Supporting information of

New Fluorescent *trans*-DihydroFluoren-3-ones from Aldol - Robinson Annulation – Regioselective Addition Involved One-Pot Reaction

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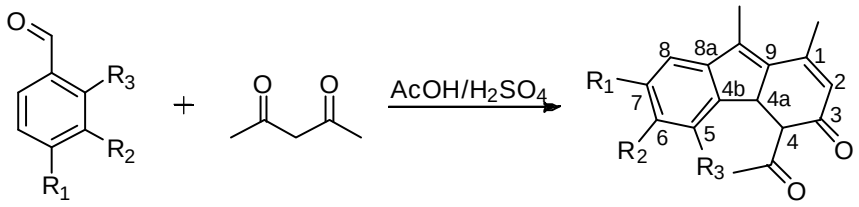
Contents

1. Chemistry

1.1 Synthesis of 2a-i, 2b-cis and 2b', 1d'

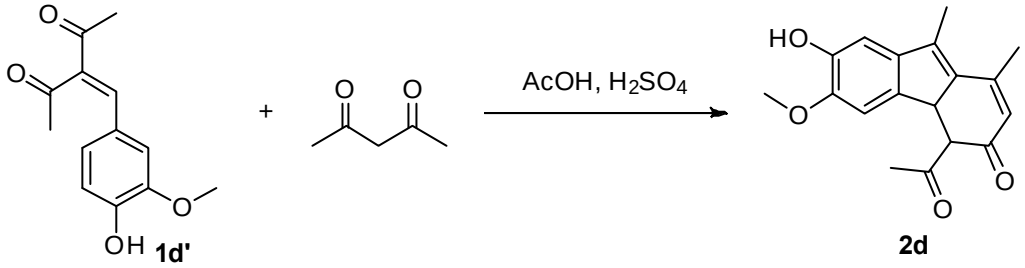
Typical procedure for synthesis of 2a-i



1a-i **2a-i**

In a 100mL flask, 10mmol substituted benzaldehydes was mixed with 30mmol acetylacetone. The mixture was diluted with 5 mL AcOH and cooled to 0℃. Then 2*eq* 98% H_2SO_4 was added dropwise to the solution. After 30 mins stirring, the reaction temperature was raised to r.t. and stirred for 4 hours until the benzaldehyde disappeared (monitored by TLC). Then the solution was diluted with 40mL EtOAc and 40mL water, neutralized with $NaHCO_3$; the organic layer was washed with 40mL water and dried with anhydrous $MgSO_4$. The crude products were purified with chromatography (support: silica gel (300~400), EA: petroleum ether=1:5) and recrystalized in ethanol, giving final products in 11%~20% isolated yields respectively.

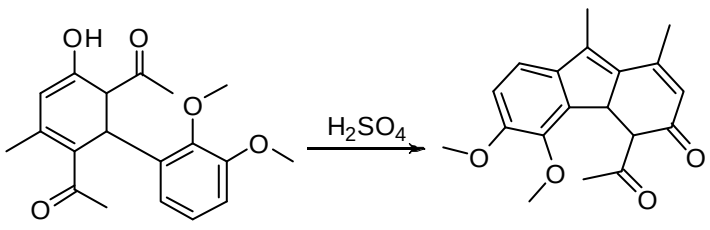
Synthesis of 2d from 1d'



1d' **2d**

In a 100mL flask, 10mmol **1d'** was mixed with 10mmol acetylacetone. The mixture was diluted with 5 mL AcOH and cooled to 0℃. Then 2*eq* 98% H_2SO_4 was added dropwise to the solution. After 30 mins the reaction was raised to r.t. and further stirred for 4 hours. The formation of **2d** was verified by isolation (isolated yield, 45%) and characterization by NMR and MS.

Synthesis of 2b, 2b-cis from 2b'

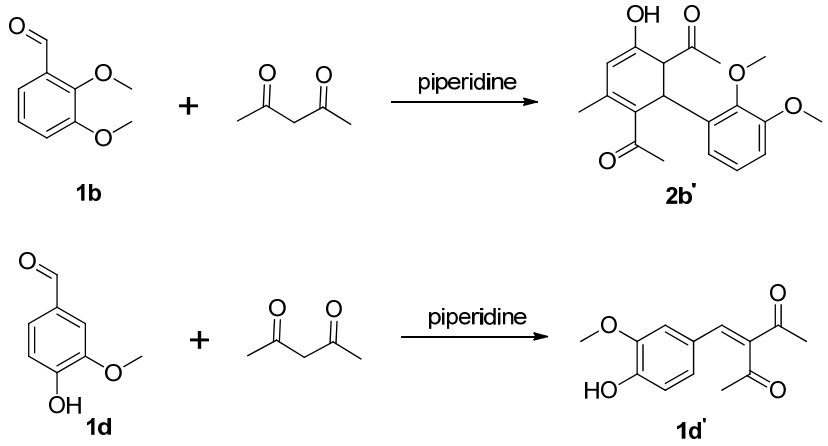


2b' **2b**

In a 100ml flask, 1.5g **2b'** was dissolved in 20ml EtOAc and 5 mL AcOH (the EtOAc was used to

dissolve the **2b'** owning to the poor solvability of **2b'** in AcOH), and 2*eq* 98% H_2SO_4 was added to the solution slowly at room temperature. The reaction mixture was stirred until **2b'** disappeared detected by TLC. The work-up and purifying procedure were similar to that of synthesis of **2b** from **1b**, and finally two fluorescent products were separated, which were identified as **2b** (isolated yield, 16%) and **2b-cis** (isolated yield, 28%) respectively.

Synthesis of 2b' and 1d'



In a 250ml flask, 42 mmol **1b** or **1d** was dissolved in 20ml acetylacetone respectively, 0.7ml piperidine was added. The solution was stirred under 110℃ for 8 hours. The reaction mixture was diluted by 50ml EtOAc, neutralized by hydrochloric acid, and washed by water for 3 times. The organic layer was separated and dried over $MgSO_4$, evaporated under vacuum and recrystallyzed in ethanol. In the case of **1b**, 3.7g pure **2b'** was obtained, yield 27%, in this condition, **2b'** presents as *trans* and *cis* mixture.

(**Ref:** *Anindra Sharma, Jyoti Pandey, R. P. Tripathi, Tetrahedron Letters 50 (2009) 1812–1816*)

In the case of **1d,** 3.8g **1d'** was obtained, yield 37%.

1.2 Optical measurements

Electronic absorption spectra were measured on a Shimadzu UV 2450 spectrophotometer. Stationary fluorescence spectra were recorded and corrected for instrumental response using a PerKin EimerTM LS 55 spectrofluorometer. The solvents: DCM, DMSO, Acetone and ethanol were checked for the presence of fluorescent impurities. For the determination of quantum yields, quinine sulfate in 1 N H_2SO_4 was used as a standard ($\Phi = 0.55$).

(Ref: *Franklyn G. Prendergast, Michael Meyer, Gerald L. Carlson, Shozo Iida and Jame D. Potter, THE JOURNAL OF BIOLOGICAL CHEMISTRY Vol. 258, No. 12, Issue of June 25, pp. 7541-7544. 1983*)

1.3 X-ray of 2b

Crystal data for 3: C19H20O4, M=312.35, green prism, 0.2 × 0.2 × 0.15 mm, orthorhombic, space group Pca21 (No. 29), a=17.8305(2), b=5.36310(10), c=16.2017(2) α=90.00°, β=90.00°, γ=90.00°, V= 1549.32(4)Å^3, Z=4, Dc=1.339mg/mm3, F(000)= 664, CuK\a radiation, λ=1.54178 Å, T=293(2)K,

$2\theta_{max}$= 71.28°, 12513 Independent reflections collected, 2896 unique (Rint = 0.0297).The structure was solved and refined using he programs SHEKXS-97 and SHELXL-97 respectively. Final GooF=1.029, R1 = 0.0285, wR2 = 0.0768, R indices based on all reflections with I>2σ (I) (refinement on F^2), 0 restraints. Lp and absorption correctionsapplied, μ=0.758mm-1

2. Stereochemistry Discussion

In this work, the obtained **2a-i** were determined as (4R,4aS), (4S,4aR) isomers based on the following discussion:

2.1. Dihedral angle θ calculation

According to Karplus equation:

$$J=7-\cos\theta+5\cos 2\theta$$

(**Ref:** *Neil E. Jacobsen, Ph.D., University of Arizona, NMR Spectroscopy Explained-Simplified Theory, Applications and Examples for Organic Chemistry and Structural Biology, John Wiley & Sons, Inc., Hoboken, New Jersey, chapter 2*)

the dihedral angle θ of H-C_{4a}-C_4-H could be calculated from J_{H4a-H4}. The J_{H4a-H4} of the rest compounds (**2a, c-i**) were close to that of **2b** ($J_{H4a-H41}$= 11.79) while the J_{H4a-H4} of **2b-cis** was 6.11Hz. We therefore calculated the θ(H-C_{4a}-C_4-H) of **2a-i** and found that the calculated θ(H-C_{4a}-C_4-H) of **2b** was 162^o, while the θ(H-C_{4a}-C_4-H) of others are near to 180^o, indicating a *trans* form of H-C_{4a}-C_4-H in **2a-i**. The calculated θ (H-C_{4a}-C_4-H) of **2b** match the measured one from its crystal structure (161.06^o). In contrast, the θ(H-C4a-C4-H) of **2b-cis** was calculated to be 46^o (*cis* H-C4a-C4-H form).

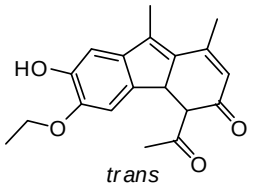
2.2. X-ray data of 2b

In the crystal of **2b**, (4R,4aS), (4S,4aR) isomers were found, see “cif file”.

3. Data of final compounds

3.1 NMR and MS

4-acetyl-6-ethoxy-7-hydroxy-1,9-dimethyl-4,4a-dihydro-3H-fluoren-3-one (2a) m.p. 177.5~180.0 ^{o}C; ^{1}H NMR (400 MHz, *CDCl$_3$*) δppm 7.00 (s, 1H), 6.74 (s, 1H), 5.77 (s, 1H), 5.73 (s, 1H), 4.32 (dd, *J* = 12.79, 1.38 Hz, 1H), 4.08 (m, 2H), 3.32 (d, *J* = 12.80 Hz, 1H), 2.42 (s, 3H), 2.37 (d, *J* = 1.17 Hz, 3H), 2.35 (d, *J* = 1.96 Hz, 3H), 1.43 (t, *J* = 6.99, 6.99 Hz, 3H); ^{13}C NMR: 207.2, 196.3, 154.0, 145.8, 145.6, 140.2, 139.9, 137.6, 136.1, 124.9, 107.7, 106.5, 64.8, 63.9, 50.0, 33.0, 22.1, 14.7, 12.7; MS (APCI) $[M+1]^{+}$: 311.0; EA, calcd. for $C_{19}H_{20}O_4 \cdot 1/4H_2O$: C% 72.02, H% 6.52; found: C% 72.30, H% 6.636.



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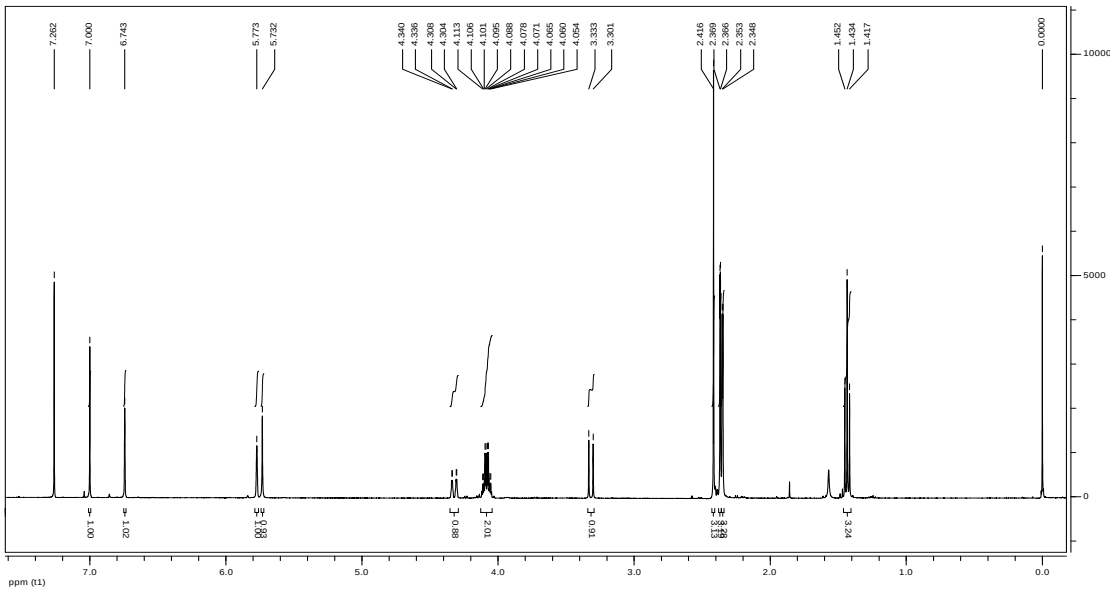
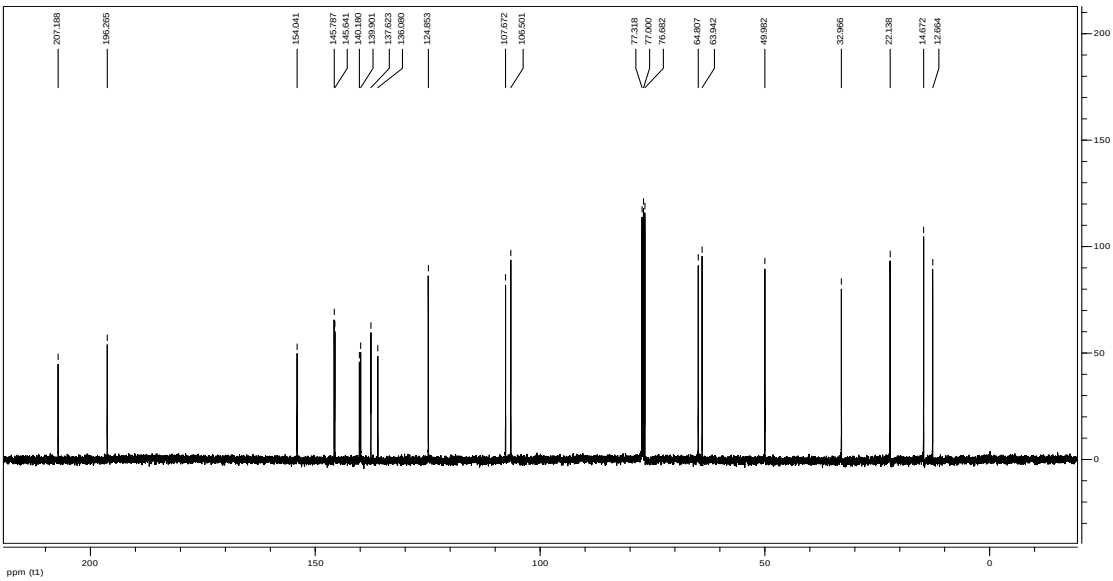


13CNMR:



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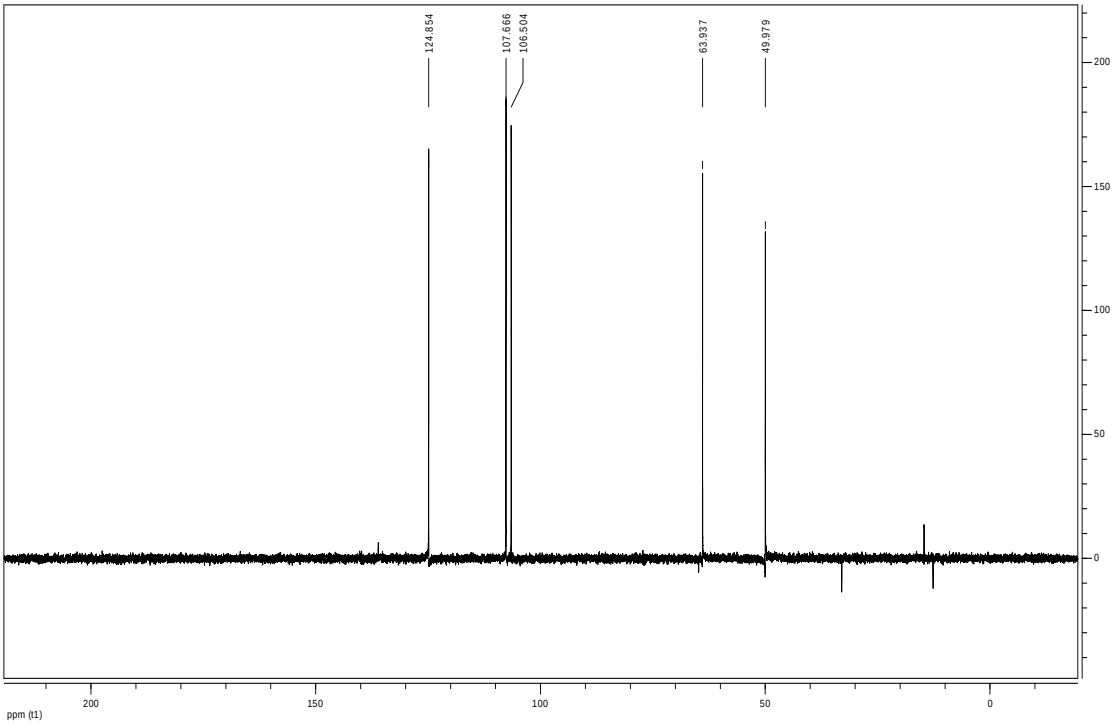

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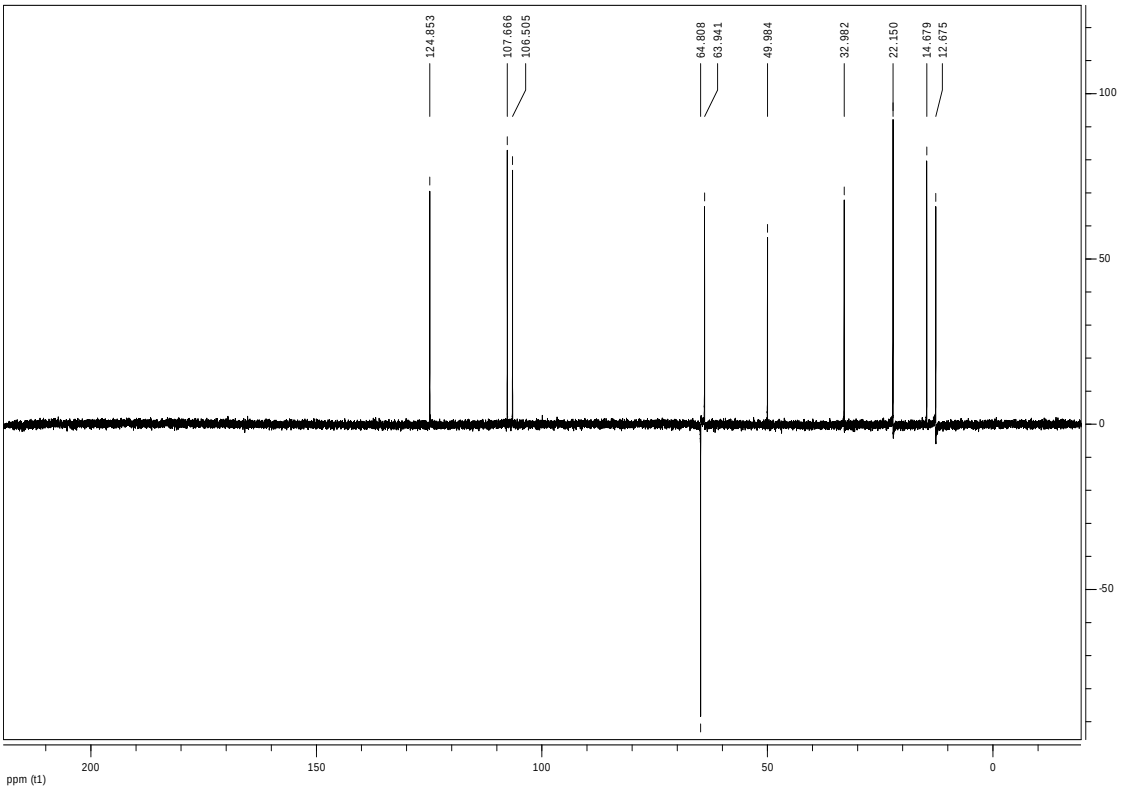

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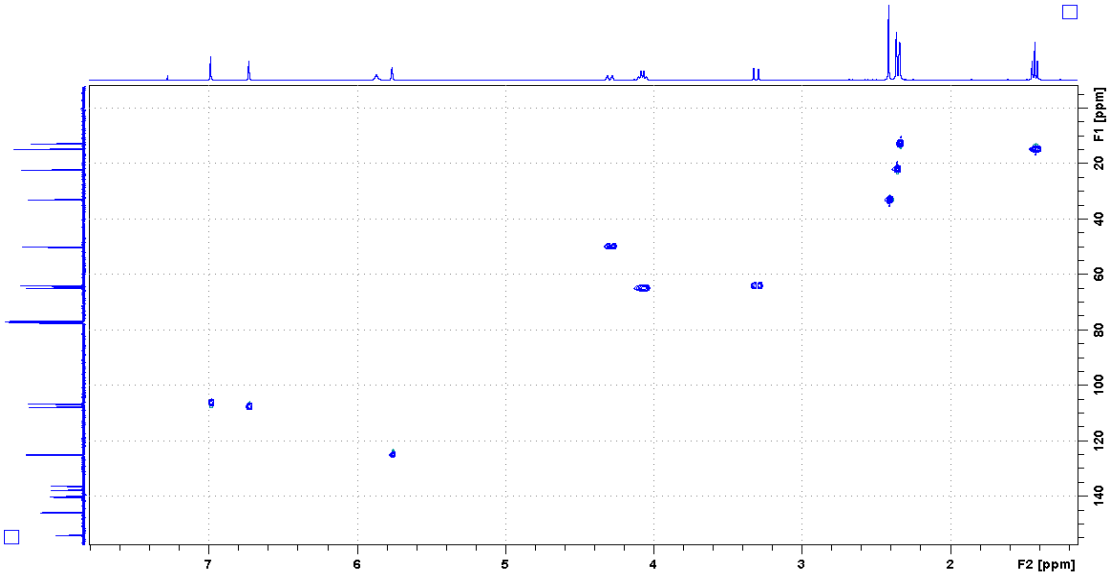

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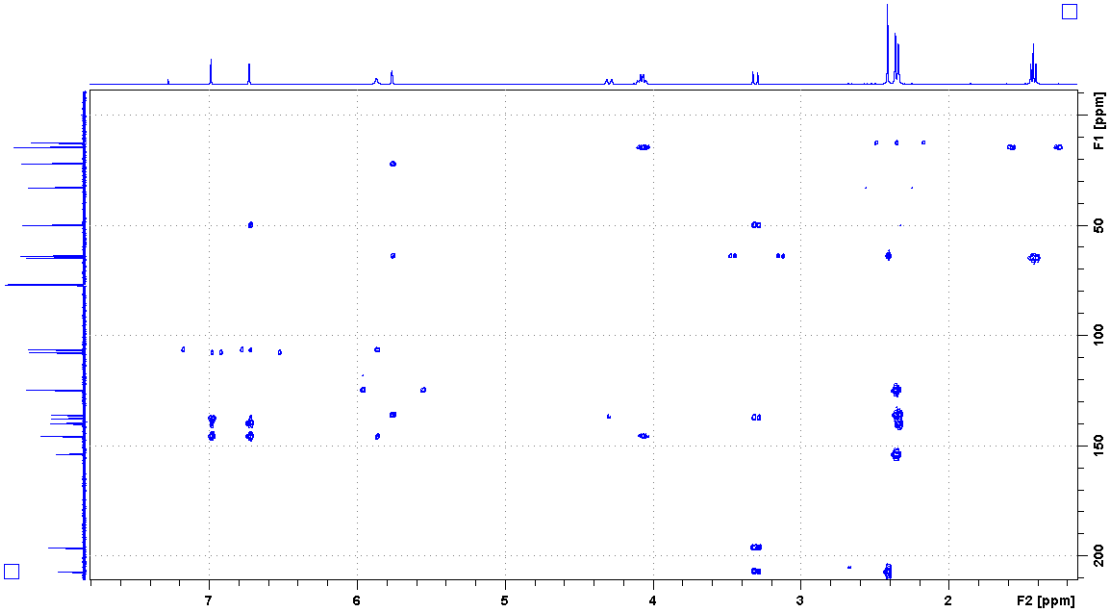

