

Supporting Information

Bifunctional Squaramide Catalyzed Stereoselective Mannich Reaction of α -Azido Ketones with Isatin-Derived Ketimines

Seda Karahan and Cihangir Tanyeli*

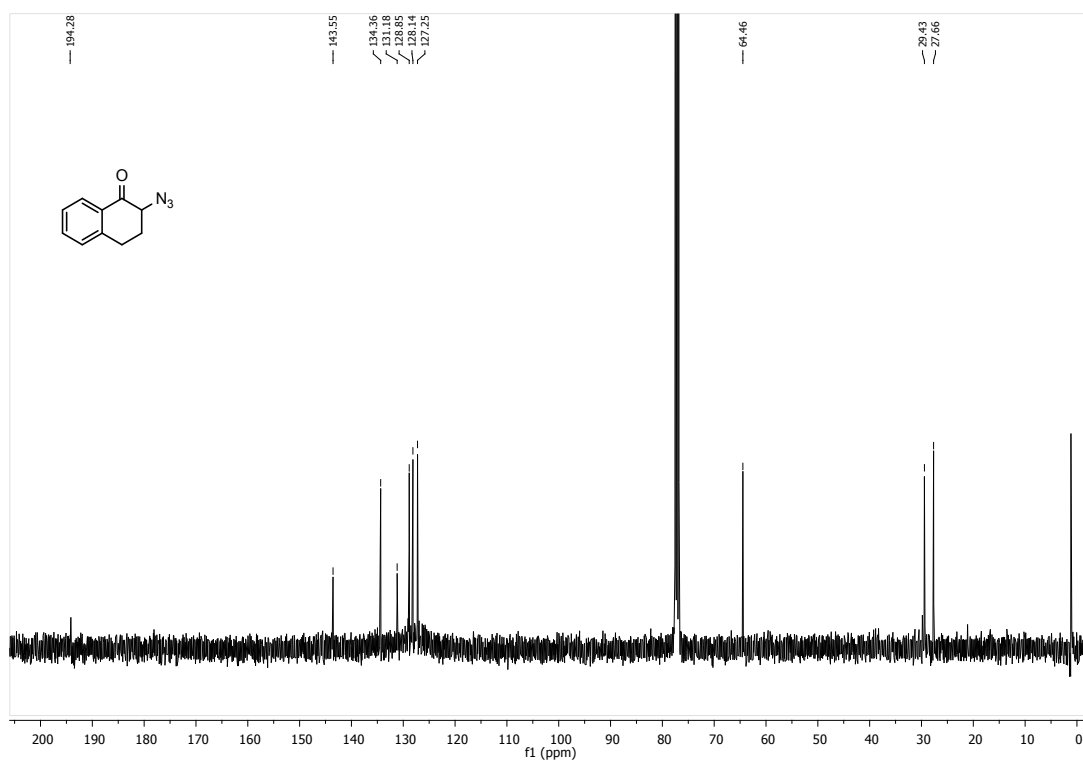
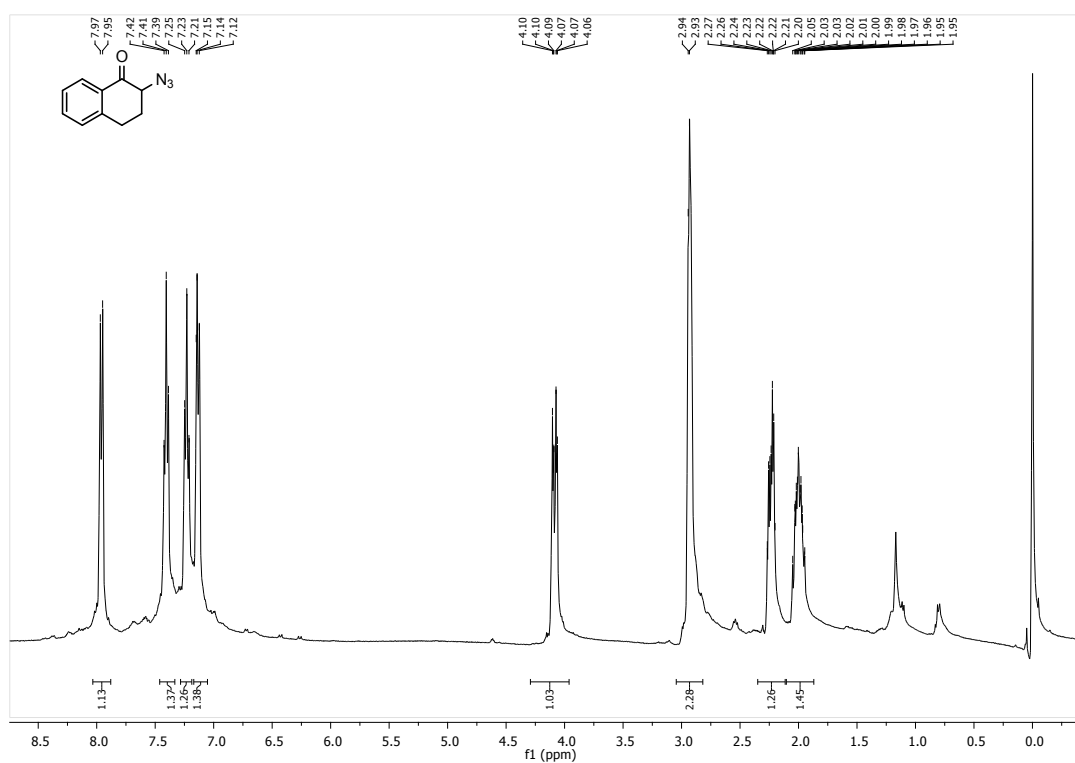
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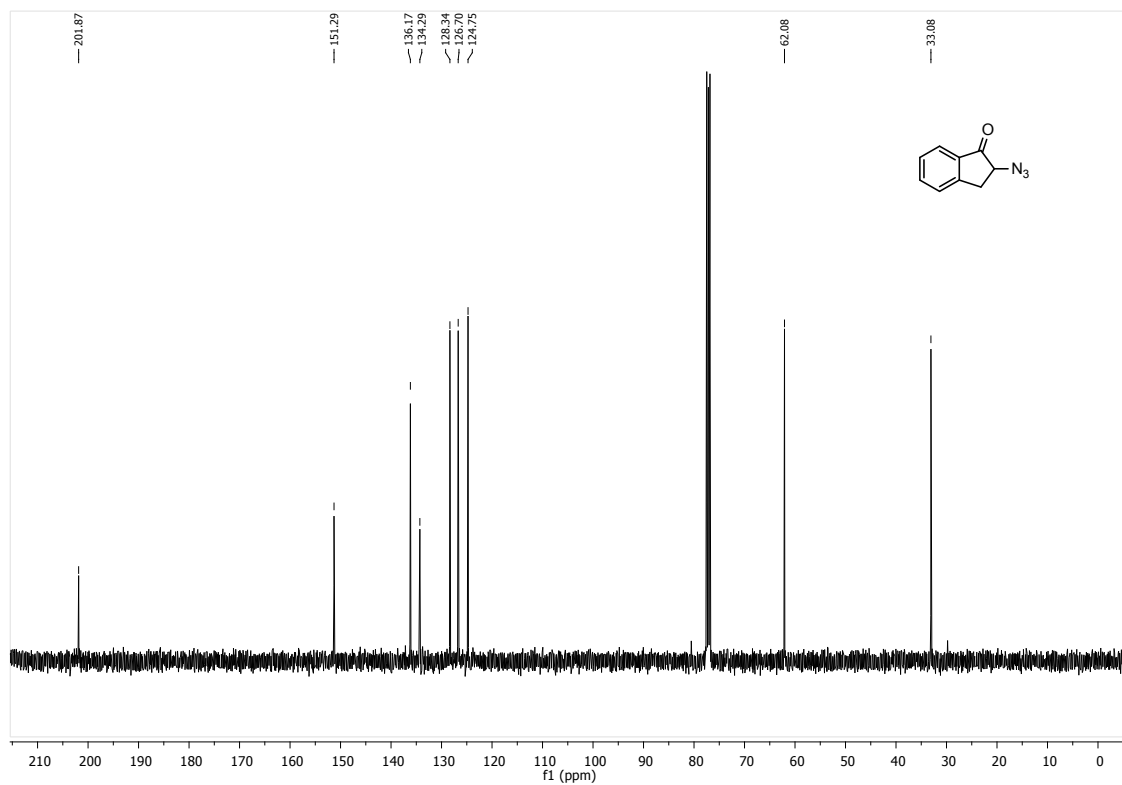
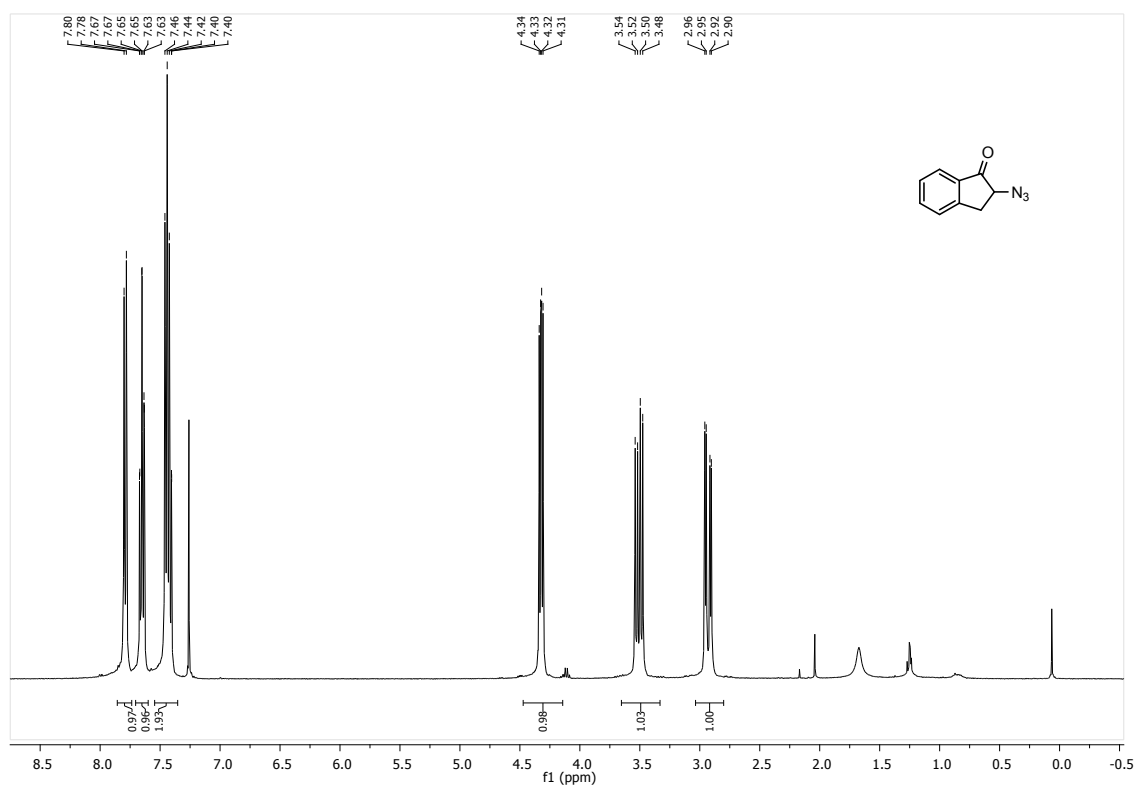
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1. NMR Spectra

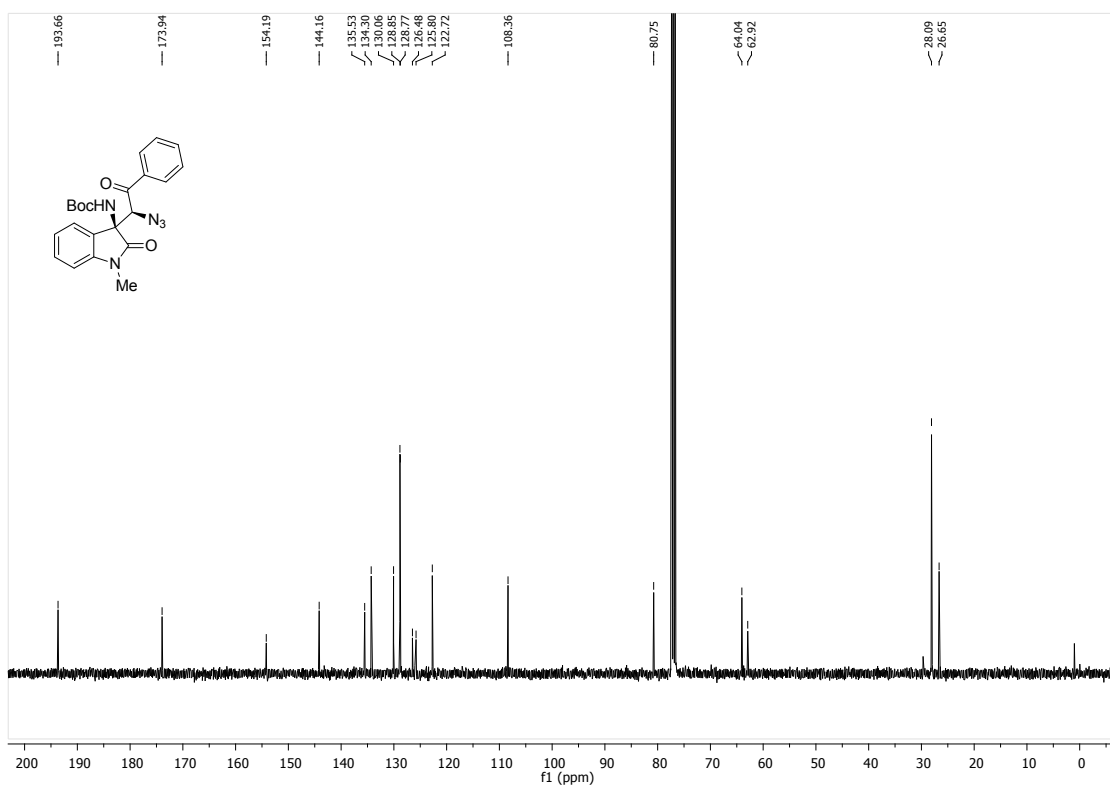
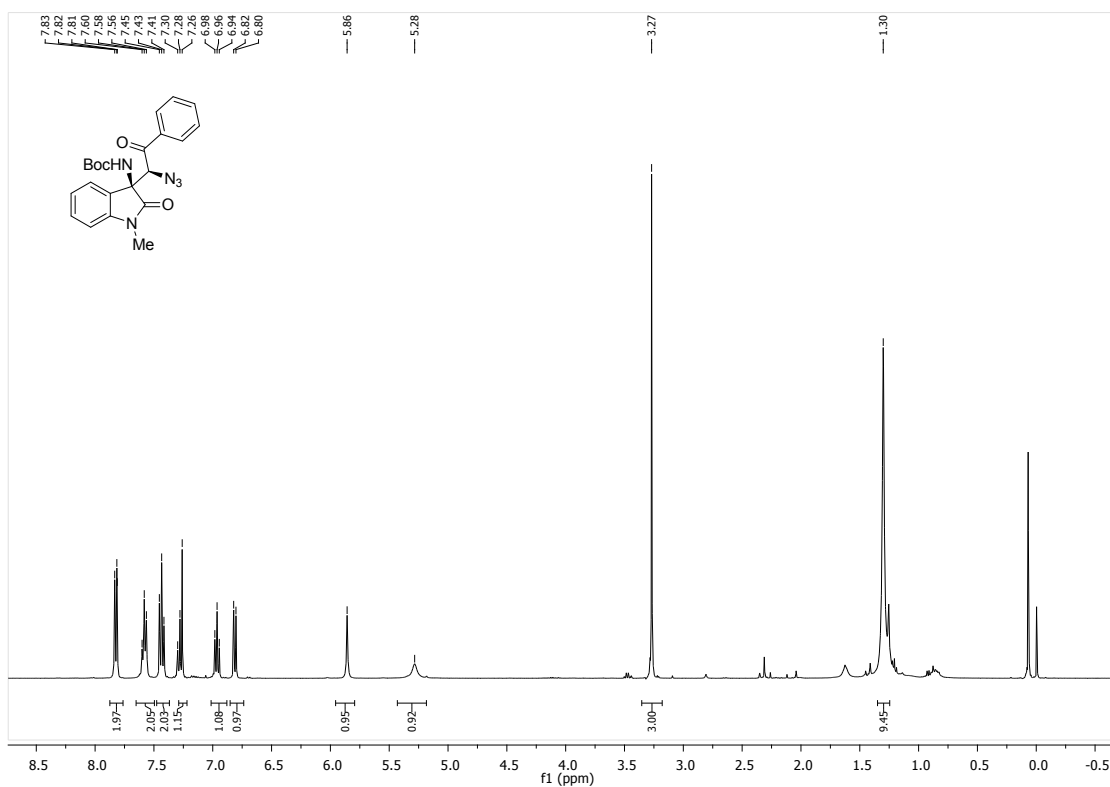
2-Azido-3,4-dihydronaphthalen-1(2H)-one



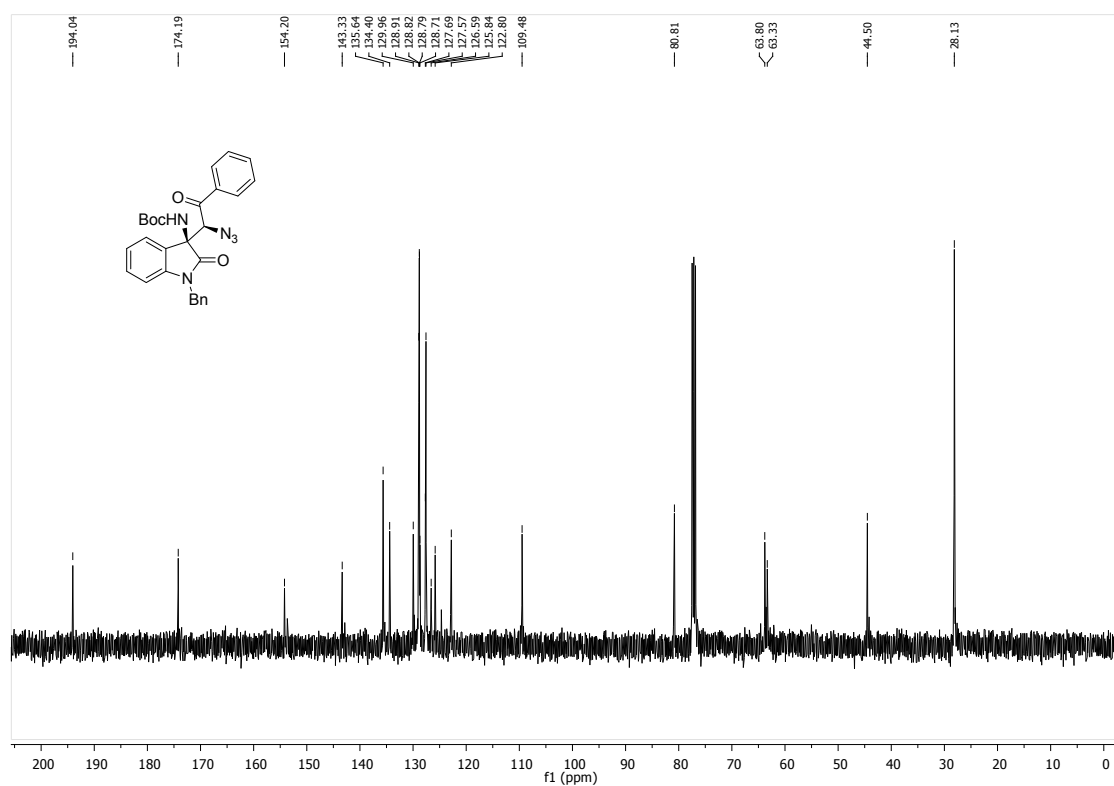
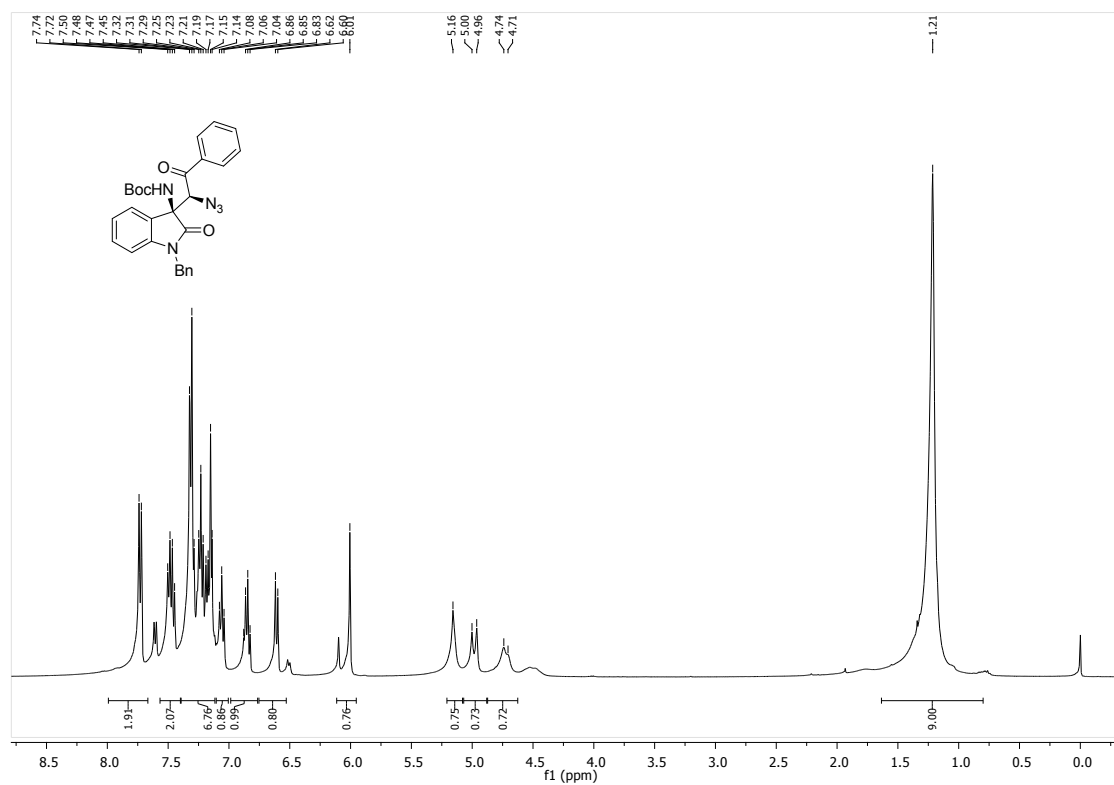
2-Azido-2,3-dihydro-1H-inden-1-one



