Supporting Information

Copper(II)-Catalyzed Tandem Reaction: Synthesis of Furo[3,2-*c*]Coumarin Derivatives and Evaluation for Photophysical Properties

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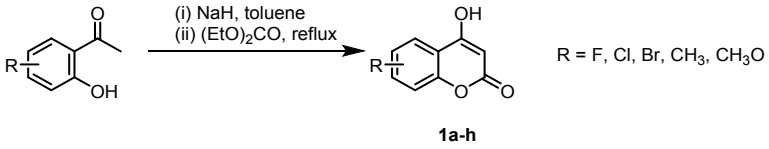
Contents:

EXPERIMENTAL SECTION

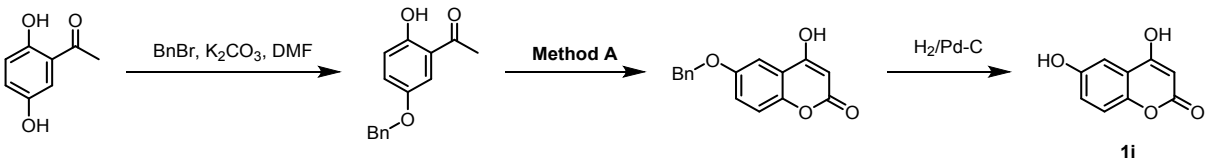
Synthesis

*Procedures for synthesis of substituted 4-hydroxy-2H-chromen-2-one (**1a–o**)*



1a-h

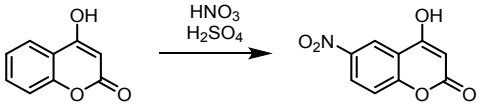
Method A. *4-Hydroxy-2H-chromen-2-one (**1a**)* was prepared according to the literature procedure.[1] NaH (2.0 g, 50 mmol, 5 equiv) in 40 mL toluene was cooled in an ice bath. To the suspension was added 2'-hydroxyacetophenone (1.36 g, 10 mmol, 1 equiv) in one portion and the result mixture was allowed to warm to room temperature and stirred for 30 min. Then diethyl carbonate (1.77 g, 15 mmol, 1.5 equiv) was added to the reaction mixture at room temperature by drop-wise. The reaction was heated to reflux and stirred for 4 h. On completing of the reaction monitored by TLC, the reaction was allowed to cool to room temperature and the precipitate was collected and washed with 1N HCl solution and water to give the crude product. It was further purified by column chromatography to give the desired 4-hydroxycoumarin (1.0 g, 65%) as a white solid. The ^{1}H NMR spectrum fits well to the reported data.[1] HRMS (ESI$^+$): calcd for $C_9H_7O_3^+$ $(M + H)^+$, 163.0390, found 163.0394. Furthermore, the substituted 4-hydroxycoumarins **1b–1h** were prepared according to the **Method A** except various 2'-hydroxyacetophenones were employed in the reaction.



1i

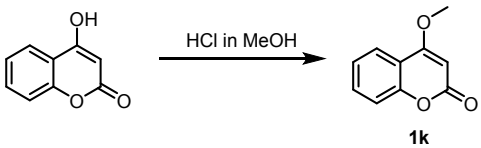
*4,6-Dihydroxy-2H-chromen-2-one (**1i**)*. Prepared according to the following procedure. A 100 mL round bottom flask was charged with 2,4-dihydroxyacetophenone (2.0 g, 13.1 mmol), potassium carbonate (2.7 g,

1.5 equiv), benzyl bromide (2.2 g, 0.99 equiv), and DMF (25 mL). The obtained mixture was the stirred at 100 ℃ for 8 h till the acetophenone was consumed. The crude mixture was quenched with water (50 mL) and extracted with EtOAc (3 × 30 mL), and the organic phases were combined and washed with water and brine. After concentration at reduced pressure, the crude product was obtained and used for next step without further purification. Then the benzyl-**1i** could be prepared according to the **Method A** (1.7 g, 48 % for two steps). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 12.55 (s, 1H). 7.48–7.32 (m, 8H), 5.59 (s, 1H), 5.17 (s, 2H) ppm. A following deprotection (10% Pd-C, H_2, rt) was performed to afford the title compound **1i** as a yellow solid (quant. yield). HRMS (ESI$^+$): calcd for $C_9H_7O_4^+$ $(M + H)^+$, 179.0339, found 179.0334.



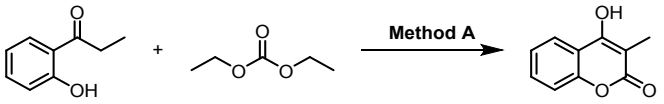
1a **1j**

*4-Hydroxy-6-nitro-2H-chromen-2-one (**1j**).* Under an ice bath, **1a** (1.0 g, 6.2 mmol) was dissolved in conc. H_2SO_4 (4 mL) followed by the addition of conc. HNO_3 (0.4 mL, 1.0 equiv) in one portion. The obtained sticky solution was stirred at room temperature for 1 h and then carefully poured into cold water (30 mL). The crude product was extracted with EtOAc (30 mL × 2) and the combined organic layer was washed with water (30 mL × 2), brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1) to provide **1j** (0.4 g, 31%) as a white solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.55 (d, J = 2.8 Hz, 1H), 8.47 (dd, J_1 = 9.1, J_2 = 2.8 Hz, 1H), 7.63 (d, J = 9.1 Hz, 1H), 5.71 (s, 1H) ppm. HRMS (ESI$^+$): calcd for $C_9H_6NO_5^+$ $(M + H)^+$, 208.0240; found 208.0241.



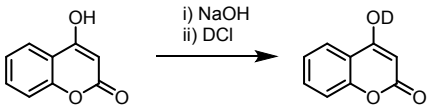
1k

*4-Methoxy-2H-chromen-2-one (**1k**).* Prepared according to a reported method.[2] A solution of **1a** in methanolic hydrogen chloride was heated to reflux for 5 h and the precipitation was filtered and dried to afford the desired product. The ^{1}H NMR spectrum fits well to the reported data.[2] HRMS (ESI$^+$): calcd for $C_{10}H_9O_3^+$ $(M + H)^+$, 177.0546, found 177.0540.



1l

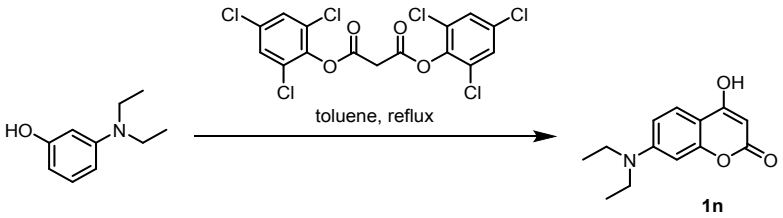
*4-Hydroxy-3-methyl-2H-chromen-2-one (**1l**)*. Prepared according to the procedure of **Method A**. NaH (0.61 g, 15 mmol, 5 equiv, 60% w/w) in 15 mL toluene was cooled at ice bath. To the suspension was added 1-(2-hydroxyphenyl)propan-1-one (0.45 g, 3 mmol, 1 equiv) as one portion. After stirred for 30 min at room temperature, diethyl carbonate (0.53 g, 4.5 mmol, 1.5 equiv) was added by drop-wise to the mixture. Then the reaction was heated to reflux for 4 h. On completing of the reaction monitored by TLC, the precipitate was collected and washed with HCl 1N solution and water to give the crude product. It was further purified by column chromatography to afford desired product (0.39 g, 74%) as a white solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 11.27 (brs, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.37–7.31 (m, 2H), 2.00 (s, 3H) ppm.



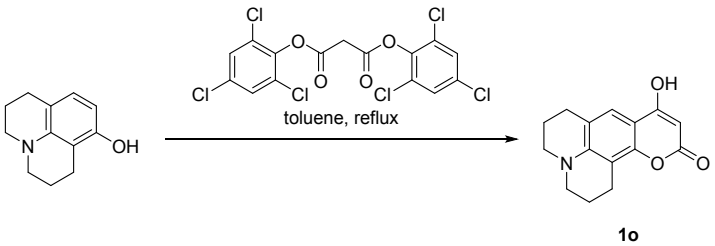
1a **1m**

*4-Hydroxy-3-methyl-2H-chromen-2-one (**1m**).* A solution of **1a** (0.97 g, 6 mmol) in MeOH (12 mL) was heated to reflux. Then 2N NaOH aqueous solution (3 mL) was added and the clear solution was stirred for 1 h. The solvent was removed *in vacuo,* and the white residue was added with EtOAc (10 mL) and stirred for 1

h. The sodium salt of **1a** was obtained as a white solid after being filtered and dried. The sodium salt was then dissolved in a DCl D_2O solution (20%, 2 mL) and extracted with EtOAc (3 mL × 2). The organic solution was combined and evaporated *in vacuo* to give the 4-OD coumarin **1m** (0.33 g, 34%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 12.60 (s, 1H), 7.87–7.78 (m, 1H), 7.71–7.60 (m, 1H), 7.42–7.30 (m, 2H), 5.62 (s, 1H) ppm. HRMS (ESI$^+$): cacld for $C_9H_6DO_3^+$ $(M + H)^+$, 164.0452; found 164.0446.



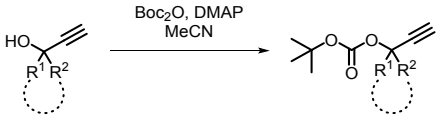
*7-(Diethylamino)-4-hydroxy-2H-chromen-2-one (**1n**).* Prepared according to a reported literature.[3] A solution of bis(2,4,6-trichlorophenyl) malonate (0.92 g, 2 mmol) and 3-(diethylamino)phenol (0.34 g, 2 mmol) in 5 mL toluene was heated to reflux for 5 h. After cooling down, the precipitation was collected and washed with cold toluene and hexane to afford the desired compound **1n** as gray solid (0.32 g, 70%). The ^{1}H NMR spectrum fits well to the reported data.[3] HRMS (ESI$^+$): calcd for $C_{13}H_{16}NO_3^+$ $(M + H)^+$, 234.1125, found 234.1120.



*9-Hydroxy-2,3,6,7-tetrahydro-1H,5H,11H-pyrano[2,3-f]pyrido[3,2,1-ij]quinolin-11-one (**1o**).* A solution of bis (2,4,6-trichlorophenyl) malonate (2.45g, 5.28mmol) and 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-ij]quinolin-8-ol (1g, 5.28mmol) in 25ml toluene was heated to reflux for 5h. After cooling down, the

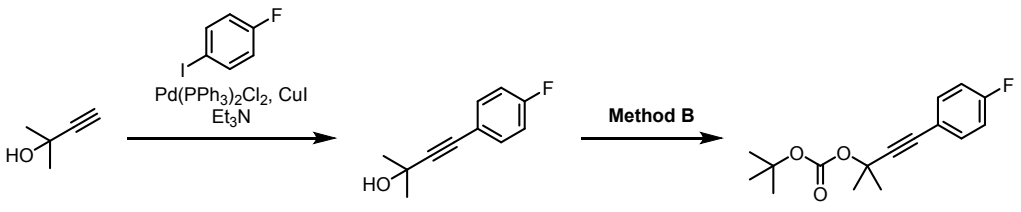
precipitation was collected and washed with cold toluene and hexane to afford the desired compound **1o** as gray solid (1.01 g, 75%). HRMS (ESI^+): calcd for $C_{15}H_{16}NO_3^+$ $(M + H)^+$, 258.1125, found 258.1129.

*Procedure for synthesis of Boc-protected propargyl alcohol (**2a–g**)*



2a-f

Method B. *Tert*-butyl (2-methylbut-3-yn-2-yl) carbonate (**2a**) was prepared according to our previously reported procedure[4]. Generally, di-*tert*-butyl decarbonate (7.85 g, 36 mmol, 1.2 equiv) was added dropwise to a solution of 2-methylbut-3-yn-2-ol (2.52 g, 30 mmol, 1.0 equiv) with 4-dimethylaminopyridine (0.36 g, 3 mmol, 0.1 equiv) in 100 mL acetonitrile. The resulting mixture was then stirred at room temperature for 12 h. Upon completion, the solvent was removed and the residue was diluted with aqueous 1N HCl solution and extracted with ethyl acetate (3 × 40 mL). The organic phases were collected, washed by water and dried with anhydrous Na_2SO_4. After being filtered and concentrated in vacuo, the crude product was further purified by a column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1) to give the desired product (2.87 g, 52%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.54 (s, 1H), 1.69 (s, 6H), 1.49 (s, 9H) ppm. Next, the Boc-protected propargyl alcohols **2b–2f** were prepared according to the **Method B** except various propargyl alcohols were employed in the reaction.



2g

*tert-Butyl (4-(4-fluorophenyl)-2-methylbut-3-yn-2-yl) carbonate (**2g**)*. 4-(4-Fluorophenyl)-2-methylbut-3-yn-2-ol was prepared through a Sonogashira reaction.[5] ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.46–7.41 (m, 2H), 7.23–7.17 (m, 2H), 5.46 (s, 1H), 1.46 (s, 6H) ppm. Then **2g** was prepared according to method B a yellow oil. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.47–7.43 (m, 2H), 7.23 (t, J = 8.8 Hz, 2H), 1.69 (s, 6H), 1.42 (s, 9H) ppm.

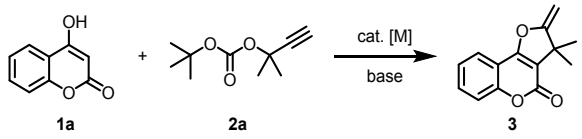
*Synthesis of 3-methyl-4-[(3-methylbuta-1,2-dien-1-yl)oxy]-2H-chromen-2-one (**3a**)*

1l (1.0 mmol) And tert-butyl (2-methylbut-3-yn-2-yl) carbonate **2a** (1.5 mmol, 1,5 equiv) were further employed in a standard reaction to afford 3-methyl-4-[(3-methylbuta-1,2-dien-1-yl)oxy]-2*H*-chromen-2-one (**3a**, 0.16 g, 67%) as a white solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.80 (d, J = 7.7 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 8.2 Hz, 1H), 2.94 (s, 1H), 1.47 (s, 1H), 1.20 (s, 1H), 1.13 (s, 1H) ppm.

*Synthesis of 3,3-dimethyl-2-(methylene-d)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (**3b**)*

1m (1.0 mmol) was treated with **2a** (1.5 mmol, 1,5 equiv) under standard method to afford title compound **3b** (0.14 g, 61%) as a white solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.82–7.67 (m, 2H), 7.52 (d, J = 8.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 4.98–4.96 (m, 1H), 4.79–4.75 (m, 1H), 1.49 (s, 6H) ppm. HRMS (APCI+): calcd for $C_{14}H_{12}DO_3^+$ $(M + H)^+$, 230.0922, found 230.0926.

Table S1. Reaction Optimization[a]



Entry	Catalyst	Base	Solvent	Temp (°C)	Yield[b]
1	$Pd(OAc)_2$	NaOAc	THF	25	NR

2	$PdCl_2$	NaOAc	THF	25	NR

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (1.5 mmol, 1.5 equiv), [M] catalyst (10 mol %), base (1.5 equiv) in solvent (15 mL) for 1 h under air. [b]Isolated yield. NR = No reaction.

REFERENCE

[1] Huang, Z.; Matsubara, O.; Jia, S.; Tokunaga, E.; Shibata, N., Difluoromethylthiolation of Phenols and Related Compounds with a Hf2cso2na/Ph2pcl/Me3sicl System. *Org Lett.* **2017**, *19*, 934-937.

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[3] Chevalier, A.; Renard, P. Y.; Romieu, A., Straightforward Access to Water-Soluble Unsymmetrical Sulfoxanthene Dyes: Application to the Preparation of Far-Red Fluorescent Dyes with Large Stokes' Shifts. *Chemistry.* **2014**, *20*, 8330-8337.

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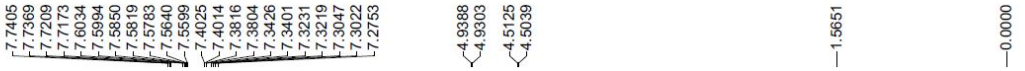
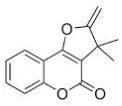
[5] Brzozowska, A.; Zubar, V.; Ganardi, R. C.; Rueping, M., Chemoselective Hydroboration of Propargylic Alcohols and Amines Using a Manganese(Ii) Catalyst. *Org Lett.* **2020**, *22*, 3765-3769.

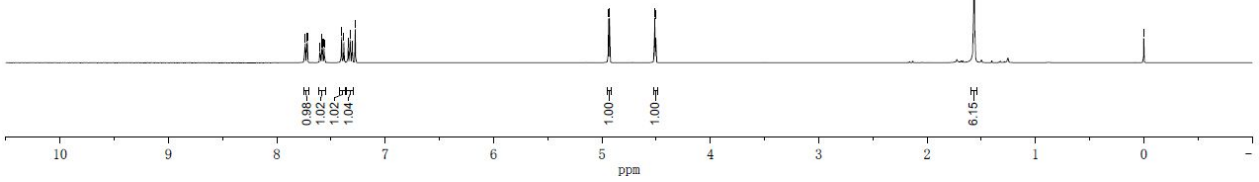
NMR and HRMS data of reported compounds

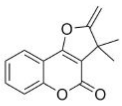
3,3-Dimethyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**3**)



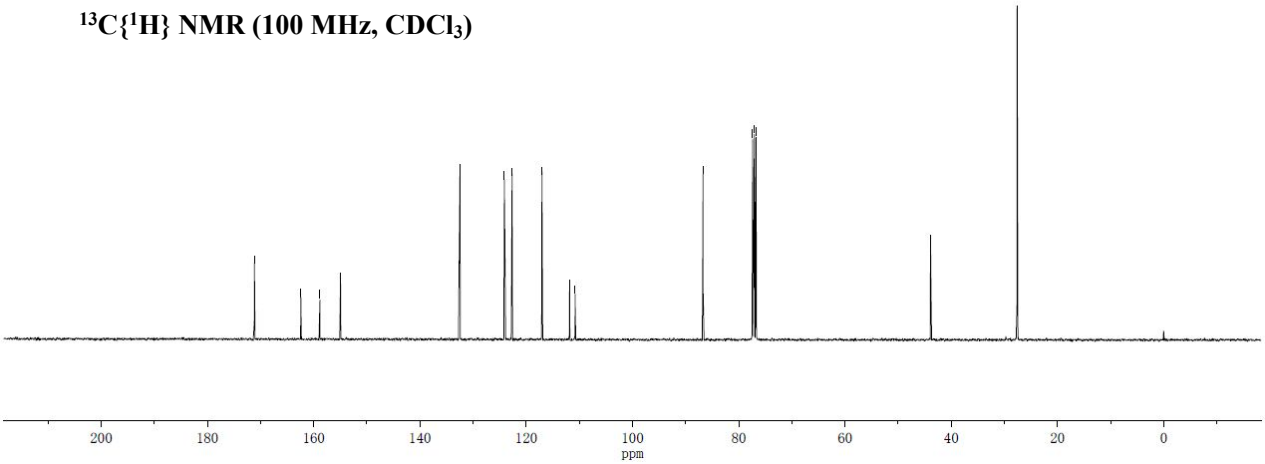


^{1}H NMR (400 MHz, $CDCl_3$)

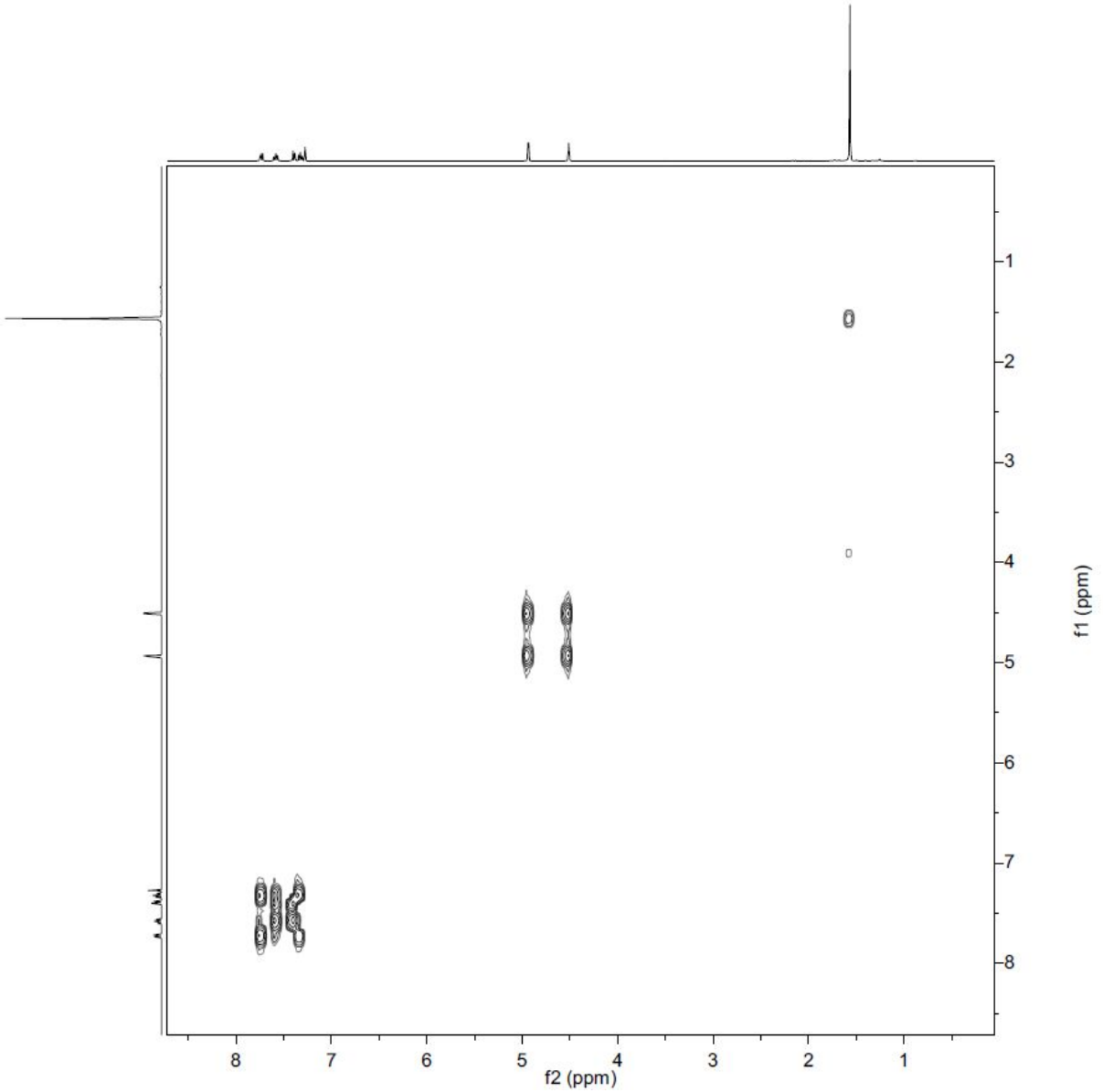




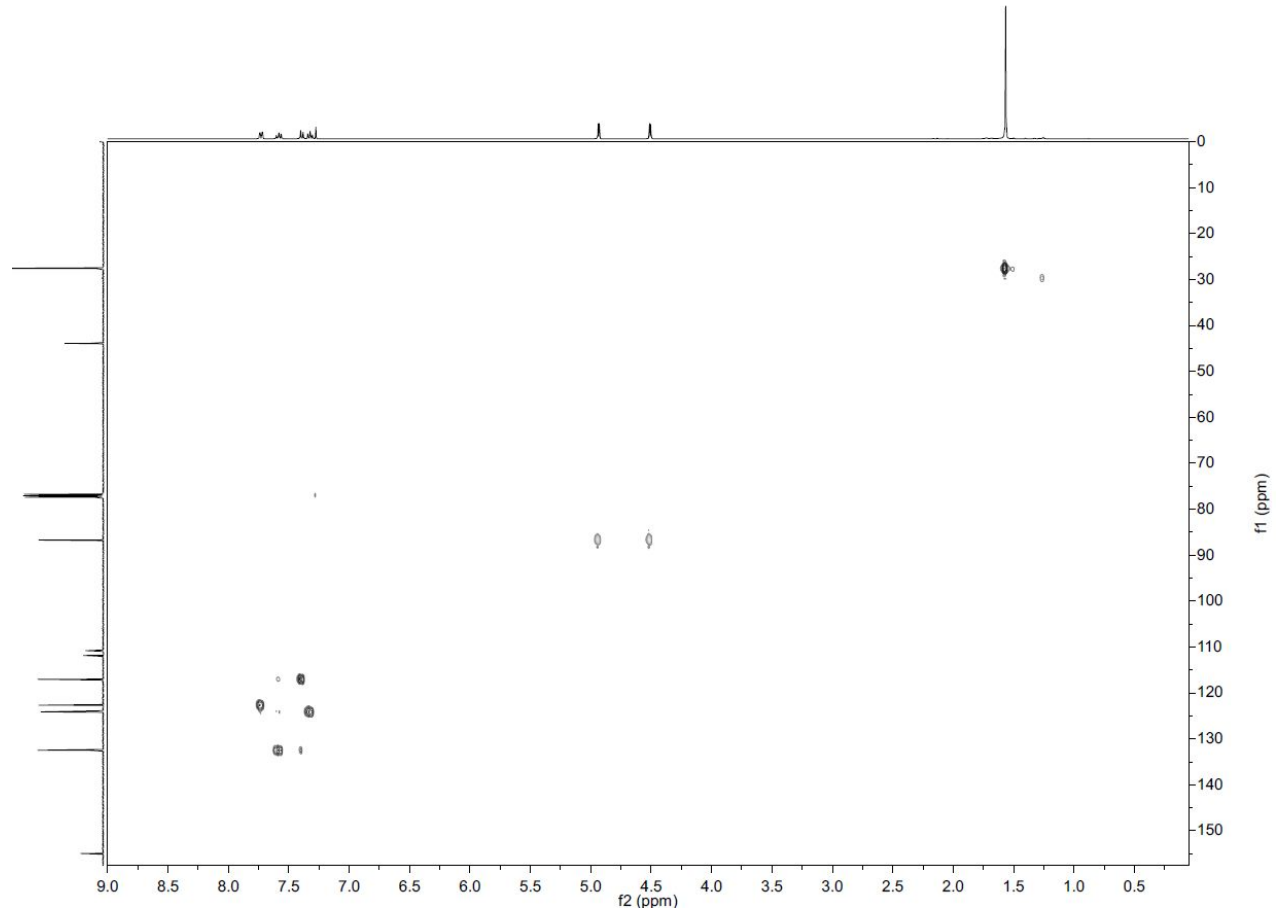
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



