

Diastereo- and Enantioselective Synthesis of Spirooxindoles with Contiguous Tetrasubstituted Stereocenters via Catalytic Coupling of Two Tertiary Radicals

Zhi-Yong Song,^{a,b} Kun-Quan Chen,^{a,b} Xiang-Yu Chen^a and Song Ye^{a,b} *

^a Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of
Molecular Recognition and Function, CAS Research/Education Center for Excellence
in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing
100190, China.

^b University of Chinese Academy of Sciences, Beijing 100049, China.

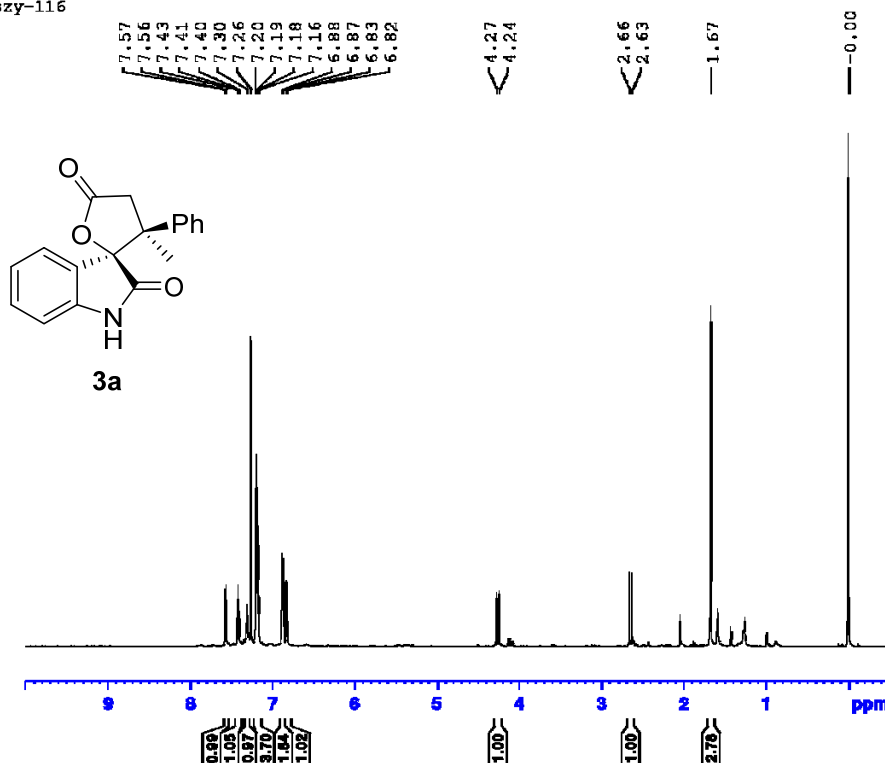
E-mail: songye@iccas.ac.cn

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Part I NMR Spectra

szy-116

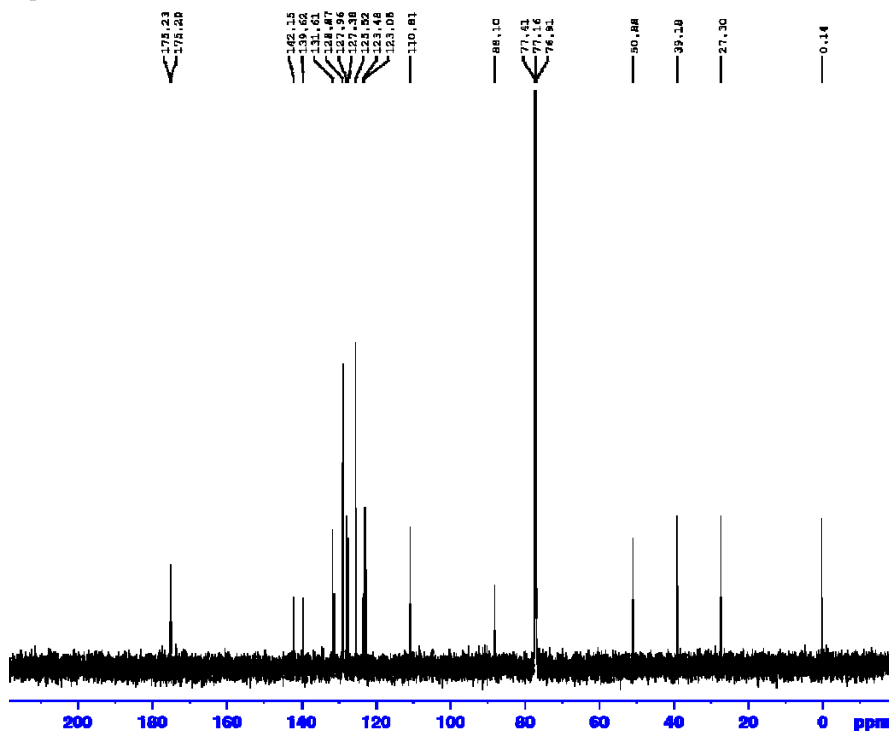


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NAME H NMR
EXPNO 56
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160321
Time 17.11 h
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 31.72
DW 50.000 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TDO 1
SFO1 500.1330895 MHz
NUC1 1H
P1 10.60 usec
PLW1 20.00000000 W

F2 - Processing parameters
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SF 500.1300120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

szy-116

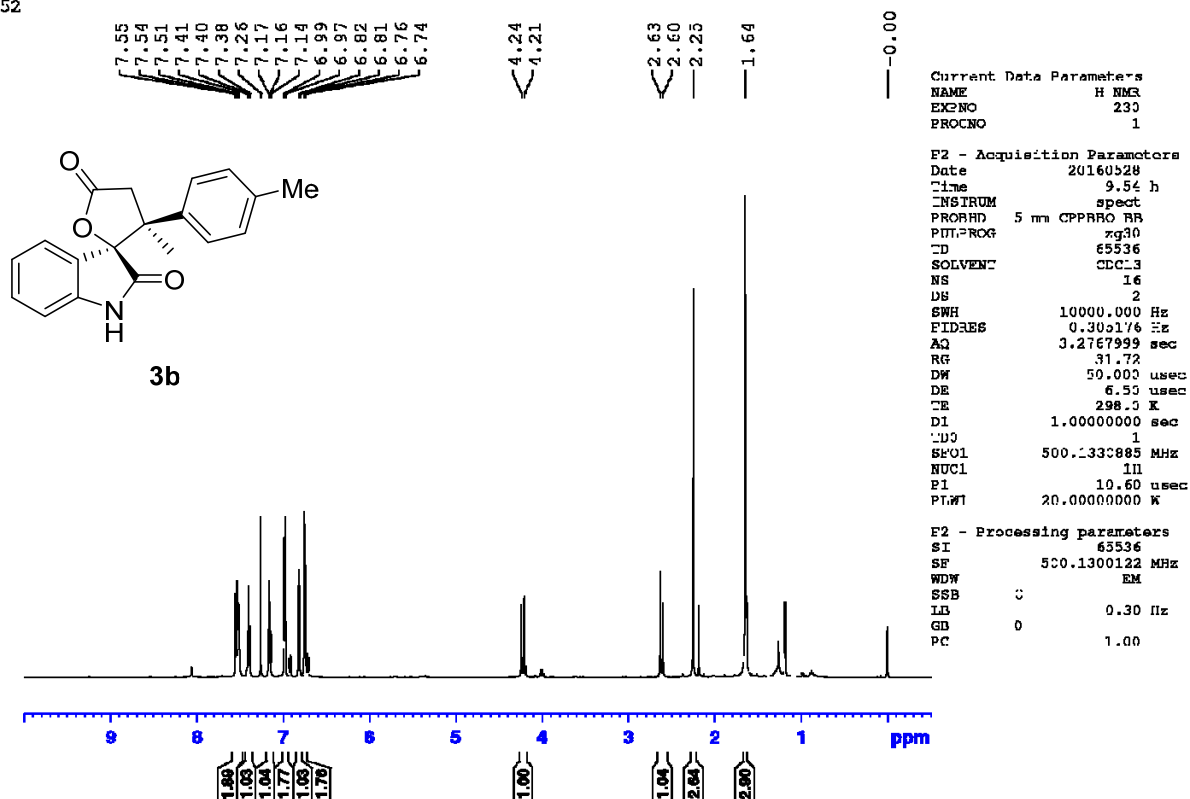


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EXPNO 57
PROCNO 1

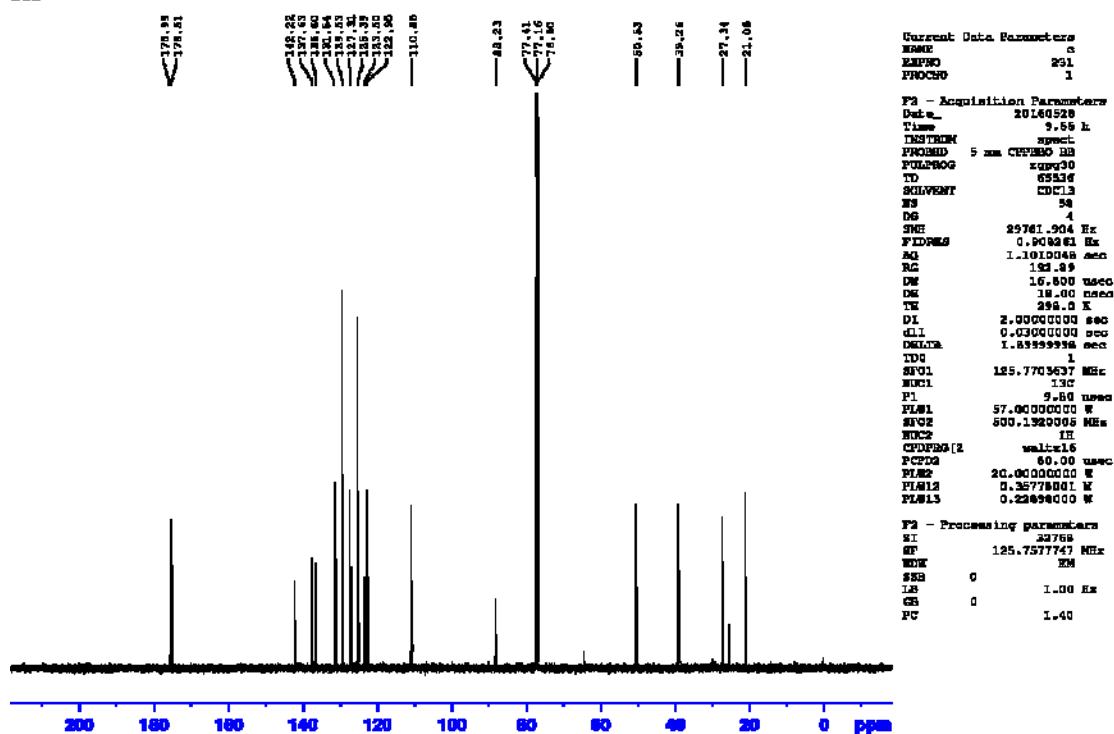
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Time 17.16 h
INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 133
DS 4
SWH 29761.904 Hz
FIDRES 0.308261 Hz
AQ 1.1019048 sec
RG 132.89
DW 16.800 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TDO 1
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
PLW1 57.00000000 W
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.35778001 W
PLW13 0.22898000 W

F2 - Processing parameters
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SF 125.7577720 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

