Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Convenient construction of polycyclic architectures by cascade cycloaddition of azomethine ylides and 2-(o-hydroxyarylidene)-1,3-indanediones

Xueyan Liu, Jing Sun, Chao-Guo Yan

Supporting Information

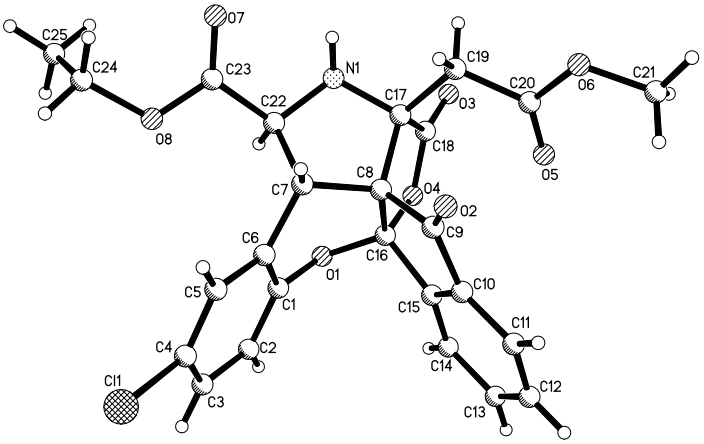


Fig. s1 Single crystal structure of the compound **4c**

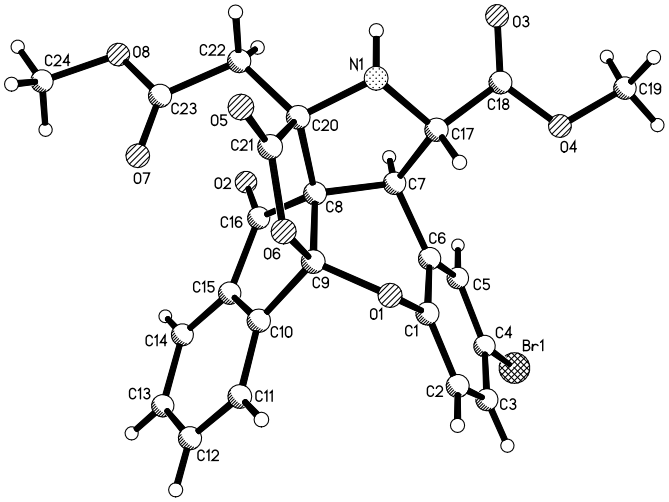


Fig. s2 Single crystal structure of the compound **4d**

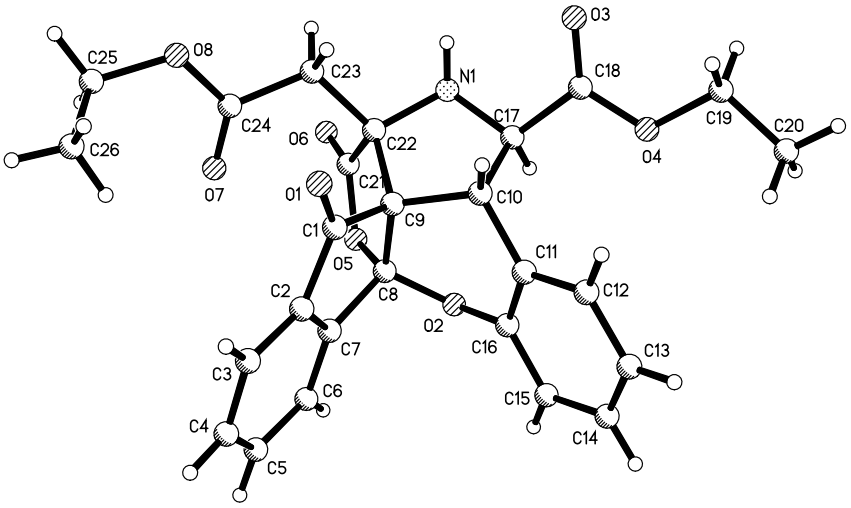


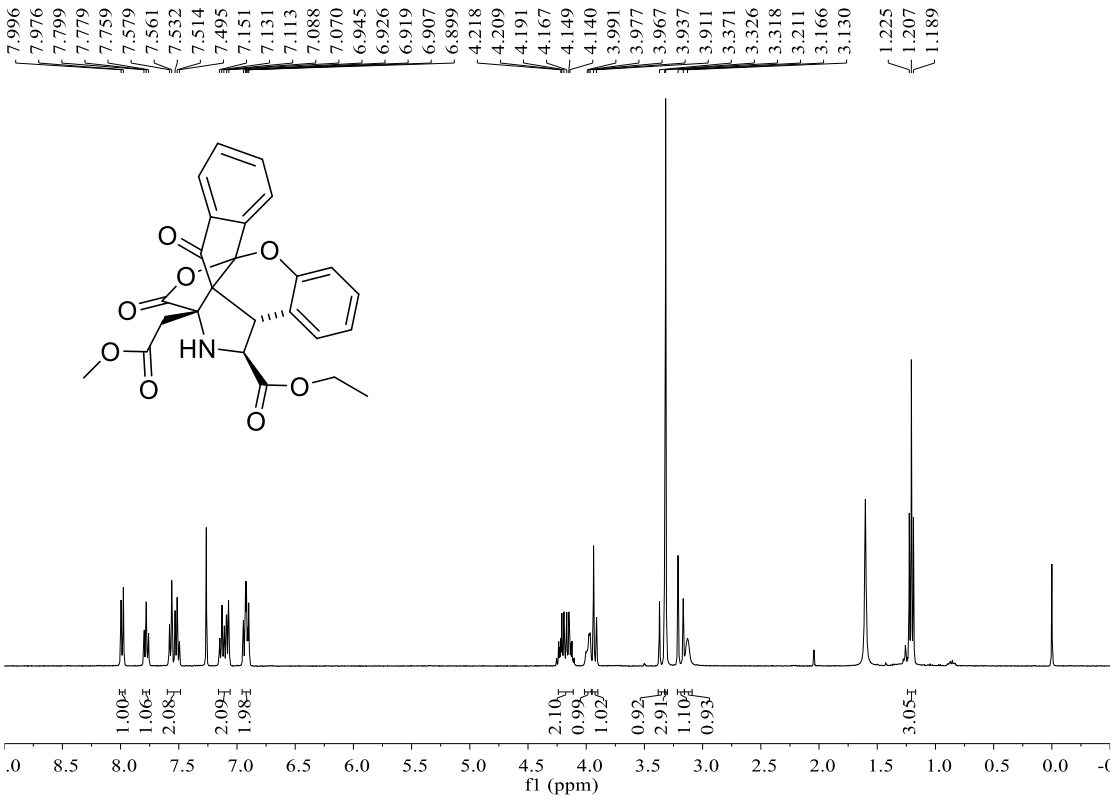
Fig. s3 Single crystal structure of the compound **4g**

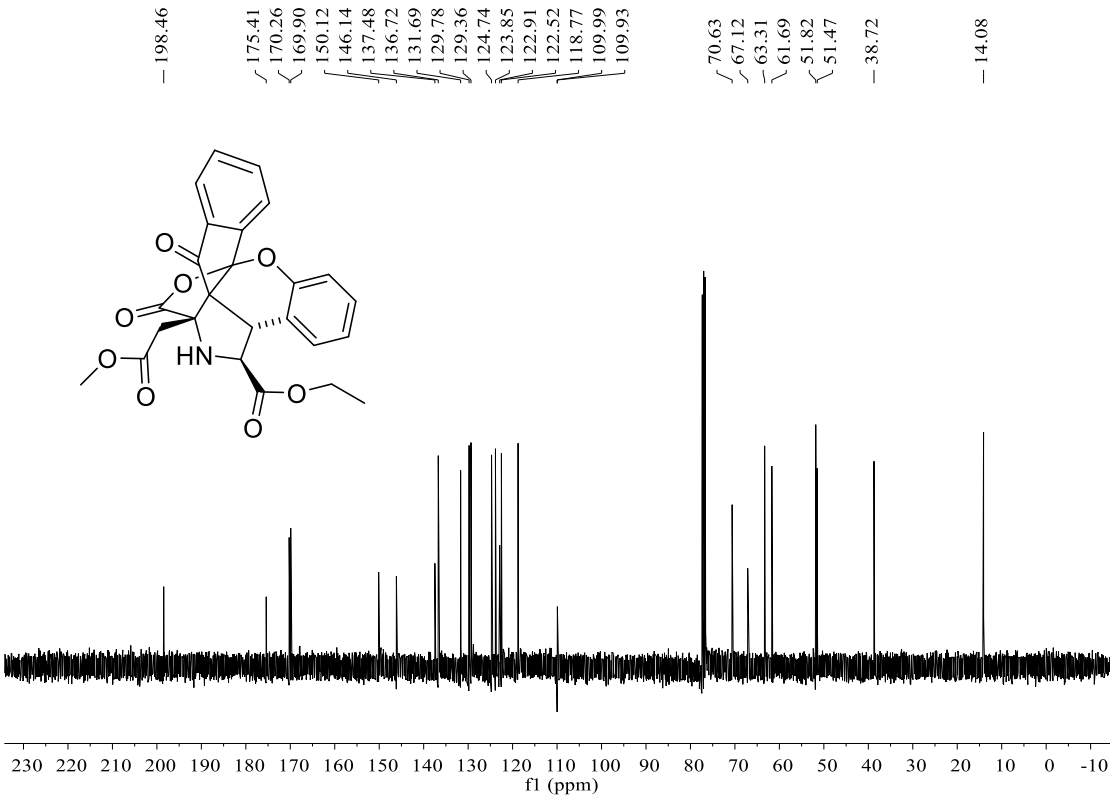
Experimental section

1. General procedure for the three-component reaction of alkyl glycinate hydrochloride, dialkyl but-2-ynedioate and 2-(o-hydroxyarylidene)-1,3-indanedione: To a round flask was added alkyl glycinate hydrochloride (1.0 mmol), dialkyl but-2-ynedioate (1.0 mml), triethylamine (1.0 mmol) and ethanol (15 mL). The mixture was stirred at room temperature for 20 minutes. Then, 2-arylidene-1,3-indanedione (0.5 mmol) was added. The solution was stirred room temperature for two days. After removing the solvent, the residue was subjected to column chromatography with ethyl acetate and petroleum ether (V/V = 3:1) as eluent to give the pure product.

2. General procedure for the four-component reaction of amino acid, dialkyl but-2-ynedioate and 2-arylidene-1,3-indanedione: To a round flask was added amino acid (1.0 mmol), dialkyl but-2-ynedioate (1.0 mml), salicylaldehyde (0.5 mmol), 1,3-indanedione (0.5 mmol), triethylamine (0.2 mmol) and ethanol (15 mL). The mixture was refluxed for twelve hours. After removing the solvent, the residue was subjected to column chromatography with ethyl acetate and petroleum ether (V/V = 3:1) as eluent to give the pure product.

Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-1-(2-methoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4a): white solid, 51%, m.p. 203-204 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.0 Hz, 1H, ArH), 7.80-7.60 (m, 1H, ArH), 7.58-7.50 (m, 2H, ArH), 7.15-7.07 (m, 2H, ArH), 7.95-6.90 (m, 2H, ArH), 4.22-4.14 (m, 2H, CH_2), 4.00-3.97 (m, 1H, CH), 3.92 (d, *J* = 10.4 Hz, 1H, CH), 3.34 (d, *J* = 18.0 Hz, 1H, CH), 3.32 (s, 3H, OCH_3), 3.18 (d, *J* = 18.0 Hz, 1H, CH), 3.13 (br.s, 1H, NH), 1.21 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.5, 175.4, 170.3, 169.9, 150.1, 146.1, 137.5, 136.7, 131.7, 129.8, 129.4, 124.7, 123.9, 122.9, 122.5, 118.8, 110.0, 70.6, 67.1, 63.3, 61.7, 51.8, 51.5, 38.7, 14.1; IR (KBr) υ: 3673, 1808, 1729, 1700, 1438, 1396, 1280, 1216, 1159, 1062, 1041, 970 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{22}NO_8$ ([M+H]$^{+}$): 464.1340, Found: 464.1355.

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122.52
118.77
109.99
109.93
70.63
67.12
63.31
61.69
51.82
51.47
38.72
14.08
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O
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O
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O
O
O
O
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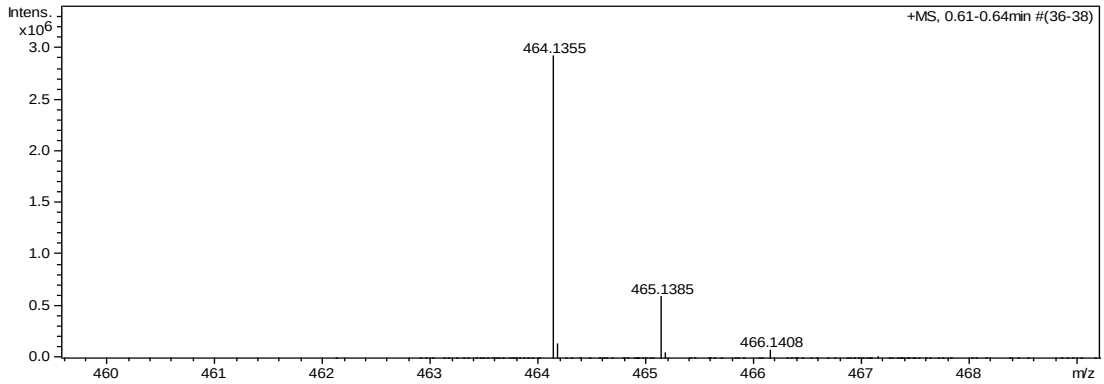
f1 (ppm)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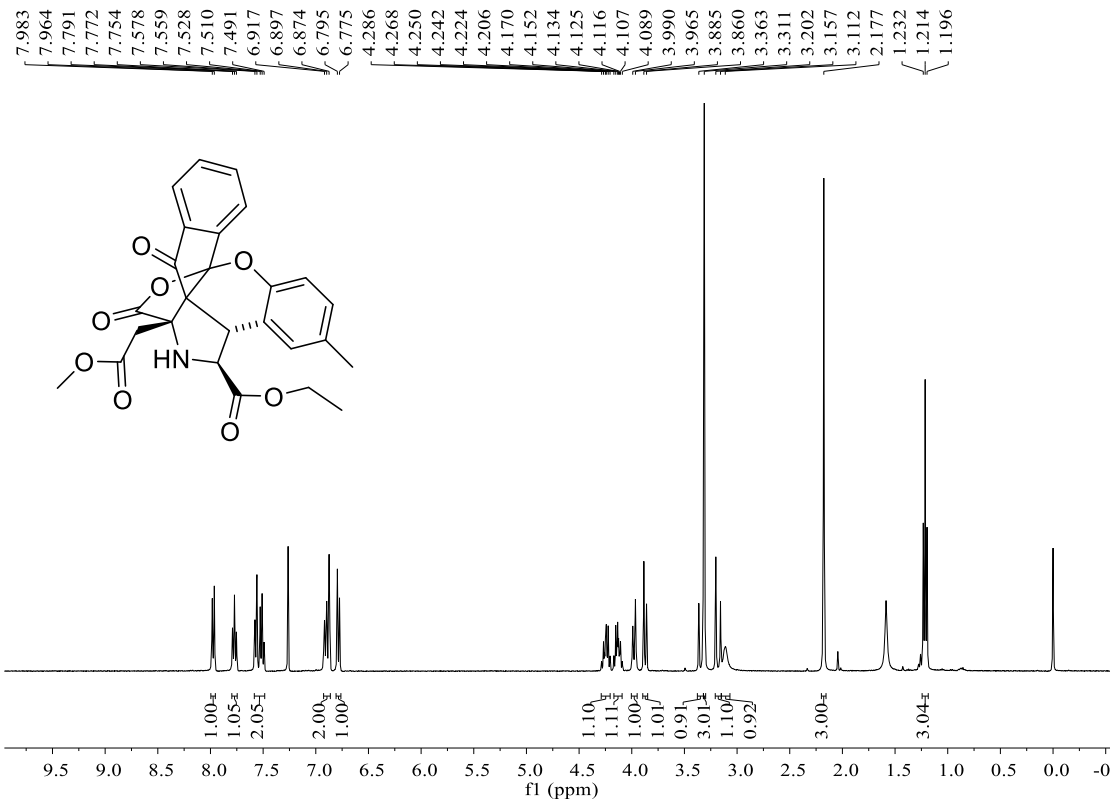
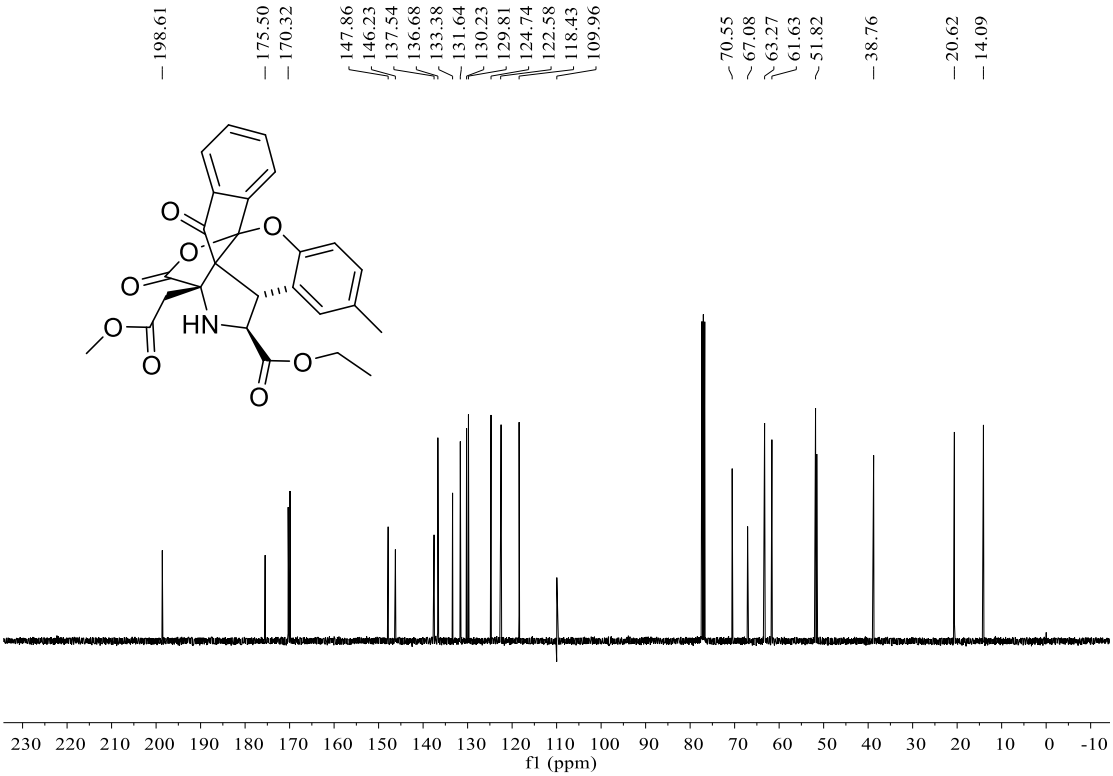
465.1385
466.1408
460
461
462
463
464
465
466
467
468
m/z

Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-1-(2-methoxy-2-oxoethyl)-5-methyl-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4b): white solid, 75%, m.p. 197-198 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 7.6 Hz, 1H, ArH), 7.79-7.75 (m, 1H, ArH), 7.58-7.49 (m, 2H, ArH), 6.92-6.87 (m, 2H, ArH), 6.98 (d, *J* = 8.0 Hz, 1H, ArH), 4.29-4.21 (m, 1H, CH), 4.17-4.09 (m, 1H, CH), 3.98 (d, *J* = 10.0 Hz, 1H, CH), 3.87 (d, *J* = 10.0 Hz, 1H, CH), 3.36 (s, 1H, CH), 3.31 (s, 3H, OCH_3), 3.18 (d, *J* = 18.0 Hz, 1H, CH), 3.11 (br.s, 1H, NH), 2.18 (s, 3H, CH_3), 1.21 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.6, 175.5, 170.3, 169.9, 147.9, 146.2, 137.5, 136.7 133.4, 131.6, 130.2, 129.8, 124.7, 122.6, 122.5, 118.4, 110.0, 70.6, 67.1, 63.3, 61.6, 51.8, 51.5, 38.8, 20.6, 14.1; IR (KBr) υ: 3666, 1810, 1720, 1770, 1657, 1577, 1446, 1390, 1286, 1222, 1163, 1069, 1046, 972, 768 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{26}H_{23}NaO_8$ ([M+Na]$^{+}$): 500.1316, Found: 500.1322.

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109.96
70.55
67.08
63.27
61.63
51.82
38.76
20.62
14.09
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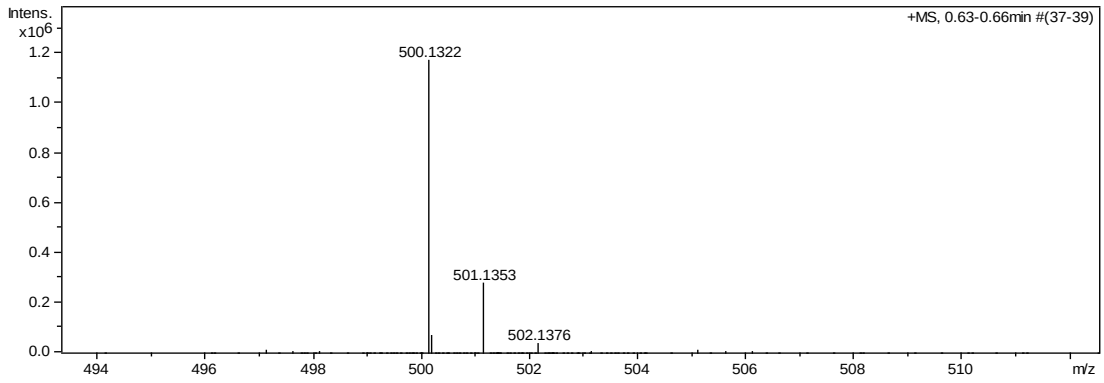
f1 (ppm)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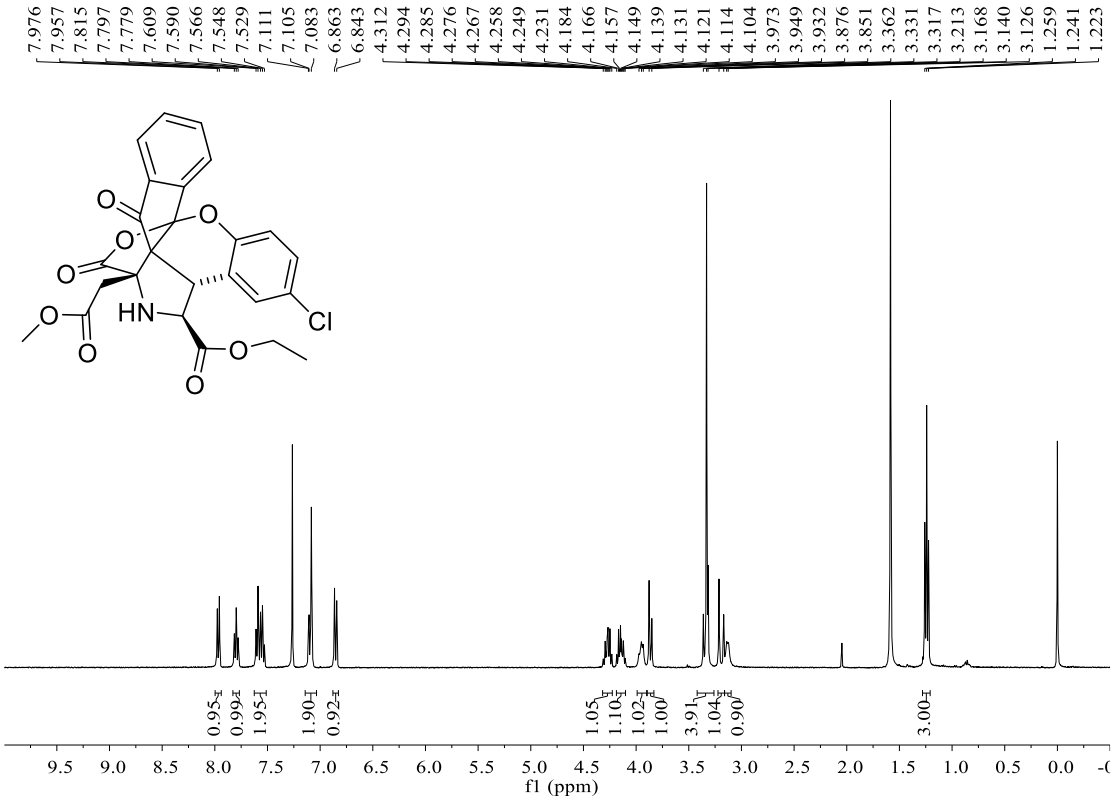
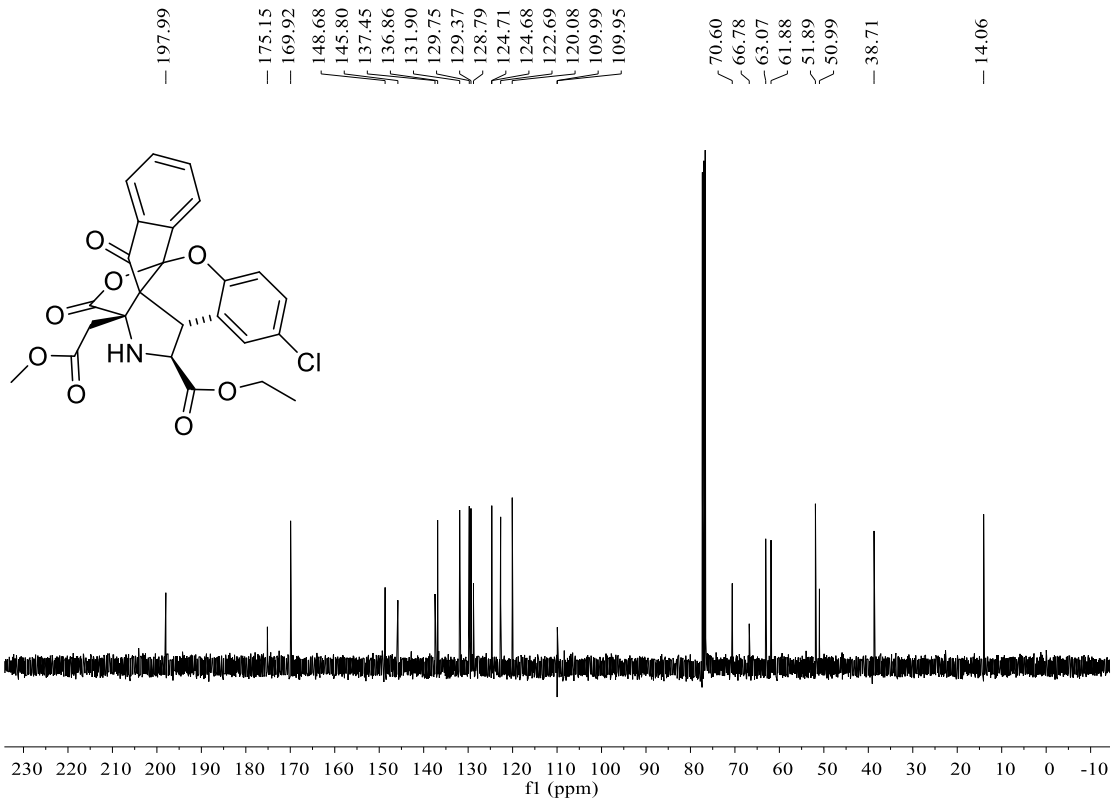
0.6
0.4
0.2
0.0
494
496
498
500
502
504
506
508
510
m/z

Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-5-chloro-1-(2-methoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4c): white solid, 53%, m.p. 177-178 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 7.6 Hz, 1H, ArH), 7.82-7.78 (m, 1H, ArH), 7.61-7.53 (m, 2H, ArH), 7.11-7.08 (m, 2H, ArH), 6.85 (d, *J* = 8.0 Hz, 1H, ArH), 4.31-4.23 (m, 1H, CH), 4.18-4.10 (m, 1H, CH), 3.97-3.93 (m, 1H, CH), 3.86 (d, *J* = 10.0 Hz, 1H, CH), 3.34 (d, *J* = 18.0 Hz, 1H, CH), 3.33 (s, 3H, OCH_3), 3.19 (d, *J* = 18.0 Hz, 1H, CH), 3.13 (d, *J* = 5.6 Hz, 1H, NH), 1.24 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.0, 175.1, 169.9, 148.7, 145.8, 137.5, 136.9, 131.9, 129.7, 129.4, 128.8, 124.7, 124.7, 122.7, 120.1, 110.0, 70.6, 66.8, 63.1, 61.9, 51.9, 51.0, 38.7, 14.1; IR (KBr) υ: 3098, 2506, 2239, 1822, 1729, 1659, 1578, 1442, 1386, 1276, 1218, 1173, 1070, 1046, 865, 743 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{20}ClNNaO_8$ ([M+Na]$^{+}$): 520.0770, Found:520.0771.

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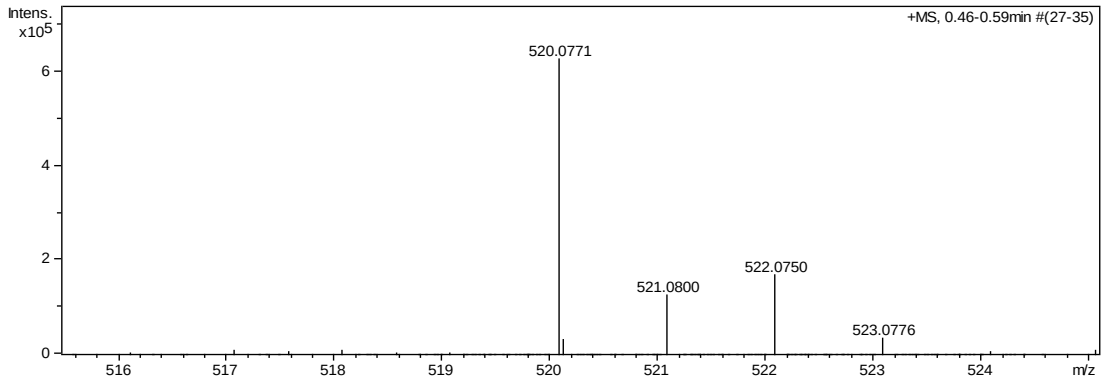
f1 (ppm)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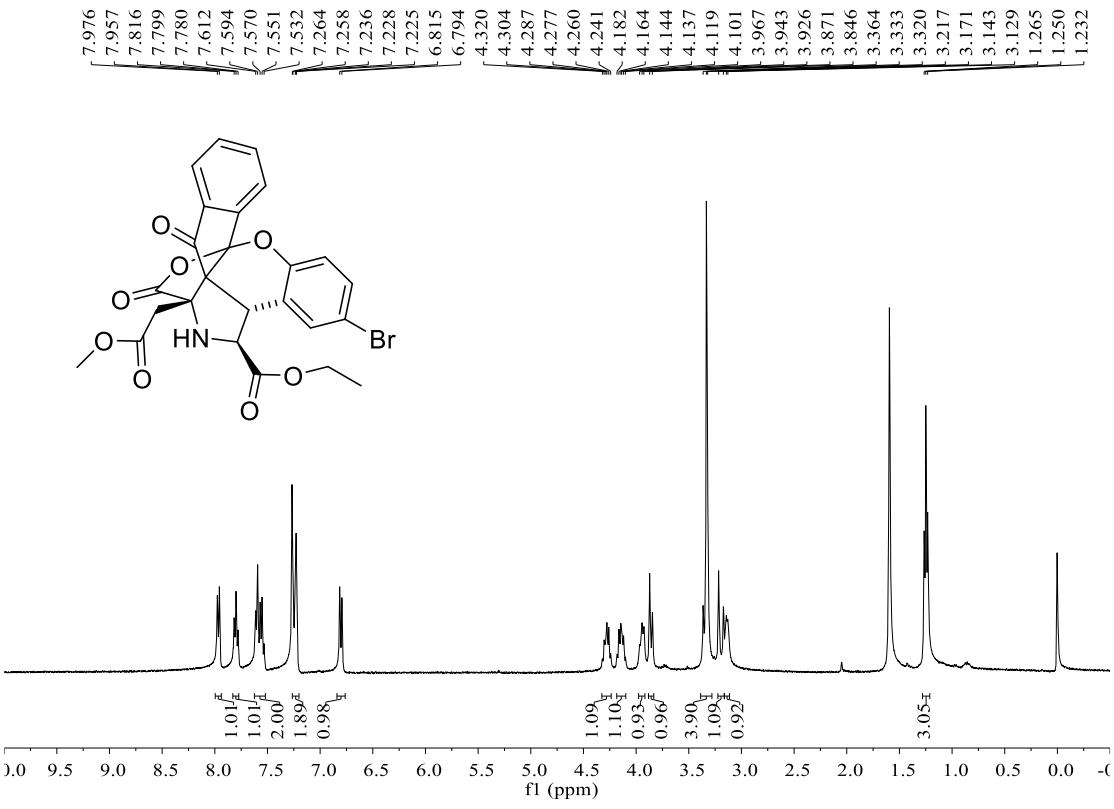
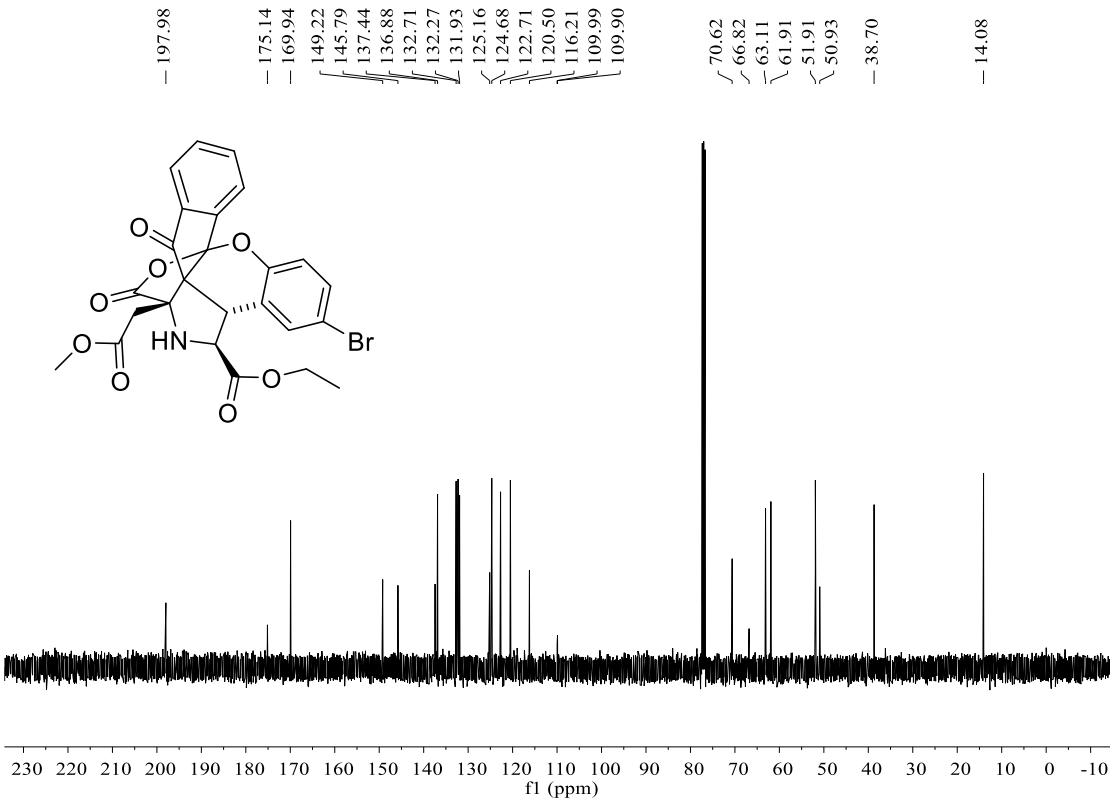
517
518
519
520
521
522
523
524
m/z

Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-5-bromo-1-(2-methoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4d): white solid, 62%, m.p. 194-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 7.6 Hz, 1H, ArH), 7.82-7.78 (m, 1H, ArH), 7.62-7.53 (m, 2H, ArH), 7.26-7.22 (m, 2H, ArH), 6.80 (d, *J* = 8.4 Hz, 1H, ArH), 4.32-4.24 (m, 1H, CH), 4.18-4.10 (m, 1H, CH), 3.97-3.93 (m, 1H, CH), 3.86 (d, *J* = 10.0 Hz, 1H, CH), 3.34 (d, *J* = 17.6 Hz, 1H, CH), 3.33 (s, 3H, OCH_3), 3.19 (d, *J* = 18.4Hz, 1H, CH), 3.14 (d, *J* = 5.6 Hz, 1H, NH), 1.25 (t, *J* = 6.0 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.0, 175.1, 169.9, 149.2, 145.8, 137.4, 136.9, 132.7, 132.3, 131.9, 125.2, 124.7, 122.7, 120.5, 116.2, 110.0, 70.6, 66.8, 63.1, 61.9, 51.9, 50.9, 38.7, 14.2; IR (KBr) υ:3198, 2516, 2244, 1987, 1734, 1667, 1576, 1443, 1390, 1274, 1209, 1173, 1076, 1048, 977, 876, 735 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{20}NNaO_8$ ($[M+Na]^+$): 564.0265, Found: 564.0258.

