

Supporting Information

Synthesis of indolyl-quinolines, indolyl-acridines and indolyl-cyclopenta[*b*]quinolines from the Baylis-Hillman adducts: An *in situ*[1,3]-sigmatropic rearrangement of an indole nucleus to access indolyl-acridines and indolyl-cyclopenta[*b*]quinolines

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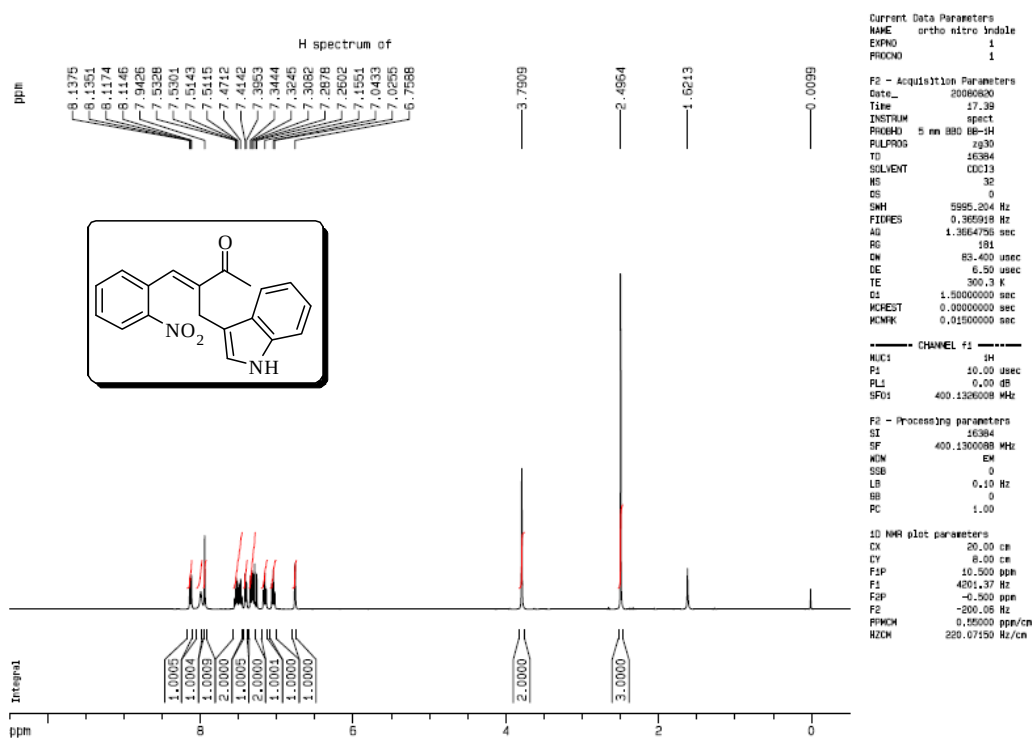
Department of Chemistry, National Taiwan Normal University, 88, Sec. 4, Tingchow Road, Taipei, Taiwan 116 R.O.C.

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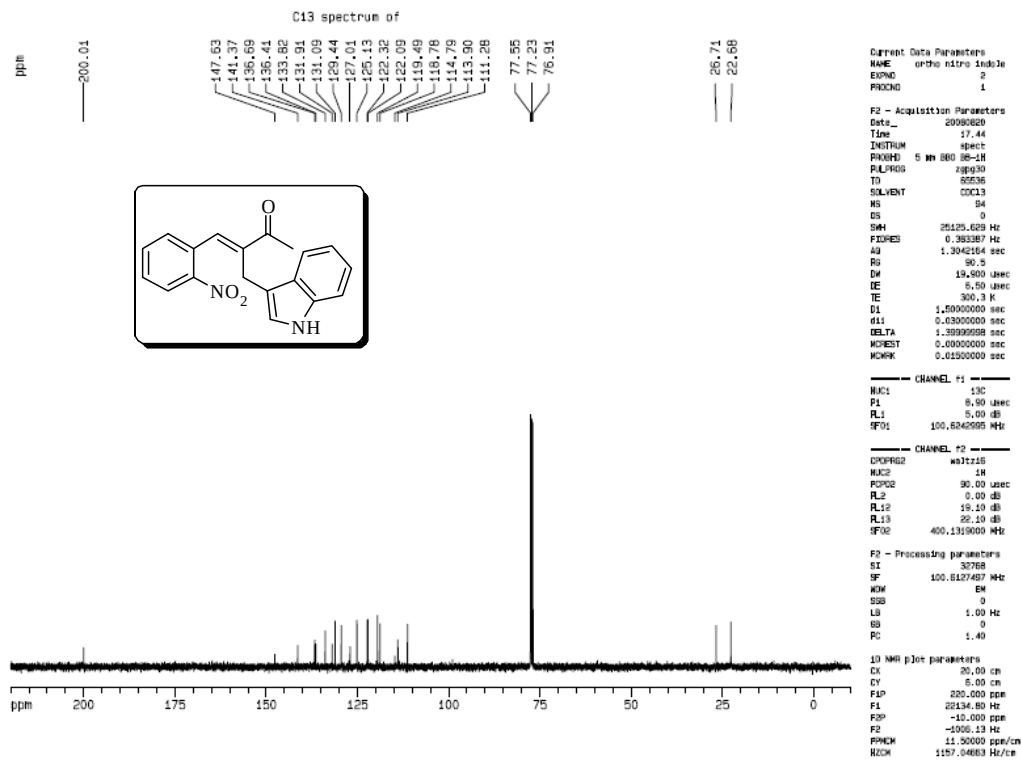
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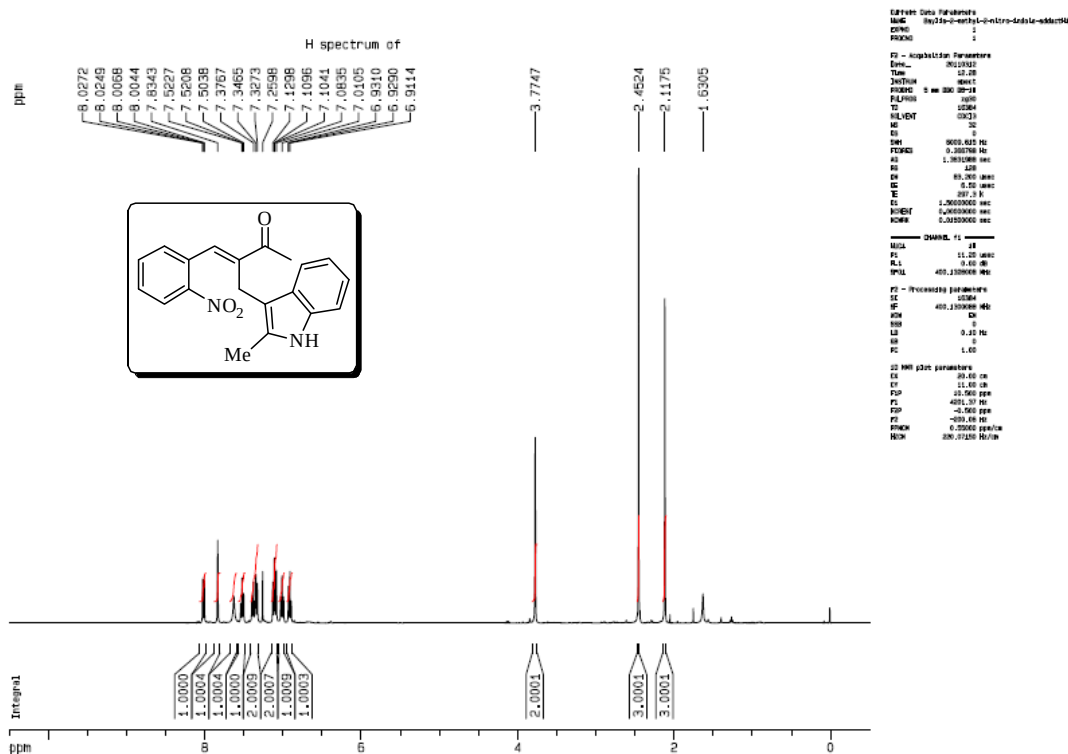
3-((1*H*-Indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (3a). ¹H NMR (400MHz, CDCl₃)



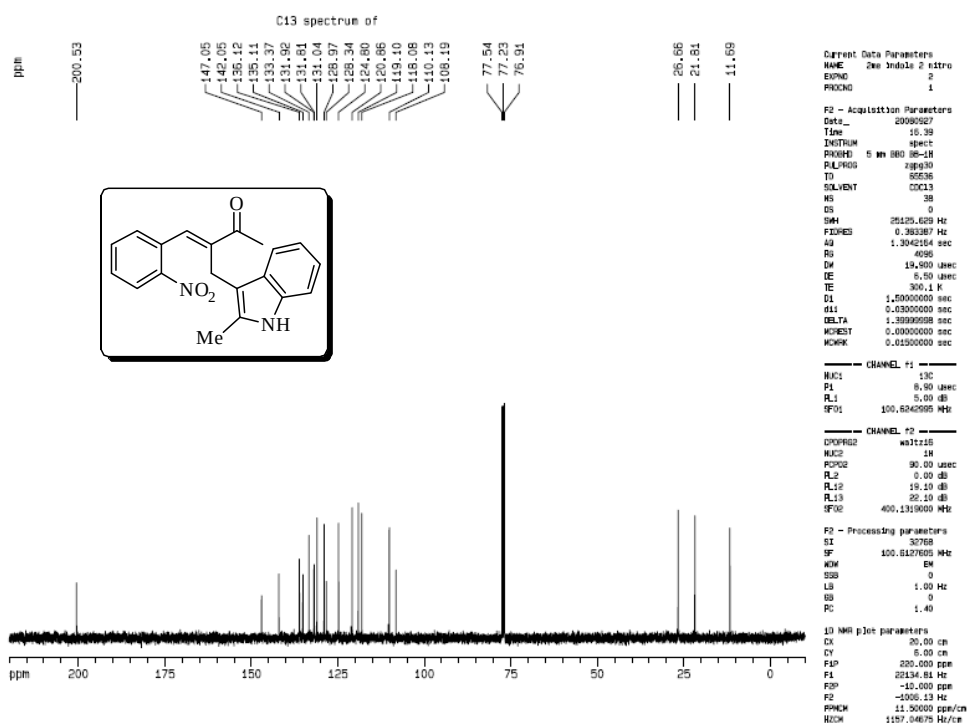
3-((1*H*-Indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (3a). ¹³C NMR (100 MHz, CDCl₃)



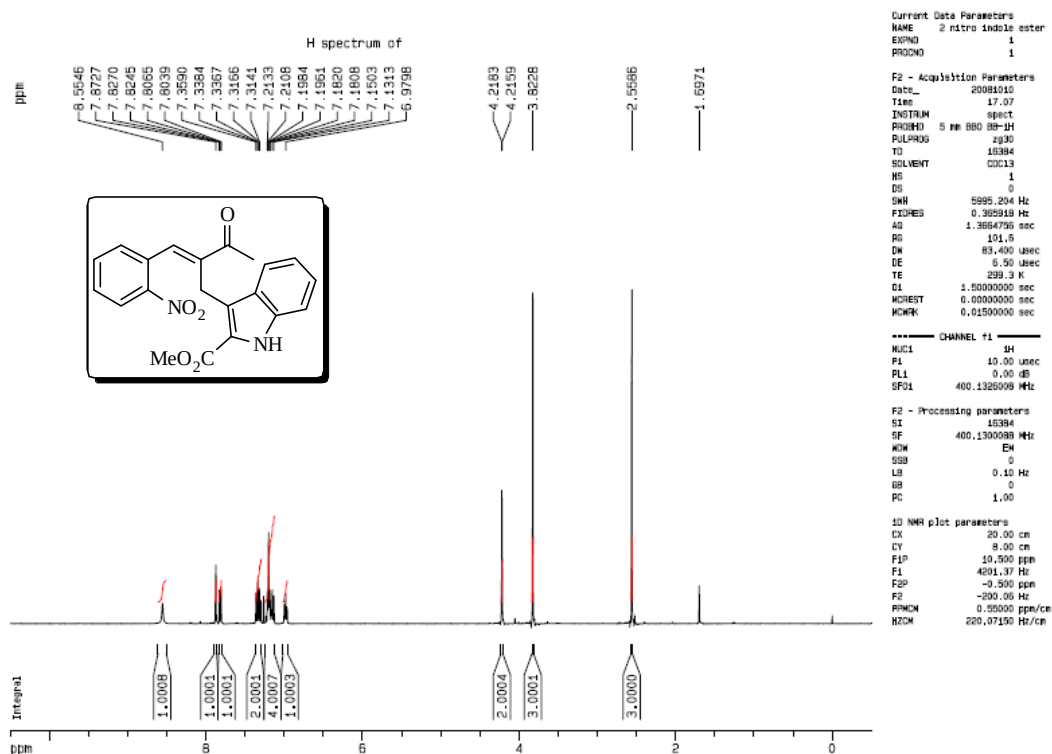
3-((2-Methyl-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (3b). ^1H NMR (400MHz, CDCl_3)



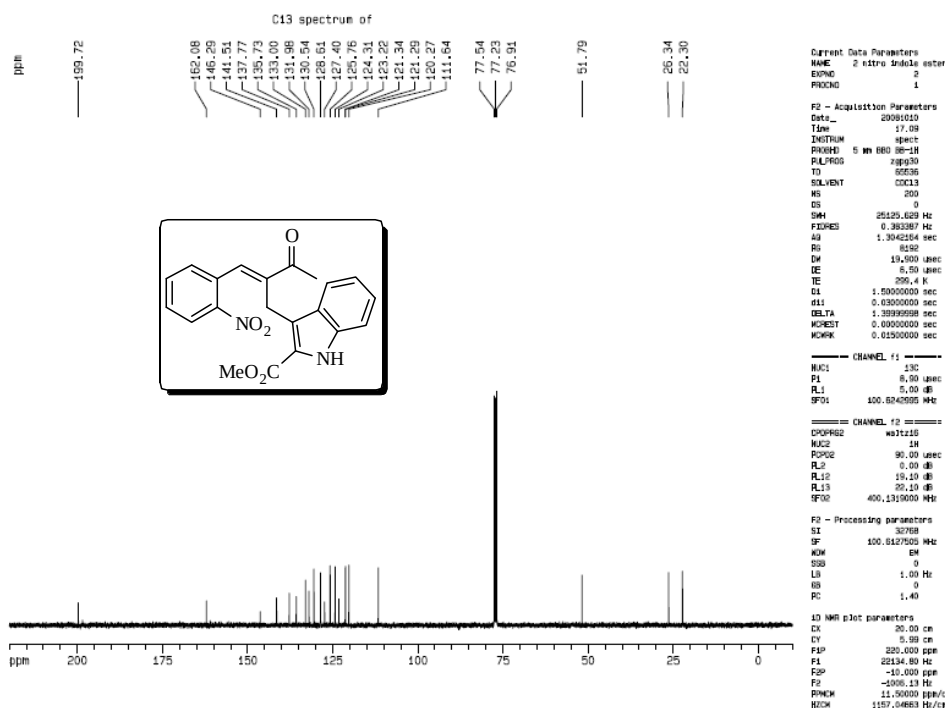
3-((2-Methyl-1H-indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (3b). ^{13}C NMR (100 MHz, CDCl_3)



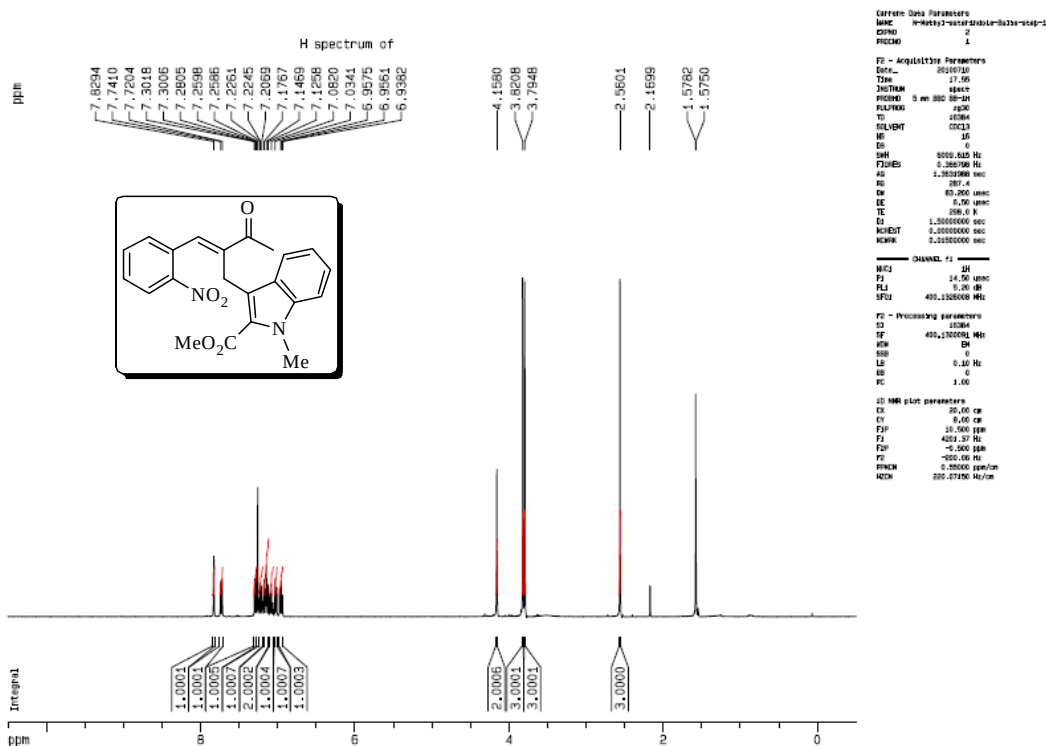
Methyl 3-(2-(2-nitrobenzylidene)-3-oxobutyl)-1H-indole-2-carboxylate (3c). ¹H NMR
(400MHz, CDCl₃)



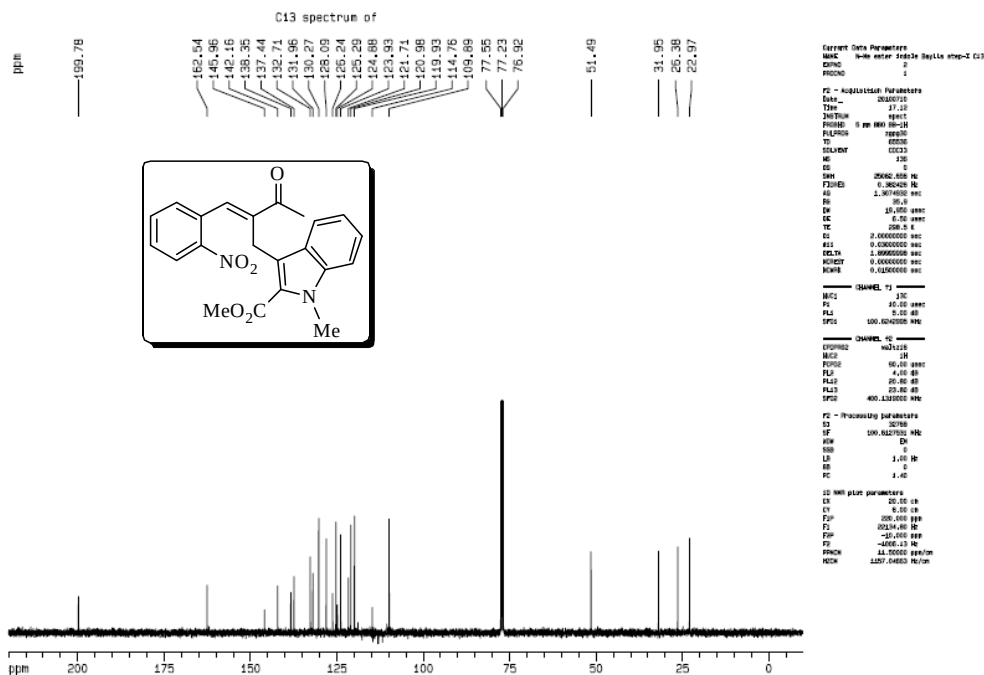
Methyl 3-(2-(2-nitrobenzylidene)-3-oxobutyl)-1H-indole-2-carboxylate (3c). ¹³C NMR (100 MHz, CDCl₃)



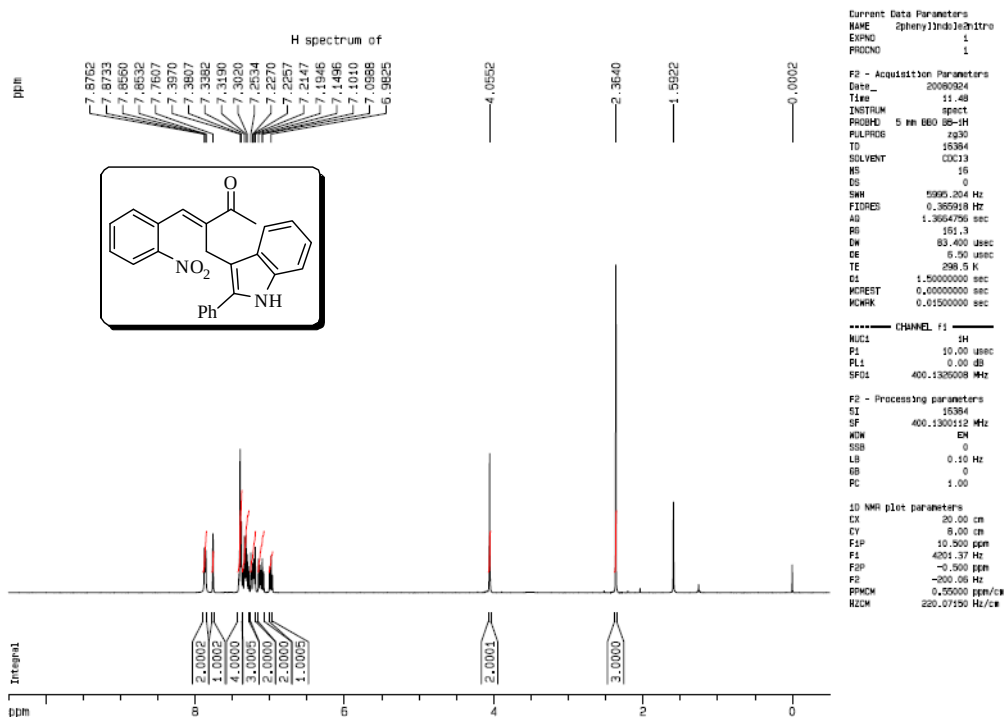
(E)-Methyl 1-methyl-3-(2-(2-nitrobenzylidene)-3-oxobutyl)-1H-indole-2-carboxylate (3d). ^1H NMR (400MHz, CDCl_3)



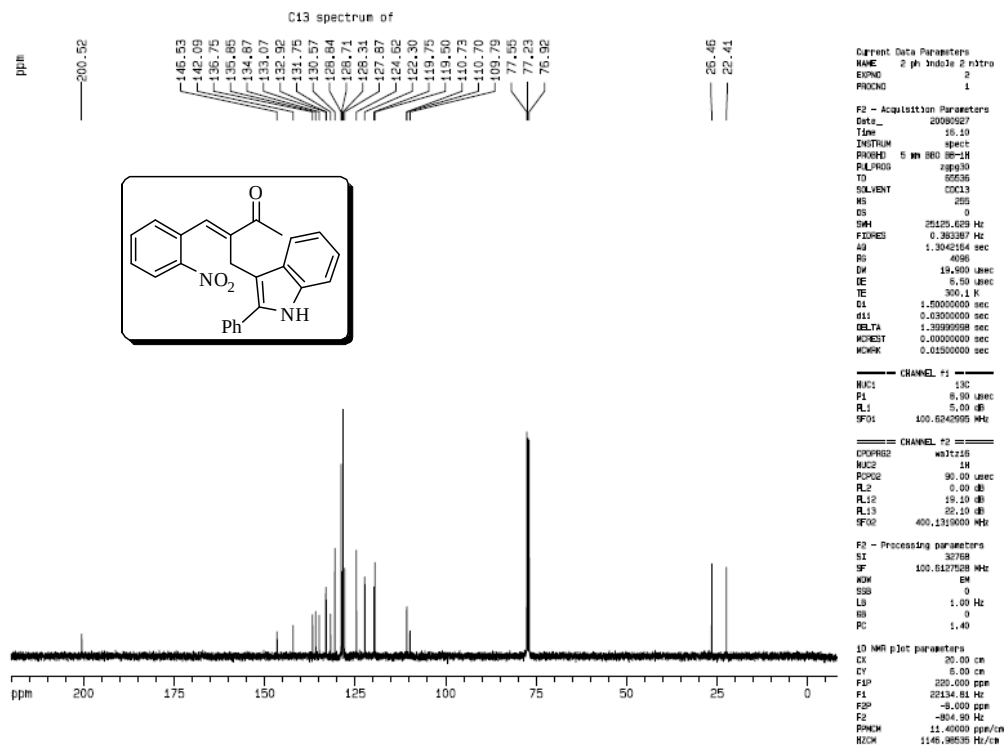
(E)-Methyl 1-methyl-3-(2-(2-nitrobenzylidene)-3-oxobutyl)-1H-indole-2-carboxylate (3d). ^{13}C NMR (100 MHz, CDCl_3)



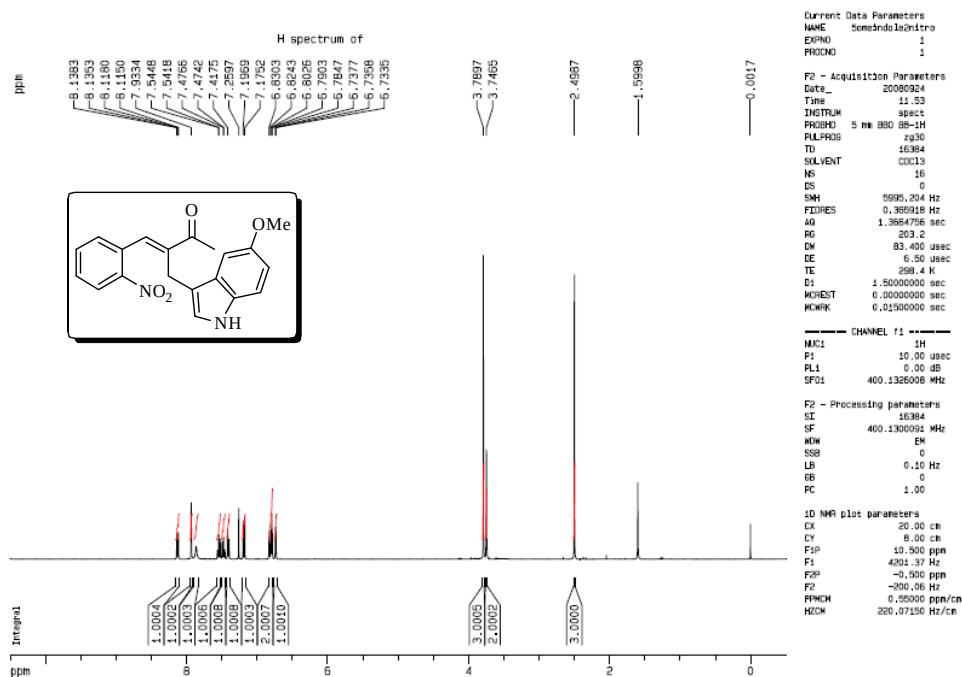
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(400MHz, CDCl₃)



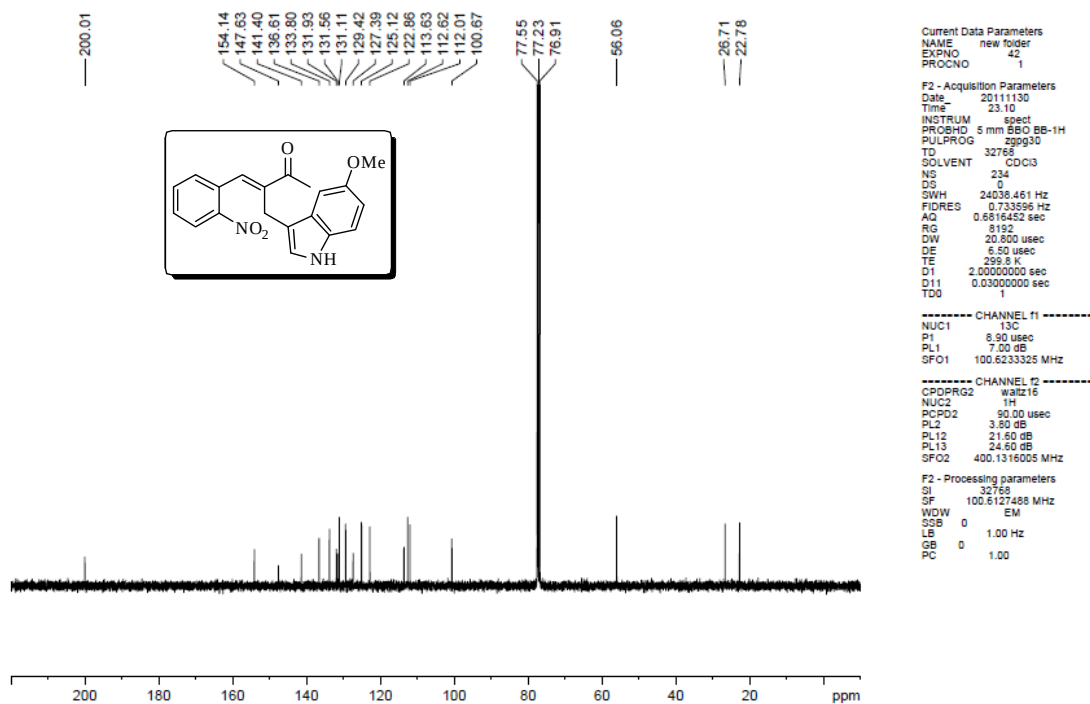
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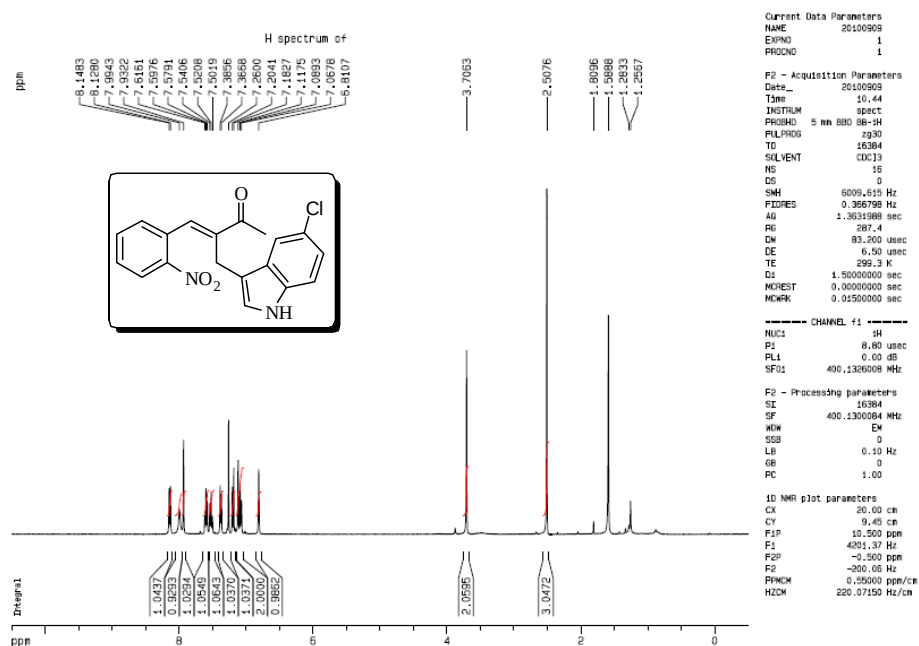
3-((5-Methoxy-1*H*-indol-3-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (3f). ¹H NMR
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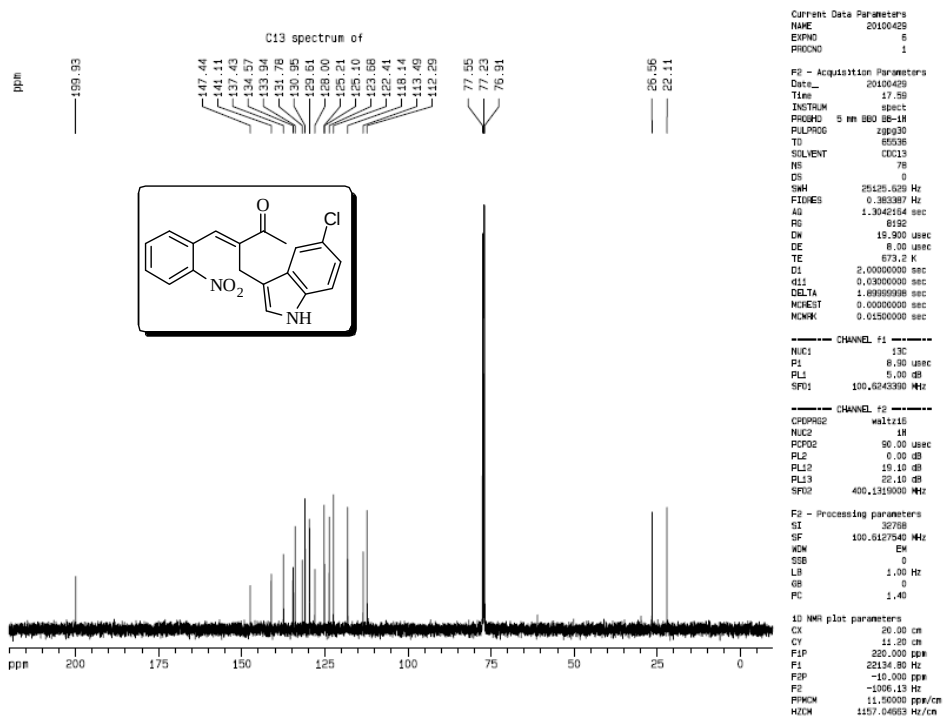
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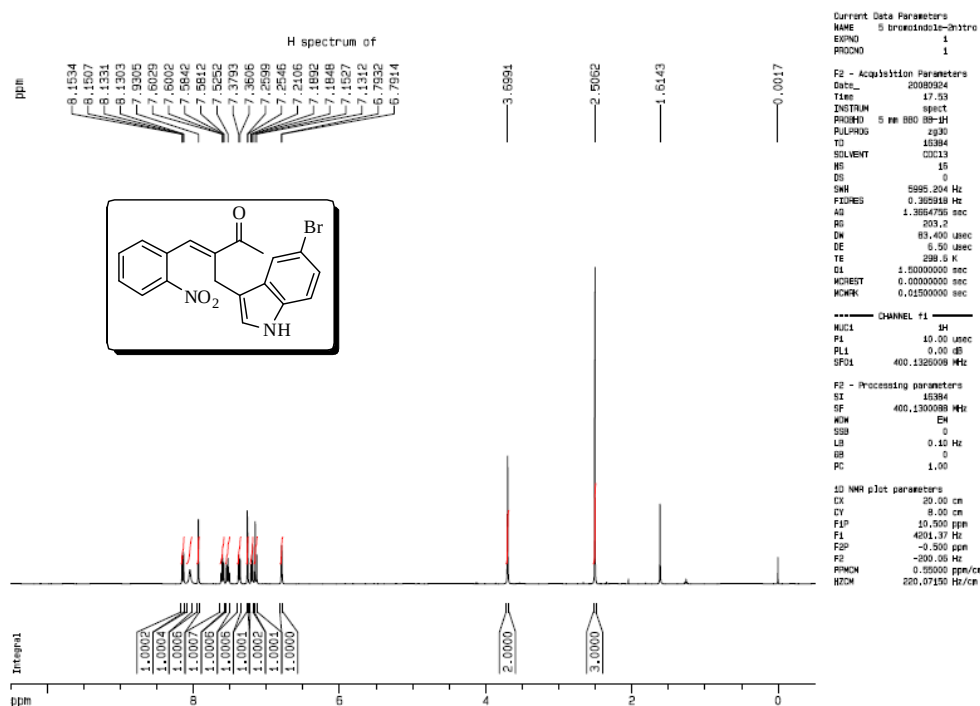
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(400MHz, CDCl_3)



