BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Convenient construction of diverse chromene frameworks via three-component reactions

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Experiment procedures, ^{1}H and ^{13}C NMR as well as HRMS spectra of the synthesized compounds

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Table S1: Single crystal data of the compounds **4c** and **4c'**.

Phase	**4c**	**4c'**
Empirical formula	$C_{35}H_{32}ClNO_7$	$C_{35}H_{32}ClNO_7$
Formula weight	614.06	614.06
Temperature/K	296(2)	296(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	P-1	Pbca
a /Å	8.6690(19)	9.0039 (14)
b / Å	11.444(3)	21.934(3)
c / Å	15.898(4)	32.455(4)
α (°)	102.664(6)	90
β (°)	93.884(6)	90
γ (°)	102.393(5)	90
V (Å ^{3})	1508.0(6)	6409.6(15)
Z	2	8
Calculated density ($g \cdot cm^{-3}$)	1.352	1.273
Absorption coefficient(mm^{-1})	0.179	0.168
F(000)	644	2576
θ range / (°)	2.397 to 25.998	1.255 to 25.997
Limiting indices	-10<=h<=10, -14<=k<=14, -19<=l<=19	-10<=h<=11, -25<=k<=27, -40<=l<=34
Reflections collected/unique	18861 / 5850	49491 / 6286
Completeness to theta	98.4 %	99.8 %
Max. and min. transmission	0.7456 and 0.6341	0.7456 and 0.6699
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5850 / 0 / 399	6286 / 0 / 399
Goodness-of-fit on F^2	1.011	1.008
Final *R* indices[I>2sigma(I)]	R1 = 0.0695, wR2 = 0.0982	R1 = 0.0810, wR2 = 0.1344
R indices (all data)	R1 = 0.1833, wR2 = 0.1266	R1 = 0.2346, wR2 = 0.1822
Largest diff. peak and hole /($e \cdot Å^{-3}$)	0.178 and -0.289	0.390 and -0.208

Table S2: Single crystal data of the compounds **6a** and **6b**.

Phase	**6a**	**6b**
Empirical formula	$C_{36}H_{34}N_2O_8S$	$C_{34}H_{32}N_2O_8S$
Formula weight	654.71	628.67
Temperature/K	200(2)	273(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	Monoclinic, P2(1)/n	Triclinic
Space group	P-1	P-1
a /Å	8.6902(12)	10.0424(14)
b / Å	33.230(5)	14.3138(19)
c / Å	13.0433(17)	14.687(2)
α (°)	90	107.338(4)
β (°)	108.568(50)	95.831(4)
γ (°)	102.393(5)	94.091(4)
V (Å ^{3})	3570.5(8)	1993.3(5)
Z	4	2
Calculated density (g·cm^{-3})	1.218	1.047
Absorption coefficient(mm^{-1})	0.142	0.125
F(000)	1376	660
θ range / (°)	2.053 to 25.361	2.667 to 24.999
Limiting indices	-10<=h<=39, 0<=k<=39, 0<=l<=15	-10<=h<=11, -17<=k<=17, -17<=l<=17
Reflections collected/unique	6382 / 6382	19141 / 6865
Completeness to theta	97.6 %	98.0 %
Max. and min. transmission	0.745209 and 0.612488	0.7456 and 0.5988
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6382 / 0 / 427	6865 / 24 / 412
Goodness-of-fit on F^2	1.095	1.053
Final *R* indices[I>2sigma(I)]	R1 = 0.0924, wR2 = 0.1715	R1 = 0.0750, wR2 = 0.1929
R indices (all data)	R1 = 0.1278, wR2 = 0.1830	R1 = 0.1736, wR2 = 0.2105
Largest diff. peak and hole /(e·Å^{-3})	0.365 and -0.594	0.370 and -0.306

Table S3: Single crystal data of the compound **8j**.

Phase	**8j**
Empirical formula	$C_{38}H_{28}ClNO_7$
Formula weight	610.03
Temperature/K	296(2)
Wavelength/ Å	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
a /Å	9.7970(10)
b / Å	24.492(2)
c / Å	13.0732(12)
α (°)	90
β (°)	106.742(3)
γ (°)	90
V (Å ^{3})	3003.9(5)
Z	4
Calculated density (g·cm^{-3})	1.178
Absorption coefficient(mm^{-1})	0.179
F(000)	1272
θ range /(°)	2.453 to 25.999
Limiting indices	-10<=h<=12, -26<=k<=30, -16<=l<=16
Reflections collected/unique	27746 / 5878
Completeness to theta	99.7 %
Max. and min. transmission	0.7456 and 0.6667
Refinement method	Full-matrix
Data/restraints/parameters	5878 / 0 / 400
Goodness-of-fit on F^2	1.019
Final *R* indices[I>2sigma(I)]	R1 = 0.0470, wR2 = 0.0989
R indices (all data)	R1 = 0.0999, wR2 = 0.1167
Largest diff. peak and hole /(e ·Å^{-3})	0.204 and -0.273

Experimental section

1. Materials and appratus:

Unless otherwise noted, the commercial reagents and solvents were used without further purification. Melting points were recorded with a micromelting point apparatus and are uncorrected. IR spectra were recorded using a Bruker Tensor 27 spectrometer (KBr disc). The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded with a Varian 400 spectrometer at 400 or 100 MHz. High-resolution mass spectra (HRMS) were recorded in ESI mode using a MicroTOF mass spectrometer. Single-crystal X-ray data were collected with a Bruker Smart APEX-2 CCD diffractometer. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were monitored by observation under UV light (254 and 365 nm). 2-(2-hydroxybenzylidene)-1,3-diarylpropane-1,3-diones[1] and 2-(2-*N*-tosylaminobenzylidene)-1,3-indanediones[2,3] were prepared according to the published methods.

[1] Y.T. Lee, Y.T. Lee, C.J. Lee, C.N. Sheu, B.Y. Lin, J.H. Wang, W.W. Lin. *Org. Biomol. Chem.* **2013**, *11*(31): 5156-5161.

[2] G.B. Kolukula, P.V. Babu, K. Premsagar, S. Sibbala. *Synth. Commun.* **2025**, *55*(8): 608-617

[3] Z.H. Wang, L.W. Shen, K.X. Xie, Y. You, J.Q Zhao, W.C. Yuan. *Org. Lett.* **2020**, *22*(8): 3114-3118

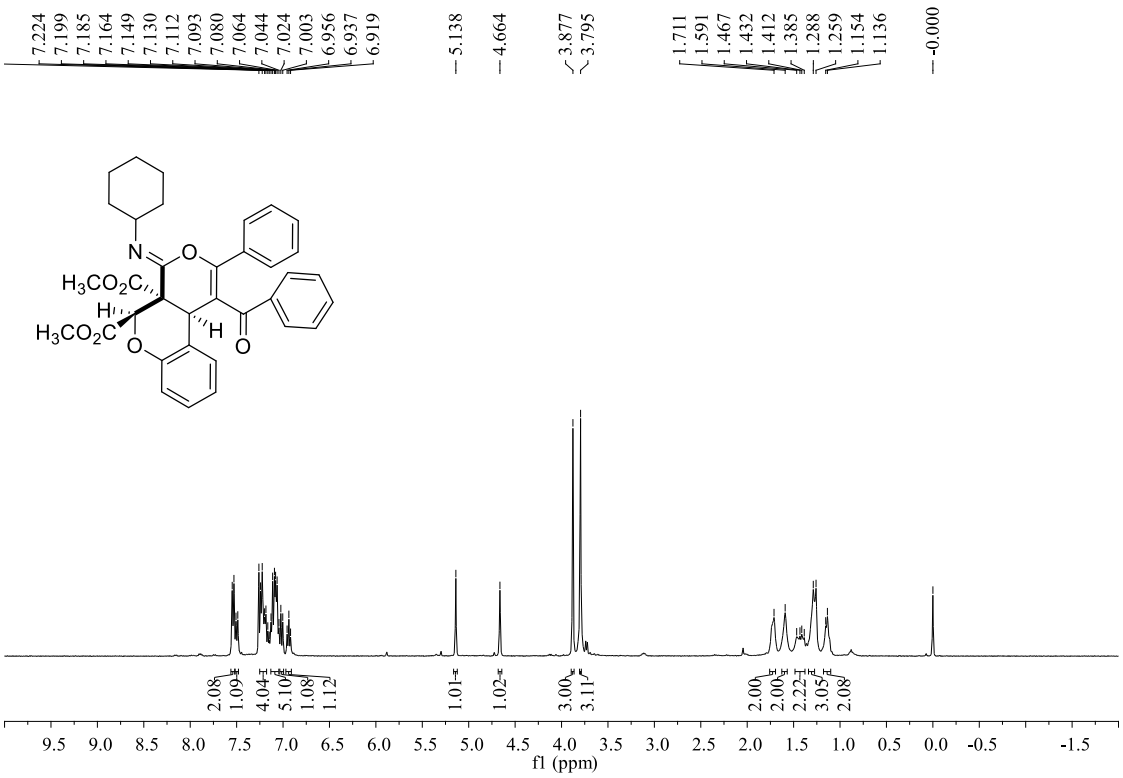
2. General procedure for the preparation of the functionalized pyrano[3,4-*c*]chromenes 4a–n and 4a'–n': To a round flask was added 2-(2-hydroxybenzylidene)-1,3-diarylpropane-1,3-dione **3** (0.2 mmol, 1.0 equiv) and tetrahydrofuran (5.0 mL). The solution was stirred at room temperature. Then, alkyl isocyanide **1** (0.2 mmol, 1.0 equiv) and dialkyl but-2-ynedioate **2** (0.4 mmol, 2.0 equiv) was added to the solution. The mixture was stirred

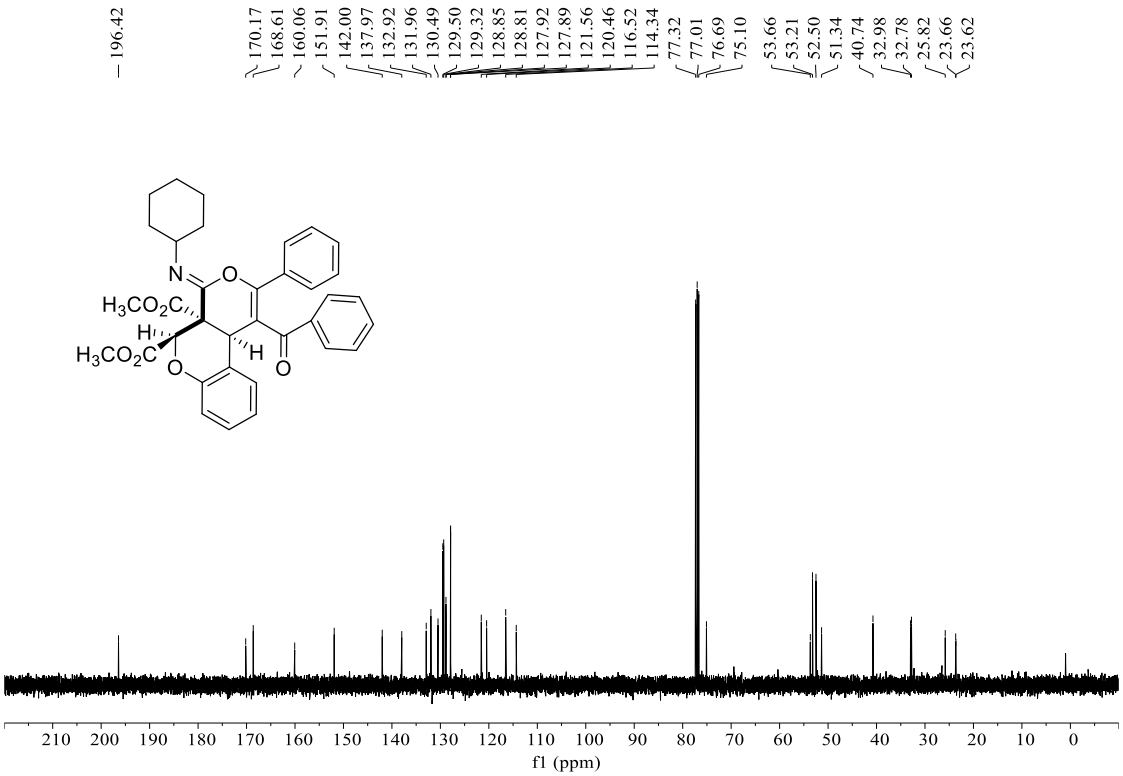
at room temperature for twenty-four hours. After removing the solvent by rotatory evaporation at reduced pressure, the residue was subjected to column chromatography with a mixture of petroleum ether, ethyl acetate and dichloromethane (6:1:3, v/v/v) to give the pure products **4a–n** and **4a'–n'** for analysis.

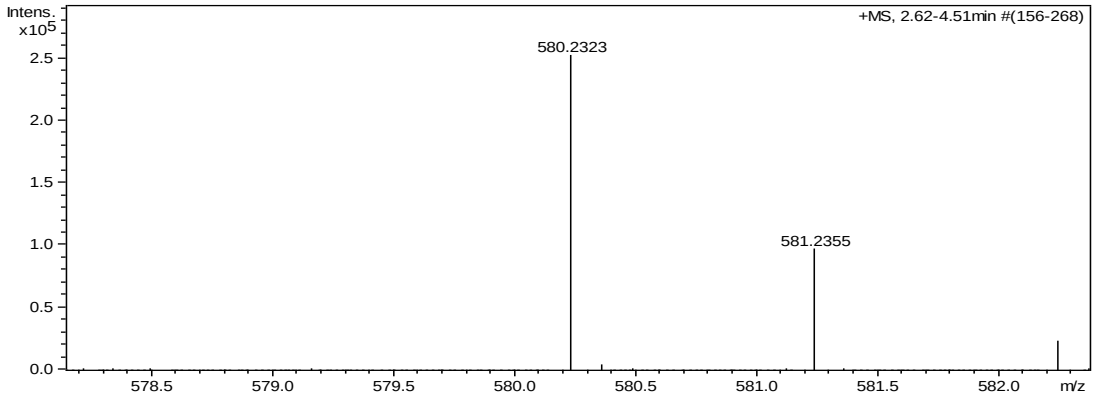
3. General procedure for the preparation of the functionalized tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinolines 6a–j: To a round flask was added 2-(2-*N*-tosylaminobenzylidene)-1,3-indanedione (**5**, 0.2 mmol, 1.0 equiv) and acetonitrile (5.0 mL). The solution was stirred at room temperature. Then, alkyl isocyanide **1** (0.2 mmol, 1.0 equiv) and dialkyl but-2-ynedioate **2** (0.5 mmol, 2.5 equiv) was added to the solution. The mixture was refluxed in an oil bath (80 °C) for three hours. After removing the solvent by rotatory evaporation at reduced pressure, the residue was subjected to column chromatography with a mixture of petroleum ether and ethyl acetate (3:1, v/v) to give the pure products **6a–j** for analysis.

4. General procedure for the preparation of the functionalized chromenes 8a–p: To a round flask was added aryl amine **7** (0.2 mmol, 1.0 equiv), dialkyl but-2-ynedioate **2** (0.4 mmol, 2.0 equiv) and dichloromethane (5.0 mL), The solution was stirred at room temperature for half hour. Then, 2-(2-hydroxybenzylidene)-1,3-diphenylpropane-1,3-dione **3** (0.2 mmol, 1.0 equiv) and $BF_3 \cdot OEt_2$ (0. 4 mmol, 0.2 equiv) was added to the solution. The mixture was refluxed (40 °C) in an oil bath for six hours. After removing the solvent by rotatory evaporation at reduced pressure, the residue was subjected to column chromatography with a mixture of petroleum ether and ethyl acetate (3:1, v/v) to give the pure products **8a–p** for analysis.

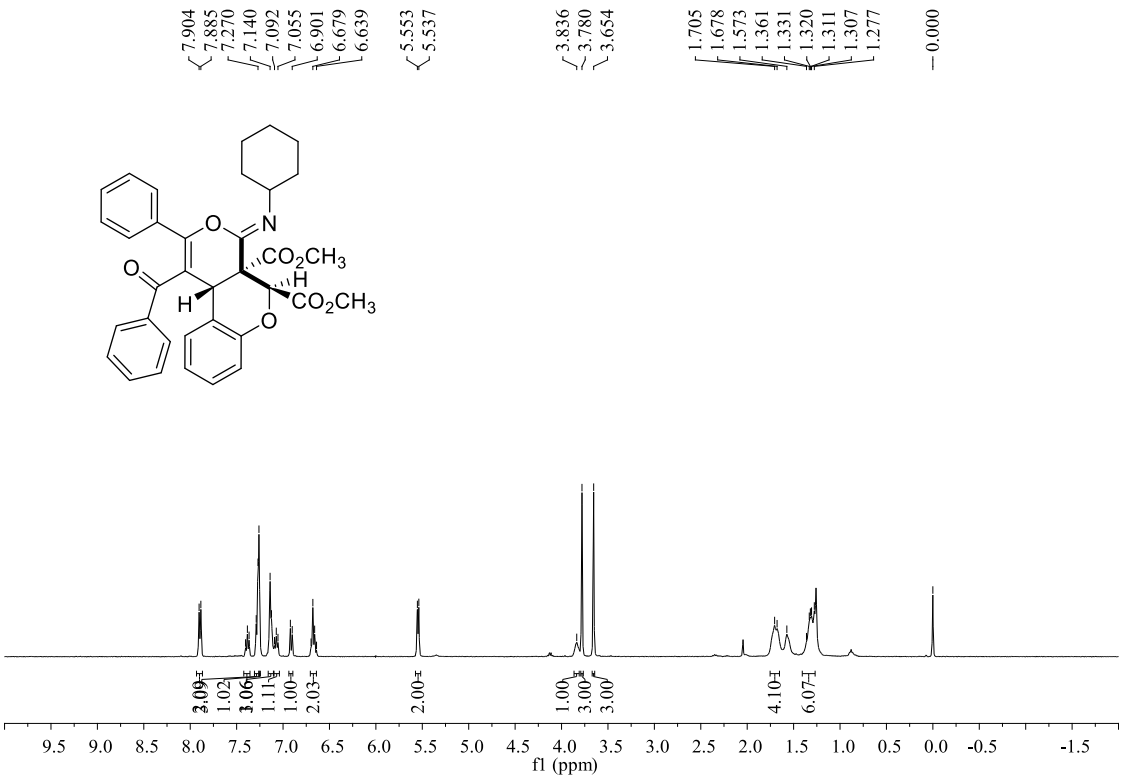
Dimethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-4-(cyclohexylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4a): Yellow solid, 52%, mp 163-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 7.6 Hz, 2H, ArH), 7.50 (d, *J* = 8.0 Hz, 1H, ArH), 7.25-7.19 (m, 4H, ArH), 7.13-7.04 (m, 5H, ArH), 7.01 (d, *J* = 8.4 Hz, 1H, ArH), 6.94 (t, *J* = 7.6 Hz, 1H, ArH), 5.14 (s, 1H, CH), 4.66 (s, 1H, CH), 3.88 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 1.75-1.69 (m, 2H, CH), 1.59 (s, 2H, CH), 1.48-1.38 (m, 2H, CH), 1.34-1.28 (m, 3H, CH), 1.17-1.10 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.4, 170.2, 168.6, 160.1, 151.9, 142.0, 138.0, 132.9, 132.0, 130.5, 129.5, 129.3, 128.9, 128.8, 127.9, 127.9, 121.6, 120.5, 116.5, 114.3, 75.1, 53.7, 53.2, 52.5, 51.3, 40.7, 33.0, 32.8, 25.8, 23.7, 23.6; IR (KBr) υ: 2946, 2848, 1748, 1712, 1614, 1597, 1487, 1457, 1446, 1363, 1341, 1277, 1230, 1188, 1161, 1119, 1043, 1033, 1015, 969, 904, 731, 713, 692, 647 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{34}NO_7$ ($[M + Na]^+$): 580.2330, found: 580.2323.

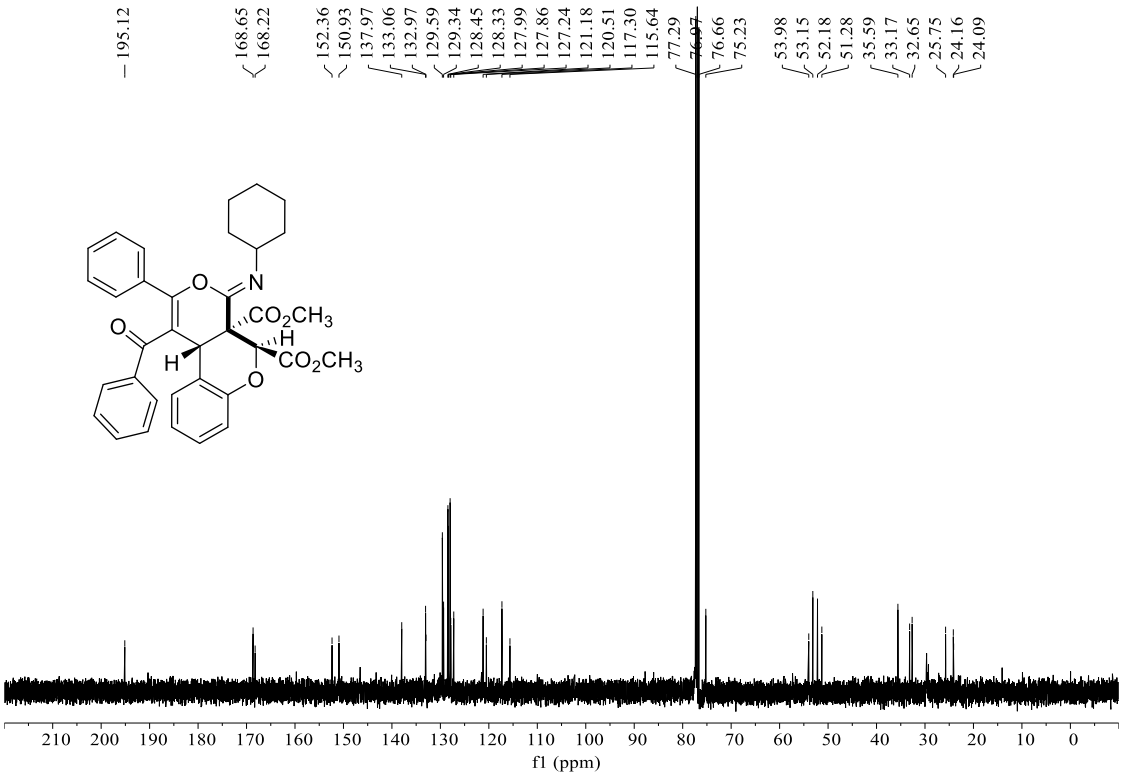


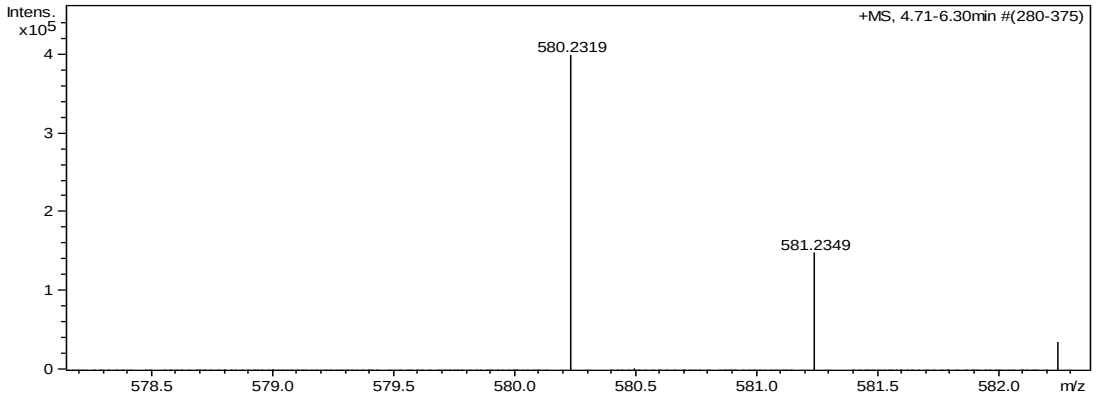

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77.32
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H3CO2C
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f1 (ppm)


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1.0
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582.0
m/z

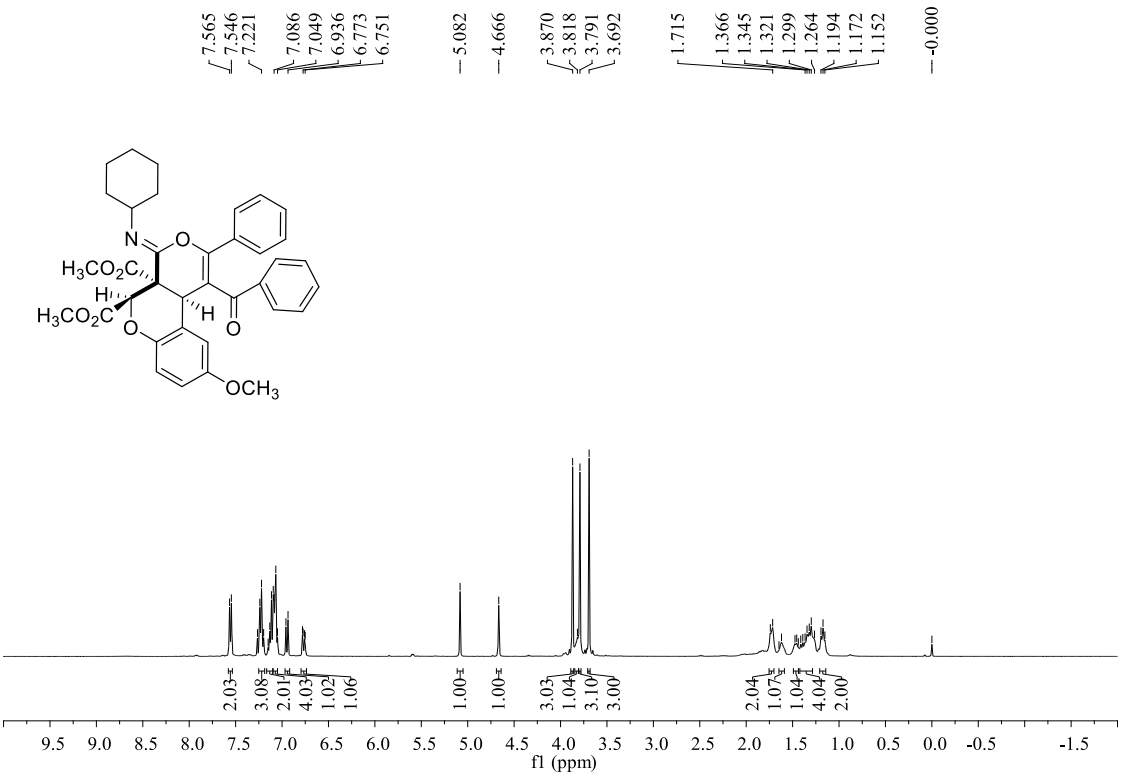
Dimethyl *rel*-(4a*S*,5*S*,10b*R*,*Z*)-1-benzoyl-4-(cyclohexylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4a'): Yellow solid, 12%, mp 181-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 7.6 Hz, 2H, ArH), 7.38 (t, *J* = 8.0 Hz, 1H, ArH), 7.30-7.27 (m, 3H, ArH), 7.25-7.24 (m, 1H, ArH), 7.16-7.10 (m, 3H, ArH), 7.09-7.04 (m, 1H, ArH), 6.91 (d, *J* = 8.0 Hz, 1H, ArH), 6.70-6.64 (m, 2H, ArH), 5.54 (d, *J* = 6.4 Hz, 2H, CH), 3.84 (s, 1H, CH), 3.78 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 1.75-1.65 (m, 4H, CH), 1.41-1.26 (m, 6H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.1, 168.7, 168.2, 152.4, 150.9, 138.0, 133.1, 133.0, 129.6, 129.3, 128.5, 128.3, 128.0, 127.9, 127.2, 121.2, 120.5, 117.3, 115.6, 75.2, 54.0, 53.2, 52.2, 51.3, 35.6, 33.2, 32.7, 25.8, 24.2, 24.1; IR (KBr) υ: 2929, 2851, 1743, 1711, 1654, 1597, 1580, 1492, 1452, 1367, 1329, 1230, 1197, 1177, 1157, 1112, 1073, 1057, 1002, 969, 908, 753, 696 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{34}NO_7$ ($[M + Na]^+$): 580.2330, found: 580.2319.

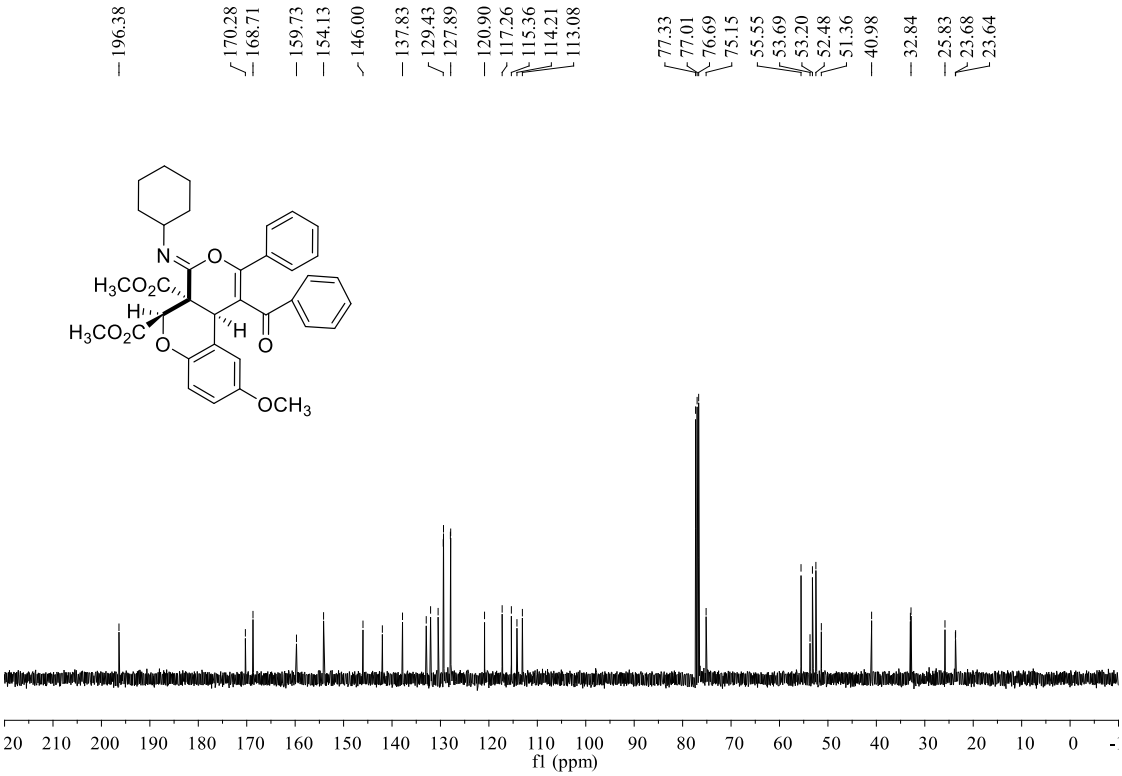


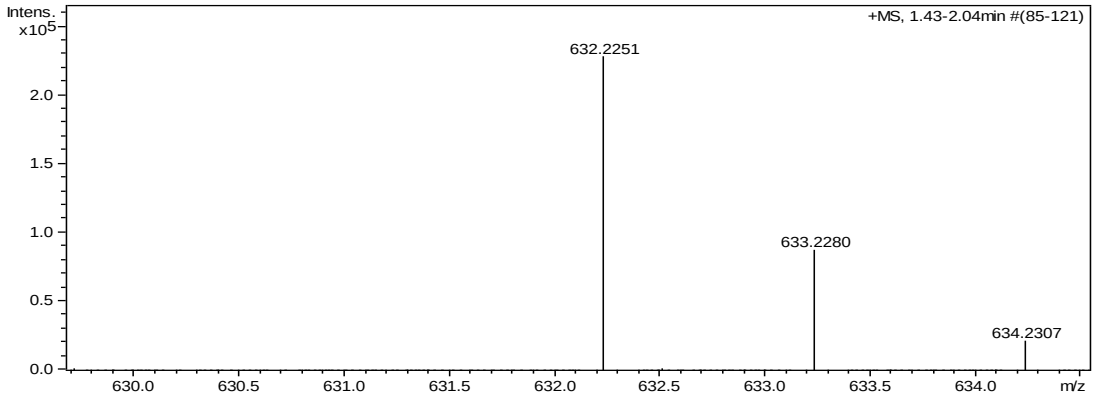

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53.98
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O
N
CO2CH3
H
O
H
CO2CH3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
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578.5 579.0 579.5 580.0 580.5 581.0 581.5 582.0 m/z

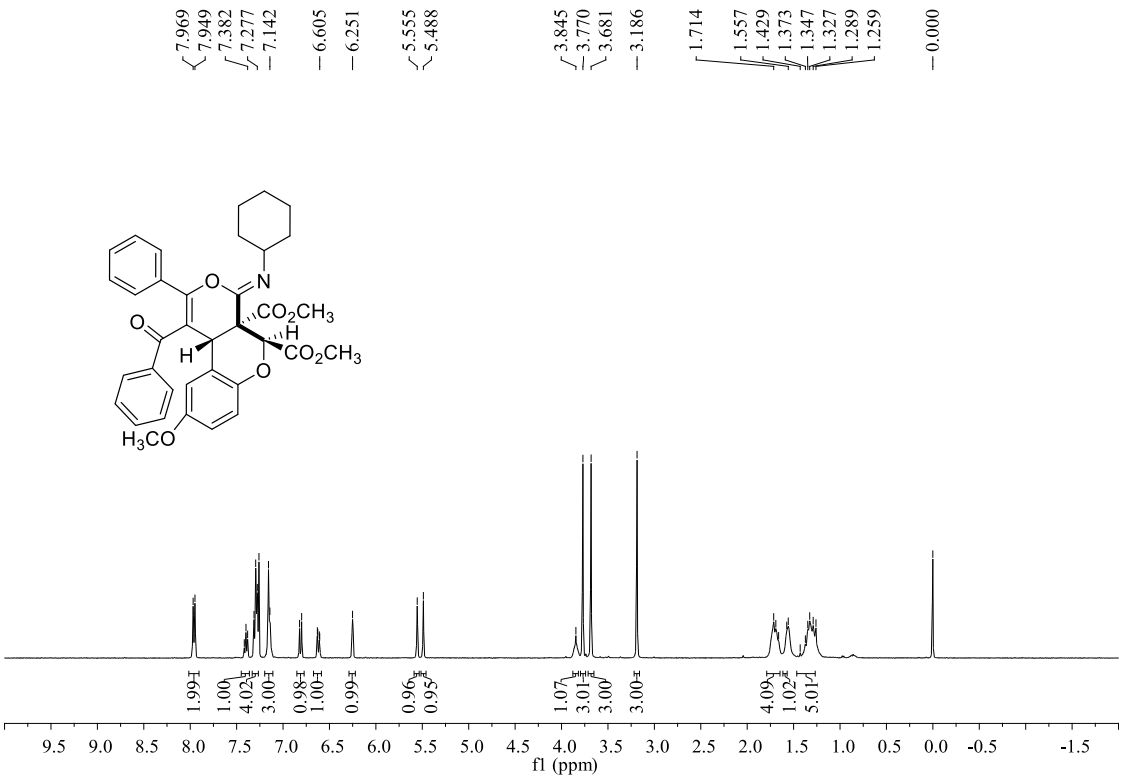
Dimethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-4-(cyclohexylimino)-9-methoxy-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4b): Yellow solid, 48%, mp 200-201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 7.6 Hz, 2H, ArH), 7.24-7.19 (m, 3H, ArH), 7.15-7.11 (m, 2H, ArH), 7.09-7.04 (m, 4H, ArH), 6.95 (d, *J* = 8.8 Hz, 1H, ArH), 6.77 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H, ArH), 5.08 (s, 1H, CH), 4.67 (s, 1H, CH), 3.87 (s, 3H, OCH_3), 3.82 (s, 1H, CH), 3.79 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 1.74-1.71 (m, 2H, CH), 1.64-1.62 (m, 1H, CH), 1.47-1.43 (m, 1H, CH), 1.41-1.29 (m, 4H, CH), 1.22-1.15 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.4, 170.3, 168.7, 159.7, 154.1, 146.0, 142.0, 137.8, 132.9, 132.0, 130.5, 129.4, 129.4, 128.0, 127.9, 120.9, 117.3, 115.4, 114.2, 113.1, 75.2, 55.6, 53.7, 53.2, 52.5, 51.4, 41.0, 33.0, 32.8, 25.8, 23.7, 23.6; IR (KBr) υ: 2934, 2848, 1732, 1705, 1639, 1495, 1447, 1435, 1362, 1328, 1297, 1189, 1170, 1145, 1120, 1100, 1072, 1035, 1013, 905, 847, 766, 726, 711, 704, 693, 655, 576 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{36}H_{35}NNaO_8$ ($[M + Na]^+$): 632.2255, found: 632.2251.

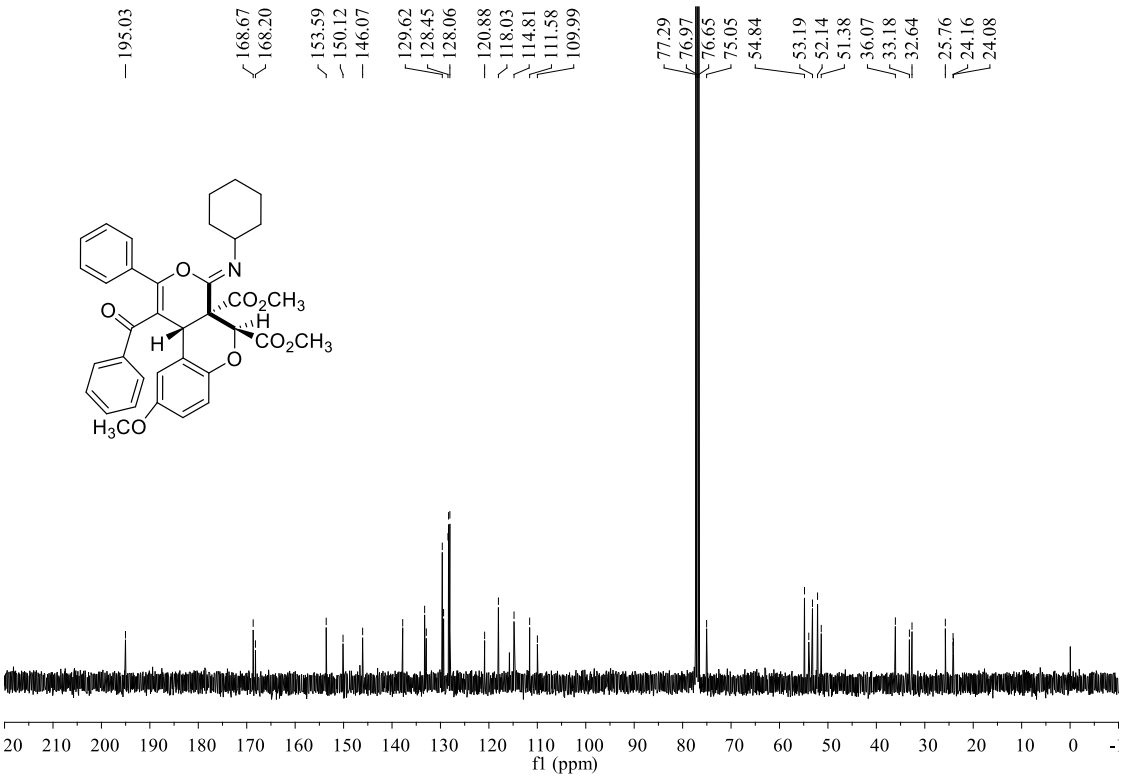


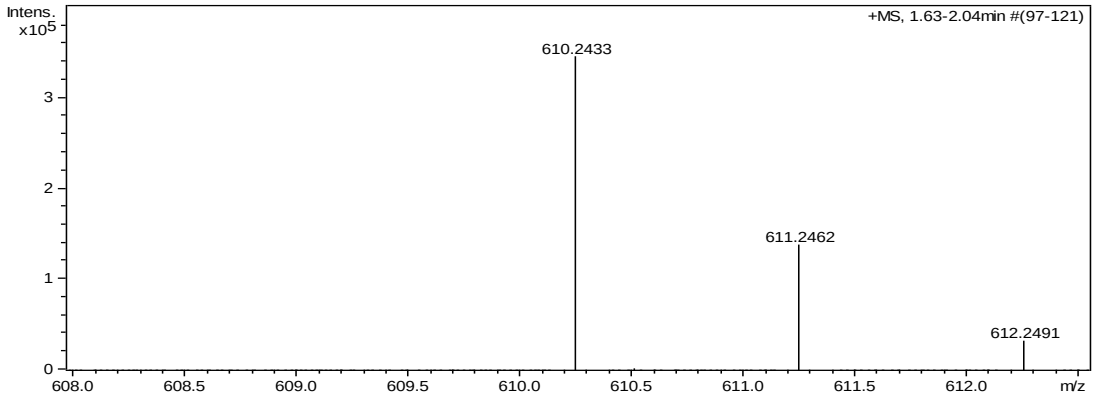

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25.83
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O
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H3CO2C
O
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f1 (ppm)


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634.0
m/z

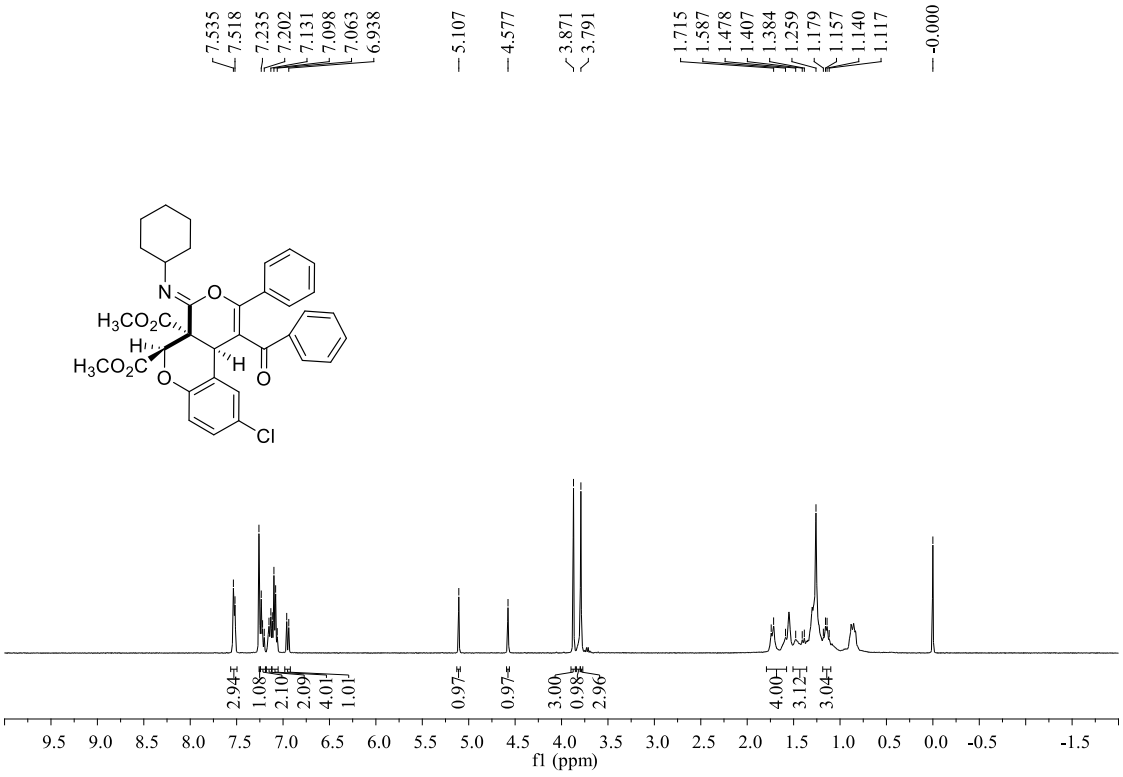
Dimethyl *rel*-(4a*S*,5*S*,10b*R*,*Z*)-1-benzoyl-4-(cyclohexylimino)-9-methoxy-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4b'): Yellow solid, 11%, mp 202-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.0 Hz, 2H, ArH), 7.40 (t, *J* = 7.6 Hz, 1H, ArH), 7.31-7.27 (m, 4H, ArH), 7.15-7.13 (m, 3H, ArH), 6.81 (d, *J* = 8.8 Hz, 1H, ArH), 6.61 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H, ArH), 6.25 (s, 1H, ArH), 5.55 (s, 1H, CH), 5.49 (s, 1H, CH), 3.85 (s, 1H, CH), 3.77 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.19 (s, 3H, OCH_3), 1.71-1.66 (m, 4H, CH), 1.61-1.57 (m, 1H, CH), 1.42-1.28 (m, 5H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.0, 168.7, 168.2, 153.6, 150.1, 146.1, 137.8, 133.3, 132.9, 129.6, 129.4, 128.5, 128.3, 128.1, 120.9, 118.0, 114.8, 111.6, 111.0, 75.1, 54.8, 54.0, 53.2, 52.1, 51.4, 36.1, 33.2, 32.6, 25.8, 24.2, 24.1; IR (KBr) υ: 2932, 2851, 1747, 1696, 1641, 1488, 1448, 1367, 1325, 1303, 1284, 1228, 1199, 1175, 1146, 1113, 1074, 1046, 1006, 903, 807, 770, 701, 674, 649, 603, 532 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{36}H_{36}NO_8$ ([M + H]$^+$): 610.2435, found: 610.2433

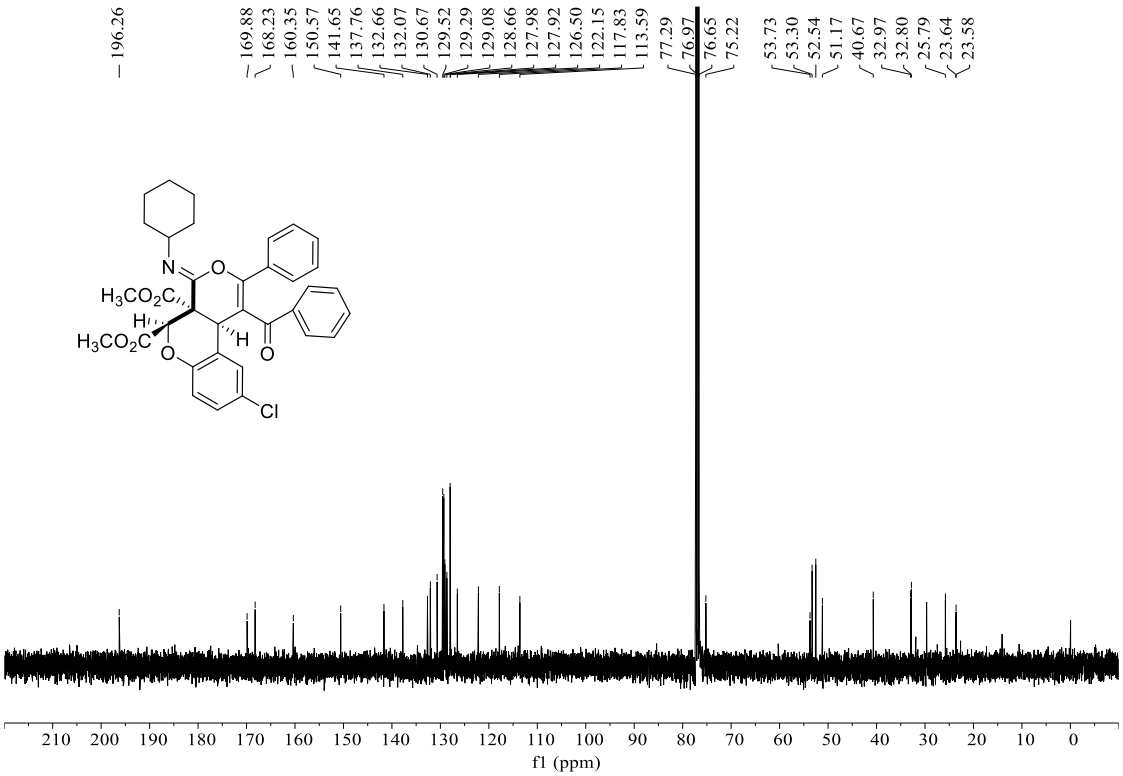


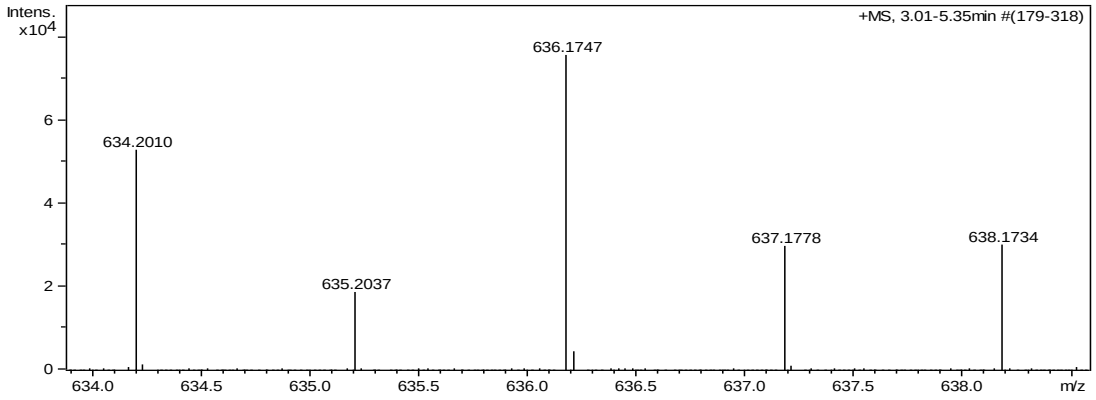

195.03
168.67
168.20
153.59
150.12
146.07
129.62
128.45
128.06
120.88
118.03
114.81
111.58
109.99
77.29
76.97
76.65
75.05
54.84
53.19
52.14
51.38
36.07
33.18
32.64
25.76
24.16
24.08
O
N
CO2CH3
H
CO2CH3
O
O
H
H3CO
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 1.63-2.04min #(97-121)
610.2433
611.2462
612.2491
0
1
2
3
608.0
608.5
609.0
609.5
610.0
610.5
611.0
611.5
612.0
m/z

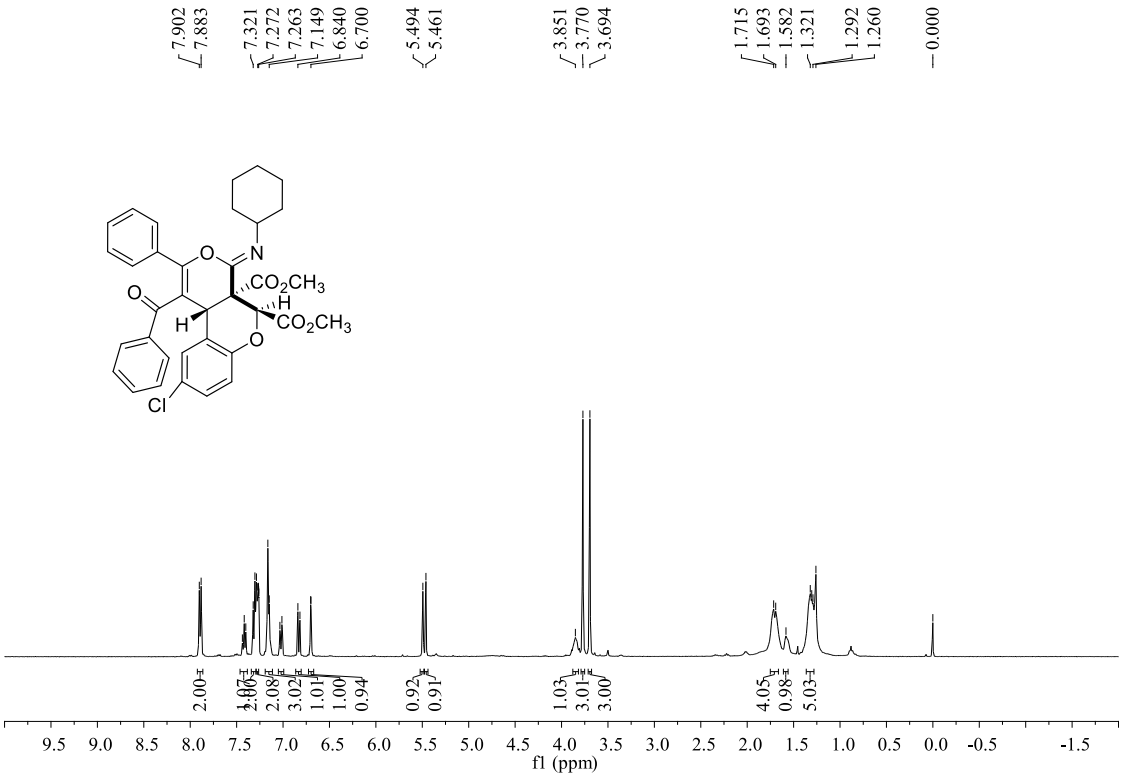
Dimethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-9-chloro-4-(cyclohexylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4c): Yellow solid, 30%, mp 205-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 6.8 Hz, 3H, ArH), 7.26-7.25 (m, 1H, ArH), 7.24-7.19 (m, 2H, ArH), 7.14 (d, *J* = 8.4 Hz, 2H, ArH), 7.11-7.06 (m, 4H, ArH), 6.95 (d, *J* = 9.2 Hz, 1H, ArH), 5.11 (s, 1H, CH), 4.58 (s, 1H, CH), 3.87 (s, 3H, OCH_3), 3.84-3.80 (m, 1H, CH), 3.79 (s, 3H, OCH_3), 1.79-1.58 (m, 4H, CH), 1.50-1.38 (m, 3H, CH), 1.18-1.12 (m, 3H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.3, 169.9, 168.2, 160.4, 150.6, 141.7, 137.8, 132.7, 132.1, 130.8, 129.5, 129.3, 129.1, 128.7, 128.0, 127.9, 126.5, 122.2, 117.8, 113.6, 75.2, 53.7, 53.3, 52.5, 51.2, 40.7, 33.0, 32.8, 25.8, 23.64, 23.58; IR (KBr) υ: 2923, 2851, 1766, 1732, 1712, 1598, 1578, 1481, 1447, 1425, 1336, 1266, 1234, 1215, 1175, 1149, 1121, 1027, 1005, 965, 904, 810, 724, 693, 649 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{32}ClNNaO_9$ ($[M + Na]^+$): 636.1760, found: 636.1747.

