

Supporting Information

Palladium-Catalyzed Regio- and Stereoselective Synthesis of Aryl and 3-Indolyl Substituted-4-Methylene- isoquinolin-1(2*H*)-ones.

V. Nori^a, A. Arcadi^a, A. Carlone^a, M. Chiarini^b, F. Marinelli^a

a) Dipartimento di Scienze Fisiche e Chimiche, Università di L'Aquila, Via Vetoio, 67010 Coppito (AQ), Italy.

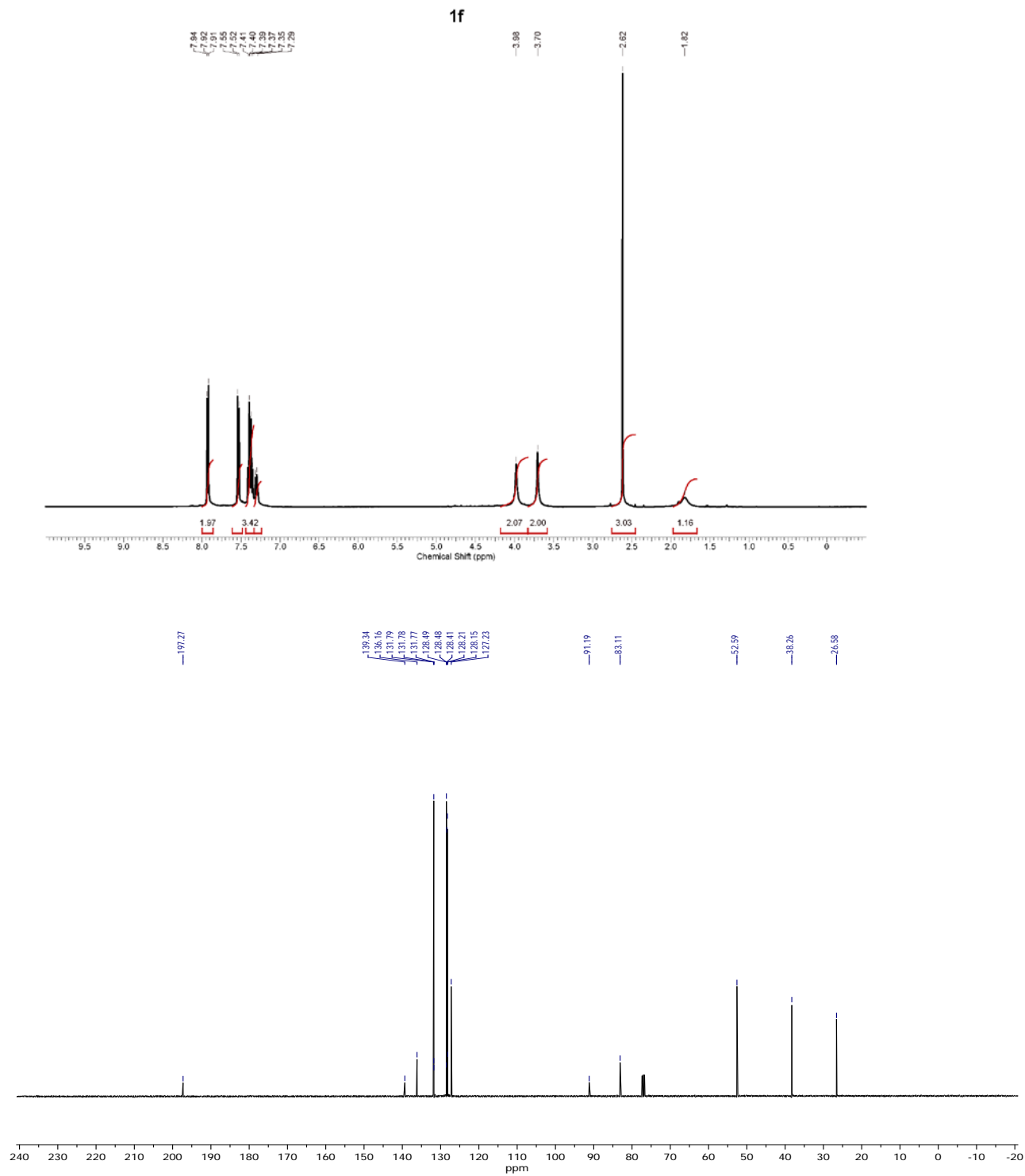
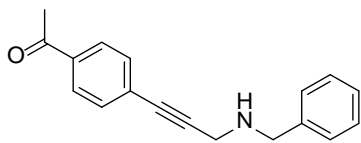
b) Facoltà di Bioscienze e Tecnologie Agro-alimentari e Ambientali, Università di Teramo, Via Balzarini 1, 64100 Teramo (Te), Italy

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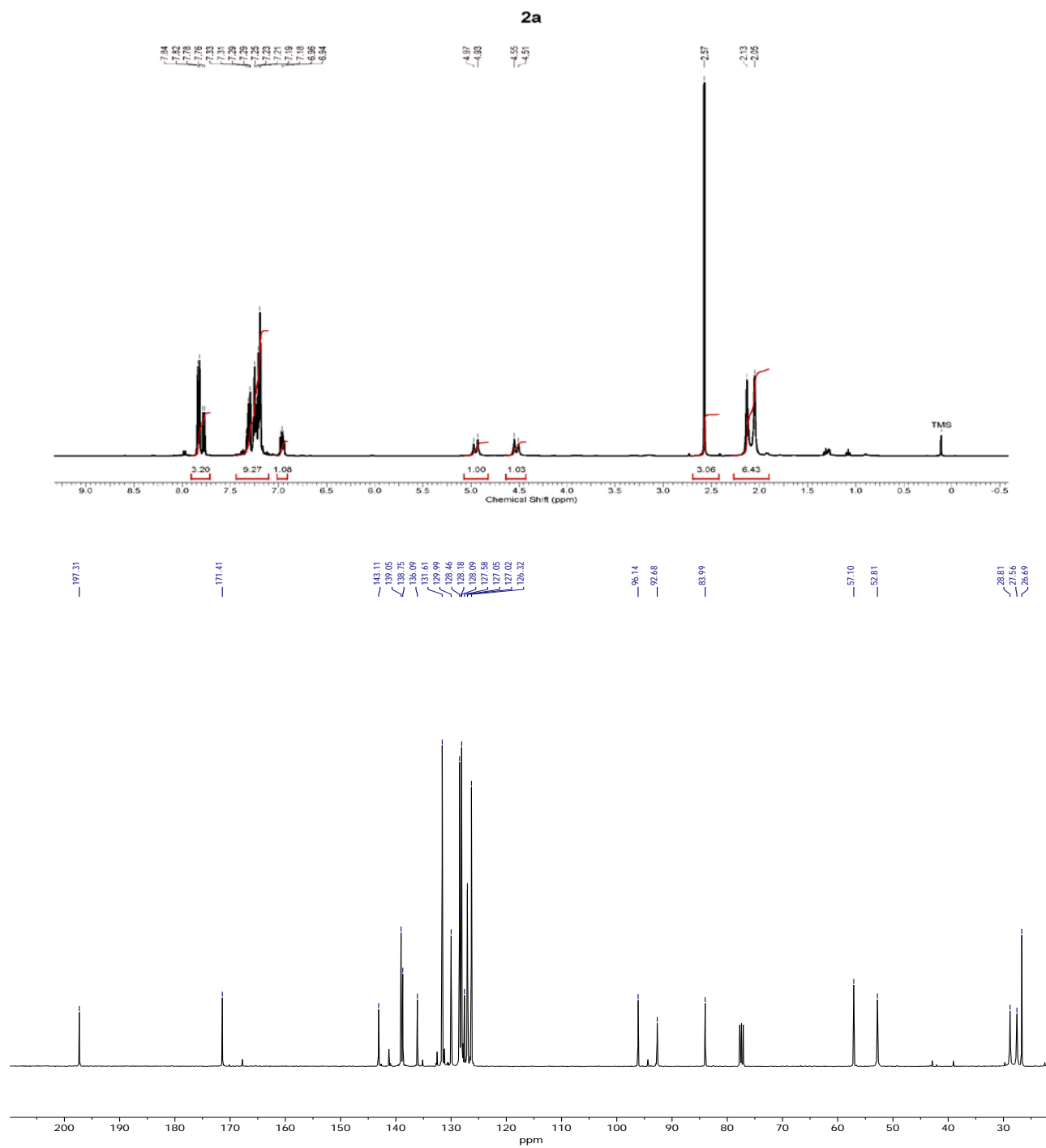
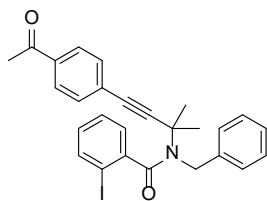
NMR data

¹ H and ¹³ C NMR of all new compounds.....	S 02-28
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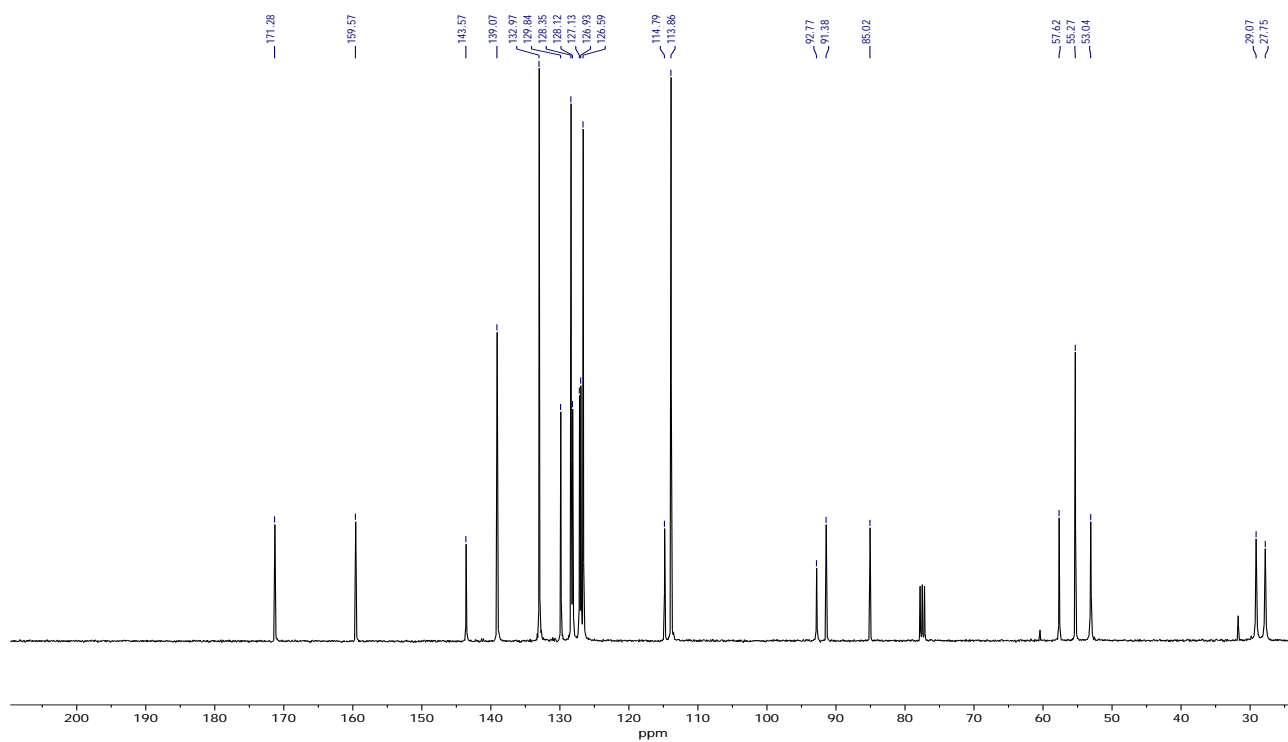
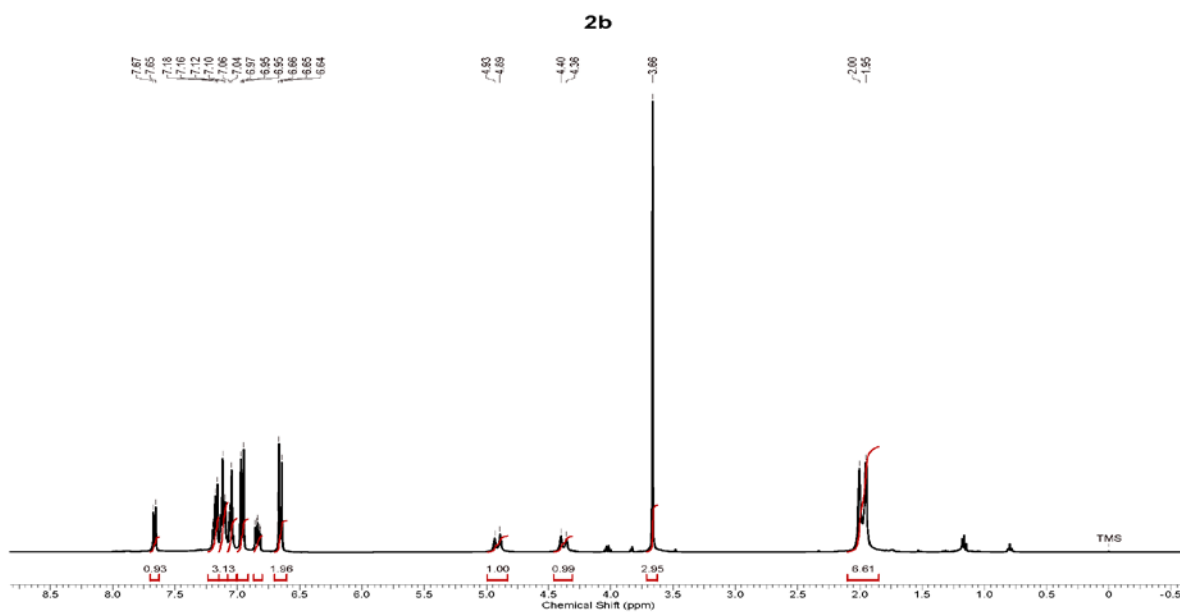
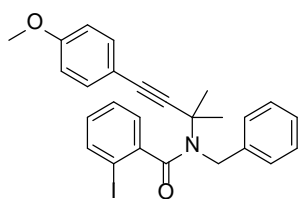
1-(4-(3-(benzylamino)prop-1-yn-1-yl)phenyl)ethenone (1f)



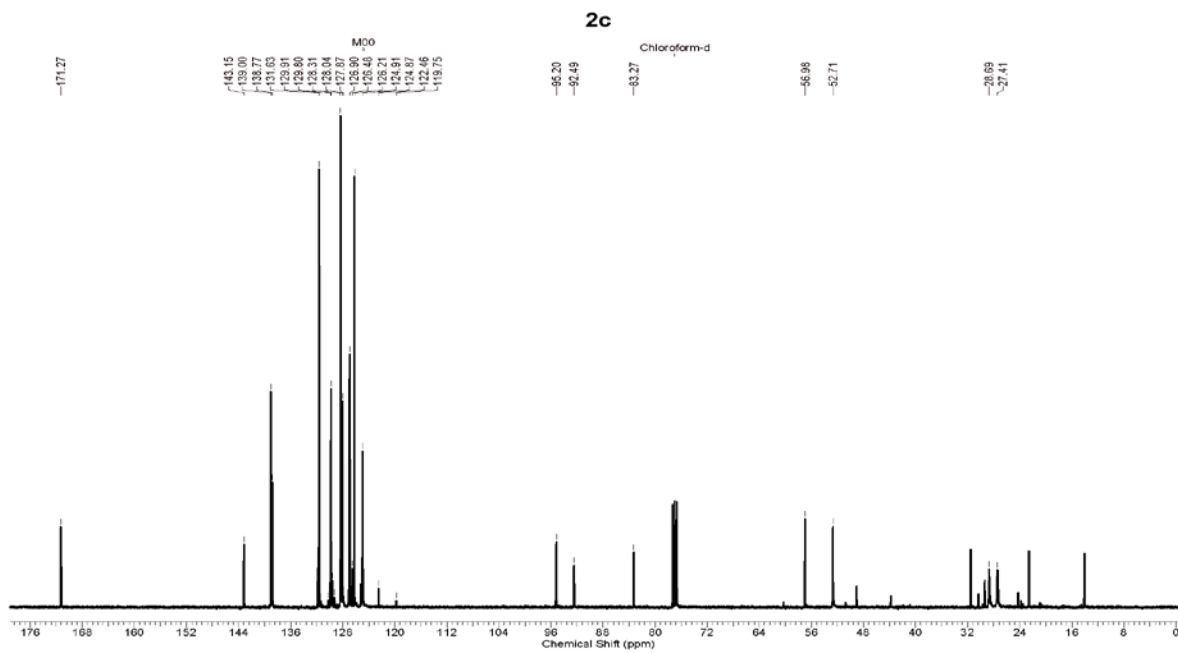
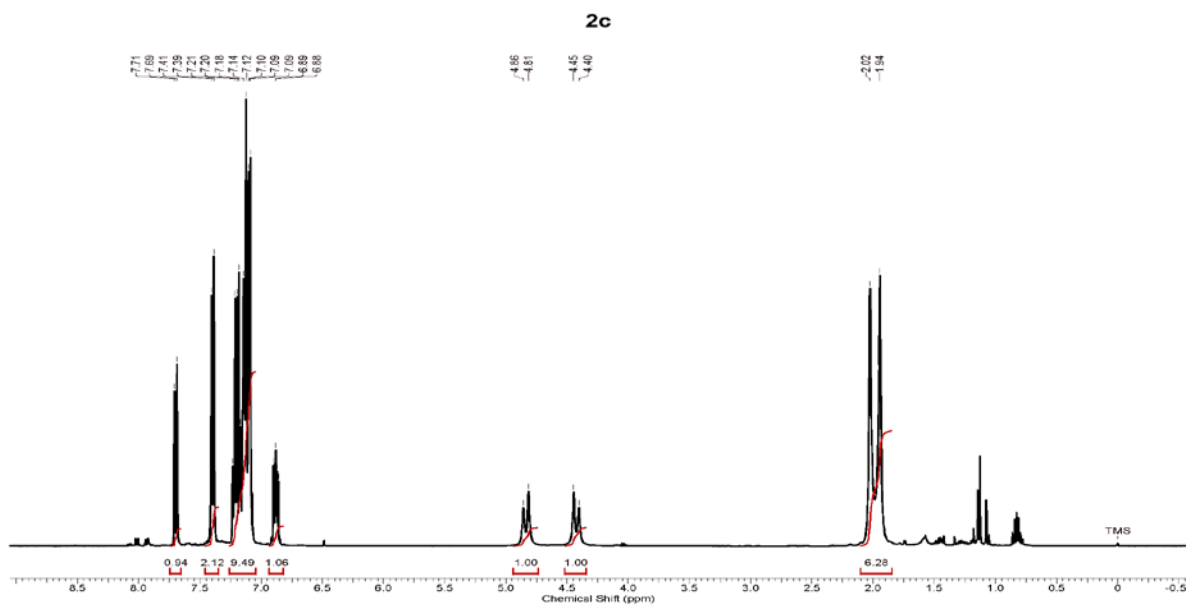
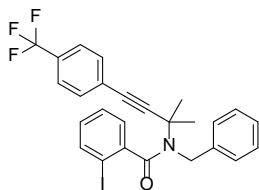
N-(4-(4-acetylphenyl)-2-methylbut-3-yn-2-yl)-N-benzyl-2-iodobenzamide (2a)