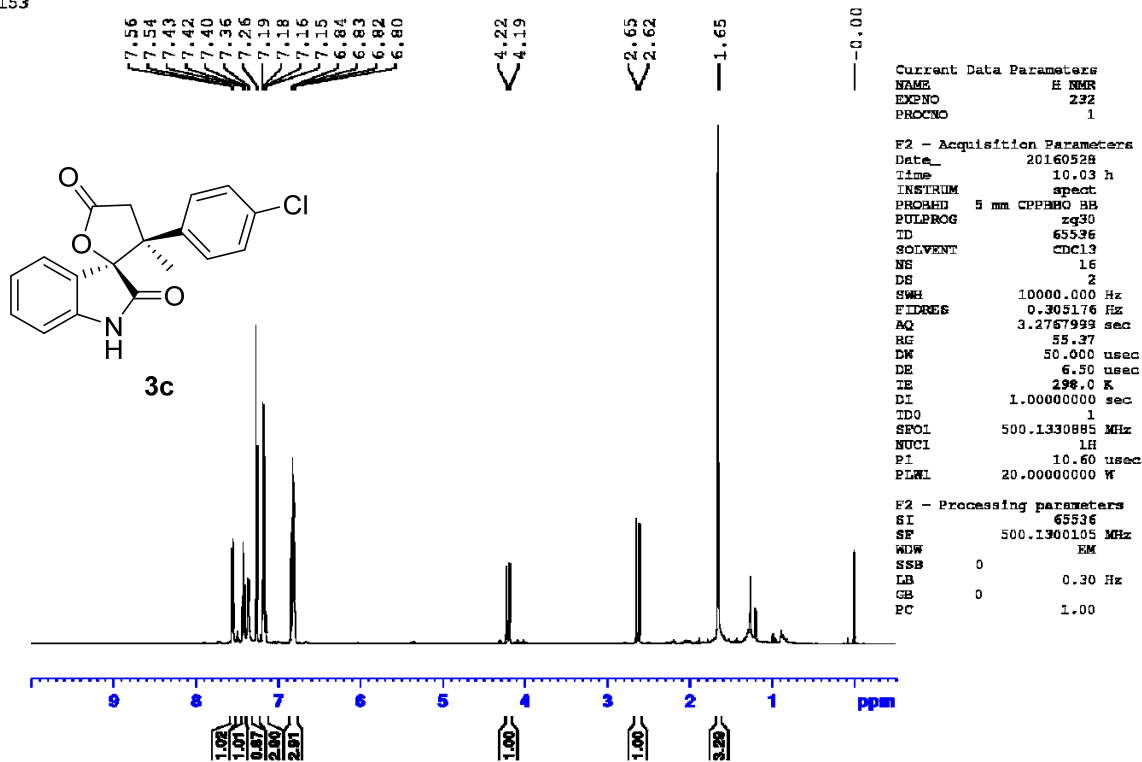
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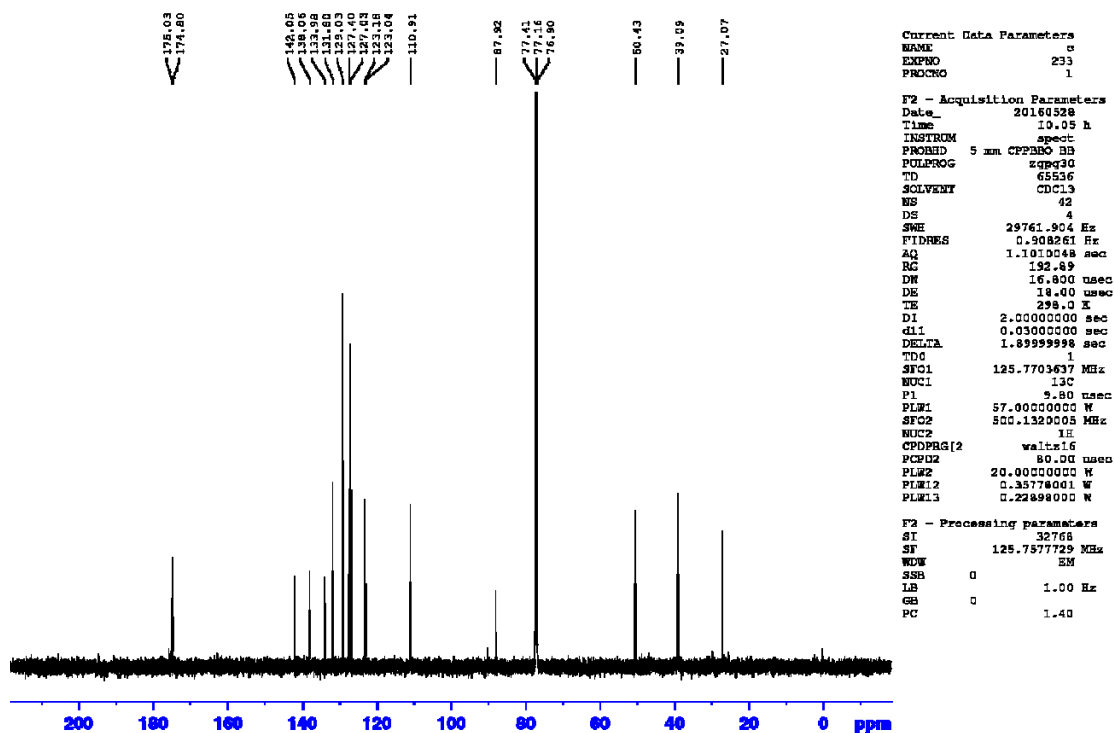
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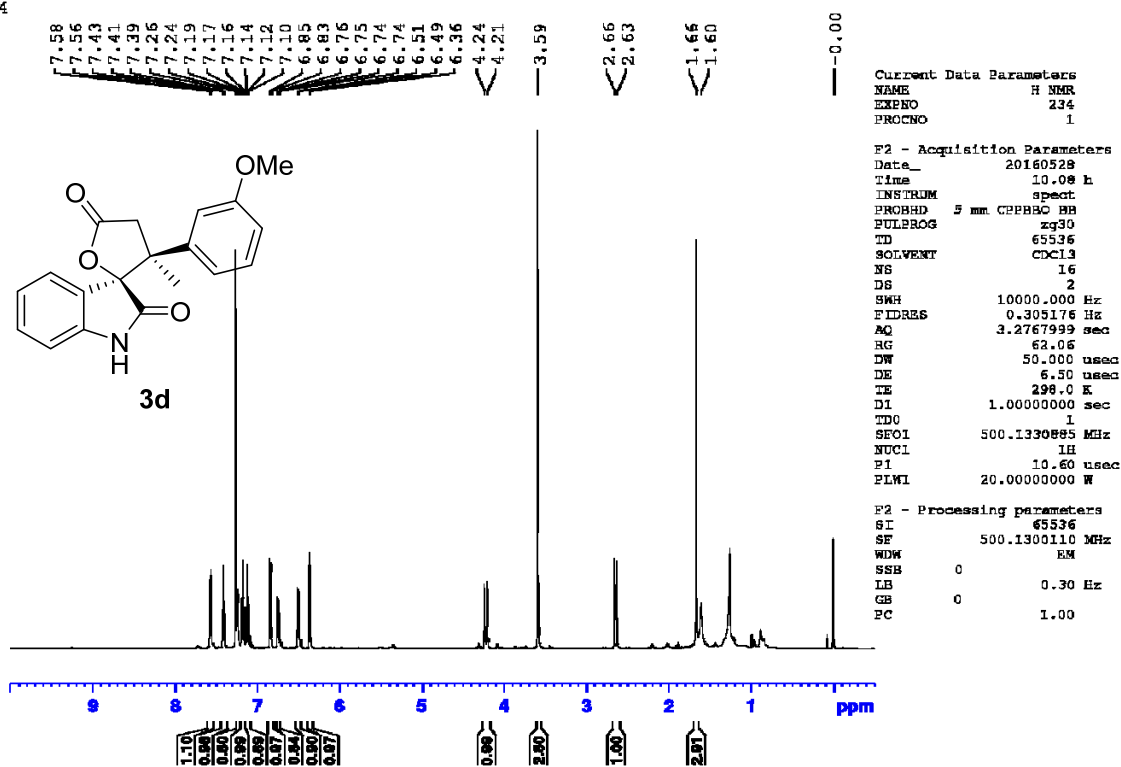
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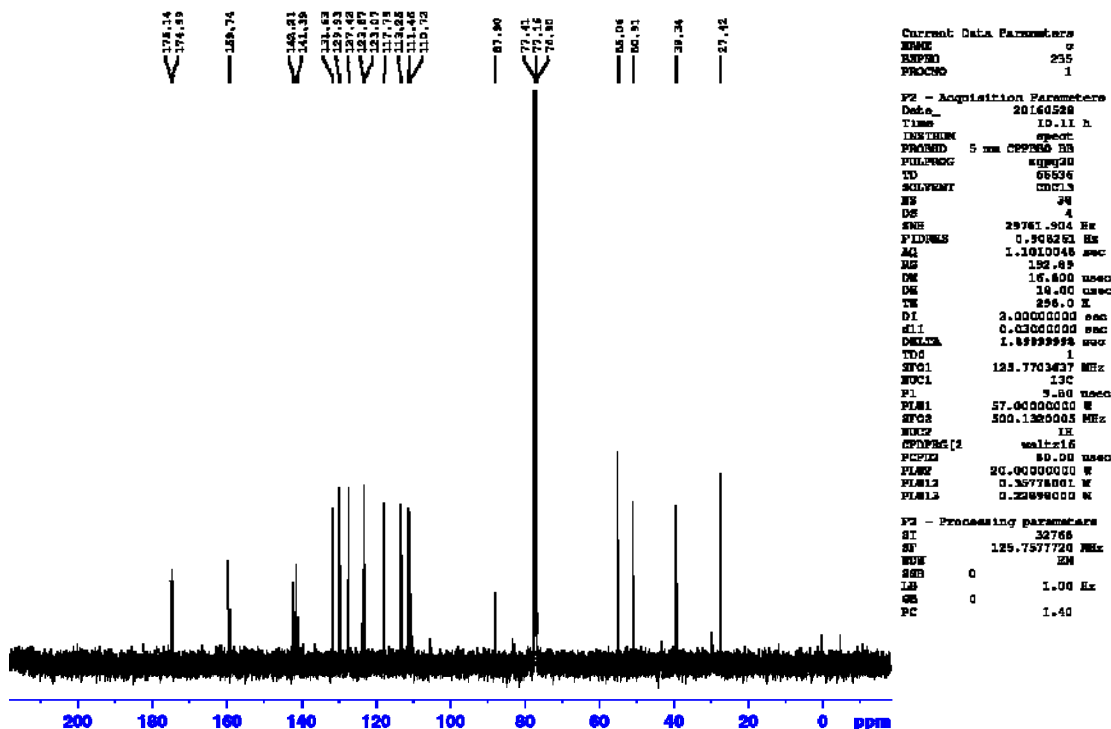
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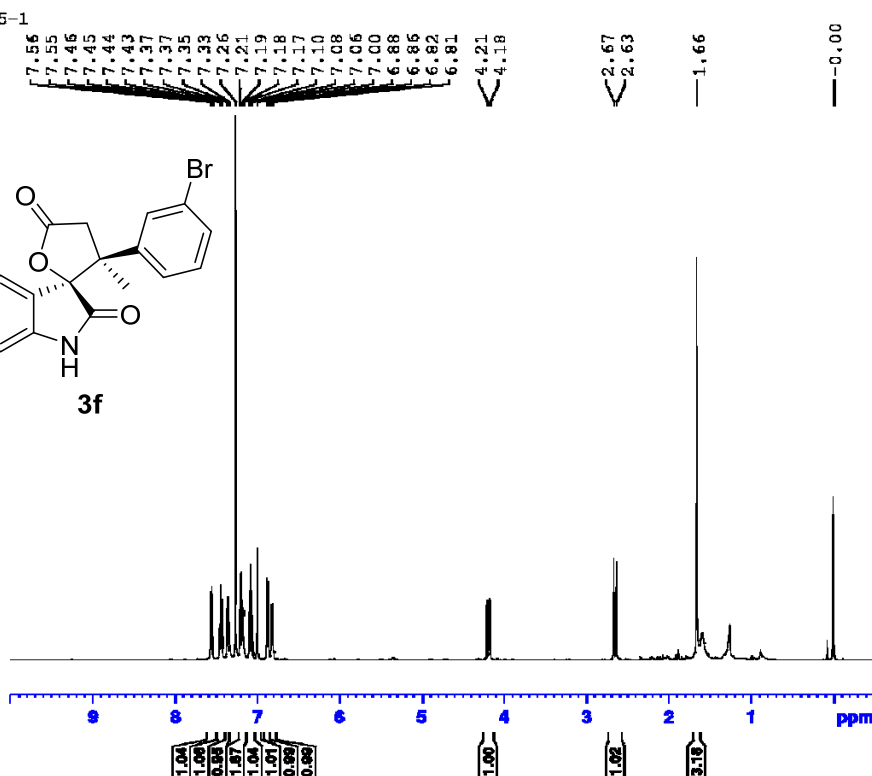
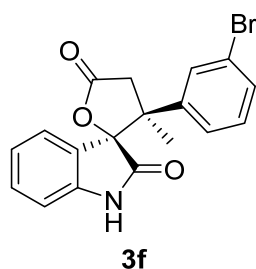
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Current Data Parameters

NAME	H NMR
EXNO	236
PROCNO	1

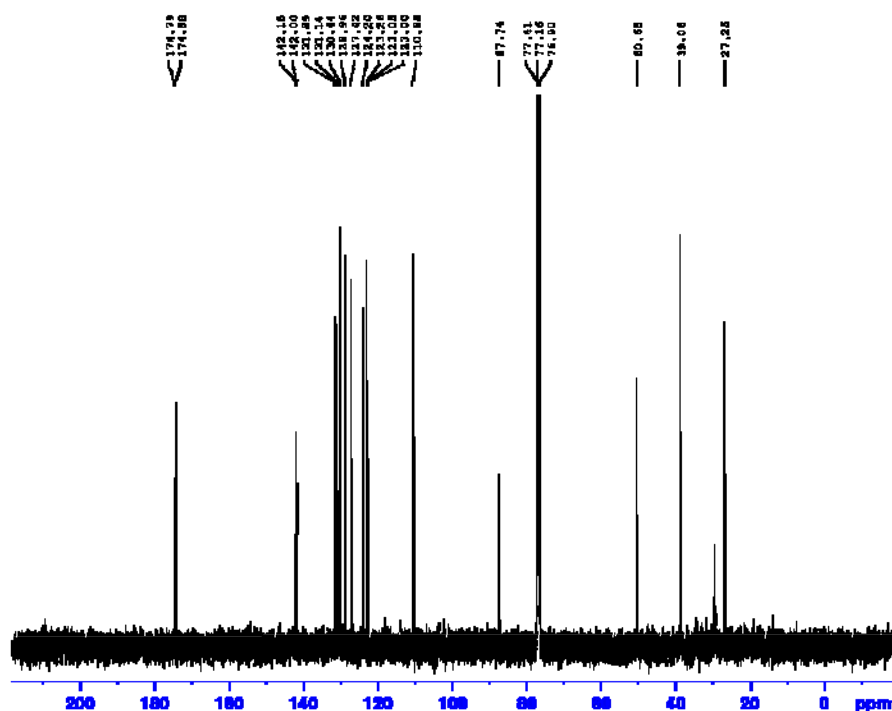
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PROBHD	5 mm CBBBO BB
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10000.000 Hz
FIDRES	0.305176 Hz
AQ	3.2767999 sec
RG	63.06
DW	50.000 used
DE	6.50 used
TE	298.0 K
D1	1.00000000 sec
TD0	1
SFO1	500.1330885 MHz
NUC1	1H
P1	10.60 usec
PL1	20.00000000 W

F2 - Processing parameters

SI	65536
SF	500.1300111 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

155

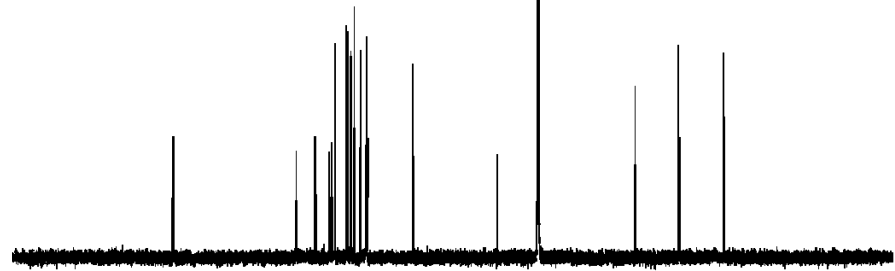
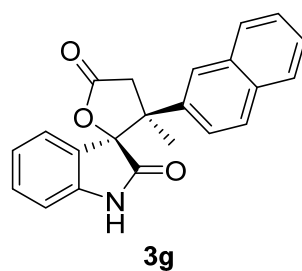


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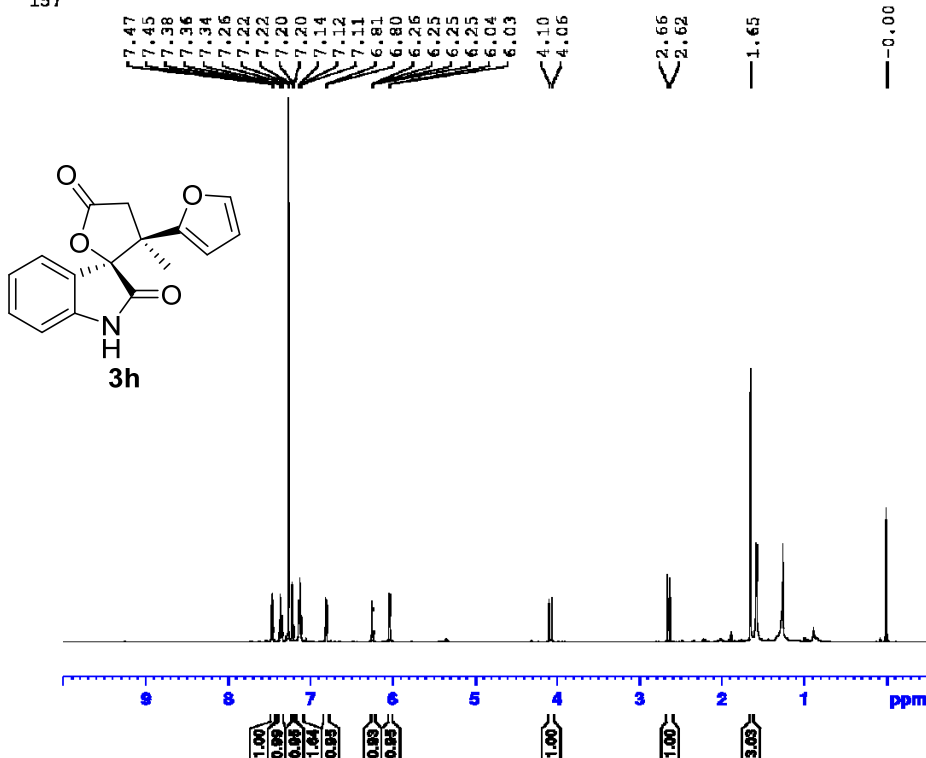
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EXNO	20
PROCNO	1

F2 - Acquisition Parameters

Date_	20160528
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INSTRUM	spect
PROBHD	5 mm CBBBO BB
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	233
DS	4



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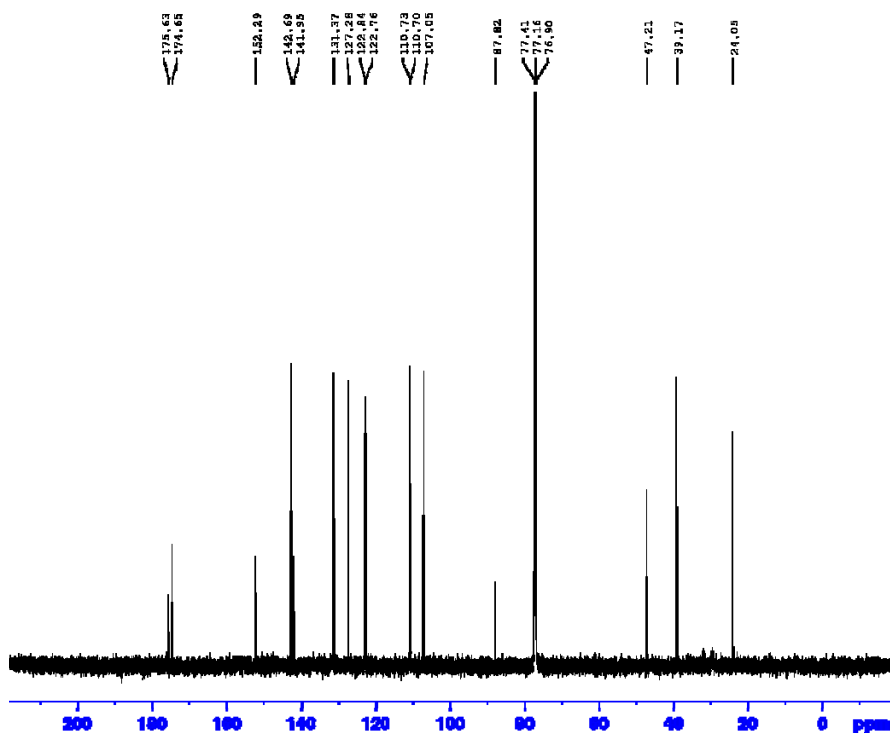


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NAME H NMR
EXNO 245
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160530
Time 21.34 h
INSTRUM spect
PROBHD 5 mm CPMBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 31.72
DW 50.000 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 500.1330885 MHz
NUC1 1H
P1 10.60 usec
PL1 20.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300114 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

