

New Journal of Chemistry

Electronic Supplementary Information

From benzofuro-, benzothieno- and 10-methylindolo- [2,3-*b*]-fused benzothiopyrano[4,3,2-*de*]quinolines to the corresponding benzothiopyrano[4,3,2-*de*]1,8-naphthyridines: Synthesis and properties of these hexacyclic heteroaromatic compounds

Nicolas Mast,^a William Erb,^{a,*} Lionel Nauton,^b Pascale Moreau,^{b,*} Olivier Mongin,^a Thierry Roisnel,^a Margaux Macaigne,^c Thomas Robert,^{c,d} Stéphane Bach,^{c,d,e} Laurent Picot,^f Valérie Thiéry,^f Jean-Pierre Hurvois,^a and Florence Mongin^{a,*}

^a *Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France. E-mail: william.erb@univ-rennes1.fr, florence.mongin@univ-rennes1.fr*

^b *Université Clermont Auvergne, CNRS, Clermont Auvergne INP, ICCF, F-63000 Clermont-Ferrand, France. E-mail: pascale.moreau@uca.fr*

^c *Sorbonne Université, CNRS, FR2424, Plateforme de criblage KISSf (Kinase Inhibitor Specialized Screening facility), Station Biologique de Roscoff, Place Georges Tessier, 29680 Roscoff, France*

^d *Sorbonne Université, CNRS, UMR8227, Integrative Biology of Marine Models Laboratory (LBI2M), Station Biologique de Roscoff, 29680 Roscoff, France*

^e *Centre of Excellence for Pharmaceutical Sciences, North-West University, Private Bag X6001, Potchefstroom 2520, South Africa*

^f *La Rochelle Université, Laboratoire Littoral Environnement et Sociétés, UMRi CNRS 7266, Université de La Rochelle, 17042 La Rochelle, France*

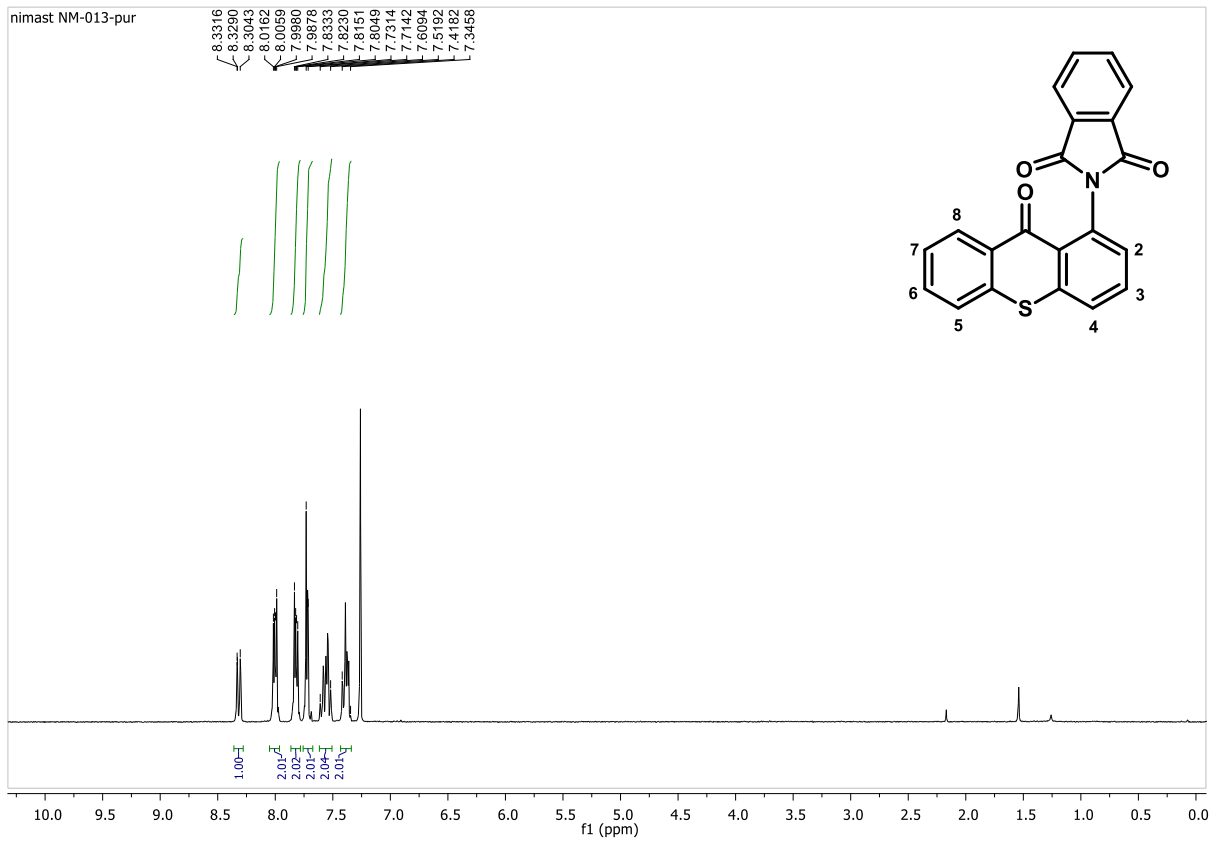
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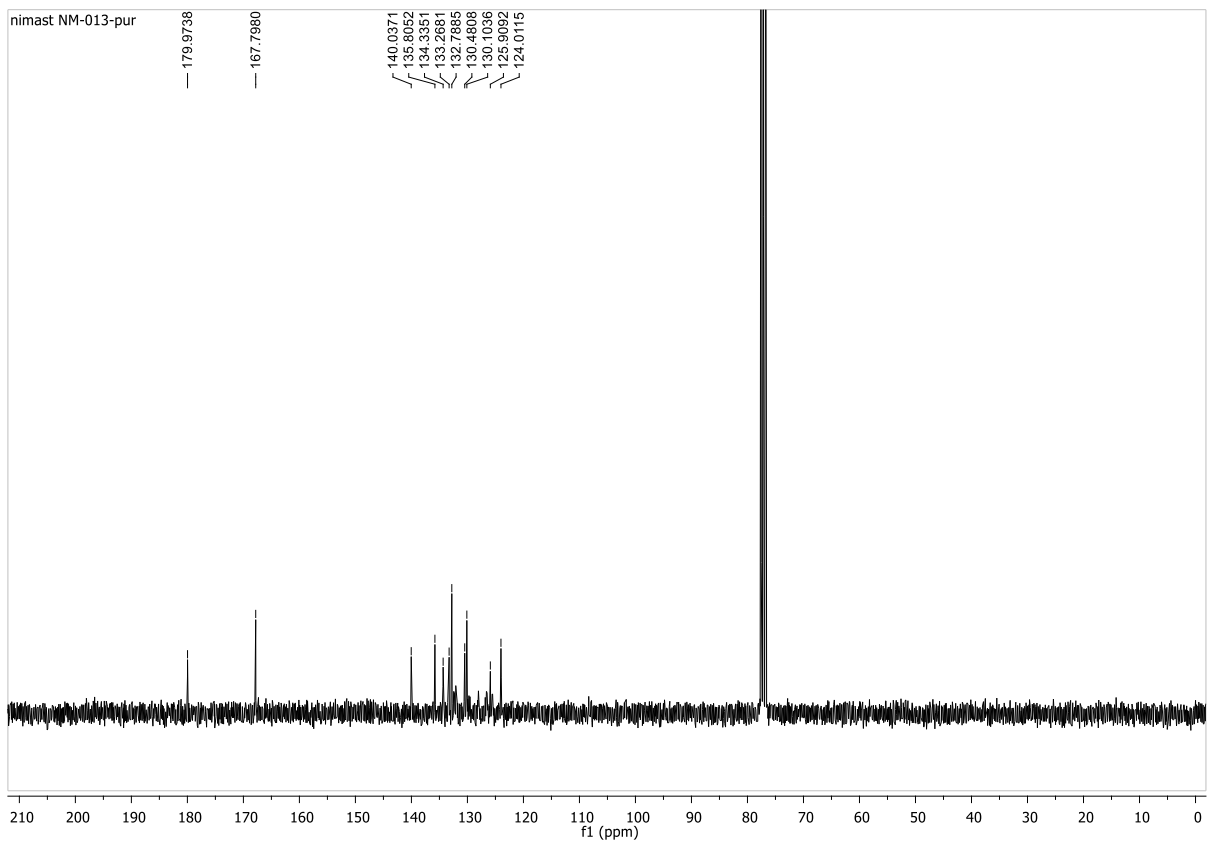
NMR spectra

1-(*N*-Phthalimido)thioxanthone (3)

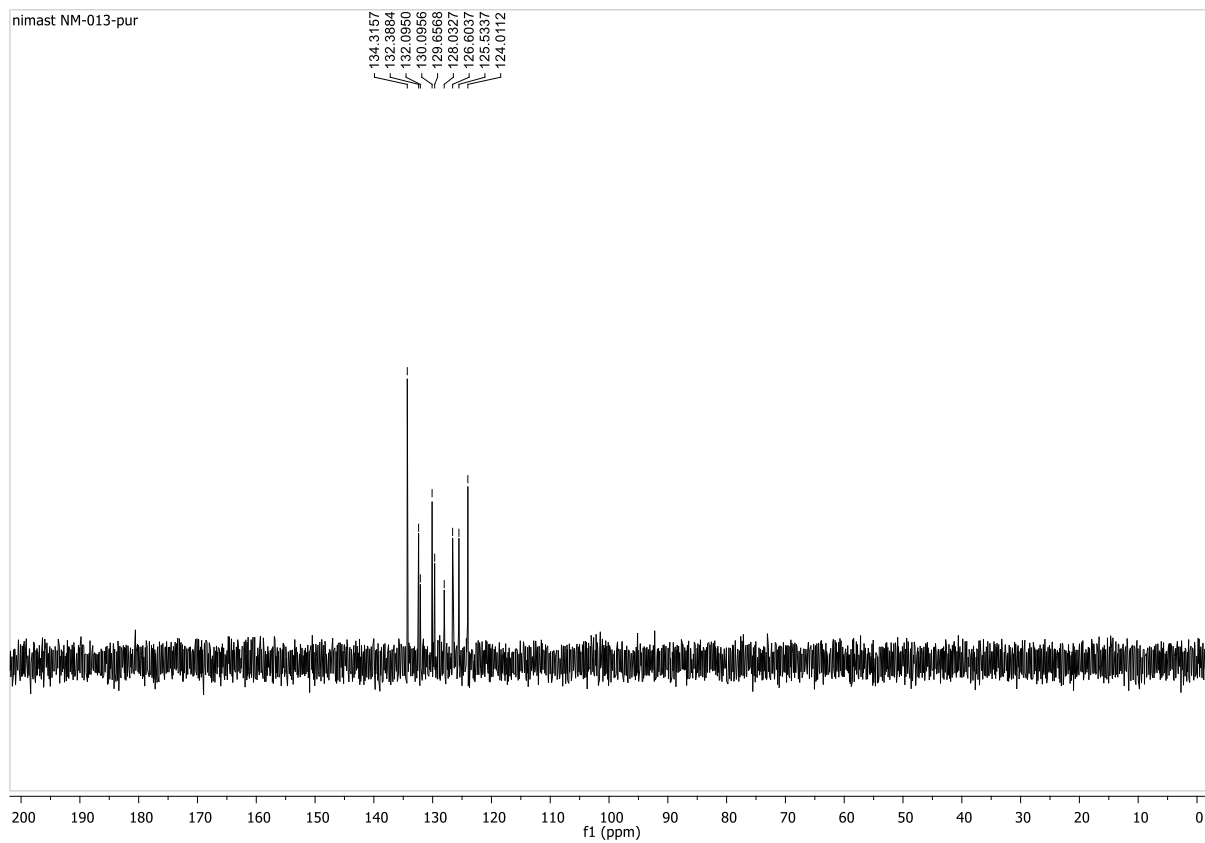
^1H (CDCl_3 , 300 K, 300 MHz)



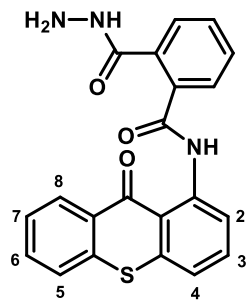
^{13}C (CDCl_3 , 300 K, 75 MHz)



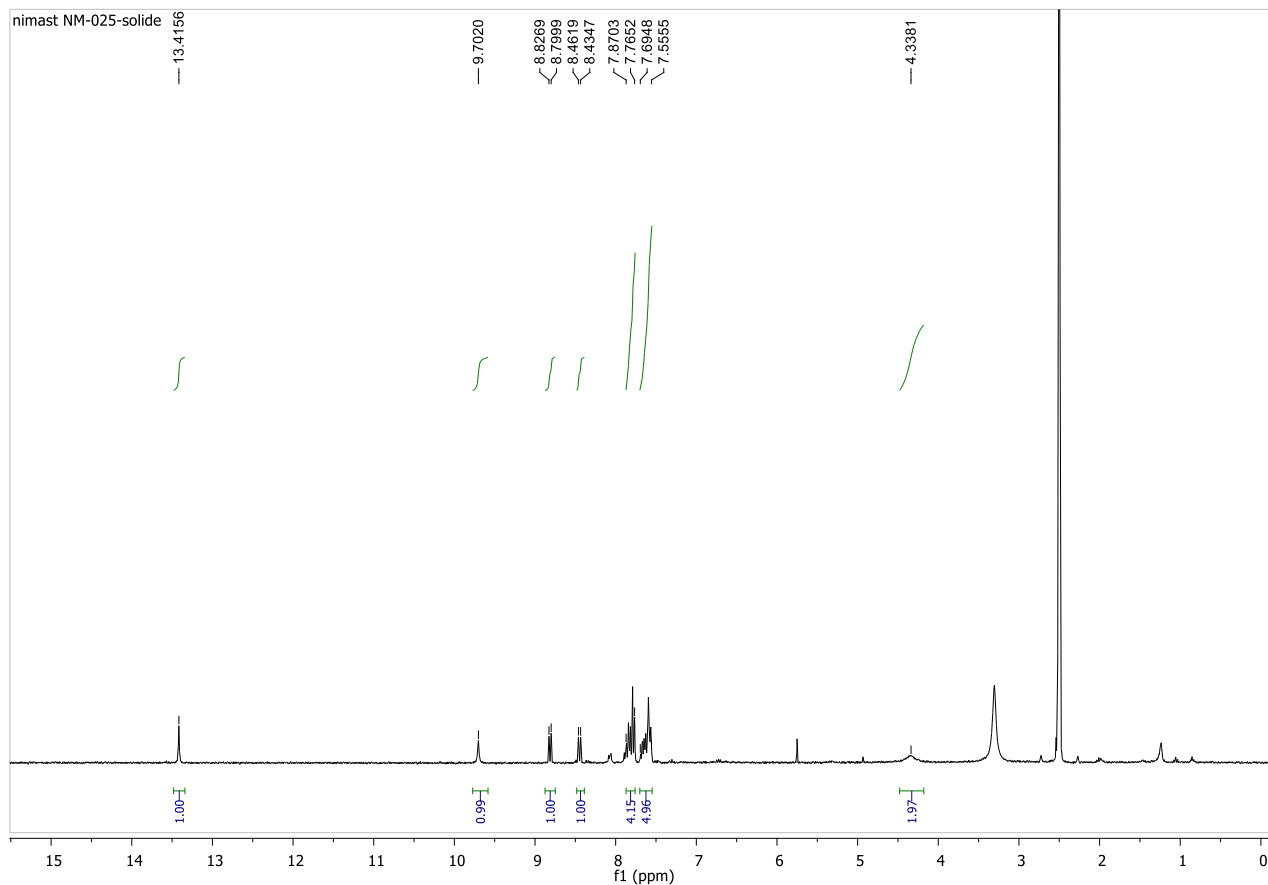
DEPT135 (CDCl₃, 300 K, 75 MHz)



1-(2-(Hydrazinocarbonyl)phenylcarbonylamino)thioxanthone (4)

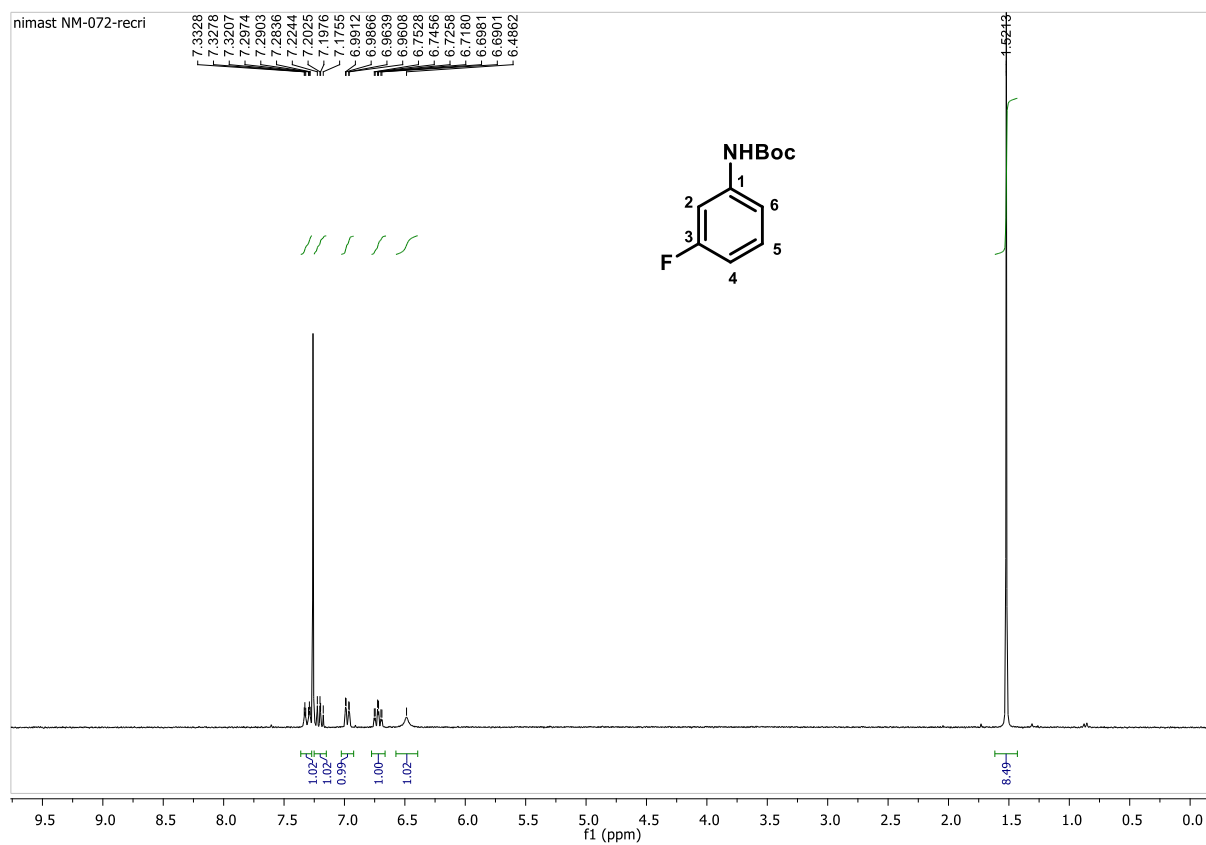


^1H ((CD_3) $_2\text{SO}$, 300 K, 300 MHz)

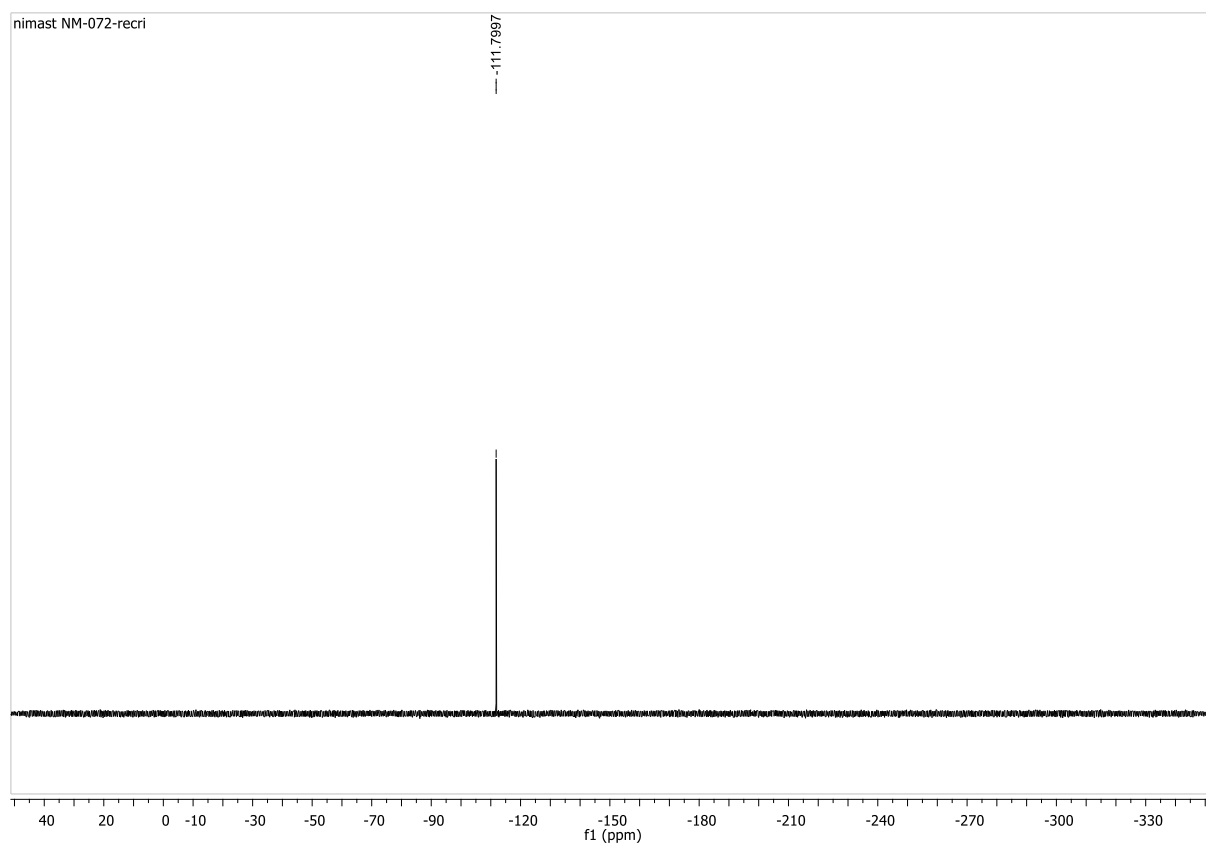


***tert*-Butyl *N*-(3-fluorophenyl)carbamate (5)**

^1H (CDCl_3 , 300 K, 300 MHz)

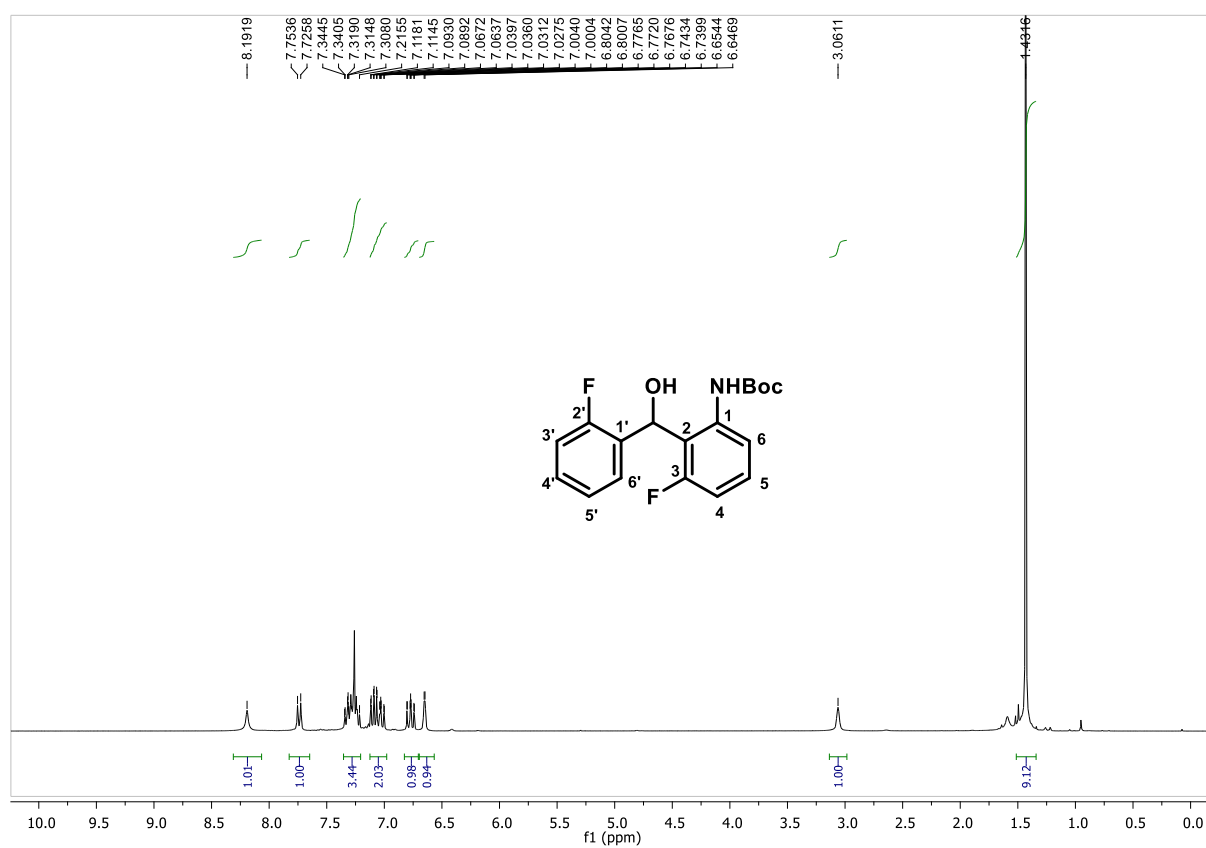


^{19}F (CDCl_3 , 300 K, 282 MHz)

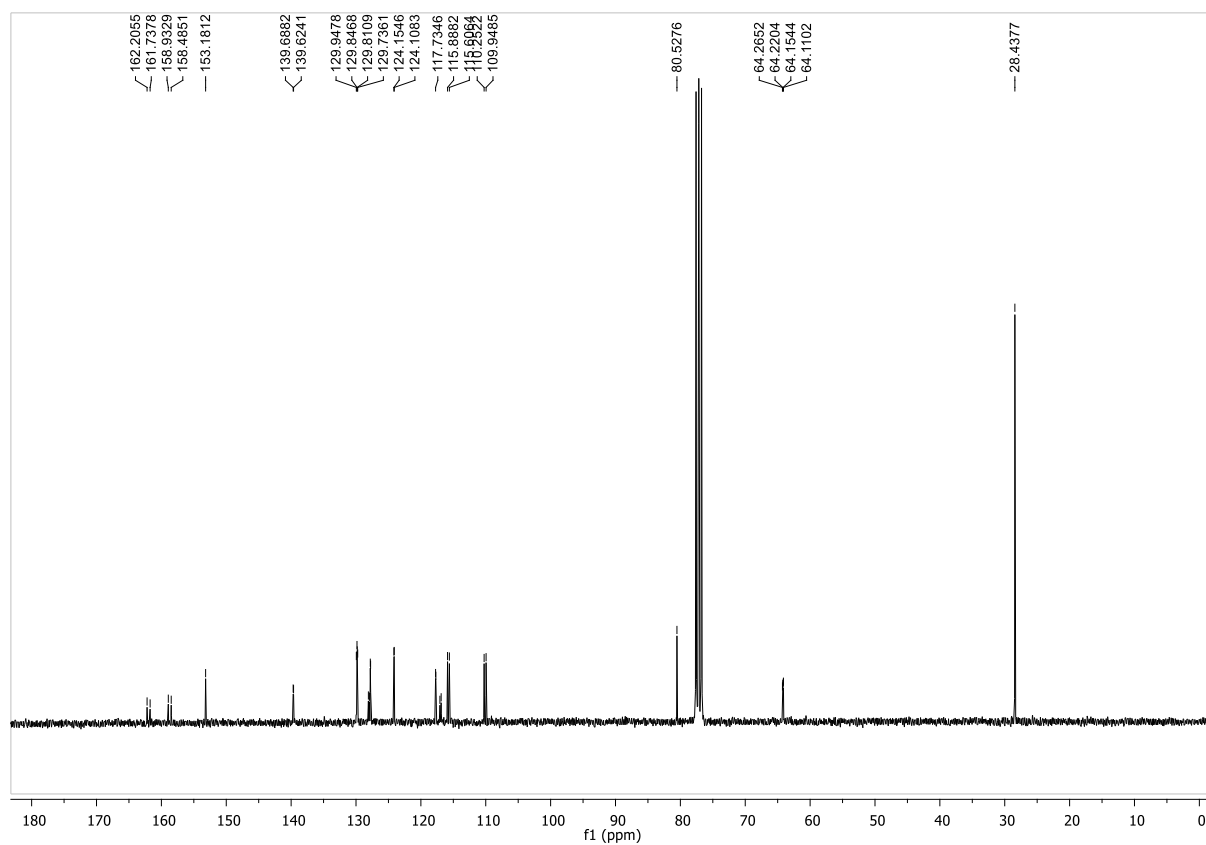


***tert*-Butyl *N*-(3-fluoro-2-((1-(2-fluorophenyl)hydroxymethyl)phenyl)carbamate (6a)**

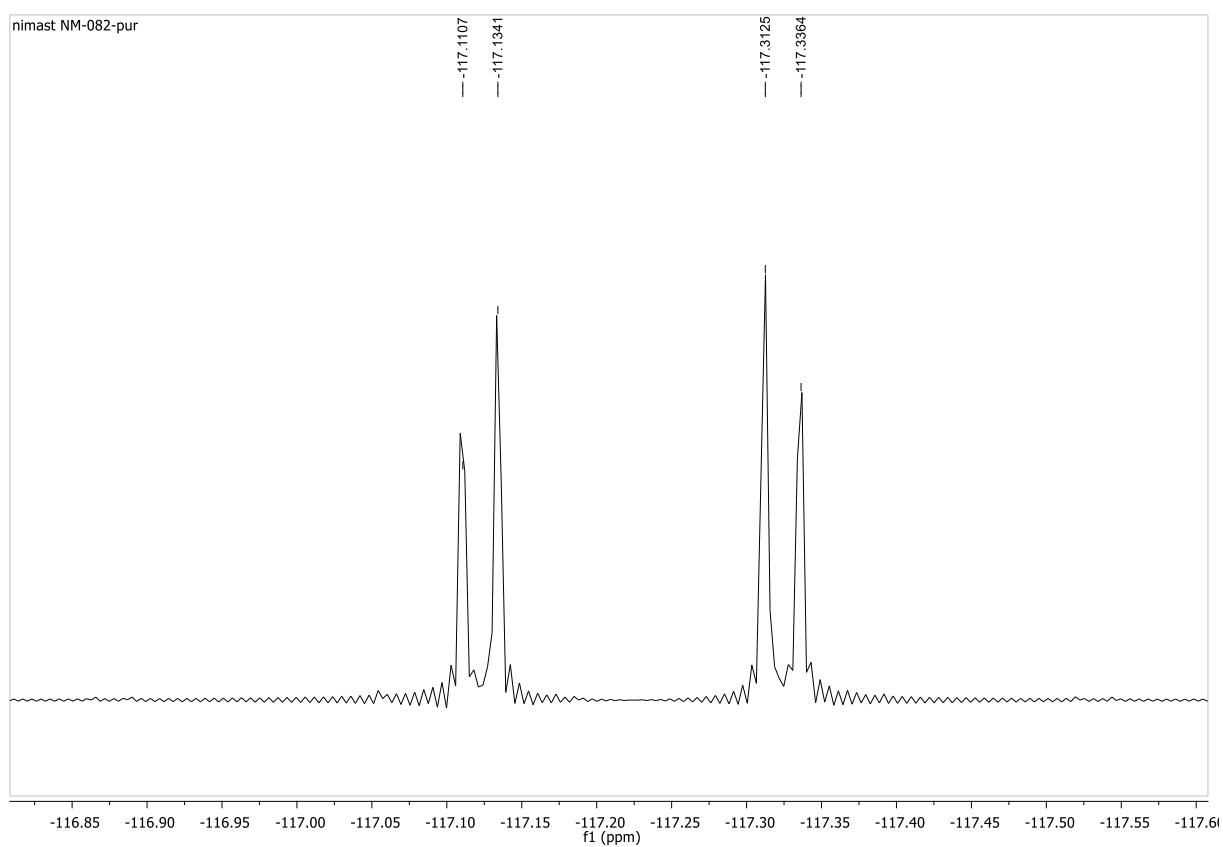
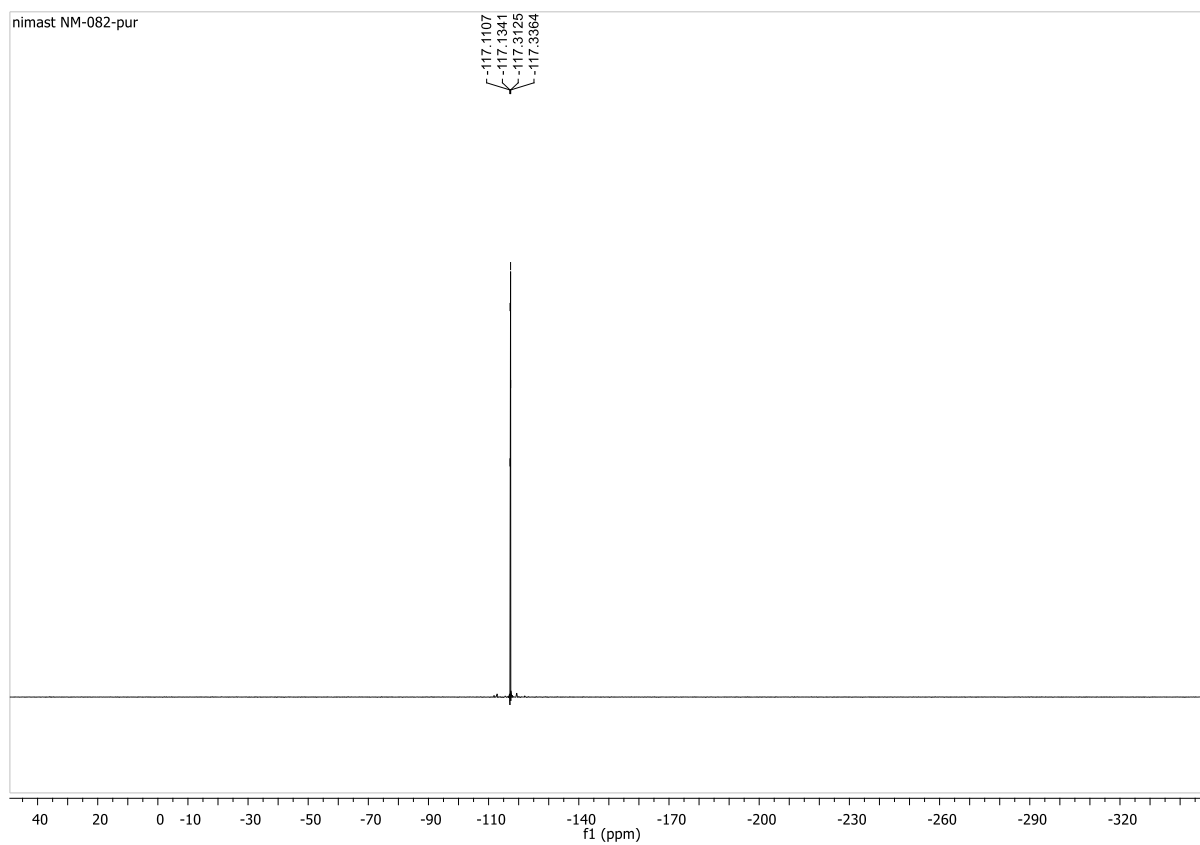
^1H (CDCl_3 , 300 K, 300 MHz)



^{13}C (CDCl_3 , 300 K, 75 MHz)

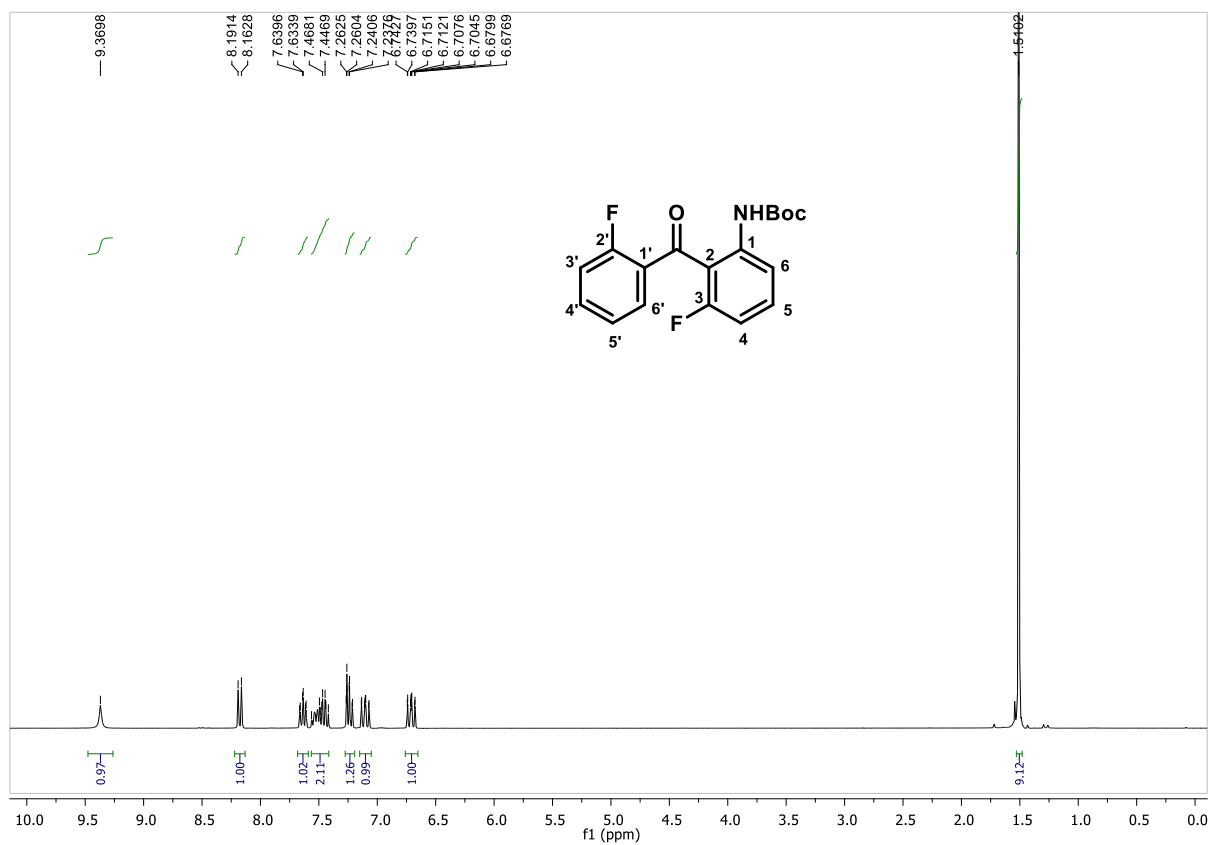


^{19}F (CDCl_3 , 300 K, 471 MHz)

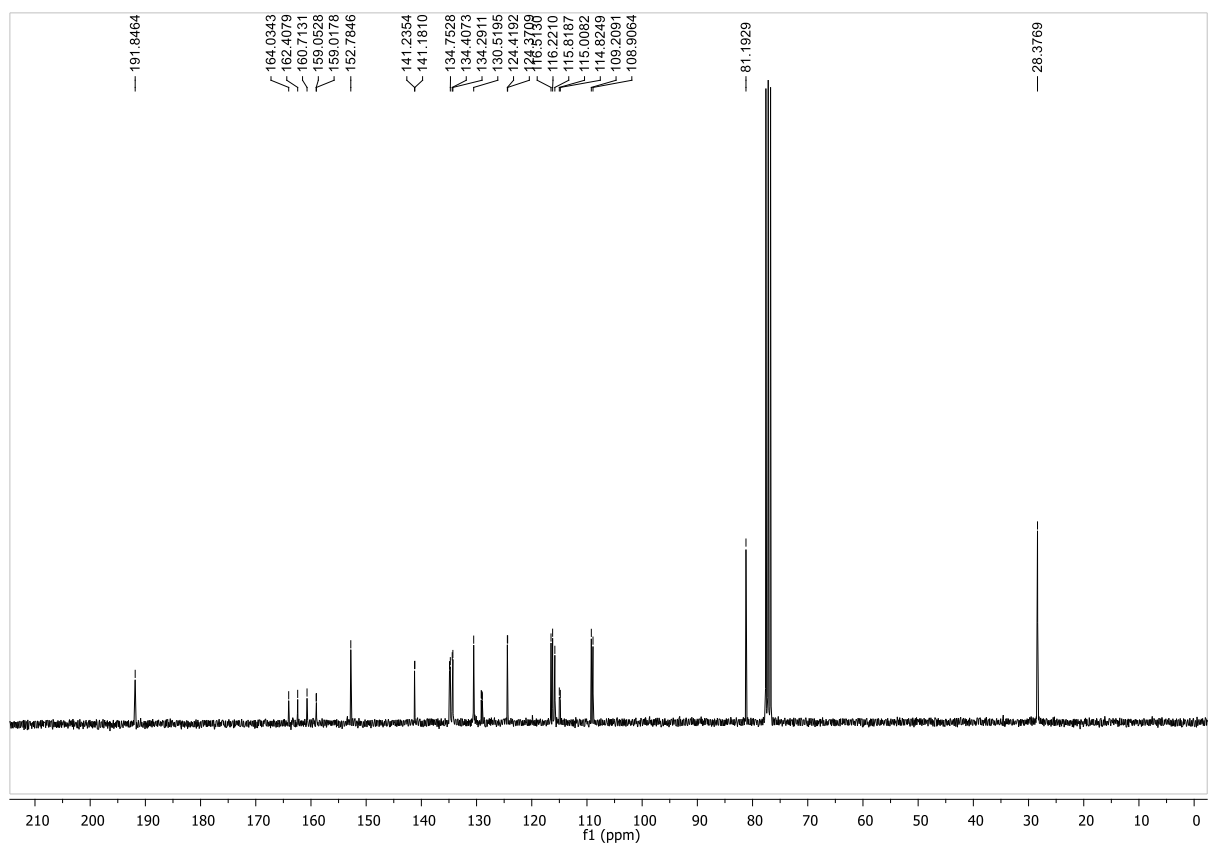


***tert*-Butyl *N*-(3-fluoro-2-(2-fluorobenzoyl)phenyl)carbamate (7)**

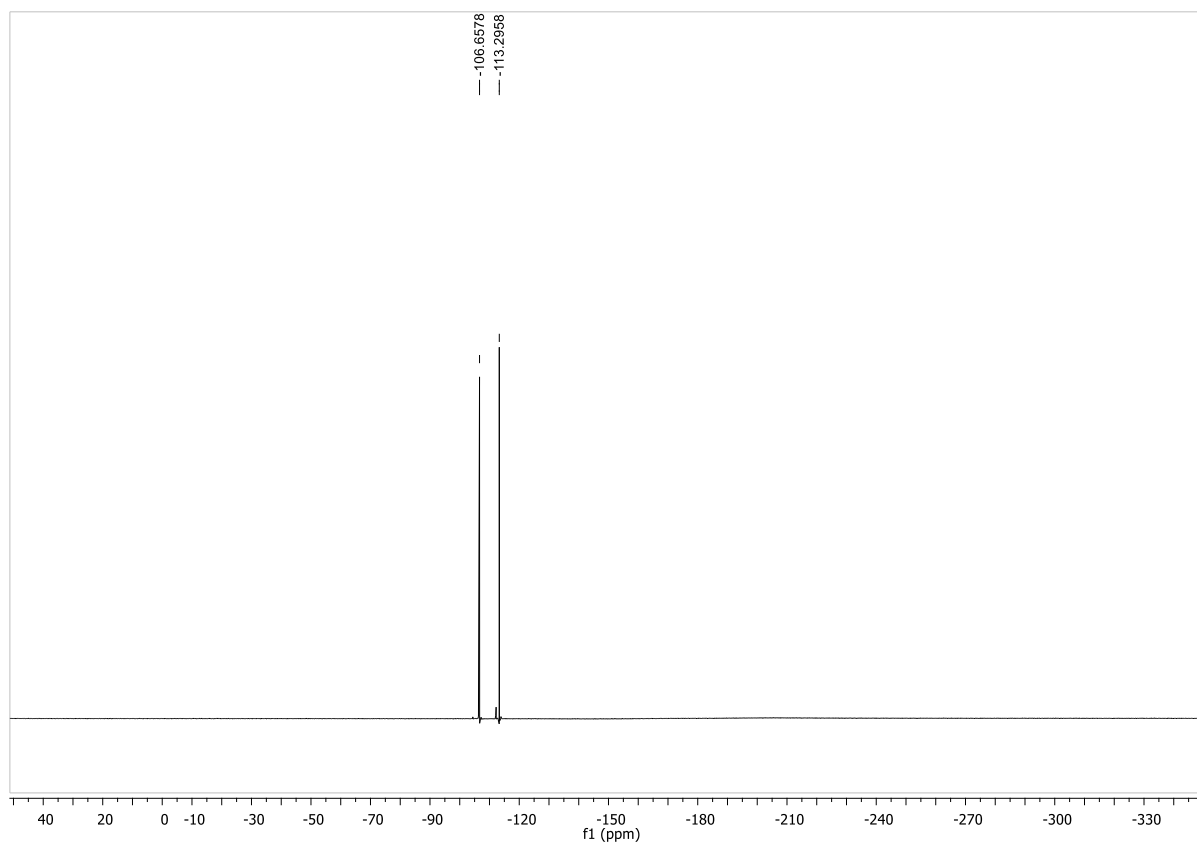
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^{13}C (CDCl_3 , 300 K, 75 MHz)

