Supporting Information For

Bran-new four-molecule and five-molecule cascade reactions for one-pot synthesis of pyrano[3,2-*c*]chromen-5-ones and spiro[benzo[*b*]-[1,4]diazepine-2,2'-pyrano[3,2-*c*]chromen]-5'-ones under catalyst- and solvent-free conditions

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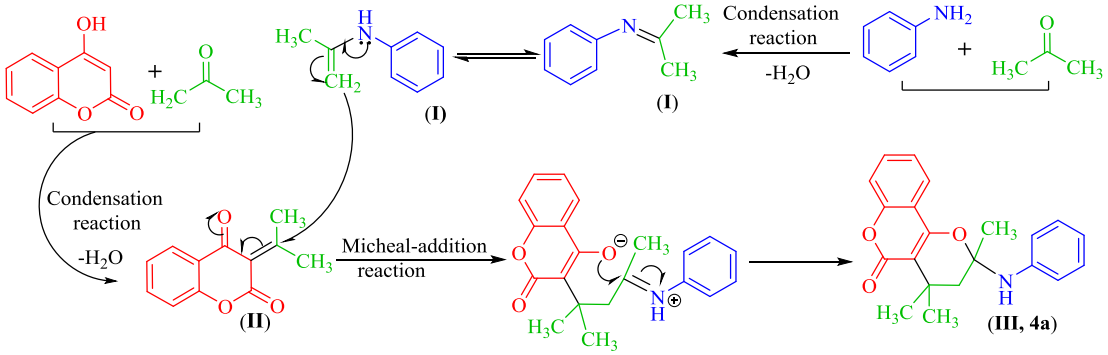
Table of Contents

1. Mechanism speculation of the reaction

For the first kind of reaction, four-molecule reaction (Scheme S1)

A mixture of acetone, aniline and 4-hydroxychromen-2-one was refluxed for 6 h, then HRMS (high resolution mass spectrometer) was run for the reaction mixture. Five peaks were found from positive ion HRMS: 134.0964 ($C_9H_{12}N^+$, cald. 134.0964) $[M+H]^+$, matched with *iso*-propylidenephenylamine (**I**), the condensed product of acetone and aniline; 203.0703 ($C_{12}H_{11}O_3^+$, cald. 203.0703) $[M+H]^+$ and 225.0524 ($C_{12}H_{10}NaO_3^+$, cald. 225.0522) $[M+Na]^+$, matched with 3-*iso*-propylidenechroman- 2,4-dione (**II**), the condensed product of acetone and 4-hydroxychromen-2-one; 336.1600 ($C_{21}H_{22}NO_3^+$, cald. 336.1594) $[M+H]^+$ and 358.1419 ($C_{21}H_{21}NNaO_3^+$, cald. 358.1414) $[M+Na]^+$, matched with target compound, 2,4,4-trimethyl-2-phenylamino-3,4-dihydro-2*H*-pyrano-[3,2-c]chromen-5-one (**III**).

Two peaks were found from negative ion HRMS: 201.0550 ($C_{12}H_9O_3^-$, cald. 201.0557) $[M-H]^-$, matched with 3-*iso*-propylidenechroman-2,4-dione (**II**); 334.1448 ($C_{21}H_{20}NO_3^-$, cald. 334.1449)$[M-H]^-$, matched with target compound 2,4,4-trimethyl-2-phenylamino-3,4-dihydro-*2H*-pyrano[3,2-c]chromen-5-one (**III**).

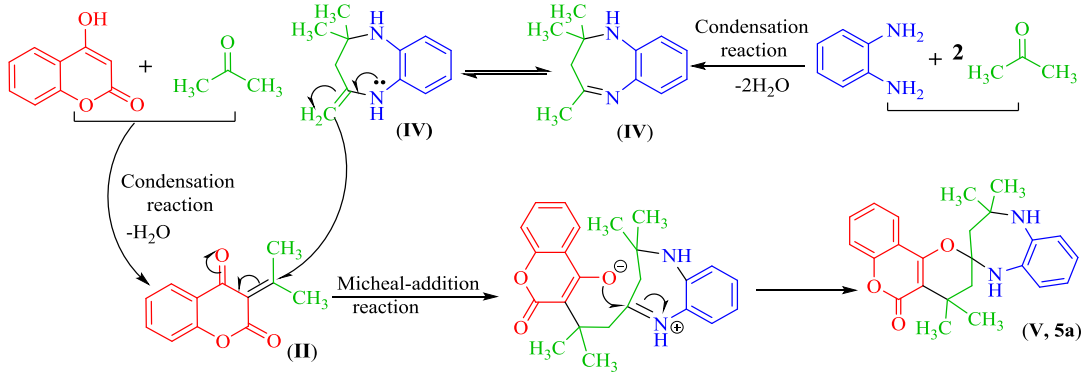


Scheme S1 Mechanism of the four-molecule cascading reaction of 4-hydroxychromen-2-one, aniline and acetone

For the second kind of reaction, five-molecule reaction (Scheme S2)

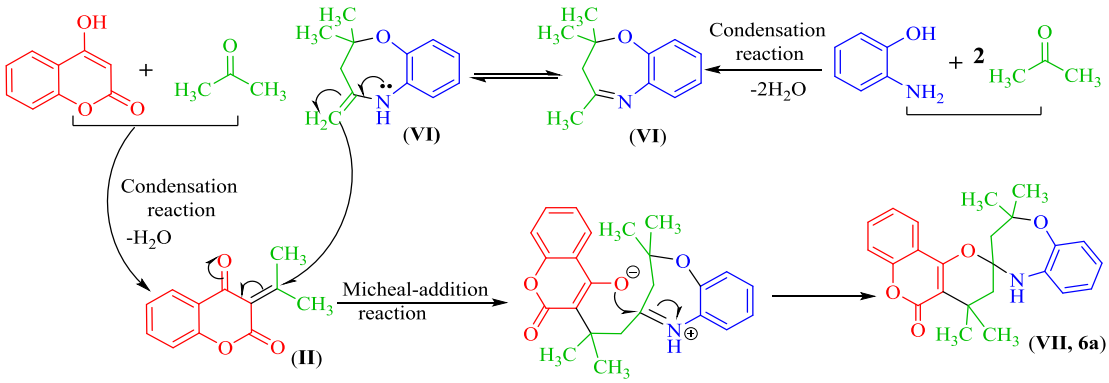
In order to verify this proposed five-molecule reaction mechanism, the key intermediate **IV** was prepared based on the reported method, then **IV** and 4-hydroxychromen-2-one in acetone were mixed and refluxed for 8h, HRMS was run for the reaction mixture. Three positive ion peaks were found: 189.1379 ($C_{12}H_{17}N_2^+$, cald. 189.1386) $[M+H]^+$,

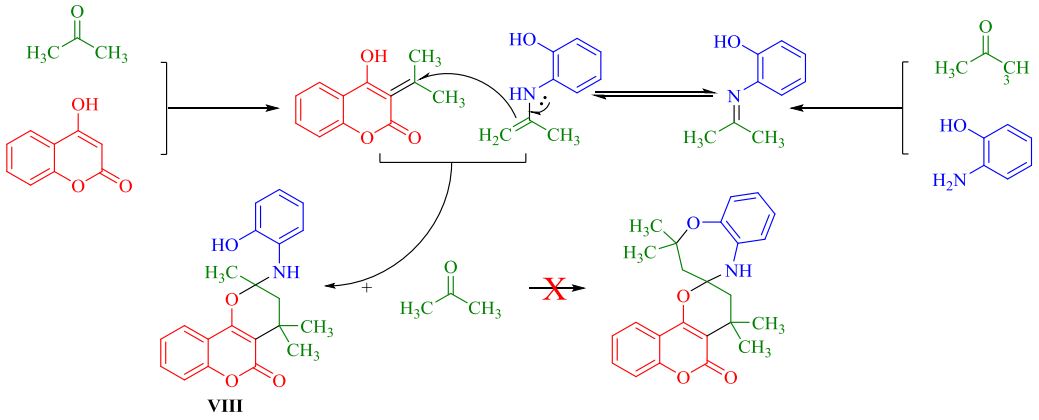
matched with **IV**; 203.0691 ($C_{12}H_{11}O_3^+$, cald. 203.0703) $[M+H]^+$, matched with **II**; 391.2001 ($C_{24}H_{27}N_2O_3^+$, cald. 391.2016)$[M+H]^+$, matched with **V**. Three negative ion peaks were found: 161.0253 ($C_9H_5O_3^-$, cald. 161.0244) $[M-H]^-$, matched with 4-hydroxychromen-2-one; 201.0552 ($C_{12}H_9O_3^-$, cald. 201.0557) $[M-H]^-$, matched with **II**; 389.1863 ($C_{24}H_{25}N_2O_3^-$, cald. 389.1871)$[M-H]^-$, matched with **V**.



Scheme S2 Mechanism of the five-molecule cascading reaction of 4-hydroxychromen-2-one, benzene-1,2-diamine and acetone

For 2,2,4',4'-tetramethyl-2,3,3',4'-tetrahydro-*5H,5'H*-spiro[benzo[*b*][1,4]-oxazepine-4,2'-pyrano[3,2-c]chromen]-5'-one (**VII**), the mechanism of its formation was presumed to be similar to that of the formation of **V**, that is, the reaction went through forming **II** and 6,6,8-trimethyl-6,7-dihydro-5-oxa-9-azabenzocycloheptene (or 6,6-dimethyl-8-methylene-6,7,8,9-tetrahydro-5-oxa-9-azabenzocycloheptene (**VI**) steps (**Scheme S3, above**).



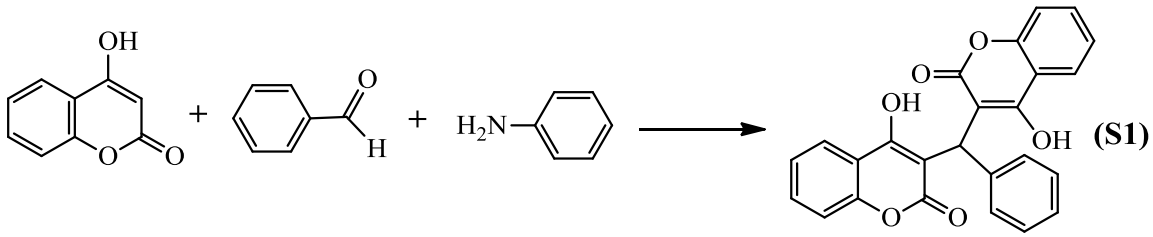


Scheme S3 Mechanism of the five-molecule cascading reaction of 4-hydroxychromen-2-one, 2-aminophenol and acetone

In order to confirm this reaction mechanism, 2-((2-hydroxyphenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one (**VIII**), as an intermediate, was synthesized, firstly, by protecting hydroxyl group, then this intermediate (**VIII**) mixed with acetone, and the mixture was refluxed for 8h. But compound **6a** was not obtained, which demonstrated that this reaction went through the forming **VI**, instead of **VIII** (**Scheme S3, below**).

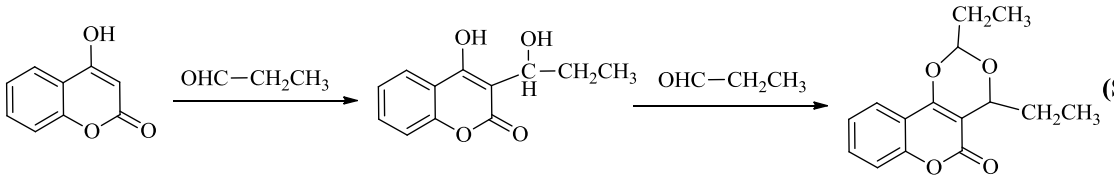
Substrate scope of ketone compounds

The reaction mixture of benzaldehyde, aniline and 4-hydroxychromen-2-one was refluxed for 8h, HRMS was run for the mixture. The result was that benzaldehyde reacted with 2-flod of 4-hydroxychromen-2-one to form 3,3'-(phenylmethylene)bis(4-hydroxy-2H-chromen-2-one) (**eqn** (**S1**)), which was confirmed by ion peaks of 411.0874 ($C_{25}H_{15}O_6^-$, cald. 411.0874 $[M-H]^-$ in the HRMS of the reacting mixture.



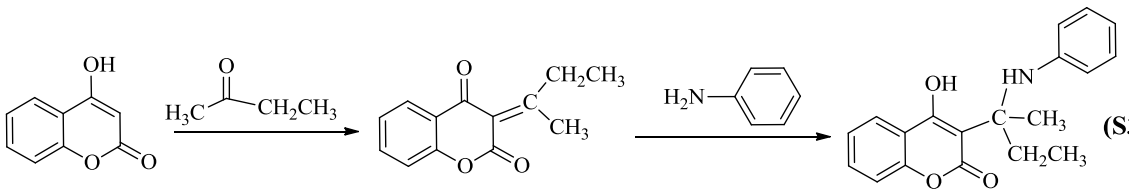
For alphatic aldehyde compounds, such as propionaldehyde, the desired target compound 4-ethyl-3-methyl-2-(phenylamino)-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]-chromen-5-one was obtained (**eqn** (**S2**)), confirmed by finding ion peak in HRMS

[334.1449 ($C_{21}H_{20}NO_3^-$, cald. 334.1421)[M-H]$^-$], but the yield was very low, due to the formation of by-products. The main by-product could be 2,4-diethyl-*4H,5H*[1,3]dioxino[5,4-c]- chromen-5-one, as ion peak, 259.0980 ($C_{15}H_{15}NO_4^-$, cald. 259.0976)[M-H]$^-$, was found.



(S2)

As butanone is structurally very similar to acetone, it was scanned for this reaction, too. The corresponding ion peak of target compound, 2,4-diethyl-4-methyl-2-phenylamino-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one [364.1907 ($C_{23}H_{26}NO_3^+$, cald. 364.1907)[M+H]$^+$], was found (**eqn** (**S3**)), but the abundance of the peak was very low, indicating that the yield was very low. Meantime, ion peaks of 3-(butan-2-ylidene)chromane-2,4-dione [215.0690 ($C_{13}H_{11}O_3^-$, cald. 215.0714)[M-H]$^-$] and its additive product with aniline, 4-hydroxy-3-(1-methyl-1-phenylamino-propyl)chromen-2-one, [310.1442 ($C_{19}H_{20}NO_3^+$, cald. 310.1438)[M+H]$^+$], were found, which demonstrated that butanone could react to form the designed compound as the acetone, but the yield for this reaction was lower, because the by-product was formed. The main by-product could be 2,4-diethyl-*4H,5H*-[1,3]-dioxino[5,4-c]chromen-5-one, because the ion peak, 310.1442 ($C_{19}H_{20}NO_3^-$, cald. 310.1438)[M-H]$^-$, was found.



(S3)

2. General experimental section

The starting materials were commercially available and were used without further purification. The products were isolated by column chromatography on silica gel. Melting points were determined by WRS-1B (Shanghai Precise Science Instrument Co. Ltd). NMR spectra were determined on Bruker 400 in $CDCl_3$. ^1H NMR and ^{13}C NMR spectra were recorded on 400 MHz spectrometers using $CDCl_3$ as solvent. Element Analysis was performed on elemental analyzer (Germany Elementar Co. Ltd). HRMS

spectra were performed on Agilent QTOF-MS 6540. Single crystals were prepared in dichloromethane at room temperature by solvent evaporation method and their structure data were collected on a Smart 1000 CCD single crystal diffractometer.

3. Experimental procedure for multicomponent reaction

General procedure for the synthesis of 4a-q

A mixture of 1.62 g (10 mmol) of 4-hydroxychromen-2-one, 10.5 mmol of the corresponding anilines, 5.80 g (100 mmol) 7.4 mL of acetone was stirred for 24 h under refluxing, then was concentrated in vacuum to obtain a residue which was separated by column chromatography with ethyl acetate and petroleum ether as the eluents to afford the corresponding products. All other compounds are synthesized in a similar manner, with the yields listed in the main text calculated from the isolated, pure products.

General procedure for the synthesis of 4a on 10-gram scale

A mixture of 16.2 g (100 mmol) of 4-hydroxychromen-2-one, 9.77 g (105 mmol) of aniline, 58.0 g (1000 mmol) 74 mL of acetone was stirred for 24 h under refluxing. The reaction mixture was cooled to room temperature, the product precipitated. The precipitated product was filtered and washed with petroleum ether to get pure product 18.0 g (yield: 54%).

General procedure for the synthesis of 5a-d and 6a-c

A mixture of 1.62 g (10.0 mmol) of 4-hydroxychromen-2-one, 10.5 mmol of the corresponding *o*-phenylenediamines or *o*-aminophenols, 5.80 g (100 mmol) 7.4 mL of acetone was stirred for 24 h under refluxing, then was concentrated in vacuum to obtain a residue which was separated by column chromatography with ethyl acetate and petroleum ether as the eluents to give the corresponding products. All other compounds are

synthesized in a similar manner, with the yields listed in the main text calculated from the isolated, pure products.

4. Single crystal data

Single crystal preparation

100mg (0.3mmol) of compound **4a** was dissolved in 2mL dichloromethane in a 5mL plastic centrifuge tube and the mixture was left standing for more than 48h. The obtained crystal was collected and analyzed. Single crystals of **5a** and **6a** were obtained as the same method.

Relevant information

The single crystal structures were analyzed and the obtained data were deposited in Cambridge Crystallographic Data Centre (CCDC). The information about these crystals was listed in **Table S1-2**.

Table S1 Information of single crystals in this work

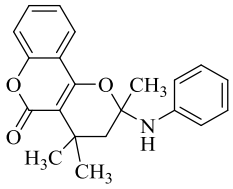
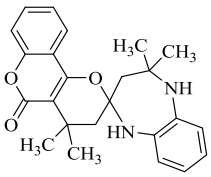
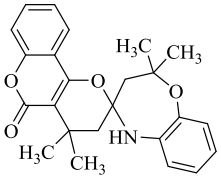
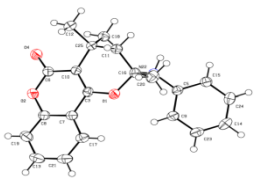
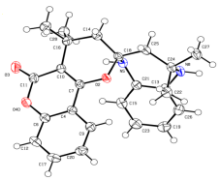
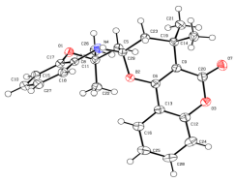
Entry	**1**	**2**	**3**
Molecular structure			
Crystal structure			
Given number by CCDC	1555403	1555401	1555402
Given name by us	MCR-H	MCR-2NH$_2$	MCR-2OH
Molecular formula	$C_{21}H_{21}NO_3$	$C_{24}H_{26}N_2O_3$	$C_{24}H_{25}NO_4$

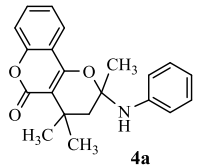
Table 2 Details of single crystals in this work

Name	MCR-H	MCR-2NH2	MCR-2OH
Empirical formula	C16 H10 N2 O2	C24 H26 N2 O3	C24 H25 N O4
Formula weight	262.26	390.47	391.45
Temperature	293(2) K	293(2) K	293(2) K

Wavelength	1.54178 A	1.54178 A	1.54178 A
Crystal system, space group	Triclinic, P-1	Monoclinic, P2(1)/n	Monoclinic, C2/c
Unit cell dimensions	a = 7.7916(3) A alpha = 68.596(4) deg. b = 8.7127(4) A beta = 77.302(4) deg. c = 10.0548(4) A gamma = 69.280(4) deg.	a = 10.63300(10) A alpha = 90 deg. b = 11.8182(2) A beta = 95.6420(10) deg. c = 16.2353(2) A gamma = 90 deg.	a = 18.1869(5) A alpha = 90 deg. b = 11.8032(3) A beta = 103.632(3) deg. c = 19.0131(5) A gamma = 90 deg.
Volume	591.17(5) A^3	2030.29(5) A^3	3966.44(19) A^3
Z, Calculated density	2, 1.473 Mg/m^3	4, 1.277 Mg/m^3	8, 1.311 Mg/m^3
Absorption coefficient	0.812 mm^-1	0.676 mm^-1	0.719 mm^-1
F(000)	272	832	1664
Crystal size	0.340 x 0.260 x 0.210 mm	0.500 x 0.320 x 0.250 mm	0.6 x 0.4 x 0.18 mm
Theta range for data collection	4.749 to 73.983 deg.	4.636 to 73.733 deg.	4.504 to 74.111 deg.
Limiting indices	-9<=h<=6, -10<=k<=10, -12<=l<=12	-12<=h<=13, -14<=k<=13, -19<=l<=20	-22<=h<=22, -11<=k<=14, -16<=l<=23
Reflections collected / unique	3791 / 2310 [R(int) = 0.0142]	20882 / 4072 [R(int) = 0.0278]	7262 / 3890 [R(int) = 0.0236]
Completeness to theta = 67.679	99.6 %	100.0 %	99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.85712	1 and 0.22983	1 and 0.74611
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2310 / 0 / 181	4072 / 0 / 275	3890 / 0 / 270
Goodness-of-fit on F^2	1.038	1.035	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1252	R1 = 0.0372, wR2 = 0.0992	R1 = 0.0397, wR2 = 0.1077
R indices (all data)	R1 = 0.0460, wR2 = 0.1299	R1 = 0.0392, wR2 = 0.1014	R1 = 0.0432, wR2 = 0.1111
Extinction coefficient	n/a	0.00083(18)	n/a
Largest diff. peak and hole	0.310 and -0.272 e.A^-3	0.314 and -0.193 e.A^-3	0.244 and -0.202 e.A^-3

5. Characterization data for the products

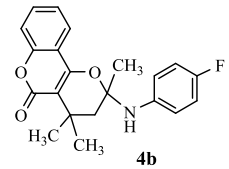
1. 2,4,4-Trimethyl-2-(phenylamino)-3,4-dihydro-*2H*,*5H*-pyrano[3,2-*c*]chromen-5-one (**4a**)



4a

Yield 58%. m.p., 168.4-168.8 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.36–7.18 (m, 4H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.92 (t, *J* = 7.3 Hz, 1H), 4.44 (br, 1H), 2.33–2.11 (m, 2H), 1.82 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 157.1, 152.6, 142.8, 131.4, 129.1, 123.7, 123.2, 121.1, 119.4, 116.3, 116.2, 108.5, 89.2, 49.6, 30.8, 28.8, 28.6, 25.4. HRMS-ESI, m/z: 336.1637 $[M+H]^+$ (Calcd. for $C_{21}H_{22}NO_3^+$, 336.1594). Anal. Calcd. For $C_{21}H_{21}NO_3$: C, 75.20; H, 6.31; N, 4.18. Found: C, 75.07; H, 6.28; N, 3.82.

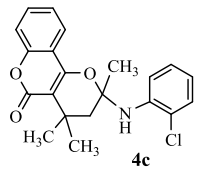
2. 2-((4-Fluorophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one (**4b**)



4b

Yield 23%. m.p.108.4-109.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.52 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.37–7.26 (m, 5H), 6.89 (d, *J* = 8.2 Hz, 2H), 4.39 (br, 1H), 2.30–2.10 (m, 2H), 1.80 (s, 3H), 1.65 (s, 3H) , 1.55 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 157.2, 157.0, 152.6, 138.5, 131.4, 123.7, 123.0, 122.9, 122.7, 116.3, 116.1, 115.7, 115.4, 108.5, 89.7, 49.5, 30.8, 28.7, 28.6, 25.3. HRMS-ESI, m/z: 354.1501 [M+H]+ (Calcd. for $C_{21}H_{21}FNO_3^+$, 354.1500). Anal. Calcd. For $C_{22}H_{23}NO_4$: C, 71.37; H, 5.70; N, 3.96. Found: C, 71.08; H, 5.69; N, 3.68.

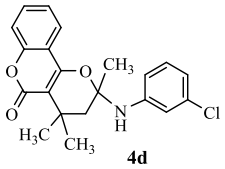
3. 2-((2-Chlorophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one (**4c**)



4c

Yield 43%. m.p. 142.2-142.4 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.53–7.47 (m, 1H), 7.40 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.32–7.27 (m, 3H), 7.16 (ddd, *J* = 8.4, 7.5, 1.6 Hz, 1H), 6.78 (td, *J* = 7.7, 1.5 Hz, 1H), 5.11 (br, 1H), 2.37–2.16 (m, 2H), 1.89 (s, 3H), 1.75 (s, 3H), 1.56 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 156.7, 152.6, 139.7, 131.4, 129.4, 127.4, 123.7, 122.9, 121.7, 120.2, 117.4, 116.3, 116.0, 109.0, 88.1, 50.1, 30.4, 29.1, 28.2, 25.4. HRMS-ESI, m/z: 370.1234 [M+H]+ (Calcd. for $C_{21}H_{21}ClNO_3^+$, 370.1204). Anal. Calcd. For $C_{21}H_{20}ClNO_3$: C, 68.20; H, 5.45; N, 3.79. Found: C, 68.44; H, 4.95; N, 2.99.