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109.99
109.90
70.62
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63.11
61.91
51.91
50.93
38.70
14.08
O
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O
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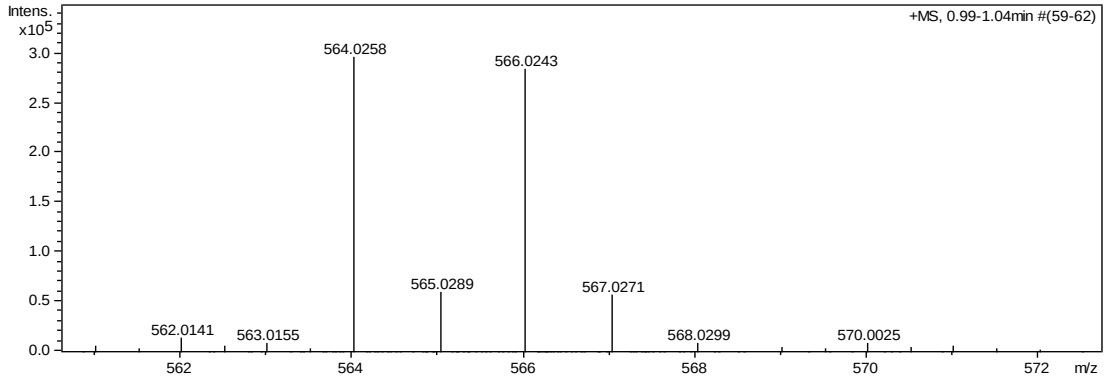
f1 (ppm)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565.0289
567.0271
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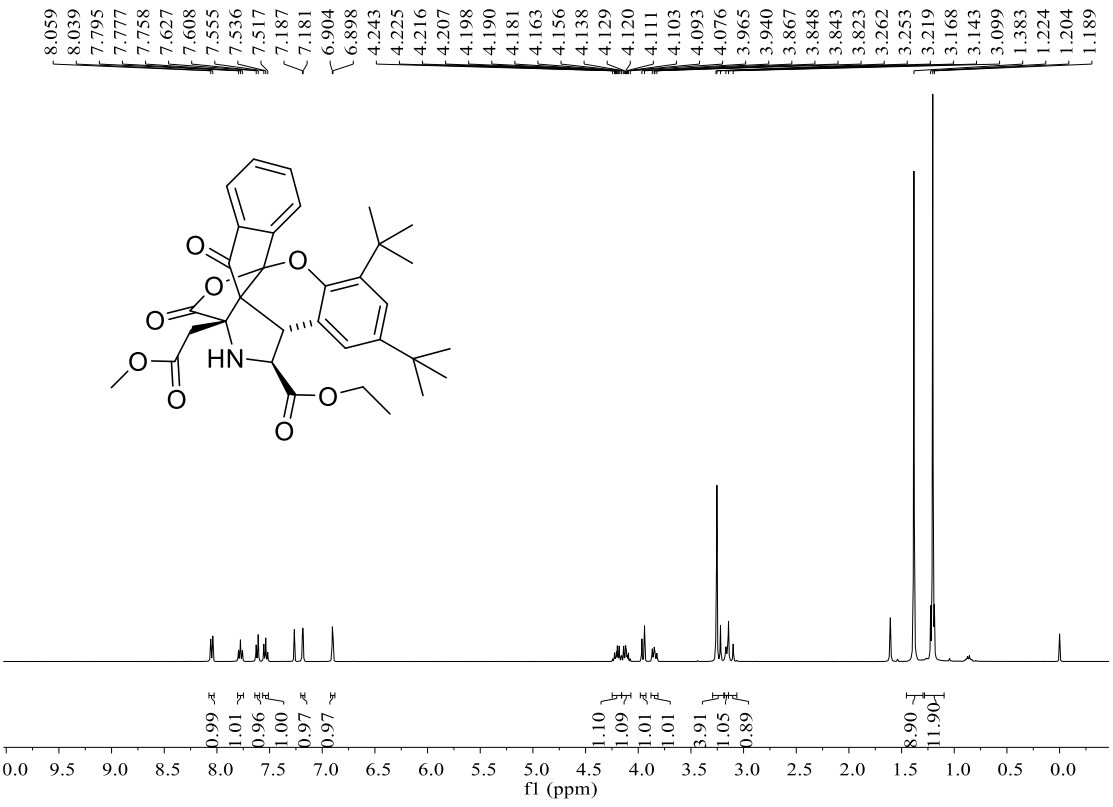
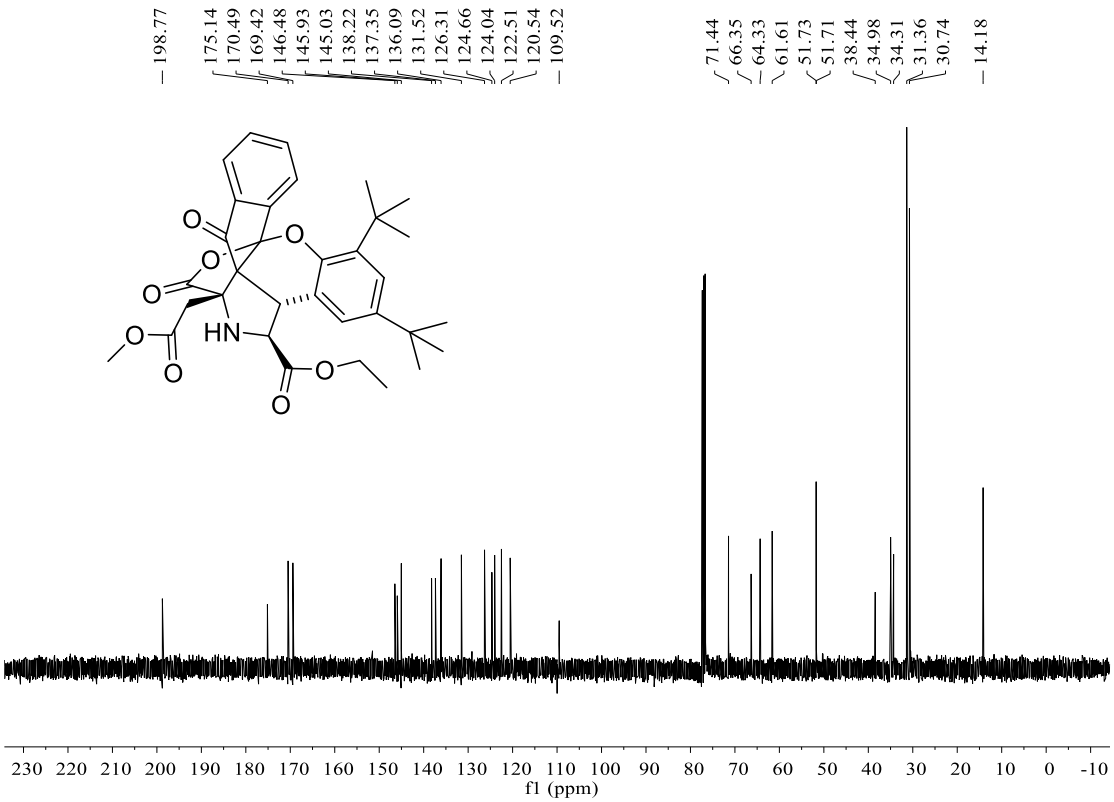
563.0155
568.0299
570.0025
562
564
566
568
570
572
m/z

Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-5,7-di-tert-butyl-1-(2-methoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4e): white solid, 61%, m.p. 137-139 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.0 Hz, 1H, ArH), 7.80-7.76 (m, 1H, ArH), 7.61 (d, *J* = 7.6 Hz, 1H, ArH), 7.56-7.52 (m, 1H, ArH), 7.18 (d, *J* = 2.4 Hz, 1H, ArH), 6.90 (d, *J* = 2.4 Hz, 1H, ArH), 4.24-4.16 (m, 1H, CH), 4.15-4.08 (m, 1H, CH), 3.95 (d, *J* = 10.0 Hz, 1H, CH), 3.87-3.82 (m, 1H, CH), 3.24 (d, *J* = 17.2 Hz, 1H, CH), 3.25 (s, 3H, OCH_3), 3.15 (d, *J* = 10.0 Hz, 1H, CH), 3.10 (s, 1H, NH), 1.38 (s, 9H, CH_3), 1.20 (t, *J* = 6.8 Hz, 12H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ:198.8, 175.1, 170.4, 169.4, 146.2, 145.9, 145.0, 138.2, 137.4, 136.1, 131.5, 126.3, 124.7, 124.0, 122.5, 120.5, 109.5, 71.4, 66.3, 64.3, 61.6, 51.7, 51.7, 38.4, 35.0, 34.3, 31.4, 30.7, 14.2; IR (KBr) υ:3188, 2510, 2240, 1988, 1723, 1650, 1576, 1435, 1399, 1267, 1237, 1080, 1035, 970, 886, 745 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{33}H_{38}NO_8$ ([M+H]$^{+}$): 576.2592, Found: 576.2593.

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64.33
61.61
51.73
51.71
38.44
34.98
34.31
31.36
30.74
14.18
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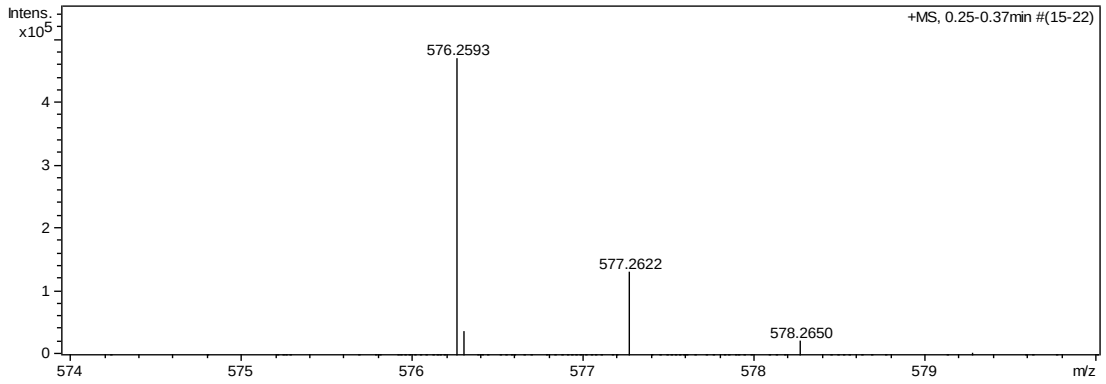
f1 (ppm)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x10^5
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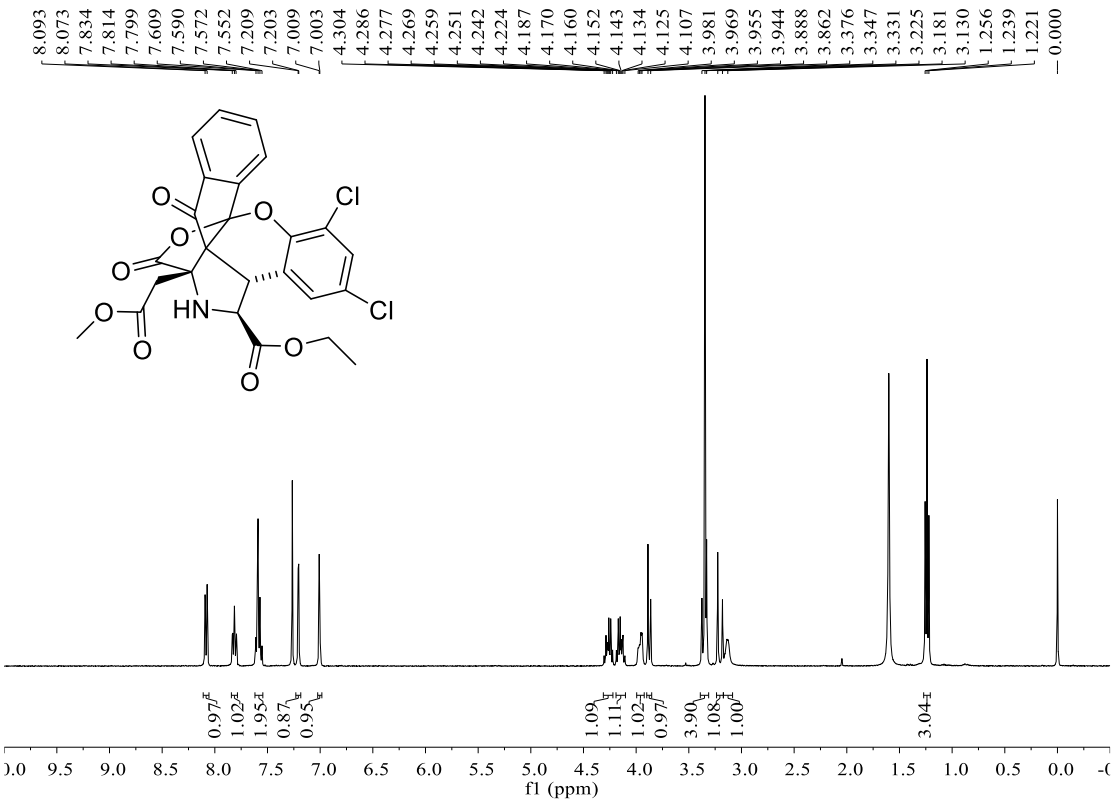
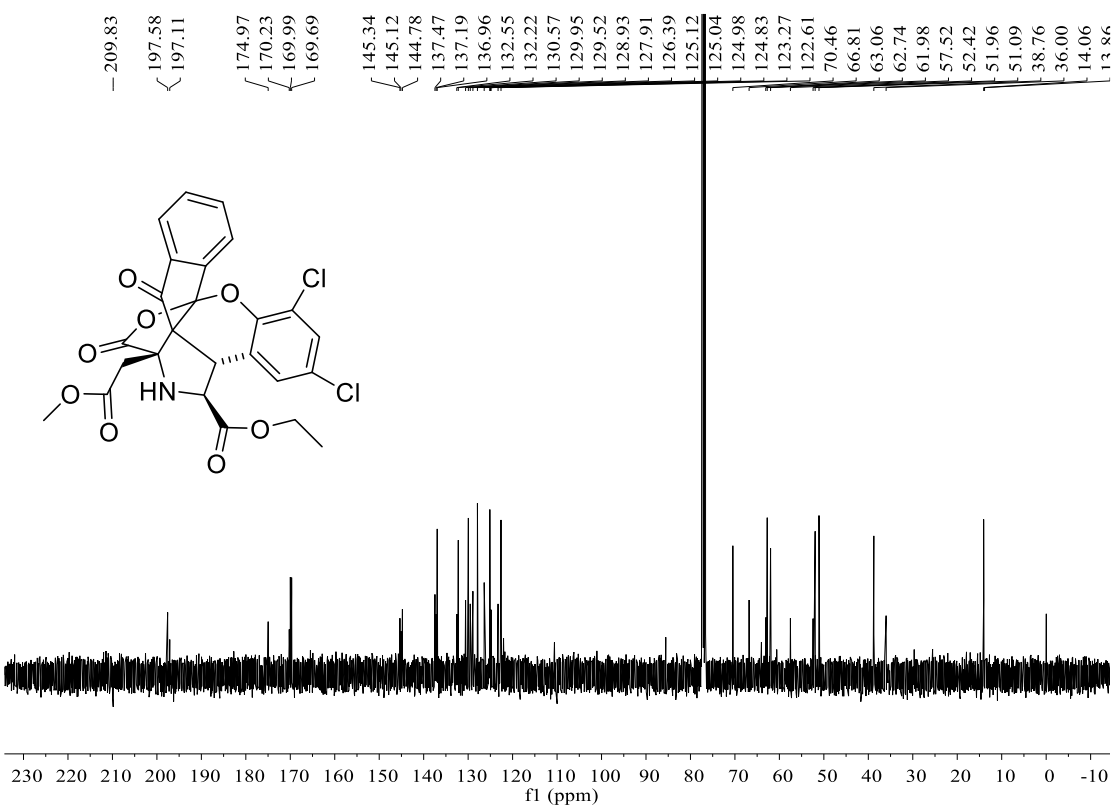
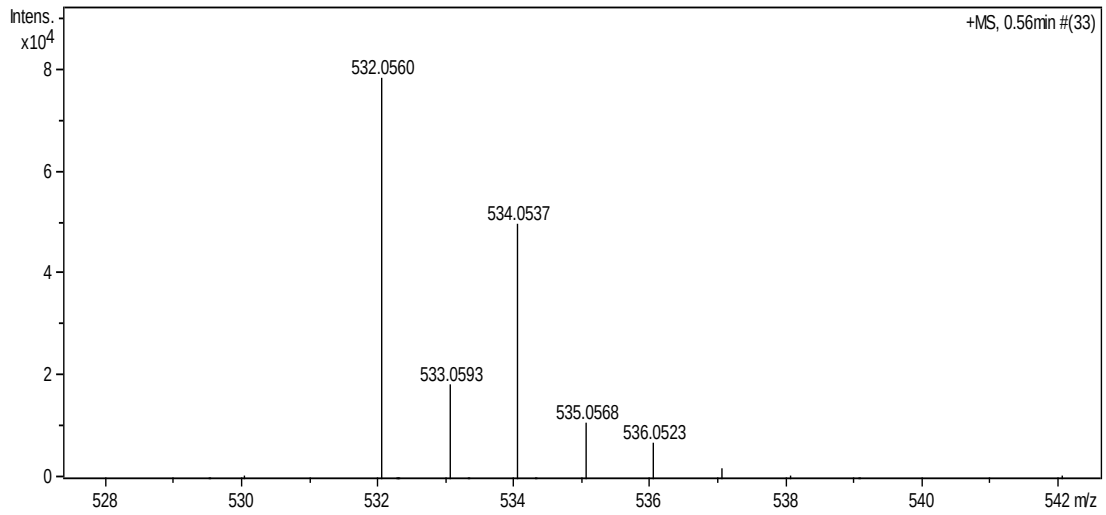
0
1
2
3
4
574
575
576
577
578
579
m/z

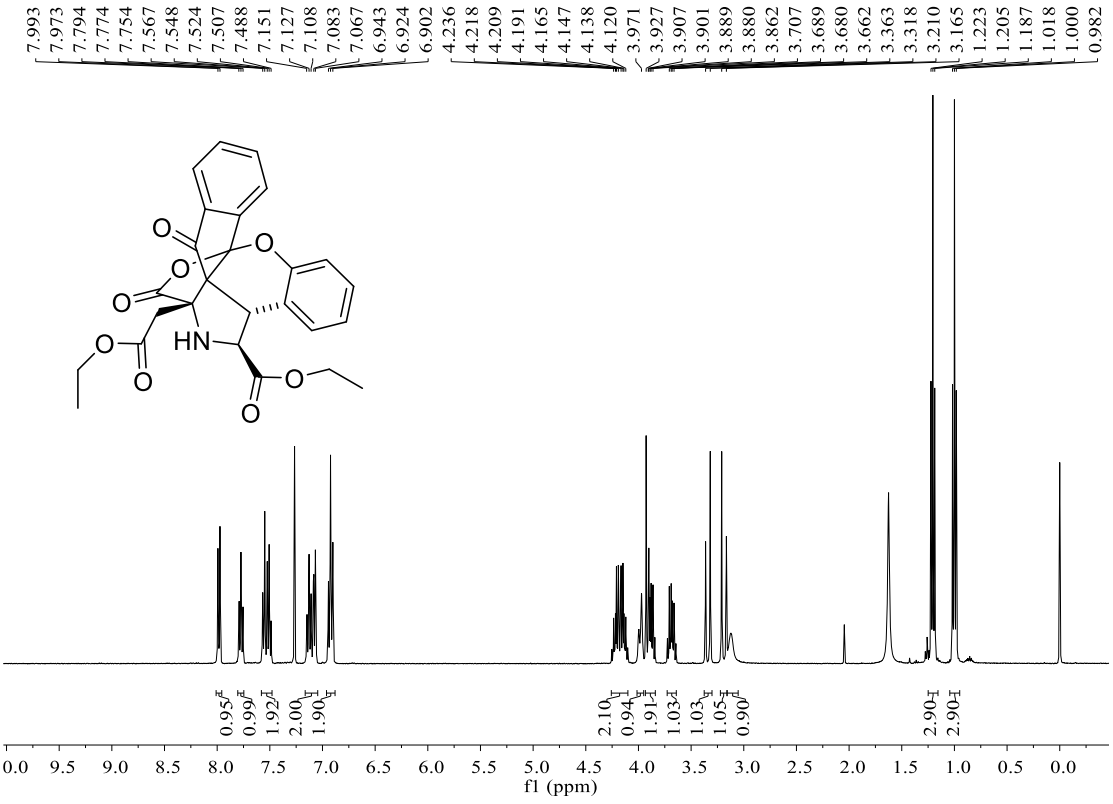
Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-5,7-dichloro-1-(2-methoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4f): white solid, 70%, m.p. 219-221 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 8.0 Hz, 1H, ArH), 7.83-7.80 (m, 1H, ArH), 7.61-7.55 (m, 2H, ArH), 7.21 (m, *J* = 2.4 Hz, 1H, ArH), 7.01 (d, *J* = 2.4 Hz, 1H, ArH), 4.30-4.22 (m, 1H, CH), 4.19-4.11 (m, 1H, CH), 3.98-3.94 (m, 1H, CH), 3.87 (d, *J* = 10.4 Hz, 1H, CH), 3.35 (d, *J* = 18.0 Hz, 1H, CH), 3.35 (s, 3H, OCH_3), 3.20 (d, *J* = 17.6 Hz, 1H, CH), 3.13 (br.s, 1H, NH), 1.24 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ:209.8, 197.6, 197.1, 175.0, 170.2, 170.0, 169.7, 145.3, 145.1, 144.8, 137.5, 137.2, 137.0, 132.6, 132.2, 130.6, 130.0, 129.5, 128.9, 127.9, 126.4, 125.1, 125.0, 125.0, 124.8, 123.3, 122.6, 111.4, 110.6, 85.6, 70.5, 66.8, 63.1, 62.7, 62.0, 57.5, 52.4, 52.0, 51.089, 38.8, 36.0, 14.1, 13.9; IR (KBr) υ: 3180, 2522, 2257, 1970, 1735, 1668, 1587, 1445, 1386, 1256, 1249, 1070, 1054, 960, 856, 776 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{20}Cl_2NO_8$ ([M+H]$^{+}$): 532.0560, Found: 532.0560.

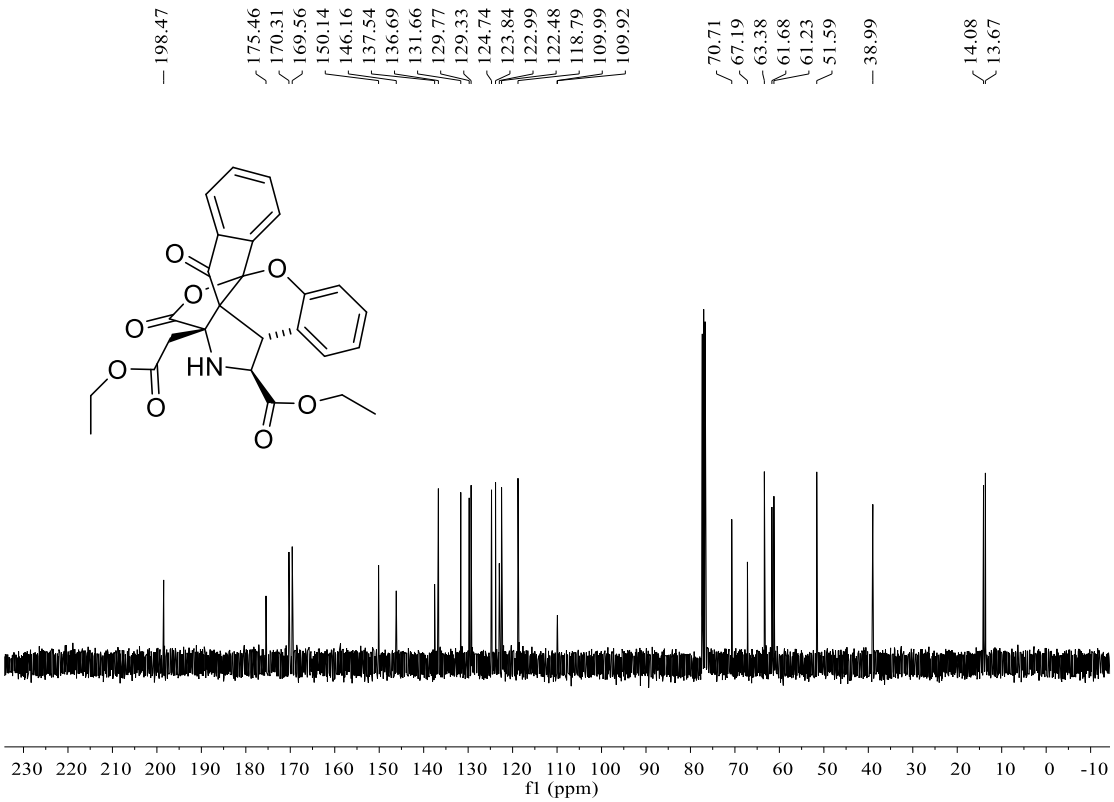


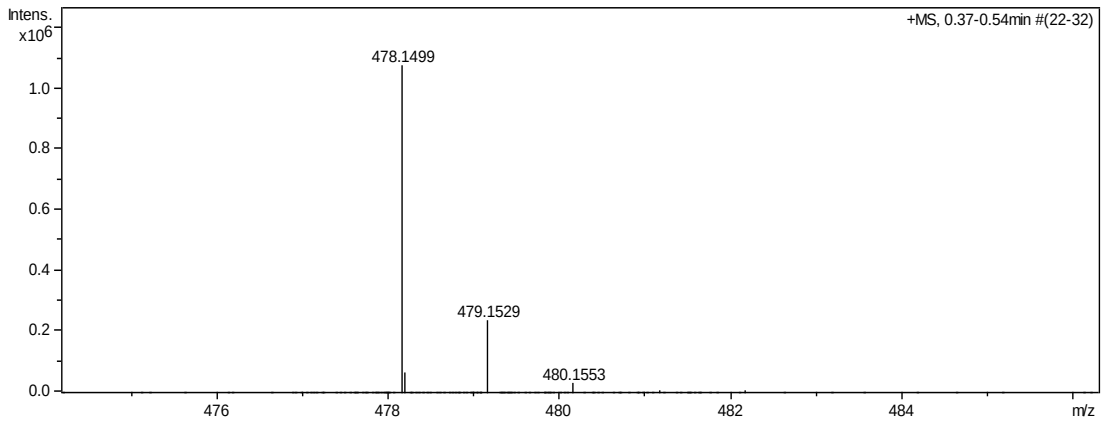

209.83
197.58
197.11
174.97
170.23
169.99
169.69
145.34
145.12
144.78
137.47
137.19
136.96
132.55
132.22
130.57
129.95
129.52
128.93
127.91
126.39
125.12
125.04
124.98
124.83
123.27
122.61
70.46
66.81
63.06
62.74
61.98
57.52
52.42
51.96
51.09
38.76
36.00
14.06
Cl
Cl
HN
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 0.56min #(33)
532.0560
534.0537
533.0593
535.0568
536.0523
0
2
4
6
8
528
530
532
534
536
538
540
542 m/z

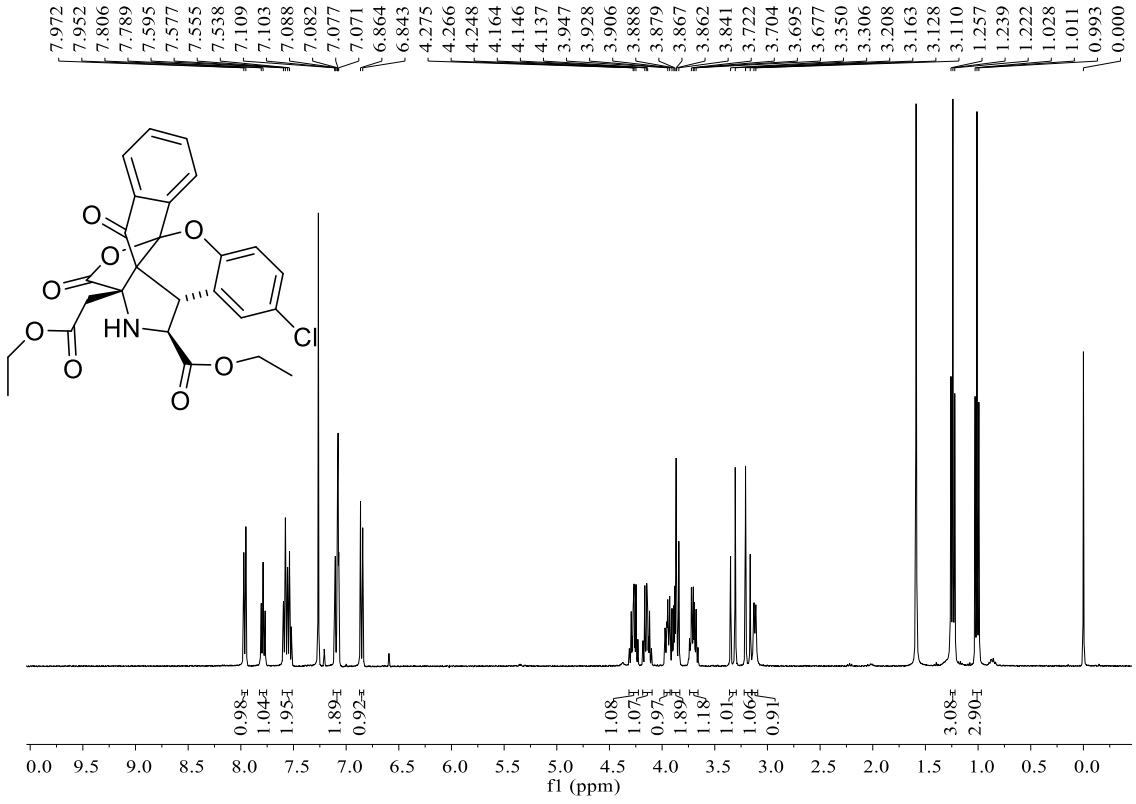
Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-1-(2-ethoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4g): white solid, 57%, m.p. 183-184 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.0 Hz, 1H, ArH), 7.79-7.75 (m, 1H, ArH), 7.57-7.49 (m, 2H, ArH), 7.15-7.07 (m, 2H, ArH), 6.94-6.90 (m, 2H, ArH), 4.25-4.10 (m, 2H, CH_2), 3.98 (d, *J* = 10.0 Hz, 1H, CH), 3.93-3.84 (m, 2H, CH_2), 3.73-3.64 (m, 1H, CH), 3.34 (d, *J* = 18.0 Hz, 1H, CH), 3.19 (d, *J* = 18.0 Hz, 1H, CH), 3.12 (br.s, 1H, NH), 1.12 (t, *J* = 7.2 Hz, 3H, CH_3), 1.00 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.5, 175.5, 170.3, 169.6, 150.1, 146.1, 137.5, 136.7, 131.7, 129.8, 129.3, 124.7, 123.8, 123.0, 122.5, 118.8, 110.0, 70.7, 67.2, 63.4, 61.7, 61.2, 51.6, 39.0, 14.1, 13.7; IR (KBr) υ: 3176, 2540 2260, 1954, 1870, 1660, 1570, 1454, 1379, 1260, 1223, 1068, 1033, 935, 825, 756 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{26}H_{24}NO_8$ ([M+H]$^{+}$): 478.1496, Found: 478.1499.

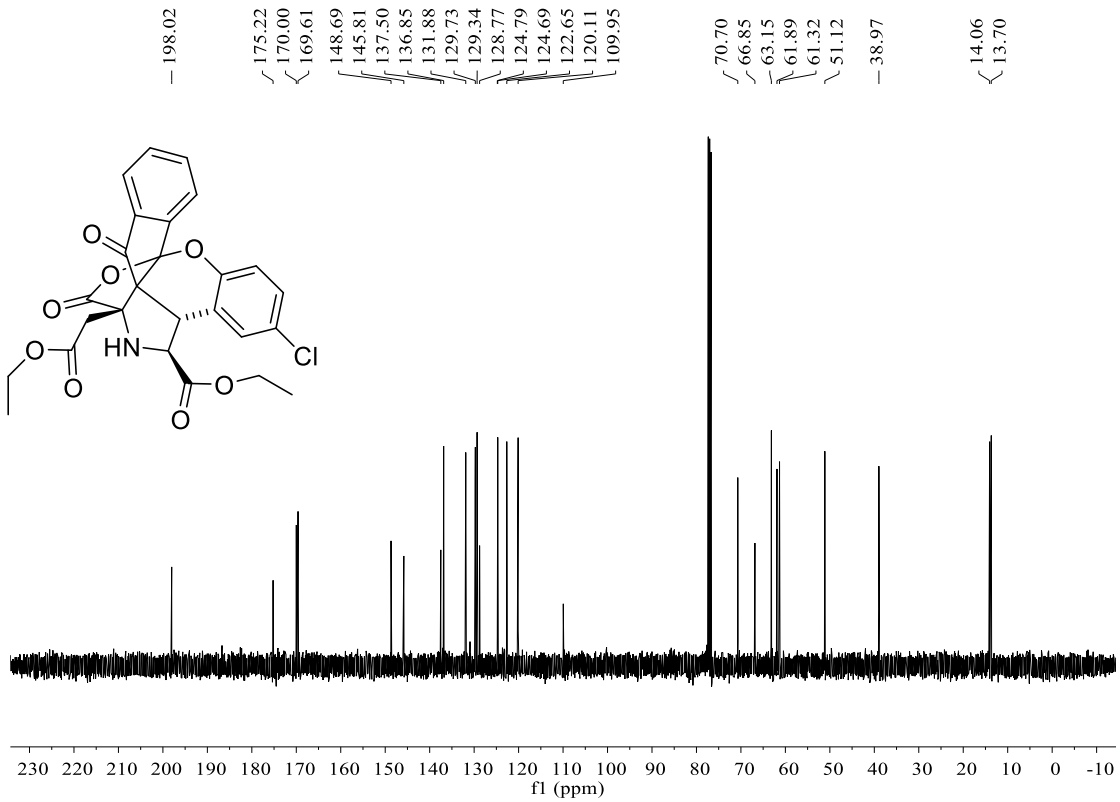


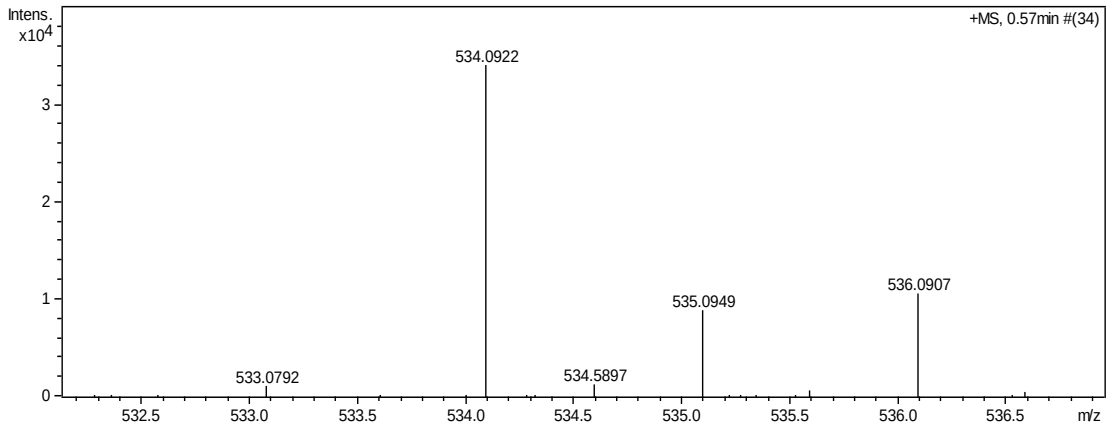

198.47
175.46
170.31
169.56
150.14
146.16
137.54
136.69
131.66
129.77
129.33
124.74
123.84
122.99
122.48
118.79
109.99
109.92
70.71
67.19
63.38
61.68
61.23
51.59
38.99
14.08
13.67
O
O
O
O
HN
O
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^6
+MS, 0.37-0.54min #(22-32)
478.1499
479.1529
480.1553
1.0
0.8
0.6
0.4
0.2
0.0
476
478
480
482
484
m/z

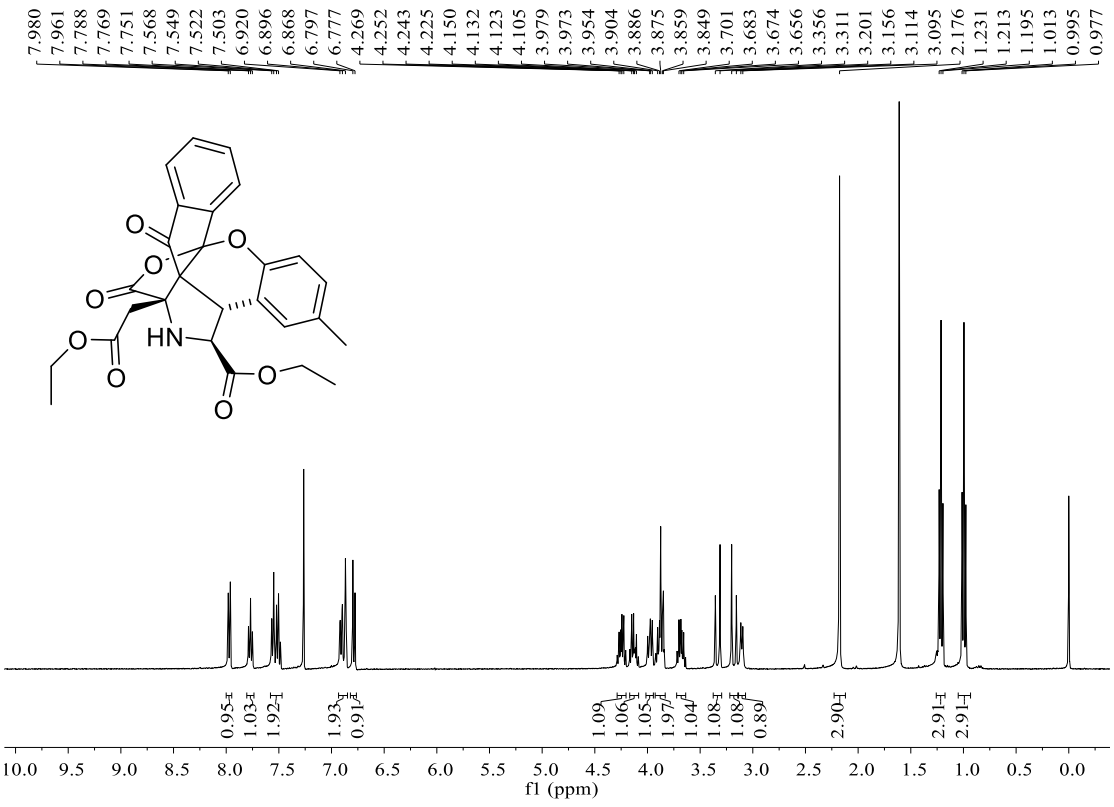
Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-5-chloro-1-(2-ethoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4i) white solid, 60%, m.p. 140-141 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.0 Hz, 1H, ArH), 7.81-7.77 (m, 1H, ArH), 7.60-7.52 (m, 2H, ArH), 7.11-7.07 (m, 2H, ArH), 6.85 (d, *J* = 8.4 Hz, 1H, ArH), 4.31-4.23 (m, 1H, CH), 4.18-4.10 (m, 1H, CH), 3.97-3.93 (m, 1H, CH), 3.91-3.84 (m, 2H, CH_2), 3.74-3.66 (m, 1H, CH), 3.33 (d, *J* = 17.6 Hz, 1H, CH), 3.18 (d, *J* = 18.0 Hz, 1H, CH), 3.12 (d, *J* = 7.2 Hz, 1H, NH), 1.24 (t, *J* = 7.2 Hz, 3H, CH_3), 1.01 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.0, 175.2, 170.0, 169.6, 148.7, 145.8, 137.5, 136.9, 131.9, 129.7, 129.3, 128.8, 124.8, 124.7, 122.7, 120.1, 110.0, 70.7, 66.9, 63.1, 61.9, 61.3, 51.1, 39.0, 14.1, 13.7; IR (KBr) υ: 3178, 2578 2256, 1934, 1877, 1658, 1565, 1420, 1370, 1256, 1209, 1060, 1030, 940, 857, 743 cm^{-1}; MS (*m*/z): HRMS (ESI-TOF) Calcd. for $C_{26}H_{22}ClNO_8$ ([M+H]$^{+}$): 534.0926, Found: 534.0922.

