

Electronic Supplementary Information

Ruthenium-catalyzed C–H functionalization of indoles and indolines with 7-azabenzonorbornadienes: access to aminodihydronaphthyl indoles and indolines

Jia-Zhen Chen and Zhong-Xia Wang*

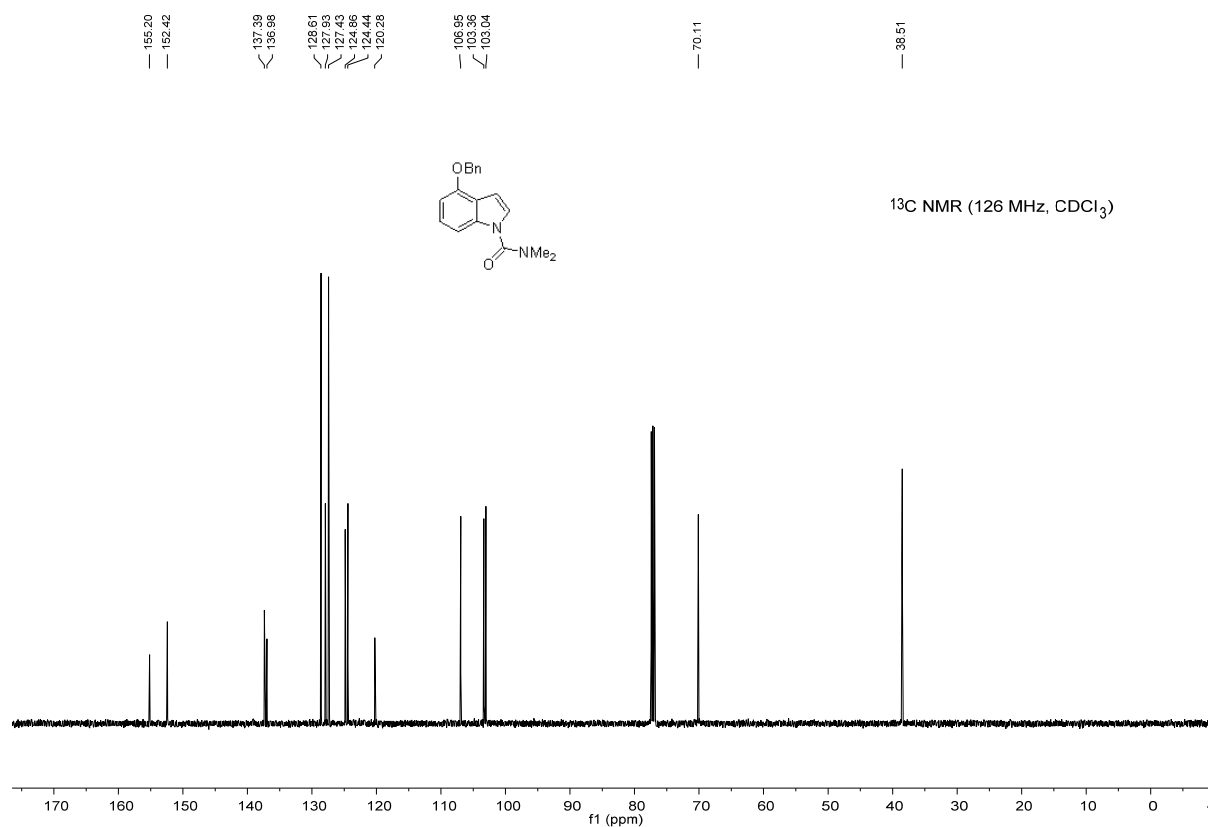
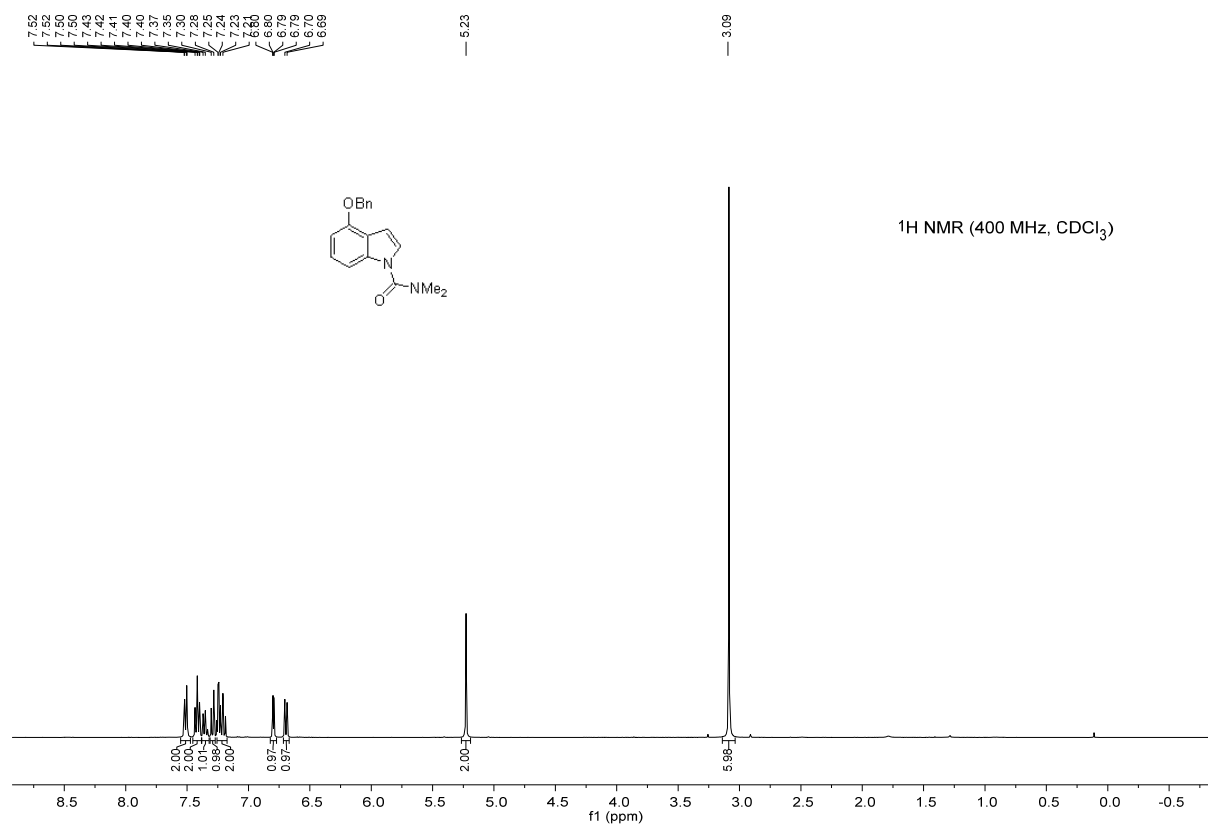
CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. Email: zxiwang@ustc.edu.cn.

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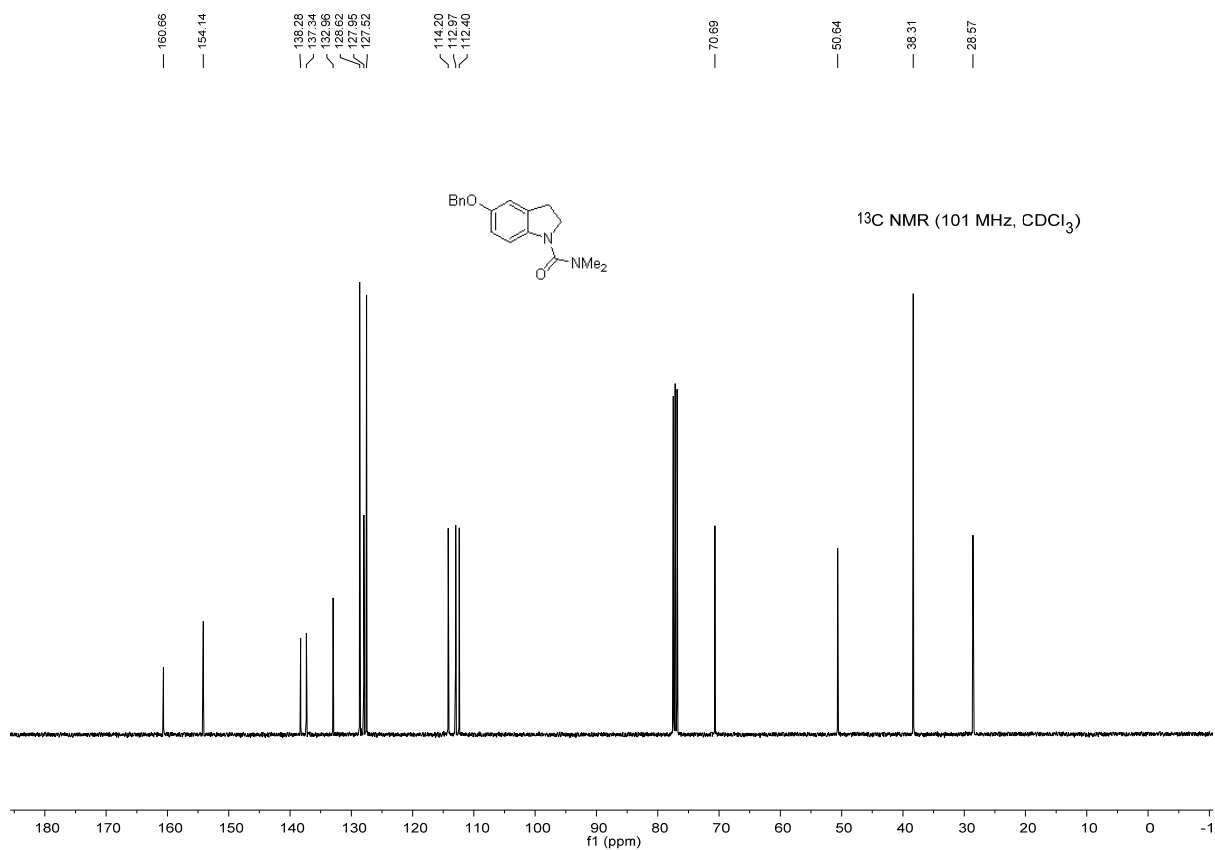
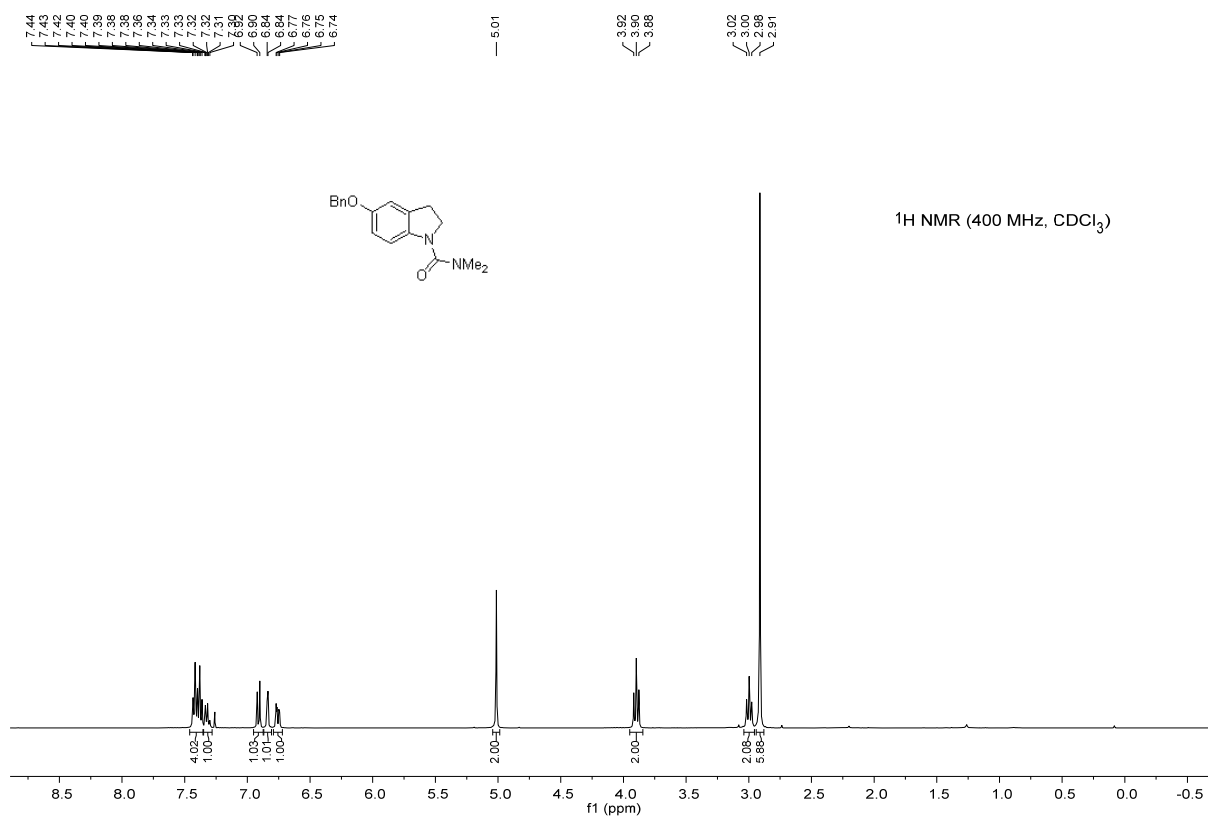
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NMR spectral copies of unreported reactants

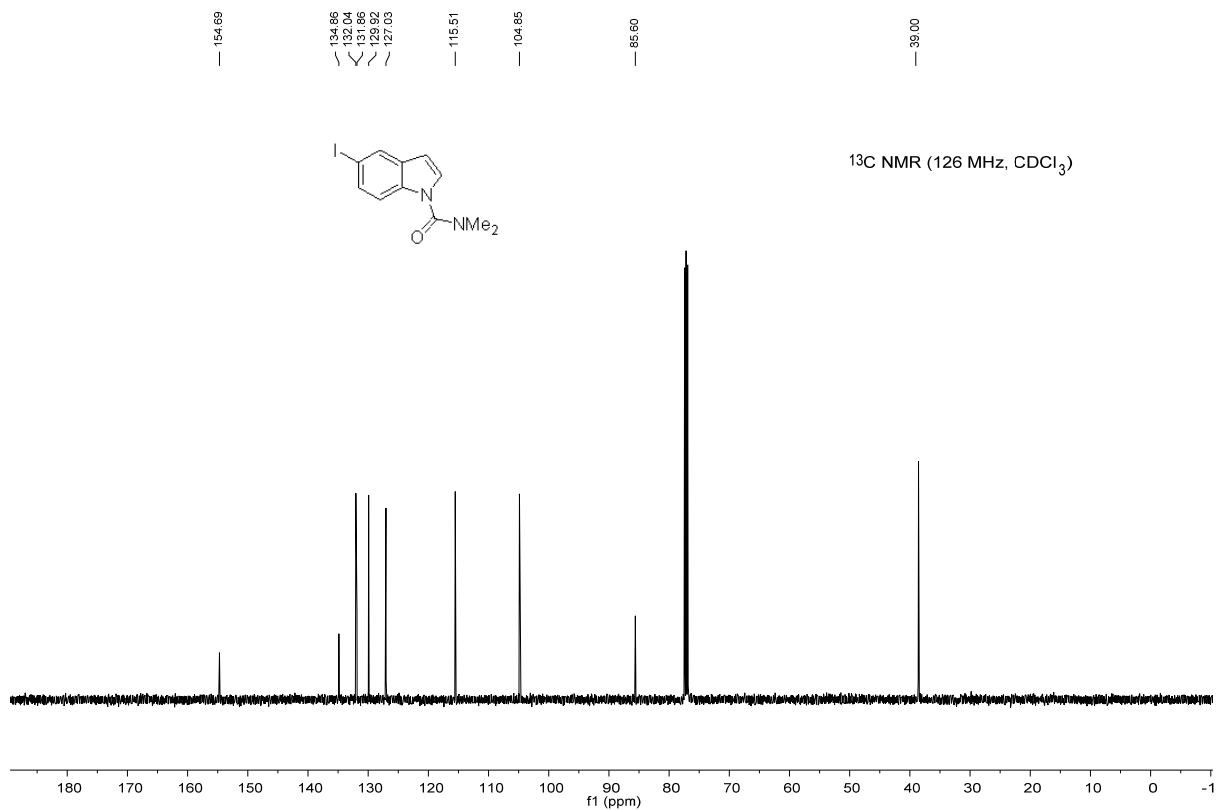
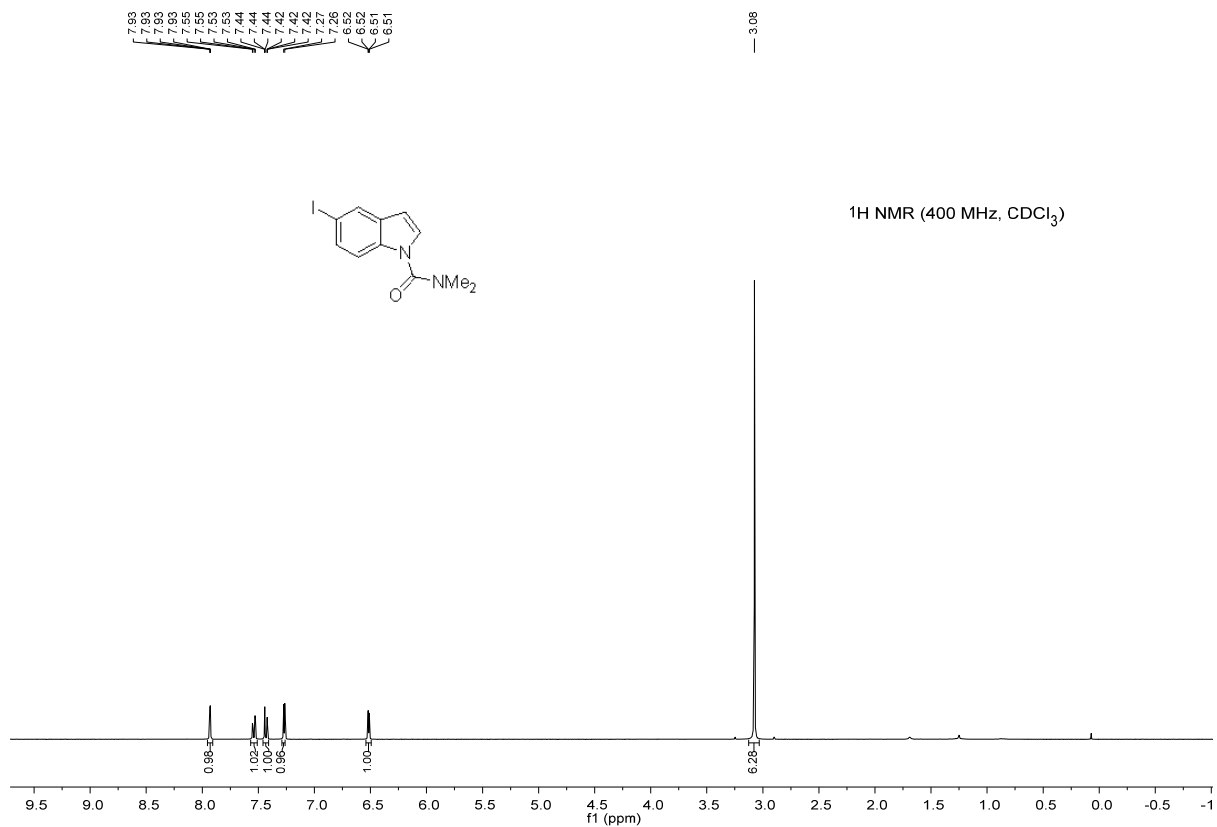
(1) 4-(benzyloxy)-*N,N*-dimethyl-1*H*-indole-1-carboxamide (**1d**)



(2) 5-(benzyloxy)-N,N-dimethylindoline-1-carboxamide (**1j**)

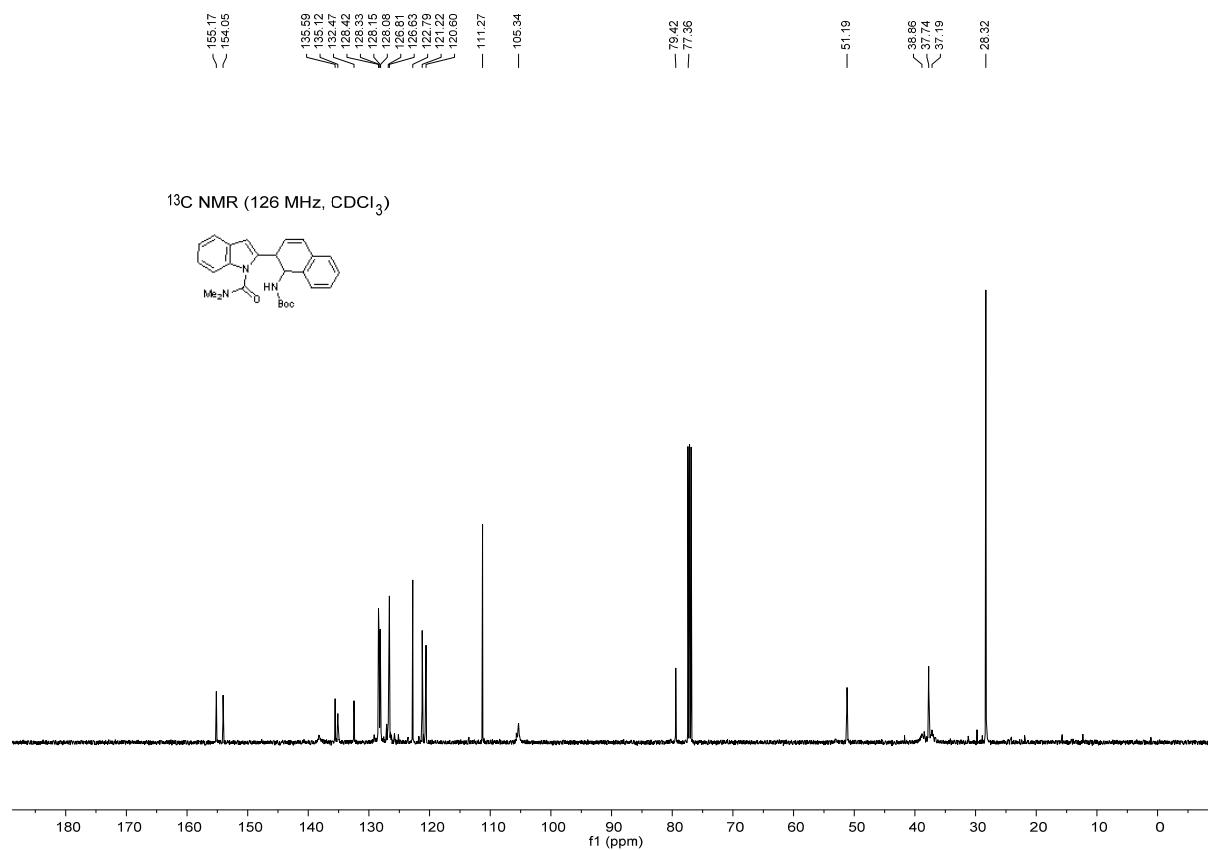
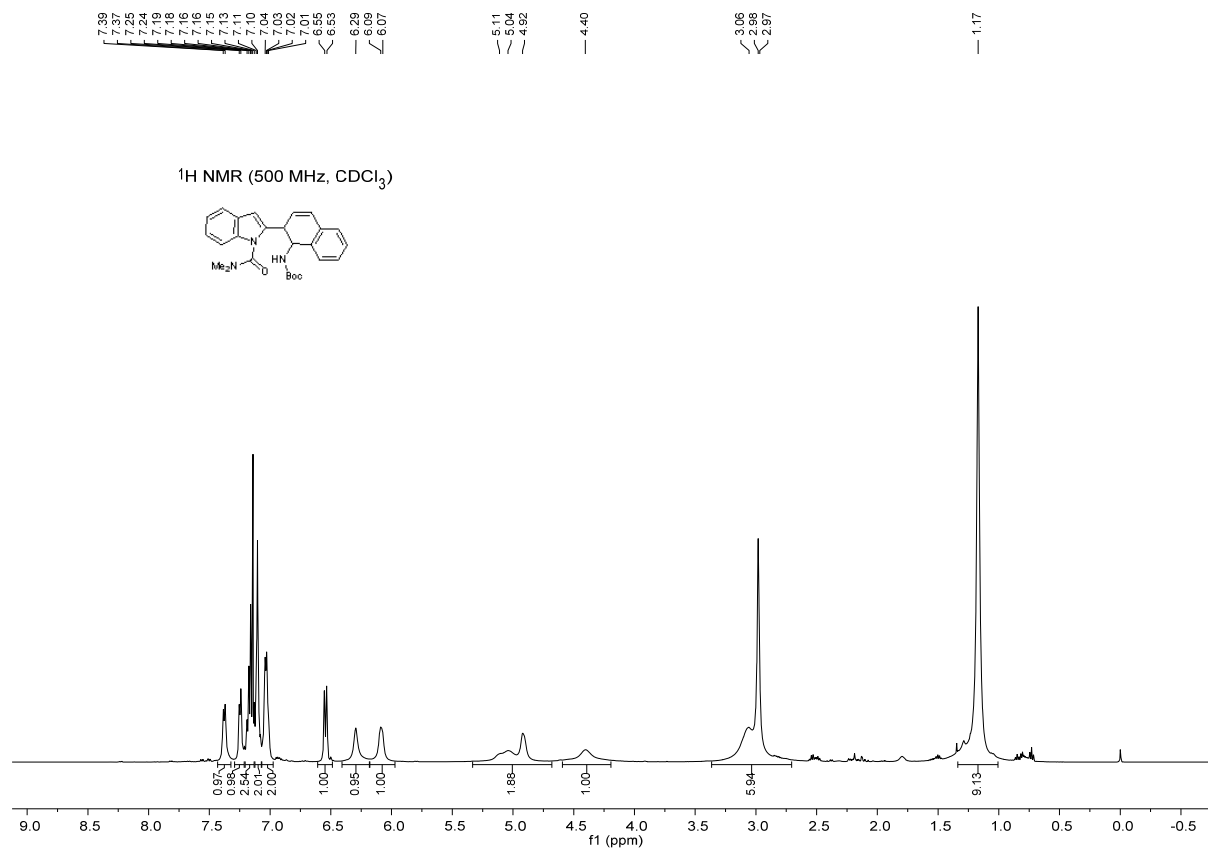


(3) 5-iodo-N,N-dimethyl-1*H*-indole-1-carboxamide (**1n**)



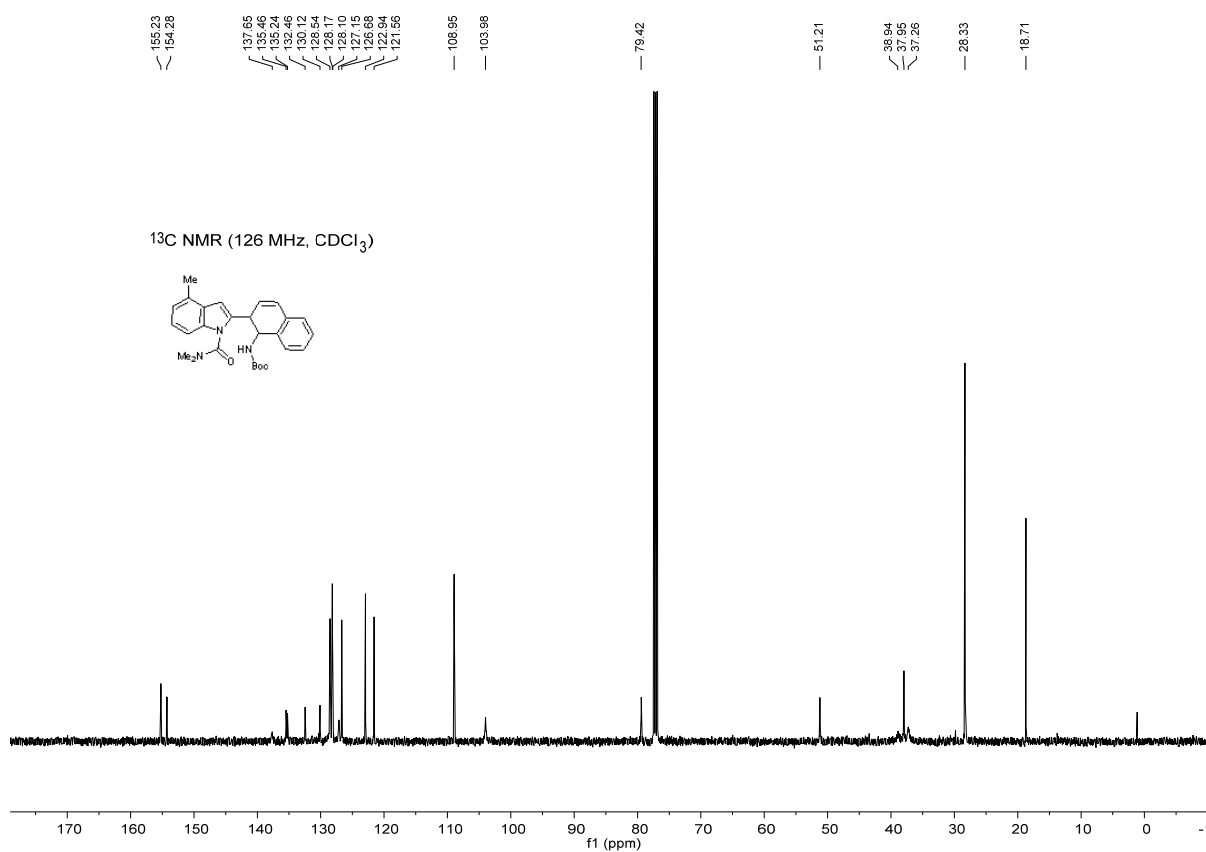
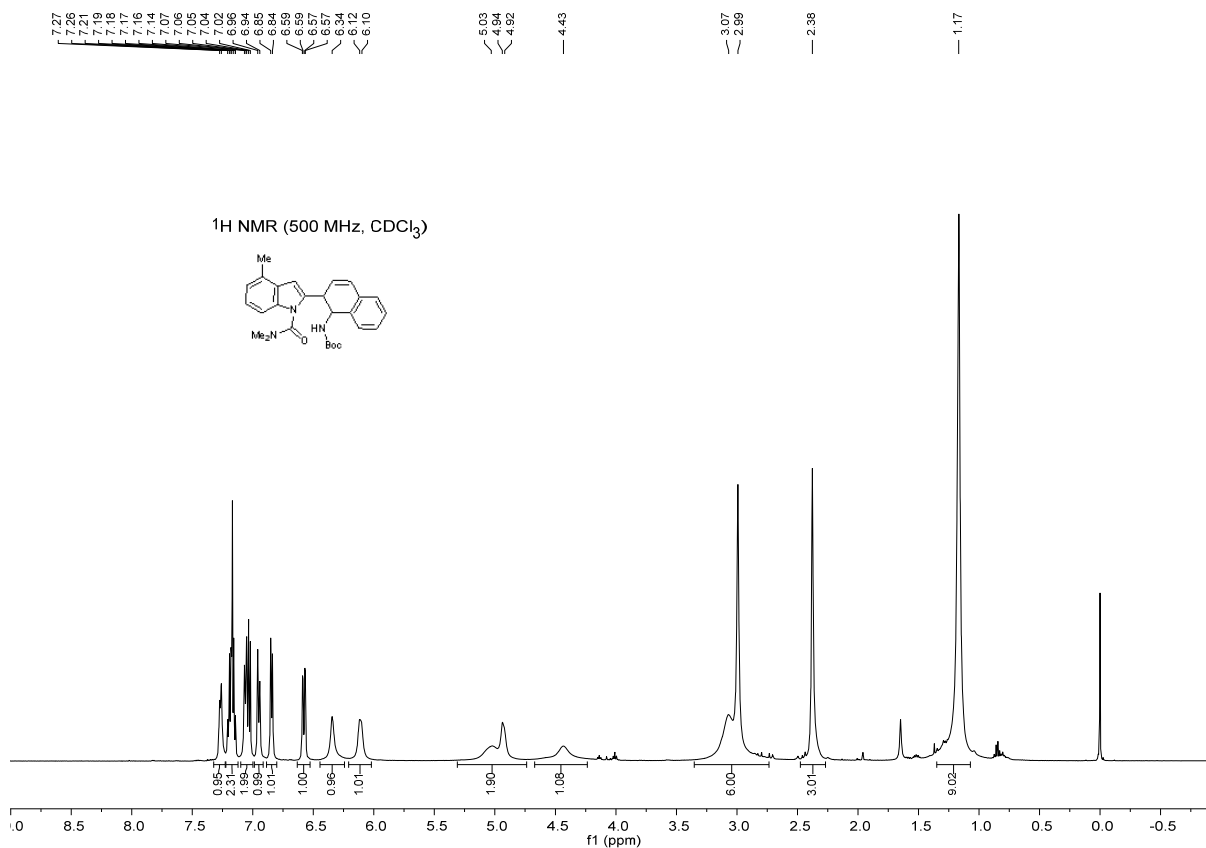
NMR spectral copies of the coupling products

(1) *tert*-butyl (2-(1-(dimethylcarbamoyl)-1H-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate (**3a**)