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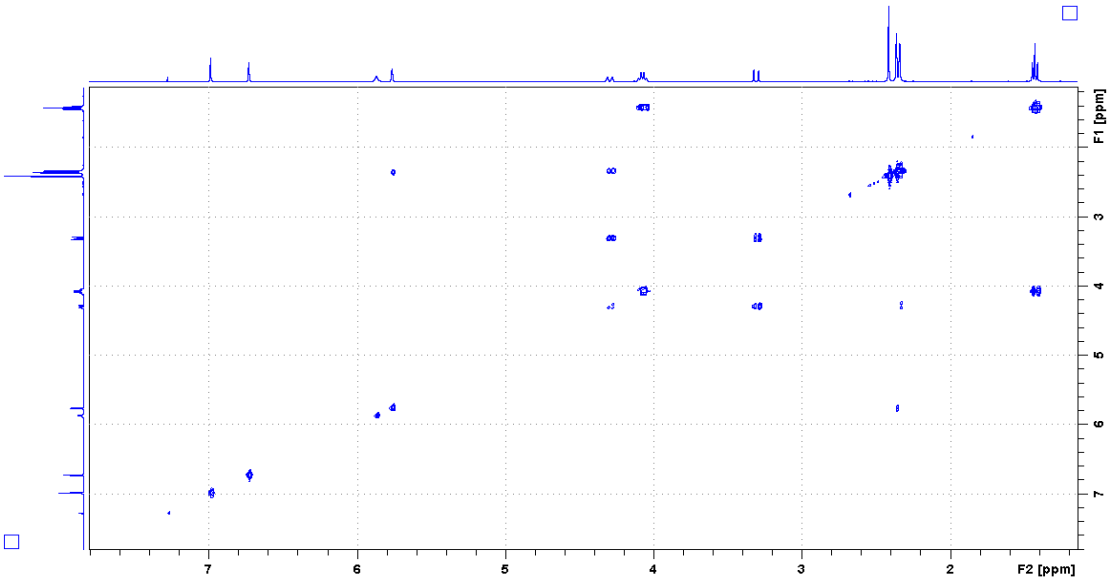

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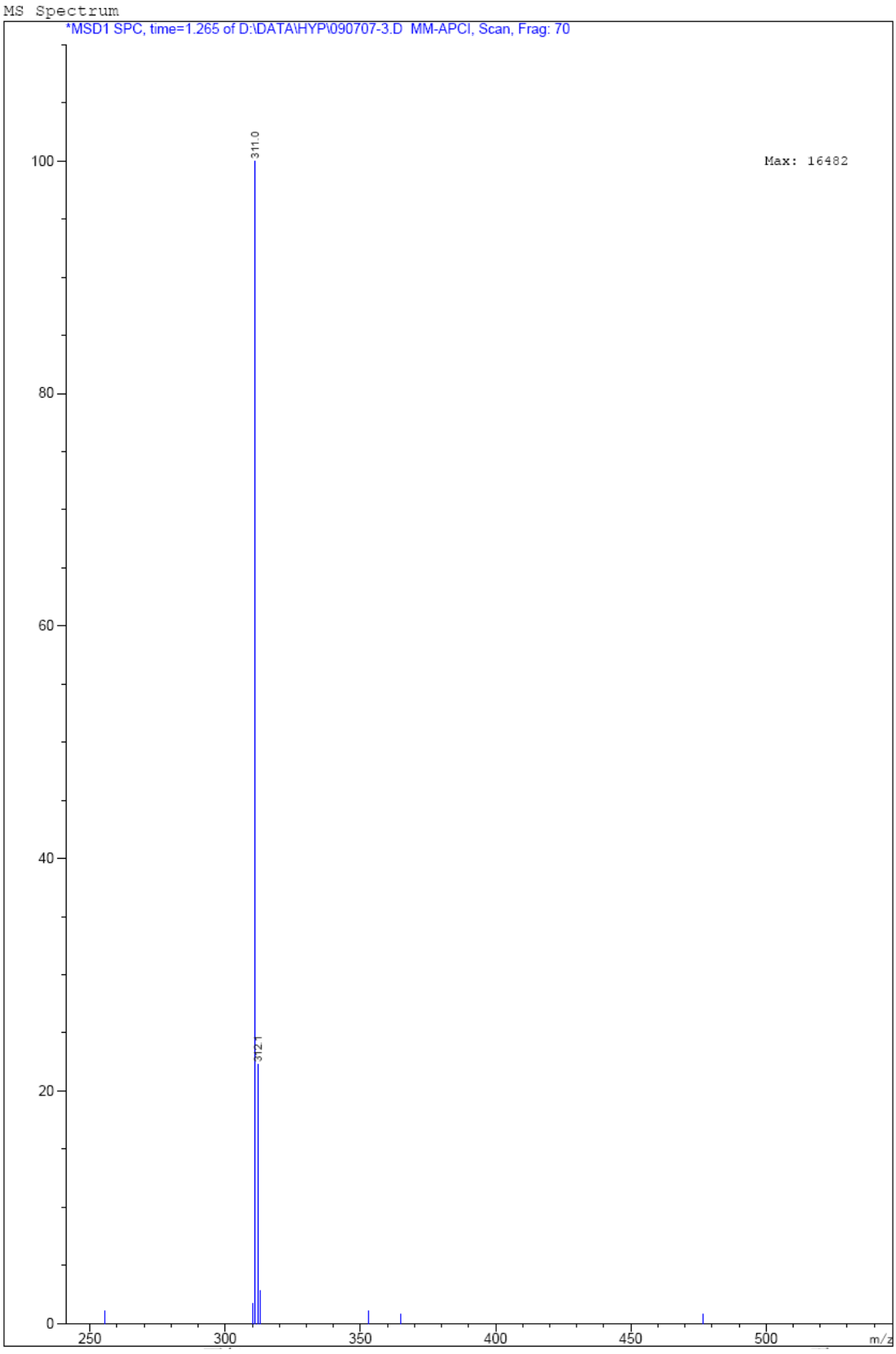
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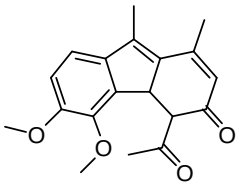
80
60
40
20
0
250
300
350
400
450
500
m/z

4-acetyl-5,6-dimethoxy-1,9-dimethyl-4,4a-dihydro-3H-fluoren-3-one (2b) m.p. 165~166.2 °C; ^{1}H NMR (400 MHz, *CDCl$_3$*) δppm 7.11 (d, *J* = 8.22 Hz, 1H), 6.91 (d, *J* = 8.24 Hz, 1H), 5.78 (s, 1H), 4.62 (dd, *J* = 11.81, 2.10 Hz, 1H), 3.89 (s, 3H), 3.66 (s, 3H), 3.46 (d, *J* = 11.79 Hz, 1H), 2.47 (s, 3H), 2.36 (d, *J* = 1.09 Hz, 3H), 2.34 (d, *J* = 2.16 Hz, 3H) ^{13}C NMR：205.3, 196.7, 153.8, 152.3 144.9, 140.4, 139.1, 137.1, 136.3, 125.6, 116.0, 111.6, 60.8, 59.3, 55.9, 48.6, 32.3, 22.3, 12.5; MS (APCI) $[M+1]^+$: 313.1; EA, calcd for $C_{19}H_{20}O_4$: C% 73.06, H% 6.45; found: C%72.79, H% 6.358.



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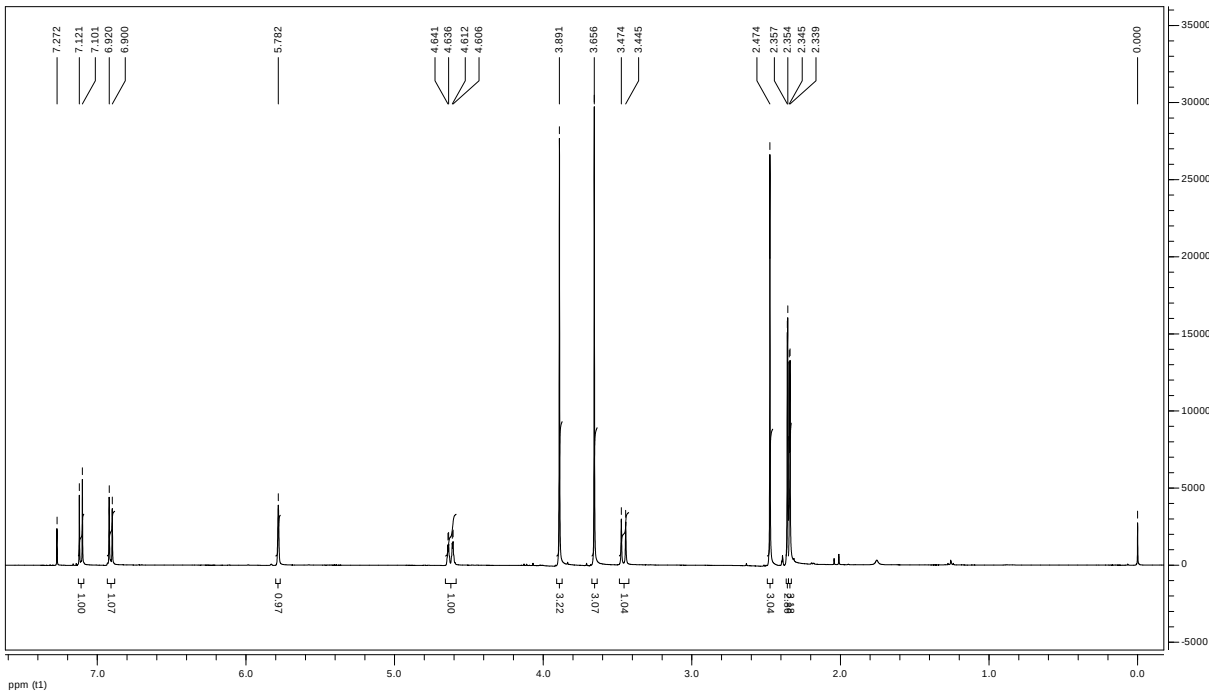

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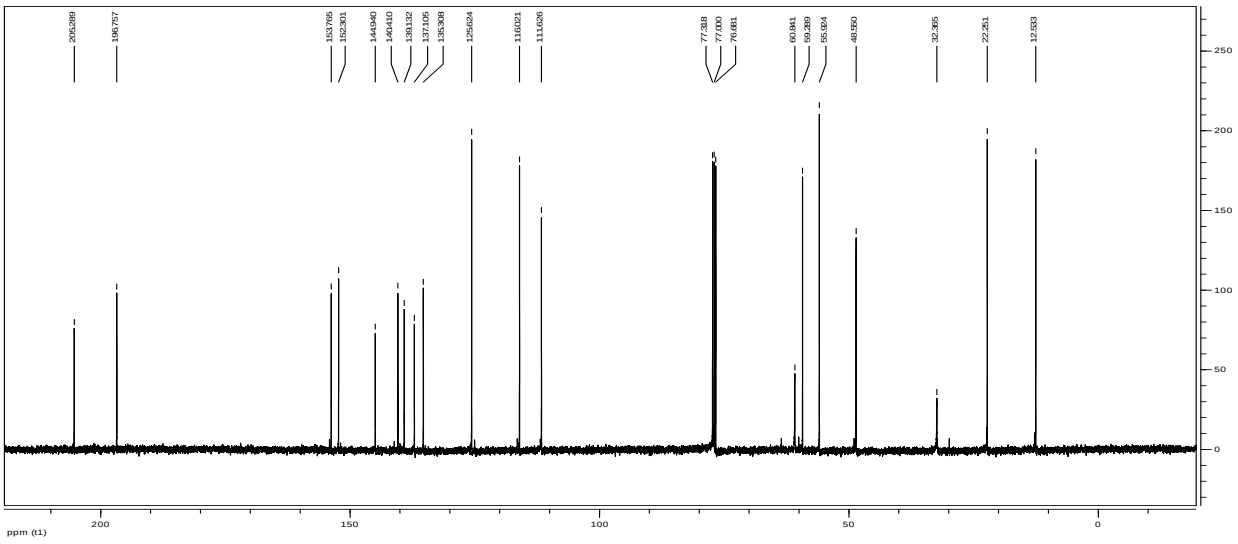

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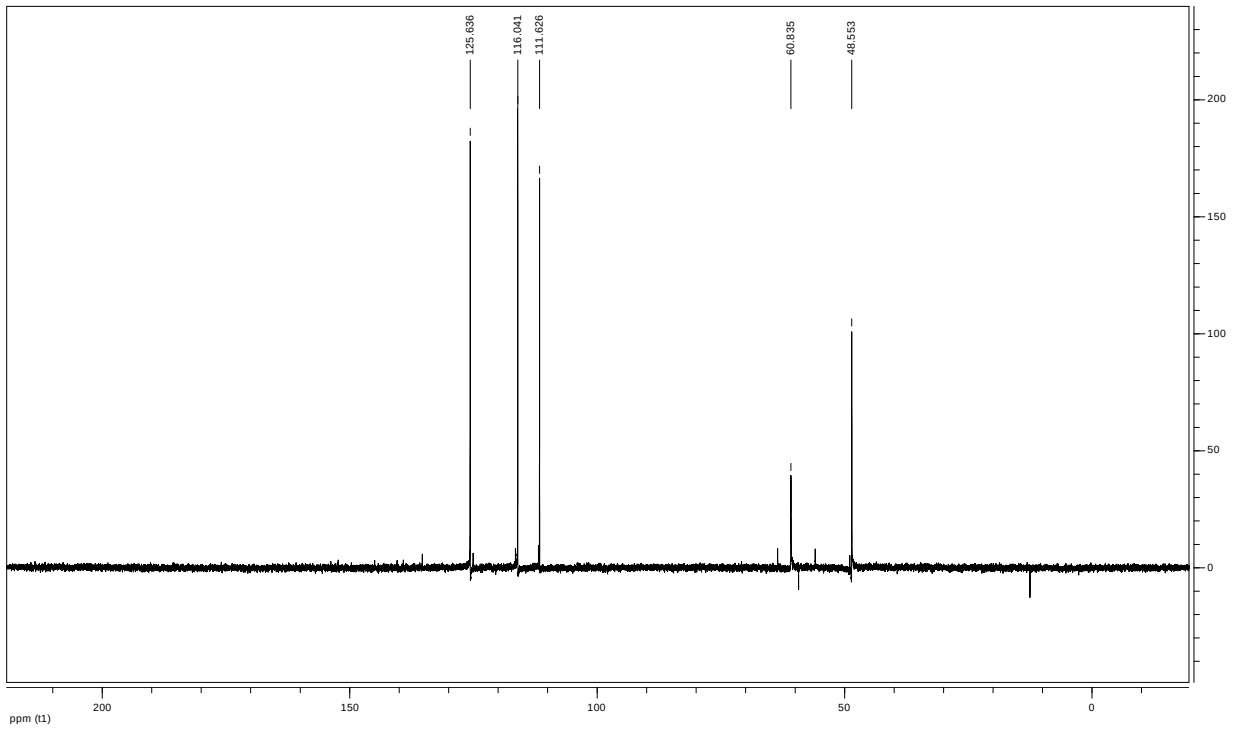

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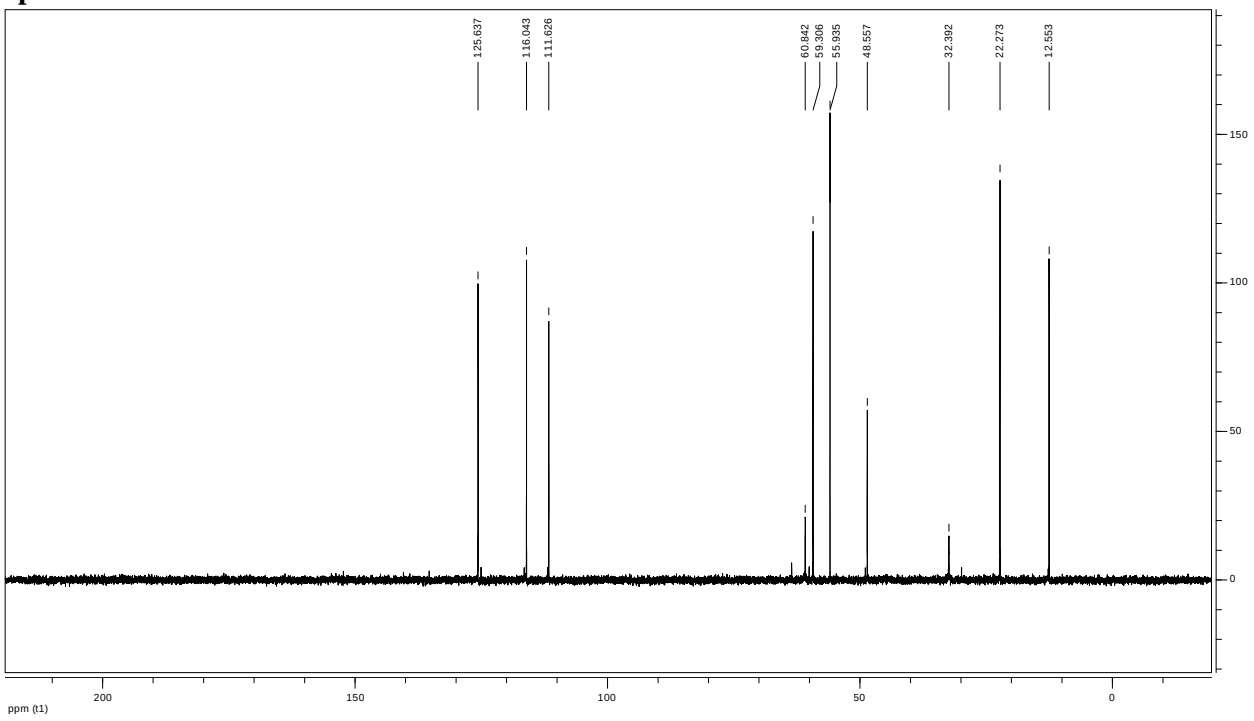

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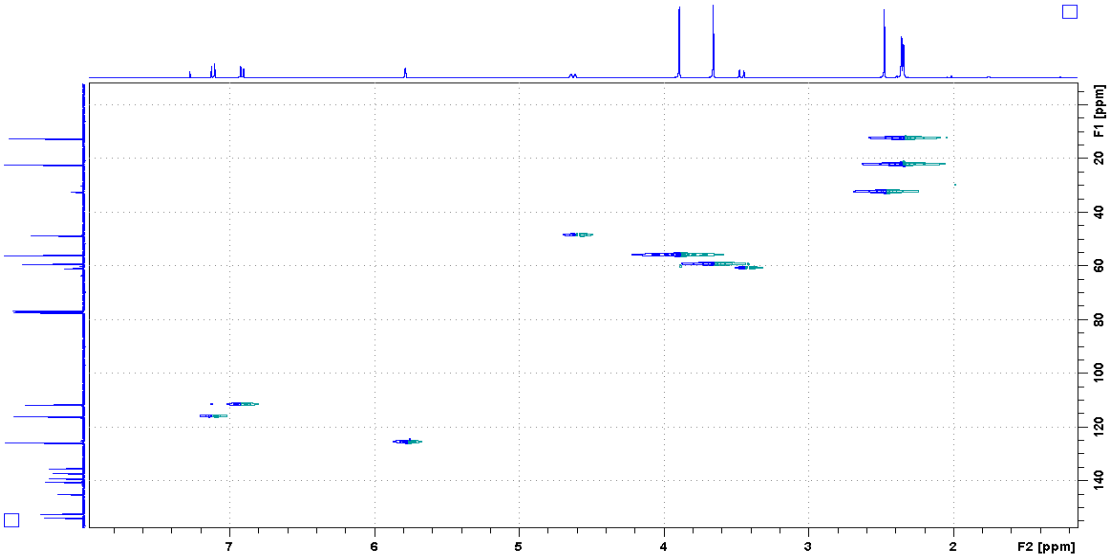

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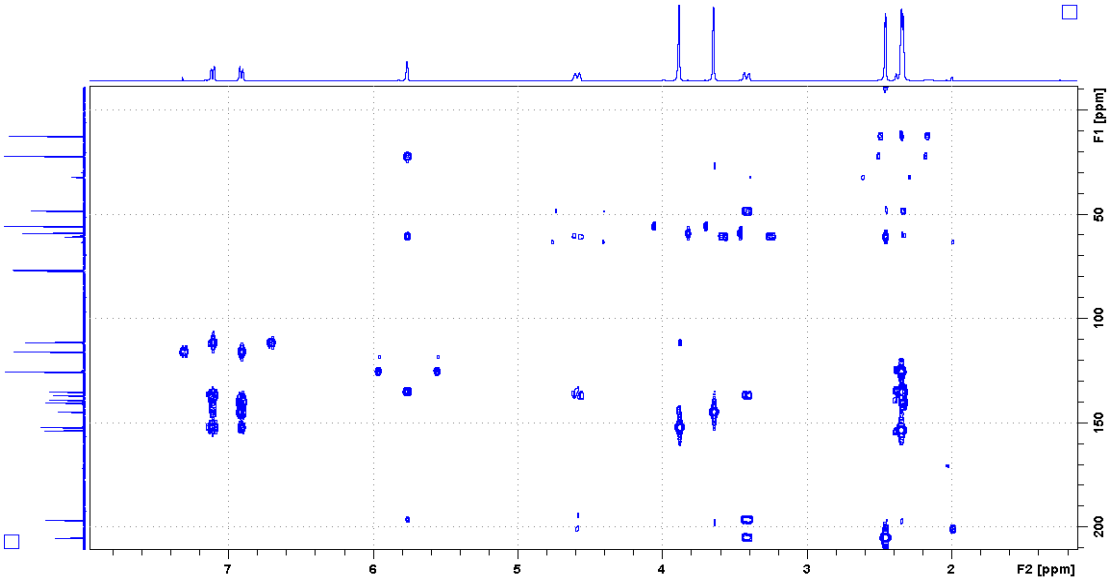

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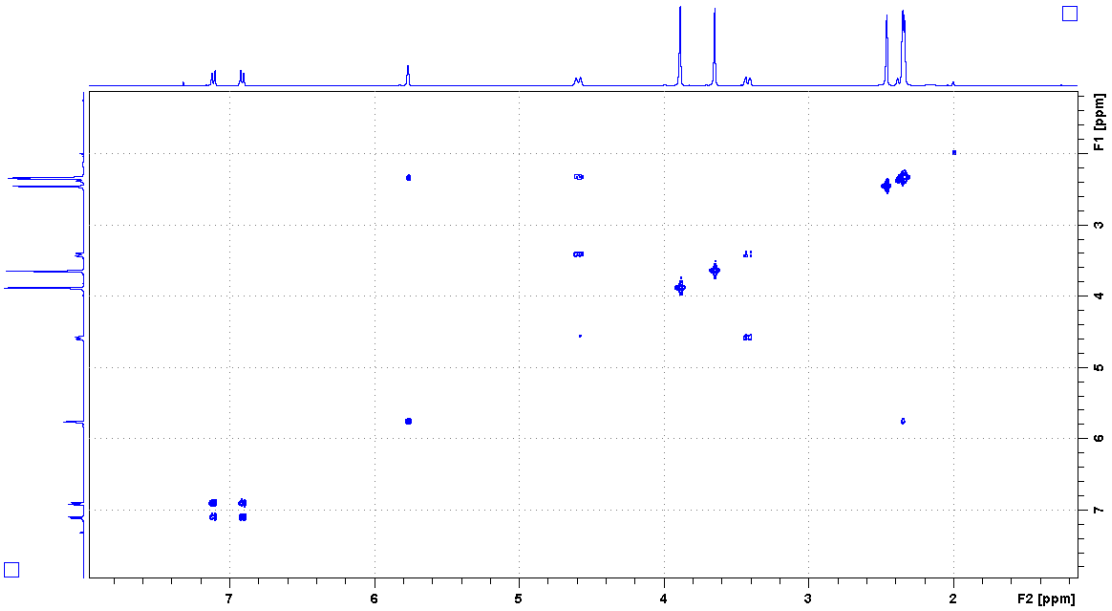

