Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Efficient Construction of Diverse Spiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridines] via [3+3] Cycloaddition of MBH Carbonates of Isatins with β-Enamino Maleimides[a]

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Supporting Information

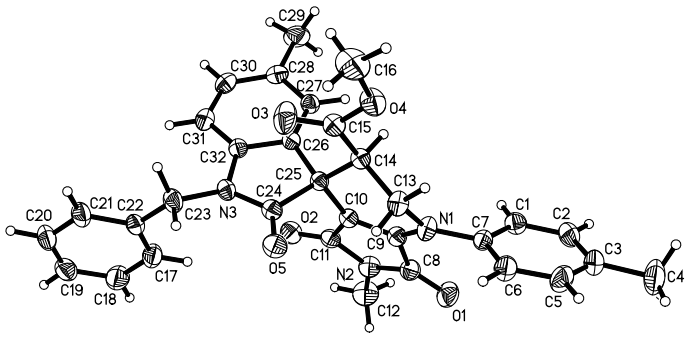


Fig. 1 Single crystal structure of the compound **3i**

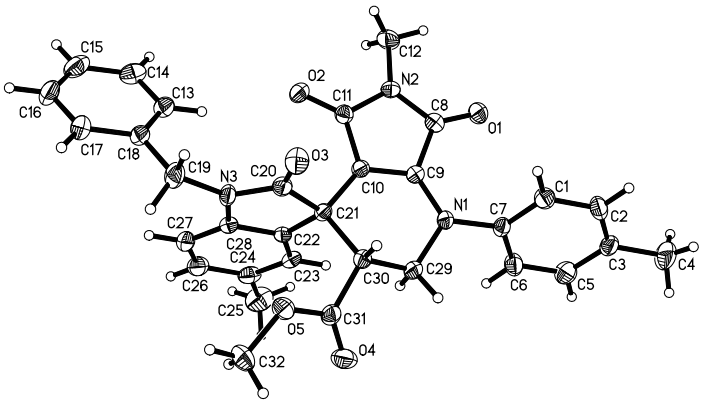


Fig. 2 Single crystal structure of the compound **3i'**

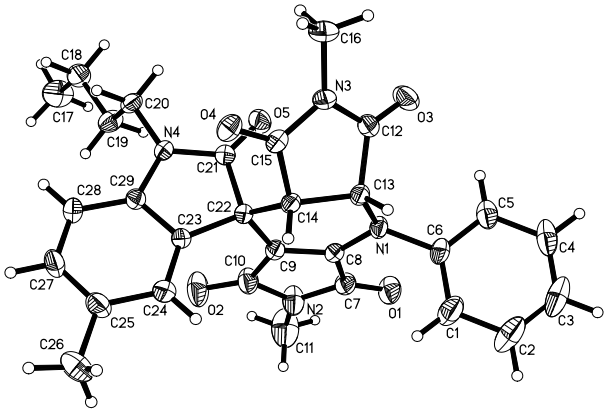


Fig. 3 Single crystal structure of the compound **5e**

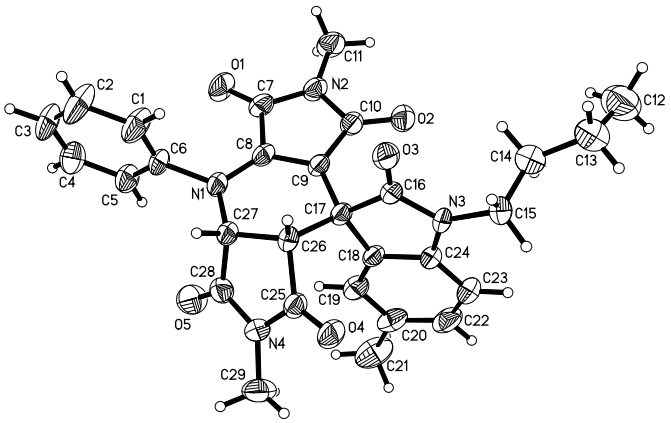


Fig. 4 Single crystal structure of the compound **5e'**

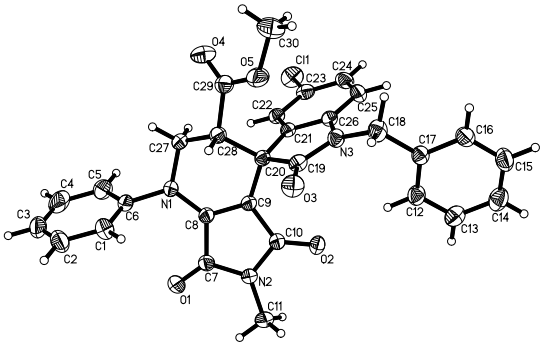


Fig. s1 Single crystal structure of the compound **3k'**

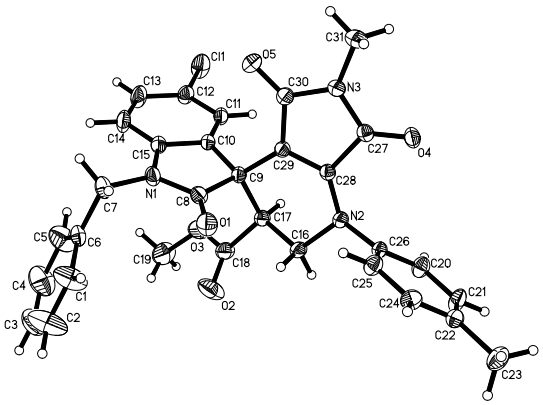


Fig. s2 Single crystal structure of the compound **3l**

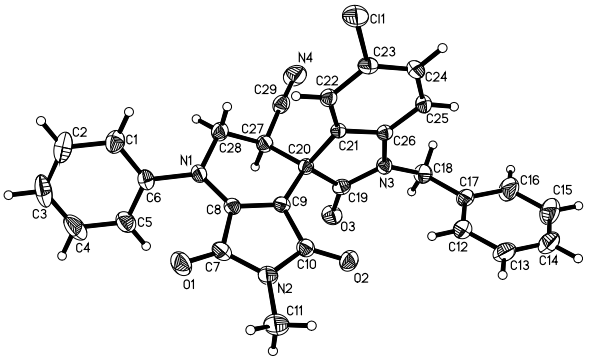


Fig. s3 Single crystal structure of the compound **4c'**

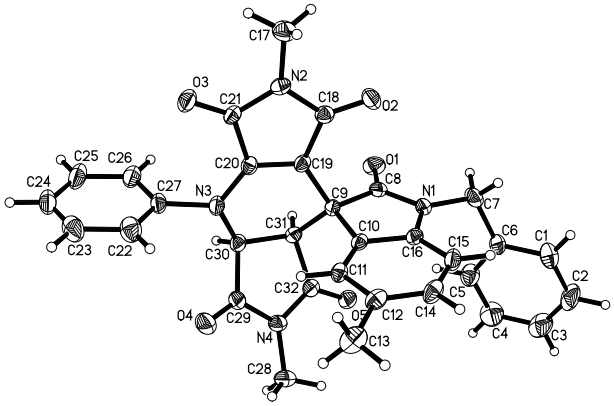


Fig. s4 Single crystal structure of the compound **5b'**

Table S1 The single crystal date of compounds **3i** and **3i'**

Phase	**3i**	**3i'**
Empirical formula	$C_{32}H_{29}N_3O_5$	$C_{32}H_{29}N_3O_5{\cdot}CHCl_3$
Formula weight	535.58	654.95
Temperature/K	296(2) K	296(2) K
Wavelength/ Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
a /Å	12.7017(18)	13.0140(14)
b / Å	20.368(3)	11.1280(11)
c / Å	10.6831(15)	21.958(3)
α (°)	90	90
β (°)	91.573(5)	94.274(4)
γ (°)	90	90
V (Å ^{3})	2762.8(7)	3171.1(6)
Z	4	4
Calculated density (g·cm^{-3})	1.288	1.372
Absorption coefficient (mm^{-1})	0.088	0.335
F(000)	1128	1360
θ range / (°)	2.153 to 25.999	2.343 to 24.997
Limiting indices	-15<=h<=14, -25<=k<=20, -13<=l<=12	-15<=h<=15, -13<=k<=13, -25<=l<=26
Reflections collected/unique	27432 / 5405 [R(int) = 0.0410]	27460 / 5577 [R(int) = 0.0672]
Completeness to theta	99.6 %	99.8 %
Max. and min. transmission	0.7456 and 0.6871	0.7456 and 0.6854
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5405 / 0 / 365	5577 / 0 / 401
Goodness-of-fit on F^2	1.020	1.075
Final *R* indices[I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1139	R1 = 0.0690, wR2 = 0.1786
R indices (all data)	R1 = 0.0850, wR2 = 0.1304	R1 = 0.1313, wR2 = 0.1993
Largest diff. peak and hole /(e ·Å^{-3})	0.239 and -0.205	0.474 and -0.679

Table S2 The single crystal date of compounds **3k'** and **3l**

Phase	**3k'**	**3l**
Empirical formula	$C_{30}H_{24}ClN_3O_5$	$C_{31}H_{26}ClN_3O_5$
Formula weight	541.97	556.00
Temperature/K	296(2) K	296(2) K
Wavelength/ Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/n	P-1
a /Å	9.4166(4)	9.2939(12)
b / Å	11.3916(5)	11.4737(17)
c / Å	24.6355(11)	13.2237(18)
α (°)	90	78.635(5)
β (°)	94.6982(15)	87.607(4)
γ (°)	90	75.843(4)
V (Å ^{3})	2633.8(2)	1340.4(3)
Z	4	2
Calculated density (g·cm^{-3})	1.367	1.378
Absorption coefficient (mm^{-1})	0.191	0.190
F(000)	1128	580
θ range / (°)	2.386 to 25.997	2.260 to 25.998
Limiting indices	-11<=h<=11, -14<=k<=12, -28<=l<=30	-11<=h<=11, -14<=k<=14, -15<=l<=16
Reflections collected/unique	24775 / 5163 [R(int) = 0.0409]	19165 / 5253 [R(int) = 0.0345]
Completeness to theta	99.7 %	99.6 %
Max. and min. transmission	0.7456 and 0.6850	0.7456 and 0.6846
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5163 / 0 / 355	5253 / 37 / 374
Goodness-of-fit on F^2	1.019	1.035
Final *R* indices[I>2sigma(I)]	R1 = 0.0435, wR2 = 0.0942	R1 = 0.0483, wR2 = 0.1079
R indices (all data)	R1 = 0.0808, wR2 = 0.1101	R1 = 0.0786, wR2 = 0.1224
Largest diff. peak and hole /(e ·Å^{-3})	0.208 and -0.188	0.200 and -0.337

Table S3 The single crystal date of compounds **4c'** and **5b'**

Phase	**4c'**	**5b'**
Empirical formula	$C_{29}H_{21}ClN_4O_3$	$C_{32}H_{26}N_4O_5$
Formula weight	508.95	546.57
Temperature/K	296(2) K	296(2) K
Wavelength/ Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
a /Å	18.3989(11)	9.0131(9)
b / Å	11.1620(7)	10.5429(11)
c / Å	12.1197(7)	14.4302(14)
α (°)	90	88.781(3)
β (°)	95.609(2)	86.492(3)
γ (°)	90	74.875(3)
V (Å ^{3})	2477.1(3)	1321.2(2)
Z	4	2
Calculated density (g·cm^{-3})	1.365	1.374
Absorption coefficient (mm^{-1})	0.194	0.095
F(000)	1056	572
θ range / (°)	1.112 to 25.999	2.345 to 25.998
Limiting indices	-22<=h<=22, -13<=k<=11, -14<=l<=14	-11<=h<=11, -12<=k<=13, 0<=l<=17
Reflections collected/unique	22796 / 4857 [R(int) = 0.0656]	5066 / 5066 [R(int) = ?]
Completeness to theta	99.6 %	99.3 %
Max. and min. transmission	0.7456 and 0.6653	0.7456 and 0.3662
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4857 / 0 / 335	5066 / 0 / 374
Goodness-of-fit on F^2	1.013	1.016
Final *R* indices[I>2sigma(I)]	R1 = 0.0511, wR2 = 0.0954	R1 = 0.0784, wR2 = 0.1841
R indices (all data)	R1 = 0.1168, wR2 = 0.1164	R1 = 0.1212, wR2 = 0.2125
Largest diff. peak and hole /(e ·Å^{-3})	0.220 and -0.221	0.258 and -0.304

Table S4 The single crystal date of compounds **5e** and **5e'**

Phase	**5e**	**5e'**
Empirical formula	$C_{29}H_{28}N_4O_5$	$C_{29}H_{28}N_4O_5$
Formula weight	512.55	512.55
Temperature/K	296(2) K	296(2) K
Wavelength/ Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
a /Å	9.6086(10)	11.1314(6)
b / Å	29.328(3)	9.2504(5)
c / Å	9.6428(11)	25.5543(16)
α (°)	90	90
β (°)	101.287(3)	100.241(2)
γ (°)	90	90
V (Å ^{3})	2664.8(5)	2589.4(3)
Z	4	4
Calculated density (g·cm^{-3})	1.278	1.315
Absorption coefficient (mm^{-1})	0.089	0.091
F(000)	1080	1080
θ range / (°)	2.563 to 25.992	2.238 to 25.000
Limiting indices	--11<=h<=10, -35<=k<=36, -11<=l<=10	-12<=h<=13, -10<=k<=11, -30<=l<=29
Reflections collected/unique	26172 / 5212 [R(int) = 0.0634]	24790 / 4546 [R(int) = 0.0488]
Completeness to theta	99.7 %	99.8 %
Max. and min. transmission	0.7456 and 0.6076	0.7456 and 0.6599
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5212 / 0 / 347	4546 / 171 / 386
Goodness-of-fit on F^2	1.018	1.062
Final *R* indices[I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1232	R1 = 0.0704, wR2 = 0.2111
R indices (all data)	R1 = 0.1006, wR2 = 0.1436	R1 = 0.1178, wR2 = 0.2351
Largest diff. peak and hole /(e ·Å^{-3})	0.205 and -0.203	0.565 and -0.513

Experimental section

1. General procedure for the reaction of MBH esters of isatins and β-enamino maleimides: To a round flask was added MBH esters of isatins (0.20 mmol), β-enamino maleimides (0.40 mmol), DABCO (0.04 mmol) and acetonitrile (6.0 mL). The mixture was stirred at room temperature for about one hour. After removing the solvent by rotatory evaporation at reduced pressure, the residue was subjected to column chromatography with ethyl acetate and petroleum ether (V/V = 1:6) as eluent to give the pure products **3a-3m** and **3a'-3m'** for analysis.。

Methyl *rel*-(3*R*,3'*R*)-1-butyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3a**): yellow solid, 47%, m.p. 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (dd, J_1 =8.4 Hz, J_2 =2.0 Hz, 1H, ArH), 7.23 (d, J = 8.0 Hz, 2H, ArH), 7.16 (d, J = 8.4 Hz, 2H, ArH), 7.08 (d, J = 2.0 Hz, 1H, ArH), 6.86 (d, J = 8.4 Hz, 1H, ArH), 4.73 (t, J = 12.0 Hz, 1H, CH), 3.97 (dd, J_1 =12.8 Hz, J_2 =3.6 Hz, 1H, CH), 3.81 ~ 3.69 (m, 2H, CH), 3.52 (s, 3H, OCH_3), 3.32 (dd, J_1=11.2 Hz, J_2=3.6 Hz, 1H, CH), 2.76 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 1.75 ~ 1.67 (m, 2H, CH), 1.49 ~ 1.39 (m, 2H, CH), 0.97 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.8, 168.7, 167.0, 163.7, 145.0, 142.9, 140.1, 137.4, 131.3, 129.8, 128.8, 127.6, 125.0, 122.6, 110.0, 109.4, 101.4, 52.4, 51.0, 46.6, 45.9, 40.5, 29.2, 23.1, 21.1, 20.1, 13.7; IR (KBr) υ: 2941, 2862, 1765, 1722, 1712, 1640, 1614, 1501, 1465, 1443, 1389, 1356, 1254, 1177, 1109, 1069, 1033, 976, 854, 791, 749 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{28}ClN_3NaO_5$ ([M+Na]$^+$): 544.1610, Found: 544.1606.

Methyl *rel*-(3*S*,3'*R*)-1-butyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3a'**): yellow solid, 35%, m.p. 215-217 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (d, J =8.8 Hz, 1H, ArH), 7.23 (d, J = 8.0 Hz, 2H, ArH), 7.17 (d, J = 8.0 Hz, 2H, ArH), 7.12 (m, 1H, ArH), 6.85 (d, J = 8.4 Hz, 2H, ArH), 4.20 ~ 4.08 (m, 2H, CH), 3.81 (t, J = 7.6 Hz, 2H, CH), 3.59 (dd, J_1 =11.2 Hz, J_2 =4.8 Hz, 1H, CH), 3.36 (s, 3H, OCH_3), 2.39 (s, 3H, CH_3), 1.80 ~ 1.73 (m, 2H, CH), 1.56 ~ 1.46 (m, 2H, CH), 1.02 (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.7, 168.6, 167.4, 163.8, 144.8, 142.5, 139.9, 137.3, 131.1, 129.8, 129.1, 127.6, 124.7, 124.5, 109.5, 103.0, 52.0, 50.8, 47.0, 45.8, 40.7, 29.2, 23.2, 21.1, 20.2, 13.8; IR (KBr) υ: 2944, 2859, 1767, 1732, 1702, 1655, 1613, 1462, 1435, 1373, 1340, 1254, 1160, 1088, 1051, 981, 846, 812, 788 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{28}ClN_3NaO_5$ ([M+Na]$^+$):

544.1610, Found: 544.1619.

Methyl *rel*-(3*R*,3'*R*)-1-butyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3b**): yellow solid, 51%, m.p. 244-246 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 ~ 7.40 (m, 2H, ArH), 7.35 ~ 7.27 (m, 4H, ArH), 7.09 (s, 1H, ArH), 6.87 (d, *J* = 8.4 Hz, 1H, ArH), 4.76 (t, *J* = 12.0 Hz, 1H, CH), 4.01 (dd, J_1 =12.8 Hz, J_2 =3.6 Hz, 1H, CH), 3.81 ~ 3.70 (m, 2H, CH), 3.53 (s, 3H, OCH_3), 3.33 (dd, J_1 =11.6 Hz, J_2 =3.6 Hz, 1H, CH), 2.76 (s, 3H, CH_3), 1.75 ~ 1.68 (m, 2H, CH), 1.49 ~ 1.40 (m, 2H, CH), 0.97 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.7, 168.6, 166.9, 163.7, 144.8, 143.0, 142.6, 131.2, 129.2, 128.8, 127.6, 127.3, 125.1, 122.6, 109.5, 102.2, 52.5, 50.9, 46.6, 46.0, 40.5, 29.2, 23.2, 20.1, 13.7; IR (KBr) υ: 2946, 2853, 1763, 1730, 1706, 1645, 1600, 1511, 1470, 1437, 1388, 1360, 1255, 1176, 1104, 1076, 1030, 981, 857, 796, 759 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}ClN_3NaO_5$ ($[M+Na]^+$): 530.1453, Found: 530.1451.

Methyl *rel*-(3*S*,3'*R*)-1-butyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3b'**): yellow solid, 32%, m.p. 266-267 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 ~ 7.41 (m, 2H, ArH), 7.35 ~ 7.24 (m, 4H, ArH), 7.14 ~ 7.11 (m, 1H, ArH), 6.86 (d, *J* = 8.4 Hz, 1H, ArH), 4.23 ~ 4.10 (m, 2H, CH), 3.81 (t, *J* = 7.6 Hz, 2H, CH), 3.60 (dd, J_1 =10.8 Hz, J_2 =5.2 Hz, 1H, CH), 3.36 (s, 3H, OCH_3), 2.80 (s, 3H, CH_3), 1.79 ~ 1.73 (m, 2H, CH), 1.56 ~ 1.47 (m, 2H, CH), 1.02 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 168.6, 167.3, 163.8, 144.6, 142.5, 142.4, 131.0, 129.2, 129.1, 127.6, 127.2, 124.8, 124.5, 109.5, 103.7, 52.0, 50.7, 47.1, 45.8, 40.7, 29.2, 23.3, 20.2, 13.8; IR (KBr) υ: 2942, 2854, 1764, 1726, 1702, 1644, 1609, 1521, 1476, 1428, 1402, 1368, 1264, 1176, 1110, 1075, 1031, 987, 862, 796, 764 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{26}ClN_3NaO_5$ ($[M+Na]^+$): 530.1453, Found: 530.1449.

Methyl *rel*-(3*R*,3'*R*)-1-butyl-5-chloro-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3c**): yellow solid, 48%, m.p. 219-221 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (dd, J_1 =8.4 Hz, J_2 =2.0 Hz, 1H, ArH), 7.23 ~ 7.19 (m, 2H, ArH), 7.08 (d, *J* = 2.0 Hz, 1H, ArH), 6.95 ~ 6.92 (m, 2H, ArH), 6.86 (d, *J* = 8.4 Hz, 1H, ArH), 4.71 (t, *J* = 12.0 Hz, 1H, CH), 3.94 (dd, J_1 =12.8 Hz, J_2 =4.0 Hz, 1H, CH), 3.84 (s, 3H,

OCH_3), 3.77 ~ 3.71 (m, 2H, CH), 3.53 (s, 3H, CH_3), 3.33 (dd, J_1 =12.8 Hz, J_2 =3.6 Hz, 1H, CH), 2.76 (s, 3H, CH_3), 1.75 ~ 1.67 (m, 2H, CH), 1.49 ~ 1.39 (m, 2H, CH), 0.7 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.9, 168.7, 167.0, 163.8, 158.8, 145.2, 142.9, 135.5, 131.3, 128.8, 127.6, 126.6, 122.6, 114.4, 109.4, 100.5, 55.5, 52.4, 51.1, 46.6, 45.9, 40.5, 29.2, 23.1, 20.1, 13.7; IR (KBr) υ: 2944, 2858, 1765, 1721, 1701, 1642, 1607, 1519, 1472, 1432, 1397, 1370, 1264, 1171, 1111, 1073, 1028, 984, 867, 799, 762 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{28}ClN_3NaO_6$ ($[M+Na]^+$): 560.1559, Found: 560.1552.

Methyl *rel*-(3*S*,3'*R*)-1-butyl-5-chloro-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate(**3c'**): yellow solid, 29%, m.p. 228-230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 ~ 7.27 (m, 1H, ArH), 7.22 (d, J = 8.8 Hz, 2H, ArH), 7.12 (d, J = 1.6 Hz, 1H, ArH), 6.95 (d, J = 8.8 Hz, 2H, ArH), 6.86 (d, J = 8.4 Hz, 1H, ArH), 4.19 ~ 4.06 (m, 2H, CH), 3.84 (s, 3H, OCH_3), 3.83 ~ 3.79 (m, 2H, CH), 3.61 (dd, J_1 =11.6 Hz, J_2 =4.4 Hz, 1H, CH), 3.36 (s, 3H, OCH_3), 2.79 (s, 3H, CH_3), 1.80 ~ 1.73 (m, 2H, CH), 1.56 ~ 1.47 (m, 2H, CH), 1.02 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.7, 168.6, 167.4, 163.9, 158.7, 144.9, 142.5, 135.3, 131.1, 129.1, 127.6, 126.3, 124.5, 114.4, 109.5, 102.2, 55.5, 52.0, 51.0, 47.0, 45.7, 40.7, 29.2, 23.2, 20.2, 13.8; IR (KBr) υ: 2939, 2857, 1762, 1727, 1697, 1641, 1603, 1527, 1478, 1431, 1404, 1372, 1267, 1174, 1107, 1073, 1032, 988, 861, 798, 763 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{28}ClN_3NaO_6$ ($[M+Na]^+$): 560.1559, Found: 560.1553.

Methyl *rel*-(3*R*,3'*R*)-1-butyl-5-chloro-1'-(4-chlorophenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3d**): yellow solid, 57%, m.p. 223-225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, J = 8.4 Hz, 2H, ArH), 7.30 (dd, J_1 =8.4 Hz, J_2 =8.4 Hz, 1H, ArH), 7.21 (d, J = 8.4 Hz, 2H, ArH), 7.08 (d, J = 1.6 Hz, 1H, ArH), 6.87 (d, J = 8.4 Hz, 1H, ArH), 4.73 (t, J = 12.0 Hz, 1H, CH), 3.96 (dd, J_1 =12.8 Hz, J_2 =4.0 Hz,, 1H, CH), 3.81 ~ 3.69 (m, 2H, CH), 3.54 (s, 3H, OCH_3), 3.32 (dd, J_1 =11.6 Hz, J_2 =3.6 Hz,, 1H, CH), 2.77 (s, 3H, CH_3), 1.75 ~ 1.67 (m, 2H, CH), 1.48 ~ 1.39 (m, 2H, CH), 0.97 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.6, 168.5, 166.8, 163.7, 144.5, 142.9, 141.0, 132.9, 131.0, 129.4, 128.9, 127.7, 126.3, 122.6, 109.5, 103.0, 52.5, 50.8, 46.5, 45.9, 40.5, 29.1, 23.2, 20.1, 13.7; IR (KBr) υ: 2939, 2851, 1766, 1729, 1705, 1647, 1603, 1519, 1477, 1430, 1398, 1362, 1265, 1174, 1105, 1078, 1028, 984, 859, 792, 756 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{25}Cl_2N_3NaO_5$ ($[M+Na]^+$):

564.1063, Found: 564.1059.

Methyl *rel*-(3*S*,3'*R*)-1-butyl-5-chloro-1'-(4-chlorophenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3d'**): yellow solid, 30%, m.p. 225-227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 8.4 Hz, 2H, ArH), 7.29 (dd, J_1 =8.0 Hz, J_2 =7.2 Hz, 1H, ArH), 7.22 (d, *J* = 8.4 Hz, 2H, ArH), 7.16~ 7.14(m, 1H, ArH), 6.86 (d, *J* =8.4 Hz, 1H, ArH), 4.20~ 4.08 (m, 2H, CH), 3.80 (t, *J* = 7.6 Hz, 2H, CH), 3.58 (dd, J_1 =11.2 Hz, J_2 =3.2 Hz, 1H, CH), 3.37 (s, 3H, OCH_3), 2.80 (s, 3H, CH_3), 1.79 ~ 1.72 (m, 2H, CH), 1.55 ~ 1.46 (m, 2H, CH), 1.02 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.5, 168.4, 167.1, 163.8, 144.2, 142.5, 140.9, 132.8, 130.7, 129.34, 129.2, 127.7, 126.0, 124.5, 109.6, 104.5, 52.1, 50.7, 47.0, 45.7, 40.7, 29.1, 23.3, 20.2, 13.8; IR (KBr) υ: 2947, 2852, 1767, 1735, 1701, 1642, 1605, 1518, 1474, 1425, 1403, 1369, 1266, 1173, 1107, 1068, 1034, 983, 865, 794, 758 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{25}Cl_2N_3NaO_5$ ($[M+Na]^+$): 564.1063, Found: 564.1062.

Methyl *rel*-(3*R*,3'*R*)-1-benzyl-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3e**): yellow solid, 27%, m.p. 203-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 ~ 7.41 (m, 4H, ArH), 7.36 ~ 7.31 (m, 4H, ArH), 7.29 (s, 1H, ArH), 7.26 ~ 7.21 (m, 2H, ArH), 7.13 (d, *J* =7.2 Hz, 1H, ArH), 7.06 ~ 7.02 (m, 1H, ArH), 6.77 (d, *J* =8.0 Hz, 1H, ArH), 5.06 ~ 4.98 (m, 2H, CH), 4.82 (t, *J* =12.0 Hz, 1H, CH), 4.02 (dd, J_1 = 12.8 Hz, J_2 = 3.6 Hz, 1H, CH), 3.44 (s, 3H, OCH_3), 3.40 (dd, J_1 = 11.6 Hz, J_2 = 3.6 Hz, 1H, CH), 2.78 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.3, 169.0, 167.1, 163.9, 144.9, 143.9, 142.7, 135.6, 129.2, 129.1, 128.9, 128.7, 127.4, 127.3, 127.2, 125.1, 122.7, 122.0, 109.6, 102.8, 52.4, 51.0, 46.7, 46.1, 44.5, 23.2; IR (KBr) υ: 2958, 2849, 1766, 1731, 1711, 1647, 1596, 1511, 1463, 1442, 1392, 1350, 1254, 1176, 1103, 1078, 1030, 979, 843, 799, 763 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{26}N_3O_5$ ($[M+H]^+$): 508.1867, Found: 508.1885.

Methyl *rel*-(3*S*,3'*R*)-1-benzyl-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3e'**): yellow solid, 40%, m.p. 135-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 7.6 Hz, 2H, ArH), 7.45 ~ 7.41 (m, 2H, ArH), 7.40 ~ 7.36 (m, 2H, ArH), 7.34 ~ 7.29 (m, 4H, ArH), 7.22 ~ 7.17 (m, 2H, ArH), 7.02 (t, *J* = 7.6 Hz, 1H, ArH), 6.79 (d, *J* = 8.0 Hz, 1H, ArH), 5.09 (d, *J* = 15.6 Hz, 1H, CH), 5.03 (d, *J* = 15.6 Hz, 1H, CH), 4.30

~ 4.23 (m, 1H, CH), 4.14 (dd, J_1 = 13.6 Hz, J_2 = 4.4 Hz, 1H, CH), 3.67 (dd, J_1 = 11.6 Hz, J_2 = 4.0 Hz, 1H, CH), 3.13 (s, 3H, OCH_3) , 2.82 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.5, 168.9, 167.5, 164.1, 144.5, 143.5, 142.6, 135.7, 129.2, 129.1, 128.7, 127.8, 127.6, 127.1, 124.8, 123.9, 122.7, 109.5, 104.6, 51.9, 50.9, 47.2, 46.0, 44.9, 23.3; IR (KBr) υ: 2956, 2866, 1749, 1735, 1700, 1640, 1608, 1512, 1464, 1432, 1376, 1349, 1248, 1178, 1097, 1065, 1033, 982, 847, 804, 761 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{26}N_3O_5$ ($[M+H]^+$): 508.1867, Found: 508.1887.

Methyl *rel*-(3*R*,3'*R*)-1-benzyl-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3f**): yellow solid, 23%, m.p. 218-220 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, *J* =7.6 Hz, 2H, ArH), 7.35 (t, *J* =7.6 Hz, 2H, ArH), 7.28 ~ 7.26 (m, 1H, ArH), 7.24 ~ 7.18 (m, 5H, ArH), 7.13 (d, *J* =7.2 Hz, 1H, ArH), 7.06 ~ 7.02 (m, 1H, ArH), 6.77 (d, *J* =8.0 Hz, 1H, ArH), 5.02 (s, 2H, CH), 4.79 (t, *J* =12.0 Hz, 1H, CH), 3.99 (dd, J_1 = 12.8 Hz, J_2 = 4.0 Hz, 1H, CH), 3.44 (s, 3H, OCH_3), 3.40 (dd, J_1 = 11.6 Hz, J_2 = 3.6 Hz, 1H, CH), 2.78 (s, 3H, CH_3), 2.39 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.4, 169.0, 167.1, 163.9, 145.1, 143.9, 140.2, 137.3, 135.7, 129.8, 129.2, 128.9, 128.7, 127.4, 127.3, 125.1, 122.7, 122.0, 109.5, 102.0, 52.3, 51.1, 46.7, 46.1, 44.4, 23.2, 21.1; IR (KBr) υ: 2943, 2855, 1751,1723, 1701, 1644, 1604, 1511, 1464, 1429, 1375, 1356, 1260, 1171, 1111, 1072, 1033, 979, 837, 789, 753 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{27}N_3NaO_5$ ($[M+Na]^+$): 544.1843, Found: 544.1835.

Methyl *rel*-(3*S*,3'*R*)-1-benzyl-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3f'**): yellow solid, 36%, m.p. 177-179 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.6 Hz, 2H, ArH), 7.38 (t, *J* =7.2 Hz, 2H, ArH), 7.32 ~ 7.28 (m, 1H, ArH), 7.24 ~ 7.17 (m, 6H, ArH), 7.03 ~ 6.99 (m, 1H, ArH), 6.79 (d, *J* =8.0 Hz, 1H, ArH), 5.09 (d, *J* = 15.6 Hz, 1H, CH), 5.03 (d, *J* = 15.6 Hz, 1H, CH), 4.27 ~ 4.21 (m, 1H, CH), 4.10 (dd, J_1 = 13.6 Hz, J_2 = 4.0 Hz, 1H, CH), 3.66 (dd, J_1 = 11.6 Hz, J_2 = 4.0 Hz, 1H, CH), 3.13 (s, 3H, OCH_3), 2.81 (s, 3H, CH_3), 2.39 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.6, 168.9, 167.5, 164.1, 144.7, 143.5, 140.1, 137.2, 135.7, 129.8, 129.1, 128.7, 127.8, 127.6, 124.7, 123.9, 122.7, 109.5, 103.7, 51.9, 50.9, 47.1, 45.9, 44.9, 23.3, 21.1; IR (KBr) υ: 2949, 2842, 1756, 1721, 1710, 1638, 1611, 1507, 1465, 1430, 1385, 1340, 1262, 1166, 1103, 1064, 1040, 992, 855, 793, 762 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{28}N_3O_5$ ($[M+H]^+$): 544.1843, Found: 544.1829.

Methyl

***rel*-(3*R*,3'*R*)-1-benzyl-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydr ospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3g**): yellow solid, 28%, m.p. 167-169 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 7.6 Hz, 2H, ArH), 7.34 (t, *J* = 7.2 Hz, 2H, ArH), 7.28 ~ 7.26 (m, 1H, ArH), 7.24 ~ 7.20 (m, 3H, ArH), 7.13 (d, *J* = 6.8 Hz, 1H, ArH), 7.06 ~ 7.02 (m, 1H, ArH), 6.94 (d, *J* = 8.8 Hz, 2H, ArH), 6.76 (d, *J* = 7.6 Hz, 1H, ArH), 5.02 (s, 2H, CH), 4.77 (t, *J* = 11.6 Hz, 1H, CH), 3.95 (dd, J_1 = 12.8 Hz, J_2 = 4.0 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 3.42 ~ 3.38 (m, 1H, CH), 2.77 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.4, 169.0, 167.1, 164.0, 158.7, 145.3, 143.8, 135.7, 135.6, 129.2, 128.9, 128.7, 127.4, 127.3, 126.7, 122.7, 122.0, 114.4, 109.5, 101.1, 55.5, 52.3, 51.2, 46.7, 46.0, 44.4, 23.1; IR (KBr) υ: 2941, 2851, 1761,1728, 1707, 1642, 1606, 1509, 1460, 1483, 1384, 1355, 1251, 1173, 1104, 1072, 1029, 990, 850, 807, 757 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{28}N_3O_6$ ([M+H]$^+$): 538.1973, Found: 538.1989.

Methyl

***rel*-(3*S*,3'*R*)-1-benzyl-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydr ospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3g'**): yellow solid, 34%, m.p. 193-195 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.2 Hz, 2H, ArH), 7.38 (t, *J* = 7.2 Hz, 2H, ArH), 7.31 ~ 7.28 (m, 1H, ArH), 7.24 ~ 7.17 (m, 4H, ArH), 7.02 ~ 6.99 (m, 1H, ArH), 6.96 ~ 6.93 (m, 2H, ArH), 6.78 (d, *J* = 7.6 Hz, 1H, ArH), 5.09 (d, *J* = 15.6 Hz, 1H, CH), 5.03 (d, *J* = 15.6 Hz, 1H, CH), 4.23 (t, *J* = 12.4 Hz,1H, CH), 4.06 (dd, J_1 = 14.0 Hz, J_2 = 4.4 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.66 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H, CH), 3.14 (s, 3H, OCH_3), 2.81 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.6, 168.9, 167.5, 164.1, 158.6, 144.8, 143.5, 135.7, 135.5, 129.2, 129.1, 128.7, 127.8, 127.6, 126.3, 123.9, 122.7, 114.4, 109.5, 103.0, 55.5, 51.8, 51.1, 47.1, 45.9, 44.9, 23.2; IR (KBr) υ: 2961, 2842, 1756,1721, 1710, 1638, 1611, 1507, 1465, 1430, 1385, 1350, 1262, 1166, 1103, 1064, 1040, 992, 855, 793, 762 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{28}N_3O_6$ ([M+H]$^+$): 538.1973, Found: 538.1986.

Methyl

***rel*-(3*R*,3'*R*)-1-benzyl-1'-(4-chlorophenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydros piro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3h**): yellow solid, 25%, m.p. 214-216 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 ~ 7.33 (m, 6H, ArH), 7.29 ~ 7.27 (m, 1H, ArH), 7.25 ~ 7.22 (m, 3H, ArH), 7.12 (d, *J* = 6.8 Hz, 1H, ArH), 7.07 ~ 7.03 (m, 1H, ArH), 6.78 (d, *J* = 8.0 Hz, 1H, ArH), 5.04 (d, *J* = 16.0 Hz, 1H, CH), 5.00 (d, *J* = 15.2 Hz, 1H, CH), 4.79 (t, *J* = 12.0

Hz, CH), 4.98 (dd, J_1 = 12.4 Hz, J_2 = 3.6 Hz, 1H, CH), 3.45 (s, 3H, OCH_3), 3.39 (dd, J_1 = 11.6 Hz, J_2 = 4.0 Hz, 1H, CH), 2.79 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.2, 168.8, 167.0, 163.9, 144.5, 143.9, 141.2, 135.6, 132.8, 129.4, 129.0, 128.9, 128.7, 127.5, 127.3, 126.4, 122.8, 122.0, 109.6, 103.5, 52.4, 50.9, 46.6, 46.1, 44.5, 23.2; IR (KBr) υ: 2952, 2855, 1762, 1724, 1709, 1642, 1609, 1497, 1455, 1420, 1388, 1353, 1247, 1187, 1116, 1083, 1033, 996, 858, 803, 764 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{24}ClN_3NaO_5$ ($[M+Na]^+$): 564.1297, Found: 564.1314.

Methyl *rel*-(3*S*,3'*R*)-1-benzyl-1'-(4-chlorophenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3h'**): yellow solid, 37%, m.p. 201-203 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 7.2 Hz, 2H, ArH), 7.40 ~ 7.36 (m, 4H, ArH), 7.32 ~ 7.28 (m, 1H, ArH), 7.25 ~ 7.16 (m, 4H, ArH), 7.03 ~ 6.99 (m, 1H, ArH), 6.80 (d, *J* = 7.6 Hz, 1H, ArH), 5.08 (d, *J* = 16.0 Hz, 1H, CH), 5.03 (d, *J* = 15.6 Hz, 1H, CH), 4.27 ~ 4.20 (m, 1H, CH), 4.09 (dd, J_1 = 13.6 Hz, J_2 = 4.4 Hz, 1H, CH), 3.65 (dd, J_1 = 12.0 Hz, J_2 = 4.4 Hz, 1H, CH), 3.13 (s, 3H, OCH_3), 2.82 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.3, 168.8, 167.3, 164.0, 144.1, 143.5, 141.0, 135.6, 132.6, 129.3, 129.3, 128.8, 128.8, 127.8, 127.7, 126.0, 123.9, 122.8, 109.6, 105.4, 51.9, 50.8, 47.1, 45.9, 44.9, 23.3; IR (KBr) υ: 2938, 2859, 1766, 1725, 1698, 1634, 1607, 1510, 1462, 1437, 1386, 1359, 1252, 1179, 1110, 1074, 1030, 991, 852, 791, 767 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{24}ClN_3NaO_5$ ($[M+Na]^+$): 564.1297, Found: 564.1297.

Methyl *rel*-(3*R*,3'*R*)-1-benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3i**): yellow solid, 35%, m.p. 236-238 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 6.8 Hz, 2H, ArH), 7.36 ~ 7.27 (m, 3H, ArH), 7.24 ~ 7.17 (m, 4H, ArH), 7.01 (d, *J* = 8.0 Hz, 1H, ArH), 6.93 (s, 1H, ArH), 6.64 (d, *J* = 7.6 Hz, 1H, ArH), 5.03 (d, *J* = 16.0 Hz, 1H, CH), 4.97 (d, *J* = 15.6 Hz, 1H, CH), 4.81 ~ 4.75 (m, 1H, CH), 4.98 (dd, J_1 = 12.8 Hz, J_2 = 4.0 Hz, 1H, CH), 3.46 (s, 3H, OCH_3), 3.37 (dd, J_1 = 11.6 Hz, J_2 = 3,6 Hz, 1H, CH), 2.78 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.4, 169.0, 167.1, 164.0, 145.0, 141.5, 140.3, 137.2, 135.8, 132.1, 129.8, 129.2, 128.7, 127.4, 127.3, 125.0, 122.8, 109.2, 102.4, 52.4, 51.2, 46.8, 46.1, 44.4, 23.2, 21.2, 21.1; IR (KBr) υ: 2947, 2860, 1746, 1731, 1712, 1650, 1600, 1509, 1444, 1411, 1373, 1358, 1255, 1182, 1117, 1084, 1043, 984, 836, 779, 753 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{30}N_3O_5$ ($[M+H]^+$): 536.2180, Found: 536.2195.

Methyl *rel*-(3*S*,3'*R*)-1-benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3i'**): yellow solid, 47%, m.p. 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 7.6 Hz, 2H, ArH), 7.39 ~ 7.35 (m, 2H, ArH), 7.30 ~ 7.27 (m, 1H, ArH), 7.24 ~ 7.18 (m, 4H, ArH), 6.98 (d, *J* = 10.4 Hz, 1H, ArH), 6.66 (d, *J* = 8.0 Hz, 1H, ArH), 5.06 (d, *J* = 15.6 Hz, 1H, CH), 5.00 (d, *J* = 15.6 Hz, 1H, CH), 4.28 ~ 4.21 (m, 1H, CH), 4.09 (dd, J_1 = 13.6 Hz, J_2 = 4.4 Hz, 1H, CH), 3.64 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H, CH), 3.15 (s, 3H, OCH_3), 2.81 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.5, 169.0, 167.5, 164.2, 144.6, 141.1, 140.2, 137.1, 135.9, 132.1, 129.8, 129.5, 129.2, 128.7, 127.8, 127.6, 124.8, 124.7, 109.2, 104.1, 51.8, 50.9, 47.2, 45.9, 44.9, 23.3, 21.2, 21.1; IR (KBr) υ: 2952, 2867, 1759, 1736, 1700, 1649, 1609, 1513, 1468, 1443, 1387, 1350, 1251, 1184, 1105, 1066, 1021, 998, 843, 784, 766 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{30}N_3O_5$ ($[M+H]^+$): 536.2180, Found: 536.2197.

Methyl *rel*-(3*R*,3'*R*)-1-benzyl-1'-(4-methoxyphenyl)-5,6'-dimethyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3j**): yellow solid, 30%, m.p. 217-219 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 7.6 Hz, 2H, ArH), 7.35 ~ 7.32 (m, 2H, ArH), 7.27 ~ 7.22 (m, 3H, ArH), 7.00 (d, *J* = 7.6 Hz, 1H, ArH), 6.96 ~ 6.95 (m, 1H, ArH), 6.93 (m, 2H, ArH), 6.64 (d, *J* = 8.0 Hz, 1H, ArH), 5.02 (d, *J* = 16.0 Hz, 1H, CH), 4.97 (d, *J* = 16.0 Hz, 1H, CH), 4.76 (t, J_1 =12.0 Hz, 1H, CH), 3.95 (dd, J_1 =12.8 Hz, J_2 =4.0 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.45 (s, 3H, OCH_3), 3.38 (dd, J_1 =11.6 Hz, J_2 =4.0 Hz, 1H, CH), 2.78 (s, 3H, CH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.4, 169.1, 167.1, 164.1, 158.7, 145.2, 141.5, 135.8, 135.7, 132.1, 129.2, 128.7, 127.4, 127.3, 126.6, 122.9, 114.4, 109.2, 101.6, 55.5, 52.4, 51.3, 46.8, 46.1, 44.4, 23.2, 21.3; IR (KBr) υ: 2944, 2862, 1765, 1720, 1694, 1633, 1601, 1517, 1469, 1433, 1391, 1362, 1255, 1176, 1102, 1077, 1028, 993, 847, 796, 771 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{30}N_3O_6$ ($[M+H]^+$): 552.2129, Found: 552.2143.

Methyl *rel*-(3*S*,3'*R*)-1-benzyl-1'-(4-methoxyphenyl)-5,6'-dimethyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3j'**): yellow solid, 45%, m.p. 232-234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 7.6 Hz, 2H, ArH), 7.39 ~ 7.35 (m, 2H, ArH), 7.30 ~ 7.27 (m, 1H, ArH), 7.25 ~ 7.22 (m, 2H, ArH), 6.99 ~ 6.94 (m, 4H, ArH), 6.66 (d, *J* =

8.0 Hz, 1H, ArH), 5.07 (d, *J* = 15.6 Hz, 1H, CH), 5.00 (d, *J* = 15.6 Hz, 1H, CH), 4.27 ~ 4.20 (m, 1H, CH), 4.06 (dd, J_1 = 13.6 Hz, J_2 = 4.4 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.65 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H, CH), 3.15 (s, 3H, OCH_3), 2.81 (s, 3H, CH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.5, 169.0, 167.5, 164.2, 158.6, 144.7, 141.1, 135.9, 135.6, 132.1, 129.5, 129.2, 128.7, 127.8, 127.6, 126.3, 124.8, 114.4, 109.2, 103.3, 55.5, 51.8, 51.1, 47.2, 45.9, 44.9, 23.2, 21.2; IR (KBr) υ: 2947, 2868, 1759,1729, 1701, 1640, 1606, 1520, 1476, 1435, 1399, 1367, 1259, 1186, 1109, 1071, 1034, 989, 856, 799, 771 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{30}N_3O_6$ ($[M+H]^+$): 552.2129, Found: 552.2141.

Methyl *rel*-(3*R*,3'*R*)-1-benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3k**): yellow solid, 53%, m.p. 208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 ~ 7.41 (m, 4H, ArH), 7.36 ~ 7.35 (m, 3H, ArH), 7.30 ~ 7.28 (m, 3H, ArH),7.17 (d, *J* = 8.0 Hz, 1H, ArH), 7.10 (s, 1H, ArH), 6.66 (d, *J* = 8.4 Hz, 1H, ArH), 5.04 (d, *J* = 15.6 Hz, 1H, CH), 4.97 (d, *J* = 16.4 Hz, 1H, CH), 4.80 (t, *J* = 11.6 Hz, 1H, CH), 4.04 (d, *J* = 12.4 Hz, 1H, CH), 3.49 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.38 (d, *J* = 10.8 Hz, 1H, CH), 2.80 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.0, 168.7, 167.0, 163.7, 144.9, 142.6, 142.5, 135.2, 131.1, 129.2, 128.8, 128.8, 128.0, 127.6, 127.4, 127.2, 125.1, 122.5, 110.4, 102.1, 52.5, 51.0, 46.7, 46.1, 44.6, 23.2; IR (KBr) υ: 2955, 2847, 1755,1722, 1709, 1637, 1610, 1518, 1465, 1433, 1377, 1349, 1262, 1175, 1109, 1072, 1033, 977, 842, 788, 754 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{25}ClN_3O_5$ ($[M+H]^+$): 542.1477, Found: 542.1493.

Methyl *rel*-(3*S*,3'*R*)-1-benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3k'**): yellow solid, 42%, m.p. 247-249 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 6.8 Hz, 2H, ArH), 7.46 ~ 7.43 (m, 2H, ArH), 7.40 ~ 7.37 (m, 2H, ArH), 7.34 ~ 7.26 (m, 4H, ArH), 7.18 ~ 7.14 (m, 2H, ArH), 6.69 (d, *J* = 7.6 Hz, 1H, ArH), 5.04 (d, *J* = 16.8 Hz, 1H, CH), 5.02 (d, *J* = 16.8 Hz, 1H, CH), 4.25 ~ 4.15 (m, 2H, CH), 3.69 ~ 3.66 (m, 1H, CH), 3.22 (s, 3H, OCH_3), 2.83 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.1, 168.5, 167.4, 163.8, 144.7, 142.4, 142.2, 135.3, 130.9, 129.2, 129.1, 128.8, 128.0, 127.8, 127.7, 127.3, 124.9, 124.4, 110.5, 103.6, 52.1, 50.8, 47.2, 46.0, 45.0, 23.3; IR (KBr) υ: 2960, 2854, 1771, 1737, 1705, 1645, 1608, 1517, 1463, 1442, 1395, 1352, 1258, 1180, 1113, 1076, 1040, 993, 848, 811, 761 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{25}ClN_3O_5$ ($[M+H]^+$): 542.1477, Found: 542.1495.

Methyl *rel*-(3*R*,3'*R*)-1-benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3l**): yellow solid, 48%, m.p. 231-233 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 6.8 Hz, 2H, ArH), 7.37 ~ 7.33 (m, 2H, ArH), 7.29 ~ 7.25 (m, 2H, ArH), 7.23 (s, 1H, ArH), 7.19 ~ 7.16 (m, 3H, ArH), 7.10 (s, 1H, ArH), 6.66 (d, *J* = 8.4 Hz, 1H, ArH), 5.03 (d, *J* = 16.0 Hz, 1H, CH), 4.96 (d, *J* = 16.0 Hz, 1H, CH), 4.77 (t, *J* = 11.6 Hz, 1H, CH), 4.00 (d, *J* = 12.8 Hz, 1H, CH), 3.49 (s, 3H, OCH_3), 3.37 (d, *J* = 10.4 Hz, 1H, CH), 2.79 (s, 3H, CH_3), 2.39 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.1, 168.8, 167.0, 163.7, 145.1, 142.6, 140.0, 137.4, 135.2, 131.2, 129.9, 128.8, 128.0, 127.6, 127.2, 125.0, 122.5, 110.4, 101.3, 52.5, 51.0, 46.7, 46.1, 44.5, 23.2, 21.1; IR (KBr) υ: 2941, 2863, 1756, 1722, 1694, 1637, 1602, 1521, 1471, 1434, 1397, 1352, 1253, 1176, 1108, 1068, 1034, 994, 856, 807, 759 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{27}ClN_3O_5$ ($[M+H]^+$): 556.1634, Found: 556.1649.

Methyl *rel*-(3*S*,3'*R*)-1-benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3l'**): yellow solid, 36%, m.p. 232-234 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 6.8 Hz, 2H, ArH), 7.40 ~ 7.37 (m, 2H, ArH), 7.32 ~ 7.29 (m, 1H, ArH), 7.26 ~ 7.23 (m, 2H, ArH), 7.20 ~ 7.13 (m, 4H, ArH), 6.69 (d, *J* = 8.4 Hz, 1H, ArH), 5.07 (d, *J* = 17.2 Hz, 1H, CH), 5.02 (d, *J* = 16.8 Hz, 1H, CH), 4.23 ~ 4.11 (m, 2H, CH), 3.68 ~ 3.65 (m, 1H, CH), 3.22 (s, 3H, OCH_3), 2.82 (s, 3H, CH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.2, 168.6, 167.4, 163.8, 144.8, 142.2, 139.9, 137.4, 135.3, 131.0, 129.9, 129.1, 128.8, 127.9, 127.8, 127.7, 124.8, 124.4, 110.4, 102.8, 52.0, 50.8, 47.1, 45.9, 45.0, 23.3, 21.1; IR (KBr) υ: 2944, 2854, 1766, 1722, 1709, 1645, 1609, 1511, 1473, 1434, 1390, 1356, 1246, 1177, 1105, 1064, 1029, 998, 849, 812, 755 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{27}ClN_3O_5$ ($[M+H]^+$): 556.1634, Found: 556.1650.