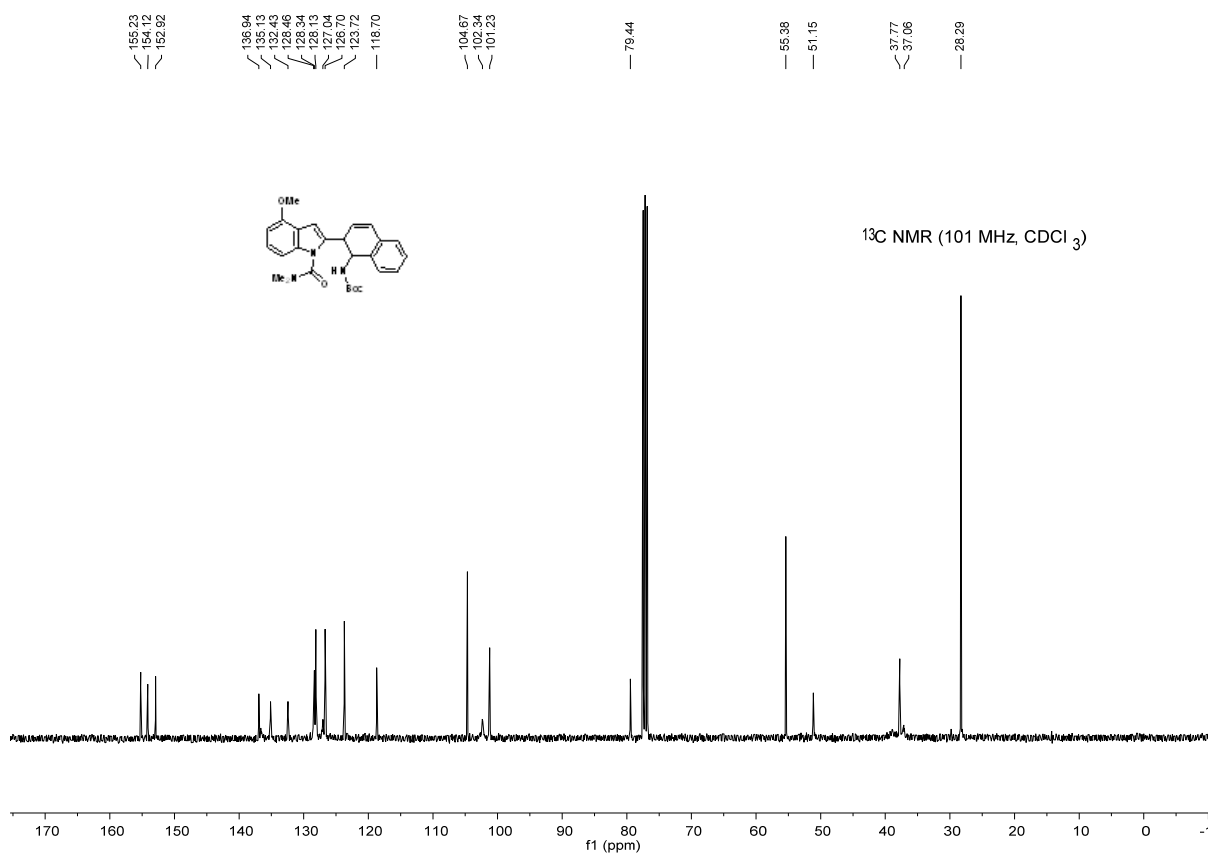
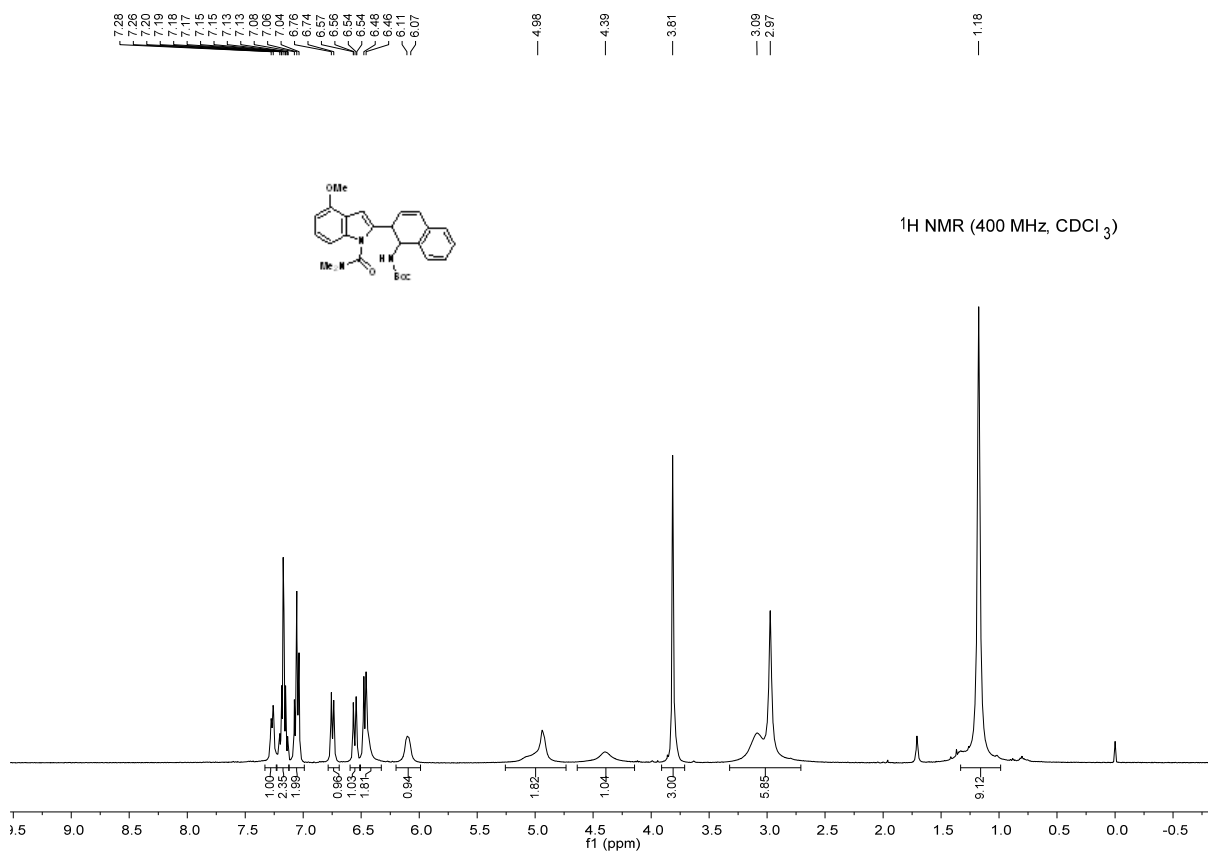


(2) *tert*-butyl (2-(1-(dimethylcarbamoyl)-4-methyl-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate

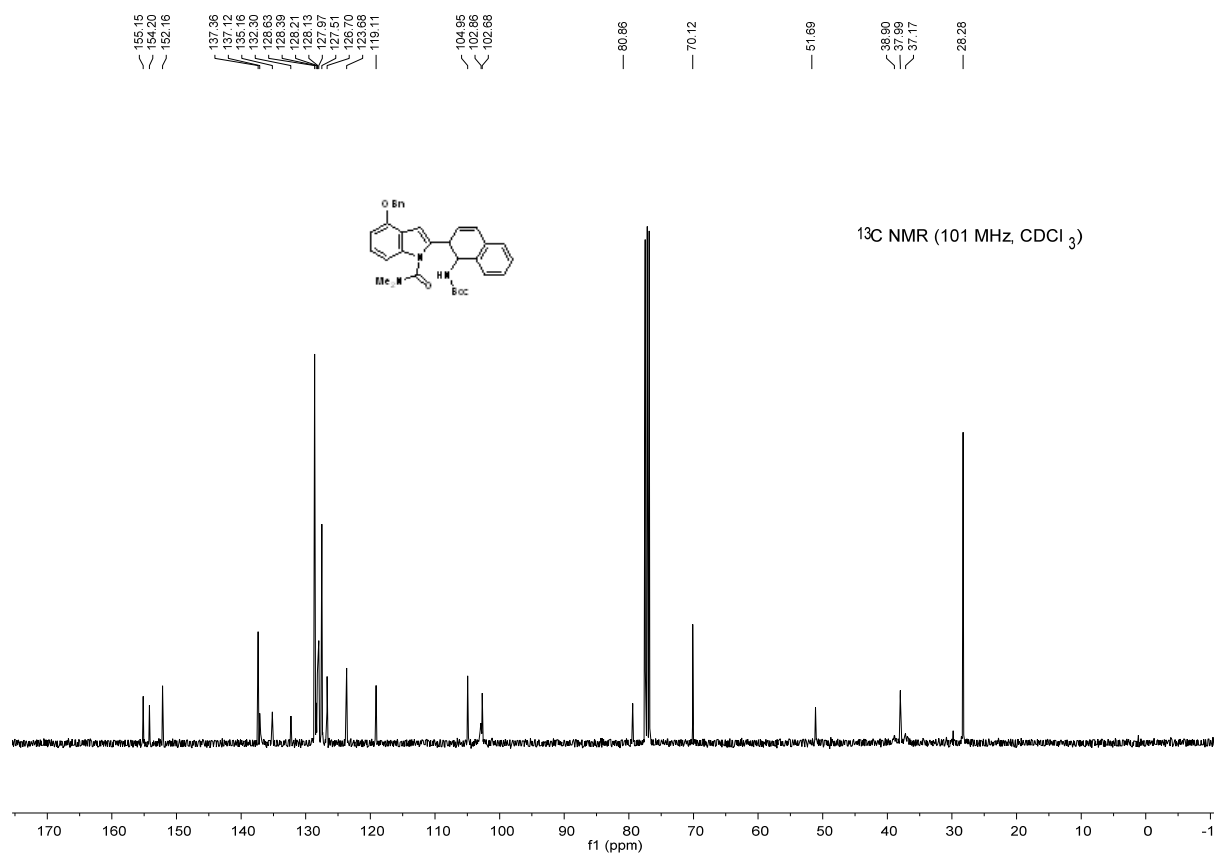
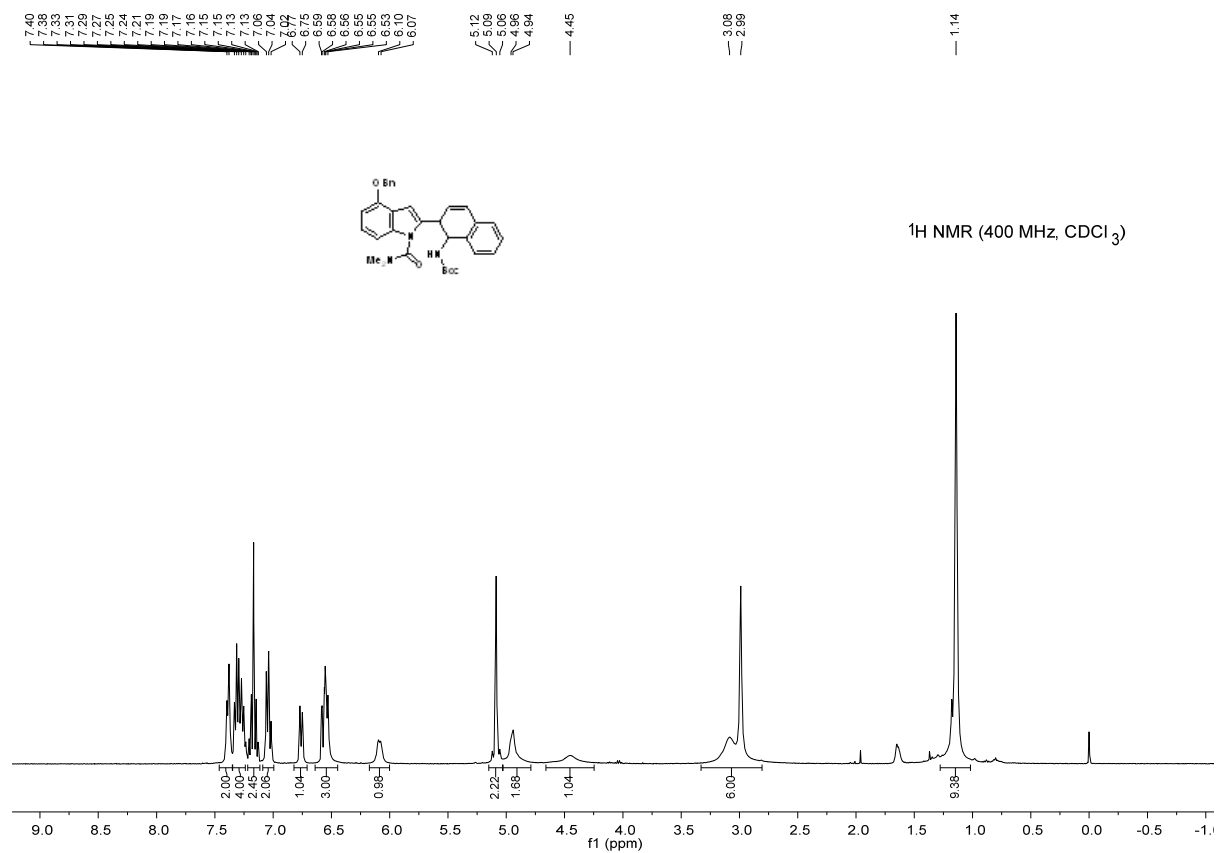
(3b)



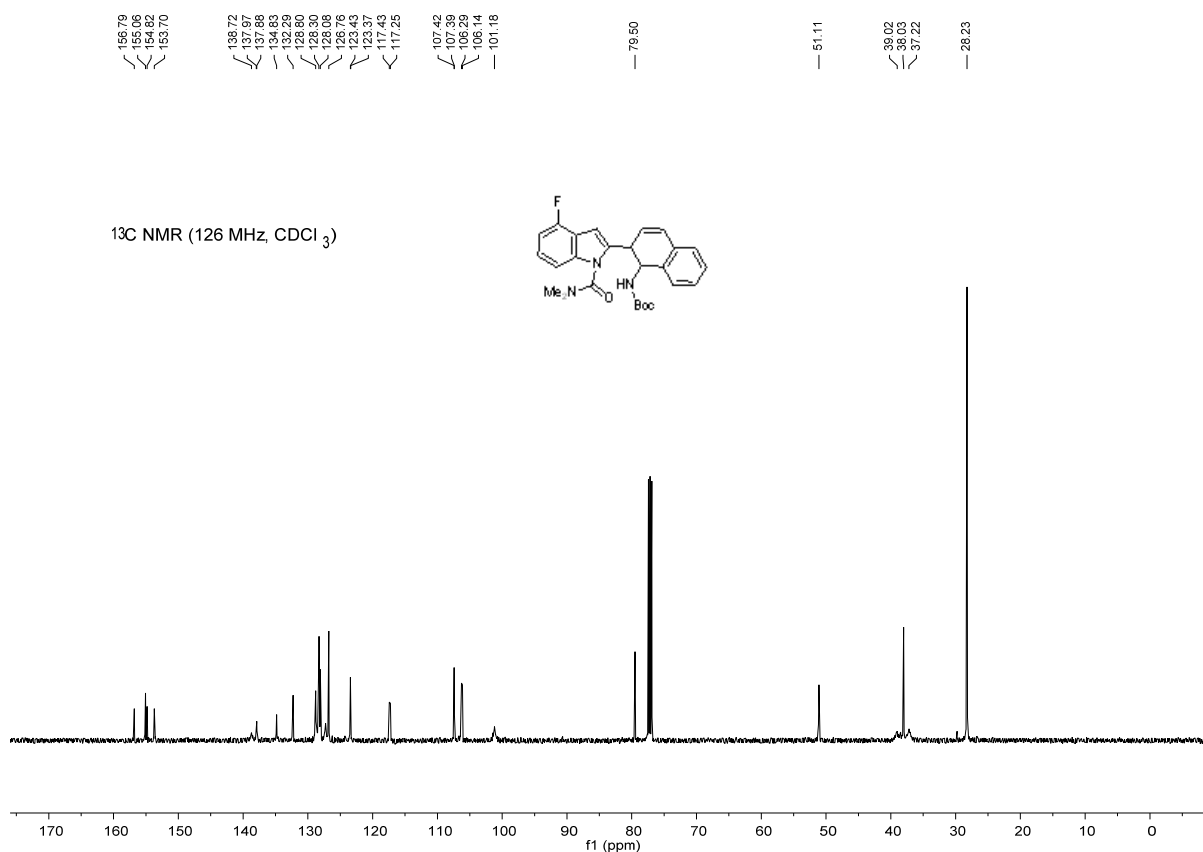
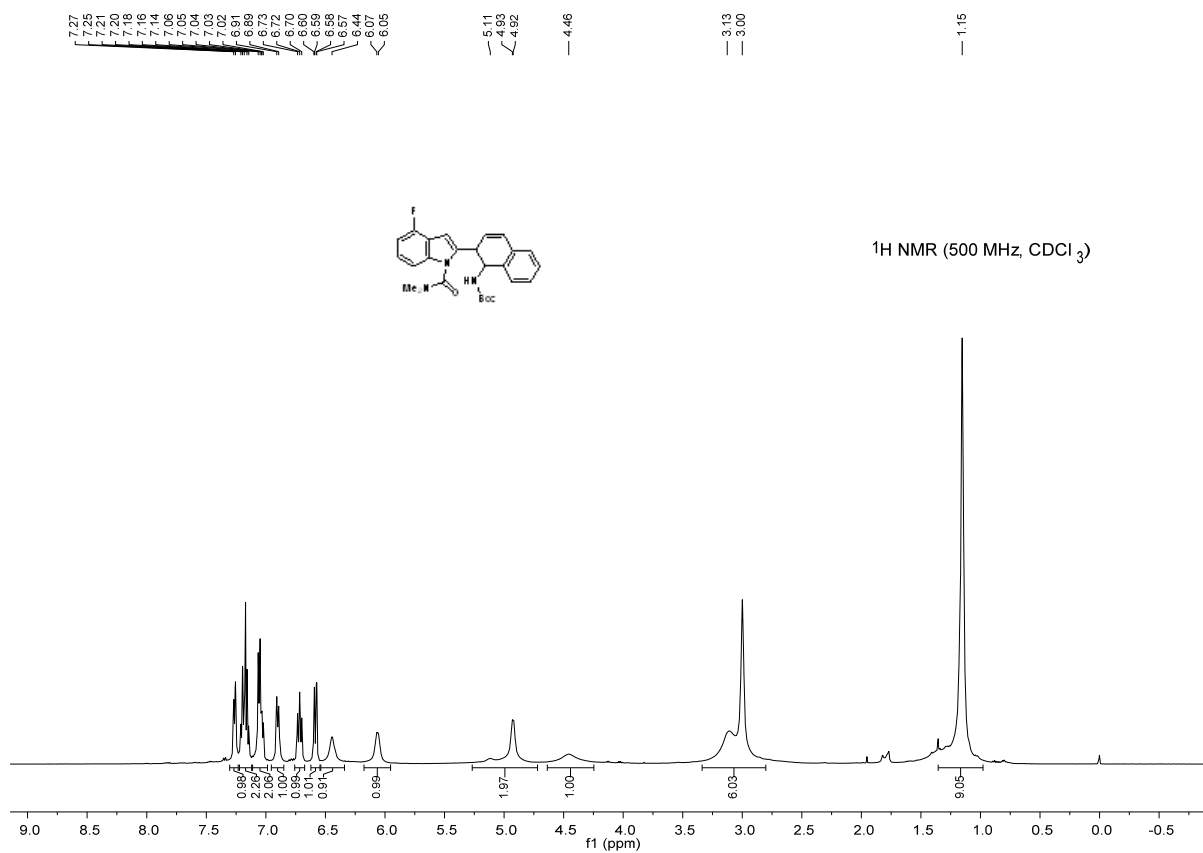
(3) *tert*-butyl(2-(1-(dimethylcarbamoyl)-4-methoxy-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(3c)

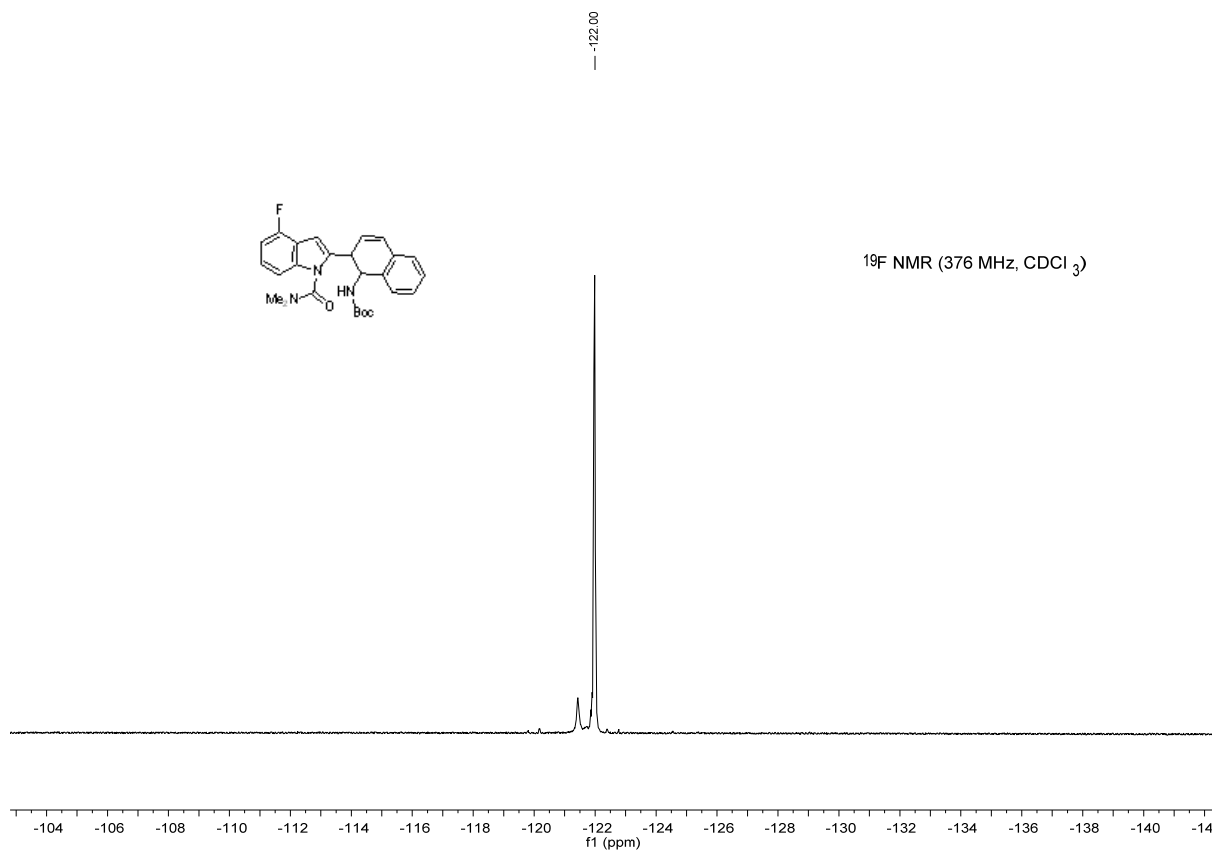


(4) *tert*-butyl (2-(4-(benzyloxy)-1-(dimethylcarbamoyl)-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate (**3d**)

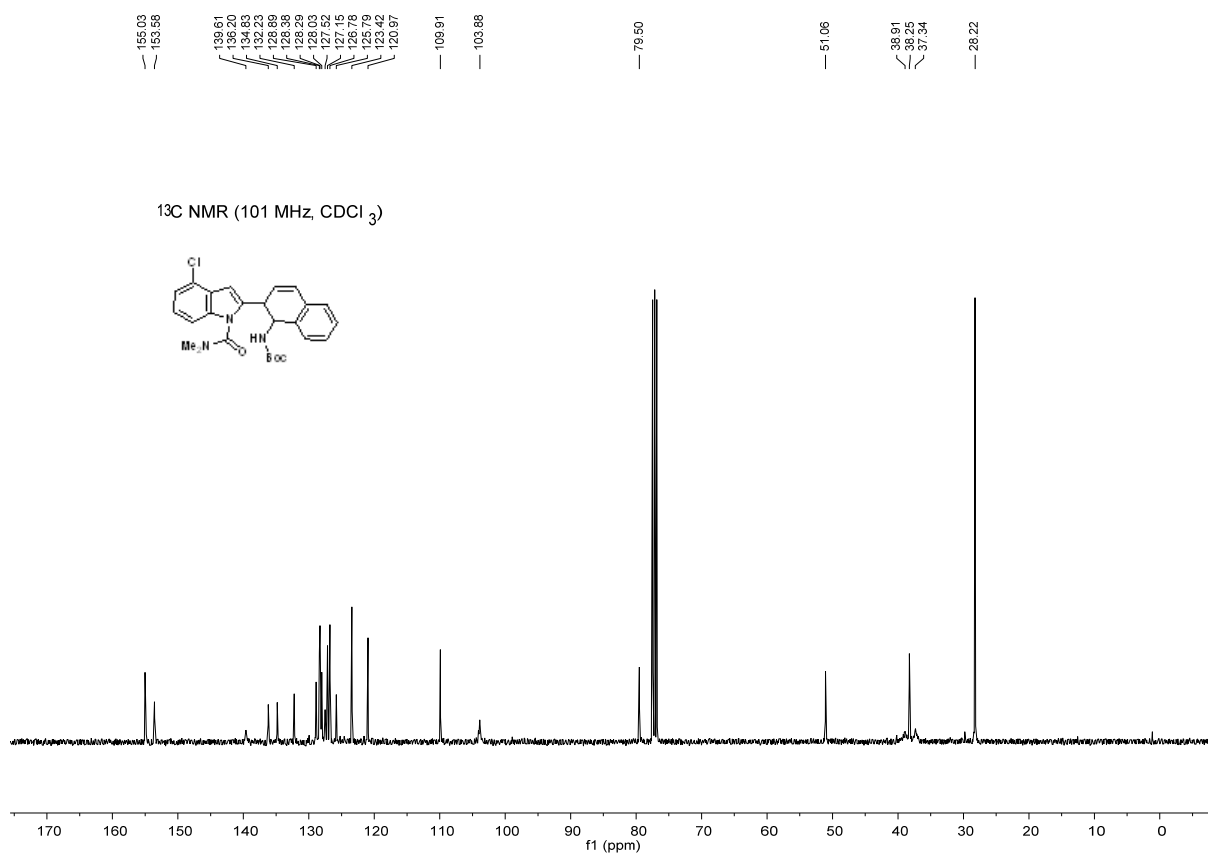
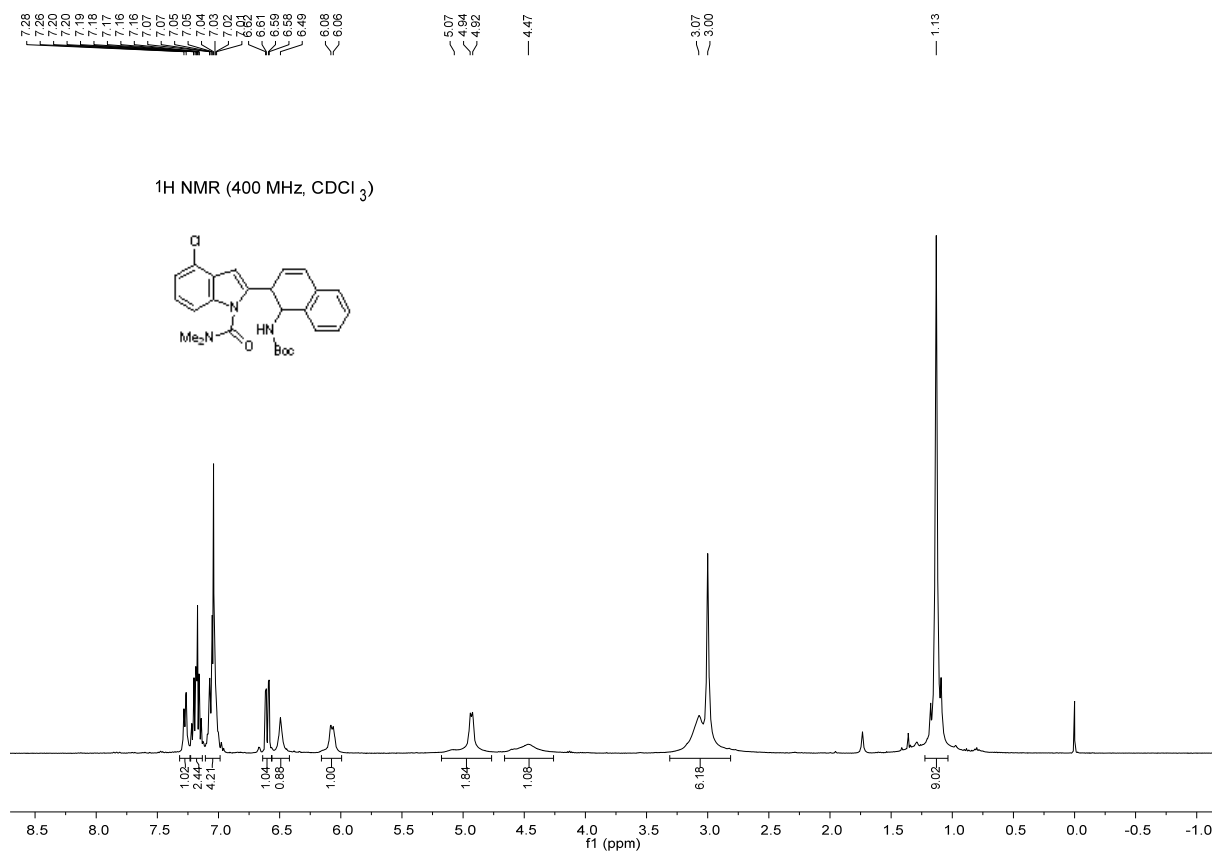


(5) *tert*-butyl (2-(1-(dimethylcarbamoyl)-4-fluoro-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(3e)

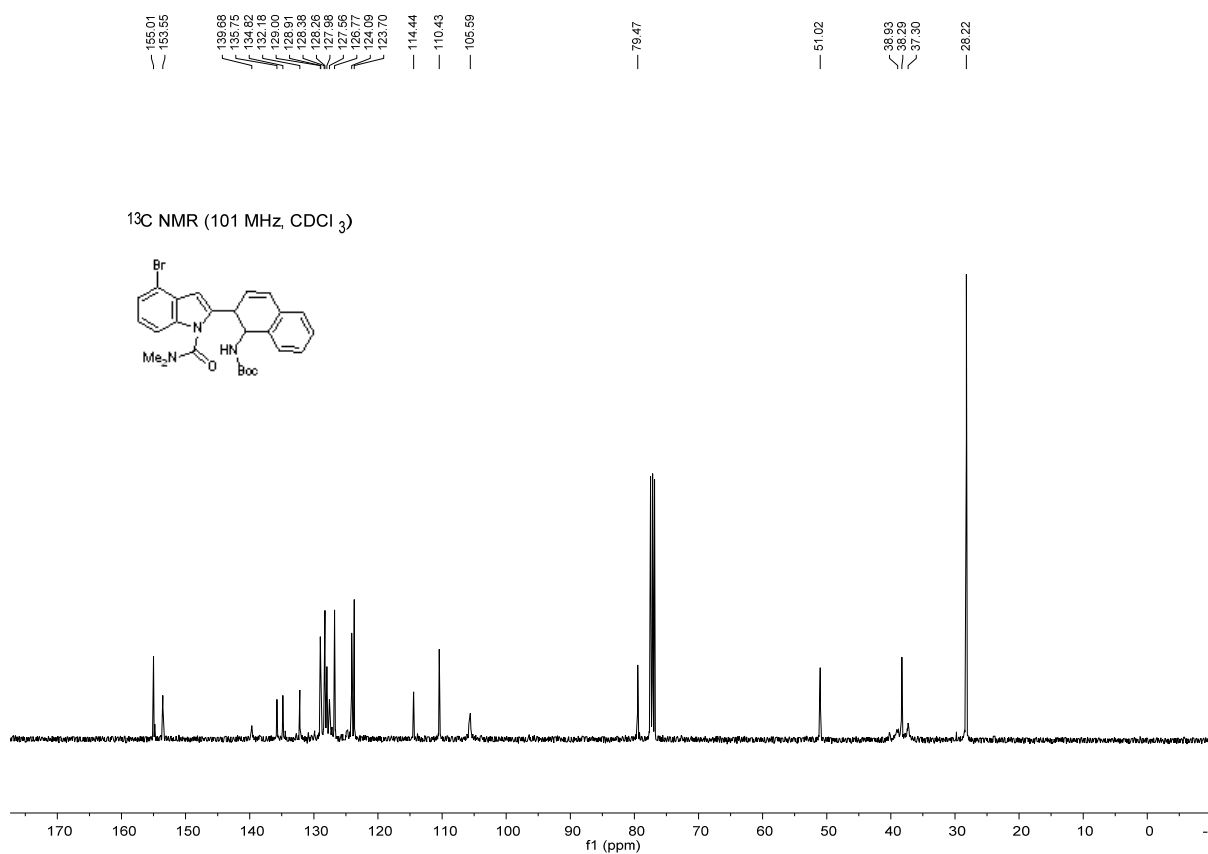
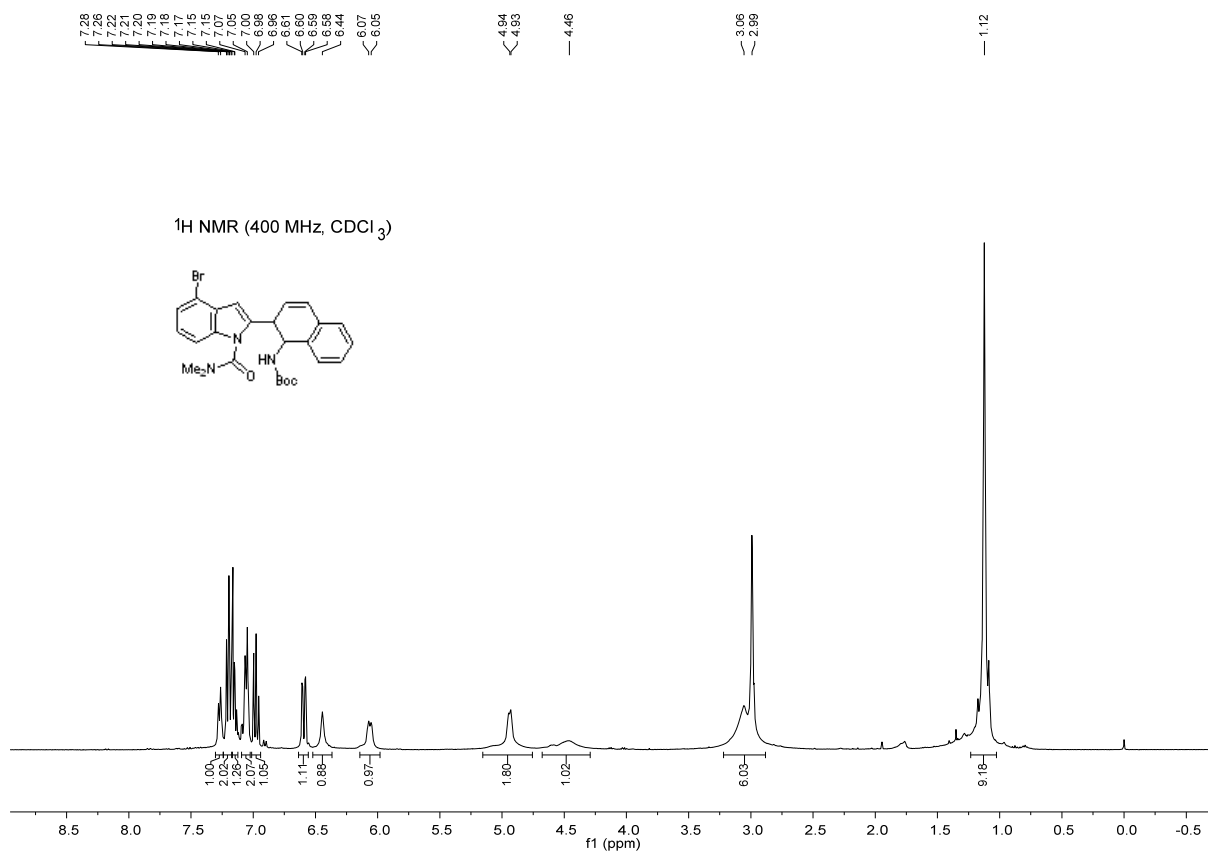