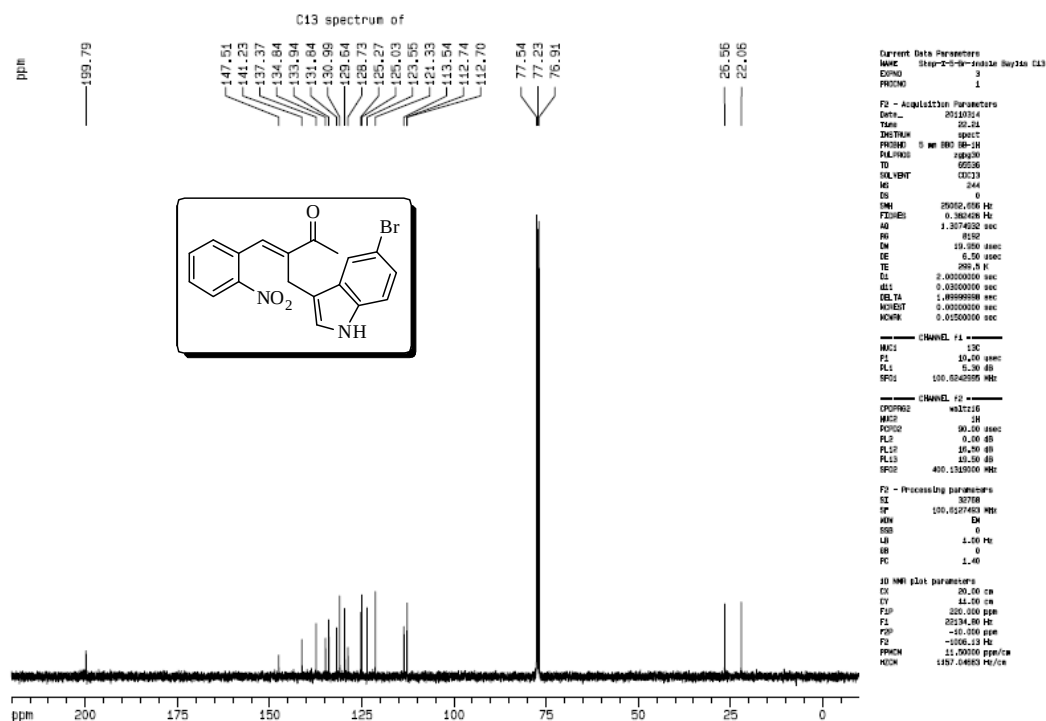
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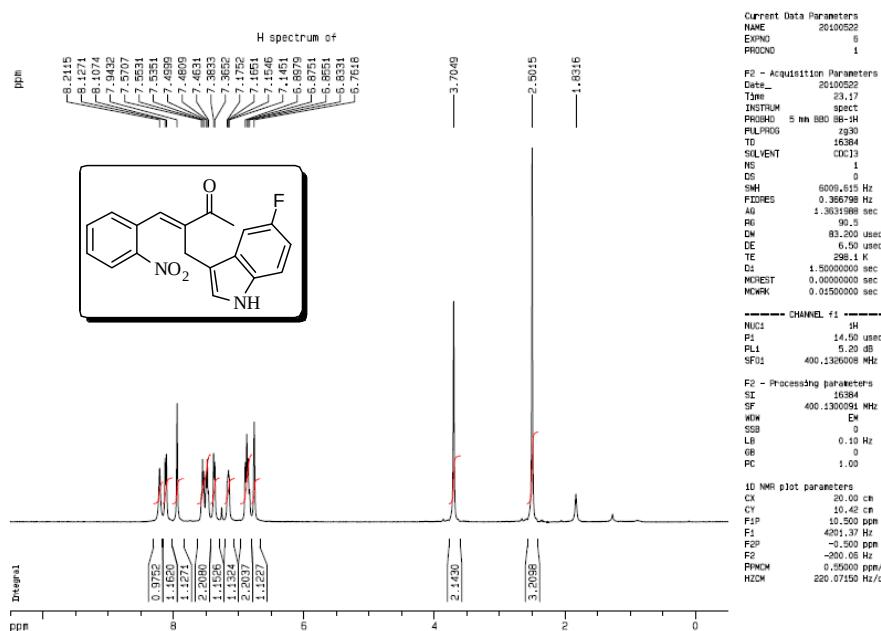
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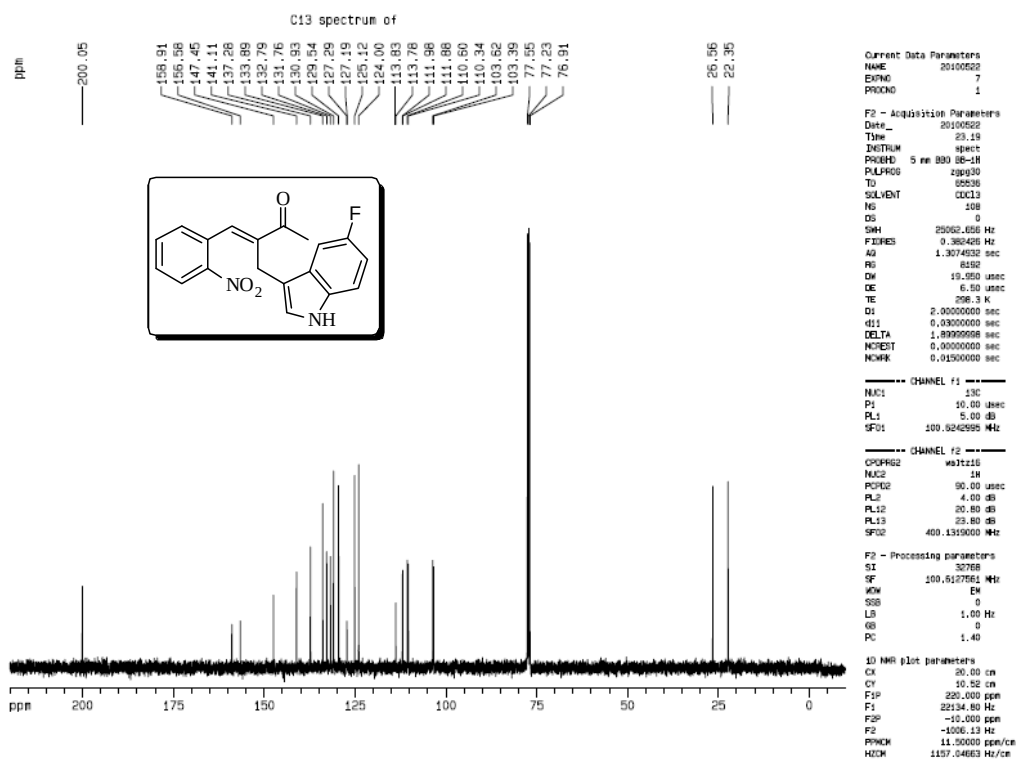
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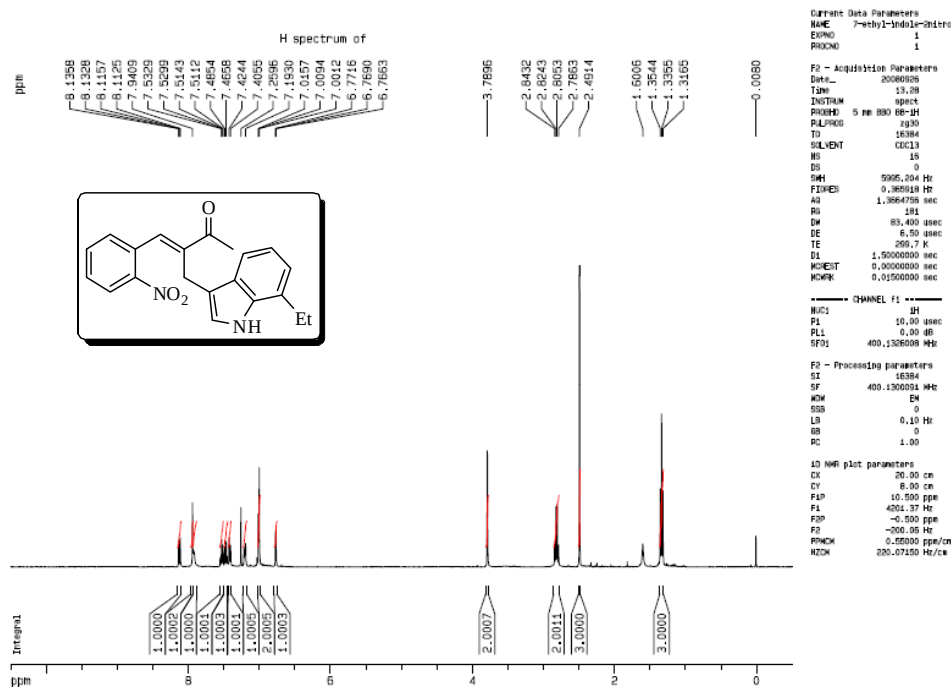
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(400MHz, CDCl_3)



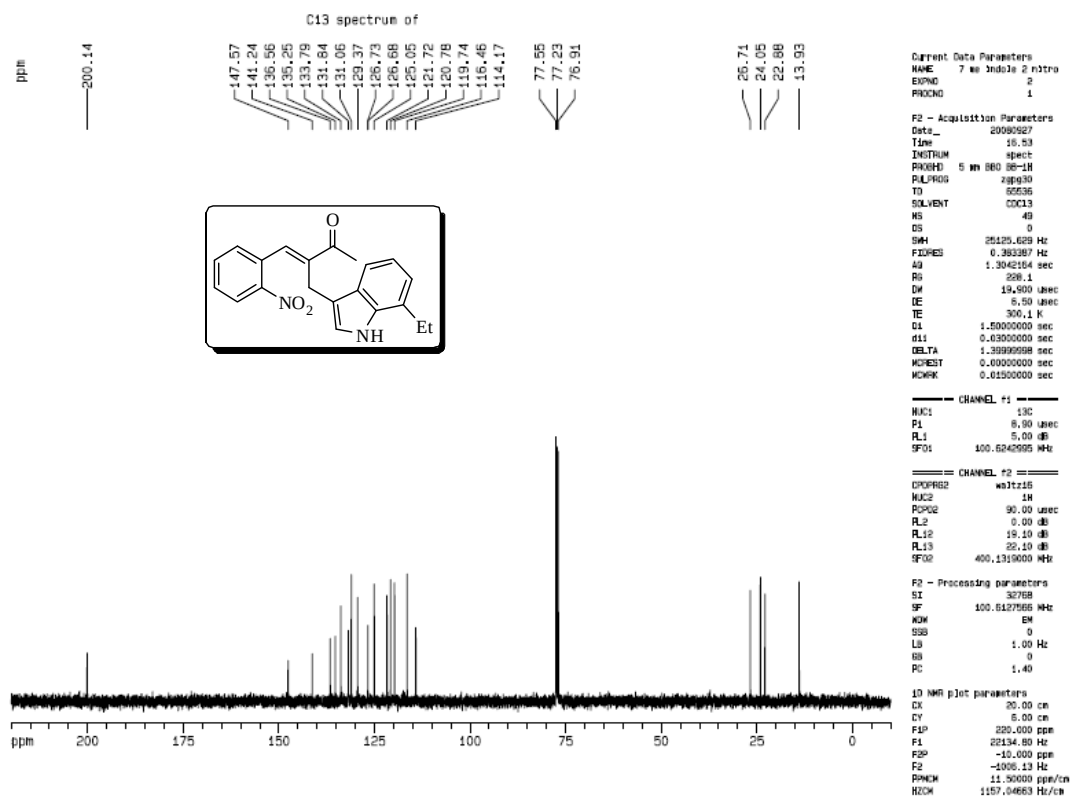
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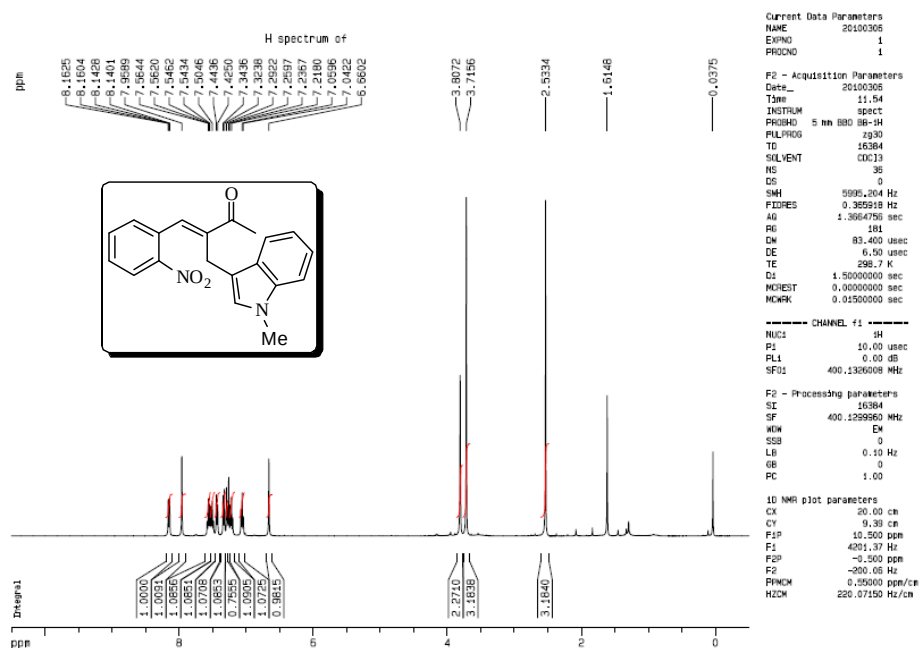
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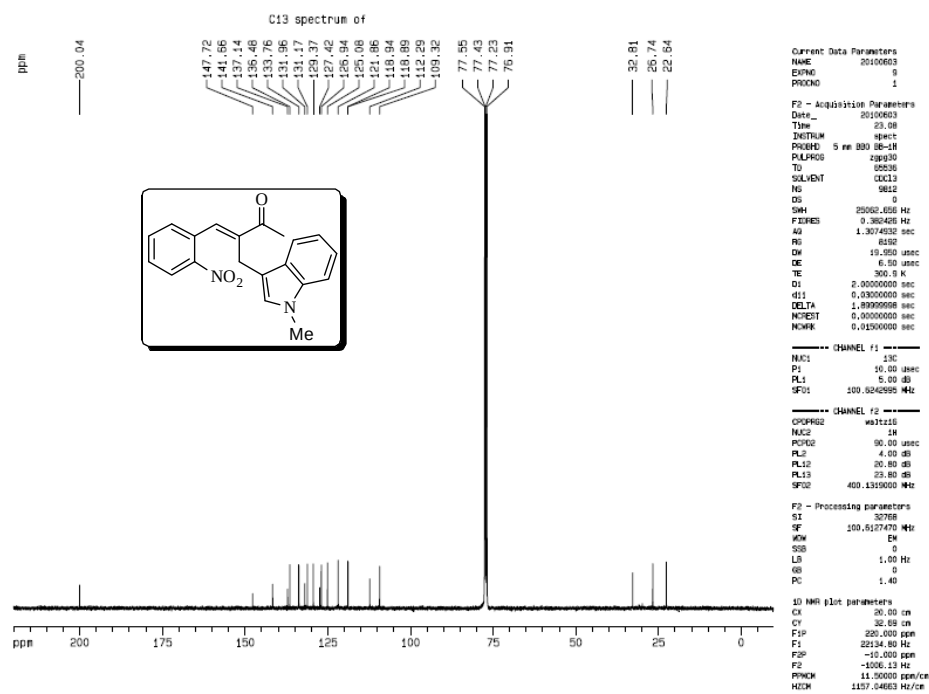
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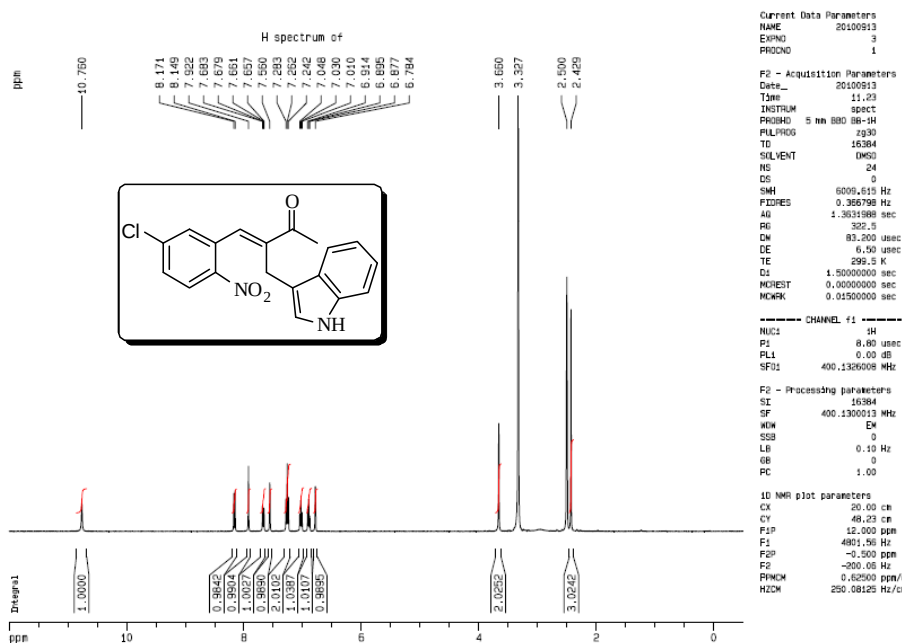
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(400MHz, CDCl_3)



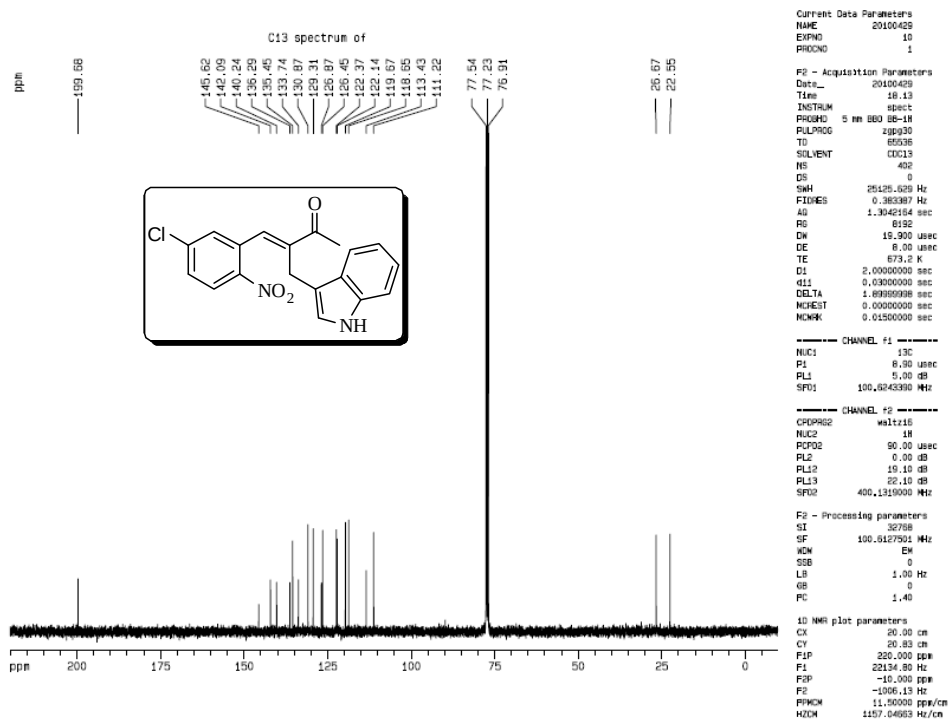
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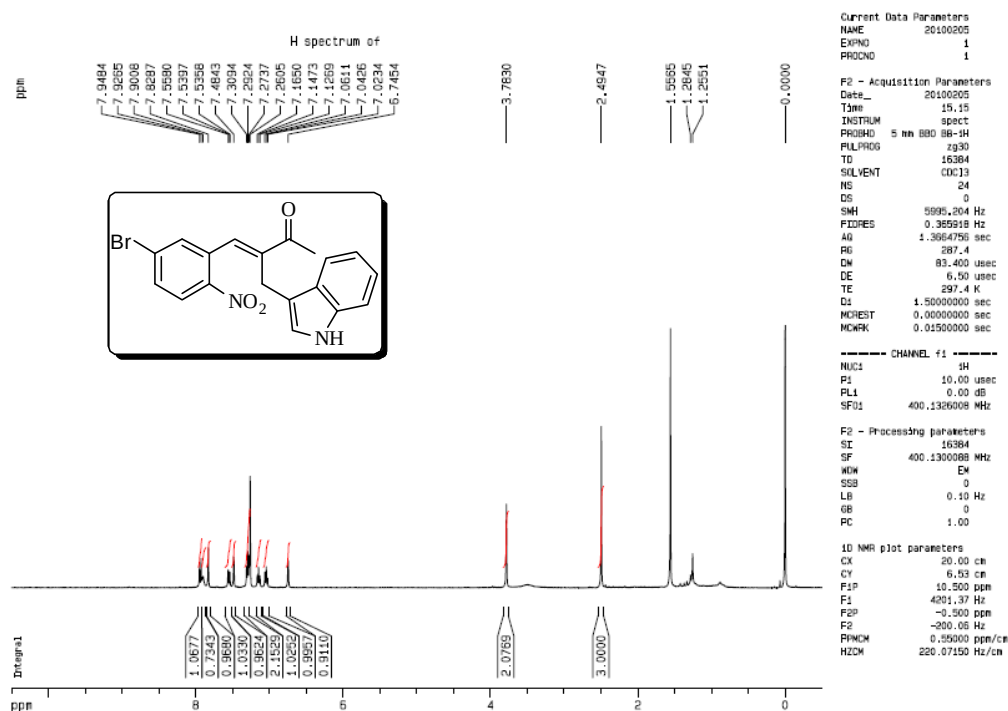
(E)-3-((1H-Indol-3-yl)methyl)-4-(5-chloro-2-nitrophenyl)but-3-en-2-one (3l). ^1H NMR
(400MHz, DMSO- d_6)



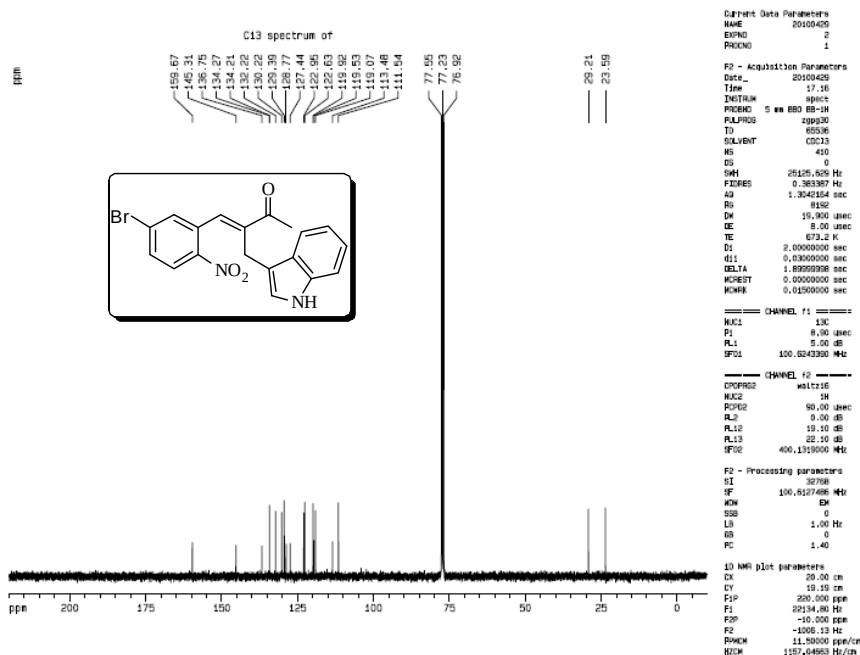
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(100MHz, CDCl_3)



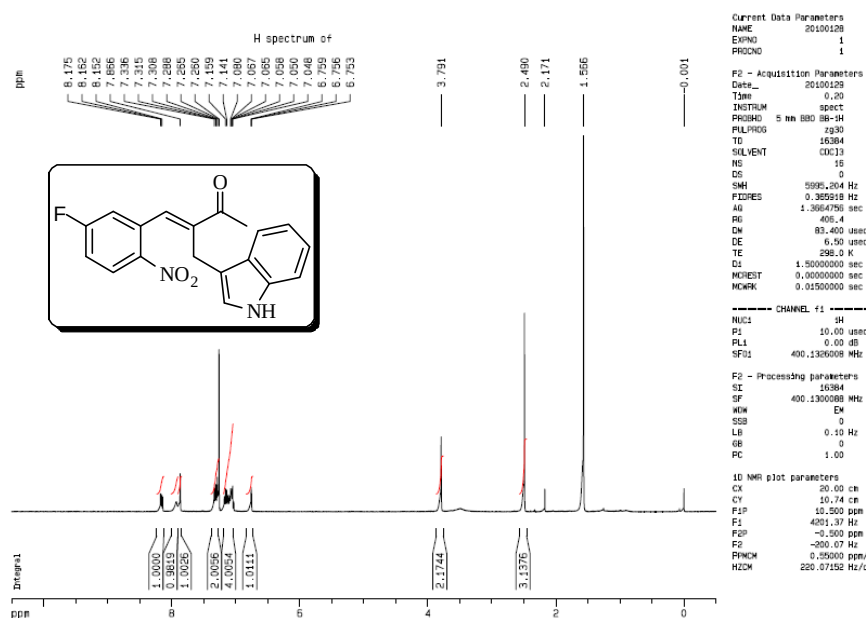
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(400MHz, CDCl_3)



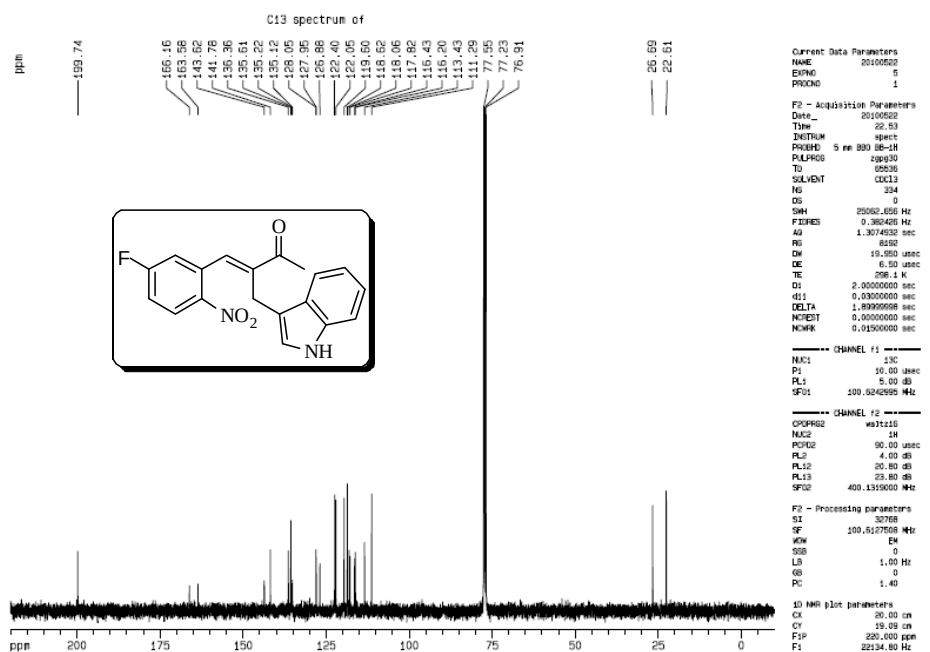
(E)-3-((1H-Indol-3-yl)methyl)-4-(5-bromo-2-nitrophenyl)but-3-en-2-one (3m). ^{13}C NMR
(100MHz, CDCl_3)



(E)-3-((1H-Indol-3-yl)methyl)-4-(5-fluoro-2-nitrophenyl)but-3-en-2-one (3n). ^1H NMR
(400MHz, CDCl_3)

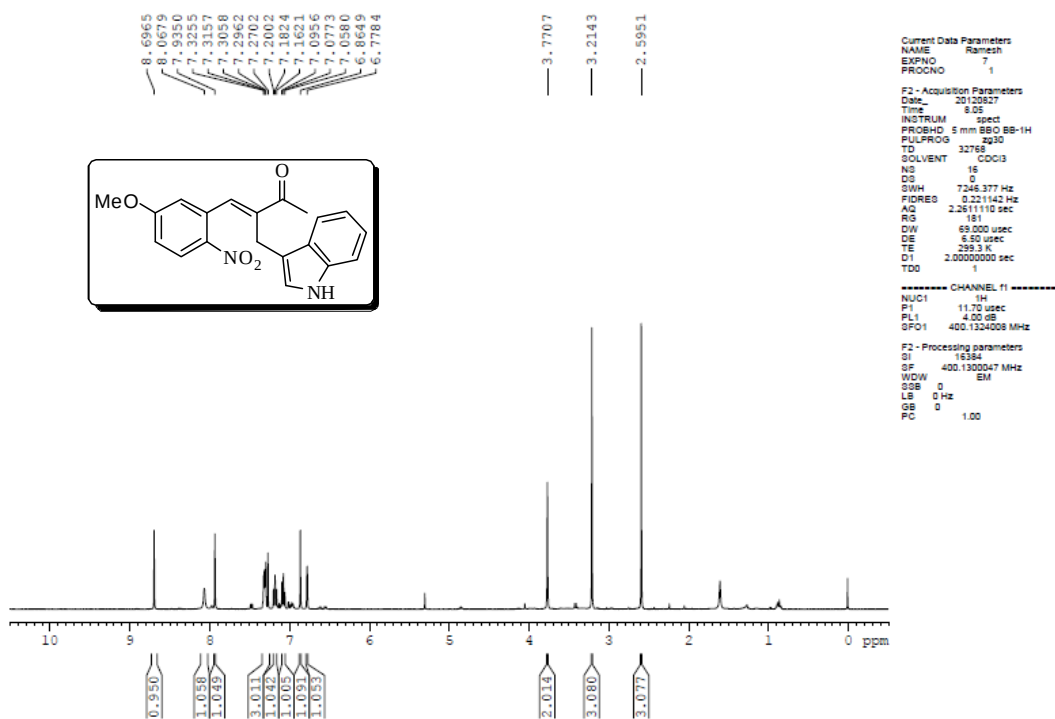


(E)-3-((1H-Indol-3-yl)methyl)-4-(5-fluoro-2-nitrophenyl)but-3-en-2-one (3n). ^{13}C NMR
(100MHz, CDCl_3)



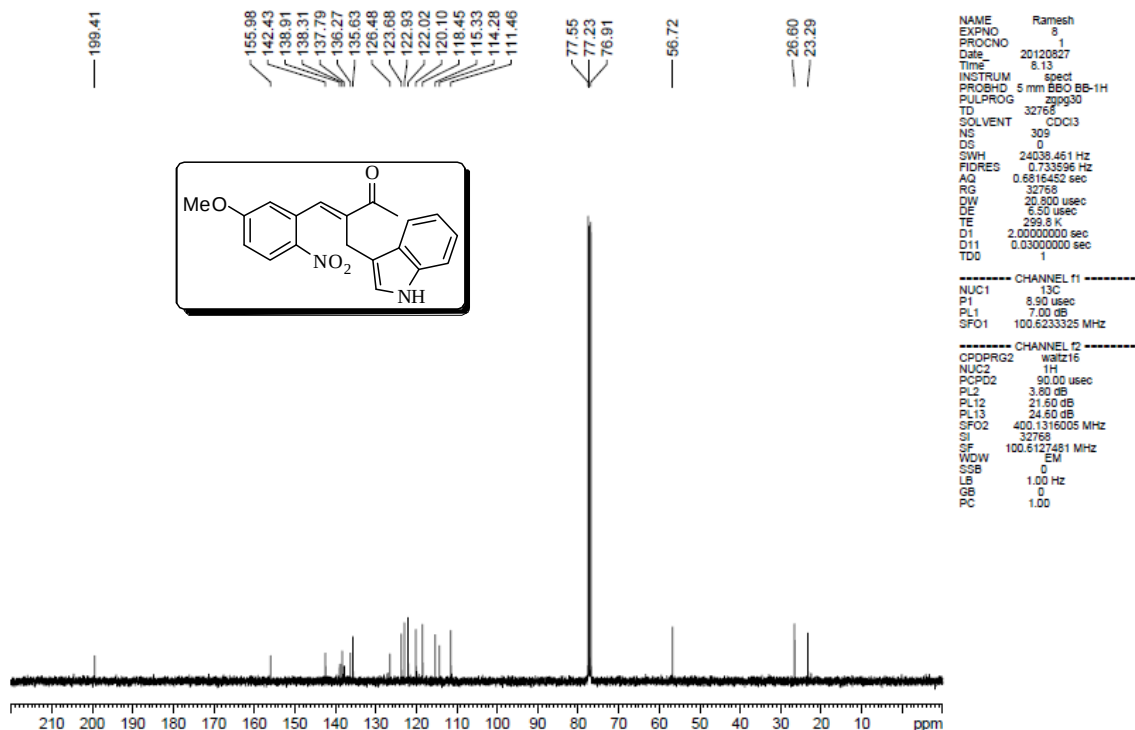
(E)-3-((1H-indol-3-yl)methyl)-4-(5-methoxy-2-nitrophenyl)but-3-en-2-one (3o).

¹H NMR (400MHz, CDCl₃)



(E)-3-((1H-indol-3-yl)methyl)-4-(5-methoxy-2-nitrophenyl)but-3-en-2-one (3o).