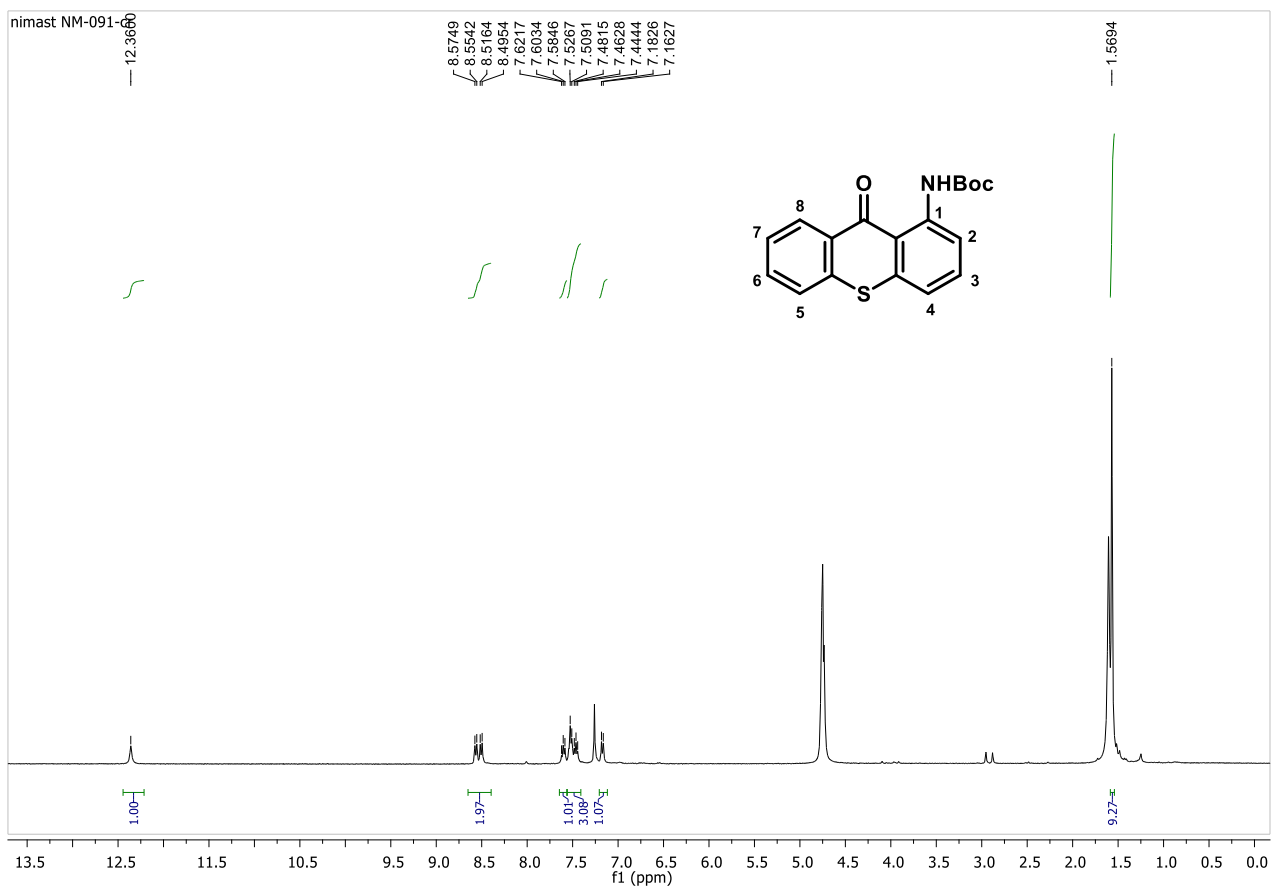


^{19}F (CDCl_3 , 300 K, 282 MHz)



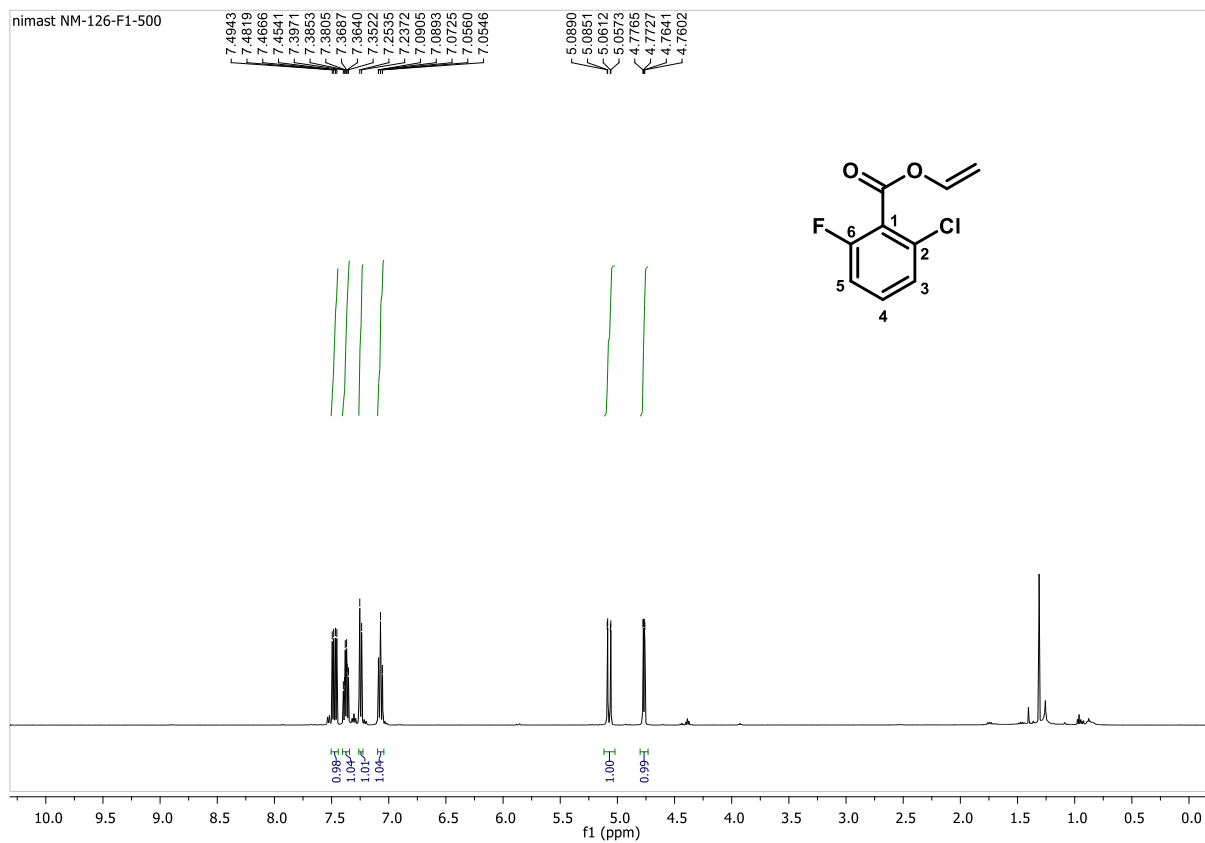
1-(*tert*-Butoxycarbonylamino)thioxanthone (**8**; crude)

^1H (CDCl₃, 300 K, 300 MHz)

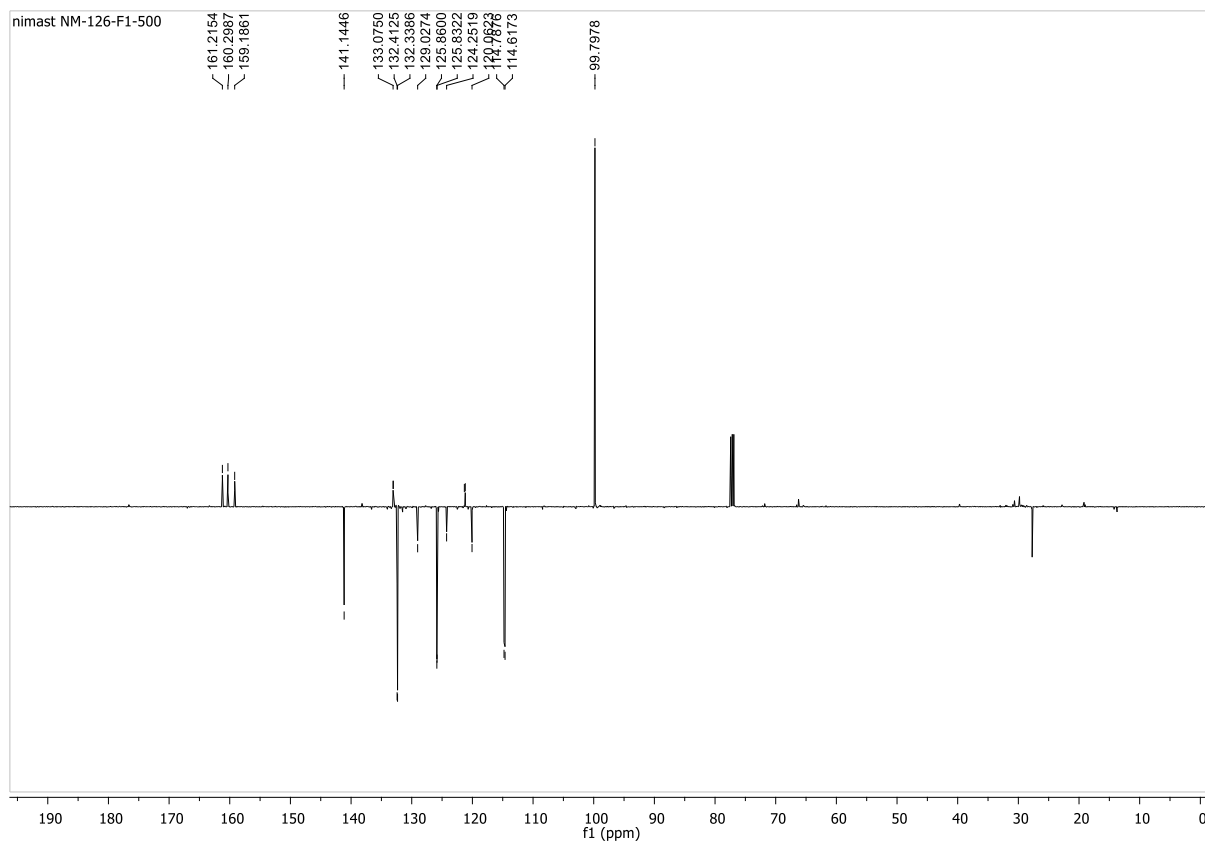


Vinyl 2-chloro-6-fluorobenzoate (9)

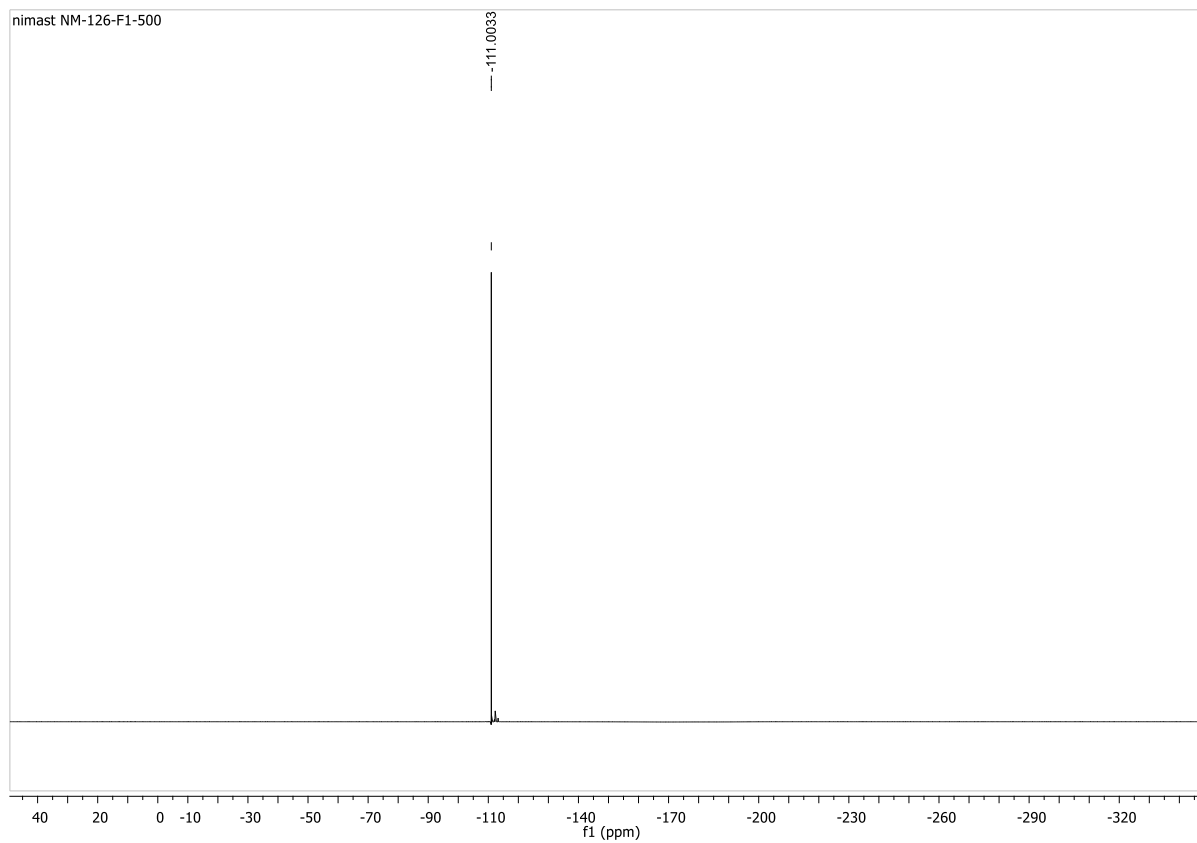
^1H (CDCl₃, 300 K, 500 MHz)



JMOD (CDCl₃, 300 K, 126 MHz)

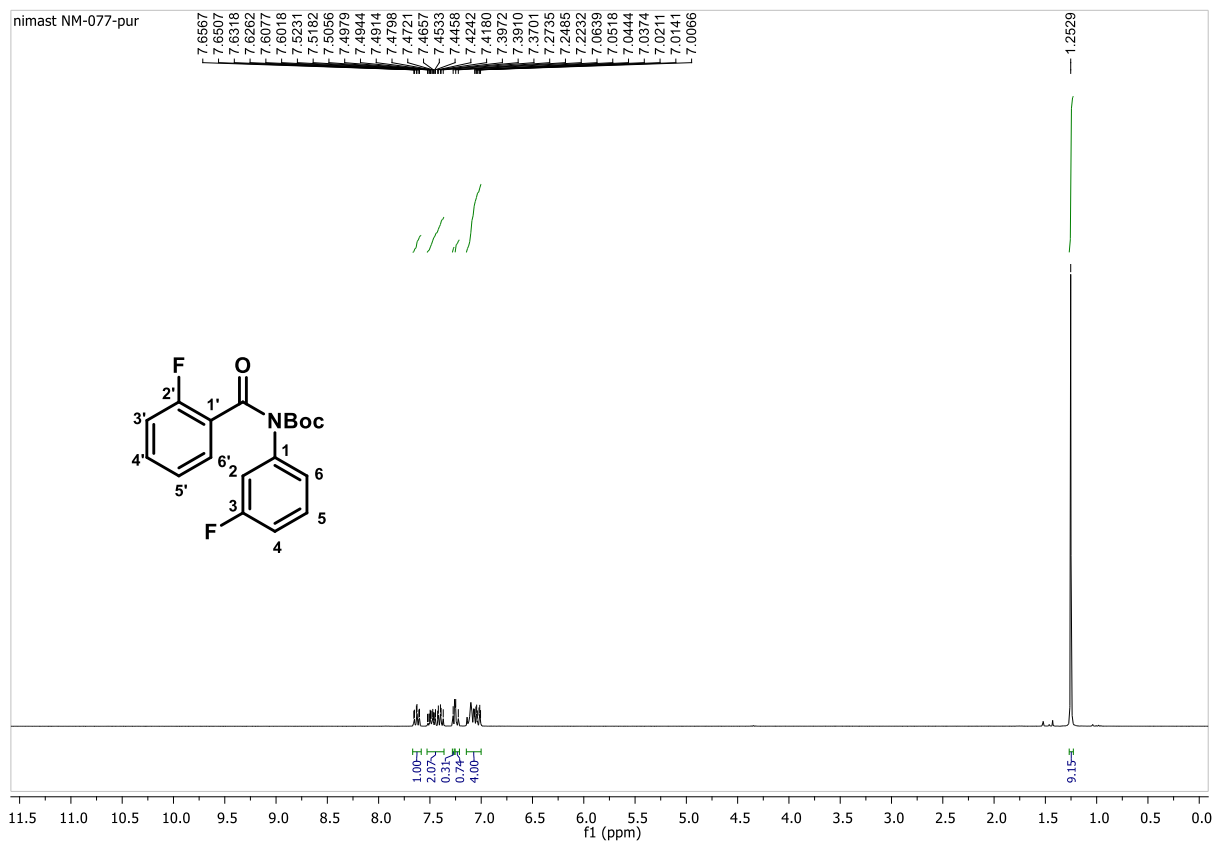


^{19}F (CDCl_3 , 300 K, 471 MHz)

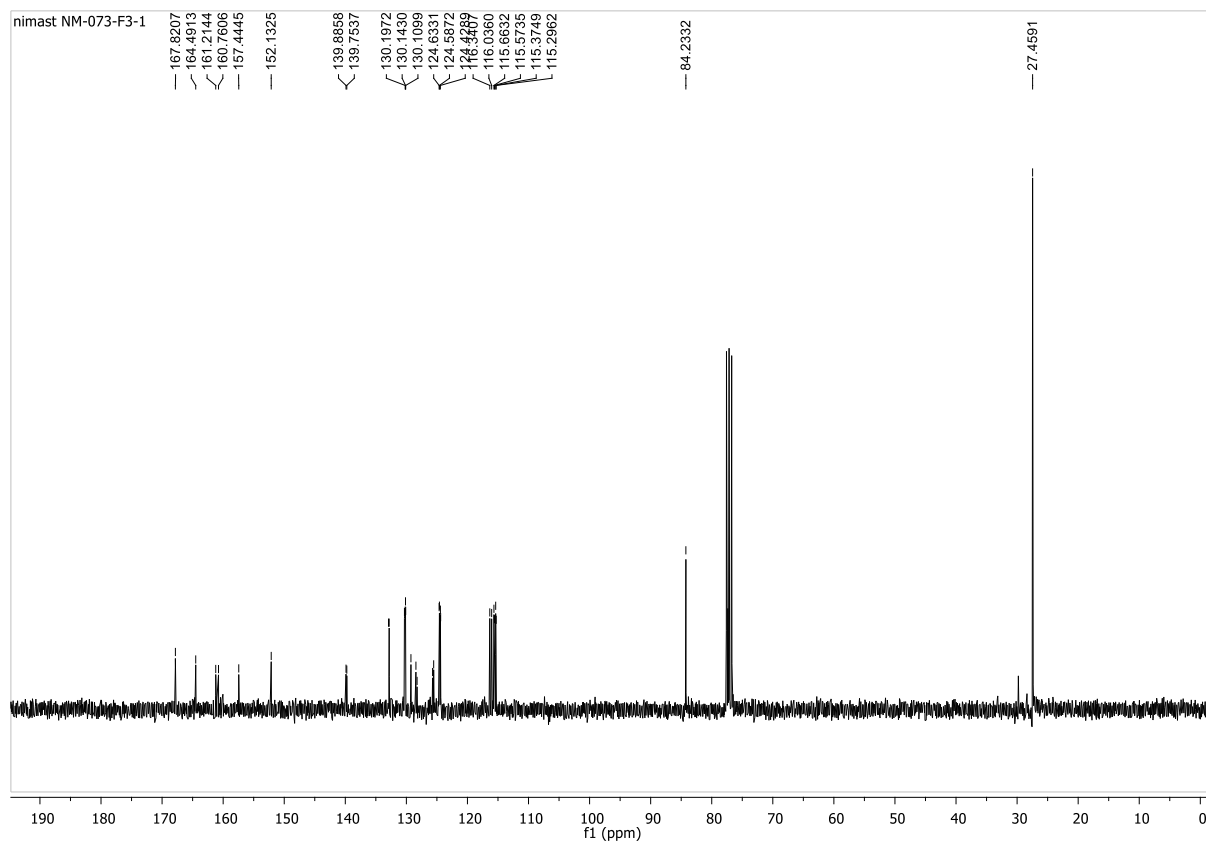


***tert*-Butyl *N*-(2-fluorobenzoyl)-*N*-(3-fluorophenyl)carbamate (10)**

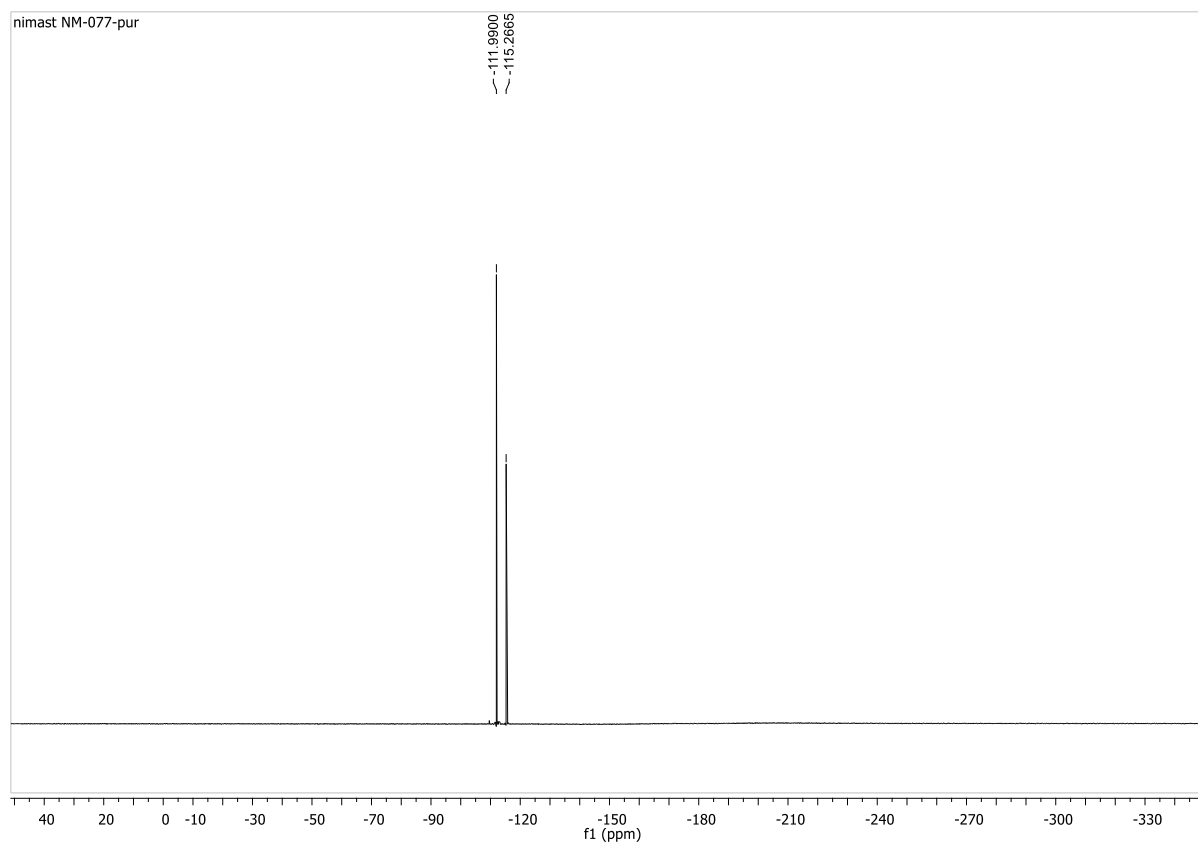
^1H (CDCl₃, 300 K, 500 MHz)



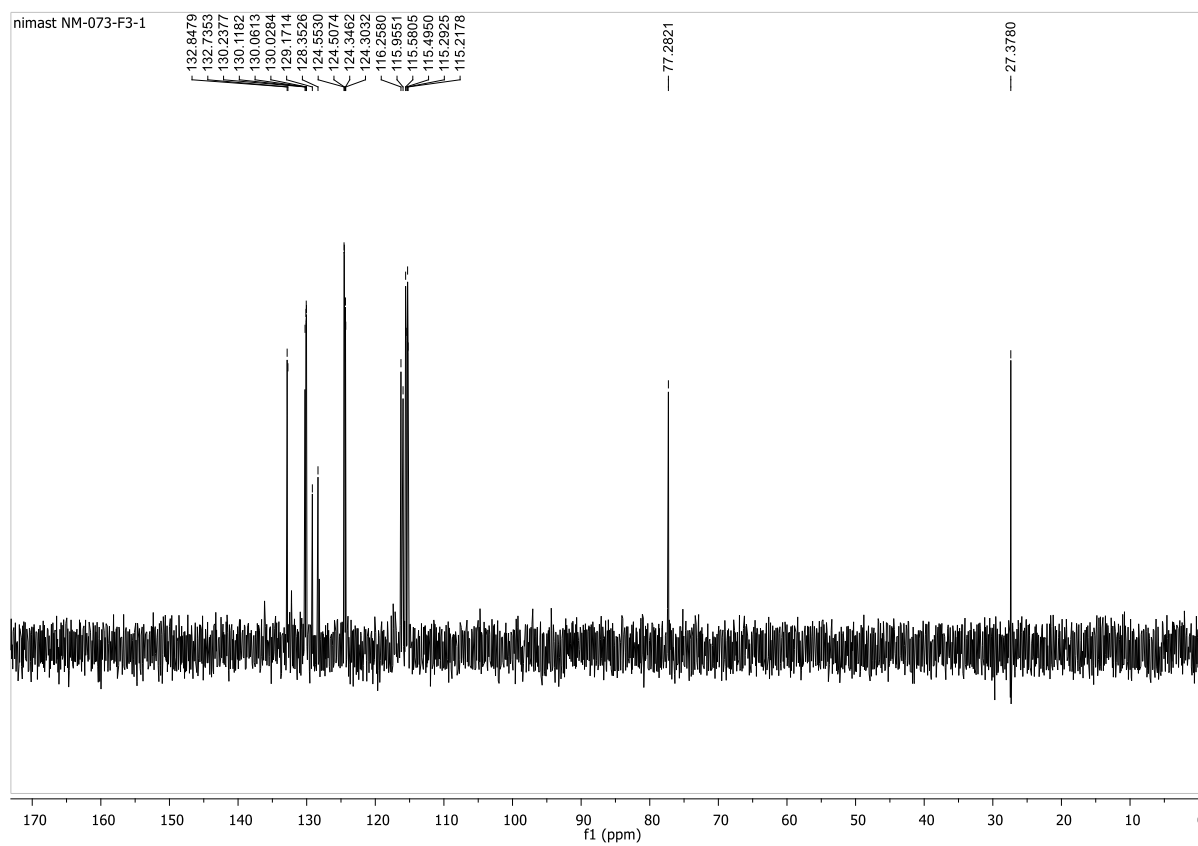
^{13}C (CDCl₃, 300 K, 126 MHz)



^{19}F (CDCl_3 , 300 K, 282 MHz)

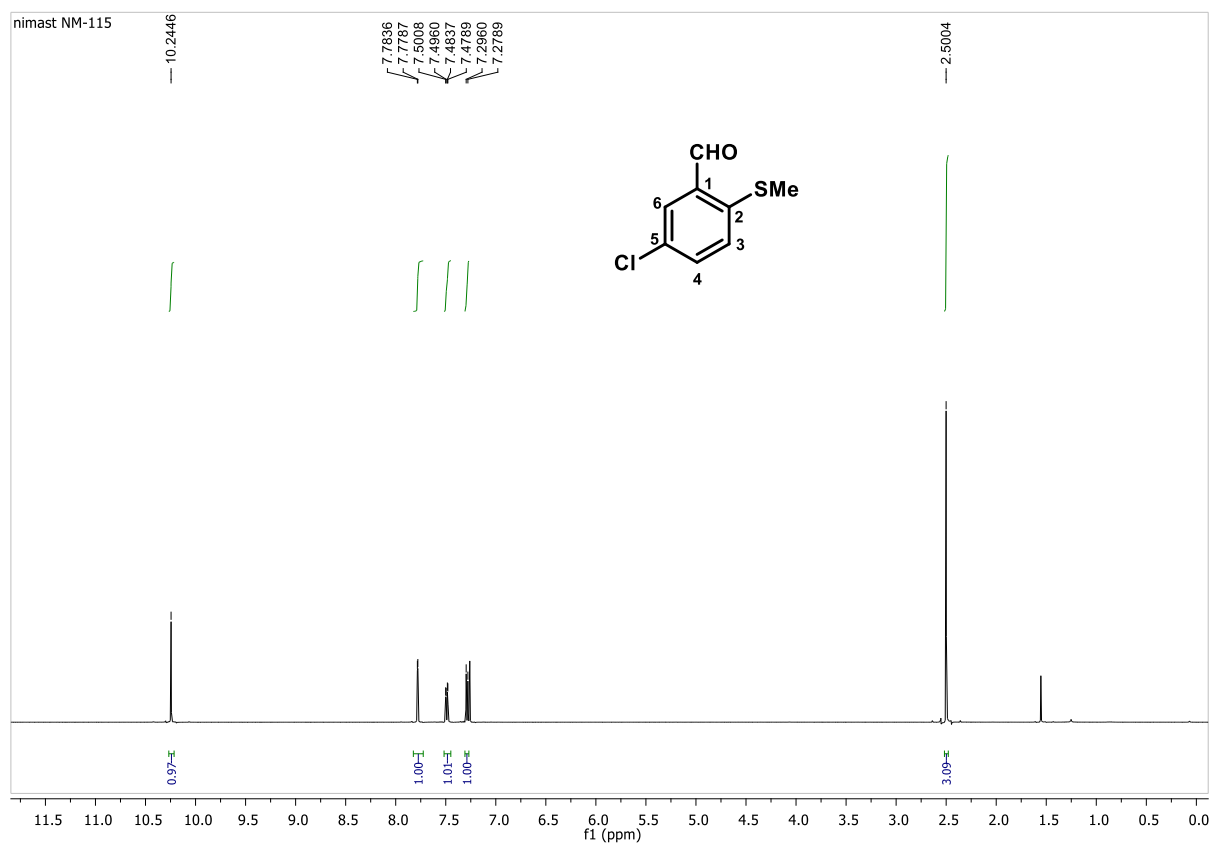


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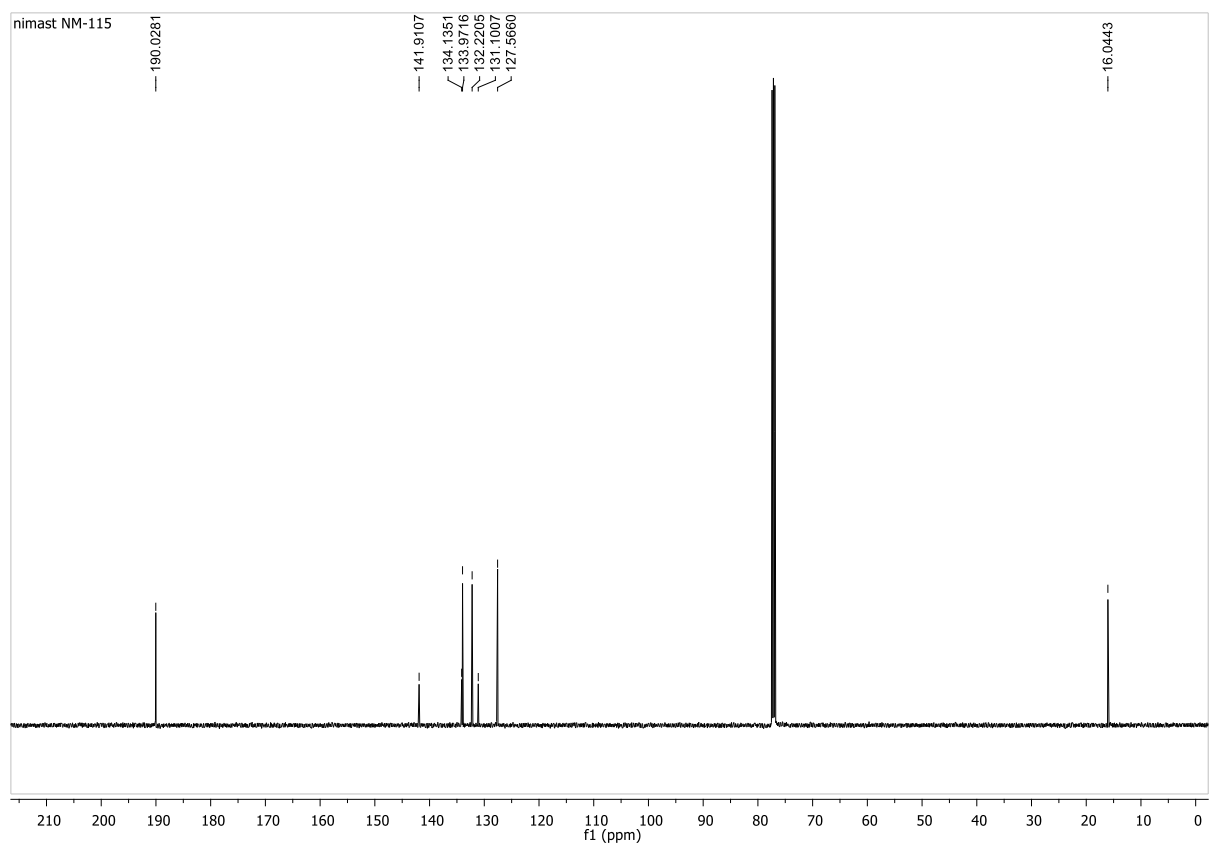


5-Chloro-2-(methylthio)benzaldehyde (11)

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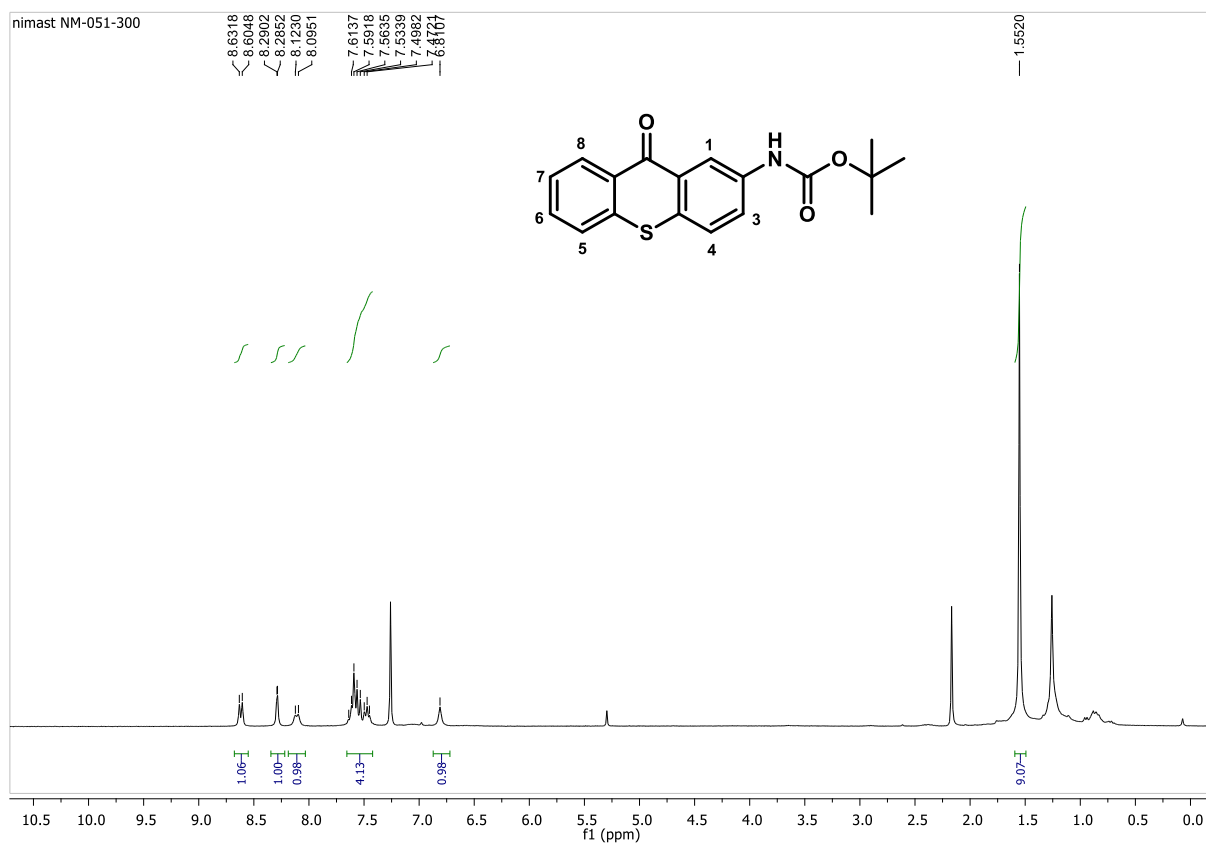


^{13}C (CDCl_3 , 300 K, 126 MHz)

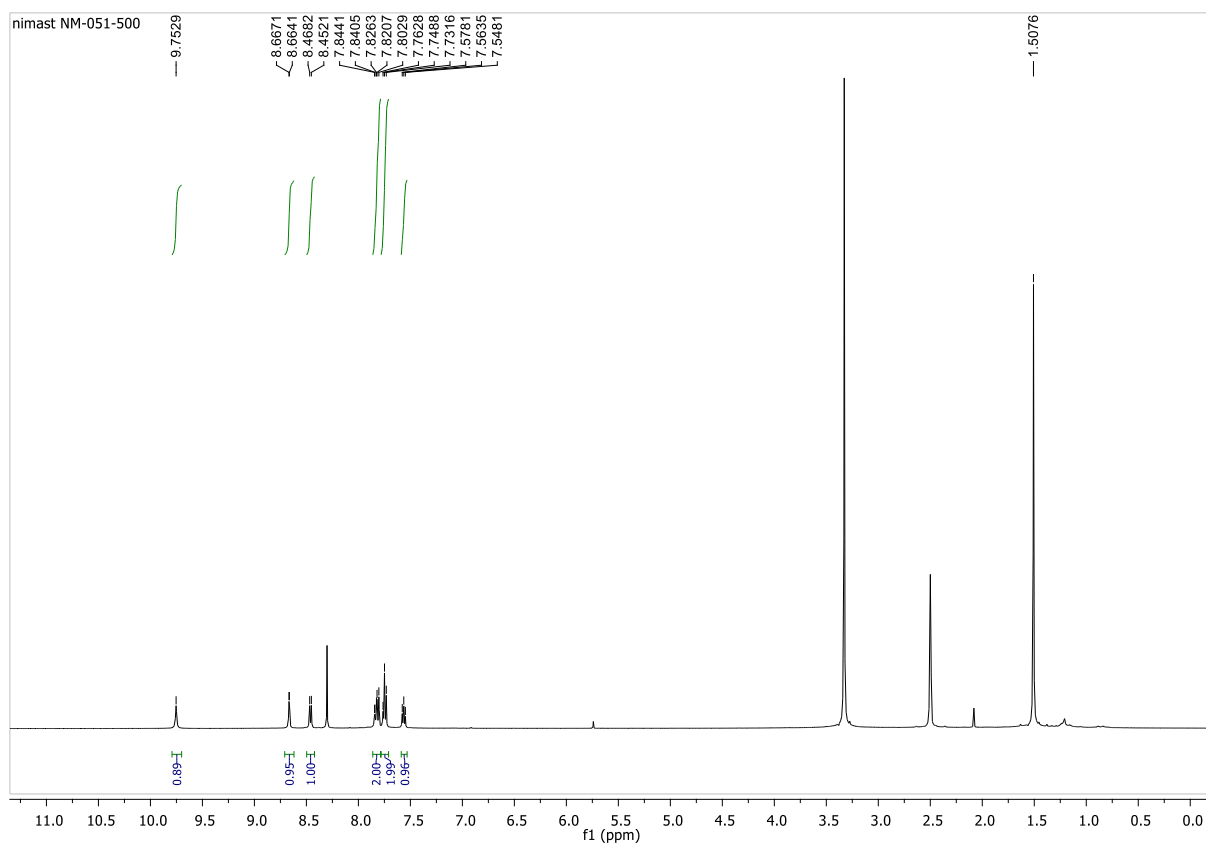


2-(*tert*-Butoxycarbonylamino)thioxanthone (12-Boc)

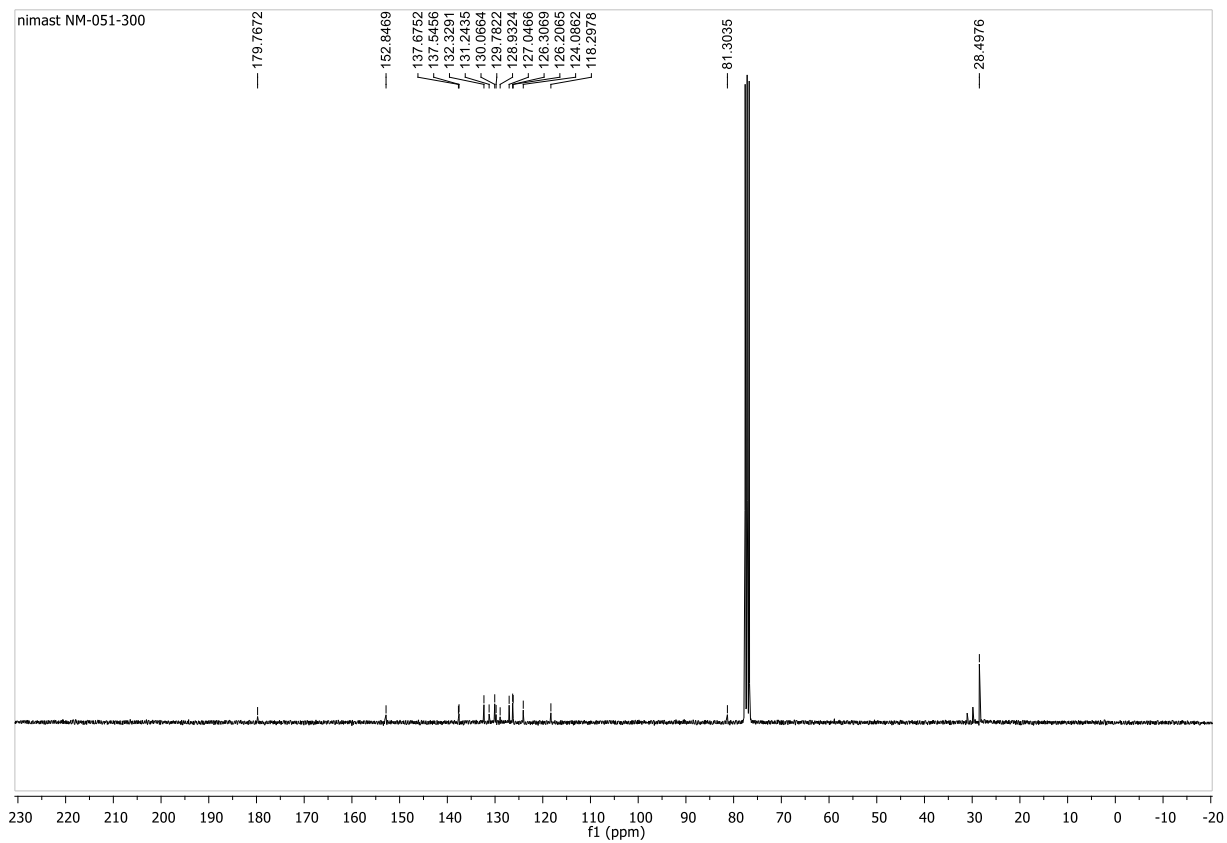
^1H (CDCl_3 , 300 K, 300 MHz)