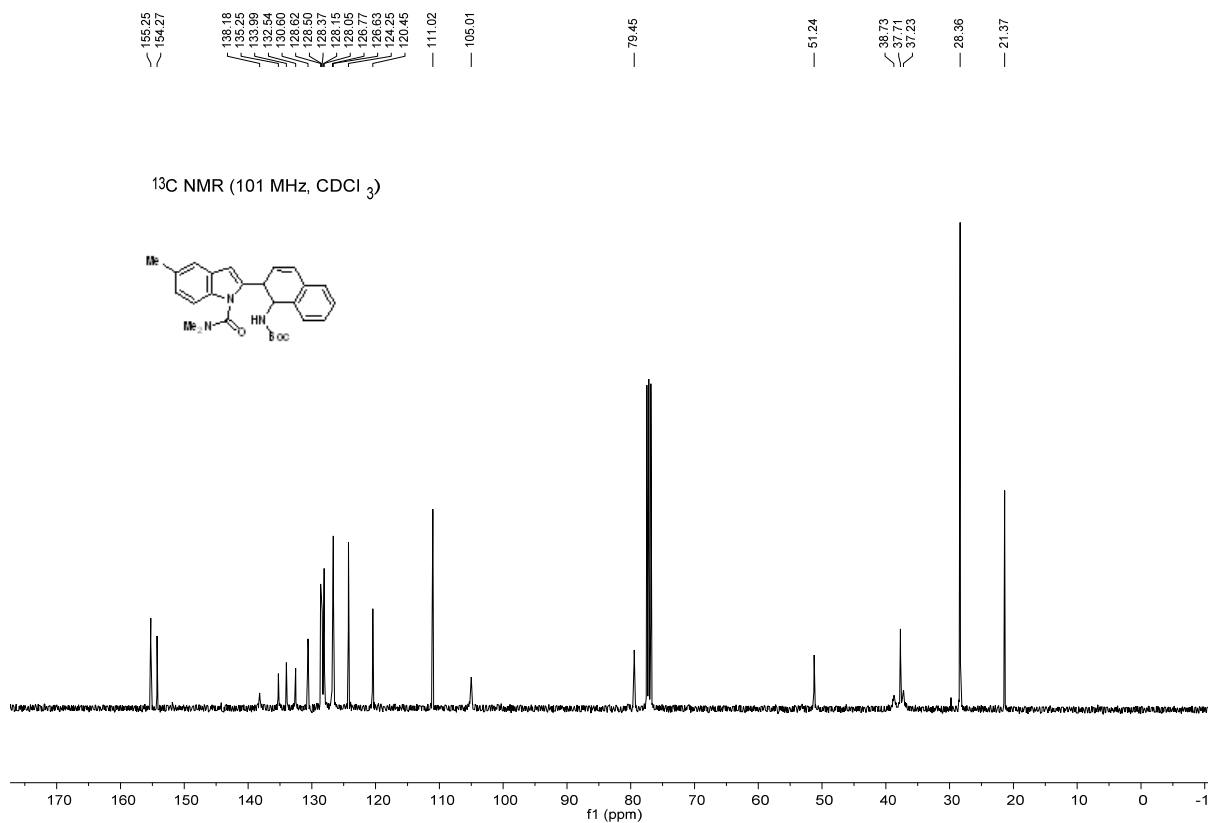
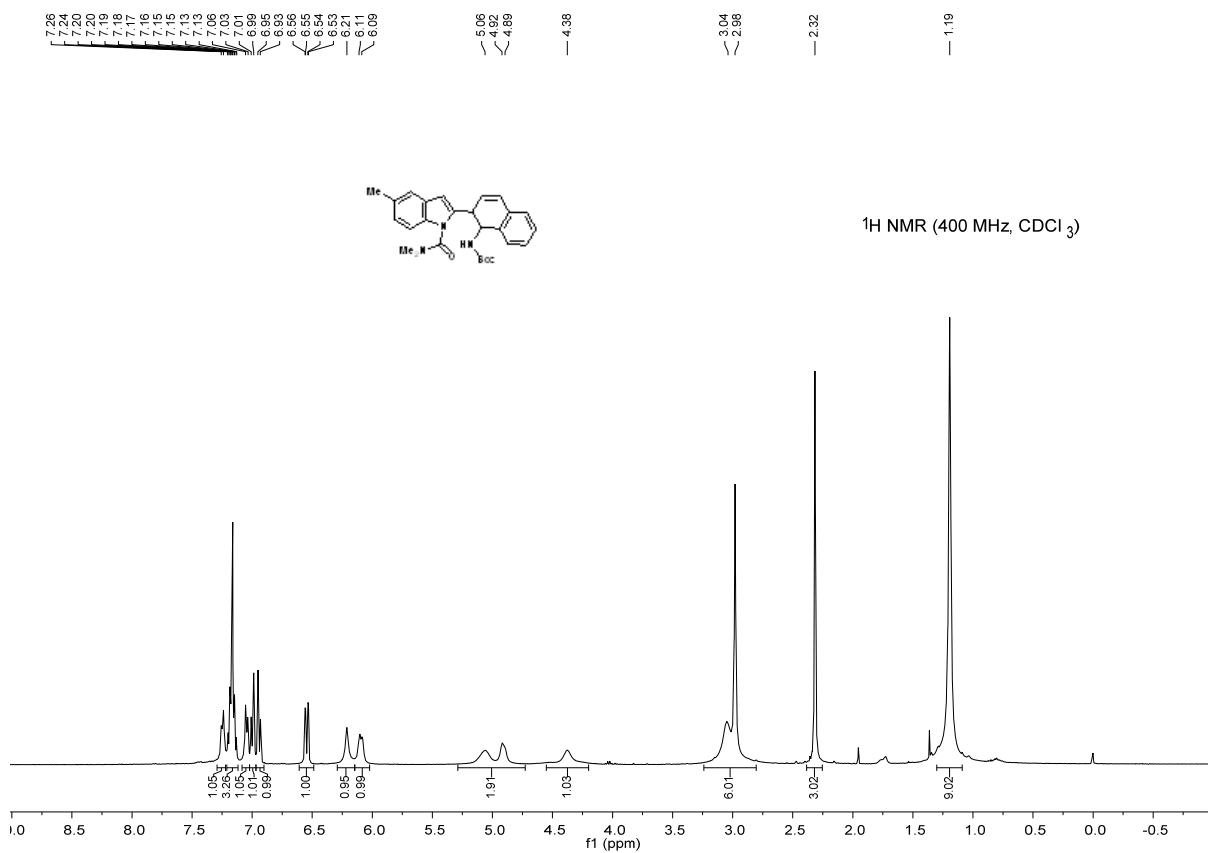
(6) *tert*-butyl (2-(4-chloro-1-(dimethylcarbamoyl)-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(3f)



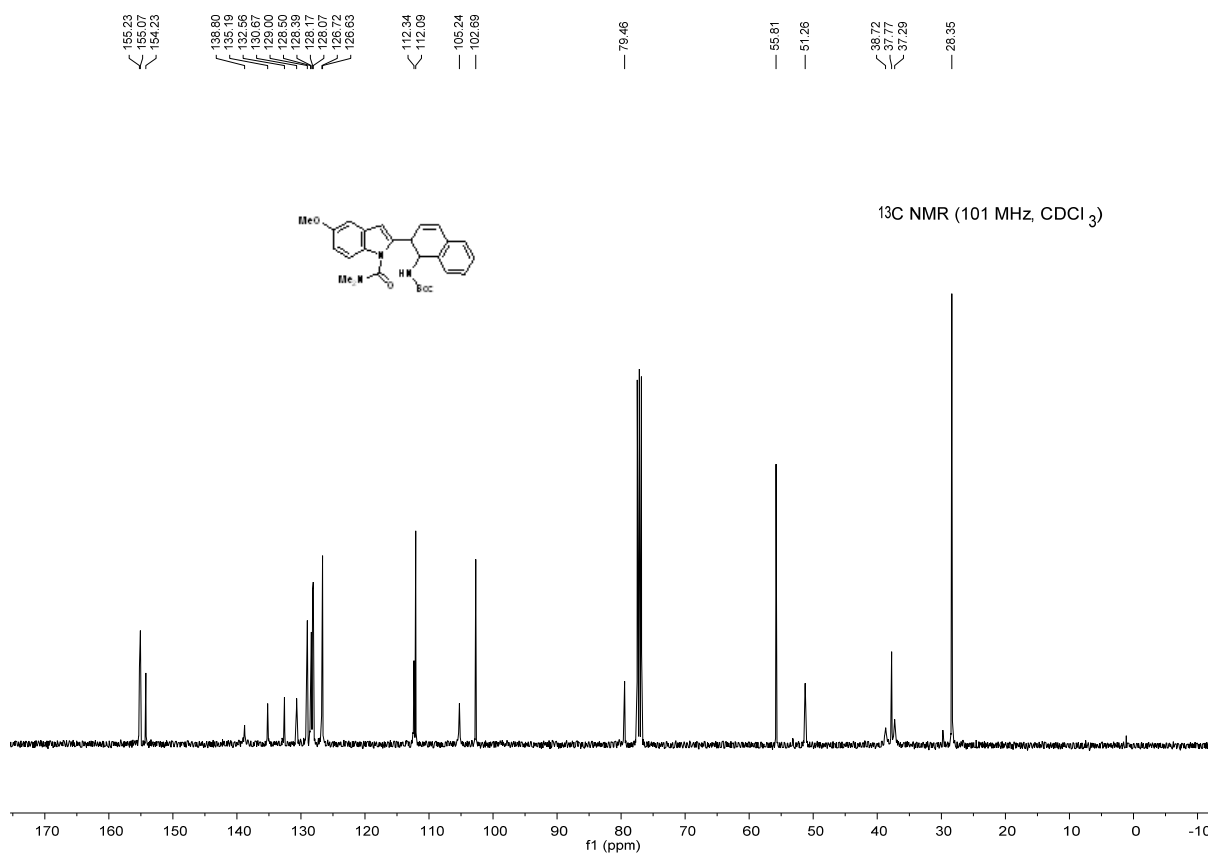
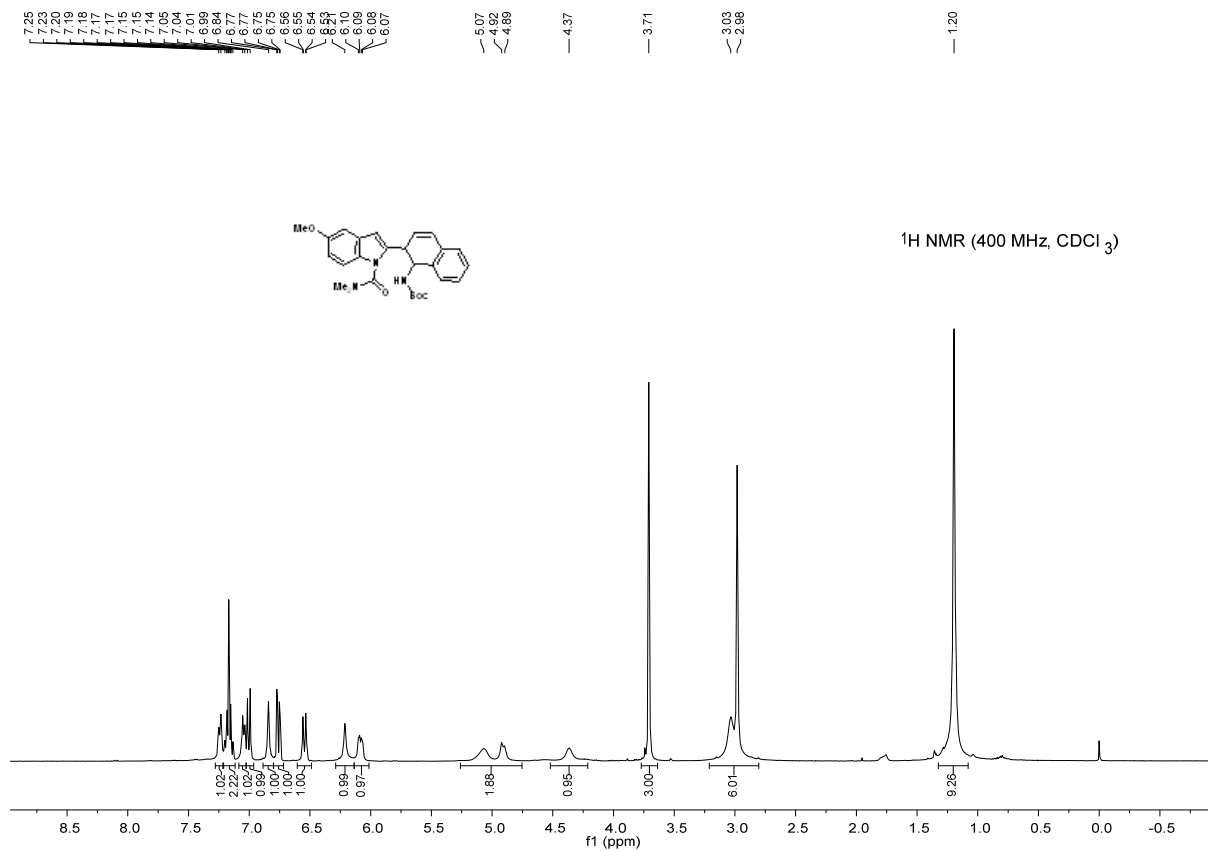
(7) *tert*-butyl (2-(4-bromo-1-(dimethylcarbamoyl)-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(3g)



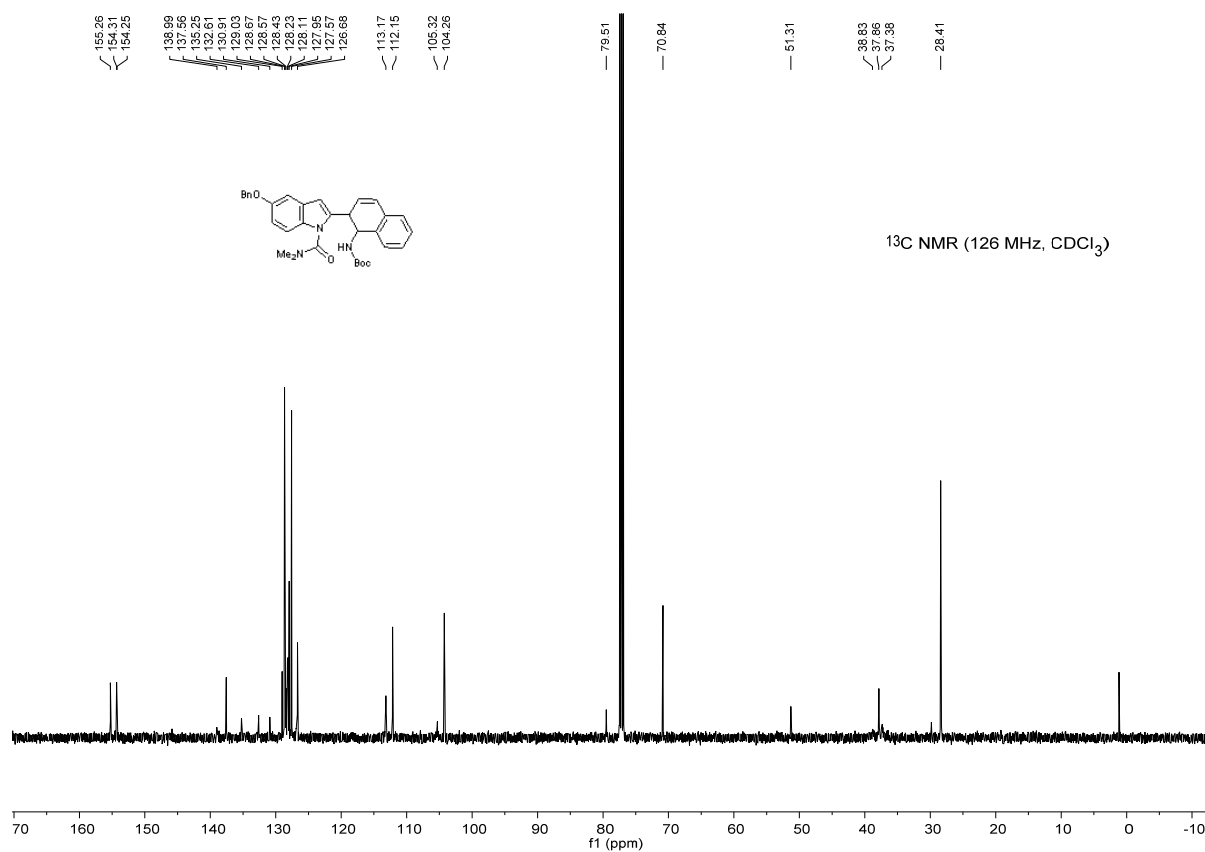
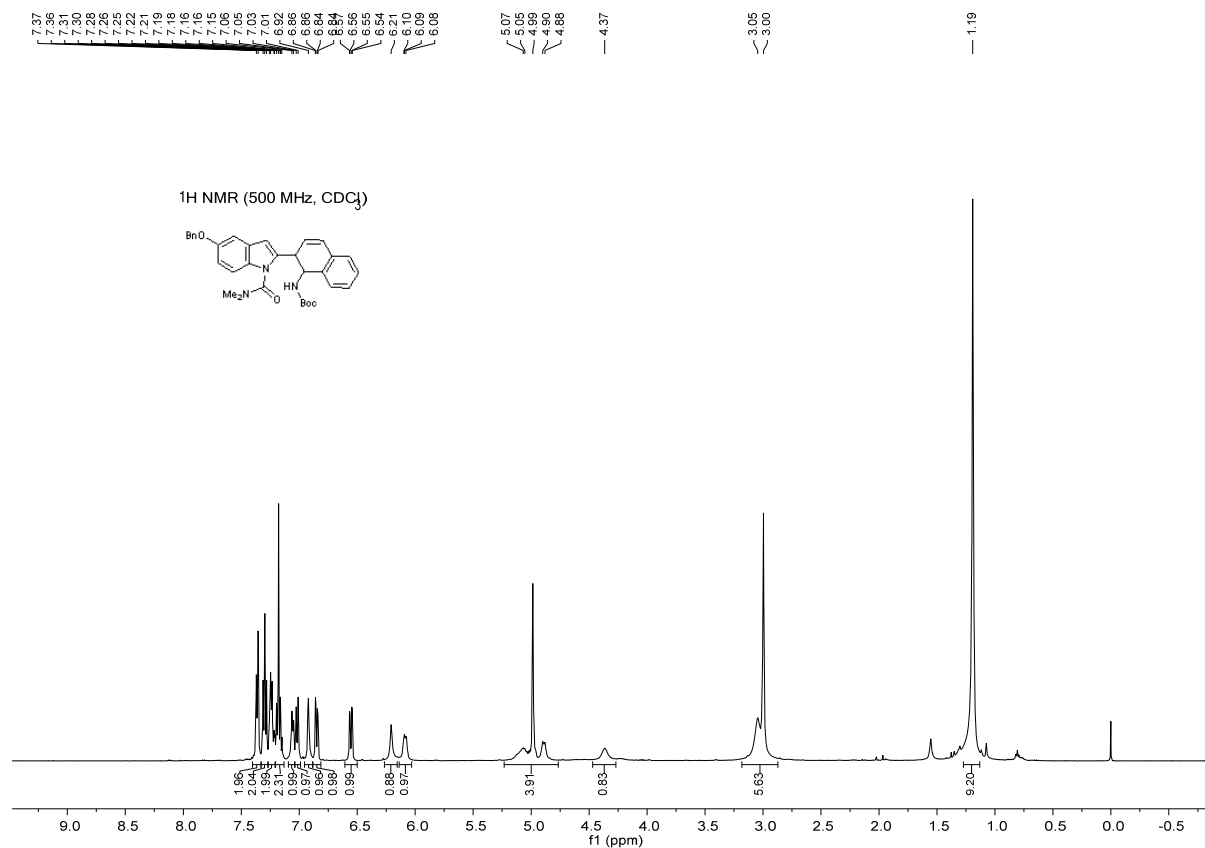
(8) *tert*-butyl (2-(1-(dimethylcarbamoyl)-5-methyl-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(3h)



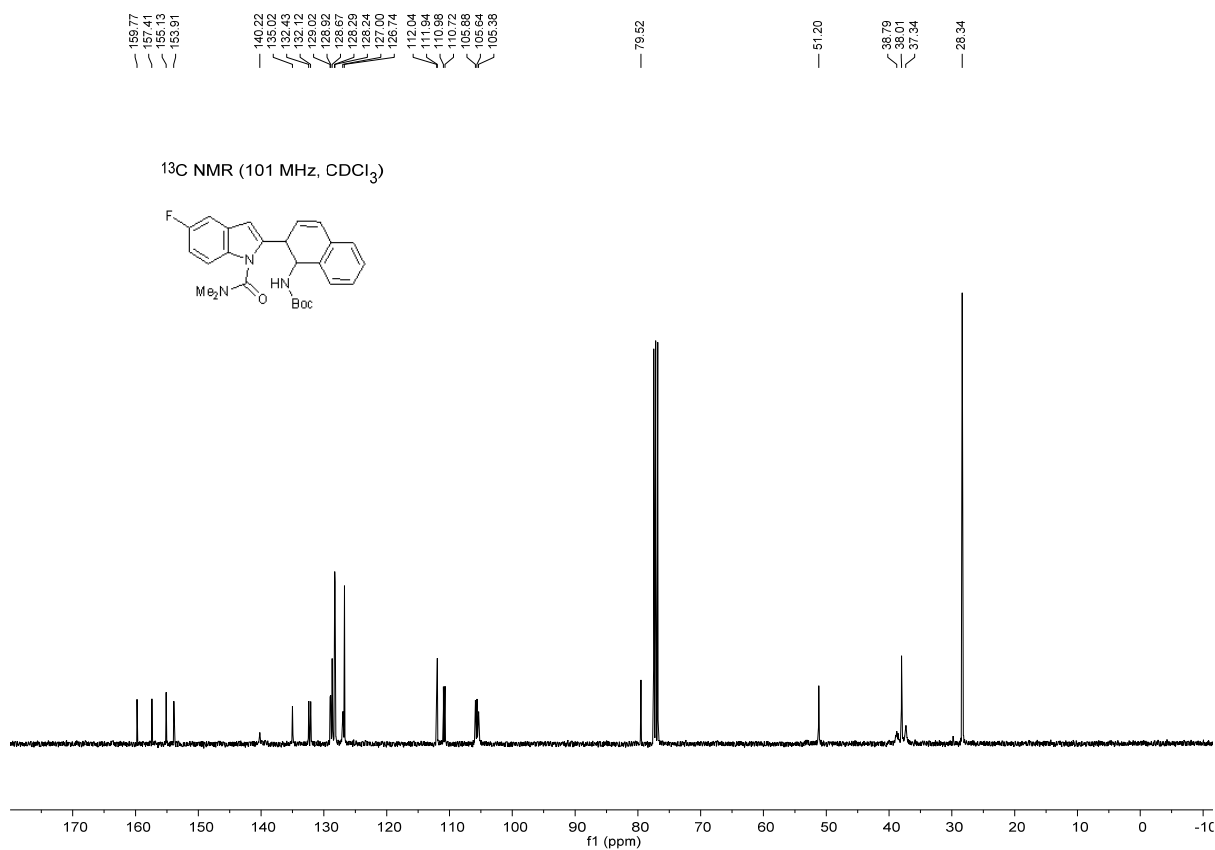
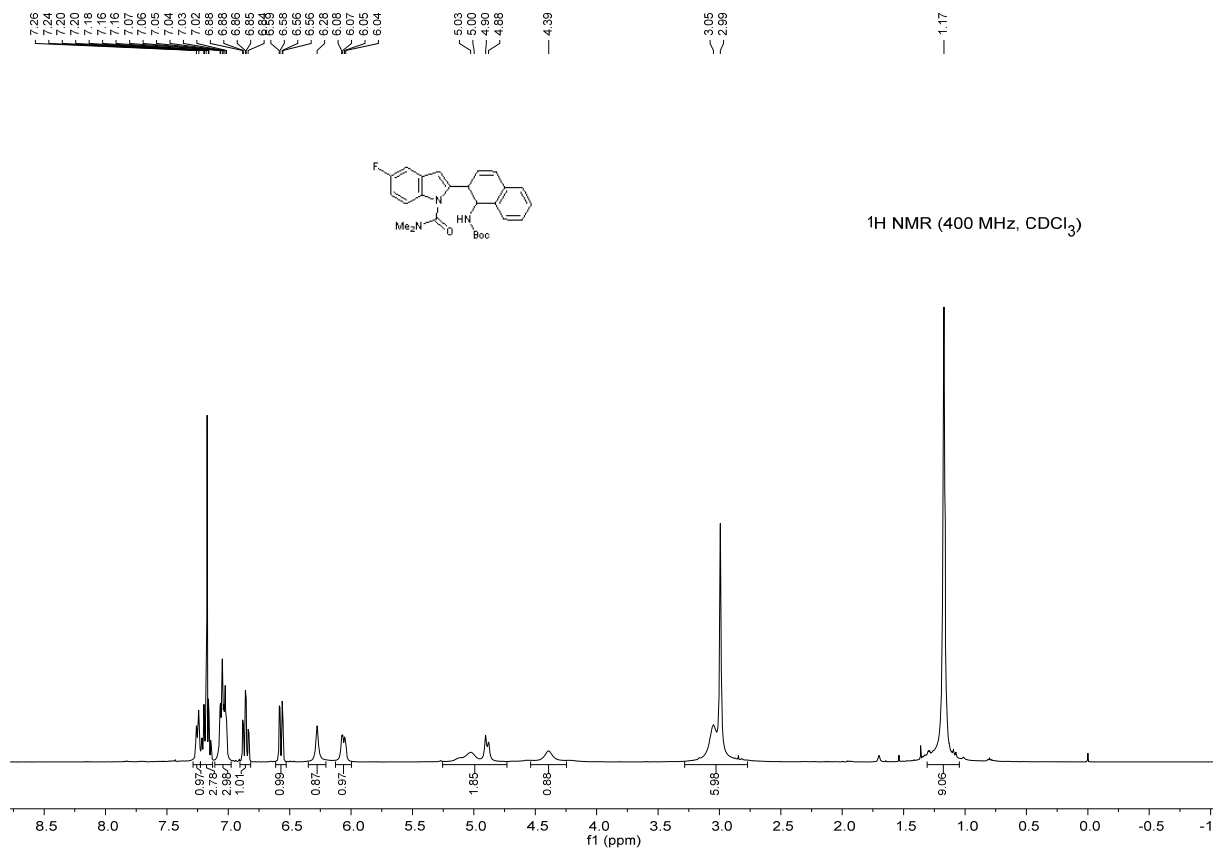
(9) *tert*-butyl (2-(1-(dimethylcarbamoyl)-5-methoxy-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(3i)

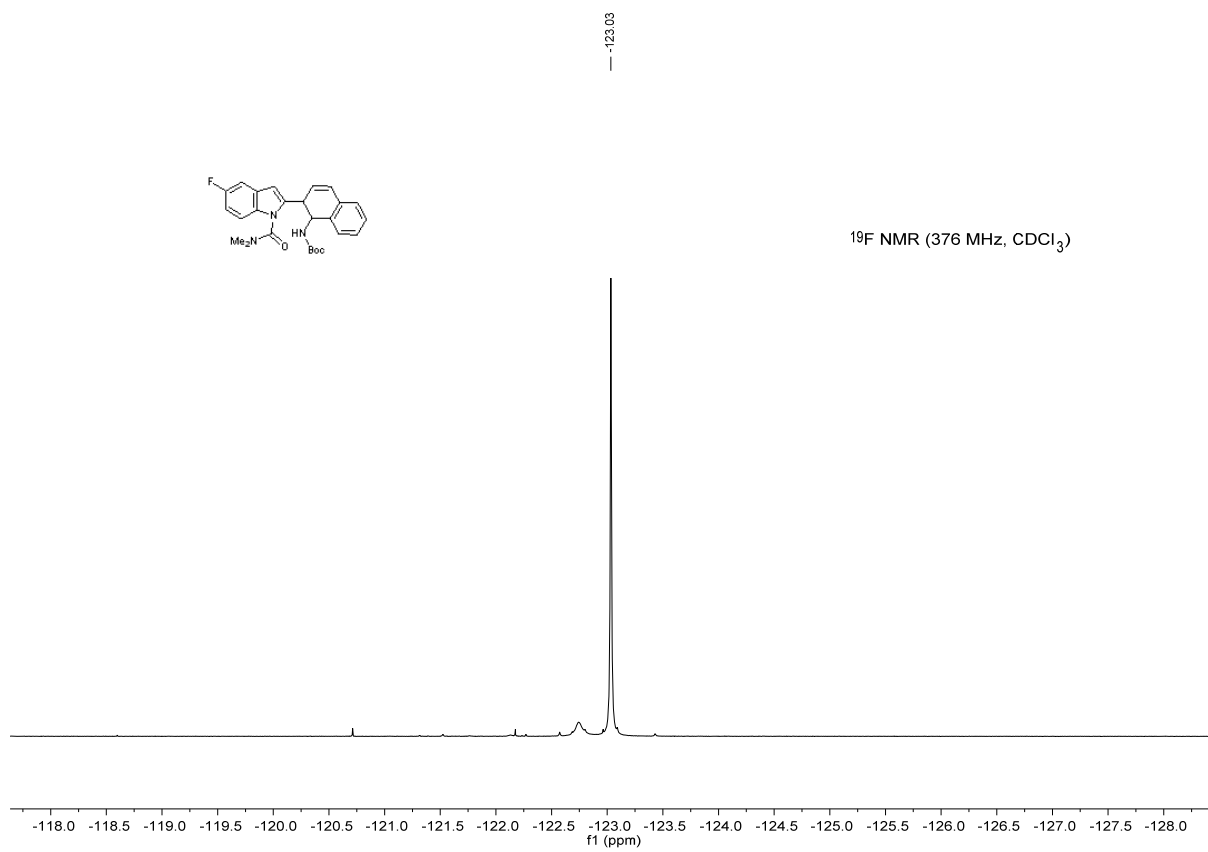


(10) *tert*-butyl (2-(5-(benzyloxy)-1-(dimethylcarbamoyl)-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl) carbamate (**3j**)



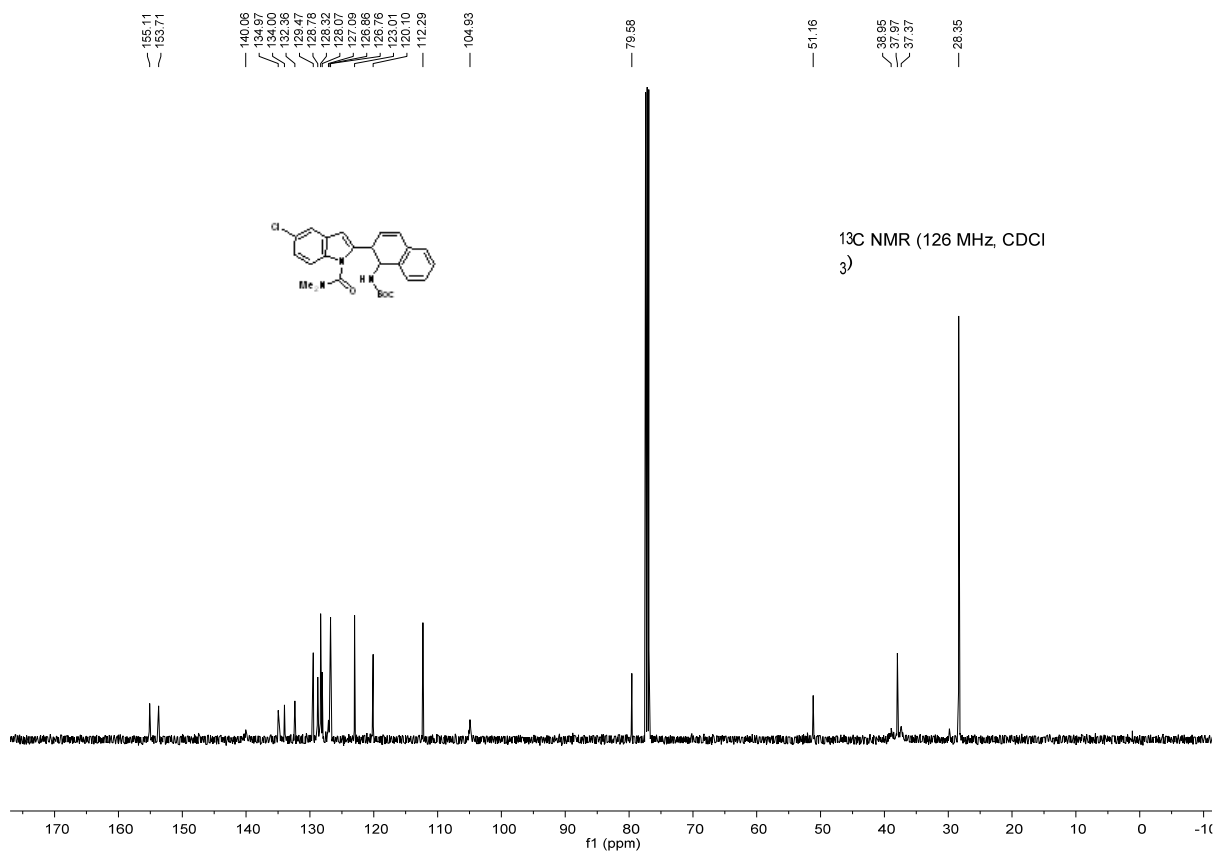
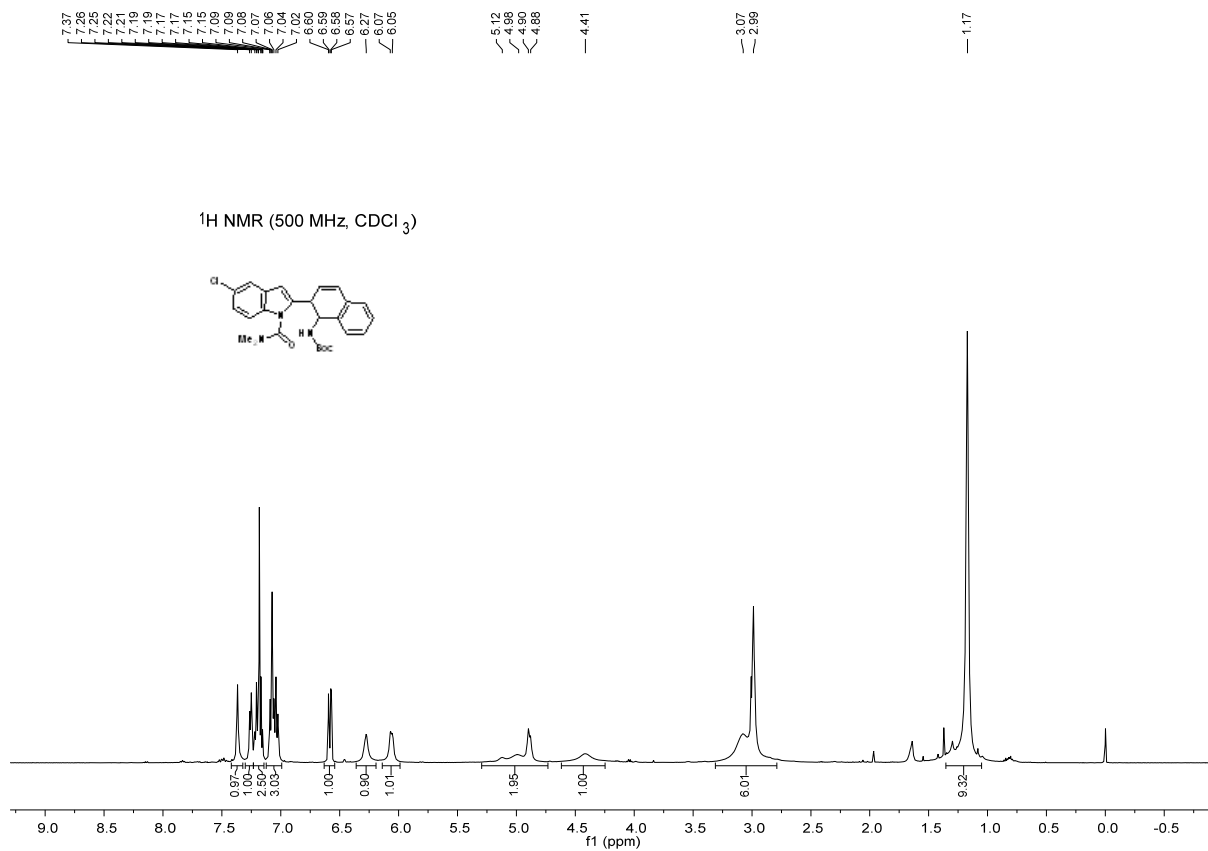
(10) *tert*-butyl (2-(1-(dimethylcarbamoyl)-5-fluoro-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(3k)