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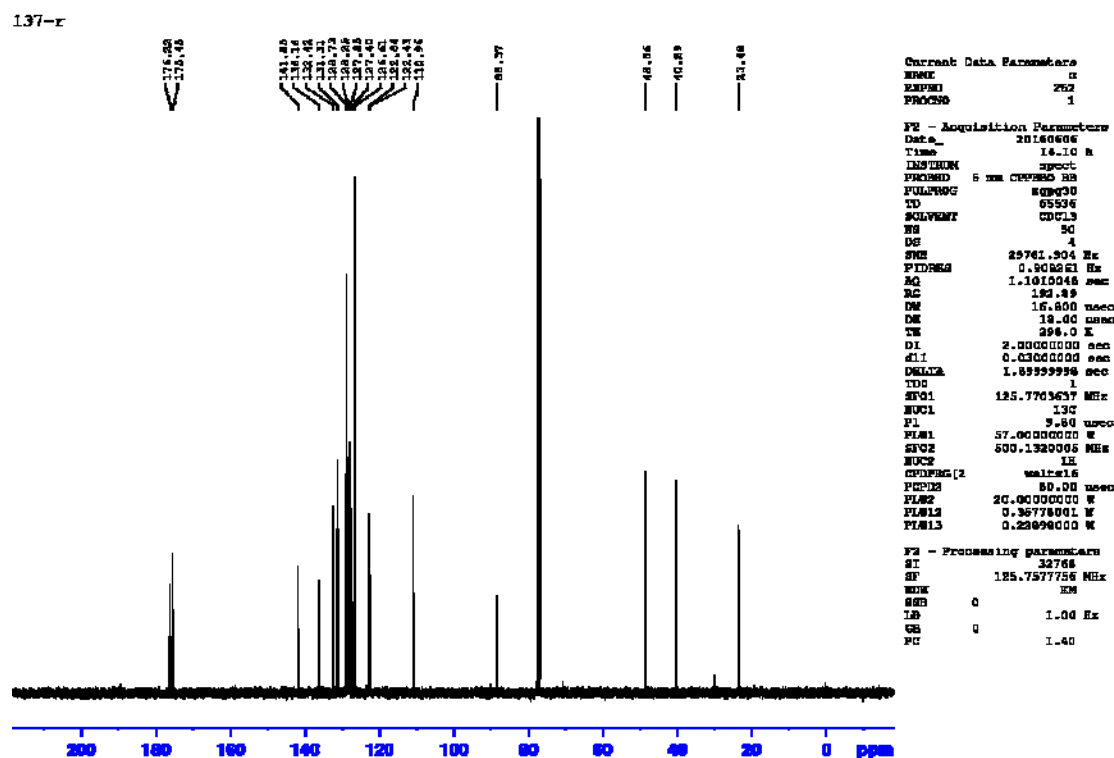
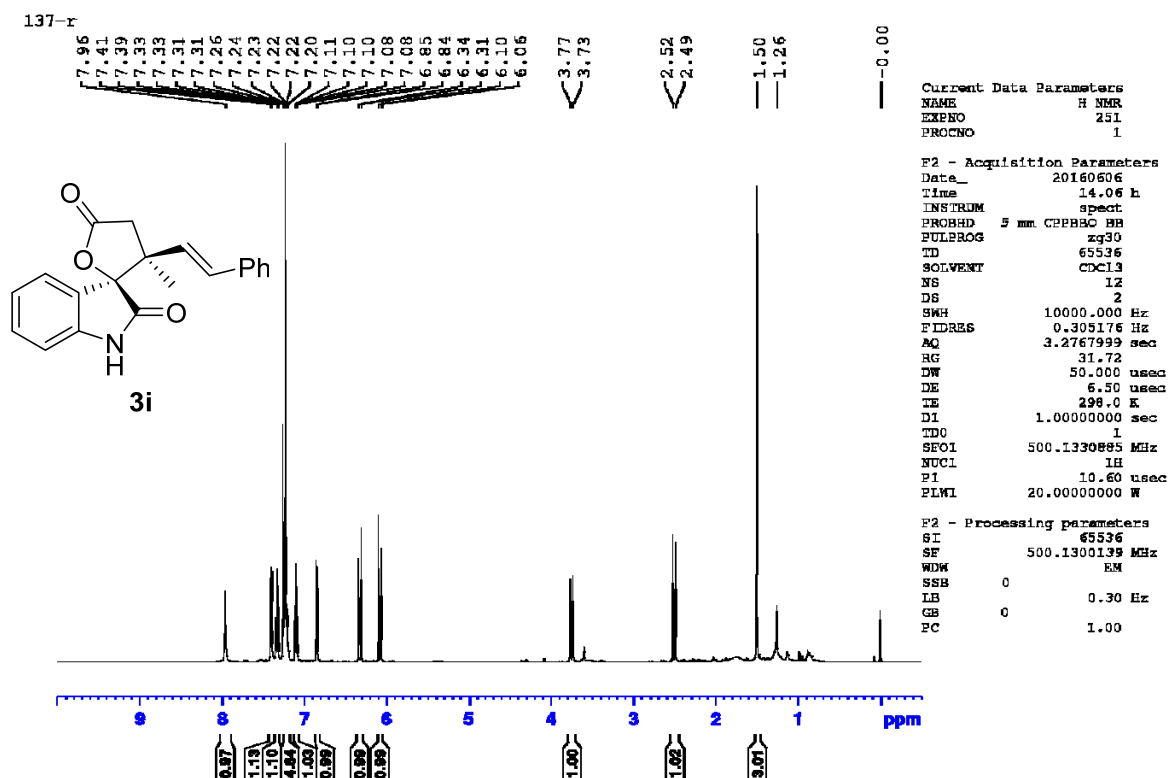
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EXNO 22
PROCNO 1

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Date_ 20160126
Time 13.32
INSTRUM spect
PROBHD 5 mm CPMBO BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 276
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 132.69
DW 16.800 usec
DE 18.00 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

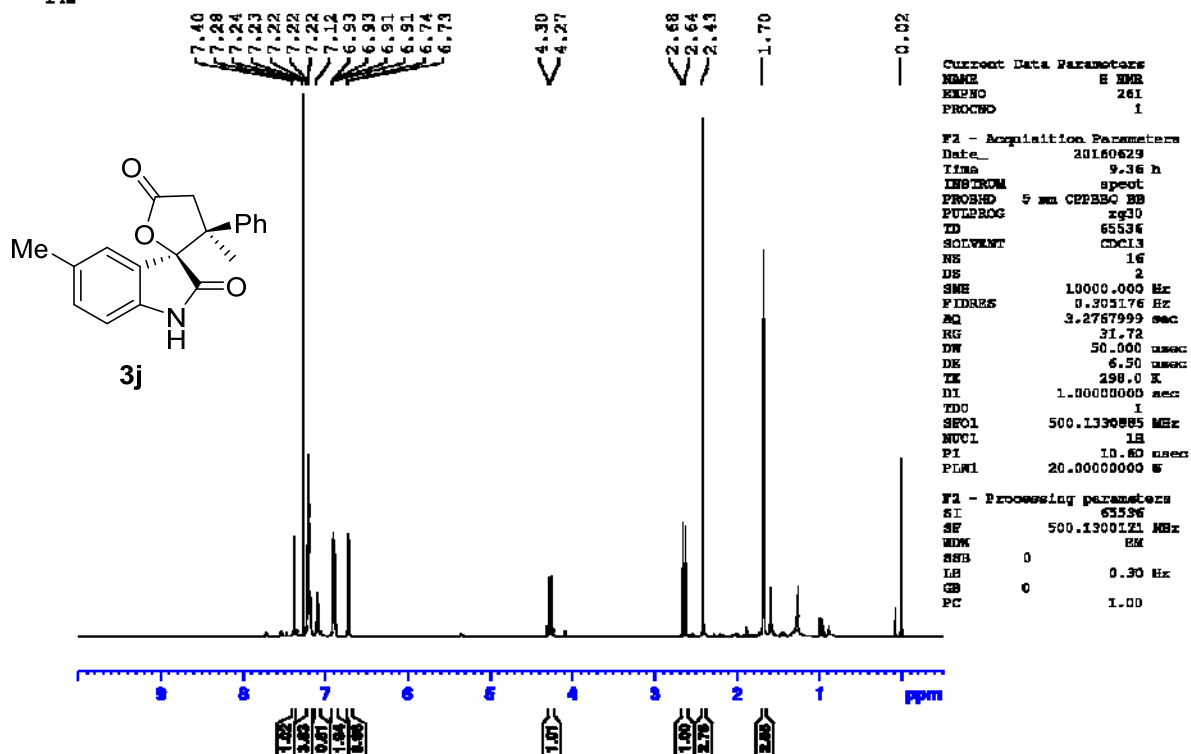
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SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
PL1 57.00000000 W

CHANNEL F2
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLF2 20.00000000 W
PLF12 0.35778001 W
PLF13 0.22898000 W

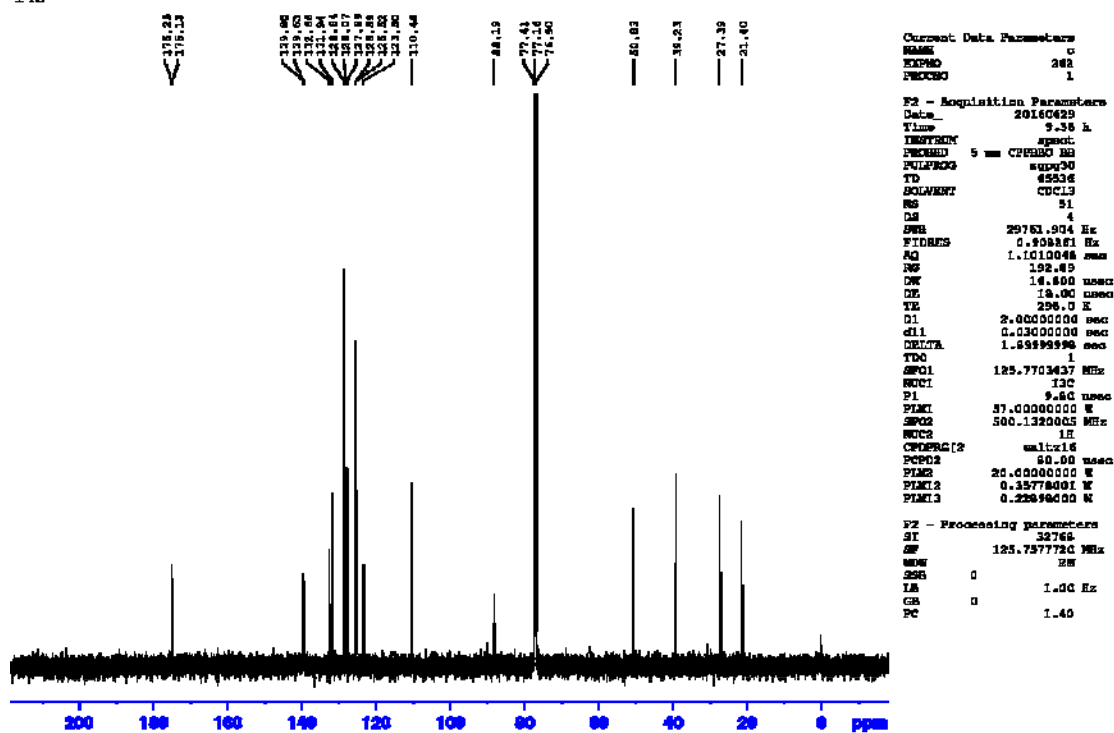
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WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



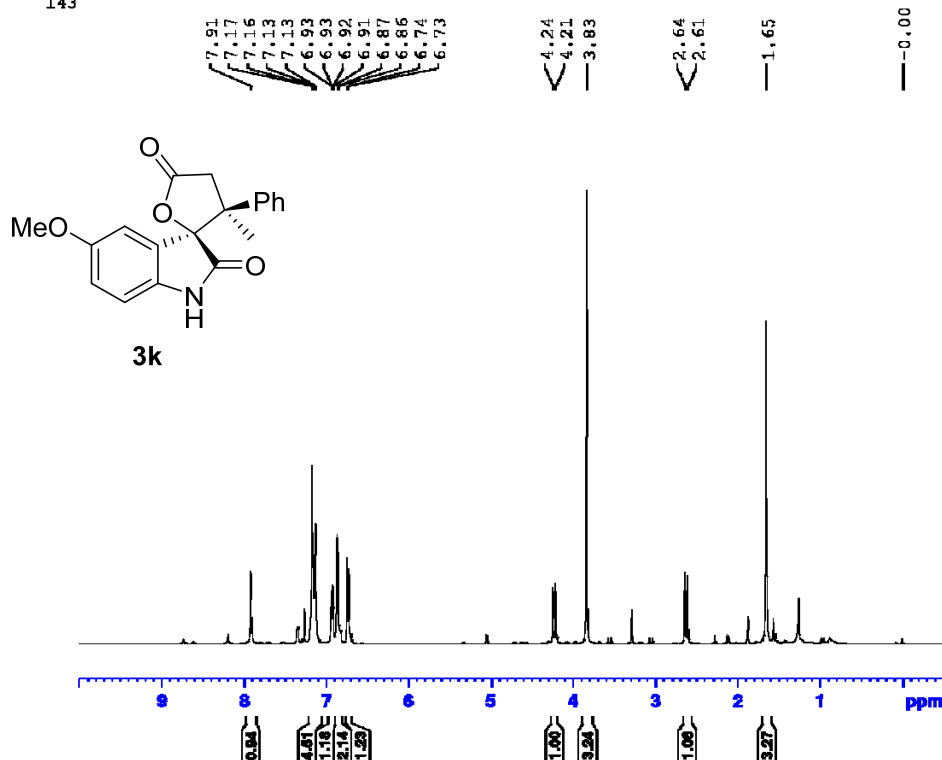
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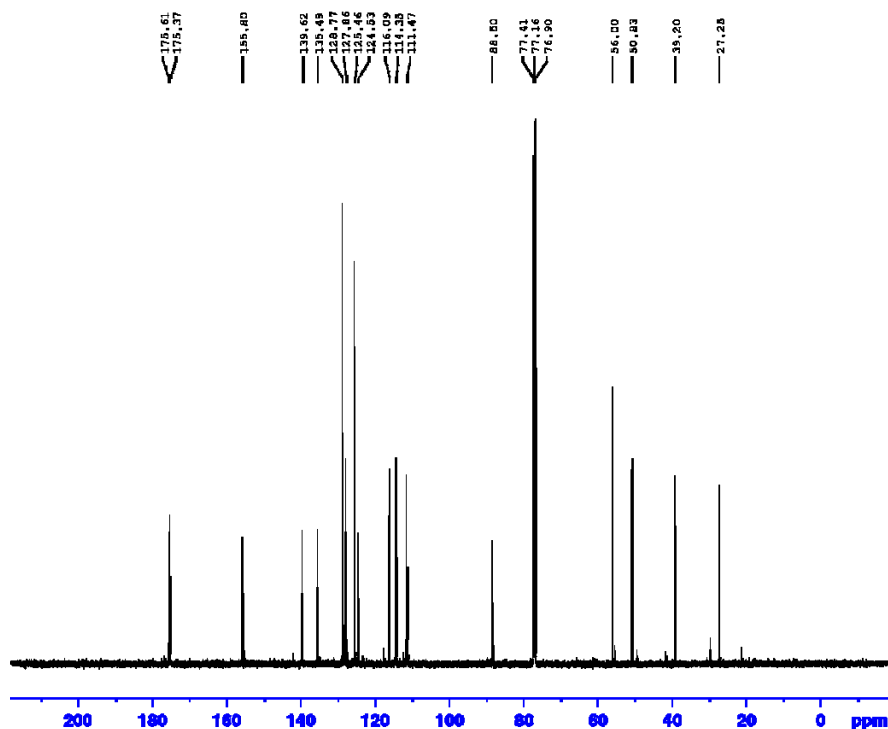
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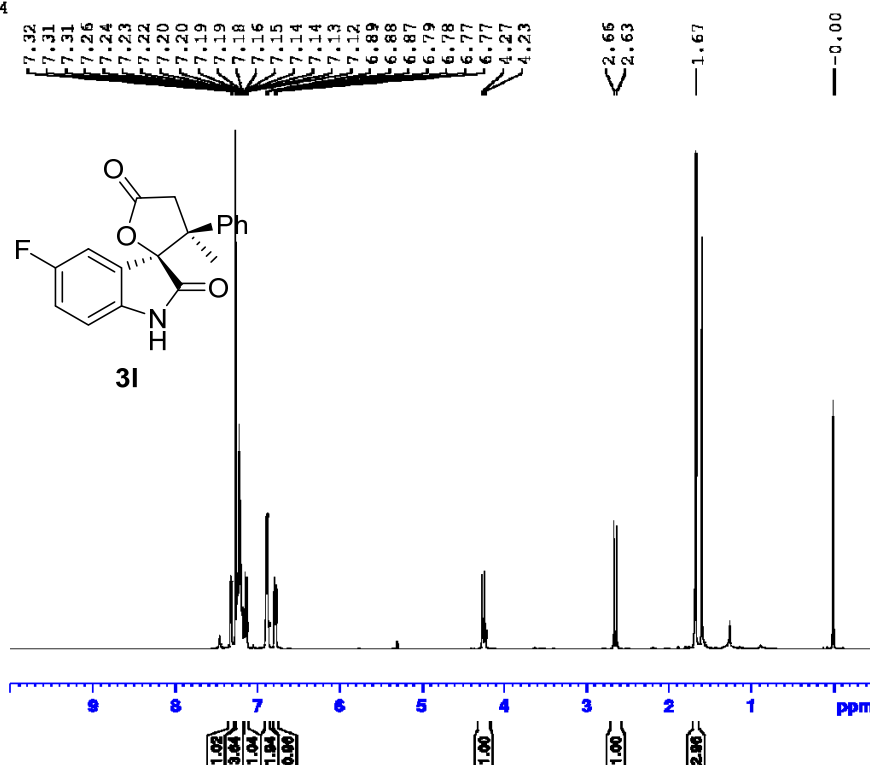
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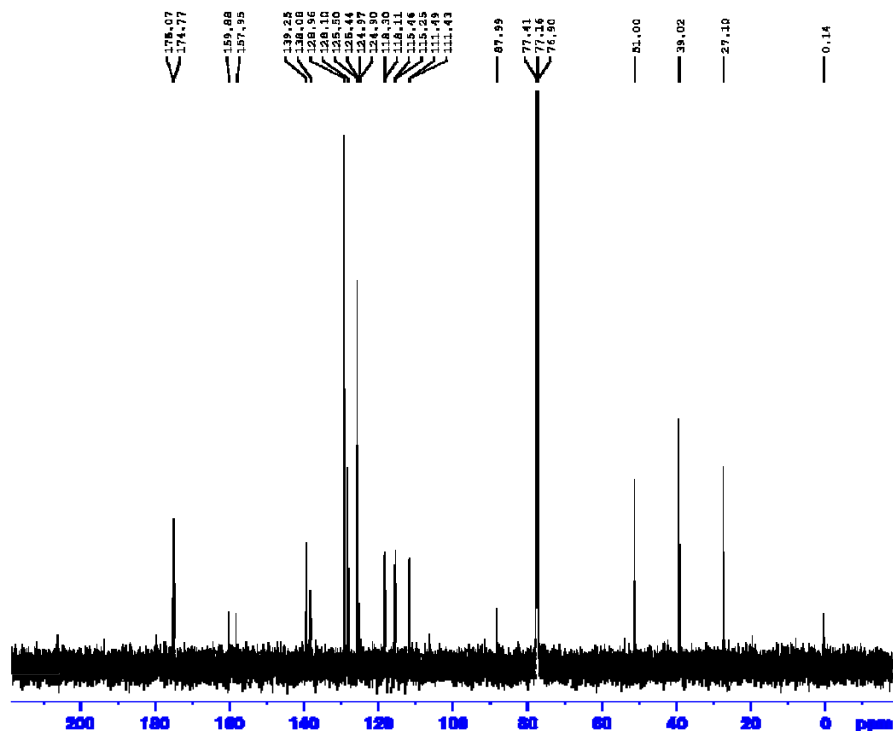


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NAME c
EXPNO 265
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160704
Time 20.25 h
INSTRUM spect
PROBHD 5 mm CPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 77.18
DW 50.000 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 500.1330885 MHz
NUC1 1H
P1 10.60 usec
PLM1 20.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300115 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