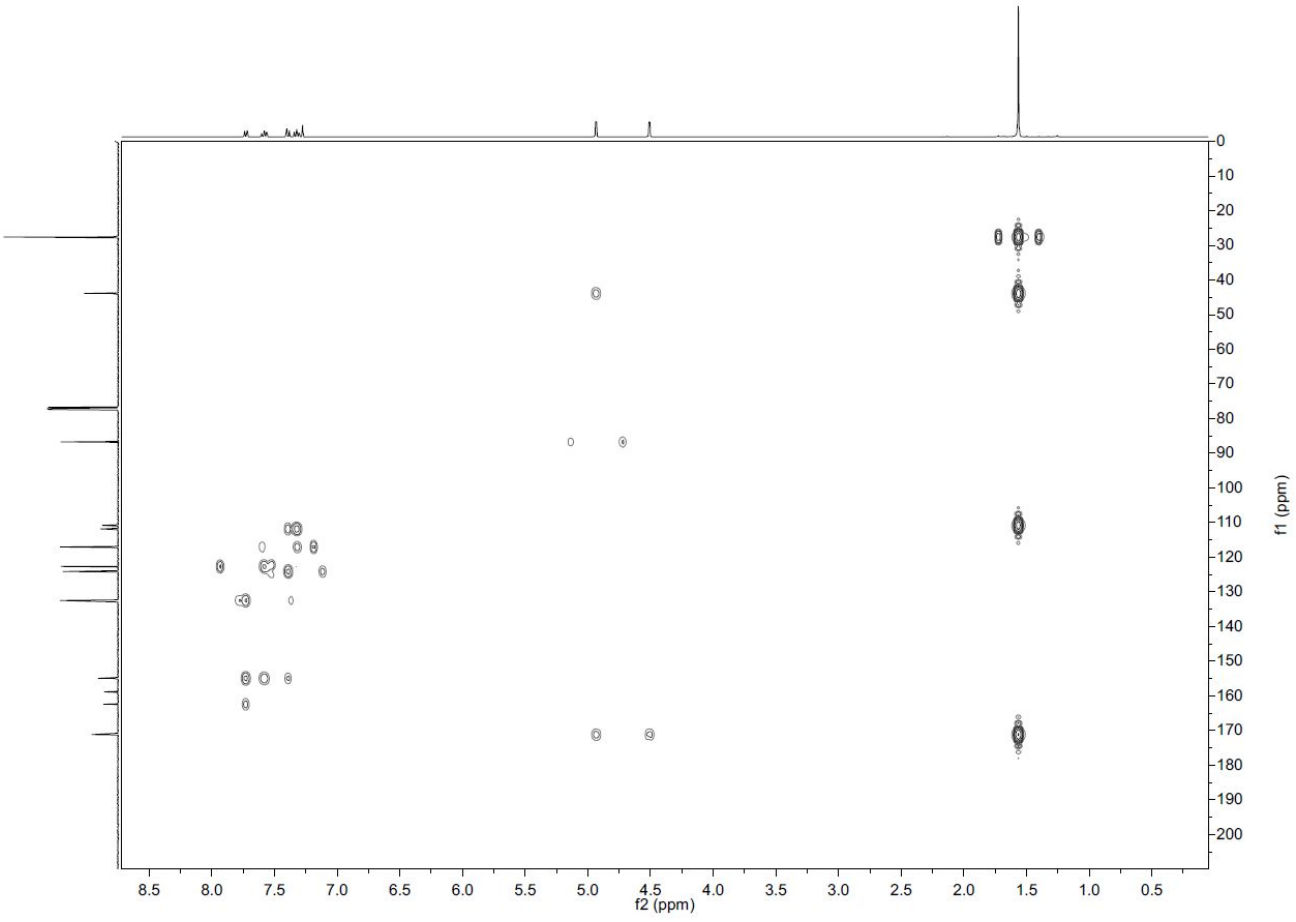
^{1}H-^{1}H Correlation Spectroscopy (COSY) of **3**



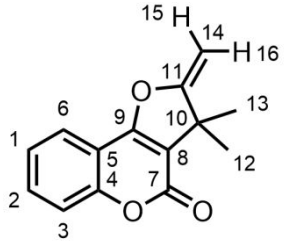
C-H Heteronuclear Single Quantum Correlation (HSQC) of **3**



C-H Heteronuclear Multiple Bond Correlation (HMBC) of **3**

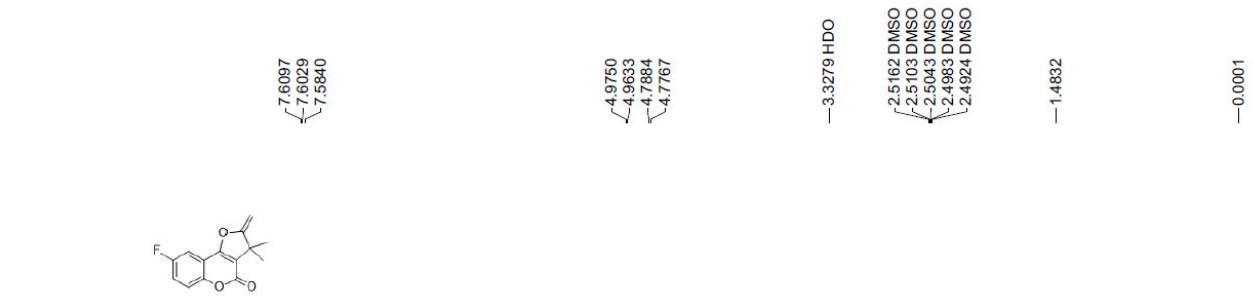


NMR spectra assignments of **3**

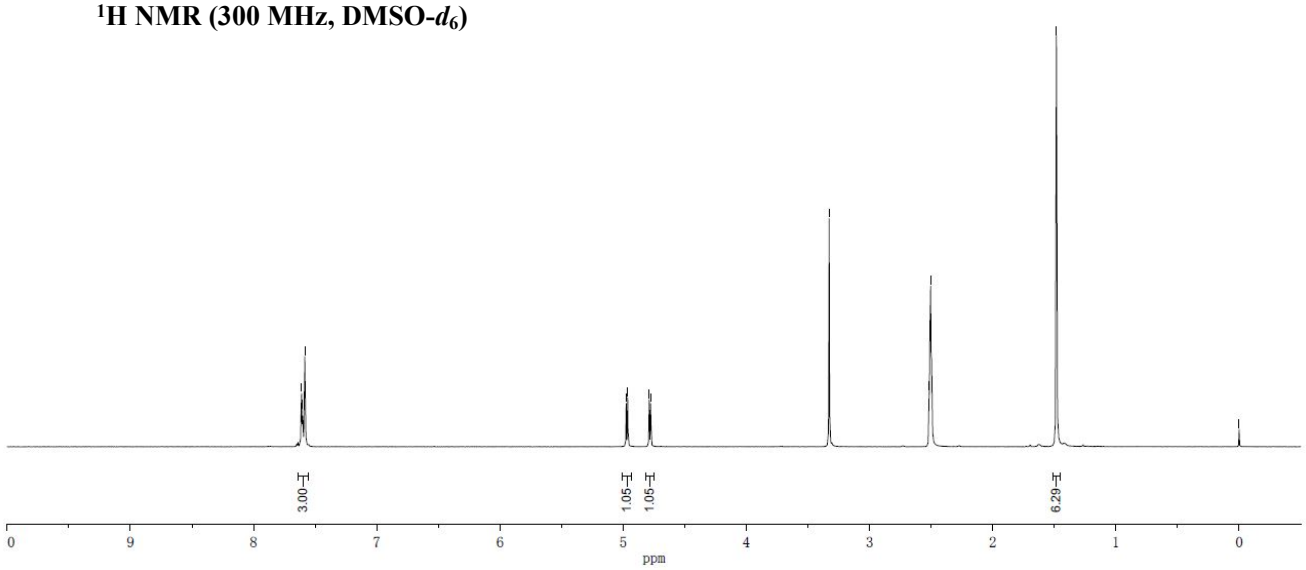


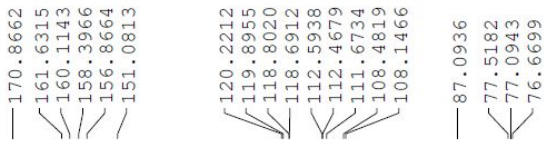
Position	^{1}H chemical shift	multiplicity	Relative intensity	Coupling constant(s) (Hz)	^{13}C{^{1}H} chemical shirt	HMBC correlations
1	7.38	dt	1H	1.0, 7.8	132.5	H1: C5, C6
2	7.59	m	1H		124.1	H2: C3, C4, C6
3	7.40	dd	1H	0.4, 8.4	122.7	H3: C1, C2, C4, C5
4					155.0	C4: H2, H3, H6
5					111.8	C5: H1, H3
6	7.74	dd	1H	1.4, 7.8	117.0	H6: C1, C4, C9
7					158.8	
8					110.8	C8: H12, H13
9					162.4	C9: H6
10					43.9	C10: H12, H13, H16
11					171.2	C11: H6, H12, H13, H15, H16
12	1.57	s	3H		27.6	H12: C8, C10, C11, C12, C13
13	1.57	*s*	3H		27.6	H12: C8, C10, C11, C12, C13
14					86.7	C14: H15, H16
15	4.51	d	1H	3.4		H15: C11, C14
16	4.94	d	1H	3.4		H16: C10, C11, C14

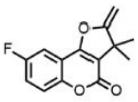
8-Fluoro-3,3-dimethyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**4**)



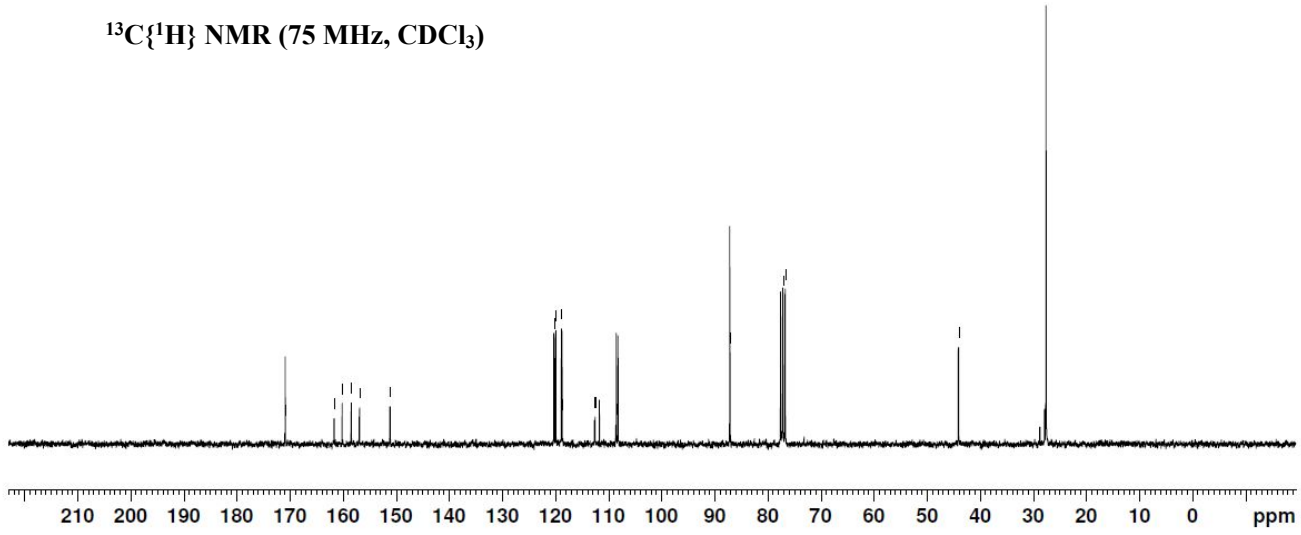
^{1}H NMR (300 MHz, DMSO-d_6)



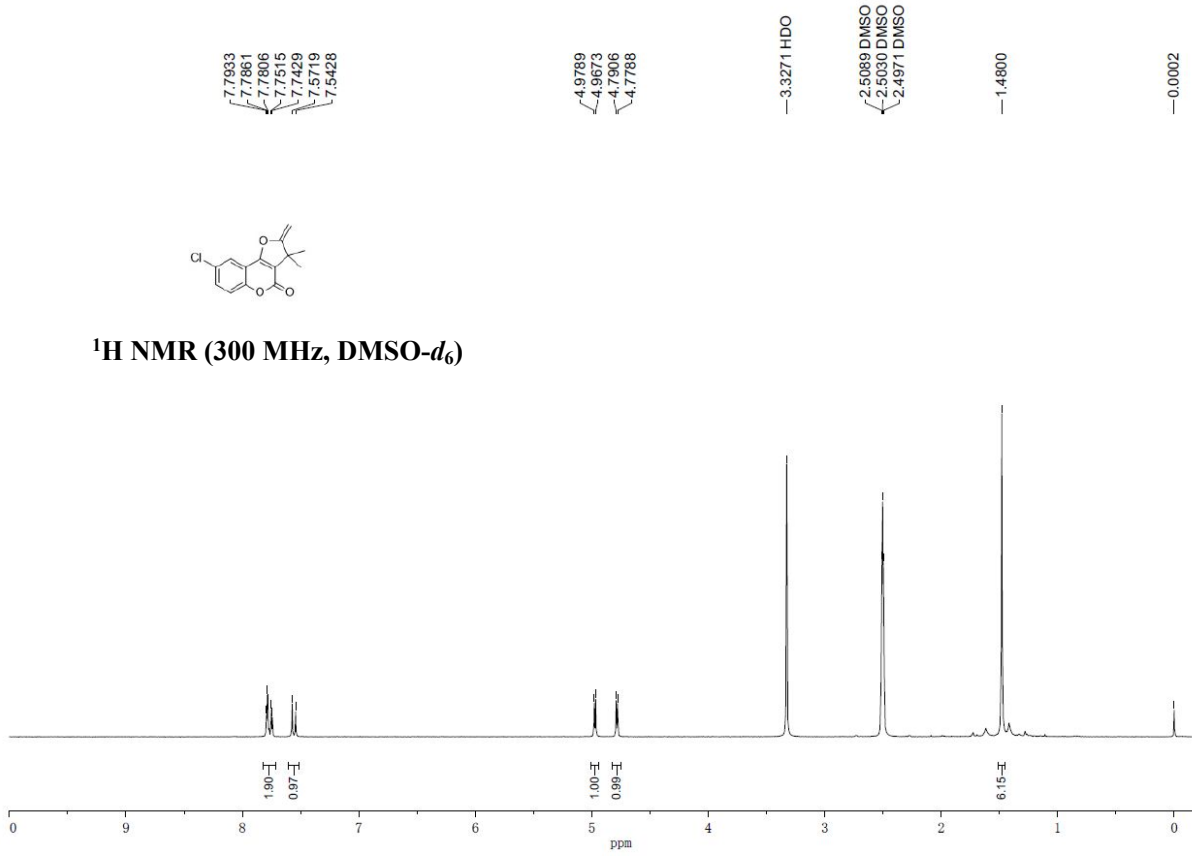




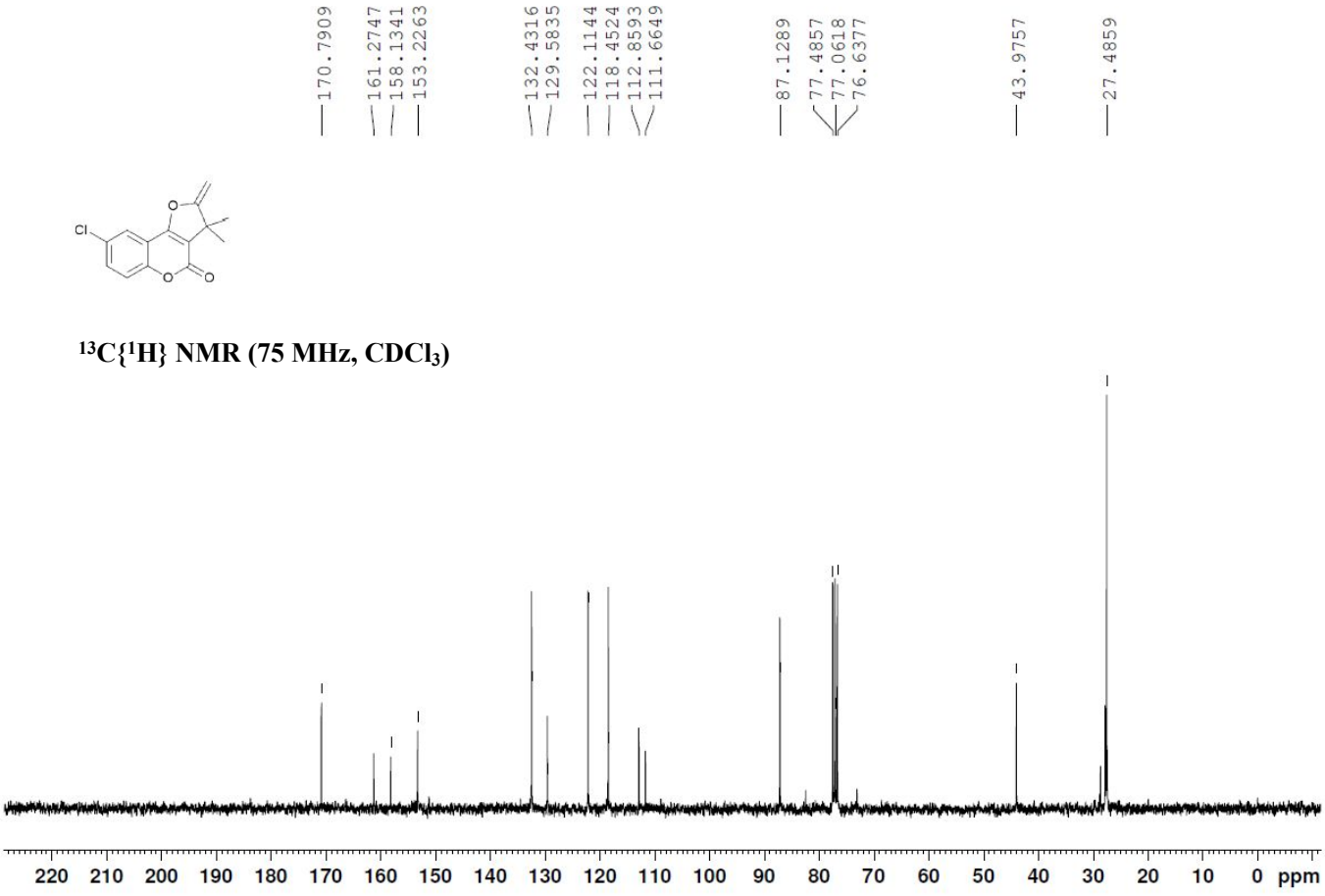
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



8-Chloro-3,3-dimethyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**5**)

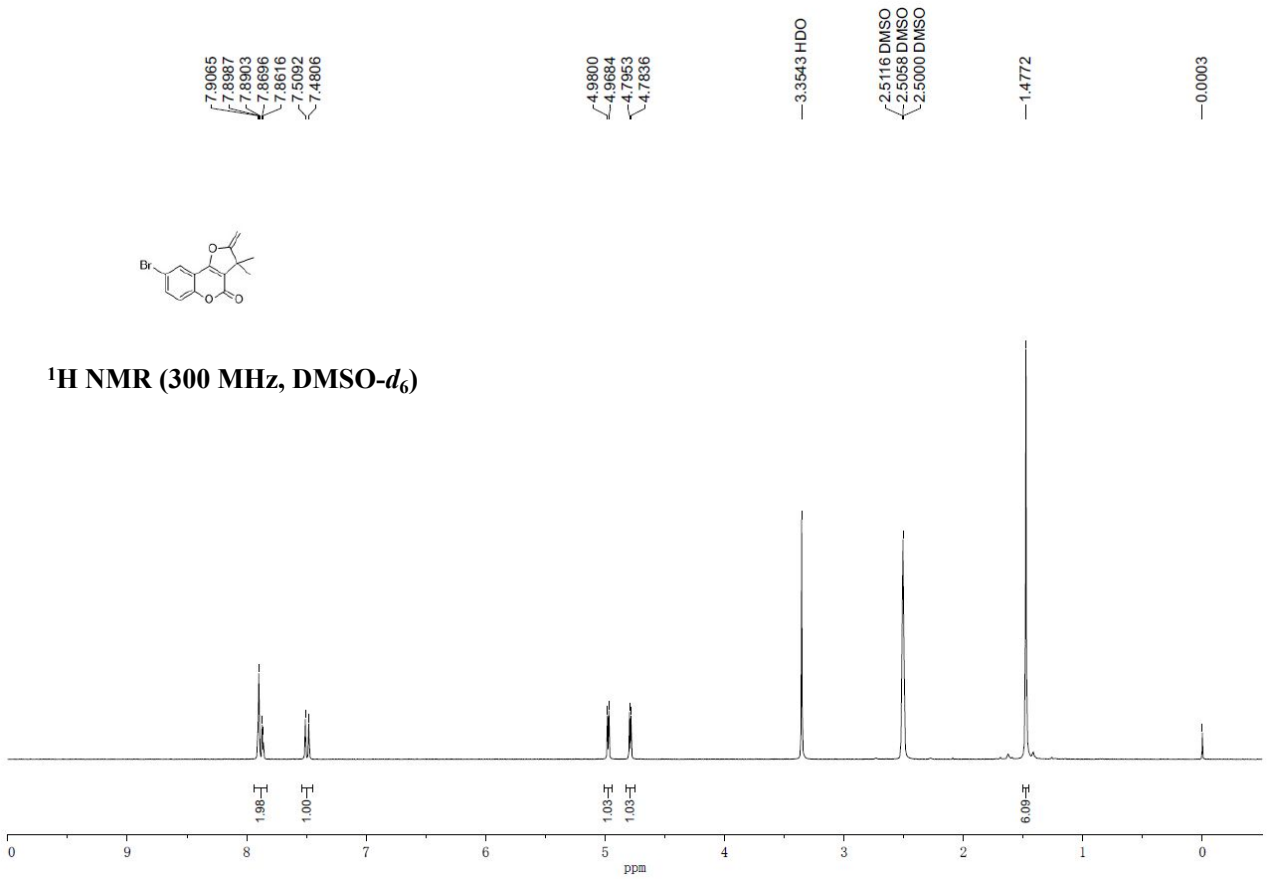


^{1}H NMR (300 MHz, DMSO-d_6)

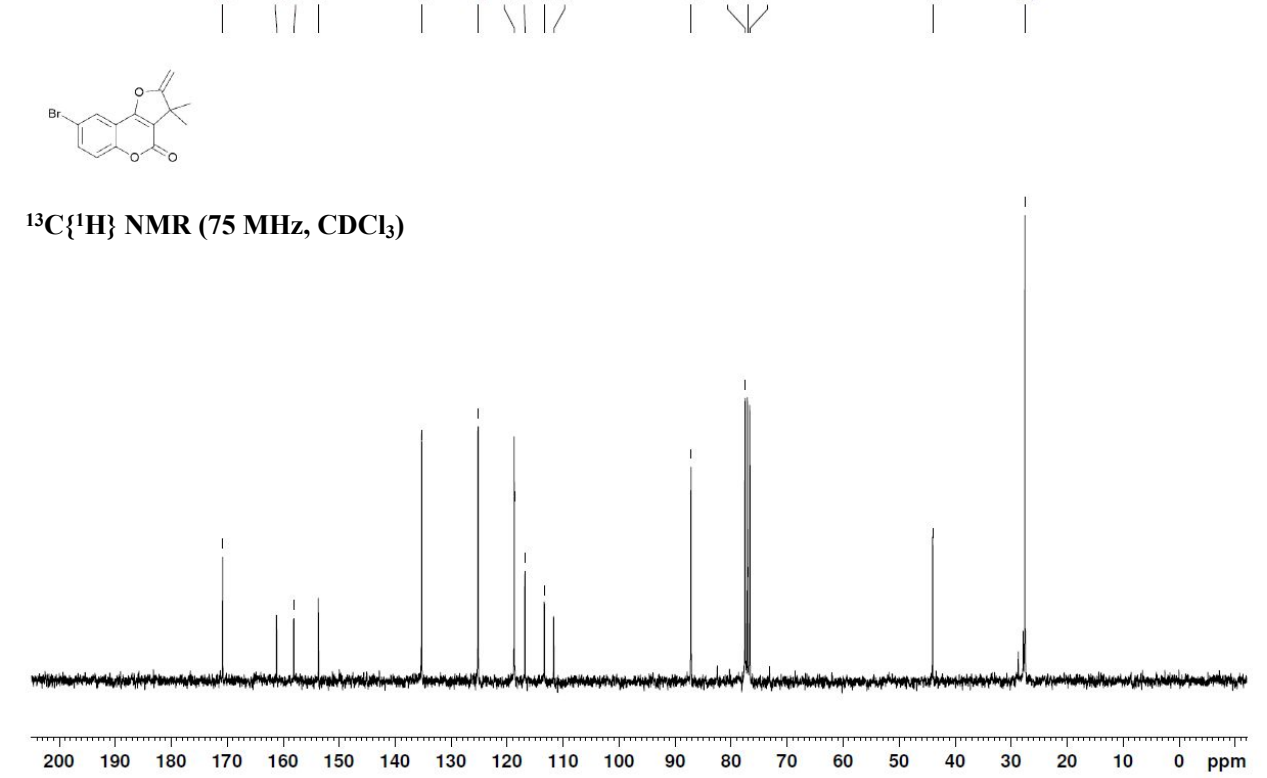


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

8-Bromo-3,3-dimethyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**6**)

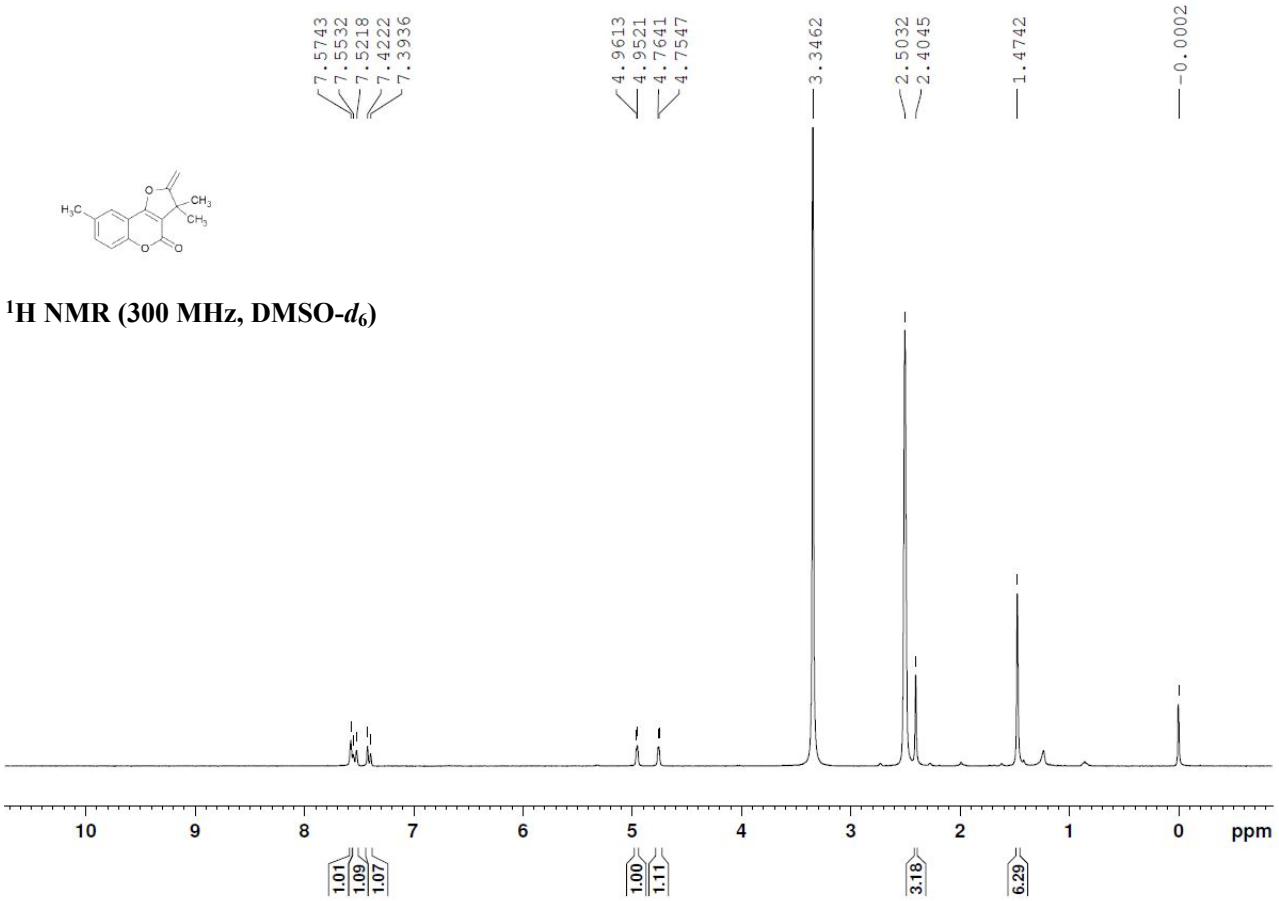


^{1}H NMR (300 MHz, DMSO-d_6)