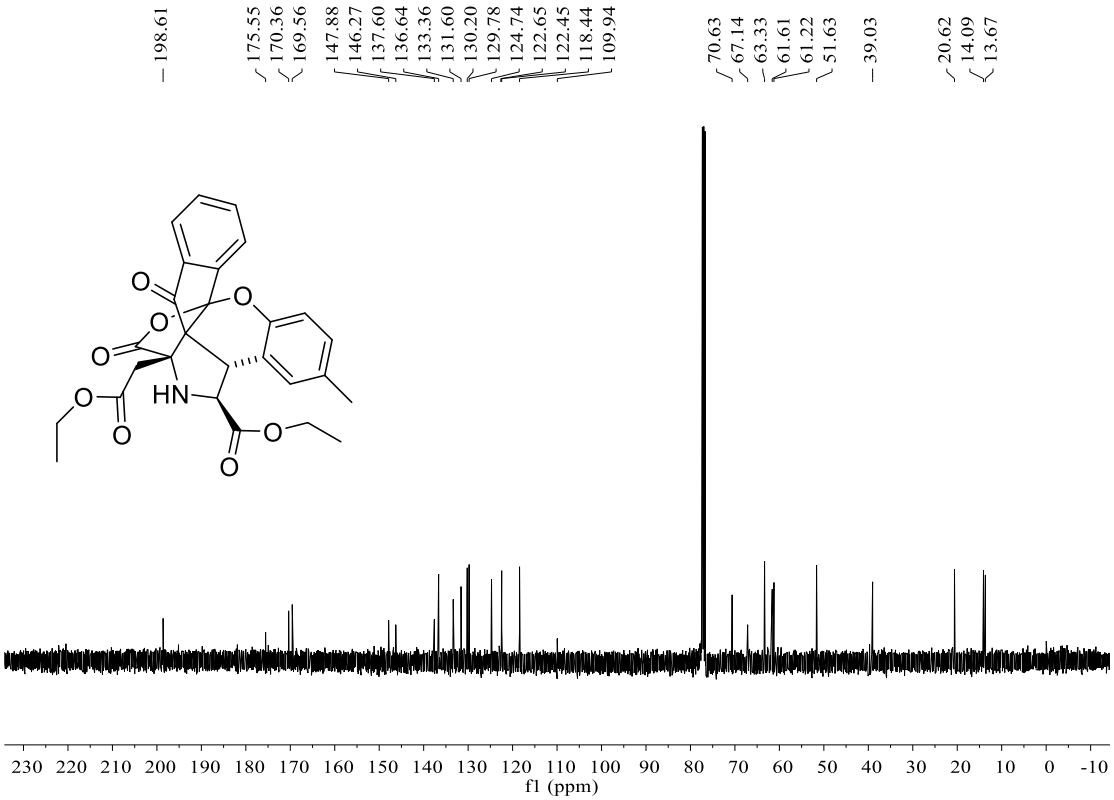


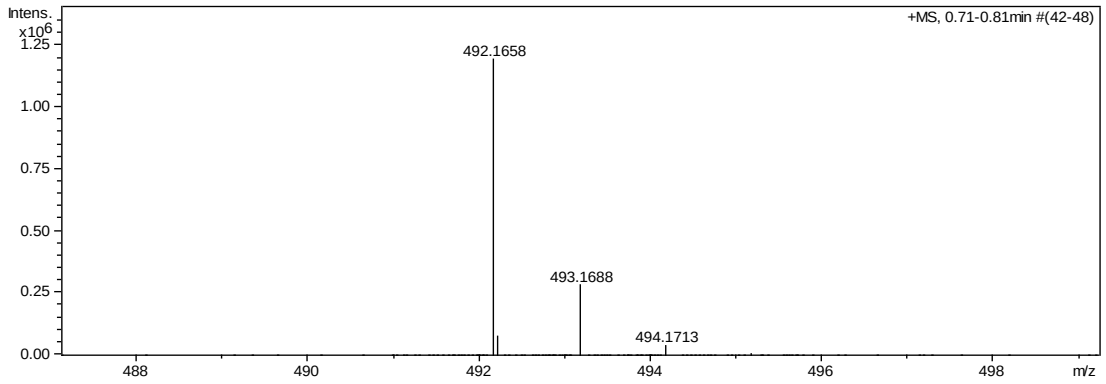

198.02
175.22
170.00
169.61
148.69
145.81
137.50
136.85
131.88
129.73
129.34
128.77
124.79
124.69
122.65
120.11
109.95
70.70
66.85
63.15
61.89
61.32
51.12
38.97
14.06
13.70
O
O
O
O
HN
O
O
O
O
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 0.57min #(34)
534.0922
536.0907
535.0949
533.0792
534.5897
0
1
2
3
532.5
533.0
533.5
534.0
534.5
535.0
535.5
536.0
536.5
m/z

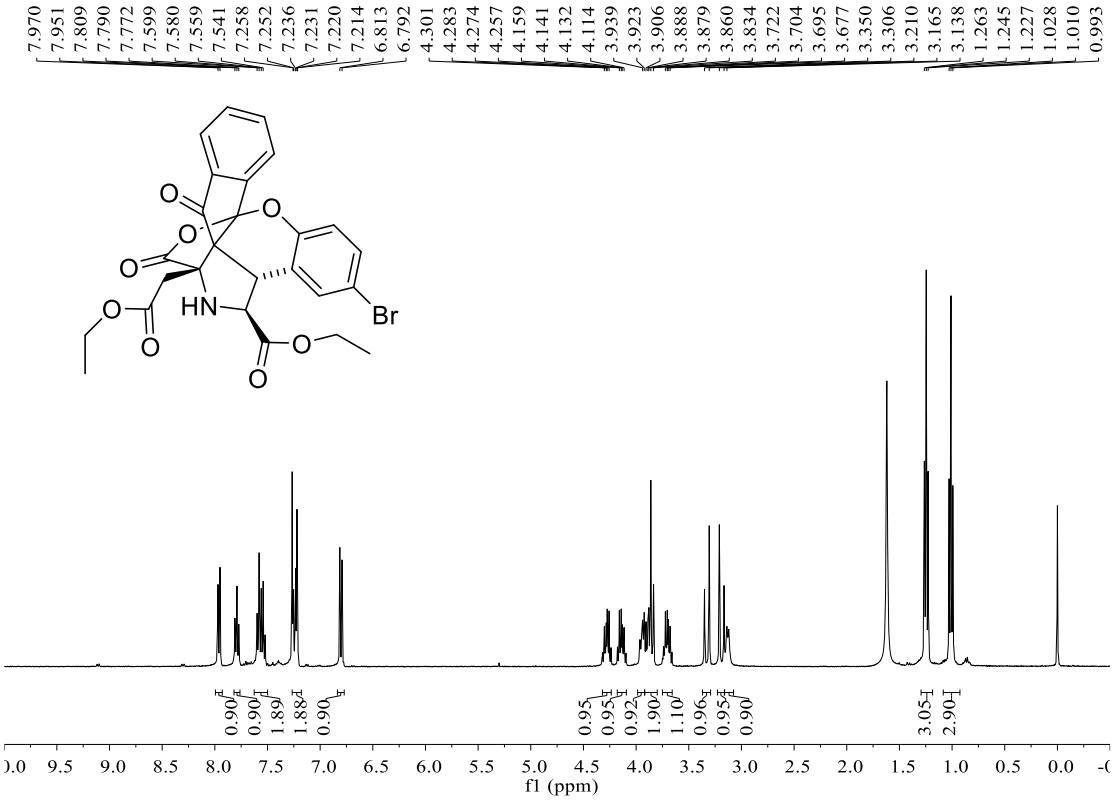
Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-1-(2-ethoxy-2-oxoethyl)-5-methyl-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4h): white solid, 37%, m.p. 140-141 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 7.6 Hz, 1H, ArH), 7.79-7.75 (m, 1H, ArH), 7.57-7.49 (m, 2H, ArH), 6.92-6.87 (m, 2H, ArH), 6.78 (d, *J* = 8.0 Hz, 1H, ArH), 4.29-4.21 (m, 1H, CH), 4.17-4.09 (m, 1H, CH), 3.99-3.95 (m, 1H, CH), 3.92-3.84 (m, 2H, CH_2), 3.72-3.64 (m, 1H, CH), 3.33 (d, *J* = 18.0 Hz, 1H, CH), 3.23 (d, *J* = 18.0 Hz, 1H, CH), 3.10 (d, *J* = 7.6 Hz, 1H, NH), 2.18 (s, 3H, CH_3), 1.21 (t, *J* = 7.2 Hz, 3H, CH_3), 1.10 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.6, 175.6, 170.3, 169.6, 147.8, 146.3, 137.6, 136.6, 133.4, 131.6, 130.2, 129.8, 124.7, 122.6, 122.50, 118.4, 110.0, 70.6, 67.1, 63.3, 61.6, 61.2, 51.6, 39.0, 20.6, 14.2, 13.7; IR (KBr) υ: 3178, 2575, 2250, 1933, 1860, 1644, 1547, 1434, 1366, 1243, 1221, 1070, 1029, 928, 820, 726 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{27}H_{25}NO_8$ ($[M+H]^+$): 492.1653, Found: 492.1658.

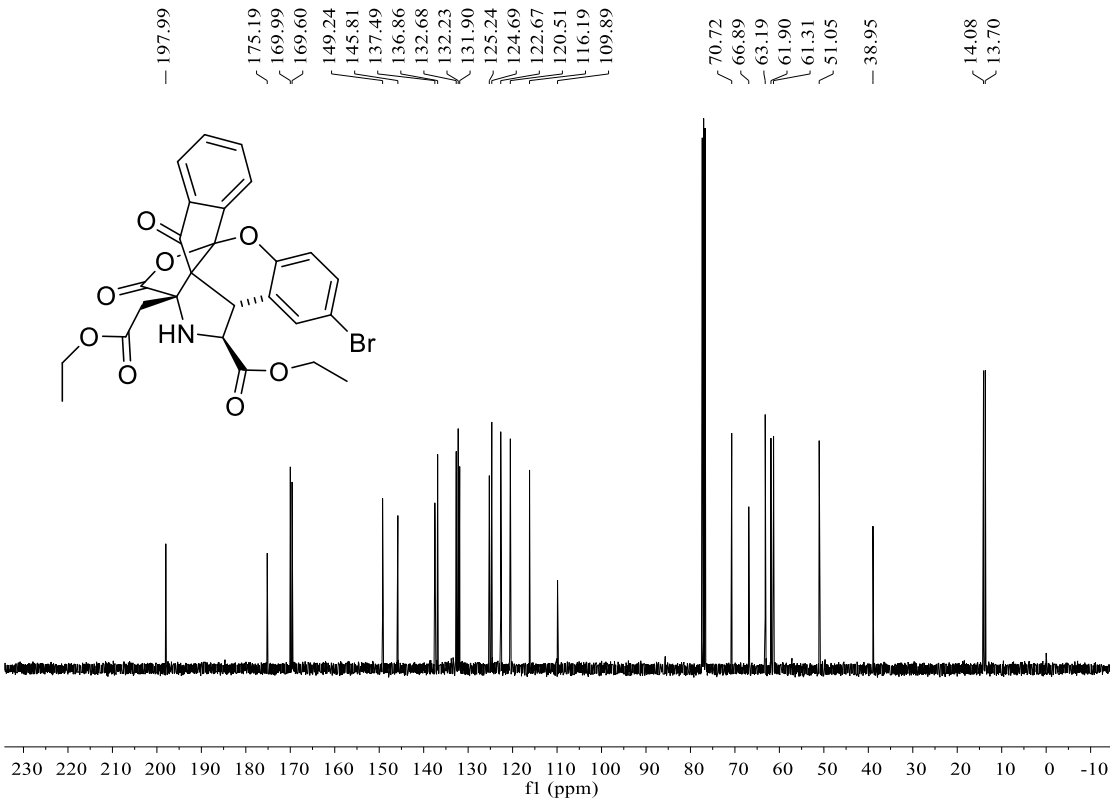


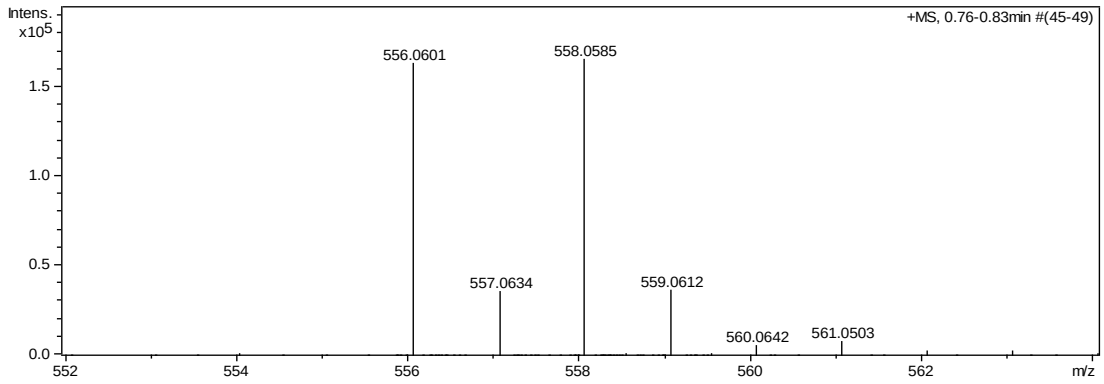

198.61
175.55
170.36
169.56
147.88
146.27
137.60
136.64
133.36
131.60
130.20
129.78
124.74
122.65
122.45
118.44
109.94
70.63
67.14
63.33
61.61
61.22
51.63
39.03
20.62
14.09
13.67
HN
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^6
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 0.71-0.81min #(42-48)
492.1658
493.1688
494.1713
488
490
492
494
496
498
m/z

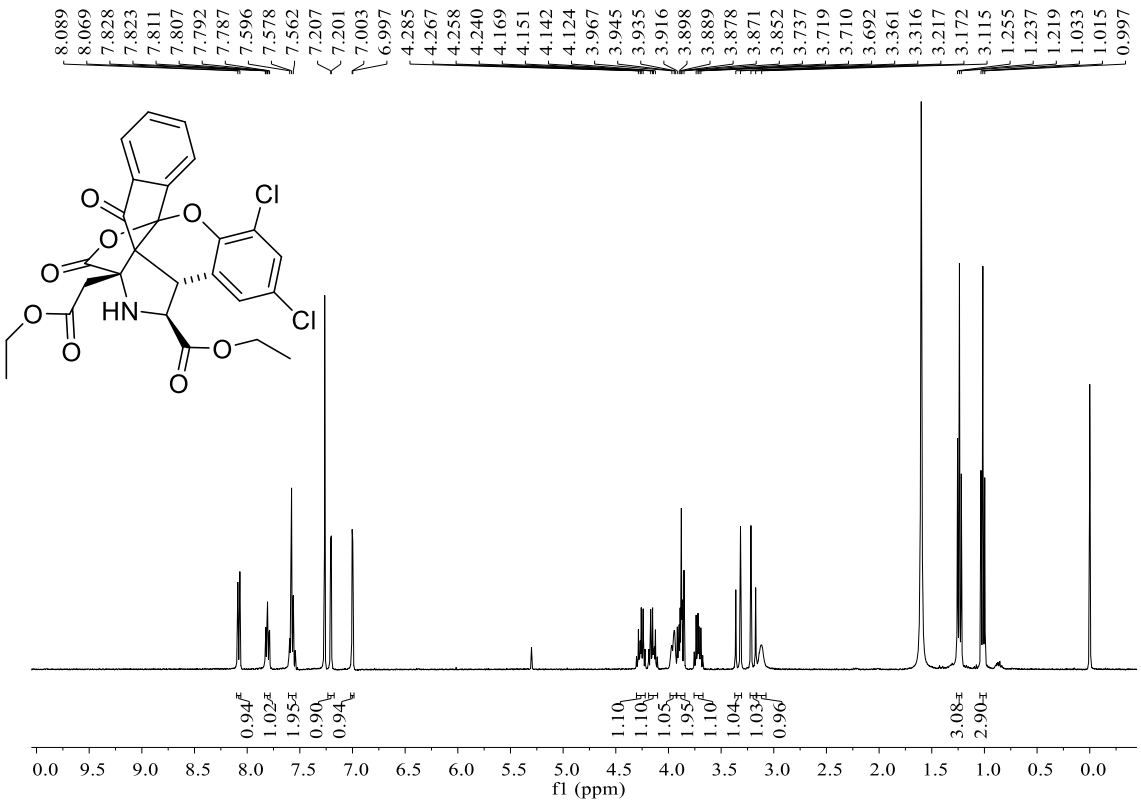
Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-5-bromo-1-(2-ethoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4j): white solid, 72%, m.p. 147-148 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 7.6 Hz, 1H, ArH), 7.81-7.77 (m, 1H, ArH), 7.60-7.52 (m, 2H, ArH), 7.26-7.21 (m, 2H, ArH), 6.80 (d, *J* = 8.4 Hz, 1H, ArH), 4.32-4.24 (m, 1H, CH), 4.18-4.10 (m, 1H, CH), 3.96-3.92 (m, 1H, CH), 3.91-3.84 (m, 2H, CH_2), 3.75-3.66 (m, 1H, CH), 3.33 (d, *J* = 17.6 Hz, 1H, CH), 3.19 (d, *J* = 18.0 Hz, 1H, CH), 3.13 (d, *J* = 6.8 Hz, 1H, NH), 1.25 (t, *J* = 7.2 Hz, 3H, CH_3), 1.01 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.0, 175.2, 170.0, 169.6, 149.2, 145.8, 137.5, 136.9, 132.7, 132.2, 131.9, 125.2, 124.7, 122.7, 120.5, 116.2, 109.9, 70.7, 66.9, 63.2, 61.9, 61.3, 51.0, 39.0, 14.1, 13.7; IR (KBr) υ: 3170, 2568, 2244, 1954, 1867, 1654, 1578, 1433, 1367, 1239, 1218, 1088, 1009, 918, 811, 719 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{26}H_{23}BrNO_8$ ([M+H]$^{+}$): 556.0602, Found: 556.0601.

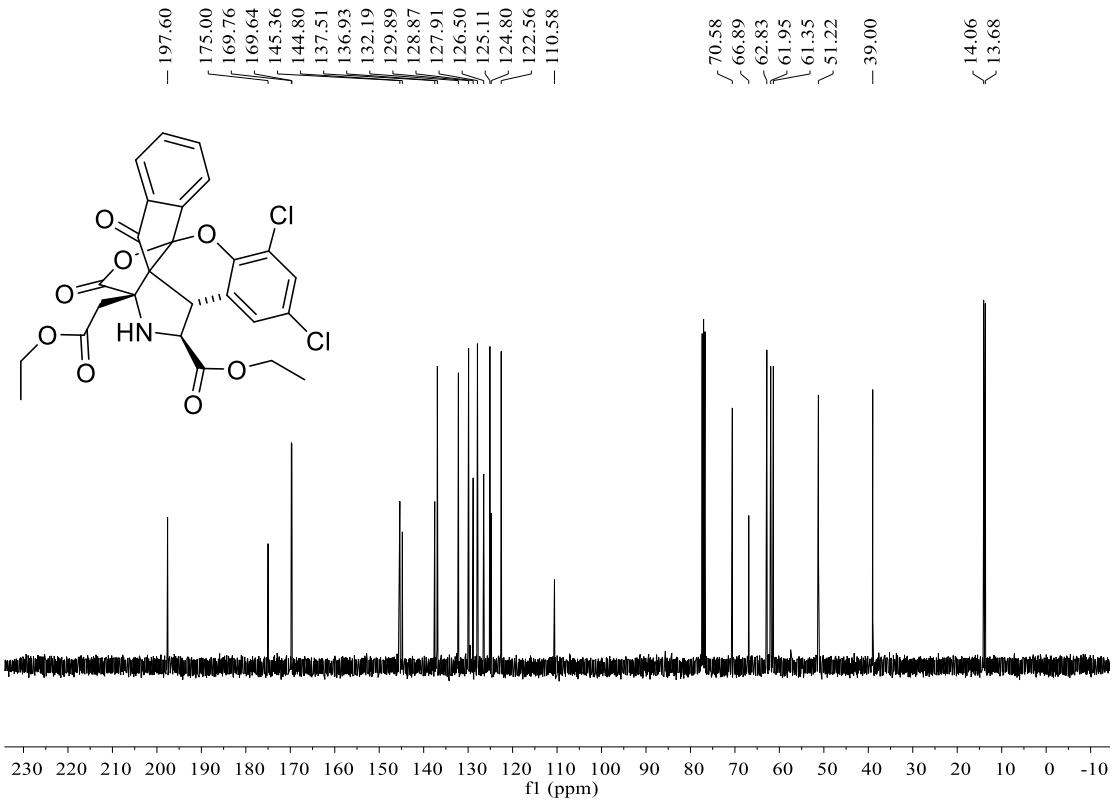


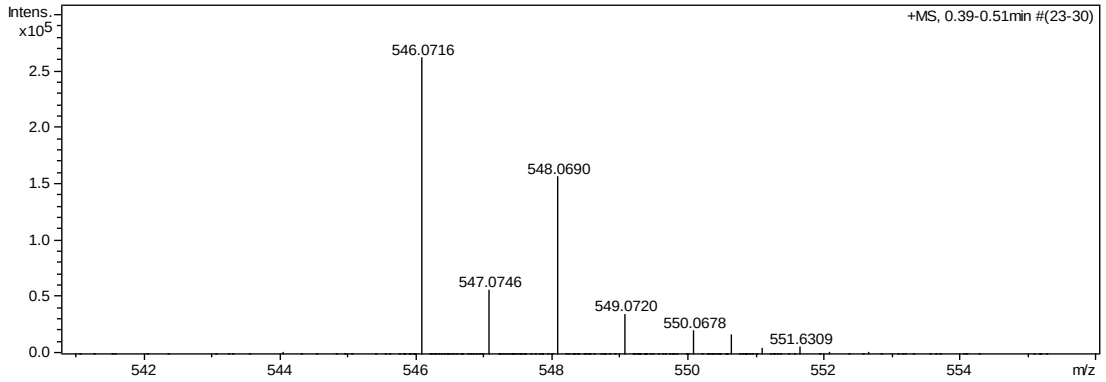

197.99
175.19
169.99
169.60
149.24
145.81
137.49
136.86
132.68
132.23
131.90
125.24
124.69
122.67
120.51
116.19
109.89
70.72
66.89
63.19
61.90
61.31
51.05
38.95
14.08
13.70
O
O
O
O
O
HN
Br
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.76-0.83min #(45-49)
556.0601
558.0585
557.0634
559.0612
560.0642
561.0503
1.5
1.0
0.5
0.0
552
554
556
558
560
562
m/z

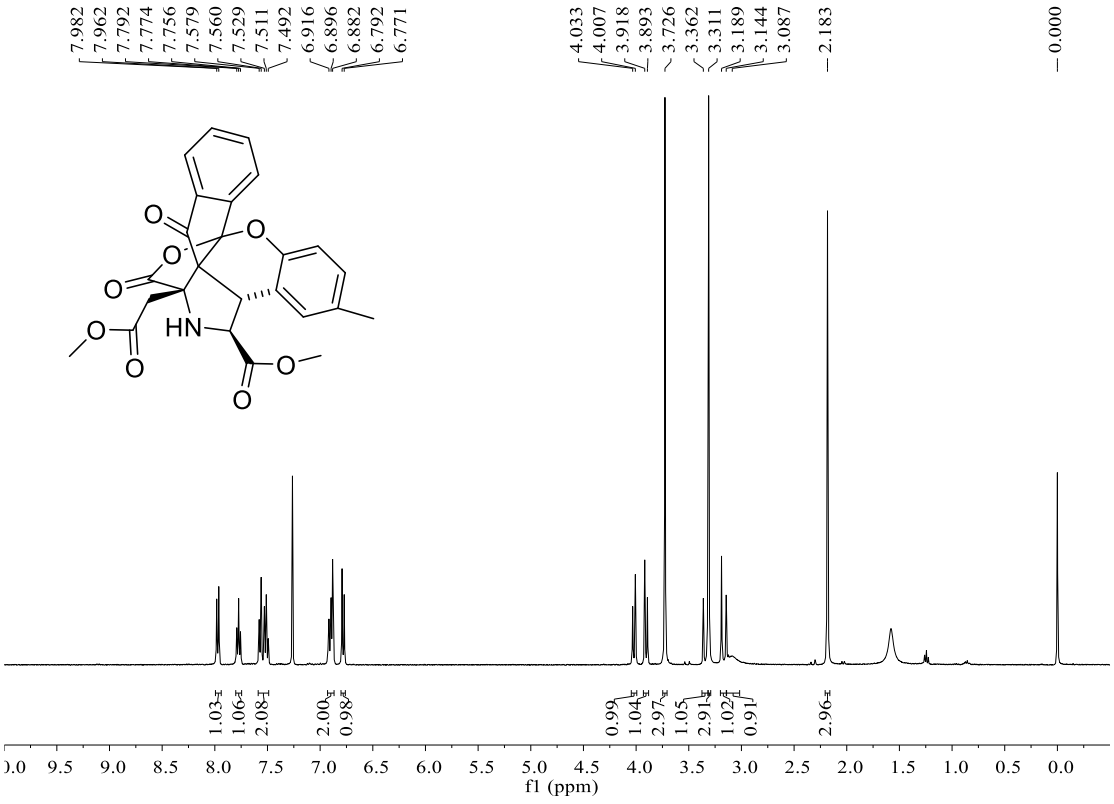
Ethyl *rel*-(1S,3S,3aS,8aR,13aS)-5,7-dichloro-1-(2-ethoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4k): white solid, 76%, m.p. 208-209 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.0 Hz, 1H, ArH), 7.83-7.79 (m, 1H, ArH), 7.60-7.54 (m, 1H, ArH), 7.20 (d, *J* = 2.4 Hz, 1H, ArH), 7.00 (d, *J* = 2.4 Hz, 1H, ArH), 4.30-4.22 (m, 1H, CH), 4.19-4.10 (m, 1H, CH), 3.97-3.94 (m, 1H, CH), 3.92-3.85 (m, 2H, CH_2), 3.76-3.68 (m, 1H, CH), 3.34 (d, *J* = 18.0 Hz, 1H, CH), 3.19 (d, *J* = 18.0 Hz, 1H, CH), 3.11 (br.s, 1H, NH), 1.24 (t, *J* = 7.2 Hz, 3H, CH_3), 1.01 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 197.6, 175.0, 169.8, 169.6, 145.4, 144.8, 137.5, 136.9, 132.2, 129.9, 128.9, 127.9, 126.5, 125.1, 124.8, 122.6, 110.6, 70.6, 66.9, 62.8, 62.0, 61.4, 51.2, 39.0, 14.1, 13.7; IR (KBr) υ: 3174, 2556, 2240, 1943, 1860, 1668, 1581, 1419, 1377, 1228, 1220, 1082, 1011, 954, 810, 720 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{26}H_{22}Cl_2NO_8$ ($[M+H]^+$): 546.0717, Found: 546.0716.

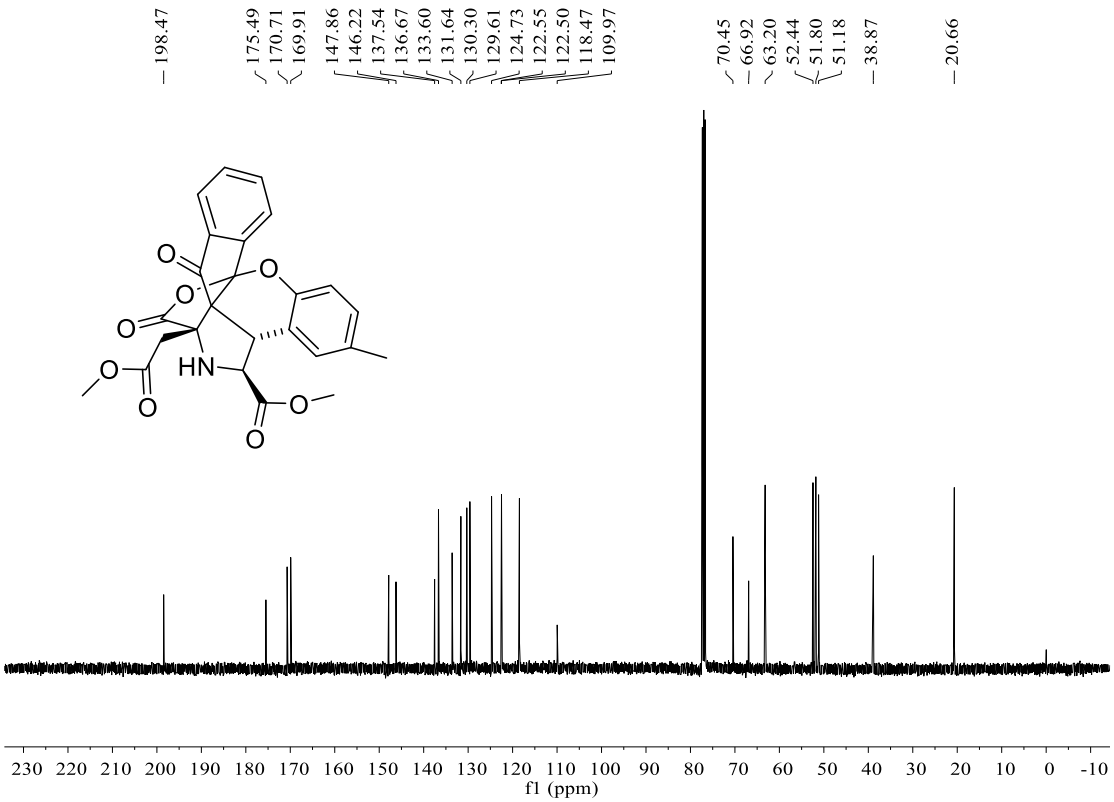


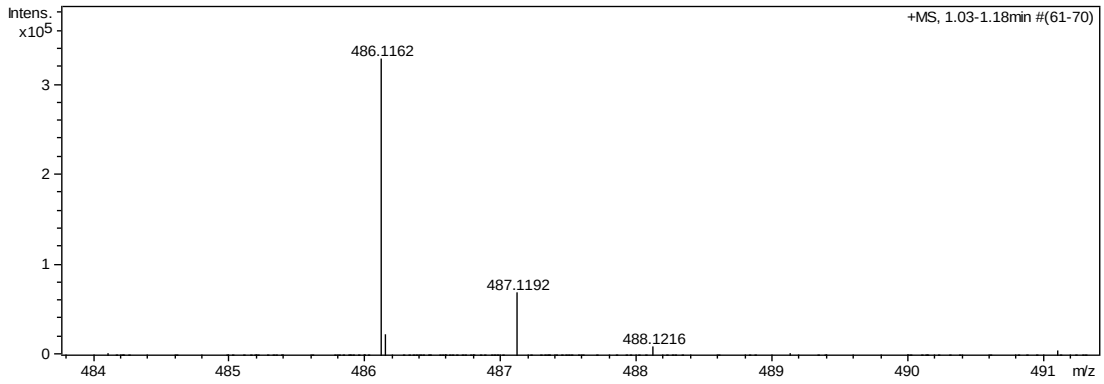

197.60
175.00
169.76
169.64
145.36
144.80
137.51
136.93
132.19
129.89
128.87
127.91
126.50
125.11
124.80
122.56
110.58
70.58
66.89
62.83
61.95
61.35
51.22
39.00
14.06
13.68
Cl
Cl
HN
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.39-0.51min #(23-30)
546.0716
548.0690
547.0746
549.0720
550.0678
551.6309
542
544
546
548
550
552
554
m/z

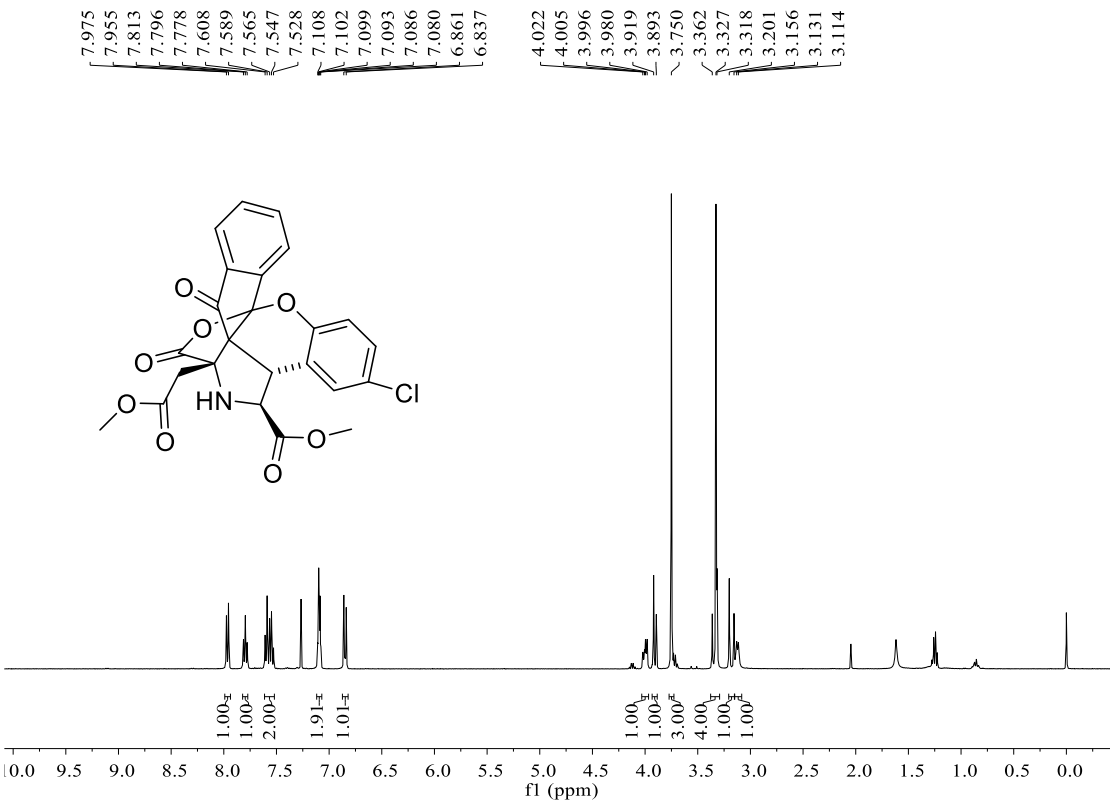
Methyl *rel*-(1S,3S,3aS,8aR,13aS)-1-(2-methoxy-2-oxoethyl)-5-methyl-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4l): white solid, 69%, m.p. 155-156 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 8.0 Hz, 1H, ArH), 7.79-7.76 (m, 1H, ArH), 7.58-7.49 (m, 2H, ArH), 6.92-6.88 (m, 2H, ArH), 6.78 (d, *J* = 8.4 Hz, 1H, ArH), 4.02 (d, *J* = 10.4 Hz, 1H, CH), 3.91 (d, *J* = 10.0 Hz, 1H, CH), 3.73 (s, 3H, OCH_3), 3.34 (d, *J* = 18.0 Hz, 1H, CH), 3.31 (s, 3H, OCH_3), 3.17 (d, *J* = 18.0 Hz, 1H, CH), 3.09 (brs, 1H, NH), 2.18 (s, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.5, 175.5, 170.7, 170.0, 147.9, 146.2, 137.5, 136.7, 133.6, 131.6, 130.3, 129.6, 124.7, 122.6, 122.5, 118.5, 110.0, 70.5, 66.9, 63.2, 52.4, 51.8, 51.2, 38.9, 20.7; IR (KBr) υ: 2965, 1795, 1729, 1602, 1446, 1398, 1334, 1280, 1218, 1164, 1068, 1041, 977, 858, 746, 711 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{21}NNaO_8$ ($[M+Na]^+$): 486.1162, Found: 486.1162.

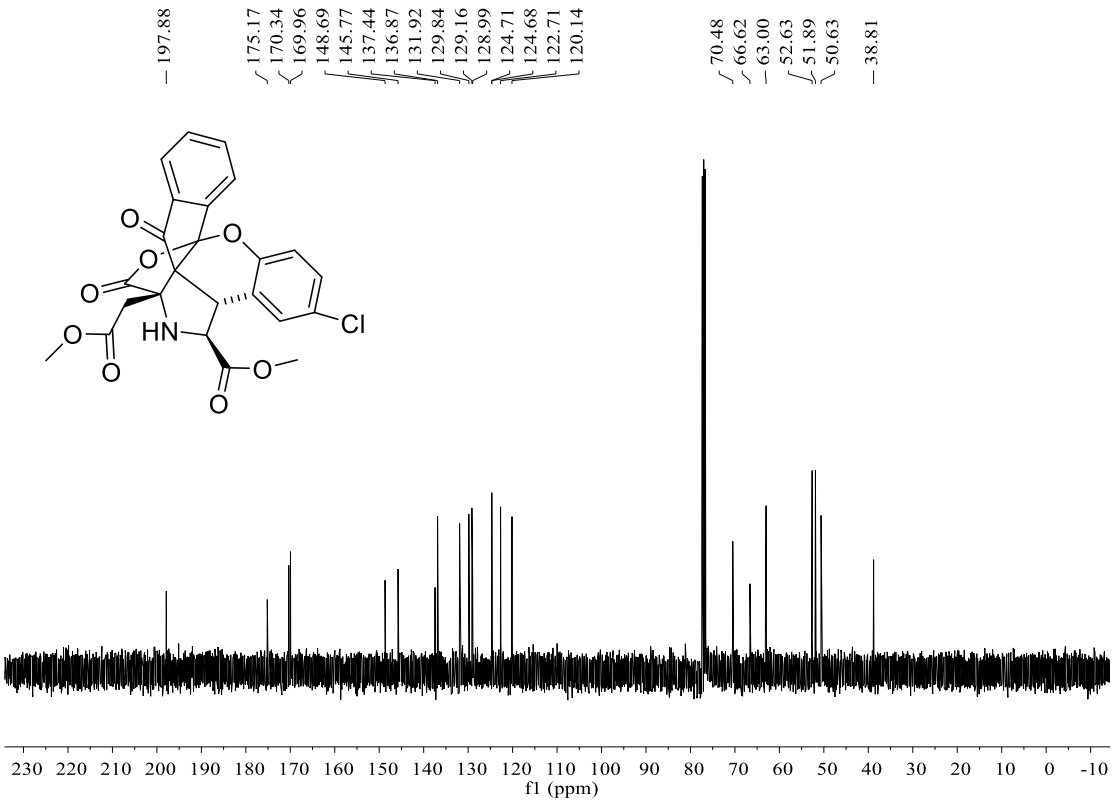


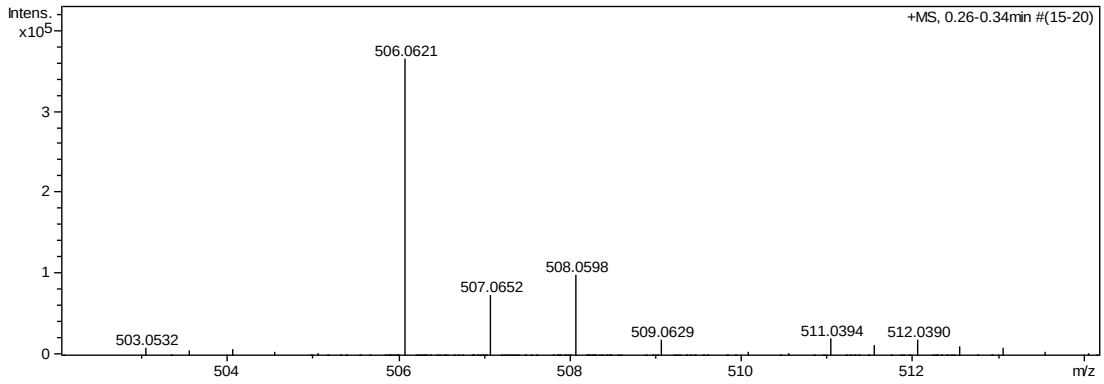

198.47
175.49
170.71
169.91
147.86
146.22
137.54
136.67
133.60
131.64
130.30
129.61
124.73
122.55
122.50
118.47
109.97
70.45
66.92
63.20
52.44
51.80
51.18
38.87
20.66
O
O
O
O
O
HN
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 1.03-1.18min #(61-70)
486.1162
487.1192
488.1216
0
1
2
3
484
485
486
487
488
489
490
491
m/z

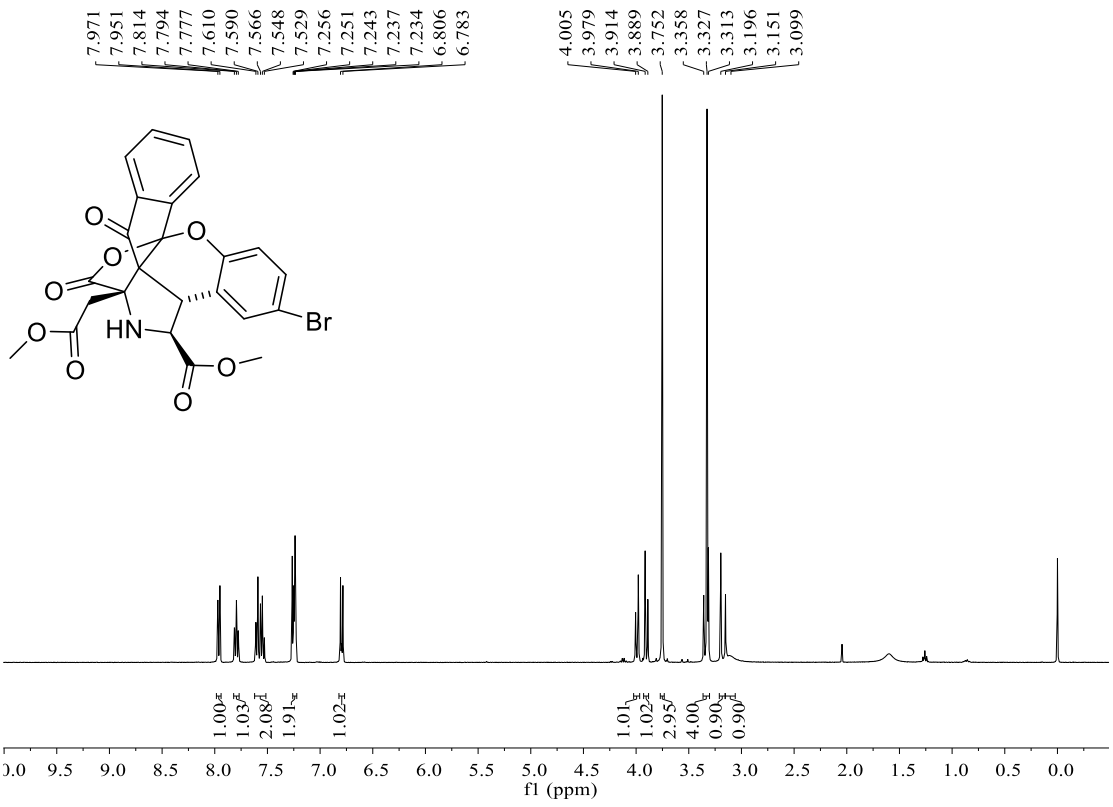
Methyl *rel*-(1S,3S,3aS,8aR,13aS)-5-chloro-1-(2-methoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4m): white solid, 40%, m.p. 207-208 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 8.0 Hz, 1H, ArH), 7.81-7.78 (m, 1H, ArH), 7.61-7.53 (m, 2H, ArH), 7.11-7.08 (m, 2H, ArH), 6.85 (d, *J* =9.6 Hz, 1H, ArH), 4.02-3.98 (m, 1H, CH), 3.91 (d, *J* = 10.4 Hz, 1H, CH), 3.75 (s, 3H, OCH_3), 3.34 (d, *J* = 17.6 Hz, 1H, CH), 3.33 (s, 3H, OCH_3), 3.18 (d, *J* = 18.0 Hz, 1H, CH), 3.12 (d, *J* = 6.8 Hz, 1H, NH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 197.9, 175.2, 170.3, 170.0, 148.7, 145.8, 137.4, 136.9, 131.9, 129.8, 129.2, 129.0, 124.7, 124.7, 122.7, 120.1, 70.5, 66.6, 63.0, 52.6, 51.9, 50.6, 38.8; IR (KBr) υ: 2960, 1793, 1725, 1611, 1445, 1370, 1335, 1280, 1220, 1160, 1062, 1045, 970, 855, 743, 716 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{18}ClNNaO_8$ ([M+Na]$^{+}$): 506.0613, Found: 506.0621.