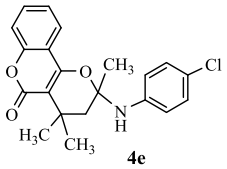
4. 2-((3-chlorophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one (**4d**)



4d

Yield 43%. m.p. 156.1-156.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.51 (td, *J* = 7.7, 7.0, 1.6 Hz, 1H), 7.35–7.27 (m, 2H), 7.13 (t, *J* = 8.1 Hz, 1H), 7.04 (t, *J* = 2.1 Hz, 1H), 6.84 (td, J = 8.5, 2.0 Hz, 2H), 4.45 (br, 1H), 2.30–2.11 (m, 2H), 1.83 (s, 3H), 1.67 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (75 MHz, CDCl3) δ 161.2, 156.8, 152.6, 144.3, 134.7, 131.5, 130.1, 123.8, 123.0, 120.4, 118.3, 116.5, 116.3, 116.0, 108.8, 88.6, 49.7, 30.6, 28.8, 28.4, 25.3. HRMS-ESI, m/z: 370.1233 $[M+H]^+$ (Calcd. for $C_{21}H_{21}ClNO_3^+$, 370.1204). Anal. Calcd. For $C_{21}H_{20}ClNO_3$: C, 68.20; H, 5.45; N, 3.79. Found: C, 67.92; H, 5.32; N, 3.40.

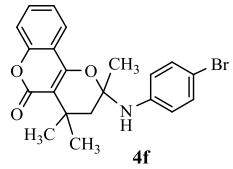
5. 2-((4-Chlorophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one (**4e**)



4e

Yield 49%. m.p. 135.4-135.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.52 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.33–7.25 (m, 2H), 7.22–7.16 (m, 2H), 6.96–6.89 (m, 2H), 4.38 (br, 1H), 2.26 (d, *J* = 14.6 Hz, 2H), 1.79 (s, 3H), 1.65 (s, 3H), 1.55 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 156.9, 152.6, 141.5, 131.5, 129.0, 126.1, 123.7, 122.9, 120.5, 116.3, 116.0, 108.6, 88.9, 49.6, 30.7, 28.7, 28.6, 25.3. HRMS-ESI, m/z: 370.1233 $[M+H]^+$ (Calcd. for $C_{21}H_{21}ClNO_3^+$, 370.1204). Anal. Calcd. For $C_{21}H_{20}ClNO_3$: C, 68.20; H, 5.45; N, 3.79. Found: C, 67.91; H, 5.30; N, 3.37.

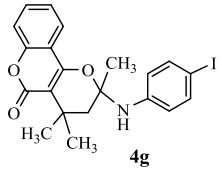
6. 2-((4-Bromophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one (**4f**)



4f

Yield 42%. m.p. 134.4-134.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.52 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.37–7.26 (m, 5H), 6.89 (d, *J* = 8.2 Hz, 2H), 4.39 (br, 1H), 2.30– 2.10 (m, 2H), 1.80 (s, 3H), 1.65 (s, 3H) , 1.55 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 161.2, 156.9, 152.6, 142.0, 131.9, 131.5, 123.8, 123.0, 120.6, 116.3, 116.0, 113.2, 108.6, 88.8, 49.6, 30.7, 28.8, 28.4, 25.3. HRMS-ESI, m/z: 414.0690 $[M+H]^+$ (Calcd. for $C_{21}H_{21}BrNO_3^+$, 414.0699). Anal. Calcd. For $C_{21}H_{20}BrNO_3$: C, 60.88; H, 4.87; N, 3.38. Found: C, 60.80; H, 4.90; N, 3.11.

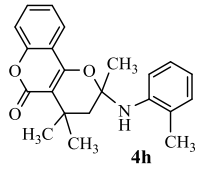
7. 2-((4-Iodophenyl) amino)-2,4,4-trimethyl-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one (**4g**)



4g

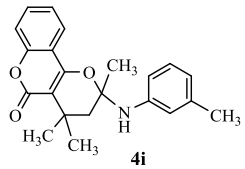
Yield 40%. m.p.130.3-130.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51 (dq, *J* = 7.3, 2.1, 1.6 Hz, 3H), 7.34–7.27 (m, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 4.34 (br, 1H), 2.31–2.10 (m, 2H), 1.81 (s, 3H), 1.64 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 156.9, 152.6, 142.7, 137.8, 131.5, 123.8, 122.9, 120.8, 116.3, 115.9, 108.7, 88.7, 82.8, 49.6, 31.6, 30.7, 28.8, 28.5, 25.3, 22.7. HRMS-ESI, m/z: 462.0592 $[M+H]^+$ (Calcd. for $C_{21}H_{21}INO_3^+$, 462.0561). Anal. Calcd. For $C_{21}H_{20}INO_3$: C, 54.68; H, 4.37; N, 3.04. Found: C, 54.41; H, 4.57; N, 2.71.

8. 2, 4, 4-Trimethyl-2-(*o*-tolylamino)-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one (**4h**)


4h

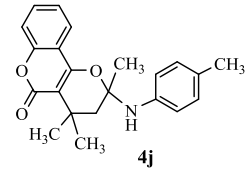
Yield 48%. m.p. 122.0-122.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.88 (m, 1H), 7.53–7.46 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.28 (d, *J* = 14.2 Hz, 2H), 7.14 (dd, *J* = 13.4, 7.2 Hz, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 4.36 (br, 1H), 2.40-2.15 (m, 5H), 1.86 (s, 3H), 1.70 (s, 3H), 1.57 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 157.2, 152.6, 141.1, 131.3, 130.6, 126.6, 126.1, 123.7, 123.2, 120.5, 118.2, 116.3, 108.5, 89.2, 50.1, 30.6, 28.9, 28.8, 25.3, 18.0. HRMS-ESI, m/z: 350.1786 $[M+H]^+$ (Calcd. for $C_{22}H_{24}NO_3^+$, 350.1751). Anal. Calcd. For $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.57; H, 6.57; N, 3.65.

9. 2,4,4-Trimethyl-2-(m-tolylamino)-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one (**4i**)


4i

Yield 46%. m.p. 141.1-141.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.35–7.24 (m, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.89–6.78 (m, 2H), 6.74 (d, *J* = 7.5 Hz, 1H), 4.41 (br, 1H), 2.30 (s, 3H), 2.28–2.11 (m, 2H), 1.82 (s, 3H), 1.67 (s, 3H), 1.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 157.1, 152.7, 142.7, 138.9, 131.4, 128.9, 123.6, 123.1, 121.9, 120.2, 116.4, 116.3, 116.2, 108.6, 89.2, 49.7, 30.7, 28.8, 28.5, 25.4, 21.5. HRMS-ESI, m/z: 350.1788 $[M+H]^+$ (Calcd. for $C_{22}H_{24}NO_3^+$, 350.1751). Anal. Calcd. For $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.69; H, 6.59; N, 3.65.

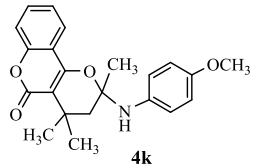
10. 2, 4, 4-Trimethyl-2-(p-tolylamino)-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one (**4j**)


4j

Yield 52%. m.p. 122.5-123.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.6 Hz, 1H),

7.50 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.32–7.25 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 4.49(br, 1H), 2.29 (s, 3H), 2.26–2.10 (m, 2H), 1.77 (s, 3H), 1.63 (s, 3H), 1.55 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 157.3, 152.6, 140.1, 131.3, 131.0, 130.5, 129.6, 128.4, 123.6, 123.2, 120.6, 116.2, 108.4, 89.7, 49.6, 30.8, 28.7, 26.9, 26.5, 25.3, 20.6. HRMS-ESI, m/z: 350.1790 $[M+H]^+$ (Calcd. for $C_{22}H_{24}NO_3^+$, 350.1751). Anal. Calcd. For $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01. Found: C, 74.94; H, 6.67; N, 3.61.

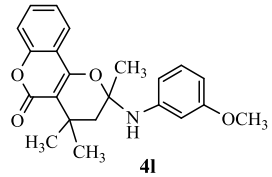
11. 2-((2-Methoxyphenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one (**4k**)



4k

Yield 52%. m.p. 183.1-183.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.87 (m, 1H), 7.48 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.30–7.24 (m, 3H), 6.88 (ddd, *J* = 7.8, 6.8, 2.2 Hz, 1H), 6.84–6.77 (m, 2H), 5.12 (br, 1H), 3.78 (s, 3H), 2.38–2.13 (m, 2H), 1.88 (s, 3H), 1.72 (s, 3H), 1.55 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 157.1, 152.6, 148.2, 132.8, 131.2, 123.6, 123.1, 120.8, 119.5, 116.7, 116.2, 109.9, 108.8, 88.6, 55.5, 49.9, 30.5, 29.1, 28.1, 25.4. HRMS-ESI, m/z: 366.1740 $[M+H]^+$ (Calcd. for $C_{22}H_{24}NO_4^+$, 366.1700). Anal. Calcd. For $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.33; H, 6.31; N, 3.47.

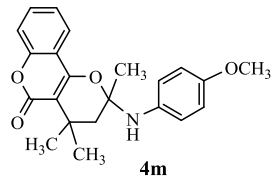
12. 2-((3-Methoxyphenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one (**4l**)



4l

Yield 52%. m.p 86.4-87.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.32–7.25 (m, 2H), 7.13 (t, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 8.3 Hz, 1H), 4.42 (br, 1H), 3.77 (s, 3H), 2.32–2.11 (m, 2H), 1.84 (s, 3H), 1.66 (s, 3H), 1.55(s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 160.4, 157.0, 152.6, 144.3, 131.4, 129.8, 123.6, 123.1, 116.3, 116.1, 111.5, 108.6, 106.1, 104.9, 88.9, 55.2, 49.8, 30.7, 28.8, 28.5, 25.4. HRMS-ESI, m/z: 366.1723 $[M+H]^+$ (Calcd. for $C_{22}H_{24}NO_4^+$, 366.1700). Anal. Calcd. For $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.33; H, 6.31; N, 3.47.

13. 2-((4-Methoxyphenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one (**4m**)

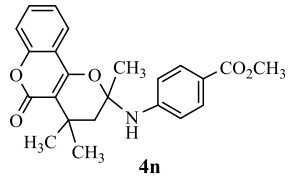


4m

Yield 56%. m.p. 99.2-99.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J*

= 7.8 Hz, 1H), 7.34–7.25 (m, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.18 (br, 1H), 3.79 (s, 3H), 2.28–2.08 (m, 2H), 1.69 (s, 3H),1.61 (s, 3H),1.56(s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 157.5, 155.8, 152.7, 135.2, 131.3, 124.6. 123.6, 123.2, 116.2, 114.2, 108.3, 90.5, 55.5, 49.3, 30.9, 28.9, 28.5, 25.3. HRMS-ESI, m/z: 366.1747 $[M+H]^+$ (Calcd. for $C_{22}H_{24}NO_4^+$, 366.1700). Anal. Calcd. For $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.31; H, 6.35; N, 3.48.

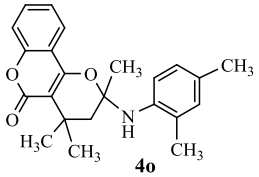
14. Methyl 4-((2,4,4-trimethyl-5-oxo-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-2-yl)amino)benzoate (**4n**)



4n

Yield 19%. m.p,180.3-180.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51 (dq, *J* = 7.3, 2.1, 1.6 Hz, 3H), 7.34–7.27 (m, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 4.34 (br, 1H), 2.31–2.10 (m, 2H), 1.81 (s, 3H), 1.64 (s, 3H), 1.55 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 161.1, 156.6, 152.6, 147.5, 131.5, 131.2, 123.8, 122.9, 121.1, 116.3, 116.0, 115.8, 108.8, 88.1, 51.7, 49.6, 30.6, 28.8, 28.3, 25.4. HRMS-ESI, m/z: 394.1652 $[M+H]^+$ (Calcd. for $C_{23}H_{25}NO_5^+$, 394.1649). Anal. Calcd. For $C_{23}H_{24}NO_5$: C, 70.21; H, 5.89; N, 3.56. Found: C, 69.74; H, 5.89; N, 3.39.

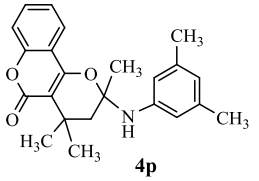
15. 2-((2,4-Dimethylphenyl)amino)-2,4,4-trimethyl-3,4-dihydro-2H,5H-pyrano[3,2-c]chromen-5-one (**4o**)



4o

Yield 61%. m.p. 169.7-169.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.53–7.46 (m, 1H), 7.32–7.20 (m, 3H), 6.95 (d, *J* = 6.6 Hz, 2H), 4.21 (br, 1H), 2.22 (d, *J* = 29.4 Hz, 8H), 1.81 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 157.4, 152.7, 138.3, 131.3, 130.5, 127.3, 127.0, 123.7, 123.2, 119.7, 116.3, 108.4, 89.8, 50.0, 30.8, 28.8, 25.2, 20.5, 18.1. HRMS-ESI, m/z: 364.1960 $[M+H]^+$ (Calcd. for $C_{23}H_{26}NO_3^+$, 364.1907). Anal. Calcd. For $C_{23}H_{25}NO_3$: C, 76.01; H, 6.93; N, 3.85. Found: C, 76.01; H, 7.06; N, 3.32.

16. 2-((3,5-Dimethylphenyl)amino)-2,4,4-trimethyl-3,4-dihydro-2H,5H-pyrano[3,2-c]chromen-5-one (**4p**)

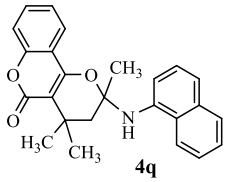


4p

Yield 59%. m.p. 176.3-176.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.33–7.24 (m, 2H), 6.61 (m, *J* = 29.9 Hz, 3H), 4.33 (br, 1H), 2.29–2.12 (m, 8H), 1.82 (s, 3H), 1.66 (s, 3H), 1.54 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 157.1, 152.7, 138.7, 131.3, 123.5, 123.1, 122.9, 117.3, 116.3, 116.2, 108.7, 89.2, 49.7, 30.7, 28.8, 28.5, 25.4,

21.4. HRMS-ESI, m/z: 364.1968 $[M+H]^+$ (Calcd. for $C_{23}H_{26}NO_3^+$, 364.1907). Anal. Calcd. For $C_{23}H_{25}NO_3$: C, 76.01; H, 6.93; N, 3.85. Found: C, 76.07; H, 6.93; N, 3.52.

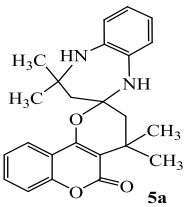
17. 2,4,4-Trimethyl-2-(naphthalen-1-ylamino)-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one (**4q**)



4q

Yield 38%. m.p. 159.7-161.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.33–7.24 (m, 2H), 6.61 (m, *J* = 29.9 Hz, 3H), 4.33 (br, 1H), 2.29–2.12 (m, 8H), 1.82 (s, 3H), 1.66 (s, 3H), 1.54 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 157.1, 152.7, 138.7, 131.3, 123.5, 123.1, 122.9, 117.3, 116.3, 116.2, 108.7, 89.2, 49.7, 30.7, 28.8, 28.5, 25.4, 21.4. HRMS-ESI, m/z: 386.1756 $[M+H]^+$ (Calcd. for $C_{25}H_{24}NO_3^+$, 386.1751). Anal. Calcd. For $C_{23}H_{25}NO_3$: C, 77.90; H, 6.01; N, 3.63. Found: C, 77.44; H, 6.13; N, 3.50.

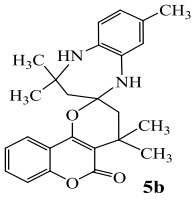
18. 4,4,4',4'-Tetramethyl-1,3,3',4,4',5-hexahydro-*5'H*-spiro[benzo-[b][1,4]diazepine-2,2'-pyrano[3,2-c]chromen]-5'-one (**5a**)



5a

Yield 66%. m.p. 151.2-151.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.37 (m, 2H), 7.31–7.24 (m, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.89 (td, *J* = 7.5, 1.4 Hz, 1H), 6.78 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.71 (td, *J* = 7.5, 1.4 Hz, 1H), 6.52 (dd, *J* = 7.7, 1.4 Hz, 1H), 4.86 (s, 1H), 3.51 (s, 1H), 2.23 (s, 2H), 2.22 (d, *J* = 29.9 Hz, 2H), 1.83–1.14 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 157.4, 152.5, 138.9, 134.0, 131.4, 123.7, 123.6, 123.3, 122.5, 122.1, 121.4, 116.1, 115.9, 108.2, 90.6, 52.1, 51.2, 50.9, 30.9, 30.5, 29.3. HRMS-ESI, m/z: 391.2041 $[M+H]^+$ (Calcd. for $C_{24}H_{27}N_2O_3^+$, 391.2016). Anal. Calcd. For $C_{24}H_{26}N_2O_3$: C, 73.82; H, 6.71; N, 7.17. Found: C, 73.45; H, 6.84; N, 6.85.

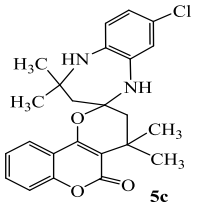
19. 4,4,4',4',7-Pentamethyl-1,3,3',4,4',5-hexahydro-*5'H*-spiro[benzo-[b][1,4]diazepine-2,2'-pyrano[3,2-*c*]chromen]-5'-one (**5b**)



5b

Yield 41%. m.p: 121.1-121.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.42 (m, 2H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.15–7.09 (m, 1H), 6.81 (d, *J* = 1.9 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 4.60 (s, 1H), 2.34–2.21 (m, 7H), 1.78–1.35 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ161.3, 157.5, 152.5, 138.9, 136.3, 134.0, 133.2, 131.5, 131.3, 124.1, 123.6, 123.4, 123.0, 122.5, 122.4, 121.9, 121.4, 116.0, 115.9, 108.2, 108.1, 90.8, 52.1, 51.9, 51.3, 51.2, 51.0, 50.9, 30.6, 29.3, 20.7, 20.4. HRMS-ESI, m/z: 405.2222 $[M+H]^+$ (Calcd. for $C_{25}H_{29}N_2O_3^+$, 405.2173). Anal. Calcd. For

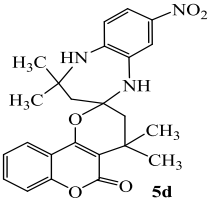
$C_{25}H_{28}N_2O_3$: C, 74.23; H, 6.98; N, 6.93. Found: C, 73.94; H, 7.12; N, 6.63.



5c

20. 7-Chloro-4,4,4',4'-tetramethyl-1,3,3',4,4',5-hexahydro-5'H-spiro-[benzo[b][1,4]diazepine-2,2'-pyrano[3,2-c]chromen]-5'-one (**5c**)

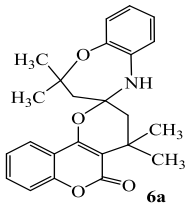
Yield 37%. m.p:155.3-156.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.39 (m, 2H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.15–7.10 (m, 1H), 6.78 (d, *J* = 2.3 Hz, 1H), 6.67 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.44 (d, *J* = 8.2 Hz, 1H), 4.81 (s, 1H), 3.56 (s, 1H), 2.31–2.06 (m, 4H), 1.77–1.24 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 157.3, 154.0, 152.5, 140.3, 132.5, 131.5, 128.2, 123.7, 123.3, 123.2, 121.5, 120.8, 116.1, 115.7, 108.2, 90.3, 52.3, 50.8, 50.7, 30.6, 30.5. HRMS-ESI, m/z: 425.1656 $[M+H]^+$ (Calcd. for $C_{24}H_{26}N_2O_3Cl^+$, 425.1626). Anal. Calcd. For $C_{24}H_{25}N_2O_3Cl$: C, 67.84; H, 5.93; N, 6.59. Found: C, 67.78; H, 6.07; N, 6.29.



5d

21. 4,4,4',4'-tetramethyl-8-nitro-1,3,3',4,4',5-hexahydro-5'H-spiro-[benzo[b][1,4]diazepine-2,2'-pyrano[3,2-c]chromen]-5'-one (**5d**)

Yield 20%. m.p:125.1-125.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.33 – 7.24 (m, 2H), 6.61 (m, *J* = 29.9 Hz, 3H), 4.33 (br, 1H), 2.29 – 2.12 (m, 8H), 1.82 (s, 3H), 1.66 (s, 3H), 1.54 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 157.1, 152.7, 138.7, 131.3, 123.5, 123.1, 122.9, 117.3, 116.3, 116.2, 108.7, 89.2, 49.7, 30.7, 28.8, 28.5, 25.4, 21.4. HRMS-ESI, m/z: 436.1867 $[M+H]^+$ (Calcd. for $C_{24}H_{26}N_3O_5^+$, 436.1867). Anal. Calcd. For $C_{24}H_{25}N_3O_5$: C, 66.19; H, 5.79; N, 9.65. Found: C, 66.46; H, 6.19; N, 9.01.

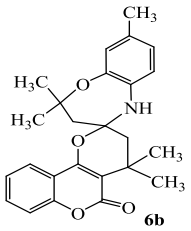


6a

22. 2,2,4',4'-Tetramethyl-2,3,3',4'-tetrahydro-*5H,5'H*-spiro-[benzo[b][1,4]oxazepine-4,2'-pyrano[3,2-c]chromen]-5'-one (**6a**)

Yield 49%. m.p: 142.0-142.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.42 (m, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.12 (td, *J* = 7.6, 1.2 Hz, 1H), 7.00 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.93 (td, *J* = 7.6, 1.6 Hz, 1H), 6.85 (td, *J* = 7.5, 1.7 Hz, 1H), 6.58 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.69 (s, 1H), 2.33 (d, *J* = 12.6 Hz, 2H), 2.26 (s, 2H), 1.70 (s, 3H), 1.56 (s, 6H), 1.41 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 157.3, 152.5, 147.3, 135.9, 131.5, 123.9, 123.7, 123.4, 123.3, 121.7, 116.1, 115.8, 108.2, 50.8, 49.8, 30.9, 30.6. HRMS-ESI, m/z: 392.1883 $[M+H]^+$ (Calcd. for $C_{24}H_{26}NO_4^+$, 392.1856). Anal. Calcd. For $C_{24}H_{25}NO_4$: C, 73.64; H, 6.44; N, 3.58. Found: C, 73.36; H, 6.54; N, 3.26.

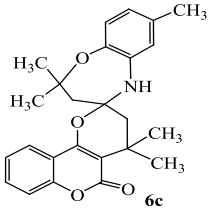
23. 2,2,4',4',8-Pentamethyl-2,3,3',4'-tetrahydro-5H,5'H-spiro-[benzo[b][1,4]oxazepine-4,2'-pyrano[3,2-c]chromen]-5'-one (**6b**)



6b

Yield 42%. m.p:155.2-155.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.42 (m, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.13 (td, *J* = 7.6, 1.1 Hz, 1H), 6.81 (d, *J* = 1.9 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 4.56 (s, 1H), 2.26 (d, *J* = 5.6 Hz, 7H), 1.76–1.35 (m, 12H).^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 157.4, 152.5, 147.2, 133.2, 131.5, 123.8, 123.7, 123.6, 123.3, 121.6, 116.1, 115.9, 108.1, 50.7, 49.6, 30.9, 30.6, 29.2, 20.6. HRMS-ESI, m/z: 406.2032 $[M+H]^+$ (Calcd. for $C_{25}H_{28}NO_4^+$, 406.2013). Anal. Calcd. For $C_{25}H_{27}NO_4$: C, 74.05; H, 6.71; N, 3.45. Found: C, 73.39; H, 6.96; N, 3.04.