¹³C NMR (100MHz, CDCl₃)



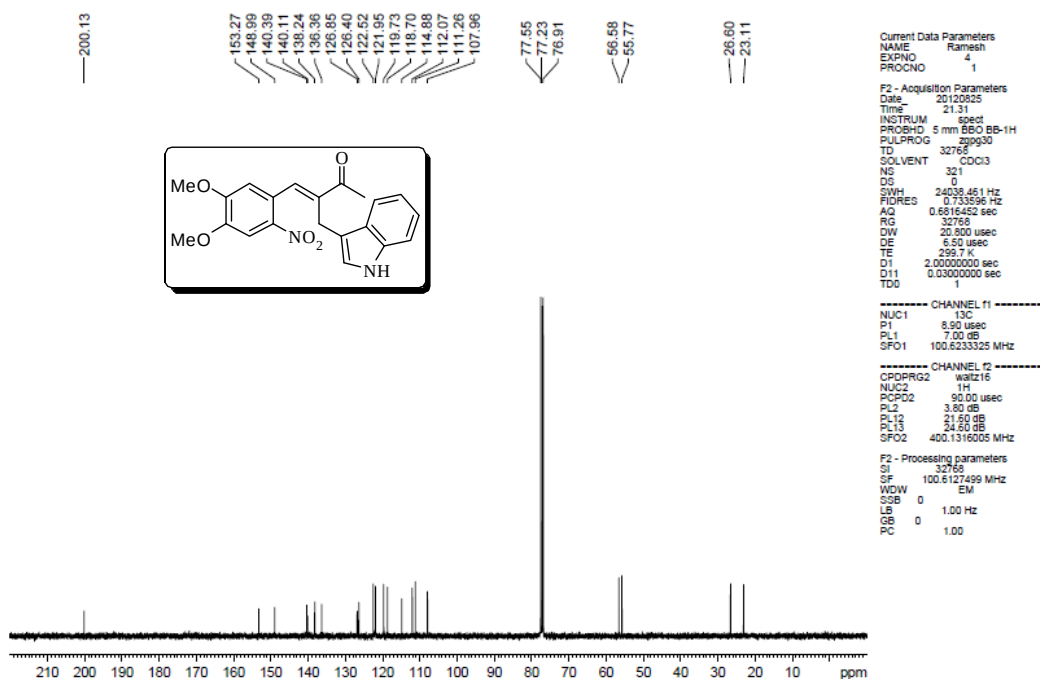
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¹H NMR (400MHz, CDCl₃)

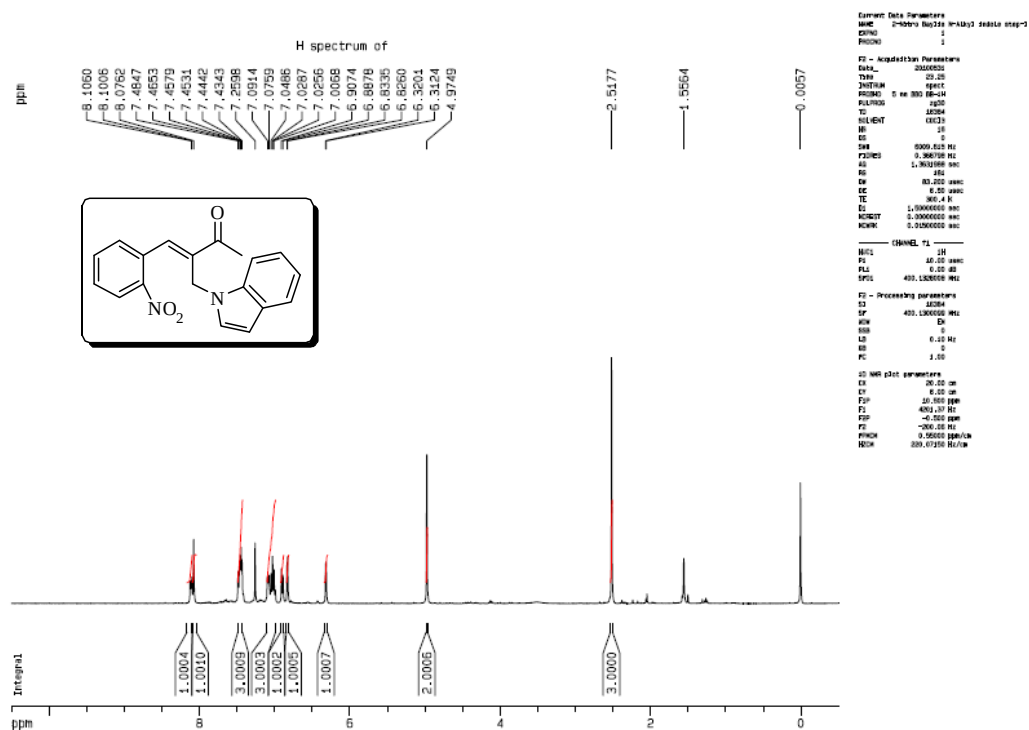


(E)-3-((1H-indol-3-yl)methyl)-4-(4,5-dimethoxy-2-nitrophenyl)but-3-en-2-one (3p).

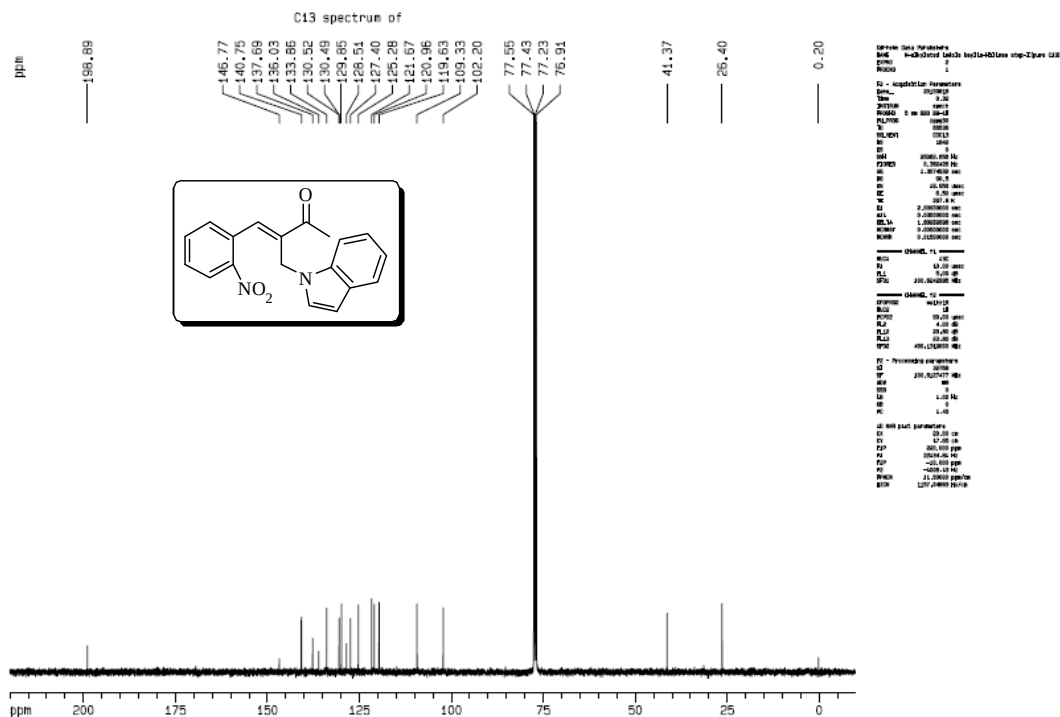
¹³C NMR (100MHz, CDCl₃)



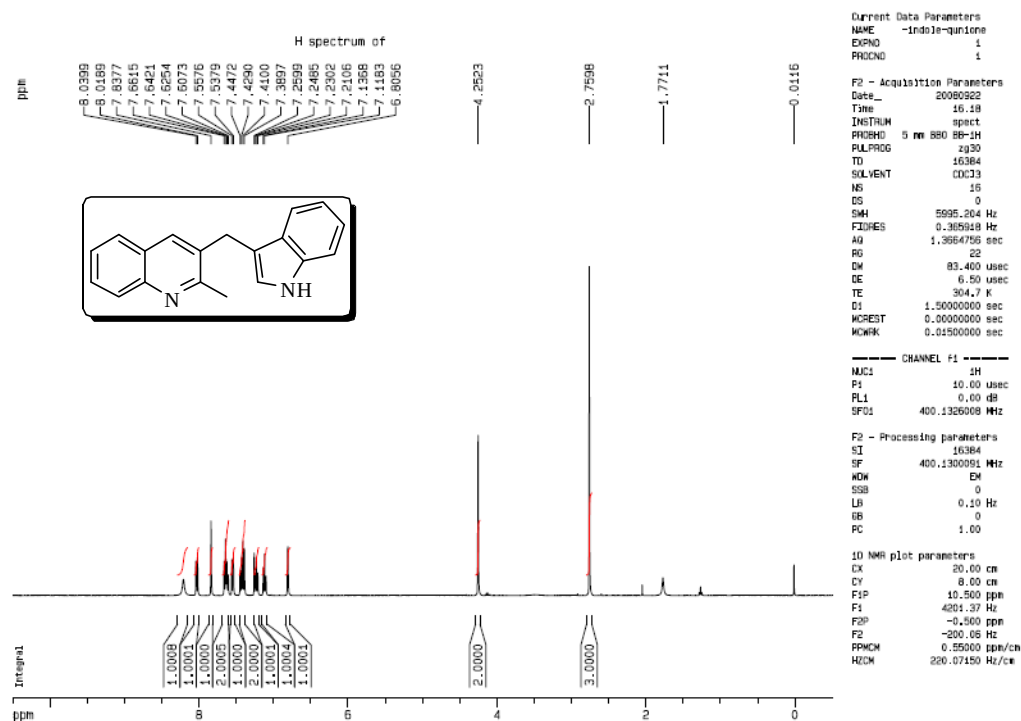
(*E*)-3-((1*H*-Indol-1-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (3q). ¹H NMR (400MHz, CDCl₃)



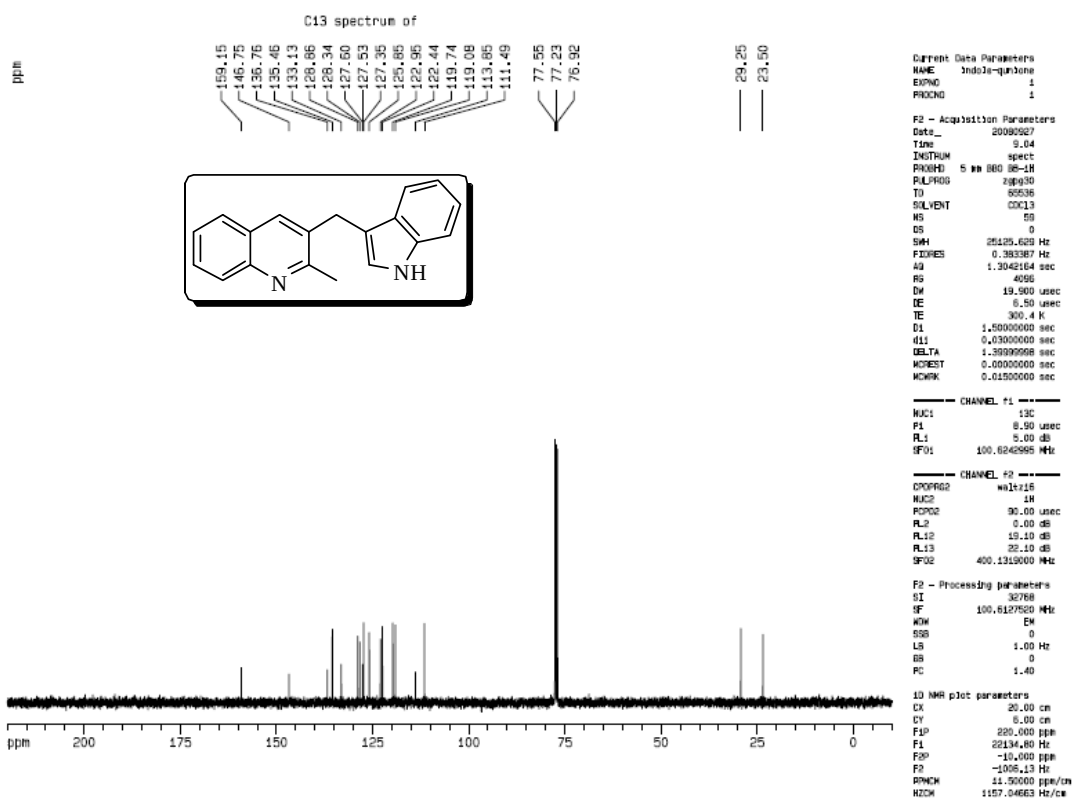
(*E*)-3-((1*H*-Indol-1-yl)methyl)-4-(2-nitrophenyl)but-3-en-2-one (3q). ¹³C NMR (100 MHz, CDCl₃)



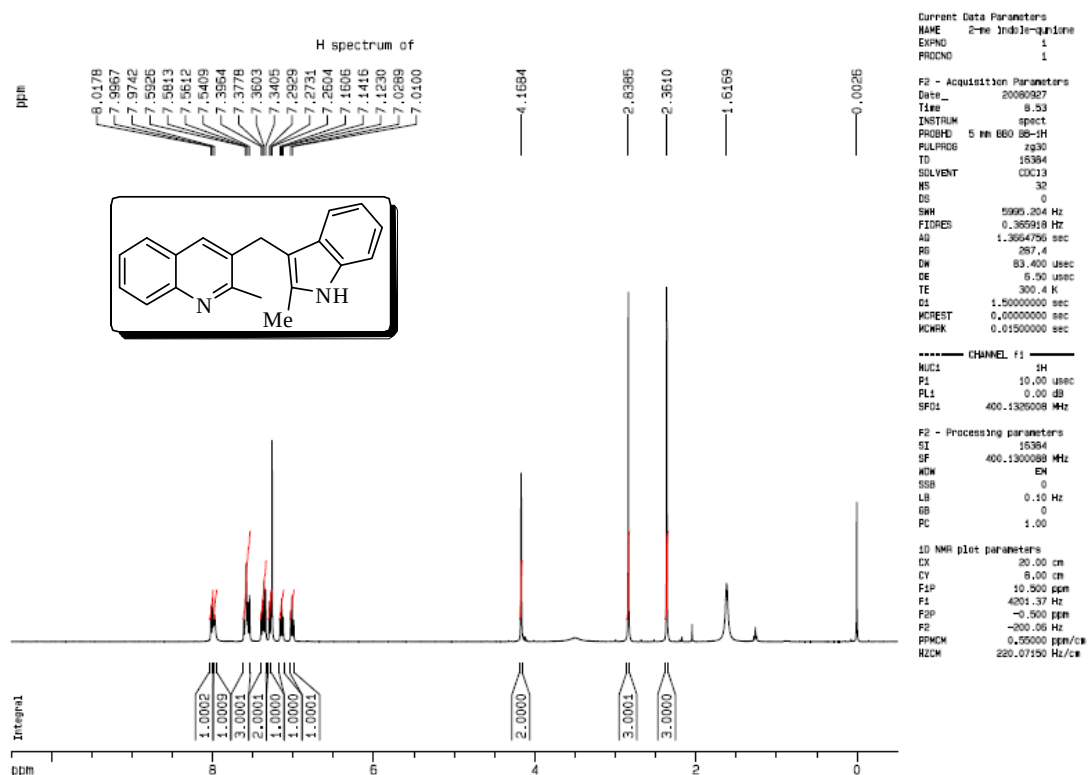
3-((1*H*-Indol-3-yl)methyl)-2-methylquinoline (3ab). ¹H NMR (400MHz, CDCl₃)



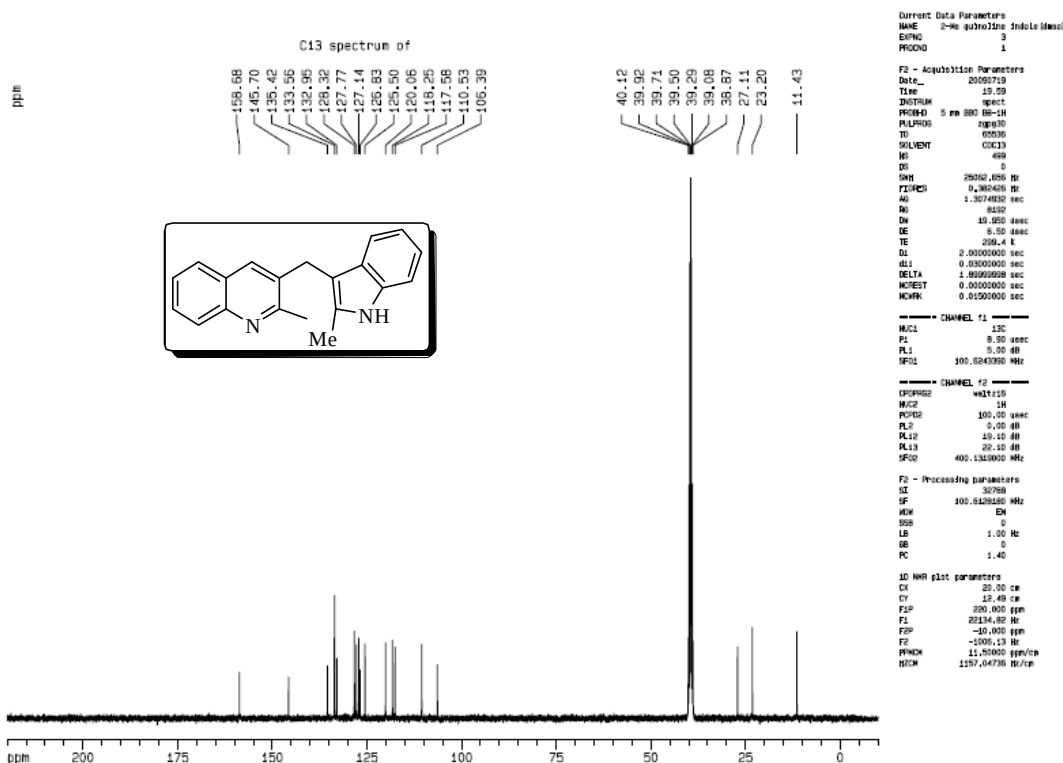
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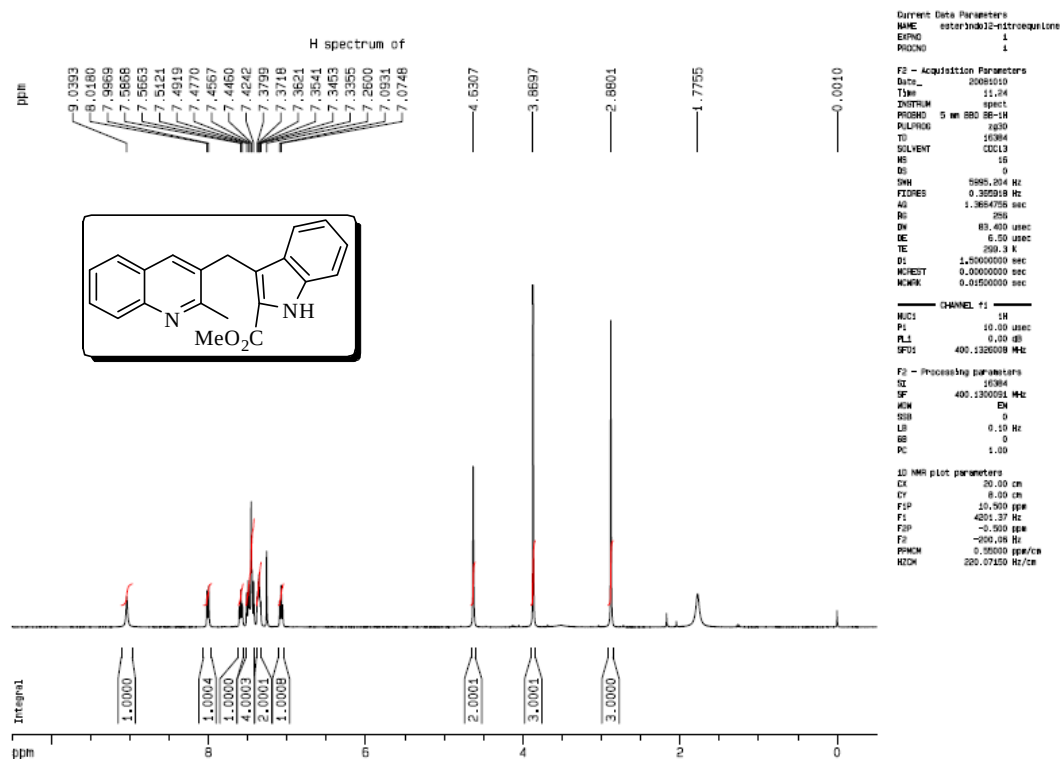
2-Methyl-3-((2-methyl-1H-indol-3-yl)methyl) quinoline (3bb). ^1H NMR (400 MHz, CDCl_3)



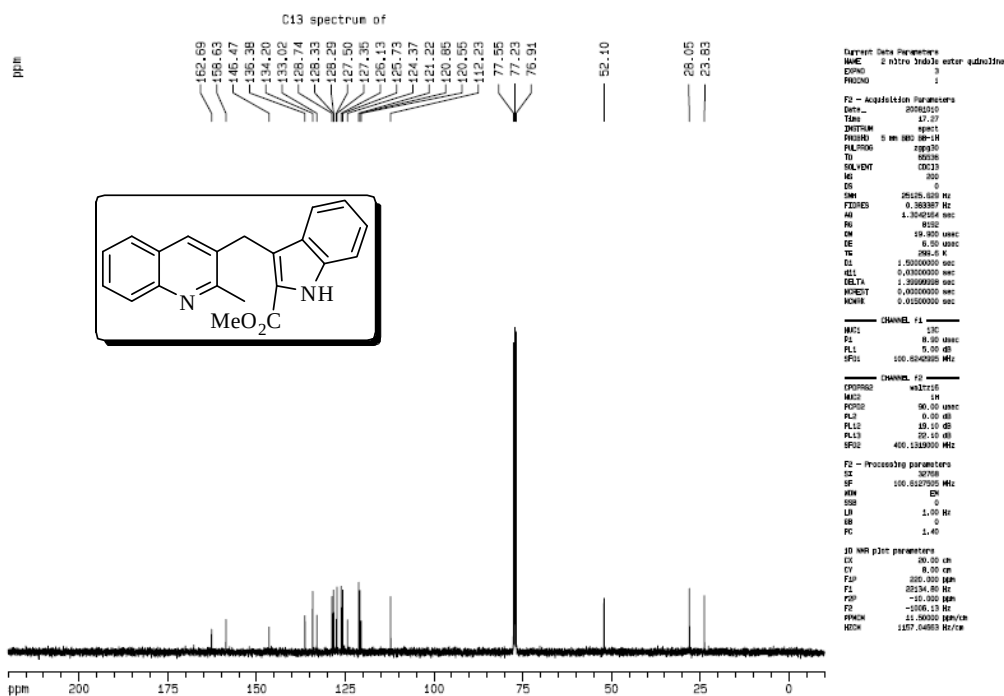
2-Methyl-3-((2-methyl-1H-indol-3-yl)methyl) quinoline (3bb). ^{13}C NMR (100 MHz, CDCl_3)



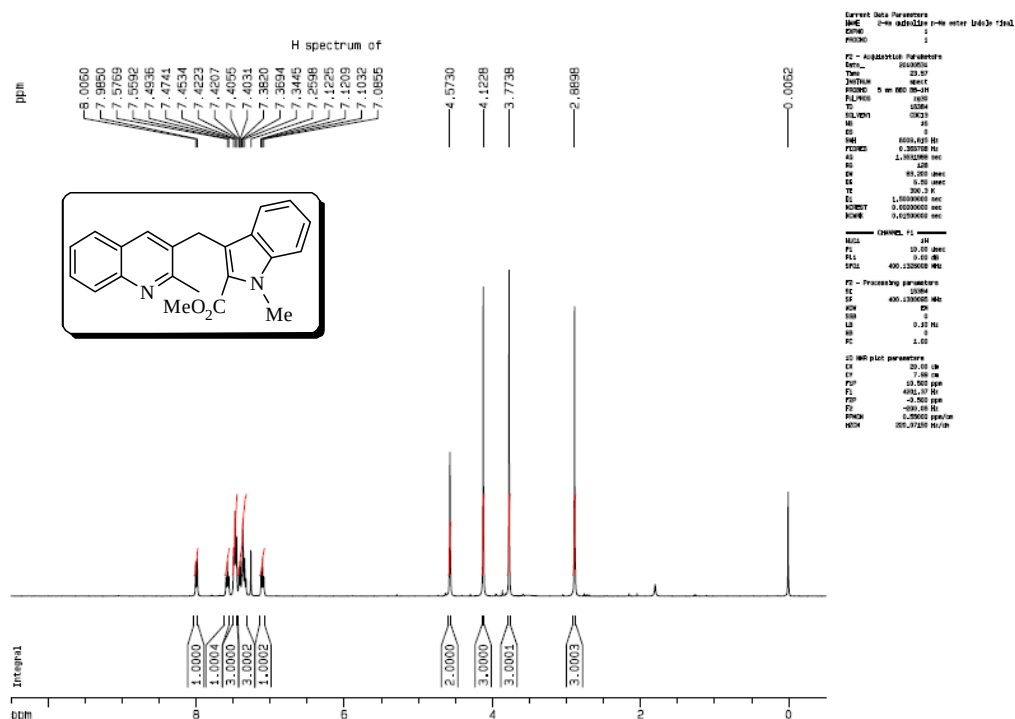
Methyl 3-((2-methylquinolin-3-yl)methyl)-1H-indole-2-carboxylate (3cb). ^1H NMR (400MHz, CDCl_3)



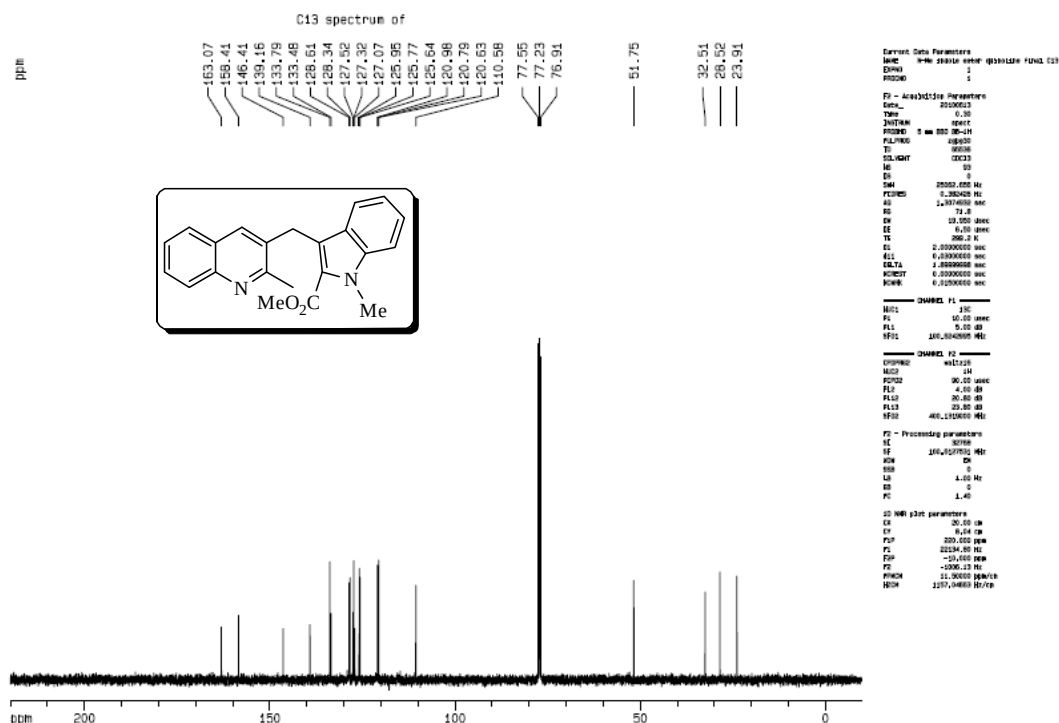
Methyl 3-((2-methylquinolin-3-yl)methyl)-1H-indole-2-carboxylate (3cb). ^{13}C NMR (100 MHz, CDCl_3)



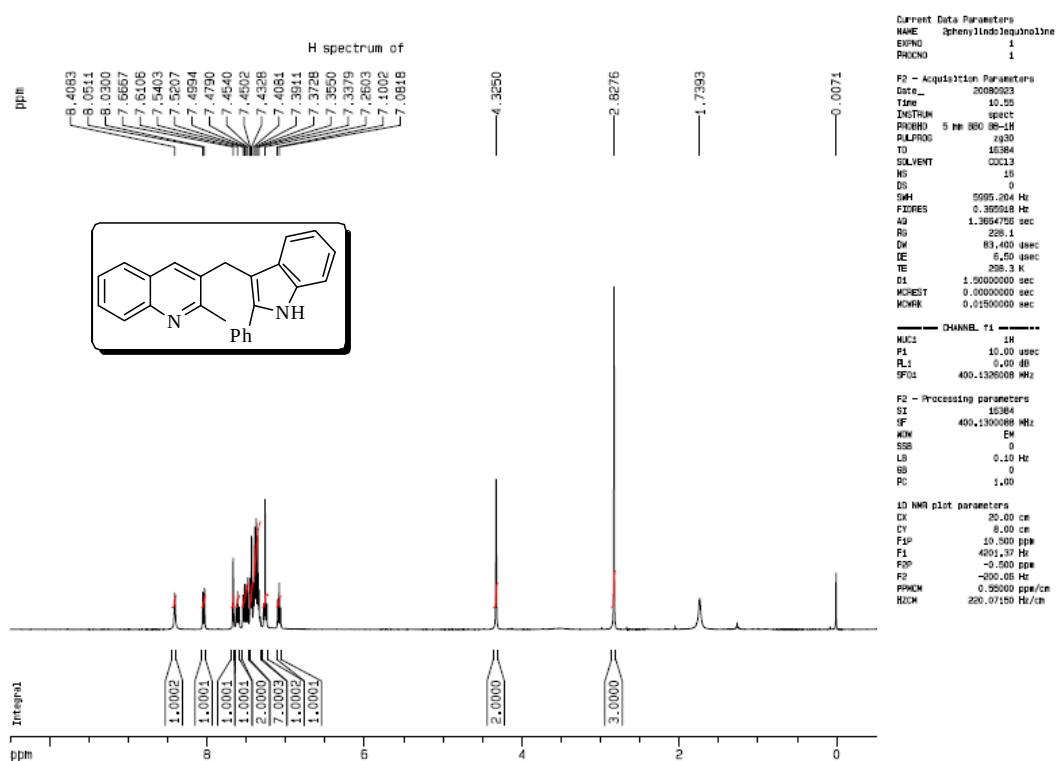
Methyl 1-methyl-3-((2-methylquinolin-3-yl)methyl)-1H-indole-2-carboxylate (3db). ¹H NMR (400MHz, CDCl₃)



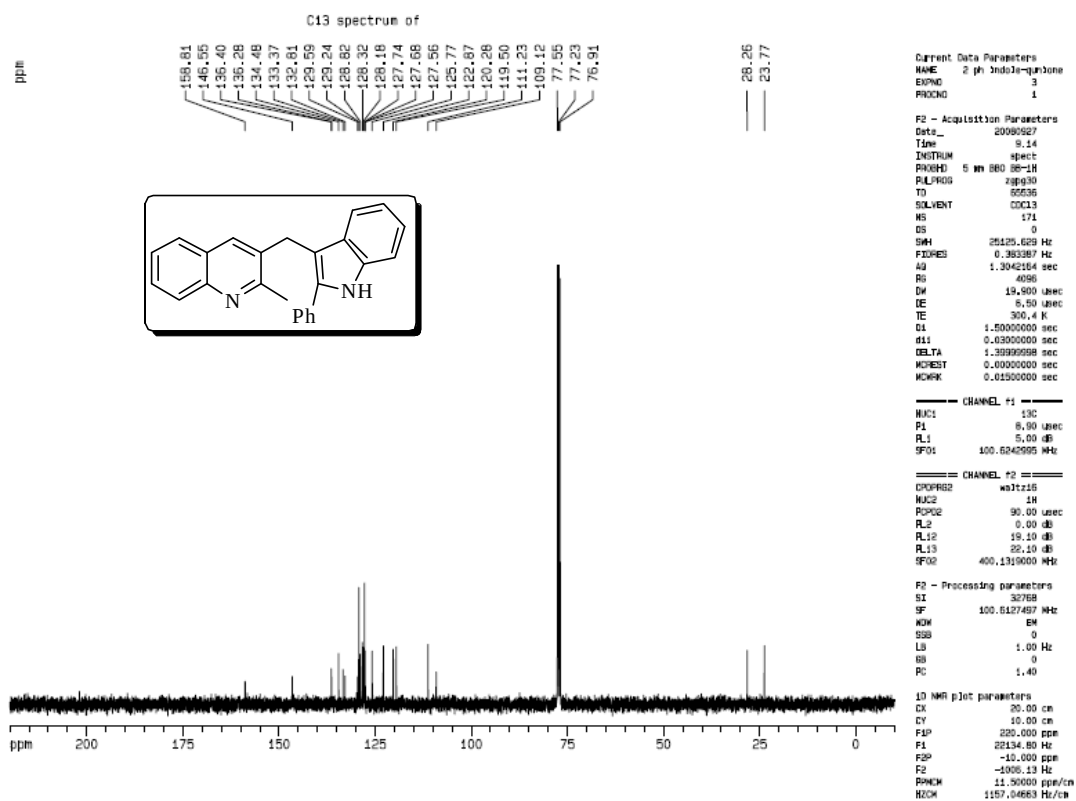
Methyl 1-methyl-3-((2-methylquinolin-3-yl)methyl)-1H-indole-2-carboxylate (3db). ¹³C NMR (100 MHz, CDCl₃)



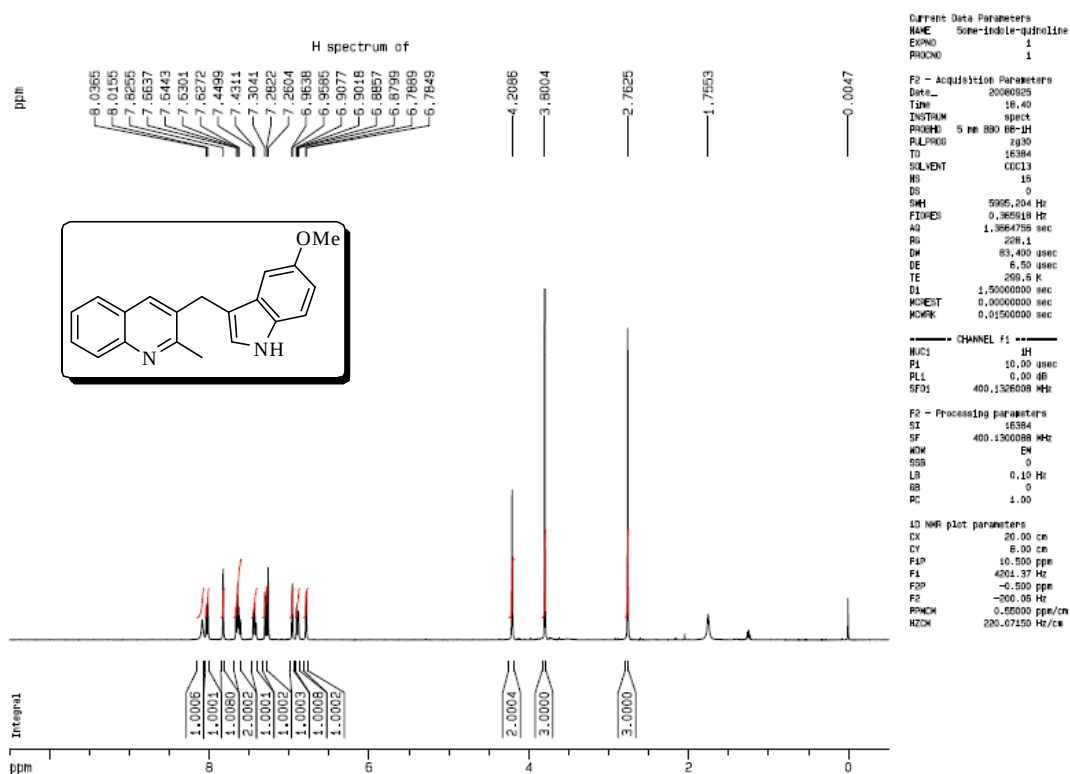
2-Methyl-3-((2-phenyl-1H-indol-3-yl)methyl)quinoline (3eb). ^1H NMR (400MHz, CDCl_3)