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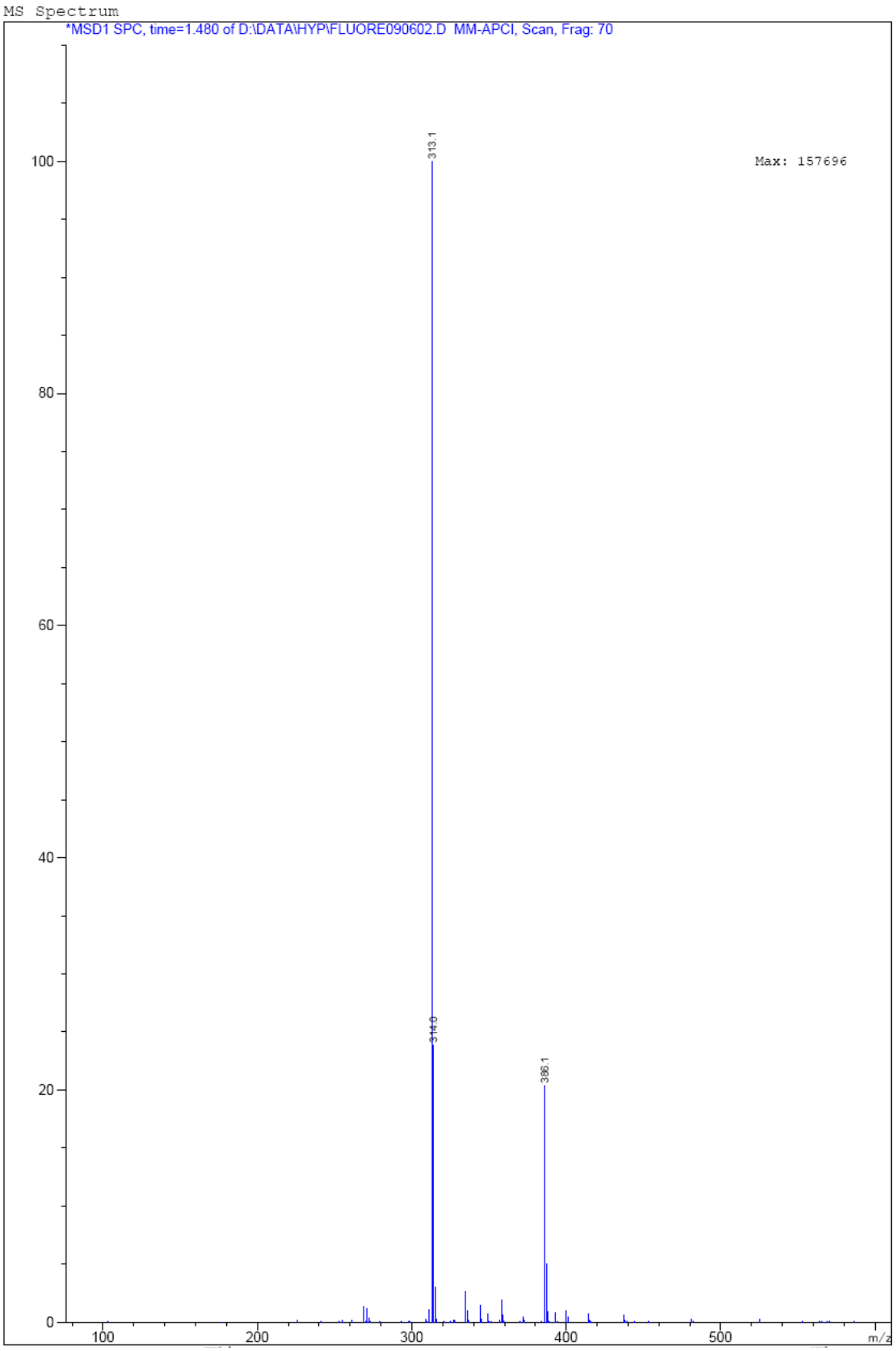
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Max: 157696
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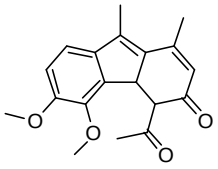
314.0
386.1
100
80
60
40
20
0
100
200
300
400
500
m/z

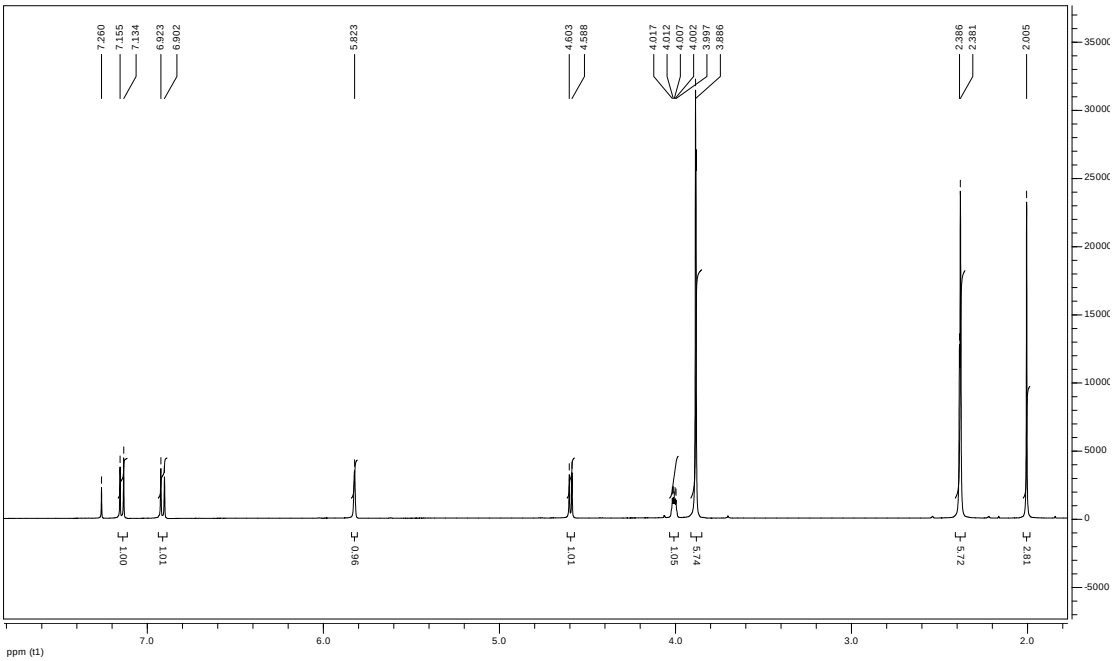
2b-cis:

m.p. 142~143.4°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 6.91 (d, J = 8.26 Hz, 1H), 7.14 (d, J = 8.24 Hz, 1H), 5.82 (s, 1H), 4.60 (d, J = 6.11 Hz, 1H), 4.01 (dd, J = 6.05, 2.13 Hz, 1H), 3.88 (m, 6H), 2.38 (m 6H), 2.00 (s, 3H); ^{13}C NMR: 201.1, 194.6, 154.1, 151.9, 144.4, 141.2, 140.0, 136.5, 134.9, 125.0, 116.5, 111.8, 63.5, 60.1, 55.9, 48.9, 29.9, 22.3, 12.7. MS (APCI) $[M+1]^+$: 313.1, Elemental Analysis of $C_{19}H_{20}O_4$: calc: C% 73.06, H% 6.45; found: C%72.87, H% 6.445.



cis

1HNMR:



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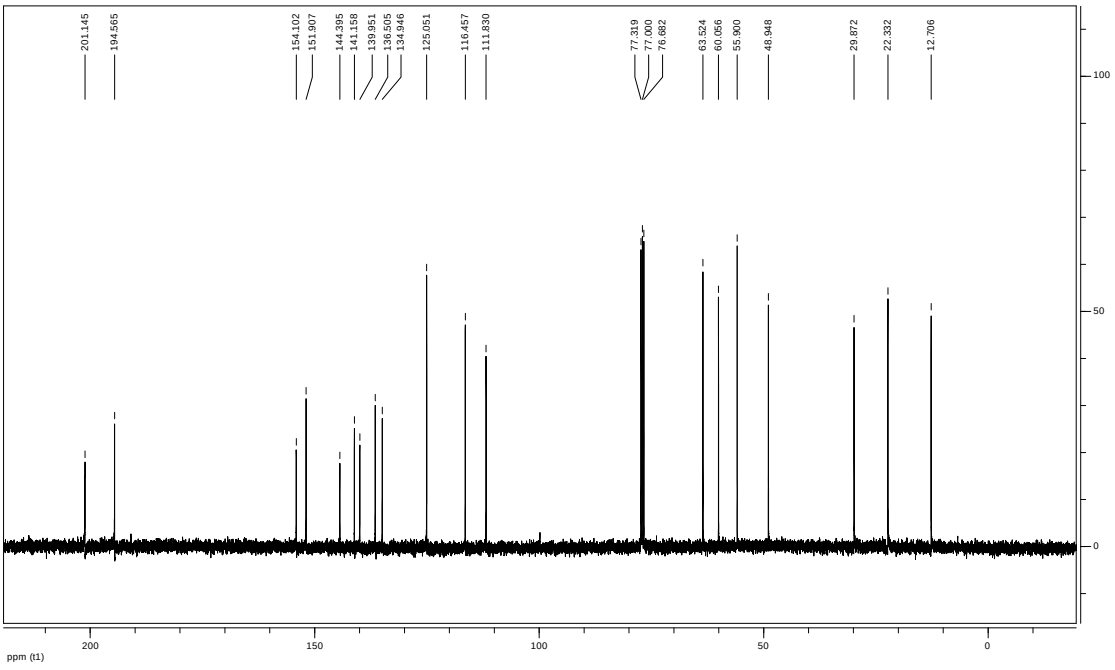

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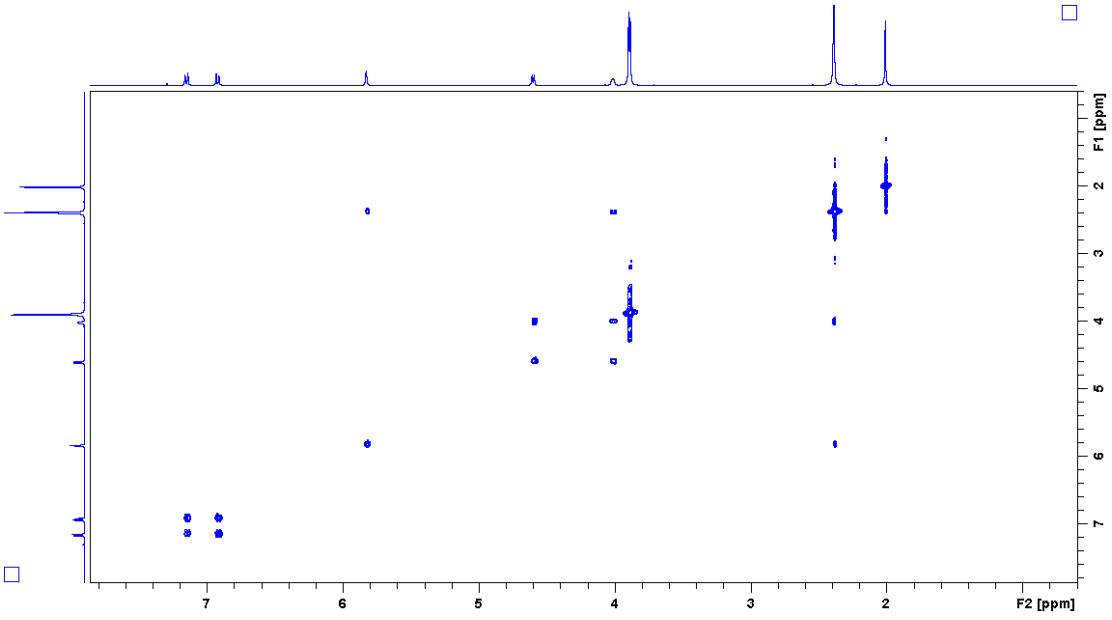

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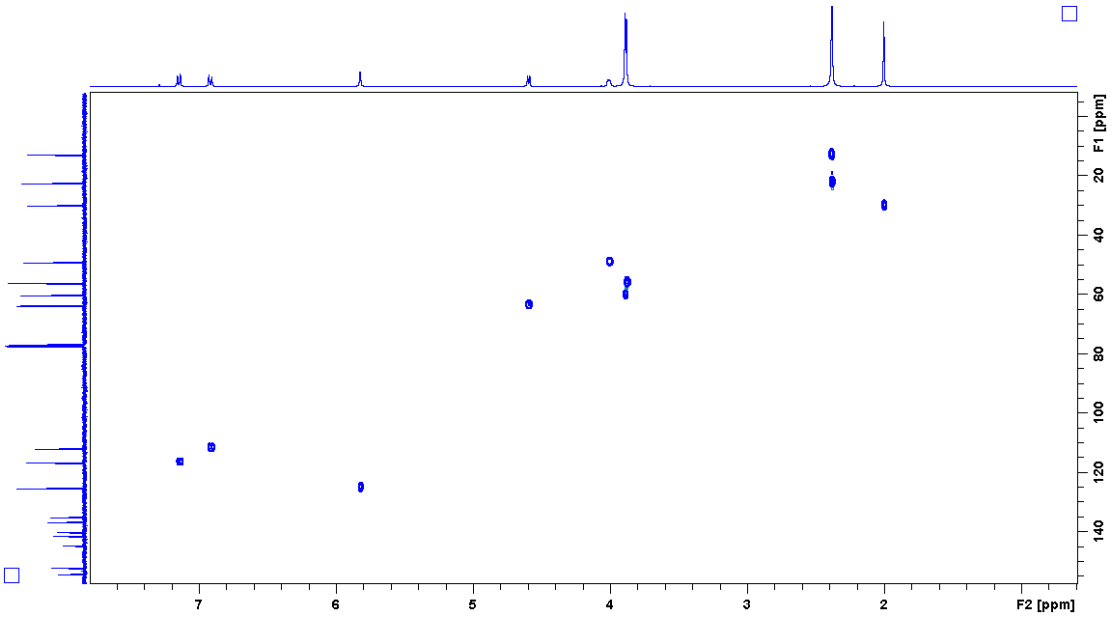

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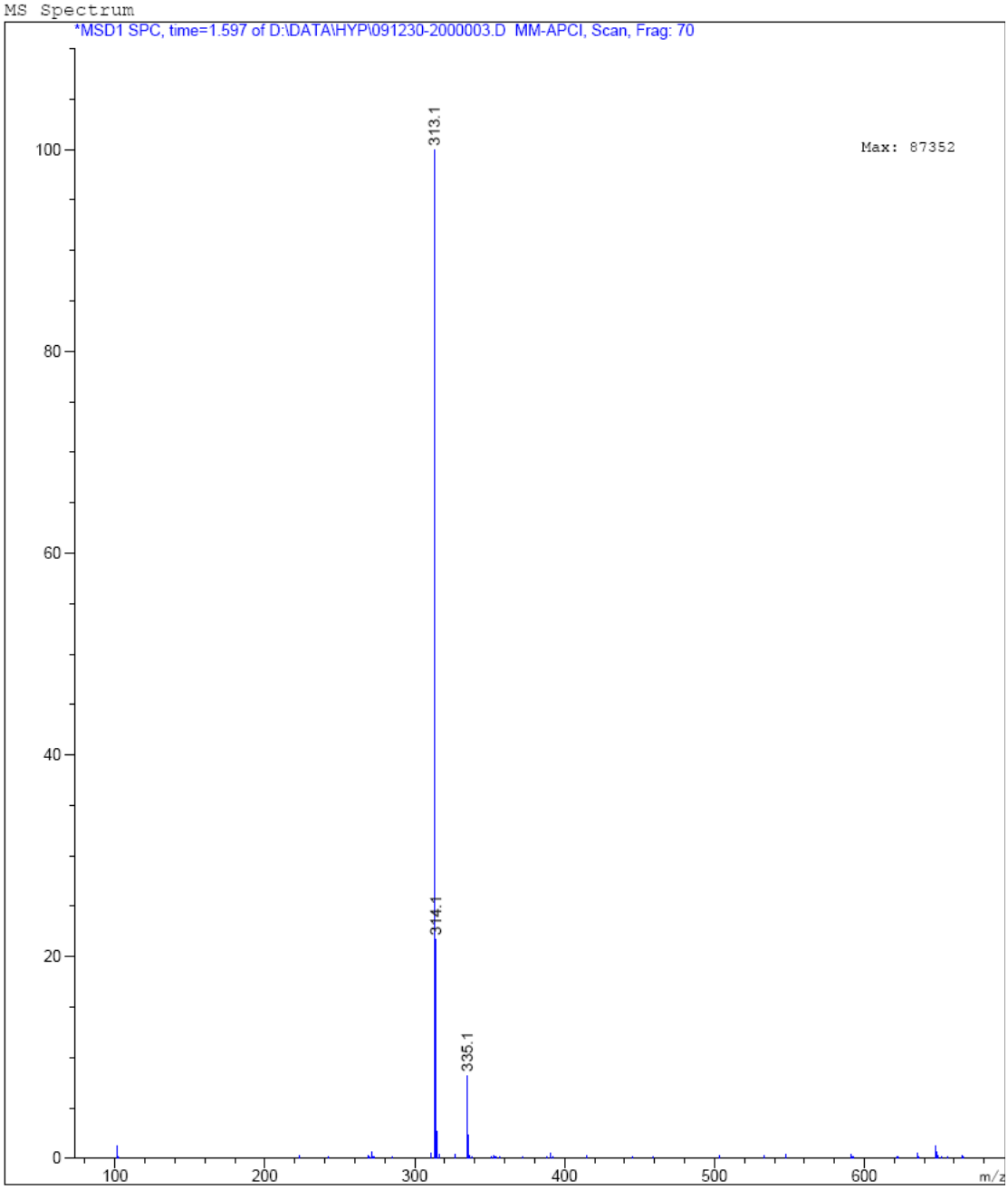
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314.1
335.1
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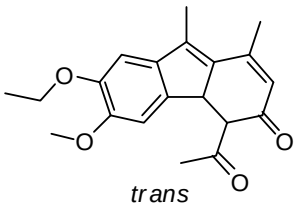
80
60
40
20
0
100
200
300
400
500
600
m/z

4-acetyl-7-ethoxy-6-methoxy-1,9-dimethyl-4,4a-dihydro-3H-fluoren-3-one (2c) m.p. 157.2~160.4 ^{o}C; ^{1}H NMR (400 MHz, *CDCl$_3$*) δppm 6.94 (s, 1H), 6.78 (s, 1H), 5.77 (s, 1H), 4.35 (dd, *J* = 12.76, 1.47 Hz, 1H), 4.15 (q, *J* = 7.02, 7.01, 7.01 Hz, 2H), 3.84 (s, 3H), 3.33 (d, *J* = 12.79 Hz, 1H), 2.43 (s, 3H), 2.38 (m, 6H), 1.49 (t, *J* = 6.99, 6.99 Hz, 3H) ^{13}C NMR: 207.0, 196.1, 153.8, 149.4, 148.4, 140.0, 139.3, 136.5, 135.9, 124.8, 107.6, 105.2, 64.6, 63.7, 56.0, 50.0, 32.9, 22.1, 14.7, 12.7; MS (APCI) $[M+1]^{+}$: 349.0; EA, calcd for $C_{20}H_{22}O_4$: C% 73.60, H% 6.79; found: C% 73.71, H% 6.686.



trans

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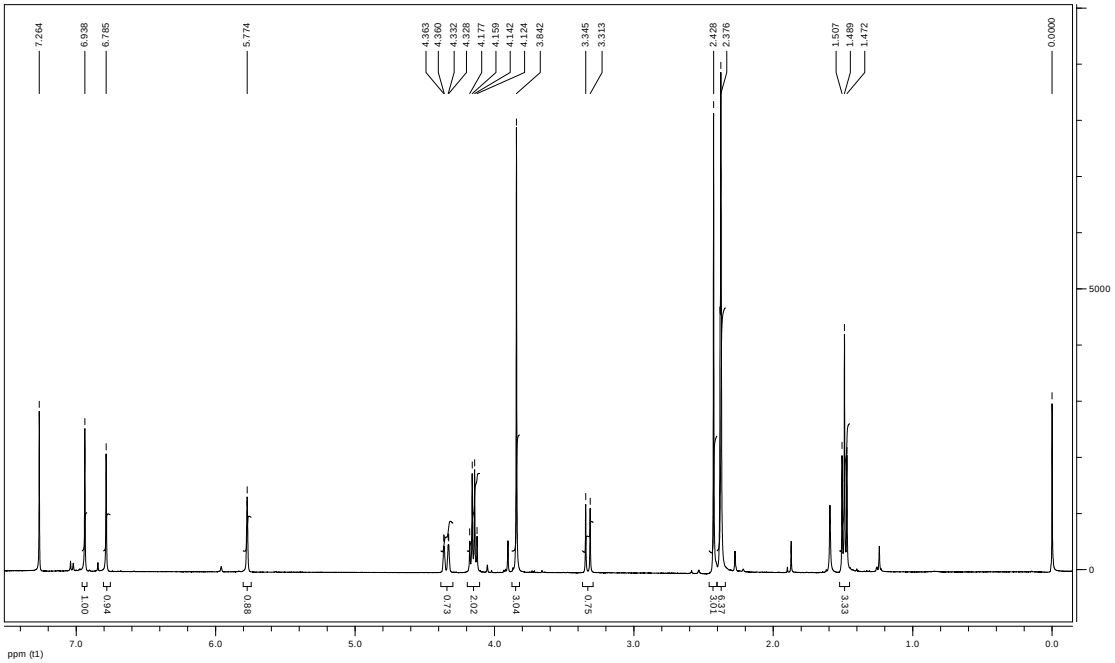

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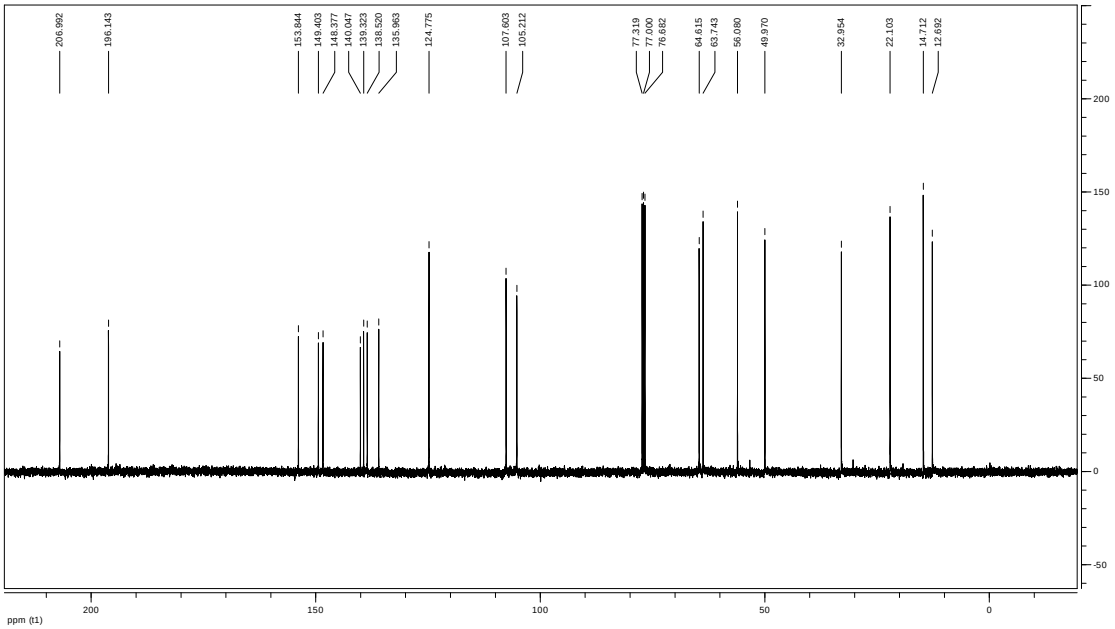

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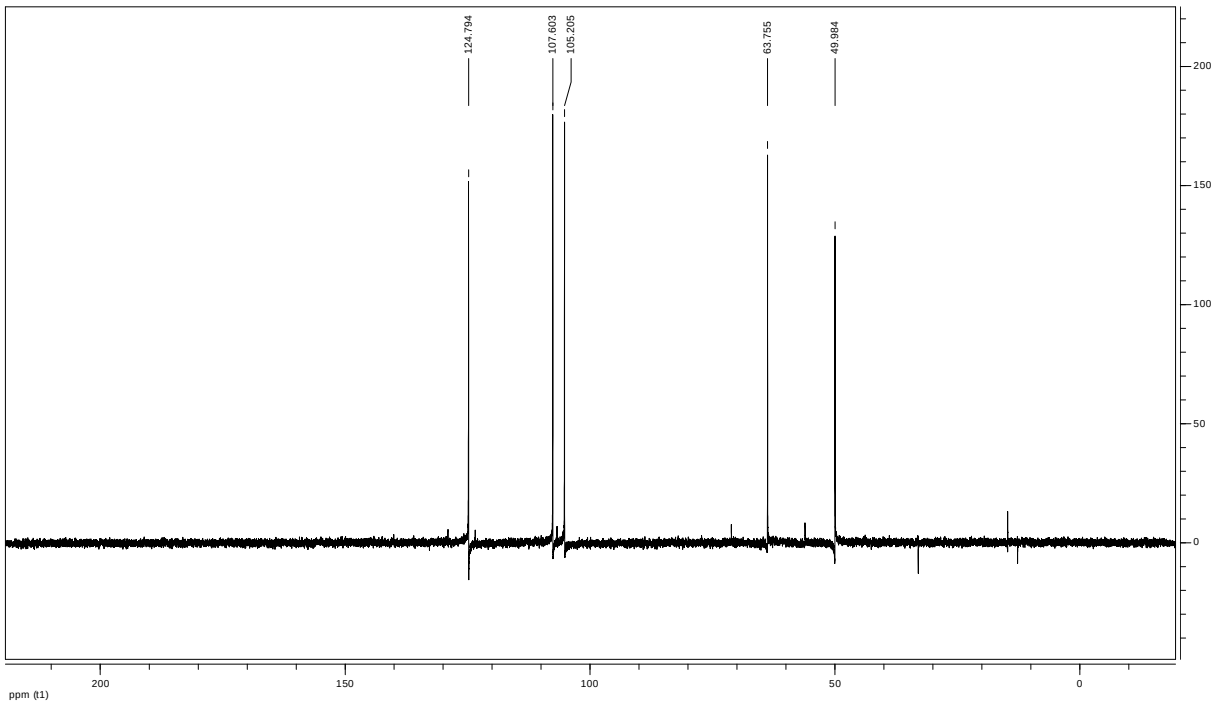