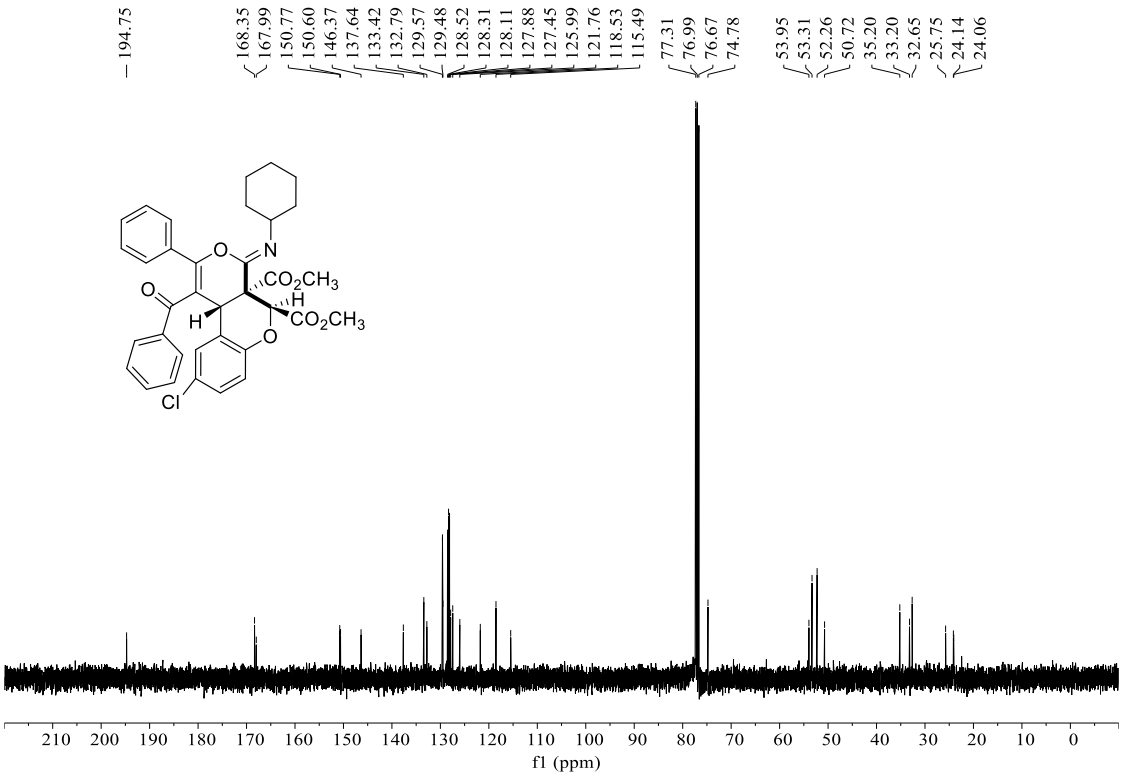


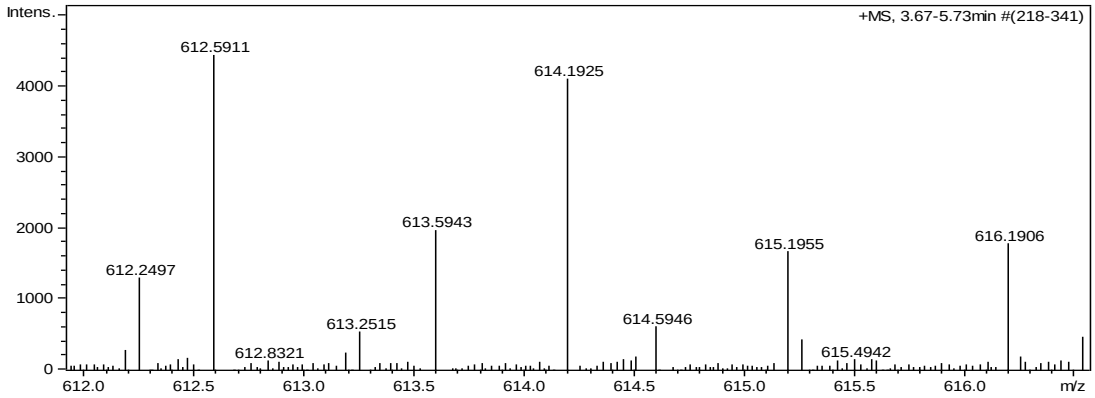

196.26
169.88
168.23
160.35
150.57
141.65
137.76
132.66
132.07
130.67
129.52
129.29
129.08
128.66
127.98
127.92
126.50
122.15
117.83
113.59
77.29
76.97
76.65
75.22
53.73
53.30
52.54
51.17
40.67
32.97
32.80
25.79
23.64
23.58
N
O
H3CO2C
H
H3CO2C
O
H
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^4
+MS, 3.01-5.35min #(179-318)
636.1747
634.2010
637.1778
638.1734
635.2037
0
2
4
6
634.0 634.5 635.0 635.5 636.0 636.5 637.0 637.5 638.0
m/z

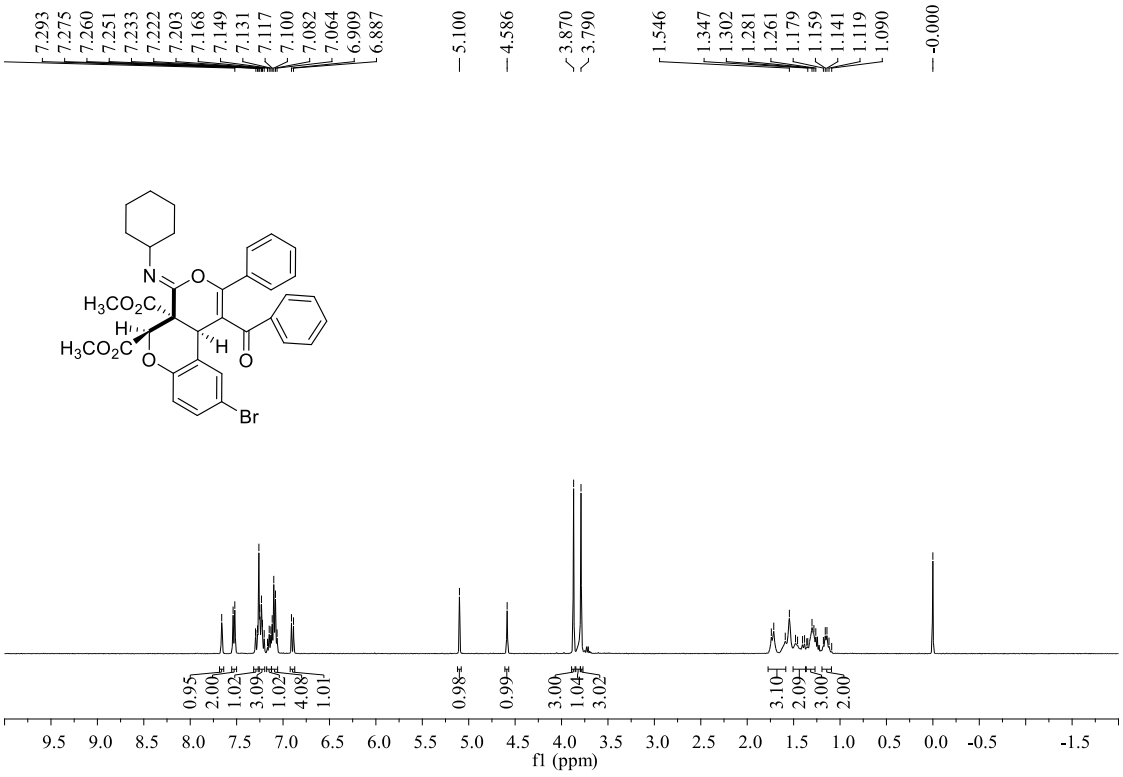
Dimethyl *rel*-(4a*S*,5*S*,10b*R*,*Z*)-1-benzoyl-9-chloro-4-(cyclohexylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4c'): Yellow solid, 24%, mp 211-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 7.6 Hz, 2H, ArH), 7.44-7.40 (m, 1H, ArH), 7.30 (d, *J* = 7.2 Hz, 2H, ArH), 7.29-7.26 (m, 2H, ArH), 7.19-7.12 (m, 3H, ArH), 7.02 (d, *J* = 8.8 Hz, 1H, ArH), 6.83 (d, *J* = 8.8 Hz, 1H, ArH), 6.70 (d, *J* = 0.8 Hz, 1H, ArH), 5.49 (s, 1H, CH), 5.46 (s, 1H, CH), 3.85 (s, 1H, CH), 3.77 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 1.71-1.67 (m, 4H, CH), 1.61-1.56 (m, 1H, CH), 1.32-1.29 (m, 5H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 194.8, 168.4, 168.0, 150.8, 150.6, 146.4, 137.6, 133.4, 132.8, 129.6, 129.5, 128.5, 128.3, 128.1, 127.9, 127.5, 126.0, 121.8, 118.5, 115.5, 74.9, 54.0, 53.3, 52.3, 50.7, 35.2, 33.2, 32.7, 25.8, 24.14, 24.06; IR (KBr) υ: 2930, 2845, 1776, 1730, 1700, 1603, 1566, 1478, 1450, 1423, 1365, 1260, 1233, 1210, 1160, 1152, 1134, 1030, 1001, 982, 900, 780, 735, 690, 650 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{33}ClNO_9$ ([M + H]$^+$): 614.1940, found: 614.1925

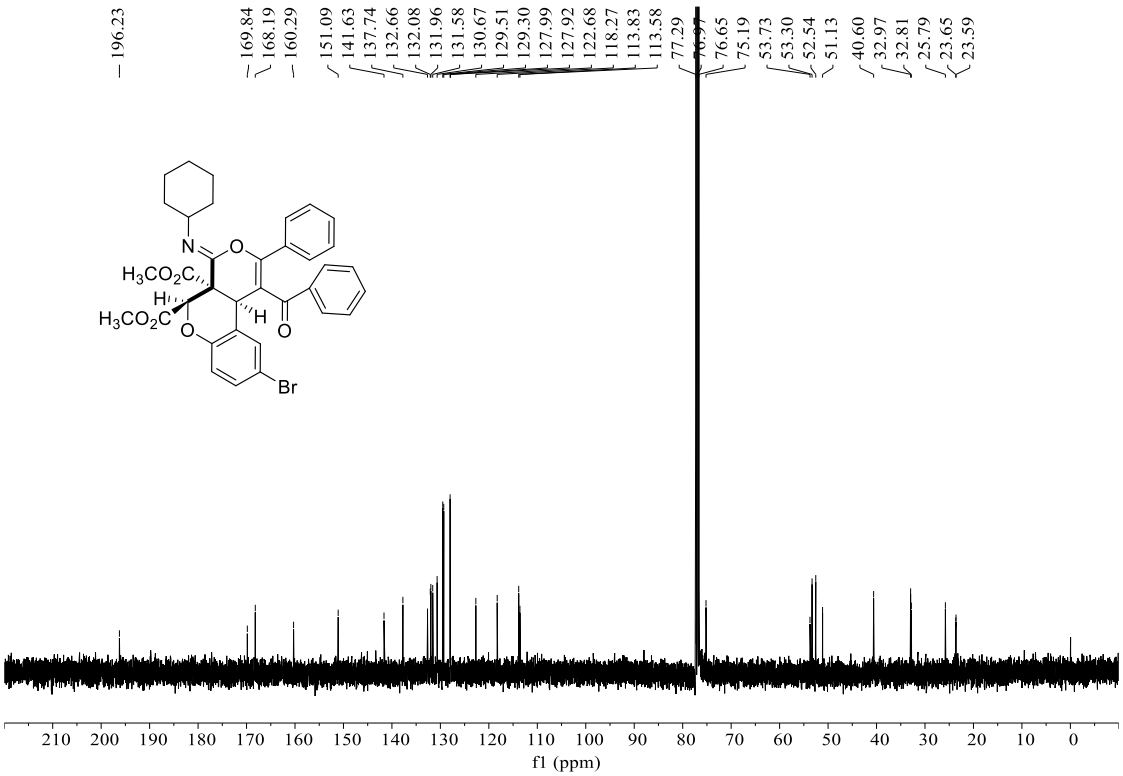


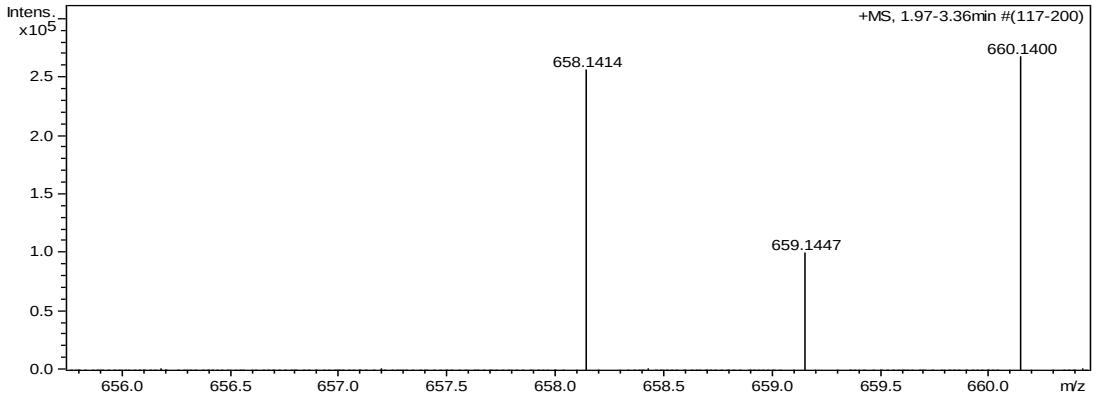

194.75
168.35
167.99
150.77
150.60
146.37
137.64
133.42
132.79
129.57
129.48
128.52
128.31
128.11
127.88
127.45
125.99
121.76
118.53
115.49
77.31
76.99
76.67
74.78
53.95
53.31
52.26
50.72
35.20
33.20
32.65
25.75
24.14
24.06
O
N
CO2CH3
H
O
H
CO2CH3
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
+MS, 3.67-5.73min #(218-341)
612.5911
614.1925
613.5943
615.1955
616.1906
612.2497
613.2515
614.5946
612.8321
615.4942
4000
3000
2000
1000
0
612.0 612.5 613.0 613.5 614.0 614.5 615.0 615.5 616.0
m/z

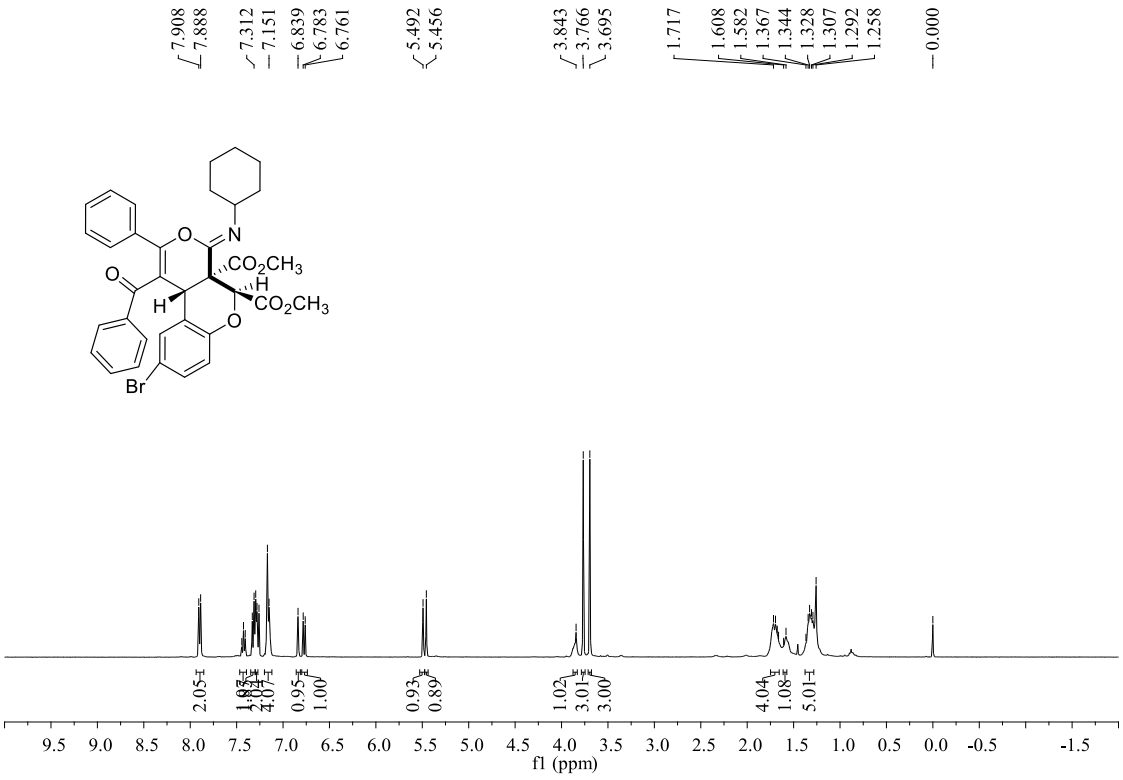
Dimethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-9-bromo-4-(cyclohexylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4d): Yellow solid, 33%, mp 216-217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (s, 1H, ArH), 7.53 (d, *J* = 7.2 Hz, 2H, ArH), 7.28-7.27 (m, 1H, ArH), 7.25-7.20 (m, 3H, ArH), 7.17-7.13 (m, 1H, ArH), 7.12-7.06 (m, 4H, ArH), 6.90 (d, *J* = 8.8 Hz, 1H, ArH), 5.10 (s, 1H, CH), 4.59 (s, 1H, CH), 3.87 (s, 3H, OCH_3), 3.84-3.80 (m, 1H, CH), 3.79 (s, 3H, OCH_3), 1.74-1.59 (m, 3H, CH), 1.48-1.38 (m, 2H, CH), 1.36-1.28 (m, 3H, CH), 1.18-1.09 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.2, 169.8, 168.2, 160.3, 151.1, 141.6, 137.7, 132.7, 132.1, 132.0, 131.6, 130.7, 129.5, 129.3, 128.0, 127.9, 122.7, 118.3, 113.8, 113.6, 75.2, 53.7, 53.3, 52.5, 51.1, 40.6, 33.0, 32.8, 25.8, 23.7, 23.6; IR (KBr) υ: 2932, 2843, 1766, 1732, 1713, 1621, 1598, 1578, 1480, 1447, 1337, 1268, 1235, 1216, 1149, 1124, 1028, 1005, 905, 809, 723, 693, 650 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{33}BrNO_7$ ($[M + H]^+$): 658.1435, found: 658.1414.

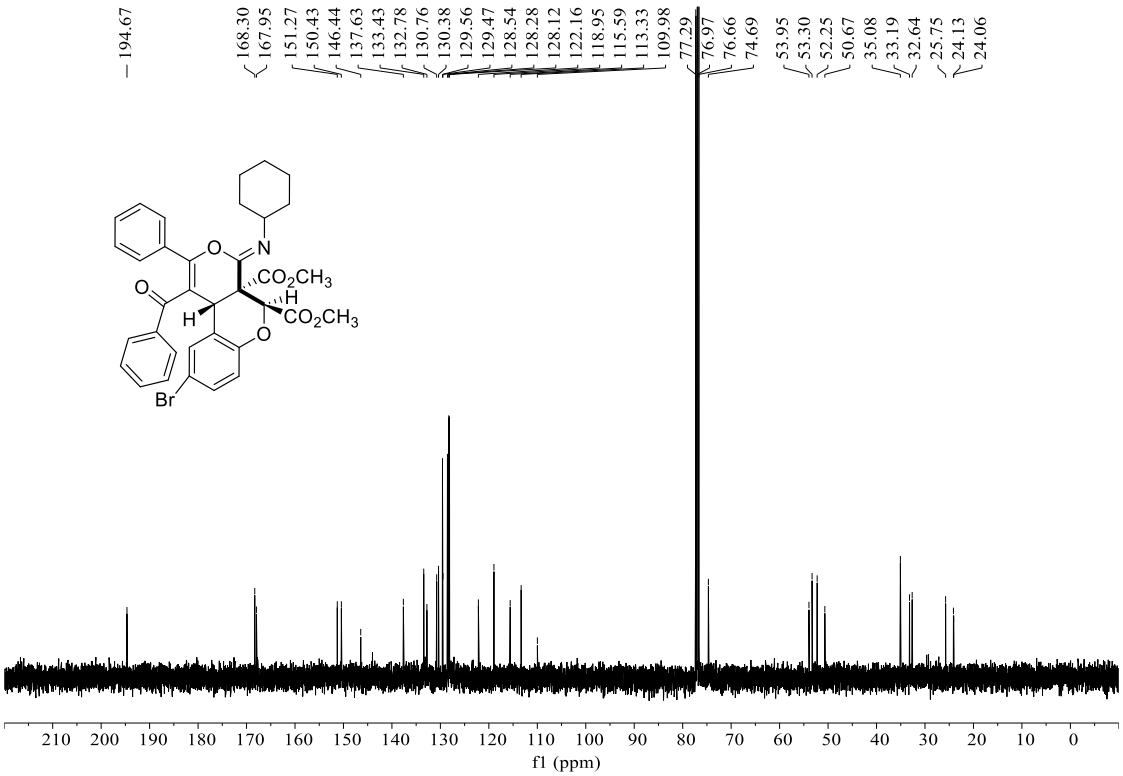


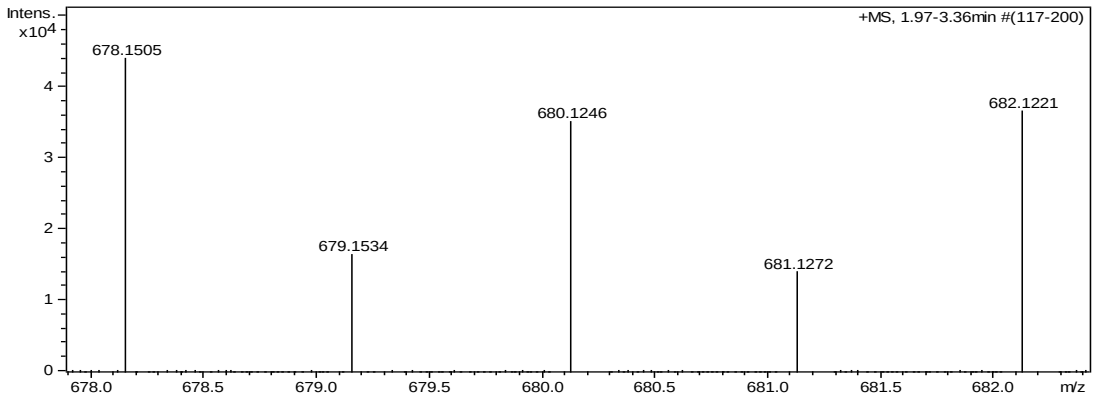

196.23
169.84
168.19
160.29
151.09
141.63
137.74
132.66
132.08
131.96
131.58
130.67
129.51
129.30
127.99
127.92
122.68
118.27
113.83
113.58
77.29
76.97
76.65
75.19
53.73
53.30
52.54
51.13
40.60
32.97
32.81
25.79
23.65
23.59
N
O
H3CO2C
H
H3CO2C
O
H
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 1.97-3.36min #(117-200)
658.1414
660.1400
659.1447
2.5
2.0
1.5
1.0
0.5
0.0
656.0
656.5
657.0
657.5
658.0
658.5
659.0
659.5
660.0
m/z

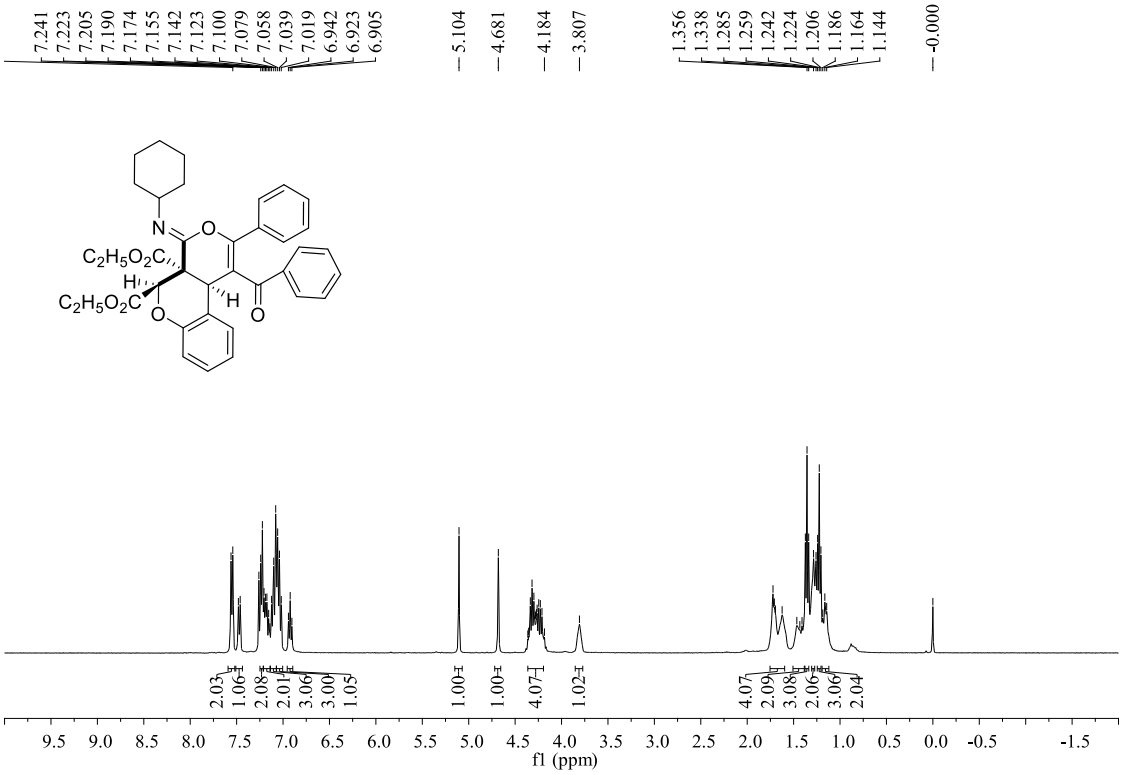
Dimethyl *rel*-(4a*S*,5*S*,10b*R*,*Z*)-1-benzoyl-9-bromo-4-(cyclohexylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4d'): Yellow solid, 24%, mp 224-225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.0 Hz, 2H, ArH), 7.44-7.41 (m, 1H, ArH), 7.32 (d, *J* = 7.6 Hz, 2H, ArH), 7.29-7.27 (m, 2H, ArH), 7.19-7.12 (m, 4H, ArH), 6.84 (s, 1H, ArH), 6.77 (d, *J* = 8.8 Hz, 1H, ArH), 5.49 (s, 1H, CH), 5.46 (s, 1H, CH), 3.84 (s, 1H, CH), 3.77 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 1.72-1.66 (m, 4H, CH), 1.61-1.58 (m, 1H, CH), 1.36-1.29 (m, 5H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 194.7, 168.3, 168.0, 151.3, 150.4, 146.4, 137.6, 133.4, 132.8, 130.8, 130.4, 129.6, 129.5, 128.6, 128.3, 128.1, 122.2, 119.0, 115.6, 113.3, 110.0, 74.7, 54.0, 53.3, 52.3, 50.7, 35.1, 33.2, 32.6, 25.8, 24.13, 24.06; IR (KBr) υ: 2966, 2843, 1782, 1744, 1607, 1598, 1561, 1482, 1432, 1423, 1340, 1269, 1238, 1211, 1154, 1150, 1130, 1017, 1000, 997, 893, 769, 740, 680, 640 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{32}BrNNaO_7$ ([M + Na]$^+$): 680.1254, found: 680.1246.

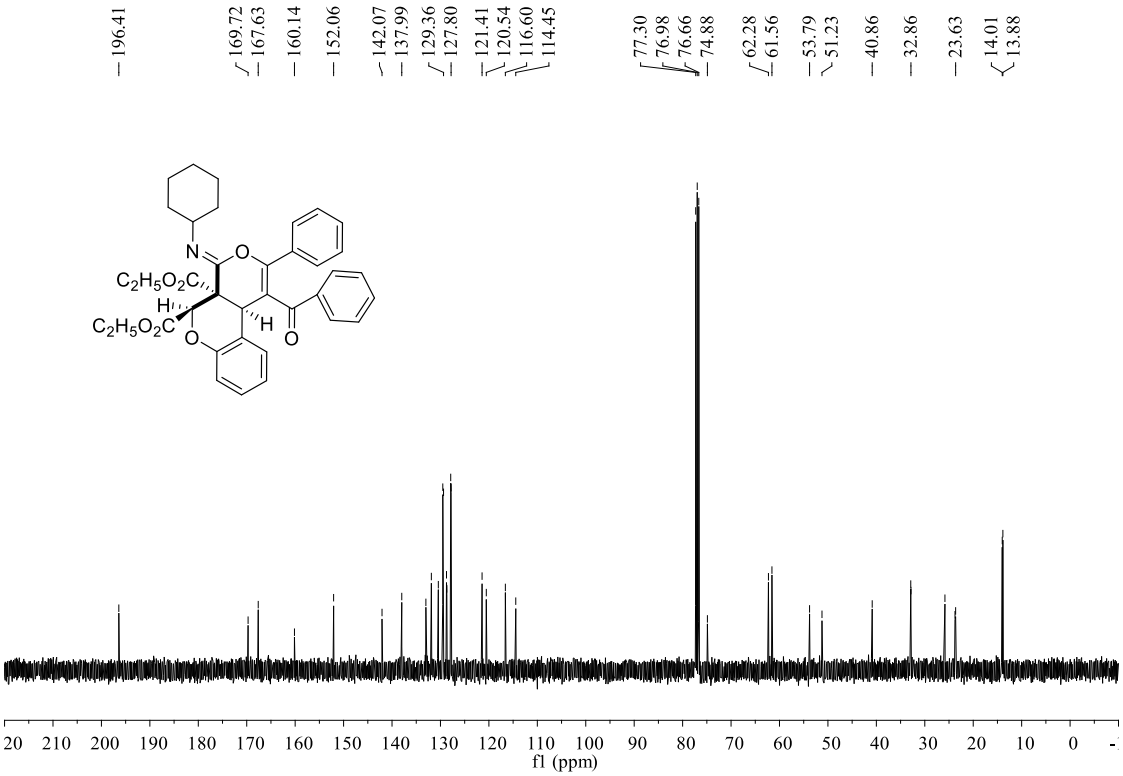


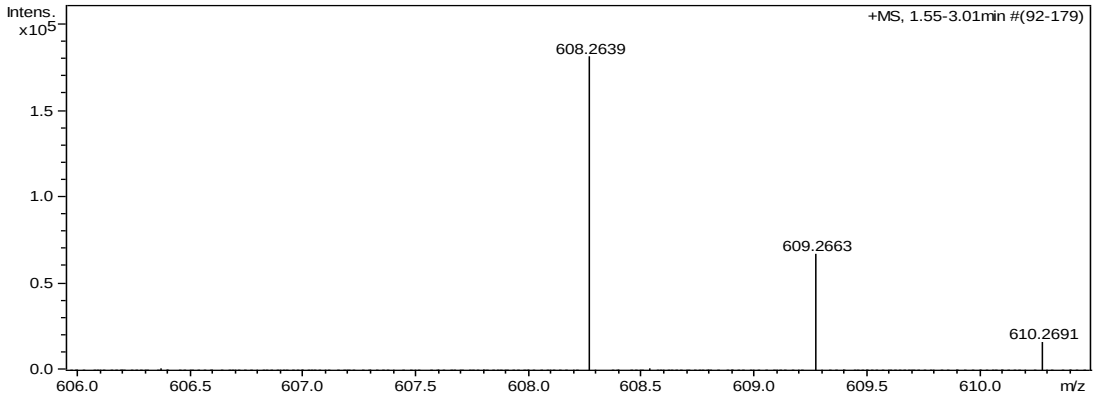

194.67
168.30
167.95
151.27
150.43
146.44
137.63
133.43
132.78
130.76
130.38
129.56
129.47
128.54
128.28
128.12
122.16
118.95
115.59
113.33
109.98
77.29
76.97
76.66
74.69
53.95
53.30
52.25
50.67
35.08
33.19
32.64
25.75
24.13
24.06
O
N
CO2CH3
H
O
H
CO2CH3
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^4
+MS, 1.97-3.36min #(117-200)
678.1505
679.1534
680.1246
681.1272
682.1221
0
1
2
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678.5
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679.5
680.0
680.5
681.0
681.5
682.0
m/z

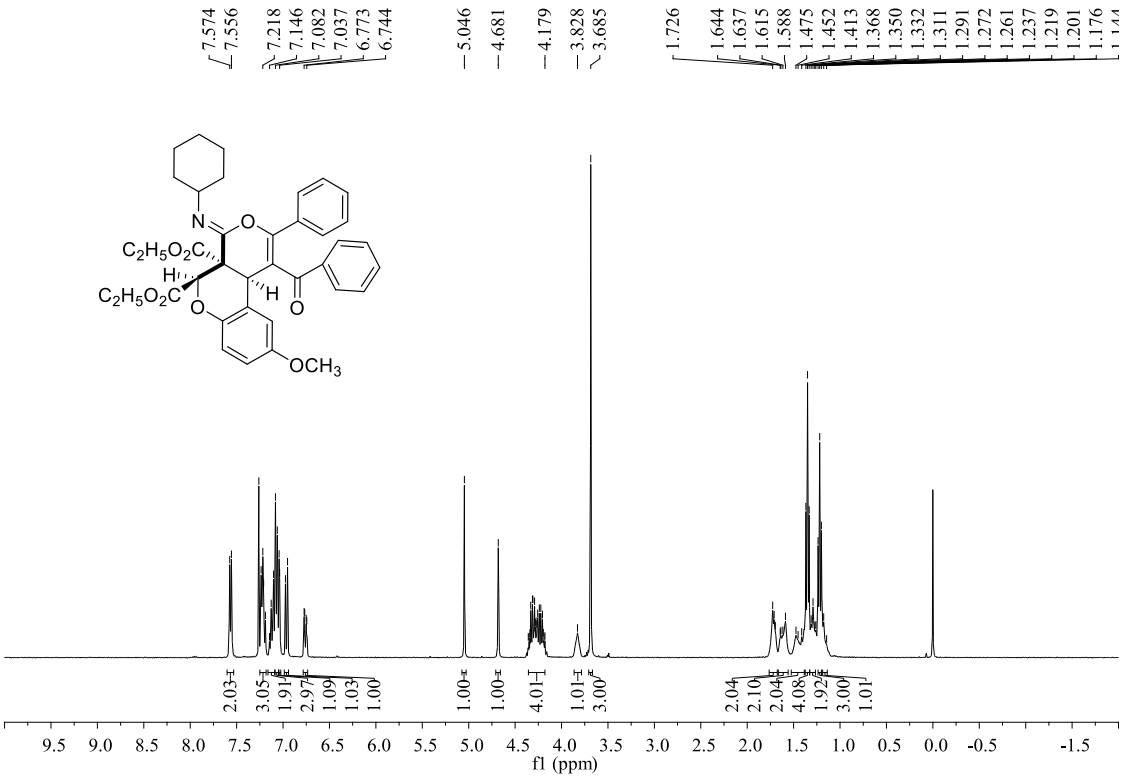
Diethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-4-(cyclohexylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4e): Yellow solid, 33%, mp 187-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 7.6 Hz, 2H, ArH), 7.47 (d, *J* = 7.6 Hz, 1H, ArH), 7.23 (d, *J* = 7.2 Hz, 2H, ArH), 7.20-7.14 (m, 2H, ArH), 7.12-7.08 (m, 3H, ArH), 7.06-7.02 (m, 3H, ArH), 6.94-6.91 (m, 1H, ArH), 5.10 (s, 1H, CH), 4.68 (s, 1H, CH), 4.36-4.18 (m, 4H, CH_2), 3.81 (s, 1H, CH), 1.72-1.62 (m, 4H, CH), 1.47-1.41 (m, 2H, CH), 1.36 (t, *J* = 6.8 Hz, 3H, CH_3), 1.29 (s, 2H, CH), 1.22 (t, *J* = 7.2 Hz, 3H, CH_3), 1.19-1.14 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.4, 169.7, 167.6, 160.1, 152.1, 142.1, 134.0, 133.0, 131.9, 130.4, 129.5, 129.4, 128.8, 128.7, 127.9, 127.8, 121.4, 120.5, 116.6, 114.5, 74.9, 62.3, 61.6, 53.8, 51.2, 40.9, 32.9, 32.9, 25.8, 23.8, 23.6, 14.0, 13.9; IR (KBr) υ: 2995, 2924, 2811, 1753, 1723, 1710, 1621, 1600, 1487, 1452, 1342, 1320, 1288, 1211, 1190, 1153, 1123, 1088, 1023, 1035, 1001, 912, 816, 754, 733, 722, 675, 632 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{37}H_{38}NO_7$ ([M + H]$^+$): 608.2643, found: 608.2639.

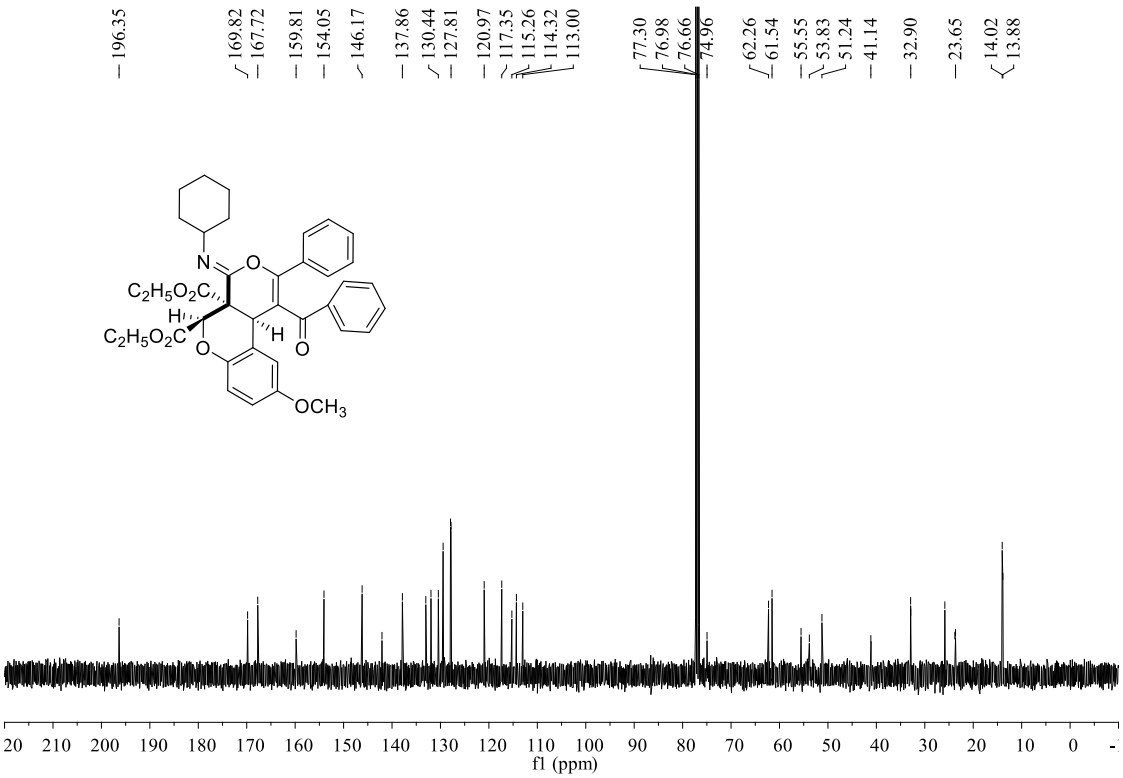


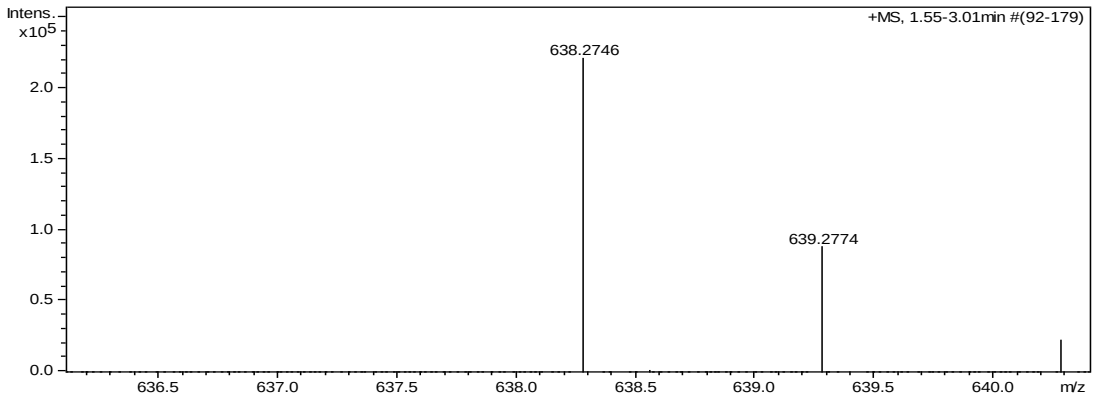

196.41
169.72
167.63
160.14
152.06
142.07
137.99
129.36
127.80
121.41
120.54
116.60
114.45
77.30
76.98
76.66
74.88
62.28
61.56
53.79
51.23
40.86
32.86
23.63
14.01
13.88
N
O
C2H5O2C
H
C2H5O2C
O
H
O
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 1.55-3.01min #(92-179)
608.2639
609.2663
610.2691
1.5
1.0
0.5
0.0
606.0
606.5
607.0
607.5
608.0
608.5
609.0
609.5
610.0
m/z

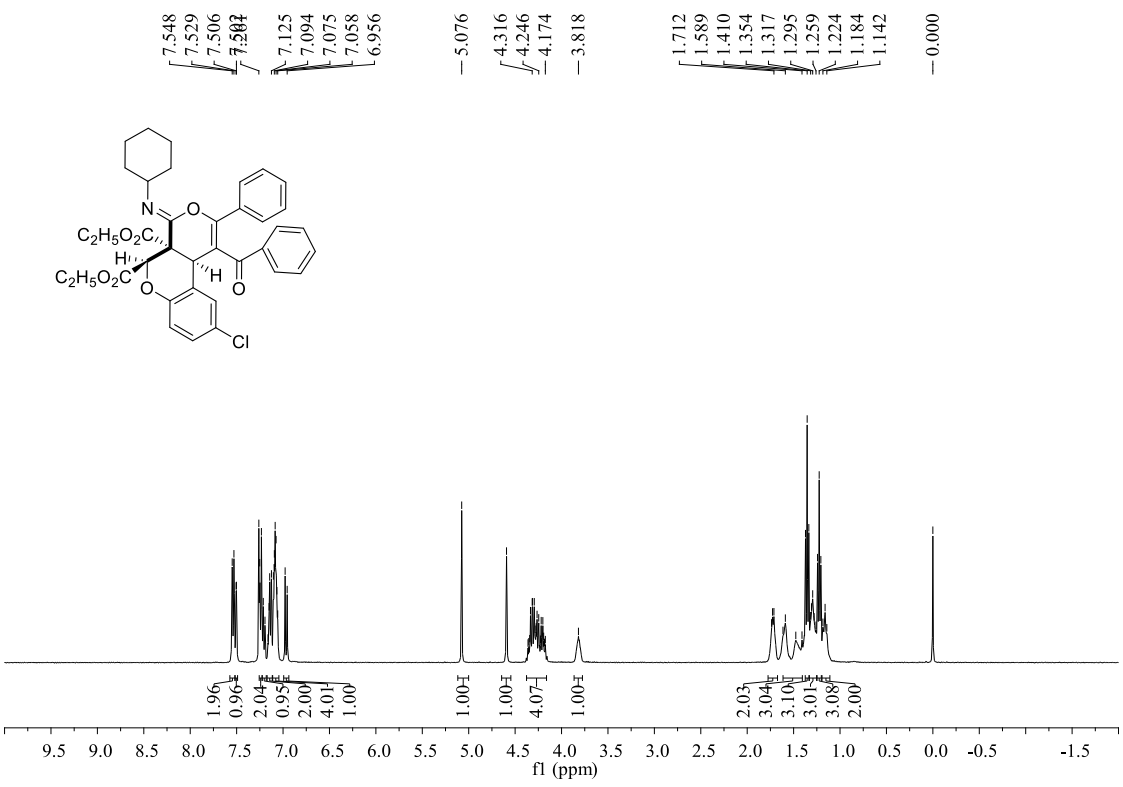
Diethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-4-(cyclohexylimino)-9-methoxy-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4f): Yellow solid, 31%, mp 149-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.2 Hz, 2H, ArH), 7.24-7.19 (m, 3H, ArH), 7.15-7.10 (m, 2H, ArH), 7.07 (d, *J* = 8.0 Hz, 2H, ArH), 7.05-7.03 (m, 2H, ArH), 6.96 (d, *J* = 8.8 Hz, 1H, ArH), 6.76 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H, ArH), 5.05 (s, 1H, CH), 4.68 (s, 1H, CH), 4.35-4.18 (m, 4H, CH_2), 3.83 (s, 1H, CH), 3.69 (s, 3H, OCH_3), 1.73-1.70 (m, 2H, CH), 1.64-1.59 (m, 2H, CH), 1.48-1.41 (m, 2H, CH), 1.35 (t, *J* = 7.2 Hz, 4H, CH_3, CH), 1.31-1.27 (m, 2H, CH), 1.22 (t, *J* = 7.2 Hz, 3H, CH_3), 1.18-1.14 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.4, 169.8, 167.7, 159.8, 154.1, 146.2, 142.1, 137.9, 133.0, 132.0, 130.4, 129.5, 127.9, 127.8, 121.0, 117.4, 115.3, 114.3, 113.0, 75.0, 62.3, 61.5, 55.6, 53.8, 51.2, 41.1, 32.92, 32.90, 25.9, 23.8, 23.7, 14.0, 13.9; IR (KBr) υ: 2987, 2930, 2845, 1763, 1733, 1712, 1621, 1598, 1497, 1447, 1351, 1337, 1276, 1214, 1168, 1142, 1118, 1094, 1072, 1039, 1003, 907, 814, 767, 726, 710, 691, 649 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{38}H_{40}NO_8$ ($[M + H]^+$): 638.2748, found: 638.2746.

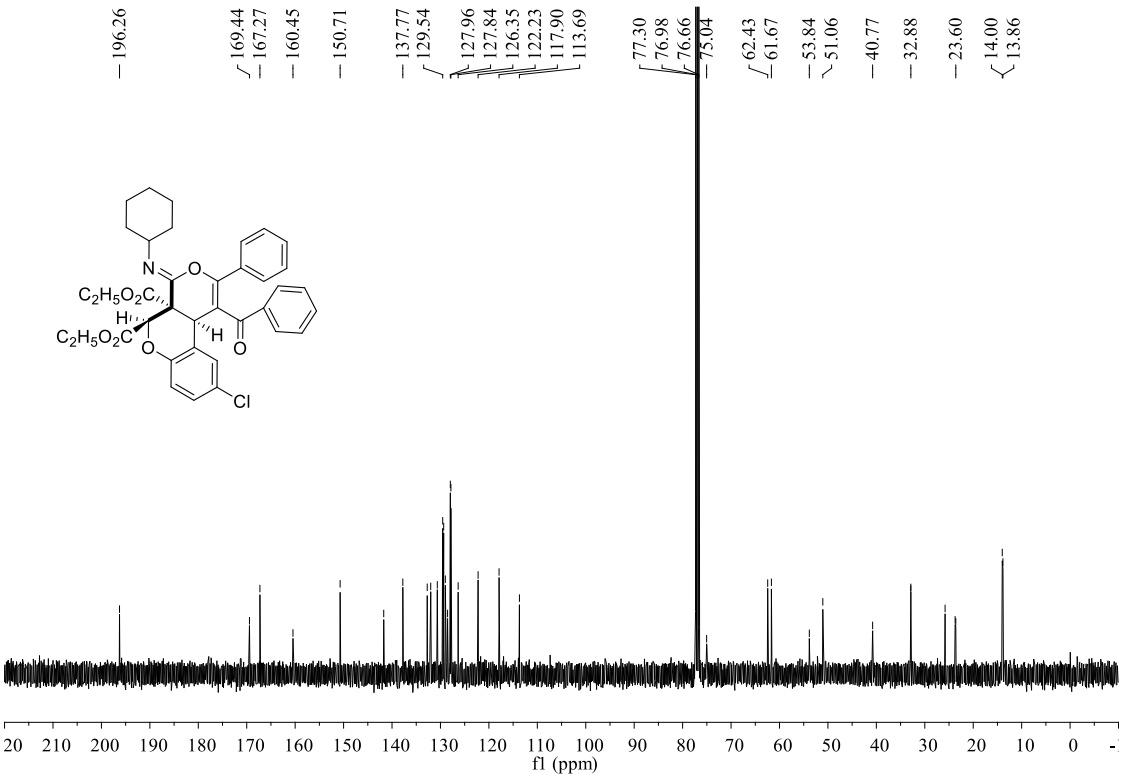


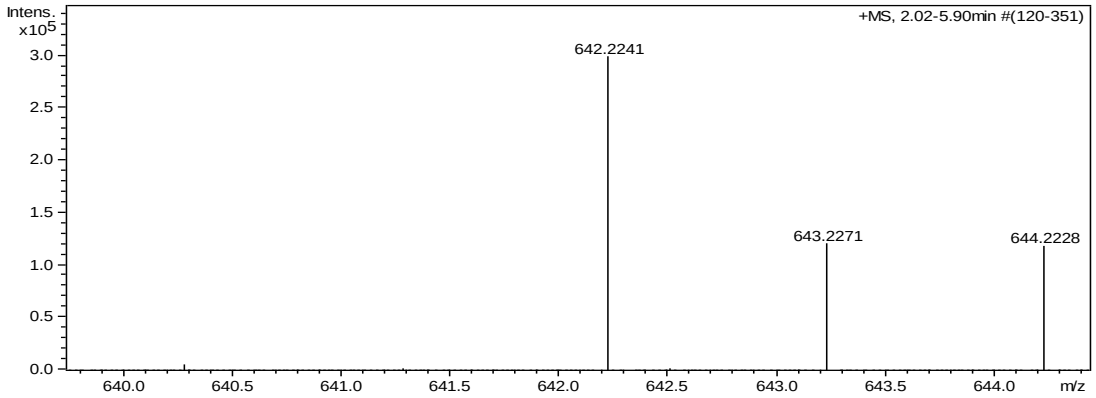

196.35
169.82
167.72
159.81
154.05
146.17
137.86
130.44
127.81
120.97
117.35
115.26
114.32
113.00
77.30
76.98
76.66
74.96
62.26
61.54
55.55
53.83
51.24
41.14
32.90
23.65
14.02
13.88
N
O
C2H5O2C
H
C2H5O2C
O
H
O
OCH3
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 1.55-3.01min #(92-179)
638.2746
639.2774
2.0
1.5
1.0
0.5
0.0
636.5
637.0
637.5
638.0
638.5
639.0
639.5
640.0
m/z

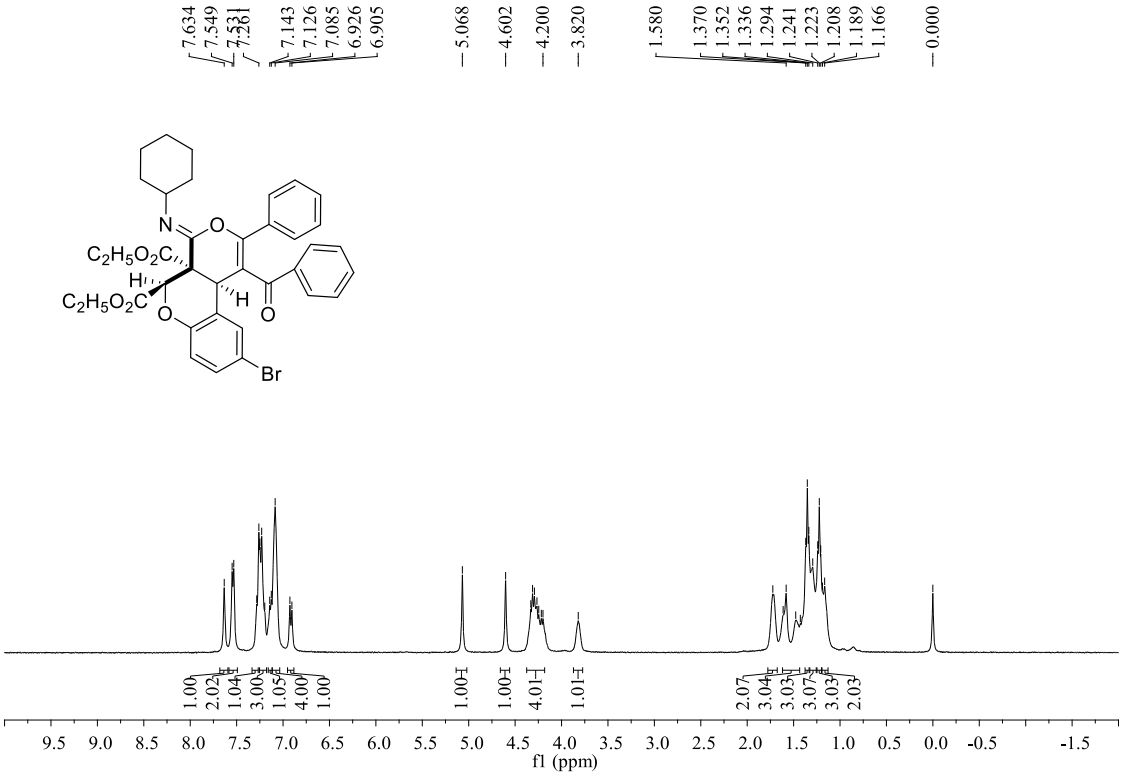
Diethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-9-chloro-4-(cyclohexylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4g): Yellow solid, 28%, mp 184-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 7.6 Hz, 2H, ArH), 7.50 (d, *J* = 1.6 Hz, 1H, ArH), 7.24 (d, *J* = 7.2 Hz, 2H, ArH), 7.20 (d, *J* = 7.2 Hz, 1H, ArH), 7.16-7.13 (m, 2H, ArH), 7.10-7.06 (m, 4H, ArH), 6.97 (d, *J* = 8.8 Hz, 1H, ArH), 5.08 (s, 1H, CH), 4.59 (s, 1H, CH), 4.33-4.17 (m, 4H, CH_2), 3.82 (s, 1H, CH), 1.73-1.71 (m, 2H, CH), 1.61-1.41 (m, 3H, CH), 1.35 (t, *J* = 7.2 Hz, 3H, CH_3), 1.32-1.28 (m, 3H, CH), 1.22 (t, *J* = 7.2 Hz, 3H, CH_3), 1.18-1.14 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.3, 169.4, 167.3, 160.5, 150.7, 141.7, 137.8, 132.7, 132.0, 130.7, 129.6, 129.3, 129.0, 128.5, 128.0, 127.8, 126.4, 122.3, 117.9, 113.7, 75.0, 62.4, 61.7, 53.8, 51.1, 40.8, 32.9, 32.88, 25.8, 23.7, 23.6, 14.0, 13.9; IR (KBr) υ: 2983, 2926, 2844, 1732, 1717, 1615, 1598, 1475, 1448, 1373, 1352, 1339, 1233, 1147, 1120, 1088, 1064, 1025, 1002, 905, 723, 700, 650, 592 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{37}H_{37}ClNO_7$ ([M + H]$^+$): 642.2253, found: 642.2241.