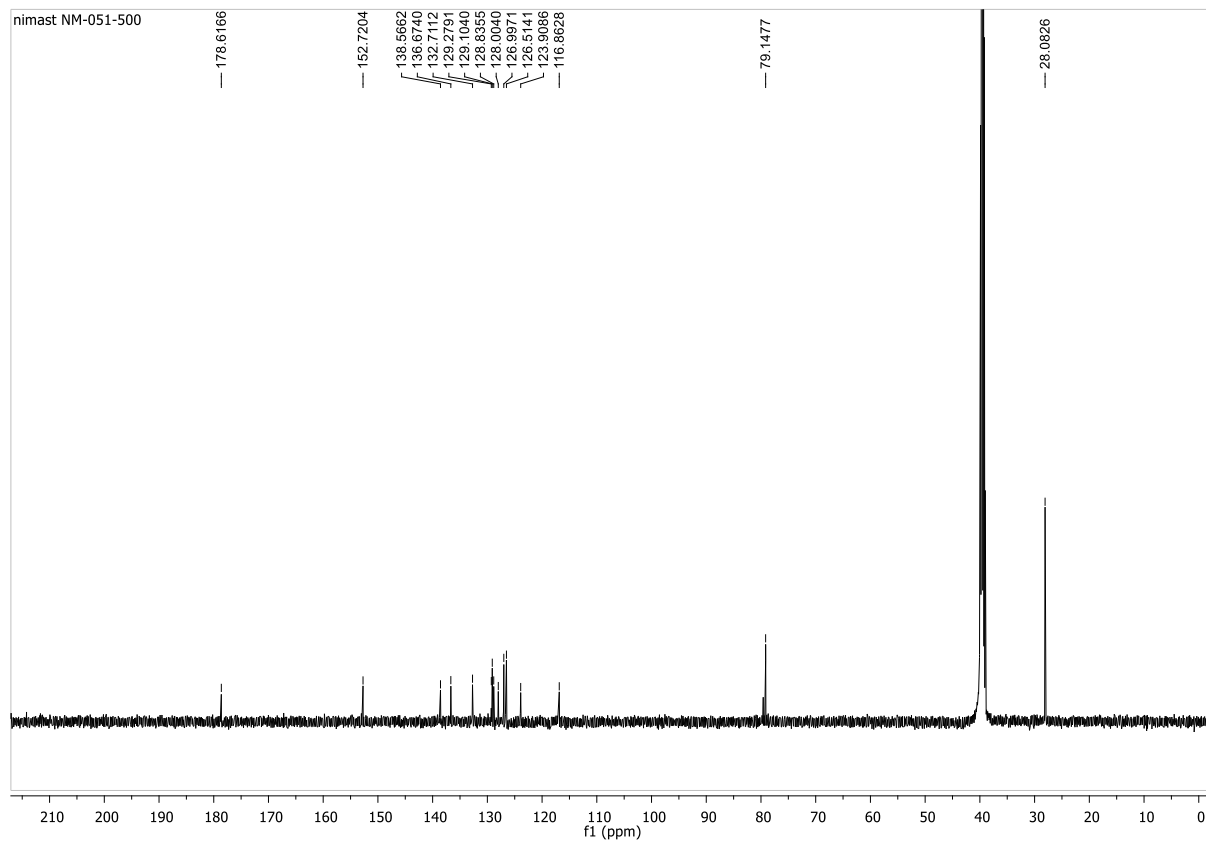
^1H ($(\text{CD}_3)_2\text{SO}$, 300 K, 500 MHz) – Presence of CHCl_3



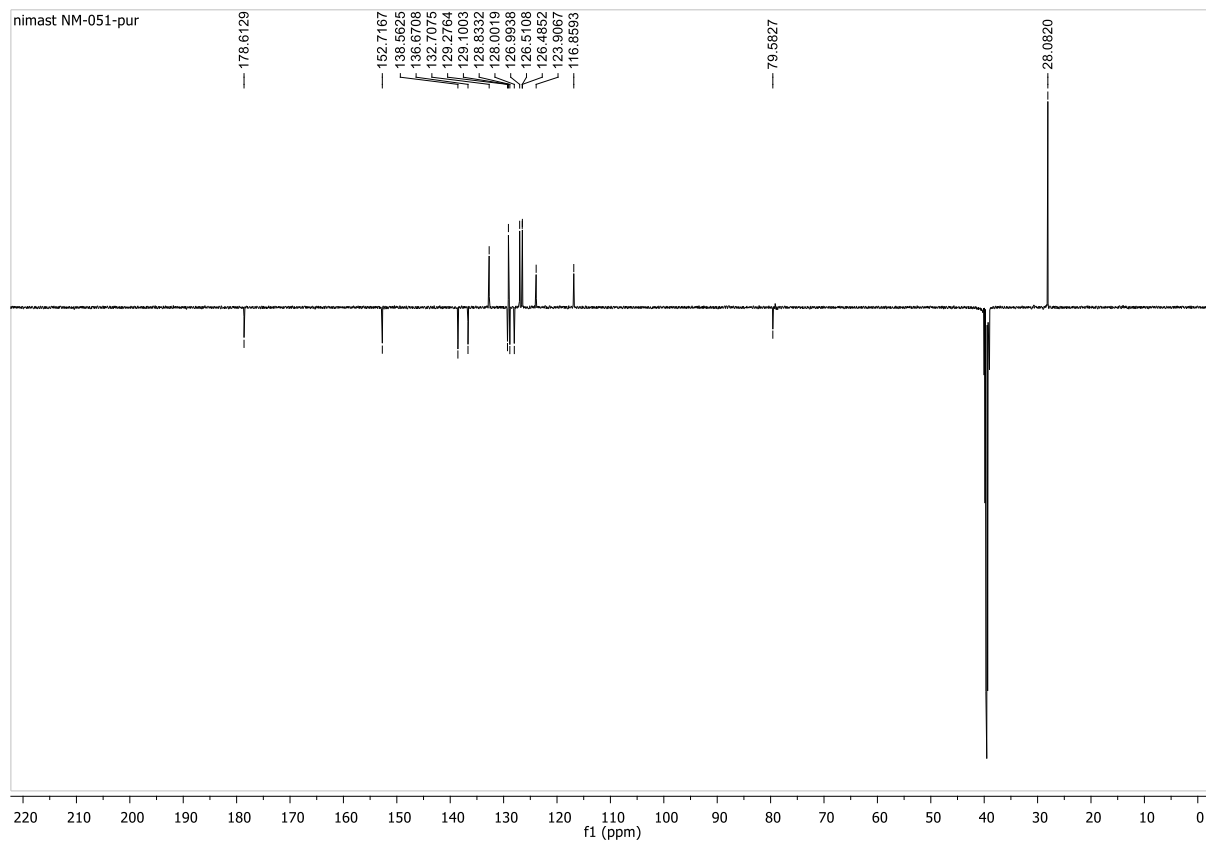
^{13}C (CDCl_3 , 300 K, 75 MHz)



^{13}C ($(\text{CD}_3)_2\text{SO}$, 300 K, 126 MHz)

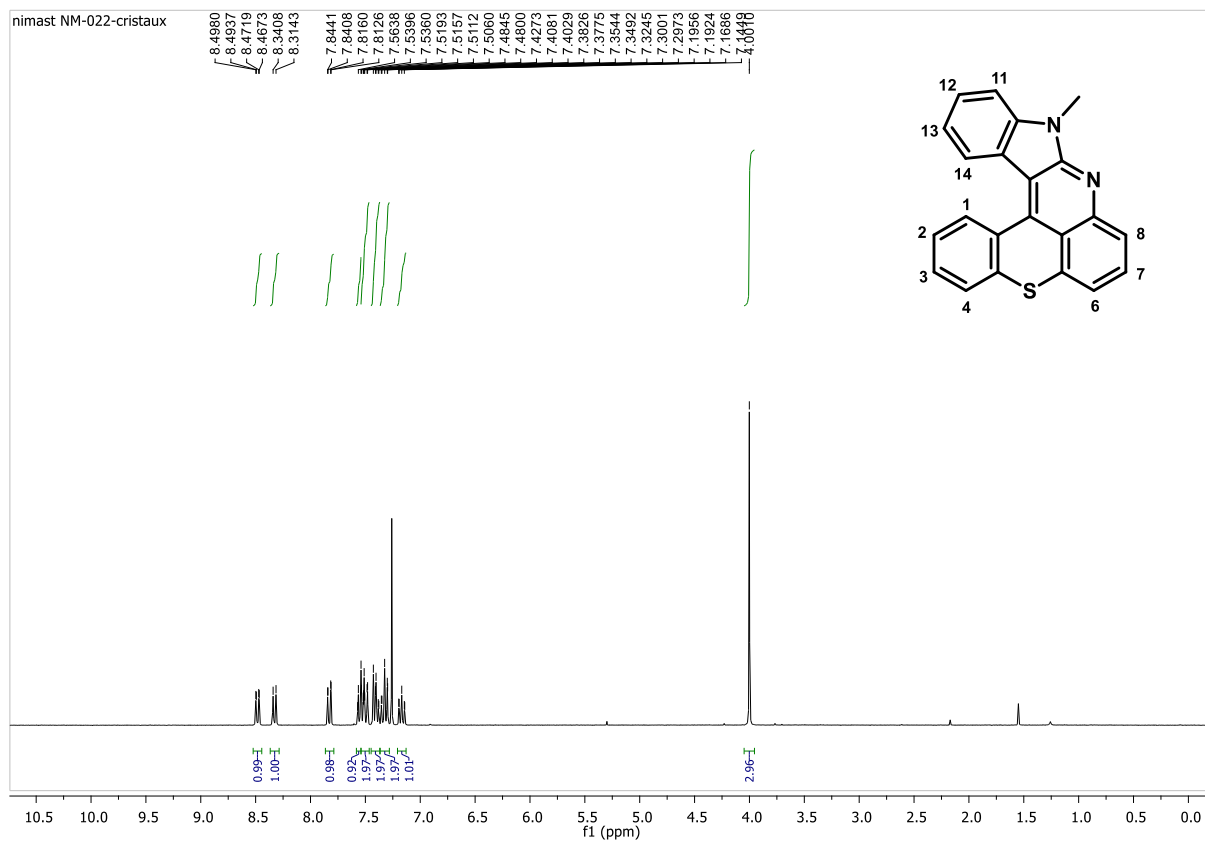


JMOD ((CD₃)₂SO, 300 K, 126 MHz)

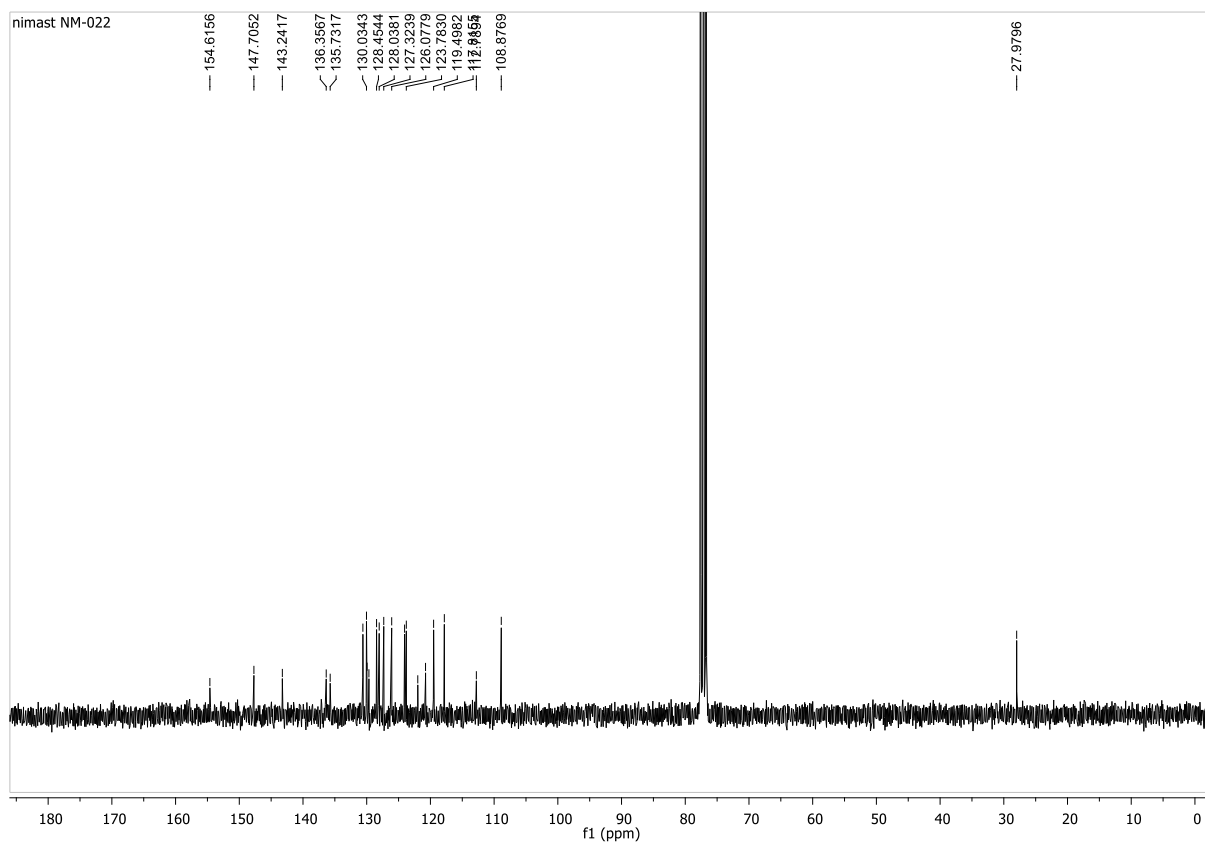


10-Methylbenzothiopyrano[4,3,2-de]indolo[2,3-b]quinoline (13)

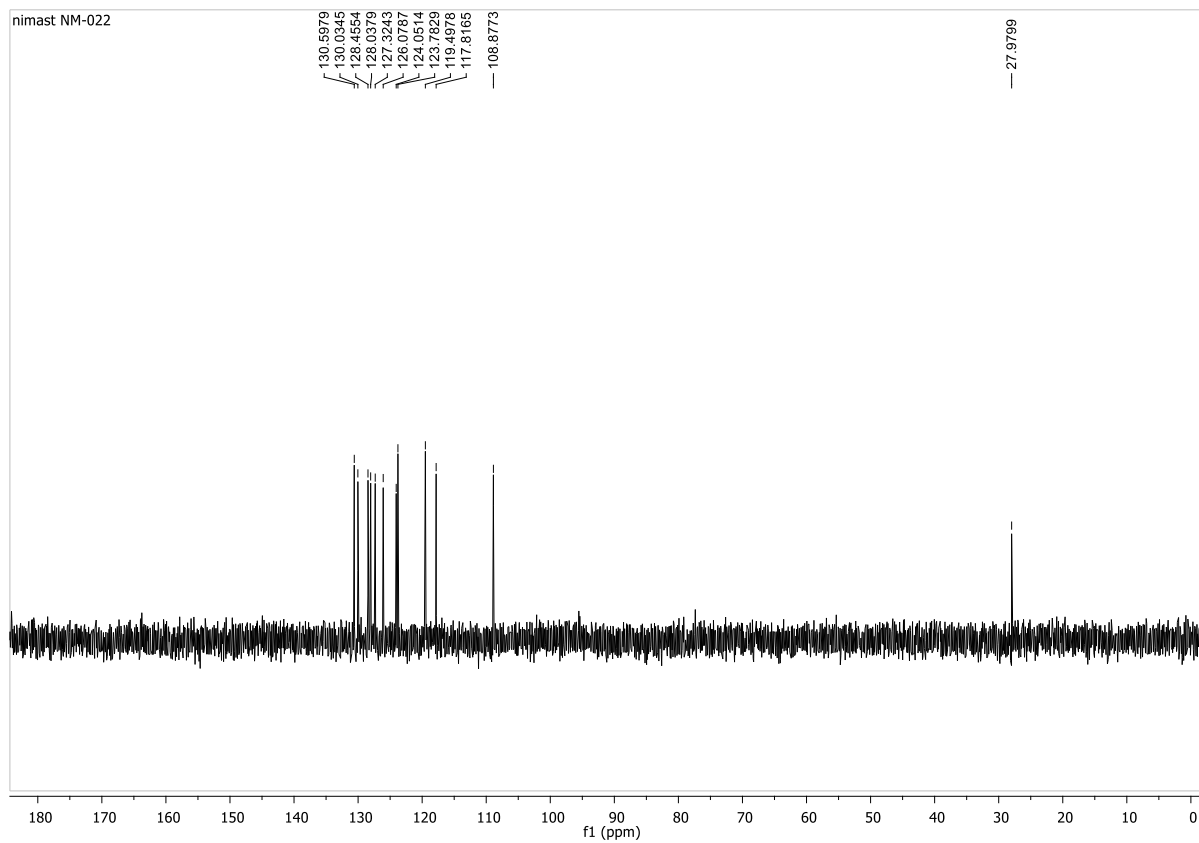
^1H (CDCl₃, 300 K, 300 MHz)



^{13}C (CDCl₃, 300 K, 75 MHz)

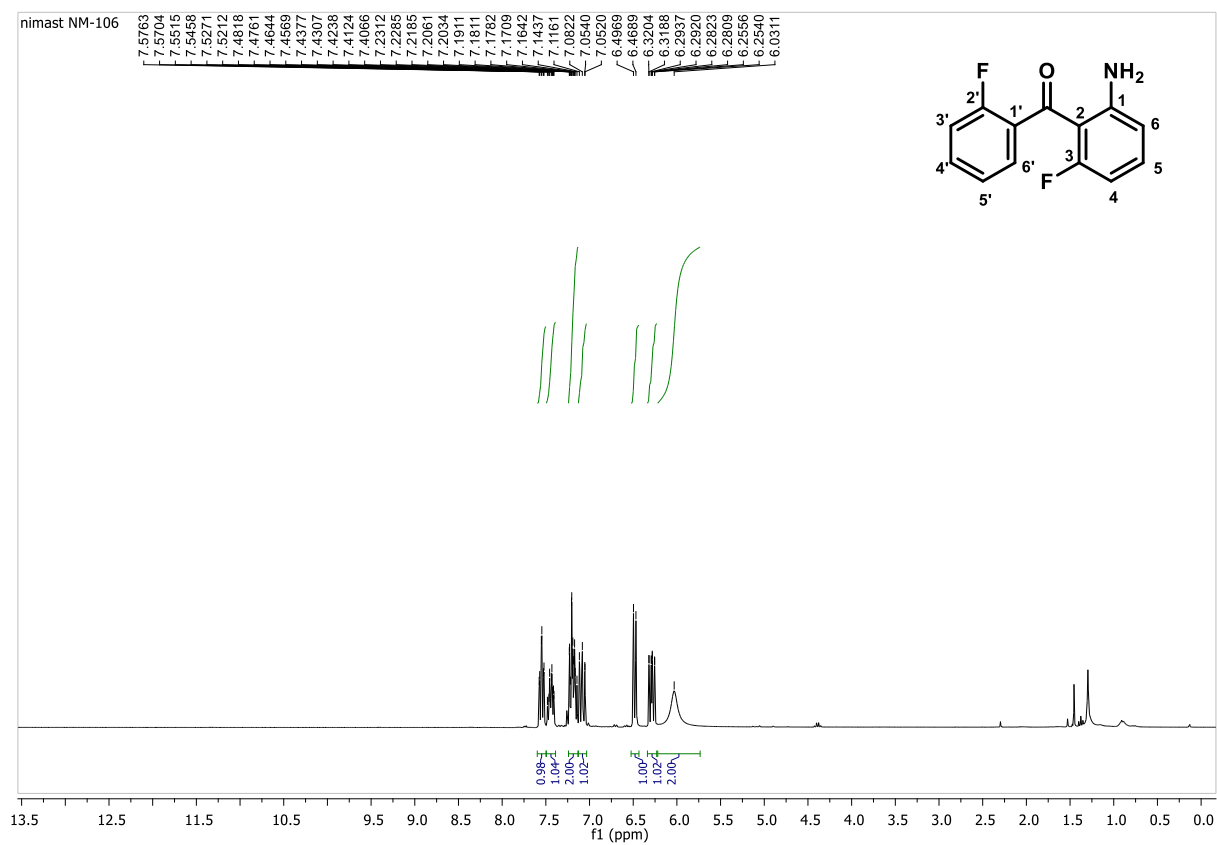


DEPT135 (CDCl₃, 300 K, 75 MHz)

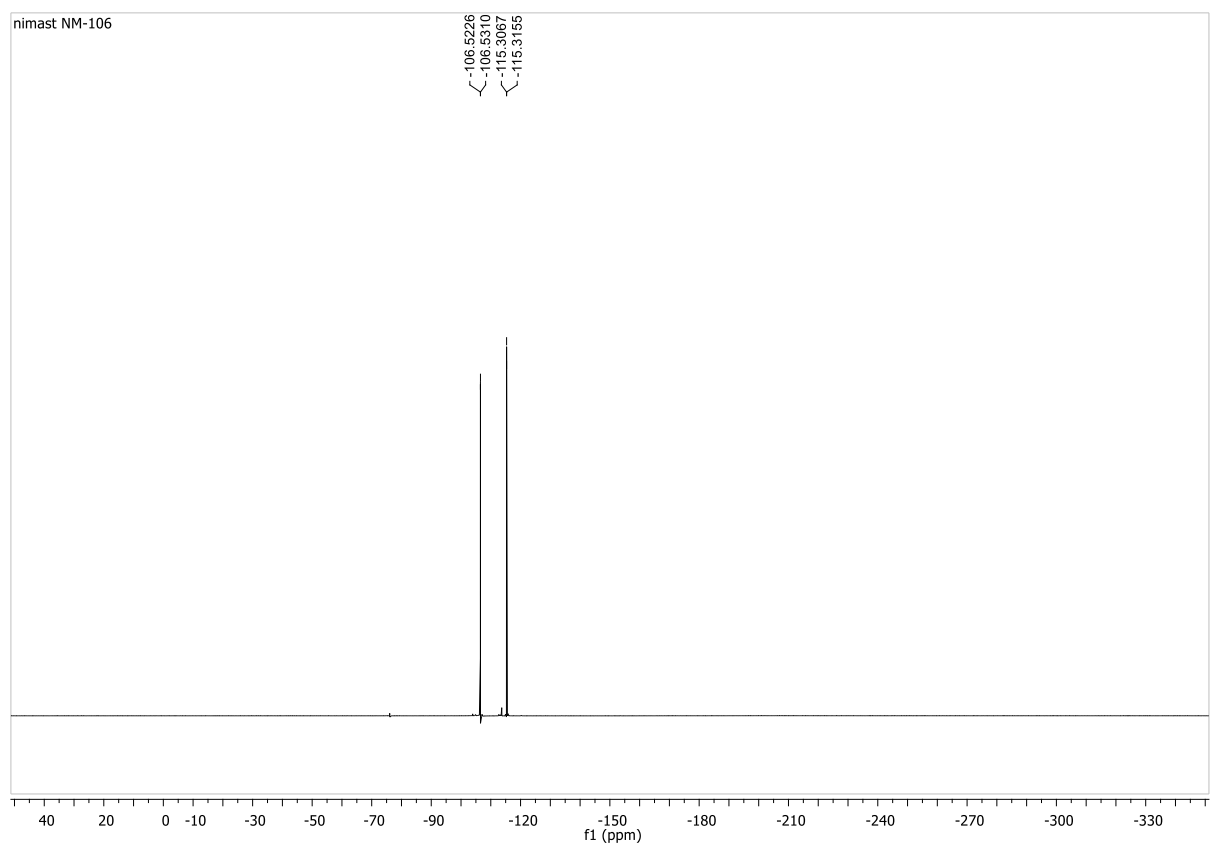


2-Amino-6,2'-difluorobenzophenone (14)

^1H (CDCl_3 , 300 K, 400 MHz)

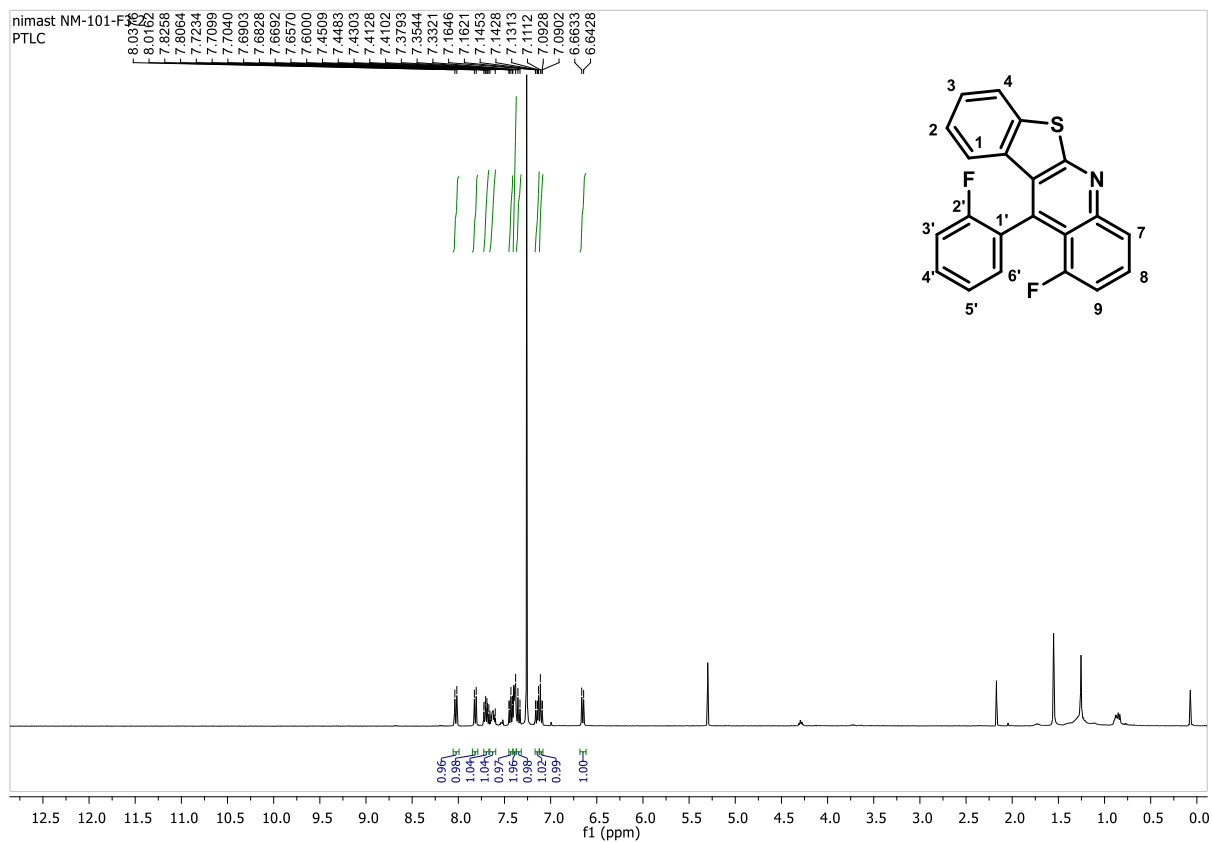


^{19}F (CDCl_3 , 300 K, 282 MHz)

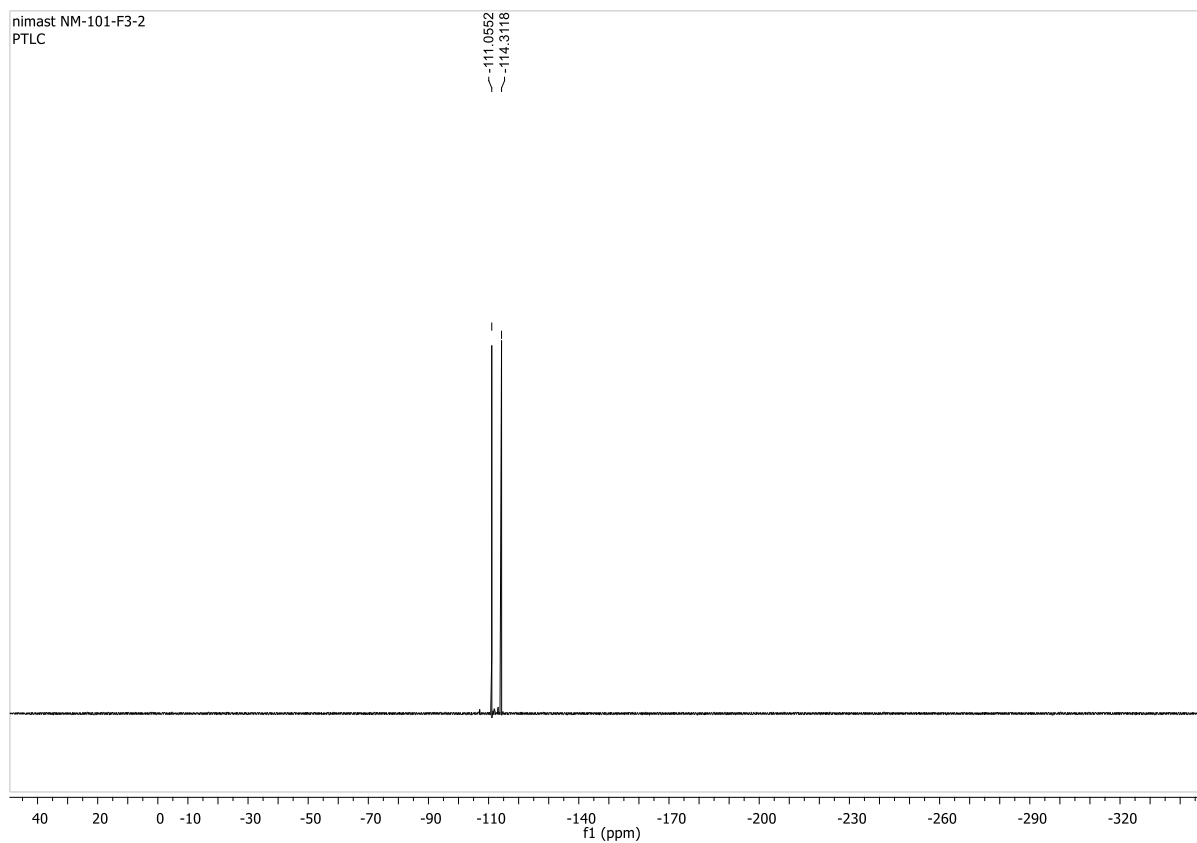


10-Fluoro-11-(2-fluorophenyl)benzothieno[2,3-b]quinoline (15a)

^1H (CDCl₃, 300 K, 400 MHz)

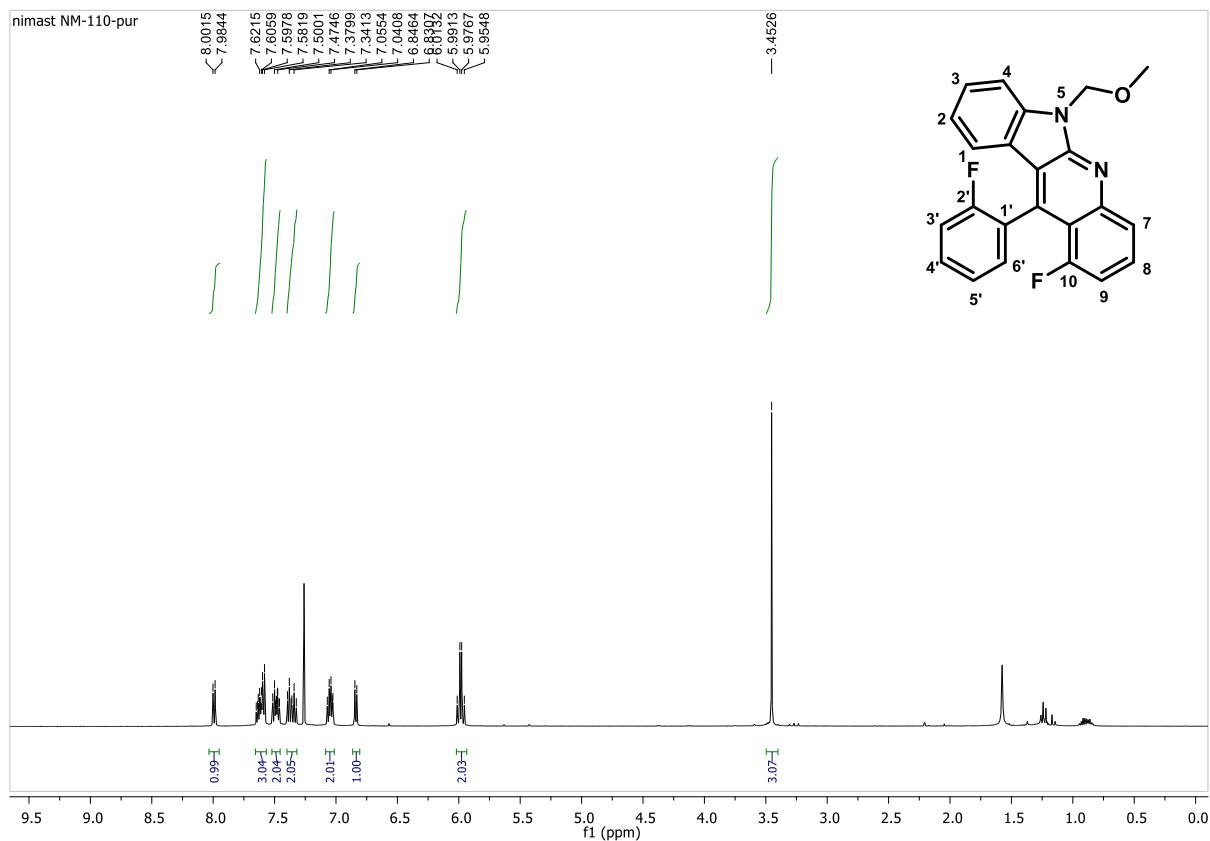


^{19}F (CDCl₃, 300 K, 376 MHz)

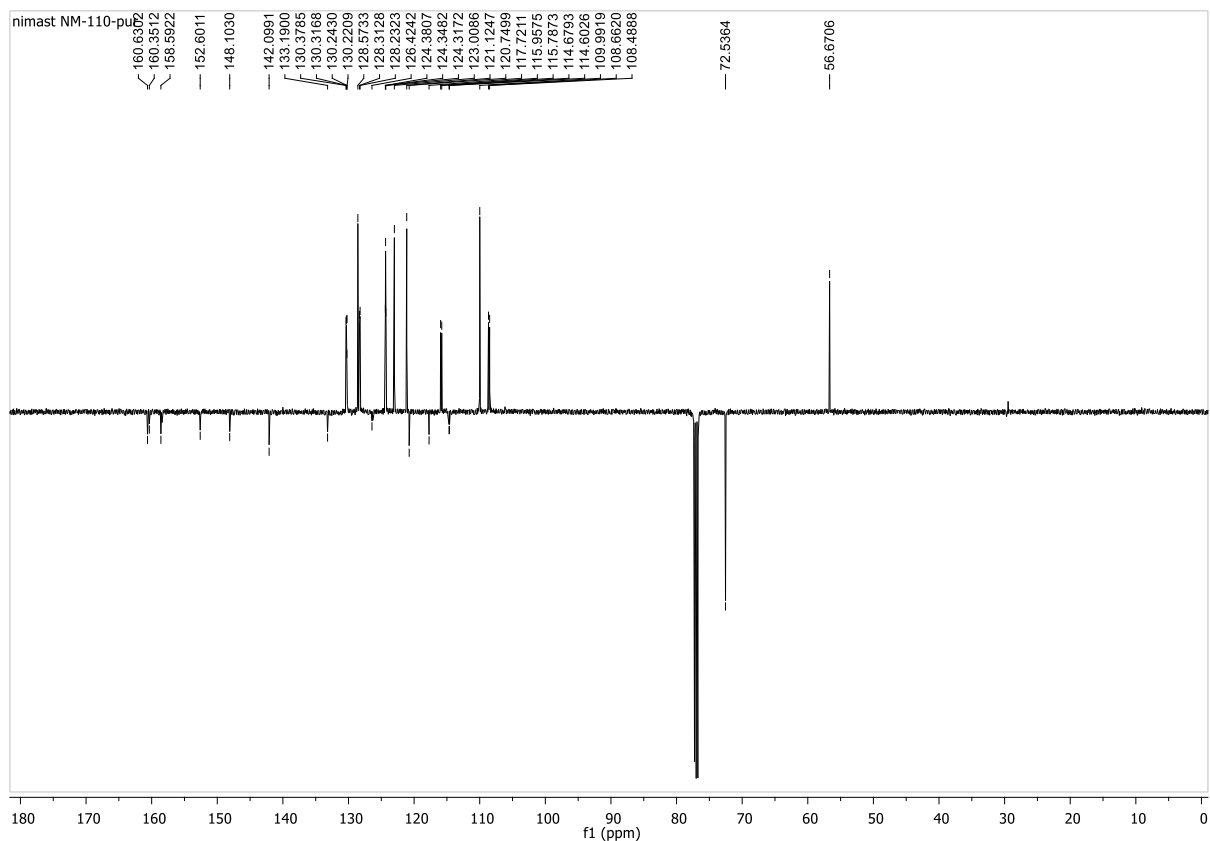


10-Fluoro-11-(2-fluorophenyl)-5-(methoxymethyl)indolo[2,3-b]quinoline (15b)

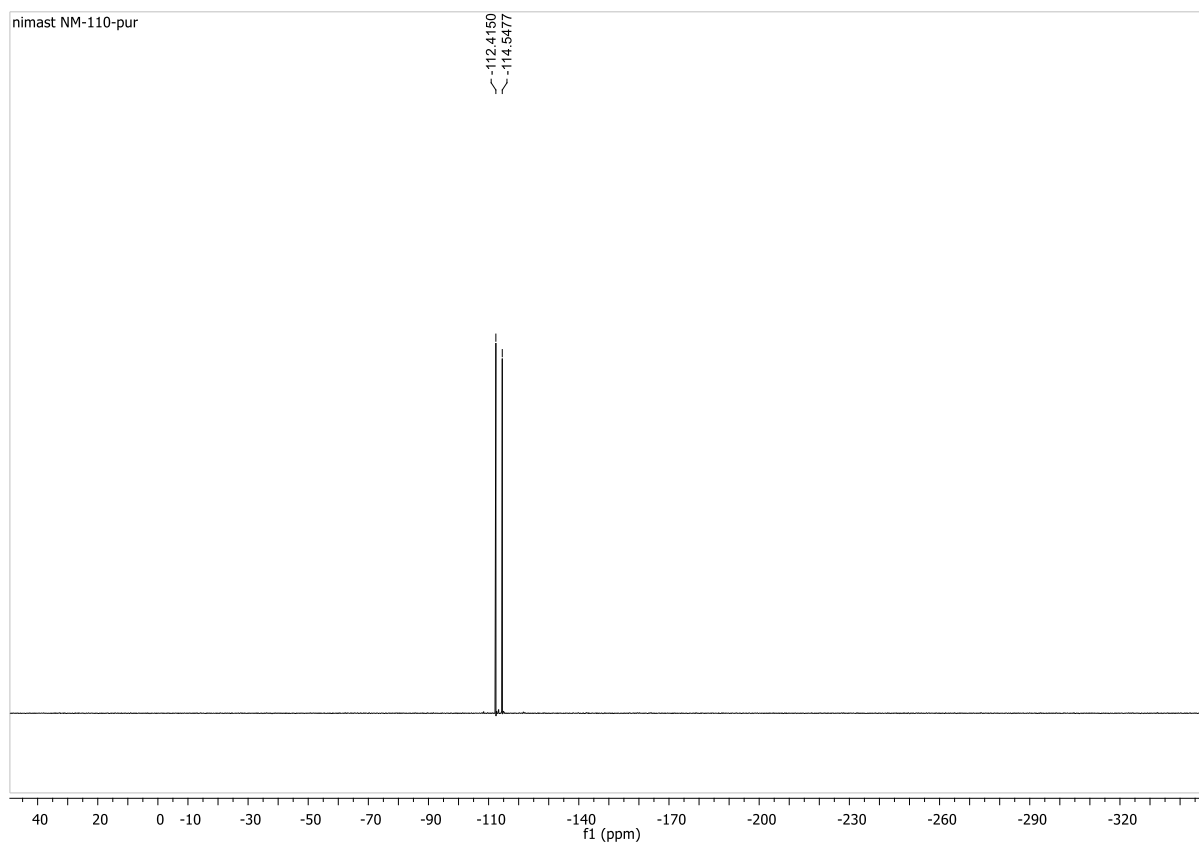
^1H (CDCl₃, 300 K, 500 MHz)



JMOD (CDCl₃, 300 K, 126 MHz)

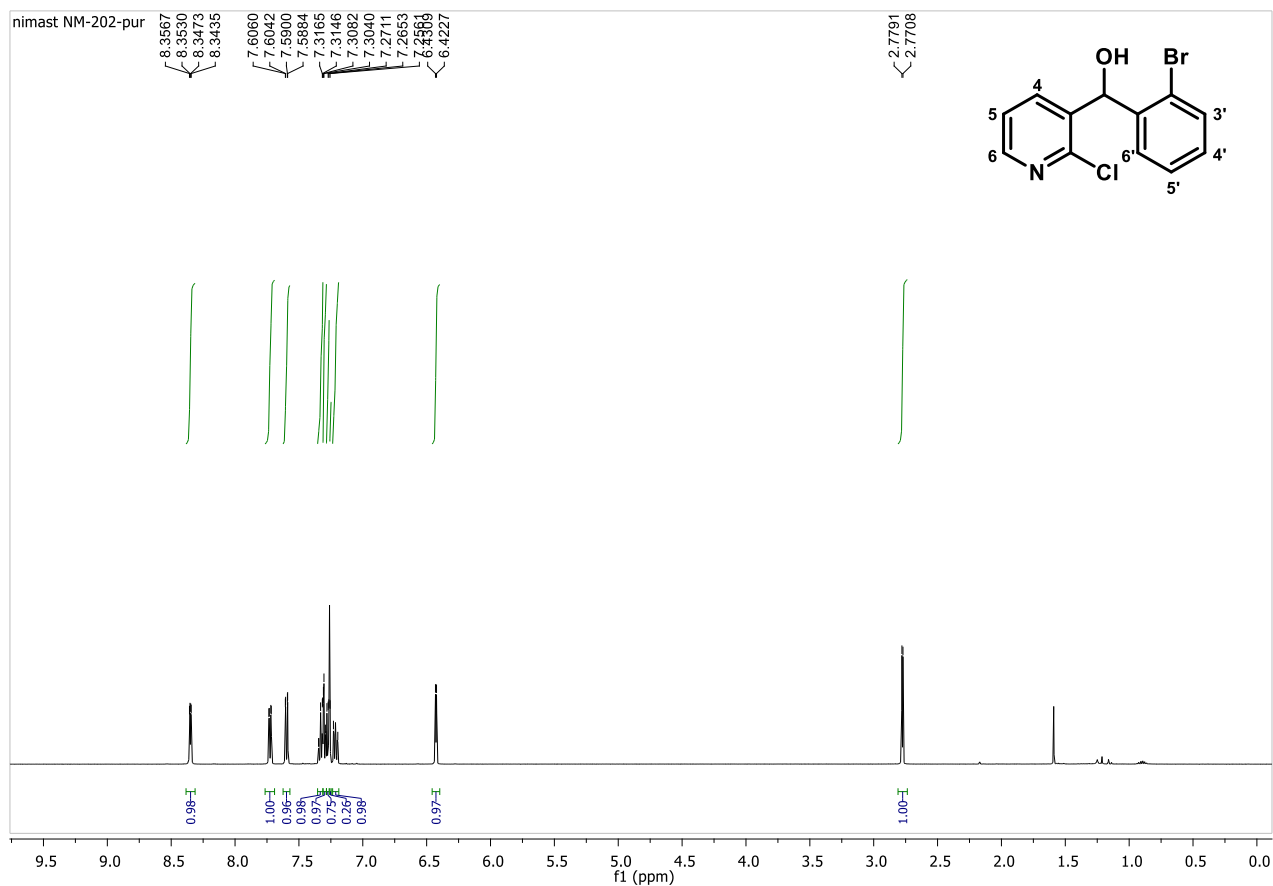


^{19}F (CDCl_3 , 300 K, 471 MHz)

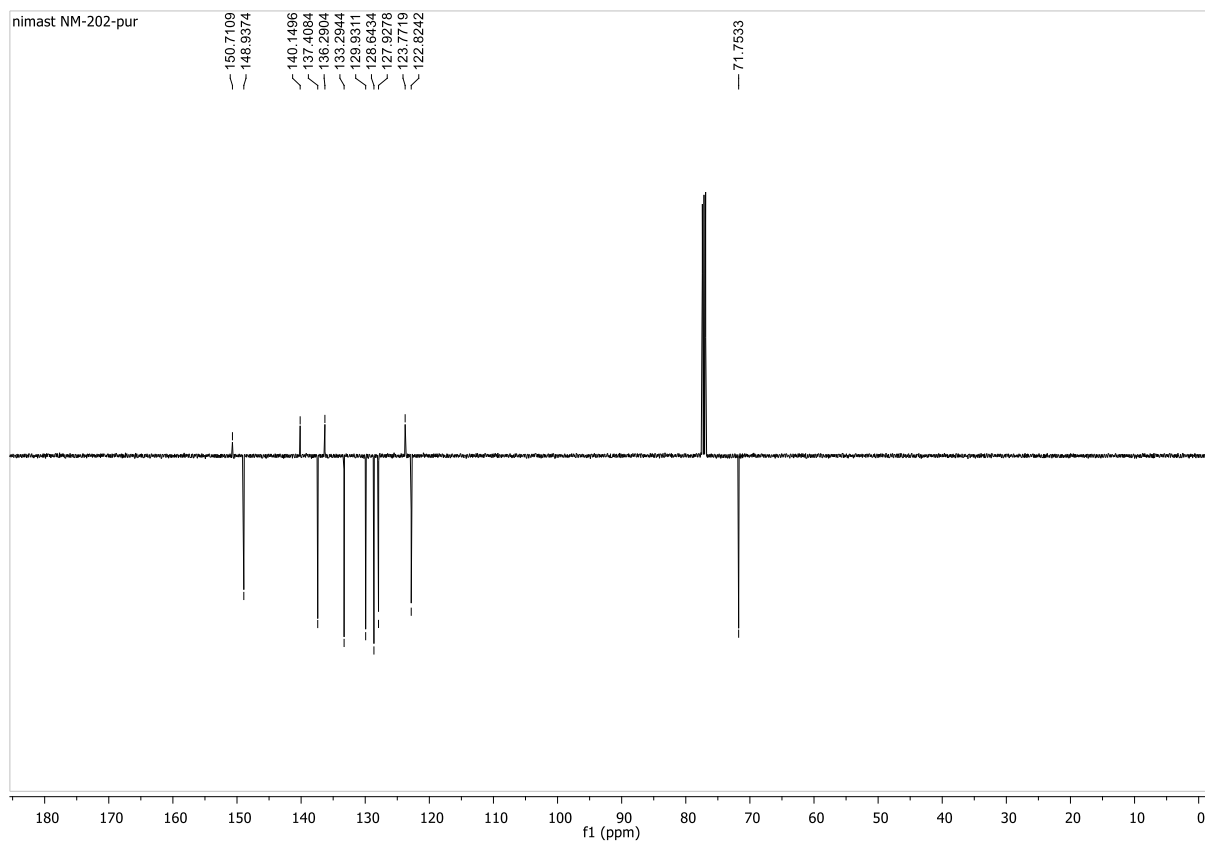


3-(1-(2-Bromophenyl)hydroxymethyl)-2-chloropyridine (16)

