Rh(II)/Brønsted Acid Cocatalyzed Intramolecular Trapping of Ammonium Ylides with Enones: Diastereoselective Synthesis of 2,2,3-Trisubstituted Indolines

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[b]*College of Chemical & Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang, 050018 People's Republic of China*

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Supporting Information

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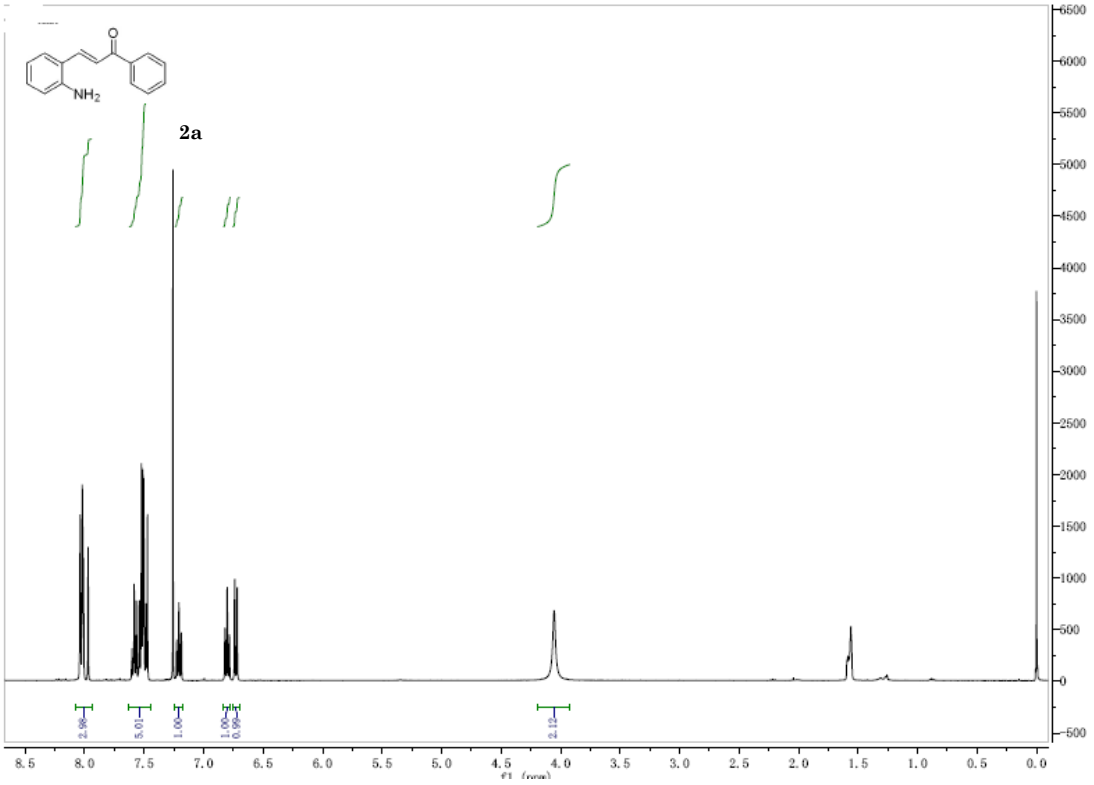
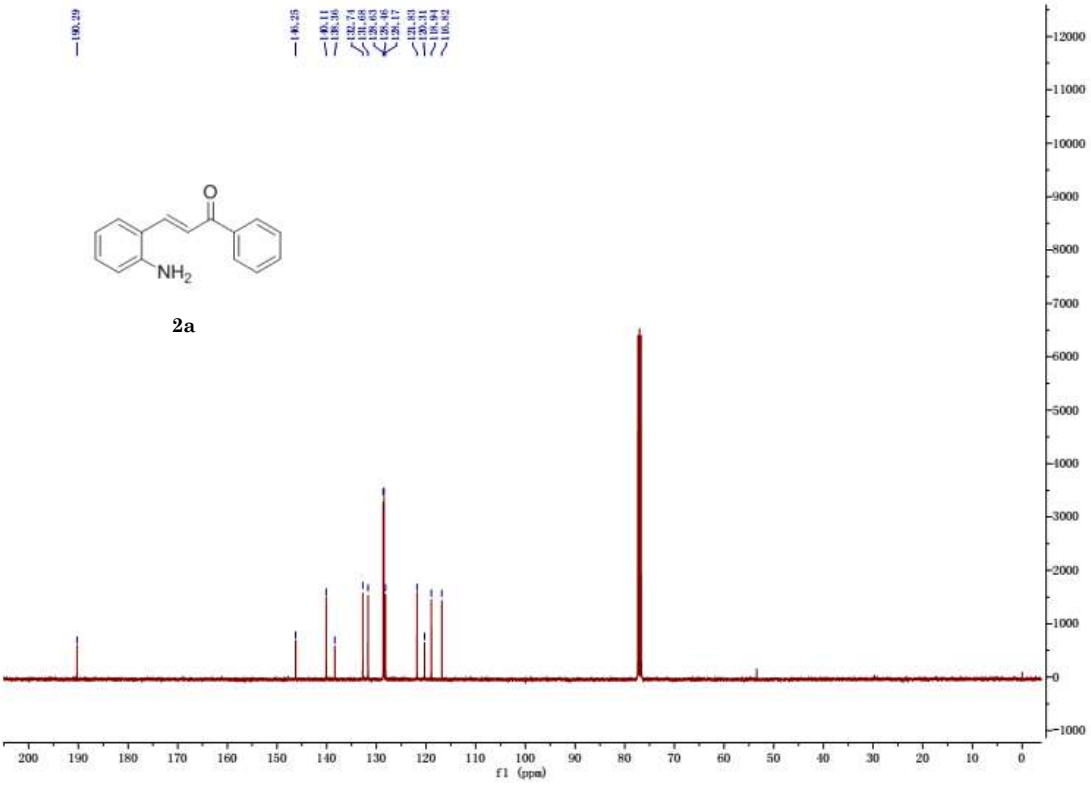
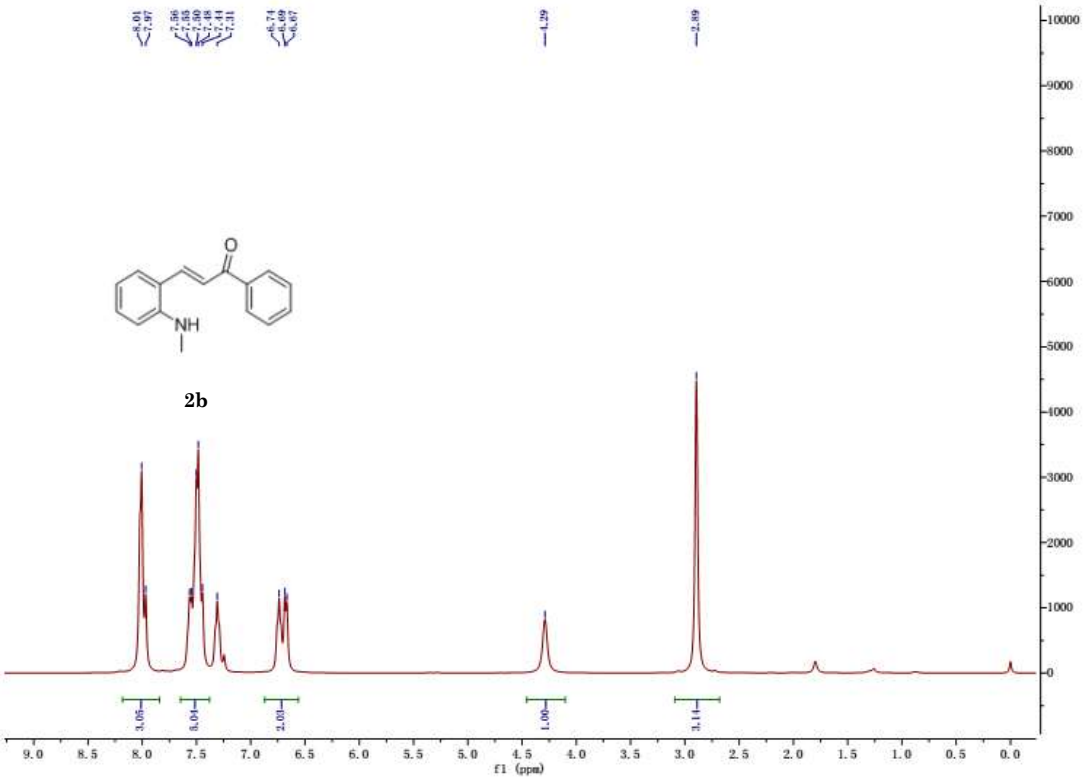
NMR spectra of compounds 1e-1h, 2b-2h



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O
NH
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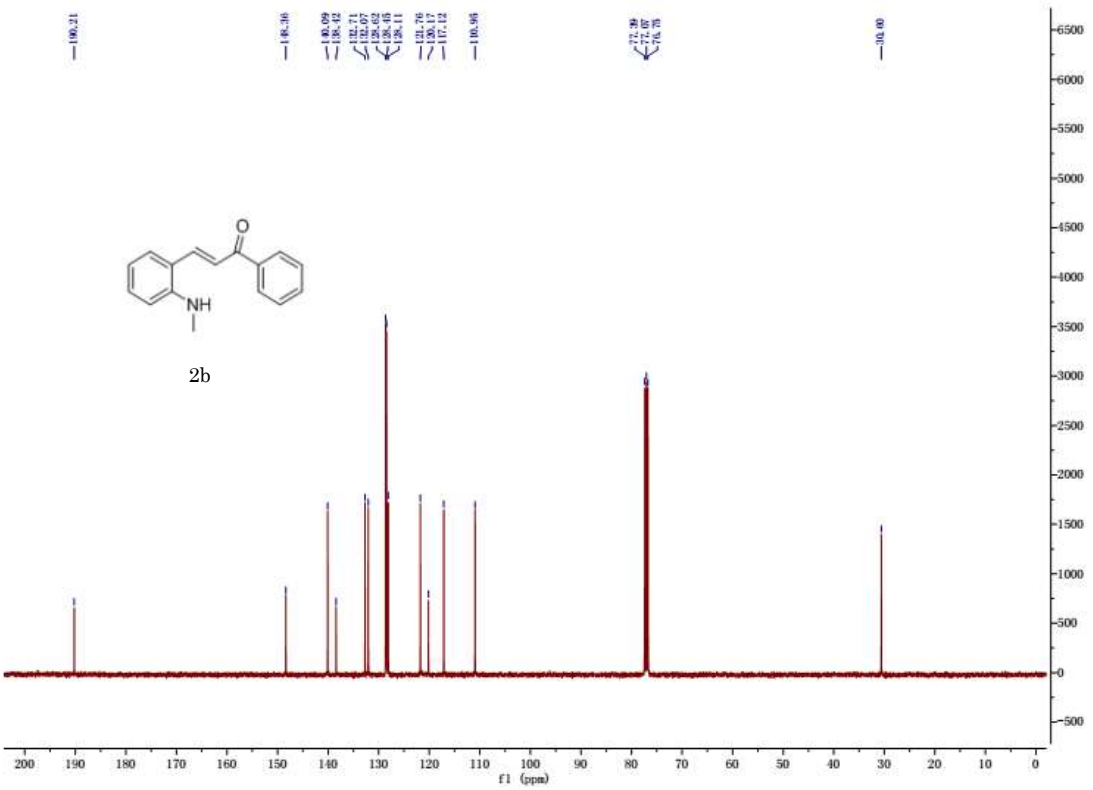
2.03
1.00
3.14
f1 (ppm)

2b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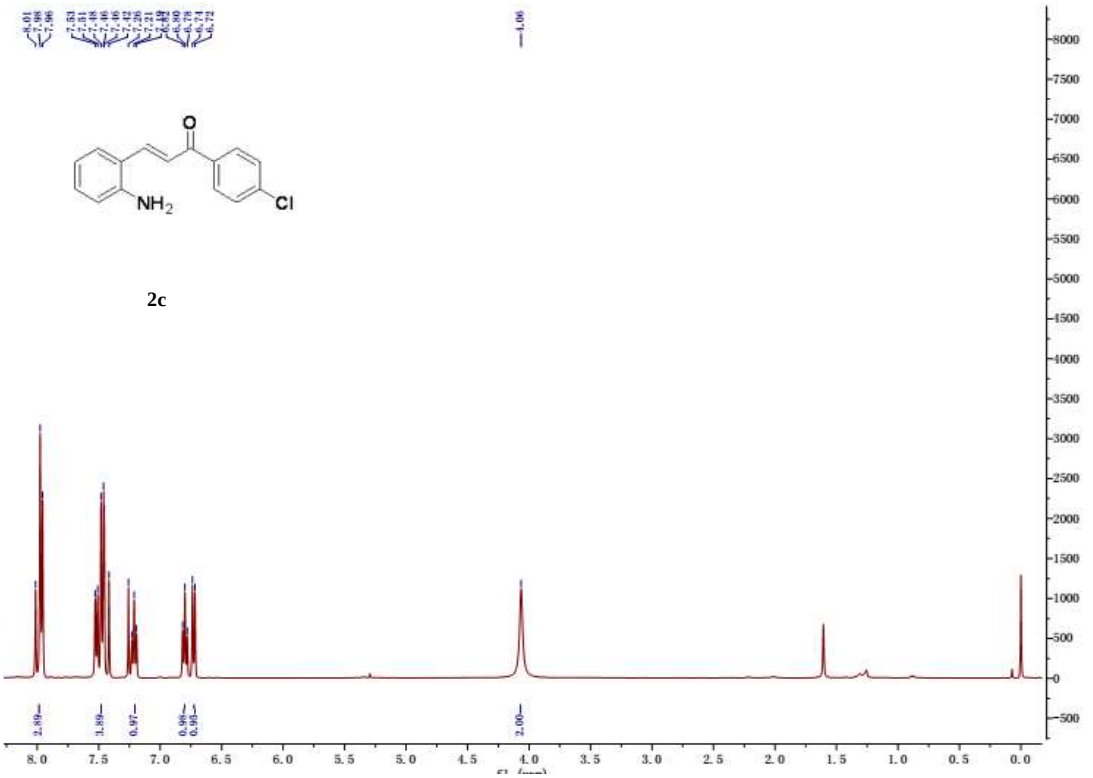
O
NH
f1 (ppm)

2b



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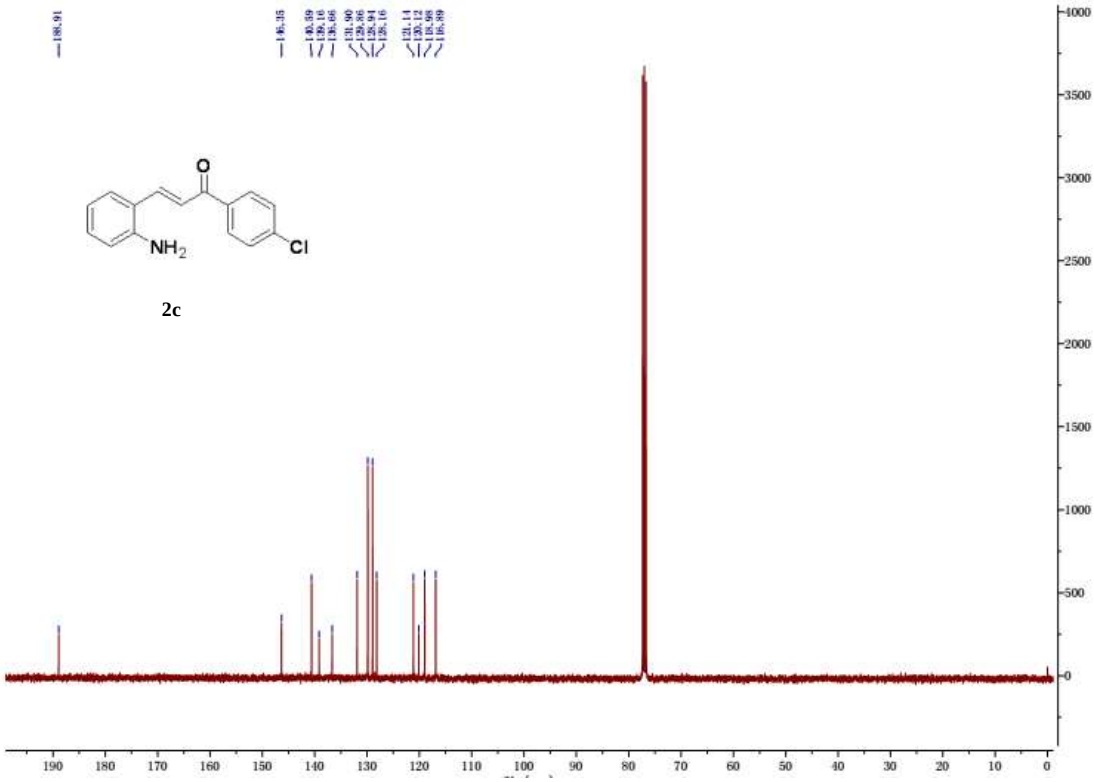

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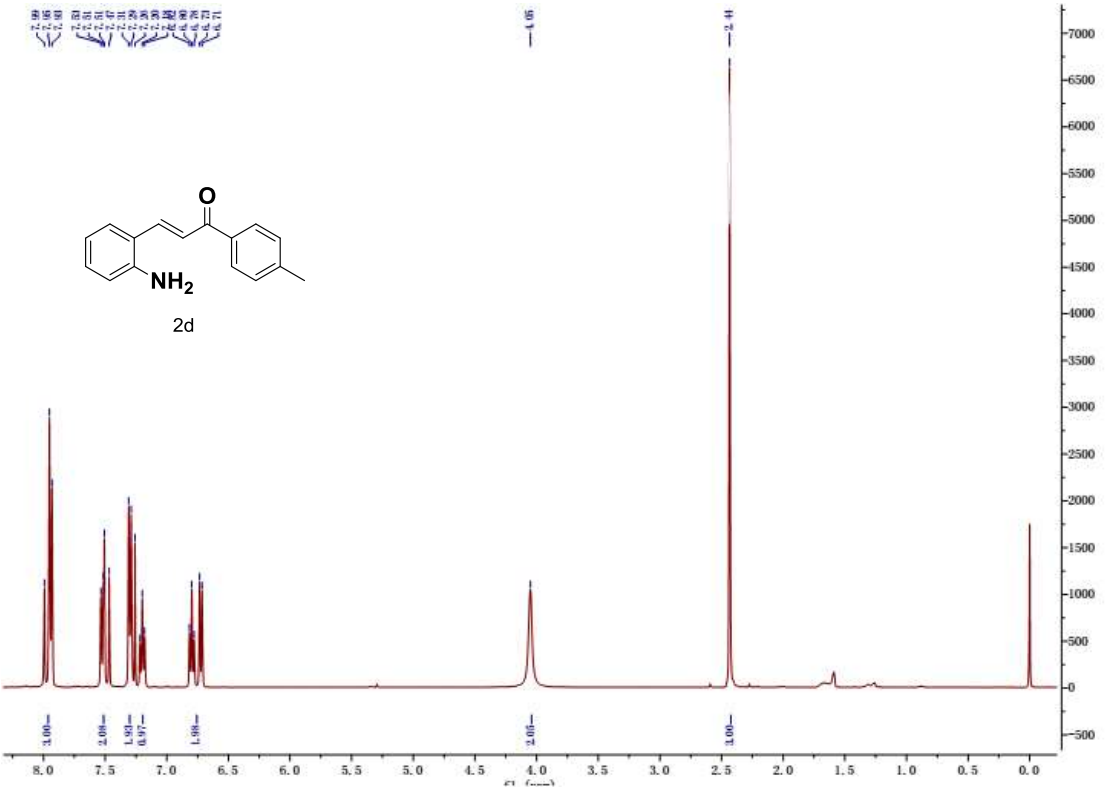

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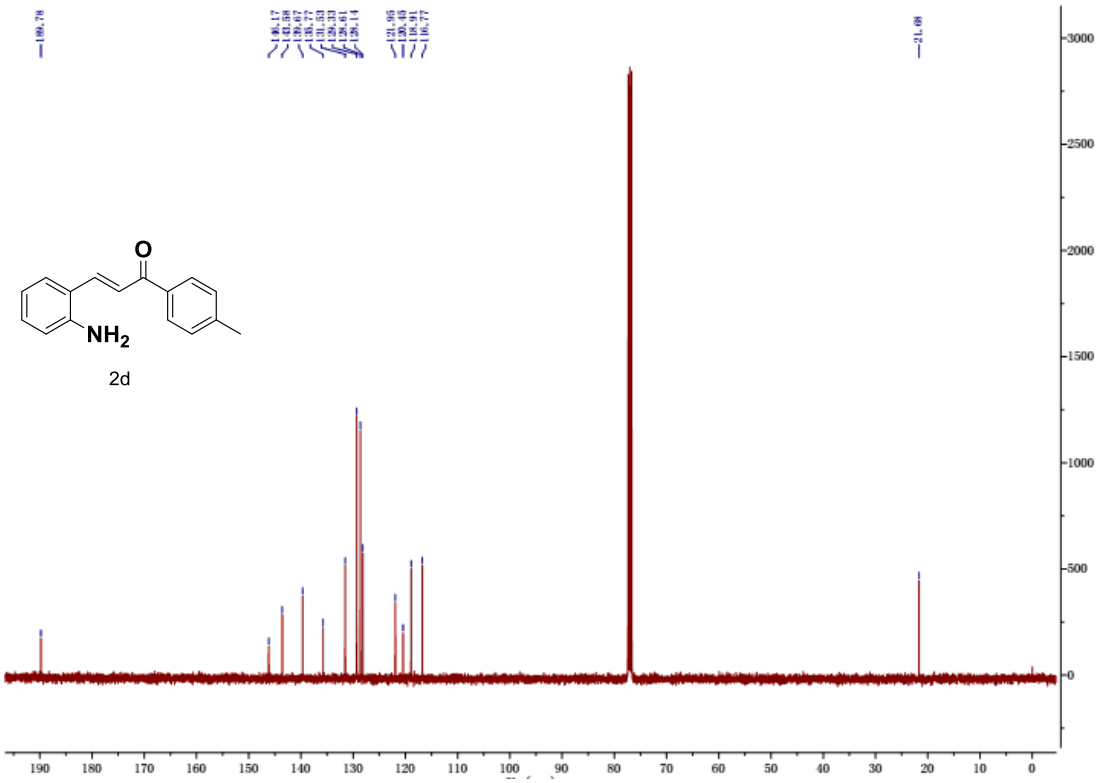

