Construction of diverse spirooxindoles via domino reaction of arylamines, but-2-ynedioates and 3-hydroxy-3-(indol-3-yl)indolin-2-ones

Ling-Yun Zhu, Jing Sun,* Dan Liu, Chao-Guo Yan*

Supporting Information

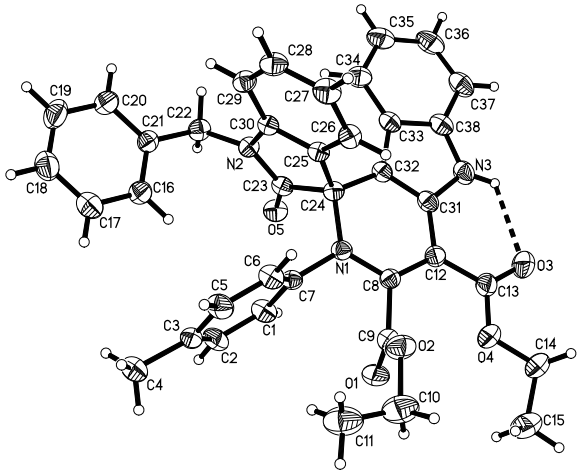


Fig. s1 Single crystal structure of the compound **4e**

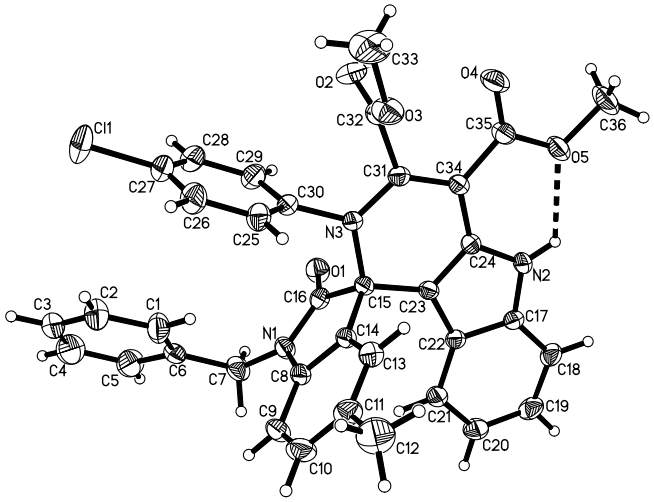


Fig. s2 Single crystal structure of the compound **4k**

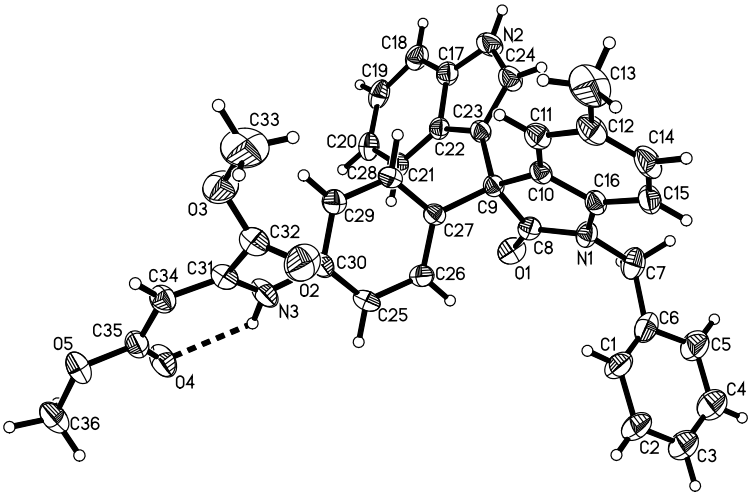


Fig. s3 Single crystal structure of the compound **5b**

Experimental section

1. General procedure for the preparation of spiro[indoline-3,1'-pyrido[4,3-*b*]indol]-2-ones 4a-4o

To a round flask was added arylamine (1.0 mmol), dialkyl but-2-ynedioate (1.0 mmol), and acetonitrile (6.0 mL). The solution was stirred at room temperature for half hour. Then, 3-hydroxy-3-(indol-3-yl)indolin-2-one (1.0 mmol) and iodine (0.3 mmol) was added. The mixture was stirred at 65 ^{o}C for twelve hours. After removing the solvent by rotatory evaporation, the residue was subjected to column chromatography with ethyl acetate and petroleum ether (V/V = 1: 2 to 1:4) as eluent to give the pure product for analysis.

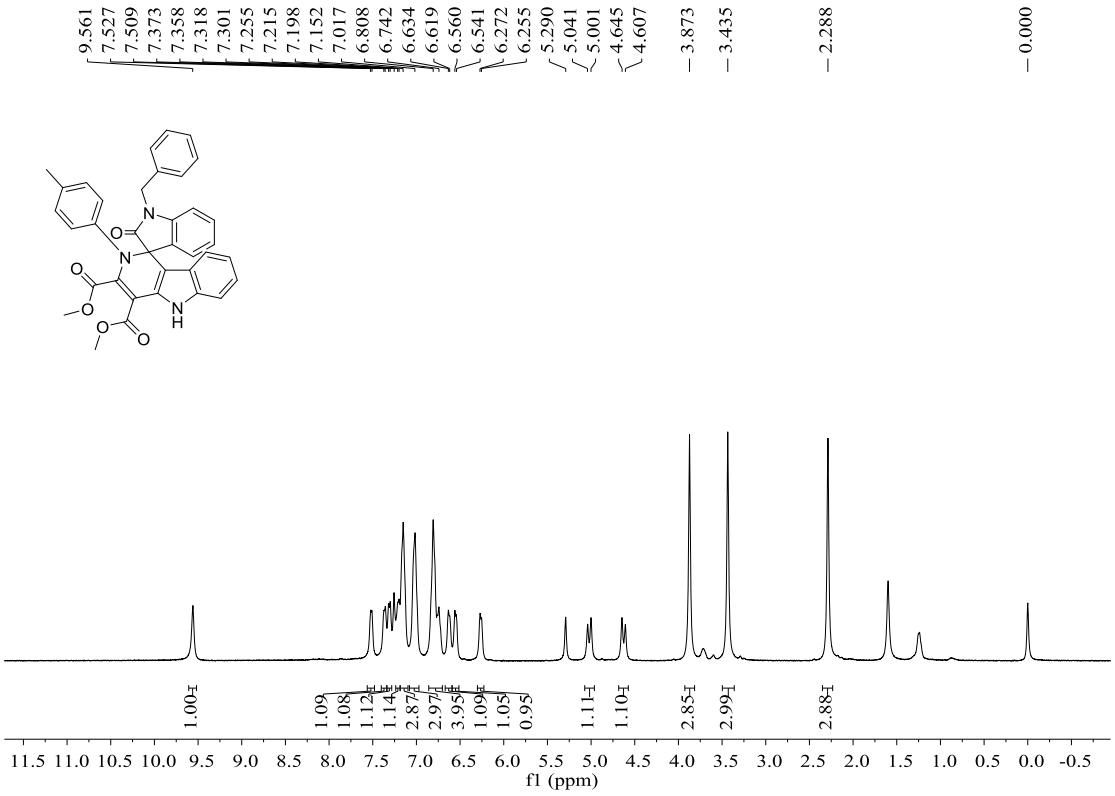
2. General procedure for the preparation of chain compounds 5a-5g