Methyl *rel*-(3*R*,3'*R*)-1-benzyl-5-chloro-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3m**): yellow solid, 60%, m.p. 229-231 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 ~ 7.40 (m, 2H, ArH), 7.36 ~ 7.33 (m, 2H, ArH), 7.29 ~ 7.26 (m, 1H, ArH), 7.22 (d, *J* = 7.6 Hz, 2H, ArH), 7.17 (d, *J* = 7.6 Hz, 1H, ArH), 7.10 (s, 1H, ArH), 6.95 (d, *J* = 7.6 Hz, 2H, ArH), 6.66 (d, *J* = 8.4 Hz, 1H, ArH), 5.03 (d, *J* = 16.4 Hz, 1H, CH), 4.97 (d, *J* = 16.0 Hz, 1H, CH), 4.75 (t, *J* = 12.0 Hz, 1H, CH), 3.97 (d, *J* = 12.4 Hz,

1H, CH), 3.84 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.38 (d, *J* = 11.2 Hz, 1H, CH), 2.79 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.2, 168.8, 167.0, 163.8, 158.8, 145.3, 142.6, 135.4, 135.2, 131.2, 128.8, 128.0, 127.6, 127.2, 126.6, 122.6, 114.4, 110.4, 100.5, 55.5, 52.5, 51.2, 46.7, 46.0, 44.5, 23.2; IR (KBr) υ: 2962, 2865, 1767, 1735, 1708, 1630, 1607, 1501, 1465, 1435, 1392, 1376, 1258, 1183, 1098, 1060, 1036, 980, 843, 797, 761 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{27}ClN_3O_6$ ($[M+H]^+$): 572.1583, Found: 572.1603.

Methyl *rel*-(3*S*,3'*R*)-1-benzyl-5-chloro-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3m'**): yellow solid, 21%, m.p. 245-247 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 6.8 Hz, 2H, ArH), 7.38 ~ 7.37 (m, 2H, ArH), 7.32 ~ 7.28 (m, 1H, ArH), 7.24 ~ 7.22 (m, 2H, ArH), 7.17 ~ 7.13 (m, 2H, ArH), 6.95 (d, *J* = 8.0 Hz, 1H, ArH), 6.69 (d, *J* = 8.4 Hz, 1H, ArH), 5.06 (d, *J* = 15.6 Hz, 1H, CH), 5.02 (d, *J* = 15.6 Hz, 1H, CH), 4.21 ~ 4.08 (m, 2H, CH), 3.84 (s, 3H, OCH_3), 3.68 ~ 3.65 (m, 1H, CH), 3.22 (s, 3H, OCH_3), 2.82 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.2, 168.6, 167.4, 163.8, 158.8, 145.0, 142.2, 135.3, 135.3, 131.1, 129.0, 128.8, 127.9, 127.8, 127.7, 126.4, 124.4, 114.5, 110.4, 102.1, 55.5, 52.0, 51.0, 47.1, 45.9, 45.0, 23.3; IR (KBr) υ: 2966, 2854, 1763, 1734, 1700, 1646, 1602, 1519, 1479, 1434, 1400, 1375, 1260, 1188, 1104, 1077, 1028, 989, 865, 794, 760 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{27}ClN_3O_6$ ($[M+H]^+$): 572.1583, Found: 572.1603.

2. General procedure for the reaction of MBH esters of isatins and β-enamino maleimides: To a round flask was added MBH nitriles of isatins (0.20 mmol), β-enamino maleimides (0.40 mmol), DABCO (0.04 mmol) and acetonitrile (6.0 mL). The mixture was stirred at room temperature for about one hour. After removing the solvent by rotatory evaporation at reduced pressure, the residue was subjected to column chromatography with ethyl acetate and petroleum ether (V/V = 1:5) as eluent to give the pure products **4a-4f** and **4a'-4f'**for analysis.

***rel*-(3*R*,3'*R*)-1-Benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro [indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4a**): yellow solid, 26%, m.p. >300 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.47 ~ 7.43 (m, 2H, ArH), 7.40 ~ 7.32 (m, 5H, ArH), 7.29 ~ 7.26 (m, 3H, ArH), 7.07 (d, *J* = 8.0 Hz, 1H, ArH), 6.99 (s,1H, ArH), 6.68 (d, *J* = 8.0 Hz, 1H, ArH), 5.04 (s, 2H, CH), 4.89 (t, *J* = 7.6 Hz, 1H, CH), 3.96 (dd, J_1 = 12.8 Hz, J_2 = 3.6 Hz, 1H, CH), 3.39 (dd, J_1 = 11.6 Hz, J_2 = 4.4 Hz, 1H, CH), 2.82 (s, 3H, CH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 166.7, 145.0, 142.0, 140.8, 134.8, 133.1, 130.5, 129.4, 128.8, 127.7, 127.6, 127.0,

126.6, 125.1, 123.4, 115.4, 110.2, 101.6, 50.2, 46.7, 44.5, 34.5, 23.3, 21.2; IR (KBr) υ: 3054, 2977, 2932, 2861, 1766, 1708, 1647, 1603, 1499, 1460, 1421, 1389, 1341, 1282, 1205, 1128, 1097, 1071, 1023, 987, 826, 752 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{25}N_4O_3$ ($[M+H]^+$): 511.1741, Found: 511.1747.

***rel*-(3*S*,3'*R*)-1-Benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro [indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4a'**): yellow solid, 29%, m.p. 276-278 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 ~ 7.44 (m, 2H, ArH), 7.38 ~ 7.26 (m, 8H, ArH), 7.21 (s, 1H, ArH), 7.08 (d, *J* = 7.6 Hz, 1H, ArH), 6.69 (d, *J* = 8.0 Hz, 1H, ArH), 5.09 (d, *J* = 15.6 Hz, 1H, CH), 4.98 (d, *J* = 15.6 Hz, 1H, CH), 4.52 (d, *J* = 12.8 Hz, 1H, CH), 4.15 ~ 4.09 (m, 1H, CH), 3.45 ~ 3.37 (m, 1H, CH), 2.84 (s, 3H, CH_3), 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.8, 167.0, 163.6, 144.7, 142.2, 140.4, 134.9, 133.1, 130.5, 129.5, 128.9, 127.8, 127.7, 127.3, 126.9, 125.4, 125.2, 115.8, 110.0, 101.7, 50.8, 46.2, 44.5, 33.7, 23.4, 21.2; IR (KBr) υ: 3044, 2980, 2942, 2870, 1764, 1701, 1645, 1600, 1492, 1465, 1427, 1395, 1342, 1290, 1211, 1121, 1107, 1070, 1038, 999, 832, 766 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{25}N_4O_3$ ($[M+H]^+$): 511.1741, Found: 511.1750.

***rel*-(3*R*,3'*R*)-1-Benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro [indoline -3,4'-pyrrolo[3,4-b]pyridine]-3'-carbonitrile** (**4b**): yellow solid, 25%, m.p. >300 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.2 Hz, 2H, ArH), 7.34 (t, *J* = 7.6 Hz, 2H, ArH), 7.28 ~ 7.26 (m, 1H, ArH), 7.26 ~ 7.23 (m, 2H, ArH), 7.16 (d, *J* = 8.0 Hz, 2H, ArH), 7.06 (d, *J* = 8.0 Hz, 1H, ArH), 6.99 (s,1H, ArH), 6.68 (d, *J* = 8.0 Hz, 1H, ArH), 5.06 (d, *J* = 16.4 Hz, 1H, CH), 5.02 (d, *J* = 16.4 Hz, 1H, CH), 4.86 (t, *J* = 11.2 Hz, 1H, CH), 3.92 (dd, J_1 = 12.8 Hz, J_2 = 3.6 Hz, 1H, CH), 3.88 (dd, J_1 = 11.6 Hz, J_2 = 4.0 Hz, 1H, CH), 2.81 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 166.8, 163.5, 145.2, 140.8, 139.5, 137.9, 134.8, 133.1, 130.4, 130.0, 128.8, 127.6, 127.0, 126.7, 125.0, 123.4, 115.5, 110.1, 100.8, 50.3, 46.7, 44.5, 34.5, 23.3, 21.2, 21.1; IR (KBr) υ: 3048, 2980, 2933, 2878, 1758, 1713, 1638, 1596, 1509, 1456, 1413, 1373, 1349, 1280, 1202, 1128, 1090, 1075, 1032, 987, 829, 766 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{27}N_4O_3$ ($[M+H]^+$): 503.2078, Found: 503.2085.

***rel*-(3*S*,3'*R*)-1-Benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro [indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4b'**): yellow solid, 33%, m.p. 244-246 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 ~ 7.33 (m, 4H, ArH), 7.29 ~ 7.25 (m, 3H, ArH), 7.21 ~ 7.19 (m, 3H, ArH), 7.08 (d, *J* = 8.0 Hz, 1H, ArH), 6.68 (d, *J* = 8.0 Hz, 1H, ArH), 5.08 (d, *J* = 16.0 Hz, 1H, CH), 4.99 (d, *J* = 16.0 Hz, 1H, CH), 4.48 (dd, J_1 = 12.8 Hz, J_2 = 3.2 Hz, 1H, CH), 4.12 ~

4.07 (m, 1H, CH), 3.44 (dd, J_1 = 7.6 Hz, J_2 = 3.2 Hz, CH), 2.84 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.34 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.9, 167.0, 163.7, 144.9, 140.4, 139.7, 137.9, 134.9, 133.0, 130.5, 130.1, 128.9, 127.7, 127.4, 126.9, 125.4, 125.1, 115.9, 110.0, 101.0, 50.8, 46.2, 44.5, 33.7, 23.4, 21.2, 21.2; IR (KBr) υ: 3068, 2982, 2943, 2873, 1766, 1708, 1641, 1590, 1487, 1462, 1426, 1382, 1356, 1289, 1214, 1116, 1088, 1065, 1033, 992, 826, 751 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{27}N_4O_3$ ($[M+H]^+$): 503.2078, Found: 503.2088.

***rel*-(3*S*,3'*R*)-1-Benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydro-spiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4c'**): yellow solid, 37%, m.p. 269-271 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 ~ 7.45 (m, 2H, ArH), 7.41 ~ 7.35 (m, 7H, ArH), 7.33 ~ 7.32 (m, 1H, ArH), 7.31 ~ 7.30 (m, 1H, ArH), 7.28 ~ 7.25 (m, 1H, ArH), 6.72 (d, *J* = 8.4 Hz, 1H, ArH), 5.10 (d, *J* = 16.0 Hz, 1H, CH), 4.99 (d, *J* = 16.0 Hz, 1H, CH), 4.51 (dd, J_1 = 13.2 Hz, J_2 = 5.2 Hz, 1H, CH), 4.14 ~ 4.09 (m, 1H, CH), 3.49 ~ 3.46 (m, 1H, CH), 2.86 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 166.9, 163.4, 144.9, 141.9, 141.4, 134.3, 130.2, 129.8, 129.5, 129.0, 129.0, 128.0, 127.9, 126.9, 125.9, 125.2, 125.1, 115.4, 111.3, 100.6, 50.7, 46.3, 44.7, 33.6, 23.5; IR (KBr) υ: 3058, 2977, 2942, 2880, 1773, 1712, 1645, 1584, 1508, 1473, 1420, 1394, 1357, 1293, 1214, 1126, 1099, 1066, 1027, 1002, 832, 768 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{22}ClN_4O_3$ ($[M+H]^+$): 509.1375, Found: 509.1385.

***rel*-(3*S*,3'*R*)-1-Benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydro-spiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4d'**): yellow solid, 39%, m.p. 232-234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 ~ 7.27 (m, 9H, ArH), 7.20 (d, *J* = 7.6 Hz, 1H, ArH), 6.71 (d, *J* = 8.4 Hz, 1H, ArH), 5.10 (d, *J* = 15.6 Hz, 1H, CH), 4.99 (d, *J* = 16.0 Hz, 1H, CH), 4.47 (d, *J* = 12.8 Hz, 1H, CH), 4.12 ~ 4.06 (m, 1H, CH), 3.47 (d, *J* =6.0 Hz, 1H, CH), 2.85 (s, 3H, CH_3), 2.41 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 166.9, 163.4, 145.1, 141.4, 139.4, 138.2, 134.3, 130.2, 130.1, 129.0, 128.9, 127.9, 126.9, 125.1, 125.1, 115.4, 111.2, 50.8, 46.3, 44.7, 33.6, 23.4, 21.2; IR (KBr) υ: 3040, 2961, 2943, 2859, 1760, 1715, 1631, 1598, 1492, 1468, 1431, 1380, 1355, 1280, 1216, 1112, 1088, 1061, 1029, 996, 826, 777 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{24}ClN_4O_3$ ($[M+H]^+$): 523.1531, Found: 523.1542.

***rel*-(3*S*,3'*R*)-1-Benzyl-5-chloro-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4e'**): yellow solid, 31%, m.p. 227-229 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 ~ 7.34 (m, 5H, ArH), 7.33 ~ 7.28 (m, 1H,

ArH), 7.27 ~ 7.23 (m, 3H, ArH), 6.97 (d, *J* = 8.8 Hz, 1H, ArH), 6.71 (d, *J* = 8.4 Hz, 1H, ArH), 5.10 (d, *J* = 16.0 Hz, 1H, CH), 4.98 (d, *J* = 16.0 Hz, 1H, CH), 4.46 (dd, J_1 = 13.2 Hz, J_2 = 3.2 Hz, 1H, CH), 4.09 ~ 4.03 (m, 1H, CH), 3.85 (s, 3H, OCH_3), 3.45 (dd, J_1 = 8.0 Hz, J_2 = 3.2 Hz, 1H, CH), 2.85 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 166.9, 163.4, 159.2, 145.2, 141.4, 134.7, 134.3, 130.1, 129.1, 129.0, 128.9, 127.9, 126.9, 126.7, 125.2, 115.5, 114.7, 111.2, 99.2, 55.5, 50.9, 46.2, 44.7, 33.5, 23.4; IR (KBr) υ: 3058, 2976, 2947, 2870, 1763, 1705, 1633, 1598, 1507, 1473, 1429, 1381, 1345, 1281, 1192, 1133, 1106, 1078, 1020, 1002, 824, 751 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{24}ClN_4O_4$ ($[M+H]^+$): 539.1481, Found: 539.1494.

***rel*-(3*R*,3'*R*)-1-Butyl-5,6'-dimethyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro [indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4f**): yellow solid, 23%, m.p. 218-220 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.46 ~ 7.42 (m, 2H, ArH), 7.37 ~ 7.34 (m, 1H, ArH), 7.28 ~ 7.25 (m, 2H, ArH), 7.20 (d, *J* = 7.2 Hz, 2H, ArH), 6.97 (s, 1H, ArH), 6.90 (d, *J* = 8.0 Hz, 1H, ArH), 4.85 (t, *J* = 11.6 Hz, 1H, CH), 3.91 (dd, J_1 = 12.4 Hz, J_2 = 3.6 Hz, 1H, CH), 3.86 ~ 3.71 (m, 2H, CH), 3.32 (dd, J_1 = 15.8 Hz, J_2 = 4.0 Hz, 1H, CH), 2.79 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 1.78 ~ 1.70 (m, 2H, CH), 1.49 ~ 1.46 (m, 1H, CH), 1.44 ~ 1.40 (m, 1H, CH), 0.96 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.0, 166.7, 163.5, 145.0, 142.1, 141.1, 132.8, 130.4, 129.4, 127.7, 126.8, 125.1, 123.5, 115.2, 109.2, 101.6, 50.1, 46.6, 40.7, 34.5, 29.7, 29.3, 23.3, 21.2, 20.1, 13.7; IR (KBr) υ: 3052, 2971, 2936, 2867, 1761, 1707, 1641, 1594, 1497, 1463, 1425, 1384, 1351, 1285, 1204, 1125, 1096, 1071, 1030, 995, 821, 758 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{27}N_4O_3$ ($[M+H]^+$): 455.2078, Found: 455.2093.

***rel*-(3*S*,3'*R*)-1-Butyl-5,6'-dimethyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro [indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4f'**): yellow solid, 54%, m.p. 227-229 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.47 ~ 7.43 (m, 2H, ArH), 7.38 ~ 7.35 (m, 1H, ArH), 7.32 ~ 7.26 (m, 2H, ArH), 7.22 ~ 7.20 (m, 2H, ArH), 6.89 (d, *J* = 8.0 Hz, 1H, ArH), 4.52 ~ 4.48 (m, 1H, CH), 4.08 (dd, J_1 = 12.8 Hz, J_2 = 3.6 Hz, 1H, CH), 3.79 (t, *J* = 7.2 Hz, 2H, CH), 3.38 ~ 3.36 (m, 1H, CH), 2.82 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 1.80 ~ 1.71 (m, 2H, CH), 1.49 ~ 1.40 (m, 1H, CH), 0.98 (t, *J* = 7.6 Hz, 1H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 167.0, 163.7, 144.6, 142.2, 140.7, 132.8, 130.5, 129.4, 127.7, 127.4, 125.5, 125.2, 115.8, 109.1, 101.8, 50.7, 46.1, 40.6, 33.6, 29.3, 23.4, 21.3, 20.1, 13.8; IR (KBr) υ: 3067, 2964, 2950, 2857, 1762, 1714, 1650, 1596, 1507, 1478, 1430, 1388, 1354, 1283, 1212, 1126, 1107, 1075, 1032, 994, 829, 763 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{27}N_4O_3$ ($[M+H]^+$): 455.2078, Found: 455.2094.

***rel*-(3*S*,3'*R*)-1-Butyl-5-fluoro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydro-spiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4g'**): yellow solid, 48%, m.p. 211-213 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 ~ 7.44 (m, 2H, ArH), 7.40 ~ 7.36 (m, 1H, ArH), 7.30 (d, *J* =7.6 Hz, 2H, ArH), 7.21 ~ 7.18 (m, 1H, ArH), 7.15 ~ 7.11 (m, 1H, ArH), 6.95 ~ 6.92 (m, 1H, ArH), 4.57 (d, *J* =13.2 Hz, 1H, CH), 4.07 ~ 4.01 (m, 1H, CH), 3.80 (t, *J* =7.6 Hz, 2H, CH), 3.37 ~ 3.35 (m, 1H, CH), 2.83 (s, 3H, CH_3), 1.76 ~ 1.70 (m, 2H, CH), 1.48 ~ 1.39 (m, 2H, CH), 0.98 (t, *J* =7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 166.9, 163.4, 159.2 (d, *J* = 246.4 Hz), 144.9, 142.0, 139.1 (d, *J* = 2.0 Hz), 129.50, 128.8 (d, *J* = 8.1 Hz), 128.0, 125.3, 116.5 (d, *J* = 23.2 Hz), 115.5, 113.2 (d, *J* = 25.3 Hz), 109.9 (d, *J* = 8.1 Hz), 100.5, 50.6, 46.1, 40.8, 33.3, 29.2, 23.4, 20.0, 13.7; IR (KBr) υ: 3058, 2969, 2942, 2865, 1765, 1700, 1632, 1609, 1516, 1463, 1436, 1382, 1357, 1283, 1210, 1129, 1091, 1068, 1035, 990, 828, 754 cm^{-1}; HRMS (ESI) Calcd. for $C_{26}H_{24}FN_4O_3$ ($[M+H]^+$): 459.1827, Found: 459.1843.

3. General procedure for the reaction of MBH imides of isatins and β-enamino maleimides: To a round flask was added MBH imides of isatins (0.20 mmol), β-enamino imides (0.40 mmol), DABCO (0.10 mmol) and acetonitrile (6.0 mL). The mixture was stirred at room temperature for about twelve hours. After removing the solvent by rotatory evaporation at reduced pressure, the residue was subjected to column chromatography with ethyl acetate and petroleum ether (V/V = 1:5) as eluent to give the pure products **5a-5g** and **5a'-5g'**for analysis.

***rel*-(3a*R*,8*R*,8a*S*)-1'-Benzyl-4-(4-chlorophenyl)-2,6-dimethyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5a**): yellow solid, 35%, m.p. 232-234 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 8.4 Hz, 2H, ArH), 7.43 (d, *J* = 8.8 Hz, 2H, ArH), 7.35 ~ 7.23 (m, 7H, ArH), 7.17 (t, *J* = 7.6 Hz, 1H, ArH), 6.80 (d, *J* = 8.0 Hz, 1H, ArH), 4.97 (d, *J* = 16.4 Hz, 1H, CH), 4.79 (d, *J* = 14.8 Hz, 1H, CH), 4.79 (d, *J* = 8.8 Hz, 1H, CH), 3.65 (d, *J* = 8.4 Hz, 1H, CH), 2.80 (s, 3H, CH_3), 2.79 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.5, 172.5, 171.0, 166.8, 163.4, 144.2, 143.6, 140.6, 134.8, 134.2, 129.7, 129.6, 128.8, 128.3, 128.1, 127.6, 126.9, 123.7, 123.0, 110.1, 102.2, 61.3, 46.3, 44.6, 44.3, 24.8, 23.4; IR (KBr) υ: 3045, 3022, 2937, 2883, 1790, 1709, 1645, 1596, 1499, 1427, 1340, 1243, 1198, 1111, 1075, 1022, 987, 924, 866, 818, 787, 751 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{23}ClN_4NaO_5$ ($[M+Na]^+$): 589.1249, Found: 589.1261.

***rel*-(3a*R*,8*S*,8a*S*)-1'-Benzyl-4-(4-chlorophenyl)-2,6-dimethyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5a'**): yellow solid, 44%,

m.p. 259-261 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 ~ 7.52 (m, 4H, ArH), 7.45 ~ 7.38 (m, 4H, ArH), 7.32 ~ 7.28 (m, 1H, ArH), 7.15 (t, *J* = 8.0 Hz, 1H, ArH), 6.3 (t, *J* = 7.6 Hz, 1H, ArH), 6.77 (d, *J* = 7.2 Hz, 1H, ArH), 6.67 (d, *J* = 8.0 Hz, 1H, ArH), 5.17 (d, *J* = 16.0 Hz, 1H, CH), 5.04 (d, *J* = 16.0 Hz, 1H, CH), 4.91 (d, *J* = 8.4 Hz, 1H, CH), 4.00 (d, *J* = 8.4 Hz, 1H, CH), 2.82 (s, 3H, CH_3), 2.57 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.9, 173.7, 171.0, 166.9, 163.6, 143.6, 143.4, 140.9, 134.8, 134.3, 130.0, 129.7, 128.8, 128.5, 127.6, 127.2, 127.0, 123.1, 122.6, 110.6, 103.7, 62.1, 45.7, 45.5, 44.9, 24.2, 23.5; IR (KBr) υ: 3048, 3030, 2938, 2881, 1788, 1721, 1648, 1594, 1495, 1426, 1341, 1240, 1180, 1104, 1076, 1012, 983, 924, 872, 828, 769, 748 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{23}ClN_4NaO_5$ ([M+Na]$^+$): 589.1249, Found: 589.1267.

***rel*-(3a*R*,8*S*,8a*S*)-1'-Benzyl-2,5',6-trimethyl-4-phenyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5b'**): yellow solid, 30%, m.p. >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 ~ 7.61 (m, 2H, ArH), 7.53 (d, *J* = 7.6 Hz, 2H, ArH), 7.51 ~ 7.47 (m, 2H, ArH), 7.45 ~ 7.37 (m, 3H, ArH), 7.31 ~ 7.27 (m, 1H, ArH), 6.95 ~ 6.93 (m, 1H, ArH), 6.59 (s, 1H, ArH), 6.54 (d, *J* = 8.0 Hz, 1H, ArH), 5.16 (d, *J* = 16.4 Hz, 1H, CH), 5.04 (d, *J* = 16.0 Hz, 1H, CH), 4.92 (d, *J* = 8.4 Hz, 1H, CH), 3.98 (d, *J* = 8.0 Hz, 1H, CH), 2.82 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.22 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.9, 173.8, 171.1, 167.1, 163.7, 143.7, 142.6, 141.2, 135.0, 132.2, 130.2, 129.5, 128.8, 128.5, 127.5, 127.4, 127.0, 123.9, 110.2, 103.4, 62.4, 45.8, 45.5, 44.9, 24.1, 23.4, 20.9; IR (KBr) υ: 3055, 3027, 2936, 2880, 1787, 1713, 1641, 1592, 1498, 1431, 1344, 1239, 1191, 1113, 1073, 1024, 988, 932, 860, 819, 786, 752 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{26}N_4NaO_5$ ([M+Na]$^+$): 569.1795, Found: 569.1802.

***rel*-(3a*R*,8*R*,8a*S*)-1'-Benzyl-4-(4-chlorophenyl)-2,5',6-trimethyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo [3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5c**): yellow solid, 28%, m.p. 243-245 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 8.4 Hz, 2H, ArH), 7.42 (d, *J* = 8.8 Hz, 2H, ArH), 7.35 ~ 7.31 (m, 2H, ArH), 7.27 ~ 7.25 (m, 3H, ArH), 7.11 ~ 7.08 (m, 2H, ArH), 6.68 (d, *J* = 7.6 Hz, 1H, ArH), 4.94 (d, *J* = 16.0 Hz, 1H, CH), 4.77 (d, *J* = 15.6 Hz, 1H, CH), 4.77 (d, *J* = 8.4 Hz, 1H, CH), 3.63 (d, *J* = 8.4 Hz, 1H, CH), 2.80 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 2.35 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 172.6, 171.1, 166.8, 163.4, 144.1, 141.2, 140.8, 135.0, 134.1, 133.3, 130.1, 129.5, 128.7, 128.3, 128.1, 127.5, 126.9, 123.9, 109.8, 102.6, 61.4, 46.4, 44.6, 44.3, 24.8, 23.4, 21.3; IR (KBr) υ: 3043, 3013, 2921, 2875, 1790, 1723, 1640,

1594, 1500, 1432, 1358, 1232, 1201, 1119, 1066, 1029, 1008, 942, 864, 820, 792, 760 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{25}ClN_4NaO_5$ ($[M+Na]^+$): 603.1406, Found: 603.1420.

***rel*-(3a*R*,8*S*,8a*S*)-1'-Benzyl-4-(4-chlorophenyl)-2,5',6-trimethyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo [3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5c'**): yellow solid, 36%, m.p. 267-269 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 ~ 7.50 (m, 4H, ArH), 7.41 ~ 7.36 (m, 4H, ArH), 7.30 ~ 7.26 (m, 1H, ArH), 6.94 (d, *J* = 8.0 Hz, 1H, ArH), 6.65 ~ 6.53 (m, 2H, ArH), 5.11 (d, *J* = 16.4 Hz, 1H, CH), 4.98 (d, *J* = 16.0 Hz, 1H, CH), 4.91 (d, *J* = 8.4 Hz, 1H, CH), 3.99 (d, *J* = 8.4 Hz, 1H, CH), 2.81 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 2.21 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.9, 173.9, 171.1, 167.0, 163.7, 143.4, 141.2, 141.0, 135.0, 134.2, 132.3, 130.2, 129.6, 128.8, 128.5, 127.6, 127.3, 126.9, 123.9, 110.2, 103.8, 62.2, 45.8, 45.5, 44.8, 24.1, 23.5, 20.9; IR (KBr) υ: 3050, 3025, 2942, 2881, 1794, 1707, 1649, 1594, 1488, 1432, 1334, 1250, 1192, 1118, 1076, 1023, 998, 928, 864, 823, 779, 750 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{25}ClN_4NaO_5$ ($[M+Na]^+$): 603.1406, Found: 603.1418.

***rel*-(3a*R*,8*R*,8a*S*)-1'-Benzyl-5'-chloro-4-(4-methoxyphenyl)-2,6-dimethyl-3a,8a-dihydro-1*H*-spiro[di-pyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5d**): yellow solid, 26%, m.p. 182-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 2.0 Hz, 1H, ArH), 7.33 ~ 7.29 (m, 3H, ArH), 7.21 ~ 7.19 (m, 2H, ArH), 7.14 (s, 1H, ArH), 7.06 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.84 (d, *J* = 8.8 Hz, 2H, ArH), 6.67 (d, *J* = 8.8 Hz, 2H, ArH), 6.43 (d, *J* = 8.4 Hz, 1H, CH), 5.93 (s, 1H, CH), 5.09 (d, *J* = 15.6 Hz, 1H, CH), 4.40 (d, *J* = 15.6 Hz, 1H, CH), 3.80 (s, 3H, OCH_3), 3.00 (s, 3H, CH_3), 2.89 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.3, 171.5, 169.1, 168.8, 167.0, 158.1, 144.9, 142.0, 140.4, 134.6, 130.8, 129.1, 129.0, 128.7, 128.1, 127.0, 126.5, 126.1, 125.7, 114.3, 110.5, 95.0, 55.5, 51.2, 44.6, 29.7, 24.1, 23.9; IR (KBr) υ: 3053, 3026, 2946, 2874, 1797, 1719, 1642, 1600, 1492, 1435, 1348, 1230, 1195, 1115, 1083, 1026, 990, 937, 855, 811, 793, 752 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{25}ClN_4NaO_6$ ($[M+Na]^+$): 619.1355, Found: 619.1358.

***rel*-(3a*R*,8*S*,8a*S*)-1'-Benzyl-5'-chloro-4-(4-methoxyphenyl)-2,6-dimethyl-3a,8a-dihydro-1*H*-spiro[di-pyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5d'**): yellow solid, 31%, m.p. 240-242 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 ~ 7.38 (m, 6H, ArH), 7.33 ~ 7.29 (m, 1H, ArH), 7.13 ~ 7.11 (m, 1H, ArH), 6.99 (d, *J* = 8.4 Hz, 2H, ArH), 6.75 (s, 1H, ArH), 6.58 (d, *J* = 8.4 Hz, 1H, ArH), 5.14 (d, *J* = 16.0 Hz, 1H, CH), 5.06 (d, *J* = 16.0 Hz, 1H,

CH), 4.89 (d, *J* = 8.4 Hz, 1H, CH), 3.97 (d, *J* = 8.4 Hz, 1H, CH), 3.86 (s, 3H, OCH_3), 2.83 (s, 3H, CH_3), 2.66 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.8, 173.6, 171.0, 167.0, 163.4, 159.6, 144.2, 142.2, 134.9, 134.5, 129.7, 129.2, 128.9, 127.9, 127.8, 127.0, 123.6, 114.6, 111.4, 101.1, 62.4, 55.5, 45.7, 45.4, 24.2, 23.4; IR (KBr) υ: 3055, 3033, 2933, 2886, 1785, 1713, 1641, 1590, 1495, 1438, 1349, 1235, 1184, 1103, 1070, 1028, 979, 934, 863, 818, 788, 752 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{25}ClN_4NaO_6$ ($[M+Na]^+$): 619.1355, Found: 619.1360.

***rel*-(3a*R*,8*R*,8a*S*)-1'-Butyl-2,5',6-trimethyl-4-phenyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*] pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5e**): yellow solid, 21%, m.p. 279-281 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* = 7.6 Hz, 1H, ArH), 7.48 ~ 7.45 (t, *J* = 7.6 Hz, 2H, ArH), 7.42 ~ 7.38 (m, 1H, ArH), 7.18 (d, *J* = 8.8 Hz, 2H, ArH), 7.05 (s, 1H, ArH), 6.83 (d, *J* = 8.0 Hz, 1H, ArH), 4.77 (d, *J* = 8.4 Hz, 1H, CH), 3.72 ~ 3.64 (m, 1H, CH), 3.60 ~ 3.53 (m, 2H, CH), 2.93 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 1.65 ~ 1.59 (m, 2H, CH), 1.40 ~ 1.31 (m, 2H, CH), 0.94 (t, *J* = 8.0 Hz, 3H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 172.7, 171.2, 166.9, 163.5, 144.3, 142.5, 141.5, 132.8, 130.0, 129.3, 128.6, 128.2, 126.9, 123.8, 108.9, 102.4, 61.6, 46.3, 44.6, 40.4, 29.3, 24.8, 23.3, 21.3, 20.0, 13.7; IR (KBr) υ: 3065, 3022, 2944, 2878, 1792, 1719, 1636, 1603, 1481, 1425, 1354, 1243, 1196, 1114, 1069, 1027, 991, 931, 868, 829, 792, 762 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{28}N_4NaO_5$ ($[M+Na]^+$): 535.1952, Found:535.1960.

***rel*-(3a*R*,8*S*,8a*S*)-1'-Butyl-2,5',6-trimethyl-4-phenyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*] pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5e'**): yellow solid, 57%, m.p. 293-295 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 6.0 Hz, 2H, ArH), 7.50 ~ 7.40 (m, 2H, ArH), 7.44 ~ 7.40 (m, 1H, ArH), 7.09 (d, *J* = 8.0 Hz, 2H, ArH), 6.57 (s, 1H, ArH), 4.88 (d, *J* = 8.4 Hz, 1H, CH), 3.89 (d, *J* = 8.0 Hz, 1H, CH), 3.83 (t, *J* = 7.6 Hz, 2H, CH), 2.79 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.84 ~ 1.76 (m, 2H, CH), 1.58 ~ 1.48 (m, 2H, CH), 1.02 (t, *J* = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 173.9, 171.1, 167.0, 163.7, 143.6, 142.7, 141.6, 131.8, 130.1, 129.4, 128.4, 127.5, 127.0, 124.1, 109.2, 103.6, 62.3, 45.7, 45.4, 40.8, 29.1, 24.0, 23.3, 20.9, 20.1, 13.8; IR (KBr) υ: 3042, 3021, 2914, 2861, 1733, 1700, 1655, 1576, 1463, 1411, 1337, 1279, 1181, 1143, 1054, 1014, 977, 932, 864, 839, 756, 711 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{28}N_4NaO_5$ ($[M+Na]^+$): 535.1952, Found: 535.1961.

***rel*-(3a*R*,8*R*,8a*S*)-1'-Butyl-4-(4-methoxyphenyl)-2,5',6-trimethyl-3a,8a-dihydro-1*H*-spiro[dip**

yrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone (**5f**): yellow solid, 16%, m.p. 189-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (s, 1H, ArH), 7.14 (s, 1H, ArH), 7.01 (d, *J* =8.0 Hz, 1H, ArH), 6.84 (d, *J* = 8.8 Hz, 2H, ArH), 6.65 (d, *J* = 8.8 Hz, 2H, ArH), 6.55 (d, *J* = 8.0 Hz, 1H, ArH), 5.98 (s, 1H, CH), 3.81 ~ 3.72 (m, 1H, CH), 3.77 (s, 3H, OCH_3), 3.31 ~ 3.24 (m, 1H, CH), 2.97 (s, 3H, CH_3), 2.88 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 1.65 ~ 1.55 (m, 2H, CH), 1.34 ~ 1.35 (m, 1H, CH), 1.34 ~ 1.30 (m, 1H, CH), 0.93 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.3, 171.5, 169.6, 169.0, 167.1, 157.8, 146.0, 141.9, 139.8, 132.7, 131.0, 129.5, 127.5, 127.0, 125.8, 125.4, 114.1, 108.7, 96.4, 55.5, 51.3, 40.5, 29.4, 24.0, 23.8, 21.2, 20.2, 13.7; IR (KBr) υ: 3058, 3038, 2930, 2878, 1779, 1715, 1643, 1597, 1502, 1440, 1345, 1236, 1188, 1110, 1074, 1033, 982, 935, 876, 822, 778 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{30}N_4NaO_6$ ([M+Na]$^+$): 565.2058, Found: 565.2063.

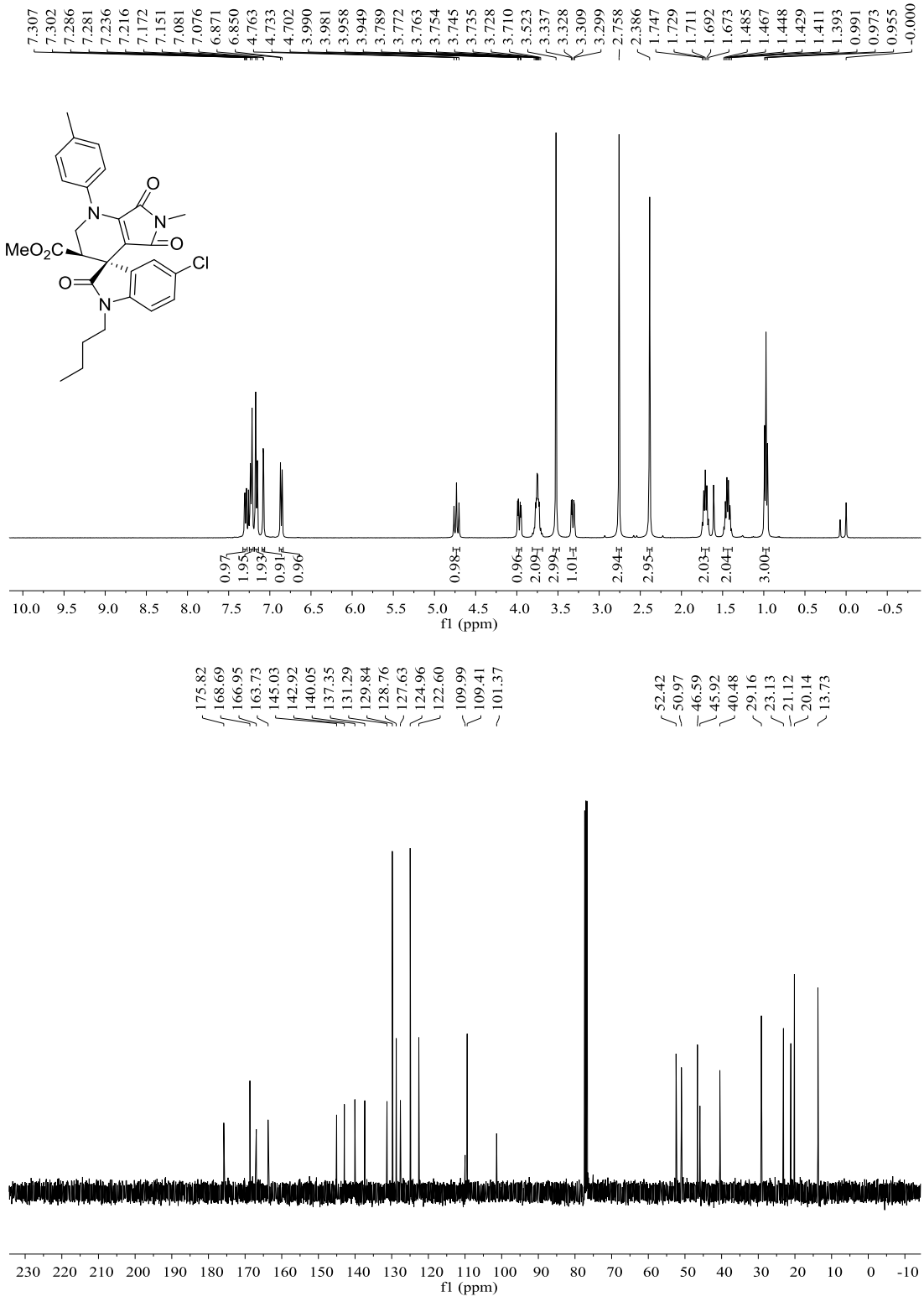
***rel*-(3a*R*,8*S*,8a*S*)-1'-Butyl-4-(4-methoxyphenyl)-2,5',6-trimethyl-3a,8a-dihydro-1*H*-spiro [dipyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5f'**): yellow solid, 54%, m.p. 123-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 8.4 Hz, 2H, ArH), 7.18 (d, *J* = 8.0 Hz, 1H, ArH), 7.06 (s, 1H, ArH), 6.97 (d, *J* = 8.8 Hz, 2H, ArH), 6.83 (d, *J* = 8.0 Hz, 1H, ArH), 4.73 (d, *J* = 8.4 Hz, 1H, CH), 3.85 (s, 3H, OCH_3), 3.72 ~ 3.64 (m, 1H, CH), 3.60 ~ 3.53 (m, 2H, CH), 2.92 (s, 3H, CH_3), 2.76 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 1.65 ~ 1.59 (m, 2H, CH), 1.40 ~ 1.36 (m, 1H, CH), 1.34 ~ 1.30 (m, 1H, CH), 0.93 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 172.7, 171.2, 166.9, 163.6, 159.4, 144.7, 141.5, 135.1, 132.9, 129.9, 128.5, 123.9, 114.4, 108.9, 100.8, 61.6, 55.5, 46.2, 44.4, 40.4, 29.3, 24.7, 23.2, 21.3, 20.0, 13.7; IR (KBr) υ: 3060, 3036, 2943, 2896, 1789, 1720, 1643, 1601, 1508, 1437, 1344, 1238, 1177, 1108, 1075, 1029, 983, 938, 862, 810, 768 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{30}N_4NaO_6$ ([M+Na]$^+$): 565.2058, Found: 565.2066.

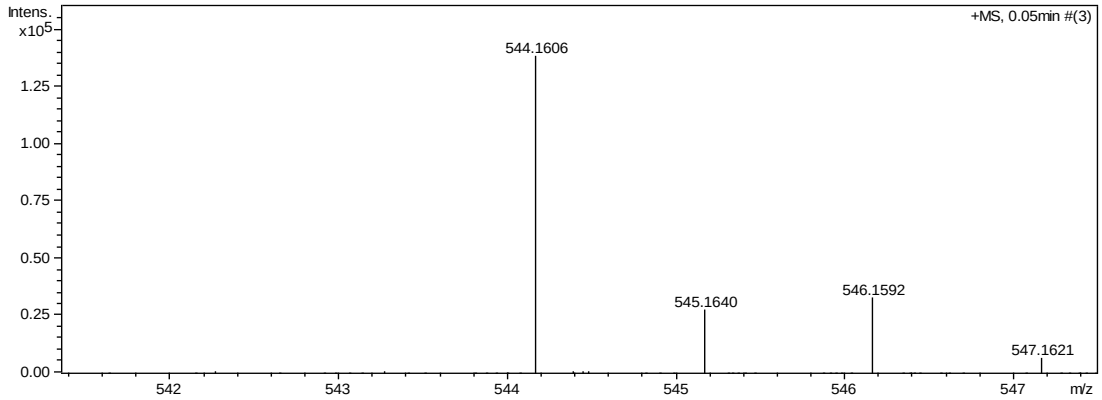
***rel*-(3a*R*,8*S*,8a*S*)-1'-Butyl-5'-chloro-2,6-dimethyl-4-phenyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo [3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5g'**): yellow solid, 48%, m.p. 290-292 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58(m, 2H, ArH), 7.49 ~ 7.40 (m, 3H, ArH), 7.29 ~ 7.26 (m, 1H, ArH), 6.85 (d, *J* = 8.4 Hz, 1H, ArH), 6.73 (m, 1H, ArH), 4.90 (d, *J* = 8.4 Hz, 1H, CH), 3.88 (d, *J* = 8.4 Hz, 1H, CH), 3.82 (t, *J* = 7.2 Hz, 2H, CH), 2.79 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 1.82 ~ 1.74 (m, 2H, CH), 1.56 ~ 1.47 (m, 2H, CH), 1.02 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 173.6, 170.9, 166.9, 163.4, 143.9, 142.7, 142.3, 129.7, 129.5,

129.3, 128.6, 127.5, 127.0, 123.8, 110.4, 102.3, 62.2, 45.6, 45.4, 41.0, 29.0, 24.2, 23.4, 20.1, 13.7; IR (KBr) υ: 3051, 3039, 2934, 2896, 1797, 1708, 1647, 1590, 1485, 1427, 1354, 1238, 1180, 1106, 1076, 1033, 982, 936, 868, 823, 780, 755 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{25}ClN_4NaO_5$ ($[M+Na]^+$): 555.1406, Found: 555.1415.