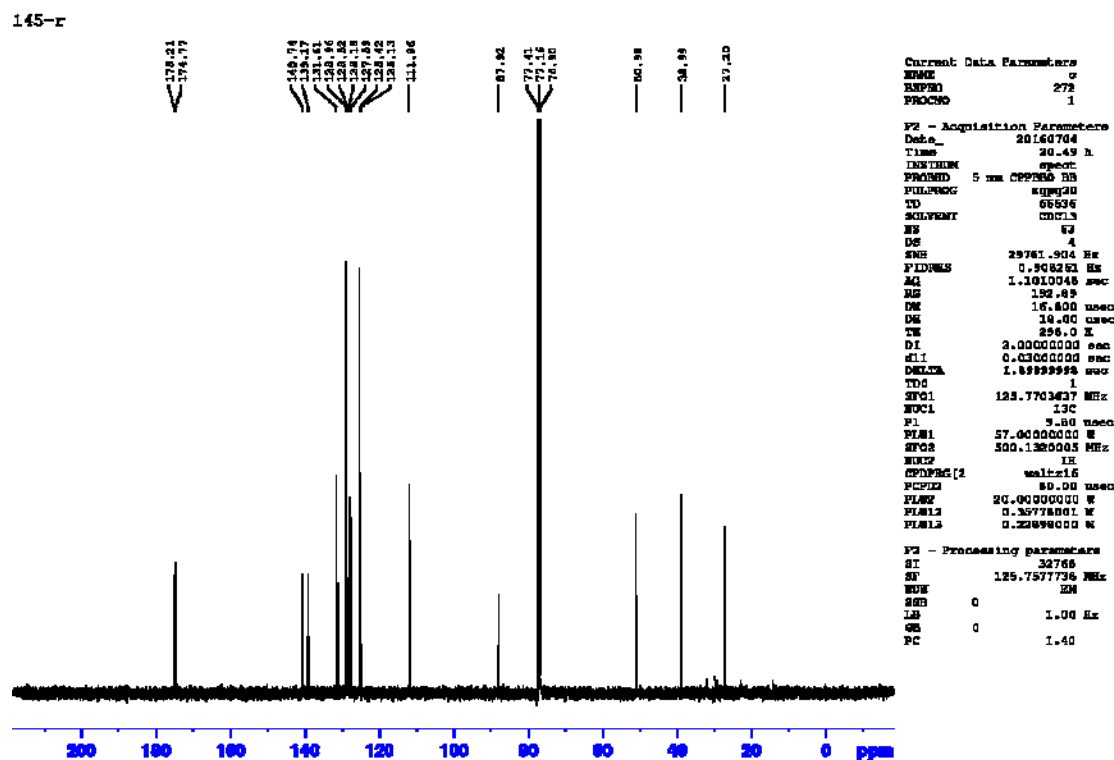
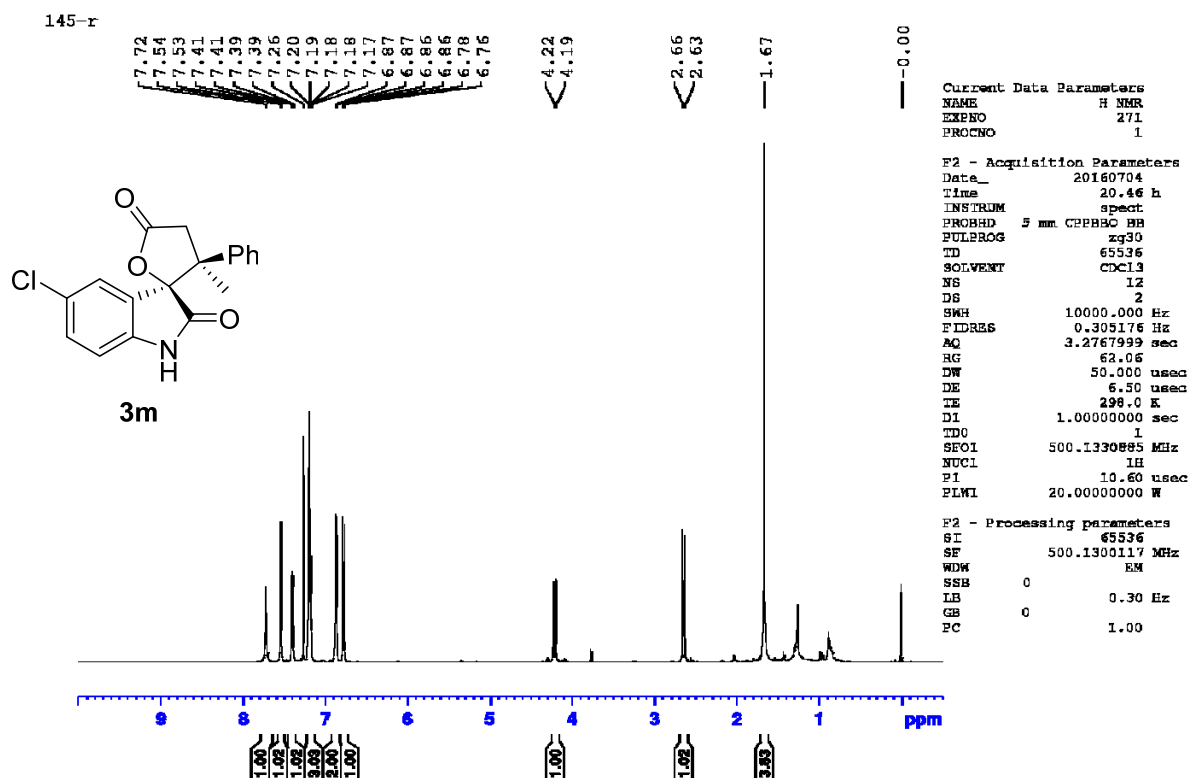
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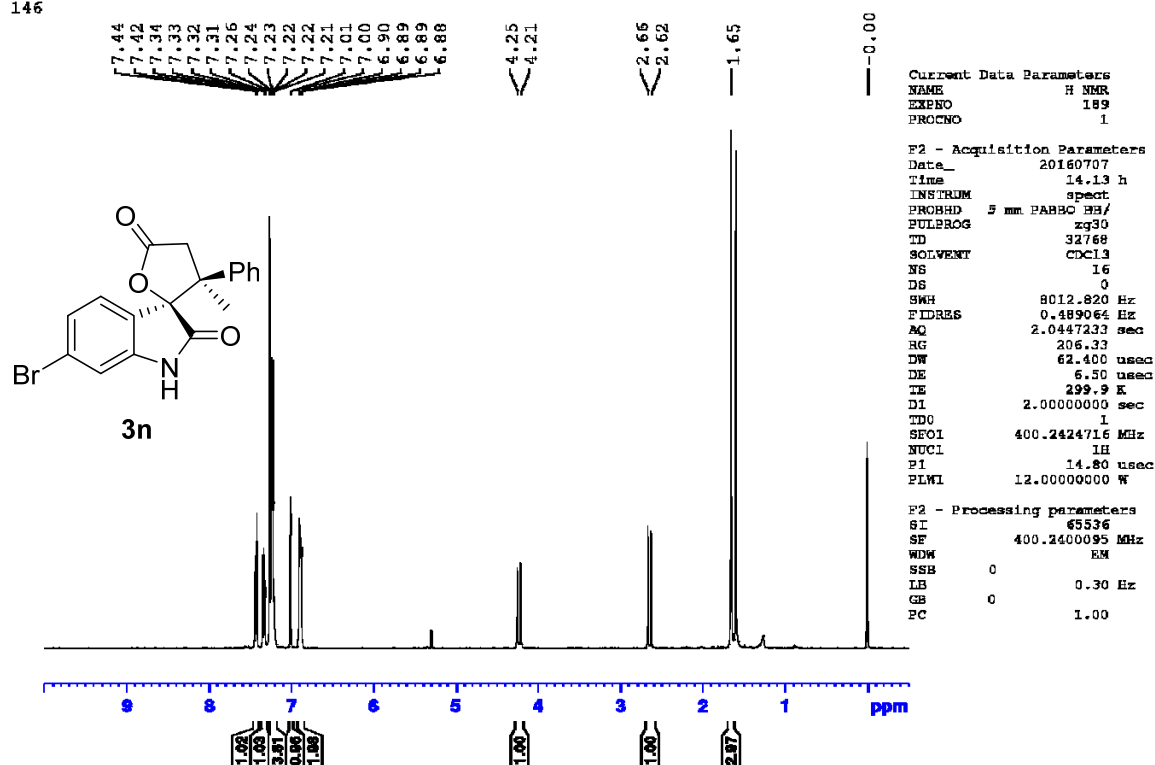
Current Data Parameters
NAME c
EXPNO 265
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160704
Time 20.28 h
INSTRUM spect
PROBHD 5 mm CPBBO BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 63
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 192.89
DW 16.800 usec
DE 18.40 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
PLM1 57.00000000 W
SFO2 500.1320005 MHz
NUC2 1H
PCPD2 wait15
PLF2 20.00000000 W
PLF12 0.35778001 W
PLF13 0.22894000 W

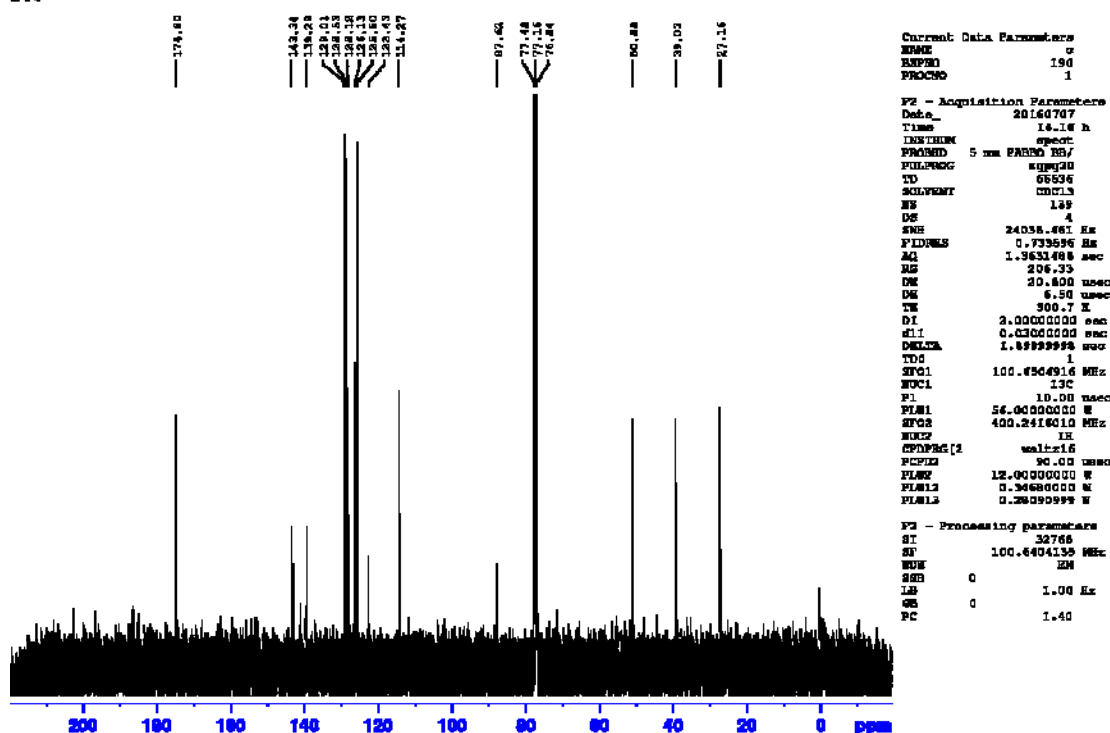
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SI 32768
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WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



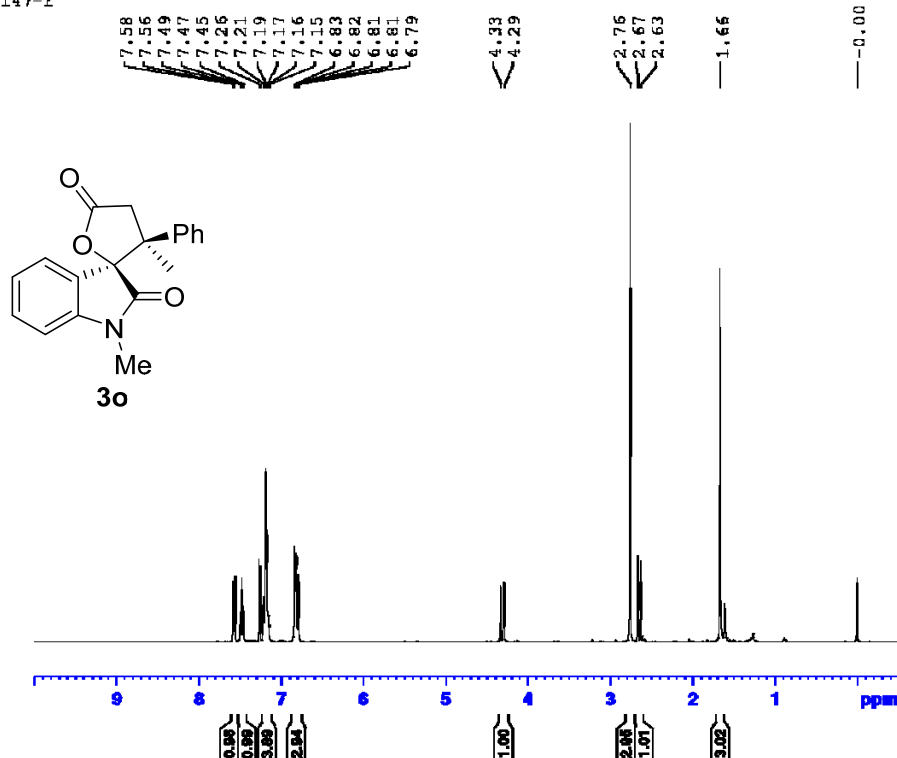
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147-z

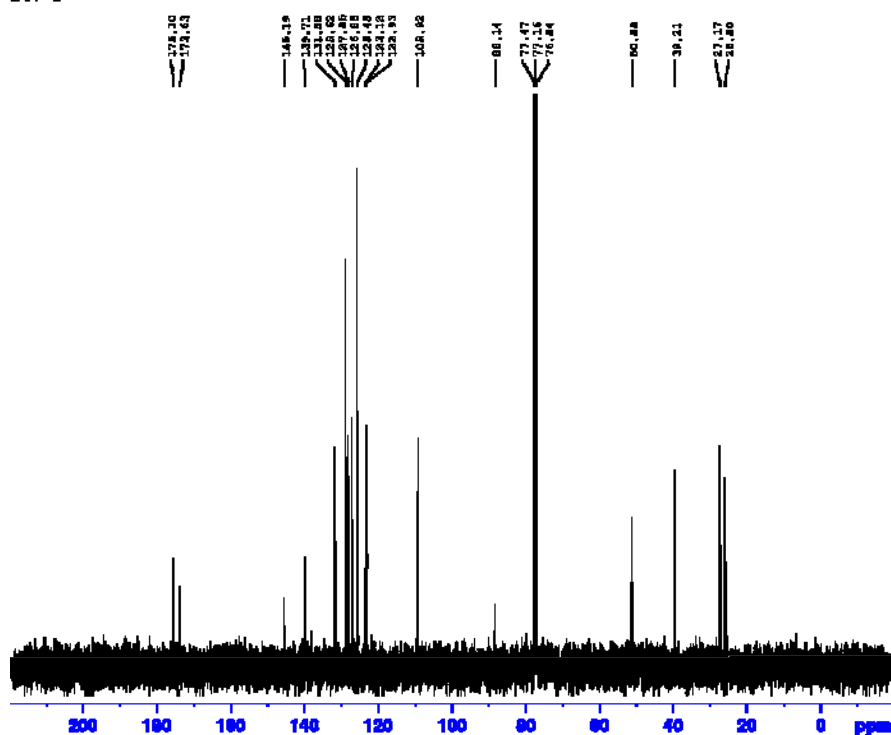


Current Data Parameters
NAME H NMR
EXPNO 220
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160811
Time 15.50 h
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 15
DS 0
SWH 8012.820 Hz
FIDRES 0.489064 Hz
AQ 2.0447233 sec
RG 102.73
DW 62.400 usec
DE 6.50 usec
TE 300.3 K
D1 2.00000000 sec
TD0 1
SFO1 400.2424716 MHz
NUC1 1H
P1 14.80 usec
PLW1 12.00000000 W

F2 - Processing parameters
SI 65536
SF 400.2400093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

147-z

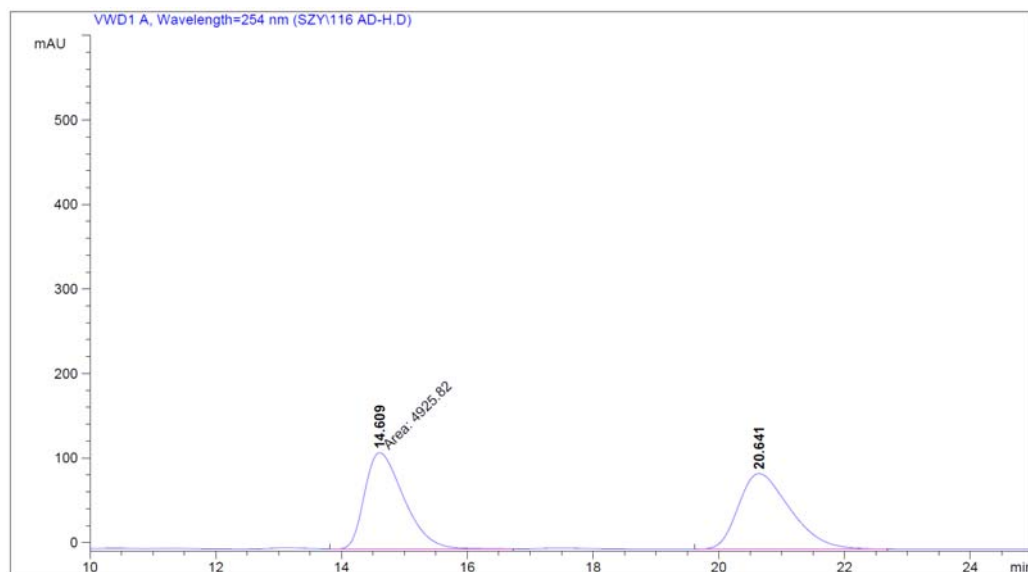
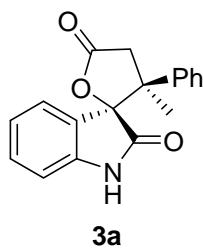