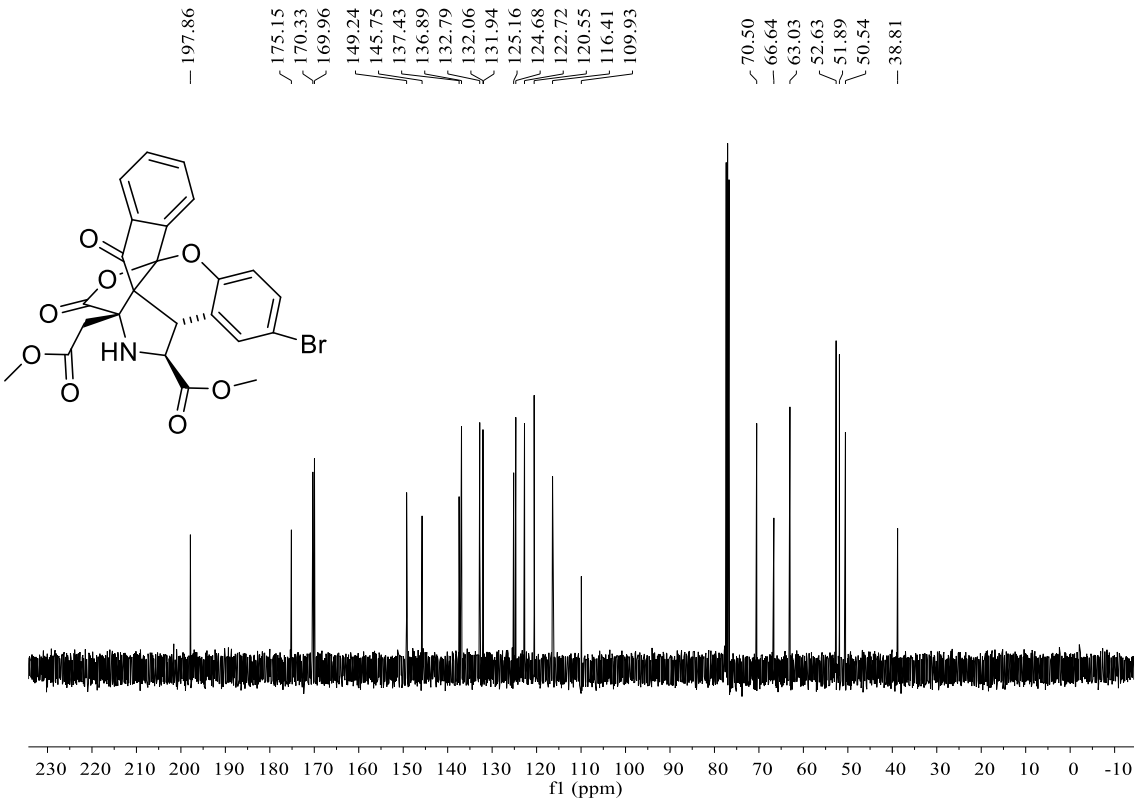


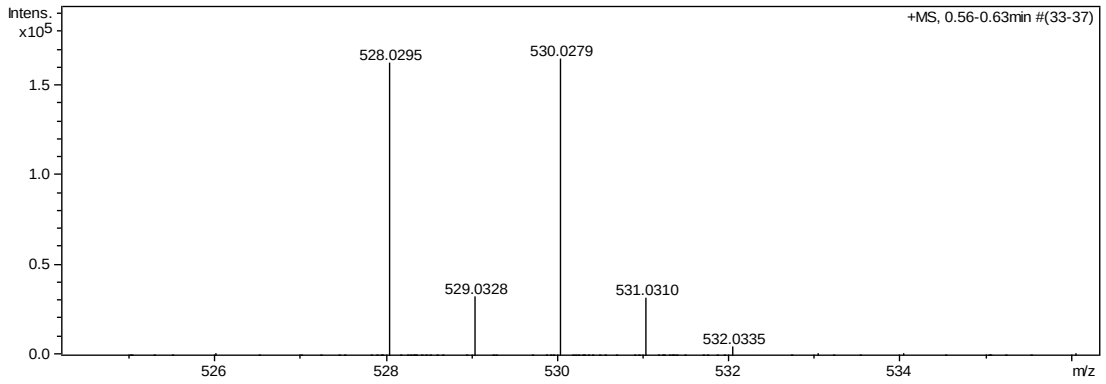

197.88
175.17
170.34
169.96
148.69
145.77
137.44
136.87
131.92
129.84
129.16
128.99
124.71
124.68
122.71
120.14
70.48
66.62
63.00
52.63
51.89
50.63
38.81
O
O
O
O
O
HN
Cl
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.26-0.34min #(15-20)
506.0621
508.0598
507.0652
503.0532
509.0629
511.0394
512.0390
0
1
2
3
504
506
508
510
512
m/z

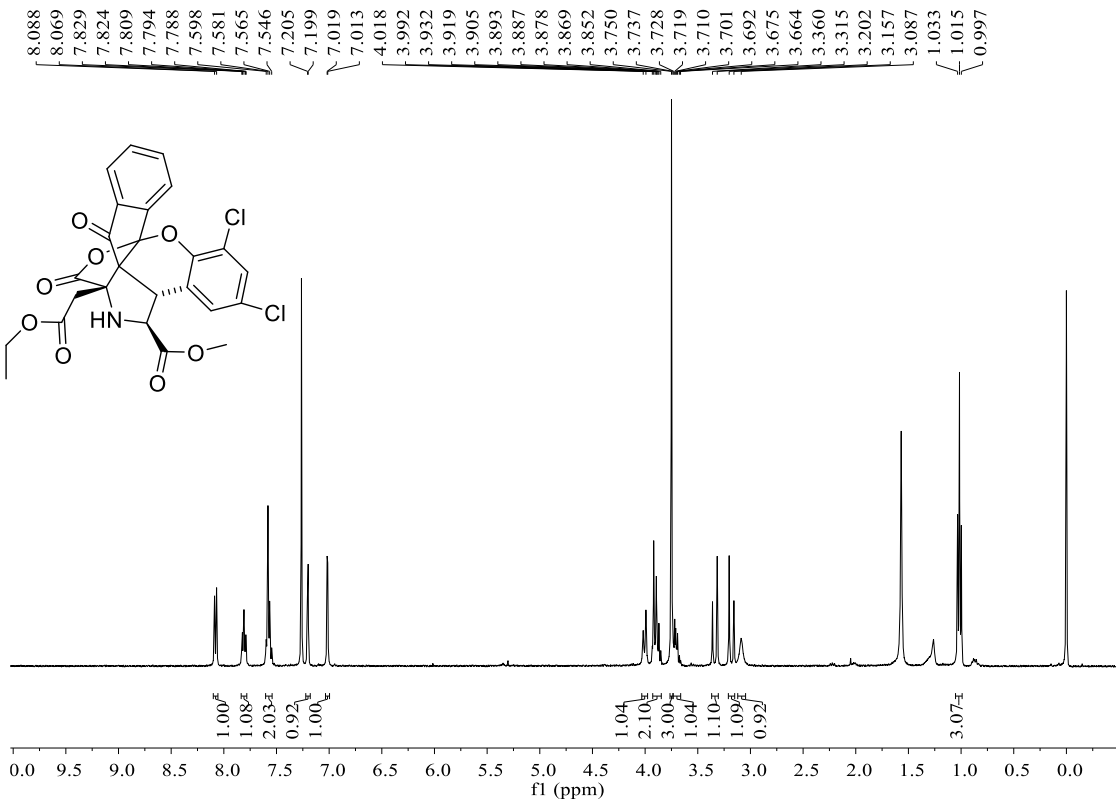
Methyl *rel*-(1S,3S,3aS,8aR,13aS)-5-bromo-1-(2-methoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4n): white solid, 57%, m.p. 209-210 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.0 Hz, 1H, ArH), 7.81-7.77 (m, 1H, ArH), 7.61-7.53 (m, 2H, ArH), 7.25-7.23 (m, 2H, ArH), 6.79 (d, *J* = 9.2 Hz, 1H, ArH), 3.99 (d, *J* = 10.4 Hz, 1H, CH), 3.90 (d, *J* = 10.0 Hz, 1H, CH), 3.75 (s, 3H, OCH_3), 3.33 (d, *J* = 18.0 Hz, 1H, C H), 3.32 (s, 3H, OCH_3), 3.17 (d, *J* = 18.0 Hz, 1H, CH), 3.10 (br.s, 1H, NH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 197.9, 175.1, 170.3, 17.0, 149.2, 145.8, 137.4, 136.9, 132.8, 132.1, 131.9, 125.2, 124.7, 122.7, 120.5, 116.4, 109.9, 70.5, 66.6, 63.0, 52.6, 51.9, 50.5, 38.8; IR (KBr) υ: 2961, 1799, 1727, 1622, 1440, 1377, 1330, 1284, 1222, 1168, 1069, 1047, 978, 856, 749, 722cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{19}BrNO_8$ ([M+H]$^{+}$): 528.0289, Found: 528.0295.

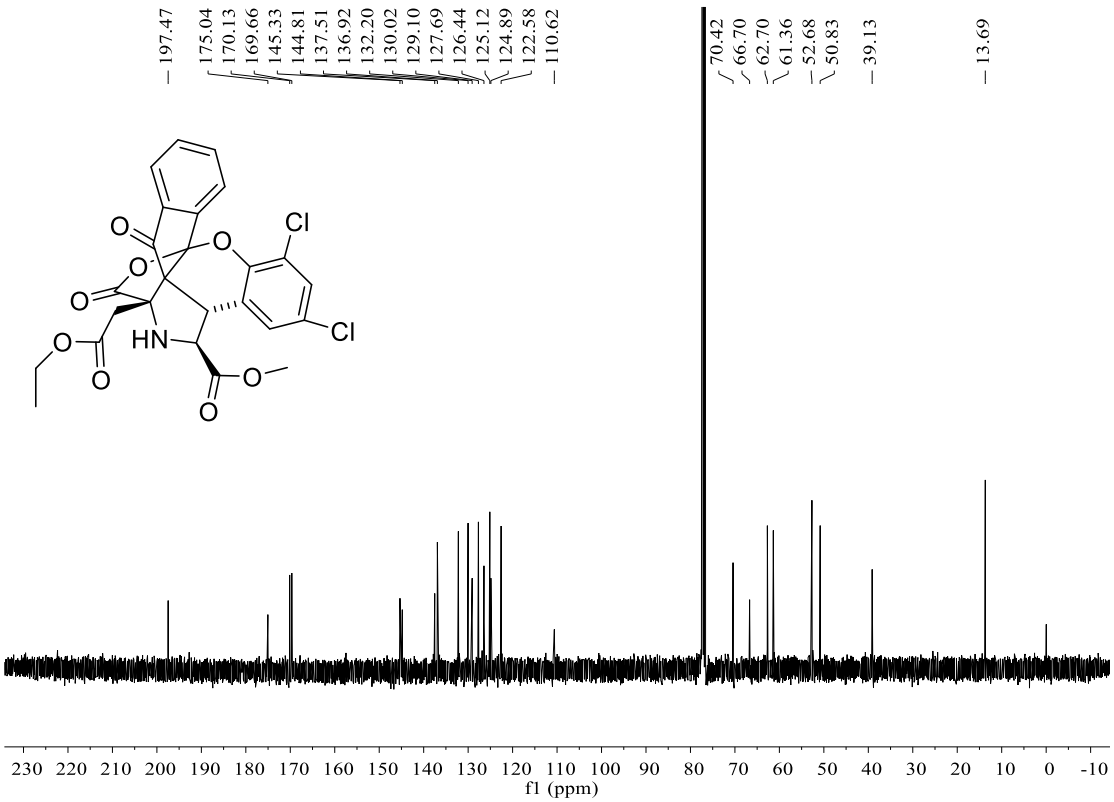


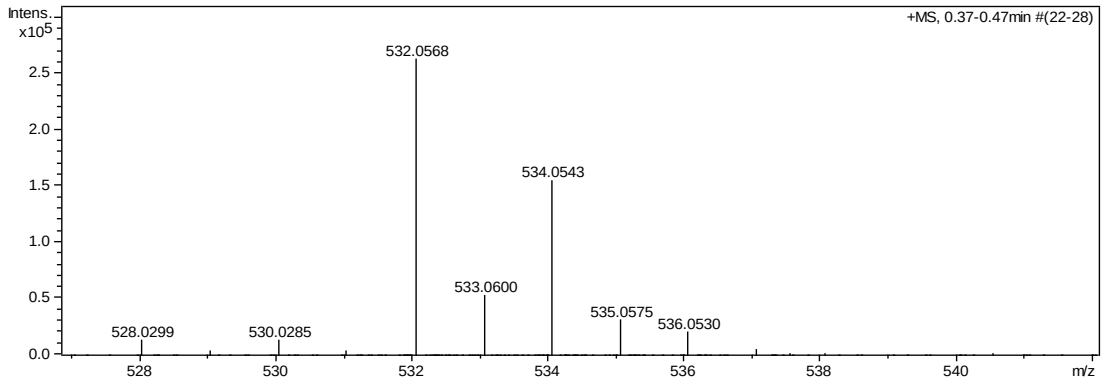

197.86
175.15
170.33
169.96
149.24
145.75
137.43
136.89
132.79
132.06
131.94
125.16
124.68
122.72
120.55
116.41
109.93
70.50
66.64
63.03
52.63
51.89
50.54
38.81
O
O
O
O
O
HN
Br
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.56-0.63min #(33-37)
528.0295
530.0279
529.0328
531.0310
532.0335
1.5
1.0
0.5
0.0
526
528
530
532
534
m/z

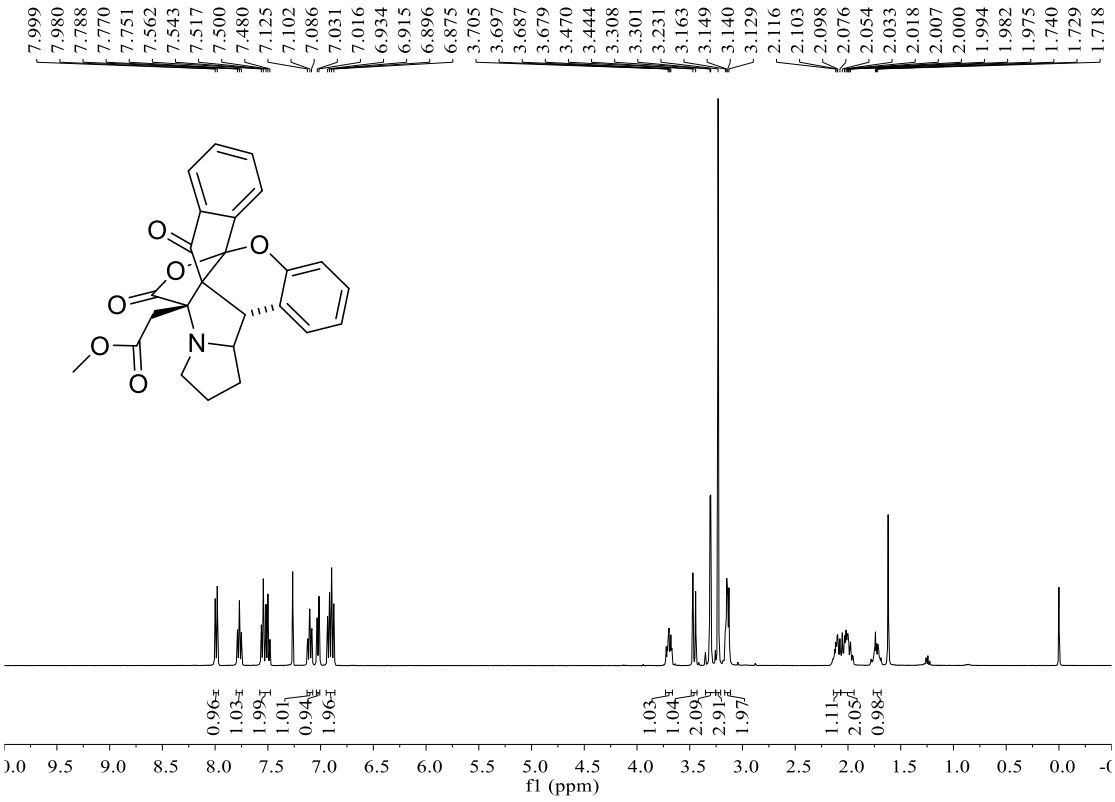
Methyl *rel*-(1S,3S,3aS,8aR,13aS)-5,7-dichloro-1-(2-ethoxy-2-oxoethyl)-13,15-dioxo-1,2,3,3a-tetrahydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrole-3-carboxylate (4o): white solid, 61%, m.p. 228-229 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, *J* = 7.6 Hz, 1H, ArH), 7.83-7.79 (m, 1H, ArH), 7.60-7.55 (m, 2H, ArH), 7.20 (d, *J* = 2.4 Hz, 1H, ArH), 7.02 (d, *J* = 2.4 Hz, 1H, ArH), 4.01 (d, *J* = 10.4 Hz, 1H, CH), 3.93-3.85 (m, 2H, CH_2), 3.75 (s, 3H, OCH_3), 3.74-3.66 (m, 1H, CH), 3.34 (d, *J* = 18.0 Hz, 1H, CH), 3.18 (d, *J* = 18.0 Hz, 1H, CH), 3.09 (br.s, 1H, NH), 1.02 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 197.5, 175.0, 170.1, 169.7, 145.3, 144.8, 137.5, 136.9, 132.2, 130.0, 129.1, 127.7, 126.4, 125.1, 124.9, 122.6, 110.6, 70.4, 66.7, 62.7, 61.4, 52.7, 50.8, 39.1, 13.7; IR (KBr) υ: 2958, 1790, 1722, 1607, 1439, 1366, 1337, 1288, 1227, 1165, 1060, 1043, 965, 854, 740 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{20}Cl_2NO_8$ ($[M+H]^+$): 532.0560, Found: 532.0568.

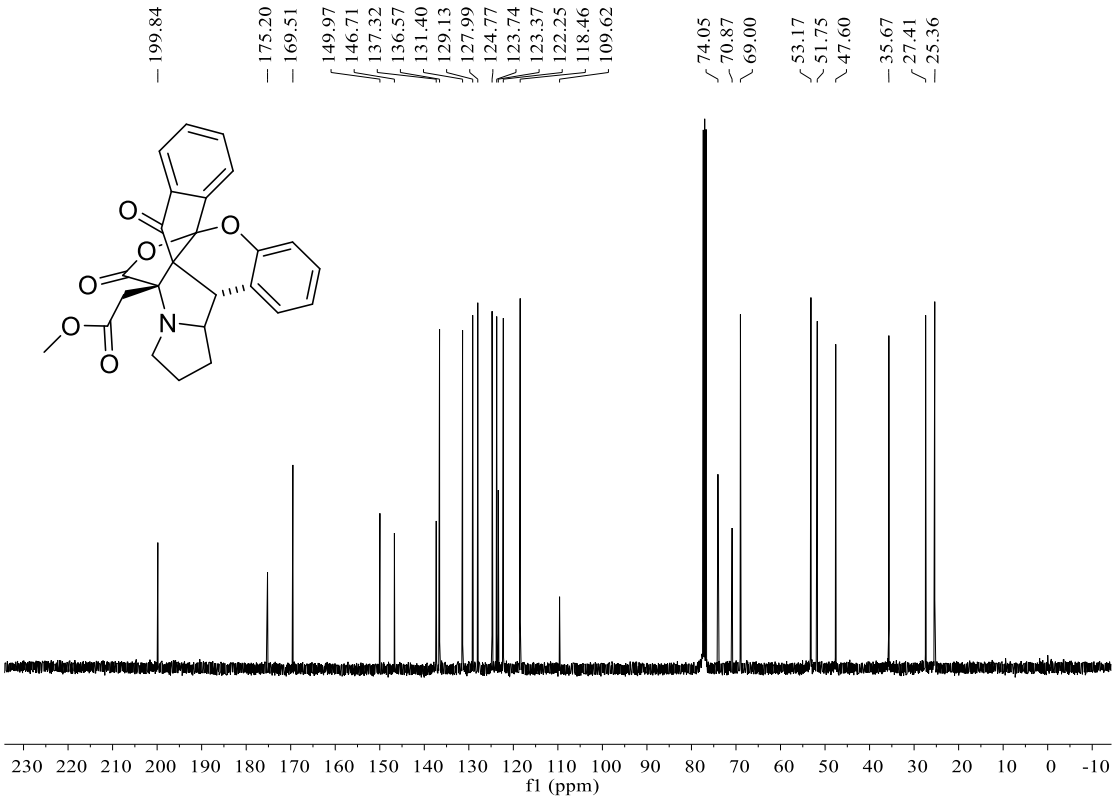


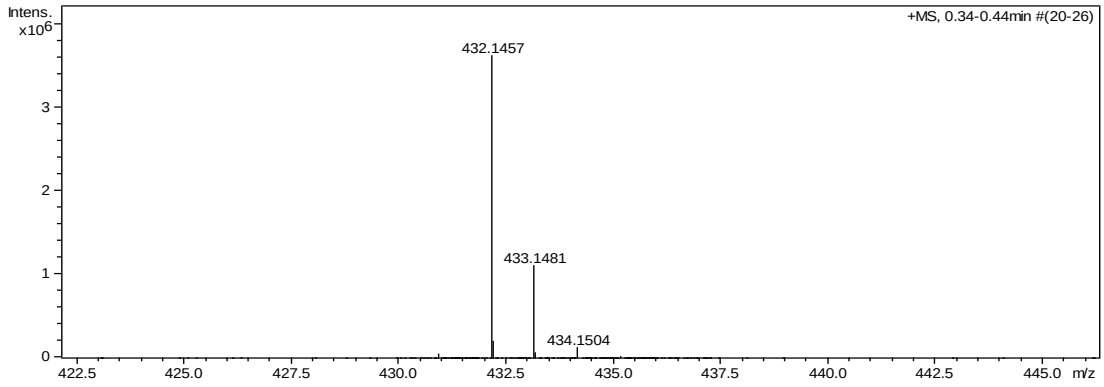

197.47
175.04
170.13
169.66
145.33
144.81
137.51
136.92
132.20
130.02
129.10
127.69
126.44
125.12
124.89
122.58
110.62
70.42
66.70
62.70
61.36
52.68
50.83
39.13
13.69
O
O
O
O
Cl
Cl
HN
O
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.37-0.47min #(22-28)
532.0568
534.0543
533.0600
535.0575
536.0530
528.0299
530.0285
2.5
2.0
1.5
1.0
0.5
0.0
528
530
532
534
536
538
540
m/z

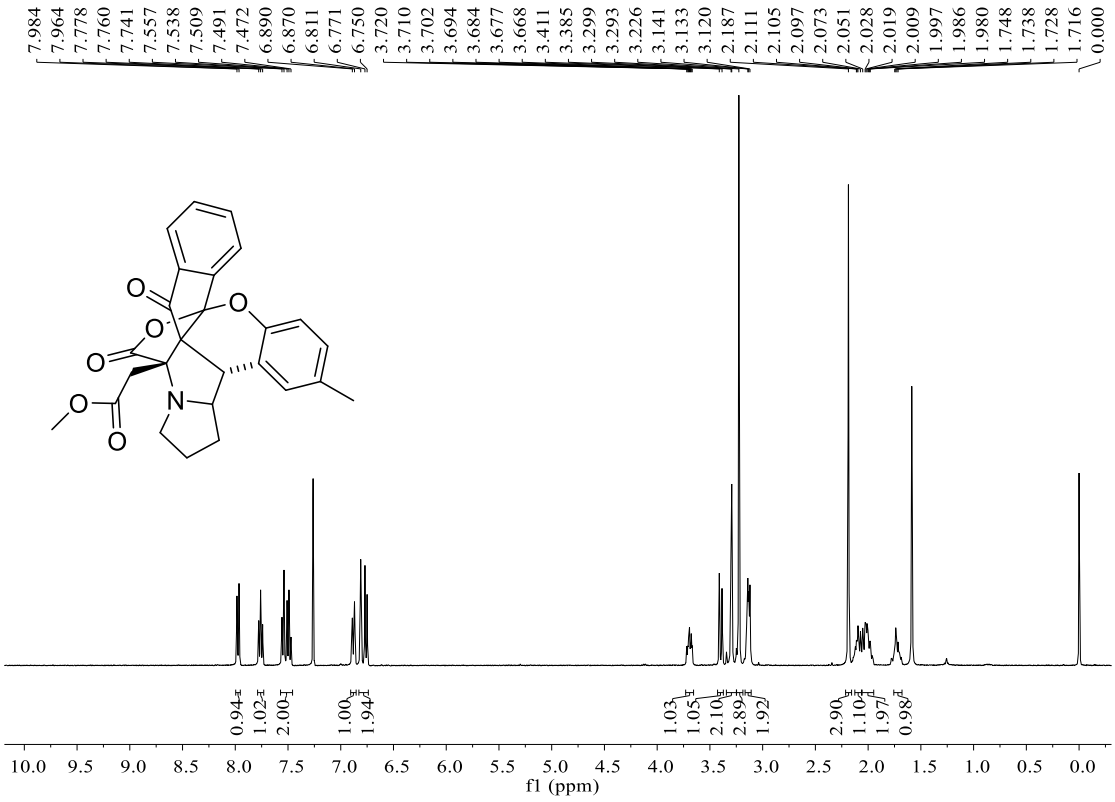
Methyl 2-(*rel*-(3bS,8aR,13aS,14S)-13,16-dioxo-2,3,3a,3b-tetrahydro-1*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1',2':2,3]chromeno[4,3-a]pyrrolizin-14-yl)acetate (6a): white solid, 67%, m.p. 190-191 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (d, *J* = 7.6 Hz, 1H, ArH), 7.79-7.75 (m, 1H, ArH), 7.56-7.48 (m, 2H, ArH), 7.13-7.09 (m, 1H, ArH), 7.02 (d, *J* = 6.0 Hz, 1H, ArH), 6.93-6.88 (m, 2H, ArH), 3.72-3.67 (m, 1H, CH), 3.46 (d, *J* = 10.4 Hz, 1H, CH), 3.30 (dd, J_1 = 17.6 Hz, J_2 = 17.2 Hz, 2H, CH_2), 3.23 (s, 3H, OCH_3), 3.16-3.13 (m, 2H, CH_2), 2.13-2.08 (m, 1H, CH), 2.05-1.95 (m, 1H, CH_2), 1.75-1.69 (m, 1H, CH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 199.8, 175.2, 169.5, 150.0, 146.7, 137.3, 136.6, 131.4, 129.1, 128.0, 124.8, 123.7, 123.4, 122.3, 118.5, 109.6, 74.1, 70.9, 69.0, 53.2, 51.7, 47.6, 35.7, 27.4, 25.4; IR (KBr) υ: 2592, 2871, 1797, 1737, 1496, 1438, 1338, 1280, 1207, 1184, 1168, 1070, 1053, 971, 883, 782 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{22}NO_6$ ($[M+H]^+$): 432.1442, Found: 432.1457.

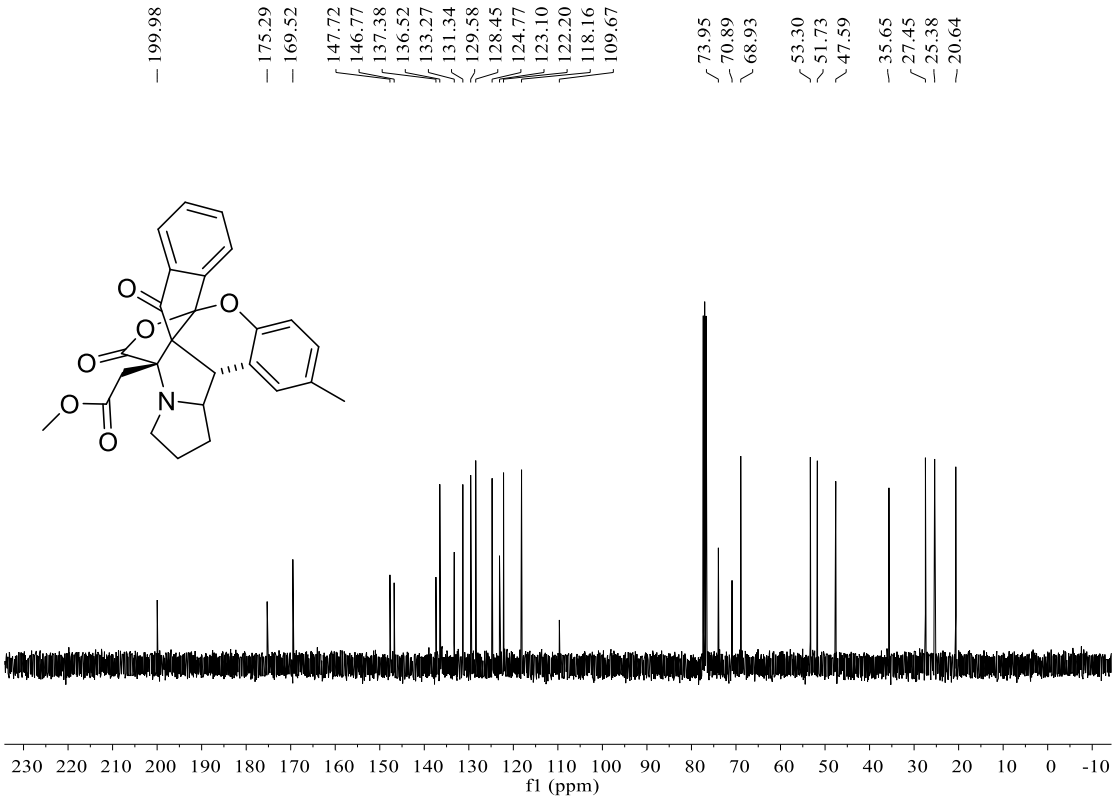


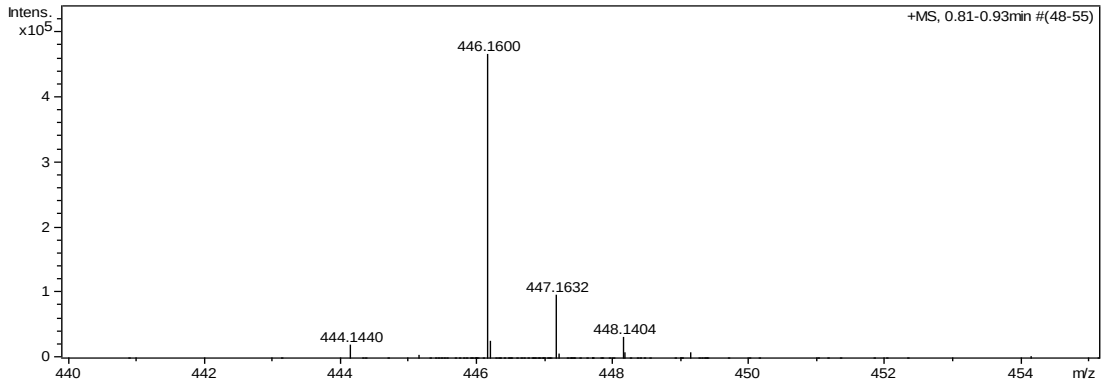

199.84
175.20
169.51
149.97
146.71
137.32
136.57
131.40
129.13
127.99
124.77
123.74
123.37
122.25
118.46
109.62
74.05
70.87
69.00
53.17
51.75
47.60
35.67
27.41
25.36
O
O
O
O
N
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^6
+MS, 0.34-0.44min #(20-26)
432.1457
433.1481
434.1504
0
1
2
3
422.5
425.0
427.5
430.0
432.5
435.0
437.5
440.0
442.5
445.0
m/z

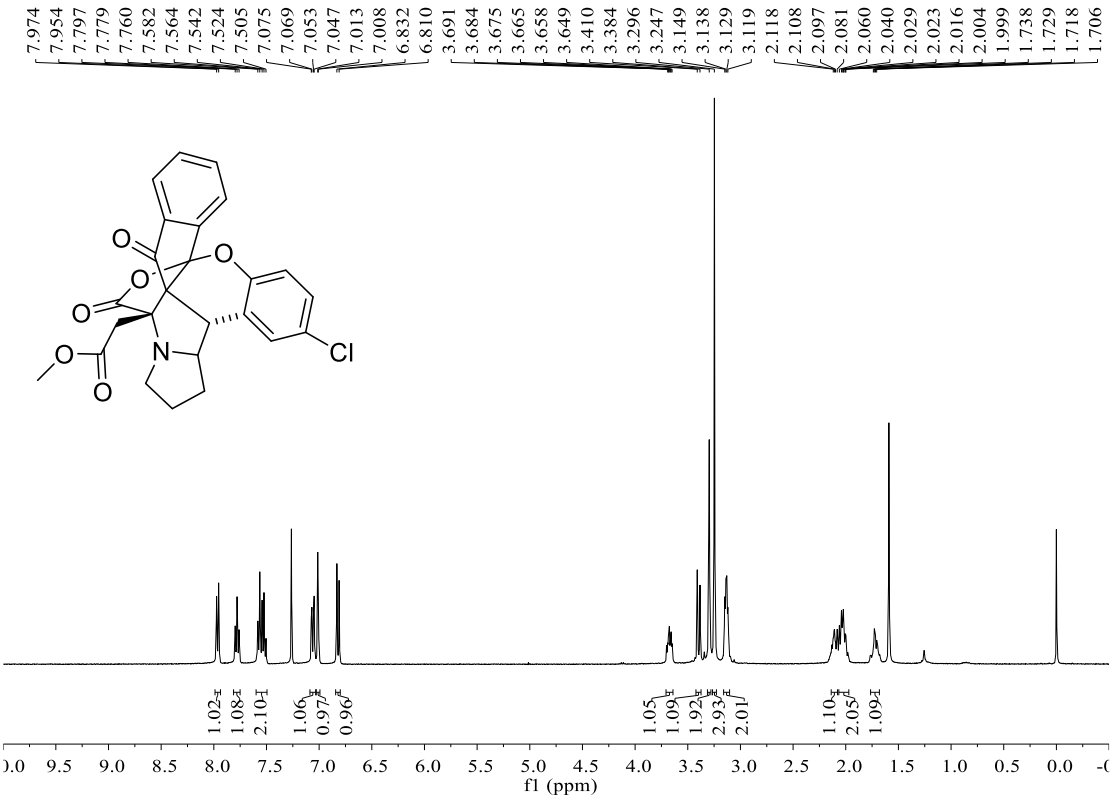
Methyl 2-(*rel*-(3bS,8aR,13aS,14S)-5-methyl-13,16-dioxo-2,3,3a,3b-tetrahydro-1*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1',2':2,3]chromeno[4,3-a]pyrrolizin-14-yl)acetate (6b): white solid, 51%, m.p. 215-216 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 8.0 Hz, 1H, ArH), 7.78-7.74 (m, 1H, ArH), 7.56-7.47 (m, 2H, ArH), 6.88 (d, *J* = 8.0 Hz, 1H ArH), 6.81-6.75 (m, 2H, ArH), 3.72-3.67 (m, 1H, CH), 3.40 (d, *J* = 10.4 Hz, 1H, CH), 3.30 (dd, J_1 = 17.6 Hz, J_2 = 17.6 Hz, 2H, CH_2), 3.23 (s, 3H, OCH_3), 3.14-3.12 (m, 2H, CH_2), 2.19 (s, 3H, CH_3), 2.12-2.07 (m, 1H, CH), 2.05-1.96 (m, 2H, CH_2), 1.75-1.69(m, 1H, CH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 200.0, 175.3, 169.5, 147.7, 146.8, 137.4, 136.5, 133.3, 131.3, 129.6, 128.4, 124.8, 123.1, 122.2, 118.2, 109.7, 74.0, 70.9, 68.9, 53.3, 51.3, 47.6, 35.7, 27.5, 25.4, 20.6; IR (KBr) υ: 2590, 2869, 1799, 1730, 1488, 1433, 1340, 1278, 1210, 1185, 1163, 1068, 1055, 974, 880, 780 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{26}H_{23}NO_6$ ([M+H]$^{+}$): 466.1598, Found: 466.1600.