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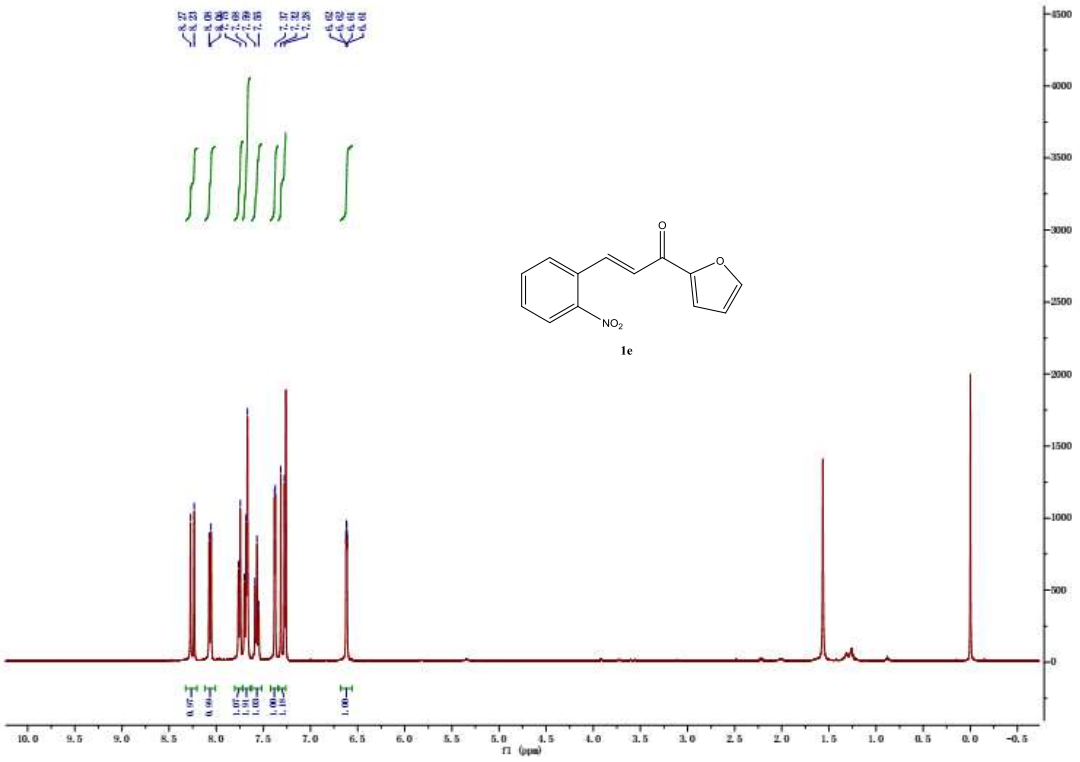
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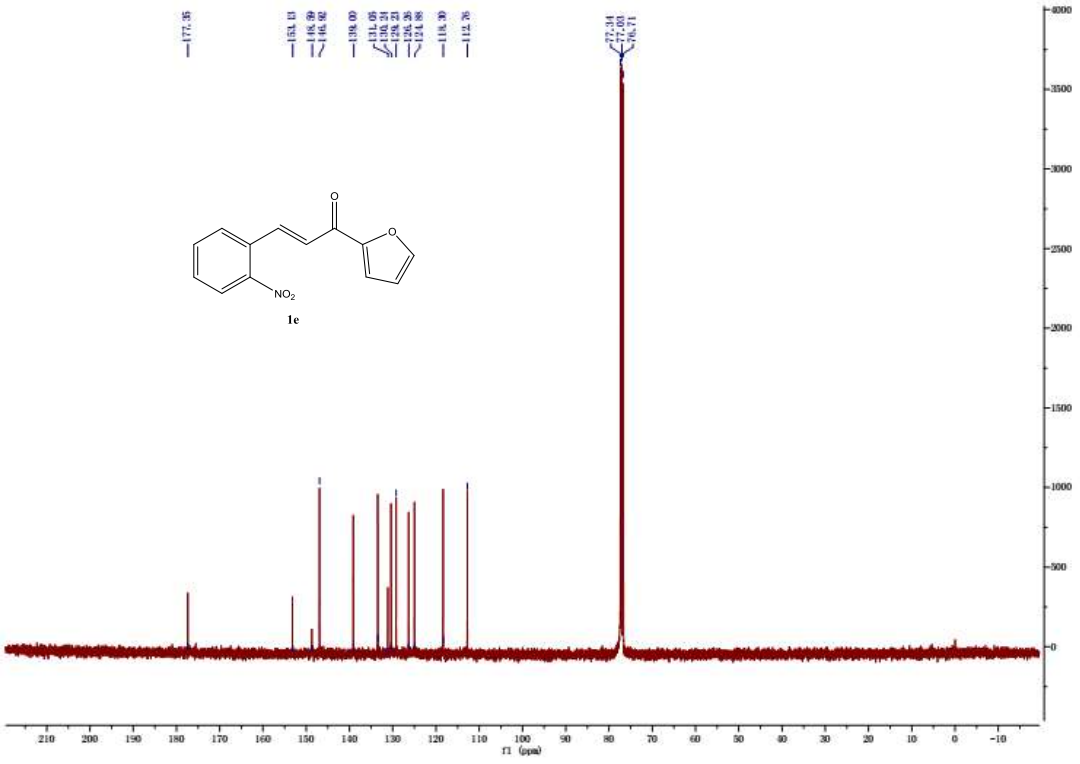
NO2
1e
f1 (ppm)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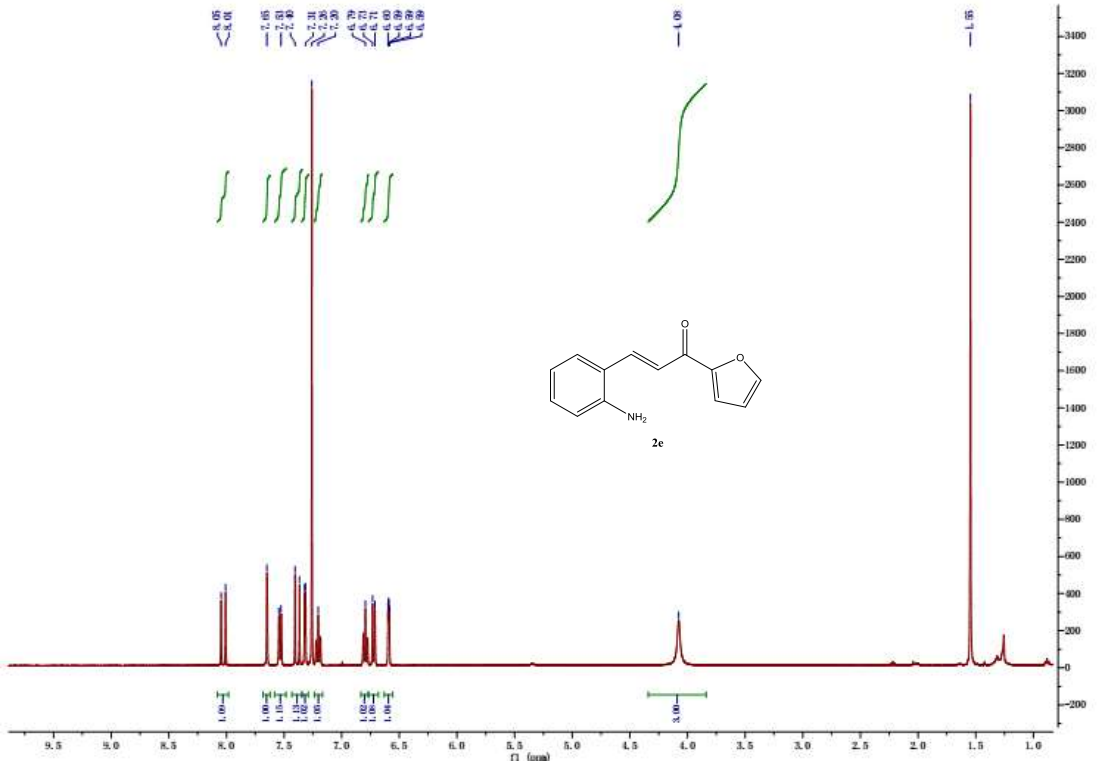
77.03
76.71
O
O
NO2
1e
f1 (ppm)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6.69
6.69
6.69
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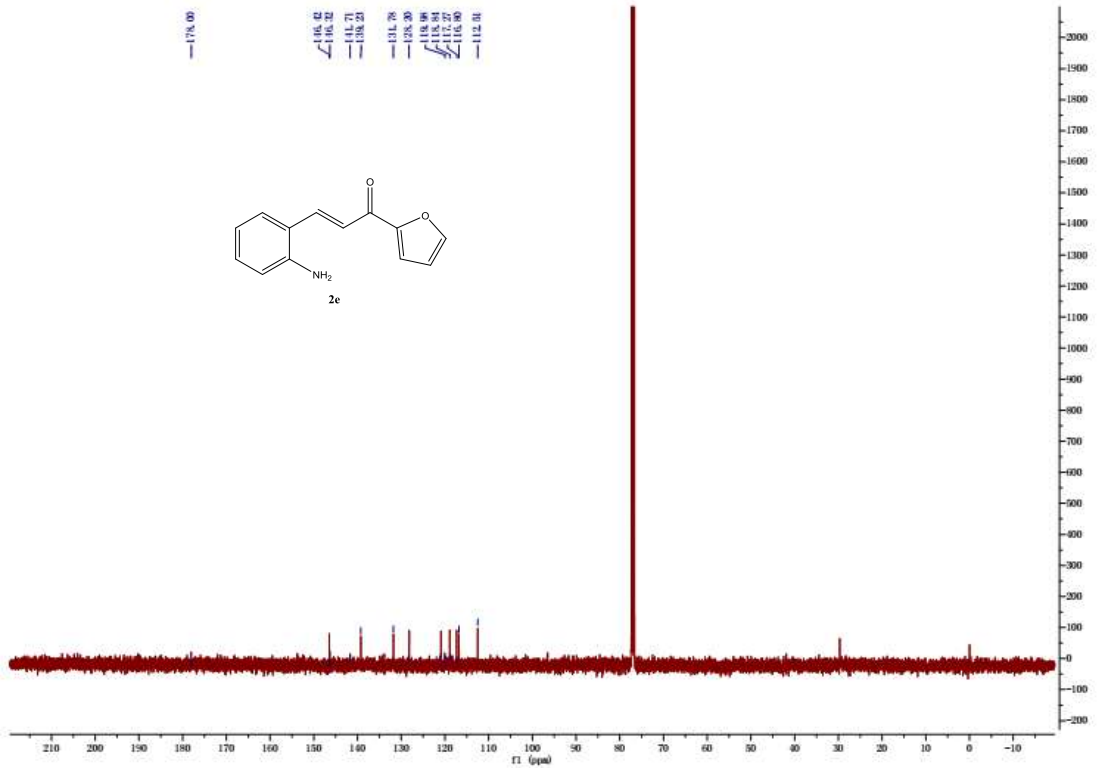
1.55
O
O
NH2
2e
f1 (ppm)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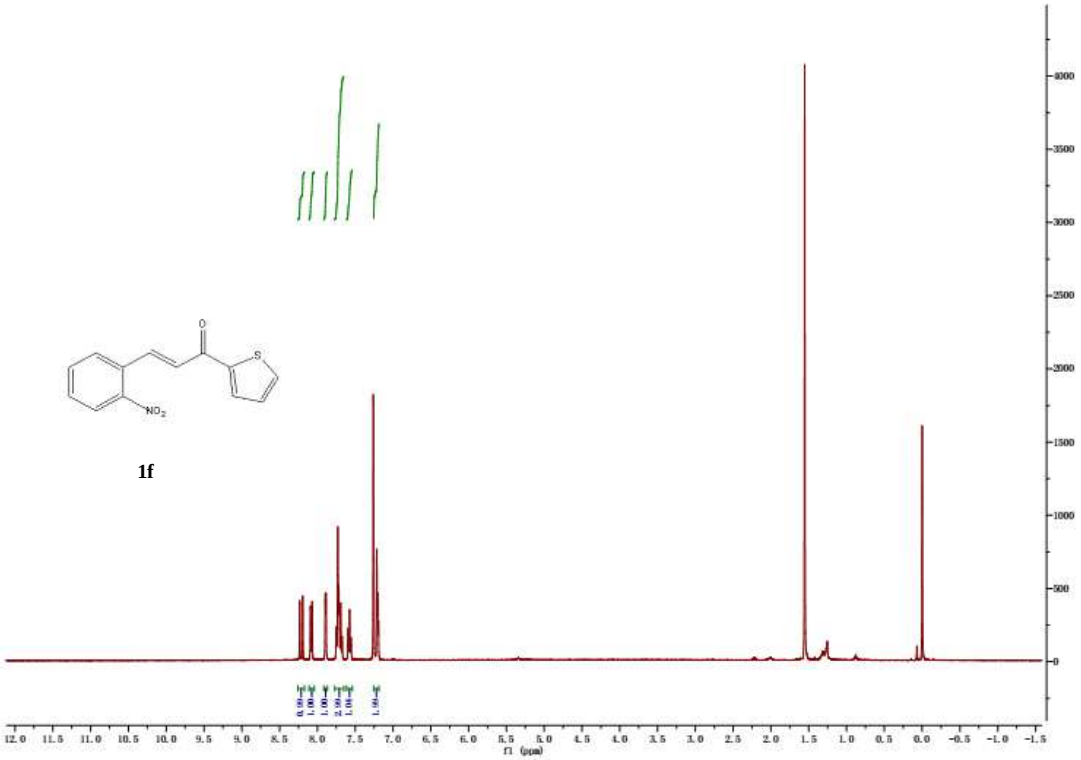
O
O
NH2
2e
f1 (ppm)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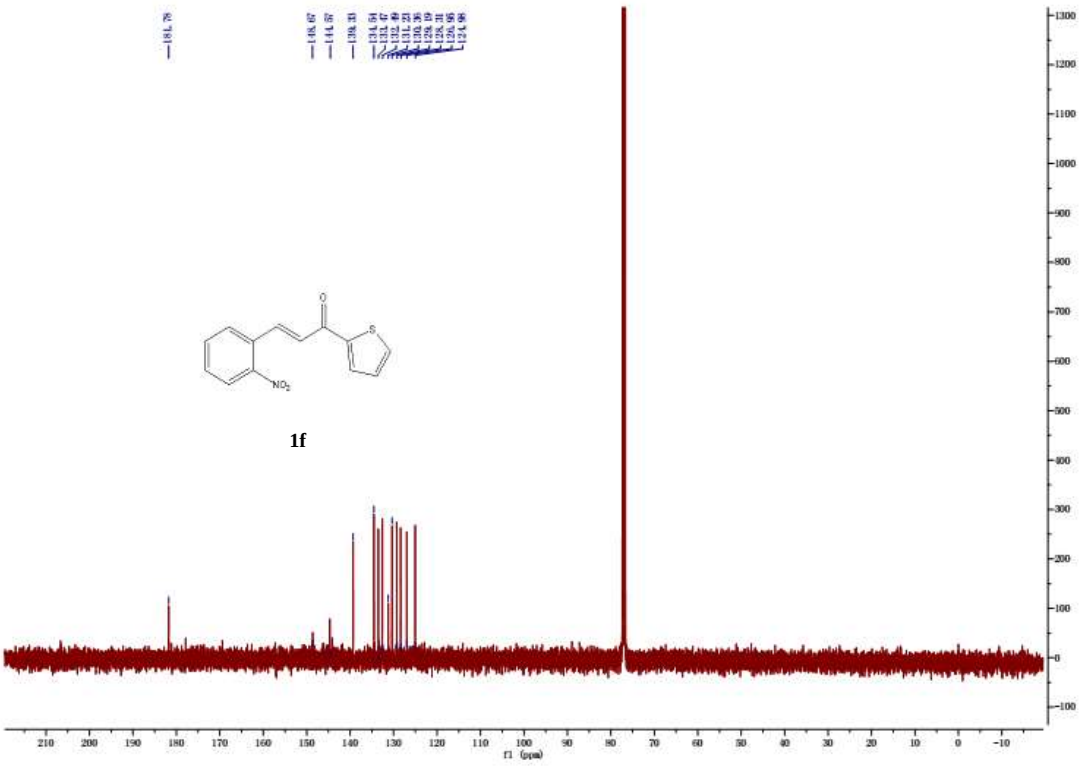
S
NO2

1f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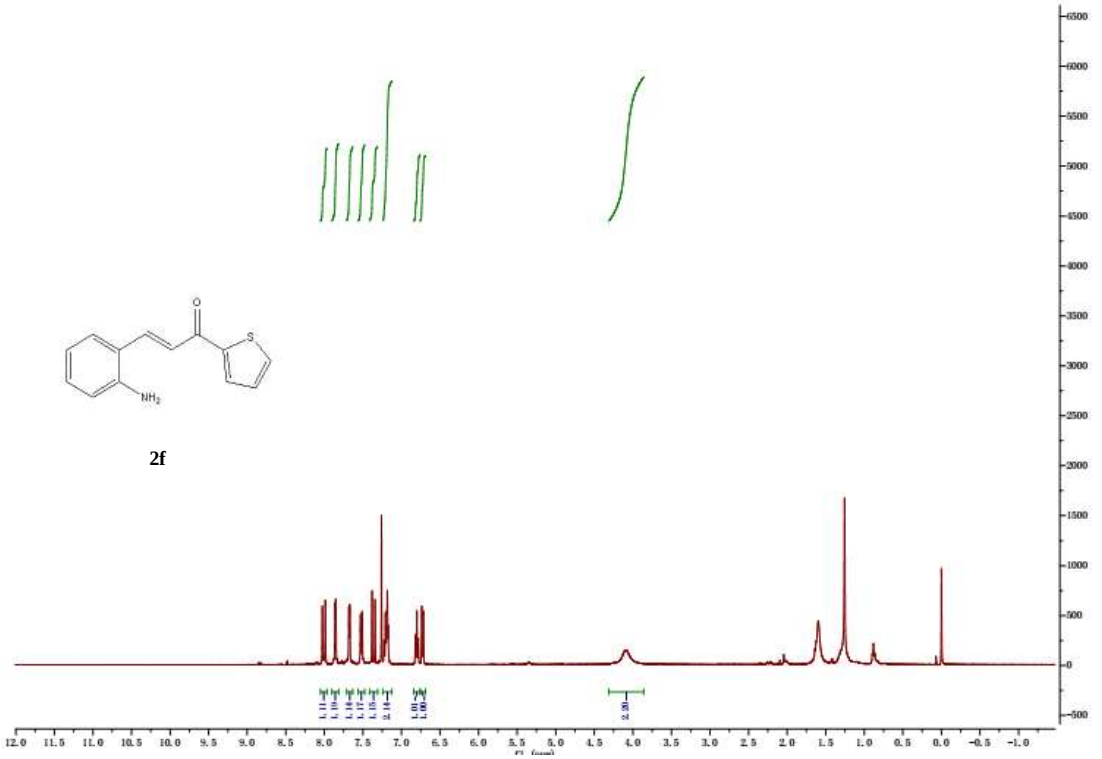
124.98
O
S
NO2

1f



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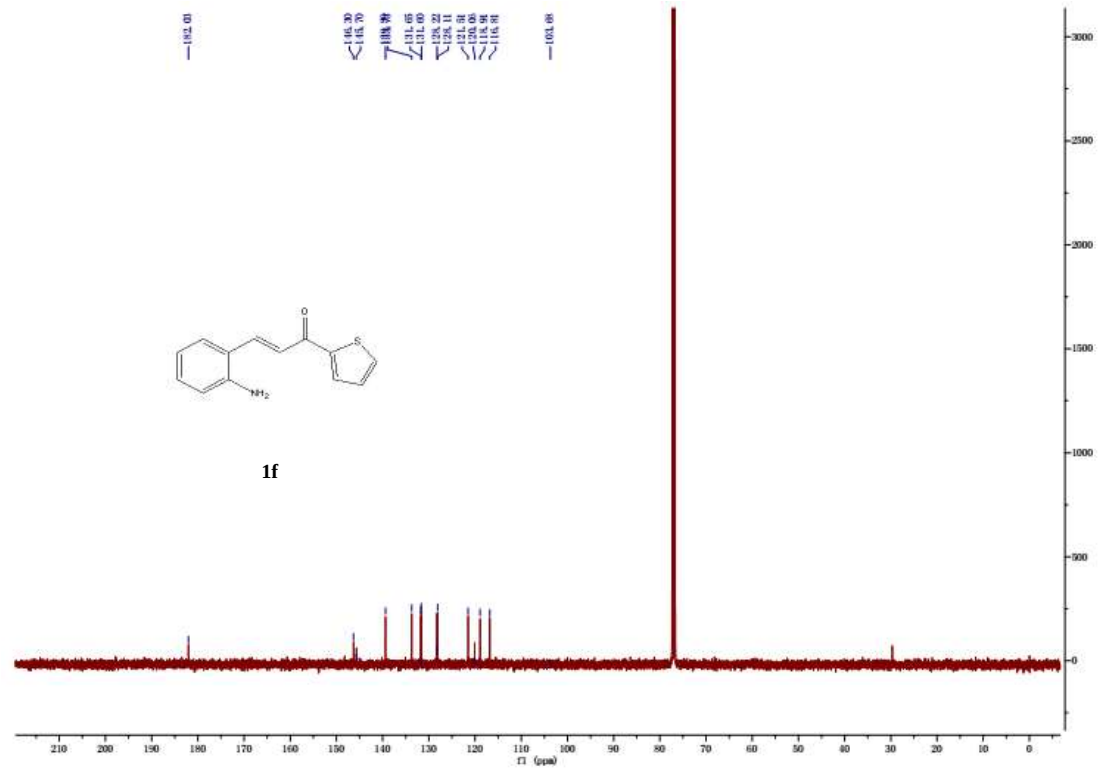

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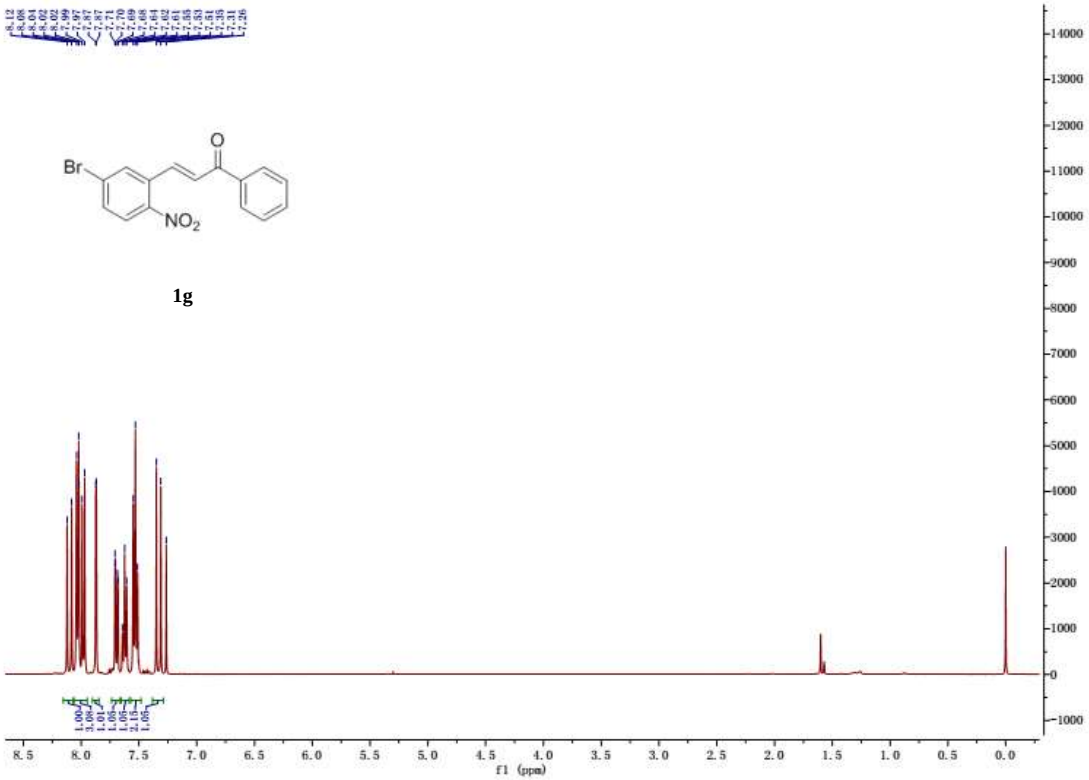

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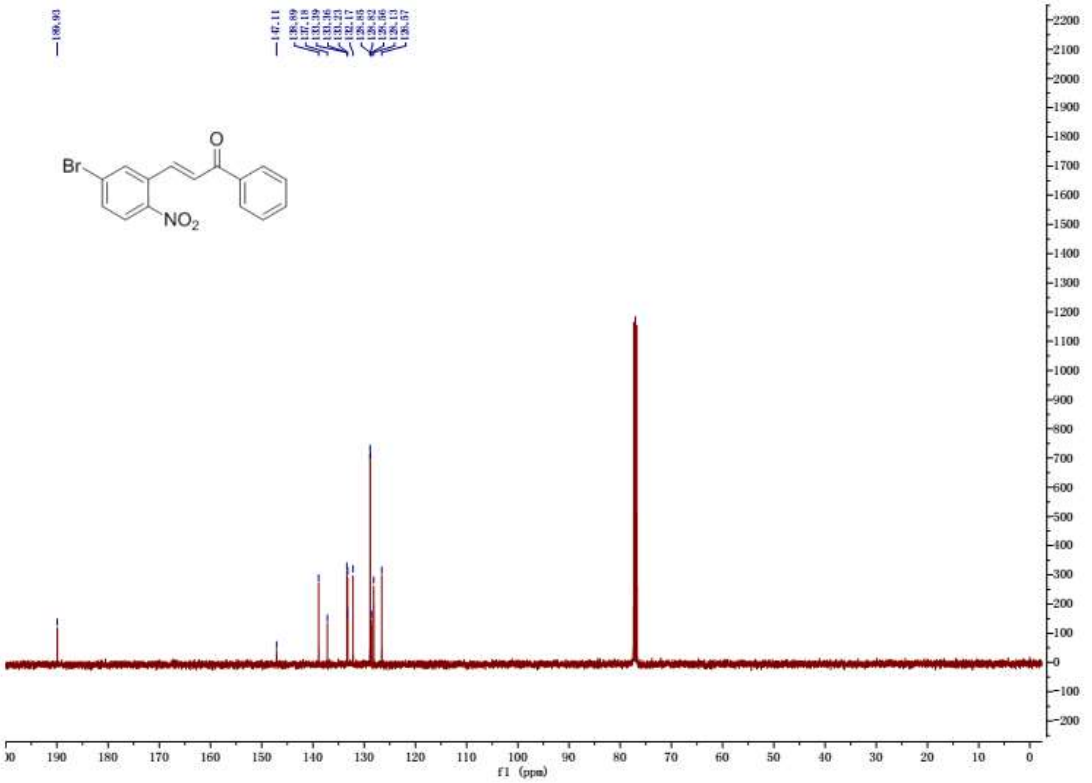

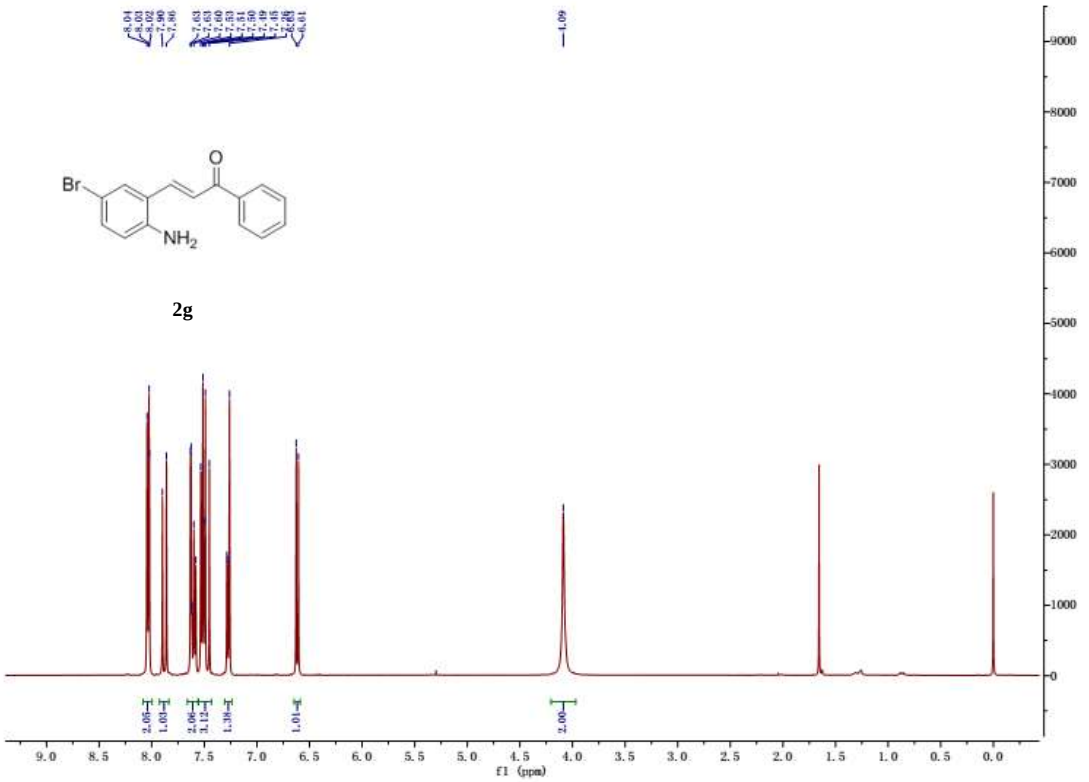

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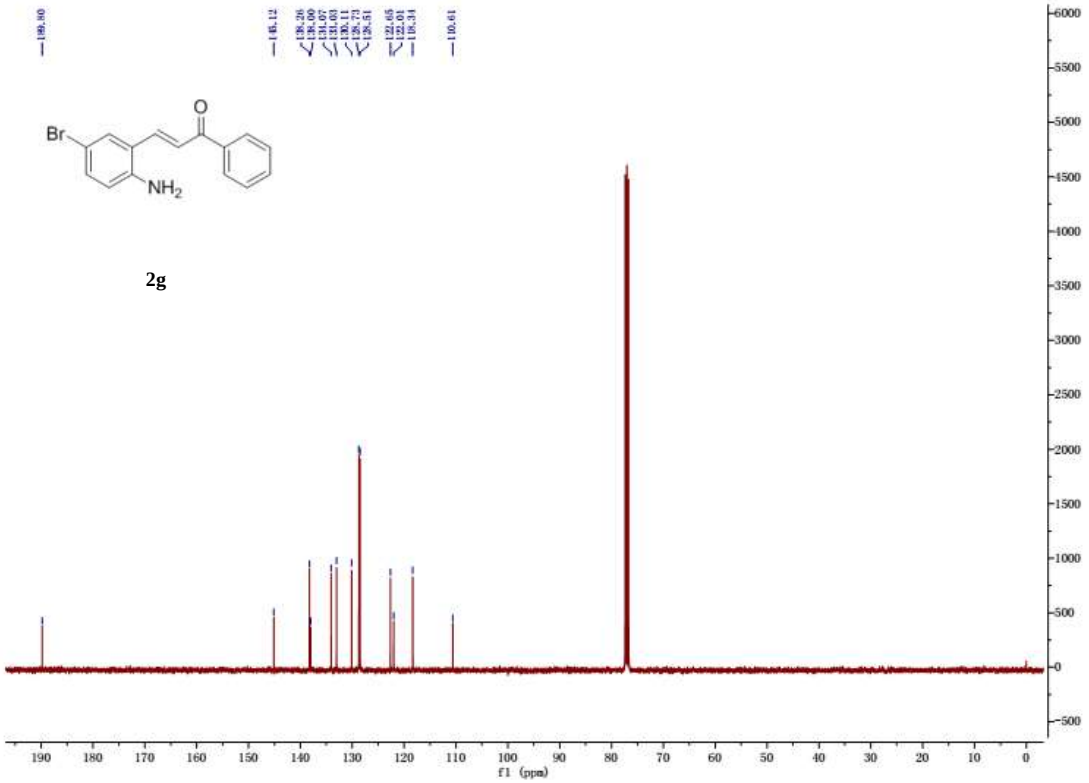