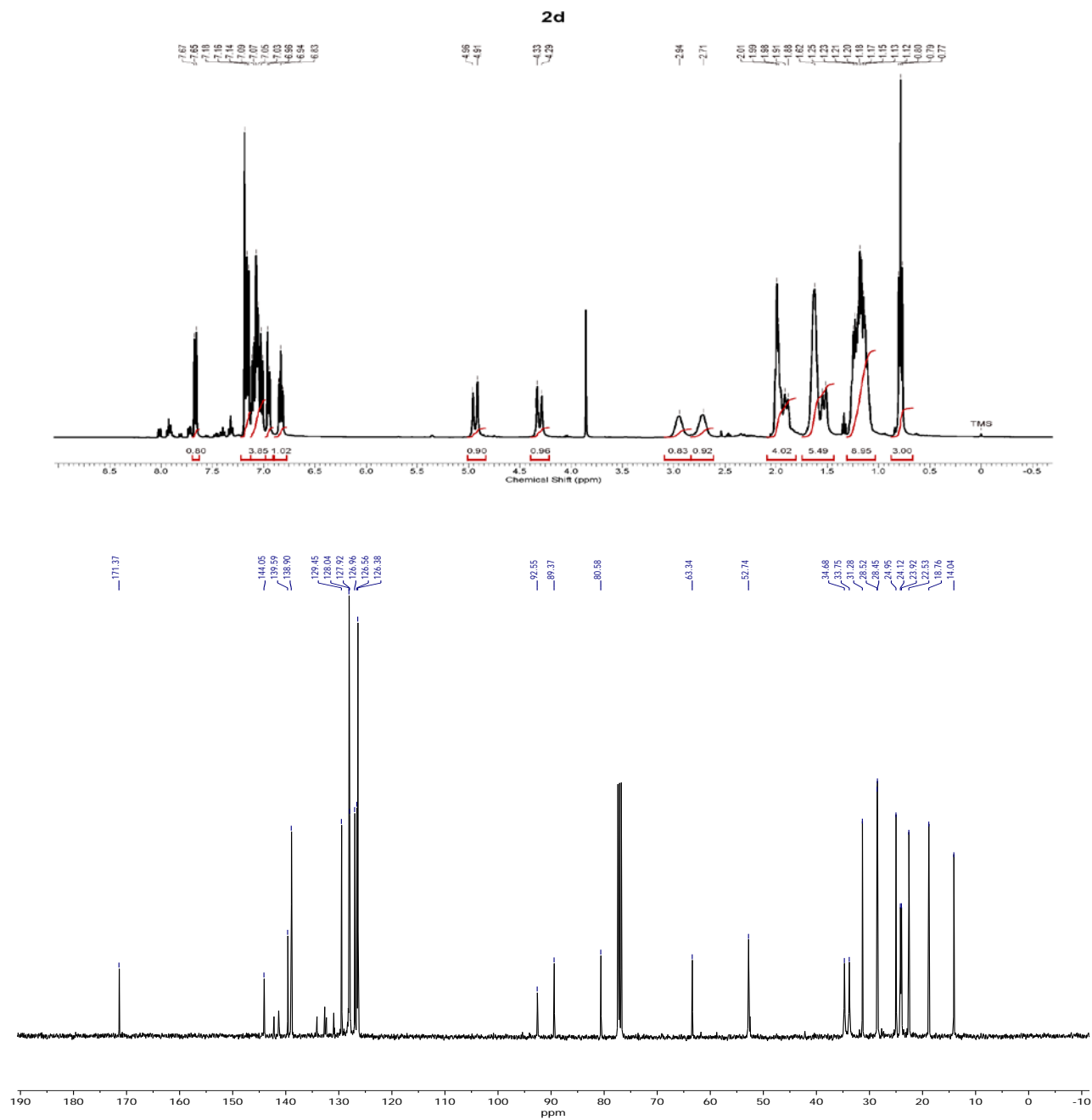
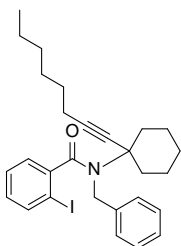
N-benzyl-2-iodo-N-(4-(4-methoxyphenyl)-2-methylbut-3-yn-2-yl)benzamide (2b)



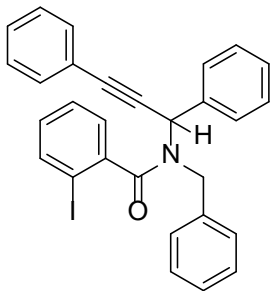
N-benzyl-2-iodo-N-(2-methyl-4-(4-(trifluoromethyl)phenyl)but-3-yn-2-yl)benzamide (2c)



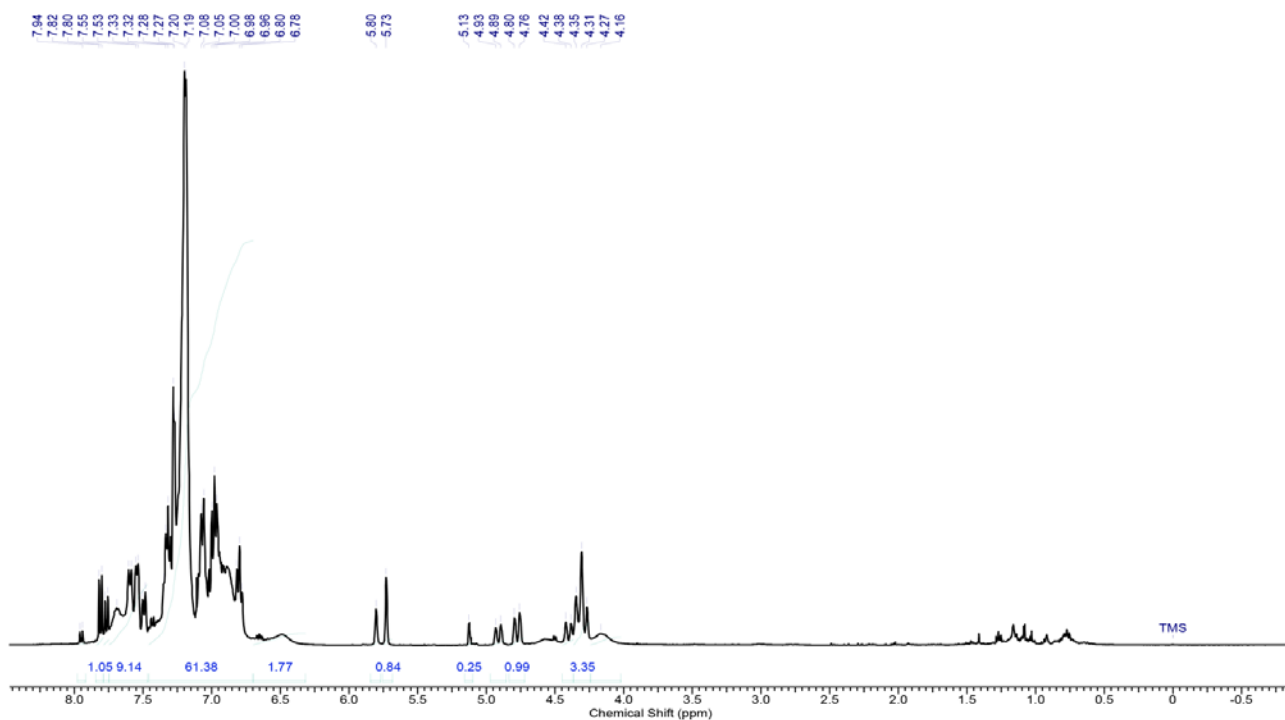
N-benzyl-2-iodo-N-(1-(oct-1-yn-1-yl)cyclohexyl)benzamide (2d)



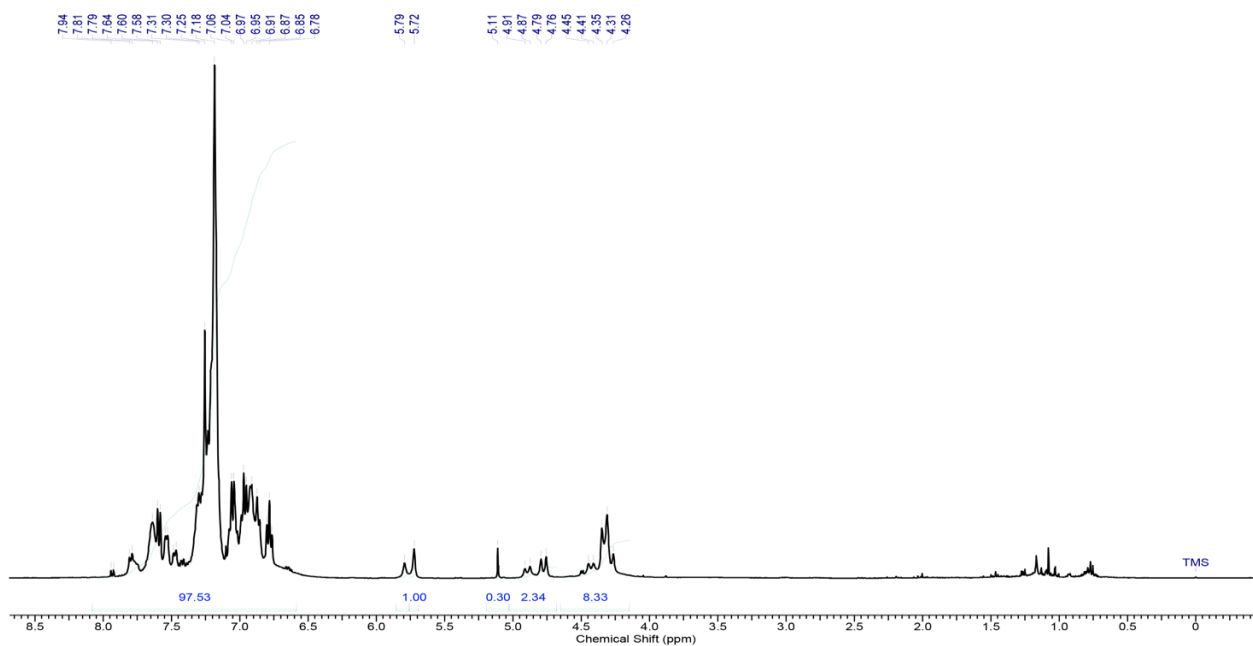
N-benzyl-N-(1,3-diphenylprop-2-yn-1-yl)-2-iodobenzamide (complex mixture of slowly interconverting amide geometric 1*S*,1*E*/1*S*,1*Z* and 1*R*,1*E*/1*R*,1*Z* isomers) (2e)