Methyl

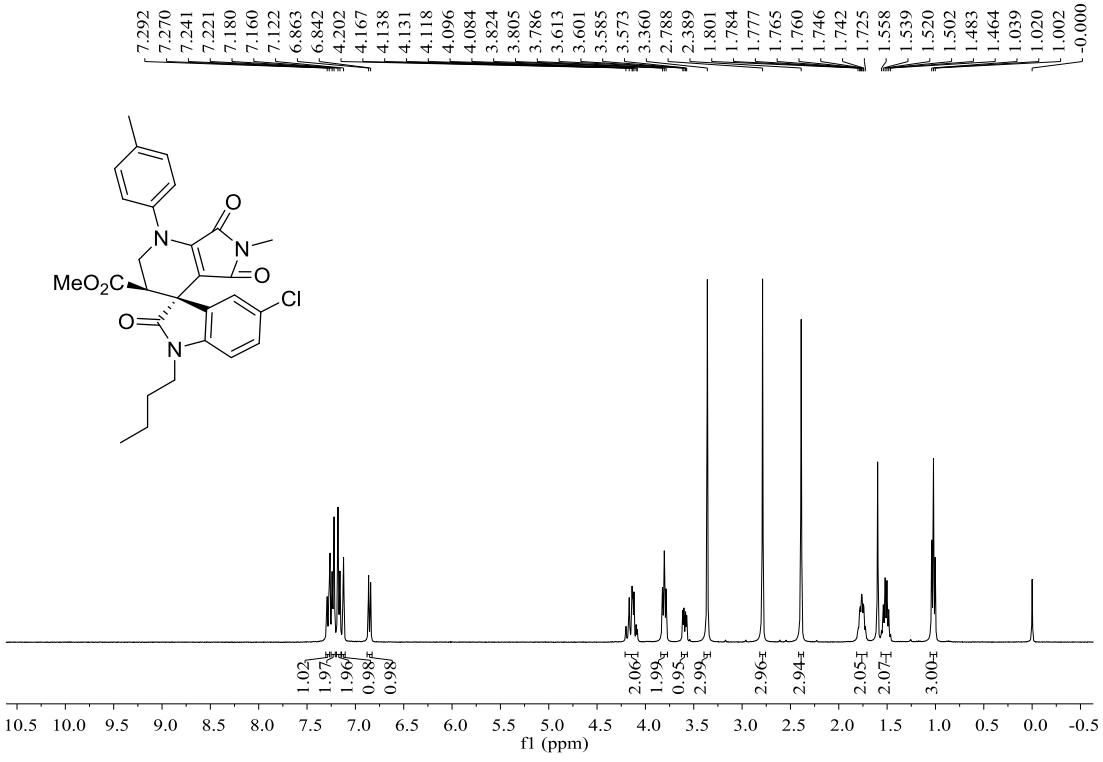
***rel*-(3*R*,3'*R*)-1-butyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3a)**:

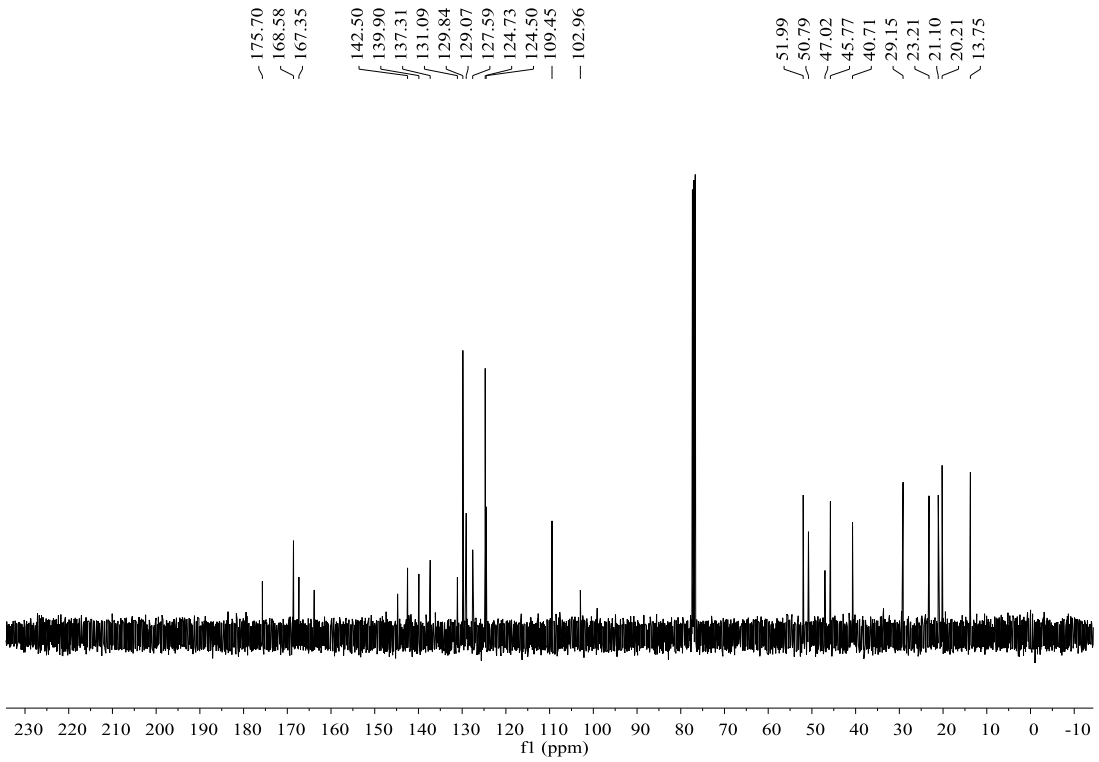




Methyl

***rel*-(3*S*,3'*R*)-1-butyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3a'**):

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102.96
51.99
50.79
47.02
45.77
40.71
29.15
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21.10
20.21
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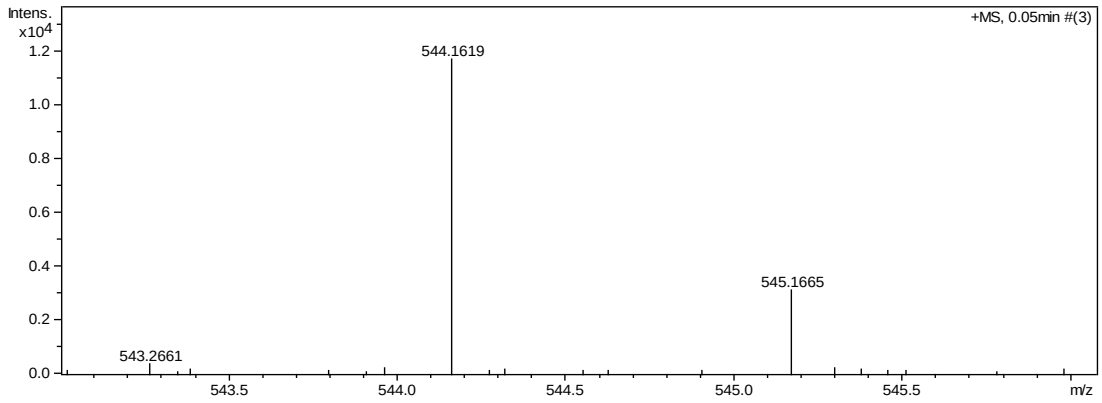
f1 (ppm)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0.6
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0.2
0.0
+MS, 0.05min #(3)
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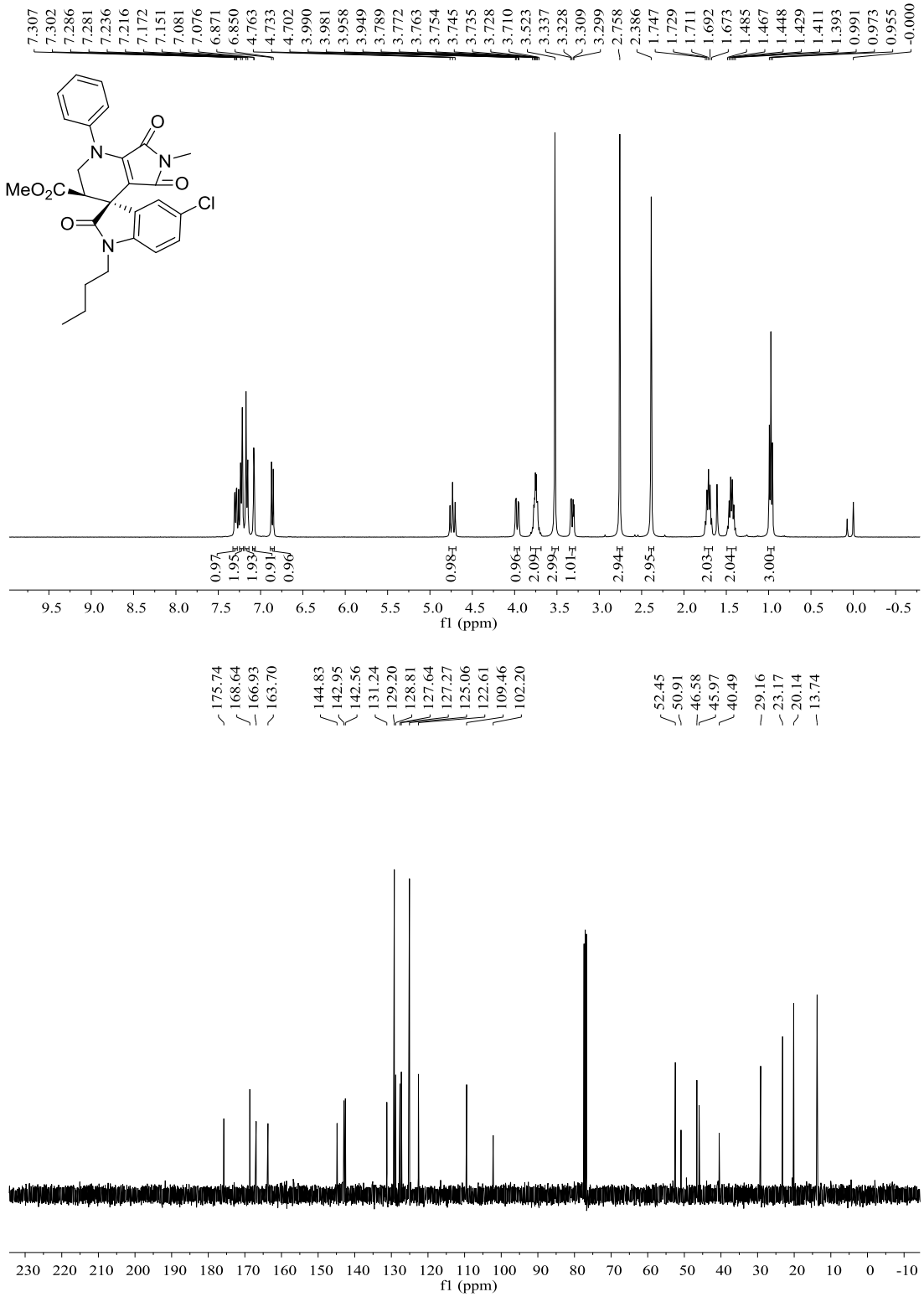
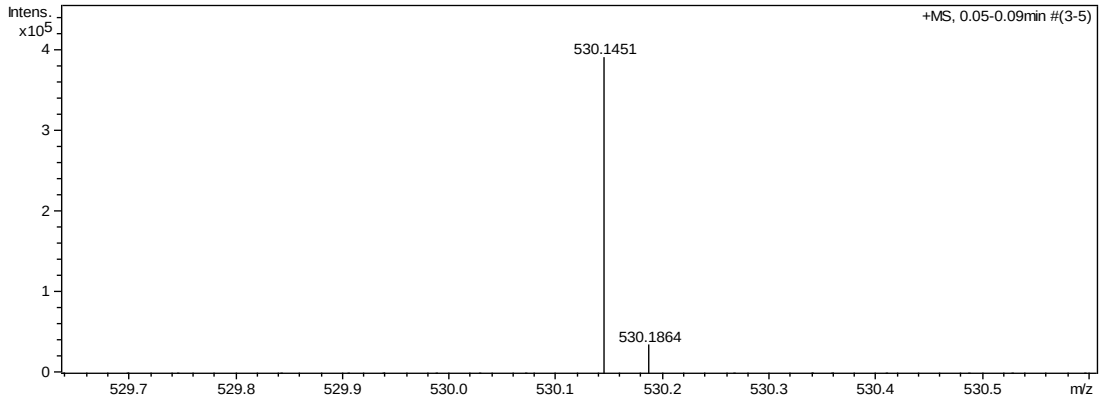
545.1665
543.2661
543.5
544.0
544.5
545.0
545.5
m/z

Methyl

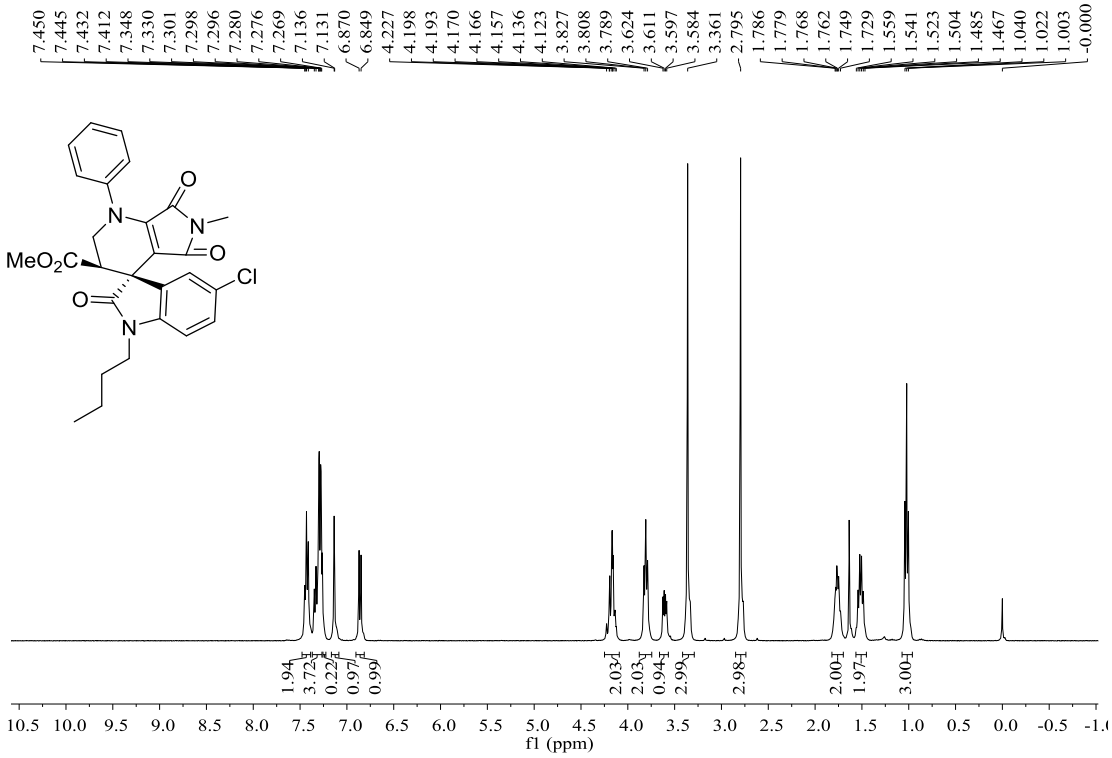
***rel*-(3*R*,3'*R*)-1-butyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3b**):

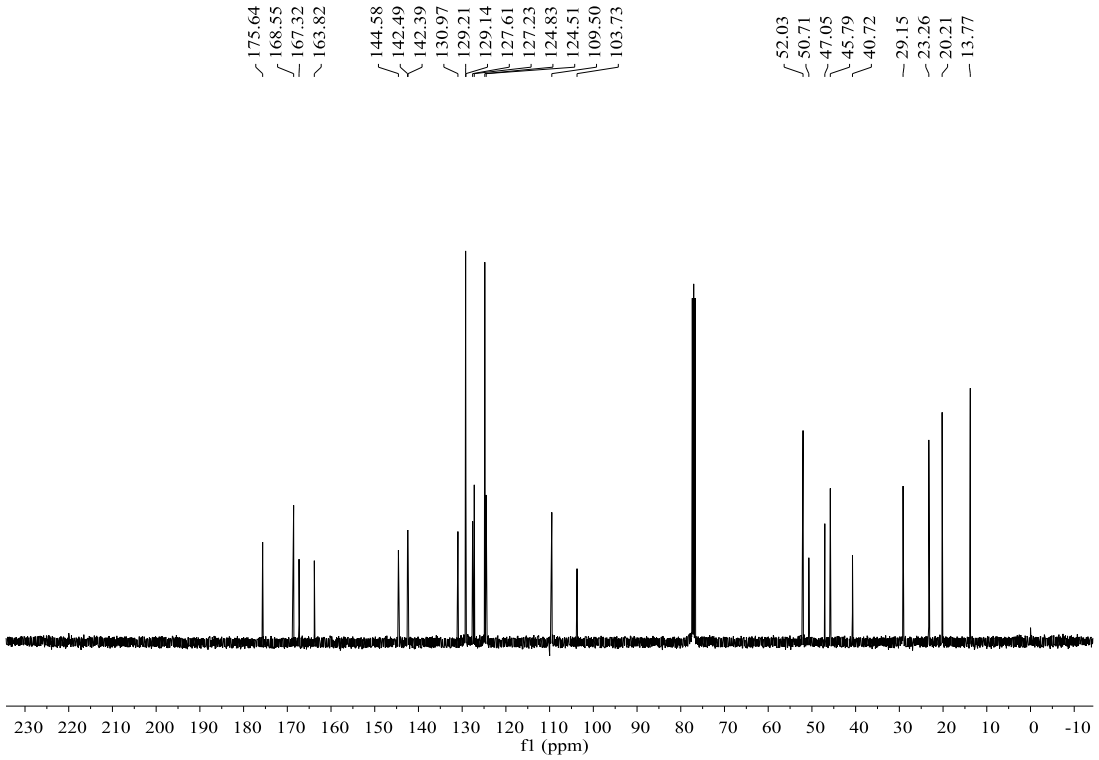


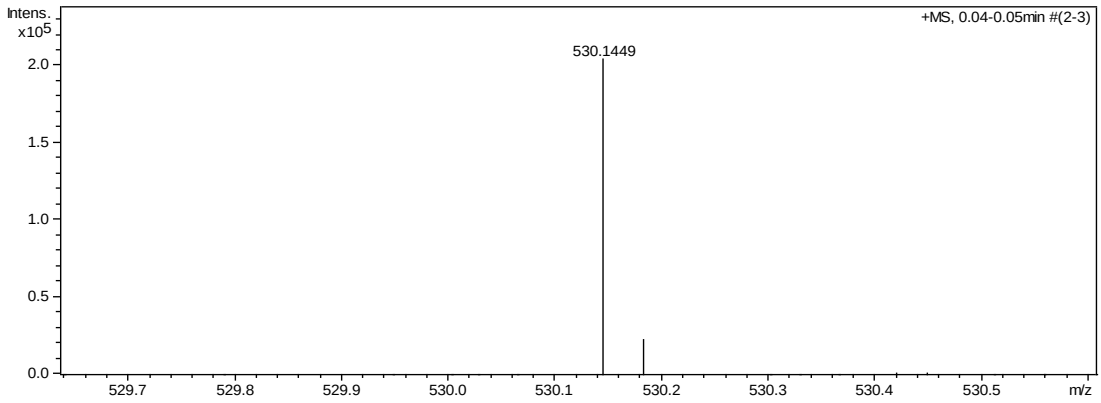


Methyl

***rel*-(3*S*,3'*R*)-1-butyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3b')**:



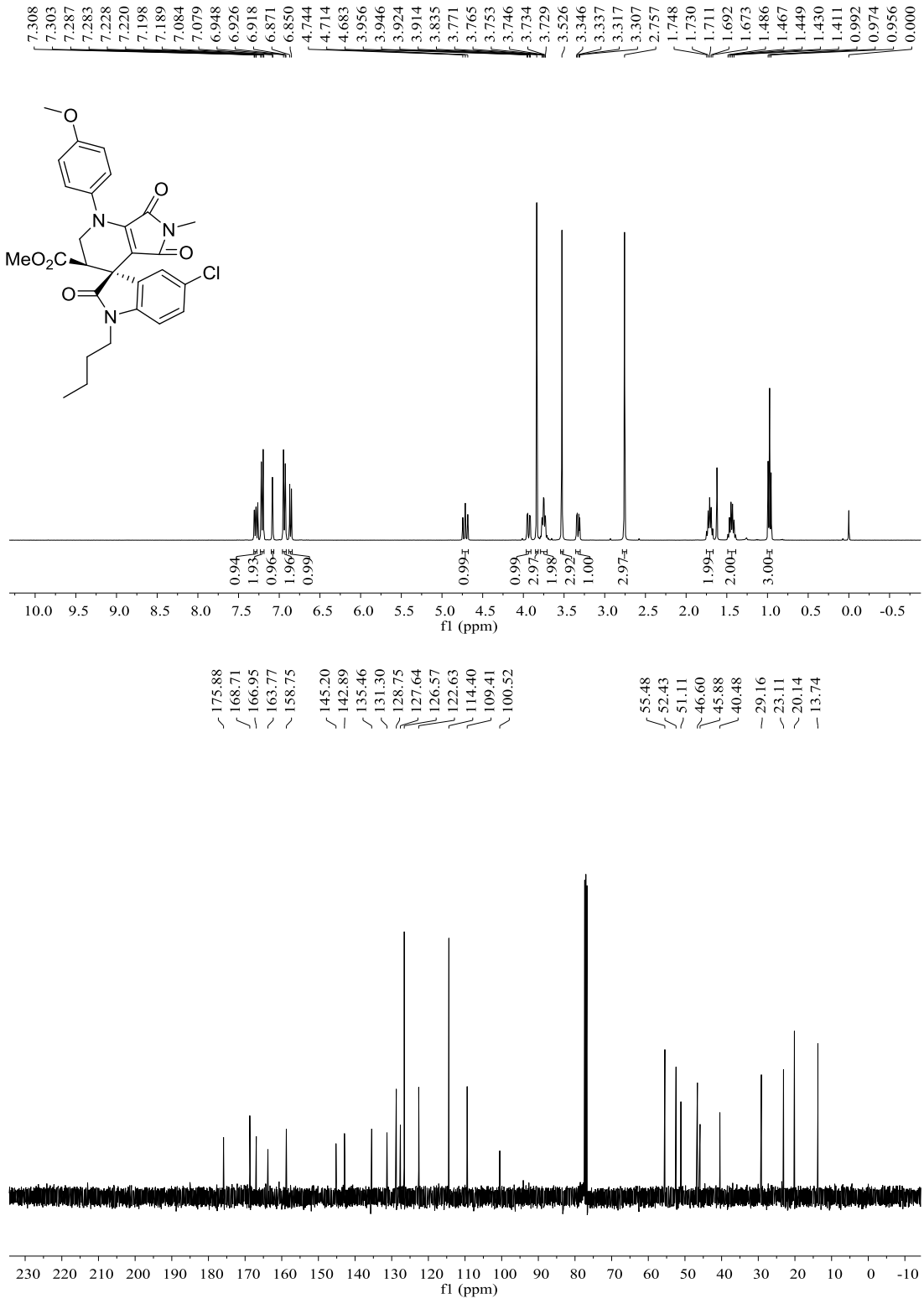

175.64
168.55
167.32
163.82
144.58
142.49
142.39
130.97
129.21
129.14
127.61
127.23
124.83
124.51
109.50
103.73
52.03
50.71
47.05
45.79
40.72
29.15
23.26
20.21
13.77
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

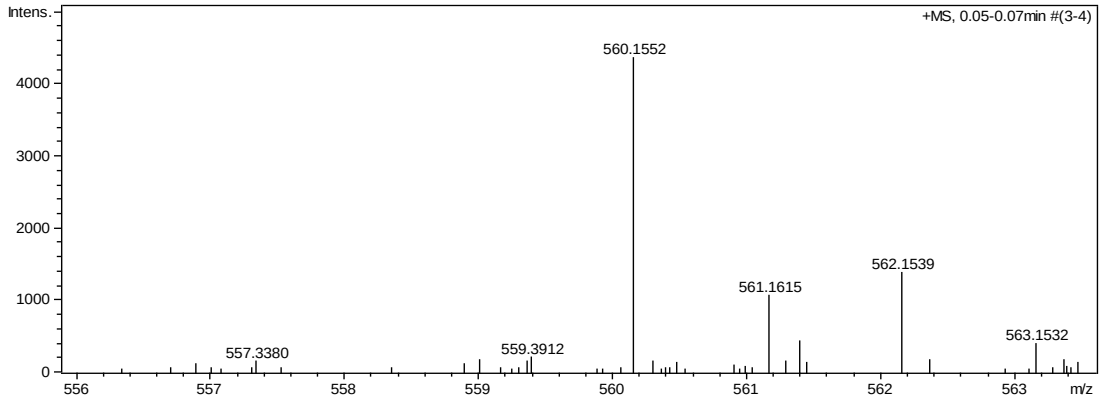

Intens.
x10^5
+MS, 0.04-0.05min #(2-3)
530.1449
2.0
1.5
1.0
0.5
0.0
529.7
529.8
529.9
530.0
530.1
530.2
530.3
530.4
530.5
m/z

Methyl

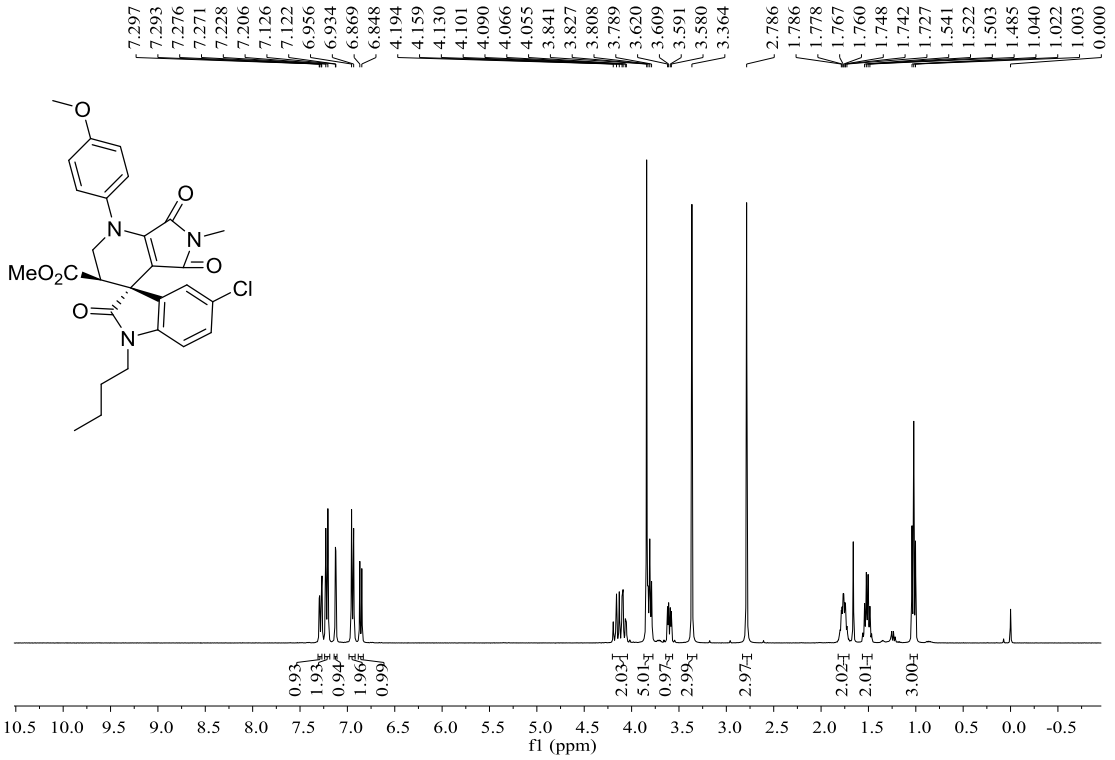
***rel*-(3*R*,3'*R*)-1-butyl-5-chloro-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-he**

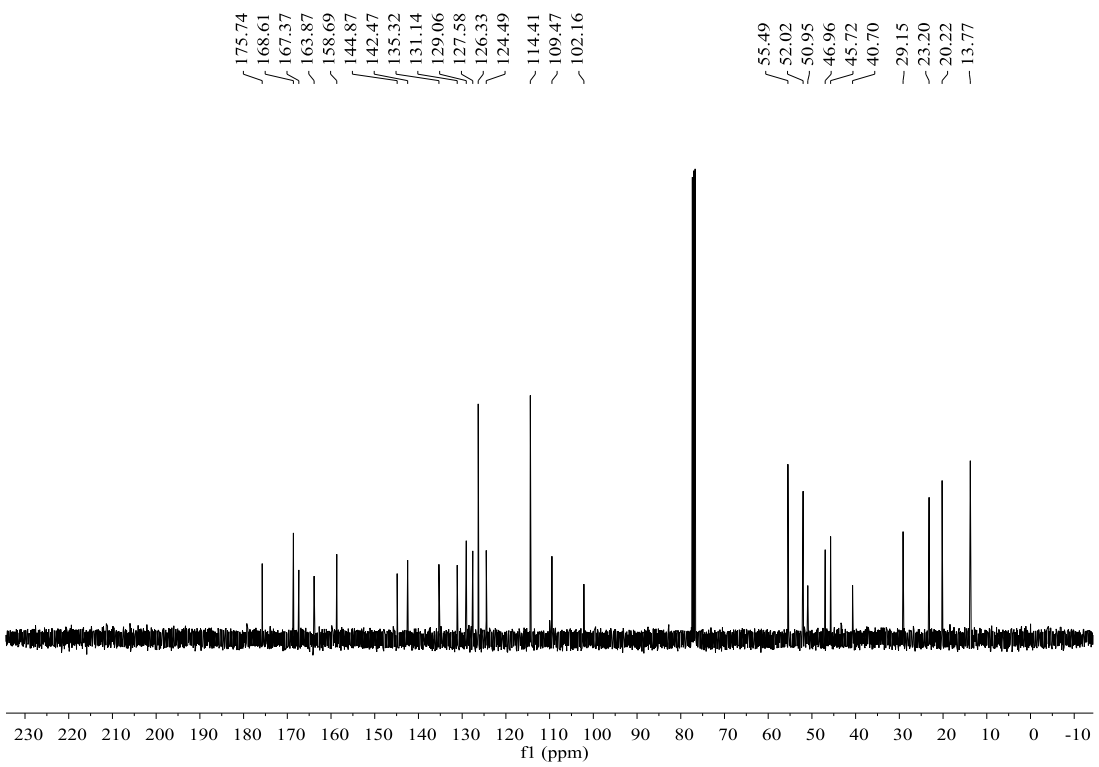
xahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3c**):

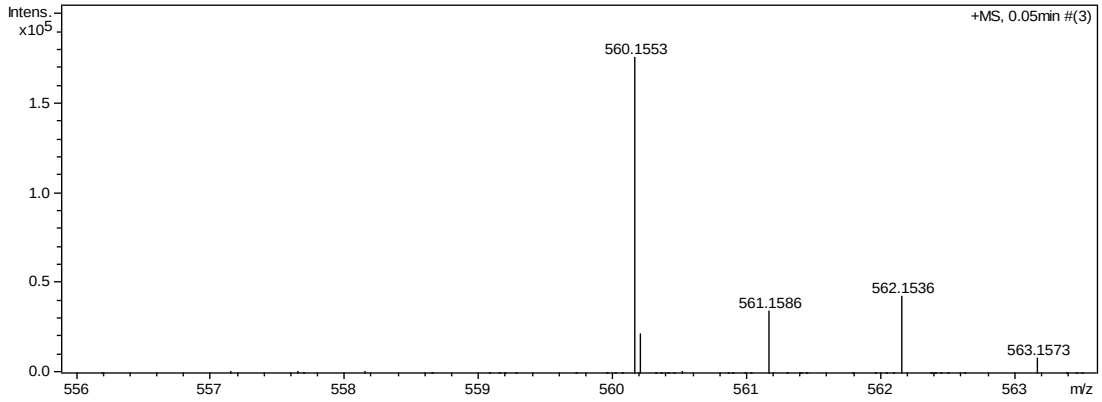




Methyl *rel*-(3*S*,3'*R*)-1-butyl-5-chloro-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate(3c'):

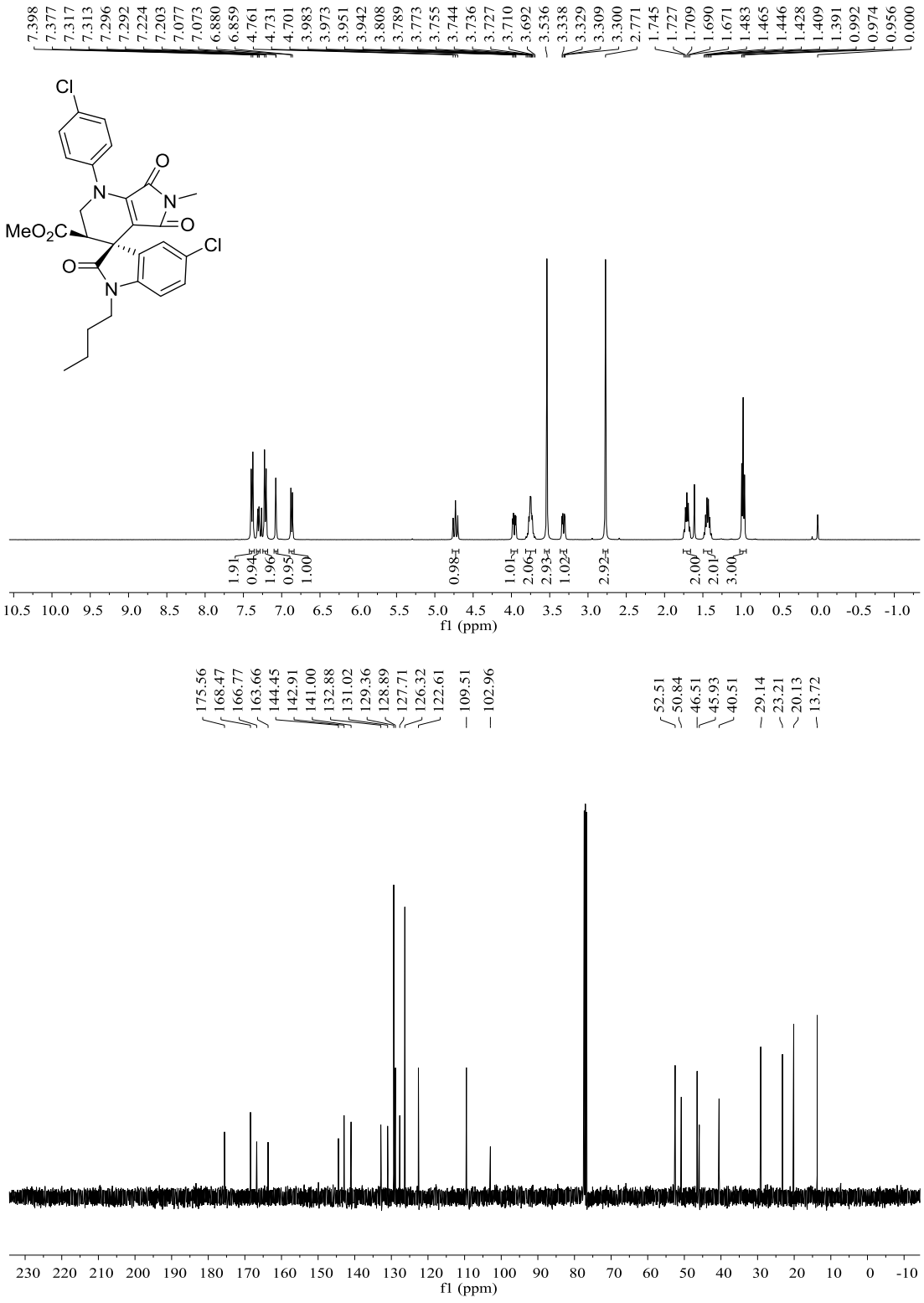


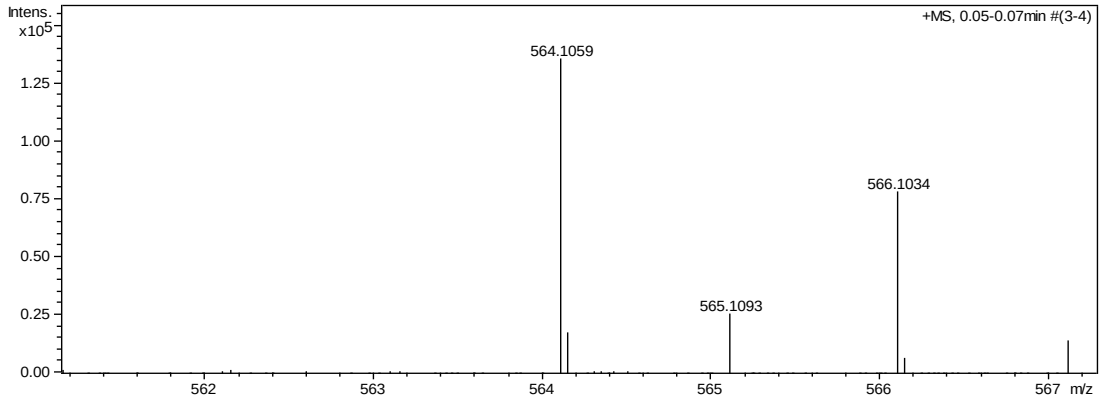

175.74
168.61
167.37
163.87
158.69
144.87
142.47
135.32
131.14
129.06
127.58
126.33
124.49
114.41
109.47
102.16
55.49
52.02
50.95
46.96
45.72
40.70
29.15
23.20
20.22
13.77
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.05min #(3)
560.1553
561.1586
562.1536
563.1573
0.0
0.5
1.0
1.5
556
557
558
559
560
561
562
563
m/z

Methyl

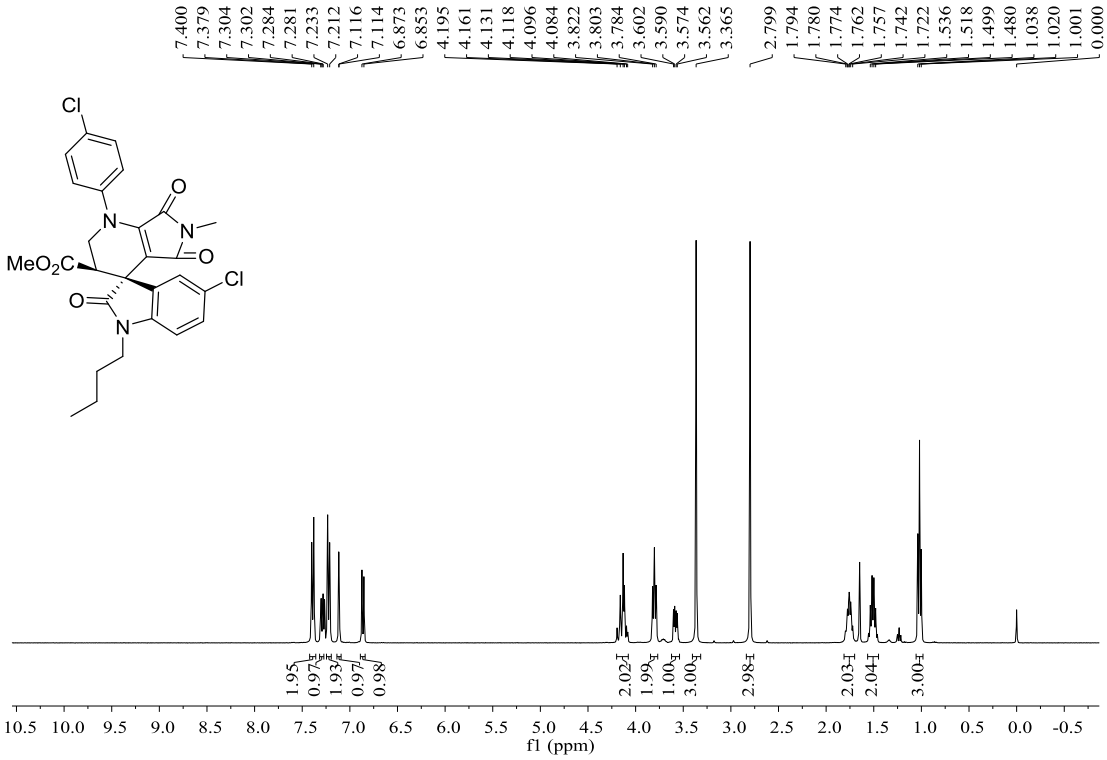
***rel*-(3*R*,3'*R*)-1-butyl-5-chloro-1'-(4-chlorophenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexa hydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3d)**:

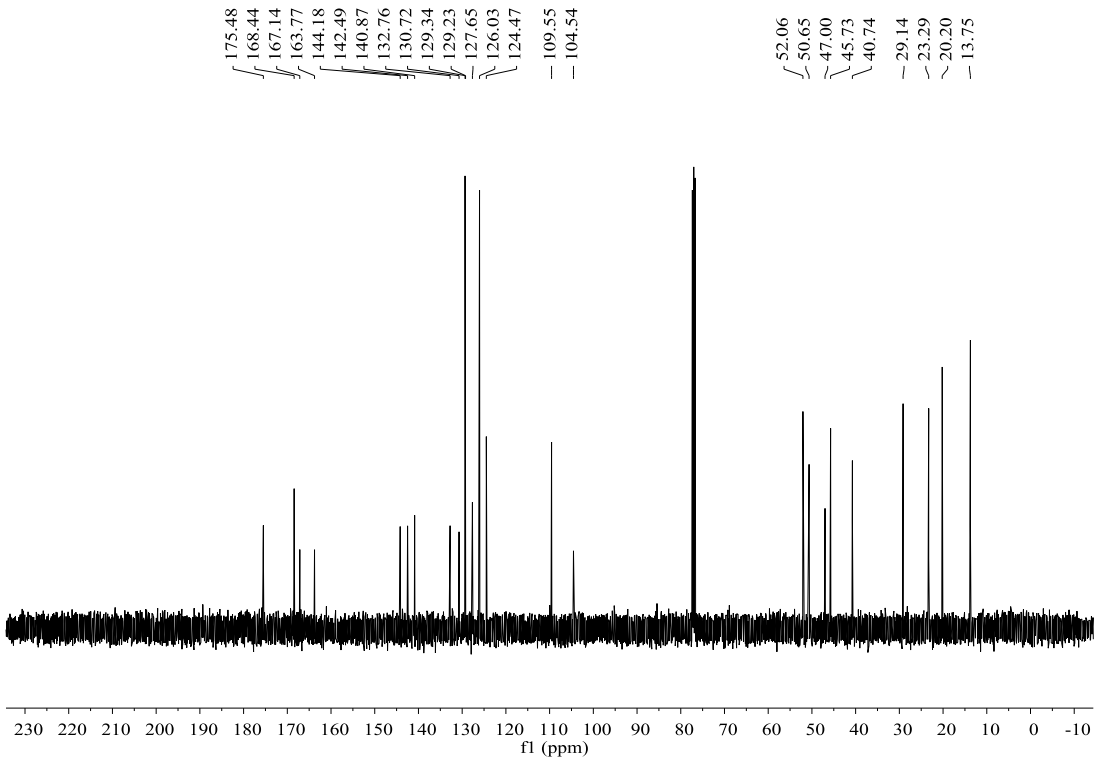


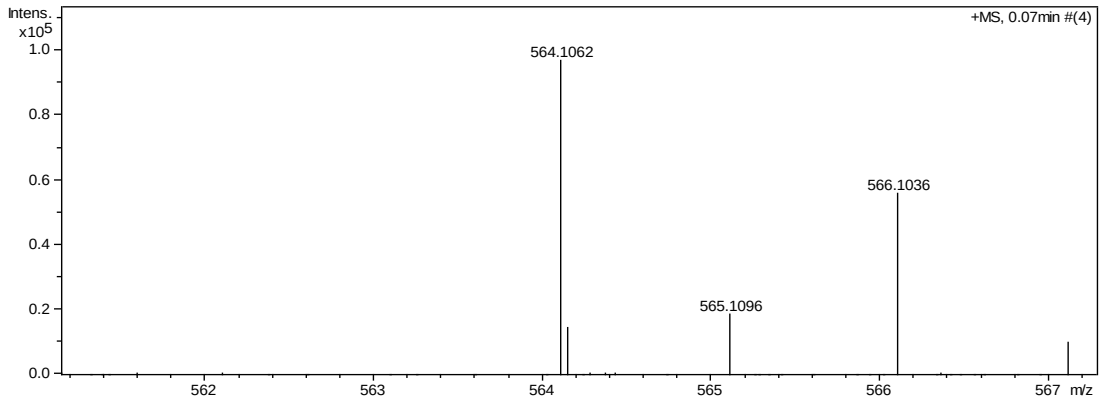


Methyl

***rel*-(3*S*,3'*R*)-1-butyl-5-chloro-1'-(4-chlorophenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexa hydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3d'**):

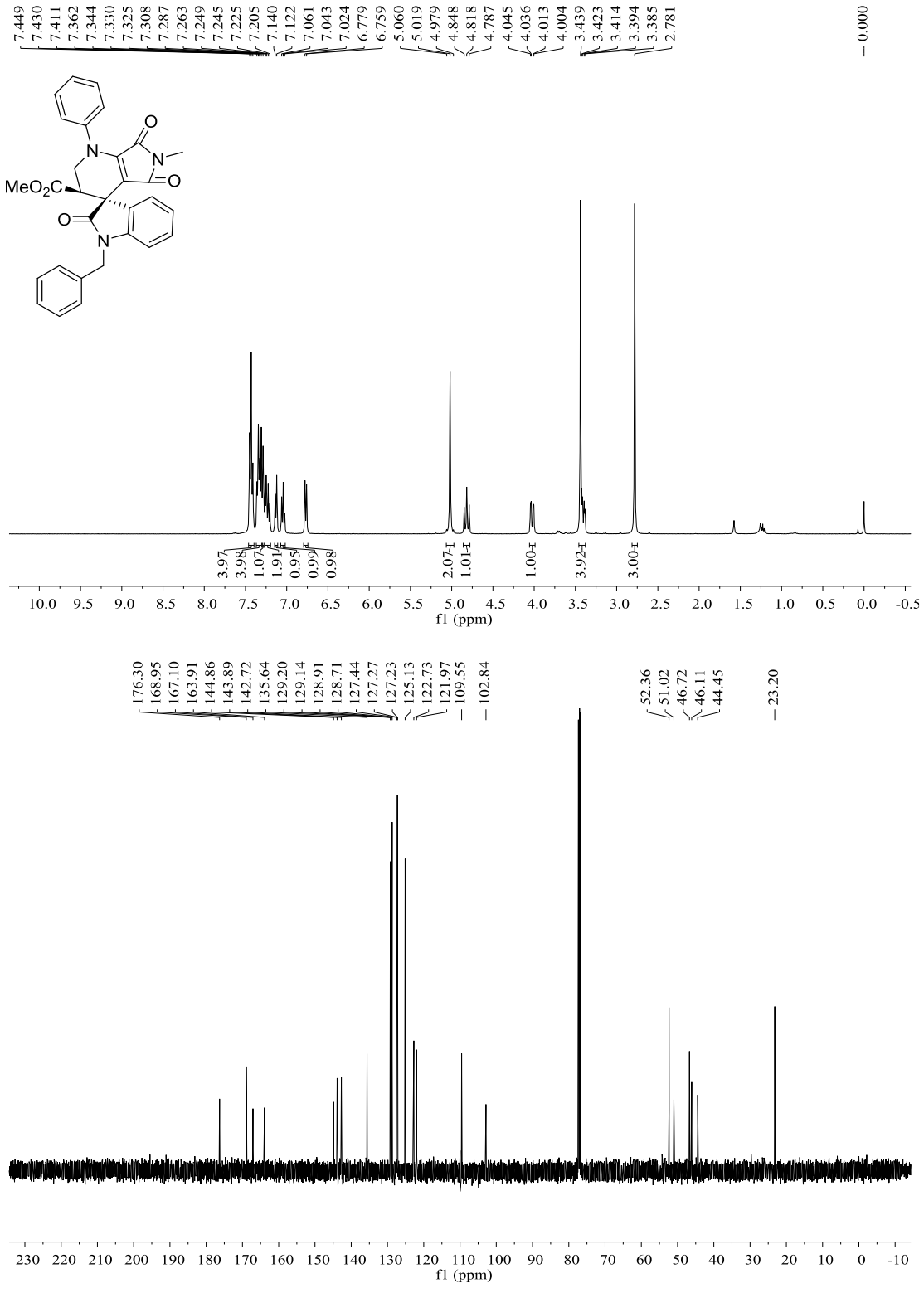


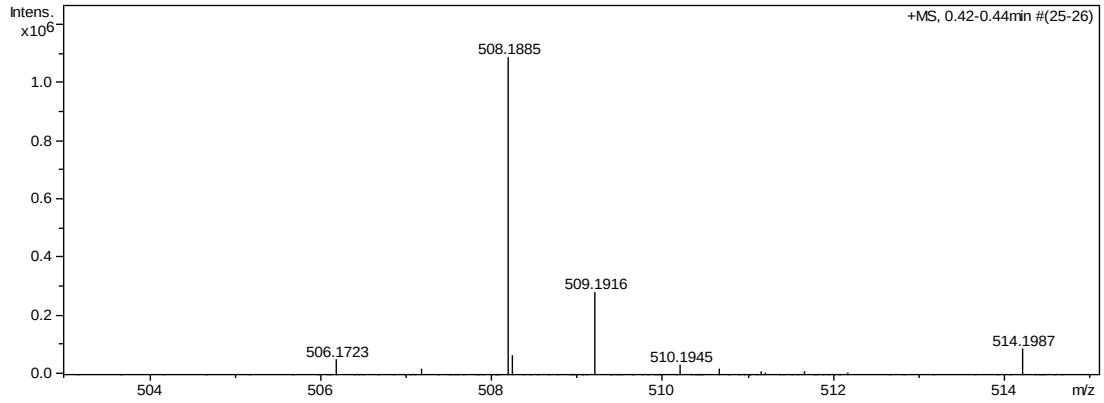

175.48
168.44
167.14
163.77
144.18
142.49
140.87
132.76
130.72
129.34
129.23
127.65
126.03
124.47
109.55
104.54
52.06
50.65
47.00
45.73
40.74
29.14
23.29
20.20
13.75
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
1.0
0.8
0.6
0.4
0.2
0.0
+MS, 0.07min #(4)
564.1062
566.1036
565.1096
562
563
564
565
566
567 m/z

Methyl

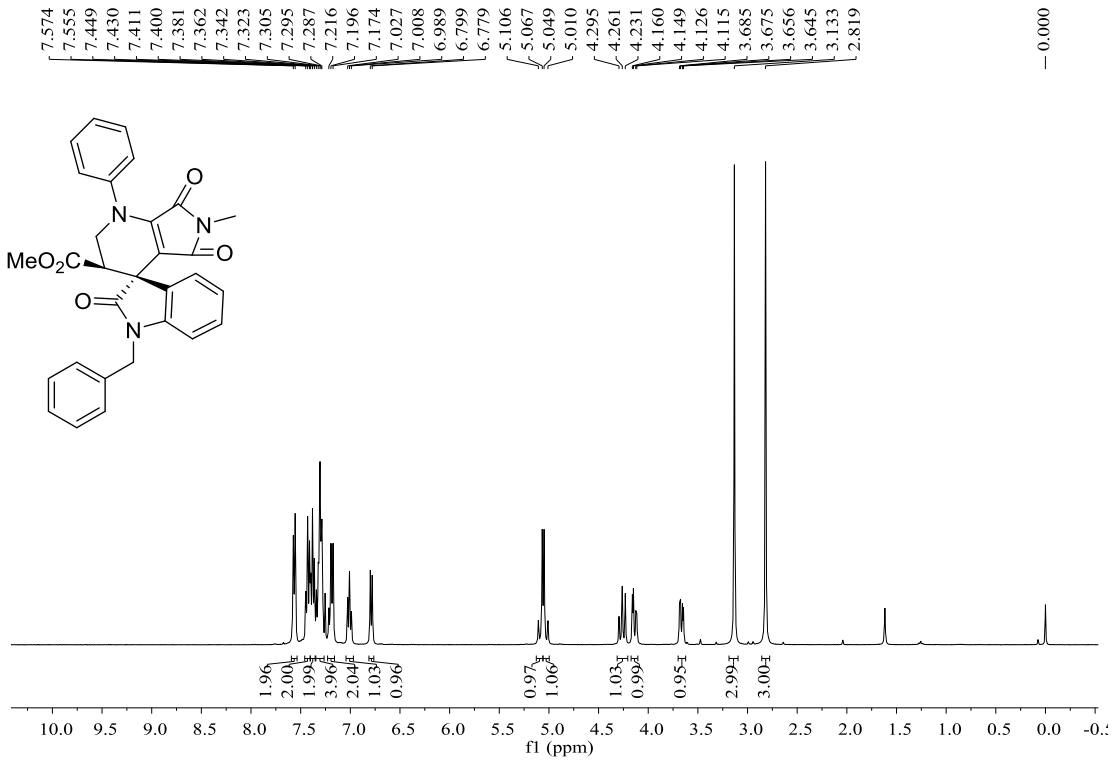
***rel*-(3*R*,3'*R*)-1-benzyl-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3e)**:

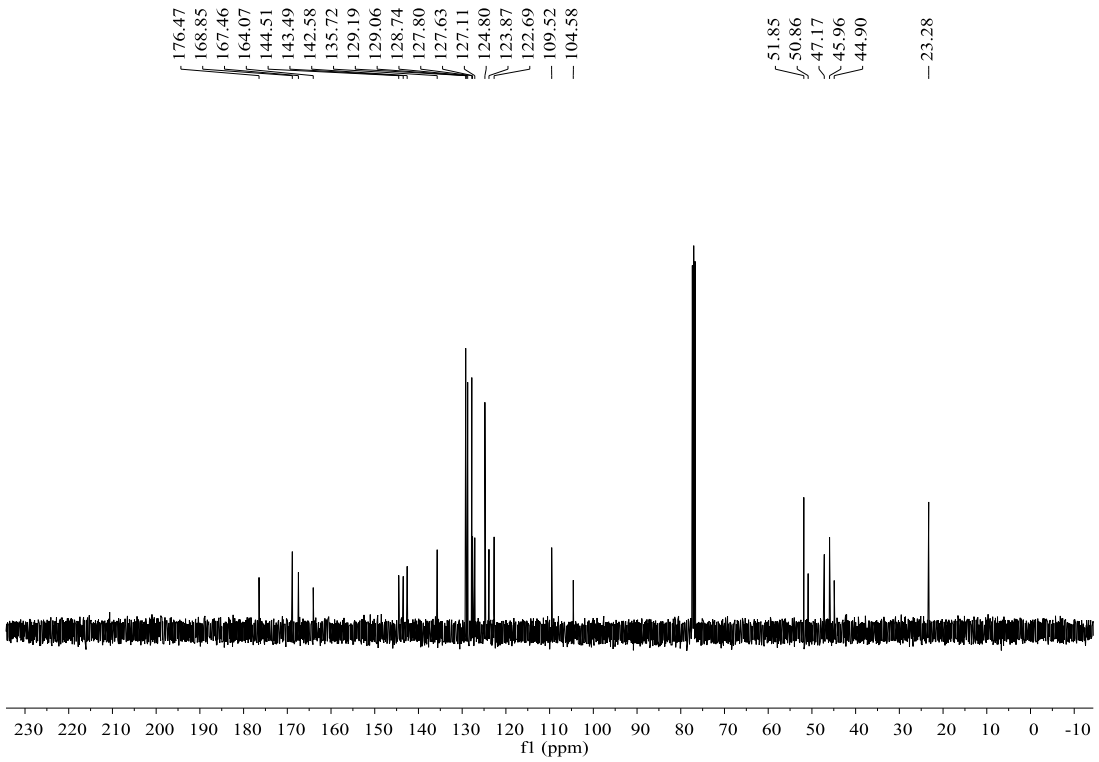


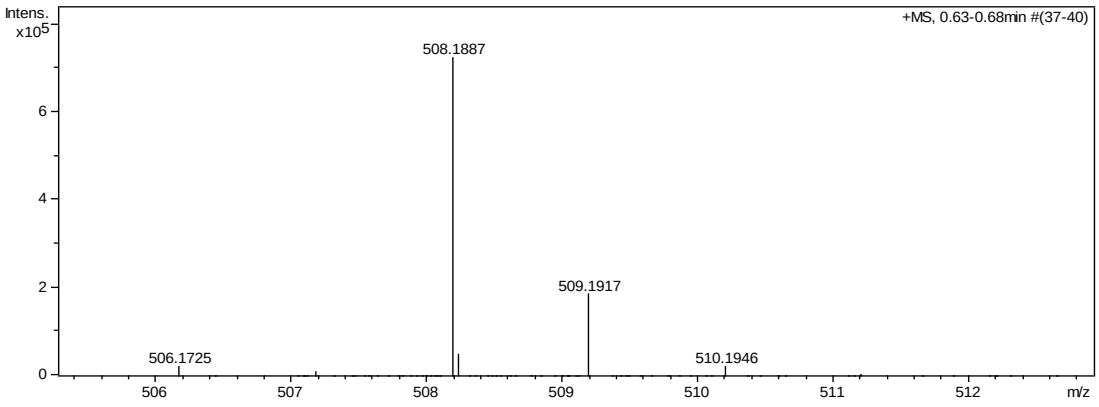


Methyl

***rel*-(3*S*,3'*R*)-1-benzyl-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3e'**):

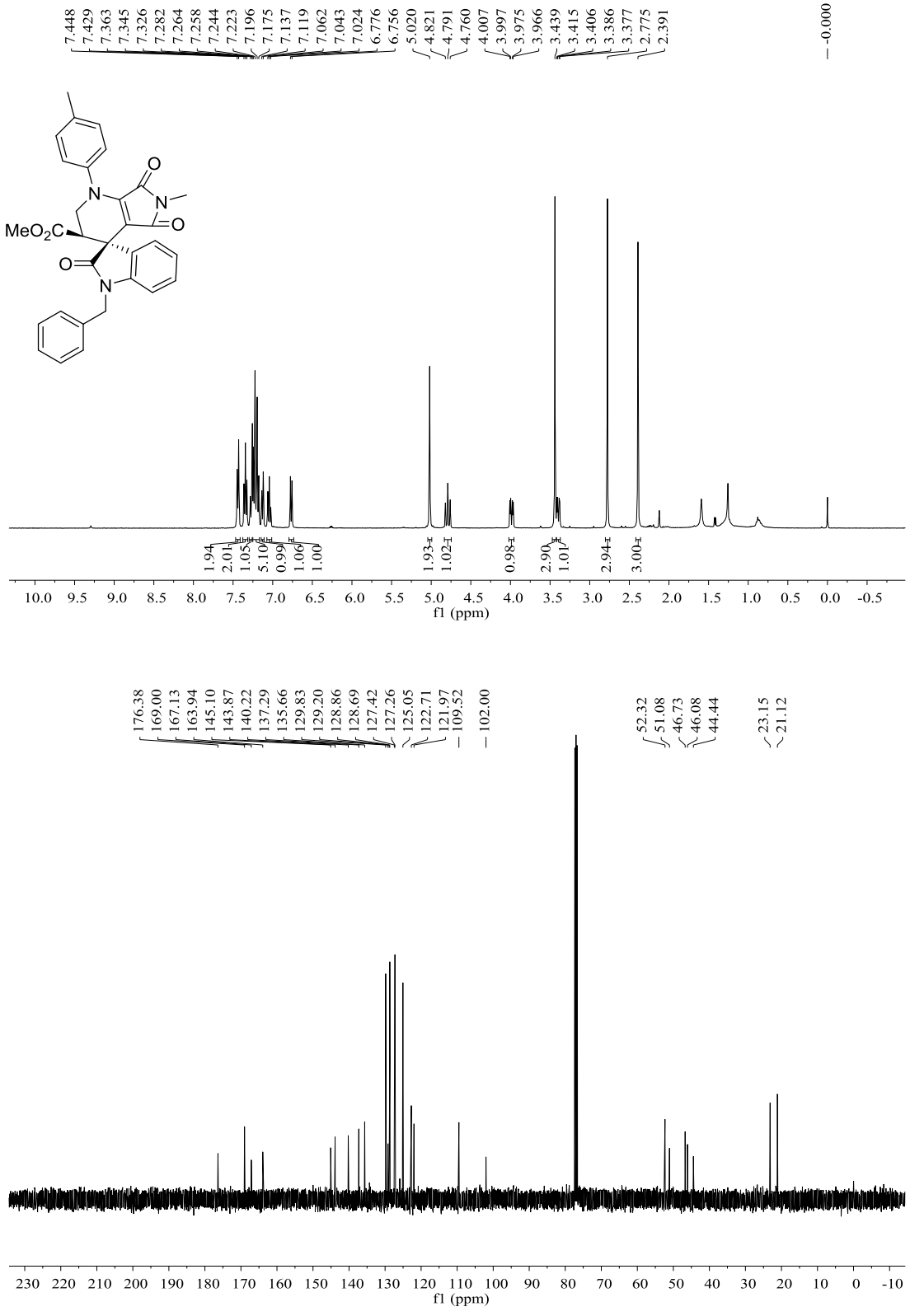


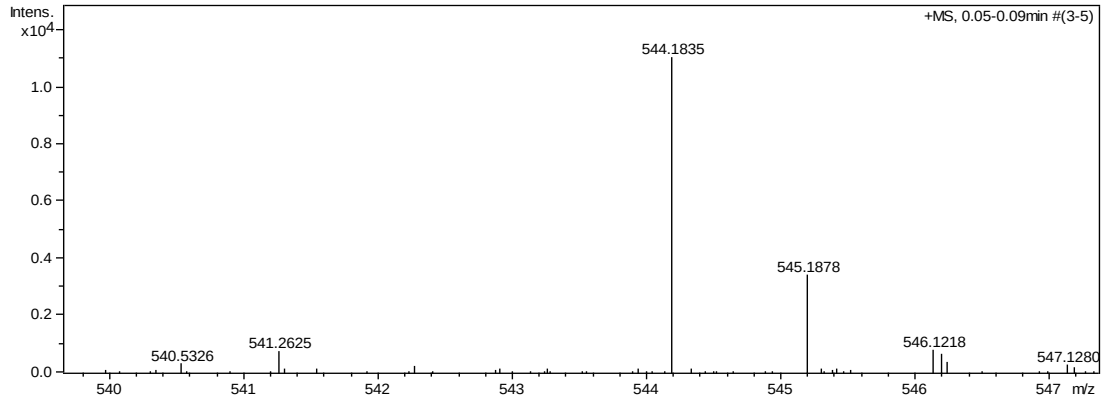

176.47
168.85
167.46
164.07
144.51
143.49
142.58
135.72
129.19
129.06
128.74
127.80
127.63
127.11
124.80
123.87
122.69
109.52
104.58
51.85
50.86
47.17
45.96
44.90
23.28
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.63-0.68min #(37-40)
508.1887
509.1917
506.1725
510.1946
0
2
4
6
506
507
508
509
510
511
512
m/z

Methyl

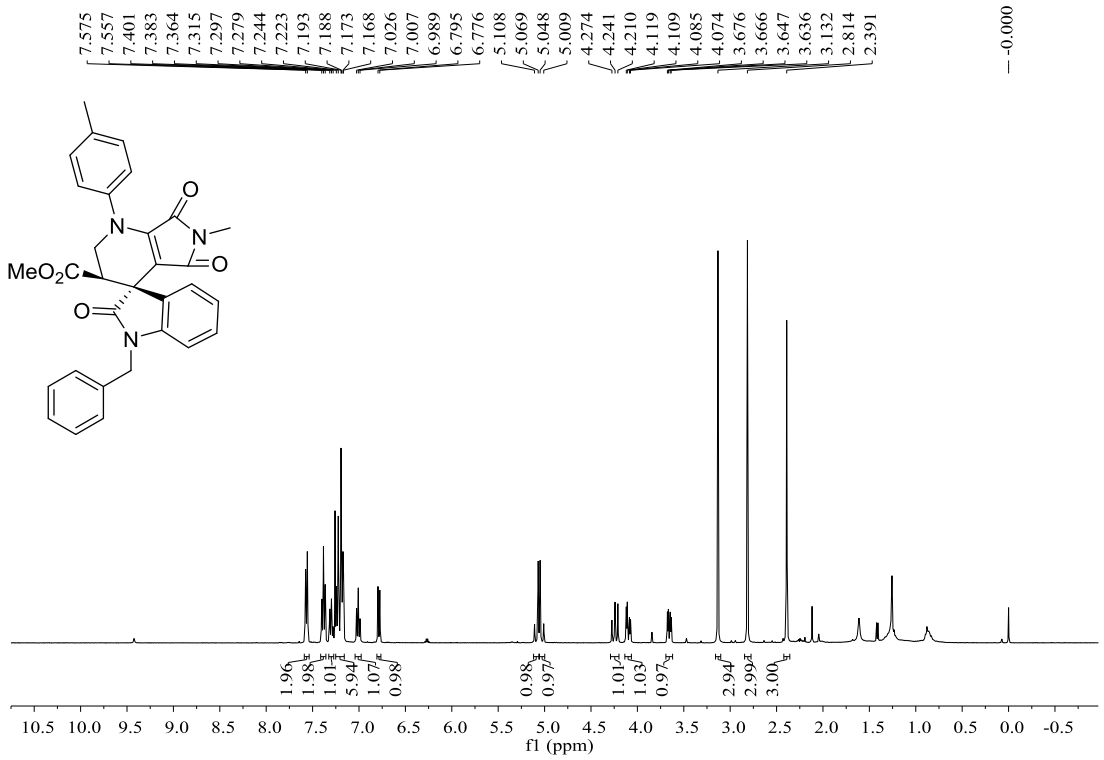
***rel*-(3*R*,3'*R*)-1-benzyl-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3f)**:

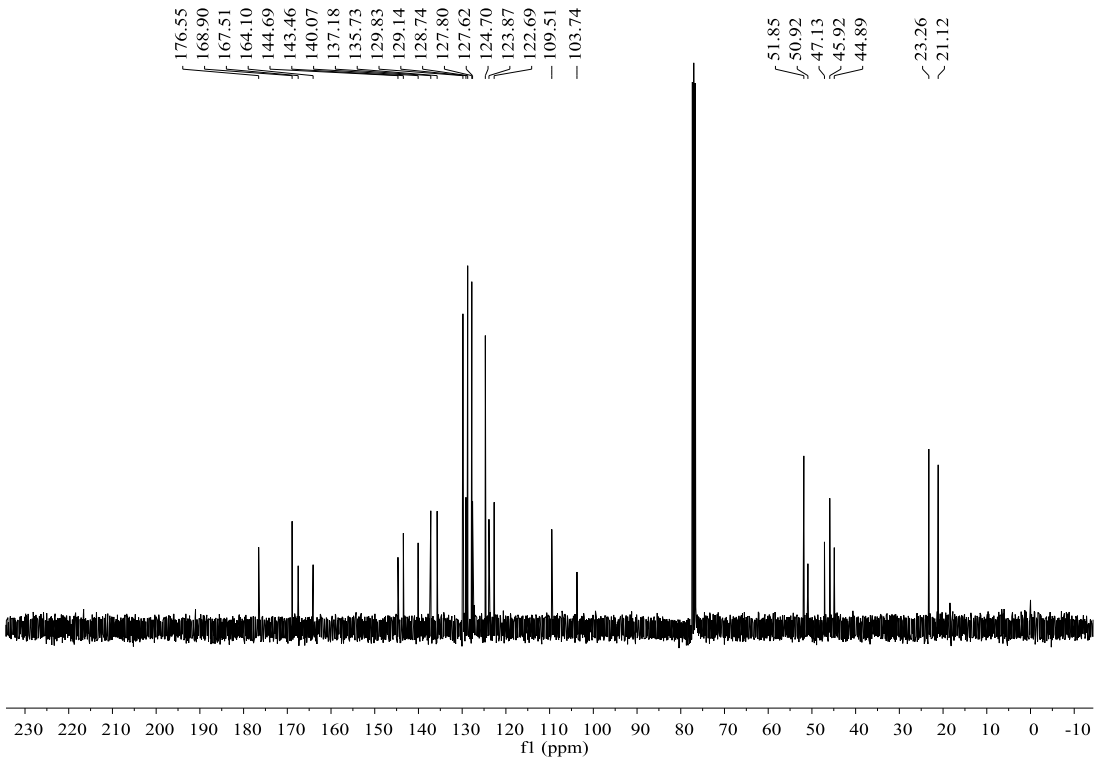


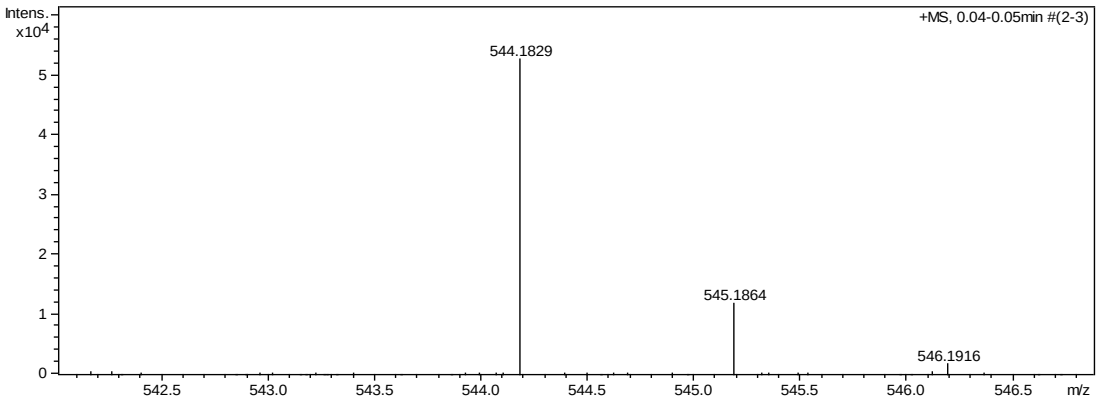


Methyl

***rel*-(3*S*,3'*R*)-1-benzyl-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3f')**:



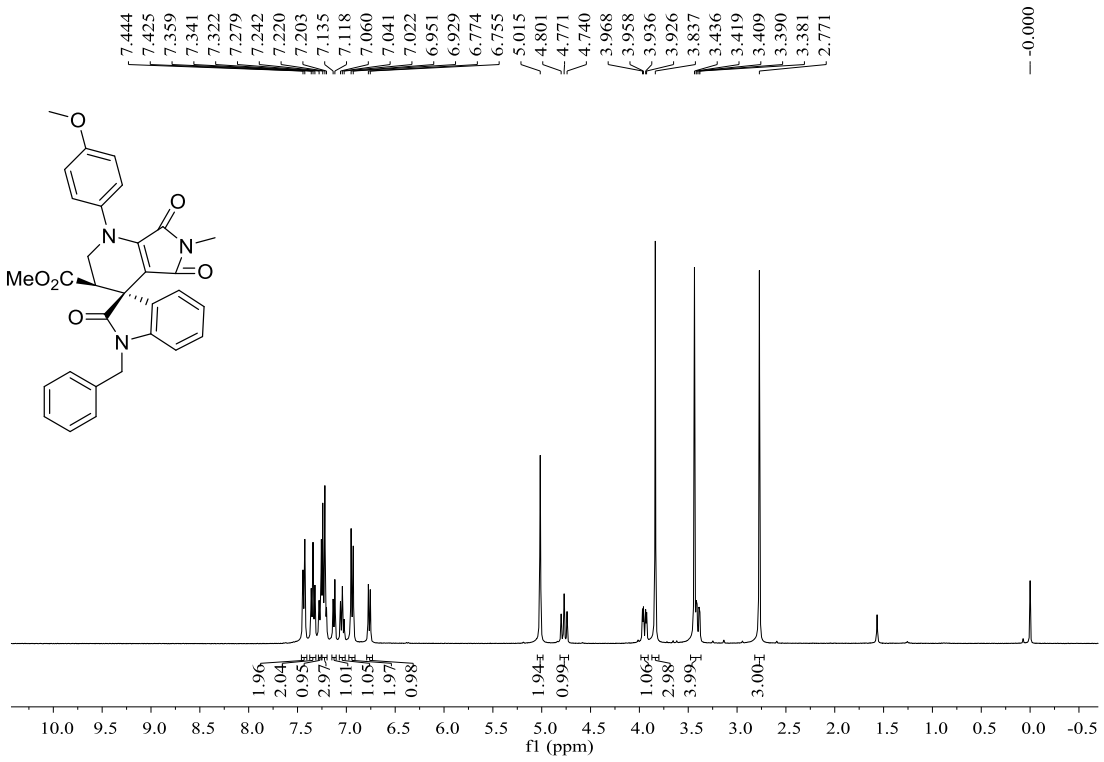

176.55
168.90
167.51
164.10
144.69
143.46
140.07
137.18
135.73
129.83
129.14
128.74
127.80
127.62
124.70
123.87
122.69
109.51
103.74
51.85
50.92
47.13
45.92
44.89
23.26
21.12
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

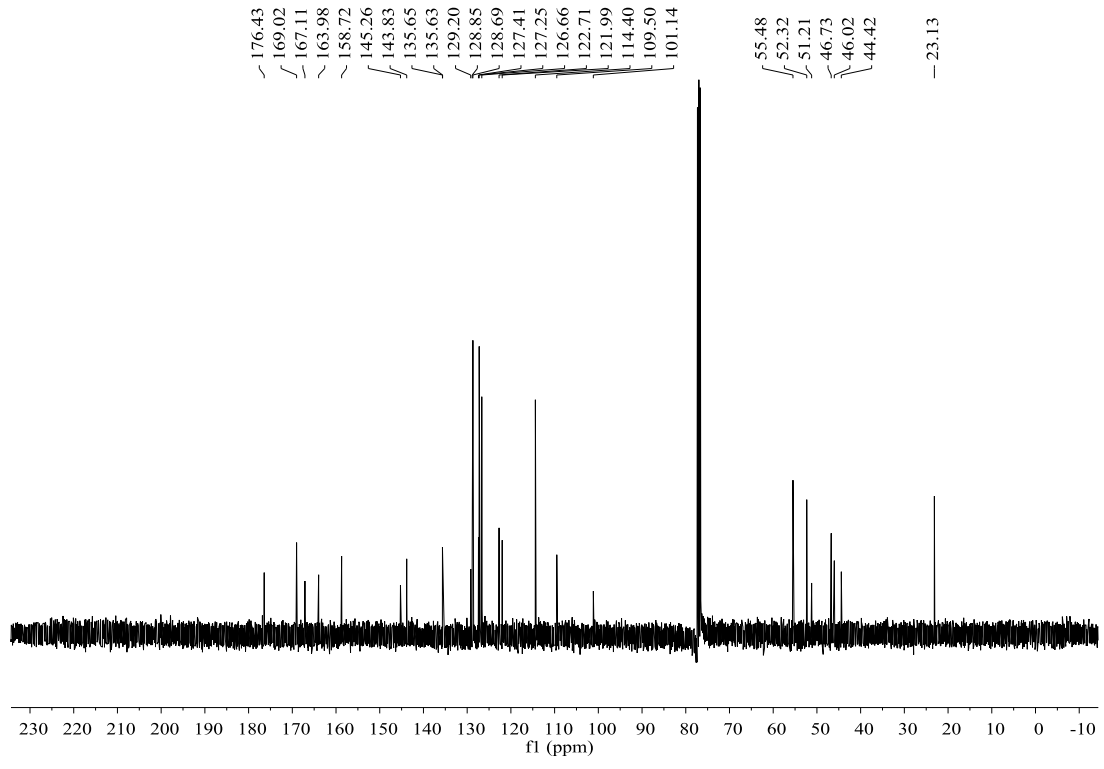

Intens.
x10^4
+MS, 0.04-0.05min #(2-3)
544.1829
545.1864
546.1916
542.5 543.0 543.5 544.0 544.5 545.0 545.5 546.0 546.5
m/z

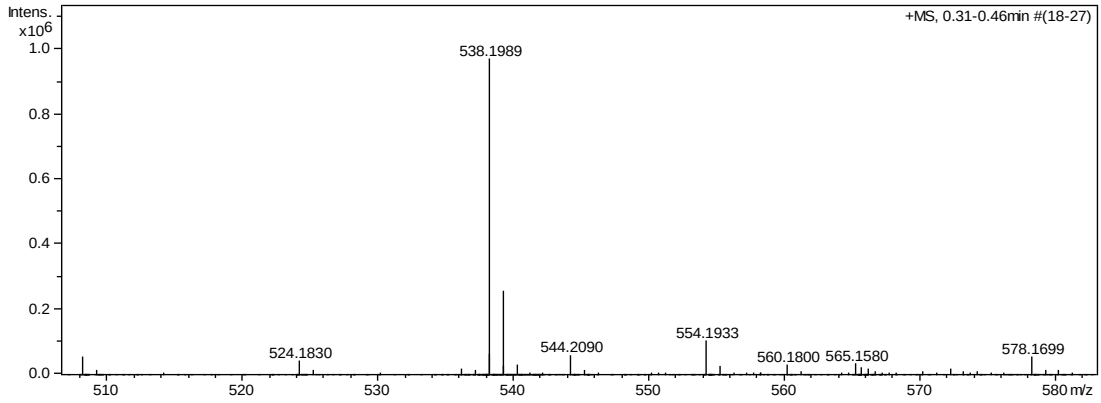
Methyl

***rel*-(3*R*,3'*R*)-1-benzyl-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydr**

ospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3g**):



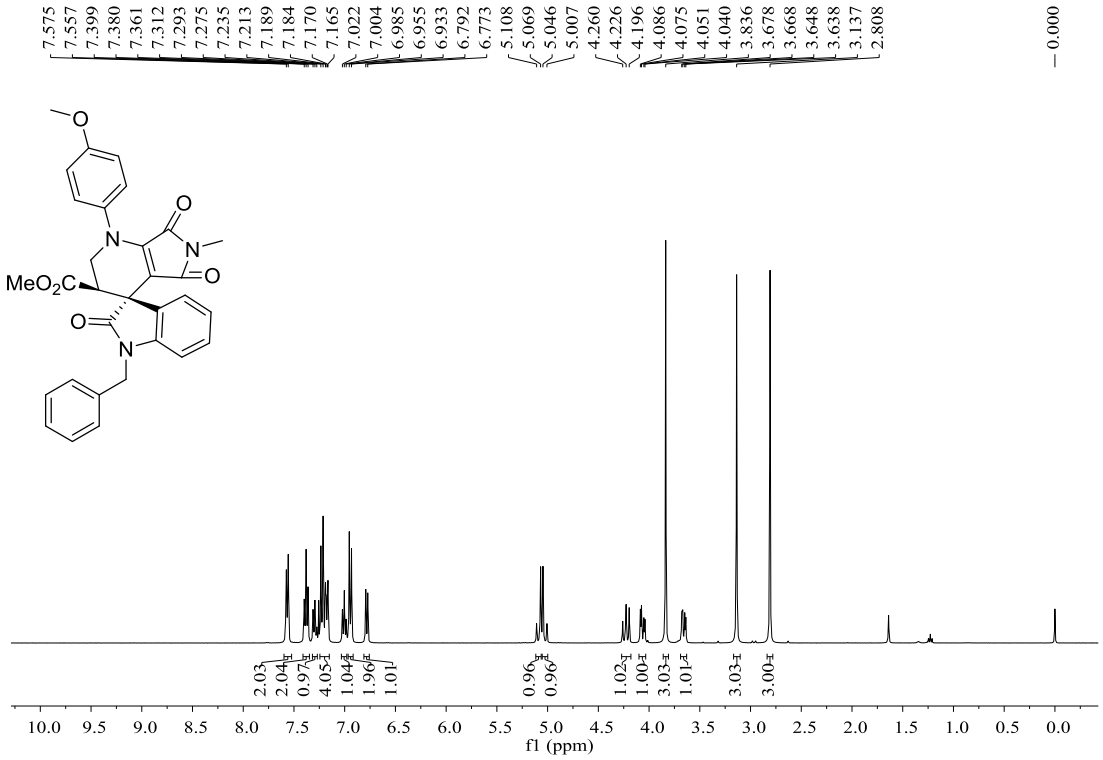


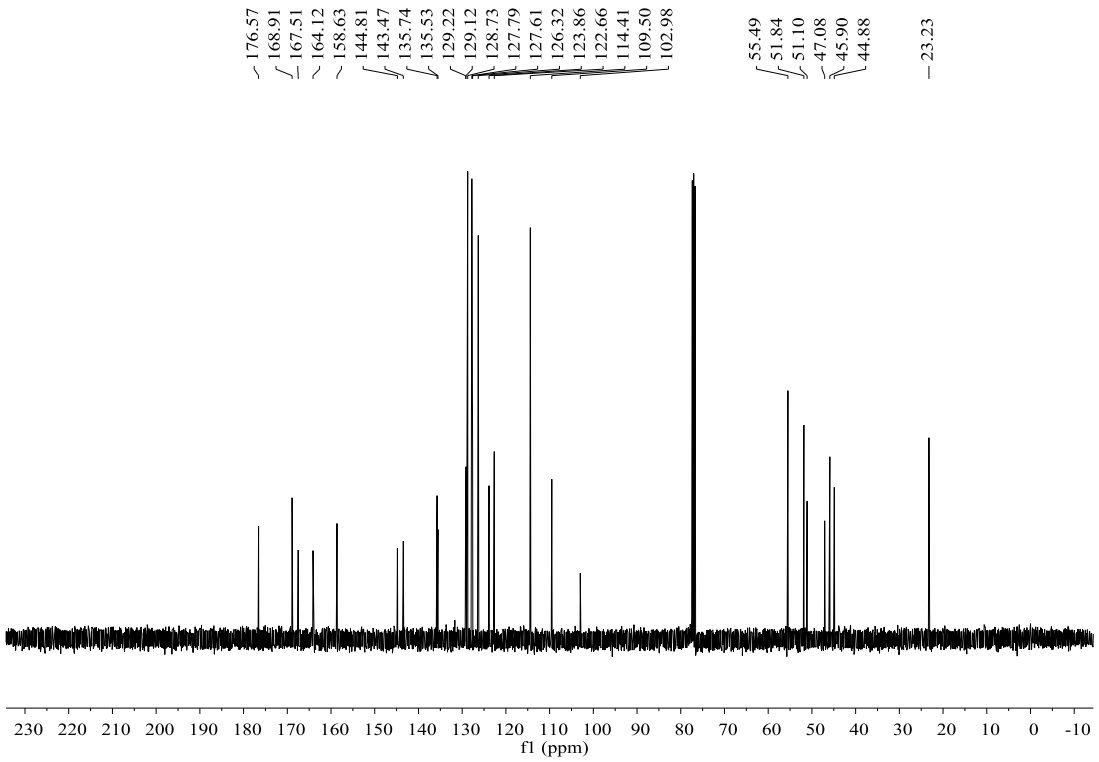


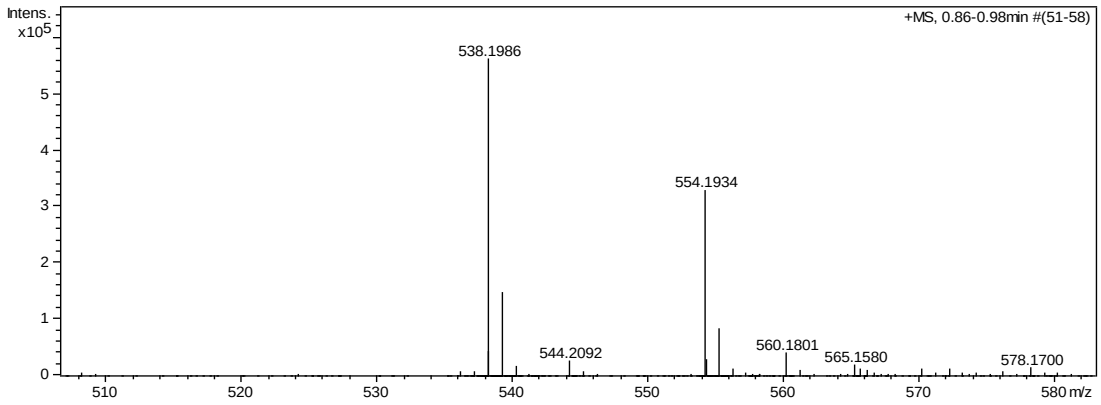
Methyl

***rel*-(3*S*,3'*R*)-1-benzyl-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydr**

ospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (**3g'**):

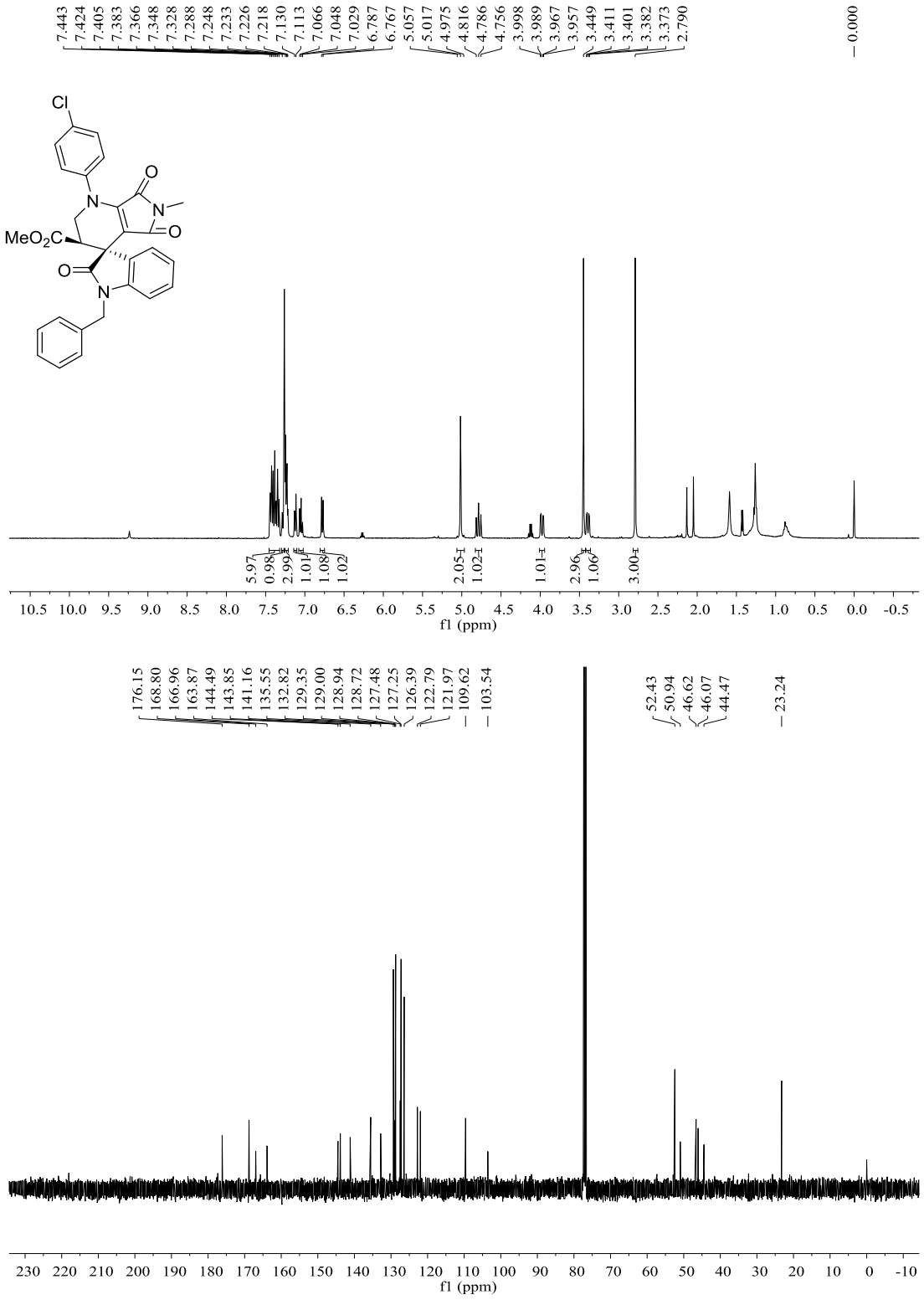


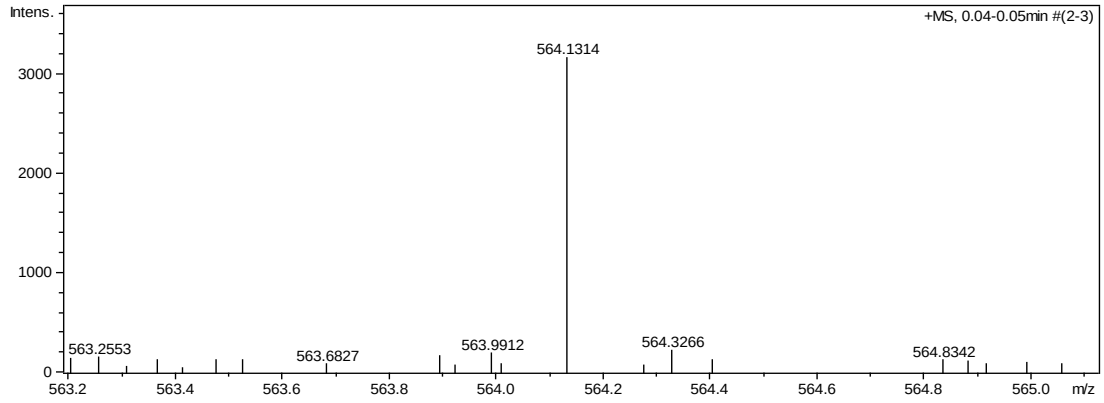

176.57
168.91
167.51
164.12
158.63
144.81
143.47
135.74
135.53
129.22
129.12
128.73
127.79
127.61
126.32
123.86
122.66
114.41
109.50
102.98
55.49
51.84
51.10
47.08
45.90
44.88
23.23
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.86-0.98min #(51-58)
538.1986
554.1934
544.2092
560.1801
565.1580
578.1700
0
1
2
3
4
5
510
520
530
540
550
560
570
580 m/z

Methyl

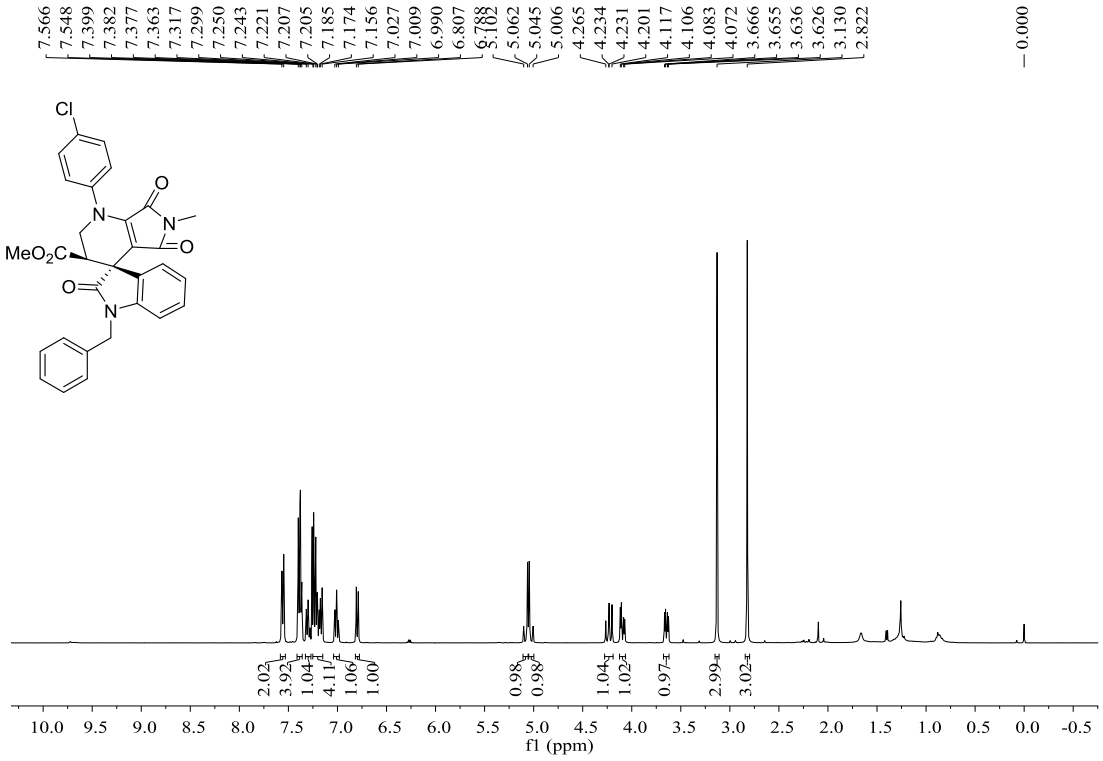
***rel*-(3*R*,3'*R*)-1-benzyl-1'-(4-chlorophenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydros piro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3h)**:

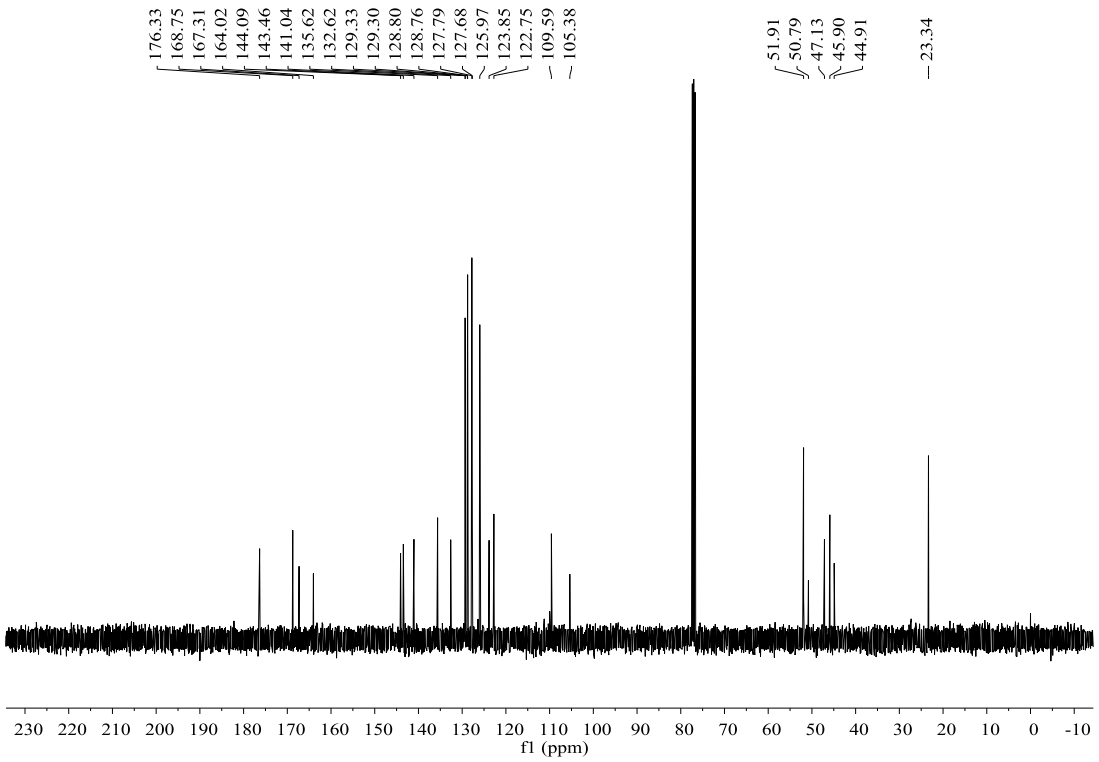


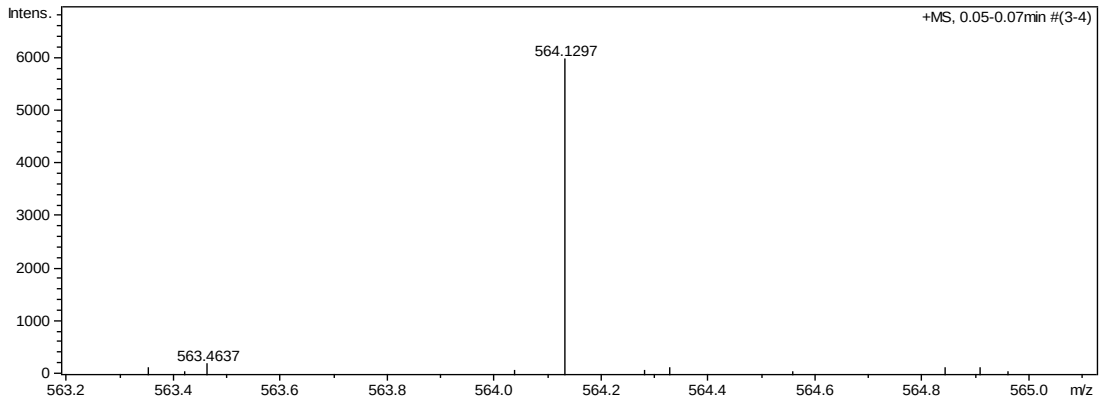


Methyl

***rel*-(3*S*,3'*R*)-1-benzyl-1'-(4-chlorophenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydros piro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3h')**:

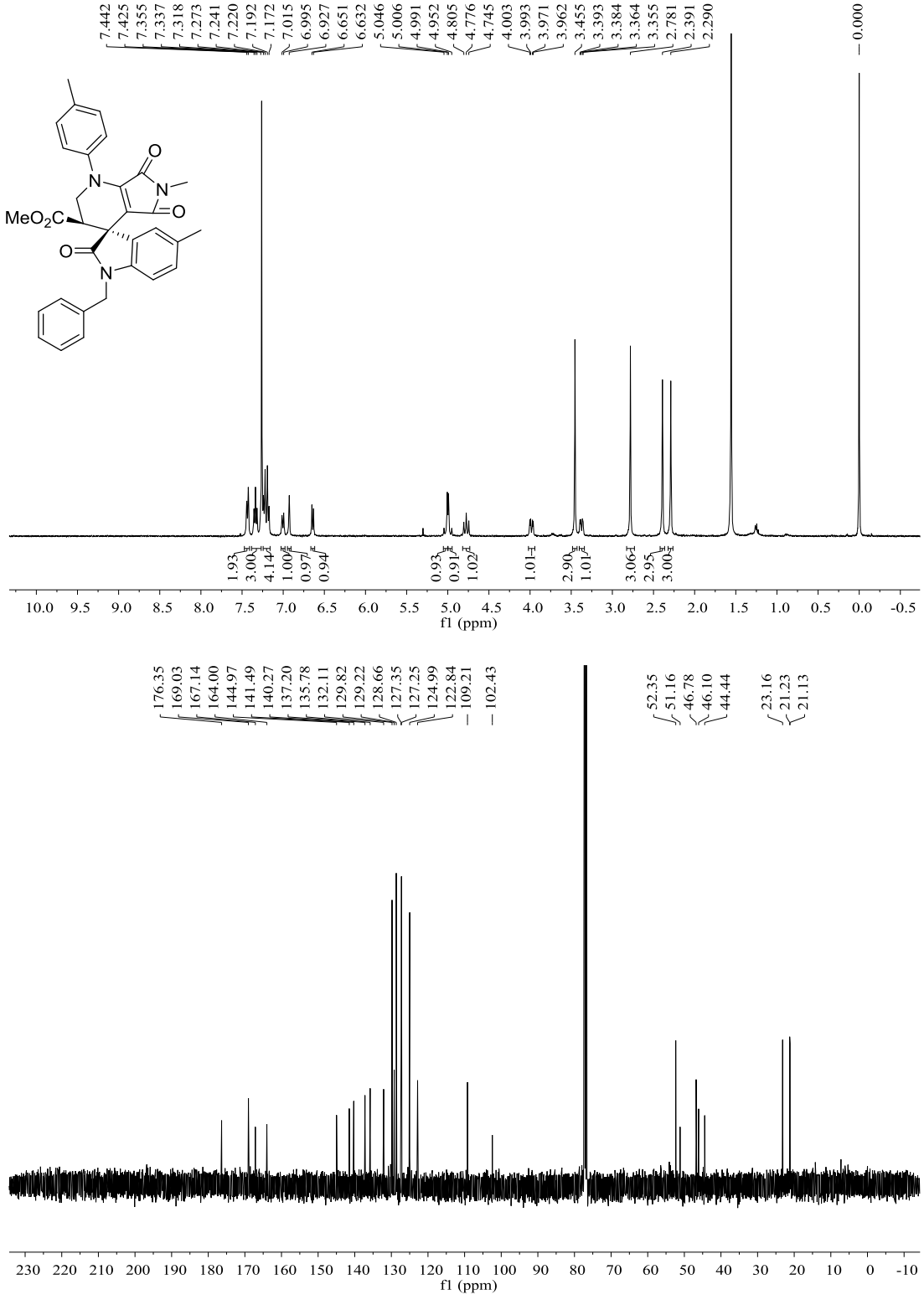


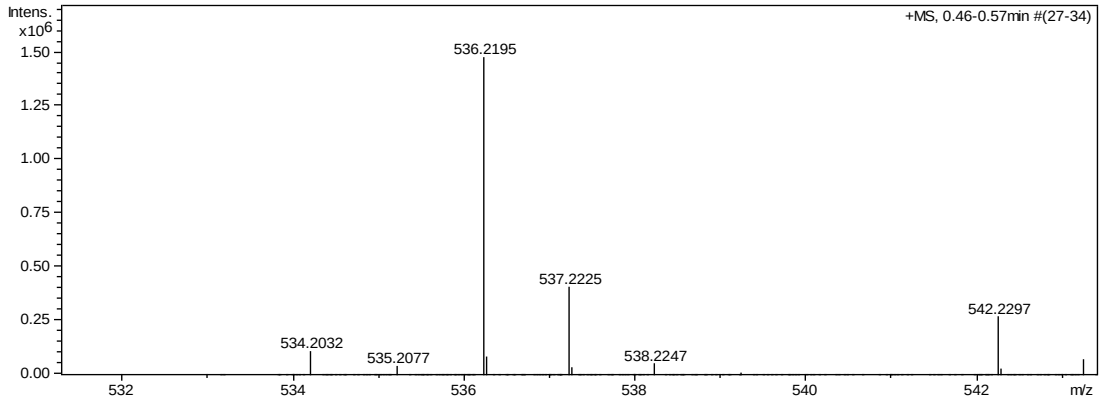

176.33
168.75
167.31
164.02
144.09
143.46
141.04
135.62
132.62
129.33
129.30
128.80
128.76
127.79
127.68
125.97
123.85
122.75
109.59
105.38
51.91
50.79
47.13
45.90
44.91
23.34
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 0.05-0.07min #(3-4)
564.1297
563.4637
6000
5000
4000
3000
2000
1000
0
563.2
563.4
563.6
563.8
564.0
564.2
564.4
564.6
564.8
565.0
m/z

Methyl

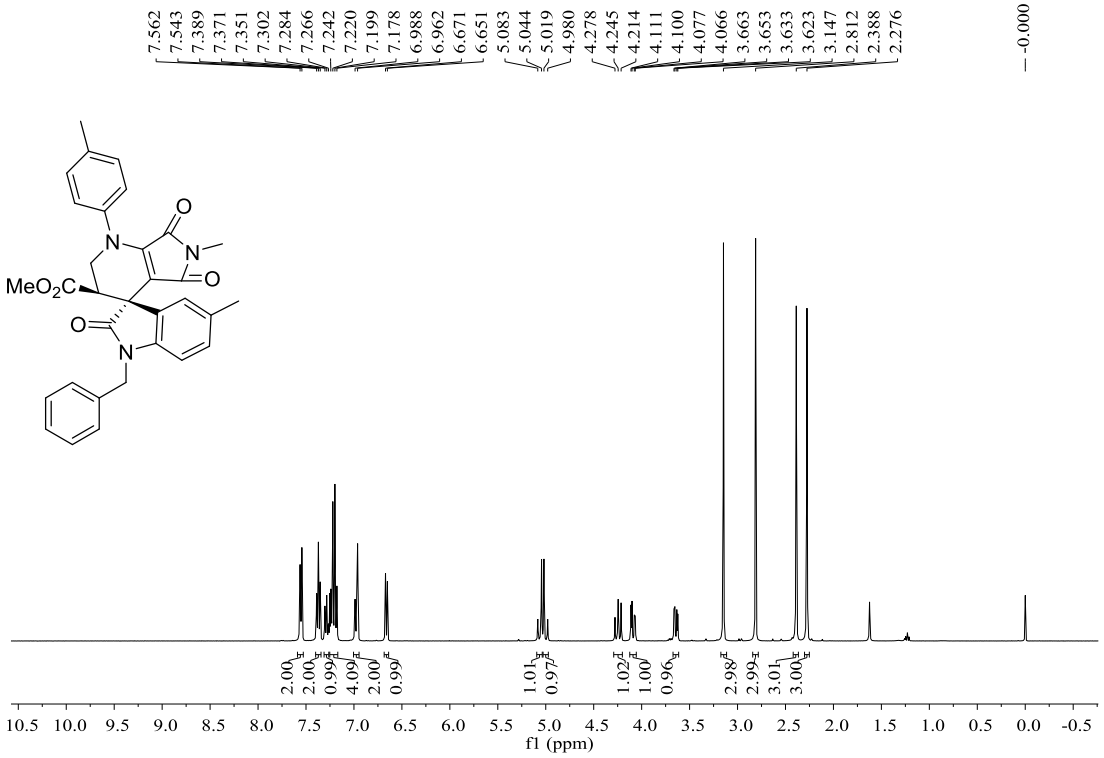
***rel*-(3*R*,3'*R*)-1-benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3i)**:

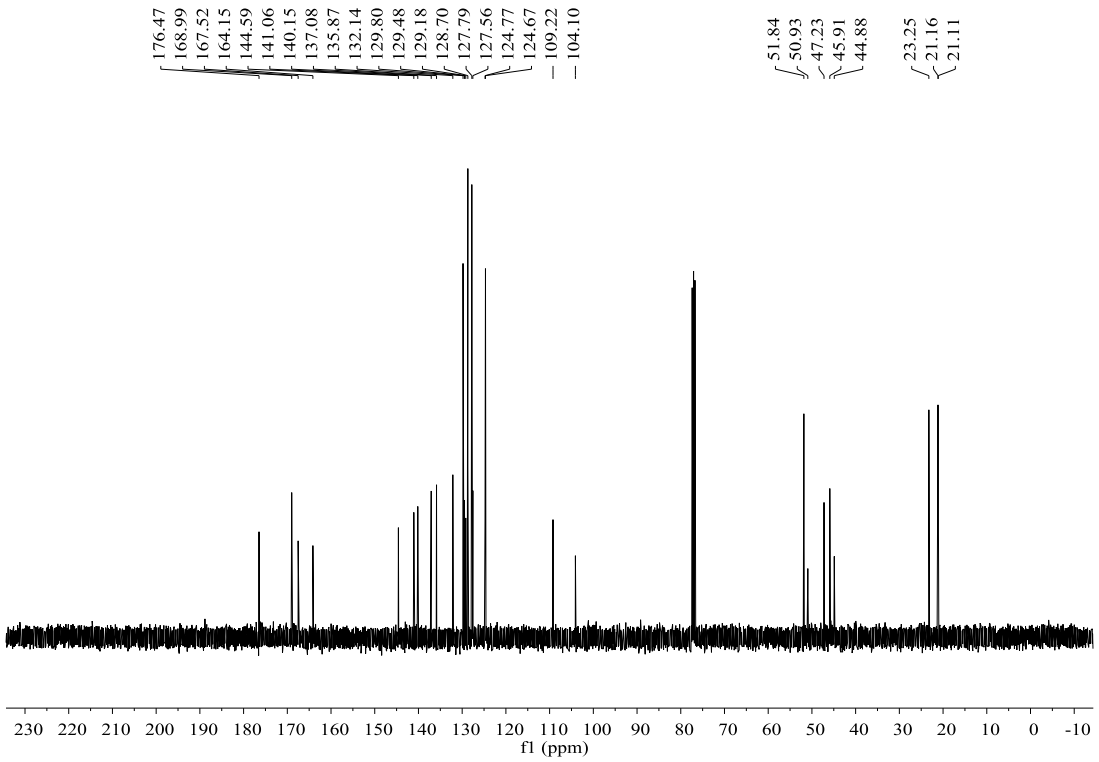


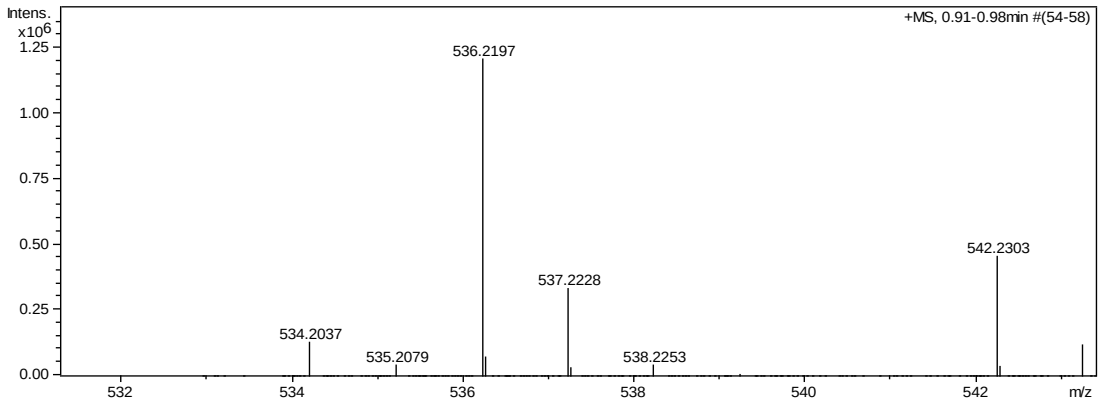


Methyl

***rel*-(3*S*,3'*R*)-1-benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3i'**):



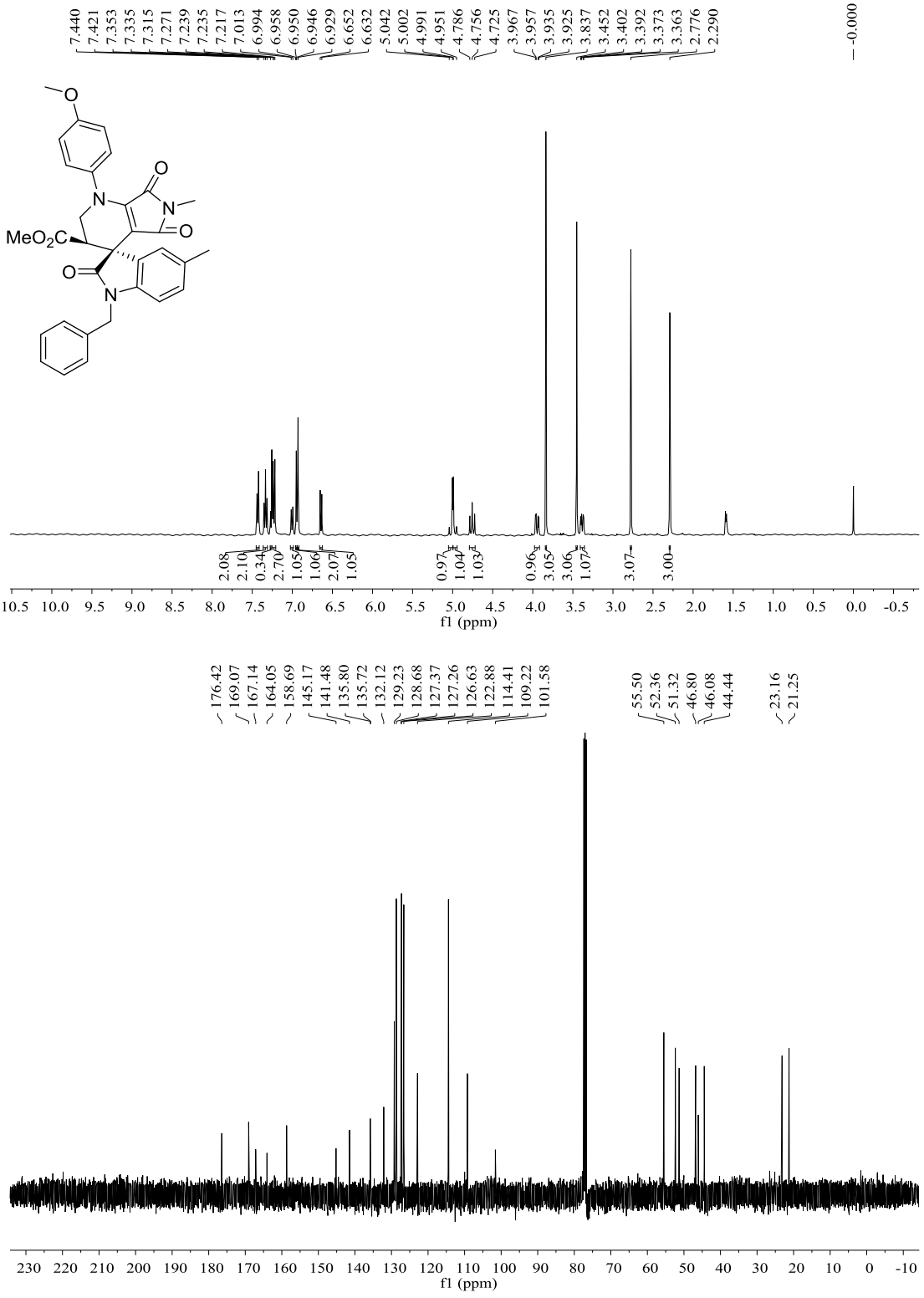

176.47
168.99
167.52
164.15
144.59
141.06
140.15
137.08
135.87
132.14
129.80
129.48
129.18
128.70
127.79
127.56
124.77
124.67
109.22
104.10
51.84
50.93
47.23
45.91
44.88
23.25
21.16
21.11
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

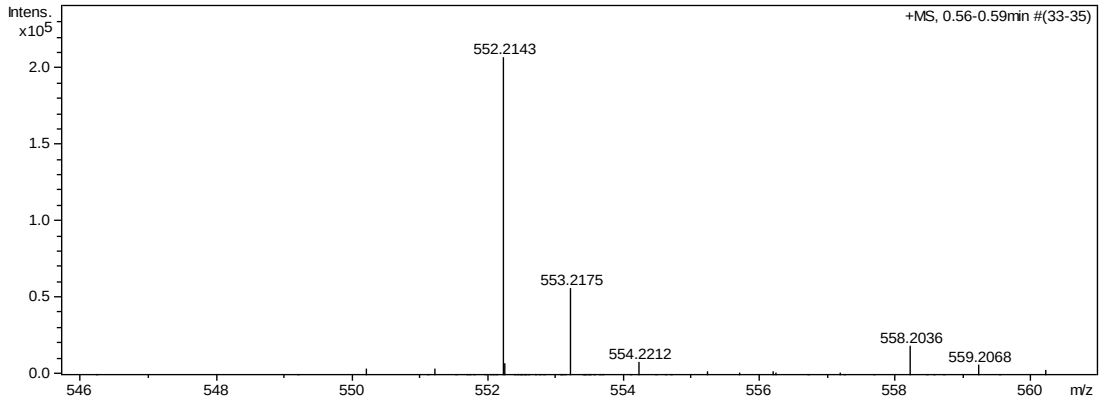

Intens.
x10^6
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 0.91-0.98min #(54-58)
536.2197
542.2303
537.2228
534.2037
535.2079
538.2253
532
534
536
538
540
542
m/z

Methyl

***rel*-(3*R*,3'*R*)-1-benzyl-1'-(4-methoxyphenyl)-5,6'-dimethyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexah**

ydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3j):

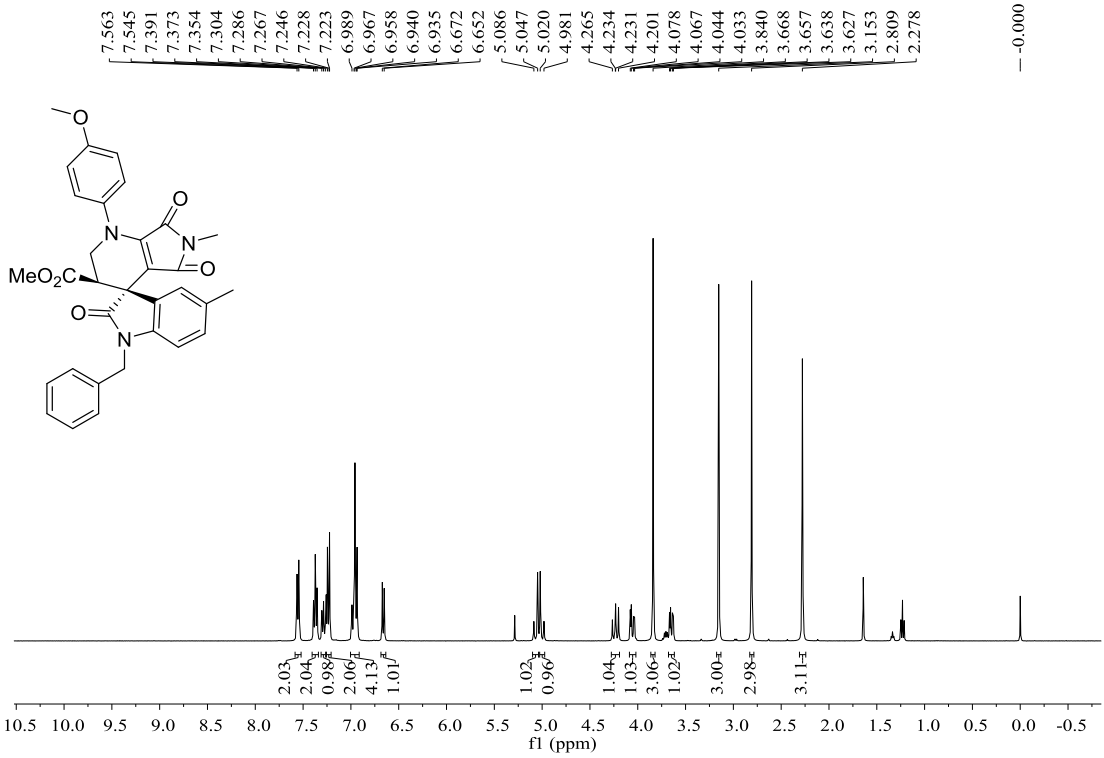


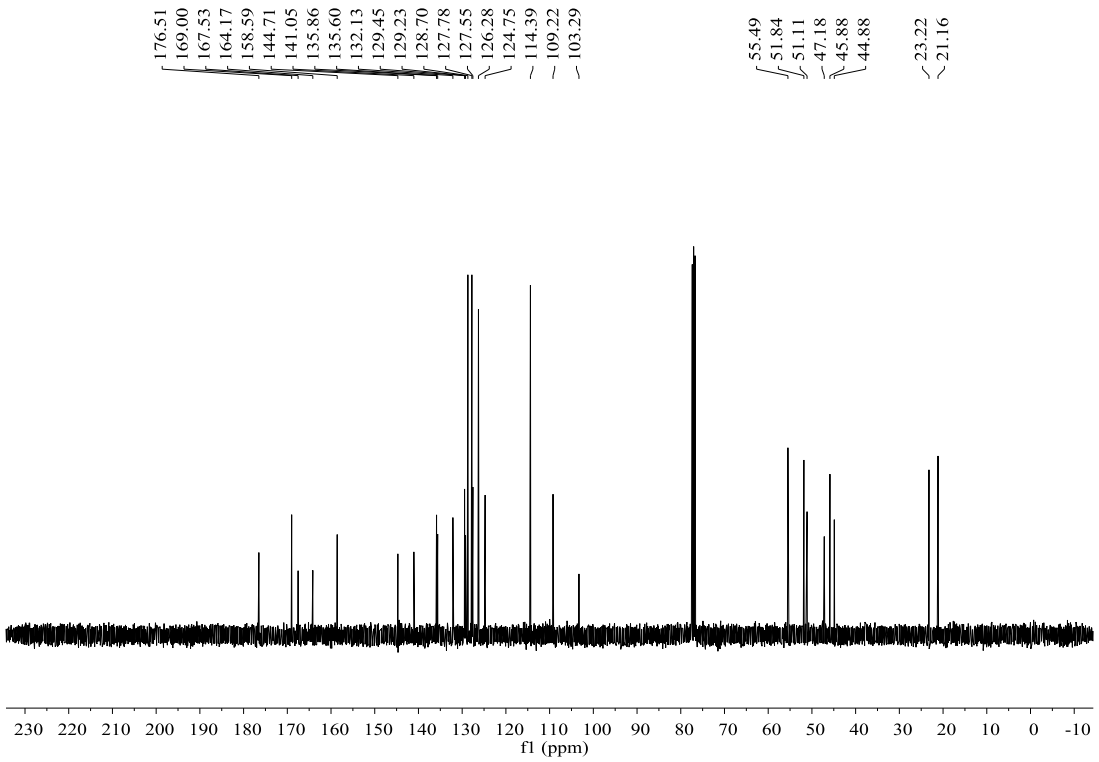


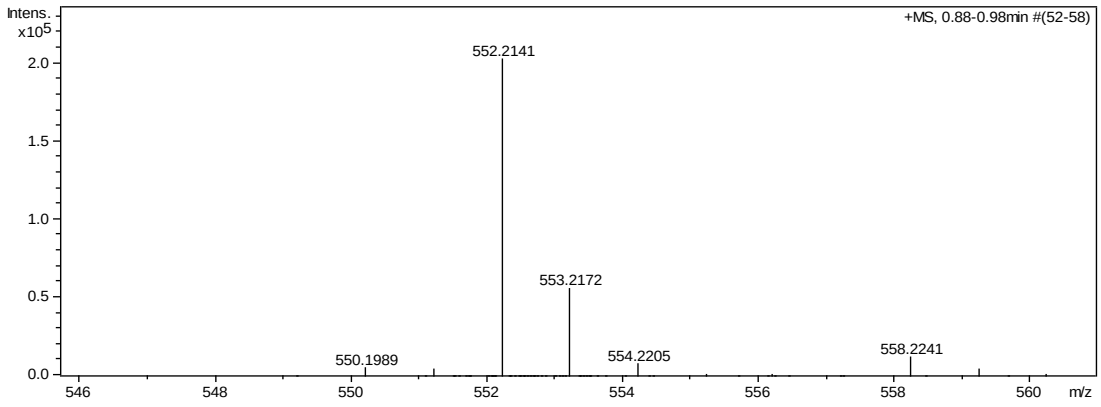
Methyl

***rel*-(3*S*,3'*R*)-1-benzyl-1'-(4-methoxyphenyl)-5,6'-dimethyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexah**

ydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3j'):

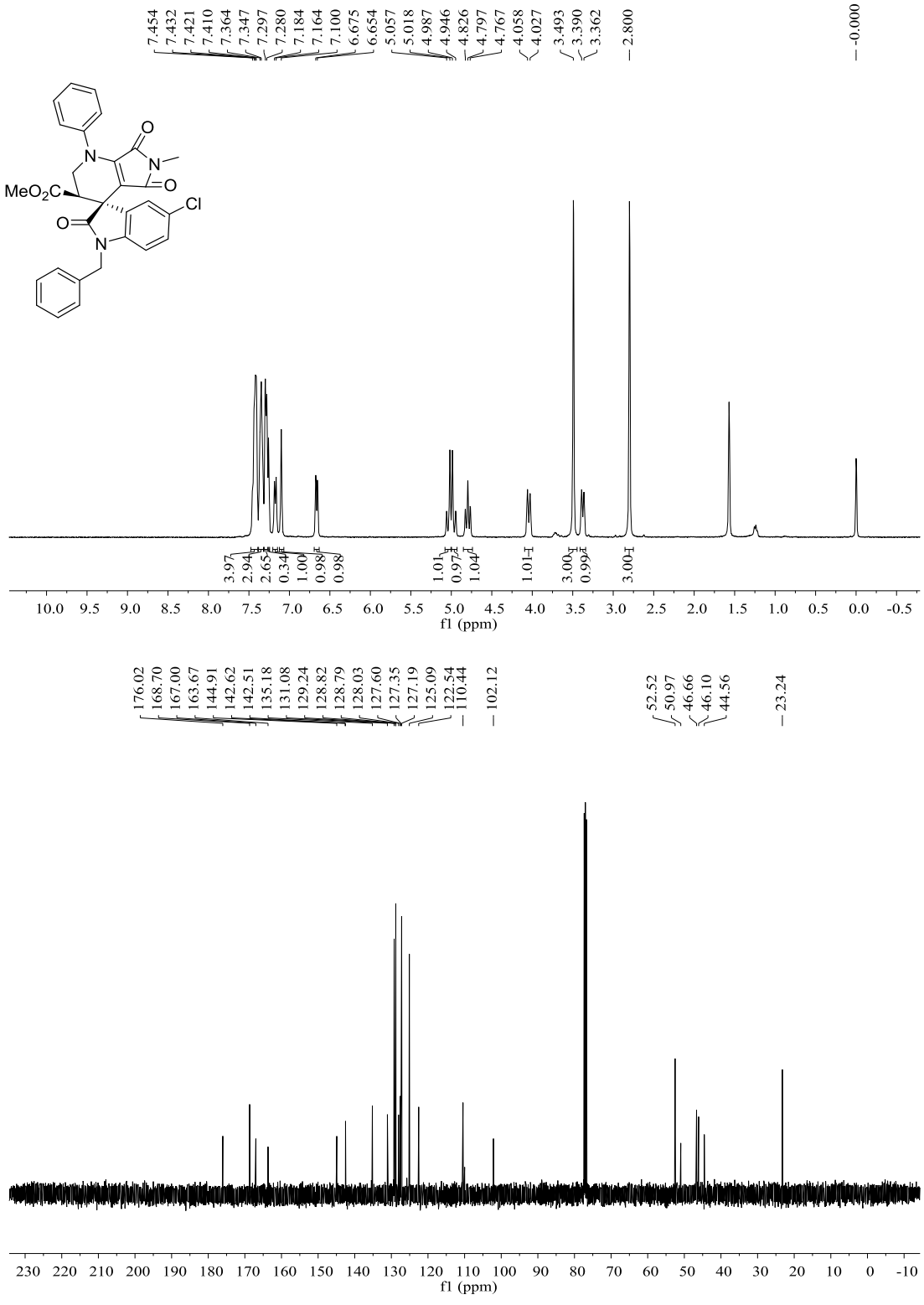


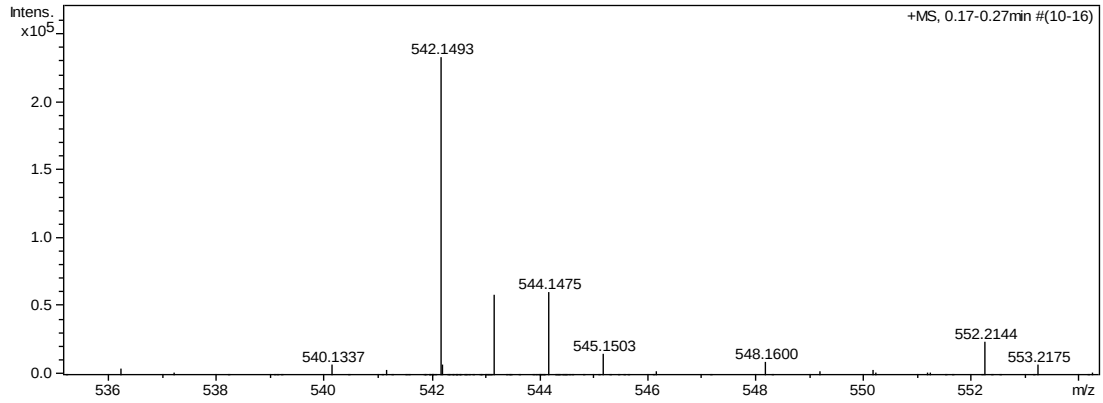

176.51
169.00
167.53
164.17
158.59
144.71
141.05
135.86
135.60
132.13
129.45
129.23
128.70
127.78
127.55
126.28
124.75
114.39
109.22
103.29
55.49
51.84
51.11
47.18
45.88
44.88
23.22
21.16
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.88-0.98min #(52-58)
552.2141
553.2172
550.1989
554.2205
558.2241
2.0
1.5
1.0
0.5
0.0
546
548
550
552
554
556
558
560
m/z

Methyl

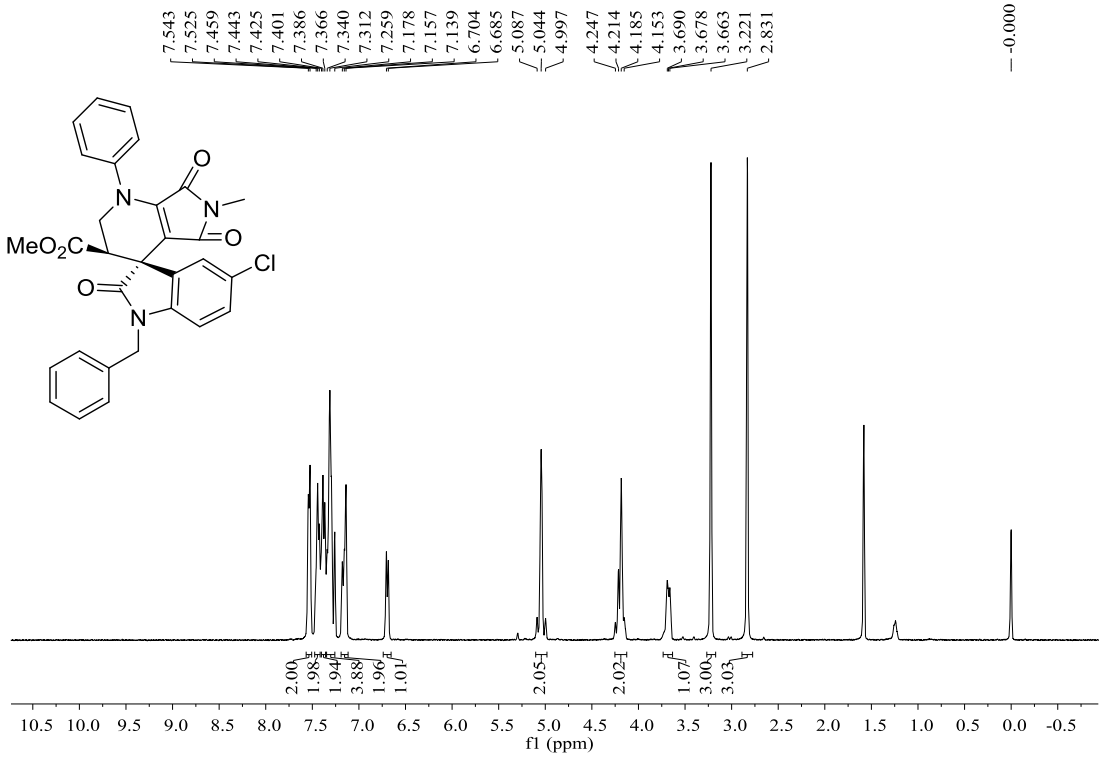
***rel*-(3*R*,3'*R*)-1-benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3k)**:

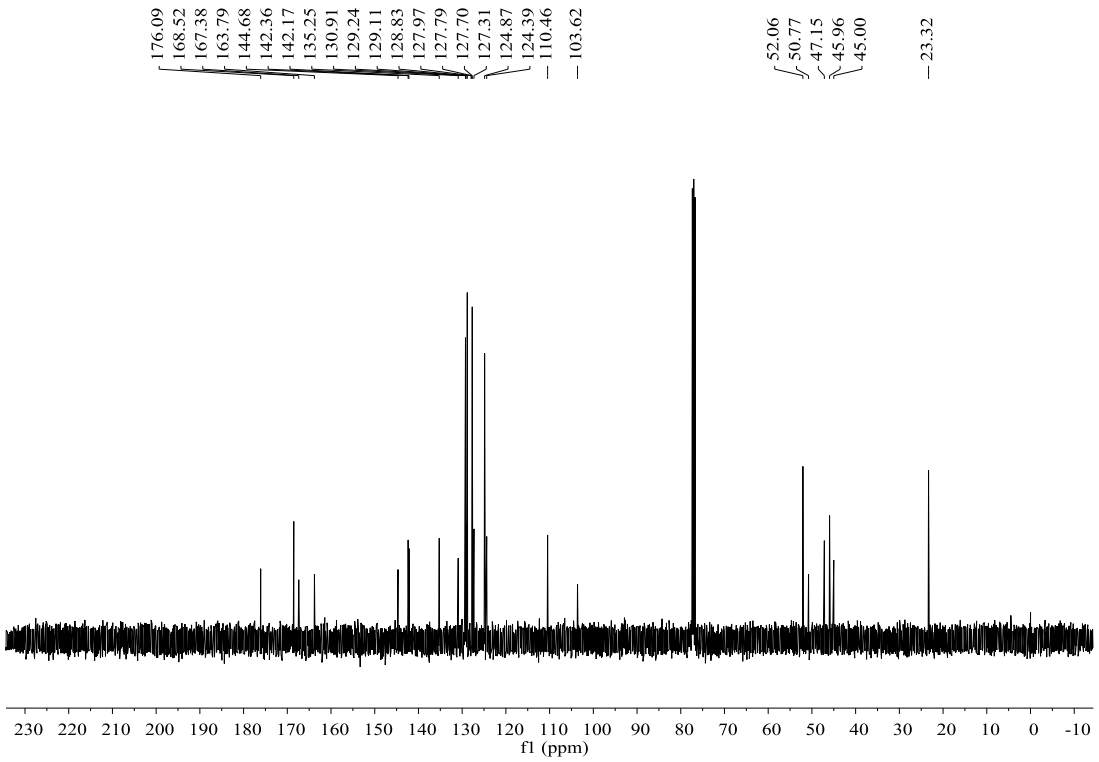


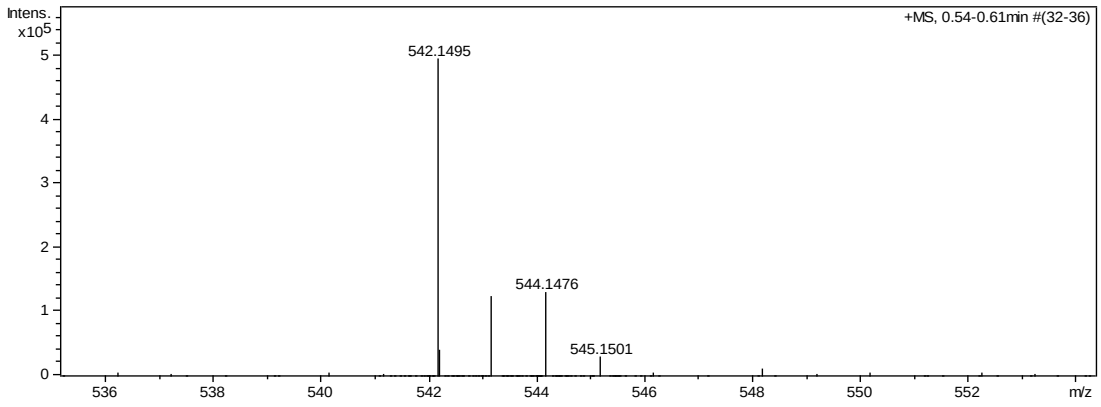


Methyl

***rel*-(3*S*,3'*R*)-1-benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3k')**:

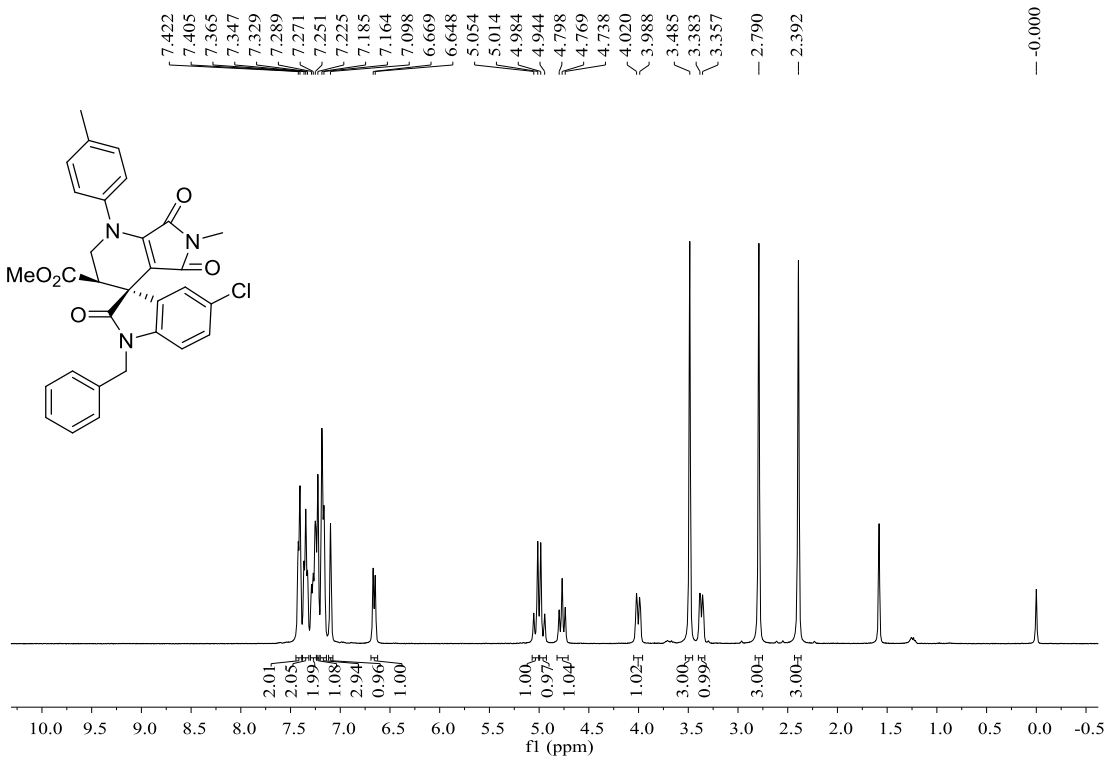


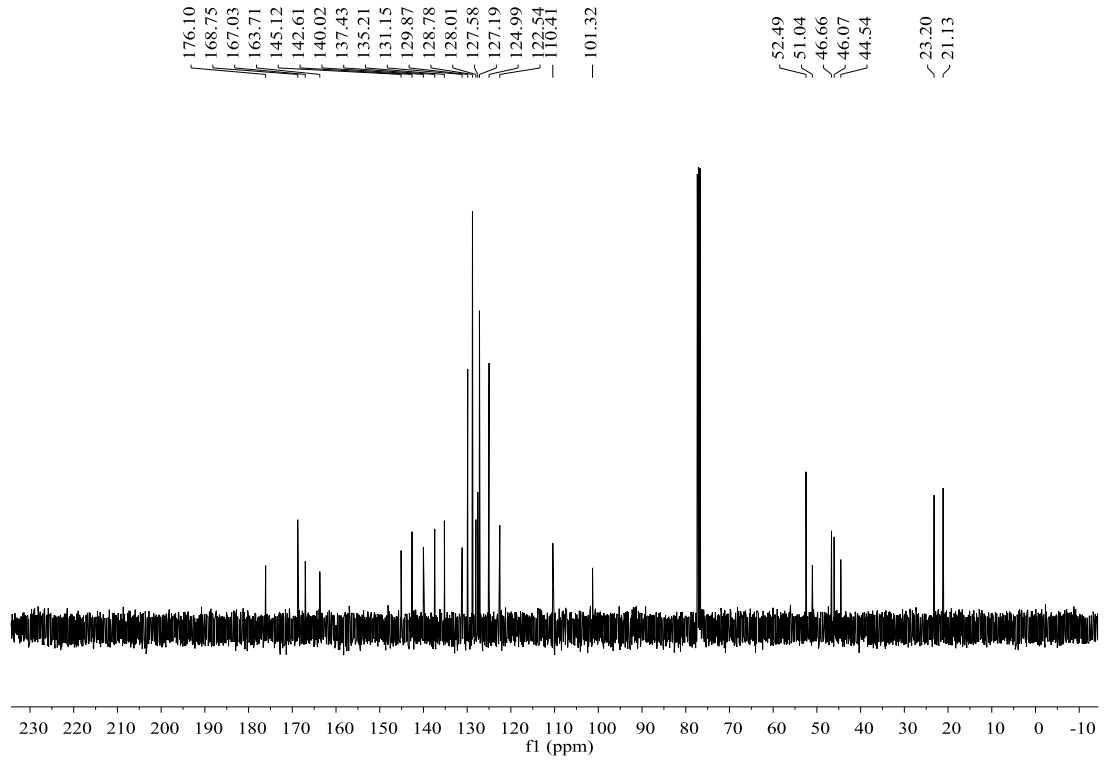

176.09
168.52
167.38
163.79
144.68
142.36
142.17
135.25
130.91
129.24
129.11
128.83
127.97
127.79
127.70
127.31
124.87
124.39
110.46
103.62
52.06
50.77
47.15
45.96
45.00
23.32
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

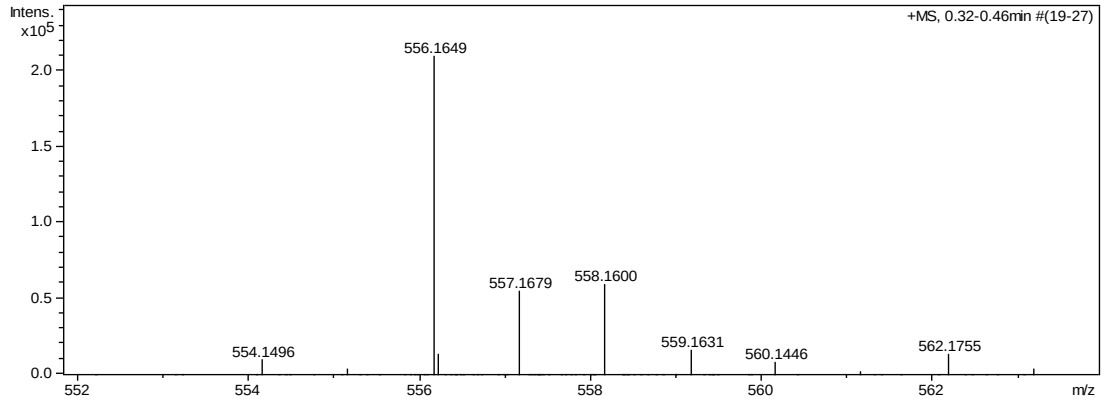

Intens.
x10^5
+MS, 0.54-0.61min #(32-36)
542.1495
544.1476
545.1501
0
1
2
3
4
5
536
538
540
542
544
546
548
550
552
m/z

Methyl

***rel*-(3*R*,3'*R*)-1-benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydros piro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate (3l)**:

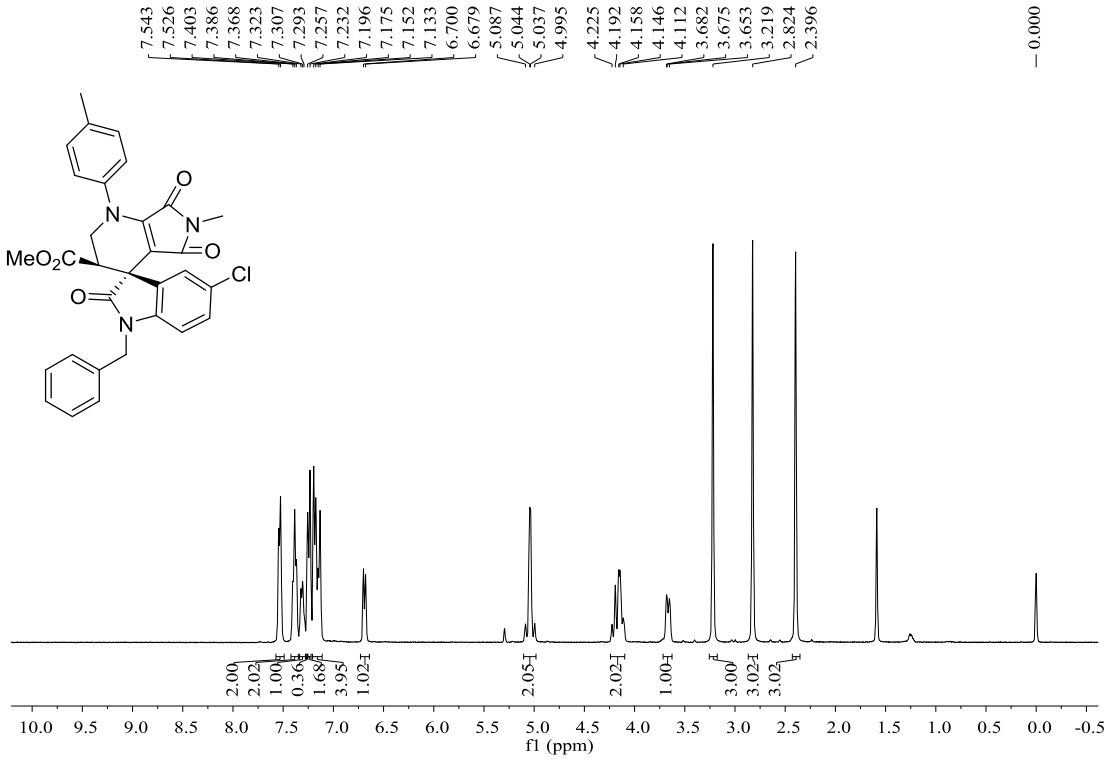


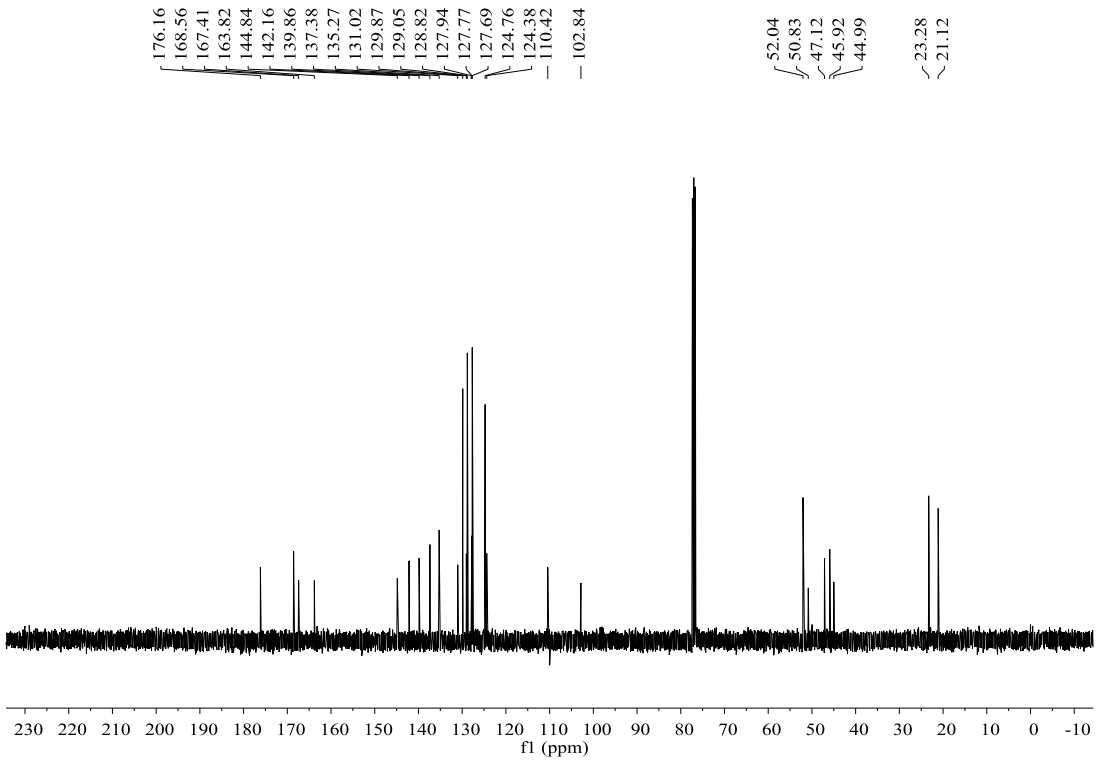


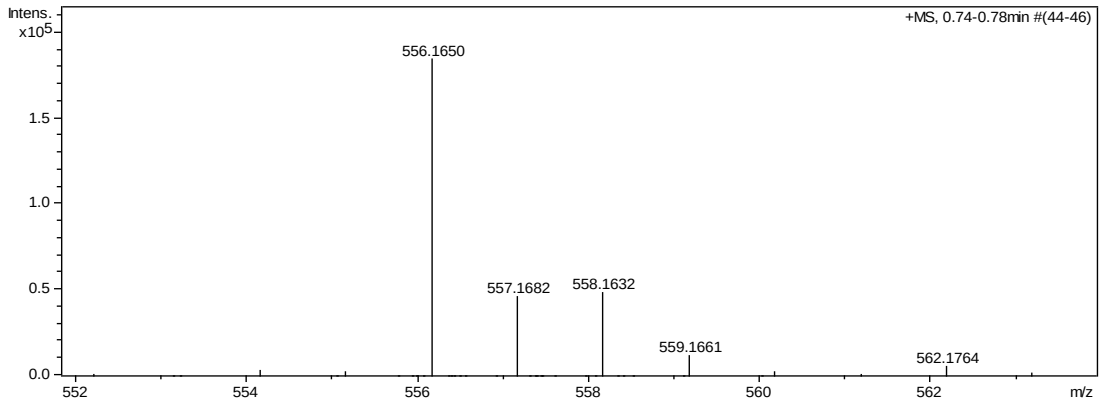


Methyl

***rel*-(3*S*,3'*R*)-1-benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydros piro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3l'**):

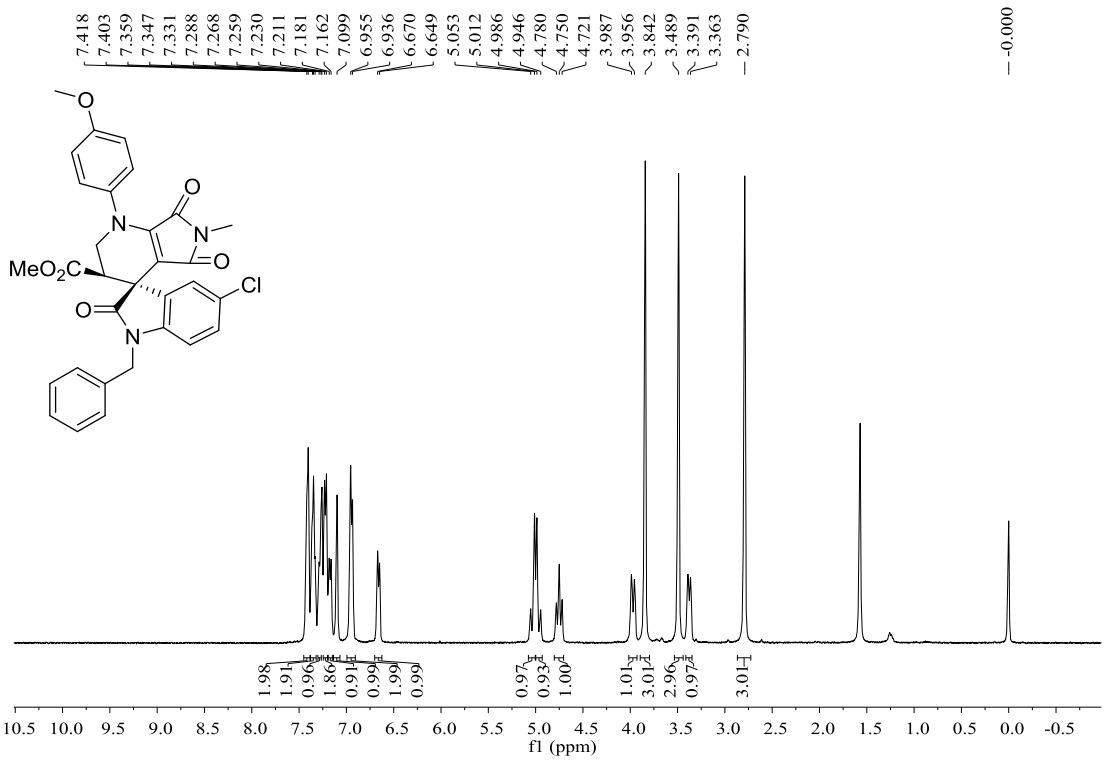


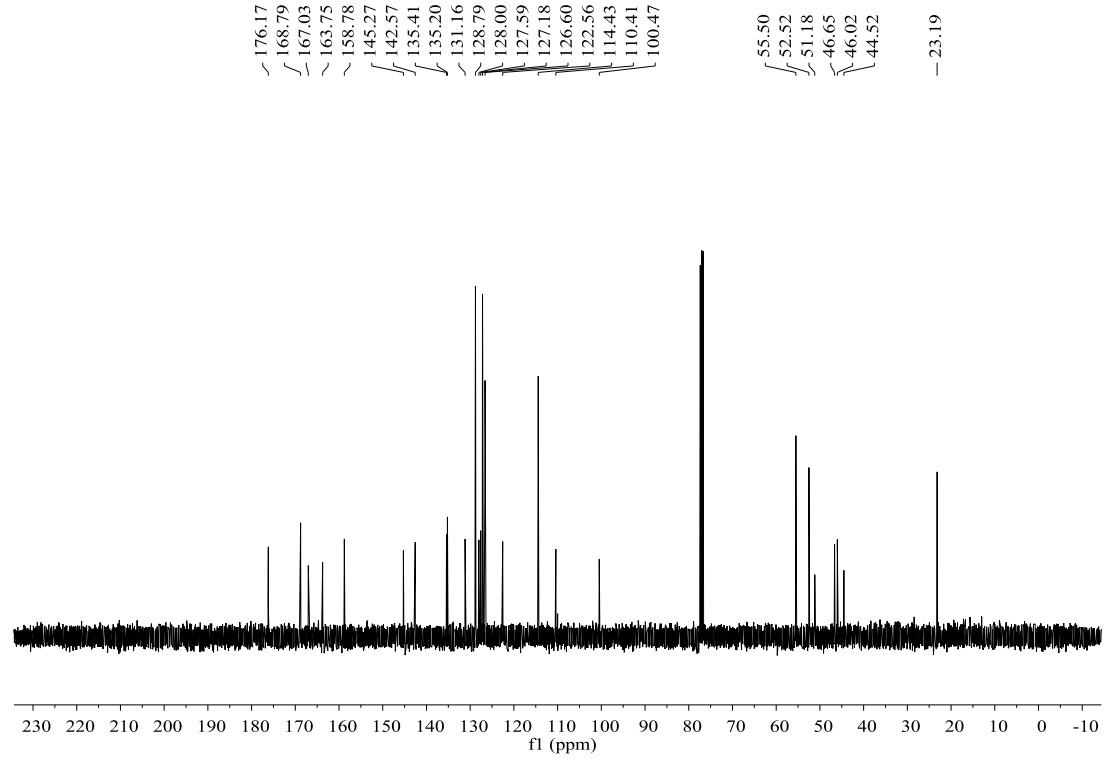

176.16
168.56
167.41
163.82
144.84
142.16
139.86
137.38
135.27
131.02
129.87
129.05
128.82
127.94
127.77
127.69
124.76
124.38
110.42
102.84
52.04
50.83
47.12
45.92
44.99
23.28
21.12
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

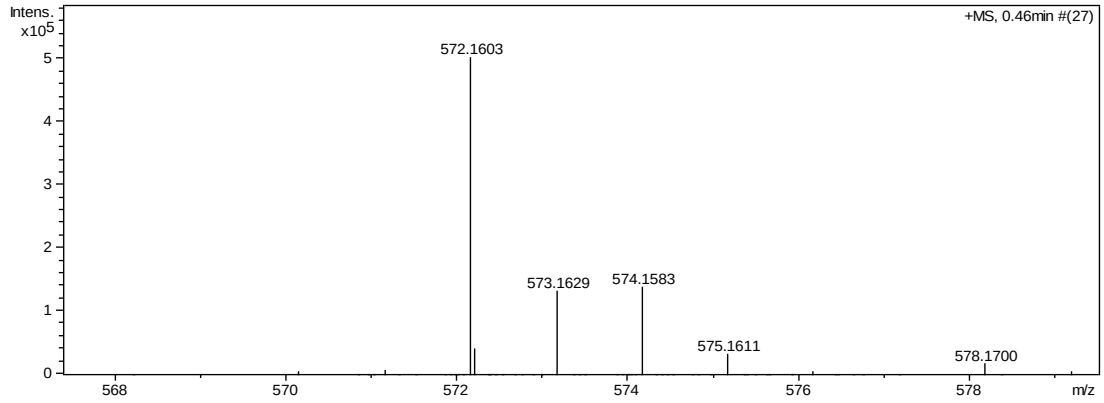

Intens.
x10^5
+MS, 0.74-0.78min #(44-46)
556.1650
557.1682
558.1632
559.1661
562.1764
0.0
0.5
1.0
1.5
552
554
556
558
560
562
m/z