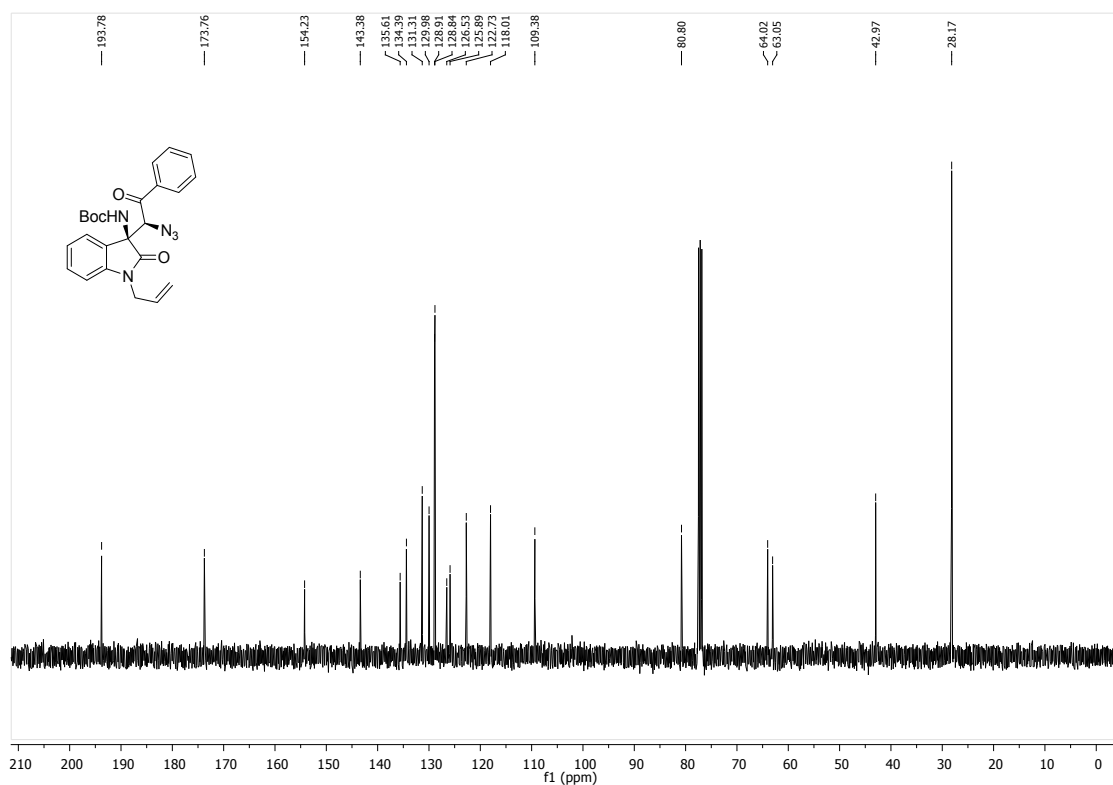
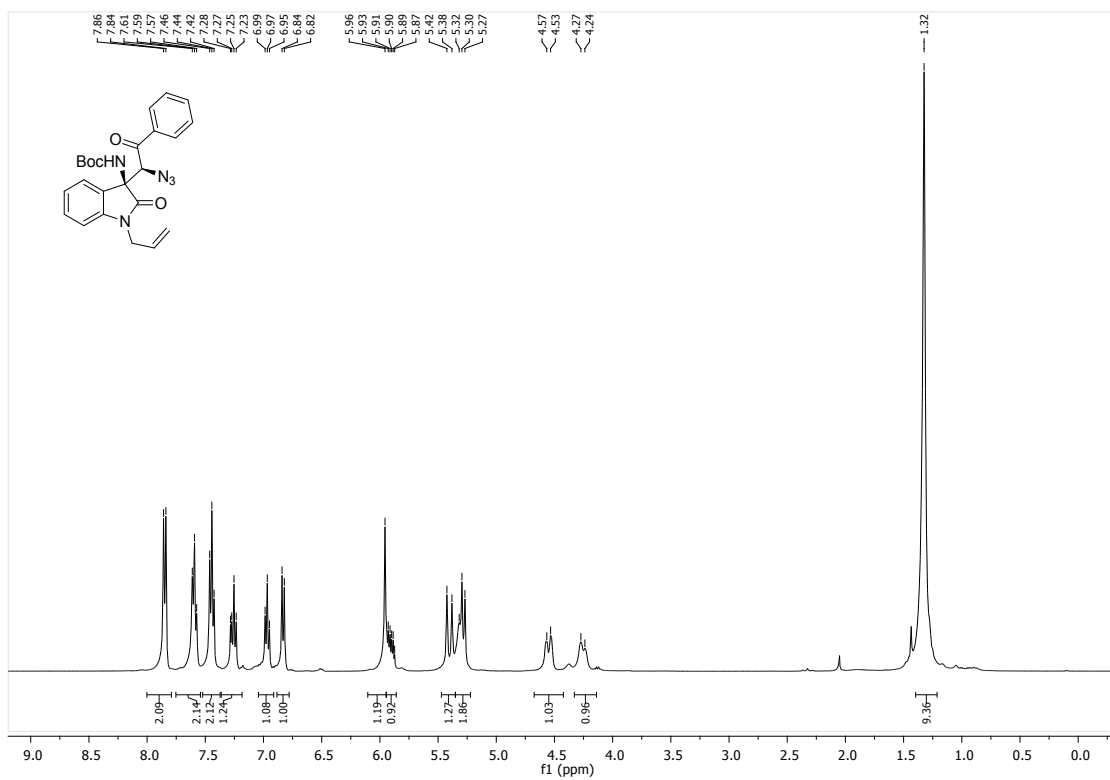
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-oxo-2-phenylethyl)-1-methyl-2-oxoindolin-3-yl)carbamate
(3a)**



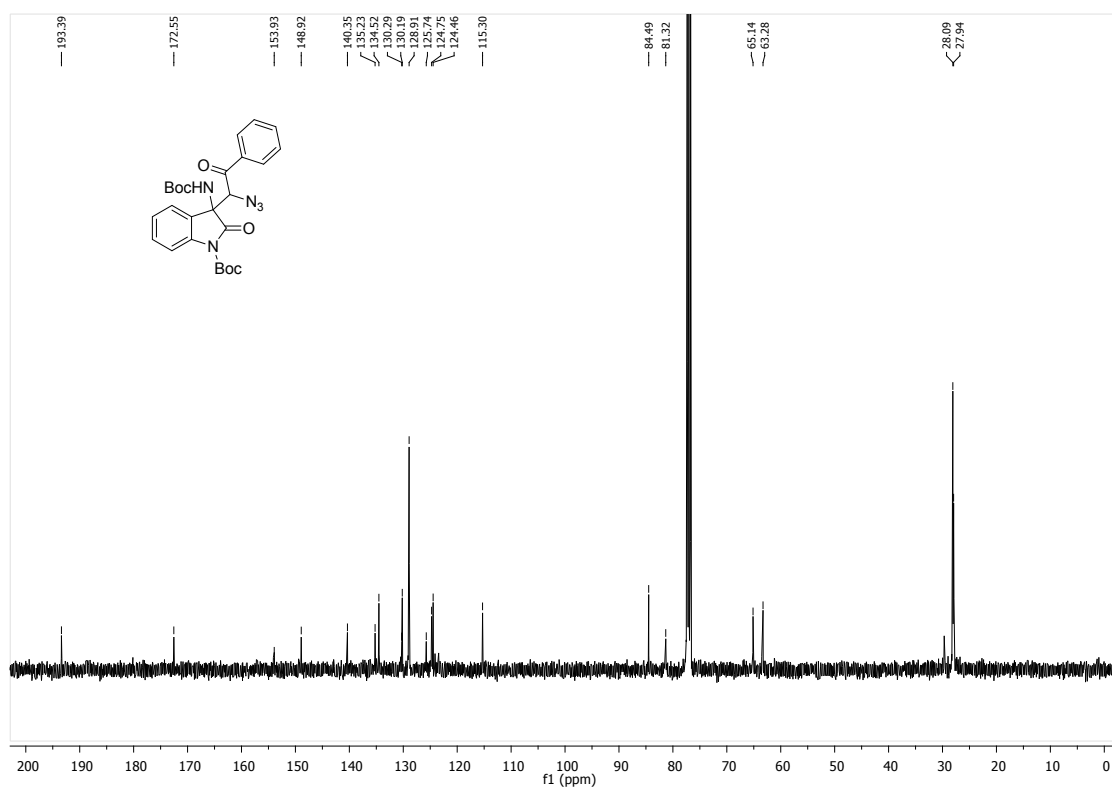
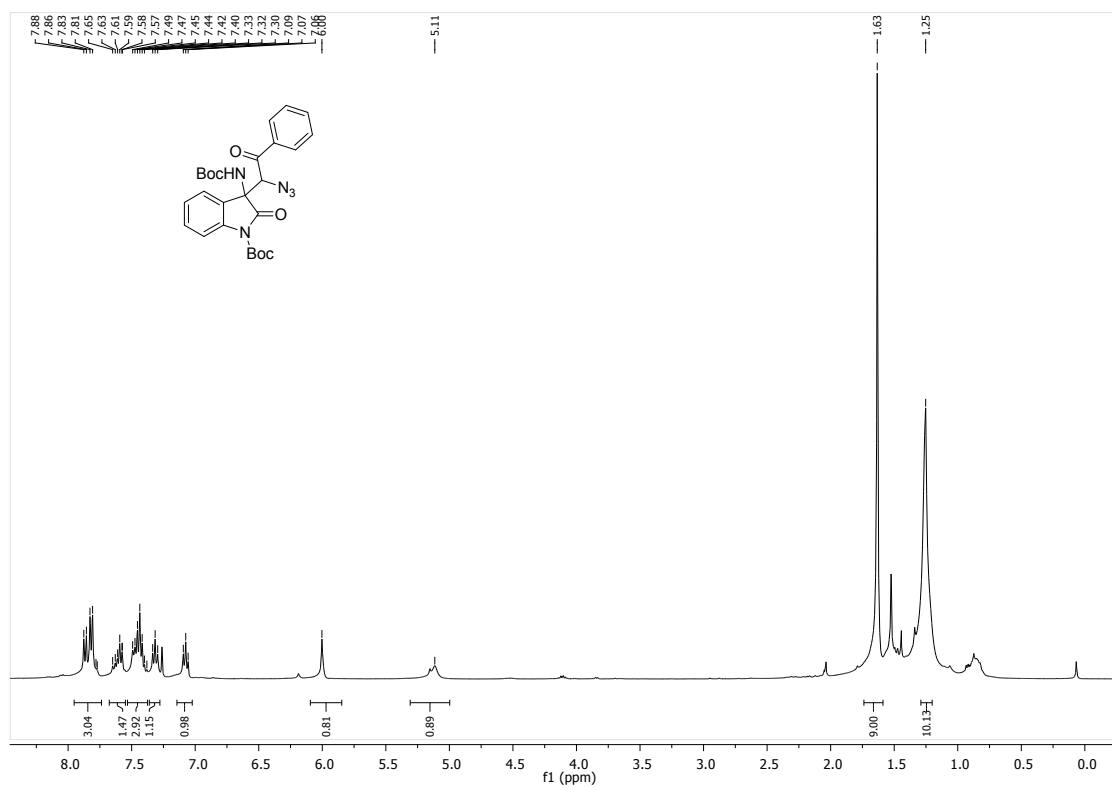
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-oxo-2-phenylethyl)-1-benzyl-2-oxoindolin-3-yl)carbamate (**3b**)**



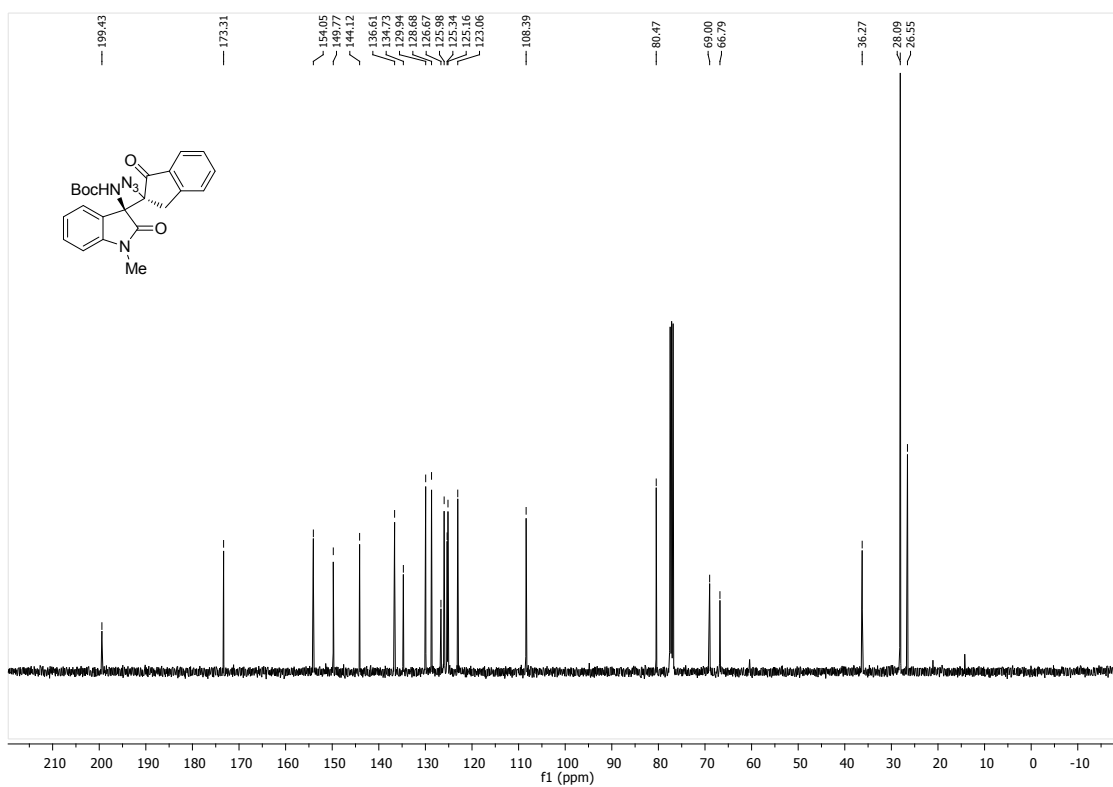
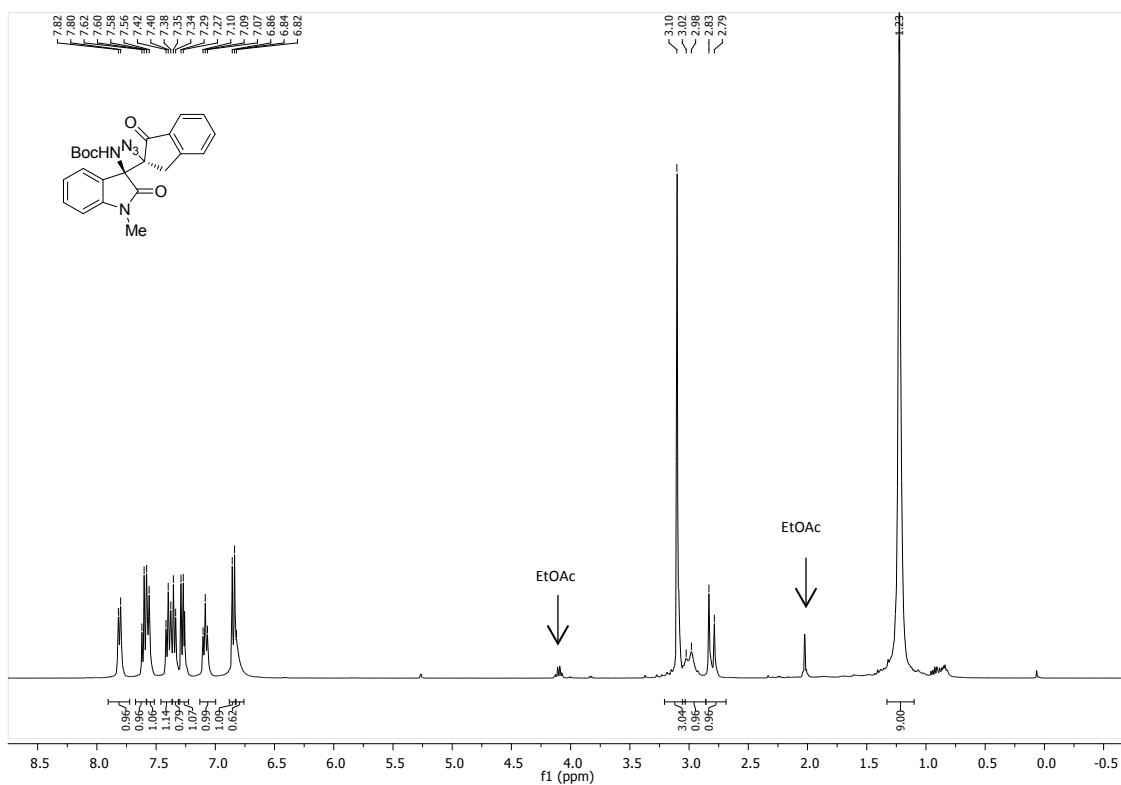
***tert*-Butyl ((*S*)-1-allyl-3-((*S*)-1-azido-2-oxo-2-phenylethyl)-2-oxoindolin-3-yl)carbamate (3c)**



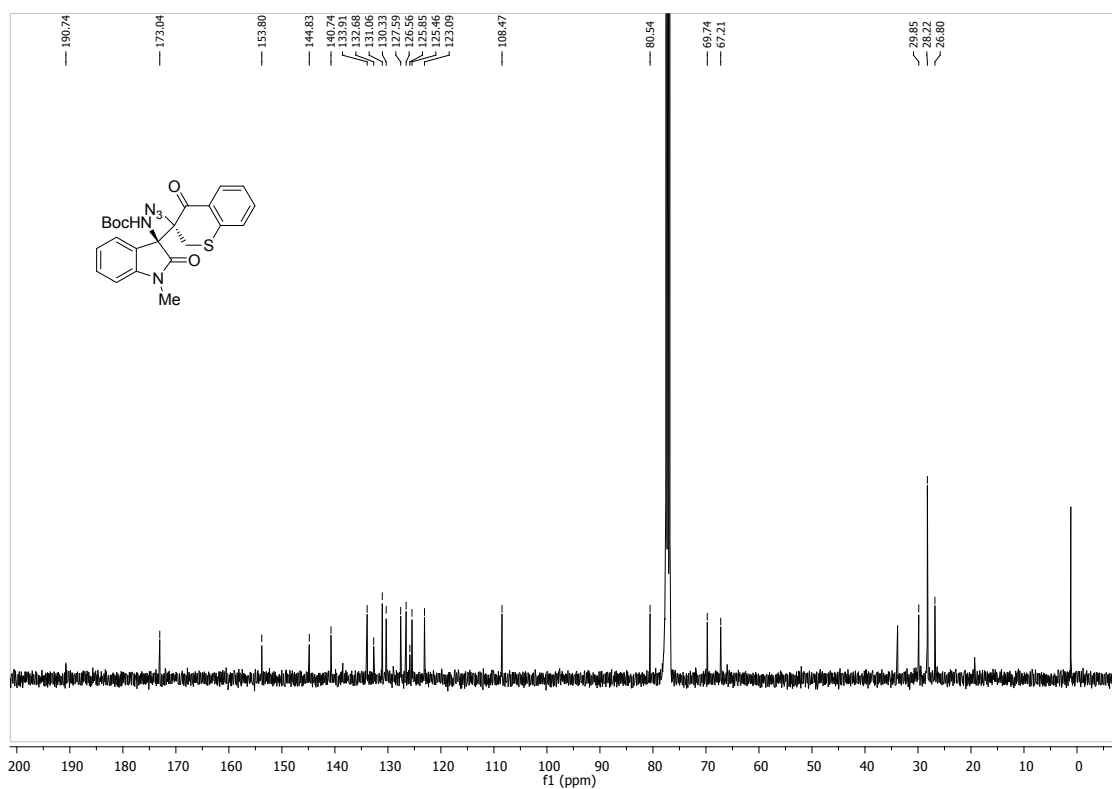
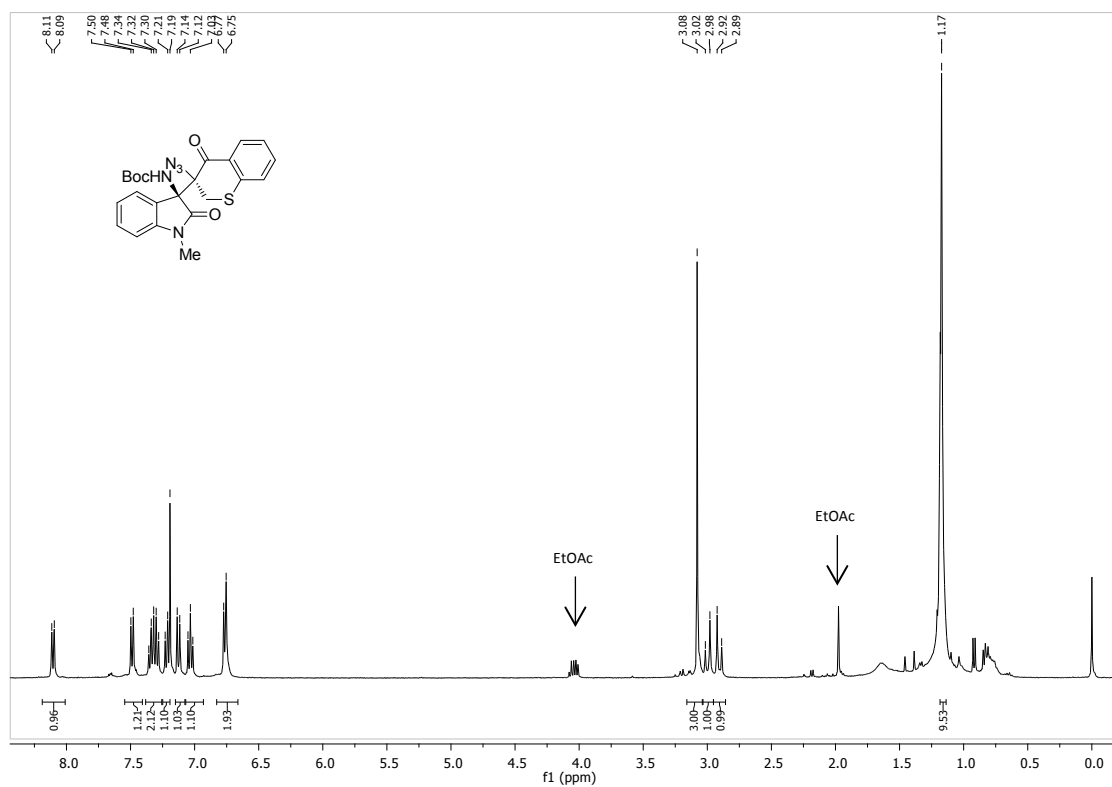
***tert*-Butyl 3-(1-azido-2-oxo-2-phenylethyl)-3-((*tert*-butoxycarbonyl)amino)-2-oxoindoline-1-carboxylate (3d)**



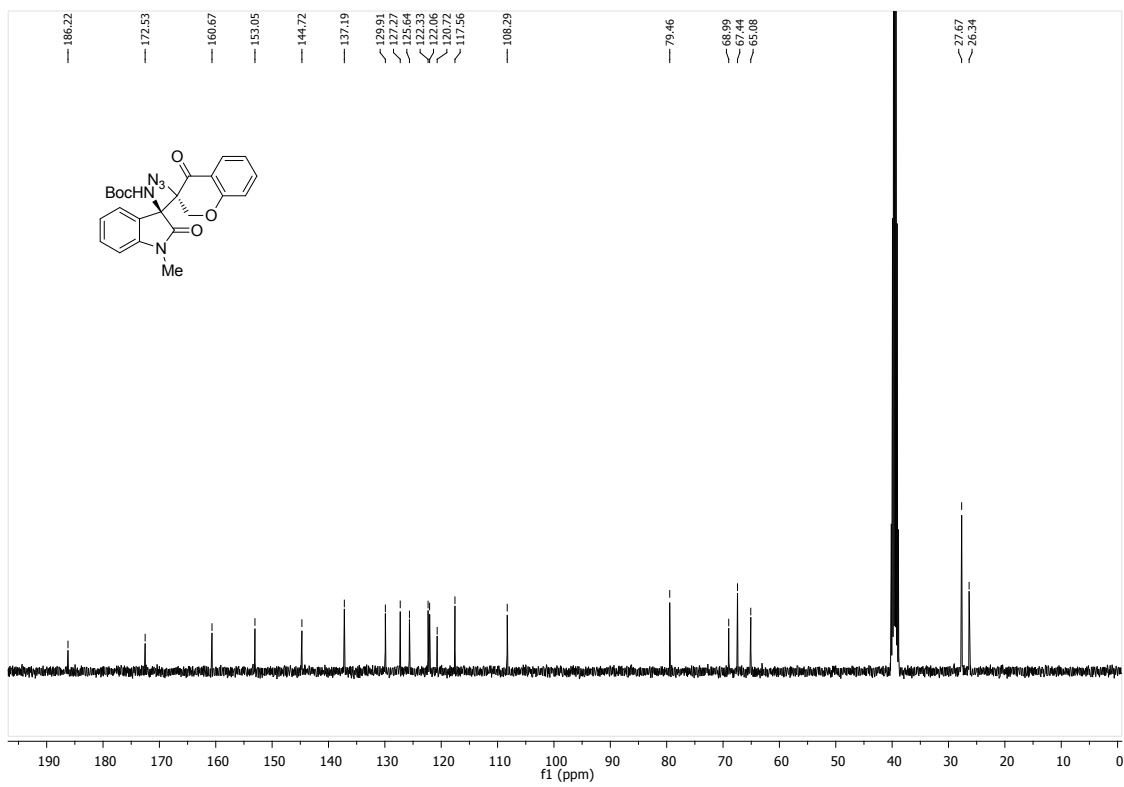
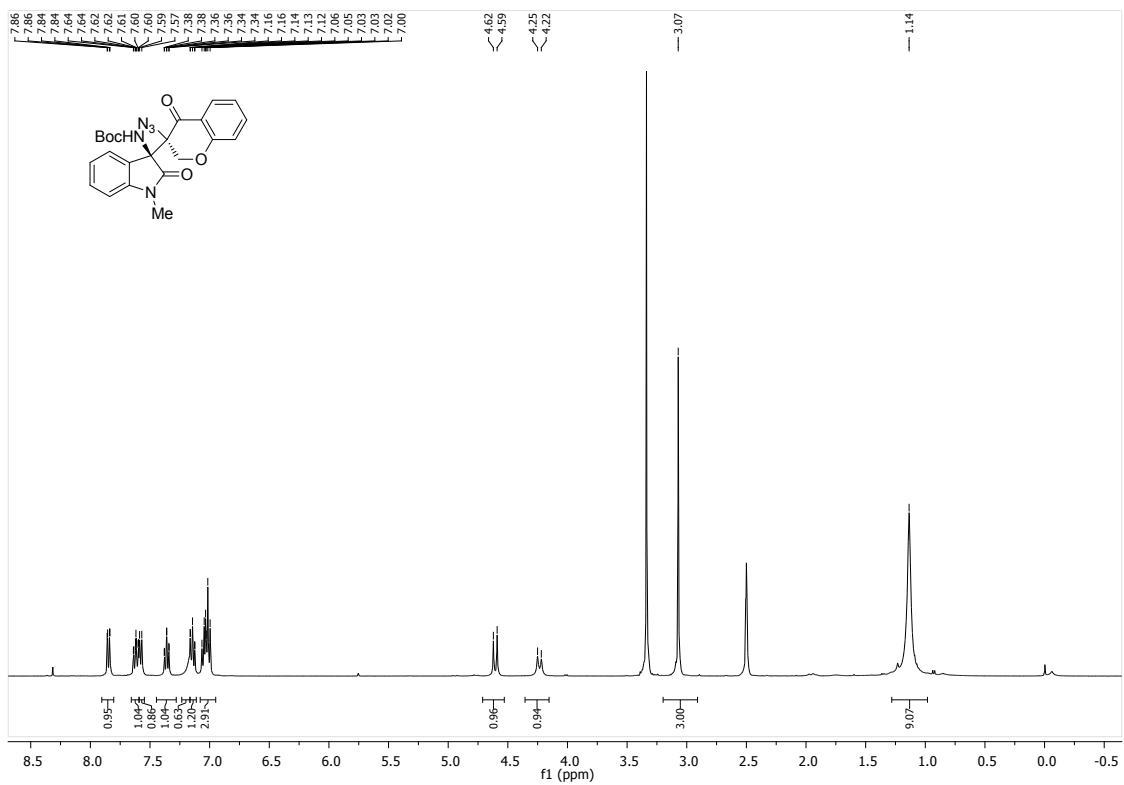
***tert*-Butyl ((*S*)-3-((*R*)-2-azido-1-oxo-2,3-dihydro-1*H*-inden-2-yl)-1-methyl-2-oxoindolin-3-yl)carbamate (**3e**)**