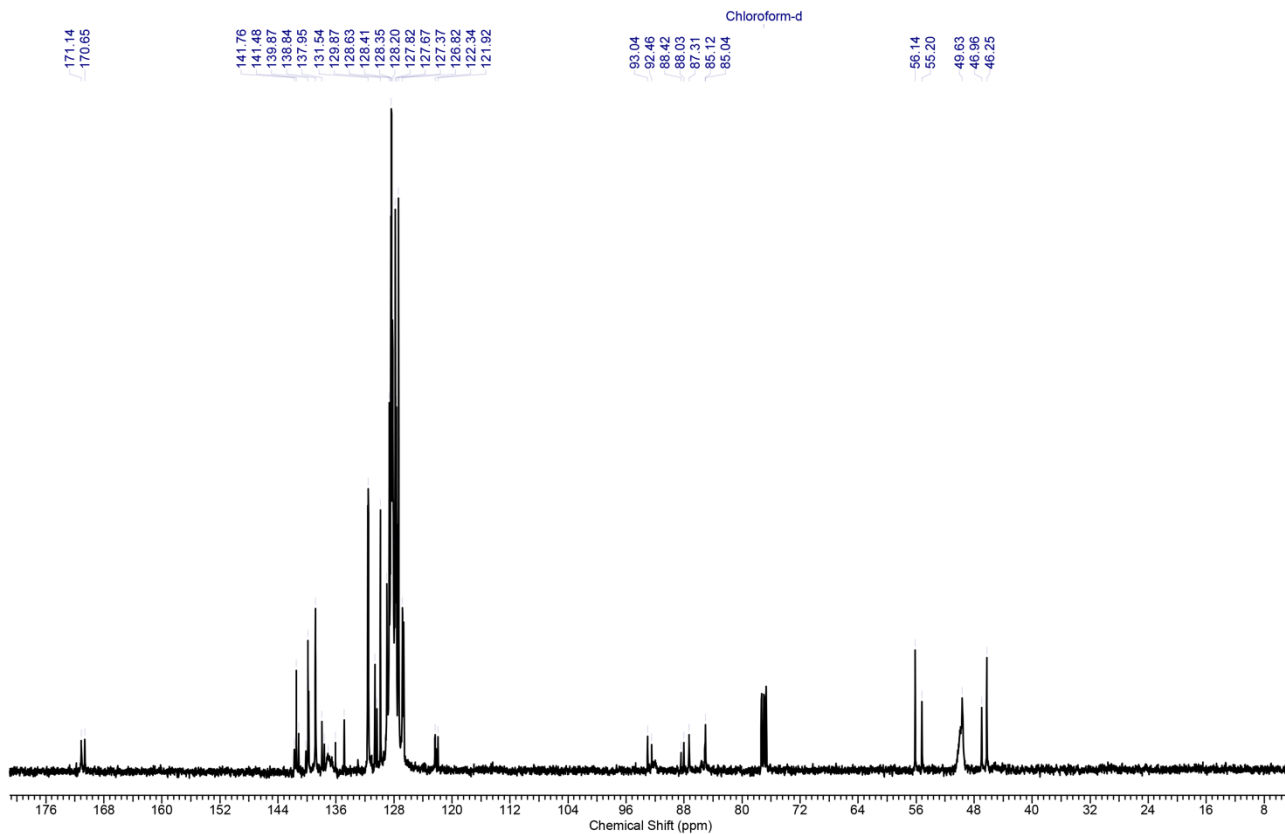
spectrum at 303 K



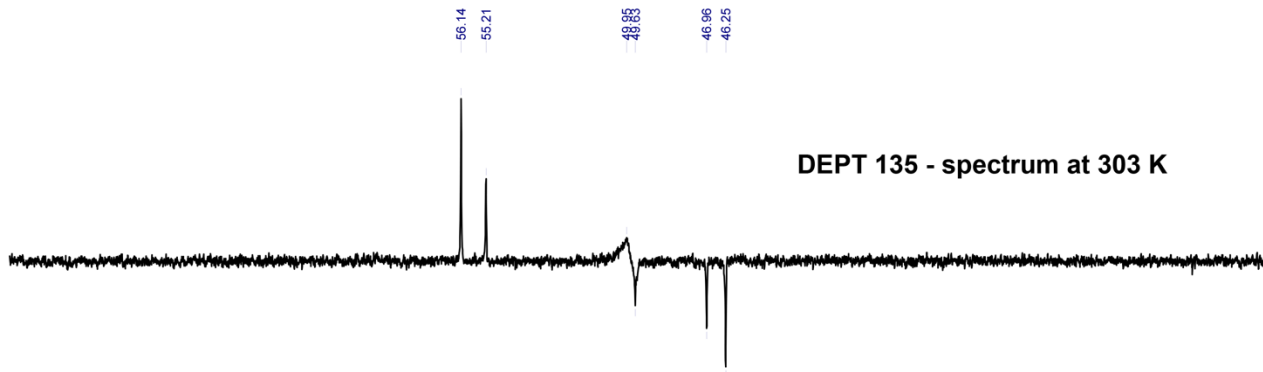
spectrum at 323 K



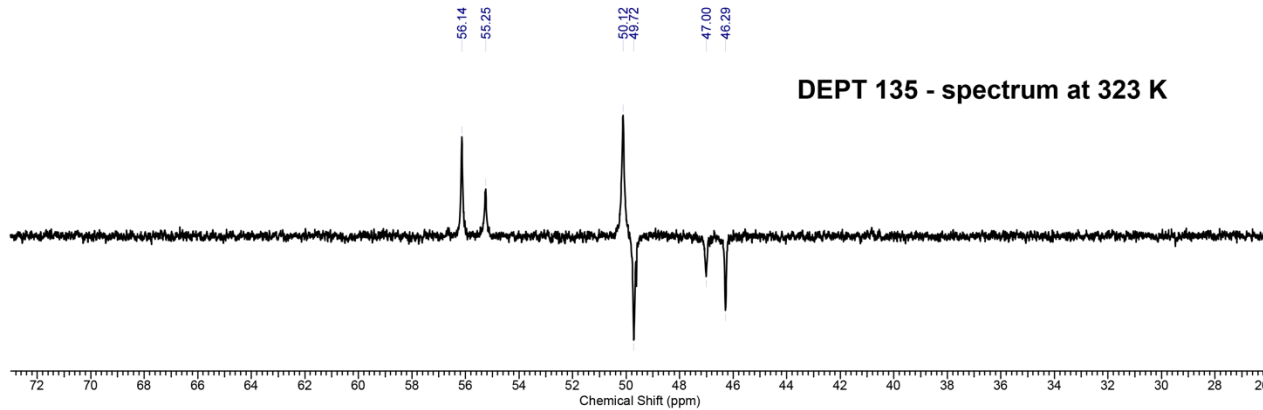
spectrum at 303 K



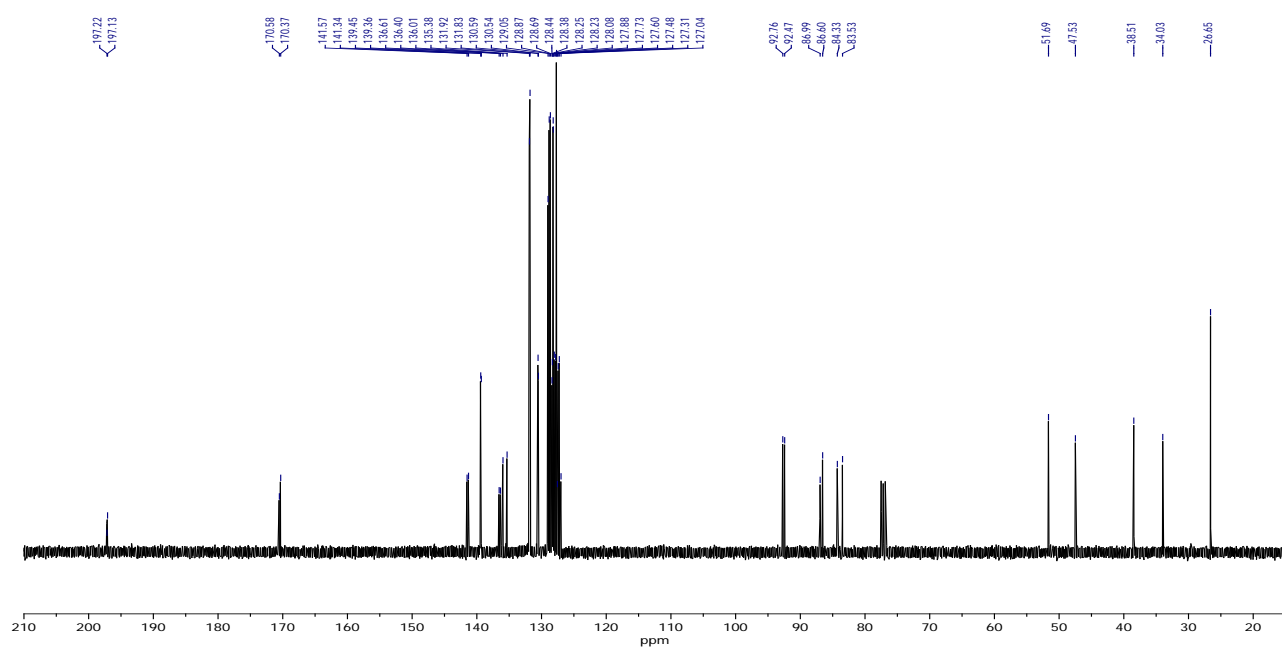
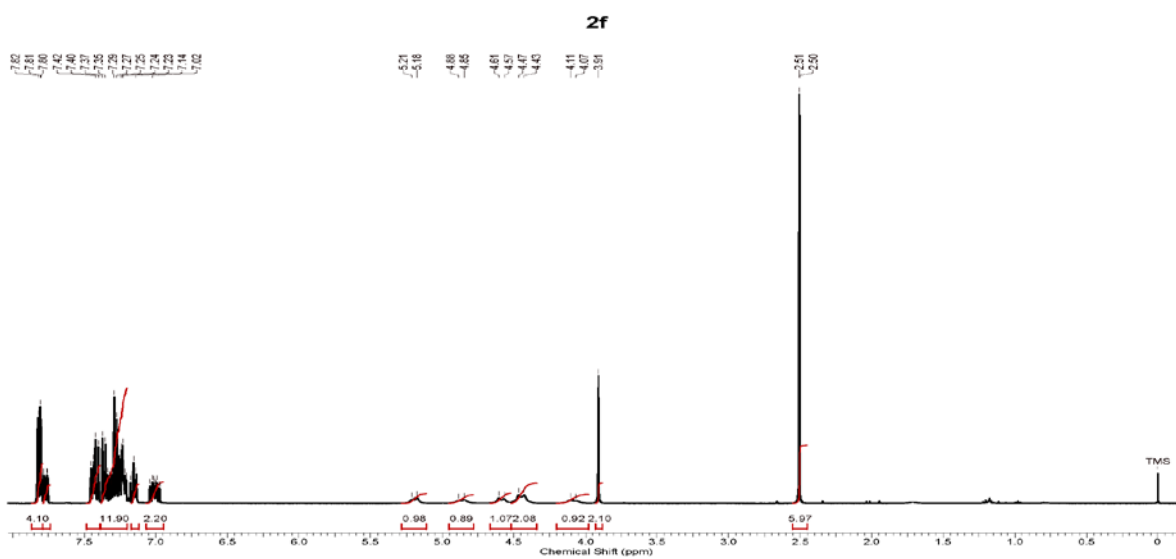
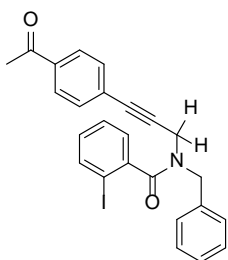
DEPT 135 - spectrum at 303 K



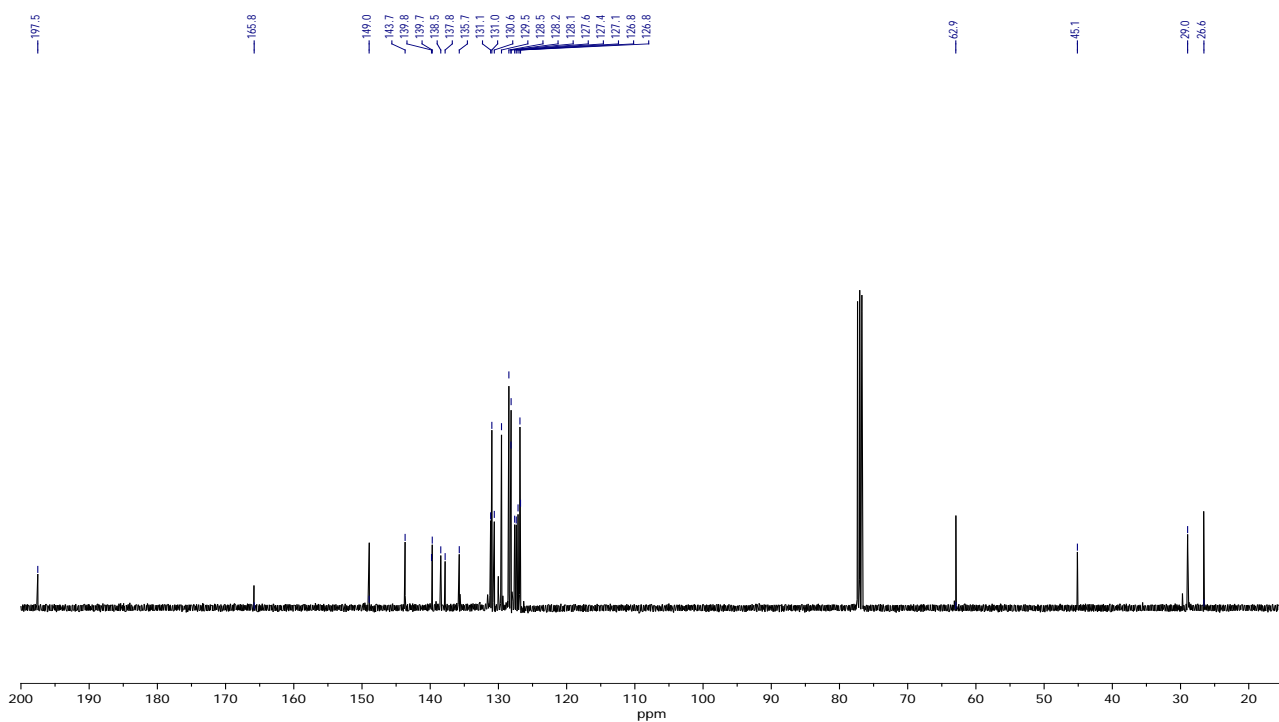
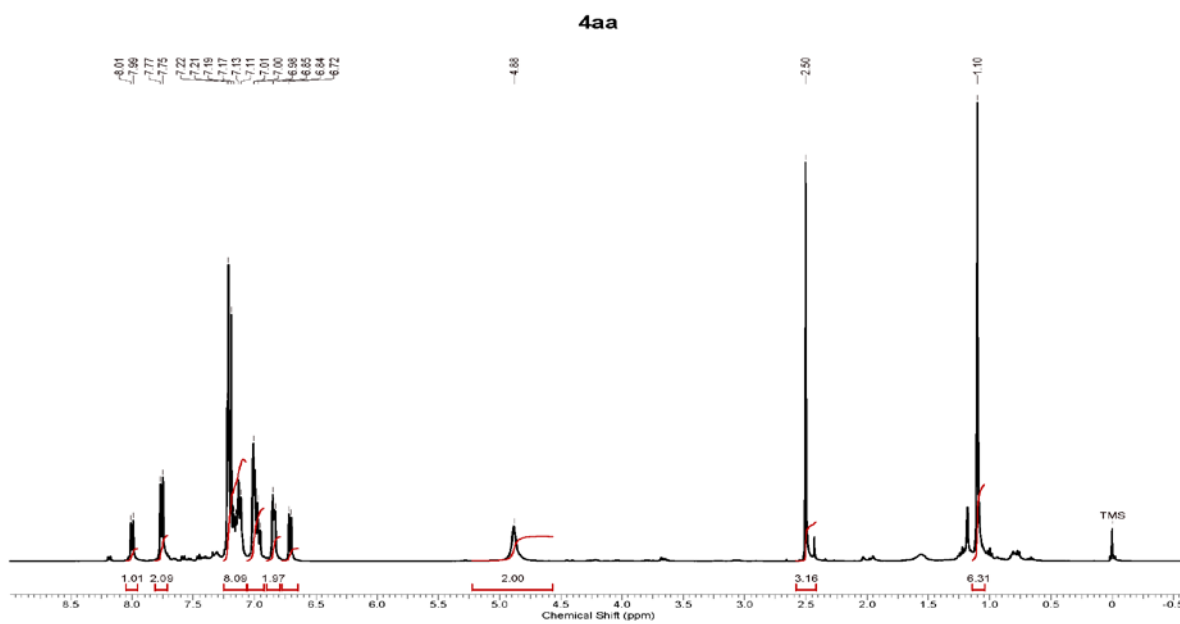
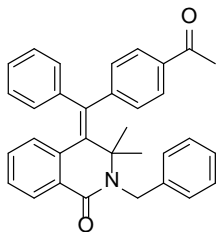
DEPT 135 - spectrum at 323 K



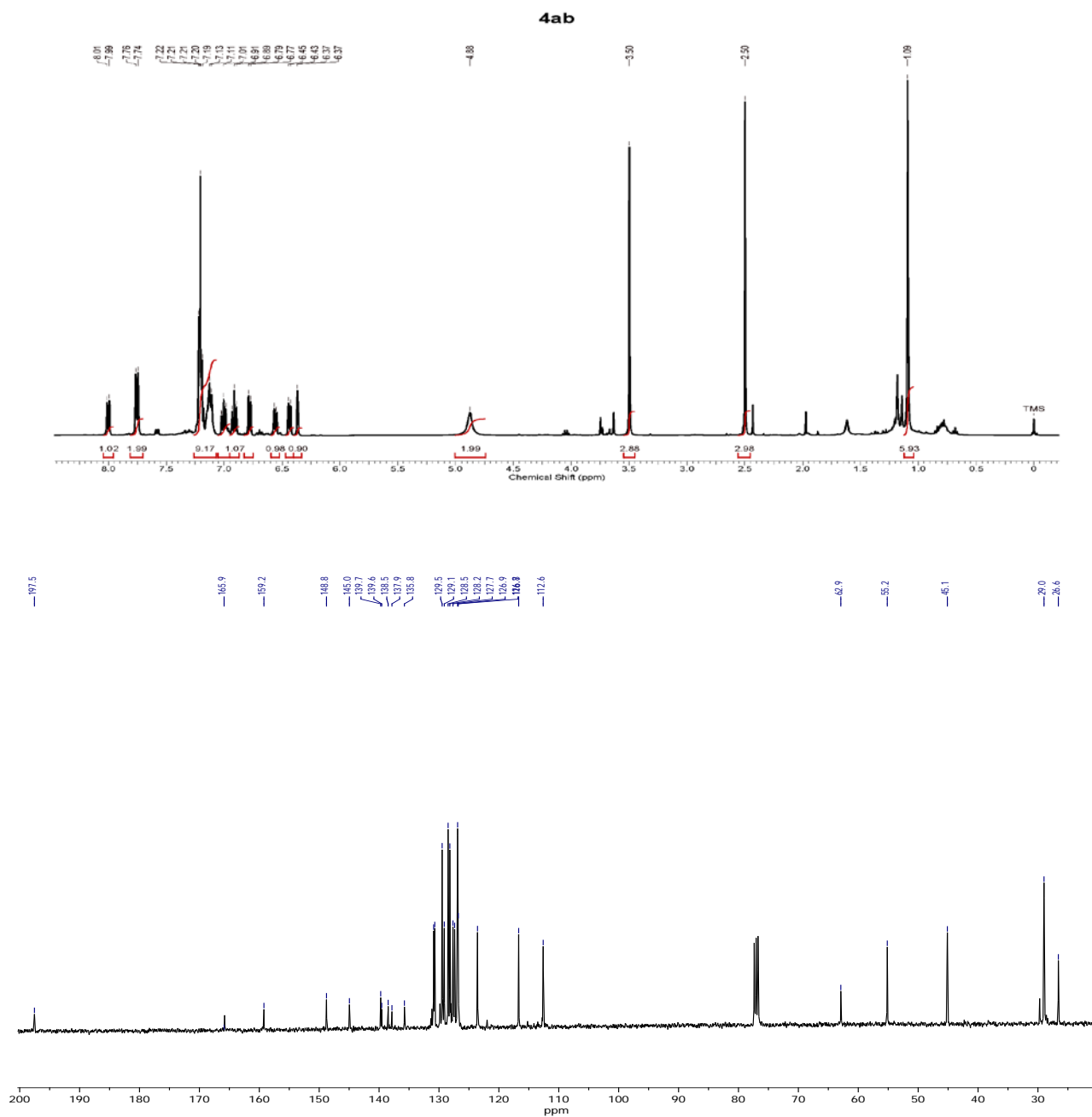
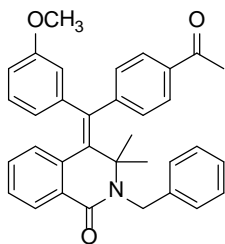
N-(3-(4-acetylphenyl)prop-2-yn-1-yl)-N-benzyl-2-iodobenzamide (mixture of slowly interconverting geometric *E/Z* isomers) (2f)



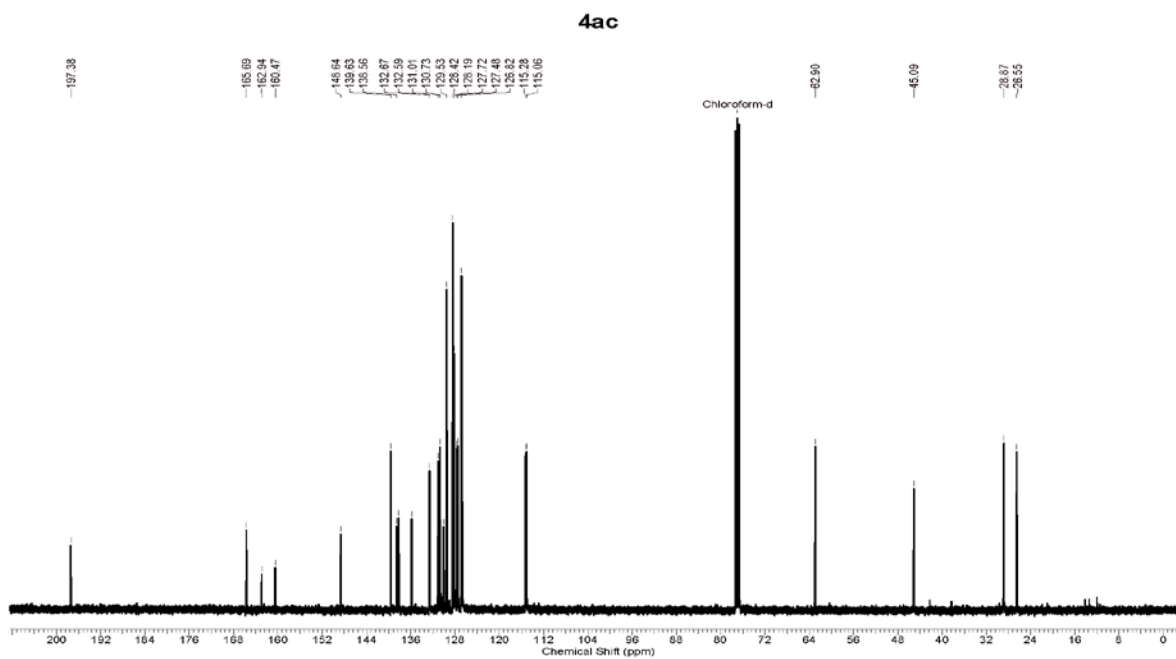
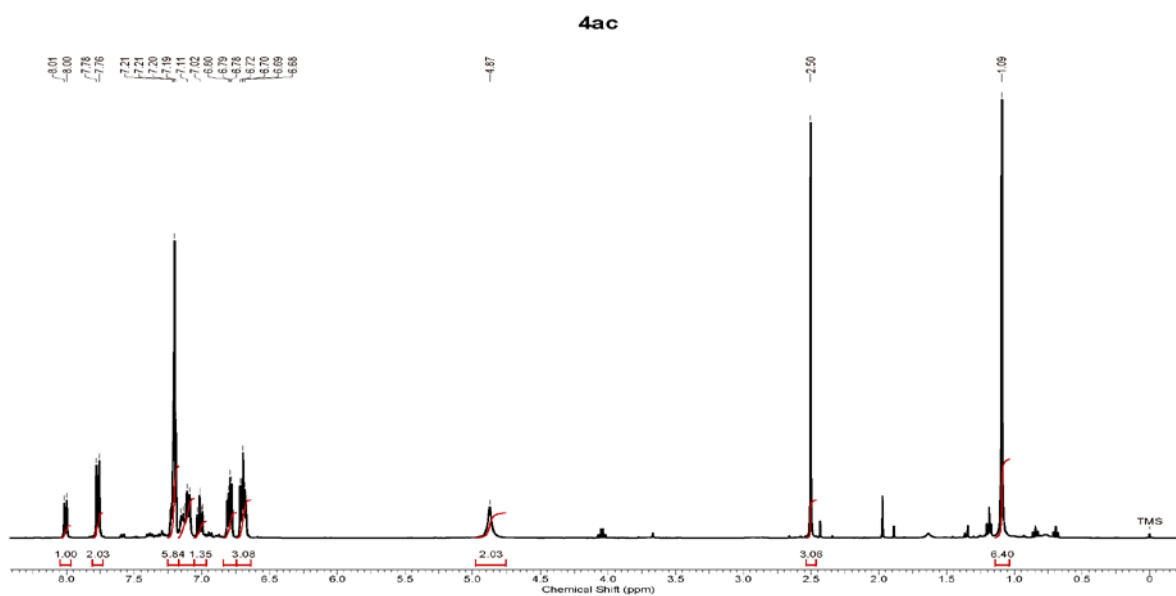
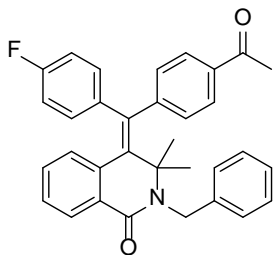
(Z)-4-((4-acetylphenyl)(phenyl)methylene)-2-benzyl-3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (4aa)