24. 2,2,4',4',7-Pentamethyl-2,3,3',4'-tetrahydro-5H,5'H-spiro-[benzo[b][1,4]oxazepine-4,2'-pyrano[3,2-c]chromen]-5'-one (**6c**)

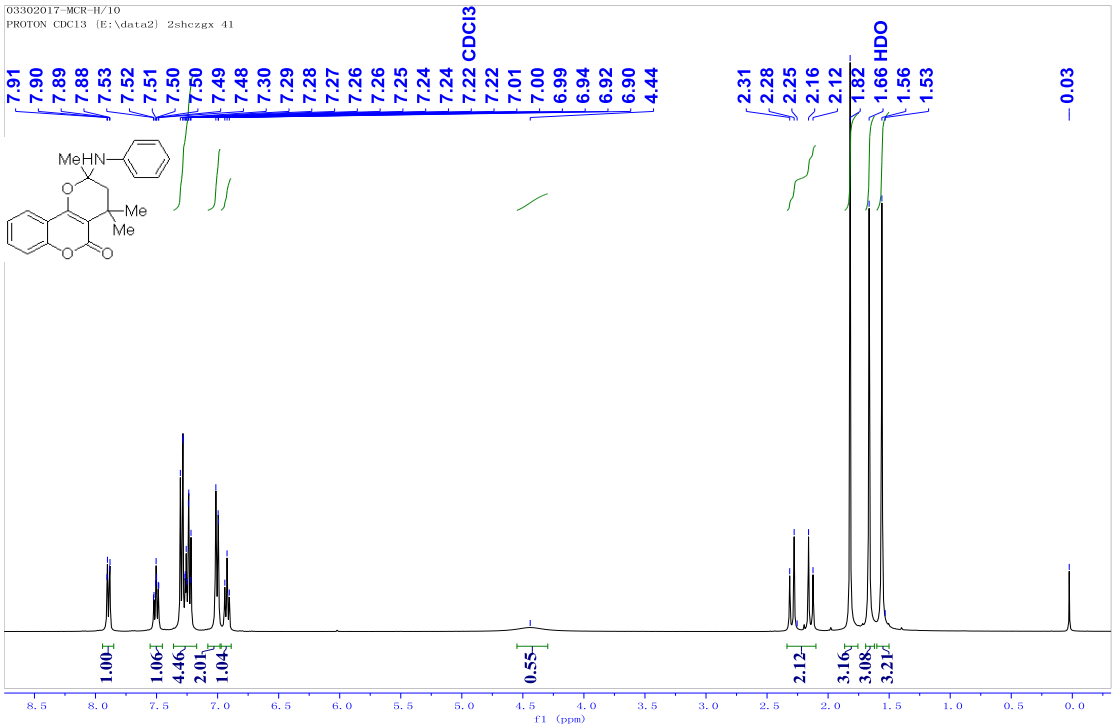


6c

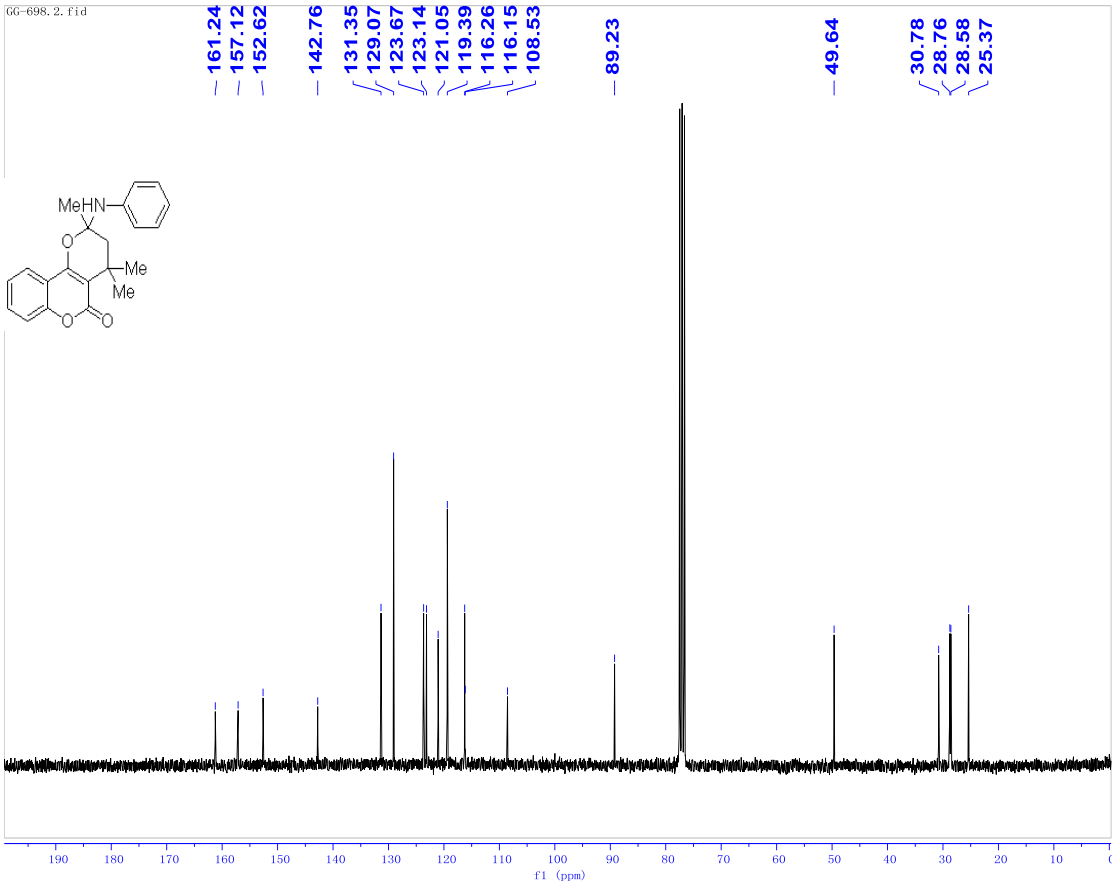
Yield 39%. m.p:152.5-152.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.43 (m, 2H), 7.30–7.25 (m, 1H), 7.16–7.10 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.72 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.37 (d, *J* = 2.0 Hz, 1H), 4.65 (s, 1H), 2.31 (d, *J* = 8.0 Hz, 2H), 2.23 (s, 2H), 2.14 (s, 3H), 1.79 – 1.35 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 157.4, 152.5, 144.8, 135.6, 133.5, 131.5, 123.7, 123.4, 123.3, 122.1, 116.1, 115.9, 108.2, 50.9, 49.9, 31.6, 30.9, 30.6, 29.2, 27.5, 22.6, 20.5. HRMS-ESI, m/z: 406.2032 $[M+H]^+$ (Calcd. for $C_{25}H_{28}NO_4^+$, 406.2013). Anal. Calcd. For $C_{25}H_{27}NO_4$: C, 74.05; H, 6.71; N, 3.45. Found: C, 73.45; H, 6.86; N, 3.29.

6. NMR Spectra of the products

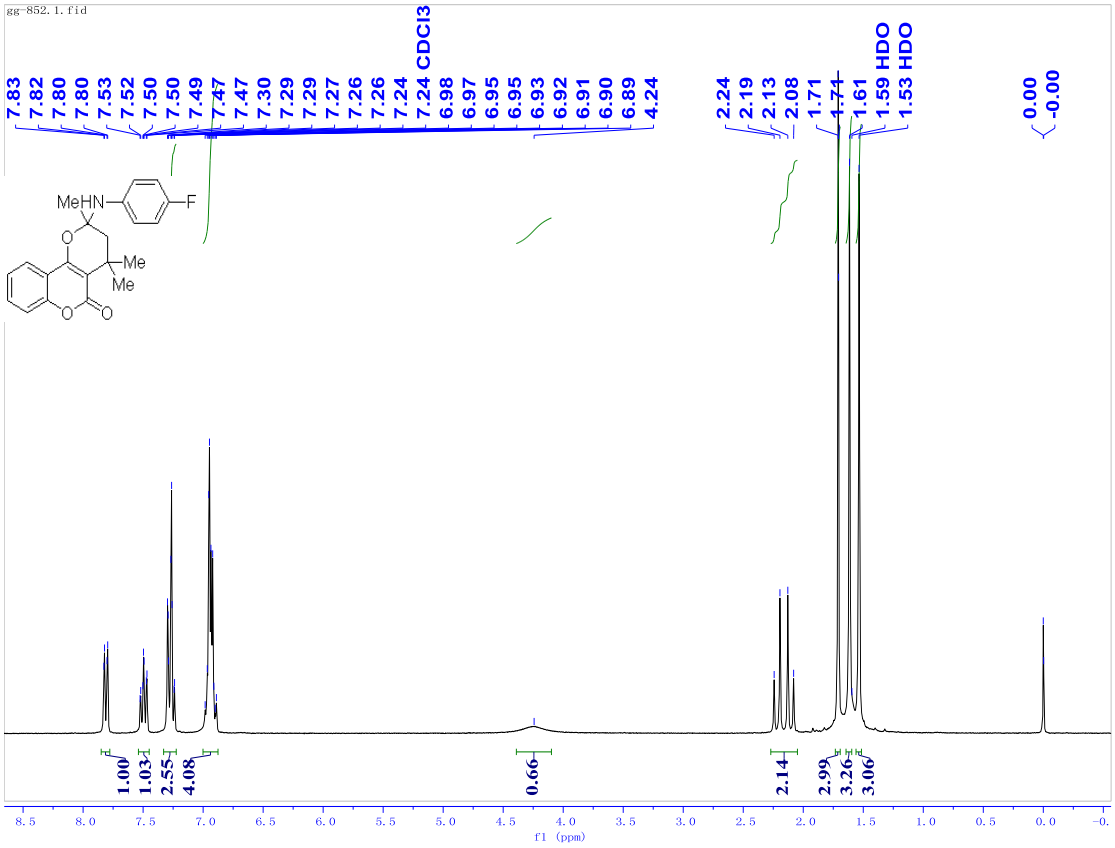
4a 2,4,4-Trimethyl-2-(phenylamino)-3,4-dihydro-*2H*,*5H*-pyrano[3,2-*c*]chromen-5-one



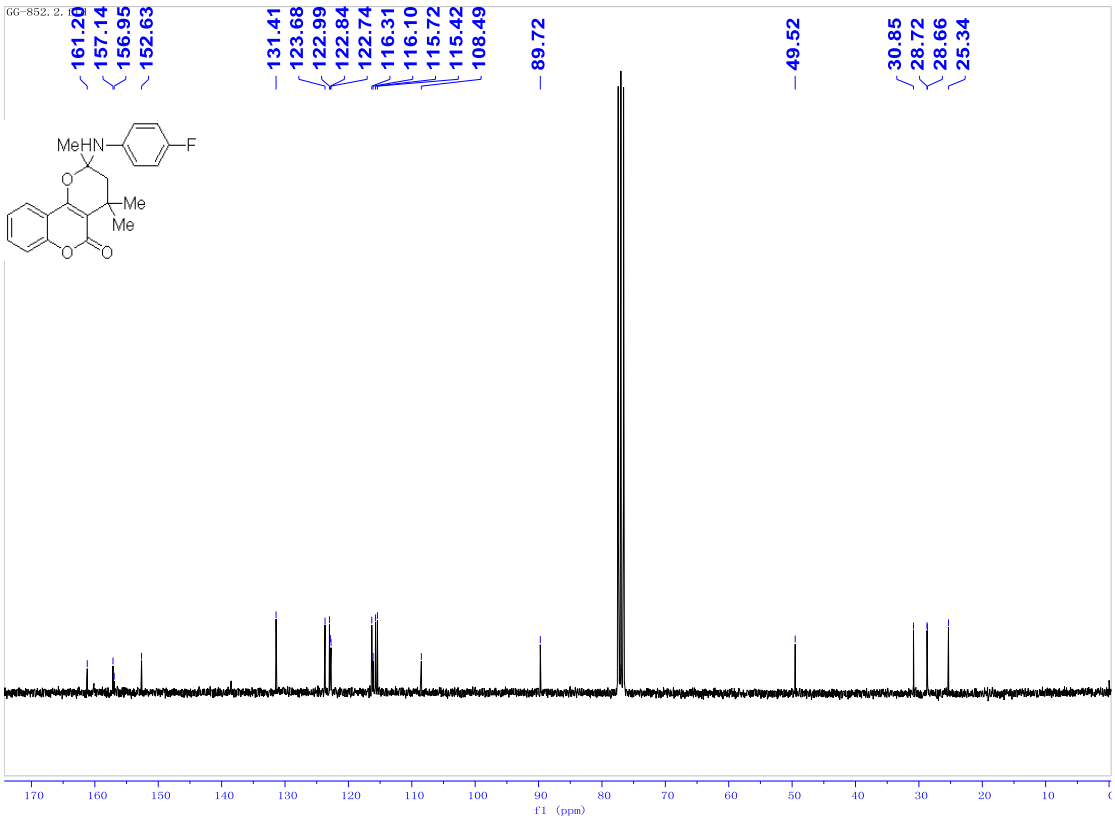
4a 2,4,4-Trimethyl-2-(phenylamino)-3,4-dihydro-*2H*,*5H*-pyrano[3,2-*c*]chromen-5-one



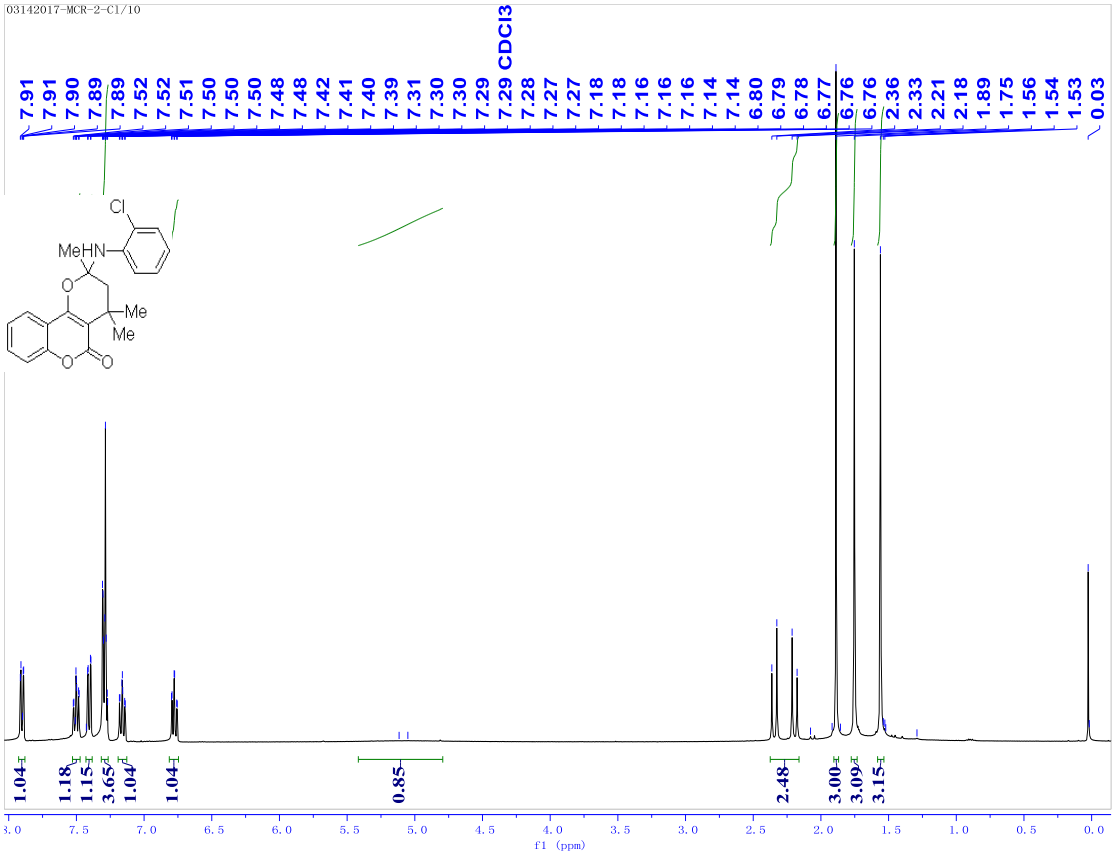
4b 2-((4-Fluorophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one



4b 2-((4-Fluorophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one



4c 2-((2-Chlorophenyl)amino)-2,4,4-trimethyl-3,4- dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



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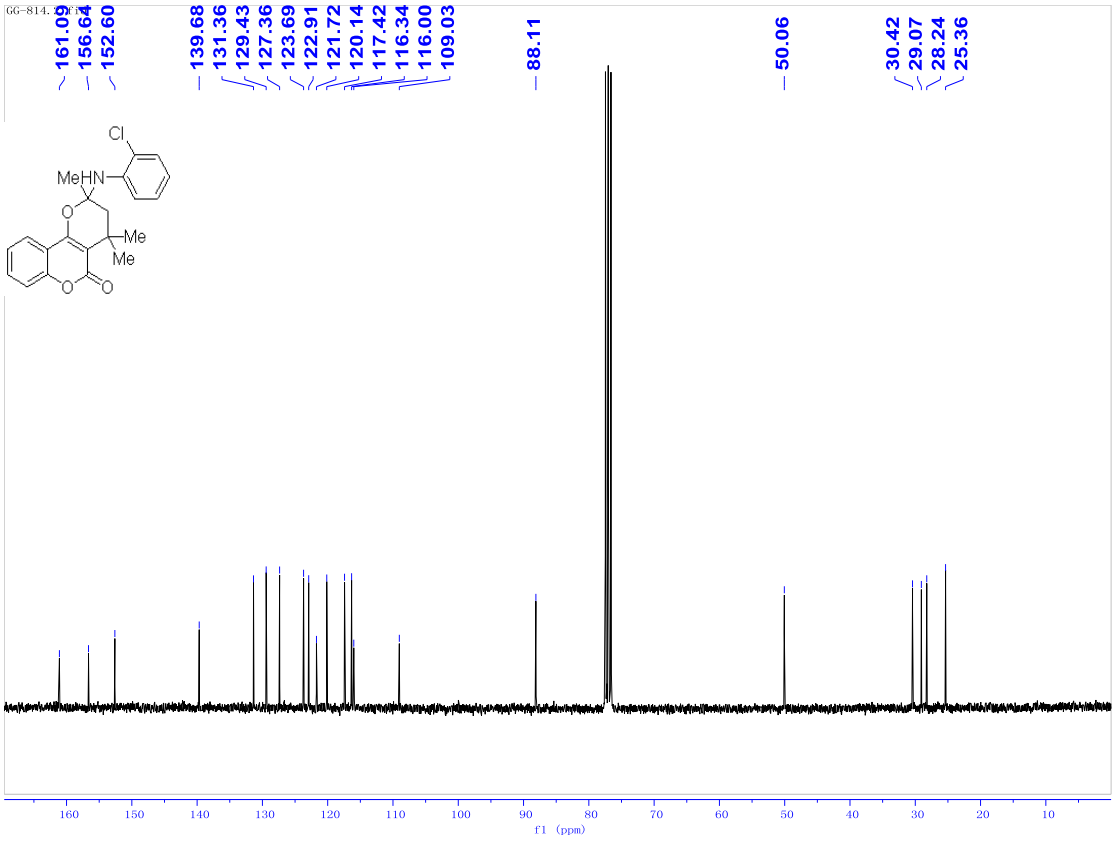
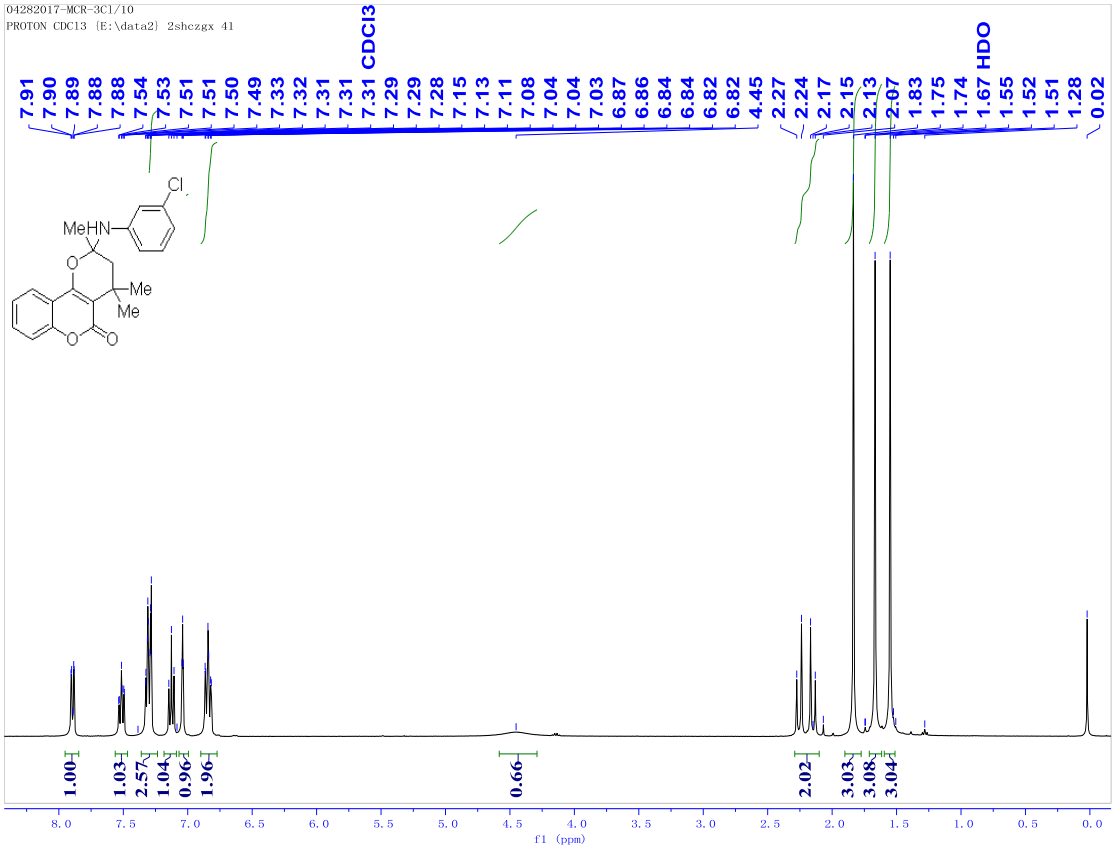
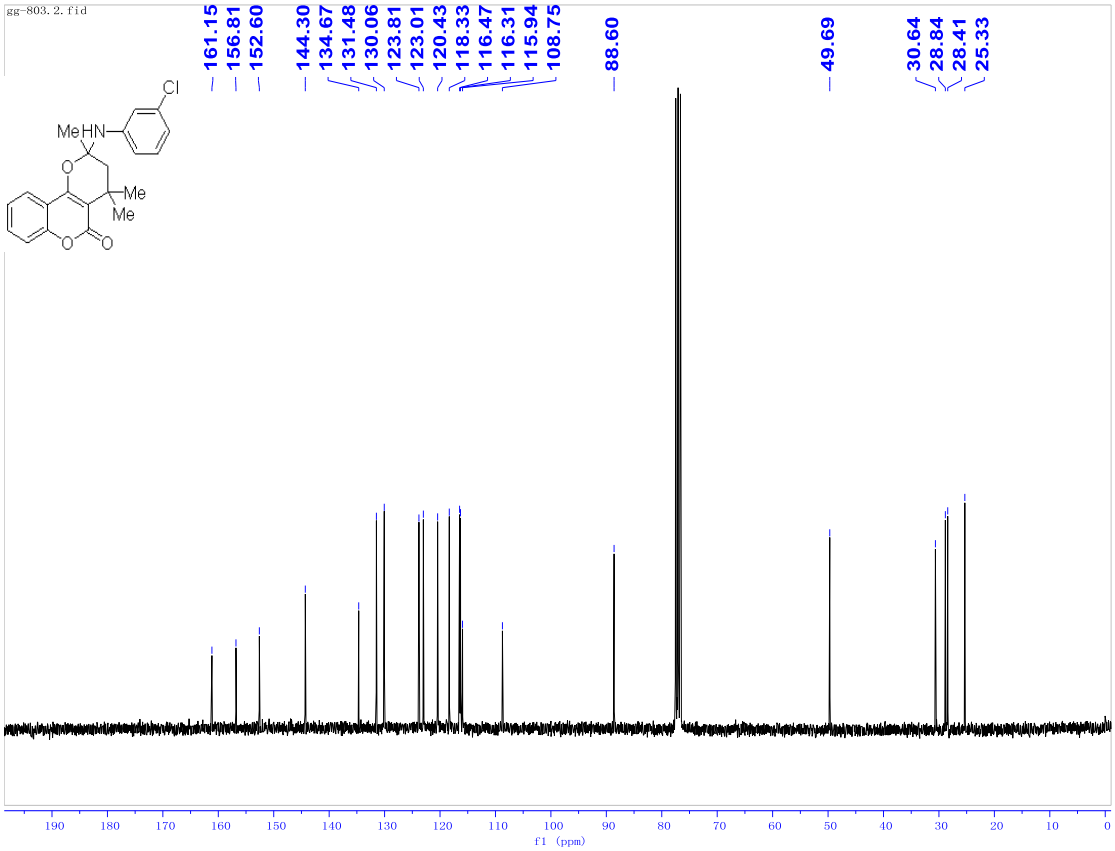


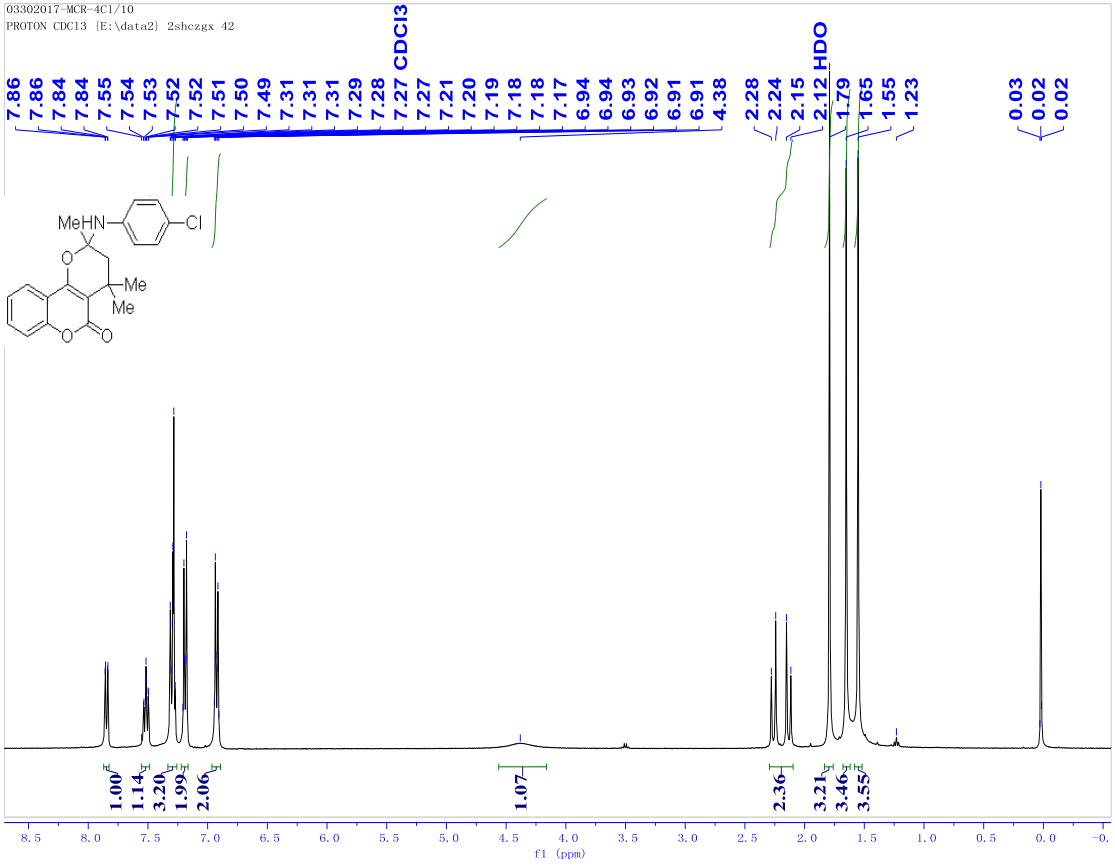
4d 2-((3-Chlorophenyl)amino)-2,4,4-trimethyl-3,4- dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