To a round flask was added arylamine (1.0 mmol), dialkyl but-2-ynedioate (1.0 mmol), and acetonitrile (6.0 mL). The solution was stirred at room temperature for half hour. Then, 3-hydroxy-3-(indol-3-yl)indolin-2-one (1.0 mmol) and iodine (0.3 mmol) was added. The mixture was stirred at 65 ^{o}C for twelve hours. After removing the solvent by rotatory evaporation, the residue was subjected to column chromatography with ethyl acetate and petroleum ether (V/V = 1: 2 to 1:4) as eluent to give the pure product for analysis.

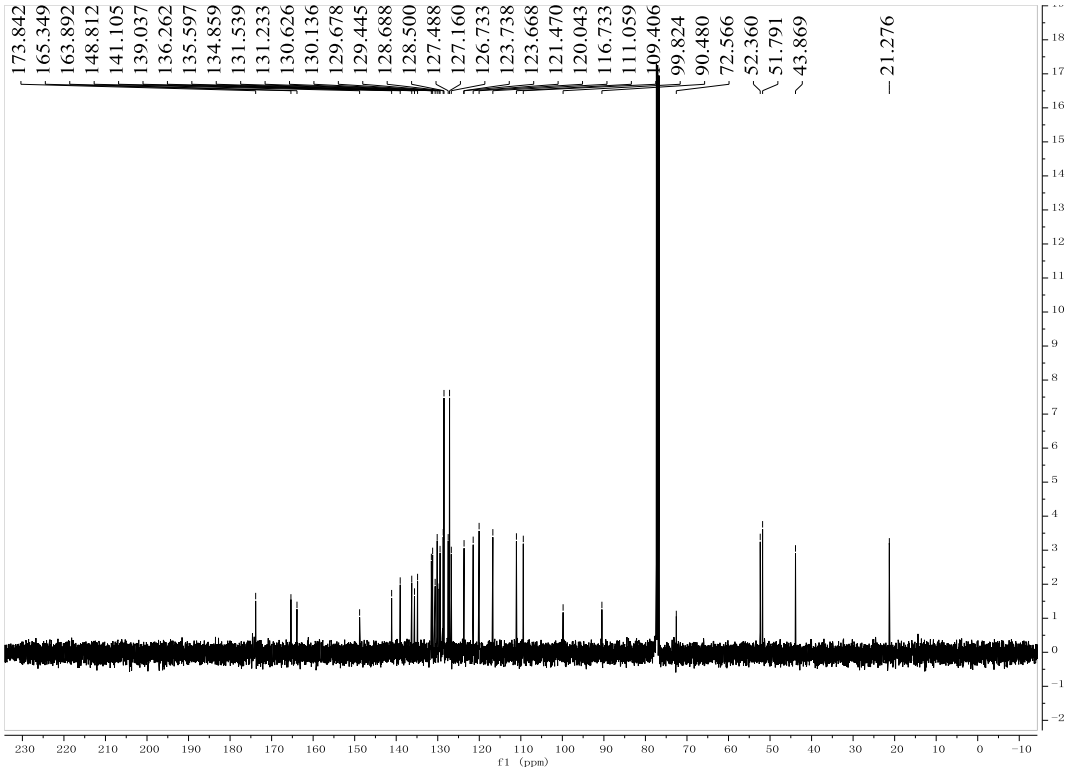
3. General procedure for the preparation of spiro[indoline-3,1'-pyrido[4,3-b]indoles] 6a-6g and spiro[indoline-3,1'-pyrano[4,3-b]indoles] 7a-7g

To a round flask was added benzylamine (1.0 mmol), dialkyl but-2-ynedioate (1.0 mmol), and acetonitrile (6.0 mL). The solution was stirred at room temperature for half hour. Then, 3-hydroxy-3-(indol-3-yl)indolin-2-one (1.0 mmol) and iodine (0.3 mmol) was added. The mixture was stirred at 65 ^{o}C for twelve hours. After removing the solvent by rotatory evaporation, the residue was subjected to column chromatography with ethyl acetate and petroleum ether (V/V = 1: 2 to 1:4) as eluent to give the pure product for analysis.