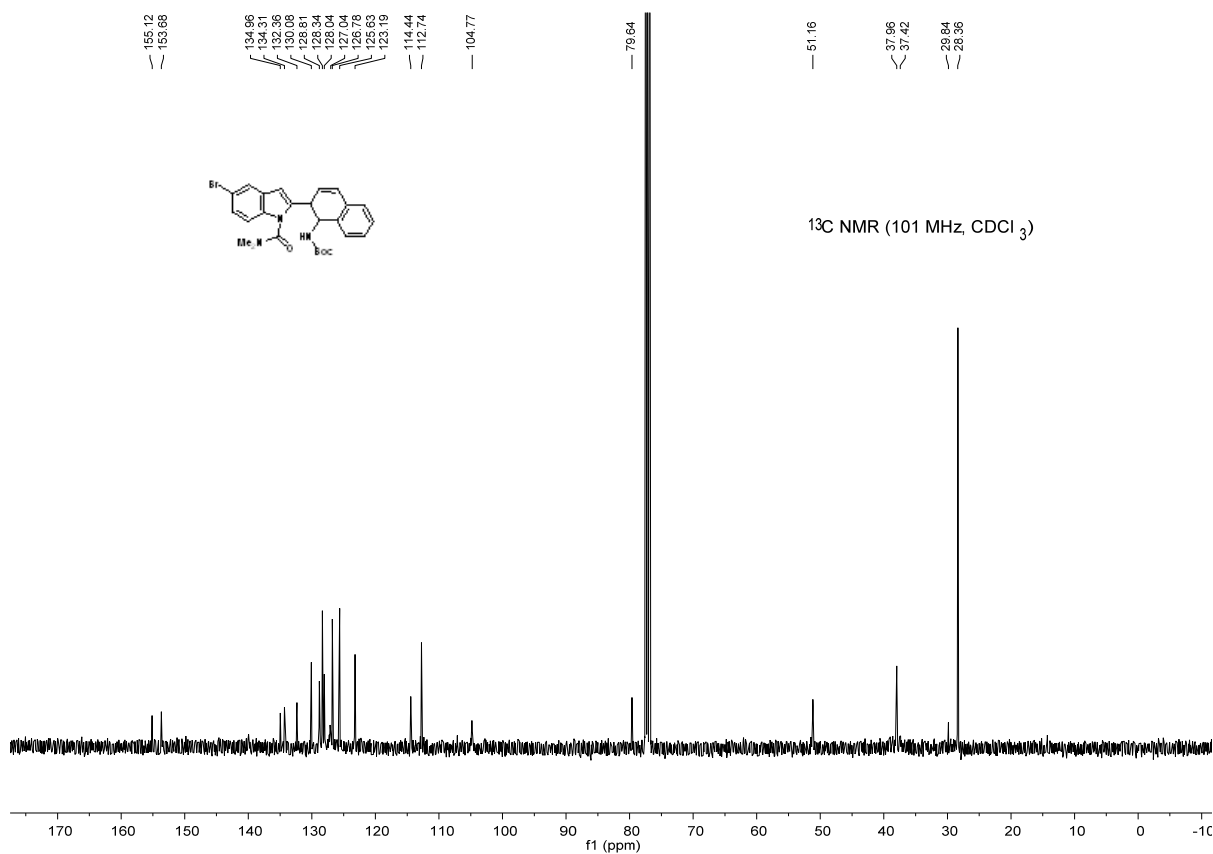
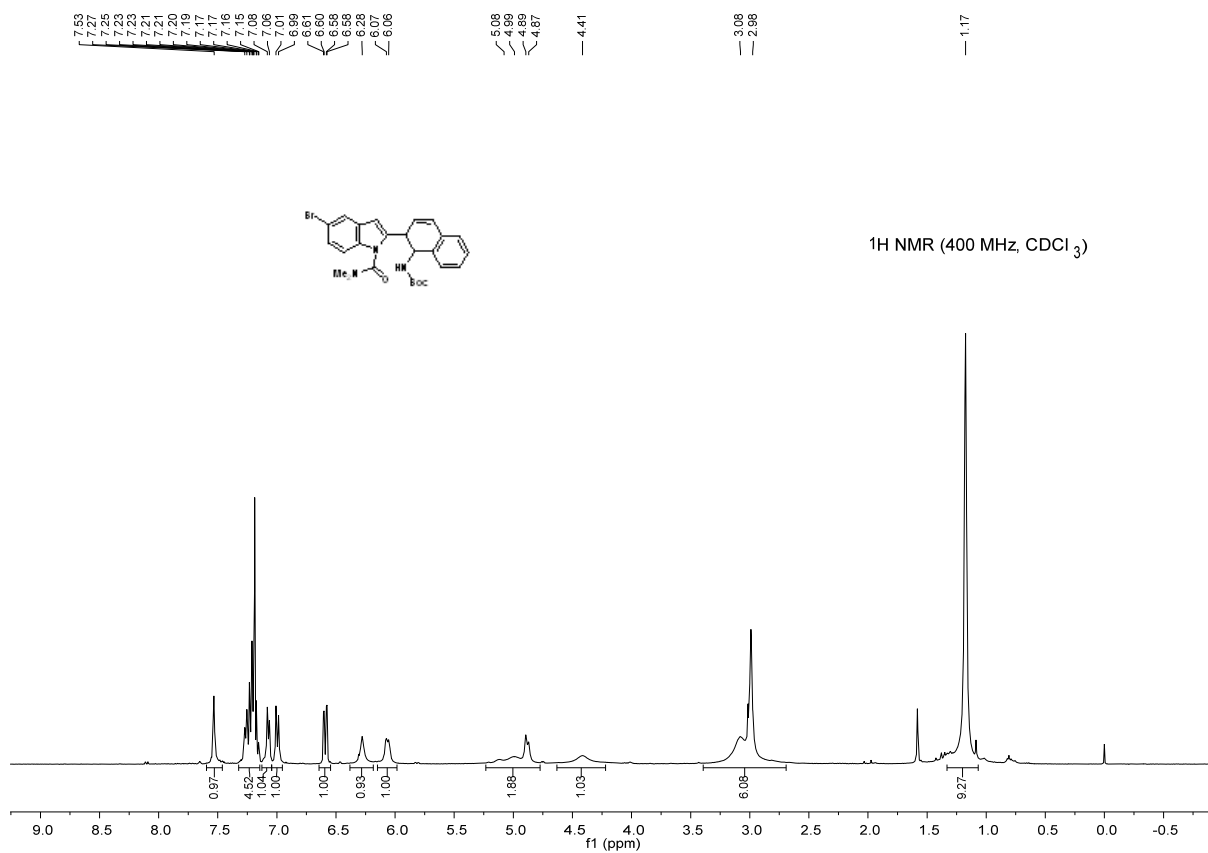


(11) *tert*-butyl (2-(5-chloro-1-(dimethylcarbamoyl)-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate

(31)

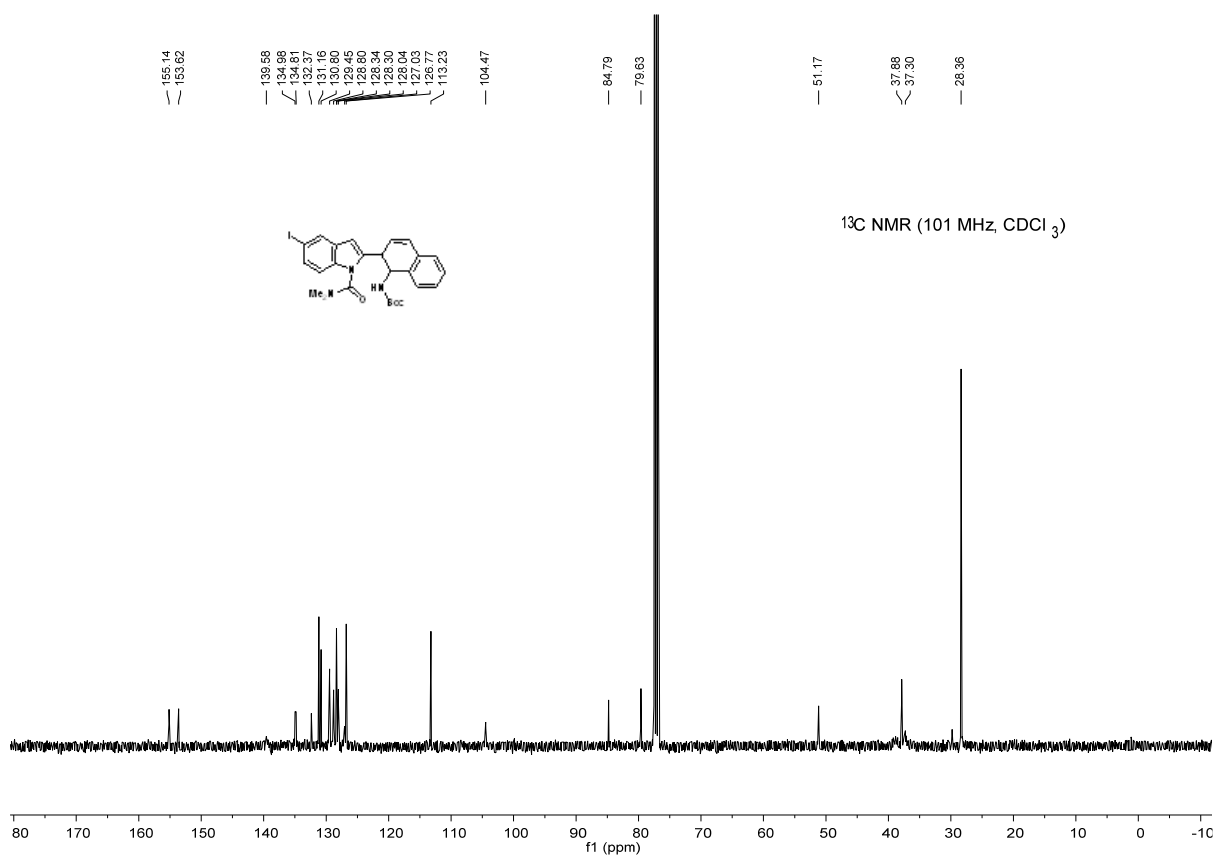
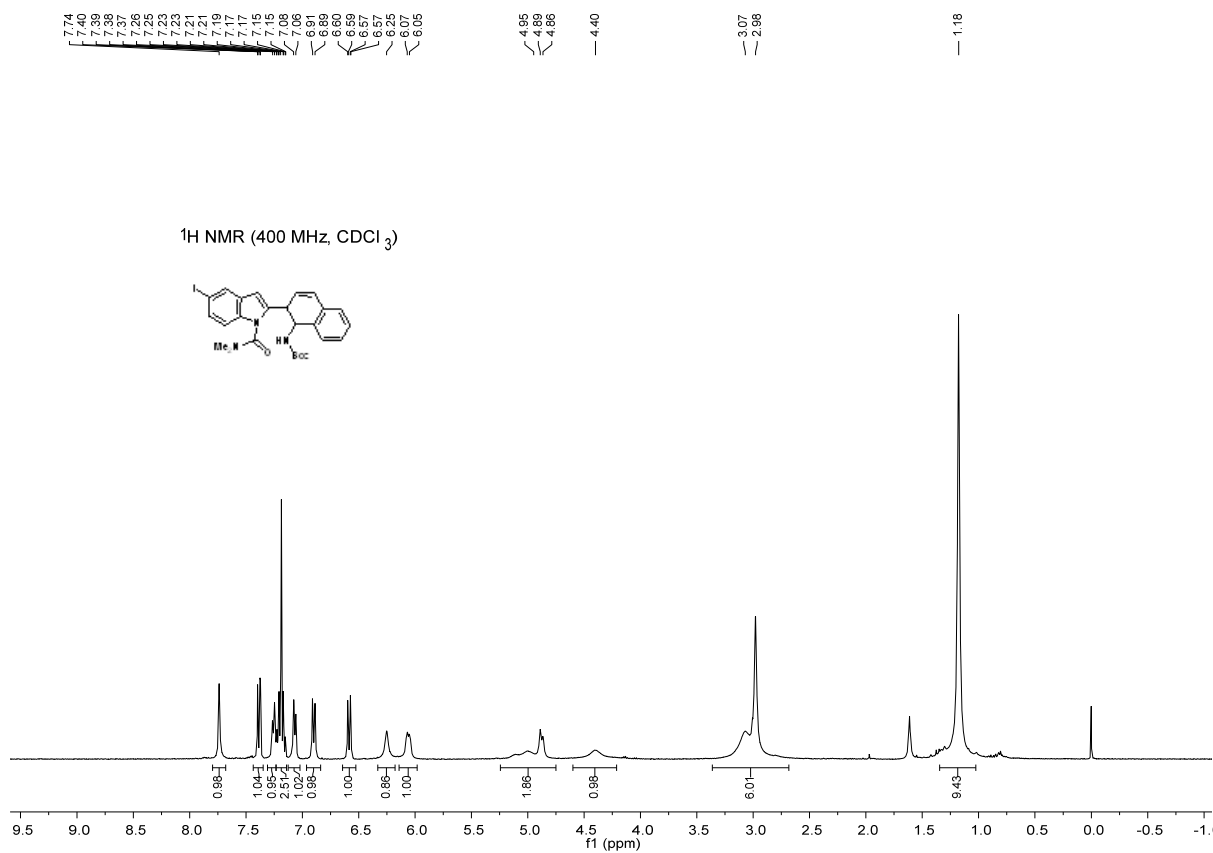


(12) *tert*-butyl (2-(5-bromo-1-(dimethylcarbamoyl)-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(3m)



(13) *tert*-butyl (2-(1-(dimethylcarbamoyl)-5-iodo-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate

(3n)

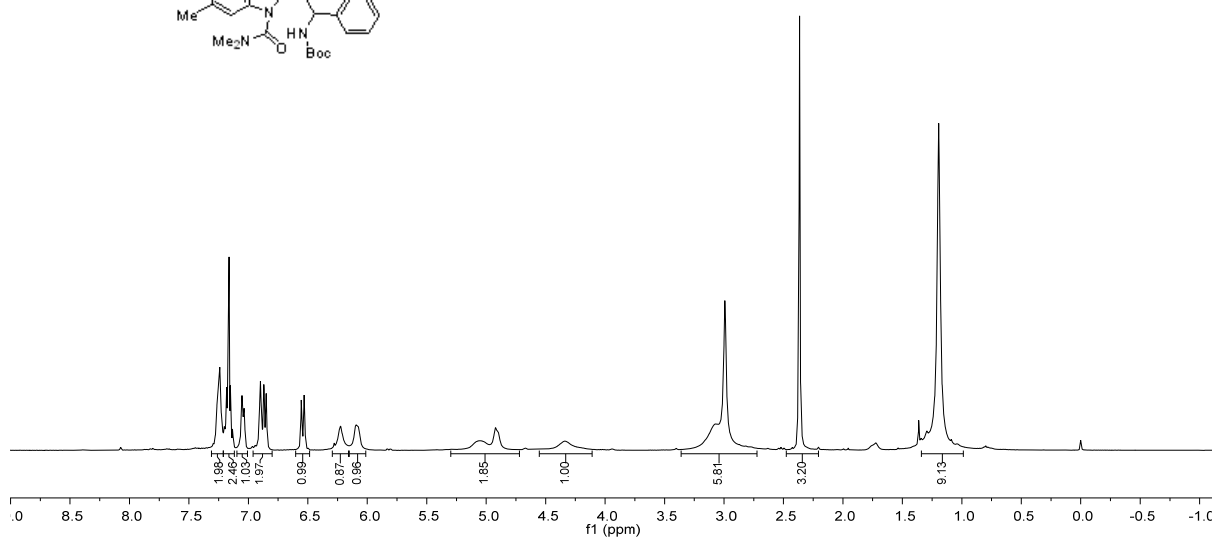
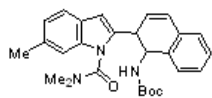


(14) *tert*-butyl (2-(1-(dimethylcarbamoyl)-6-methyl-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate

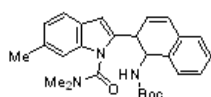
(30)

7.25
7.24
7.20
7.20
7.18
7.17
7.15
7.15
7.13
7.13
7.05
7.04
6.90
6.87
6.85
6.85
6.53
6.53
6.23
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5.01
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4.34
3.07
2.99
2.36
1.19

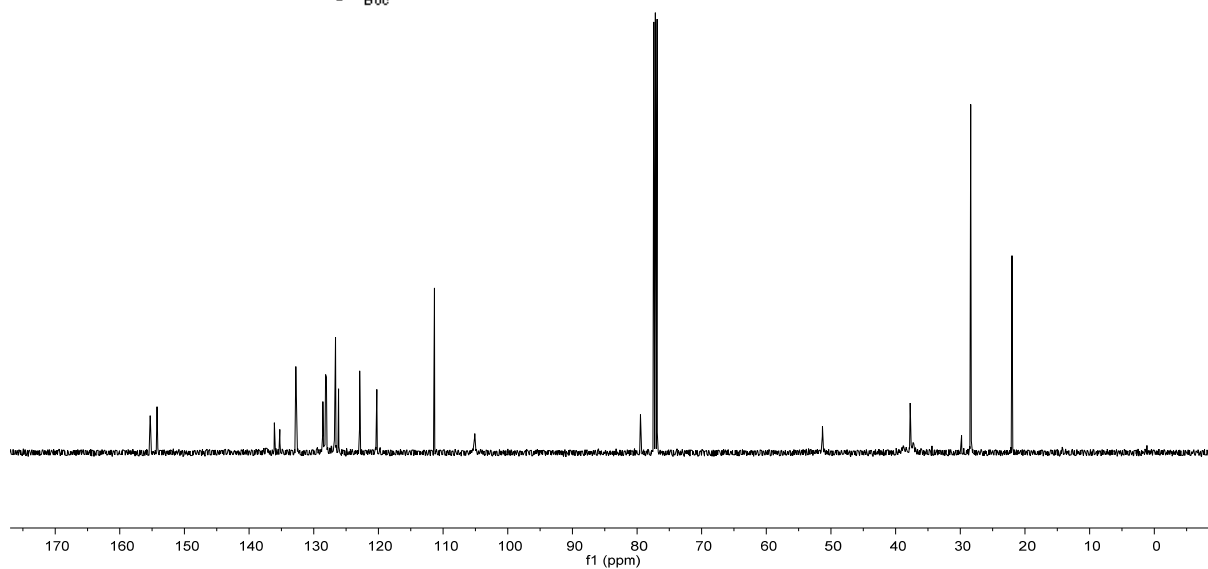
¹H NMR (400 MHz, CDCl₃)



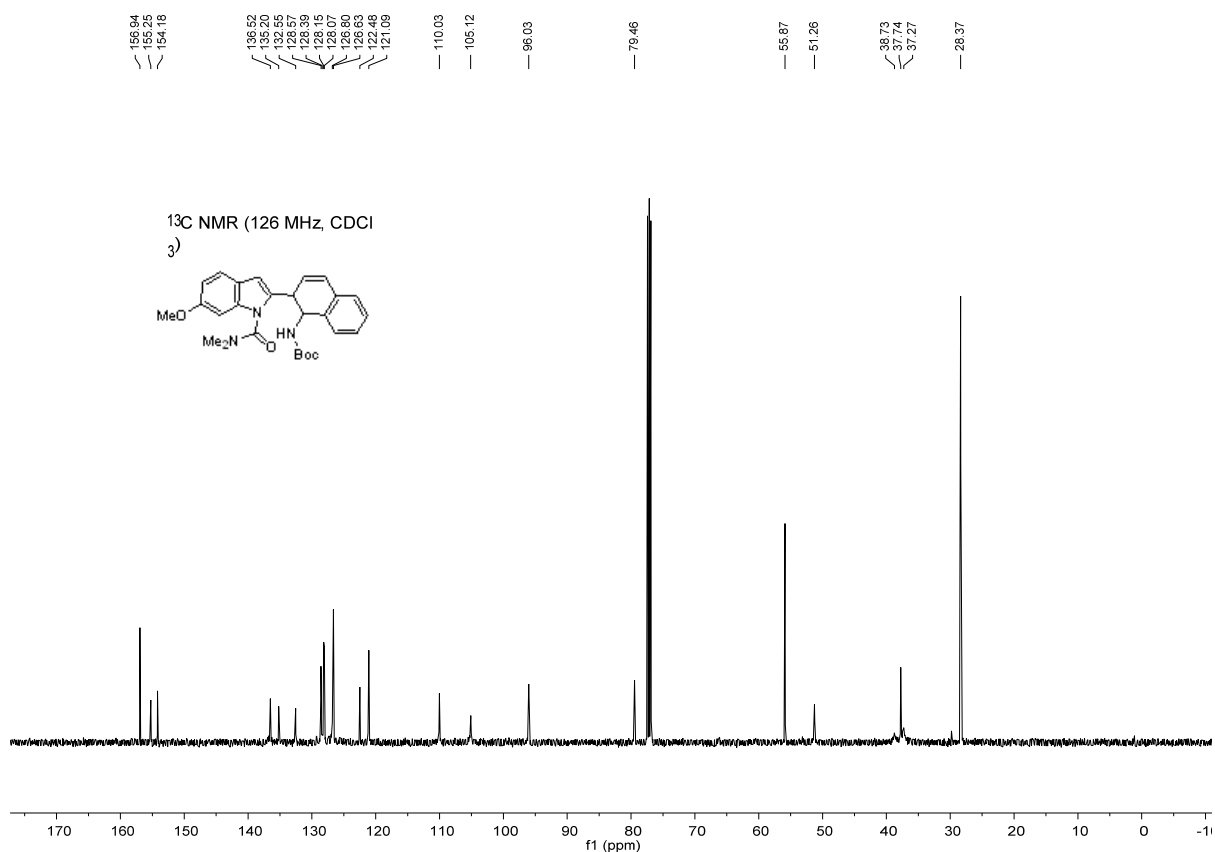
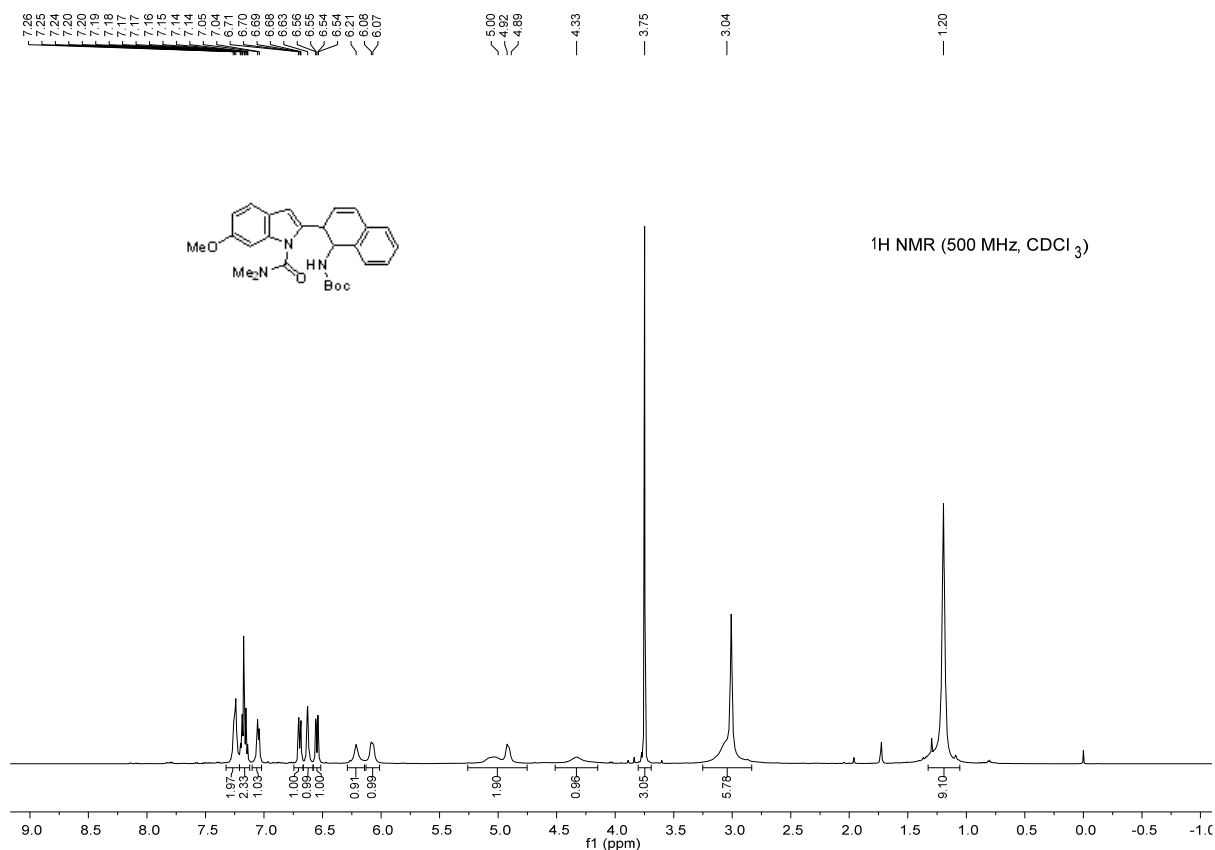
155.30
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136.08
132.77
132.60
128.59
128.36
128.17
128.06
128.15
128.15
122.89
120.25
111.34
105.10
79.48
77.36
51.30
38.74
37.74
37.24
28.39
22.00



¹³C NMR (126 MHz, CDCl₃)

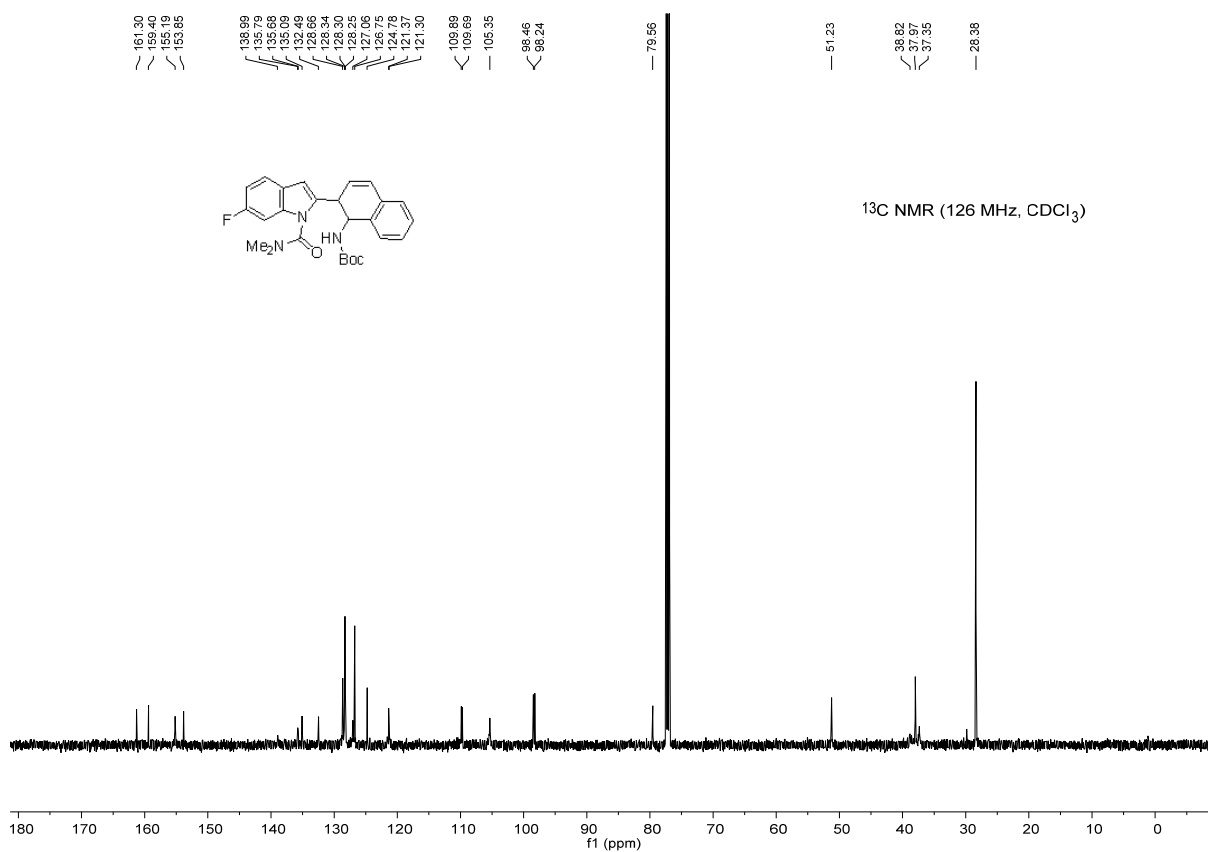
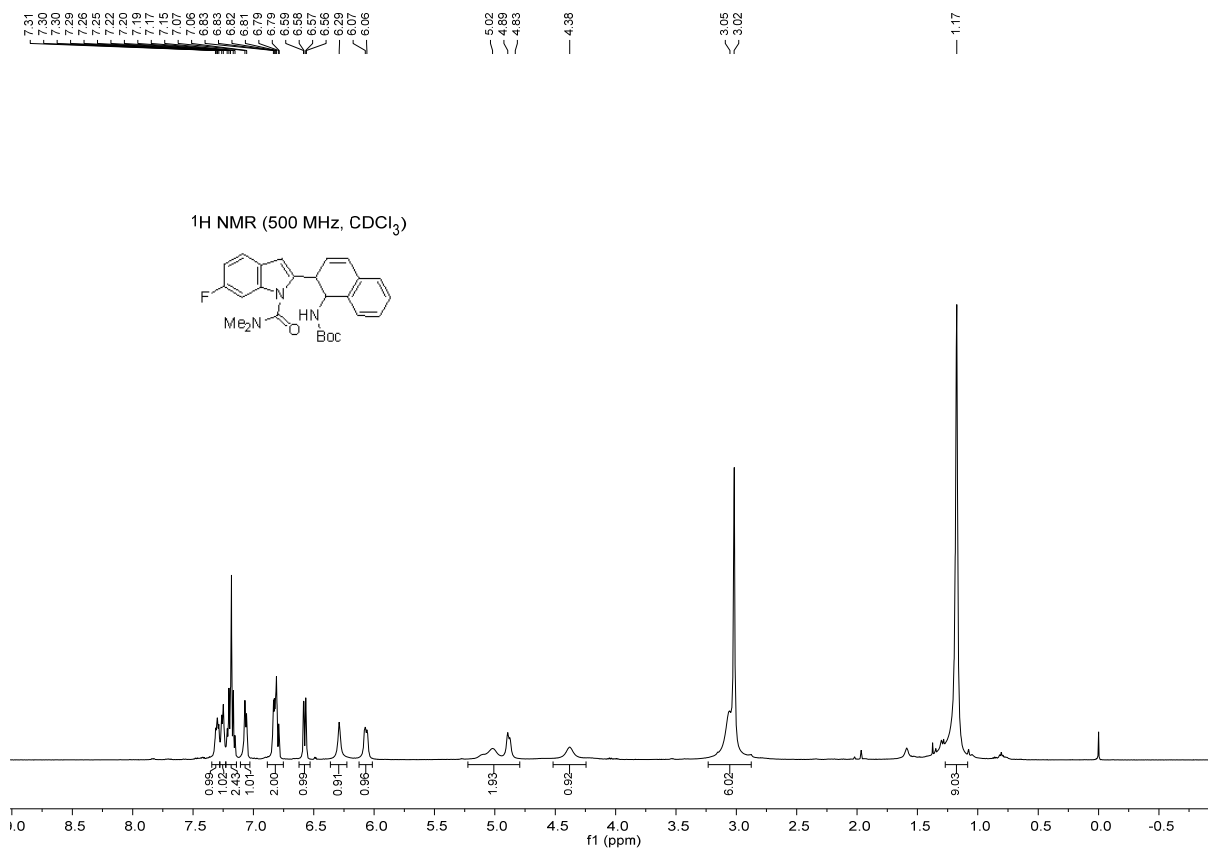


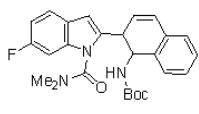
(15) *tert*-butyl (2-(1-(dimethylcarbamoyl)-6-methoxy-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate (**3p**)