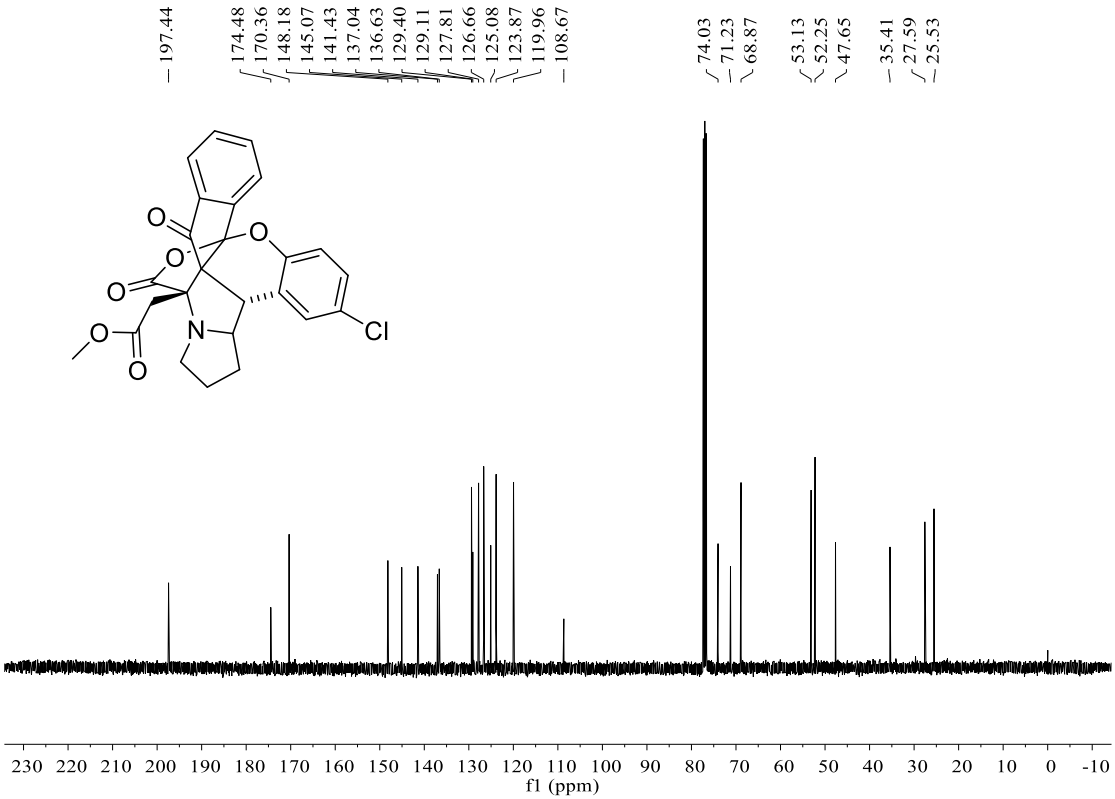


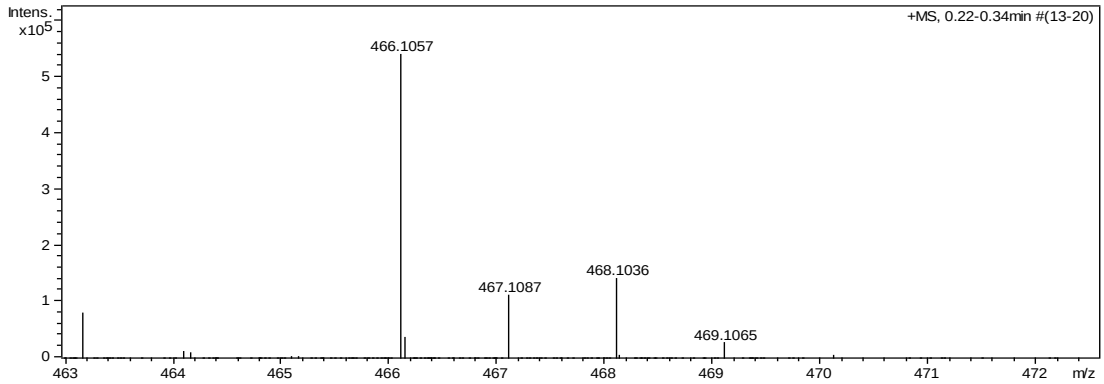

199.98
175.29
169.52
147.72
146.77
137.38
136.52
133.27
131.34
129.58
128.45
124.77
123.10
122.20
118.16
109.67
73.95
70.89
68.93
53.30
51.73
47.59
35.65
27.45
25.38
20.64
O
O
O
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.81-0.93min #(48-55)
446.1600
447.1632
448.1404
444.1440
0
1
2
3
4
440
442
444
446
448
450
452
454
m/z

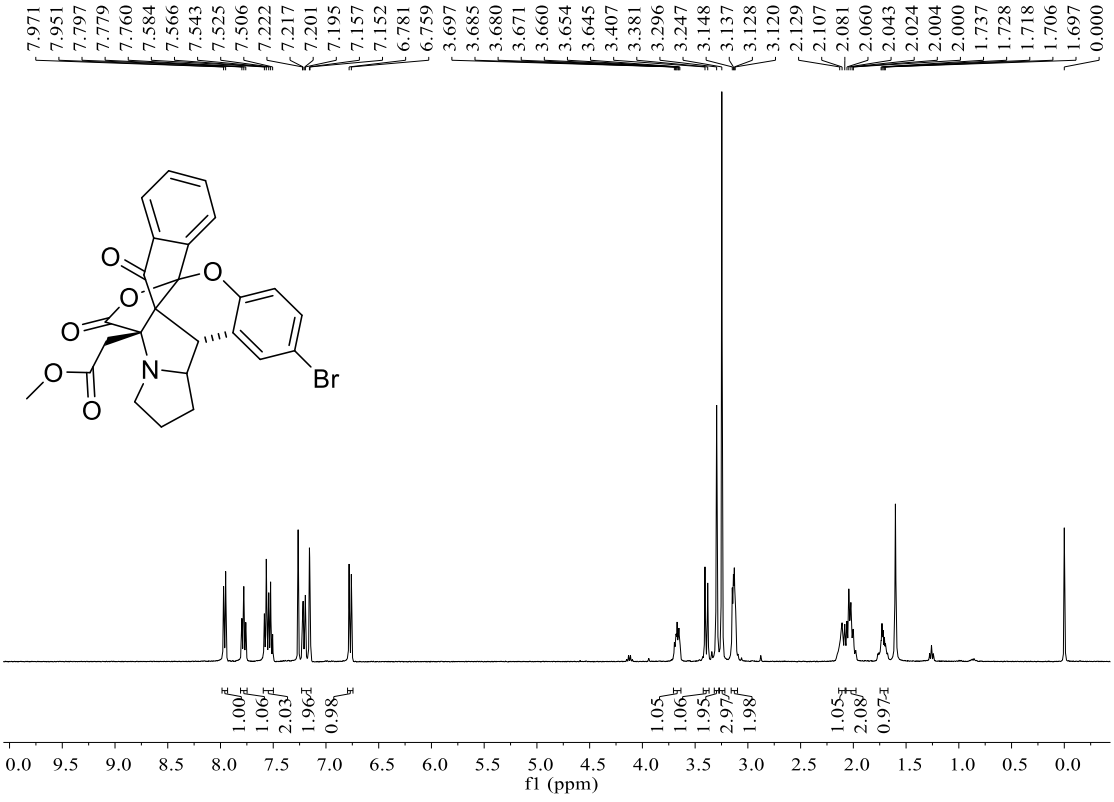
Methyl 2-(*rel*-(3bS,8aR,13aS,14S)-5-chloro-13,16-dioxo-2,3,3a,3b-tetrahydro-1*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1',2':2,3]chromeno[4,3-a]pyrrolizin-14-yl)acetate (6c): white solid, 64%, m.p. 209-210 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.0 Hz, 1H, ArH), 7.80-7.76 (m, 1H, ArH), 7.58-7.51 (m, 2H, ArH), 7.08-7.05 (m, 1H, ArH), 7.01 (d, *J* = 2.0 Hz, 1H, ArH), 6.82 (d, *J* = 8.8 Hz, 1H, ArH), 3.70-3.65 (m, 1H, CH), 3.40 (d, *J* = 10.4 Hz, 1H, CH), 3.30 (s, 2H, CH_2), 3.25 (s, 3H, OCH_3), 3.15-3.12 (m, 2H, CH_2), 2.14-2.08 (m, 1H, CH), 2.06-1.98 (m, 2H, CH_2), 1.77-1.68 (m, 1H, CH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 197.4, 174.5, 170.4, 148.2, 145.1, 141.4, 137.0, 136.6, 129.4, 129.1, 127.8, 126.7, 125.1, 123.9, 120.0, 108.7, 74.0, 71.2, 68.9, 53.1, 52.2, 47.7, 35.4, 27.6, 25.5; IR (KBr) υ: 25957, 2873, 1792, 1731, 1496, 1434, 1339, 1285, 1204, 1187, 1170, 1071, 1054, 976, 881, 787 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{21}ClNO_6$ ($[M+H]^+$): 466.1052, Found: 466.1057.

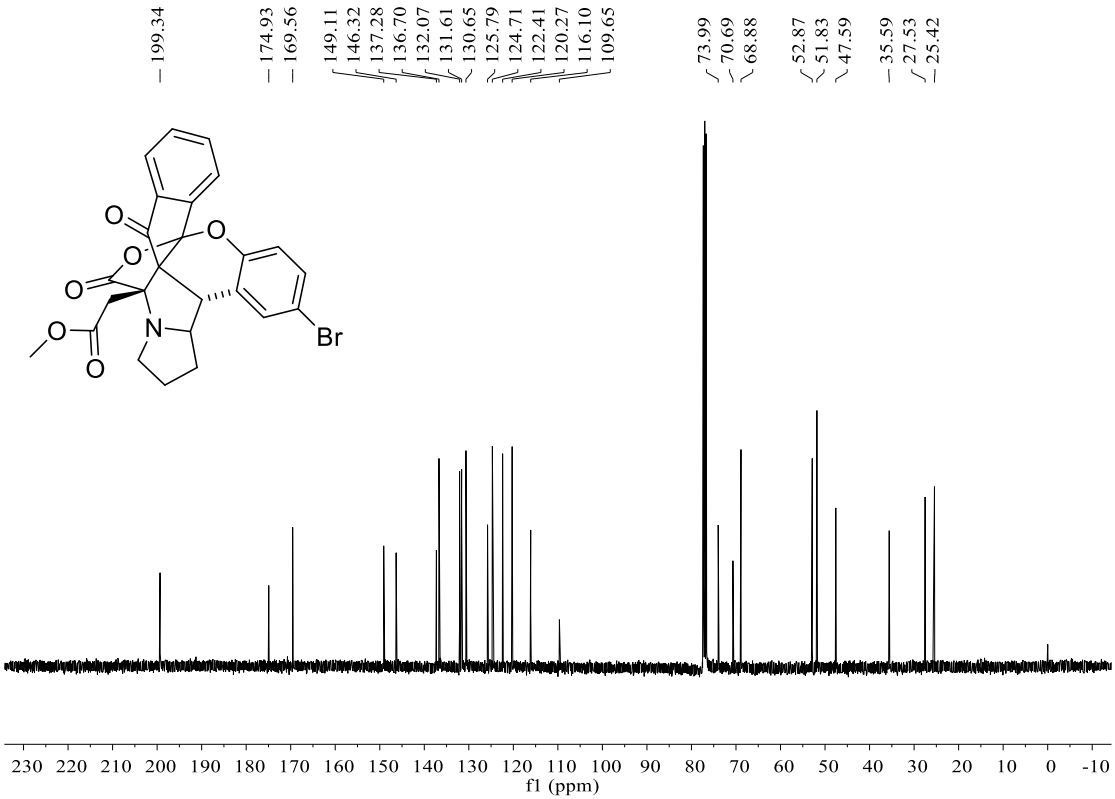


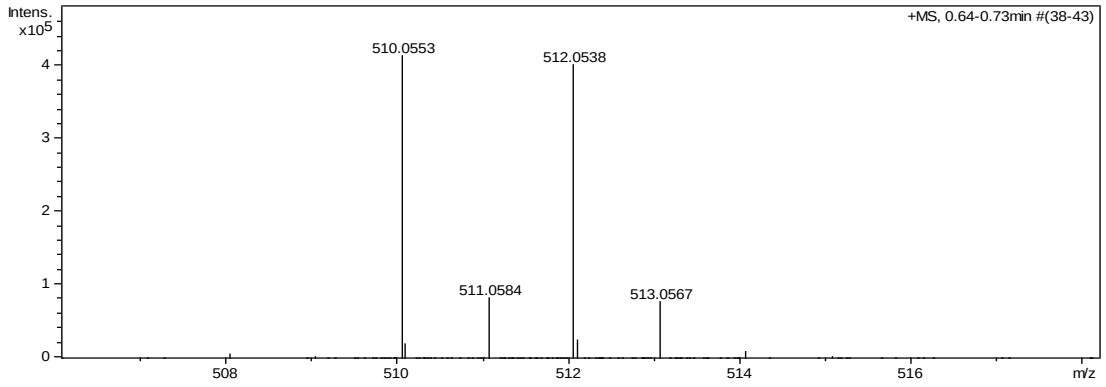

197.44
174.48
170.36
148.18
145.07
141.43
137.04
136.63
129.40
129.11
127.81
126.66
125.08
123.87
119.96
108.67
74.03
71.23
68.87
53.13
52.25
47.65
35.41
27.59
25.53
O
O
O
O
N
O
O
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.22-0.34min #(13-20)
466.1057
467.1087
468.1036
469.1065
0
1
2
3
4
5
463
464
465
466
467
468
469
470
471
472
m/z

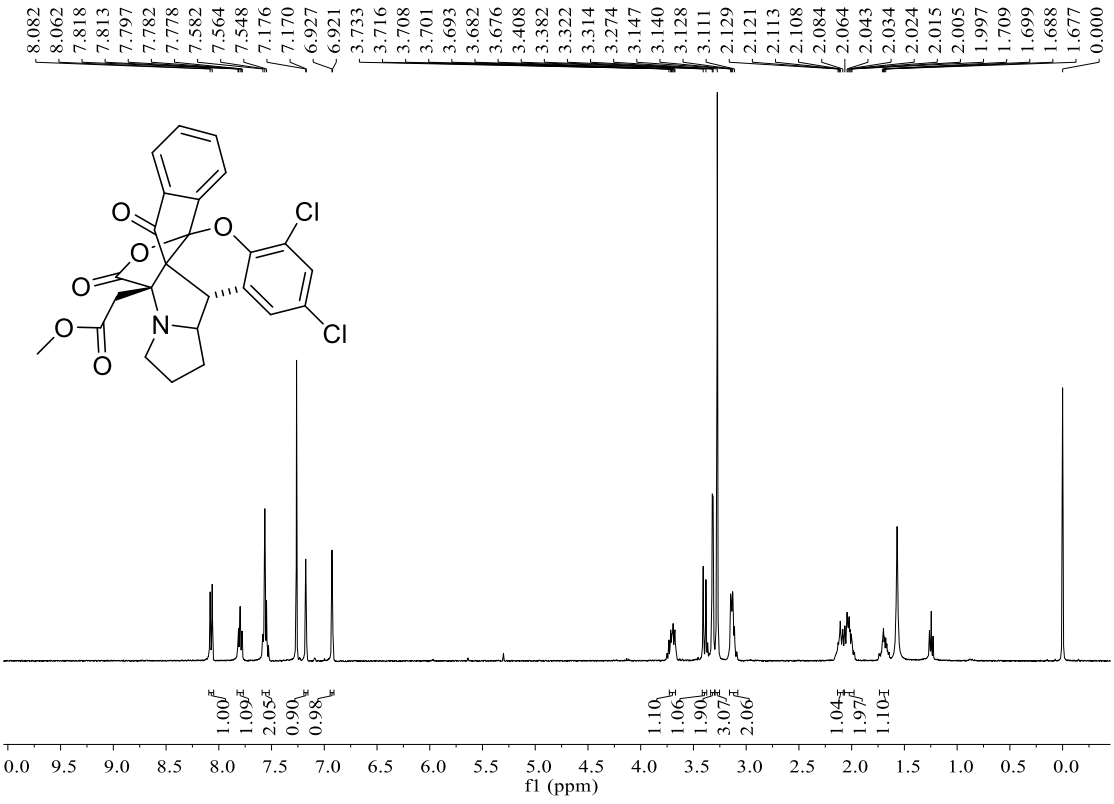
methyl *rel*-2-(*rel*-(3bS,8aR,13aS,14S)-5-bromo-13,16-dioxo-2,3,3a,3b-tetrahydro-1*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1',2':2,3]chromeno[4,3-a]pyrrolizin-14-yl)acetate (6d): white solid, 59%, m.p. 207-208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.0 Hz, 1H, ArH), 7.80-7.76 (m, 1H, ArH), 7.58-7.51 (m, 2H, ArH), 7.22-7.15 (m, 2H, ArH), 6.77 (d, *J* = 8.8 Hz, 1H ArH), 3.70-3.65 (m, 1H, CH), 3.40 (d, *J* = 10.4 Hz, 1H, CH), 3.30 (s, 2H, CH_2), 3.25 (s, 3H, OCH_3), 3.15-3.12 (m, 2H, CH_2), 2.13-2.08 (m, 1H, CH), 2.06-1.98 (m, 2H, CH_2), 1.74-1.68 (m, 1H, CH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 199.3, 175.0, 169.6, 149.1, 146.3, 137.3, 136.7, 132.1, 131.6, 130.6, 125.8, 124.7, 122.4, 120.3, 116.1, 109.7, 74.0, 70.7, 68.9, 52.9, 51.8, 47.6, 35.6, 27.5, 25.4; IR (KBr) υ: 2592, 2871, 1797, 1737, 1496, 1438, 1338, 1280, 1207, 1184, 1168, 1070, 1053, 971, 883, 782 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{21}BrNO_6$ ([M+H]$^+$): 510.0547, Found: 510.0553.

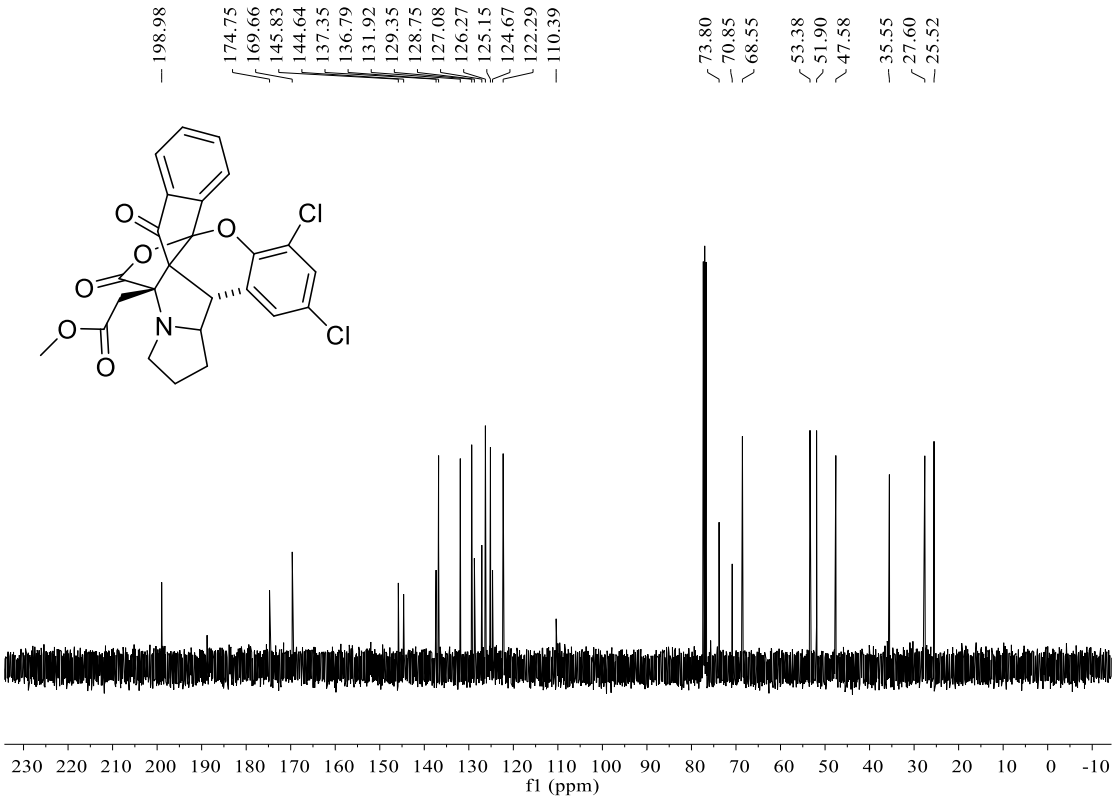


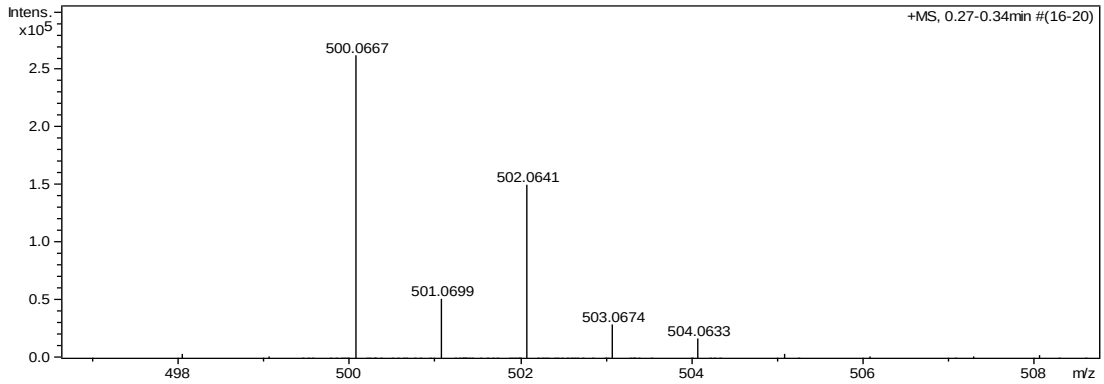

199.34
174.93
169.56
149.11
146.32
137.28
136.70
132.07
131.61
130.65
125.79
124.71
122.41
120.27
116.10
109.65
73.99
70.69
68.88
52.87
51.83
47.59
35.59
27.53
25.42
O
O
O
O
N
O
O
Br
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.64-0.73min #(38-43)
510.0553
512.0538
511.0584
513.0567
0
1
2
3
4
508
510
512
514
516
m/z

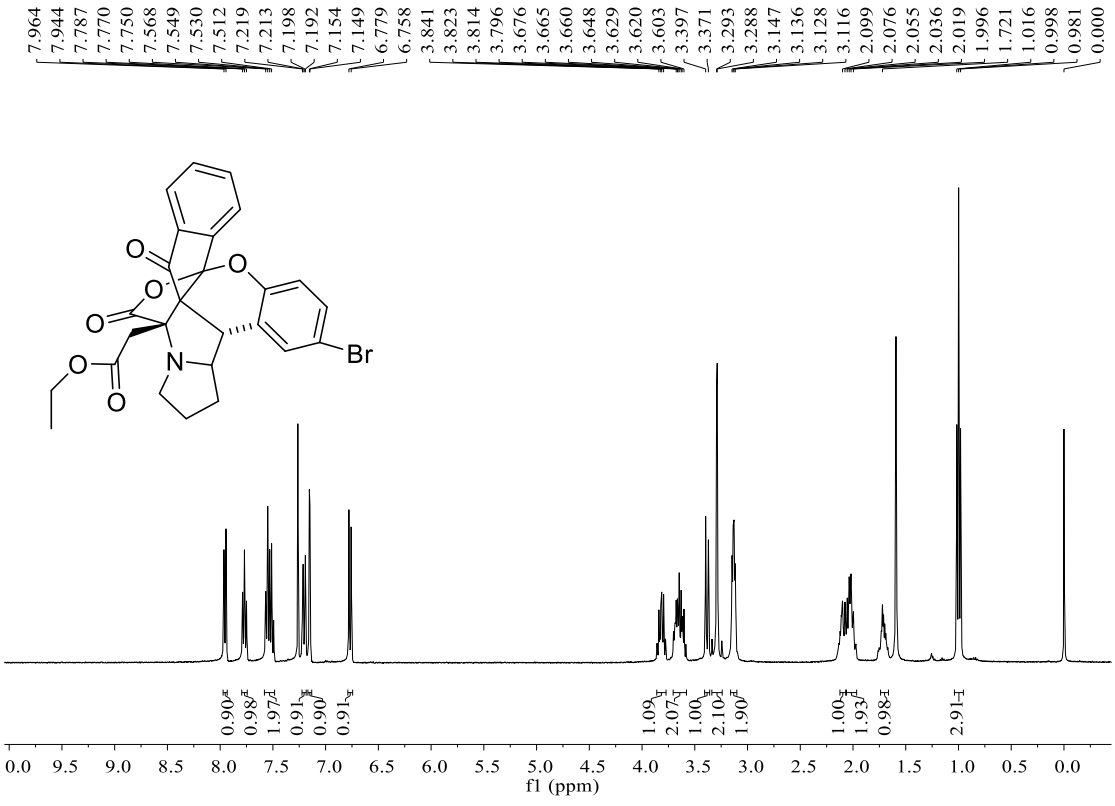
Methyl 2-(*rel*-(3bS,8aR,13aS,14S)-5,7-dichloro-13,16-dioxo-2,3,3a,3b-tetrahydro-1*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1',2':2,3]chromeno[4,3-a]pyrrolizin-14-yl)acetate (6e): white solid, 41%, m.p. 201-202 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.0 Hz, 1H, ArH), 7.82-7.78 (m, 1H, ArH), 7.58-7.53 (m, 2H, ArH), 7.17 (d, *J* = 2.4 Hz, 1H, ArH), 6.92 (d, *J* = 2.4 Hz, 1H, ArH), 3.73-3.67 (m, 1H, CH), 3.39 (d, *J* = 10.4 Hz, 1H, CH), 3.32 (d, *J* = 3.2 Hz, 2H, CH_2), 3.27 (s, 3H, OCH_3), 3.15-3.09 (m, 2H, CH_2), 2.15-2.08 (m, 1H, CH), 2.06-1.97 (m, 2H, CH_2), 1.74-1.65 (m, 1H, CH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 199.0, 174.8, 169.7, 145.8, 144.6, 137.4, 136.8, 131.9, 129.4, 128.8, 127.1, 126.3, 125.1, 124.7, 122.3, 110.4, 73.8, 70.8, 68.6, 53.4, 51.897, 47.6, 35.6, 27.6, 25.5; IR (KBr) υ: 2591, 2874 1795, 1735, 1490, 1432, 1334, 1289, 1206, 1187, 1167, 1073, 1057, 976, 886, 784 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{20}Cl_2NO_6$ ($[M+Na]^+$): 500.0662, Found: 500.0667.

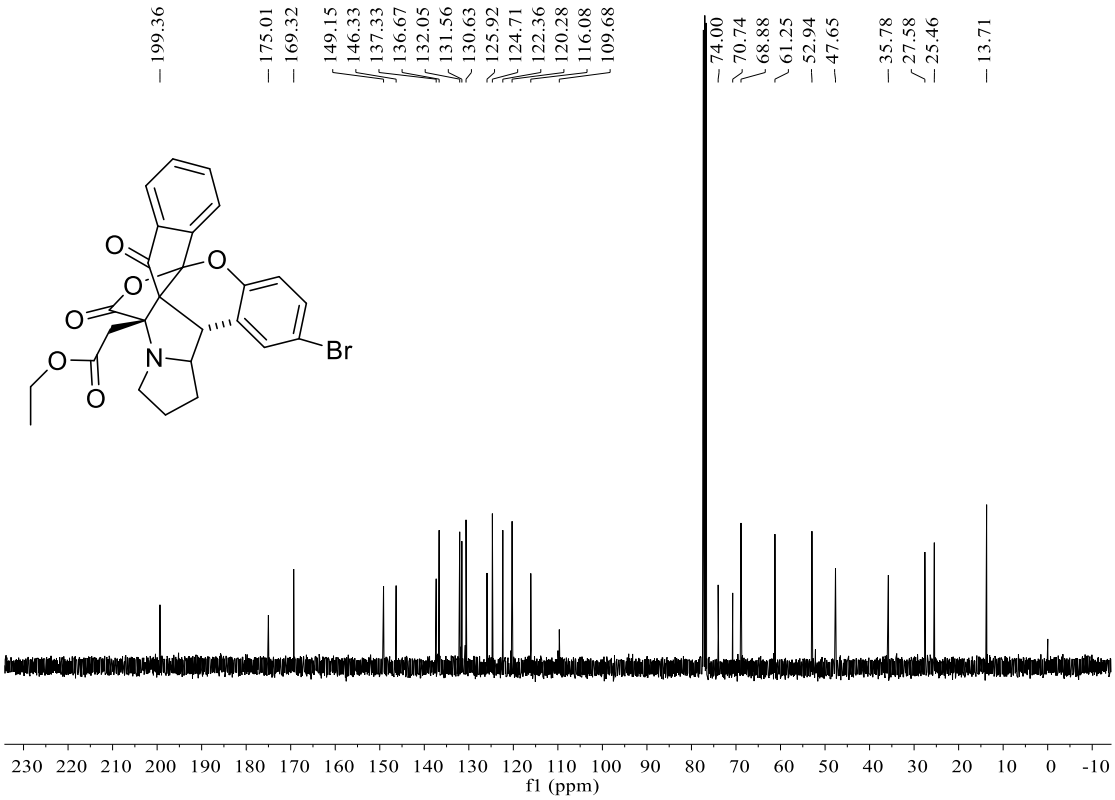


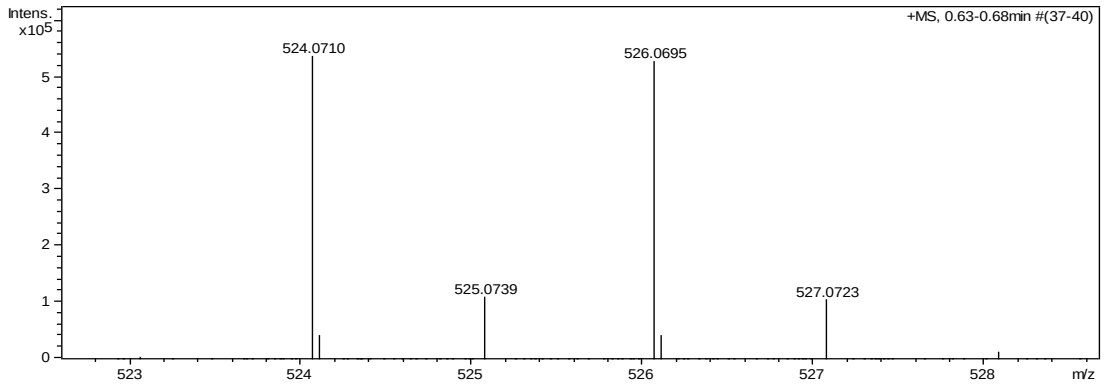

198.98
174.75
169.66
145.83
144.64
137.35
136.79
131.92
129.35
128.75
127.08
126.27
125.15
124.67
122.29
110.39
73.80
70.85
68.55
53.38
51.90
47.58
35.55
27.60
25.52
O
O
O
O
O
N
Cl
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.27-0.34min #(16-20)
500.0667
502.0641
501.0699
503.0674
504.0633
2.5
2.0
1.5
1.0
0.5
0.0
498
500
502
504
506
508
m/z

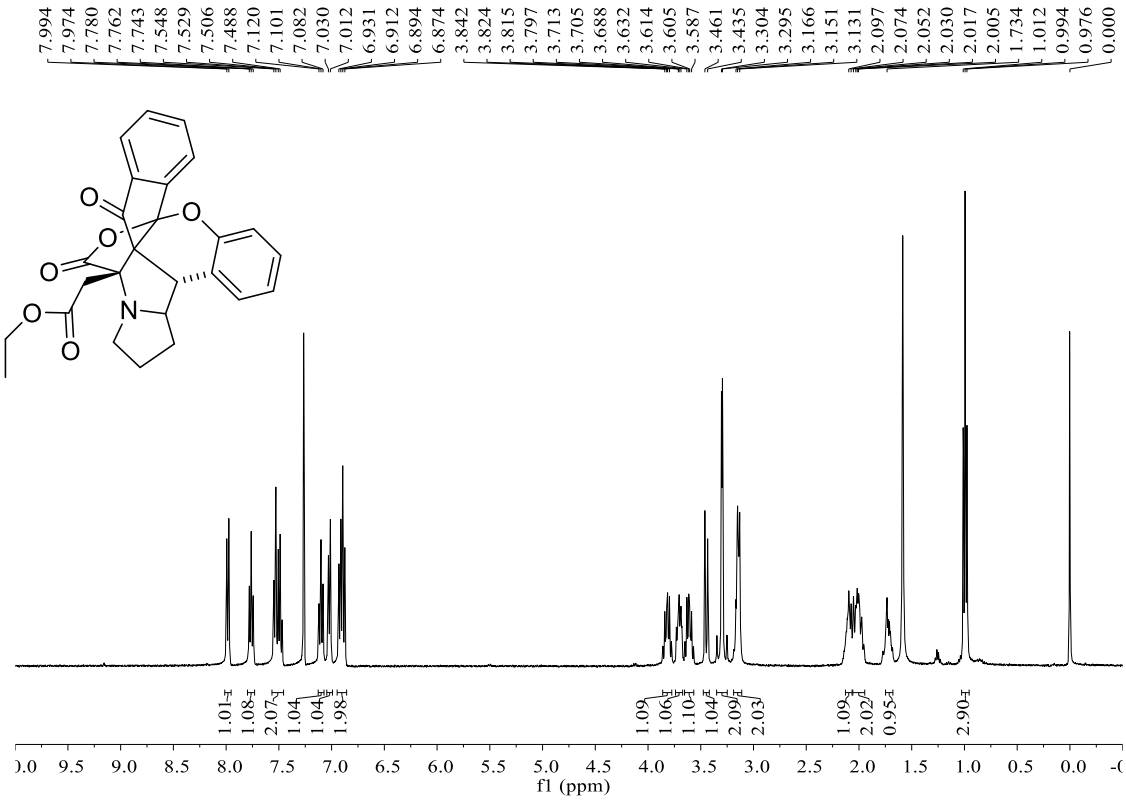
Ethyl 2-(*rel*-(3bS,8aR,13aS,14S)-5-bromo-13,16-dioxo-2,3,3a,3b-tetrahydro-1*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1',2':2,3]chromeno[4,3-a]pyrrolizin-14-yl)acetate (6f): white solid, 58%, m.p. 170-171 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 8.0 Hz, 1H, ArH), 7.79-7.75 (m, 1H, ArH), 7.57-7.49 (m, 2H, ArH), 7.22-7.19 (m, 1H, ArH), 7.15 (d, *J* = 2.0 Hz, 1H, ArH), 6.77 (d, *J* = 8.4 Hz, 1H, ArH), 3.86-3.78 (m, 1H, CH), 3.70-3.59 (m, 2H, CH_2), 3.38 (d, *J* = 10.4 Hz, 1H, CH), 3.29 (dd, J_1 = 17.6 Hz, J_2 = 17.6, 2H, CH_2), 3.15-3.12 (m, 2H, CH_2), 2.12-2.08 (m, 1H, CH), 2.06-1.97 (m, 2H, CH_2), 1.73-1.67 (m, 1H, CH), 1.00 (t, *J* = 2.0 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 199.4, 175.0, 169.3, 149.1, 146.3, 137.3, 136.7, 132.0, 131.6, 130.6, 125.9, 124.7, 122.3, 120.3, 116.1, 109.7, 74.0, 70.7, 68.9, 61.3, 52.9, 47.7, 35.8, 27.6, 25.5, 13.7; IR (KBr) υ: 2599, 2874, 1799, 1740, 1497, 1435, 1344, 1288, 1211, 1179, 1170, 1077, 1060, 965, 888, 779 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{26}H_{23}BrNO_6$ ([M+H]$^{+}$): 524.0703, Found:524.0710.

