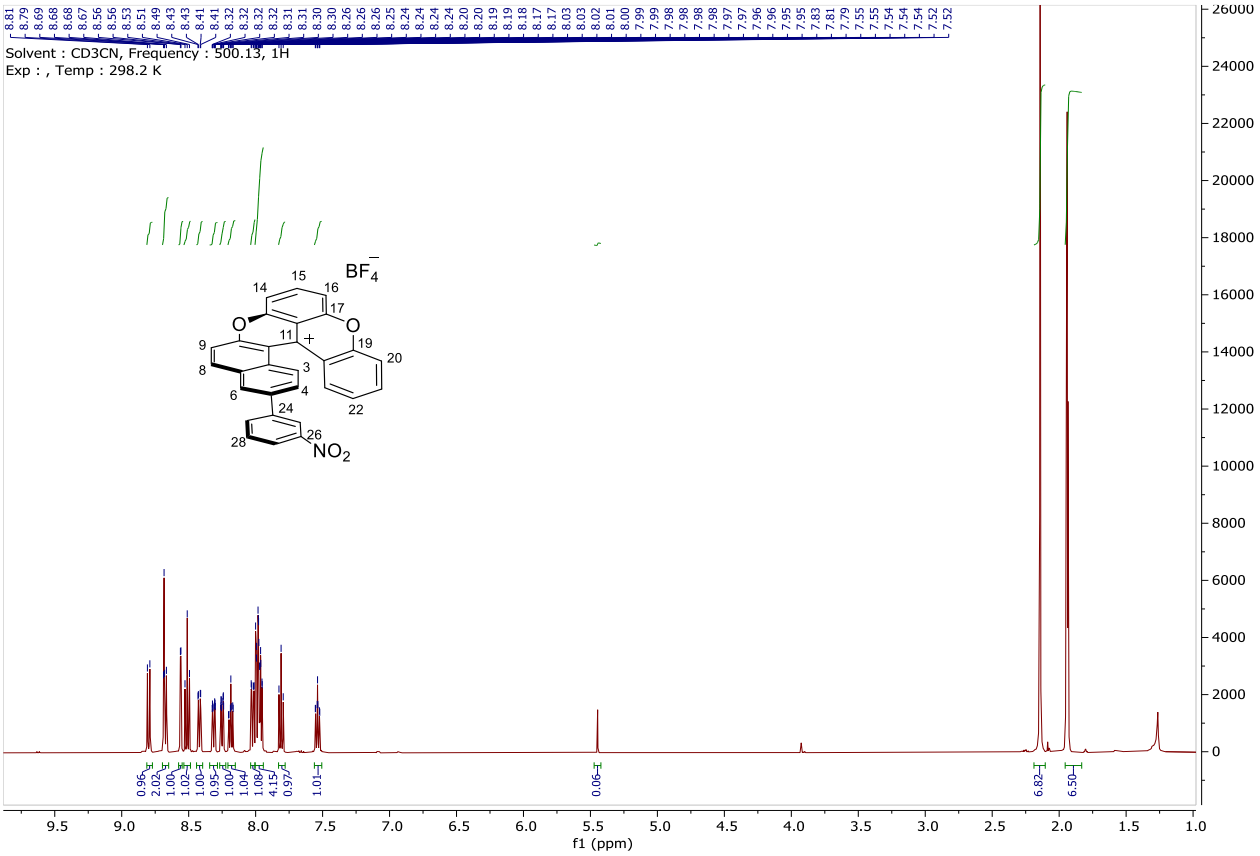
Submitter:	MARINOVA	Date of reception:	03/06/14
Sample name:	MMD5805	Date of certificate:	04/06/14
Sample number:	7187	Data filename:	SMS10GE-140604-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

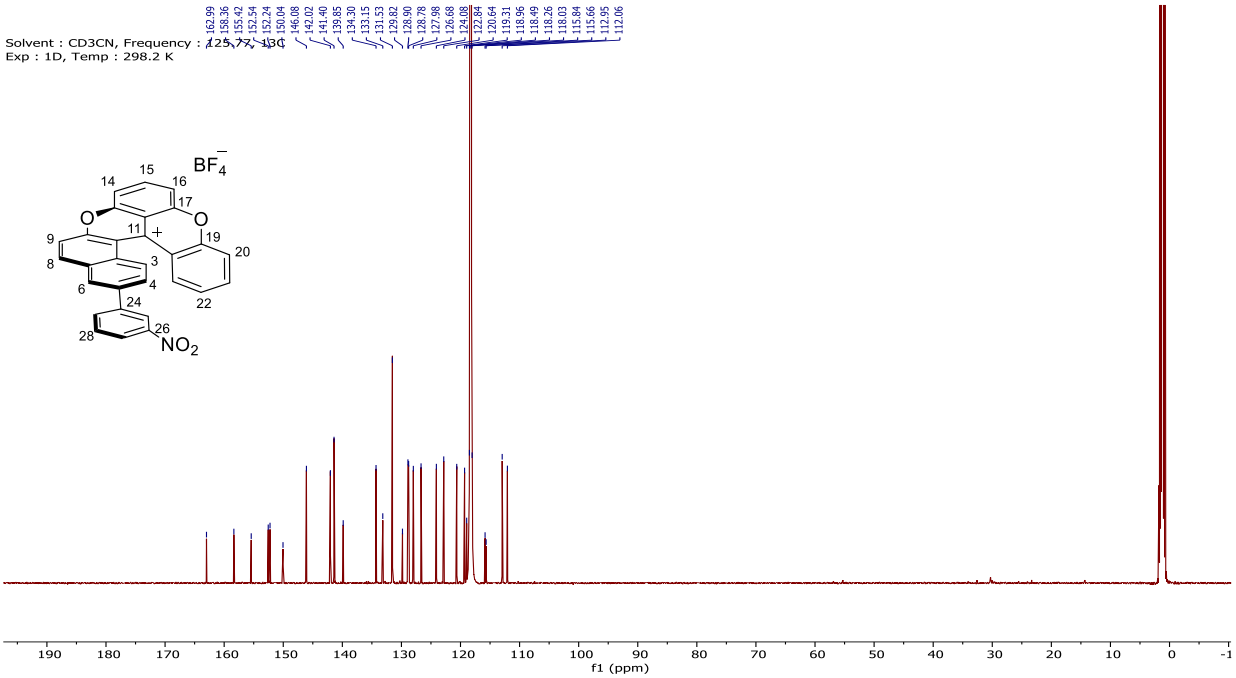
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{29}H_{16}NO_4$	442.1069	442.1074	-1.0





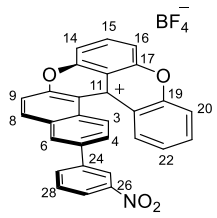
14-(3-Nitrophenyl)-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (20c)

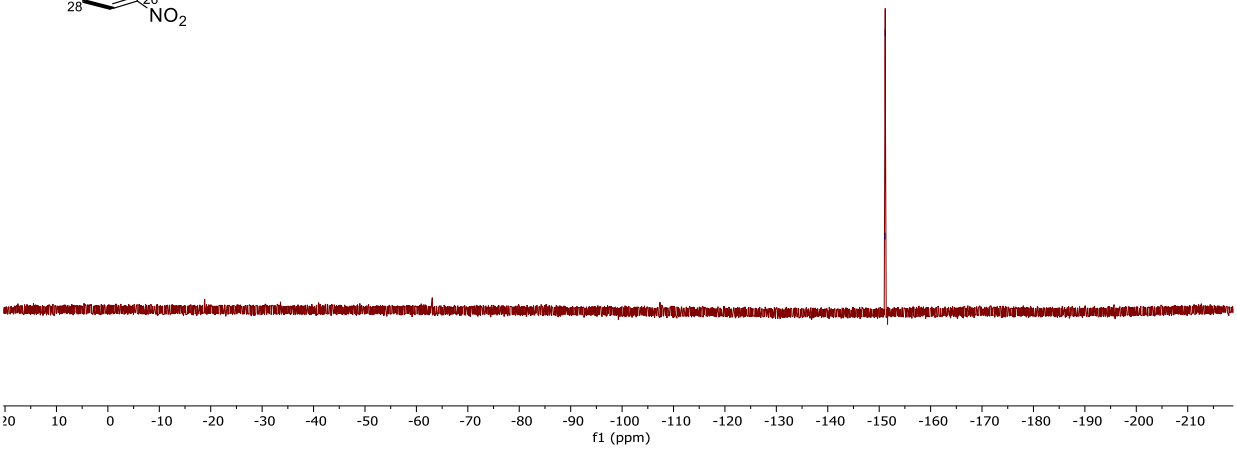




Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K

-151.12
-151.17





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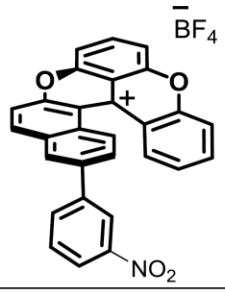
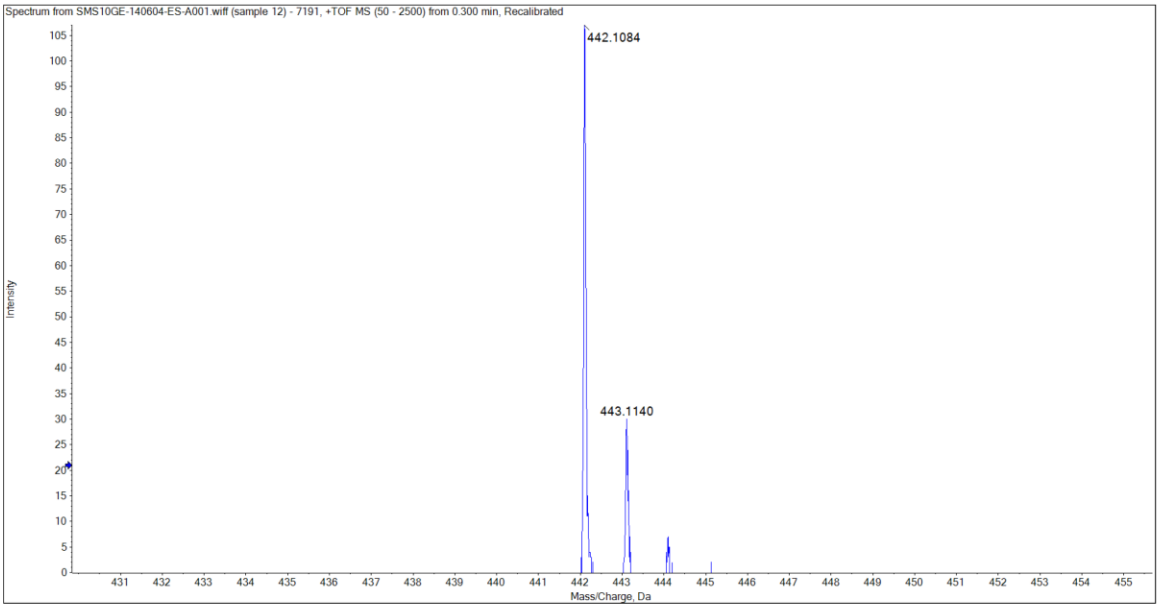
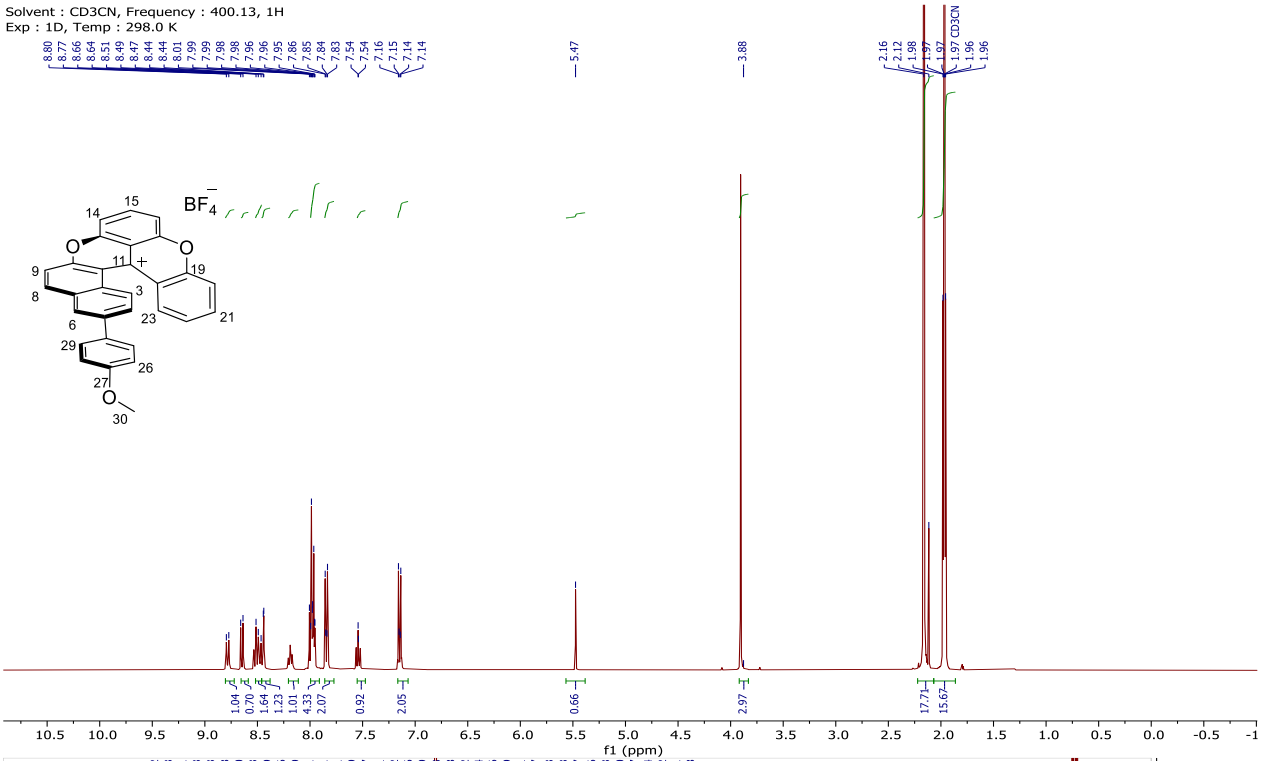
Submitter:	MARINOVA	Date of reception:	03/06/14
Sample name:	MMD69	Date of certificate:	04/06/14
Sample number:	7191	Data filename:	SMS10GE-140604-ES-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

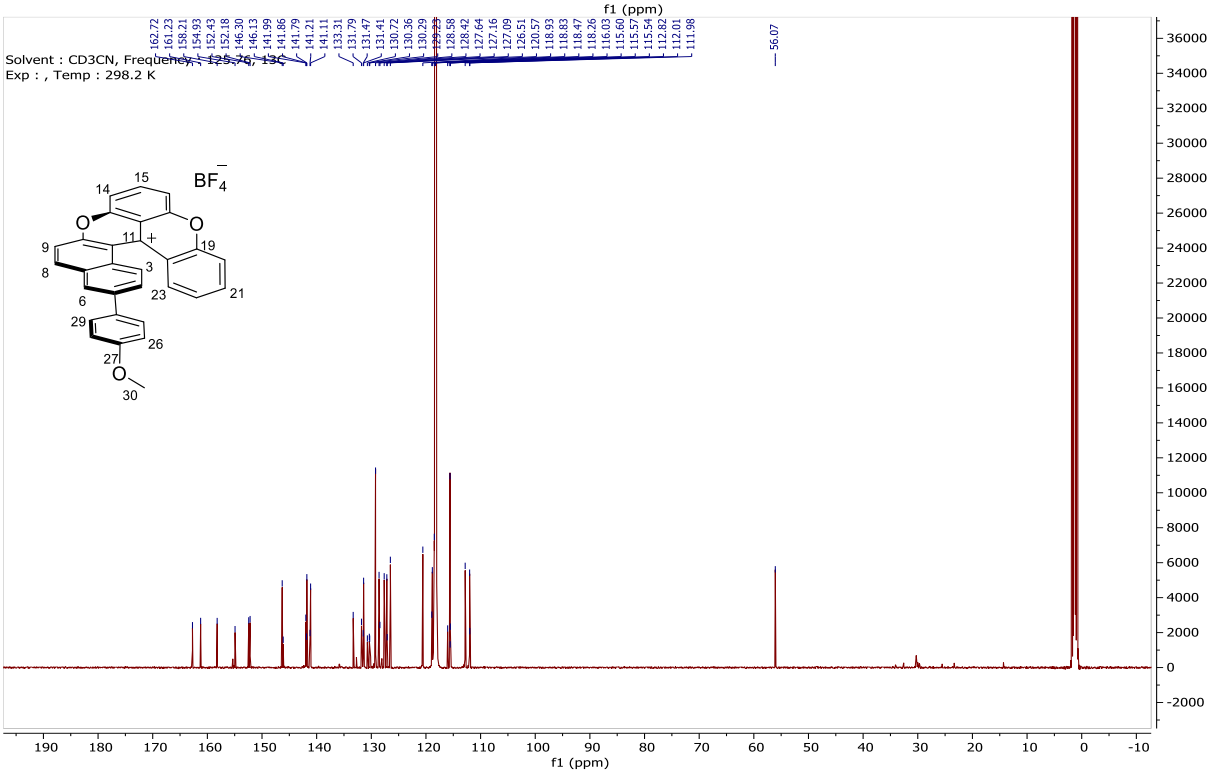
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{29}H_{16}NO_4$	442.1084	442.1074	2.2



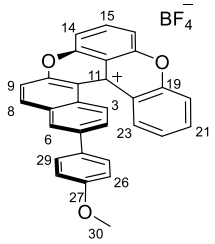


14-(4-Methoxyphenyl)-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (20d)





Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K



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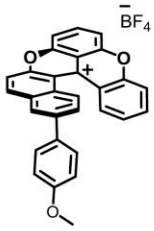
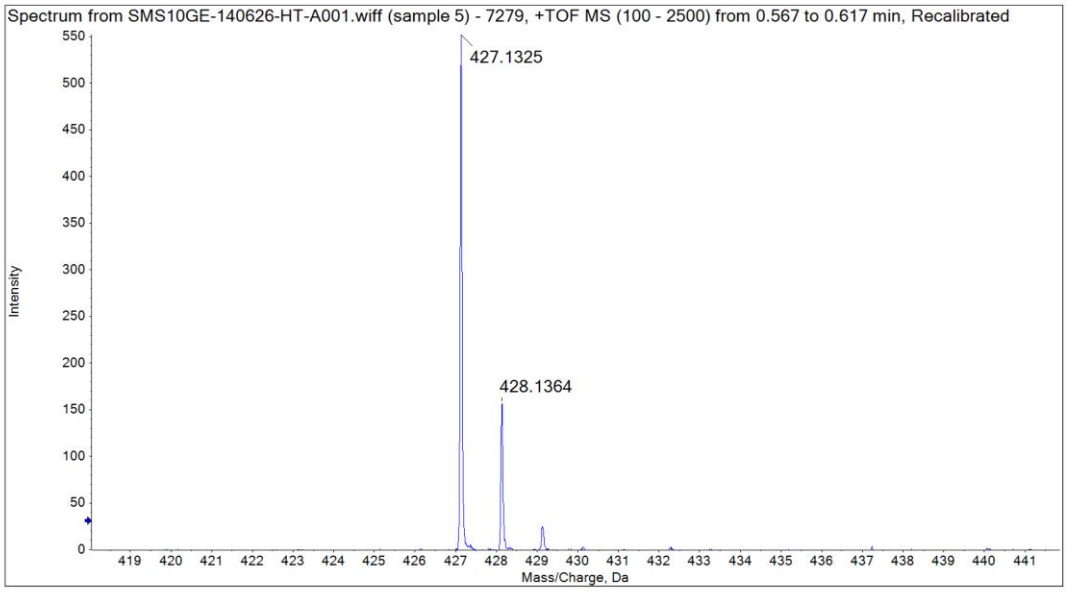
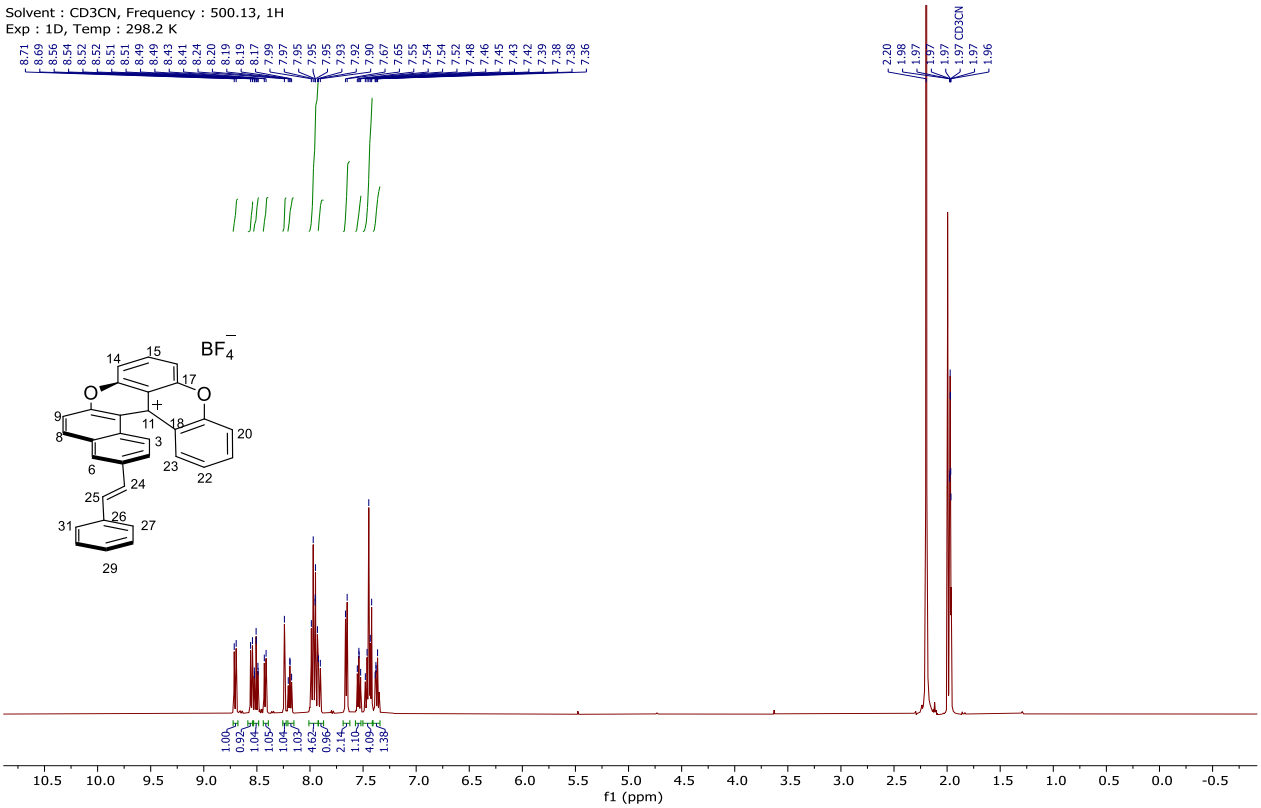
Submitter:	MARINOVA	Date of reception:	25/06/14
Sample name:	MMD8702	Date of certificate:	30/06/14
Sample number:	7279	Data filename:	SMS10GE-140626-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

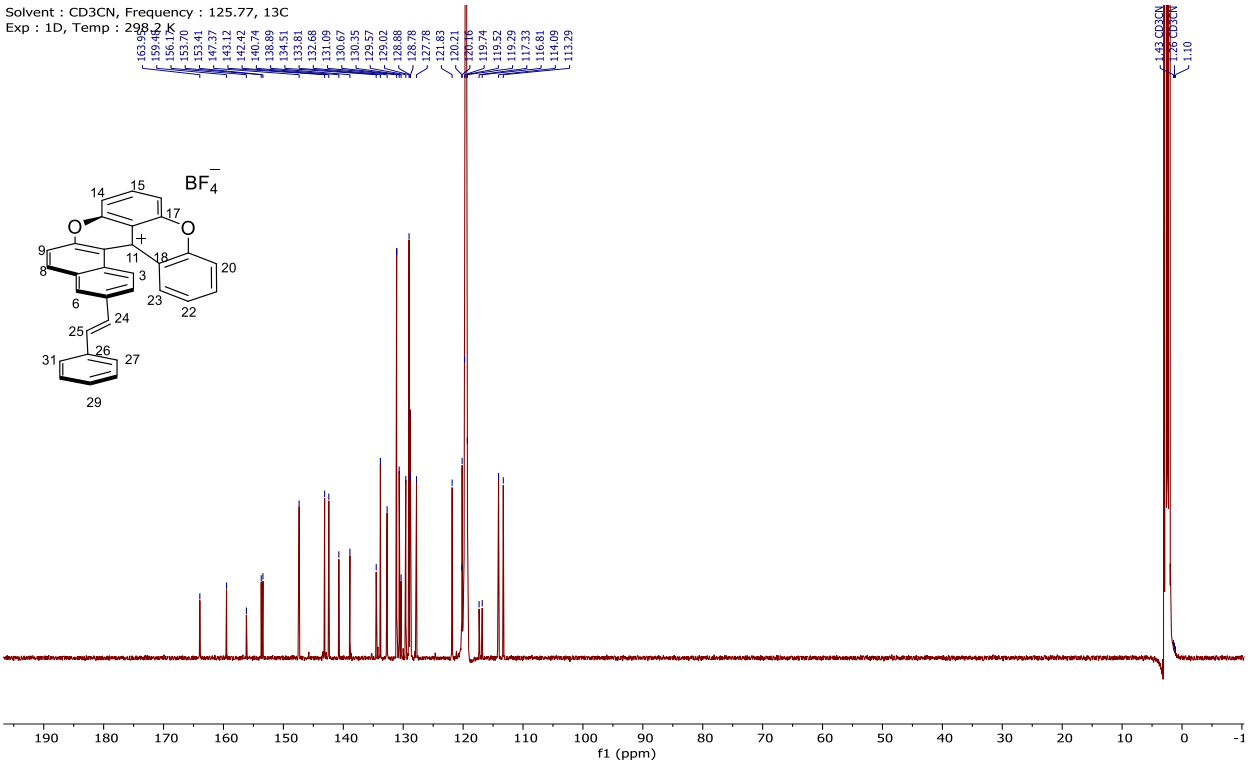
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{30}H_{19}O_3$	427.1325	427.1329	-1.0