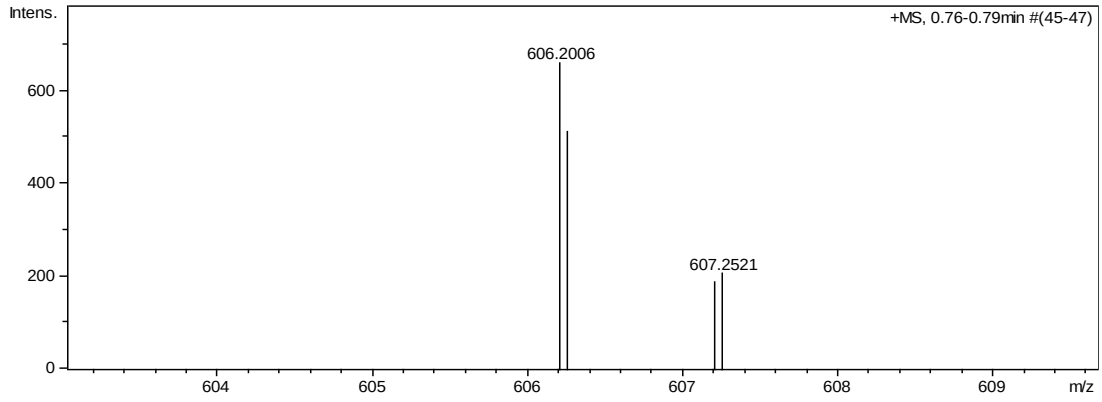
Dimethyl 1-benzyl-2-oxo-2'-(*p*-tolyl)-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (4a): yellow solid, 65%, m.p. 177-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.56 (s, 1H, NH), 7.52 (d, *J* = 7.6 Hz, 1H, ArH), 7.37 (d, *J* = 8.0 Hz, 1H, ArH), 7.31 (d, *J* = 8.0 Hz, 1H, ArH), 7.24-7.20 (m, 1H, ArH), 7.15 (t, *J* = 8.4 Hz, 3H, ArH), 7.03-6.99 (m, 3H, ArH), 6.83-6.79 (m, 3H, ArH), 6.76-6.72 (m, 1H, ArH), 6.63 (d, *J* = 8.0 Hz, 1H, ArH), 6.55 (d, *J* = 8.0 Hz, 1H, ArH), 6.26 (d, *J* = 8.0 Hz, 1H, ArH), 5.02 (d, *J* = 16.0 Hz, 1H, CH), 4.63 (d, *J* = 15.6 Hz, 1H, CH), 3.87 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.8, 165.3, 163.9, 148.8, 141.1, 139.0, 136.3, 135.6, 134.9, 131.5, 131.2, 130.6, 130.1, 129.7, 129.4, 128.7, 128.5, 127.5, 127.2, 126.7, 123.7, 123.7, 121.5, 120.0, 116.7, 111.1, 109.4, 99.8, 90.5, 77.4, 77.0, 76.7, 72.6, 52.4, 51.8, 43.9, 21.3 ppm; IR (KBr) υ: 3411, 3030, 1732, 1712, 1697, 1610, 1585, 1571, 1549, 1507, 1488, 1467, 1433, 1386, 1359, 1331, 1315, 1226, 1178, 1148, 1090, 753 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{29}N_3NaO_5$ ([M+Na]$^+$): 606.2000, Found: 606.2006.



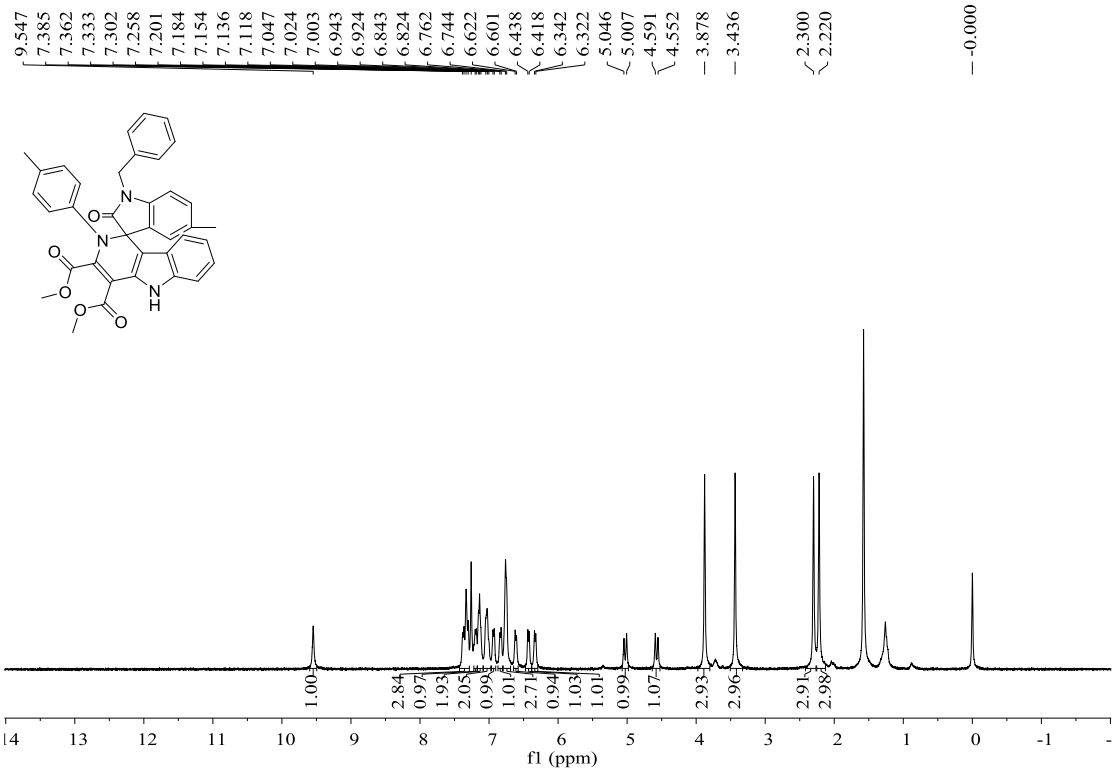
^{1}H NMR (400 MHz, $CDCl_3$)



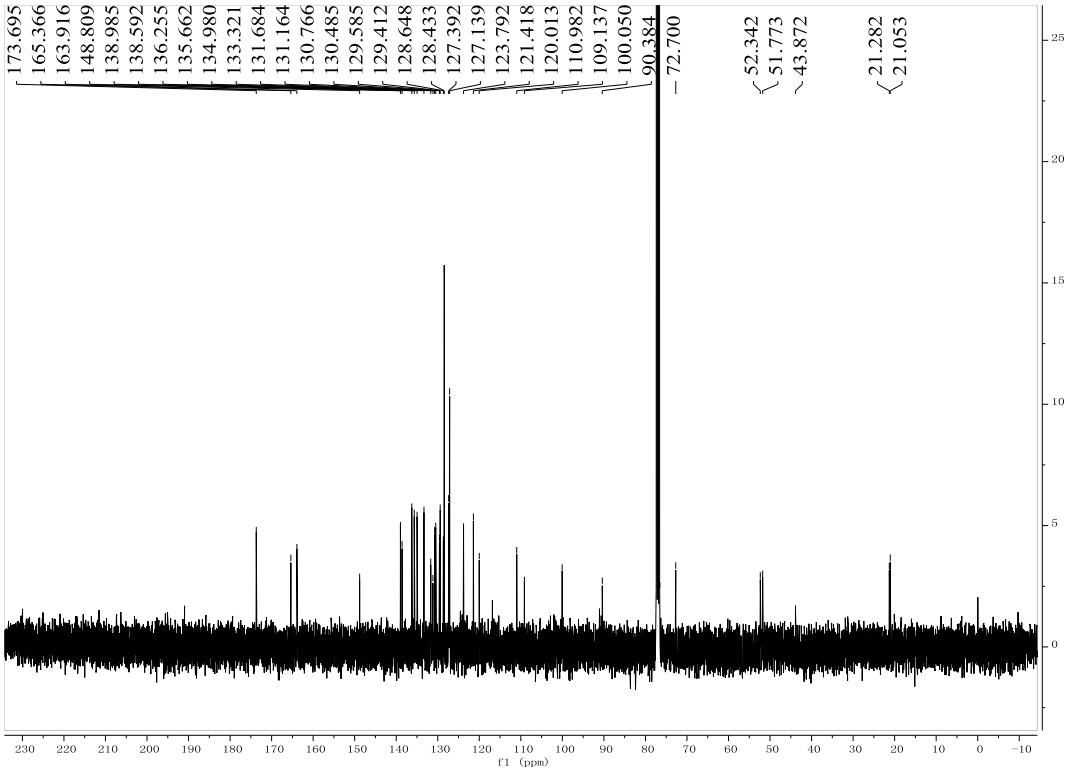
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