^1H (CDCl_3 , 300 K, 500 MHz)

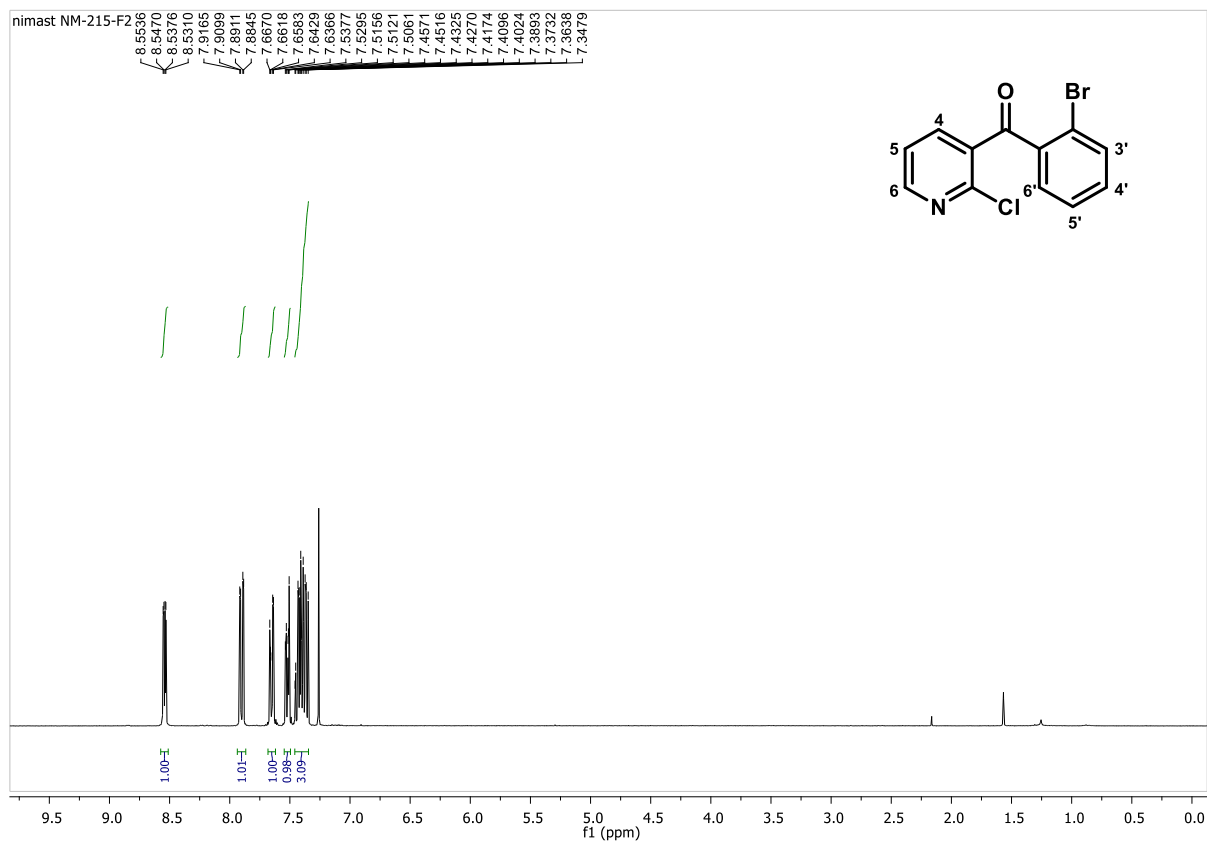


JMOD (CDCl_3 , 300 K, 126 MHz)

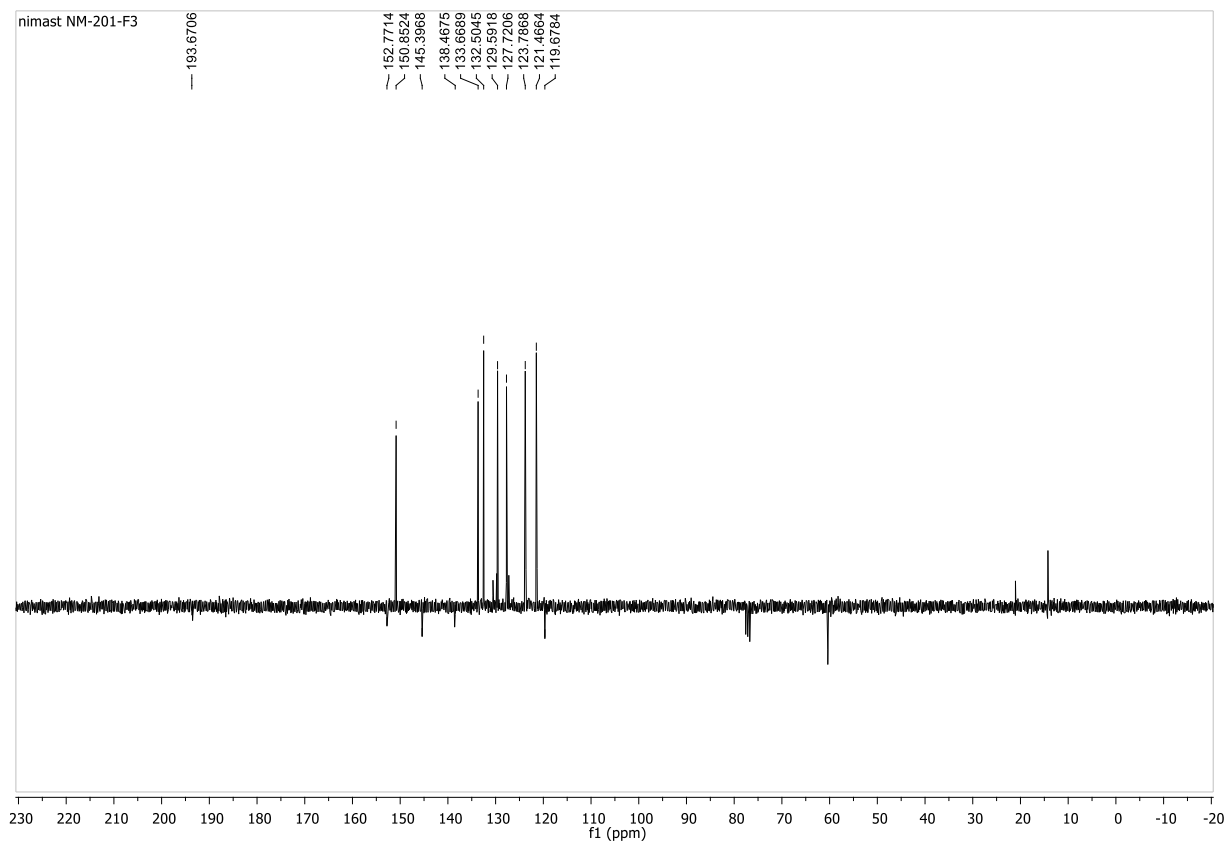


3-(2-Bromobenzoyl)-2-chloropyridine (17)

^1H (CDCl_3 , 300 K, 300 MHz)

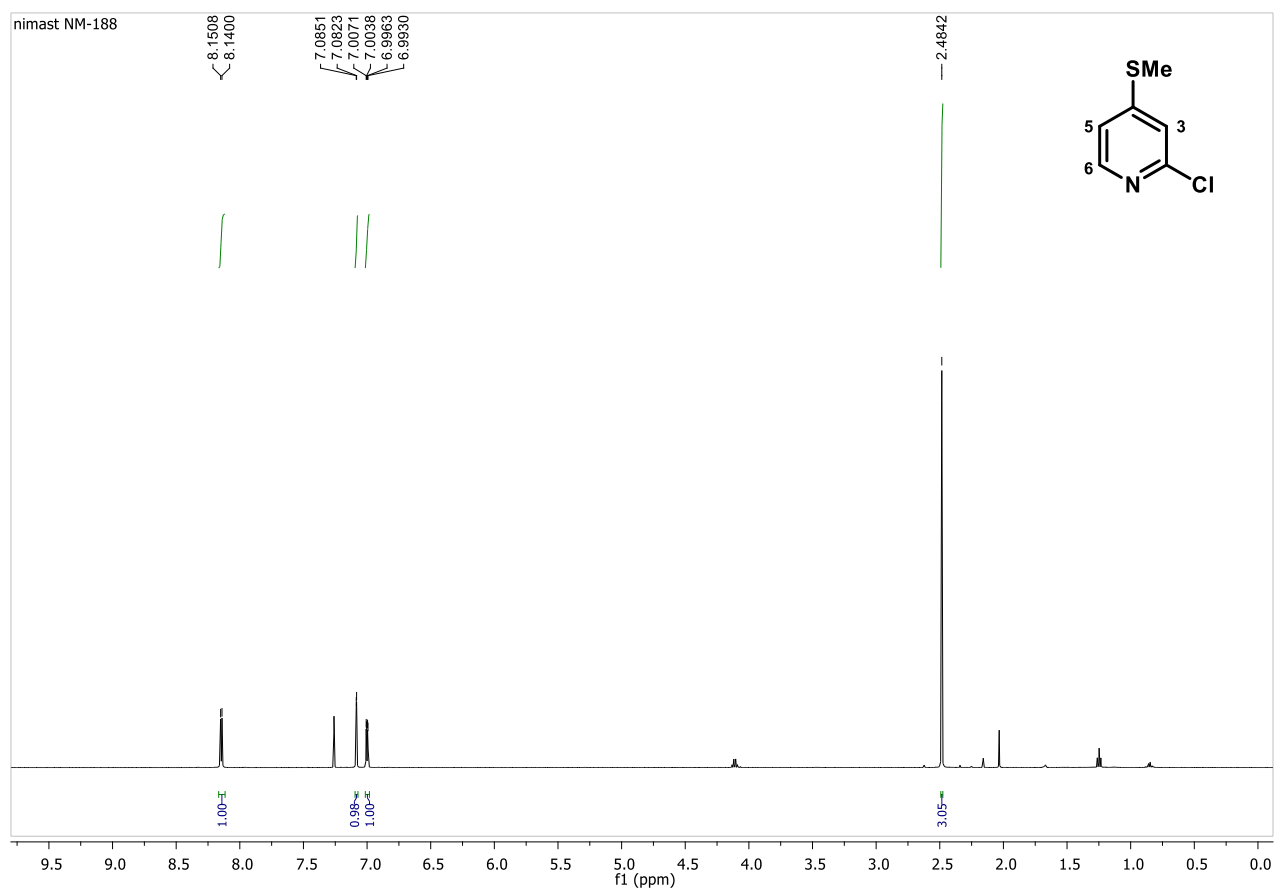


JMOD (CDCl_3 , 300 K, 126 MHz)

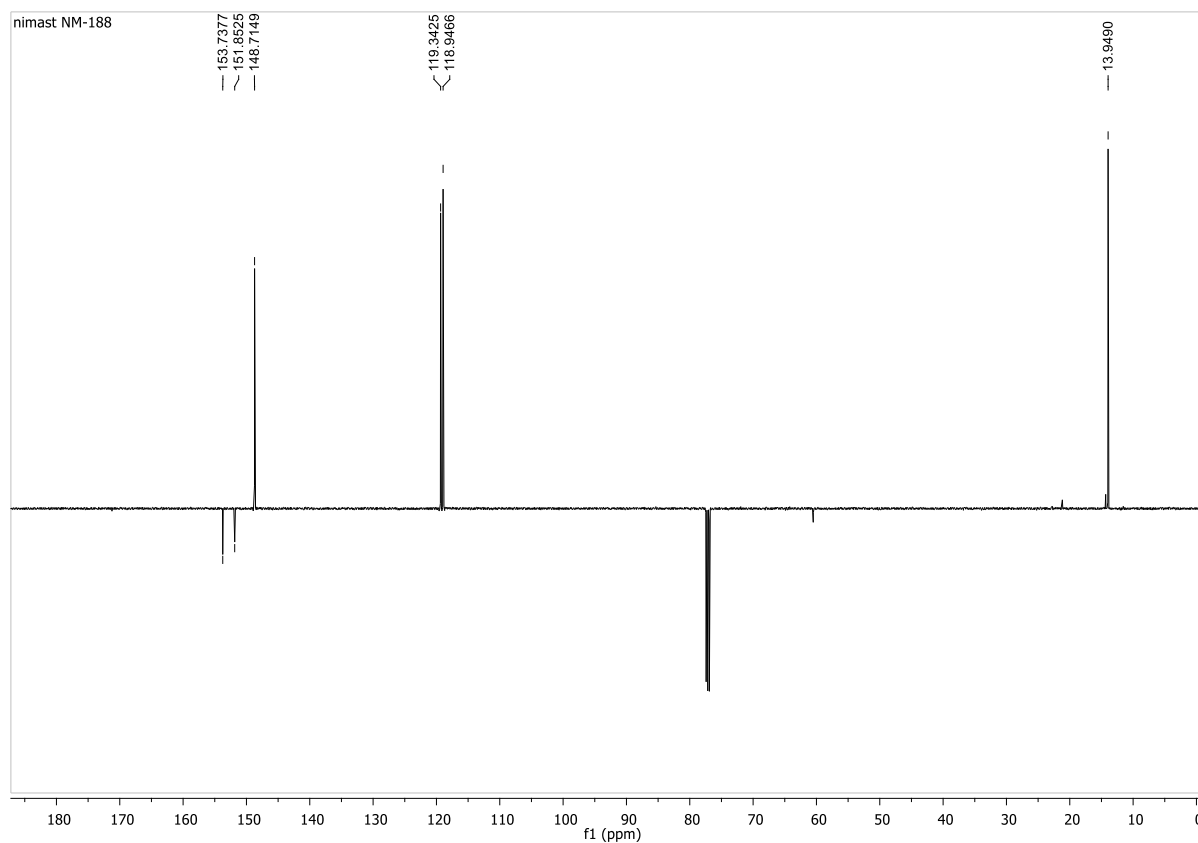


2-Chloro-4-(methylthio)pyridine

^1H (CDCl_3 , 300 K, 500 MHz)

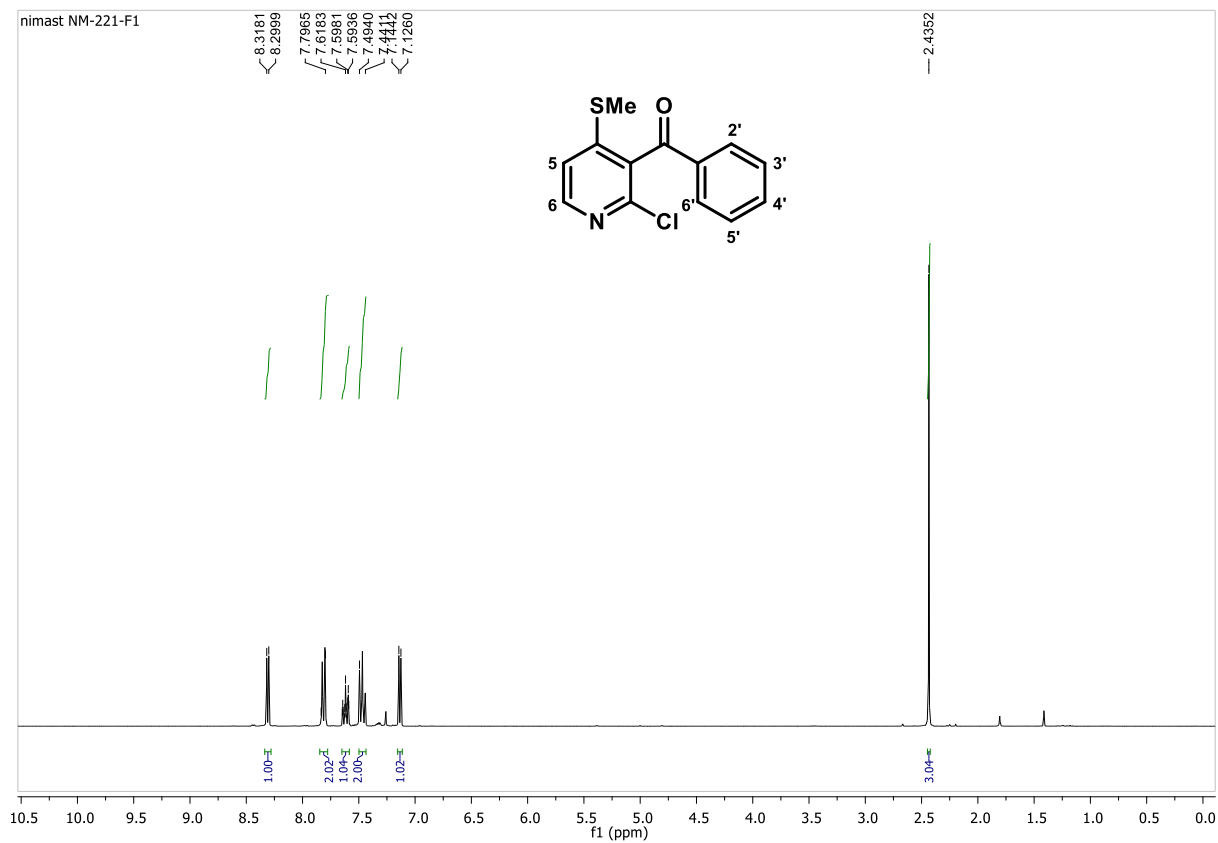


JMOD (CDCl_3 , 300 K, 126 MHz)

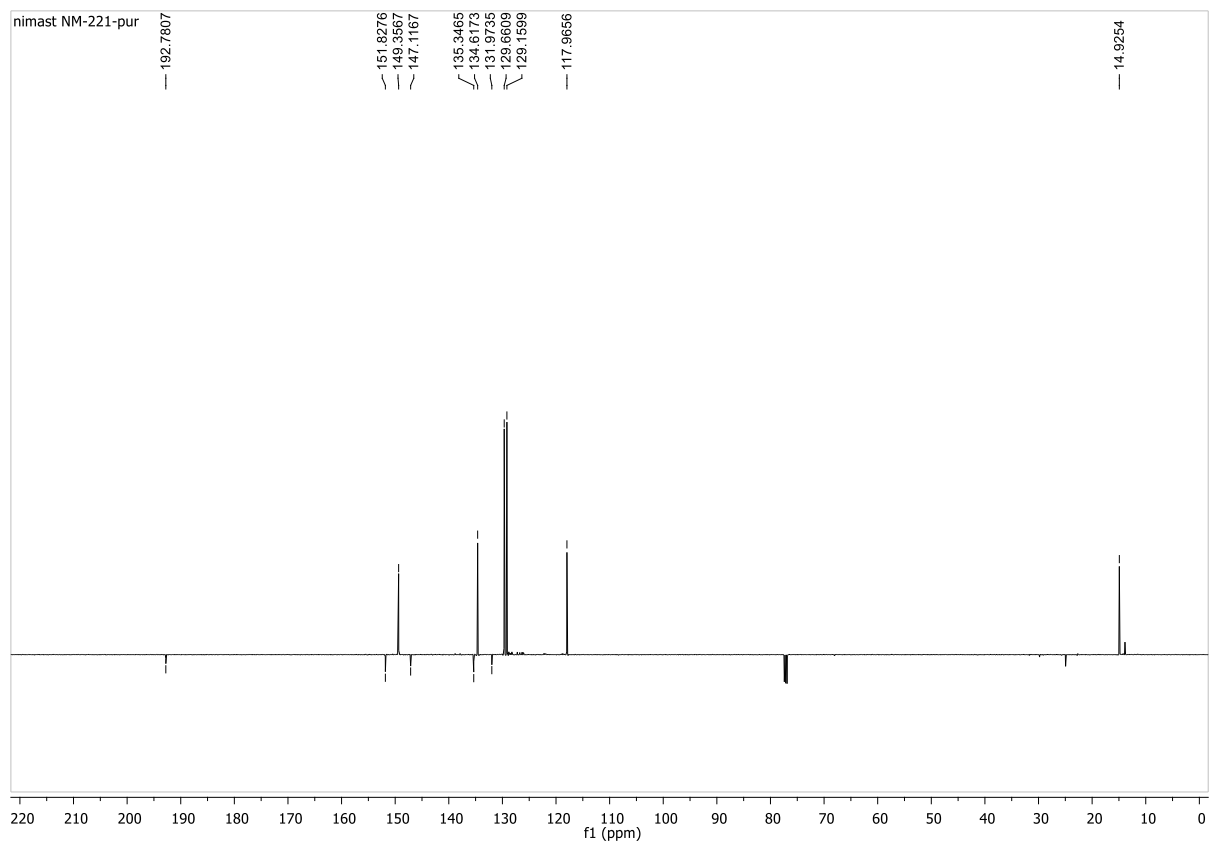


3-Benzoyl-2-chloro-4-(methylthio)pyridine (21)

^1H (CDCl_3 , 300 K, 300 MHz)

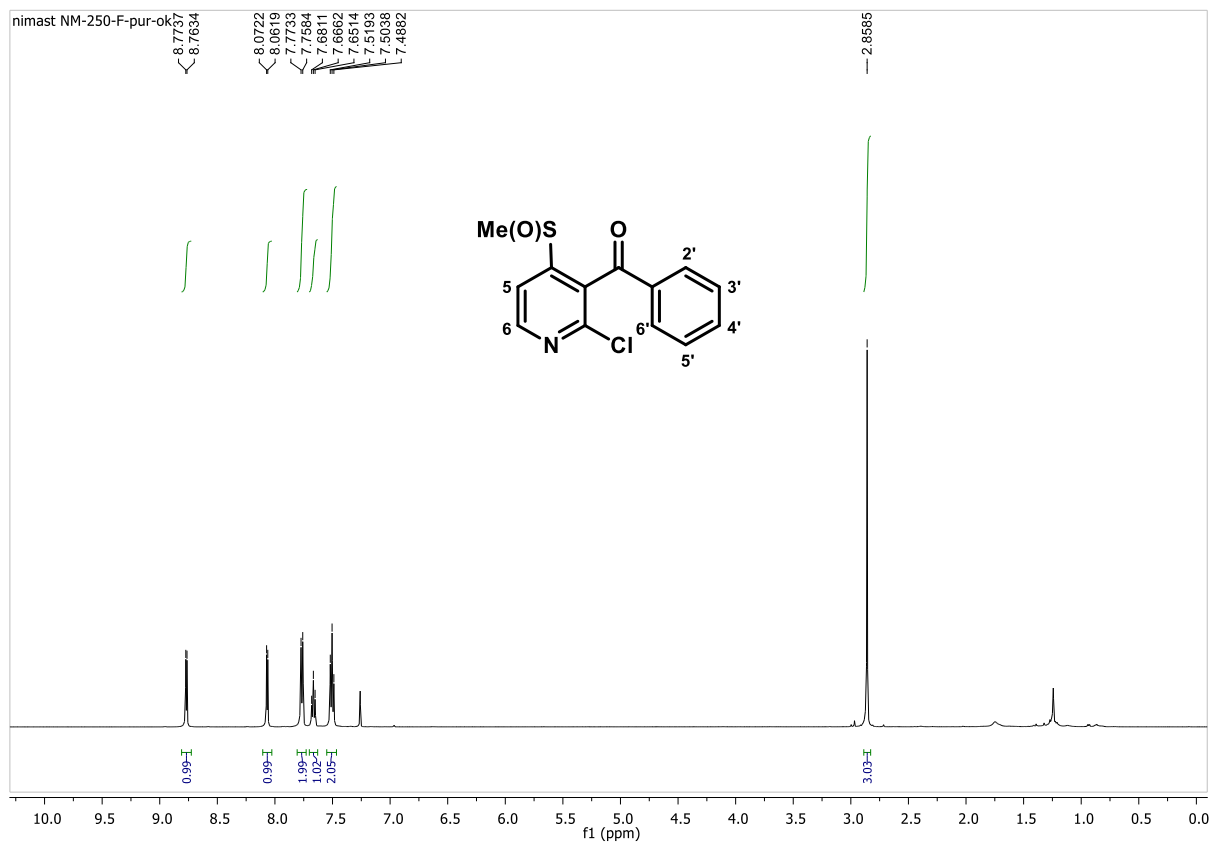


JMOD (CDCl_3 , 300 K, 126 MHz)

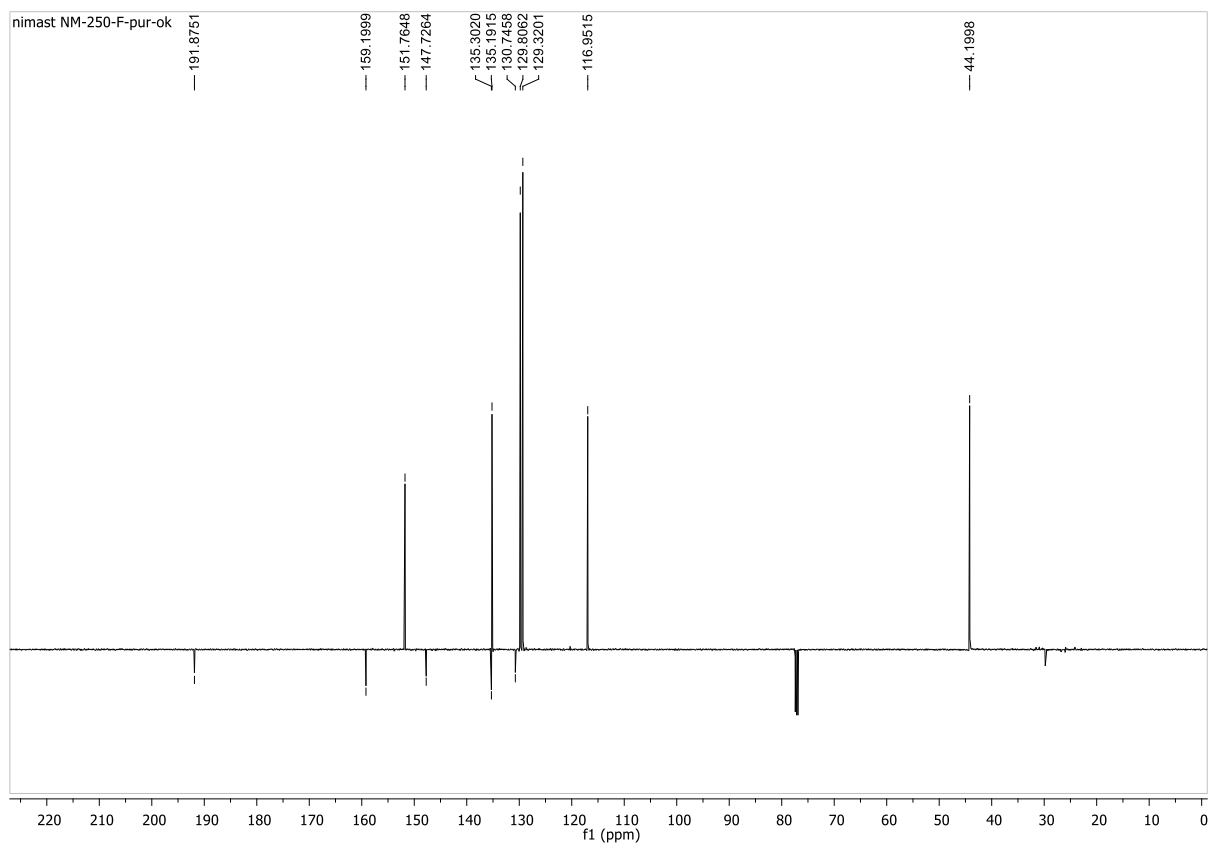


3-Benzoyl-2-chloro-4-(methylsulfinyl)pyridine (22a)

^1H (CDCl_3 , 300 K, 500 MHz)

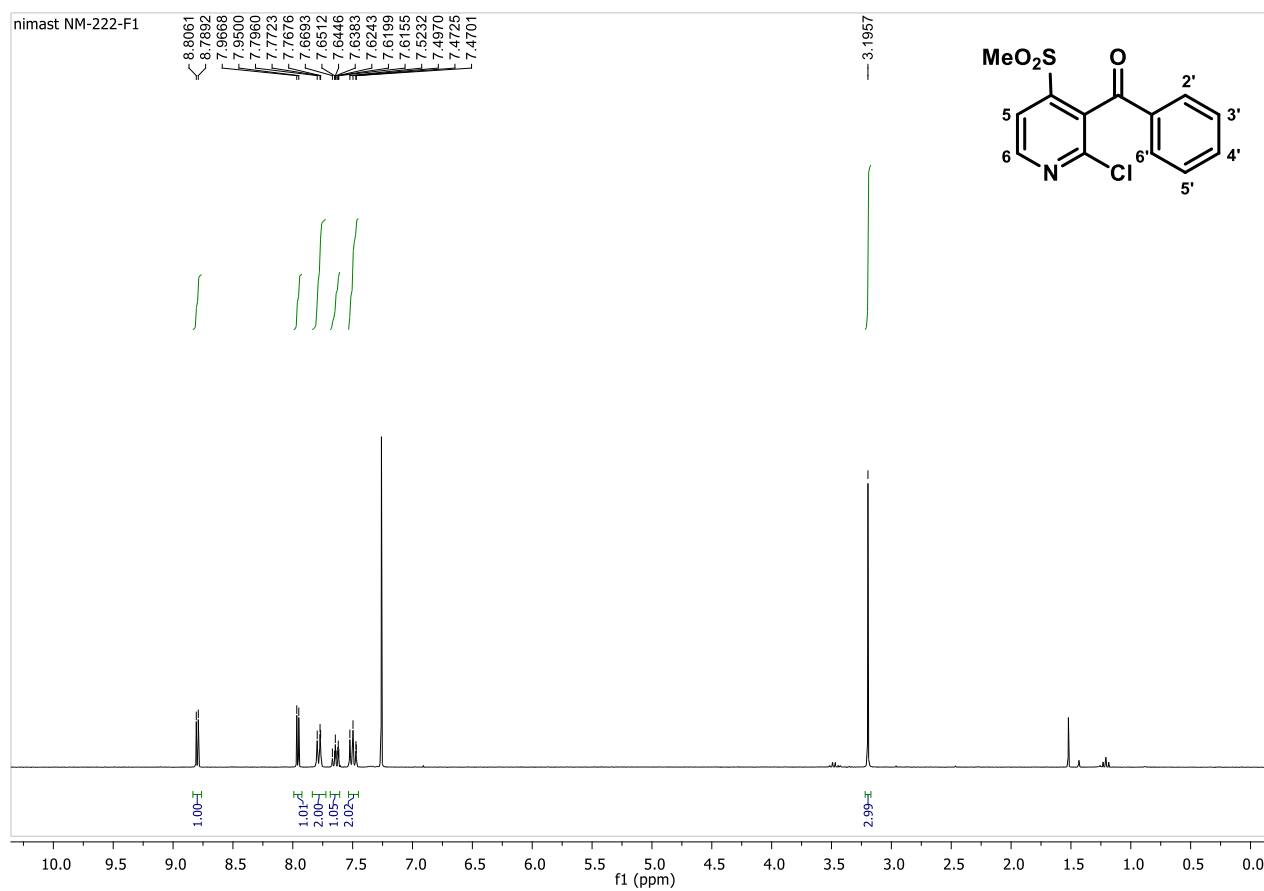


JMOD (CDCl_3 , 300 K, 126 MHz)



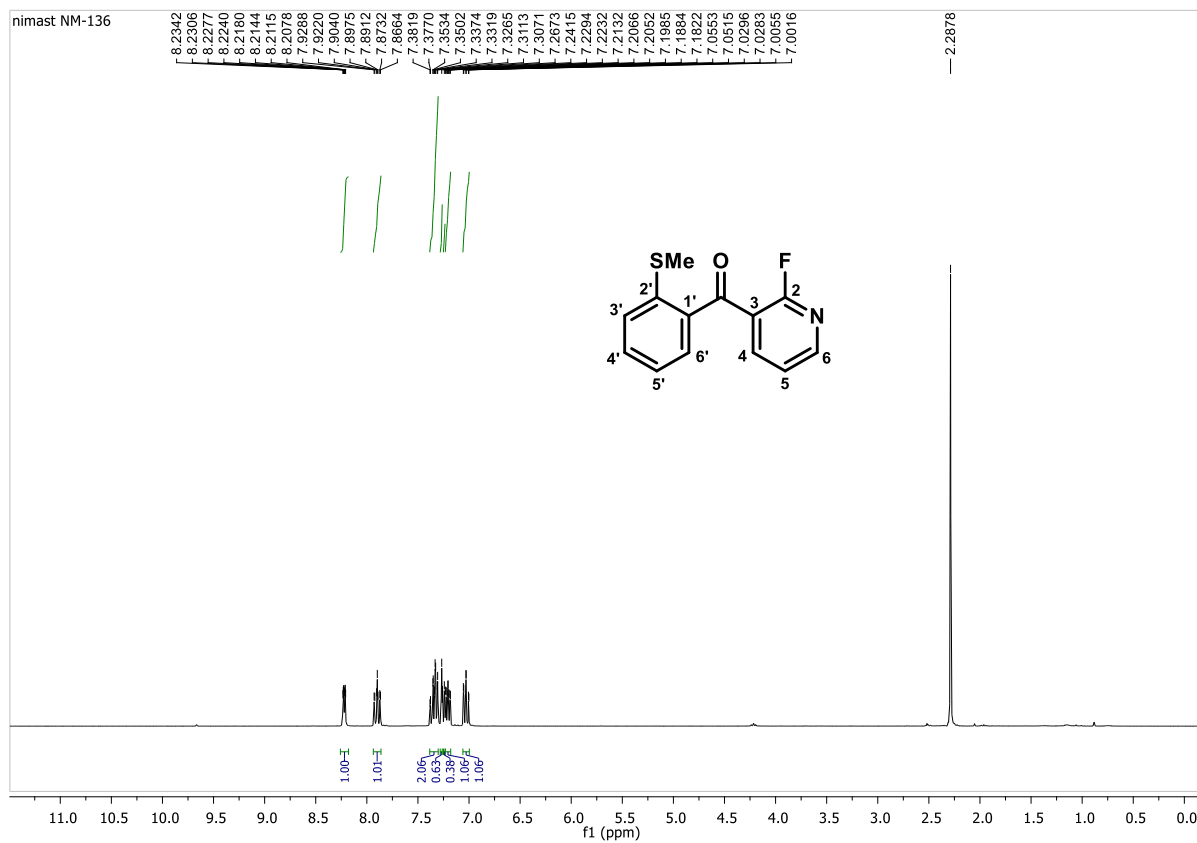
3-Benzoyl-2-chloro-4-(methanesulfonyl)pyridine (22b)

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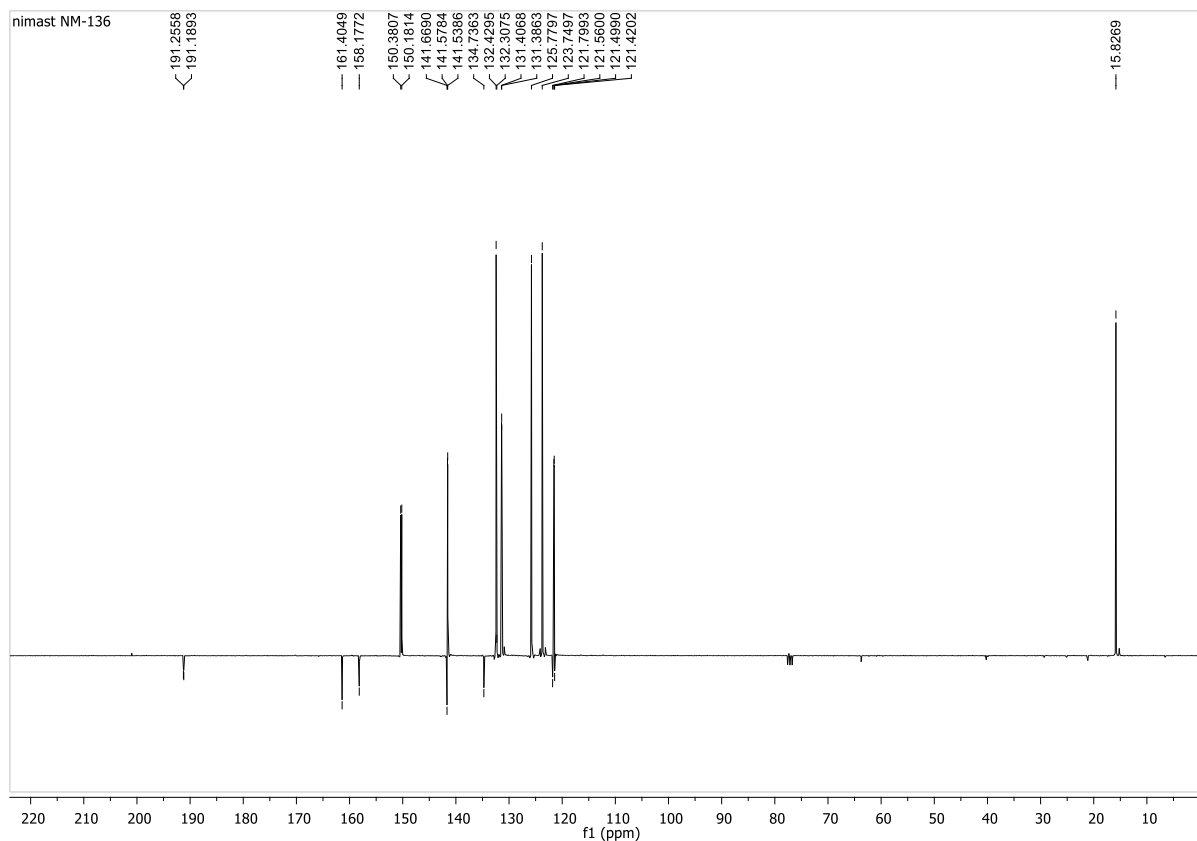


2-Fluoro-3-(2-(methylthio)benzoyl)pyridine (24a)

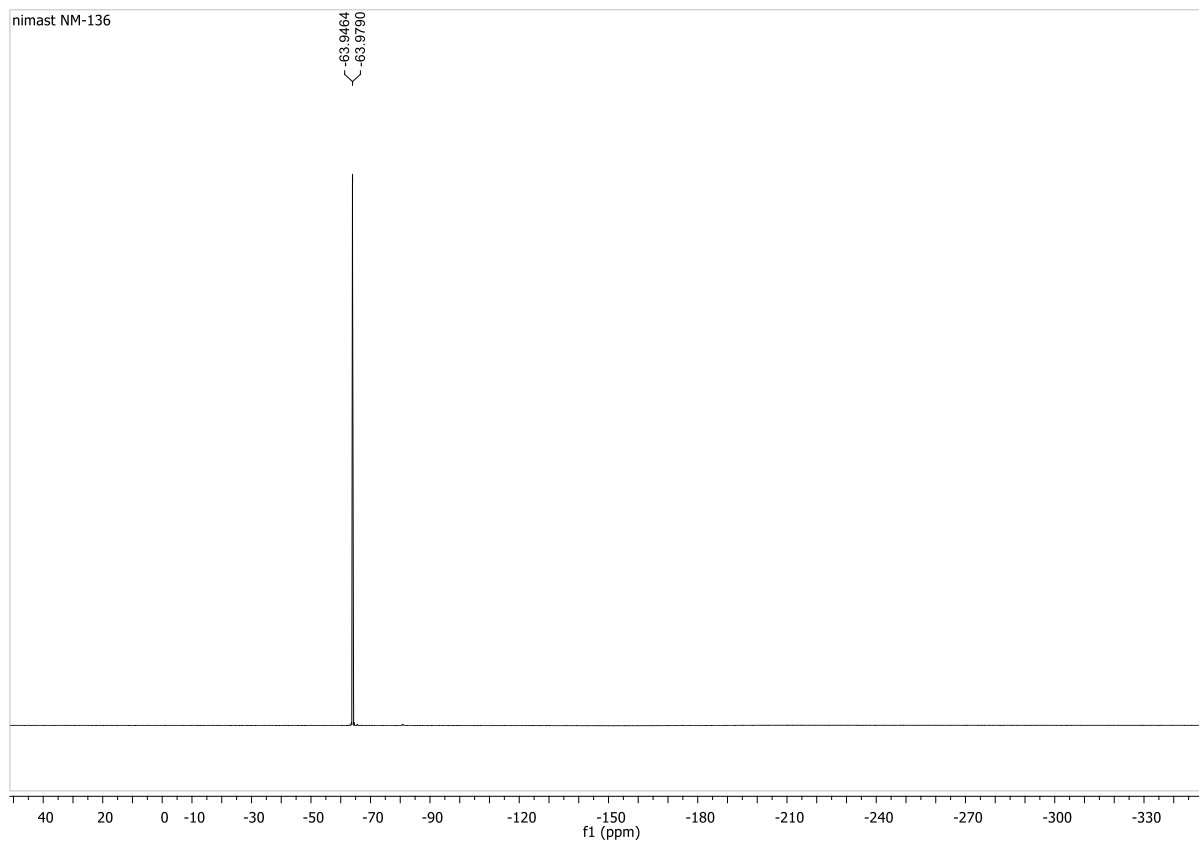
^1H (CDCl_3 , 300 K, 300 MHz)



JMOD (CDCl_3 , 300 K, 75 MHz)

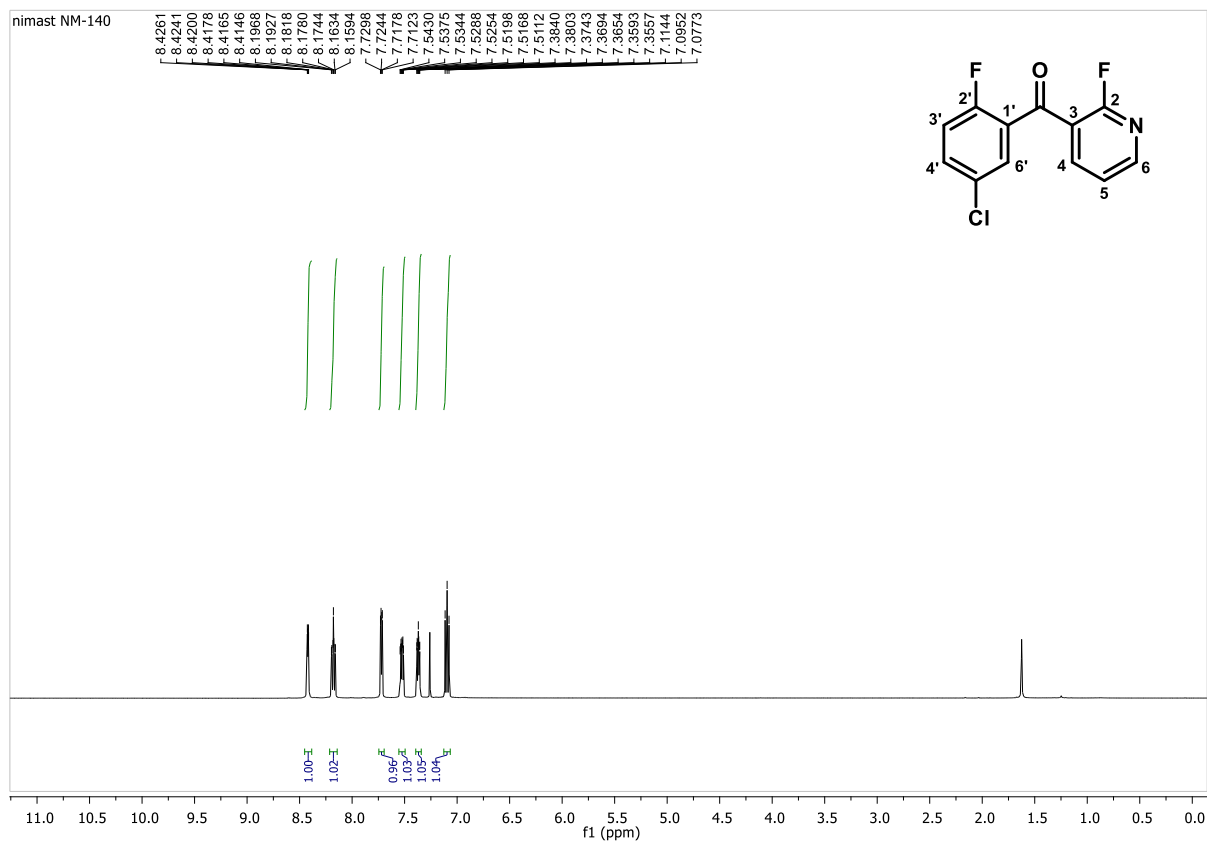


^{19}F (CDCl_3 , 300 K, 282 MHz)