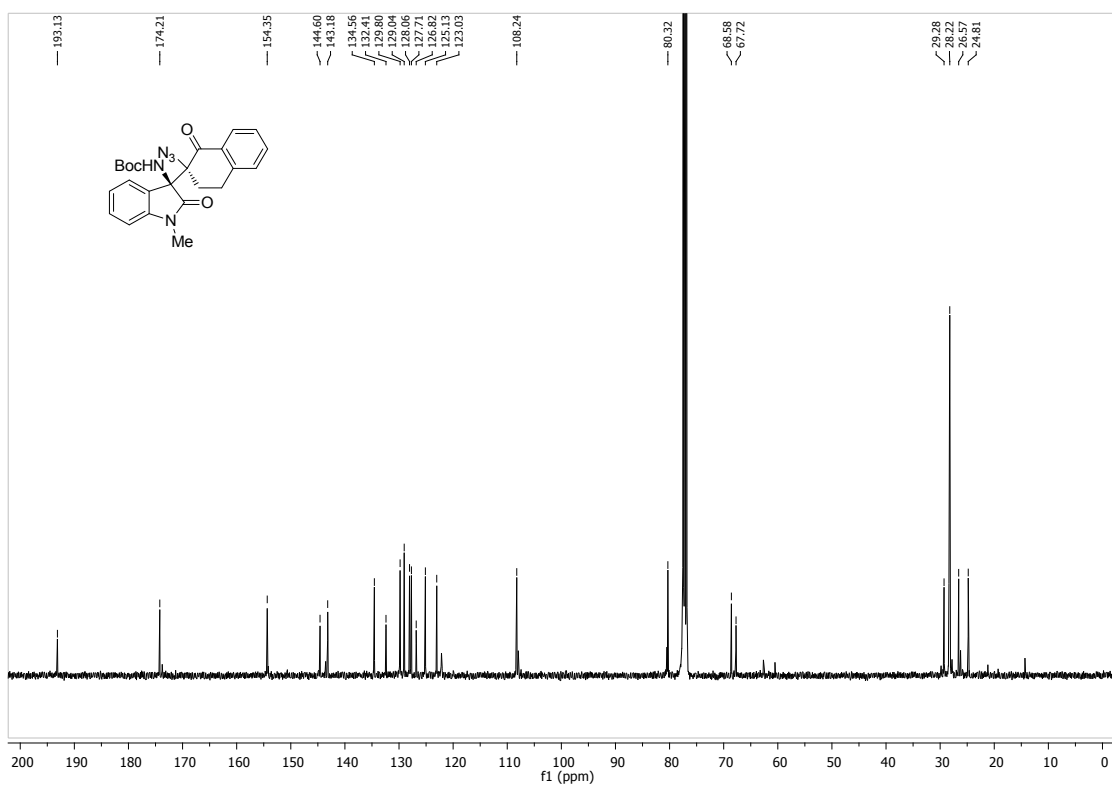
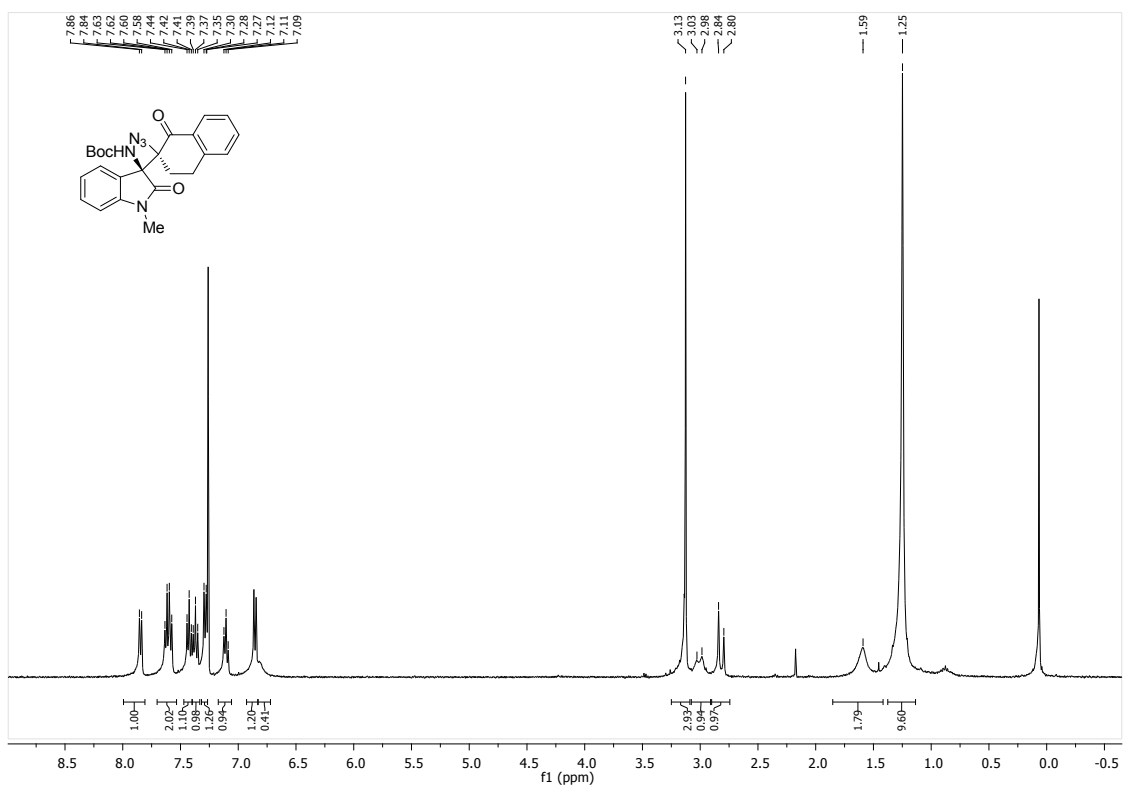
***tert*-Butyl ((*S*)-3-((*R*)-3-azido-4-oxothiochroman-3-yl)-1-methyl-2-oxindolin-3-yl)carbamate (3f)**



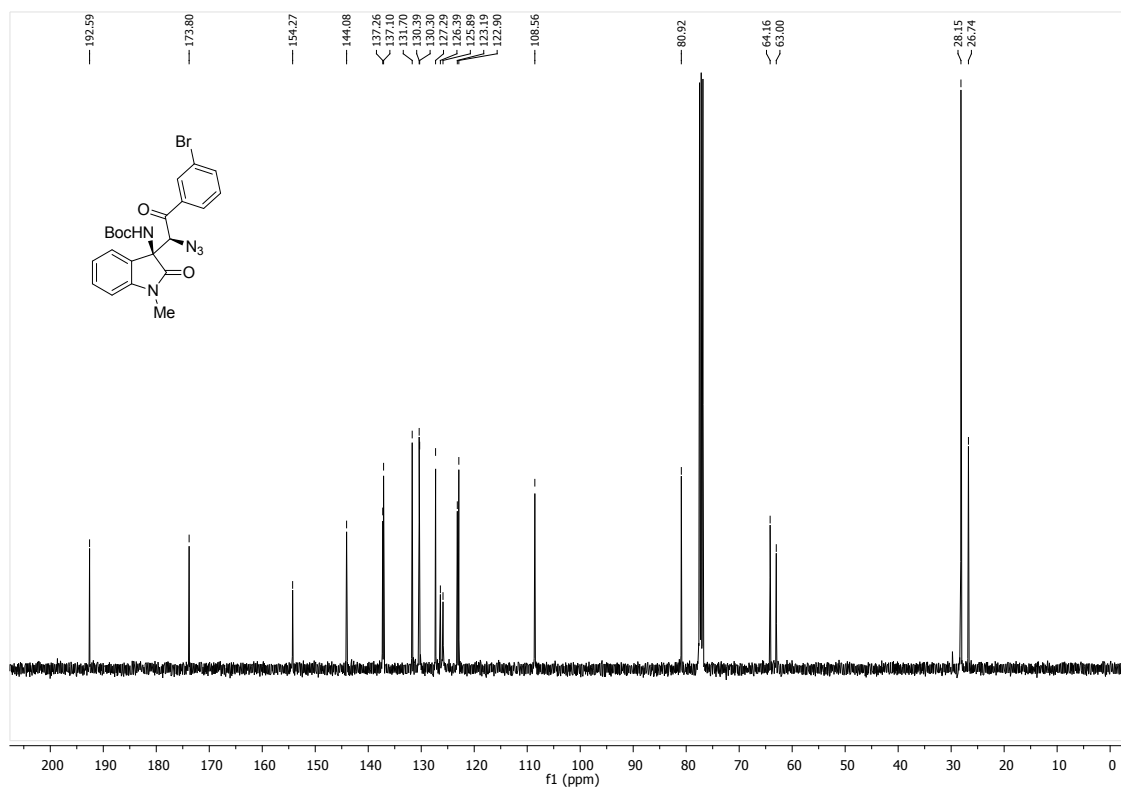
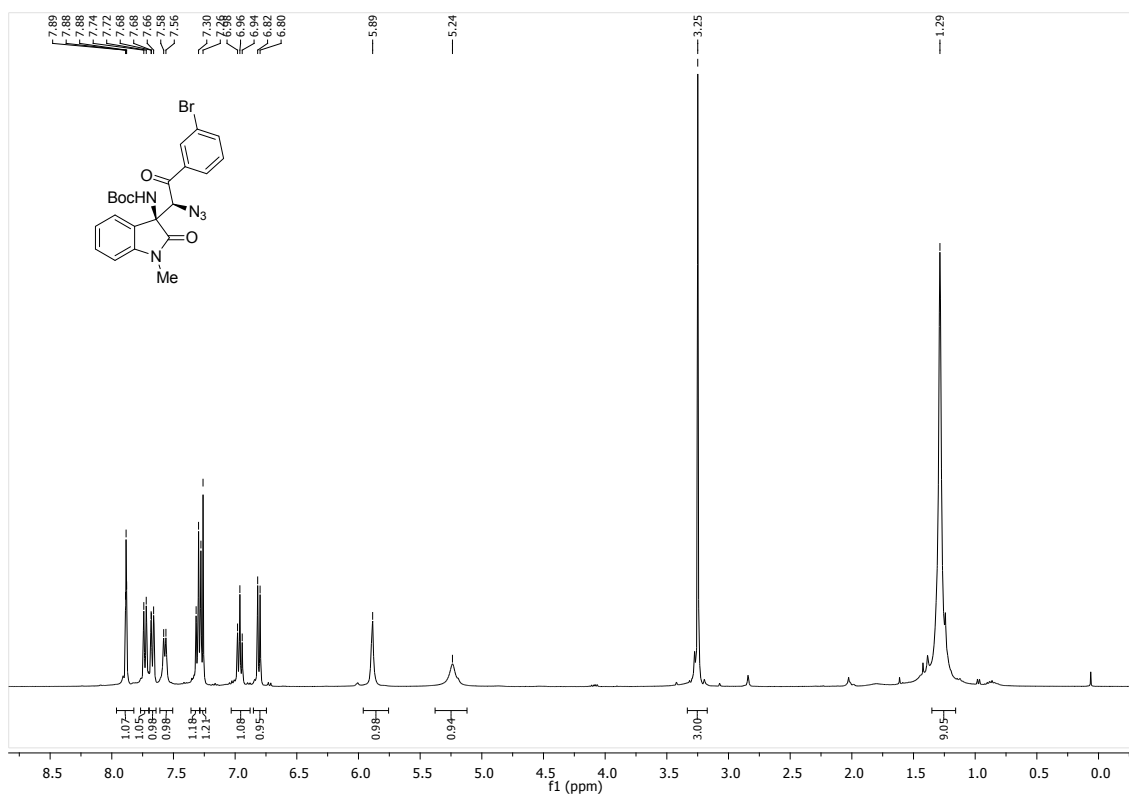
(3g)



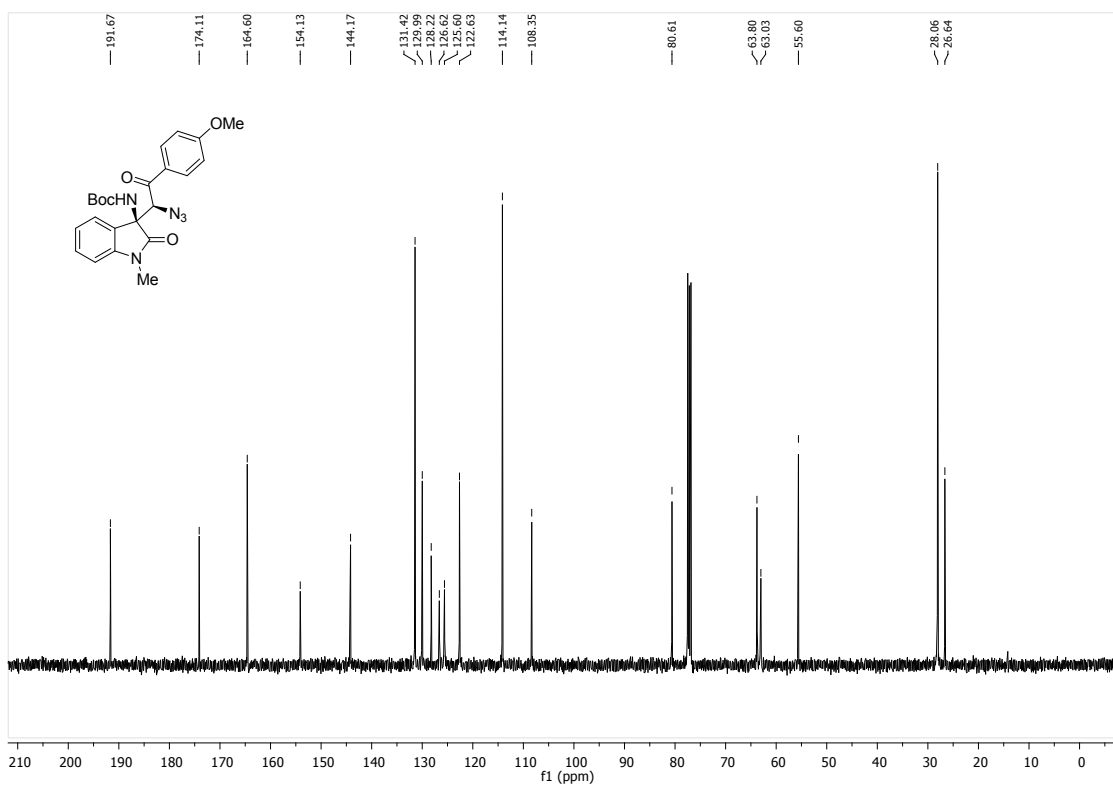
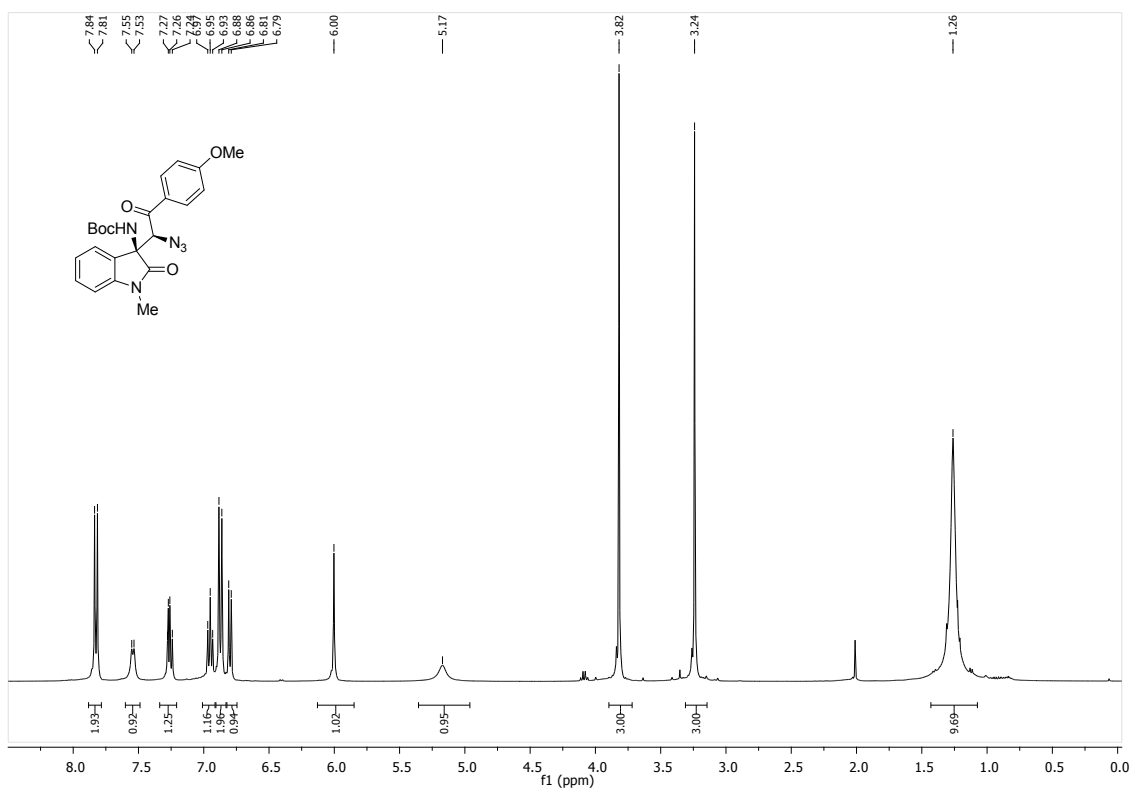
***tert*-Butyl ((*S*)-3-((*R*)-2-azido-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-1-methyl-2-oxoindolin-3-yl)carbamate (3h)**



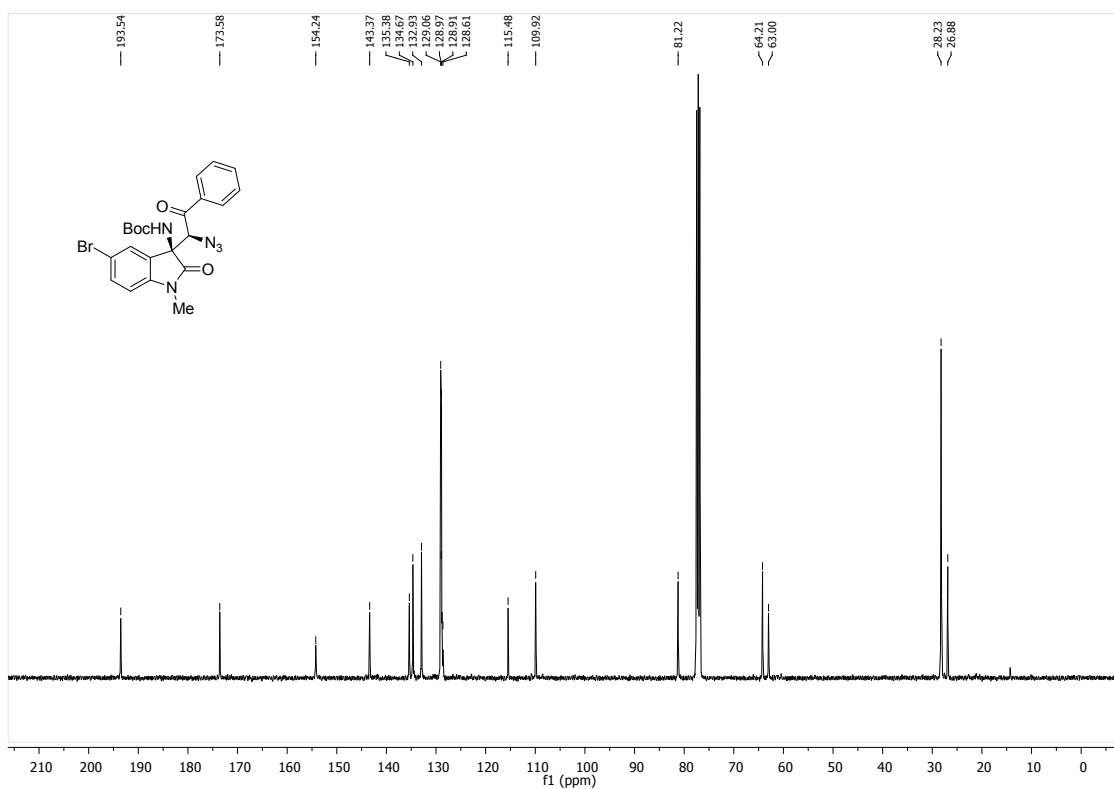
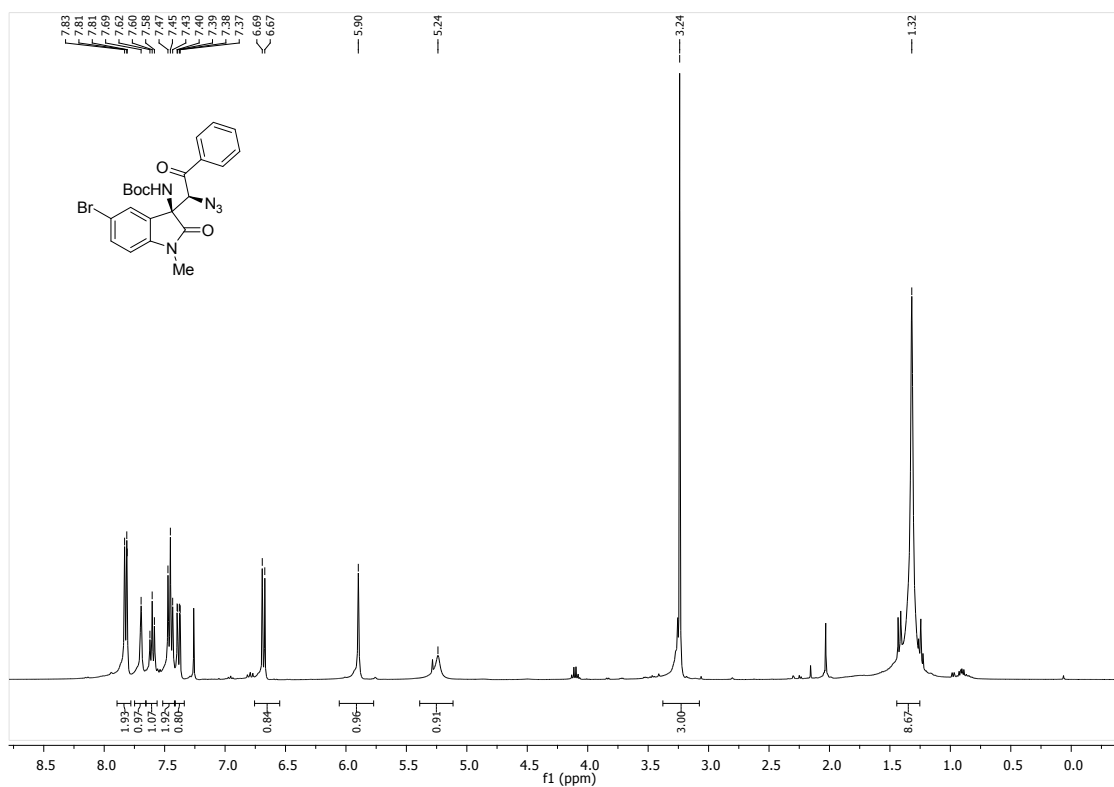
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-(3-bromophenyl)-2-oxoethyl)-1-methyl-2-oxindolin-3-yl)carbamate (**3i**)**