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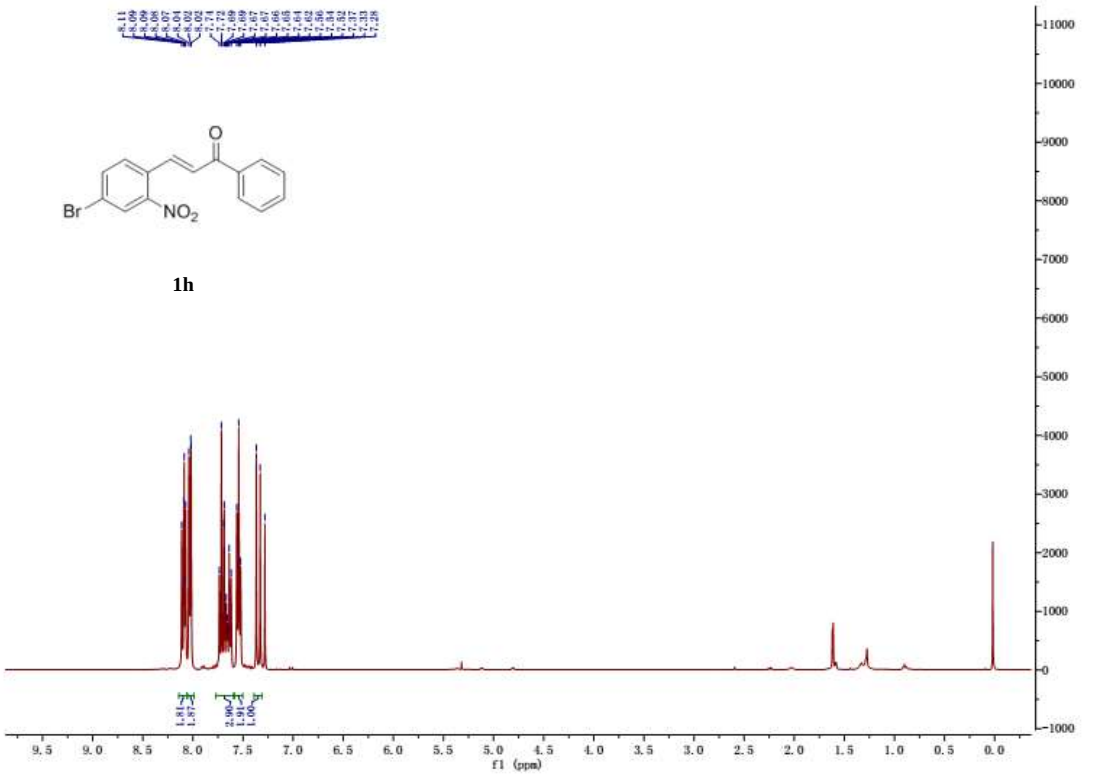

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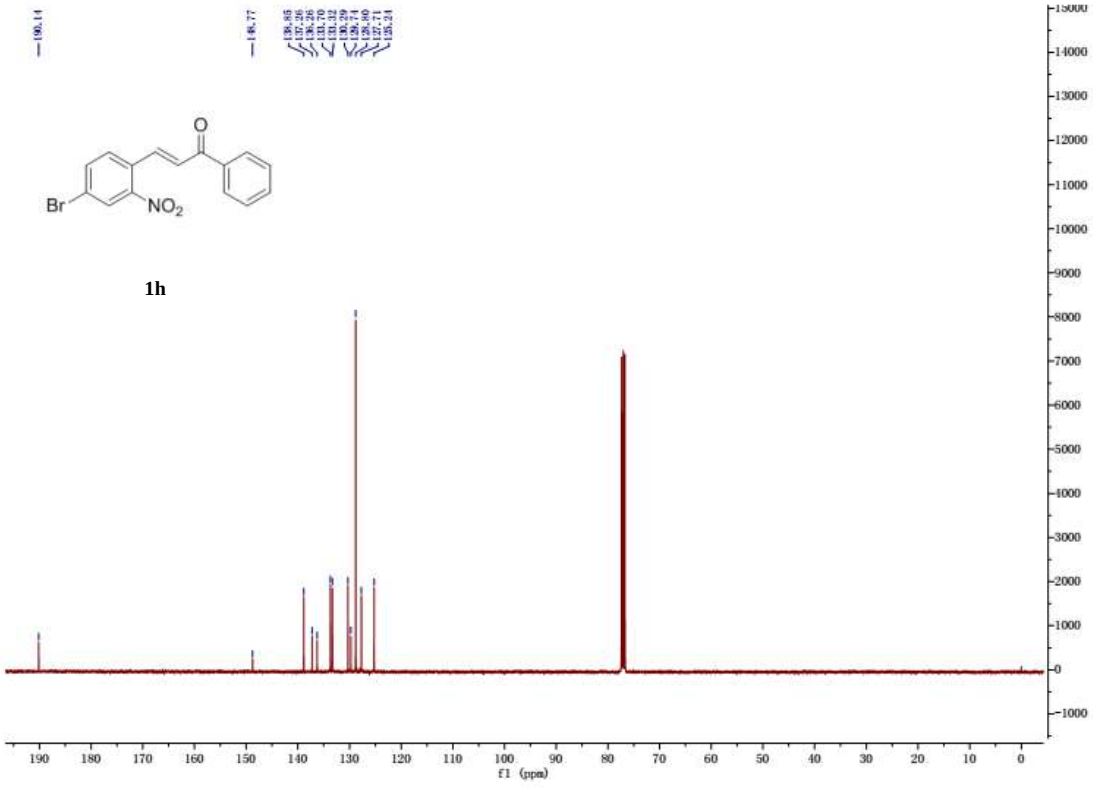

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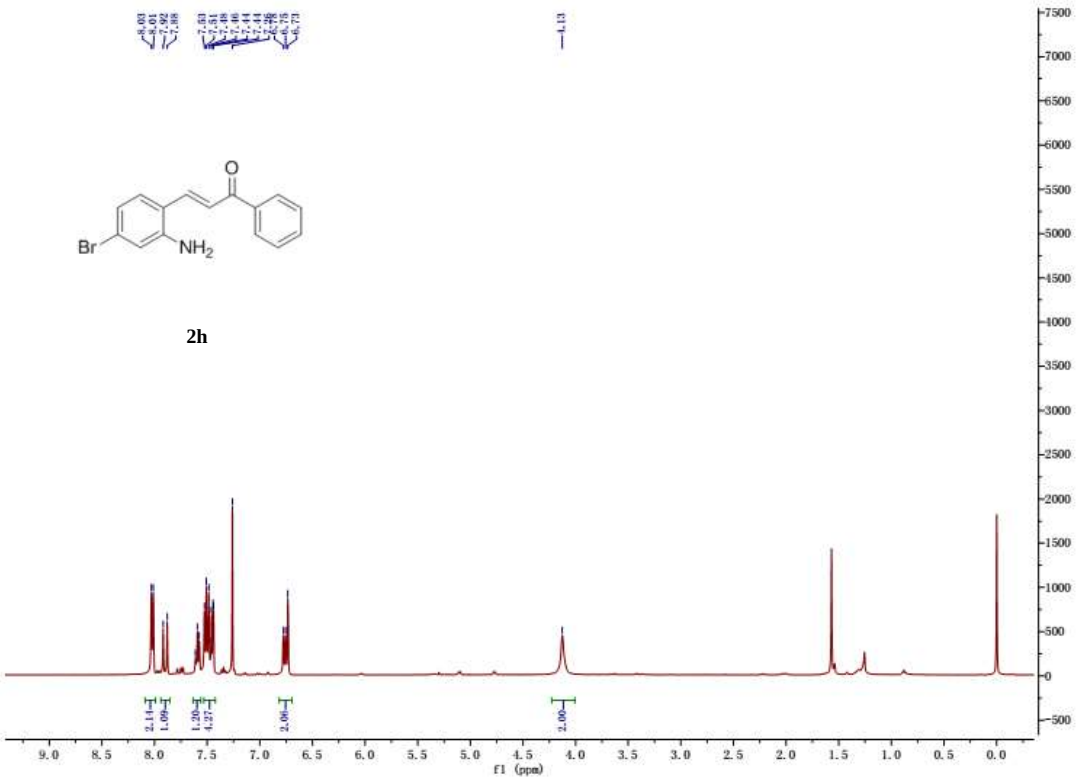

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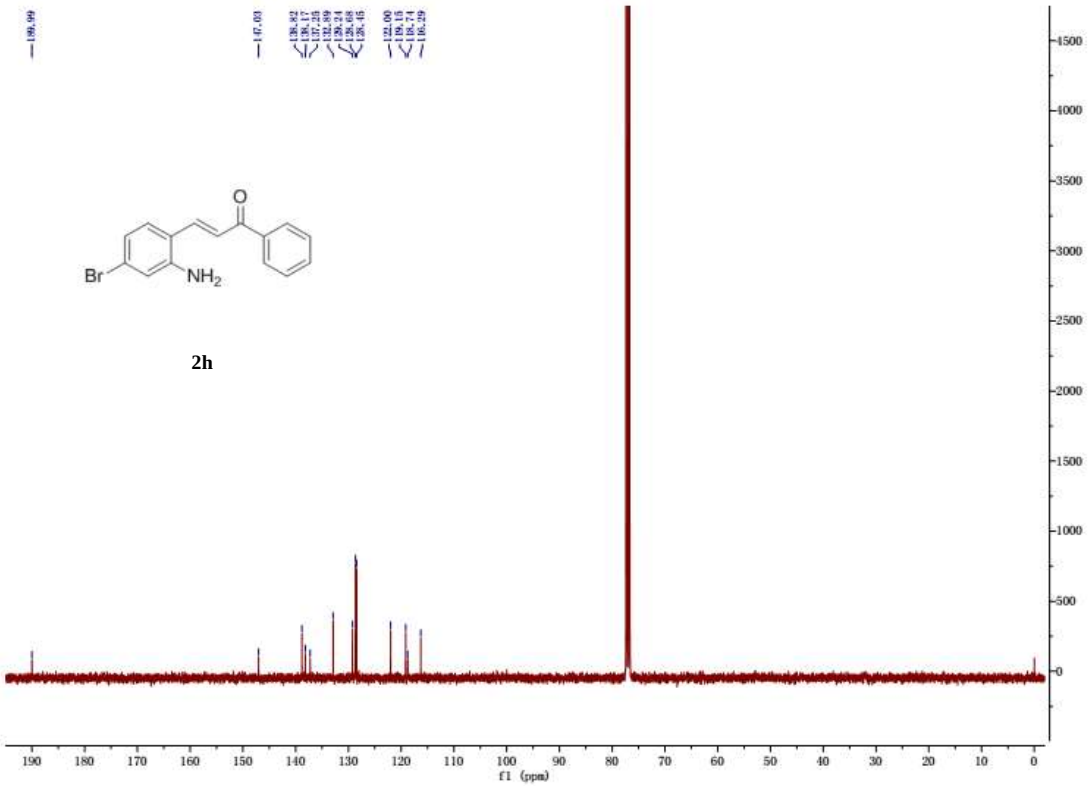

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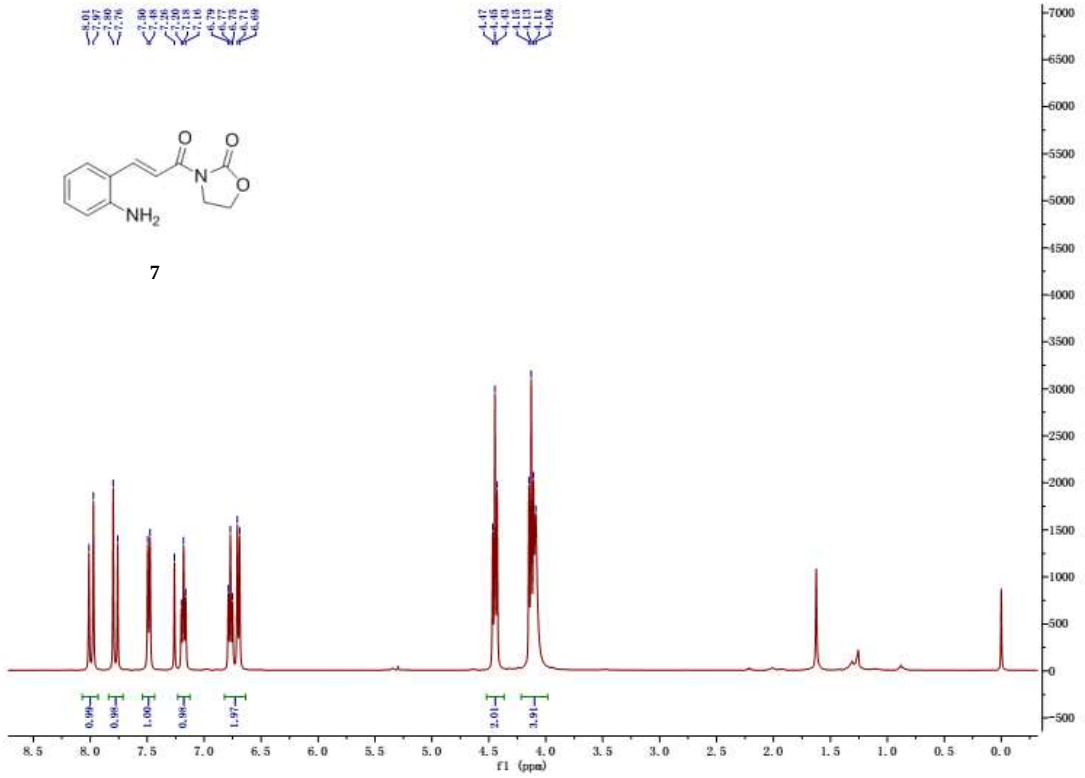
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6.71
4.69
4.47
4.45
4.43
4.15
4.13
4.11
4.09
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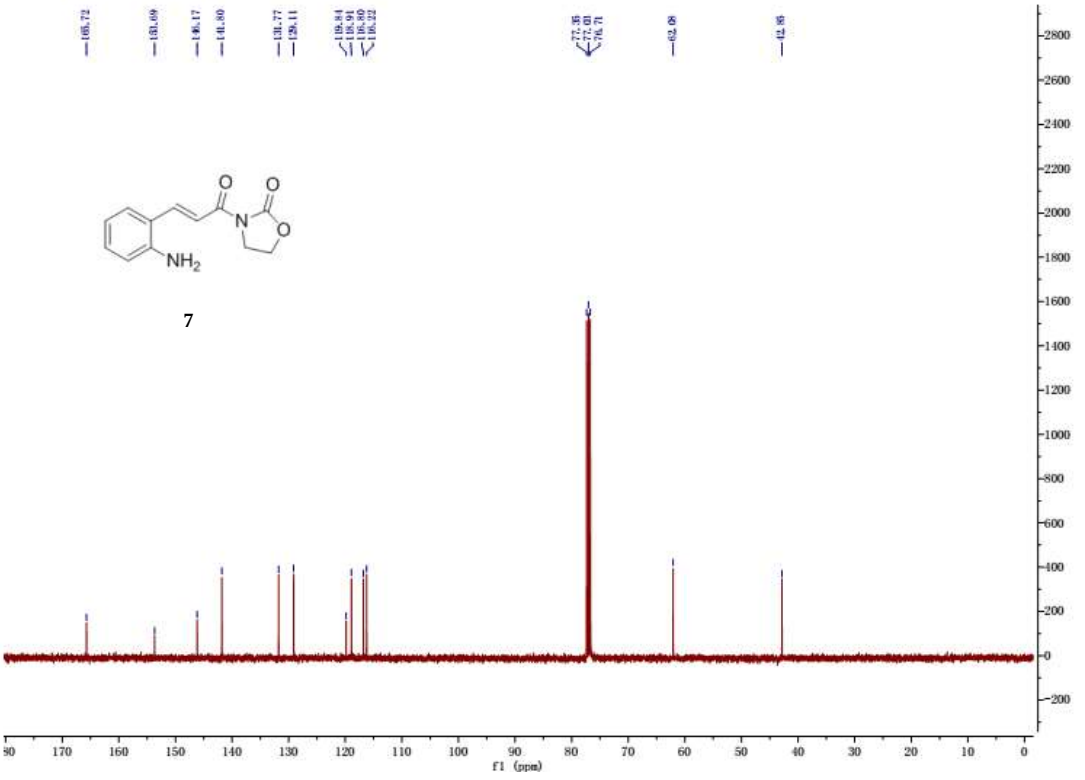
f1 (ppm)

7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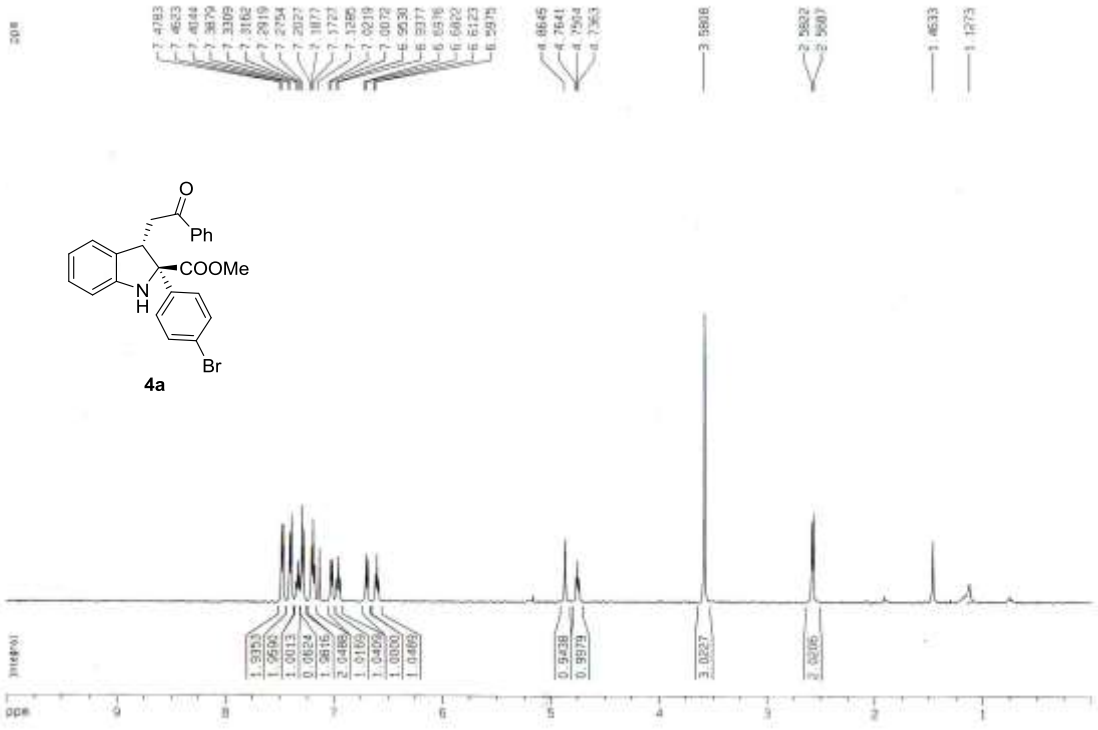
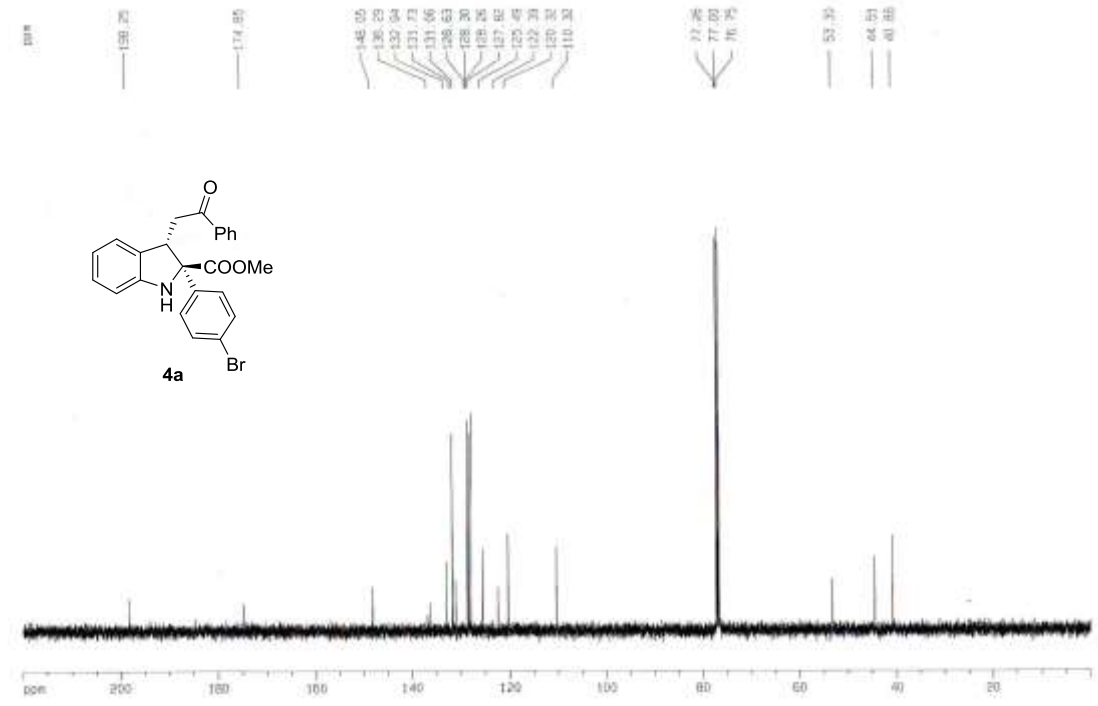
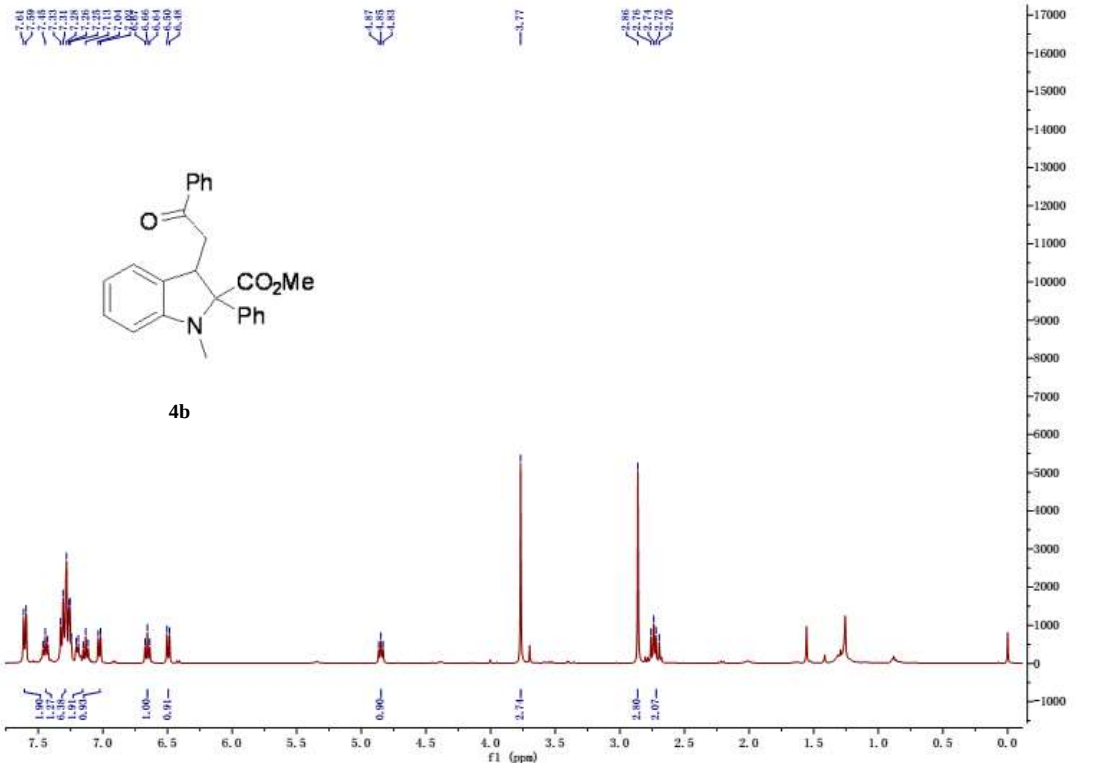
O
O
N
O
NH2
f1 (ppm)