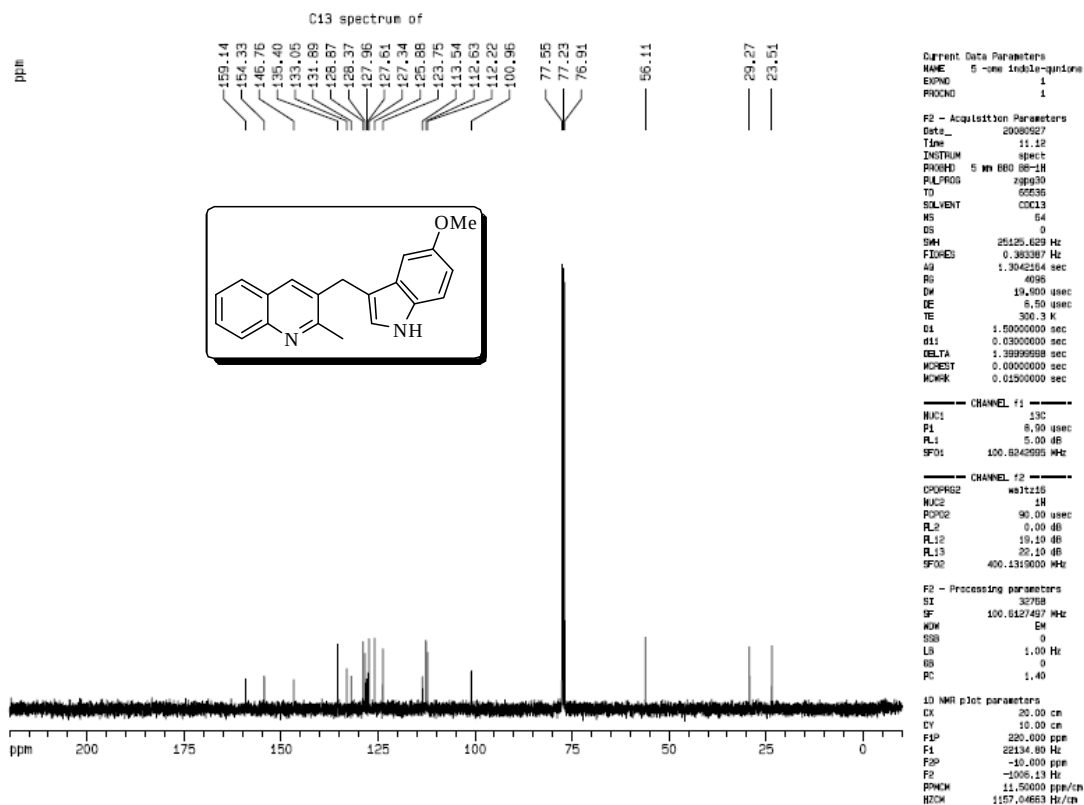
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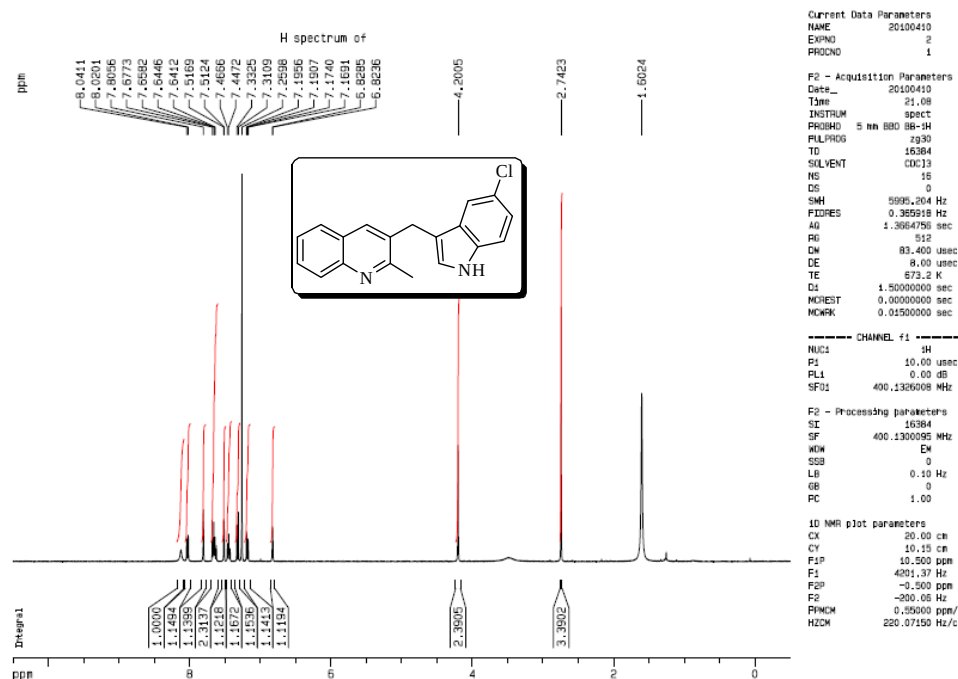
3-((5-Methoxy-1*H*-indol-3-yl)methyl)-2-methylquinoline (3fb). ¹H NMR (400MHz, CDCl₃)



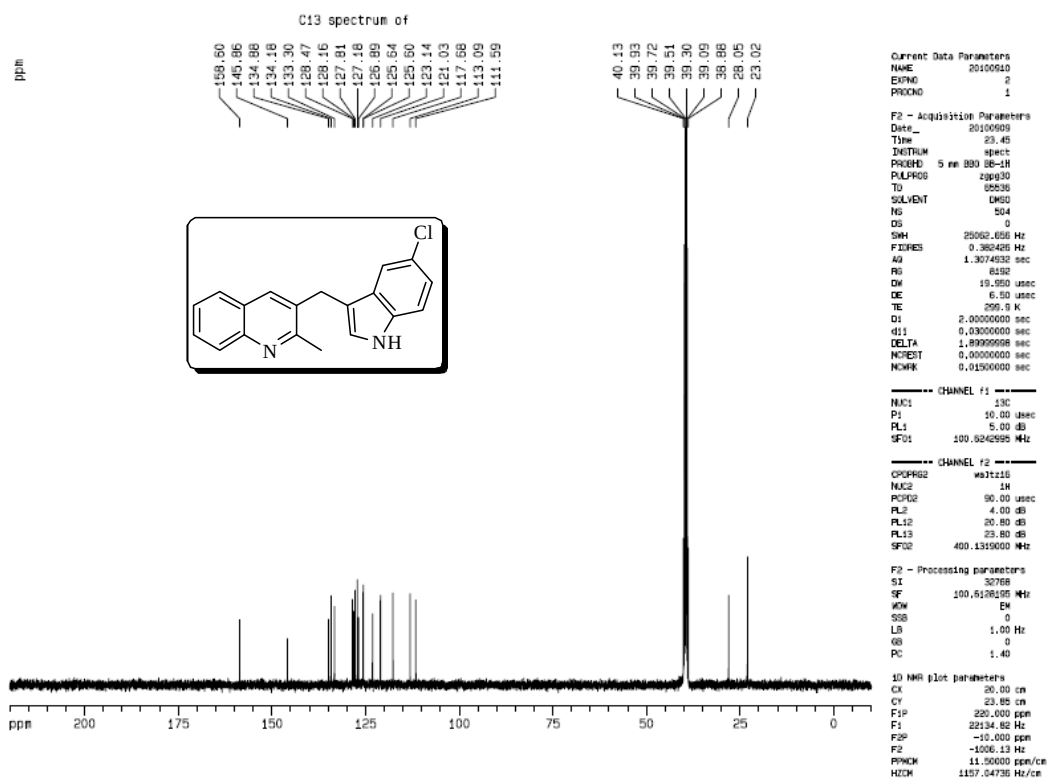
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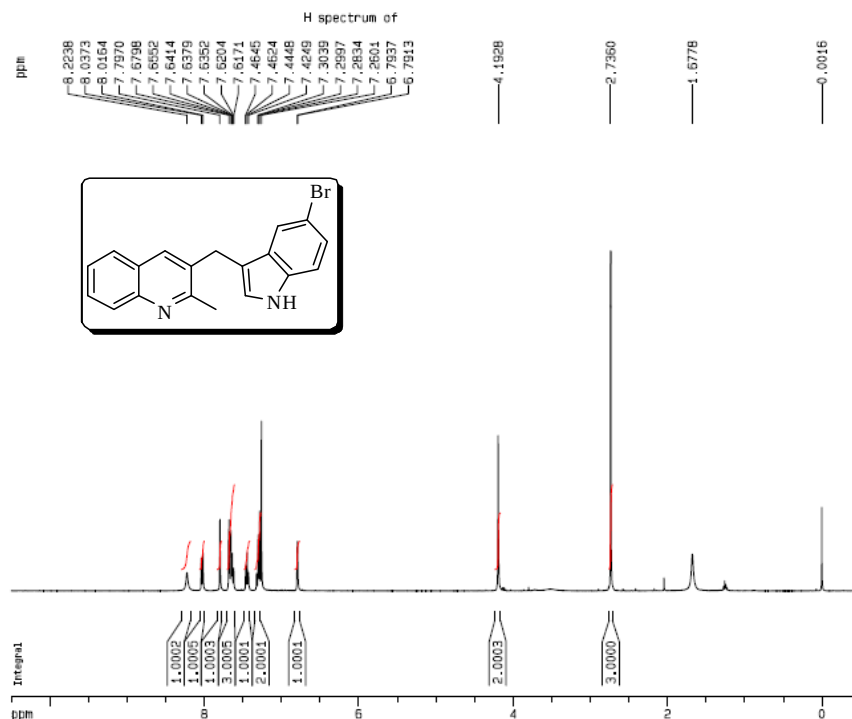
3-((5-Chloro-1*H*-indol-3-yl)methyl)-2-methylquinoline (3gb). ¹H NMR (400MHz, CDCl₃)



3-((5-Chloro-1*H*-indol-3-yl)methyl)-2-methylquinoline (3gb). ¹³C NMR(100MHz, CDCl₃)



3-((5-Bromo-1*H*-indol-3-yl)methyl)-2-methyl quinoline (3hb). ¹H NMR (400MHz, CDCl₃)



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PROCNO 1

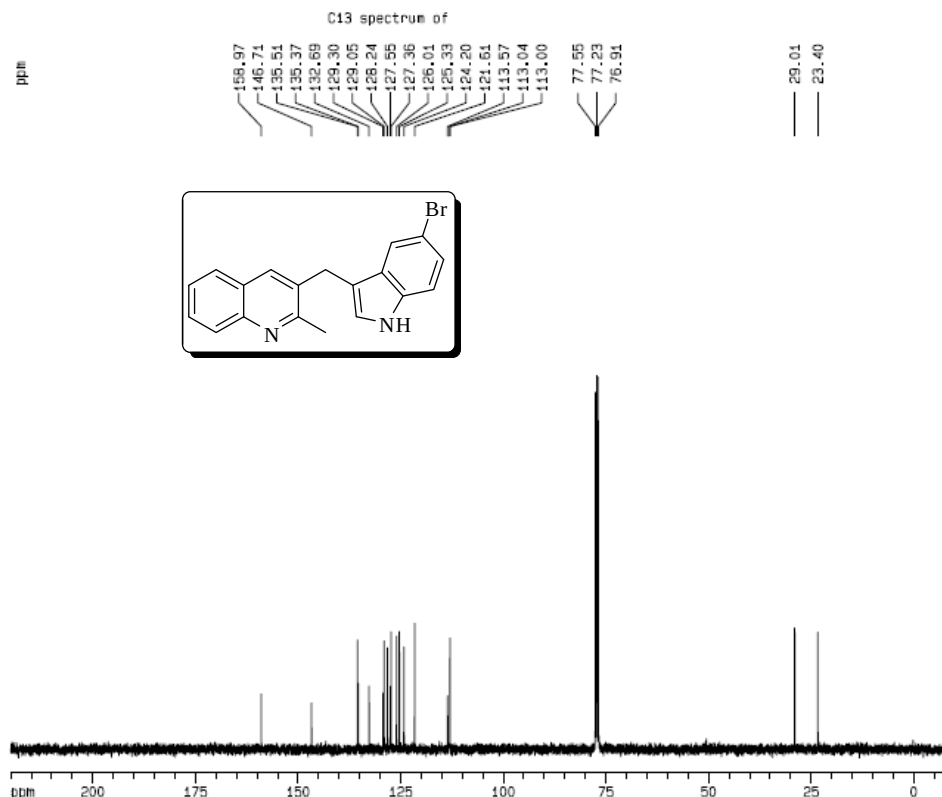
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DE 6.50 usec
TE 299.7 K
D1 1.50000000 sec
MCHST 0.00000000 sec
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PL1 0.00 dB
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3-((5-Bromo-1*H*-indol-3-yl)methyl)-2-methyl quinoline (3hb). ¹³C NMR (100 MHz, CDCl₃)



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EXPNO 2
PROCNO 1

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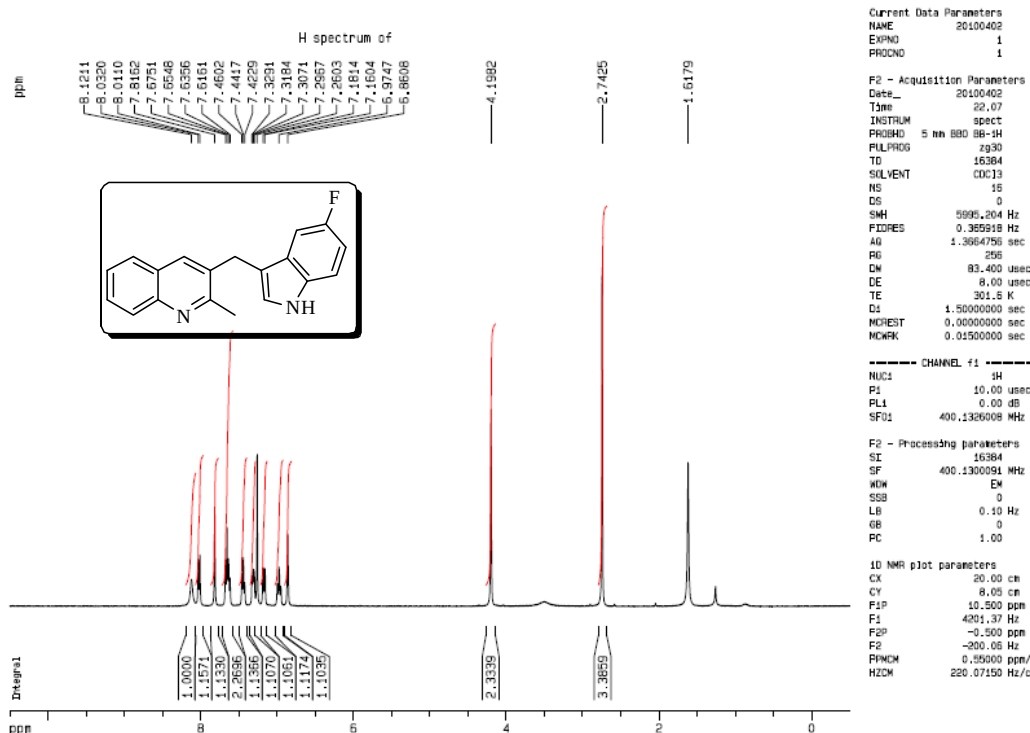
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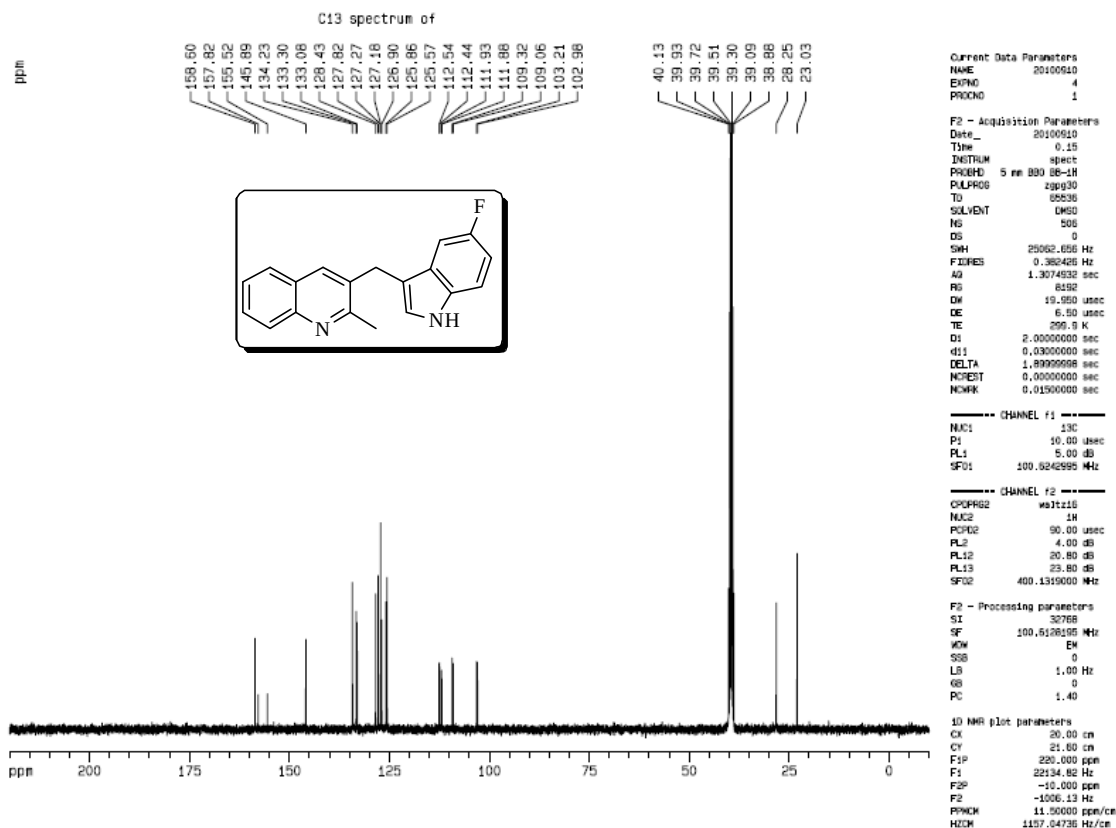
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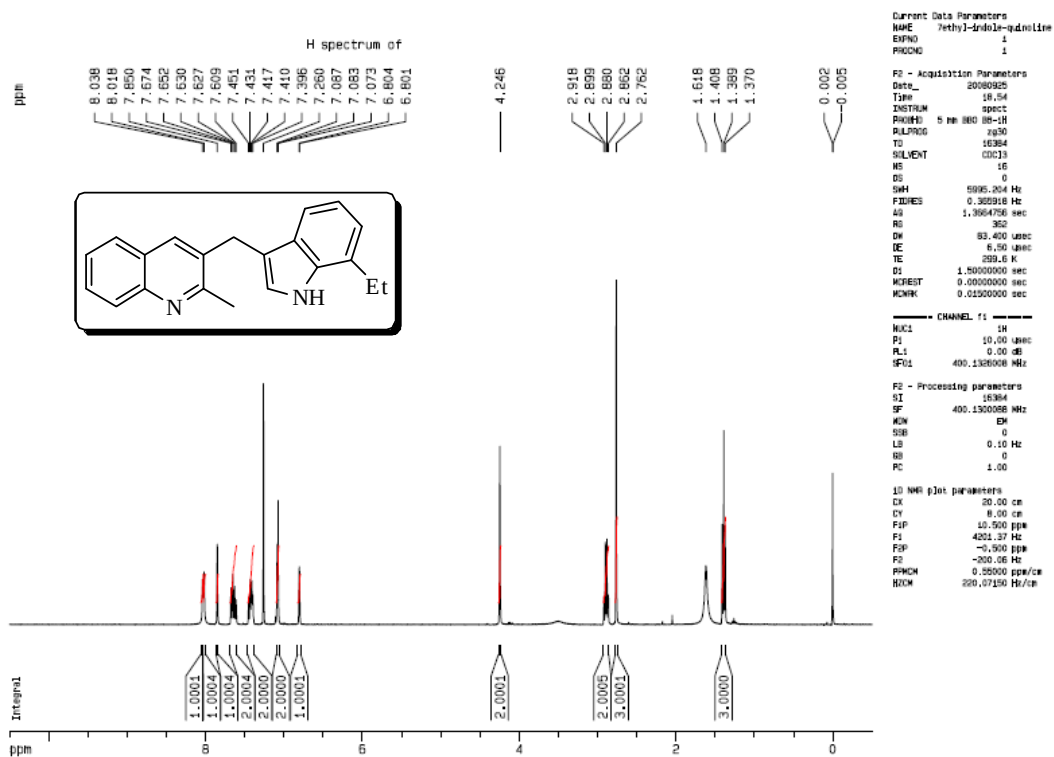
3-((5-Fluoro-1H-indol-3-yl)methyl)-2-methylquinoline(3ib). ¹H NMR (400MHz, CDCl₃)



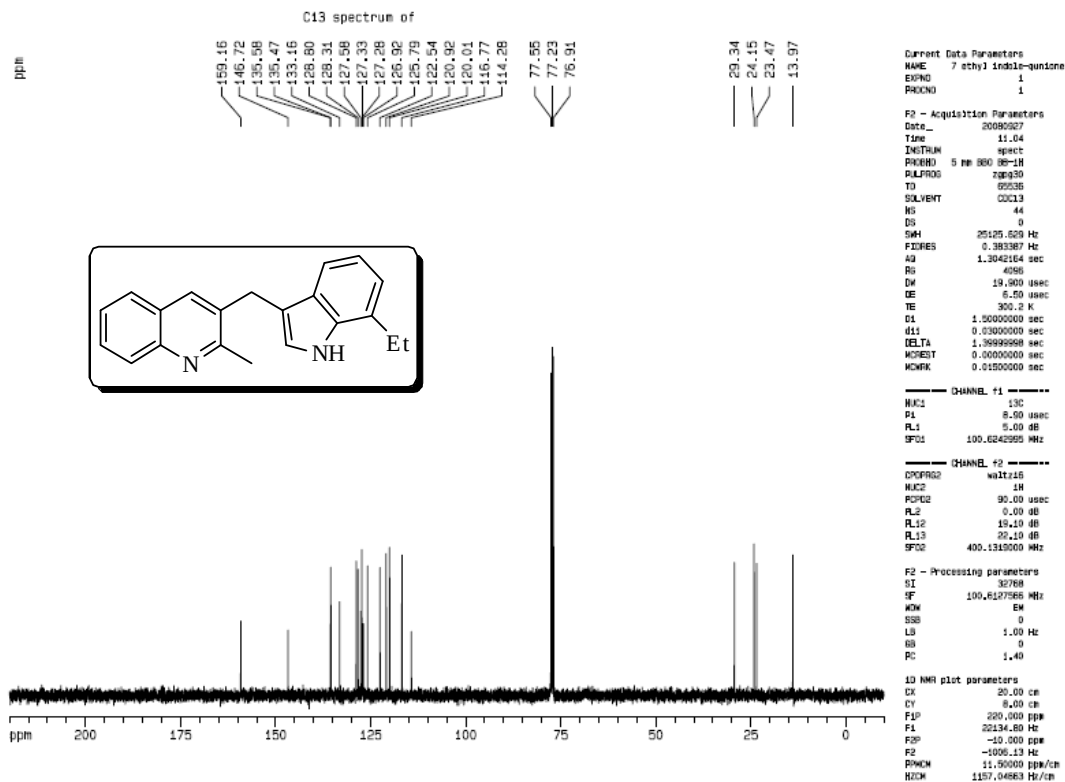
3-((5-Fluoro-1H-indol-3-yl)methyl)-2-methylquinoline(3ib). ¹³C NMR (100 MHz, CDCl₃)



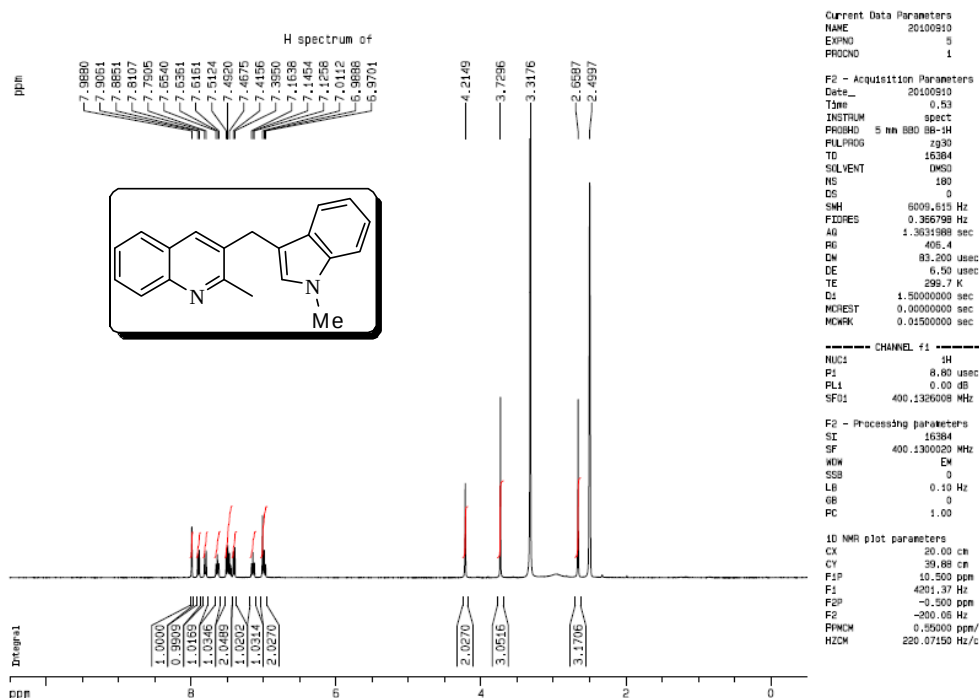
3-((7-Ethyl-1H-indol-3-yl)methyl)-2-methylquinoline (3jb). ^1H NMR (400MHz, CDCl_3)



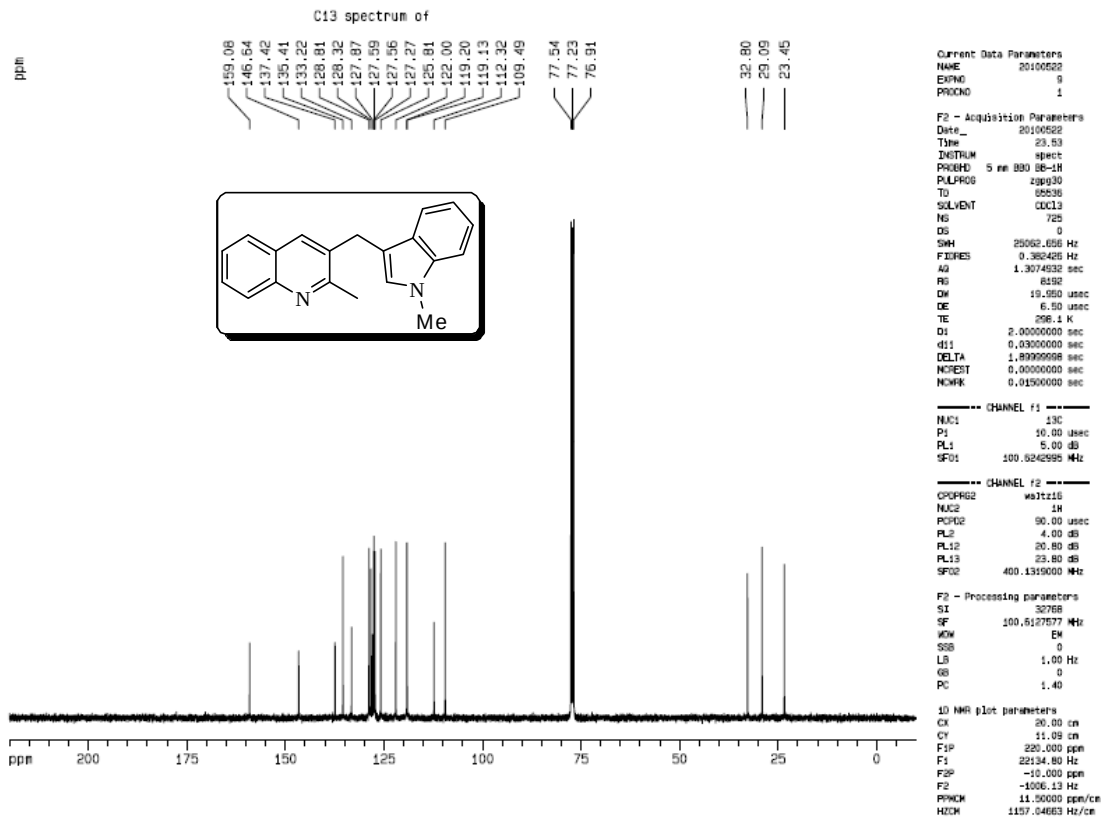
3-((7-Ethyl-1H-indol-3-yl)methyl)-2-methylquinoline (3jb). ^{13}C NMR (100 MHz, CDCl_3)



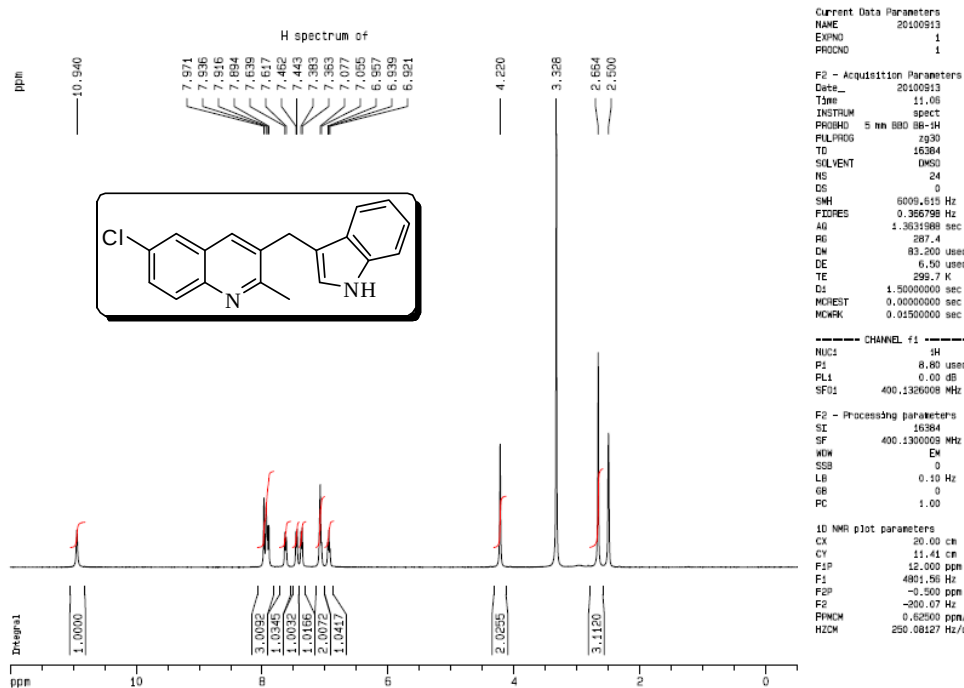
2-Methyl-3-((1-methyl-1H-indol-3-yl)methyl)quinoline (3kb). ^1H NMR (400MHz, $\text{DMSO}-d_6$)



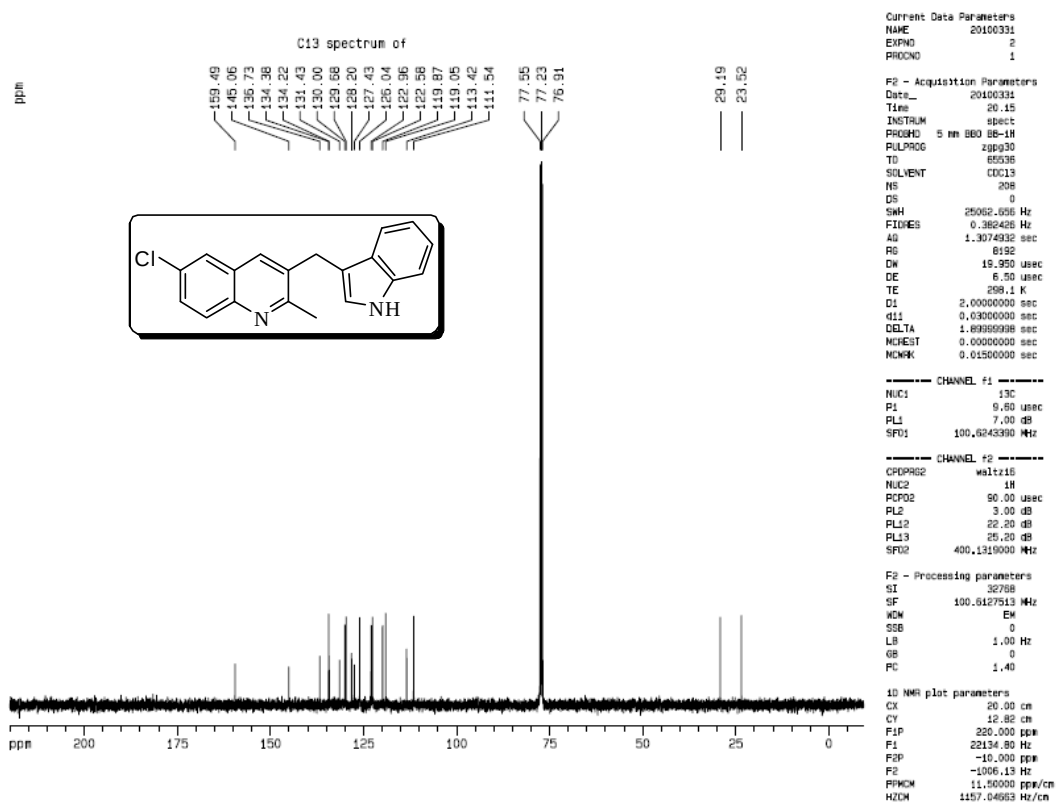
2-Methyl-3-((1-methyl-1H-indol-3-yl)methyl)quinoline (3kb). ^{13}C NMR (100 MHz, CDCl_3)



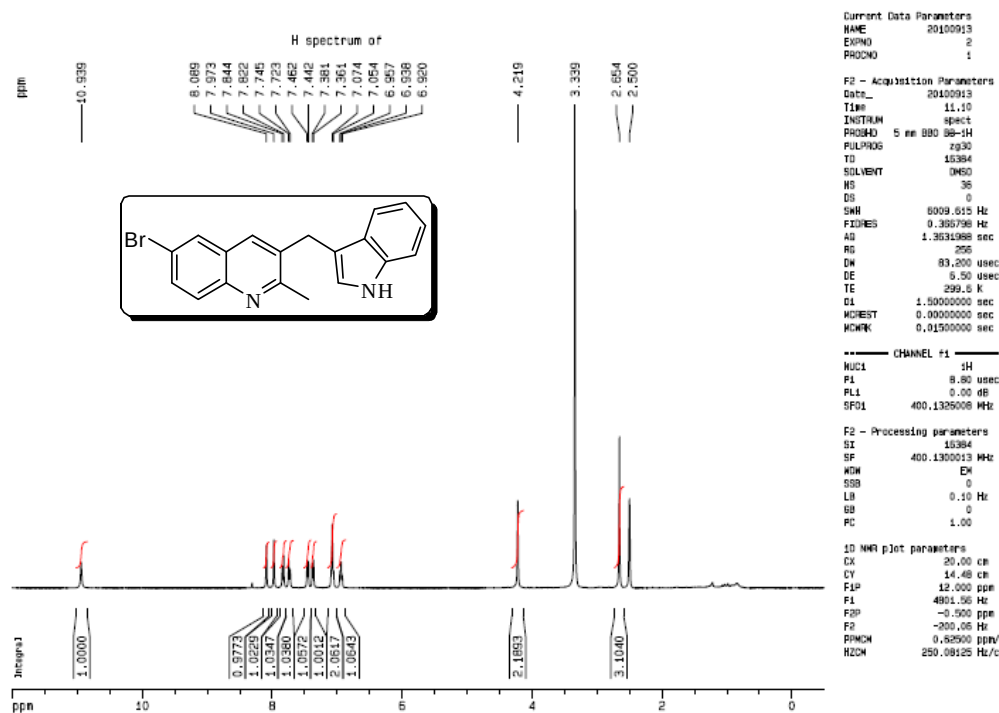
3-((1*H*-Indol-3-yl)methyl)-6-chloro-2-methylquinoline (3lb). ¹H NMR (400MHz, CDCl₃)