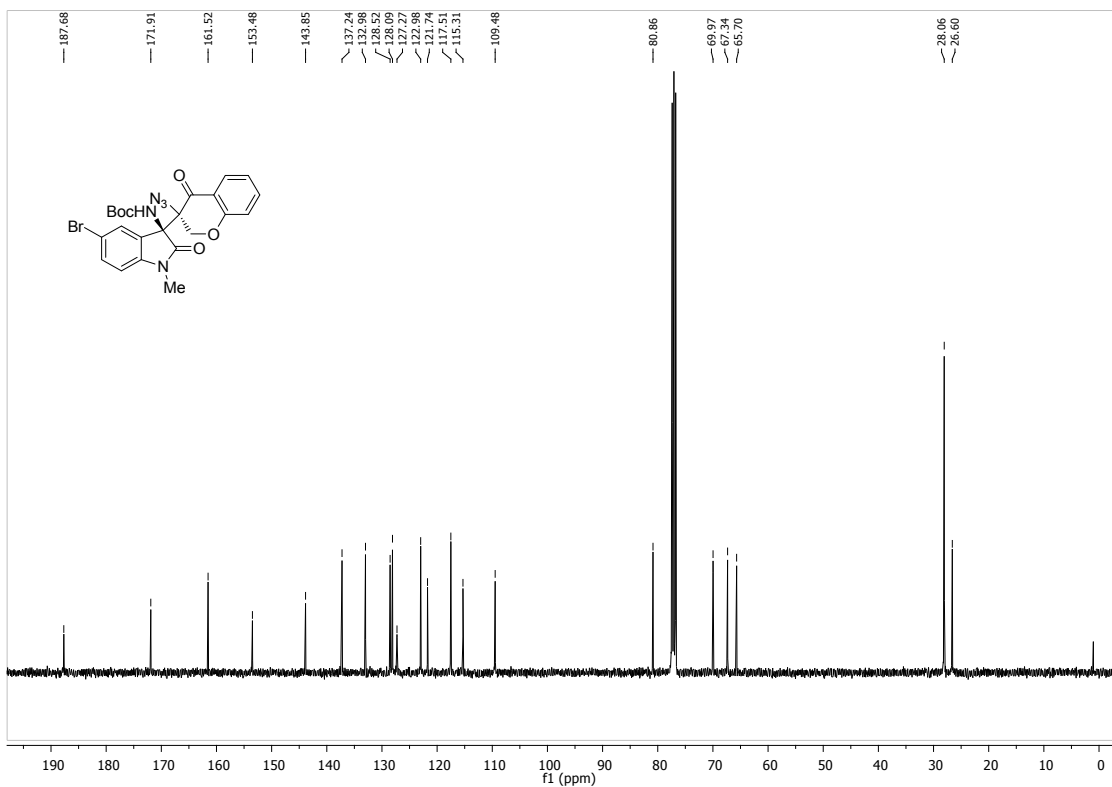
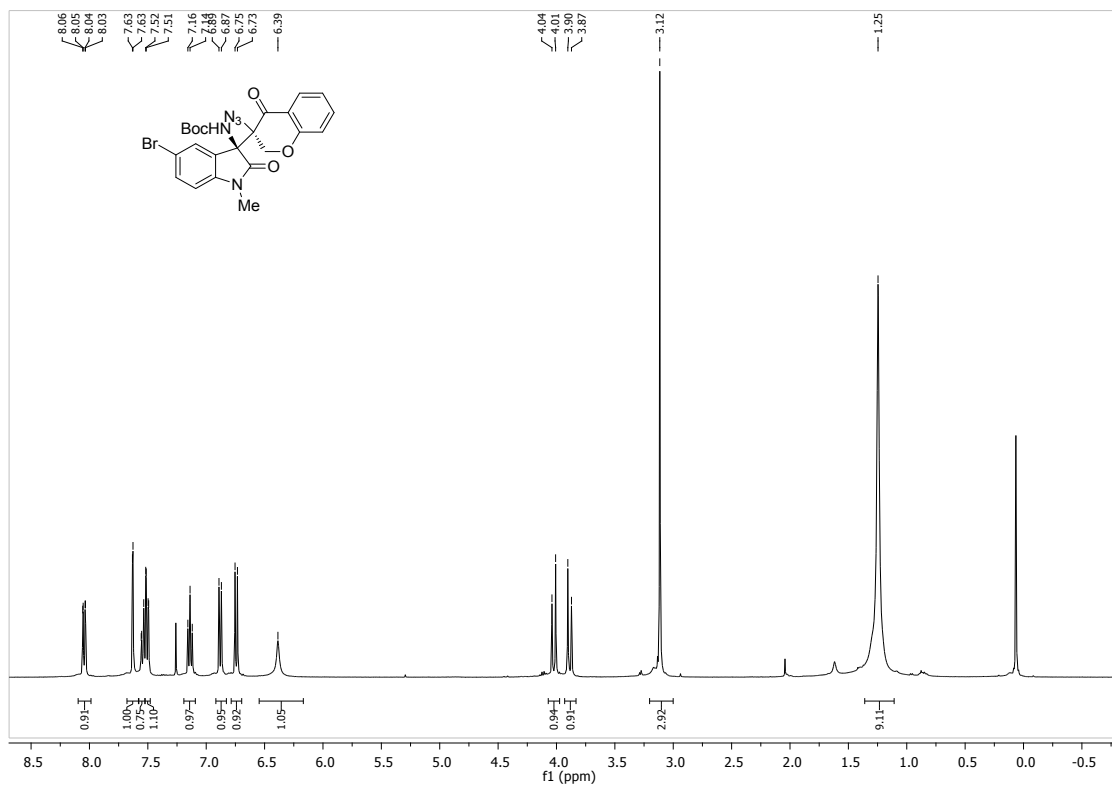
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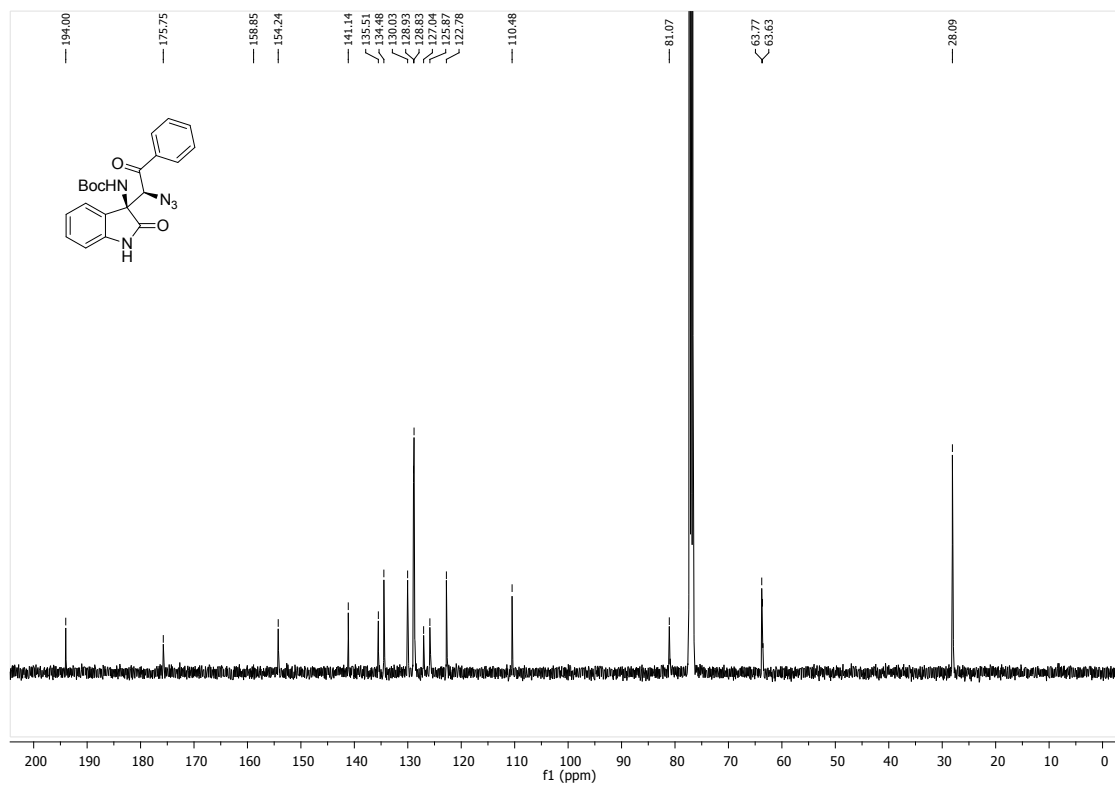
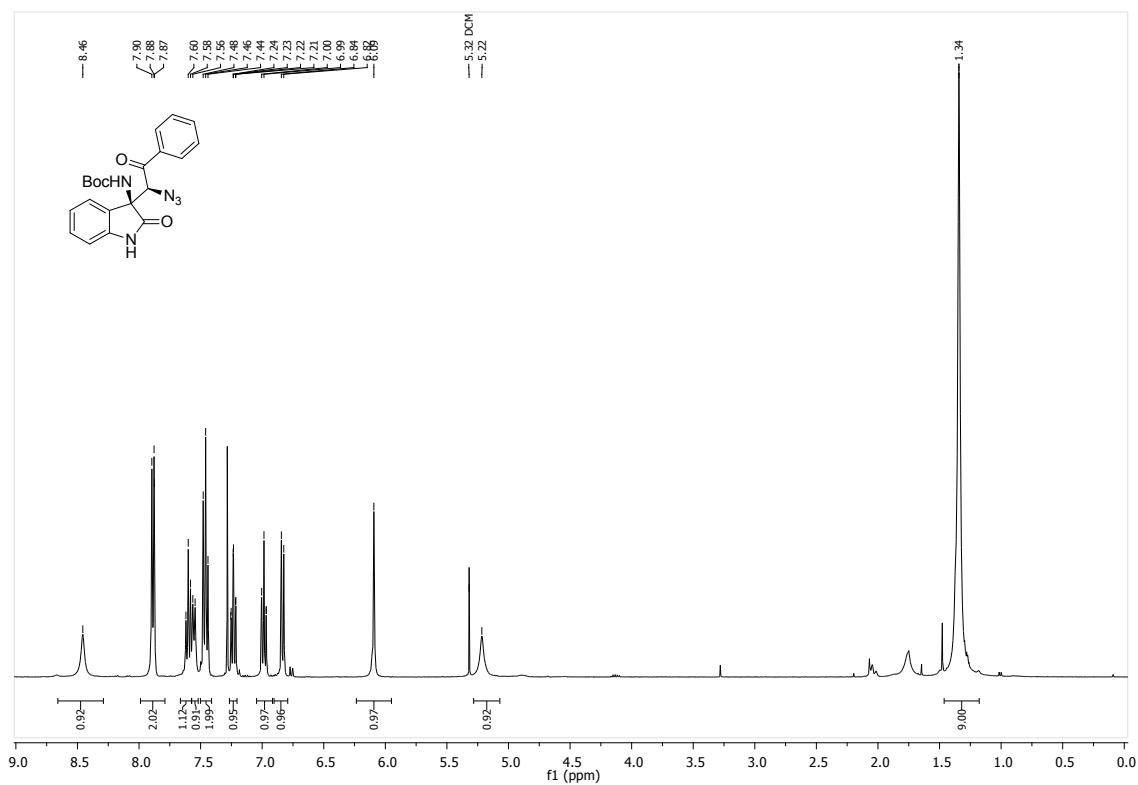
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-oxo-2-phenylethyl)-5-bromo-1-methyl-2-oxoindolin-3-yl)carbamate (3k)**



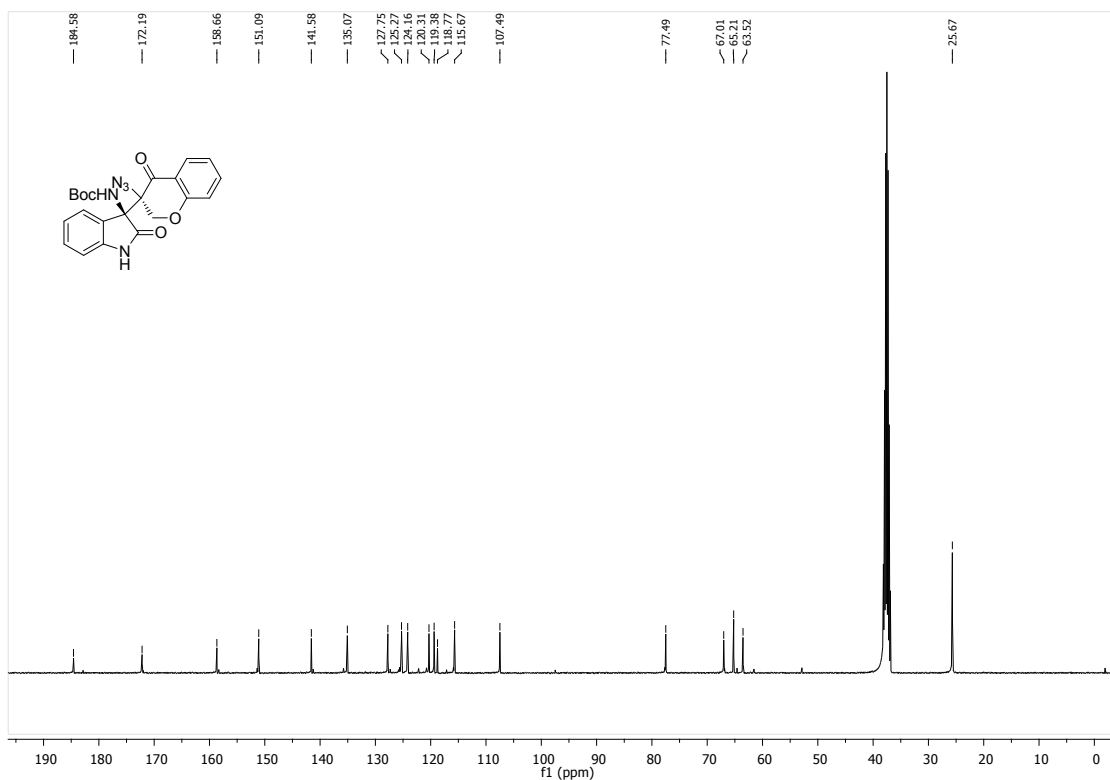
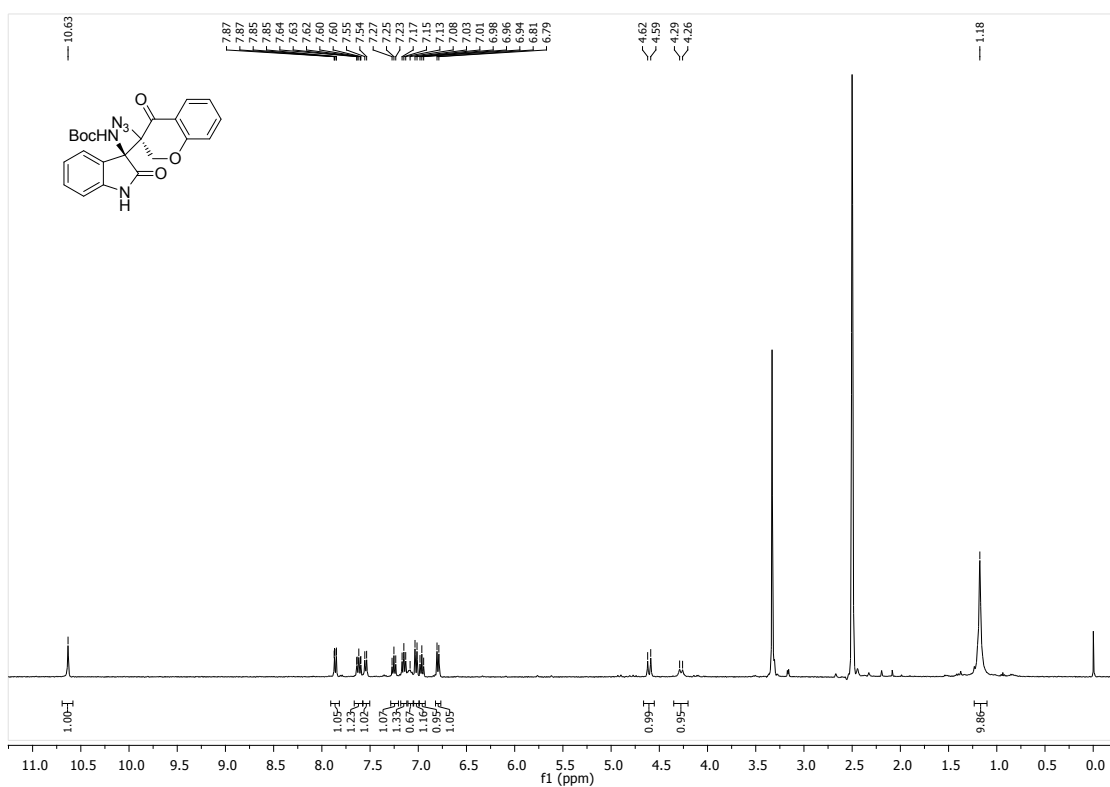
***tert*-Butyl ((*S*)-3-((*S*)-3-azido-4-oxochroman-3-yl)-5-bromo-1-methyl-2-oxoindolin-3-yl)carbamate (**3l**)**