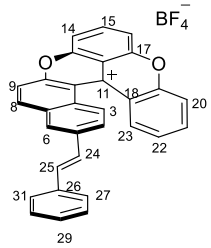


(*E*)-14-styryl-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (21a)





Solvent : C6D6, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K



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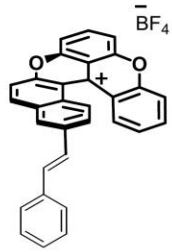
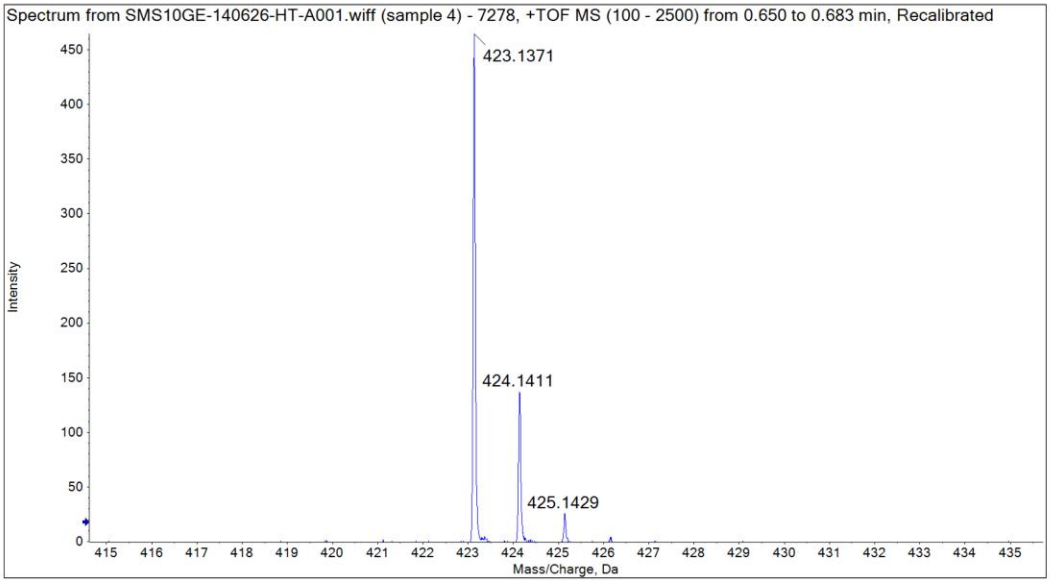
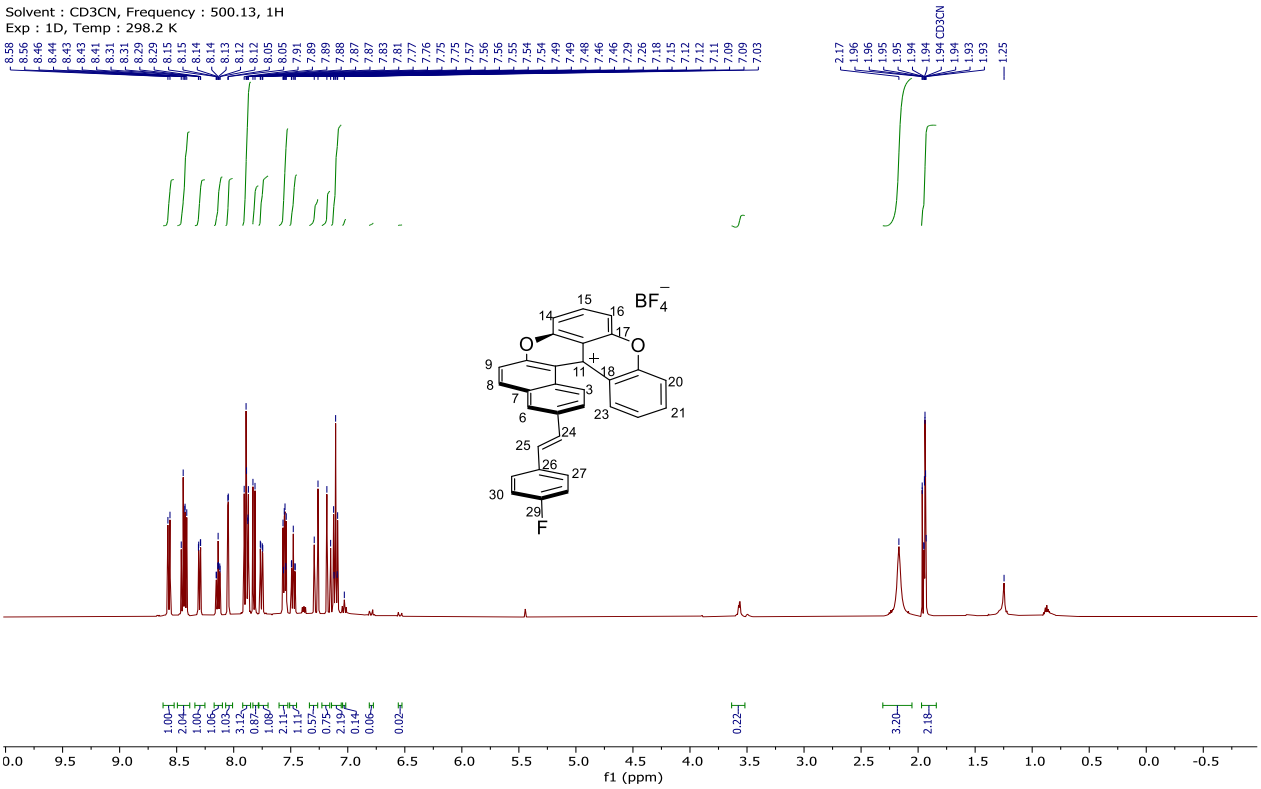
Submitter:	MARINOVA	Date of reception:	25/06/14
Sample name:	MMD7903	Date of certificate:	30/06/14
Sample number:	7278	Data filename:	SMS10GE-140626-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

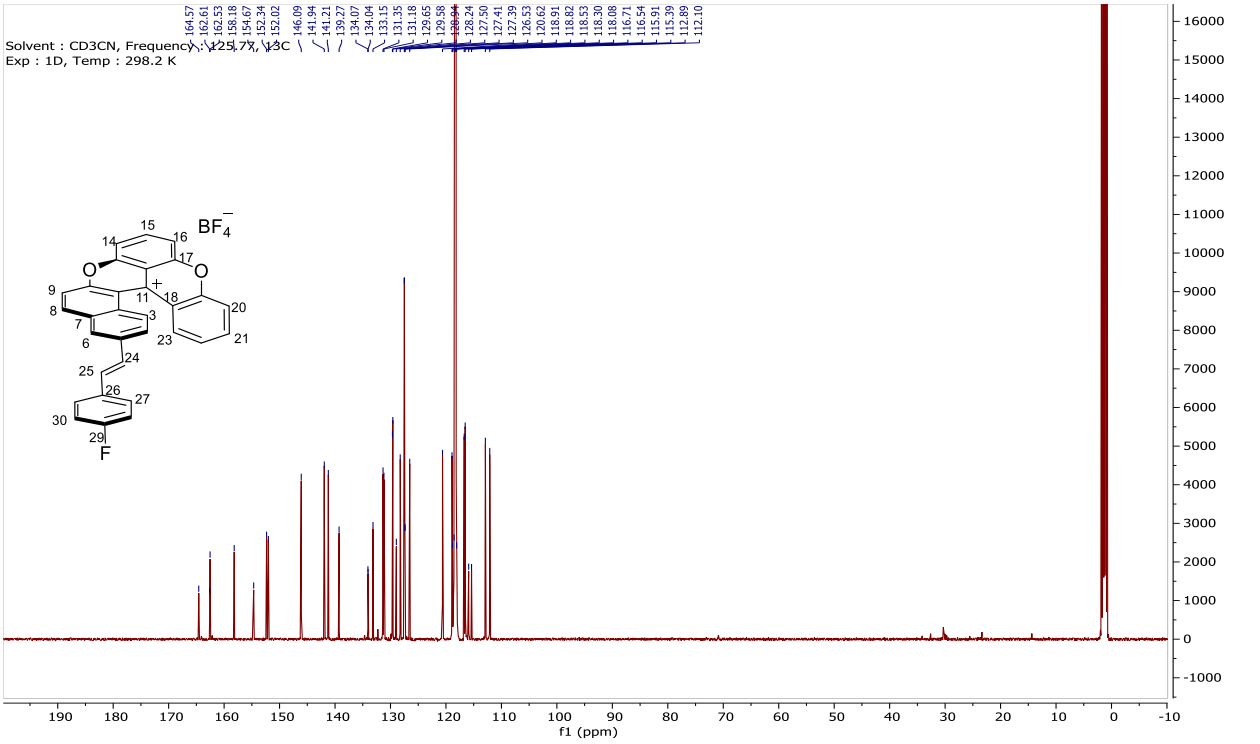
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{31}H_{19}O_2$	423.1371	423.1380	-2.1



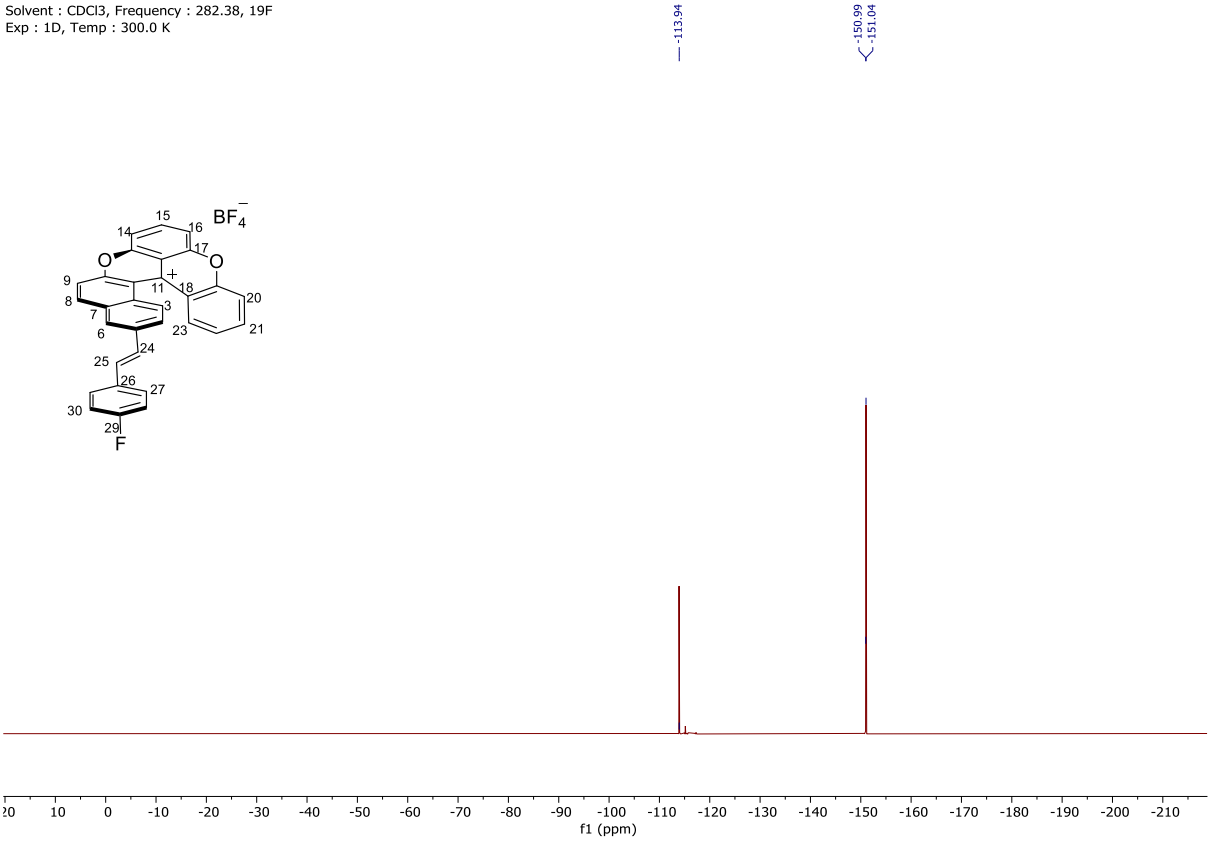


(*E*)-14-(4-fluorostyryl)-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (21b)





Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K



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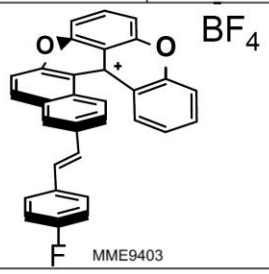
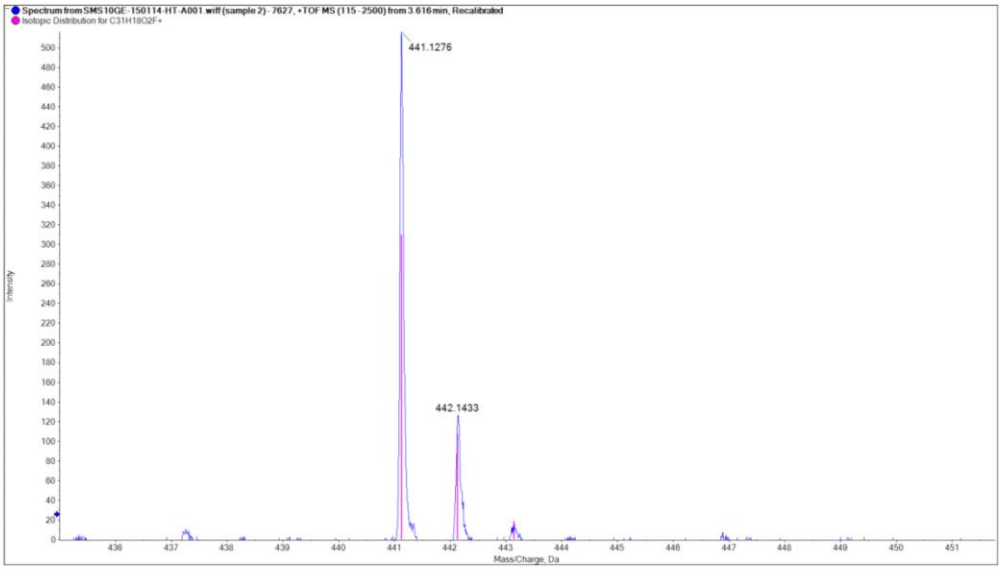
Submitter:	MARINOVA	Date of reception:	05/01/15
Sample name:	MME9403	Date of certificate:	16/01/15
Sample number:	7627	Data filename:	SMS10GE-150114-HT-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

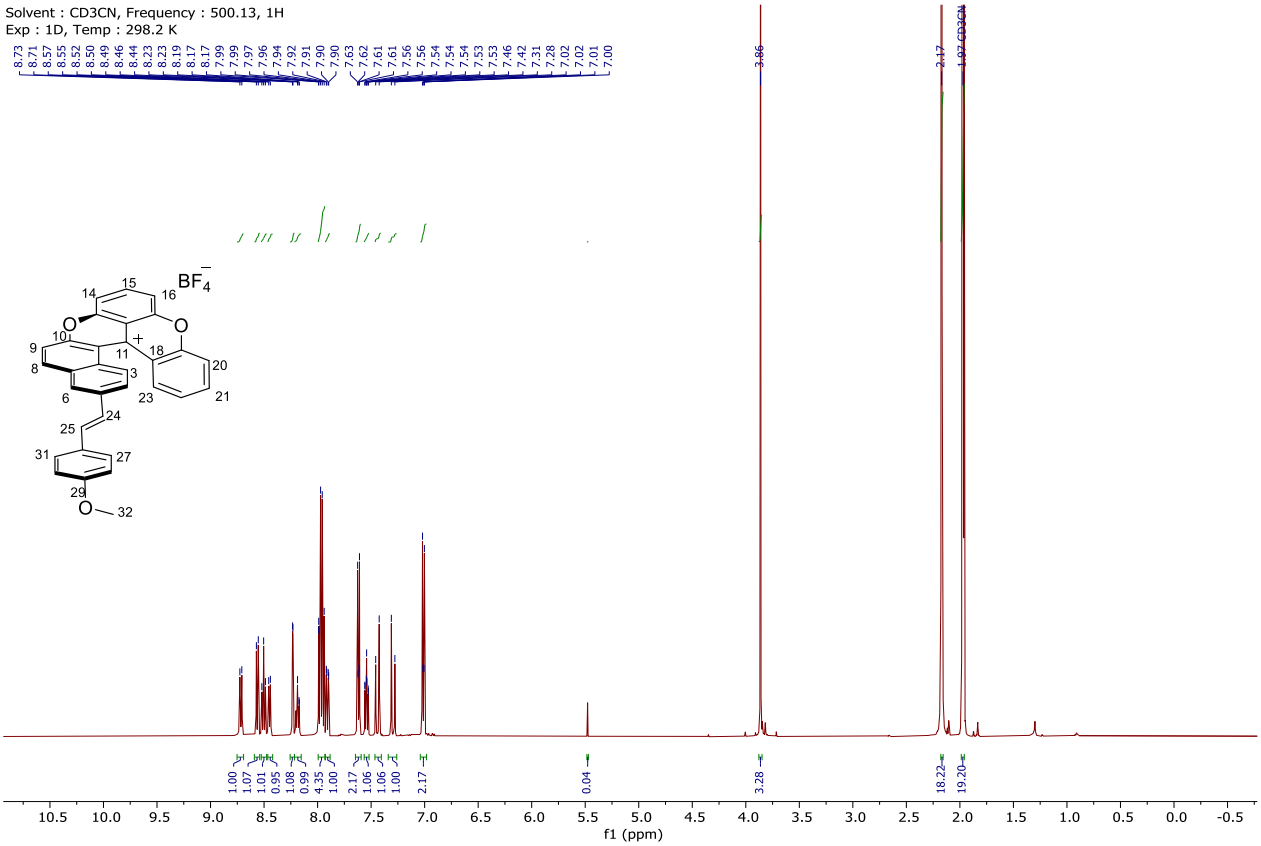
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{31}H_{18}O_2F$	441.1276	441.1285	-2.1

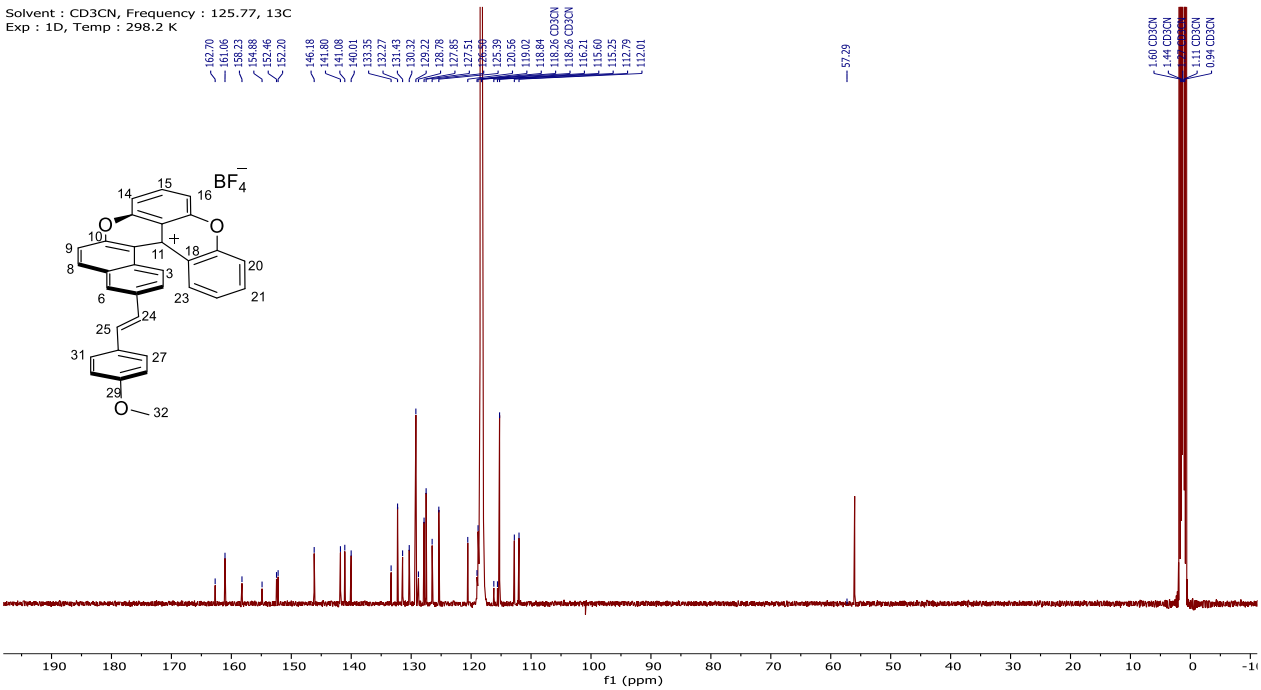


MME9403

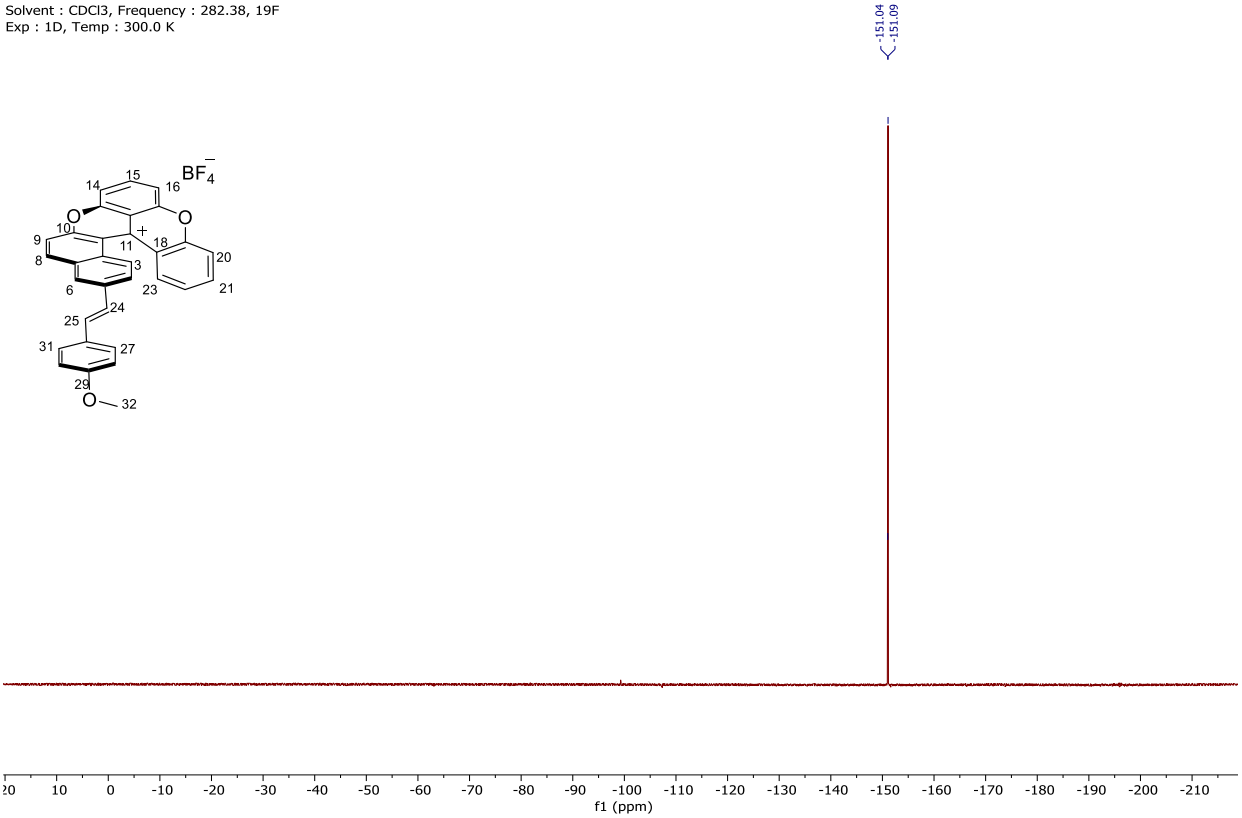


(*E*)-14-(4-methoxystyryl)-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthen-11b-ylium tetrafluoroborate (21c)





Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K



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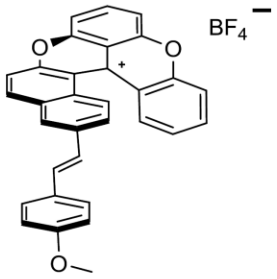
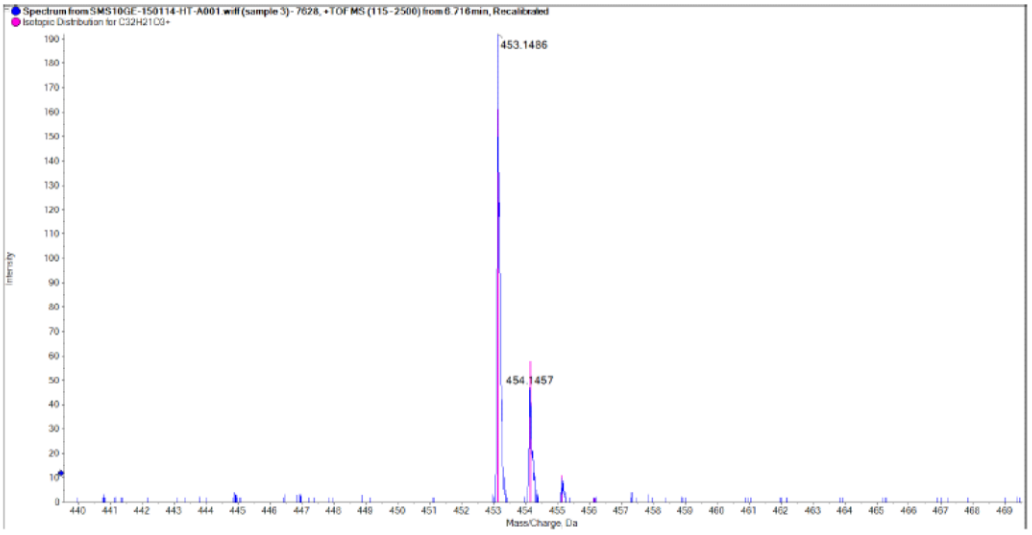
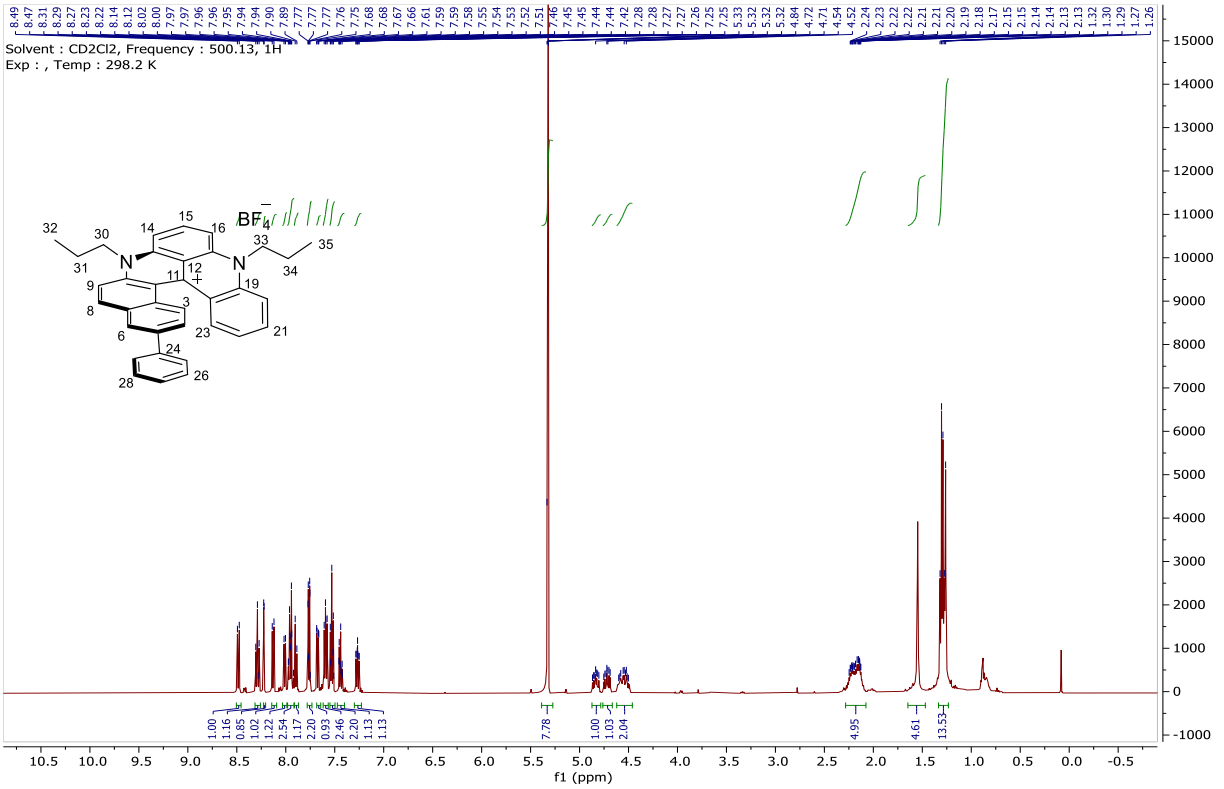
Submitter:	MARINOVA	Date of reception:	05/01/15
Sample name:	MME9305	Date of certificate:	16/01/15
Sample number:	7628	Data filename:	SMS10GE-150114-HT-A001
Operator:	Eliane Sandmeier	Instrument:	QSTAR Pulsar (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

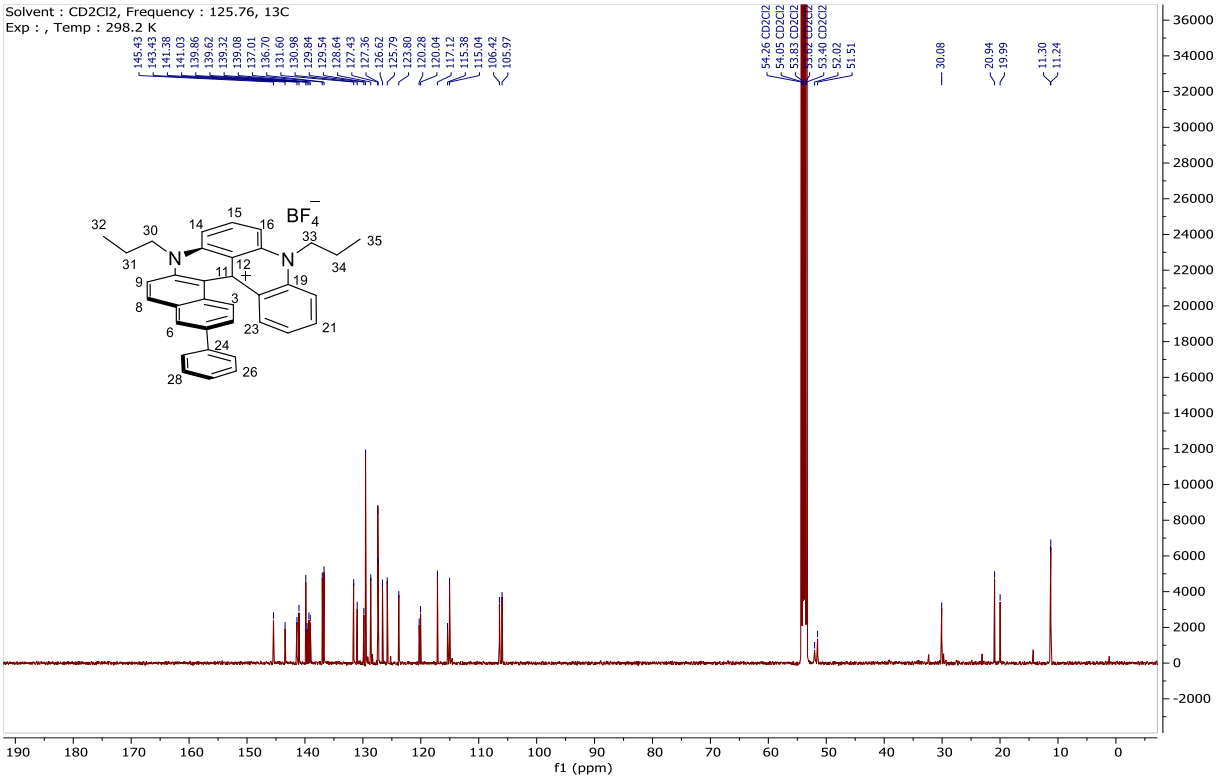
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{32}H_{21}O_3$	453.1486	453.1485	0.1

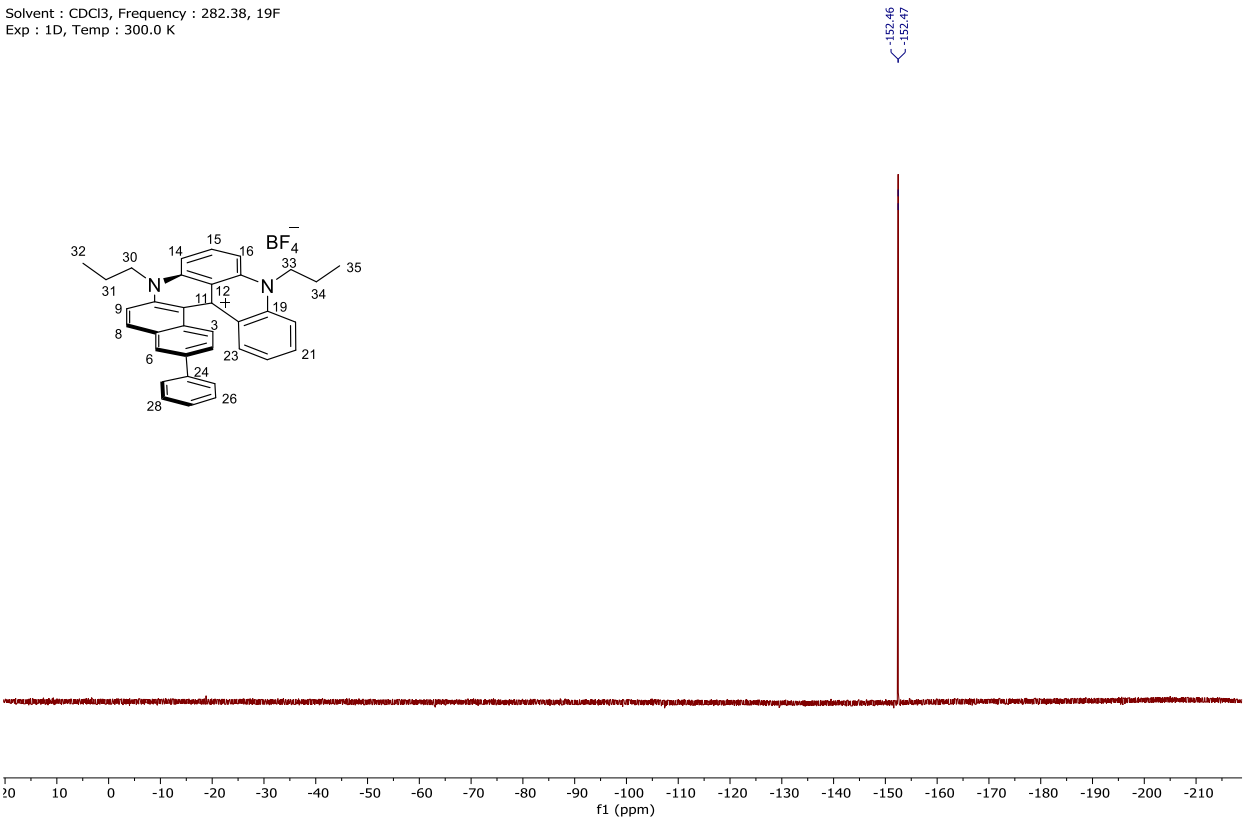


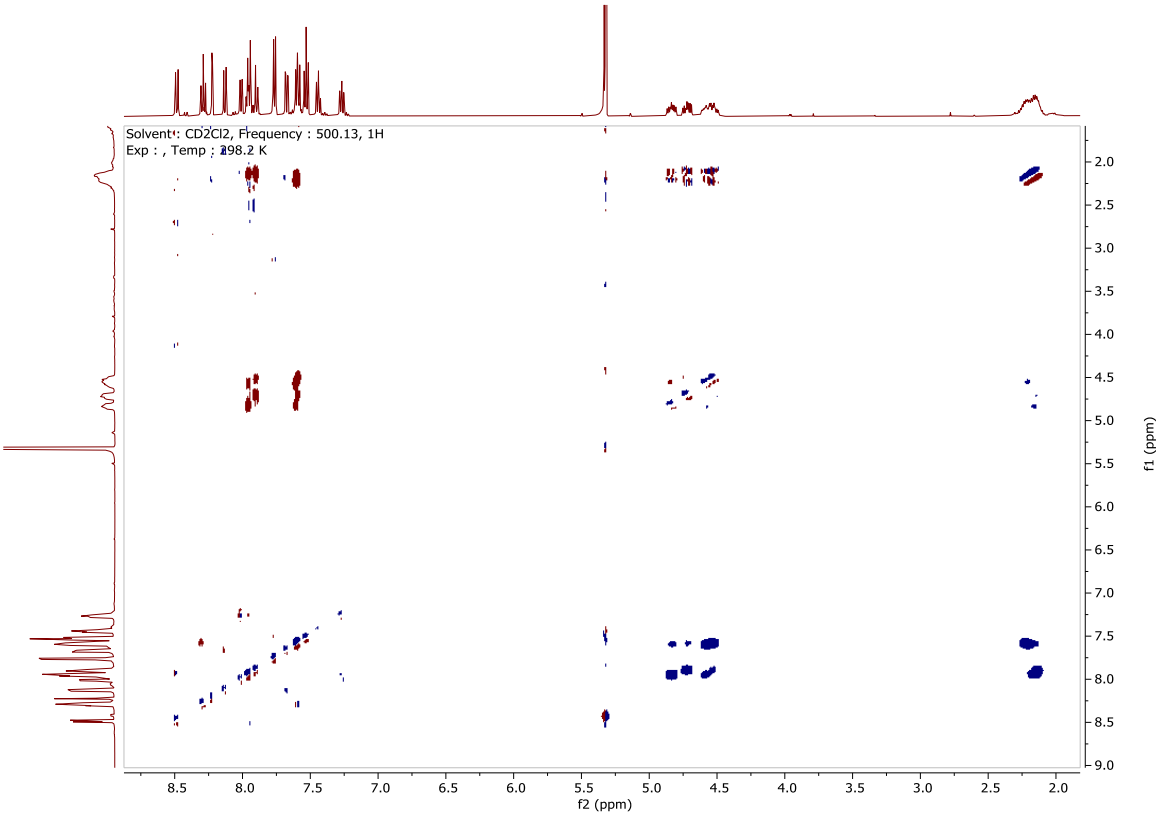


14-Phenyl-3,7-dipropyl-3,7-dihydro-11b*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridin-11b-ylium tetrafluoroborate (22a)






Solvent : CDCl3, Frequency : 282.38, 19F
Exp : 1D, Temp : 300.0 K
-152.46
-152.47
BF4
f1 (ppm)


Solvent: CD2Cl2, Frequency : 500.13, 1H
Exp : , Temp : 298.2 K
f2 (ppm)
f1 (ppm)

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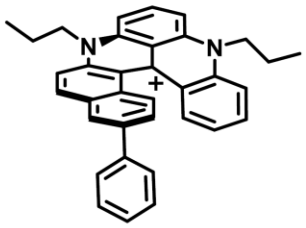
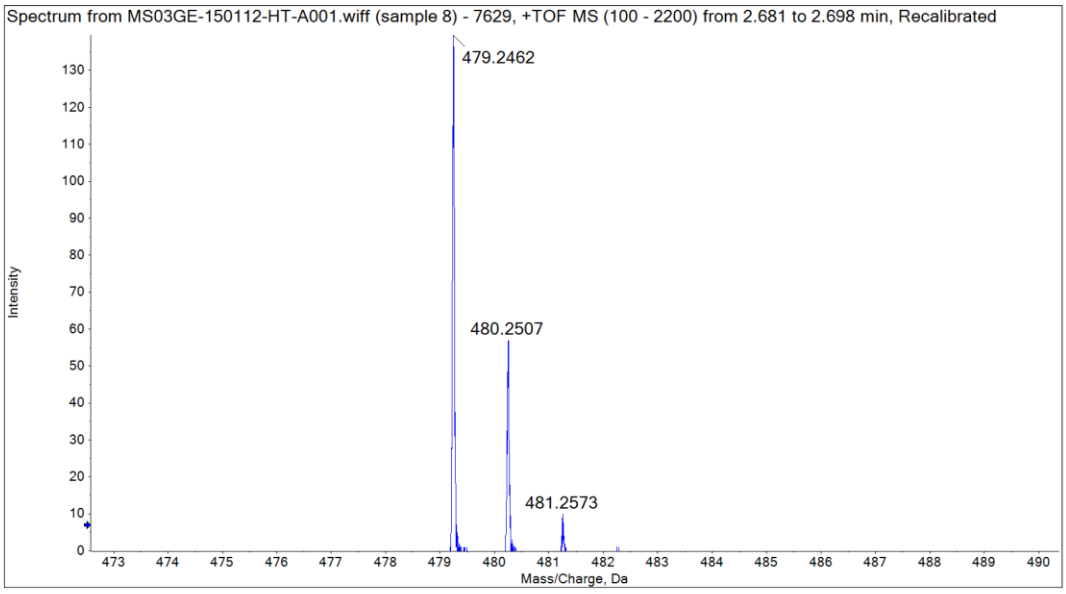
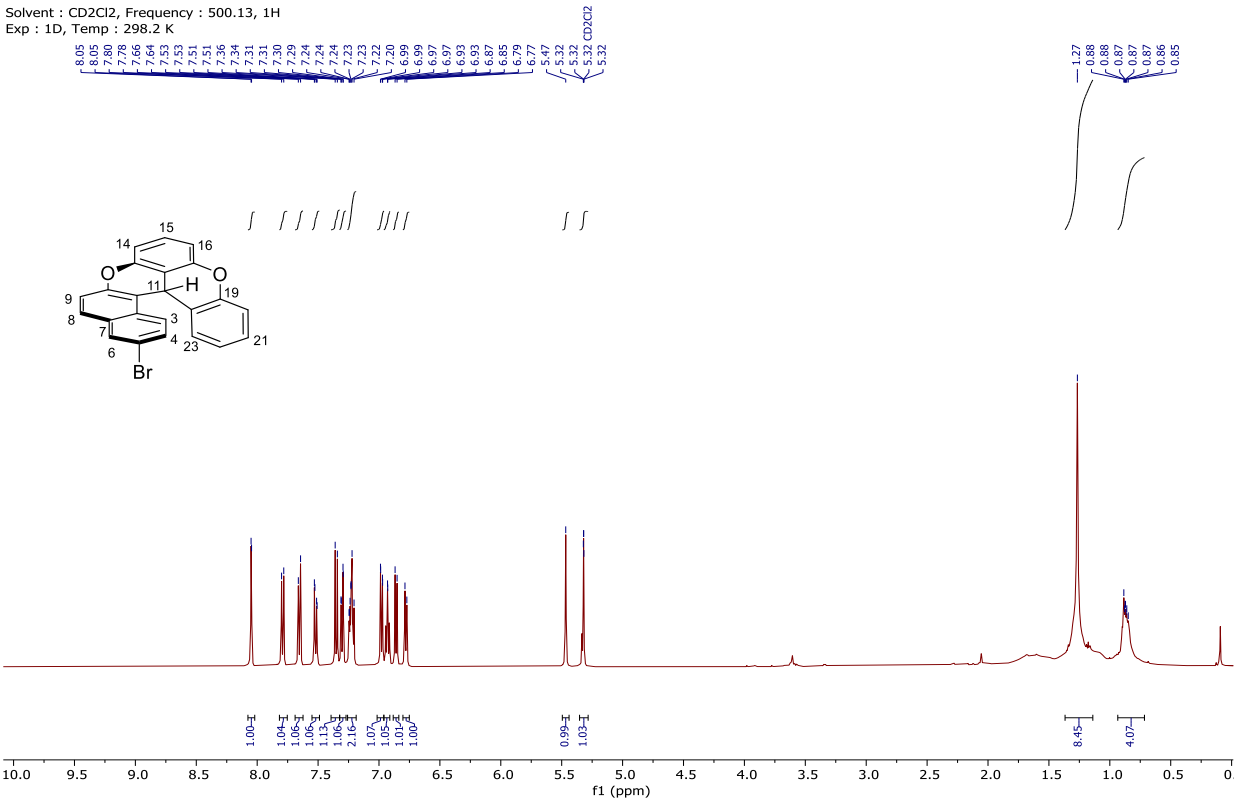
Submitter:	Maya MARINOVA	Date of reception:	05/01/15
Sample name:	MME2605	Date of certificate:	13/01/15
Sample number:	7629	Data filename:	MS03GE-150112-HT-A001
Operator:	Harry Théraulaz	Instrument:	QSTAR XL (AB/MDS Sciex)
Principal investigator:	Dr. Sophie Michalet	Ionisation mode:	ESI (positive mode)

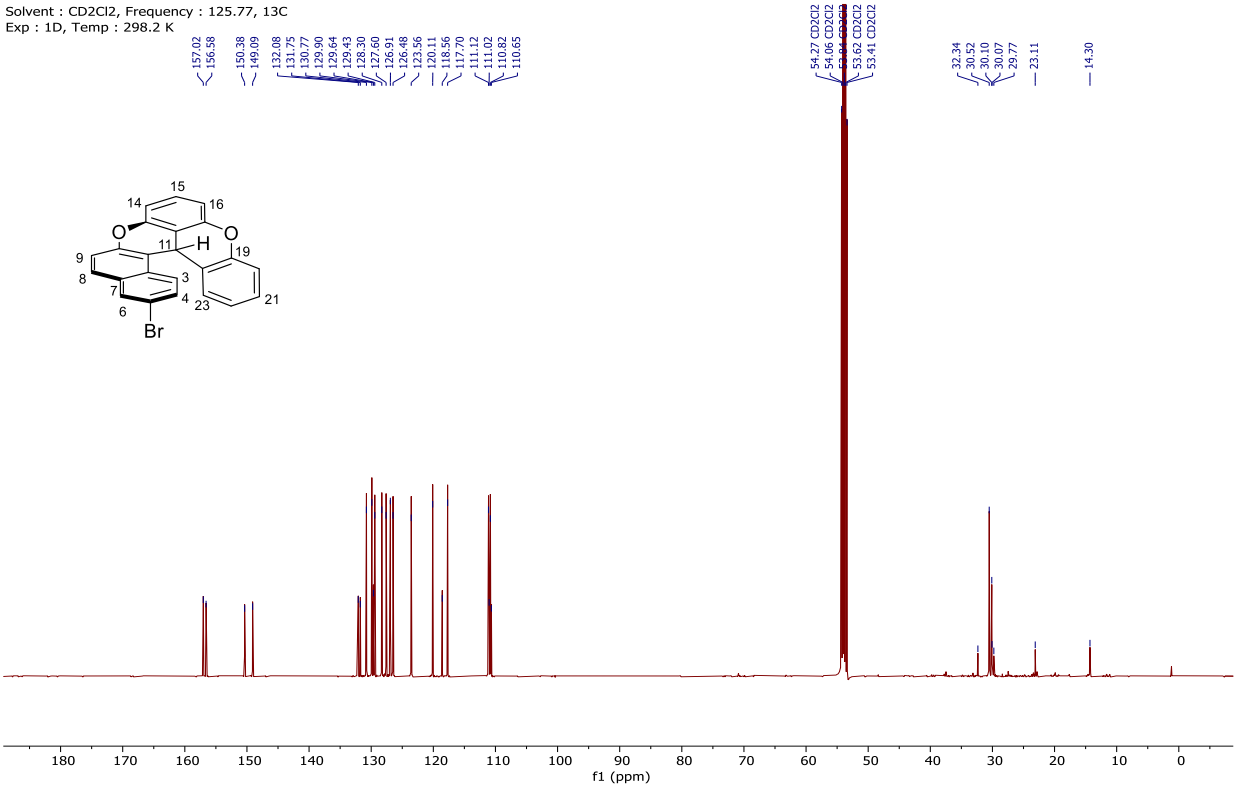
Expected Formula	Observed *m/z* $[M]^+$	Expected *m/z* (amu)	Accuracy (ppm)
$C_{35}H_{31}N_2$	479.2462	479.2482	-4.1

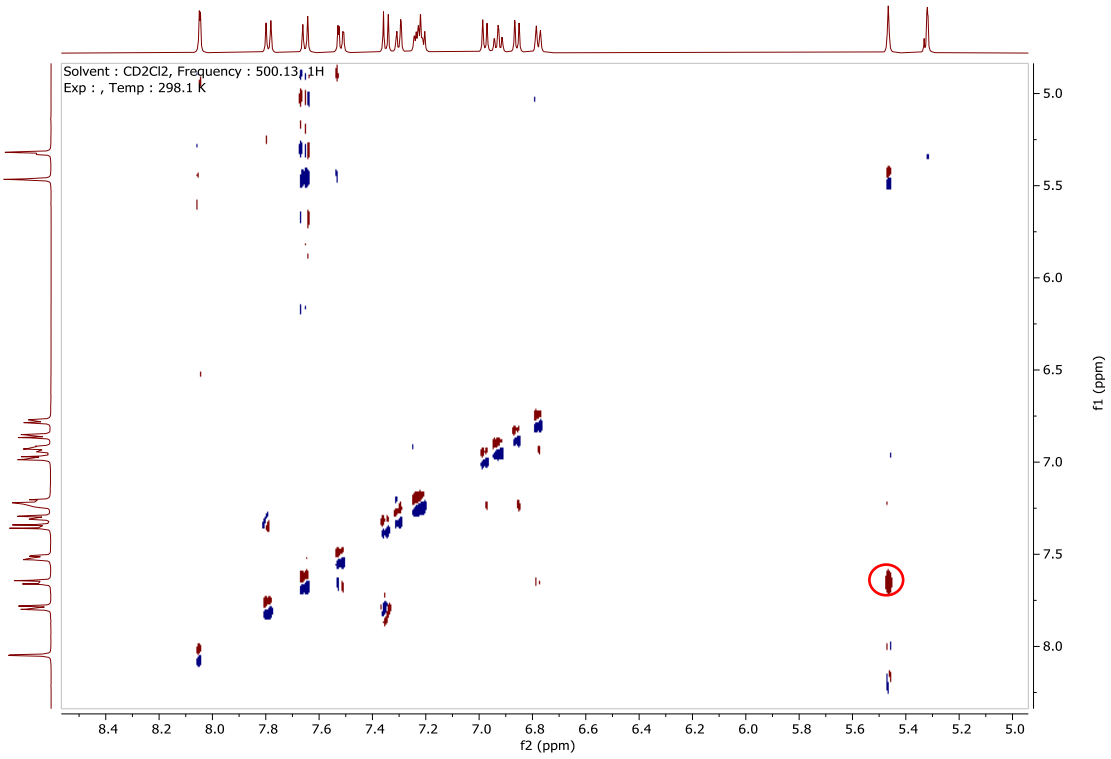




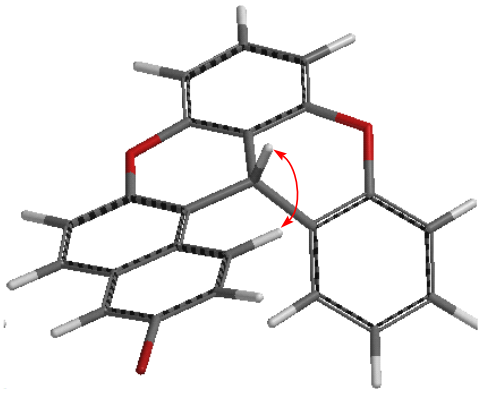
14-Bromo-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthene (23A)