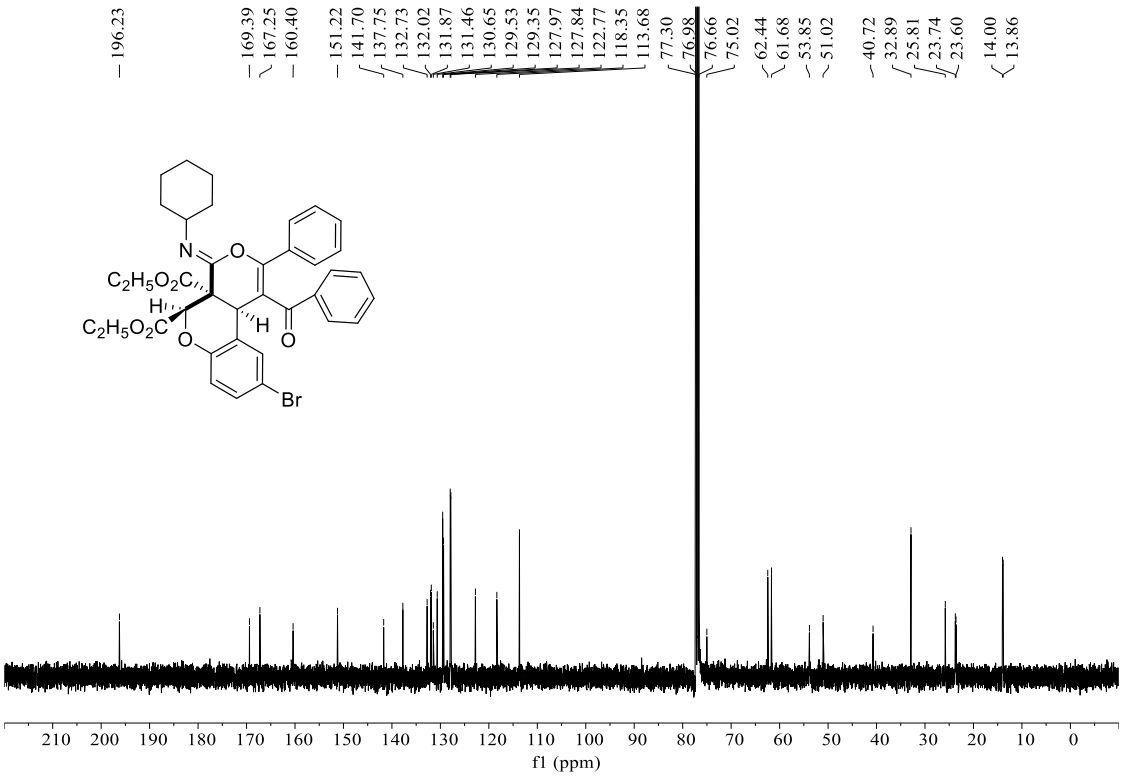


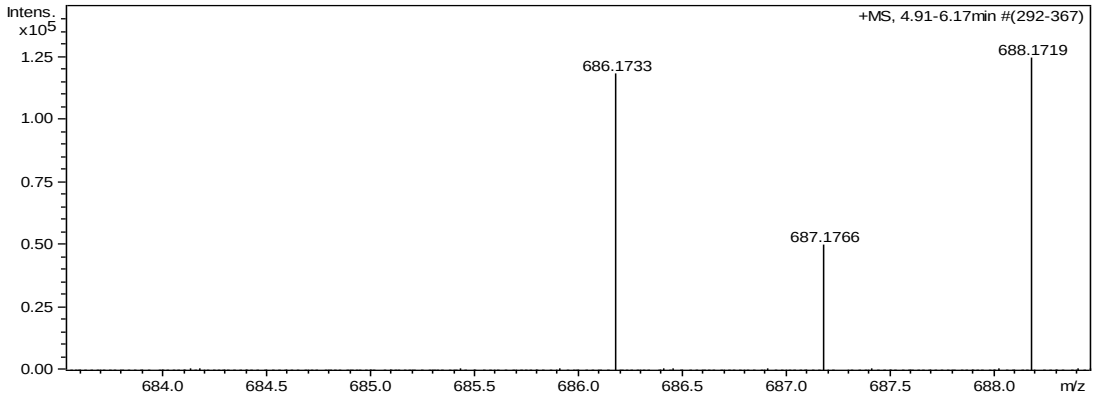

196.26
169.44
167.27
160.45
150.71
137.77
129.54
127.96
127.84
126.35
122.23
117.90
113.69
77.30
76.98
76.66
75.04
62.43
61.67
53.84
51.06
40.77
32.88
23.60
14.00
13.86
N
O
C2H5O2C
H
C2H5O2C
O
H
O
Cl
f1 (ppm)


Intens.
x10^5
+MS, 2.02-5.90min #(120-351)
642.2241
643.2271
644.2228
m/z

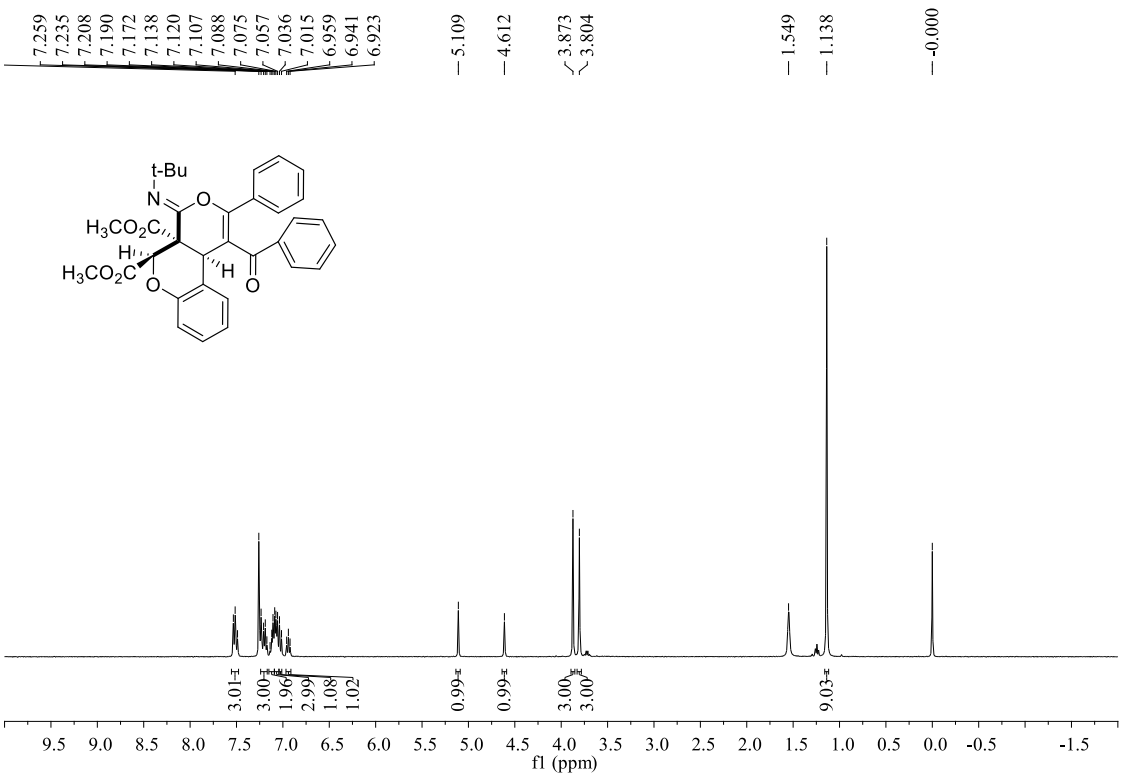
Diethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-9-bromo-4-(cyclohexylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4h): Yellow solid, 30%, mp 193-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (s, 1H, ArH), 7.54 (d, *J* = 7.2 Hz, 2H, ArH), 7.34-7.27 (m, 1H, ArH), 7.25-7.20 (m, 3H, ArH), 7.13 (d, *J* = 6.8 Hz, 1H, ArH), 7.01 (s, 4H, ArH), 6.92 (d, *J* = 8.4 Hz, 1H, ArH), 5.07 (s, 1H, CH), 4.60 (s, 1H, CH), 4.33-4.20 (m, 4H, CH_2), 3.82 (s, 1H, CH), 1.72 (s, 2H, CH), 1.62-1.43 (m, 3H, CH), 1.35 (t, *J* = 7.2 Hz, 3H, CH_3), 1.33-1.26 (m, 3H, CH), 1.22 (t, *J* = 7.2 Hz, 3H, CH_3), 1.19-1.16 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.2, 169.4, 167.3, 160.4, 151.2, 141.7, 137.8, 132.7, 132.0, 131.9, 131.5, 130.7, 129.5, 129.4, 128.0, 127.8, 122.8, 118.4, 113.7, 75.0, 62.4, 61.7, 53.9, 51.0, 40.7, 32.9, 25.8, 23.7, 23.6, 14.0, 13.9; IR (KBr) υ: 2983, 2929, 2844, 1732, 1716, 1616, 1598, 1474, 1448, 1407, 1373, 1352, 1339, 1232, 1187, 1147, 1120, 1025, 910, 723, 698, 650, 591 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{37}H_{37}BrNO_7$ ([M + H]$^{+}$): 686.1748, found: 686.1733.

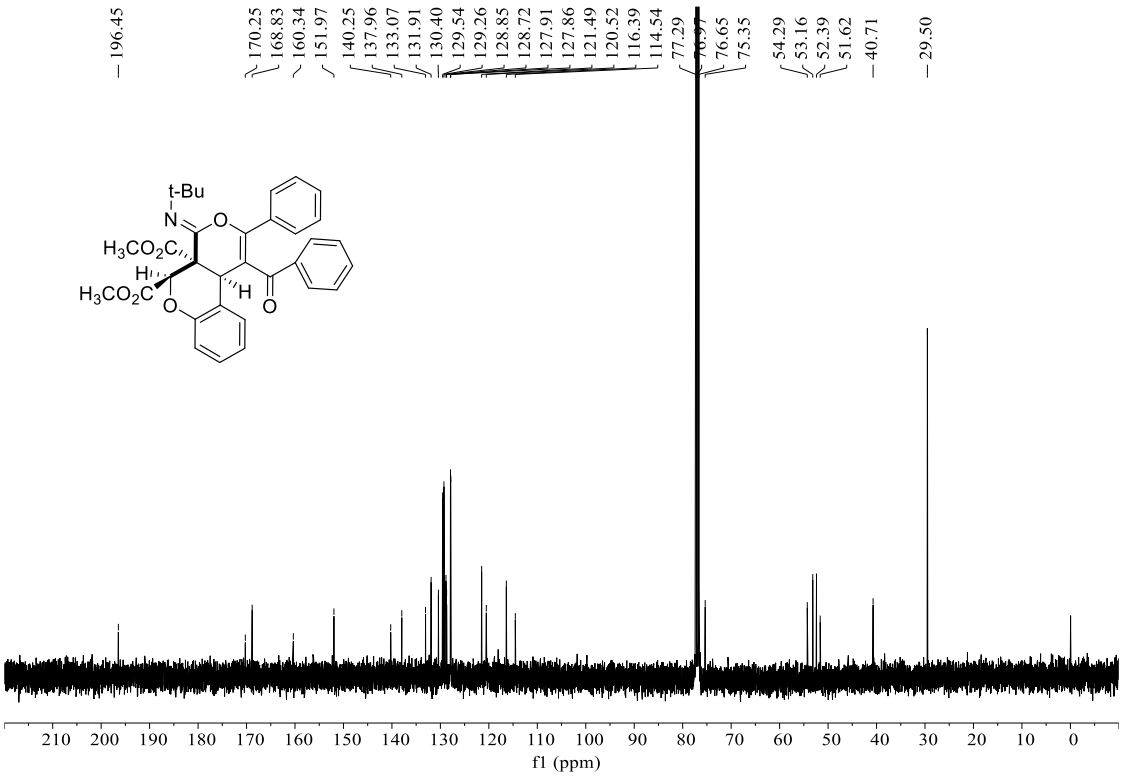


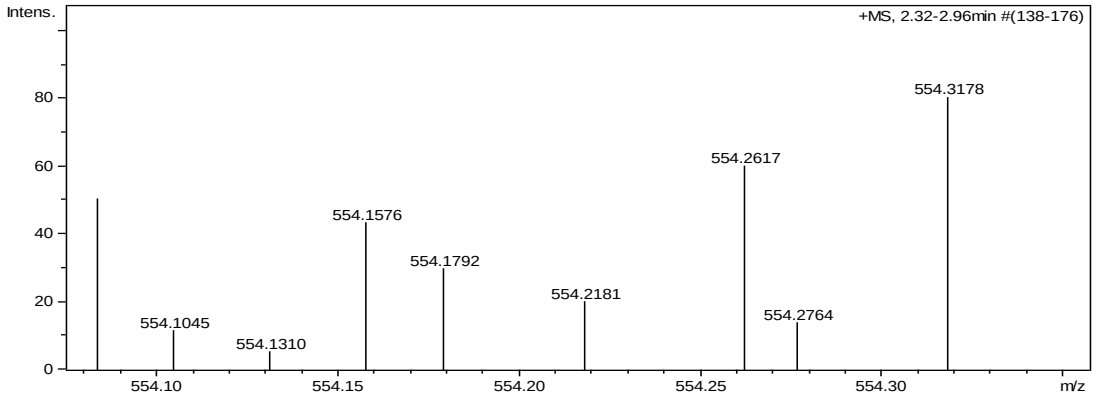

196.23
169.39
167.25
160.40
151.22
141.70
137.75
132.73
132.02
131.87
131.46
130.65
129.53
129.35
127.97
127.84
122.77
118.35
113.68
77.30
76.98
76.66
75.02
62.44
61.68
53.85
51.02
40.72
32.89
25.81
23.74
23.60
14.00
13.86
N
O
C2H5O2C
H
C2H5O2C
O
H
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 4.91-6.17min #(292-367)
1.25
1.00
0.75
0.50
0.25
0.00
686.1733
688.1719
687.1766
684.0 684.5 685.0 685.5 686.0 686.5 687.0 687.5 688.0
m/z

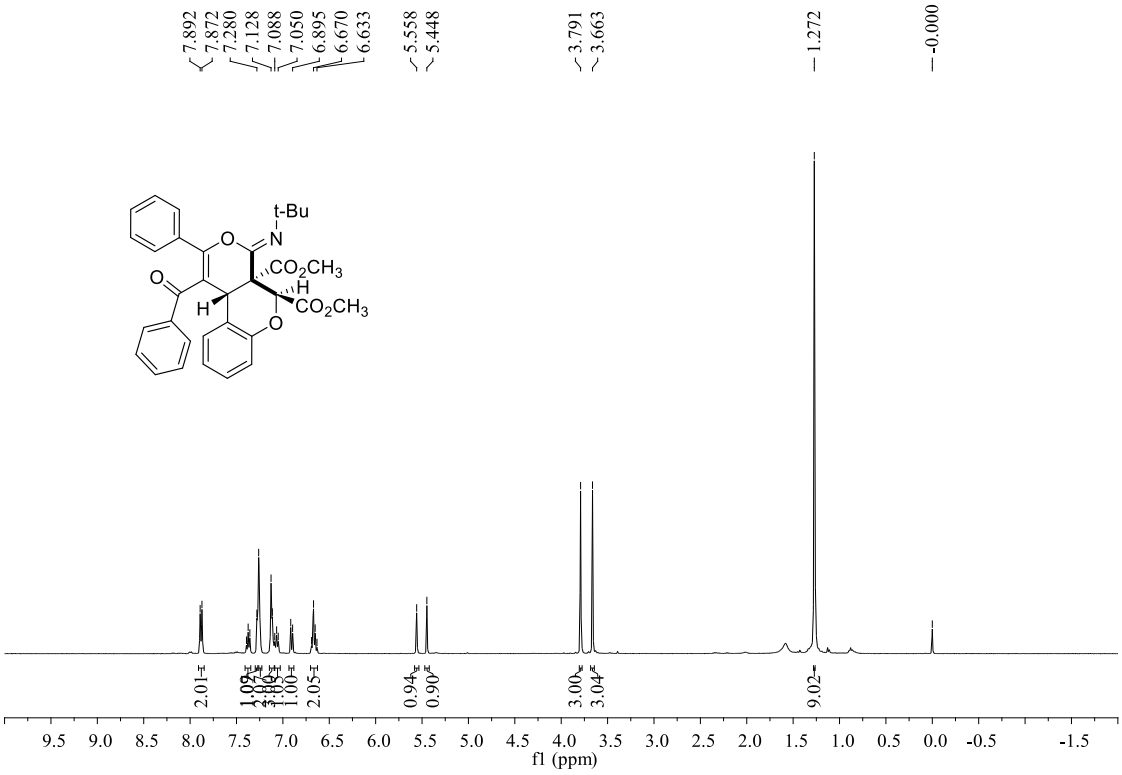
Dimethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-4-(*tert*-butylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4i): Yellow solid, 39%, mp 205-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (t, *J* = 7.6 Hz, 3H, ArH), 7.24-7.17 (m, 3H, ArH), 7.14-7.11 (m, 2H, ArH), 7.09-7.06 (m, 3H, ArH), 7.03 (d, *J* = 8.4 Hz, 1H, ArH), 6.94 (t, *J* = 7.1 Hz, 1H, ArH), 5.11 (s, 1H, CH), 4.61 (s, 1H, CH), 3.87 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 1.14 (s, 9H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.5, 170.3, 168.8, 160.3, 152.0, 140.3, 138.0, 133.1, 131.9, 130.4, 129.5, 129.3, 128.9, 128.7, 127.9, 127.9, 121.5, 120.5, 116.4, 114.5, 75.4, 54.3, 53.2, 52.4, 51.6, 40.7, 29.5; IR (KBr) υ: 2986, 2967, 2877, 1764, 1746, 1721, 1625, 1595, 1586, 1578, 1486, 1435, 1427, 1355, 1330, 1268, 1236, 1191, 1065, 1037, 1003, 929, 770, 747, 738, 694, 652, 595 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{33}H_{32}NO_7$ ($[M + H]^+$): 554.2173, found: 554.2181.

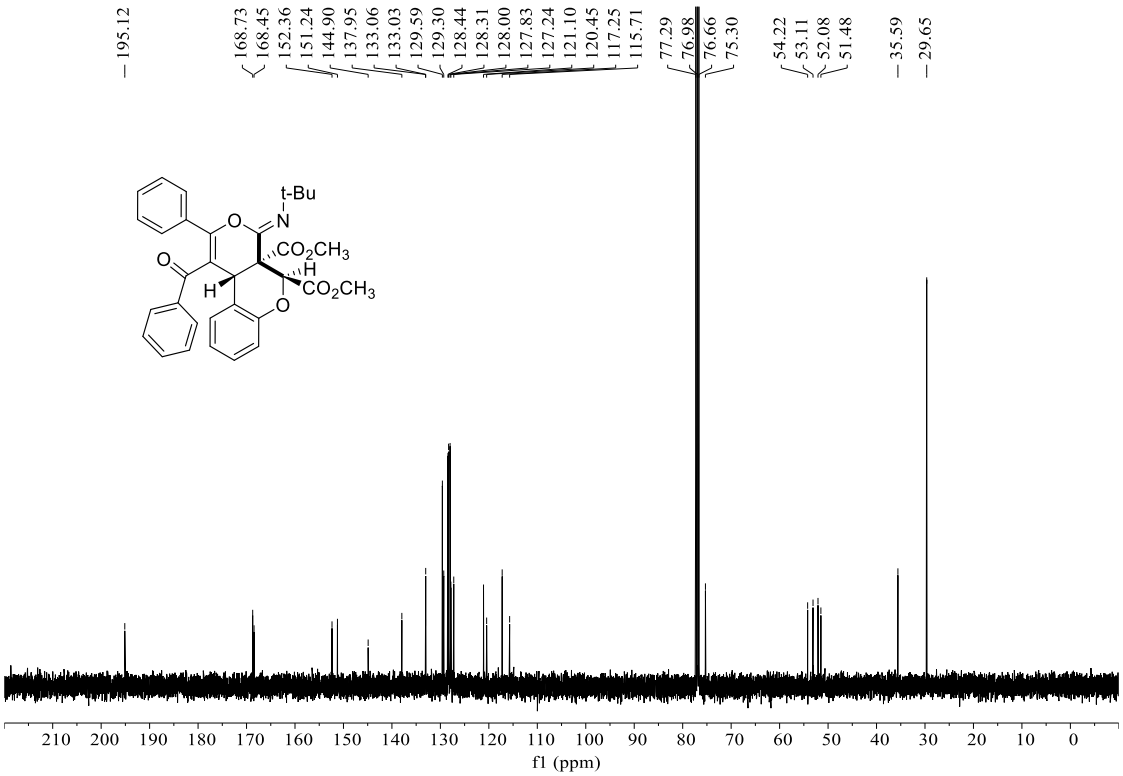


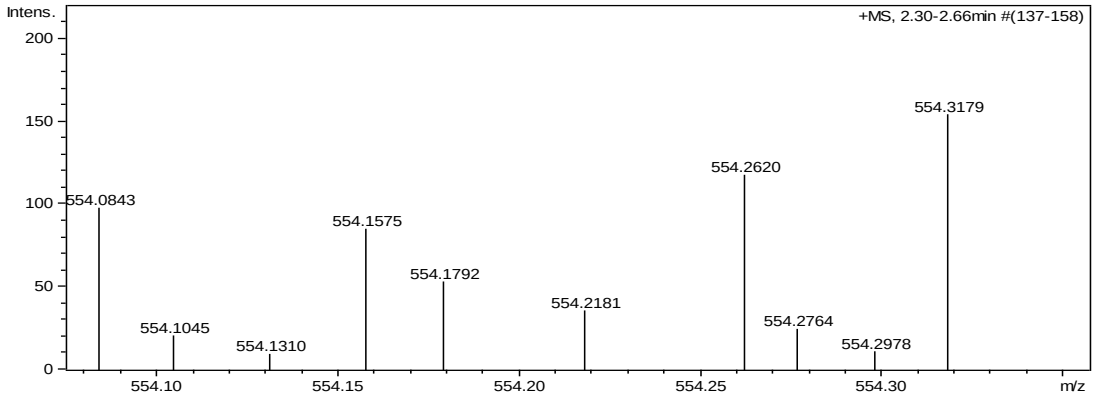

196.45
170.25
168.83
160.34
151.97
140.25
137.96
133.07
131.91
130.40
129.54
129.26
128.85
128.72
127.91
127.86
121.49
120.52
116.39
114.54
77.29
76.97
76.65
75.35
54.29
53.16
52.39
51.62
40.71
29.50
t-Bu
N
O
H3CO2C
H
H3CO2C
O
H
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
+MS, 2.32-2.96min #(138-176)
554.3178
554.2617
554.1576
554.1792
554.2181
554.2764
554.1045
554.1310
0
20
40
60
80
554.10
554.15
554.20
554.25
554.30
m/z

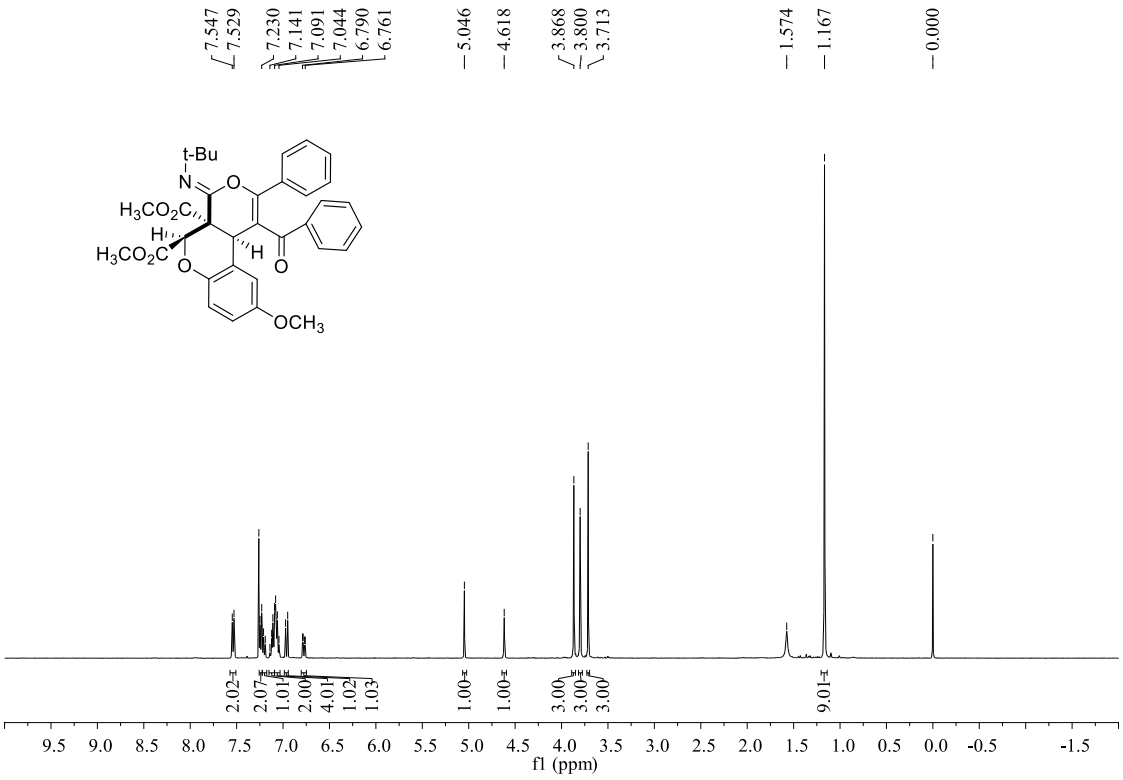
Dimethyl *rel*-(4a*S*,5*S*,10b*R*,*Z*)-1-benzoyl-4-(*tert*-butylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4i'): Yellow solid, 13%, mp 196-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.0 Hz, 2H, ArH), 7.37 (t, *J* = 7.2 Hz, 1H, ArH), 7.28-7.27 (m, 1H, ArH), 7.26-7.23 (m, 2H, ArH), 7.13-7.11 (m, 3H, ArH), 7.09-7.05 (m, 1H, ArH), 6.91 (d, *J* = 8.0 Hz, 1H, ArH), 6.69-6.63 (m, 2H, ArH), 5.56 (s, 1H, CH), 5.45 (s, 1H, CH), 3.79 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 1.27 (s, 9H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.1, 168.7, 168.5, 152.4, 151.2, 144.9, 138.0, 133.1, 133.0, 129.6, 129.3, 128.4, 128.3, 128.0, 127.8, 127.2, 121.1, 120.5, 117.3, 115.7, 75.3, 54.2, 53.1, 52.1, 51.5, 35.6, 29.7; IR (KBr) υ: 2995, 2932, 2830, 1750, 1722, 1630, 1612, 1466, 1450, 1410, 1365, 1345, 1310, 1222, 1190, 1155, 1123, 1019, 909, 714, 670, 623, 560 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{33}H_{32}NO_7$ ([M + H]$^+$): 554.2173, found: 554.2181.

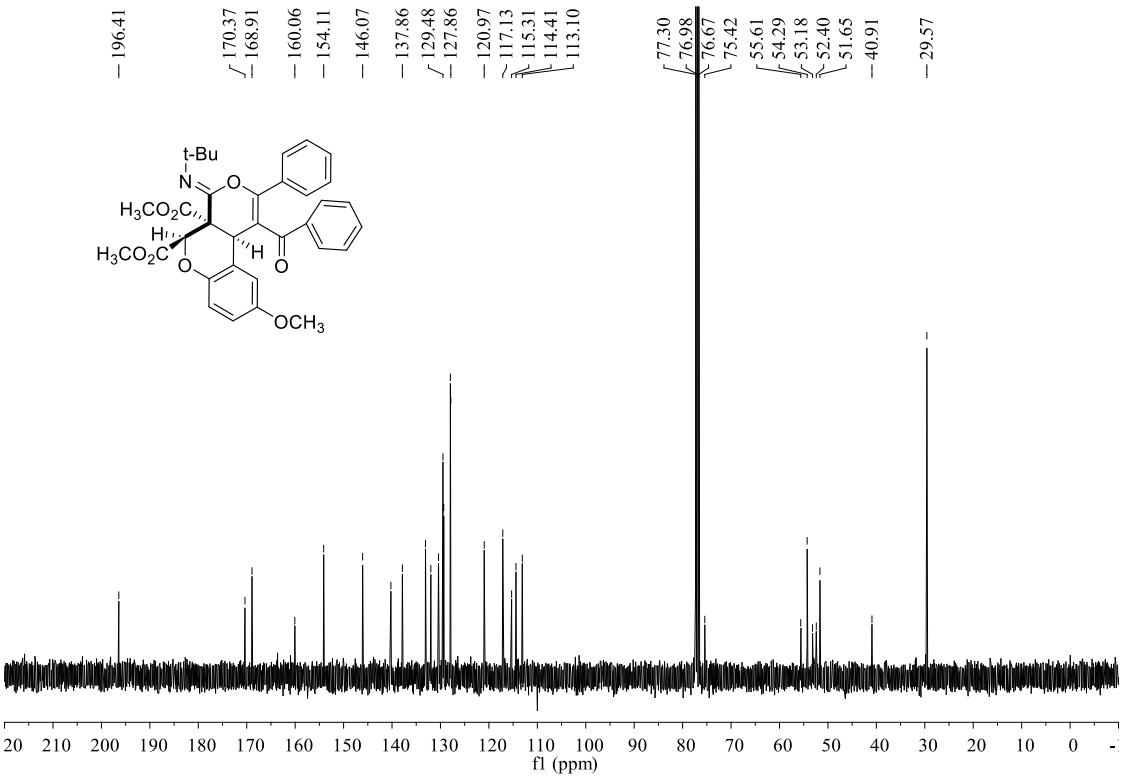


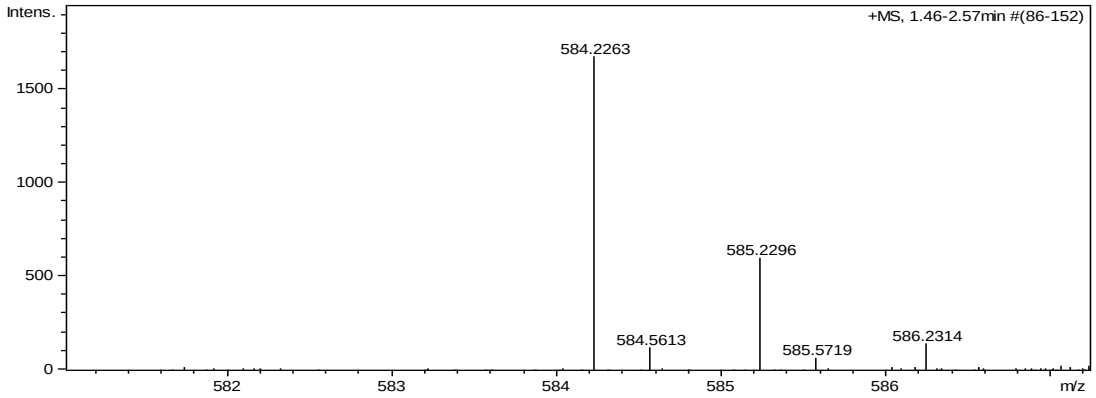

195.12
168.73
168.45
152.36
151.24
144.90
137.95
133.06
133.03
129.59
129.30
128.44
128.31
128.00
127.83
127.24
121.10
120.45
117.25
115.71
77.29
76.98
76.66
75.30
54.22
53.11
52.08
51.48
35.59
29.65
t-Bu
N
O
CO2CH3
H
O
H
CO2CH3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
+MS, 2.30-2.66min #(137-158)
200
150
100
50
0
554.0843
554.1045
554.1310
554.1575
554.1792
554.2181
554.2620
554.2764
554.2978
554.3179
554.10
554.15
554.20
554.25
554.30
m/z

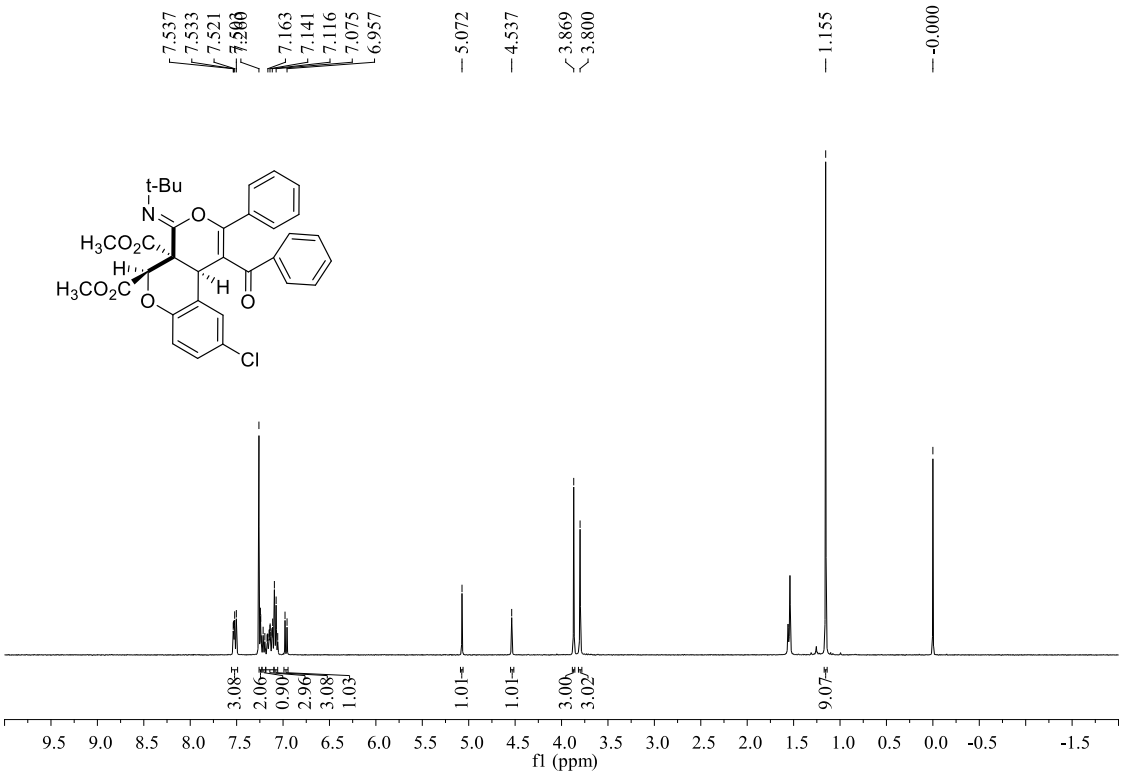
Dimethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-4-(*tert*-butylimino)-9-methoxy-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4j): Yellow solid, 26%, mp 199-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 7.2 Hz, 2H, ArH), 7.24 (d, *J* = 7.2 Hz, 2H, ArH), 7.20 (d, *J* = 7.2 Hz, 1H, ArH), 7.14-7.11 (m, 2H, ArH), 7.09-7.04 (m, 4H, ArH), 6.96 (d, *J* = 8.8 Hz, 1H, ArH), 6.78 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H, ArH), 5.05 (s, 1H, CH), 4.62 (s, 1H, CH), 3.87 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 1.17 (s, 9H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.4, 170.4, 168.9, 160.1, 154.1, 146.1, 140.2, 137.9, 133.1, 132.0, 130.4, 129.5, 129.3, 128.0, 127.9, 121.0, 117.1, 115.3, 114.4, 113.1, 75.4, 55.6, 54.3, 53.2, 52.4, 51.7, 40.9, 29.6; IR (KBr) υ: 33006, 2965, 1731, 1640, 1623, 1595, 1575, 1498, 1473, 1447, 1359, 1327, 1264, 1220, 1169, 1139, 1115, 1098, 1034, 1012, 933, 877, 846, 772, 726, 655, 576, 560 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{34}H_{34}NO_8$ ($[M+H]^+$): 584.2279, found: 584.2263.

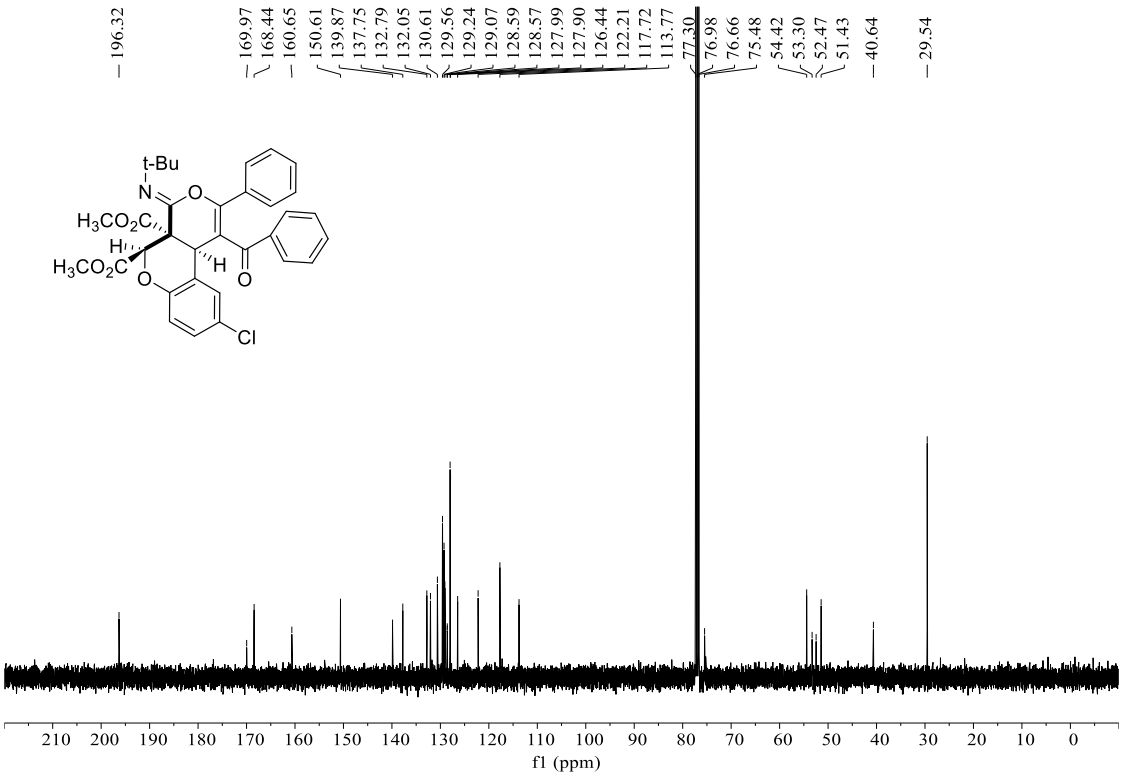


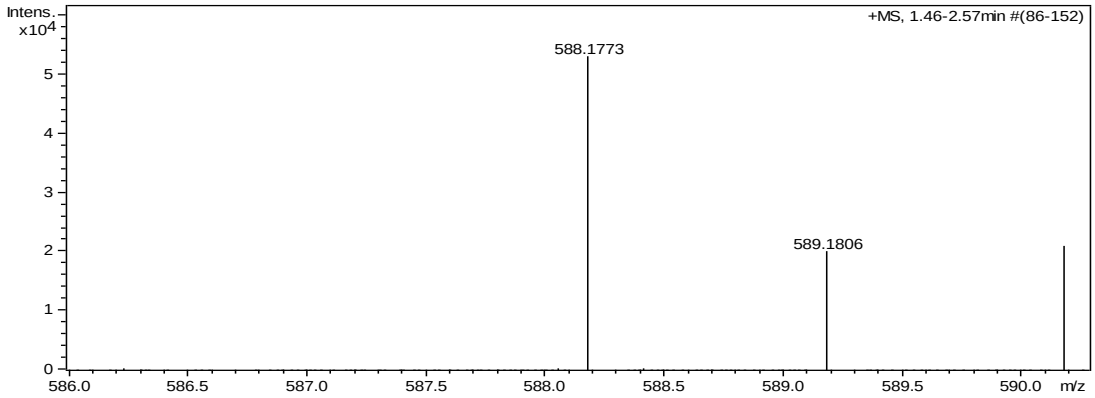

196.41
170.37
168.91
160.06
154.11
146.07
137.86
129.48
127.86
120.97
117.13
115.31
114.41
113.10
77.30
76.98
76.67
75.42
55.61
54.29
53.18
52.40
51.65
40.91
29.57
t-Bu
N
O
H3CO2C
H
H3CO2C
O
H
O
OCH3
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
+MS, 1.46-2.57min #(86-152)
584.2263
1500
1000
585.2296
500
584.5613
586.2314
585.5719
0
582
583
584
585
586
m/z

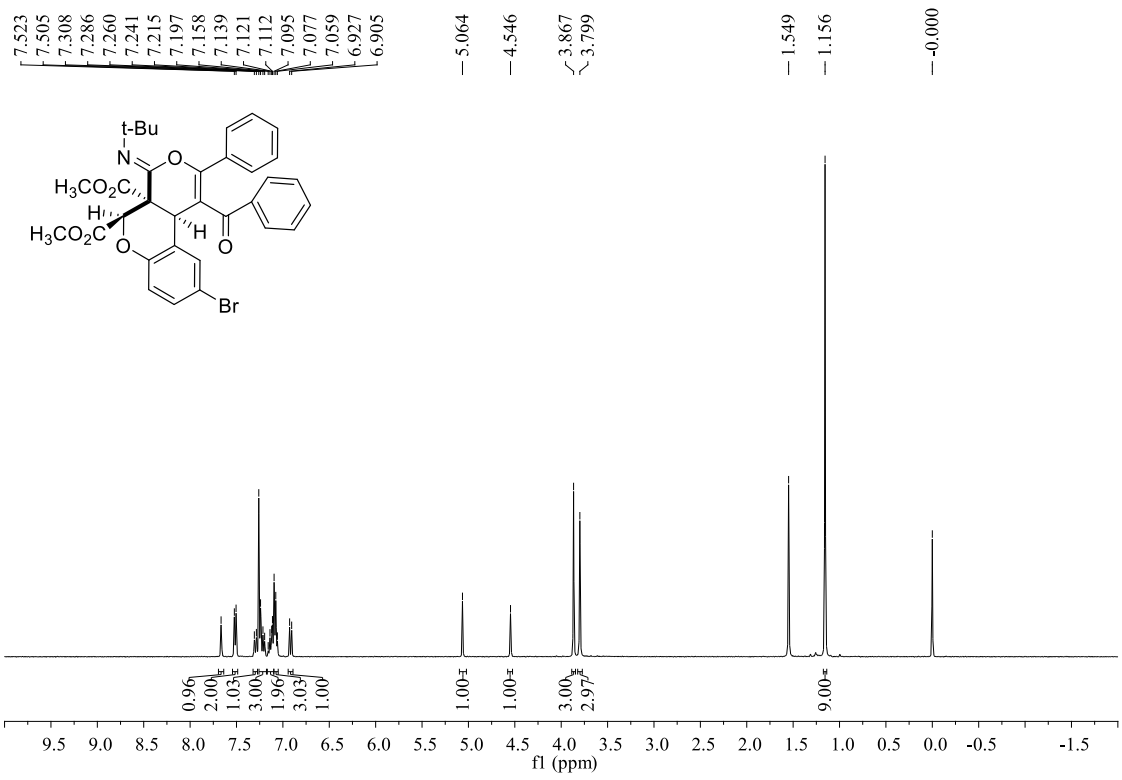
Dimethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-4-(*tert*-butylimino)-9-chloro-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4k): Yellow solid, 30%, mp 207-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.50 (m, 3H, ArH), 7.24-7.23 (m, 2H, ArH), 7.21 (d, *J* = 7.6 Hz, 1H, ArH), 7.17-7.11 (m, 3H, ArH), 7.09-7.06 (m, 3H, ArH), 6.97 (d, *J* = 8.8 Hz, 1H, ArH), 5.07 (s, 1H, CH), 4.54 (s, 1H, CH), 3.87 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 1.15 (s, 9H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.3, 170.0, 168.4, 160.7, 150.6, 139.9, 137.8, 132.8, 132.1, 130.6, 129.6, 129.2, 129.1, 128.59, 128.57, 128.0, 127.9, 126.4, 122.2, 117.7, 113.8, 75.5, 54.4, 53.3, 52.5, 51.4, 40.6, 29.5; IR (KBr) υ: 2967, 2950, 2923, 1795, 1741, 1617, 1483, 1362, 1341, 1279, 1261, 1238, 1179, 1149, 1120, 1038, 1015, 932, 817, 724, 694, 652 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{33}H_{31}ClNO_7$ ([M + H]$^+$): 588.1784, found: 588.1773.

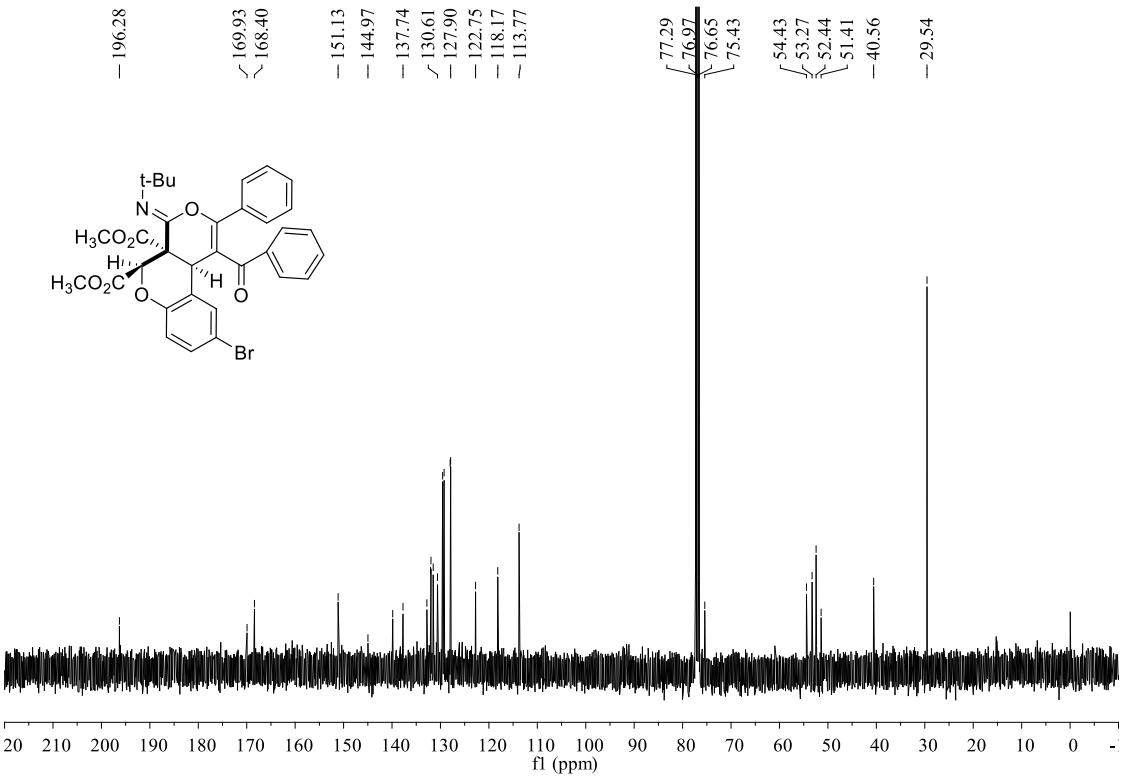


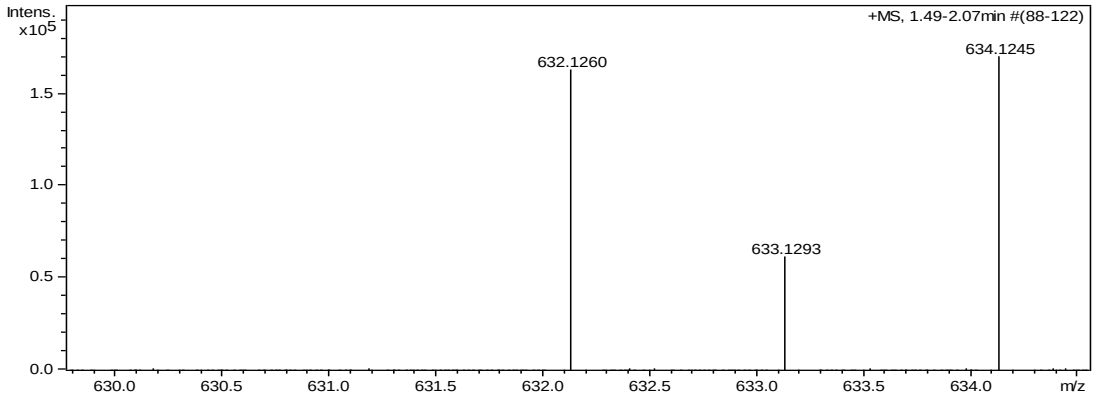

196.32
169.97
168.44
160.65
150.61
139.87
137.75
132.79
132.05
130.61
129.56
129.24
129.07
128.59
128.57
127.99
127.90
126.44
122.21
117.72
113.77
77.30
76.98
76.66
75.48
54.42
53.30
52.47
51.43
40.64
29.54
t-Bu
N
O
H3CO2C
H
H3CO2C
O
H
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^4
+MS, 1.46-2.57min #(86-152)
588.1773
589.1806
0
1
2
3
4
5
586.0 586.5 587.0 587.5 588.0 588.5 589.0 589.5 590.0 m/z

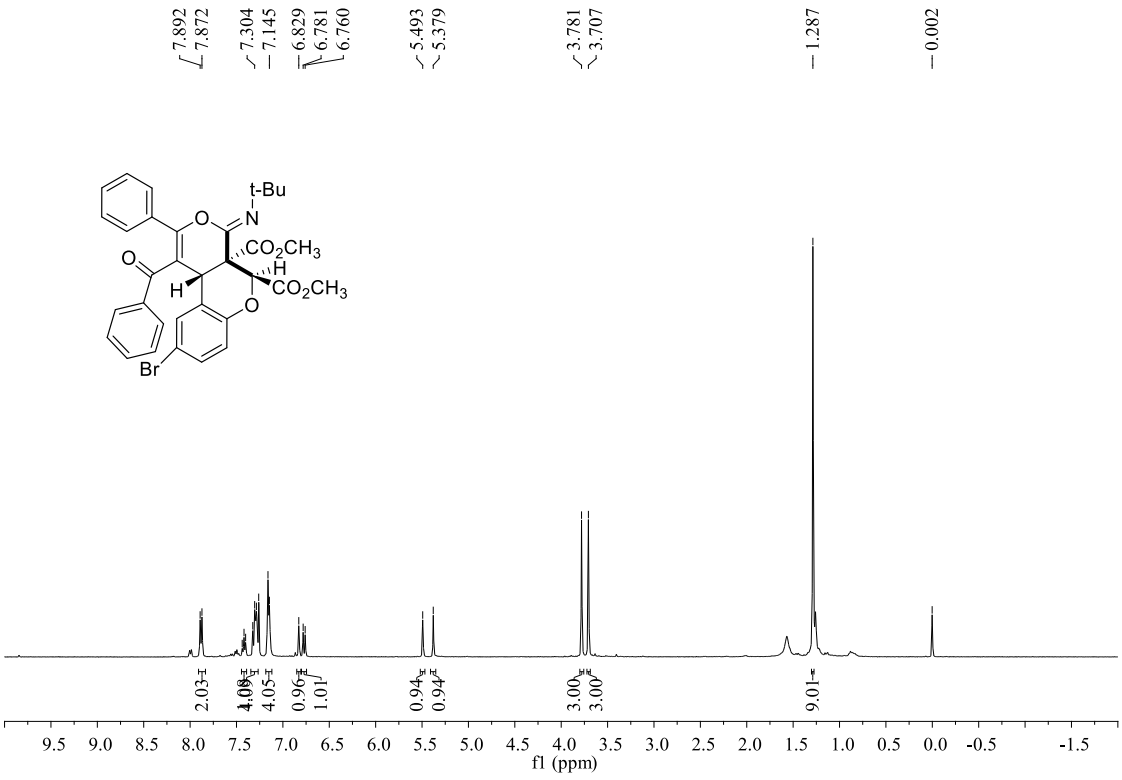
Dimethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-1-benzoyl-9-bromo-4-(*tert*-butylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4l): Yellow solid, 32%, mp 205-206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 1H, ArH), 7.51 (d, *J* = 7.2 Hz, 2H, ArH), 7.30 (d, *J* = 8.8 Hz, 1H, ArH), 7.24-7.20 (m, 3H, ArH), 7.16-7.11 (m, 2H, ArH), 7.10-7.06 (m, 3H, ArH), 6.92 (d, *J* = 8.8 Hz, 1H, ArH), 5.06 (s, 1H, CH), 4.55 (s, 1H, CH), 3.87 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 1.16 (s, 9H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.3, 169.9, 168.4, 151.1, 145.0, 139.9, 137.7, 132.8, 132.1, 132.0, 131.5, 130.6, 129.6, 129.3, 128.0, 127.9, 122.8, 118.2, 113.8, 75.4, 54.4, 53.3, 52.4, 51.4, 40.6, 29.5; IR (KBr) υ: 3063, 2967, 2950, 1741, 1637, 1617, 1598, 1481, 1448, 1361, 1341, 1309, 1261, 1238, 1180, 1148, 1120, 1074, 1053, 1015, 932, 879, 819, 723, 694, 653 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{33}H_{31}BrNO_7$ ([M + H]$^+$): 632.1278, found: 632.1260.