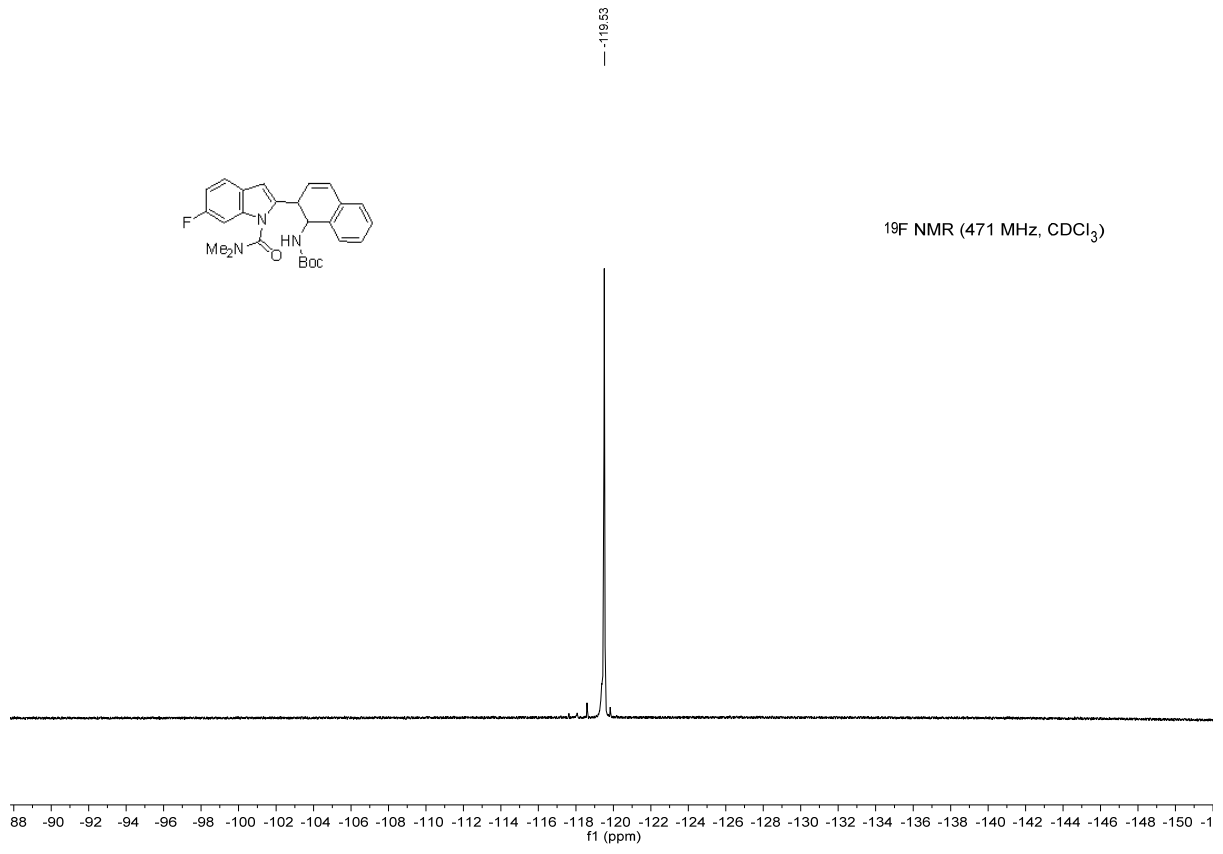
(16) *tert*-butyl (2-(1-(dimethylcarbamoyl)-6-fluoro-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate

(3q)

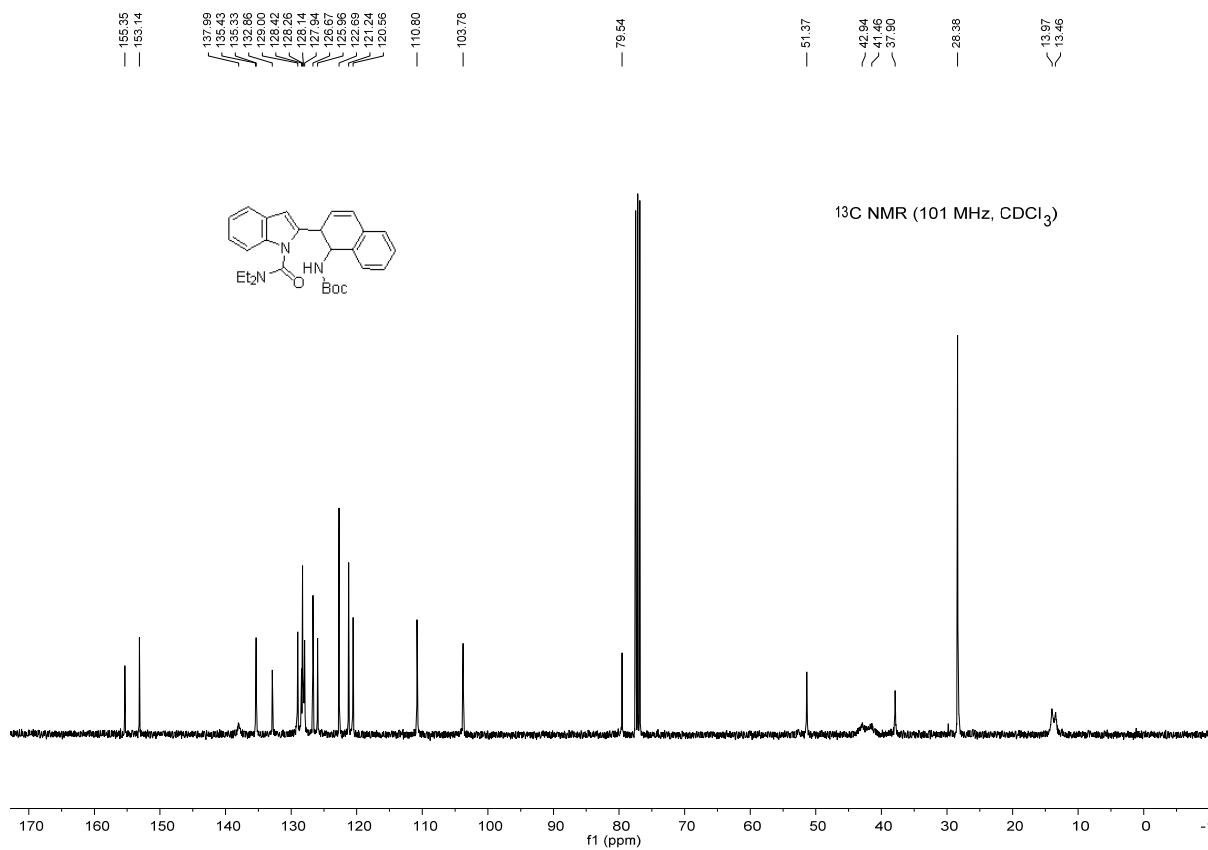
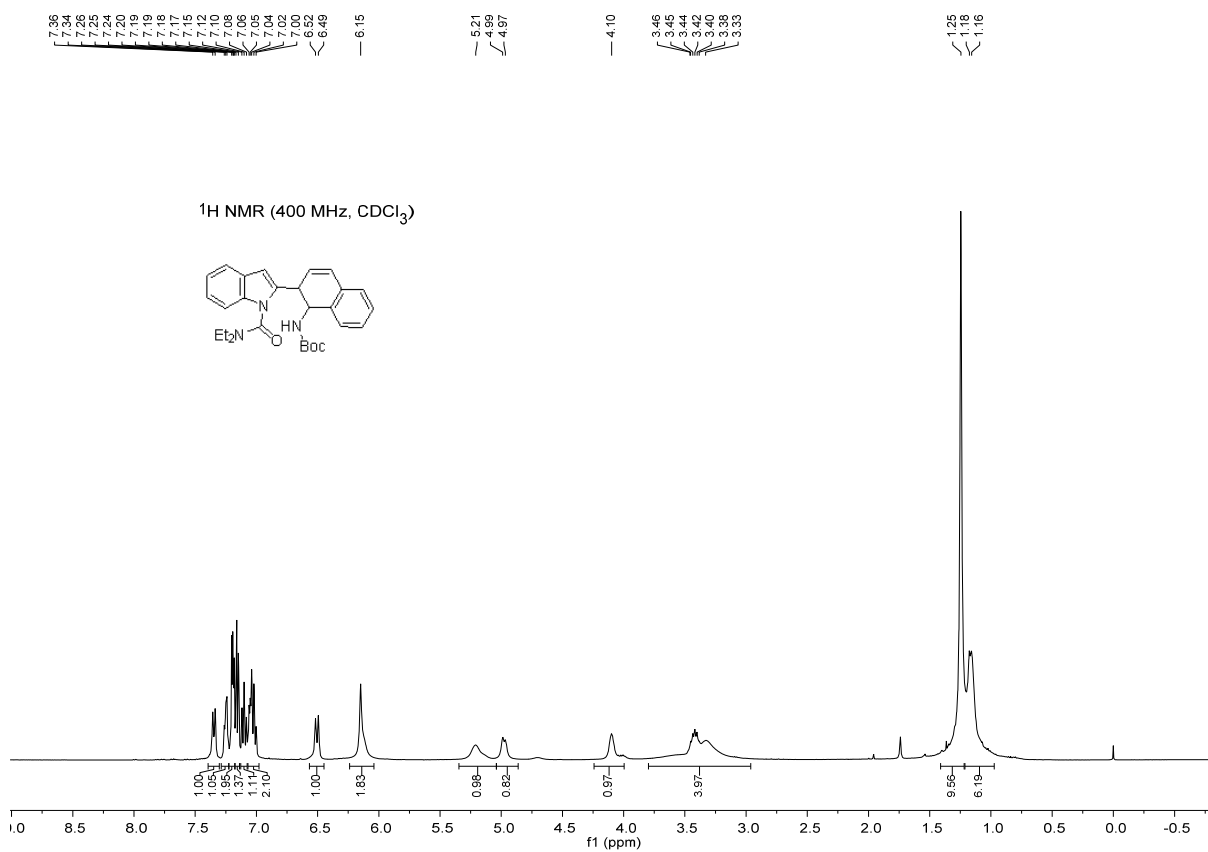




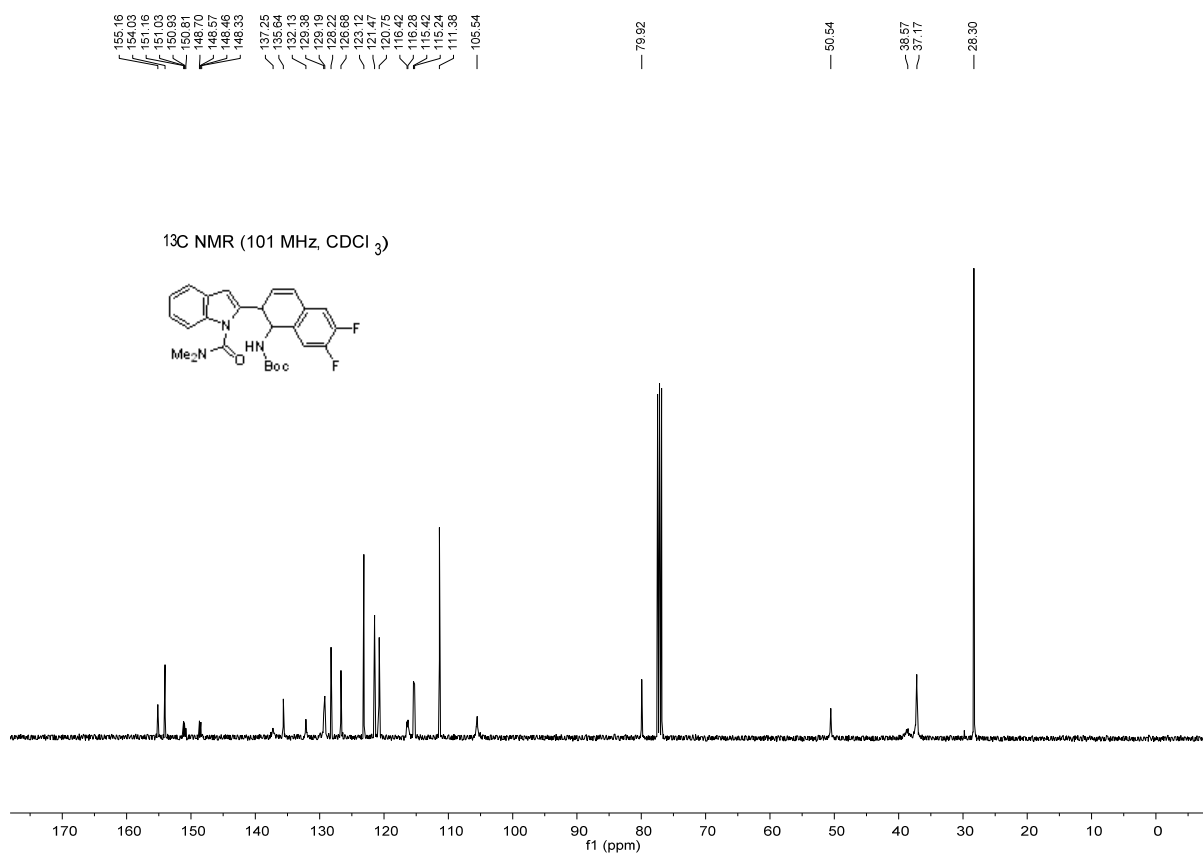
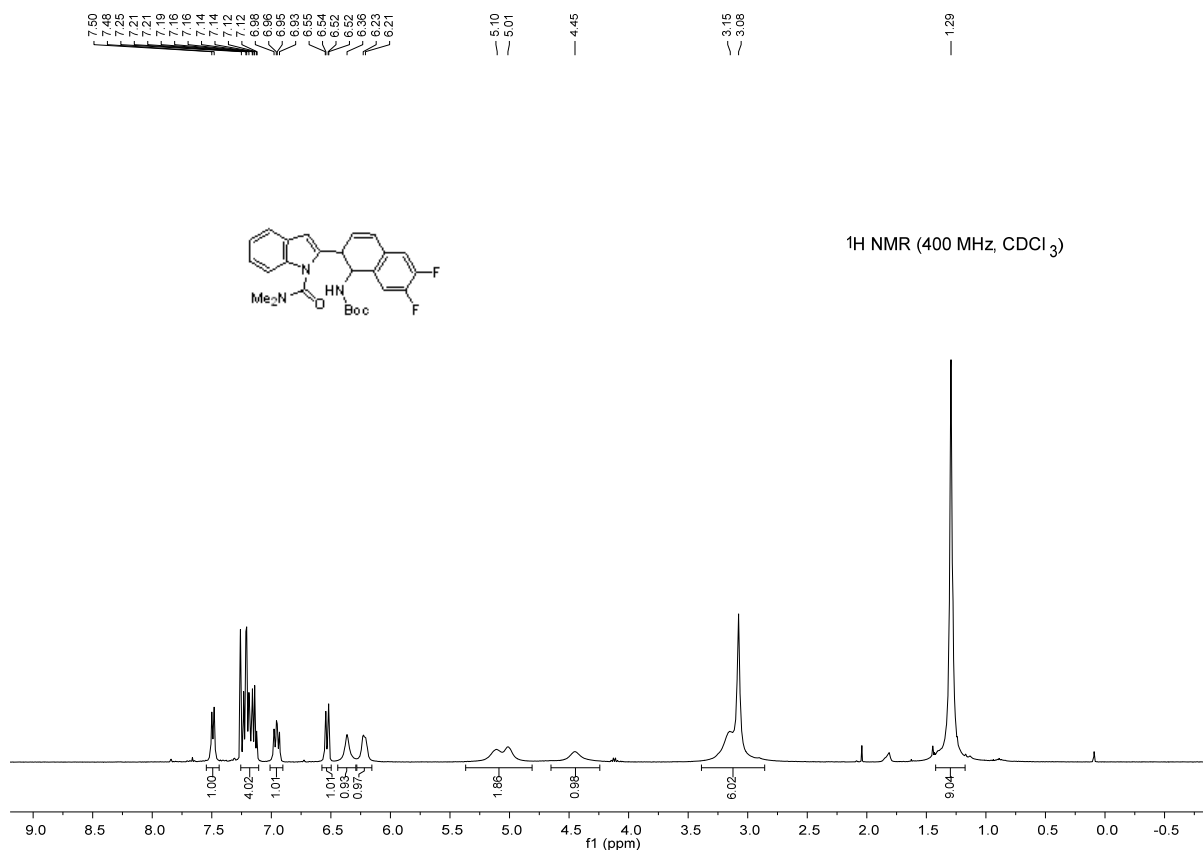
¹⁹F NMR (471 MHz, CDCl₃)

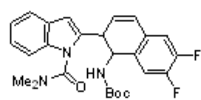


(17) *tert*-butyl (2-(1-(diethylcarbamoyl)-1*H*-indol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate (**3r**)

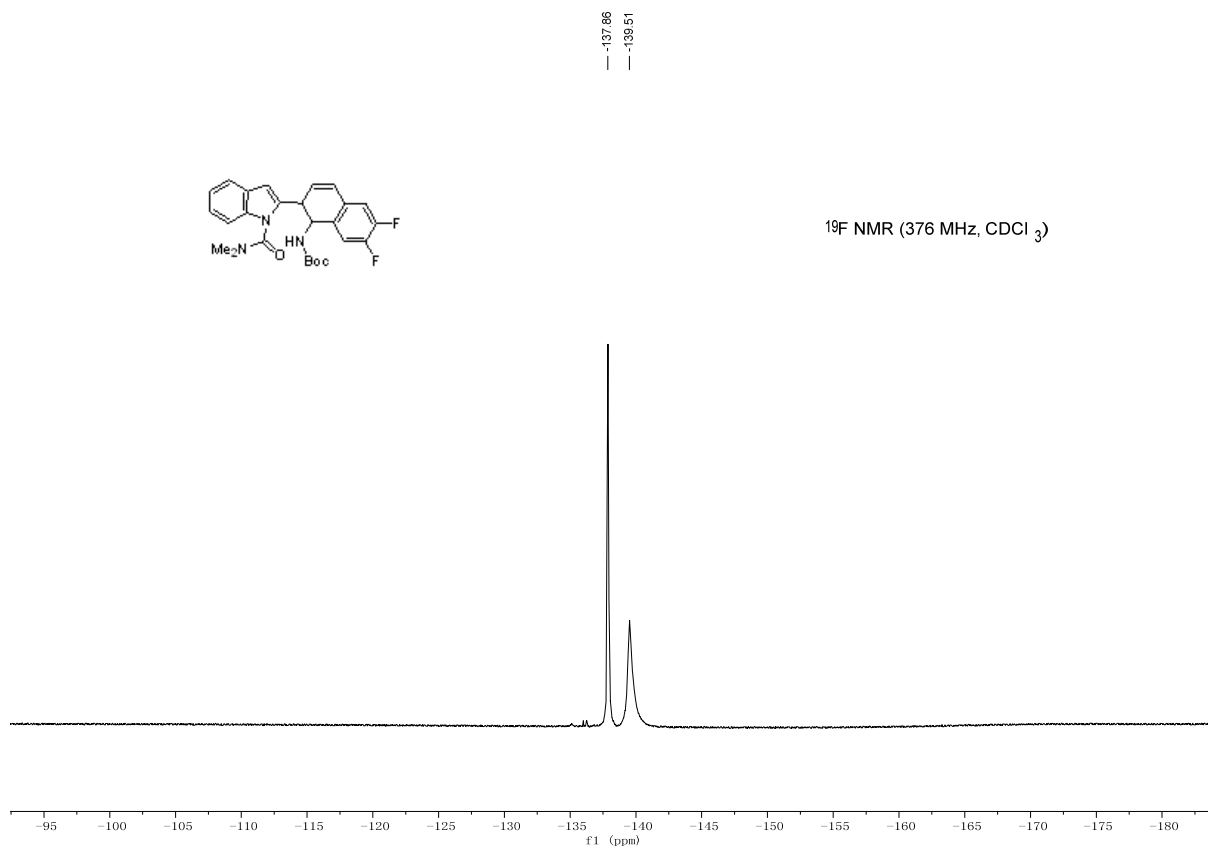


(18) *tert*-butyl (2-(1-(dimethylcarbamoyl)-1*H*-indol-2-yl)-6,7-difluoro-1,2-dihydronaphthalen-1-yl)carbamate (**3s**)

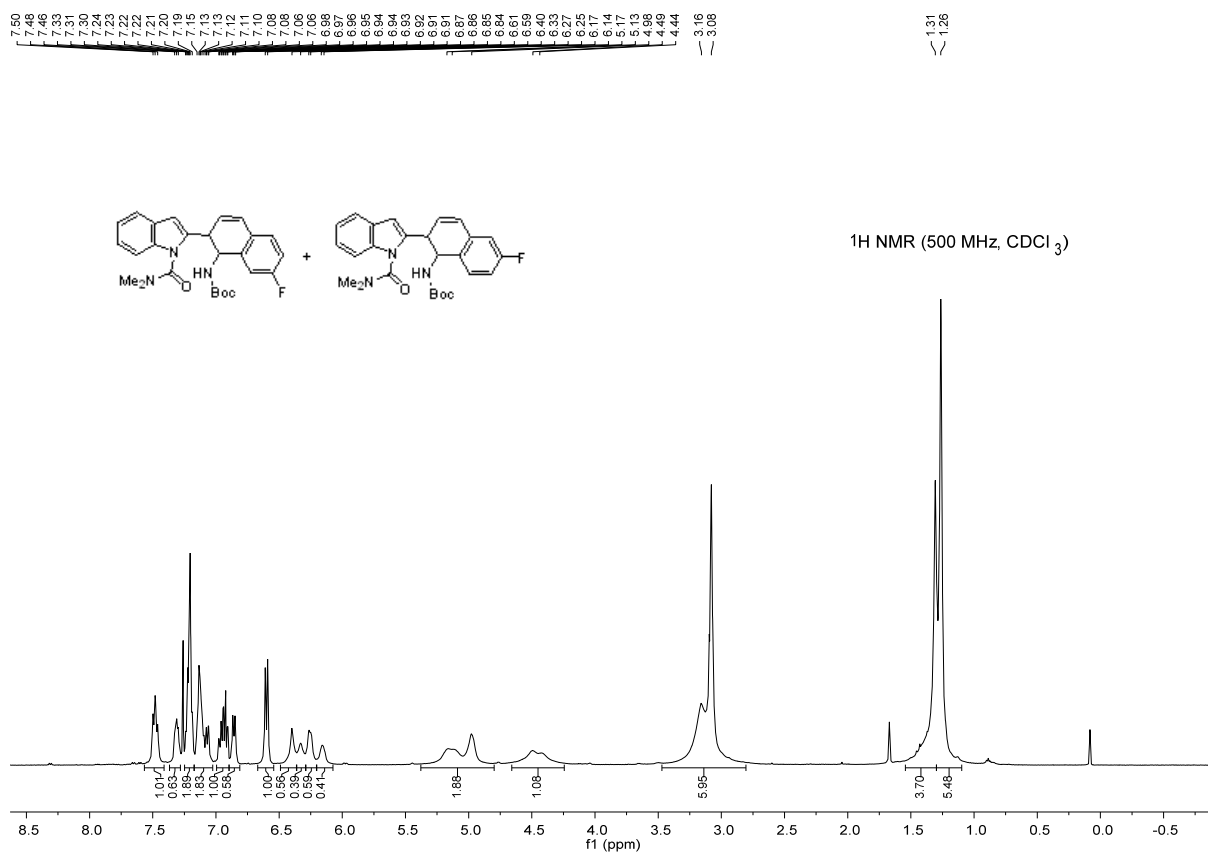


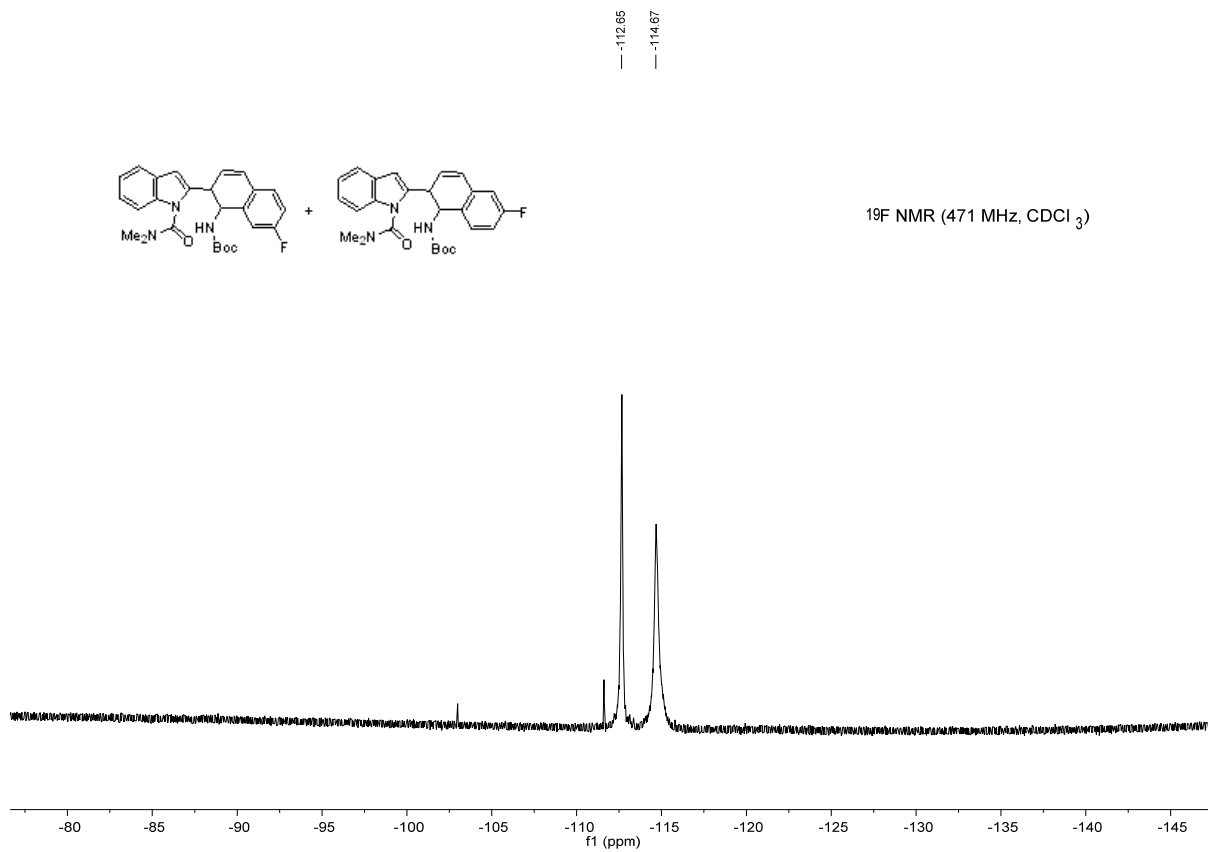
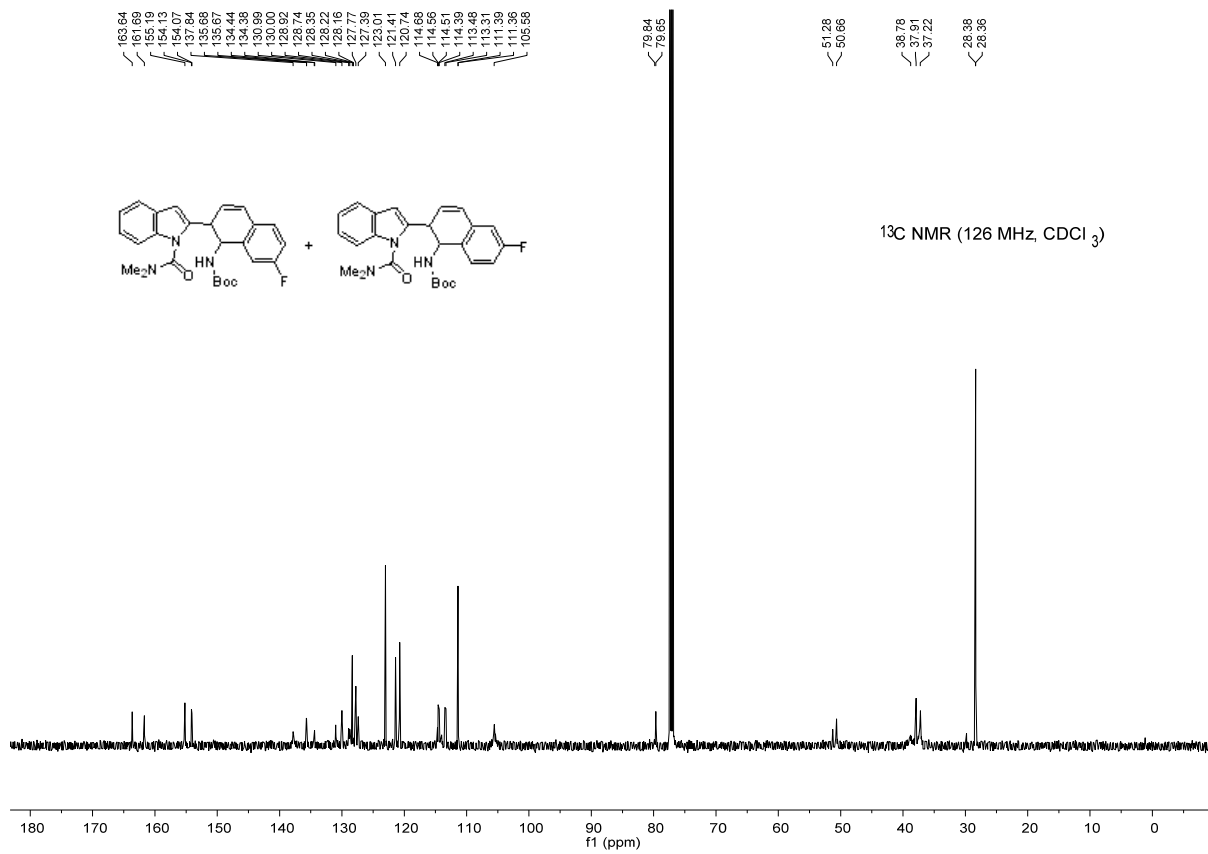


¹⁹F NMR (376 MHz, CDCl₃)

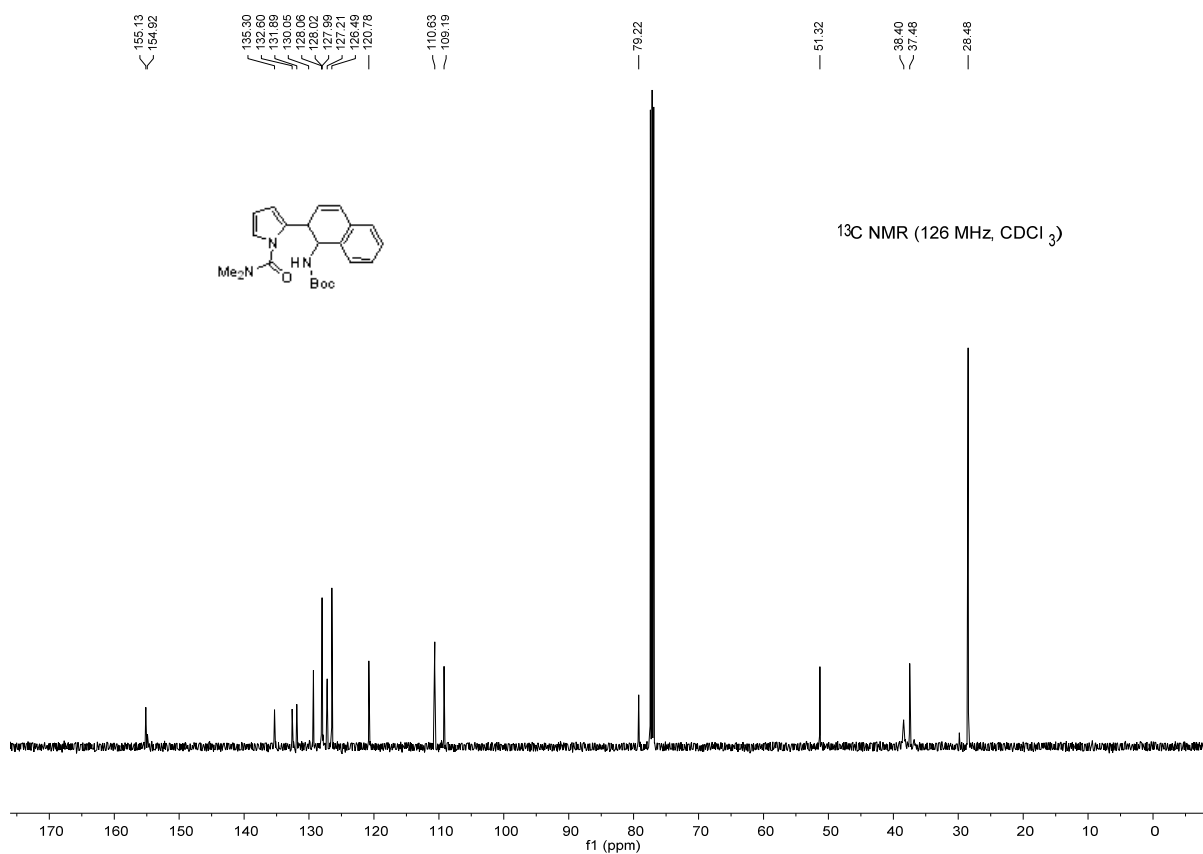
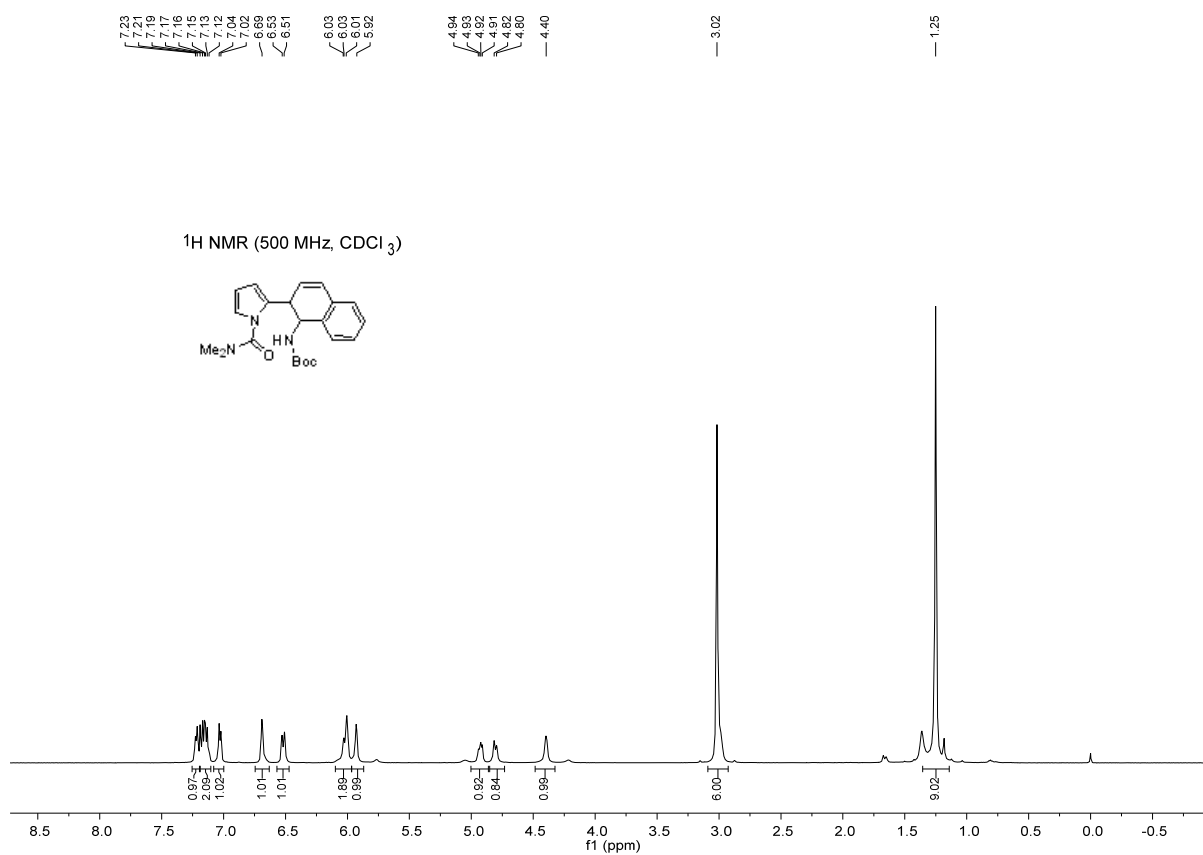