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NAME c
EXPNO 221
PROCNO 1

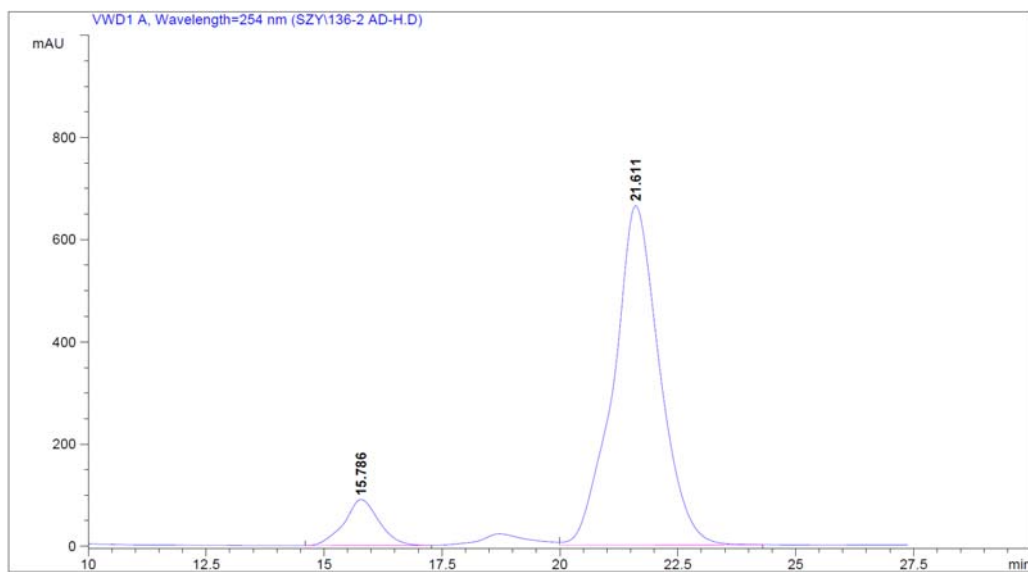
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Time 15.52 h
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 22
DS 4
SWH 24058.861 Hz
FIDRES 0.738696 Hz
AQ 1.3631488 sec
RG 206.33
DW 20.800 usec
DE 6.50 usec
TE 300.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999999 sec
TD0 1
SFO1 100.6264916 MHz
NUC1 13C
P1 10.00 usec
PLW1 56.00000000 W
SFO2 400.2416010 MHz
NUC2 1H
SFOFREQ[2] waltz16
PCP22 90.00 usec
PLW2 12.00000000 W
PLW12 0.34680000 W
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WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

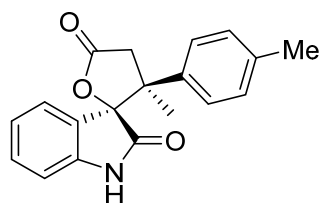
Part II HPLC Spectra



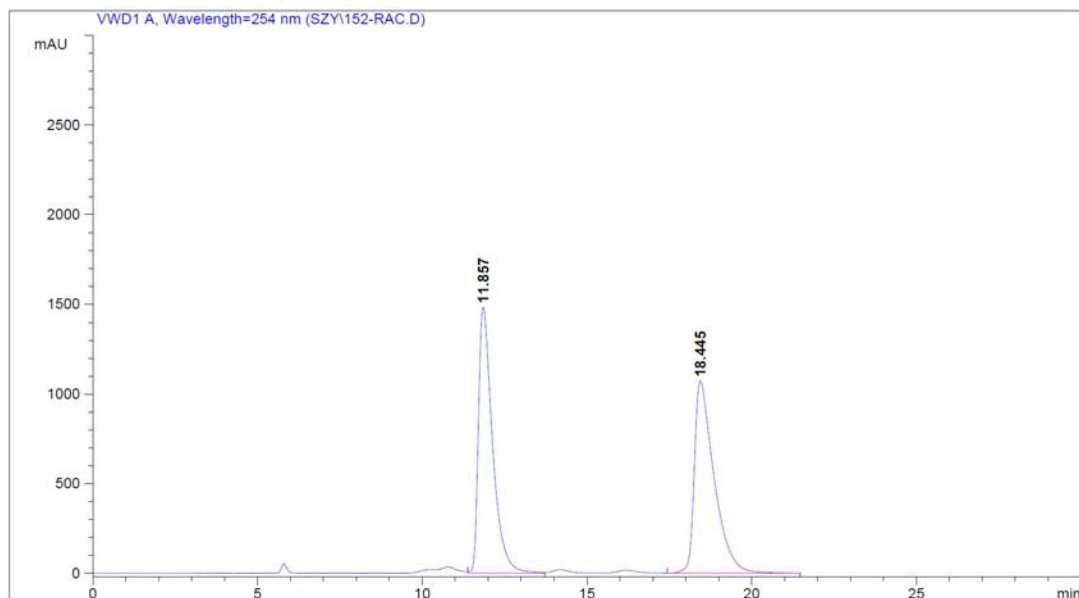
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2	20.641	BB	0.8848	5078.70996	89.30438	50.7641



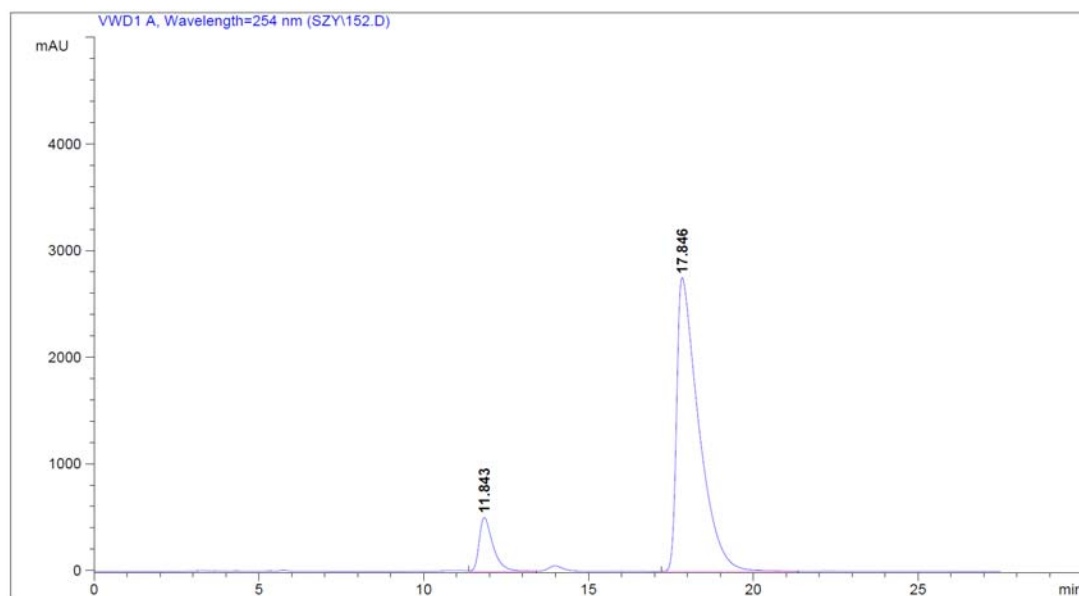
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1	15.786	BV	0.7574	4637.69922	90.15678	9.2877
2	21.611	VB	0.9912	4.52963e4	663.78375	90.7123



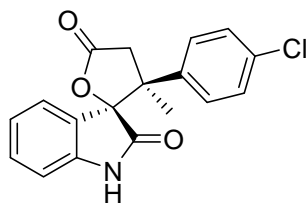
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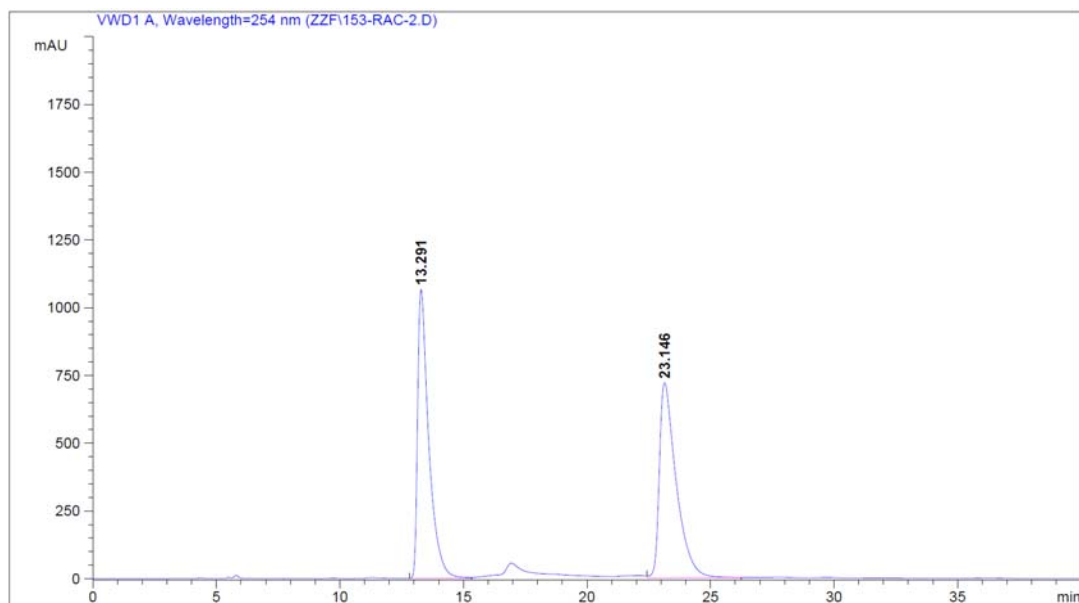
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1	11.857	VV	0.4494	4.41399e4	1482.06738	49.6193
2	18.445	VBA	0.6119	4.48172e4	1074.32593	50.3807



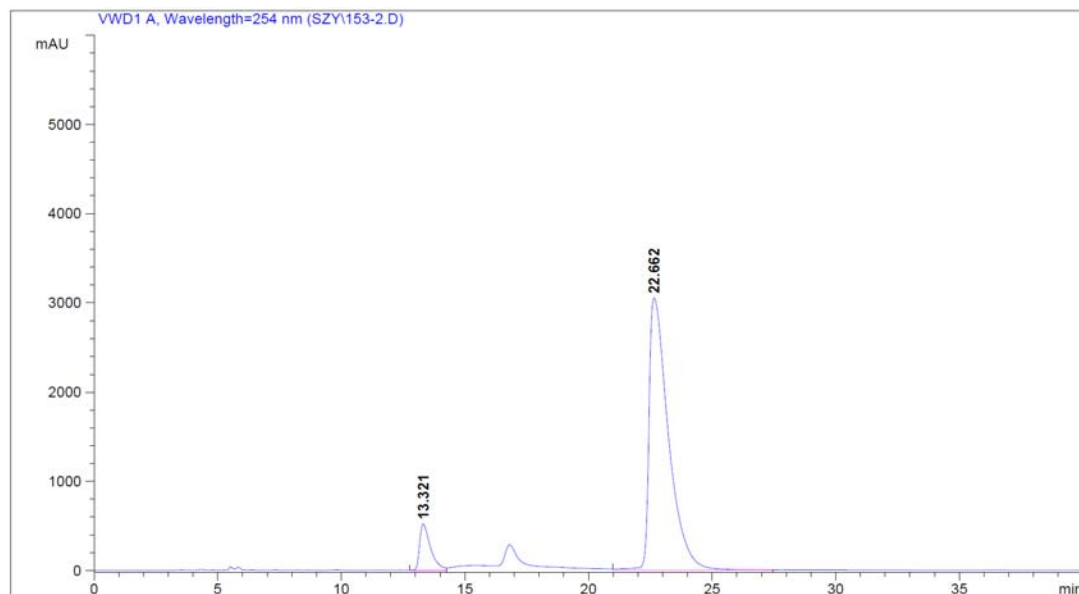
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1	11.843	VV	0.4344	1.47241e4	505.66925	10.3571
2	17.846	BB	0.6535	1.27441e5	2753.64331	89.6429



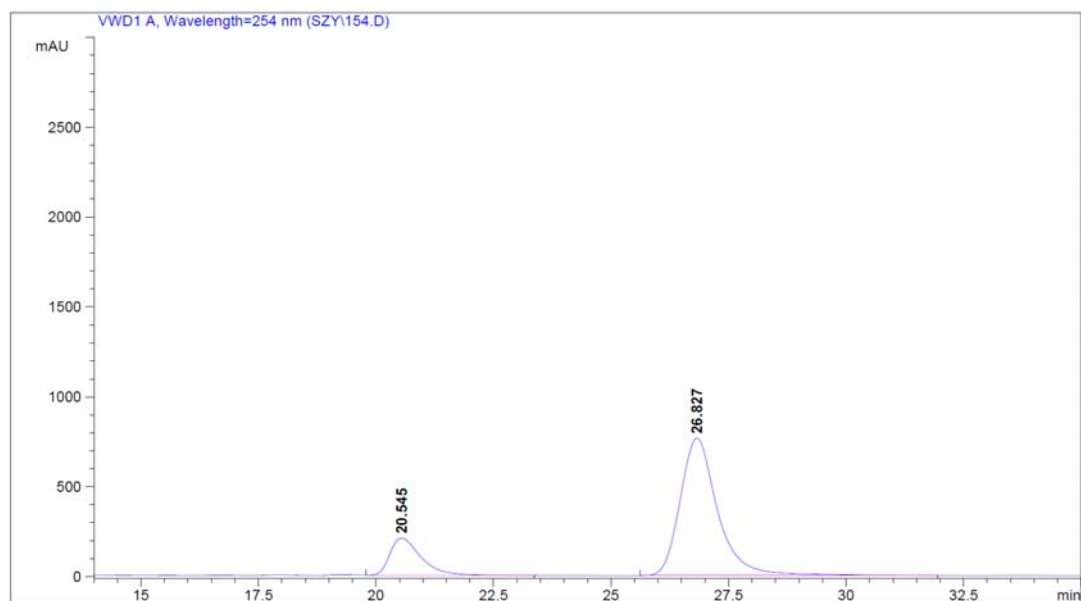
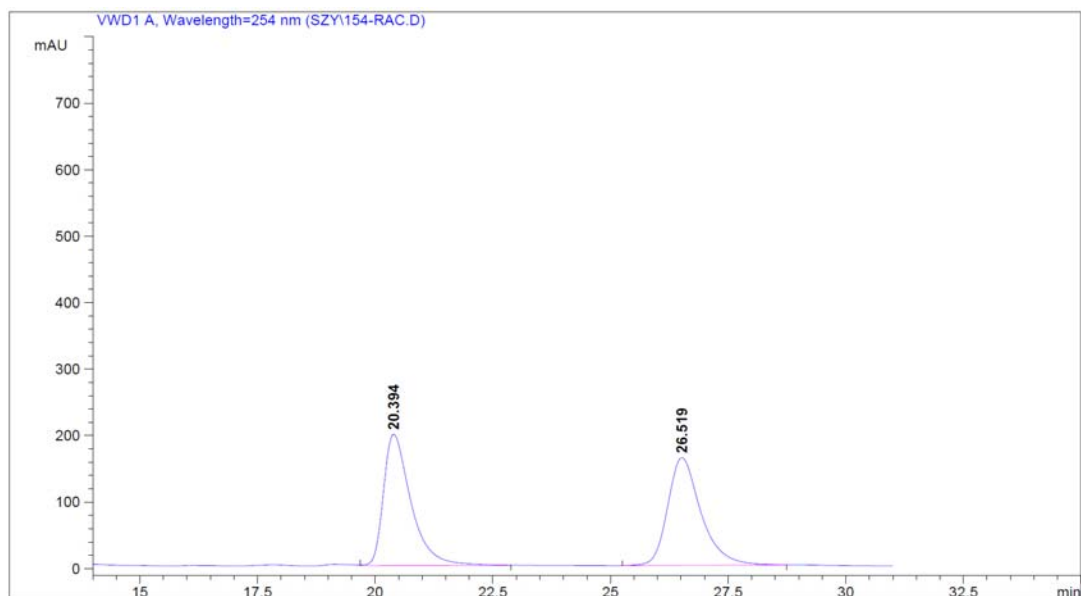
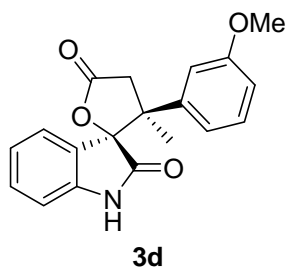
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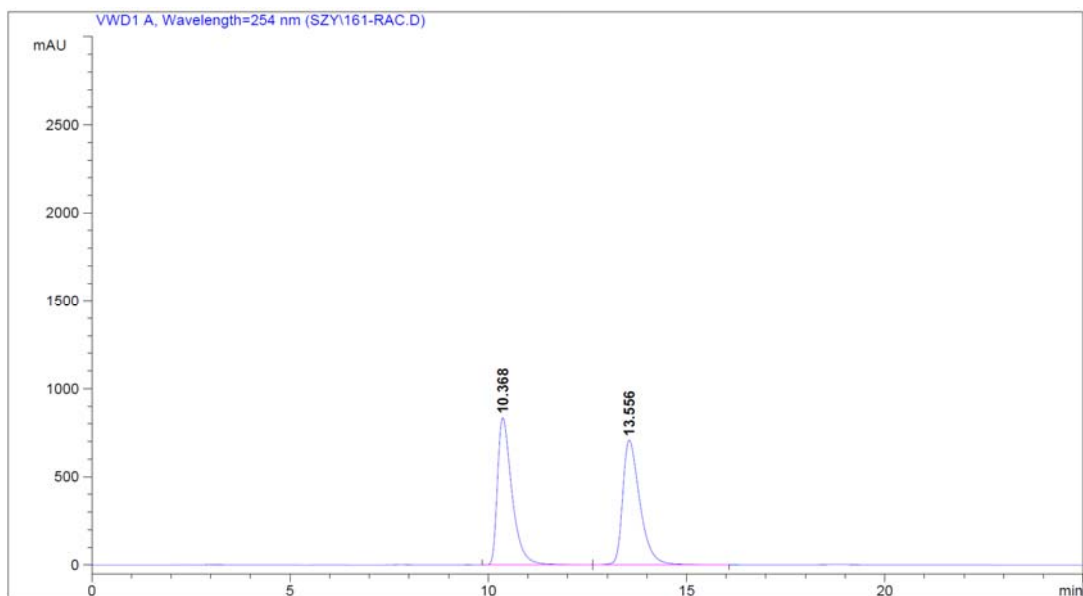
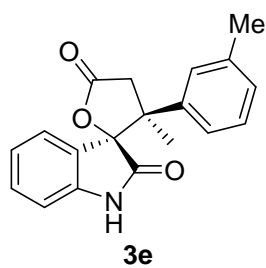


Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	13.291	BV	0.4618	3.34298e4	1066.34363	49.6720
2	23.146	VB	0.6923	3.38713e4	719.01141	50.3280

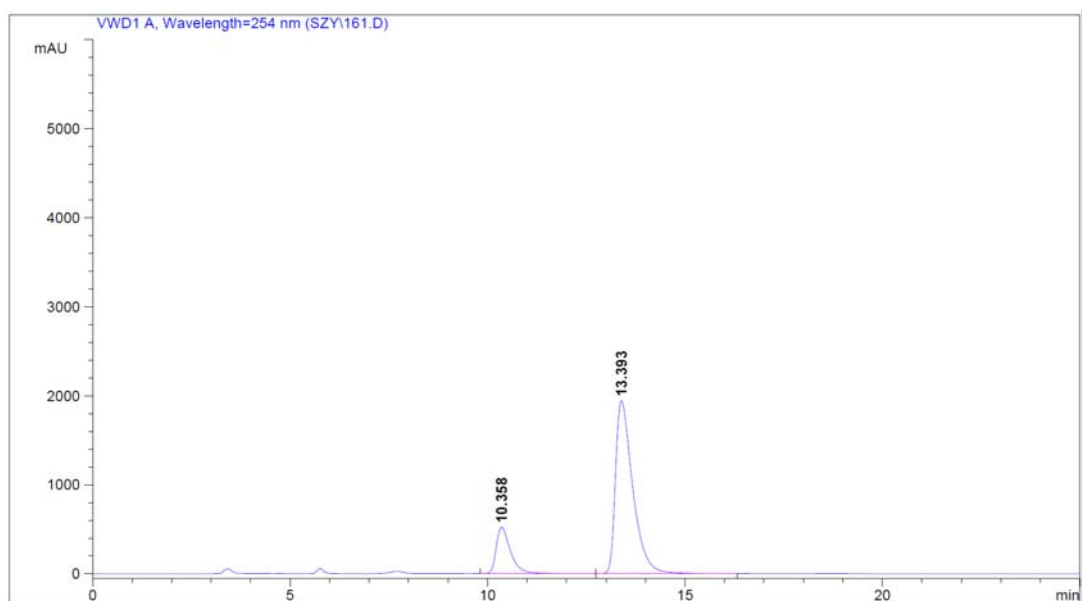


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1	13.321	VV	0.4550	1.58778e4	520.35559	8.6817
2	22.662	VB	0.8198	1.67011e5	3048.25000	91.3183

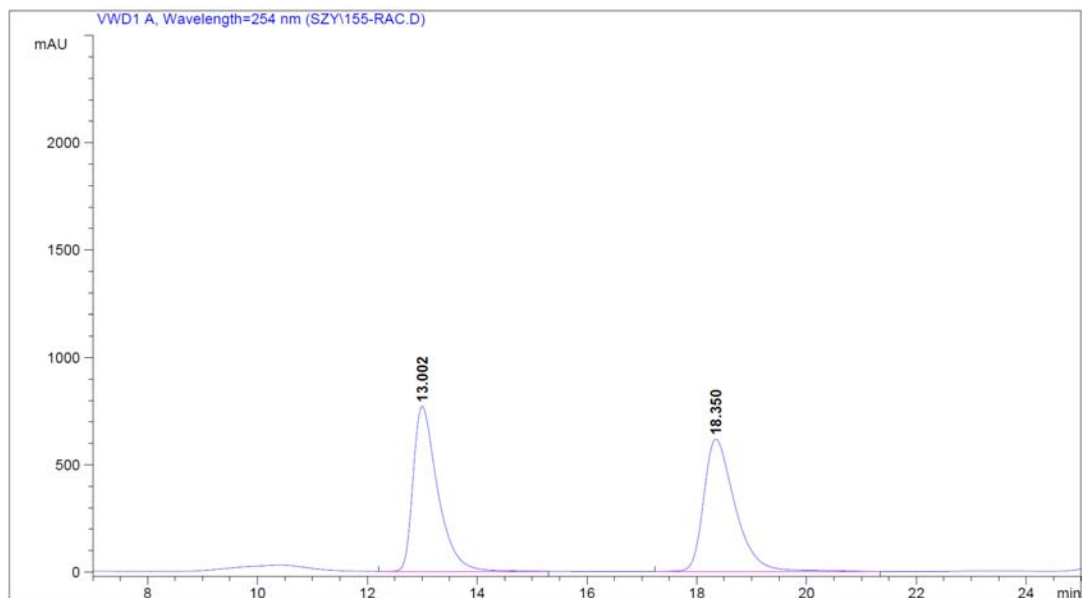
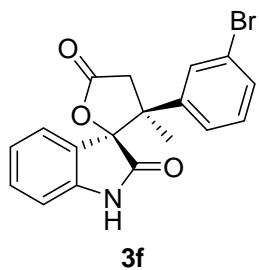




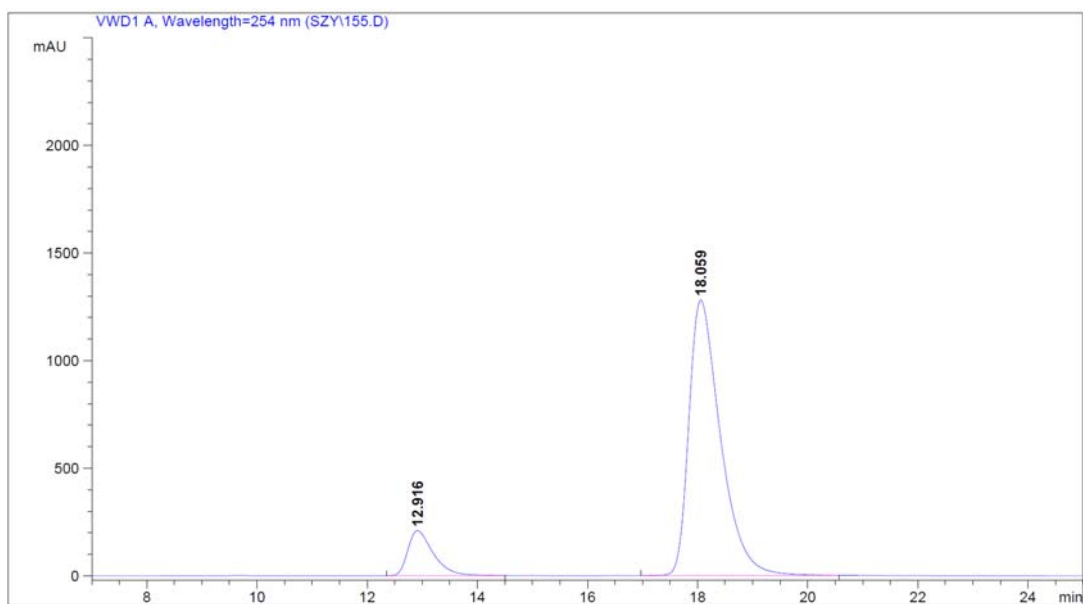
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	10.368	VV	0.3875	2.12447e4	833.81036	49.7770
2	13.556	VB	0.4612	2.14350e4	707.53735	50.2230



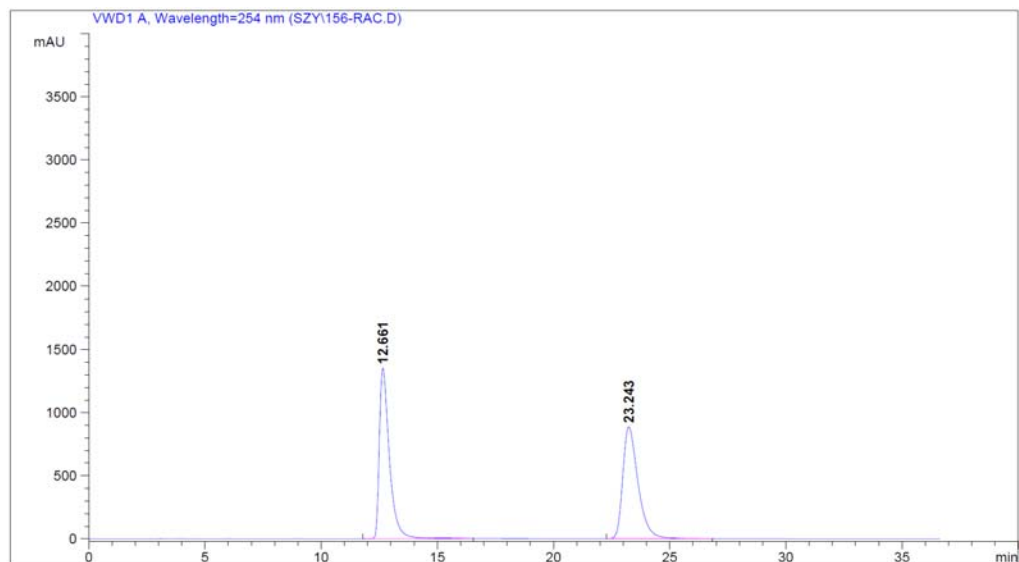
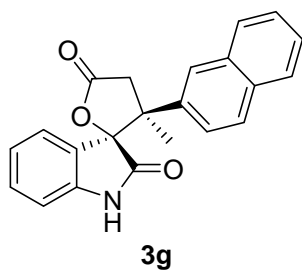
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1	10.358	VV	0.3837	1.34245e4	523.35620	18.5322
2	13.393	VB	0.4561	5.90145e4	1944.18701	81.4678



Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	13.002	VB	0.4679	2.39556e4	769.84241	49.4146
2	18.350	BB	0.6019	2.45232e4	617.10406	50.5854

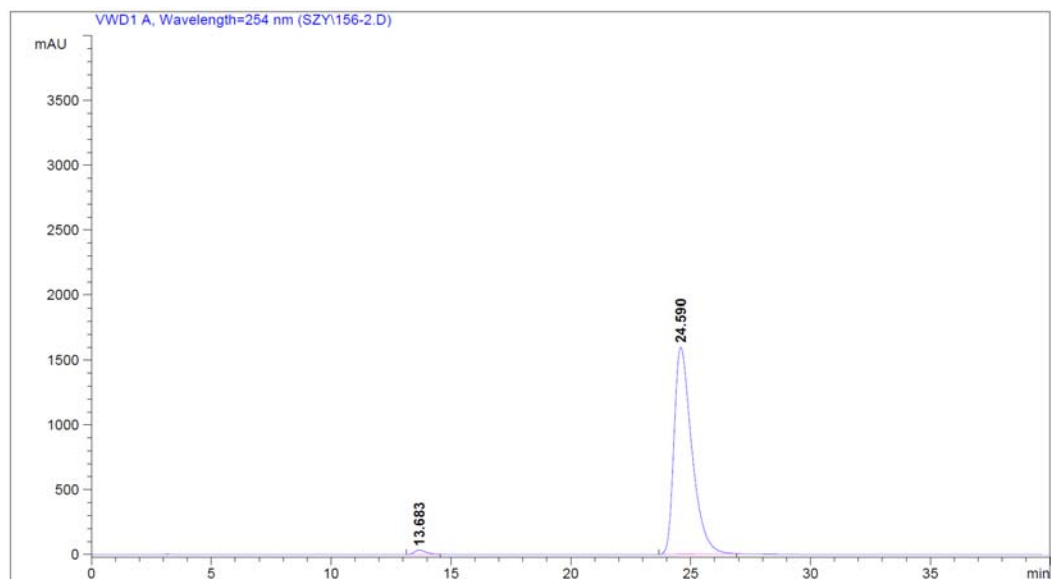


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1	12.916	BB	0.4834	6710.67236	209.22375	11.6227
2	18.059	BB	0.6021	5.10271e4	1279.52307	88.3773

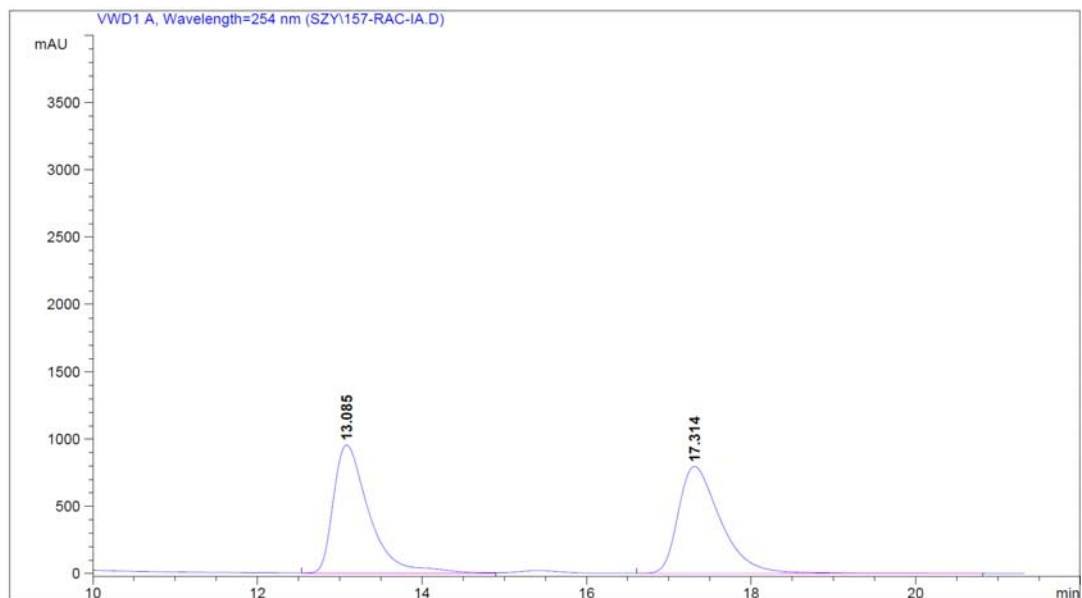
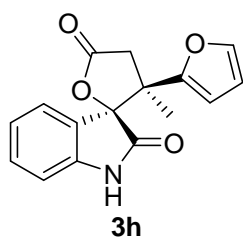


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.661	BB	0.4511	4.08719e4	1354.30322	50.1640
2	23.243	BB	0.6973	4.06047e4	886.82135	49.8360

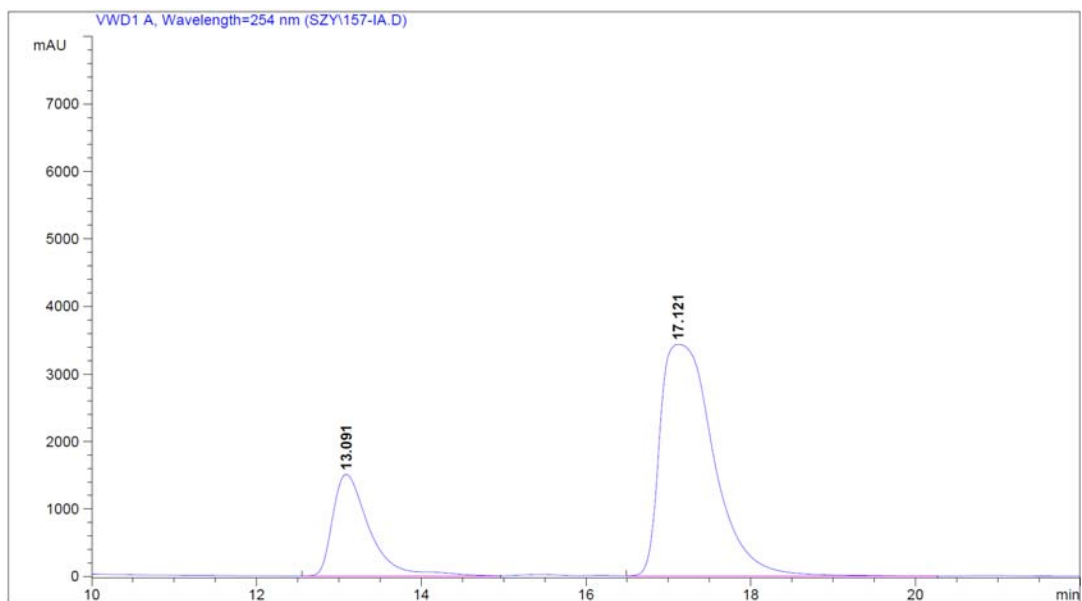
3g After recrystallization



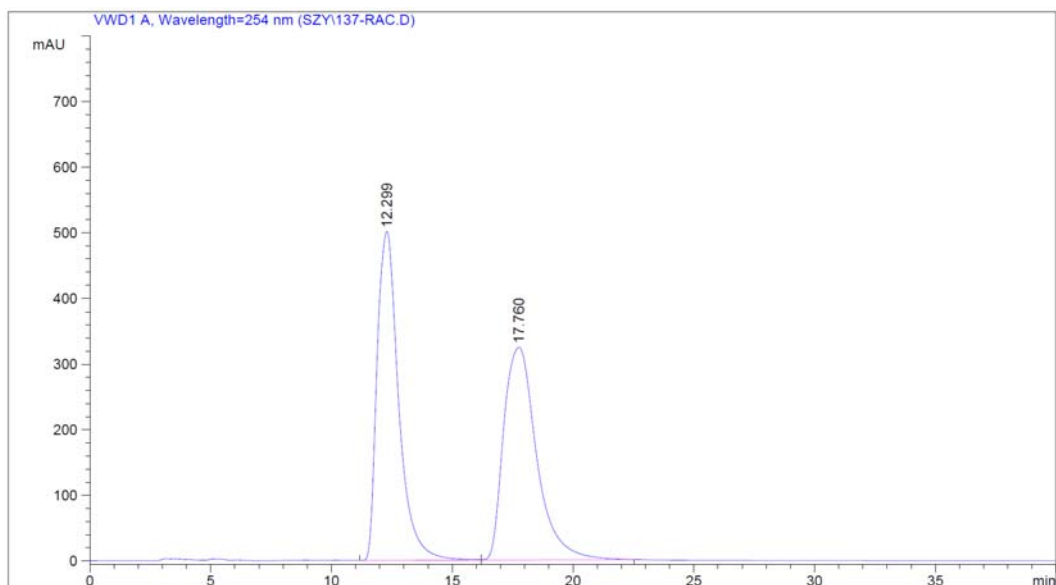
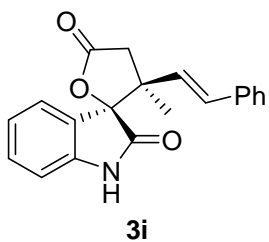
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.683	BB	0.5184	1160.13171	34.04530	1.3848
2	24.590	BB	0.7763	8.26146e4	1598.18567	98.6152