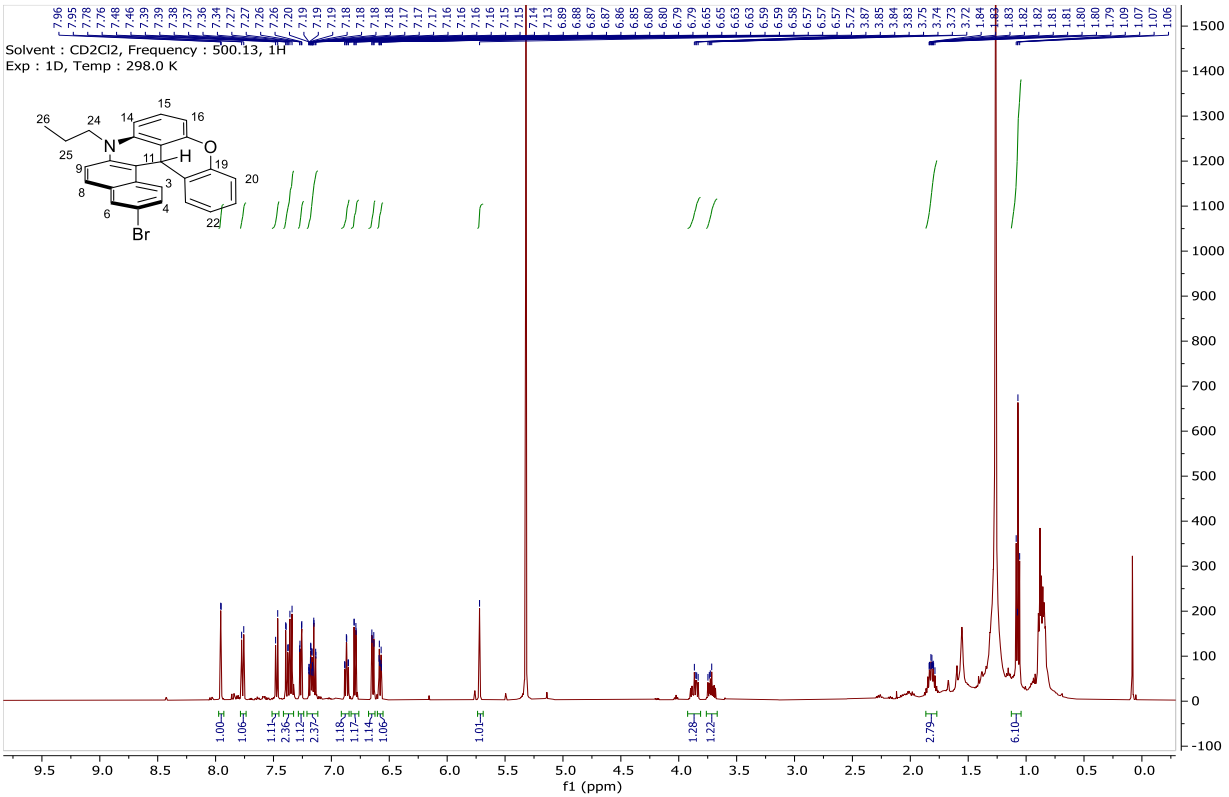


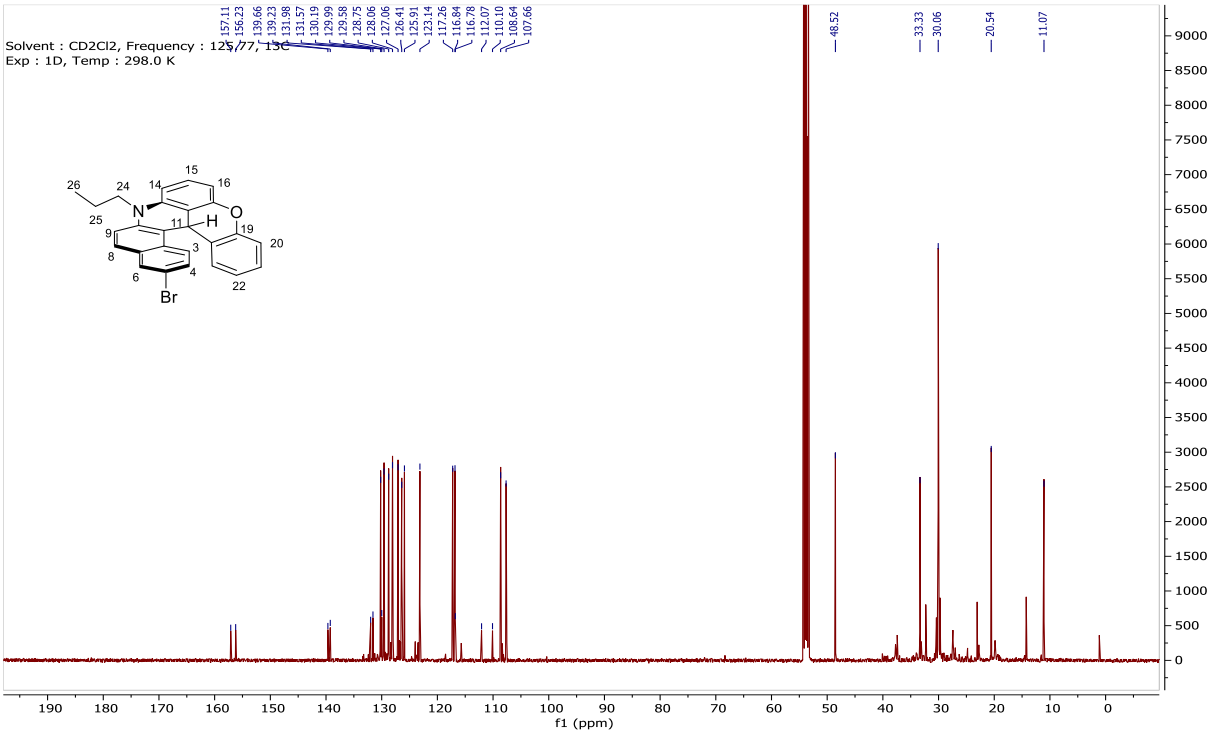


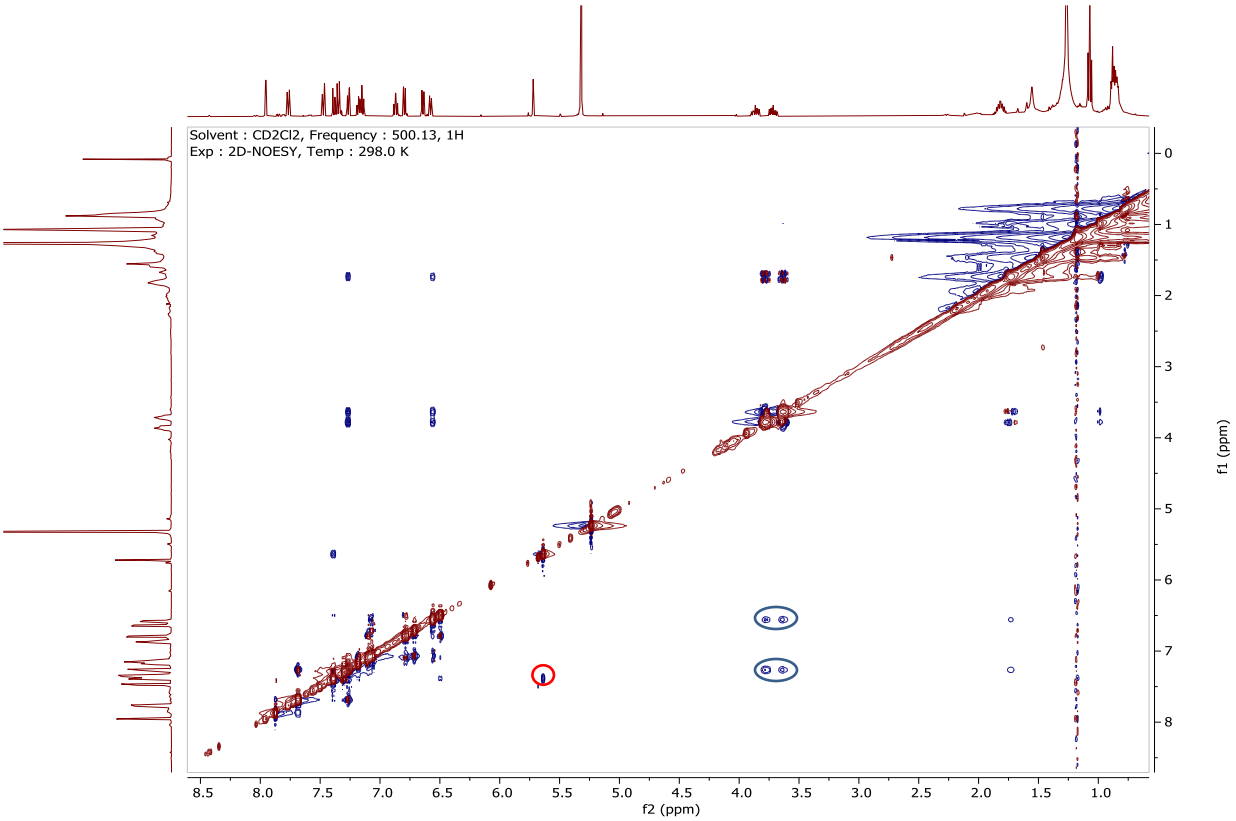
The NOE cross pick signal of H-11 and H-3 (the red arrow) is illustrated in the figure.



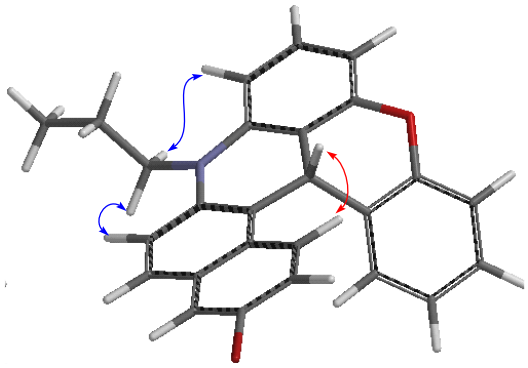
14-Bromo-3-propyl-3,11b-dihydrobenzo[*a*]chromeno[2,3,4-*kl*]acridine (24A)



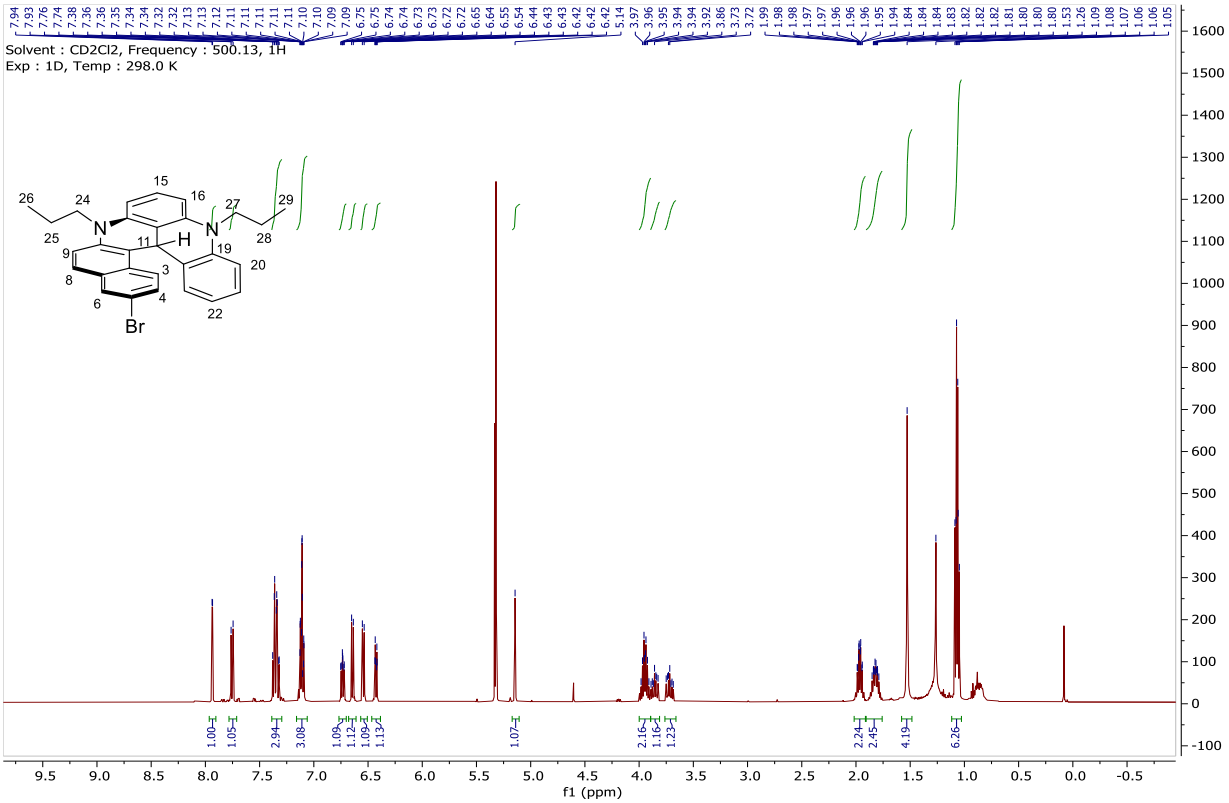


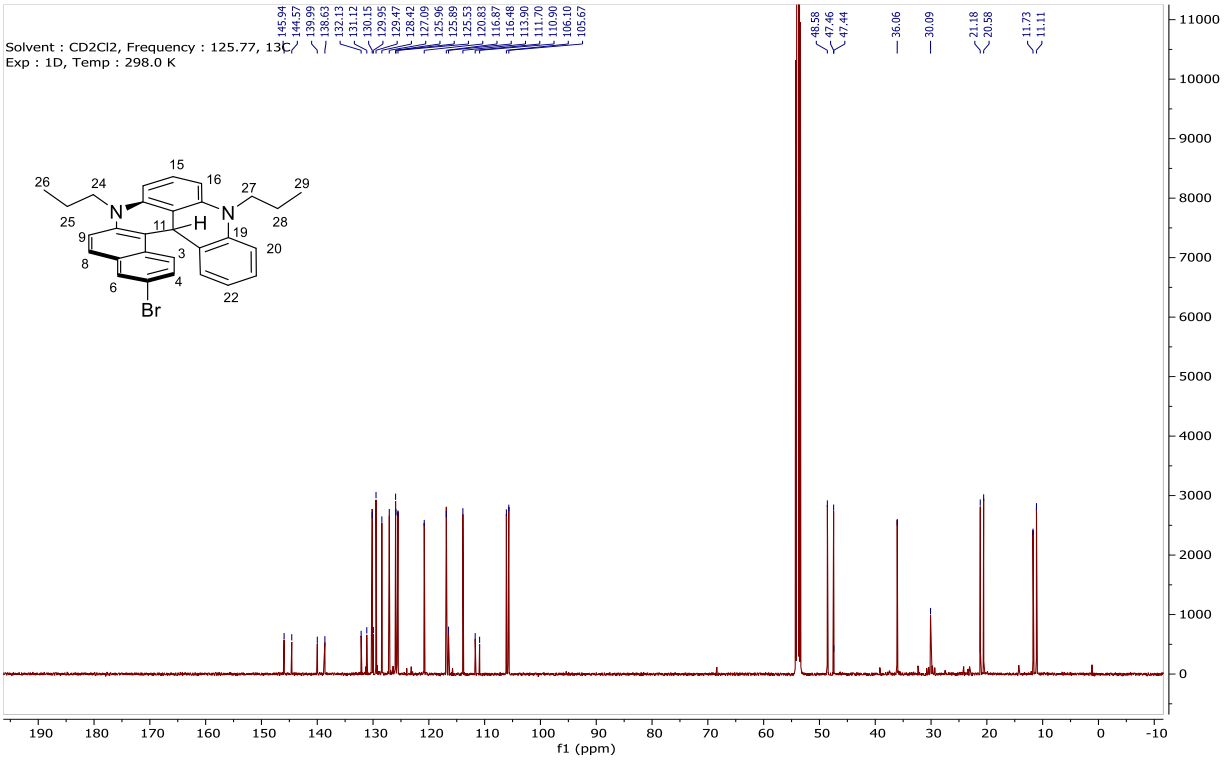


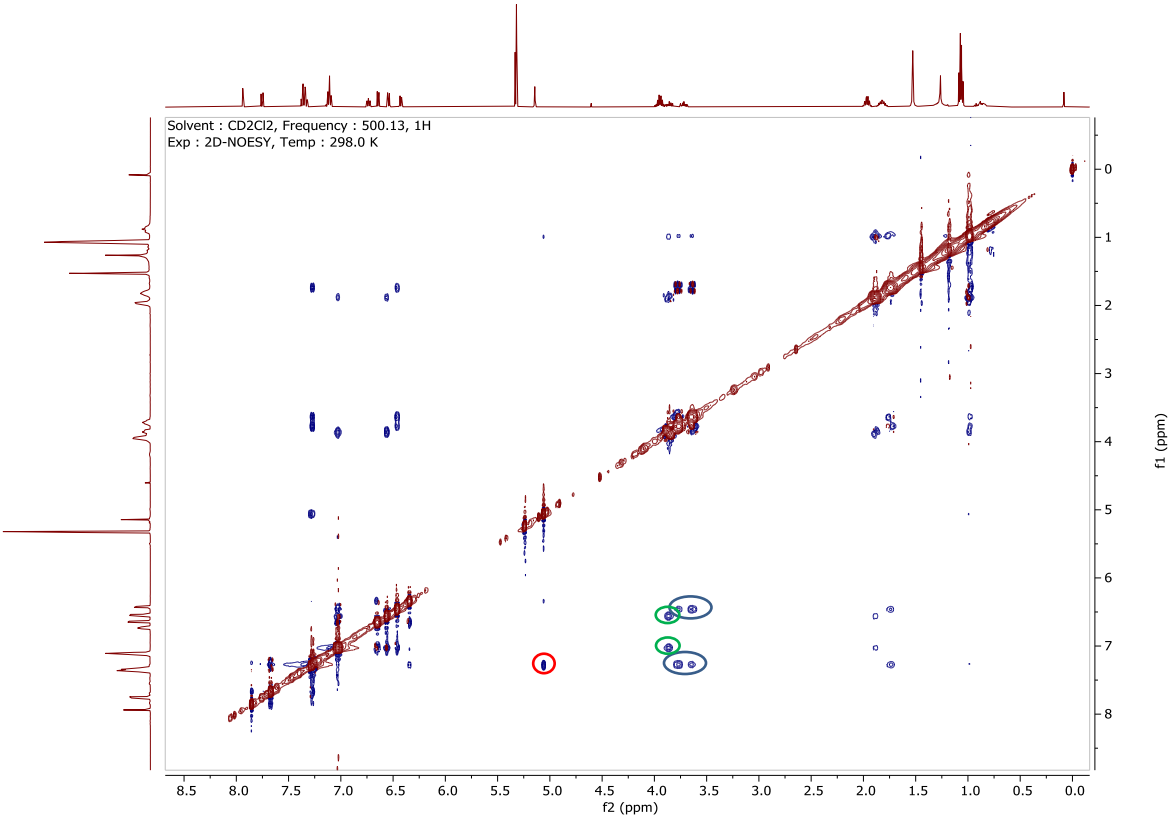
The NOE's cross peak signals of H-11 and H-3 (the red arrow), cross peak signals of H-24 and H-14 and H-24 and H-9 (the blue arrows) are illustrated in the figure.



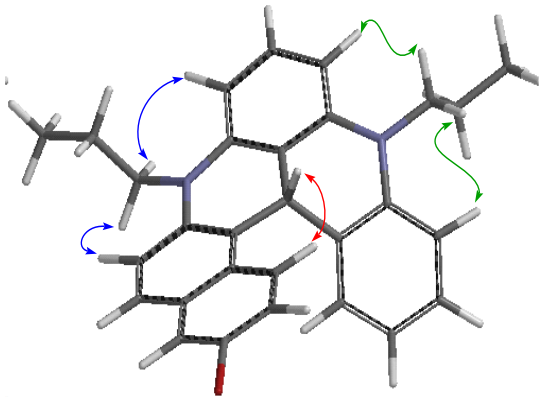
14-Bromo-3,7-dipropyl-7,11b-dihydro-3*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridine (25A)