(19) *tert*-butyl (2-(1-(dimethylcarbamoyl)-1*H*-indol-2-yl)-7-fluoro-1,2-dihydronaphthalen-1-yl)carbamate and *tert*-butyl (2-(1-(dimethylcarbamoyl)-1*H*-indol-2-yl)-6-fluoro-1,2-dihydronaphthalen-1-yl)carbamate (3t)

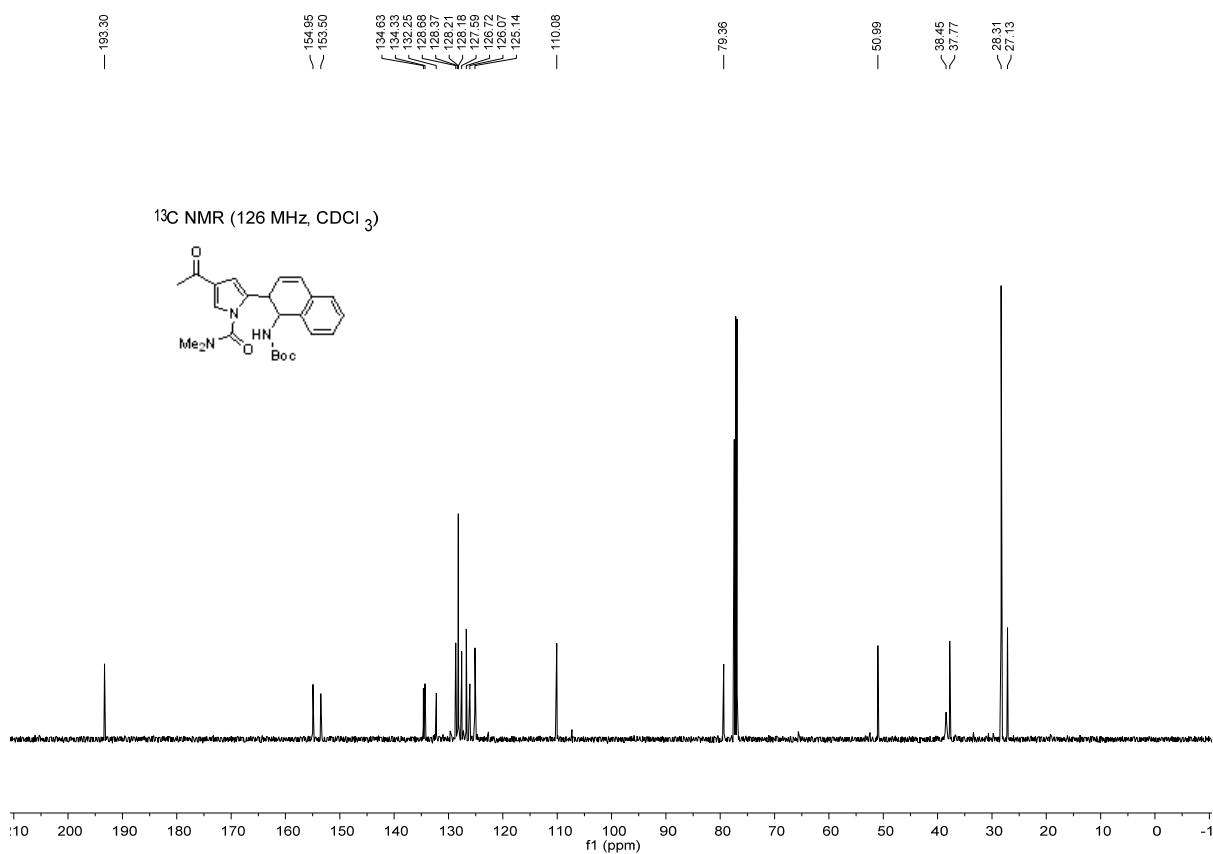
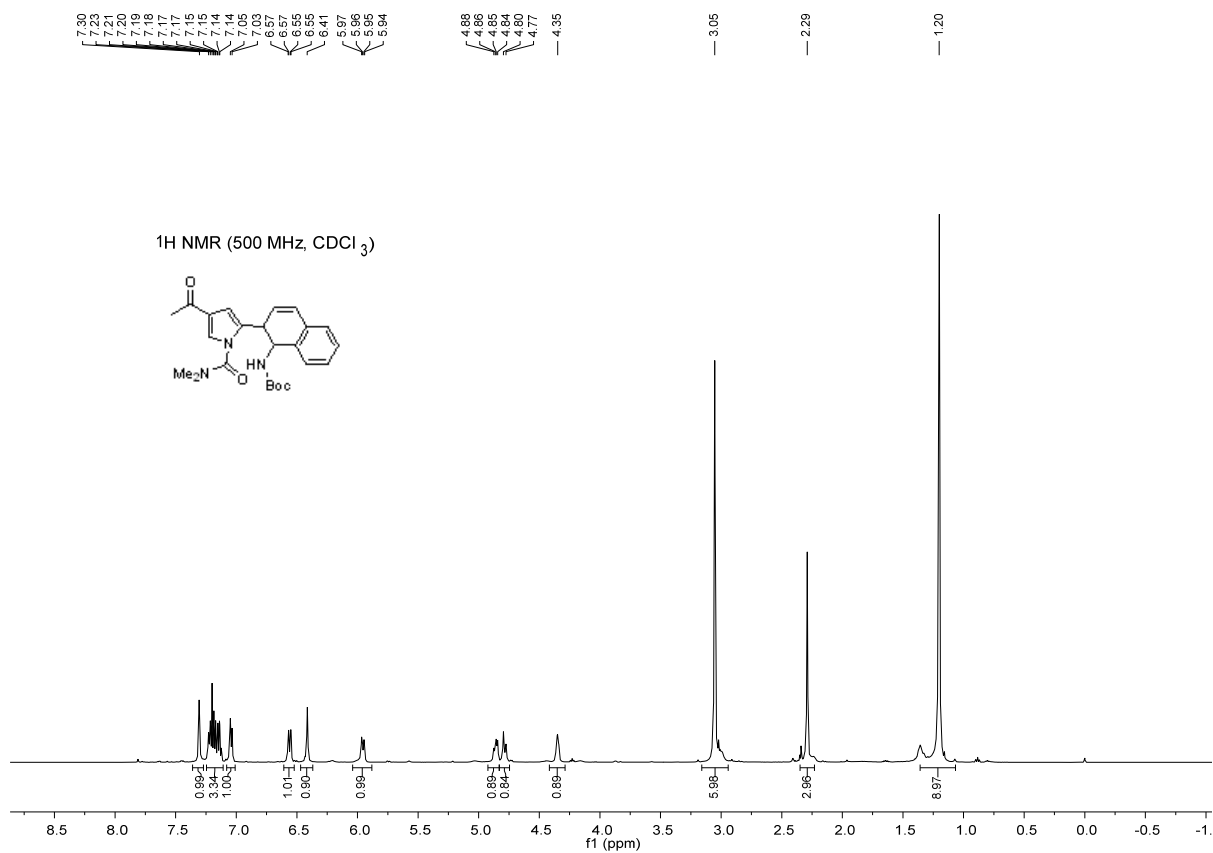




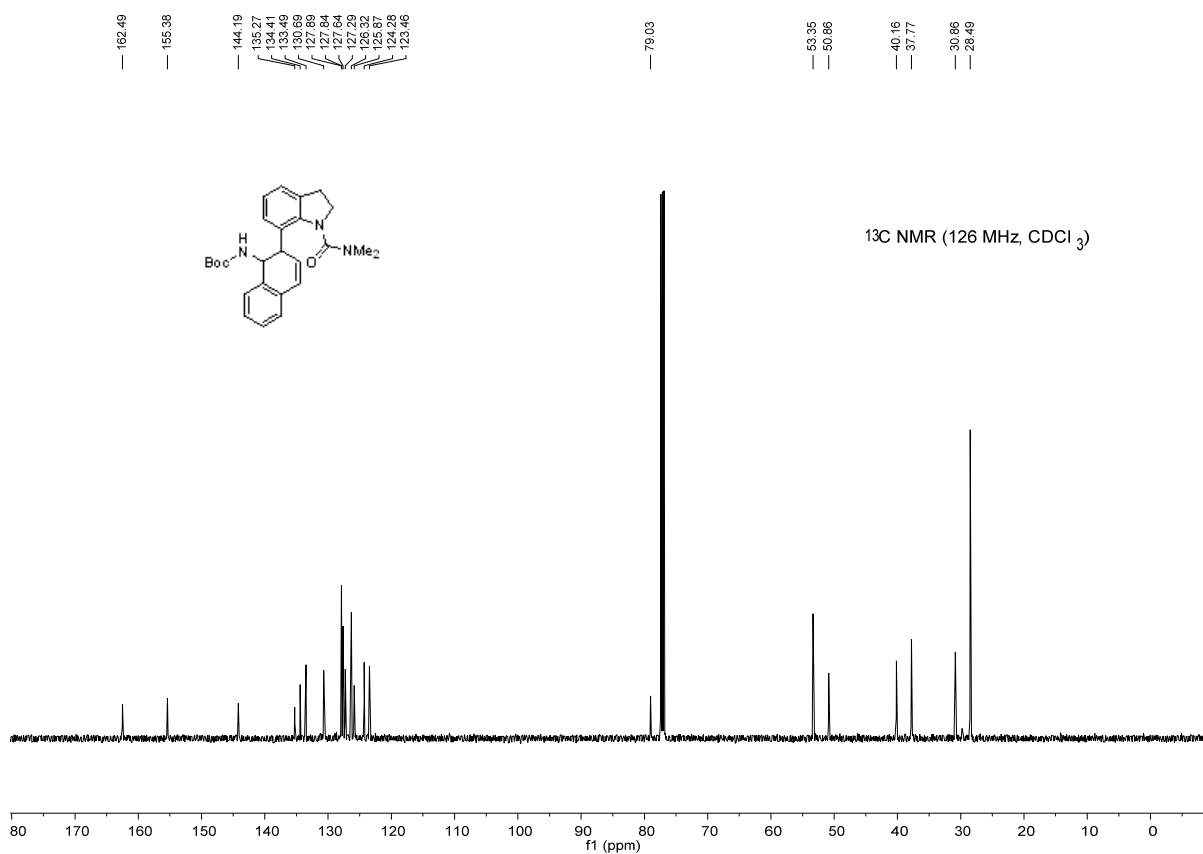
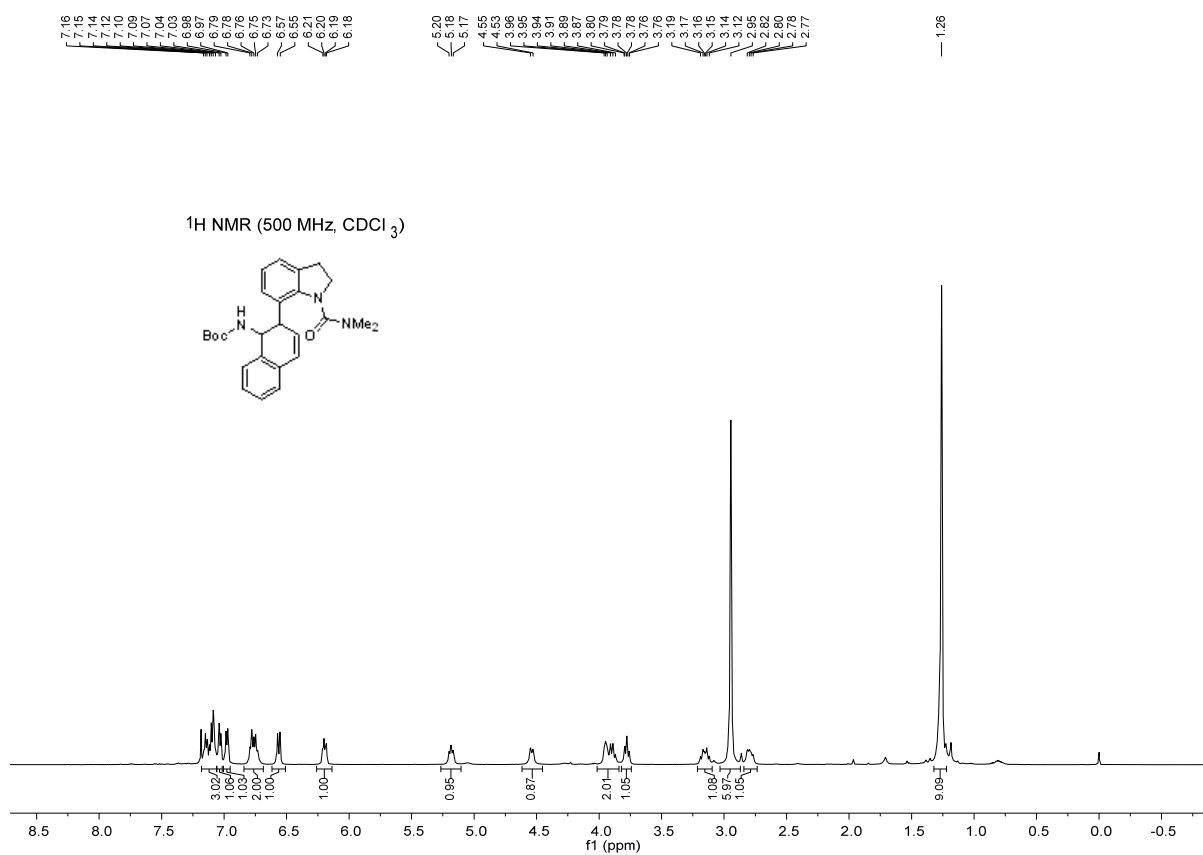
(20) *tert*-butyl (2-(1-(dimethylcarbamoyl)-1*H*-pyrrol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate (**3u**)



(21) *tert*-butyl (2-(4-acetyl-1-(dimethylcarbamoyl)-1*H*-pyrrol-2-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(3v)

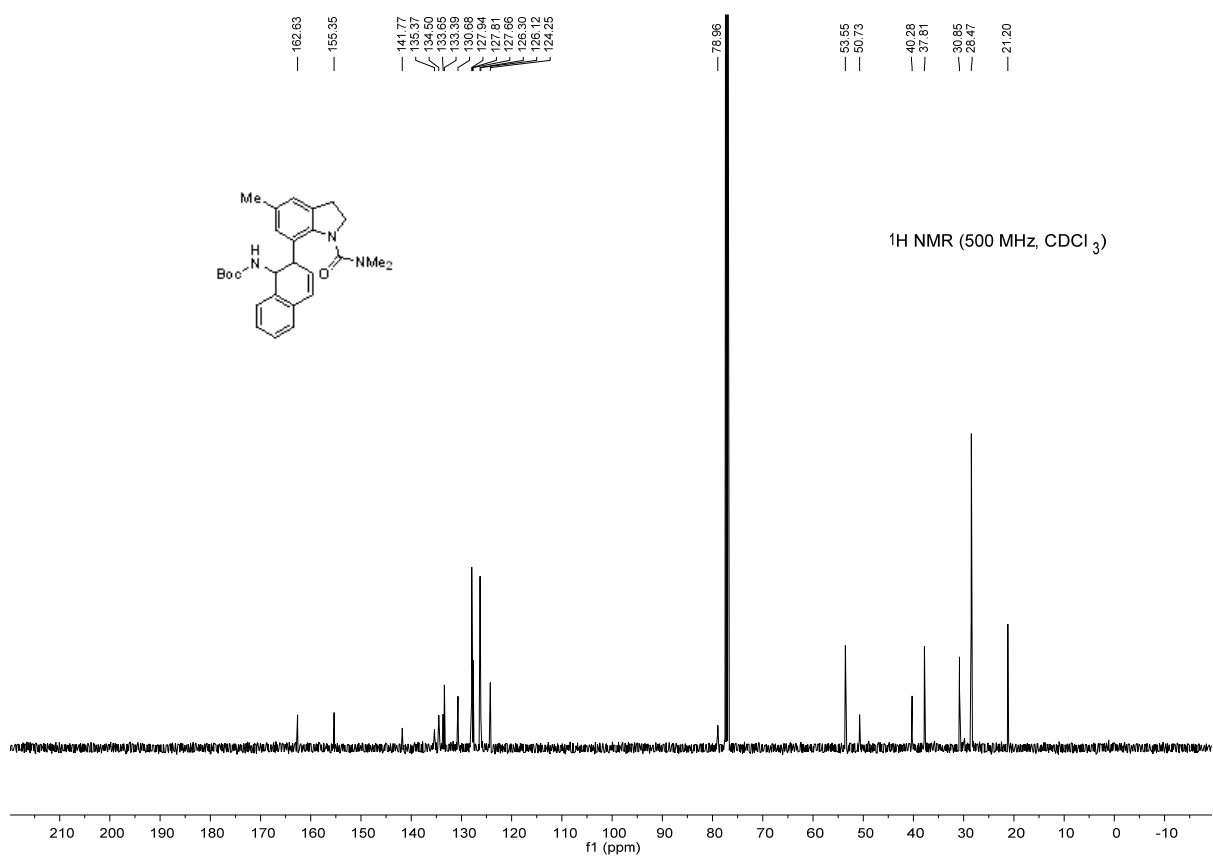
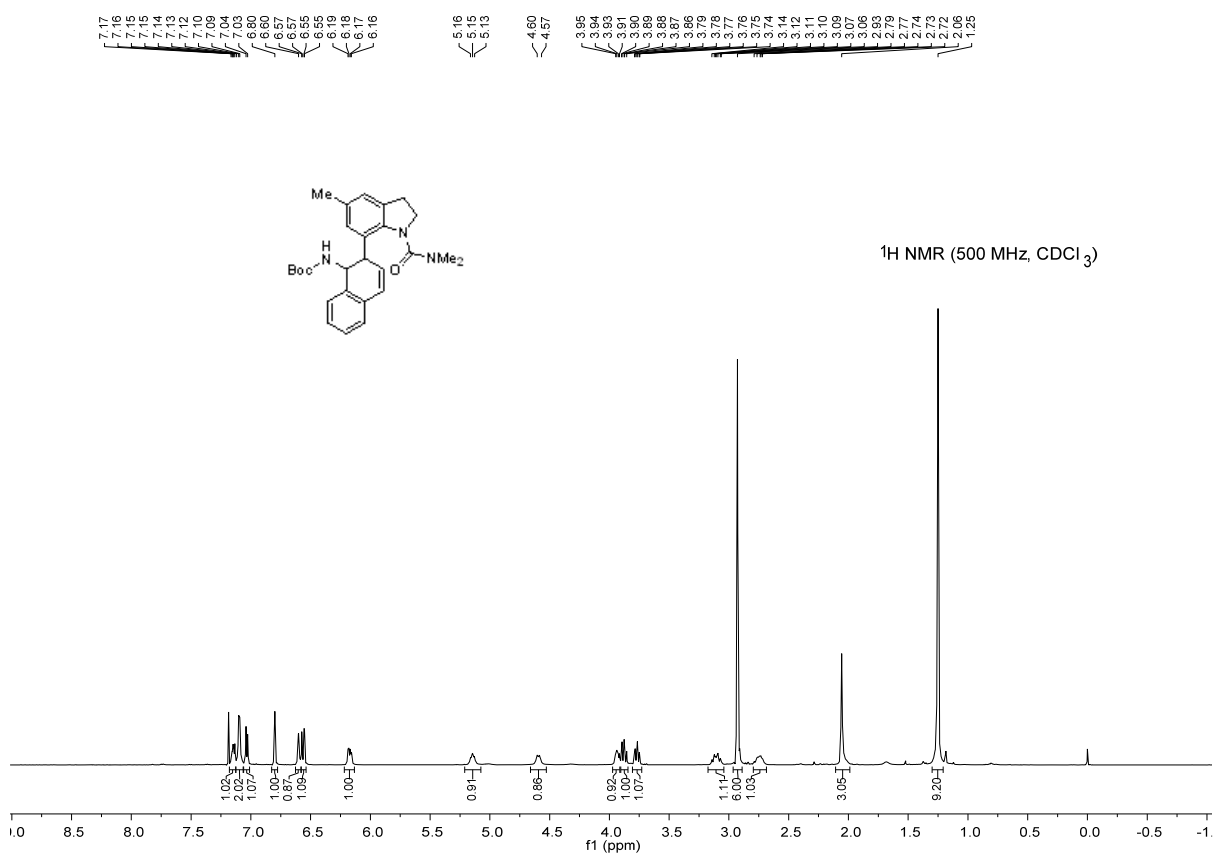


(22) *tert*-butyl (2-(1-(dimethylcarbamoyl)indolin-7-yl)-1,2-dihydronaphthalen-1-yl)carbamate (**5a**)

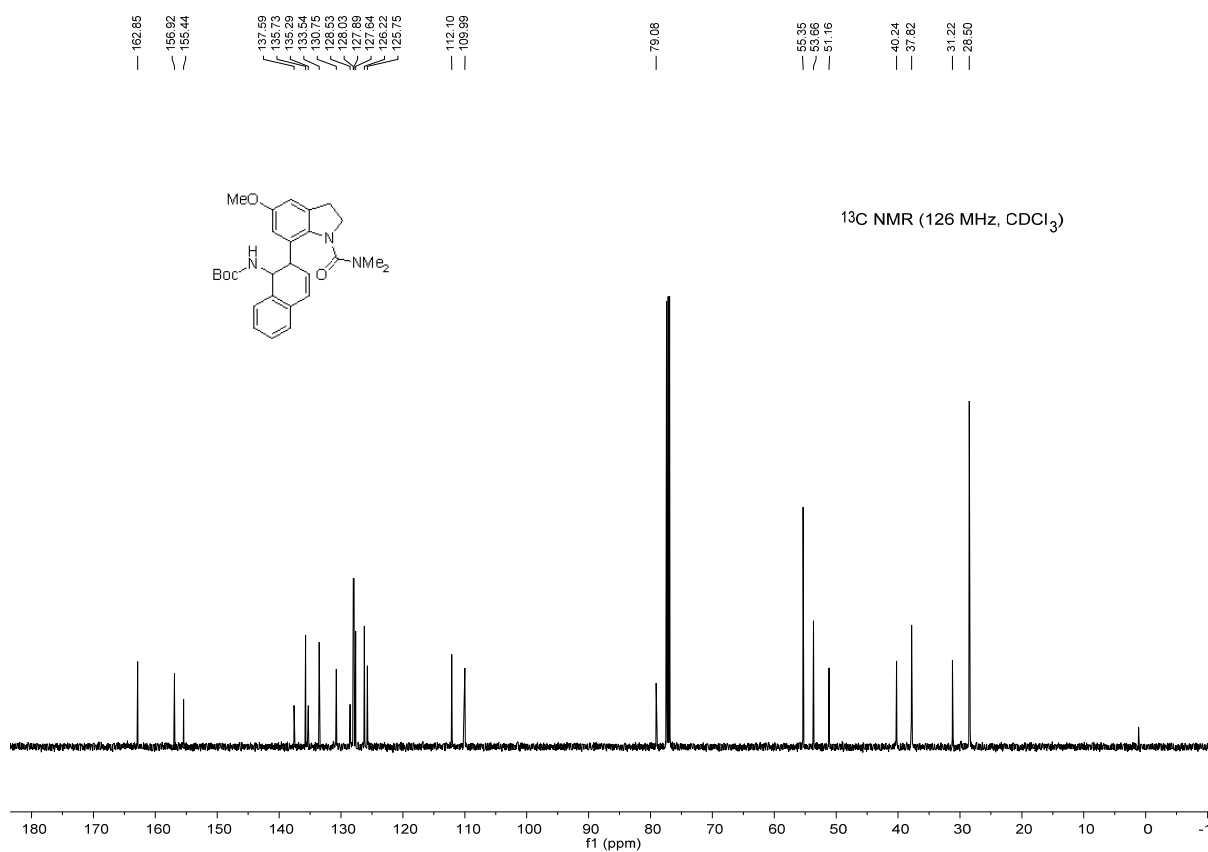
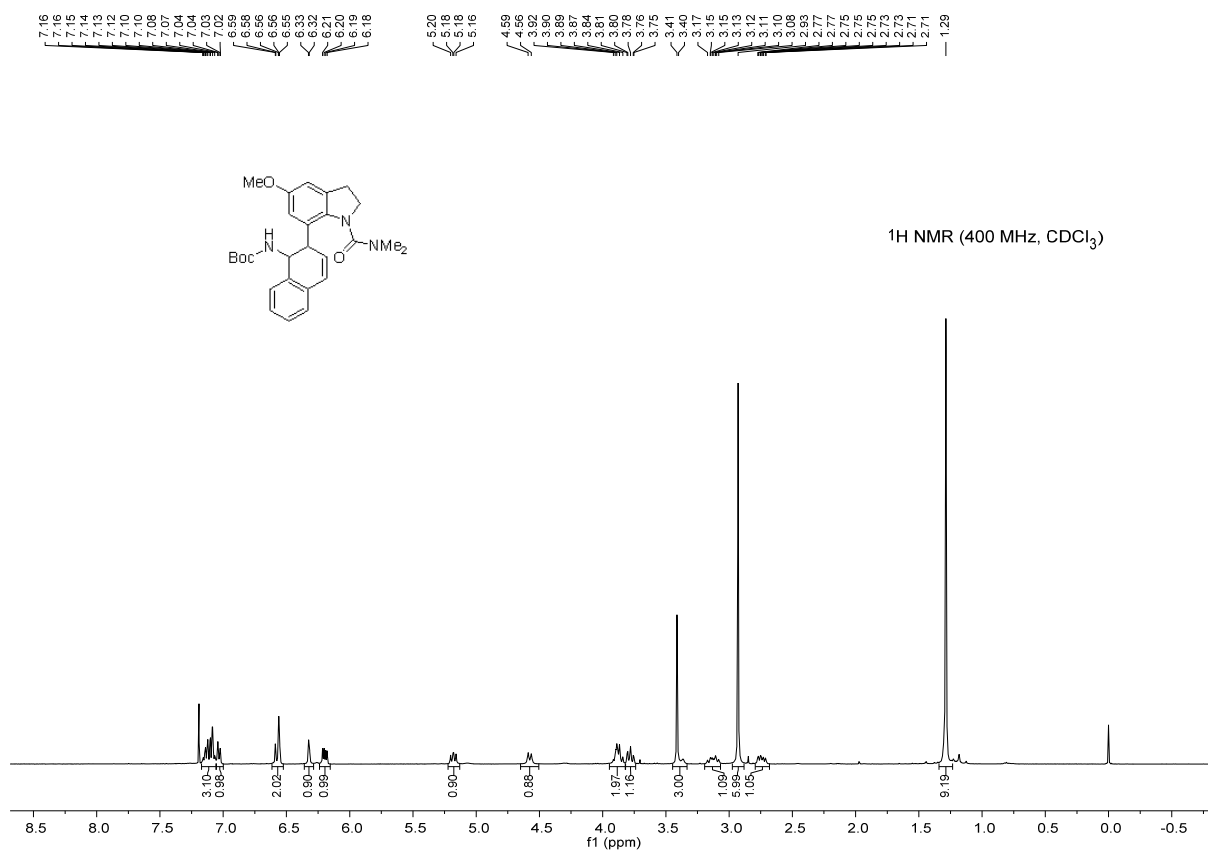


(23) *tert*-butyl (2-(1-(dimethylcarbamoyl)-5-methylindolin-7-yl)-1,2-dihydronaphthalen-1-yl)carbamate

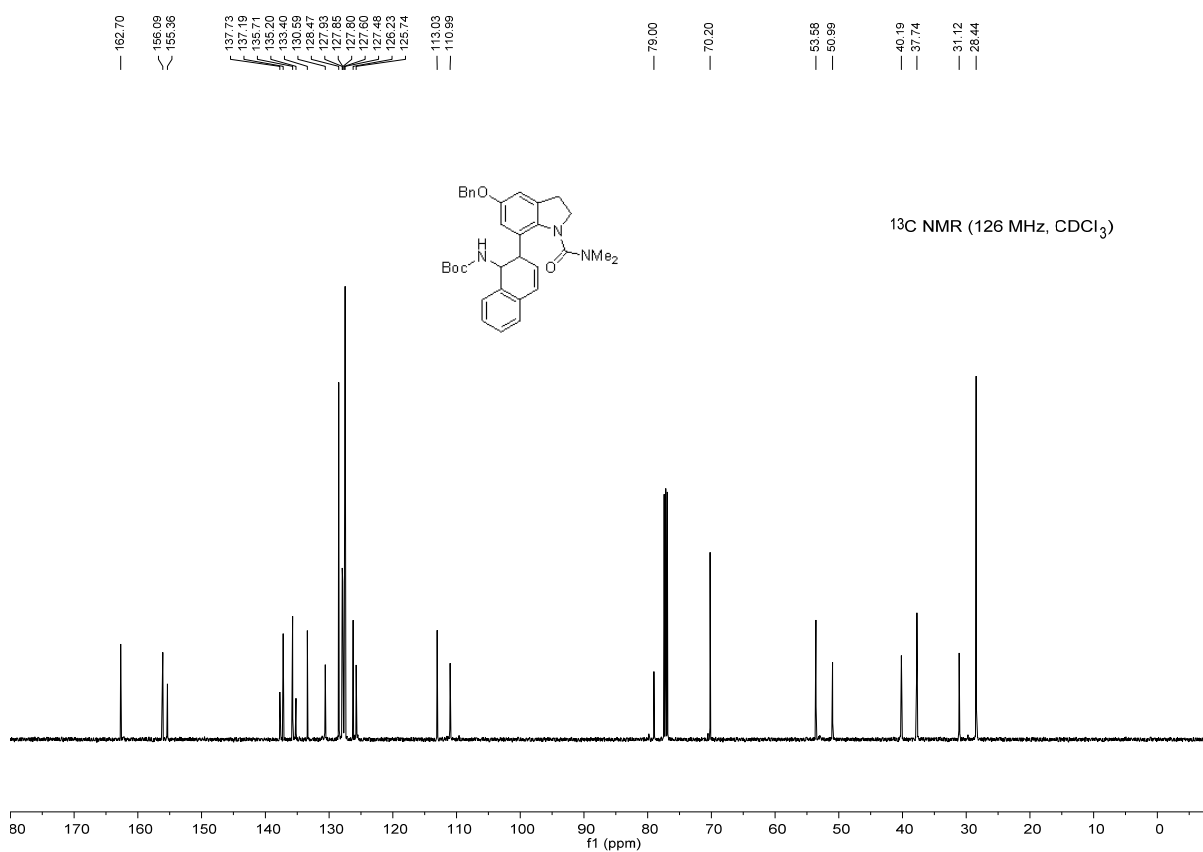
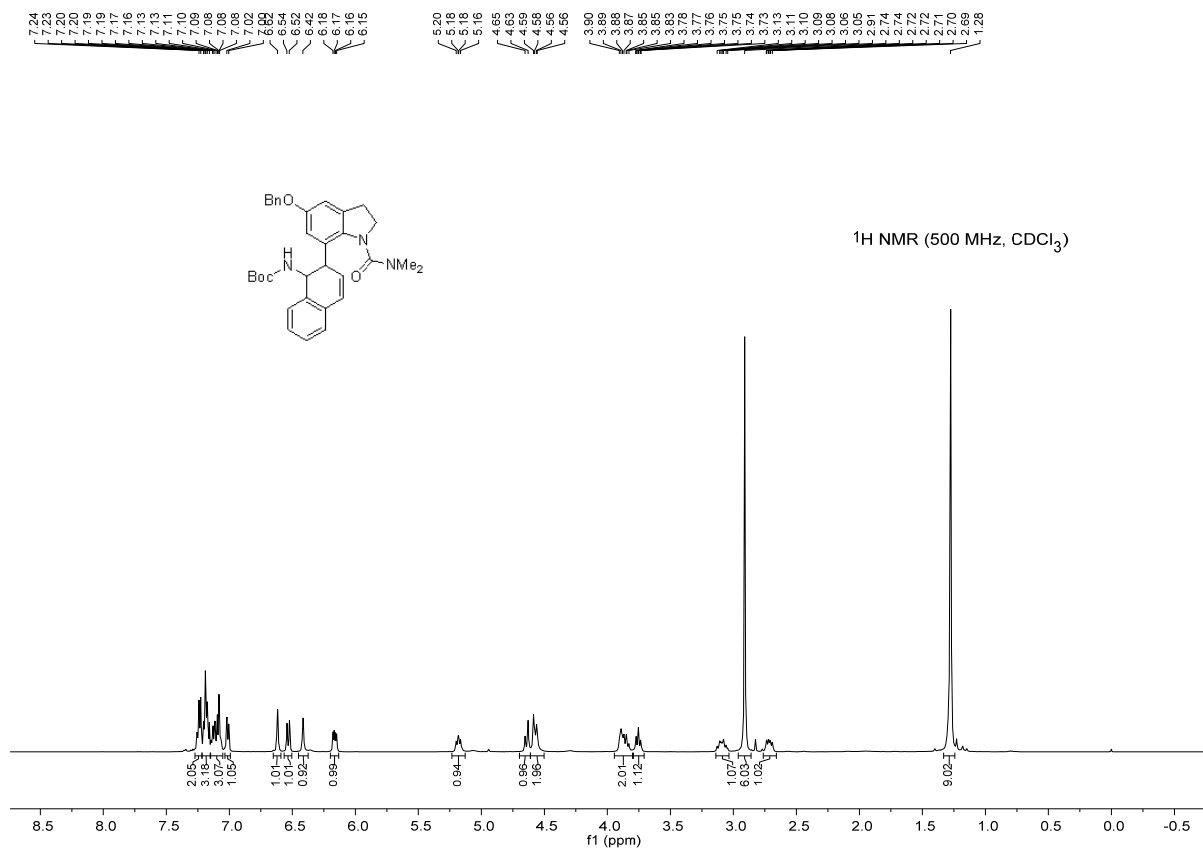
(5b)