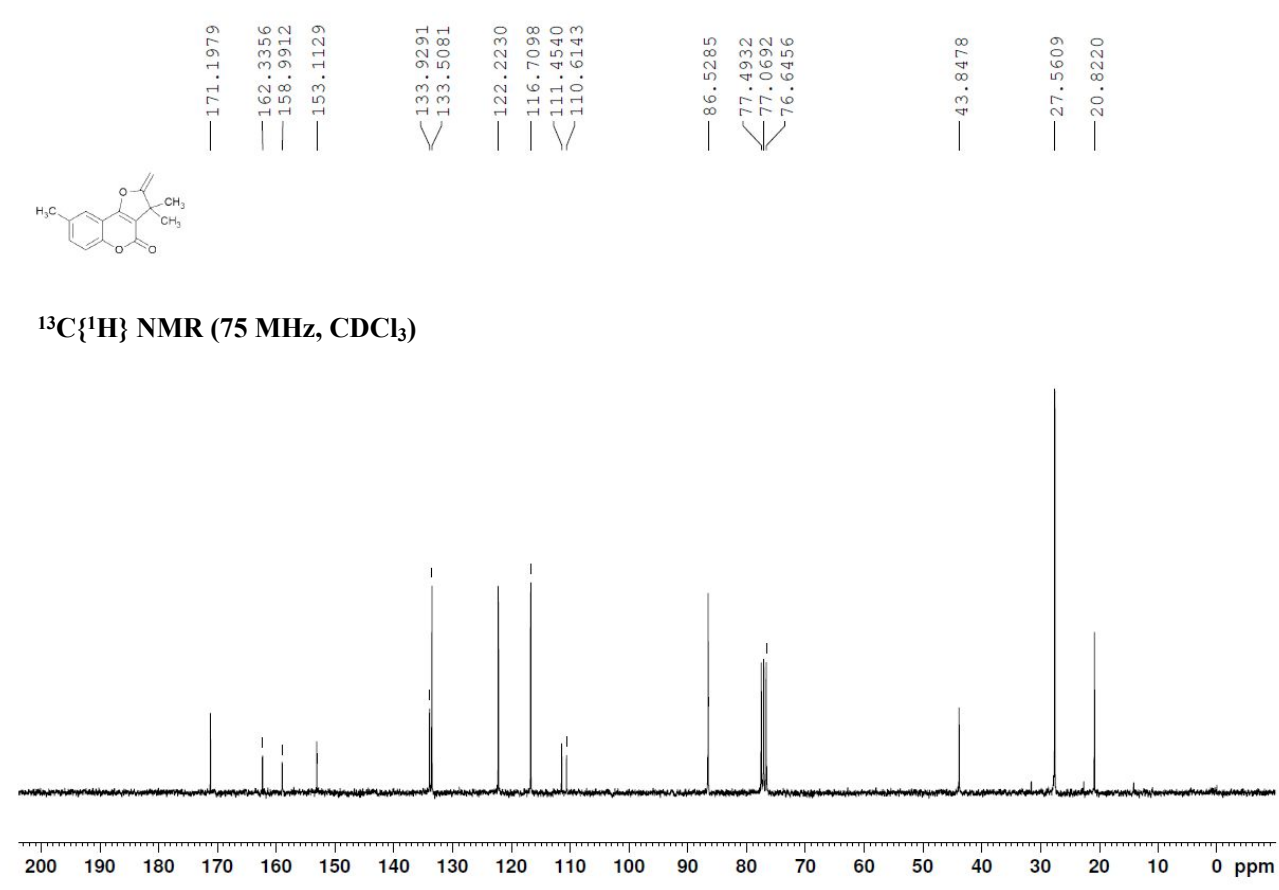


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

3,3,8-Trimethyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**7**)

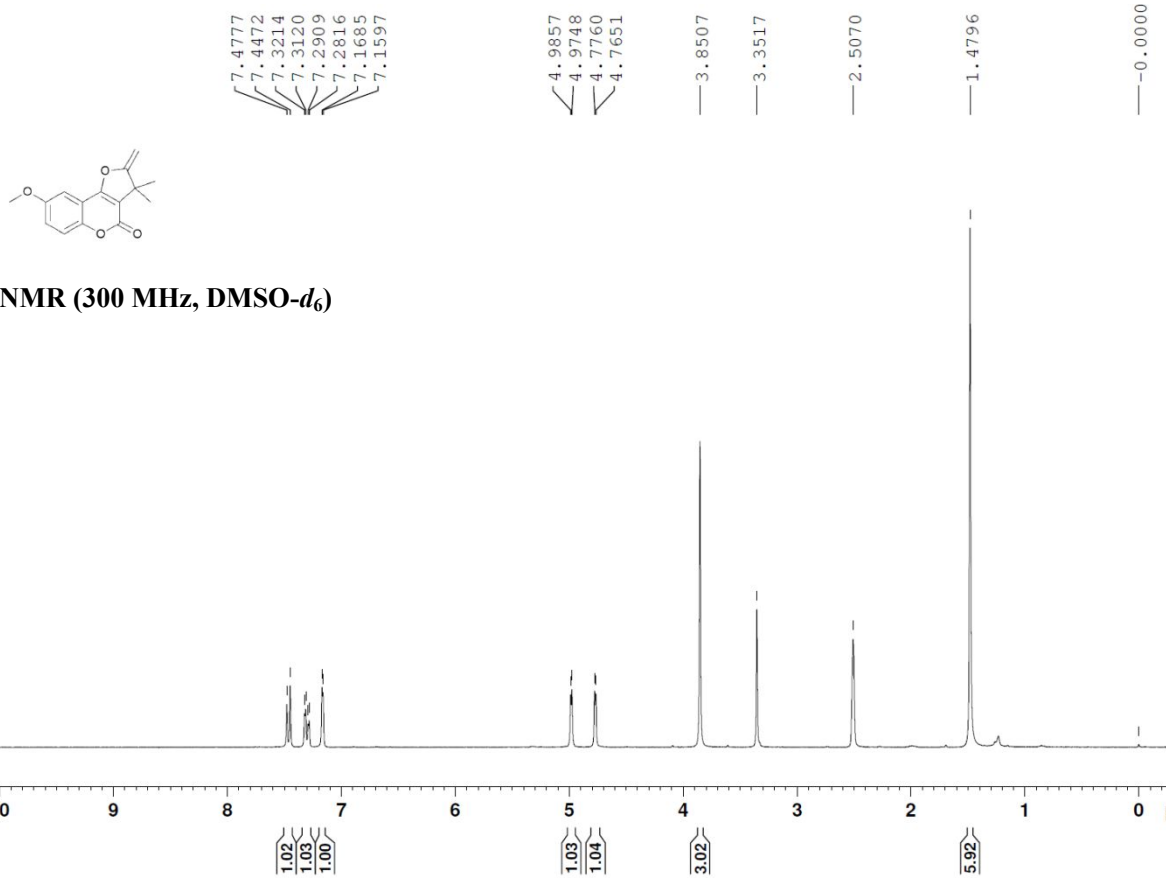


^{1}H NMR (300 MHz, DMSO-d_6)

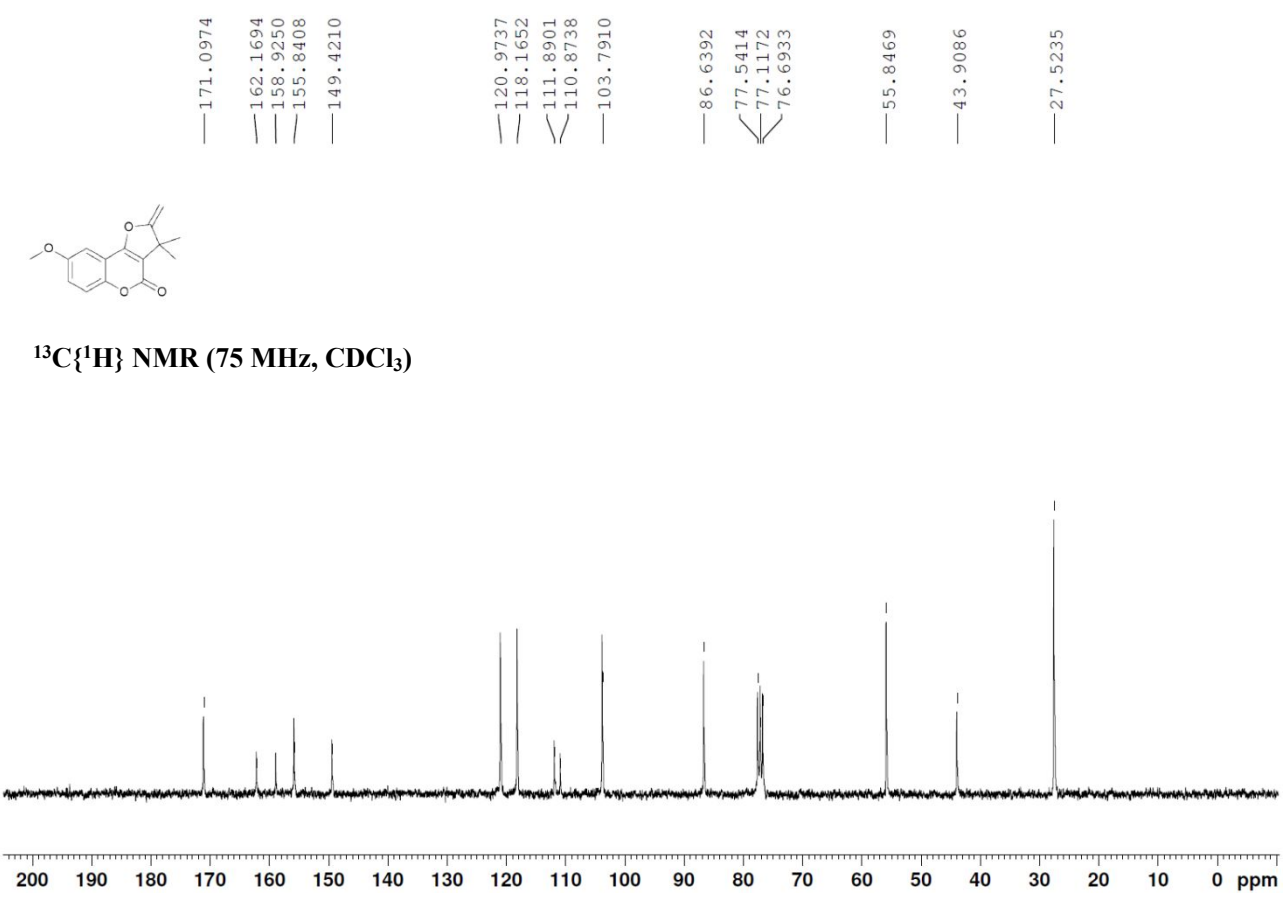


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

8-Methoxy-3,3-dimethyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**8**)

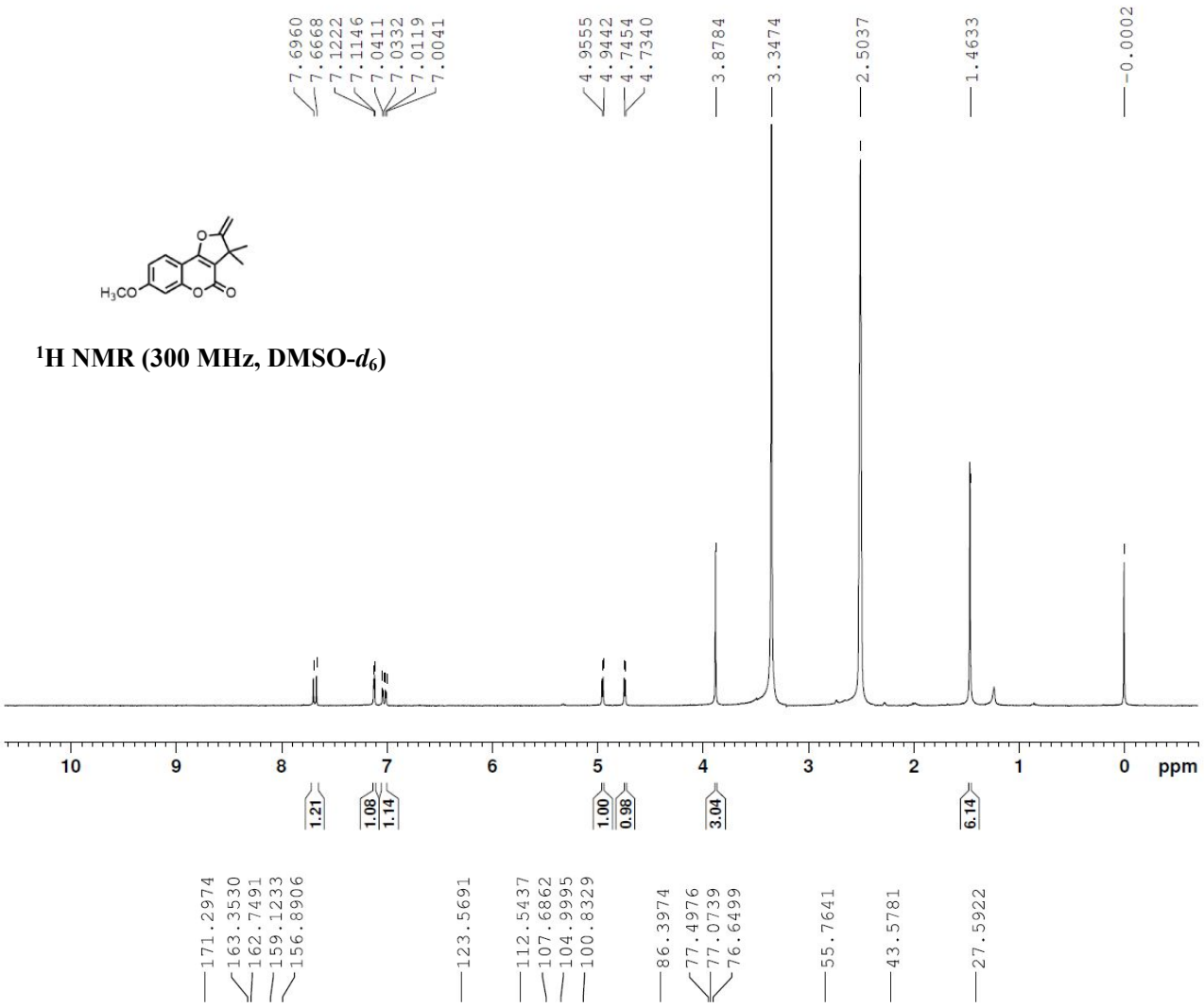


^{1}H NMR (300 MHz, DMSO-d_6)

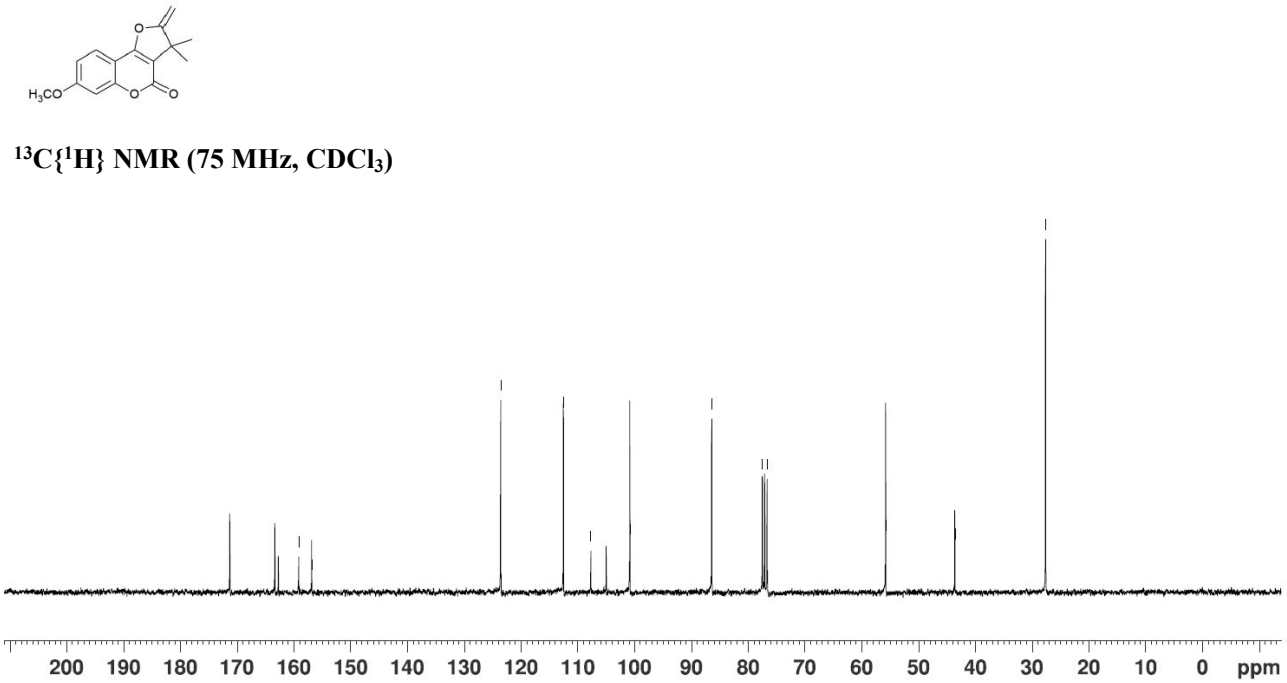


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

7-Methoxy-3,3-dimethyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**9**)

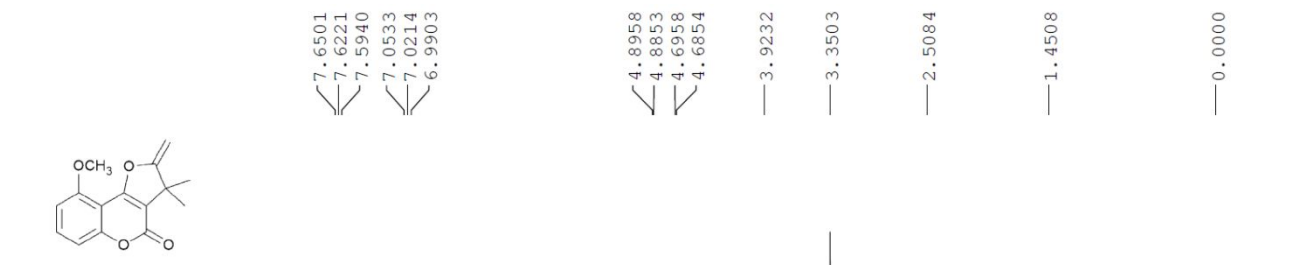


^{1}H NMR (300 MHz, DMSO-d_6)

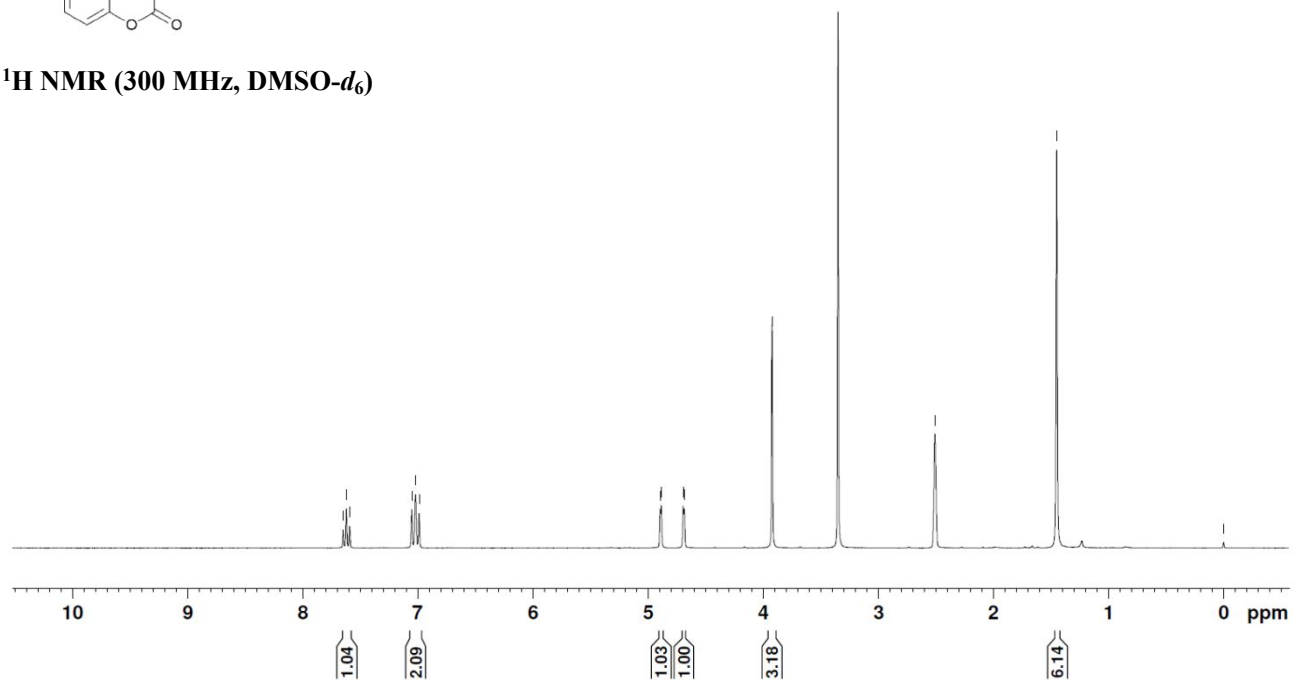


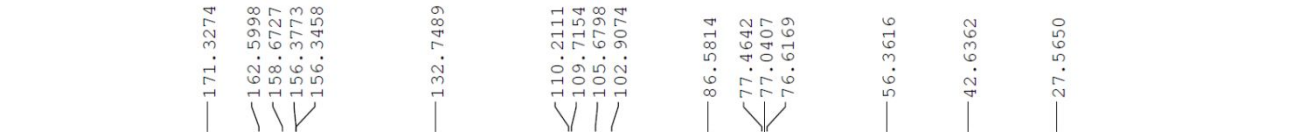
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

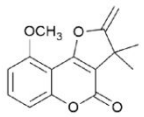
9-Methoxy-3,3-dimethyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**10**)



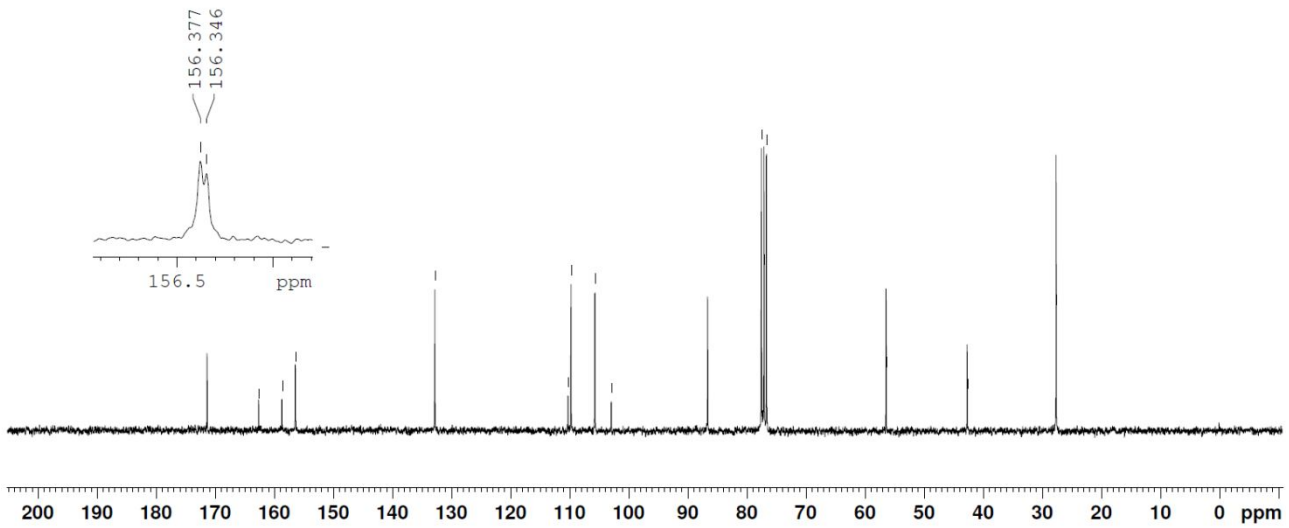
^{1}H NMR (300 MHz, DMSO-d_6)