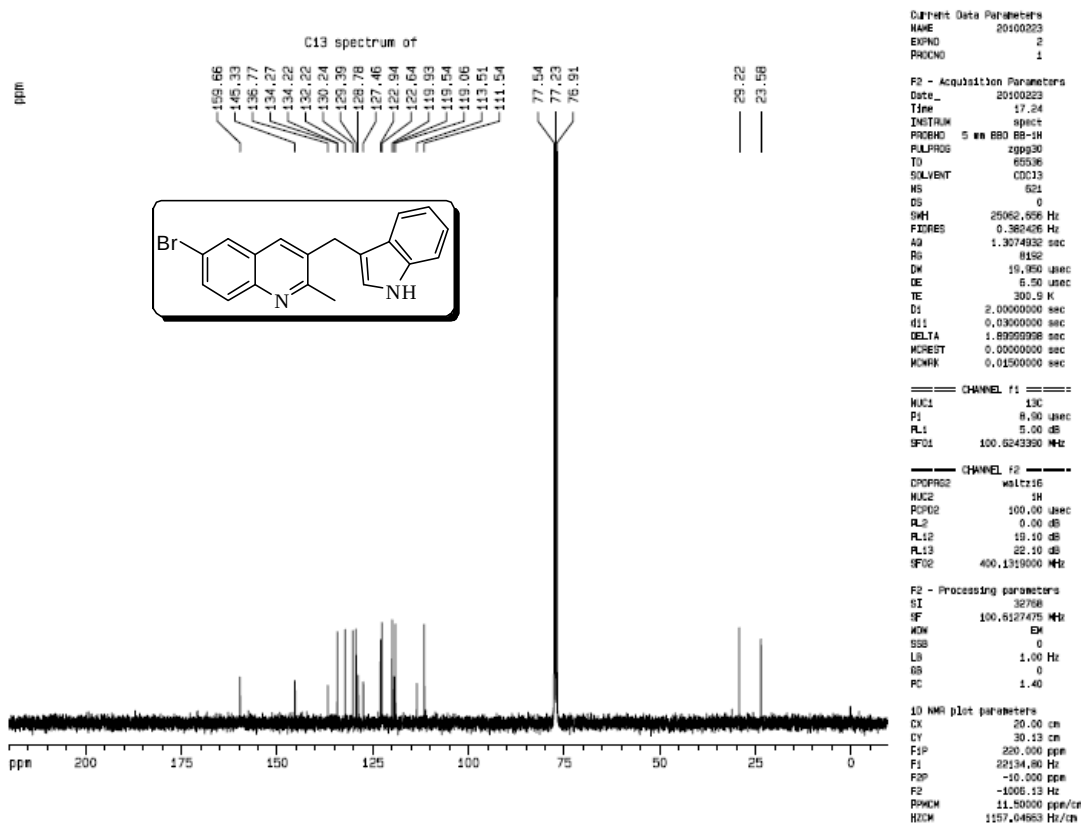
3-((1*H*-Indol-3-yl)methyl)-6-chloro-2-methylquinoline (3lb). ¹³C NMR (100 MHz, CDCl₃)



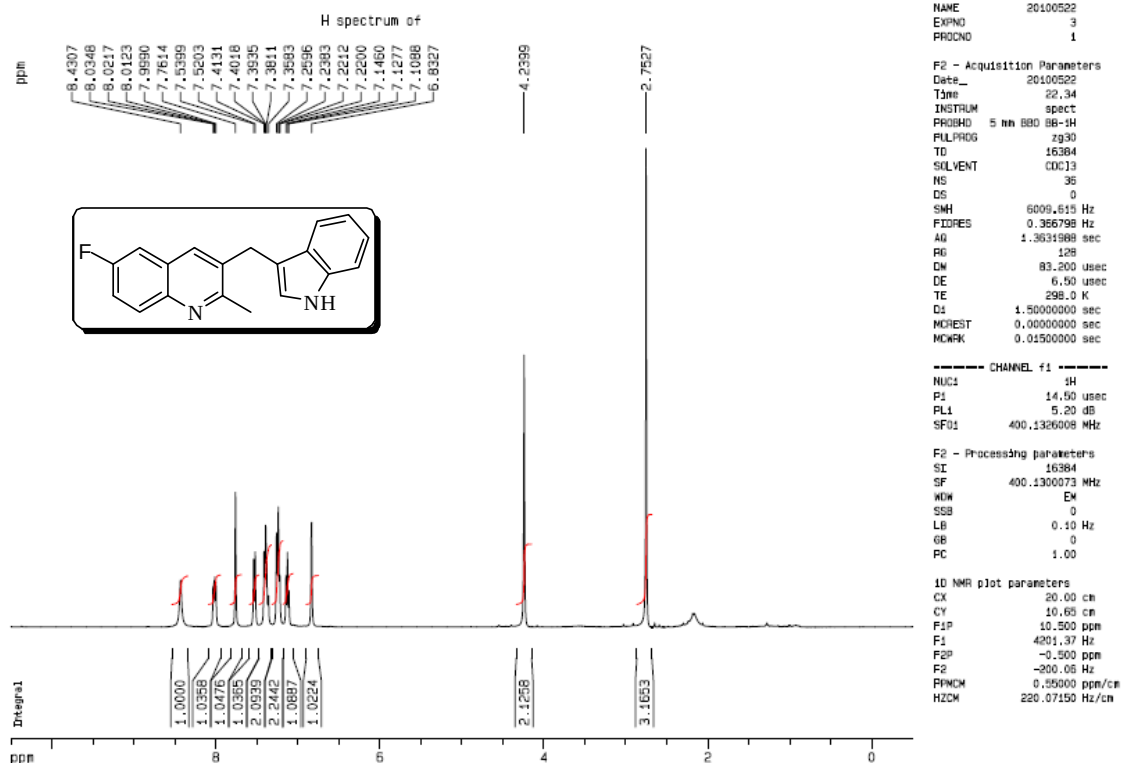
3-((1*H*-Indol-3-yl)methyl)-6-bromo-2-methylquinoline (3mb). ¹H NMR (400MHz, CDCl₃)



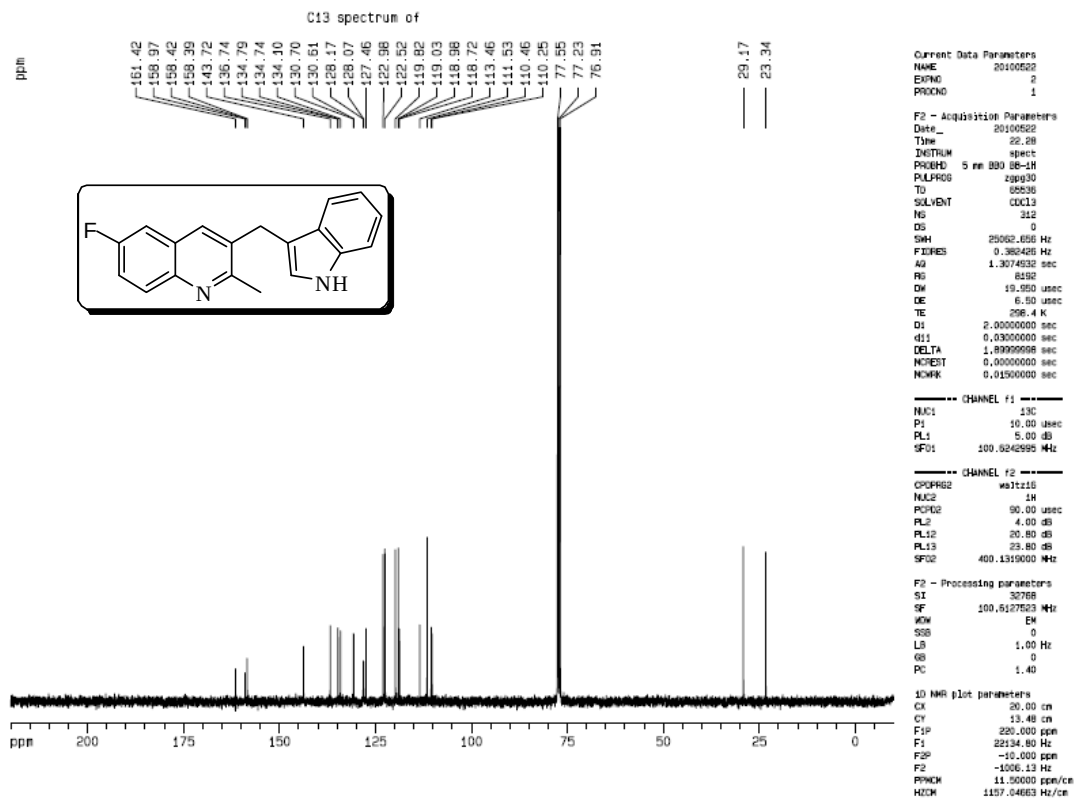
3-((1*H*-Indol-3-yl)methyl)-6-bromo-2-methylquinoline (3mb). ¹³C NMR (100 MHz, CDCl₃)



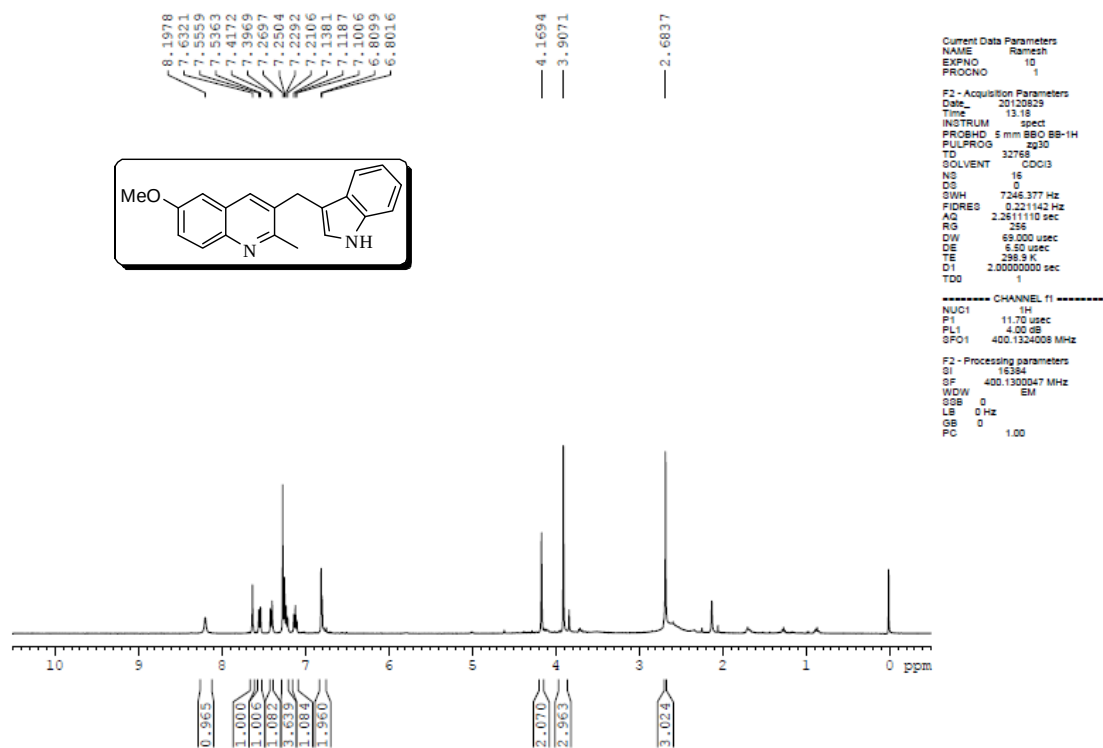
3-((1*H*-Indol-3-yl)methyl)-6-fluoro-2-methylquinoline (3nb). ¹H NMR (400MHz, CDCl₃)



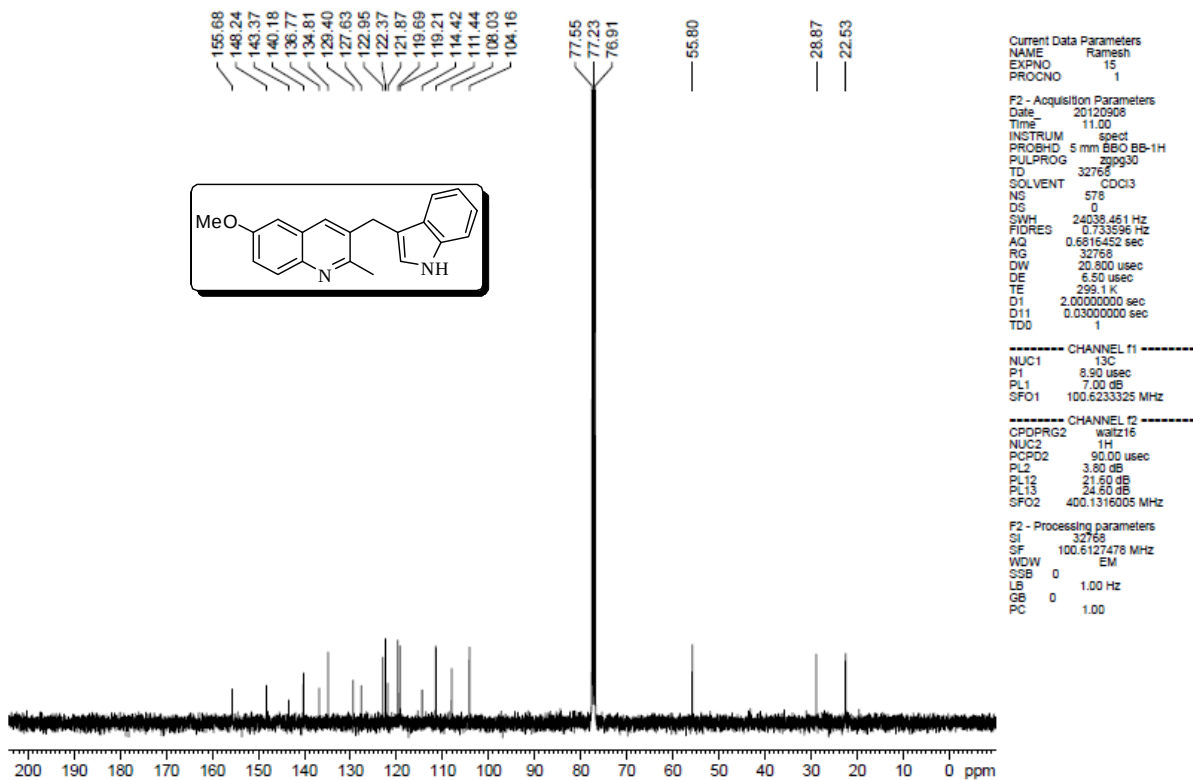
3-((1*H*-Indol-3-yl)methyl)-6-fluoro-2-methylquinoline (3nb). ¹³C NMR (400MHz, CDCl₃)



3-((1*H*-Indol-3-yl)methyl)-6-methoxy-2-methylquinoline (3ob). ¹H NMR (400MHz, CDCl₃)



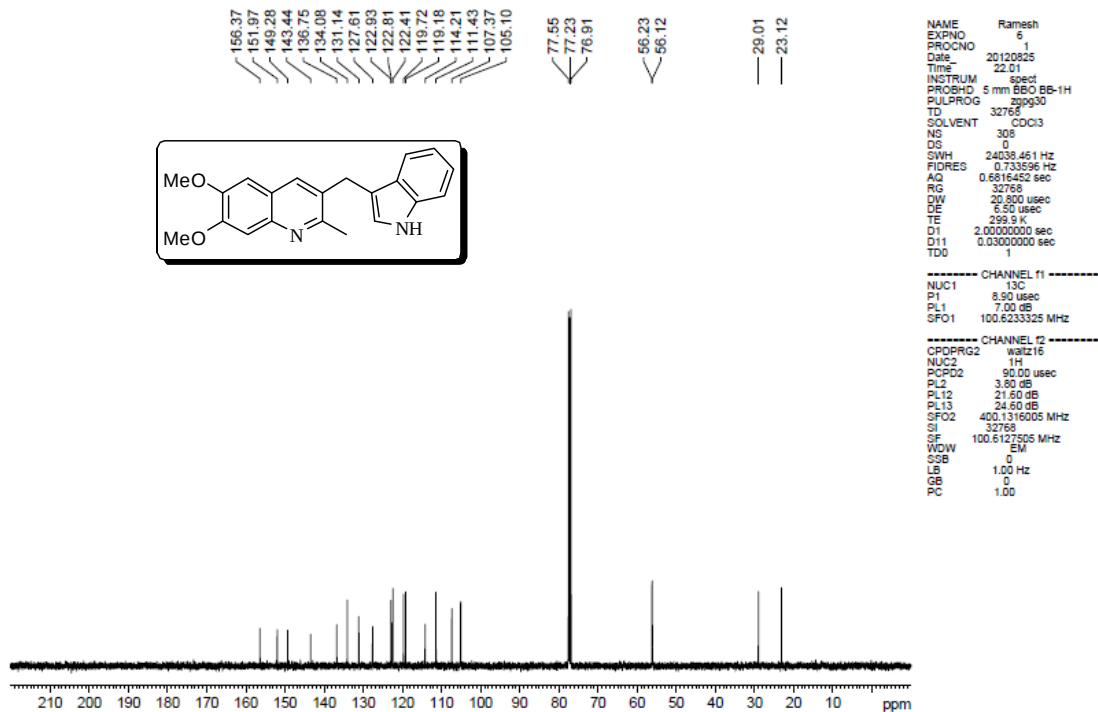
3-((1*H*-Indol-3-yl)methyl)-6-methoxy-2-methylquinoline (3ob). ¹³C NMR (400MHz, CDCl₃)



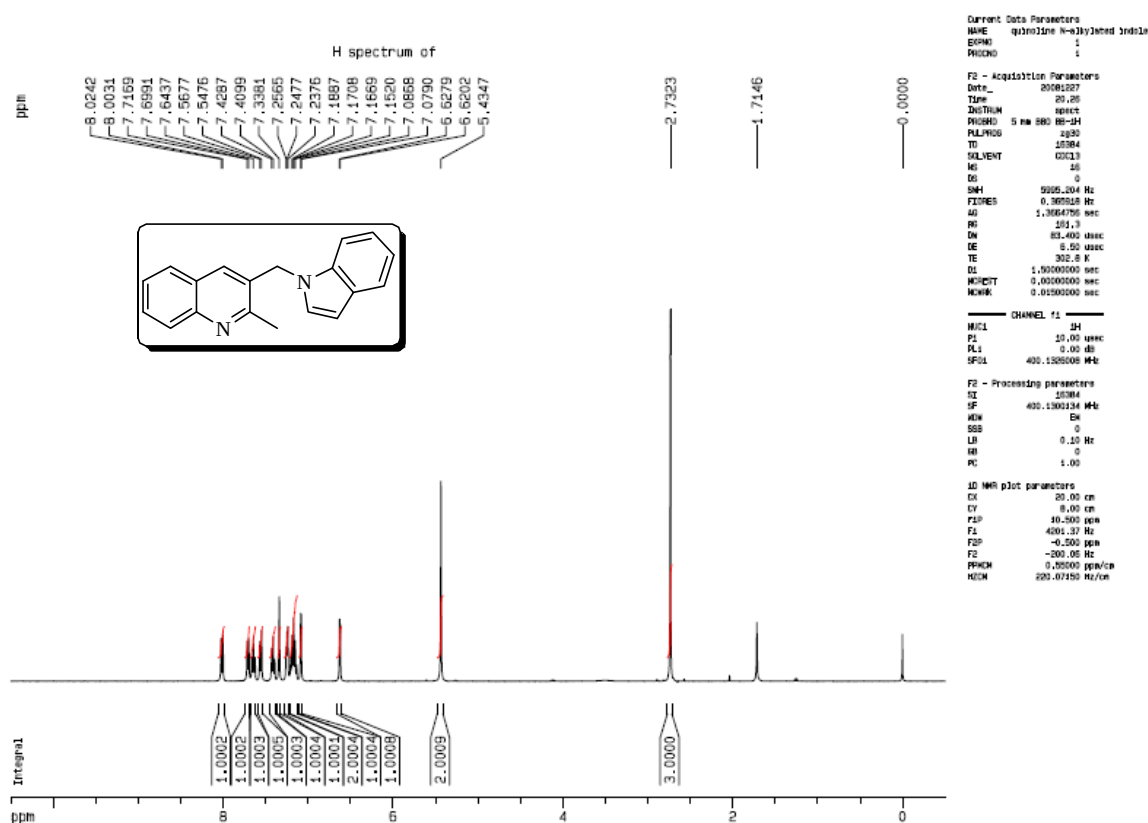
3-((1*H*-Indol-3-yl)methyl)-6,7-dimethoxy-2-methylquinoline (3pb). ¹H NMR (400MHz, CDCl₃)



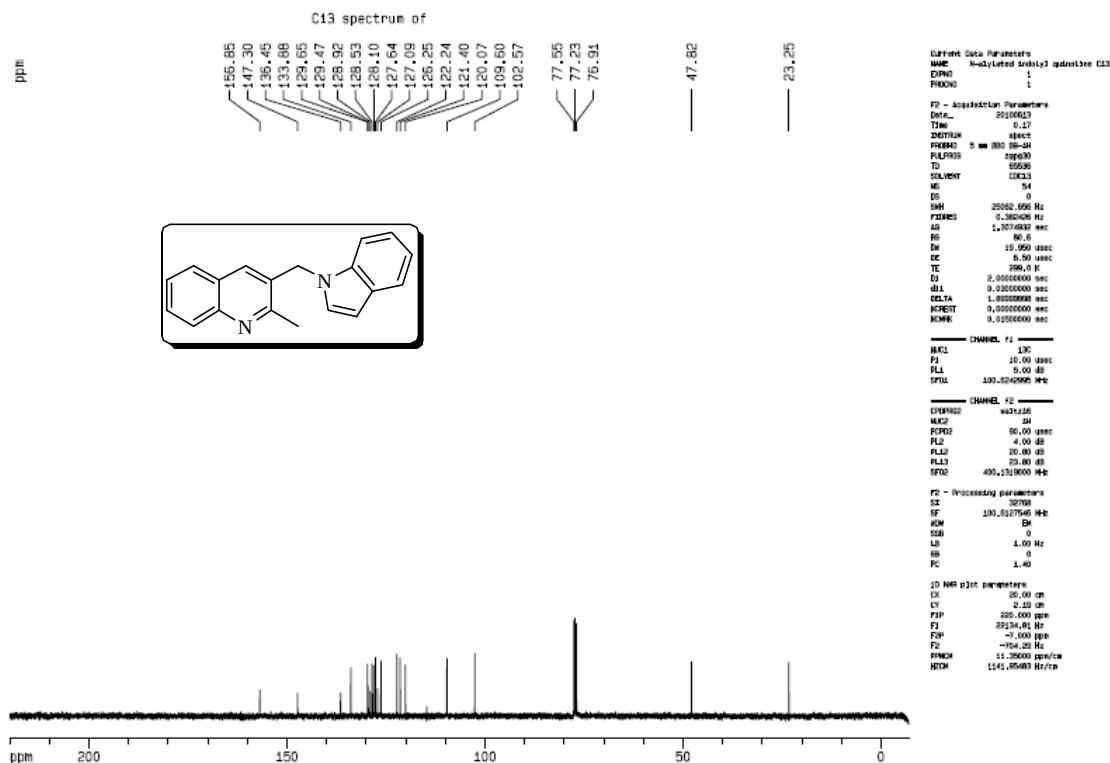
3-((1*H*-Indol-3-yl)methyl)-6,7-dimethoxy-2-methylquinoline (3pb). ¹³C NMR (400MHz, CDCl₃)



3-((1*H*-Indol-1-yl)methyl)-2-methylquinoline (3qb). ¹H NMR (400MHz, CDCl₃)

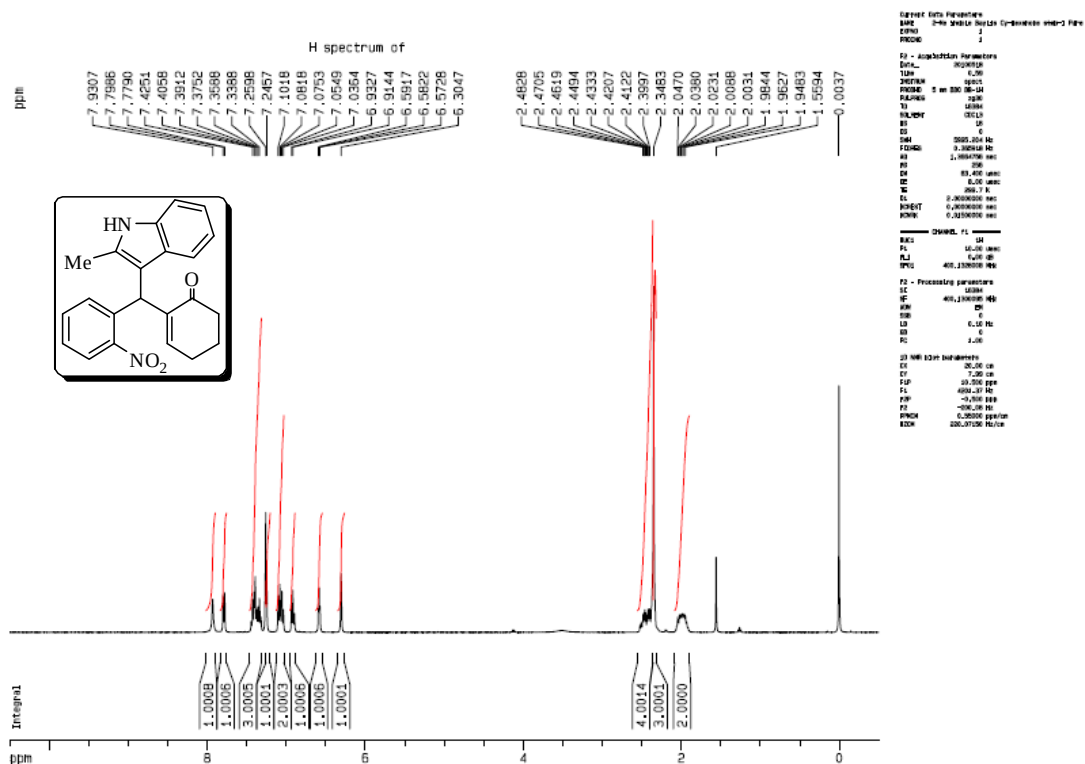


3-((1*H*-Indol-1-yl)methyl)-2-methylquinoline (3qb). ¹³C NMR (100 MHz, CDCl₃)



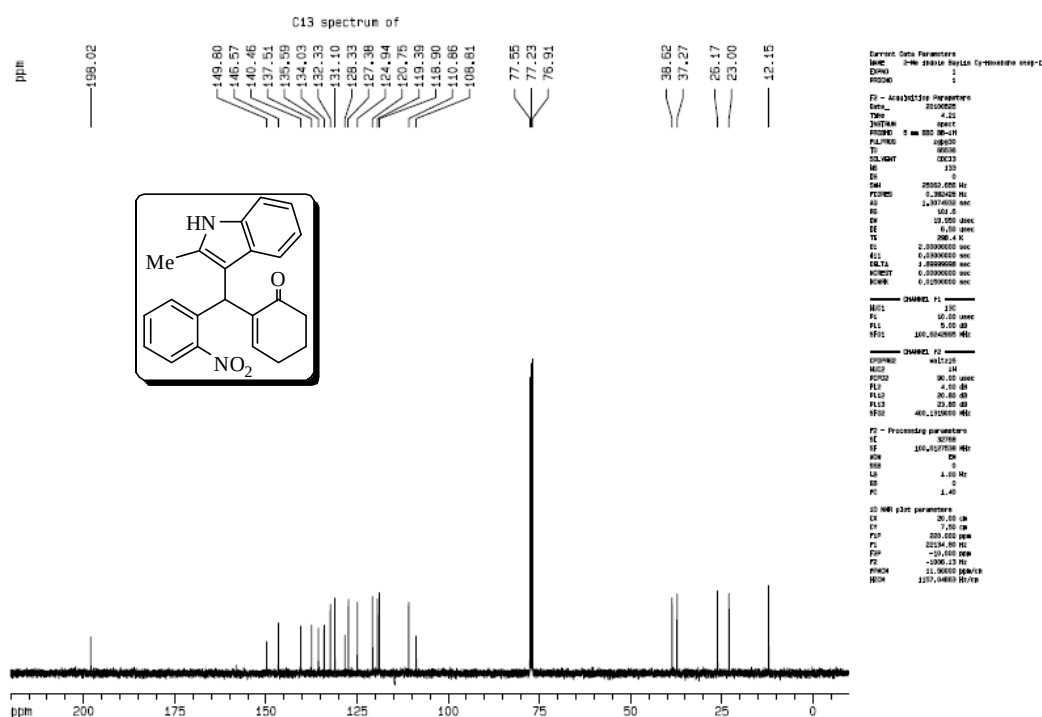
2-((2-Methyl-1H-indol-3-yl)(2-nitrophenyl)methyl)cyclohex-2-enone(4a).
(400MHz, CDCl₃)

¹H NMR

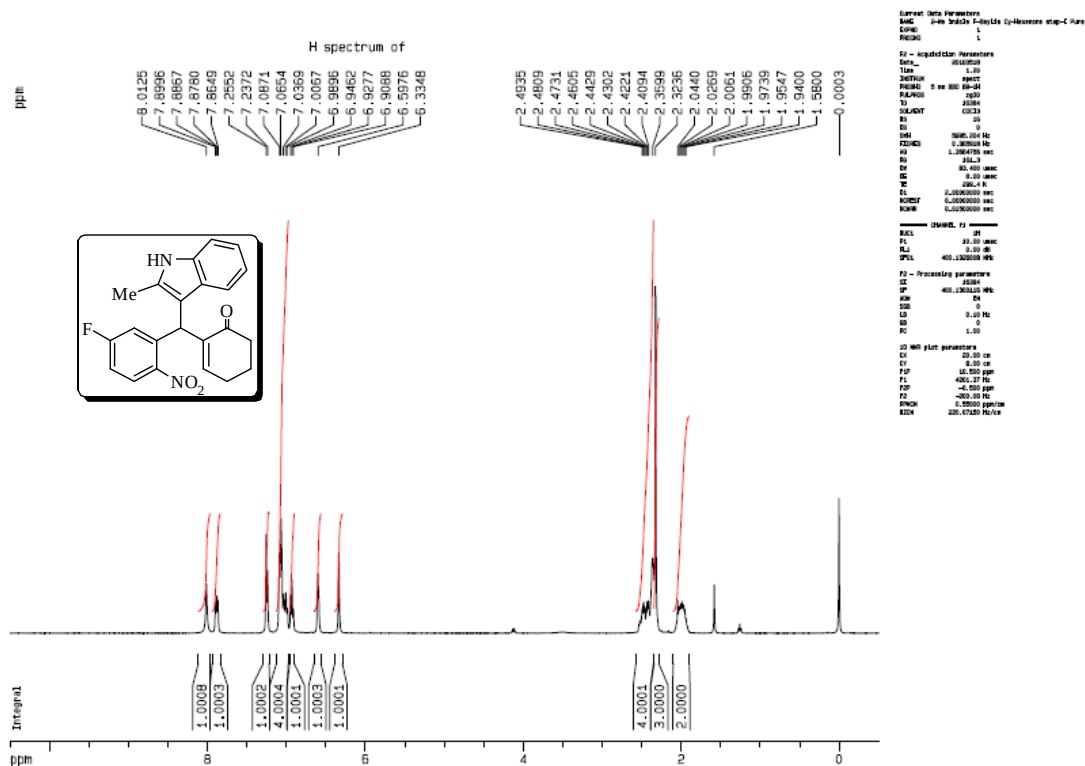


2-((2-Methyl-1H-indol-3-yl)(2-nitrophenyl)methyl)cyclohex-2-enone(4a).
(100 MHz, CDCl₃)

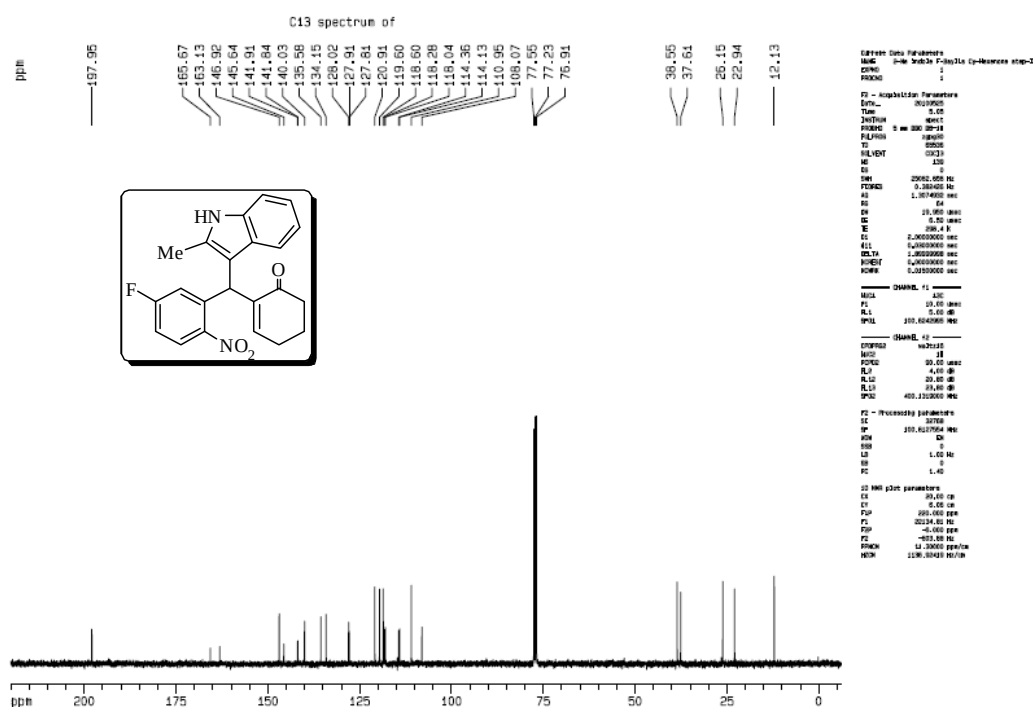
¹³C NMR (100



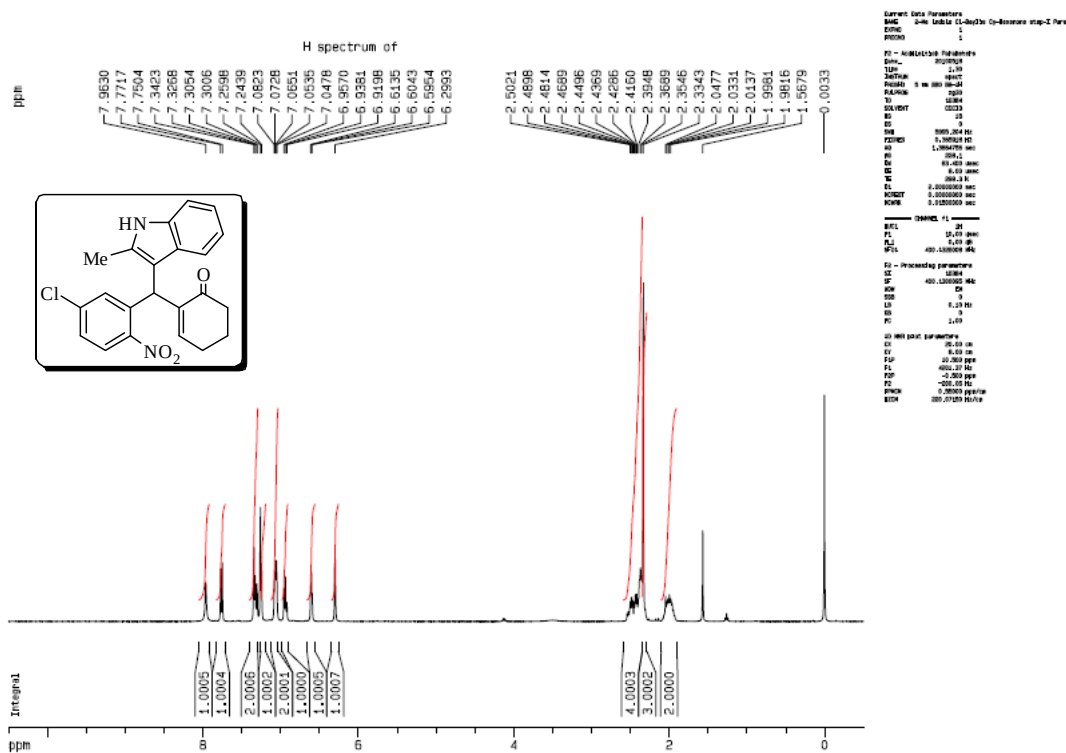
2-((5-Fluoro-2-nitrophenyl)(2-methyl-1*H*-indol-3-yl)methyl)cyclohex-2-enone (**4b**). ¹H NMR (400MHz, CDCl₃)