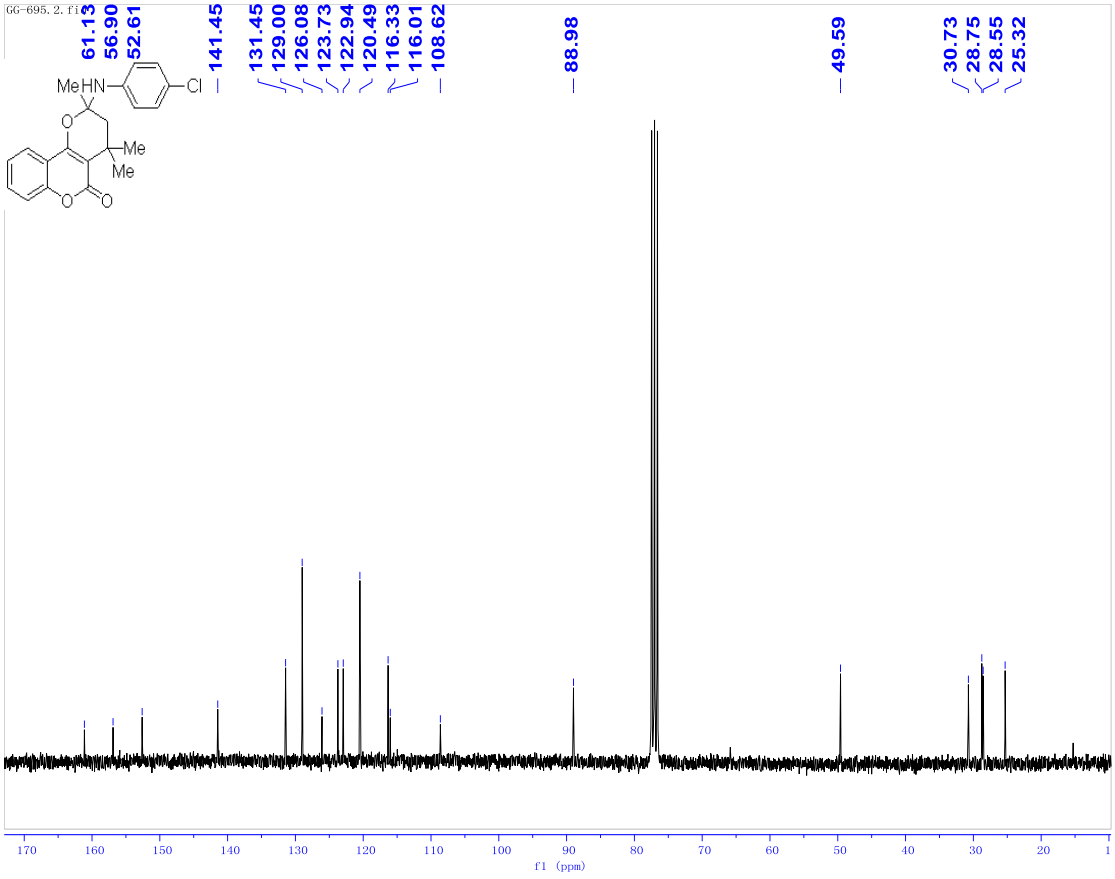
4d 2-((3-Chlorophenyl)amino)-2,4,4-trimethyl-3,4- dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



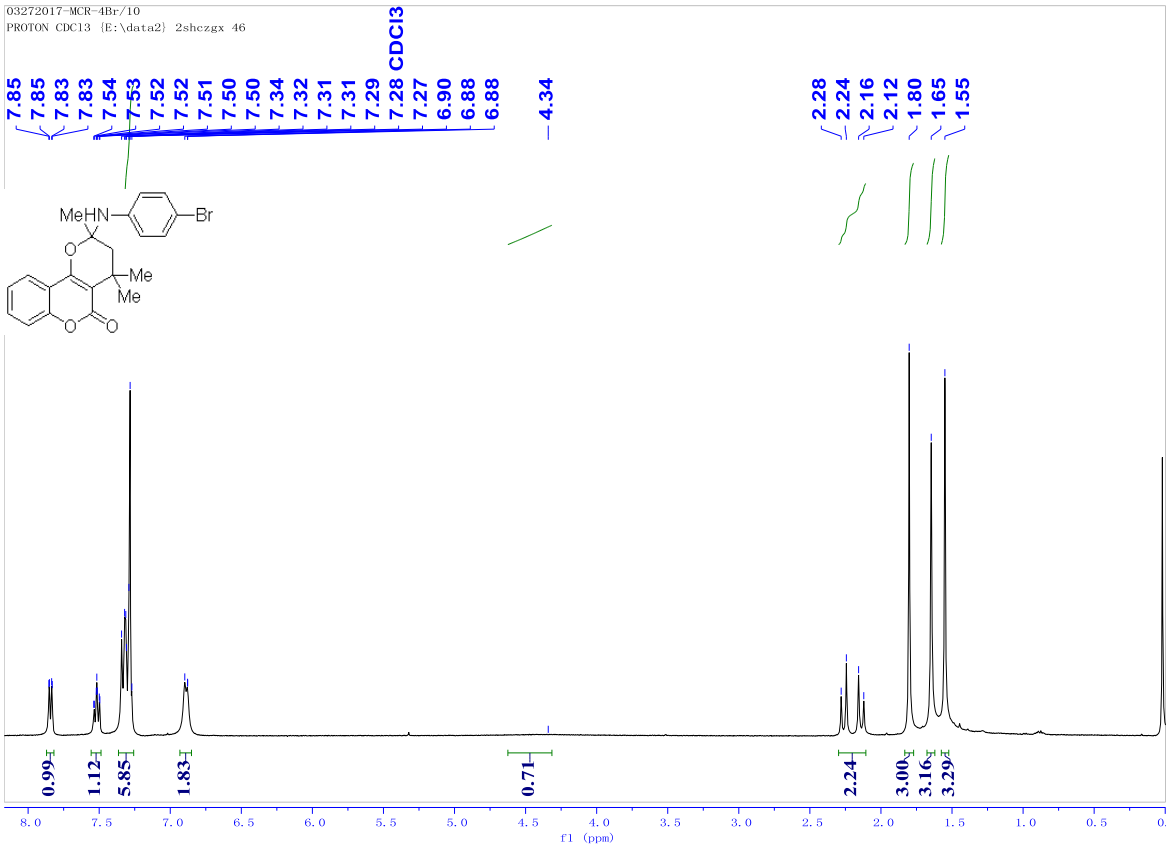
4e 2-((4-Chlorophenyl)amino)-2,4,4-trimethyl-3,4- dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



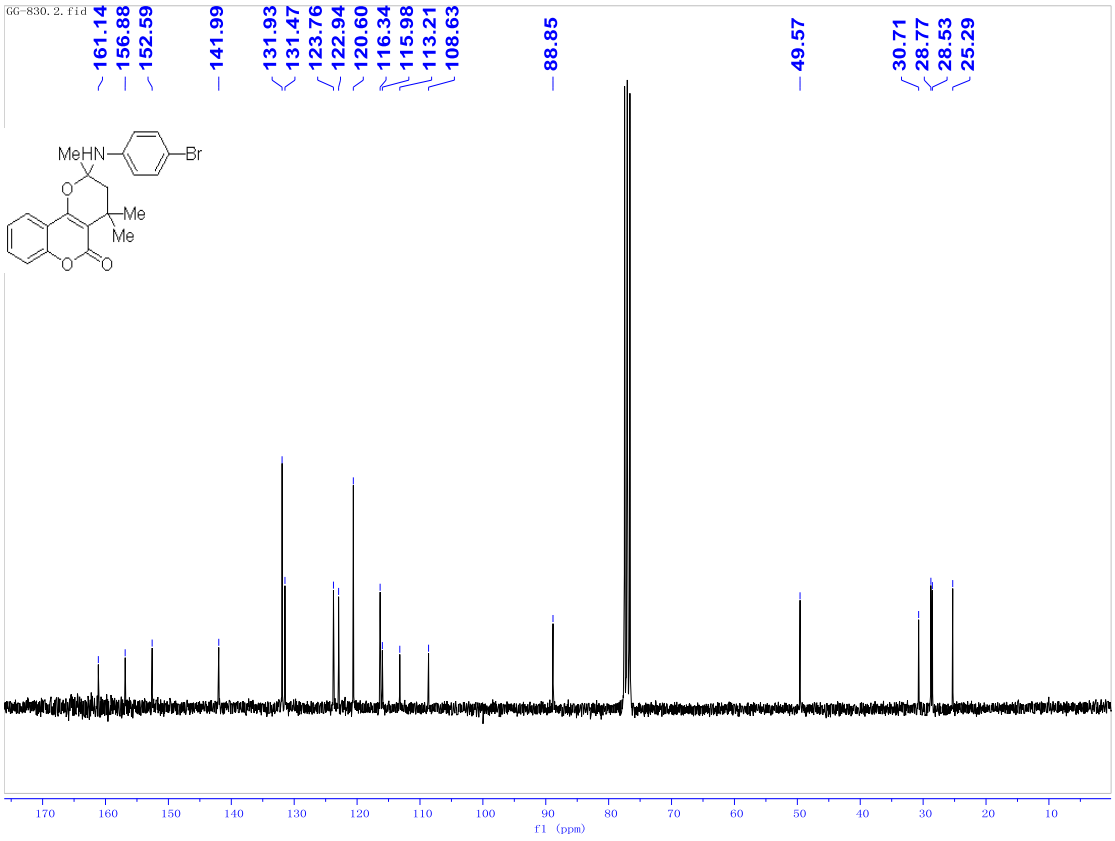
4e 2-((4-Chlorophenyl)amino)-2,4,4-trimethyl-3,4- dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



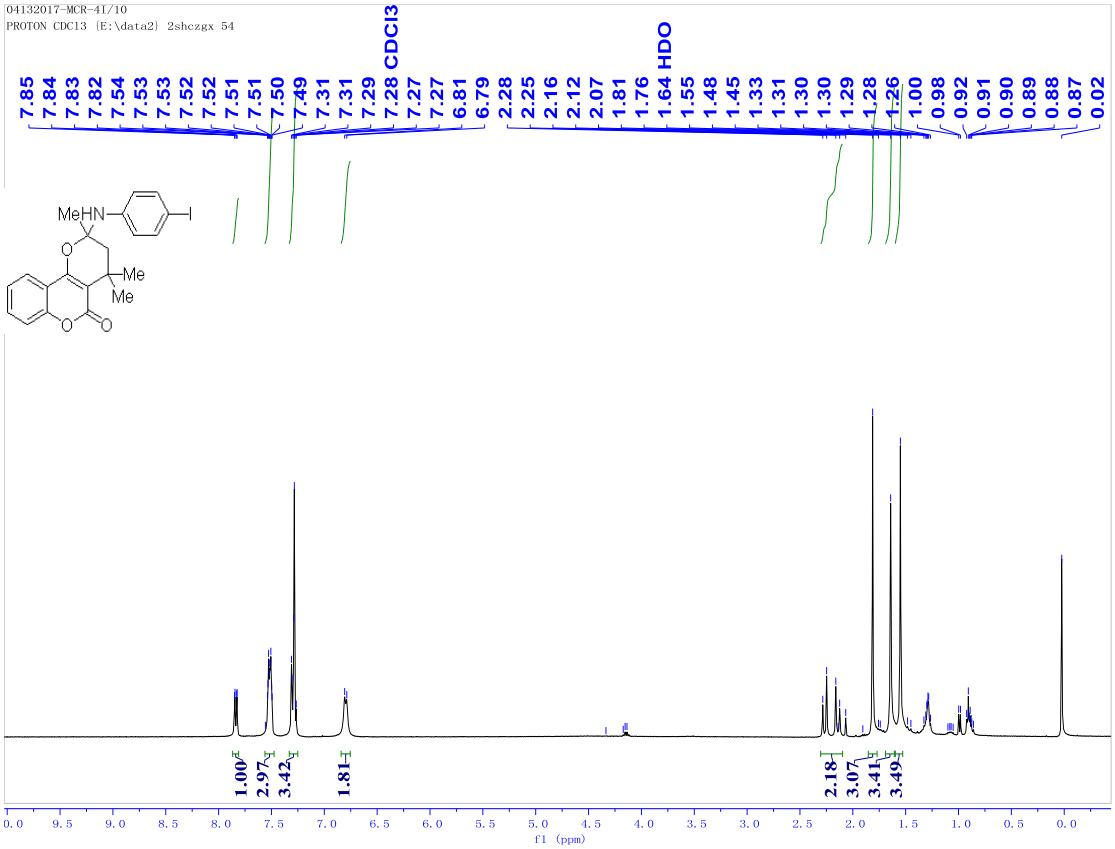
4f 2-((4-Bromophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



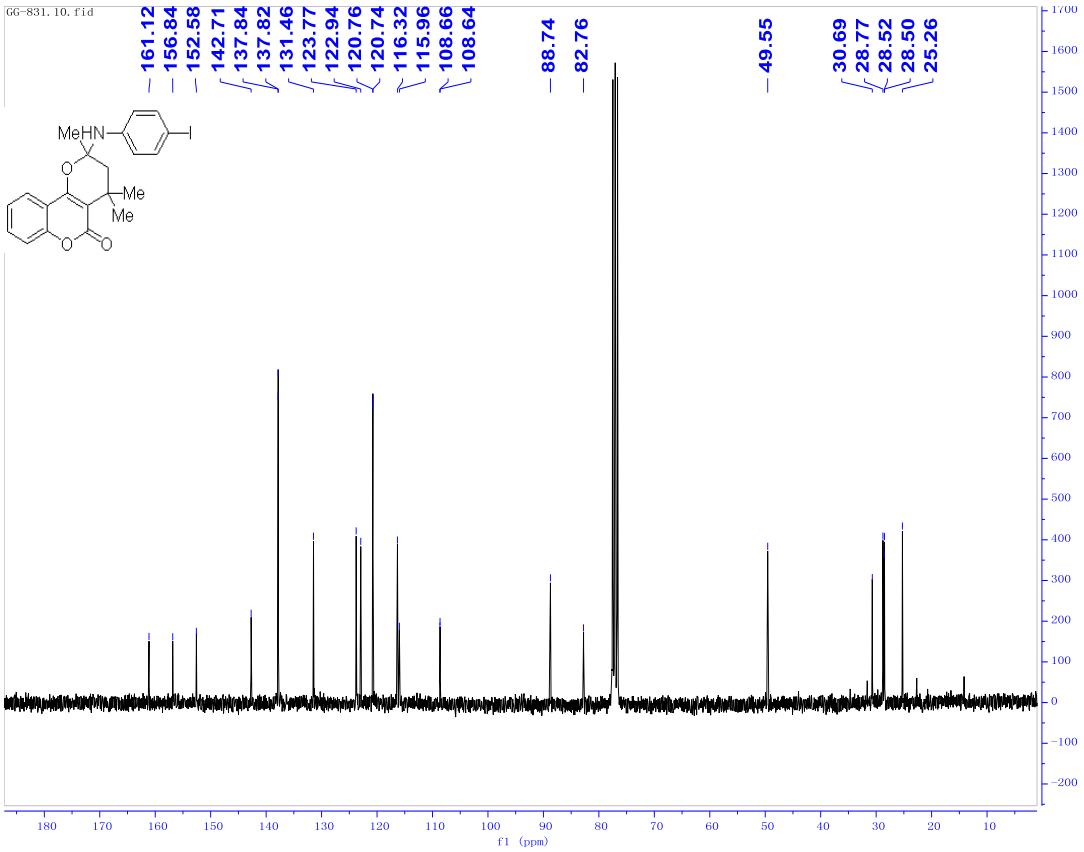
4f 2-((4-Bromophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



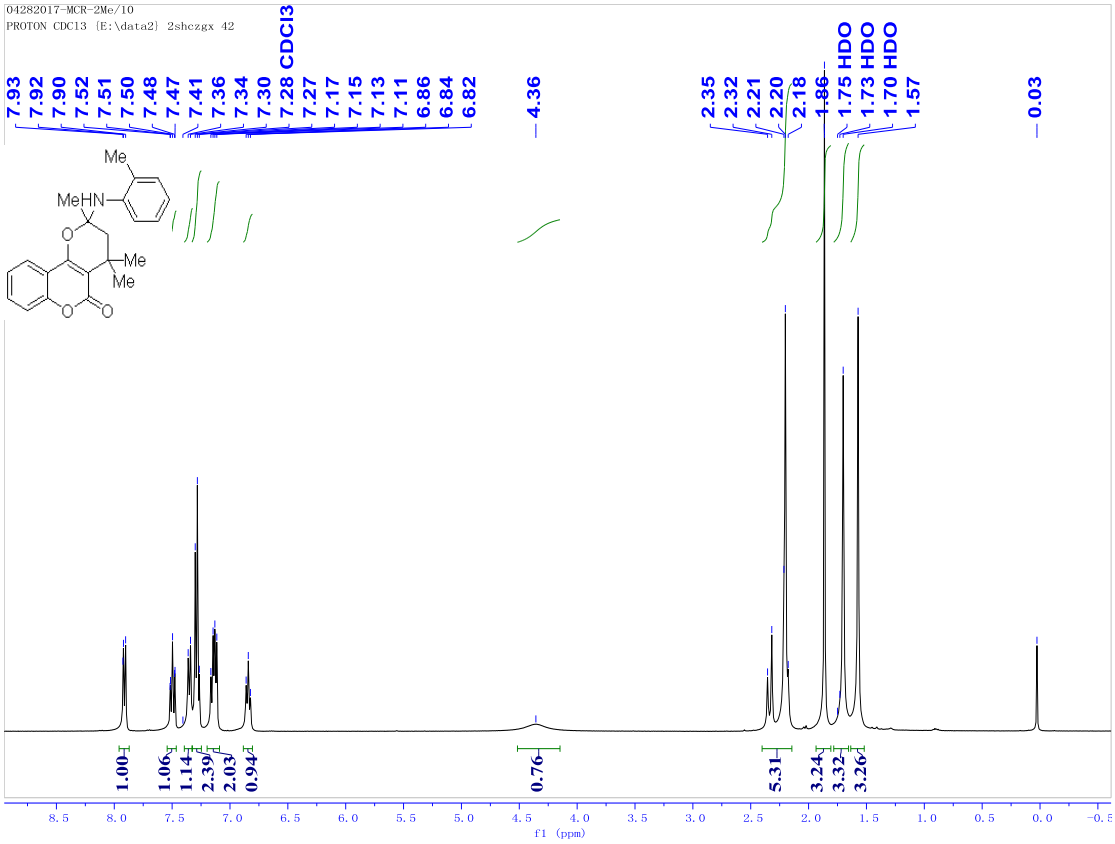
4g 2-((4- Iodophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



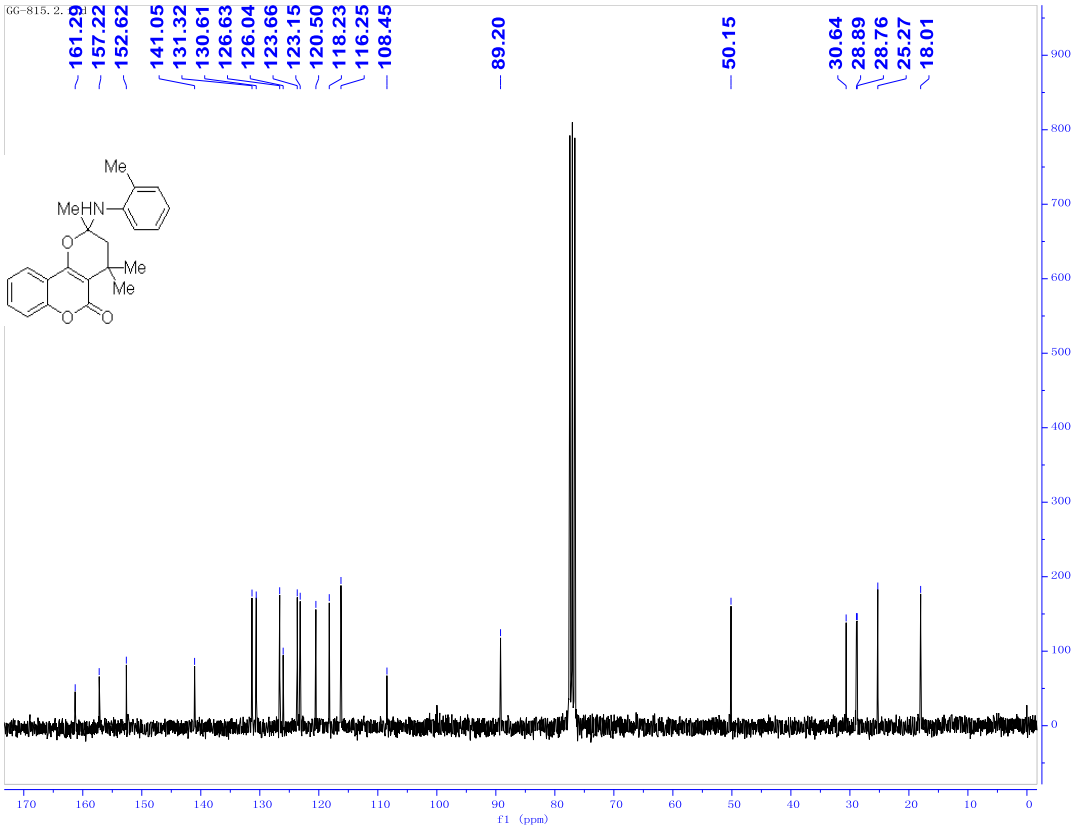
4g 2-((4- Iodophenyl)amino)-2,4,4-trimethyl-3,4-dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



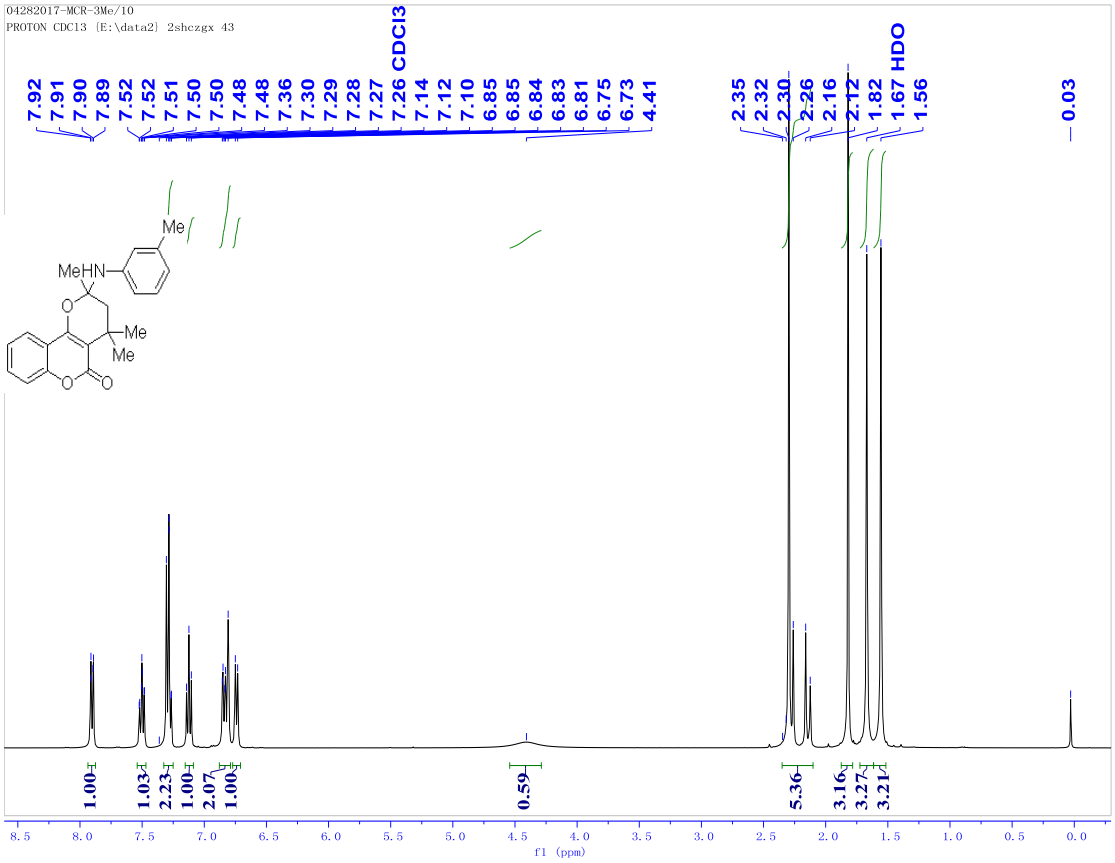
4h 2, 4, 4-Trimethyl-2-(*o*-tolylamino)-3,4- dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