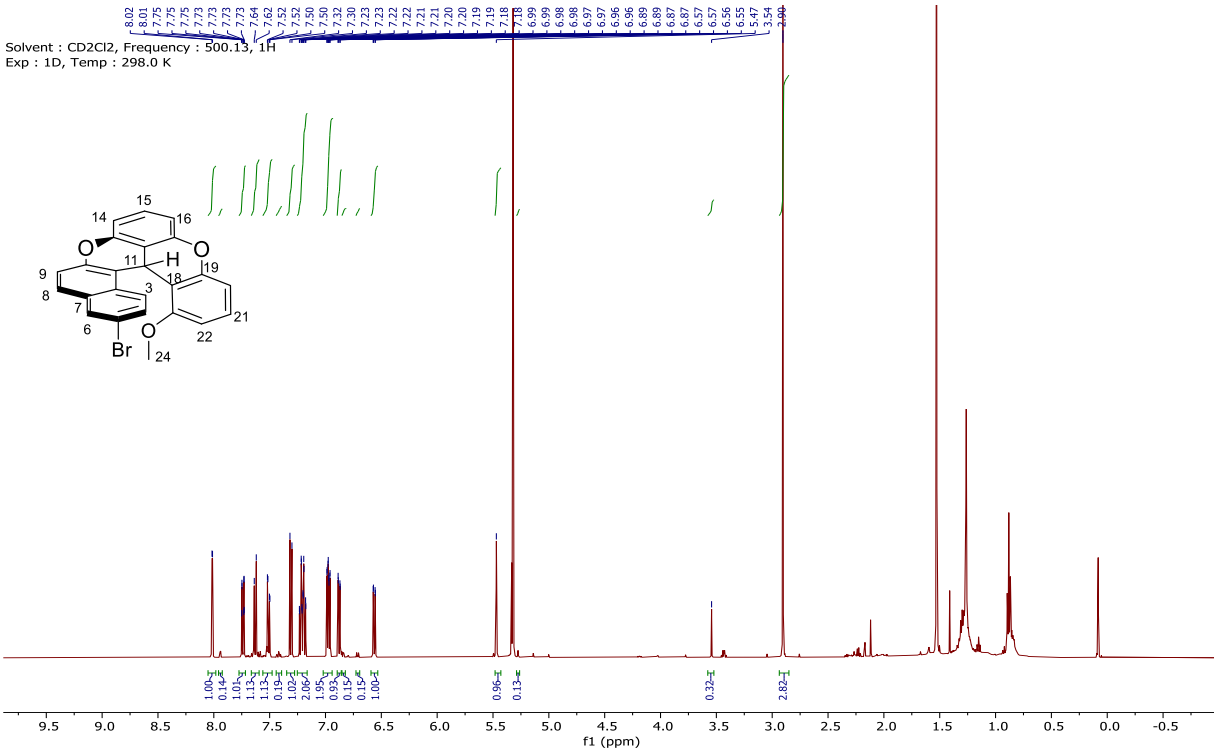


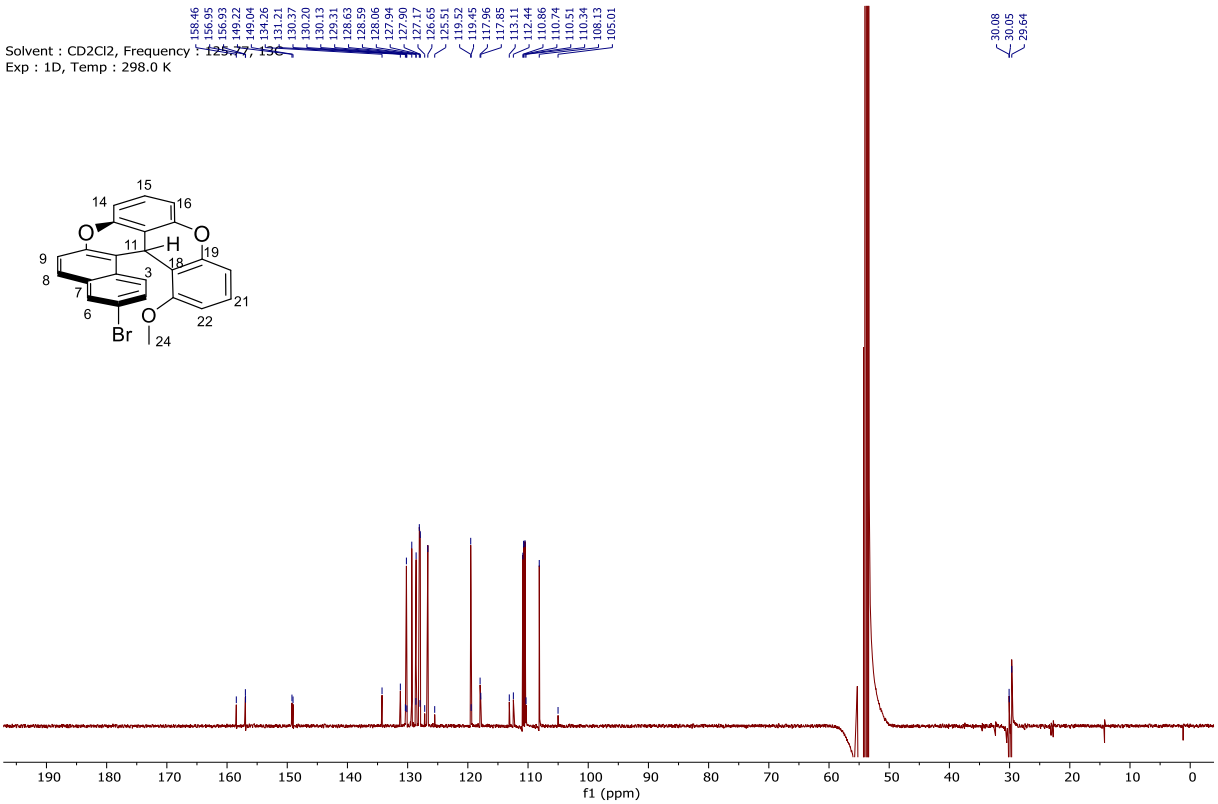


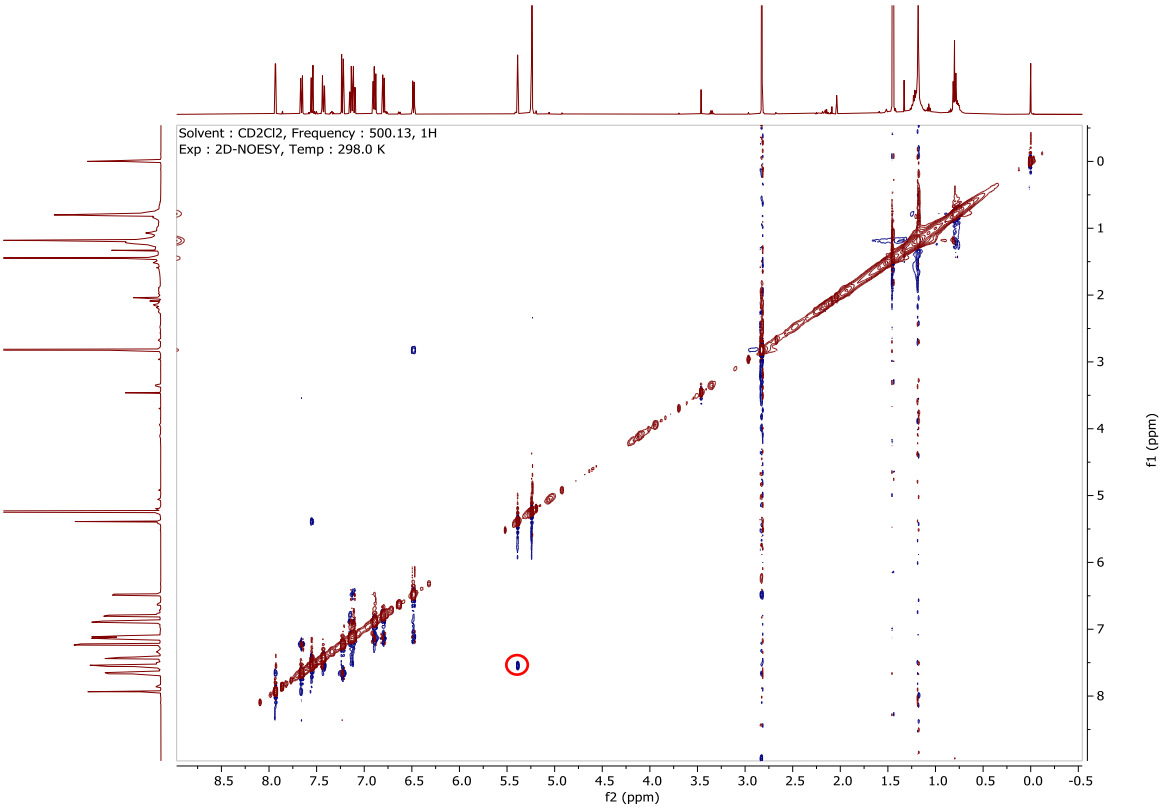
The NOE's cross peak signals of H-11 and H-3 (the red arrow), cross peak signals of H-24 and H-14, H-24 and H-9 (the blue arrows), cross peak H-16 and H-27, H-20 and H-27 (green arrows) are illustrated in the figure.



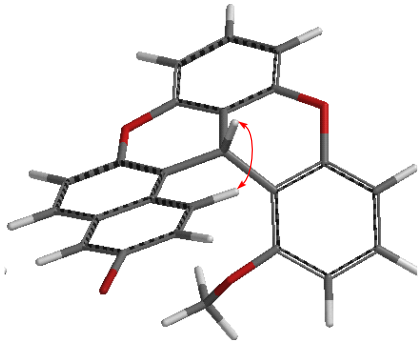
14-bromo-11-methoxy-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthene (23B)



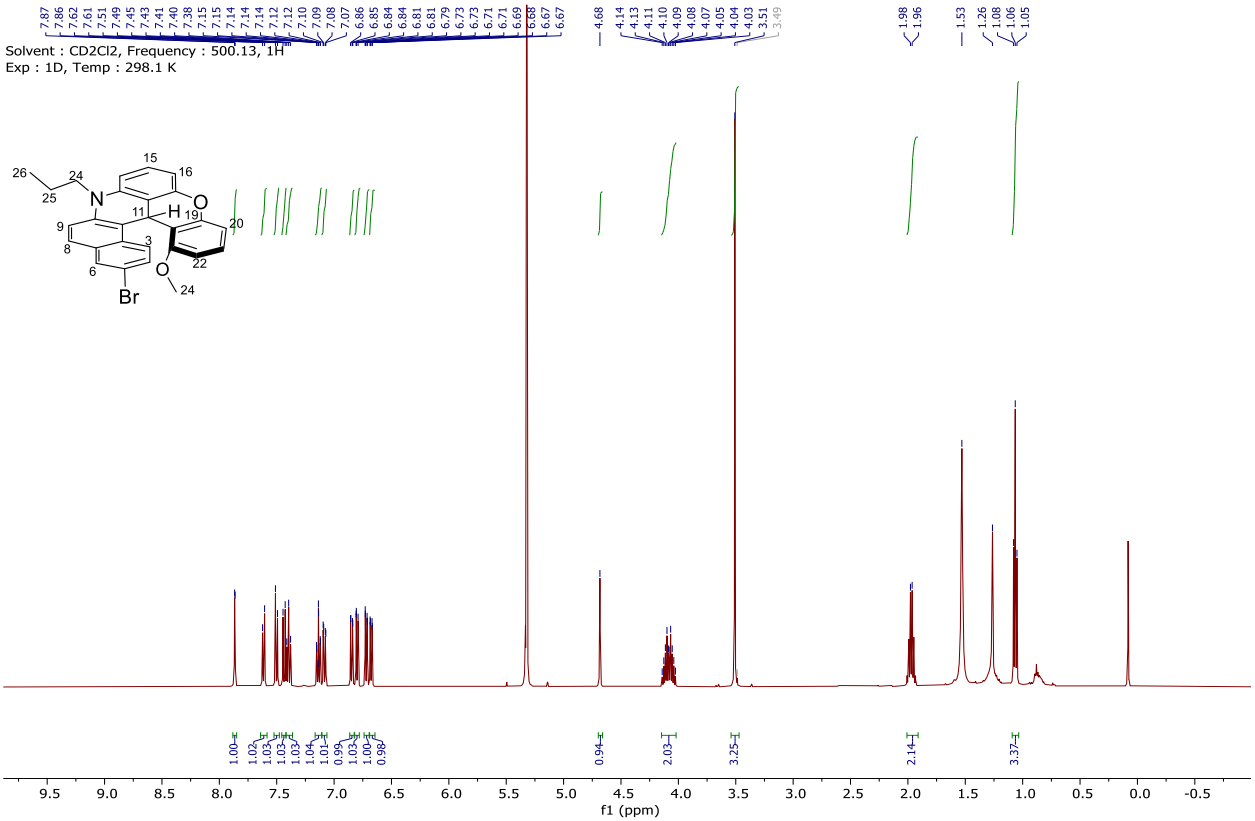


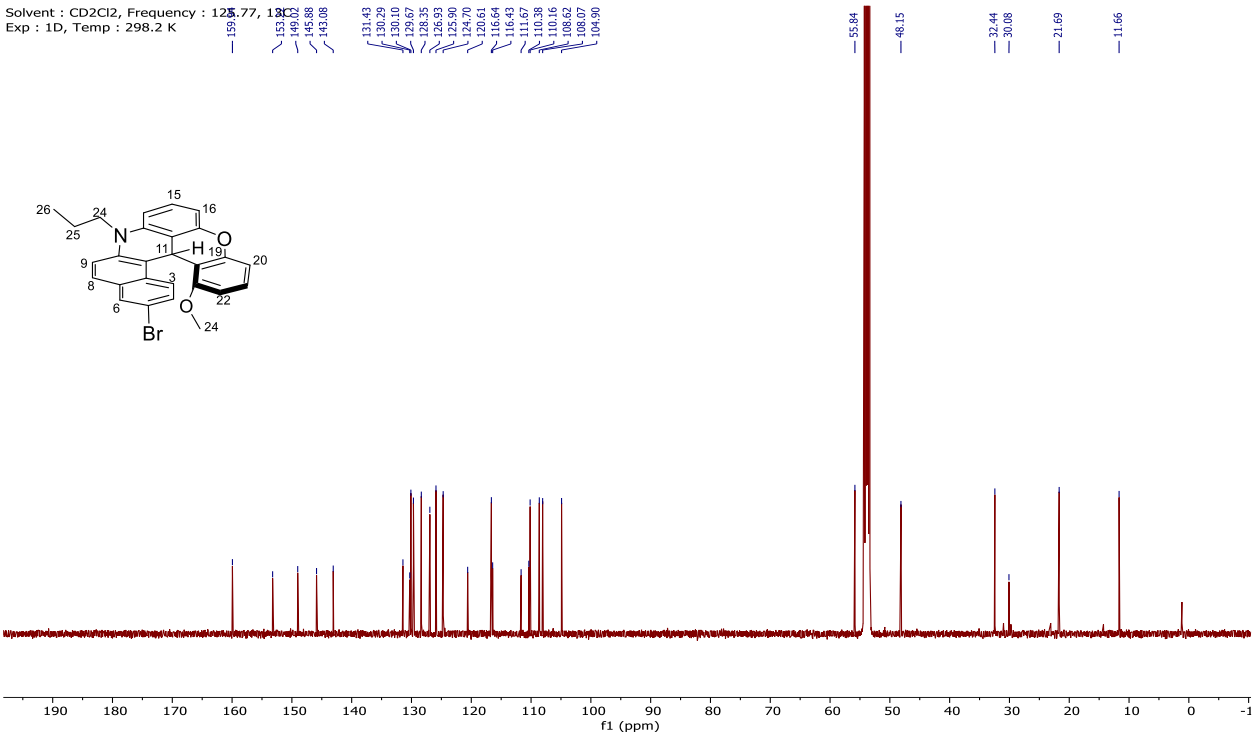


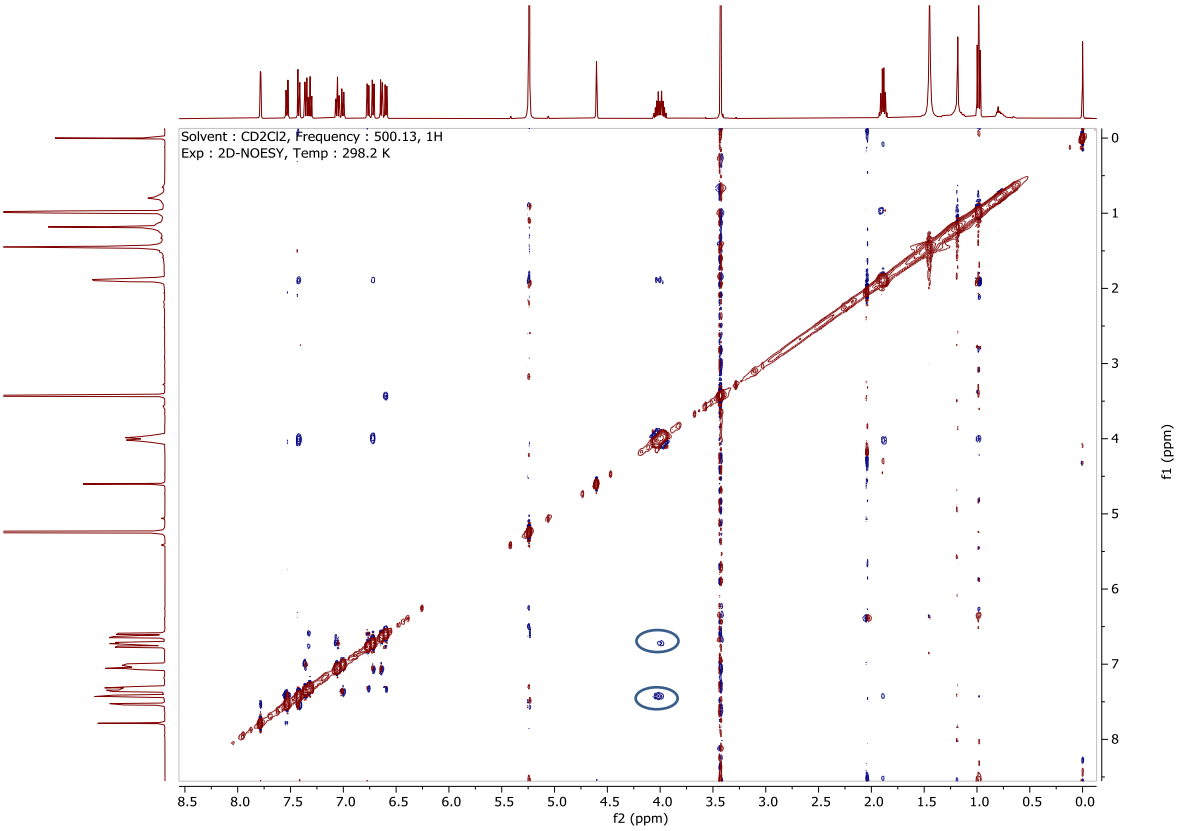
The NOE cross peak signal of H-11 and H-3 is illustrated in the figure (the red arrow).



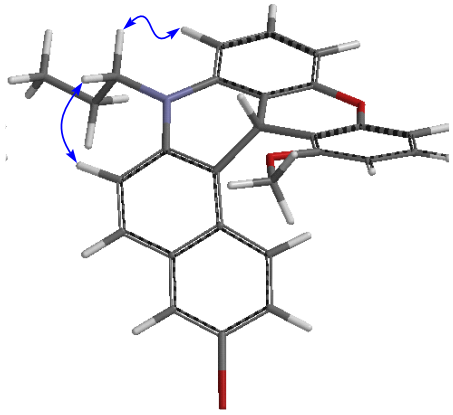
(*m*)-(*R*)-14-bromo-11-methoxy-3-propyl-3,11b-dihydrobenzo[a]chromeno[2,3,4-kl]acridine (*m*-24B)



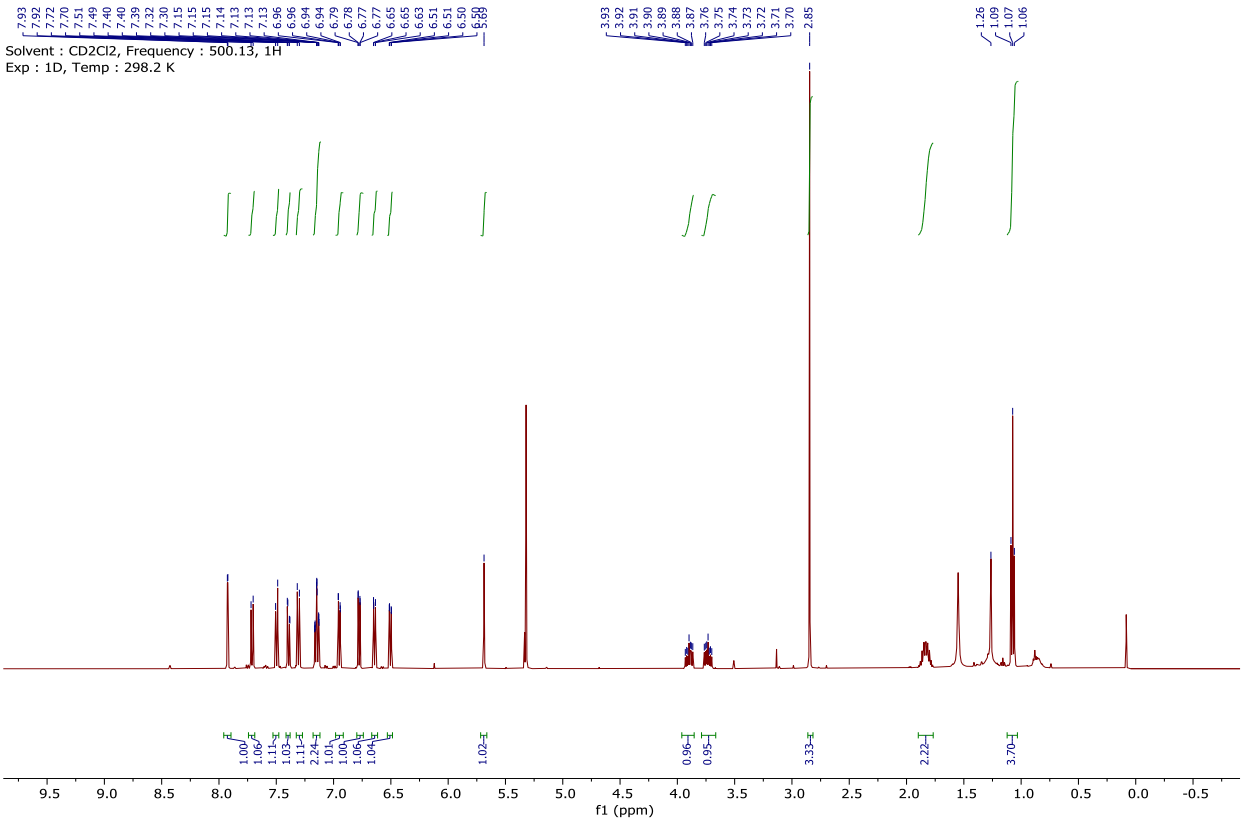


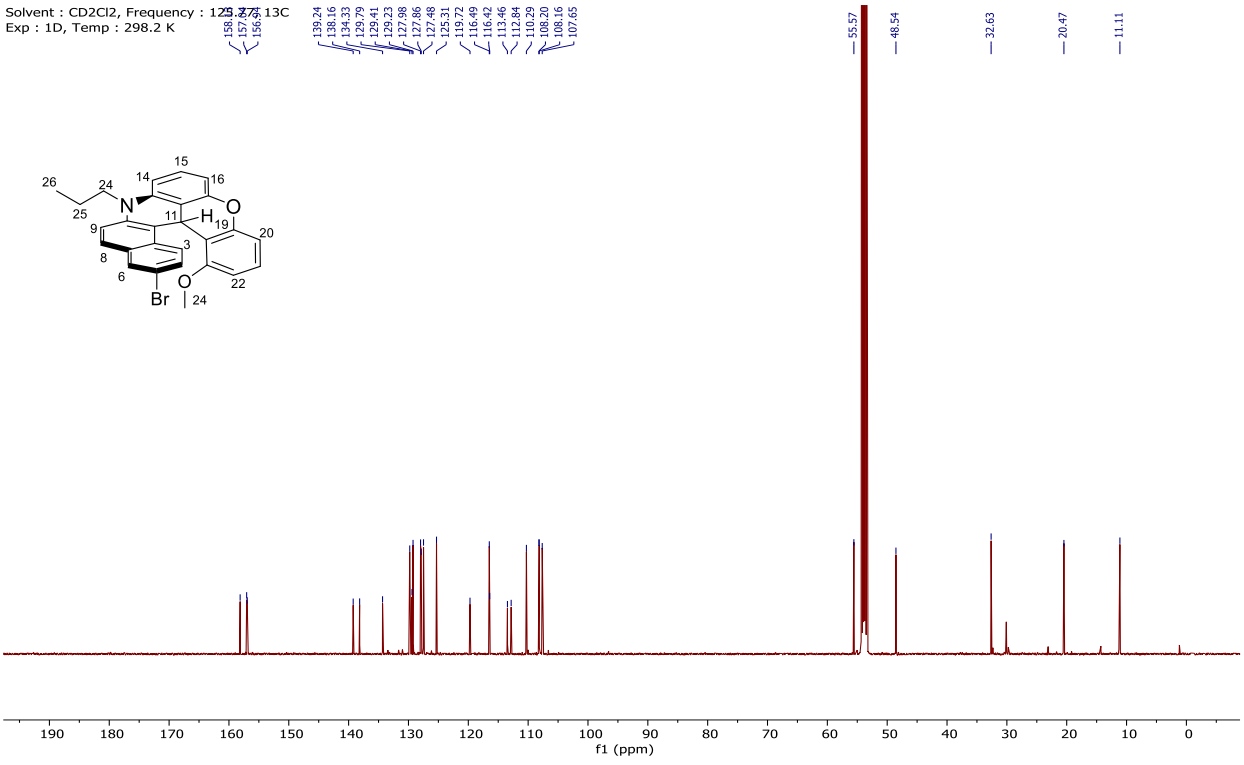


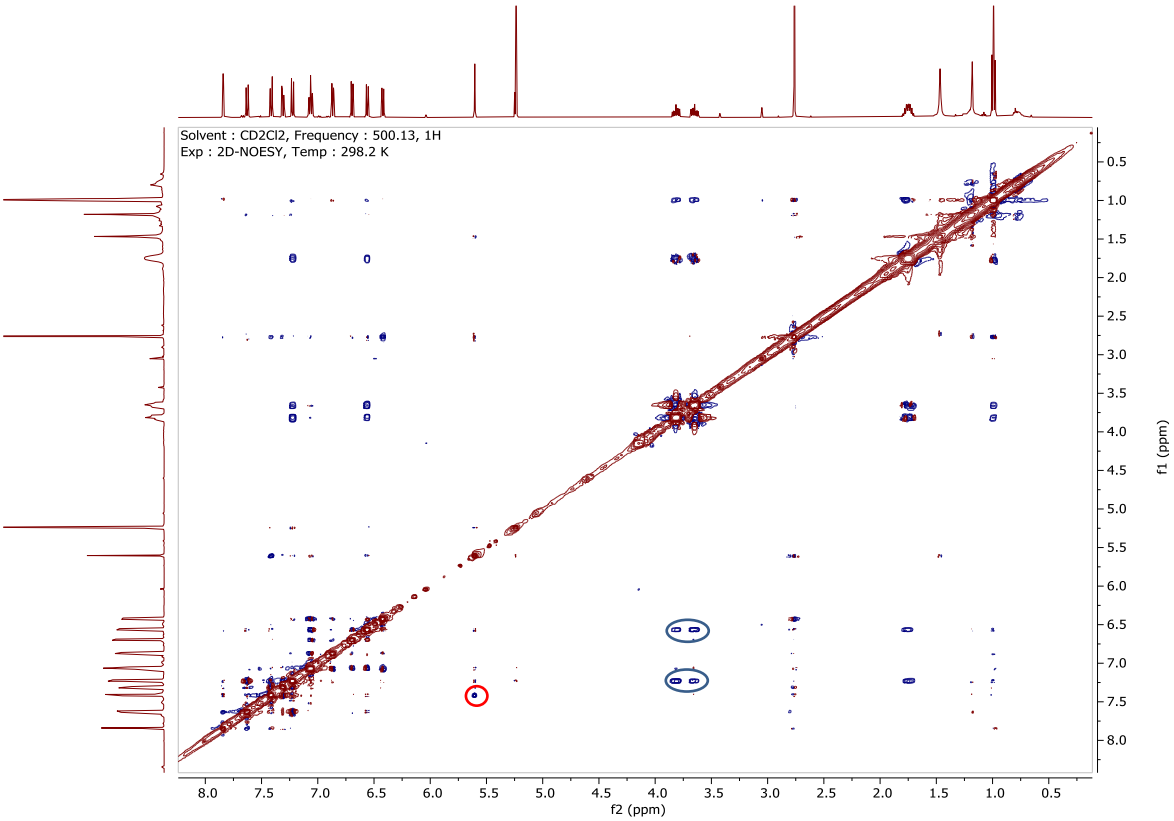
The NOE's cross peak signals of H-24 and H-14, H-24 and H-9 (the blue arrows) are illustrated in the figure.