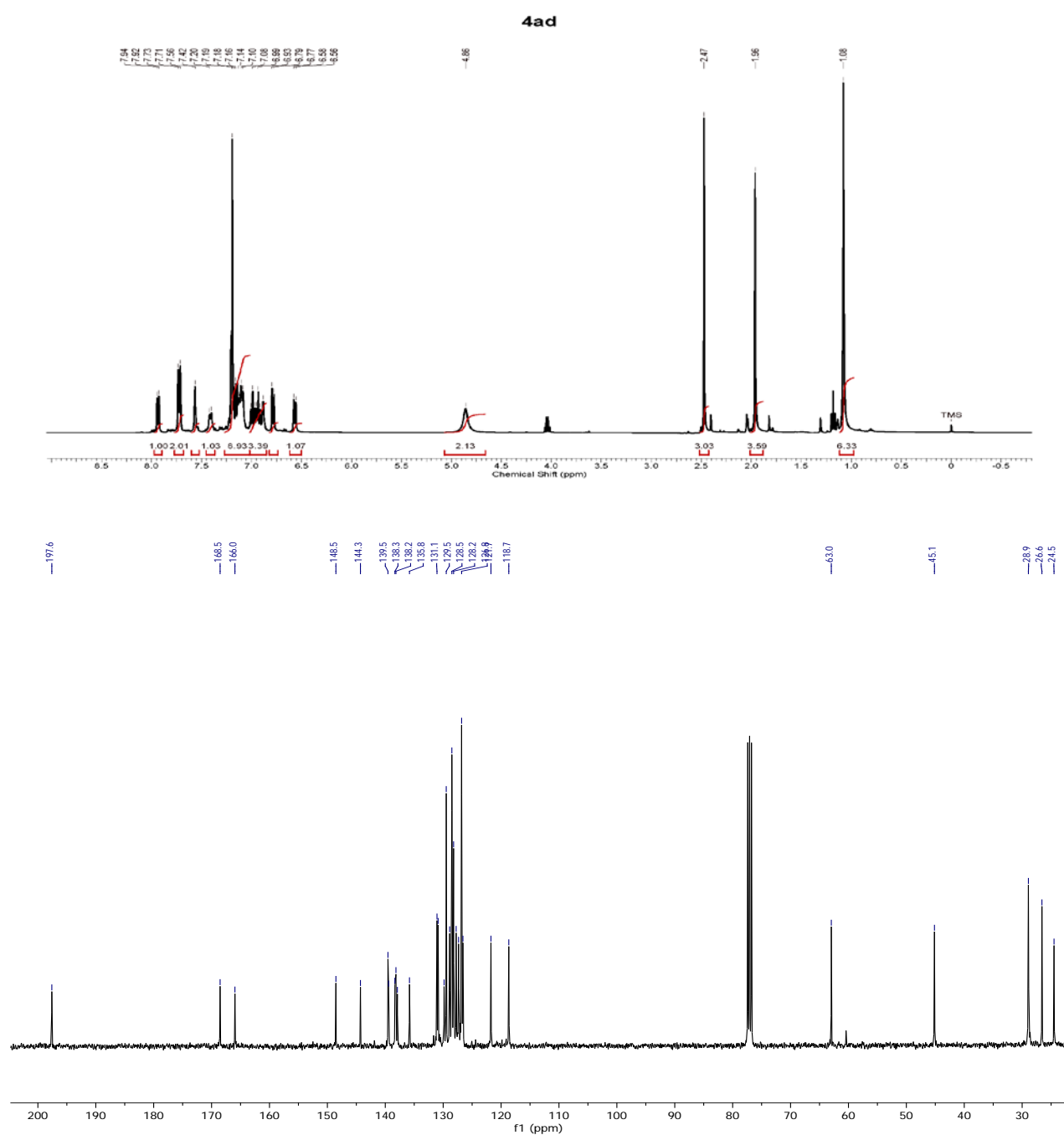
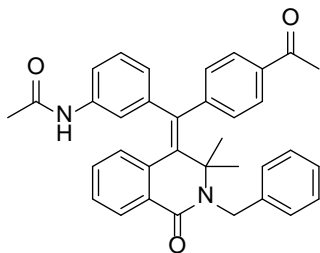
(E)-4-((4-acetylphenyl)(3-methoxyphenyl)methylene)-2-benzyl-3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (4ab)



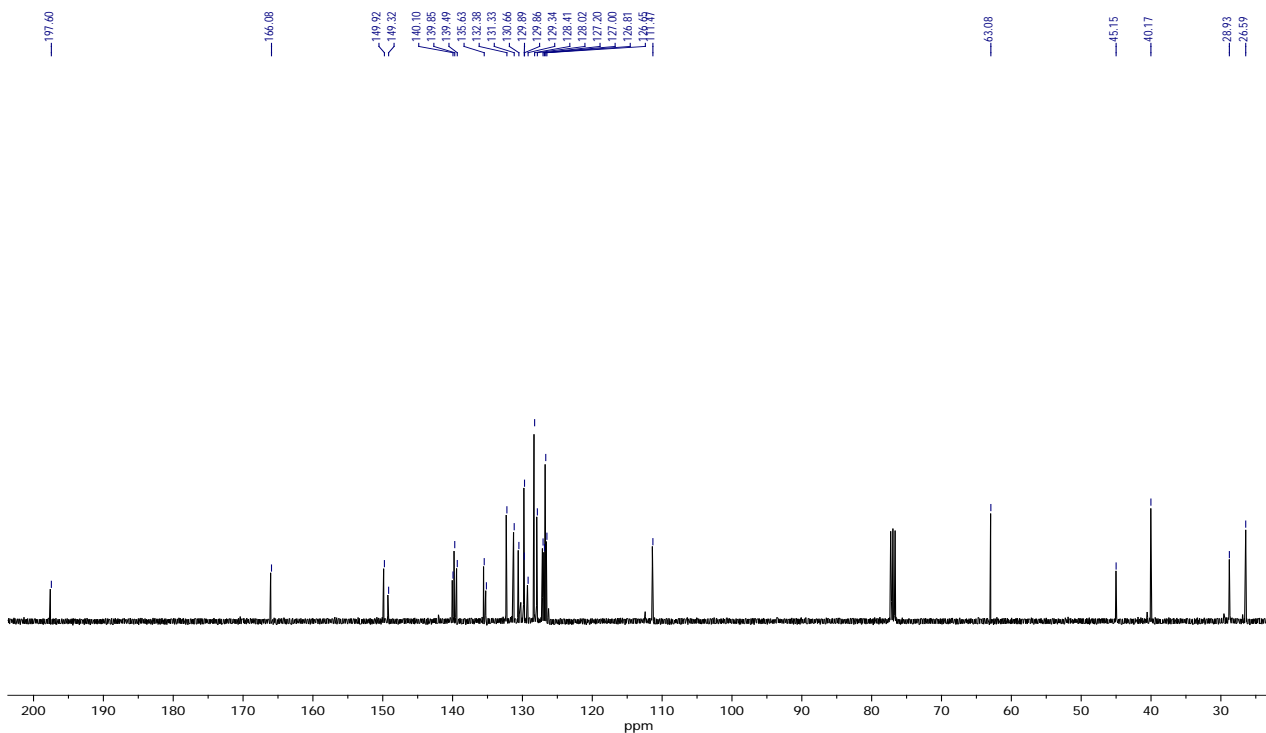
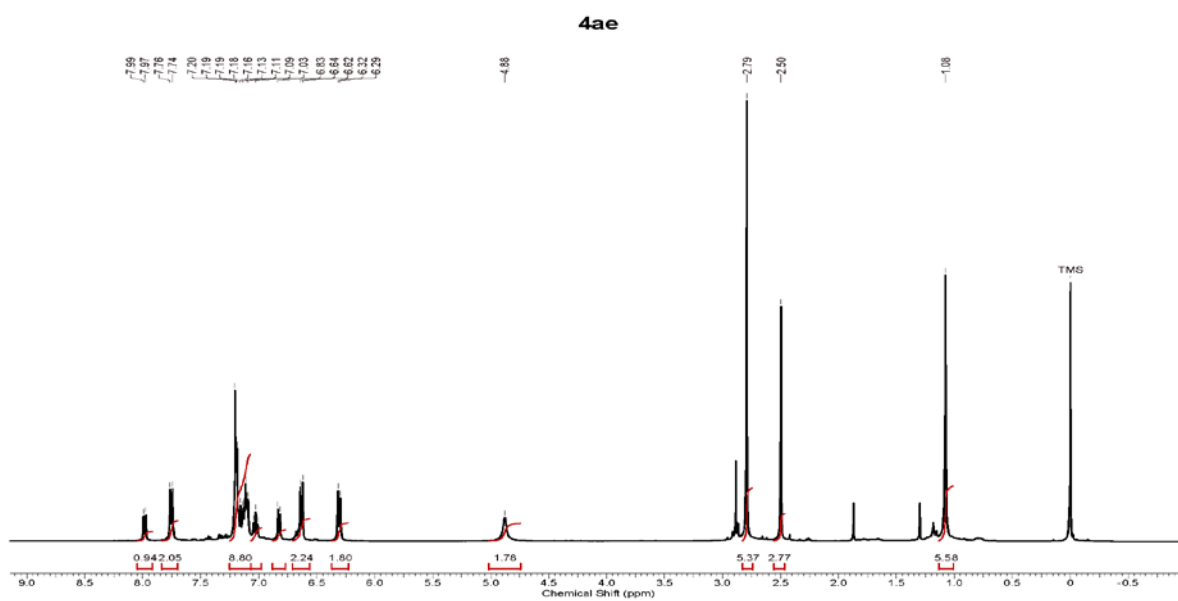
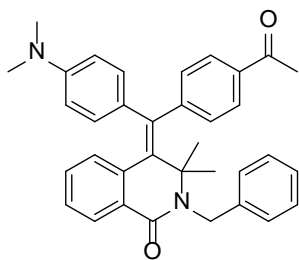
(E)-4-((4-acetylphenyl)(4-fluorophenyl)methylene)-2-benzyl-3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (4ac)



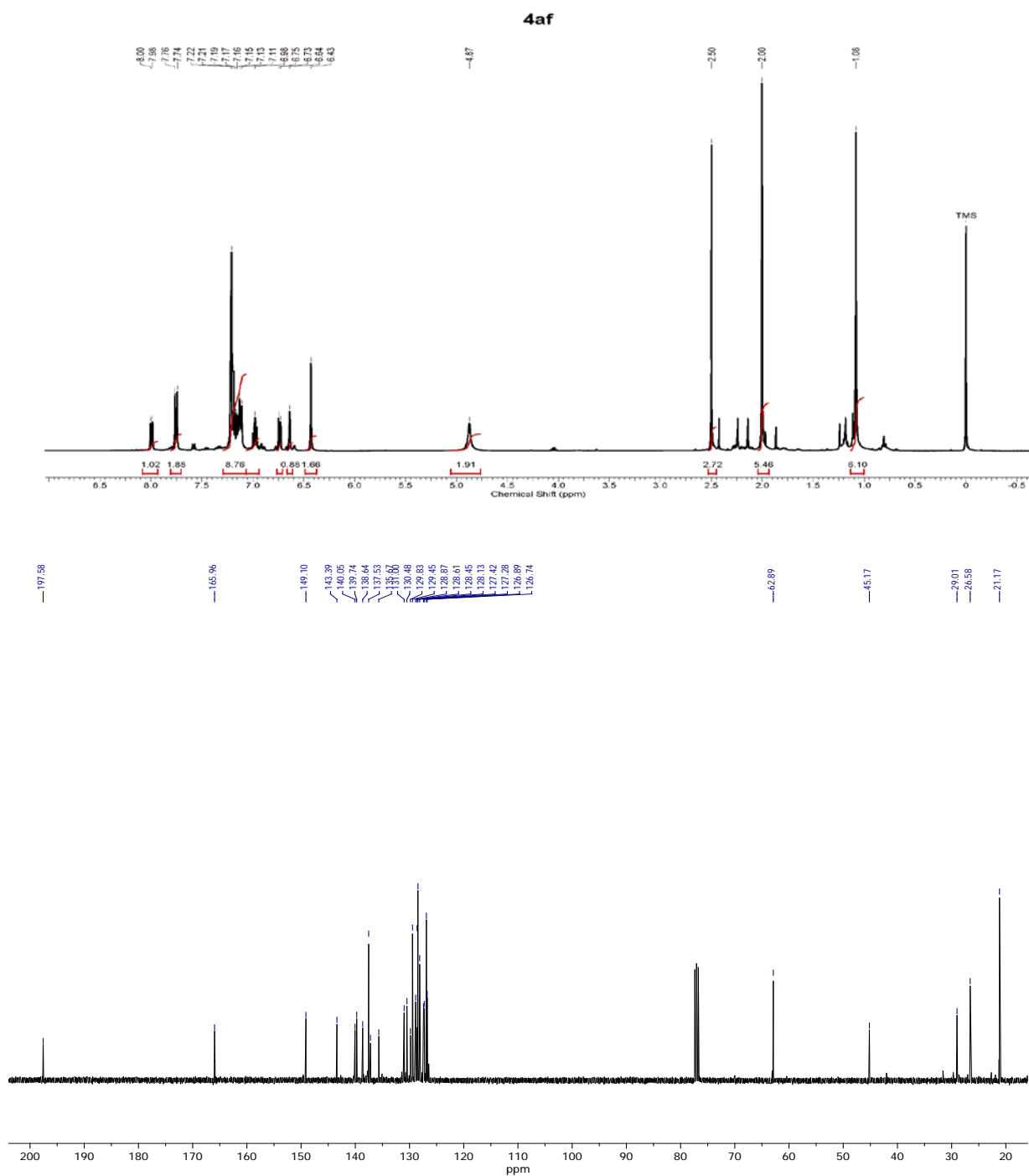
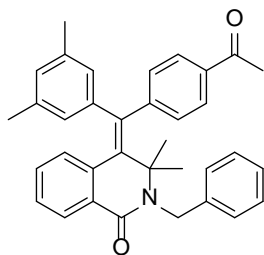
(E)-N-(3-((4-acetylphenyl)(2-benzyl-3,3-dimethyl-1-oxo-2,3-dihydroisoquinolin-4(1H)ylidene)methyl)phenyl)acetamide (4ad)



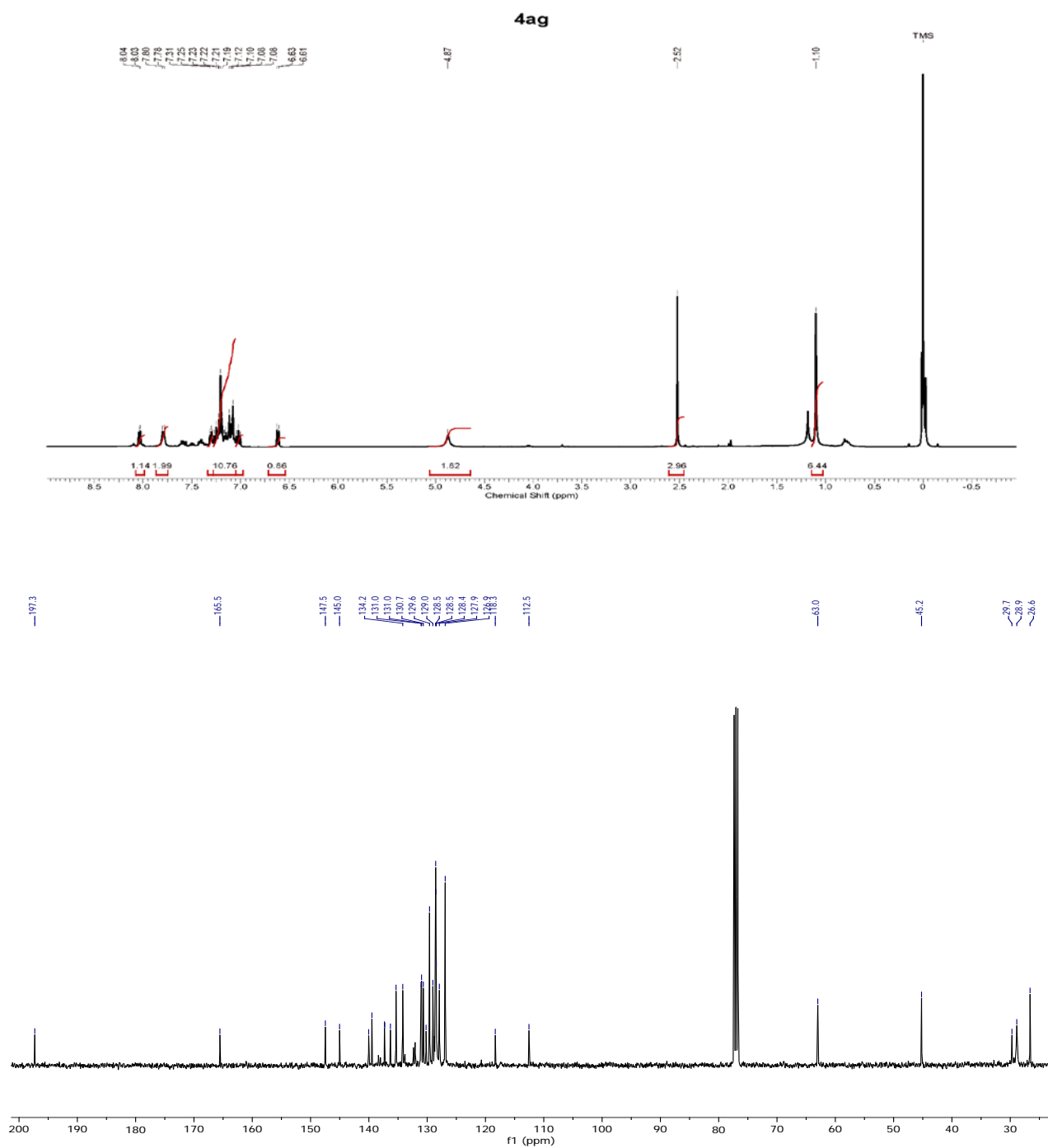
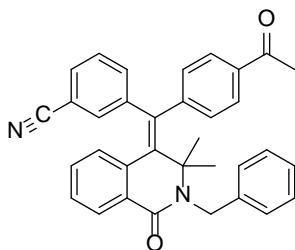
(E)-4-((4-acetylphenyl)(4-(dimethylamino)phenyl)methylene)-2-benzyl-3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (4ae)