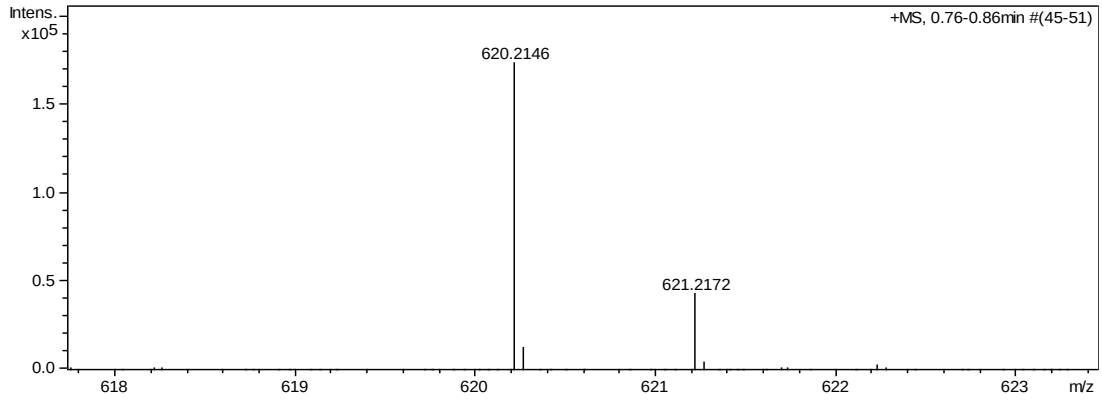
Dimethyl 1-benzyl-5-methyl-2-oxo-2'-(*p*-tolyl)-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*] indole]-3',4'-dicarboxylate (4b): yellow solid, 58%, m.p.186-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.55 (s, 1H, NH), 7.39-7.26 (m, 3H, ArH), 7.19 (d, *J* = 6.8 Hz, 1H, ArH), 7.15-7.14(m, 2H, ArH), 7.05-7.00 (m, 2H, ArH), 6.93 (d, *J* = 7.6 Hz, 1H, ArH), 6.83 (d, *J* = 7.6 Hz, 1H, ArH), 6.75 (d, *J* = 7.2 Hz, 3H, ArH), 6.61 (d, *J* = 8.4 Hz, 1H, ArH), 6.43 (d, *J* = 8.0 Hz, 1H, ArH), 6.33 (d, *J* = 8.0 Hz, 1H, ArH), 5.03 (d, *J* = 15.6 Hz, 1H, CH), 4.57 (d, *J* = 15.6 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3), 2.22 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.7, 165.4, 163.9, 148.8, 139.0, 138.6 136.3, 135.7, 135.0, 133.3, 131.7, 131.2, 130.8, 130.5, 129.6, 129.4, 128.7, 128.4, 127.4, 127.1, 123.8, 121.4, 120.0, 111.0, 109.1, 100.1, 90.4, 77.3, 77.0, 76.7, 72.7, 52.3, 51.8, 43.9, 21.3, 21.1 ppm; IR (KBr) υ: 3416, 1753, 1731, 1711, 1584, 1570, 1552, 1507, 1481, 1423, 1385, 1316, 1211, 1176, 1125, 1093, 1017, 998, 956, 879, 812, 773 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{37}H_{31}N_3NaO_5$ ($[M+Na]^+$): 620.2156, Found: 620.2146.



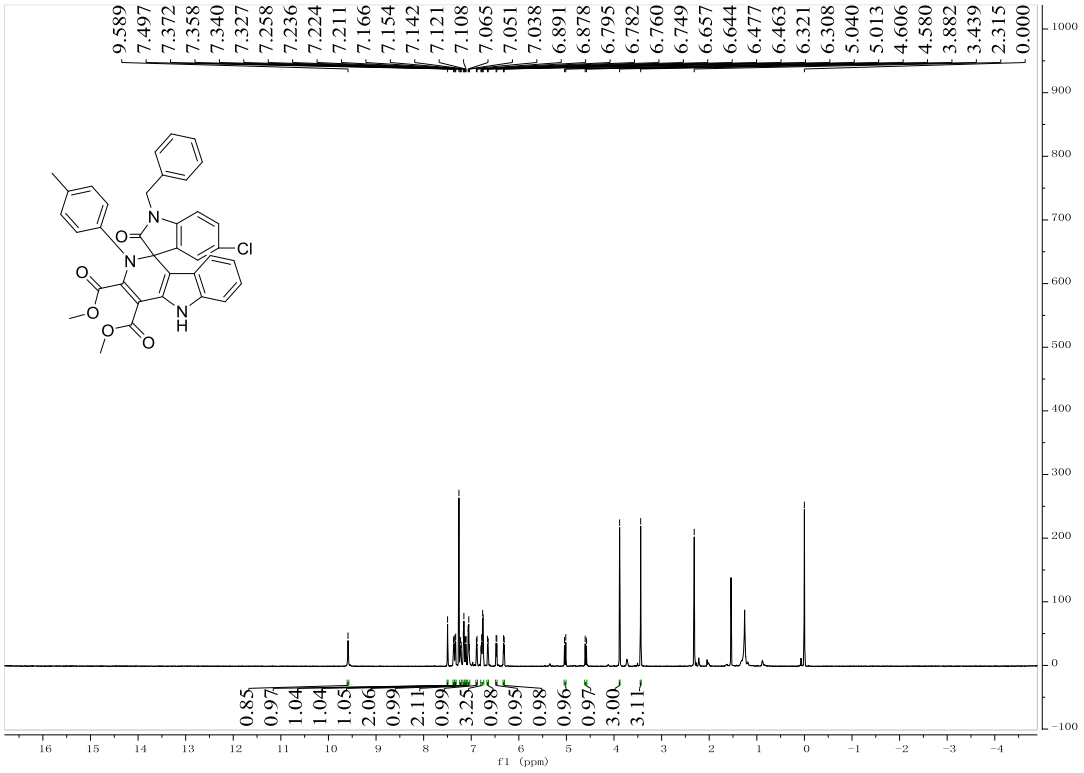
^{1}H NMR (400 MHz, $CDCl_3$)