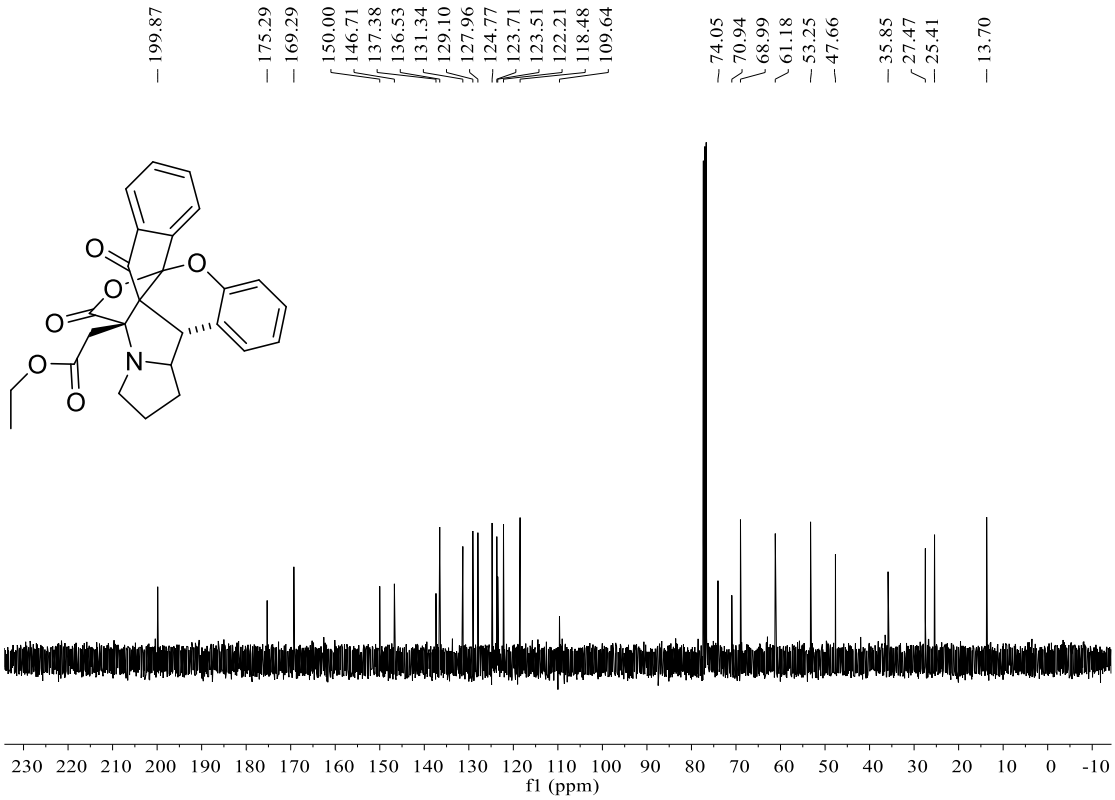


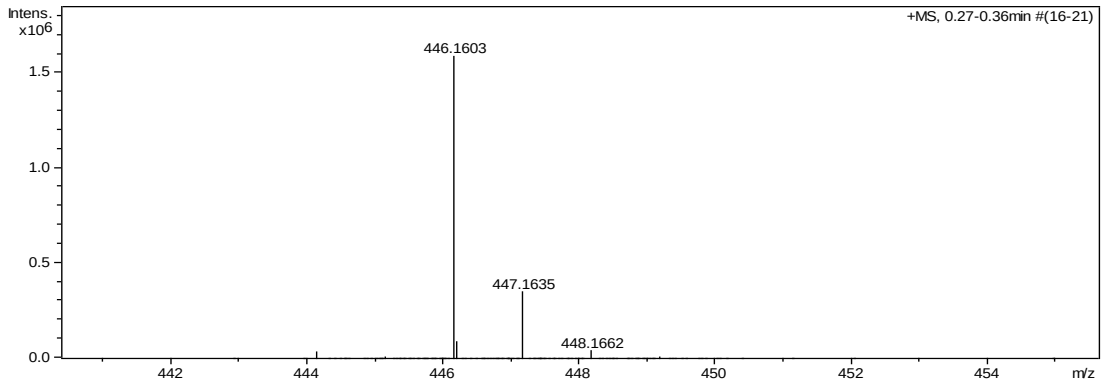

199.36
175.01
169.32
149.15
146.33
137.33
136.67
132.05
131.56
130.63
125.92
124.71
122.36
120.28
116.08
109.68
74.00
70.74
68.88
61.25
52.94
47.65
35.78
27.58
25.46
13.71
O
O
O
O
O
N
Br
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.63-0.68min #(37-40)
524.0710
526.0695
525.0739
527.0723
0
1
2
3
4
5
523
524
525
526
527
528
m/z

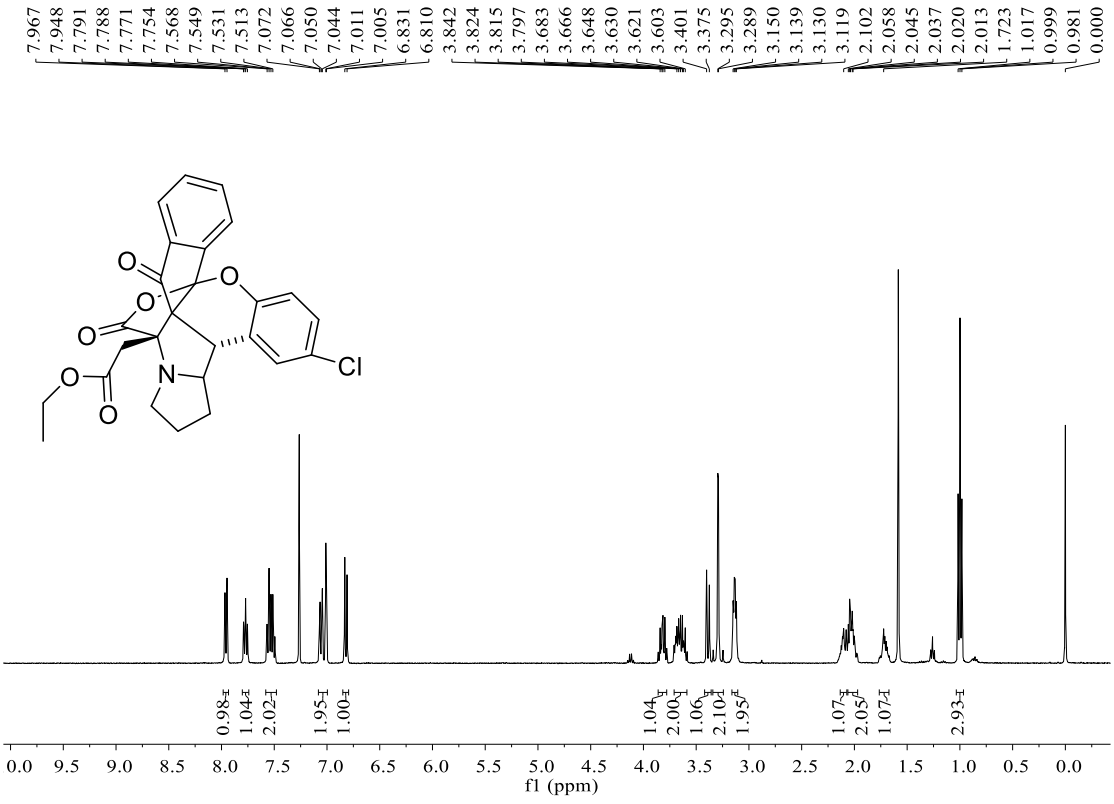
Ethyl 2-(*rel*-(3bS,8aR,13aS,14S)-13,16-dioxo-2,3,3a,3b-tetrahydro-1*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1',2':2,3]chromeno[4,3-a]pyrrolizin-14-yl)acetate (6g): white solid, 48%, m.p. 183-184 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.0 Hz, 1H, ArH), 7.78-7.43 (m, 1H, ArH), 7.55-7.47 (m, 1H, ArH), 7.12-7.08 (m, 1H, ArH), 7.02 (d, *J* = 7.2 Hz, 1H, ArH), 6.93-6,87 (m, 2H, ArH), 3.86-3.78 (m, 1H, CH), 3.73-3.68 (m, 1H, CH), 3.45 (d, *J* = 10.4 Hz, 1H, CH), 3.30 (dd, J_1 = 17.2 Hz, J_2 = 17.6, 2H, CH_2), 3.19-3.13 (m, 2H, CH_2), 2.12-2.07 (m, 1H, CH), 2.05-1.95 (m, 2H, CH_2), 1.74-1.68 (m, 1H, CH), 0.99 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 199.9, 175.3, 169.3, 150.0, 146.7, 137.3, 136.5, 131.3, 129.1, 128.0, 124.8, 123.7, 123.5, 122.2, 118.5, 109.6, 74.0, 70.9, 69.0, 61.2, 53.3, 47.67, 35.8, 27.5, 25.4, 13.7; IR (KBr) υ: 2588, 2868, 1790, 1744, 1500, 1430, 1331, 1287, 1202, 1187, 1160, 1068, 1066, 972, 880, 787 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{26}H_{24}NO_6$ ([M+H]$^{+}$): 446.1598, Found: 446.1603.

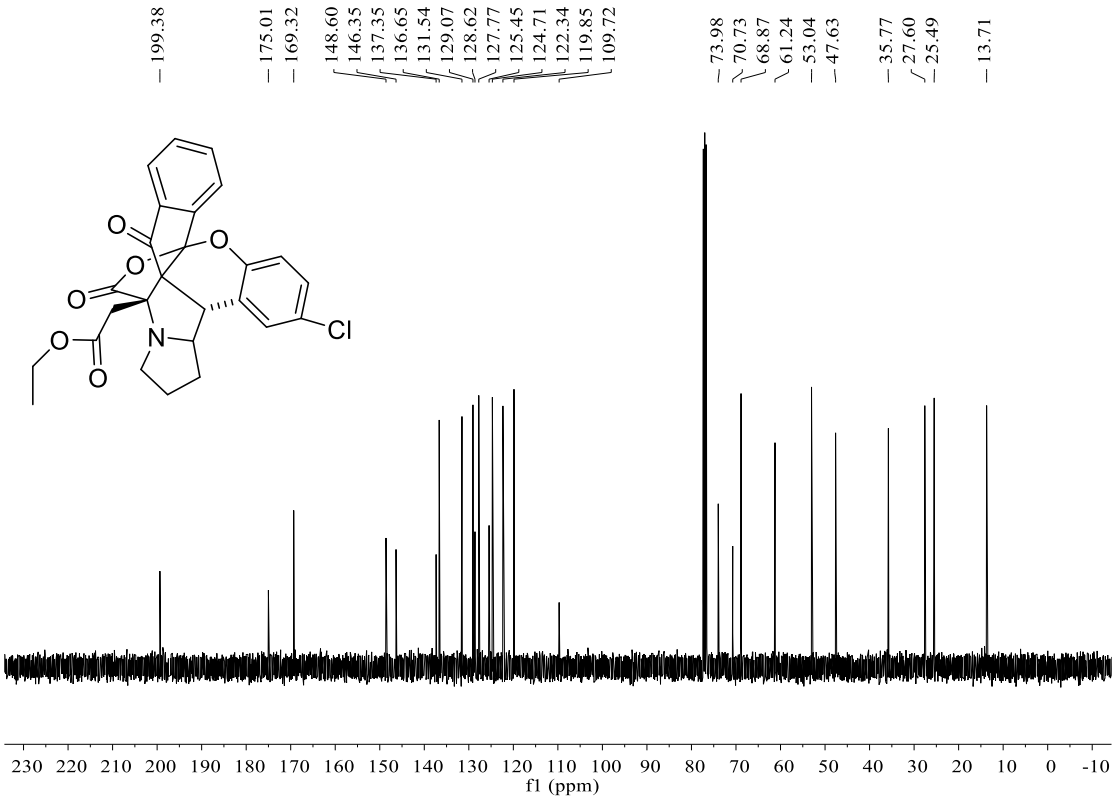


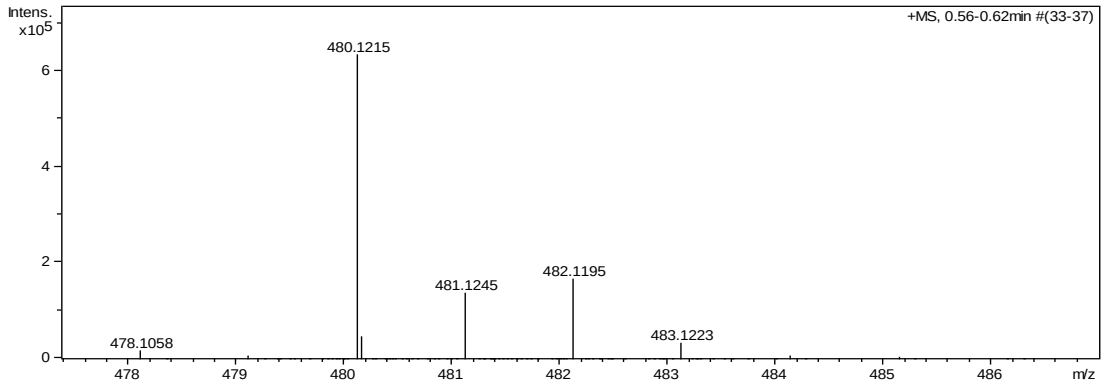

199.87
175.29
169.29
150.00
146.71
137.38
136.53
131.34
129.10
127.96
124.77
123.71
123.51
122.21
118.48
109.64
74.05
70.94
68.99
61.18
53.25
47.66
35.85
27.47
25.41
13.70
O
O
O
O
O
N
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^6
+MS, 0.27-0.36min #(16-21)
446.1603
447.1635
448.1662
1.5
1.0
0.5
0.0
442
444
446
448
450
452
454
m/z

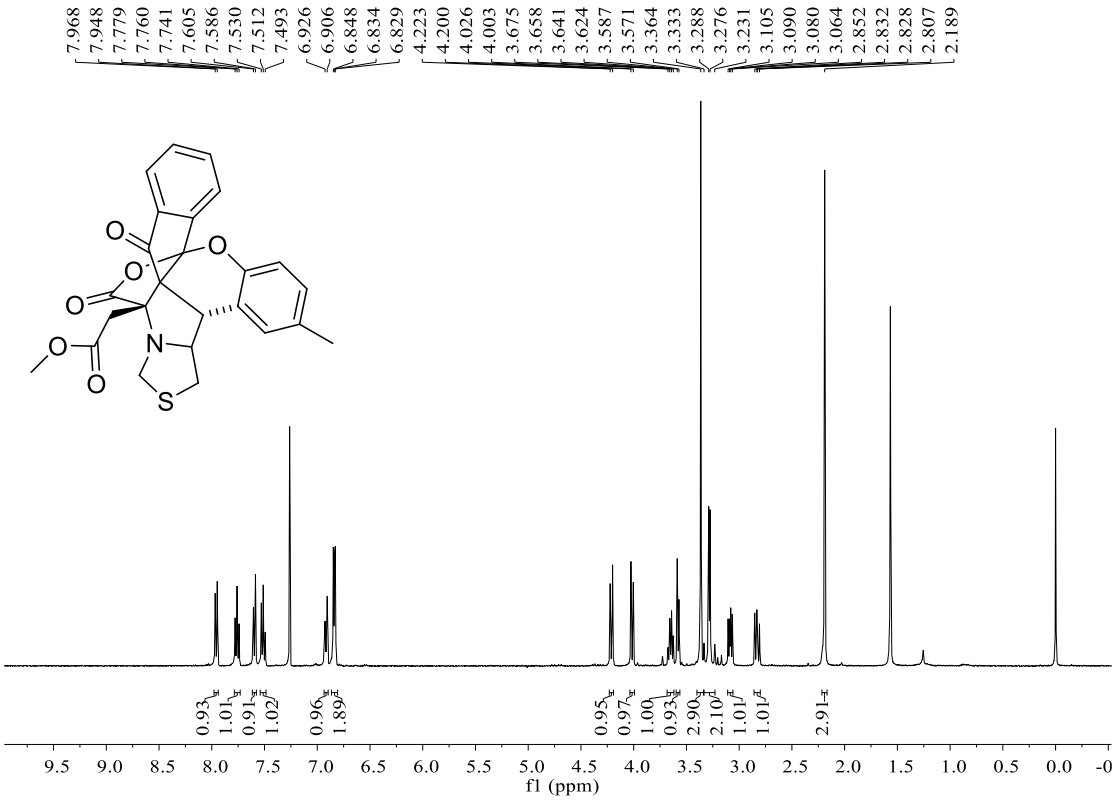
Ethyl 2-(*rel*-(3bS,8aR,13aS,14S)-5-chloro-13,16-dioxo-2,3,3a,3b-tetrahydro-1*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1',2':2,3]chromeno[4,3-a]pyrrolizin-14-yl)acetate (6h): white solid, 65%, m.p. 189-190 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 7.6 Hz, 1H, ArH), 7.79-7.75 (m, 1H, ArH), 7.57-7.49 (m, 2H, ArH), 7.07-7.01 (m, 2H, ArH), 6.82 (d, *J* = 8. 4Hz, 1H, ArH), 3.86-3,78 (m, 1H, CH), 3.71-3.59 (m, 2H, CH_2), 3.39 (d, *J* = 10.4 Hz, 1H, CH), 3.29 (dd, J_1 = 17.6Hz, J_2 = 17.6Hz, 2H, CH_2), 3.15-3.12 (m, 2H, CH_2), 2.13-2.08 (m, 1H, CH), 2.06-1.97 (m, 2H, CH_2), 1.76-1.67 (m, 1H, CH), 1.00 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 199.4, 175.0, 169.3, 148.6, 146.3, 137.3, 136.7, 131.5, 129.1, 128.6, 127.8, 125.5, 124.7, 122.3, 119.9, 109.7, 74.0, 70.7, 68.9, 61.2, 53.0, 47.6, 35.8, 27.6, 25.5, 13.7; IR (KBr) υ: 2587, 2868, 1800, 1744, 1490, 1433, 1341, 1287, 1217, 1187, 1171, 1077, 1055, 976, 887, 784 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{26}H_{23}ClNO_6$ ([M+H]$^{+}$): 480.1208, Found: 480.1215.

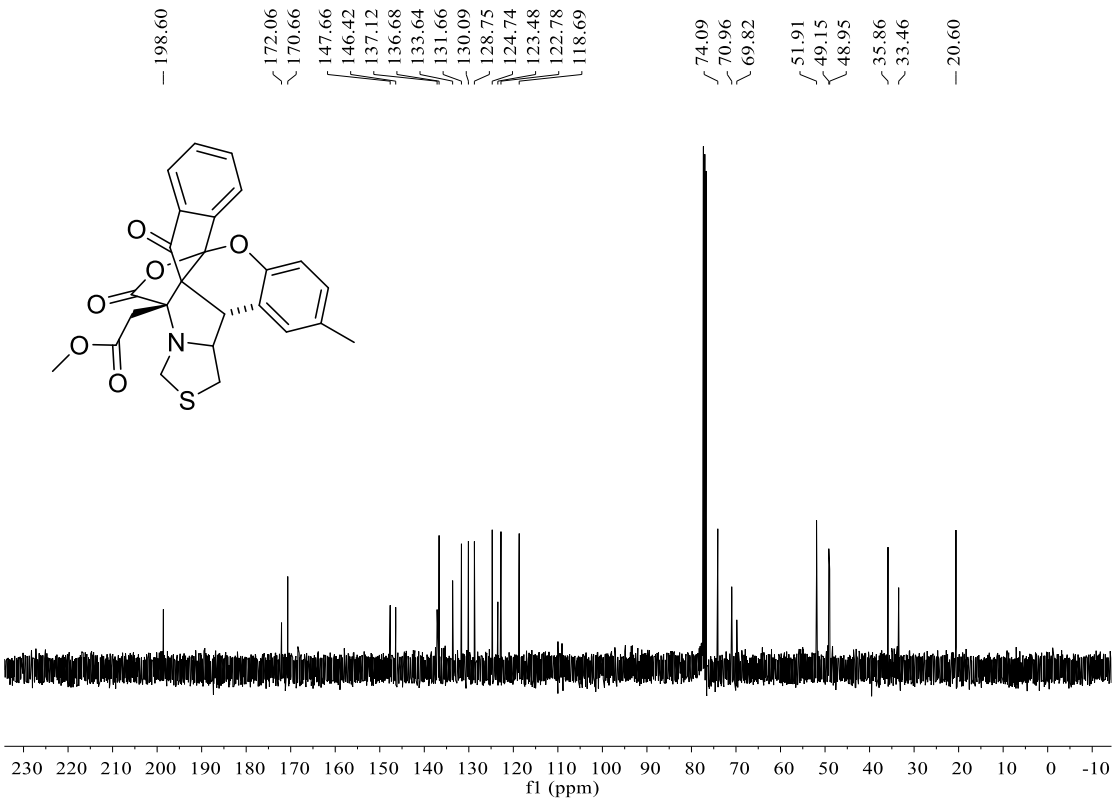


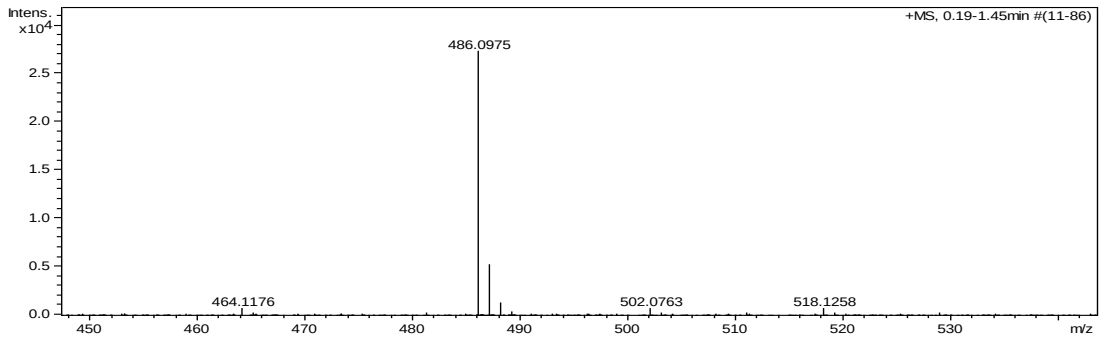

199.38
175.01
169.32
148.60
146.35
137.35
136.65
131.54
129.07
128.62
127.77
125.45
124.71
122.34
119.85
109.72
73.98
70.73
68.87
61.24
53.04
47.63
35.77
27.60
25.49
13.71
O
O
O
O
O
N
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.56-0.62min #(33-37)
480.1215
481.1245
482.1195
478.1058
483.1223
0
2
4
6
478
479
480
481
482
483
484
485
486
m/z

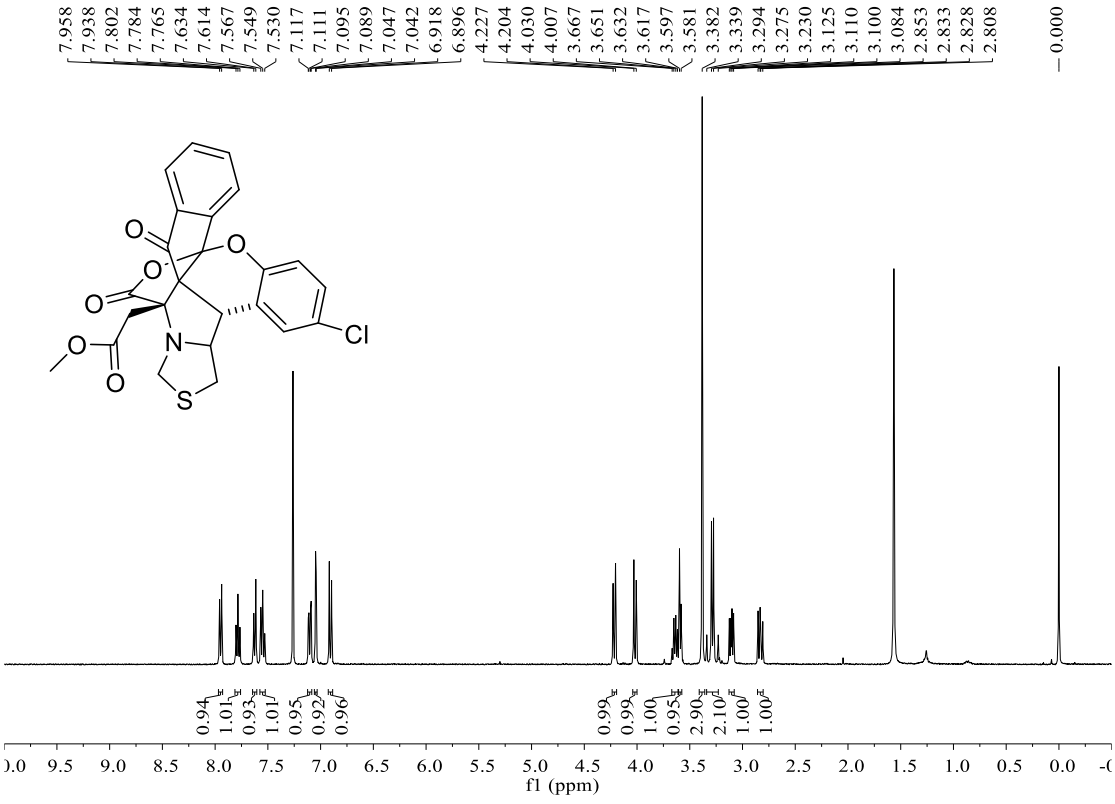
Methyl 2-(*rel*-(3bS,8aR,13aS,14S)-5-methyl-13,16-dioxo-3a,3b-dihydro-1*H*,3*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1'',2'':2',3']chromeno[4',3':3,4]pyrrolo[1,2-c]thiazol-14-yl)acetate (6i): white solid, 78%, m.p. 205-207 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 8.0 Hz, 1H, ArH), 7.78-7.74 (m, 1H, ArH), 7.59 (d, *J* = 7.6 Hz, 1H, ArH), 7.53-7.49 (m, 1H, ArH), 6.91 (d, *J* = 8.0 Hz, 1H, ArH), 6.85-6.83 (m, 2H, ArH), 4.21 (d, *J* = 9.2 Hz, 1H, CH), 4.01 (d, *J* = 9.2 Hz, 1H, CH), 3.68-3.62 (m, 1H, CH), 3.58 (m, 1H, CH), 3.36 (s, 3H, OCH_3), 3.28 (dd, J_1 = 18.0 Hz, J_2 = 18.0 Hz, 2H, CH_2), 3.11-3.06 (m, 1H, CH), 2.85-2.81 (m, 1H, CH), 2.19 (s, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.6, 172.1, 170.7, 147.7, 146.4, 137.1, 136.7, 133.6, 131.7, 130.1, 128.7, 124.7, 123.5, 122.8, 118.7, 74.1, 71.0, 69.8, 51.9, 49.2, 49.0, 35.7, 33.5, 20.6; IR (KBr) υ: 2592, 1799, 1683, 1602, 1438, 1355, 1280, 1247, 1170, 1149, 1068, 973, 887, 788, 769 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{21}NaNO_6S$ ([M+Na]$^{+}$): 486.0982, Found: 486.0975.

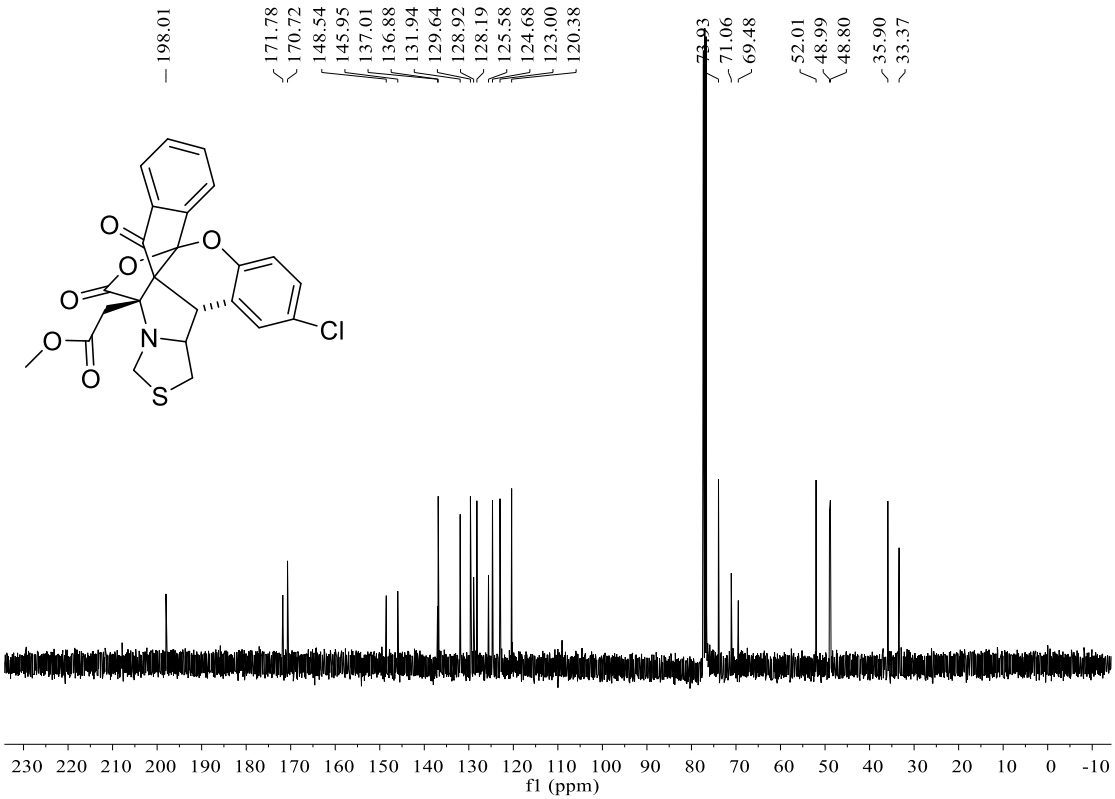


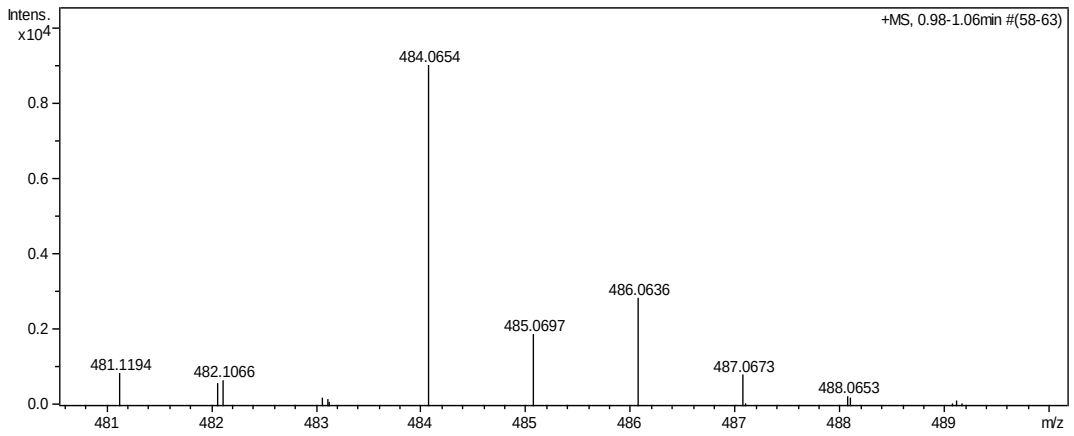

198.60
172.06
170.66
147.66
146.42
137.12
136.68
133.64
131.66
130.09
128.75
124.74
123.48
122.78
118.69
74.09
70.96
69.82
51.91
49.15
48.95
35.86
33.46
20.60
O
O
O
O
N
O
O
S
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 0.19-1.45min #(11-86)
486.0975
464.1176
502.0763
518.1258
2.5
2.0
1.5
1.0
0.5
0.0
450
460
470
480
490
500
510
520
530
m/z

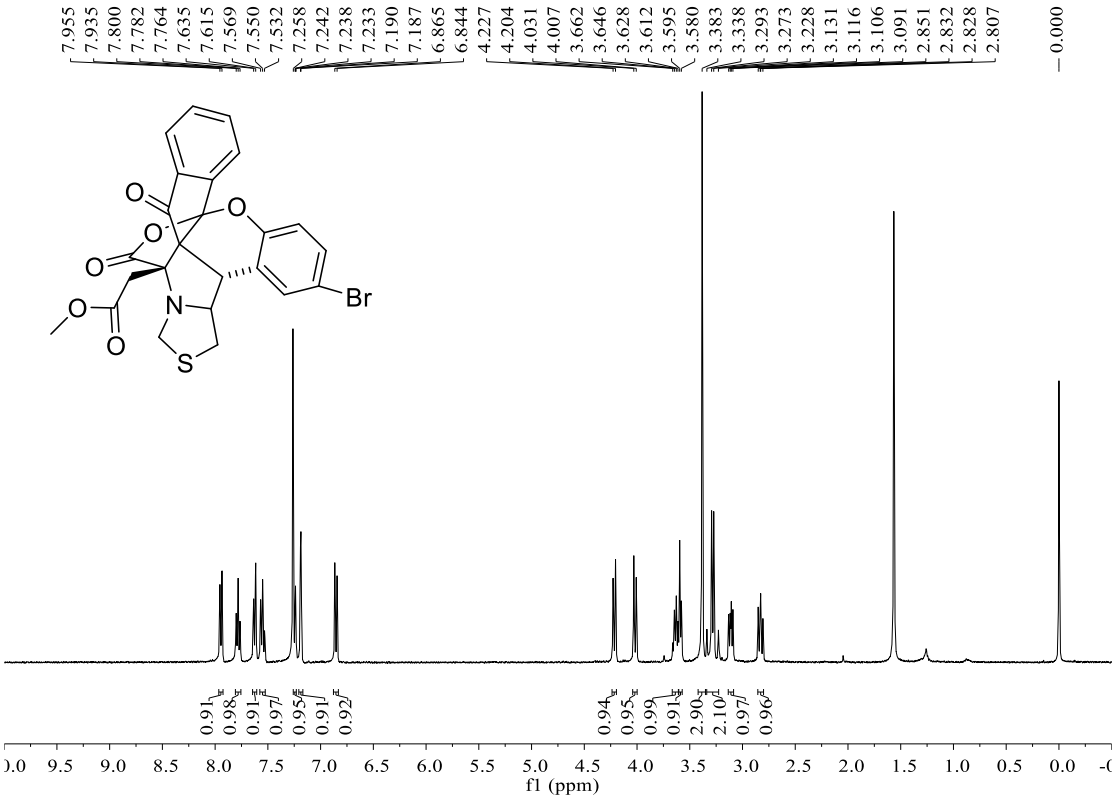
Methyl 2-(*rel*-(3bS,8aR,13aS,14S)-5-chloro-13,16-dioxo-3a,3b-dihydro-1*H*,3*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1'',2'':2',3']chromeno[4',3':3,4]pyrrolo[1,2-c]thiazol-14-yl)acetate (6j): white solid, 70%, m.p. 228-230 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.0 Hz, 1H, ArH), 7.80-7.76 (m, 1H, ArH), 7.62 (d, *J* = 8.0 Hz, 1H, ArH), 7.57-7.53 (m, 1H, ArH), 7.12-7.09 (m, 1H, ArH), 7.04 (d, *J* = 2.0 Hz, 1H, ArH), 6.90 (d, *J* = 8.8 Hz, 1H, ArH), 4.22 (d, *J* = 9.2 Hz, 1H, CH), 4.02 (d, *J* = 9.2 Hz, 1H, CH), 3.67-3.62 (m, 1H, CH), 3.59 (d, *J* = 6.4 Hz, 1H, CH), 3.38 (s, 3H, OCH_3), 3.28 (dd, J_1 = 18.0 Hz, J_2 = 18.0 Hz, 2H, CH_2), 3.13-3.08 (m, 1H, CH), 2.85-2.81 (m, 1H, CH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.0, 171.8, 170.7, 148.5, 146.0, 137.0, 136.9, 131.9, 129.6, 128.9, 128.2, 125.6, 124.7, 123.0, 120.4, 74.0, 71.1, 69.5, 52.0, 49.0, 48.8, 35.9, 33.4; IR (KBr) υ: 2595, 1792, 1688, 1609, 1440, 1357, 1287, 1243, 1177, 1150, 1069, 976, 889, 791, 764 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{19}ClNO_6$ ($[M+H]^+$): 484.0616, Found: 484.0654.

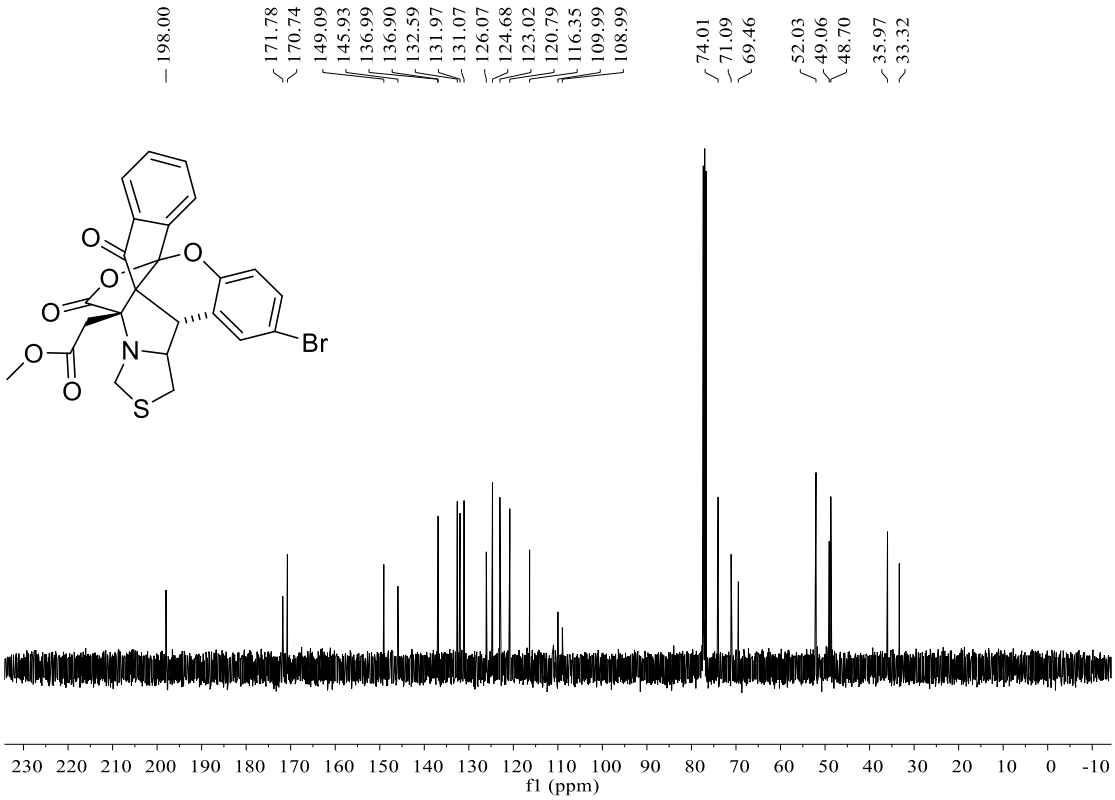


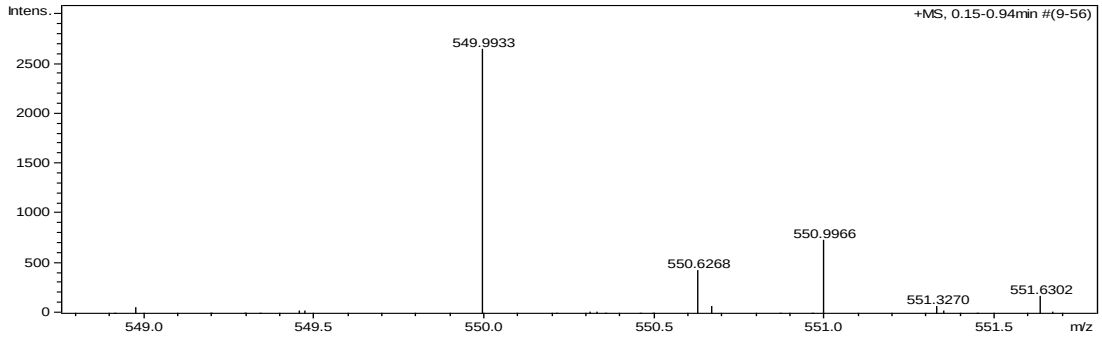

198.01
171.78
170.72
148.54
145.95
137.01
136.88
131.94
129.64
128.92
128.19
125.58
124.68
123.00
120.38
73.93
71.06
69.48
52.01
48.99
48.80
35.90
33.37
O
O
O
O
O
N
S
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 0.98-1.06min #(58-63)
484.0654
486.0636
485.0697
481.1194
482.1066
487.0673
488.0653
0.0
0.2
0.4
0.6
0.8
481
482
483
484
485
486
487
488
489
m/z

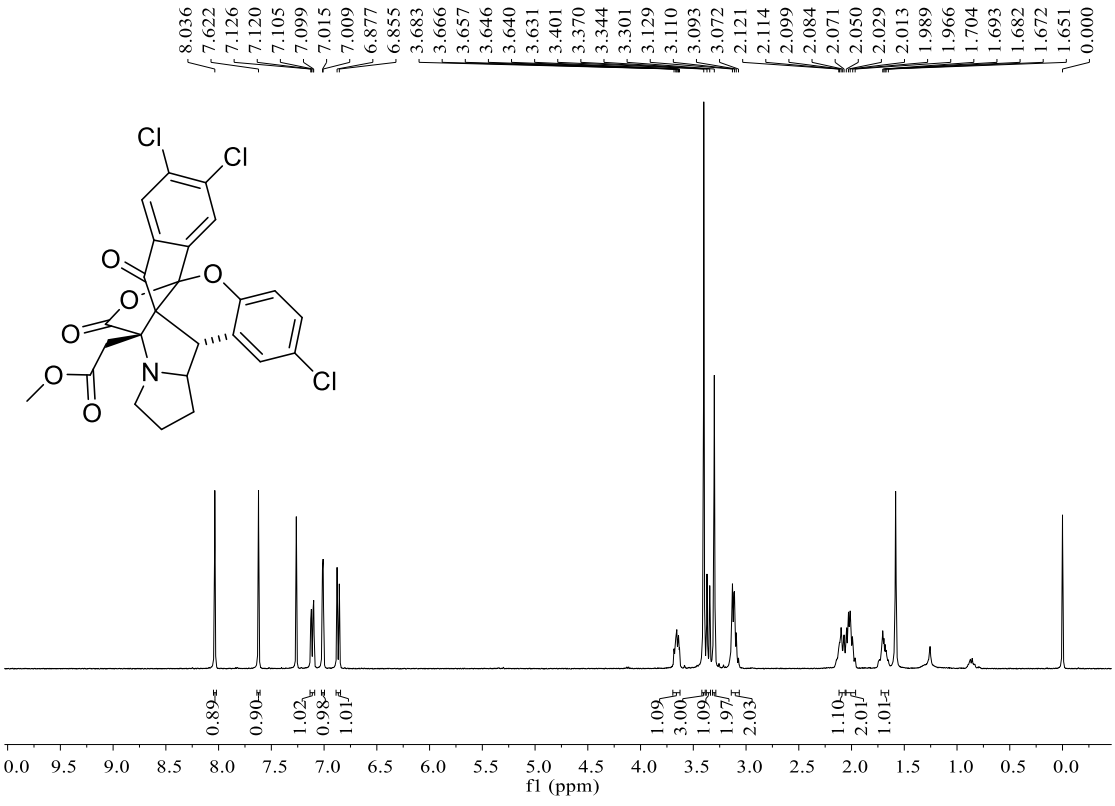
Methyl 2-(*rel*-(3bS,8aR,13aS,14S)-5-bromo-13,16-dioxo-3a,3b-dihydro-1*H*,3*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1'',2'':2',3']chromeno[4',3':3,4]pyrrolo[1,2-c]thiazol-14-yl)acetate (6k): white solid, 55%, m.p. 200-202 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.0 Hz, 1H, ArH), 7.80-7.76 (m, 1H, ArH), 7.62 (d, *J* = 8.0 Hz, 1H, ArH), 7.57-7.53 (m, 1H, ArH), 7.25-7.23 (m, 1H, ArH), 7.19 (d, *J* = 1.2 Hz, 1H, ArH), 6.85 (d, *J* = 8.4 Hz, 1H, ArH), 4.21 (d, *J* = 9.2 Hz, 1H, CH), 4.02 (d, *J* = 9.2 Hz, 1H, CH), 3.66-3.61 (m, 1H, CH), 3.59 (d, *J* = 6.0 Hz, 1H, CH), 3.38 (s, 3H, OCH_3), 3.28 (dd, J_1 = 18.0 Hz, J_2 = 18.0 Hz, 2H, CH_2), 3.13-3.09 (m, 1H, CH), 2.85-2.81 (m, 1H, CH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.0, 171.8, 170.7, 149.1, 145.9, 137.0, 136.9, 132.6, 132.0, 131.1, 126.1, 124.7, 123.0, 120.8, 116.3, 110.0, 109.0, 74.0, 71.1, 69.5, 52.0, 49.1, 48.7, 36.0, 33.32; IR (KBr) υ: 2597, 1791, 1687, 1610, 1432, 1358, 1287, 1242, 1176, 1152, 1064, 978, 882, 786, 771 cm^{-1}; MS (*m*/z): HRMS (ESI-TOF) Calcd. for $C_{24}H_{18}BrNNaO_6S$ ([M+Na]$^{+}$): 549.9930, Found: 549.9933.