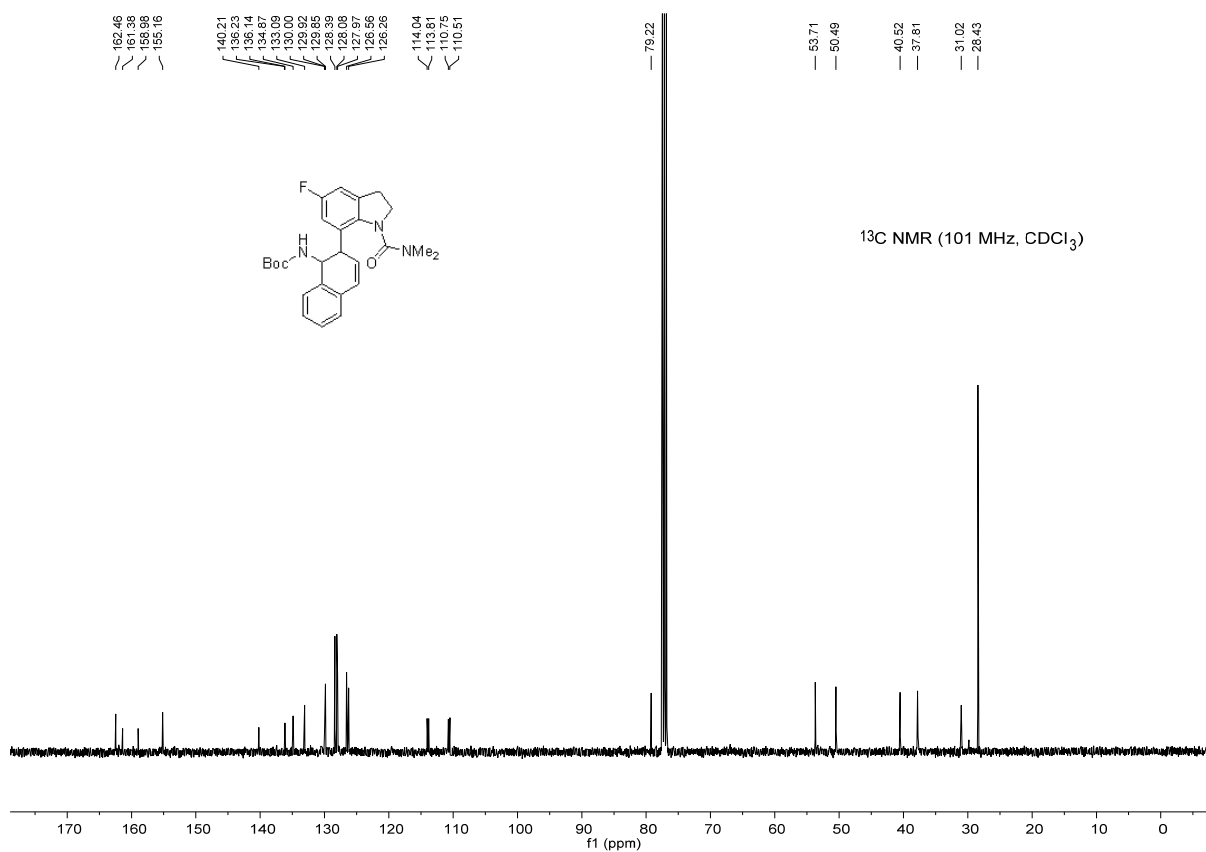
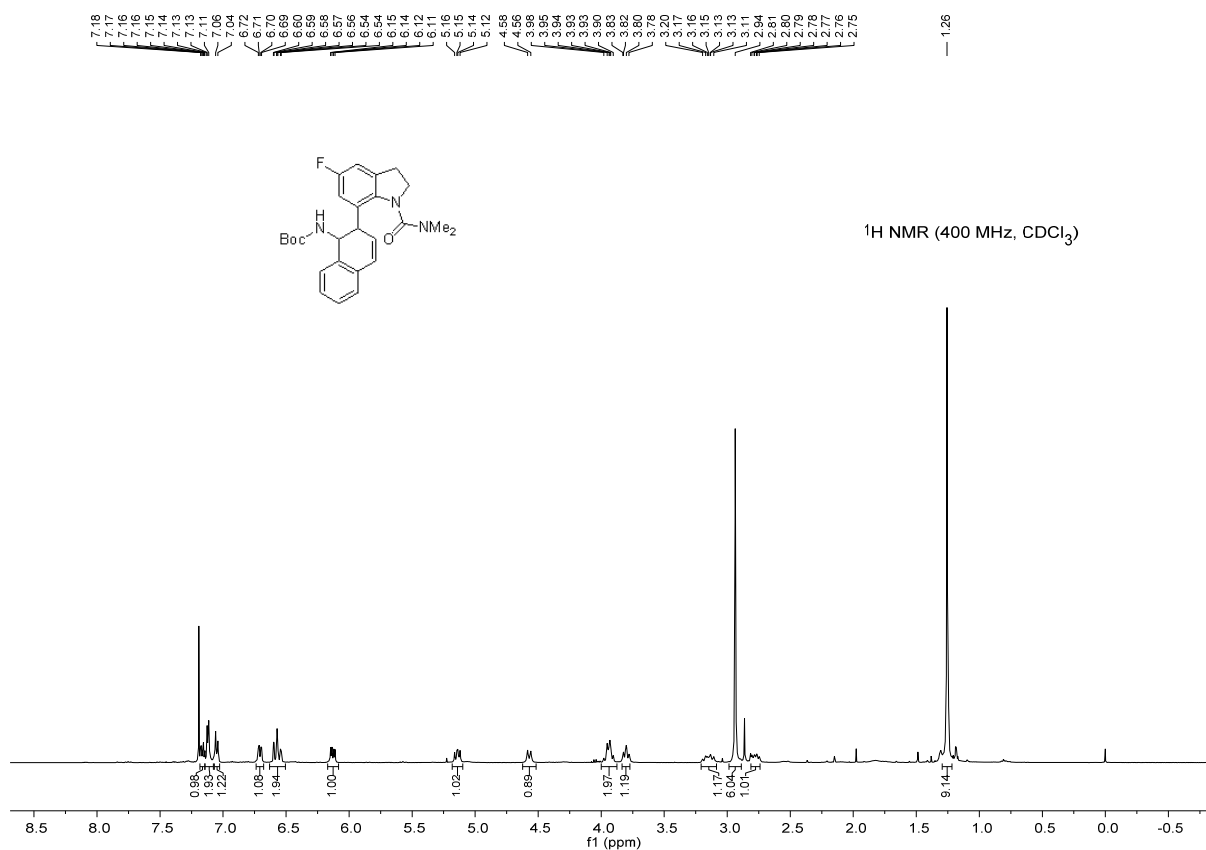
(24) *tert*-butyl (2-(1-(dimethylcarbamoyl)-5-methoxyindolin-7-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(5c)

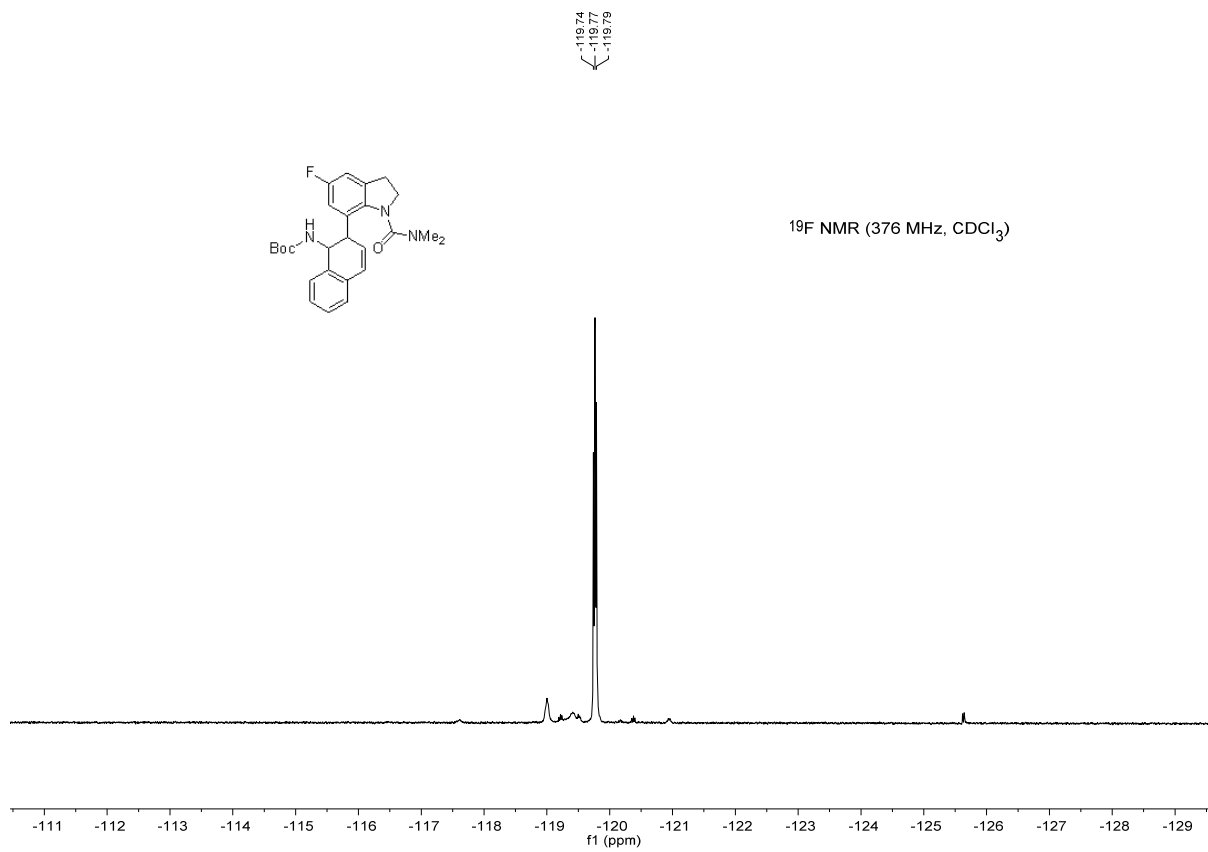


(25) *tert*-butyl (2-(5-(benzyloxy)-1-(dimethylcarbamoyl)indolin-7-yl)-1,2-dihydronaphthalen-1-yl)carbamate (**5d**)

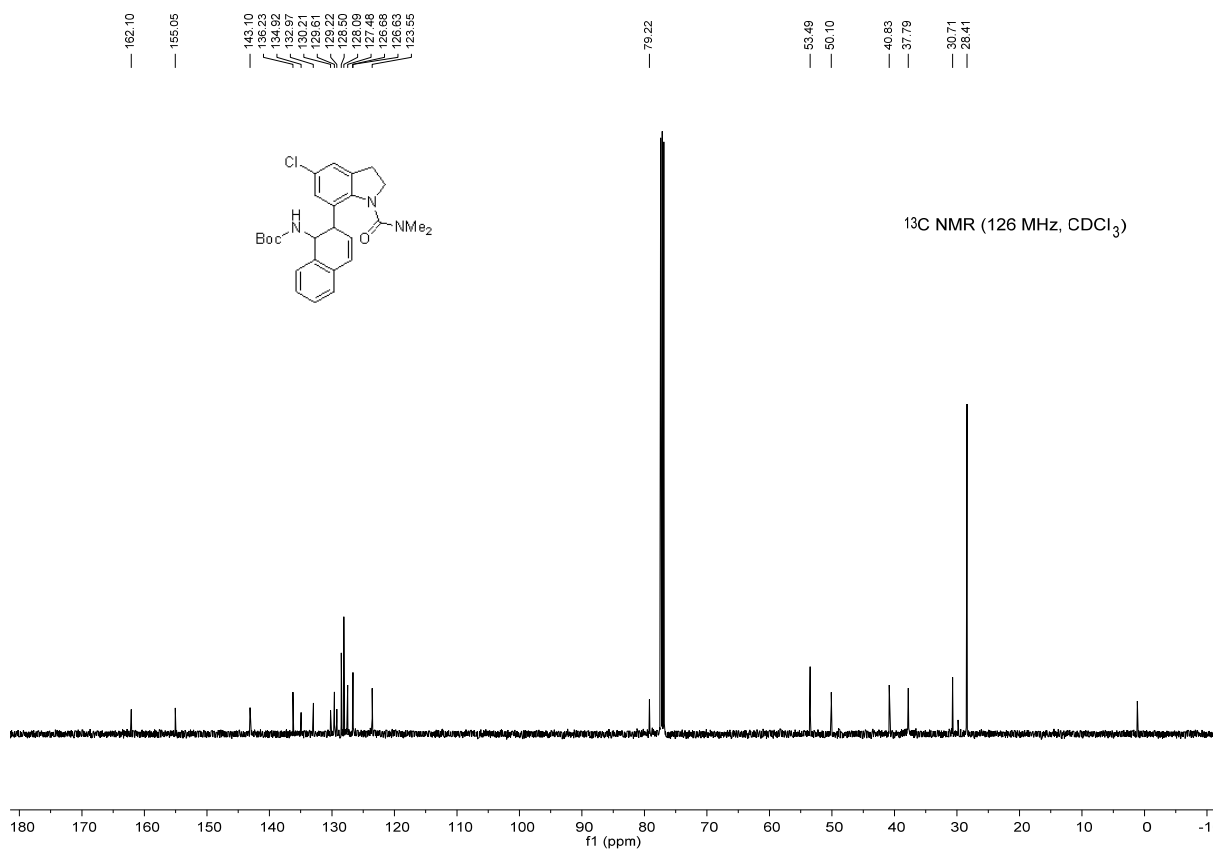
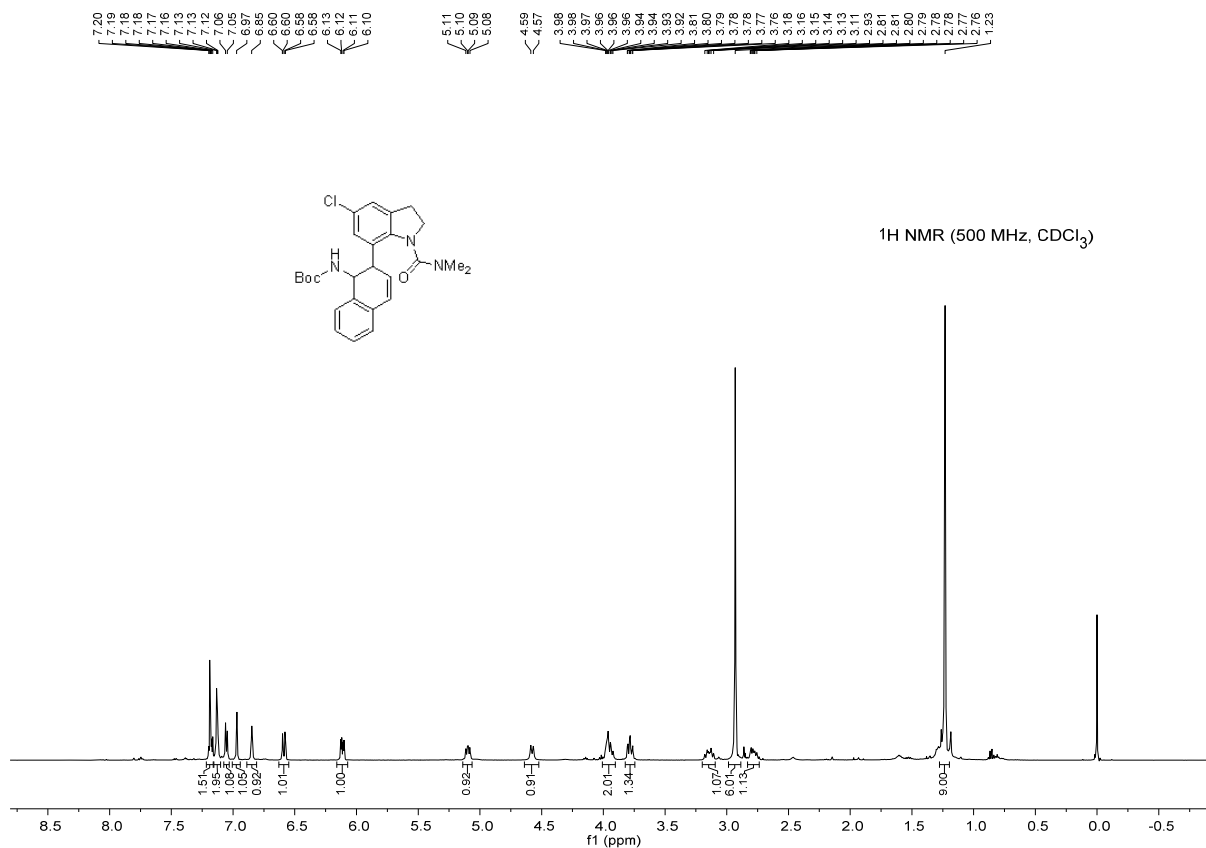


(26) *tert*-butyl (2-(1-(dimethylcarbamoyl)-5-fluoroindolin-7-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(5e)



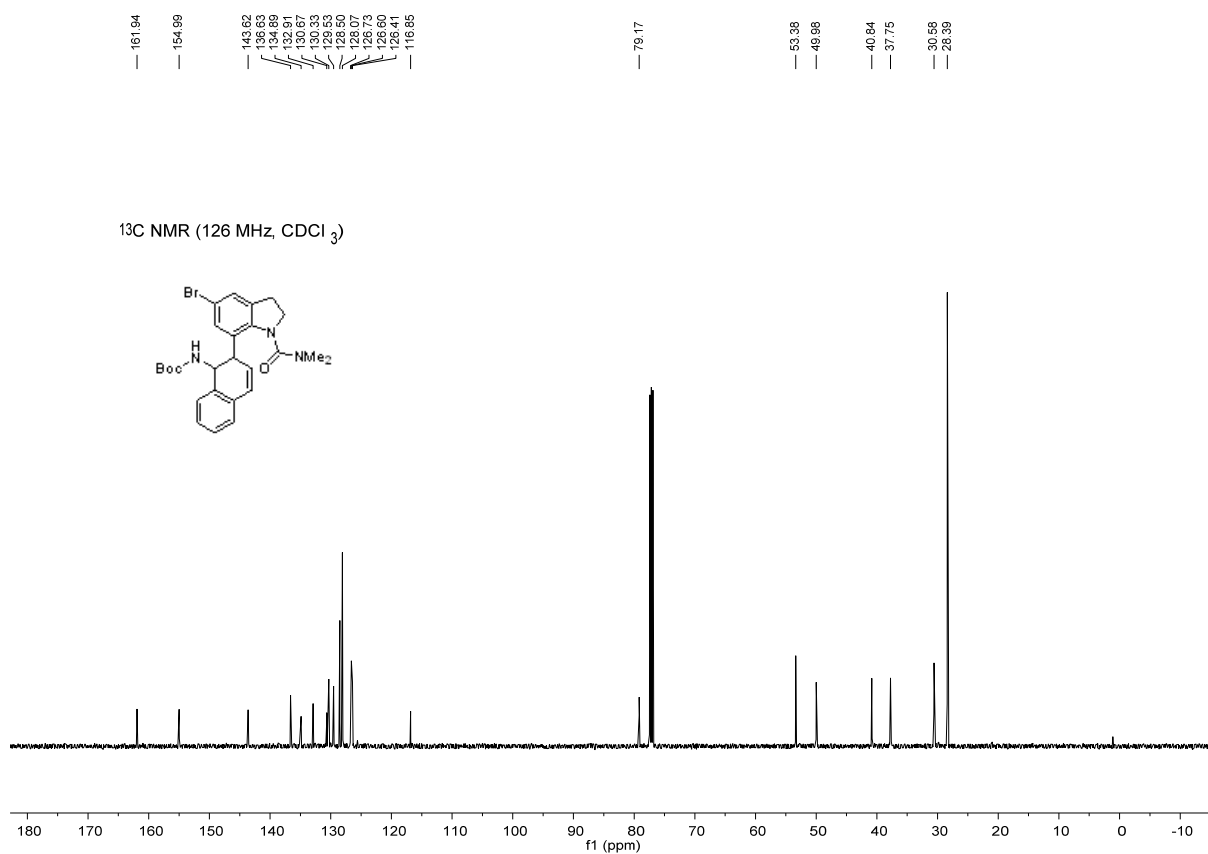
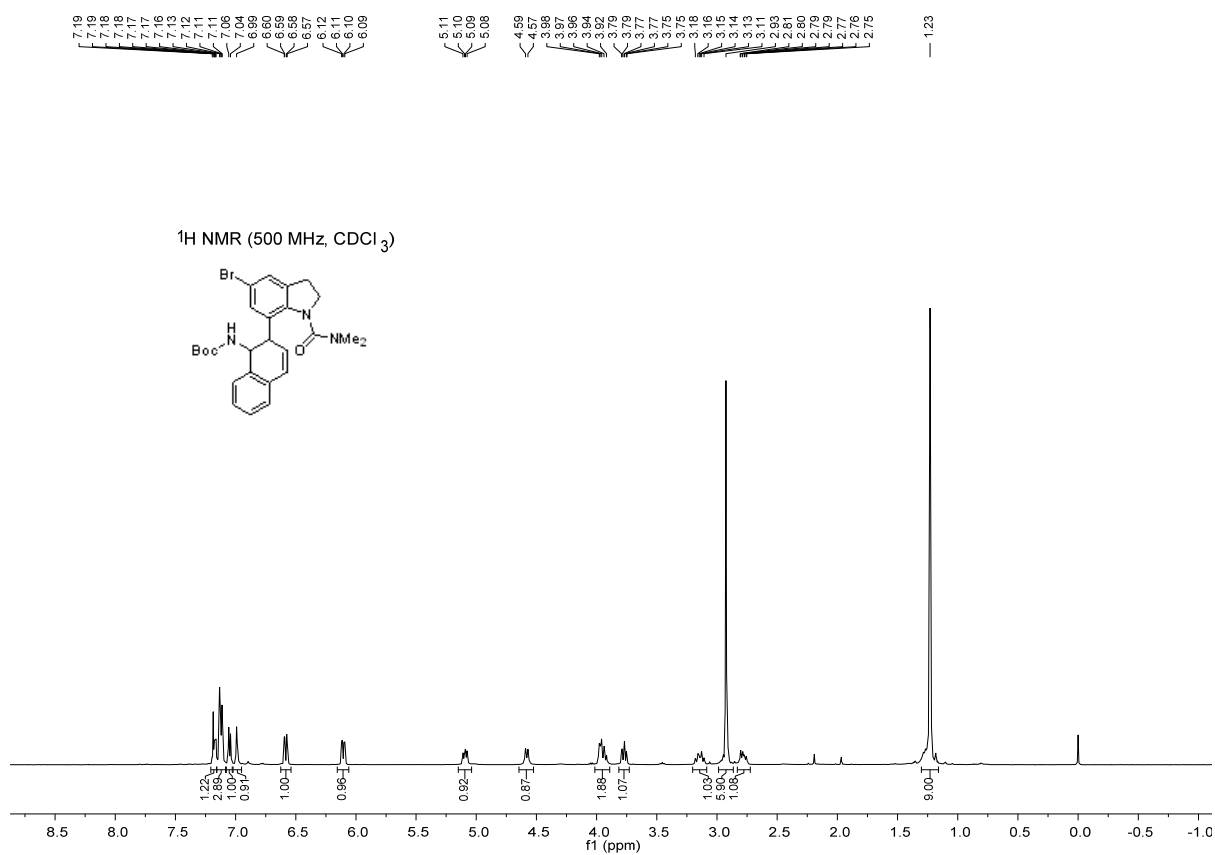


(27) *tert*-butyl (2-(5-chloro-1-(dimethylcarbamoyl)indolin-7-yl)-1,2-dihydronaphthalen-1-yl)carbamate
(5f)



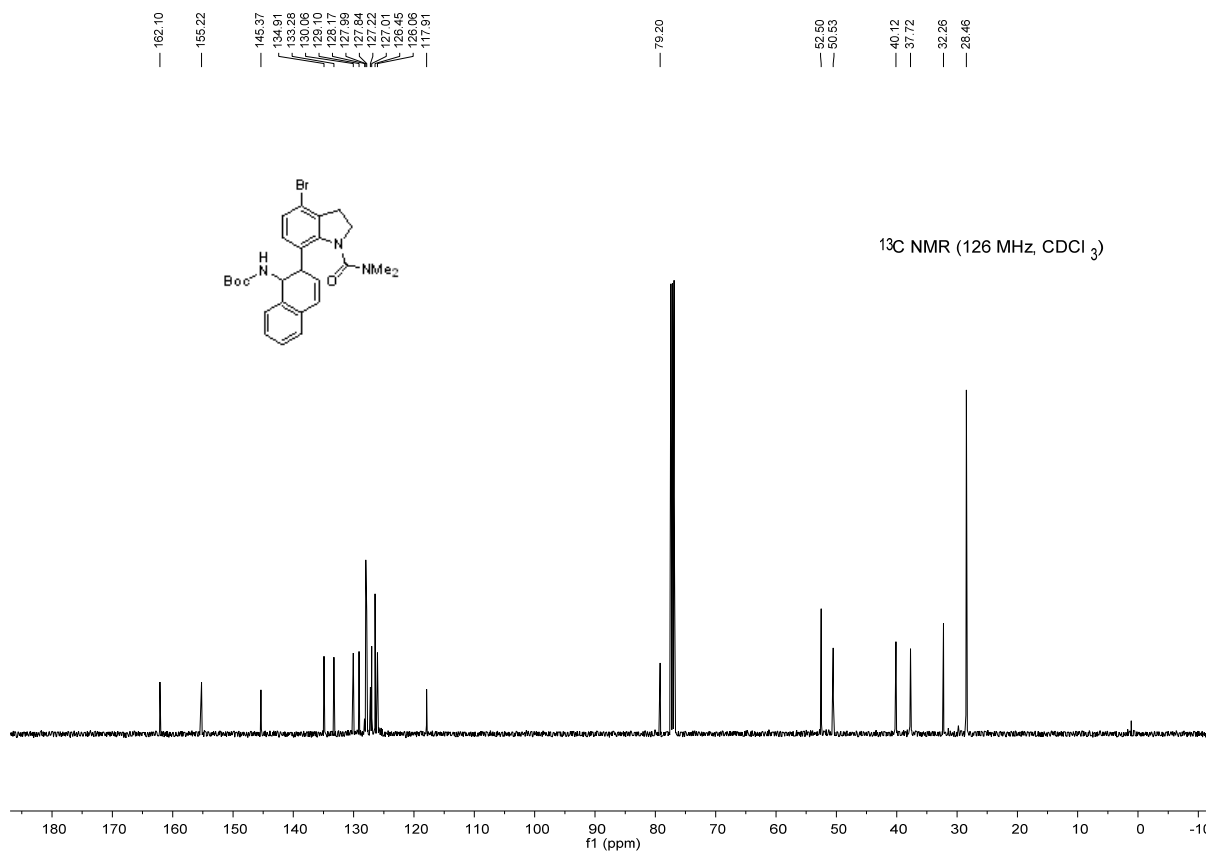
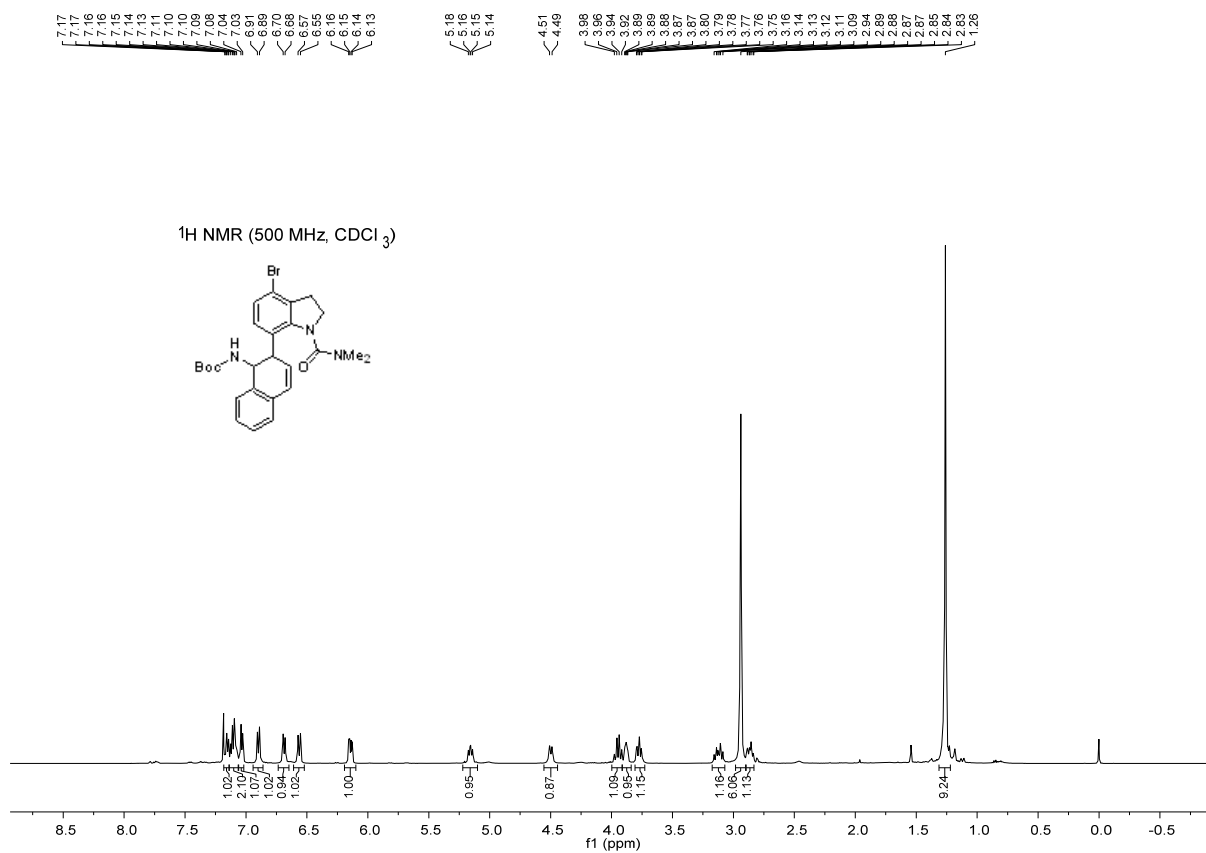
(28) *tert*-butyl (2-(5-bromo-1-(dimethylcarbamoyl)indolin-7-yl)-1,2-dihydronaphthalen-1-yl)carbamate

(5g)

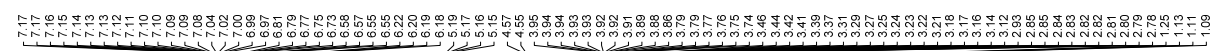


(29) *tert*-butyl (2-(4-bromo-1-(dimethylcarbamoyl)indolin-7-yl)-1,2-dihydronaphthalen-1-yl)carbamate

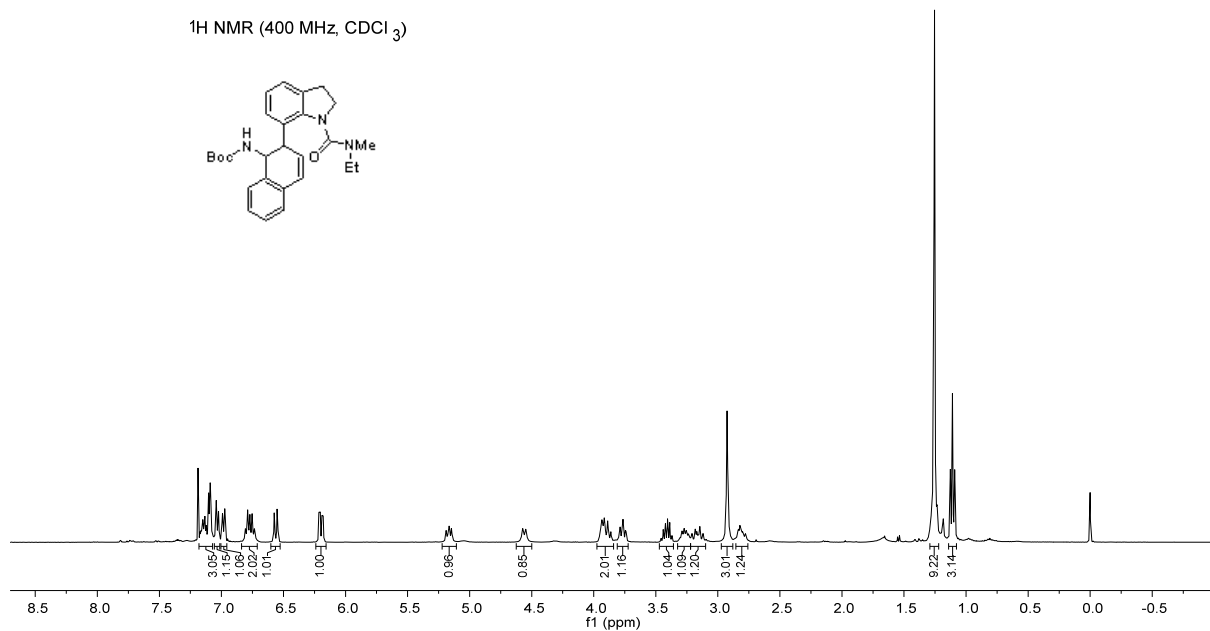
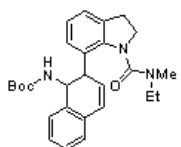
(5h)