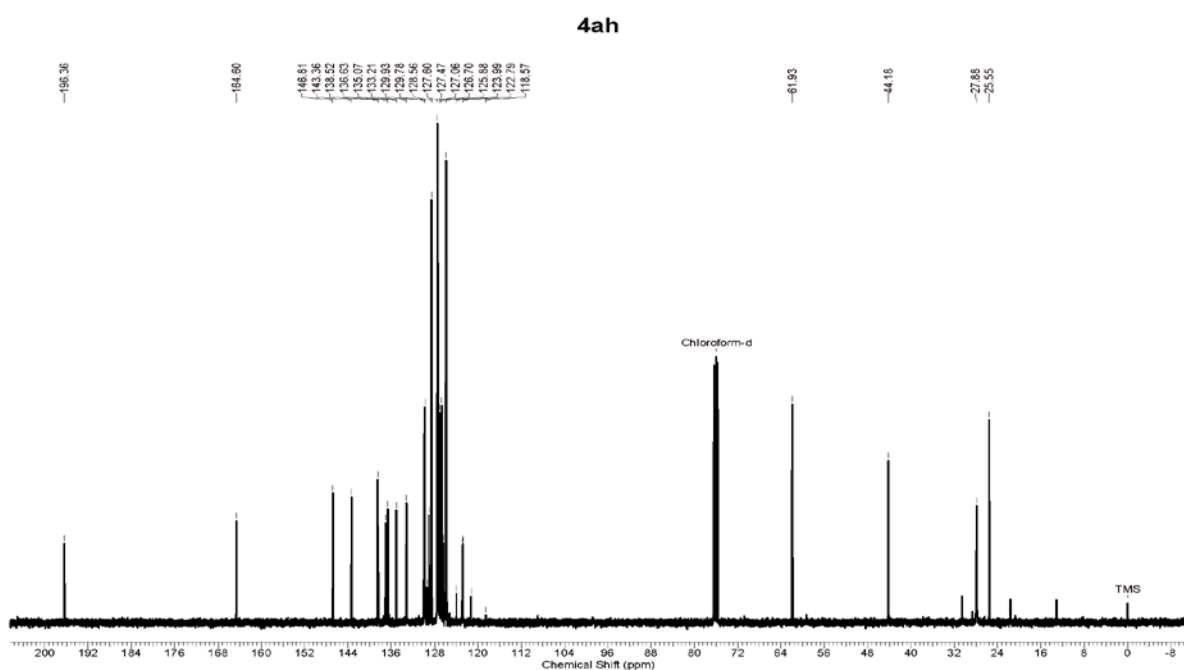
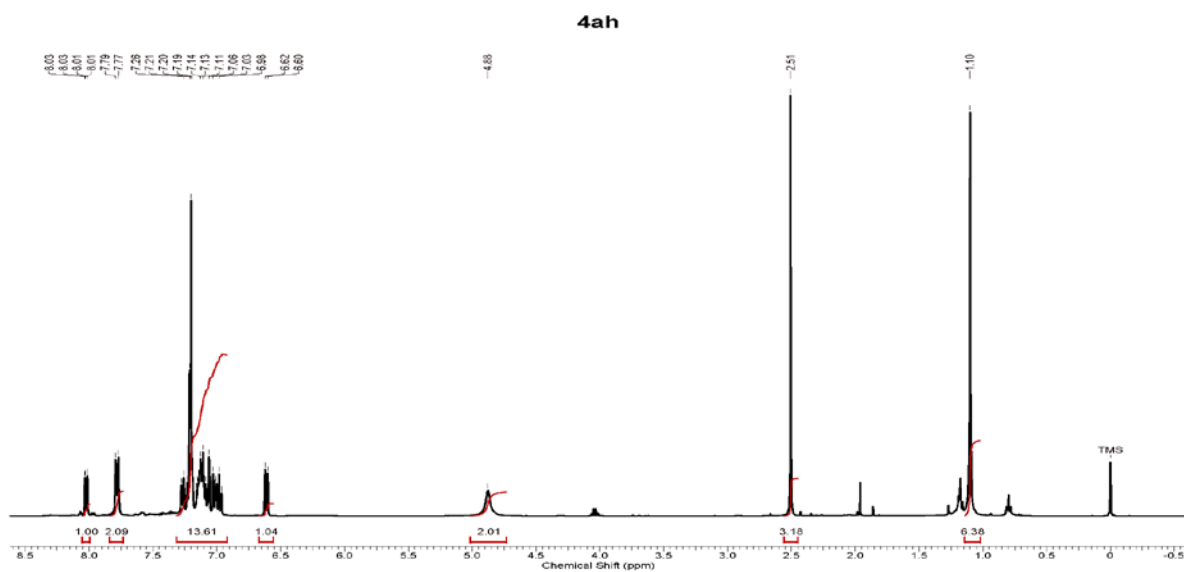
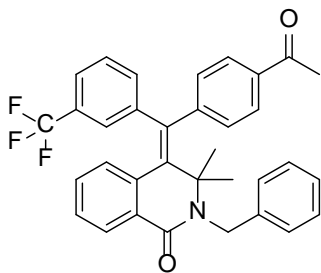
(E)-4-((4-acetylphenyl)(3,5-dimethylphenyl)methylene)-2-benzyl-3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (4af)



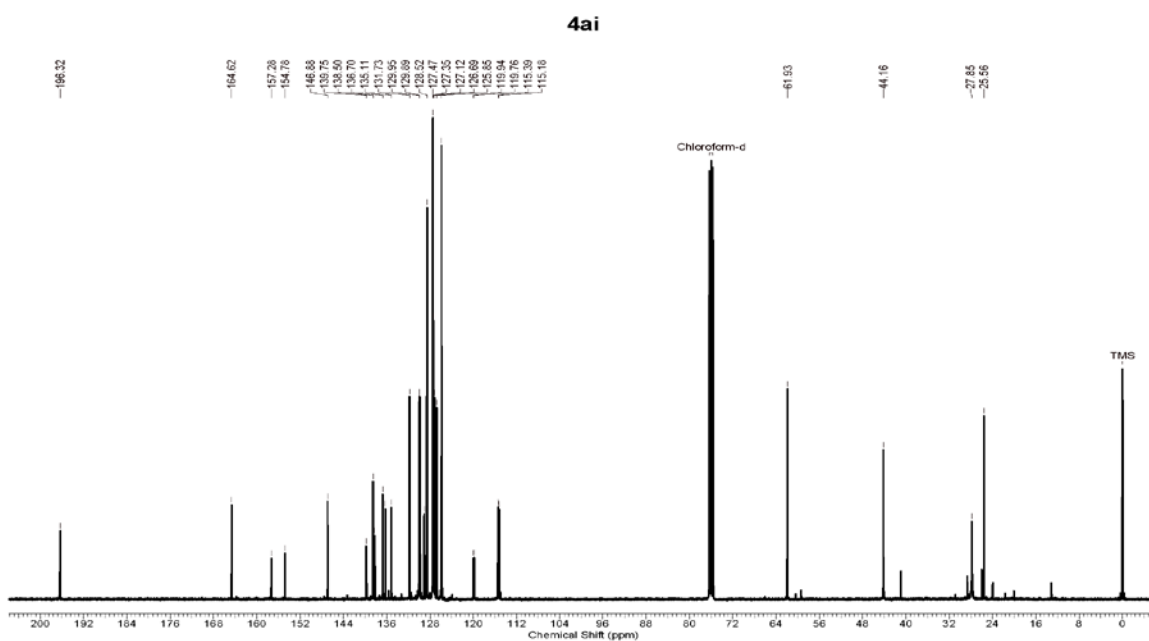
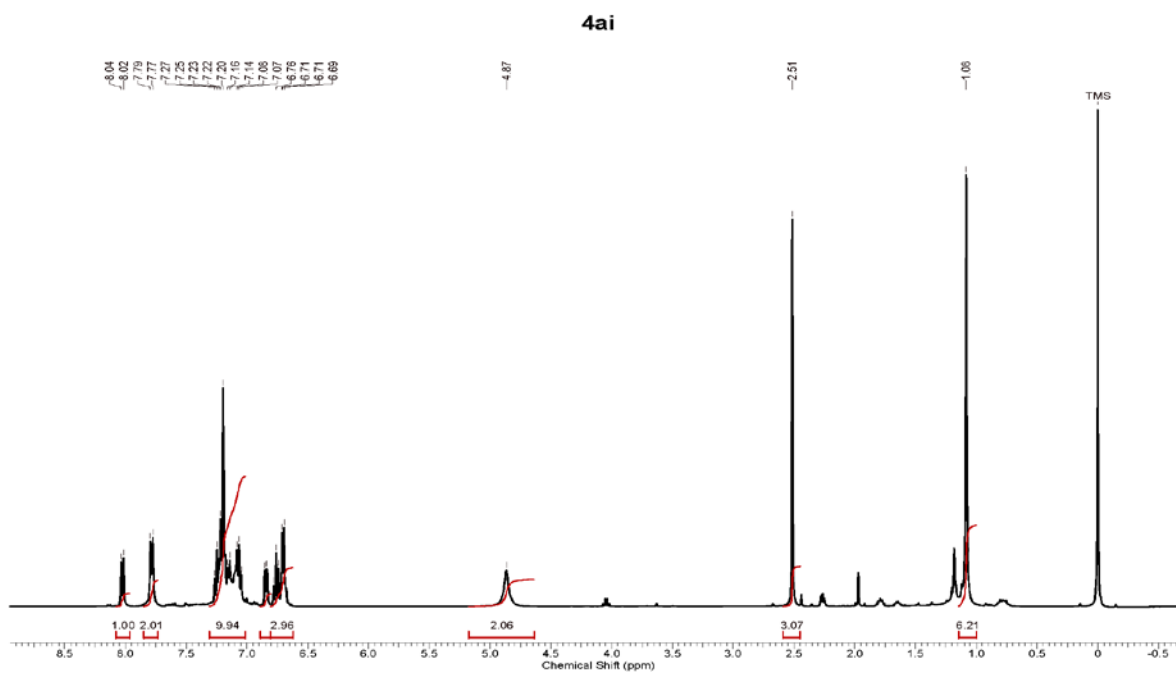
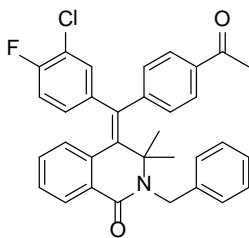
(E)-3-((4-acetylphenyl)(2-benzyl-3,3-dimethyl-1-oxo-2,3-dihydroisoquinolin-4(1H)-ylidene)methyl)benzonitrile (4ag)



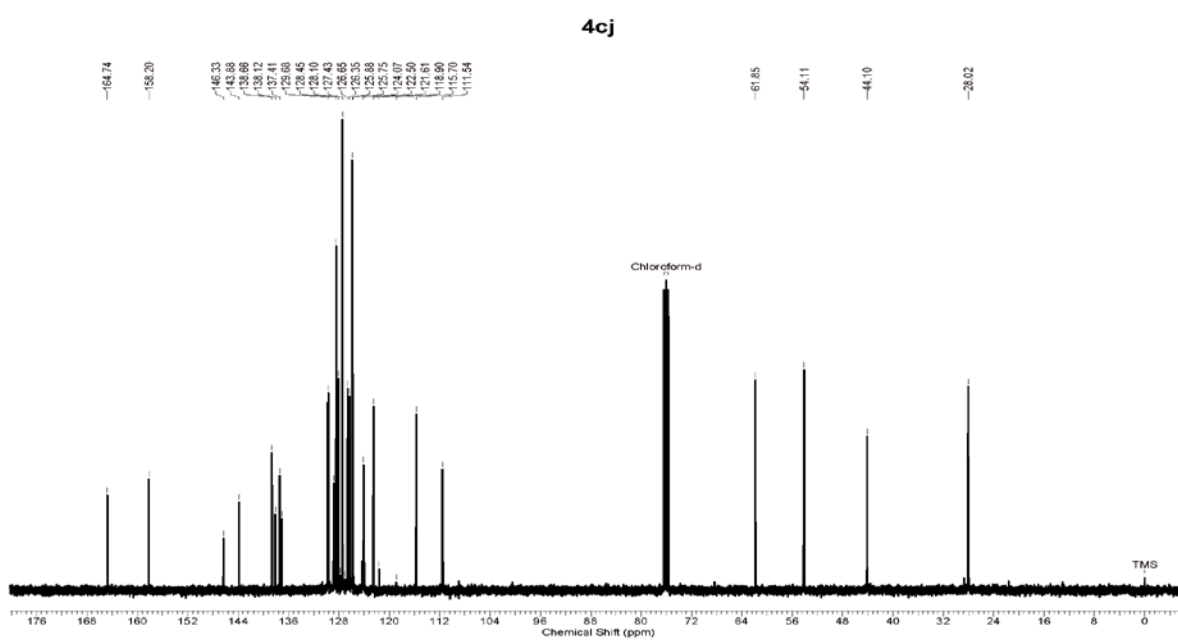
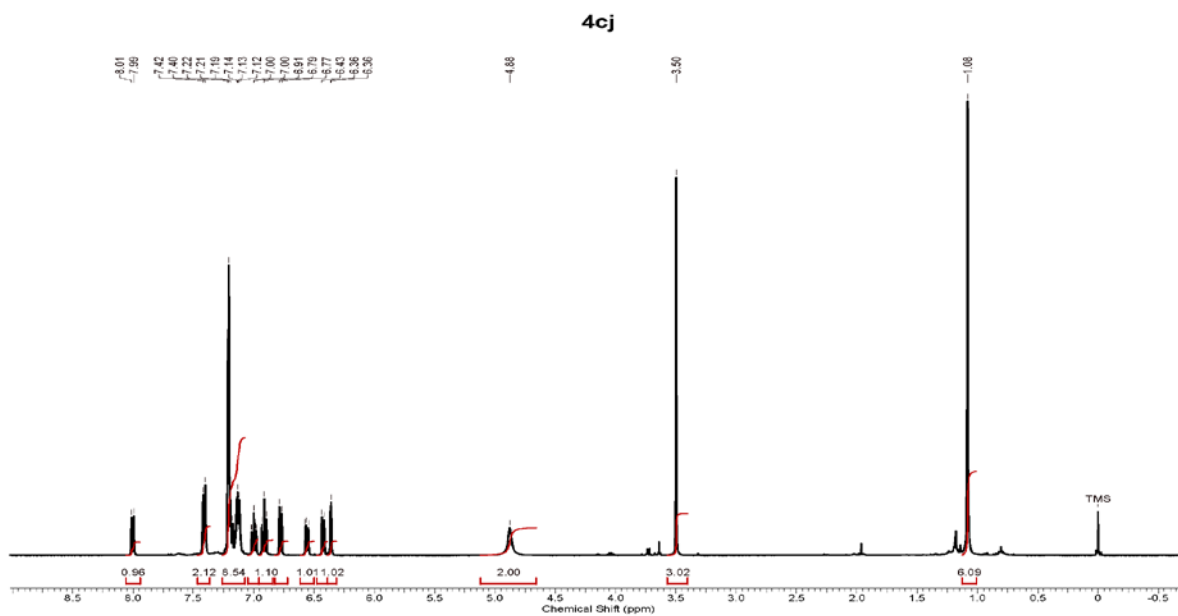
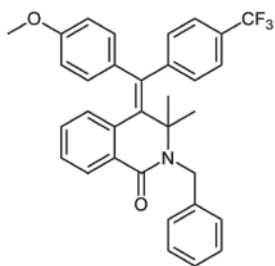
(E)-4-((4-acetylphenyl)(3-(trifluoromethyl)phenyl)methylene)-2-benzyl-3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (4ah)



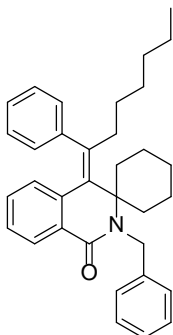
(E)-4-((4-acetylphenyl)(3-chloro-4-fluorophenyl)methylene)-2-benzyl-3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (4ai)