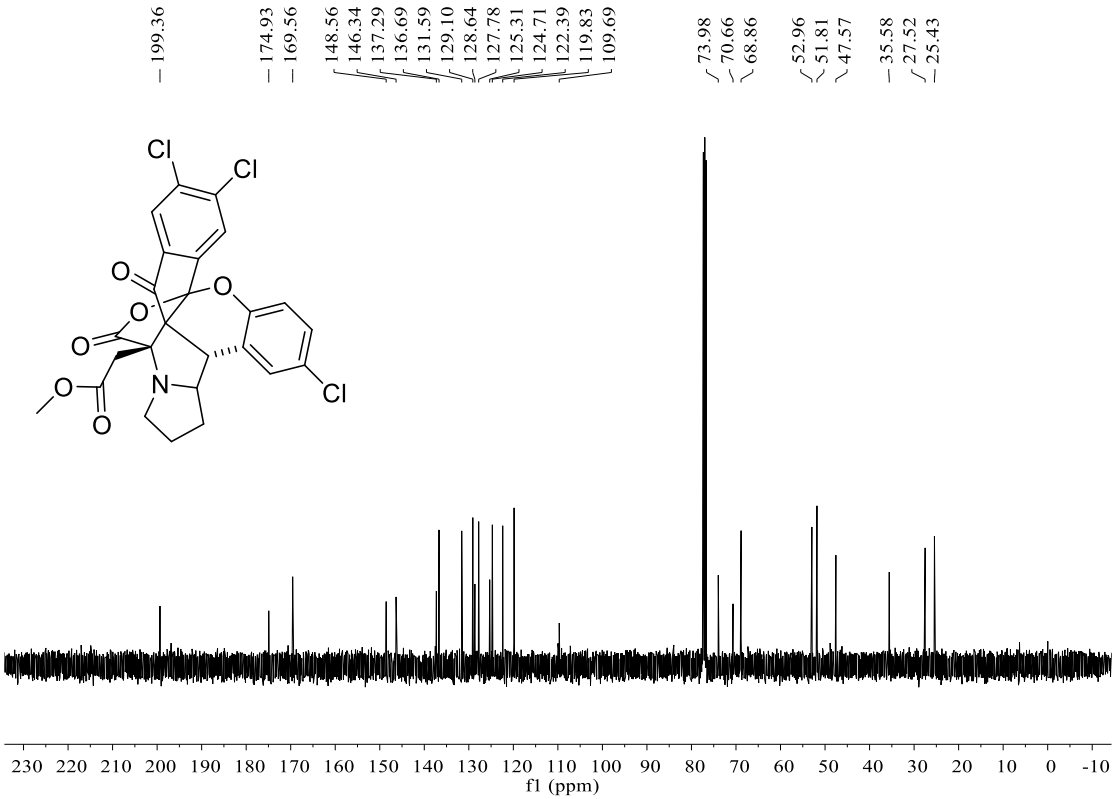


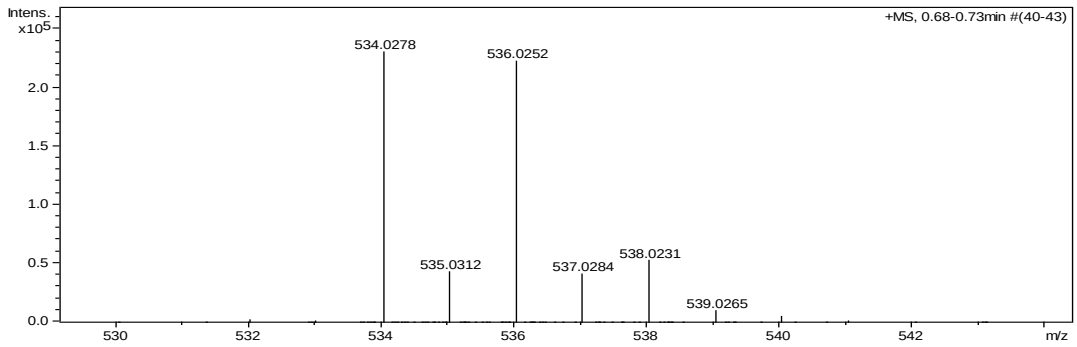

198.00
171.78
170.74
149.09
145.93
136.99
136.90
132.59
131.97
131.07
126.07
124.68
123.02
120.79
116.35
109.99
108.99
74.01
71.09
69.46
52.03
49.06
48.70
35.97
33.32
O
O
O
O
O
N
S
Br
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 0.15-0.94min #(9-56)
549.9933
550.6268
550.9966
551.3270
551.6302
2500
2000
1500
1000
500
0
549.0
549.5
550.0
550.5
551.0
551.5
m/z

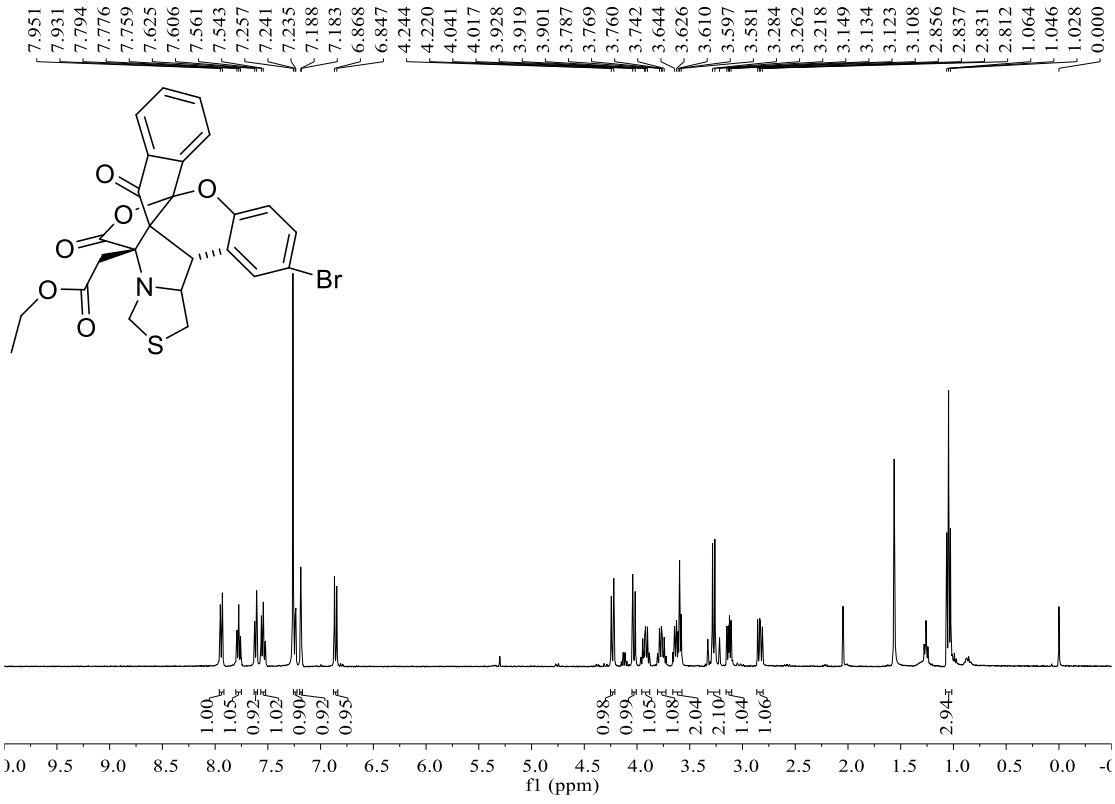
Methyl 2-(*rel*-(3bS,8aR,13aS,14S)-5,10,11-trichloro-13,16-dioxo-2,3,3a,3b-tetrahydro-1*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1',2':2,3]chromeno[4,3-a]pyrrolizin-14-yl)acetate (6l): white solid, 38%, m.p. 203-204 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (s, 1H, ArH), 7.62 (s, 1H, ArH), 7.13-7.10 (m, 1H, ArH), 7.10 (d, *J* = 2.4 Hz, 1H, ArH), 6.86 (d, *J* = 8.8 Hz, 1H, ArH), 3.68-3.63 (m, 1H, CH), 3.40 (s, 3H, OCH_3), 3.36 (d, *J* = 10.4 Hz, 1H, CH), 3.30 (s, 2H, CH_2), 3.13-3.07 (m, 2H, CH_2), 2.12-2.07 (m, 1H, CH), 2.05-1.97 (m, 2H, CH_2), 1.70-1.65 (m, 1H, CH); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ:199.4, 174.9, 169.6, 148.6, 146.3, 137.3, 136.7, 131.6, 129.1, 128.6, 127.8, 125.3, 124.7, 122.4, 119.8, 109.7, 74.0, 70.7, 68.9, 53.0, 51.8, 47.6, 35.6, 27.5, 25.4; IR (KBr) υ: 2596, 2877, 1790, 1740, 1495, 1435, 1332, 1290, 1214, 1188, 1164, 1077, 1058, 972, 885, 779 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{25}H_{19}Cl_3NO_6$ ([M+H]$^+$): 534.0272, Found: 534.0278.

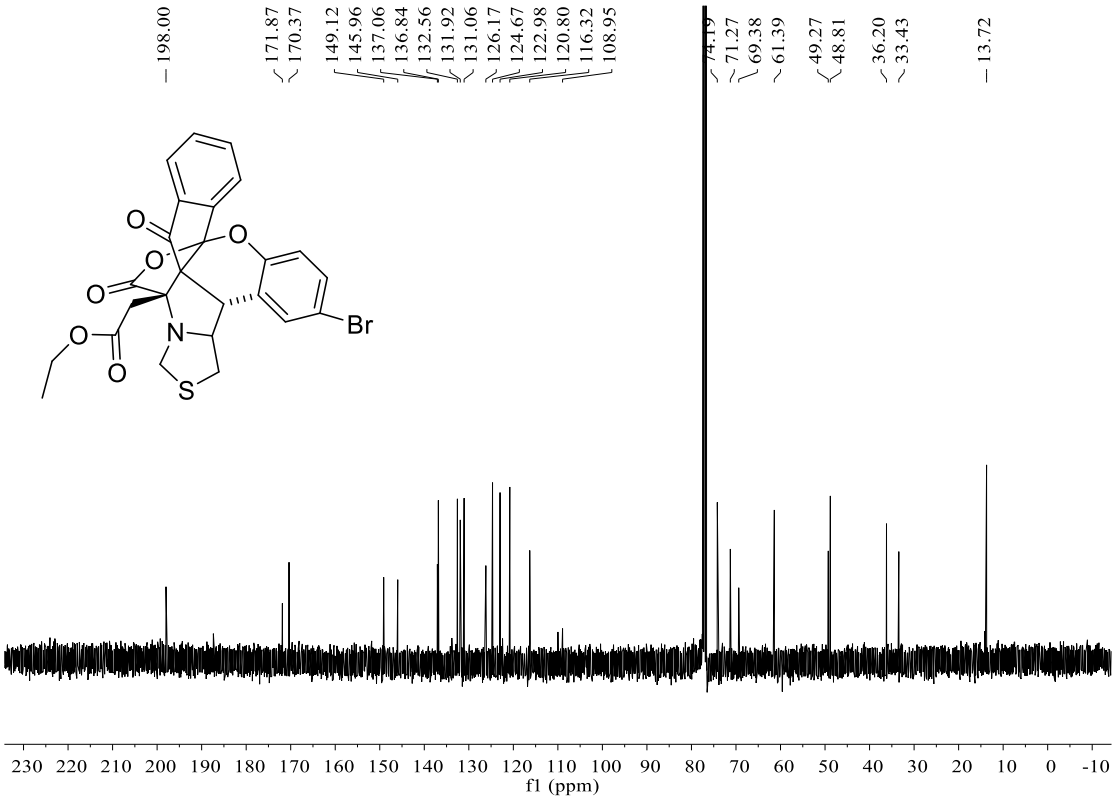


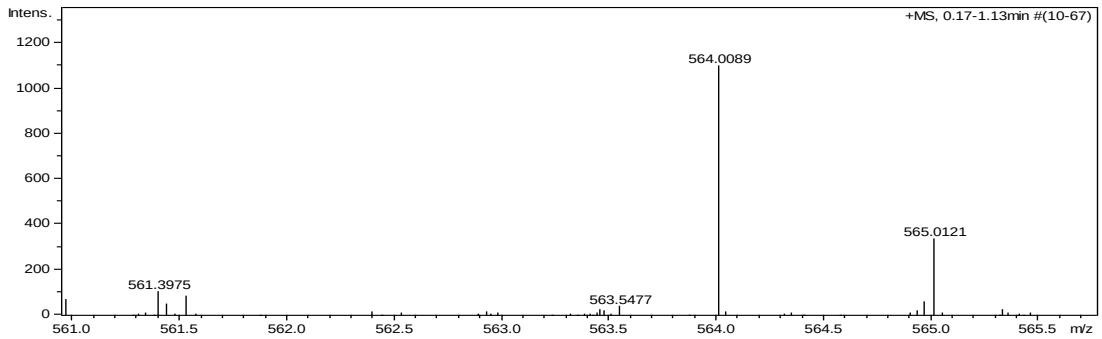

199.36
174.93
169.56
148.56
146.34
137.29
136.69
131.59
129.10
128.64
127.78
125.31
124.71
122.39
119.83
109.69
73.98
70.66
68.86
52.96
51.81
47.57
35.58
27.52
25.43
Cl
Cl
O
O
O
O
O
N
O
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.68-0.73min #(40-43)
534.0278
536.0252
535.0312
537.0284
538.0231
539.0265
2.0
1.5
1.0
0.5
0.0
530
532
534
536
538
540
542
m/z

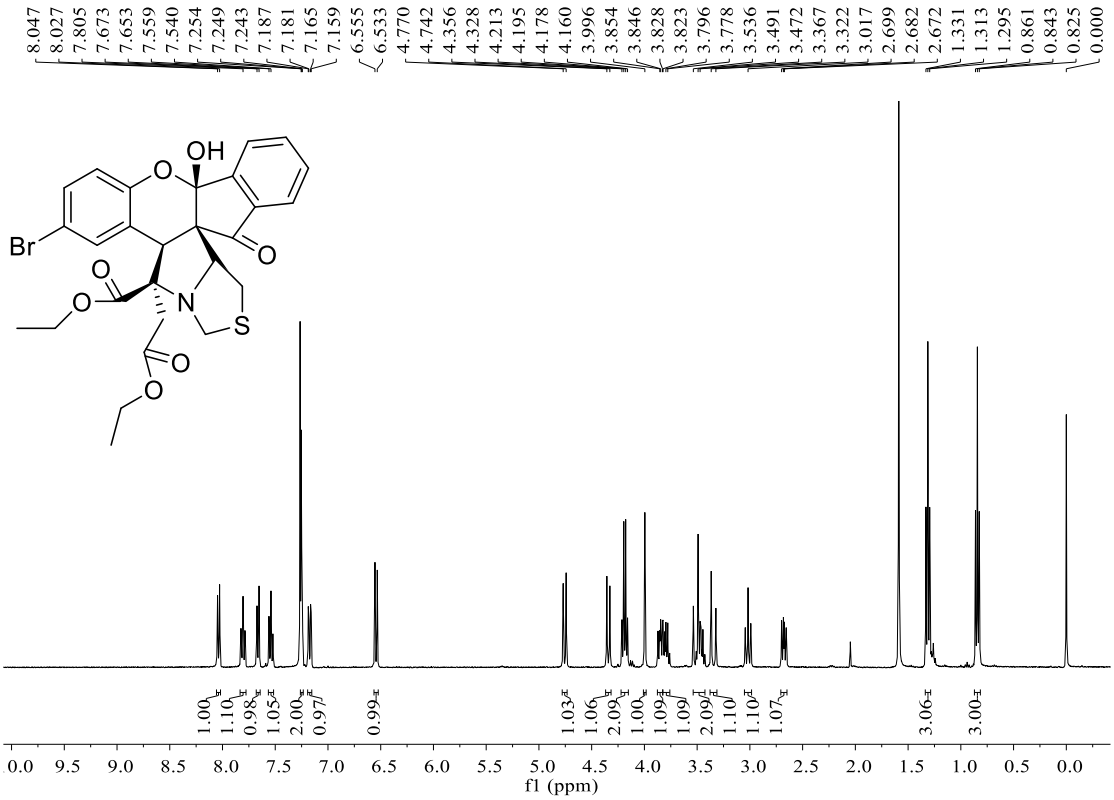
Ethyl 2-(*rel*-(3bS,8aR,13aS,14S)-5-bromo-13,16-dioxo-3a,3b-dihydro-1*H*,3*H*,13*H*,14*H*-8a,14-(epoxymethano)indeno[1'',2'':2',3']chromeno[4',3':3,4]pyrrolo[1,2-c]thiazol-14-yl)acetate (6m): white solid, 21%, m.p. 204-206 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.0 Hz, 1H, ArH), 7.79-7.76 (m, 1H, ArH), 7.61 (d, *J* = 7.6 Hz, 1H, ArH), 7.56-7.52 (m, 1H, ArH), 7.26-7.24 (m, 1H, ArH), 7.18 (d, *J* = 2.0 Hz, 1H, ArH), 6.85 (d, *J* = 8.4 Hz, 1H, ArH), 4.23 (d, *J* = 9.6 Hz, 1H, CH), 4.03 (d, *J* = 9.6 Hz, 1H, CH), 3.95-3.88 (m, 1H, CH), 3.81-3.73 (m, 1H, CH), 3.66-3.58 (m, 2H, CH_2), 3.27 (dd, J_1 = 18.0 Hz, J_2 = 17.6 Hz, 2H, CH_2), 3.15-3.11 (m, 1H, CH), 2.86-2.81 (m, 1H, CH), 1.05(t, *J* = 2.0 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.0, 171.9, 170.4, 149.1, 146.0, 137.1, 136.8, 132.6, 131.9, 131.1, 126.2, 124.7, 123.0, 120.8, 116.3, 108.9, 74.2, 71.3, 69.4, 61.4, 49.3, 48.8, 36.2, 33.4, 13.7; IR (KBr) υ: 2597, 1800, 1688, 1607, 1432, 1352, 1283, 1249, 1168, 1143, 1063, 970, 885, 786, 770 cm^{-1}; MS (*m*/z): HRMS (ESI-TOF) Calcd. for $C_{25}H_{20}BrNaNO_6S$ ([M+Na]$^{+}$): 564.0087, Found: 564.0089.

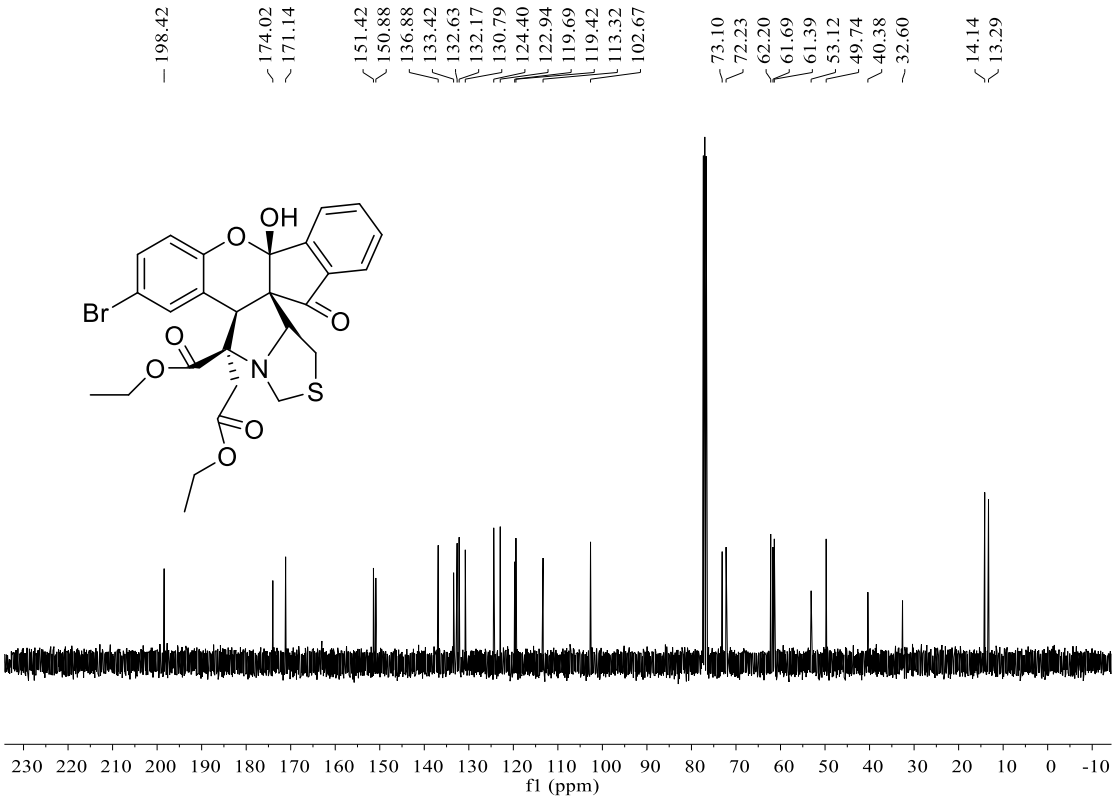


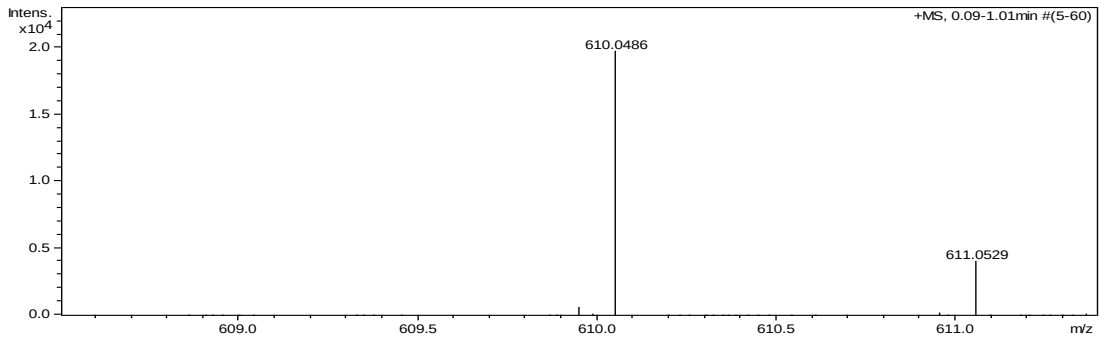

198.00
171.87
170.37
149.12
145.96
137.06
136.84
132.56
131.92
131.06
126.17
124.67
122.98
120.80
116.32
108.95
74.19
71.27
69.38
61.39
49.27
48.81
36.20
33.43
13.72
O
O
O
O
O
N
S
Br
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 0.17-1.13min #(10-67)
1200
1000
800
600
400
200
0
564.0089
565.0121
561.3975
563.5477
561.0
561.5
562.0
562.5
563.0
563.5
564.0
564.5
565.0
565.5
m/z

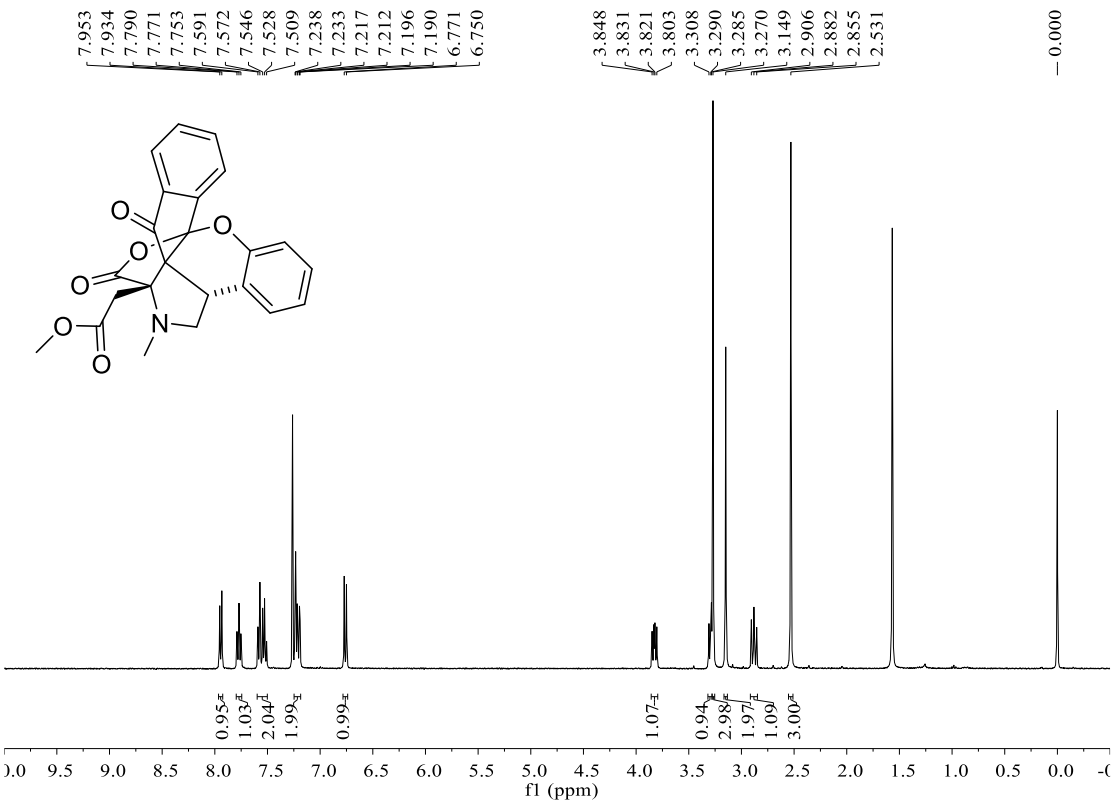
Ethyl *rel*-(5R,5aS,10aR,15aR,15bR)-7-bromo-5-(2-ethoxy-2-oxoethyl)-10a-hydroxy-15-oxo-1,5,5a,10a,15,15b-hexahydro-3*H*-indeno[1'',2'':2',3']chromeno[3',4':3,4]pyrrolo[1,2-c]thiazole-5-carboxylate (k): white solid, 67%, m.p. 203-204 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 8.0 Hz, 1H, ArH), 7.83-7.79 (m, 1H, ArH), 7.64 (d, *J* = 8.0 Hz, 1H, ArH), 7.56-7.52 (m, 1H, ArH), 7.25-7.24 (m, 2H, ArH), 7.19-7.16 (m, 1H, ArH), 6.54 (d, *J* = 8.8 Hz, 1H, ArH), 4.75 (d, *J* = 11.2 Hz, 1H, CH), 4.34 (d, *J* = 11.2 Hz, 1H, CH), 4.19 (dd, J_1 = 7.2 Hz, J_2 = 7.2 Hz, 2H, CH_2), 3.40 (s, 1H, OH), 3.87-3.83 (m, 1H, CH), 3.82-3.67 (m, 1H, CH), 3.54-3.43 (m, 2H, CH_2), 3.64 (d, *J* = 18.0 Hz, 1H, CH), 3.04-2.99 (m, 1H, CH), 2.70-2.65 (m, 1H, CH), 1.31 (t, *J* = 7.2 Hz, 3H, CH_3), 0.84 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.4, 174.0, 171.1, 151.4, 150.9, 136.9, 133.4, 132.6, 132.2, 130.8, 124.4, 122.9, 119.7, 119.4, 113.3, 102.7, 73.1, 72.2, 62.2, 61.7, 61.4, 53.1, 49.7, 40.4, 32.6, 14.1, 13.3; IR (KBr) υ: 2929, 2904, 1733, 1606, 1479, 1427, 1396, 1324, 1294, 1261, 1199, 1135, 1079, 995, 871, 769 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{27}H_{26}BrNaNO_7S$ ([M+Na]$^{+}$): 610.0506, Found: 610.0486.

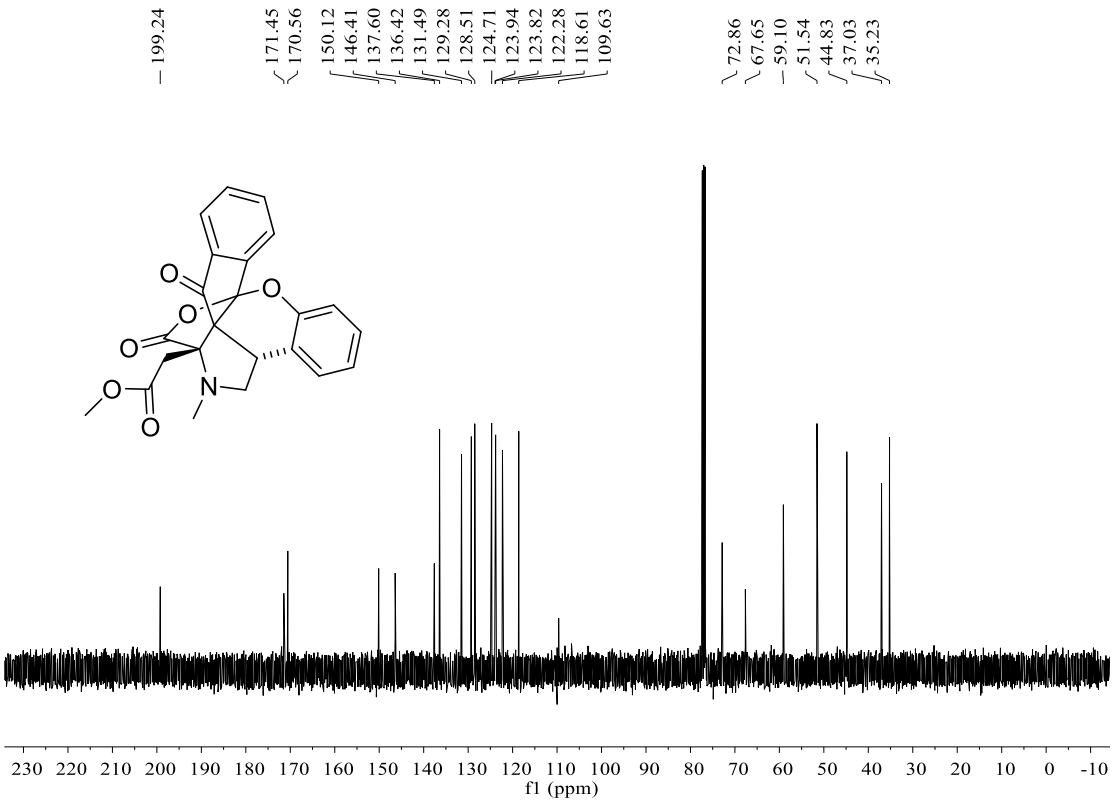


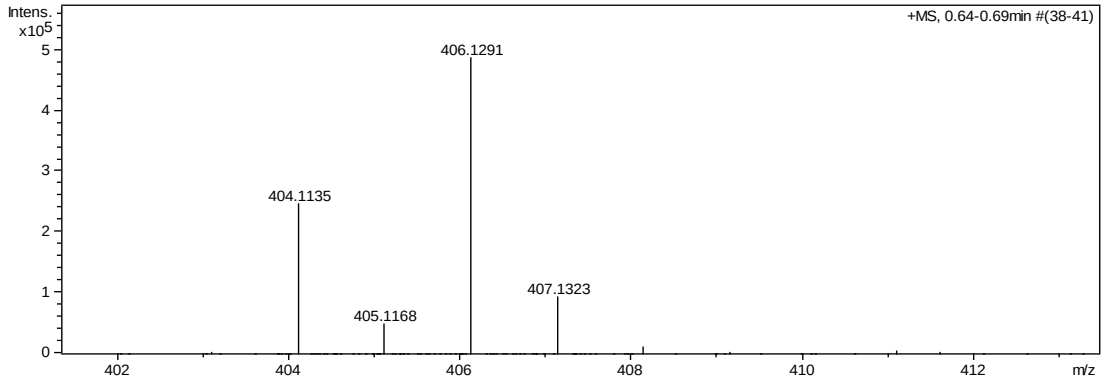

198.42
174.02
171.14
151.42
150.88
136.88
133.42
132.63
132.17
130.79
124.40
122.94
119.69
119.42
113.32
102.67
73.10
72.23
62.20
61.69
61.39
53.12
49.74
40.38
32.60
14.14
13.29
OH
O
Br
O
O
N
S
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
2.0
1.5
1.0
0.5
0.0
+MS, 0.09-1.01min #(5-60)
610.0486
611.0529
609.0
609.5
610.0
610.5
611.0
m/z

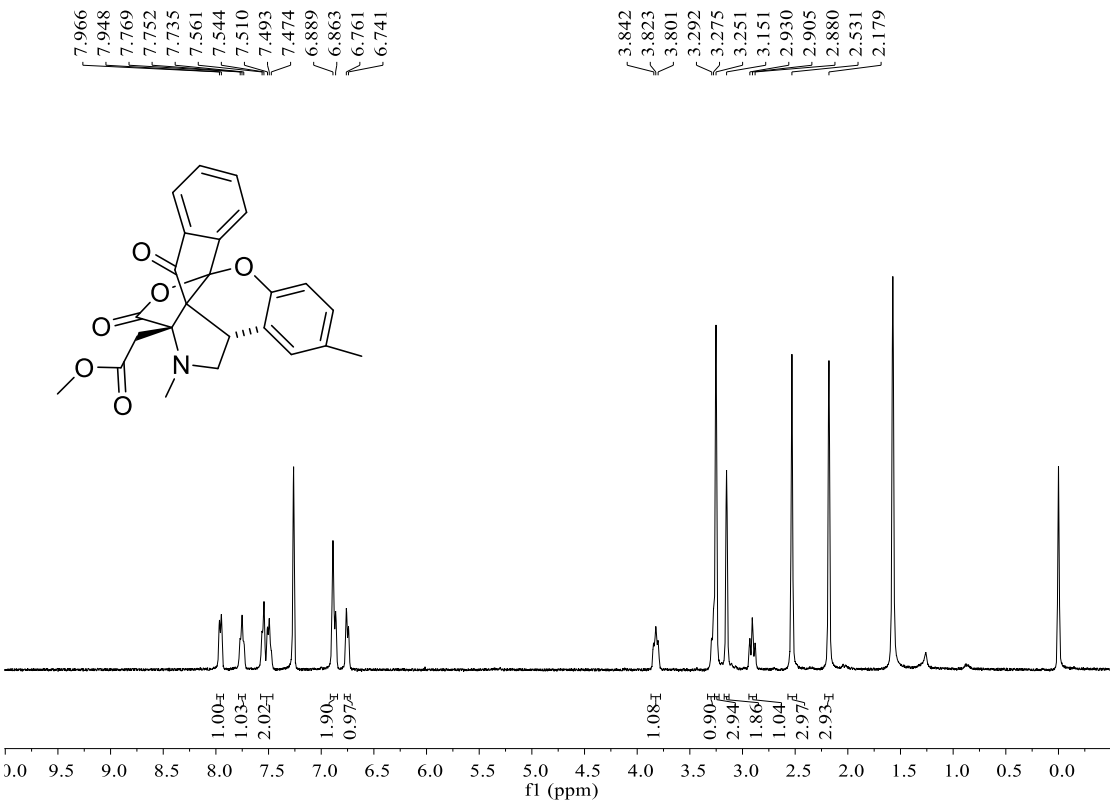
Methyl 2-(*rel*-(1S,3aS,8aR,13aS)-2-methyl-13,15-dioxo-3,3a-dihydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrol-1(2*H*)-yl)acetate (7a): white solid, 49%, m.p. 235-236 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 7.6 Hz, 1H, ArH), 7.77-7.74 (m, 1H, ArH), 7.56-7.48 (m, 2H, ArH), 7.10 (d, *J* = 6.0 Hz, 2H, ArH), 6.93-6.86 (m, 2H, ArH), 3.90-3.86 (m, 1H, CH), 3.30 (d, *J* = 7.6 Hz, 1H, CH), 3.26 (s, 3H, OCH_3), 3.16 (s, 2H, CH_2), 3.94-2.89 (m, 1H, CH), 2.54 (s, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 199.2, 171.5, 170.6, 150.1, 146.4, 137.6, 136.4, 131.5, 129.3, 128.5, 124.7, 123.9, 123.8, 122.3, 118.6, 109.6, 72.9, 67.6, 59.1, 51.5, 44.8, 37.0, 35.2; IR (KBr) υ: 2985, 2859, 1791, 1685, 1448, 1398, 1346, 1278, 1199, 1135, 1070, 1024, 985, 885, 775, 707 cm^{-1}; MS (*m*/z): HRMS (ESI-TOF) Calcd. for $C_{23}H_{20}NO_6$ ([M+H]$^{+}$): 406.1285, Found: 406.1291.