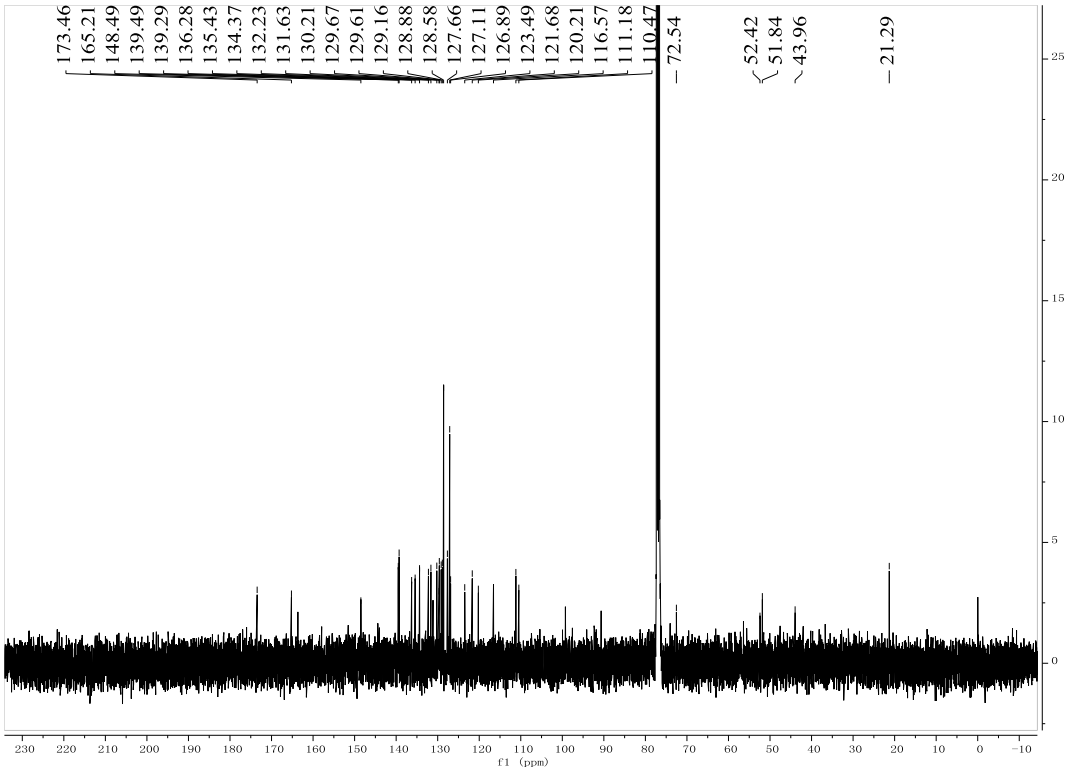
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



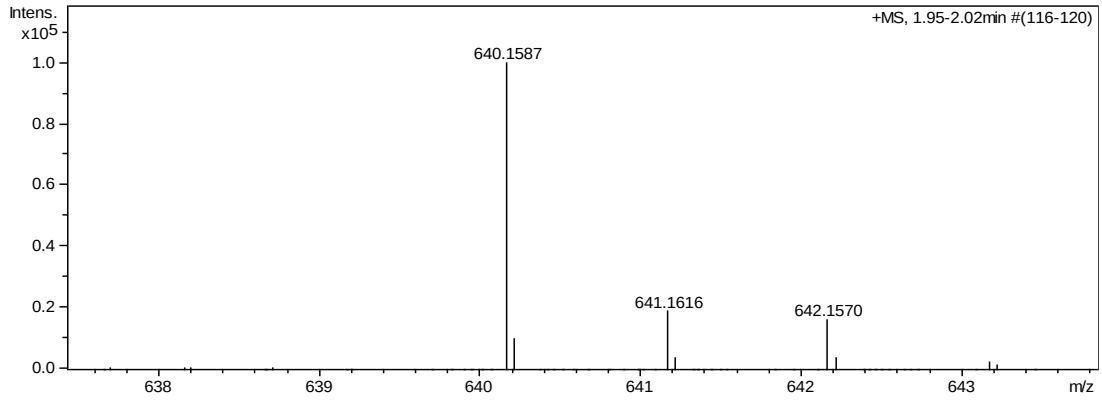
Dimethyl 1-benzyl-5-chloro-2-oxo-2'-(*p*-tolyl)-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (4c): yellow solid, 63%, m.p. 180-184 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.59 (s, 1H, NH), 7.50 (s, 1H, ArH), 7.37 (d, *J* = 8.4 Hz, 1H, ArH), 7.33 (d, *J* = 7.8 Hz, 1H, ArH), 7.22 (d, *J* = 7.2 Hz, 1H, ArH), 7.15 (d, *J* = 7.2 Hz, 1H, ArH), 7.11 (d, *J* = 7.8 Hz, 1H, ArH), 7.07-7.04 (m, 2H, ArH), 6.88 (d, *J* = 7.8 Hz, 1H, ArH), 6.80-6.75 (m, 3H, ArH), 6.65 (d, *J* = 7.8 Hz, 1H, ArH), 6.47 (d, *J* = 8.4 Hz, 1H, ArH), 6.31 (d, *J* = 7.8 Hz, 1H, ArH), 5.03 (d, *J* = 16.2 Hz, 1H, CH), 4.59 (d, *J* = 15.6 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 2.32 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.5, 165.2, 148.5, 139.5, 139.3, 136.3, 135.4, 134.4, 132.2, 131.6, 130.2, 129.7, 129.6, 129.2, 128.9, 128.6, 127.7, 127.1, 126.9, 123.5, 121.7, 120.2, 116.6, 111.2, 110.5, 77.3, 77.0, 76.7, 72.5, 52.4, 51.8, 44.0, 21.3 ppm; IR (KBr) υ: 1744, 1698, 1620, 1571, 1549, 1489, 1436, 1339, 1266, 1222, 1175, 1117, 1031, 812, 786 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{28}ClN_3NaO_5$ ([M+Na]$^+$): 640.1610, Found: 640.1587.