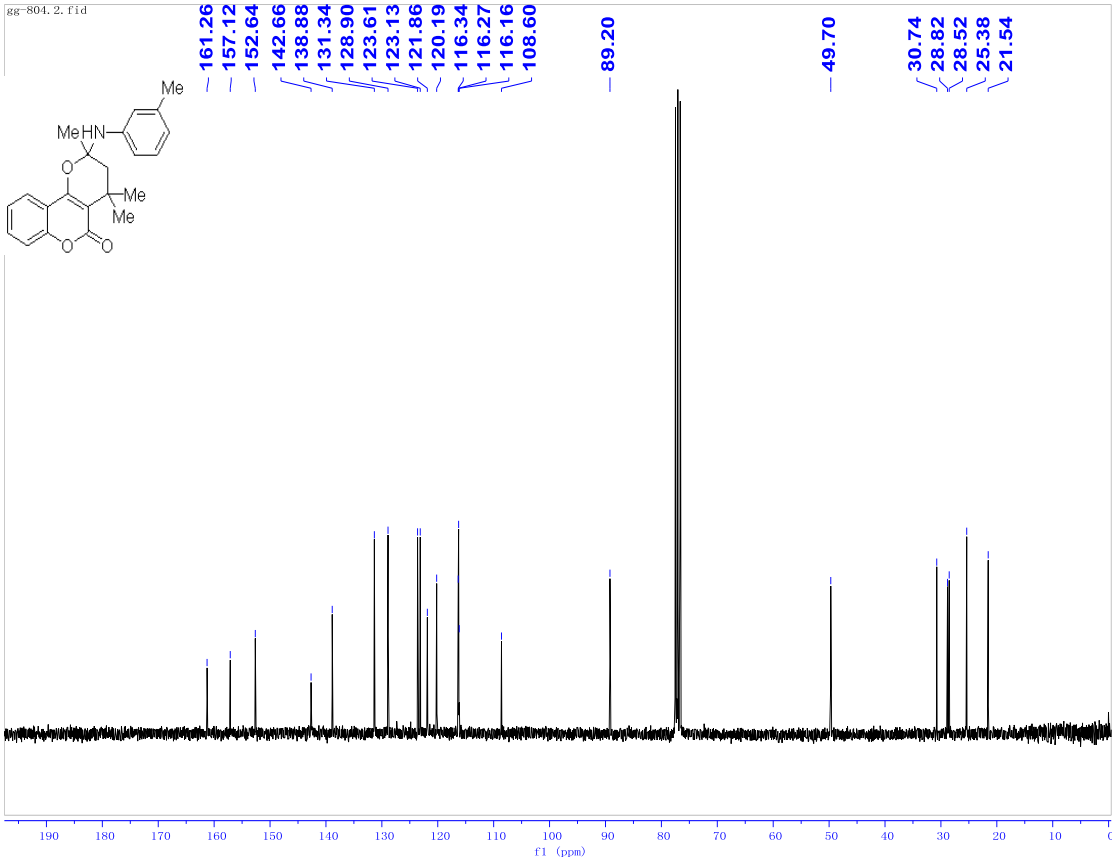
4h 2, 4, 4-Trimethyl-2-(*o*-tolylamino)-3,4- dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



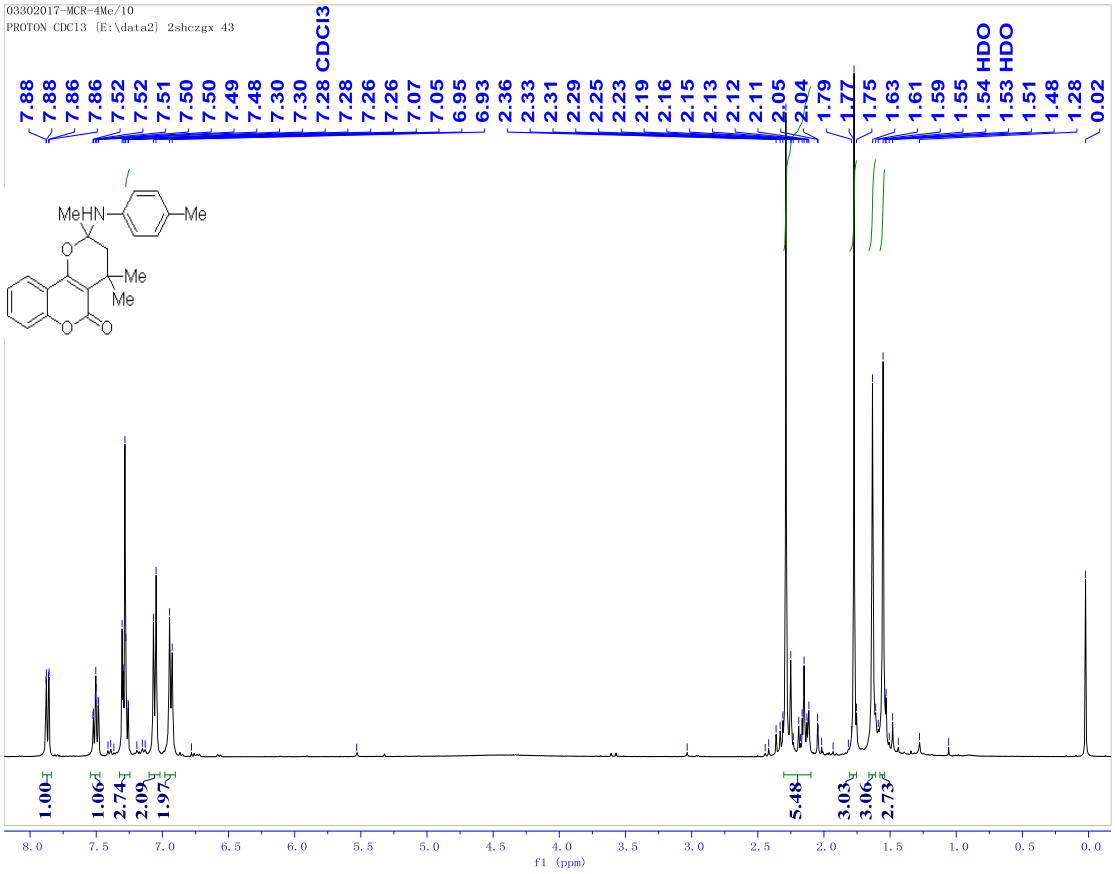
4i 2, 4, 4-Trimethyl-2-(*m*-tolylamino)-3,4- dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one



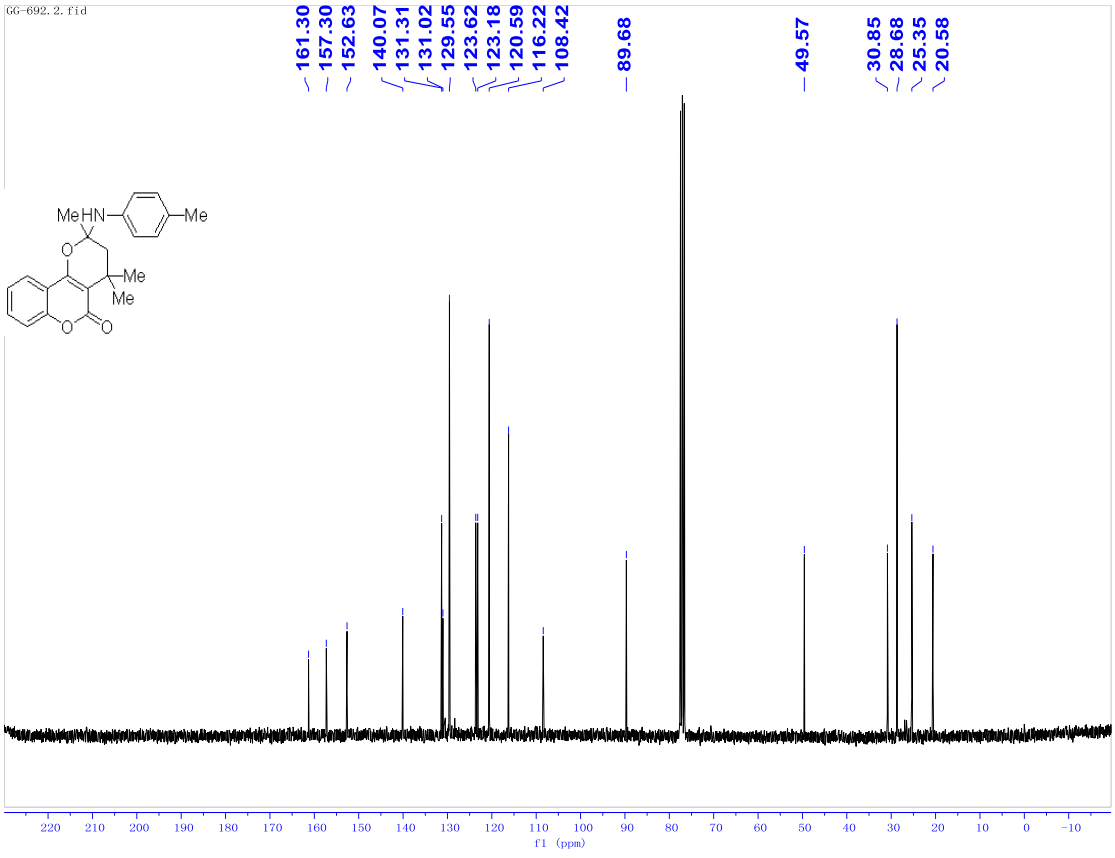
4i 2, 4, 4-Trimethyl-2-(*m*-tolylamino)-3,4-dihydro-*2H,5H*-pyrano[3,2-c]chromen-5-one



4j 2, 4, 4-Trimethyl-2-(p-tolylamino)-3,4- dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



4j 2, 4, 4-Trimethyl-2-(p-tolylamino)-3,4- dihydro-*2H*,*5H*-pyrano[3,2-c]chromen-5-one



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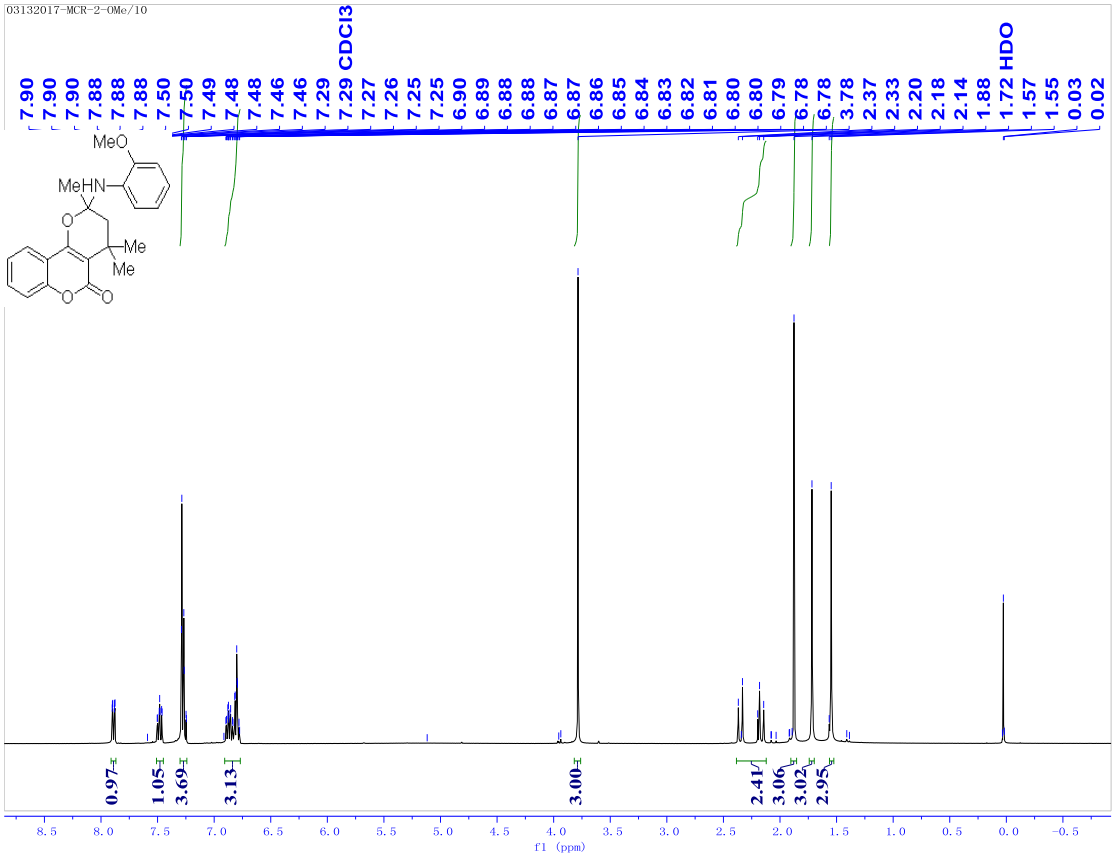

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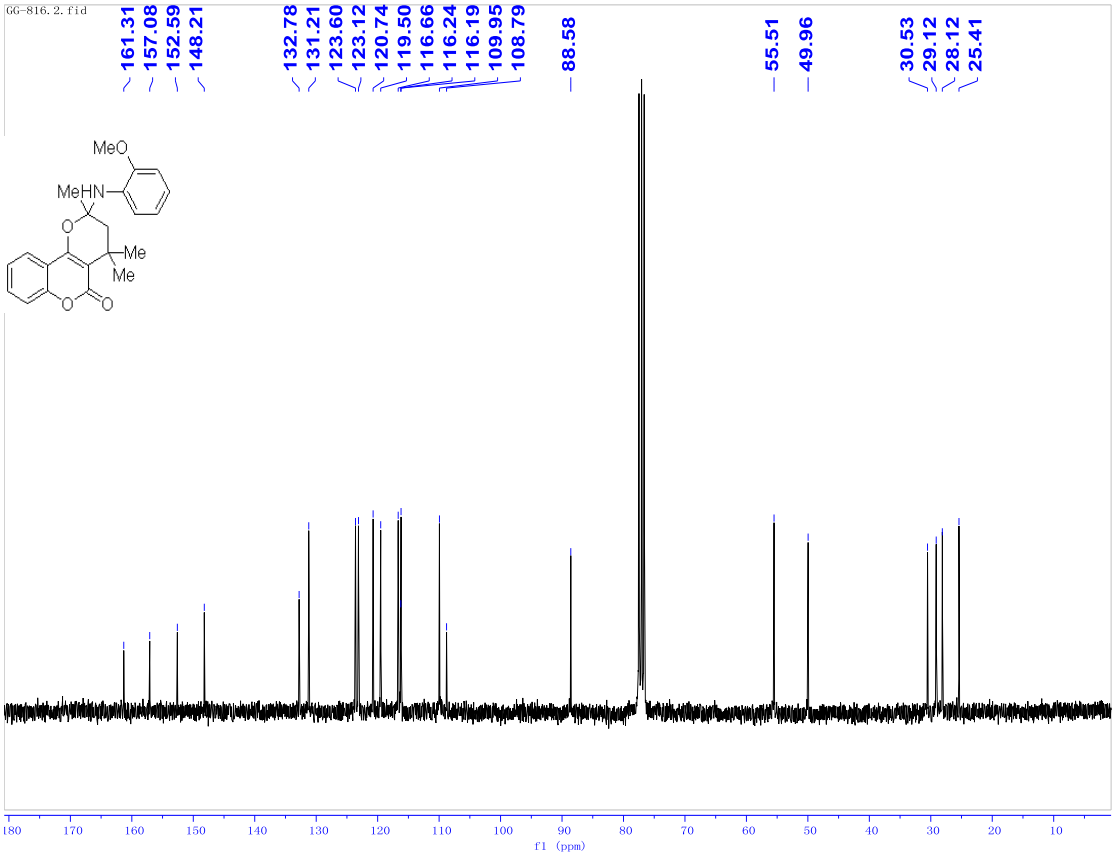

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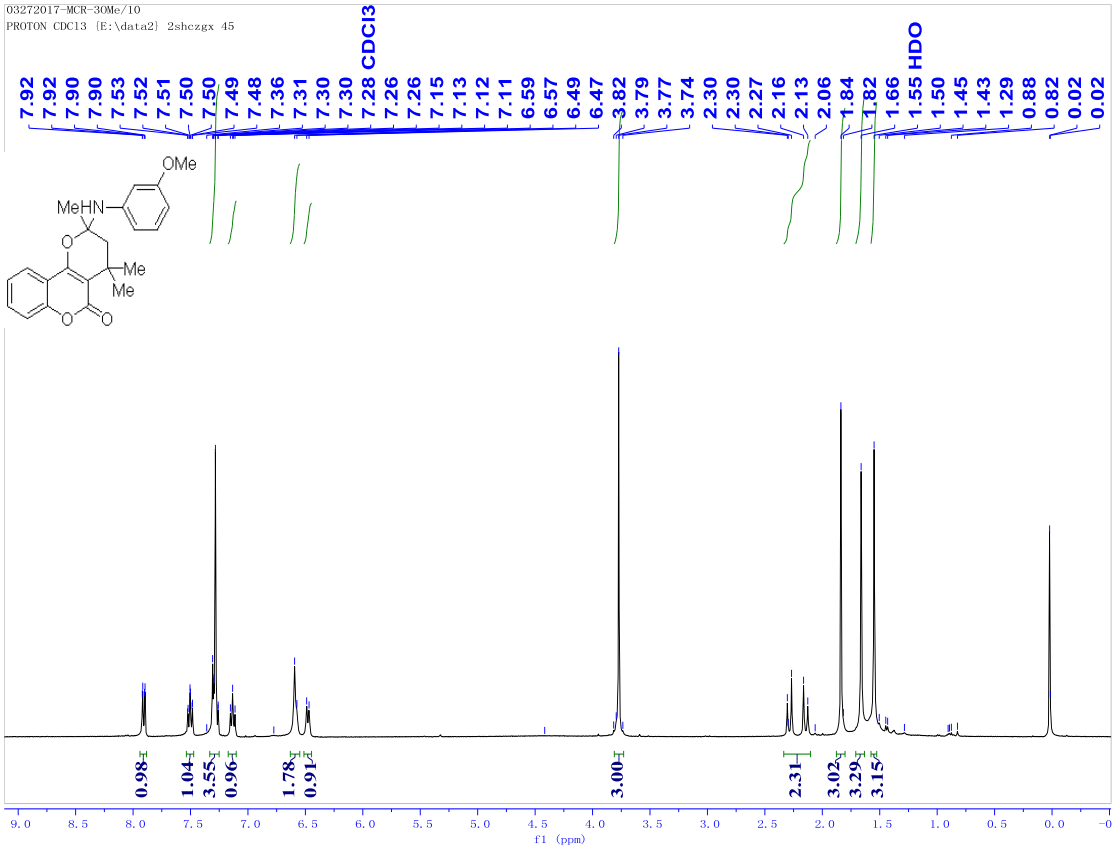

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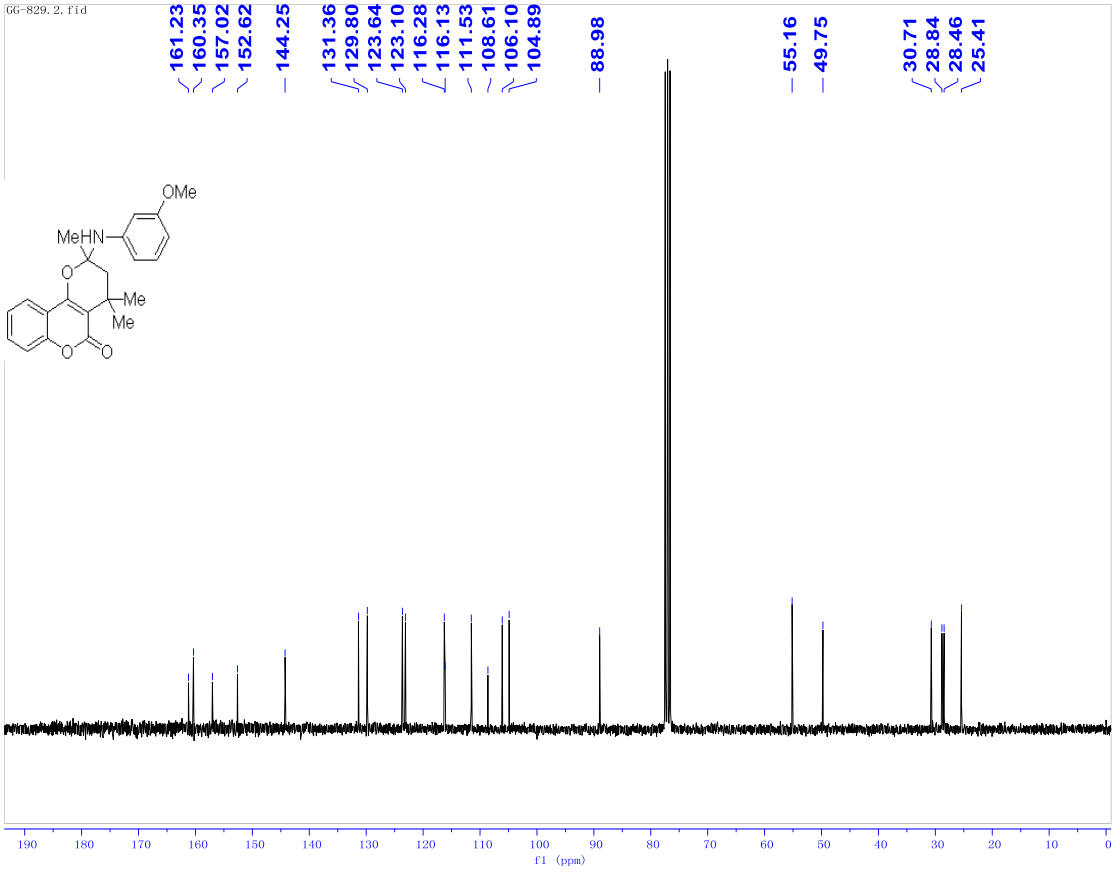

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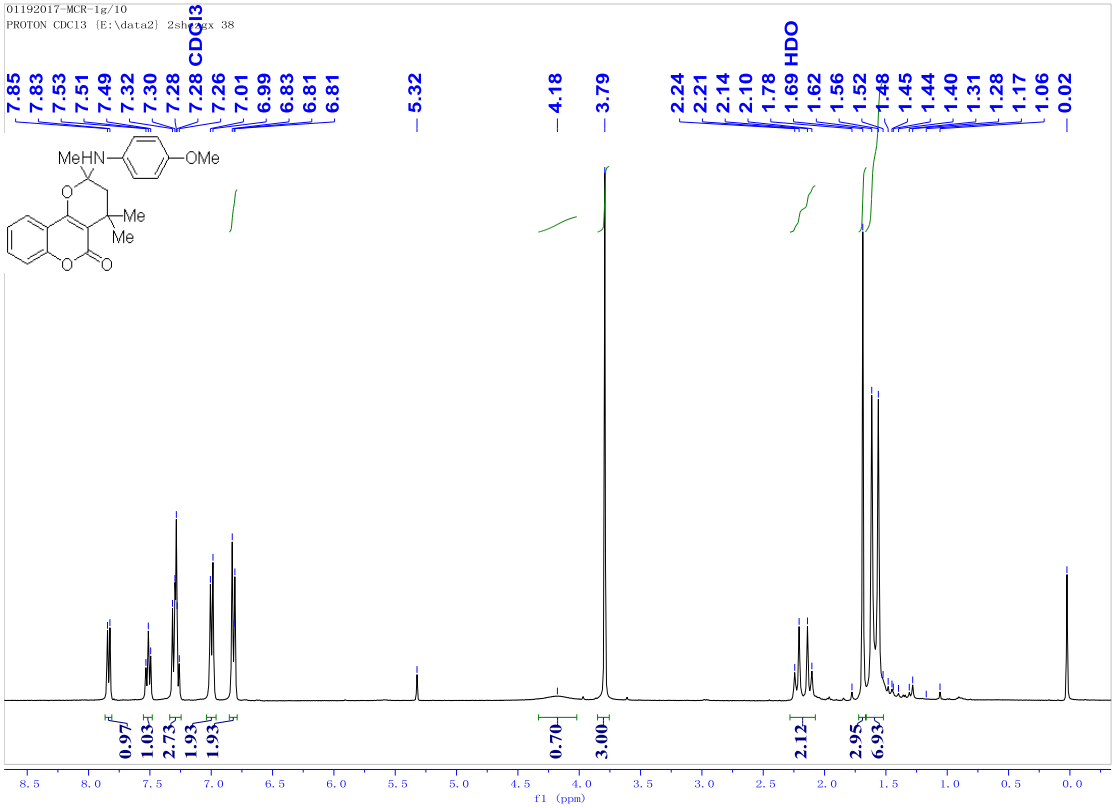