7

NMR spectra of products 4







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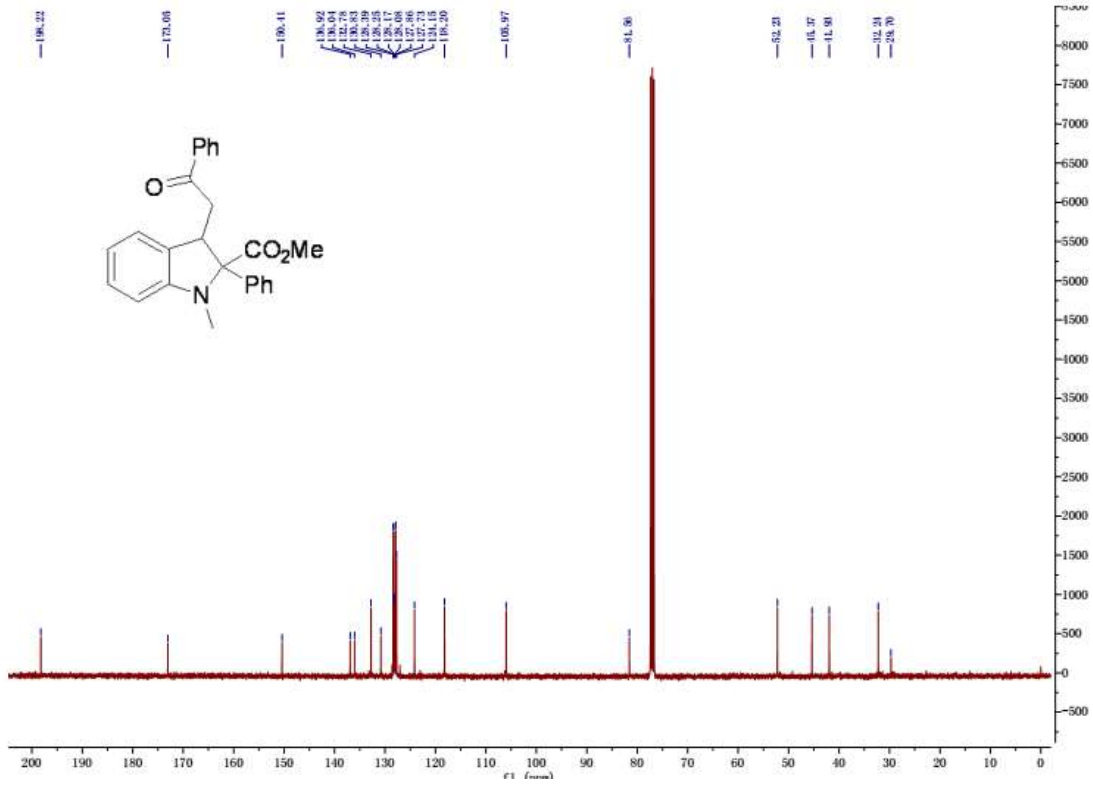