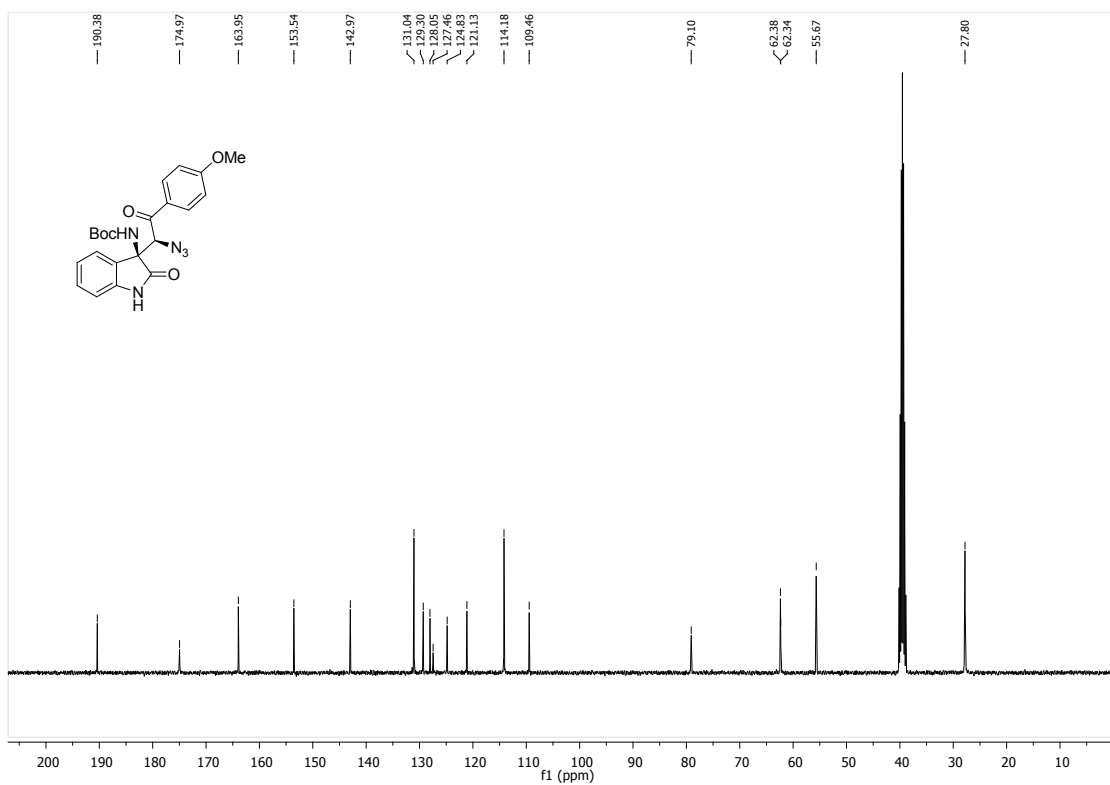
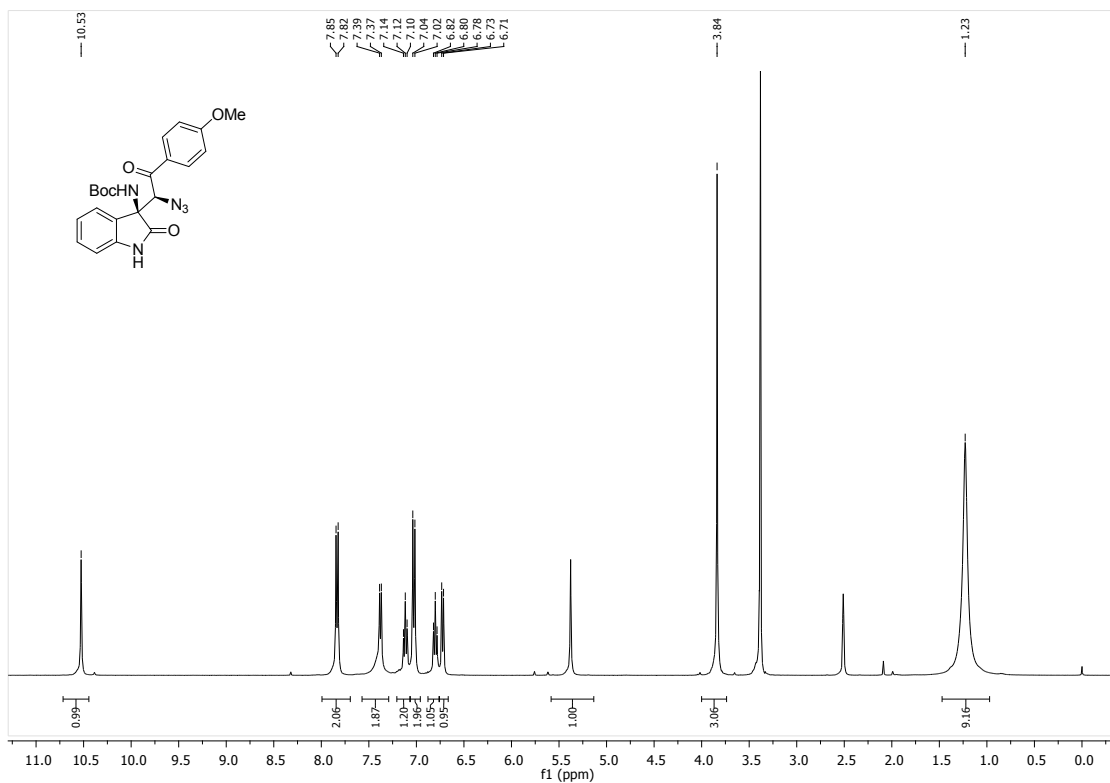
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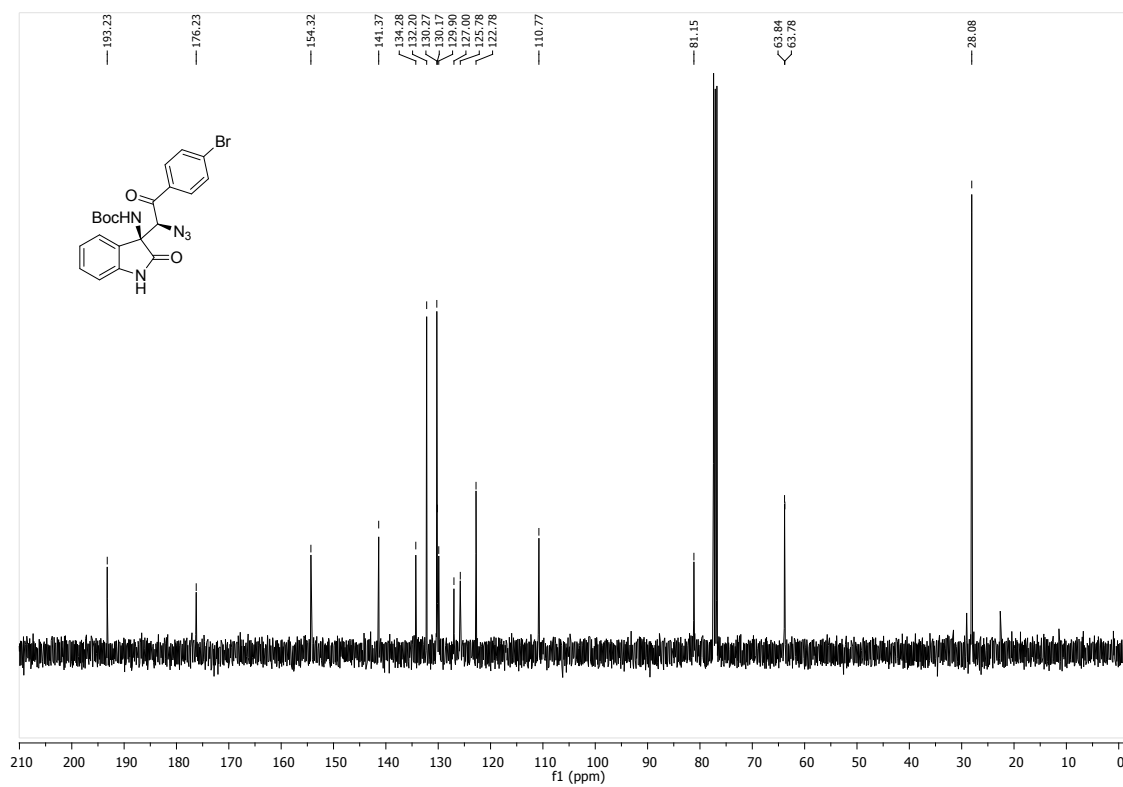
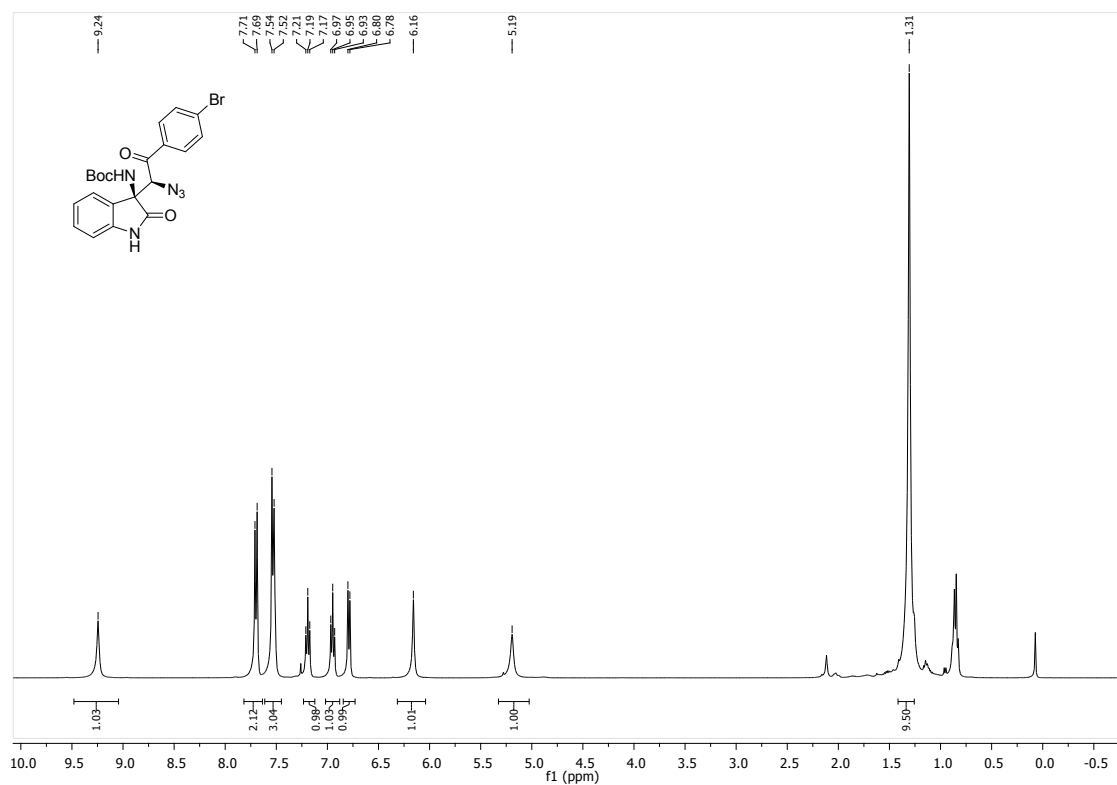
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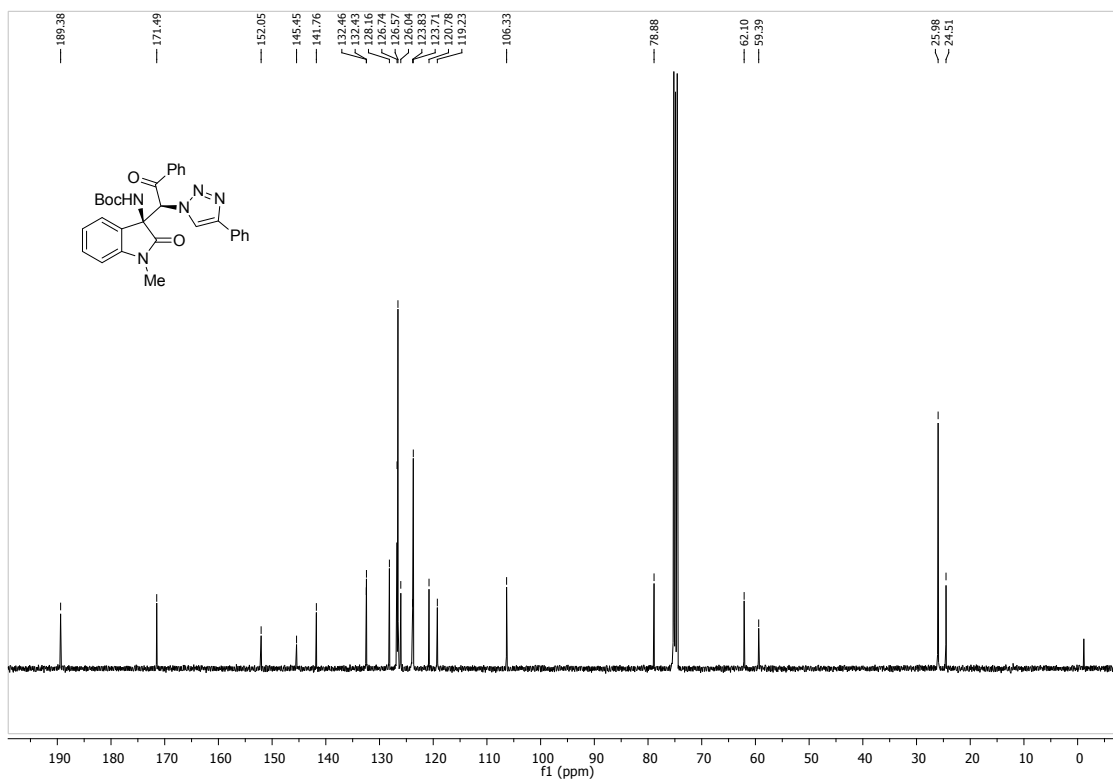
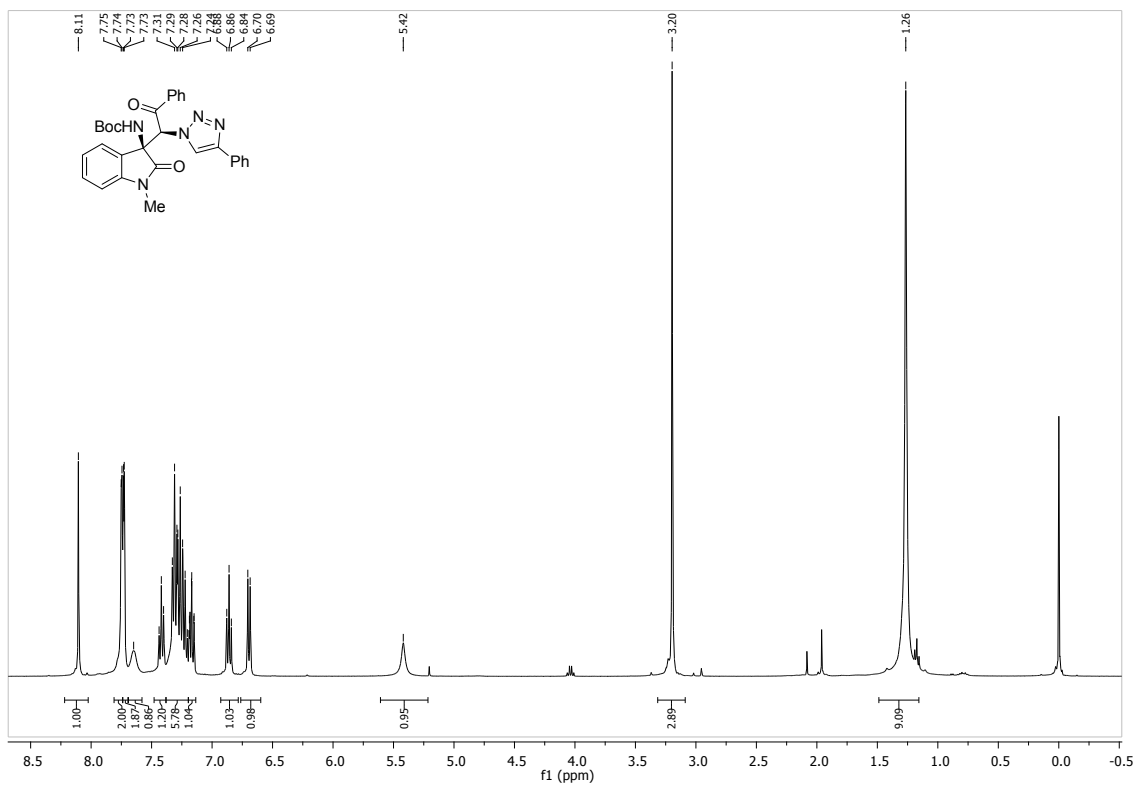
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-(4-methoxyphenyl)-2-oxoethyl)-2-oxoindolin-3-yl)carbamate (3o)**



***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-(4-bromophenyl)-2-oxoethyl)-2-oxoindolin-3-yl)carbamate
(3p)**

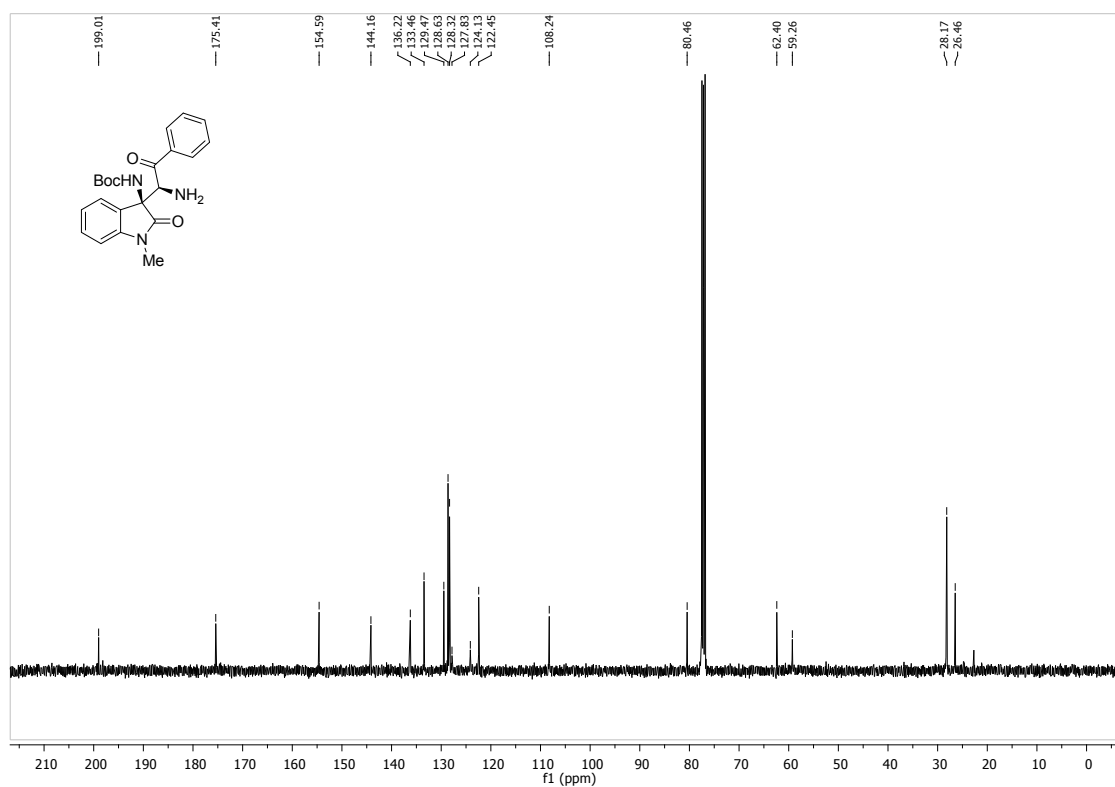
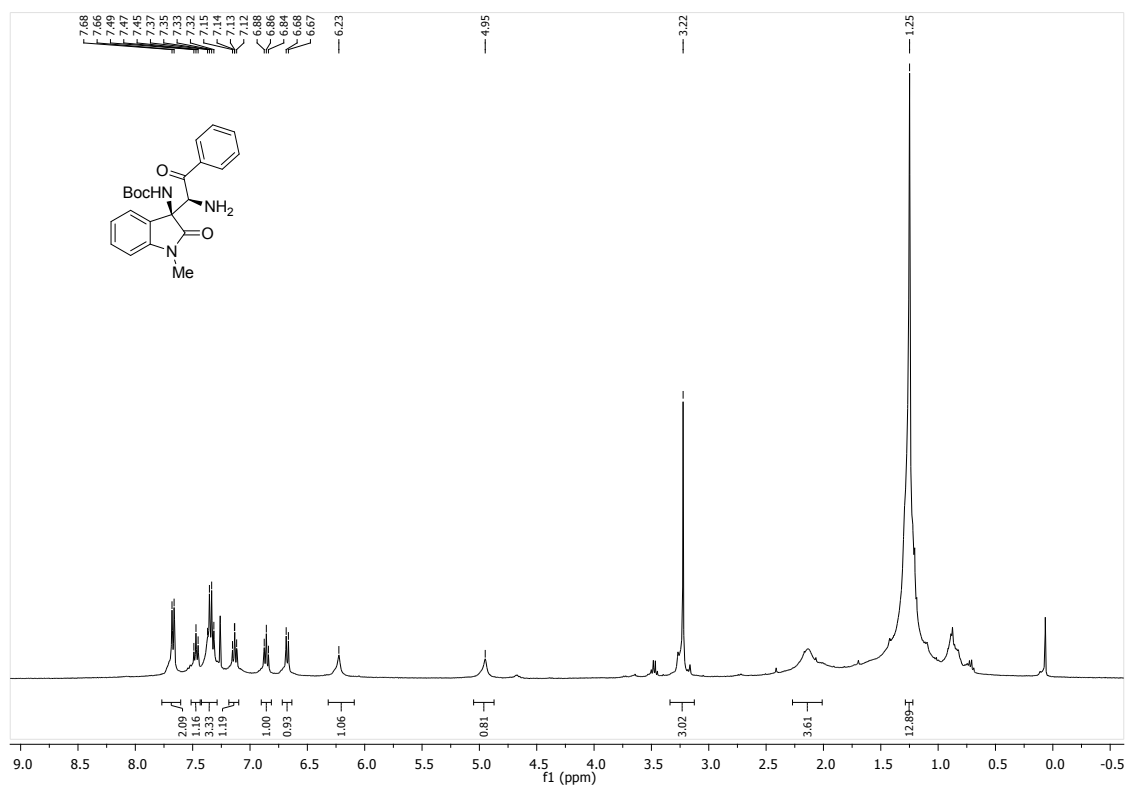


***tert*-Butyl ((*S*)-1-methyl-2-oxo-3-((*S*)-2-oxo-2-phenyl-1-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethyl)indolin-3-yl)carbamate (4)**

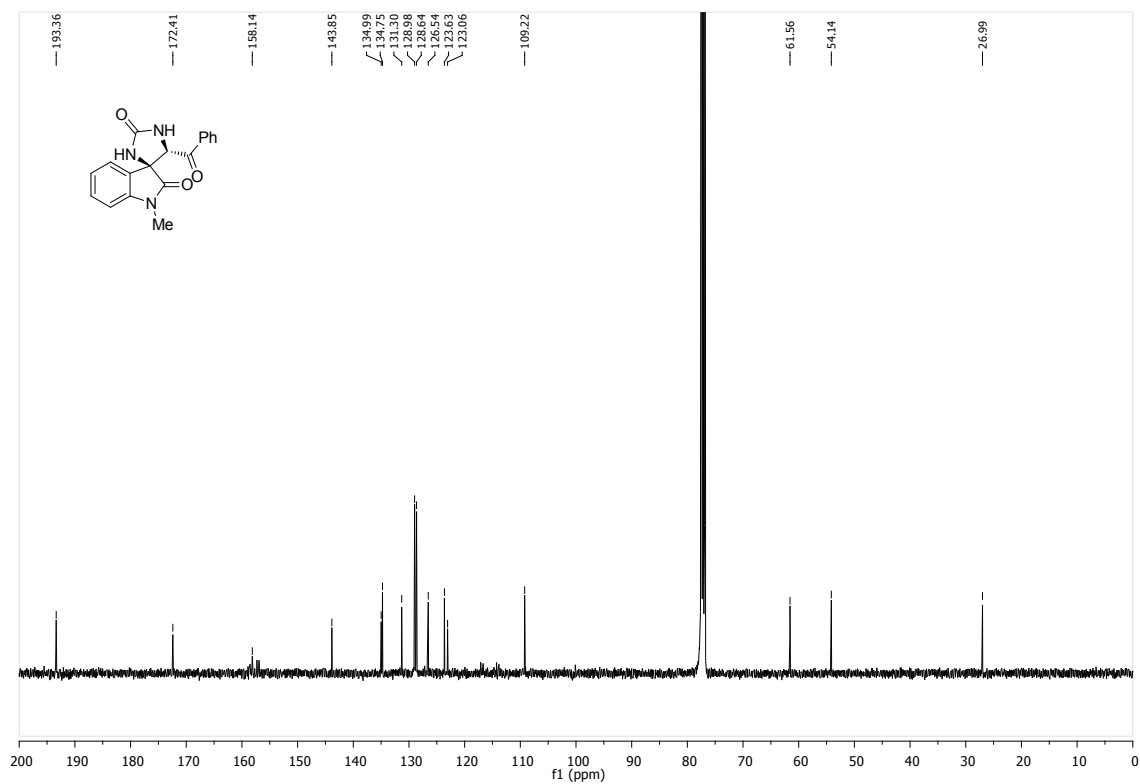
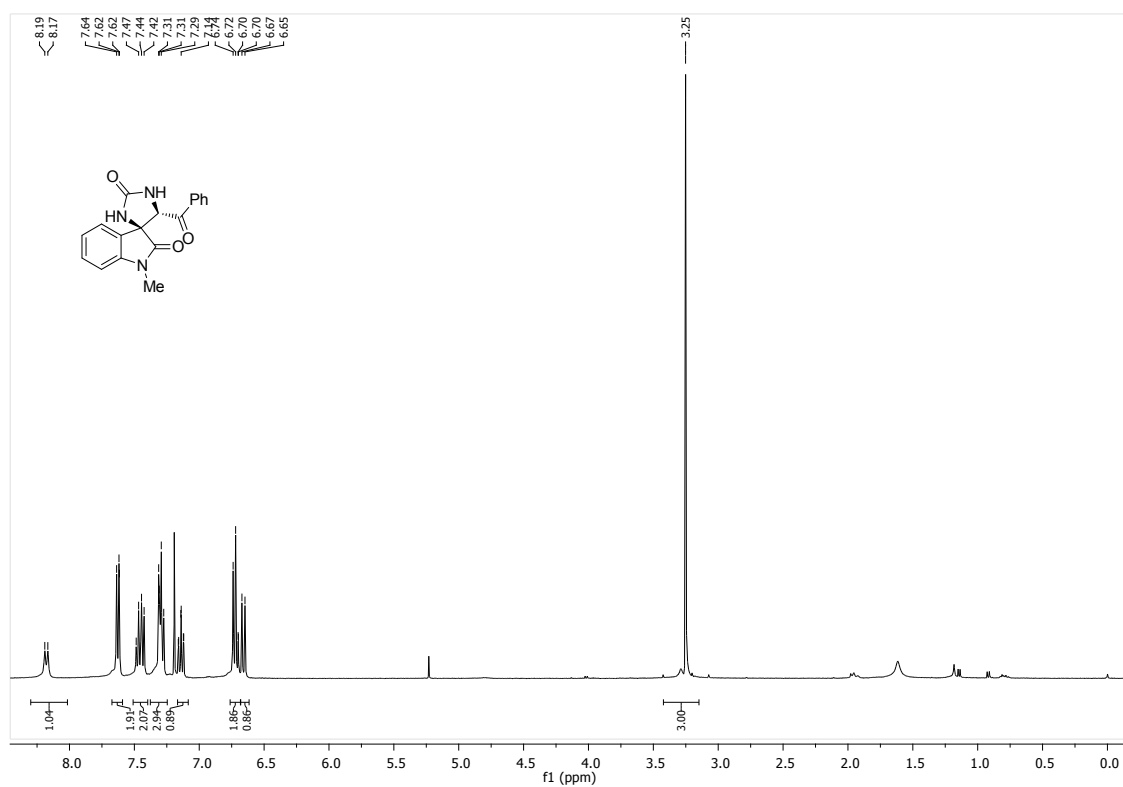


***tert*-Butyl ((*S*)-3-((*S*)-1-amino-2-oxo-2-phenylethyl)-1-methyl-2-oxoindolin-3-yl)carbamate**

(5)