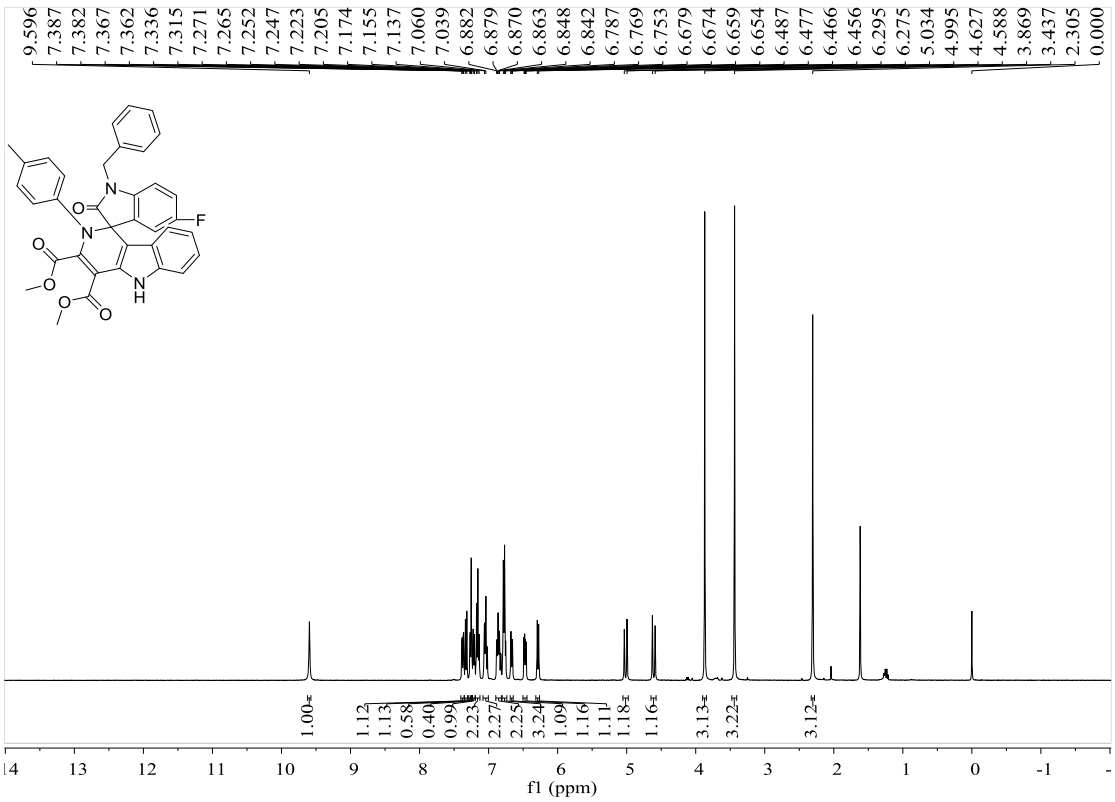
^{1}H NMR (600 MHz, $CDCl_3$)



$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



Dimethyl 1-benzyl-5-fluoro-2-oxo-2'-(*p*-tolyl)-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*] indole]-3',4'-dicarboxylate (4d): yellow solid, 66%, m.p. 291-293 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.60 (s, 1H, NH), 7.38 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, ArH), 7.33 (d, J = 8.4 Hz, 1H, ArH), 7.27-7.25 (m, 1H, ArH), 7.21 (d, J = 7.2 Hz, 1H, ArH), 7.16 (t, J = 7.6 Hz, 2H, ArH), 7.07-7.02 (m, 2H, ArH), 6.88-6.82 (m, 2H, ArH), 6.79-6.75 (m, 3H, ArH), 6.67 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, ArH), 6.47 (dd, J_1 = 8.4 Hz, J_2 = 4.0 Hz, 1H, ArH), 6.29 (d, J = 8.0 Hz, 1H, ArH), 5.01 (d, J = 15.6 Hz, 1H, CH), 4.61(d, J =15.6 Hz, 1H, CH), 3.87 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.4, 165.2, 163.7, 159.7 (d, J = 242.3 Hz), 148.6, 139.3, 137.0 (d, J = 1.9 Hz), 136.3, 135.5, 134.5, 132.1 (d, J = 6.8 Hz), 131.6, 131.1, 129.7, 128.9, 128.6, 127.6, 127.1, 123.6, 121.7, 120.2, 116.8 (d, J = 24.7 Hz), 114.5 (d, J = 24.9 Hz), 111.2, 110.2 (d, J = 7.0 Hz), 99.4, 90.7, 77.3, 77.0, 76.7, 72.7, 52.4, 51.9, 44.1, 21.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -118.4 ppm; IR (KBr) υ: 3430, 1732, 1618, 1585, 1569, 1508, 1489, 1454, 1435, 1362, 1332, 1261, 1216, 1176, 1084, 813, 788 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{28}FN_3NaO_5$ ([M+Na]$^{+}$): 624.1906, Found: 624.1892.



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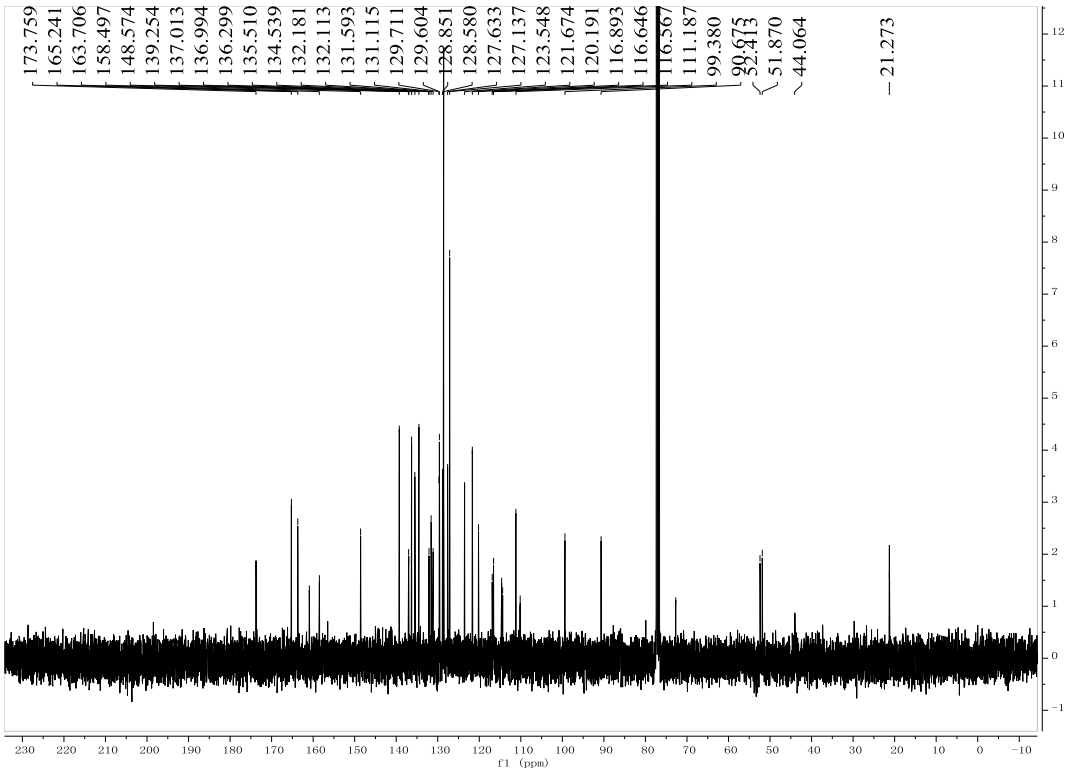