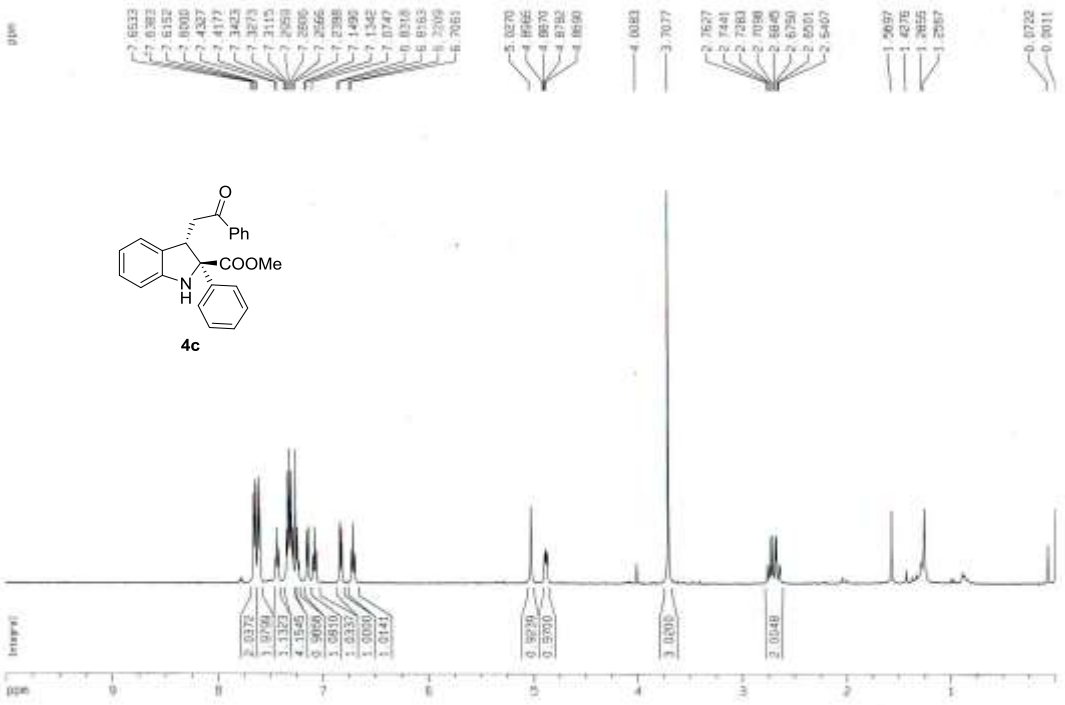
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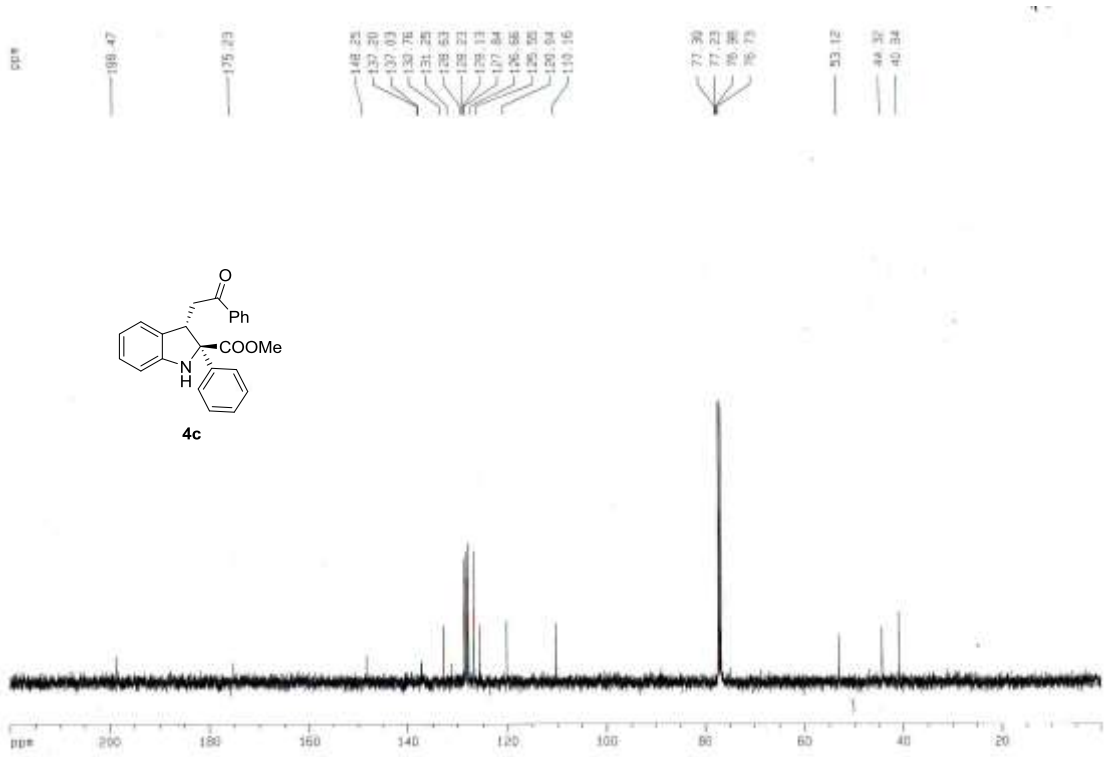
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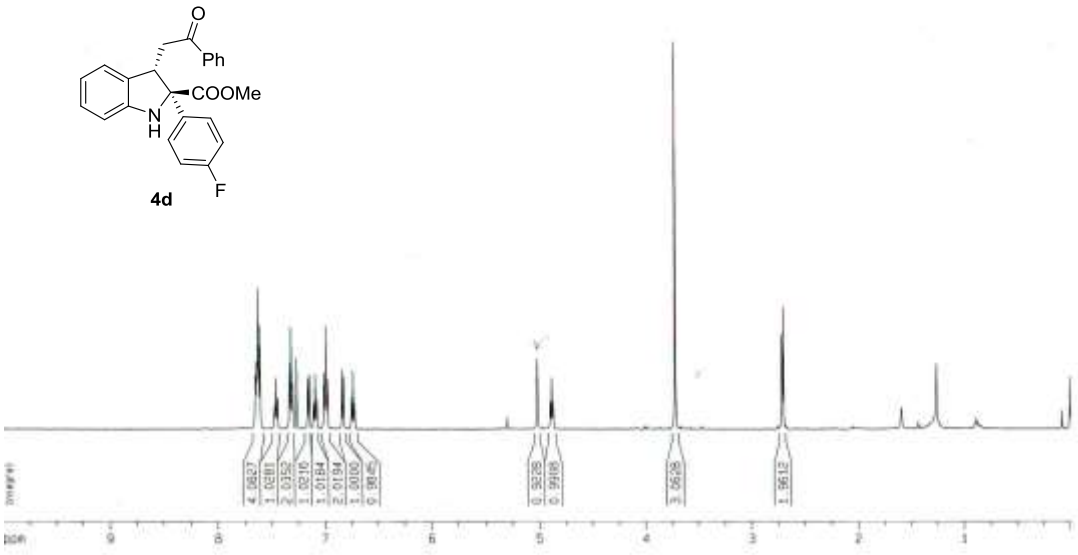
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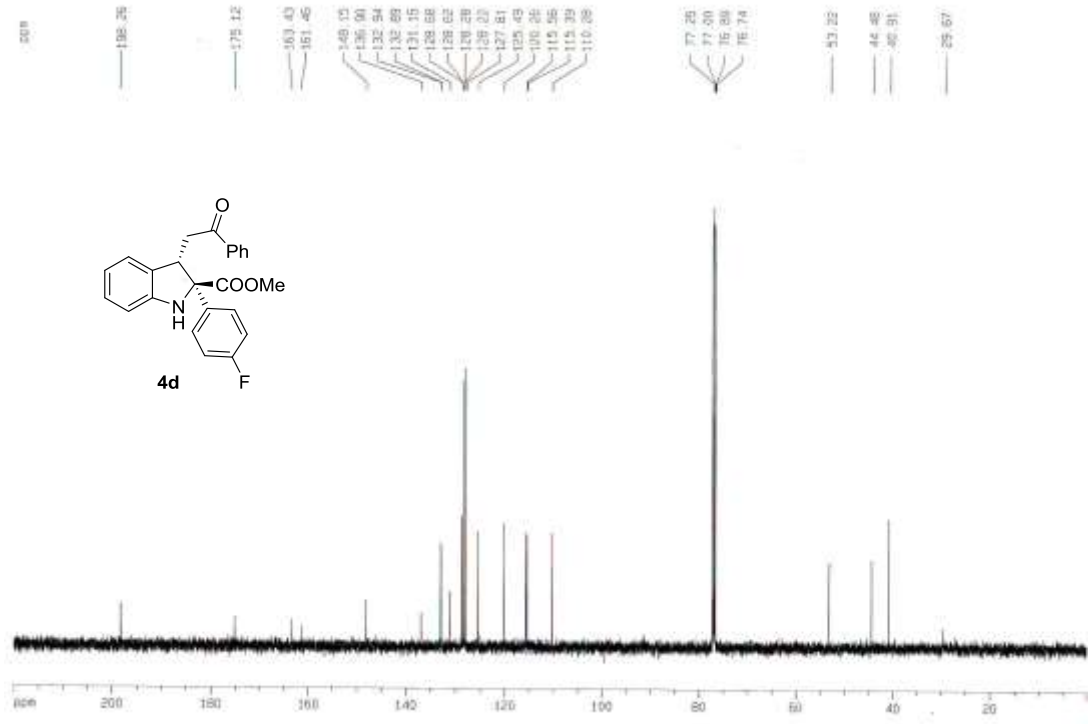
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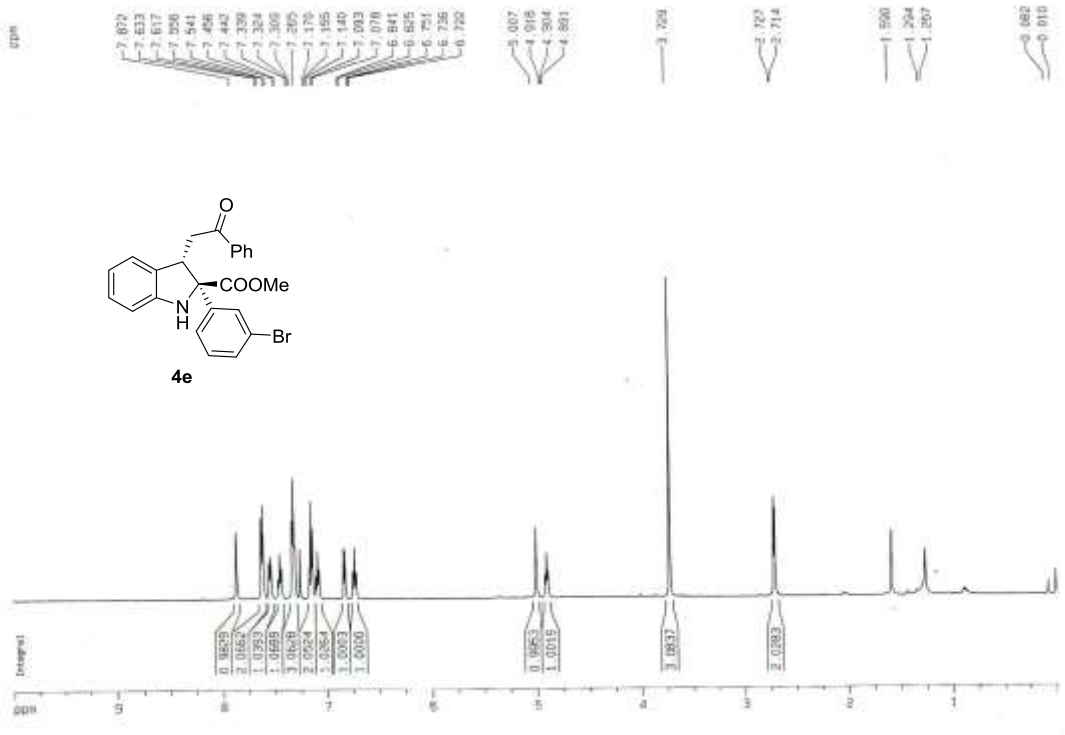
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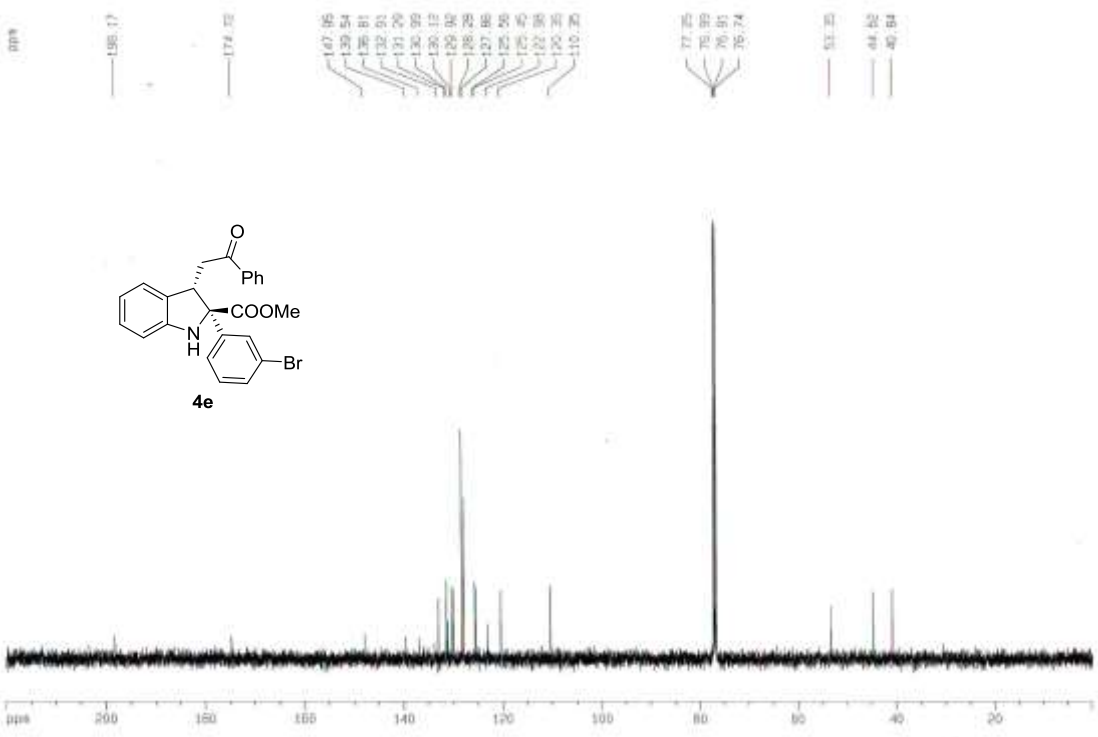
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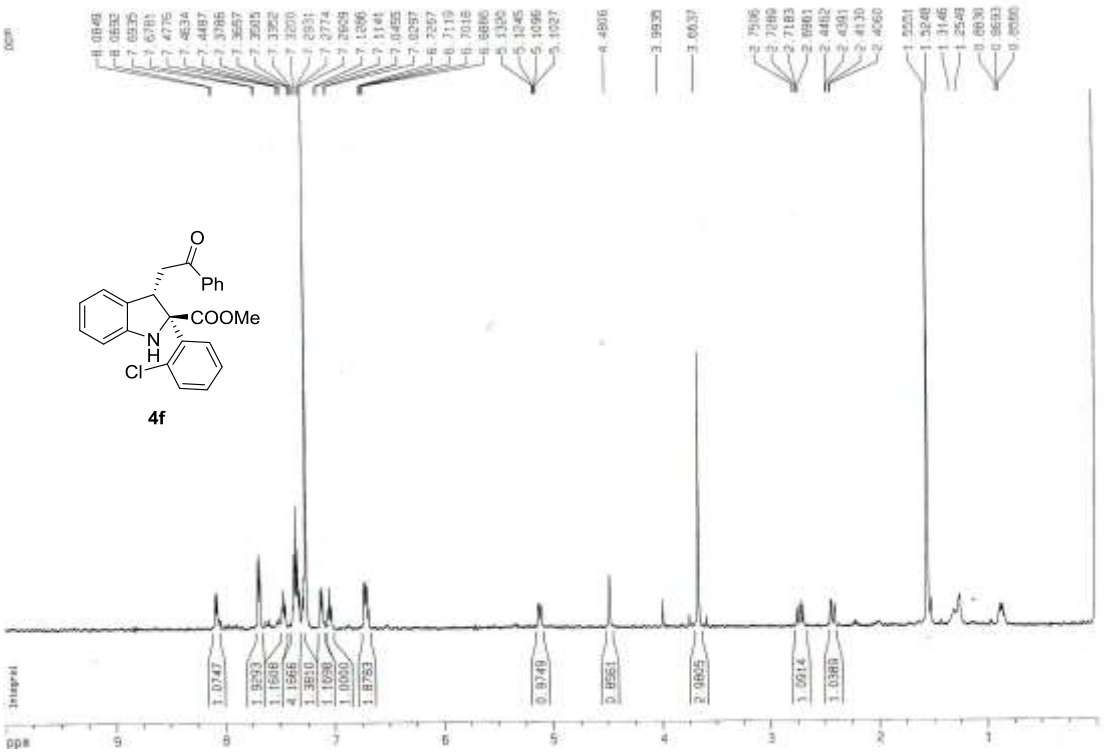
Br
4e
ppm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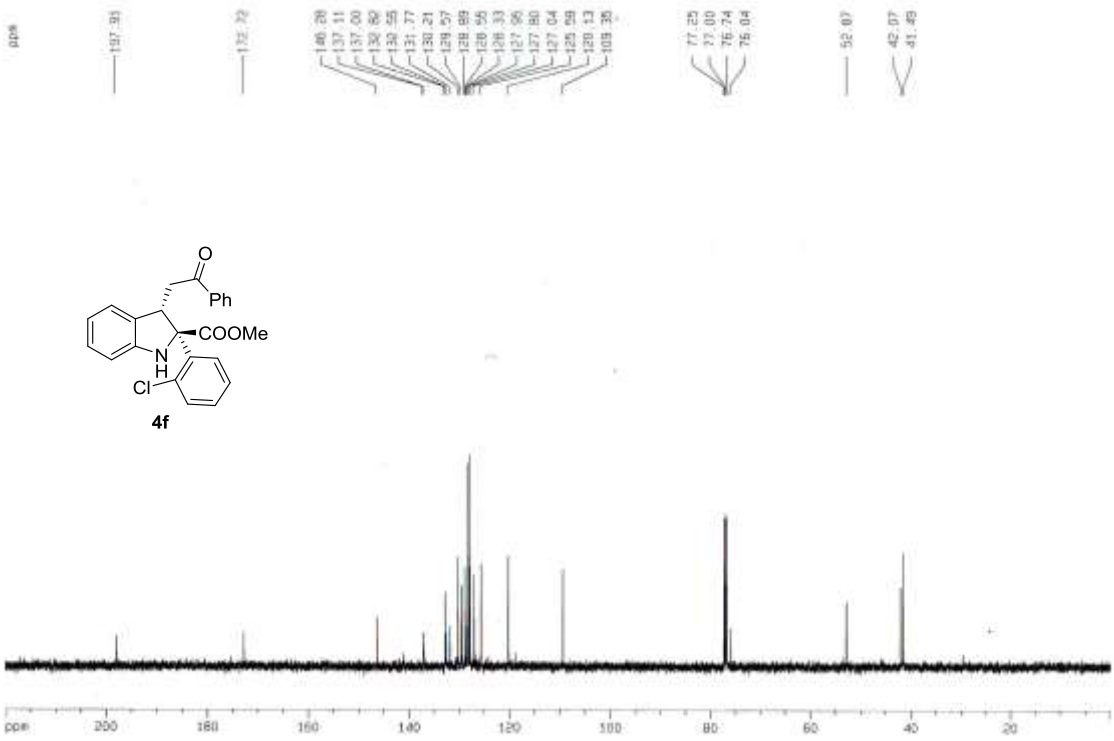
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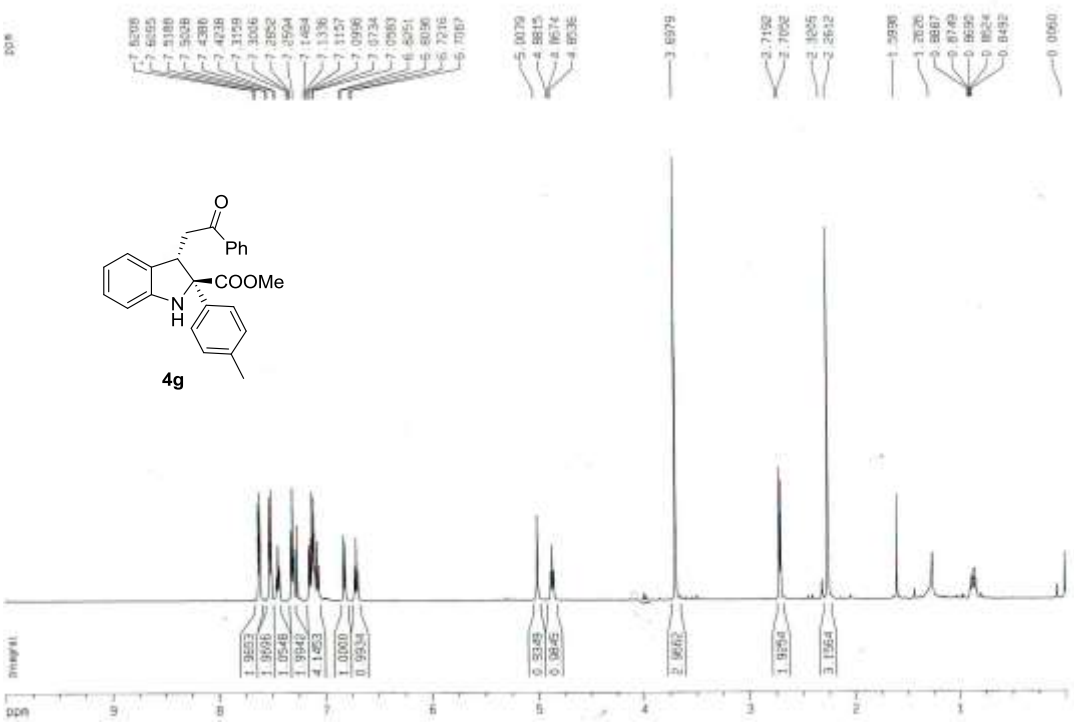
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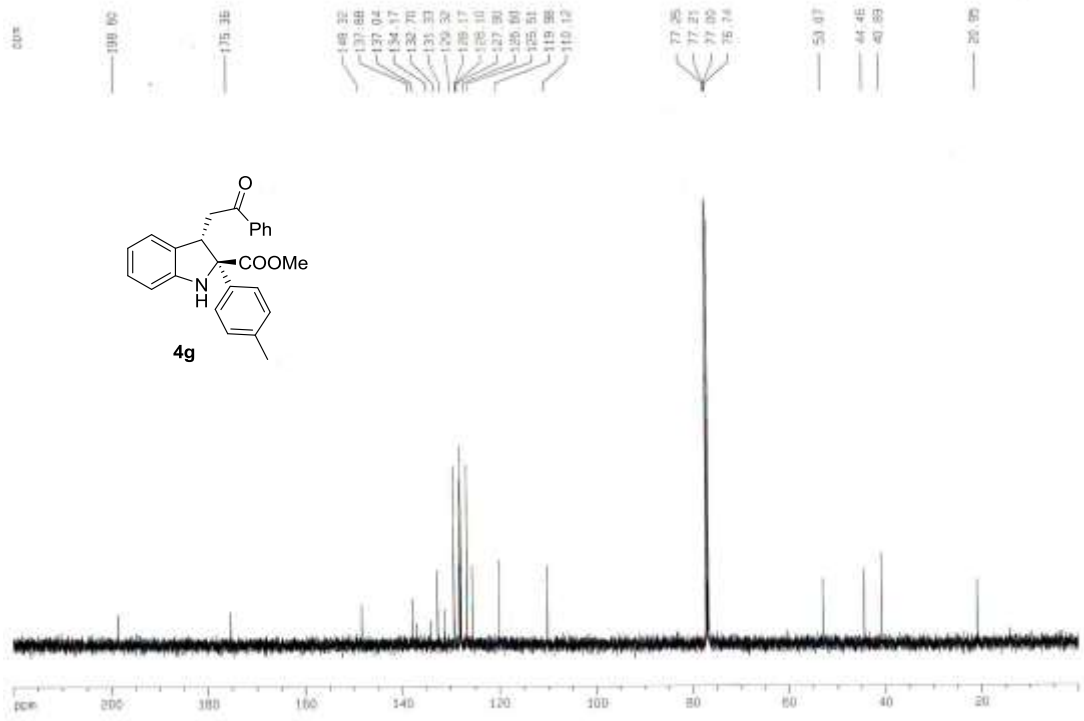
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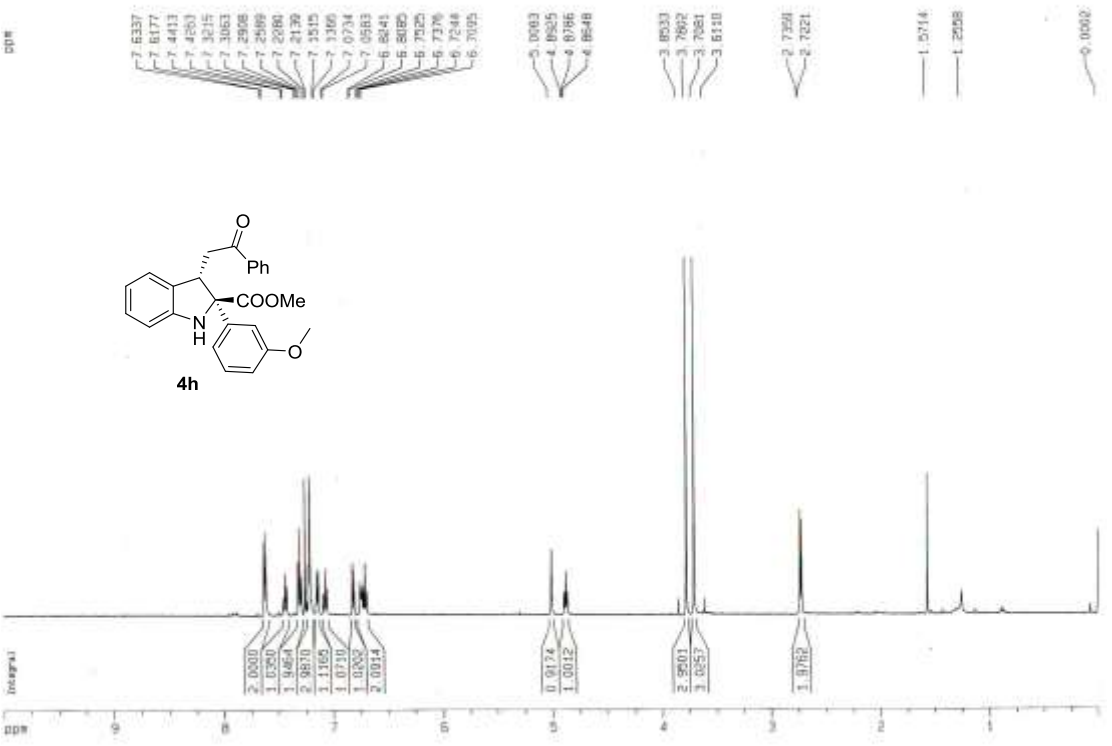
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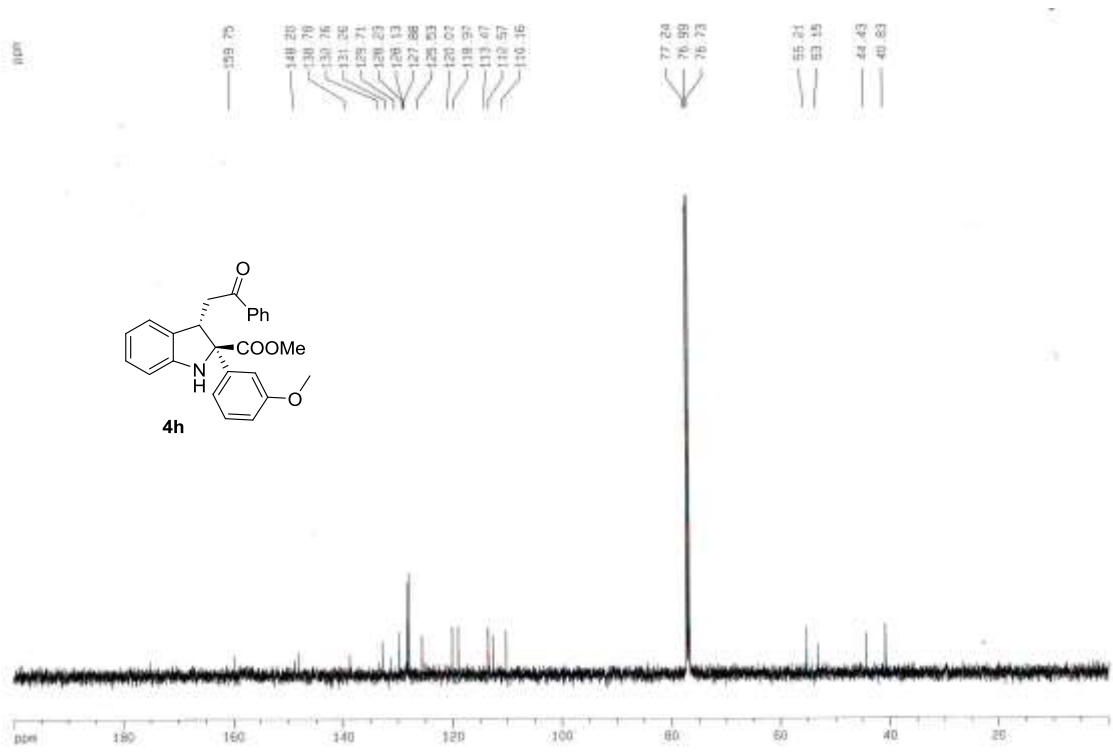
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Ph
COOMe
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4h
ppm
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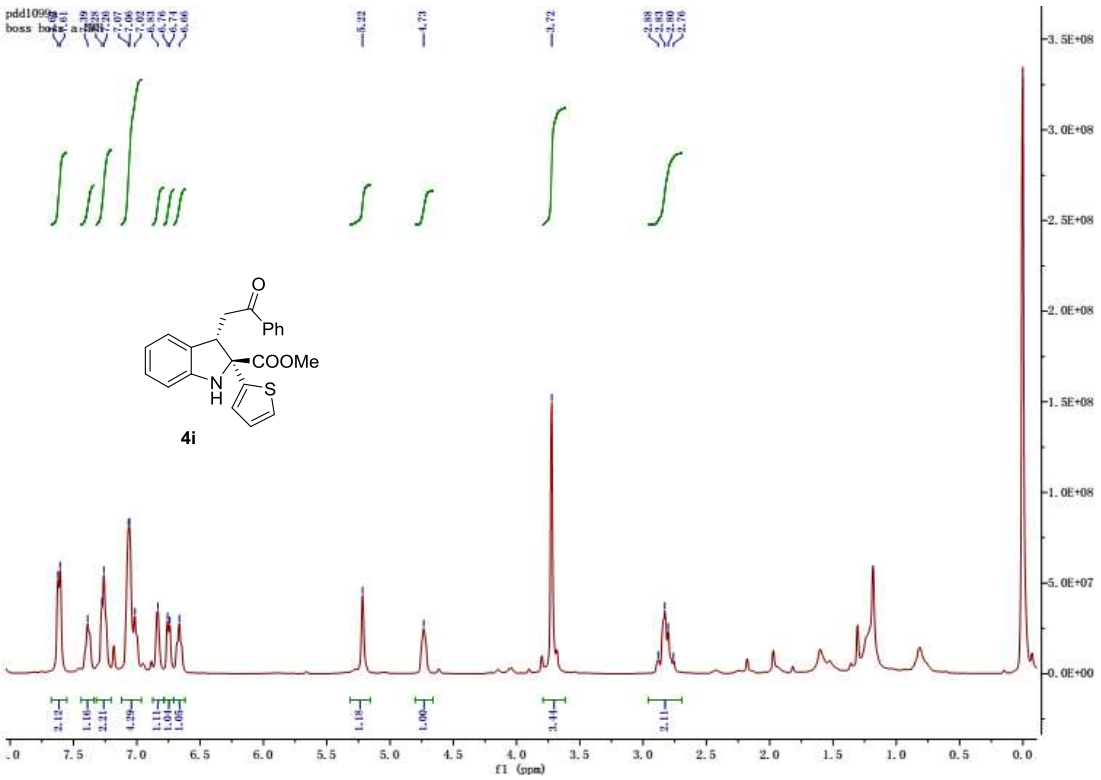
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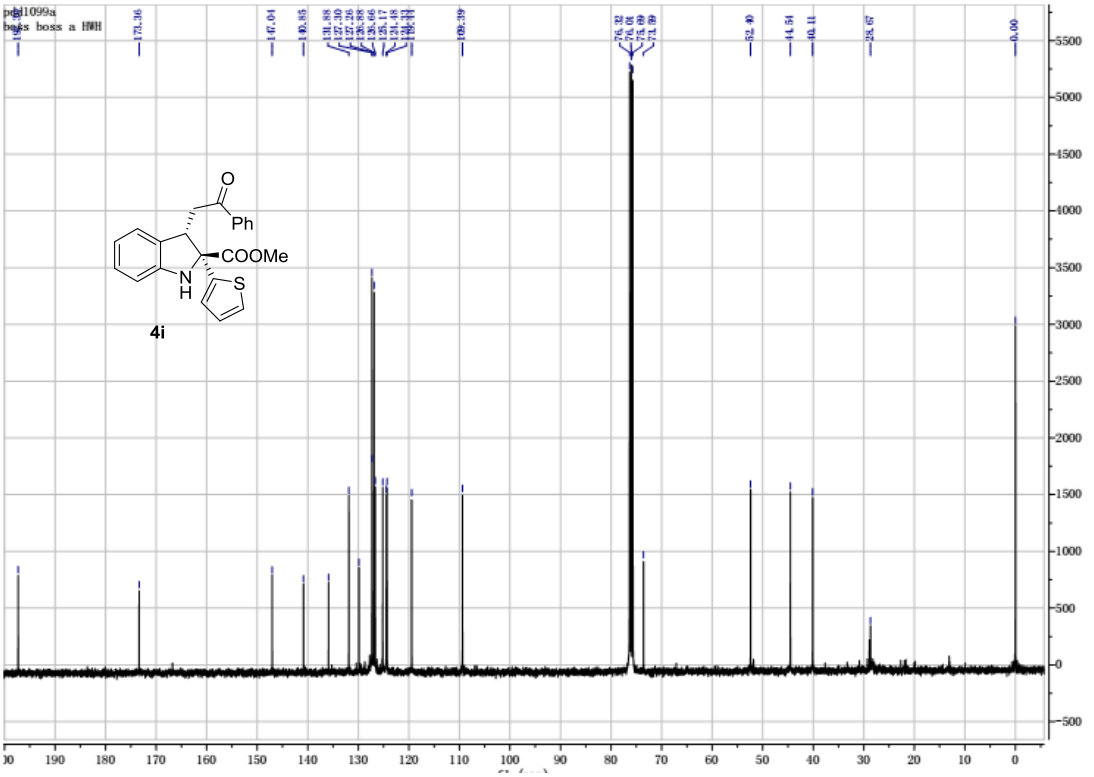
COOMe
N
H
S
4i
f1 (ppm)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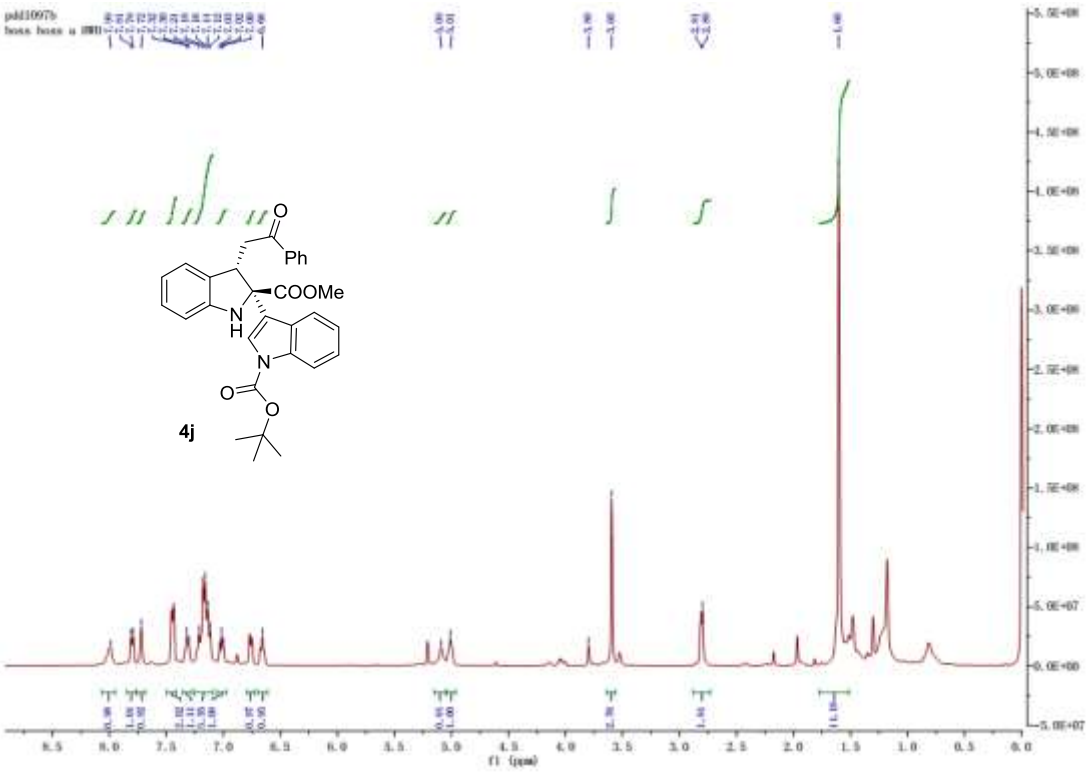
4i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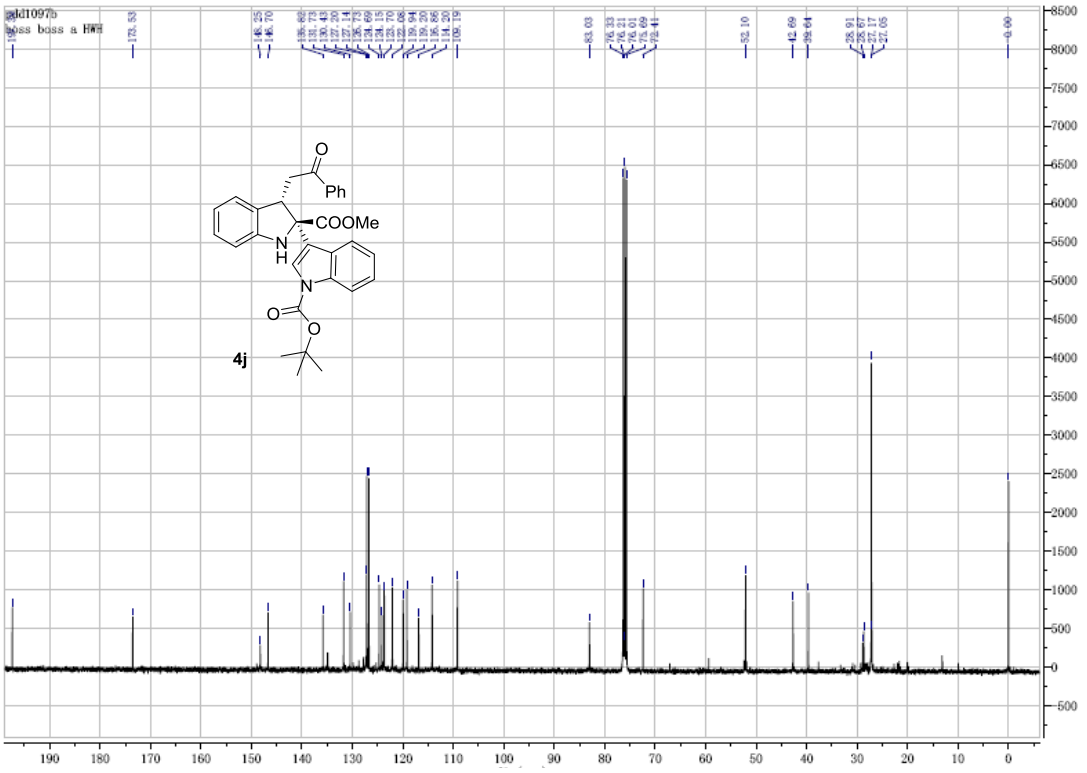
4j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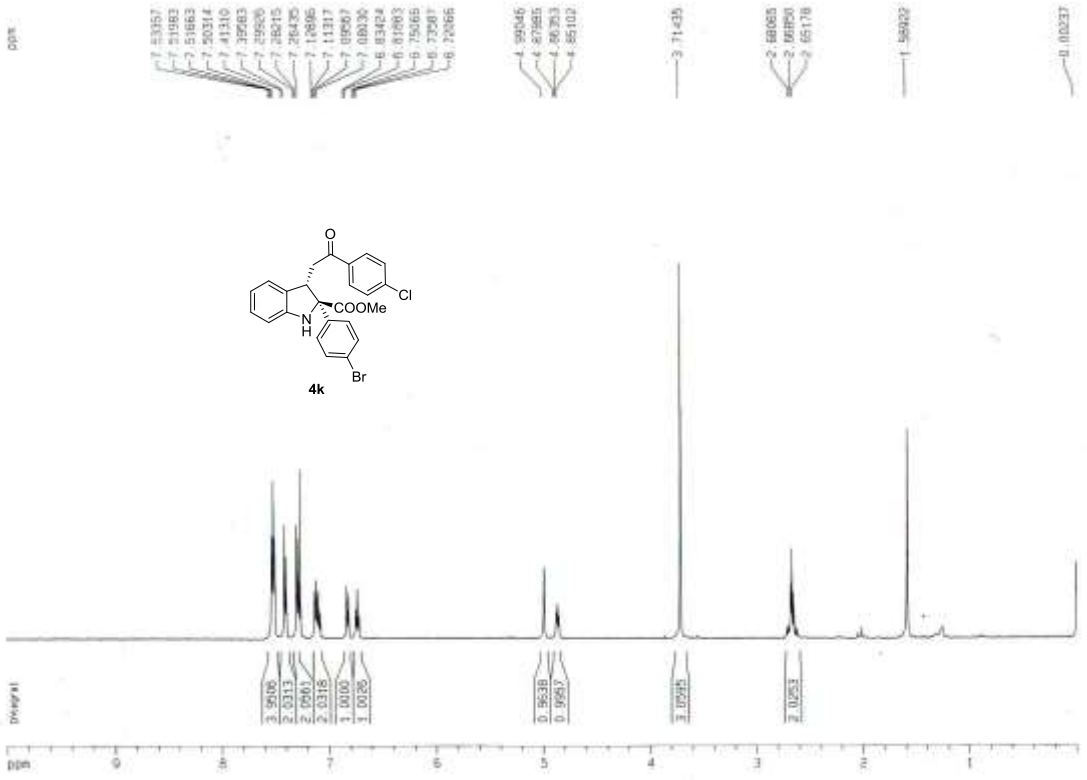
4j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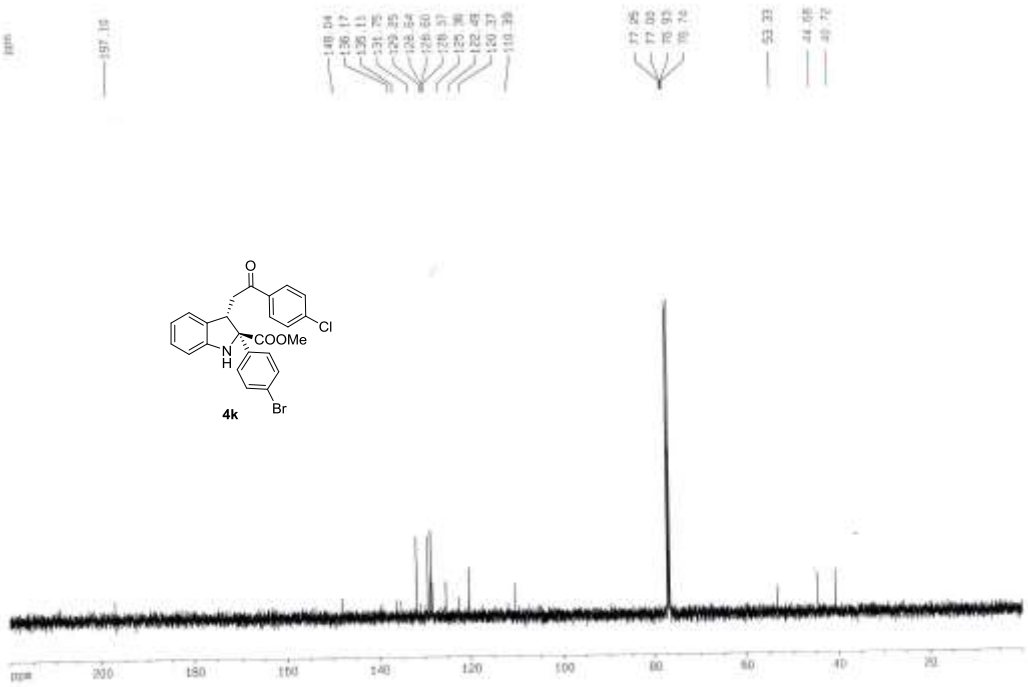
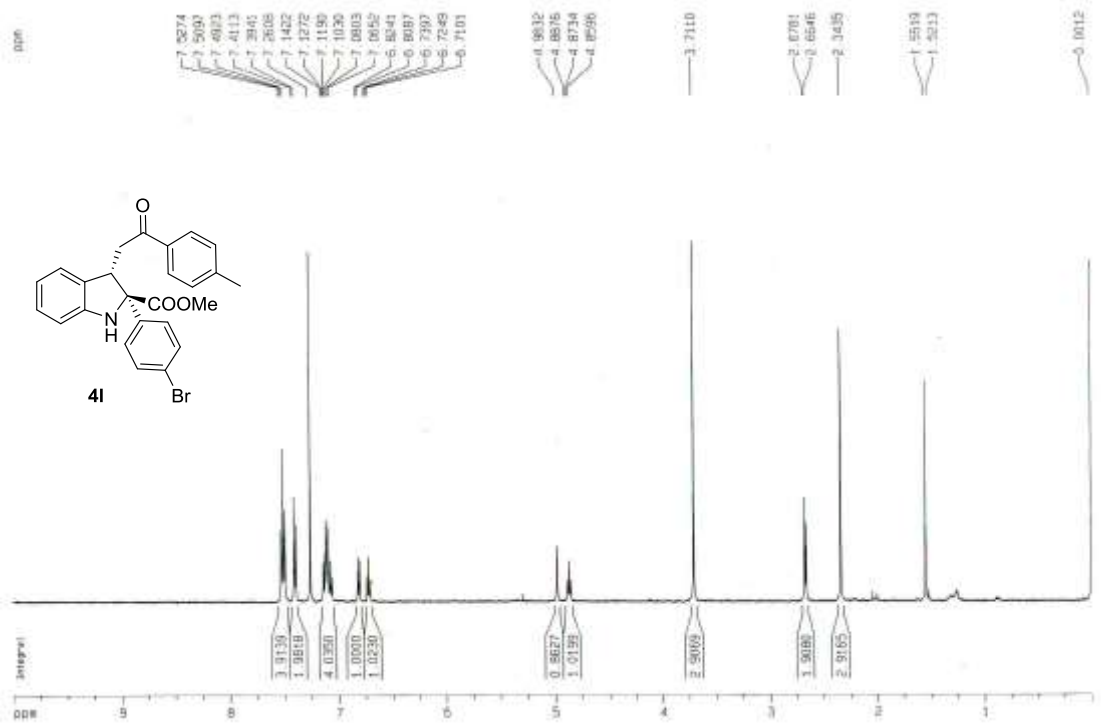
Cl
COOMe
N
H
Br