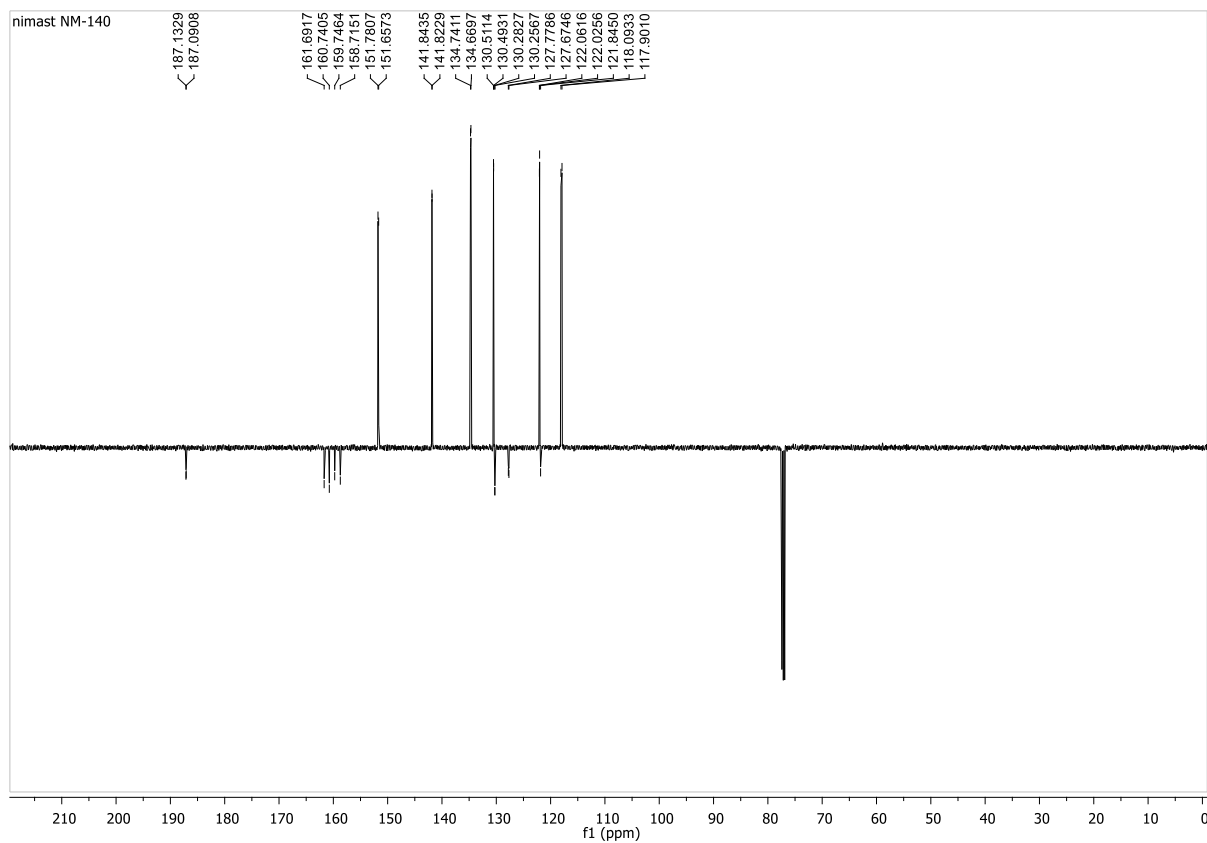


2-Fluoro-3-(5-chloro-2-fluorobenzoyl)pyridine (24b)

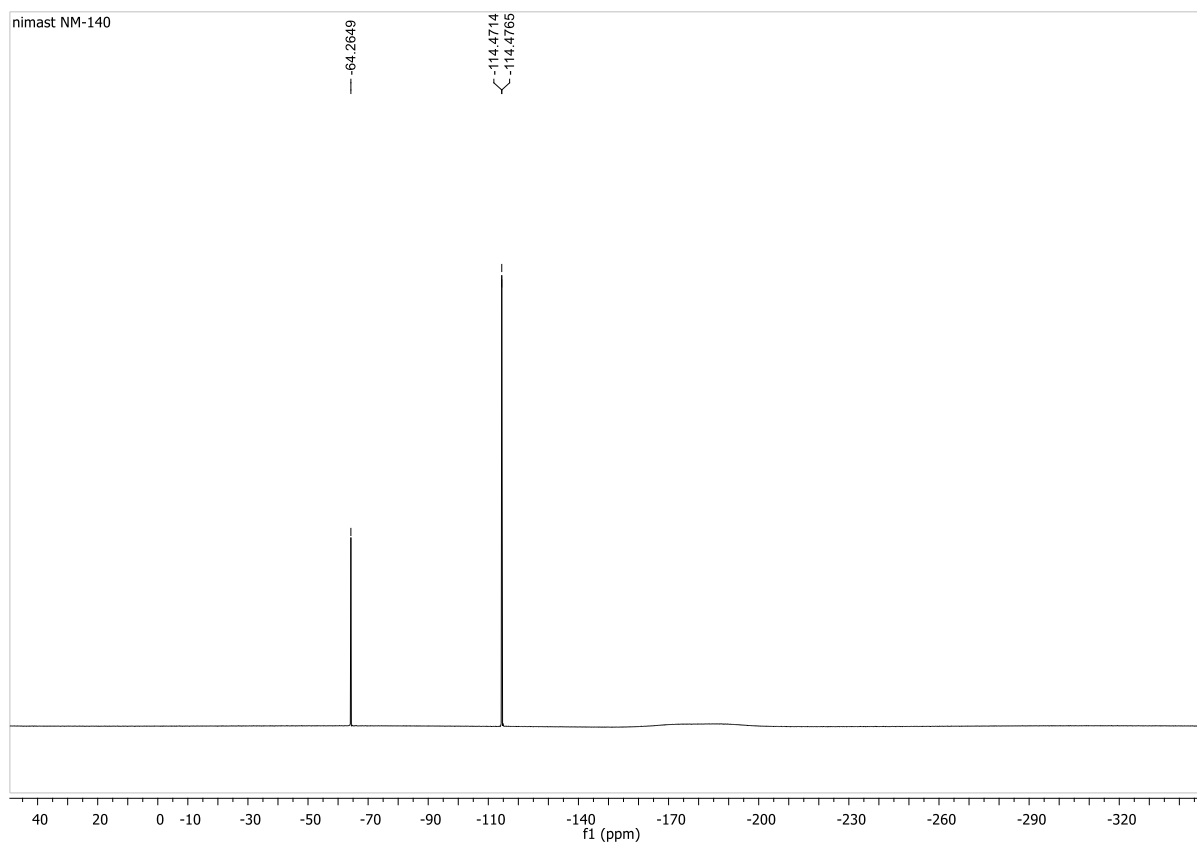
^1H (CDCl_3 , 300 K, 500 MHz)



JMOD (CDCl_3 , 300 K, 126 MHz)

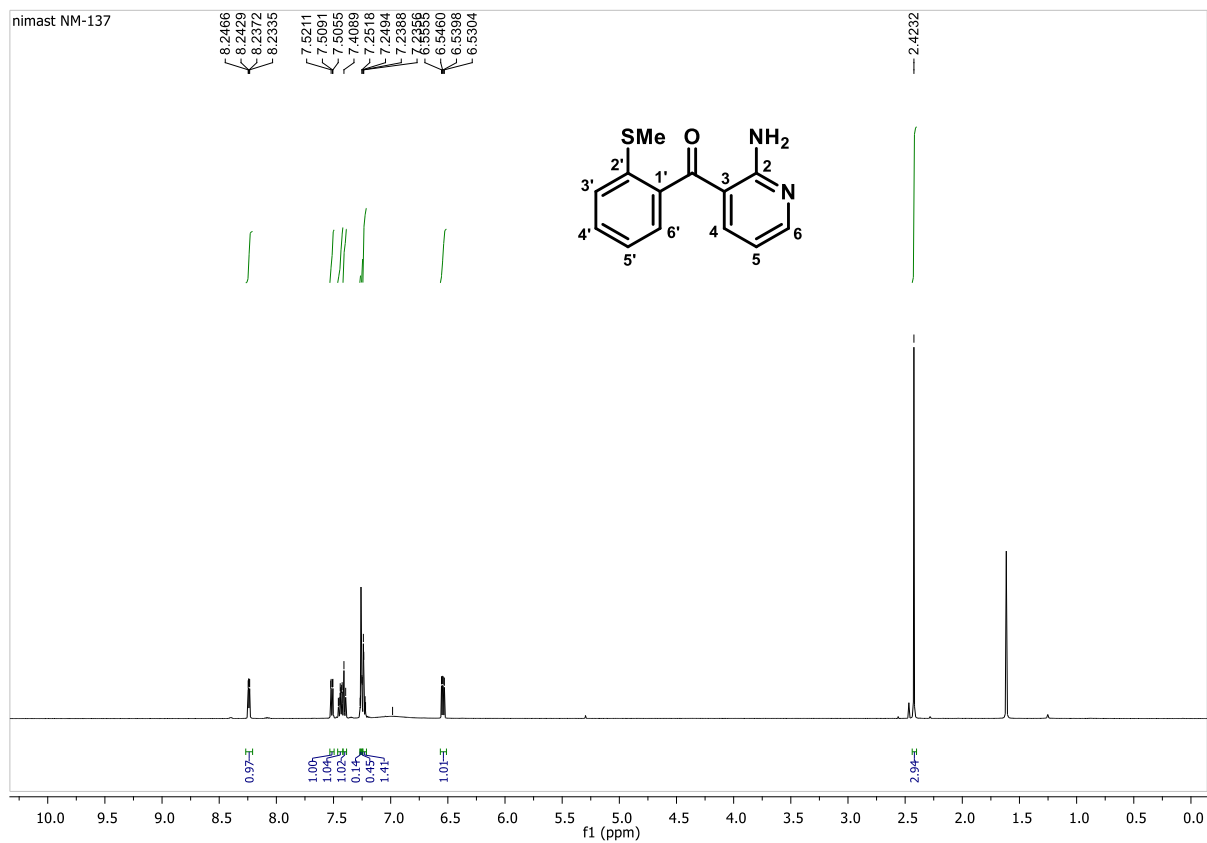


^{19}F (CDCl_3 , 300 K, 471 MHz)

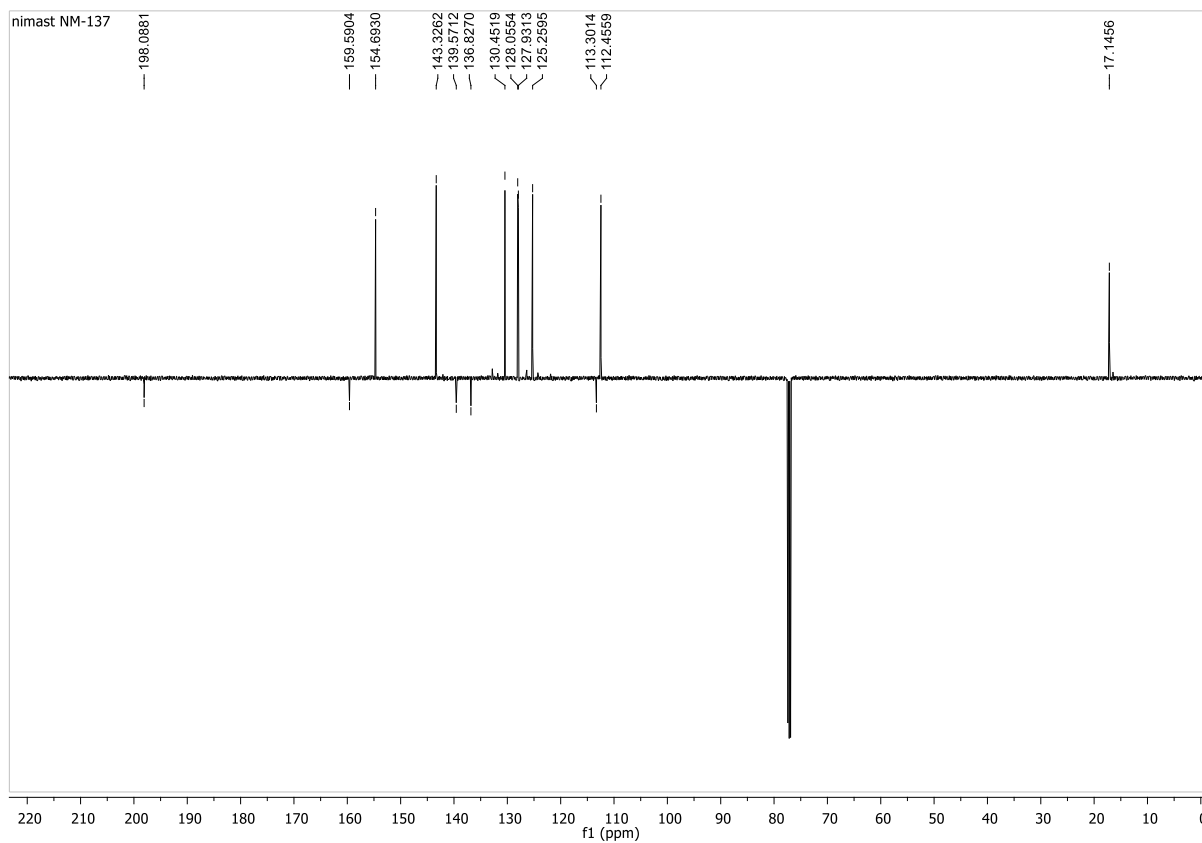


2-Amino-3-(2-(methylthio)benzoyl)pyridine (23)

^1H (CDCl_3 , 300 K, 500 MHz)

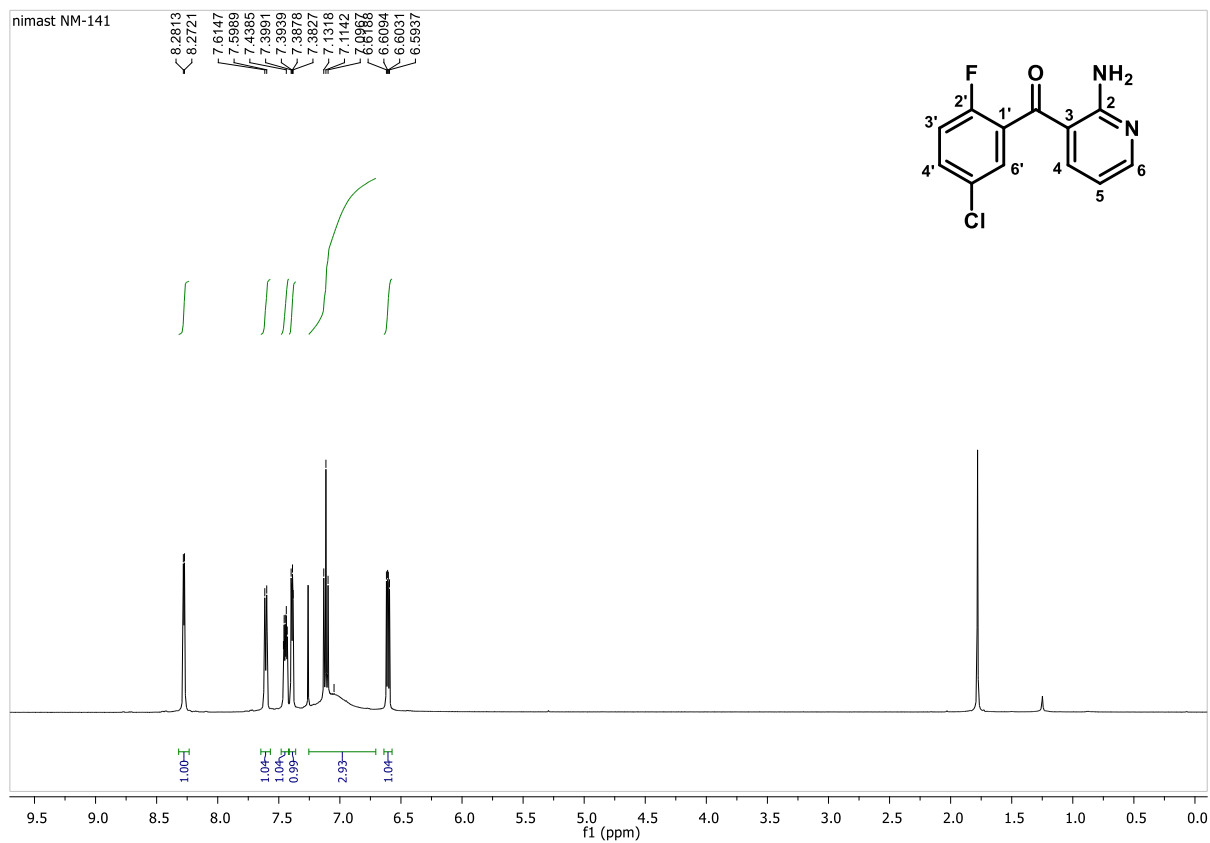


JMOD (CDCl_3 , 300 K, 126 MHz)

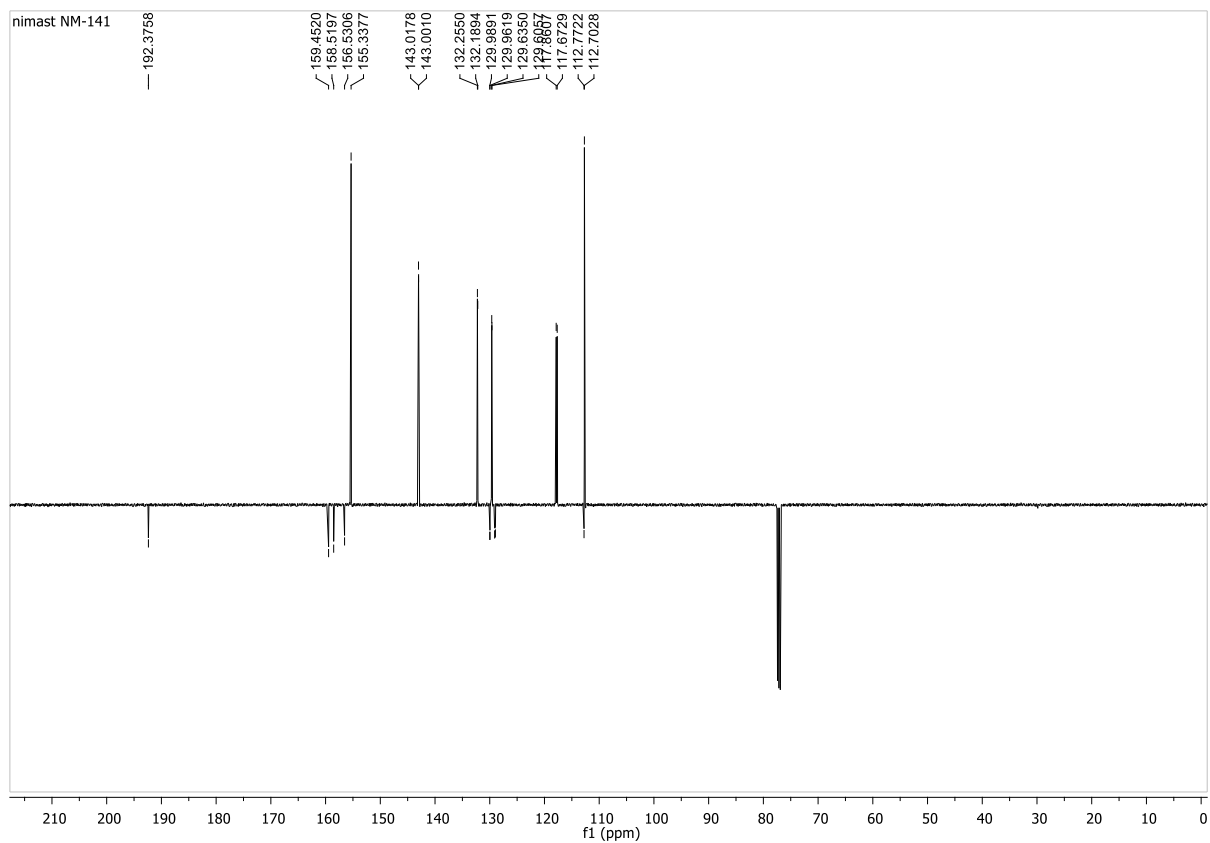


2-Amino-3-(5-chloro-2-fluorobenzoyl)pyridine (25)

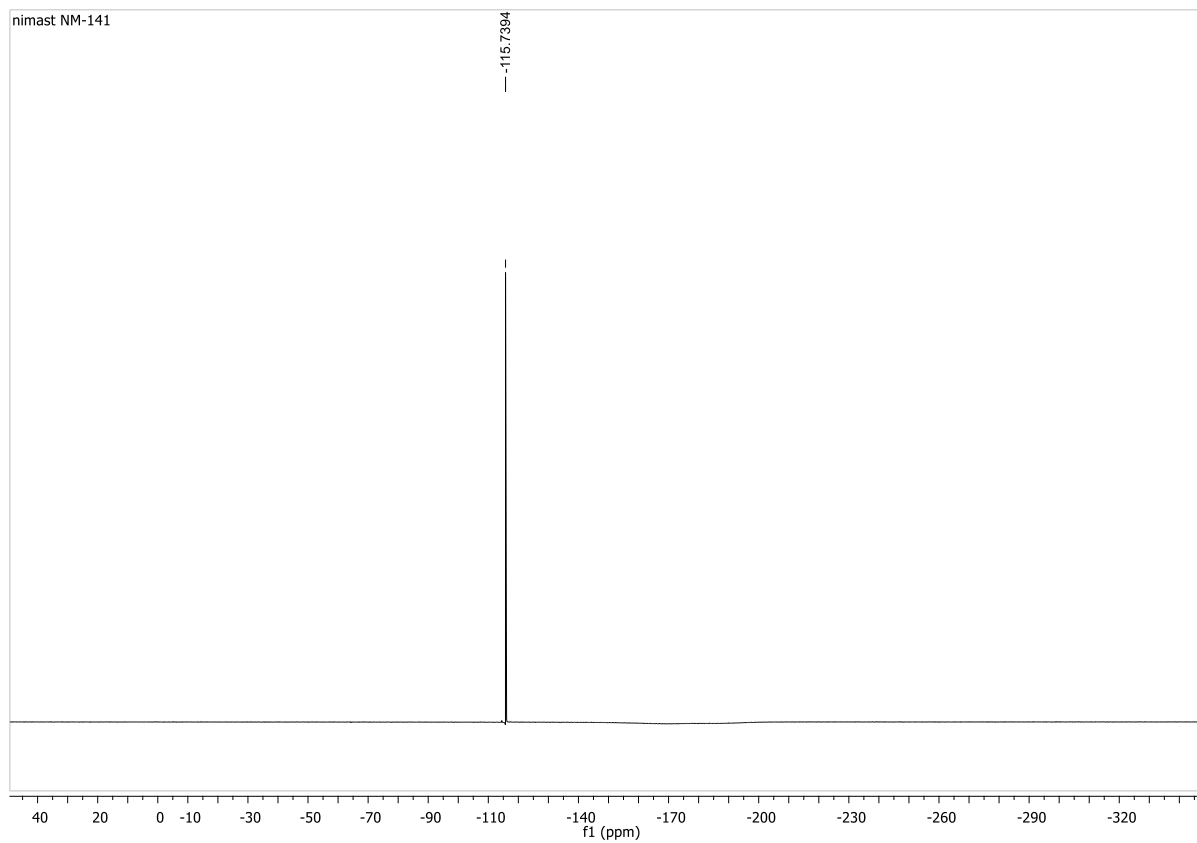
^1H (CDCl_3 , 300 K, 500 MHz)



JMOD (CDCl_3 , 300 K, 126 MHz)

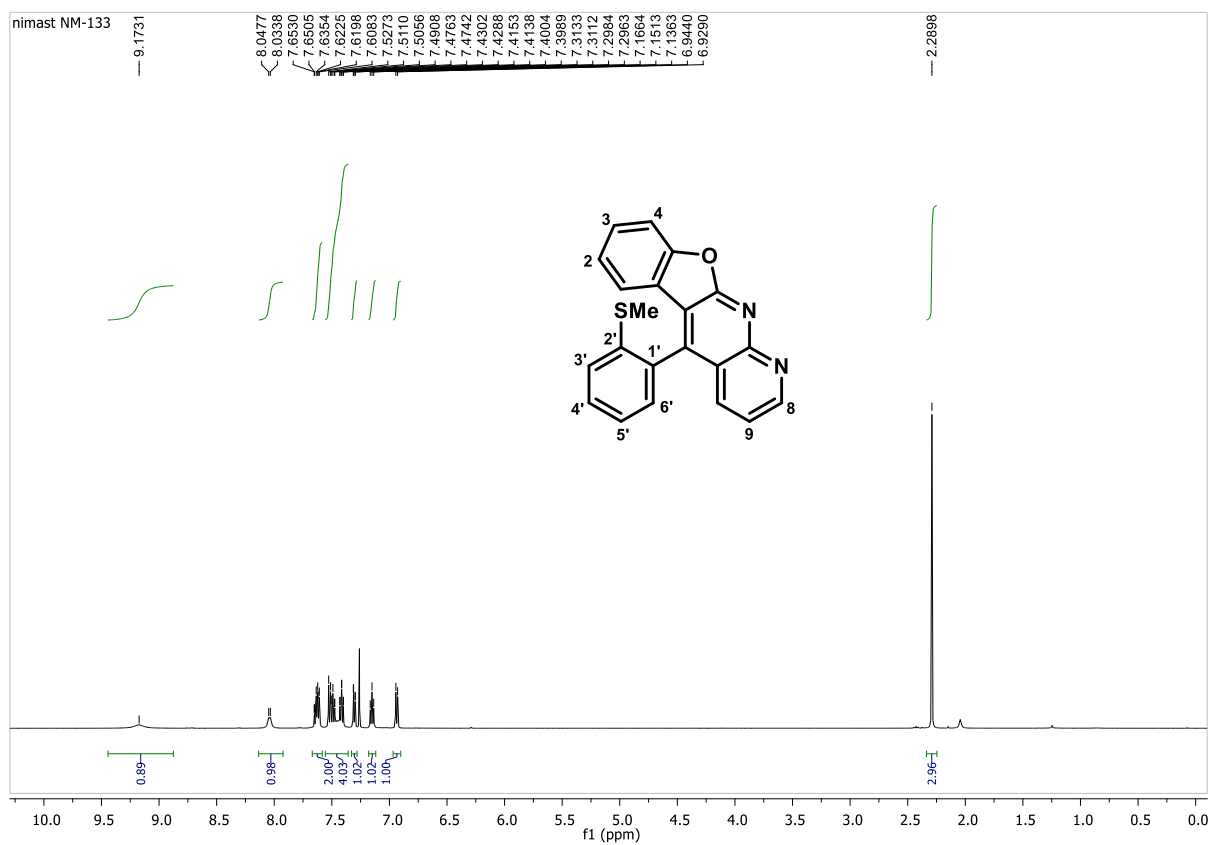


^{19}F (CDCl_3 , 300 K, 471 MHz)

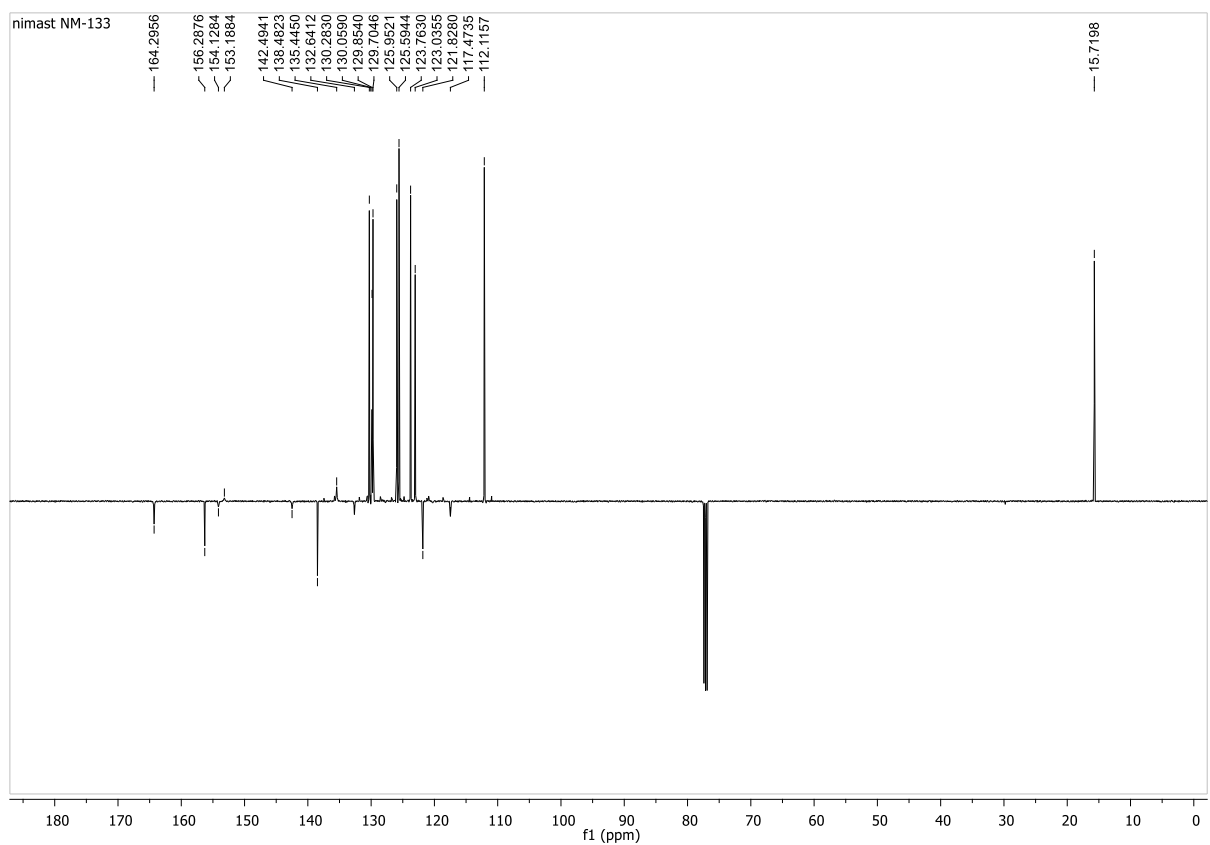


11-(2-(Methylthio)phenyl)benzofuro[2,3-b]1,8-naphthyridine (26)

^1H (CDCl₃, 300 K, 500 MHz)

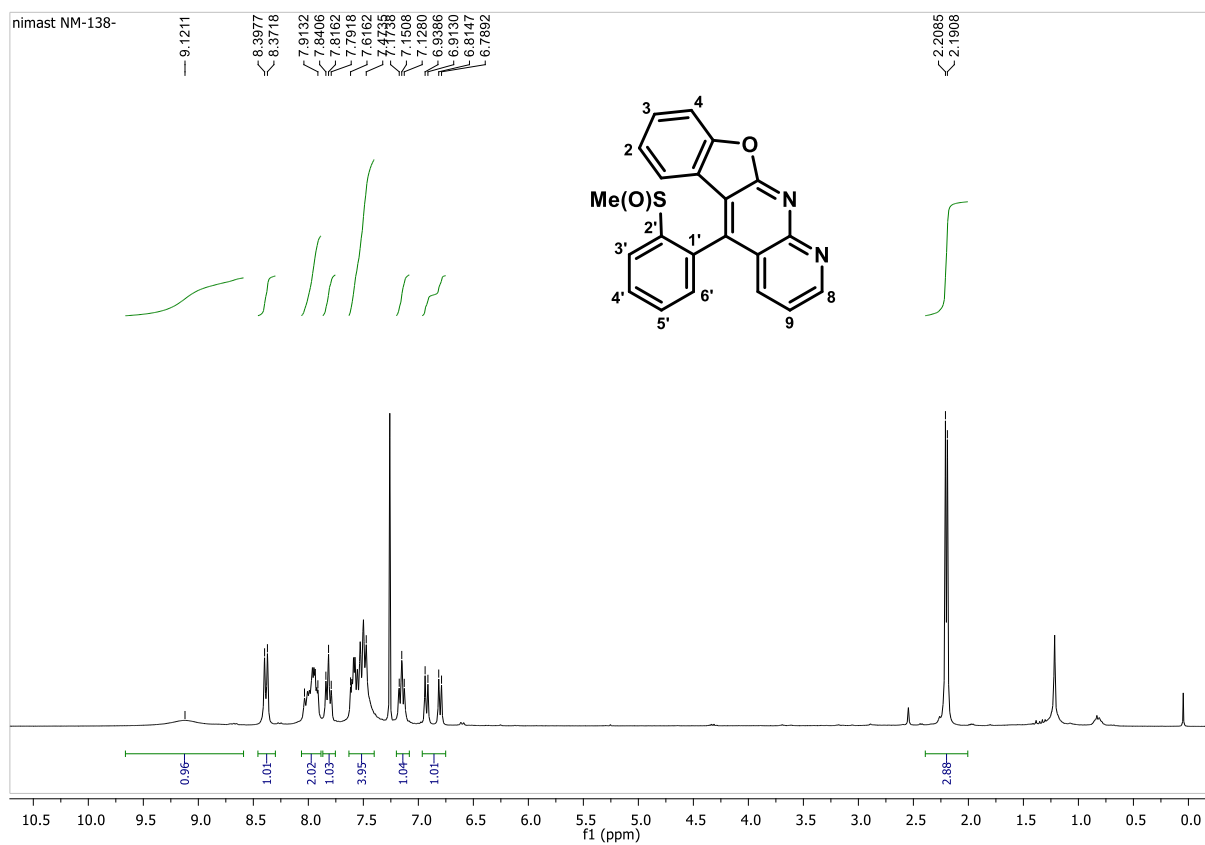


JMOD (CDCl₃, 300 K, 126 MHz)

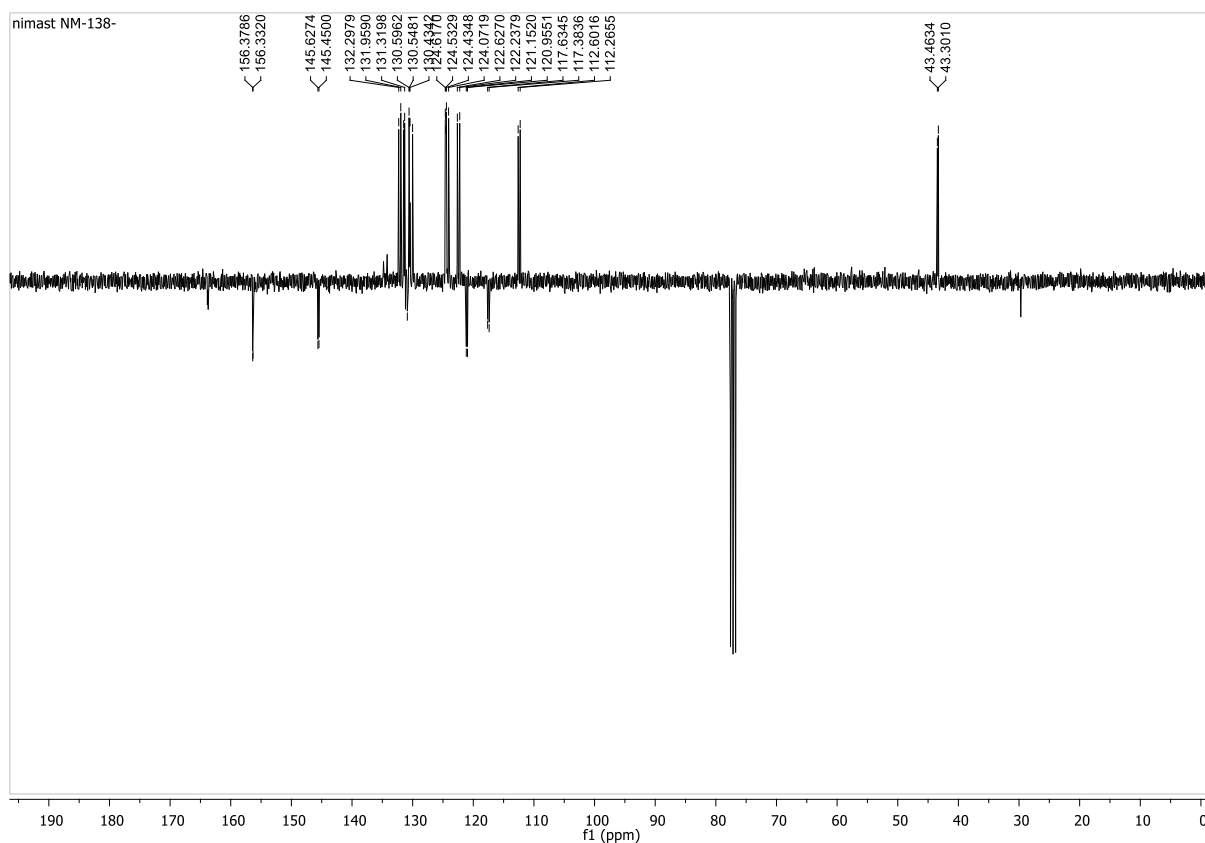


11-(2-(Methylsulfinyl)phenyl)benzofuro[2,3-b]1,8-naphthyridine (27)

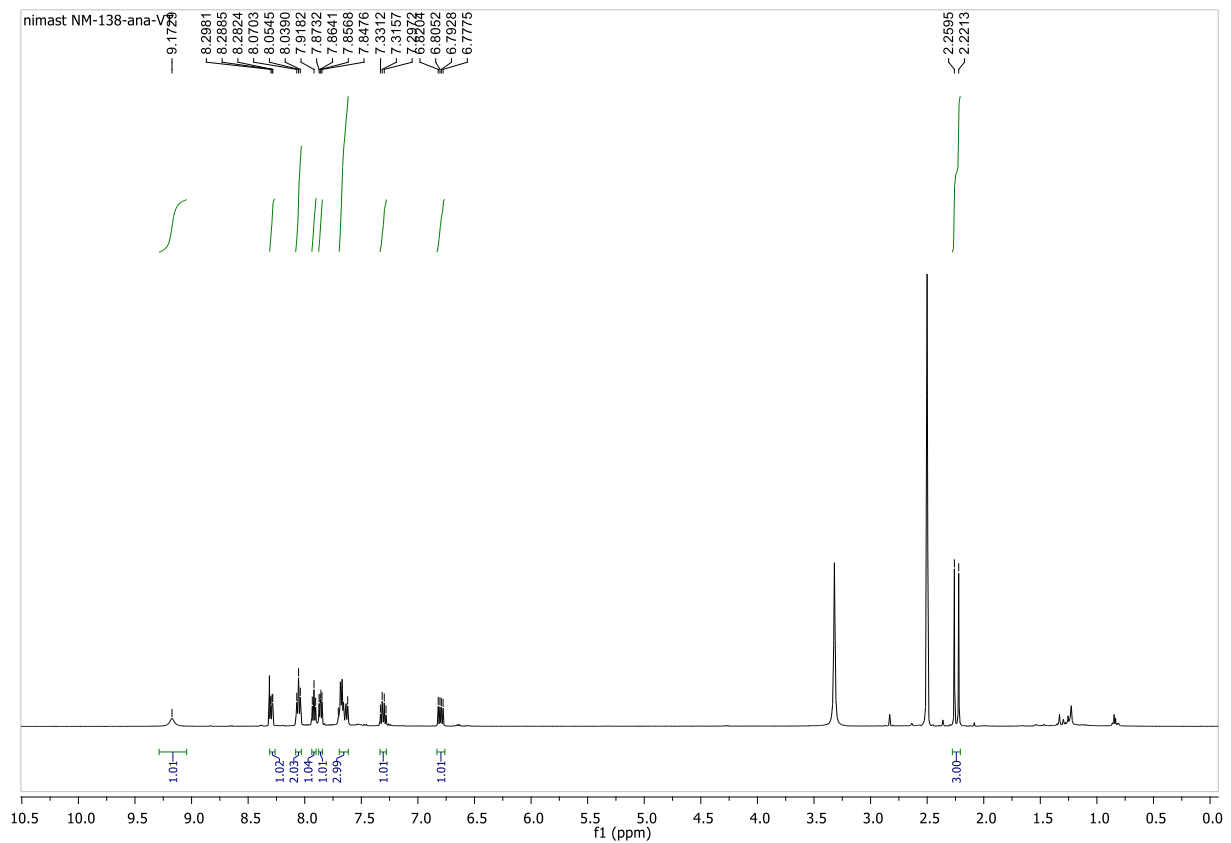
^1H (CDCl₃, 300 K, 300 MHz)



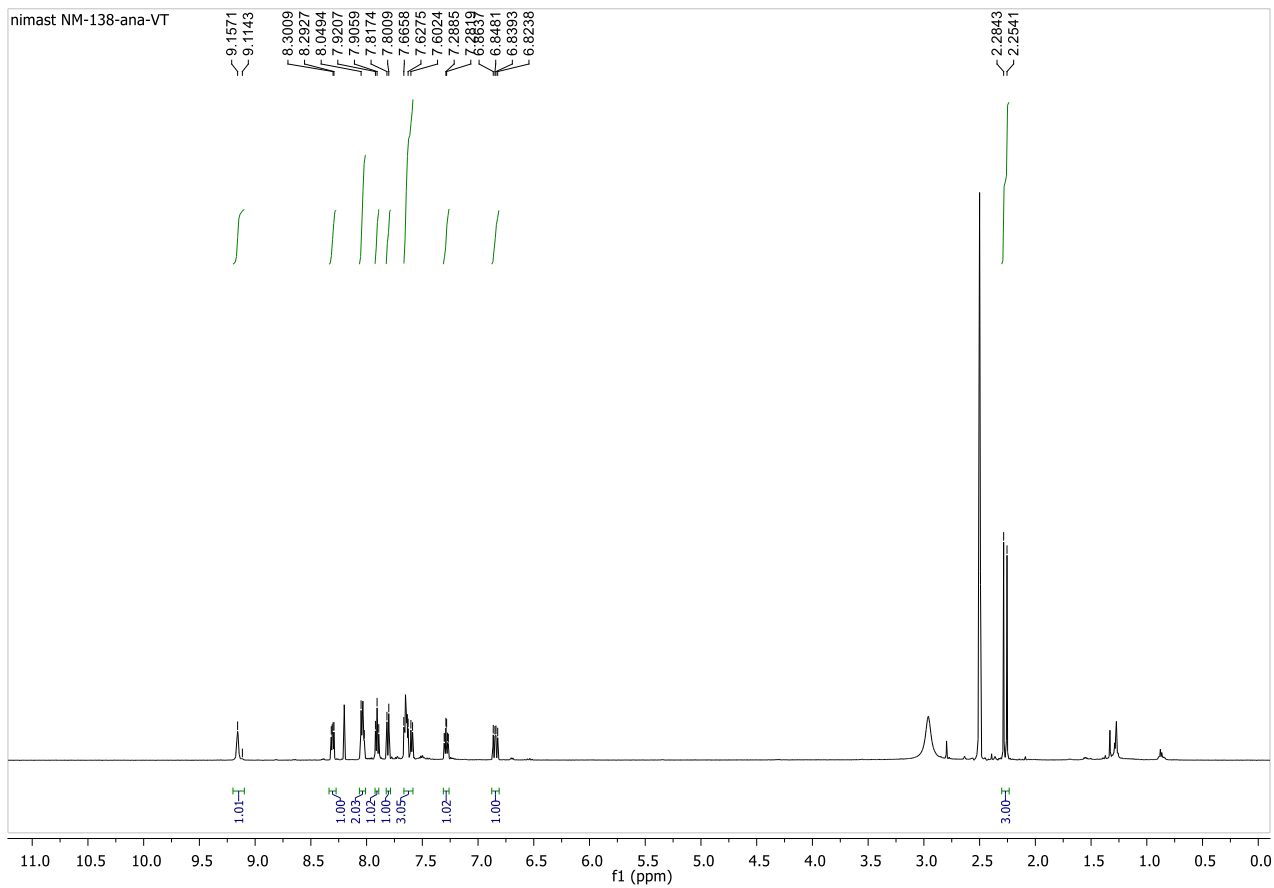
JMOD (CDCl₃, 300 K, 126 MHz)



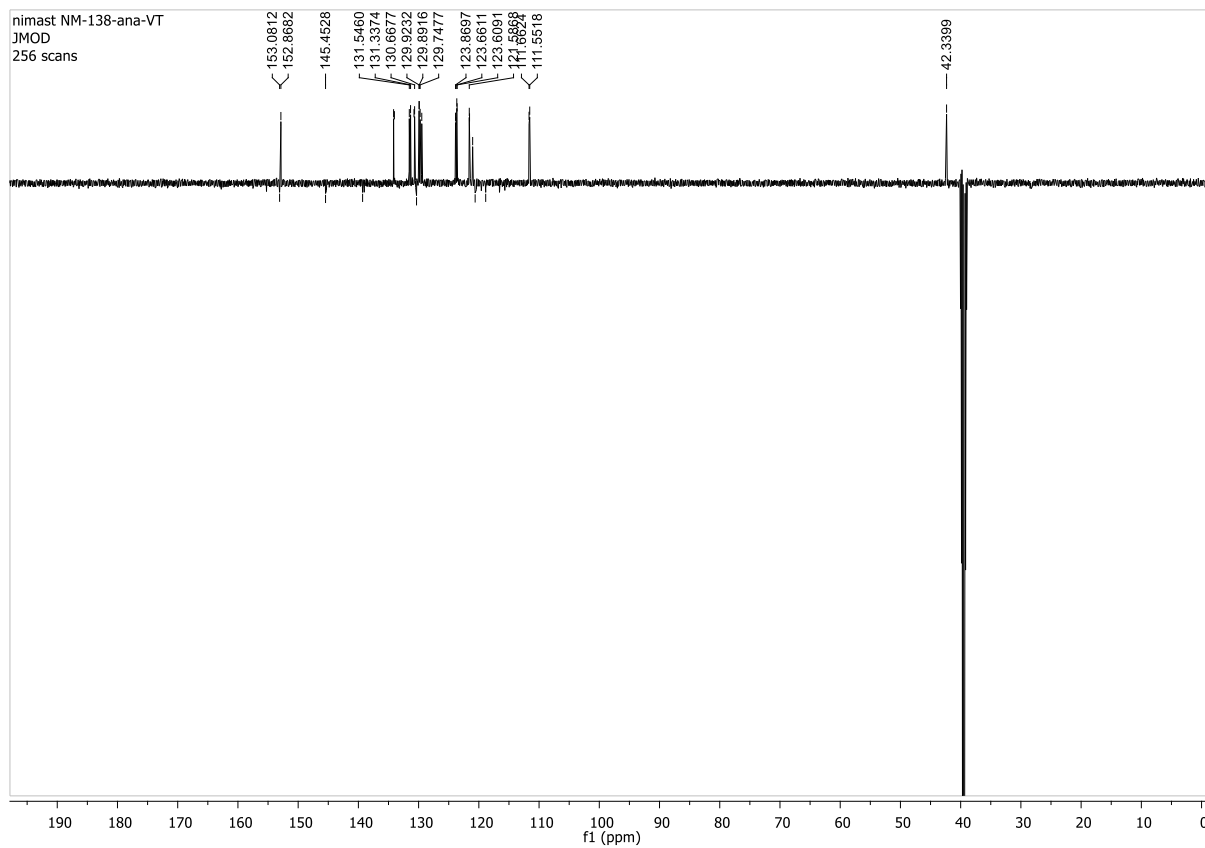
^1H ($(\text{CD}_3)_2\text{SO}$, 300 K, 500 MHz)