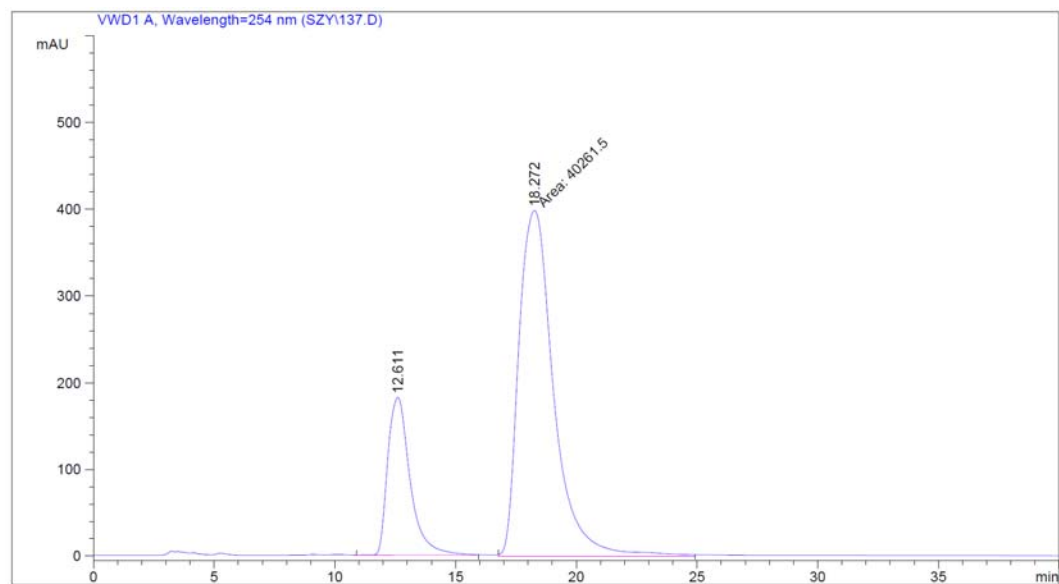
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	13.085	VV	0.4601	2.91109e4	955.92969	50.5445
2	17.314	BB	0.5428	2.84838e4	795.71655	49.4555



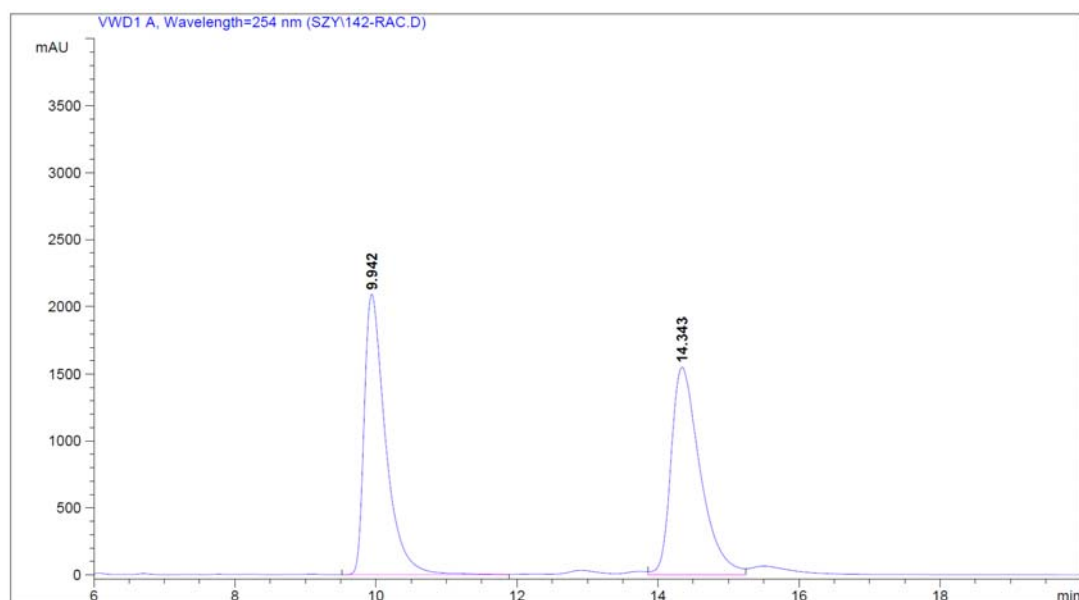
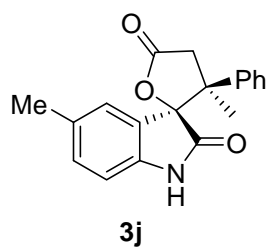
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	13.091	VV	0.4752	4.72771e4	1512.87195	23.3100
2	17.121	VV	0.7022	1.55541e5	3440.24902	76.6900



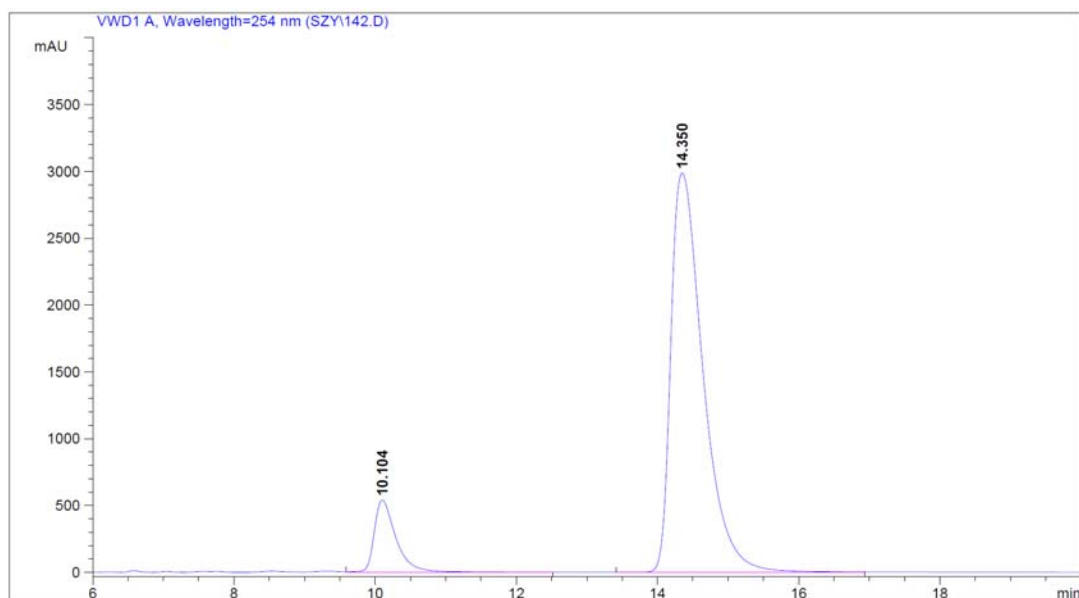
Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	12.299	BV	0.9649	3.10522e4	500.96567	50.1359
2	17.760	VB	1.4850	3.08839e4	324.79883	49.8641



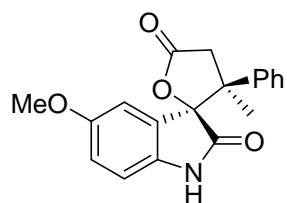
Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	12.611	VB	1.0038	1.17159e4	182.13161	22.5404
2	18.272	MM	1.6823	4.02615e4	398.87576	77.4596



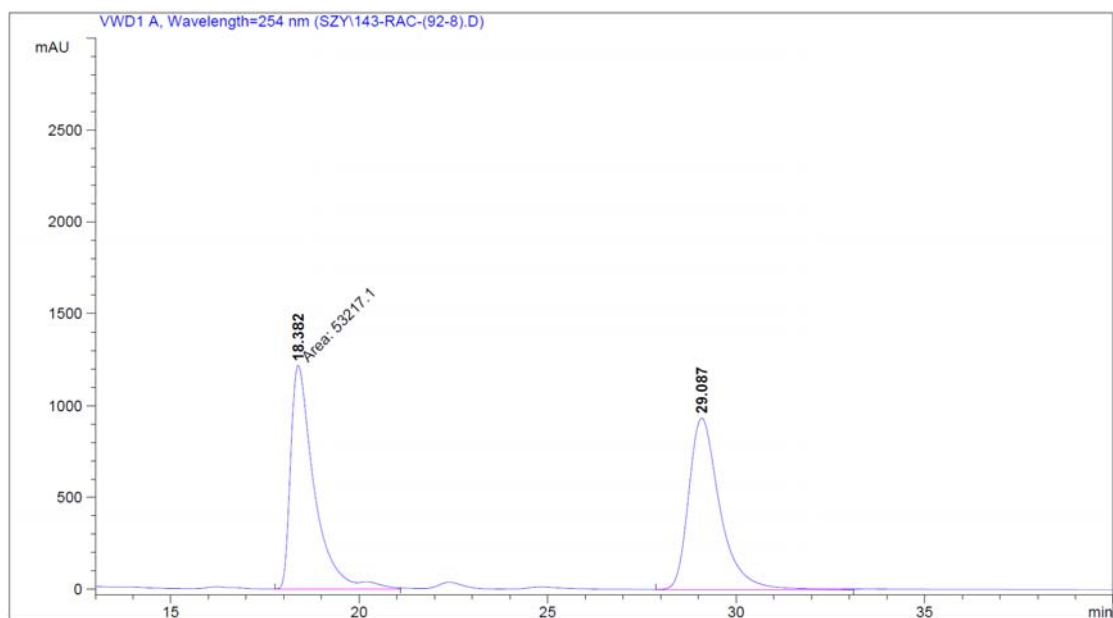
Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	9.942	VV	0.3151	4.39131e4	2089.35205	49.8067
2	14.343	VV	0.4322	4.42540e4	1549.33899	50.1933



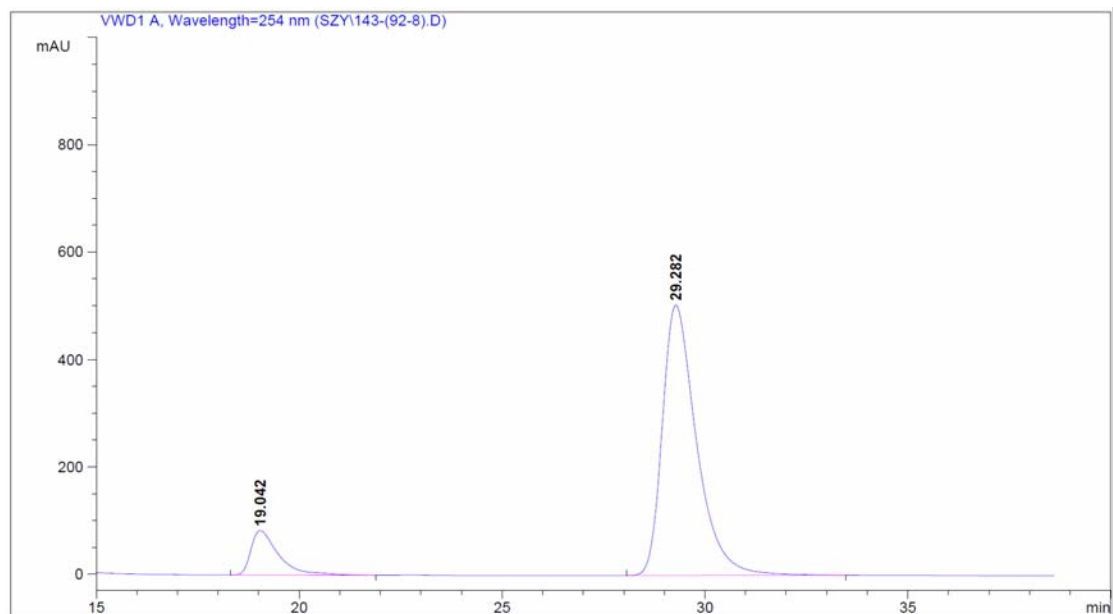
Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	10.104	VB	0.3242	1.17806e4	540.54309	11.0712
2	14.350	VB	0.4803	9.46264e4	2986.71313	88.9288



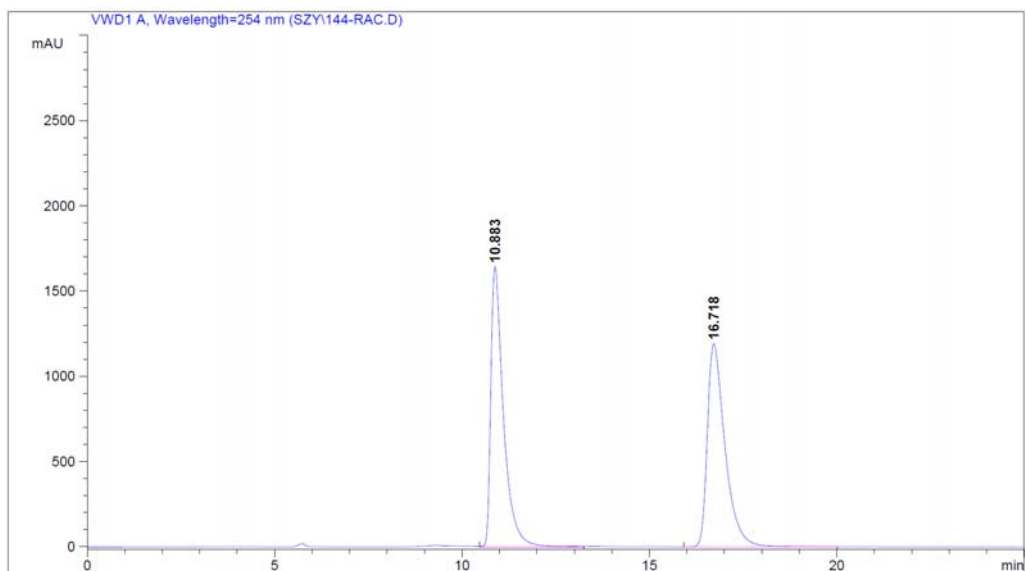
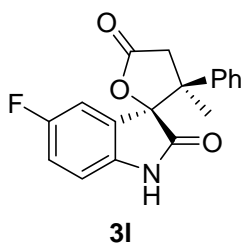
3k



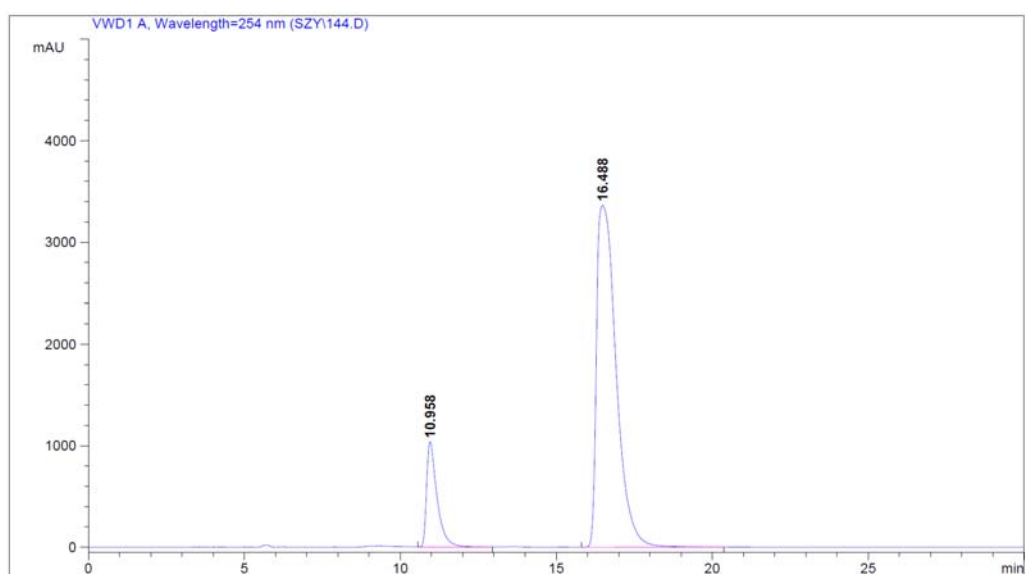
Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	18.382	MM	0.7266	5.32171e4	1220.61145	49.7805
2	29.087	BB	0.8739	5.36864e4	934.74786	50.2195