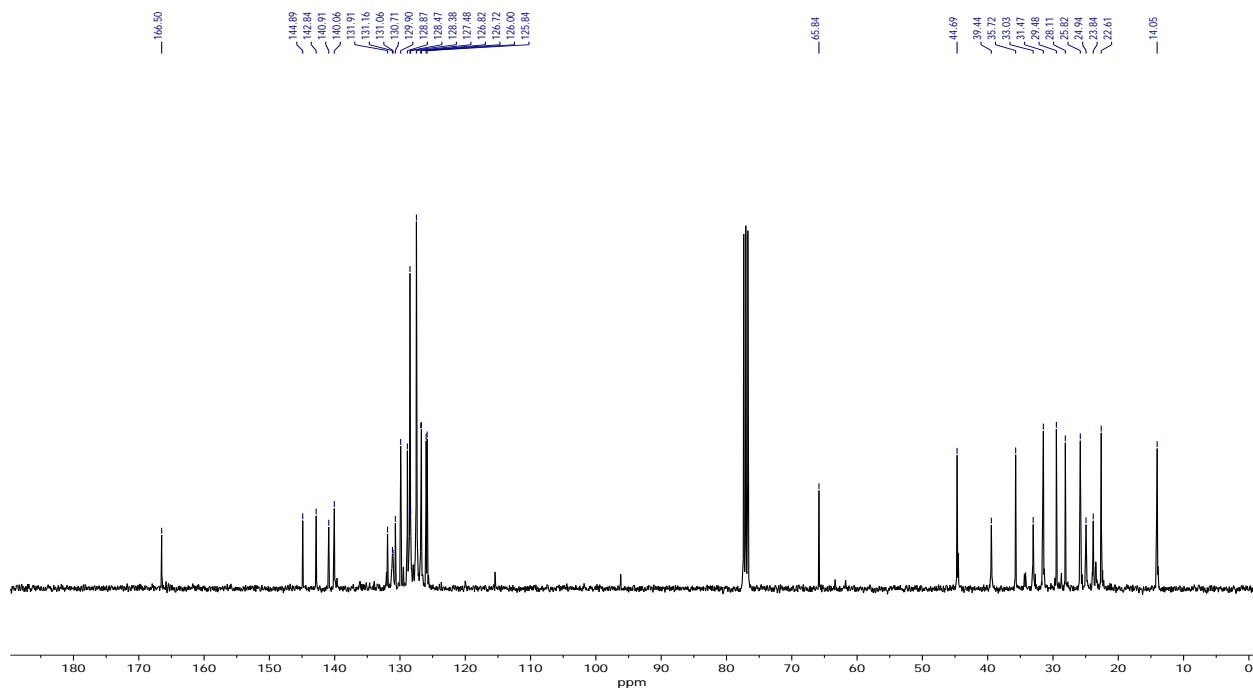
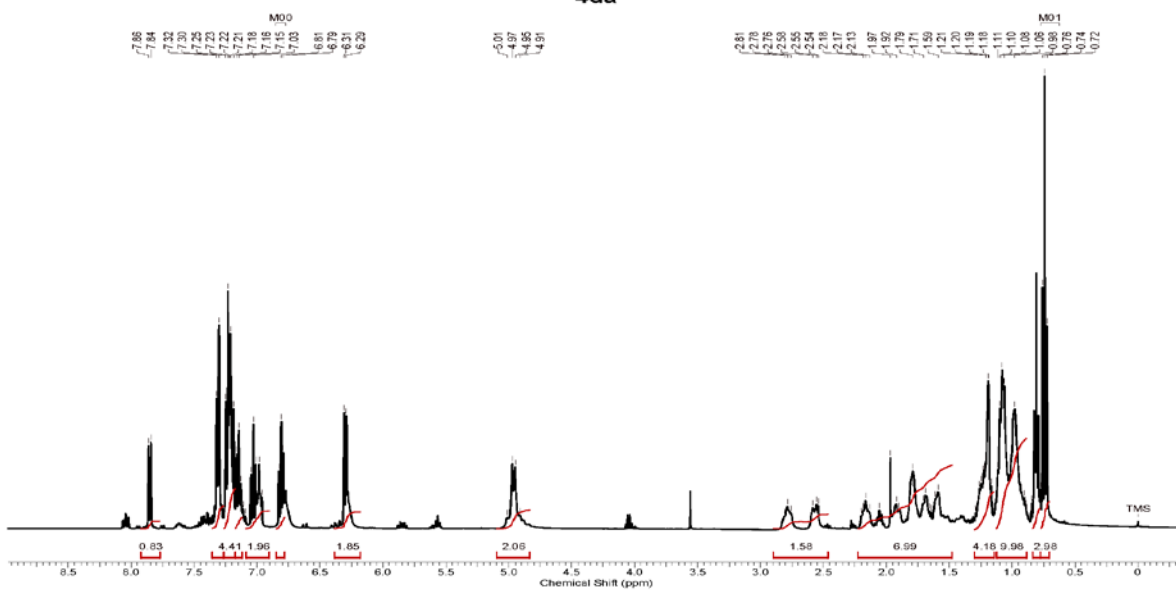
(E)-2-benzyl-4-((4-methoxyphenyl)(4-(trifluoromethyl)phenyl)methylene)-3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (4cj)



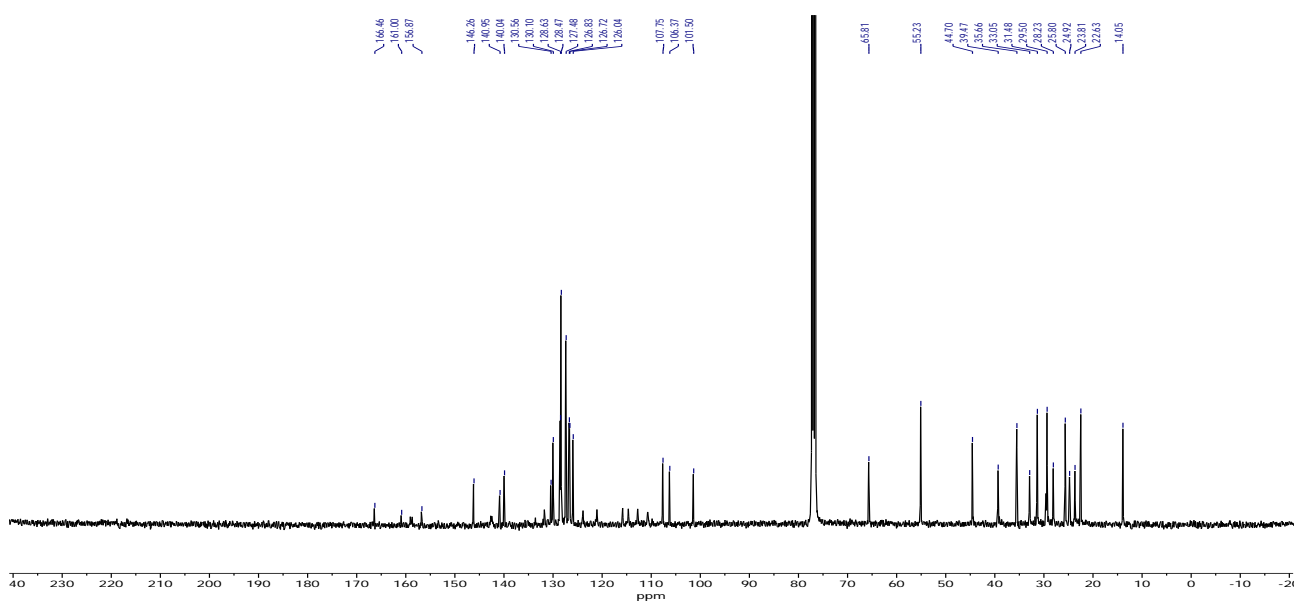
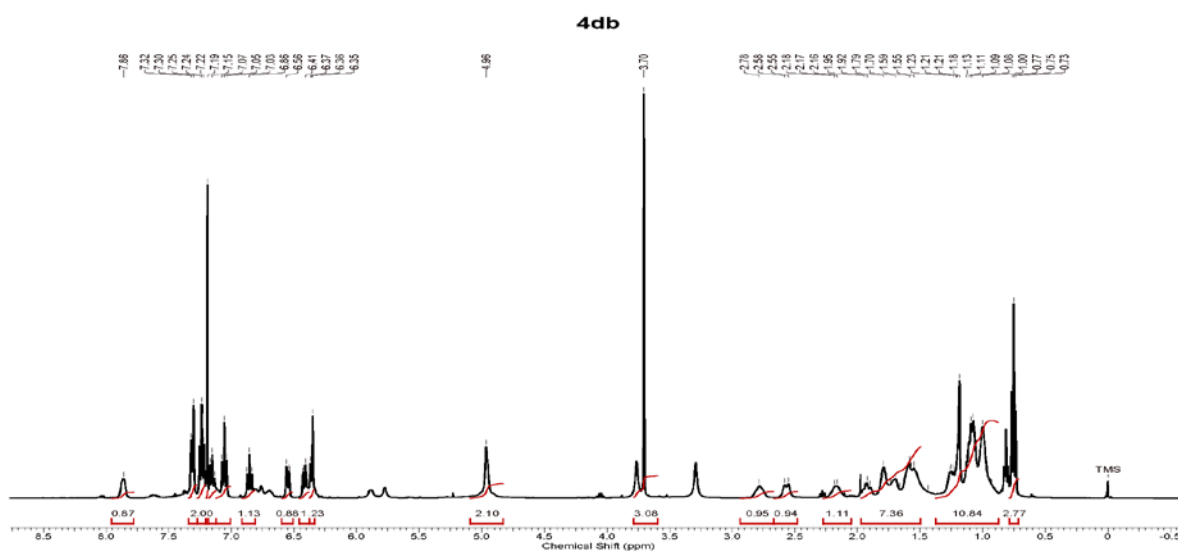
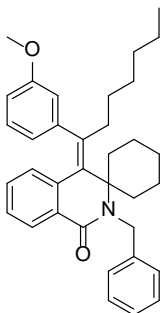
(E)-2'-benzyl-4'-(1-phenylheptylidene)-2',4'-dihydro-1'H-spiro[cyclohexane-1,3'-isoquinolin]-1'-one (4da)



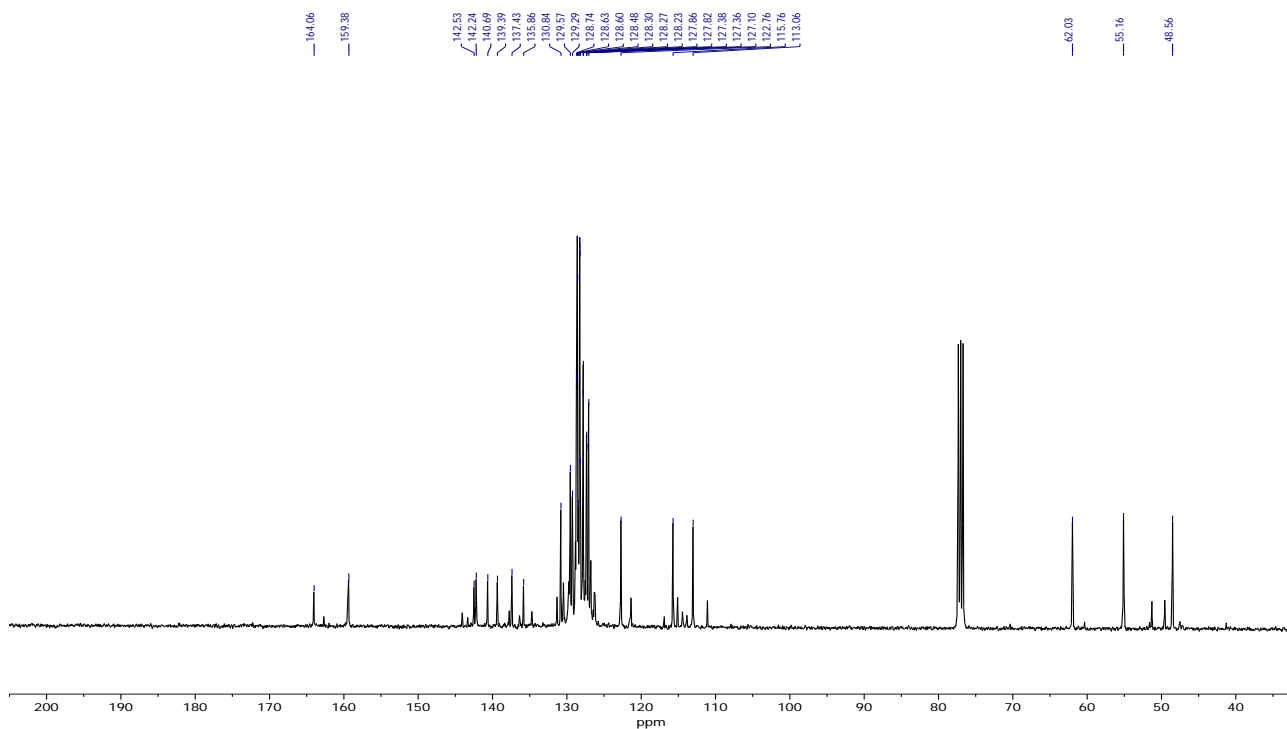
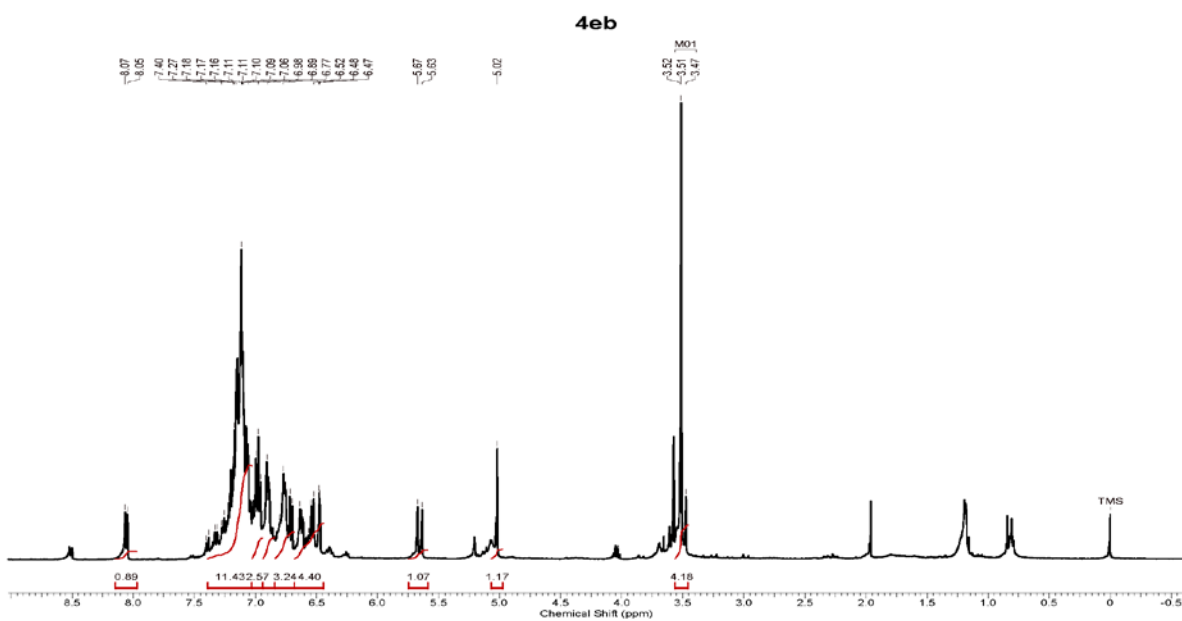
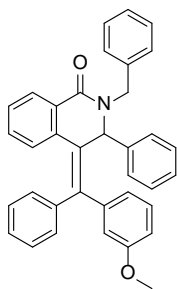
4da



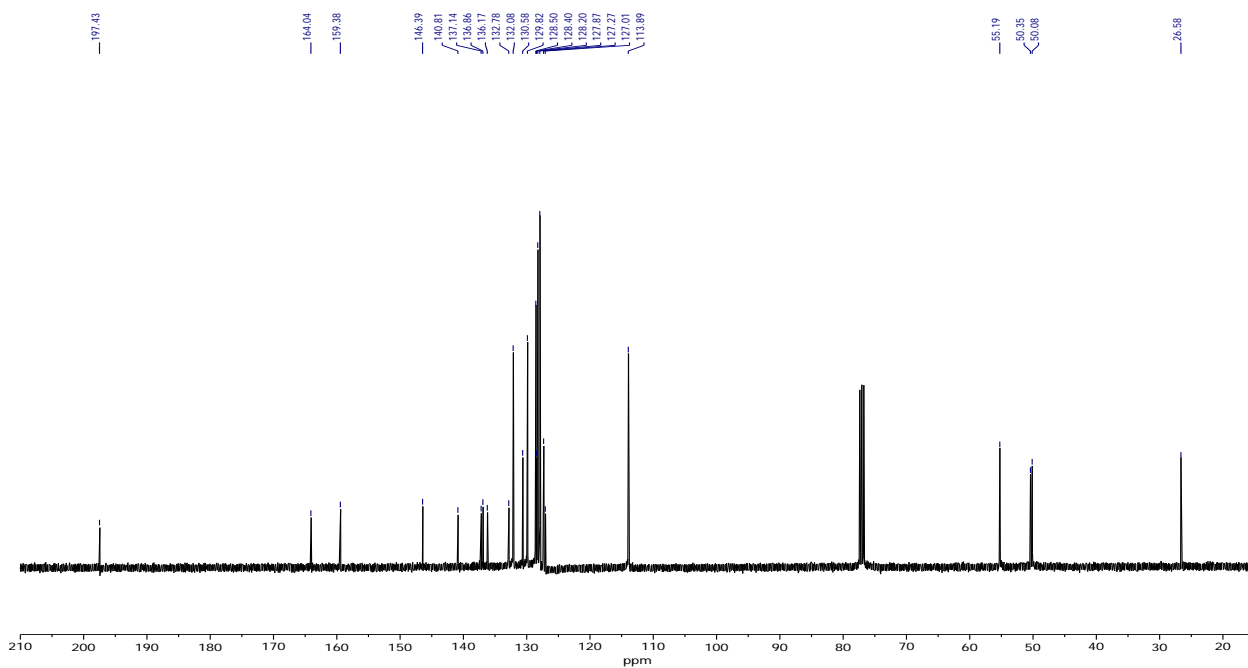
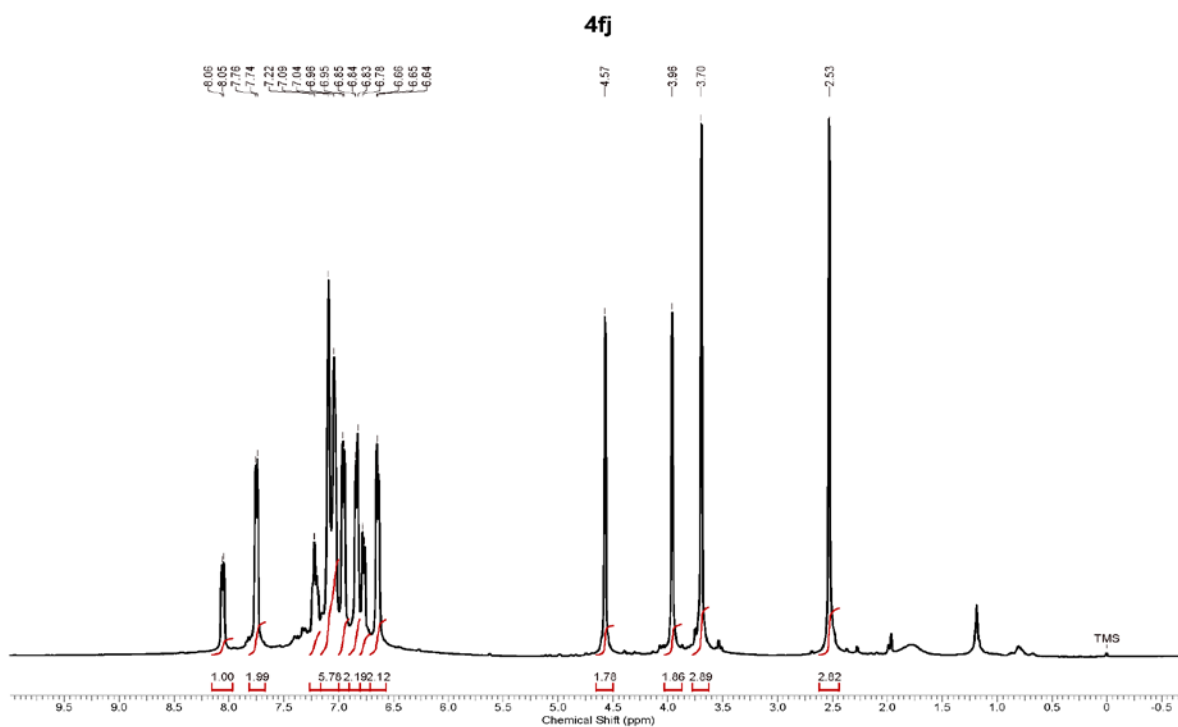
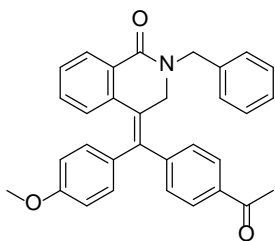
(E)-2'-benzyl-4'-(1-(3-methoxyphenyl)heptylidene)-2',4'-dihydro-1'H-spiro[cyclohexane-1,3'-isoquinolin]-1'-one (4db)