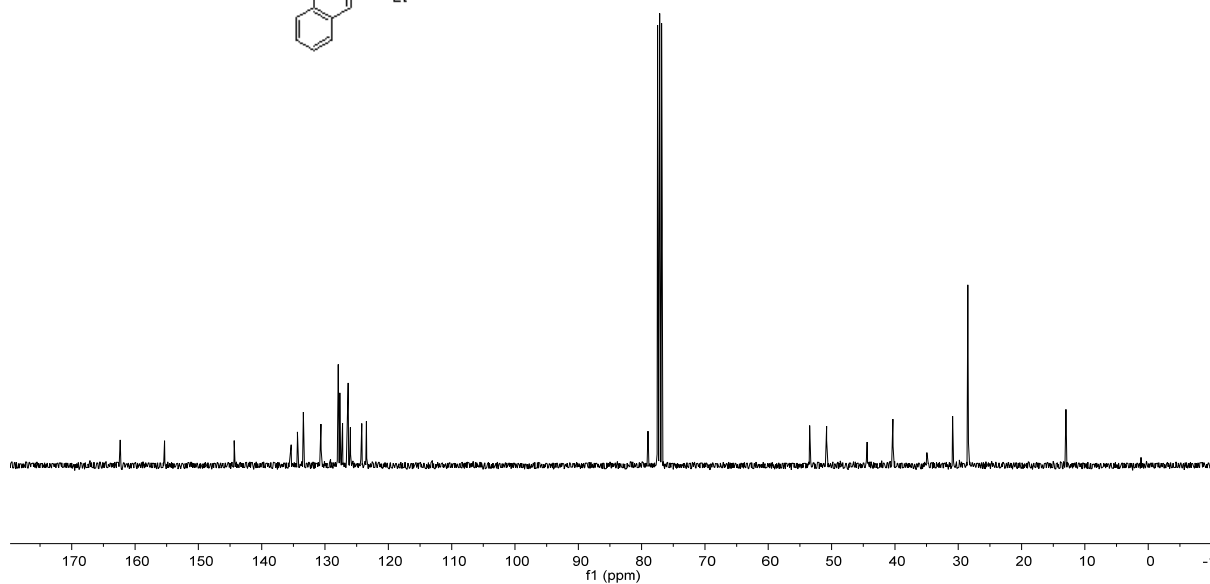
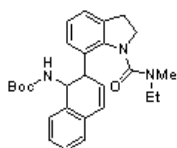
(30) *tert*-butyl (2-(1-(ethyl(methyl)carbamoyl)indolin-7-yl)-1,2-dihydronaphthalen-1-yl)carbamate (**5i**)



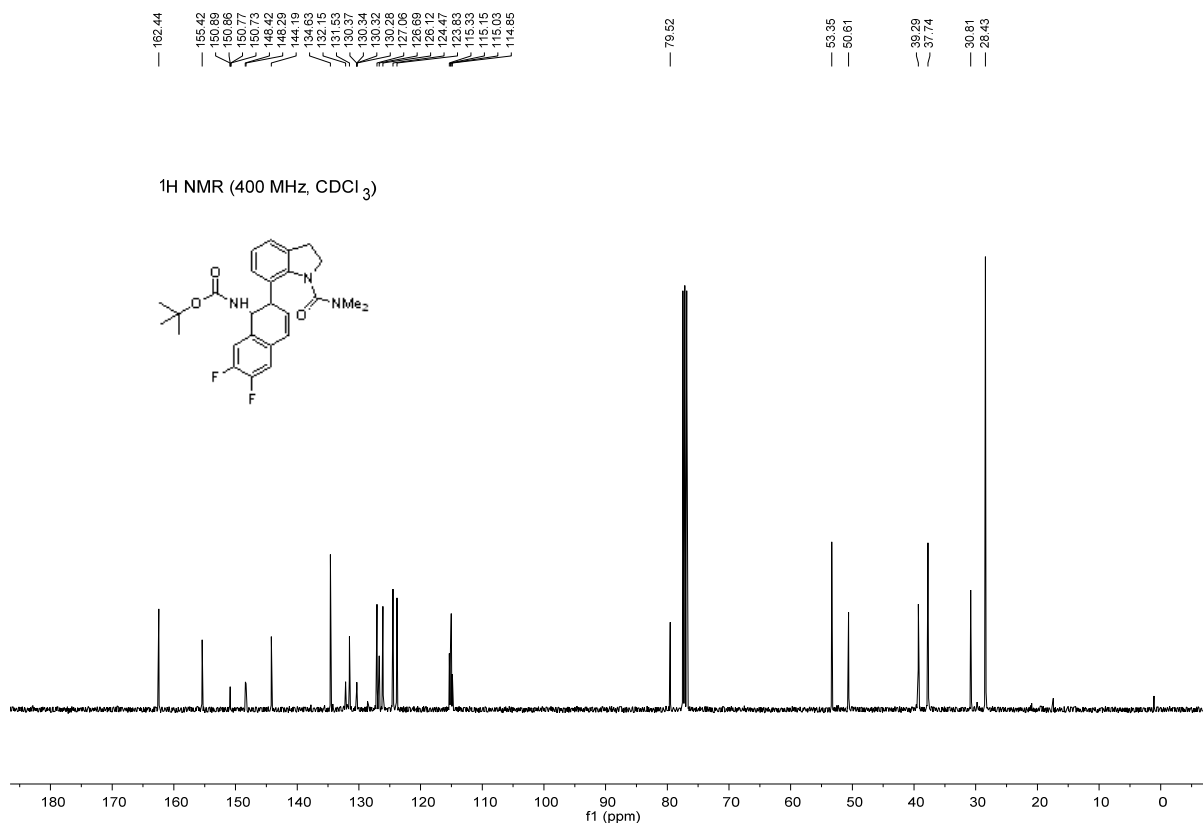
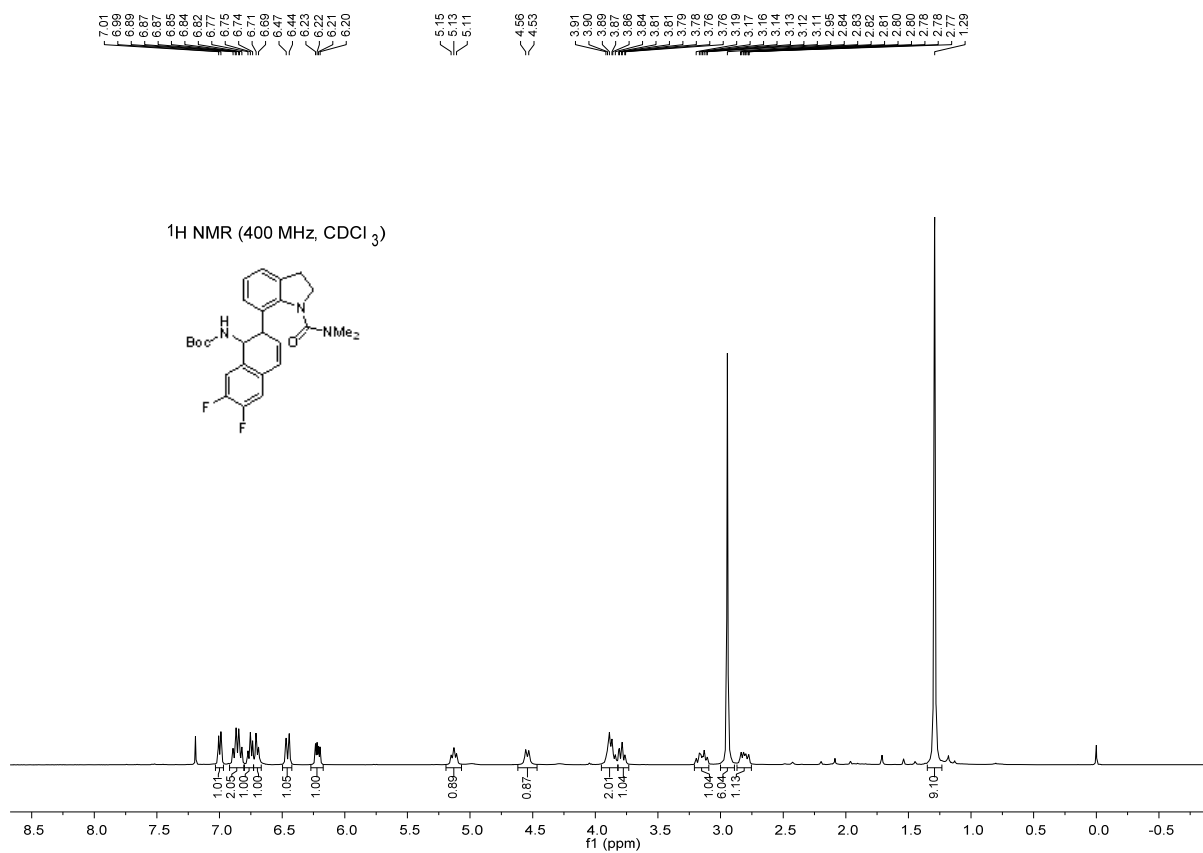
¹H NMR (400 MHz, CDCl₃)

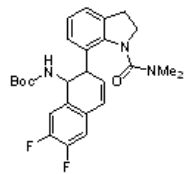


¹³C NMR (101 MHz, CDCl₃)

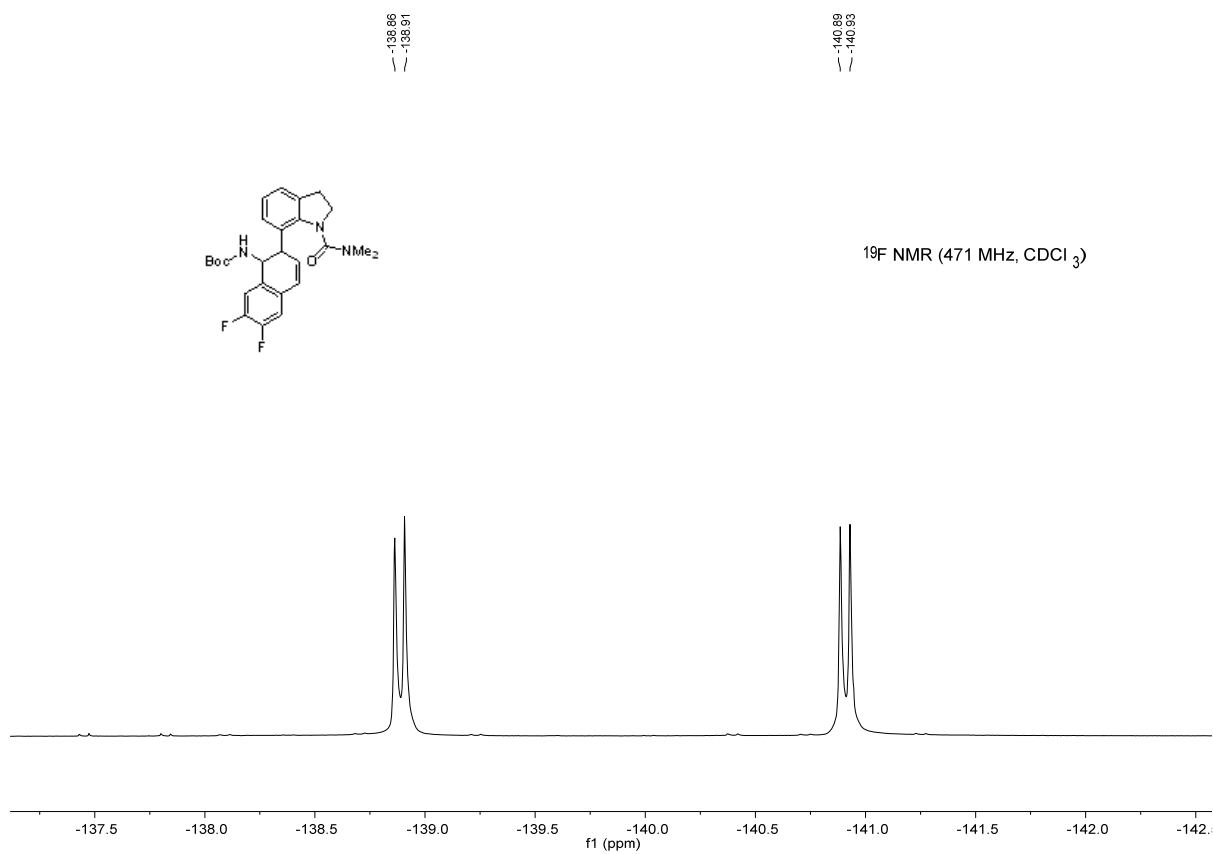


(31) *tert*-butyl (2-(1-(dimethylcarbamoyl)indolin-7-yl)-6,7-difluoro-1,2-dihydronaphthalen-1-yl)carbamate
(5j)

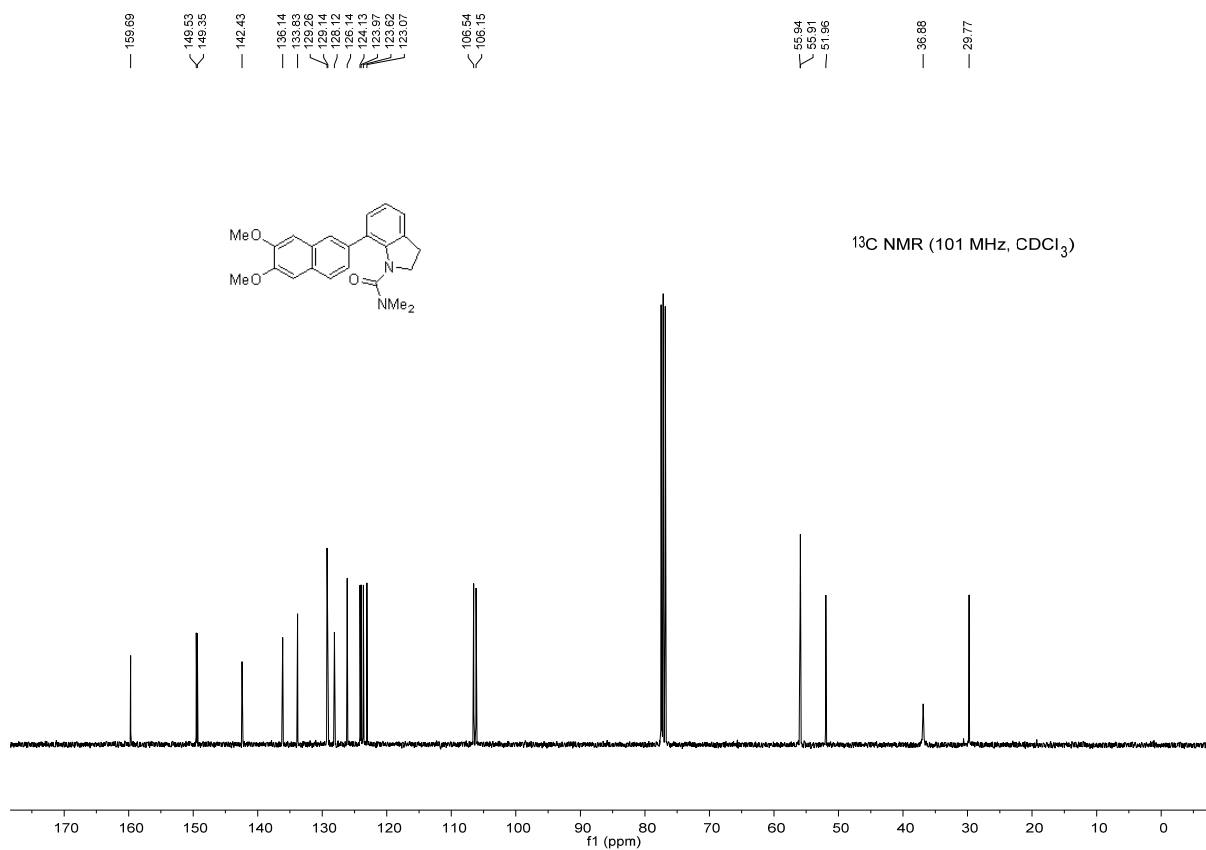
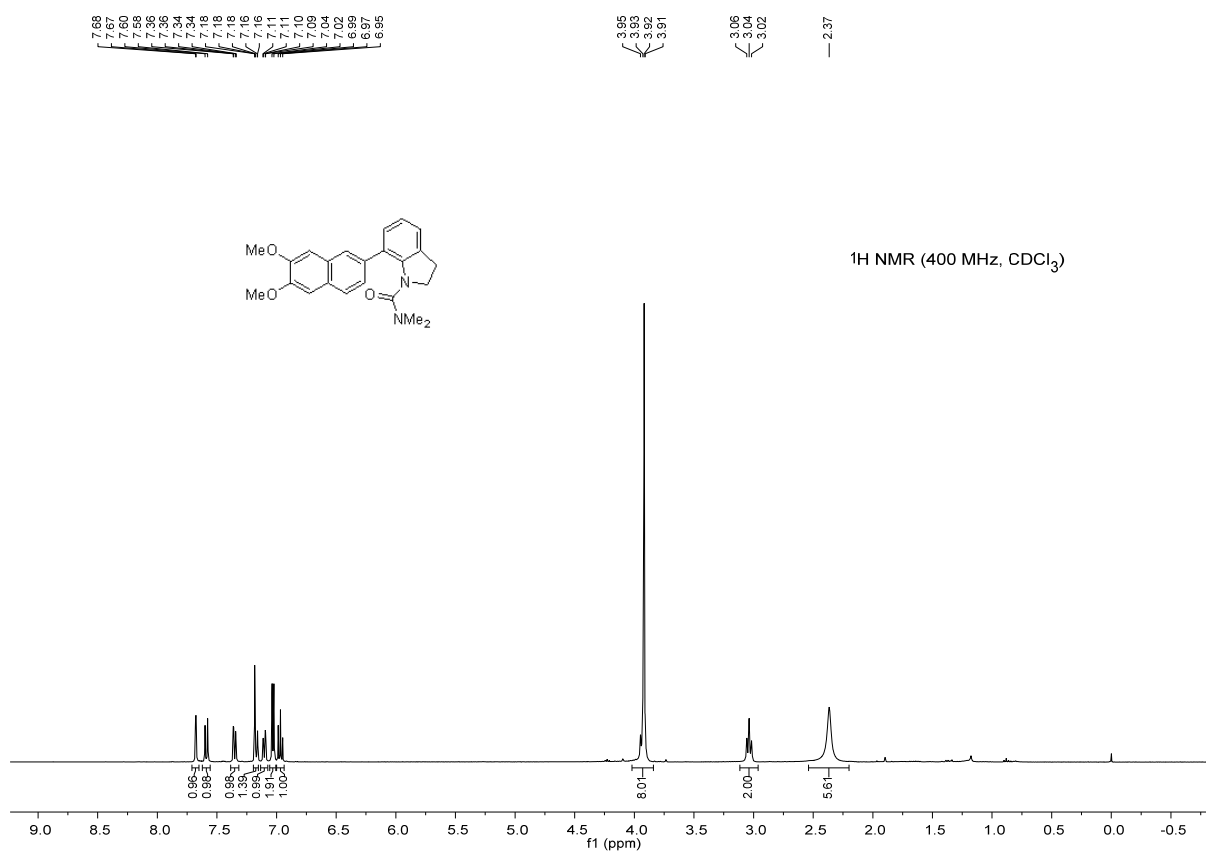




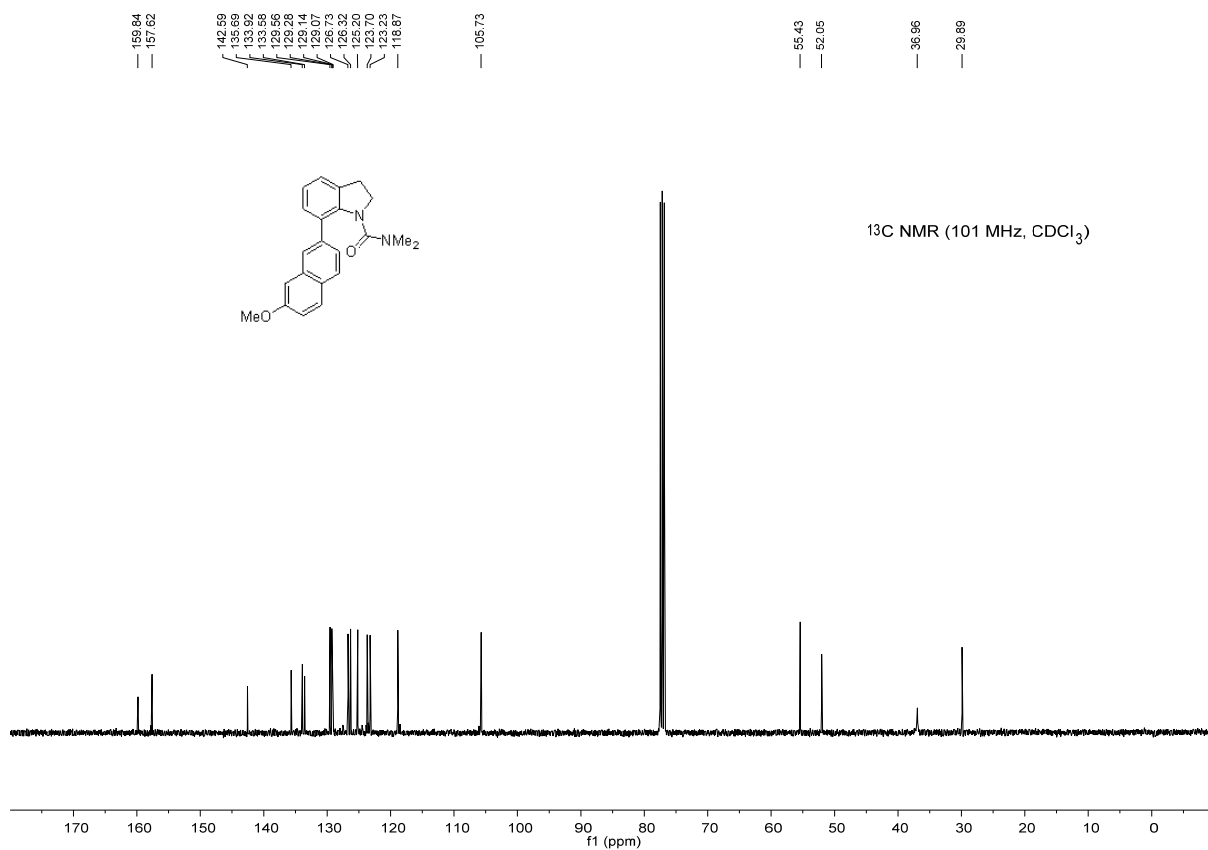
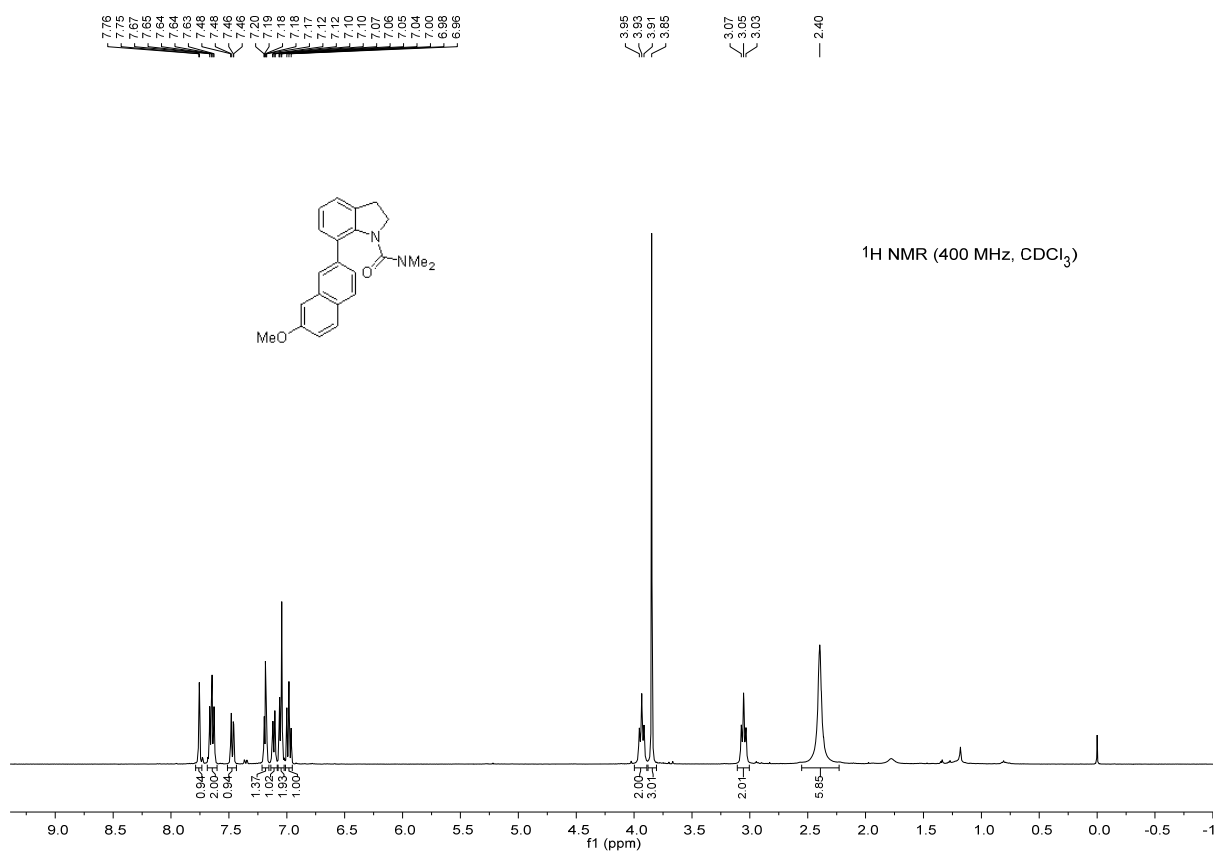
^{19}F NMR (471 MHz, CDCl_3)



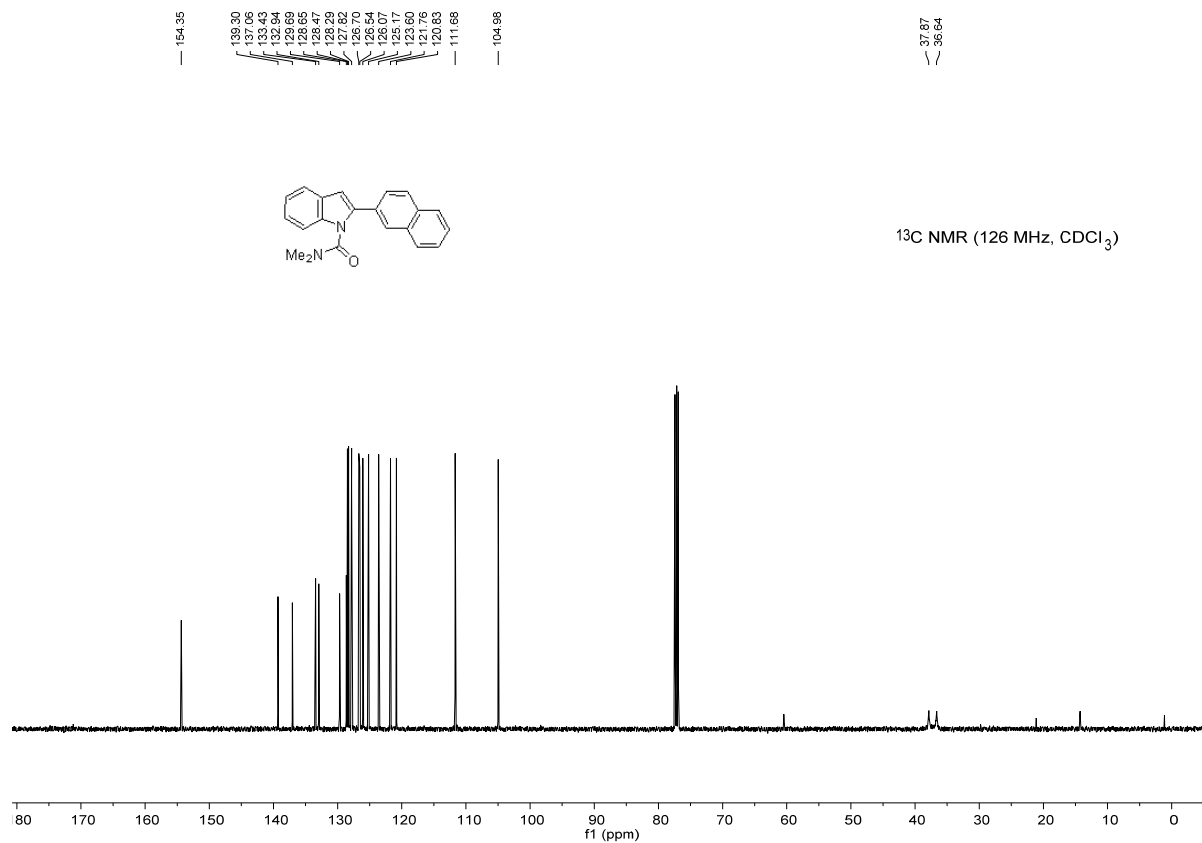
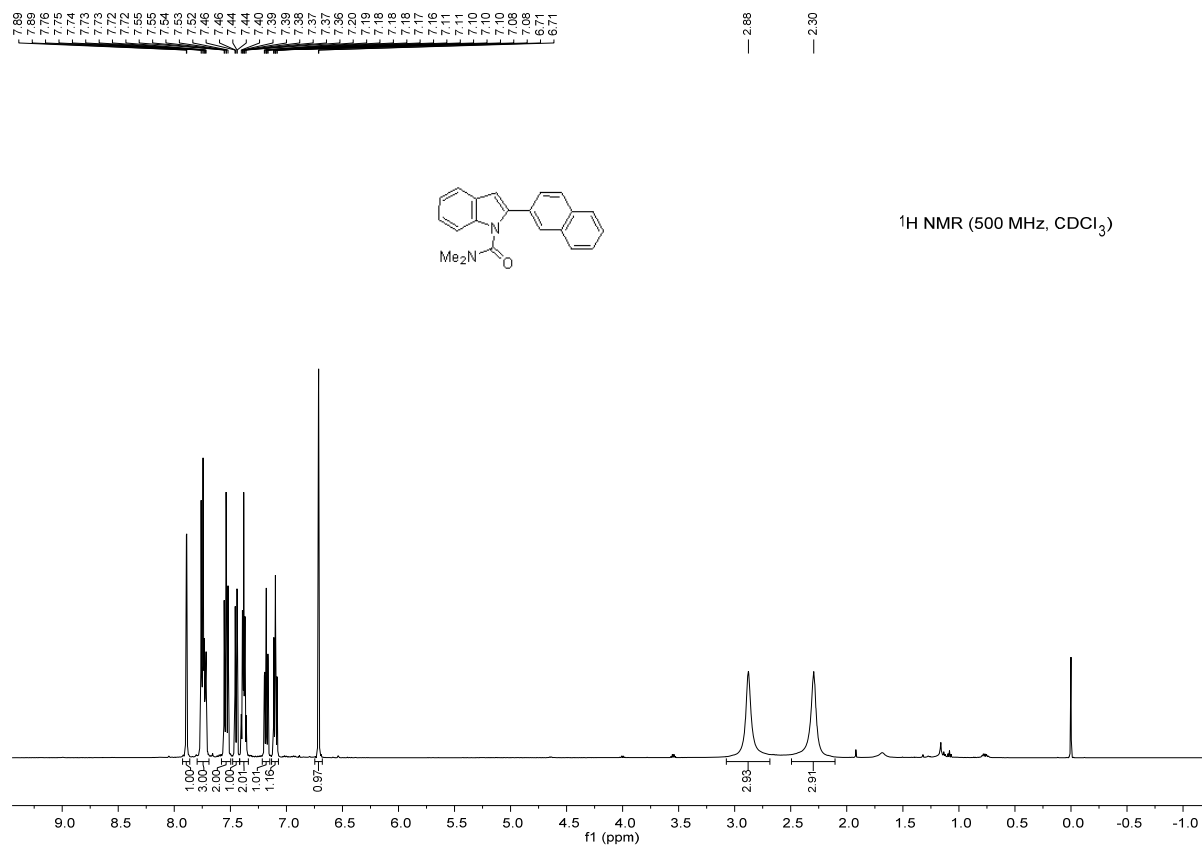
(32) 7-(6,7-dimethoxynaphthalen-2-yl)-N,N-dimethylindoline-1-carboxamide (**5k**)



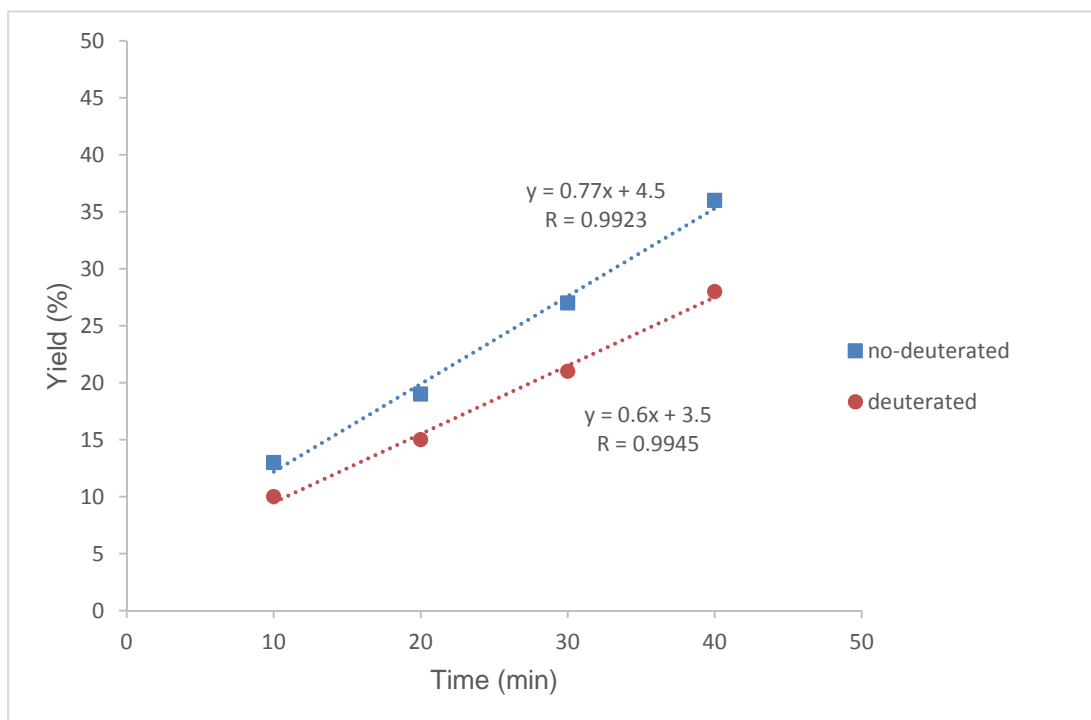
(33) 7-(7-methoxynaphthalen-2-yl)-N,N-dimethylindoline-1-carboxamide (**51**)



NMR spectral copies of compound 6 (through reaction of 3a with KOH)



Kinetic Isotope Effect (KIE) experiment



HRMS copy of intermediate I

20240122HESI+cjz-14 #21 RT: 0.30 AV: 1 NL: 4.88E6
T: FTMS + c ESI Full ms [200.00-800.00]