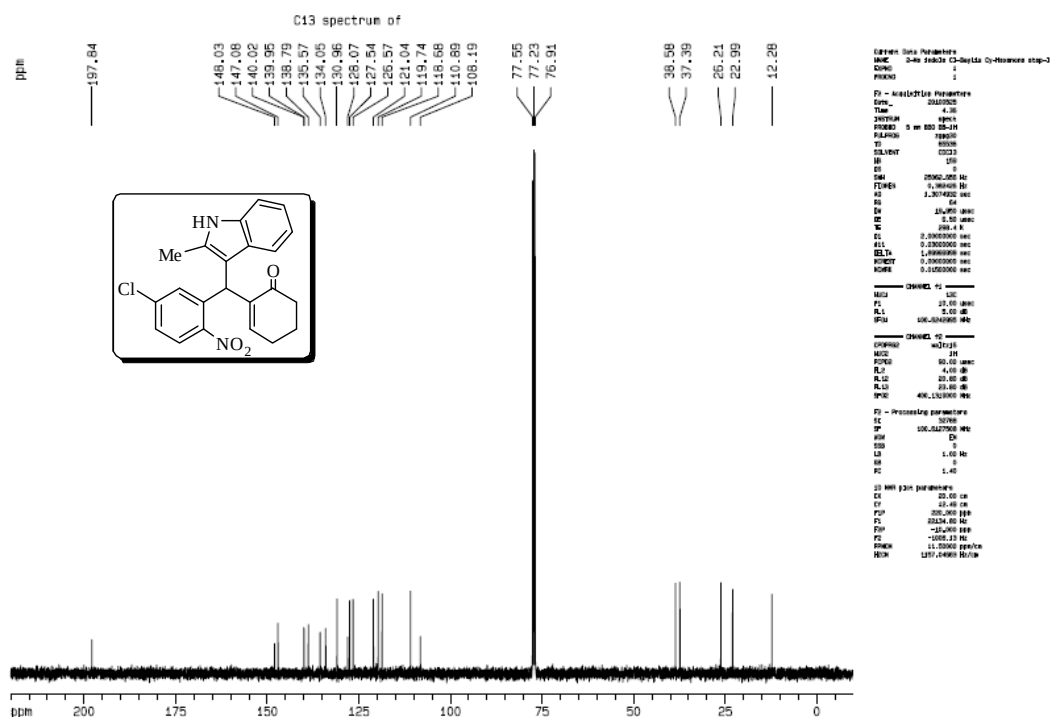
2-((5-Fluoro-2-nitrophenyl)(2-methyl-1*H*-indol-3-yl)methyl)cyclohex-2-enone (4b). ¹³C
NMR (100 MHz, CDCl₃)



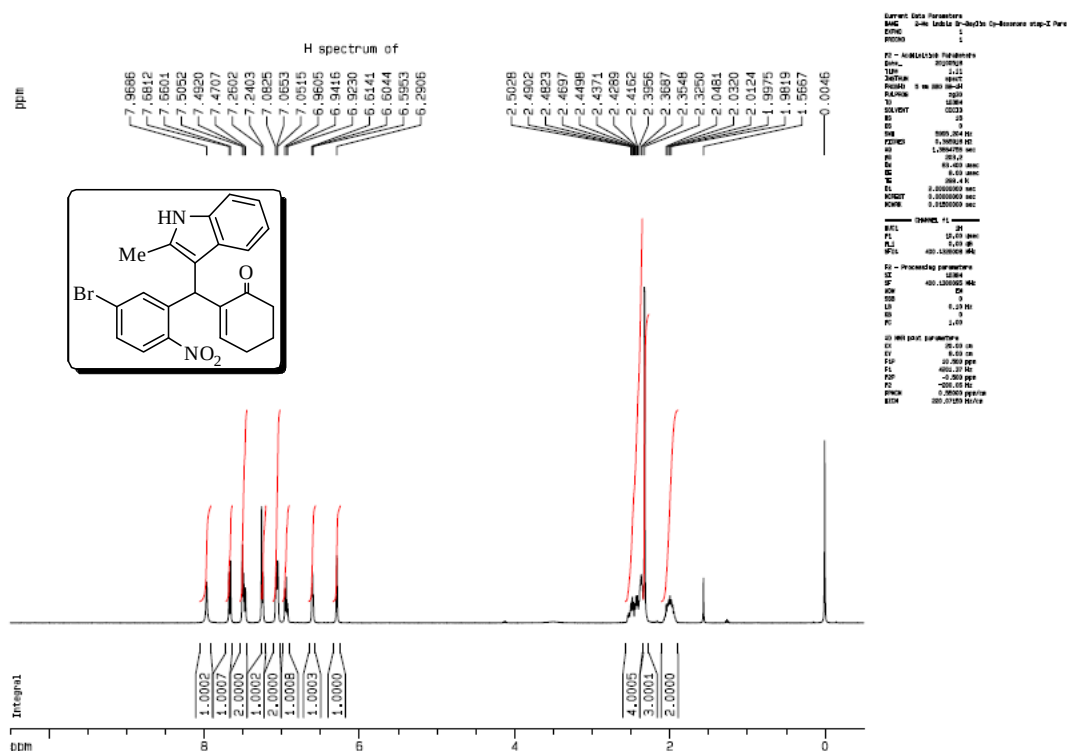
2-((5-Chloro-2-nitrophenyl)(2-methyl-1H-indol-3-yl)methyl)cyclohex-2-enone (4c). ¹H NMR (400MHz, CDCl₃)



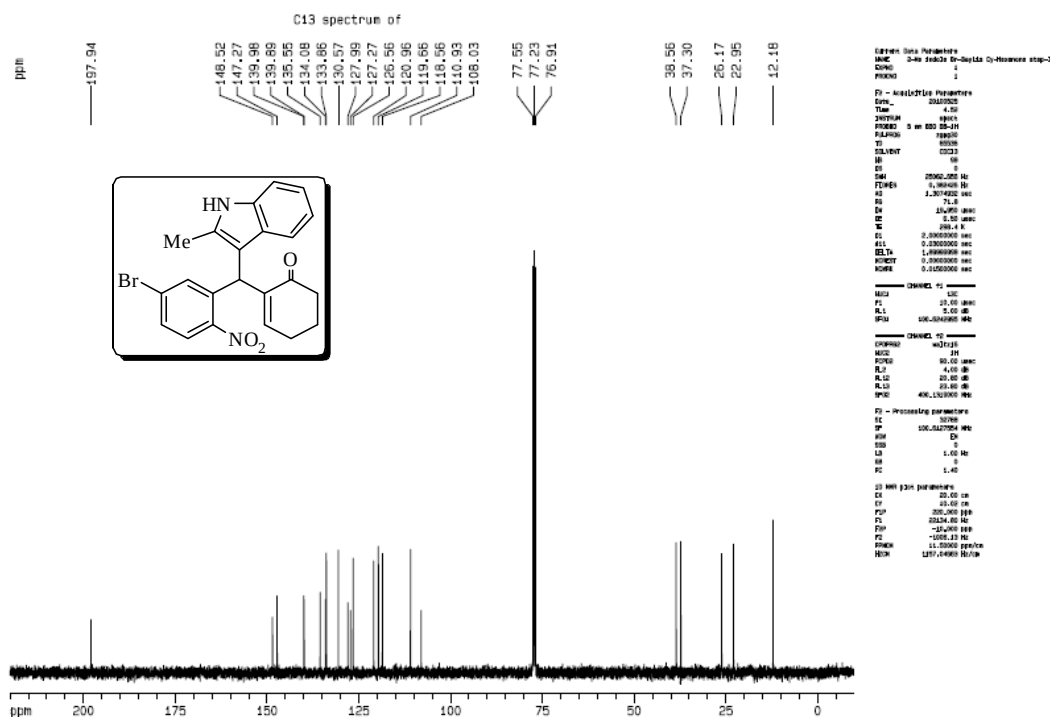
2-((5-Chloro-2-nitrophenyl)(2-methyl-1H-indol-3-yl)methyl)cyclohex-2-enone (4c). ¹³C NMR (100 MHz, CDCl₃)



2-((5-Bromo-2-nitrophenyl)(2-methyl-1*H*-indol-3-yl)methyl)cyclohex-2-enone (4d). ¹H NMR (400MHz, CDCl₃)

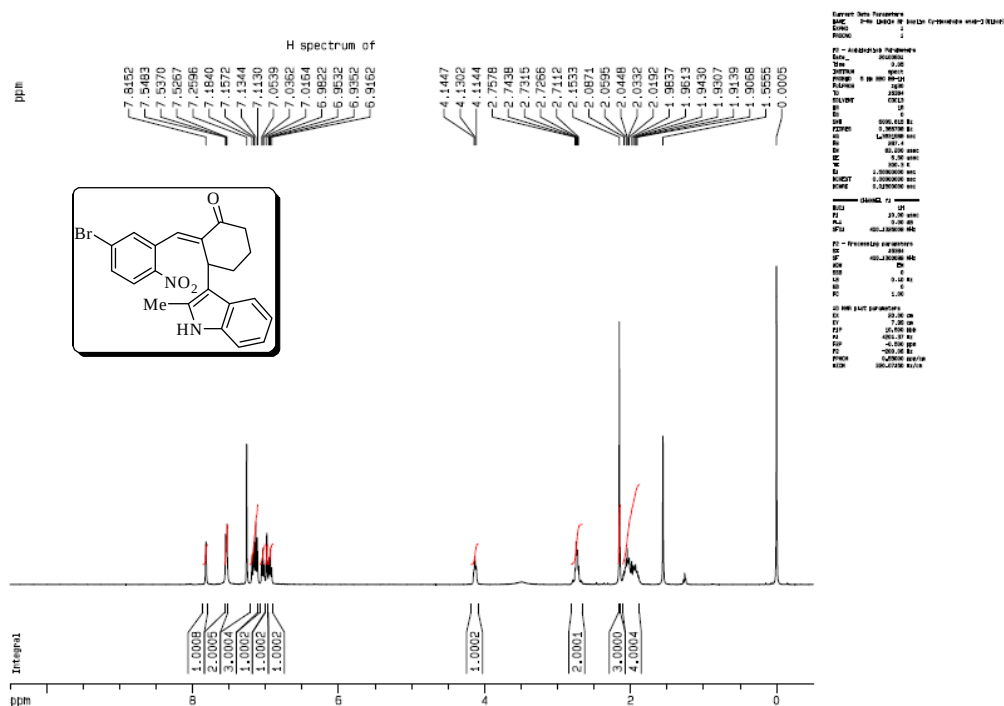


2-((5-Bromo-2-nitrophenyl)(2-methyl-1*H*-indol-3-yl)methyl)cyclohex-2-enone (4d). ¹³C NMR (100 MHz, CDCl₃)

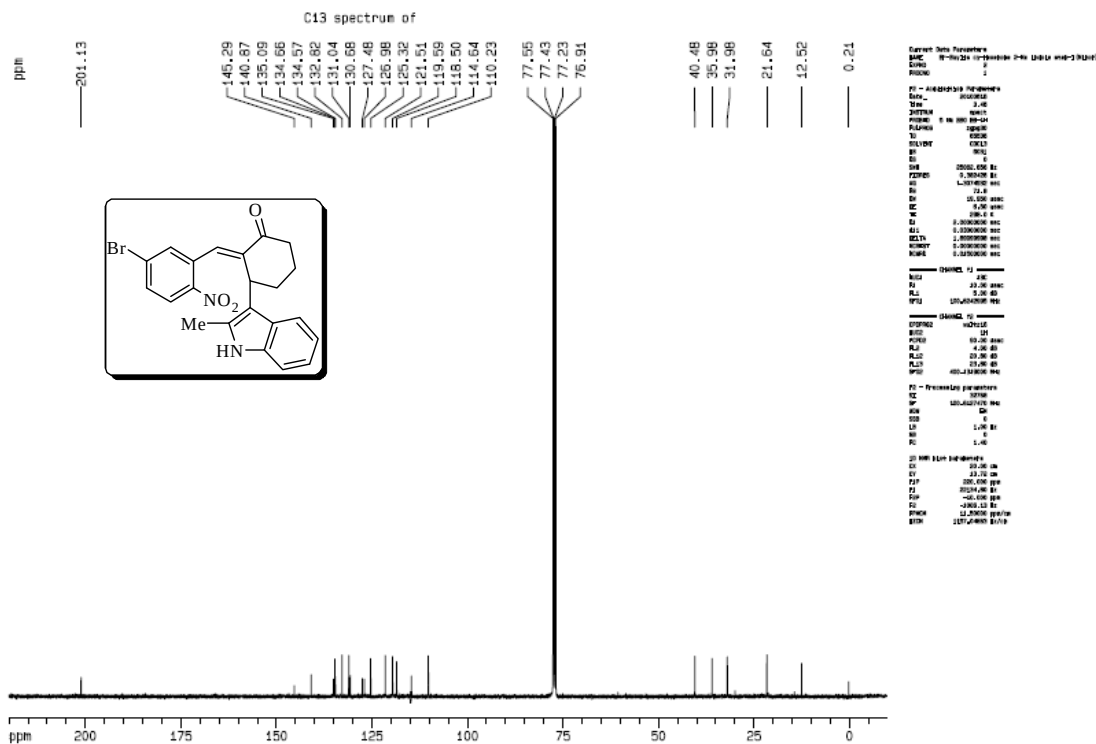


${}^1\text{H}$

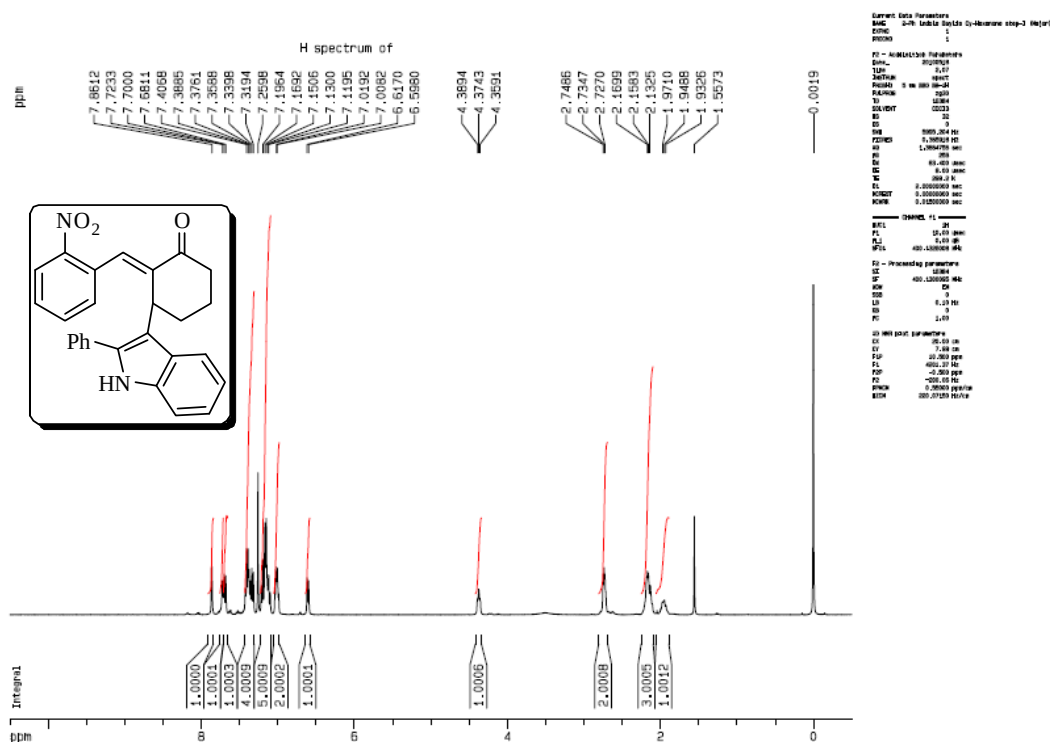
NMR (400MHz, CDCl₃)

 ^{13}C

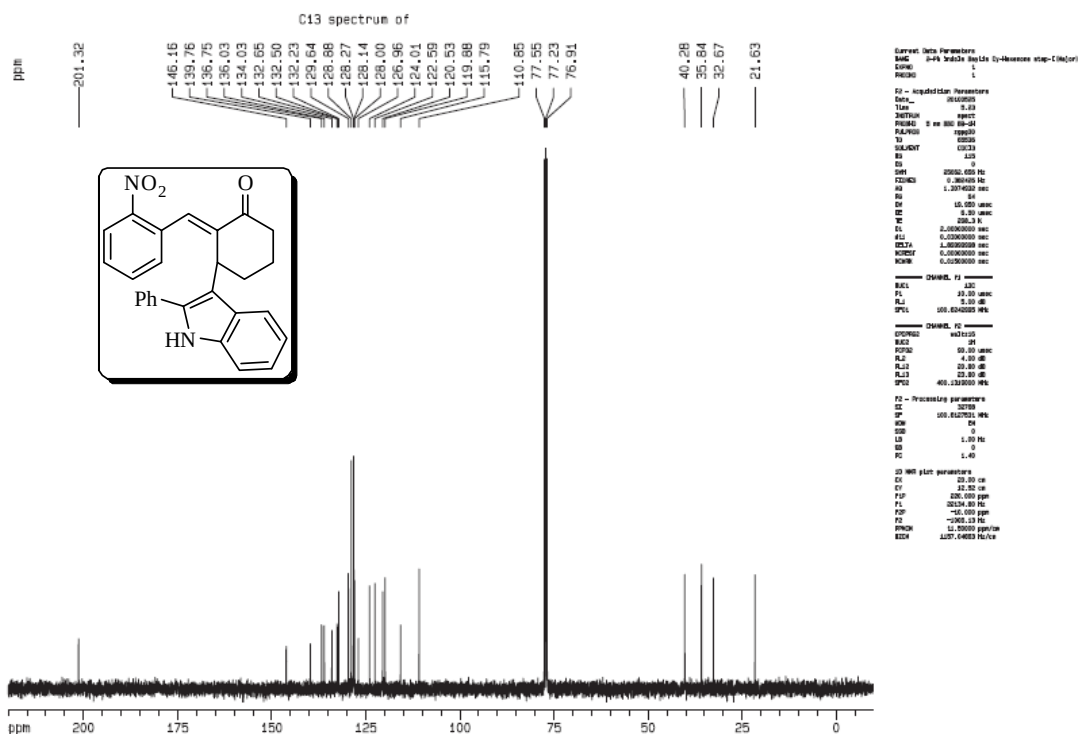
NMR (100 MHz, CDCl₃)



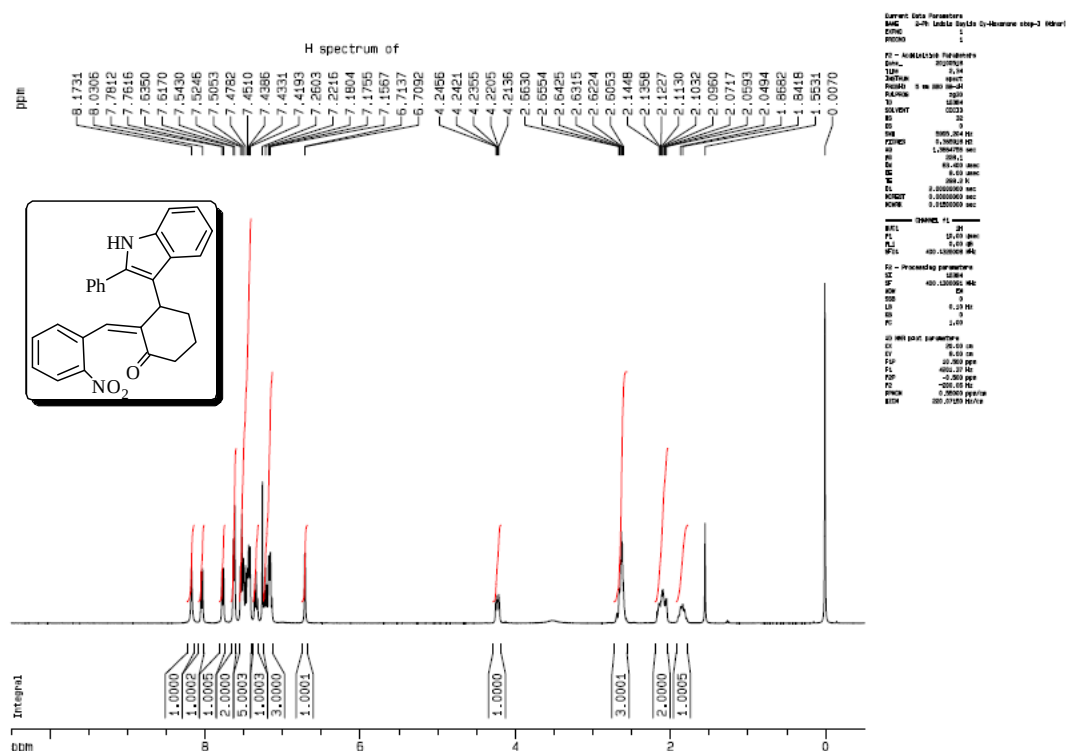
(E)-2-(2-Nitrobenzylidene)-3-(2-phenyl-1H-indol-3-yl)cyclohexanone (5e). ^1H NMR (400MHz, CDCl_3)



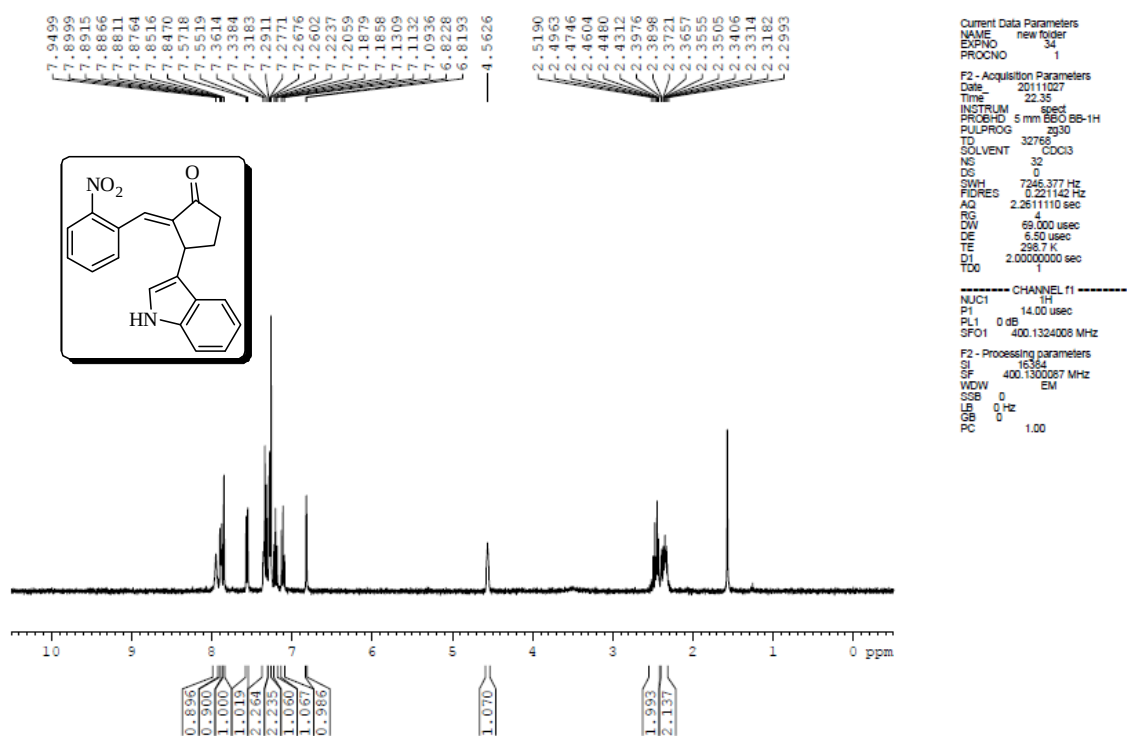
(E)-2-(2-Nitrobenzylidene)-3-(2-phenyl-1H-indol-3-yl)cyclohexanone (5e). ^{13}C NMR (100 MHz, CDCl_3)



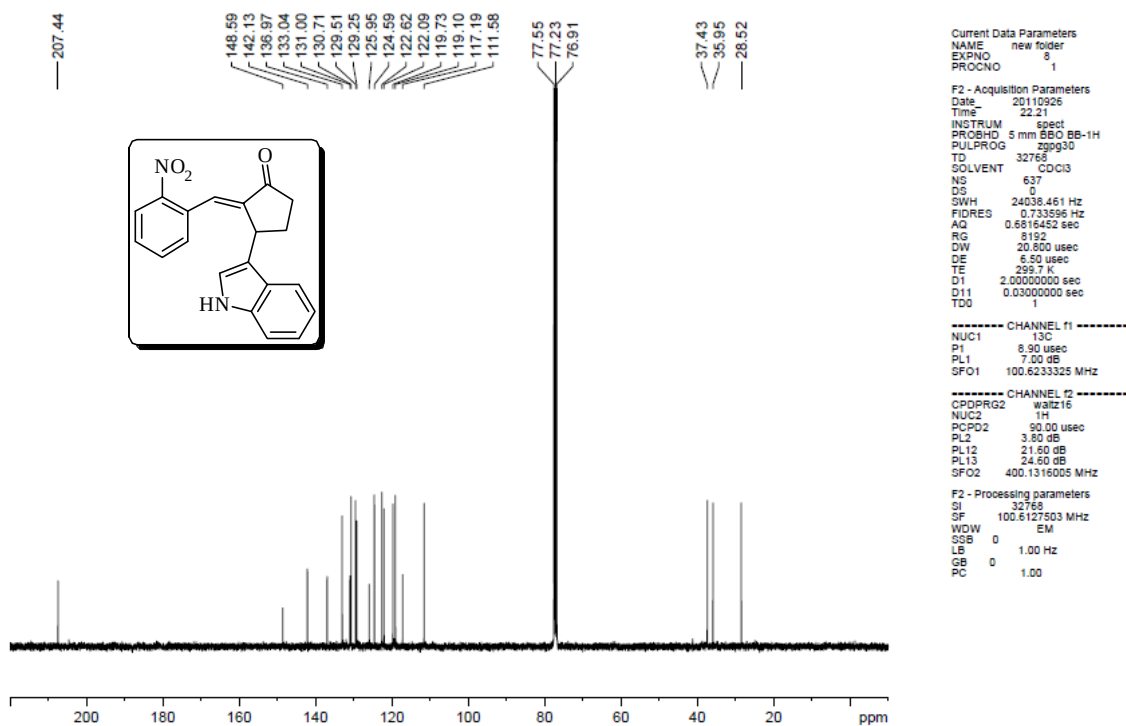
(Z)-2-(2-Nitrobenzylidene)-3-(2-phenyl-1H-indol-3-yl)cyclohexanone (5e'). ¹H NMR (400MHz, CDCl₃)



(E)-3-(1H-Indol-3-yl)-2-(2-nitrobenzylidene)cyclopentanone (6a). ^1H NMR (400MHz, CDCl_3)

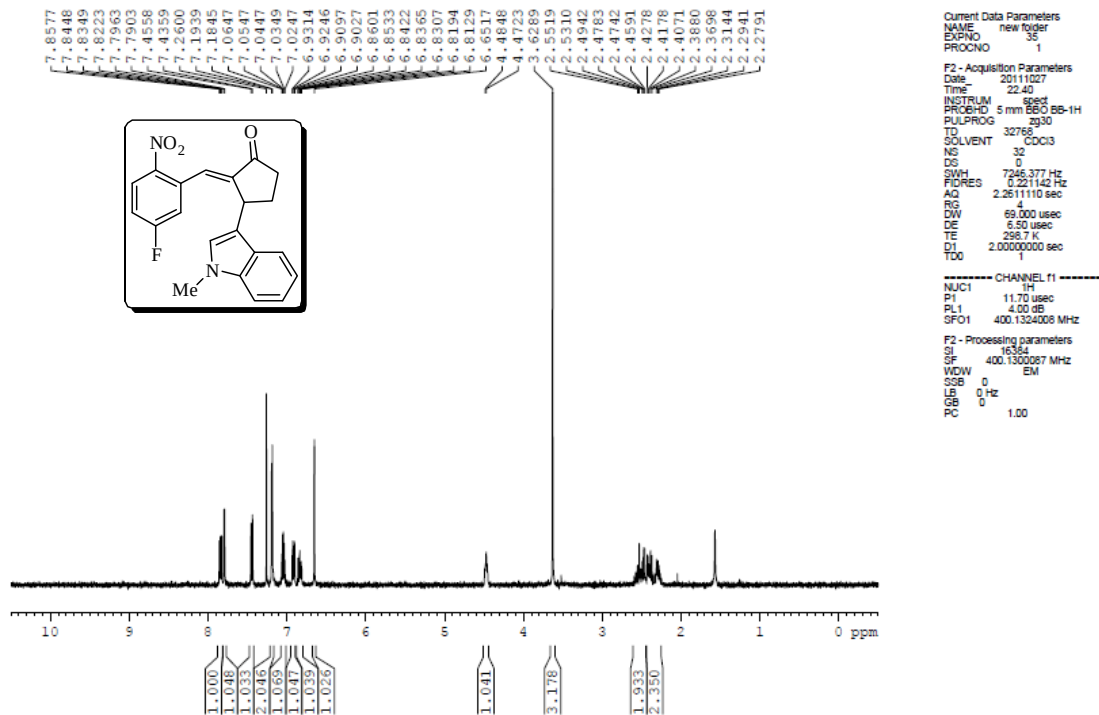


(E)-3-(1H-Indol-3-yl)-2-(2-nitrobenzylidene)cyclopentanone (6a). ^{13}C NMR (100 MHz, CDCl_3)



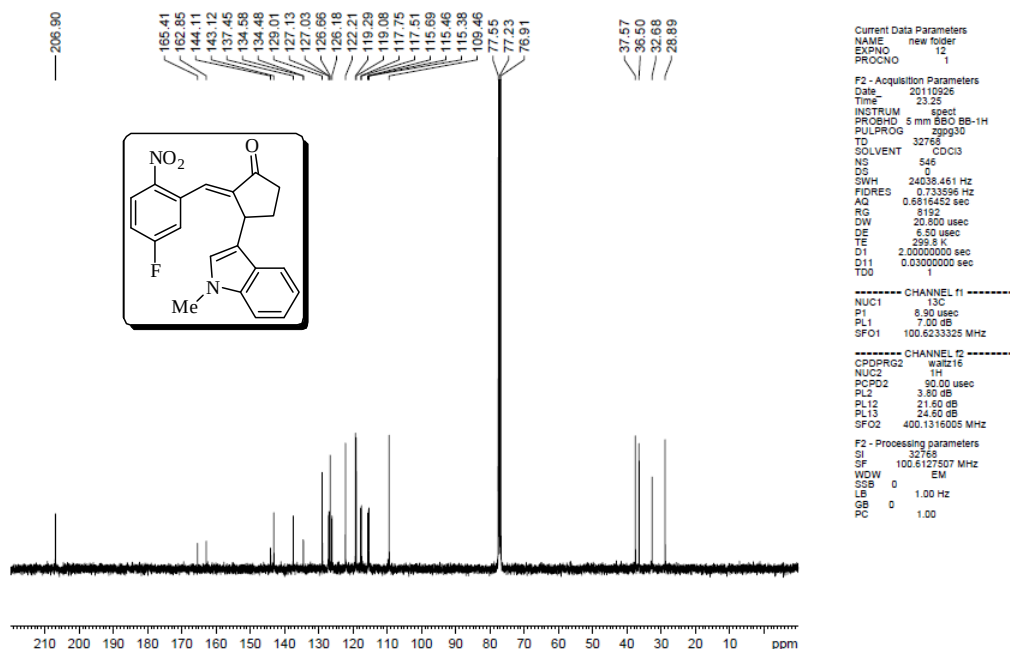
(E)-2-(5-Fluoro-2-nitrobenzylidene)-3-(1-methyl-1H-indol-3-yl)cyclopentanone (6b). ^1H

NMR (400MHz, CDCl_3)

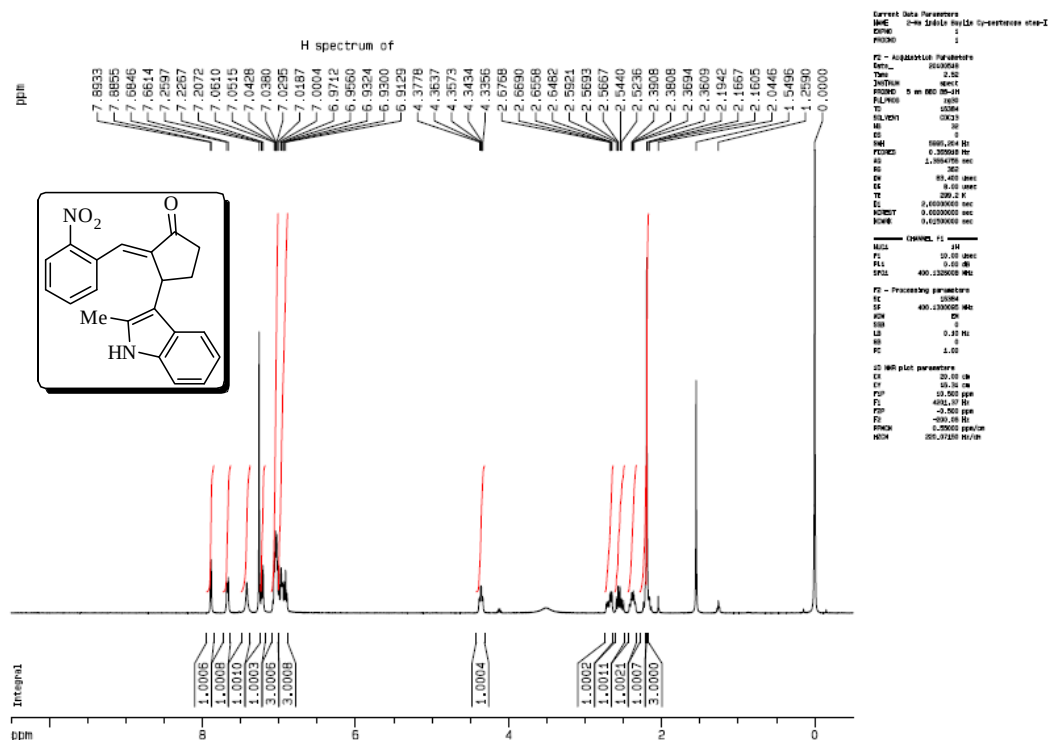


(E)-2-(5-Fluoro-2-nitrobenzylidene)-3-(1-methyl-1H-indol-3-yl)cyclopentanone (6b). ^{13}C