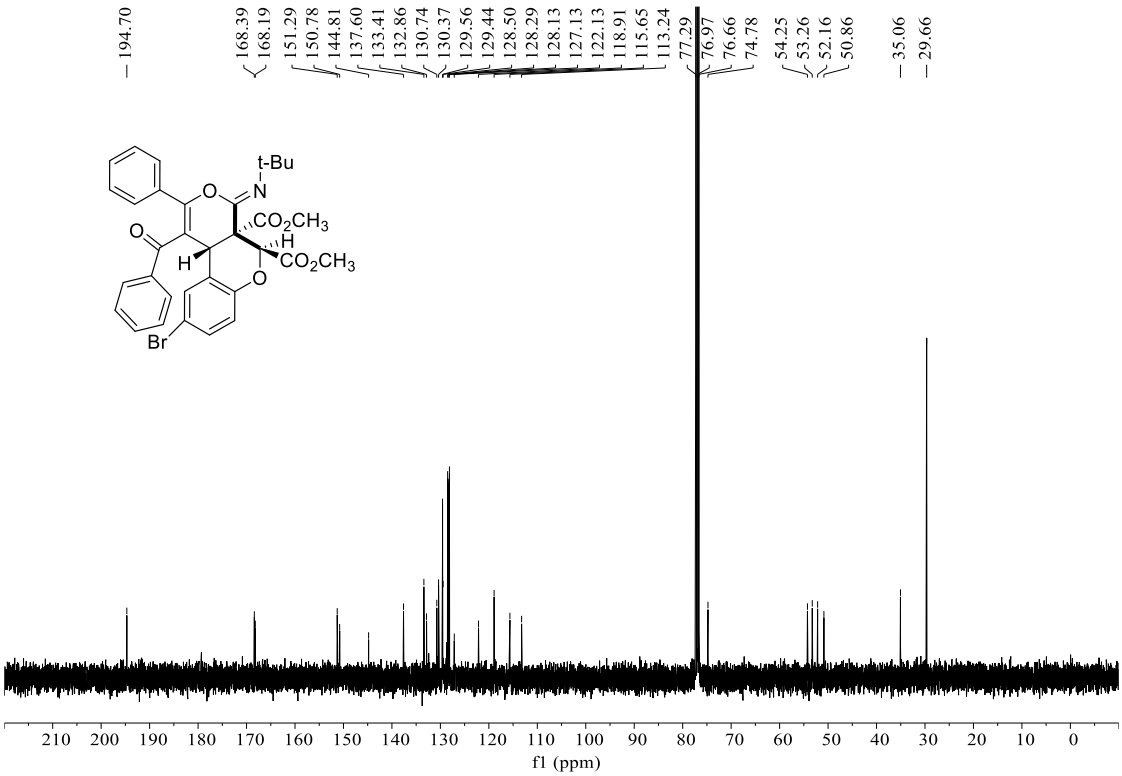


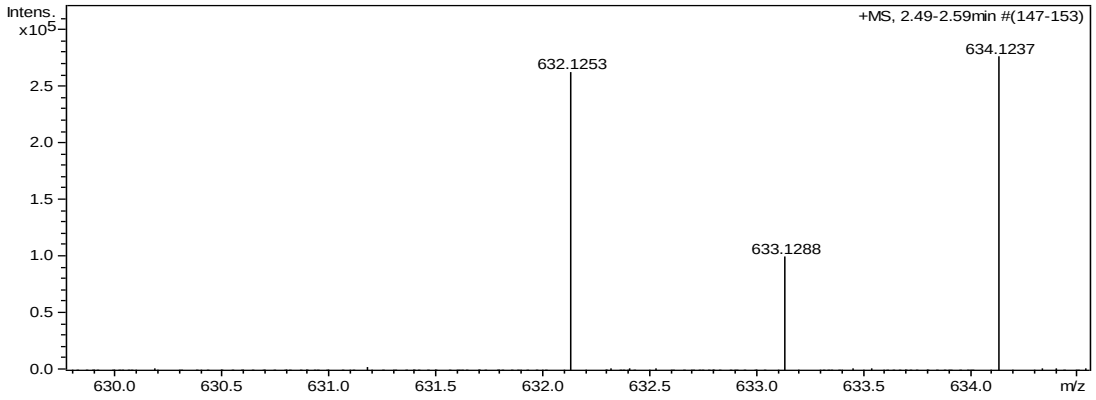

196.28
169.93
168.40
151.13
144.97
137.74
130.61
127.90
122.75
118.17
113.77
77.29
76.97
76.65
75.43
54.43
53.27
52.44
51.41
40.56
29.54
t-Bu
N
O
H3CO2C
H
H3CO2C
O
H
O
Br
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 1.49-2.07min #(88-122)
632.1260
634.1245
633.1293
1.5
1.0
0.5
0.0
630.0
630.5
631.0
631.5
632.0
632.5
633.0
633.5
634.0
m/z

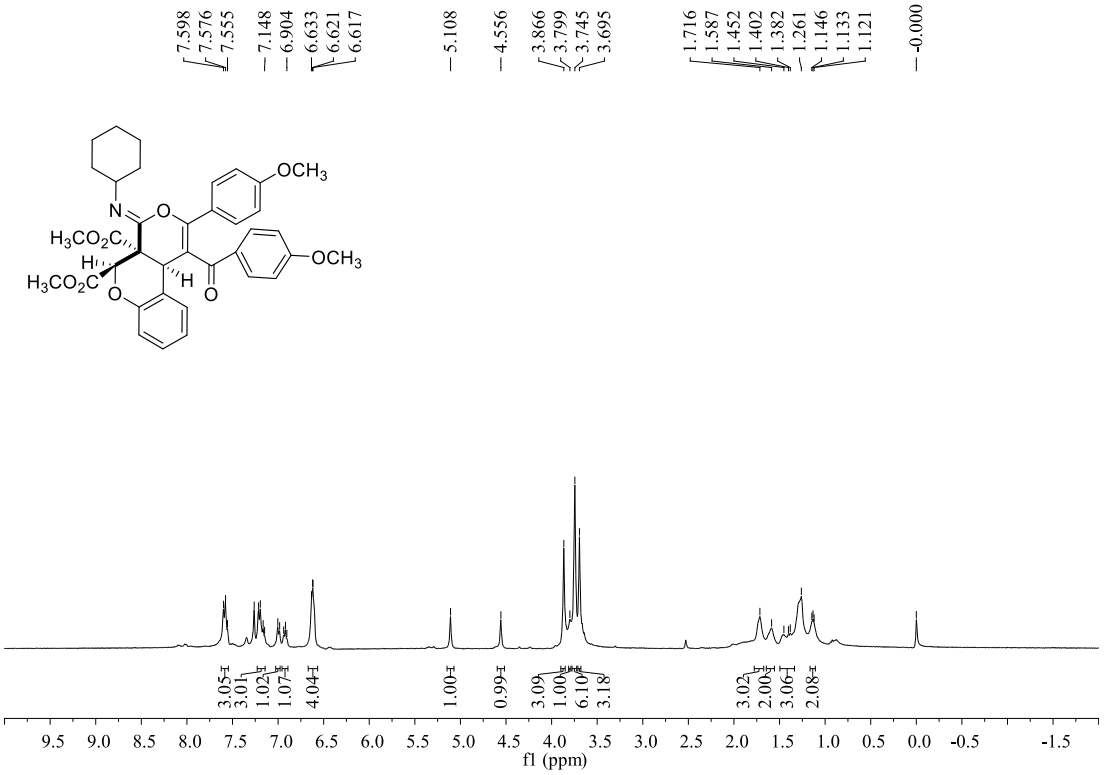
Dimethyl *rel*-(4a*S*,5*S*,10b*R*,*Z*)-1-benzoyl-9-bromo-4-(*tert*-butylimino)-2-phenyl-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4l'): Yellow solid, 10%, mp 198-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.0 Hz, 2H, ArH), 7.42 (t, *J* = 7.6 Hz, 1H, ArH), 7.32-7.29 (m, 4H, ArH), 7.15 (d, *J* = 6.4 Hz, 4H, ArH), 6.83 (s, 1H, ArH), 6.77 (d, *J* = 8.4 Hz, 1H, ArH), 5.49 (s, 1H, CH), 5.38 (s, 1H, CH), 3.78 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 1.29 (s, 9H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 194.7, 168.4, 168.2, 151.3, 150.8, 144.8, 137.6, 133.4, 132.9, 130.7, 130.4, 129.6, 129.4, 128.5, 128.3, 128.1, 127.1, 122.1, 118.9, 115.7, 113.2, 77.3, 54.3, 53.3, 52.2, 50.9, 35.1, 29.7; IR (KBr) υ: 2976, 2918, 2850, 1762, 1735, 1654, 1577, 1561, 1546, 1479, 1408, 1372, 1328, 1240, 1193, 1154, 1102, 1046, 1015, , 932, 853, 724, 688, 640 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{33}H_{31}BrNO_7$ ([M + H]$^+$): 632.1278, found: 632.1253.

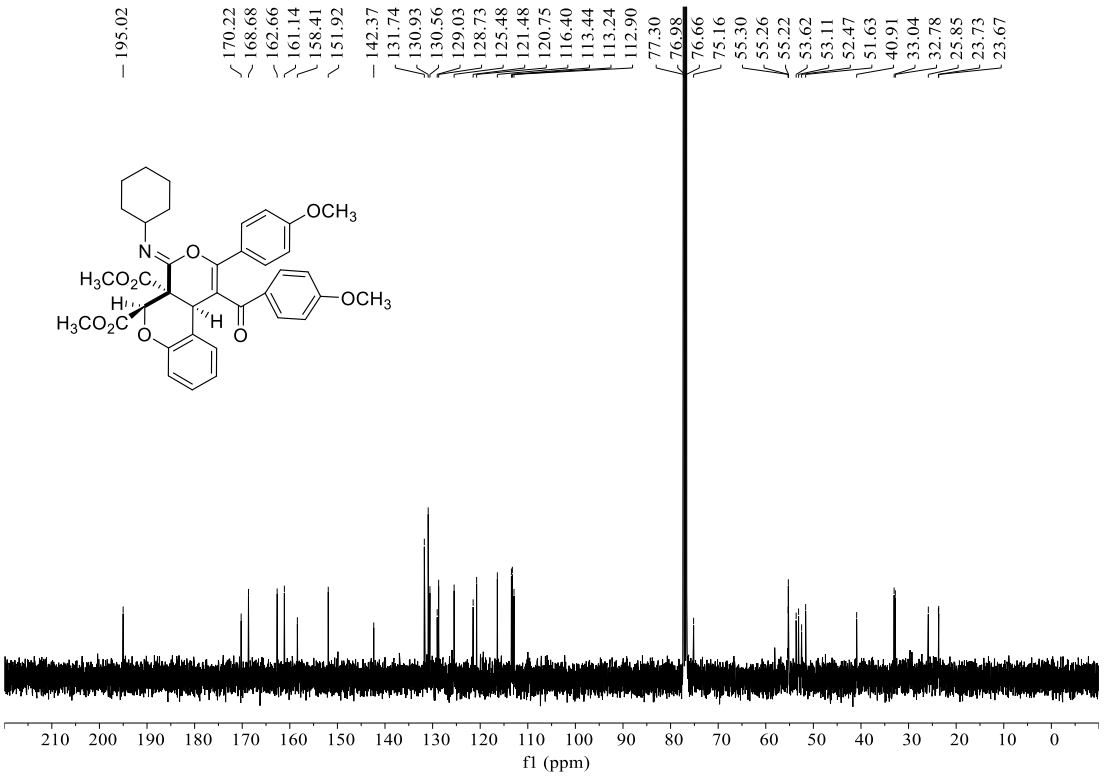


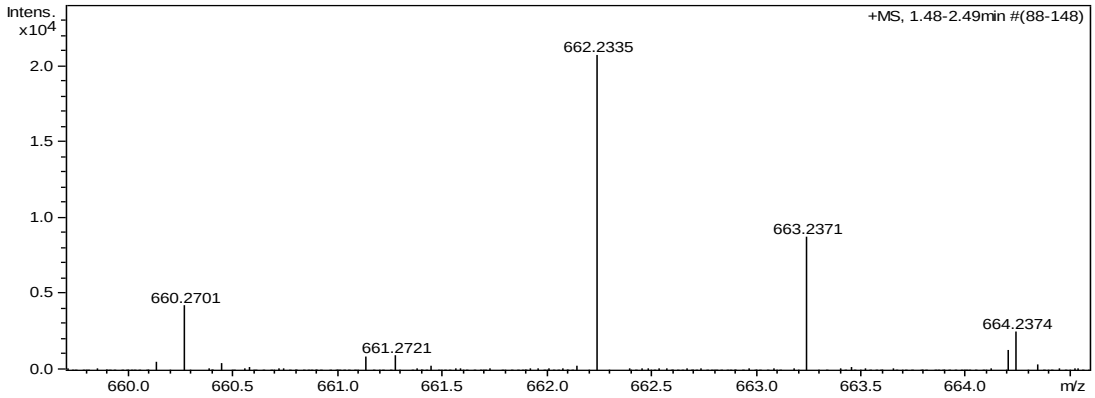

194.70
168.39
168.19
151.29
150.78
144.81
137.60
133.41
132.86
130.74
130.37
129.56
129.44
128.50
128.29
128.13
127.13
122.13
118.91
115.65
113.24
77.29
76.97
76.66
74.78
54.25
53.26
52.16
50.86
35.06
29.66
t-Bu
N
O
CO2CH3
H
O
H
CO2CH3
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 2.49-2.59min #(147-153)
632.1253
634.1237
633.1288
2.5
2.0
1.5
1.0
0.5
0.0
630.0 630.5 631.0 631.5 632.0 632.5 633.0 633.5 634.0
m/z

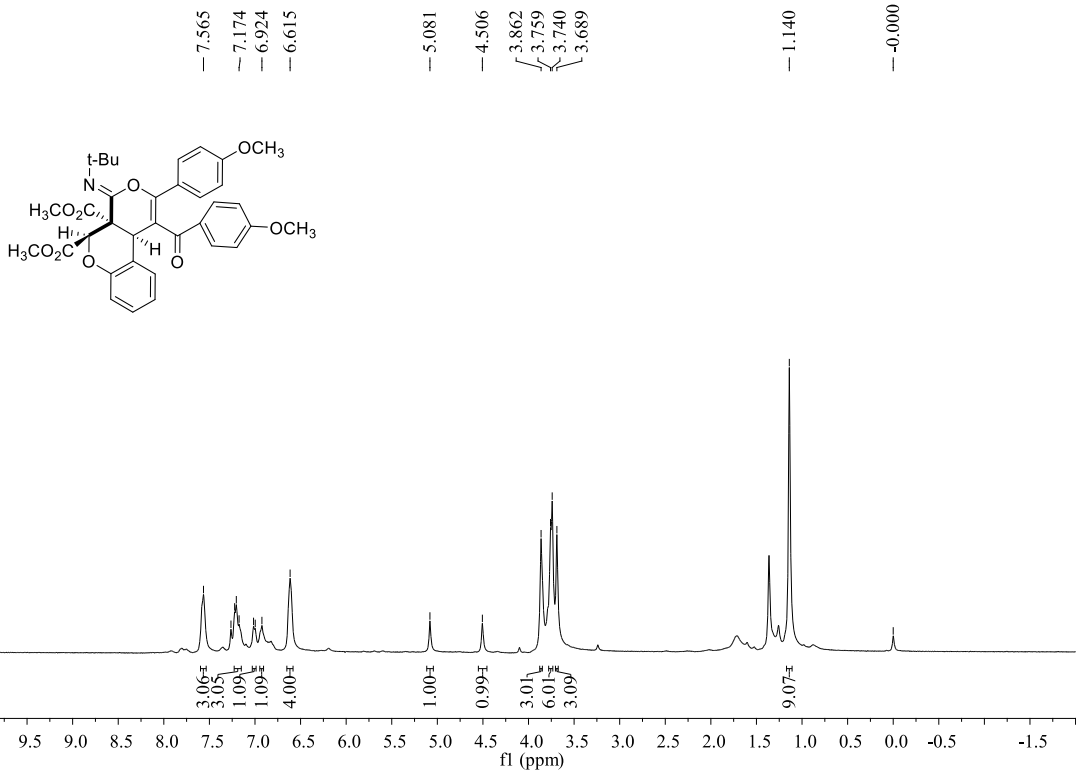
Dimethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-4-(cyclohexylimino)-1-(4-methoxybenzoyl)-2-(4-methoxyphenyl)-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4m): Yellow solid, 30%, mp 202-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60-7.56 (m, 3H, ArH), 7.21-7.15 (m, 3H, ArH), 6.99 (d, *J* = 8.0 Hz, 1H, ArH), 6.92 (t, *J* = 7.6 Hz, 1H, ArH), 6.63-6.62 (m, 4H, ArH), 5.11 (s, 1H, CH), 4.56 (s, 1H, CH), 3.87 (s, 3H, OCH_3), 3.80 (s, 1H, CH), 3.74 (s, 6H, OCH_3), 3.69 (s, 3H, OCH_3), 1.72 (s, 3H, CH), 1.59 (s, 2H, CH), 1.45-1.38 (m, 3H, CH), 1.15-1.12 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.0, 170.2, 168.7, 162.7, 161.1, 158.4, 151.9, 142.4, 131.7, 130.9, 130.6, 129.0, 128.7, 125.5, 121.5, 120.8, 116.4, 113.4, 113.2, 112.9, 75.2, 55.3, 55.3, 55.2, 53.6, 53.1, 52.5, 51.6, 40.9, 33.0, 32.8, 25.9, 23.7, 23.7; IR (KBr) υ: 2918, 2850, 1735, 1708, 1654, 1599, 1512, 1492, 1463, 1456, 1443, 1398, 1341, 1279, 1287, 1259, 1172, 1114, 1083, 1029, 983, 926, 751, 738, 701, 653, 612 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{37}H_{37}NaO_9$ ([M + Na]$^{+}$): 662.2361 found: 662.2335.

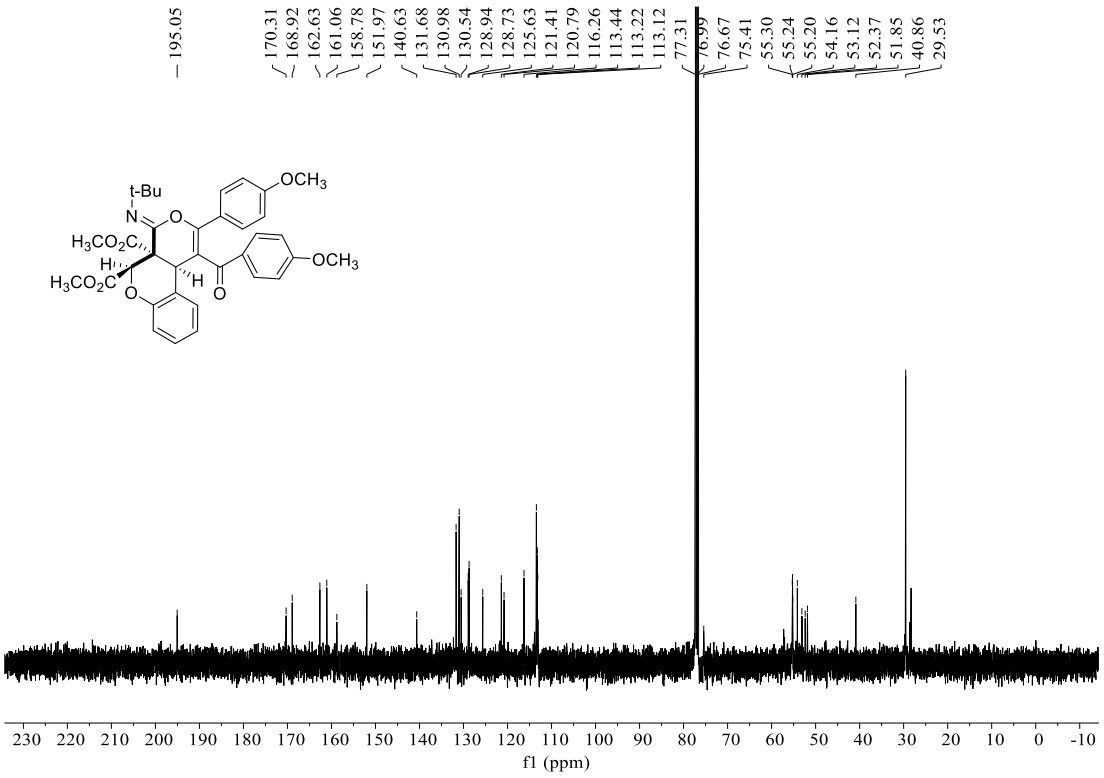


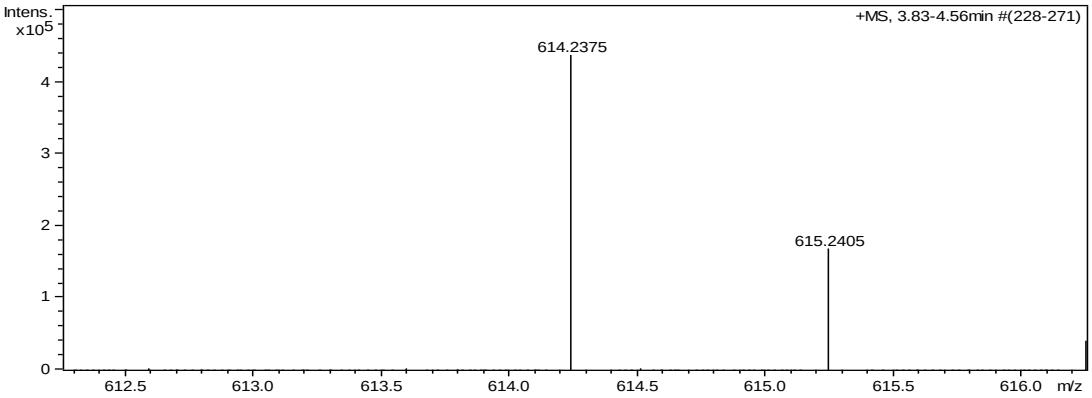

195.02
170.22
168.68
162.66
161.14
158.41
151.92
142.37
131.74
130.93
130.56
129.03
128.73
125.48
121.48
120.75
116.40
113.44
113.24
112.90
77.30
76.98
76.66
75.16
55.30
55.26
55.22
53.62
53.11
52.47
51.63
40.91
33.04
32.78
25.85
23.73
23.67
OCH3
OCH3
N
O
H3CO2C
H
H3CO2C
O
H
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^4
+MS, 1.48-2.49min #(88-148)
662.2335
663.2371
660.2701
664.2374
661.2721
2.0
1.5
1.0
0.5
0.0
660.0 660.5 661.0 661.5 662.0 662.5 663.0 663.5 664.0
m/z

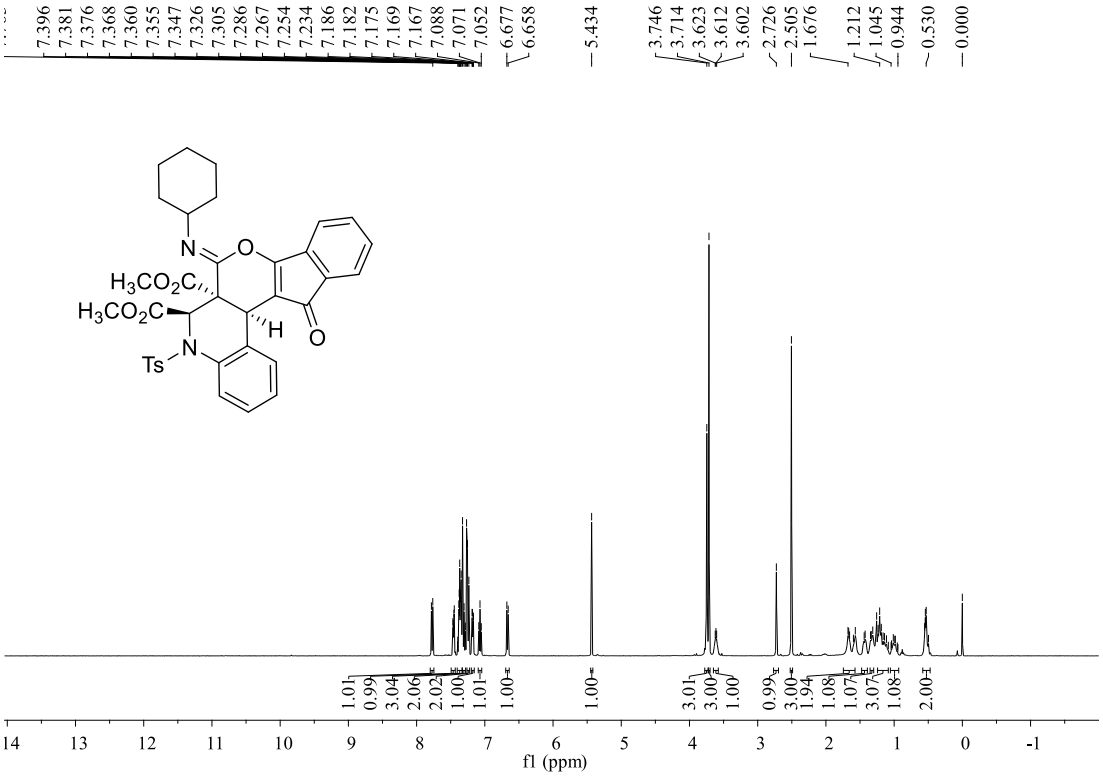
Dimethyl *rel*-(4a*R*,5*R*,10b*R*,*Z*)-4-(*tert*-butylimino)-1-(4-methoxybenzoyl)-2-(4-methoxyphenyl)-4*H*,5*H*-pyrano[3,4-*c*]chromene-4a,5(10b*H*)-dicarboxylate (4n): Yellow solid, 28%, mp 208-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (s, 3H, ArH), 7.22-7.18 (m, 3H, ArH), 7.01 (d, *J* = 7.6 Hz, 1H, ArH), 6.92 (s, 1H, ArH), 6.62 (s, 4H, ArH), 5.08 (s, 1H, CH), 4.51 (s, 1H, CH), 3.86 (s, 3H, OCH_3), 3.75 (d, *J* = 7.6 Hz, 6H, OCH_3), 3.69 (s, 3H, OCH_3), 1.14 (s, 9H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.1, 170.3, 168.9, 162.6, 161.1, 158.8, 152.0, 140.6, 131.7, 131.0, 130.5, 128.9, 128.7, 125.6, 121.4, 120.8, 116.3, 113.4, 113.1, 113.2, 75.4, 55.3, 55.2, 55.2, 54.2, 53.1, 52.4, 51.9, 40.9, 29.5; IR (KBr) υ: 2967, 2917, 2864, 1782, 1744, 1730, 1657, 1603, 1596, 1549, 1507, 1467, 1446, 1347, 1323, 1268, 1253, 1248, 1230, 1159, 1073, 1048, 995, 938, 803, 764, 728, 698, 665 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{36}NO_9$ ([M + H]$^+$): 614.2385, found: 614.2375.

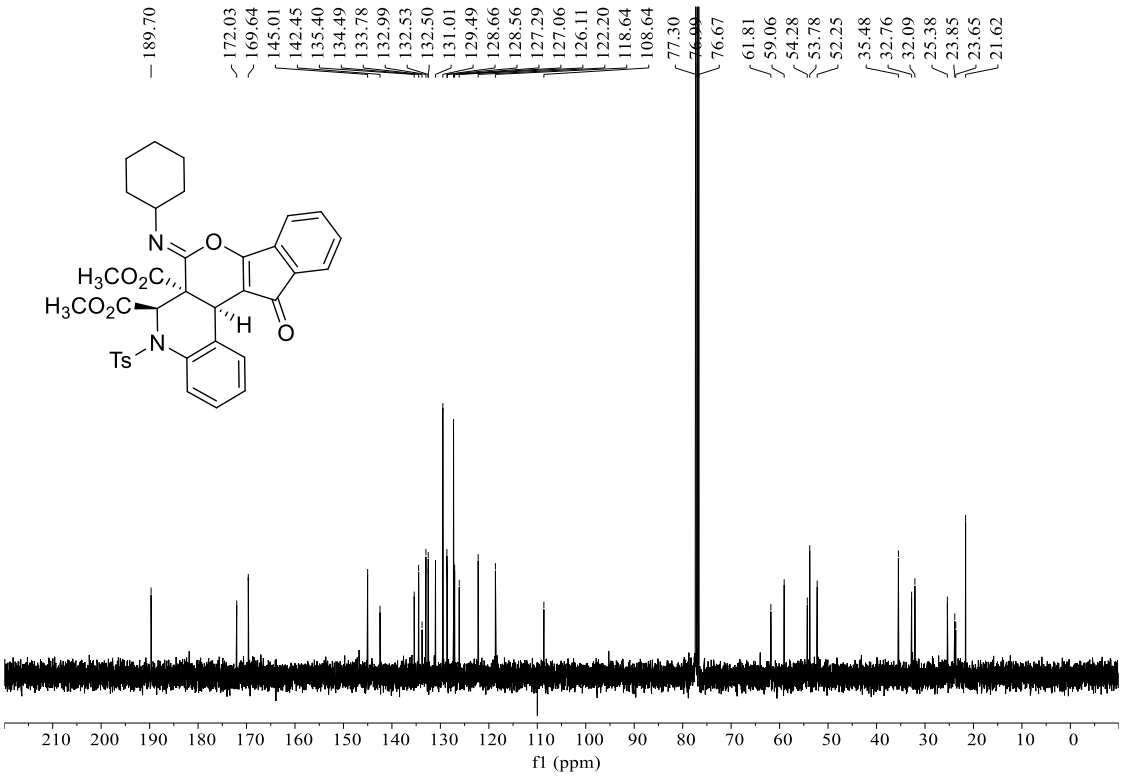


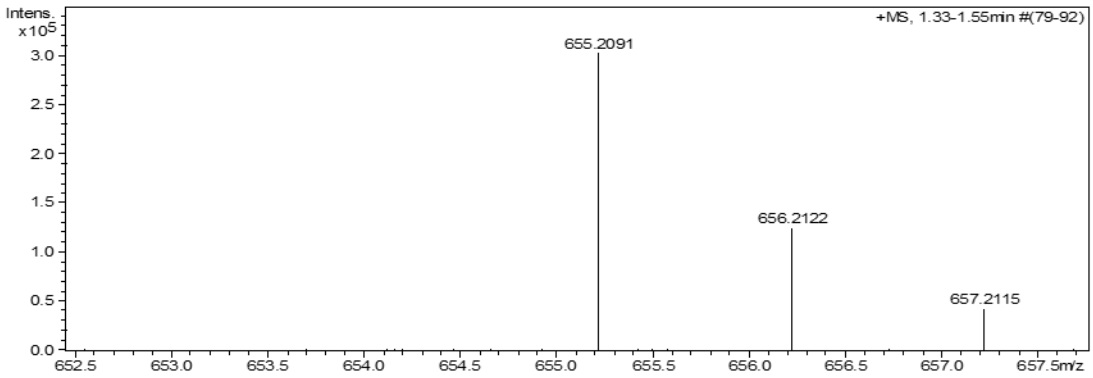

195.05
170.31
168.92
162.63
161.06
158.78
151.97
140.63
131.68
130.98
130.54
128.94
128.73
125.63
121.41
120.79
116.26
113.44
113.22
113.12
77.31
76.99
76.67
75.41
55.30
55.24
55.20
54.16
53.12
52.37
51.85
40.86
29.53
t-Bu
N
O
H_3CO_2C
H
H_3CO_2C
O
H
O
OCH_3
OCH_3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 3.83-4.56min #(228-271)
614.2375
615.2405
0
1
2
3
4
612.5
613.0
613.5
614.0
614.5
615.0
615.5
616.0
m/z

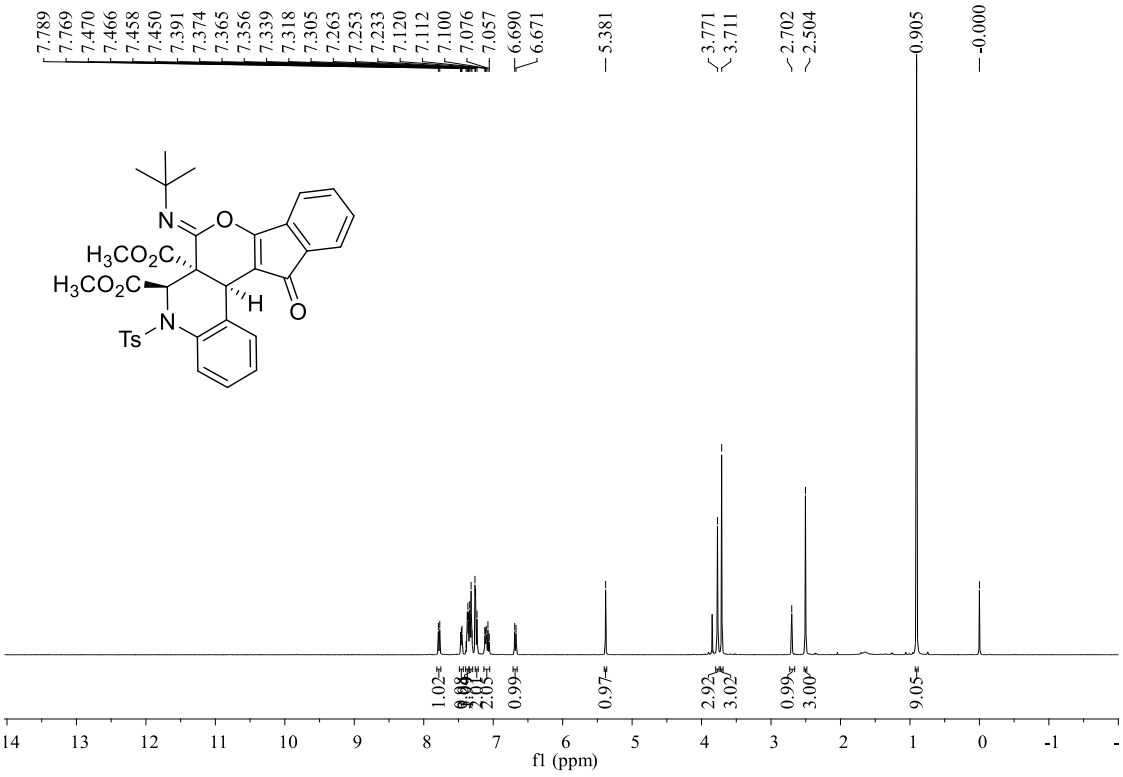
Dimethyl *rel*-(6*R*,6a*R*,13b*R*,*Z*)-7-(cyclohexylimino)-13-oxo-5-tosyl-5,6,13,13b-tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinoline-6,6a(7*H*)-dicarboxylate (6a): Yellow solid, 60%, mp 208-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 8.0 Hz, 2H, ArH), 7.47-7.45 (m, 1H, ArH), 7.40-7.35 (m, 3H, ArH), 7.33-7.29 (m, 2H, ArH), 7.24 (d, *J* = 8.0 Hz, 2H, ArH), 7.19-7.17 (m, 1H, ArH), 7.07 (t, *J* = 6.8 Hz, 1H, ArH), 6.67 (d, *J* = 7.6 Hz, 1H, ArH), 5.43 (s, 1H, CH), 3.75 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.64-3.58 (m, 1H, CH), 2.73 (s, 1H, CH), 2.51 (s, 3H, CH_3), 1.68-1.57 (m, 2H, CH), 1.47-1.39 (m, 1H, CH), 1.35-1.31 (m, 1H, CH), 1.24-1.09 (m, 3H, CH), 1.15-0.94 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.7, 172.0, 169.6, 145.0, 142.5, 135.4, 134.5, 133.8, 133.0, 132.53, 132.50, 131.0, 129.5, 128.7, 128. 6, 127.3, 127.1, 126.1, 122.2, 118.6, 108.6, 61.8, 59.1, 54.3, 53. 8, 52.3, 35.5, 32.7, 32.1, 25.4, 23.9, 23.7, 21.6; IR (KBr) υ: 2930, 2850, 1769, 1744, 1705, 1638, 1596, 1396, 1362, 1266, 1242, 1207, 1172, 1117, 1084, 1022, 999, 879, 811, 767, 723, 665, 580 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{36}H_{35}N_2O_8S$ ([M + H]$^+$): 655.2109, found: 655.2091.

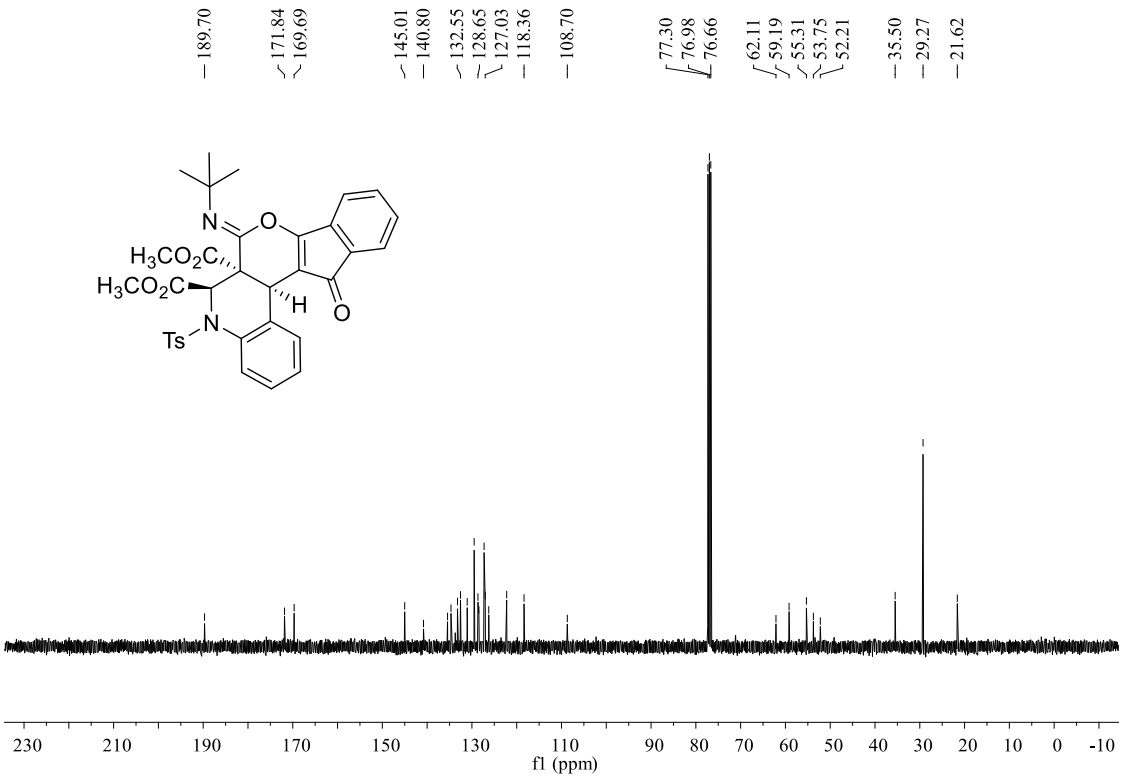


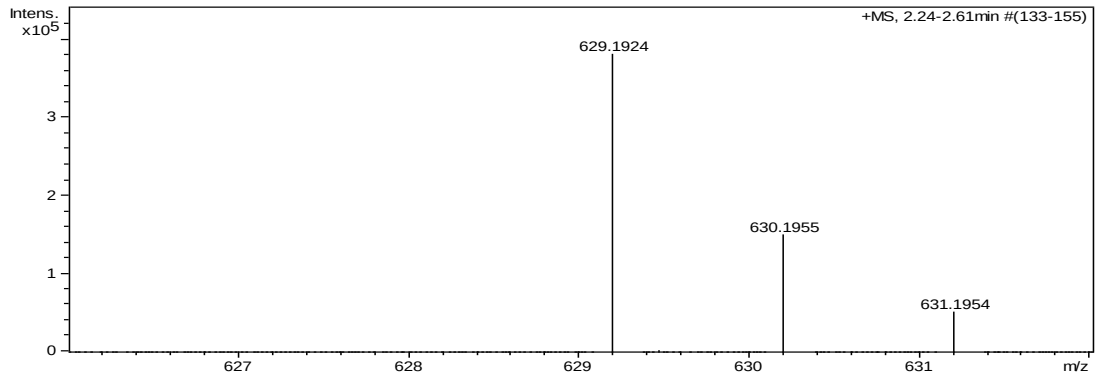

189.70
172.03
169.64
145.01
142.45
135.40
134.49
133.78
132.99
132.53
132.50
131.01
129.49
128.66
128.56
127.29
127.06
126.11
122.20
118.64
108.64
77.30
76.99
76.67
61.81
59.06
54.28
53.78
52.25
35.48
32.76
32.09
25.38
23.85
23.65
21.62
N
O
H3CO2C
H3CO2C
H
O
N
Ts
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 1.33-1.55min #(79-92)
655.2091
656.2122
657.2115
3.0
2.5
2.0
1.5
1.0
0.5
0.0
652.5 653.0 653.5 654.0 654.5 655.0 655.5 656.0 656.5 657.0 657.5m/z

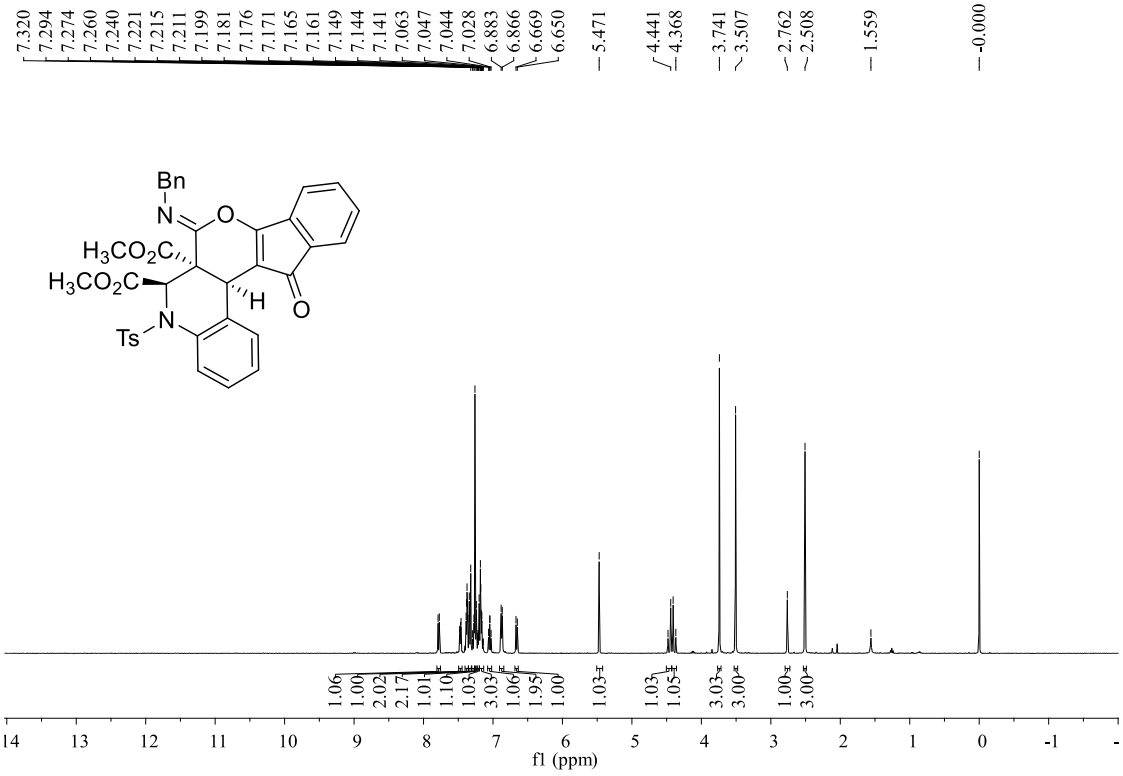
Dimethyl *rel*-(6*R*,6a*R*,13b*R*,*Z*)-7-(*tert*-butylimino)-13-oxo-5-tosyl-5,6,13,13b-tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinoline-6,6a(7*H*)-dicarboxylate (6b): Yellow solid, 54%, mp 200-201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.0 Hz, 1H, ArH), 7.47-7.45 (m, 1H, ArH), 7.39-7.36 (m, 2H, ArH), 7.34-7.31 (m, 3H, ArH), 7.24 (d, *J* = 8.0 Hz, 2H, ArH), 7.12-7.06 (m, 2H, ArH), 6.68 (d, *J* = 7.6 Hz, 1H, ArH), 5.38 (s, 1H, CH), 3.77 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 2.70 (s, 1H, CH), 2.50 (s, 3H, CH_3), 0.90 (m, 9H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.7, 171.8, 169.7, 145.0, 135.4, 134.7, 133.2, 132.6, 131.1, 129.5, 128.7, 128.4, 127.3, 127.0, 126.2, 122.2, 118.4, 108.7, 71.1, 62.1, 59.2, 55.3, 53.8, 52.2, 35.5, 29.3, 21.6; IR (KBr) υ: 3053, 2964, 1764, 1748, 1704, 1643, 1599, 1399, 1356, 1238, 1212, 1170, 1107, 1084, 1000, 907, 862, 768, 725, 665, 581 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{34}H_{33}N_2O_8S$ ([M + H]$^+$): 629.1952, found: 629.1924.

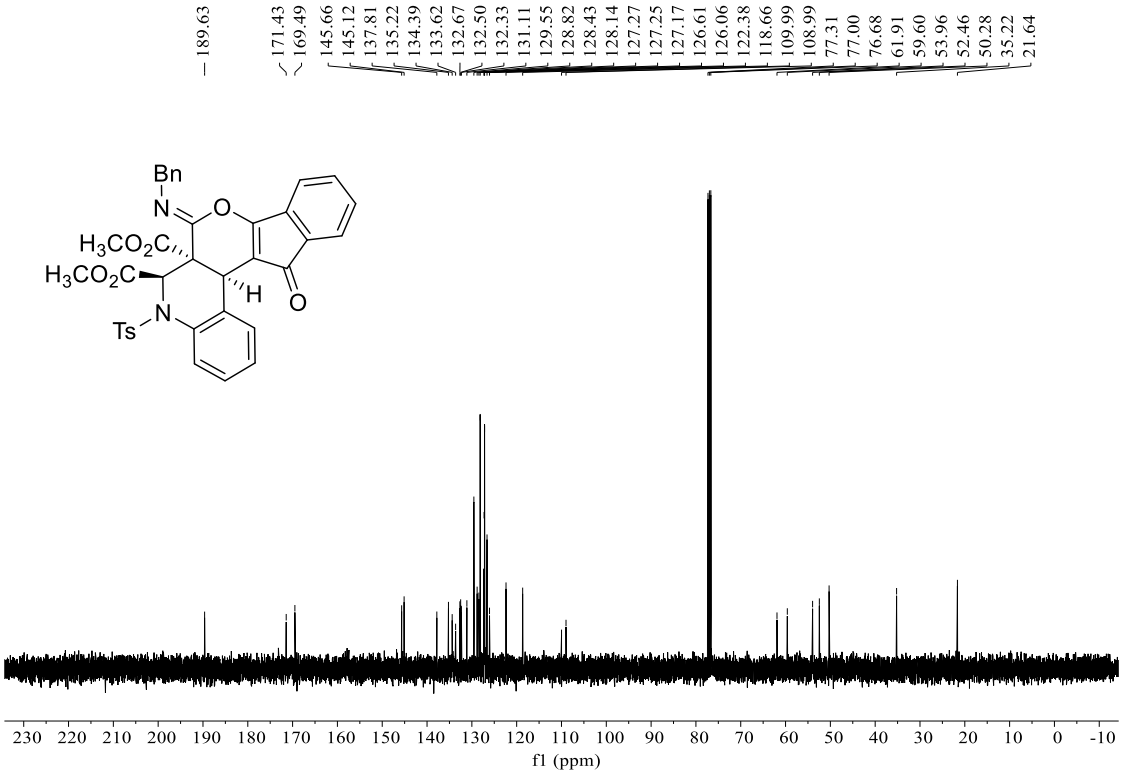


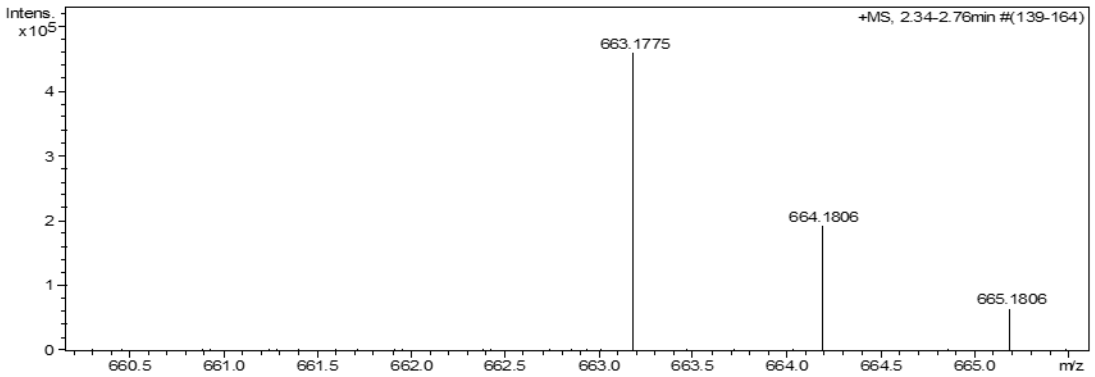

189.70
171.84
169.69
145.01
140.80
132.55
128.65
127.03
118.36
108.70
77.30
76.98
76.66
62.11
59.19
55.31
53.75
52.21
35.50
29.27
21.62
N
O
H3CO2C
H3CO2C
H
O
N
Ts
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Intens.
x10^5
+MS, 2.24-2.61min #(133-155)
629.1924
630.1955
631.1954
3
2
1
0
627
628
629
630
631
m/z

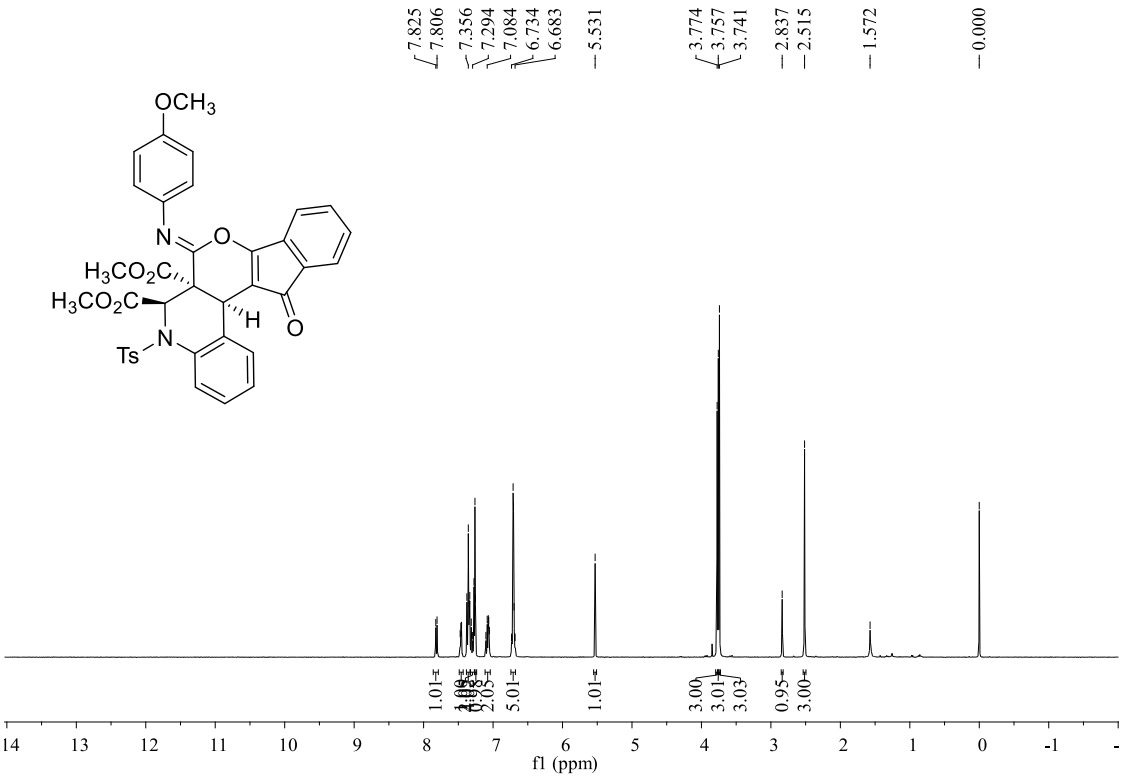
Dimethyl *rel*-(6*R*,6a*R*,13b*R*,*Z*)-7-(benzylimino)-13-oxo-5-tosyl-5,6,13,13b-tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinoline-6,6a(7*H*)-dicarboxylate (6c): Yellow solid, 40%, mp 217-218 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.0 Hz, 1H, ArH), 7.48-7.46 (m, 1H, ArH), 7.89-7.36 (m, 2H, ArH), 7.33 (d, *J* = 8.4 Hz, 2H, ArH), 7.31-7.27 (m, 1H, ArH), 7.25-7.23 (m, 1H, ArH), 7.22-7.20 (m, 1H, ArH), 7.18-7.14 (m, 3H, ArH), 7.05 (t, *J* = 7.6 Hz, 1H, ArH), 6.87 (d, *J* = 6.8 Hz, 2H, ArH), 6.66 (d, *J* = 7.6 Hz, 1H, ArH), 5.47 (s, 1H, CH), 4.46 (d, *J* = 15.6 Hz, 1H, CH_2), 4.39 (d, *J* = 15.6 Hz, 1H, CH_2), 3.74 (s, 3H, OCH_3), 3.51 (s, 3H, OCH_3), 2.76 (s, 1H, CH), 2.51 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.6, 171.4, 169.5, 145.7, 145.1, 137.8, 135.2, 134.4, 133.6, 132.7, 132.5, 132.3, 131.1, 129.6, 128.8, 128.4, 128.1, 127.27, 127.25, 127.2, 126.6, 126.1, 122.4, 118.7, 110.0, 109.0, 61.9, 59.6, 54.0, 52.5, 50.3, 35.2, 21.6; IR (KBr) υ: 2952, 2917, 1775, 1722, 1705, 1639, 1595, 1455, 1393, 1363, 1257, 1172, 1119, 1083, 1025, 1002, 881, 769, 733, 720, 665, 621, 582, 571 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{37}H_{31}N_2O_8S$ ([M + H]$^+$): 663.1796, found: 663.1775.