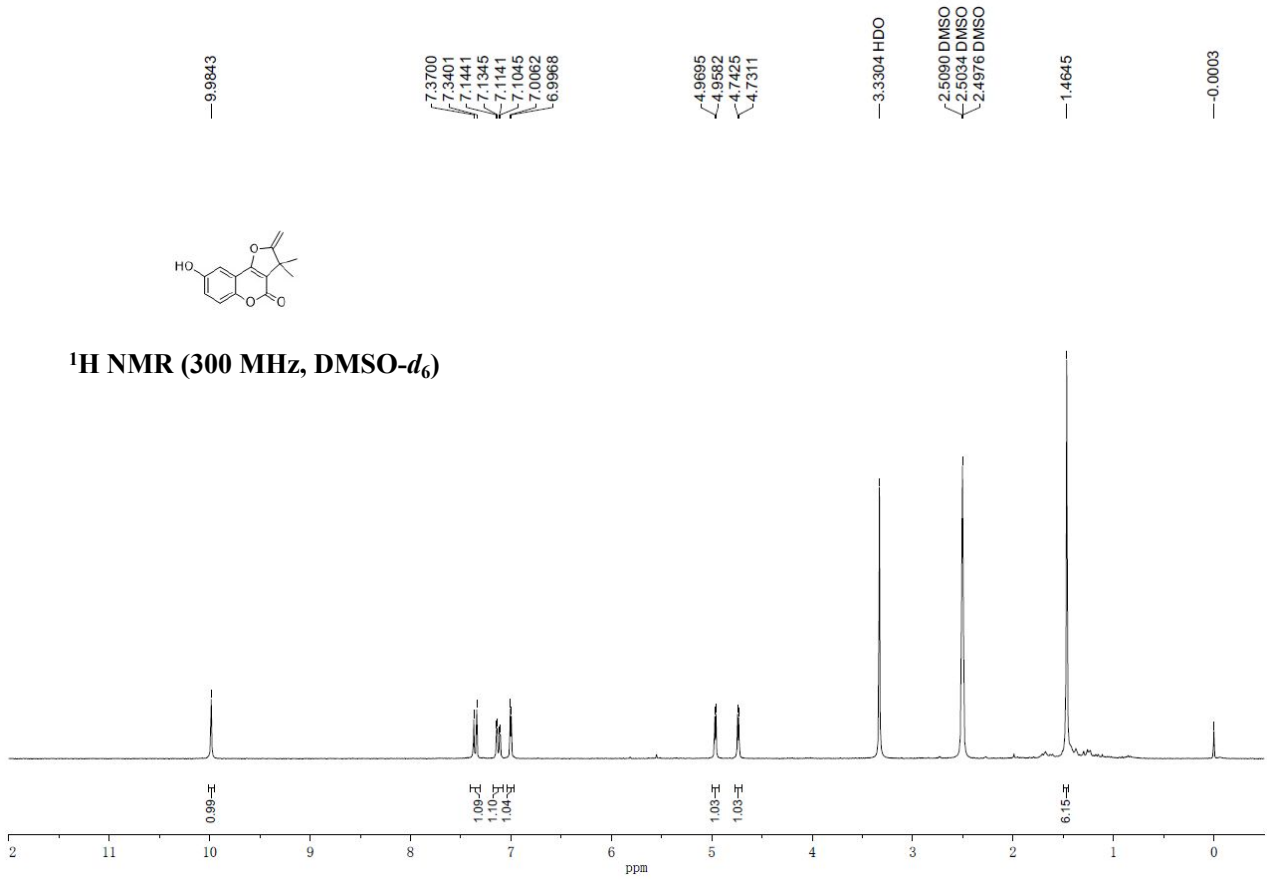




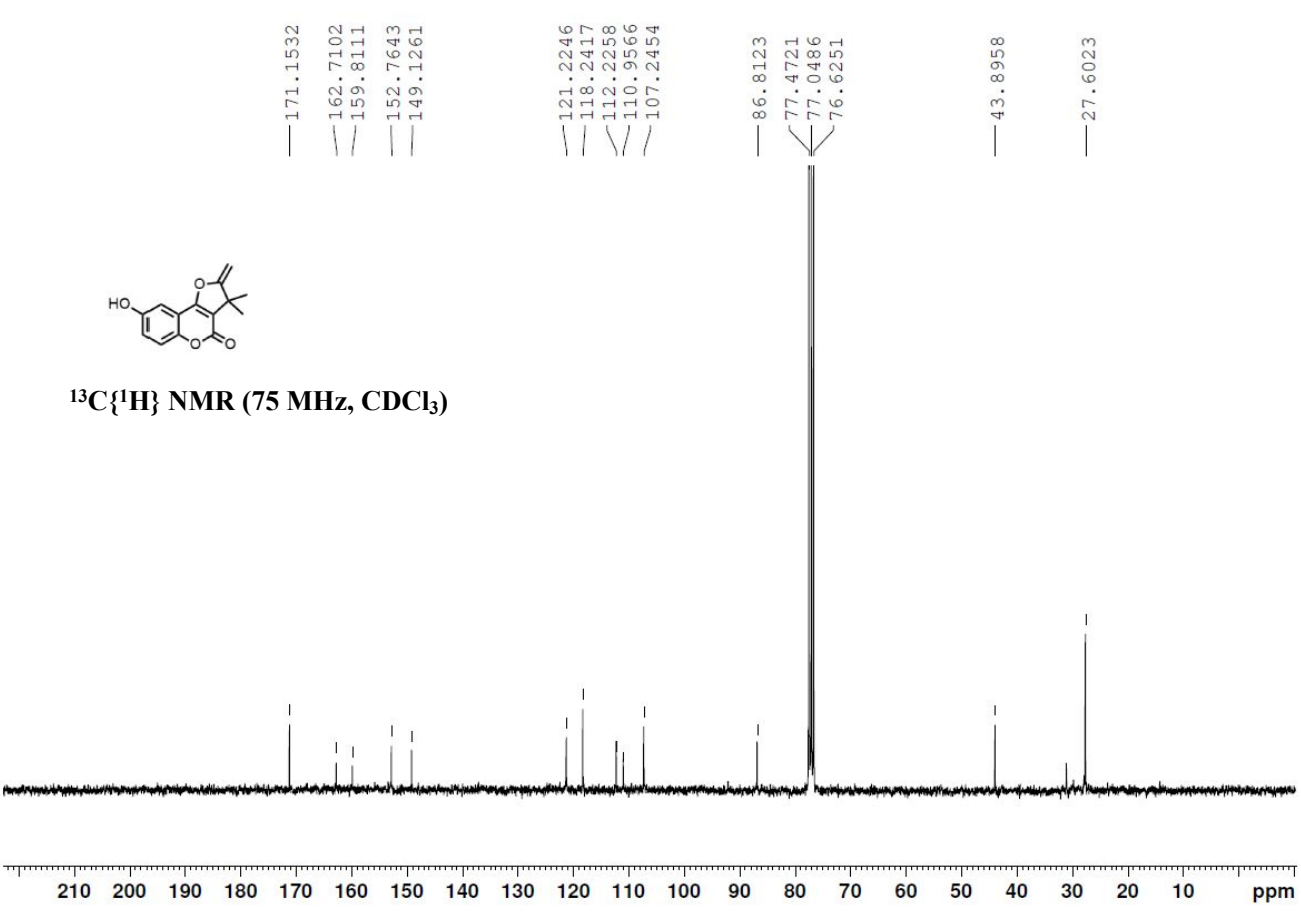
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



8-hydroxy-3,3-dimethyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**11**)

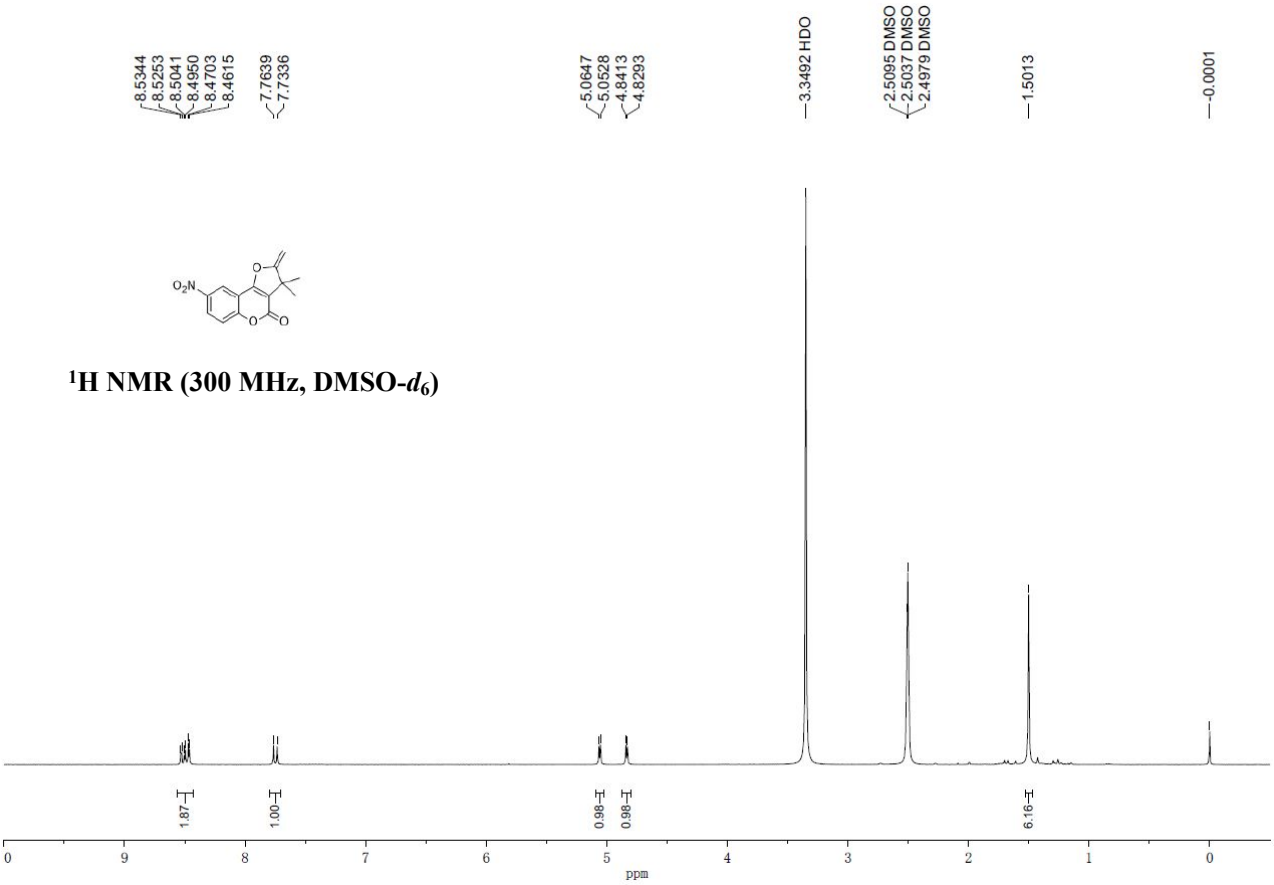


^{1}H NMR (300 MHz, DMSO-d_6)

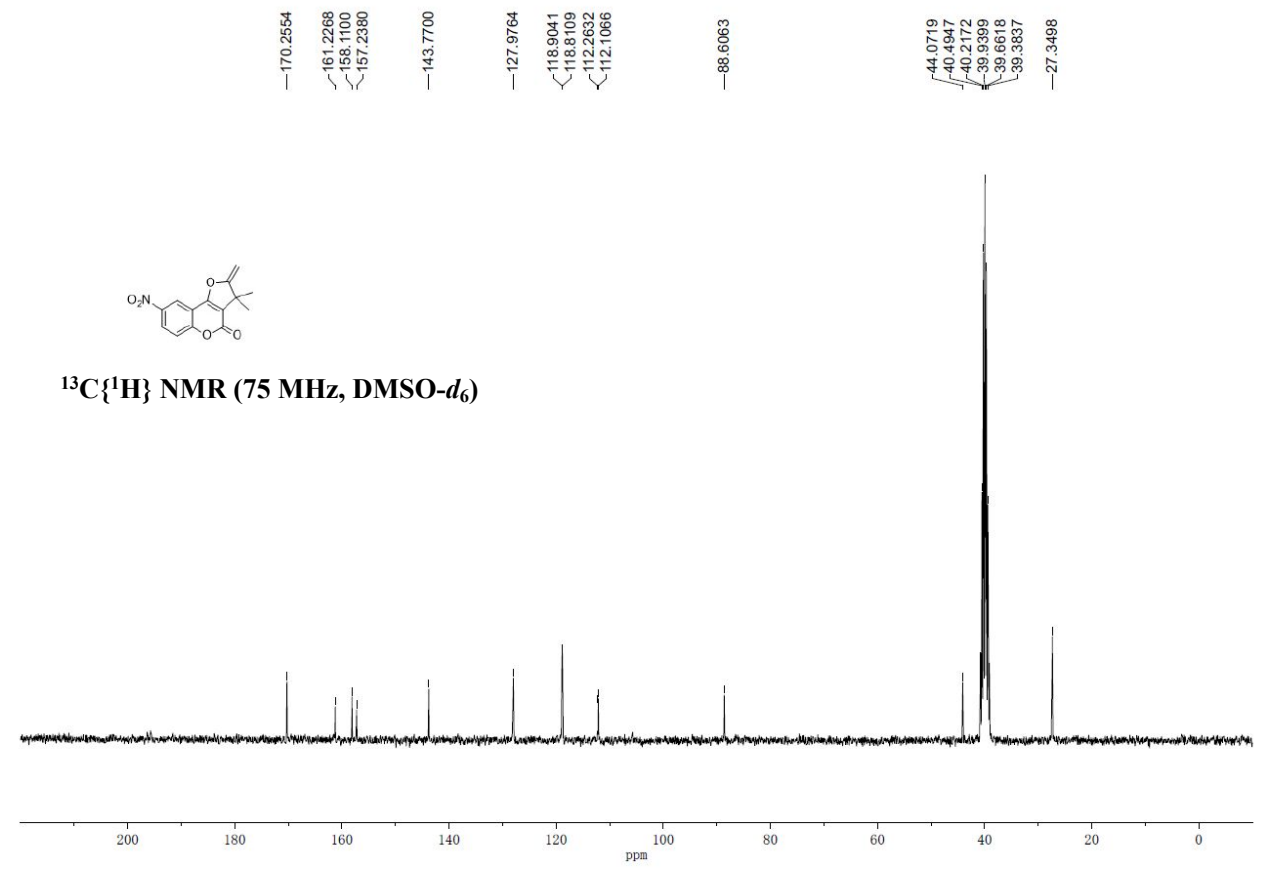


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

3,3-Dimethyl-2-methylene-8-nitro-2,3-dihydro-4H-furo[3,2-*c*]chromen-4-one (**12**)

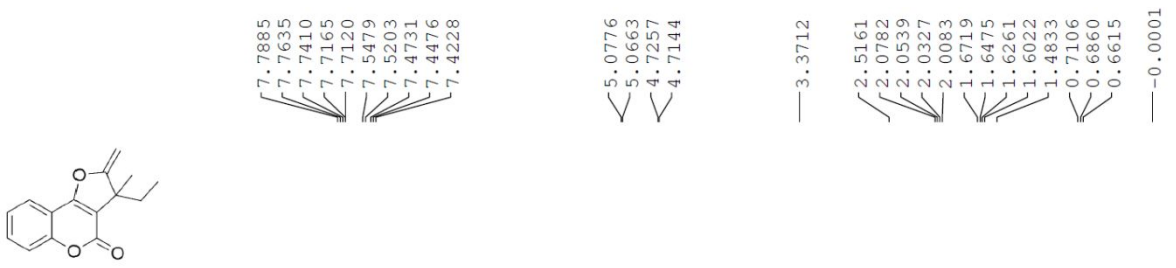


^{1}H NMR (300 MHz, DMSO-d_6)

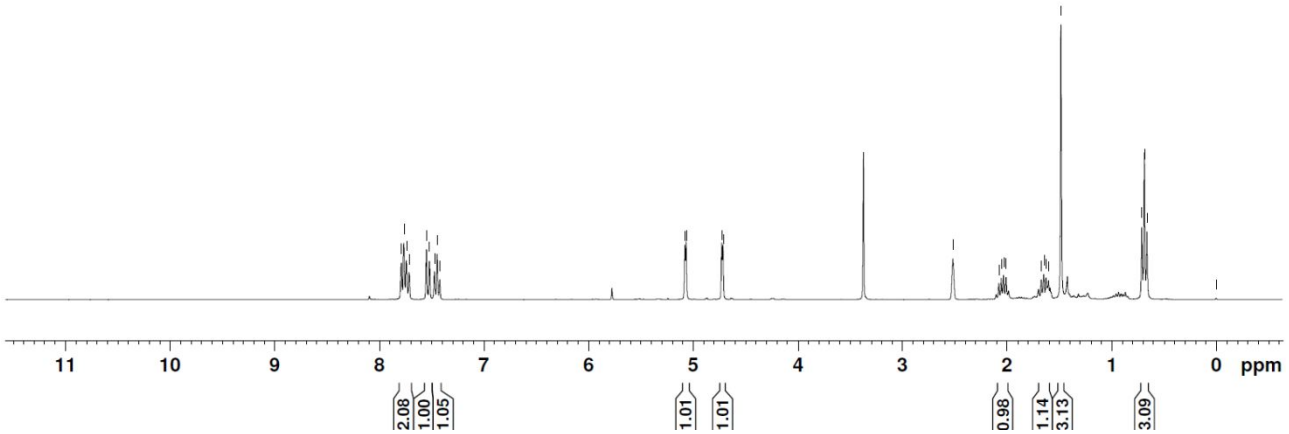


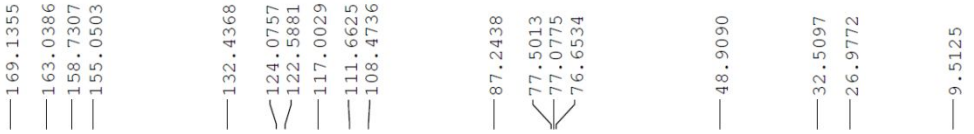
^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6)

3-Ethyl-3-methyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**13**)

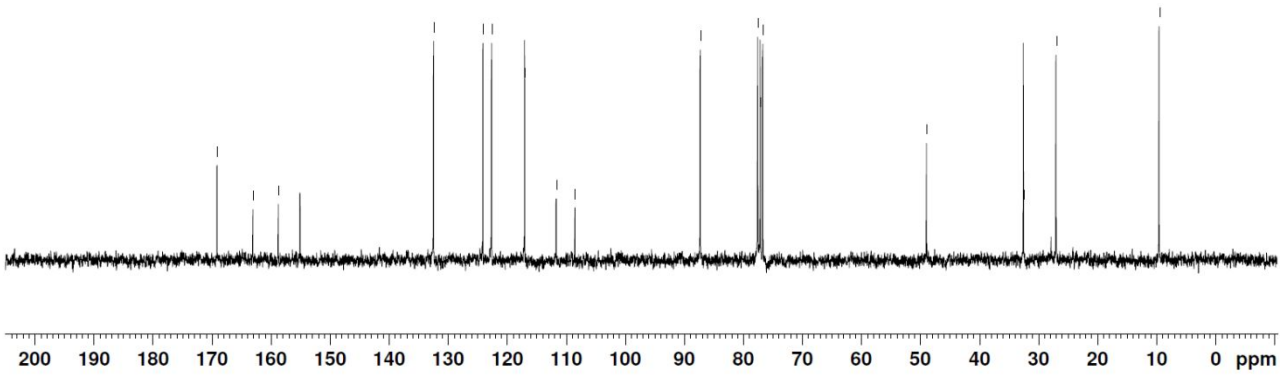


^{1}H NMR (300 MHz, DMSO-d_6)

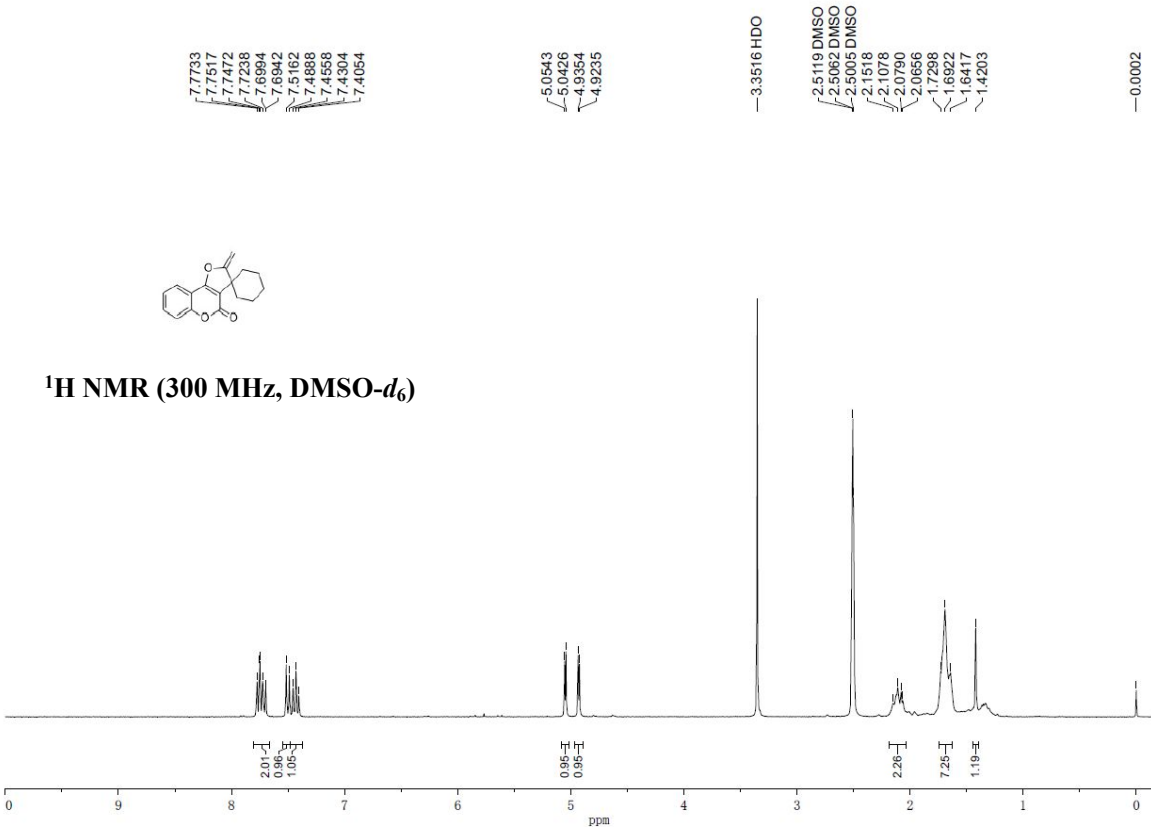




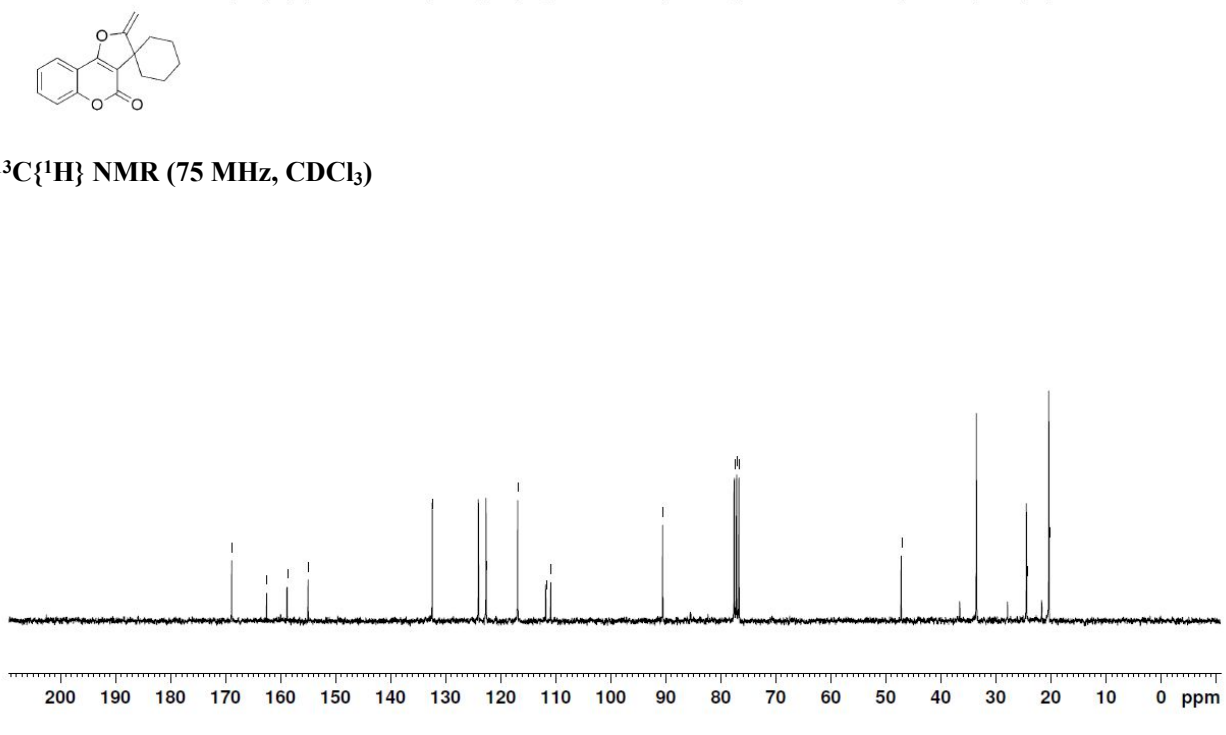
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



2'-Methylene-2'*H*,4'*H*-spiro[cyclohexane-1,3'-furo[3,2-*c*]chromen]-4'-one (**14**)

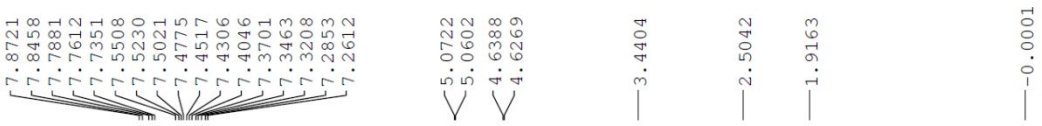


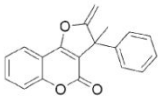
^{1}H NMR (300 MHz, DMSO-d_6)



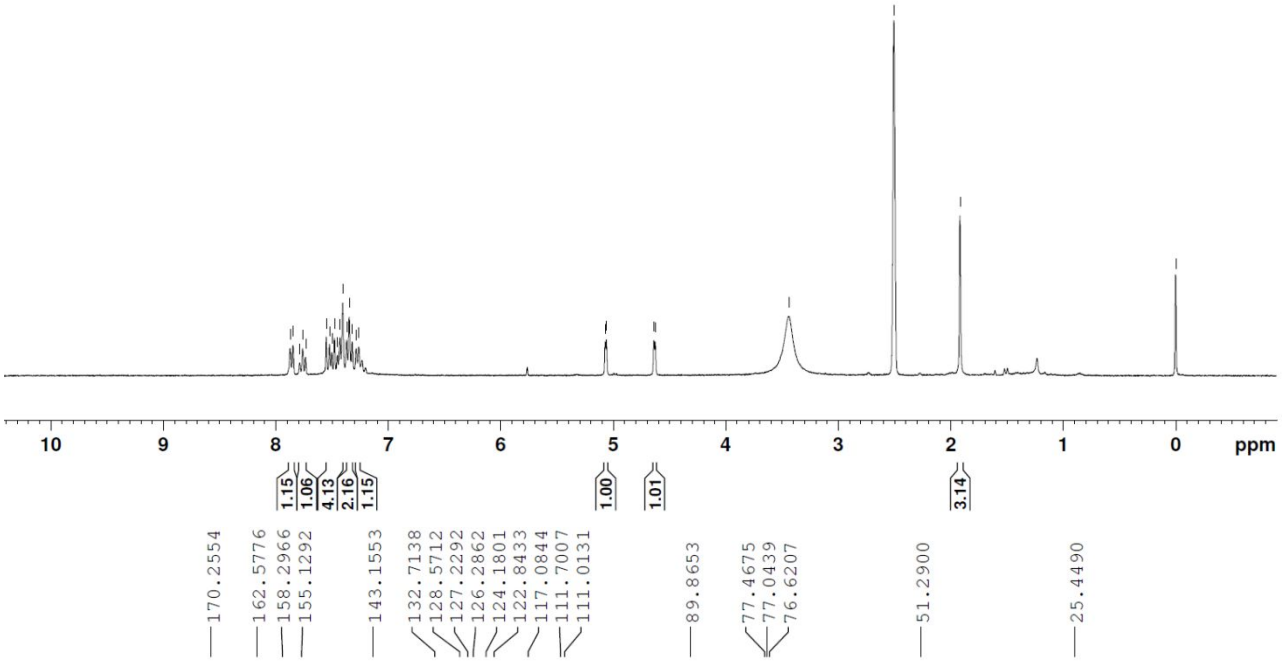
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