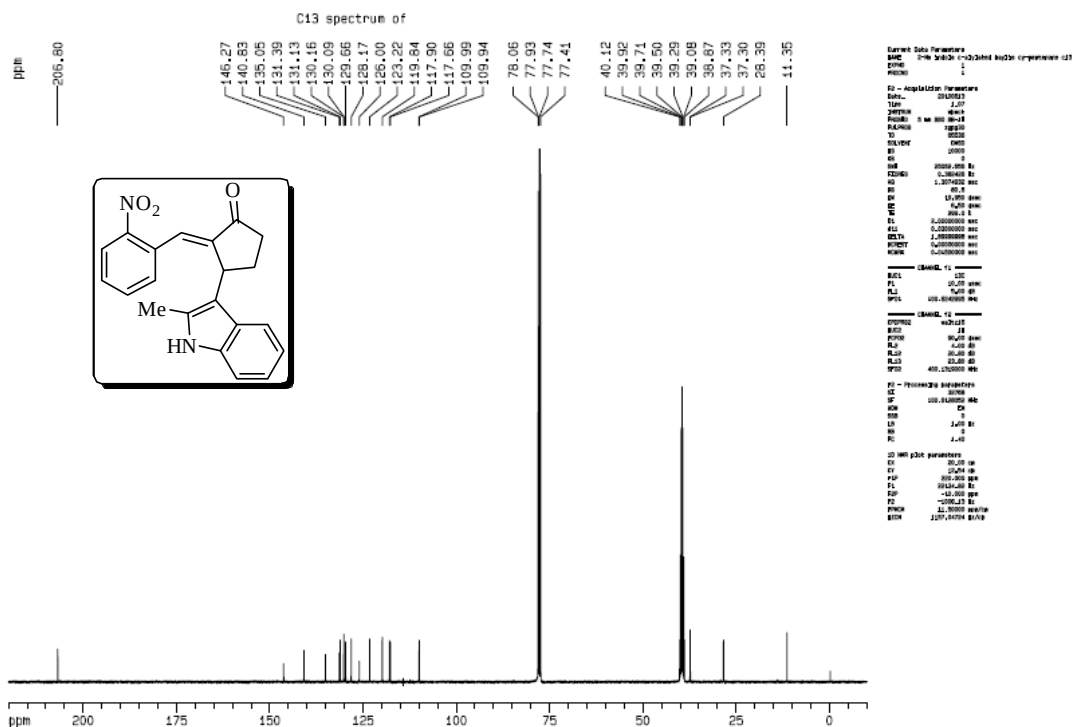
NMR (100 MHz, CDCl_3)



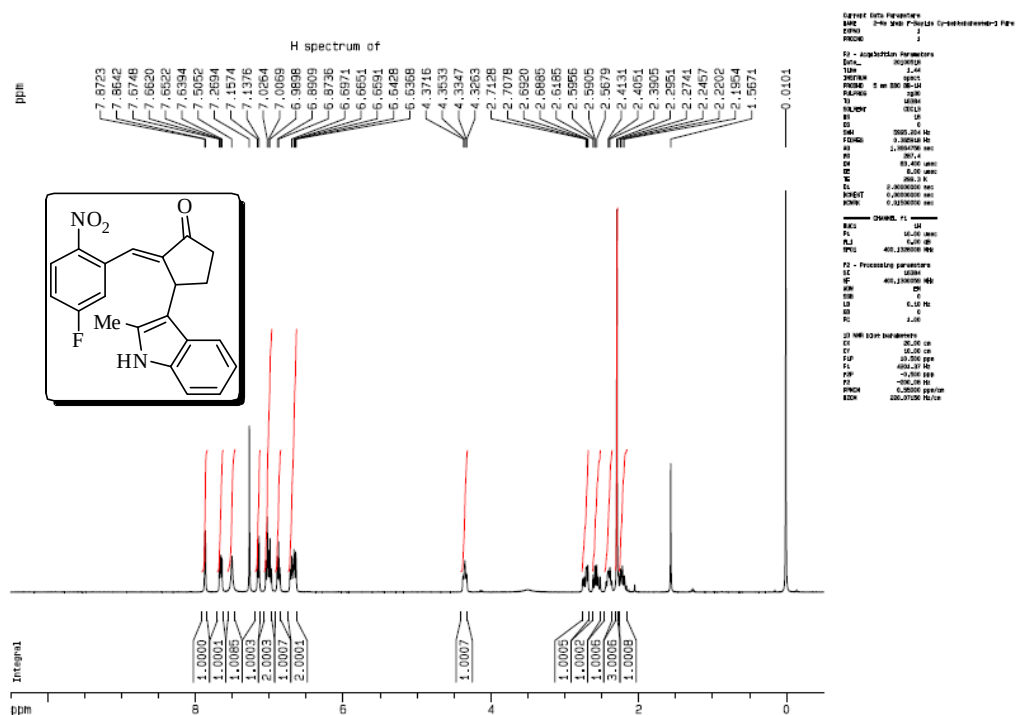
(*E*)-3-(2-Methyl-1*H*-indol-3-yl)-2-(2-nitrobenzylidene)cyclopentanone (6c). ¹H NMR (400MHz, CDCl₃)



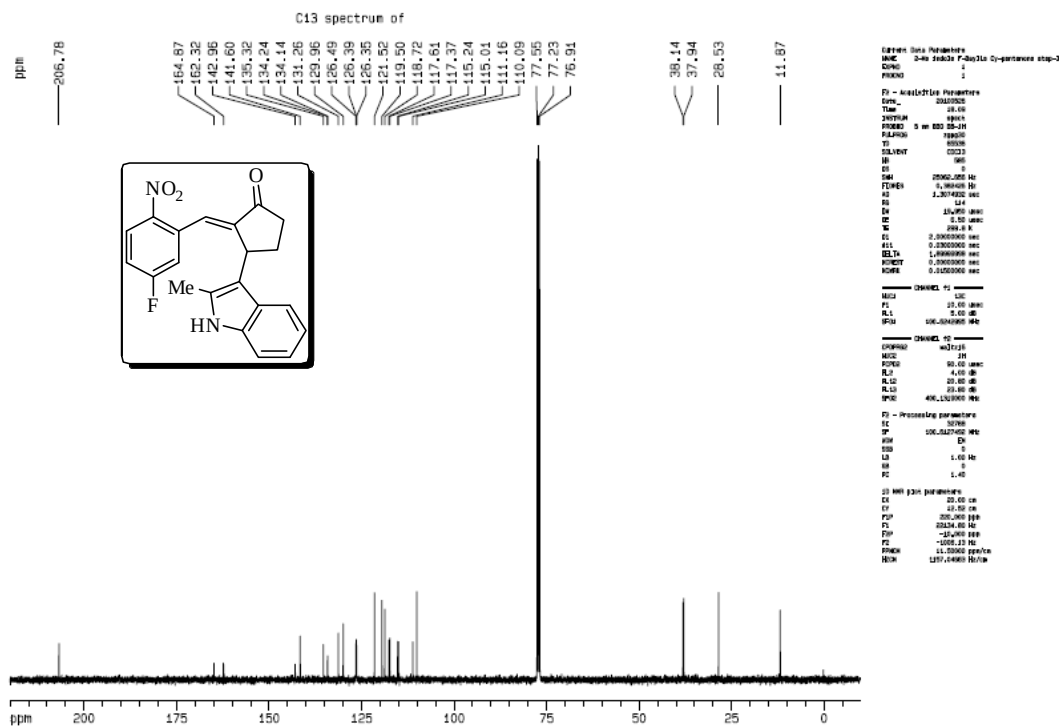
(*E*)-3-(2-Methyl-1*H*-indol-3-yl)-2-(2-nitrobenzylidene)cyclopentanone (6c). ¹³C NMR (100 MHz, CDCl₃ and DMSO-*d*₆)



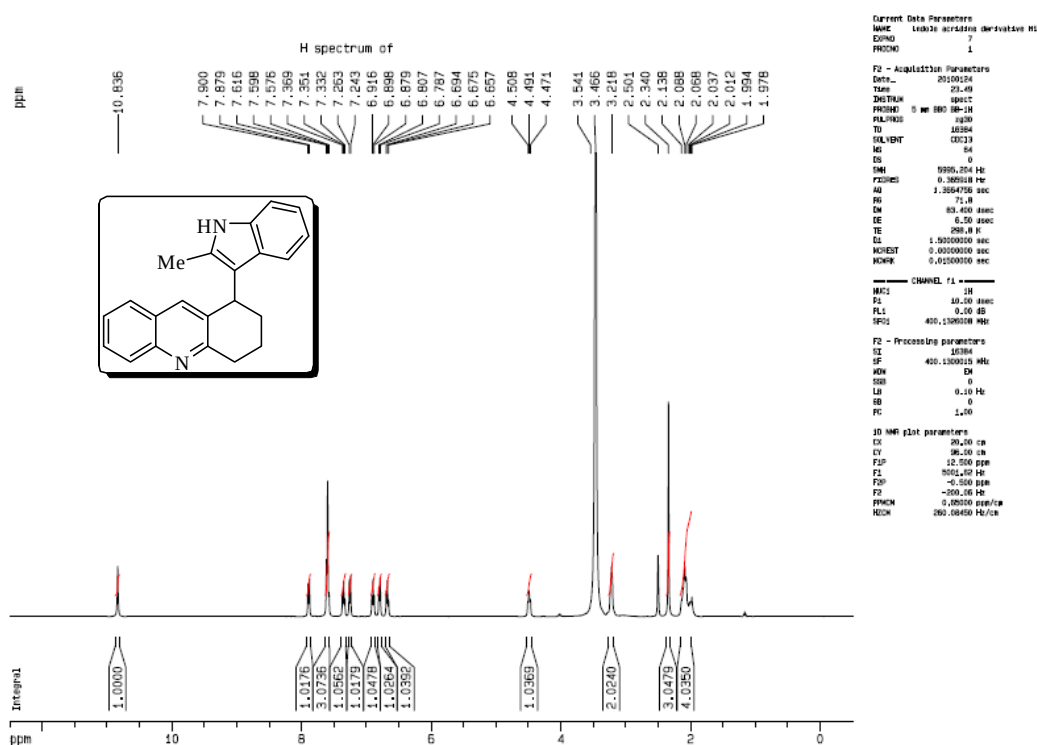
(E)-2-(5-Fluoro-2-nitrobenzylidene)-3-(2-methyl-1H-indol-3-yl)cyclopentanone (6d). ^1H
NMR (400MHz, CDCl_3)



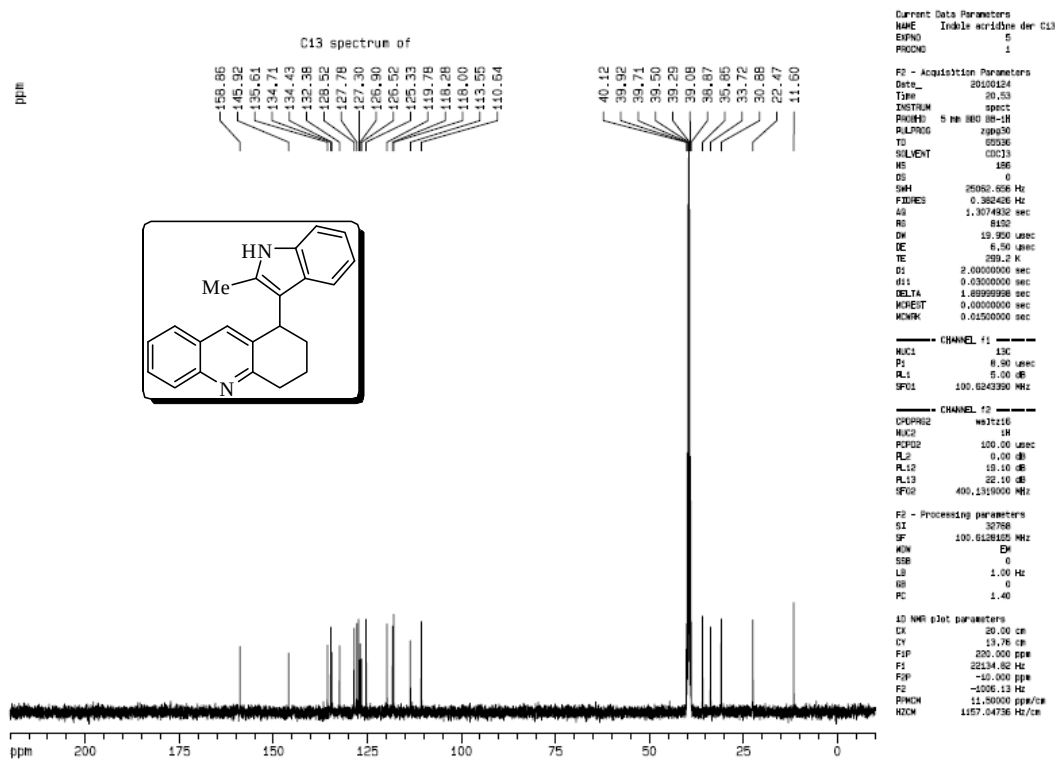
(E)-2-(5-Fluoro-2-nitrobenzylidene)-3-(2-methyl-1H-indol-3-yl)cyclopentanone (6d). ^{13}C
NMR (100 MHz, CDCl_3)



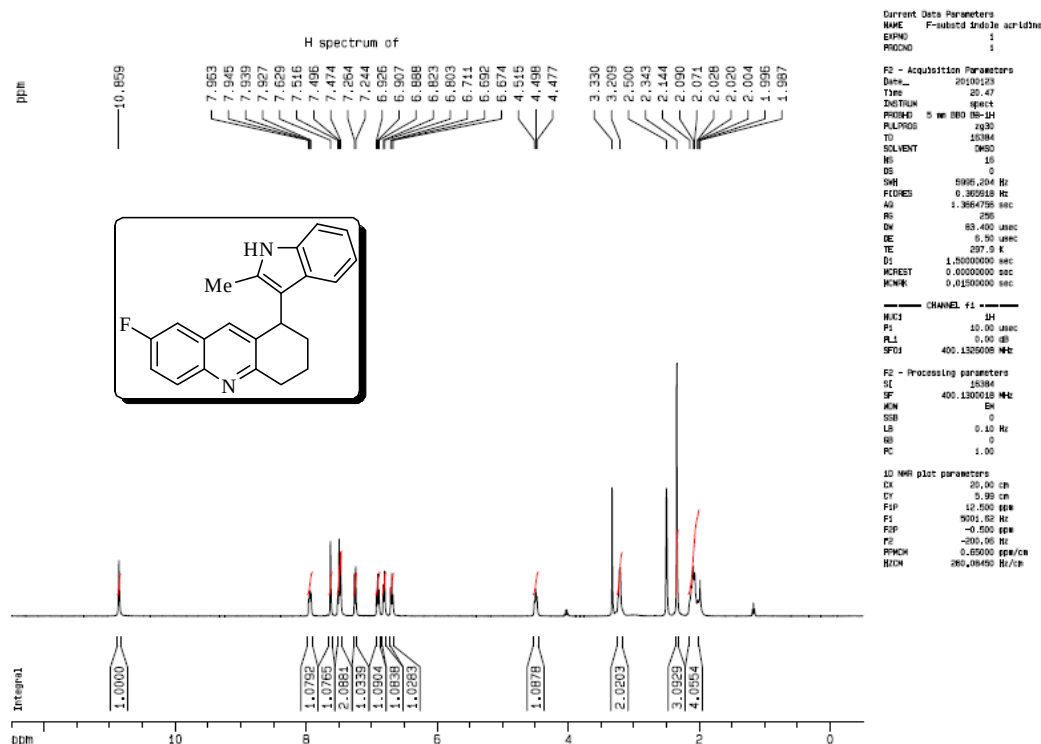
1-(2-Methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroacridine (8a). ^1H NMR (400MHz, $\text{DMSO}-d_6$)



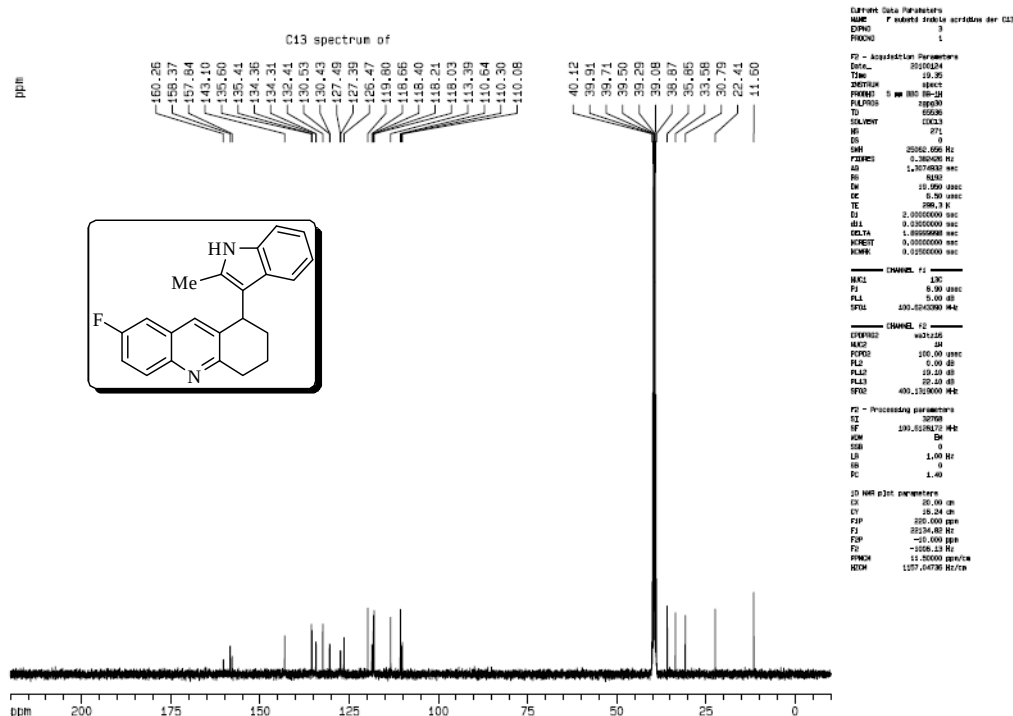
1-(2-Methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroacridine (8a). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)



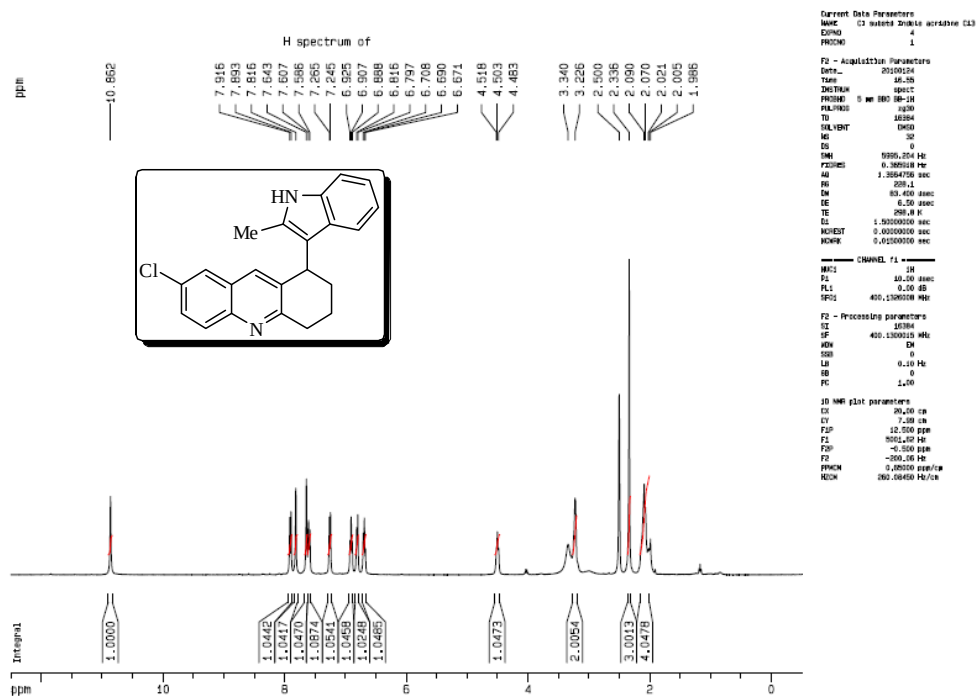
7-Fluoro-1-(2-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8b). ^1H NMR (400MHz, $\text{DMSO}-d_6$)



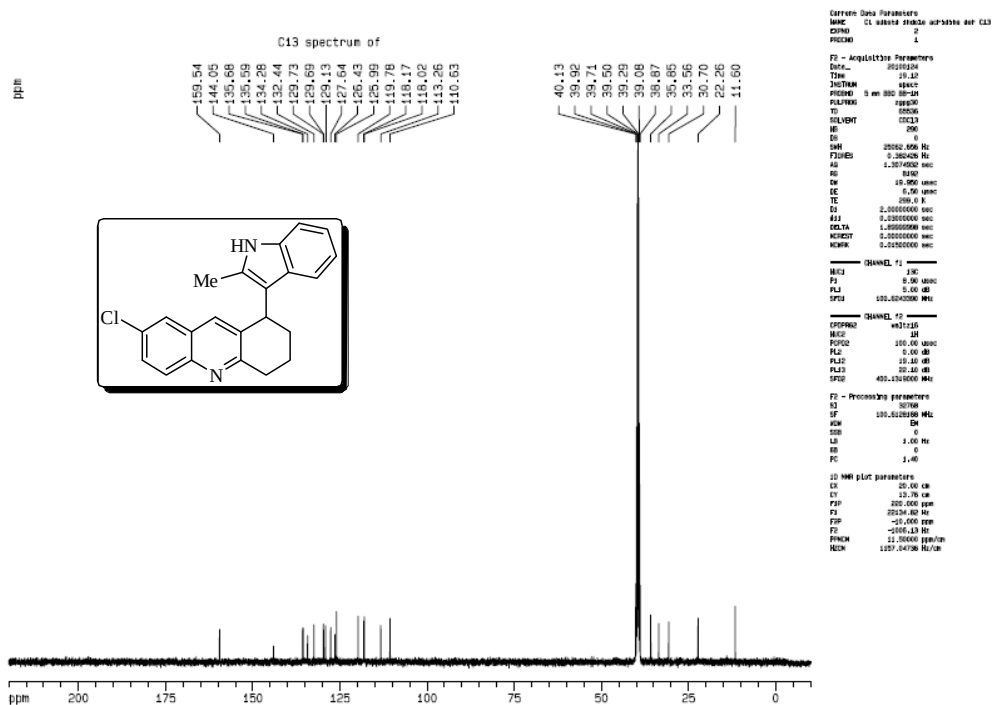
7-Fluoro-1-(2-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8b). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$)



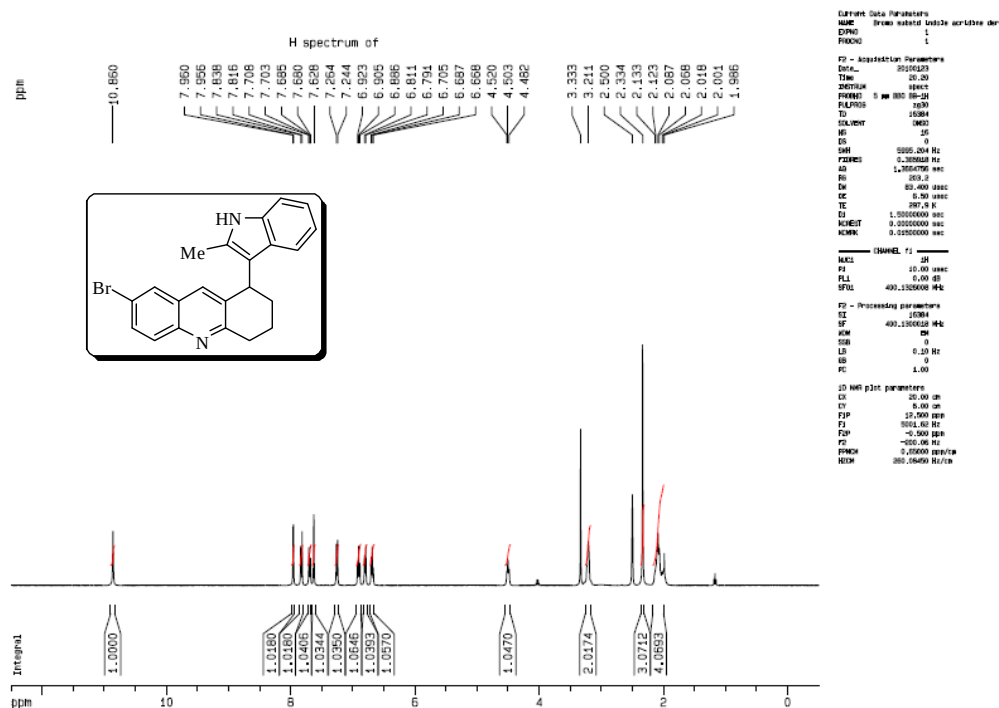
7-Chloro-1-(2-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8c). ¹H NMR (400MHz, DMSO-*d*₆)



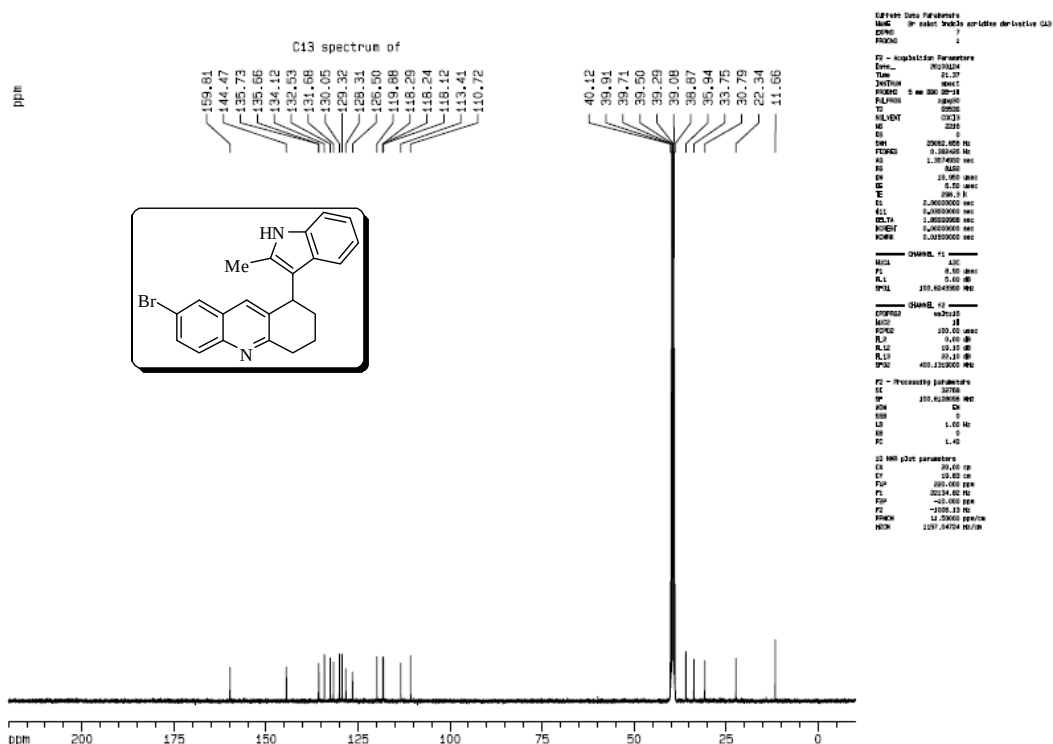
7-Chloro-1-(2-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8c). ¹³C NMR (100 MHz, DMSO-*d*₆)



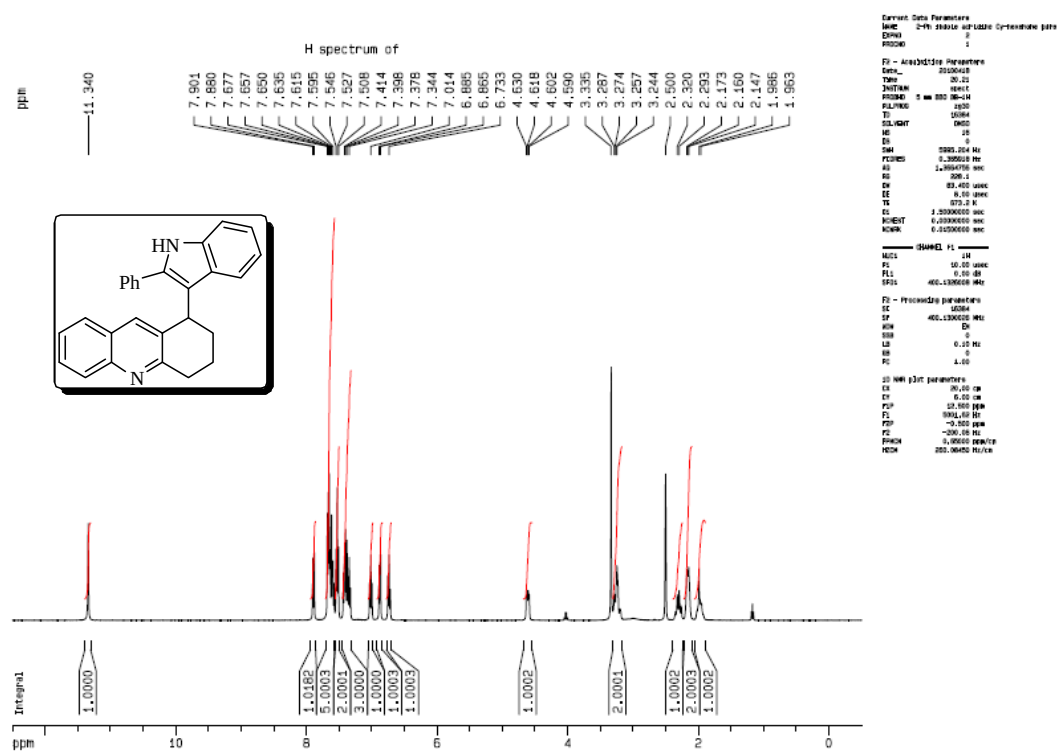
7-Bromo-1-(2-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8d). ¹H NMR (400MHz, DMSO-*d*₆)



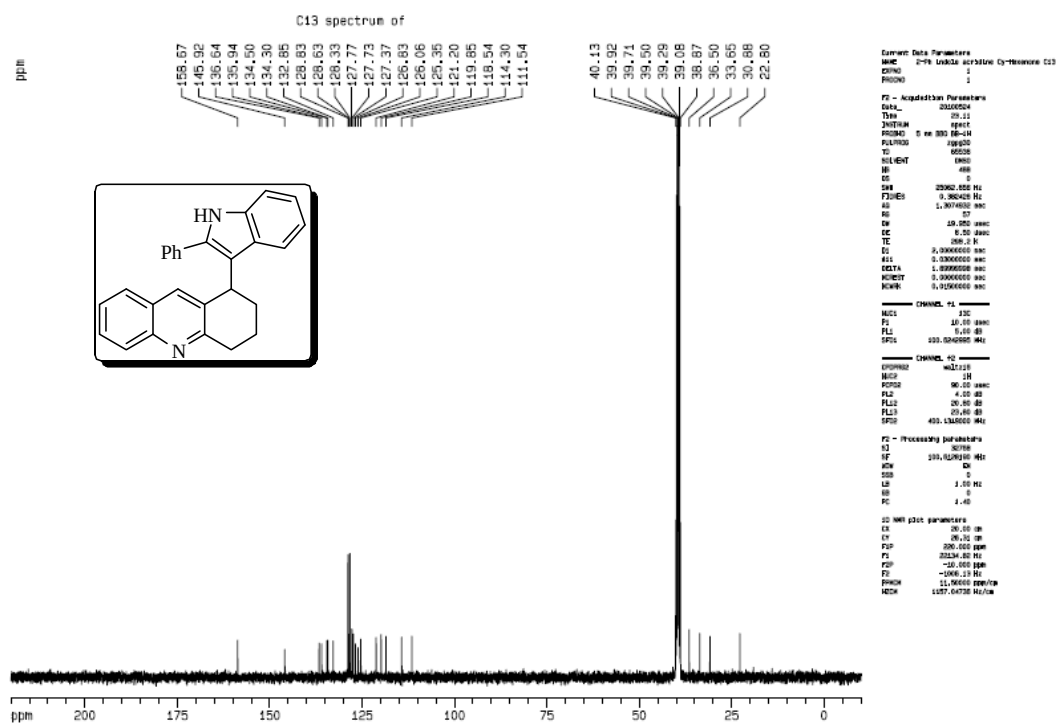
7-Bromo-1-(2-methyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8d). ¹³C NMR (400MHz, DMSO-*d*₆)



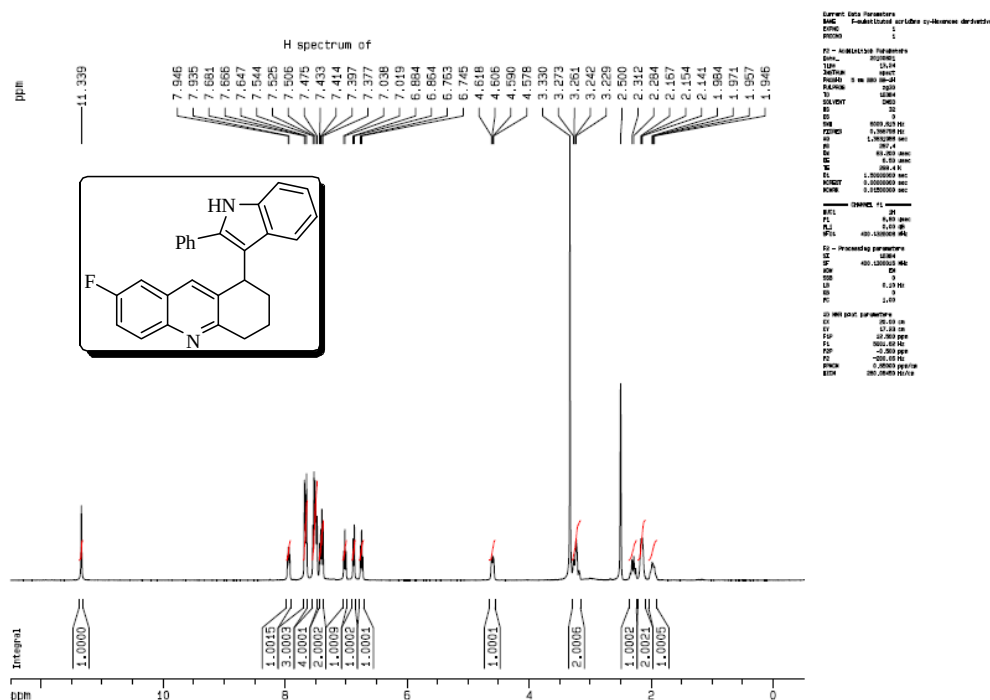
1-(2-Phenyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8e). ¹H NMR (400MHz, DMSO-*d*₆)