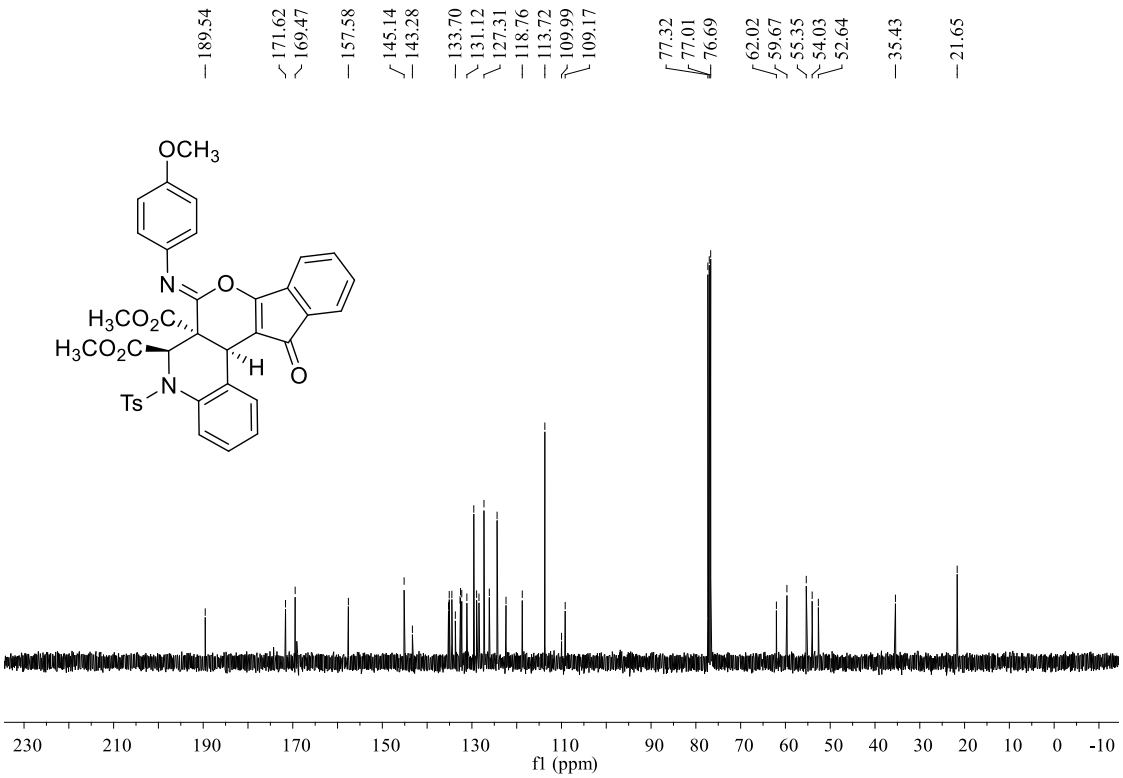


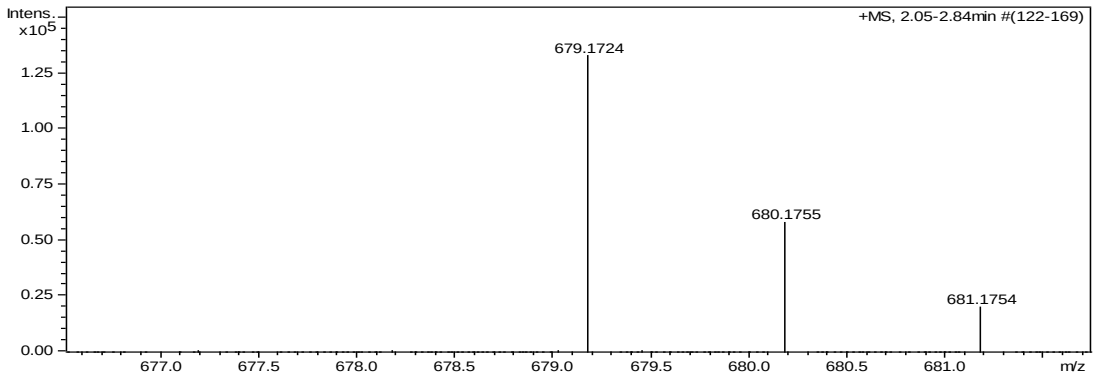

189.63
171.43
169.49
145.66
145.12
137.81
135.22
134.39
133.62
132.67
132.50
132.33
131.11
129.55
128.82
128.43
128.14
127.27
127.25
127.17
126.61
126.06
122.38
118.66
109.99
108.99
77.31
77.00
76.68
61.91
59.60
53.96
52.46
50.28
35.22
21.64
Bn
N
O
H3CO2C
H3CO2C
H
O
N
Ts
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 2.34-2.76min #(139-164)
663.1775
664.1806
665.1806
0
1
2
3
4
660.5 661.0 661.5 662.0 662.5 663.0 663.5 664.0 664.5 665.0
m/z

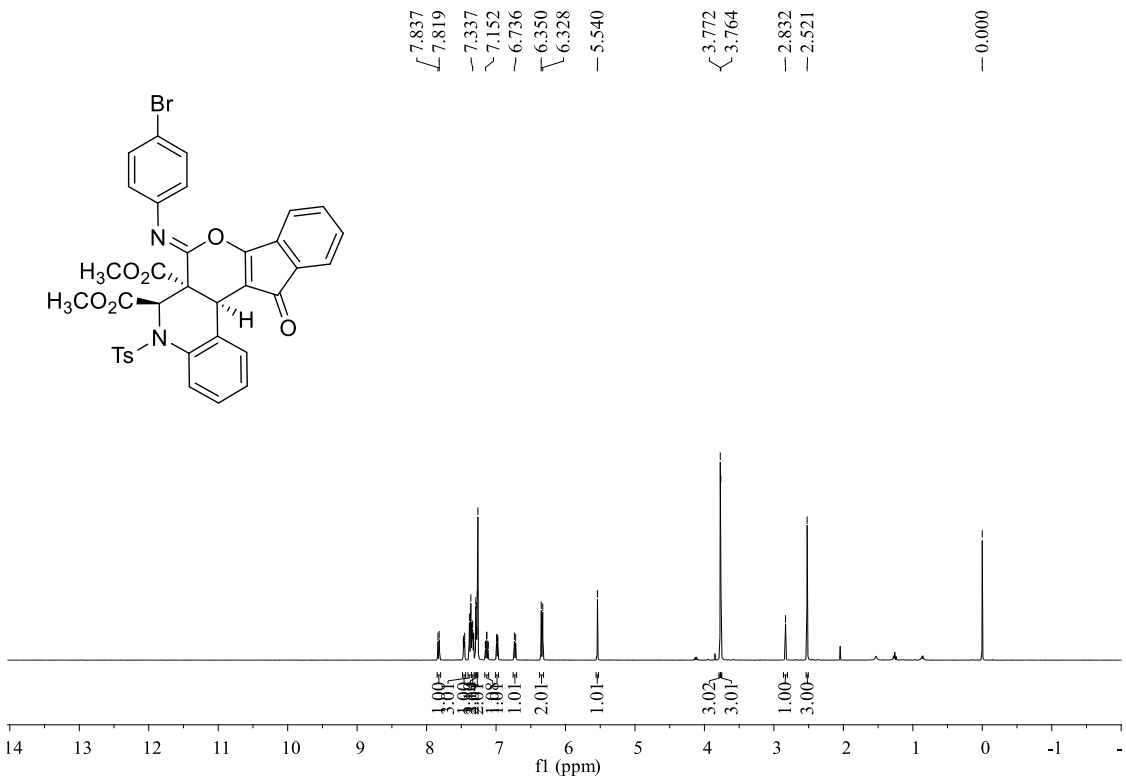
Dimethyl *rel*-(6*R*,6a*R*,13b*R*,*Z*)-7-((4-methoxyphenyl)imino)-13-oxo-5-tosyl-5,6,13,13b-tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinoline-6,6a(7*H*)-dicarboxylate (6d): Yellow solid, 45%, mp 198-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 7.6 Hz, 1H, ArH), 7.47-7.45 (m, 1H, ArH), 7.38-7.34 (m, 4H, ArH), 7.31-7.28 (m, 2H, ArH), 7.25-7.24 (m, 1H, ArH), 7.10-7.05 (m, 2H, ArH), 6.73-6.68 (m, 5H, ArH), 5.53 (s, 1H, CH), 3.77 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 2.84 (s, 1H, CH), 2.52 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.5, 171.6, 169.5, 157.6, 145.1, 143.3, 135.2, 135.1, 134.5, 133.7, 132.7, 132.5, 132.3, 131.1, 129.6, 129.0, 128.4, 127.3, 126.1, 124.4, 122.4, 118.8, 113.7, 110.0, 109.2, 62.0, 59.7, 55.4, 54.0, 52.6, 35.4, 21.7; IR (KBr) υ: 2948, 2930, 1764, 1748, 1705, 1650, 1603, 1507, 1456, 1394, 1360, 1250, 1230, 1118, 1082, 1022, 1000, 892, 848, 817, 721, 663, 577, 543, 523 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{38}H_{31}N_2O_9S$ ([M + H]$^+$): 679.1745, found: 679.1724.

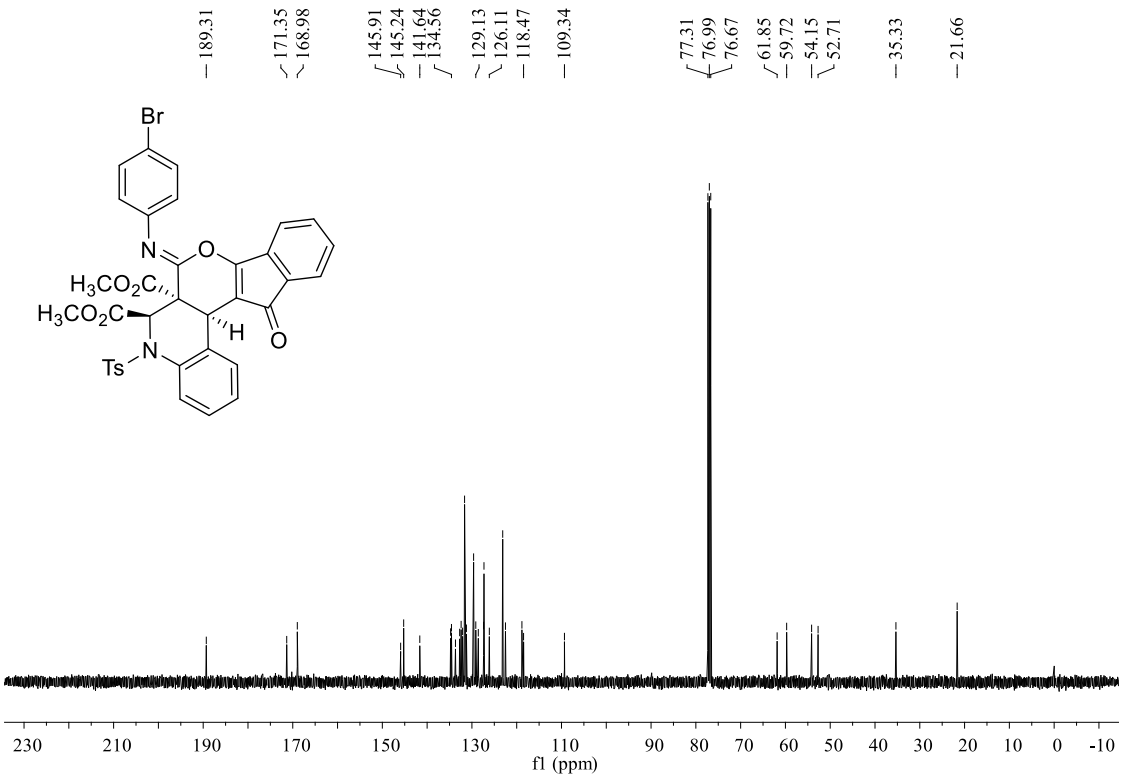


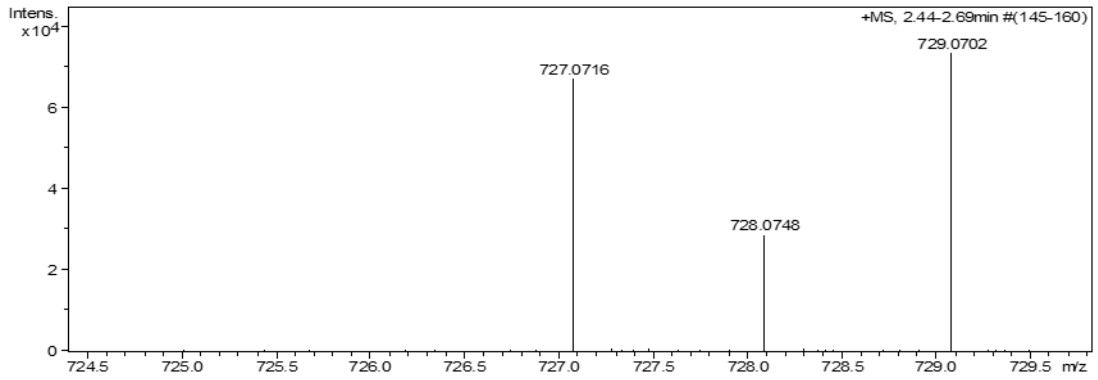

189.54
171.62
169.47
157.58
145.14
143.28
133.70
131.12
127.31
118.76
113.72
109.99
109.17
77.32
77.01
76.69
62.02
59.67
55.35
54.03
52.64
35.43
21.65
OCH3
N
O
H3CO2C
H3CO2C
H
O
N
Ts
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Intens.
x10^5
+MS, 2.05-2.84min #(122-169)
679.1724
680.1755
681.1754
1.25
1.00
0.75
0.50
0.25
0.00
677.0
677.5
678.0
678.5
679.0
679.5
680.0
680.5
681.0
m/z

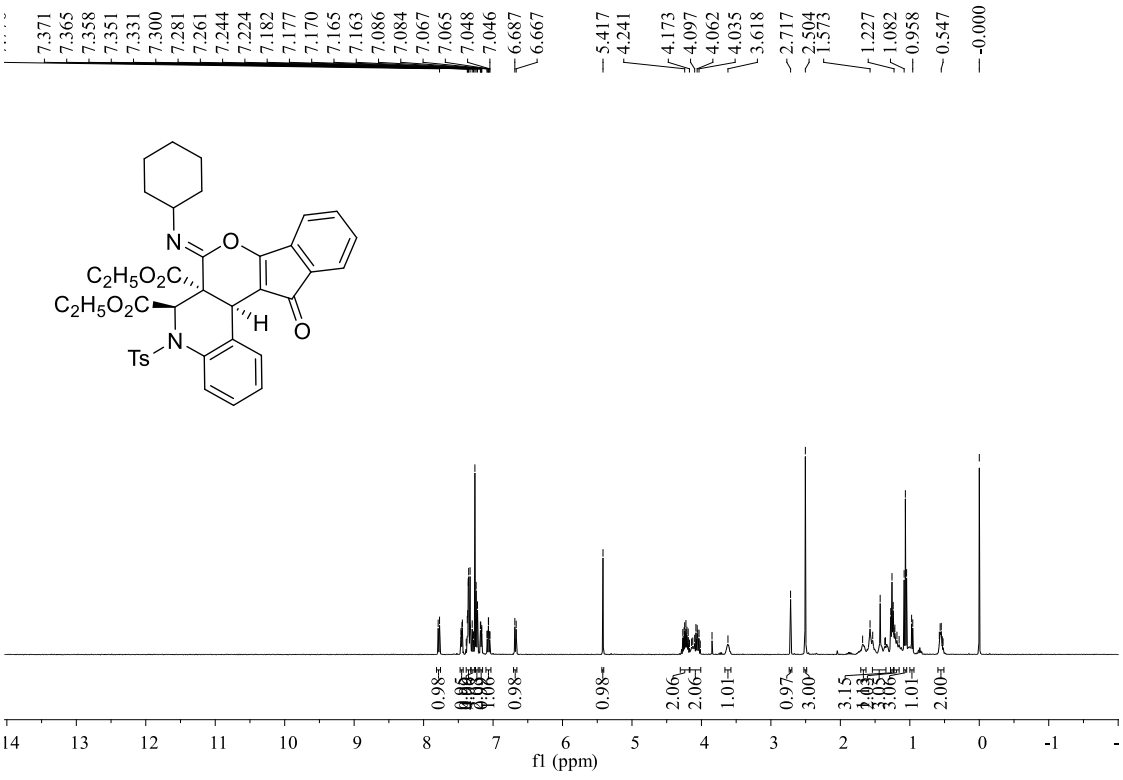
Dimethyl *rel*-(6*R*,6a*R*,13b*R*,*Z*)-7-((4-bromophenyl)imino)-13-oxo-5-tosyl-5,6,13,13b-tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinoline-6,6a(7*H*)-dicarboxylate (6e): Yellow solid, 38%, mp 239-240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 7.2 Hz, 1H, ArH), 7.47-7.45 (m, 1H, ArH), 7.38-7.36 (m, 3H, ArH), 7.35-7.32 (m, 2H, ArH), 7.30-7.28 (m, 2H, ArH), 7.27-7.26 (m, 2H, ArH), 7.14 (t, *J* = 7.6 Hz, 1H, ArH), 6.99-6.97 (m, 1H, ArH), 6.73 (d, *J* = 7.6 Hz, 1H, ArH), 5.54 (s, 1H, CH), 3.76 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 2.83 (s, 1H, CH), 2.52 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.3, 171.4, 169.0, 145.9, 145.2, 141.6, 134.8, 134.6, 133.7, 132.7, 132.4, 132.1, 131.6, 131.2, 129.6, 129.1, 128.6, 127.4, 127.3, 126.1, 123.1, 122.5, 118.8, 118.5, 109.3, 61.9, 59.7, 54.2, 52.7, 35.3, 21.7; IR (KBr) υ: 2981, 2951, 1765, 1746, 1708, 1644, 1596, 1484, 1394, 1358, 1254, 1232, 1207, 1169, 1118, 1088, 1005, 891, 804, 767, 725, 665, 577, 552, 518 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{36}H_{28}BrN_2O_8S$ ($[M + H]^+$): 727.0744, found: 727.0716.

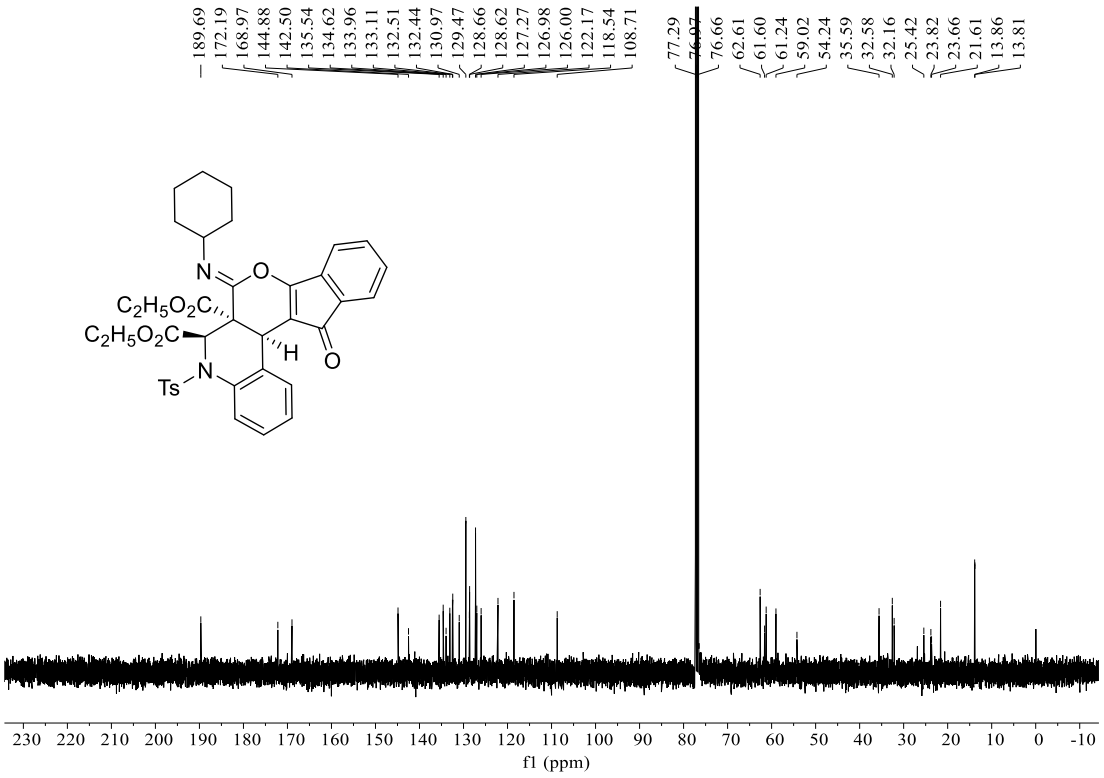


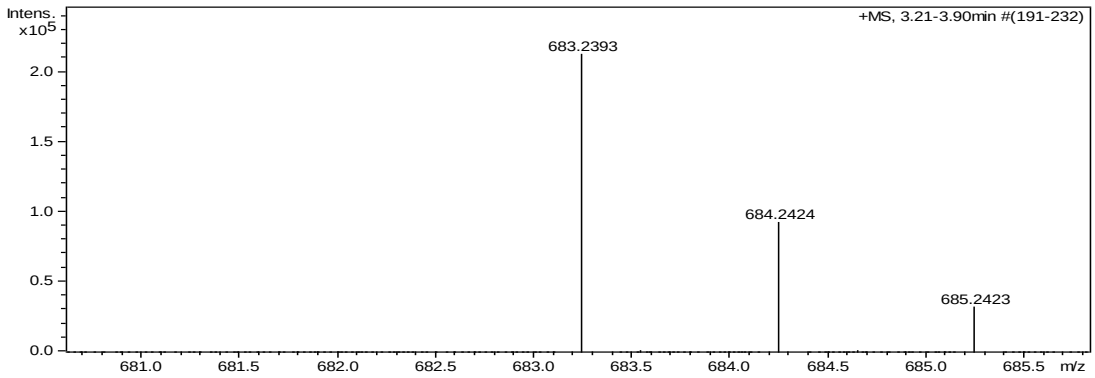

189.31
171.35
168.98
145.91
145.24
141.64
134.56
129.13
126.11
118.47
109.34
77.31
76.99
76.67
61.85
59.72
54.15
52.71
35.33
21.66
Br
N
O
H3CO2C
H3CO2C
H
O
N
Ts
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Intens.
x10^4
+MS, 2.44-2.69min #(145-160)
729.0702
727.0716
728.0748
6
4
2
0
724.5
725.0
725.5
726.0
726.5
727.0
727.5
728.0
728.5
729.0
729.5
m/z

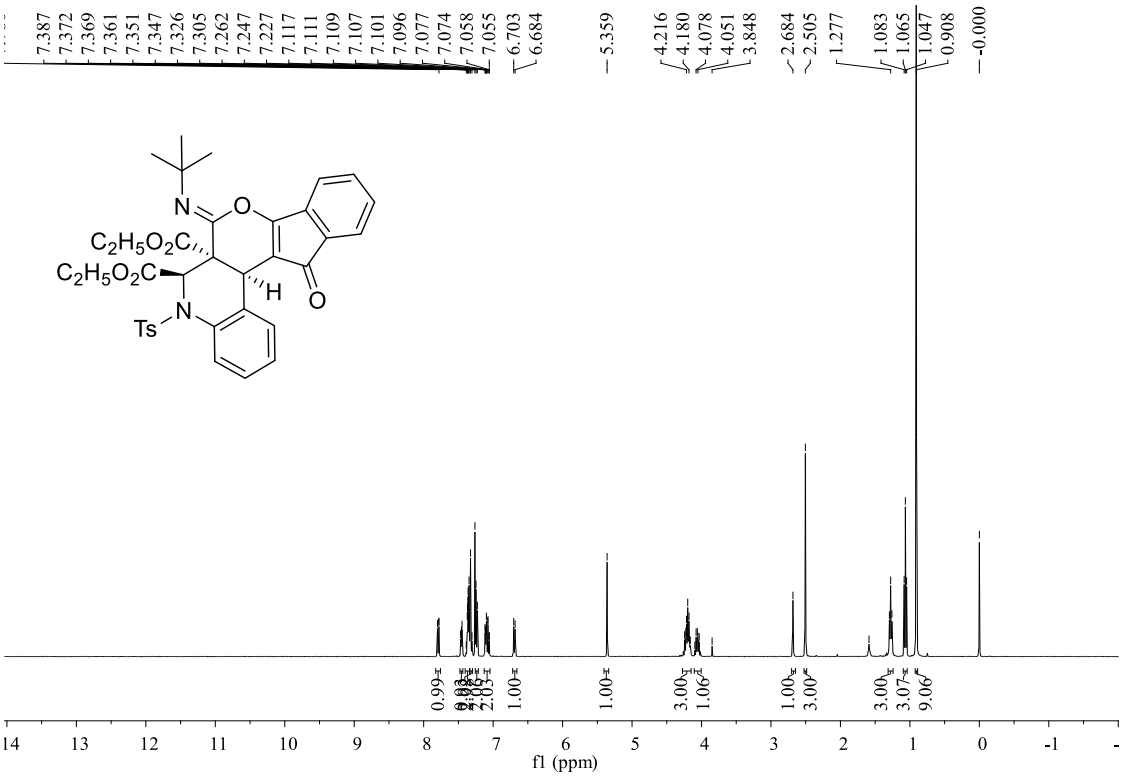
Diethyl *rel*-(6*R*,6a*R*,13b*R*,*Z*)-7-(cyclohexylimino)-13-oxo-5-tosyl-5,6,13,13b-tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinoline-6,6a(7*H*)-dicarboxylate (6f): Yellow solid, 47%, mp 161-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.0 Hz, 1H, ArH), 7.46-7.44 (m, 1H, ArH), 7.39-7.33 (m, 4H, ArH), 7.31-7.28 (m, 1H, ArH), 7.23 (d, *J* = 8.0 Hz, 2H, ArH), 7.18-7.16 (m, 1H, ArH), 7.07 (t, *J* = 7.6 Hz, 1H, ArH), 6.68 (d, *J* = 8.0 Hz, 1H, ArH), 5.42 (s, 1H, CH), 4.29-4.20 (m, 2H, CH_2), 4.14-4.02 (m, 2H, CH_2), 3.65-3.59 (m, 1H, CH), 2.72 (s, 1H, CH), 2.50 (s, 3H, CH_3), 1.70-1.63 (m, 1H, CH), 1.53-1.35 (m, 3H, CH), 1.26 (t, *J* = 6.8 Hz, 3H, CH_3), 1.21-1.15 (m, 2H, CH), 1.06 (t, *J* = 7.2 Hz, 3H, CH_3), 0.99-0.96 (m, 1H, CH), 0.56-0.52 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.7, 172.2, 169.0, 144.9, 142.5, 135.5, 134.0, 134.6, 133.1, 132.5, 132.4, 131.0, 129.5, 128.7, 128.6, 127.3, 127.0, 126.0, 122.2, 118.5, 108.7, 62.6, 61.6, 61.2, 59.0, 54.2, 35.6, 32.6, 32.2, 25.4, 23.8, 23.7, 21.6, 13.9, 13.8; IR (KBr) υ: 2930, 2854, 1764, 1742, 1704, 1639, 1596, 1458, 1397, 1366, 1232, 1204, 1171, 1117, 1084, 1022, 1002, 889, 864, 770, 723, 714, 664, 578, 524 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{38}H_{39}N_2O_8S$ ($[M + H]^+$): 683.2422, found: 683.2393.

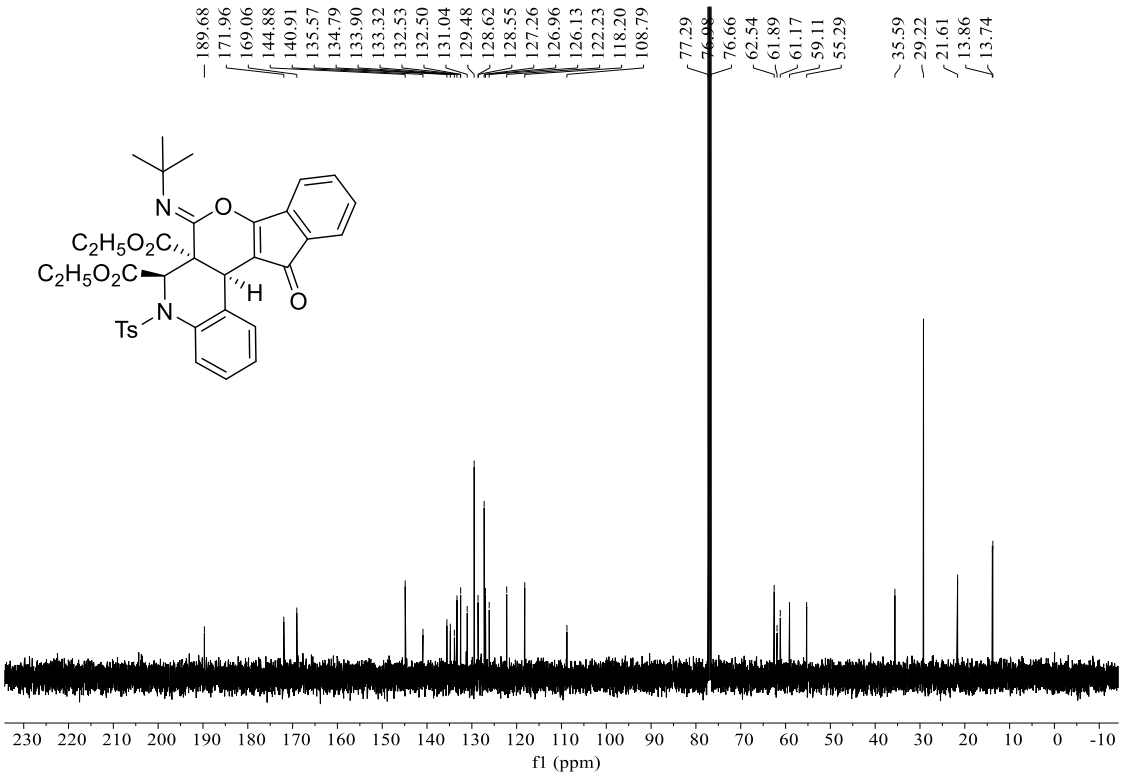


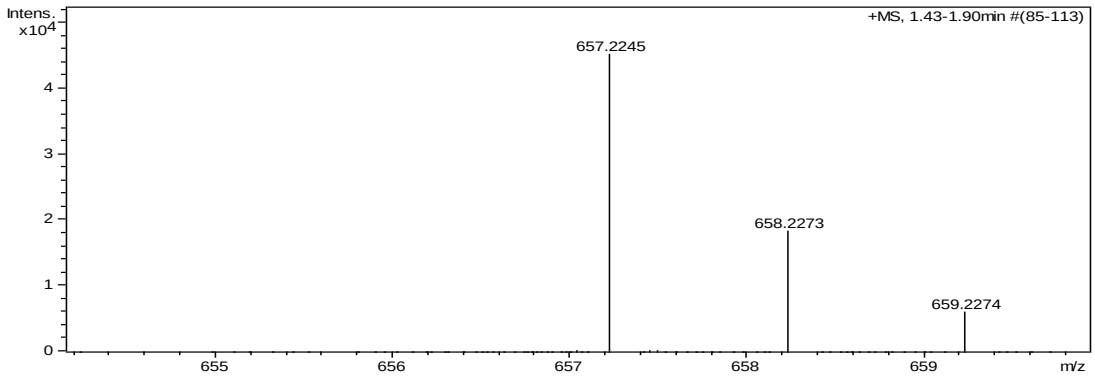

189.69
172.19
168.97
144.88
142.50
135.54
134.62
133.96
133.11
132.51
132.44
130.97
129.47
128.66
128.62
127.27
126.98
126.00
122.17
118.54
108.71
77.29
76.97
76.66
62.61
61.60
61.24
59.02
54.24
35.59
32.58
32.16
25.42
23.82
23.66
21.61
13.86
13.81
N
O
C2H5O2C
C2H5O2C
H
O
N
Ts
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 3.21-3.90min #(191-232)
683.2393
684.2424
685.2423
2.0
1.5
1.0
0.5
0.0
681.0 681.5 682.0 682.5 683.0 683.5 684.0 684.5 685.0 685.5 m/z

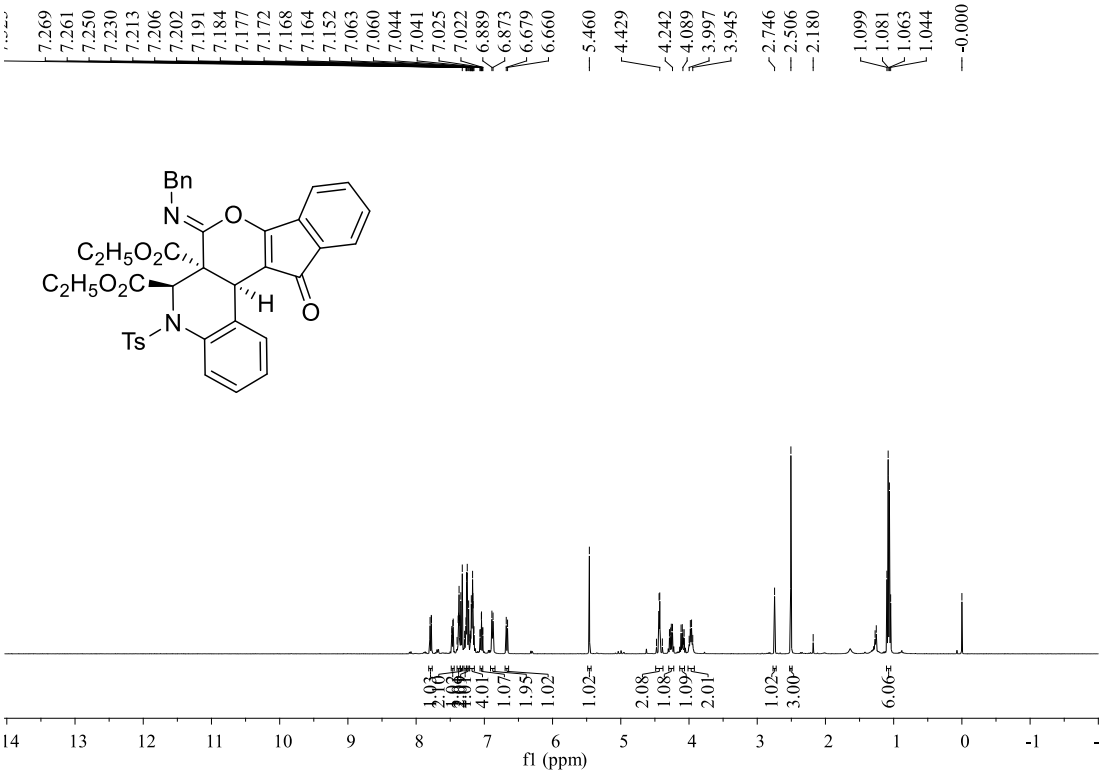
Diethyl *rel*-(6*R*,6a*R*,13b*R*,*Z*)-7-(*tert*-butylimino)-13-oxo-5-tosyl-5,6,13,13b-tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinoline-6,6a(7*H*)-dicarboxylate (6g): Yellow solid, 40%, mp 190-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.0 Hz, 1H, ArH), 7.47-7.45 (m, 1H, ArH), 7.39-7.35 (m, 3H, ArH), 7.33-7.30 (m, 2H, ArH), 7.24 (d, *J* = 8.0 Hz, 2H, ArH), 7.12-7.06 (m, 2H, ArH), 6.69 (d, *J* = 7.6 Hz, 1H, ArH), 5.36 (s, 1H, CH), 4,24-4.16 (m, 3H, CH_2), 4,10-4.02 (m, 1H, CH_2), 2.68 (s, 1H, CH), 2.50 (s, 3H, CH_3), 1.28 (t, *J* = 7.2 Hz, 3H, CH_3), 1.06 (t, *J* = 7.2 Hz, 3H, CH_3), 0.91 (m, 9H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.7, 172.0, 169.1, 144.9, 140.9, 135.6, 134.8, 133.9, 133.3, 132.53, 132.50, 131.0, 129.5, 128.6, 128.6, 127.3, 127.0, 126.1, 122.2, 118.2, 108.8, 62.5, 61. 9, 61.2, 59.1, 55.3, 35.6, 29.2, 21.6, 13.9, 13.7; IR (KBr) υ: 2980, 2931, 1767, 1740, 1707, 1637, 1595, 1398, 1358, 1274, 1236, 1210, 1169, 1152, 1115, 1089, 1021, 998, 931, 911, 722, 663, 617, 579, 543 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{36}H_{37}N_2O_8S$ ($[M + H]^+$): 657.2265, found: 657.2245.

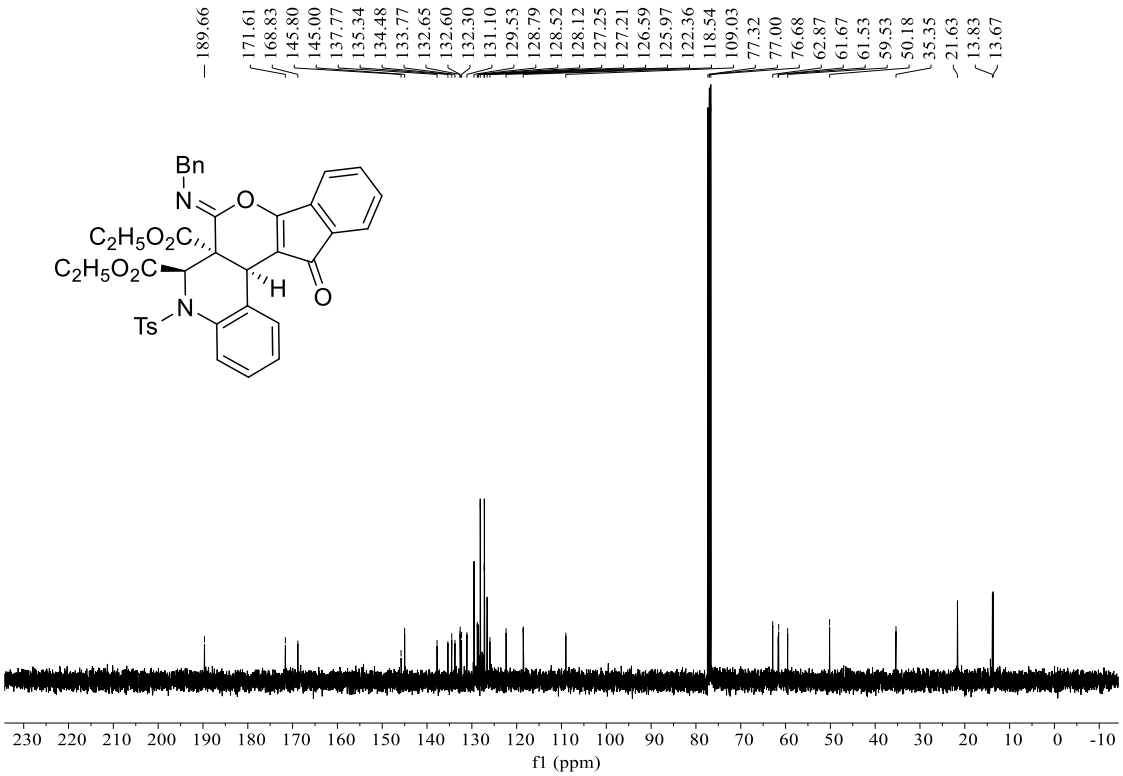


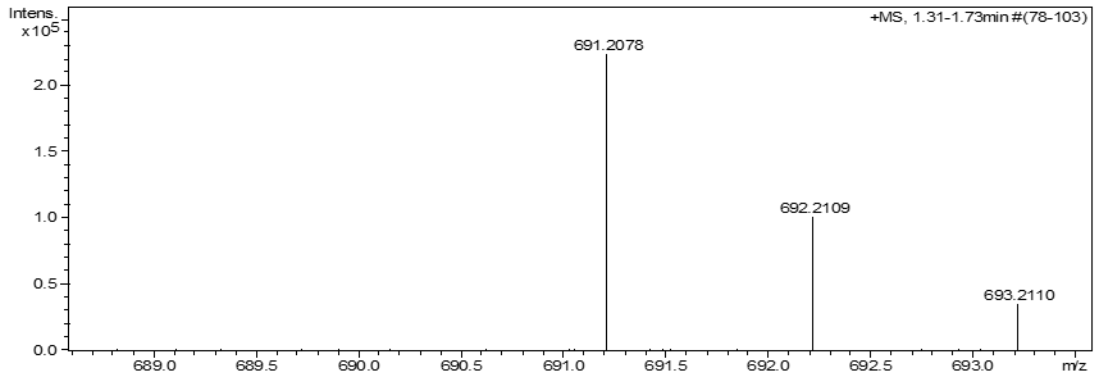

189.68
171.96
169.06
144.88
140.91
135.57
134.79
133.90
133.32
132.53
132.50
131.04
129.48
128.62
128.55
127.26
126.96
126.13
122.23
118.20
108.79
77.29
76.08
76.66
62.54
61.89
61.17
59.11
55.29
35.59
29.22
21.61
13.86
13.74
N
O
C2H5O2C
C2H5O2C
H
O
N
Ts
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 1.43-1.90min #(85-113)
657.2245
658.2273
659.2274
4
3
2
1
0
655
656
657
658
659
m/z

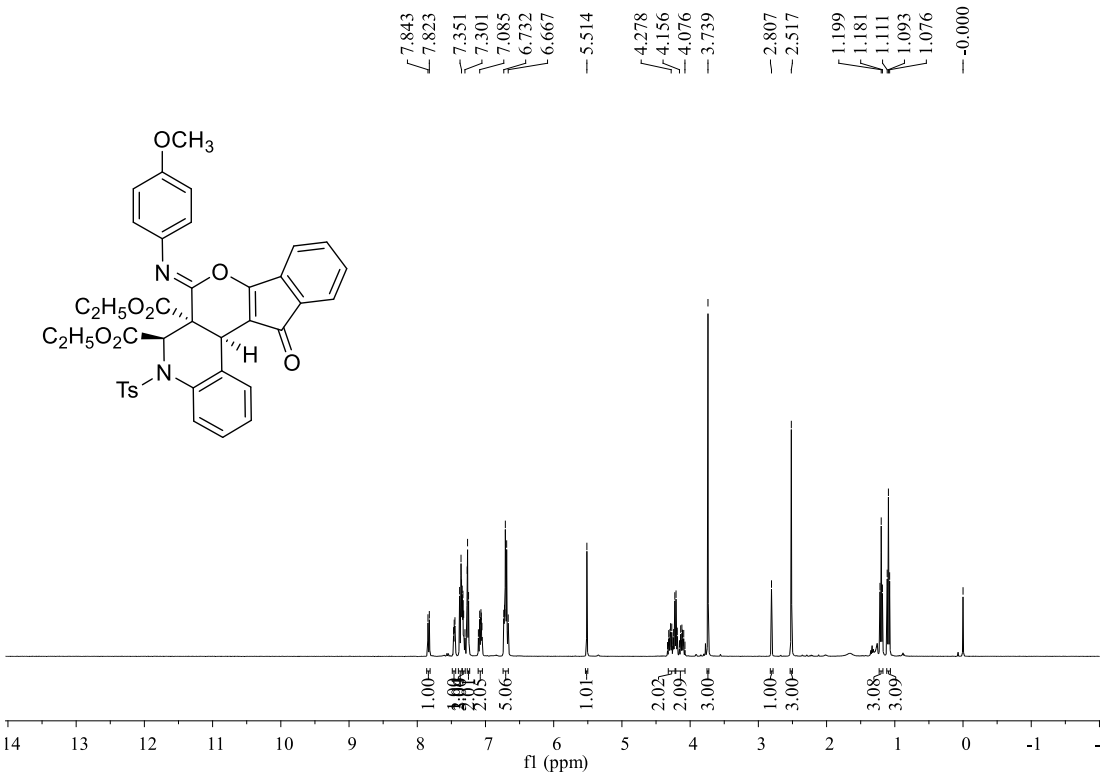
Diethyl *rel*-(6R,6aR,13bR,Z)-7-(benzylimino)-13-oxo-5-tosyl-5,6,13,13b-tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinoline-6,6a(7*H*)-dicarboxylate (6h): Yellow solid, 23%, mp 197-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* = 8.4 Hz, 1H, ArH), 7.48-7.46 (m, 1H, ArH), 7.40-7.36 (m, 2H, ArH), 7.33 (d, *J* = 8.4 Hz, 2H, ArH), 7.30-7.26 (m, 1H, ArH), 7.25-7.23 (m, 1H, ArH), 7.21-7.15 (m, 4H, ArH), 7.04 (t, *J* = 7.6 Hz, 1H, ArH), 6.88 (d, *J* = 6.8 Hz, 2H, ArH), 6.67 (d, *J* = 7.6 Hz, 1H, ArH), 5.46 (s, 1H, CH), 4.46 (d, *J* = 15.2 Hz, 1H, CH_2), 4.41 (d, *J* = 15.2 Hz, 1H, CH_2), 4.29-4.24 (m, 1H, CH_2), 4.12-4.07 (m, 1H, CH_2), 4.00-3.95 (m, 2H, CH_2), 2.75 (s, 1H, CH), 2.51 (s, 3H, CH_3), 1.21 (q, *J* = 7.2 Hz, 6H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.7, 171.6, 168.8, 145.8, 145.0, 137.8, 135.3, 134.5, 133.8, 132.7, 132.60, 132.3, 131.1, 129.5, 128.8, 128.5, 128.1, 127.3, 127.2, 126.6, 126.0, 122.4, 118.5, 109.0, 62.9, 61.7, 61.5, 59.5, 50.2, 35.4, 21.6, 13.8, 13.7; IR (KBr) υ: 2917, 2849, 1734, 1705, 1667, 1589, 1492, 1472, 1460, 1395, 1362, 1209, 1187, 1170, 1055, 1039, 1011, 902, 785, 753, 731, 687, 658, 604, 577, 549, 528 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{39}H_{35}N_2O_8S$ ($[M + H]^+$): 691.2109, found: 691.2078.