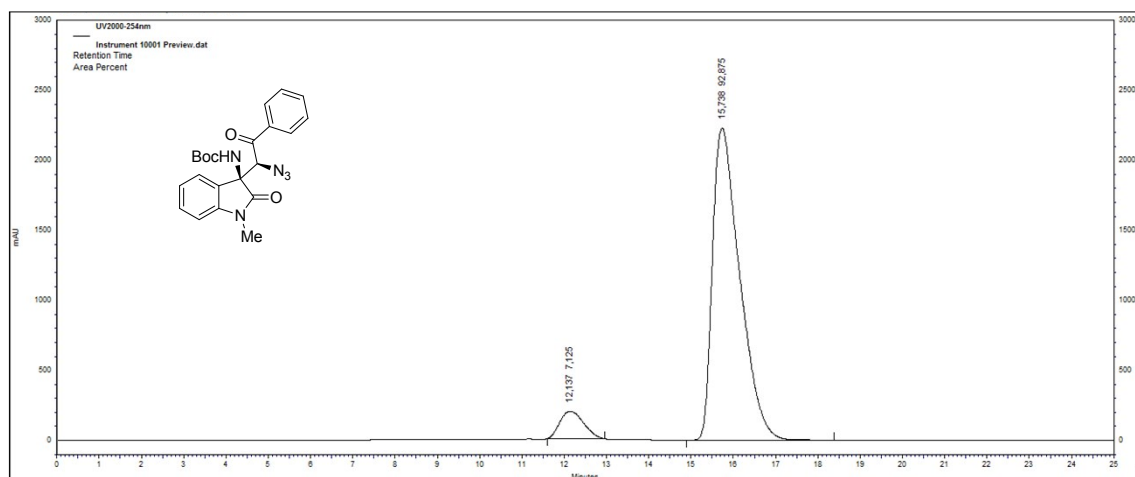
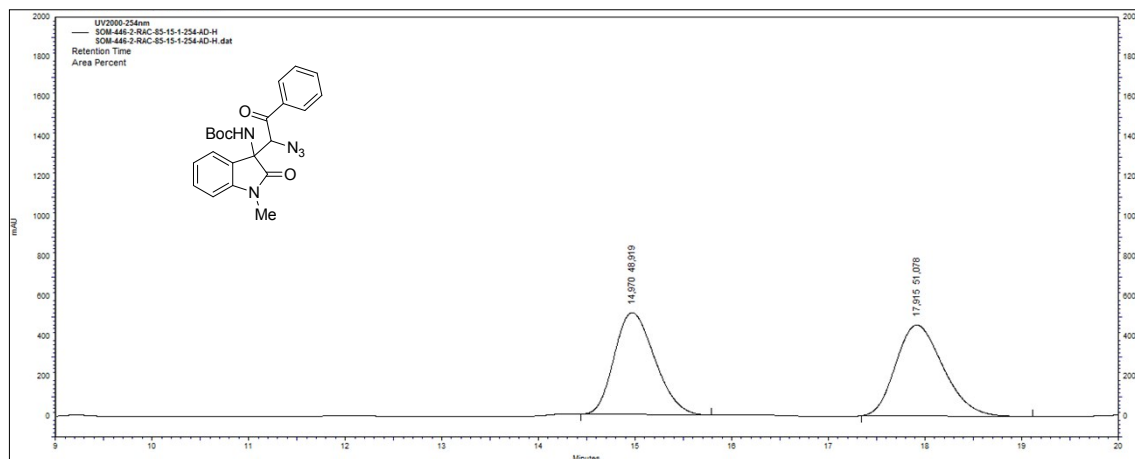


(3'S,5S)-5-Benzoyl-1'-methylspiro[imidazolidine-4,3'-indoline]-2,2'-dione (6)

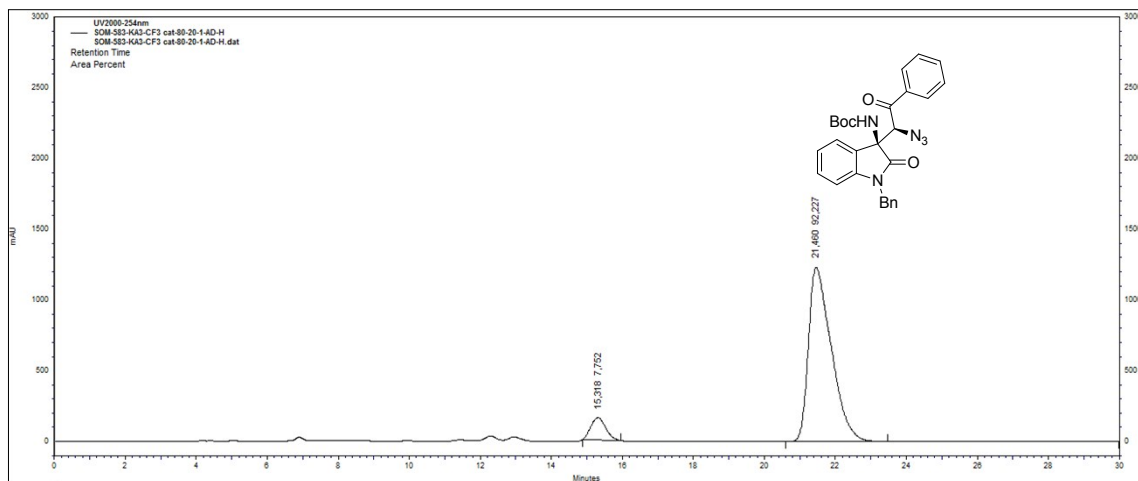
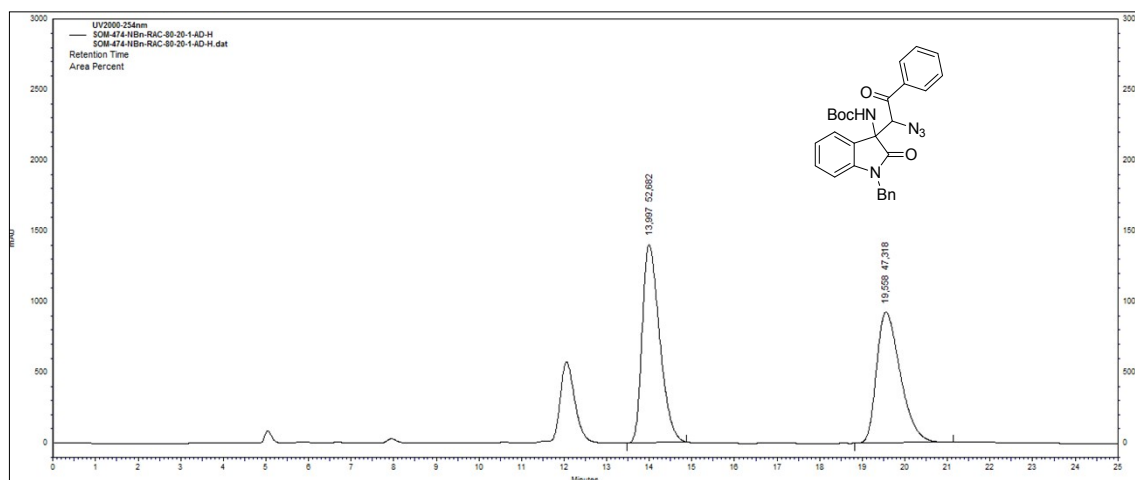


2. HPLC Chromatograms

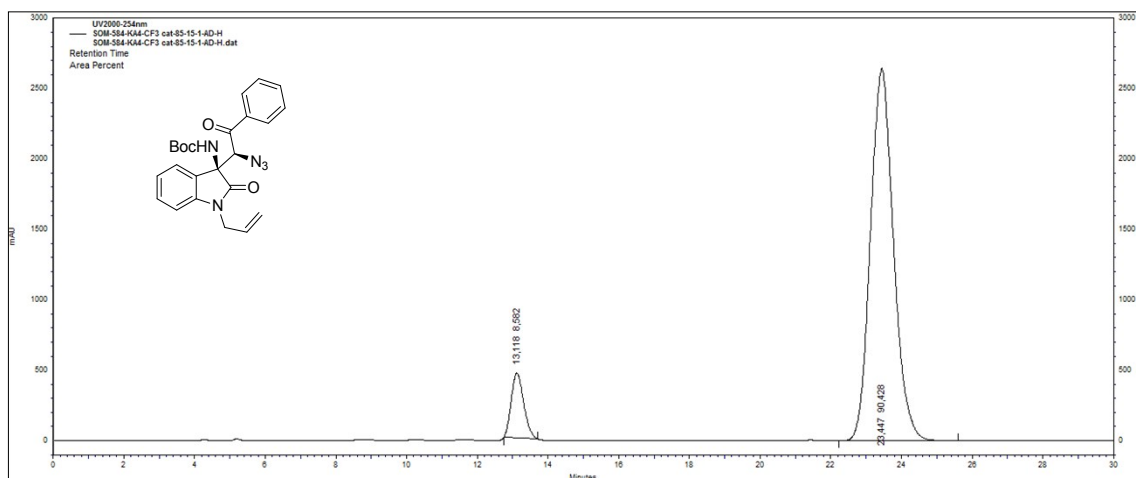
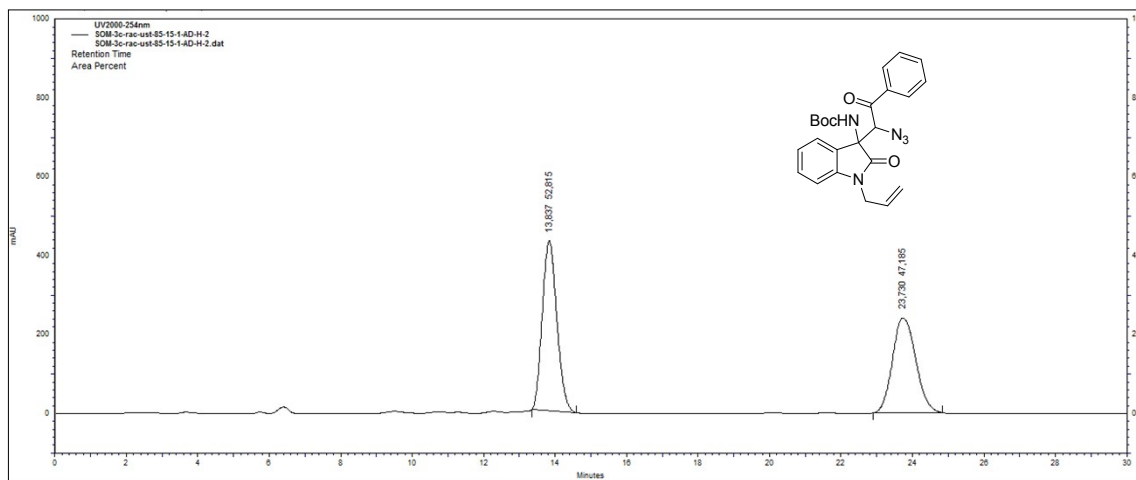
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-oxo-2-phenylethyl)-1-methyl-2-oxoindolin-3-yl)carbamate
(3a)**



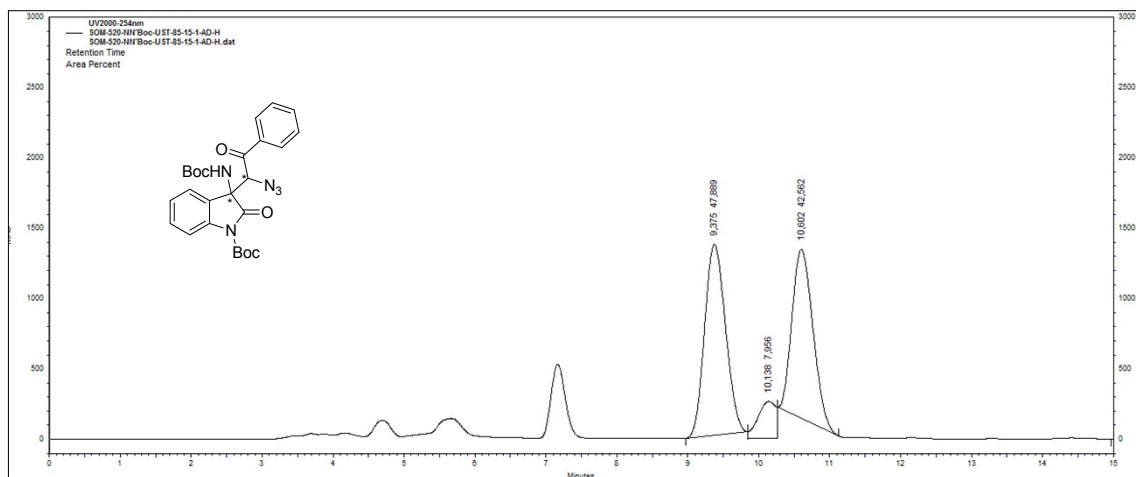
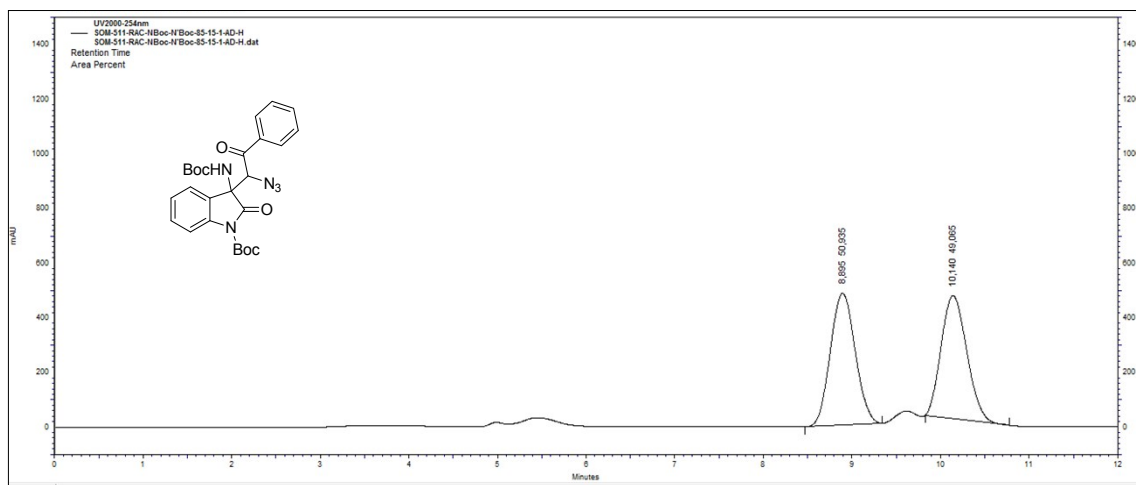
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-oxo-2-phenylethyl)-1-benzyl-2-oxoindolin-3-yl)carbamate
(3b)**



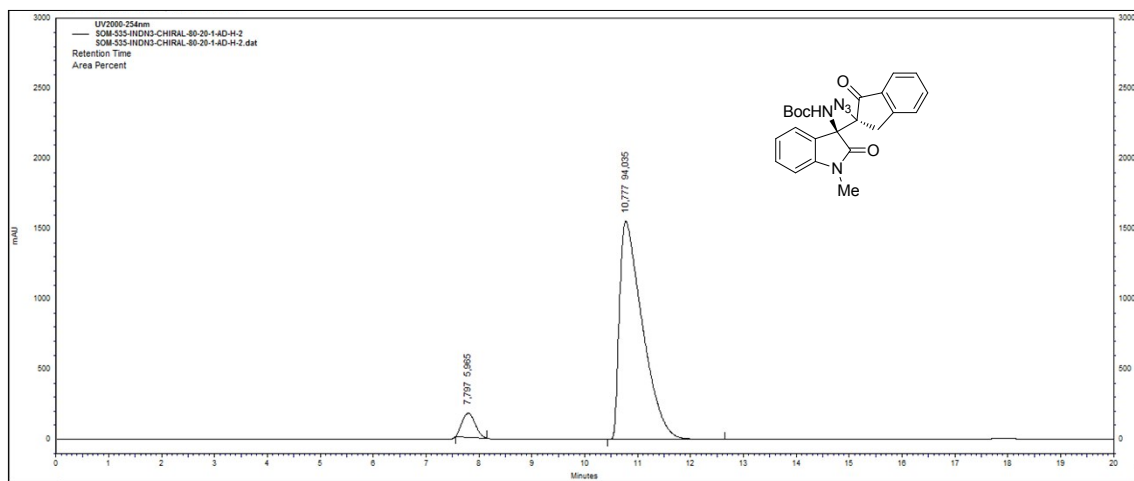
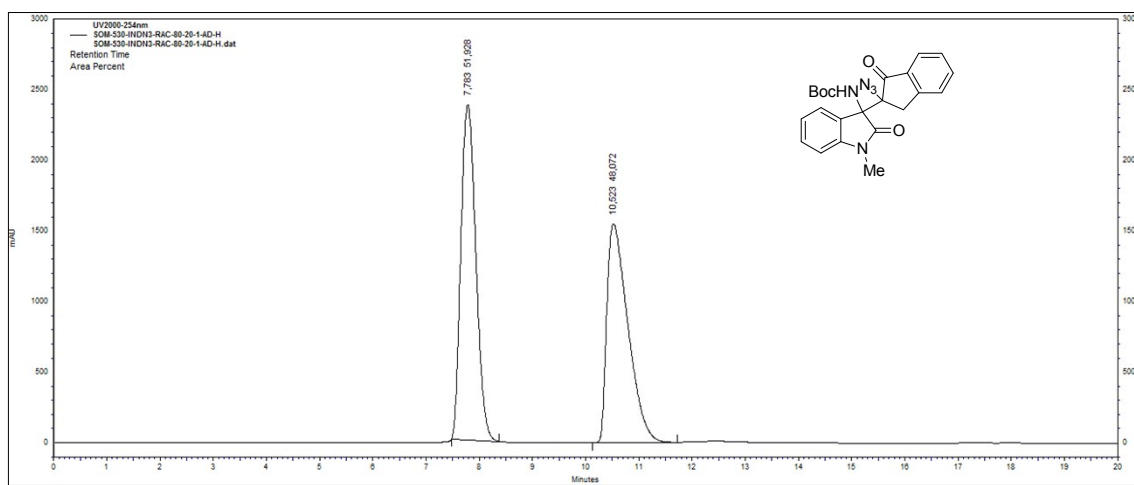
***tert*-Butyl ((*S*)-1-allyl-3-((*S*)-1-azido-2-oxo-2-phenylethyl)-2-oxoindolin-3-yl)carbamate (3c)**



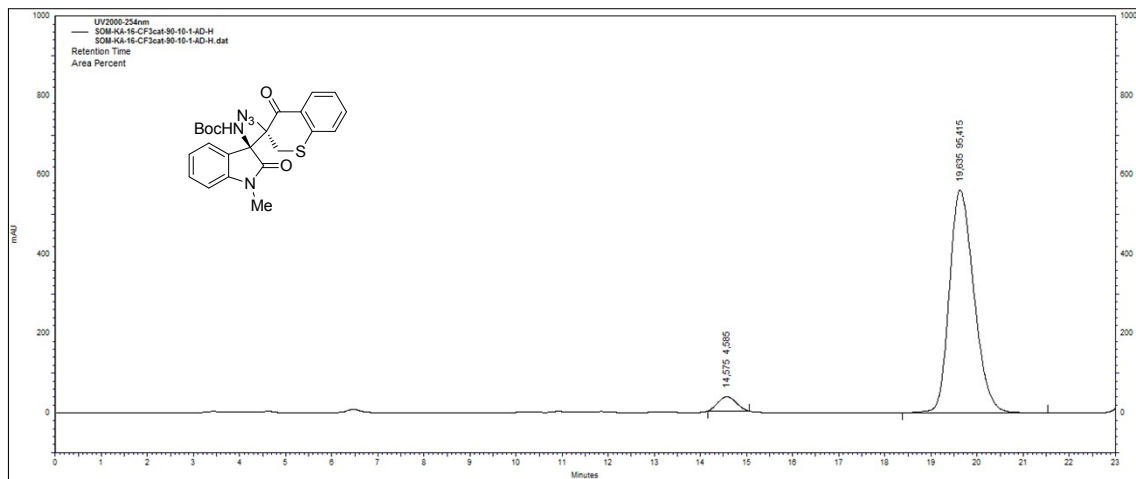
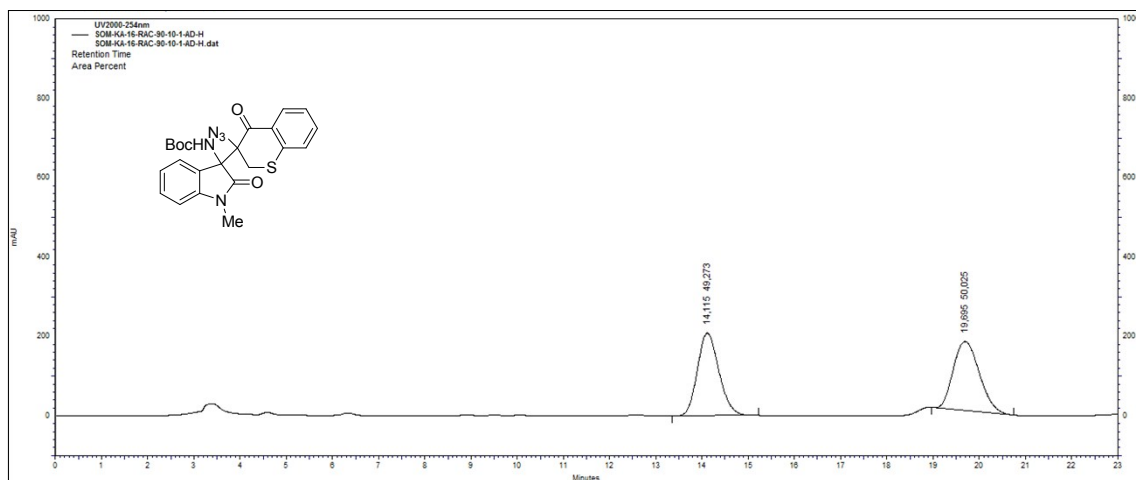
***tert*-Butyl 3-(1-azido-2-oxo-2-phenylethyl)-3-((*tert*-butoxycarbonyl)amino)-2-oxindoline-1-carboxylate (3d)**



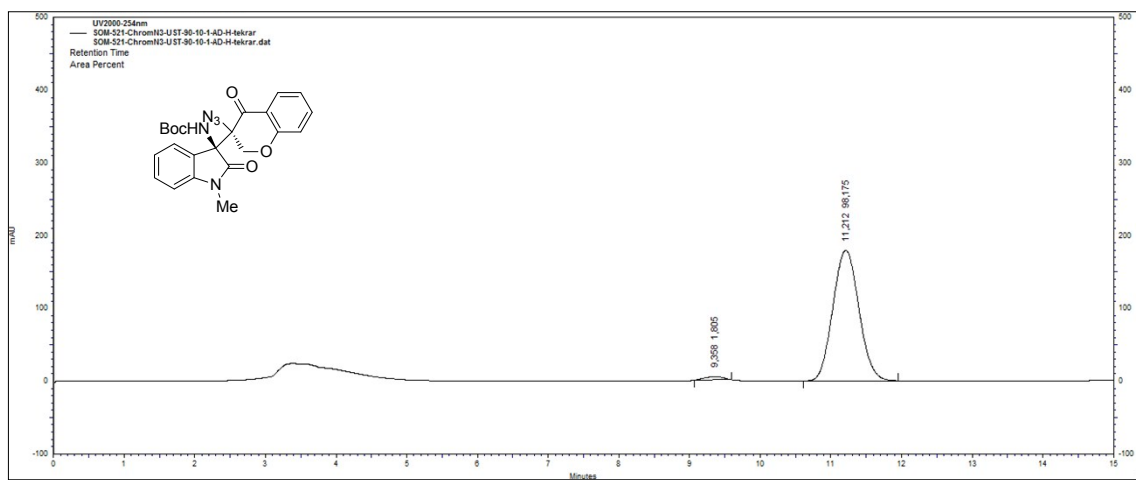
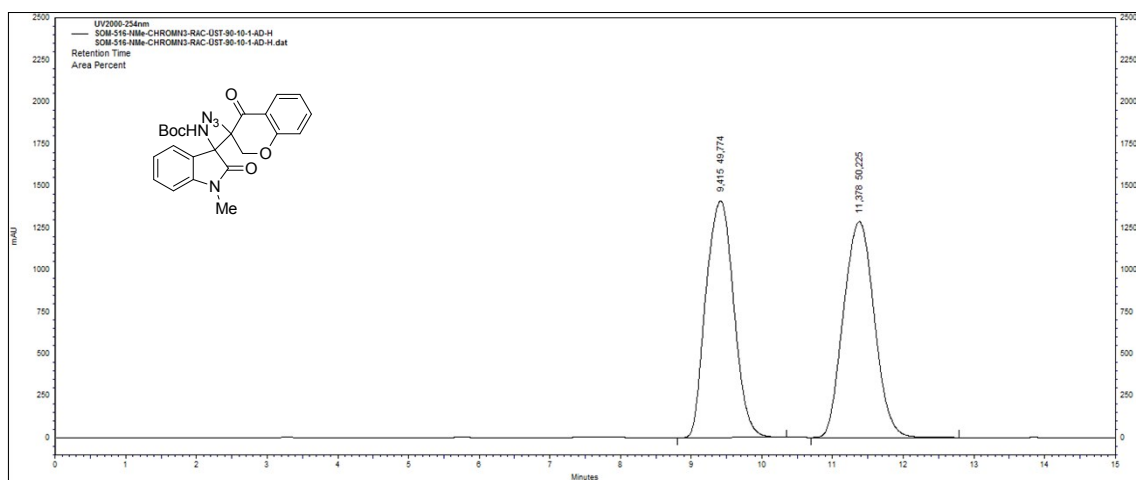
***tert*-Butyl ((*S*)-3-((*R*)-2-azido-1-oxo-2,3-dihydro-1H-inden-2-yl)-1-methyl-2-oxindolin-3-yl)carbamate (3e)**