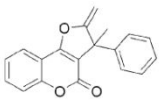
3-Methyl-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**15**)



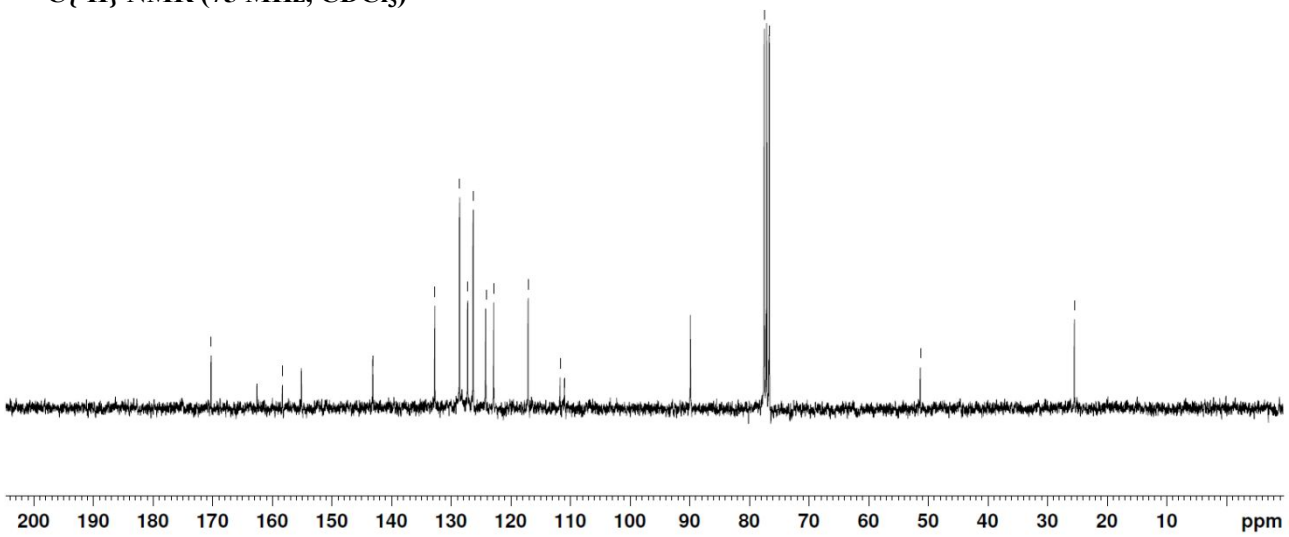


^{1}H NMR (300 MHz, DMSO-d_6)

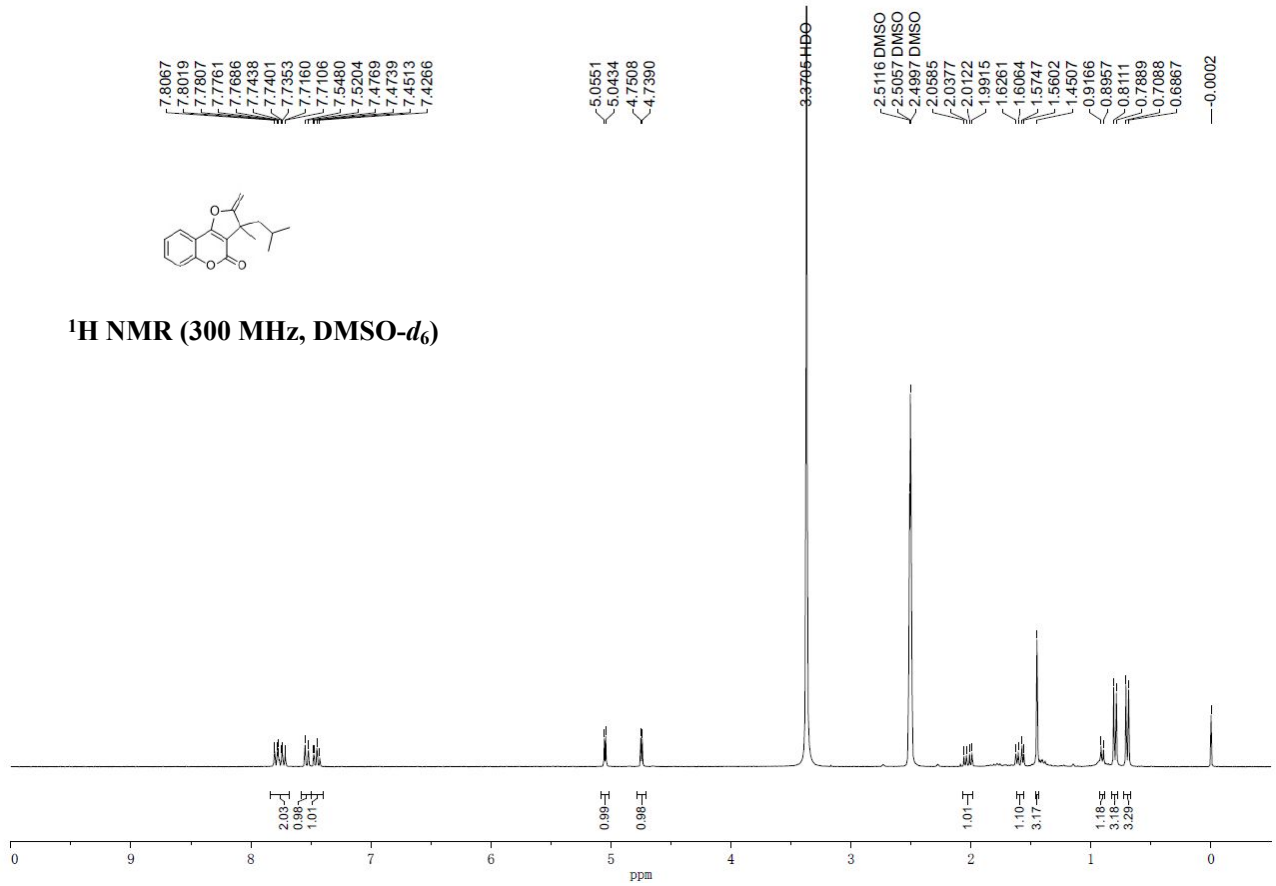




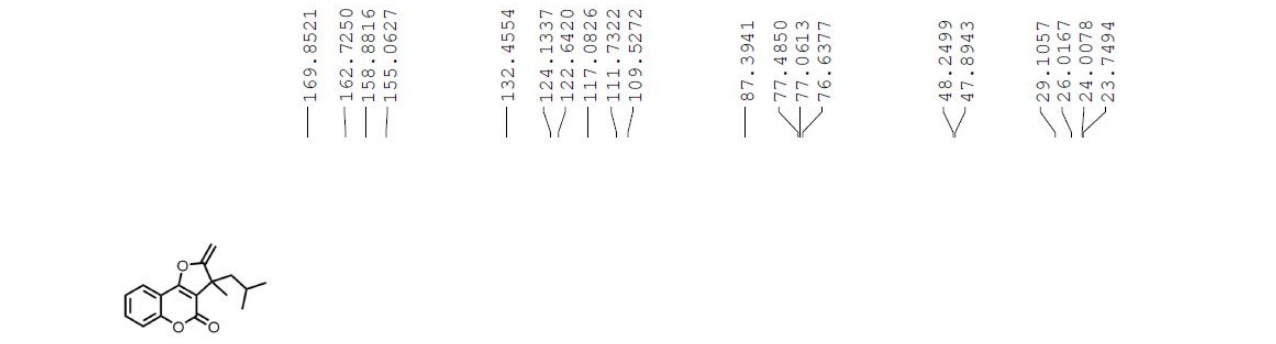
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



3-Isobutyl-3-methyl-2-methylene-2,3-dihydro-4H-furo[3,2-*c*]chromen-4-one (**16**)

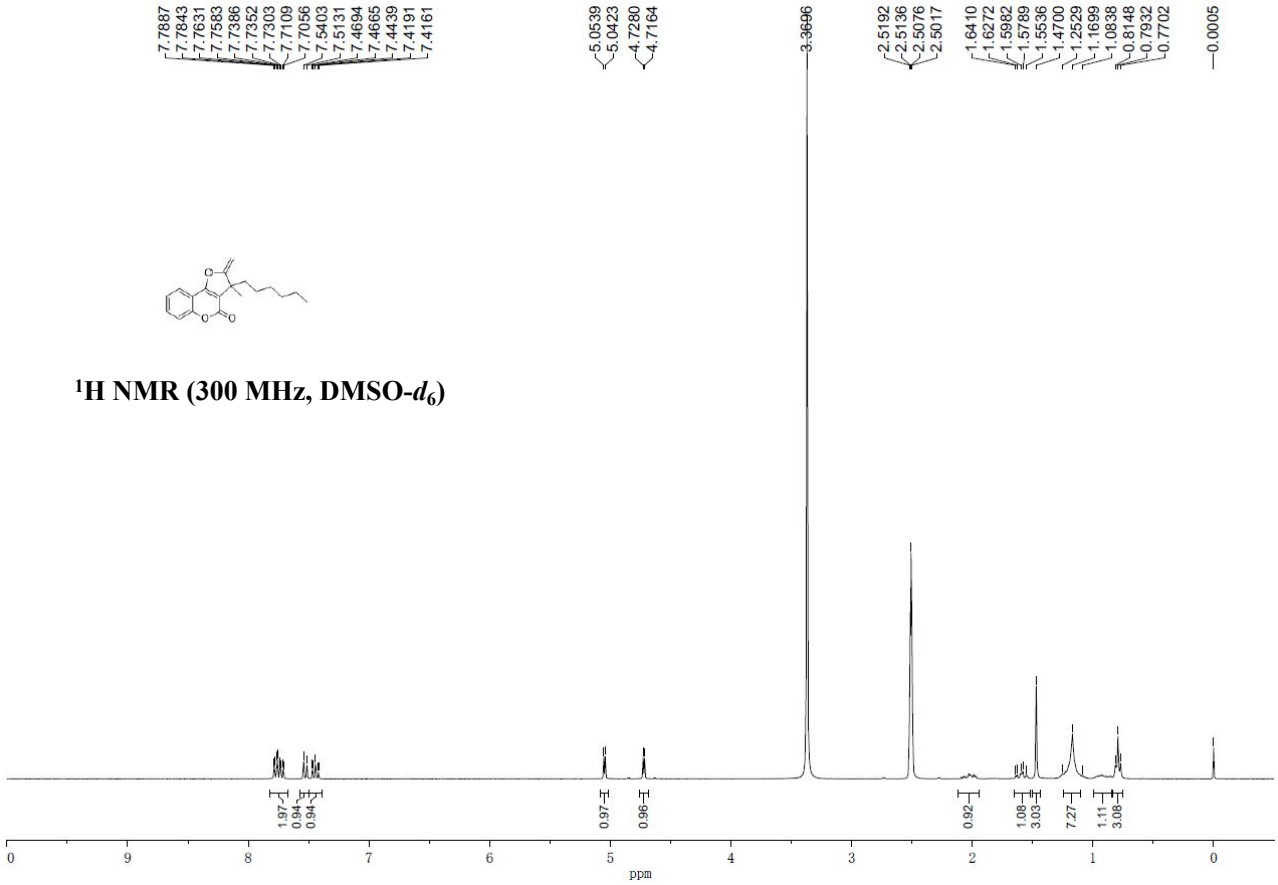


^{1}H NMR (300 MHz, DMSO-d_6)



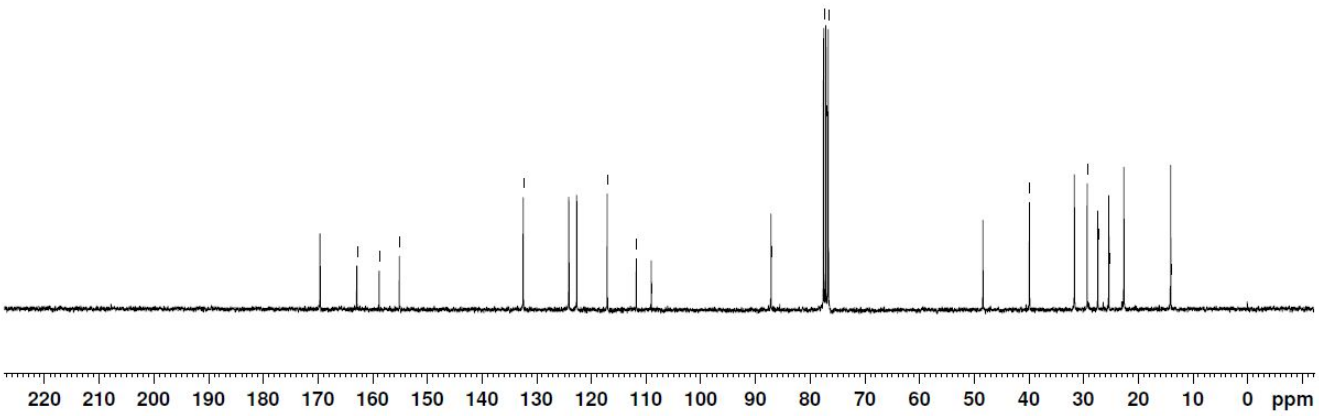
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

3-Hexyl-3-methyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**17**)

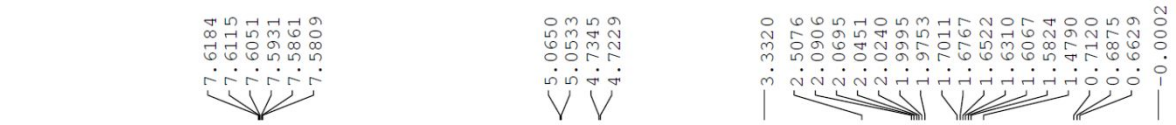


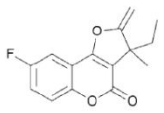
^{1}H NMR (300 MHz, DMSO-d_6)

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

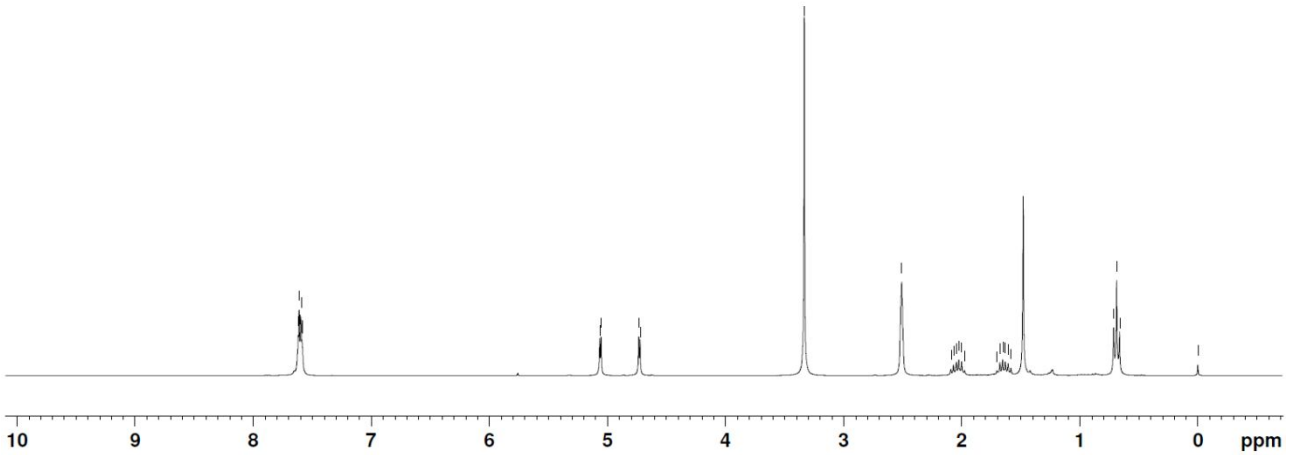


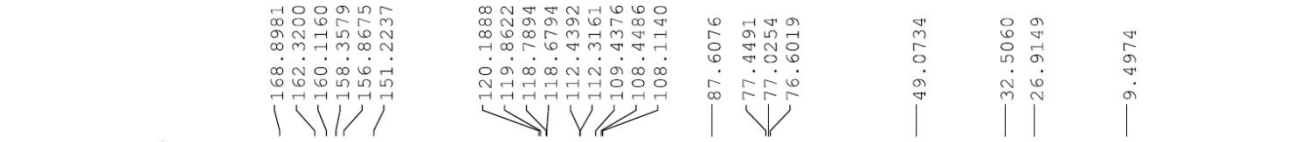
3-Ethyl-8-fluoro-3-methyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**18**)

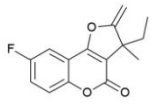




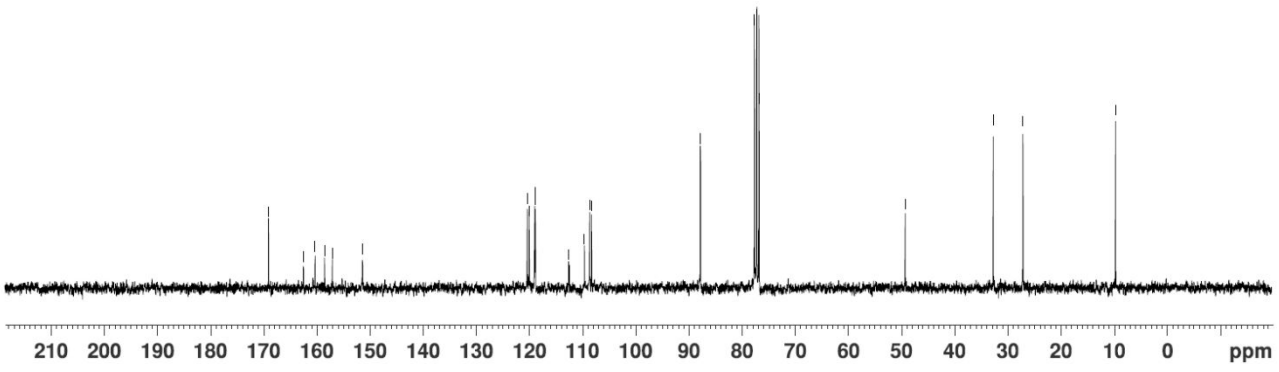
^{1}H NMR (300 MHz, DMSO-d_6)



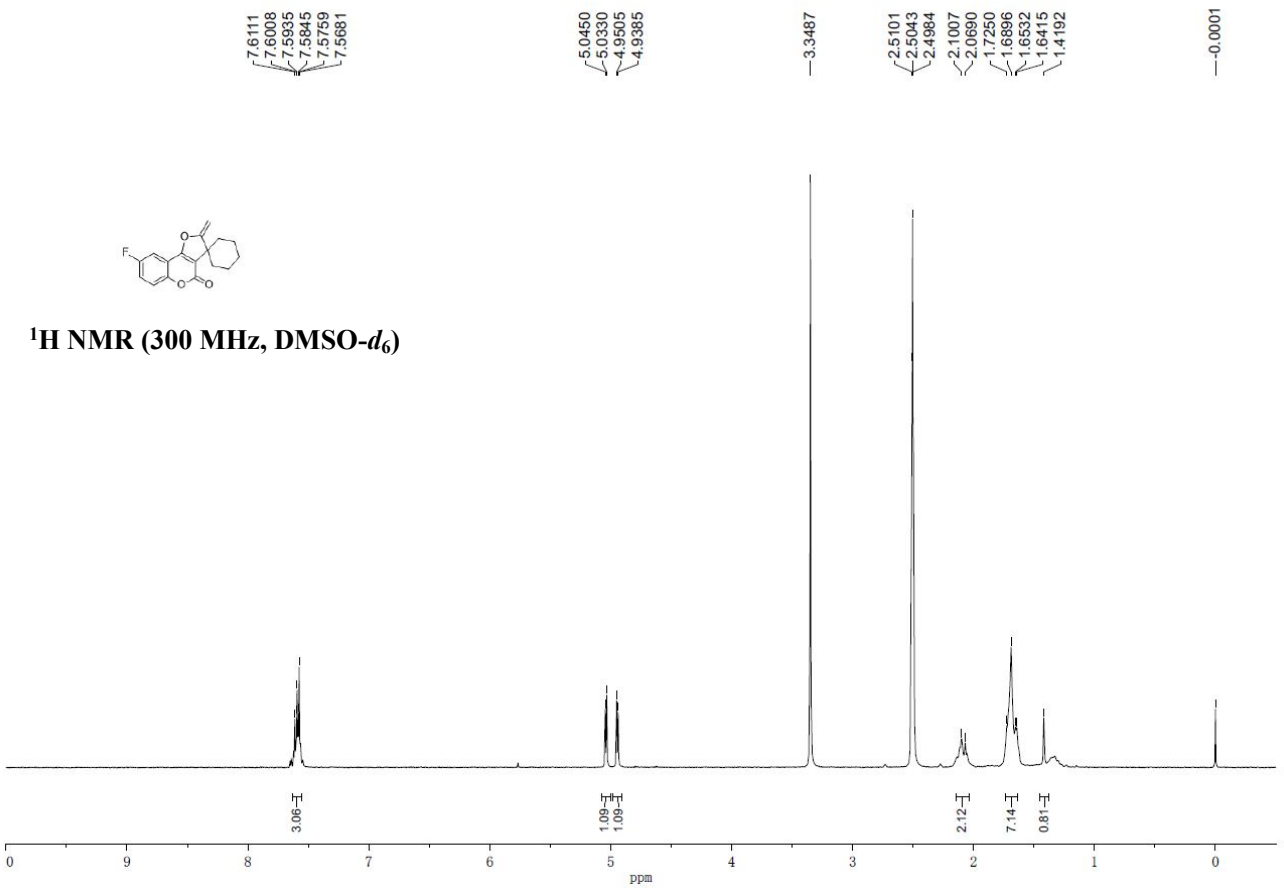




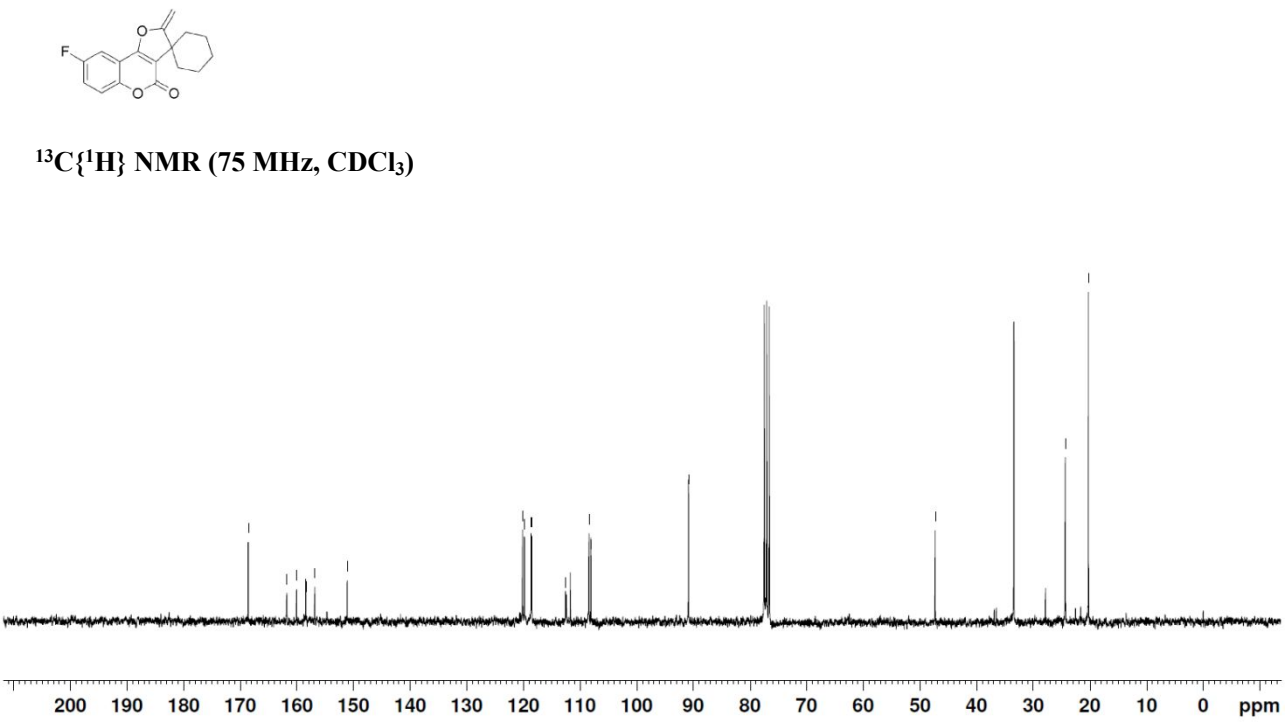
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



8'-Fluoro-2'-methylene-2'*H*,4'*H*-spiro[cyclohexane-1,3'-furo[3,2-*c*]chromen]-4'-one (**19**)

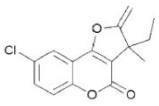


^{1}H NMR (300 MHz, DMSO-d_6)

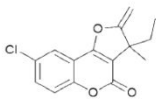


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

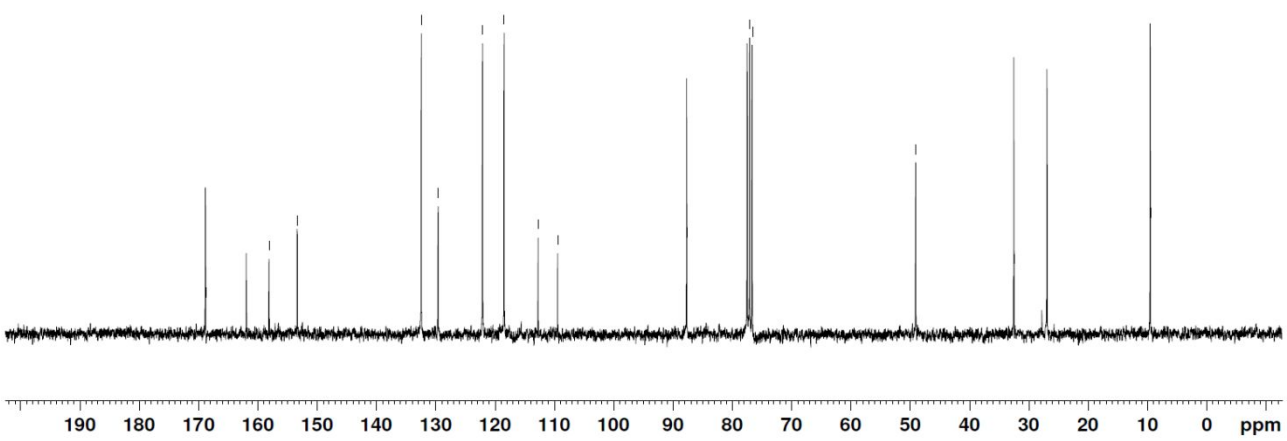
8-Chloro-3-ethyl-3-methyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**20**)