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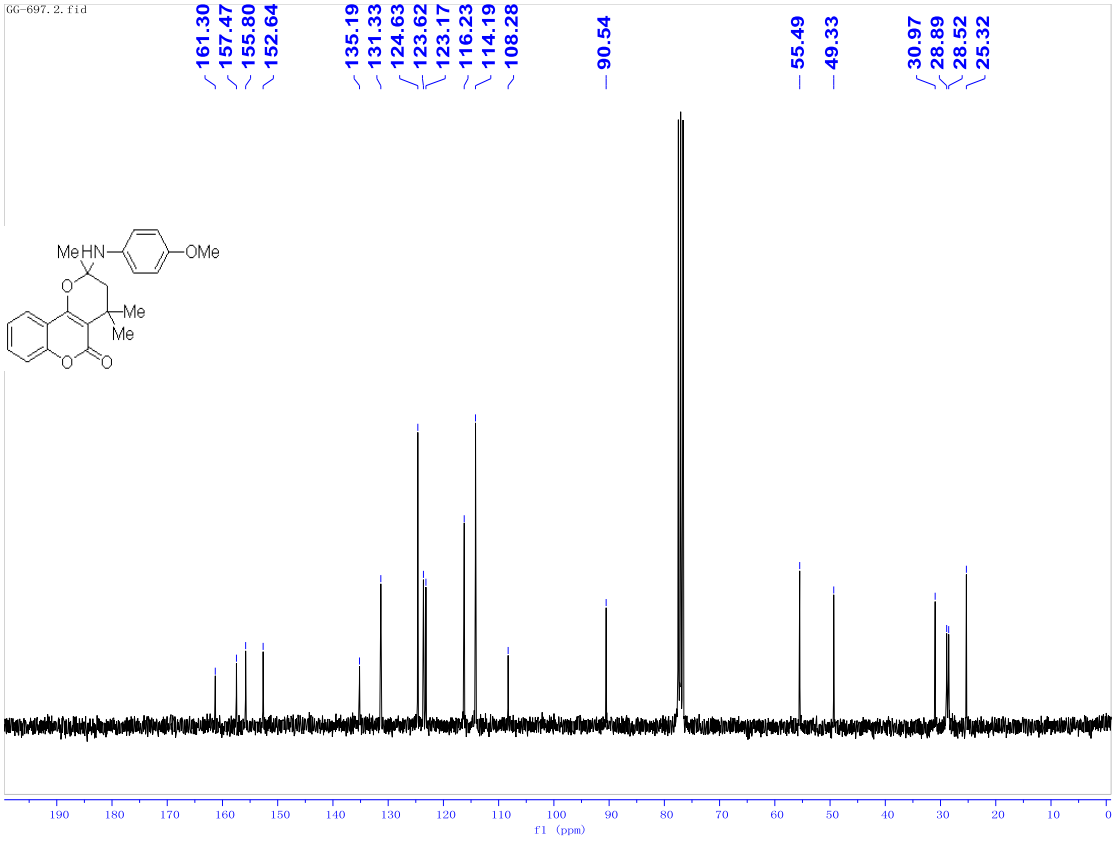

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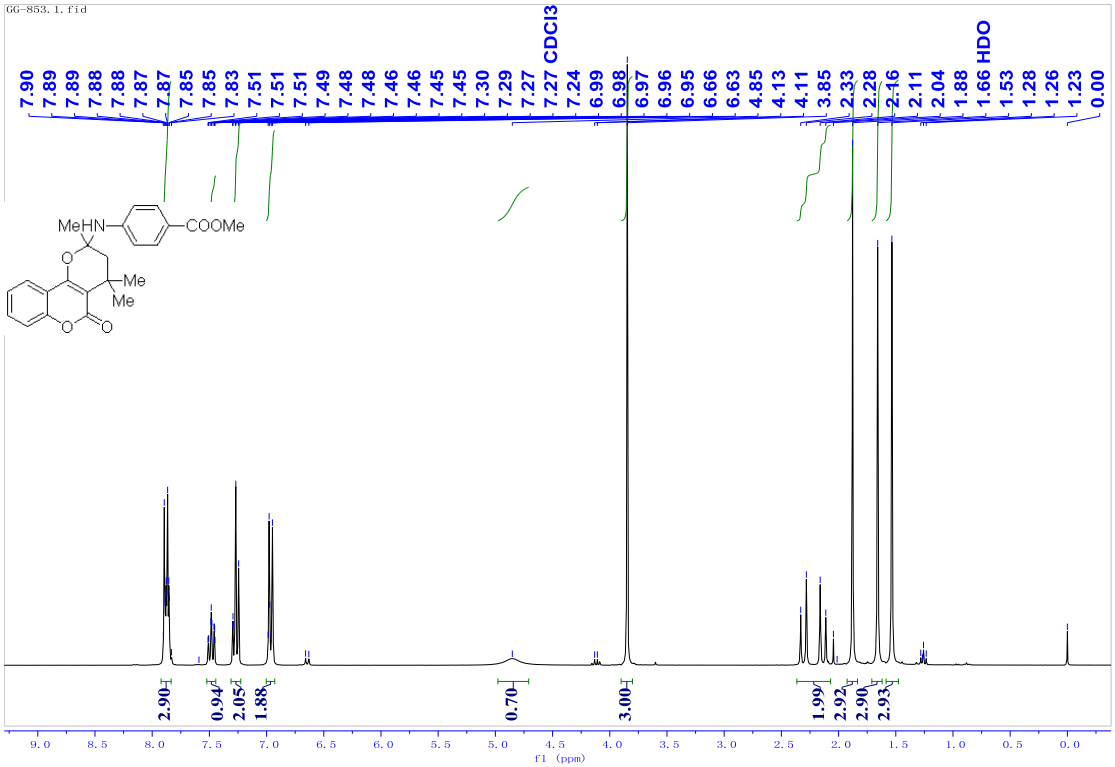

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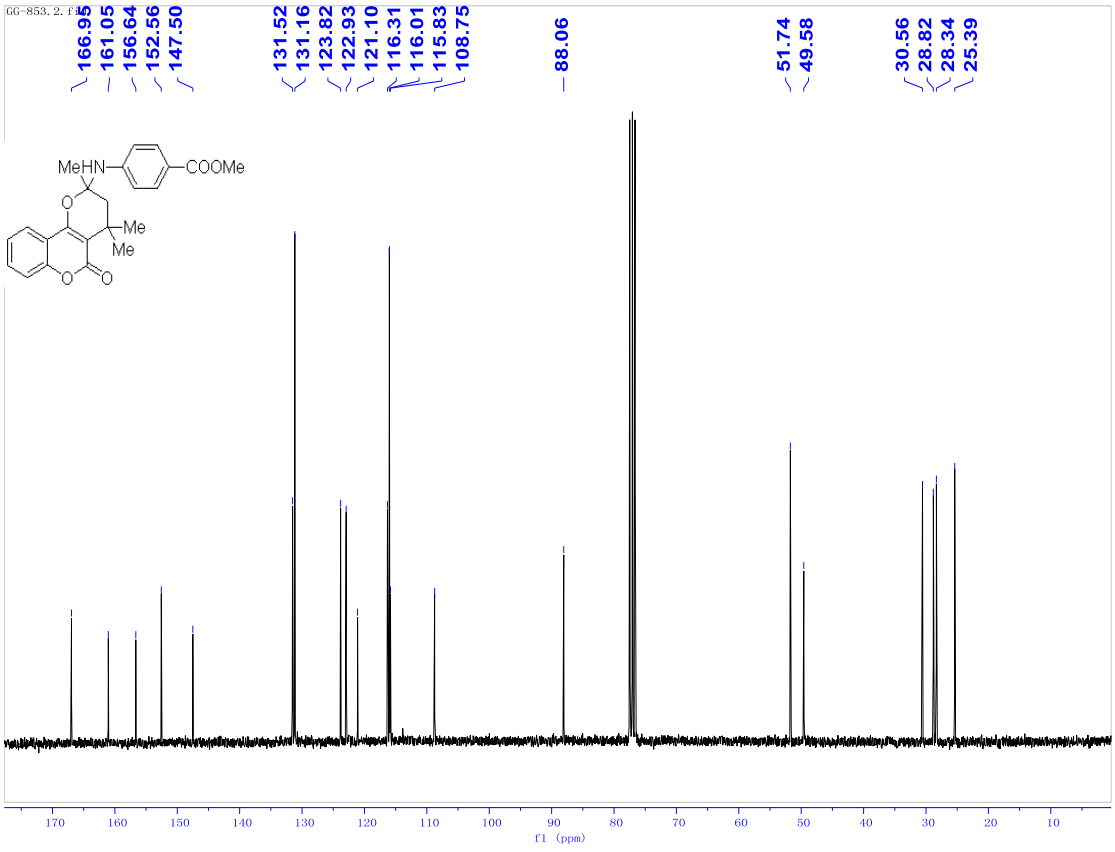

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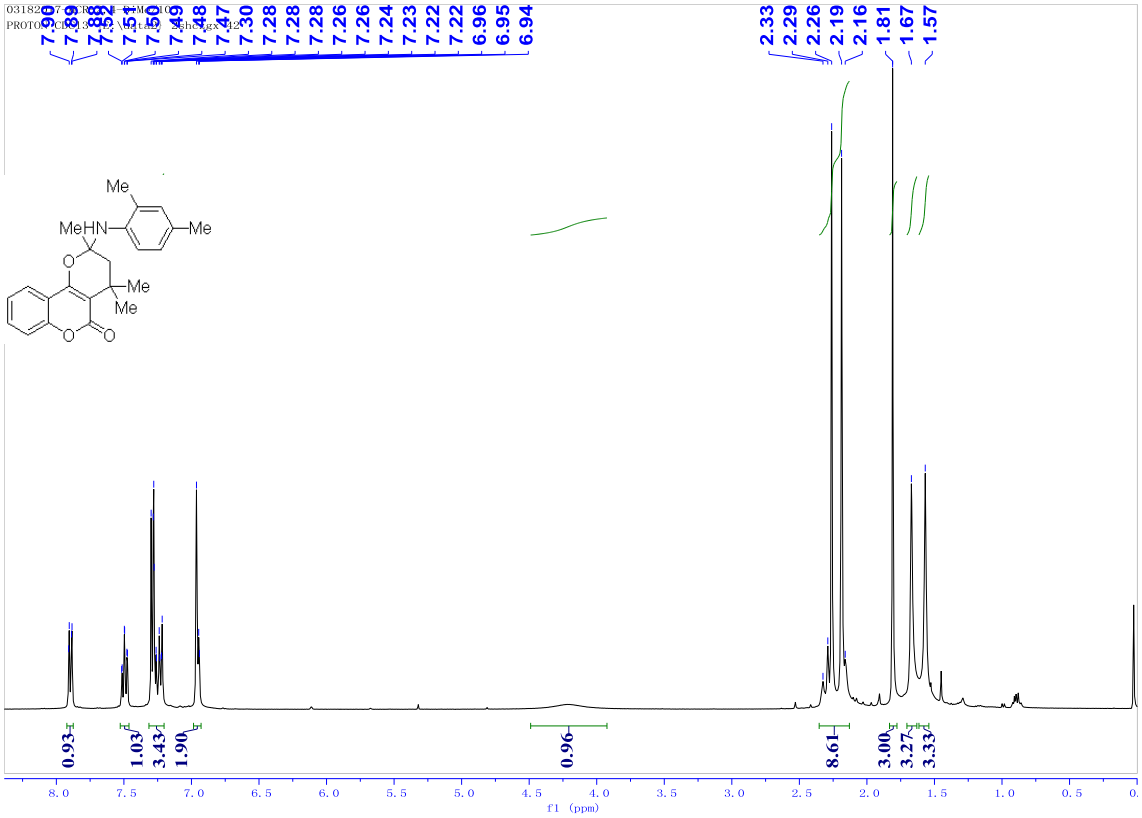

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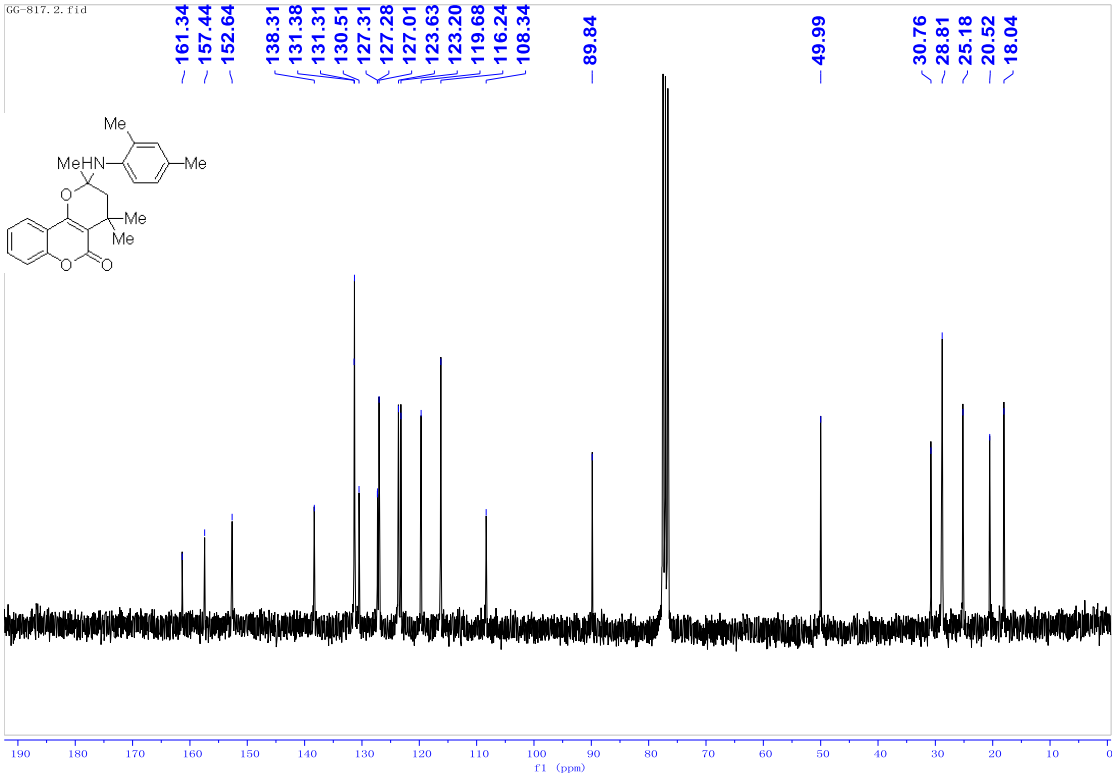

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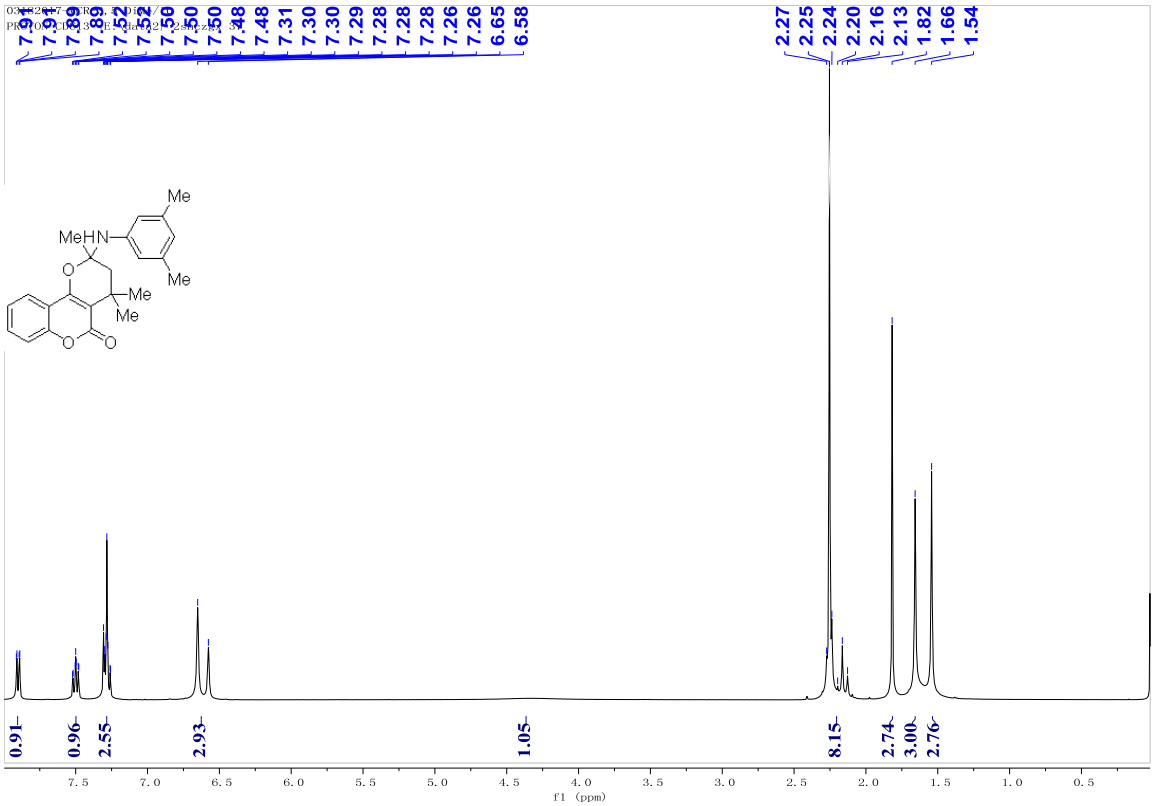

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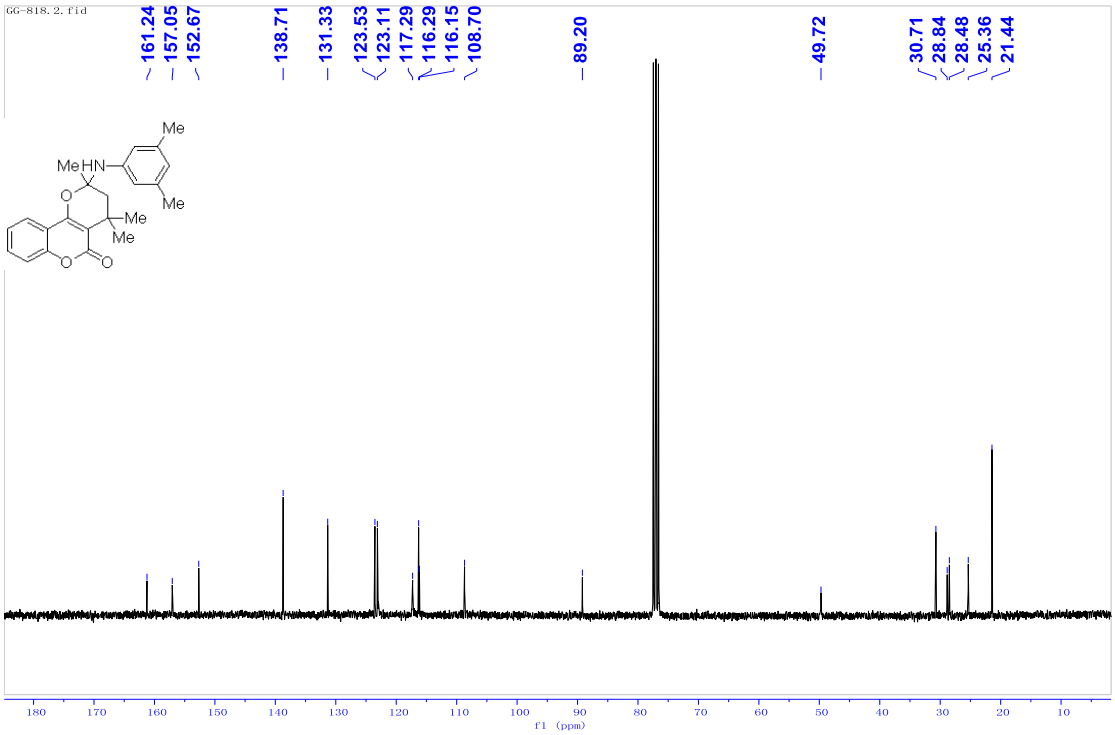

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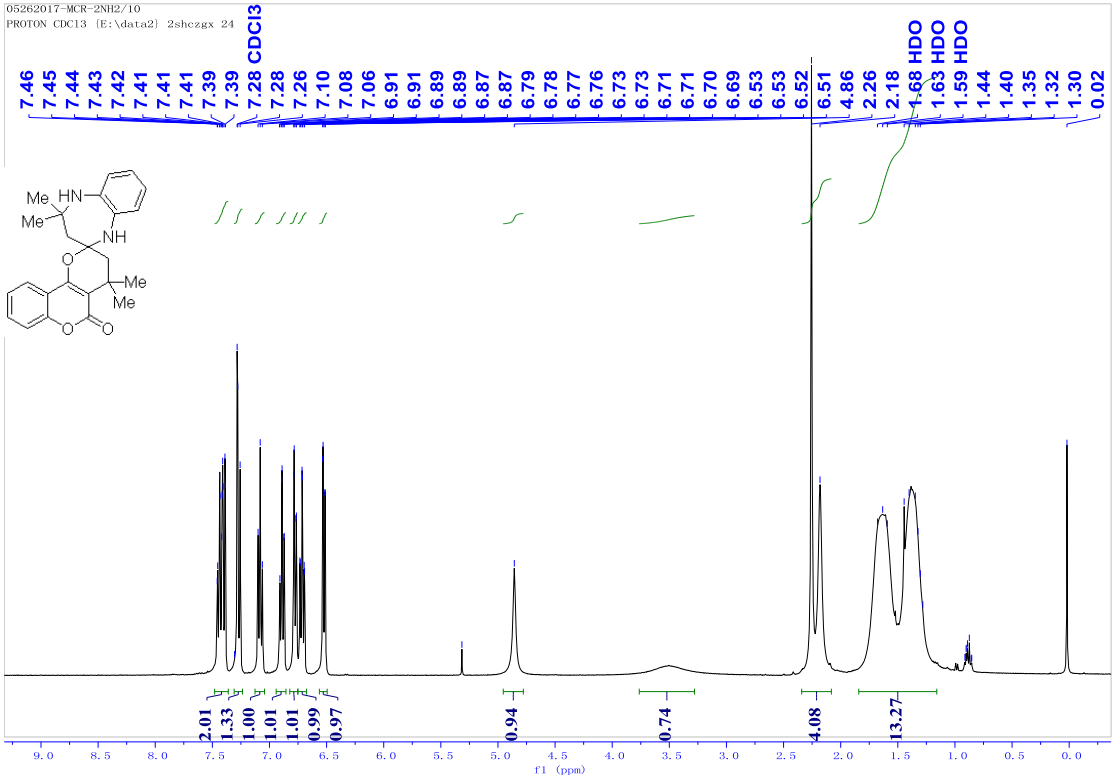
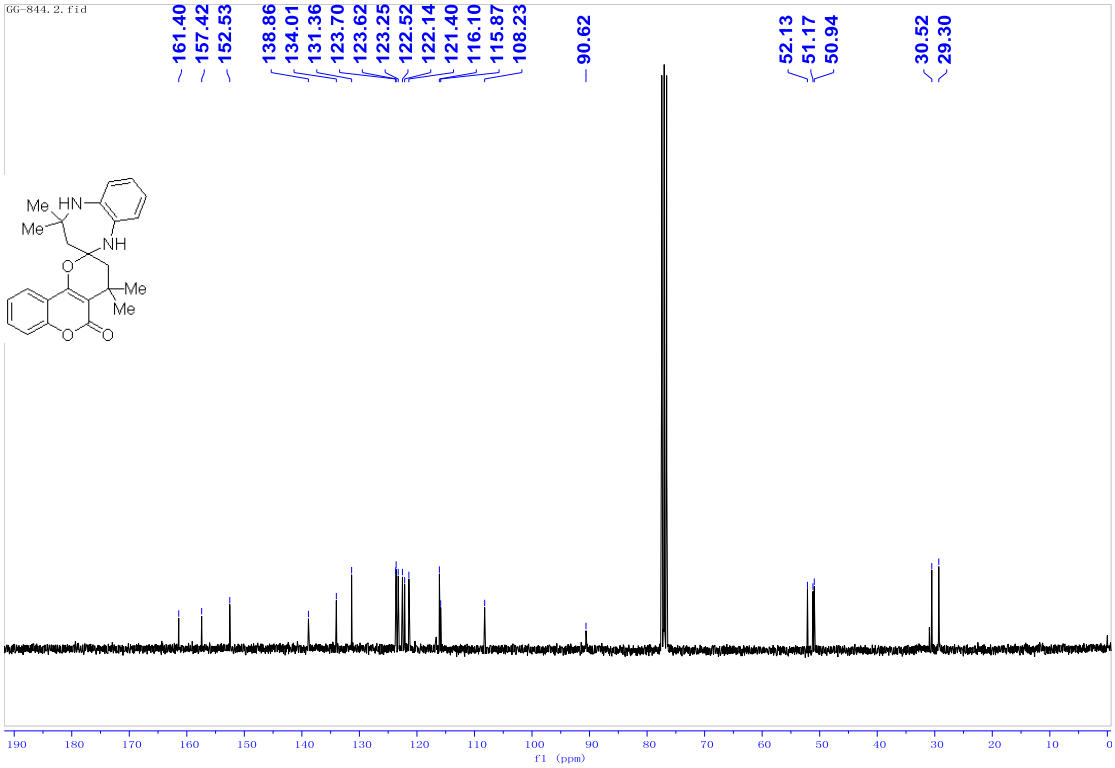