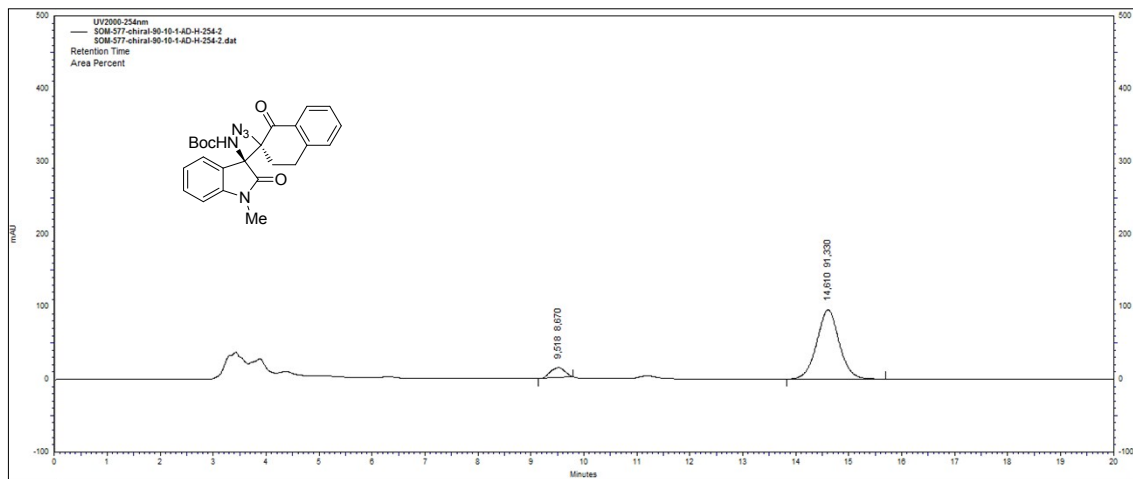
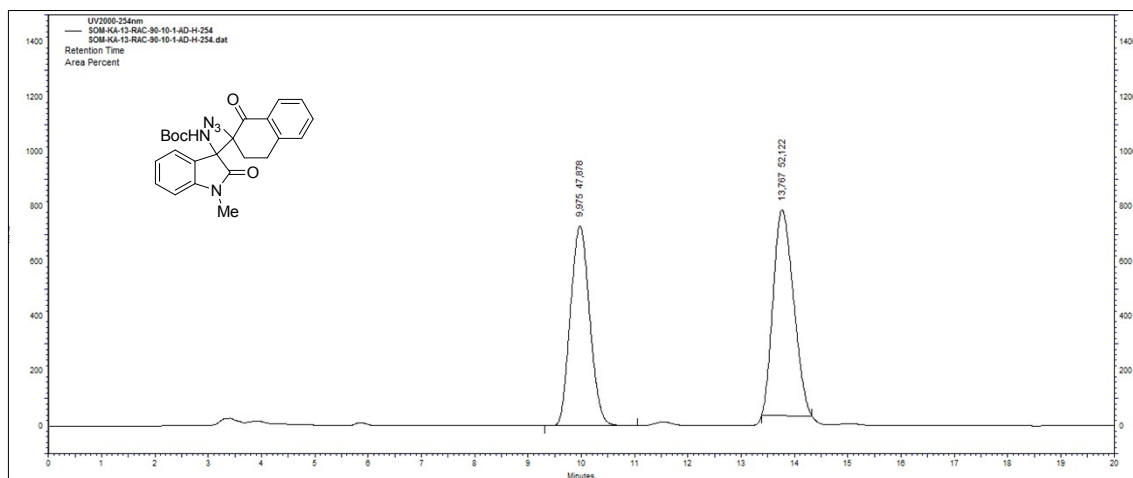
***tert*-Butyl ((*S*)-3-((*R*)-3-azido-4-oxothiochroman-3-yl)-1-methyl-2-oxindolin-3-yl)carbamate (**3f**)**



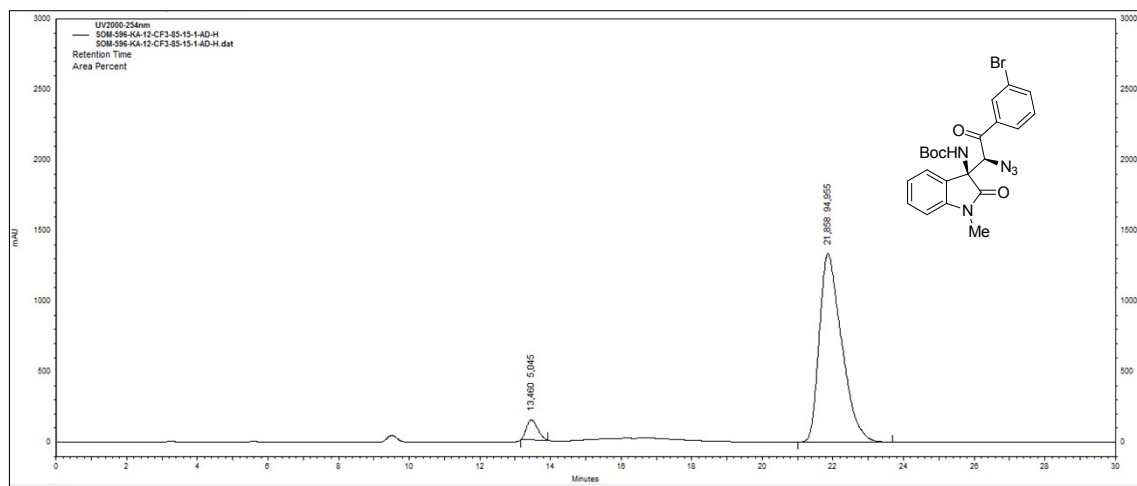
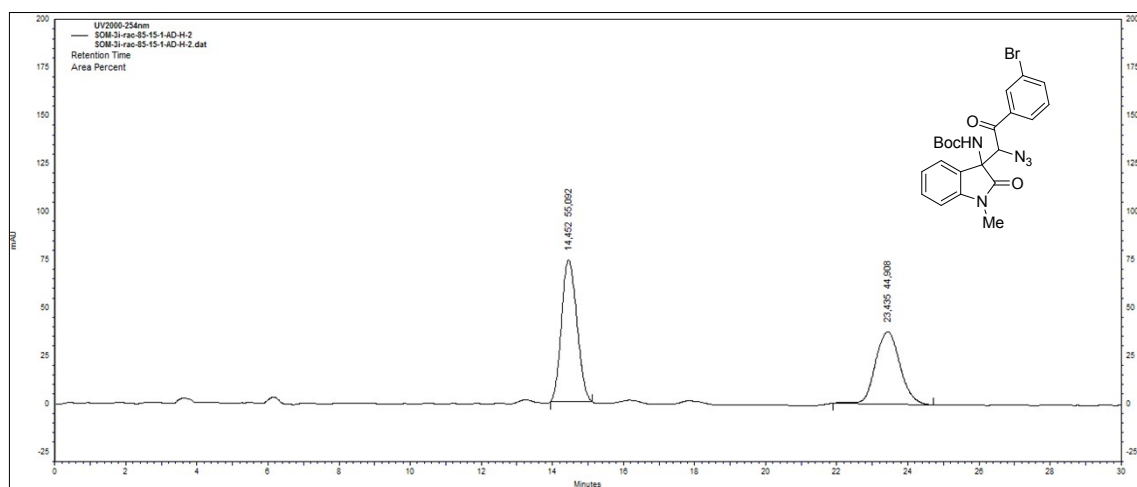
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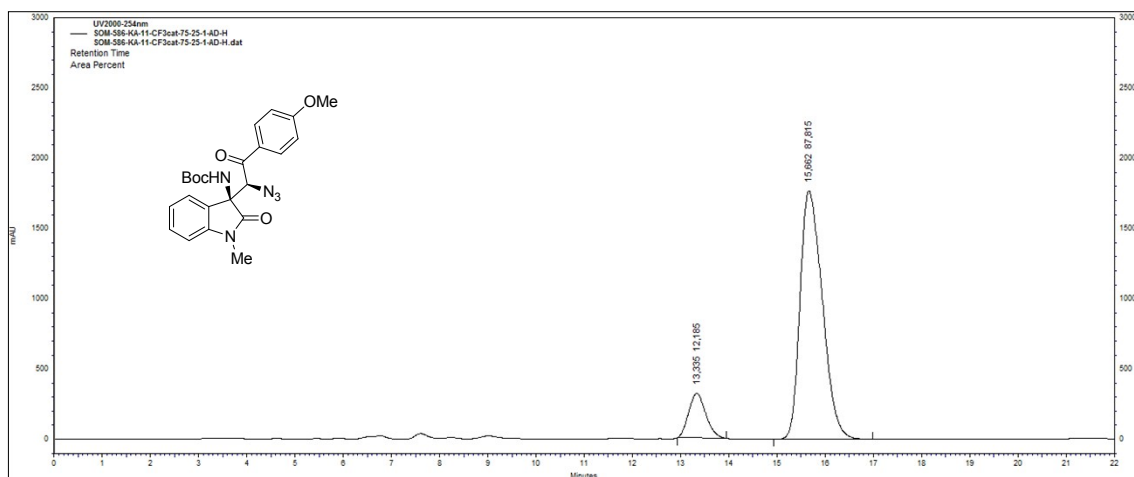
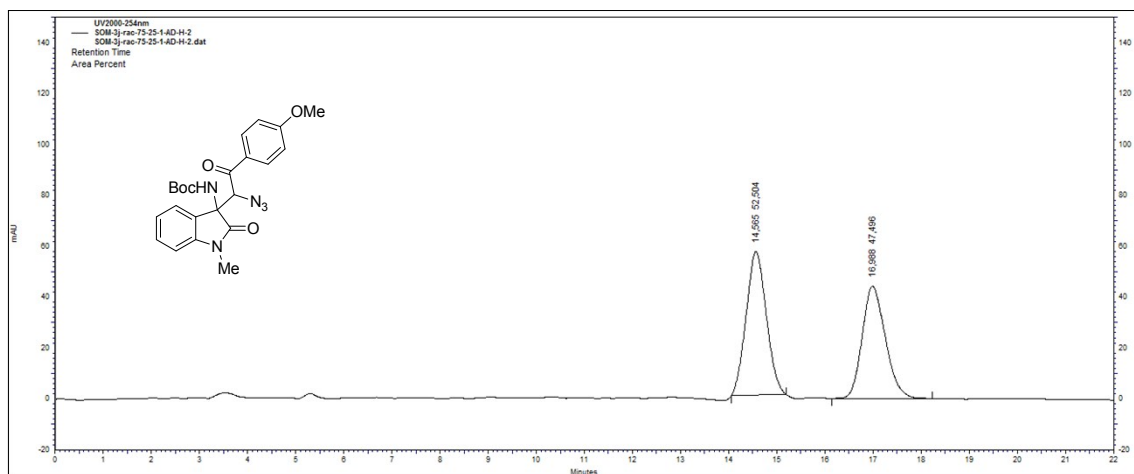
***tert*-Butyl ((*S*)-3-((*R*)-2-azido-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)-1-methyl-2-oxoindolin-3-yl)carbamate (3h)**



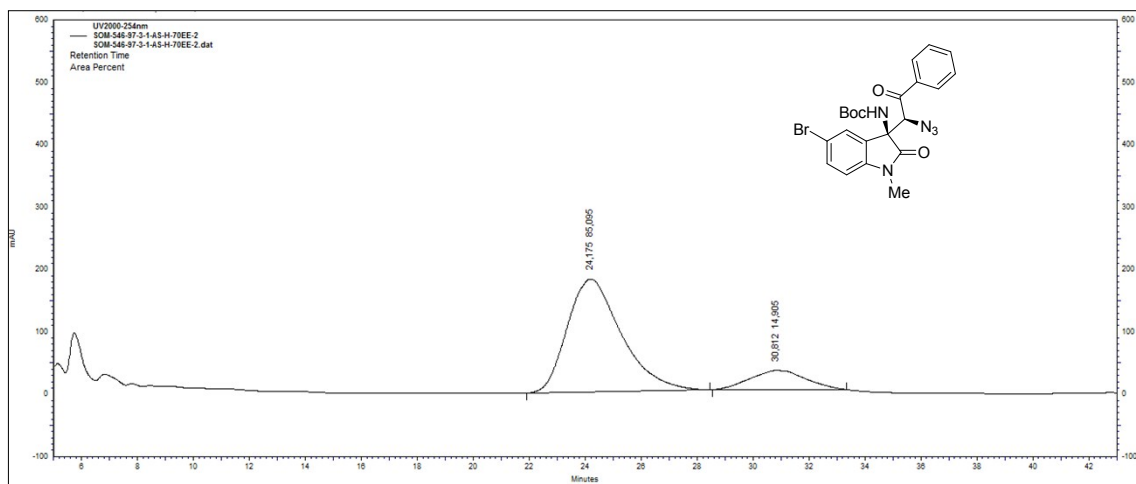
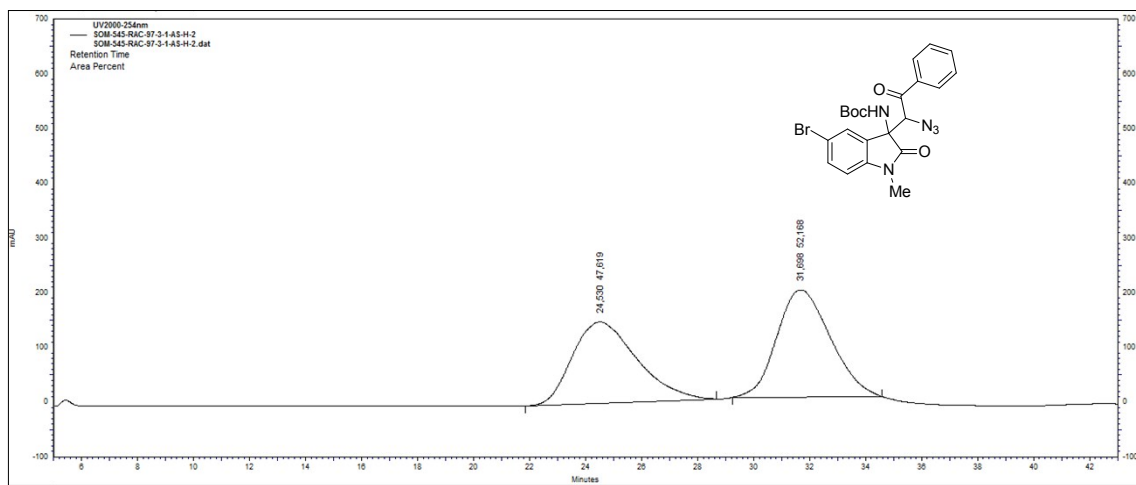
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-(3-bromophenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3i)**



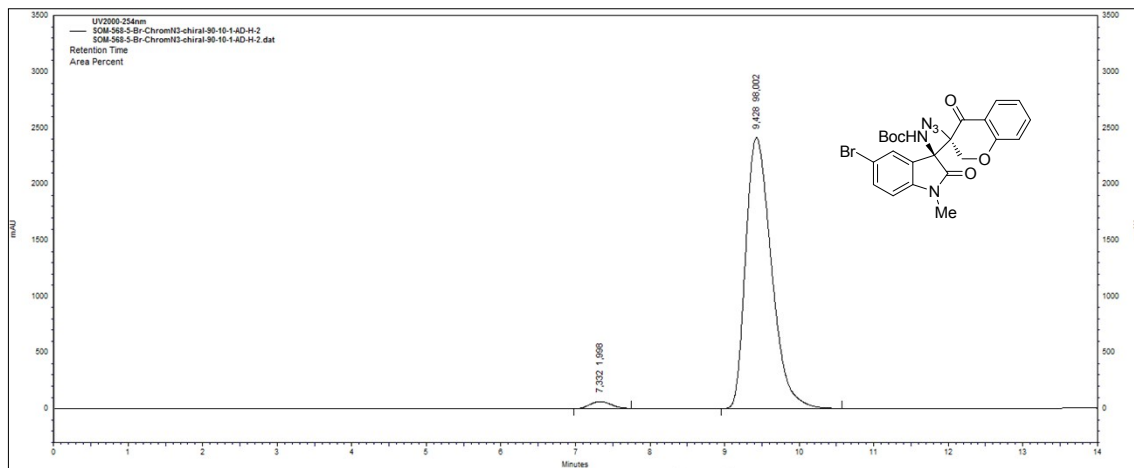
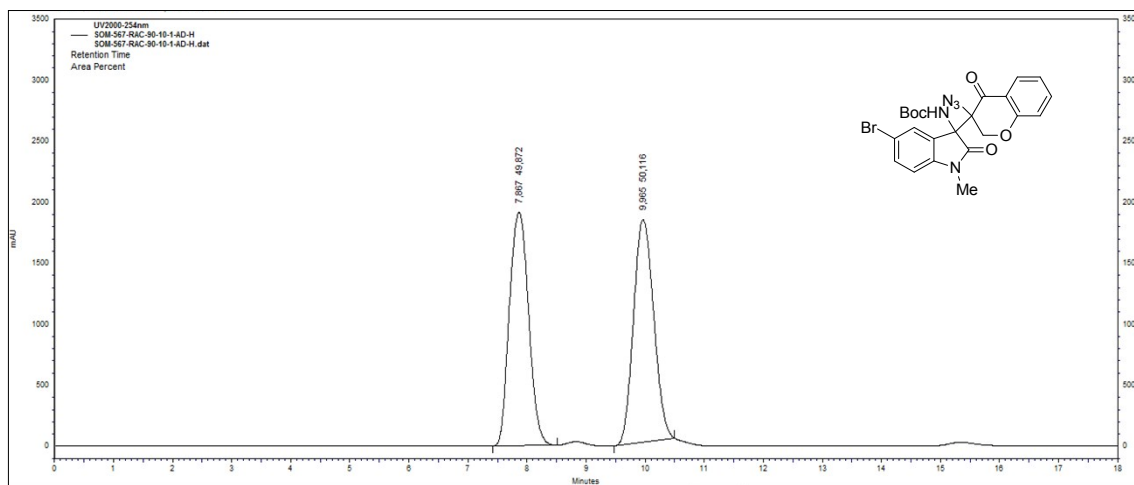
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-(4-methoxyphenyl)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)carbamate (**3j**)**



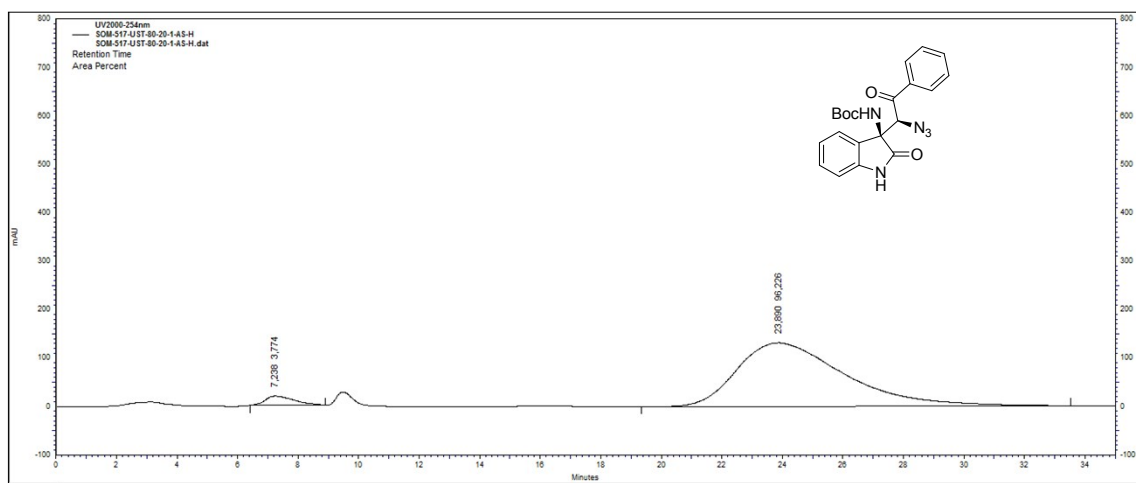
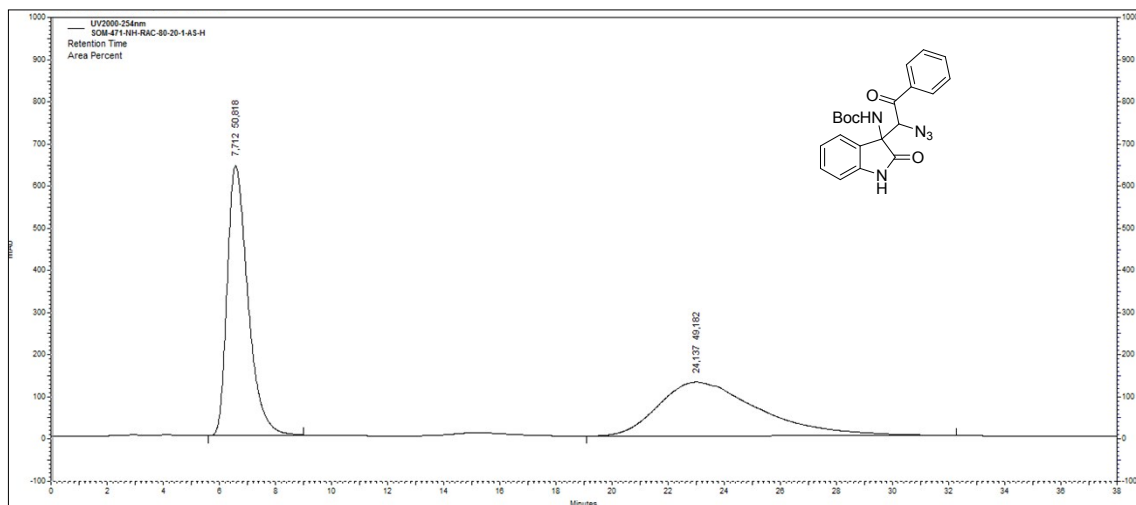
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-oxo-2-phenylethyl)-5-bromo-1-methyl-2-oxoindolin-3-yl)carbamate (3k)**



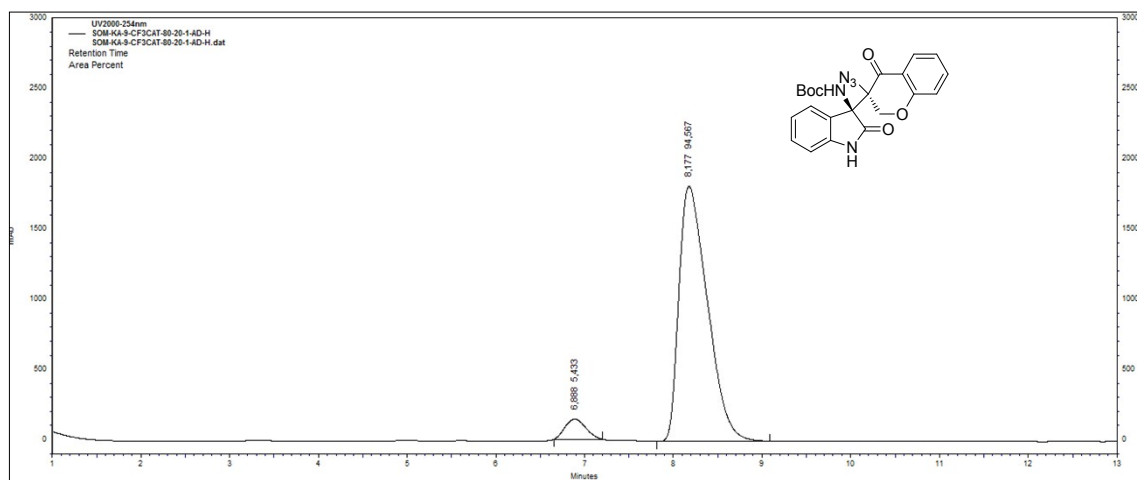
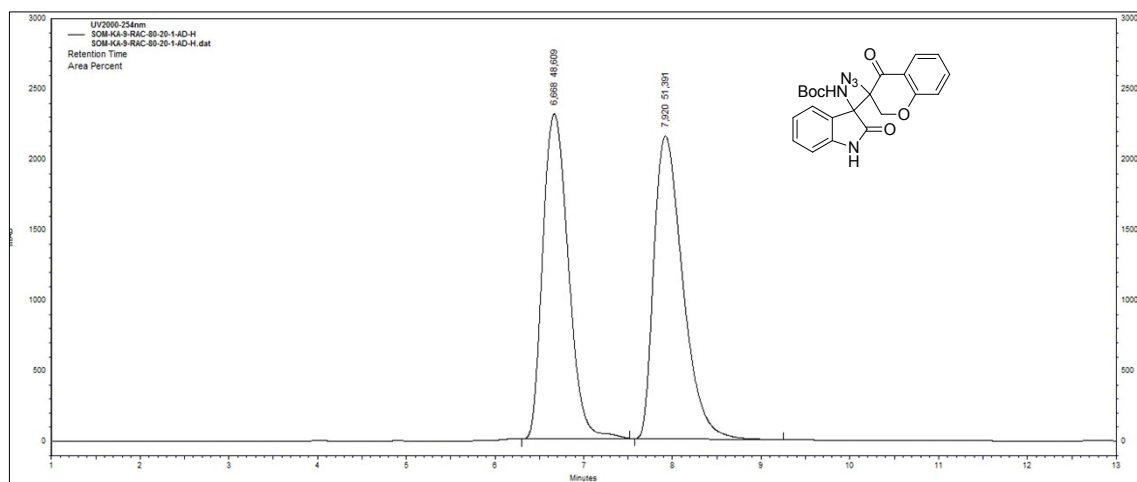
***tert*-Butyl ((*S*)-3-((*S*)-3-azido-4-oxochroman-3-yl)-5-bromo-1-methyl-2-oxoindolin-3-yl)carbamate (3I)**