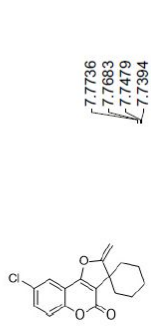
^{1}H NMR (300 MHz, DMSO-d_6)



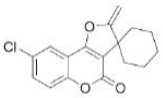
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



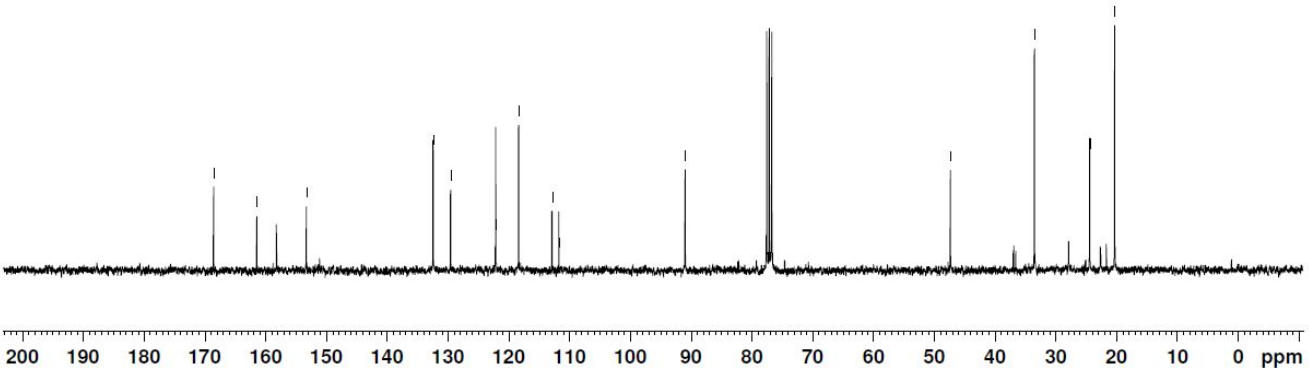
8'-chloro-2'-methylene-2'*H*,4'*H*-spiro[cyclohexane-1,3'-furo[3,2-*c*]chromen]-4'-one (**21**)



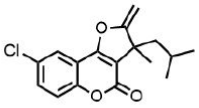
^{1}H NMR (300 MHz, DMSO-d_6)



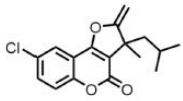
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



8-Chloro-3-isobutyl-3-methyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**22**)

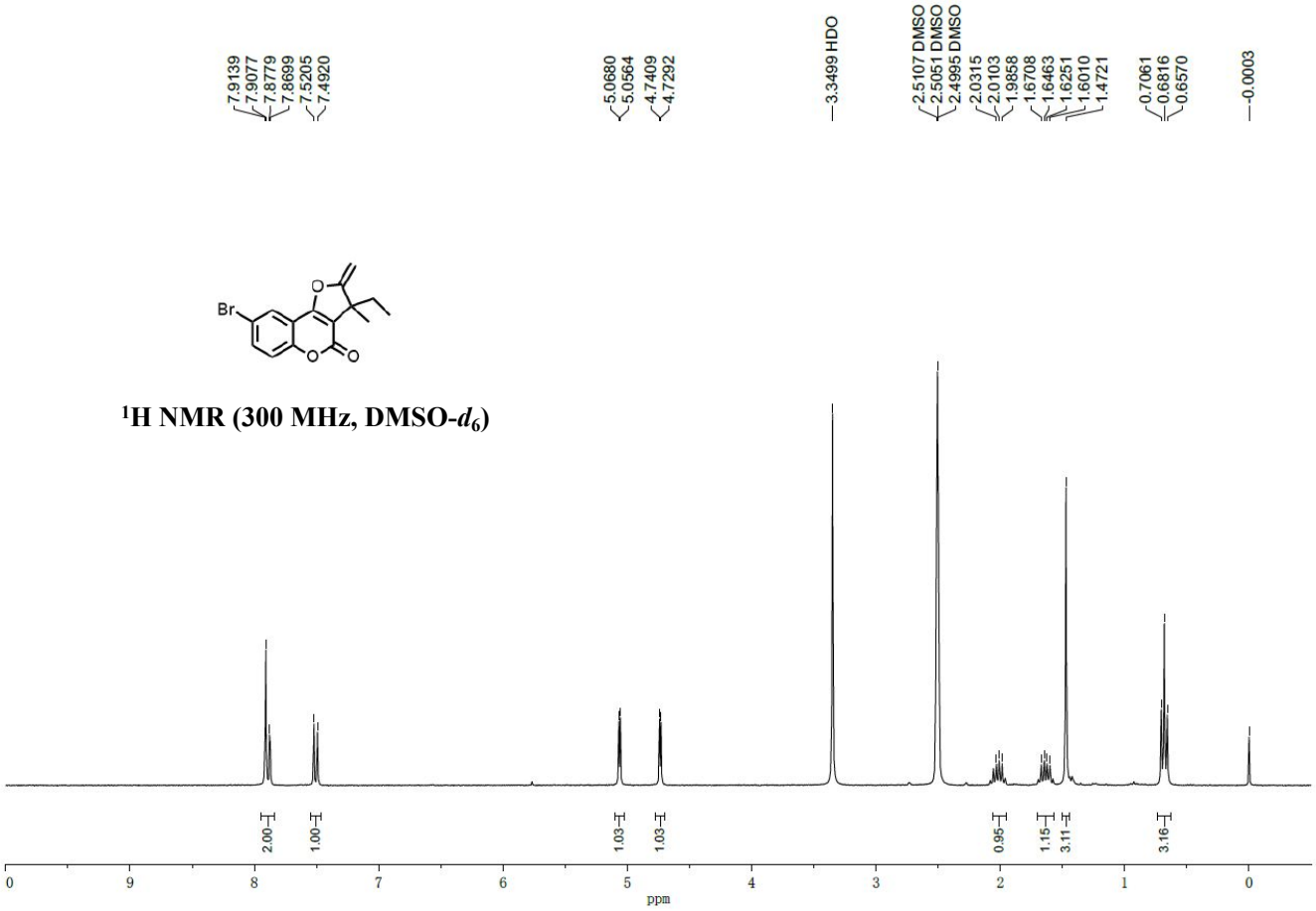


^{1}H NMR (300 MHz, DMSO-d_6)

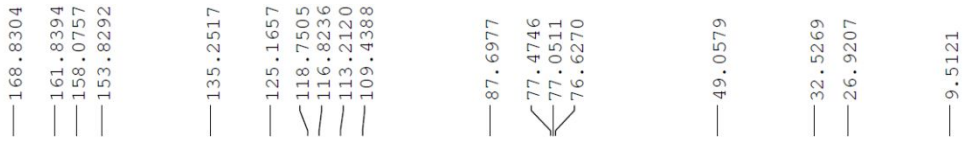


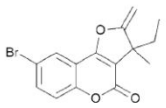
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

8-Bromo-3-ethyl-3-methyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**23**)

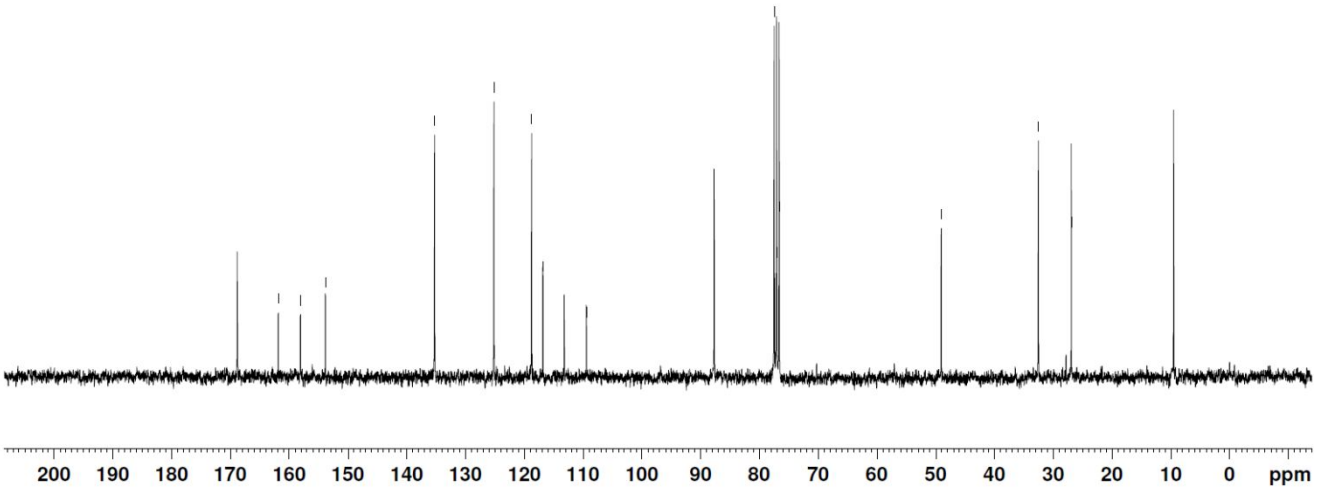


^{1}H NMR (300 MHz, DMSO-d_6)

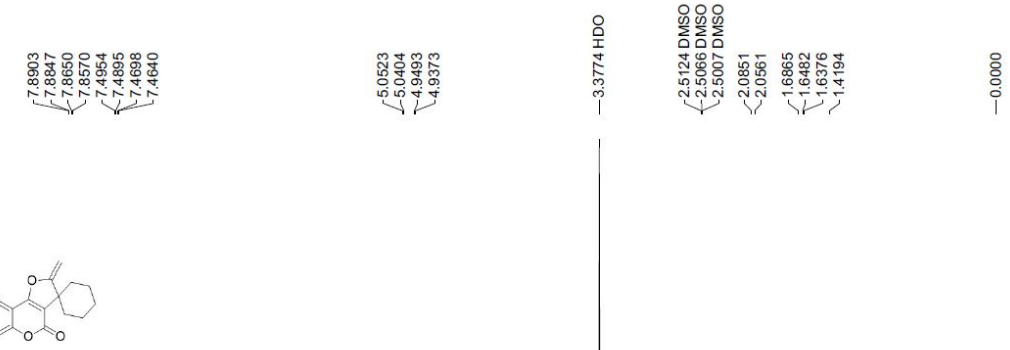




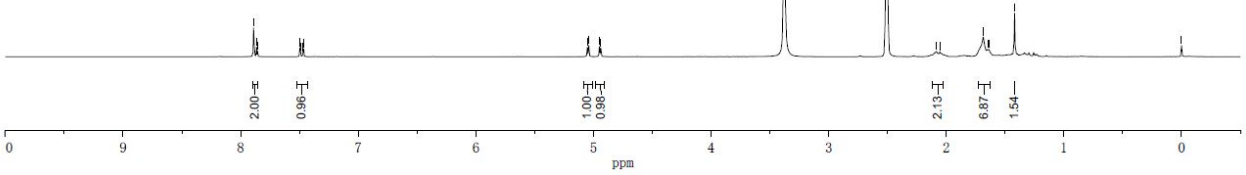
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

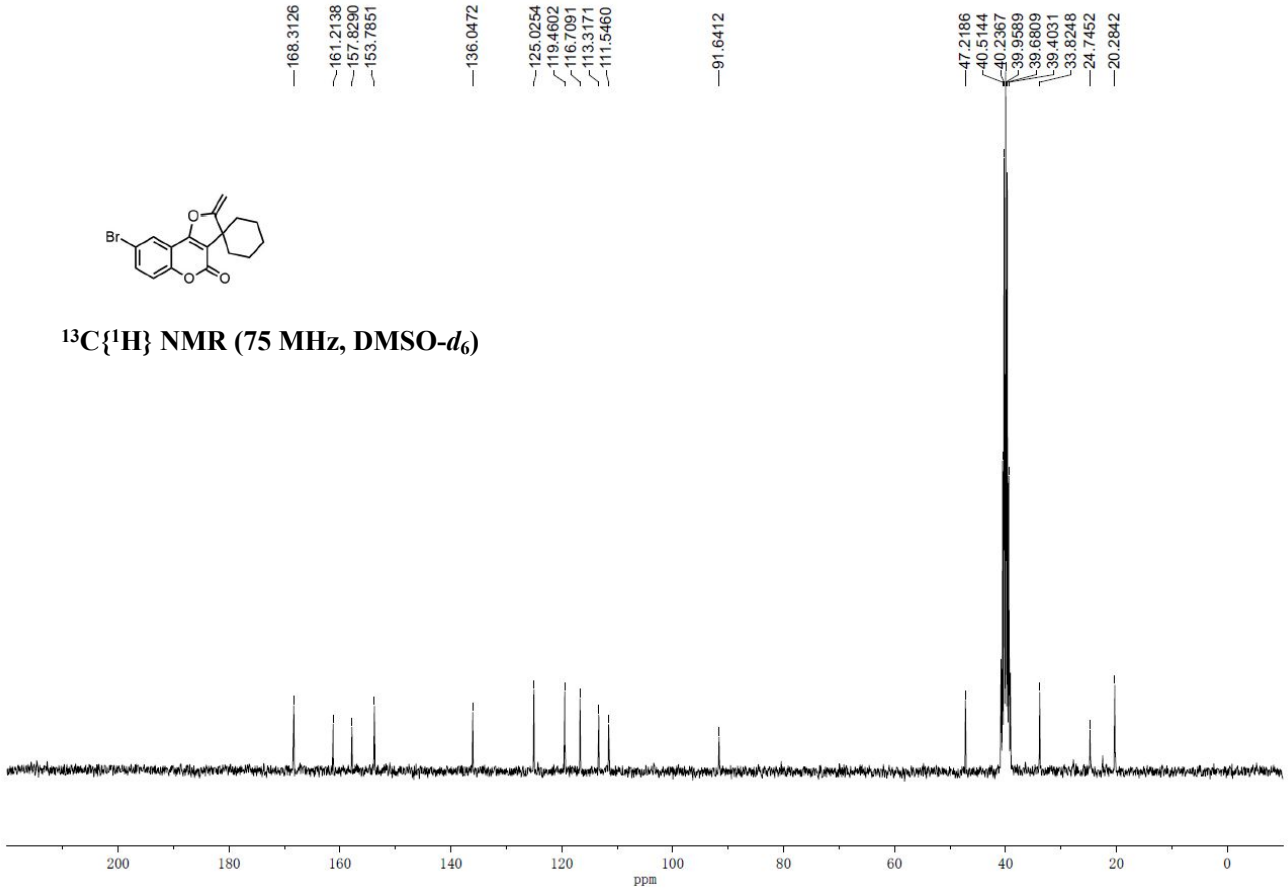


8'-bromo-2'-methylene-2'*H*,4'*H*-spiro[cyclohexane-1,3'-furo[3,2-*c*]chromen]-4'-one (**24**)



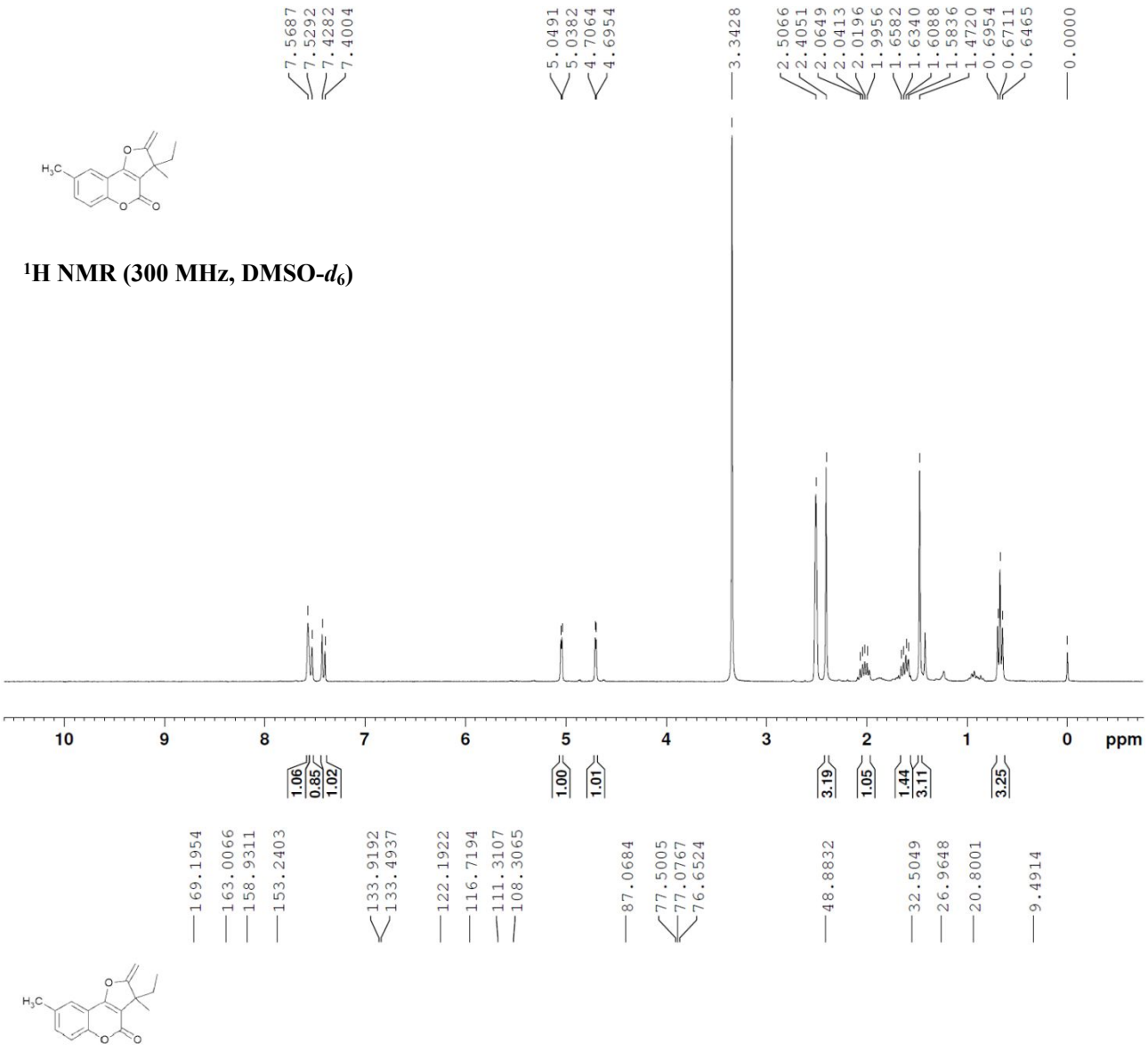
^{1}H NMR (300 MHz, DMSO-d_6)





$^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6)

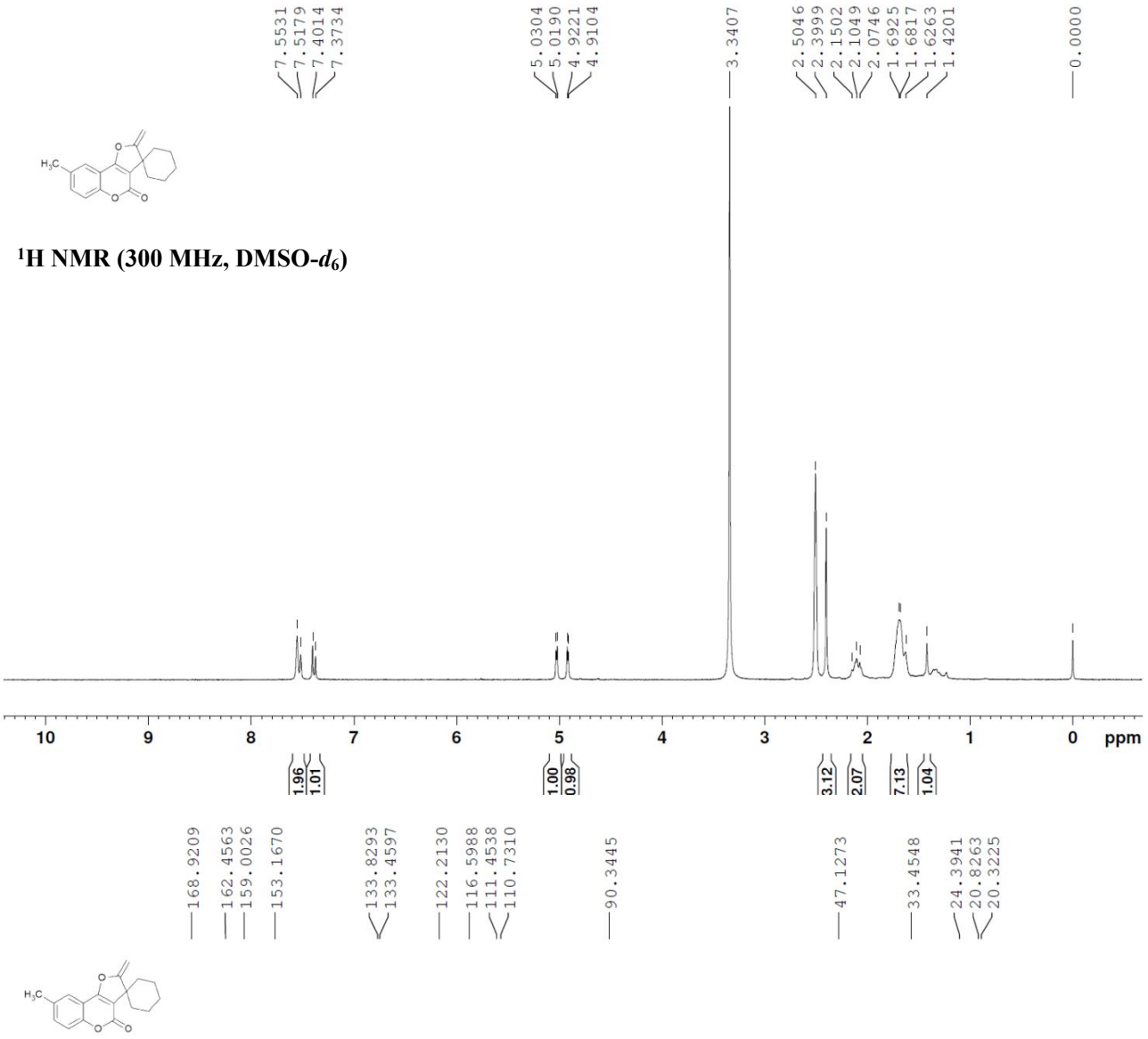
3-Ethyl-3,8-dimethyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**25**)



^{1}H NMR (300 MHz, DMSO-d_6)

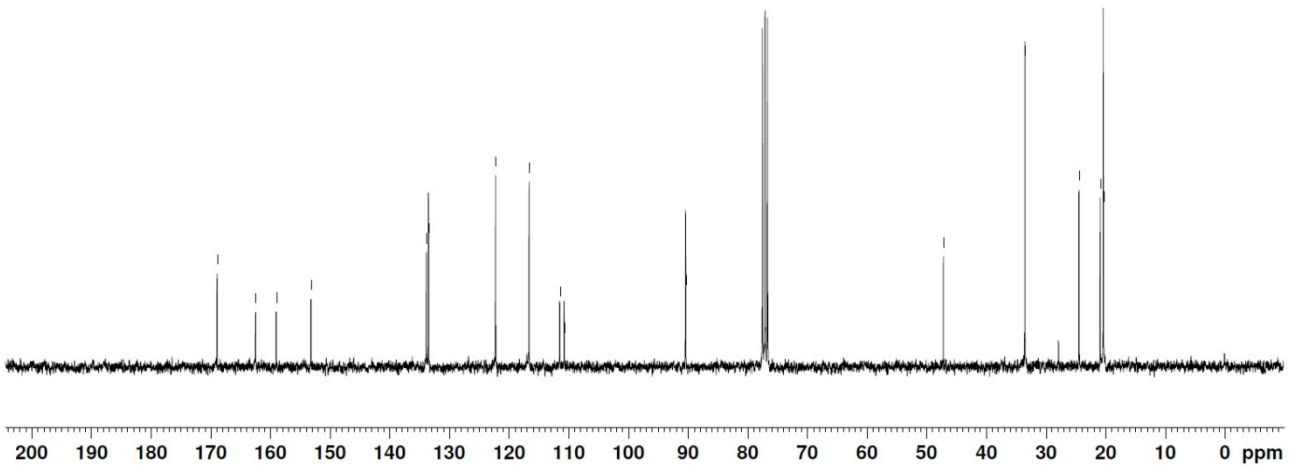
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

8'-Methyl-2'-methylene-2'*H*,4'*H*-spiro[cyclohexane-1,3'-furo[3,2-*c*]chromen]-4'-one (**26**)

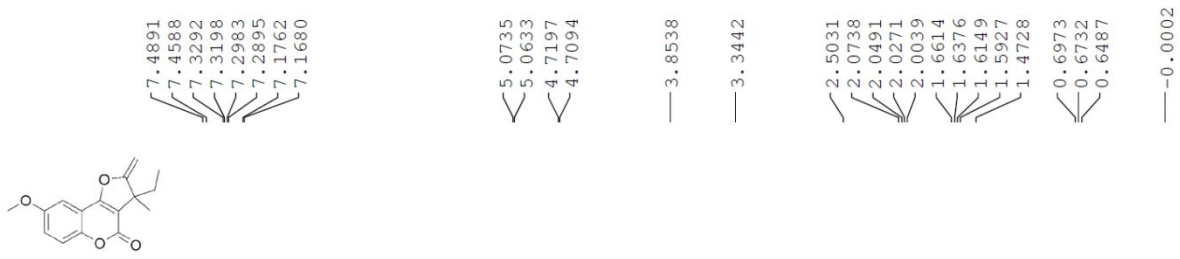


^{1}H NMR (300 MHz, DMSO-d_6)