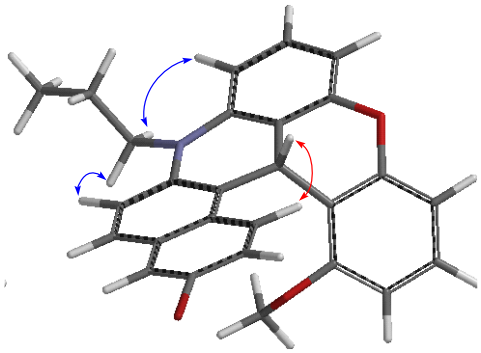
(*p*)-(*R*)-14-bromo-11-methoxy-3-propyl-3,11b-dihydrobenzo[a]chromeno[2,3,4-kl]acridine (*p*-24B)



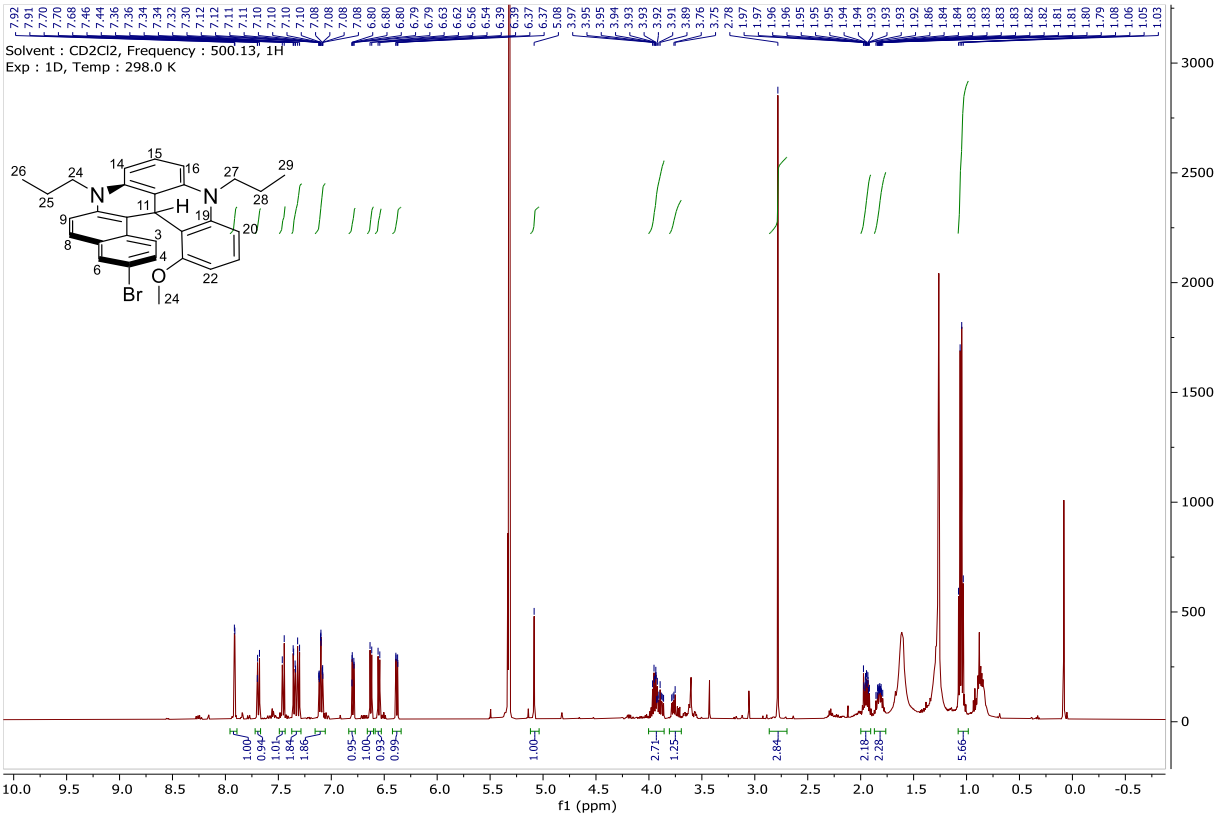


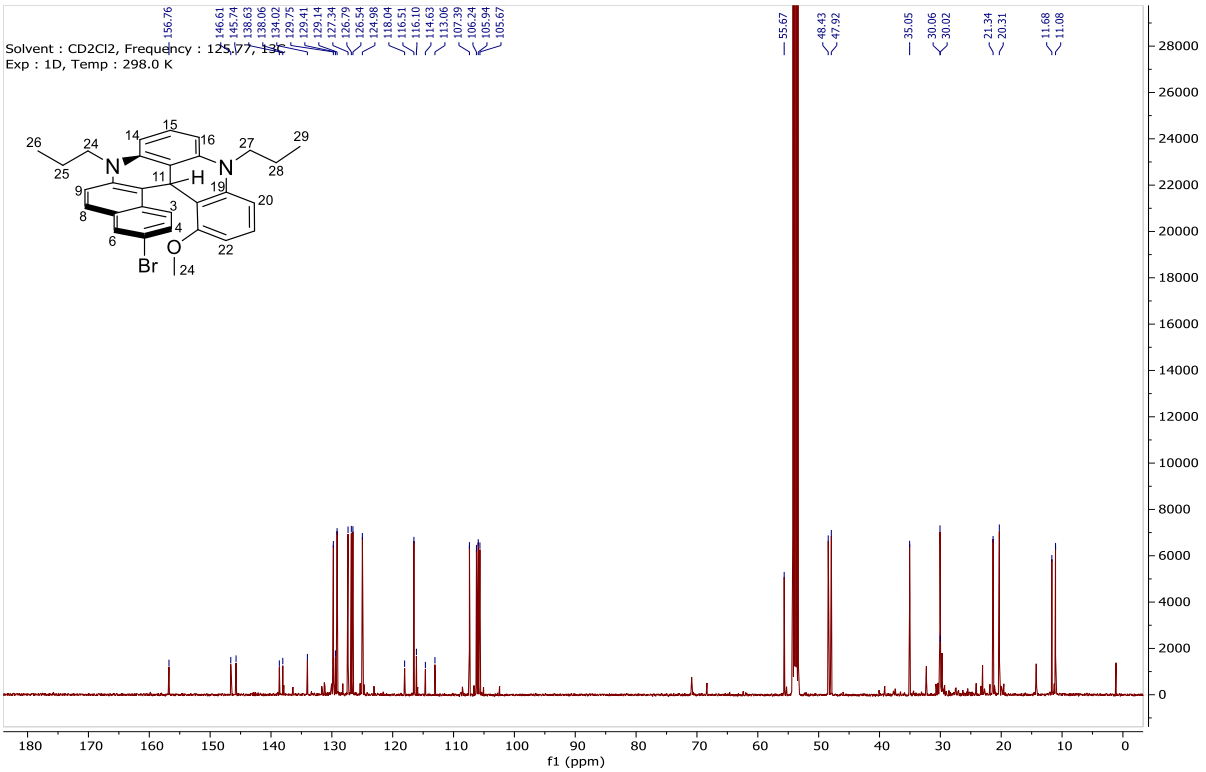


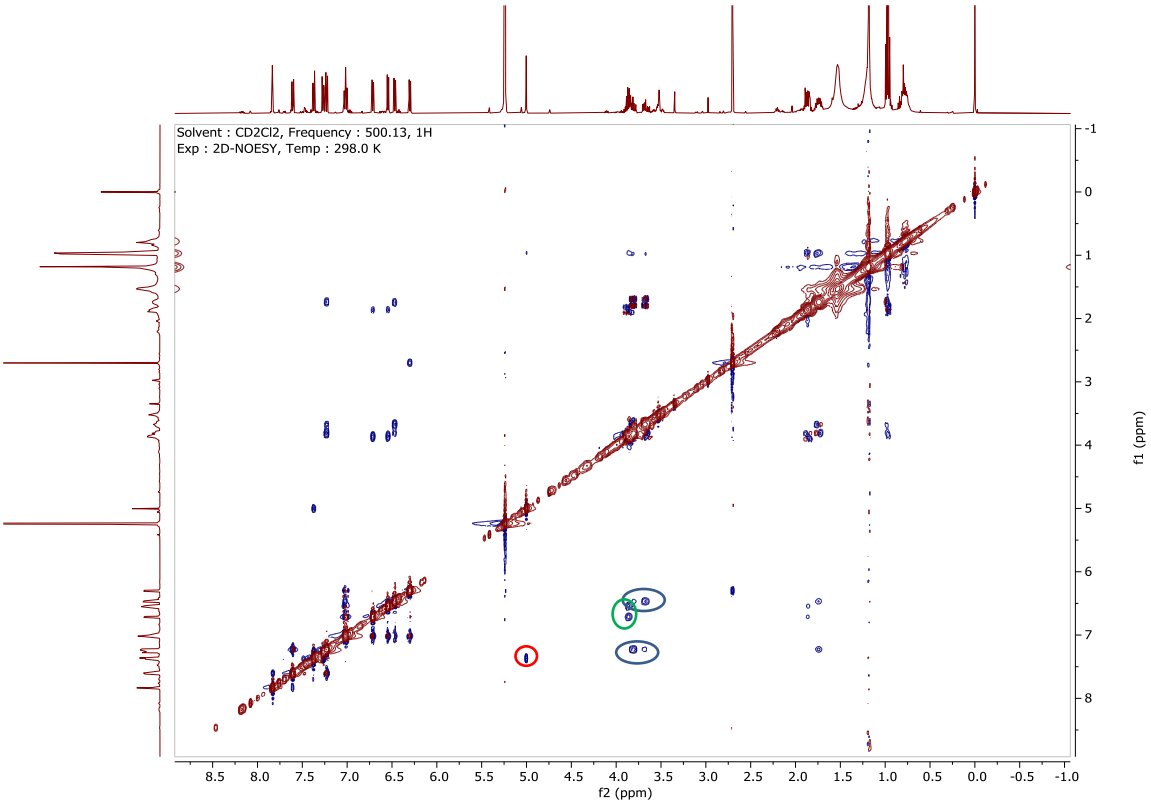
The NOE's cross peak signals of H-11 and H-3 (the red arrow), cross peak signals of H-24 and H-14, H-24 and H-9 (the blue arrows) are illustrated in the figure.



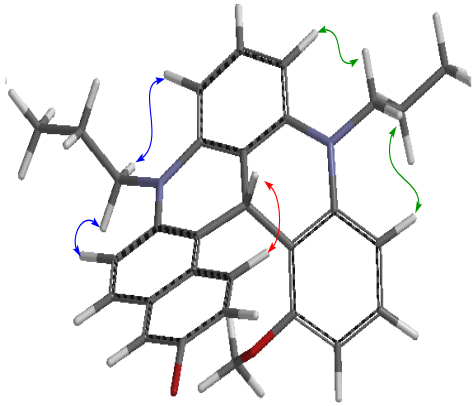
14-bromo-11-methoxy-3,7-dipropyl-7,11*b*-dihydro-3*H*-benzo[a]quinolino[2,3,4-*kl*]acridine (25B)







The NOE's cross peak signals of H-11 and H-3 (the red arrow), cross peak signals of H-24 and H-14, H-24 and H-9 (the blue arrows), cross peak H-16 and H-27, H-20 and H-27 (green arrows) are illustrated in the figure.



S-II. X-Ray Data

The compounds were crystalized as follows:

For compounds **8A**and **16B**, crystals were obtained by slow evaporation at room temperature of the acetonitrile solvent.

For compounds **9A**, **10B** and **24B**, crystals were obtained by diffusion of pentane into CH_2Cl_2 solutions.

For compounds **8B** and**15B**, crystals were obtained by diffusion of toluene into CH_2Cl_2 solutions.

Data were collected on an Agilent supernova detector using Cu Kα (all data except 16B) or Mo Kα (16B) radiation. Details for the refinement for each structure can be found below with, for each structure, a representation of the content of the asymmetric units shown as displacement ellipsoids drawn at 50 percent probability. For disordered/twinned structures, comments on the modelling of the disorder are included below this drawing. More detailed information can be found in the deposited cif files which can be obtained free of charge at the CCDC.

Crystal data and structure refinement for 8A

Identification code	8A	
Empirical formula	C23 H12 B Br F4 O2	
Formula weight	487.05	
Temperature	180(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4060(5) Å	a= 89.549(6)°.
	b = 8.4660(7) Å	b= 77.343(5)°.
	c = 14.6974(10) Å	g = 66.477(7)°.
Volume	932.01(12) $Å^3$	
Z	2	
Density (calculated)	1.736 Mg/m^3	
Absorption coefficient	3.544 mm^{-1}	
F(000)	484	
Crystal size	0.3484 x 0.2057 x 0.025 mm^3	
Theta range for data collection	3.094 to 72.421°	
Index ranges	-10<=h<=9, -10<=k<=8, -16<=l<=18	
Reflections collected	6907	
Independent reflections	3568 [R(int) = 0.0263]	
Completeness to theta = 67.500°	99.6 %	
Absorption correction	Analytical	
Max. and min. transmission	0.914 and 0.446	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3568 / 0 / 280	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1347	
R indices (all data)	R1 = 0.0527, wR2 = 0.1402	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.302 and -0.481 $e.Å^{-3}$	

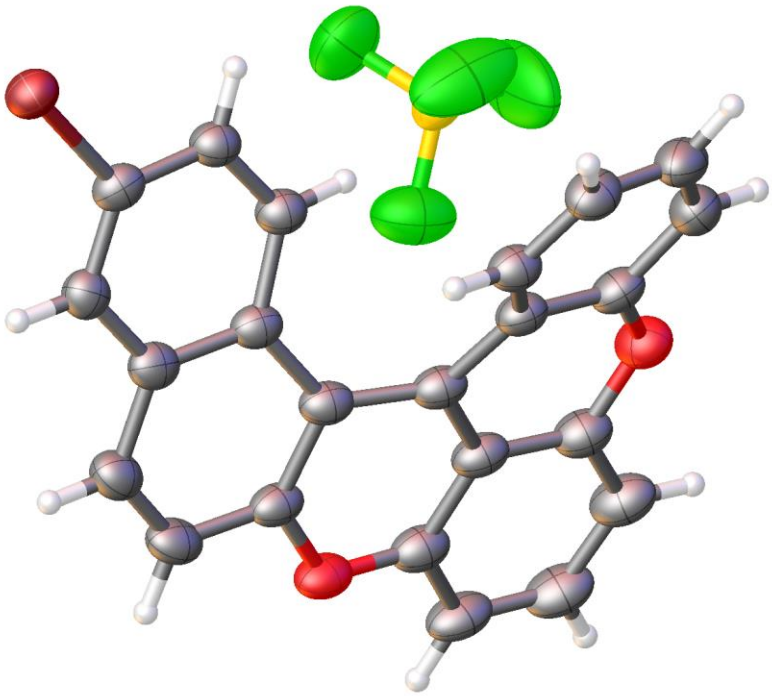


Figure S1 – View of the asymmetric units shown (displacement ellipsoids drawn at 50 percent probability level).

Crystal data and structure refinement for 8B

Identification code	8B	
Empirical formula	C24 H14 B Br F4 O3	
Formula weight	517.07	
Temperature	290.56(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.8561(5) Å	a= 91.724(4)°.
	b = 9.3777(5) Å	b= 98.862(4)°.
	c = 14.1453(5) Å	g = 116.907(6)°.
Volume	1028.42(10) $Å^3$	
Z	2	
Density (calculated)	1.670 Mg/m^3	
Absorption coefficient	3.289 mm^{-1}	
F(000)	516	
Crystal size	0.291 x 0.168 x 0.109 mm^3	
Theta range for data collection	3.182 to 73.466°.	
Index ranges	-10<=h<=10, -11<=k<=11, -17<=l<=11	
Reflections collected	6622	
Independent reflections	4003 [R(int) = 0.0168]	
Completeness to theta = 67.684°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.79381	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4003 / 93 / 335	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.0917	
R indices (all data)	R1 = 0.0397, wR2 = 0.0959	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.533 and -0.480 $e.Å^{-3}$	

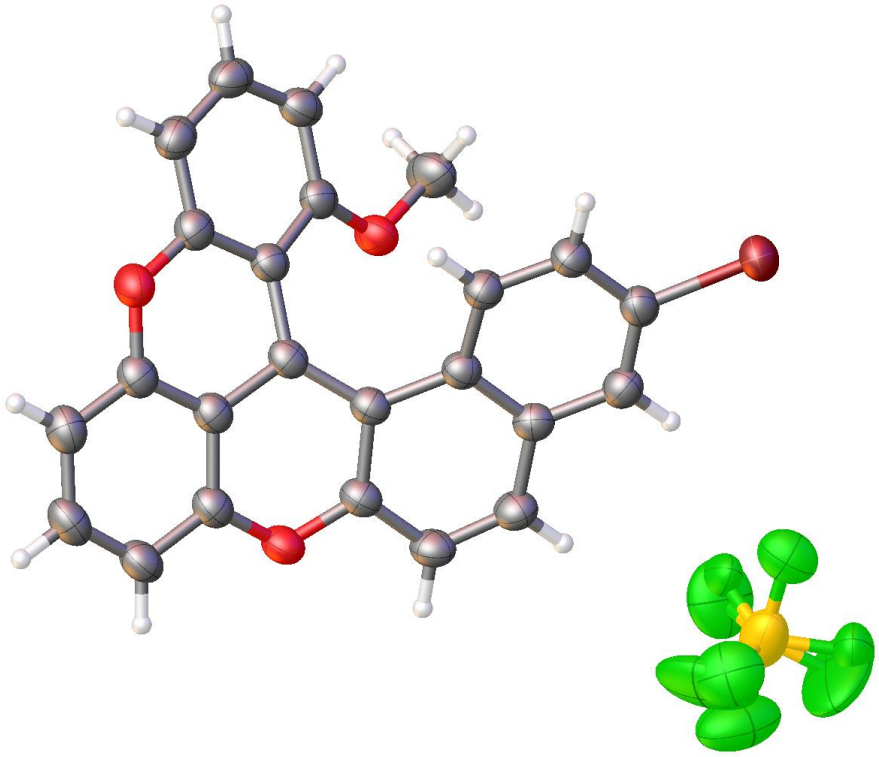


Figure S2 – View of the asymmetric units shown (displacement ellipsoids drawn at 50 percent probability level).

Remark: one disordered BF_4^- refined using 8 fluorides atoms. SADI restraints on B-F and F-F distances. RIGU restraints on anisotropic displacement parameters.

Crystal data and structure refinement for 9A

Identification code	9A	
Empirical formula	C29 H26 B Br F4 N2	
Formula weight	569.24	
Temperature	179.95(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.7765(3) Å	a= 77.279(4)°.
	b = 16.0668(6) Å	b= 80.071(3)°.
	c = 17.3836(7) Å	g = 80.432(3)°.
Volume	3398.0(2) $Å^3$	
Z	4	
Density (calculated)	1.113 Mg/m^3	
Absorption coefficient	1.978 mm^{-1}	
F(000)	1160	
Crystal size	0.3395 x 0.2228 x 0.0181 mm^3	
Theta range for data collection	3.475 to 74.015°.	
Index ranges	-15<=h<=11, -19<=k<=19, -19<=l<=21	
Reflections collected	23721	
Independent reflections	13315 [R(int) = 0.0493]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.965 and 0.640	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13315 / 0 / 671	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0619, wR2 = 0.1771	
R indices (all data)	R1 = 0.0720, wR2 = 0.1909	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.150 and -1.182 $e.Å^{-3}$	

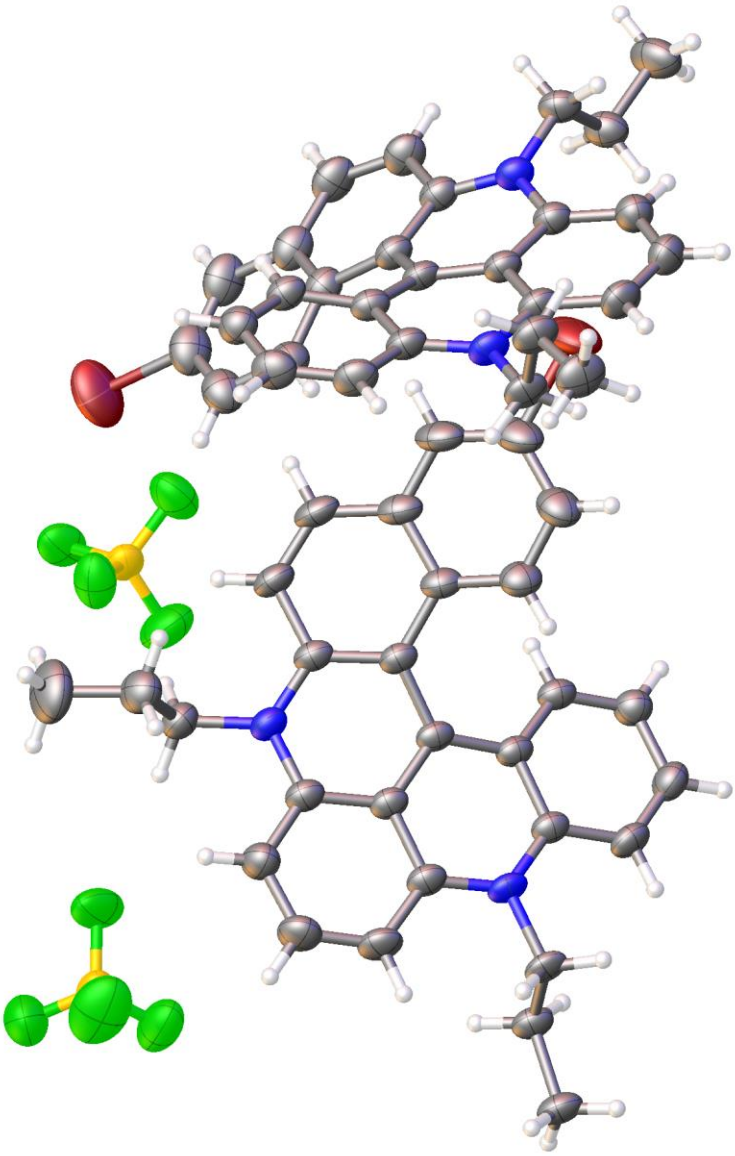


Figure S3 – View of the asymmetric units shown (displacement ellipsoids drawn at 50 percent probability level).

Crystal data and structure refinement for 10B

Identification code	10B	
Empirical formula	C55 H44 B2 Br2 Cl2 F8 N2 O4	
Formula weight	1201.26	
Temperature	179.95(10) K	
Wavelength	1.5418 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 7.7507(4) Å	a= 104.972(5)°.
	b = 12.3048(5) Å	b= 95.439(4)°.
	c = 13.5177(8) Å	g = 94.459(4)°.
Volume	1232.79(11) $Å^3$	
Z	1	
Density (calculated)	1.618 Mg/m^3	
Absorption coefficient	3.787 mm^{-1}	
F(000)	606	
Crystal size	0.265 x 0.1635 x 0.0374 mm^3	
Theta range for data collection	3.409 to 73.599°.	
Index ranges	-9<=h<=9, -14<=k<=14, -16<=l<=16	
Reflections collected	15209	
Independent reflections	15209 [R(int) = ?]	
Completeness to theta = 67.680°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.64059	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15209 / 202 / 761	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0651, wR2 = 0.1789	
R indices (all data)	R1 = 0.0694, wR2 = 0.1829	
Absolute structure parameter	n/a	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.607 and -0.660 e.$Å^{-3}$	

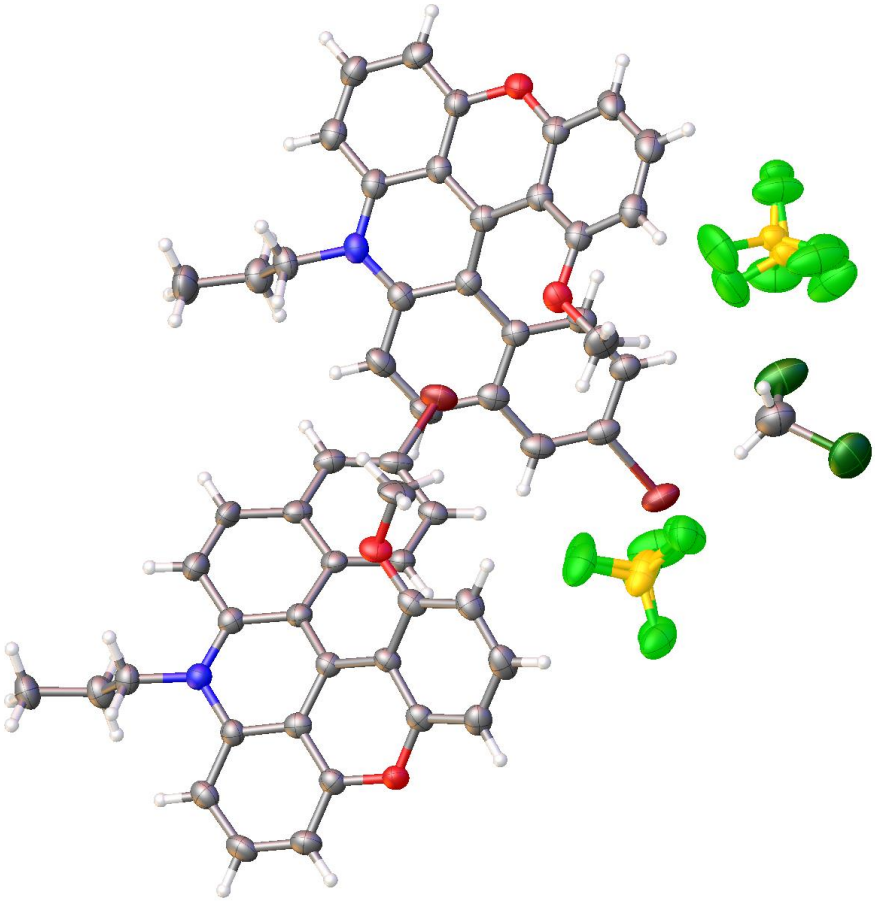


Figure S4 – View of the asymmetric units shown (displacement ellipsoids drawn at 50 percent probability level).