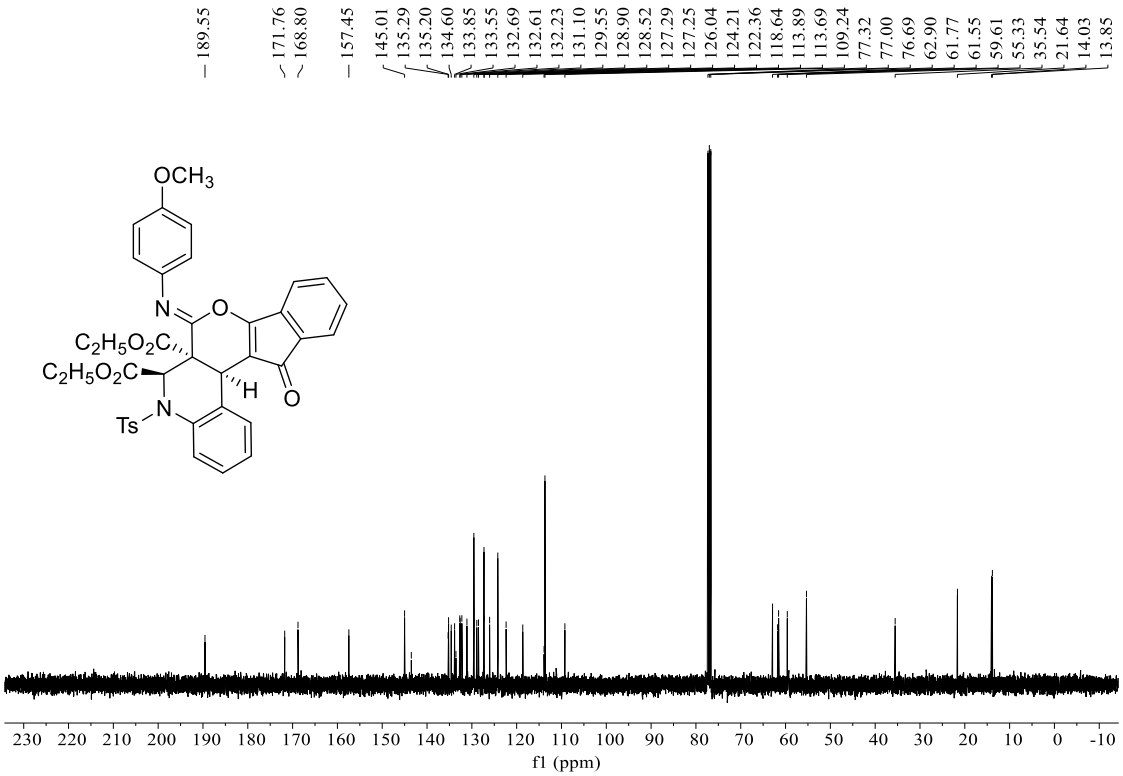


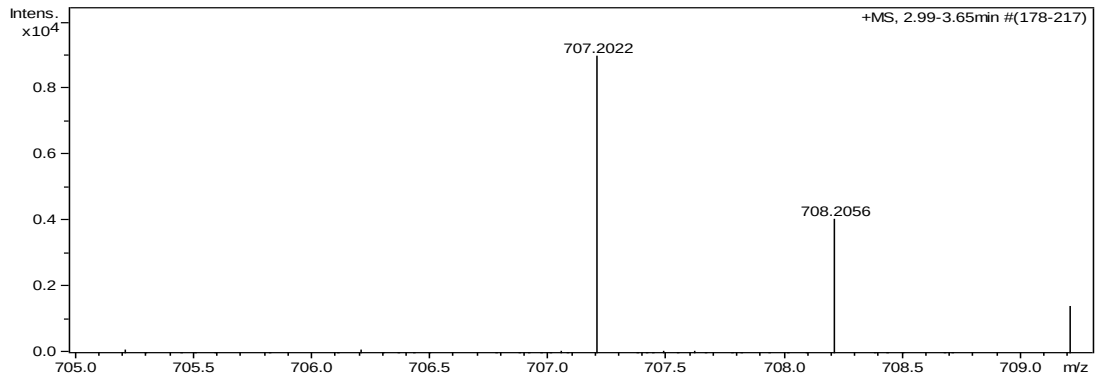

189.66
171.61
168.83
145.80
145.00
137.77
135.34
134.48
133.77
132.65
132.60
132.30
131.10
129.53
128.79
128.52
128.12
127.25
127.21
126.59
125.97
122.36
118.54
109.03
77.32
77.00
76.68
62.87
61.67
61.53
59.53
50.18
35.35
21.63
13.83
13.67
Bn
N
O
$C_2H_5O_2C$
$C_2H_5O_2C$
H
O
N
Ts
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 1.31-1.73min #(78-103)
691.2078
692.2109
693.2110
2.0
1.5
1.0
0.5
0.0
689.0
689.5
690.0
690.5
691.0
691.5
692.0
692.5
693.0
m/z

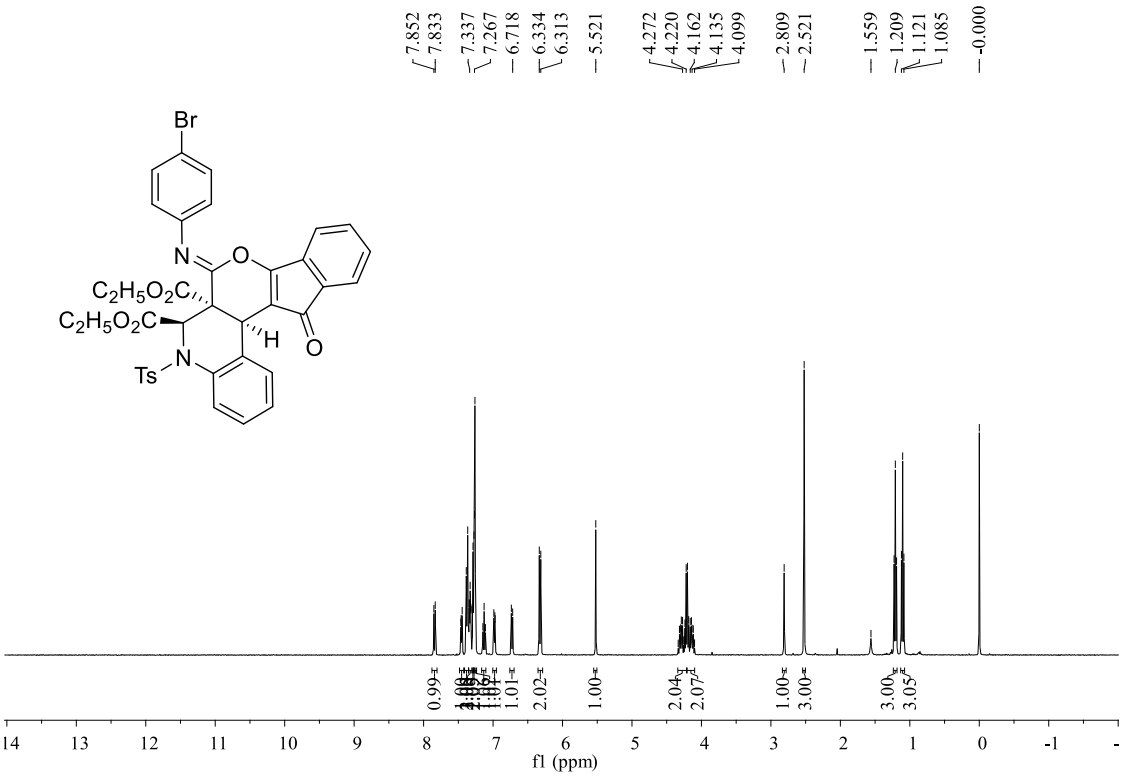
Diethyl *rel*-(6*R*,6a*R*,13b*R*,*Z*)-7-((4-methoxyphenyl)imino)-13-oxo-5-tosyl-5,6,13,13b-tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinoline-6,6a(7*H*)-dicarboxylate (6i): Yellow solid, 37%, mp 216-217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.0 Hz, 1H, ArH), 7.47-7.45 (m, 1H, ArH), 7.38-7.35 (m, 3H, ArH), 7.34-7.30 (m, 2H, ArH), 7.26-7.25 (m, 2H, ArH), 7.10-7.05 (m, 2H, ArH), 6.73-6.67 (m, 5H, ArH), 5.51 (s, 1H, CH), 4,33-4.23 (m, 2H, CH_2), 4,21-4.08 (m, 2H, CH_2), 3.74 (s, 3H, OCH_3), 2.81 (s, 1H, CH), 2.52 (s, 3H, CH_3), 1.20 (t, *J* = 7.2 Hz, 3H, CH_3), 1.09 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.6, 171.8, 168.8, 157.5, 145.0, 143.5, 135.3, 135.2, 134.6, 133.9, 133.6, 132.7, 132.6, 132.2, 131.1, 129.6, 128.9, 128.5, 127.3, 127.3, 126.0, 124.2, 122.4, 118.6, 113.9, 113.7, 109.2, 62.9, 61.8, 61.6, 59.6, 55.3, 35.5, 21.6, 14.0, 13.9; IR (KBr) υ: 2968, 2954, 1766, 1732, 1699, 1643, 1595, 1512, 1460, 1455, 1451, 1402, 1347, 1262, 1230, 1183, 1109, 1034, 1002, 898, 853, 824, 738, 603, 582, 557, 532 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{39}H_{35}N_2O_9S$ ([M + H]$^+$): 707.2058, found: 707.2022.

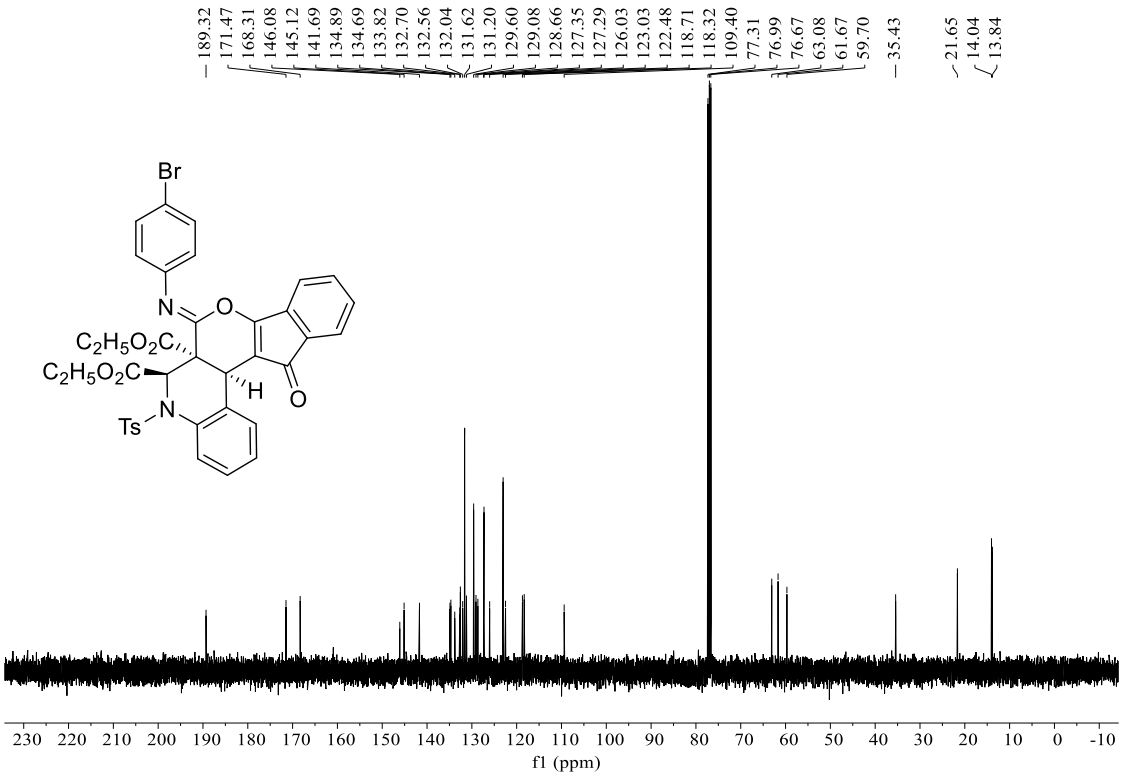


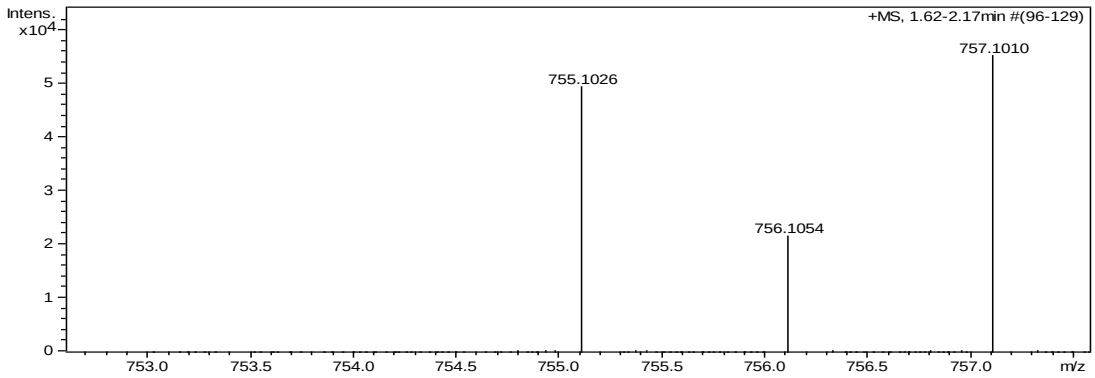

189.55
171.76
168.80
157.45
145.01
135.29
135.20
134.60
133.85
133.55
132.69
132.61
132.23
131.10
129.55
128.90
128.52
127.29
127.25
126.04
124.21
122.36
118.64
113.89
113.69
109.24
77.32
77.00
76.69
62.90
61.77
61.55
59.61
55.33
35.54
21.64
14.03
13.85
OCH3
N
O
C2H5O2C
C2H5O2C
H
O
N
Ts
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 2.99-3.65min #(178-217)
707.2022
708.2056
0.0
0.2
0.4
0.6
0.8
705.0
705.5
706.0
706.5
707.0
707.5
708.0
708.5
709.0
m/z

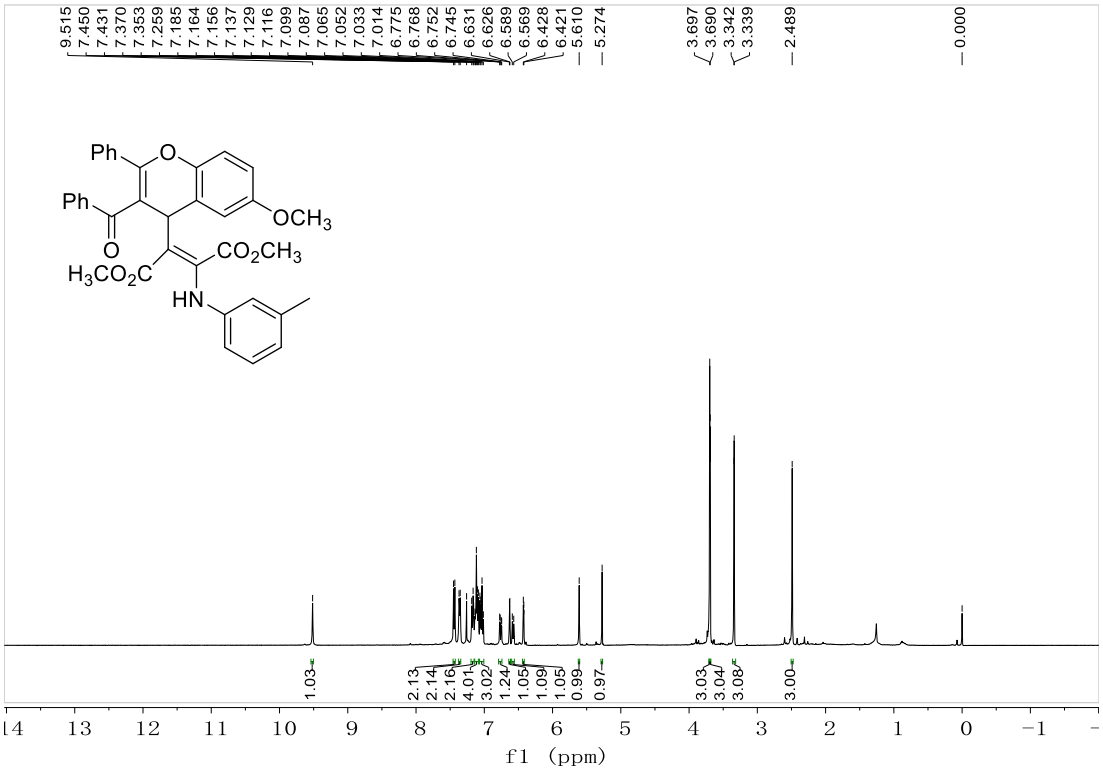
Diethyl *rel*-(6*R*,6a*R*,13b*R*,*Z*)-7-((4-bromophenyl)imino)-13-oxo-5-tosyl-5,6,13,13b-tetrahydroindeno[2',1':5,6]pyrano[3,4-*c*]quinoline-6,6a(7*H*)-dicarboxylate (6j): Yellow solid, 28%, mp 254-255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.6 Hz, 1H, ArH), 7.46-7.45 (m, 1H, ArH), 7.39-7.35 (m, 3H, ArH), 7.34-7.32 (m, 2H, ArH), 7.30-7.29 (m, 1H, ArH), 7.27-7.26 (m, 2H, ArH), 7.13 (t, *J* = 7.6 Hz, 1H, ArH), 6.99-6.97 (m, 1H, ArH), 6.73 (d, *J* = 7.6 Hz, 1H, ArH), 6.32 (d, *J* = 8.4 Hz, 1H, ArH), 5.52 (s, 1H, CH), 4,33-4.22 (m, 2H, CH_2), 4,20-4.10 (m, 2H, CH_2), 2.81 (s, 1H, CH), 2.52 (s, 3H, CH_3), 1.21 (t, *J* = 6.8 Hz, 3H, CH_3), 1.10 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.3, 171.5, 168.3, 146.1, 145.1, 141.7, 134.9, 134.7, 133.8, 132.7, 132.6, 132.4, 131.6, 131.2, 129.6, 129.1, 128.7, 127.4, 127.3, 126.3, 123.0, 122.5, 118.7, 118.3, 109.4, 63.1, 61.7, 59.7, 35.4, 21.6, 14.0, 13.8; IR (KBr) υ: 2996, 2971, 1766, 1741, 1708, 1646, 1598, 1484, 1458, 1393, 1250, 1212, 1168, 1119, 1090, 1022, 1006, 896, 844, 810, 767, 725, 665, 577, 552, 518 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{38}H_{32}BrN_2O_8S$ ([M + H]$^+$): 755.1057, found: 755.1026.

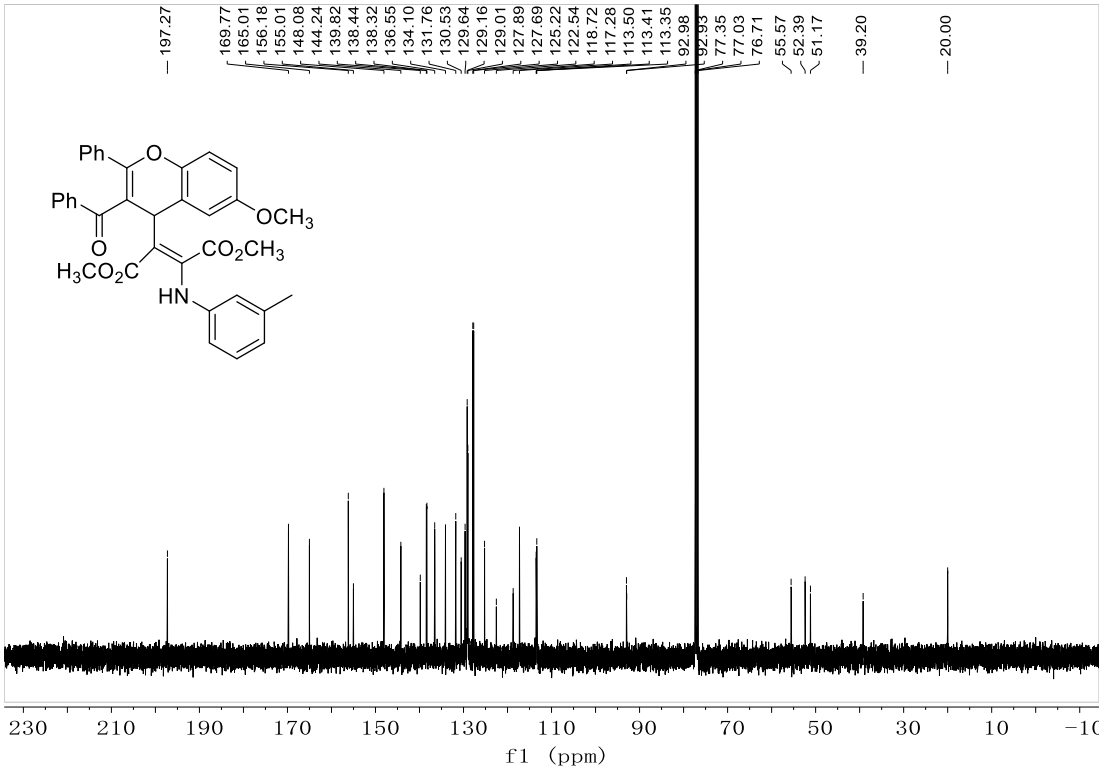


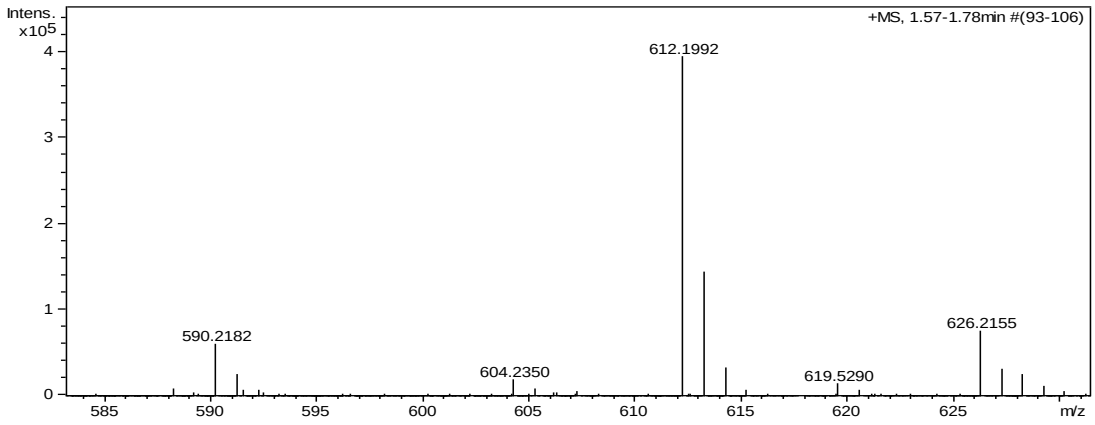

189.32
171.47
168.31
146.08
145.12
141.69
134.89
134.69
133.82
132.70
132.56
132.04
131.62
131.20
129.60
129.08
128.66
127.35
127.29
126.03
123.03
122.48
118.71
118.32
109.40
77.31
76.99
76.67
63.08
61.67
59.70
35.43
21.65
14.04
13.84
Br
N
O
C2H5O2C
C2H5O2C
H
O
N
Ts
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 1.62-2.17min #(96-129)
757.1010
755.1026
756.1054
0
1
2
3
4
5
753.0
753.5
754.0
754.5
755.0
755.5
756.0
756.5
757.0
m/z

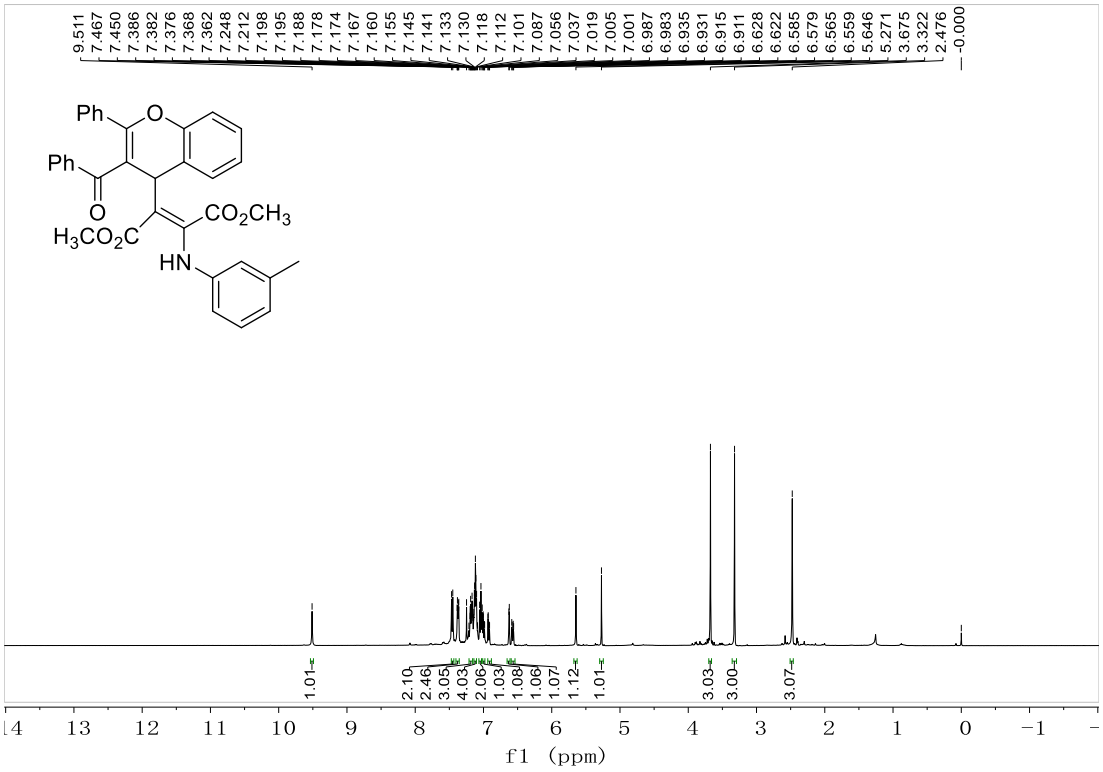
Dimethyl 2-(3-benzoyl-6-methoxy-2-phenyl-4*H*-chromen-4-yl)-3-(*m*-tolylamino)fumarate (8a): Yellow solid, 62%, mp 187-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.52 (s, 1H, NH), 7.44 (d, *J* = 7.6 Hz, 2H, ArH), 7.36 (d, *J* = 6.8 Hz, 2H, ArH), 7.19-7.15 (m, 2H, ArH), 7.14-7.09 (m, 4H, ArH), 7.07-7.01 (m, 3H, ArH), 6.76 (dd, J_1 = 9.2 Hz, J_2= 2.8 Hz, 1H, ArH), 6.63 (d, *J* = 2.0 Hz, 1H, ArH), 6.58 (d, *J* = 8.0 Hz, 1H, ArH), 6.42 (d, *J* = 2.8 Hz, 1H, ArH), 5.61 (s, 1H, ArH), 5.27 (s, 1H, CH), 3.70 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 2.49 (s, 3H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.3, 169.8, 165.0, 156.2, 155.0, 148.1, 144.2, 139.8, 138.4, 138.3, 136.6, 134.1, 131.8, 130.5, 129.6, 129.2, 129.0, 127.9, 127.7, 125.2, 122.5, 118.7, 117.3, 113.5, 113.4, 113.4, 93.0, 92.9, 55.6, 52.4, 51.2, 39.2, 20.0 ppm; IR (KBr) υ: 3721, 3464, 3376, 2324, 1636, 1733, 1676, 1611, 1542, 1513, 1509, 1428, 1337, 1320, 1193, 1152, 1123, 1043, 1011, 1002, 921, 822, 792, 753, 726 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{36}H_{31}NNaO_7$ ([M + Na]$^+$): 612.1993, found: 612.1992.

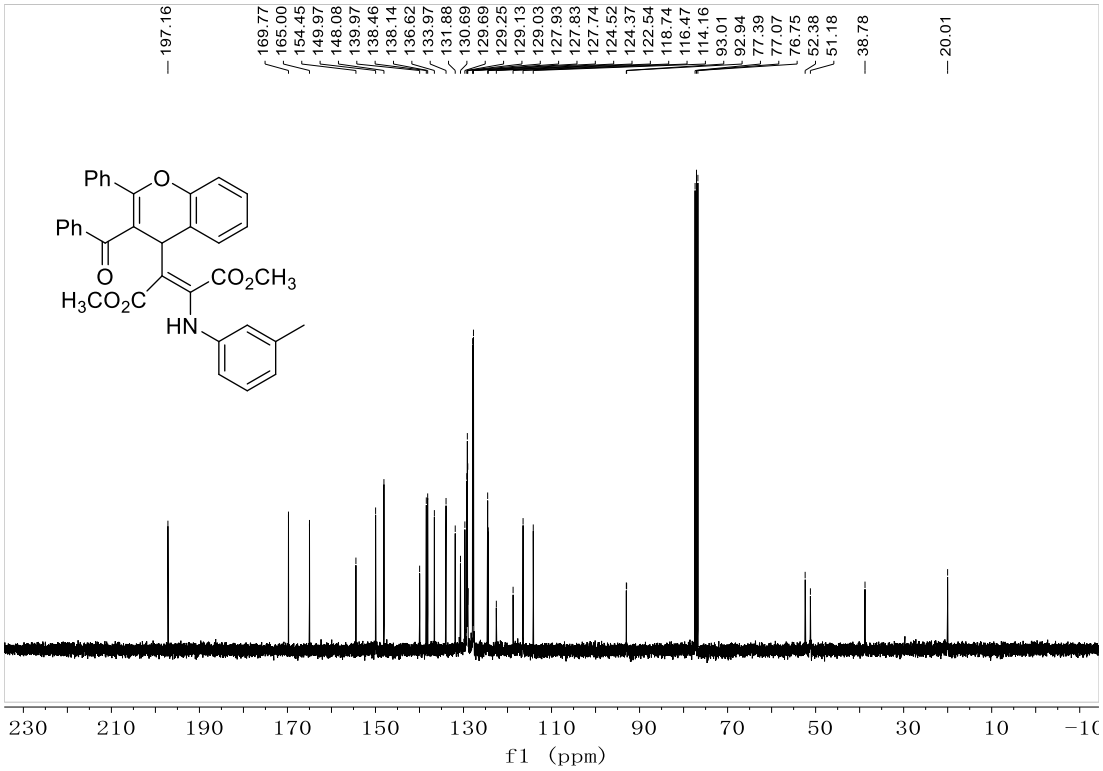


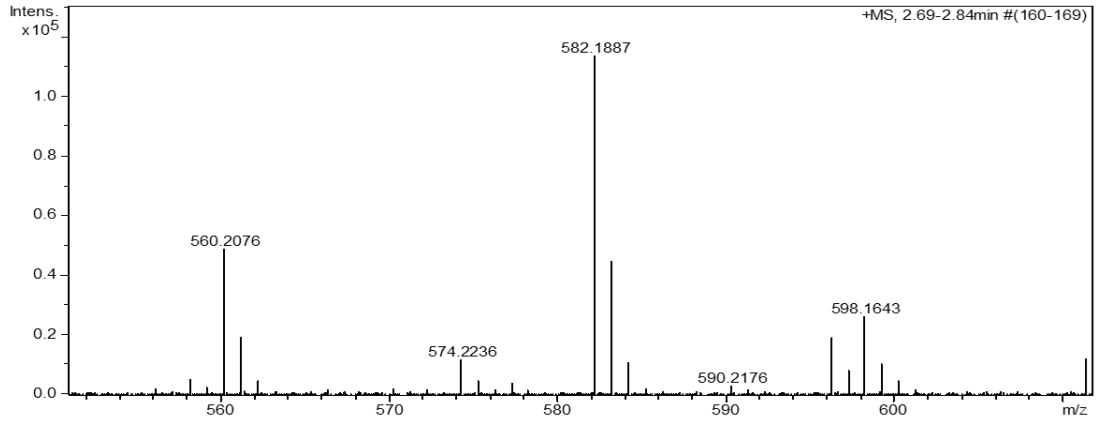

197.27
169.77
165.01
156.18
155.01
148.08
144.24
139.82
138.44
138.32
136.55
134.10
131.76
130.53
129.64
129.16
129.01
127.89
127.69
125.22
122.54
118.72
117.28
113.50
113.41
113.35
92.98
92.93
77.35
77.03
76.71
55.57
52.39
51.17
39.20
20.00
Ph
O
Ph
OCH3
O
CO2CH3
H3CO2C
HN
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^5
+MS, 1.57-1.78min #(93-106)
612.1992
590.2182
604.2350
619.5290
626.2155
m/z

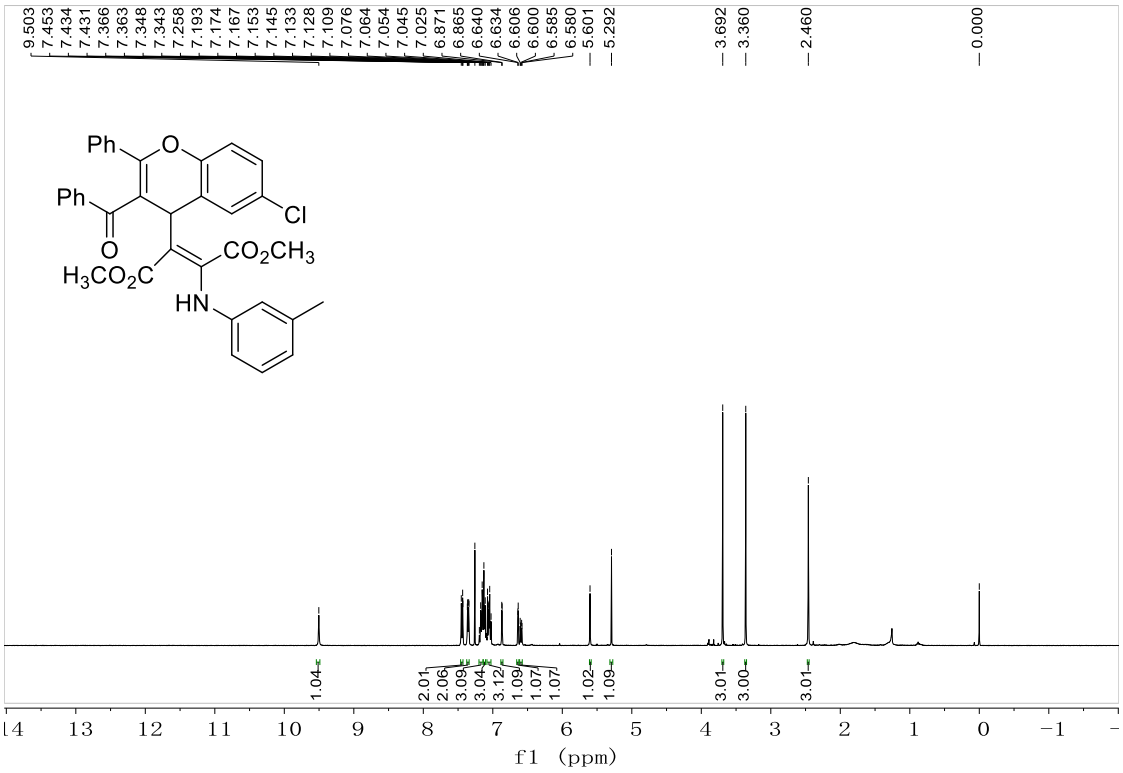
Dimethyl 2-(3-benzoyl-2-phenyl-4*H*-chromen-4-yl)-3-(*m*-tolylamino)fumarate (8b): Yellow solid, 57%, mp 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.51 (s, 1H, NH), 7.46 (d, *J* = 6.8 Hz, 2H, ArH), 7.39-7.36 (m, 2H, ArH), 7.21-7.17 (m, 3H, ArH), 7.15-7.10 (m, 4H, ArH), 7.05 (d, *J* = 7.6 Hz, 1H, ArH), 6.99 (dd, J_1 = 7.2 Hz, J_2= 1.6 Hz, 1H, ArH), 6.92 (d, *J* = 7,6 Hz, 2H, ArH), 6.62 (d, *J* = 2.4 Hz, 1H, ArH), 6.57 (dd, J_1 = 8.0 Hz, J_2= 2.4 Hz, 1H, ArH), 5.65 (s, 1H, ArH), 5.27 (s, 1H, CH), 3.68 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 2.45 (s, 3H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.2, 169.8, 165.0, 154.5, 150.0, 148.1, 140.0, 138.5, 138.1, 136.6, 134.0, 131.9, 130.7, 129.7, 129.3, 129.1, 129.0, 127.9, 127.8, 127.7, 124.5, 124.4, 122.5, 118.7, 116.5, 114.2, 93.0, 92.9, 52.4, 51.2, 38.8, 20.0 ppm; IR (KBr) υ: 3824, 3530, 3376, 2904, 2843, 1787, 1532, 1509, 1435, 1327, 1300, 1289, 1200, 1172, 1198, 1103, 1082, 1024, 1011, 936, 820, 797, 783, 609 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{29}NNaO_6$ ([M + Na]$^+$): 582.1887, ound: 582.1887.

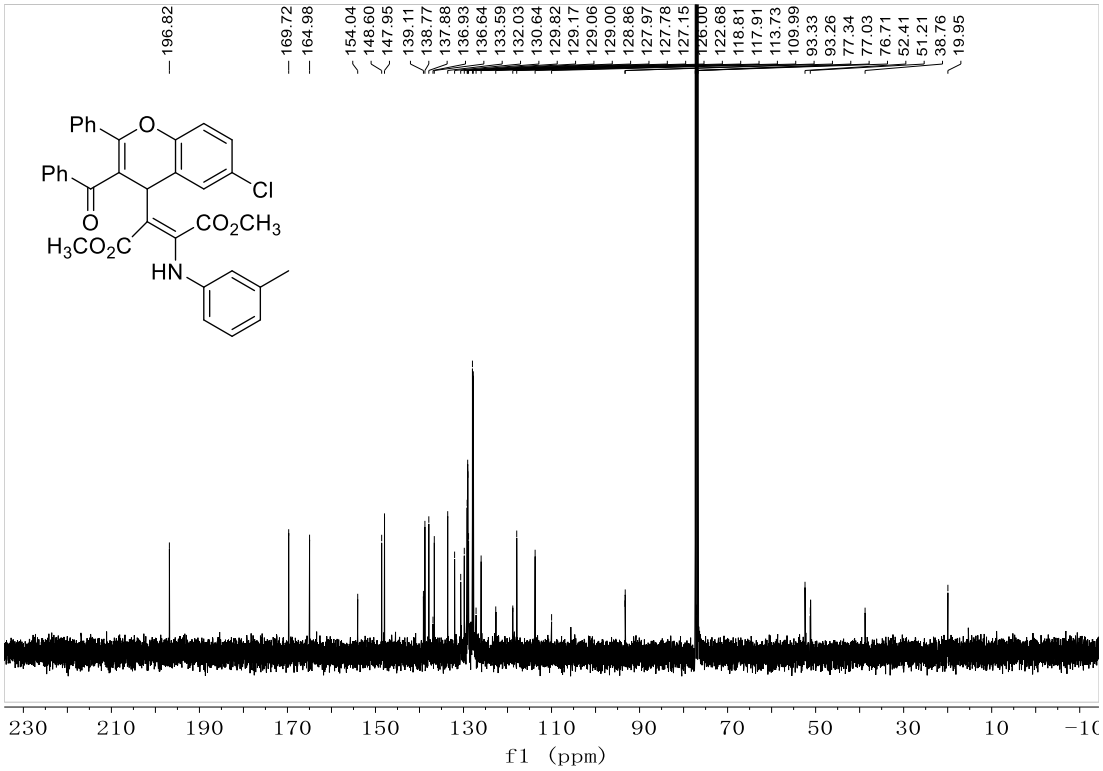


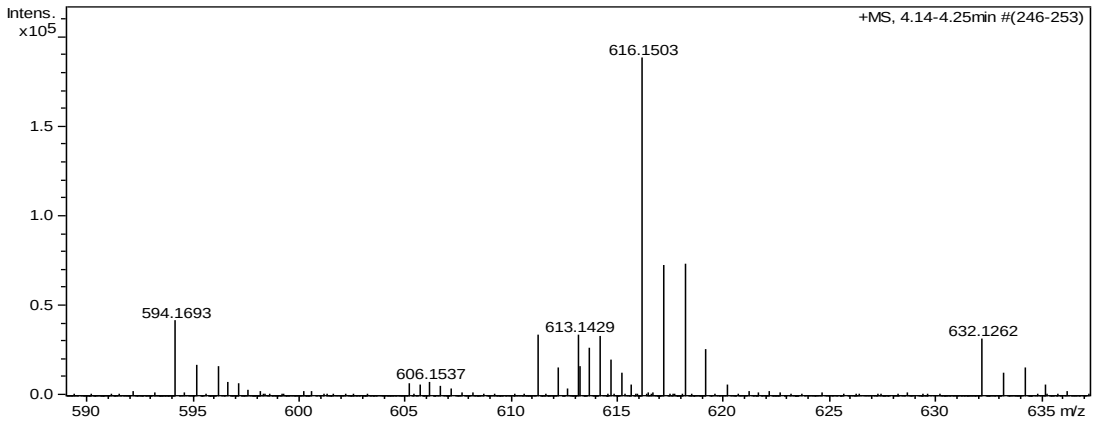

197.16
169.77
165.00
154.45
149.97
148.08
139.97
138.46
138.14
136.62
133.97
131.88
130.69
129.69
129.25
129.13
129.03
127.93
127.83
127.74
124.52
124.37
122.54
118.74
116.47
114.16
93.01
92.94
77.39
77.07
76.75
52.38
51.18
38.78
20.01
Ph
O
Ph
O
H_3CO_2C
CO_2CH_3
HN
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^5
+MS, 2.69-2.84min #(160-169)
582.1887
560.2076
574.2236
590.2176
598.1643
1.0
0.8
0.6
0.4
0.2
0.0
560
570
580
590
600
m/z

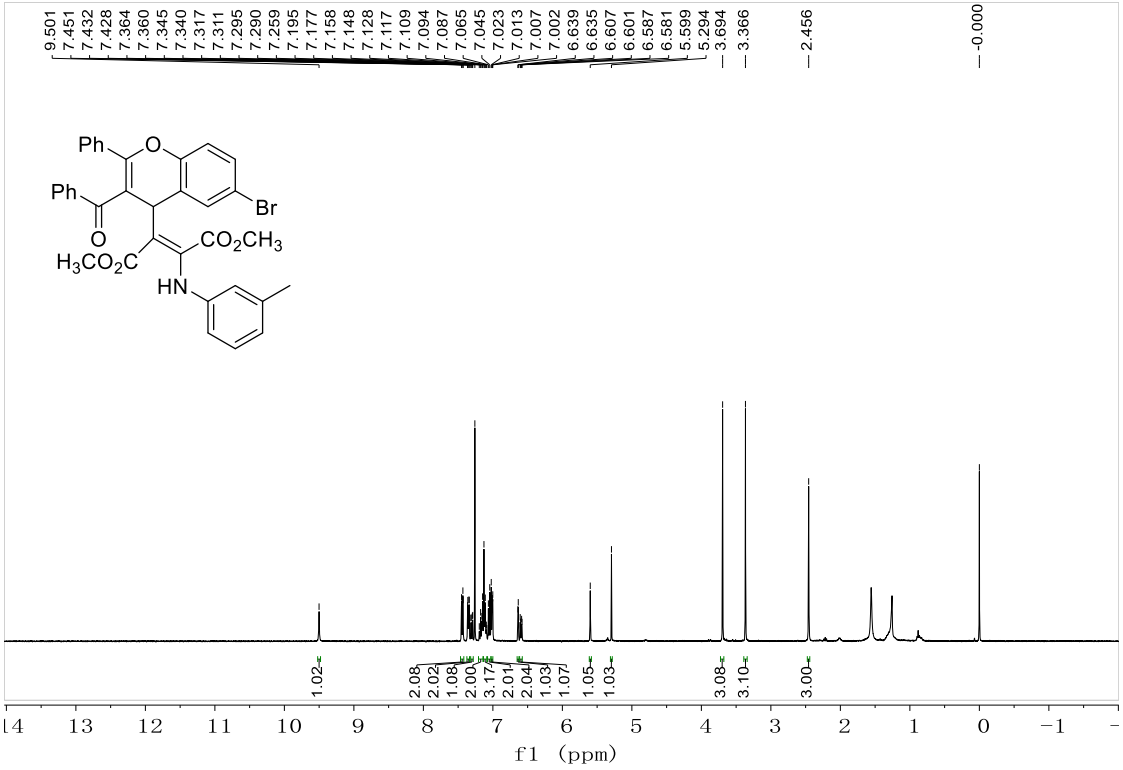
Dimethyl 2-(3-benzoyl-6-chloro-2-phenyl-4*H*-chromen-4-yl)-3-(*m*-tolylamino)fumarate (8c): Yellow solid, 45%, mp 201-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.50 (s, 1H, NH), 7.53-7.31 (m, 2H, ArH), 7.35 (dd, J_1 = 7.2 Hz, J_2= 1.2 Hz, 2H, ArH), 7.19-7.15 (m, 3H, ArH), 7.13-7.11 (m, 3H, ArH), 7.08-7.03 (m, 3H, ArH), 6.87 (d, J = 2.4 Hz, 1H, ArH), 6.64 (d, J = 2.4 Hz, 1H, ArH), 6.59 (dd, J_1 = 8.4 Hz, J_2= 2.4 Hz, 1H, ArH), 5.60 (s, 1H, ArH), 5.29 (s, 1H, CH), 3.69 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3), 2.46 (s, 3H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.8, 169.7, 165.0, 154.0, 148.6, 148.0, 139.1, 138.8, 137.9, 136.9, 136.6, 133.6, 132.0, 130.6, 129.8, 129.2, 129.1, 129.0, 128.9, 128.0, 127.8, 127.2, 126.0, 122.7, 118.8, 117.9, 113.7, 110.0, 93.3, 93.3, 52.4, 51.2, 38.8, 20.0 ppm; IR (KBr) υ: 3826, 3521, 3469, 2230, 1789, 1724, 1680, 1653, 1609, 1528, 1509, 1430, 1398, 1320, 1208, 1162, 1095, 1043, 1021, 1004, 931, 843, 780, 733, 716 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{28}ClNNaO_6$ ([M + Na]$^+$): 616.1497, found: 616.1503.

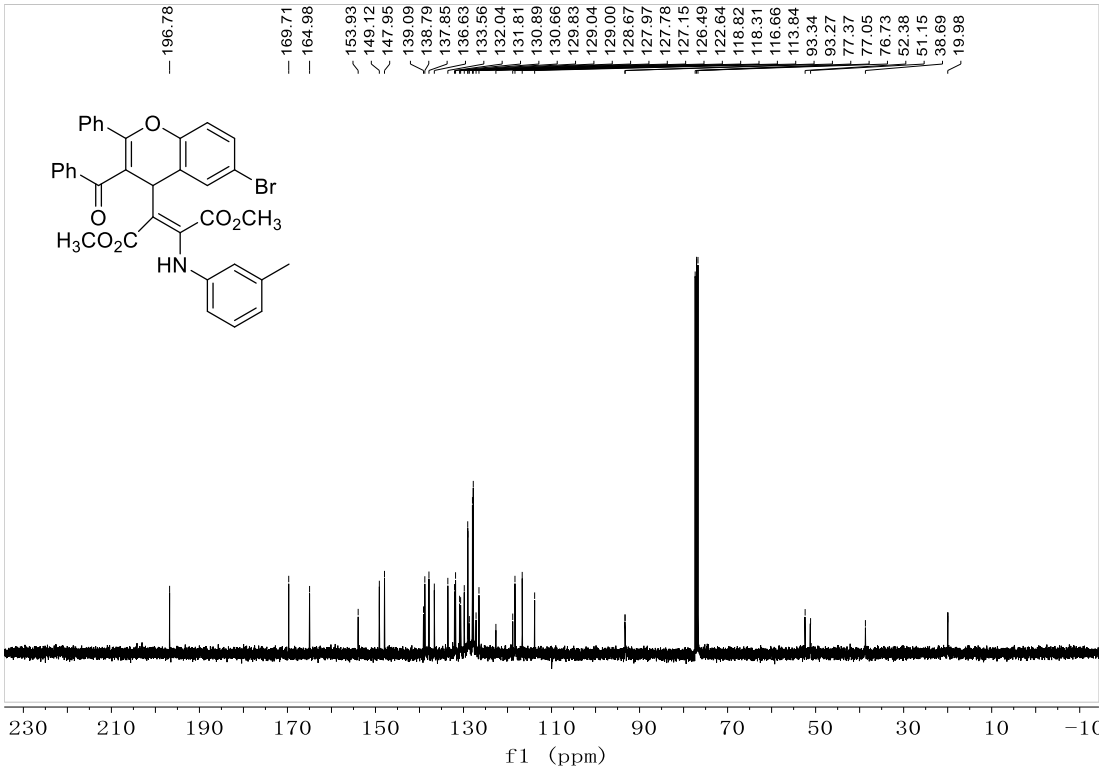


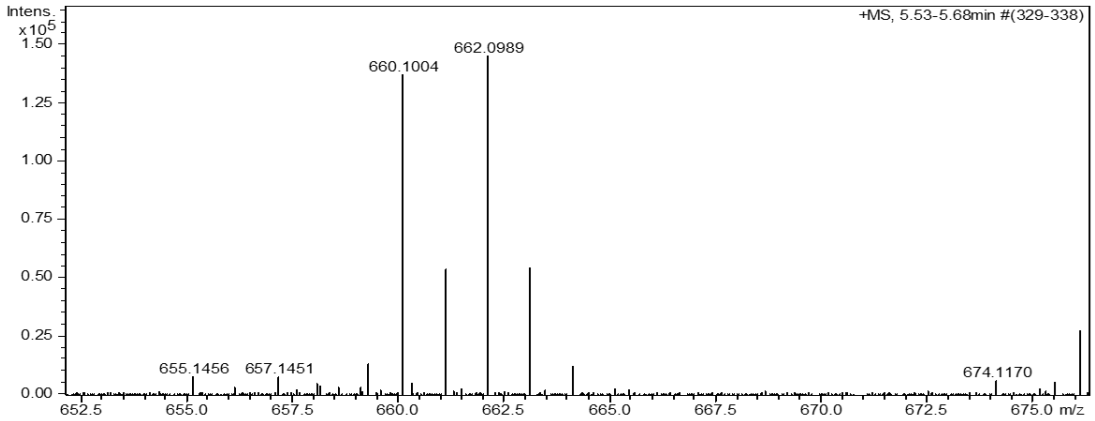

196.82
169.72
164.98
154.04
148.60
147.95
139.11
138.77
137.88
136.93
136.64
133.59
132.03
130.64
129.82
129.17
129.06
129.00
128.86
127.97
127.78
127.15
126.00
122.68
118.81
117.91
113.73
109.99
93.33
93.26
77.34
77.03
76.71
52.41
51.21
38.76
19.95
Ph
O
Ph
Cl
O
CO_2CH_3
H_3CO_2C
HN
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^5
+MS, 4.14-4.25min #(246-253)
616.1503
1.5
1.0
0.5
0.0
594.1693
613.1429
632.1262
606.1537
590
595
600
605
610
615
620
625
630
635 m/z

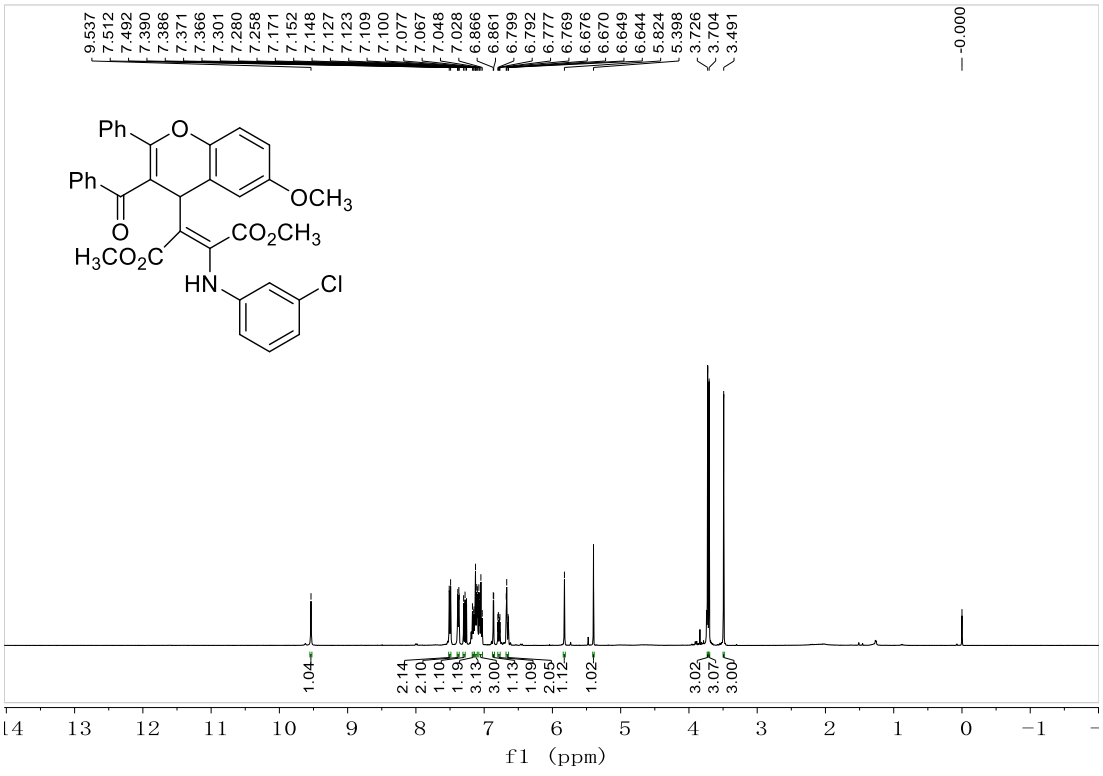
Dimethyl 2-(3-benzoyl-6-bromo-2-phenyl-4*H*-chromen-4-yl)-3-(*m*-tolylamino)fumarate (8d): Yellow solid, 40%, mp 186-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.50 (s, 1H, NH), 7.45-7.43 (m, 2H, ArH), 7.35 (dd, J_1 = 7.6 Hz, J_2= 1.6 Hz, 2H, ArH), 7.30 (dd, J_1 = 8.8 Hz, J_2= 2.4 Hz, 1H, ArH), 7.20-7.15 (m, 2H, ArH), 7.13-7.09 (m, 3H, ArH), 7.05 (d, J = 8.0 Hz, 2H, ArH), 7.02-7.00 (m, 2H, ArH), 5.60 (s, 1H, ArH), 5.60 (s, 1H, ArH), 5.29 (s, 1H, CH), 3.69 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 2.46 (s, 3H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.8, 169.7, 165.0, 153.9, 149.1, 148.0, 139.1, 138.8, 137.9, 136.6, 133. 6, 132.0, 131.8, 130.9, 130.7, 129.8, 129.0, 129.0, 128.7, 128.0, 127.8, 127.2, 126.5, 122.6, 118.8, 118.3, 116.7, 113.8, 93.4, 93.3, 52.4, 51.2, 38.7, 20.0 ppm; IR (KBr) υ: 3810, 3456, 3408, 2489, 1823, 1705, 1654, 1631, 1602, 1530, 1524, 1487, 1430, 1349, 1320, 1194, 1138, 1098, 1025, 1009, 976, 903, 824, 787, 766, 730 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{28}BrNNaO_6$ ([M + Na]$^+$): 660.0992, found: 660.1004.