5a 4,4,4',4'-Tetramethyl-1,3,3',4,4',5-hexahydro-*5'H*-spiro[benzo-[b][1,4]diazepine-2,2'-pyrano[3,2-c]chromen]-5'-one



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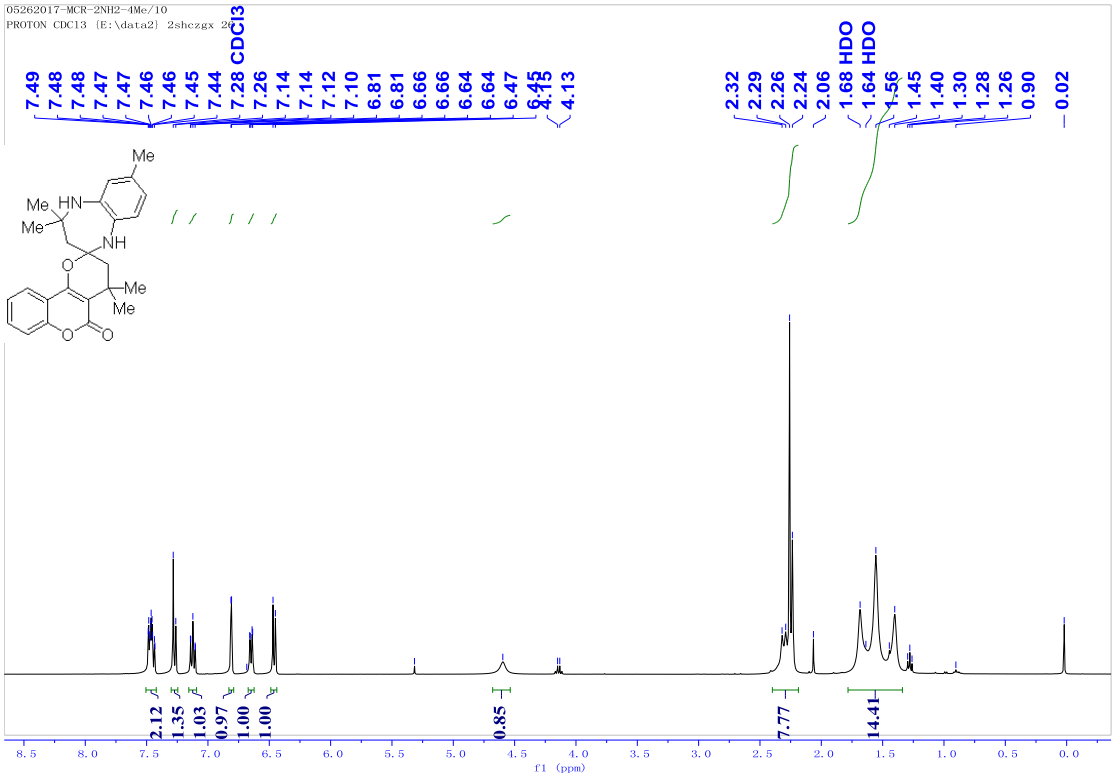

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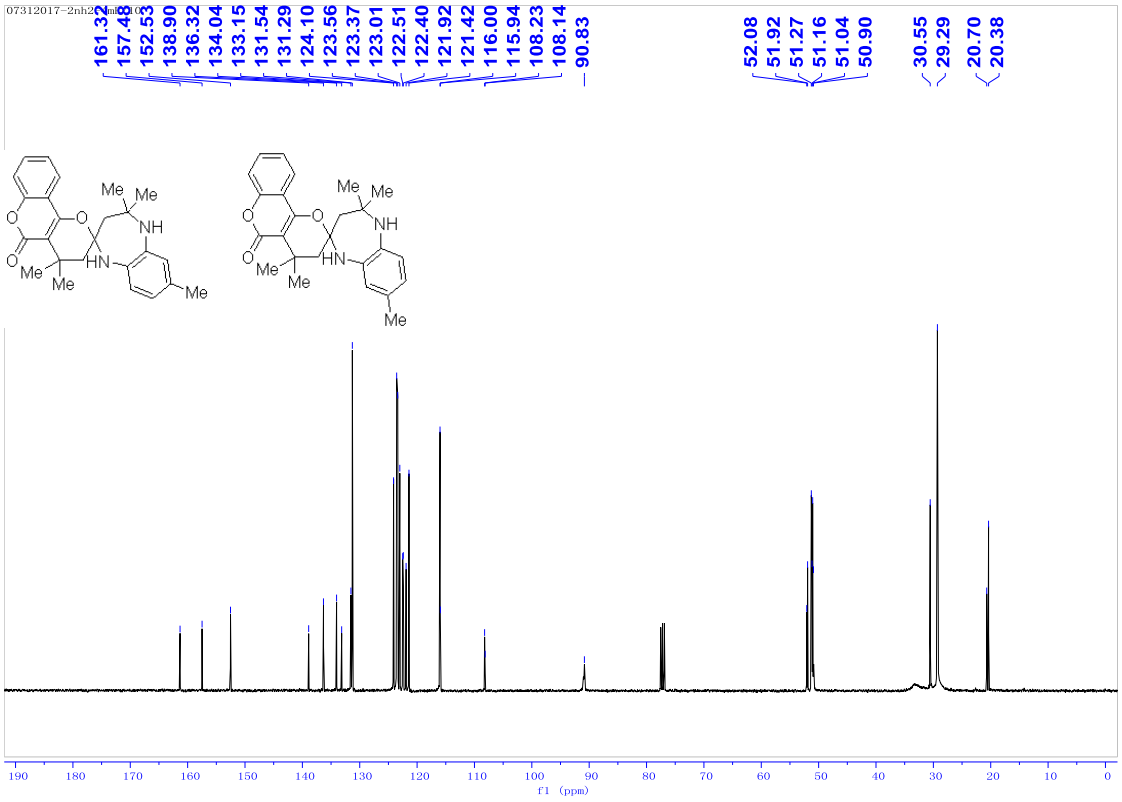
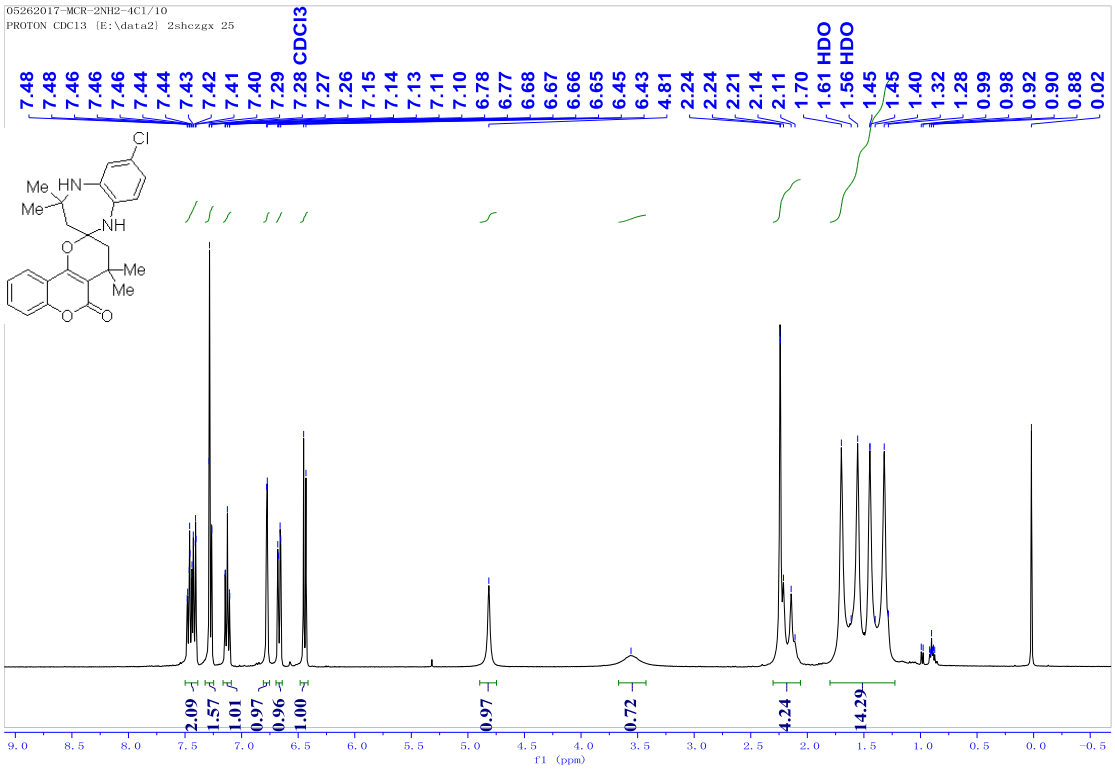


5c 7-Chloro-4,4,4',4'-tetramethyl-1,3,3',4,4',5-hexahydro-5'H-spiro-[benzo[b][1,4]diazepine-2,2'-pyrano[3,2-c]chromen]-5'-one



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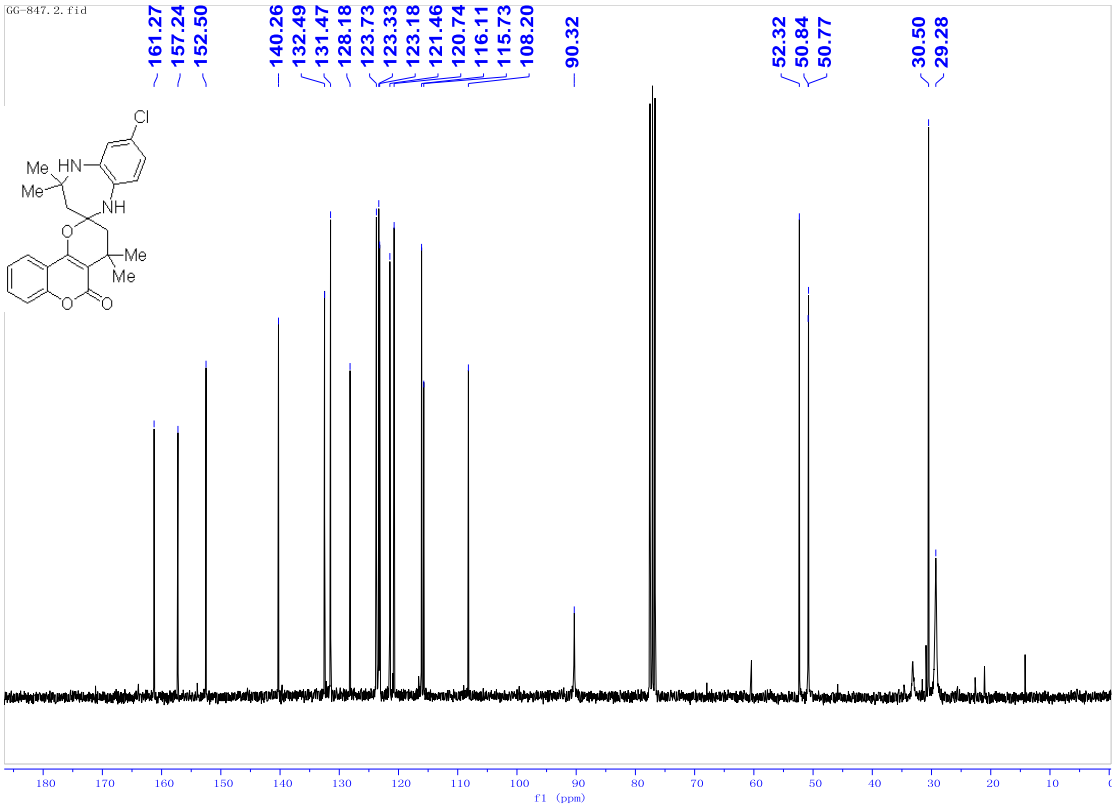
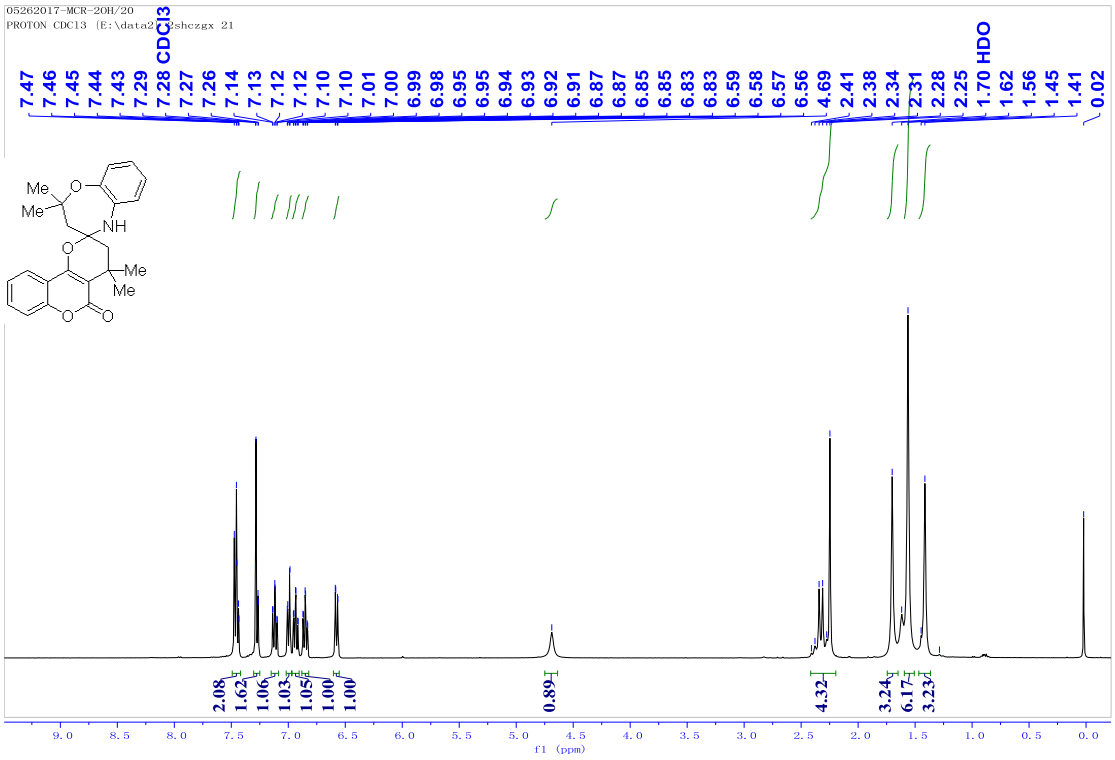


6a 2,2,4',4'-Tetramethyl-2,3,3',4'-tetrahydro-*5H,5'H*-spiro-[benzo[b][1,4]oxazepine-4,2'-pyrano[3,2-c]chromen]-5'-one



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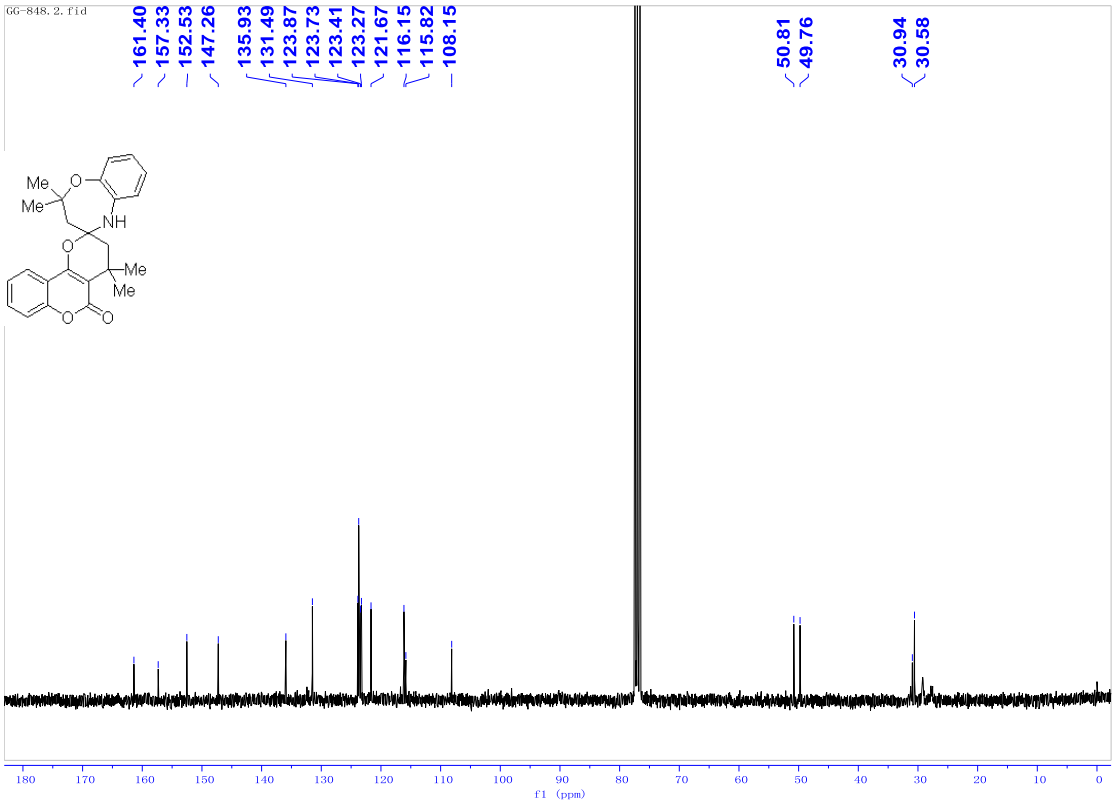

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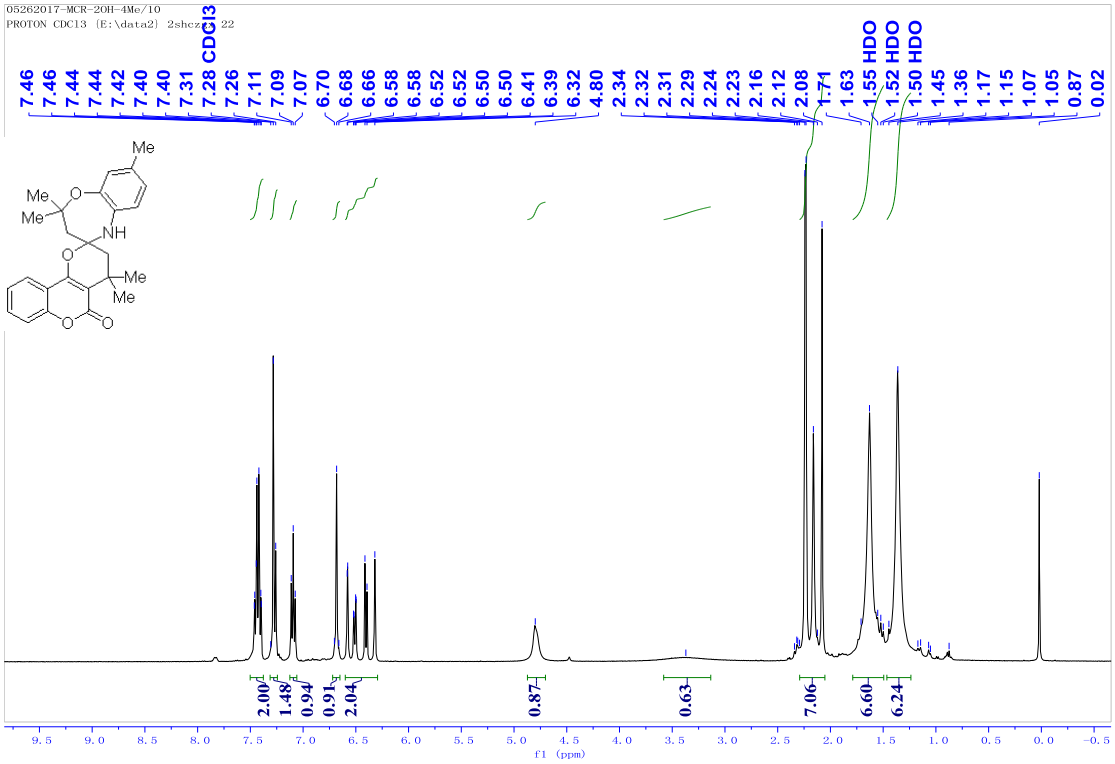

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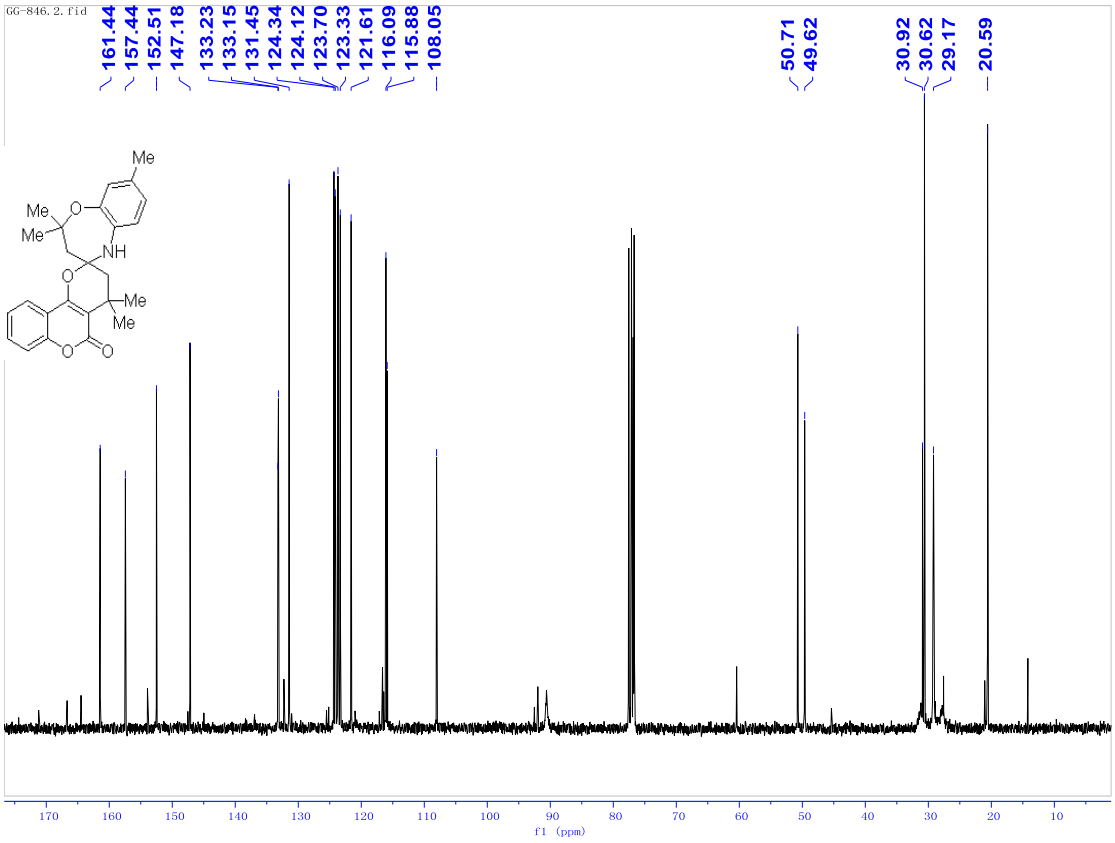
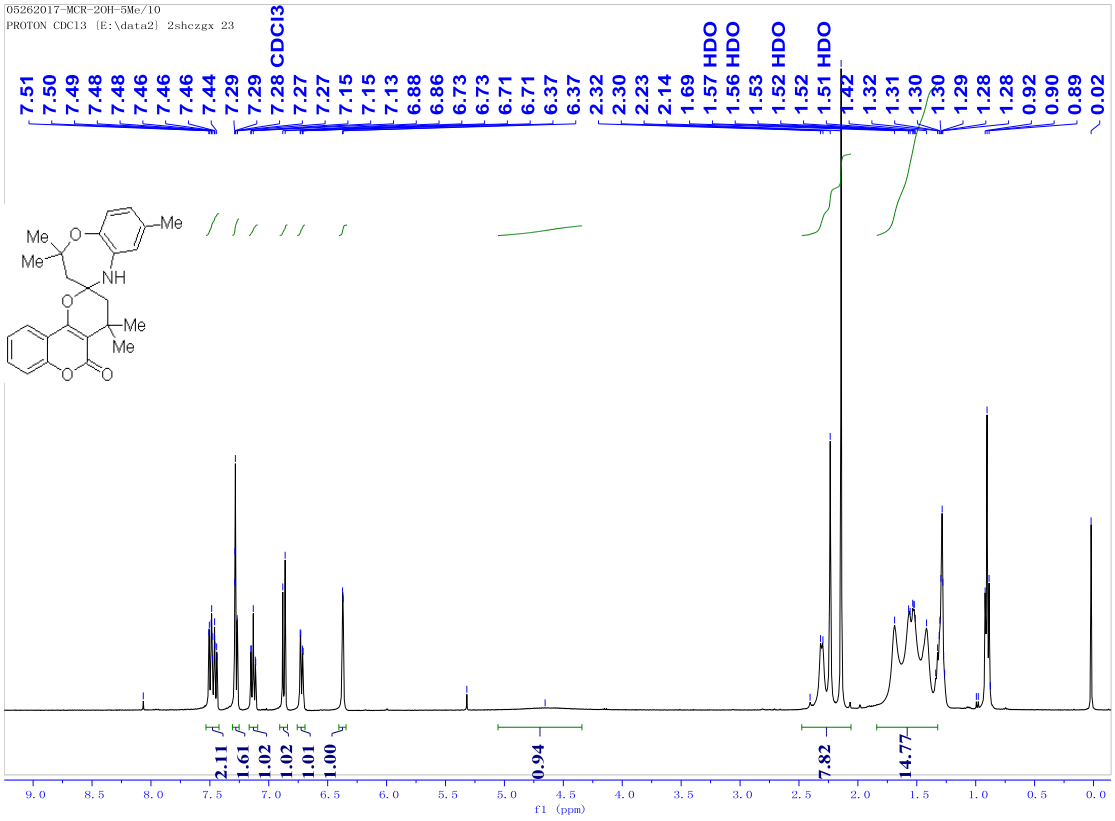