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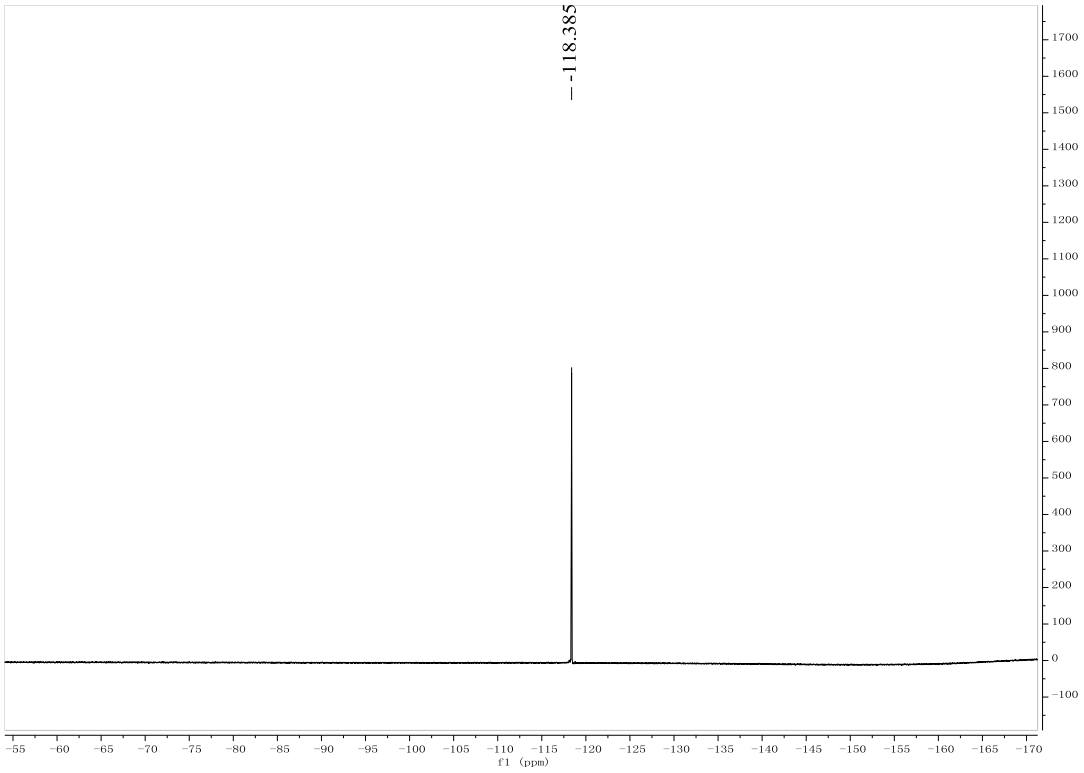
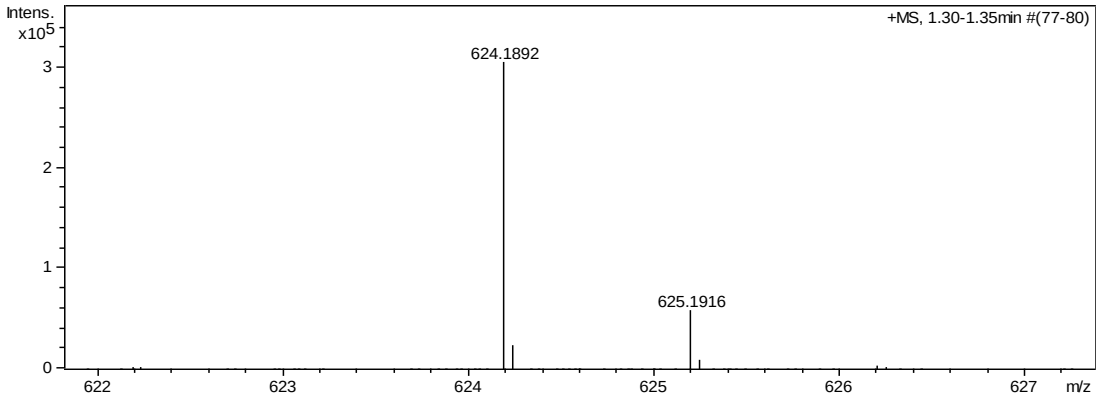