4k
Cl
COOMe
N
H
Br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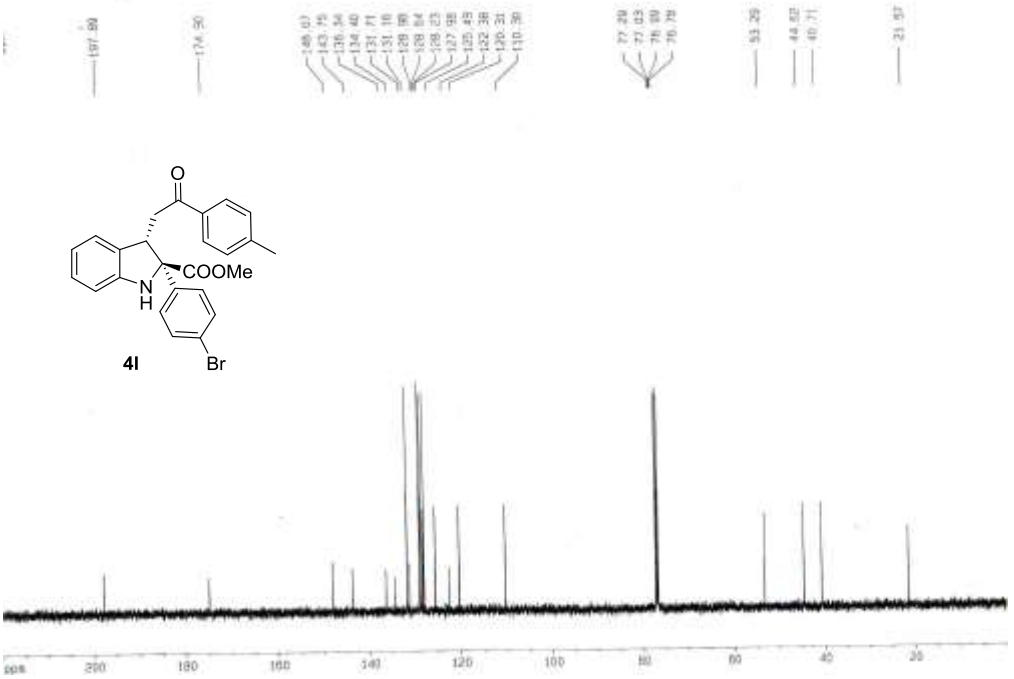
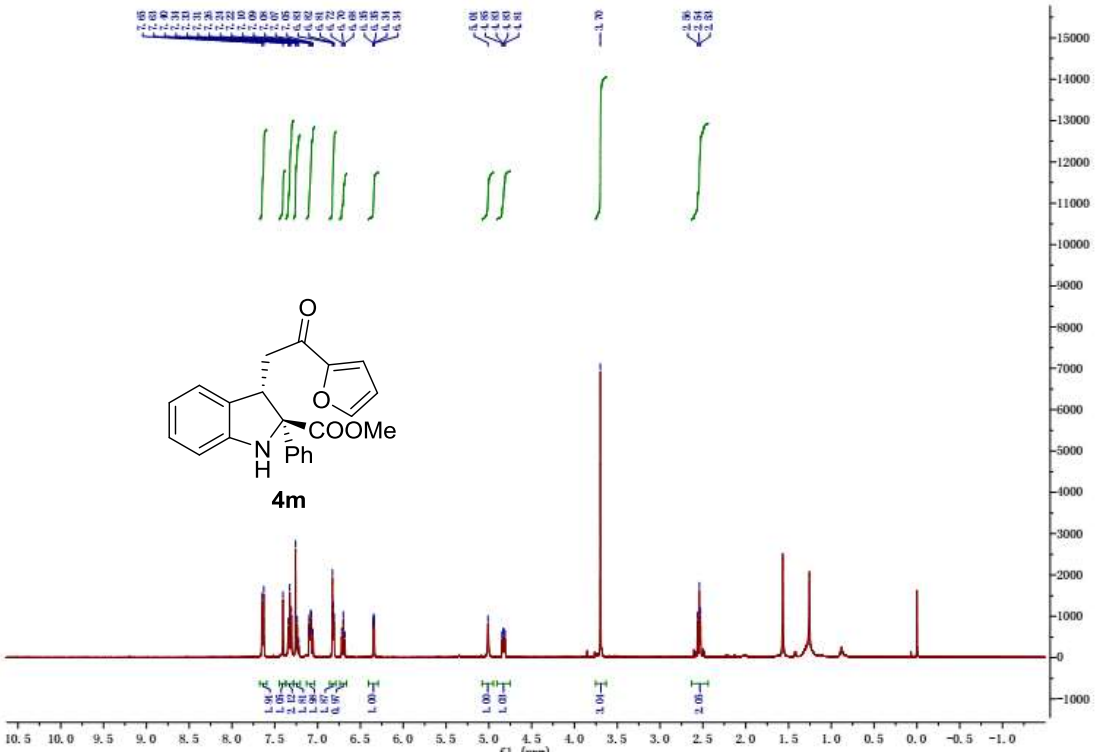
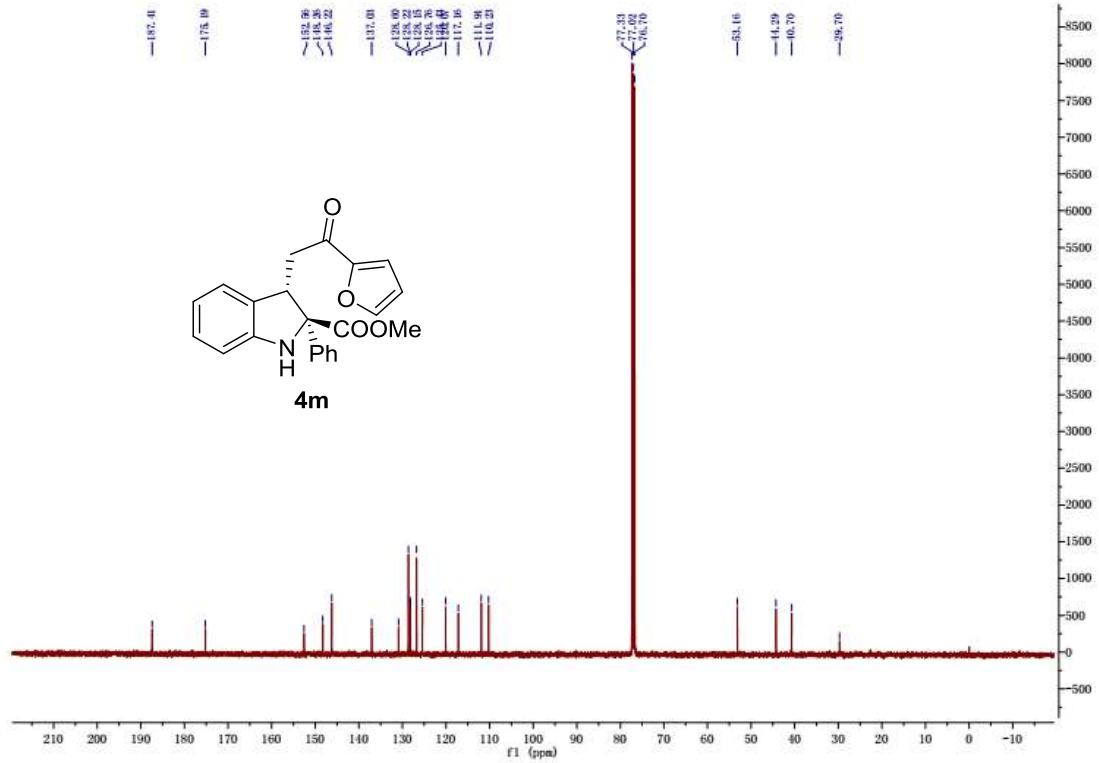
COOMe
N
H
Br
4l

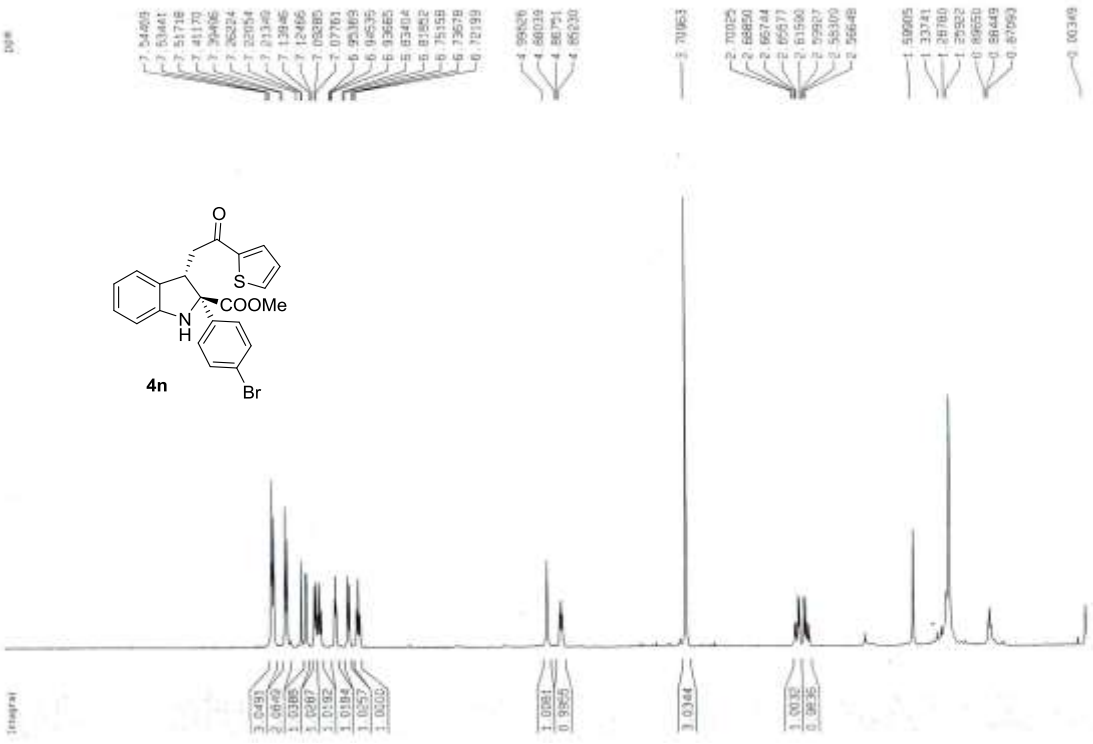

O
COOMe
N
H
Br
4l

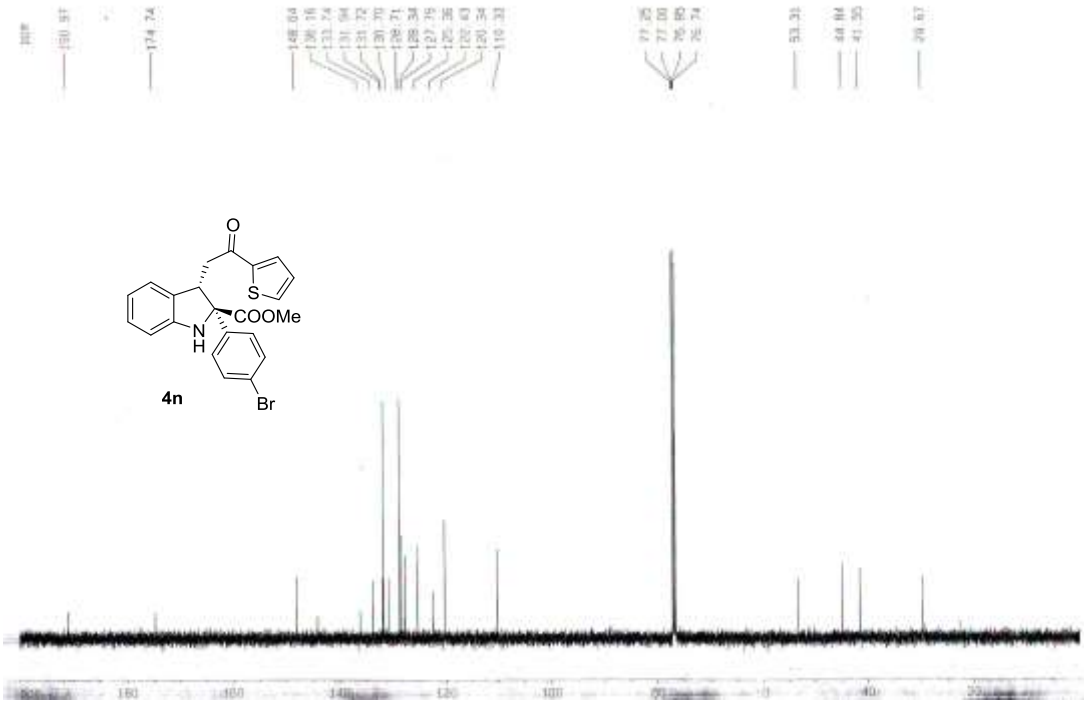


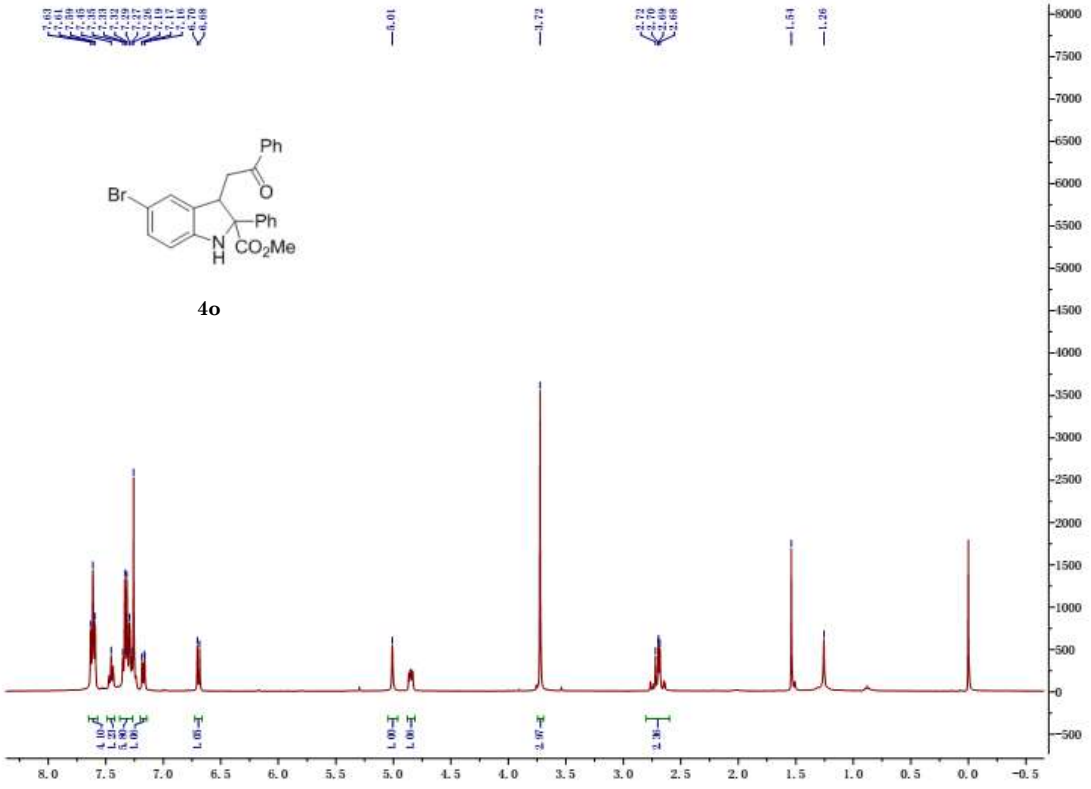
4m



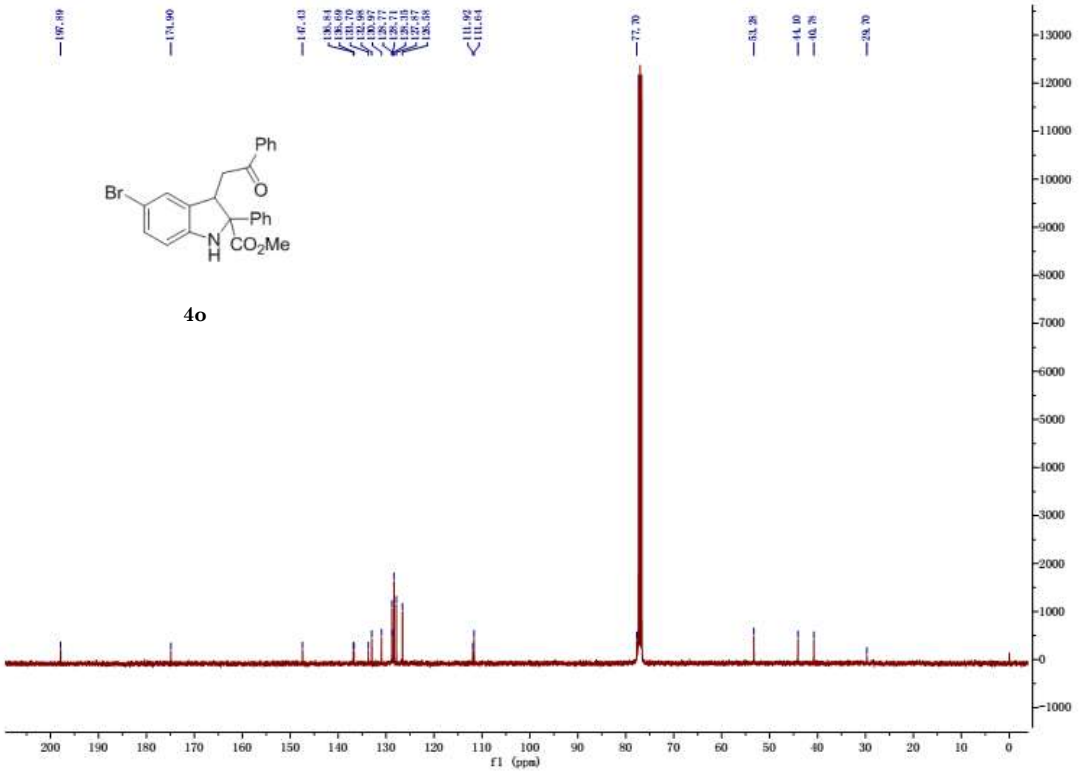
4m


4n
O
S
COOMe
N
H
Br

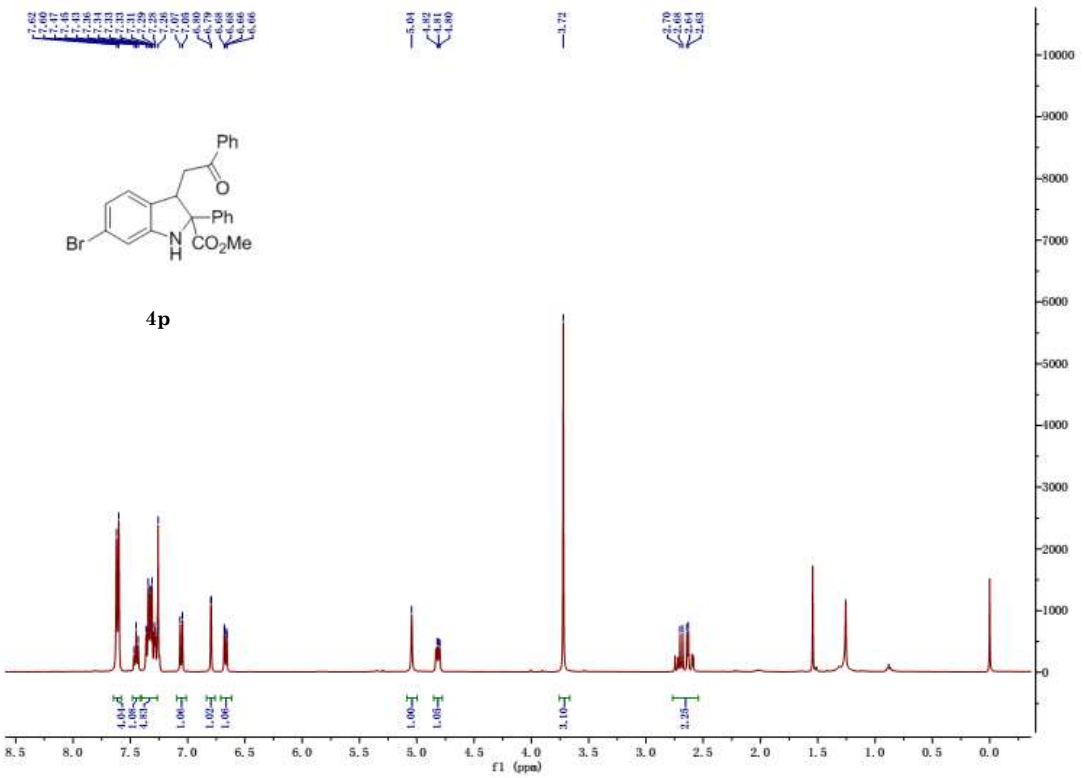

4n
O
S
COOMe
N
H
Br



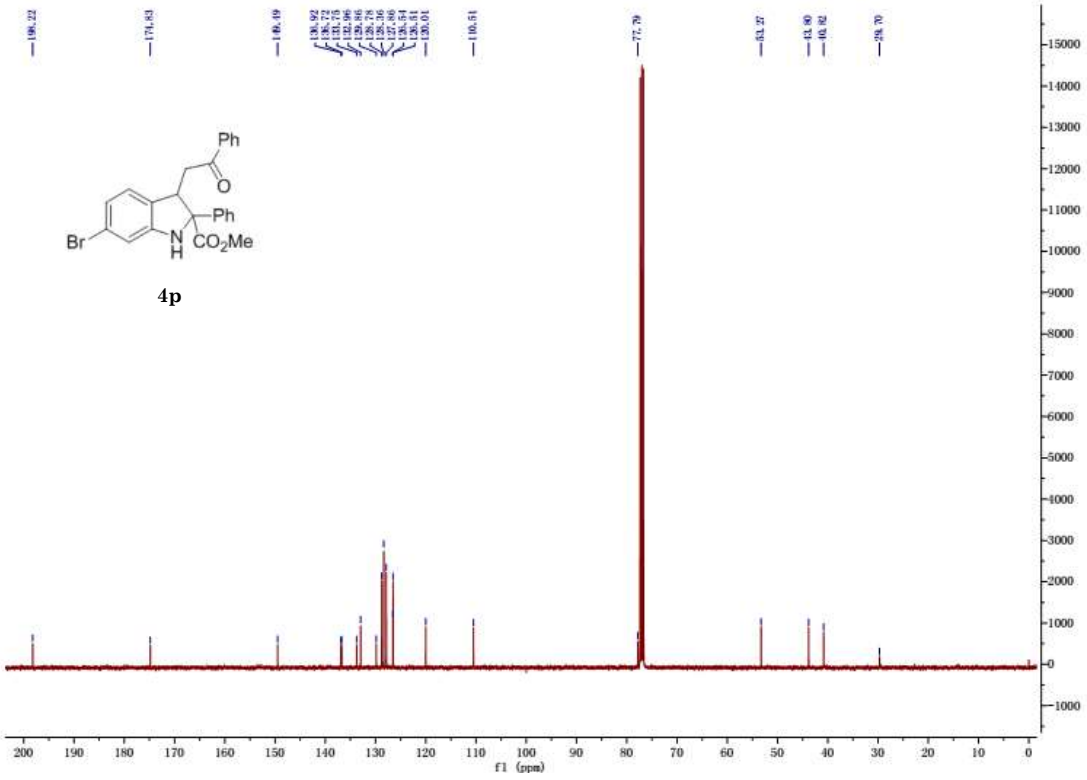
4o



4o



4p

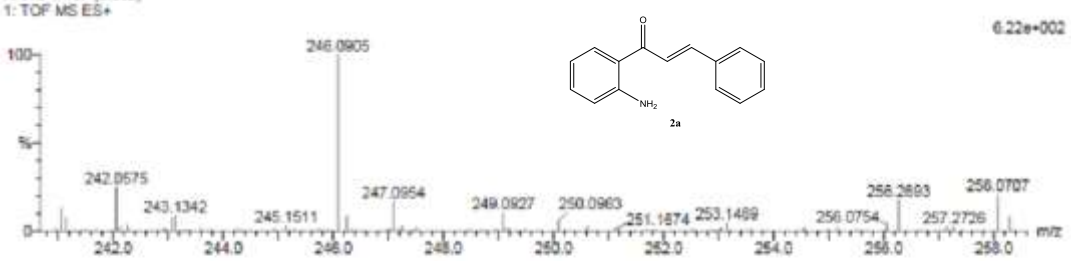


4p

HRMS of compounds **1e-1h**, **2b2h, 4a-4p**

Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

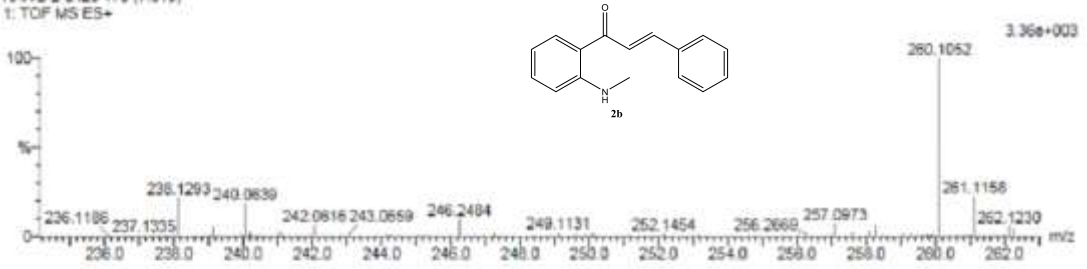
Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-15 H: 10-15 N: 1-1 O: 1-1 Na: 0-1
KANG-1 197 (8.662)
1: TOF MS ES+



Minimum:				-1.5					
Maximum:		500.0	10.0	50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula		
246.0905	246.0895	1.0	4.1	9.5	87.7	0.0	C15	H13	N O Na

Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-16 H: 12-23 N: 1-1 O: 1-1 Na: 0-1
KANG-2-0423 178 (7.619)
1: TOF MS ES+

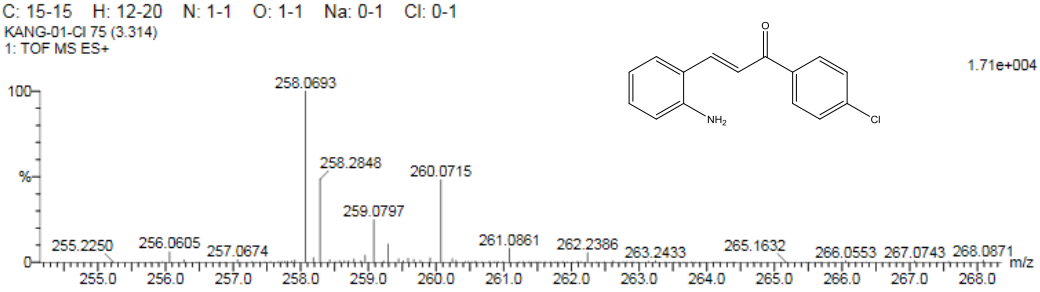


Minimum:				-1.5					
Maximum:		500.0	10.0	50.0					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula		
260.1052	260.1051	0.1	0.4	9.5	147.6	0.0	C16	H15	N O Na

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 15-15 H: 12-20 N: 1-1 O: 1-1 Na: 0-1 Cl: 0-1
KANG-01-Cl 75 (3.314)
1: TOF MS ES+