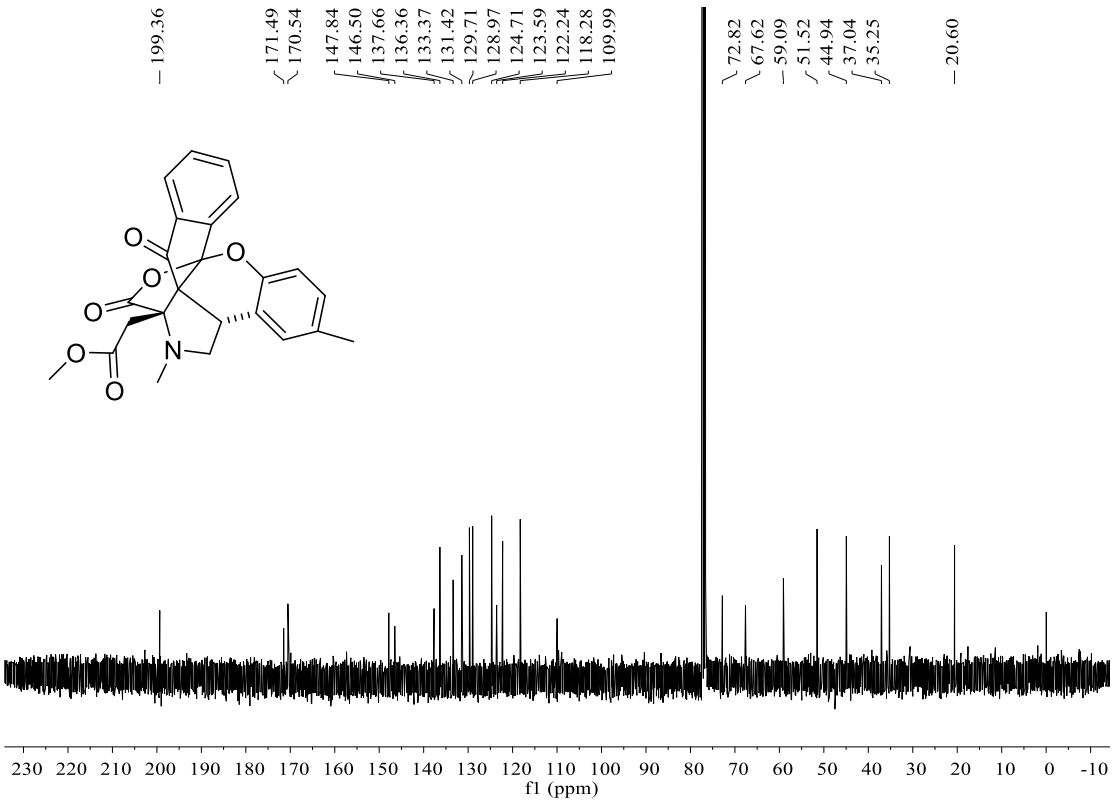


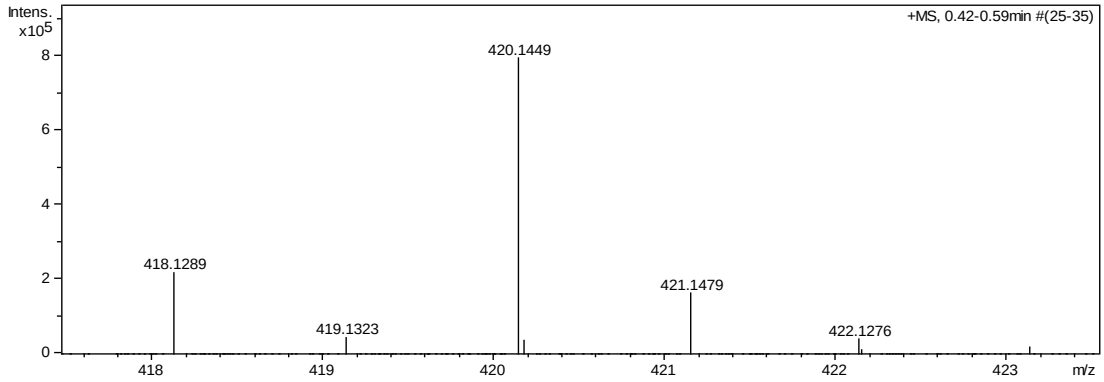

199.24
171.45
170.56
150.12
146.41
137.60
136.42
131.49
129.28
128.51
124.71
123.94
123.82
122.28
118.61
109.63
72.86
67.65
59.10
51.54
44.83
37.03
35.23
O
O
O
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.64-0.69min #(38-41)
406.1291
404.1135
407.1323
405.1168
0
1
2
3
4
5
402
404
406
408
410
412
m/z

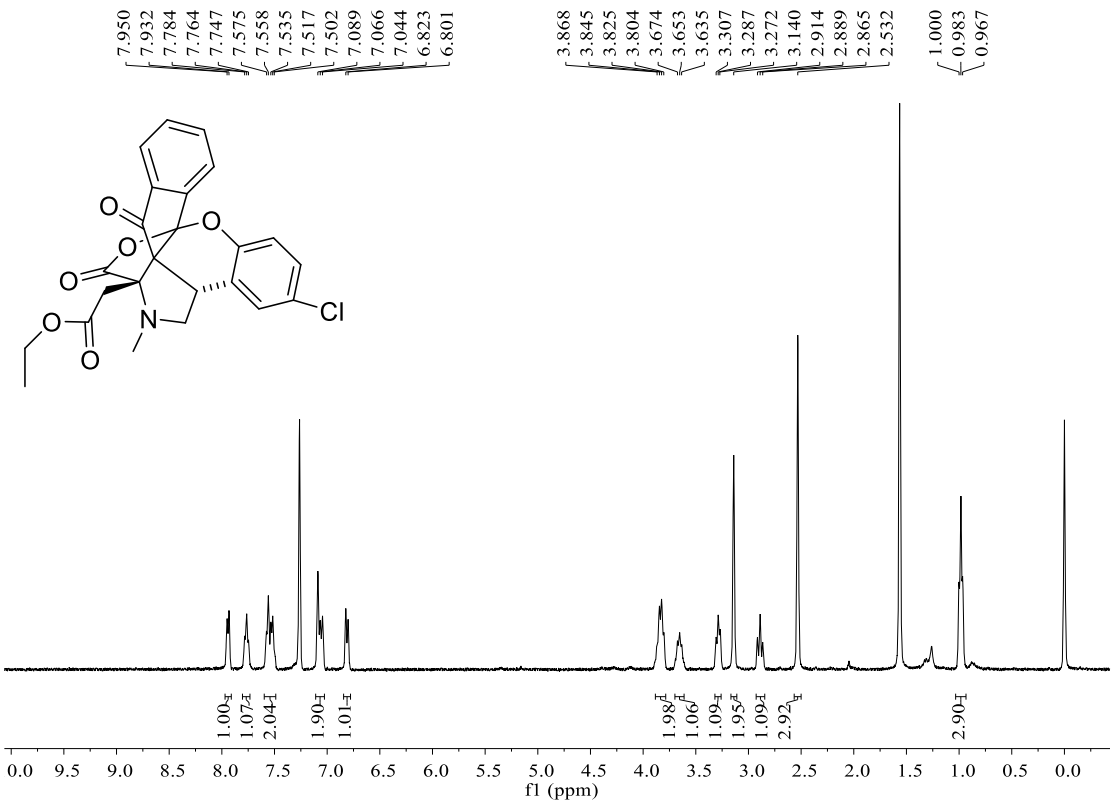
Methyl 2-(*rel*-(1S,3aS,8aR,13aS)-2,5-dimethyl-13,15-dioxo-3,3a-dihydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrol-1(2*H*)-yl)acetate (7b): white solid, 31%, m.p. 247-249 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95 (d, *J* = 7.2 Hz, 1H, ArH), 7.67-7.74 (m, 1H, ArH), 7.56-7.47 (m, 2H, ArH), 6.87 (d, *J* = 10.4 Hz, 2H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 3.84-3.80 (m, 1H, CH), 3.29-3.28 (m, 1H, CH), 3.25 (s, 3H, OCH_3), 3.15 (s, 2H, CH_2), 2.93-2.88 (m, 1H, CH), 2.53 (s, 3H, CH_3), 2.18(s, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 199.4, 171.5, 170.5, 147.8, 146.5, 137.7, 136.4, 133.4, 131.4, 129.7, 129.0, 124.7, 123.6, 122.2, 118.3, 110.0, 72.8, 67.6, 59.1, 51.5, 44.9, 37.0, 35.3, 20.6; IR (KBr) υ: 2984, 2863, 1794, 1682, 1449, 1393, 1347, 1273, 1194, 1138, 1073, 1028, 984, 887, 775, 708 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{22}NO_6$ ([M+H]$^{+}$): 420.1442, Found: 420.1449.

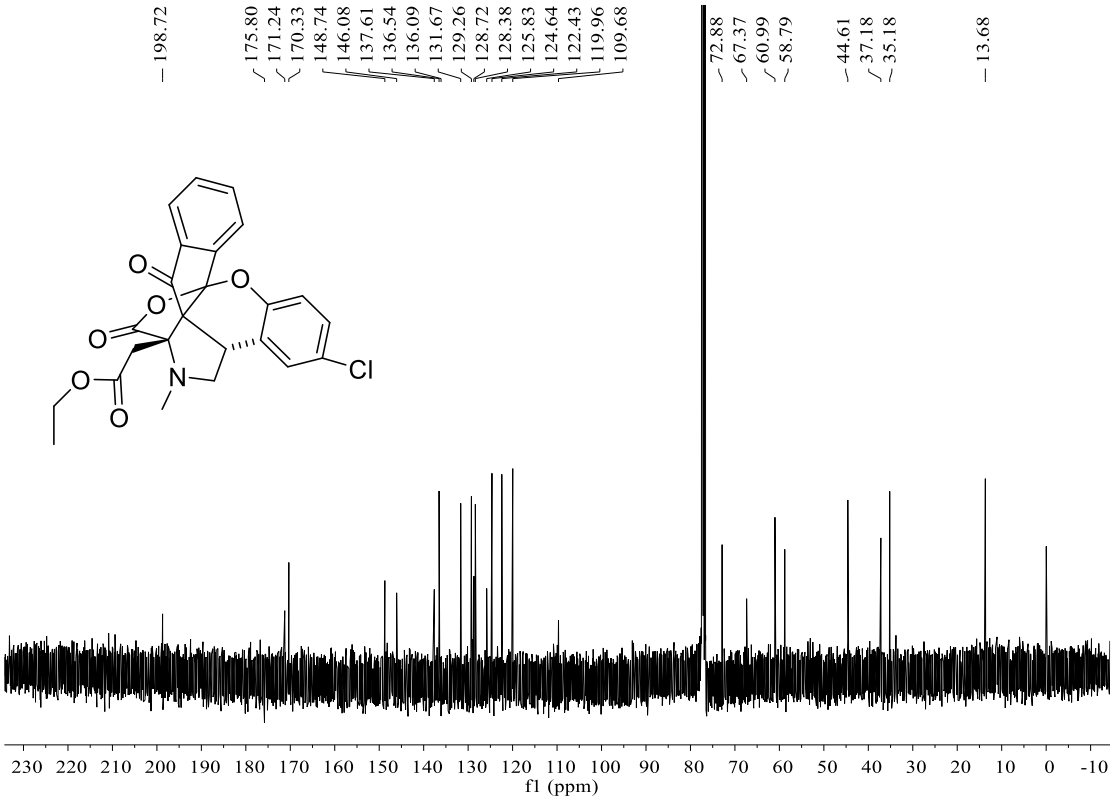


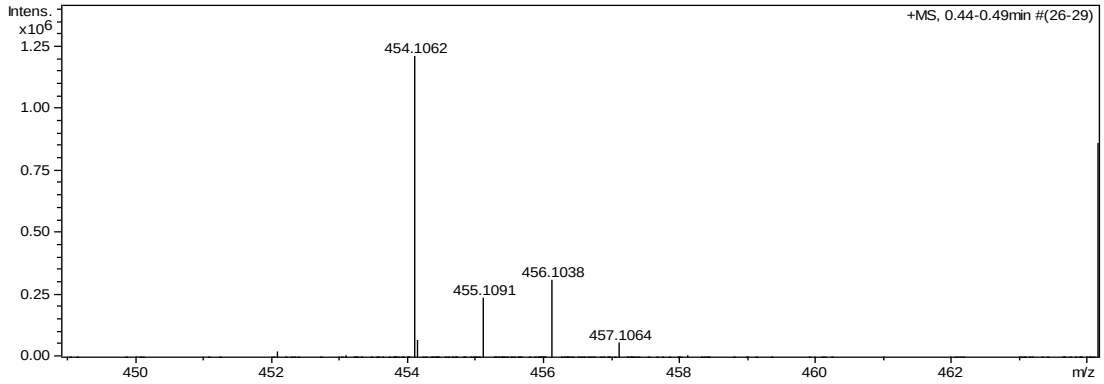

199.36
171.49
170.54
147.84
146.50
137.66
136.36
133.37
131.42
129.71
128.97
124.71
123.59
122.24
118.28
109.99
72.82
67.62
59.09
51.52
44.94
37.04
35.25
20.60
O
O
O
O
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.42-0.59min #(25-35)
420.1449
418.1289
421.1479
419.1323
422.1276
0
2
4
6
8
418
419
420
421
422
423
m/z

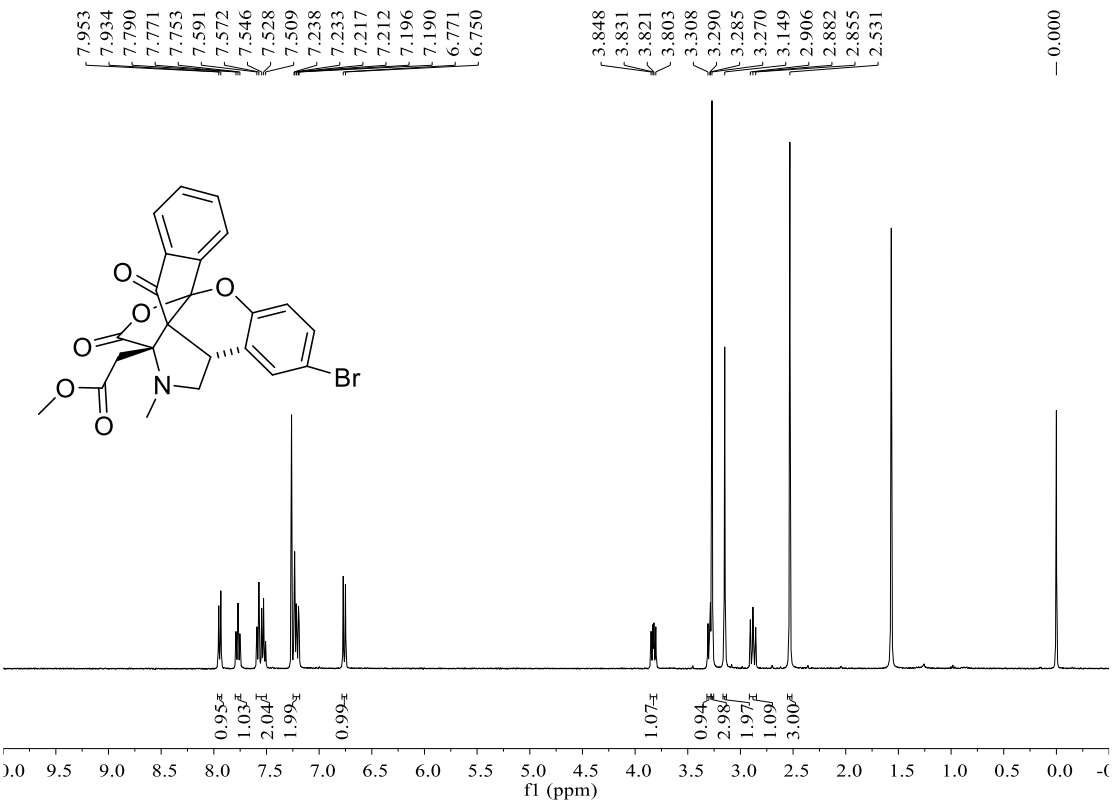
Ethyl 2-(*rel*-(1S,3aS,8aR,13aS)-5-chloro-2-methyl-13,15-dioxo-3,3a-dihydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrol-1(2*H*)-yl)acetate (7c): white solid, 53%, m.p. 239-240 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.2 Hz, 1H, ArH), 7.78-7.75 (m, 1H, ArH), 7.58-7.50 (m, 2H, ArH), 7.09-7.04 (m, 2H, ArH), 6.81 (d, *J* = 8.8 Hz, 1H, ArH), 3.87-3.80 (m, 2H, CH_2), 3.67-3.64 (m, 1H, CH), 3.31-3.27 (m, 1H, CH), 3.14 (s, 2H, CH_2), 2.91-2.87 (m, 1H, CH), 2.53 (s, 3H, CH_3), 0.98 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ: 198.7, 175.8, 171.2, 170.3, 148.7, 146.1, 137.6, 136.5, 136.1, 131.7, 129.3, 128.7, 128.4, 125.8, 124.6, 122.4, 120.0, 109.7, 72.9, 67.4, 61.0, 58.8, 44.6, 37.2, 35.2, 13.7; IR (KBr) υ: 2988, 2861, 1790, 1687, 1450, 1392, 1345, 1278, 1199, 1140, 1078, 1023, 982, 881, 777, 702 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{21}ClNO_6$ ([M+H]$^{+}$): 454.1052, Found: 454.1062.

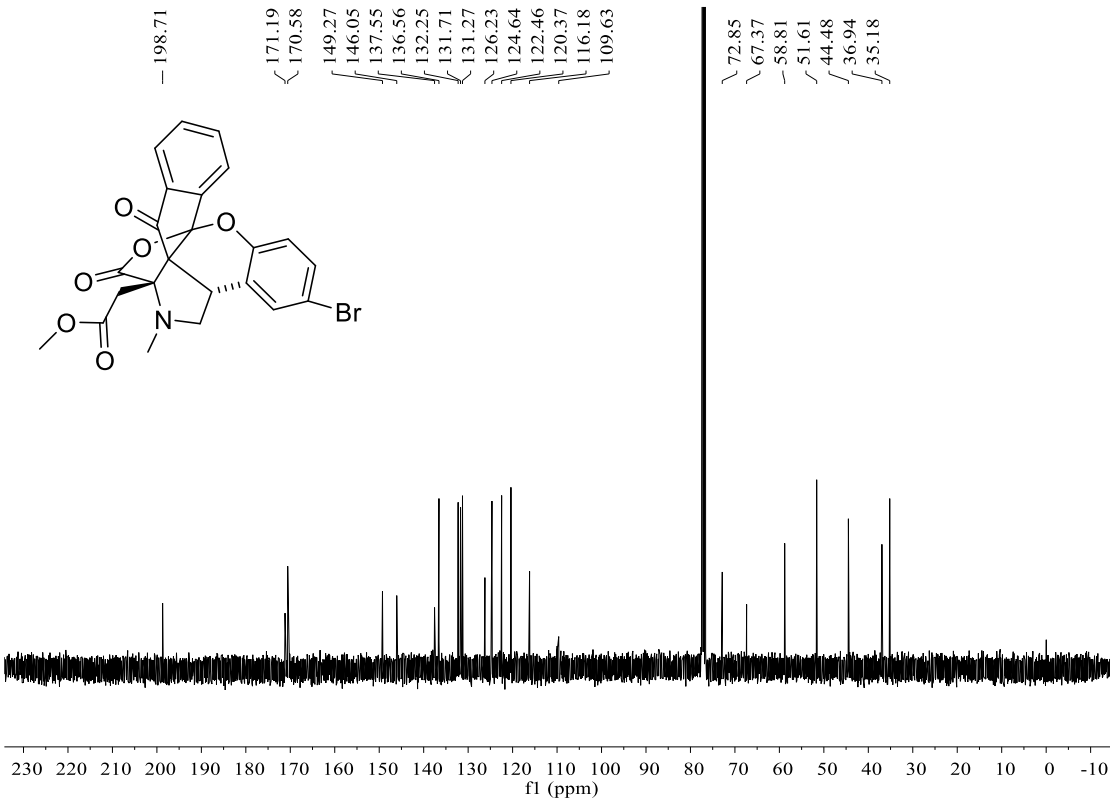


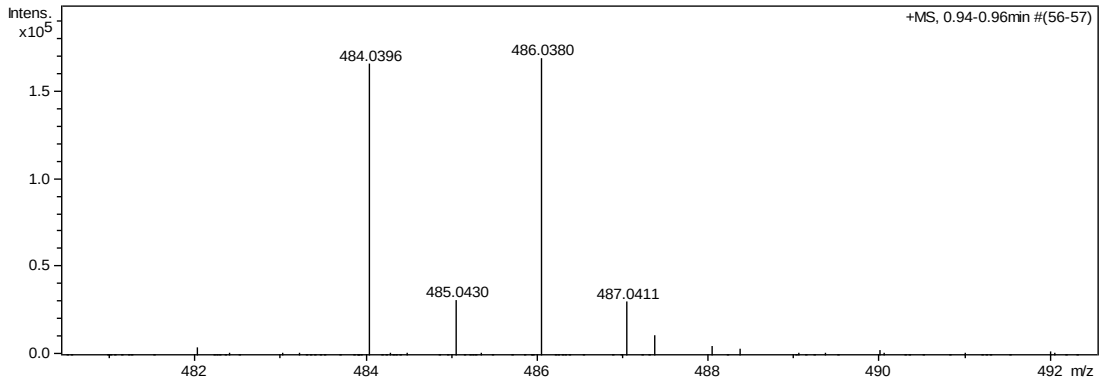

198.72
175.80
171.24
170.33
148.74
146.08
137.61
136.54
136.09
131.67
129.26
128.72
128.38
125.83
124.64
122.43
119.96
109.68
72.88
67.37
60.99
58.79
44.61
37.18
35.18
13.68
O
O
O
O
O
N
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^6
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 0.44-0.49min #(26-29)
454.1062
456.1038
455.1091
457.1064
450
452
454
456
458
460
462
m/z

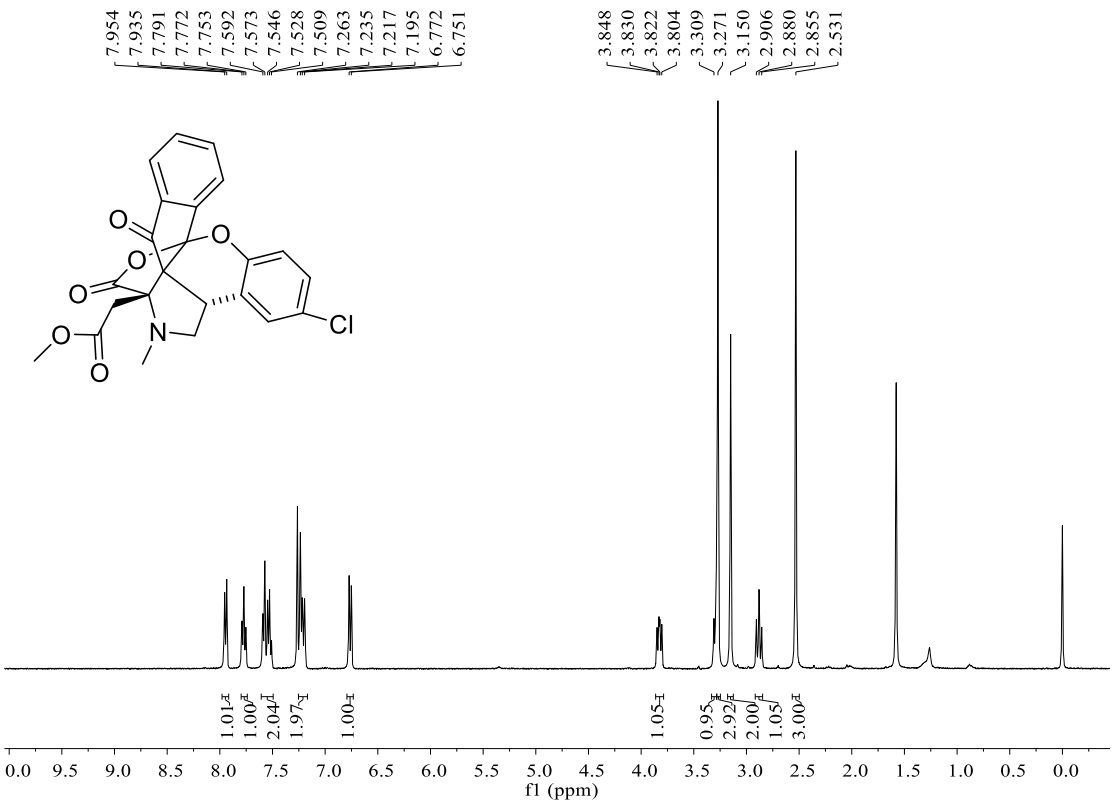
Methyl 2-(*rel*-(1S,3aS,8aR,13aS)-5-bromo-2-methyl-13,15-dioxo-3,3a-dihydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrol-1(2*H*)-yl)acetate (7d): white solid, 35%, m.p. 240-241 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.6 Hz, 1H, ArH), 7.79-7.75 (m, 1H, ArH), 7.59-7.51 (m, 2H, ArH), 7.24-7.19 (m, 2H, ArH), 7.76 (d, *J* = 8.4 Hz, 1H, ArH), 3.85-3.80 (m, 1H, CH), 3.31-3.28 (m, 1H, CH), 3.27 (s, 3H, OCH_3), 3.15 (s, 2H, CH_2), 2.91-2.86 (m, 1H, CH), 2.53 (s, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.7, 171.2, 170.6, 149.3, 146.1, 137.6, 136.6, 132.3, 131.7, 131.3, 126.2, 124.6, 122.5, 120.4, 116.2, 109.6, 72.8, 67.4, 58.8, 51.6, 44.5, 37.0, 35.2; IR (KBr) υ: 2981, 2868, 1795, 1688, 1443, 1388, 1344, 1277, 1190, 1137, 1075, 1023, 979, 886, 779, 710 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{23}H_{19}BrNO_6$ ([M+H]$^{+}$): 484.0390, Found: 484.0396.

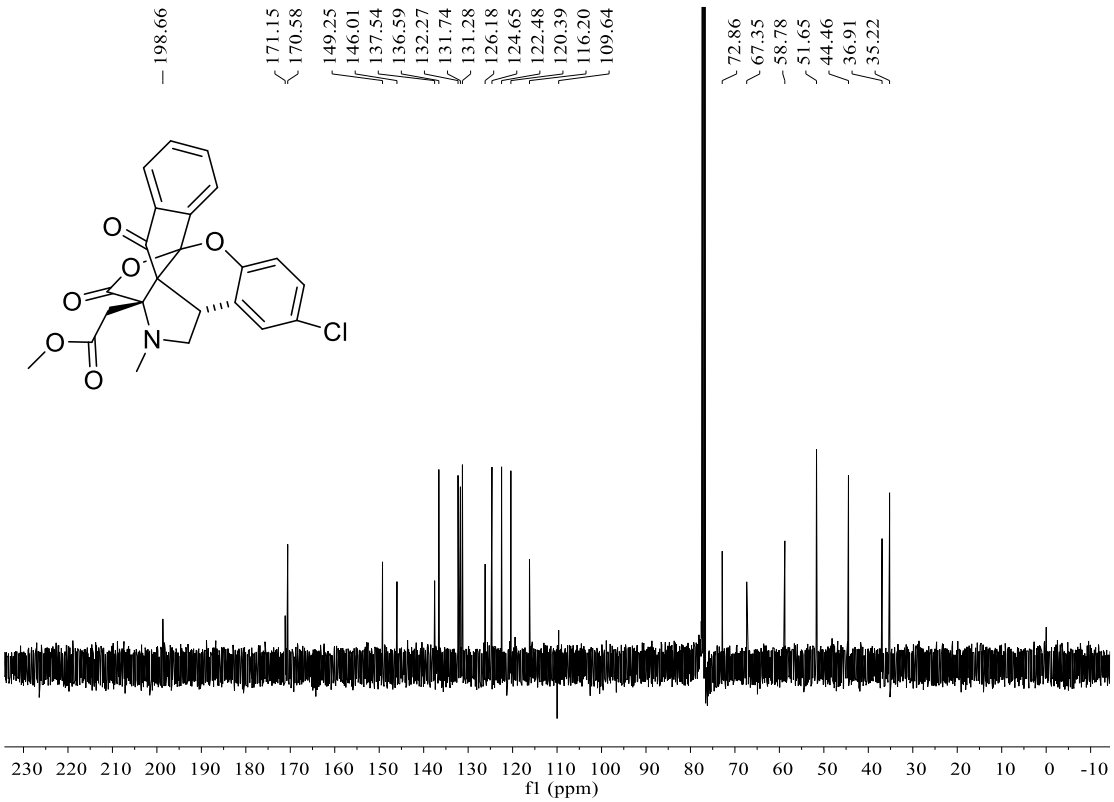


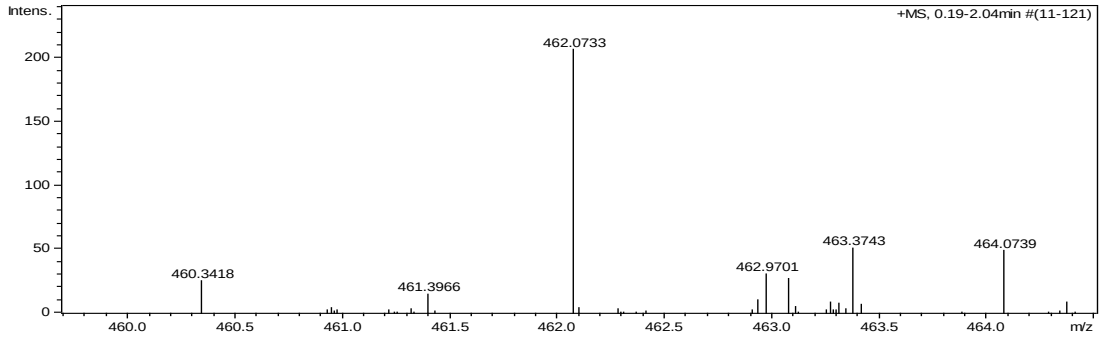

198.71
171.19
170.58
149.27
146.05
137.55
136.56
132.25
131.71
131.27
126.23
124.64
122.46
120.37
116.18
109.63
72.85
67.37
58.81
51.61
44.48
36.94
35.18
O
O
O
O
O
N
Br
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.94-0.96min #(56-57)
484.0396
486.0380
485.0430
487.0411
1.5
1.0
0.5
0.0
482
484
486
488
490
492 m/z

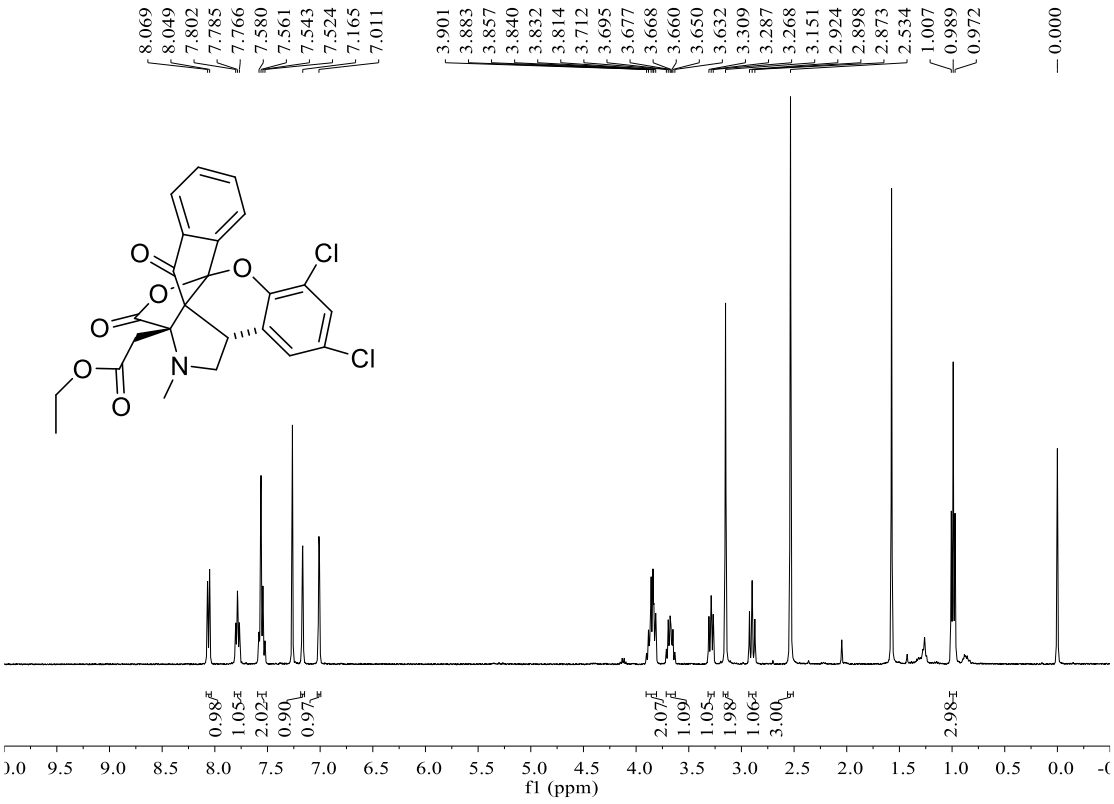
Methyl 2-(*rel*-(1S,3aS,8aR,13aS)-5-chloro-2-methyl-13,15-dioxo-3,3a-dihydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrol-1(2*H*)-yl)acetate (7e): white solid, 63%, m.p. 258-259 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.6 Hz, 1H, ArH), 7.79-7.75 (m, 1H, ArH), 7.59-7.51 (m, 2H, ArH), 7.26-7.20 (m, 2H, ArH), 6.76 (d, *J* = 8.4 Hz, 1H, ArH), 3.85-3.80 (m, 1H, CH), 3.33 (d, *J* = 9.6 Hz, 1H, CH), 3.27 (s, 3H, OCH_3), 3.15 (s, 2H, CH_2), 2.91-2.86 (m, 1H, CH), 2.53 (s, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.7, 171.1, 170.6, 149.3, 146.0, 137.5, 136.6, 132.3, 131.7, 131.3, 126.2, 124.6, 122.5, 120.4, 116.2, 109.6, 72.9, 67.3, 58.8, 51.6, 44.5, 36.9, 35.2; IR (KBr) υ: 2988, 2865, 1797, 1687, 1450, 1397, 1344, 1277, 1191, 1134, 1079, 1022, 980, 885, 773, 710 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{23}H_{18}ClNaNO_6$ ($[M+Na]^+$): 462.0715, Found: 462.0733.

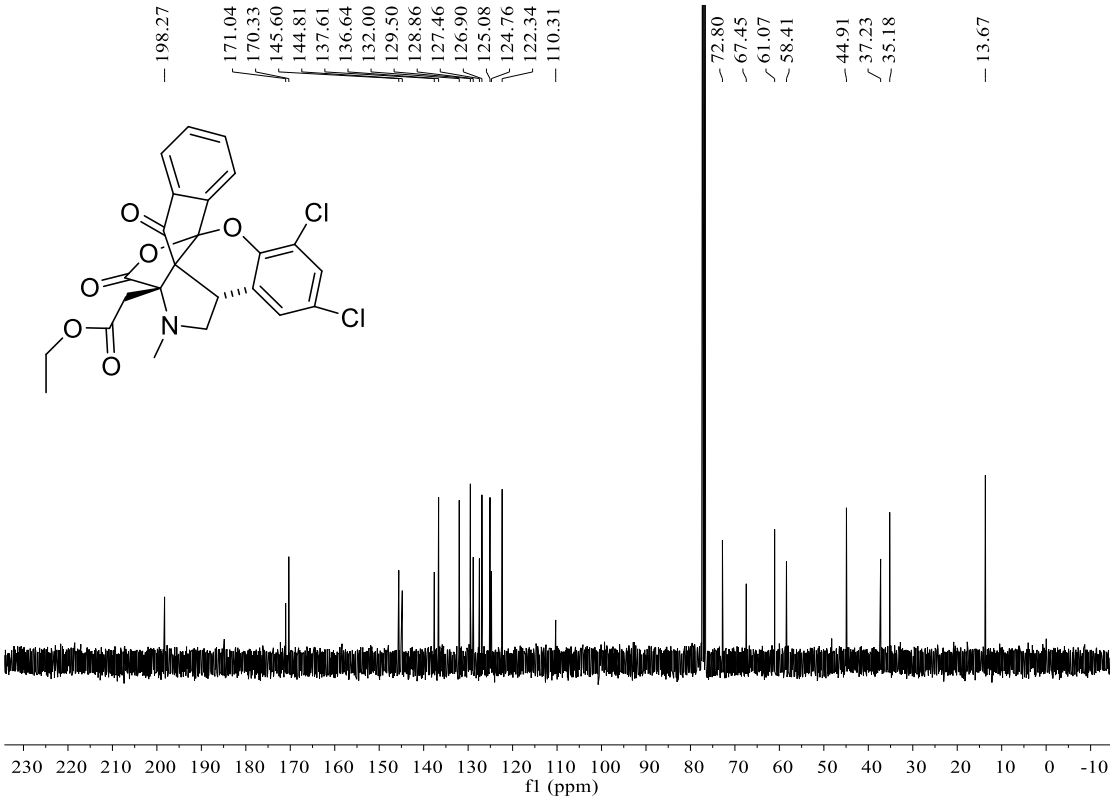


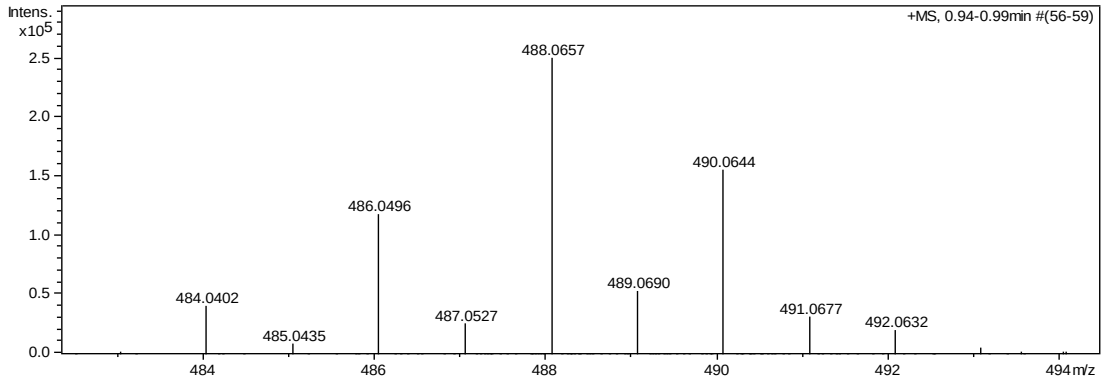

198.66
171.15
170.58
149.25
146.01
137.54
136.59
132.27
131.74
131.28
126.18
124.65
122.48
120.39
116.20
109.64
72.86
67.35
58.78
51.65
44.46
36.91
35.22
O
O
O
O
O
N
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 0.19-2.04min #(11-121)
462.0733
460.3418
461.3966
462.9701
463.3743
464.0739
200
150
100
50
0
460.0
460.5
461.0
461.5
462.0
462.5
463.0
463.5
464.0
m/z

Ethyl 2-(*rel*-(1S,3aS,8aR,13aS)-5,7-dichloro-2-methyl-13,15-dioxo-3,3a-dihydro-13*H*-8a,1-(epoxymethano)indeno[1',2':2,3]chromeno[3,4-c]pyrrol-1(2*H*)-yl)acetate (7f): white solid, 64%, m.p. 236-237 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 8.0 Hz, 1H, ArH), 7.80-7.77 (m, 1H, ArH), 7.58-7.52 (m, 2H, ArH), 7.17 (s, 1H, ArH), 7.01 (s, 1H, ArH), 3.90-3.81 (m, 2H, CH_2), 3.71-3.63 (m, 1H, CH), 3.31-3.27 (m, 1H, CH), 3.15 (s, 2H, CH_2), 2.92-2.87 (m, 1H, CH), 2.53 (s, 3H, CH_3), 0.99 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 198.3, 171.0, 170.3, 145.6, 144.8, 137.6, 136.6, 132.0, 129.5, 128.9, 127.5, 126.9, 125.1, 124.8, 122.3, 110.3, 72.8, 67.4, 61.1, 58.4, 44.9, 37.2, 35.1, 13.7; IR (KBr) υ: 2988, 2867, 1790, 1678, 1451, 1398, 1355, 1276, 1197, 1140, 1074, 1030, 987, 882, 771, 710 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{24}H_{20}Cl_2NO_6$ ([M+H]$^{+}$): 488.0662, Found: 488.0657.




198.27
171.04
170.33
145.60
144.81
137.61
136.64
132.00
129.50
128.86
127.46
126.90
125.08
124.76
122.34
110.31
72.80
67.45
61.07
58.41
44.91
37.23
35.18
13.67
O
O
O
O
O
N
Cl
Cl
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, 0.94-0.99min #(56-59)
488.0657
490.0644
486.0496
489.0690
484.0402
491.0677
487.0527
492.0632
485.0435
0.0
0.5
1.0
1.5
2.0
2.5
484
486
488
490
492
494 m/z