Methyl

***rel*-(3*R*,3'*R*)-1-benzyl-5-chloro-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3m**):

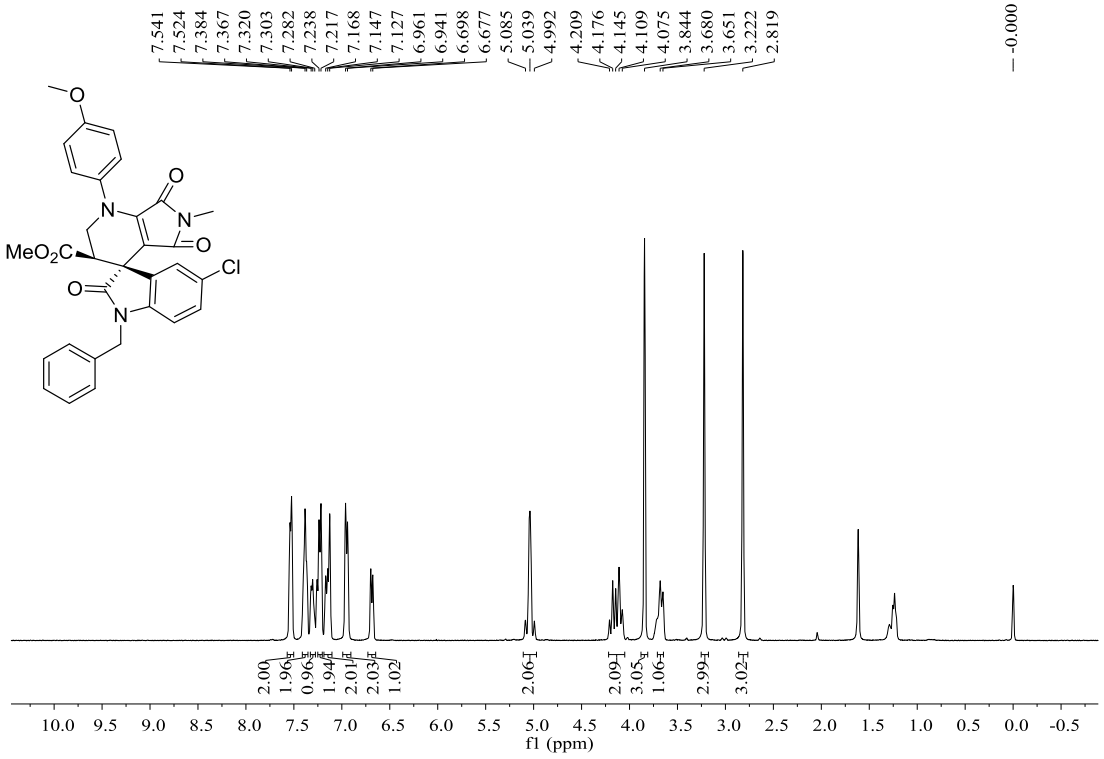


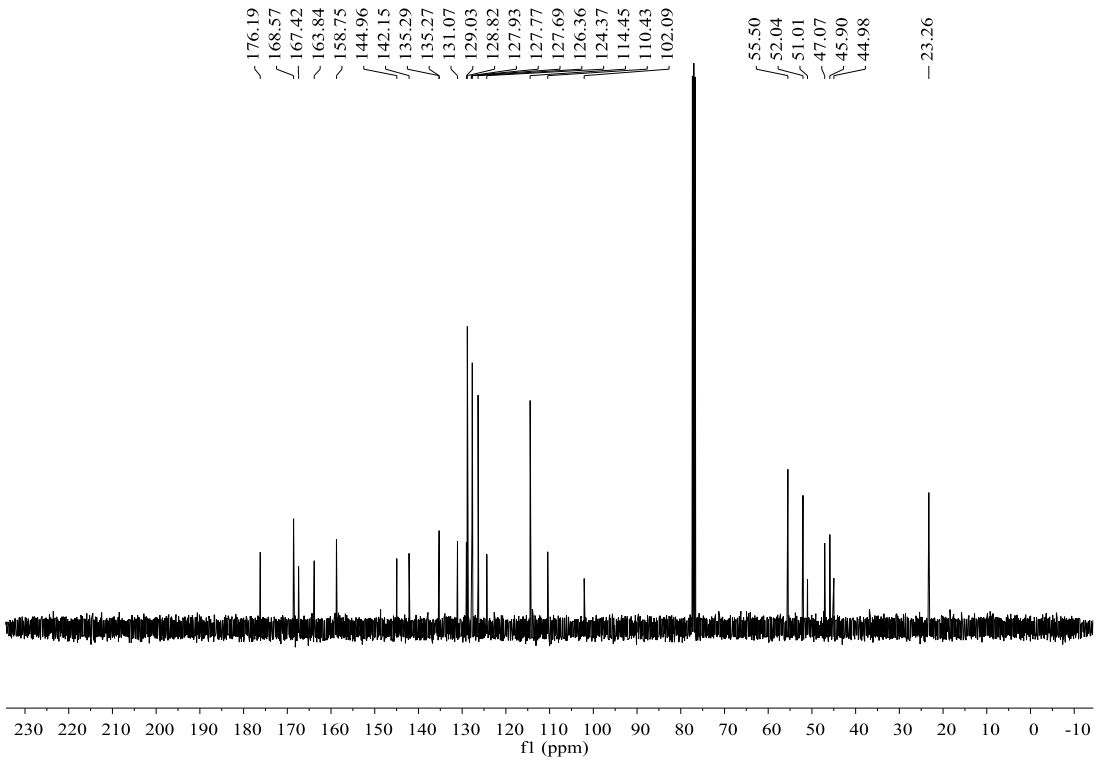


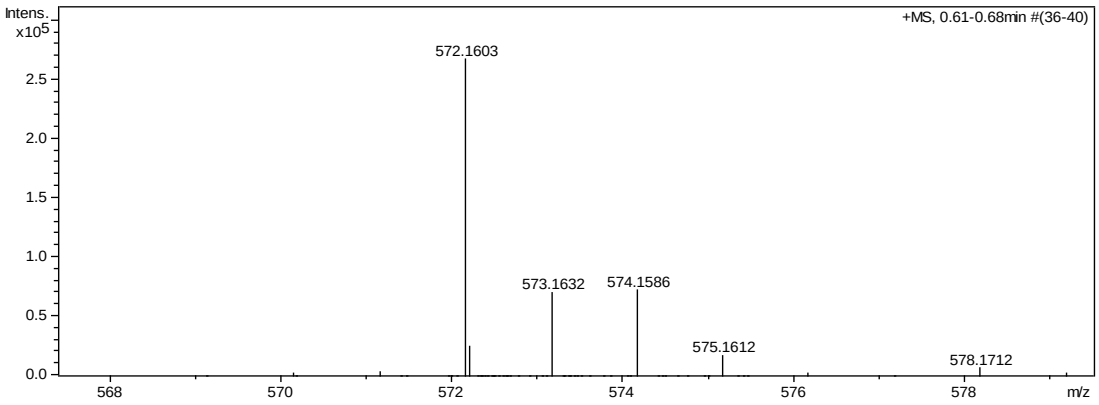


Methyl

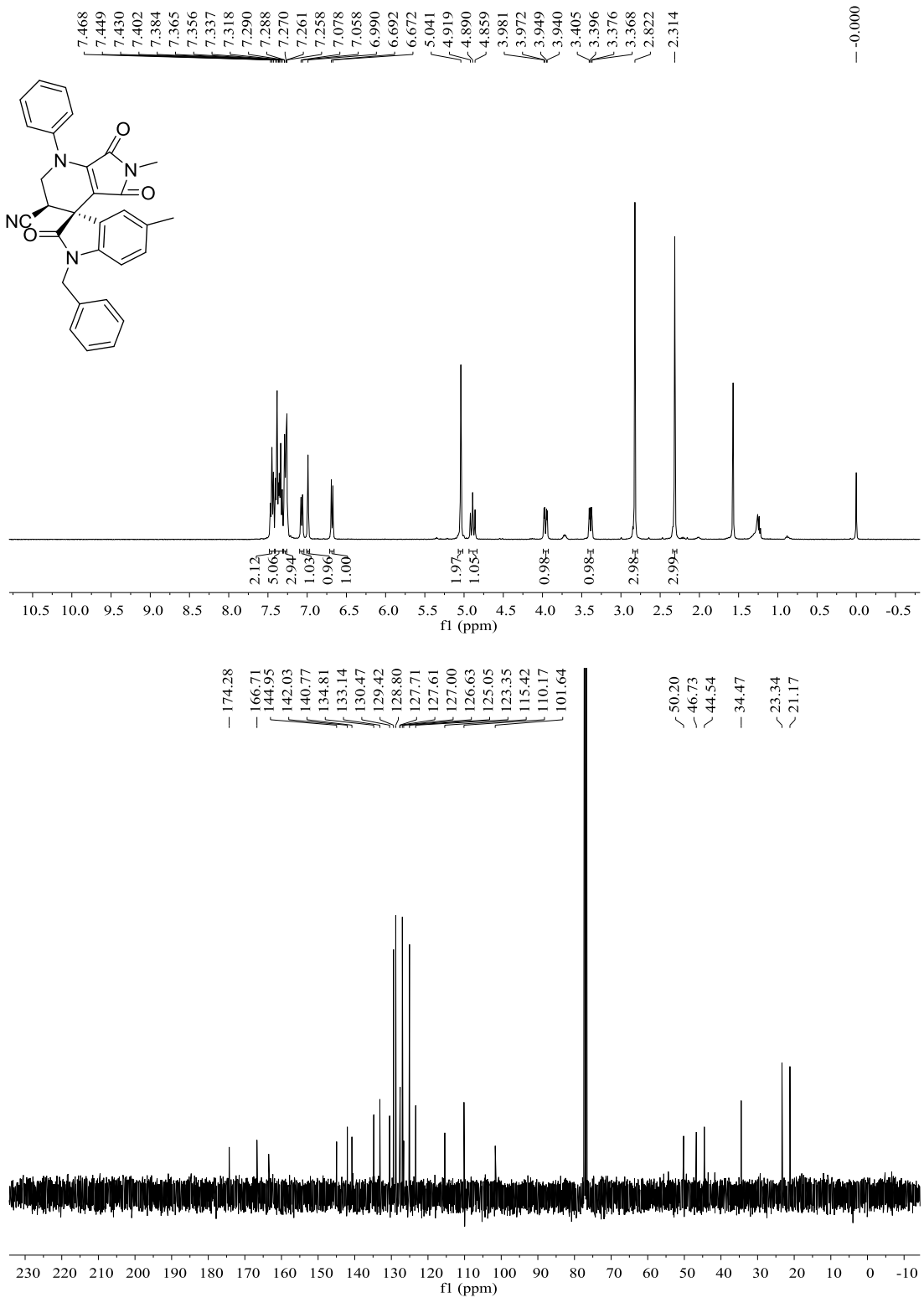
***rel*-(3*S*,3'*R*)-1-benzyl-5-chloro-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-hexahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carboxylate** (**3m'**):

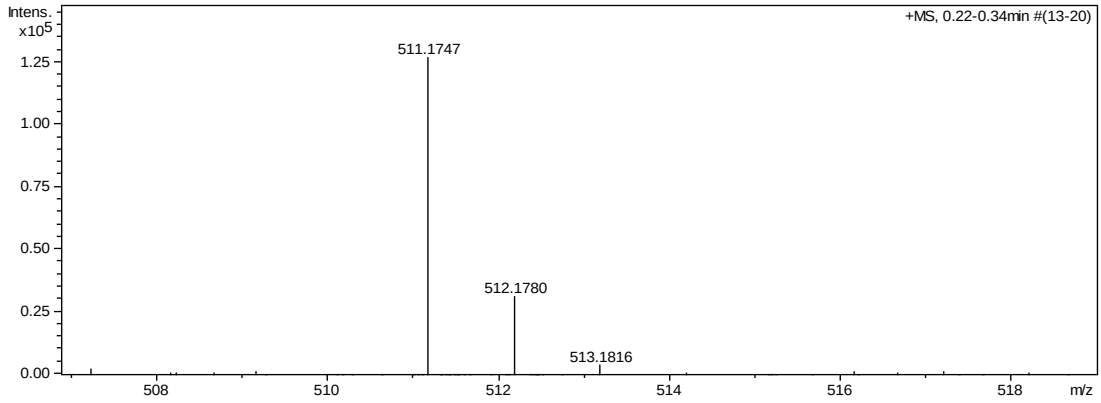



176.19
168.57
167.42
163.84
158.75
144.96
142.15
135.29
135.27
131.07
129.03
128.82
127.93
127.77
127.69
126.36
124.37
114.45
110.43
102.09
55.50
52.04
51.01
47.07
45.90
44.98
23.26
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

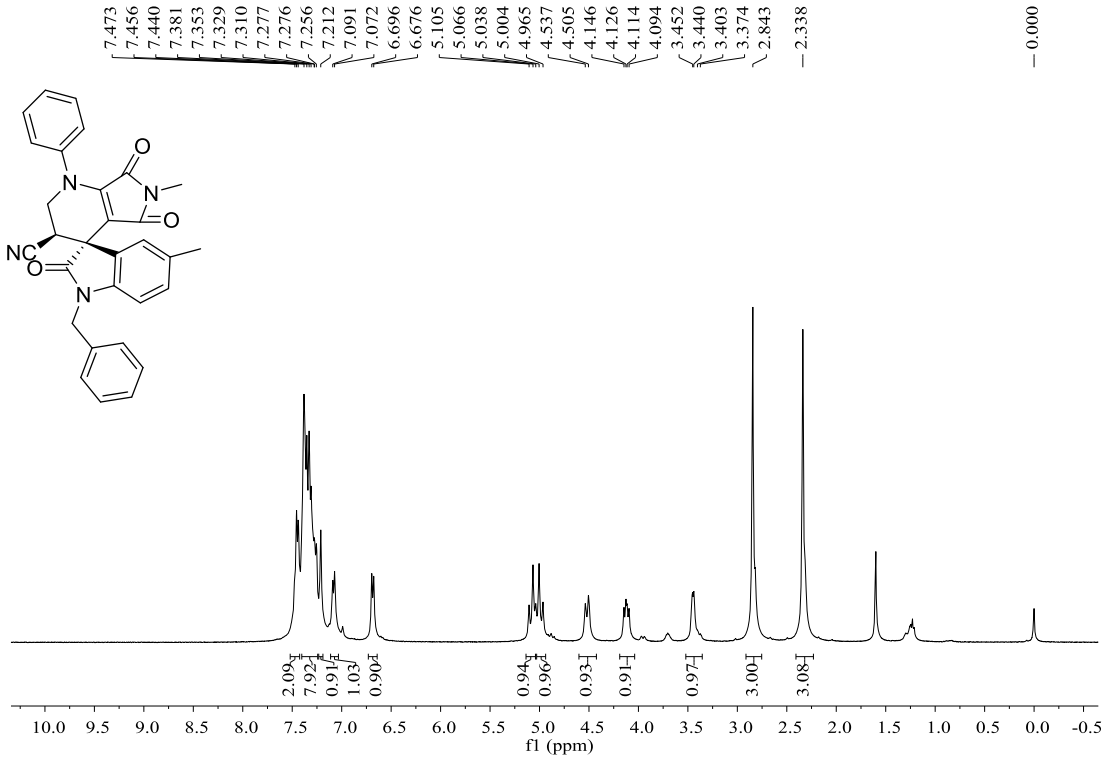

Intens.
x10^5
+MS, 0.61-0.68min #(36-40)
572.1603
573.1632
574.1586
575.1612
578.1712
2.5
2.0
1.5
1.0
0.5
0.0
568
570
572
574
576
578
m/z

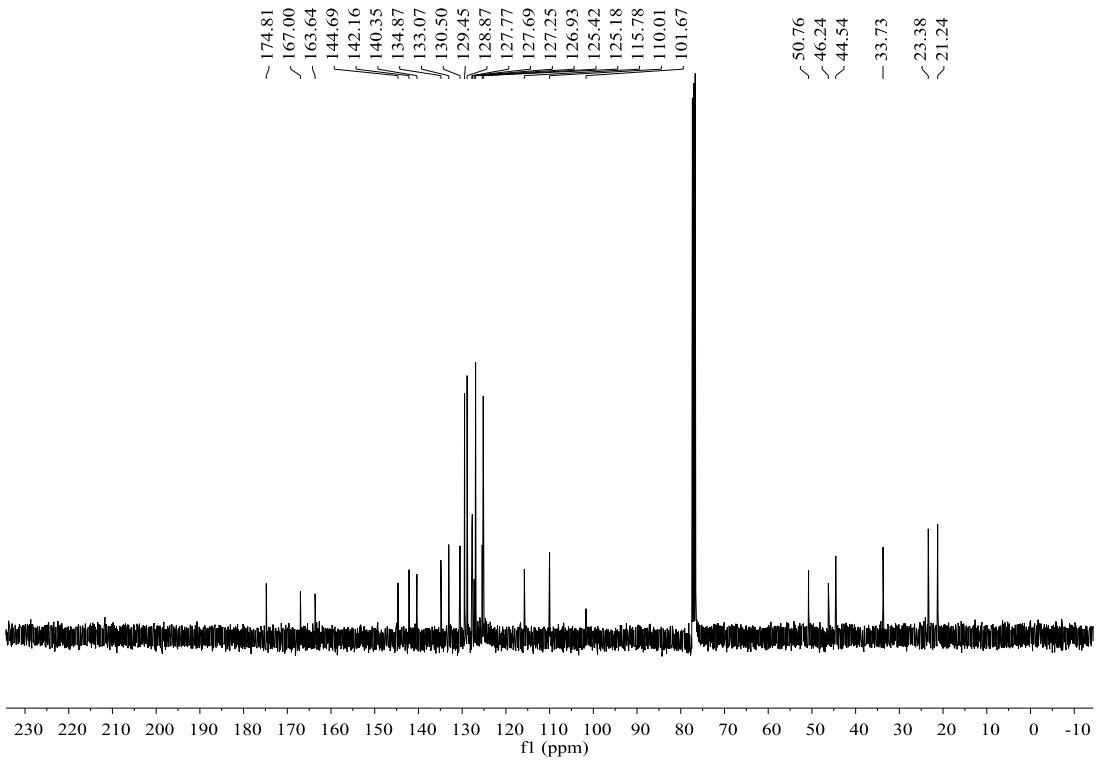
***rel*-(3*R*,3'*R*)-1-benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro [indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4a**):

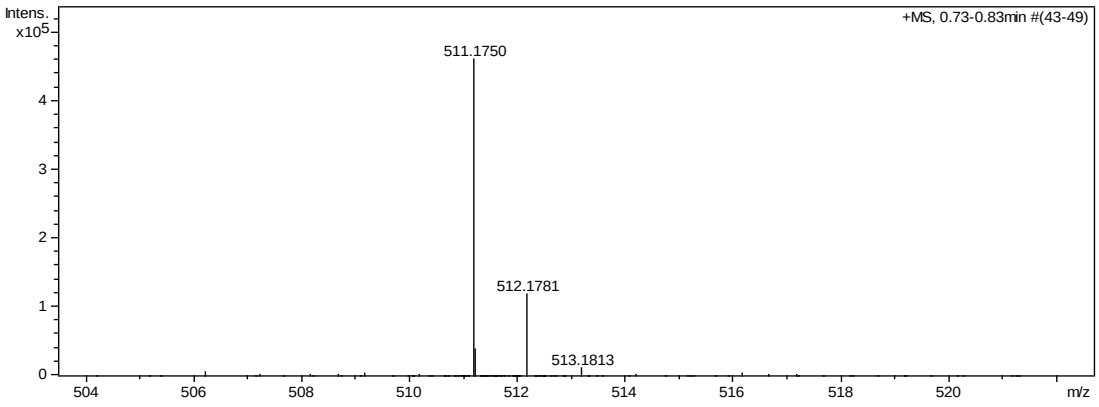




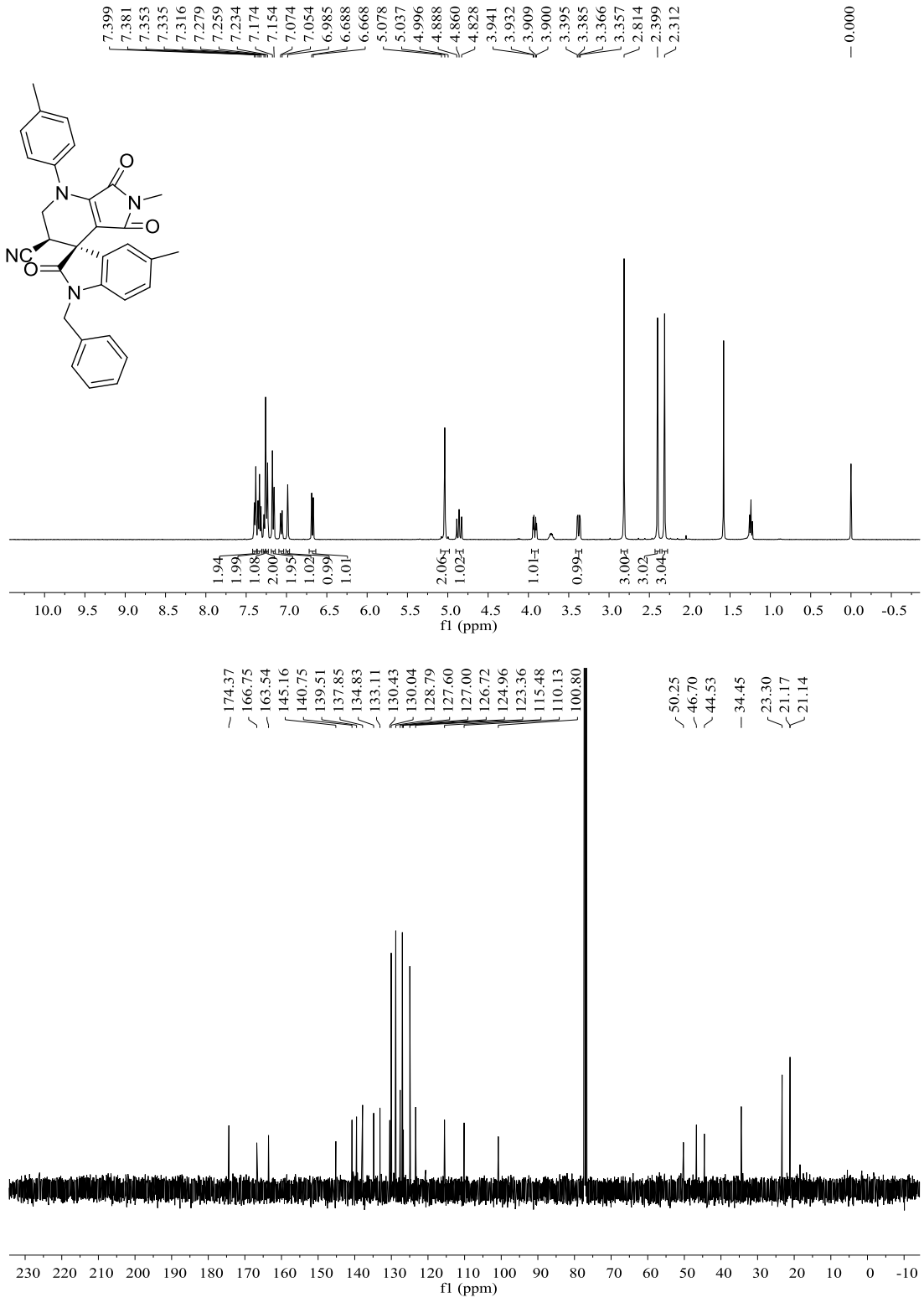
***rel*-(3*S*,3'*R*)-1-benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro [indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile (4a')**:

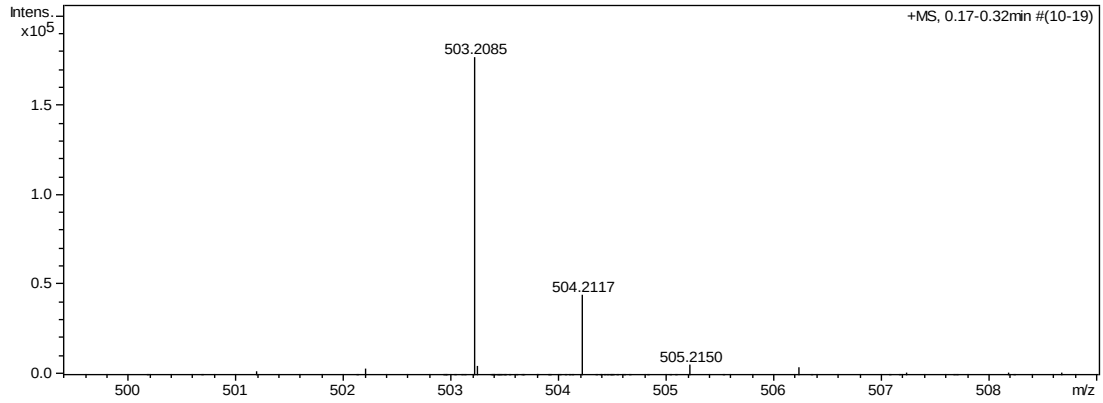



174.81
167.00
163.64
144.69
142.16
140.35
134.87
133.07
130.50
129.45
128.87
127.77
127.69
127.25
126.93
125.42
125.18
115.78
110.01
101.67
50.76
46.24
44.54
33.73
23.38
21.24
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

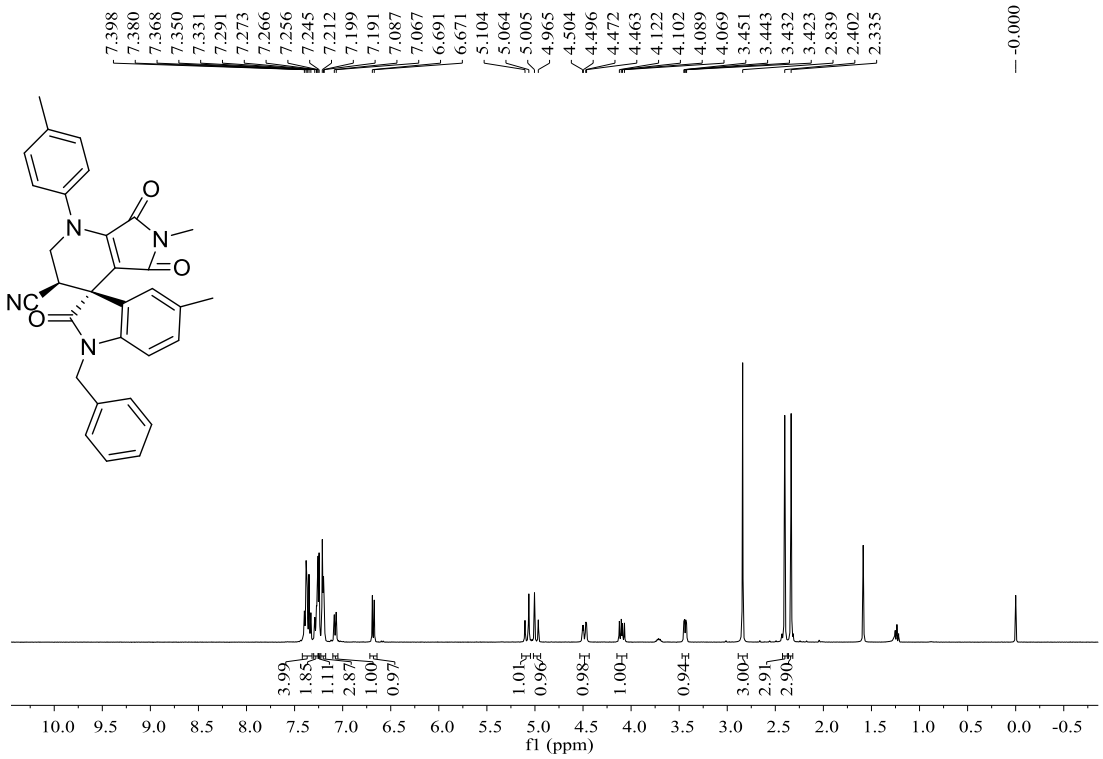

Intens.
x10^5
+MS, 0.73-0.83min #(43-49)
511.1750
512.1781
513.1813
0
1
2
3
4
504 506 508 510 512 514 516 518 520
m/z

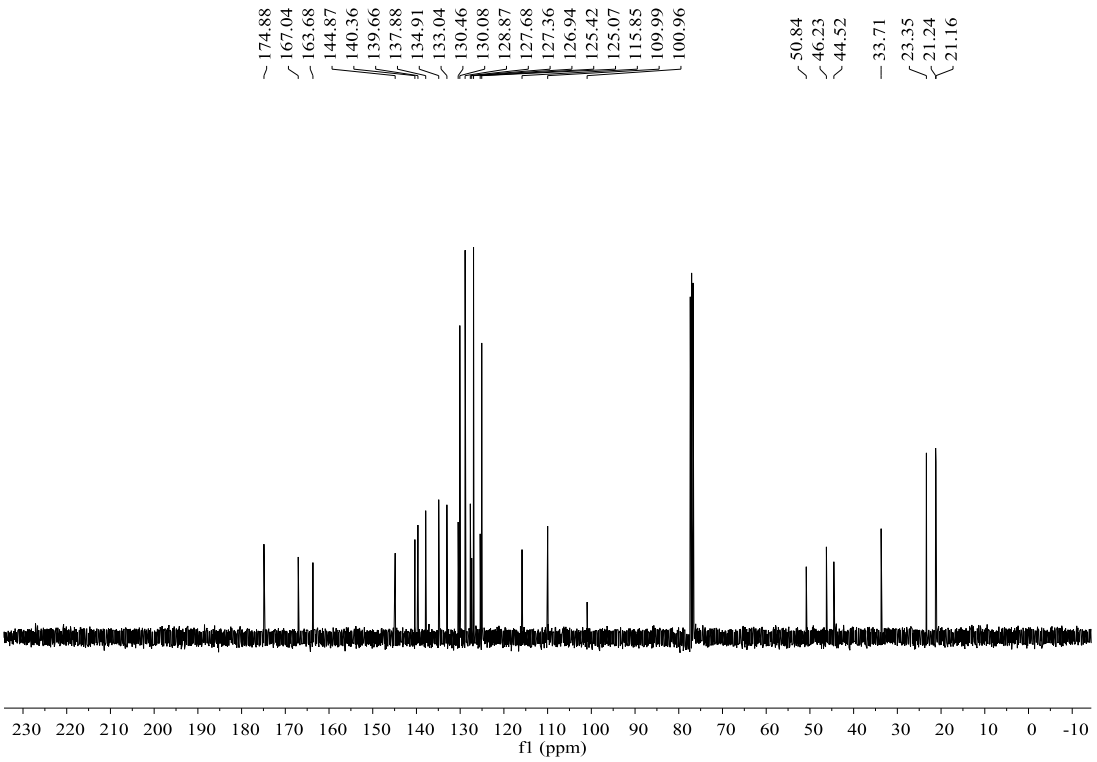
***rel*-(3*R*,3'*R*)-1-benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro [indoline -3,4'-pyrrolo[3,4-b]pyridine]-3'-carbonitrile (4b)**:

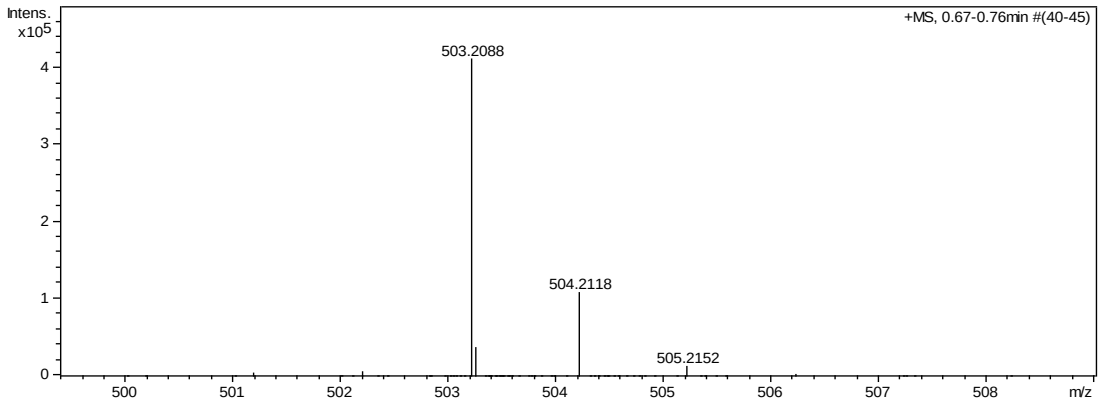




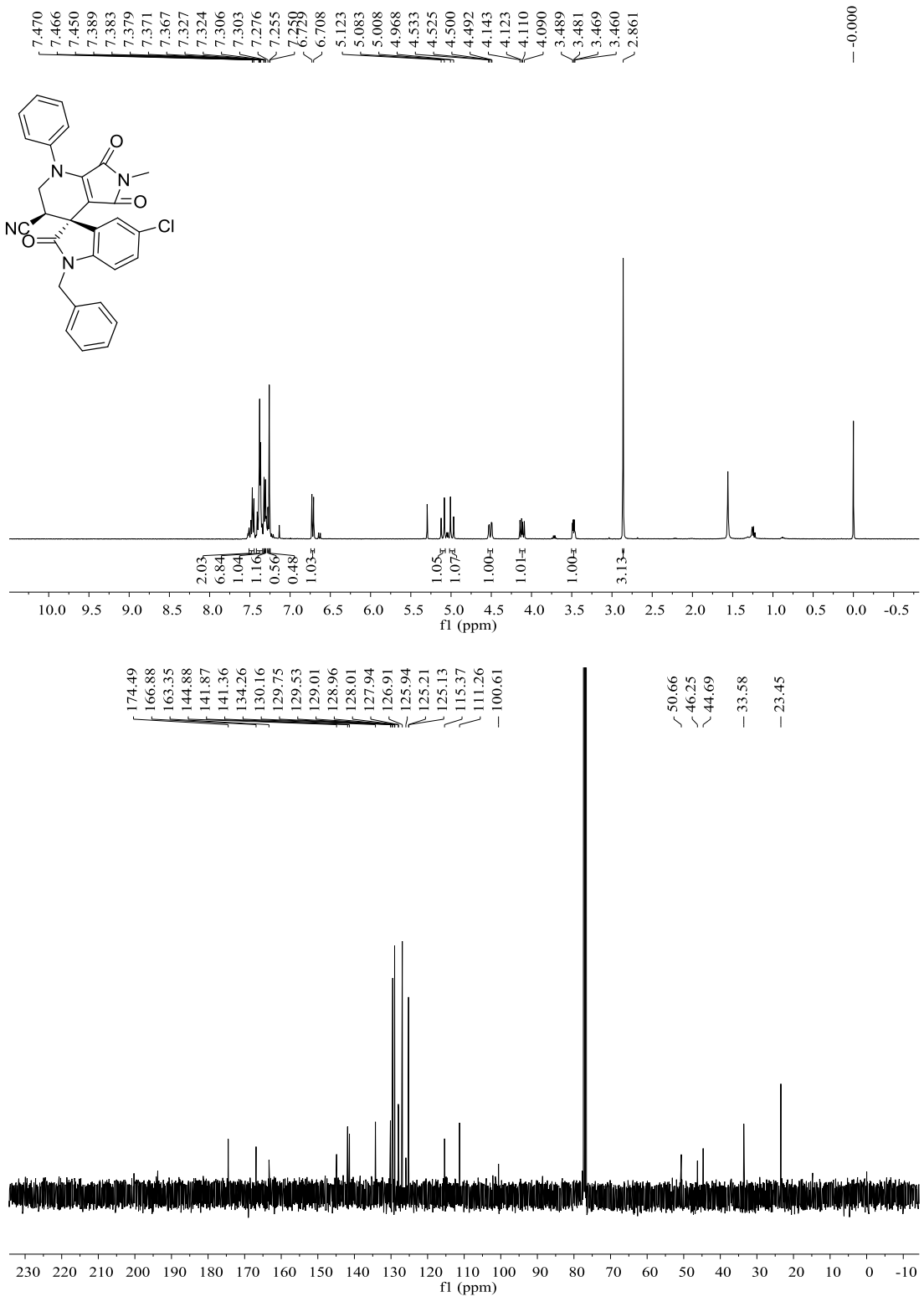
***rel*-(3*S*,3'*R*)-1-benzyl-5,6'-dimethyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydrospiro [indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4b'**):

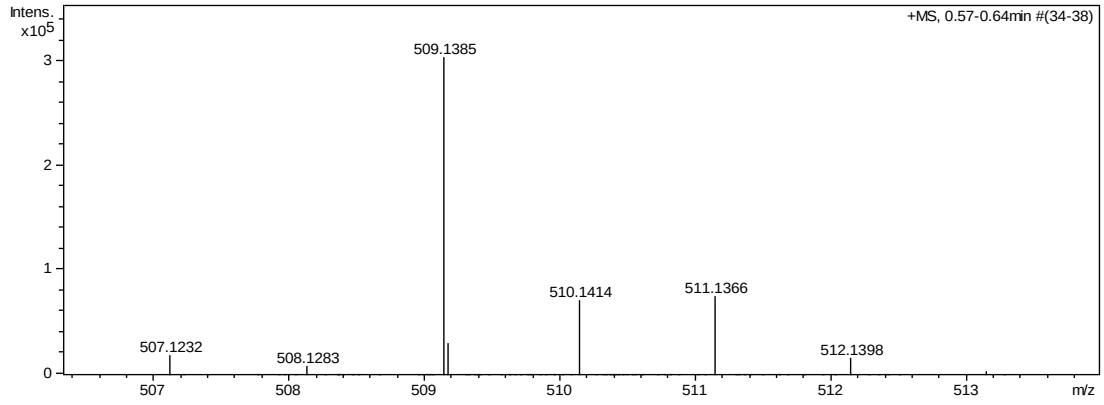



174.88
167.04
163.68
144.87
140.36
139.66
137.88
134.91
133.04
130.46
130.08
128.87
127.68
127.36
126.94
125.42
125.07
115.85
109.99
100.96
50.84
46.23
44.52
33.71
23.35
21.24
21.16
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

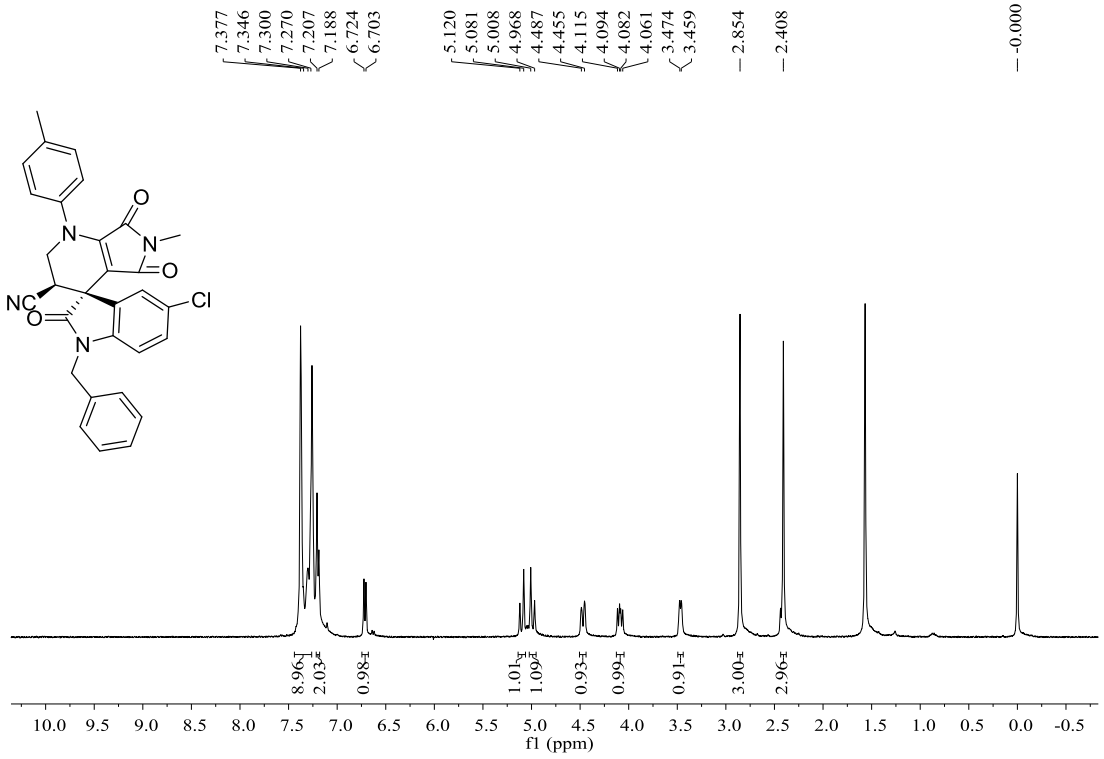

Intens.
x10^5
+MS, 0.67-0.76min #(40-45)
503.2088
504.2118
505.2152
0
1
2
3
4
500
501
502
503
504
505
506
507
508
m/z

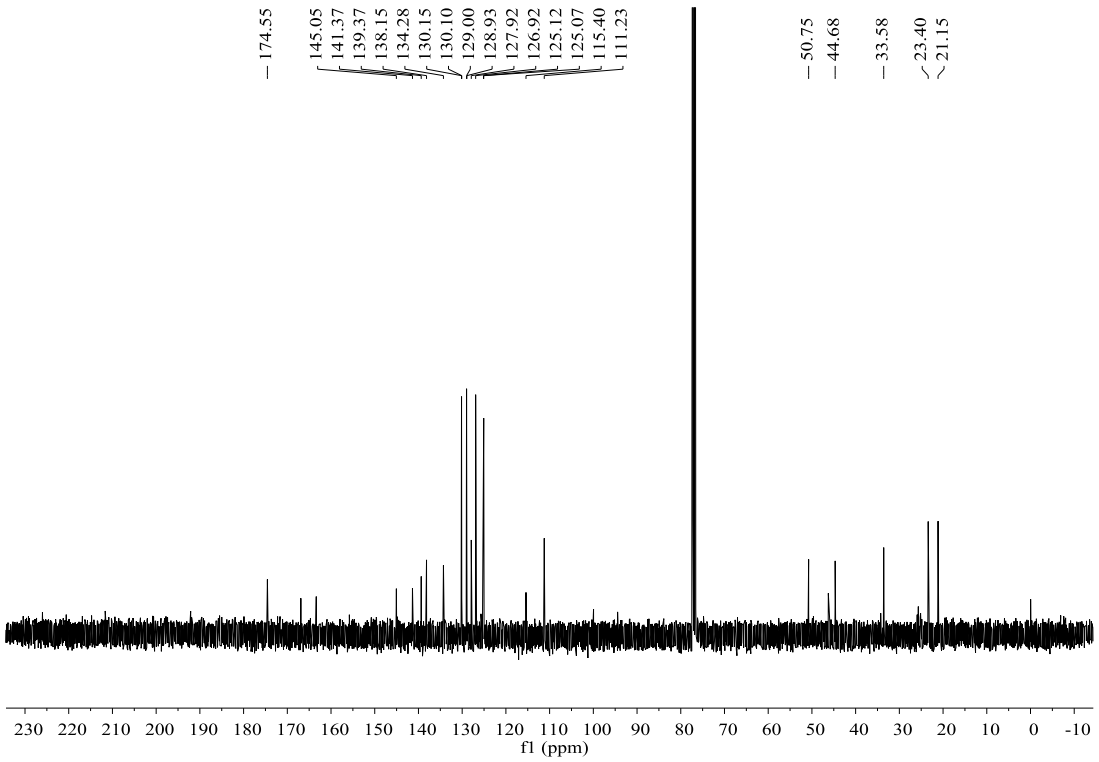
***rel*-(3*S*,3'*R*)-1-benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydro-spiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4c'**):

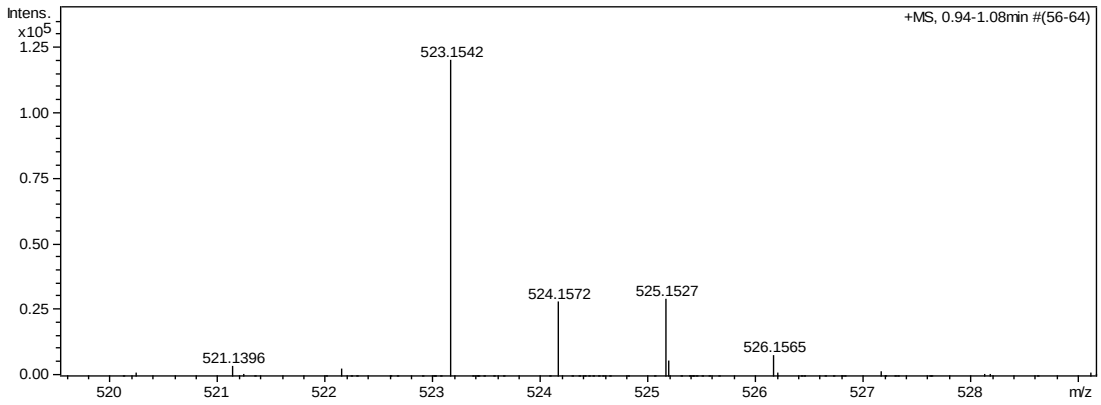




***rel*-(3*S*,3'*R*)-1-benzyl-5-chloro-6'-methyl-2,5',7'-trioxo-1'-(*p*-tolyl)-1',2',3',5',6',7'-hexahydro-spiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile** (**4d'**):

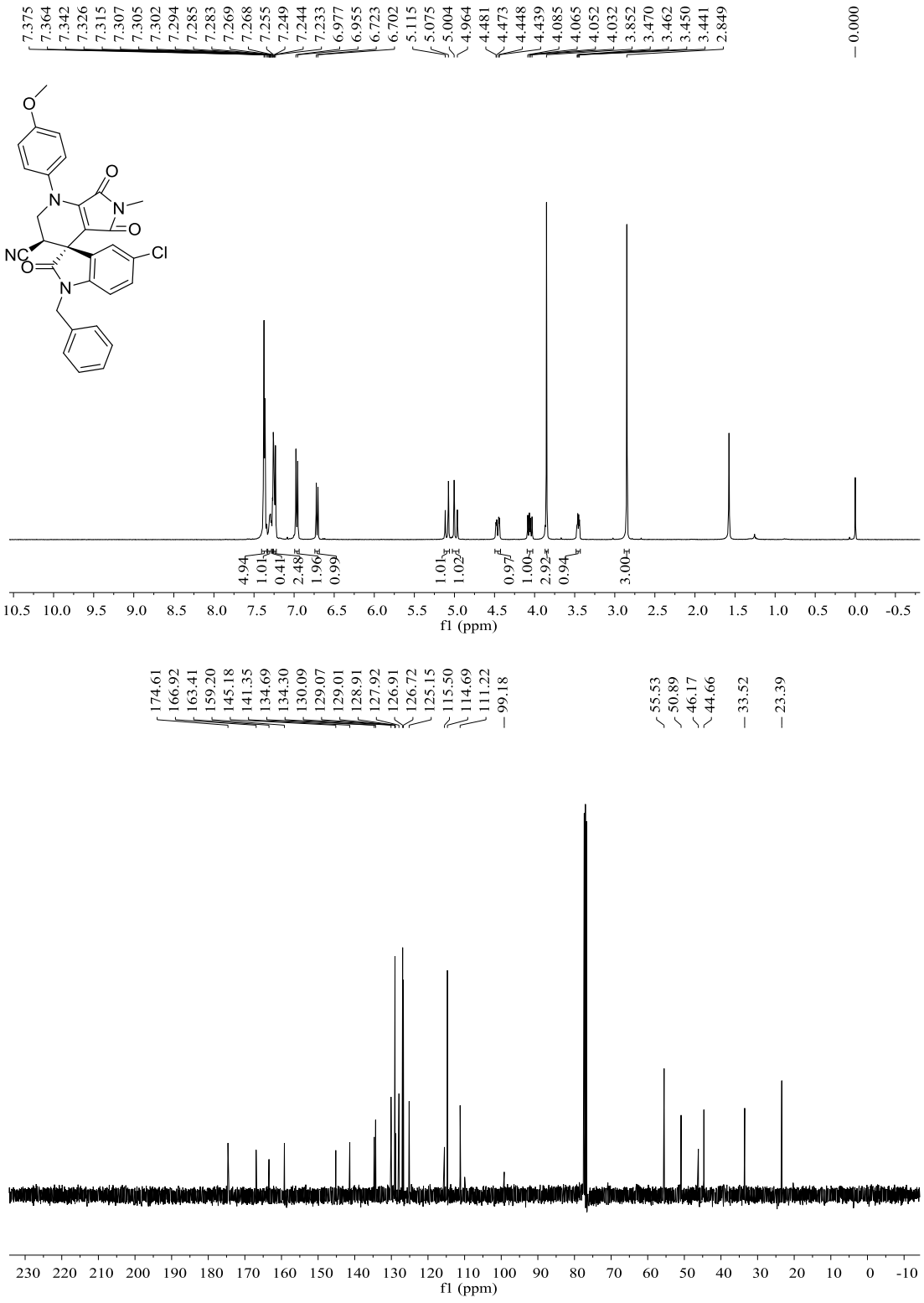


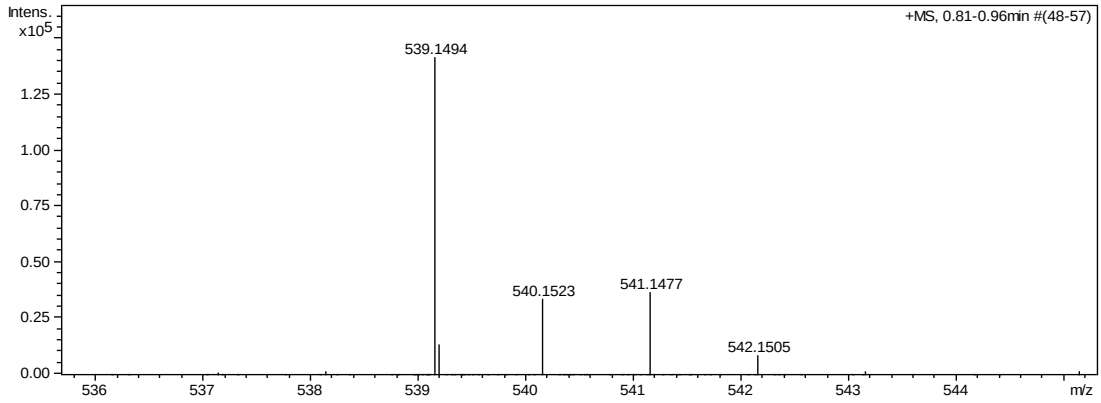

174.55
145.05
141.37
139.37
138.15
134.28
130.15
130.10
129.00
128.93
127.92
126.92
125.12
125.07
115.40
111.23
50.75
44.68
33.58
23.40
21.15
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 0.94-1.08min #(56-64)
523.1542
524.1572
525.1527
521.1396
526.1565
520
521
522
523
524
525
526
527
528
m/z