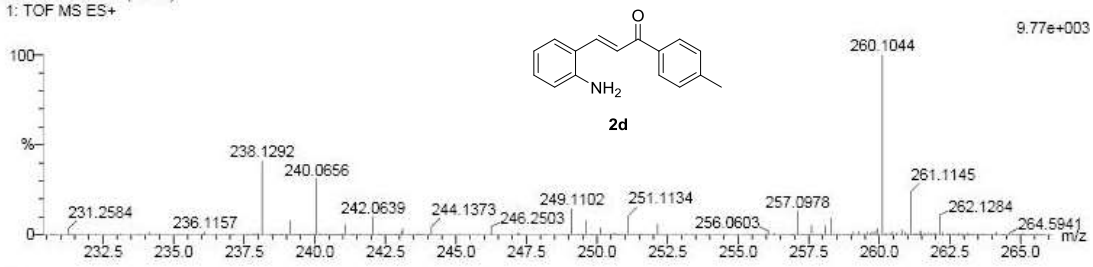


Minimum:				-1.5			
Maximum:		500.0	1000.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
258.0693	258.0686	0.7	2.7	9.5	274.8	0.0	C15 H13 N O Cl

Elemental Composition Report

Single Mass Analysis
Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 15-16 H: 12-20 N: 1-1 O: 1-1 Na: 0-1
KANG-02-ME 21 (0.947)
1: TOF MS ES+

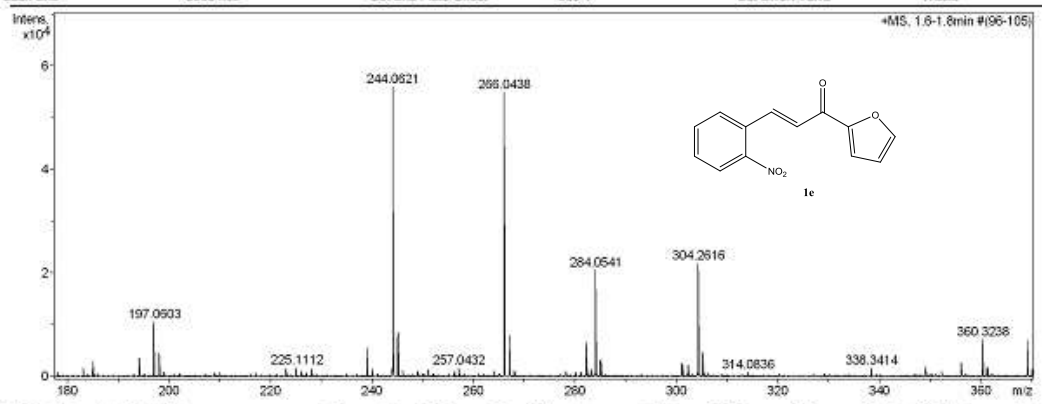


2d

Minimum:				-1.5			
Maximum:		500.0	1000.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
260.1044	260.1051	-0.7	-2.7	9.5	228.6	0.0	C16 H15 N O Na

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



1e

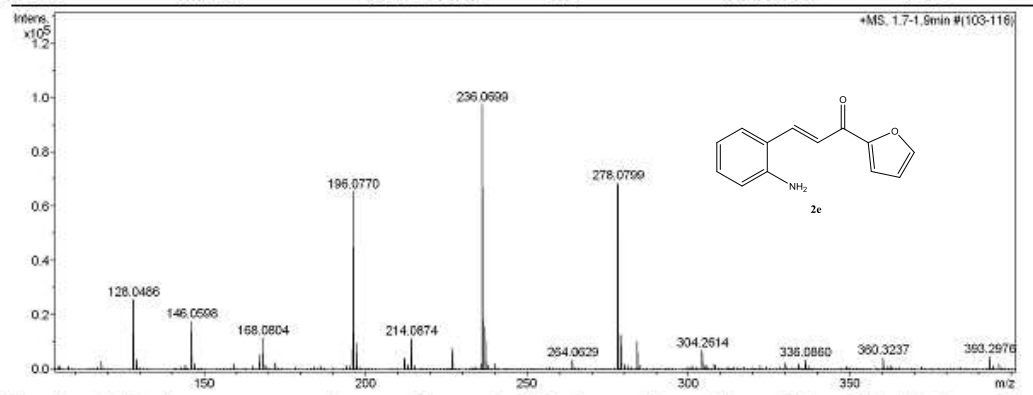
Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
266.0438														
	1	C 13 H 9 N Na O 4	266.0424	-5.4	-5.1	9.5	ok	even	0.50	0.0008	0.0014	0.0006	0.0006	0.3598

Analysis Info

Analysis Name	D:\Data\HWH-20140523\JLQ-19-2_43_01_3136.d	Acquisition Date	5/23/2014 1:45:08 PM
Method	tune_low_for_lc-15min-seg.m	Operator and analyzer	ECNU.CHEM. G.D.Yang
Sample Name	JLQ-19-2	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



2e

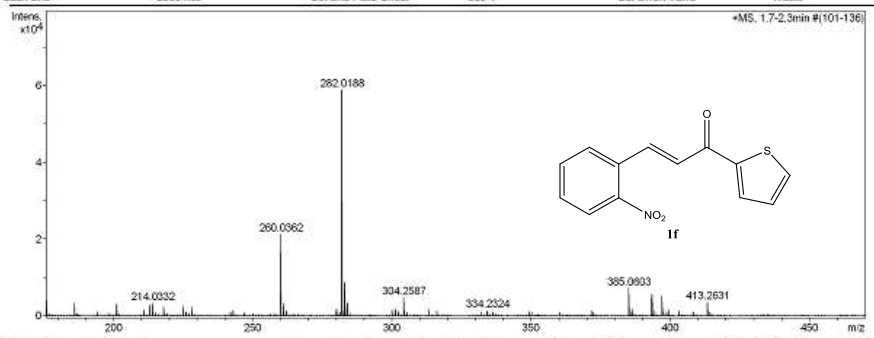
Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
236.0699														
	1	C 13 H 11 N Na O 2	236.0682	-7.3	-6.9	8.5	ok	even	9.02	0.0175	0.0017	0.0071	0.0009	0.5336

Analysis Info

Analysis Name	D:\Data\HWH-20140603\JLQ-02-3_51_01_3144.d	Acquisition Date	6/3/2014 10:03:19 AM
Method	tune_low_for_lc-15min-seg.m	Operator and analyzer	ECNU.CHEM. G.D.Yang
Sample Name	JLQ-02-3	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



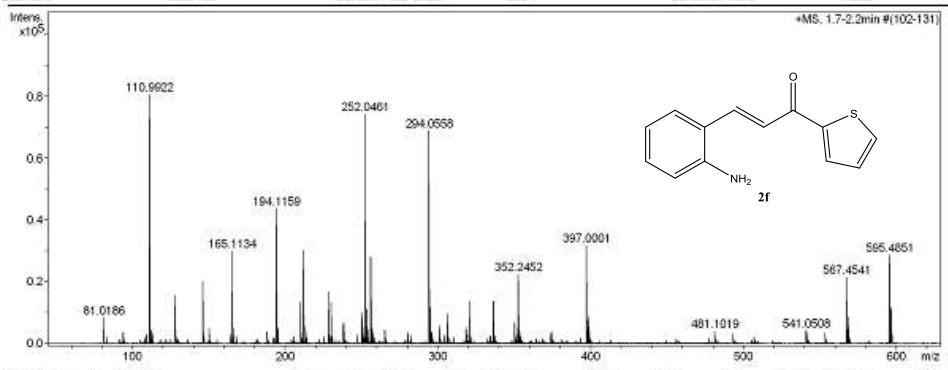
Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
282.0188	1	C 13 H 9 N Na O 3 S	282.0195	2.7	3.2	9.5	ok	even	2.12	0.0048	0.0012	0.0018	0.0021	0.4148

Analysis Info

Analysis Name	D:\Data\hwh-20140605\jlq-20-3_31_01_3161.d	Acquisition Date	6/6/2014 3:28:55 PM
Method	tune_low_for_lc-15min-seg.m	Operator and analyzer	ECNU.CHEM. G.D.Yang
Sample Name	jlq-20-3	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

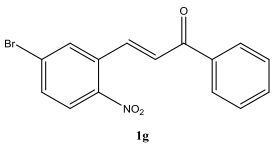
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
252.0461	1	C 13 H 11 N Na O S	252.0454	-2.9	-3.3	8.5	ok	even	2.18	0.0044	0.0015	0.0020	0.0039	0.4420

Single Mass Analysis
Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

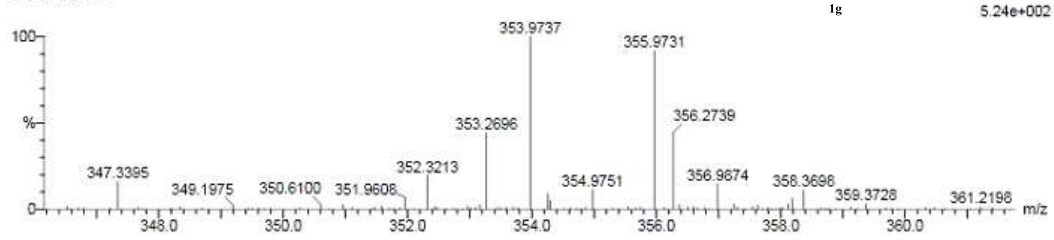
Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-15 H: 10-22 N: 1-1 O: 1-3 Na: 0-1 Br: 0-1



1g

KANGZH-02-010 77 (3.402)
1: TOF MS ES+

5.24e+002



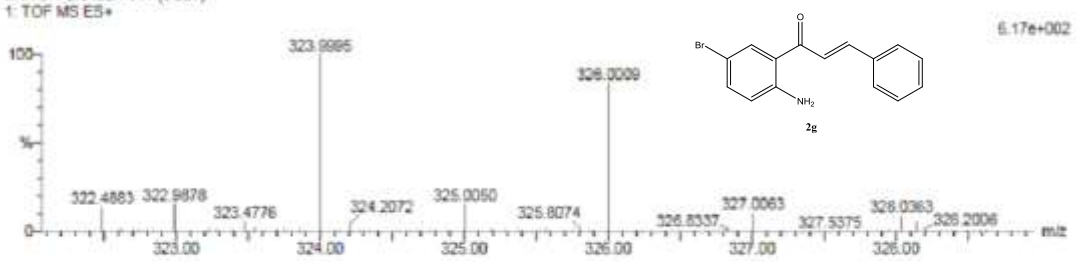
Minimum:				-1.5			
Maximum:		500.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
353.9737	353.9742	-0.5	-1.4	10.5	72.5	0.0	C15 H10 N O3 Na Br

Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-15 H: 12-23 N: 1-1 O: 1-1 Na: 0-1 Br: 1-1

KANG-4-3-0423A 141 (6.207)
1: TOF MS ES+

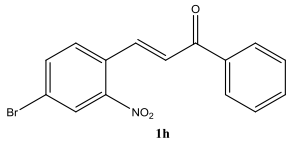
6.17e+002



2g

Minimum:				-1.5			
Maximum:		500.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
323.9995	324.0000	-0.5	-1.5	9.5	83.2	0.0	C15 H12 N O Na Br

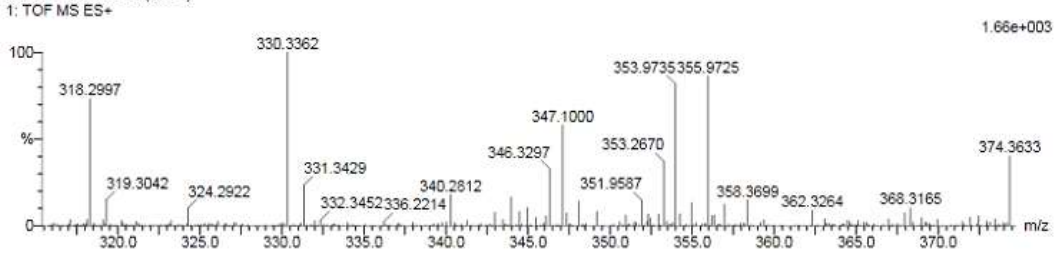
Single Mass Analysis
Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3



1h

Monoisotopic Mass, Even Electron Ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-15 H: 10-22 N: 1-1 O: 1-3 Na: 0-1 Br: 0-1

KANGZH-02-016 88 (3.874)
1: TOF MS ES+

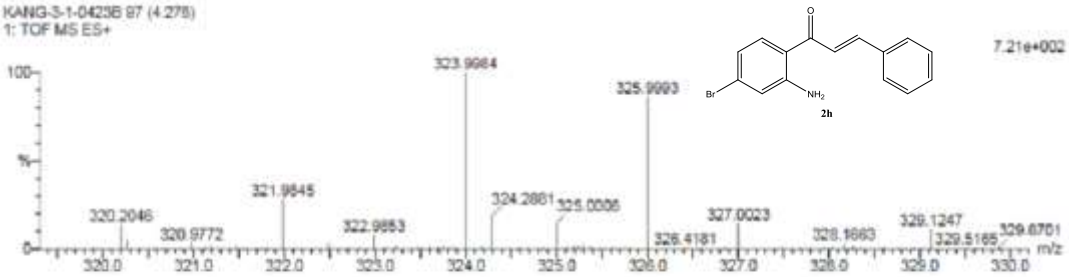


Minimum:				-1.5			
Maximum:		500.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
353.9735	353.9742	-0.7	-2.0	10.5	78.8	0.0	C15 H10 N O3 Na Br

Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-24 H: 12-14 N: 1-1 O: 1-3 Na: 0-1 Br: 1-1

KANG-3-1-04236 97 (4.276)
1: TOF MS ES+



2h

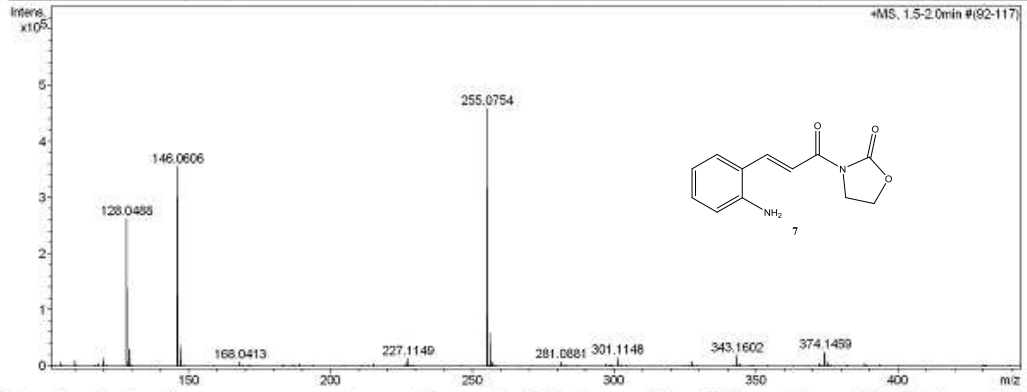
Minimum:				-1.5			
Maximum:		500.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
323.9984	324.0000	-1.6	-4.9	9.5	78.4	0.0	C15 H12 N O Na Br

Analysis Info

Analysis Name	D:\Data\HWH-20140523\JLQ-02-03_44_01_3137.d	Acquisition Date	5/23/2014 2:01:52 PM
Method	tune_low_for_lc-15min-seg.m	Operator and analyzer	ECNU.CHEM. G.D.Yang
Sample Name	JLQ-02-03	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

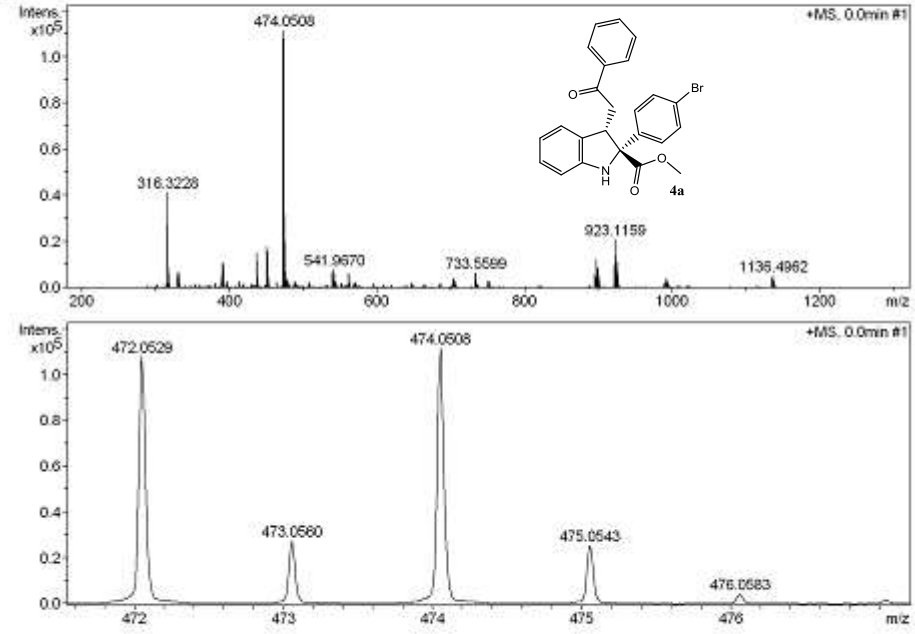
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
255.0754														
	1	C 12 H 12 N 2 Na O 3	255.0740	-5.3	-4.1	7.5	ok	even	4.66	0.0091	0.0013	0.0037	0.0024	0.5156

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



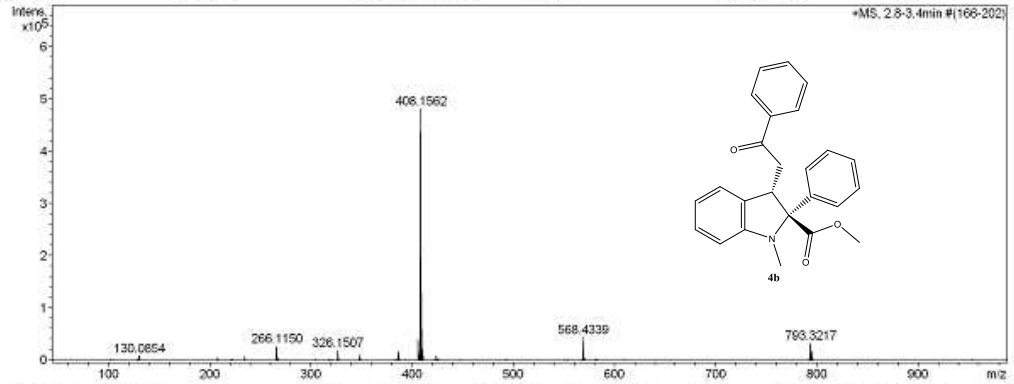
Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e¡¥ Conf	mSigma	Std Mean m/z
472.0529										
	1	C 24 H 20 Br N Na O 3	472.0519	-2.2	-2.0	14.5	ok	even	15.23	0.0010

Analysis Info

Analysis Name	D:\Data\hwh-20140605\kang-jiang_81_01_3153.d	Acquisition Date	6/5/2014 2:35:01 PM
Method	tune_low_for_lc-15min-seg.m	Operator and analyzer	ECNU.CHEM. G.D.Yang
Sample Name	kang-jiang	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

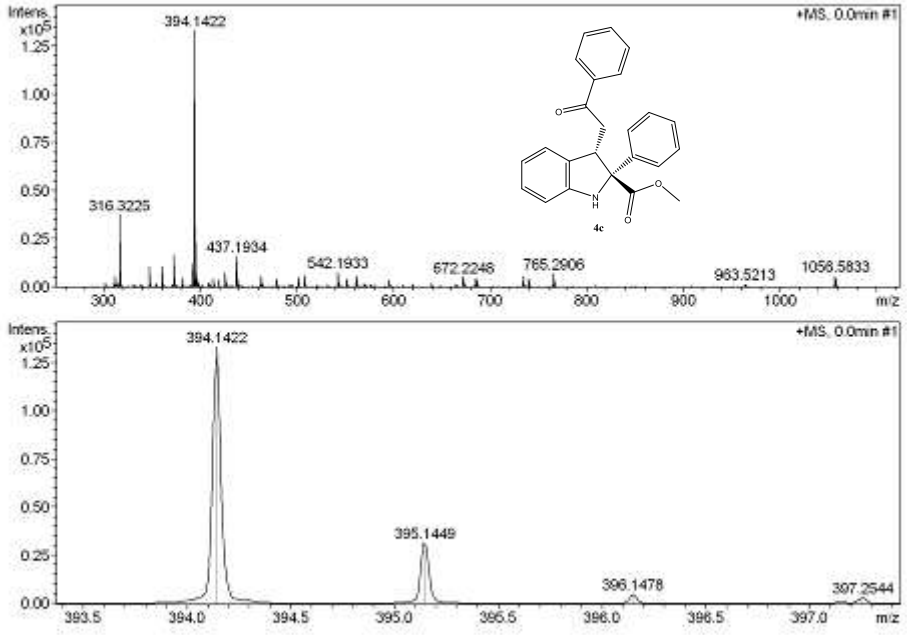
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
408.1562	1	C 25 H 23 N Na O 3	408.1570	2.0	3.3	14.5	ok	even	13.03	0.0195	0.0017	0.0084	0.0020	0.5115

Acquisition Parameter

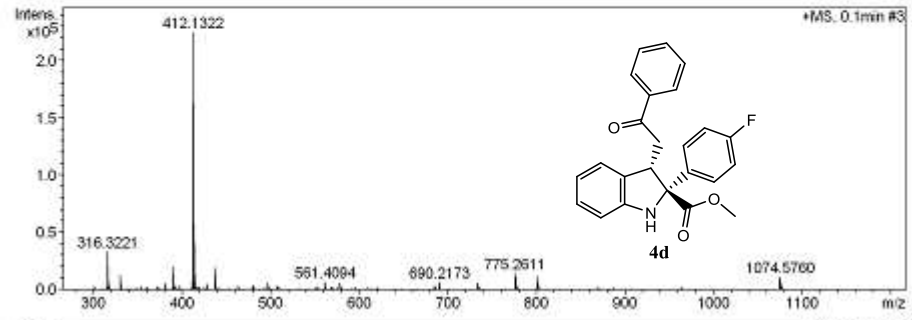
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

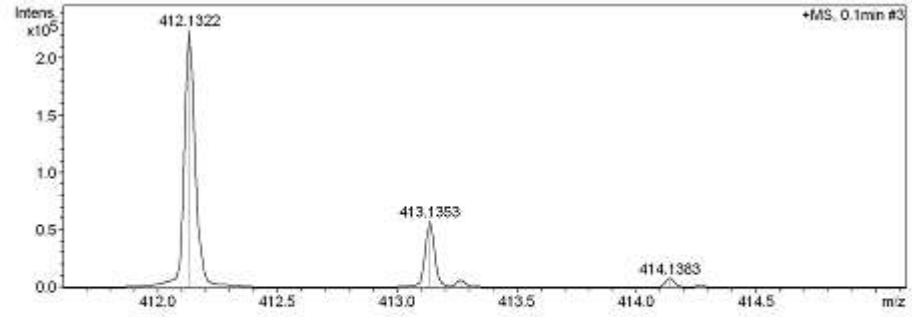


Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std Mean m/z
394.1422	1	C 24 H 21 N Na O 3	394.1414	-2.0	-1.7	14.5	ok	even	15.07	0.0007

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



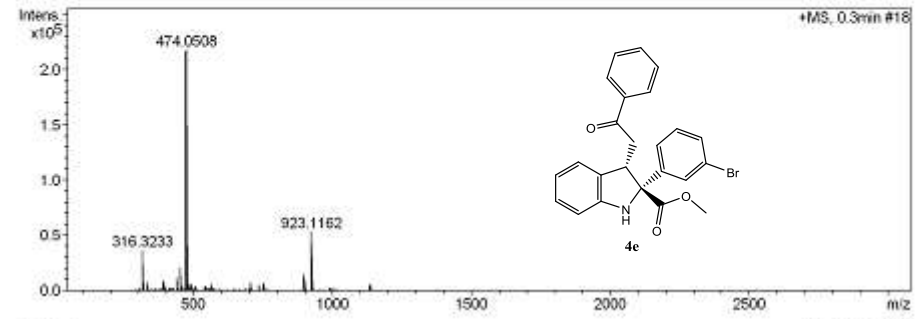


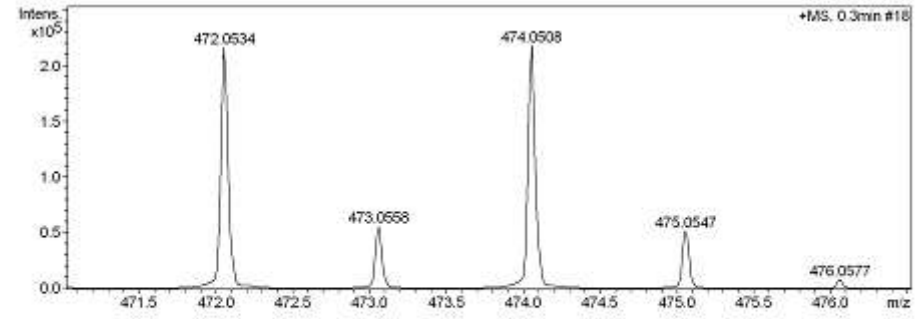
4d

Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e¡¥ Conf	mSigma	Std Mean m/z
412.1322										
	1	C 24 H 20 F N Na O 3	412.1319	-0.6	-0.4	14.5	ok	even	4.71	0.0002

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source





4e

Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e¡¥ Conf	mSigma	Std Mean m/z
472.0534										
	1	C 24 H 20 Br N Na O 3	472.0519	-3.2	-2.4	14.5	ok	even	9.68	0.0012

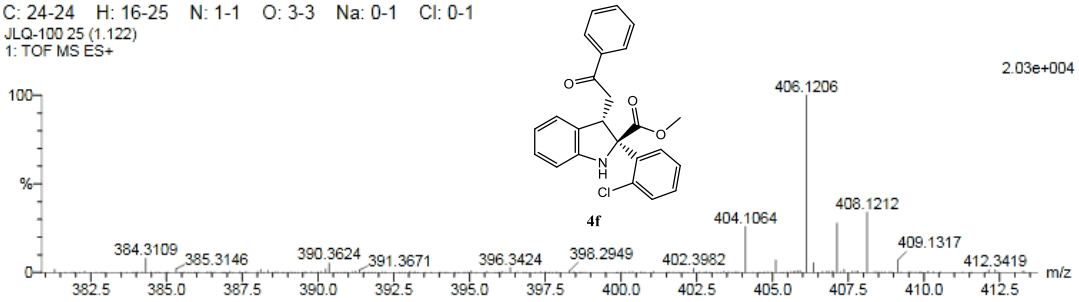
Elemental Composition Report

Single Mass Analysis

Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 24-24 H: 16-25 N: 1-1 O: 3-3 Na: 0-1 Cl: 0-1