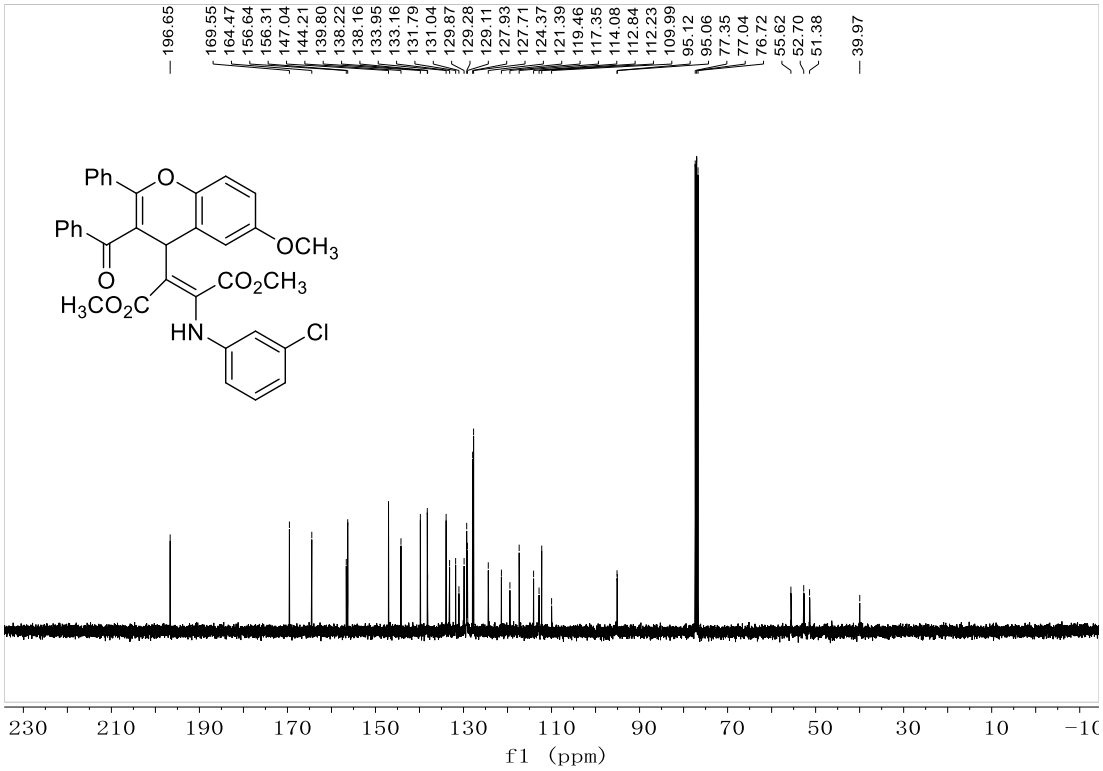


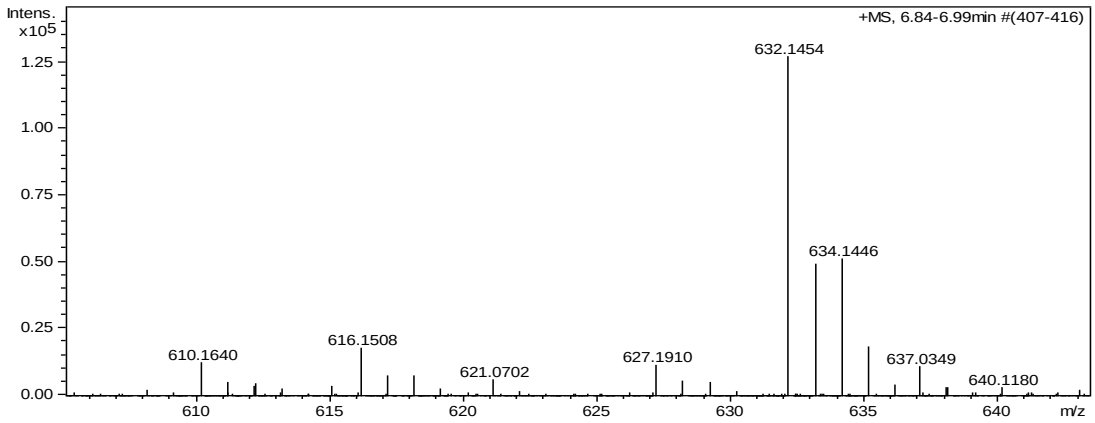

196.78
169.71
164.98
153.93
149.12
147.95
139.09
138.79
137.85
136.63
133.56
132.04
131.81
130.89
130.66
129.83
129.04
129.00
128.67
127.97
127.78
127.15
126.49
122.64
118.82
118.31
116.66
113.84
93.34
93.27
77.37
77.05
76.73
52.38
51.15
38.69
19.98
Ph
O
Ph
Br
O
CO2CH3
H3CO2C
HN
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^5
1.50
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 5.53-5.68min #(329-338)
662.0989
660.1004
655.1456
657.1451
674.1170
652.5
655.0
657.5
660.0
662.5
665.0
667.5
670.0
672.5
675.0 m/z

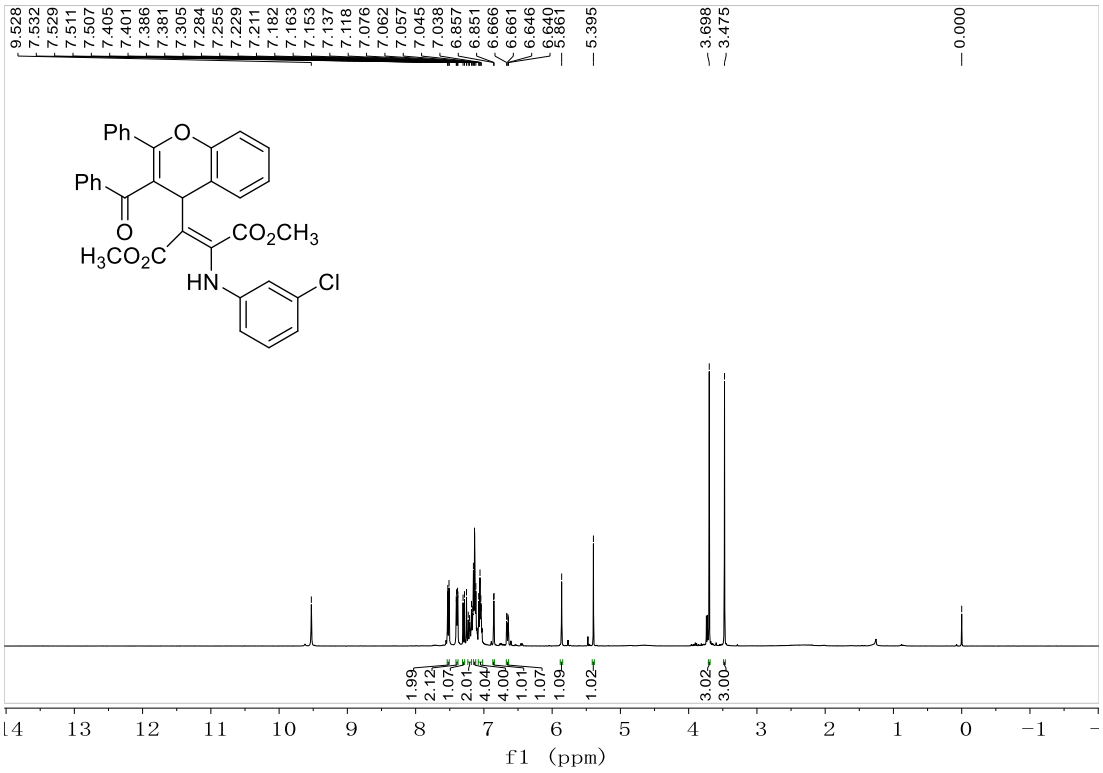
Dimethyl 2-(3-benzoyl-6-methoxy-2-phenyl-4*H*-chromen-4-yl)-3-((3-chlorophenyl)amino)fumarate (8e): Yellow solid, 65%, mp 187-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.54 (s, 1H, NH), 7.50 (d, *J* = 8.0 Hz, 2H, ArH), 7.38 (dd, J_1 = 7.6 Hz, J_2= 1.6 Hz, 2H, ArH), 7.29 (d, *J* = 7.6 Hz, 1H, ArH), 7.17-7.15 (m, 1H, ArH), 7.13-7.10 (m, 3H, ArH), 7.08-7.03 (m, 3H, ArH), 6.86 (d, *J* = 2.0 Hz, 2H, ArH), 6.78 (dd, J_1 = 8.8 Hz, J_2= 2.8 Hz, 1H, ArH), 6.68-6.44 (m, 2H, ArH), 5.82 (s, 1H, ArH), 5.40 (s, 1H, CH), 3.73 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.7, 169.6, 164.5, 156.6, 156.3, 147.0, 144.2, 139.8, 138.2, 138.2, 134.0, 133.2, 131.8, 131.0, 129.9, 129.3, 129.1, 127.9, 127.7, 124.4, 121.4, 119.5, 117.4, 114.1, 112.8, 112.2, 110.0, 95.1, 95.1, 55.6, 52.7, 51.4, 40.0 ppm; IR (KBr) υ: 3903, 3745, 3421, 3092, 2941, 1820, 1735, 1781, 1754, 1632, 1598, 1523, 1467, 1368, 1321, 1280, 1235, 1182, 1160, 1132, 1089, 1077, 1020, 933, 867, 785, 772, 730 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{28}ClNNaO7$ ([M + Na]$^+$): 632.1447, found: 632.1454.

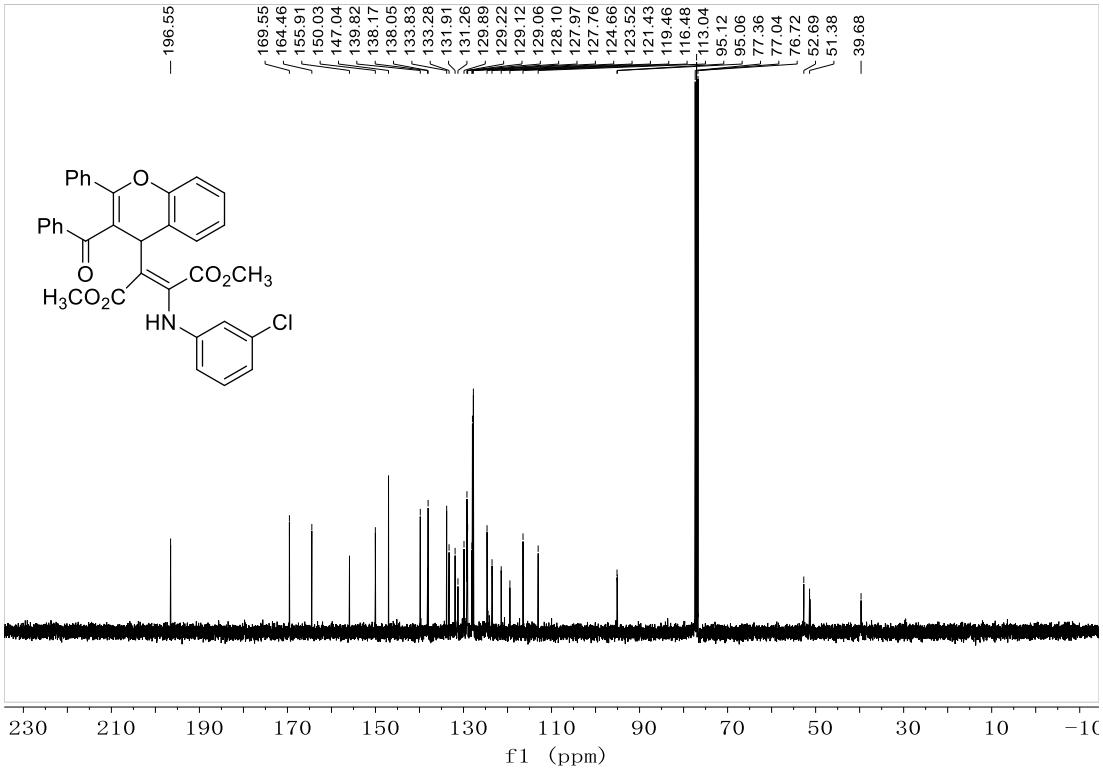


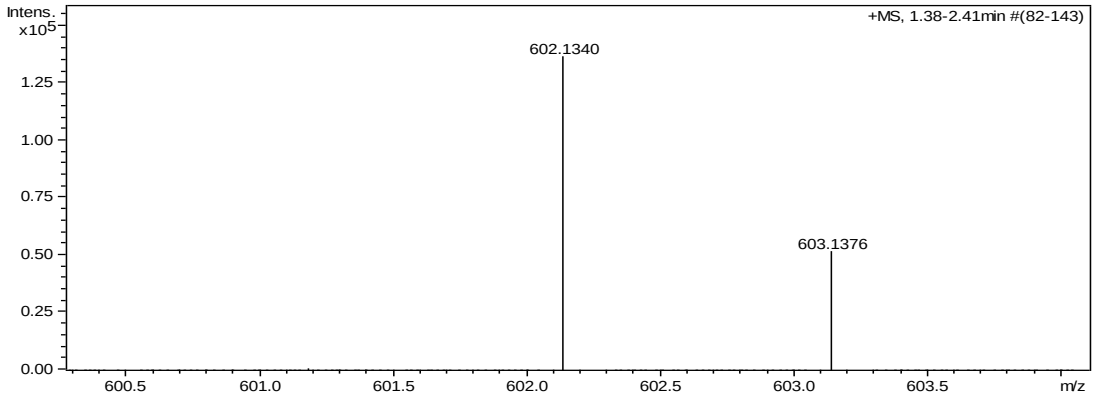

196.65
169.55
164.47
156.64
156.31
147.04
144.21
139.80
138.22
138.16
133.95
133.16
131.79
131.04
129.87
129.28
129.11
127.93
127.71
124.37
121.39
119.46
117.35
114.08
112.84
112.23
109.99
95.12
95.06
77.35
77.04
76.72
55.62
52.70
51.38
39.97
Ph
O
Ph
OCH3
O
CO2CH3
H3CO2C
HN
Cl
230
210
190
170
150
130
110
90
70
50
30
10
−10
f1 (ppm)


Intens.
x10^5
+MS, 6.84-6.99min #(407-416)
632.1454
634.1446
637.0349
640.1180
627.1910
616.1508
610.1640
621.0702
1.25
1.00
0.75
0.50
0.25
0.00
610
615
620
625
630
635
640
m/z

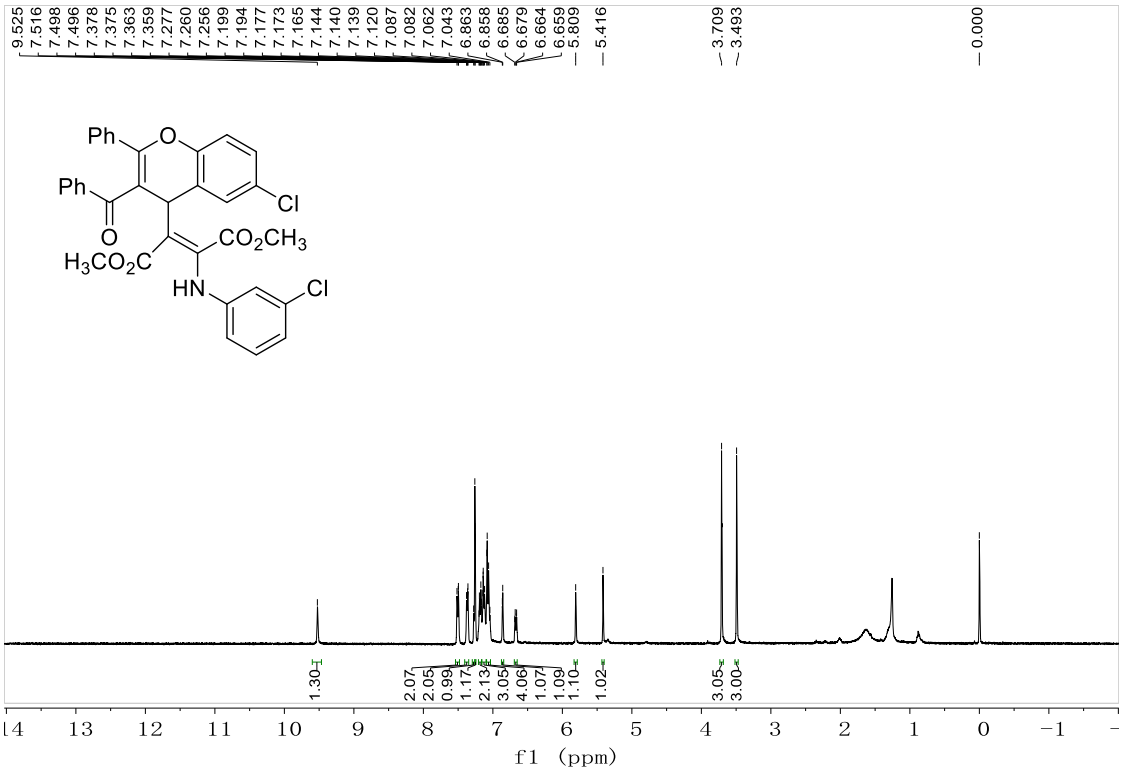
Dimethyl 2-(3-benzoyl-2-phenyl-4*H*-chromen-4-yl)-3-((3-chlorophenyl)amino)fumarate (8f): Yellow solid, 60%, mp 198-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.53 (s, 1H, NH), 7.52 (d, J = 7.2 Hz, 2H, ArH), 7.39 (dd, J_1 = 7.6 Hz, J_2= 1.6 Hz, 2H, ArH), 7.29 (d, J = 7.6 Hz, 1H, ArH), 7.23-7.18 (m, 2H, ArH), 7.15-7.12 (m, 4H, ArH), 7.08-7.04 (m, 4H, ArH), 6.85 (d, J = 2.4 Hz, 2H, ArH), 6.65 (dd, J_1 = 8.0 Hz, J_2= 2.0 Hz, 1H, ArH), 5.86 (s, 1H, ArH), 5.40 (s, 1H, CH), 3.70 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.6, 169.6, 164.5, 155.9, 150.0, 147.0, 139.8, 138.2, 138.0, 133.8, 133.3, 131.9, 131.3, 129.9, 129.2, 129.1, 129.1, 128.1, 128.0, 127.8, 124.7, 123.5, 121.4, 119.5, 116.5, 113.0, 95.12, 95.06, 52.7, 51.4, 39.7 ppm; IR (KBr) υ: 3789, 3677, 3523, 2953, 2830, 1743, 1711, 1632, 1611, 1580, 1291, 1221, 1197, 1150, 1095, 1076, 1029, 1008, 922, 851, 807, 725, 708 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{34}H_{26}ClNNaO_6$ ([M + Na]$^+$): 602.1341, found: 602.1340.

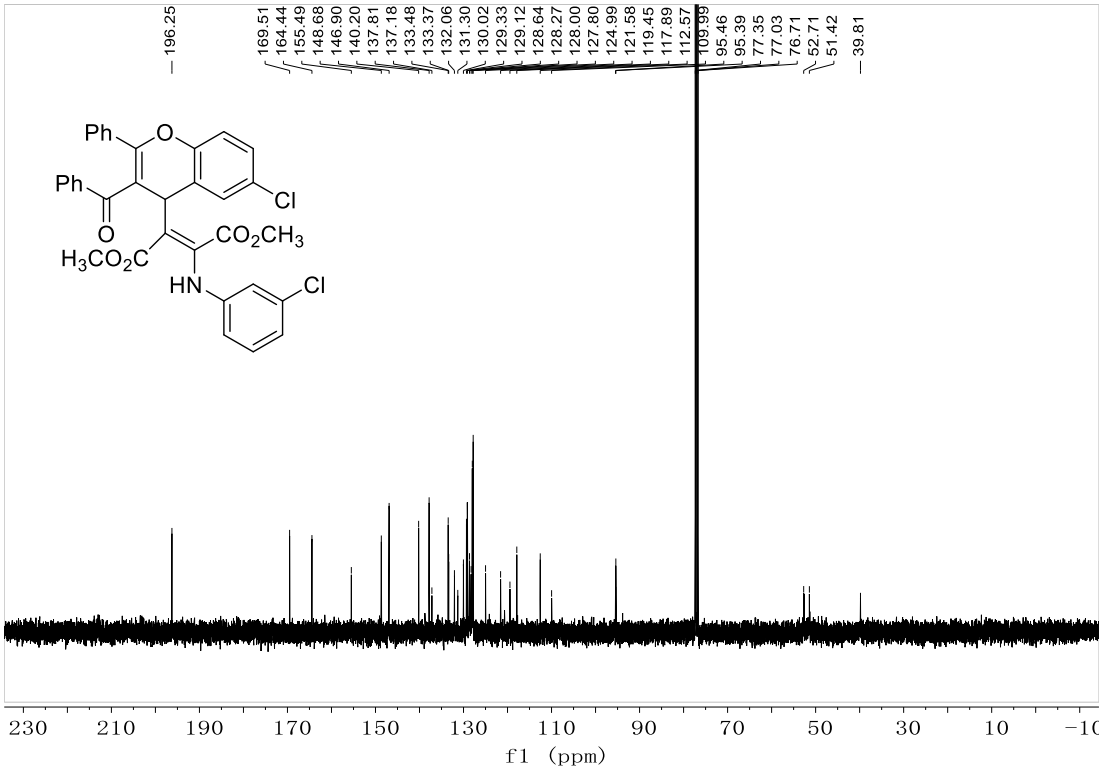


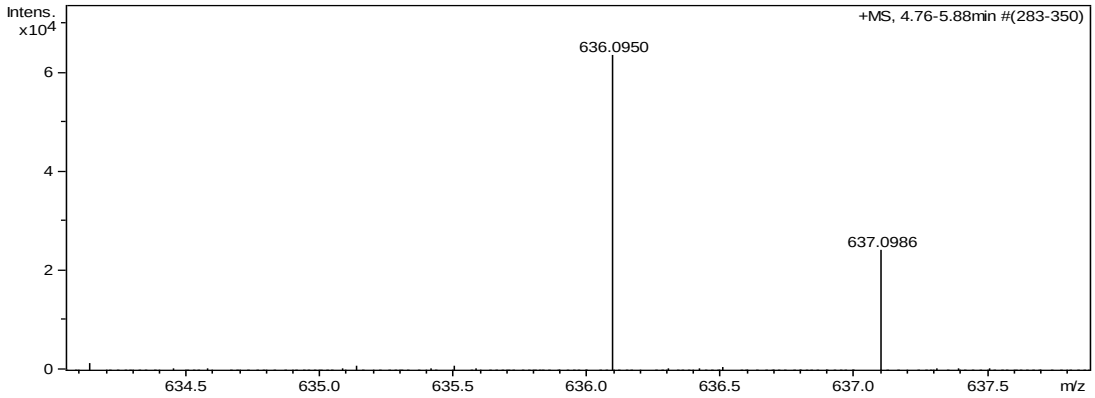

196.55
169.55
164.46
155.91
150.03
147.04
139.82
138.17
138.05
133.83
133.28
131.91
131.26
129.89
129.22
129.12
129.06
128.10
127.97
127.76
124.66
123.52
121.43
119.46
116.48
113.04
95.12
95.06
77.36
77.04
76.72
52.69
51.38
39.68
Ph
O
Ph
O
CO_2CH_3
H_3CO_2C
HN
Cl
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^5
+MS, 1.38-2.41min #(82-143)
602.1340
603.1376
1.25
1.00
0.75
0.50
0.25
0.00
600.5
601.0
601.5
602.0
602.5
603.0
603.5
m/z

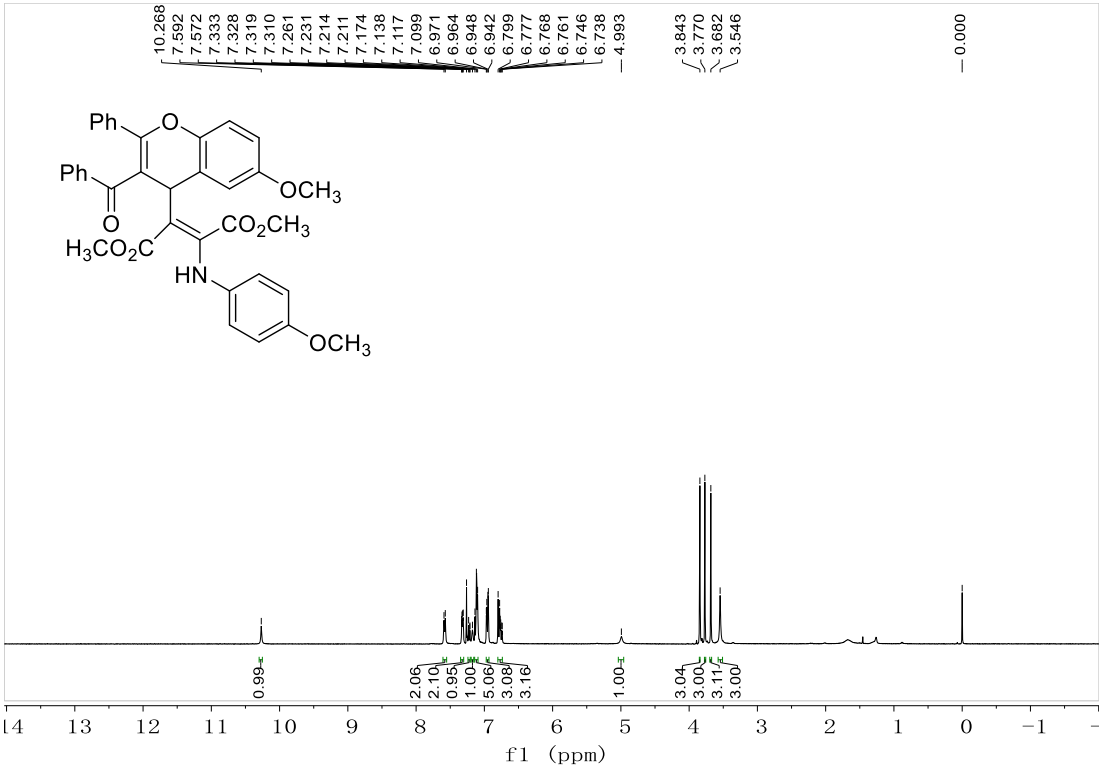
Dimethyl 2-(3-benzoyl-6-chloro-2-phenyl-4*H*-chromen-4-yl)-3-((3-chlorophenyl)amino)fumarate (8g): Yellow solid, 41%, mp 188-189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.52 (s, 1H, NH), 7.52-7.50 (m, 2H, ArH), 7.37 (dd, J_1 = 6.0 Hz, J_2= 1.2 Hz, 2H, ArH), 7.30-7.26 (m, 1H, ArH), 7.25-7.24 (m, 1H, ArH), 7.20-7.17 (m, 2H, ArH), 7.14-7.12 (m, 3H, ArH), 7.09-7.04 (m, 2H, ArH), 6.86 (d, J = 2.0 Hz, 1H, ArH), 6.67 (dd, J_1 = 8.4 Hz, J_2= 2.4 Hz, 1H, ArH), 5.81 (s, 1H, ArH), 5.42 (s, 1H, CH), 3.71 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.3, 169.5, 164.4, 155.5, 148.7, 146.9, 140.2, 137.8, 137.2, 133.5, 133.4, 132.1, 131.3, 130.0, 129.3, 129.1, 128.6, 128.8, 128.0, 127.8, 125.0, 121.6, 119.5, 117.9, 112.6, 110.0, 95.5, 95.4, 52.7, 51.4, 39.8 ppm; IR (KBr) υ: 3926, 3823, 3650, 2897, 2832, 1798, 1705, 1687, 1625, 1611, 1580, 1513, 1277, 1221, 1190, 1143, 1121, 1059, 1043, 1027, 906, 834, 767, 749, 720 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{34}H_{25}Cl_2NNaO_6$ ([M + Na]$^+$): 636.0951, found: 636.0950.

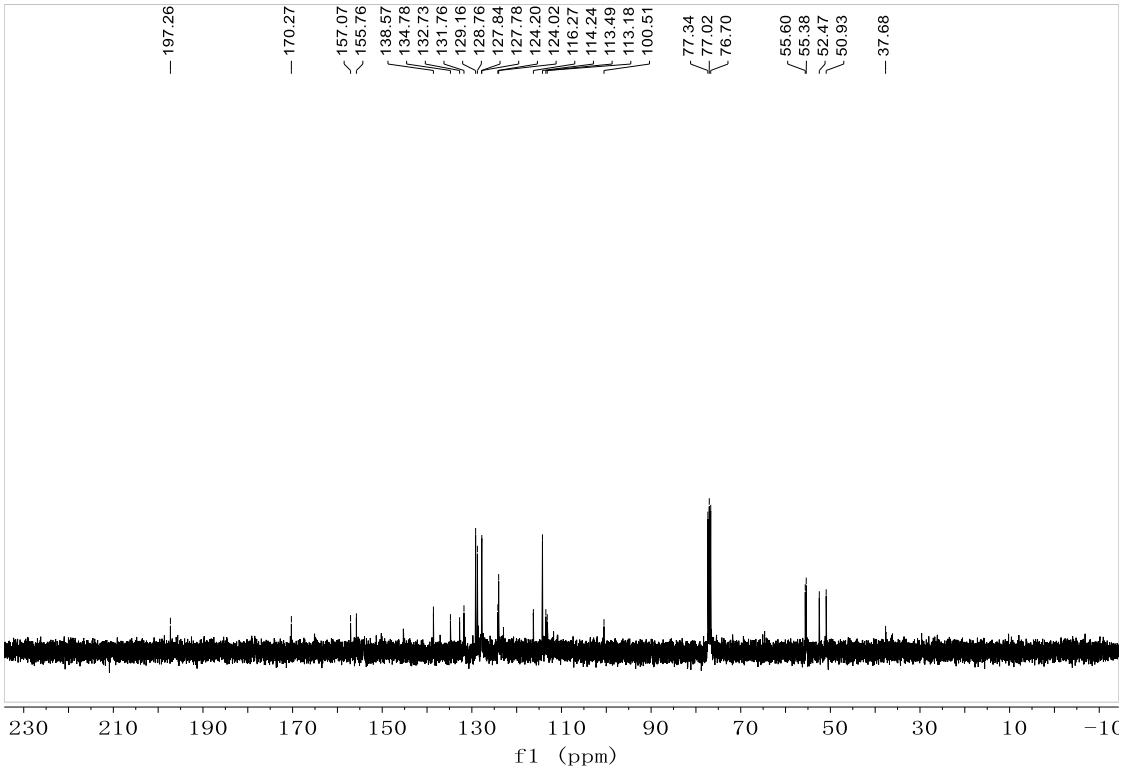


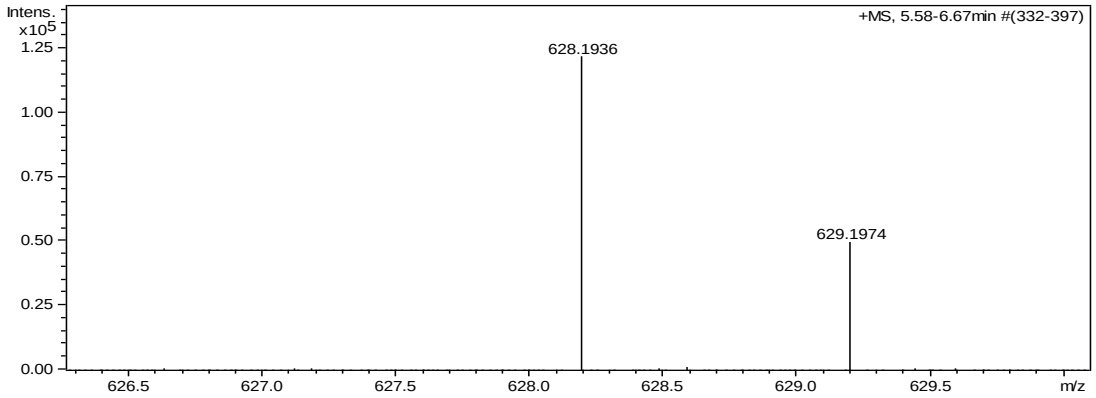

196.25
169.51
164.44
155.49
148.68
146.90
140.20
137.81
137.18
133.48
133.37
132.06
131.30
130.02
129.33
129.12
128.64
128.27
128.00
127.80
124.99
121.58
119.45
117.89
112.57
109.99
95.46
95.39
77.35
77.03
76.71
52.71
51.42
39.81
Ph
O
Ph
Cl
O
CO2CH3
H3CO2C
HN
Cl
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^4
+MS, 4.76-5.88min #(283-350)
636.0950
637.0986
6
4
2
0
634.5
635.0
635.5
636.0
636.5
637.0
637.5
m/z

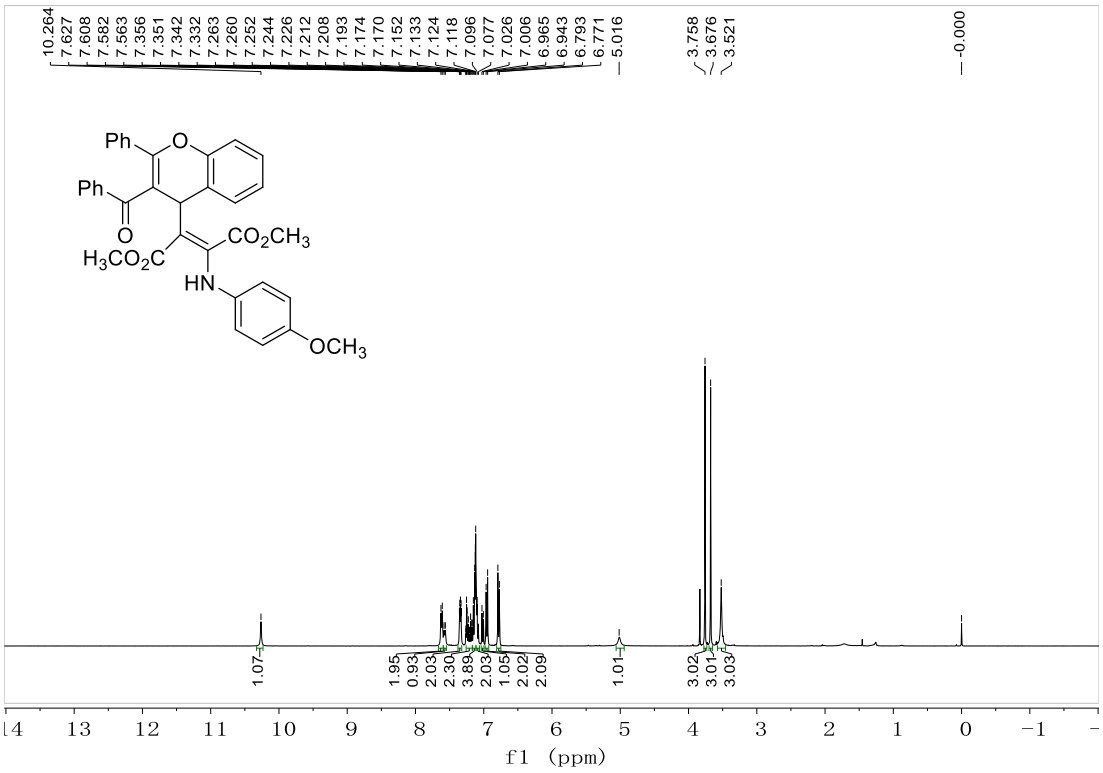
Dimethyl 2-(3-benzoyl-6-methoxy-2-phenyl-4*H*-chromen-4-yl)-3-((4-methoxyphenyl)amino)fumarate (8h): Yellow solid, 53%, mp 203-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.27 (s, 1H, NH), 7.58 (d, *J* = 8.0 Hz, 2H, ArH), 7.33-7.31 (m, 2H, ArH), 7.23-7.21 (m, 1H, ArH), 7.17 (s, 1H, ArH), 7.14-7.10 (m, 5H, ArH), 6,96 (dd, J_1 = 9.2 Hz, J_2= 2.0 Hz, 3H, ArH), 6.80-6.34 (m, 3H, ArH), 4.99 (s, 1H, CH), 3.84 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.3, 170.3, 157.1, 155.8, 138.6, 134.8, 132.7, 131.8, 129.2, 128.8, 127.84, 127.78, 124.2, 124.0, 116.3, 114.2, 113.5, 113.2, 100.5, 55.6, 55.4, 52.5, 51.0, 37.7 ppm; IR (KBr) υ: 3932, 3864, 3670, 2978, 2832, 1801, 1759, 1637, 1428, 1324, 1311, 1247, 1232, 1193, 1143, 1103, 1076, 1054, 1022, 938, 850, 783, 765, 703 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{36}H_{31}NNaO_8$ ([M + Na]$^+$): 628.1942, found: 628.1936.

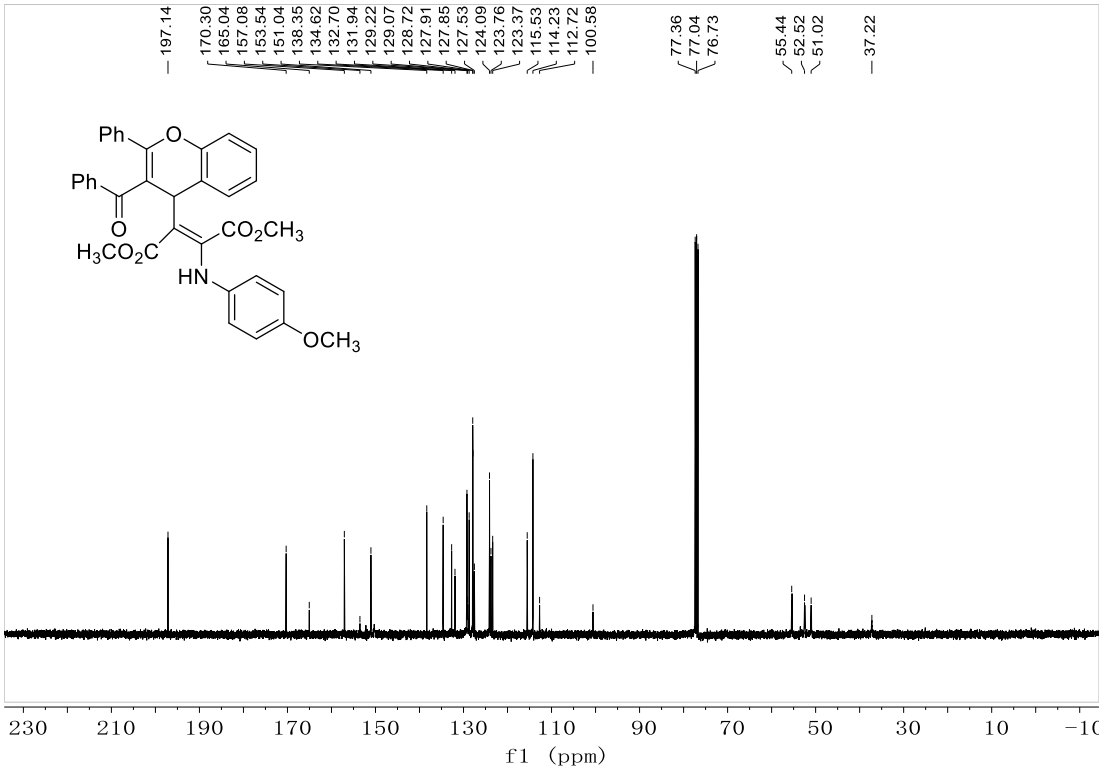


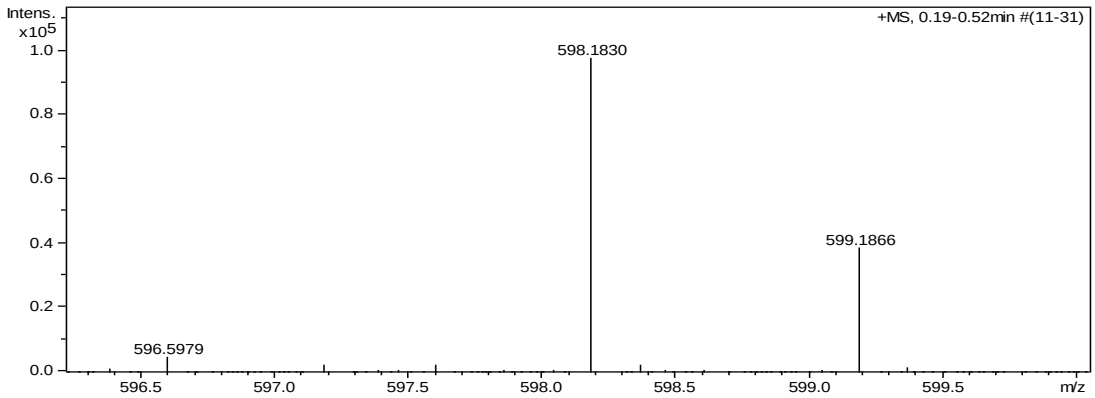

197.26
170.27
157.07
155.76
138.57
134.78
132.73
131.76
129.16
128.76
127.84
127.78
124.20
124.02
116.27
114.24
113.49
113.18
100.51
77.34
77.02
76.70
55.60
55.38
52.47
50.93
37.68
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^5
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 5.58-6.67min #(332-397)
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629.1974
626.5
627.0
627.5
628.0
628.5
629.0
629.5
m/z

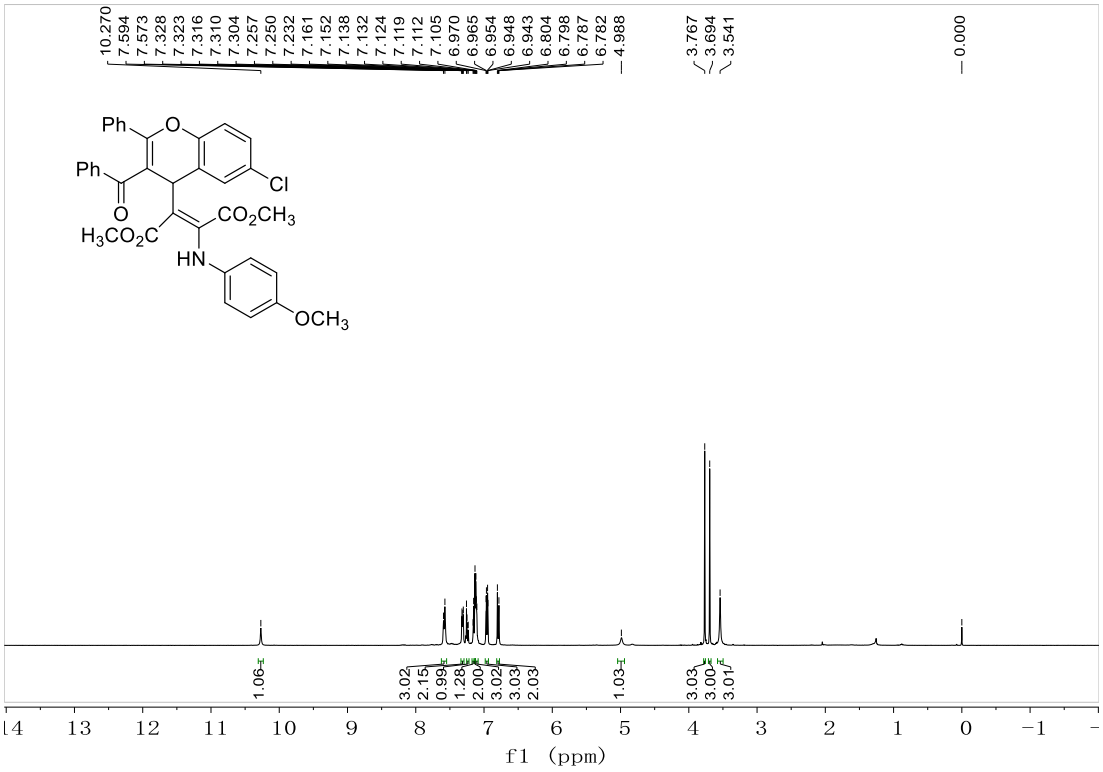
Dimethyl 2-(3-benzoyl-2-phenyl-4*H*-chromen-4-yl)-3-((4-methoxyphenyl)amino)fumarate (8i): Yellow solid, 45%, mp 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.26 (s, 1H, NH), 7.62 (d, *J* = 7.6 Hz, 2H, ArH), 7.57 (d, *J* = 7.6 Hz, 1H, ArH), 7.37-7.33 (m, 2H, ArH), 7.25-7.17 (m, 2H, ArH), 7.15-7.12 (m, 4H, ArH), 7.11-7.08 (m, 4H, ArH), 7.02 (d, *J* = 8.0 Hz, 2H, ArH), 6,95 (d, *J* = 8.8 Hz, 2H, ArH), 6,78 (d, *J* = 8.8 Hz, 2H, ArH), 5.02 (s, 1H, CH), 3.76 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.1, 170.3, 165.0, 157.1, 153.5, 151.0, 138.4, 134.6, 132.7, 131.9, 129.2, 129.1, 128.7, 127.9, 127.9, 127.5, 124.1, 123.8, 123.4, 115.5, 114.3, 112.7, 100.6, 55.4, 52.5, 51.0, 37.2 ppm; IR (KBr) υ: 3903, 3862, 3570, 3088, 2953, 1853, 1744, 1687, 1633, 1607, 1593, 1557, 1430, 1328, 1304, 1288, 1254, 1203, 1174, 1155, 1062, 1031, 1024, 953, 842, 806, 753, 723 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{29}NNaO_7$ ($[M + Na]^+$): 598.1836, found: 598.1830.

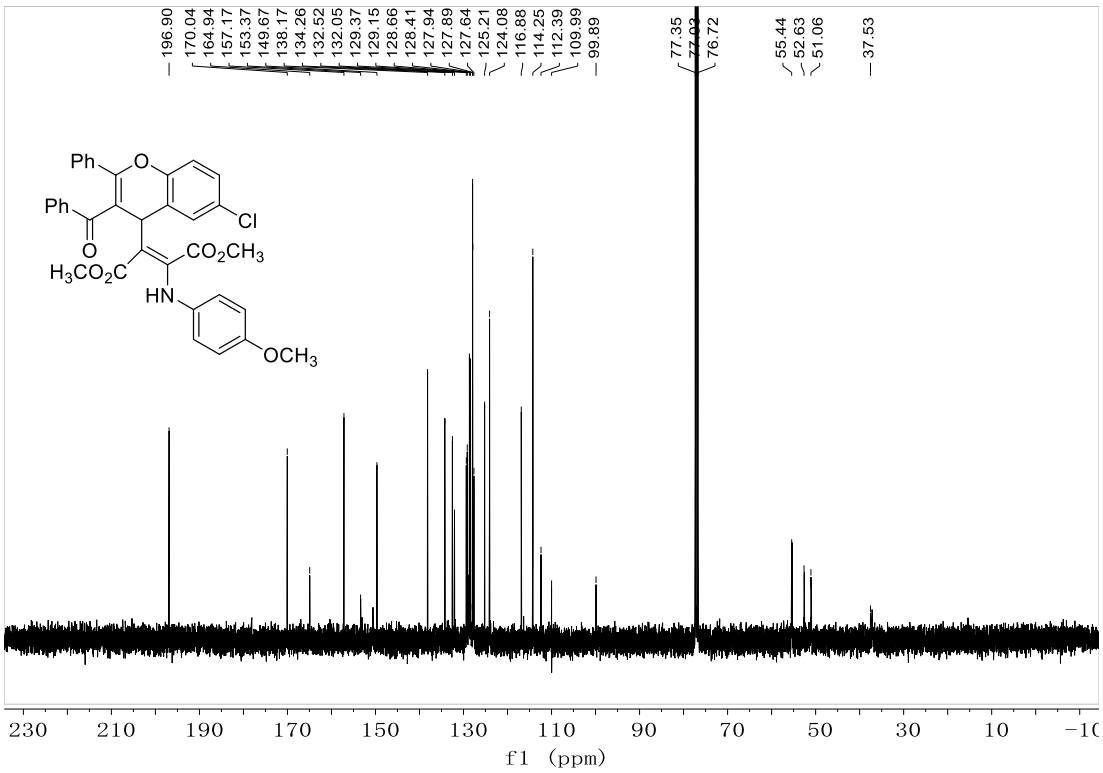


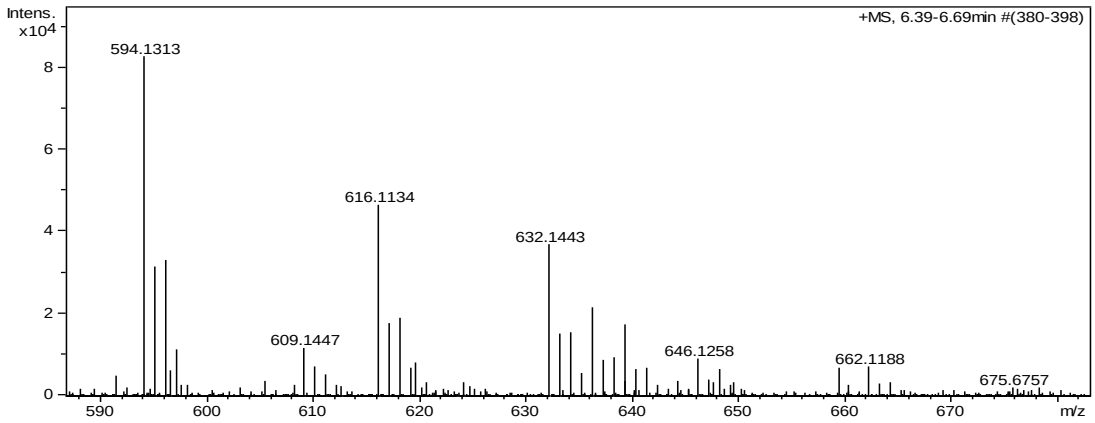

197.14
170.30
165.04
157.08
153.54
151.04
138.35
134.62
132.70
131.94
129.22
129.07
128.72
127.91
127.85
127.53
124.09
123.76
123.37
115.53
114.23
112.72
100.58
77.36
77.04
76.73
55.44
52.52
51.02
37.22
Ph
O
Ph
O
CO_2CH_3
H_3CO_2C
HN
OCH_3
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^5
+MS, 0.19-0.52min #(11-31)
598.1830
599.1866
596.5979
1.0
0.8
0.6
0.4
0.2
0.0
596.5
597.0
597.5
598.0
598.5
599.0
599.5
m/z

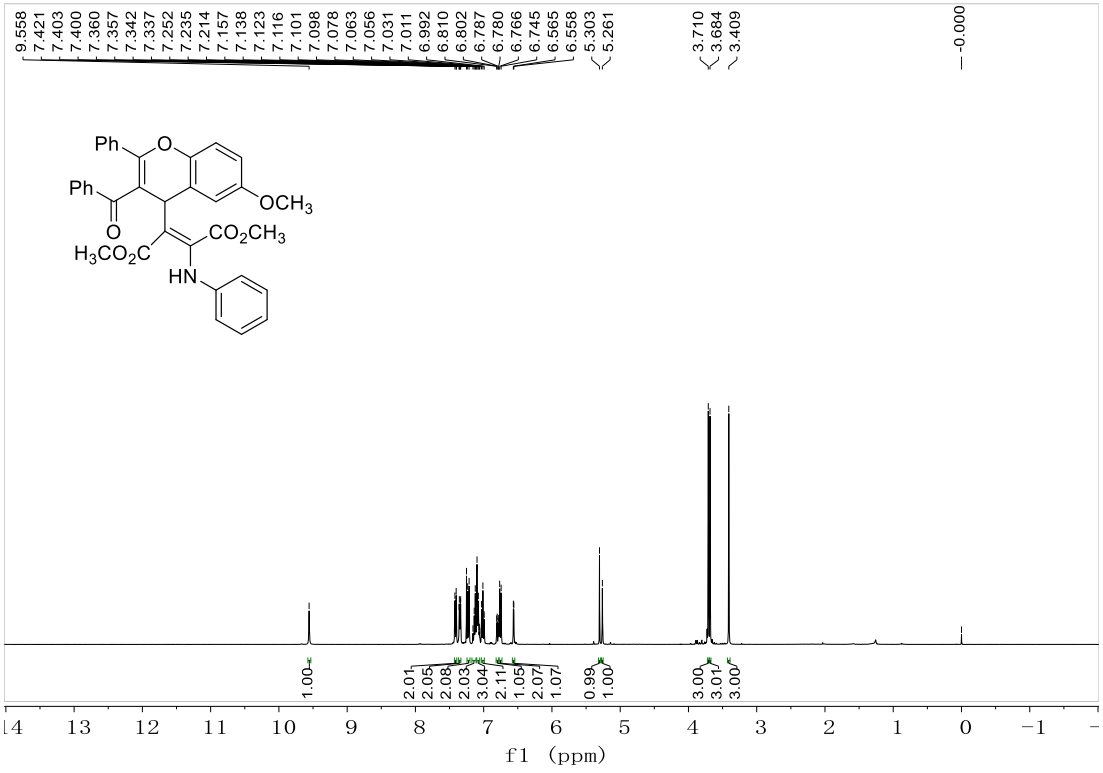
Dimethyl 2-(3-benzoyl-6-chloro-2-phenyl-4*H*-chromen-4-yl)-3-((4-methoxyphenyl)amino)fumarate (8j): Yellow solid, 40%, mp 210-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.26 (s, 1H, NH), 7.58 (d, *J* = 8.4 Hz, 3H, ArH), 7.33-7.30 (m, 2H, ArH), 7.24 (d, *J* = 7.2 Hz, 1H, ArH), 7.16 (d, *J* = 7.6 Hz, 1H, ArH), 7.14-7.13 (m, 2H, ArH), 7.12-7.11 (m, 3H, ArH), 6.97-6.94 (m, 3H, ArH), 6.79 (d, *J* = 7.2 Hz, 2H, ArH), 4.99 (s, 1H, CH), 3.77 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.9, 170.0, 164.9, 157.2, 153.4, 149.7, 138.2, 134.3, 132.5, 132.1, 129.4, 129.2, 128.7, 128.4, 127.9, 127.9, 127.6, 125.2, 124.1, 116.9, 114.3, 112.4, 110.0, 99.9, 55.4, 52.6, 51.1, 37.5 ppm; IR (KBr) υ: 3940, 3834, 3699, 2980, 2835, 1730, 1703, 1688, 1621, 1601, 1580, 1533, 1423, 1329, 1305, 1288, 1201, 1181, 1103, 1185, 1077, 1028, 1008, 982, 878, 792, 765, 723 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{28}ClNNaO_7$ ([M + Na]$^{+}$): 632.1447, found: 632.1443.