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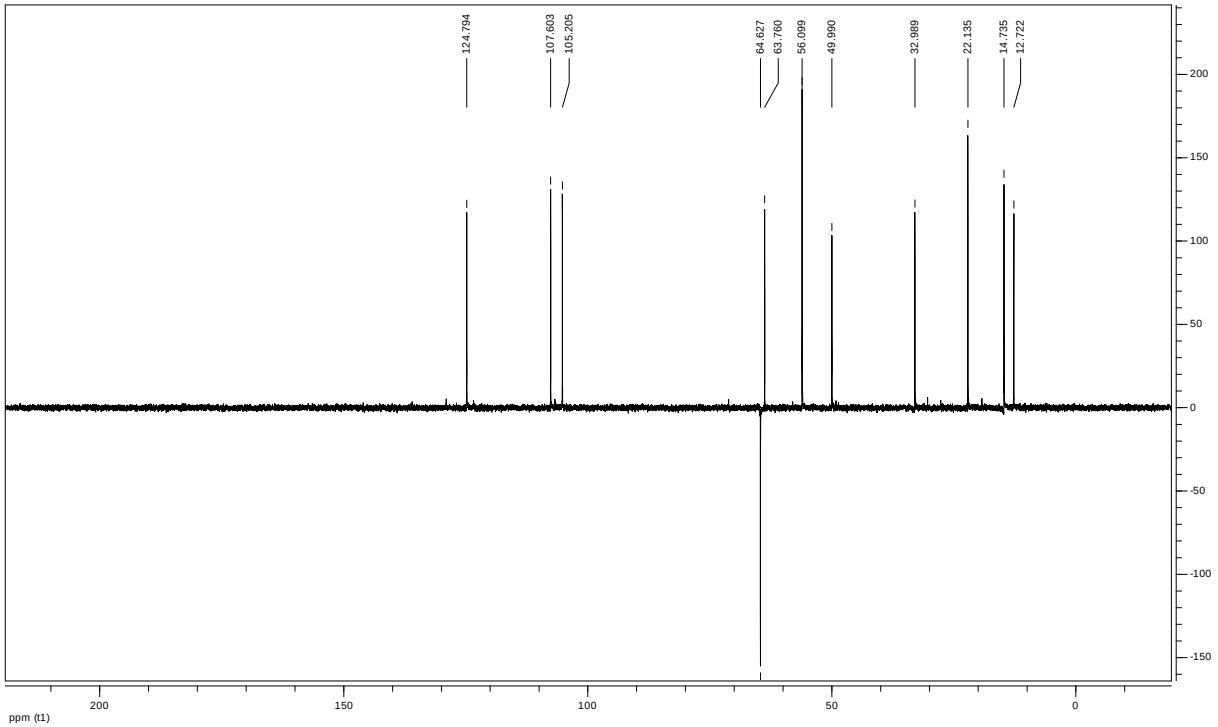

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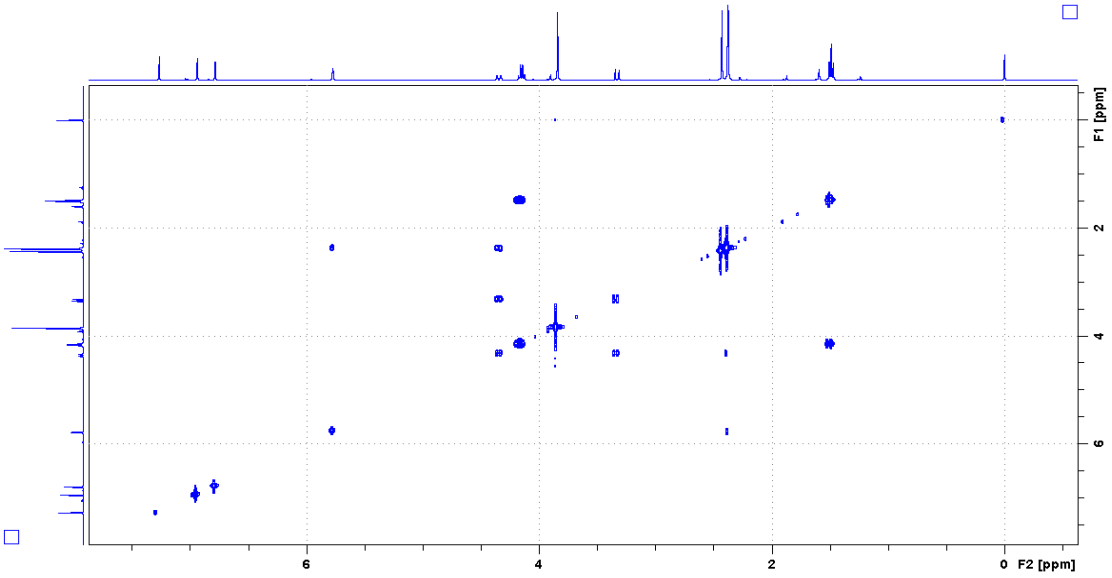
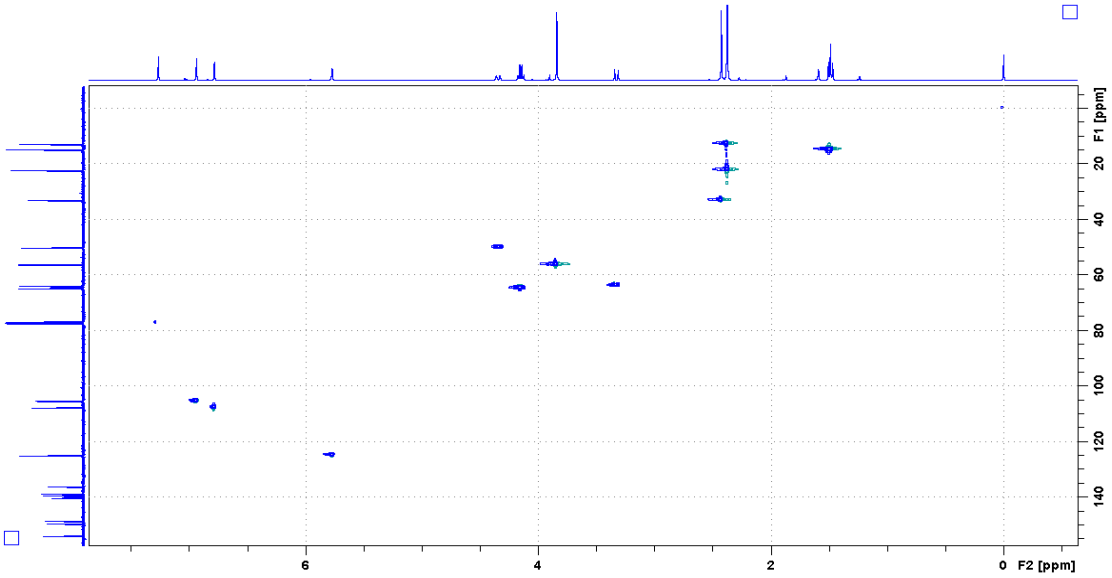
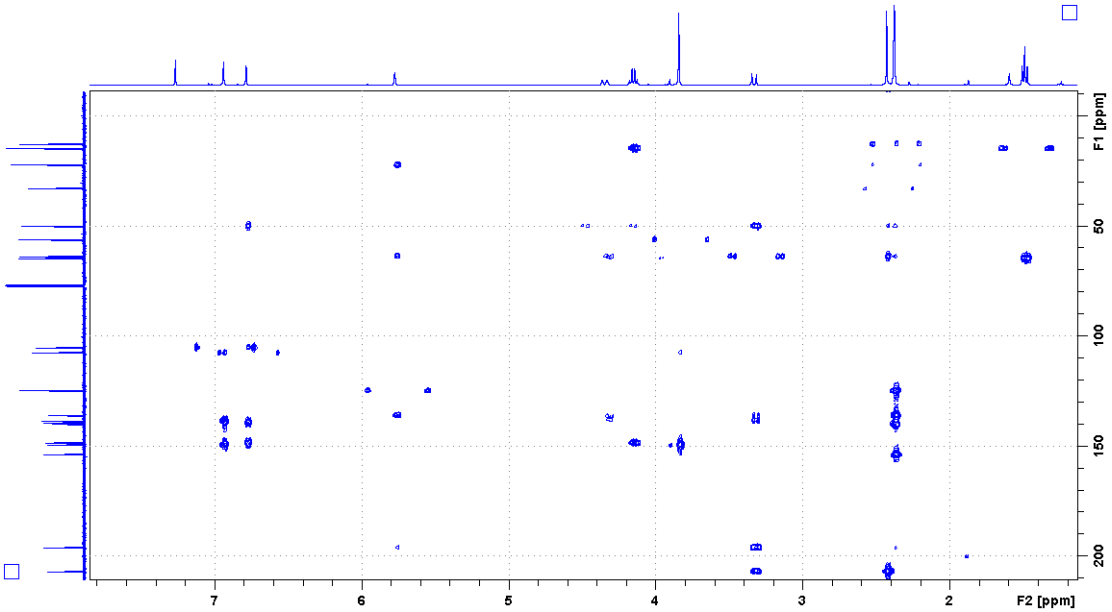


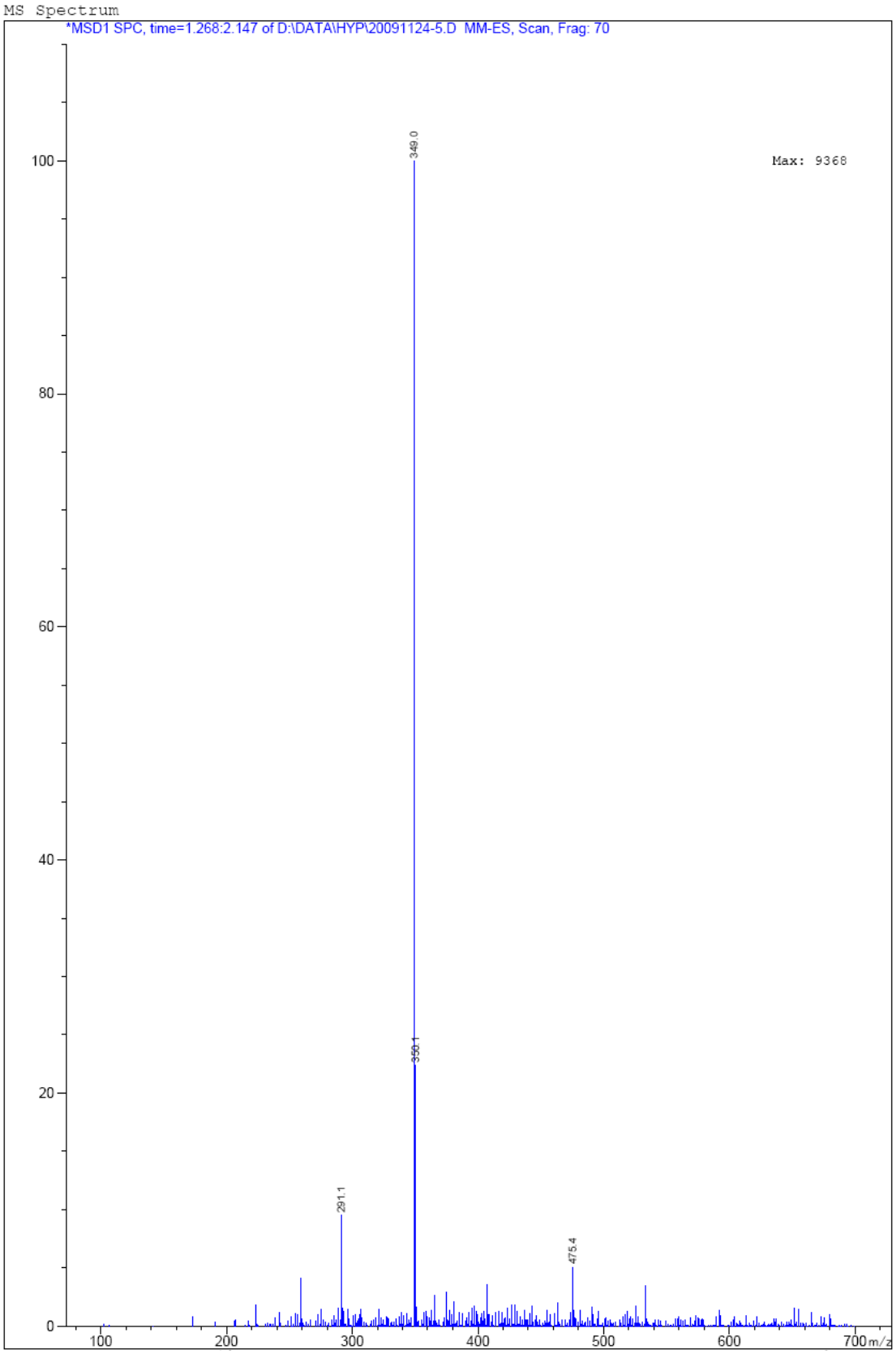
HSQC:



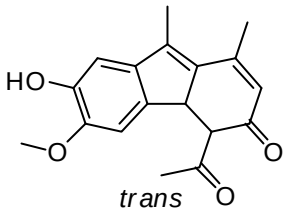
HMBC:



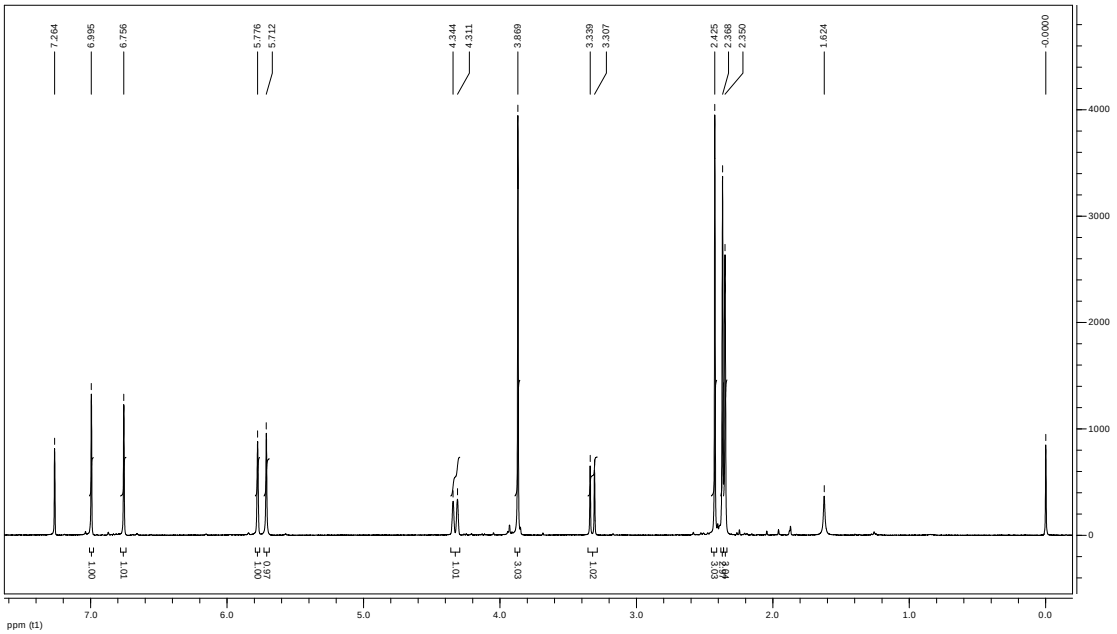
MS:


MS Spectrum
*MSD1 SPC, time=1.268:2.147 of D:\DATA\HYP\20091124-5.D MM-ES, Scan, Frag: 70
Max: 9368
349.0
350.1
291.1
475.4
100
80
60
40
20
0
100
200
300
400
500
600
700 m/z

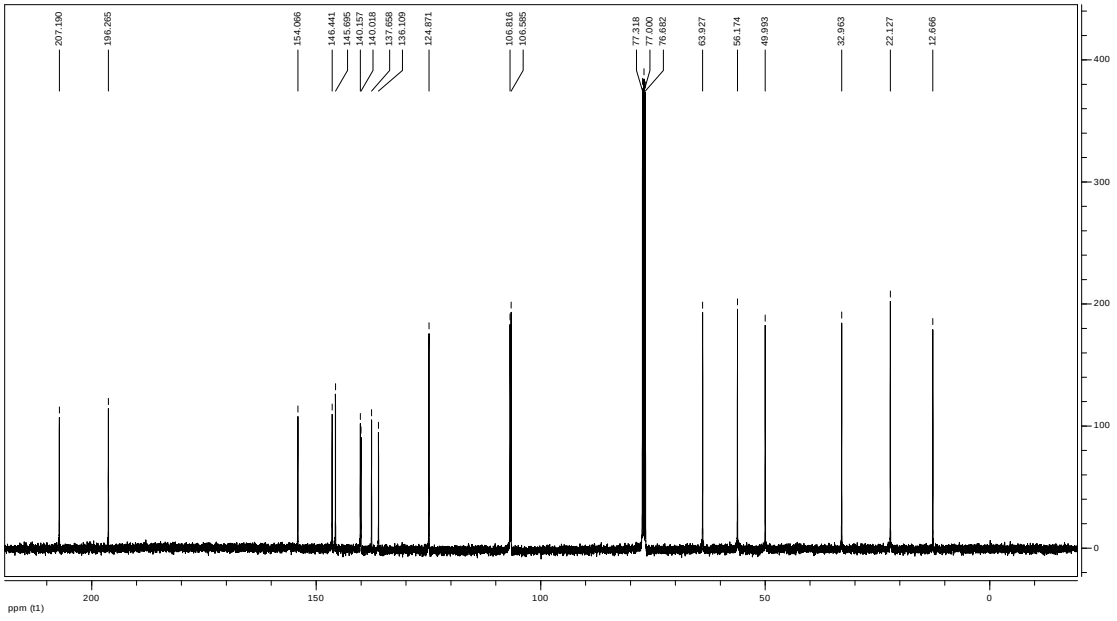
4-acetyl-7-hydroxy-6-methoxy-1,9-dimethyl-4,4a-dihydro-3H-fluoren-3-one (2d) m.p. 163.9~165.5 °C; ^{1}H NMR (400 MHz, *CDCl$_3$*) δppm 6.99 (s, 1H), 6.76 (s, 1H), 5.78 (s, 1H), 5.71 (s, 1H), 4.33 (d, *J* = 12.87 Hz, 1H), 3.87 (s, 3H), 3.32 (d, *J* = 12.79 Hz, 1H), 2.43 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H); ^{13}C NMR:207.2, 196.3, 154.1, 146.4, 145.7, 140.2, 140.0, 137.6, 136.1, 124.9, 106.8, 106.6, 63.9, 56.2, 50.0, 33.0, 22.1, 12.7; MS (APCI) $[M+1]^+$: 299.1; EA, calcd. For $C_{18}H_{18}O_4$: C% 72.47, H% 6.08%, found: C%72.20, H% 6.151.



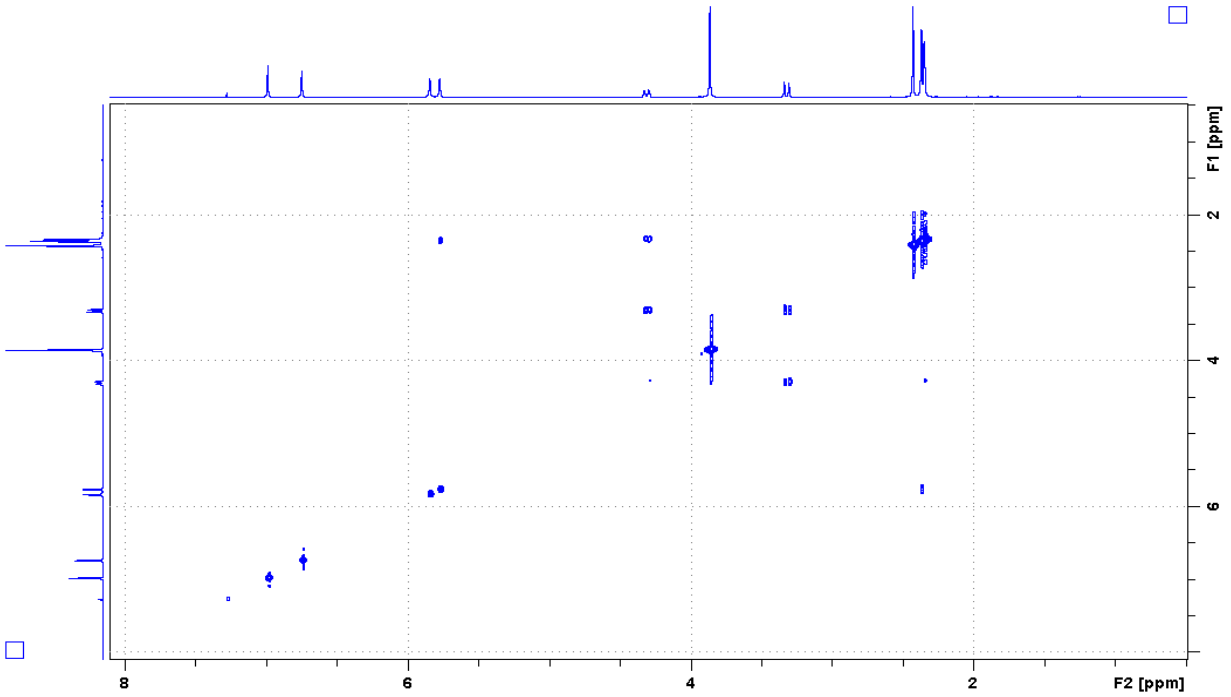
1HNMR:



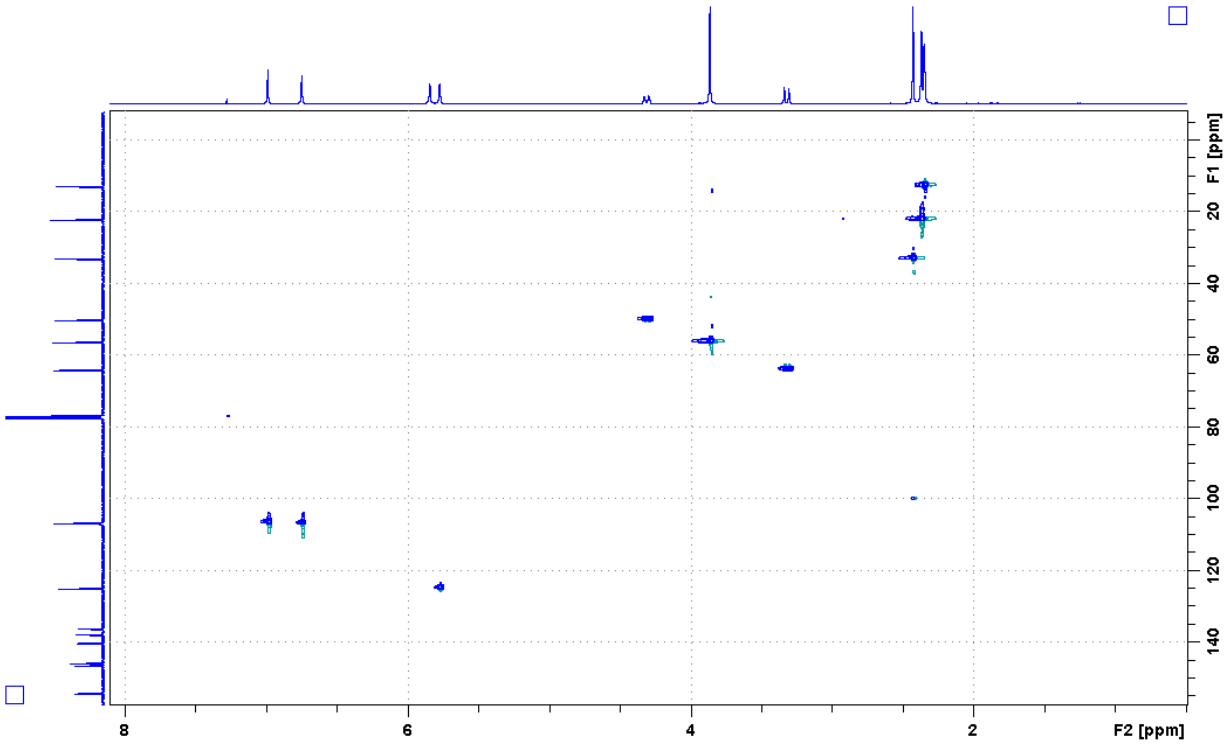
13CNMR:



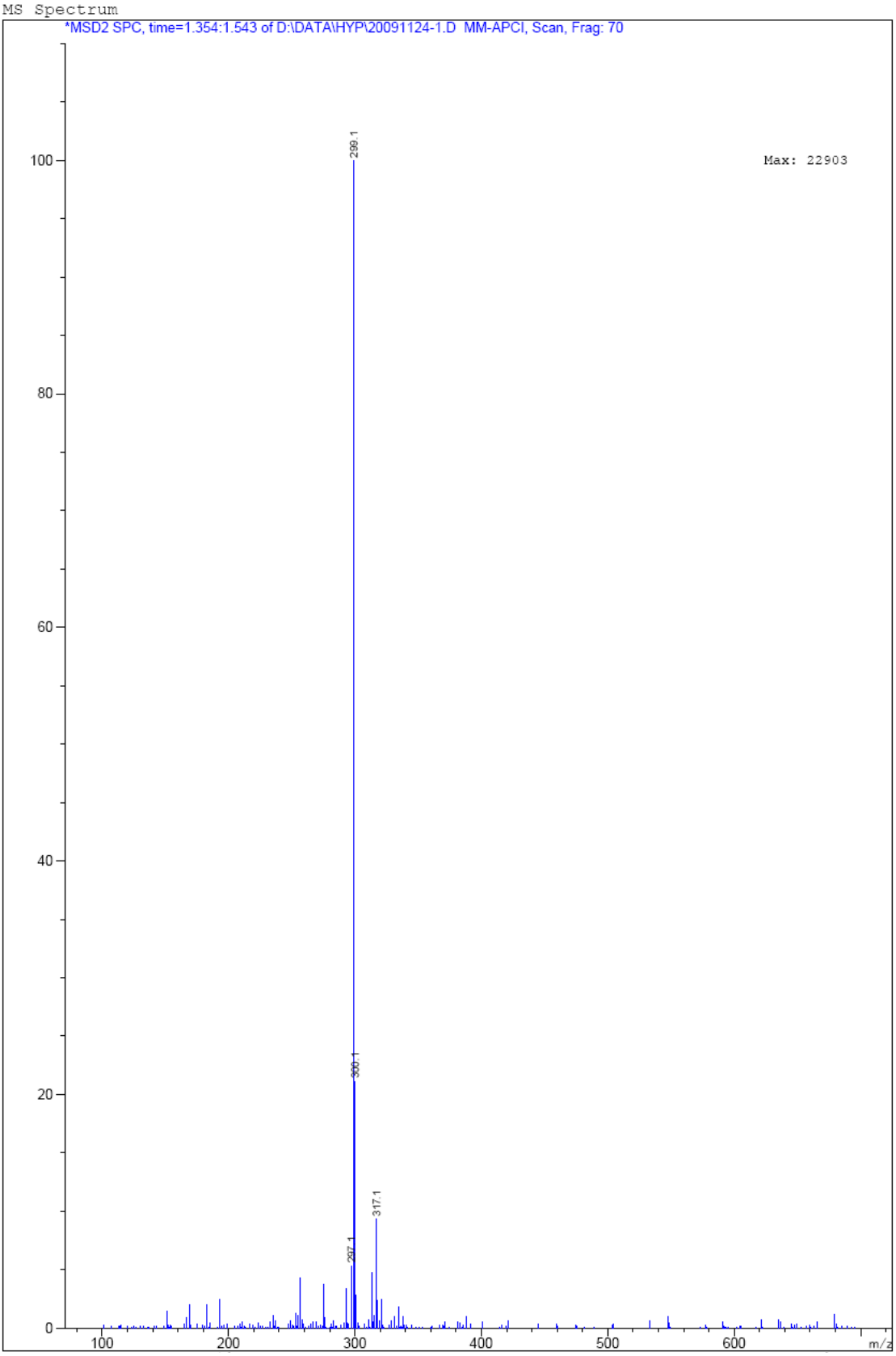
COSY:



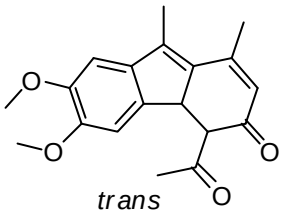
HSQC:



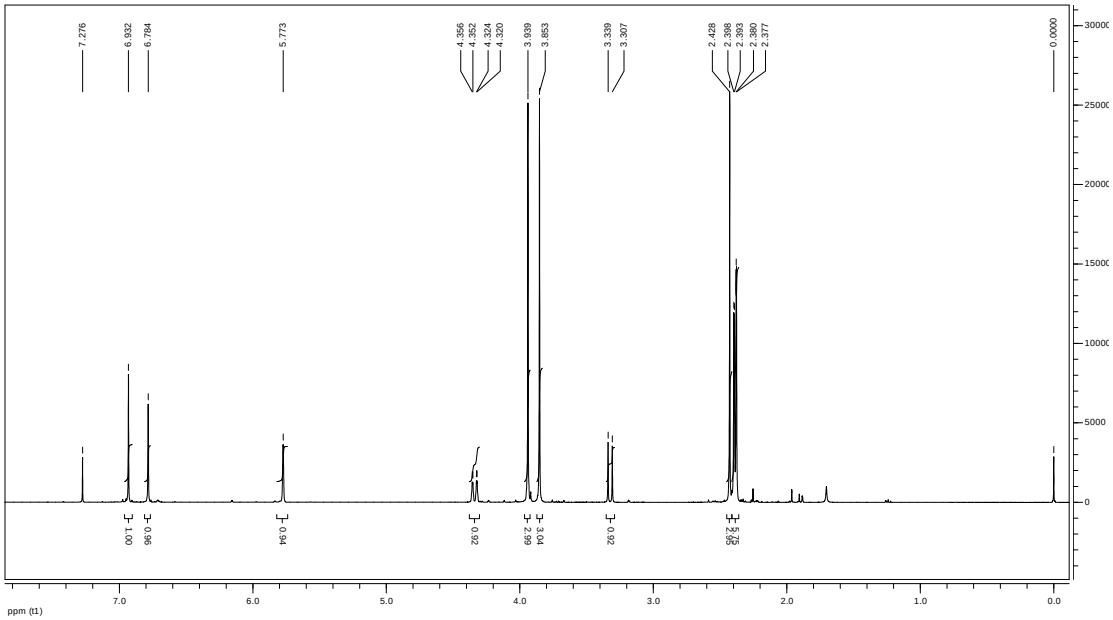
MS:


MS Spectrum
*MSD2 SPC, time=1.354:1.543 of D:\DATA\HYP\20091124-1.D MM-APCI, Scan, Frag: 70
Max: 22903
299.1
300.1
317.1
282.1
100
80
60
40
20
0
100
200
300
400
500
600
m/z

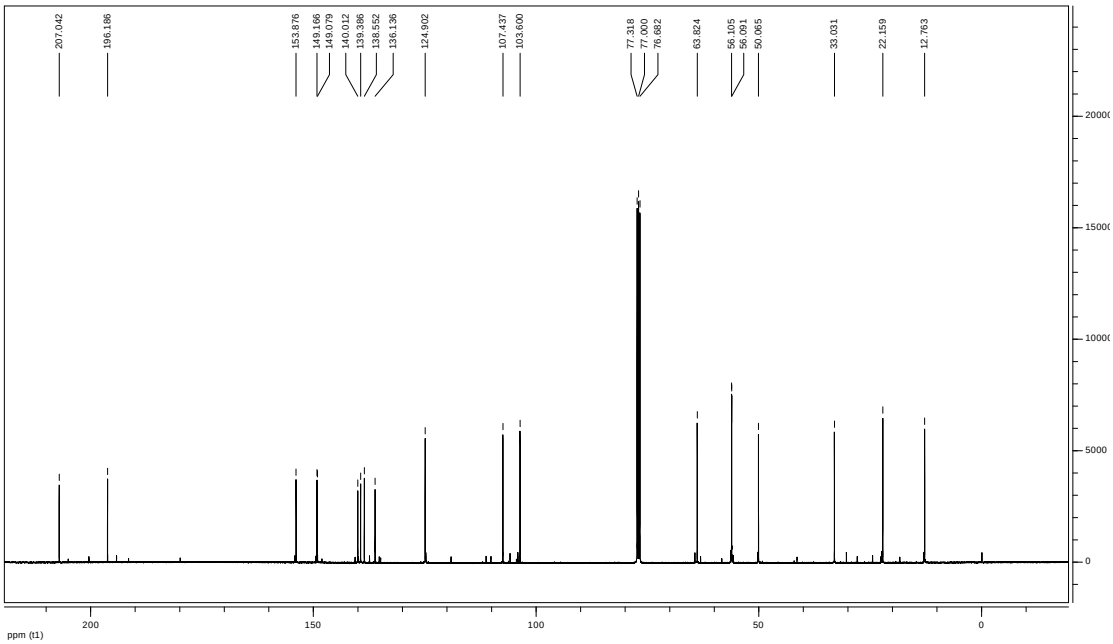
4-acetyl-6,7-dimethoxy-1,9-dimethyl-4,4a-dihydro-3H-fluoren-3-one (2e) m.p. 159.2~161.4 °C; ^{1}H NMR (400 MHz,*CDCl*$_3$) δ ppm 6.93 (s, 1H), 6.78 (s, 1H), 5.77 (s, 1H), 4.34 (dd, *J* = 12.77, 1.54 Hz, 1H), 3.94 (s, 3H), 3.85 (s, 3H), 3.32 (d, *J* = 12.79 Hz, 1H), 2.43 (s, 3H), 2.40 (d, *J* = 1.93 Hz, 3H), 2.38 (d, *J* = 1.09 Hz, 3H); ^{13}C NMR: 207.0, 196.2, 153.9, 149.2, 149.1, 140.0, 139.4, 138.5, 136.1, 124.9, 107.4, 103.6, 63.8, 56.1, 50.1, 33.0, 22.1, 12.8; MS (APCI) $[M+1]^+$: 313.2; EA, calcd. for $C_{19}H_{20}O_4$: C% 73.06, H% 6.45; found: C% 73.19, H% 6.593.



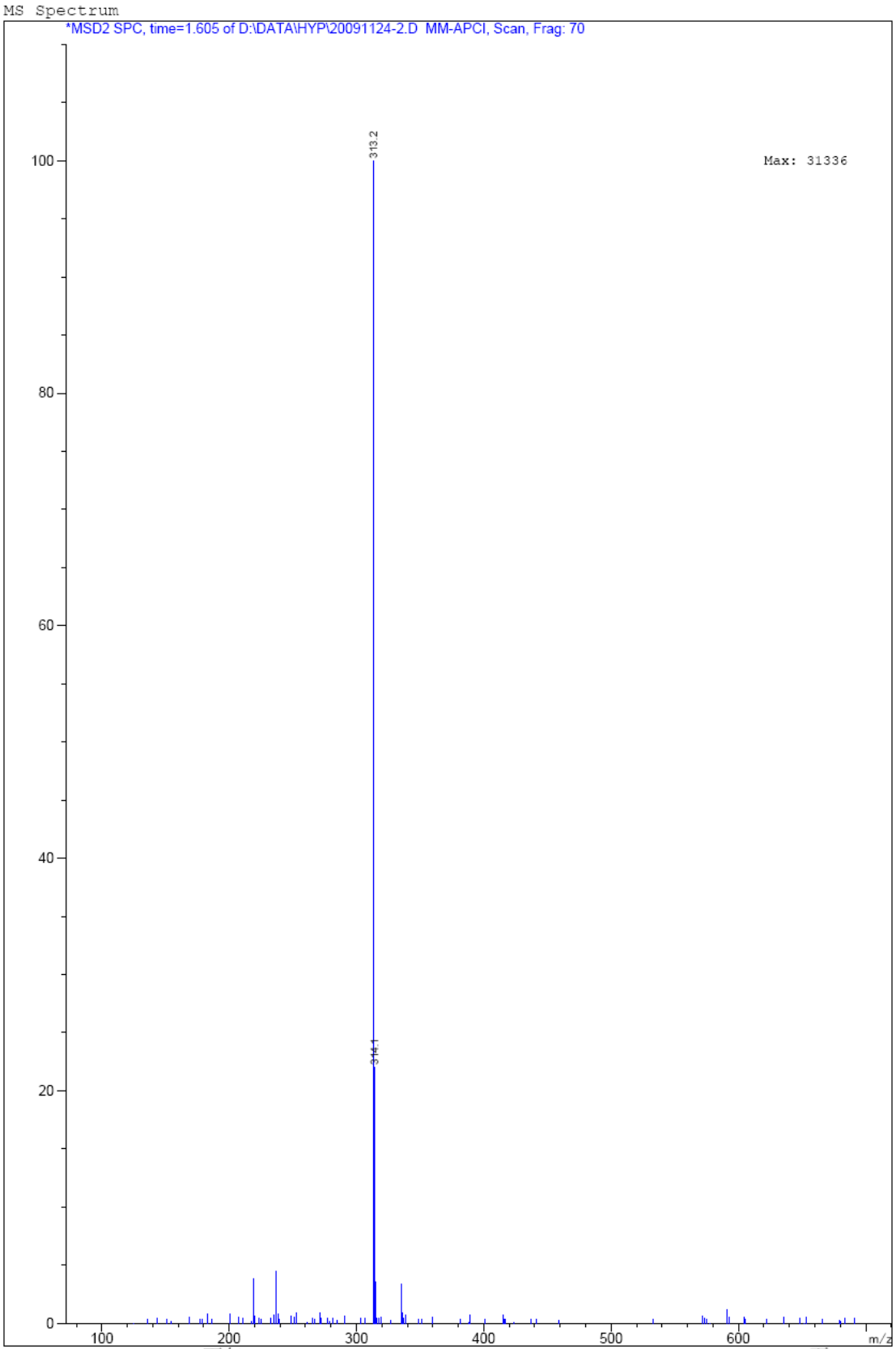
1HNMR:



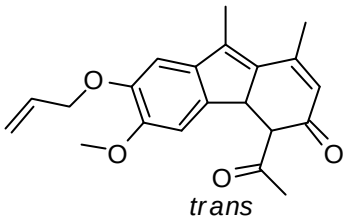
13CNMR:



MS:

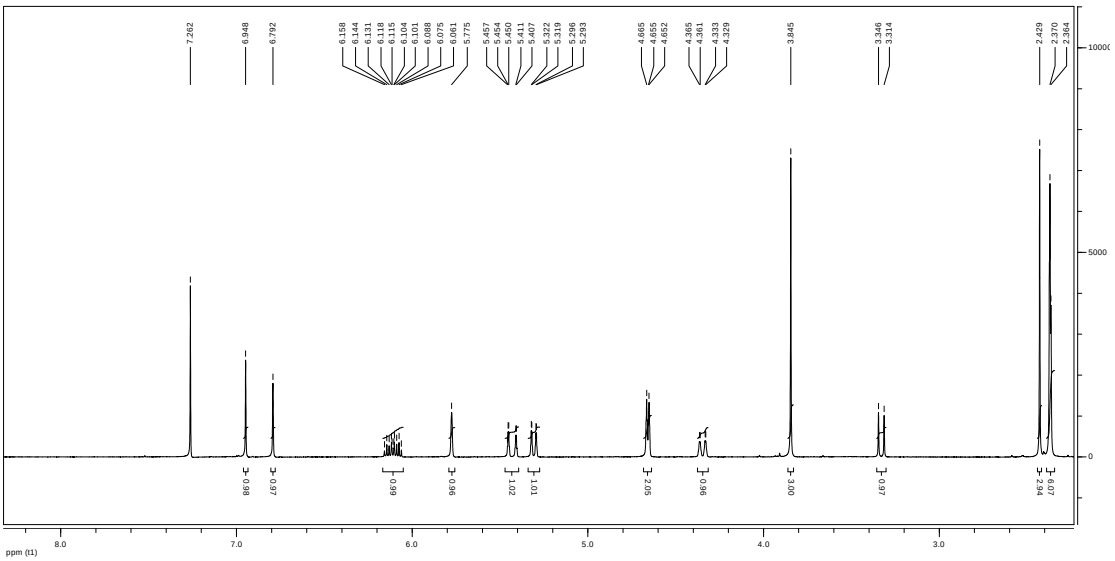

MS Spectrum
*MSD2 SPC, time=1.605 of D:\DATA\HYP\20091124-2.D MM-APCI, Scan, Frag: 70
Max: 31336
313.2
314.1
100
80
60
40
20
0
100
200
300
400
500
600
m/z

4-acetyl-7-(allyloxy)-6-methoxy-1,9-dimethyl-4,4a-dihydro-3H-fluoren-3-one (2f) m.p. 131.8~133.2 °C; ^{1}H NMR (400 MHz, *CDCl$_3$*) δppm 6.95 (s, 1H), 6.79 (s, 1H), 6.11 (tdd, *J* = 17.13, 10.67, 5.43, 5.43 Hz, 1H), 5.78 (s, 1H), 5.43 (dd, *J* = 17.26, 1.50 Hz, 1H), 5.31 (dd, *J* = 10.48, 1.32 Hz, 1H), 4.66 (d, *J* = 5.43 Hz, 2H), 4.35 (dd, *J* = 12.79, 1.44 Hz, 1H), 3.85 (s, 3H), 3.33 (d, *J* = 12.79 Hz, 1H), 2.43 (s, 3H), 2.37 (m, , 6H); ^{13}C NMR: 207.0, 196.2, 153.9, 149.7, 148.1, 140.0, 139.4, 139.0, 136.1, 133.2, 124.9, 118.0, 107.9, 106.1, 70.7, 63.8, 56.2, 50.1, 33.0, 22.2, 12.7; MS (APCI) $[M+1]^+$: 339.1; EA, calcd. for $C_{21}H_{22}O_4$: C% 74.54, H% 6.55; found: C% 74.40, H% 6.436.

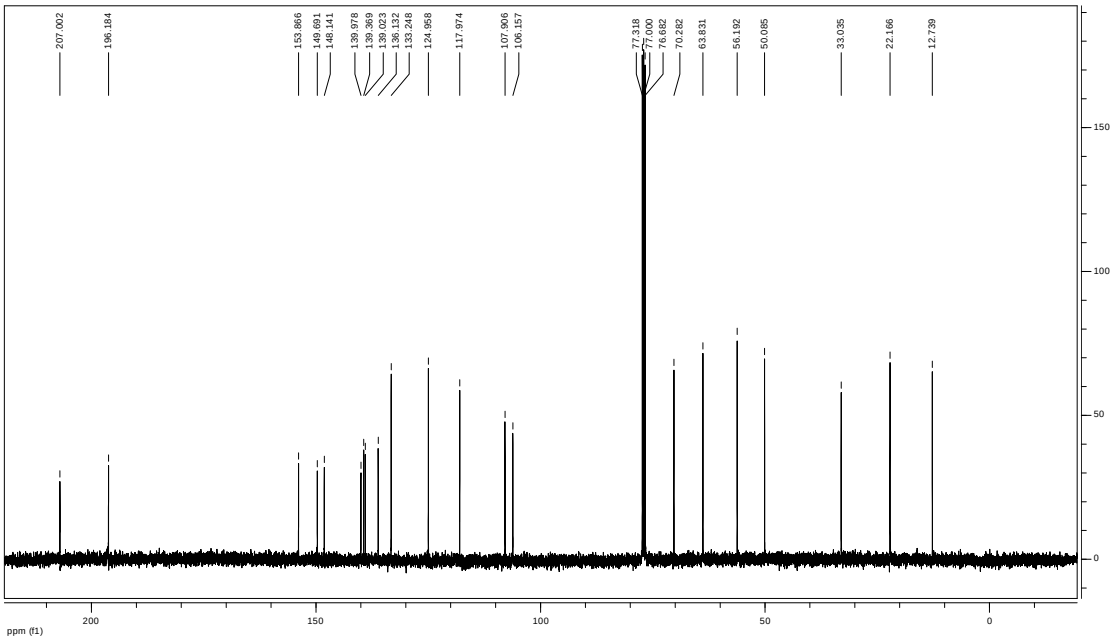


trans

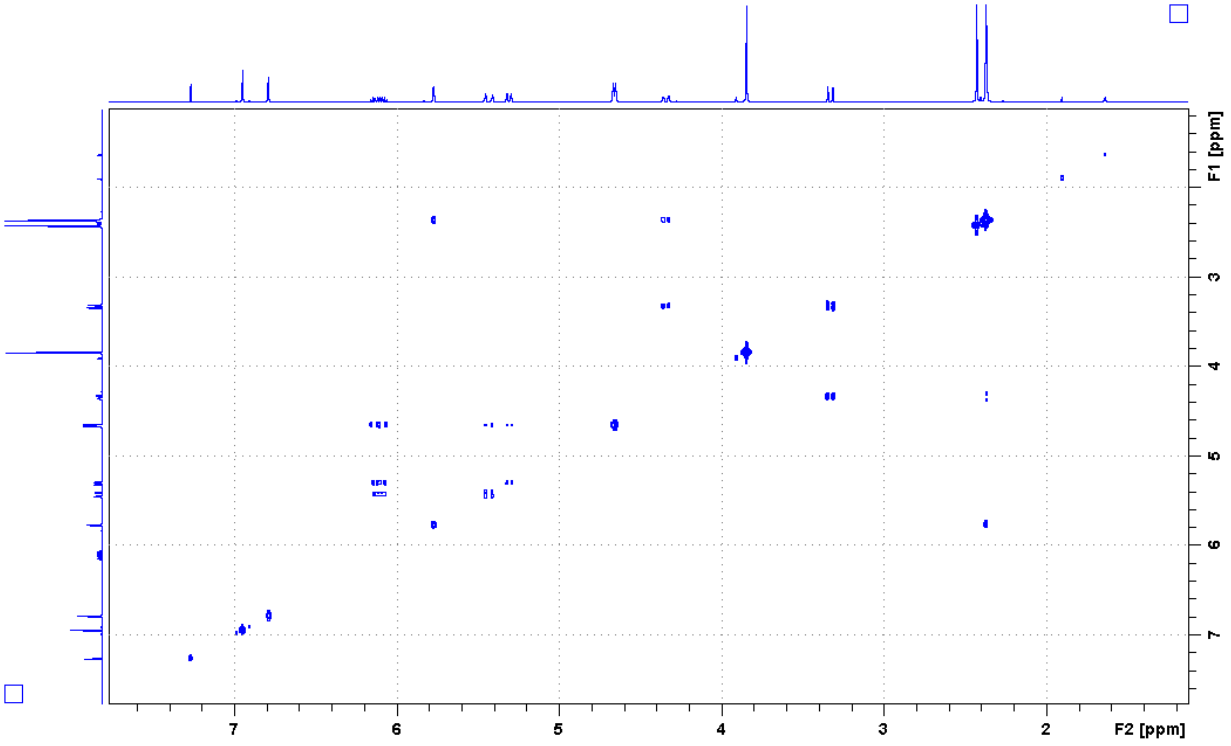
1HNMR:



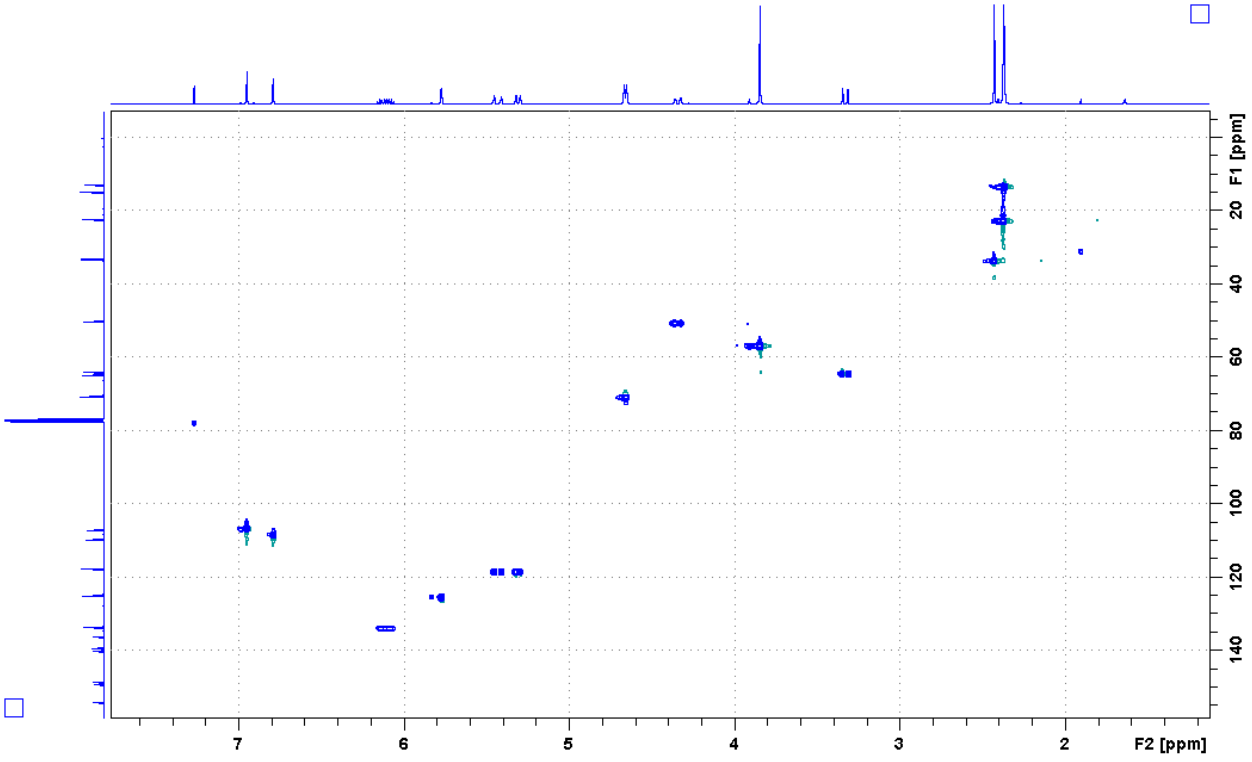
13CNMR:



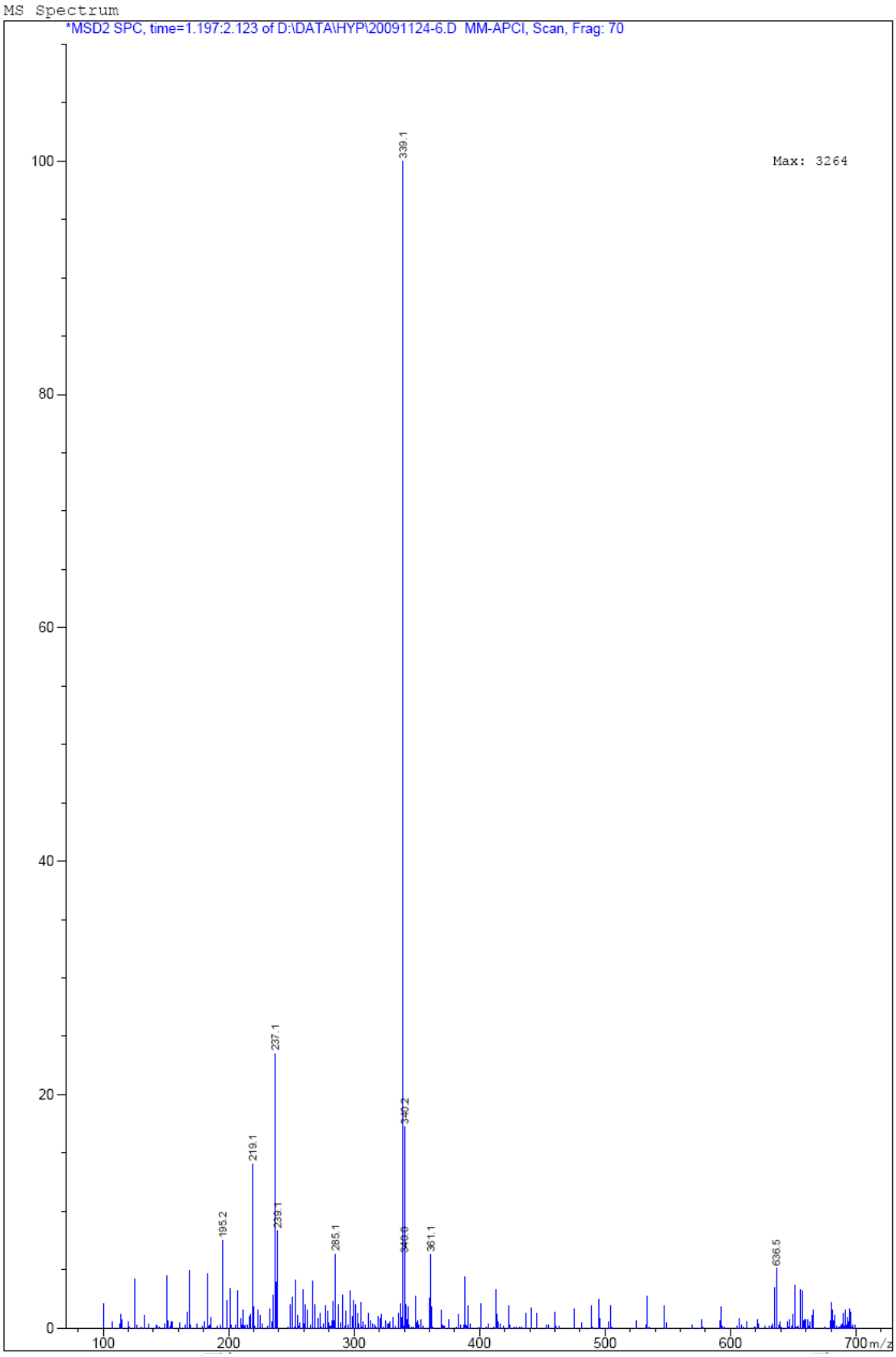
COSY:


F1 [ppm]
3
4
5
6
7
F2 [ppm]
7
6
5
4
3
2

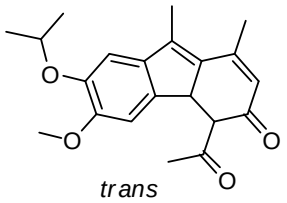
HSQC:


F1 [ppm]
20
40
60
80
100
120
140
F2 [ppm]
7
6
5
4
3
2

MS:

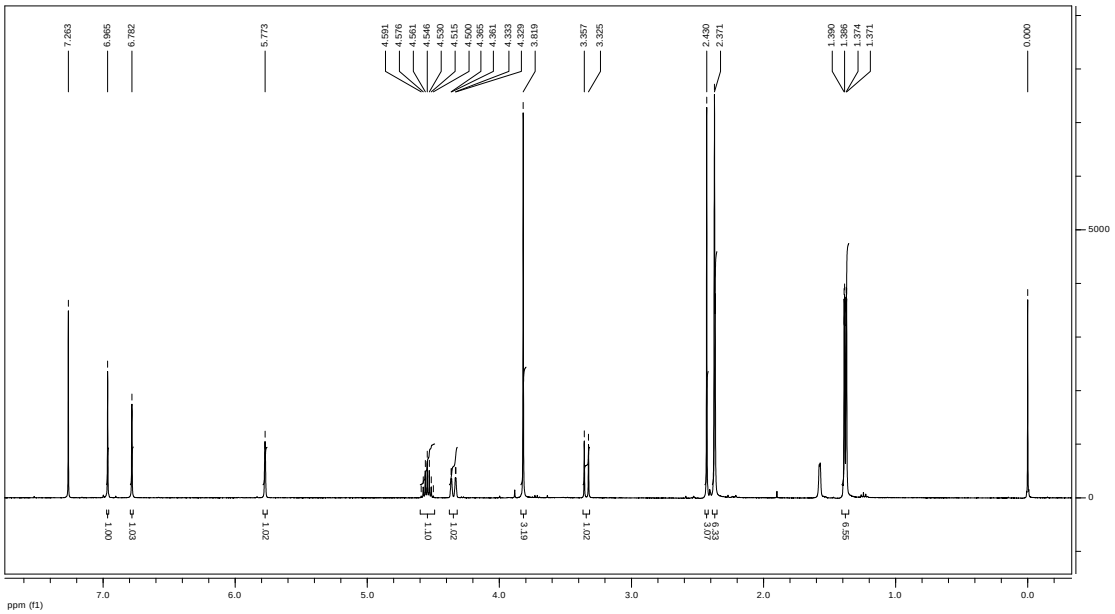

MS Spectrum
*MSD2 SPC, time=1.197:2.123 of D:\DATA\HYP\20091124-6.D MM-APCI, Scan, Frag: 70
Max: 3264
339.1
340.2
237.1
219.1
239.1
195.2
285.1
341.1
636.5
100
80
60
40
20
0
100
200
300
400
500
600
700 m/z

4-acetyl-7-isopropoxy-6-methoxy-1,9-dimethyl-4,4a-dihydro-3H-fluoren-3-one (2g) m.p. 138.9~140.8 °C; ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 6.96 (s, 1H), 6.78 (s, 1H), 5.77 (s, 1H), 4.55 (sept., J = 6.13, 6.13, 6.13, 6.13, 6.09, 6.09 Hz, 1H), 4.35 (dd, J = 12.80, 1.59 Hz, 1H), 3.82 (s, 3H), 3.34 (d, J = 12.81 Hz, 1H), 2.43 (s, 3H), 2.37 (m, 6H), 1.38 (dd, J = 6.08, 1.42 Hz, 6H); ^{13}C NMR: 207.0, 196.2, 153.9, 150.8, 147.3, 140.1, 139.4, 139.2, 135.0, 124.9, 109.0, 108.2, 72.1, 63.8, 56.2, 50.1, 33.0, 22.2, 22.1, 12.8; MS (APCI) $[M+1]^{+}$: 431.1; EA, calcd. for $C_{21}H_{24}O_4$: C% 74.09, H% 7.11; found: C% 73.85, H% 7.107.

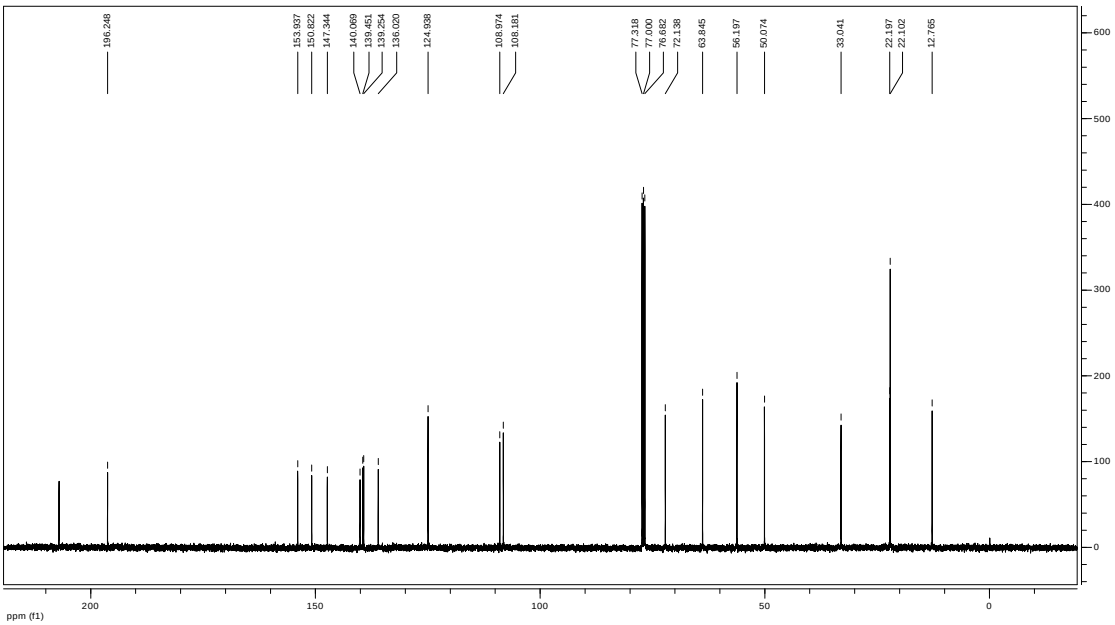


trans

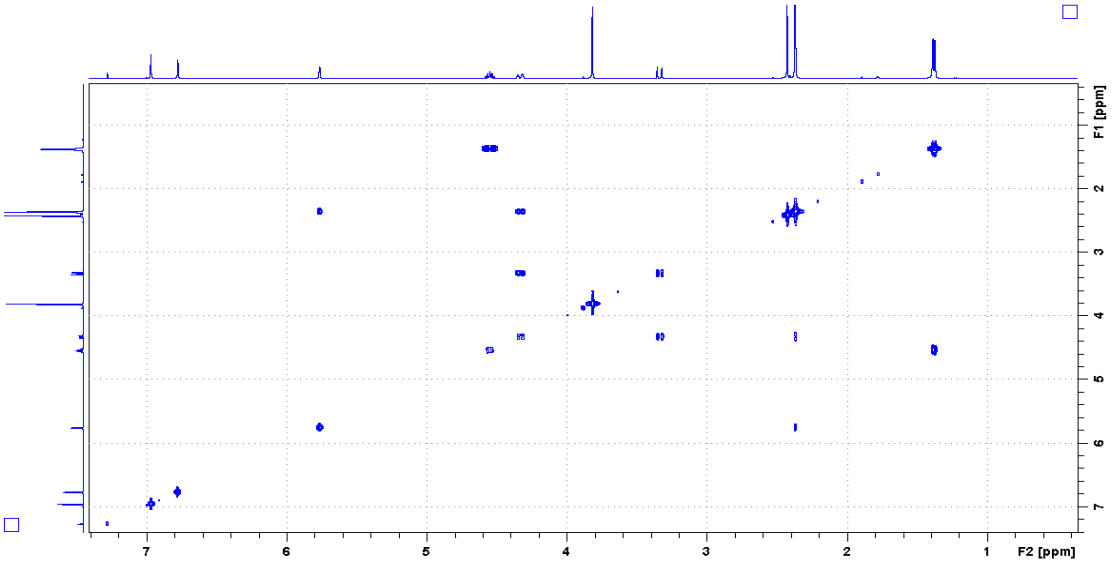
1HNMR:



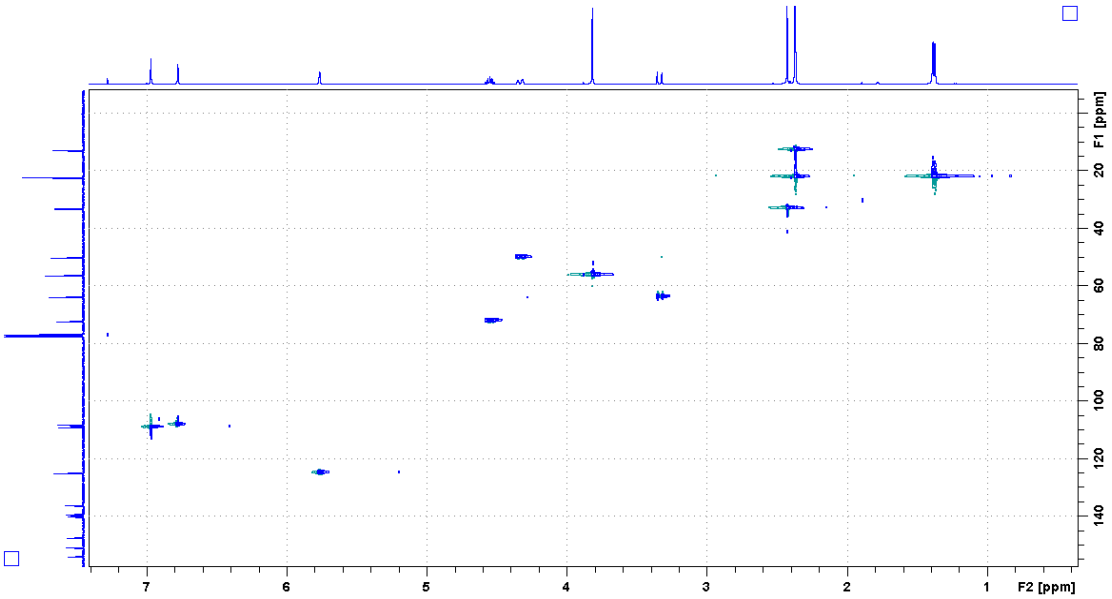
13CNMR:



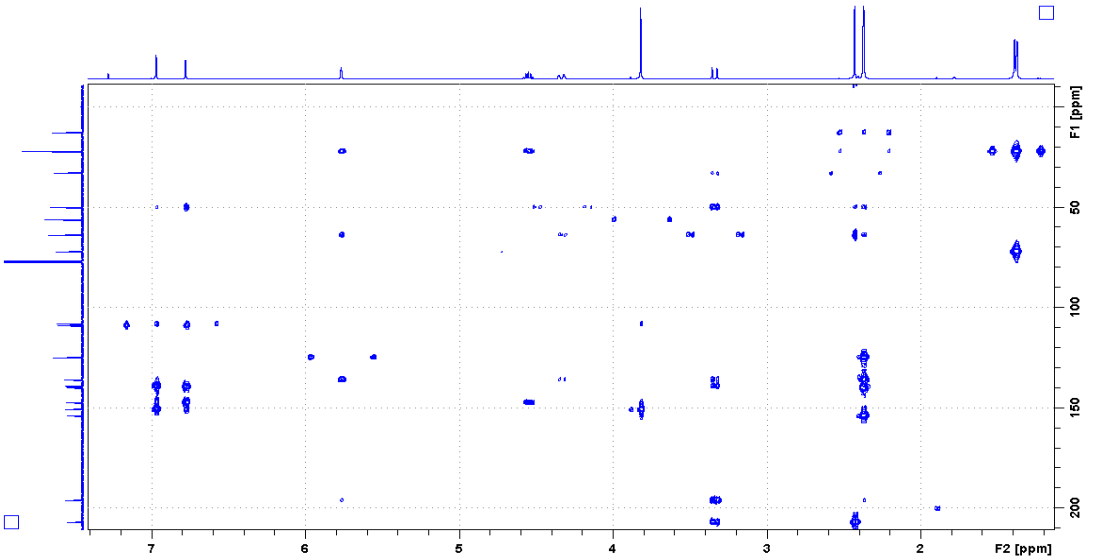
H-H COSY:



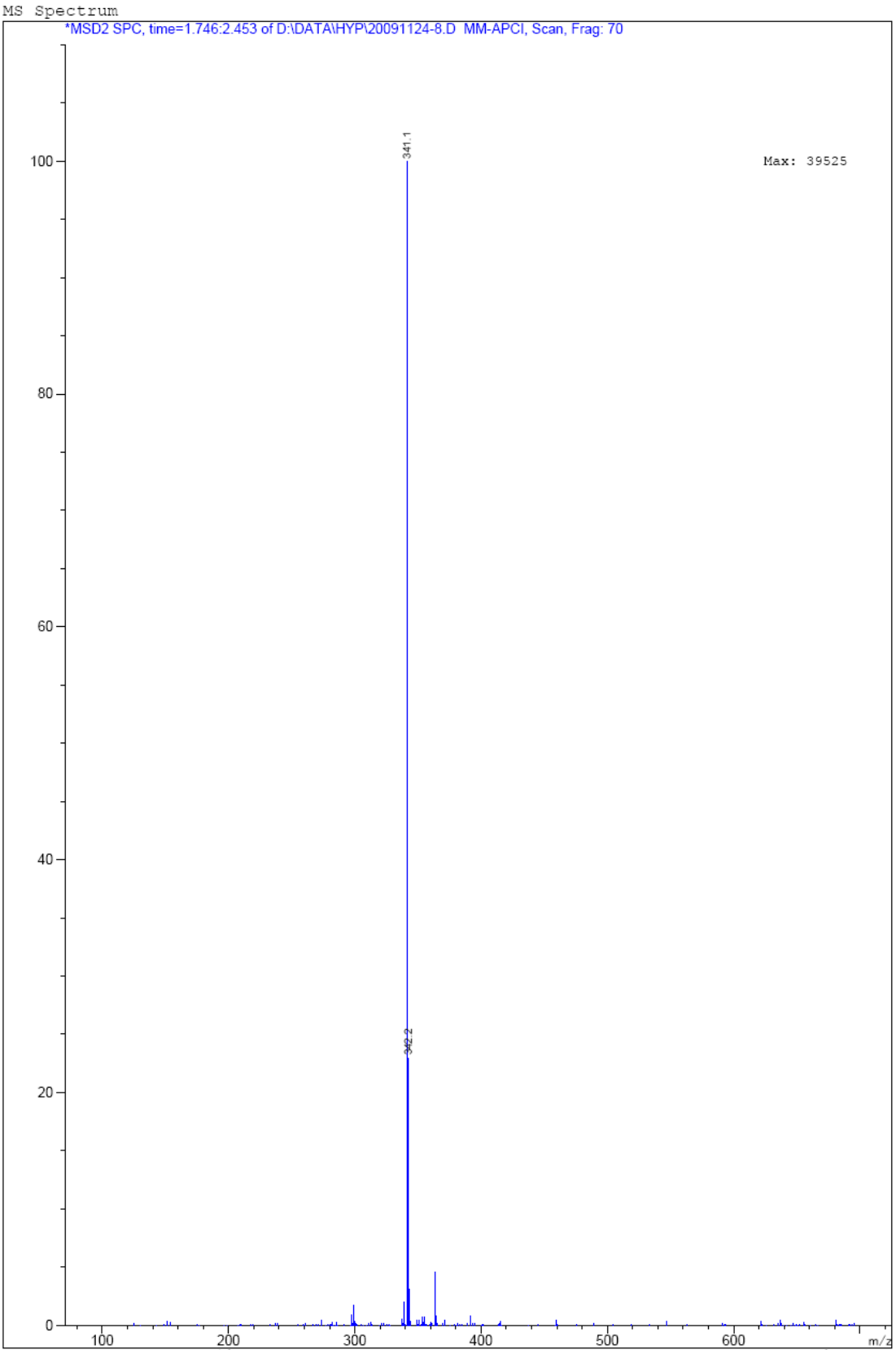
HSQC:



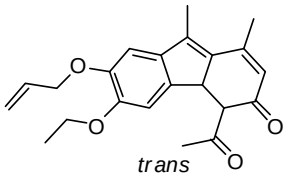
HMBC:



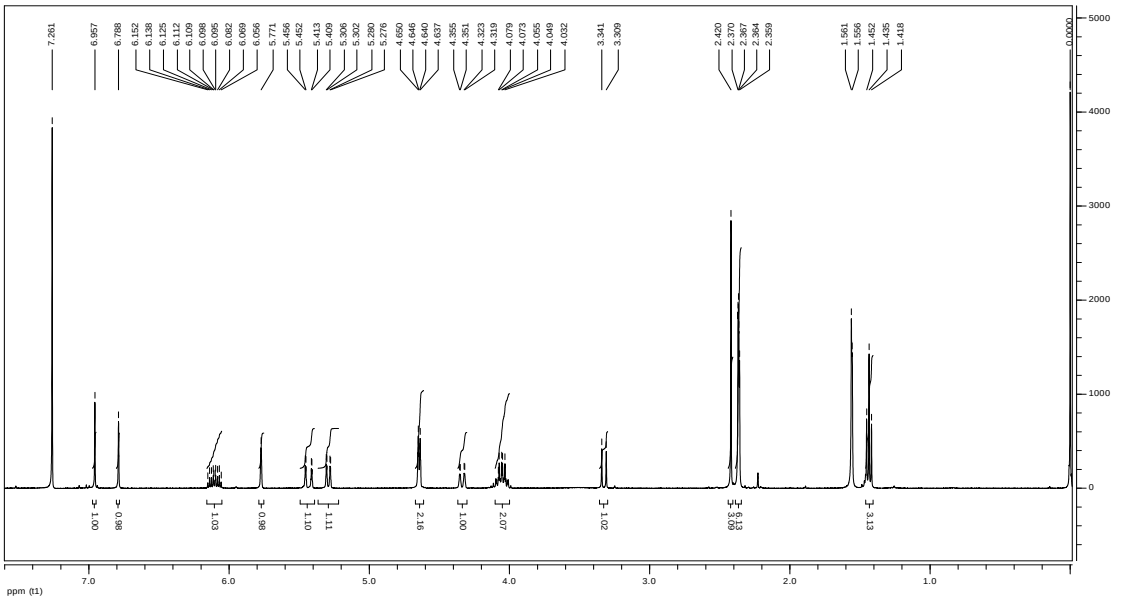
MS:


MS Spectrum
*MSD2 SPC, time=1.746:2.453 of D:\DATA\HYP\20091124-8.D MM-APCI, Scan, Frag: 70
Max: 39525
341.1
342.2
100
80
60
40
20
0
100
200
300
400
500
600
m/z

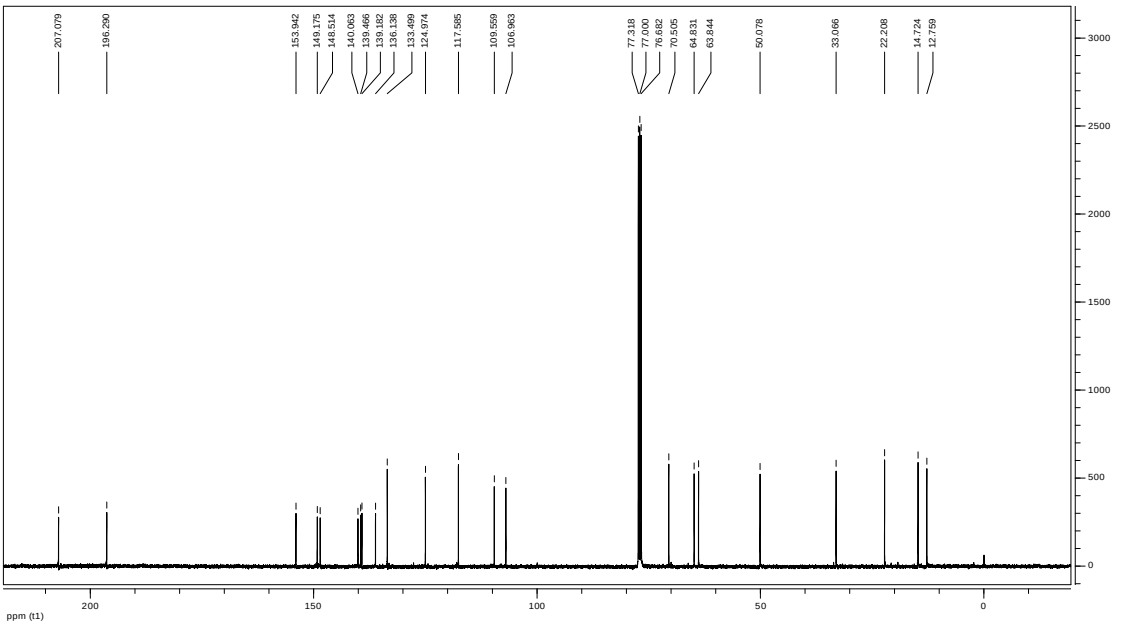
4-acetyl-7-(allyloxy)-6-ethoxy-1,9-dimethyl-4,4a-dihydro-3H-fluoren-3-one (2h) m.p. 126.9~130.4 ^{o}C; ^{1}H NMR (400 MHz, *CDCl$_3$*) δppm 6.96 (s, 1H), 6.79 (s, 1H), 6.10 (tdd, *J* = 17.08, 10.58, 5.33, 5.33 Hz, 1H), 5.77 (s, 1H), 5.43 (dd, *J* = 17.27, 1.55 Hz, 1H), 5.29 (dd, *J* = 10.51, 1.38 Hz, 1H), 4.64 (td, *J* = 5.15, 1.28, 1.28 Hz, 2H), 4.34 (dd, *J* = 12.80, 1.71 Hz, 1H), 4.05 (dddd, *J* = 16.54, 9.55, 7.02, 2.53 Hz, 2H), 3.33 (d, *J* = 12.80 Hz, 1H), 2.42 (s, 3H), 2.36 (m, 6H), 1.43 (t, *J* = 6.98, 6.98 Hz, 3H); ^{13}C NMR: 207.1, 196.3, 153.9, 149.2, 148.5, 140.0, 139.5, 139.2, 136.1, 133.5, 125.0, 117.6, 109.7, 107.0, 70.5, 64.8, 63.8, 50.1, 33.1, 22.2, 14.7, 12.8; MS (APCI) $[M+1]^{+}$: 353.1, EA, calcd. for $C_{22}H_{24}O_4 \cdot 1/3H_2O$: C% 73.72, H% 6.94; found: C% 73.47, H% 6.785.