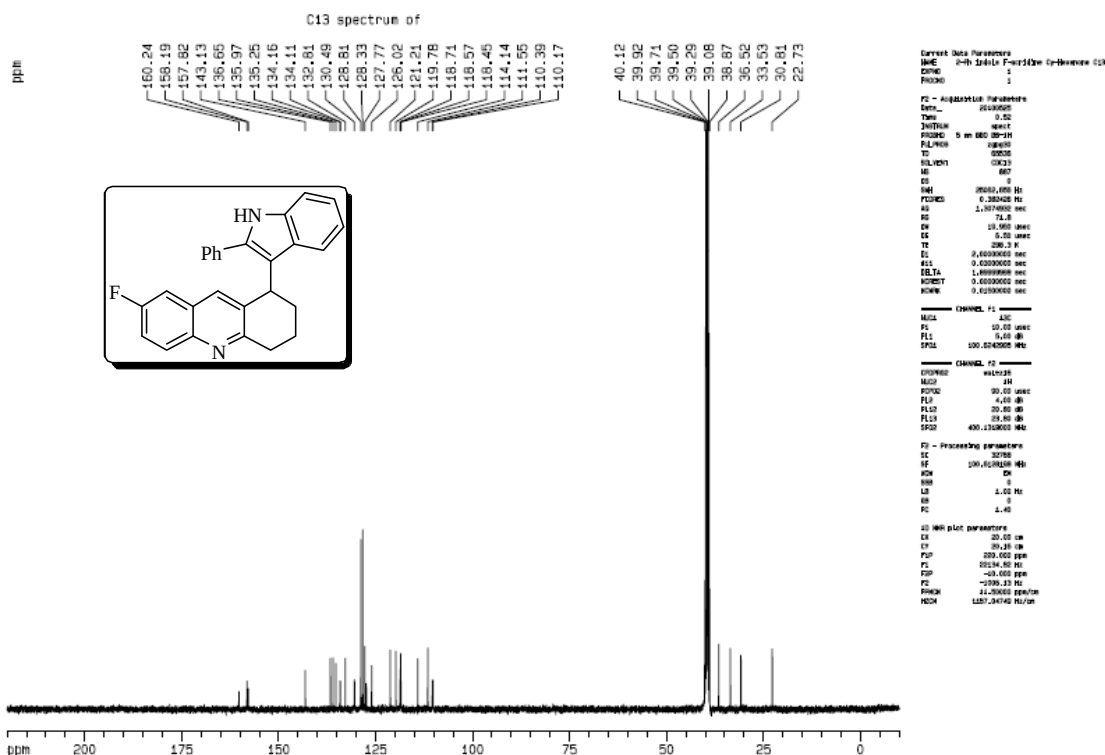
1-(2-Phenyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8e). ¹³C NMR (100 MHz, DMSO-*d*₆)



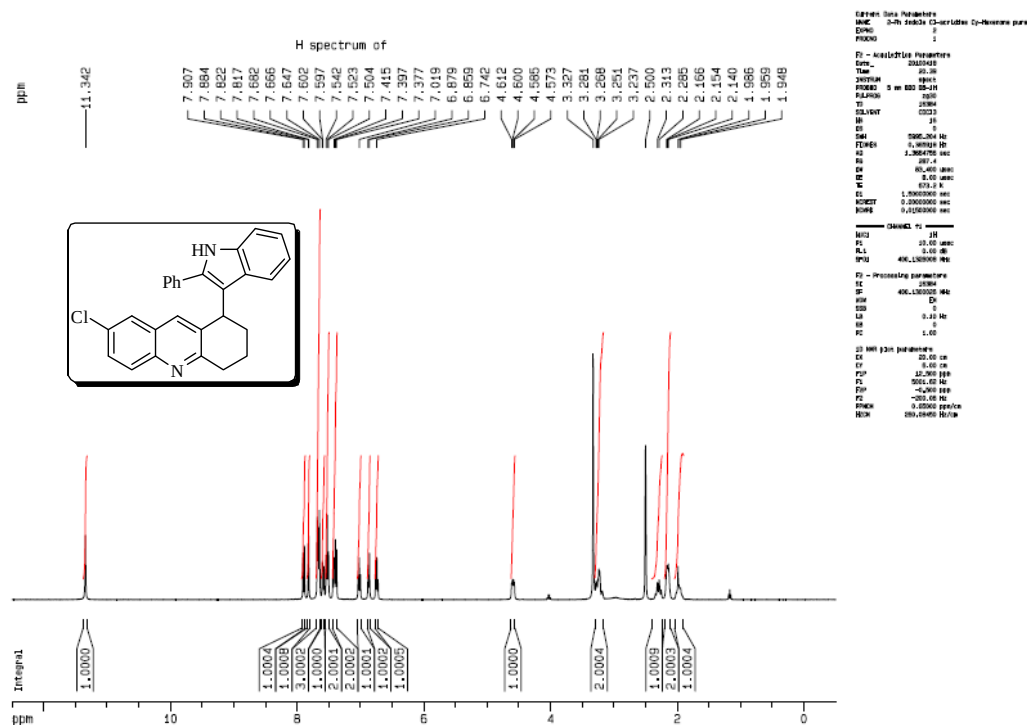
7-Fluoro-1-(2-phenyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8f). ¹H NMR (400MHz, DMSO-*d*₆)



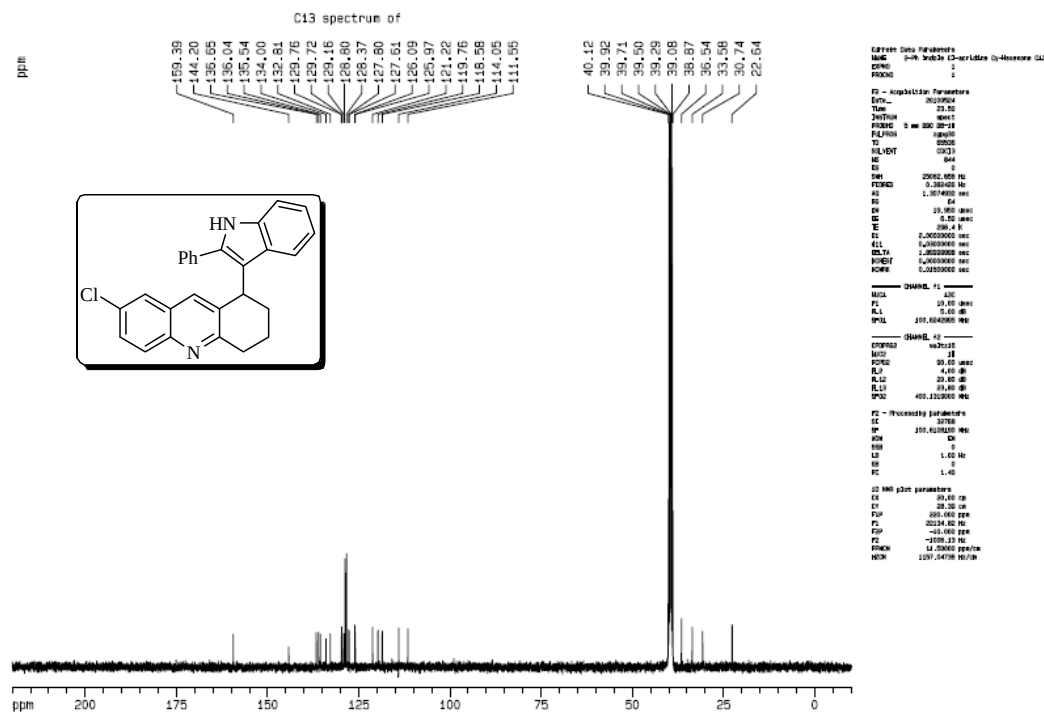
7-Fluoro-1-(2-phenyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8f). ¹³C NMR (100 MHz, DMSO-*d*₆)



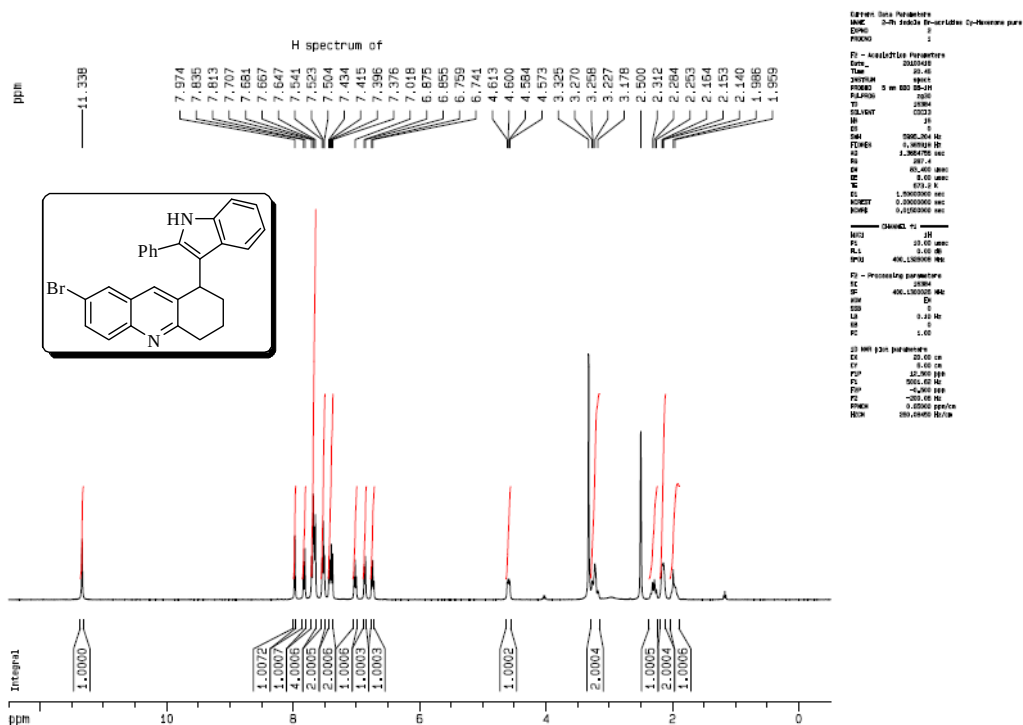
7-Chloro-1-(2-phenyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8g). ¹H NMR (400MHz, DMSO-*d*₆)



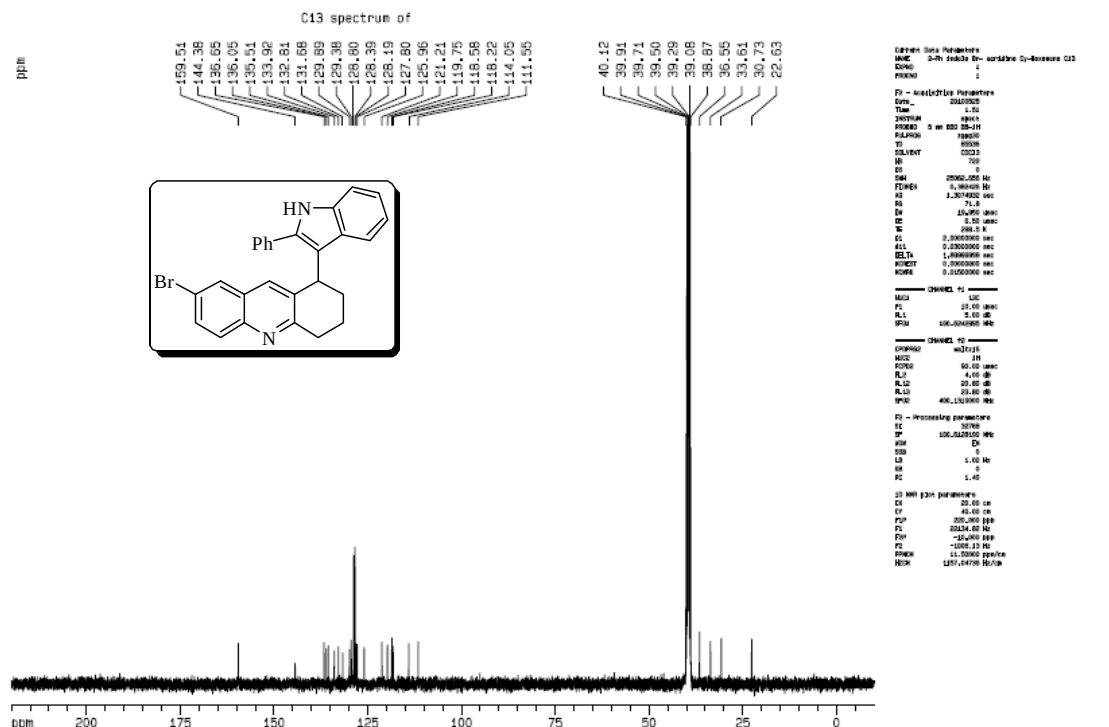
7-Chloro-1-(2-phenyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8g). ¹³C NMR (100 MHz, DMSO-*d*₆)



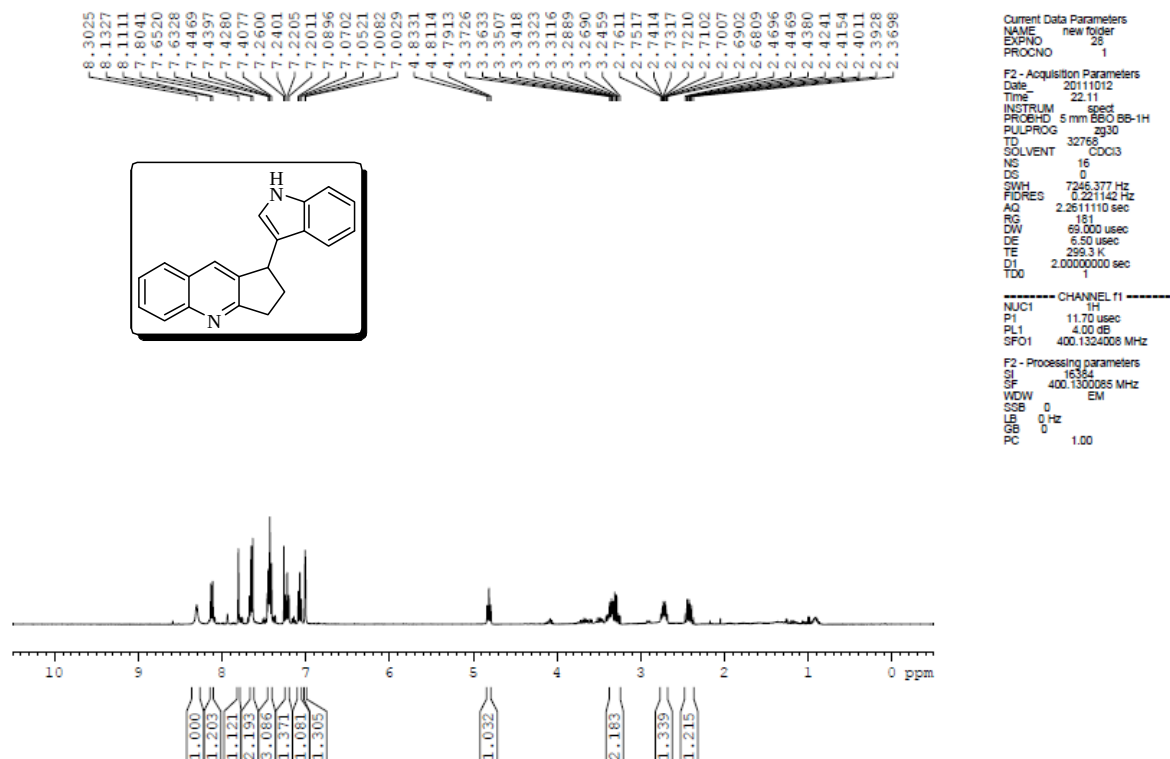
7-Bromo-1-(2-phenyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8h). ¹H NMR (400MHz, DMSO-*d*₆)



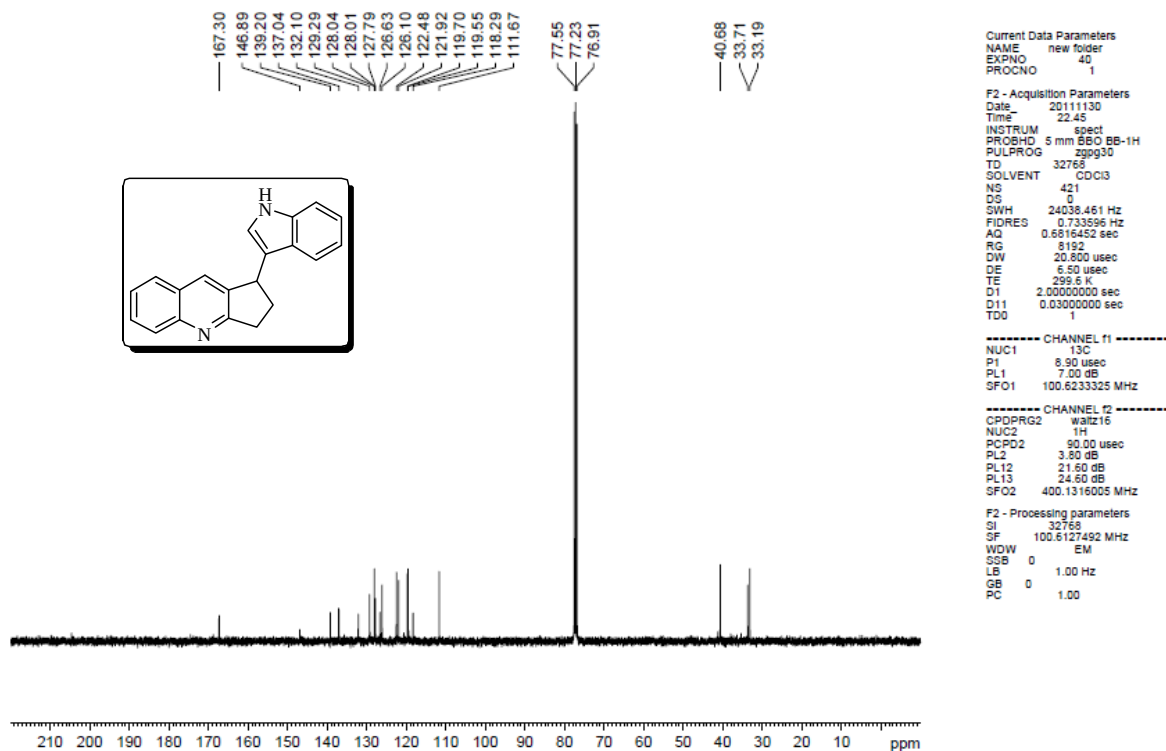
7-Bromo-1-(2-phenyl-1*H*-indol-3-yl)-1,2,3,4-tetrahydroacridine (8h). ¹³C NMR (100 MHz, DMSO-*d*₆)



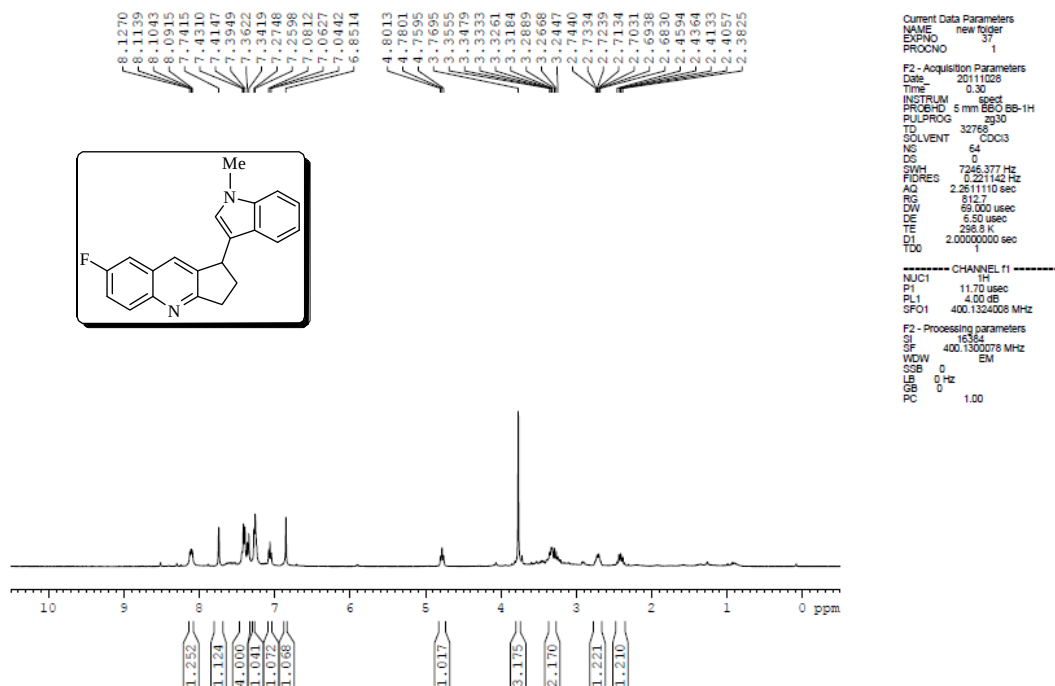
1-(1*H*-Indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (8i). ¹H NMR (400MHz, CDCl₃)



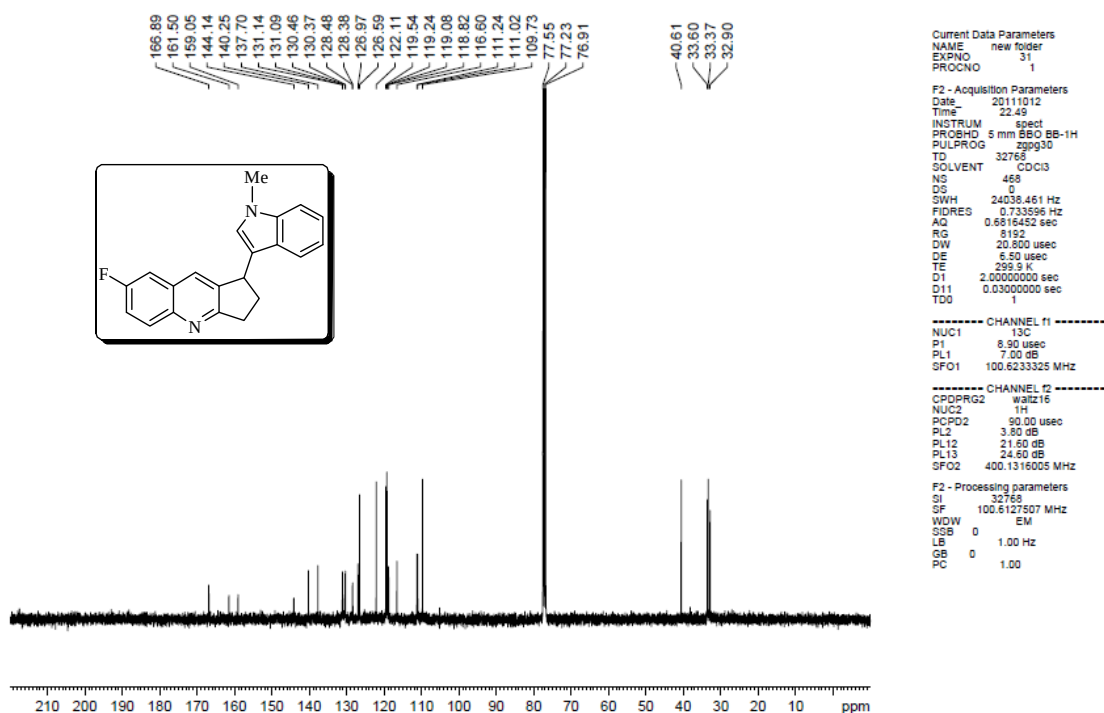
1-(1*H*-Indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (8i). ¹³C NMR (400MHz, CDCl₃)



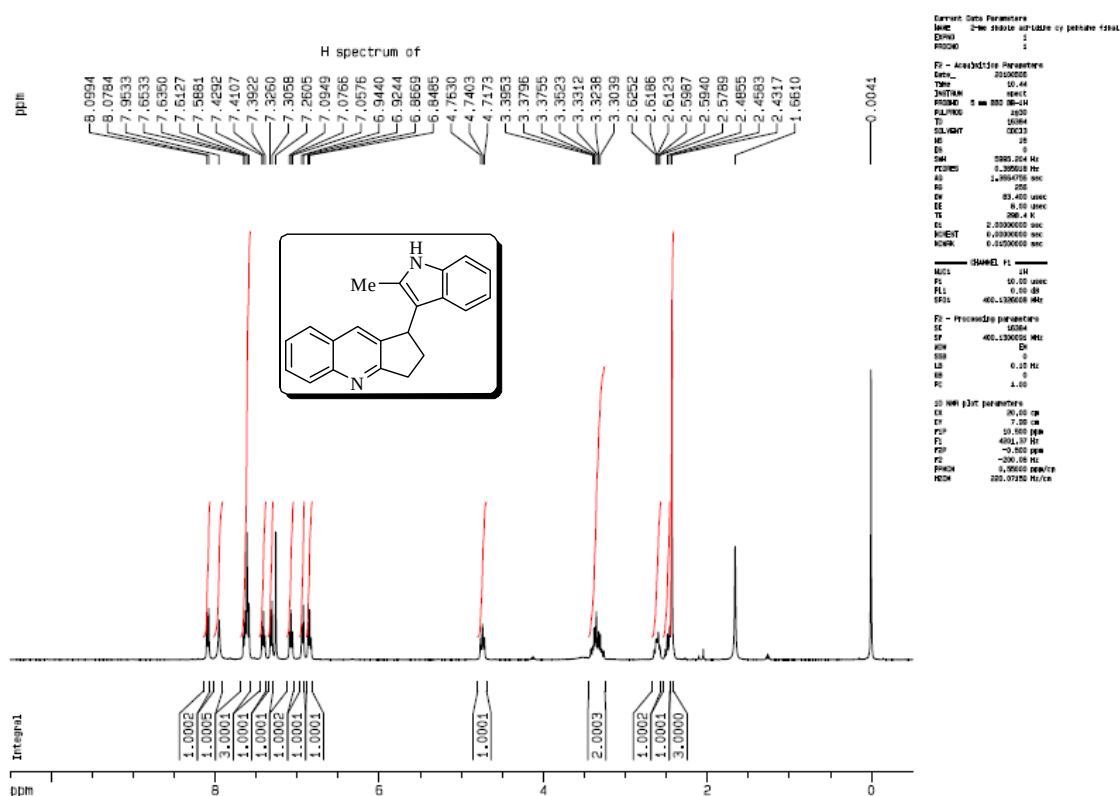
7-Fluoro-1-(1-methyl-1*H*-indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (8j). ¹H NMR (400MHz, CDCl₃)



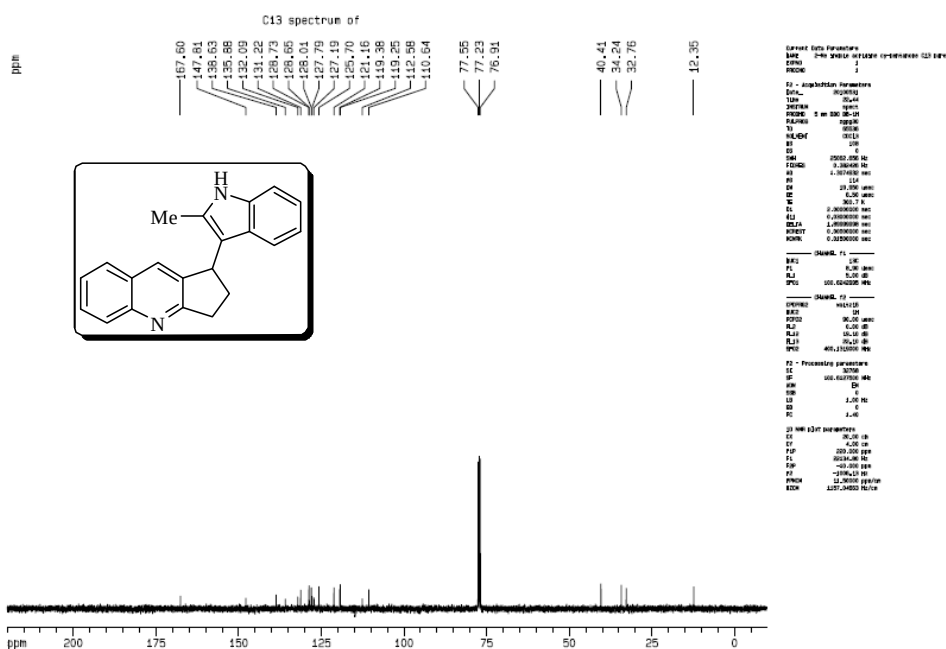
7-Fluoro-1-(1-methyl-1*H*-indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (8j). ¹³C NMR (400MHz, CDCl₃)



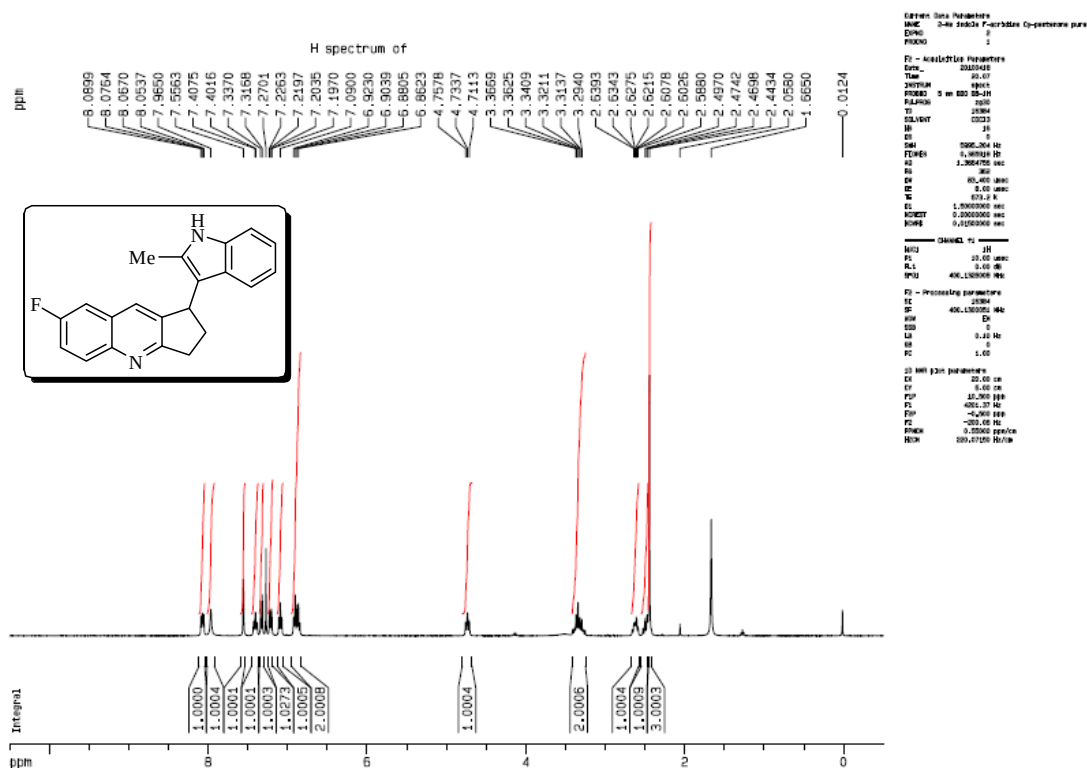
1-(2-Methyl-1*H*-indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (8k). ¹H NMR (400MHz, CDCl₃)



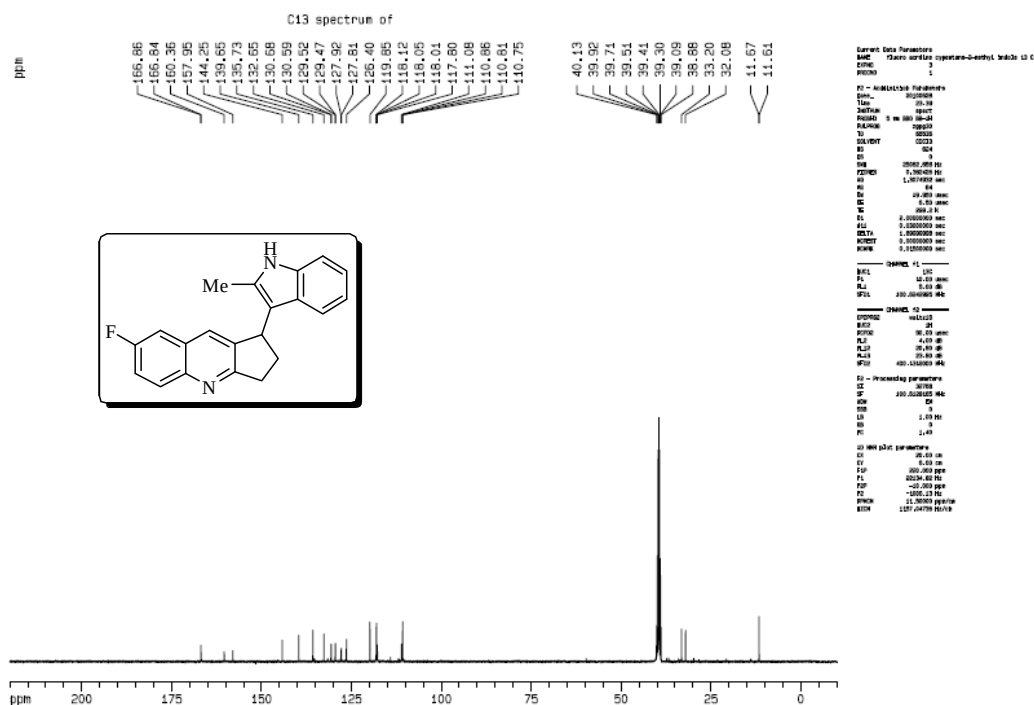
1-(2-Methyl-1*H*-indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (8k). ¹³C NMR (100 MHz, CDCl₃)



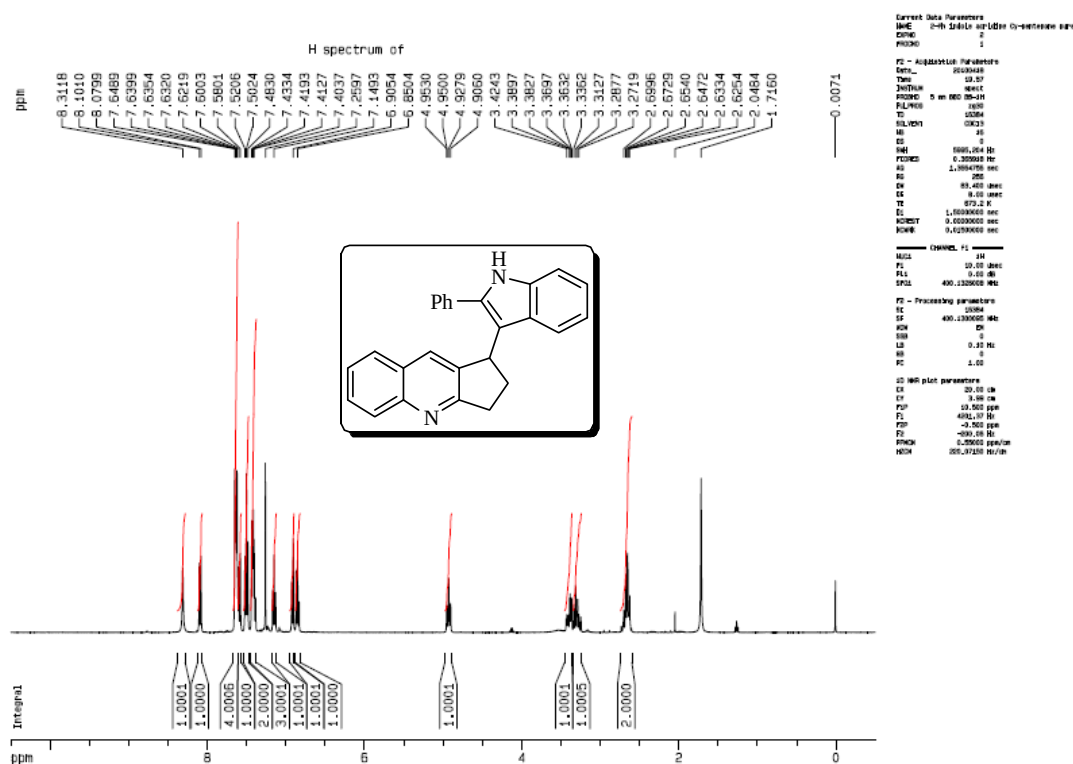
7-Fluoro-1-(2-methyl-1*H*-indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (8l). ¹H NMR (400MHz, CDCl₃)



7-Fluoro-1-(2-methyl-1*H*-indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (8l). ¹³C NMR (100 MHz, DMSO-*d*₆)



1-(2-Phenyl-1*H*-indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline(8m). ¹H NMR (400MHz, CDCl₃)



1-(2-Phenyl-1*H*-indol-3-yl)-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (8m). ¹³C NMR (100 MHz, CDCl₃)