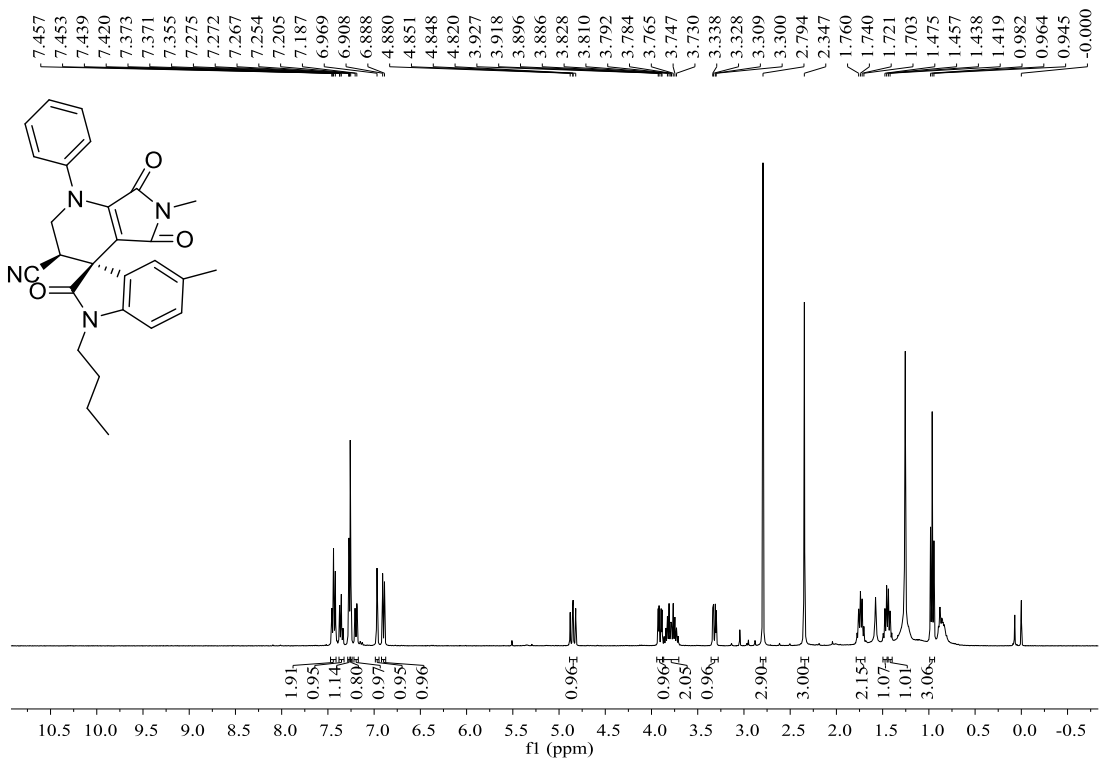
***rel*-(3*S*,3'*R*)-1-benzyl-5-chloro-1'-(4-methoxyphenyl)-6'-methyl-2,5',7'-trioxo-1',2',3',5',6',7'-h**

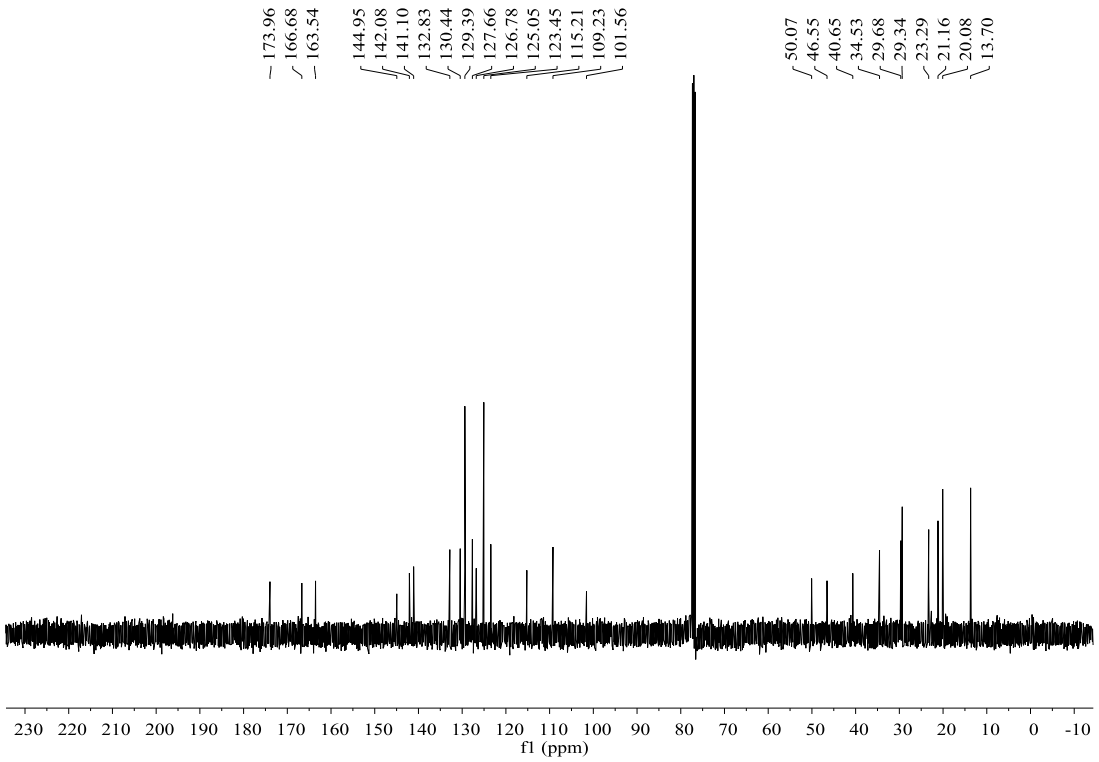
exahydrospiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile (**4e'**):

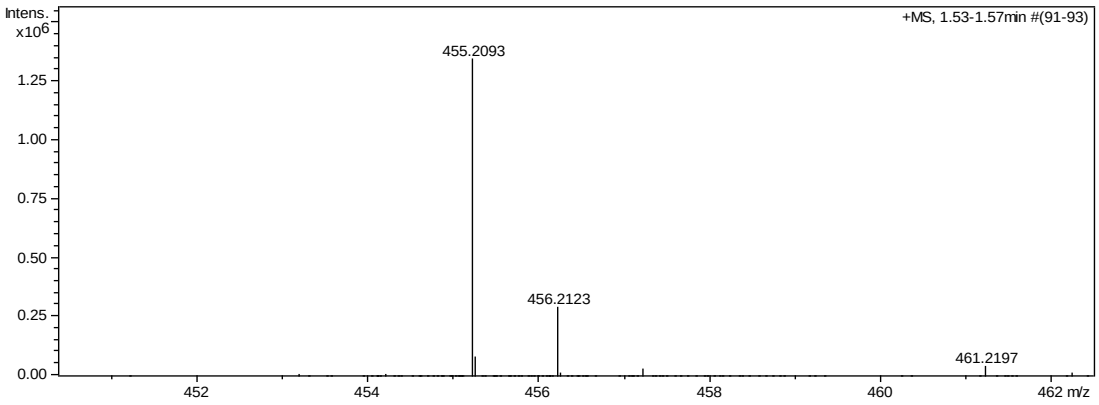




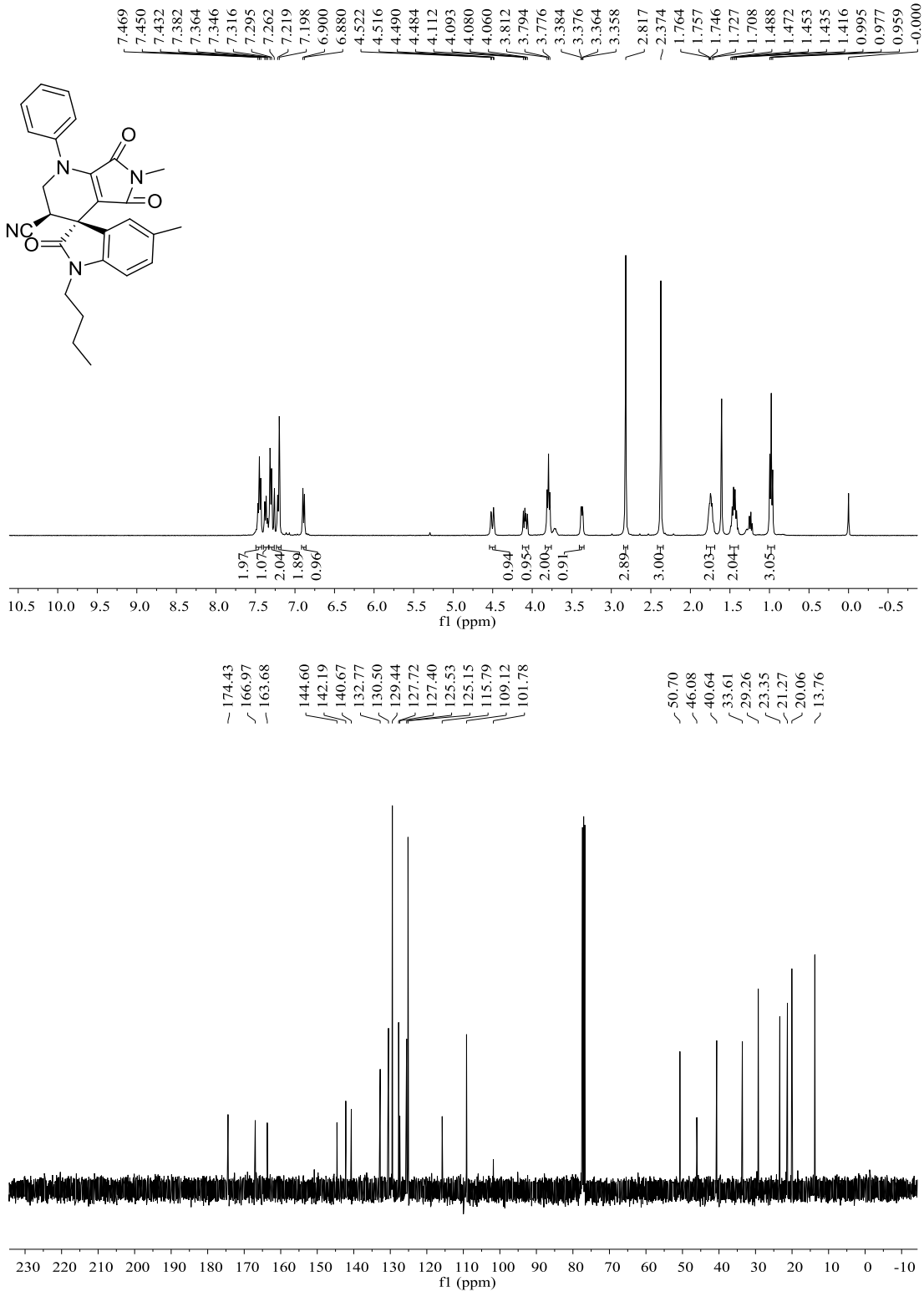
***rel*-(3*R*,3'*R*)-1-butyl-5,6'-dimethyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro [indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile (4f)**:

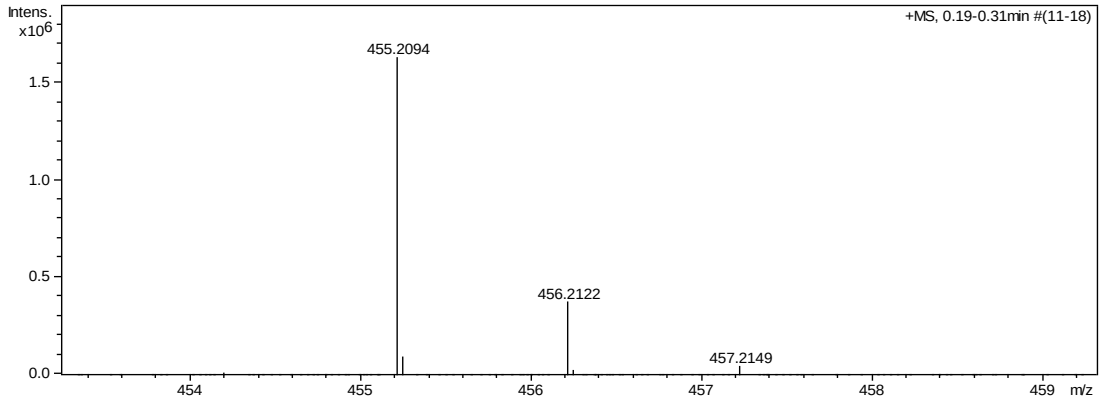



173.96
166.68
163.54
144.95
142.08
141.10
132.83
130.44
129.39
127.66
126.78
125.05
123.45
115.21
109.23
101.56
50.07
46.55
40.65
34.53
29.68
29.34
23.29
21.16
20.08
13.70
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

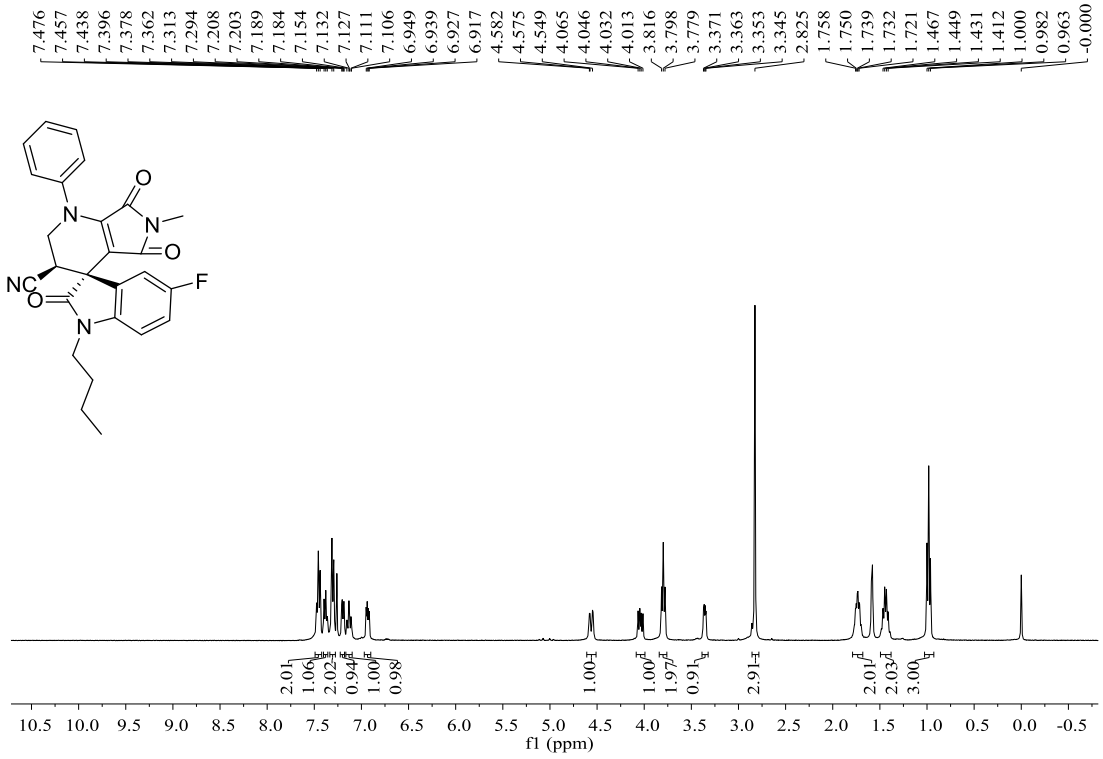

Intens.
x10^6
+MS, 1.53-1.57min #(91-93)
455.2093
456.2123
461.2197
1.25
1.00
0.75
0.50
0.25
0.00
452
454
456
458
460
462 m/z

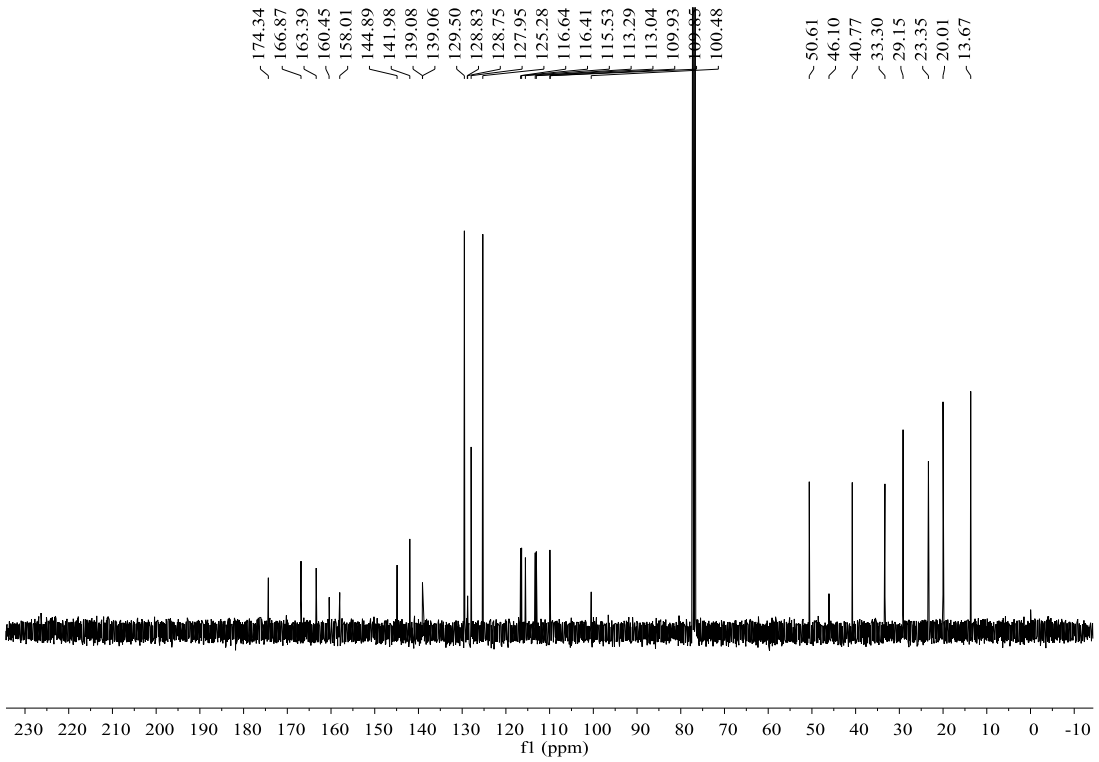
***rel*-(3*S*,3'*R*)-1-butyl-5,6'-dimethyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydrospiro [indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile (4f')**:

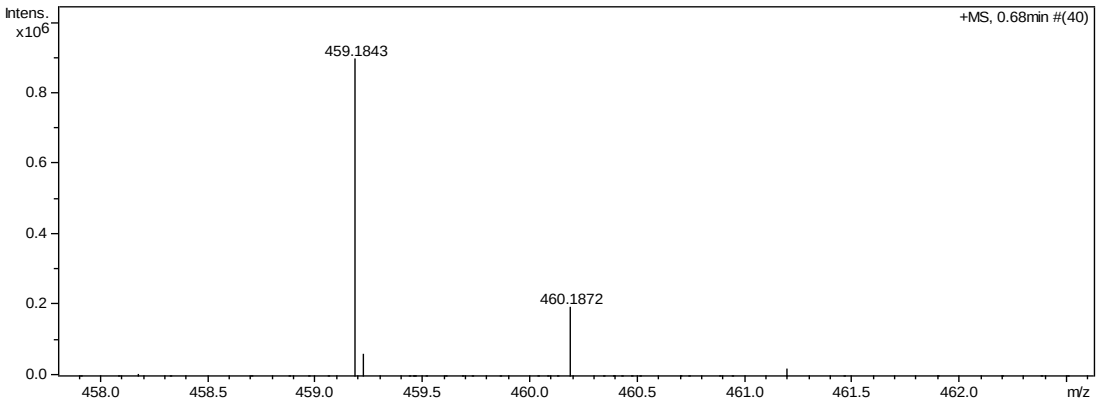




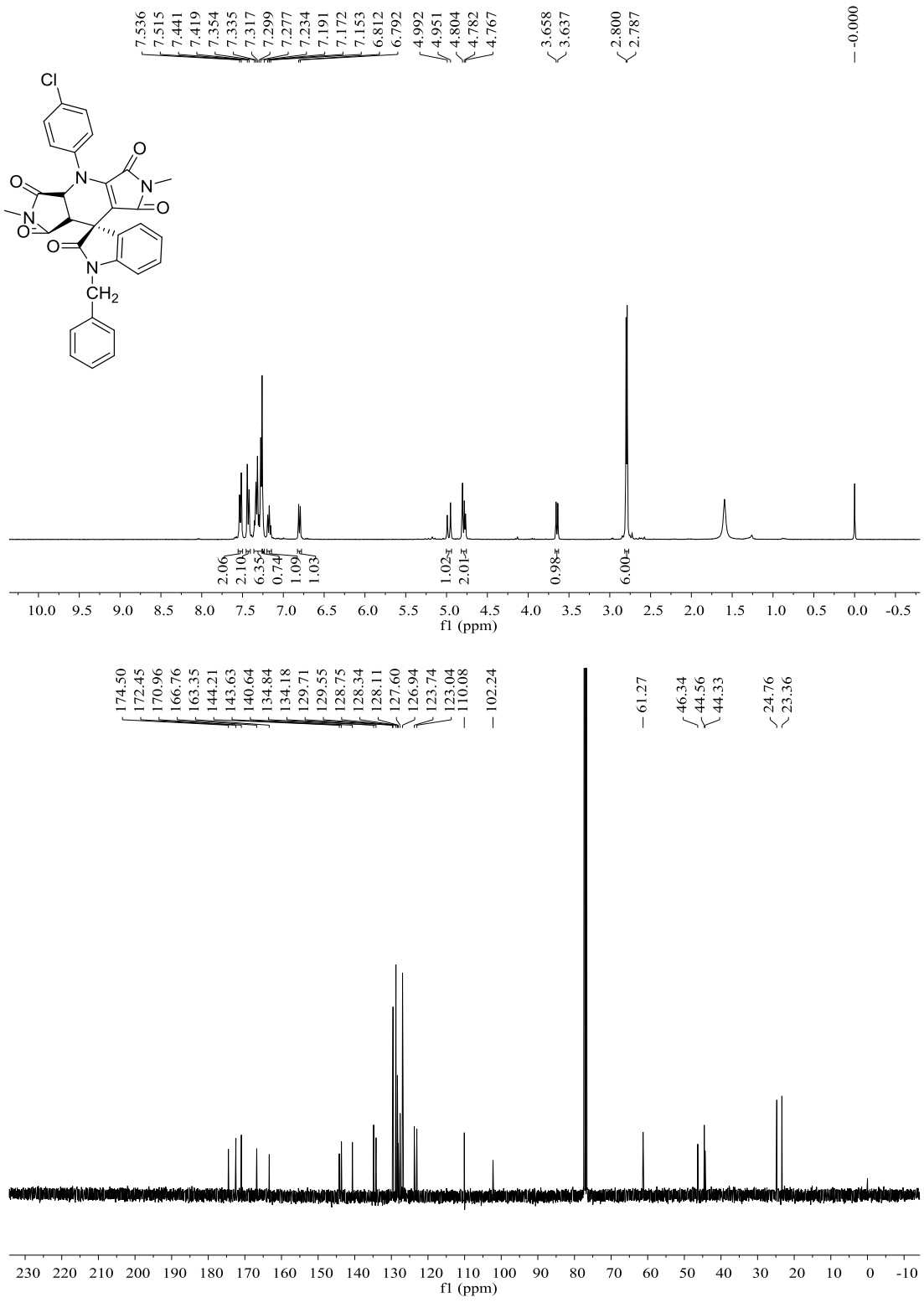
***rel*-(3*S*,3'*R*)-1-butyl-5-fluoro-6'-methyl-2,5',7'-trioxo-1'-phenyl-1',2',3',5',6',7'-hexahydro-spiro[indoline-3,4'-pyrrolo[3,4-*b*]pyridine]-3'-carbonitrile (4g')**:

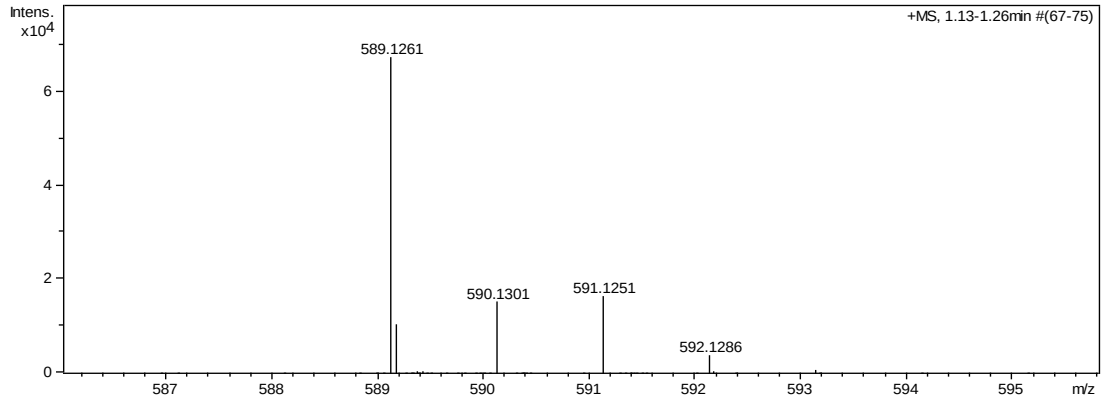



174.34
166.87
163.39
160.45
158.01
144.89
141.98
139.08
139.06
129.50
128.83
128.75
127.95
125.28
116.64
116.41
115.53
113.29
113.04
109.93
100.48
50.61
46.10
40.77
33.30
29.15
23.35
20.01
13.67
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

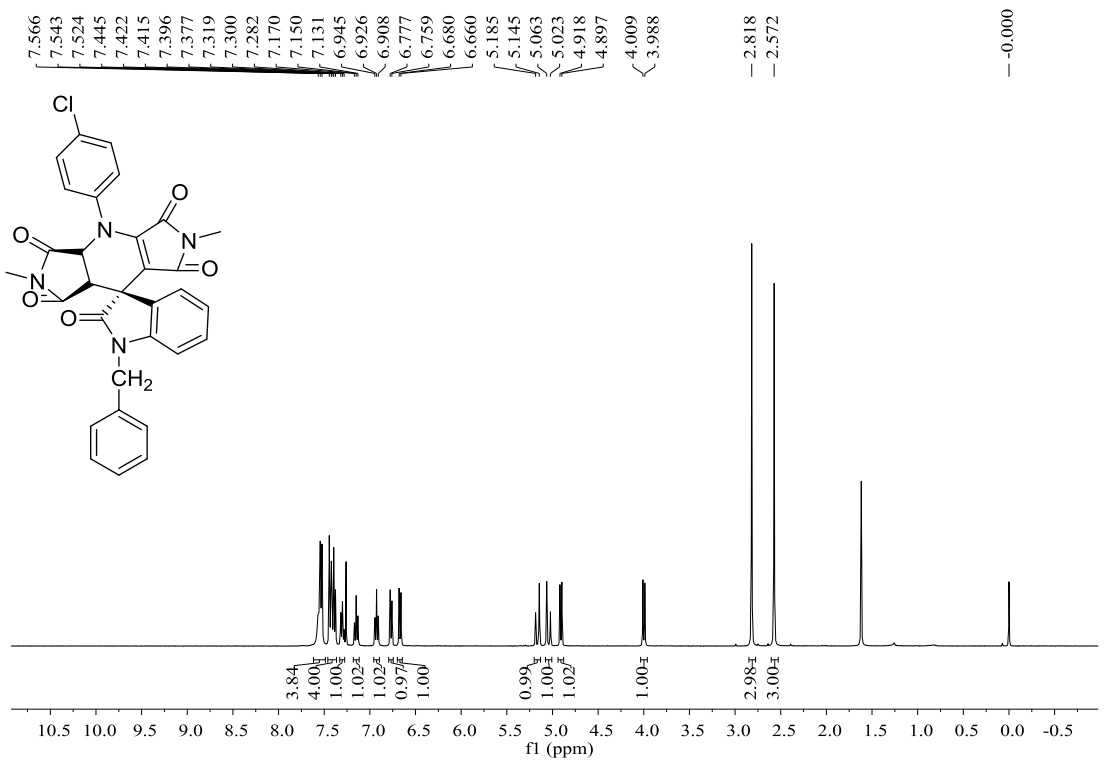

Intens.
x10^6
+MS, 0.68min #(40)
459.1843
460.1872
0.0
0.2
0.4
0.6
0.8
458.0
458.5
459.0
459.5
460.0
460.5
461.0
461.5
462.0
m/z

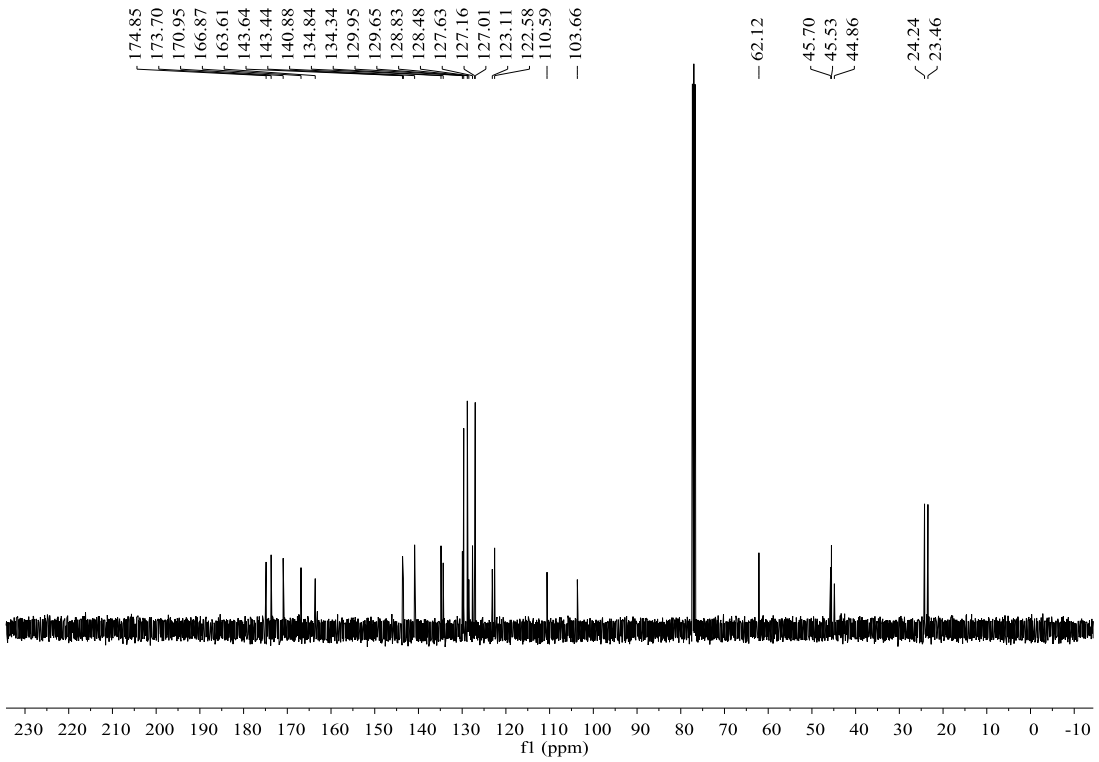
***rel*-(3a*R*,8*R*,8a*S*)-1'-benzyl-4-(4-chlorophenyl)-2,6-dimethyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5a**):

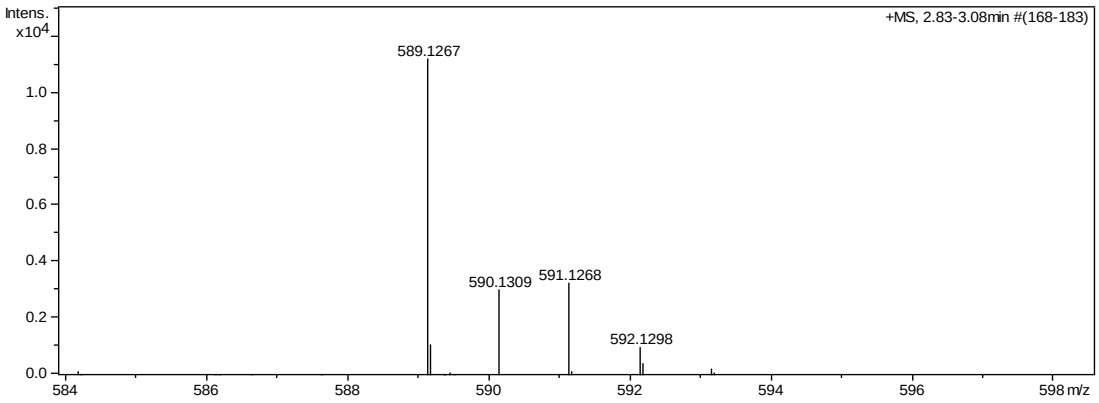




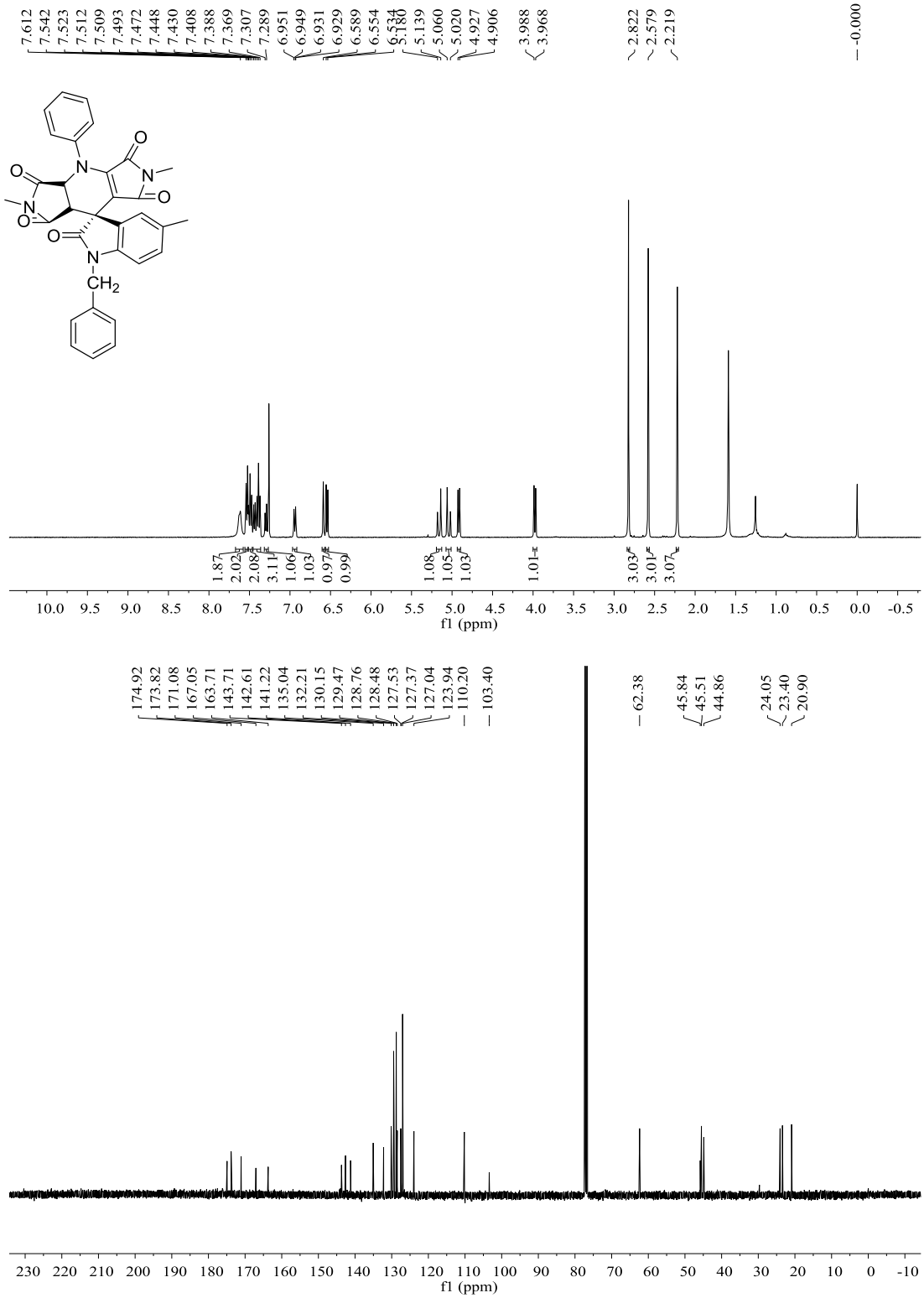
***rel*-(3a*R*,8*S*,8a*S*)-1'-benzyl-4-(4-chlorophenyl)-2,6-dimethyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5a'**):

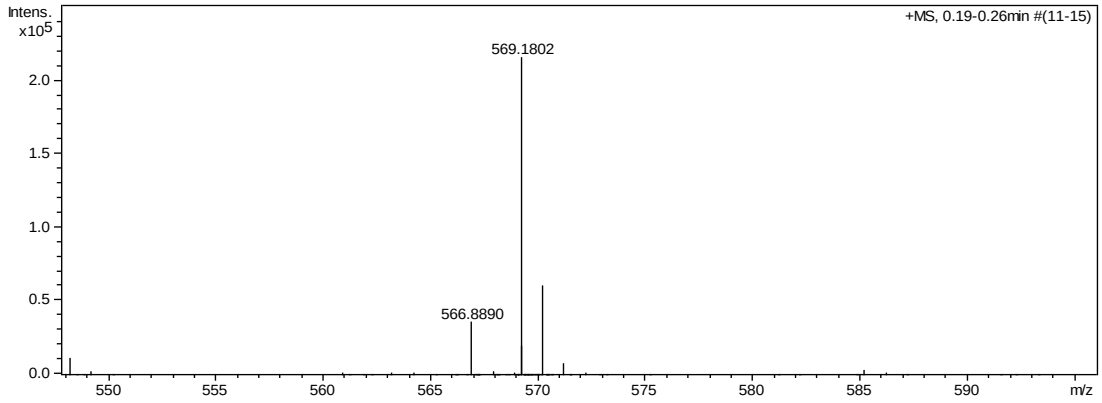



174.85
173.70
170.95
166.87
163.61
143.64
143.44
140.88
134.84
134.34
129.95
129.65
128.83
128.48
127.63
127.16
127.01
123.11
122.58
110.59
103.66
62.12
45.70
45.53
44.86
24.24
23.46
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

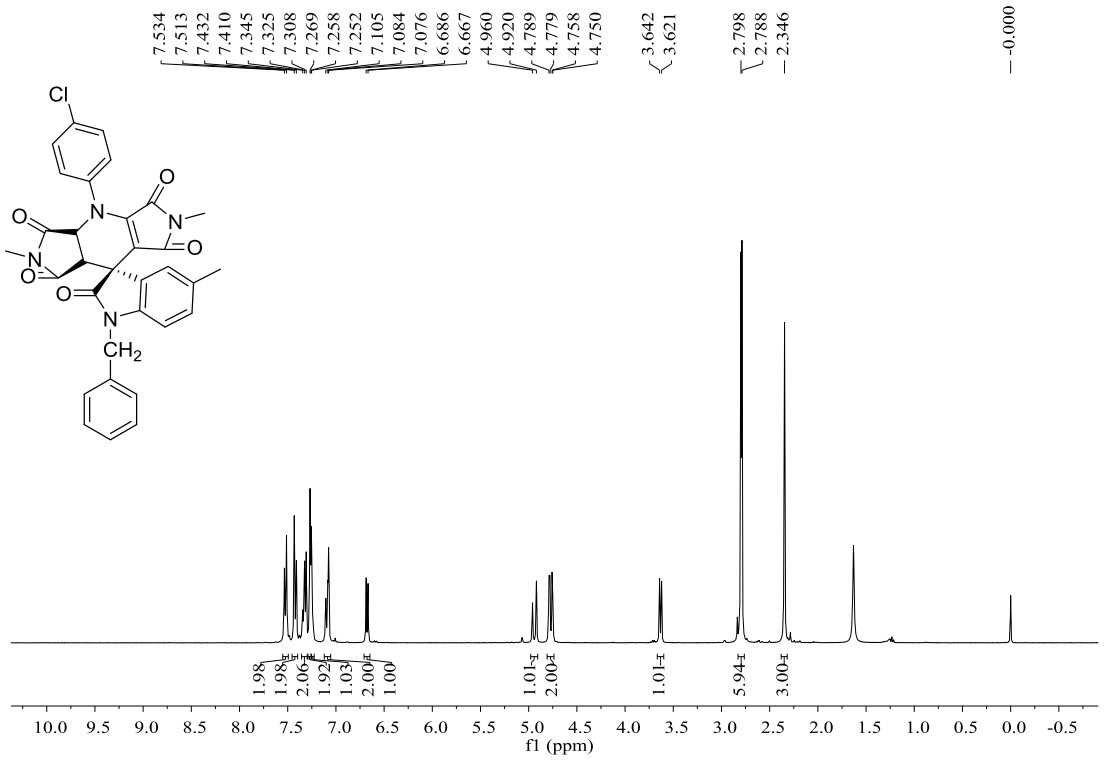

Intens.
x10^4
+MS, 2.83-3.08min #(168-183)
589.1267
590.1309
591.1268
592.1298
1.0
0.8
0.6
0.4
0.2
0.0
584
586
588
590
592
594
596
598 m/z

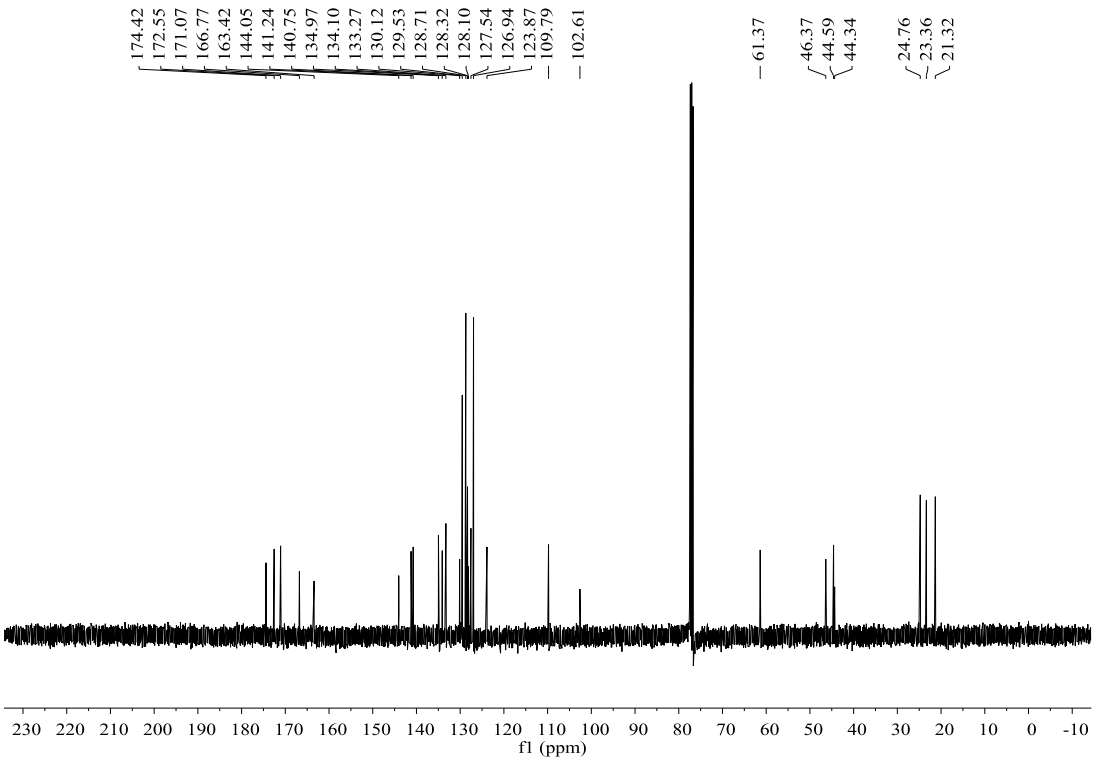
***rel*-(3a*R*,8*S*,8a*S*)-1'-benzyl-2,5',6-trimethyl-4-phenyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5b'**):

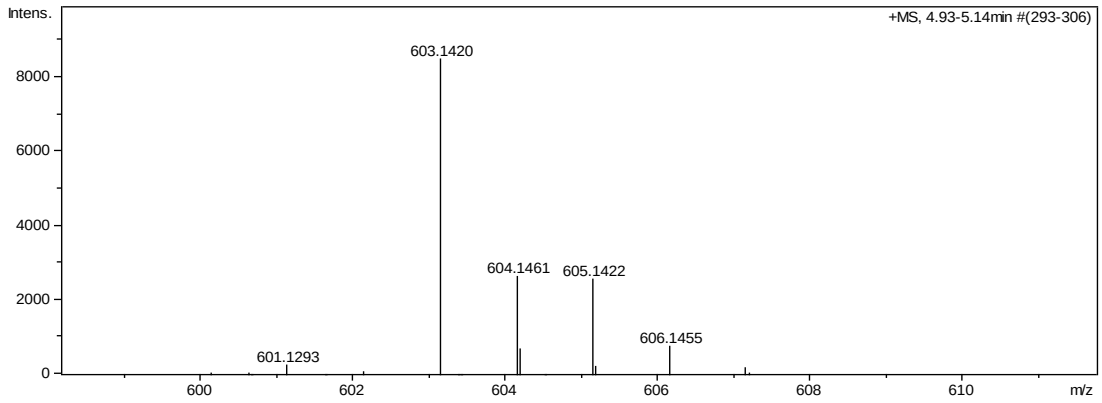




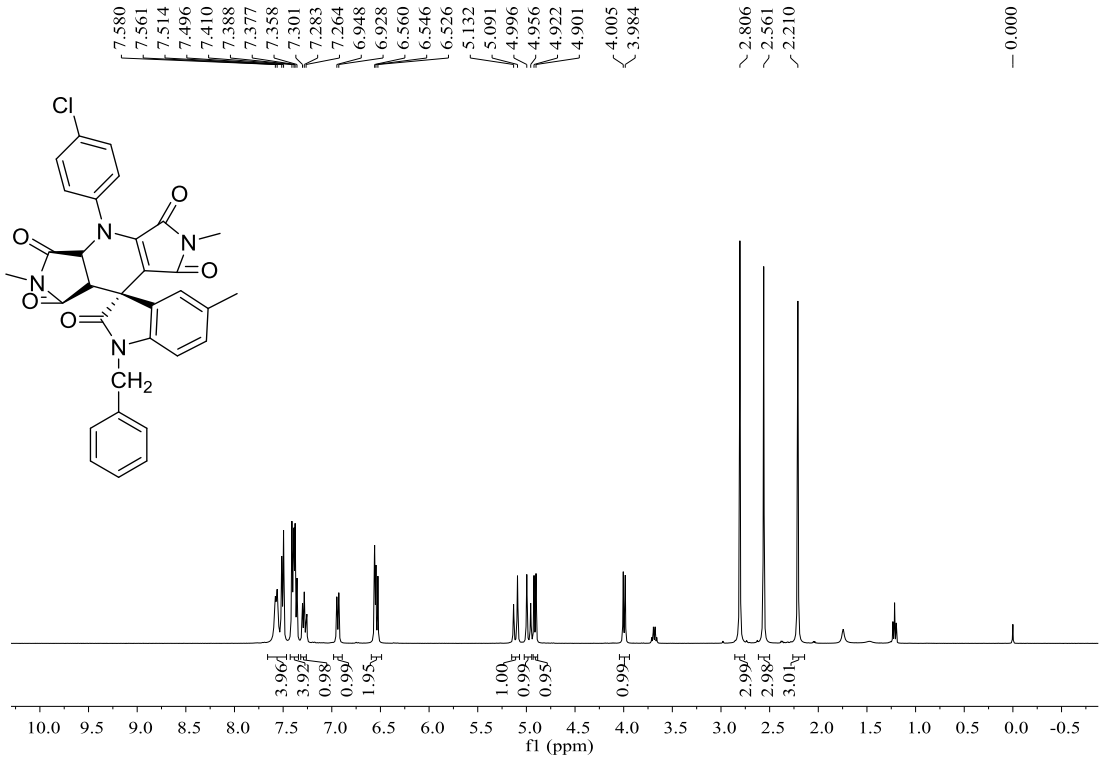
***rel*-(3a*R*,8*R*,8a*S*)-1'-benzyl-4-(4-chlorophenyl)-2,5',6-trimethyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo [3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5c**):

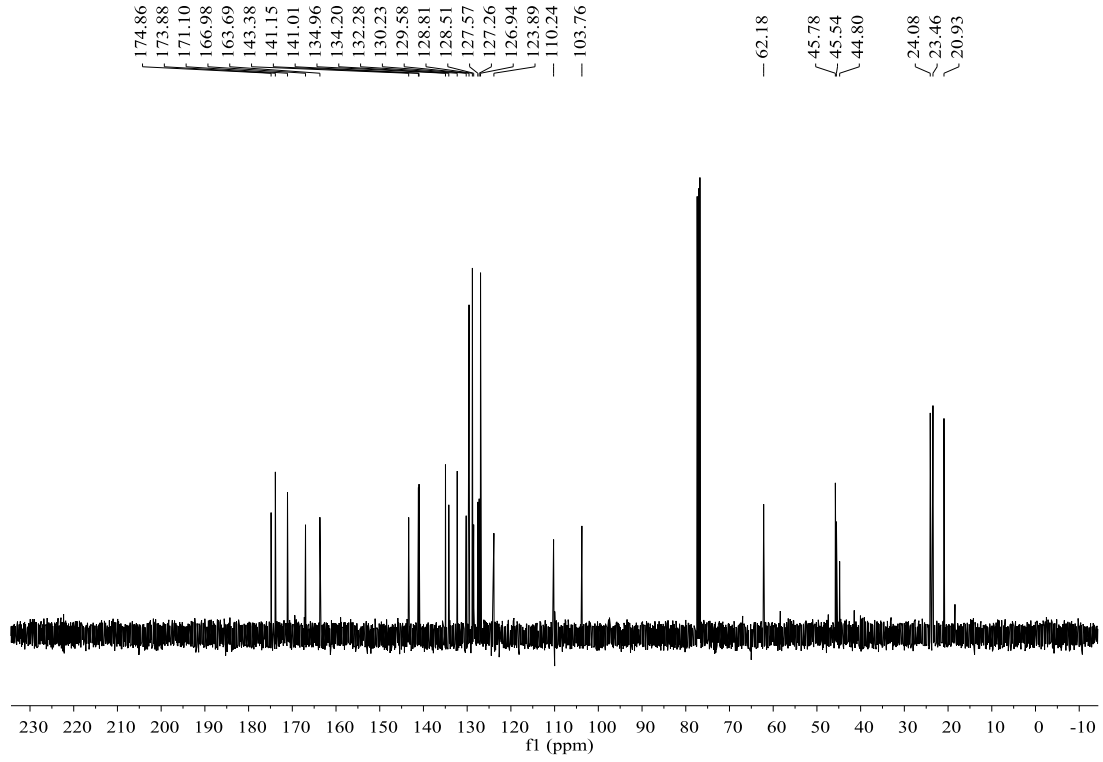


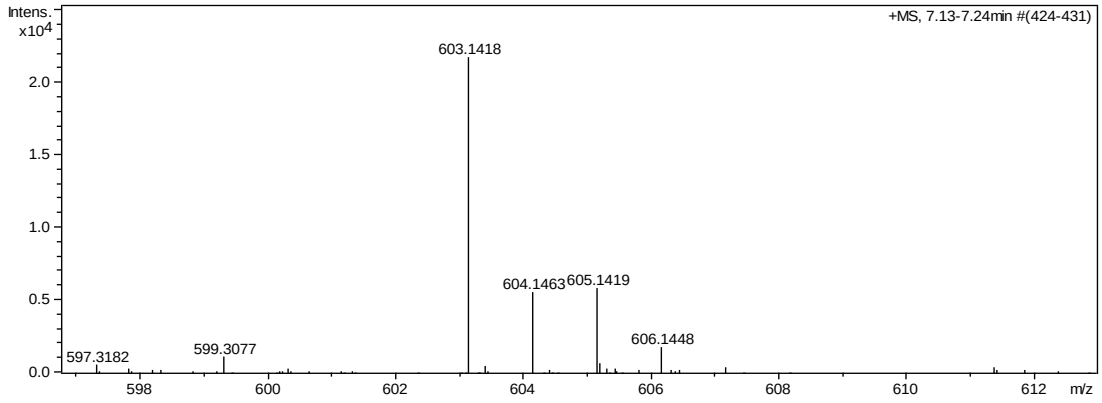

174.42
172.55
171.07
166.77
163.42
144.05
141.24
140.75
134.97
134.10
133.27
130.12
129.53
128.71
128.32
128.10
127.54
126.94
123.87
109.79
102.61
61.37
46.37
44.59
44.34
24.76
23.36
21.32
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 4.93-5.14min #(293-306)
603.1420
604.1461
605.1422
606.1455
601.1293
8000
6000
4000
2000
0
600
602
604
606
608
610
m/z