^1H ($(\text{CD}_3)_2\text{SO}$, 375 K, 500 MHz)

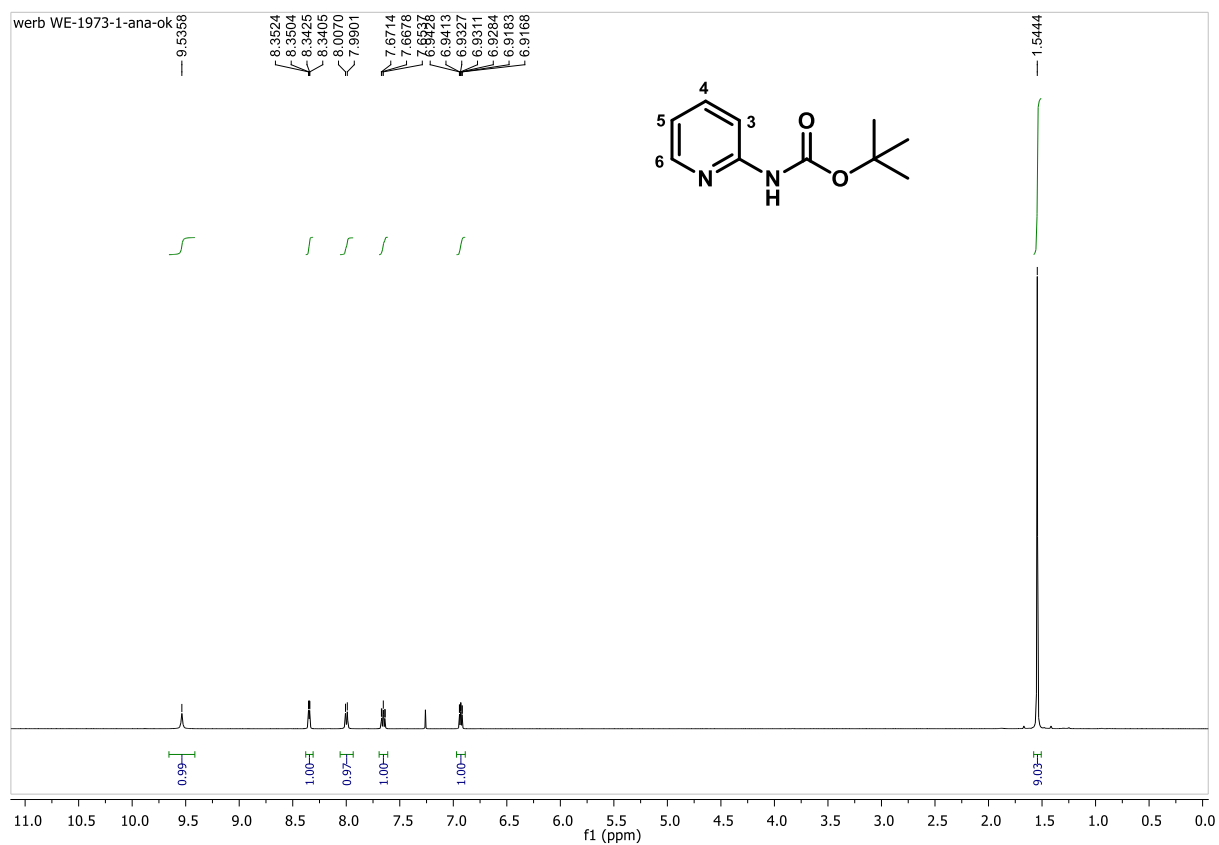


JMOD ((CD₃)₂SO, 375 K, 126 MHz)

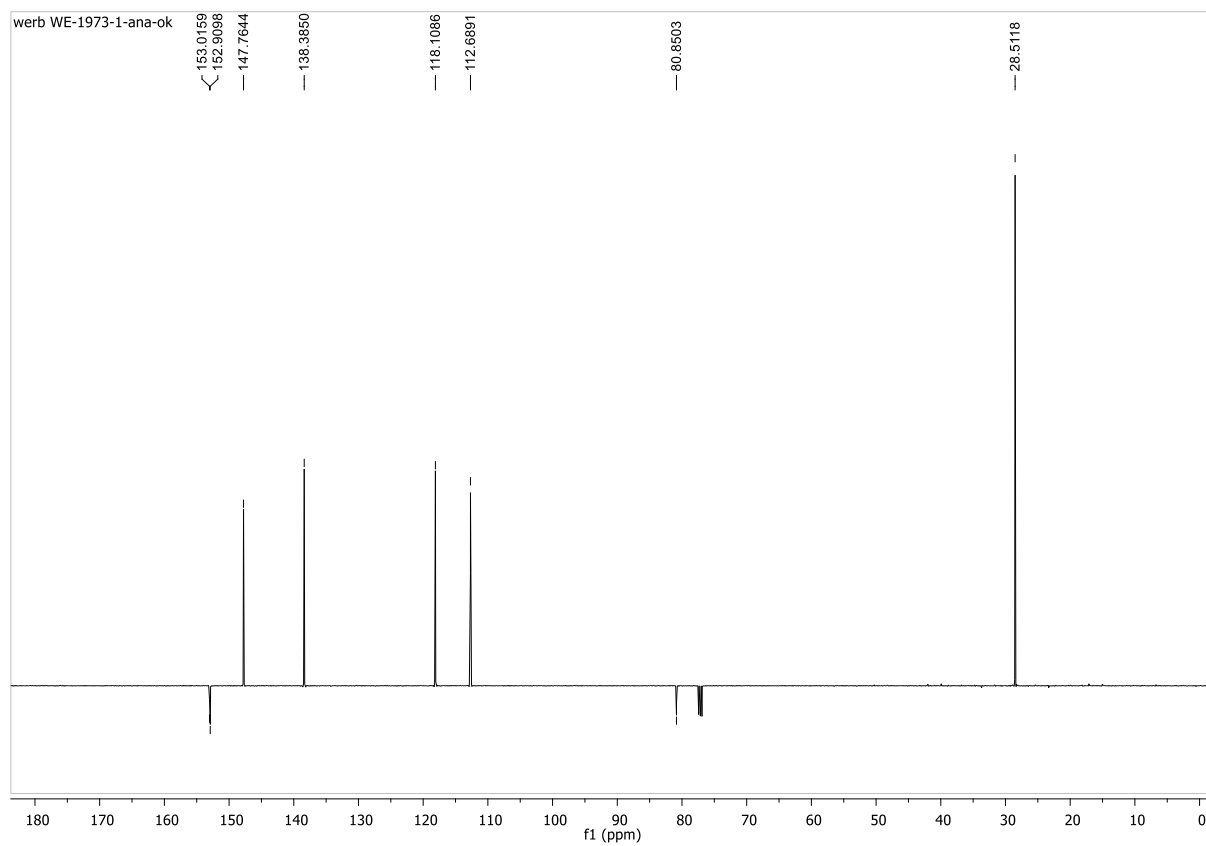


***tert*-Butyl *N*-(2-pyridyl)carbamate**

^1H (CDCl₃, 300 K, 500 MHz)

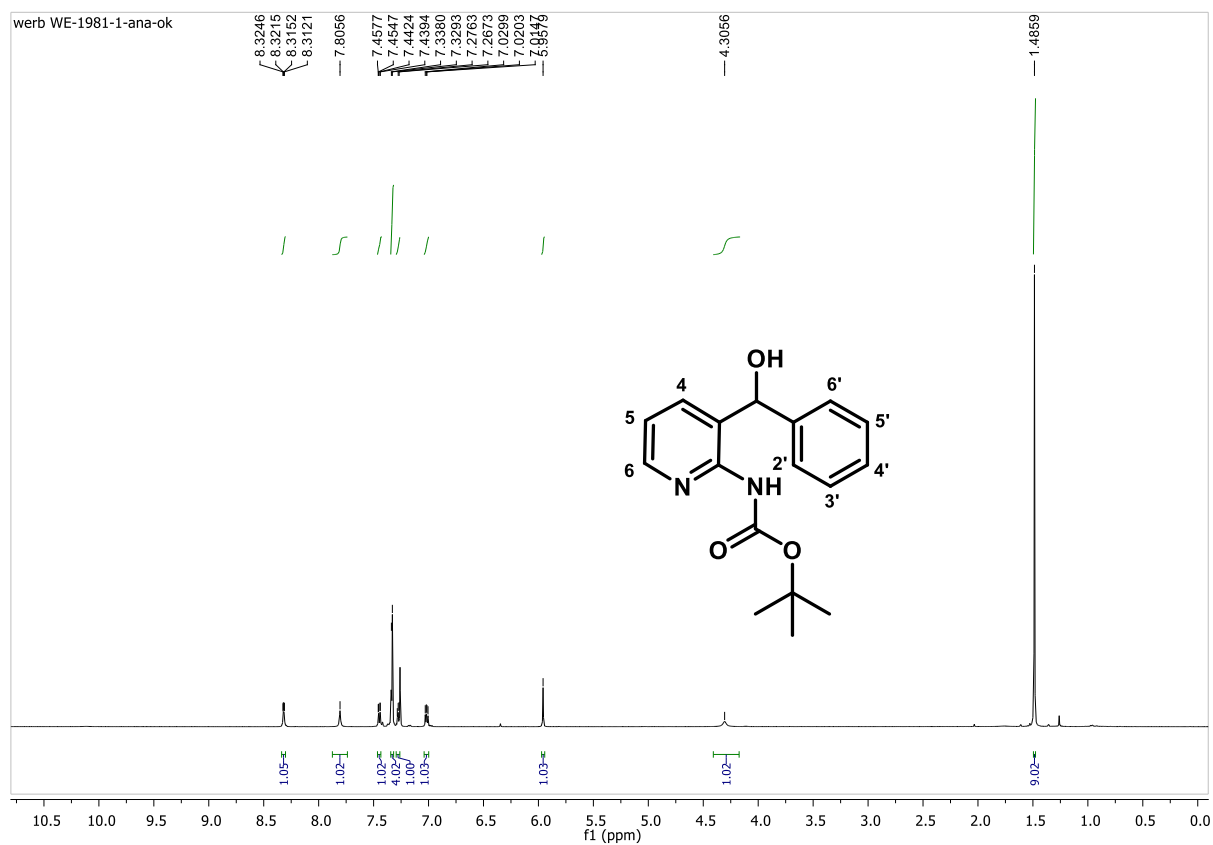


JMOD (CDCl₃, 300 K, 126 MHz)

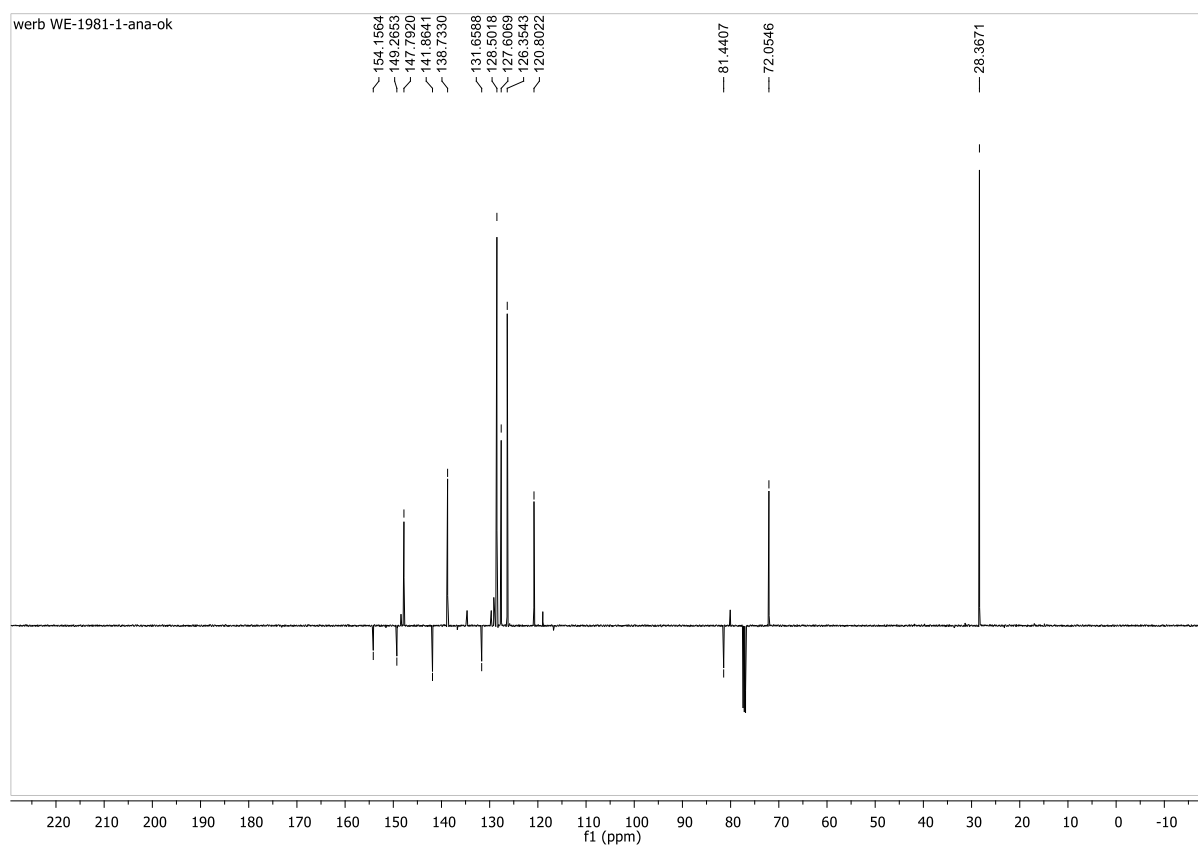


2-(*tert*-Butoxycarbonylamino)-3-((1-phenyl)hydroxymethyl)pyridine (29)

^1H (CDCl_3 , 300 K, 500 MHz)

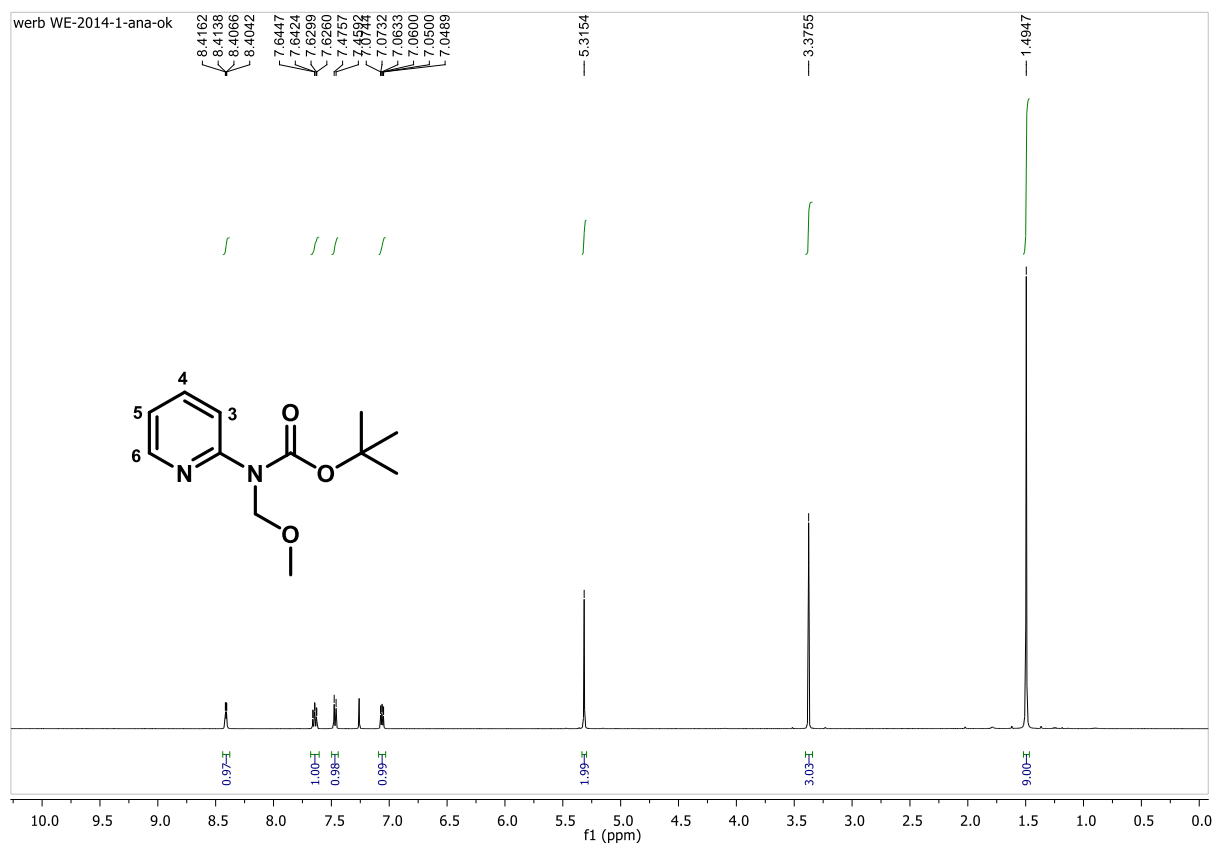


JMOD (CDCl_3 , 300 K, 126 MHz)

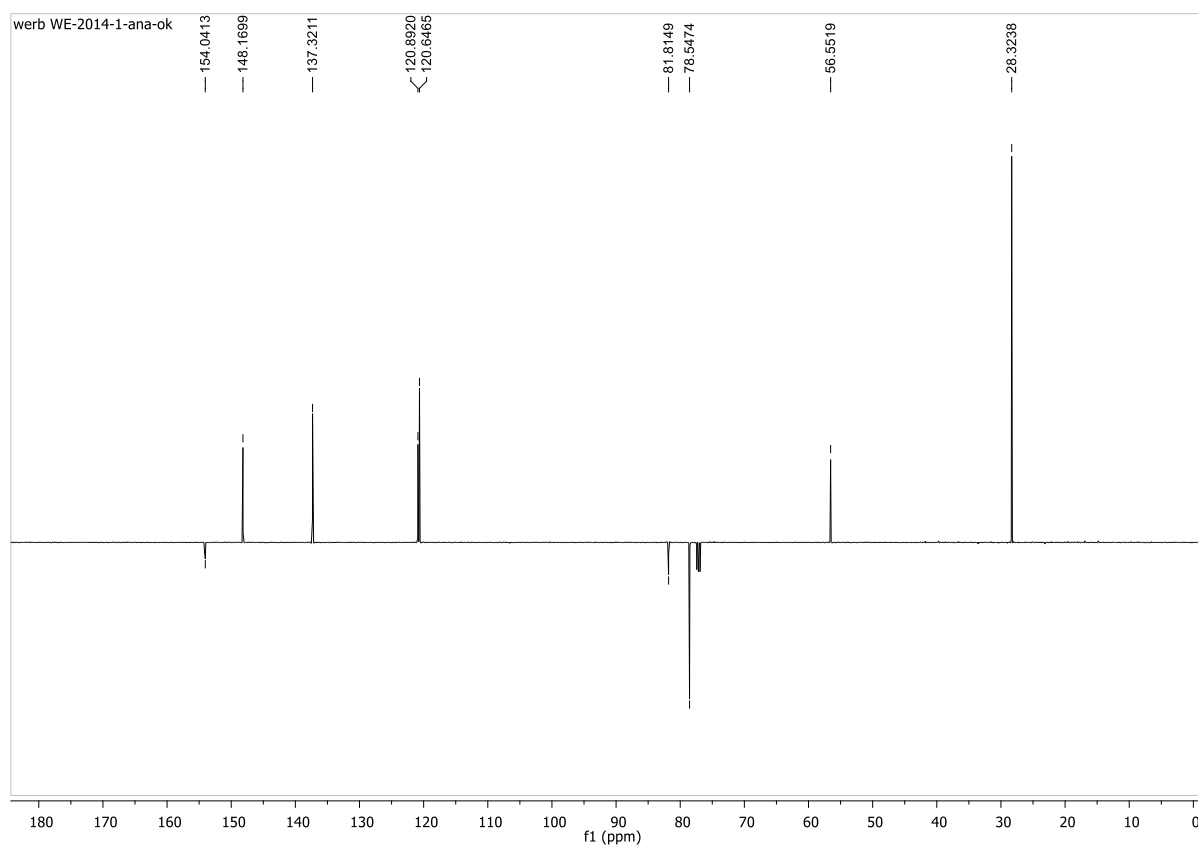


2-((*tert*-Butoxycarbonyl)(methoxymethyl)amino)pyridine

^1H (CDCl_3 , 300 K, 500 MHz)

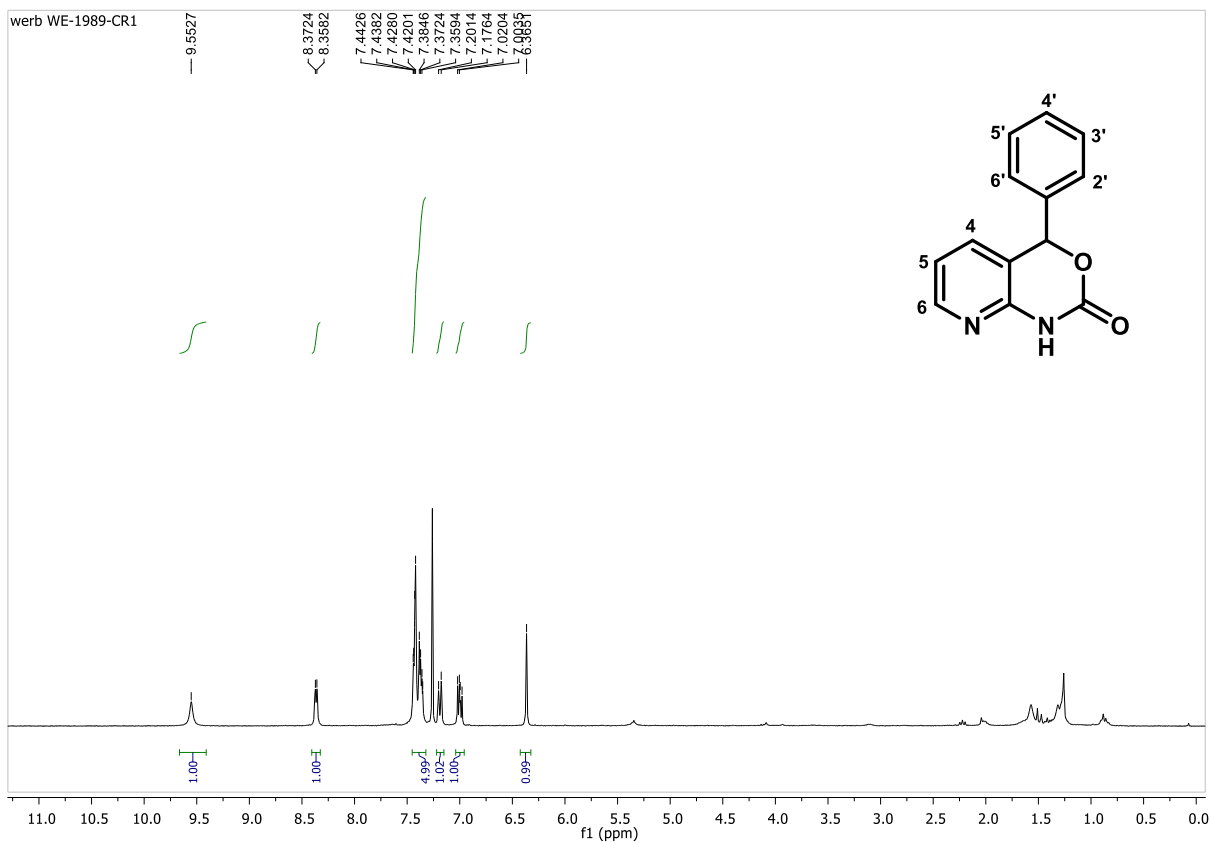


JMOD (CDCl_3 , 300 K, 126 MHz)



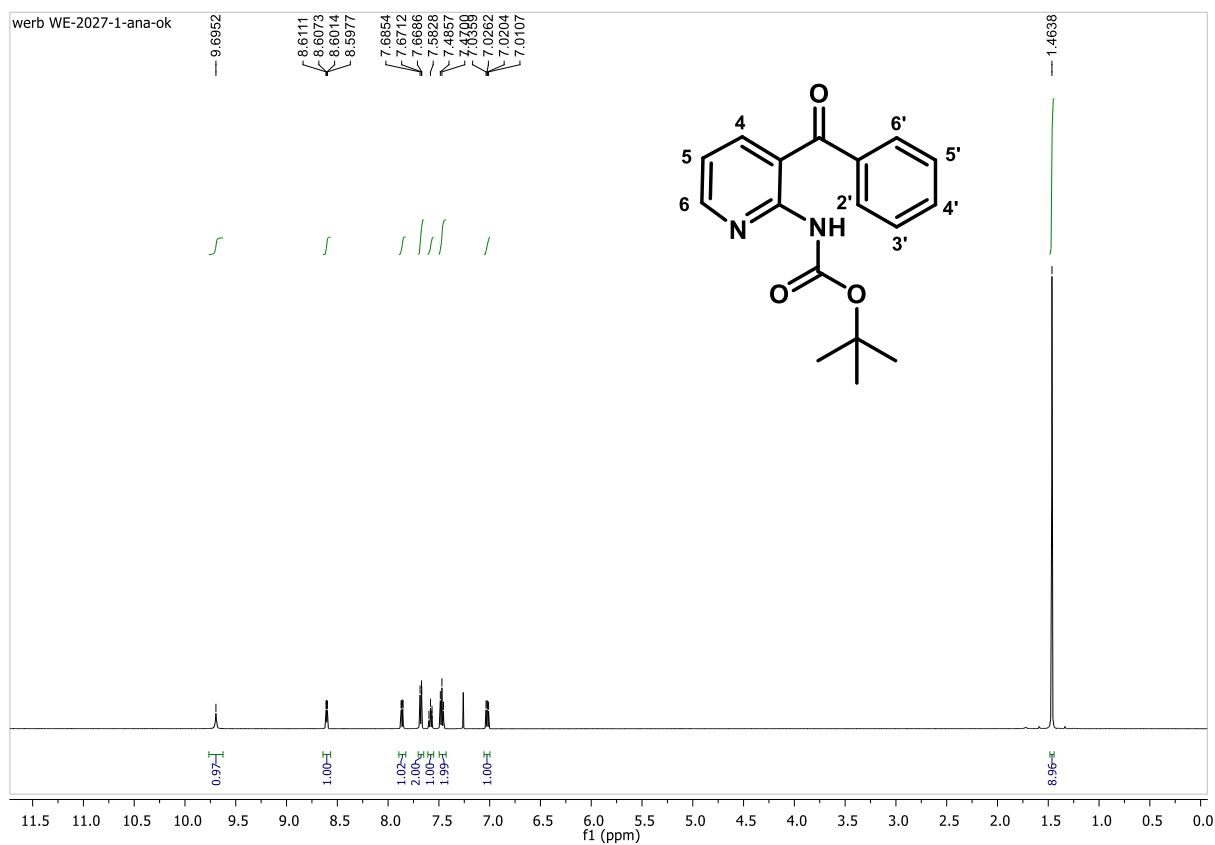
1,4-Dihydro-4-phenylpyrido[2,3-d][1,3]2-oxazinone

^1H (CDCl₃, 300 K, 500 MHz)

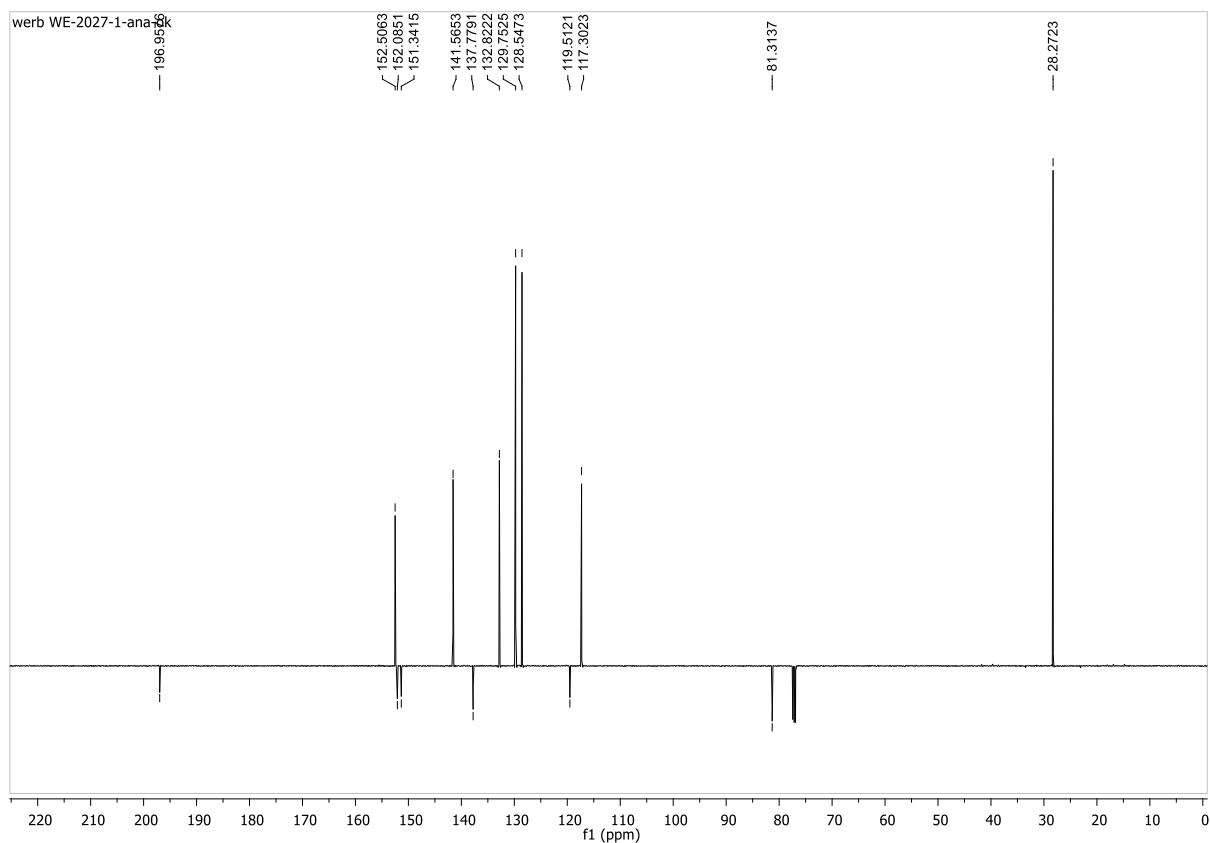


3-Benzoyl-2-(*tert*-butoxycarbonylamino)pyridine (30)

^1H (CDCl_3 , 300 K, 500 MHz)

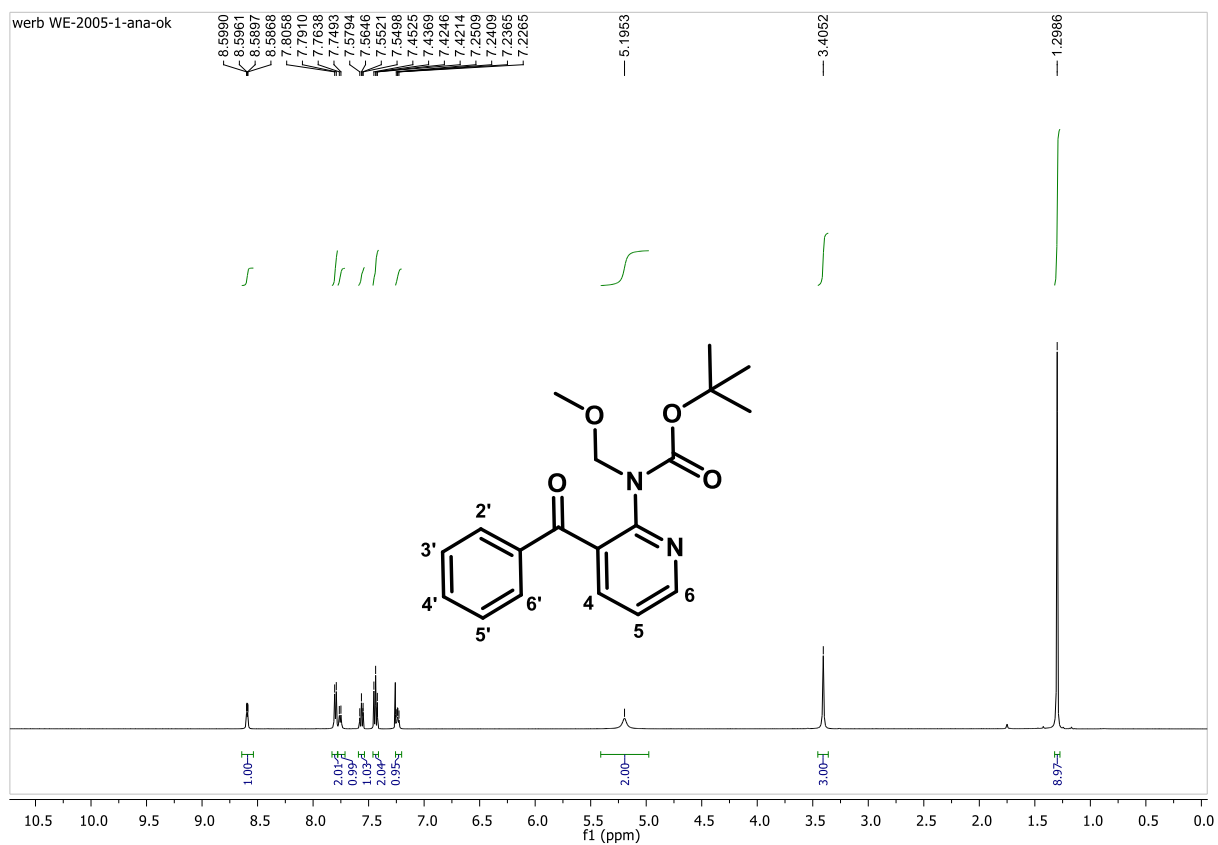


JMOD (CDCl_3 , 300 K, 126 MHz)

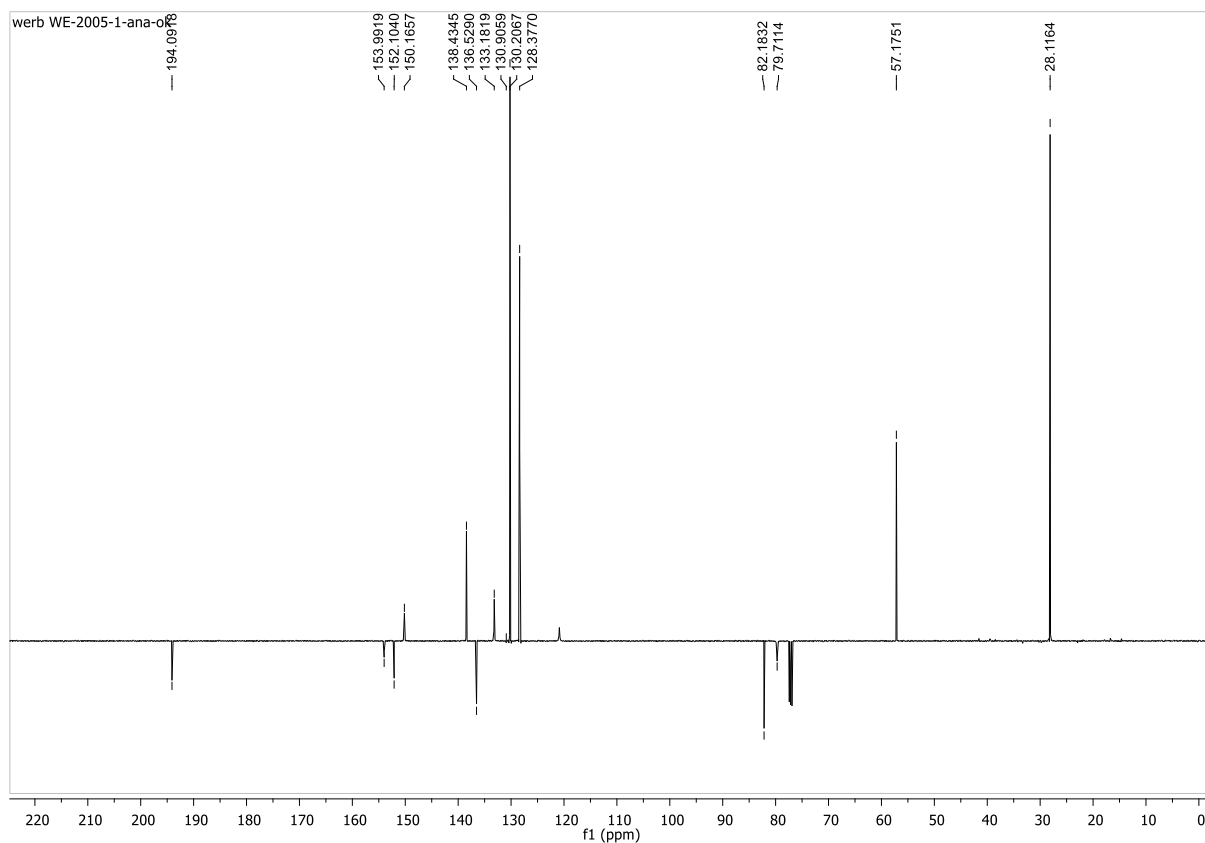


3-Benzoyl-2-((tert-butoxycarbonyl)(methoxymethyl)amino)pyridine (31)

^1H (CDCl_3 , 300 K, 500 MHz)

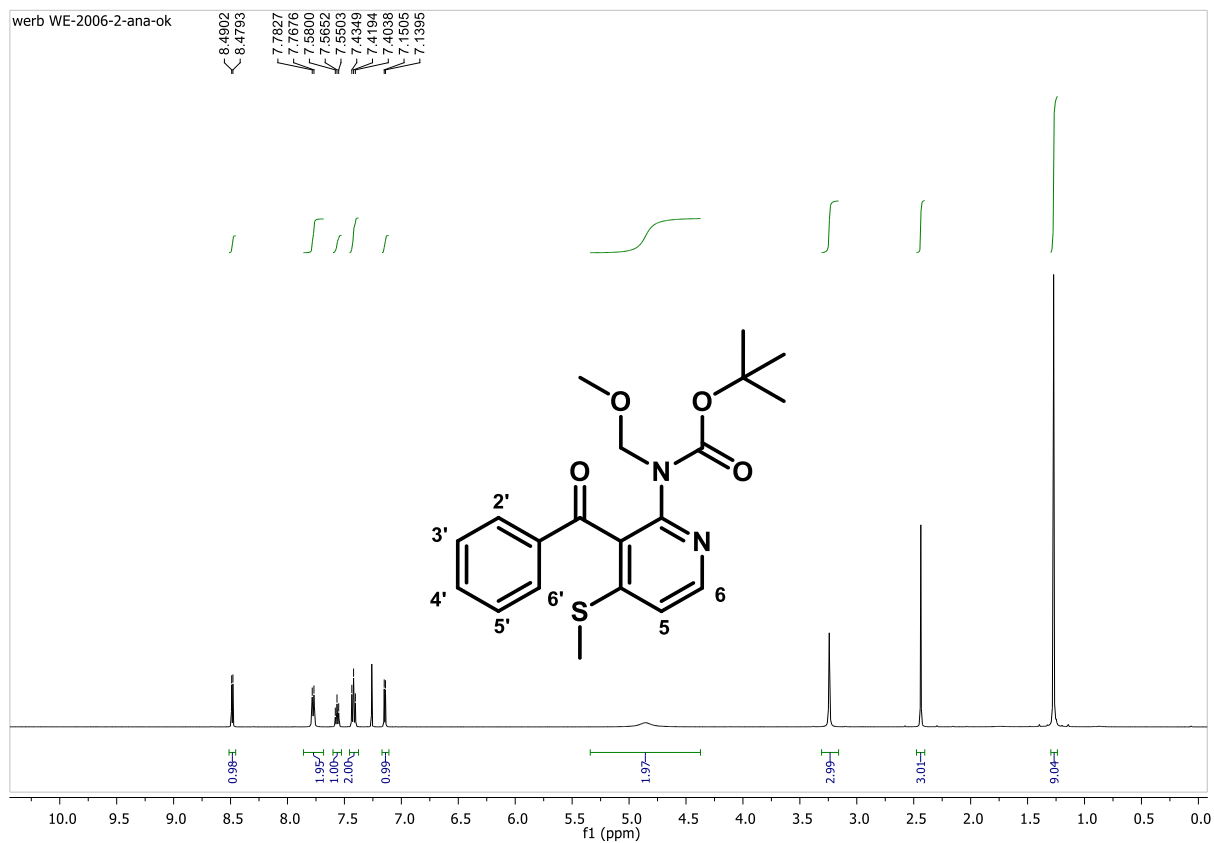


JMOD (CDCl_3 , 300 K, 126 MHz)

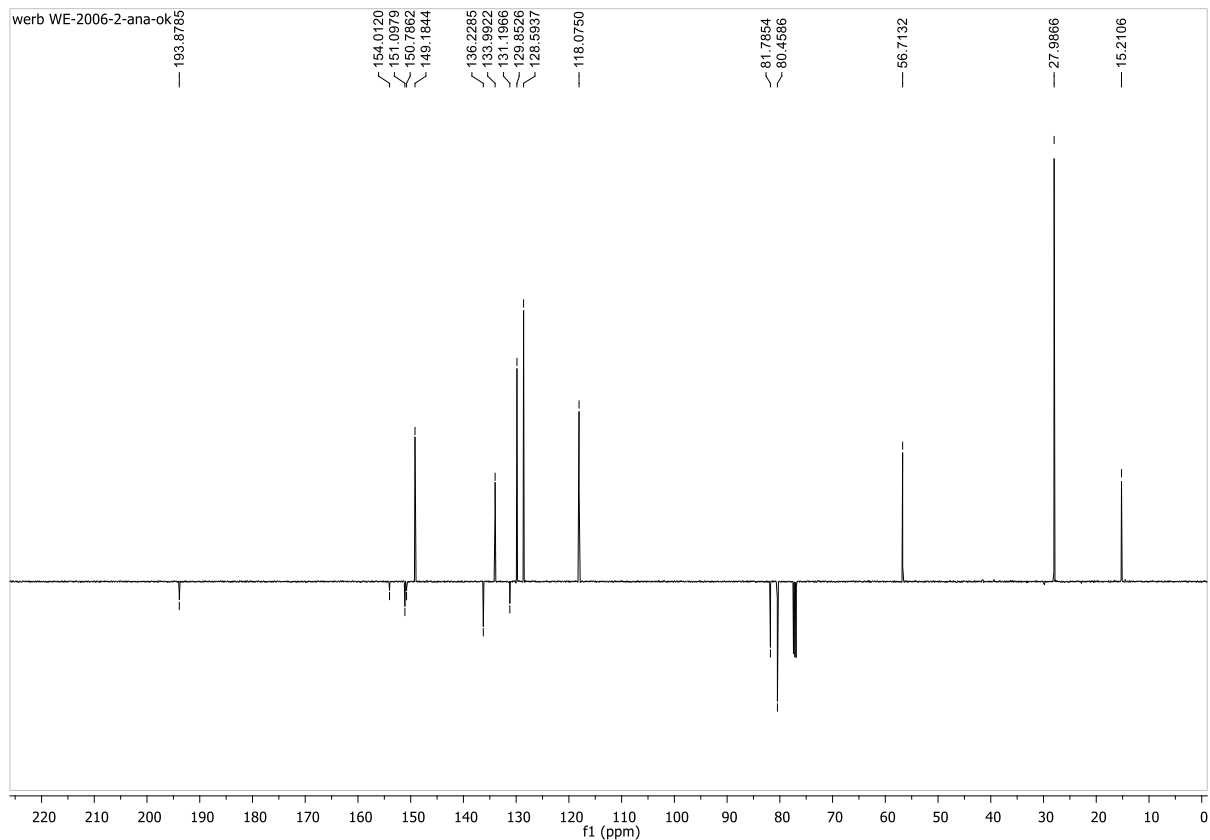


3-Benzoyl-2-((*tert*-butoxycarbonyl)(methoxymethyl)amino)-4-(methylthio)pyridine (32)

^1H (CDCl_3 , 300 K, 500 MHz)