JLQ-100 25 (1.122)
1: TOF MS ES+

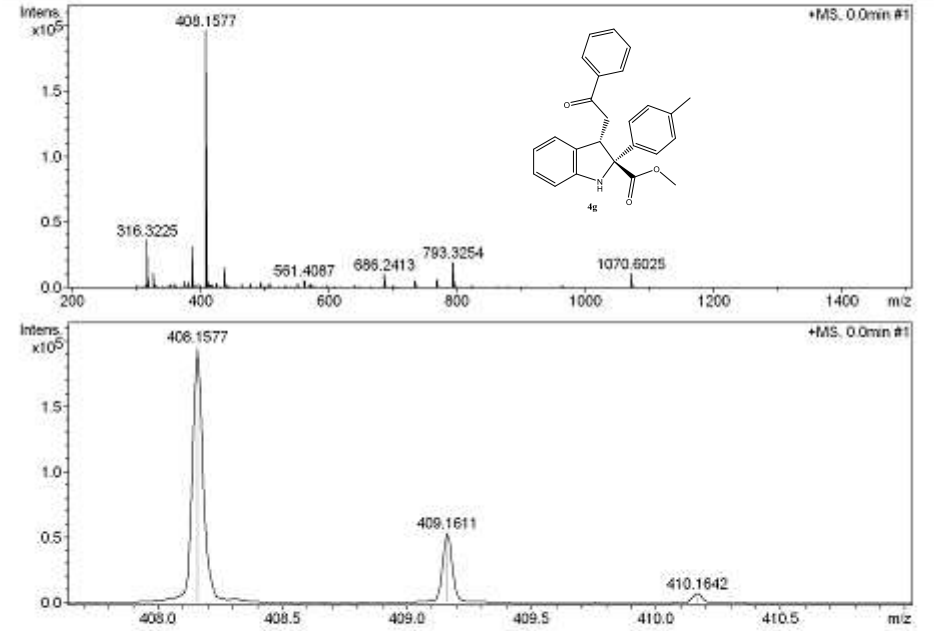


4f

Minimum:				-1.5			
Maximum:		500.0	1000.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
406.1206	406.1210	-0.4	-1.0	14.5	136.1	0.0	C24 H21 N O3 Cl

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

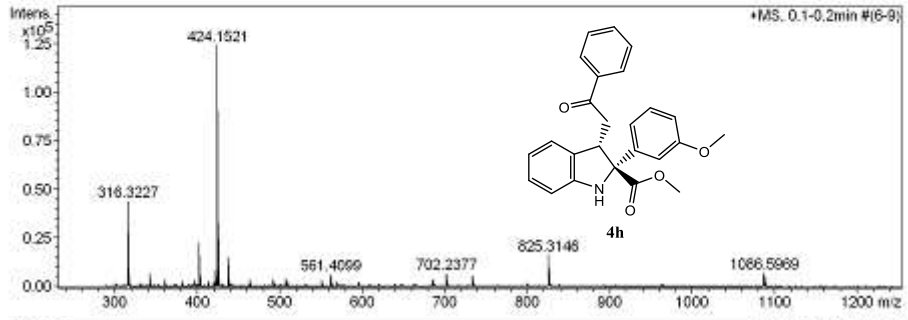


4g

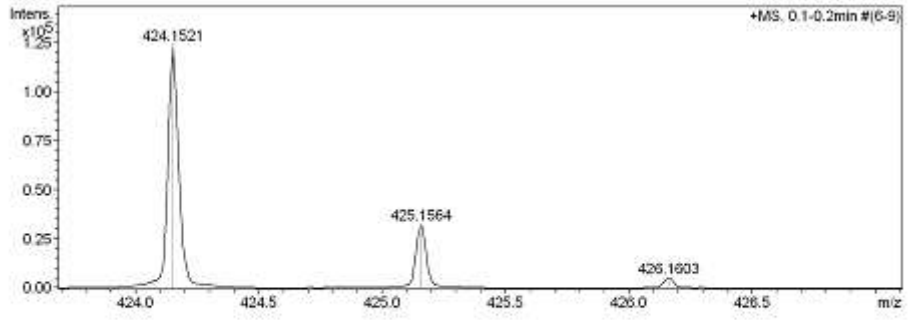
Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std Mean m/z
408.1577	1	C 25 H 23 N Na O 3	408.1570	-1.7	-1.7	14.5	ok	even	2.18	0.0007

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



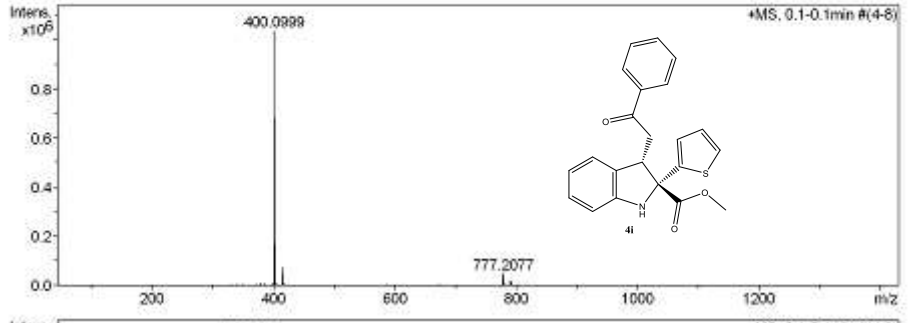
4h



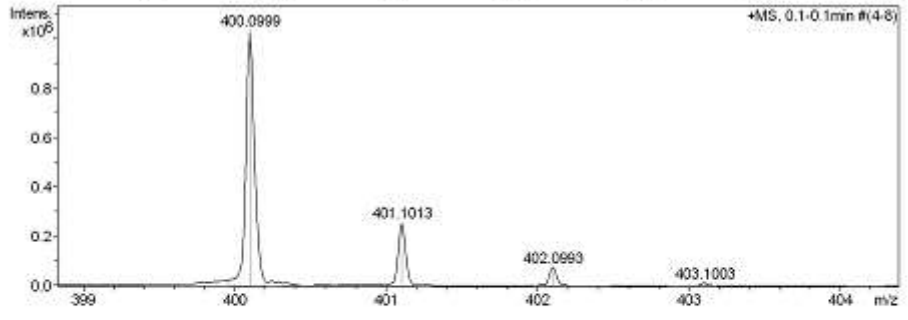
Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std Mean m/z
424.1521										
	1	C 25 H 23 N Na O 4	424.1519	-0.5	-1.0	14.5	ok	even	7.85	0.0006

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



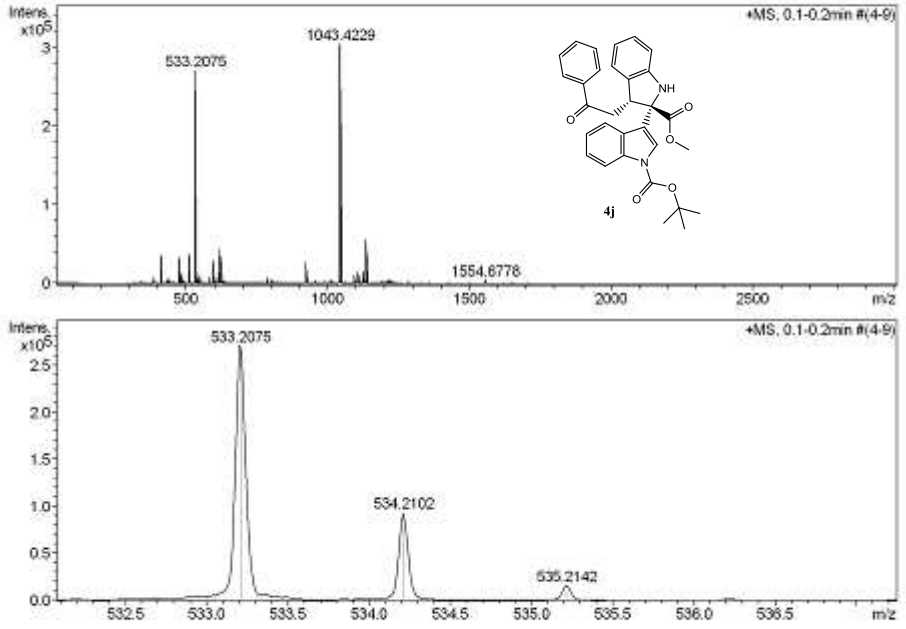
4i



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
400.0999														
	1	C 22 H 19 N Na O 3 S	400.0978	-5.4	-5.0	13.5	ok	even	4.31	0.0084	0.0023	0.0035	0.0030	0.8427

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

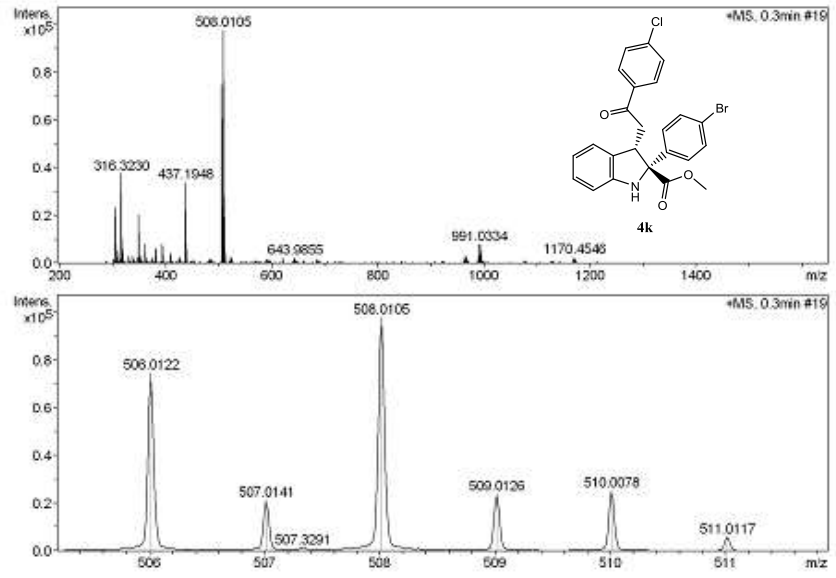


4j

Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e¡¥ Conf	mSigma	Std Mean m/z
533.2075										
	1	C 32 H 26 N 6 Na O	533.2060	-2.8	-2.5	22.5	ok	even	11.91	0.0014

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



4k

Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e¡¥ Conf	mSigma	Std Mean m/z
506.0122										
	1	C 24 H 19 Br Cl N Na O 3	506.0129	1.4	1.4	14.5	ok	even	11.19	0.0009

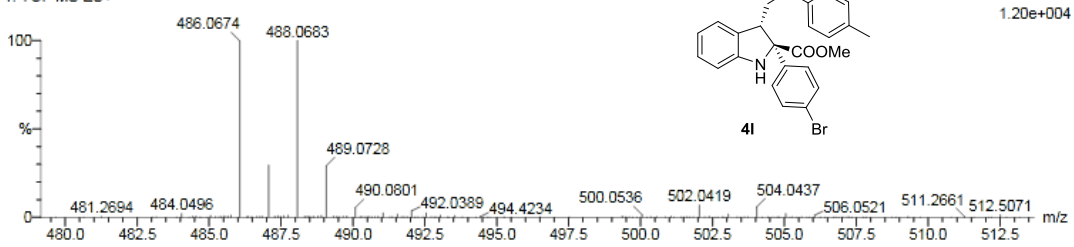
Elemental Composition Report

Single Mass Analysis

Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
5 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 25-25 H: 16-25 N: 1-1 O: 3-4 Na: 0-1 Br: 0-1

JLQ-101A 59 (2.613)
1: TOF MS ES+



4l

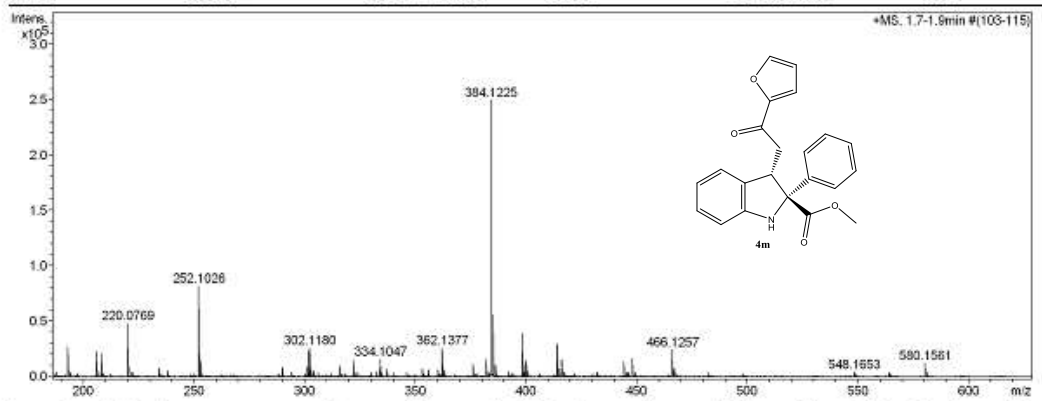
Minimum:				-1.5			
Maximum:		500.0	1000.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
486.0674	486.0681	-0.7	-1.4	14.5	135.7	0.0	C25 H22 N O3 Na Br

Analysis Info

Analysis Name	D:\Data\HWH-20140523\JLQ-13-3_41_01_3134.d	Acquisition Date	5/23/2014 1:11:40 PM
Method	tune_low_for_lc-15min-seg.m	Operator and analyzer	ECNU.CHEM. G.D.Yang
Sample Name	JLQ-13-3	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

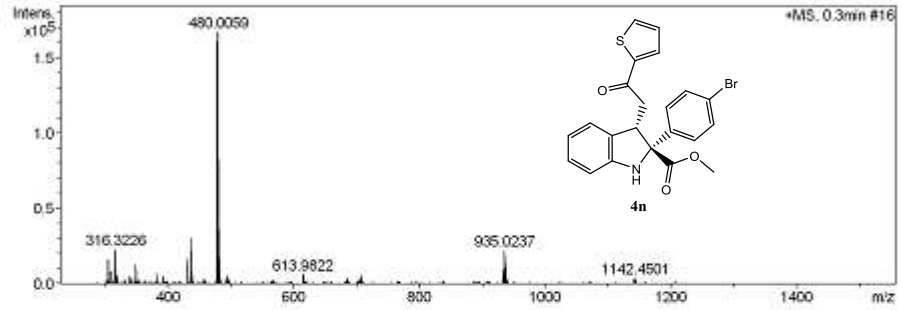
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



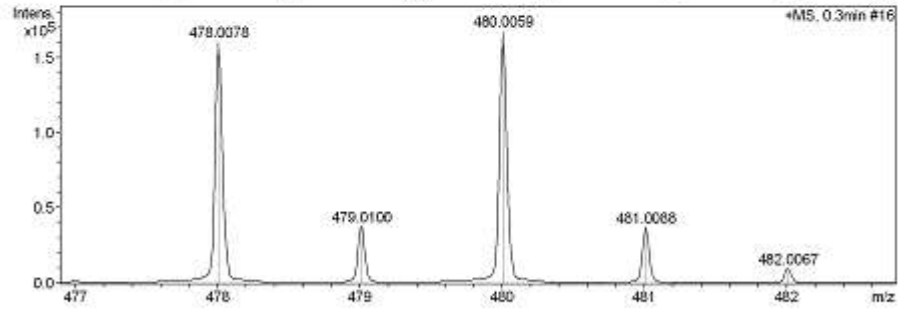
Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
384.1225	1	C 22 H 19 N Na O 4	384.1206	-4.7	-2.6	13.5	ok	even	11.14	0.0158	0.0021	0.0077	0.0030	0.6126

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



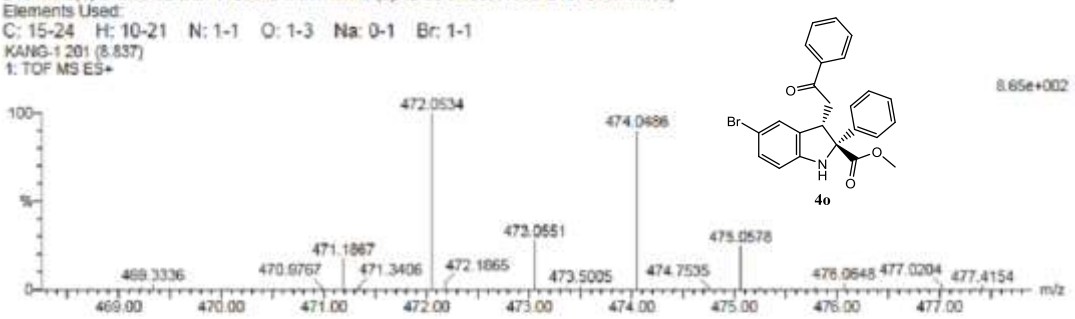
4n



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std Mean m/z
478.0078										
	1	C 22 H 18 Br N Na O 3 S	478.0083	1.1	1.0	13.5	ok	even	12.24	0.0010

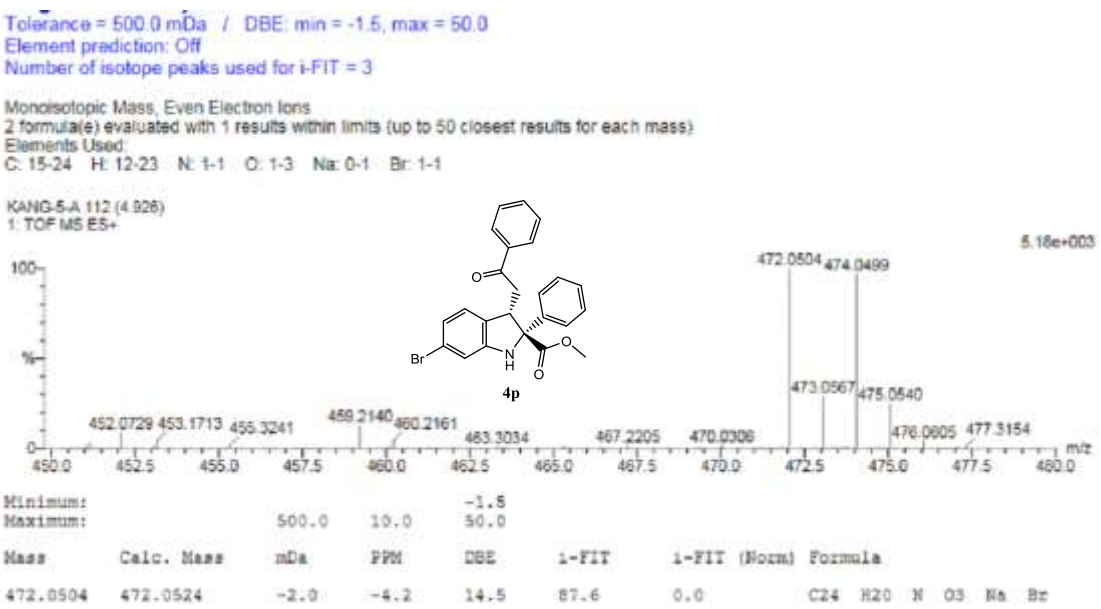
Tolerance = 500.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 15-24 H: 10-21 N: 1-1 O: 1-3 Na: 0-1 Br: 1-1
KANG-1 201 (8.837)
1: TOF MS ES+



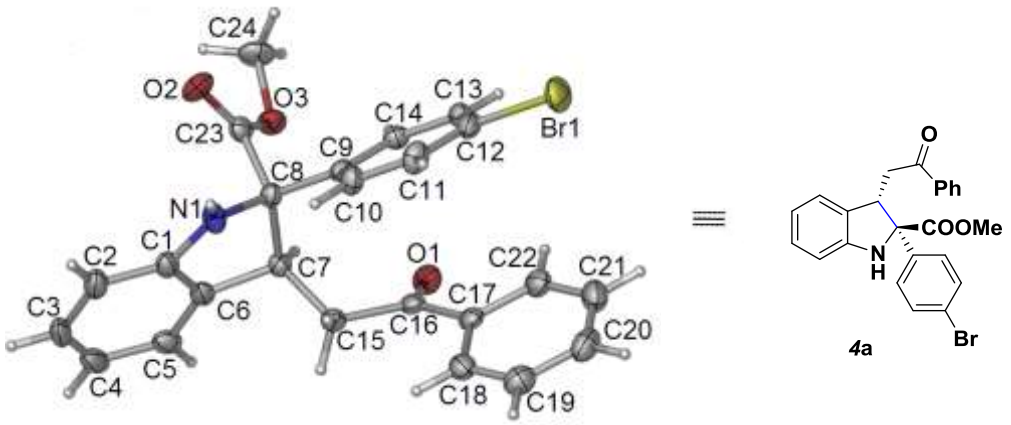
4o

Minimum:				-1.5			
Maximum:		500.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
472.0534	472.0524	1.0	2.1	14.5	64.0	0.0	C24 H20 N O3 Na Br



X-ray diffraction parameters and data

X-ray diffraction parameters and data of (2*R**, 3*S**)4a



The relative stereochemistry of **4a** was determined to be *anti* by single-crystal X-ray data analysis above.

Bond precision:	C-C = 0.0035 A		Wavelength=0.71073
Cell:	a=8.5954(6)	b=21.9171(16)	c=10.9128(8)
	alpha=90	beta=105.471(2)	gamma=90
Temperature: 173 K			

	Calculated	Reported
Volume	1981.3(2)	1981.3(2)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C24 H20 Br N O3	?
Sum formula	C24 H20 Br N O3	C24 H20 Br N O3
Mr	450.31	450.32
Dx,g cm-3	1.510	1.510
Z	4	4
Mu (mm-1)	2.101	2.101
F000	920.0	920.0
F000'	919.23	
h,k,lmax	10,26,12	10,26,12
Nref	3484	3479
Tmin,Tmax	0.623,0.730	0.644,0.743
Tmin'	0.611	

Correction method= MULTI-SCAN

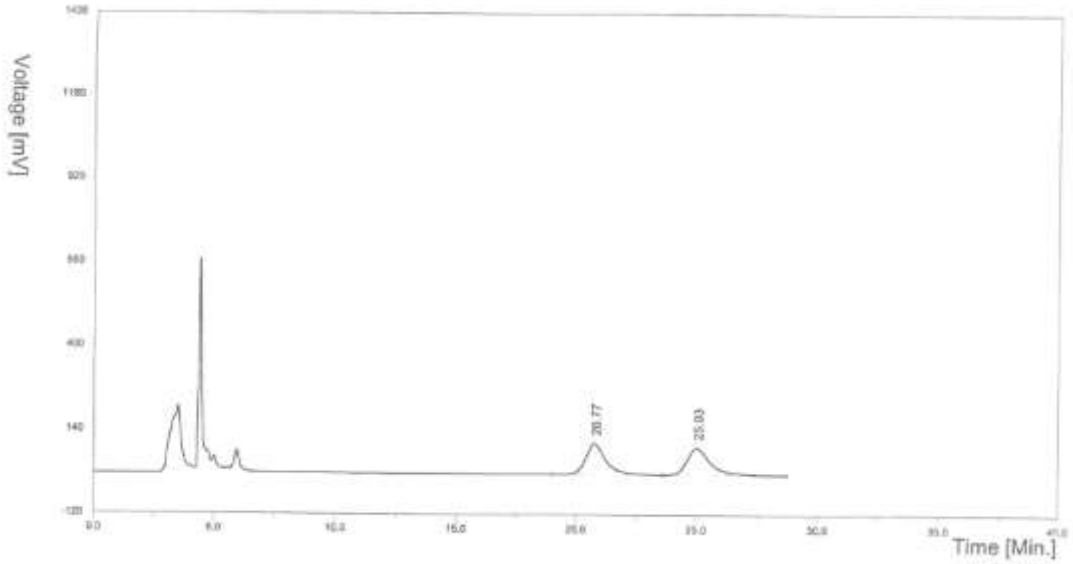
Data completeness= 0.999 Theta(max)= 25.010

R(reflections)= 0.0314(2892) wR2(reflections)= 0.0774(3479)

S = 1.029 Npar= 262

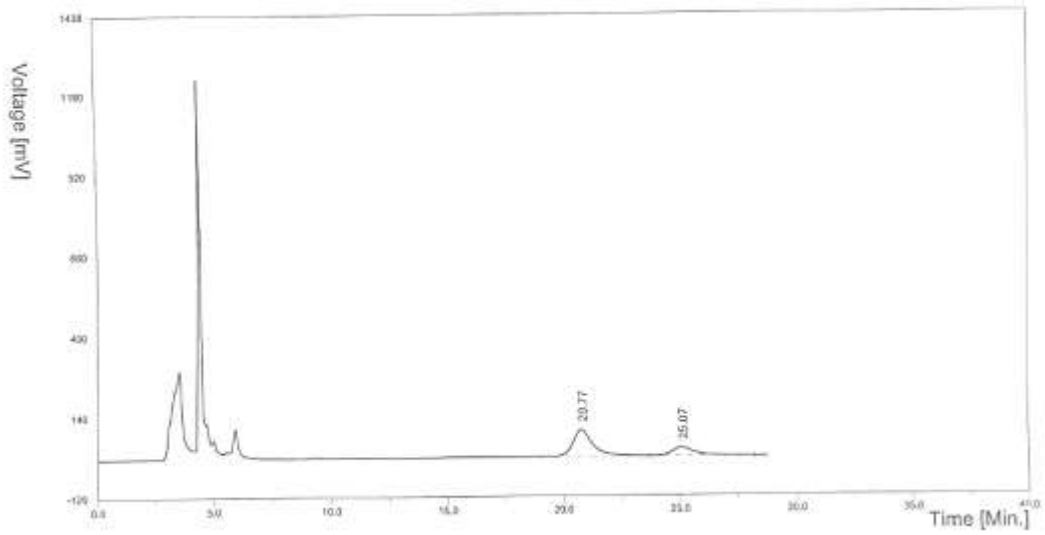
CCDC number: 944673

HPLC chromatograms of 4a



Component table 1

Peak#	Component name	Retention time(min)	Height (mv)	Area(mv.sec)	Area (%)
1	Unknow	20.77	97.06	5741.52	50.2655
2	Unknow	25.03	83.50	5680.86	49.7345
Total			180.56	11422.38	100



Component table 2

Peak#	Component name	Retention time(min)	Hight (mv)	Area(mv.sec)	Area (%)
1	Unknow	20.77	86.07	5084.97	73.3979
2	Unknow	25.03	26.95	1842.98	26.6021
Total			113.02	6927.95	100

HPLC (Chiral IA, λ = 254 nm, hexane/isopropanol = 95/5, Flow rate = 1.0 mL/min), t_{major} = 20.77 min, t_{minor} = 25.07 min.