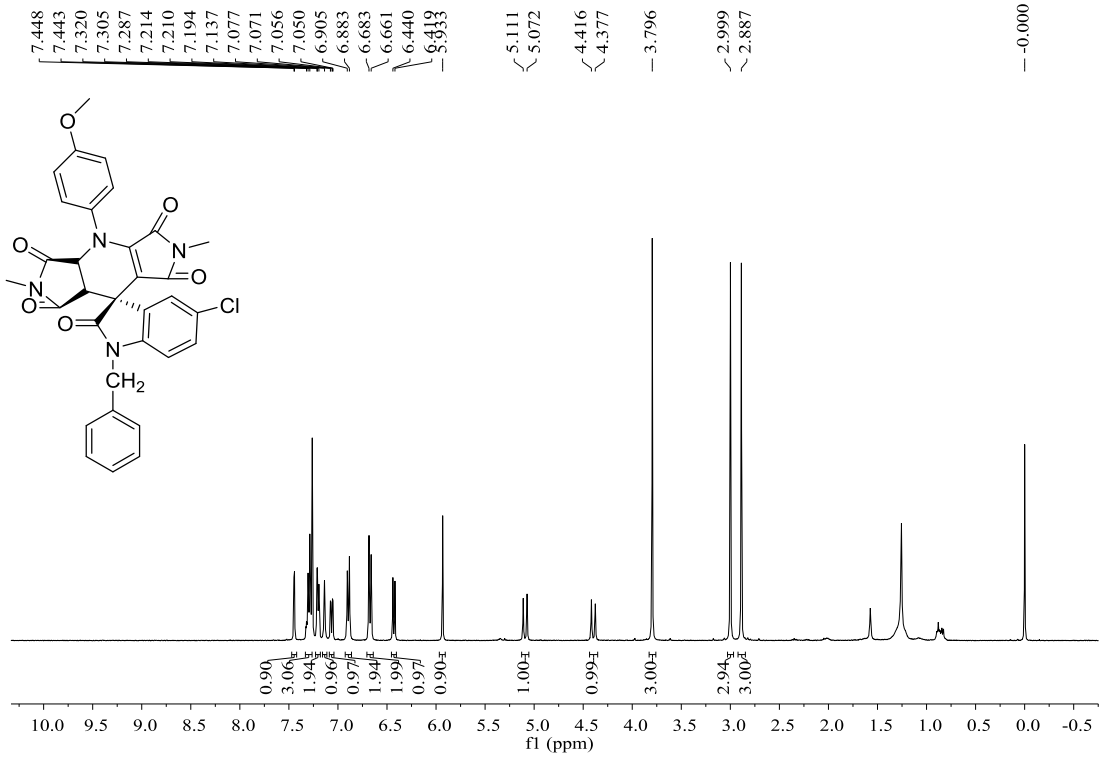
***rel*-(3a*R*,8*S*,8a*S*)-1'-benzyl-4-(4-chlorophenyl)-2,5',6-trimethyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo [3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5c'**):

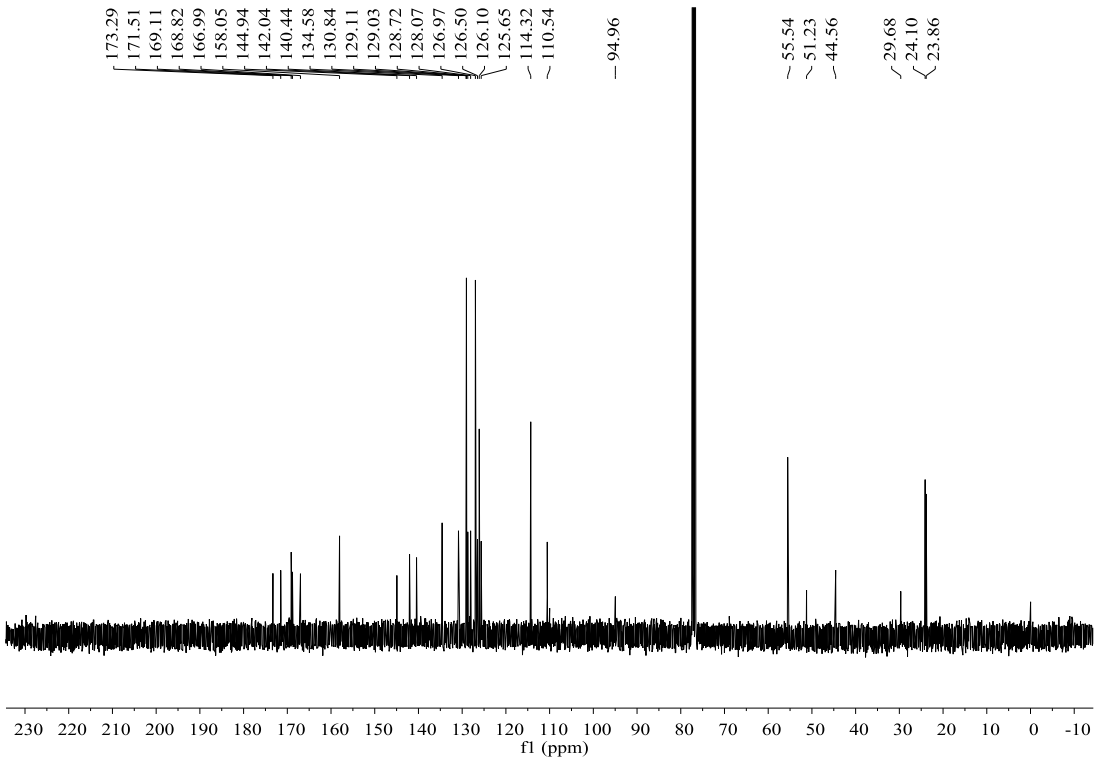


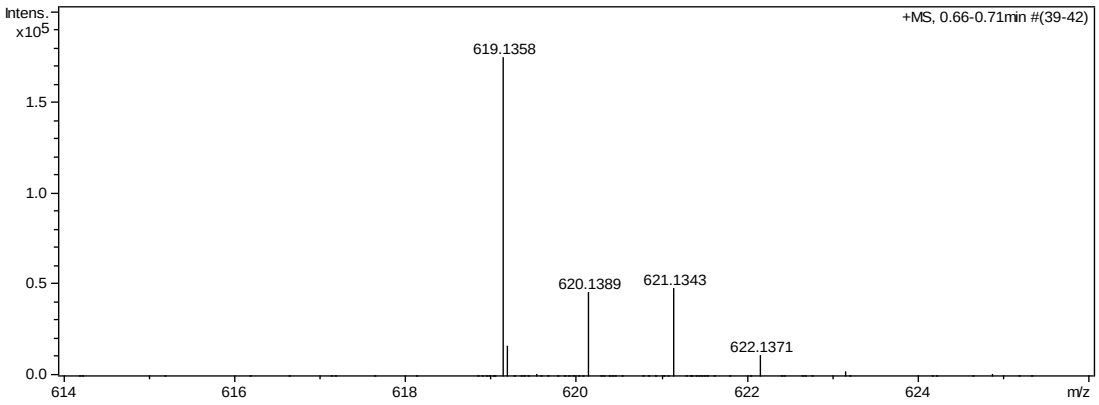




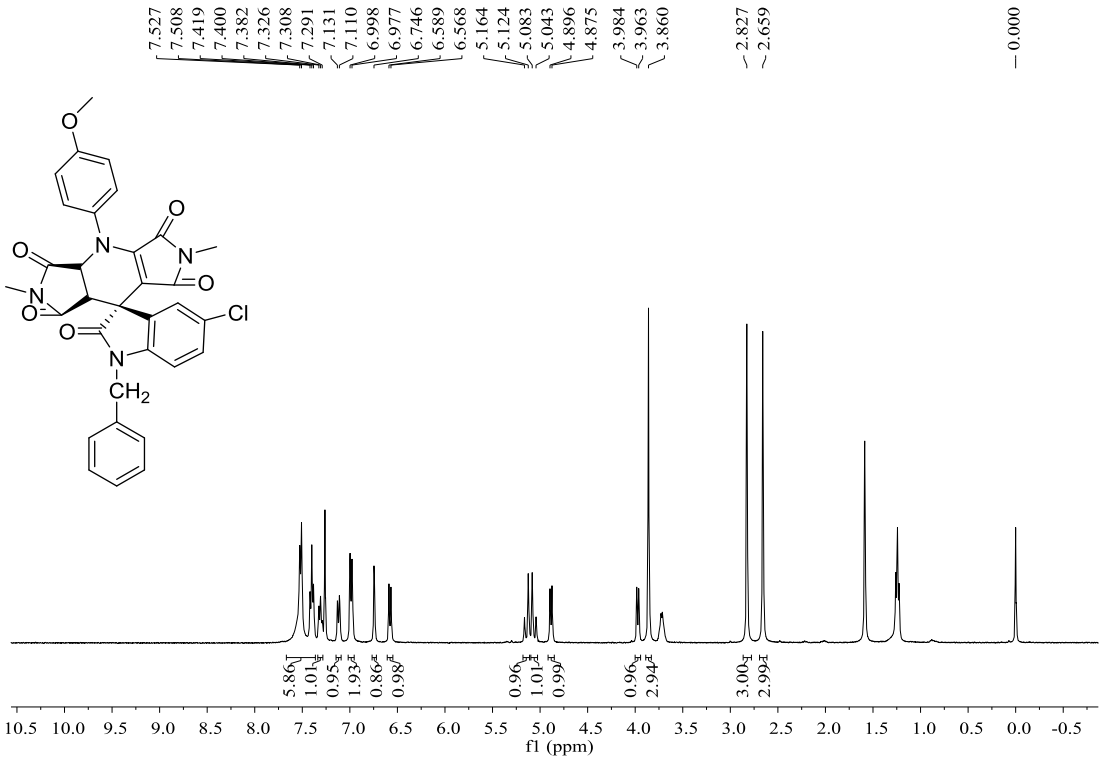
***rel*-(3a*R*,8*R*,8a*S*)-1'-benzyl-5'-chloro-4-(4-methoxyphenyl)-2,6-dimethyl-3a,8a-dihydro-1*H*-spiro[di-pyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5d**):

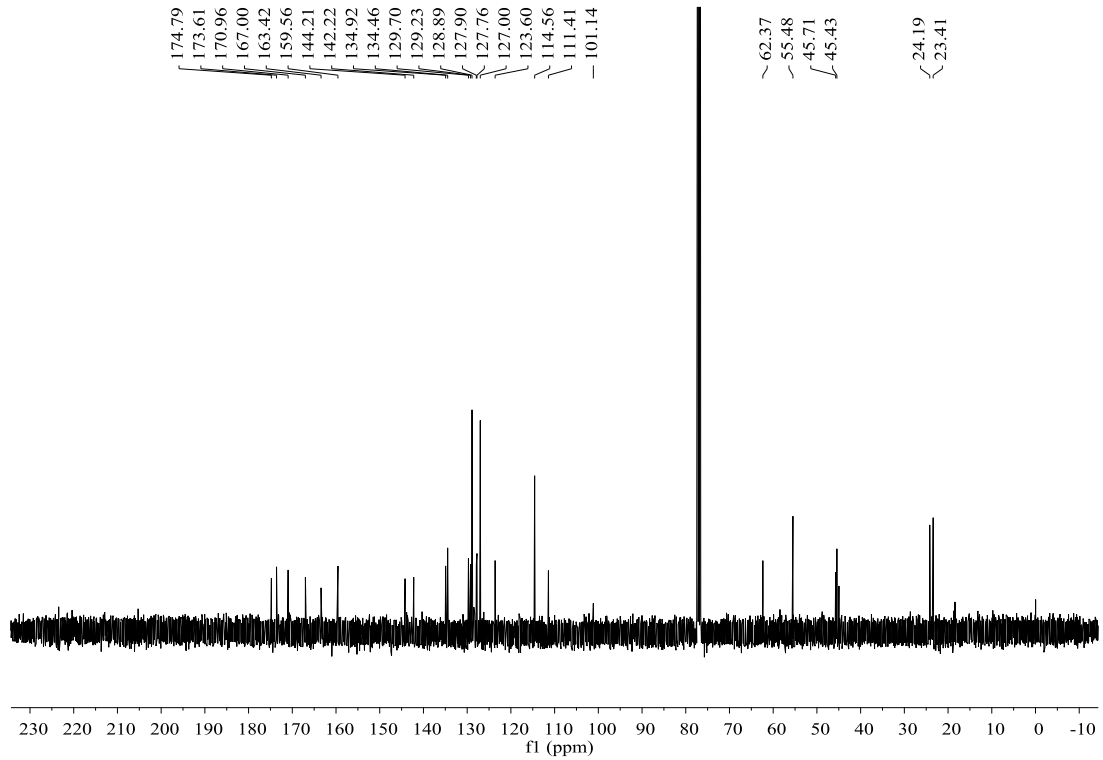


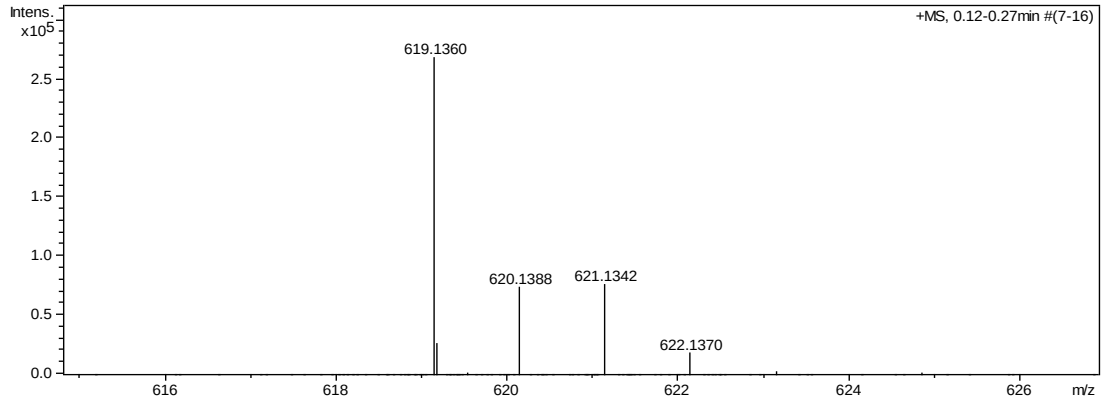

173.29
171.51
169.11
168.82
166.99
158.05
144.94
142.04
140.44
134.58
130.84
129.11
129.03
128.72
128.07
126.97
126.50
126.10
125.65
114.32
110.54
94.96
55.54
51.23
44.56
29.68
24.10
23.86
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.66-0.71min #(39-42)
619.1358
620.1389
621.1343
622.1371
1.5
1.0
0.5
0.0
614
616
618
620
622
624
m/z

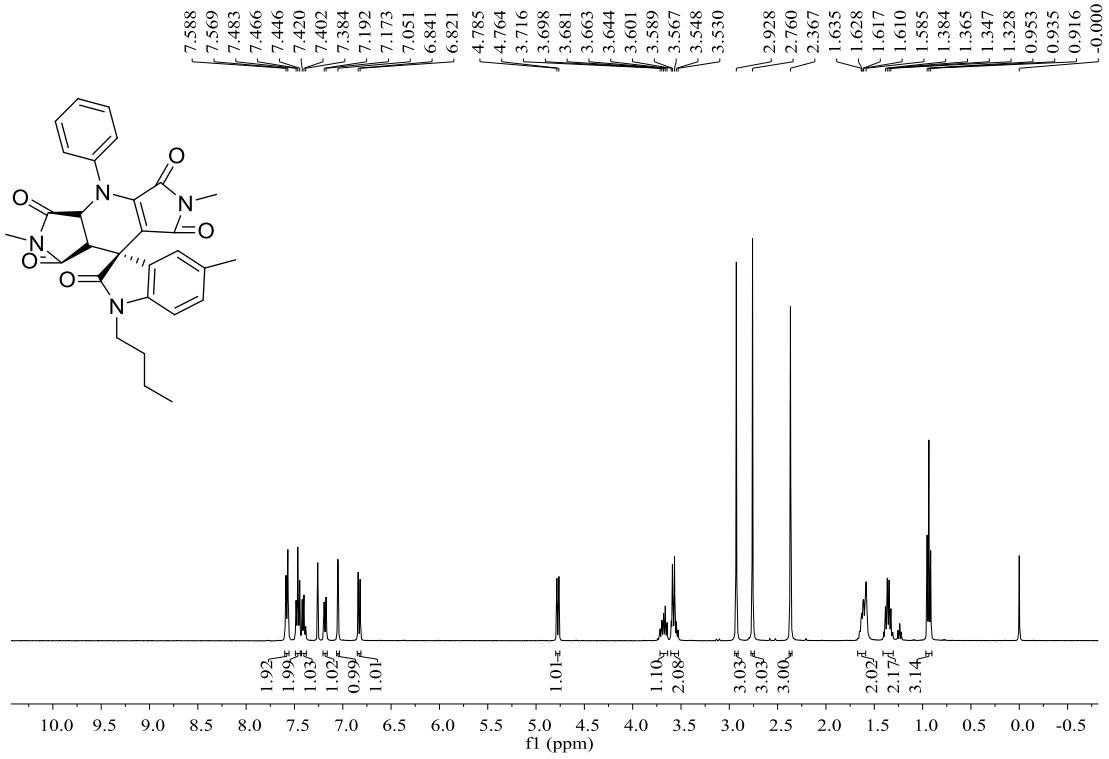
***rel*-(3a*R*,8*S*,8a*S*)-1'-benzyl-5'-chloro-4-(4-methoxyphenyl)-2,6-dimethyl-3a,8a-dihydro-1*H*-spiro[di-pyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5d'**):

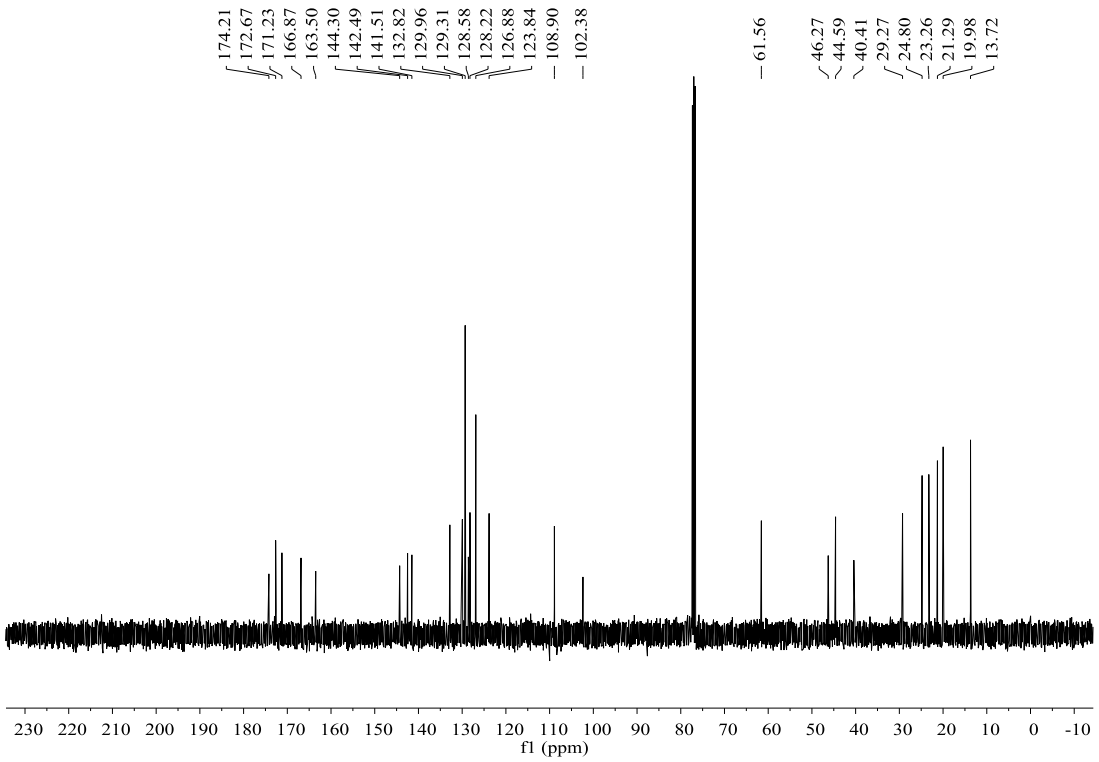


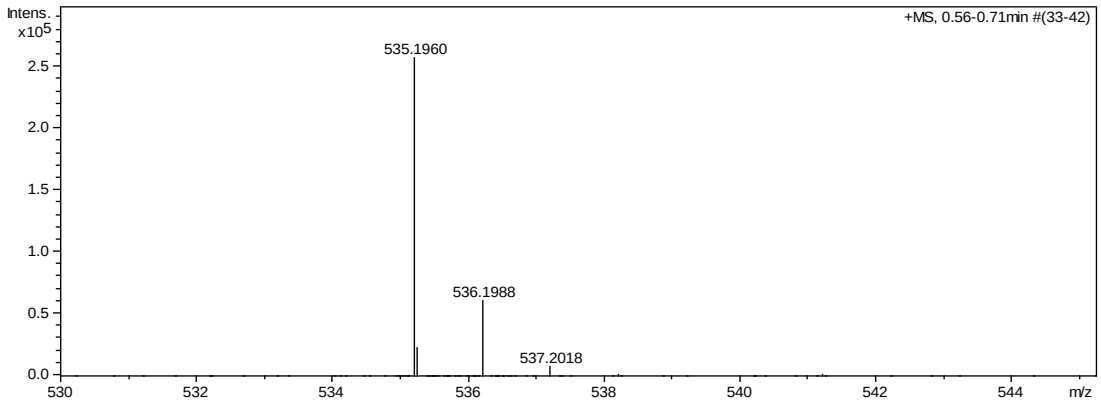




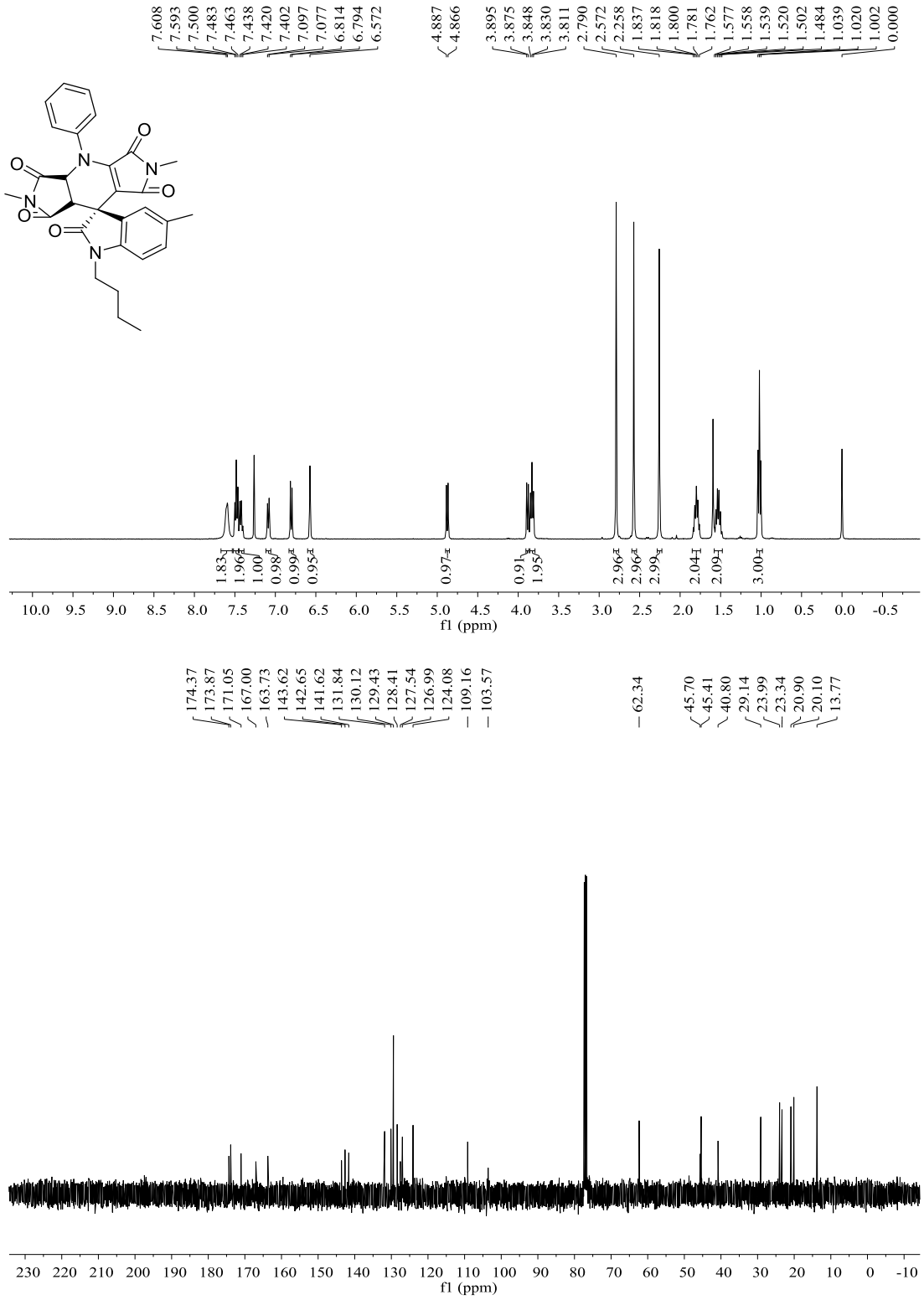
***rel*-(3a*R*,8*R*,8a*S*)-1'-butyl-2,5',6-trimethyl-4-phenyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*] pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5e**):

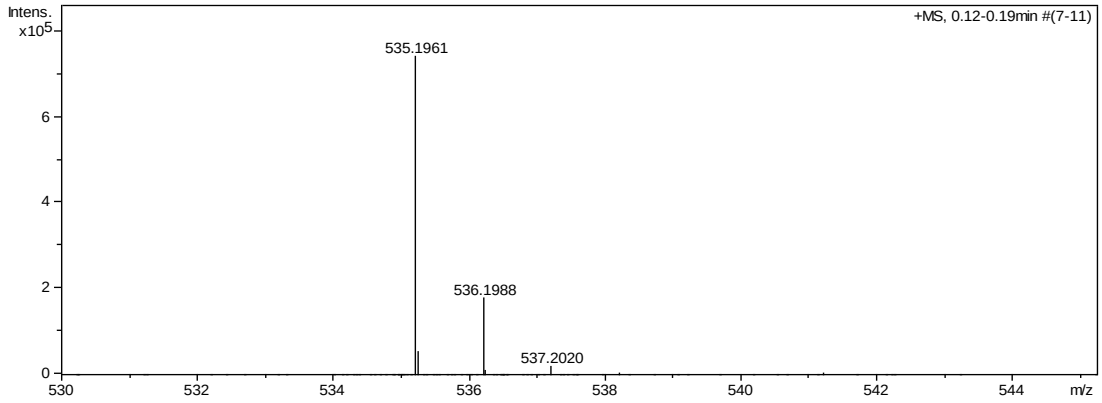



174.21
172.67
171.23
166.87
163.50
144.30
142.49
141.51
132.82
129.96
129.31
128.58
128.22
126.88
123.84
108.90
102.38
61.56
46.27
44.59
40.41
29.27
24.80
23.26
21.29
19.98
13.72
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

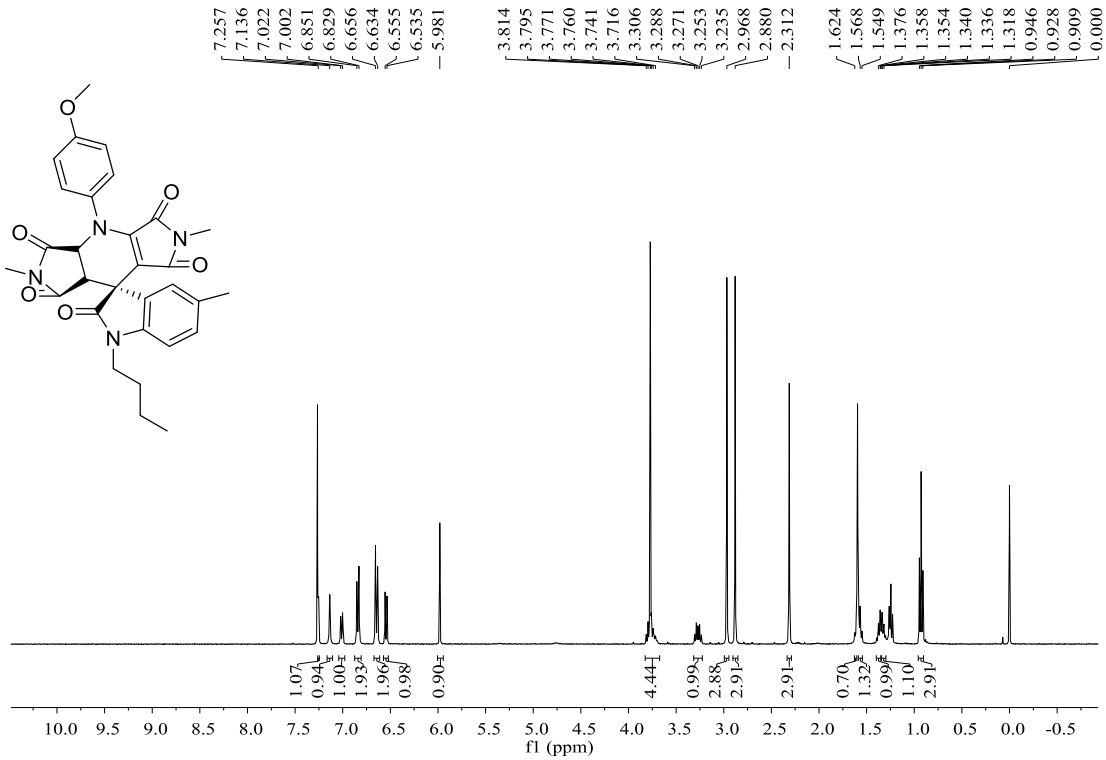

Intens.
x10^5
+MS, 0.56-0.71min #(33-42)
535.1960
536.1988
537.2018
2.5
2.0
1.5
1.0
0.5
0.0
530
532
534
536
538
540
542
544
m/z

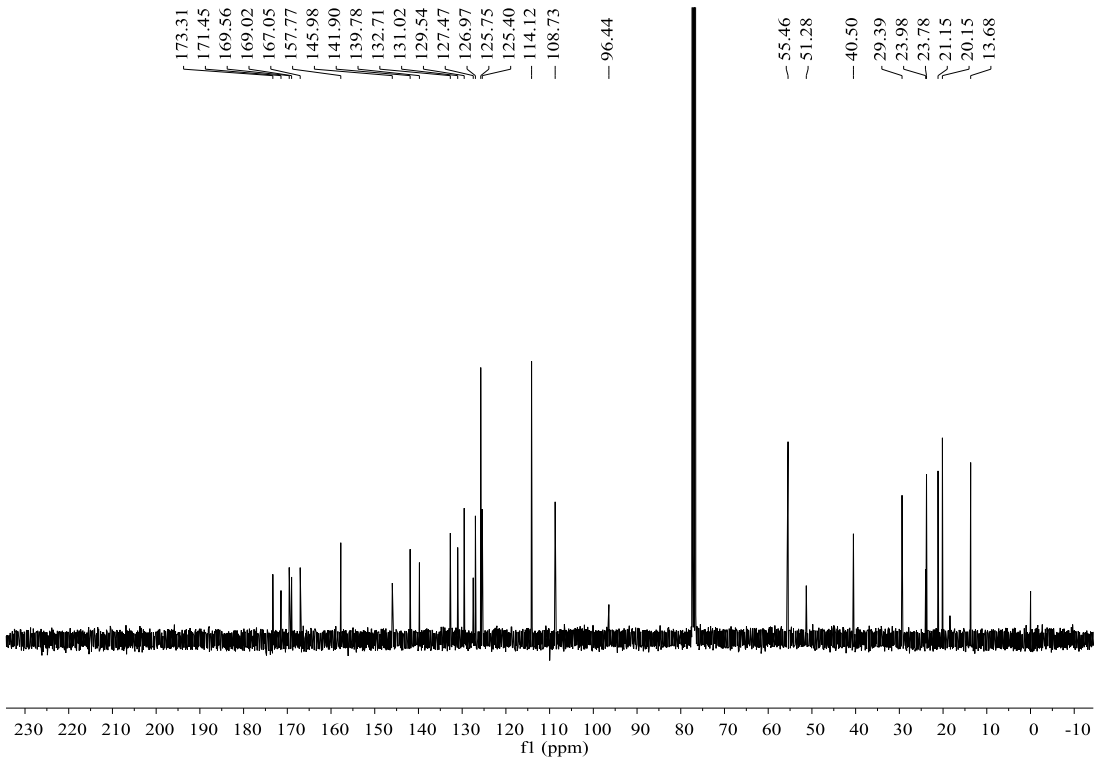
***rel*-(3a*R*,8*S*,8a*S*)-1'-butyl-2,5',6-trimethyl-4-phenyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*] pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5e'**):

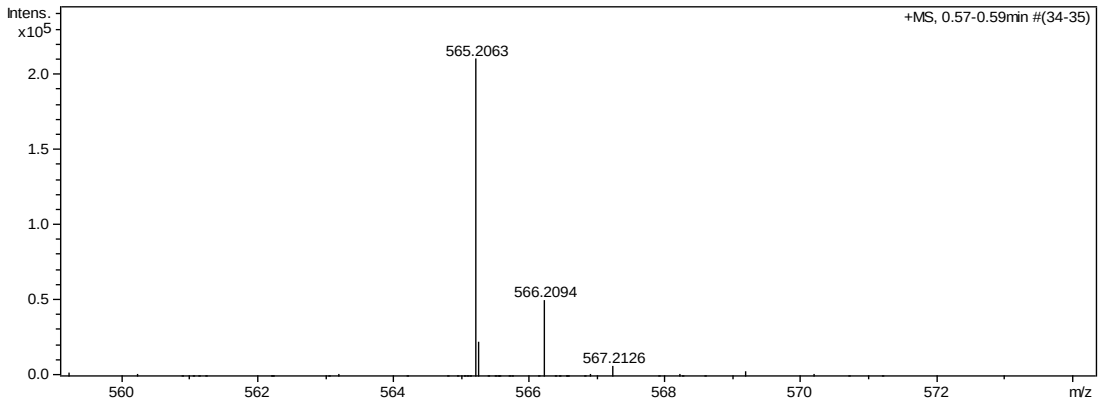




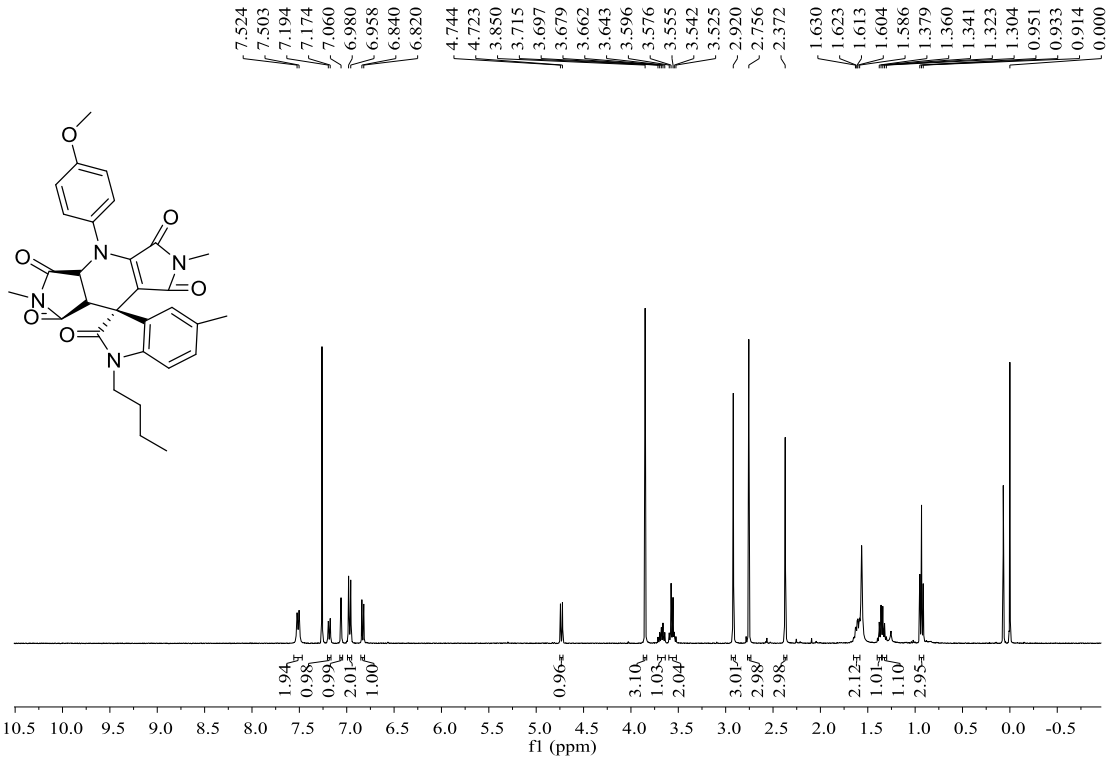
***rel*-(3a*R*,8*R*,8a*S*)-1'-butyl-4-(4-methoxyphenyl)-2,5',6-trimethyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5f**):

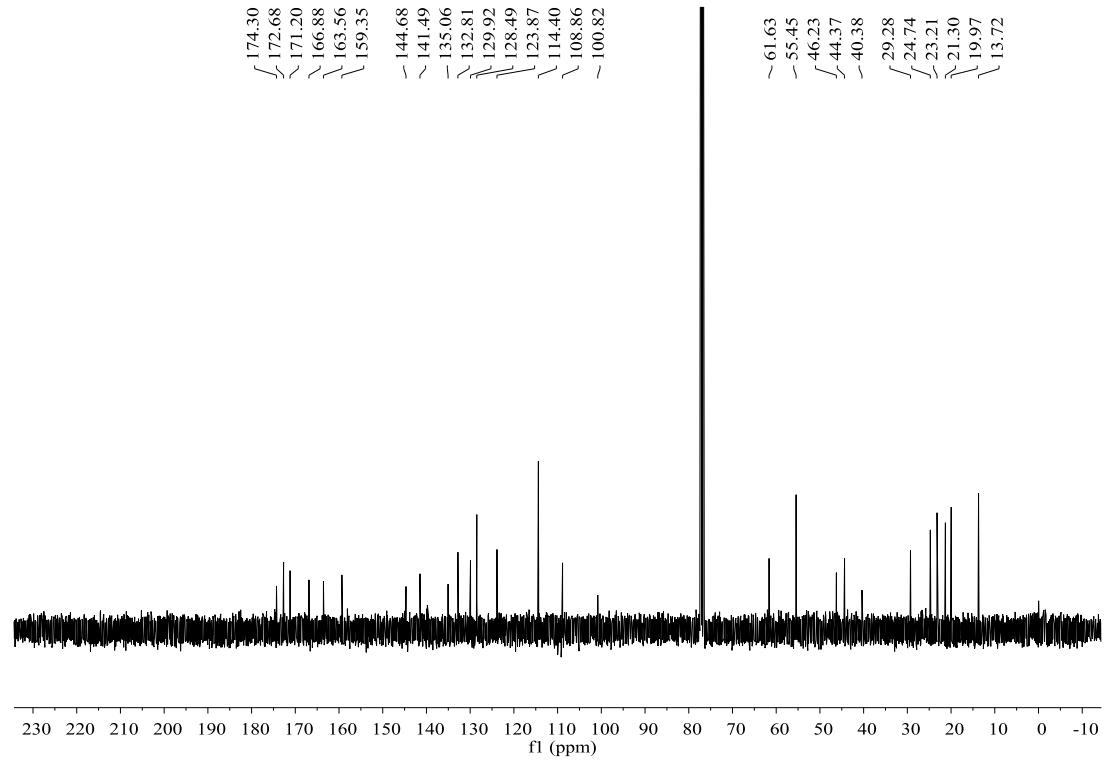


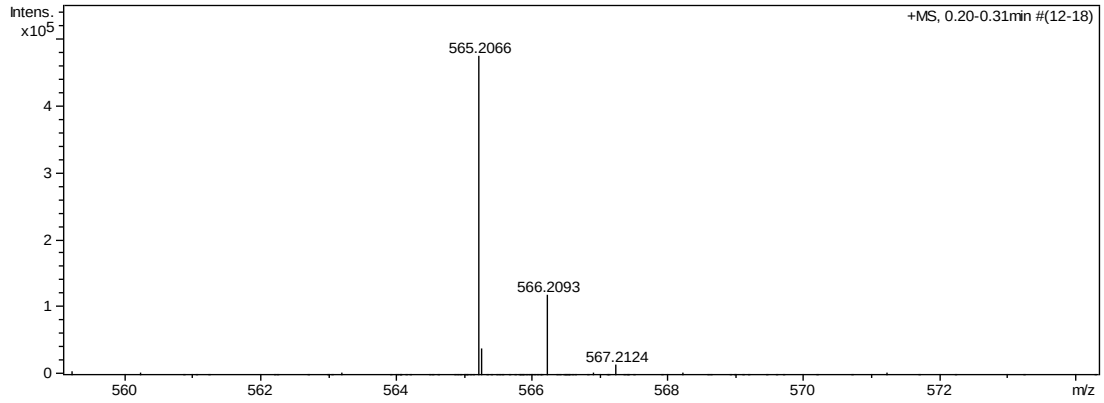

173.31
171.45
169.56
169.02
167.05
157.77
145.98
141.90
139.78
132.71
131.02
129.54
127.47
126.97
125.75
125.40
114.12
108.73
96.44
55.46
51.28
40.50
29.39
23.98
23.78
21.15
20.15
13.68
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.57-0.59min #(34-35)
565.2063
566.2094
567.2126
2.0
1.5
1.0
0.5
0.0
560
562
564
566
568
570
572
m/z

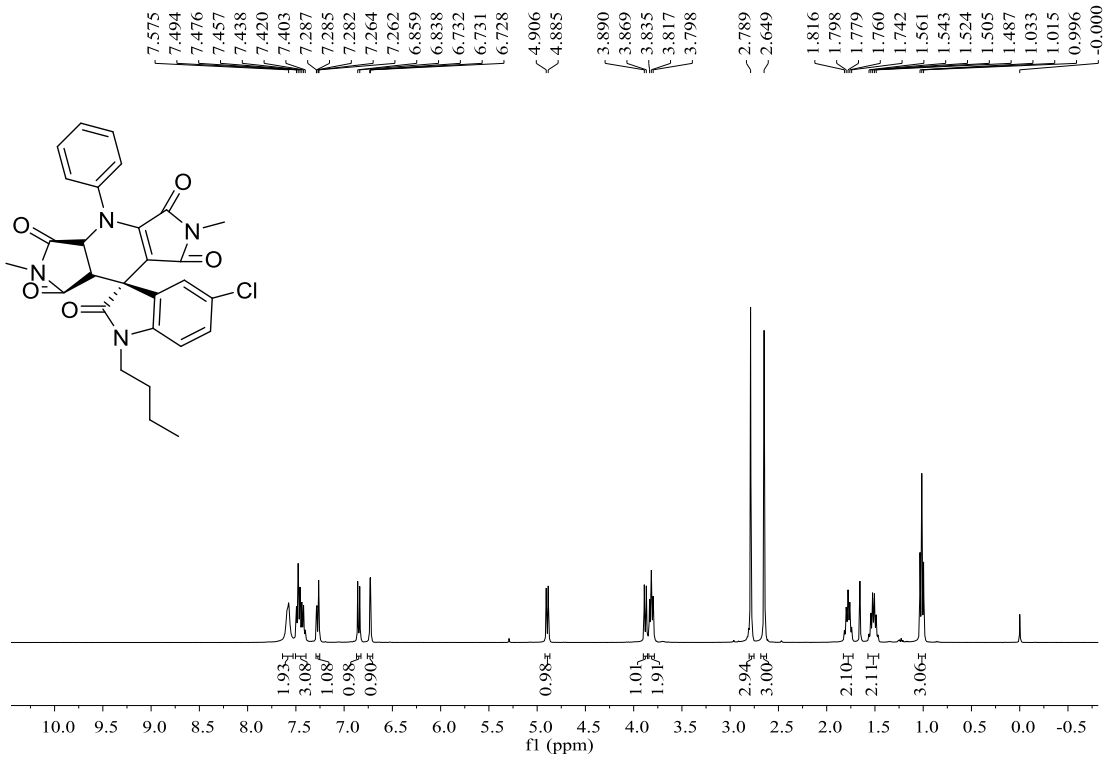
***rel*-(3a*R*,8*S*,8a*S*)-1'-butyl-4-(4-methoxyphenyl)-2,5',6-trimethyl-3a,8a-dihydro-1*H*-spiro [dipyrrolo[3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5f'**):

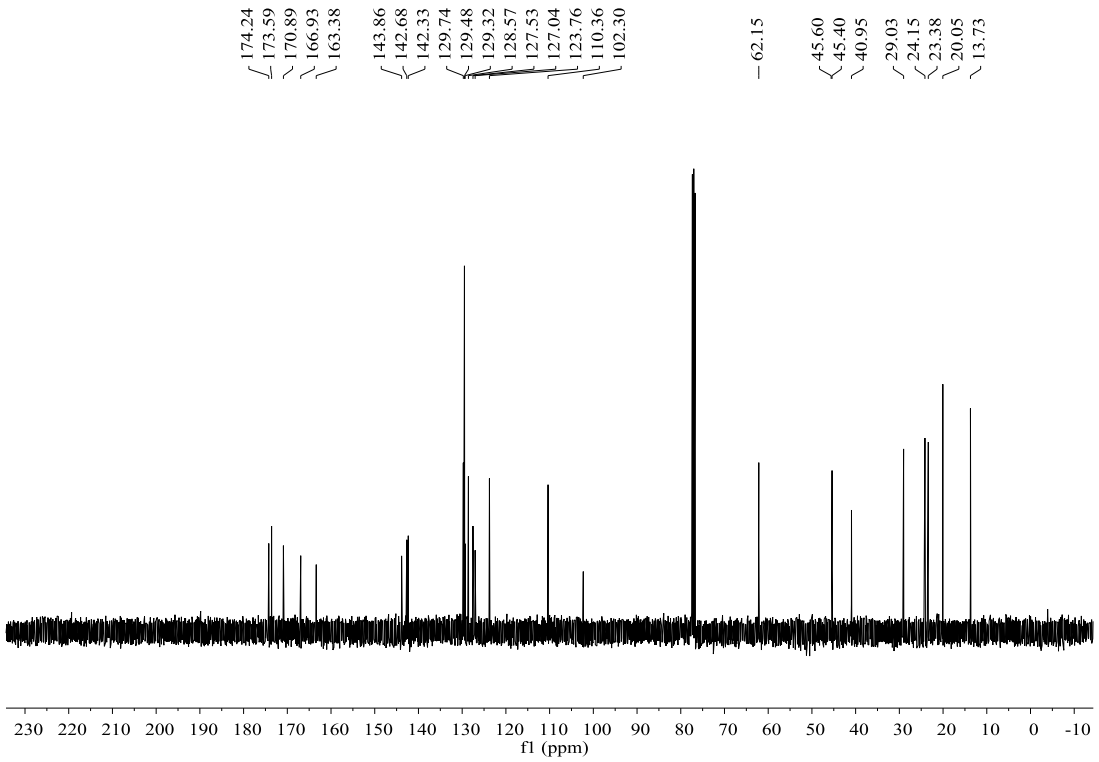


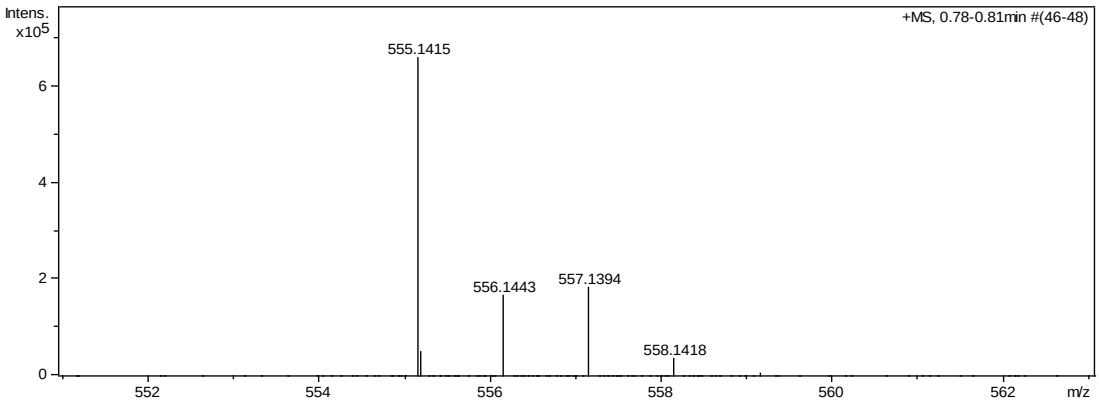




***rel*-(3a*R*,8*S*,8a*S*)-1'-butyl-5'-chloro-2,6-dimethyl-4-phenyl-3a,8a-dihydro-1*H*-spiro[dipyrrolo [3,4-*b*:3',4'-*e*]pyridine-8,3'-indoline]-1,2',3,5,7(2*H*,4*H*,6*H*)-pentaone** (**5g'**):




174.24
173.59
170.89
166.93
163.38
143.86
142.68
142.33
129.74
129.48
129.32
128.57
127.53
127.04
123.76
110.36
102.30
62.15
45.60
45.40
40.95
29.03
24.15
23.38
20.05
13.73
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, 0.78-0.81min #(46-48)
555.1415
556.1443
557.1394
558.1418
0
2
4
6
552
554
556
558
560
562
m/z