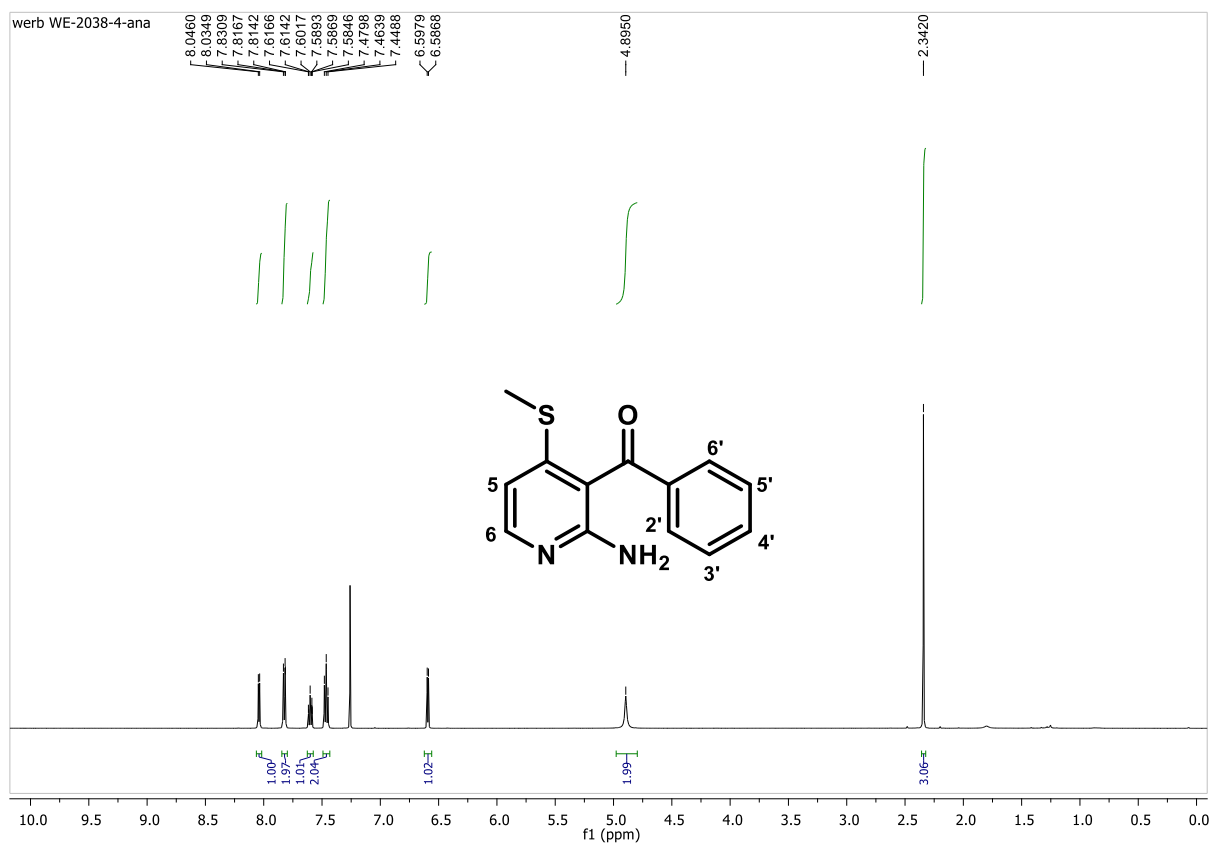


JMOD (CDCl_3 , 300 K, 126 MHz)

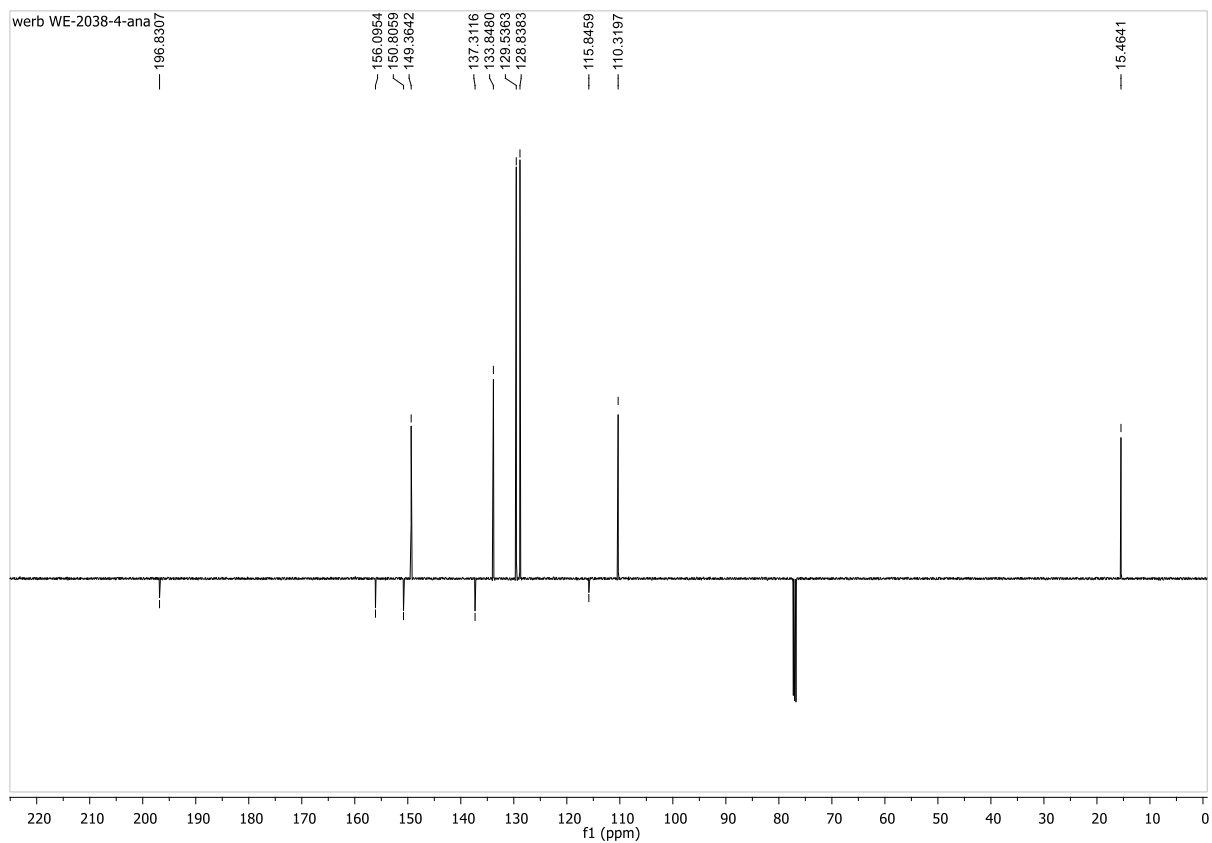


2-Amino-3-benzoyl-4-(methylthio)pyridine (20)

^1H (CDCl_3 , 300 K, 500 MHz)

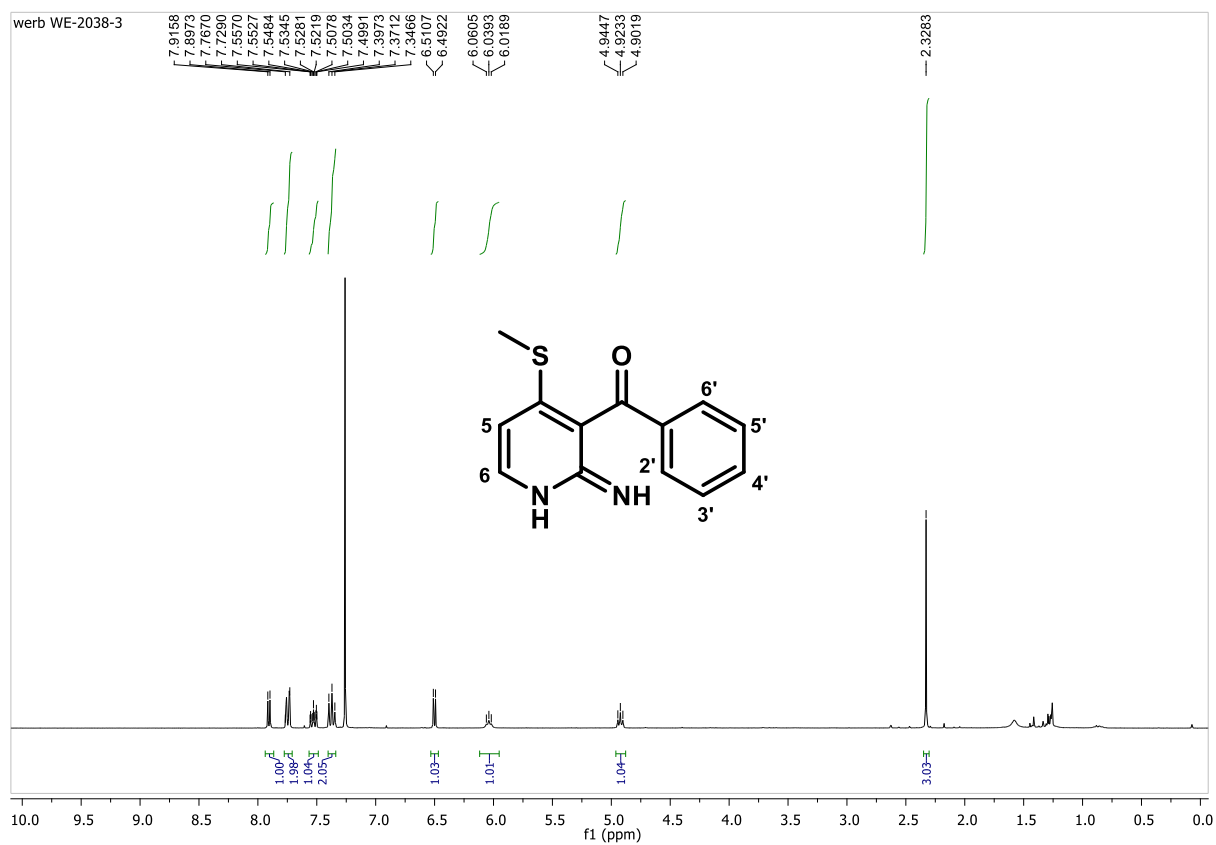


JMOD (CDCl_3 , 300 K, 126 MHz)

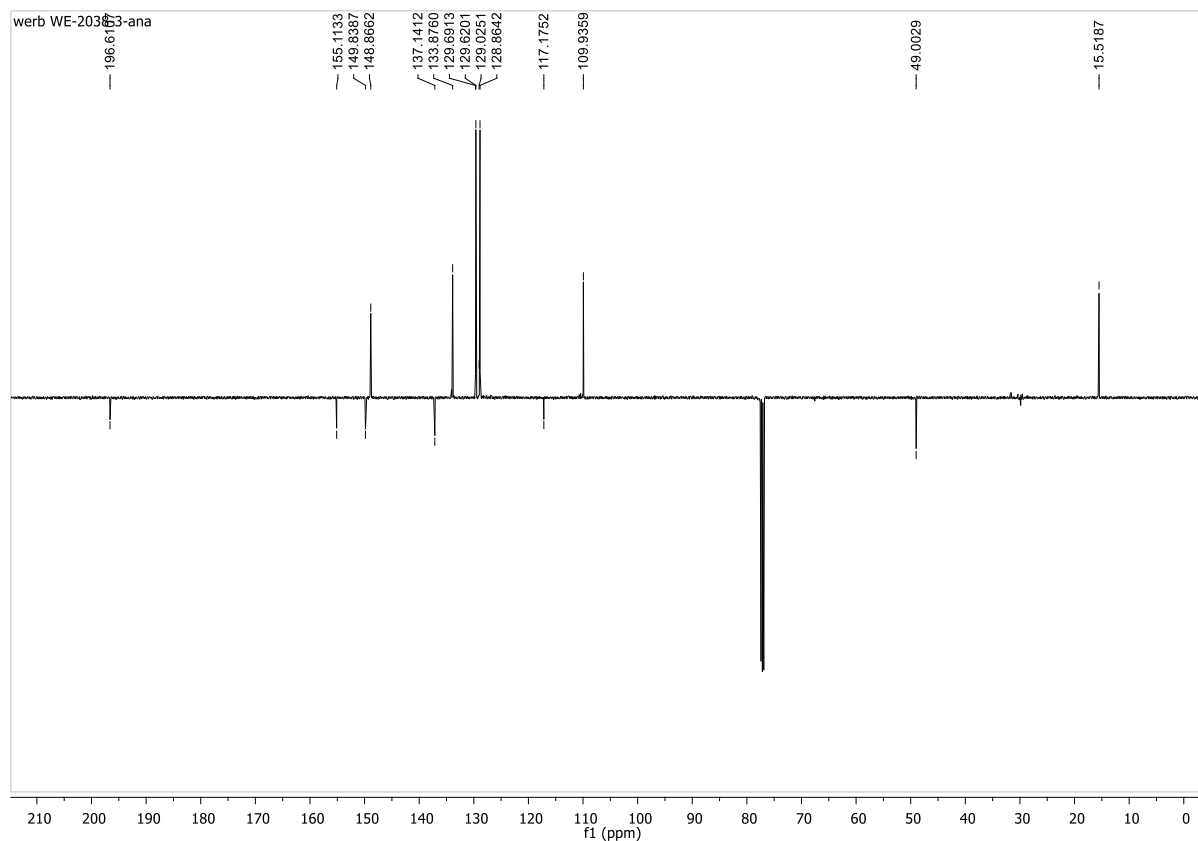


3-Benzoyl-2-imino-4-(methylthio)-1,2-dihydropyridine (20')

^1H (CDCl_3 , 300 K, 500 MHz)

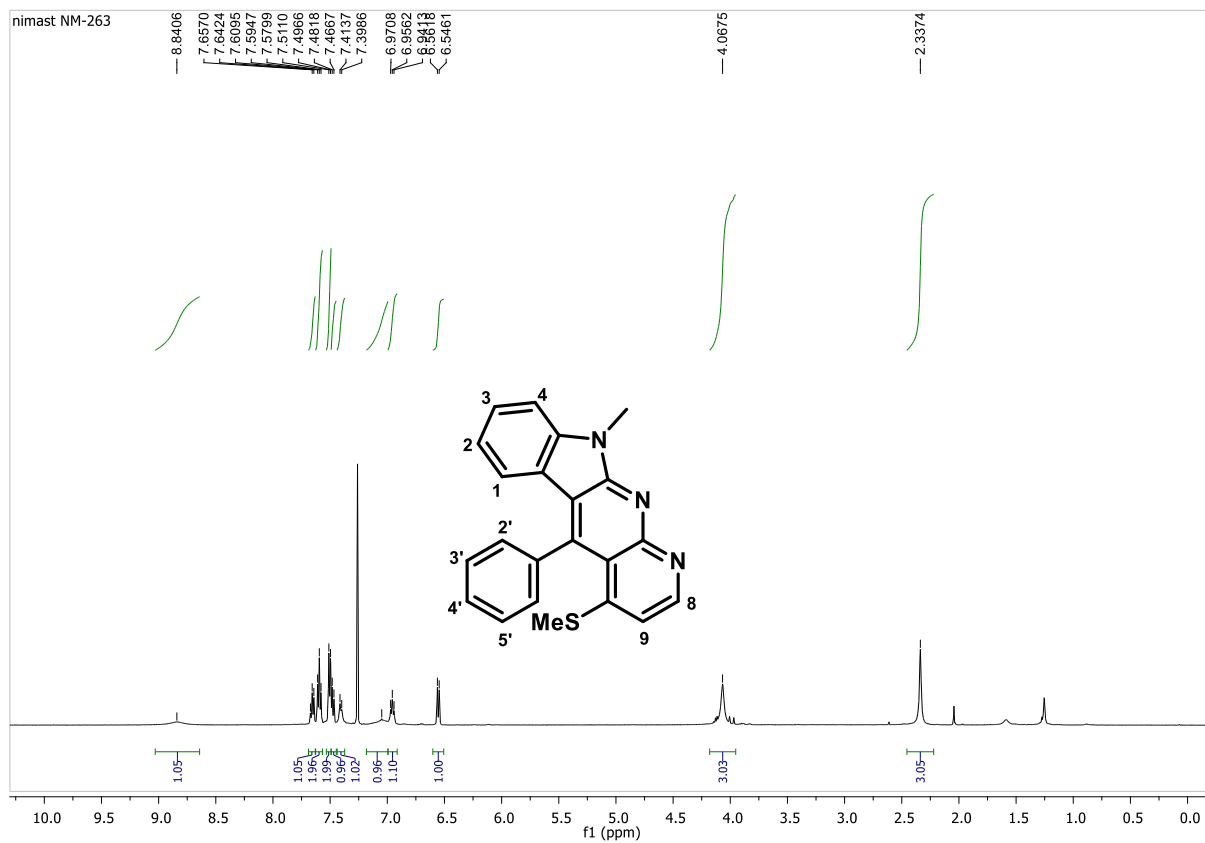


JMOD (CDCl₃, 300 K, 126 MHz)

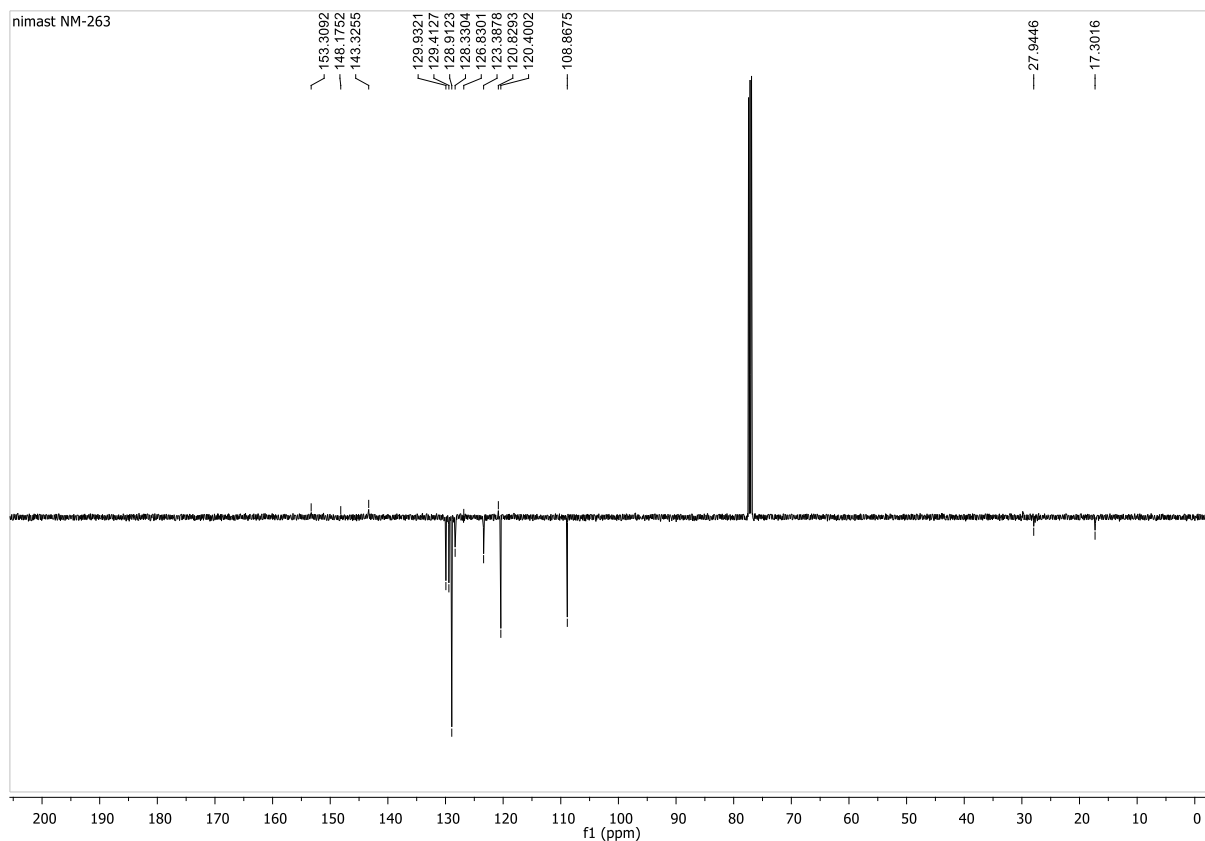


5-Methyl-10-(methylthio)-11-phenylindolo[2,3-*b*]1,8-naphthyridine (33)

^1H (CDCl₃, 300 K, 500 MHz)

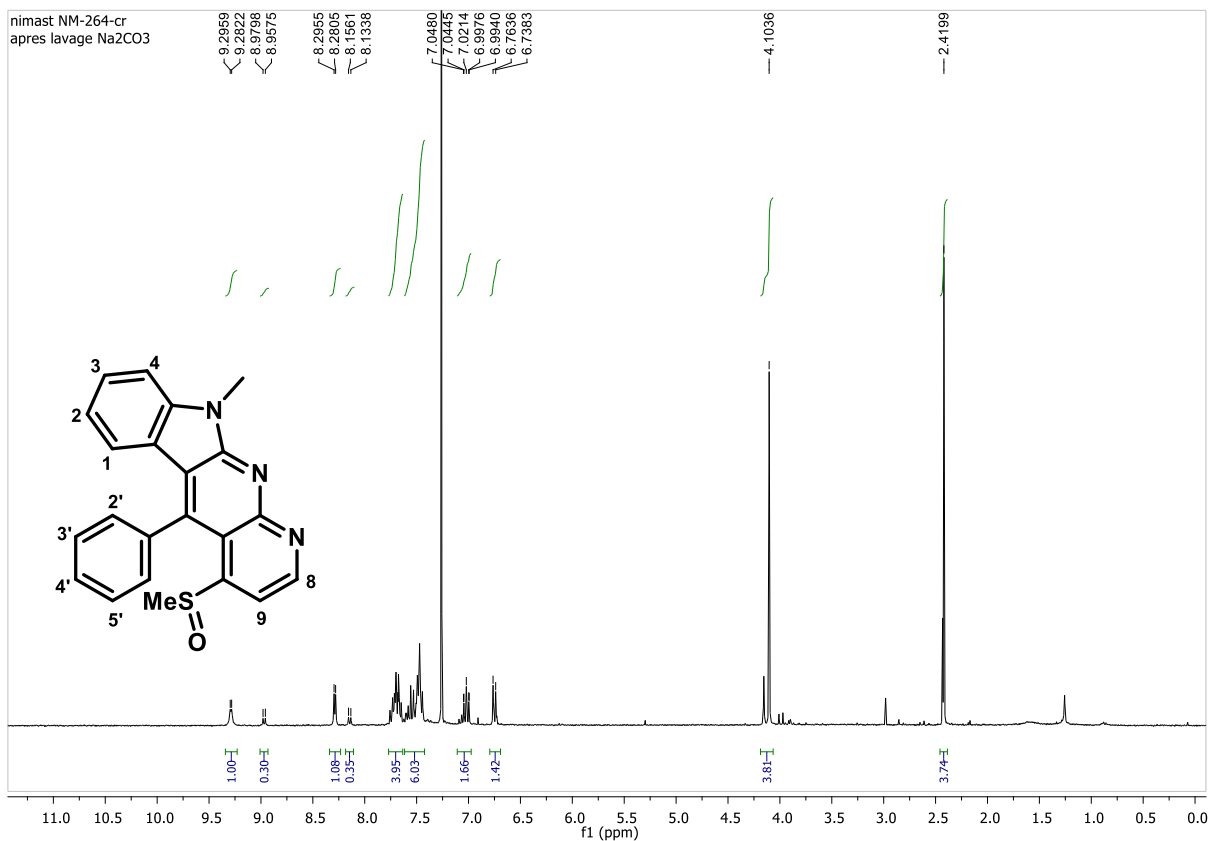


JMOD (CDCl₃, 300 K, 126 MHz)

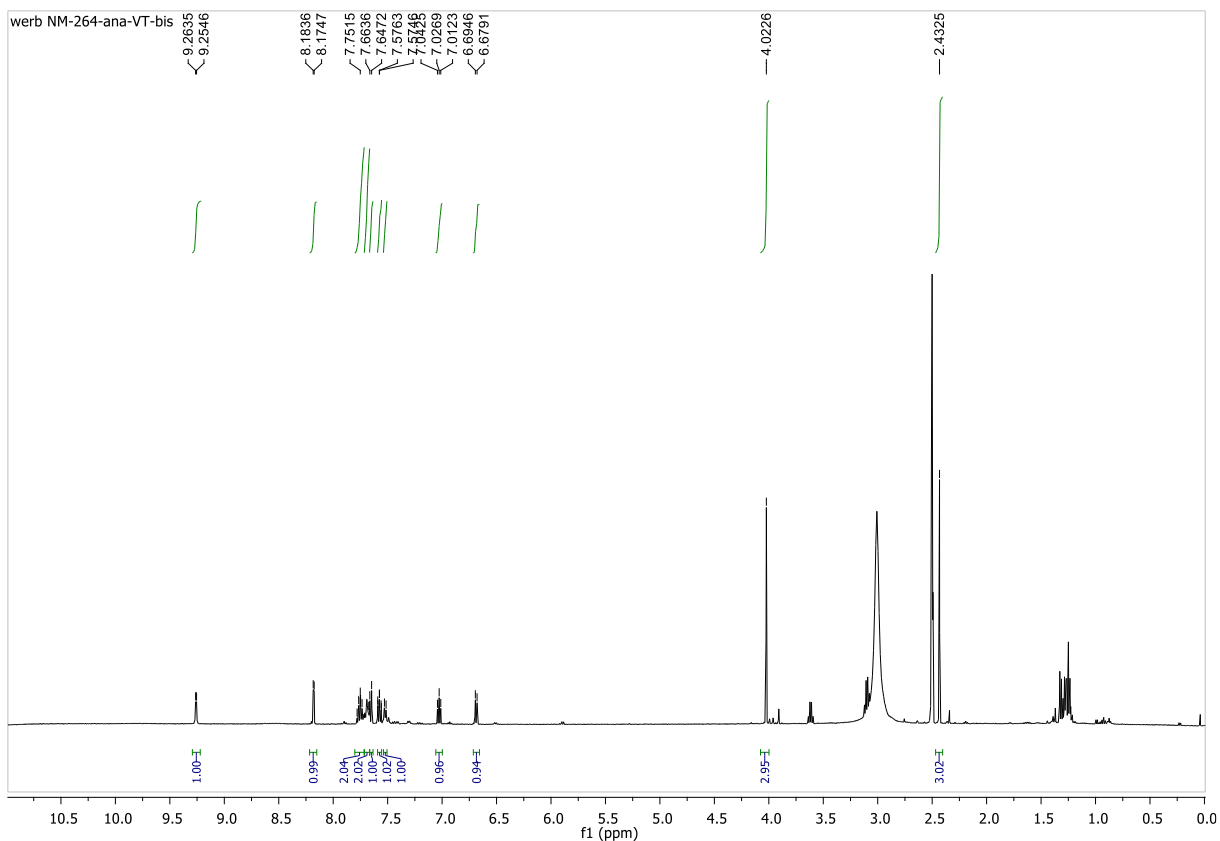


5-Methyl-10-(methylsulfinyl)-11-phenylindolo[2,3-*b*]1,8-naphthyridine (34)

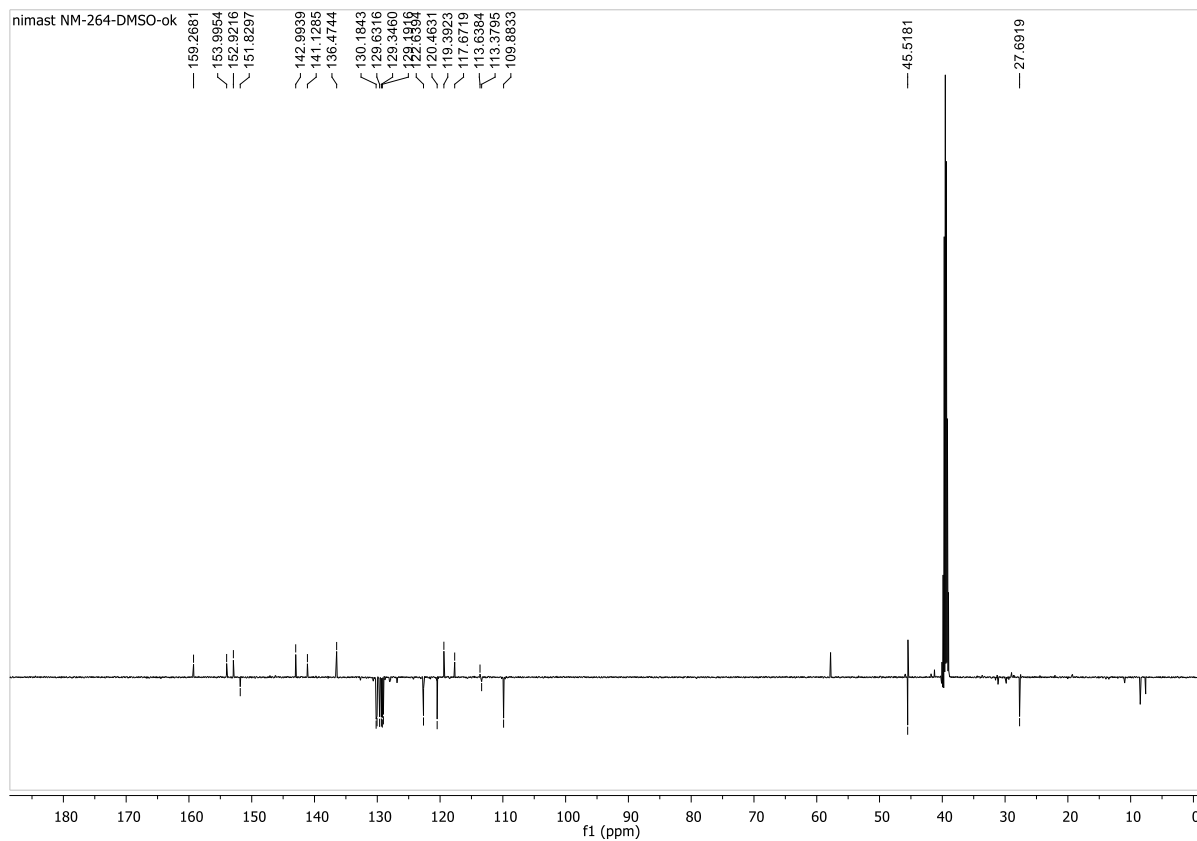
^1H (CDCl₃, 300 K, 500 MHz)



^1H ((CD₃)₂SO, 375 K, 500 MHz)

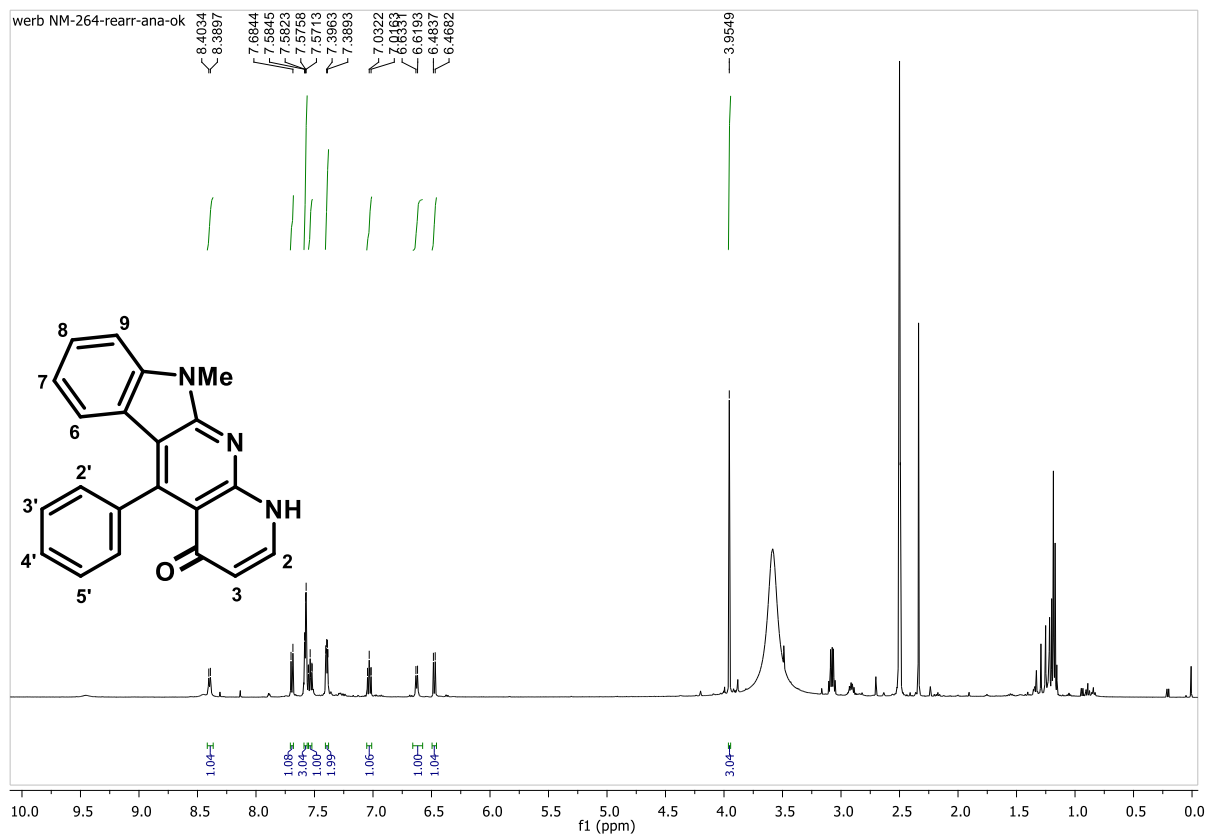


JMOD ((CD₃)₂SO, 300 K, 126 MHz)

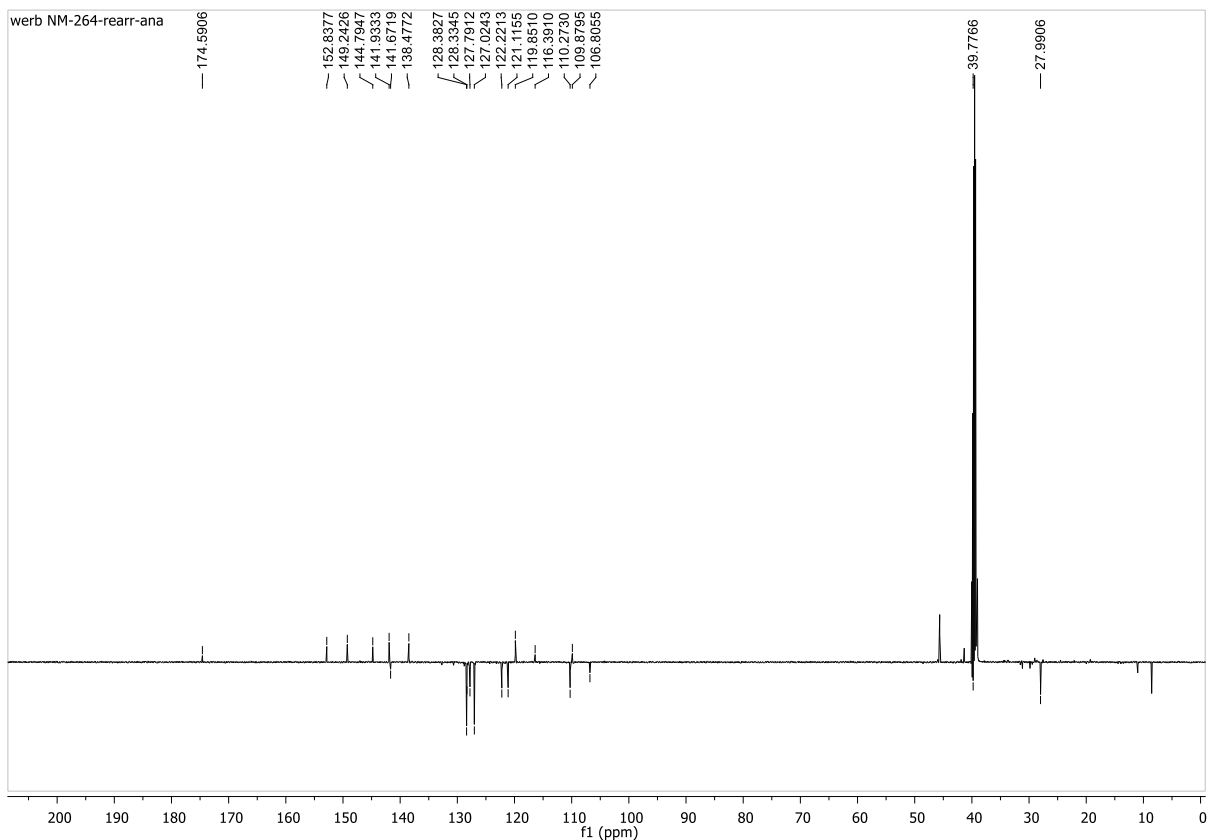


Putative 10-Methyl-5-phenyl-1,10-dihydro-4H-indolo[2,3-b]1,8-naphthyridin-4-one (34')

^1H ((CD_3) $_2\text{SO}$, 300 K, 500 MHz)

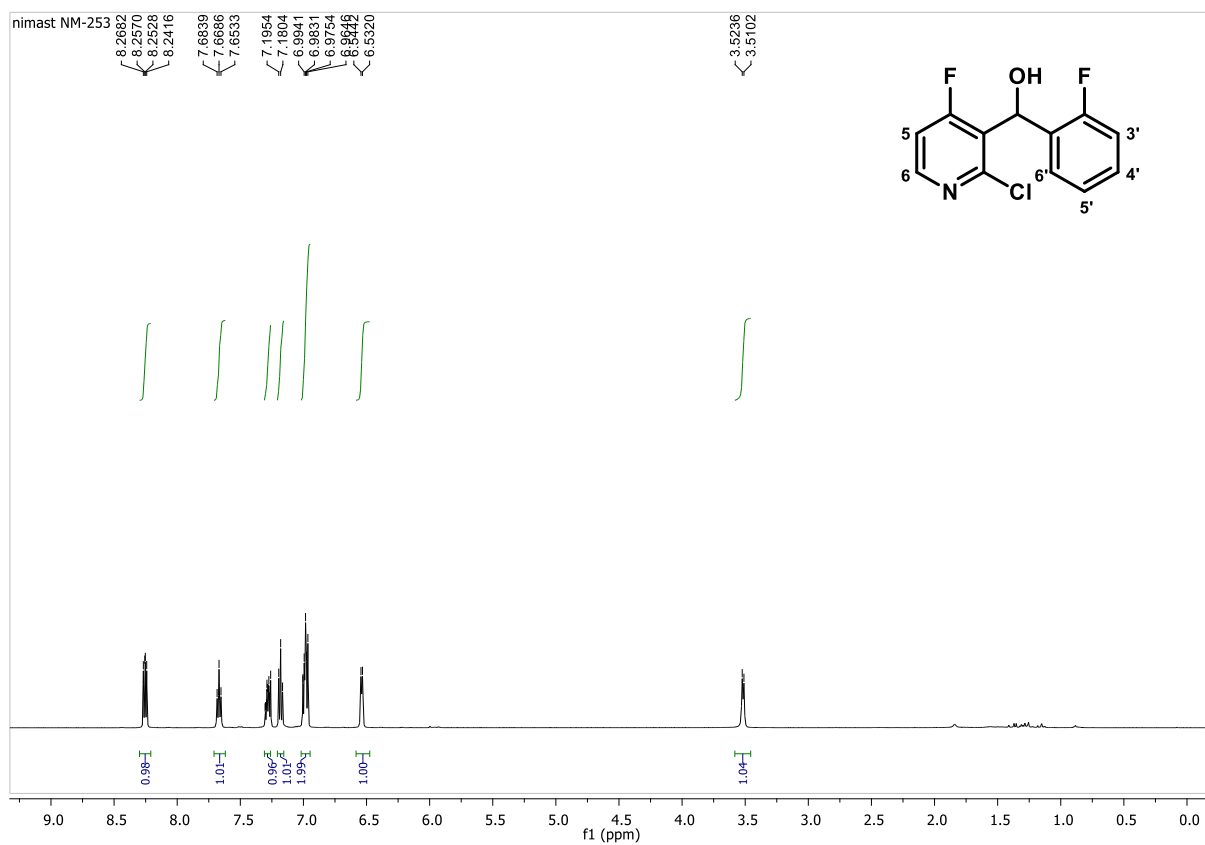


JMOD ((CD_3) $_2\text{SO}$, 300 K, 126 MHz)

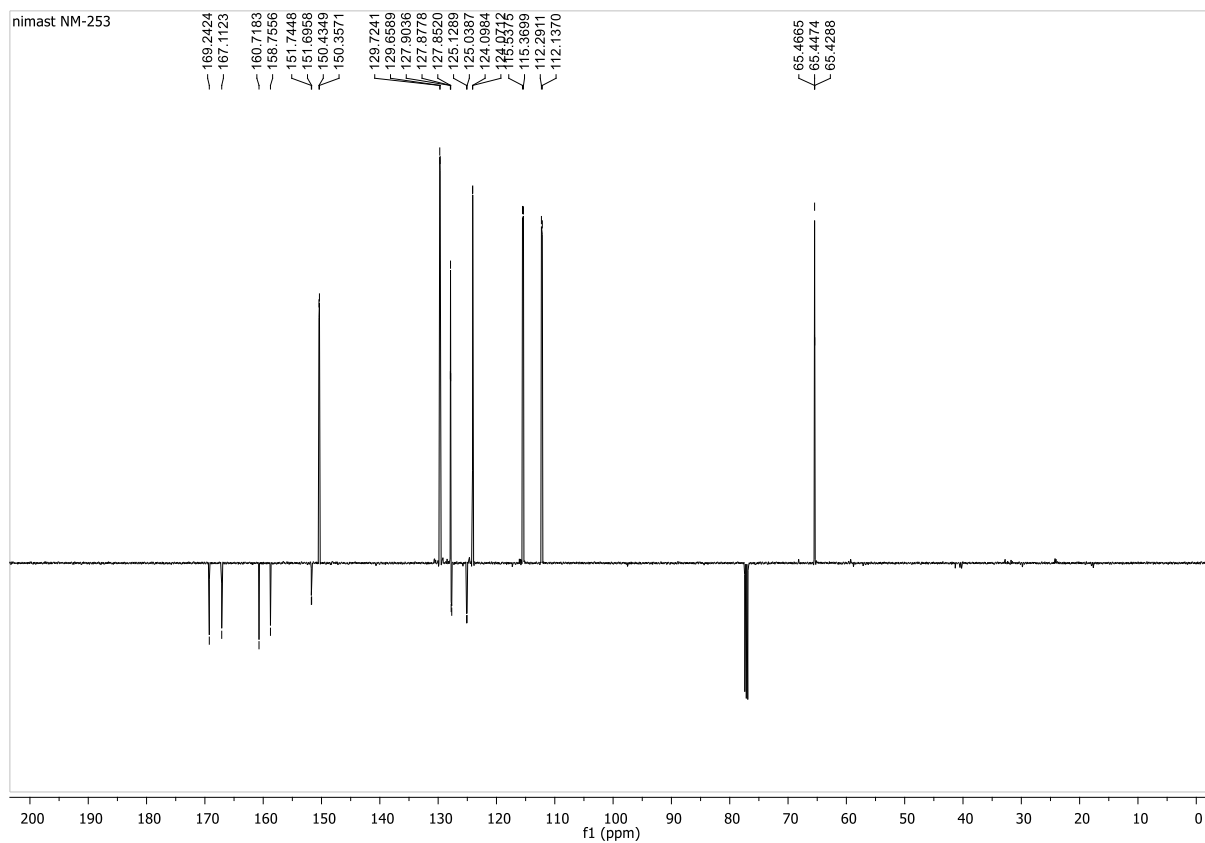


2-Chloro-4-fluoro-3-(1-(2-fluorophenyl)hydroxymethyl)pyridine (36)

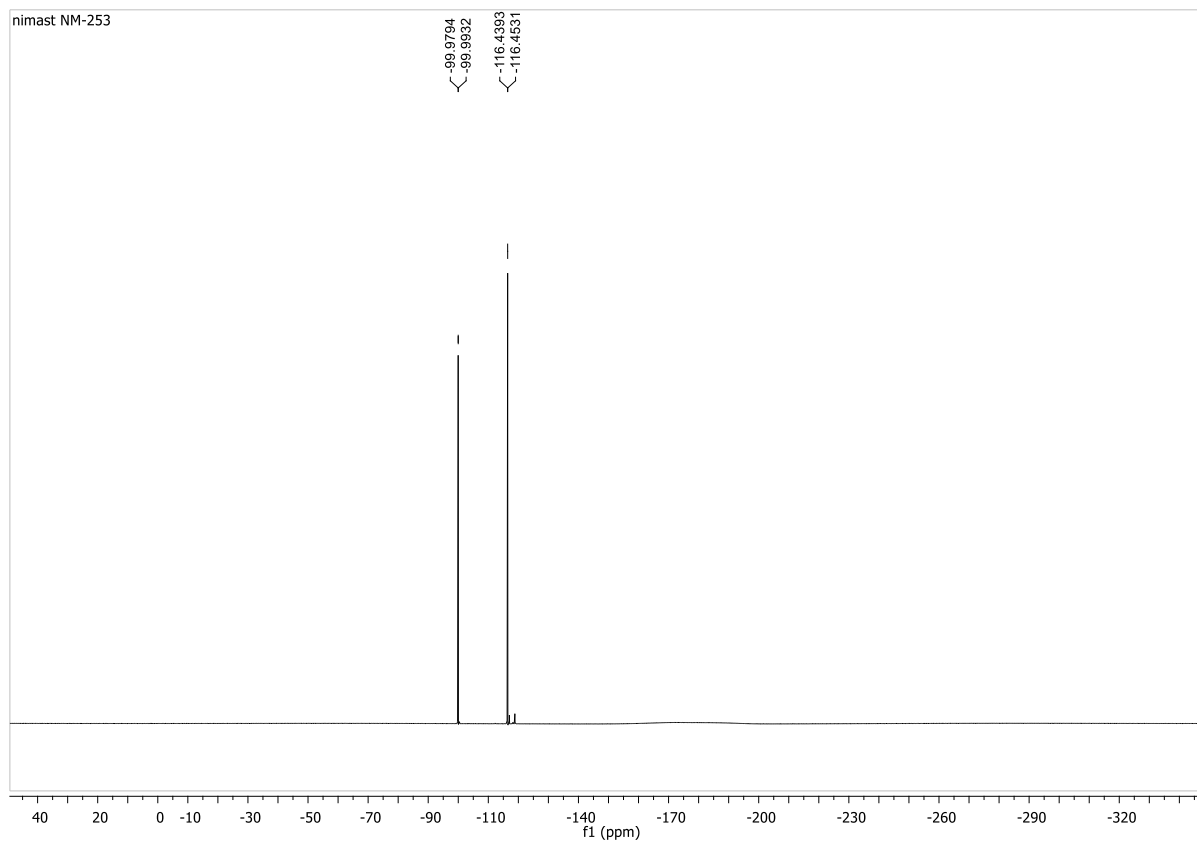
^1H (CDCl₃, 300 K, 500 MHz)