Remark: crystal is a non merohedral twin. Both components were integrated into a single HKLF5 file. No attempt was made to refine the absolute structure from the twinned data. The flack parameter on the major twin refined to -0.01(5). BF_4^- anion are disordered and were refined. SADI restraints were used on 1-2 and 1-3 distances and RIGU restraints were used on anisotropic displacement parameters. EADP constraints were applied to boron displacement parameters.

Crystal data and structure refinement for 15B

Identification code	15B	
Empirical formula	C23 H11 Br O3	
Formula weight	415.23	
Temperature	180.15 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 20.2508(3) Å	□= 90°.
	b = 4.24318(7) Å	□= 106.1860(17)°.
	c = 19.0965(3) Å	□ = 90°.
Volume	1575.88(5) $Å^3$	
Z	4	
Density (calculated)	1.750 Mg/m^3	
Absorption coefficient	3.753 mm^{-1}	
F(000)	832	
Crystal size	0.625 x 0.171 x 0.033 mm^3	
Theta range for data collection	4.547 to 73.469°.	
Index ranges	-22<=h<=24, -5<=k<=3, -23<=l<=23	
Reflections collected	4791	
Independent reflections	3081 [R(int) = 0.0152]	
Completeness to theta = 67.684°	99.8 %	
Absorption correction	Analytical	
Max. and min. transmission	0.888 and 0.340	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3081 / 0 / 244	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0782	
R indices (all data)	R1 = 0.0337, wR2 = 0.0817	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.368 and -0.659 $e.Å^{-3}$	

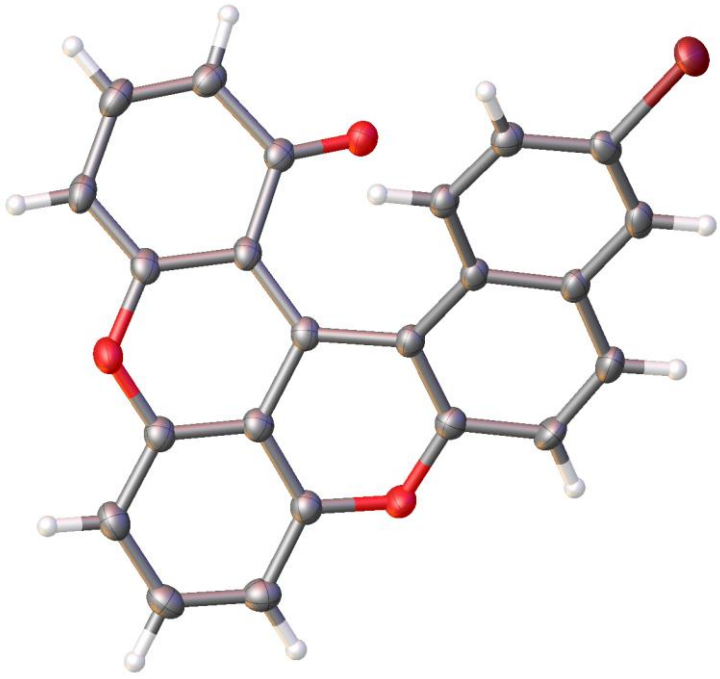


Figure S5 – View of the asymmetric units shown (displacement ellipsoids drawn at 50 percent probability level).

Crystal data and structure refinement for 16B

Identification code	16B	
Empirical formula	C29 H28 Br N O4	
Formula weight	534.43	
Temperature	290 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.9485(3) Å	□= 90°.
	b = 21.3763(5) Å	□= 99.059(3)°.
	c = 13.2147(3) Å	□ = 90°.
Volume	2496.26(12) $Å^3$	
Z	4	
Density (calculated)	1.422 Mg/m^3	
Absorption coefficient	1.683 mm^{-1}	
F(000)	1104	
Crystal size	0.3 x 0.2 x 0.15 mm^3	
Theta range for data collection	2.980 to 29.504°.	
Index ranges	-10<=h<=12, -29<=k<=27, -18<=l<=17	
Reflections collected	35238	
Independent reflections	6364 [R(int) = 0.0367]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.67536	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6364 / 0 / 324	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1038	
R indices (all data)	R1 = 0.0845, wR2 = 0.1185	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.566 and -0.725 $e.Å^{-3}$	

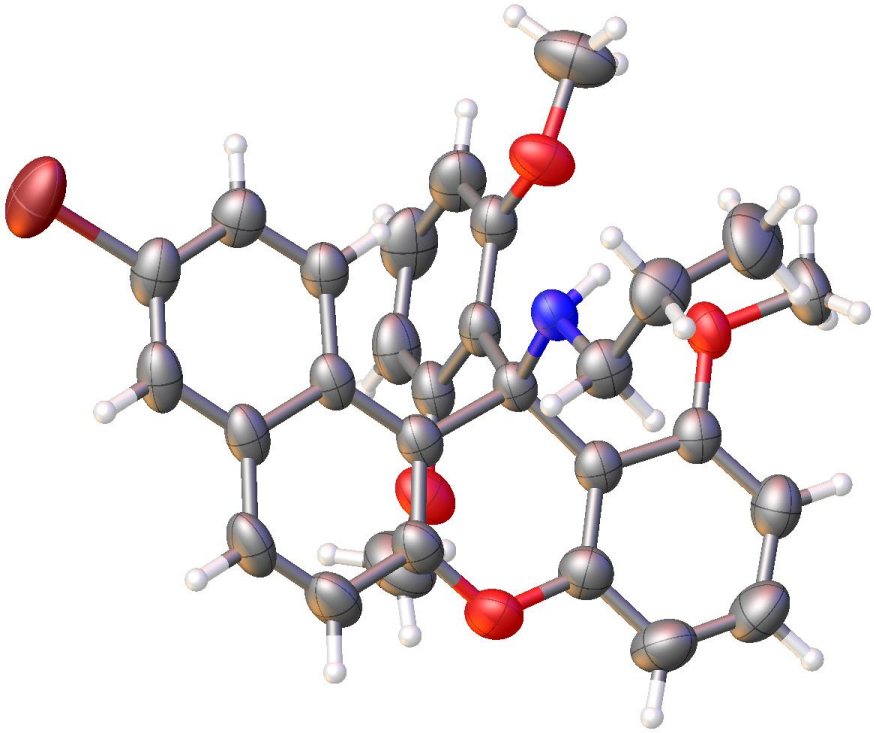


Figure S6 – View of the asymmetric units shown (displacement ellipsoids drawn at 50 percent probability level).

Crystal data and structure refinement for 24B

Identification code	24B	
Empirical formula	C28 H24 Br Cl2 N O2	
Formula weight	557.29	
Temperature	180.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9075(7) Å	□= 110.420(6)°.
	b = 11.5025(7) Å	□= 95.401(5)°.
	c = 12.5629(8) Å	□ = 112.560(6)°.
Volume	1195.28(15) $Å^3$	
Z	2	
Density (calculated)	1.548 Mg/m^3	
Absorption coefficient	4.617 mm^{-1}	
F(000)	568	
Crystal size	0.98 x 0.487 x 0.351 mm^3	
Theta range for data collection	3.892 to 73.642°.	
Index ranges	-11<=h<=8, -12<=k<=14, -15<=l<=15	
Reflections collected	7481	
Independent reflections	4648 [R(int) = 0.0333]	
Completeness to theta = 67.684°	99.6 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.364 and 0.102	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4648 / 0 / 310	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1321	
R indices (all data)	R1 = 0.0509, wR2 = 0.1338	
Extinction coefficient	0.0204(11)	
Largest diff. peak and hole	1.460 and -0.829 $e.Å^{-3}$	

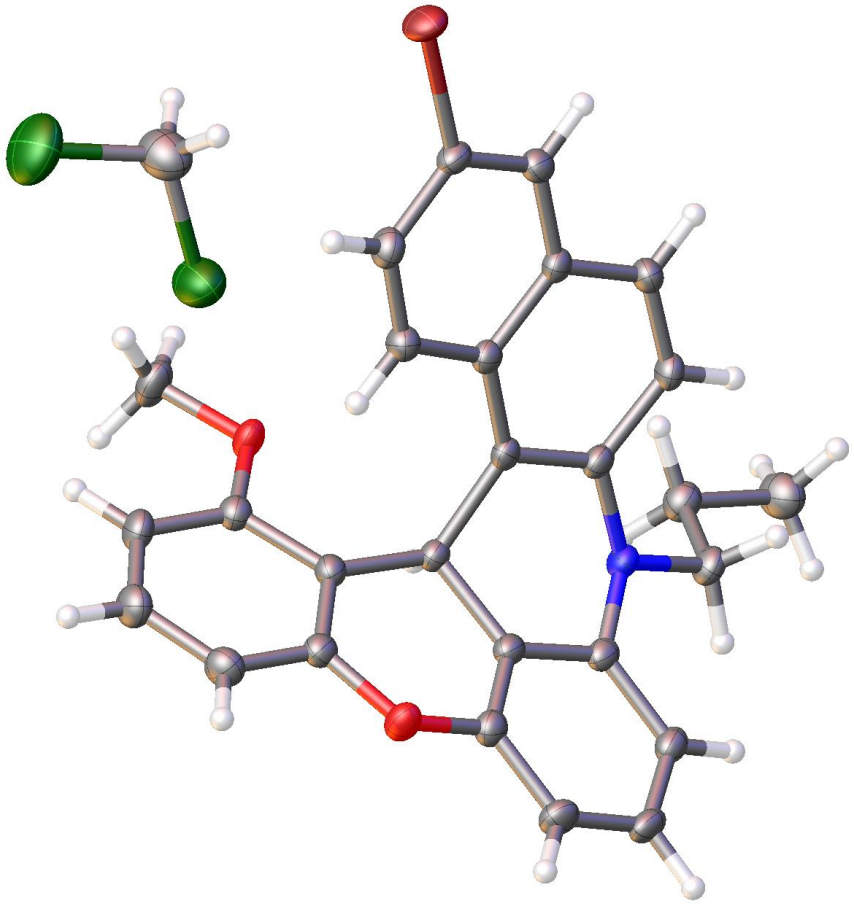
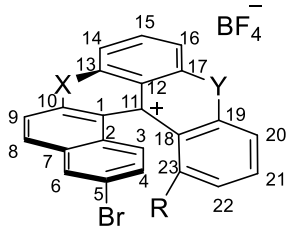


Figure S7 – View of the asymmetric units shown (displacement ellipsoids drawn at 50 percent probability level).

Relevant geometrical data.



Molecule	X	Y	R	Helical pitch / Å C(3)-C(23)	Helical angle / °	Dihedral angle Φ C(2)-C(1)-C(11)-C(18) / °	Dihedral angle Φ C(1)-C(11)-C(18)-C(23) / °
8A	O	O	H	2.940	37.5	21.7	19.5
8B	O	O	OMe	3.061	42.3	24.7	23.7
15B	O	O	O	3.039	43.6	29.5	18.2
9A	N	N	H	2.892	45	28.5	18.1
10B	N	O	OMe	3.082	51.4	28.3	25.6

The helical pitch is the distance between the first two overlapping atoms of the helicene (carbons 3 and 23). The helical angle calculated for two planes generated from the first and the last rings, counting as part of the helicene framework.

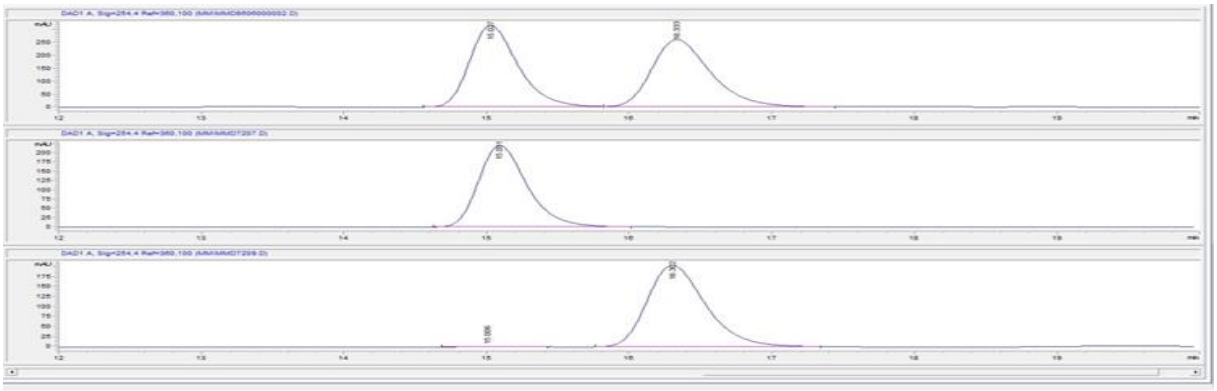
S-III. Resolution, enantiomeric purity determination, ECD spectra

Resolution of the enantiomers of 14-Bromo-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthene (23A)

The enantiomers of compound **23A** were separated by using semi preparative Chiralcel IA column (1 x 25 cm) under the following conditions: 10 mg of **23A** dissolved in 900 µL of eluent; eluent hexane:THF 93:7; injection 3 x 250 µL; flow rate 2 ml/min.

Isolated fractions within 3 injections:
(+)-**23A** – 2.1 mg, retention time 15.0 min (>99 % ee)
(+)-**23A** /(-)-**23A** – 3.1 mg (ratio 63:37, respectively)
(-)-**23A** – 1.1 mg, retention time 16.3 min (>99 % ee)

Enantiomeric purity determination:
The enantiomeric purity was determined by CSP-HPLC (Chiralcel IA column, hexane:THF 93:7, 2 ml/min flow rate, 23°C, diode array detector).



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Acq. Instrument  : HPLC Prep                      Location : Vial 4
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                                                  Inj Volume : 50.0 µl
Acq. Method      : C:\CHEM32\2\METHODS\SG\IA_SEMI_MAYA_R.M
Last changed     : 28/05/2014 13:24:55 by  Maya
                   (modified after loading)
Analysis Method  : C:\CHEM32\2\METHODS\SG\IA_SEMI_MAYA.M
Last changed     : 18/06/2014 15:26:14 by sté
                   (modified after loading)
Sample Info      : IA semi-prep; n-Hex/THF 93/7; 2mL/min; 25 °C; Inj :50
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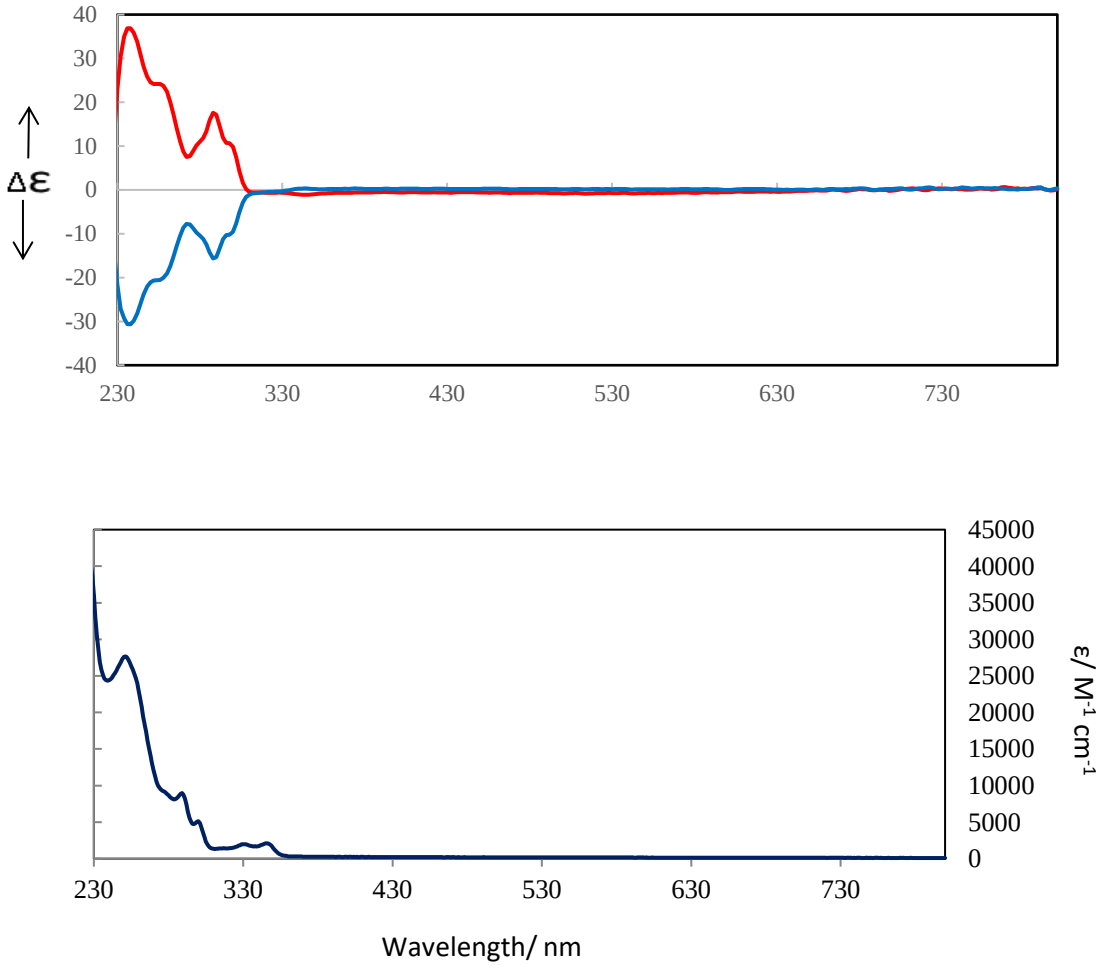
Electronic circular dichroism of 14-Bromo-11b*H*-benzo[*a*]chromeno[2,3,4-*kl*]xanthene (23A)

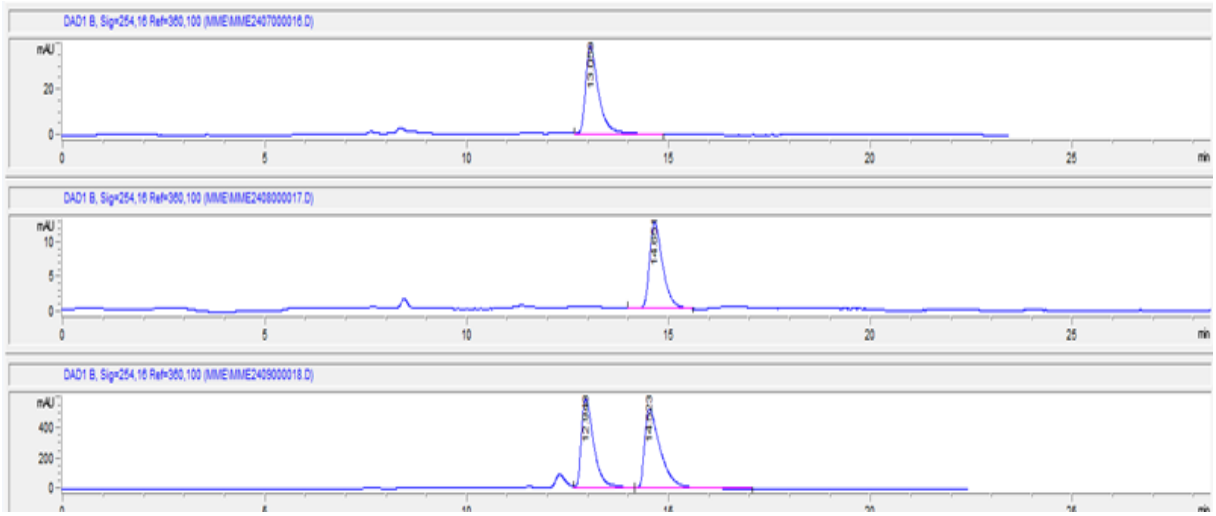
ECD spectra of compounds derived from the first and second eluted enantiomers of reduced dioxa **23A** recorded in CH_2Cl_2 solutions (2.10^{-5} M) at 20 °C.



Resolution of the enantiomers of 14-Bromo-3,7-dipropyl-7,11b-dihydro-3*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridine (25A)

The enantiomers of compound **25A** were separated by using semi preparative Chiralcel Ib column (1 x 25 cm) under the following conditions: 12 mg of **25A** dissolved in 900 µL of eluent; eluent hexane:THF 99:1; injection 3 x 250 µL; flow rate 0.5 ml/min.
Isolated was the cationic form of **25A** within 3 injections:
25A-a – 1.2 mg, retention time 12.9 min (>99 % ee)
25A-b – 1.1 mg, retention time 14.5 min (>99 % ee)

Enantiomeric purity determination:
The enantiomeric purity was determined by CSP-HPLC (Chiralcel IB column, hexane:THF 99:1, 0.5 ml/min flow rate, 23°C, diode array detector).



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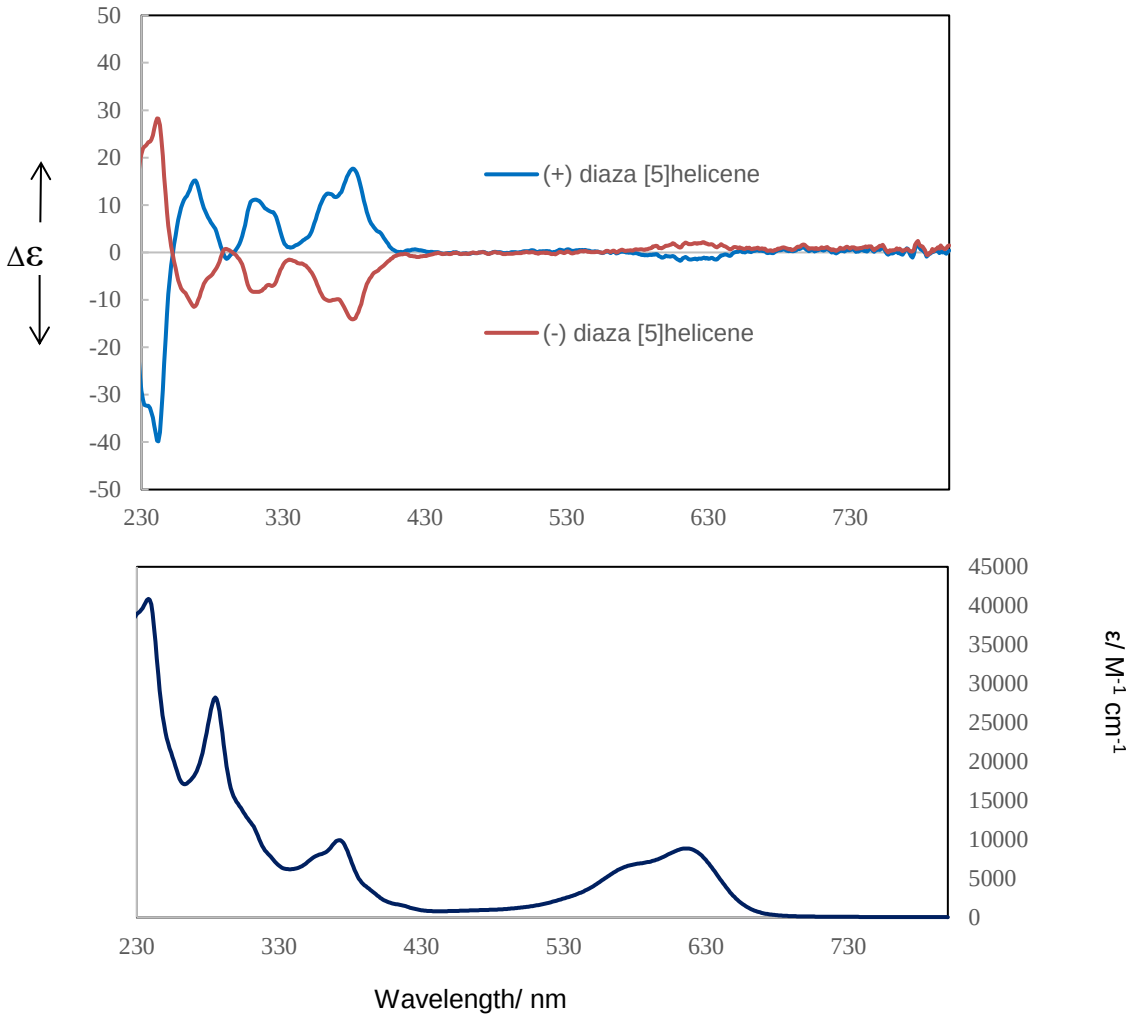
Barcode	
Operator	maya
Method	MM_IBTHF1.M
Analysis Time	23.467 min
Sampling Rate	0.0067 min (0.402 sec), 3521 datapoints

Electronic circular dichroism of the cationic species generated from 25A-a and 25A-b in CH_2Cl_2.

The enantiomers of cationic species of **14-Bromo-3,7-dipropyl-7,11b-dihydro-3H-benzo[a]quinolino[2,3,4-kl]acridine** (**9A**) form spontaneously the corresponding cationic species, under air oxidation. The change is easily recognizable by the modification of the color from translucid in the neutral form (reduced) to dark blue in cationic state (oxidized). ECD spectra of compounds derived from the first and second eluted enantiomers of cationic diaza [5]helicene **9A** generated from **25A** are recorded in CH_2Cl_2 solutions (2.10^{-5} M) at 20 °C.