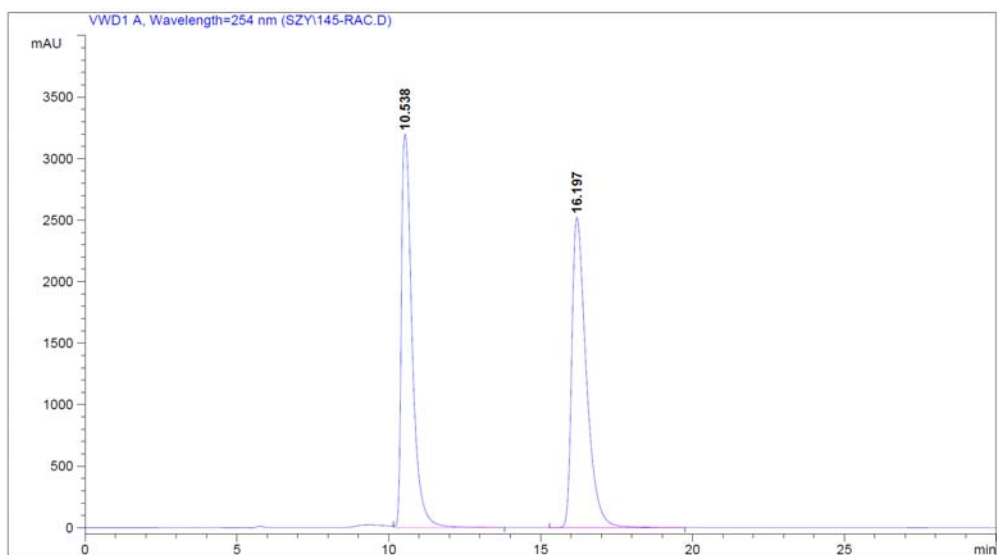
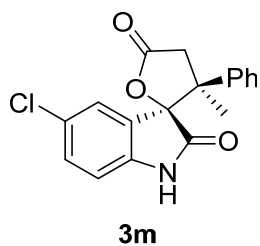
Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	19.042	BB	0.7047	3937.55835	83.03534	11.7620
2	29.282	BB	0.8916	2.95394e4	503.22089	88.2380



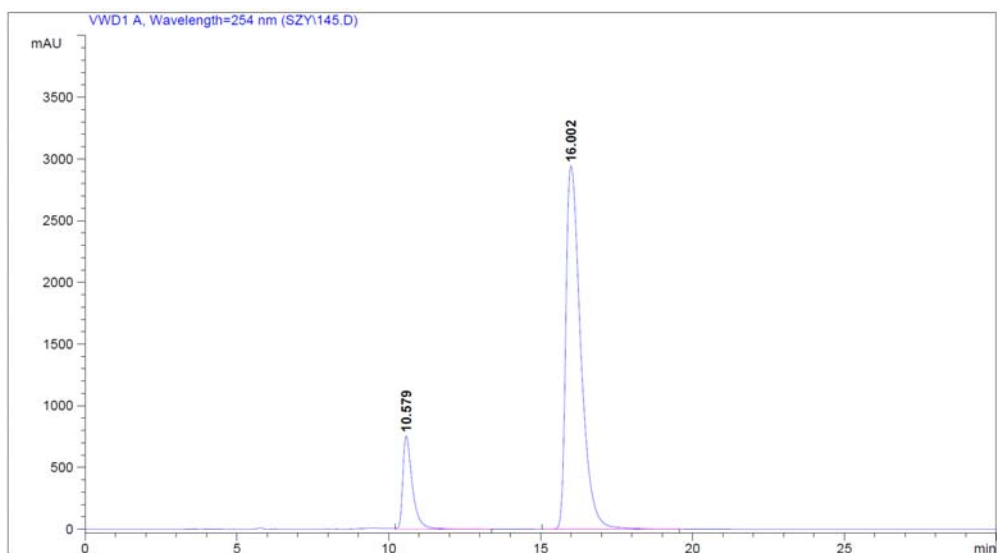
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	10.883	VV	0.3465	3.85791e4	1644.42456	49.7182
2	16.718	VB	0.4923	3.90164e4	1192.74805	50.2818



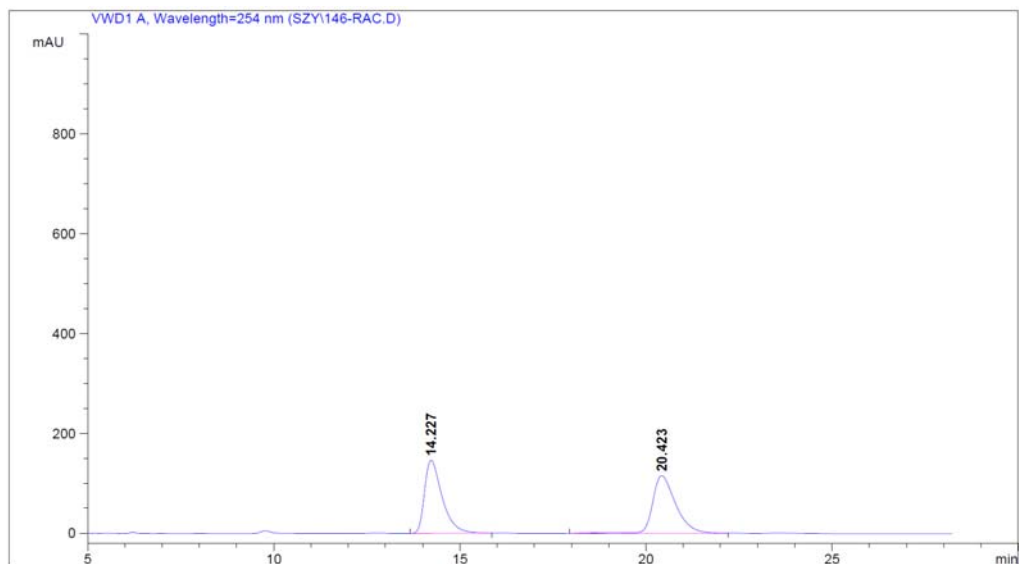
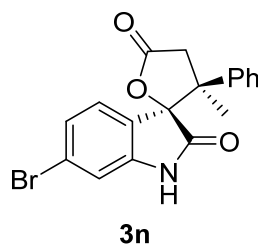
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	10.958	VB	0.3509	2.45155e4	1039.36255	14.3208
2	16.488	VB	0.6715	1.46673e5	3365.31372	85.6792



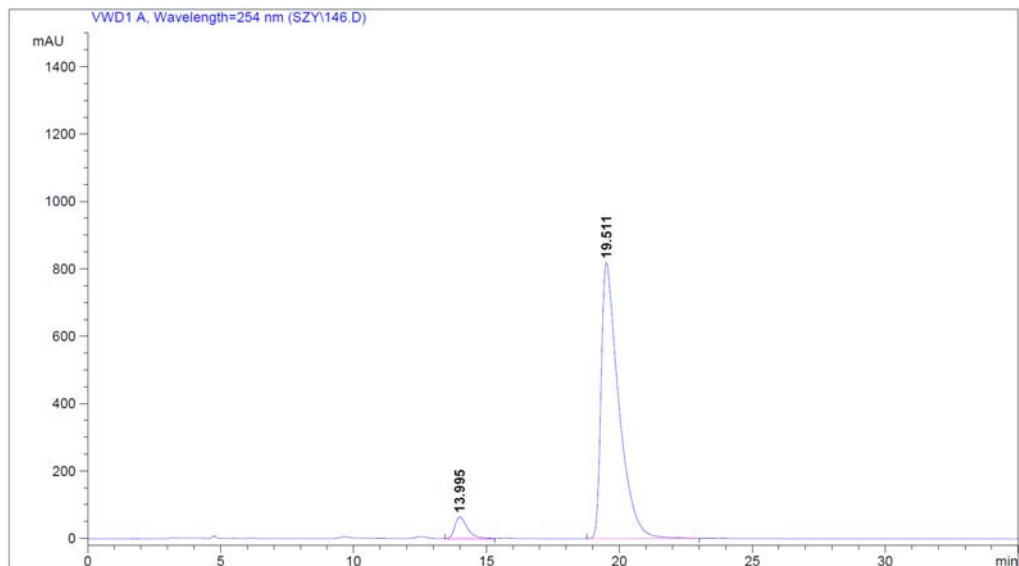
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	10.538	VB	0.3719	7.87900e4	3197.45532	48.5832
2	16.197	BB	0.4965	8.33855e4	2521.00757	51.4168



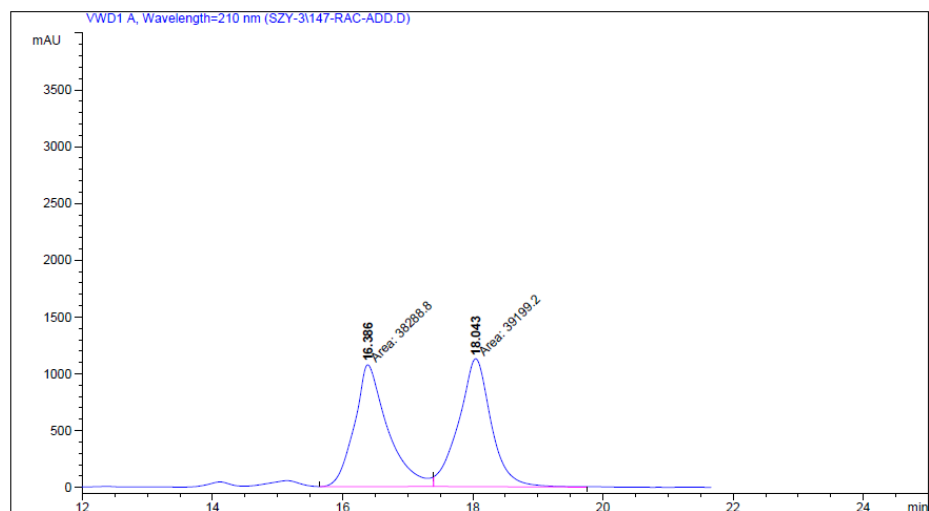
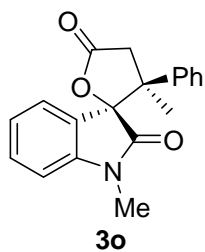
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	10.579	VB	0.3291	1.65816e4	754.81628	14.2232
2	16.002	VB	0.5159	9.99998e4	2942.04370	85.7768



Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	14.227	BB	0.4971	4830.33008	146.93402	49.1971
2	20.423	BB	0.6486	4988.00244	115.69173	50.8029



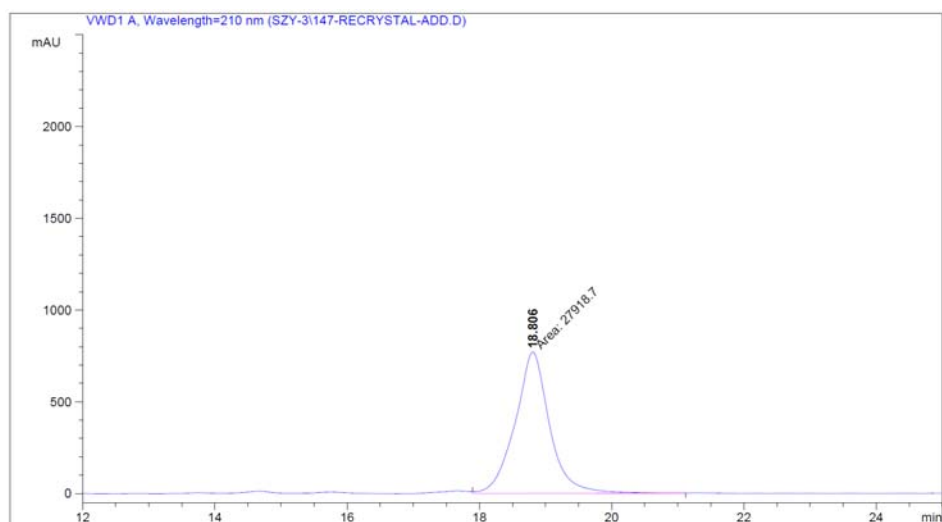
Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	13.995	BV	0.4987	2118.41553	64.66824	5.3372
2	19.511	BB	0.6689	3.75733e4	819.39923	94.6628



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	16.386	MM	0.5943	3.82888e4	1073.82190	49.4125
2	18.043	MM	0.5793	3.91992e4	1127.84668	50.5875

Totals : 7.74880e4 2201.66858

3o After recrystallization:



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	18.806	MM	0.6036	2.79187e4	770.92432	100.0000

Totals : 2.79187e4 770.92432

Part III X-ray crystallographic data of cycloadduct 3f

Crystals of the compound **3f** were obtained by slow evaporation of a hexane/ethyl acetate solution. *Data Collection.* Measurements were made on a MM007HF Saturn724+ diffractometer equipped with Saturn724+ CCD detector, a Graphite Monochromator with MoK α radiation, Montel mirrors and a Cryostream Plus low temperature device (T = 173K). Full-sphere data collection was used with ω and ϕ scans.

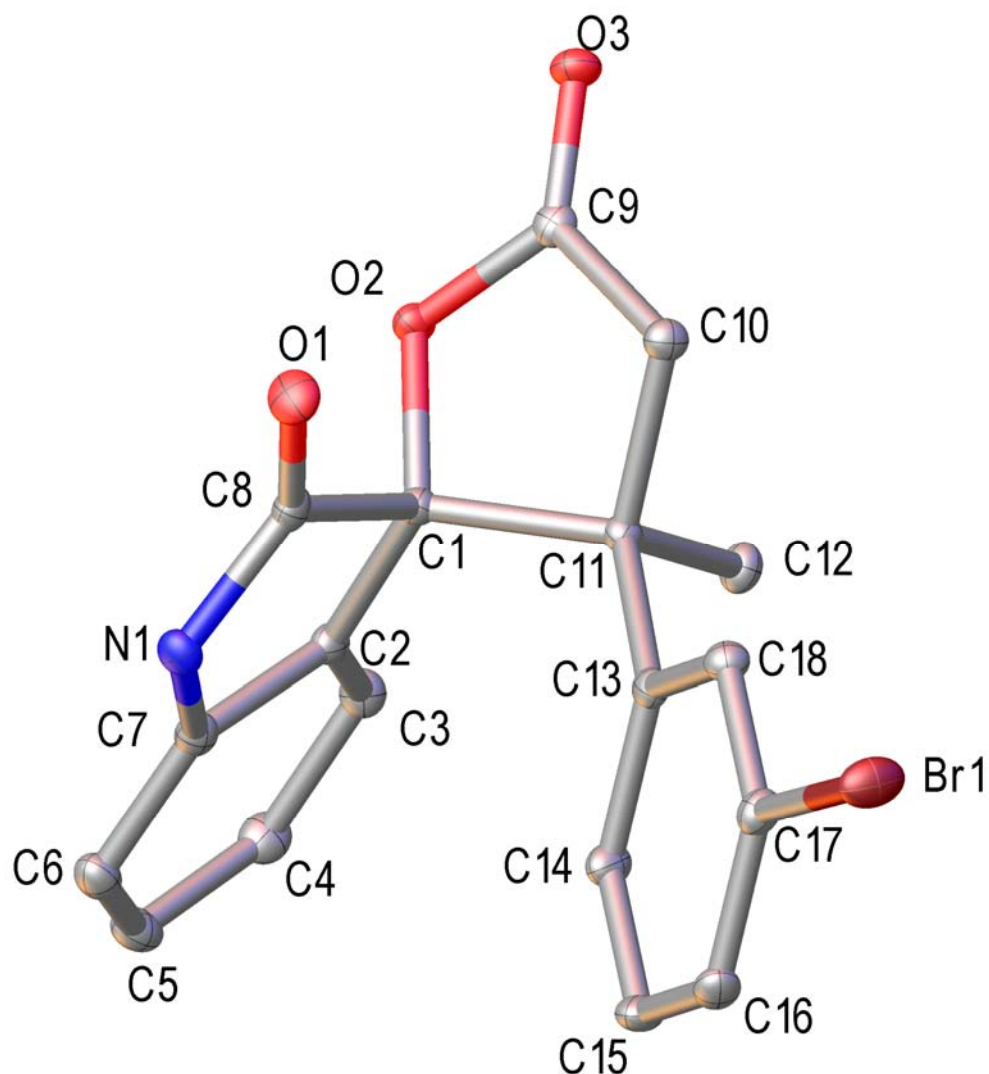


Figure S1 ORTEP of cycloadduct 3f (30% ellipsoid)

Table 1. Crystal data and structure refinement for **3f**.

Empirical formula	C ₁₈ H ₁₄ Br N O ₃	
Formula weight	372.21	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2 ₁ /c 1	
Unit cell dimensions	a = 8.351(2) Å	α = 90°.
	b = 10.255(3) Å	β = 98.302(3)°.
	c = 18.062(6) Å	γ = 90°.
Volume	1530.7(8) Å ³	
Z	4	
Density (calculated)	1.615 Mg/m ³	
Absorption coefficient	2.700 mm ⁻¹	
F(000)	752	
Crystal size	0.233 x 0.084 x 0.067 mm ³	
Theta range for data collection	3.023 to 27.477°.	
Index ranges	-9 ≤ h ≤ 10, -13 ≤ k ≤ 13, -23 ≤ l ≤ 22	
Reflections collected	9765	
Independent reflections	3464 [R(int) = 0.0400]	
Completeness to theta = 26.000°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.78393	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3464 / 0 / 209	
Goodness-of-fit on F ²	1.135	
Final R indices [I > 2σ(I)]	R ₁ = 0.0464, wR ₂ = 0.0818	
R indices (all data)	R ₁ = 0.0542, wR ₂ = 0.0848	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.371 and -0.395 e.Å ⁻³	