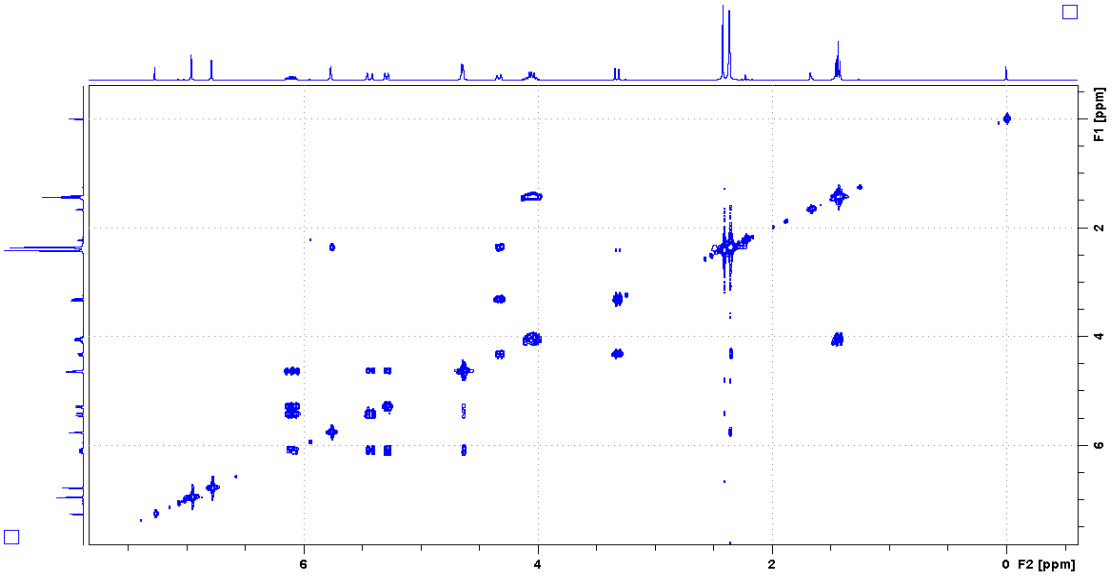
1HNMR:



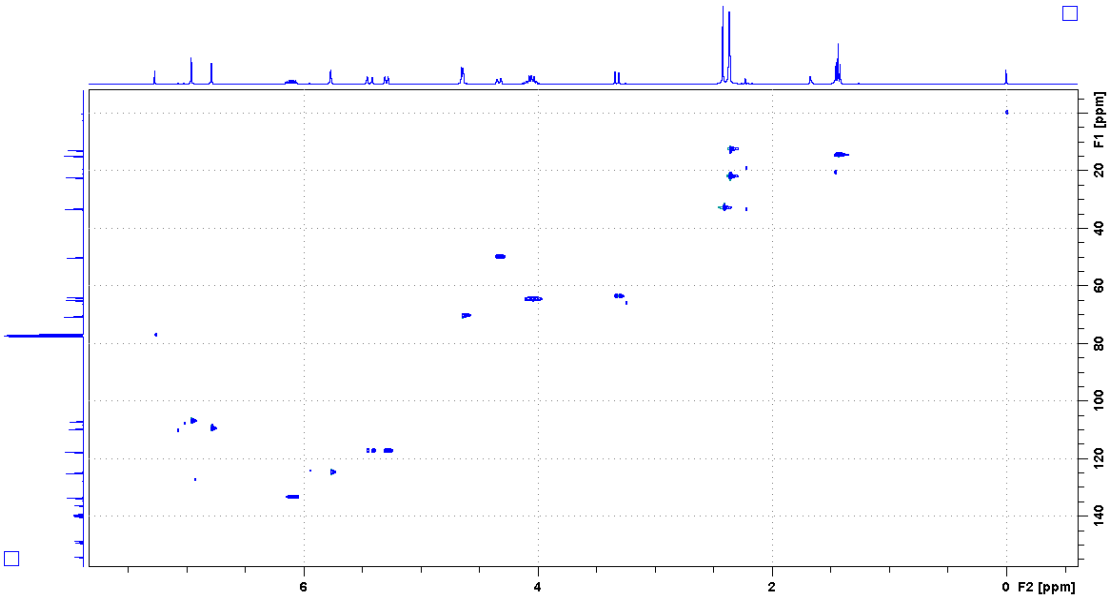
13CNMR:



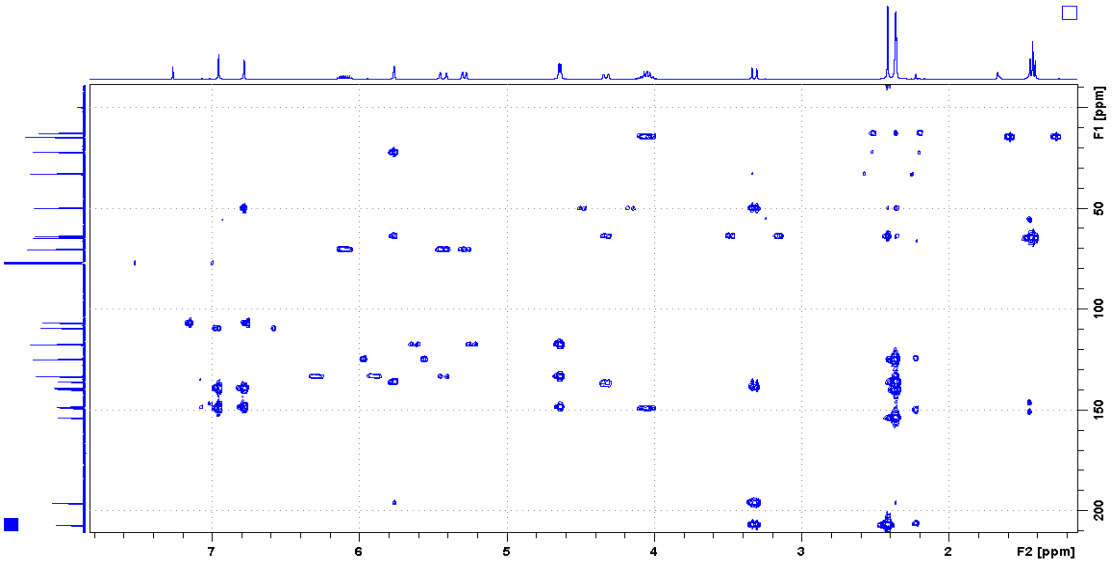
COSY:



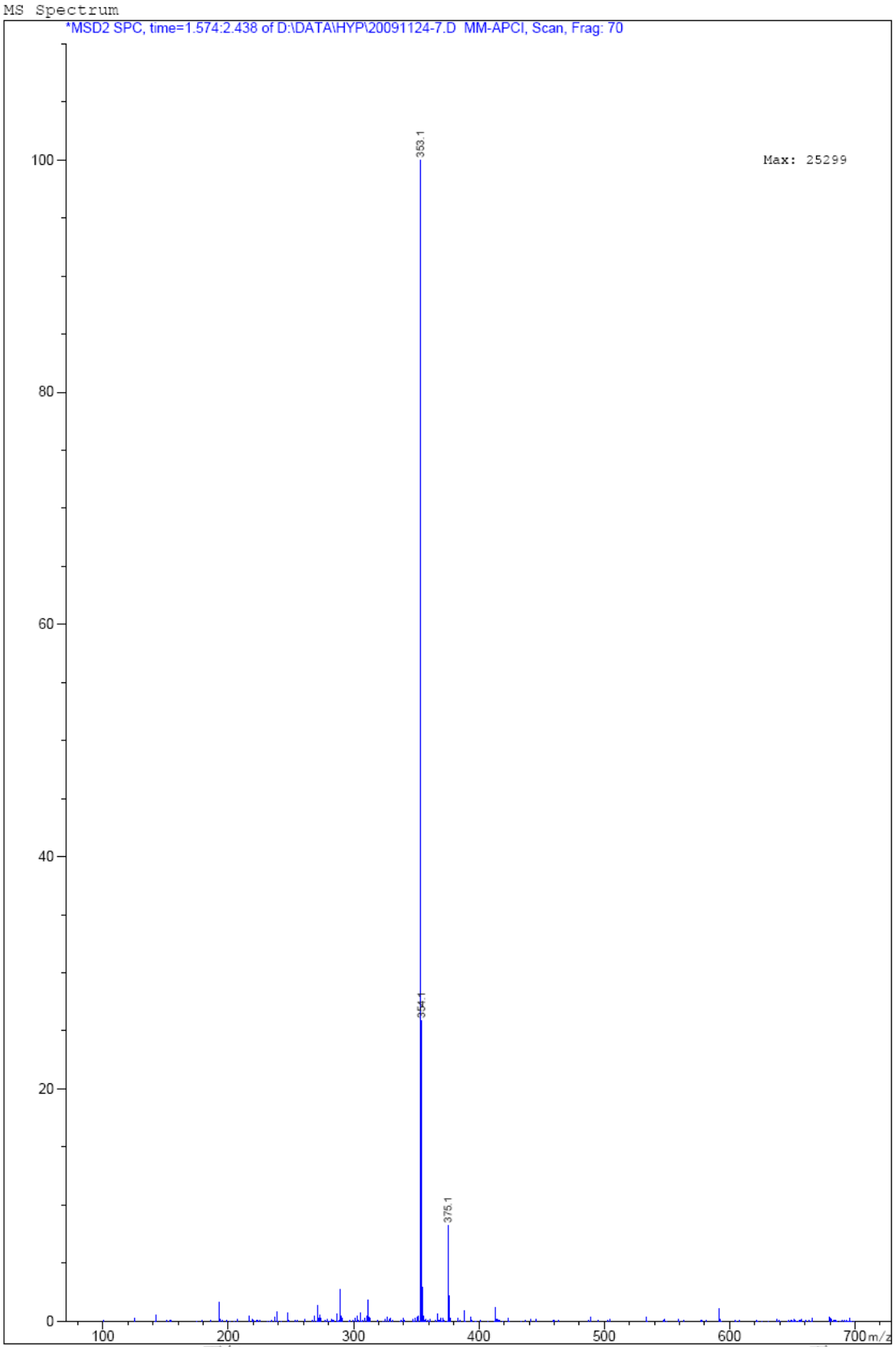
HSQC:



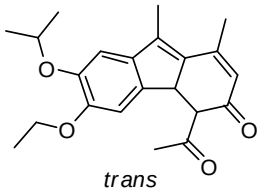
HMBC:



MS:

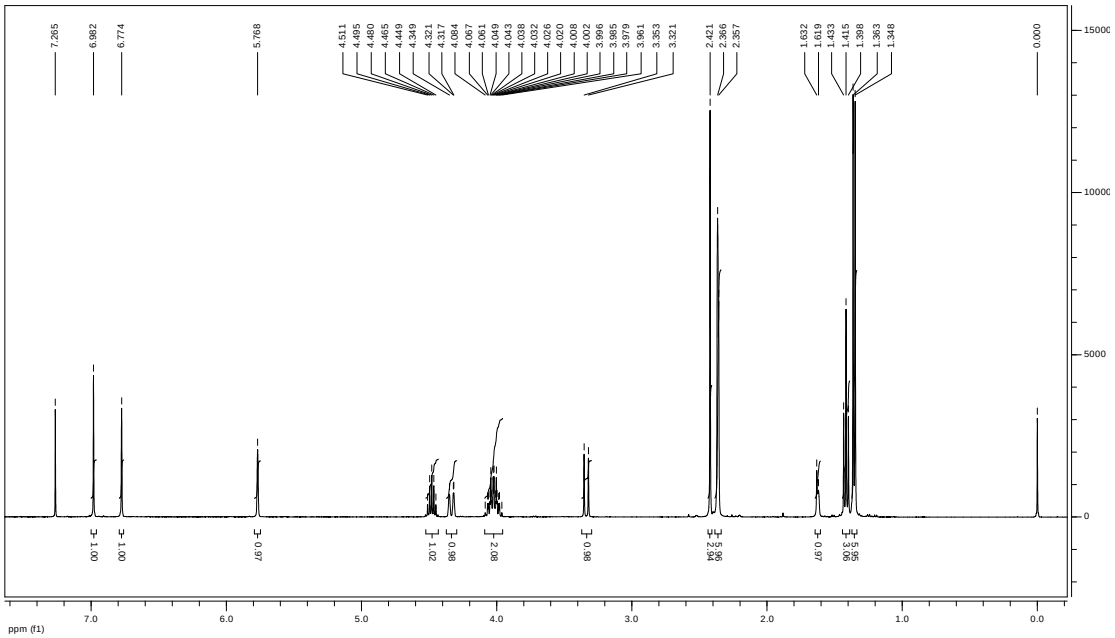

MS Spectrum
*MSD2 SPC, time=1.574:2.438 of D:\DATA\HYP\20091124-7.D MM-APCI, Scan, Frag: 70
Max: 25299
353.1
354.1
375.1
100
80
60
40
20
0
100
200
300
400
500
600
700 m/z

4-acetyl-6-ethoxy-7-isopropoxy-1,9-dimethyl-4,4a-dihydro-3H-fluoren-3-one (2i) m.p. 101.0~103.7 °C; ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 6.98 (s, 1H), 6.77 (s, 1H), 5.77 (s, 1H), 4.48 (sept., *J* = 6.09, 6.09, 6.06, 6.06, 6.06, 6.06 Hz, 1H), 4.33 (dd, *J* = 12.75, 1.55 Hz, 1H), 4.04 (m, 2H), 3.34 (d, *J* = 12.82 Hz, 1H), 2.42 (s, 3H), 2.36 (m, 6H), 1.63 (d, *J* = 4.96 Hz, 1H), 1.42 (t, *J* = 6.97, 6.97 Hz, 3H), 1.36 (d, *J* = 6.11 Hz, 6H); ^{13}C NMR: 207.0, 196.3, 153.9, 150.6, 147.7, 140.1, 139.7, 139.6, 136.0, 124.9, 110.7, 109.9, 72.9, 64.8, 63.8, 50.0, 33.0, 22.2, 14.7, 12.7; MS (APCI) $[M+1]^+$: 355.2; EA, calcd. for $C_{22}H_{26}O_4$: C% 74.55, H% 7.39; found: C% 74.43, H% 7.360.

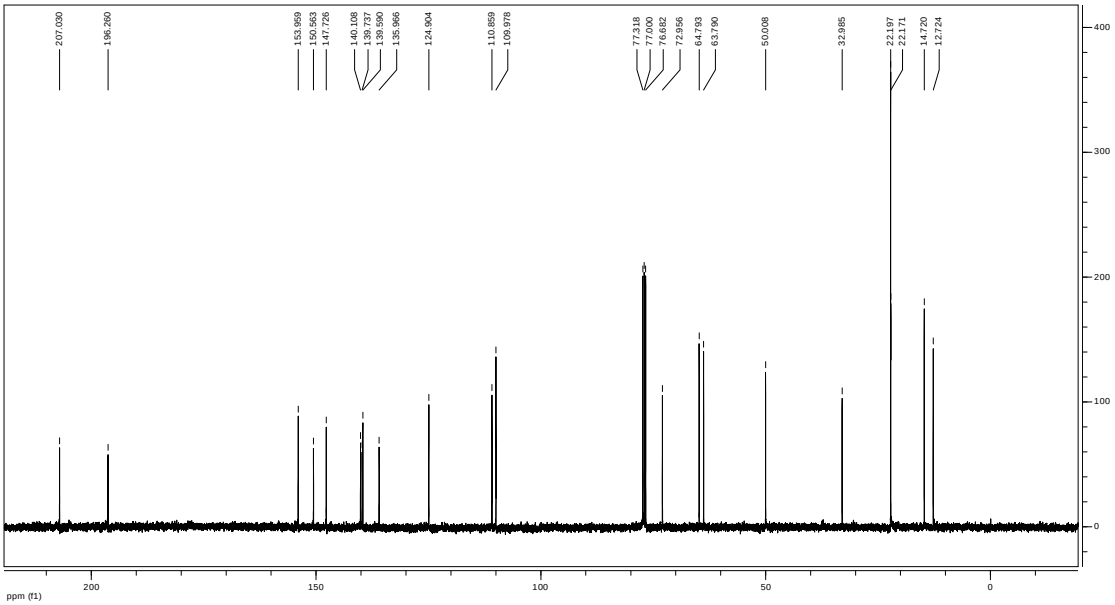


trans

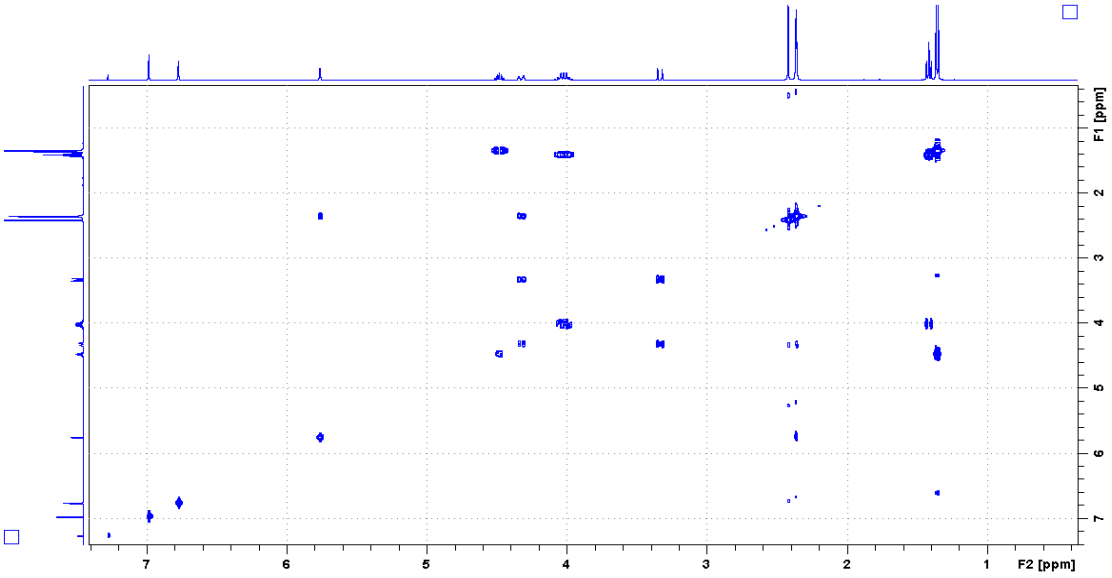
1HNMR:



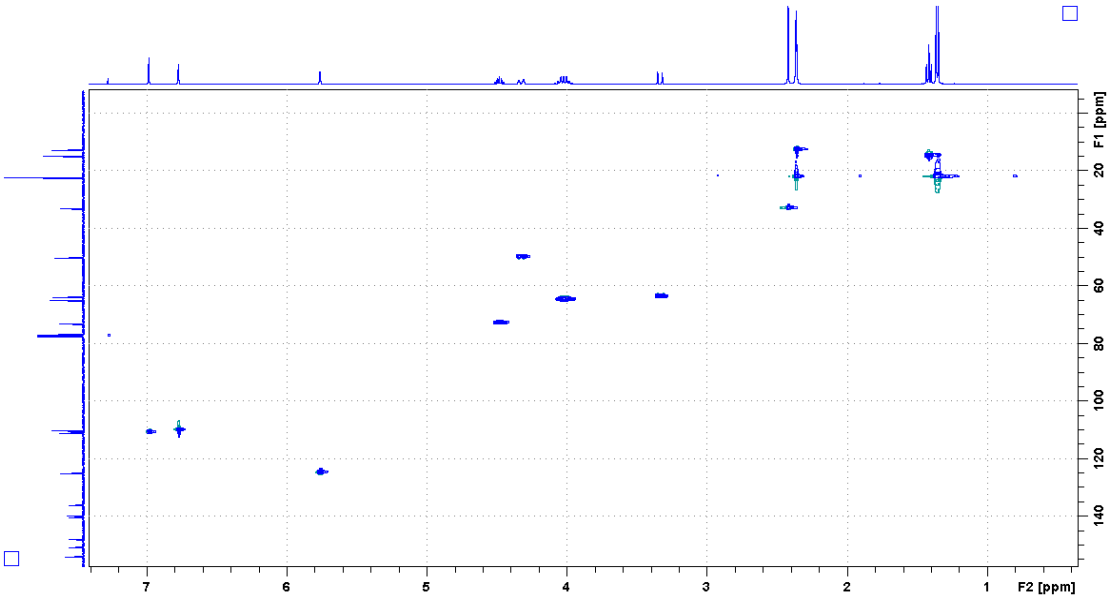
13CNMR:



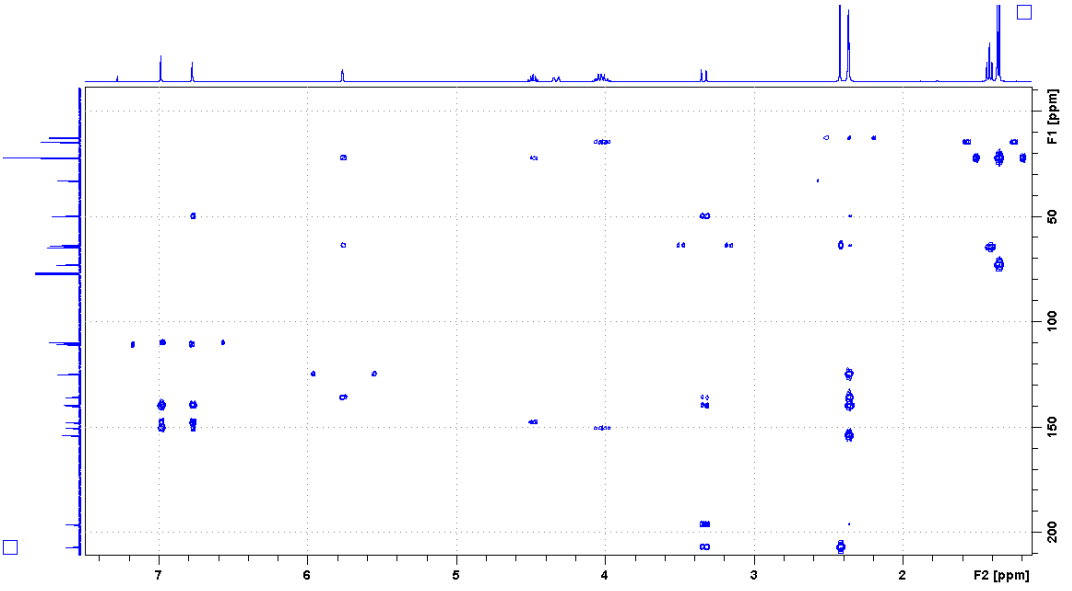
Cosy:



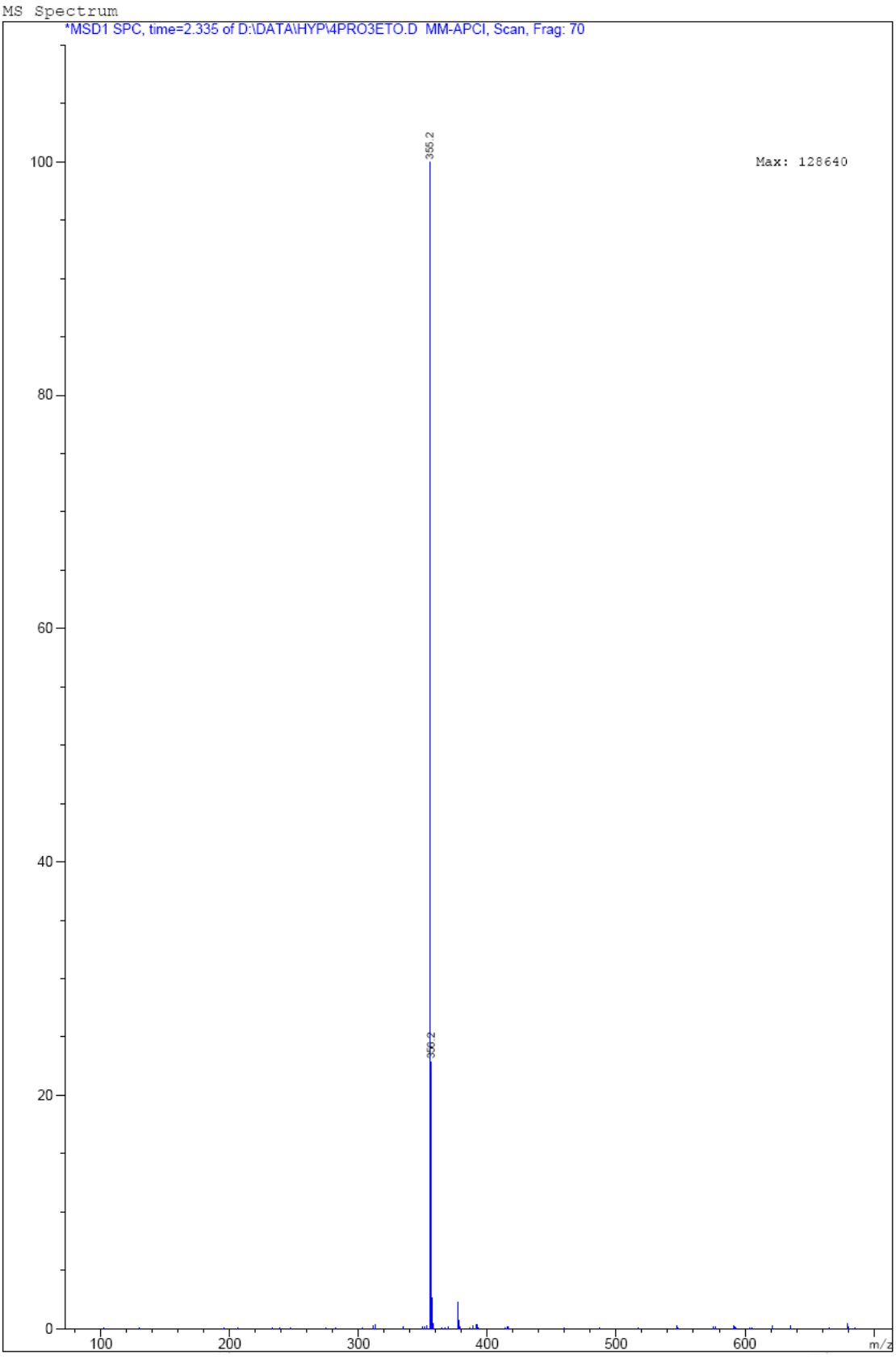
HSQC:



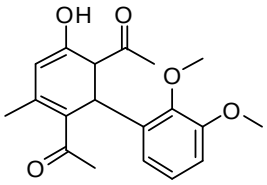
HMBC:



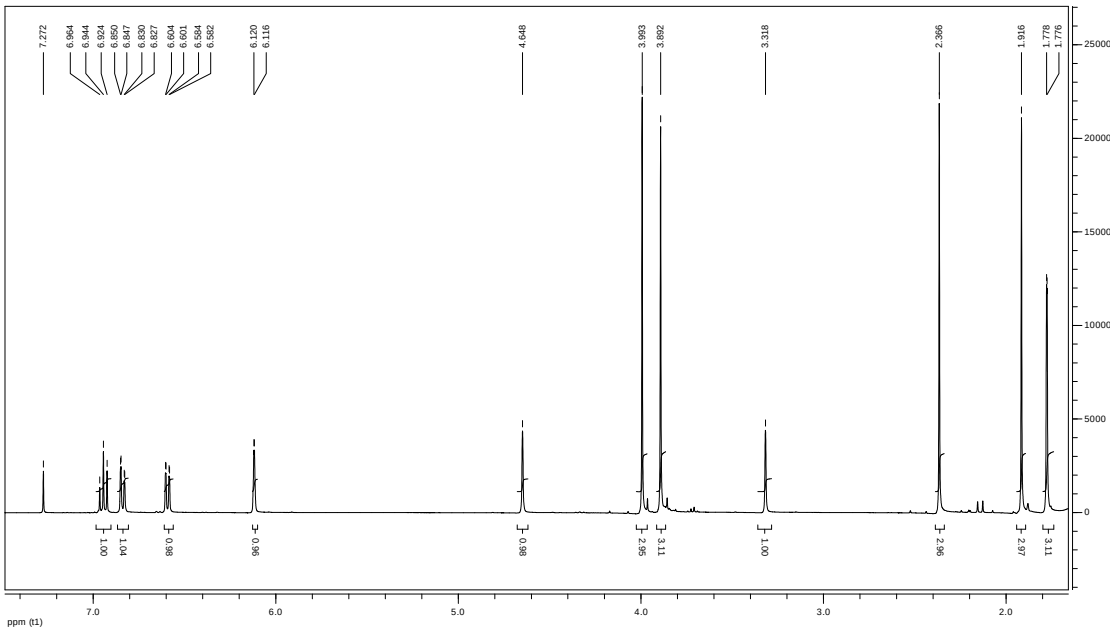
MS:


MS Spectrum
*MSD1 SPC, time=2.335 of D:\DATA\HYP\4PRO3ETO.D MM-APCI, Scan, Frag: 70
Max: 128640
355.2
356.2
100
80
60
40
20
0
100
200
300
400
500
600
m/z

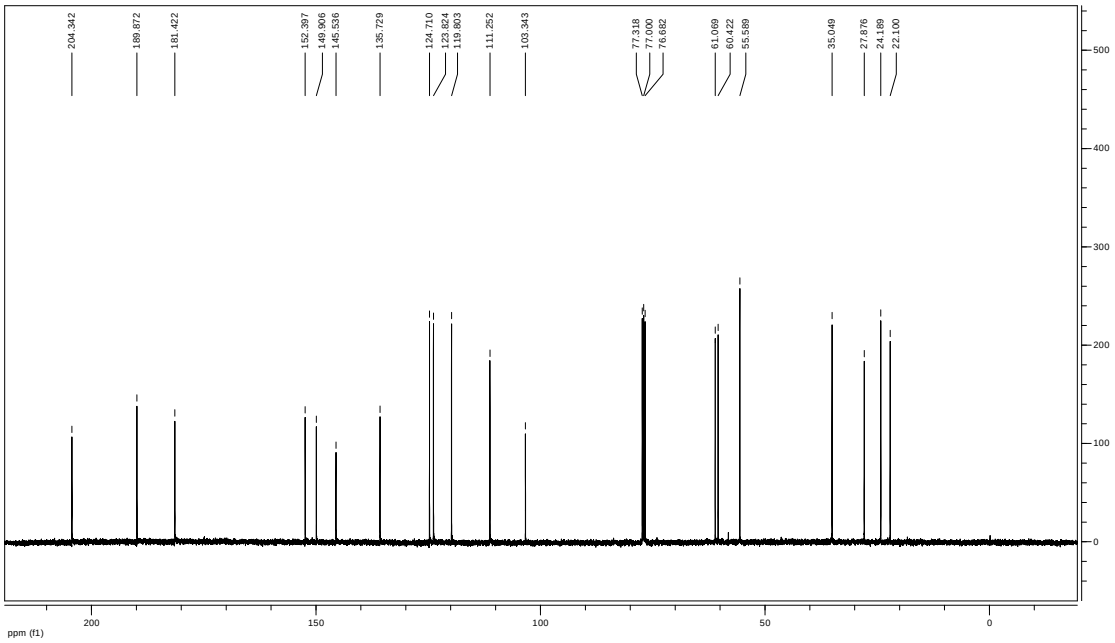
1,1'-(3-hydroxy-2',3'-dimethoxy-5-methyl-1,2-dihydro-[1,1'-biphenyl]-2,6-diyl)diethanone (2b')
m.p. 97~98.9°C; ^{1}H NMR (400 MHz, *CDCl$_3$*) δ ppm 6.94 (t, *J* = 8.00, 8.00 Hz, 1H), 6.84 (dd, *J* = 8.14, 1.07 Hz, 1H), 6.59 (dd, *J* = 7.77, 1.05 Hz, 1H), 6.12 (d, *J* = 1.23 Hz, 1H), 4.65 (s, 1H), 3.99 (s, 3H), 3.89 (s, 3H), 3.32 (s, 1H), 2.37 (s, 3H), 1.92 (s, 3H), 1.78 (d, *J* = 1.02 Hz, 3H); ^{13}C NMR: 204.3, 189.9, 181.4, 152.4, 149.9, 145.5, 135.7, 124.7, 123.8, 119.8, 111.2, 103.3, 61.1, 60.4, 55.7, 36.0, 27.9, 24.2, 22.1. MS (APCI) $[M+1]^+$: 331.1, EA, calcd. for $C_{19}H_{22}O_5$: C% 69.07, H% 6.71; found: C% 69.25, H% 6.658.



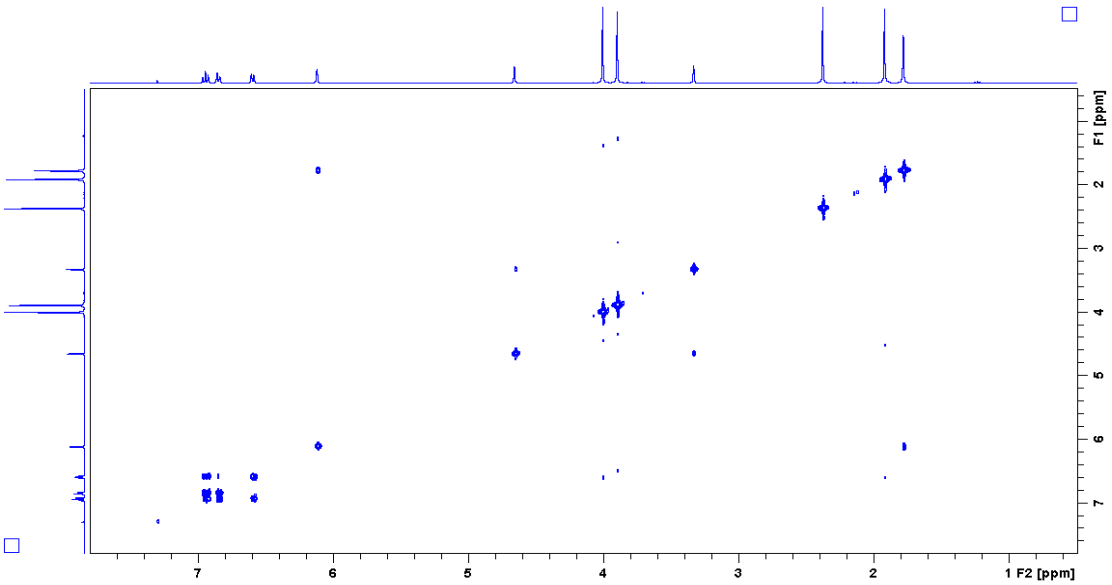
1HNMR:



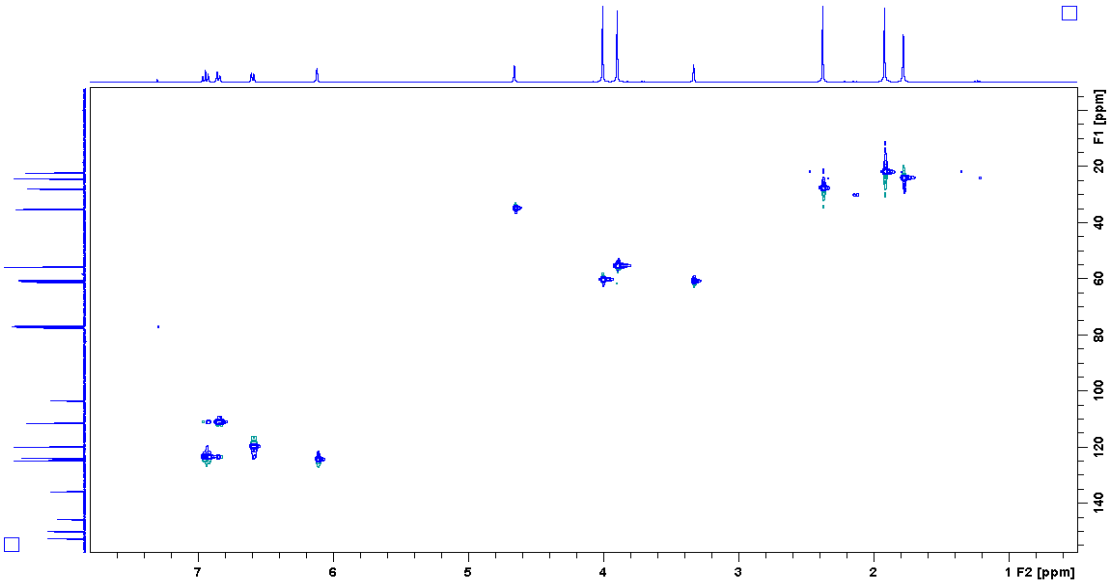
13CNMR:



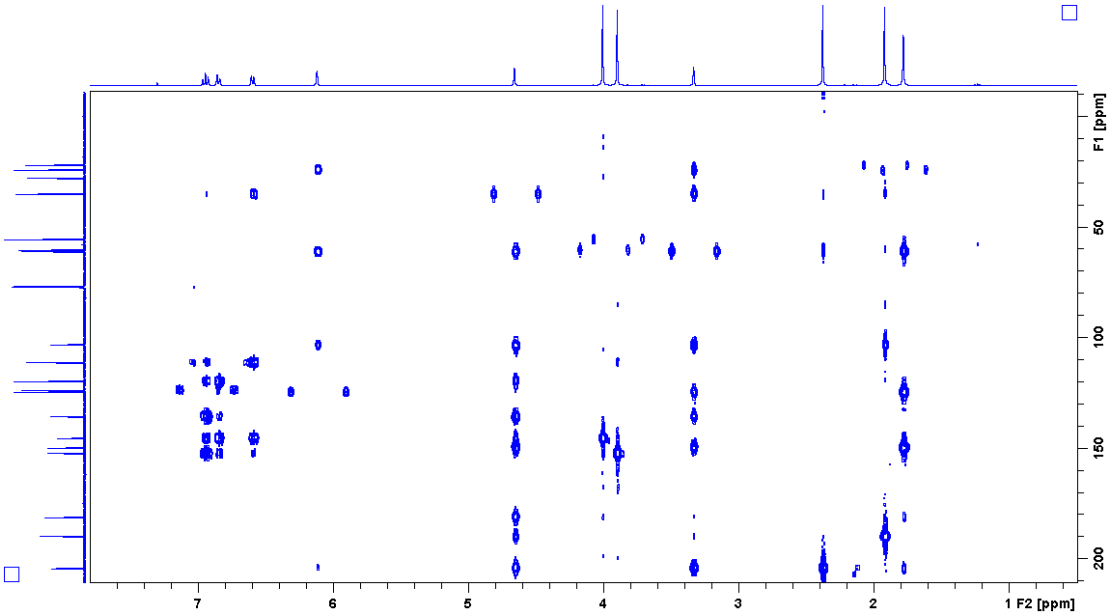
COSY



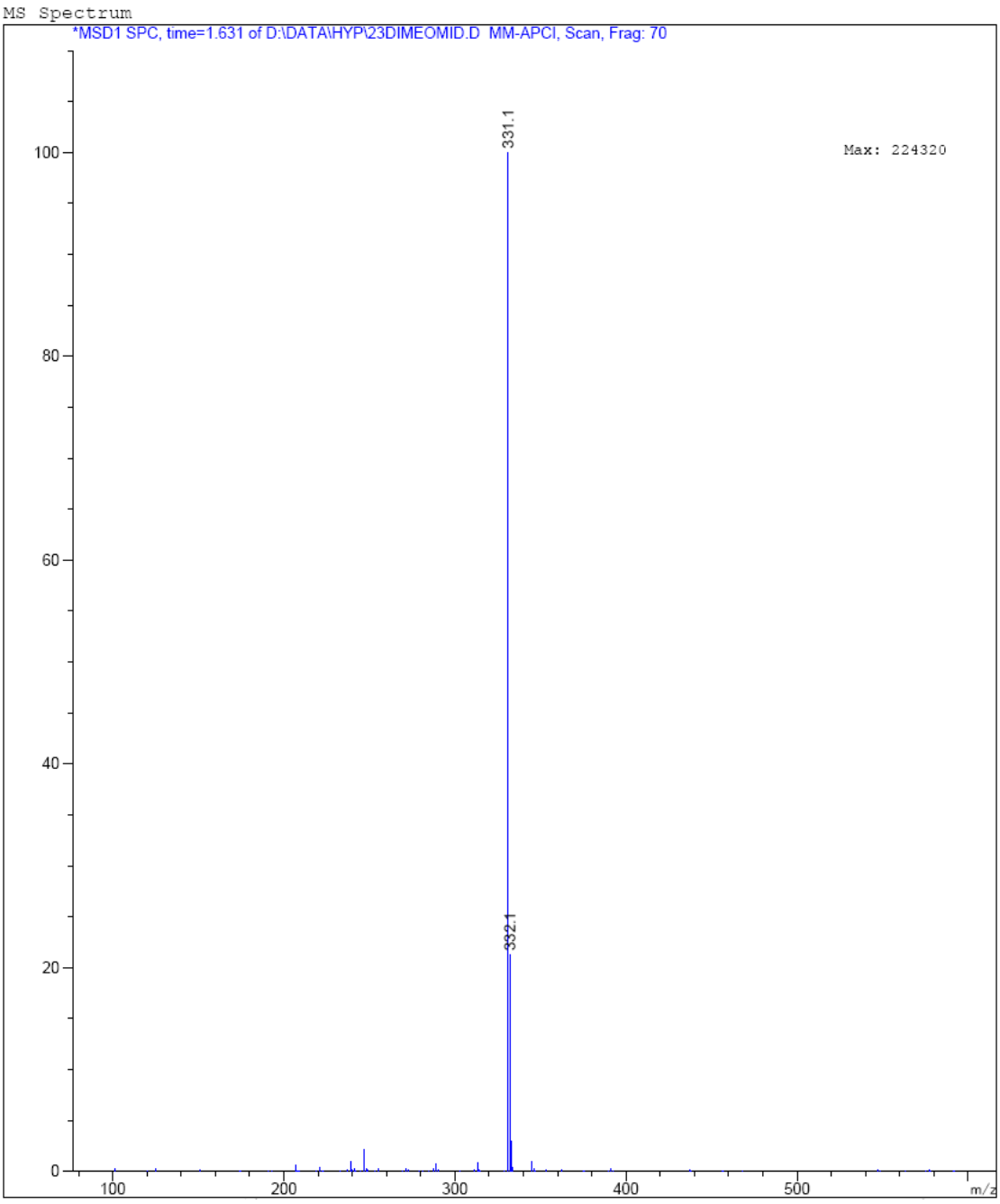
HSQC:



HMBC:



MS:


MS Spectrum
*MSD1 SPC, time=1.631 of D:\DATA\HYP\23DIMEOMID.D MM-APCI, Scan, Frag: 70
Max: 224320
331.1
332.1
100
80
60
40
20
0
100
200
300
400
500
m/z

3.2 Element analysis of new compounds

CHN元素含量测定值 07.11.09
德国Elementar公司Vario EL元素分析仪

No.	Name		Weight [mg]	Info	O2 Fact.	Prot. Fact.	Prot. [%]	C/N Ratio	User1	User2		Content [%]	Peak Area	Blank Value	Daily Factor
24	(4)	2f	1.8280	Nu	1	0.000	0.000	2646	0.000	0.000	N:	0.028	103	90	0.9909
											C:	74.40	40586	0	1.0274
											H:	6.436	11271	700	0.9769
25	(5)	2a (~~2b~~)	1.8570	Nu	1	0.000	0.000	2397	0.000	0.000	N:	0.030	104	90	1.0027
											C:	72.30	40069	0	1.0274
											H:	6.636	11830	700	0.9769
26	(6)	(2c)	1.8540		1	0.000	0.000	0.000	0.000	0.000	N:	0.000	82	90	1.0027
											C:	73.71	40782	0	1.0274
											H:	6.686	11904	700	0.9769
27	(7)	2b (~~2d~~)	1.8510		1	0.000	0.000	0.000	0.000	0.000	N:	0.000	81	90	1.0027
											C:	72.79	40211	0	1.0274
											H:	6.358	11275	700	0.9769
28	(9)	2g	1.5980		1	0.000	0.000	0.000	0.000	0.000	N:	0.000	87	90	1.0027
											C:	73.85	35230	0	1.0274
											H:	7.107	10862	700	0.9769
29	(10)	2i	1.5210	Nu	1	0.000	0.000	28299	0.000	0.000	N:	0.003	91	90	1.0027
											C:	74.43	33800	0	1.0274
											H:	7.360	10700	700	0.9769
~~30~~	~~(11)~~	~~(2k)~~	~~1.8600~~		~~1~~	~~0.000~~	~~0.000~~	~~0.000~~	~~0.000~~	~~0.000~~	~~N:~~	~~0.000~~	~~80~~	~~90~~	~~1.0027~~
											~~C:~~	~~70.30~~	~~39027~~	~~0~~	~~1.0274~~
											~~H:~~	~~6.387~~	~~11385~~	~~700~~	~~0.9769~~
51	(8)	2h	0.7990	Nu	1	0.000	0.000	366.9	0.000	0.000	N:	0.200	130	90	1.0027
											C:	73.47	17538	0	1.0274
											H:	6.785	5120	700	0.9769

Elementar Analysensysteme GmbH VarioEL V4.01 20.Aug. 2002 CHN Mode Page 1
Document: D:\DATA\2009年\CHN\测试日期 2009-11-06(CHN).dat

CHN元素含量测定值 06.11.09
德国Elementar公司Vario EL元素分析仪

No.	Name	Weight [mg]	Info	O2 Fact.	Prot. [%]	Prot.	C/N Ratio	User1	User2		Content [%]	Peak Area	Blank Value	Daily Factor
49	1 (2d)	1.9410	Nu	1	0.000	0.000	1005	0.000	0.000	N:	0.072	135	100	0.9986
										C:	72.20	41903	0	1.0254
										H:	6.151	11235	600	0.9860
~~50~~	~~3 (2e)~~	~~1.7960~~		~~1~~	~~0.000~~	~~0.000~~	~~0.000~~	~~0.000~~	~~0.000~~	~~N:~~	~~0.000~~	~~80~~	~~100~~	~~0.9986~~
										~~C:~~	~~69.94~~	~~37565~~	~~0~~	~~1.0254~~
										~~H:~~	~~6.515~~	~~10998~~	~~600~~	~~0.9860~~
71	2 2e	1.2070	Nu	1	0.000	0.000	11086	0.000	0.000	N:	0.007	102	100	0.9986
										C:	73.19	26435	0	1.0254
										H:	6.593	7355	600	0.9860

Elementar Analysensysteme GmbH VarioEL V4.01 20.Aug. 2002 CHN Mode Page 1
Document: D:\DATA\2009年\CHN\测试日期 2009-11-05(CHN).dat

CHN元素含量测定值 14.01.10

德国Elementar公司Vario EL元素分析仪

No.	Name	Weight [mg]	Info	O2	Prot. Fact.	Prot. [%]	C/N Ratio	User1	User2		Content [%]	Peak Area	Blank Value	Daily Factor
~~41~~	~~4EtO3MeO-Fu~~	~~1.5460~~		~~1~~	~~0.000~~	~~0.000~~	~~0.000~~	~~0.000~~	~~0.000~~	~~N:~~	~~0.000~~	~~47~~	~~50~~	~~0.9878~~
										~~C:~~	~~69.40~~	~~33111~~	~~0~~	~~0.9939~~
										~~H:~~	~~6.918~~	~~10320~~	~~800~~	~~0.9754~~
42	2,3diMeO-Mid	1.7100	Nu 2b ~~2b-cis~~	1	0.000	0.000	6010	0.000	0.000	N:	0.012	55	50	0.9878
										C:	69.25	36541	0	0.9939
										H:	6.658	11009	800	0.9754
43	2,3-DiMeO-Cis	1.8430	2b-cis	1	0.000	0.000	0.000	0.000	0.000	N:	0.000	35	50	0.9878
										C:	72.87	41430	0	0.9939
										H:	6.445	11502	800	0.9754