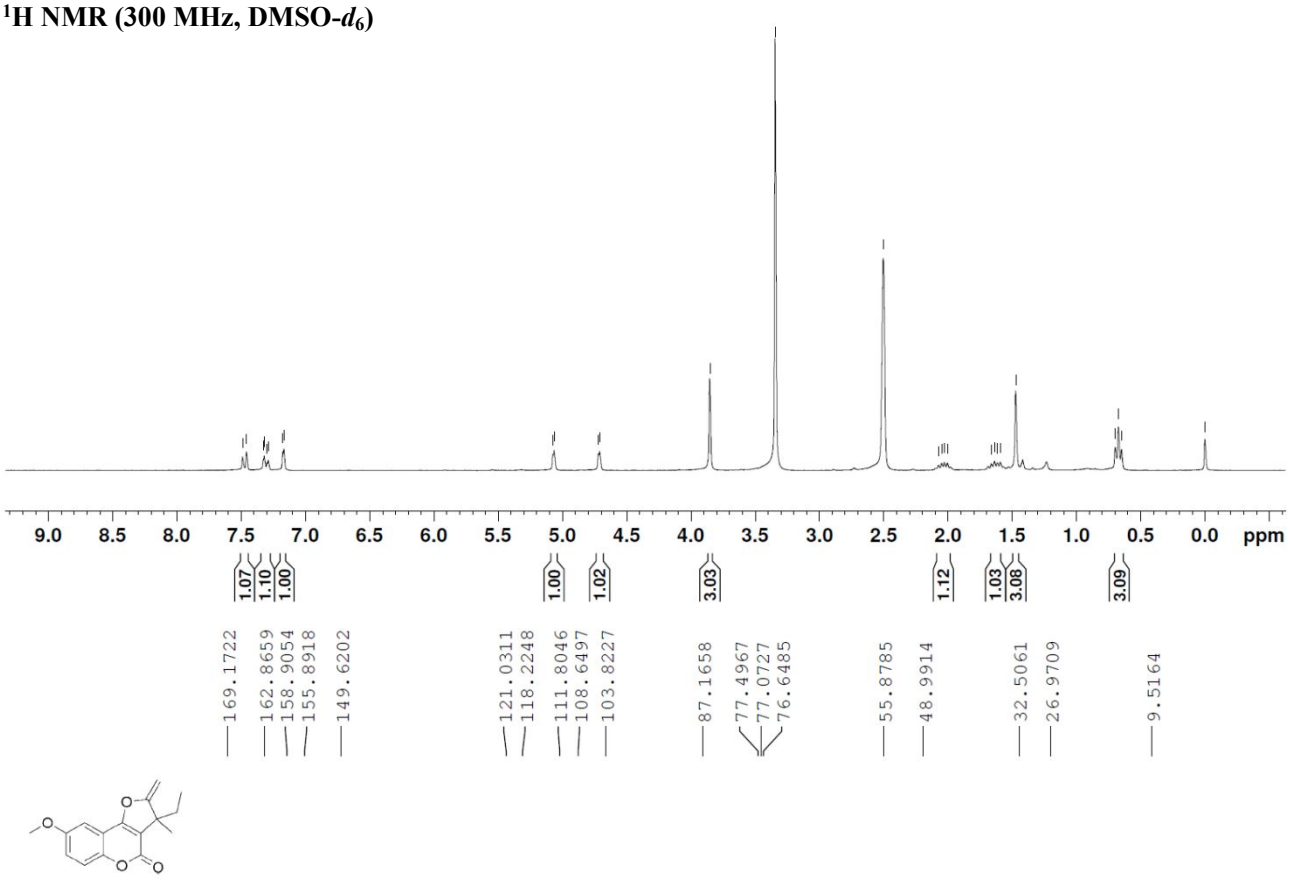
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



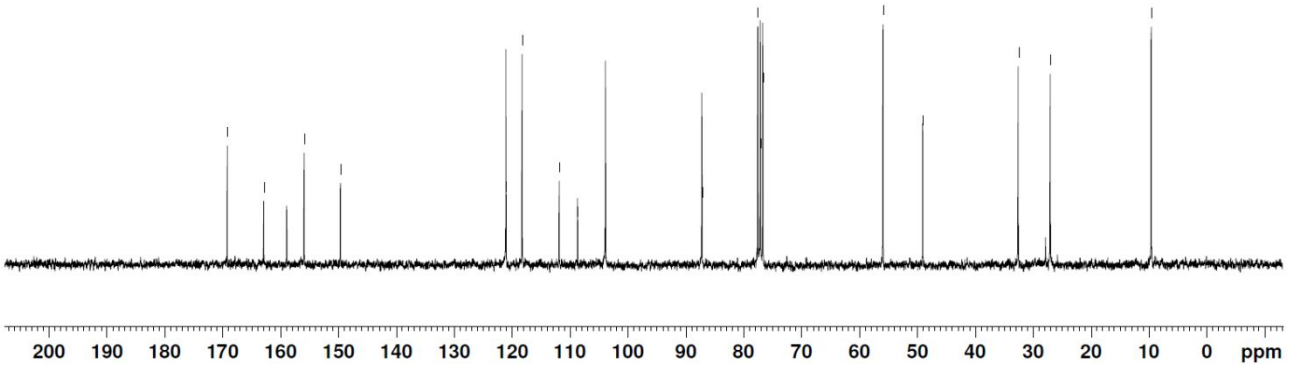
3-Ethyl-8-methoxy-3-methyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**27**)



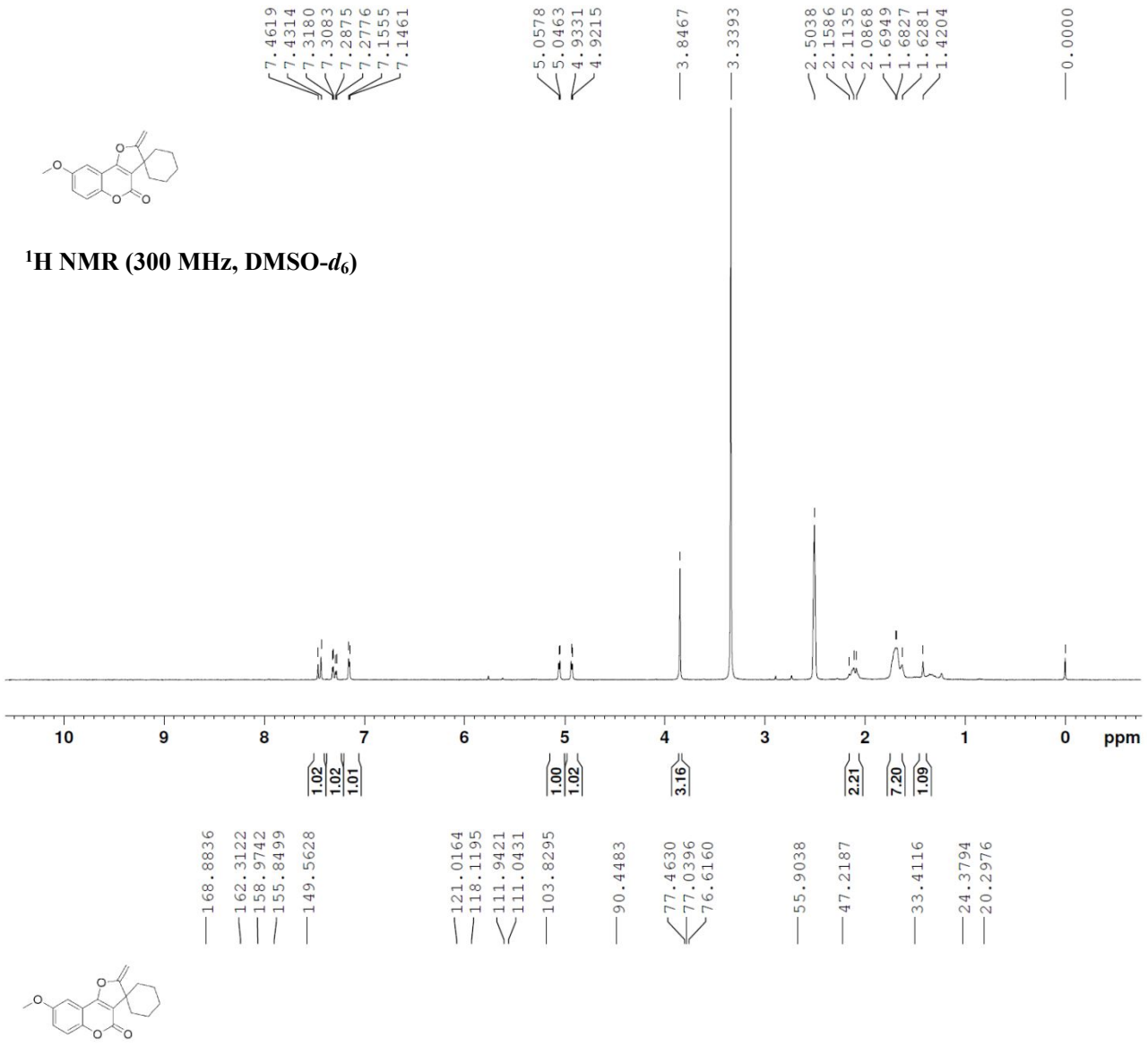
^{1}H NMR (300 MHz, DMSO-d_6)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

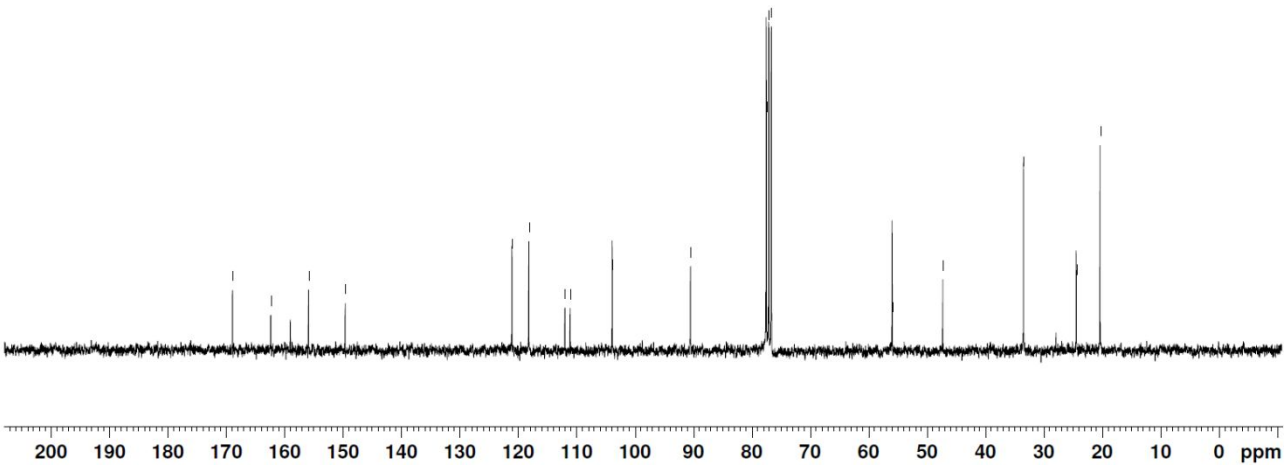


8'-Methoxy-2'-methylene-2'*H*,4'*H*-spiro[cyclohexane-1,3'-furo[3,2-*c*]chromen]-4'-one (**28**)

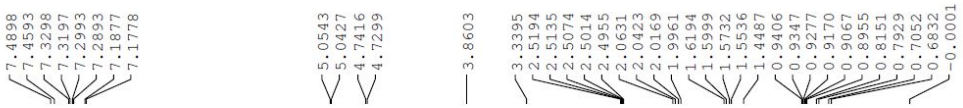


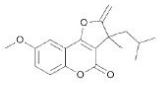
^{1}H NMR (300 MHz, DMSO-d_6)

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

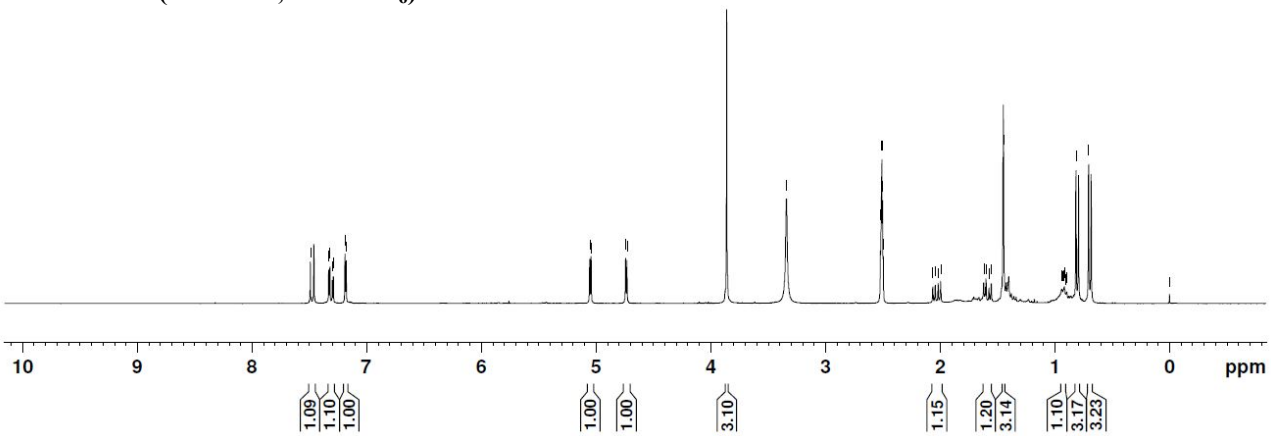


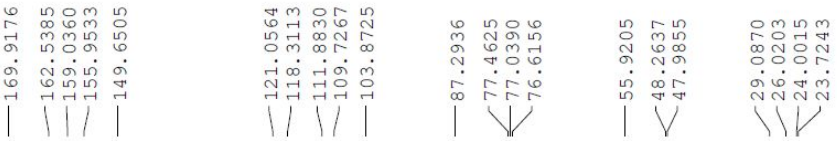
3-Isobutyl-8-methoxy-3-methyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**29**)

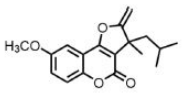




^{1}H NMR (300 MHz, DMSO-d_6)

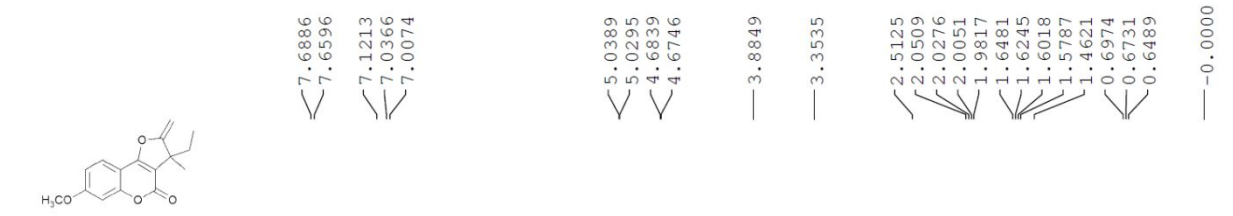




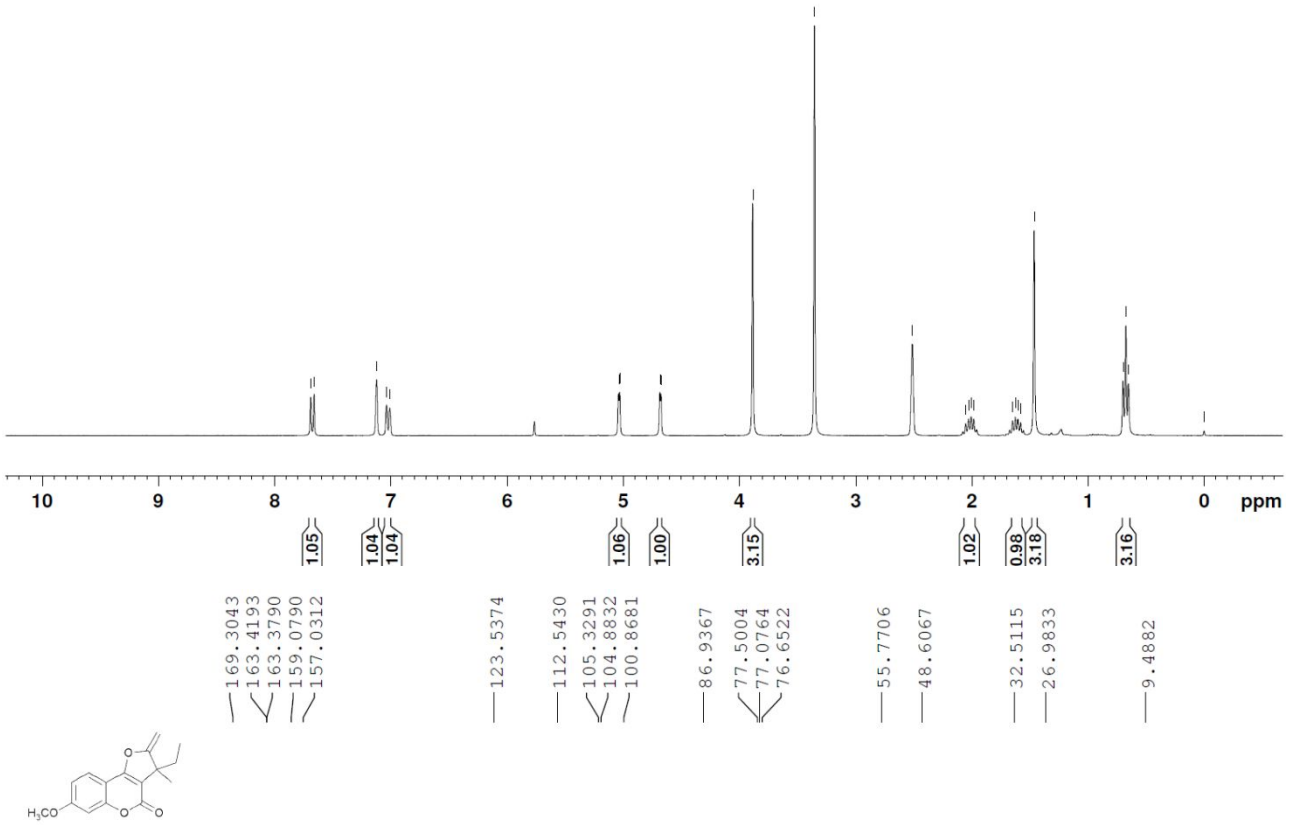


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

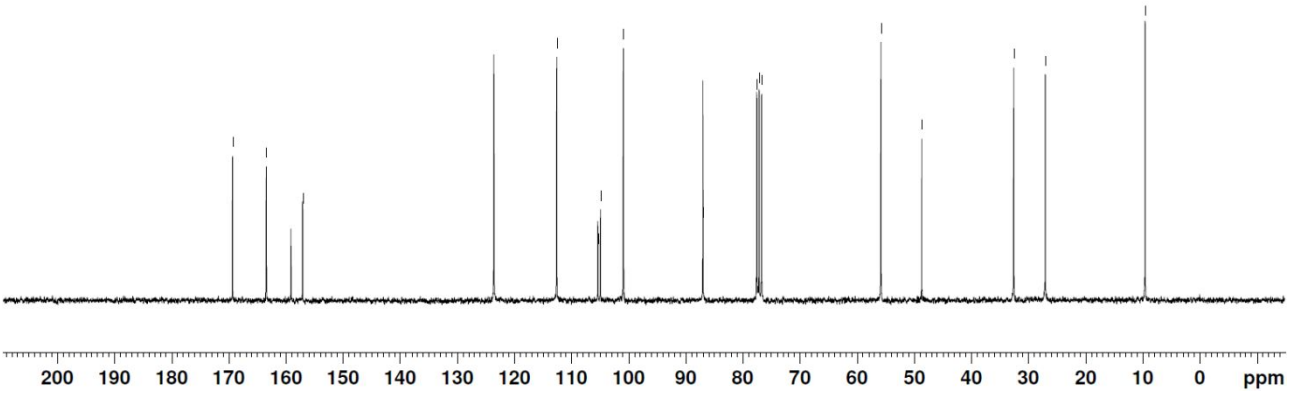
3-Ethyl-7-methoxy-3-methyl-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**30**)



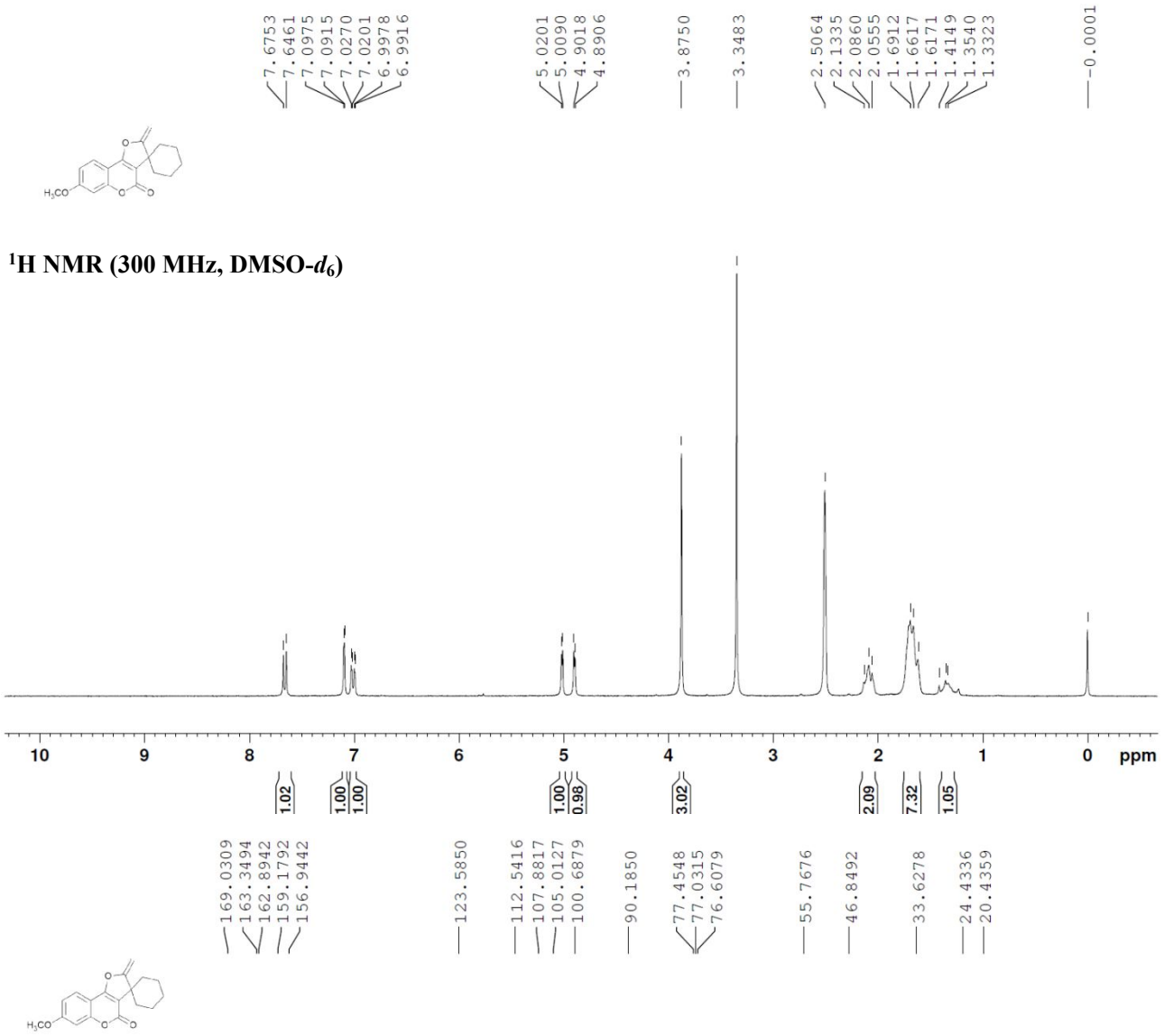
^{1}H NMR (300 MHz, DMSO-d_6)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

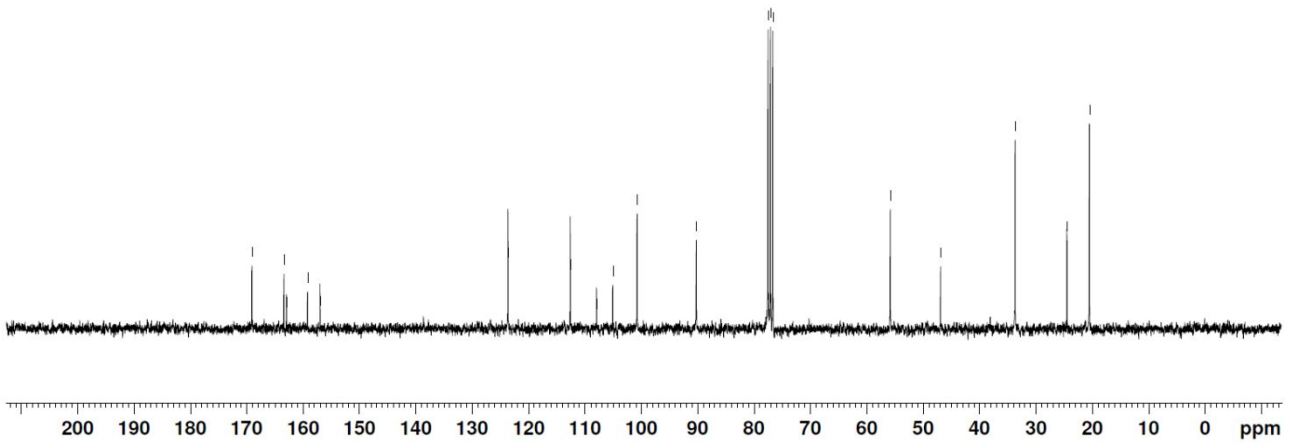


7'-Methoxy-2'-methylene-2'*H*,4'*H*-spiro[cyclohexane-1,3'-furo[3,2-*c*]chromen]-4'-one (**31**)