JMOD (CDCl₃, 300 K, 126 MHz)

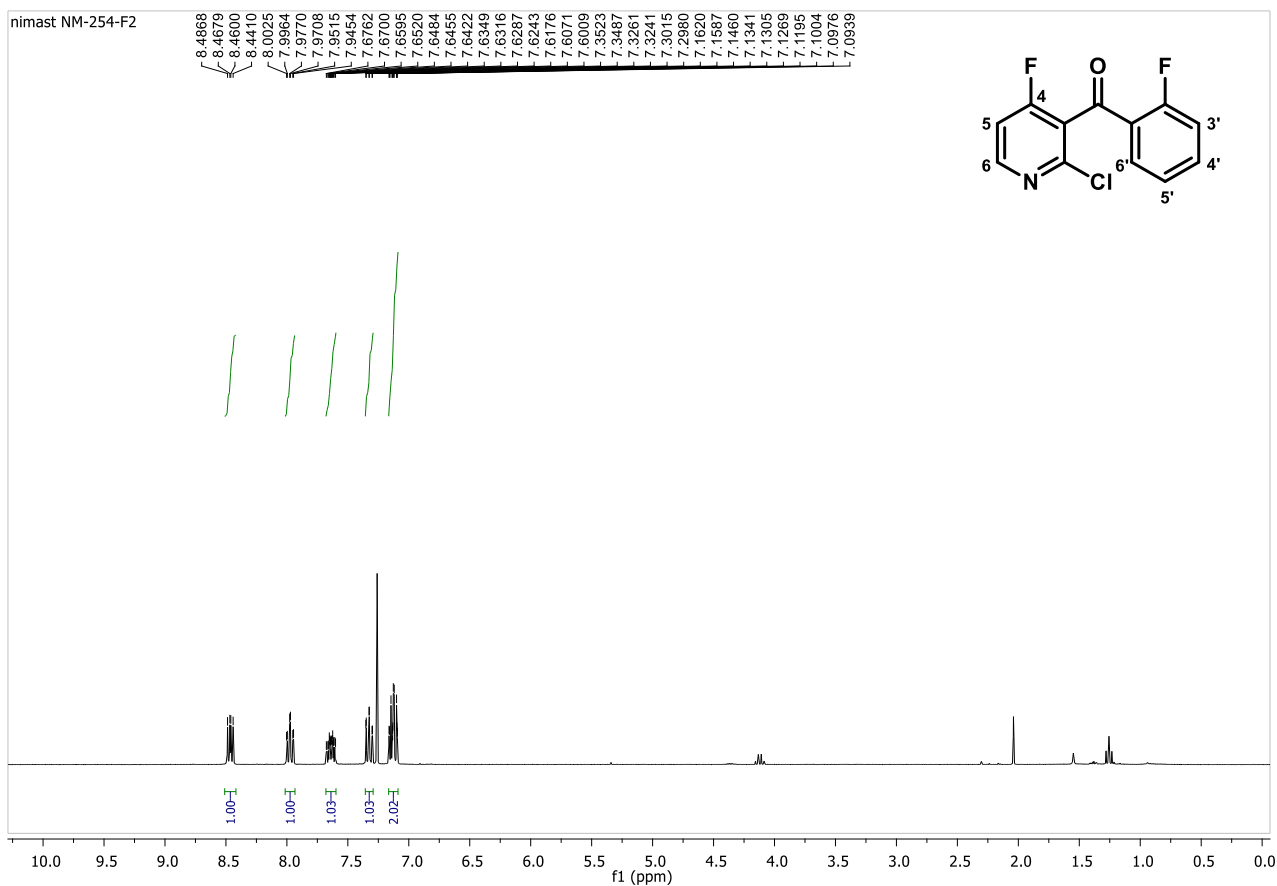


^{19}F (CDCl_3 , 300 K, 471 MHz)

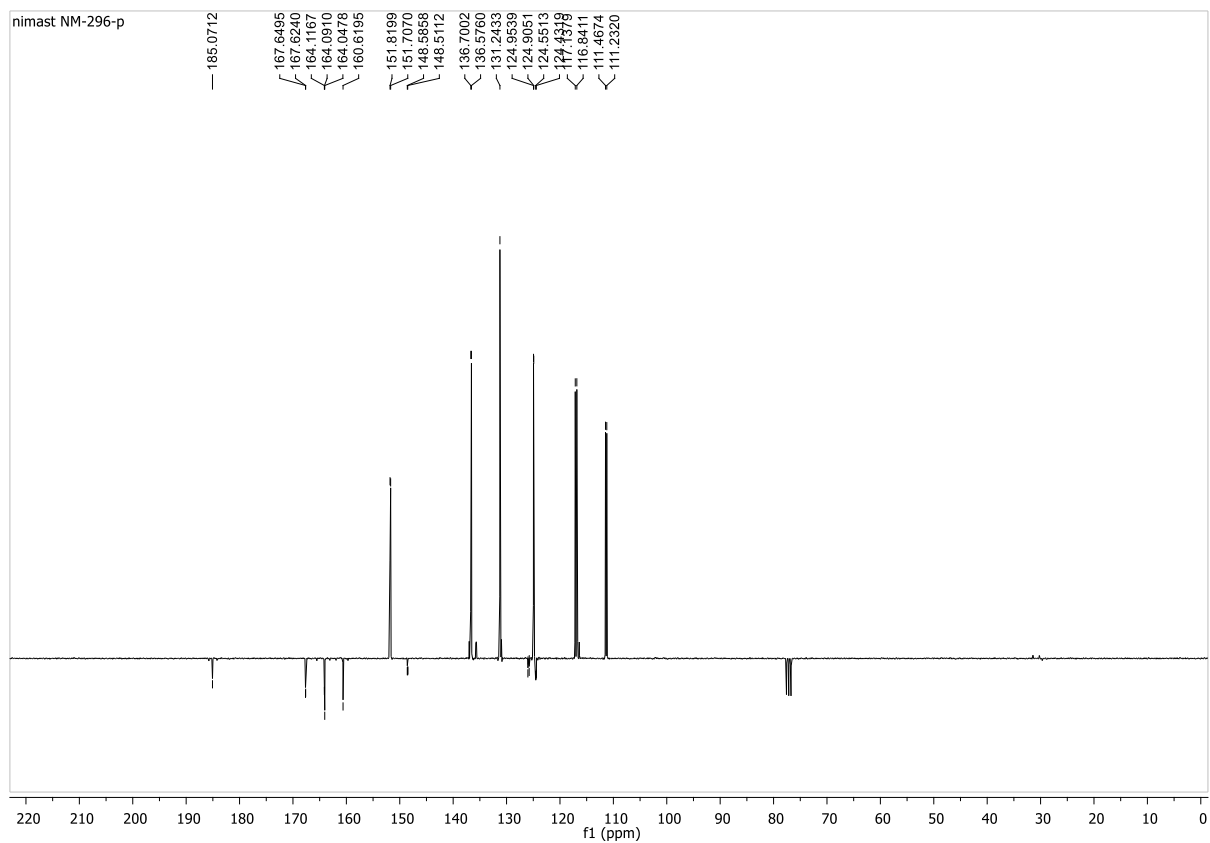


2-Chloro-4-fluoro-3-(2-fluorobenzoyl)pyridine (37)

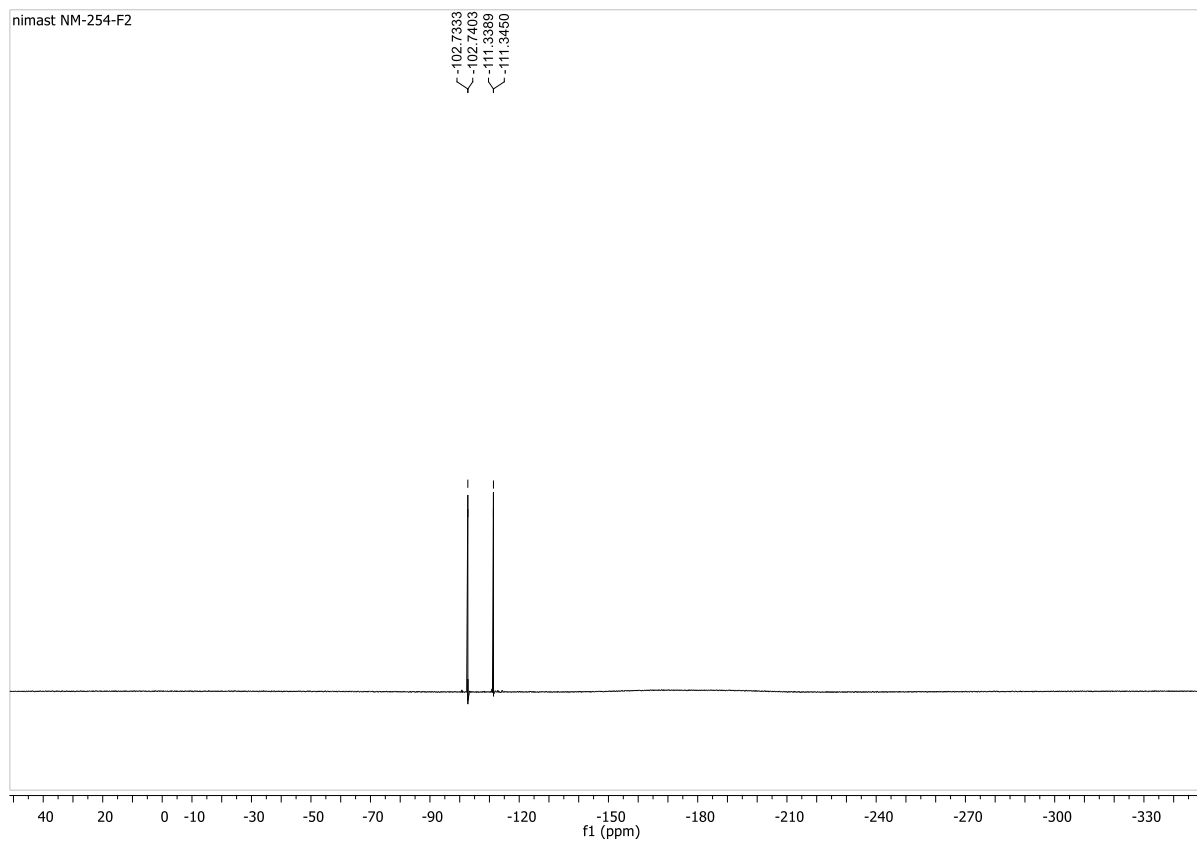
^1H (CDCl_3 , 300 K, 300 MHz)



JMOD (CDCl_3 , 300 K, 75 MHz)

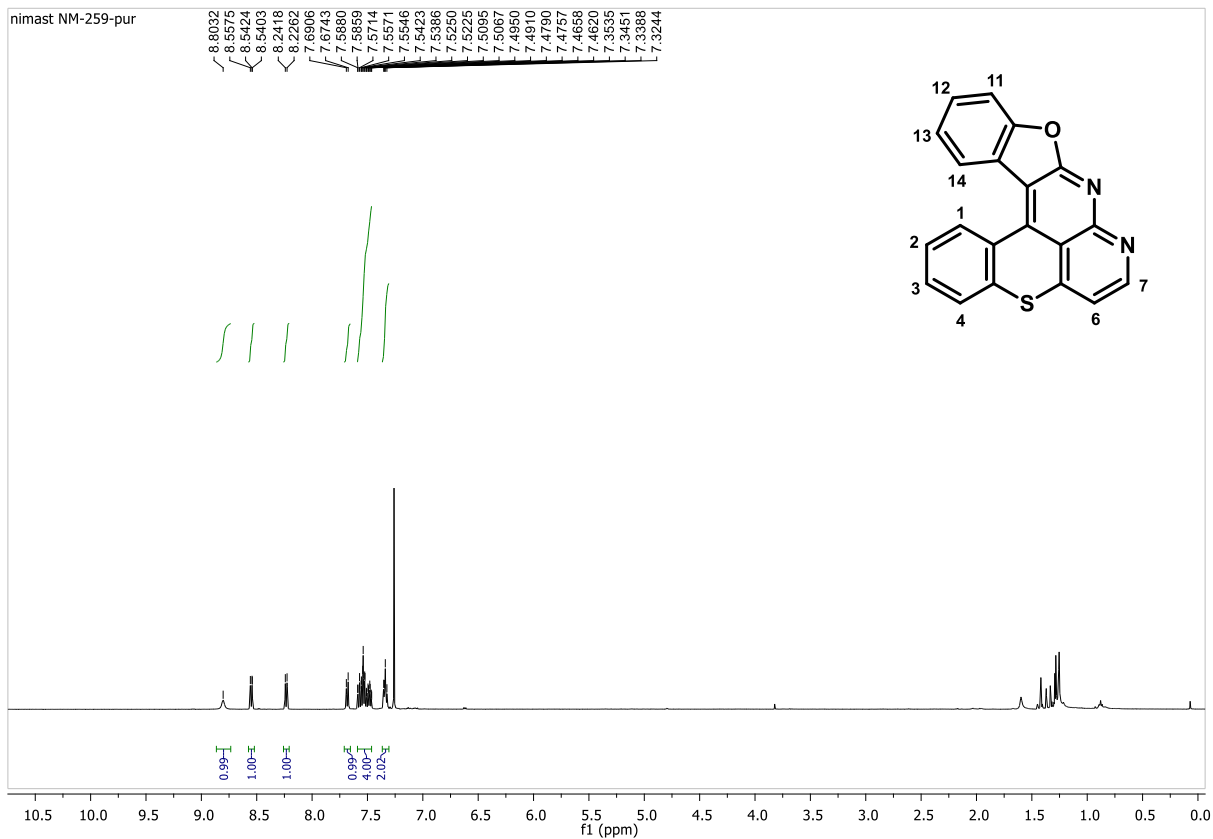


^{19}F (CDCl_3 , 300 K, 282 MHz)

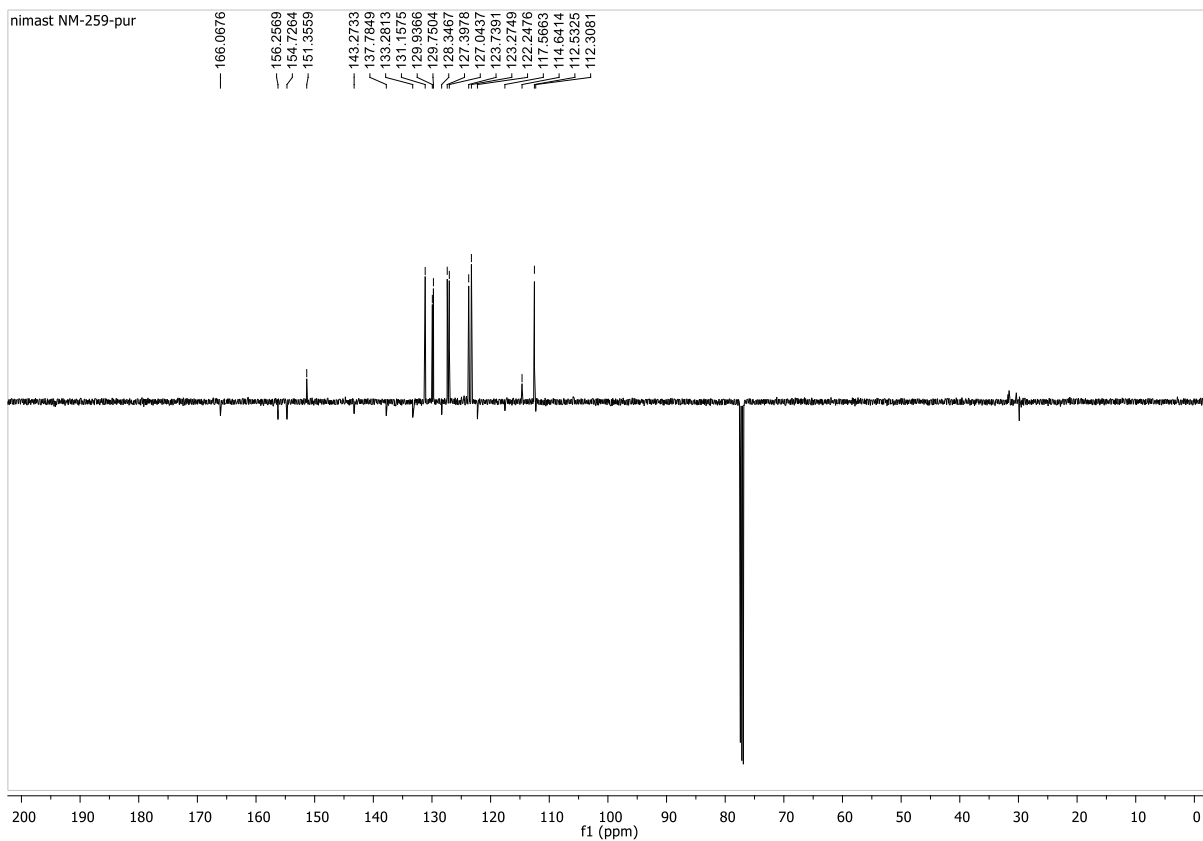


Benzofuro[2,3-*b*]benzothiopyrano[4,3,2-*de*]1,8-naphthyridine (28)

^1H (CDCl₃, 300 K, 500 MHz)

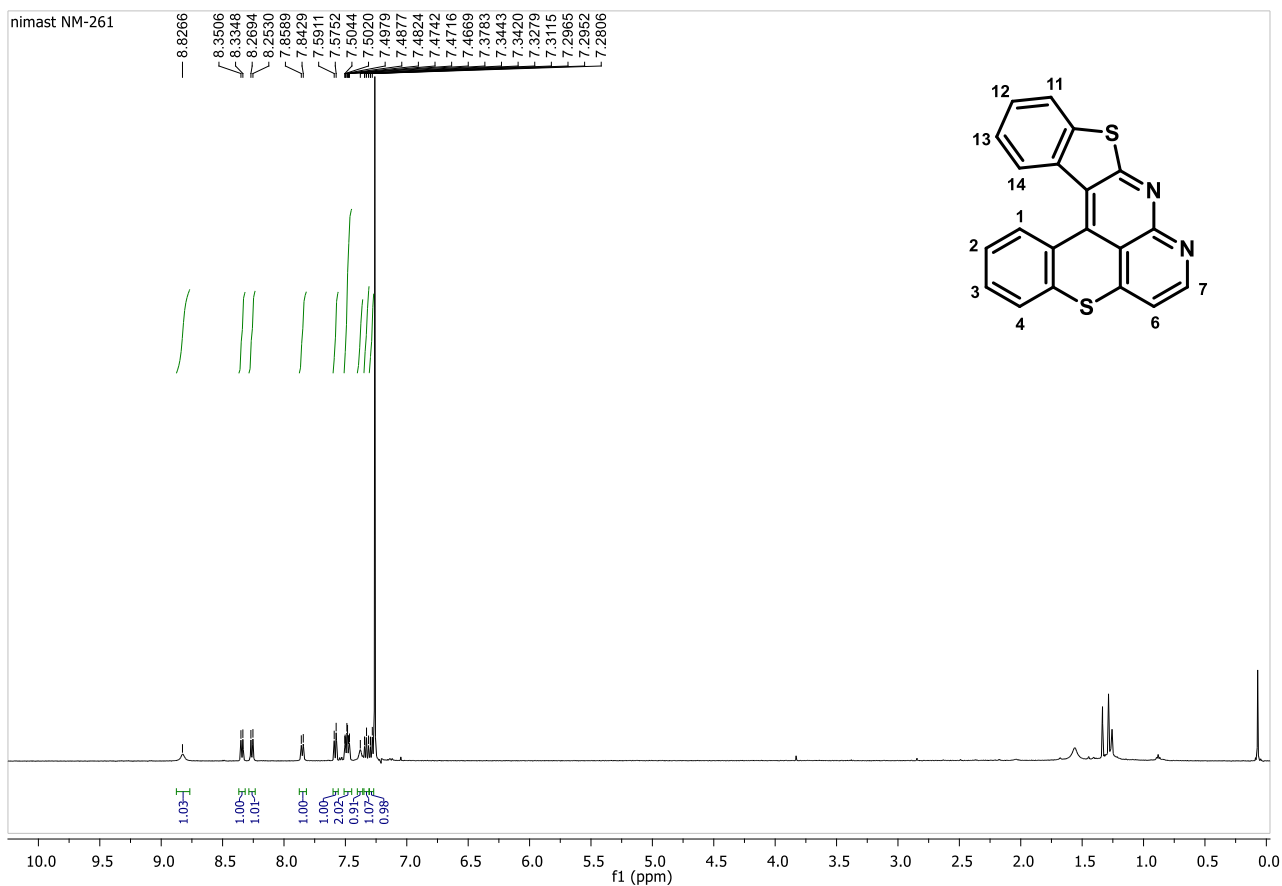


JMOD (CDCl₃, 300 K, 126 MHz)

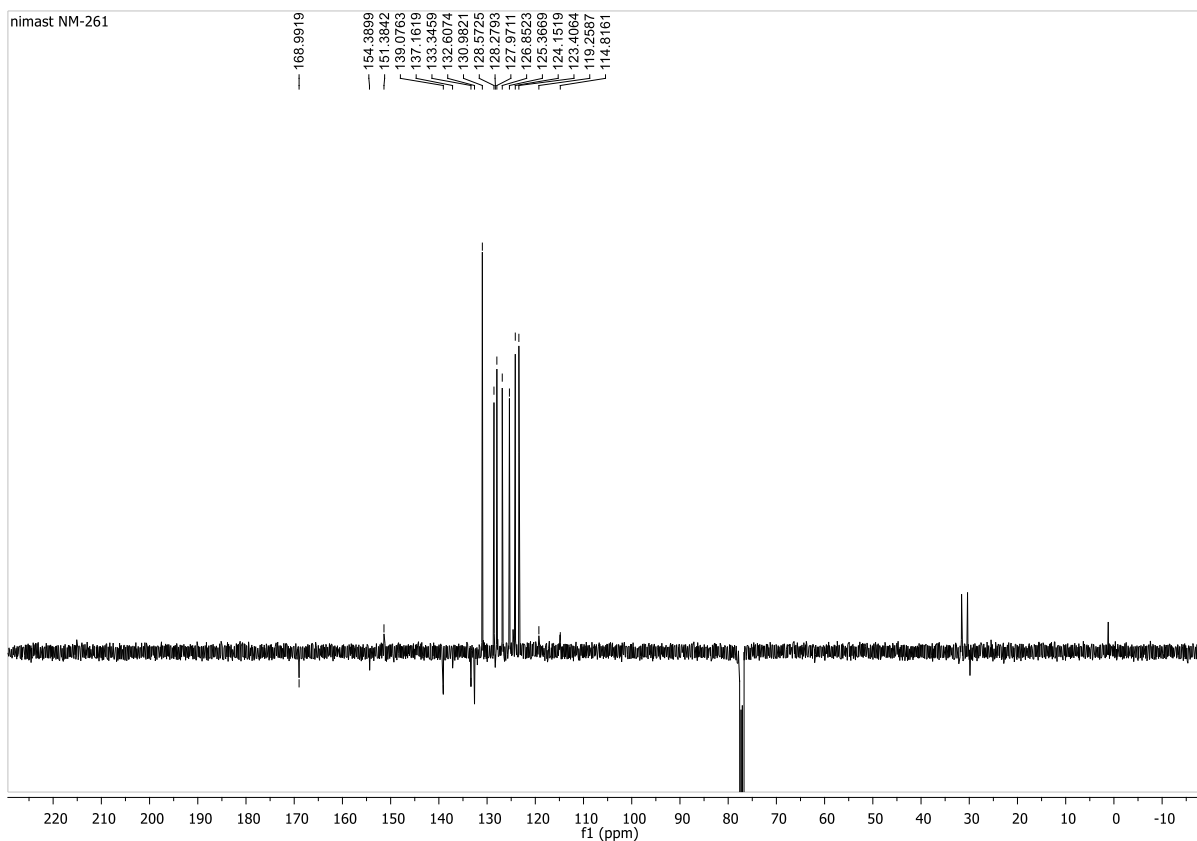


Benzothieno[2,3-*b*]benzothiopyrano[4,3,2-*de*]1,8-naphthyridine (39)

^1H (CDCl_3 , 300 K, 500 MHz)

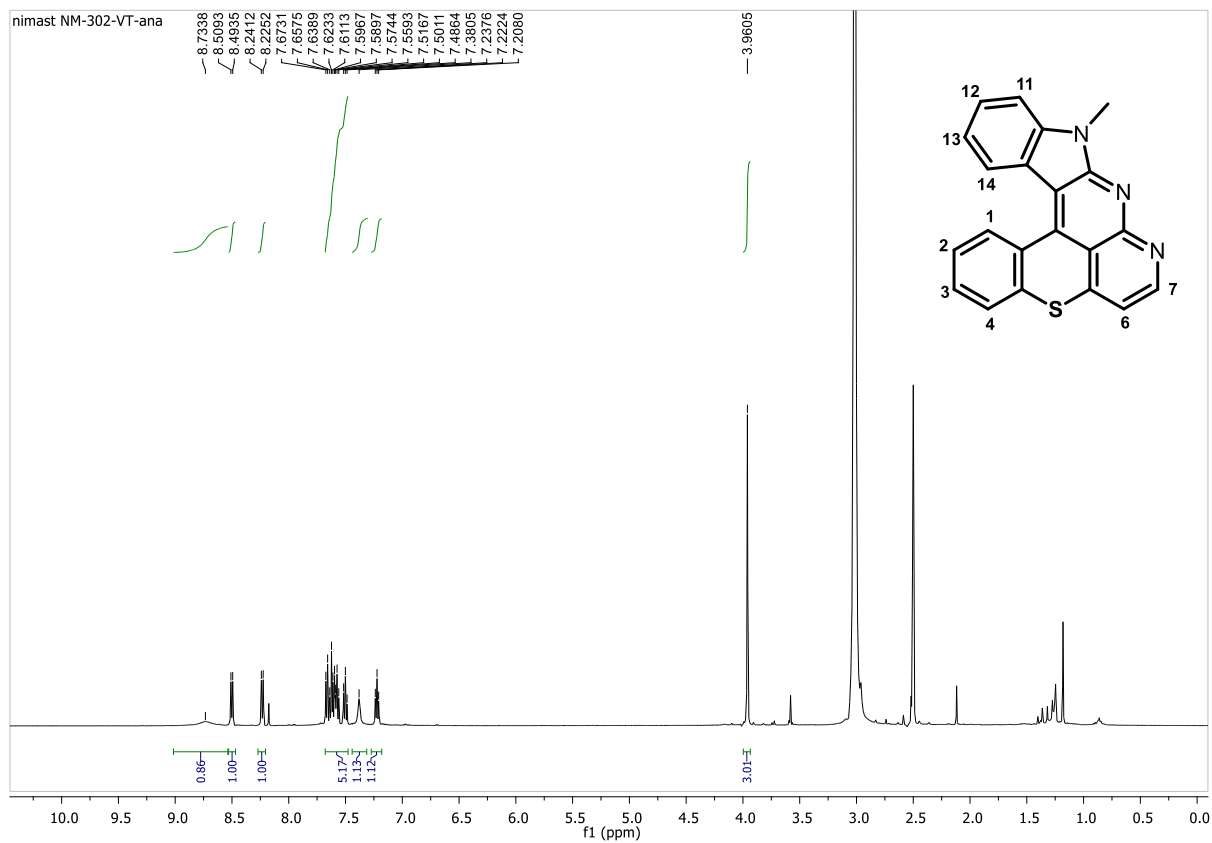


JMOD (CDCl_3 , 300 K, 126 MHz)

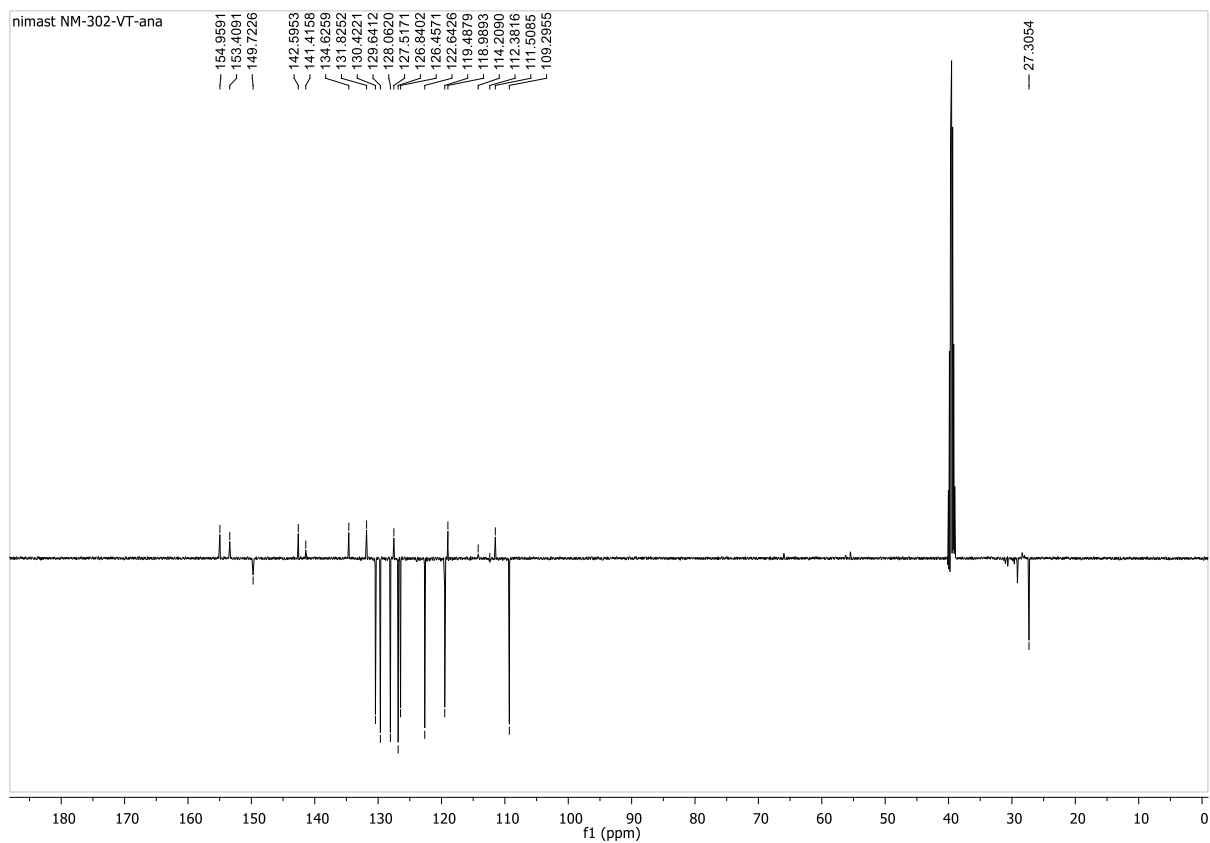


11-Methylbenzothiopyrano[4,3,2-de]indolo[2,3-b]1,8-naphthyridine (35)

^1H ($(\text{CD}_3)_2\text{SO}$, 375 K, 500 MHz)

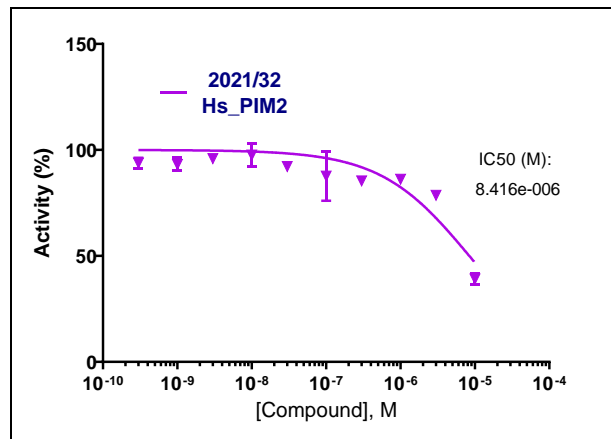
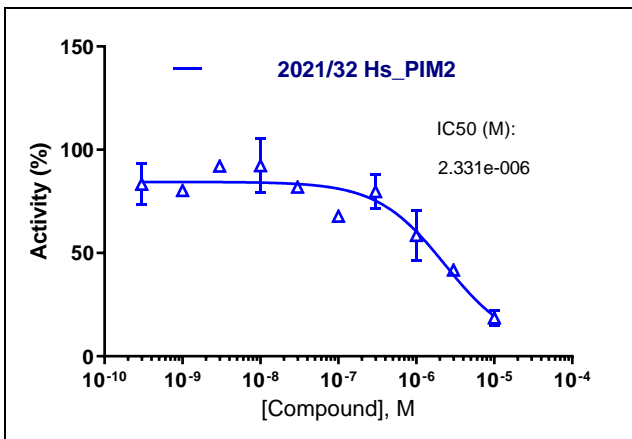
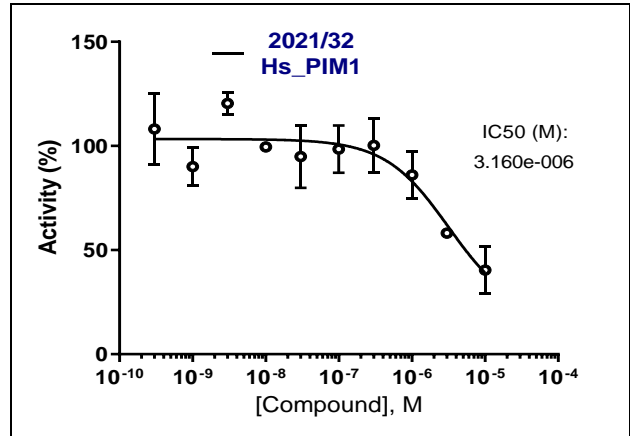
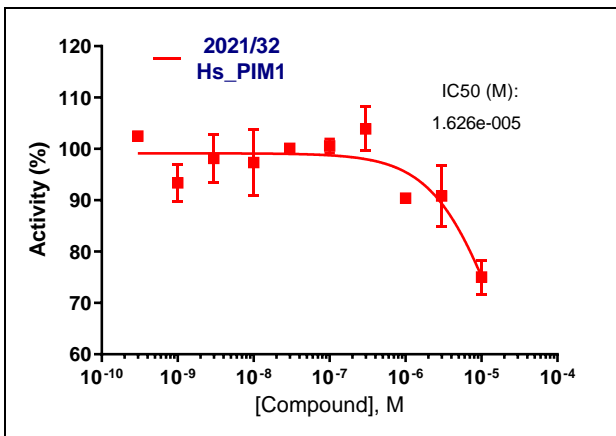


JMOD ($(\text{CD}_3)_2\text{SO}$, 375 K, 126 MHz)

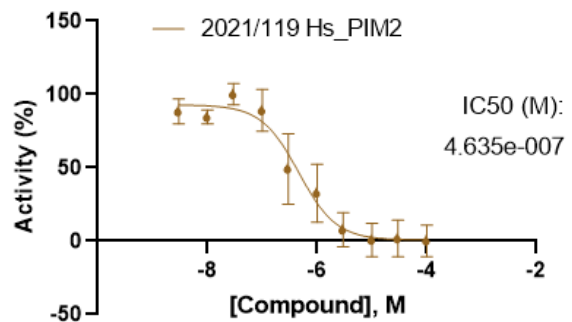
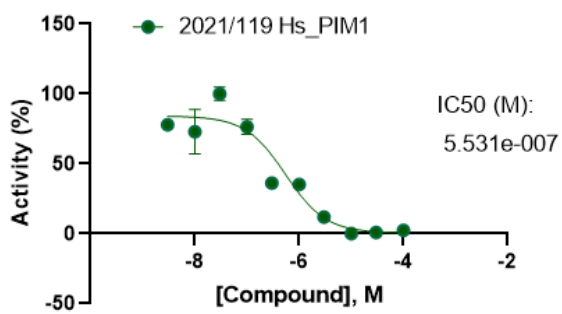


Titration curves for IC₅₀ determination

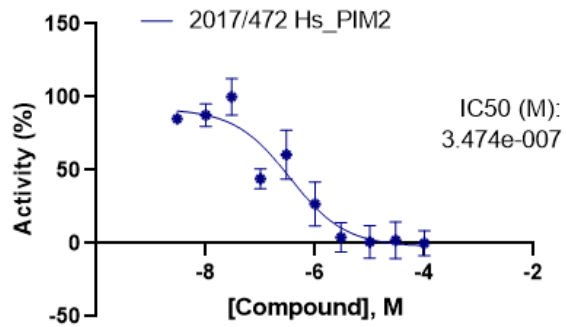
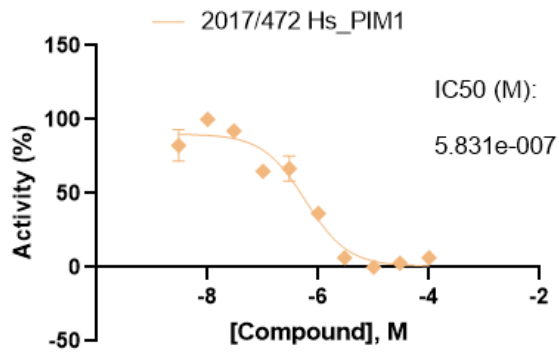
Compound NM-049



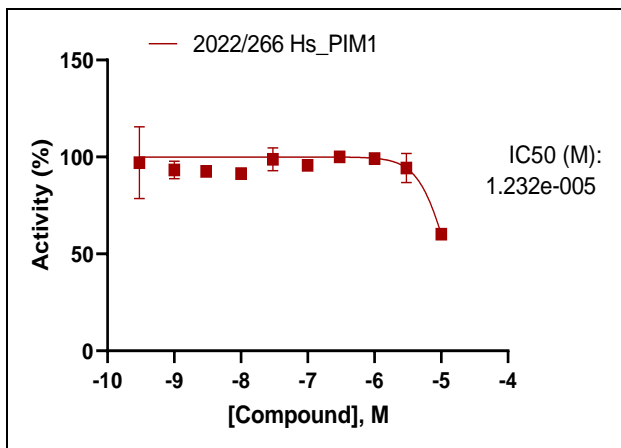
Compound MN65-45



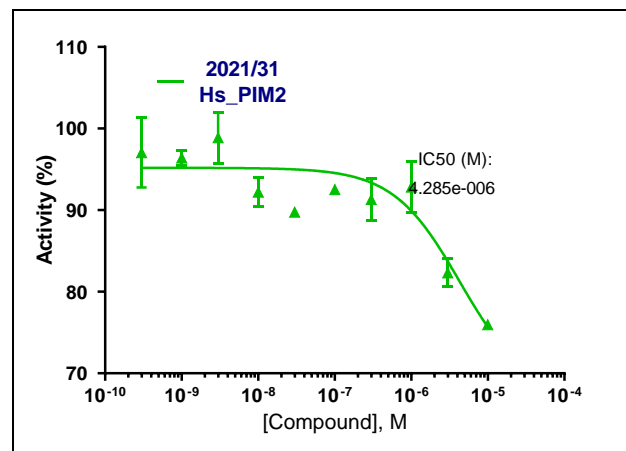
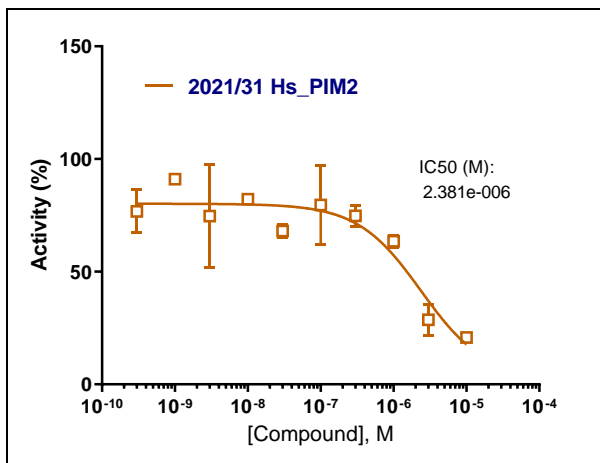
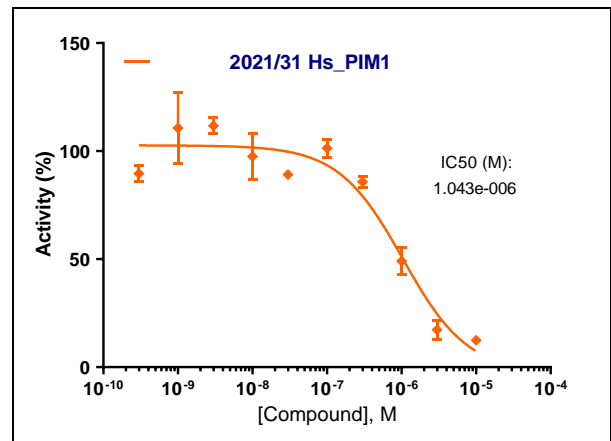
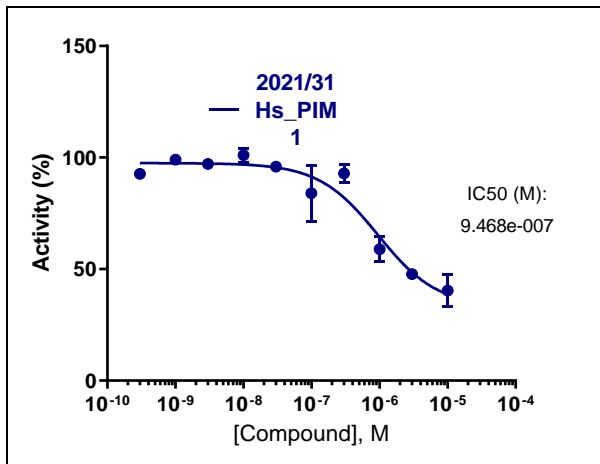
Compound MN64-44



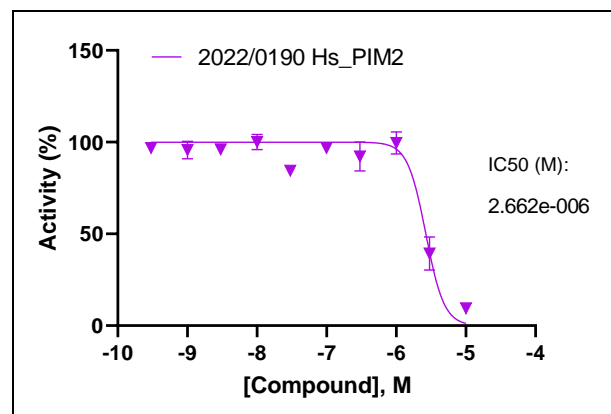
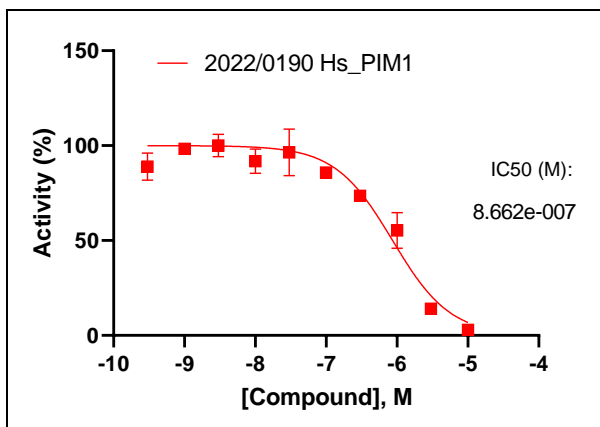
Compound 33 or NM-263



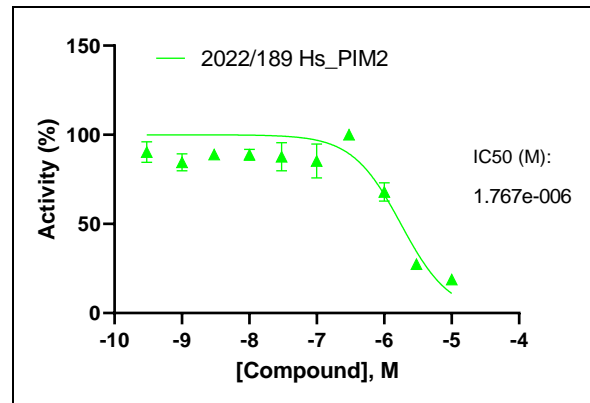
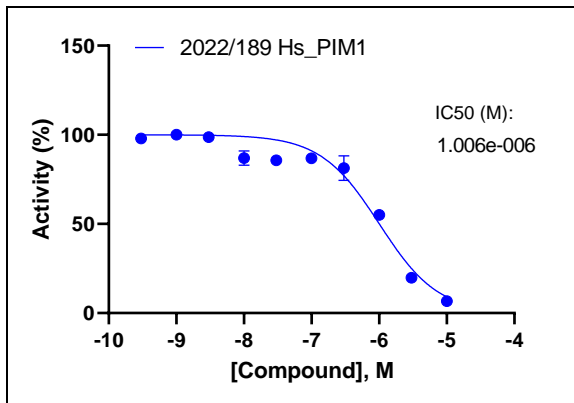
Compound 13 or NM-022



Compound 39 or NM-261



Compound 28 or NM-259



Compound 35 or NM-302