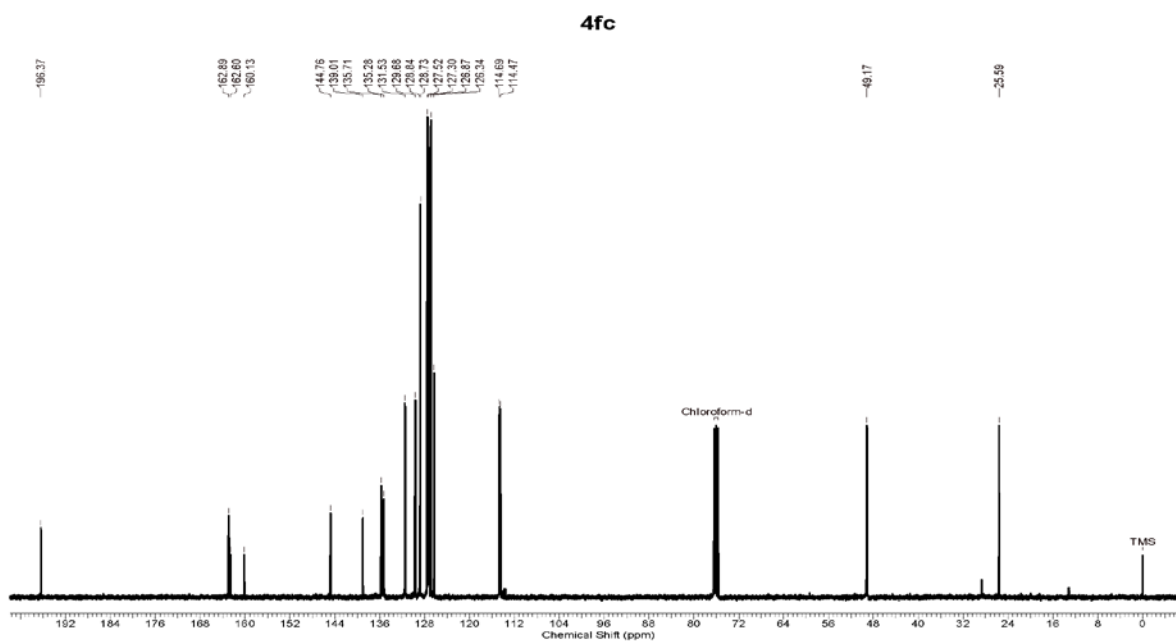
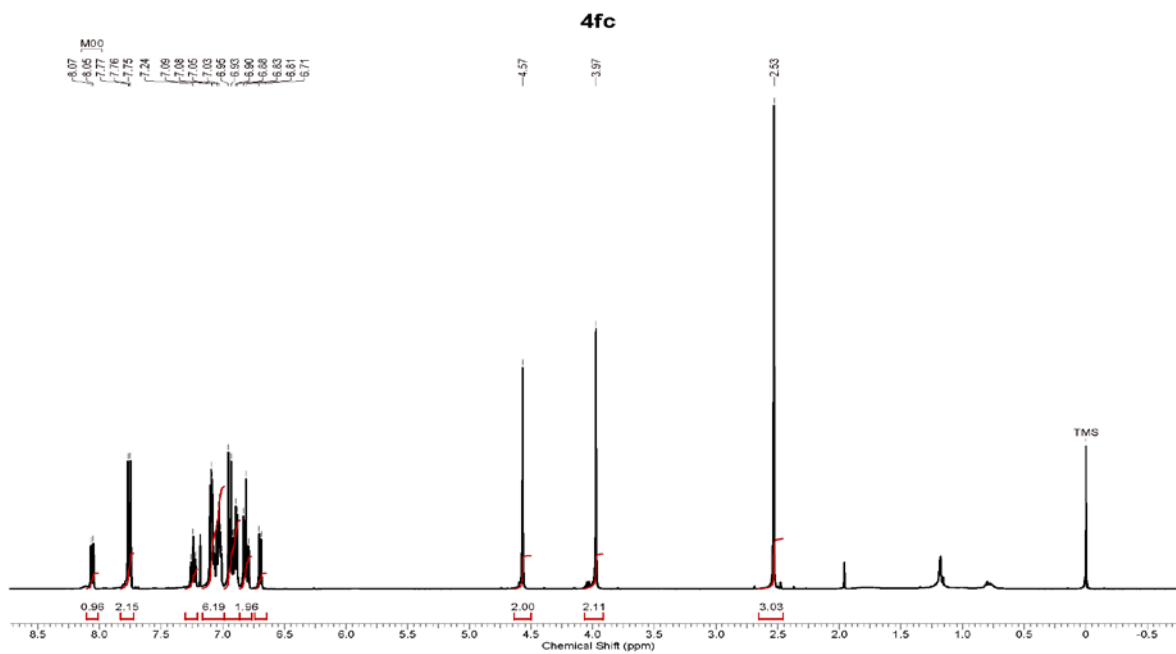
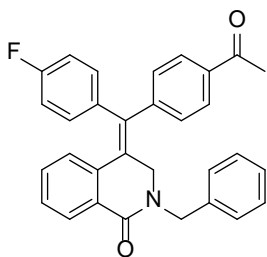
(Z)-2-benzyl-4-((3-methoxyphenyl)(phenyl)methylene)-3-phenyl-3,4-dihydroisoquinolin-1(2H)-one (4eb)



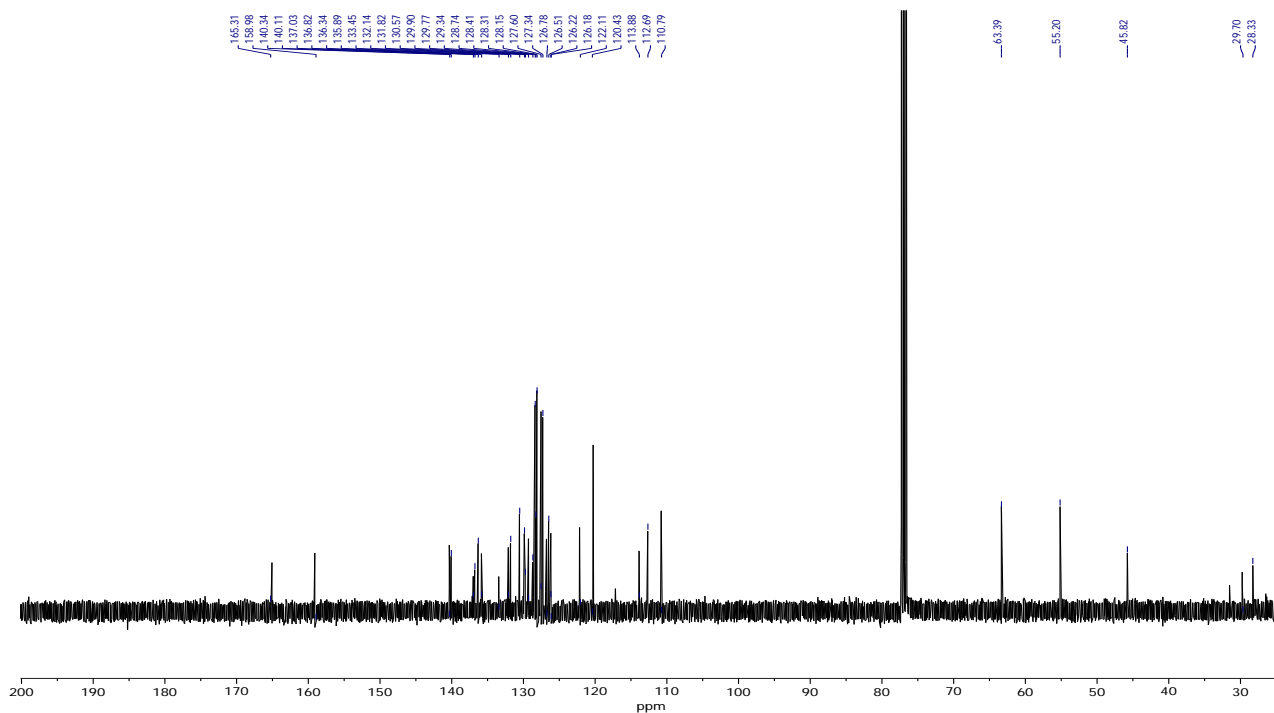
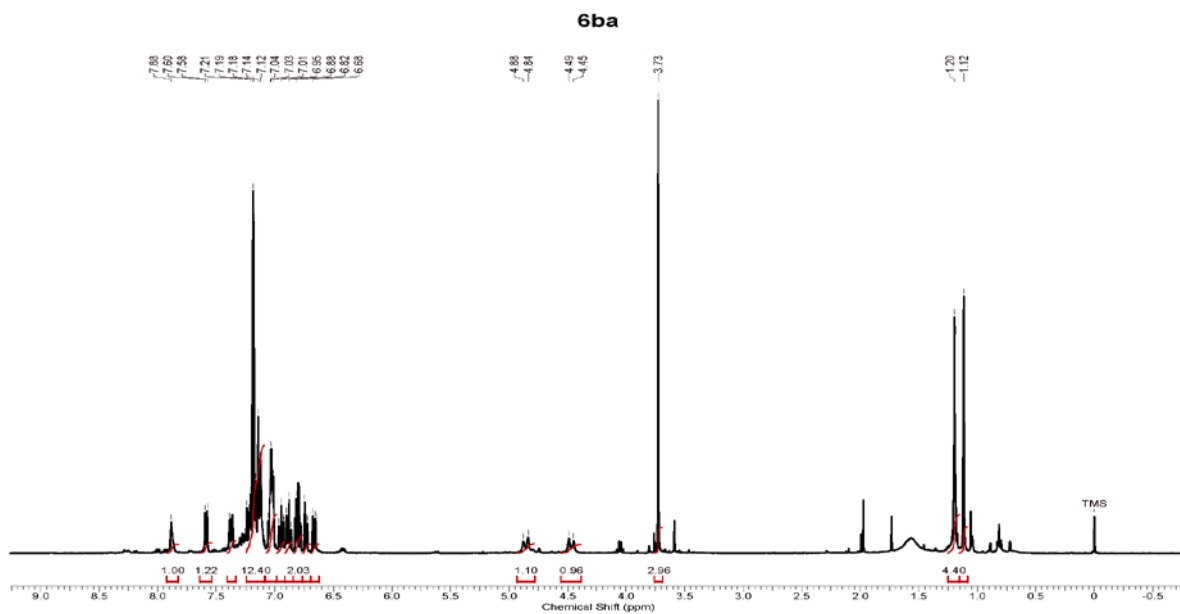
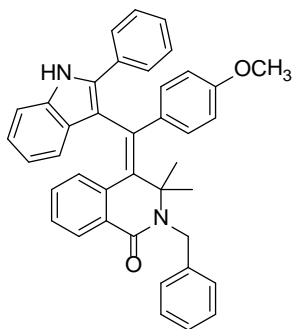
(E)-4-((4-acetylphenyl)(4-methoxyphenyl)methylene)-2-benzyl-3,4-dihydroisoquinolin-1(2H)-one (4fj)



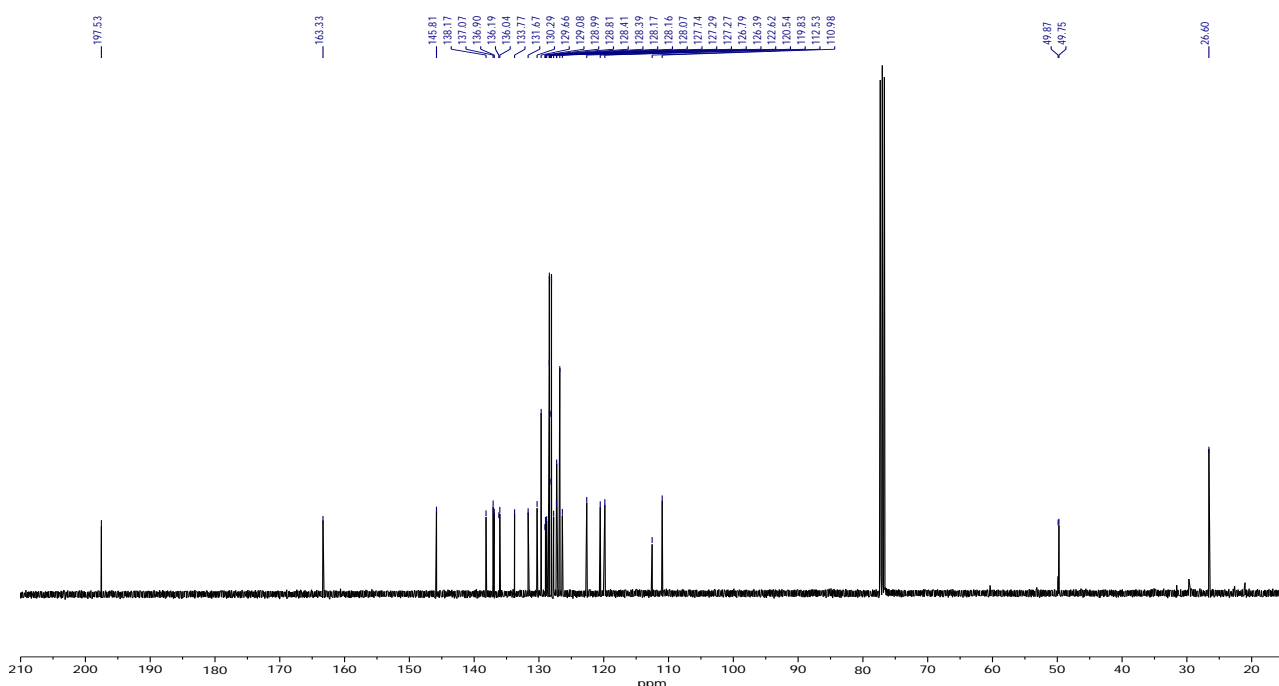
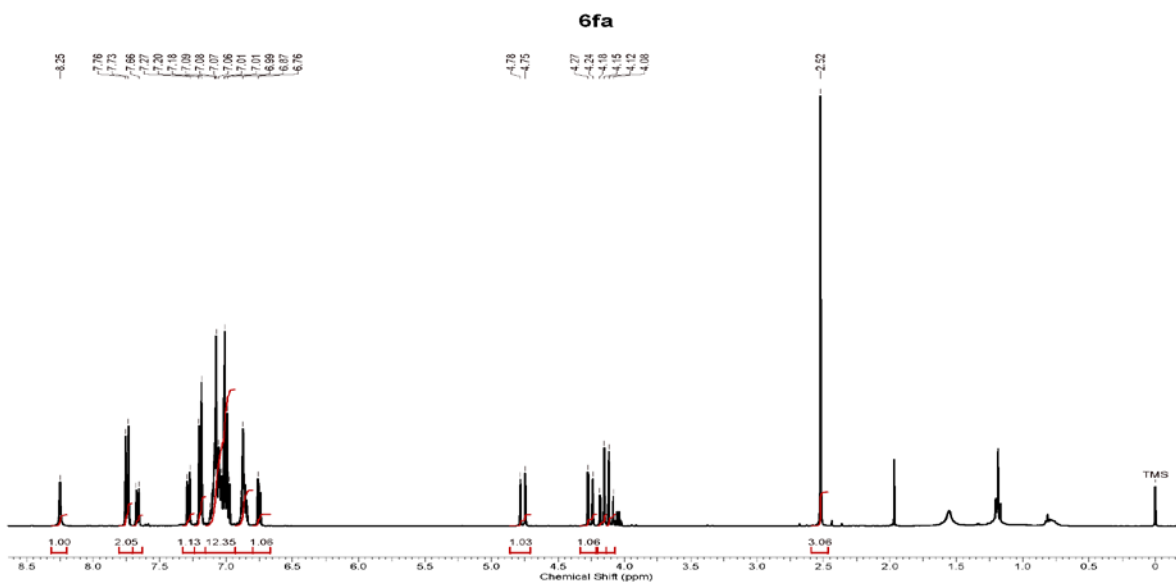
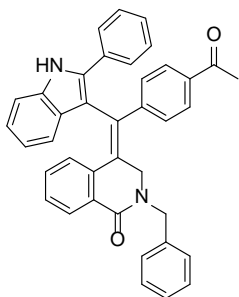
(E)-4-((4-acetylphenyl)(4-fluorophenyl)methylene)-2-benzyl-3,4-dihydroisoquinolin-1(2H)-one (4fc)