S-IV. Racemization barrier determination and VT-HPLC

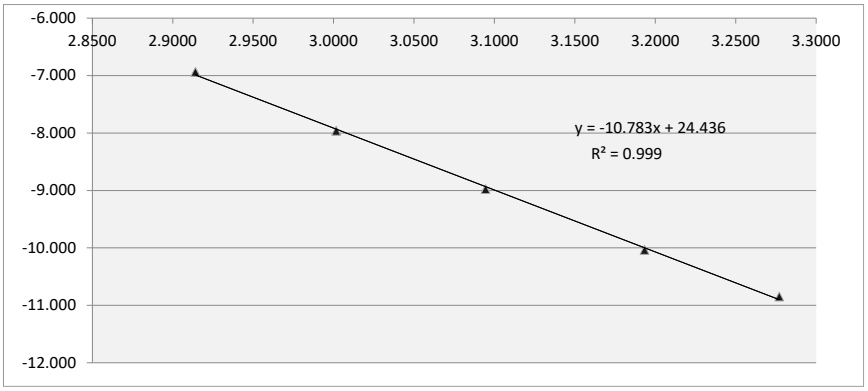
Determination of the kinetic barrier of racemization of 9A

General procedure for the racemization of the cationic species of 14-bromo-3,7-dipropyl-3,7-dihydro-11b*H*-benzo[*a*]quinolino[2,3,4-*kl*]acridin-11b-ylium salt (9A)

Circular dichroism "time course measurement" of cationic species of **(+)-9A** and **(–)-9A** (379 nm, c ~ 10^{-4} *M*, dimethyl sulfoxide) were recorded at 32 °C, 40 °C, 50 °C, 60 °C and 70 °C during 1000 s at single wavelength of 400 nm. The kinetic barrier of racemization was determined by mathematical treatment. In the scheme is shown the racemization barrier of cationic form of **(–)-9A.**
Activation parameters for the racemization of cationic form of (**9A**)- ln(k)=f(1000/T)

T [°C]	T [K]	1000/T	k (sec--1)	ln(k)	R-Square	DG	t1/2
32	305.15	3.2771	1.95E-05	-10.846	0.203119	102.3 kJ/mol	9.8828 h
40	313.15	3.1934	4.39E-05	-10.033	0.551	102.9 kJ/mol	4.3841 h
50	323.15	3.0945	0.000126	-8.977	0.887	103.5 kJ/mol	1.5239 h
60	333.15	3.0017	0.000349	-7.961	0.977	104.0 kJ/mol	0.5519 h
70	343.15	2.9142	0.000972	-6.936	0.988	104.2 kJ/mol	0.1980 h

slope=	-10.78 ±	0.20	- Ea/R	
intercept=	24.44 ±	0.61	Ln(A)	
T	70	°C		
Ea	89.7 ±	1.6	kJ/mol	21.4 ± 0.4 kcal/mol
A	4.1E+10 ±	1.0E+09		
ΔH# = Ea - RT		86.8 ±	-1.6 kJ/mol	20.8 ± -0.4 kcal/mol
ΔS# = R [ln(h*A/k*T)-1]		-51.2 ±	-1.3 $J.K^{-1}.mol^{-1}$	-12.3 ± -0.3 $cal.K^{-1}.mol^{-1}$
ΔG#		104.4 ±	-1.1 kJ/mol	25.0 ± -0.3 kcal/mol



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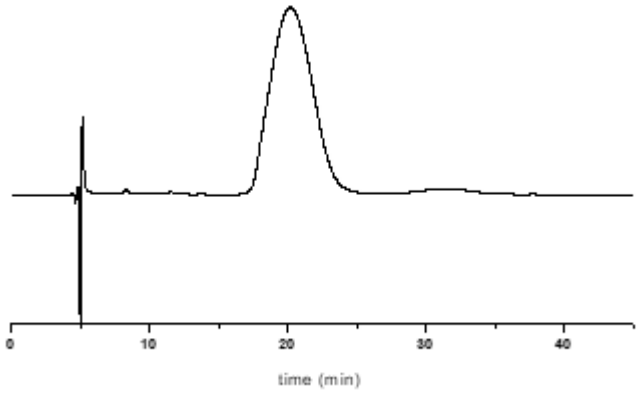
Determination of the kinetic barrier of racemization of dioxa 8A

Preliminary CSP HPLC experiments

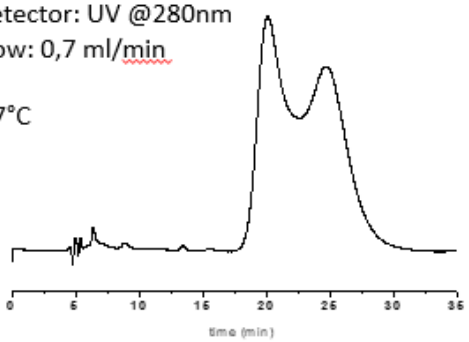
Column: Chiralpak IA 250x4.6 mm
Eluent: MeOH + 0.6%TFA / 0.4% TEA
Detector: UV @280nm
Flow: 0,7 ml/min
T = 25°C



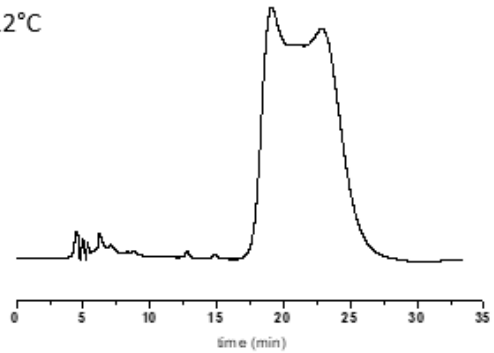
VT-HPLC

Column: Chiralpak IA 250x4.6 cm
Eluent: MeOH + 0.6%TFA / 0.4% TEA
Detector: UV @280nm
Flow: 0,7 ml/min

T 7°C



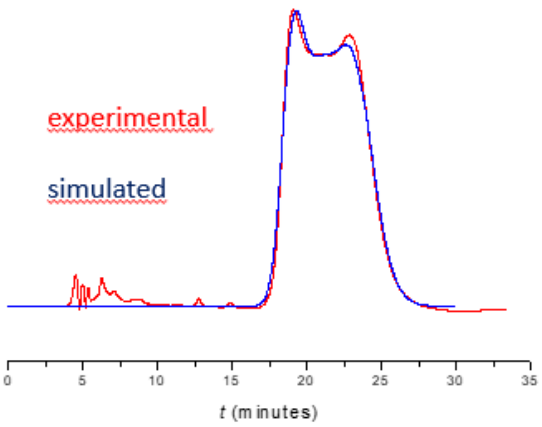
T 12°C



Experimental and simulated
HPLC plots for di-oxa 8A T=12°C

deltaGap#1-2 = 20.6441 Kcal 86.2922 KJ
deltaGap#2-1 = 20.7697 Kcal 86.8172 KJ

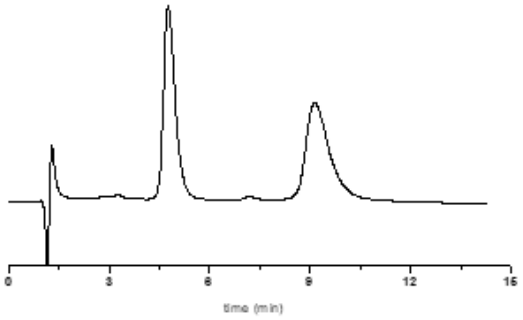
kap12 = .5368311E-01
kap21 = .4301145E-01



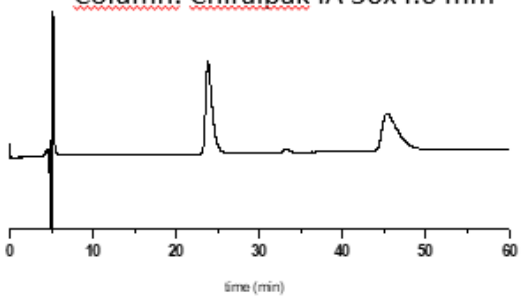
Determination of the kinetic barrier of racemization of dioxa 8B

Preliminary CSP HPLC experiments

Column: Chiralpak IA 250x4,6 mm
Eluent: MeOH + 0.6%TFA / 0.4% TEA
Detector: UV @280nm
Flow: 0,7 ml/min
T = 25°C

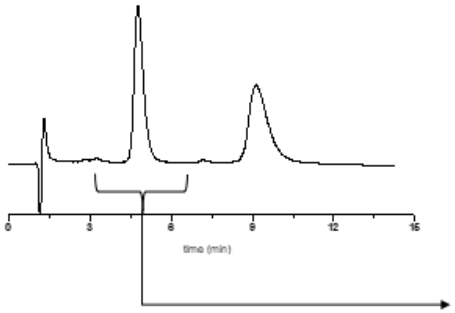


Column: Chiralpak IA 50x4.6 mm

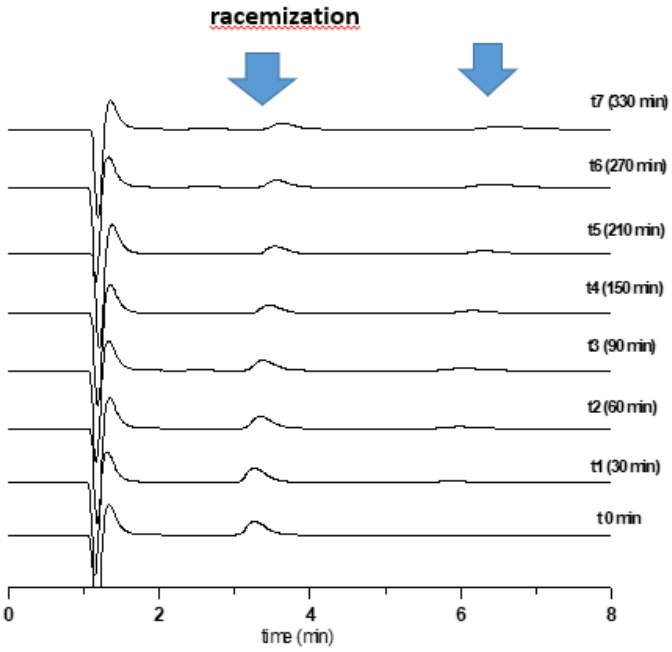


CSP Resolution and subsequent racemization study

Column: Chiralpak IA 50x4.6 mm
Eluent: MeOH + 0.06%TFA / 0.04% TEA
Detector: UV @280nm
Flow: 0,7 ml/min



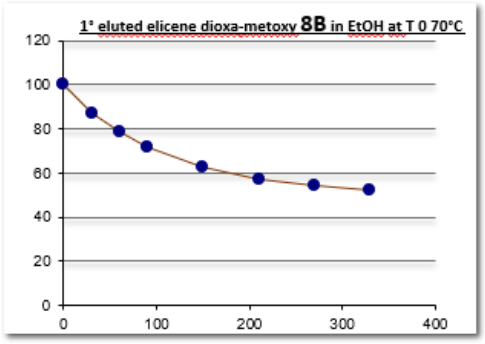
Single enantiomer obtained
by semiprep HPLC on
Chiralpak IA 250*10 mm

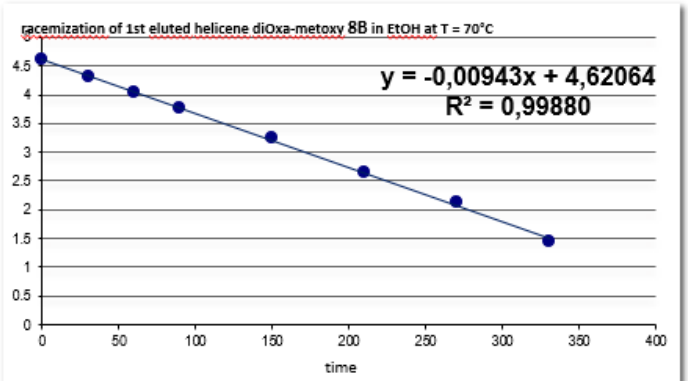


Column: Chiralpak IA 50*4.6 mm
Eluent: MeOH TFA 0,06% TEA 0,04%
Flow: 0.7 ml/min
Detector: UV@280 nm

T°C column: 25°C
T°C sample: 70°C
Reaction solvent: EtOH

Racemization parameters





T 70 °C

k_{rac} min^{-1}	$DG^{\neq}_{rac}$ (kcal/mol)
0,0094	26,15

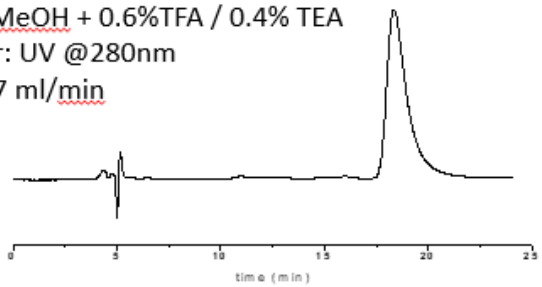
Calculated $k_{en} = k_{rac}/2 = 0{,}0047\ min^{-1}$

$\Delta G^{\neq}_{en}$ (kcal/mol) = 26,63

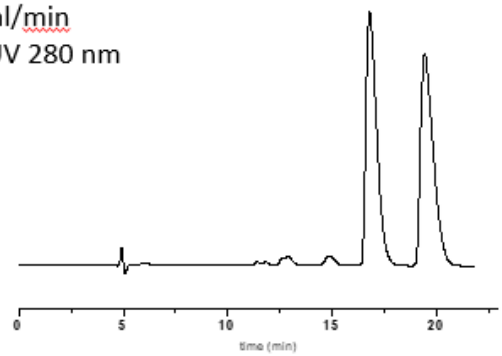
Determination of the kinetic barrier of racemization of dioxa 9B

Preliminary CSP HPLC experiments

Column: Chiralpak IA 250x4.6 cm
Eluent: MeOH + 0.6%TFA / 0.4% TEA
Detector: UV @280nm
Flow: 0,7 ml/min
T = 25°C

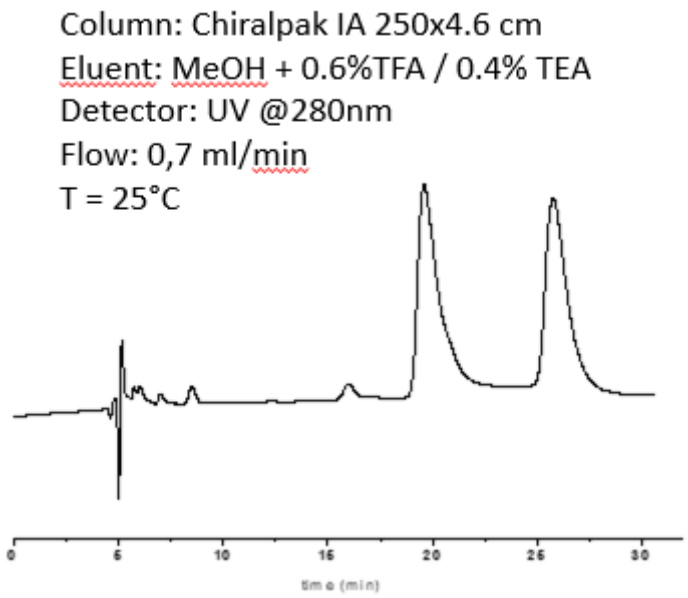


Column: Chiralpak IC (250x4.6 mm)
Eluent: MeOH/ACN/TFA/TEA 80:20:0,06:0,04
Flow: 0,7 ml/min
Detector: UV 280 nm
T = 25°C

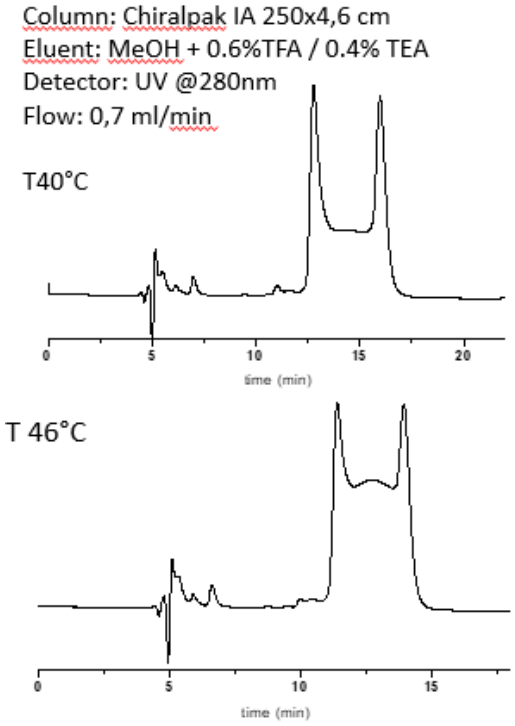


Determination of the kinetic barrier of racemization of dioxa 10A

Preliminary CSP HPLC experiments

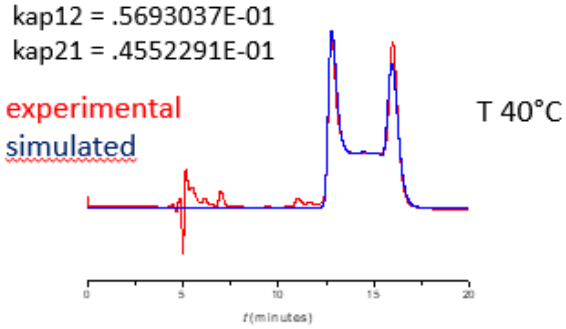


VT-HPLC

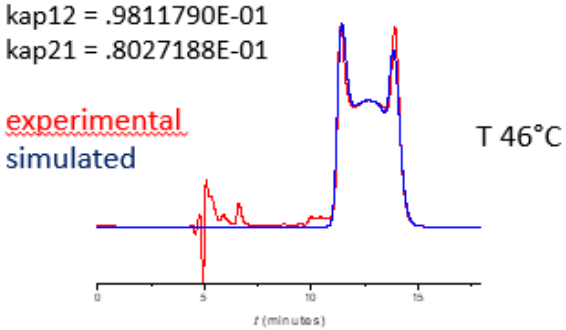


Experimental and simulated
HPLC plots for aza-oxa 10A T=40°C & T=46°C

deltaGap#1-2 = 22.6929 Kcal 94.8565 KJ
deltaGap#2-1 = 22.8321 Kcal 95.4381 KJ
kap12 = .5693037E-01
kap21 = .4552291E-01



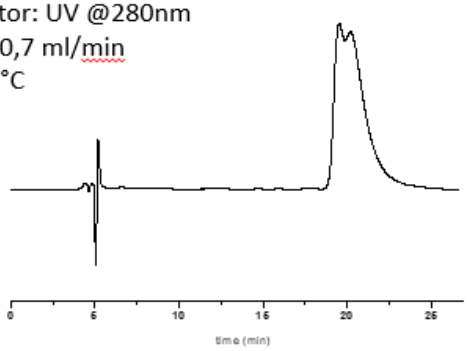
deltaGap#1-2 = 22.7945 Kcal 95.2812 KJ
deltaGap#2-1 = 22.9219 Kcal 95.8134 KJ
kap12 = .9811790E-01
kap21 = .8027188E-01



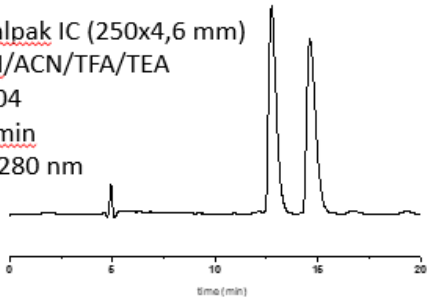
Determination of the kinetic barrier of racemization of dioxa 10B

Preliminary CSP HPLC experiments

Column: Chiralpak IA 250x4,6 cm
Eluent: MeOH + 0.6%TFA / 0.4% TEA
Detector: UV @280nm
Flow: 0,7 ml/min
T = 25°C

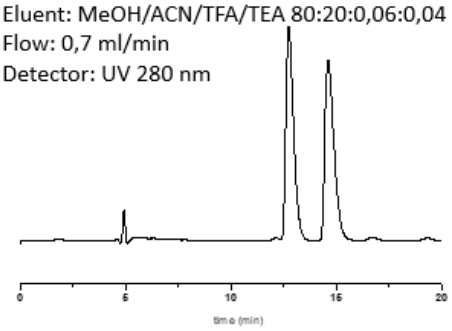


Column: Chiralpak IC (250x4,6 mm)
Eluent: MeOH/ACN/TFA/TEA
80:20:0,06:0,04
Flow: 0,7 ml/min
Detector: UV 280 nm
T = 25°C

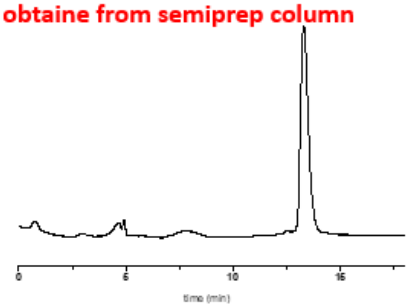


CSP Resolution and subsequent racemization study

Column: Chiralpak IC (250x4.6 mm)
Eluent: MeOH/ACN/TFA/TEA 80:20:0,06:0,04
Flow: 0,7 ml/min
Detector: UV 280 nm

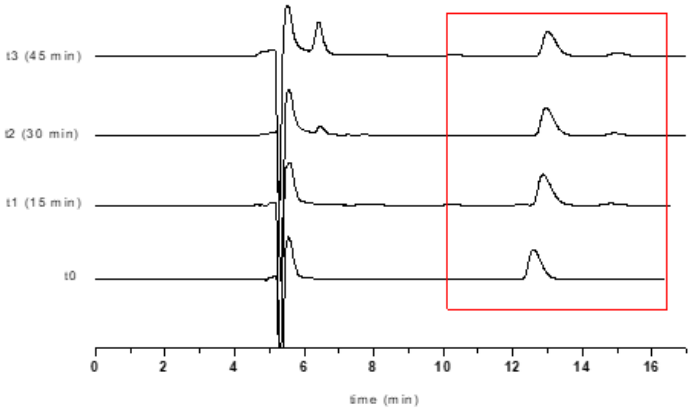


1st eluted fron Chiralpak IC obtaine from semiprep column

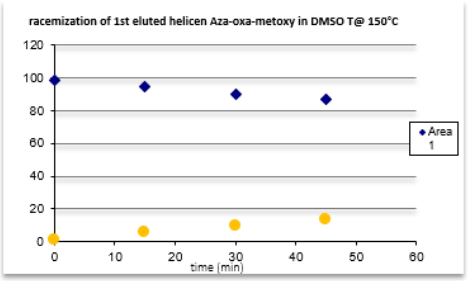


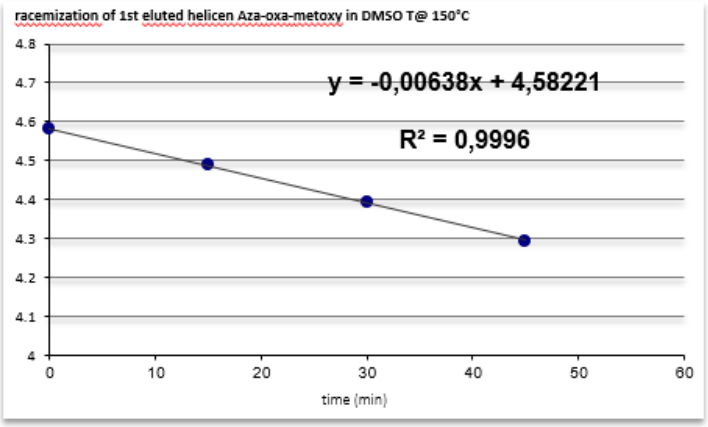
Solvent: DMSO
T°C reaction: 150°C
Column: Chiralpak IC 250x4.6 mm
Eluent: MeOH/ACN/TFA/TEA 80:20:0,06:0,04
Flow: 0,7 ml/min
Detector: UV 280 nm

Racemization of 10B



Racemization parameters





T 150 °C

k_{rac} min^{-1}	$DG^{\neq}_{rac}$ (kcal/mol)
0,00638	32,75

Calculated $k_{en} = k_{rac}/2 = 0,0032\ min^{-1}$

$\Delta G^{\neq}_{en}$ (kcal/mol) = 33,33

Table S 1. Enantiomerization by dynamic HPLC on Chiralpak IA. Racemization after enantiomer isolation by HPLC. *

		ENANTIOMERIZATION							RACEMIZATION		
compound	T (°C)	$k_{en\ 12}$ min^{-1}	$\Delta G^{\neq}_{en\ 12}$ (kcal/mol)	$k_{en\ 21}$ min^{-1}	$\Delta G^{\neq}_{en\ 21}$ (kcal/mol)	$k_{en\ av}$ min^{-1}	$\Delta G^{\neq}_{en\ av}$ (kcal/mol)	solvent	T (°C)	k_{rac} min^{-1}	$\Delta G^{\neq}_{rac}$ (kcal/mol)
										calculated from $k_{rac}=2*k_{en\ av}$	
DIOXA **8A**	12	0,054	20,64	0,043	20,77	0,048	20,705	Mix*	12	0,0970	20,31
DIOXA-MeO **8B**						0,0047	26,63	EtOH	70	0,0094	26,15
AZAOXA **10A**	40	0,057	22,69	0,045	22,83	0,051	22,76	Mix*	40	0,1025	22,32
AZAOXA **10A**	46	0,098	22,79	0,08	22,92	0,089	22,855	Mix*	46	0,1780	22,41
AZAOXA-MeO **10B**						0,0032	33,33	DMSO	150	0,0064	32,75
DIAZA **9A**								DMSO	40-70		24,38
DIAZA-MeO **9B**								DMSO	150	e.e. unchanged after 1h	

*Mix is the HPLC eluent: MeOH + CF_3COOH 0.6% + Et_3N 0.4 %.