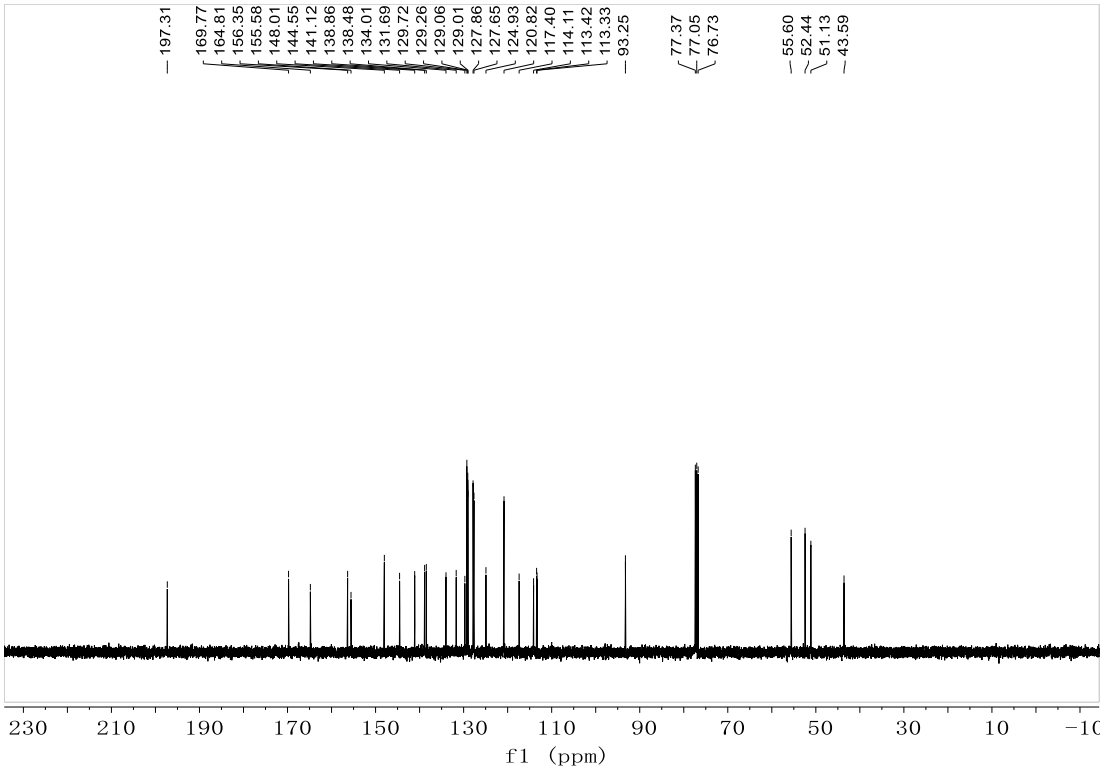


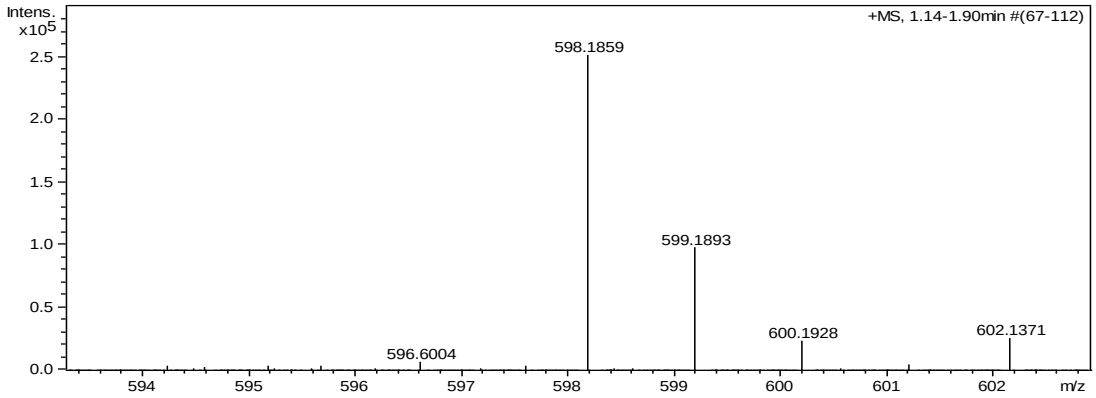

196.90
170.04
164.94
157.17
153.37
149.67
138.17
134.26
132.52
132.05
129.37
129.15
128.66
128.41
127.94
127.89
127.64
125.21
124.08
116.88
114.25
112.39
109.99
99.89
77.35
77.03
76.72
55.44
52.63
51.06
37.53
Ph
O
Ph
Cl
O
CO2CH3
H3CO2C
HN
OCH3
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^4
+MS, 6.39-6.69min #(380-398)
594.1313
616.1134
632.1443
609.1447
646.1258
662.1188
675.6757
0
2
4
6
8
590
600
610
620
630
640
650
660
670
m/z

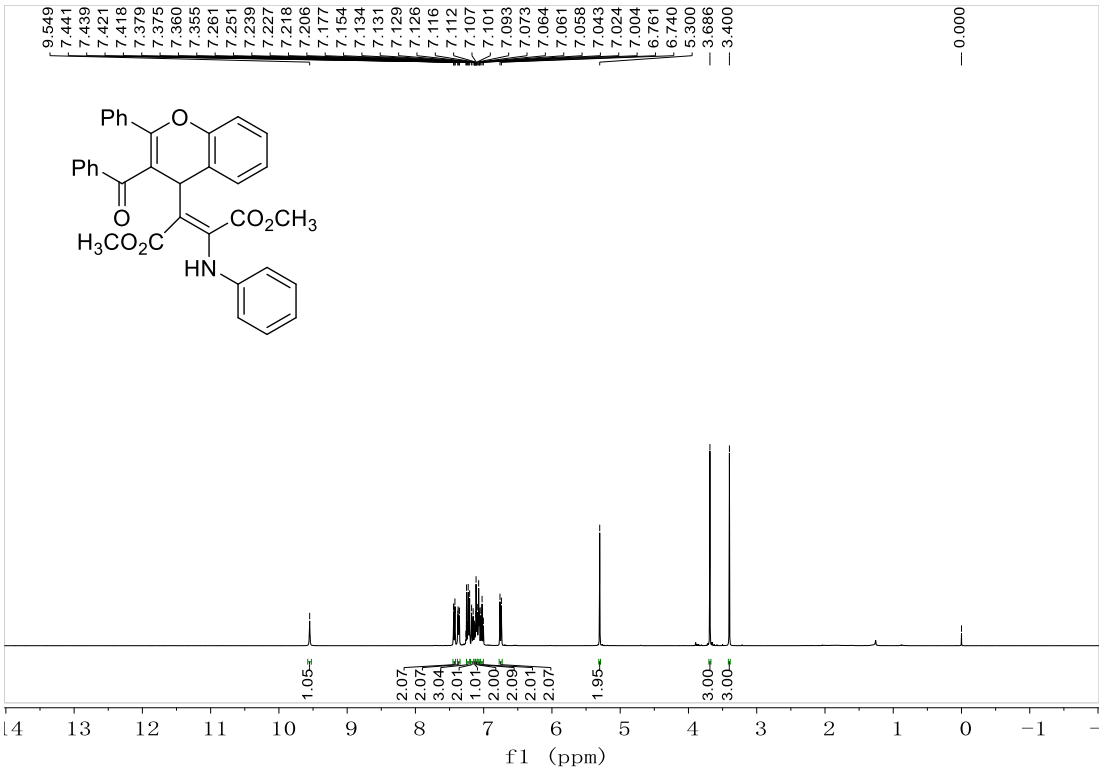
Dimethyl 2-(3-benzoyl-6-methoxy-2-phenyl-4*H*-chromen-4-yl)-3-(phenylamino)fumarate (8k): Yellow solid, 64%, mp 175-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.56 (s, 1H, NH), 7.42-7.40 (m, 2H, ArH), 7.35 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 2H, ArH), 7.22 (d, J = 8.4 Hz, 2H, ArH), 7.16-7.12 (m, 2H, ArH), 7.10-7.06 (m, 3H, ArH), 7.01 (t, J = 8.0 Hz, 2H, ArH), 6.79 (dd, J_1 = 9.2 Hz, J_2 = 3.2 Hz, 1H, ArH), 6.76 (d, J = 8.4 Hz, 2H, ArH), 6.56 (d, J = 2.8 Hz, 1H, ArH), 5.30 (s, 1H, ArH), 5.26 (s, 1H, CH), 3.71 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.3, 169.8, 164.8, 156.4, 155.6, 148.0, 144.6, 141.1, 138.9, 138.5, 134.0, 131.7, 129.7, 129.3, 129.1, 129.0, 127.9, 127.7, 124.9, 120.8, 117.4, 114.1, 113.4, 113.3, 93.3, 55.6, 52.4, 51.1, 43.6 ppm; IR (KBr) υ: 3380, 2924, 2807, 1685, 1561, 1472, 1330, 1304, 1287, 1211, 1173, 1115, 1084, 1035, 1009, 954, 806, 772, 682, 633 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{29}NNaO_7$ ([M + Na]$^+$): 598.1836, found: 598.1859.

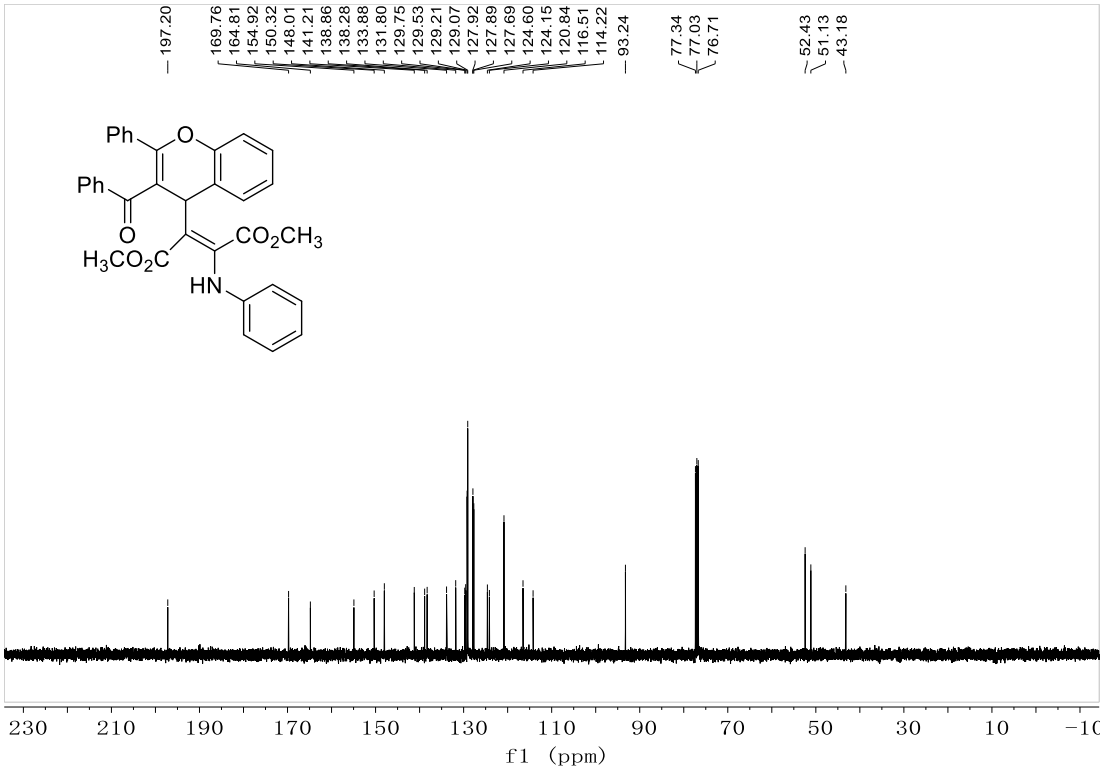


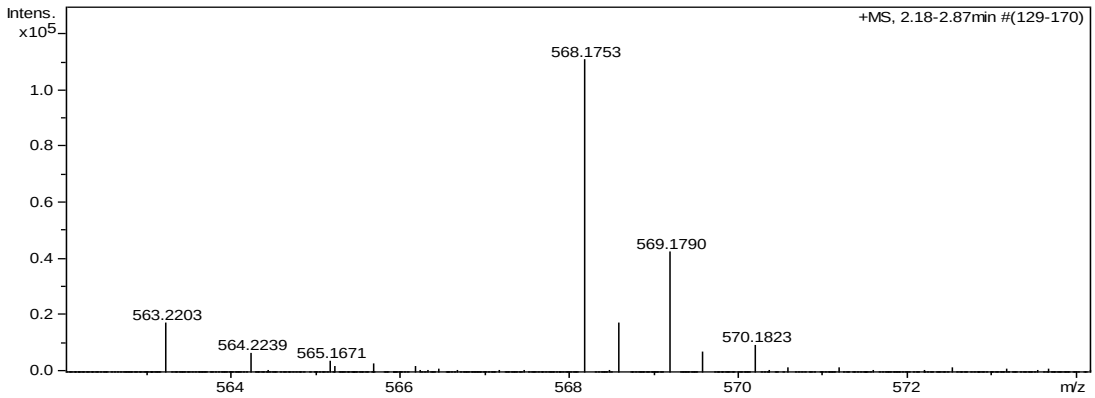

197.31
169.77
164.81
156.35
155.58
148.01
144.55
141.12
138.86
138.48
134.01
131.69
129.72
129.26
129.06
129.01
127.86
127.65
124.93
120.82
117.40
114.11
113.42
113.33
93.25
77.37
77.05
76.73
55.60
52.44
51.13
43.59
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^5
+MS, 1.14-1.90min #(67-112)
598.1859
599.1893
600.1928
602.1371
596.6004
2.5
2.0
1.5
1.0
0.5
0.0
594
595
596
597
598
599
600
601
602
m/z

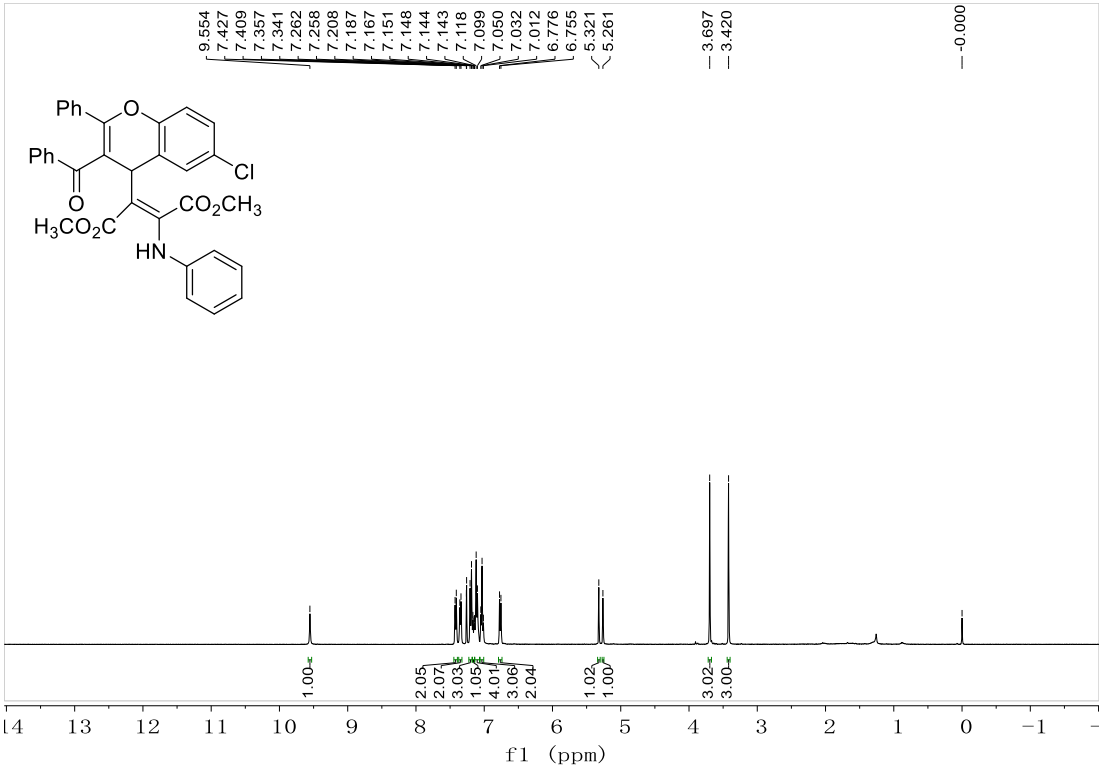
Dimethyl 2-(3-benzoyl-2-phenyl-4*H*-chromen-4-yl)-3-(phenylamino)fumarate (8l): Yellow solid, 60%, mp 179-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.55 (s, 1H, NH), 7.44-7.42 (m, 2H, ArH), 7.37 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H, ArH), 7.25-7.21 (m, 3H, ArH), 7.17 (d, J = 9.2 Hz, 2H, ArH), 7.13-7.12 (m, 1H, ArH), 7.11-7.09 (m, 2H, ArH), 7.07-7.06 (m, 2H, ArH), 6.02 (t, J = 7.2 Hz, 2H, ArH), 6.75 (d, J = 8.4 Hz, 2H, ArH), 5.30 (s, 2H, ArH, CH), 3.69 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.2, 169.8, 164.8, 154.9, 150.3, 148.0, 141.2, 138.9, 138.3, 133.9, 131.8, 129.8, 129.5, 129.2, 129.1, 127.9, 127.9, 127.7, 124.6, 124.2, 120.8, 116.5, 114.2, 93.2, 52.4, 51.1, 43.1 ppm; IR (KBr) υ: 3402, 2931, 2871, 1821, 1683, 1623, 1530, 1422, 1342, 1276, 1215, 1197, 1109, 1073, 1011, 952, 830, 789, 664, 609cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{34}H_{27}NNaO_6$ ([M + Na]$^+$): 568.1731, found: 568.1753.

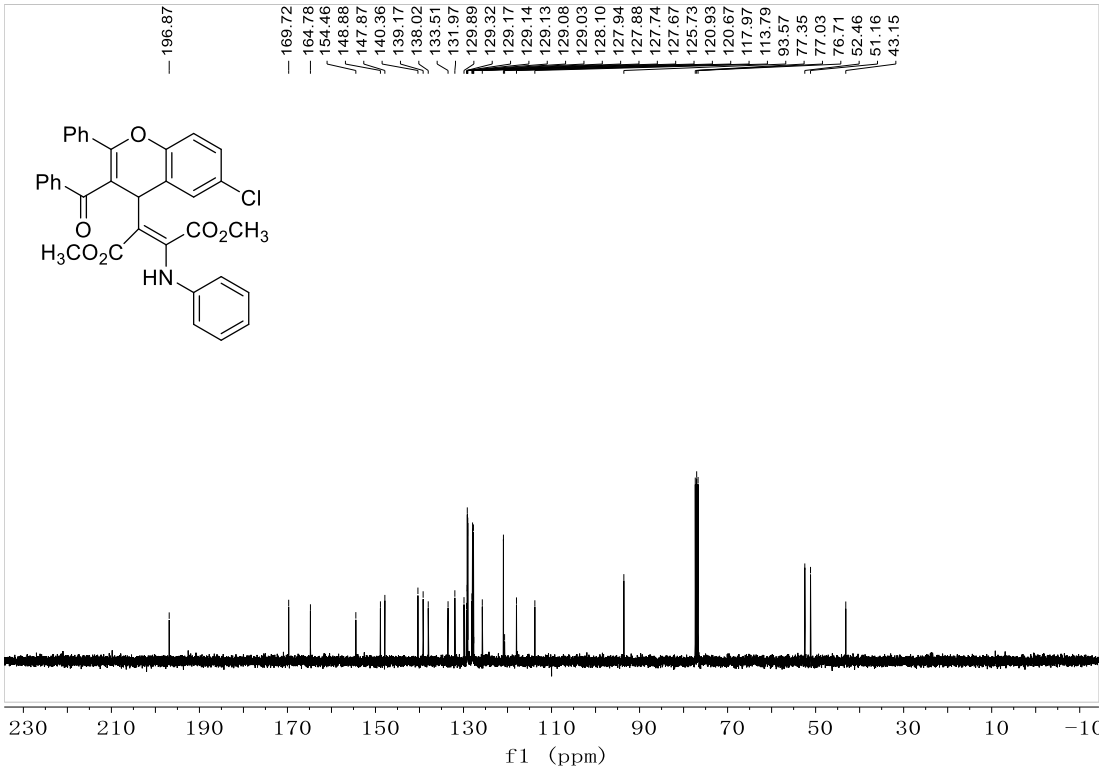


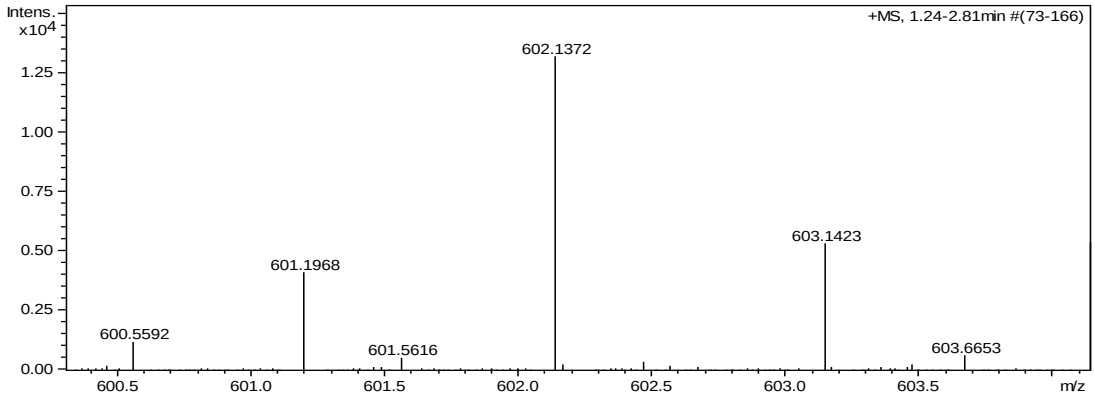

197.20
169.76
164.81
154.92
150.32
148.01
141.21
138.86
138.28
133.88
131.80
129.75
129.53
129.21
129.07
127.92
127.89
127.69
124.60
124.15
120.84
116.51
114.22
93.24
77.34
77.03
76.71
52.43
51.13
43.18
Ph
O
Ph
O
H3CO2C
CO2CH3
HN
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^5
+MS, 2.18-2.87min #(129-170)
568.1753
569.1790
563.2203
564.2239
565.1671
570.1823
1.0
0.8
0.6
0.4
0.2
0.0
564
566
568
570
572
m/z

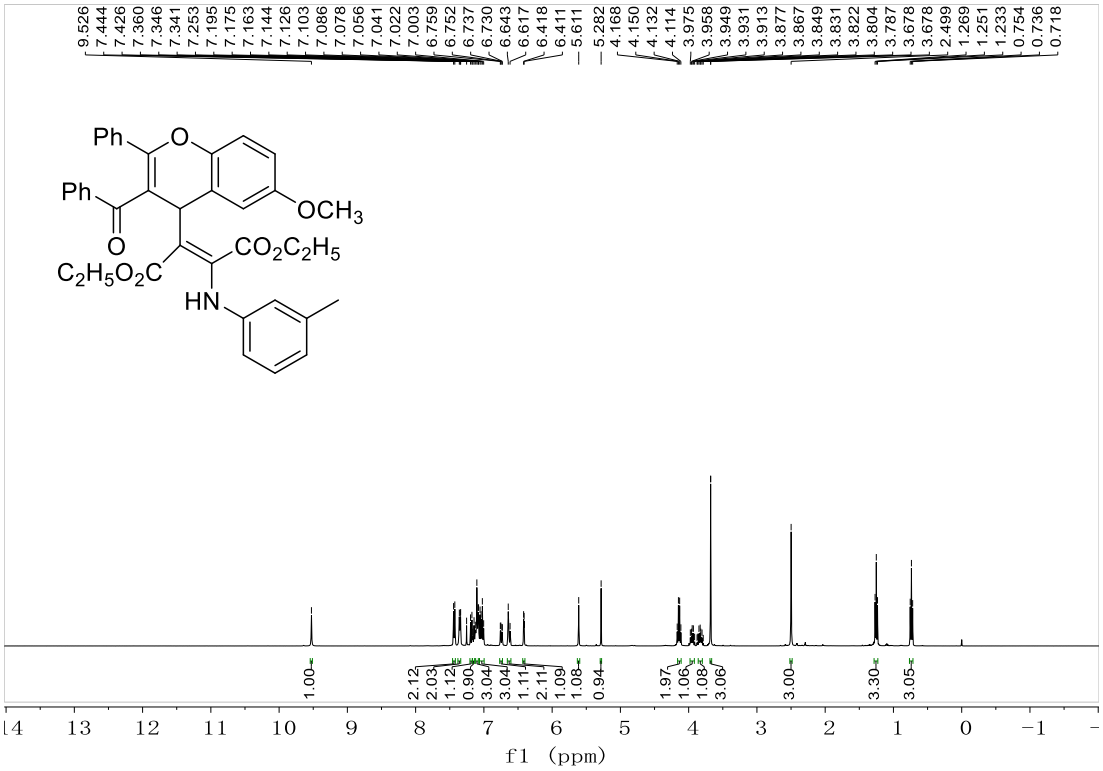
Dimethyl 2-(3-benzoyl-6-chloro-2-phenyl-4*H*-chromen-4-yl)-3-(phenylamino)fumarate (8m): Yellow solid, 52%, mp 193-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.55 (s, 1H, NH), 7.42 (d, *J* = 7.2 Hz, 2H, ArH), 7.35 (d, *J* = 6.4 Hz, 2H, ArH), 7.20 (d, *J* = 8.4 Hz, 3H, ArH), 7.17-7.14 (m, 1H, ArH), 7.11 (d, *J* = 7.6 Hz, 4H, ArH), 7.05-7.01 (m, 3H, ArH), 6.77 (d, *J* = 8.4 Hz, 2H, ArH), 5.32 (s, 1H, ArH), 5.26 (s, 1H, CH), 3.70 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.9, 169.7, 164.8, 154.5, 148.9, 147.9, 140.4, 139.2, 138.0, 133.5, 132.0, 130.0, 129.3, 129.2, 129.14, 129.13, 129.08, 129.0, 128.1, 127.94, 127.88, 127.74, 127.67, 125.73, 120.9, 120.7, 118.0, 113.8, 93.6, 52.5, 51.2, 43.2 ppm; IR (KBr) υ: 3382, 2809, 2751, 1809, 1676, 1611, 1530, 1460, 1357, 1331, 1216, 1190, 1092, 936, 862, 805, 748, 726cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{34}H_{26}ClNnaO_6$ ([M + Na]$^{+}$): 602.1341, found: 602.1372.

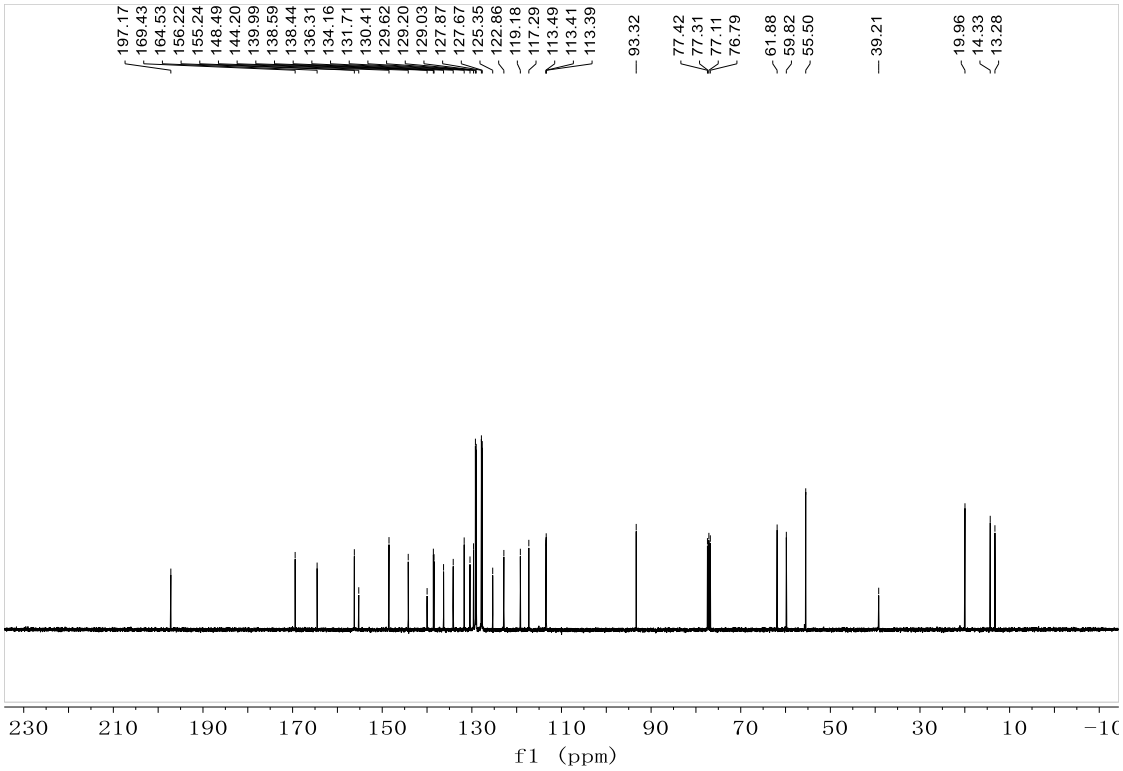


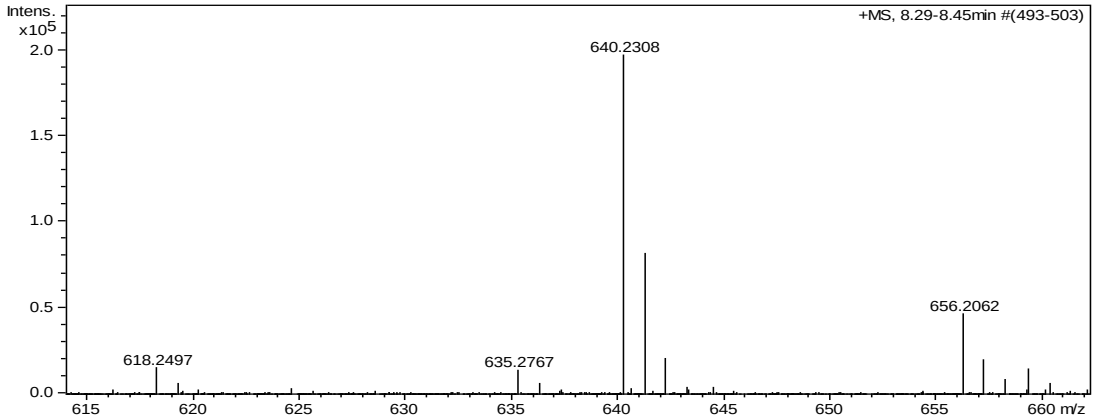

196.87
169.72
164.78
154.46
148.88
147.87
140.36
139.17
138.02
133.51
131.97
129.89
129.32
129.17
129.14
129.13
129.08
129.03
128.10
127.94
127.88
127.74
127.67
125.73
120.93
120.67
117.97
113.79
93.57
77.35
77.03
76.71
52.46
51.16
43.15
Ph
O
Ph
Cl
O
CO2CH3
H3CO2C
HN
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^4
+MS, 1.24-2.81min #(73-166)
602.1372
603.1423
601.1968
600.5592
601.5616
603.6653
1.25
1.00
0.75
0.50
0.25
0.00
600.5
601.0
601.5
602.0
602.5
603.0
603.5
m/z

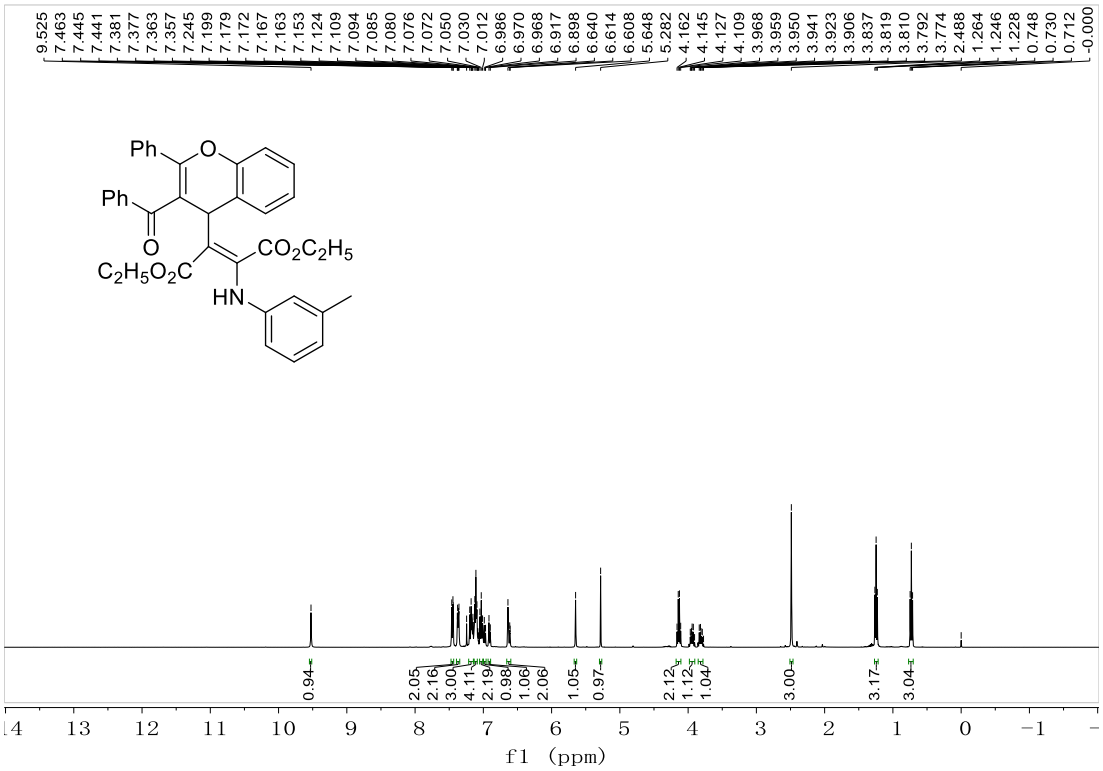
Diethyl 2-(3-benzoyl-6-methoxy-2-phenyl-4*H*-chromen-4-yl)-3-(*m*-tolylamino)fumarate (8n): Yellow solid, 49%, mp 198-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.53 (s, 1H, NH), 7.44 (d, *J* = 7.2 Hz, 2H, ArH), 7.36-7.34 (m, 2H, ArH), 7.19 (d, *J* = 8.0 Hz, 1H, ArH), 7.16-7.13 (m, 1H, ArH), 7.12-7.08 (m, 3H, ArH), 7.06-7.00 (m, 3H, ArH), 6.74 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 6.63 (d, *J* = 10.0 Hz, 2H, ArH), 6.41 (d, *J* = 2.8 Hz, 1H, ArH), 5.61 (s, 1H, ArH), 5.28 (s, 1H, CH), 4.17-4.11 (m, 2H, CH_2), 3.98-3.91 (m, 1H, CH_2), 3.85-3.80 (m, 1H, CH_2), 3.68 (s, 3H, OCH_3), 2.50 (s, 3H, CH_3), 1.25 (t, *J* = 7.2 Hz, 3H, CH_3), 0.74 (t, *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.2, 169.4, 164.5, 156.2, 155.2, 148.5, 144.2, 140.0, 138.6, 138.4, 136.3, 134.2, 131.7, 130.4, 129.6, 129.2, 129.0, 127.9, 127.7, 125.4, 122.9, 119.2, 117.3, 113.5, 113.4, 113.4, 93.3, 77.3, 61.9, 59.8, 55.5, 39.2, 20.0, 14.3, 13.3 ppm; IR (KBr) υ: 3902, 3788, 3645, 2980, 2867, 1765, 1720, 1660, 1602, 1593, 1567, 1459, 1377, 1346, 1234, 1209, 1180, 1122, 1099, 1076, 1022, 1006, 928, 820, 797, 781, 732 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{38}H_{35}NNaO_7$ ([M + Na]$^+$): 640.2306, found: 640.2308.

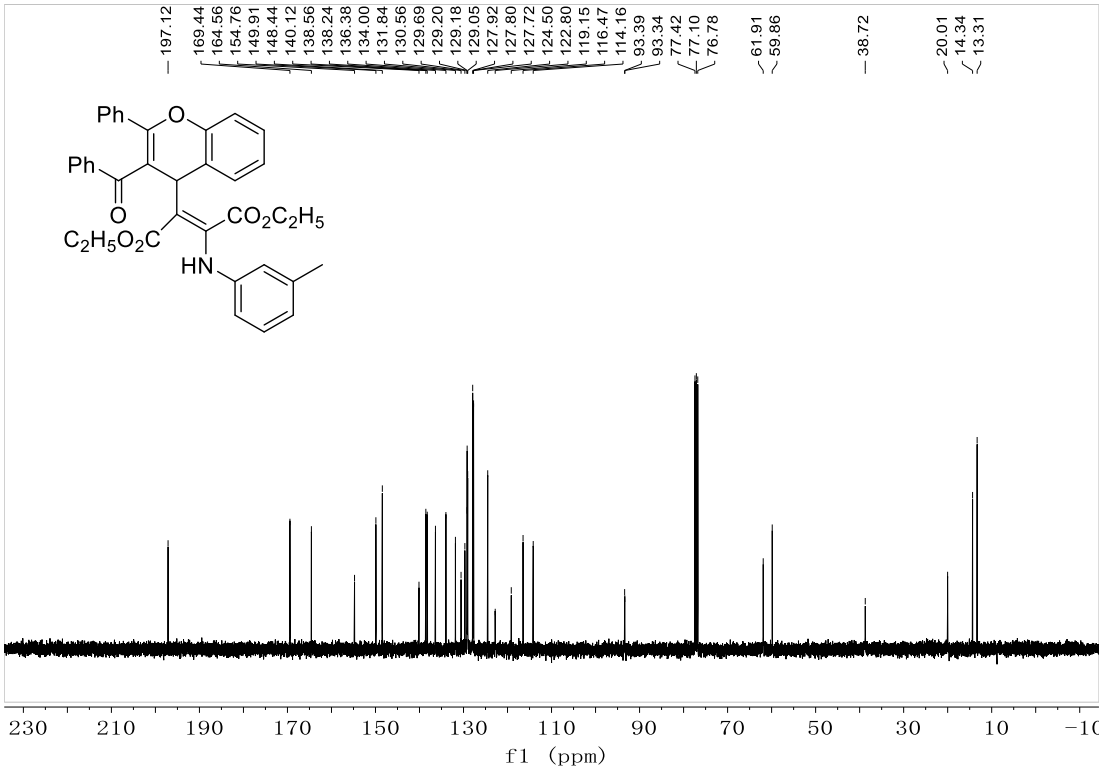


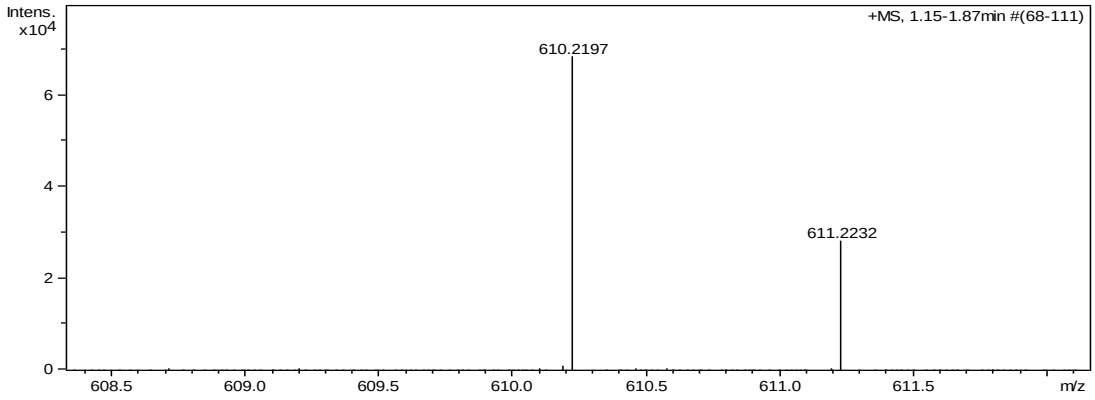

197.17
169.43
164.53
156.22
155.24
148.49
144.20
139.99
138.59
138.44
136.31
134.16
131.71
130.41
129.62
129.20
129.03
127.87
127.67
125.35
122.86
119.18
117.29
113.49
113.41
113.39
93.32
77.42
77.31
77.11
76.79
61.88
59.82
55.50
39.21
19.96
14.33
13.28
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^5
2.0
1.5
1.0
0.5
0.0
+MS, 8.29-8.45min #(493-503)
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656.2062
618.2497
635.2767
615
620
625
630
635
640
645
650
655
660 m/z

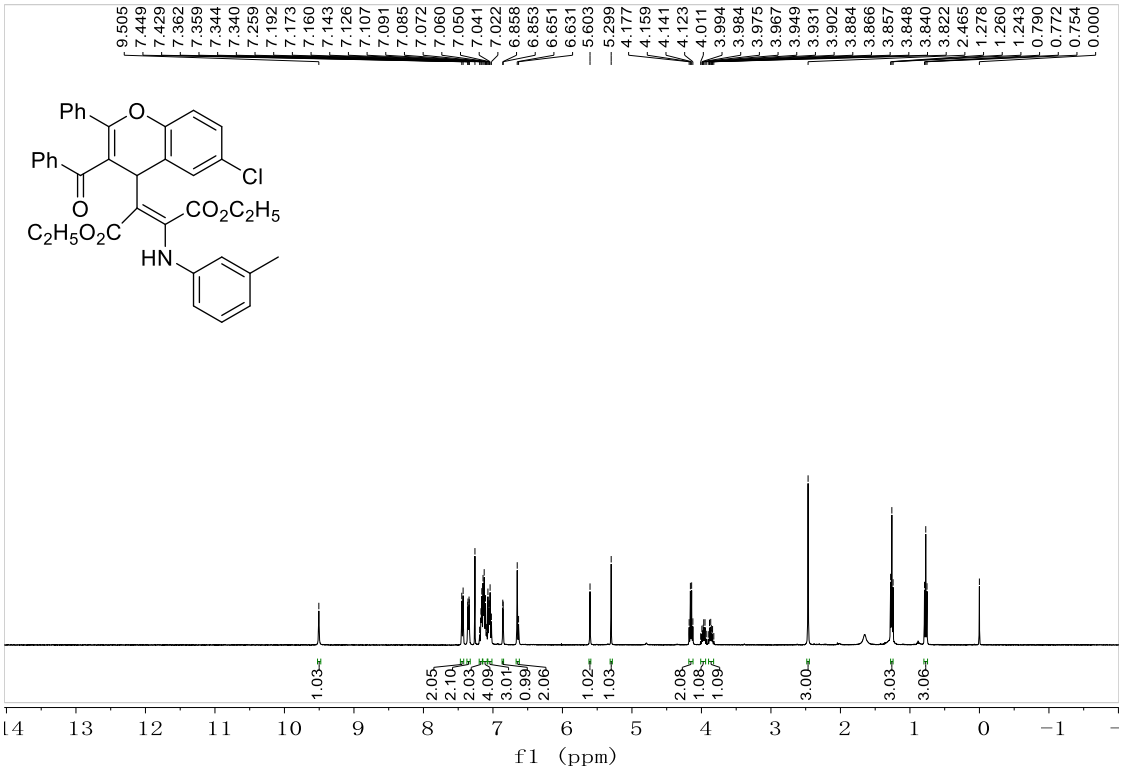
Diethyl 2-(3-benzoyl-2-phenyl-4*H*-chromen-4-yl)-3-(*m*-tolylamino)fumarate (8o): Yellow solid, 45%, mp 193-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.52 (s, 1H, NH), 7.46-7.44 (m, 2H, ArH), 7.37 (dd, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 2H, ArH), 7.20-7.15 (m, 3H, ArH), 7.12-7.07 (m, 4H, ArH), 7.05-7.01 (m, 2H, ArH), 6.99-6.97 (m, 1H, ArH), 6.91 (d, J = 7.6 Hz, 1H, ArH), 6.64-6.61 (m, 1H, ArH), 5.65 (s, 1H, ArH), 5.28 (s, 1H, CH), 4.17-4.11 (m, 2H, CH_2), 3.97-3.92 (m, 1H, CH_2), 3.83-3.77 (m, 1H, CH_2), 2.49 (s, 3H, CH_3), 1.25 (t, J = 7.2 Hz, 3H, CH_3), 0.74 (t, J = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ : 197.1, 169.4, 164.6, 154.8, 149.9, 148.4, 140.1, 138.6, 138.2, 136.4, 134.0, 131.8, 130.6, 129.7, 129.20, 129.18, 129.0, 127.9, 127.8, 127.7, 124.5, 122.8, 119.15, 116.5, 114.2, 93.4, 93.3, 61.9, 59.9, 38.7, 20.0, 14.3, 13.3 ppm; IR (KBr) υ: 3887, 3702, 3643, 2987, 2840, 1769, 1748, 1698, 1655, 1624, 1594, 1553, 1421, 1357, 1298, 1287, 1234, 1167, 1143, 1125, 1088, 1054, 1020, 927, 878, 792, 765, 732 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{37}H_{33}NNaO_6$ ([M + Na]$^{+}$): 610.2200, found: 610.2197.

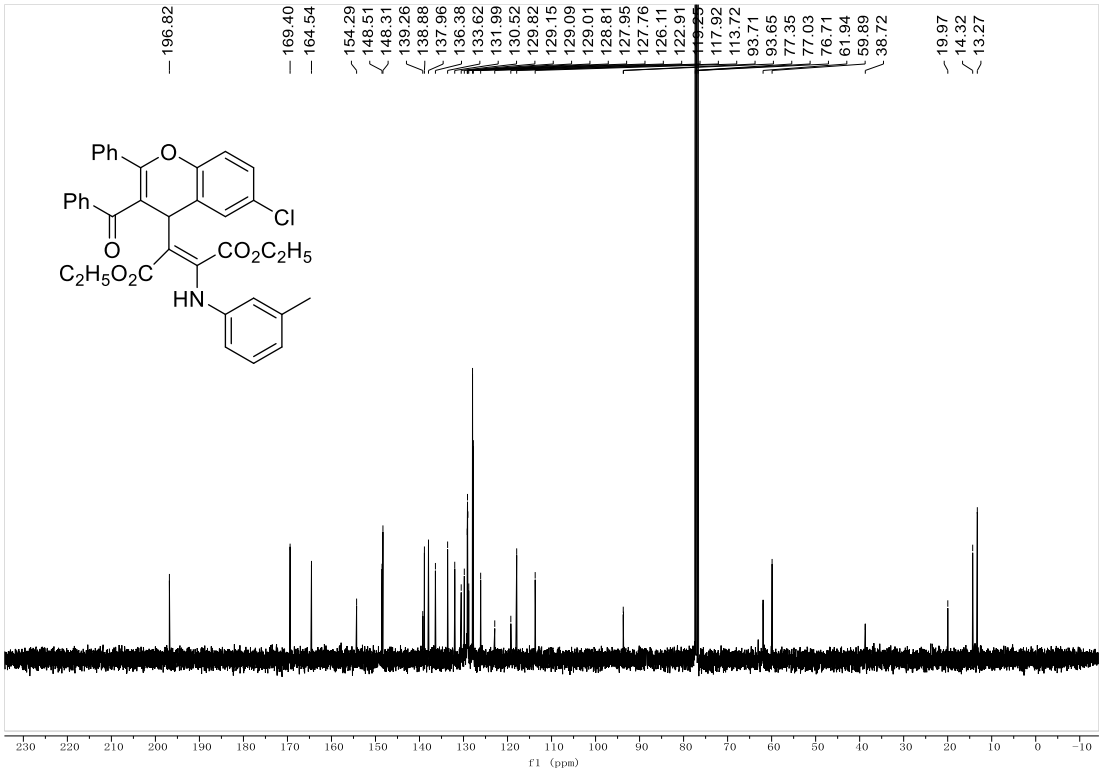


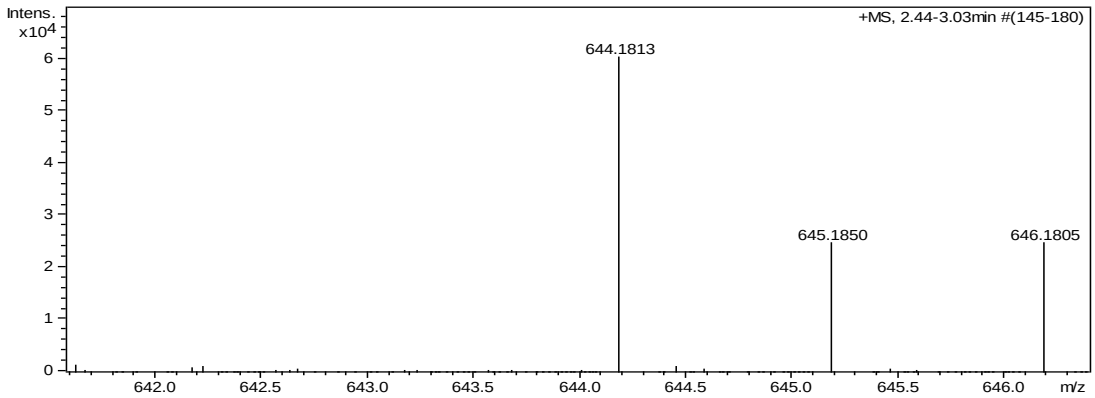

197.12
169.44
164.56
154.76
149.91
148.44
140.12
138.56
138.24
136.38
134.00
131.84
130.56
129.69
129.20
129.18
129.05
127.92
127.80
127.72
124.50
122.80
119.15
116.47
114.16
93.39
93.34
77.42
77.10
76.78
61.91
59.86
38.72
20.01
14.34
13.31
Ph
O
Ph
O
$CO_2C_2H_5$
$C_2H_5O_2C$
HN
230
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


Intens.
x10^4
+MS, 1.15-1.87min #(68-111)
610.2197
611.2232
6
4
2
0
608.5
609.0
609.5
610.0
610.5
611.0
611.5
m/z

Diethyl 2-(3-benzoyl-6-chloro-2-phenyl-4H-chromen-4-yl)-3-(*m*-tolylamino)fumarate (8p): Yellow solid, 40%, mp 203-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.51 (s, 1H, NH), 7.44 (d, J = 8.0 Hz, 2H, ArH), 7.35 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 2H, ArH), 7.19-7.16 (m, 2H, ArH), 7.13-7.09 (m, 4H, ArH), 7.07-7.02 (m, 3H, ArH), 6.86 (d, J = 2.0 Hz, 1H, ArH), 6.64 (d, J = 8.0 Hz, 2H, ArH), 5.60 (s, 1H, ArH), 5.30 (s, 1H, CH), 4.18-4.12 (m, 2H, CH_2), 4.01-3.93 (m, 1H, CH_2), 3.90-3.82 (m, 1H, CH_2), 2.47 (s, 3H, CH_3), 1.27 (t, J = 7.2 Hz, 3H, CH_3), 0.77 (t, J = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ : 196.8, 169.4, 164.5, 154.3, 148.5, 148.3, 139.3, 138.9, 138.0, 136.4, 133.6, 132.0, 130.5, 129.8, 129.2, 129.1, 129.0, 128.8, 128.0, 127.8, 126.1, 122.9, 119.3, 117.9, 113.7, 93.7, 93.7, 61.9, 59.9, 38.7, 20.0, 14.3, 13.3 ppm; IR (KBr) υ: 3913, 3723, 3528, 2976, 2822, 1803, 1741, 1680, 1622, 1601, 1569, 1498, 1453, 1328, 1302, 1233, 1205, 1176, 1169, 1143, 1081, 1024, 1009, 933, 876, 781, 756, 724 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{37}H_{32}ClNNaO_6$ ([M + Na]$^{+}$): 644.1810, found: 644.1813.




196.82
169.40
164.54
154.29
148.51
148.31
139.26
138.88
137.96
136.38
133.62
131.99
130.52
129.82
129.15
129.09
129.01
128.81
127.95
127.76
126.11
122.91
117.92
113.72
93.71
93.65
77.35
77.03
76.71
61.94
59.89
38.72
19.97
14.32
13.27
Ph
O
Ph
Cl
O
CO2C2H5
C2H5O2C
HN
f1 (ppm)


Intens.
x10^4
+MS, 2.44-3.03min #(145-180)
644.1813
645.1850
646.1805
m/z