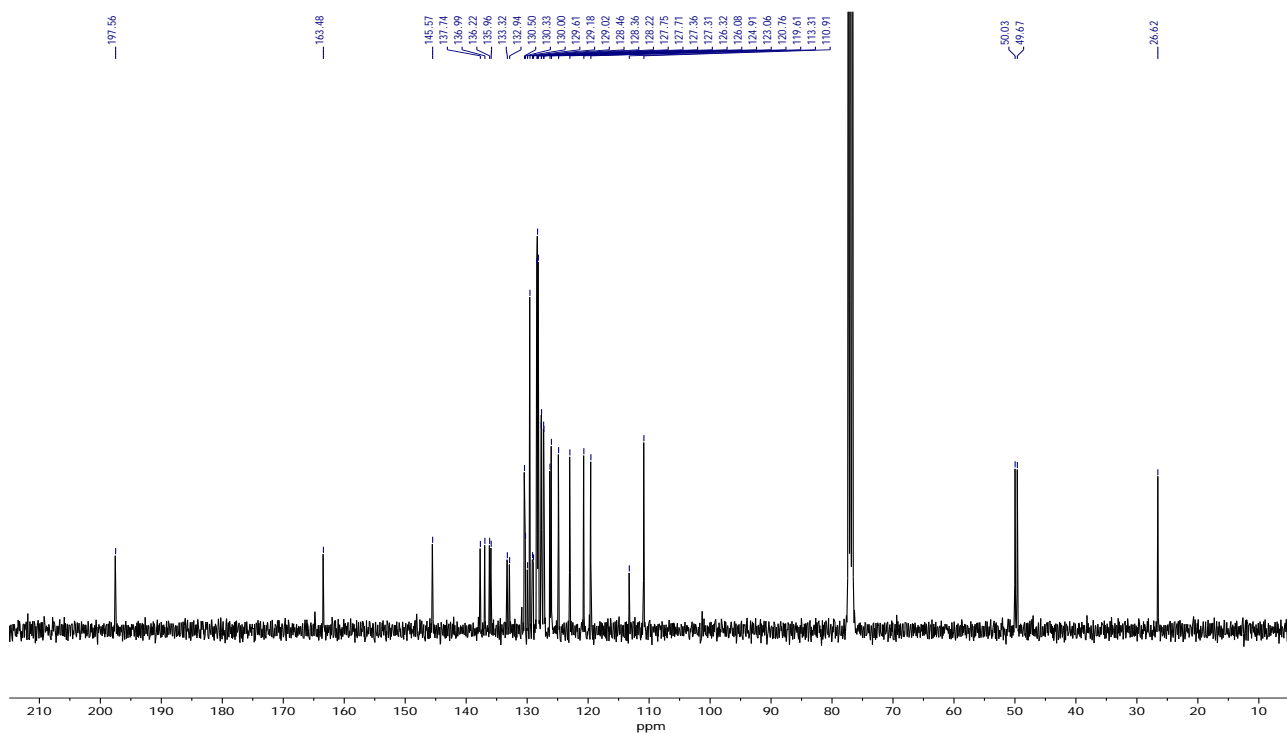
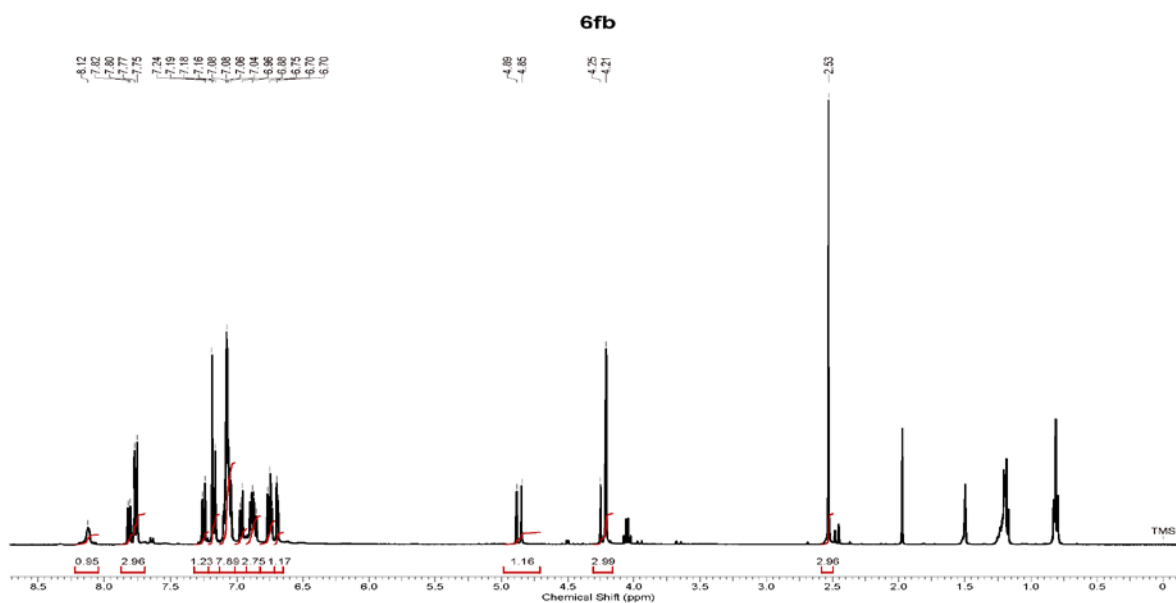
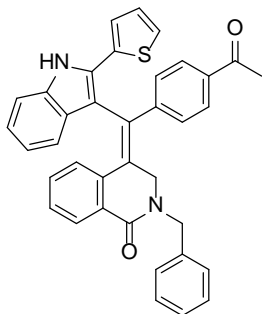
(E)-2-benzyl-4-((4-methoxyphenyl)(2-phenyl-1H-indol-3-yl)methylene)-3,3-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (6ba)



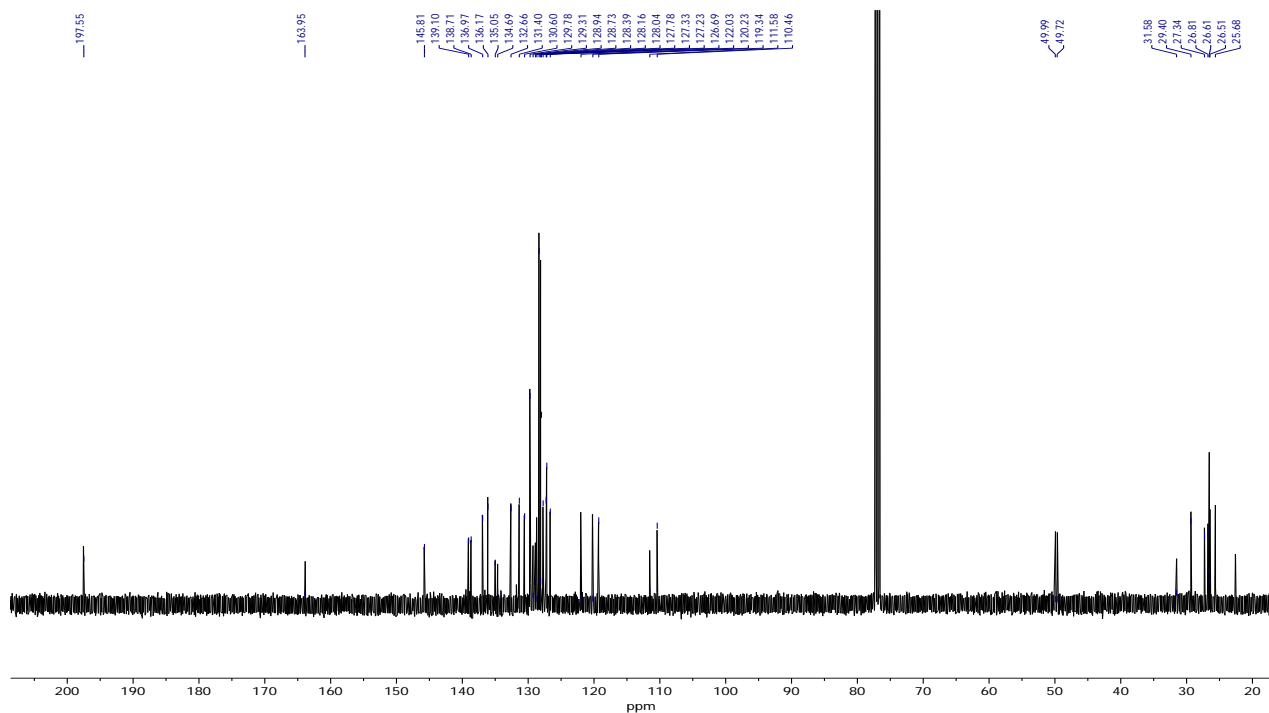
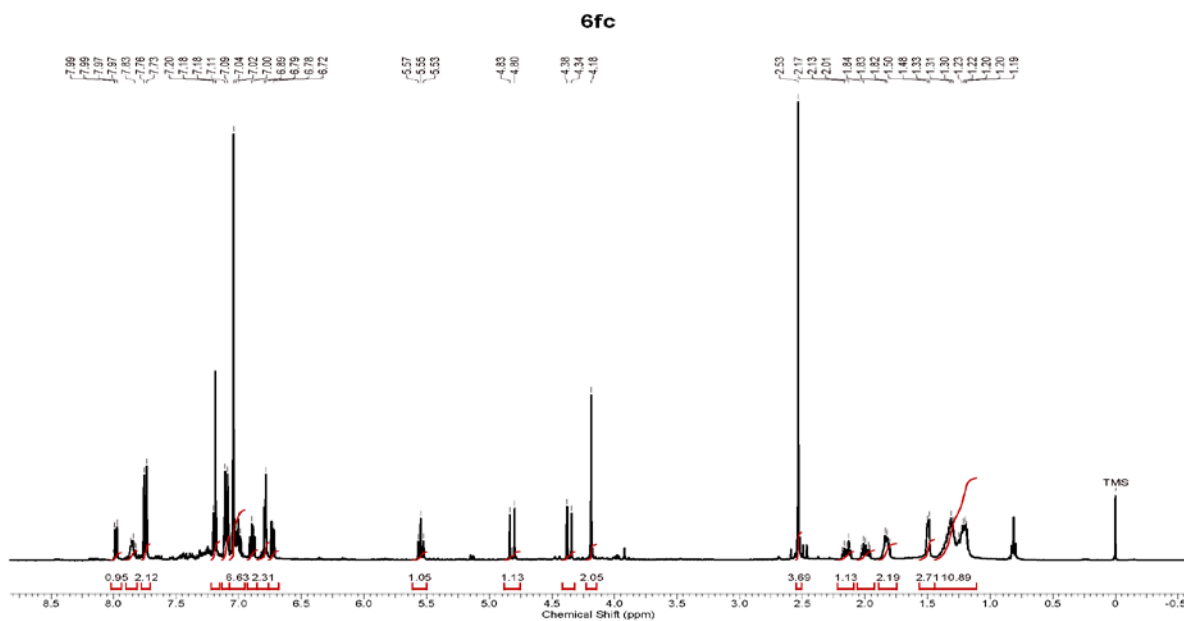
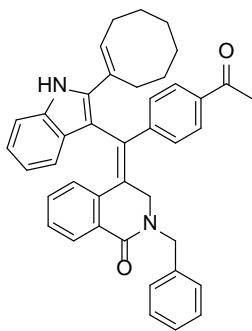
(E)-4-((4-acetylphenyl)(2-phenyl-1H-indol-3-yl)methylene)-2-benzyl-3,4-dihydroisoquinolin-1(2H)-one (6fa)



(E)-4-((4-acetylphenyl)(2-(thiophen-2-yl)-1H-indol-3-yl)methylene)-2-benzyl-3,4-dihydroisoquinolin-1(2H)-one (6fb)



(*E*)-4-((4-acetylphenyl)(2-((*E*)-cyclooct-1-en-1-yl)-1H-indol-3-yl)methylene)-2-benzyl-3,4-dihydroisoquinolin-1(2H)-one (6fc)



Determination of double bond configuration:

The absolute stereochemistry of the double bonds for **4fj** and **6fa**, as model compounds, was assigned by NOESY experiment, which demonstrated, for both, the E configuration.

In order to assign the correct stereochemistry it is necessary to have the attribution of ^1H NMR and ^{13}C NMR signals that has been performed by homonuclear 2D NMR experiments (Cosy and Noesy) and heteronuclear 2D NMR experiments (HSQC).

(E)-4-((4-acetylphenyl)(4-methoxyphenyl)methylene)-2-benzyl-3,4-dihydroisoquinolin-1(2H)-one (**4fj**)

Key NOE interactions to establish the absolute stereochemistry for **4fj** were those of proton 7 and methylene 10 (for structure numbering see Fig. S01) of dihydroisoquinolinone with the substituents 4-methoxyphenyl and 4-acetylphenyl. Noesy showed, proximity between proton 7 of dihydroisoquinolin-1(2H)-one and protons 27,31 of 4-methoxyphenyl and proximity of methylene 10 and protons 21,25 of 4-acetylphenyl (see Fig. S01)

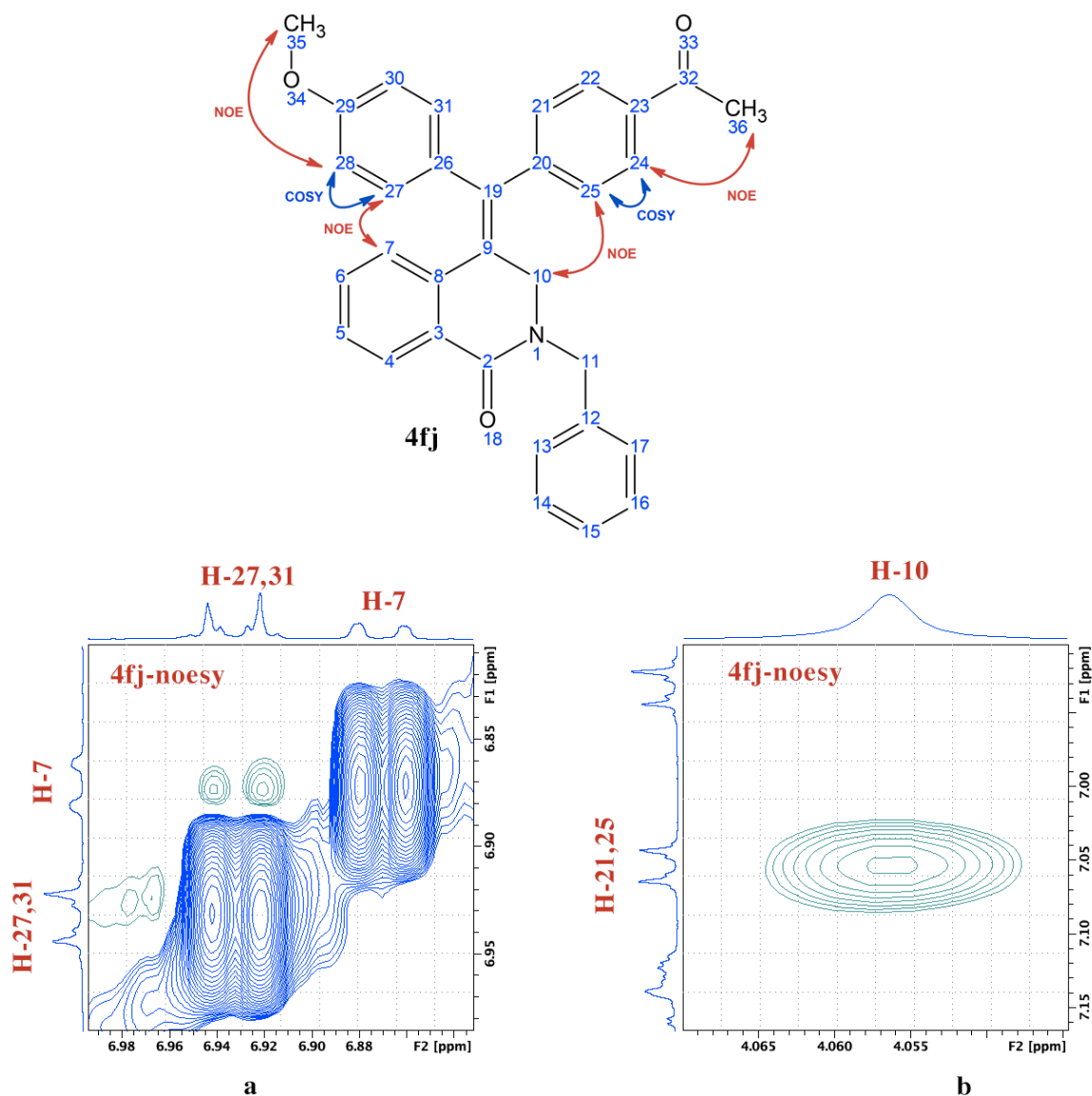


Fig. S01 . Structure numbering and key NOESY and COSY correlations of **4fj**. (a) Correlation H₁-27,28/H₁-7; (b) correlation H₁-21,25/H₂-10.

(E)-4-((4-acetylphenyl)(2-phenyl-1H-indol-3-yl)methylene)-2-benzyl-3,4-dihydroisoquinolin-1(2H)-one (6fa)

Key NOE interactions to establish the absolute stereochemistry for **6fa** were those of proton 7 and methylene 10 (for structure numbering see Fig. S02) of dihydroisoquinolone with the substituents phenylindolyl and 4-acetylphenyl. The crowded spectra for resonance of phenylindolyl did not allow unequivocal attribution of noesy signals, instead was clear the proximity between methylene protons, 10, and protons 30,34 of 4-acetylphenyl (see Fig. S02)

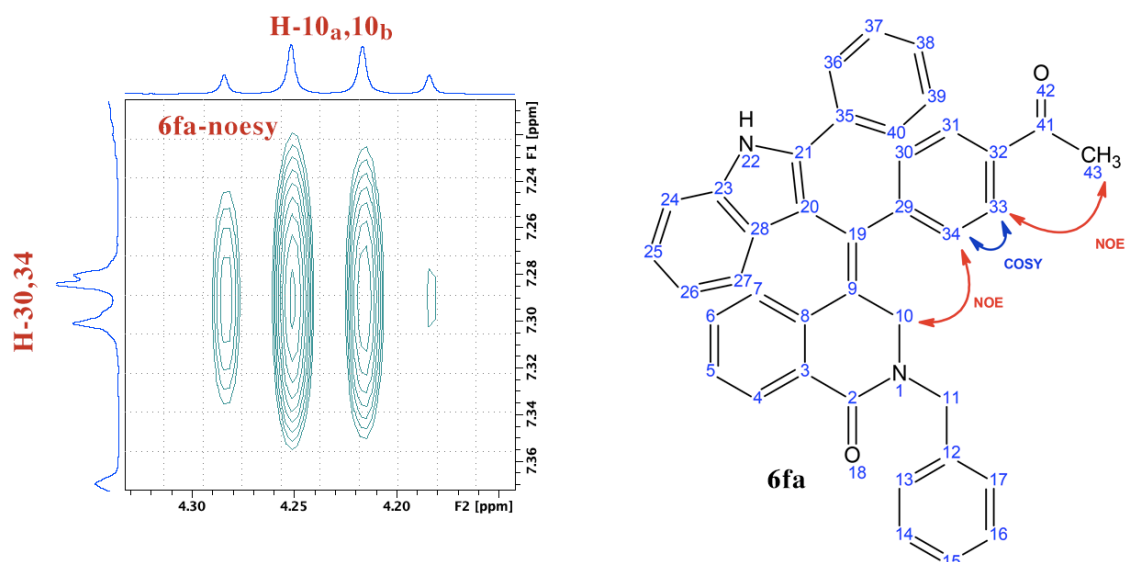


Fig. S02. Structure numbering and key NOESY and COSY correlations of **6fa**. correlation H₁-30,34/H_{a,b}-10.