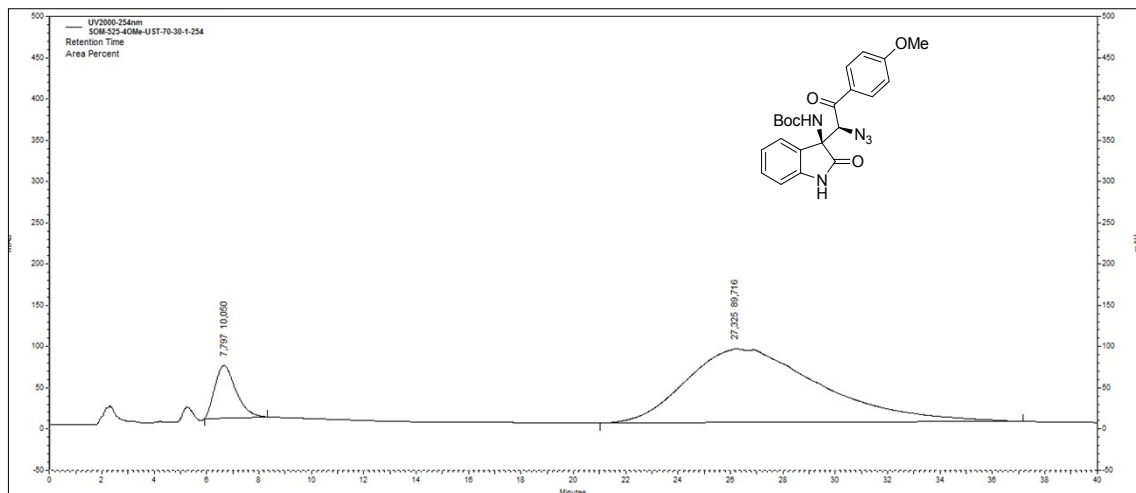
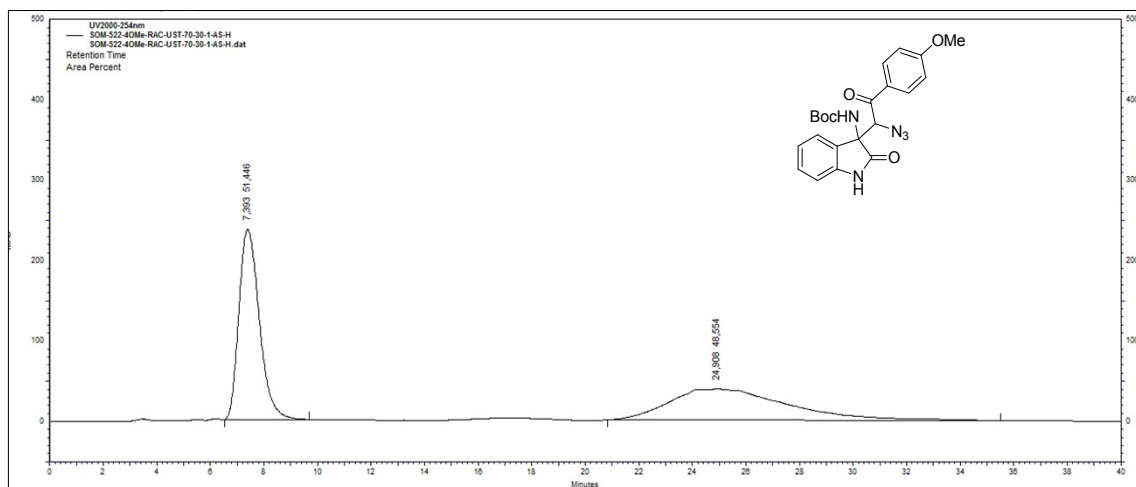
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-oxo-2-phenylethyl)-2-oxoindolin-3-yl)carbamate (3m)**



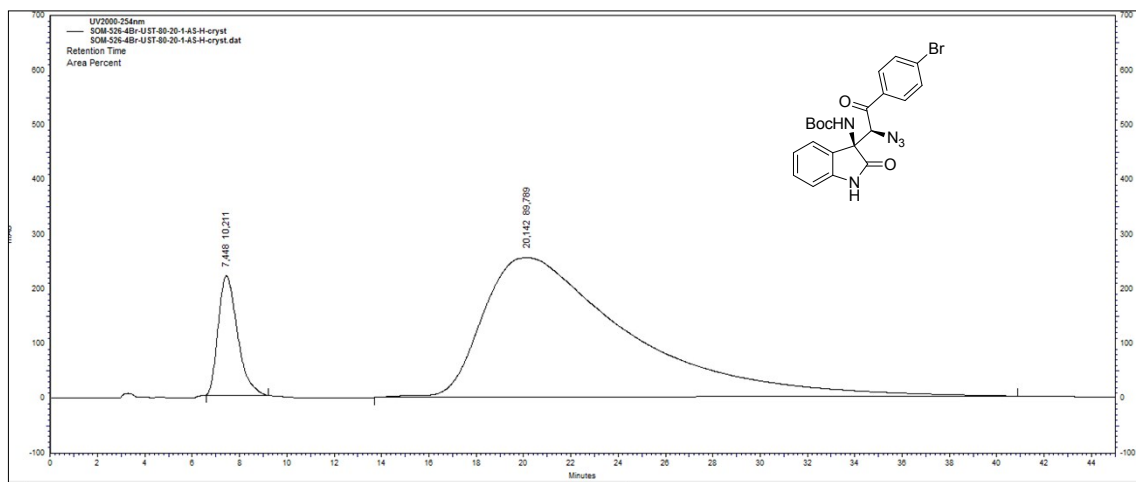
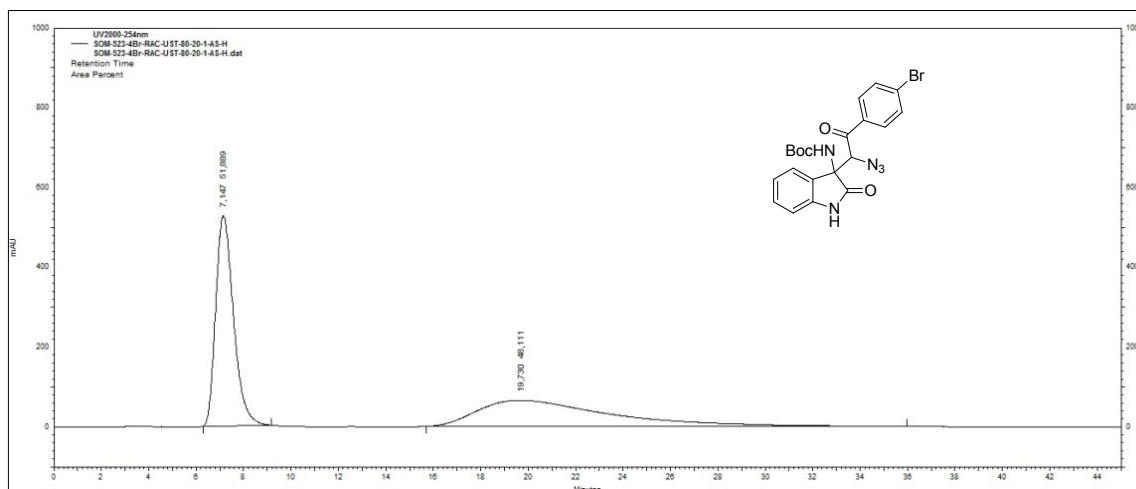
***tert*-Butyl ((*S*)-3-((*S*)-3-azido-4-oxochroman-3-yl)-2-oxoindolin-3-yl)carbamate (**3n**)**



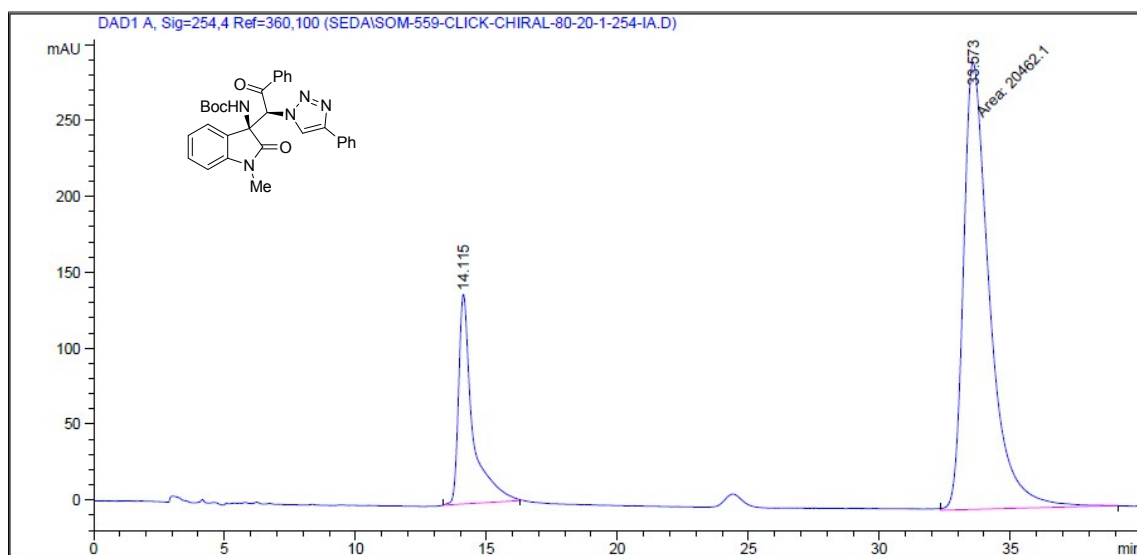
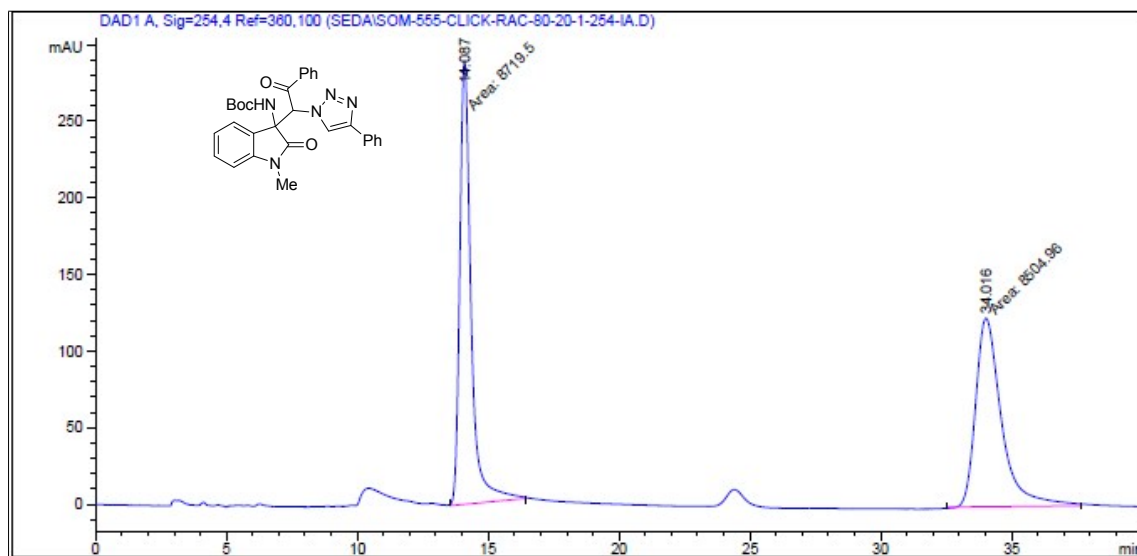
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-(4-methoxyphenyl)-2-oxoethyl)-2-oxoindolin-3-yl)carbamate (3o)**



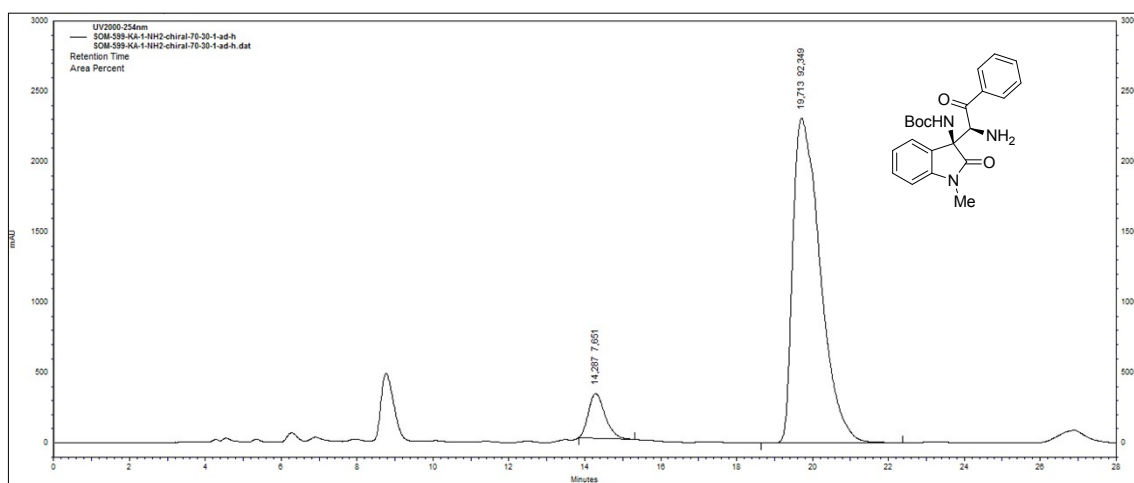
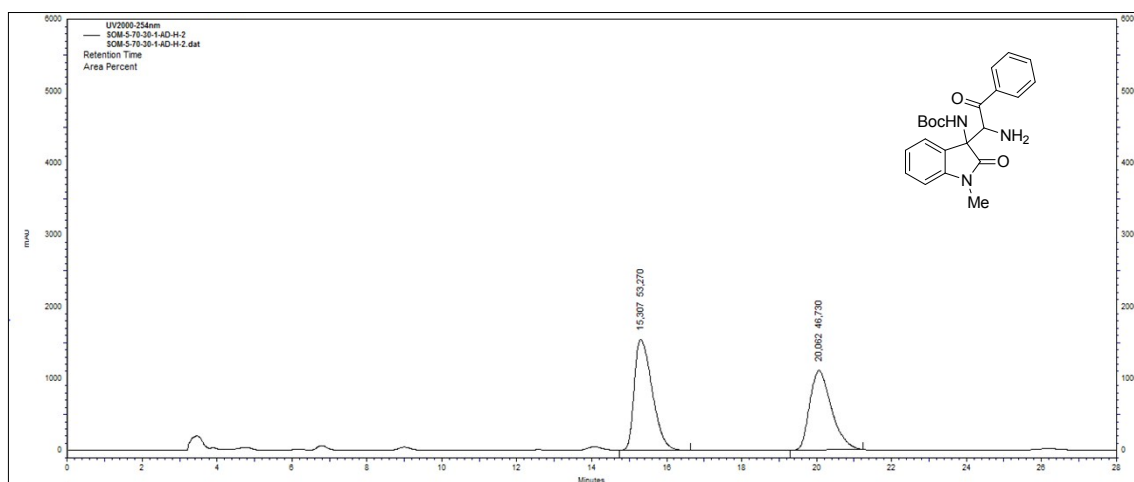
***tert*-Butyl ((*S*)-3-((*S*)-1-azido-2-(4-bromophenyl)-2-oxoethyl)-2-oxoindolin-3-yl)carbamate
(3p)**



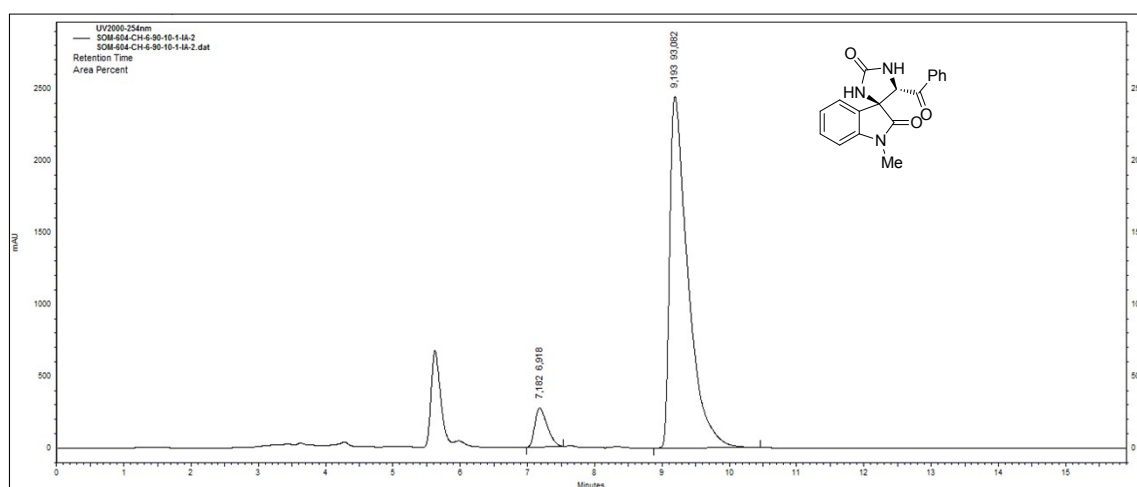
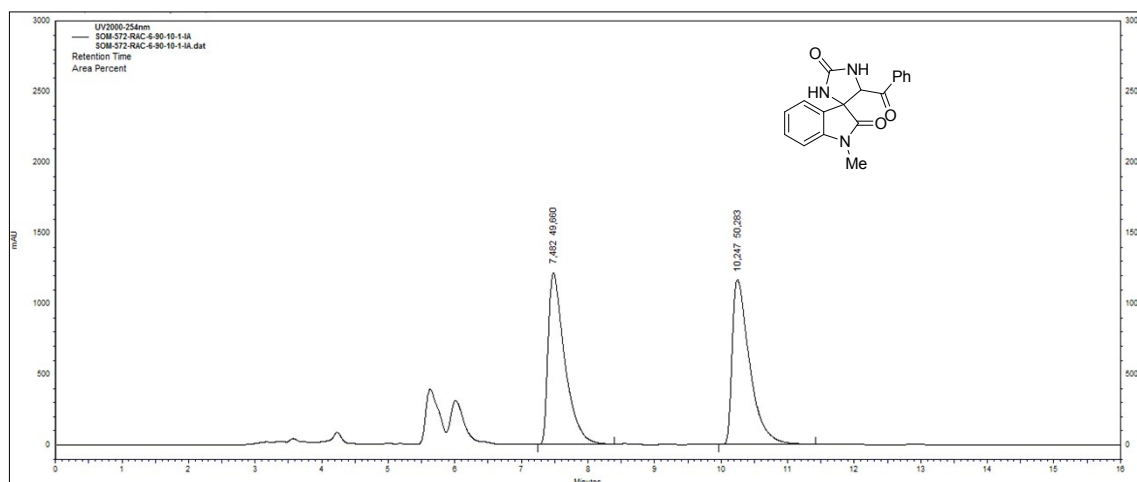
***tert*-Butyl ((*S*)-1-methyl-2-oxo-3-((*S*)-2-oxo-2-phenyl-1-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethyl)indolin-3-yl)carbamate (**4**)**



***tert*-Butyl ((*S*)-3-((*S*)-1-amino-2-oxo-2-phenylethyl)-1-methyl-2-oxoindolin-3-yl)carbamate**
(5)



(3'S,5S)-5-Benzoyl-1'-methylspiro[imidazolidine-4,3'-indoline]-2,2'-dione (6)



3. X-Ray Crystallographic Data for 3g

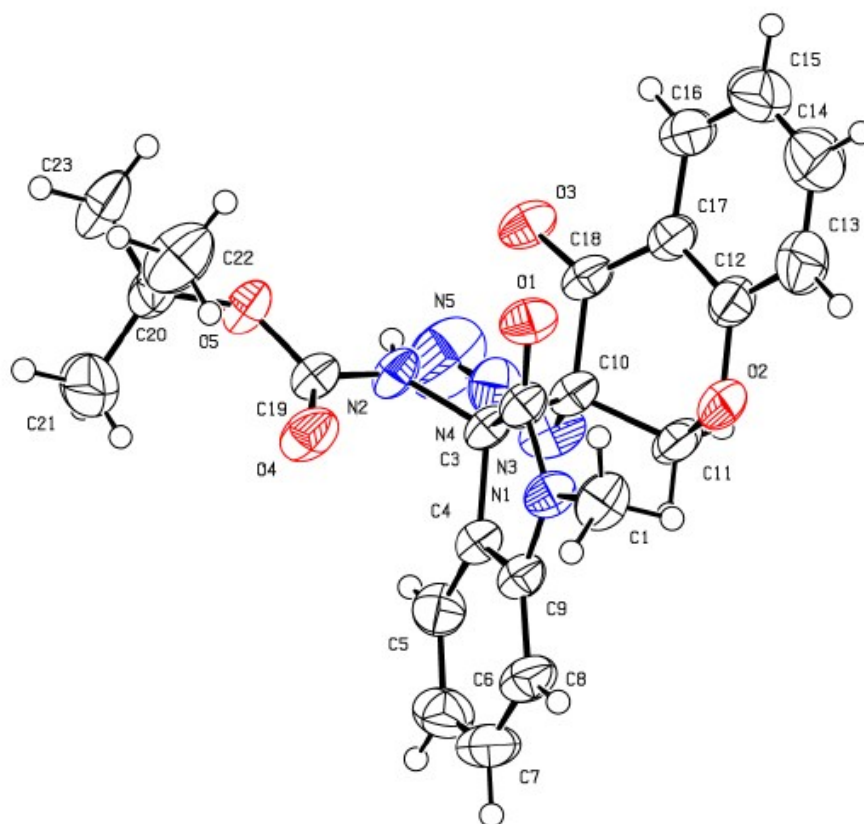


Figure 1. ORTEP plot for the X-ray structure of compound **3g**.

CCDC 1919849

Bond precision:	C-C = 0.0023 Å	Wavelength=	0.71075
Cell:	a=10.2450(2)	b=10.9607(2)	c=11.1338(7)
	alpha=74.014(5)	beta=74.695(5)	gamma=72.702(5)
Temperature:	295 K		
	Calculated	Reported	
Volume	1124.73(9)	1124.73(9)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C ₂₃ H ₂₃ N ₅ O ₅	C ₂₃ H ₂₃ N ₅ O ₅	
Sum formula	C ₂₃ H ₂₃ N ₅ O ₅	C ₂₃ H ₂₃ N ₅ O ₅	
Mr	449.46	449.47	
D _x , g cm ⁻³	1.327	1.327	

Z	2	2	
Mu (mm-1)	0.096	0.096	
F000	472.0	472.2	
F000'	472.22		
h,k,lmax	13,14,14	13,14,14	
Nref	5570	5552	
Tmin,Tmax	0.917,0.949		
Tmin'	0.917		
Correction method=	Not given		
Data completeness=	0.997	Theta(max)=	28.260
R(reflections)=	0.0588(4872)	wR2(reflections)=	0.1599(5552)
S =	1.070	Npar=	302