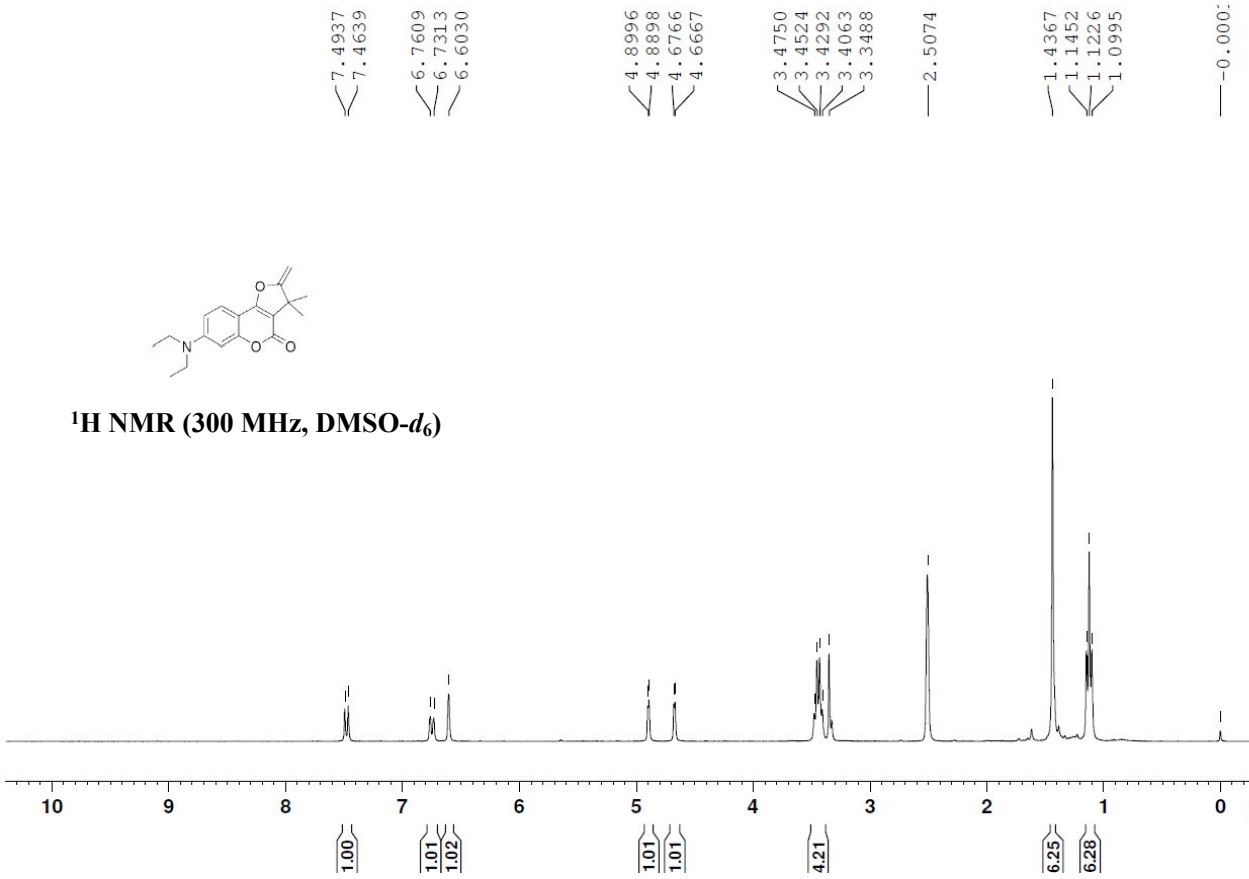


^{1}H NMR (300 MHz, DMSO-d_6)

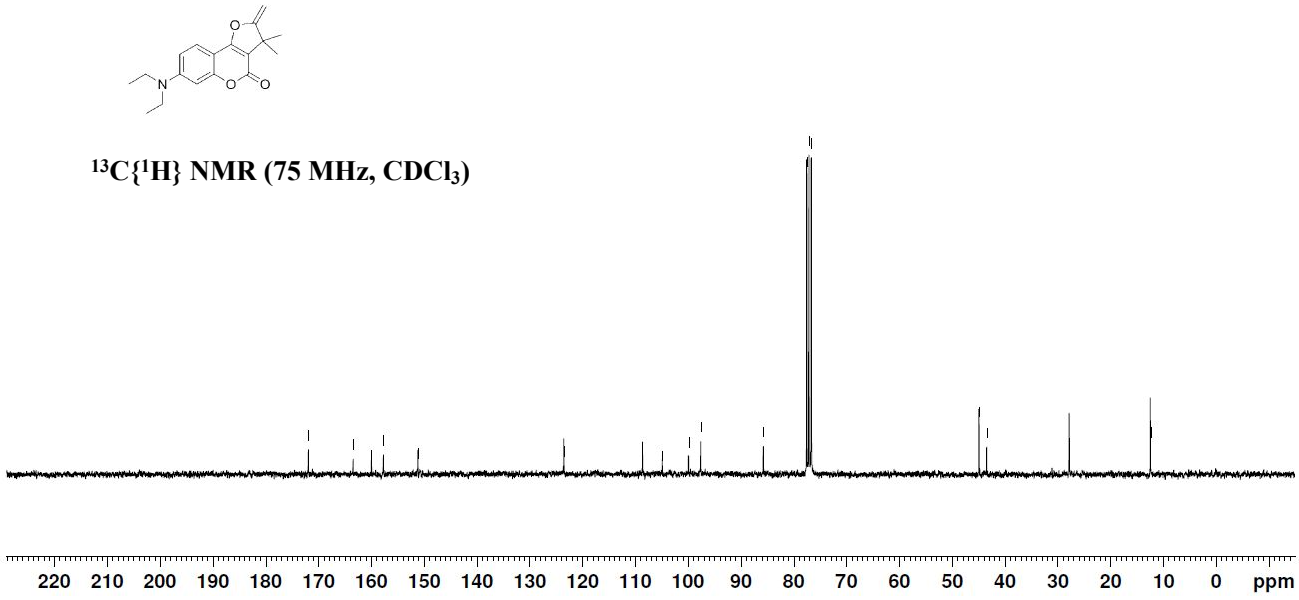
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



7-(Diethylamino)-3,3-dimethyl-2-methylene-2,3-dihydro-4H-furo[3,2-*c*]chromen-4-one (**32**)

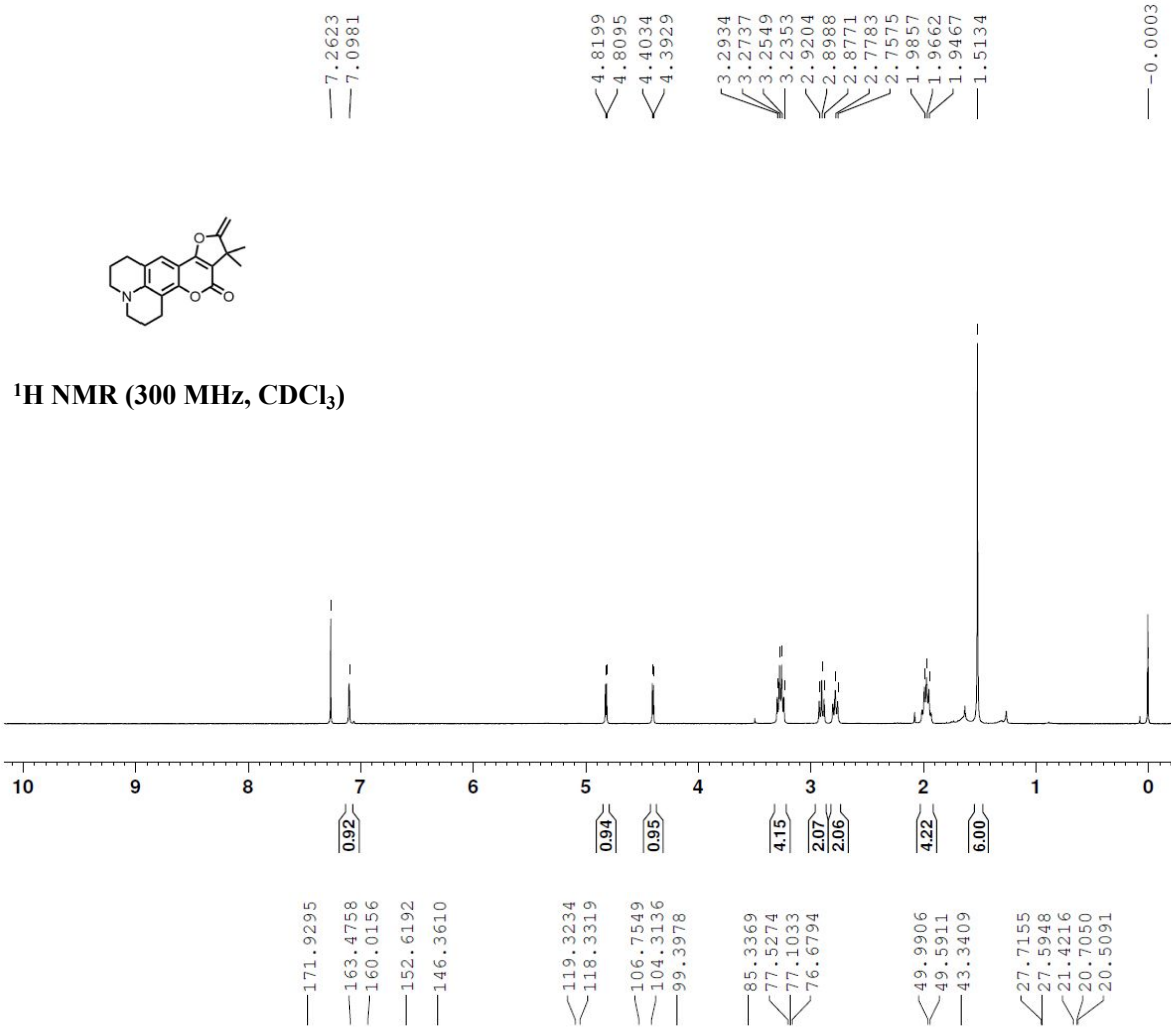


^{1}H NMR (300 MHz, DMSO-d_6)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

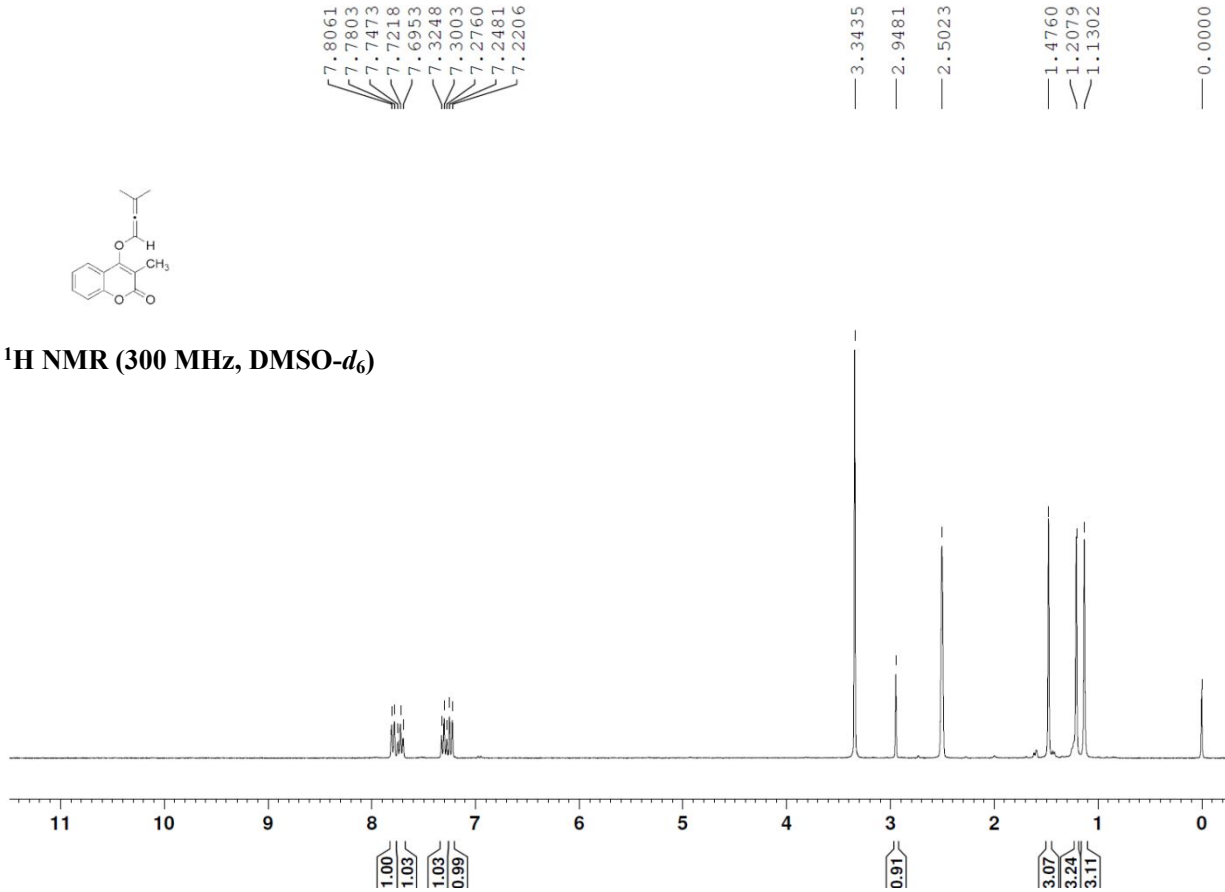
3,3-Dimethyl-2-methylene-2,3,7,8,11,12-hexahydro-4*H*,6*H*,10*H*-furo[2',3':4,5]pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-4-one (**33**)



^{1}H NMR (300 MHz, $CDCl_3$)

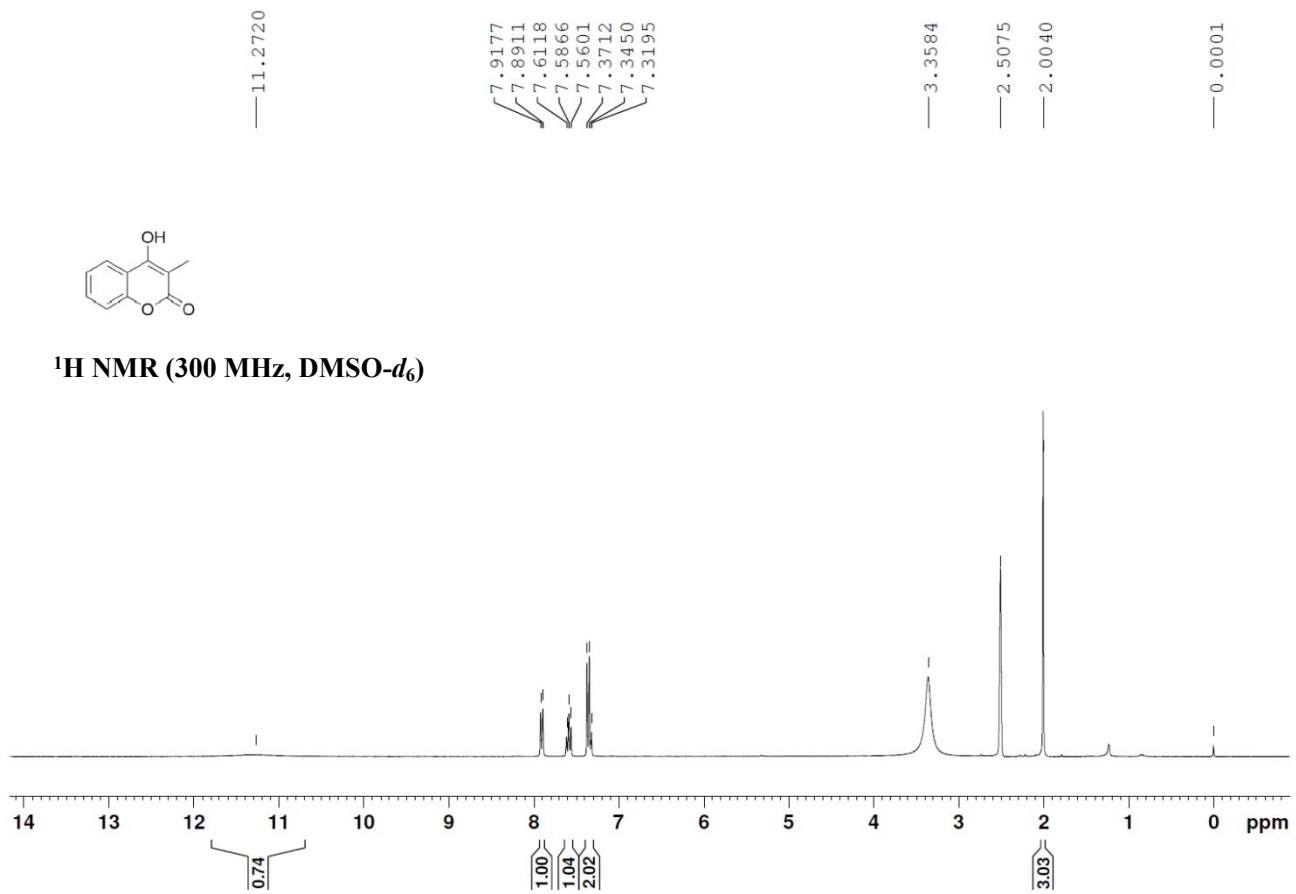
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

3-Methyl-4-[(3-methylbuta-1,2-dien-1-yl)oxy]-2*H*-chromen-2-one (**3a**)



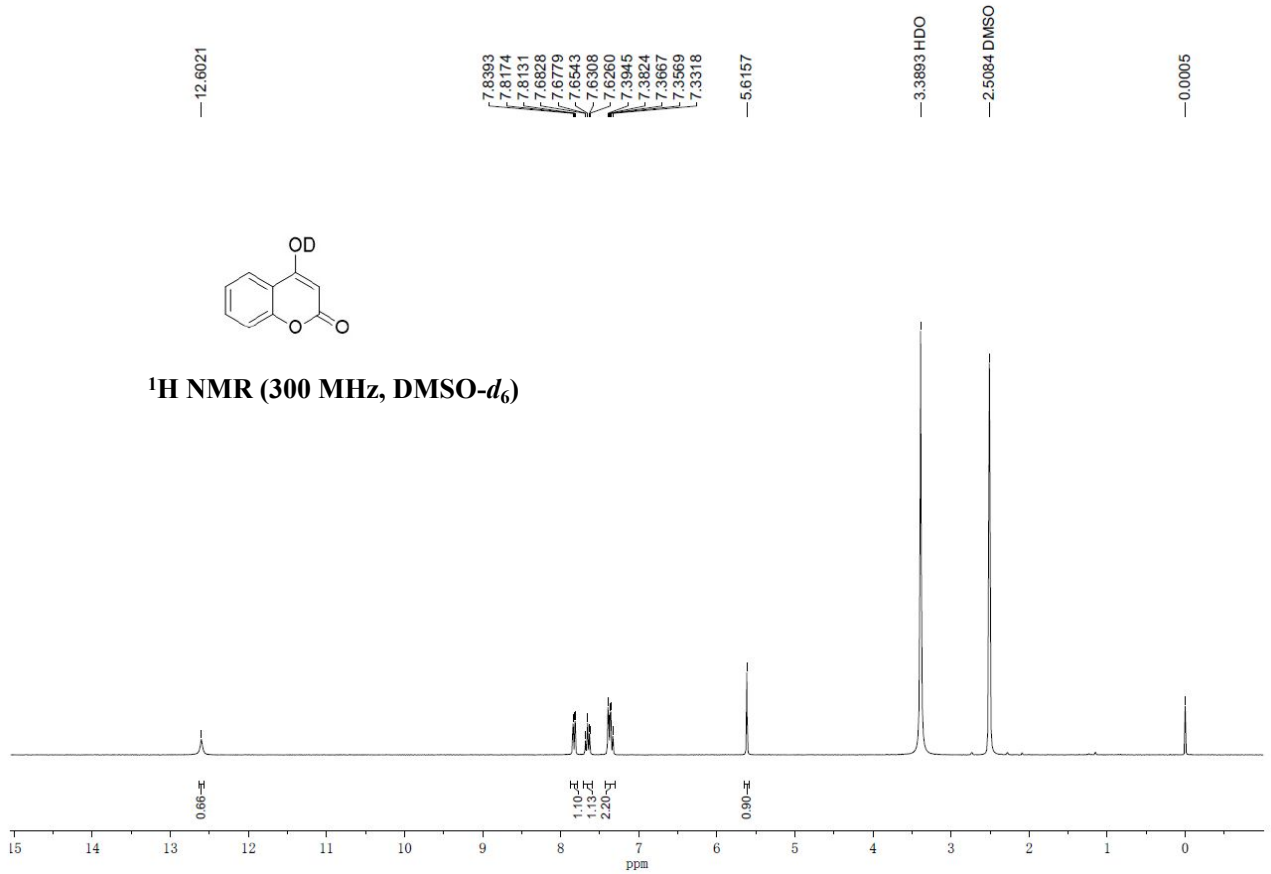
^{1}H NMR (300 MHz, DMSO-d_6)

4-Hydroxy-3-methyl-2*H*-chromen-2-one (**1l**)

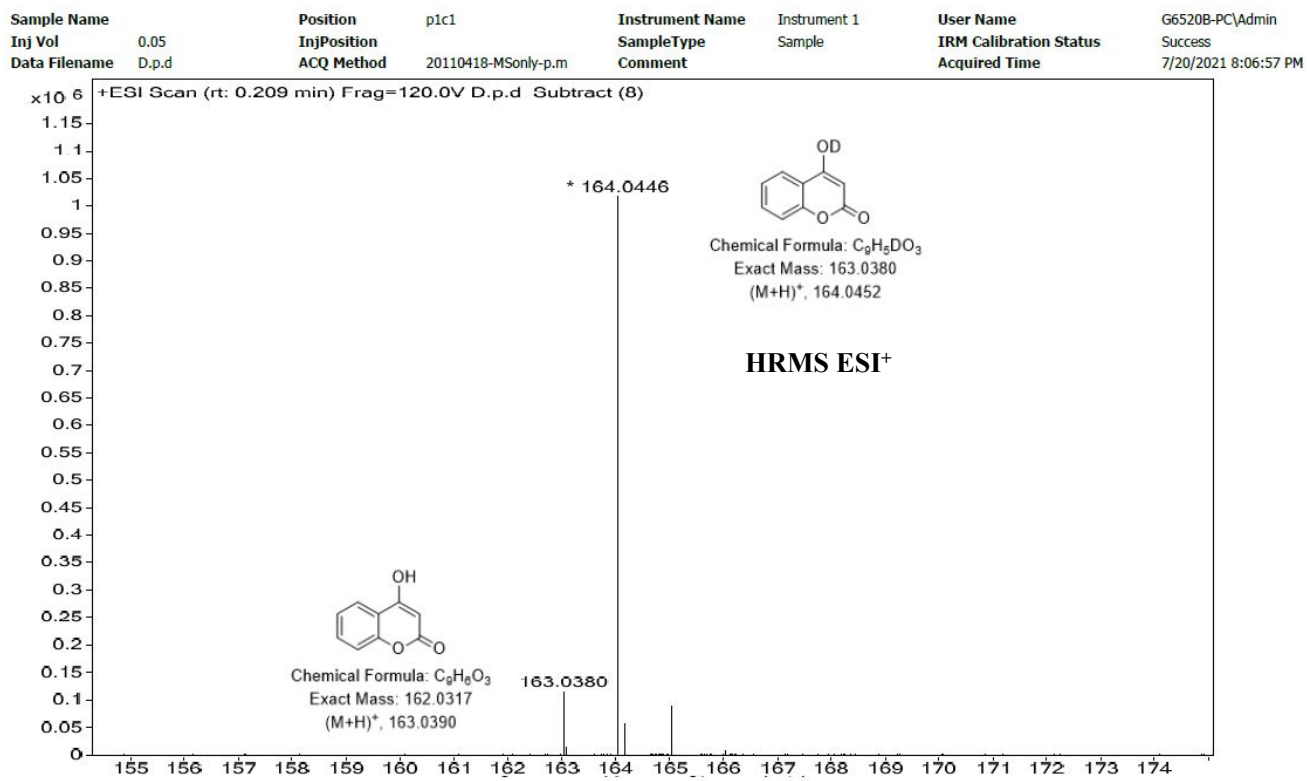


^{1}H NMR (300 MHz, DMSO-d_6)

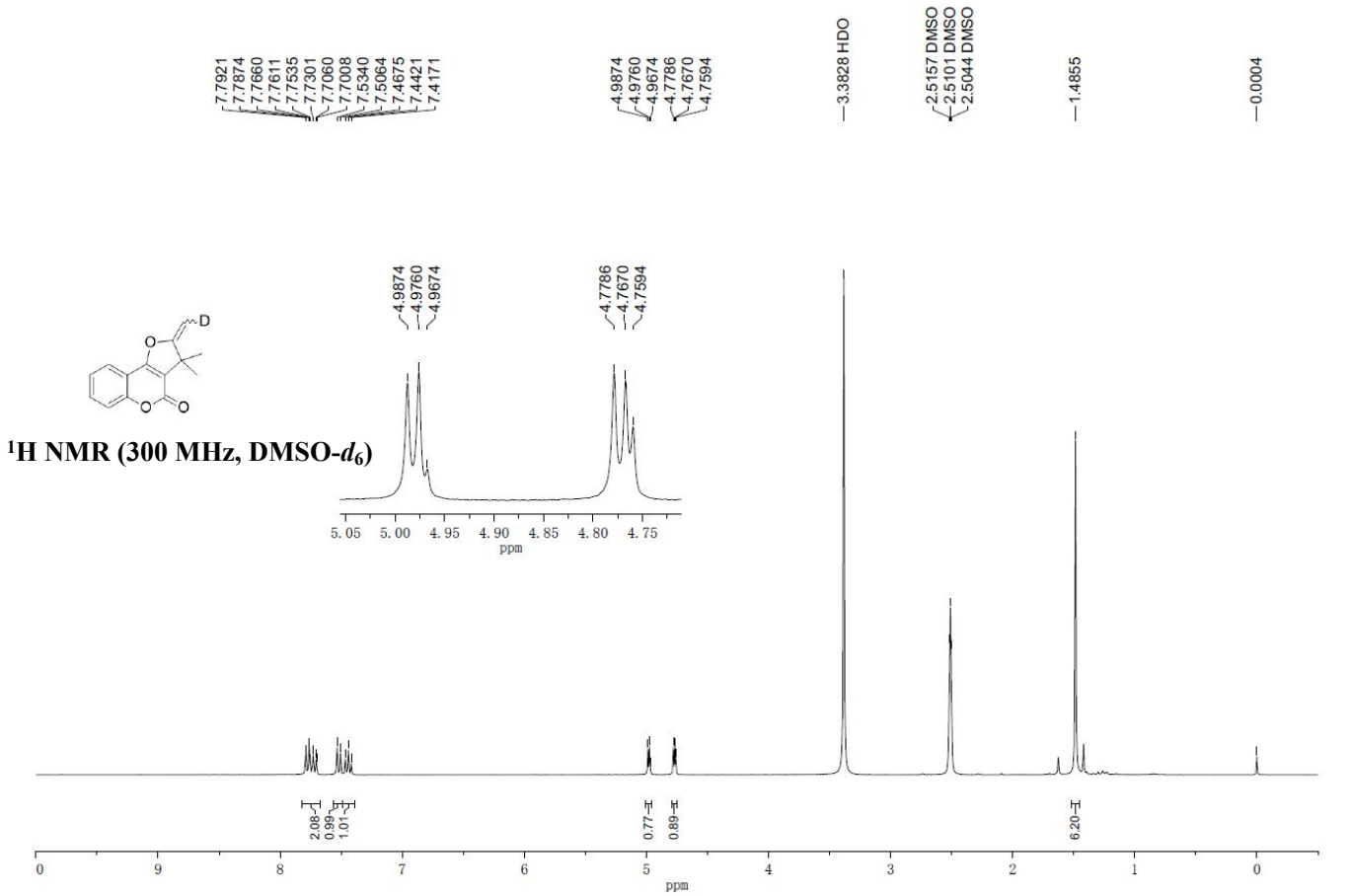
4-(Hydroxy-d)-2*H*-chromen-2-one (**1m**)



^{1}H NMR (300 MHz, DMSO-d_6)



3,3-dimethyl-2-(methylene-*d*)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (**3b**)



^{1}H NMR (300 MHz, DMSO-d_6)

Sample Name		**Position**	p1b7	**Instrument Name**	Instrument 1	**User Name**	G6520B-PC\Admin
Inj Vol	0.5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	f-D-apci-p.d	**ACQ Method**	20110418-MSonly-APCI	**Comment**		**Acquired Time**	7/27/2021 3:35:20 PM