6c 2,2,4',4',7-Pentamethyl-2,3,3',4'-tetrahydro-5H,5'H-spiro-[benzo[b][1,4]oxazepine-4,2'-pyrano[3,2-c]chromen]-5'-one



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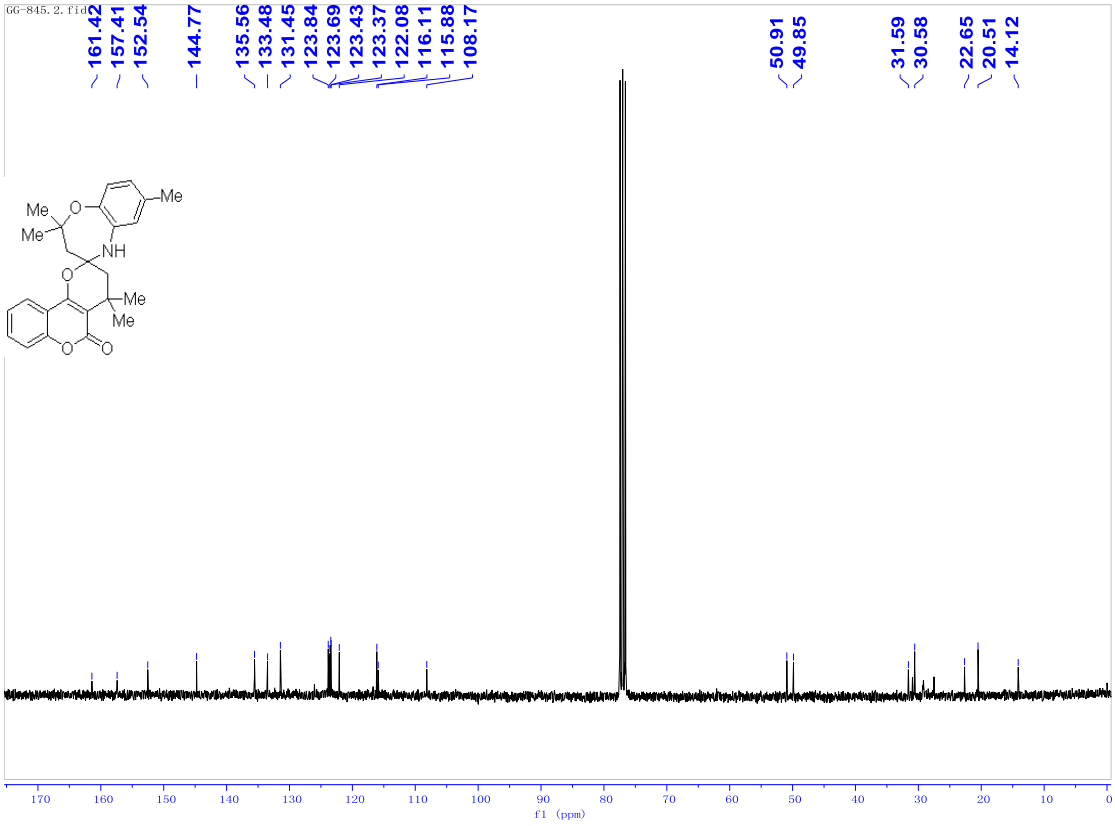


7. HRMS spectra used for the speculation of mechanism

Supporting information Figures

Figure S1

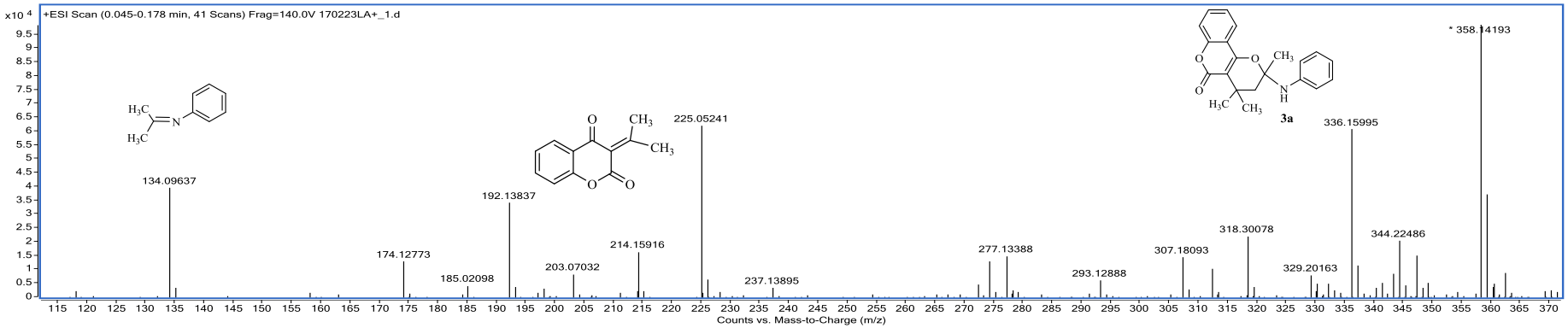


Figure S2

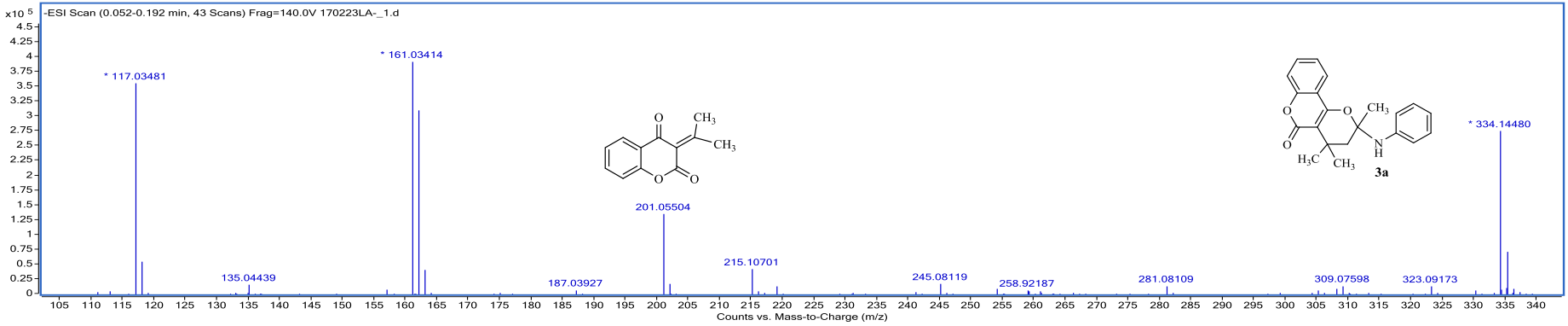
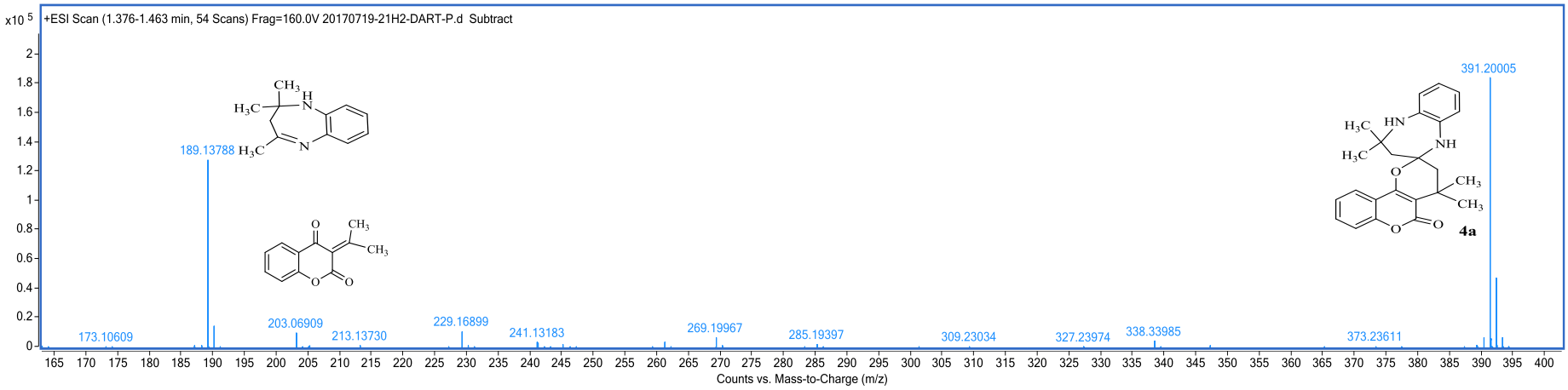


Figure S3



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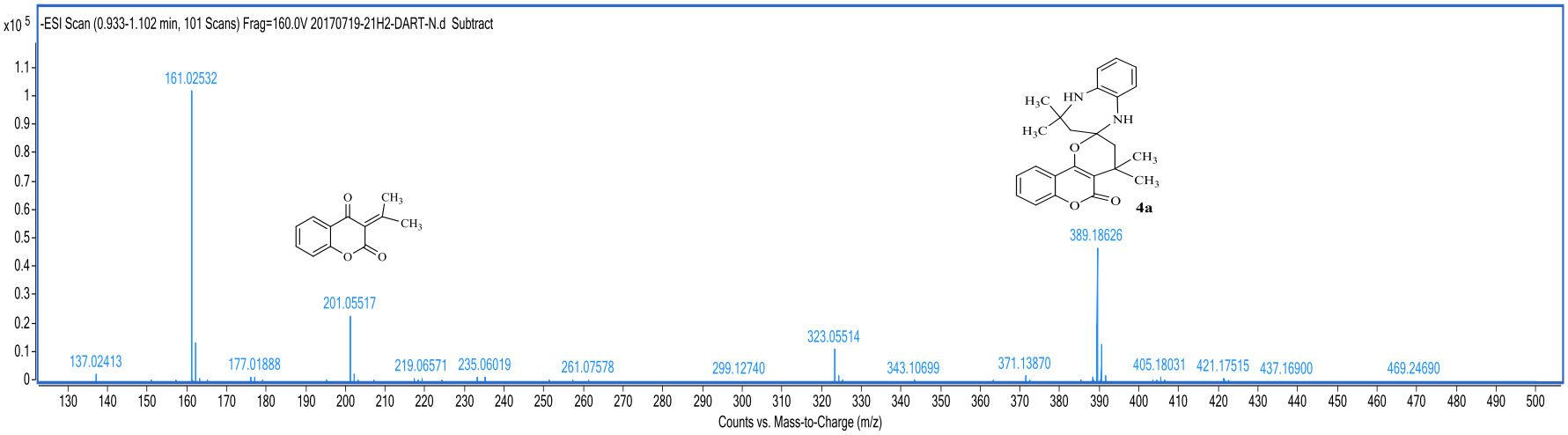

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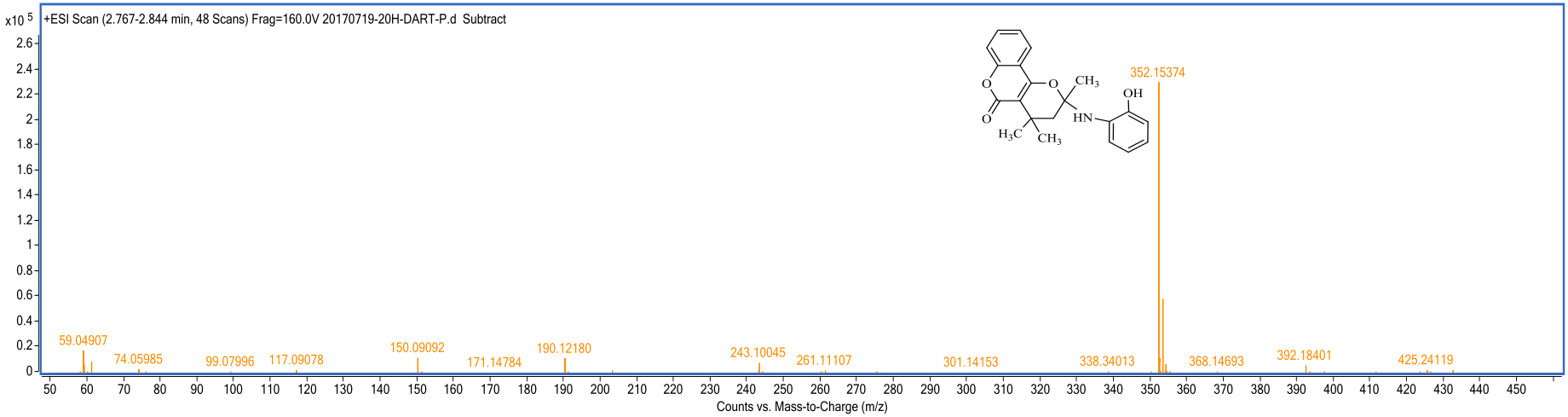

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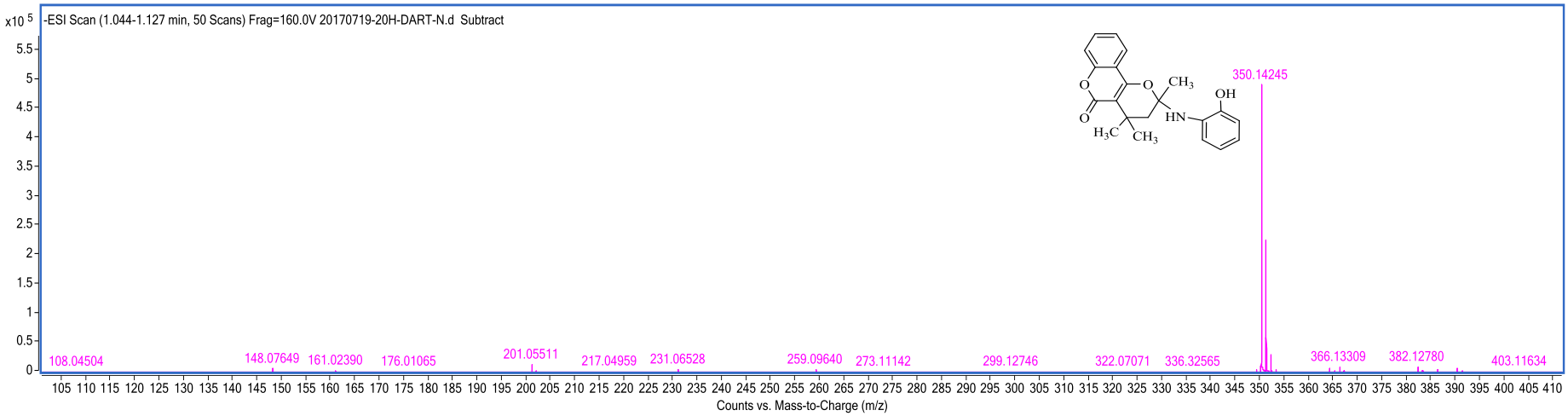

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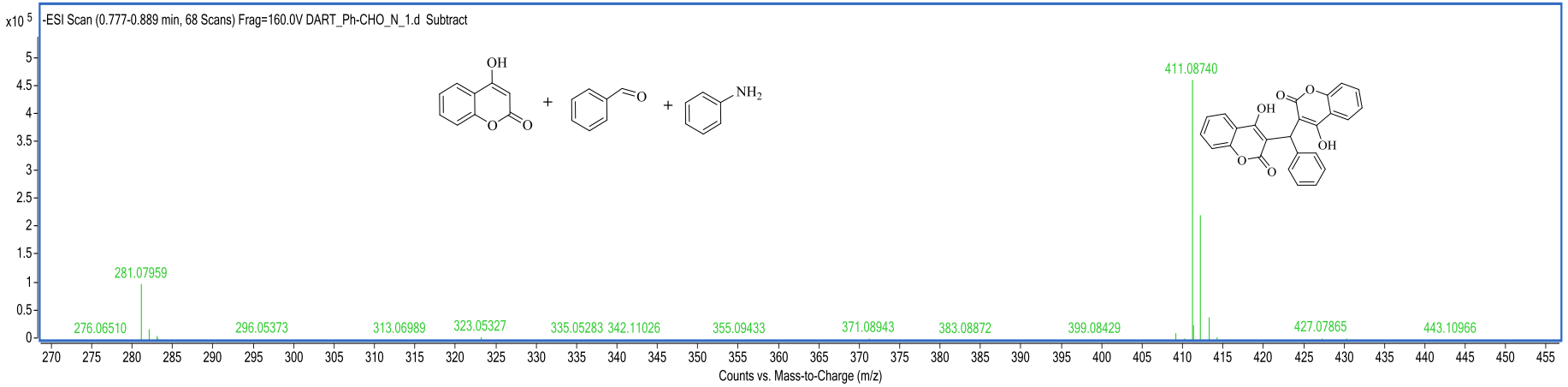

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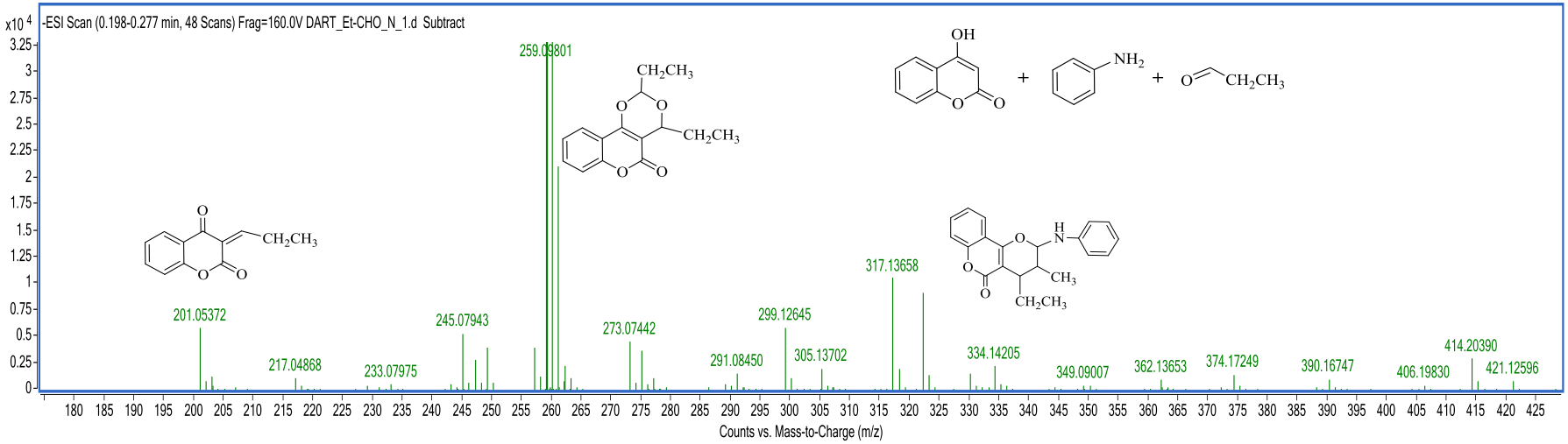


Figure S9

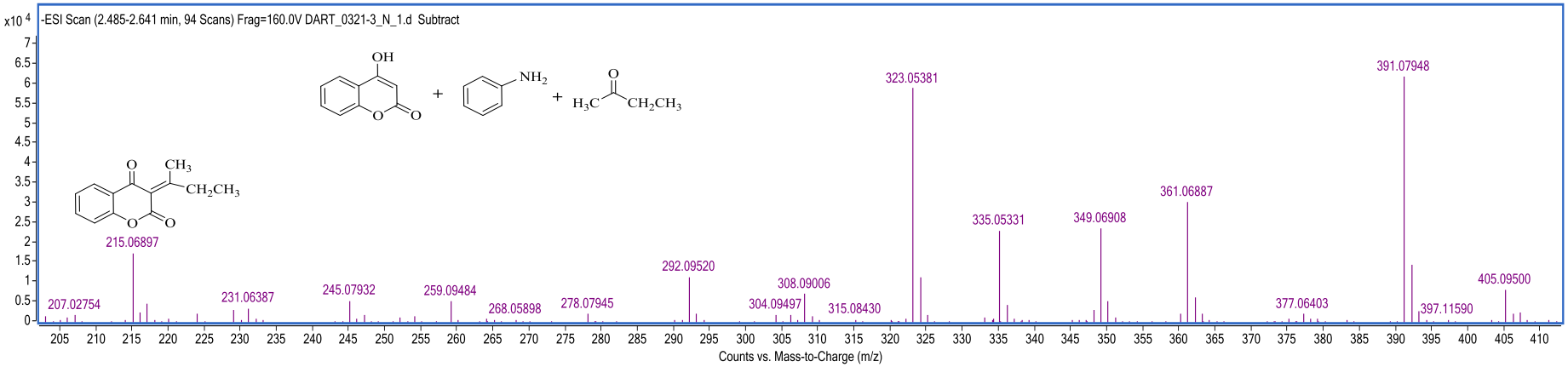


Figure S10

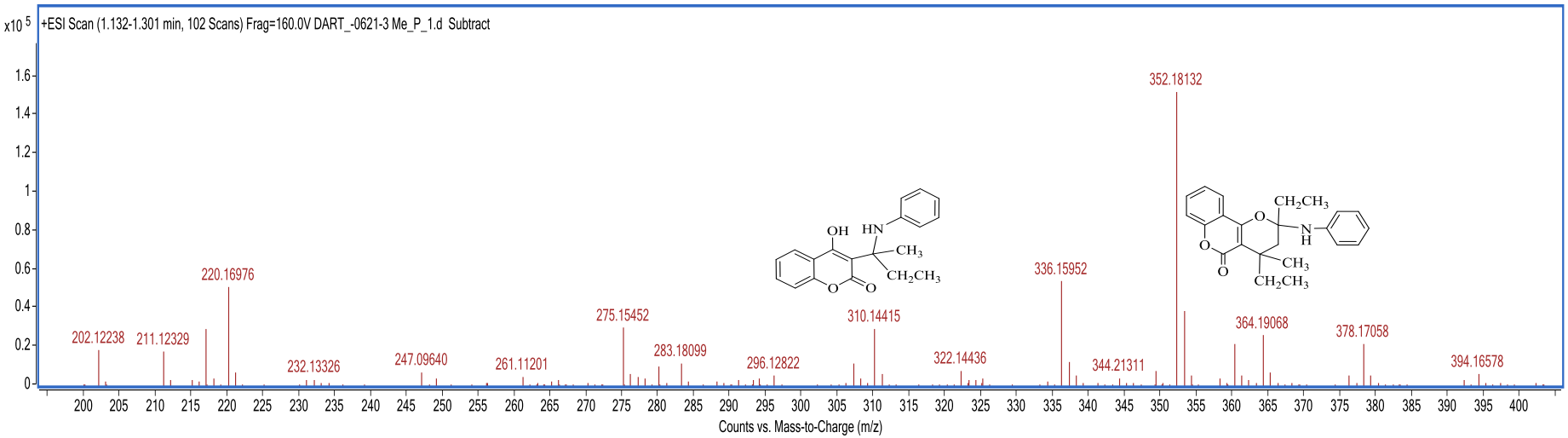
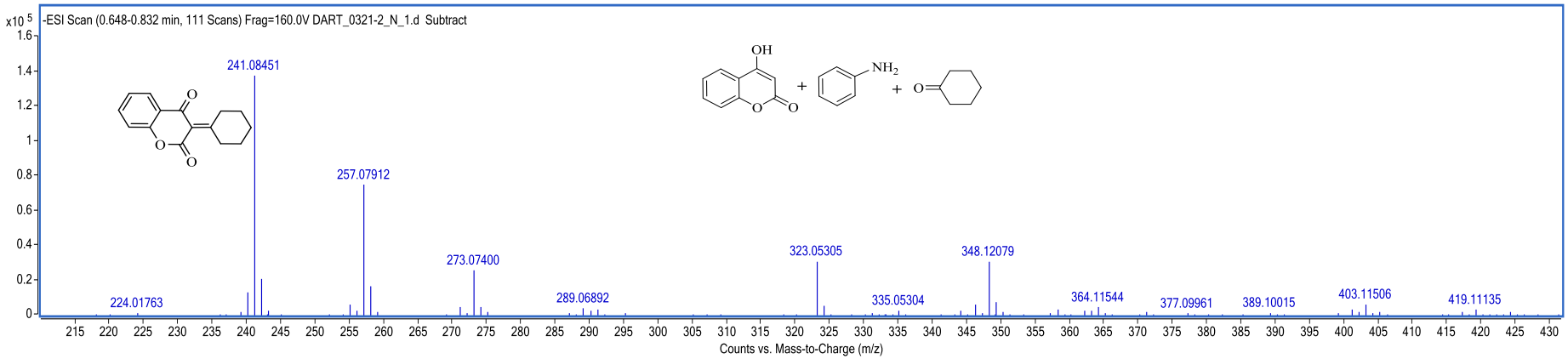


Figure S11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OH
NH2
O
Counts vs. Mass-to-Charge (m/z)