^{19}F NMR (376 MHz, $CDCl_3$)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3
2
1
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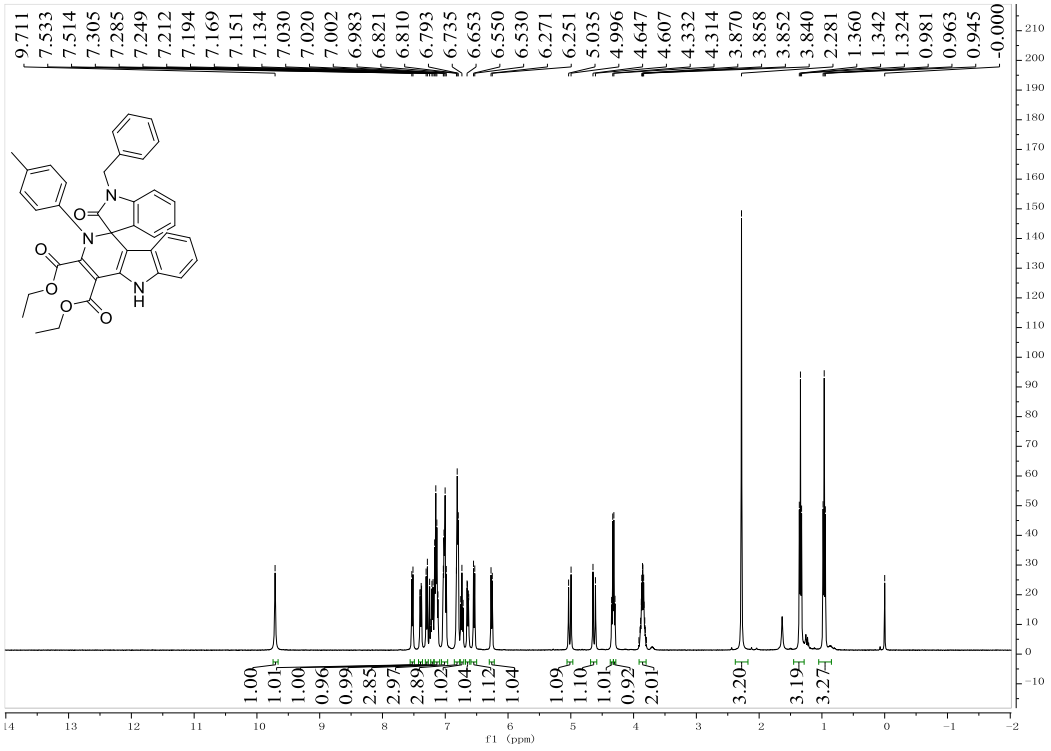
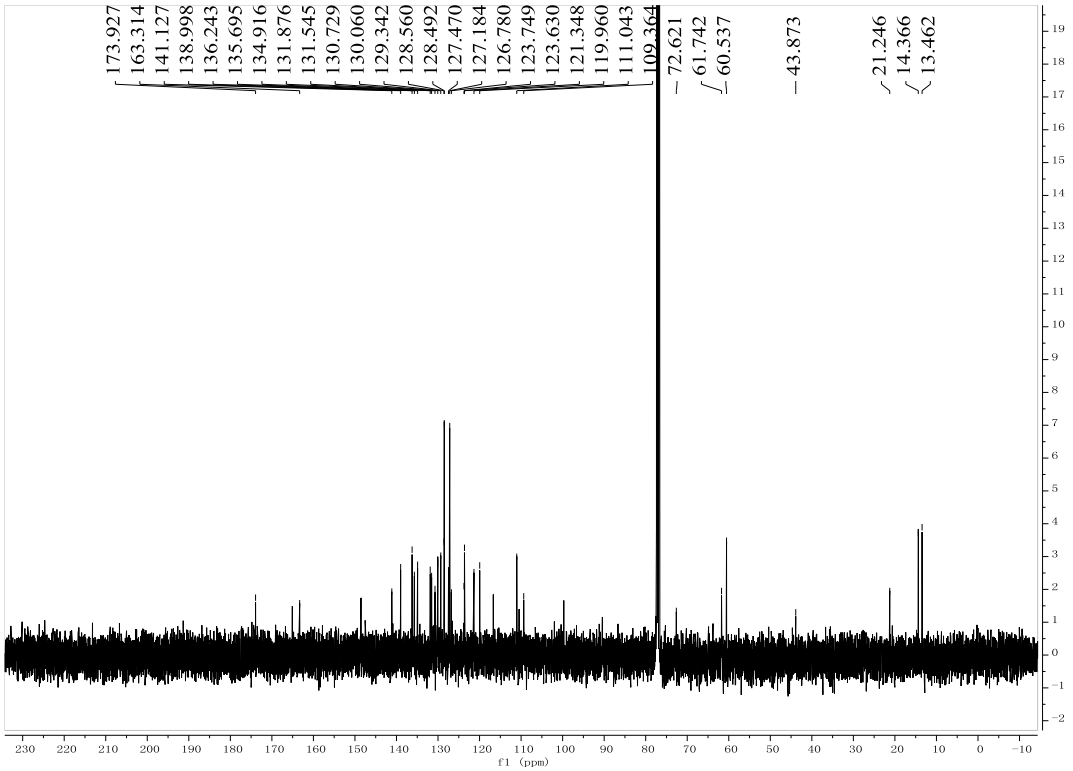
622
623
624
625
626
627
m/z

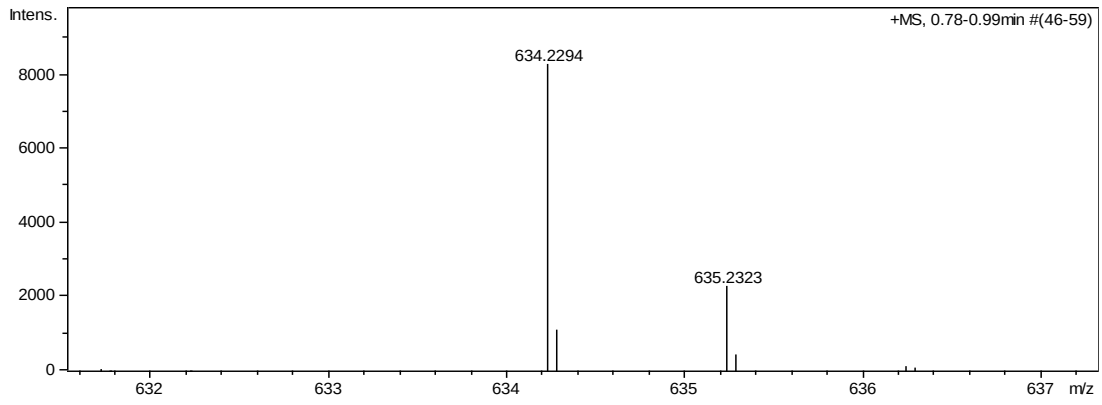
Diethyl 1-benzyl-2-oxo-2'-(*p*-tolyl)-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (4e): yellow solid, 58%, m.p. 223-228 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.71 (s, 1H, NH), 7.52 (d, *J* = 7.6 Hz, 1H, ArH), 7.39 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, ArH), 7.30 (d, *J* = 8.0 Hz, 1H, ArH), 7.23-7.19 (m, 1H, ArH), 7.17-7.12 (m, 3H, ArH), 7.00-6.98 (m, 3H, ArH), 6.82-6.79 (m, 3H, ArH), 6.74 (t, *J* = 7.6 Hz, 1H, ArH), 6.64 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.40 (d, *J* = 8.0 Hz, 1H, ArH), 6.26 (d, *J* = 8.0 Hz, 1H, ArH), 5.02 (d, *J* = 15.6 Hz, 1H, CH), 4.63 (d, *J* = 15.6 Hz, 1H, CH), 4.34 (d, *J* = 7.2 Hz, 1H, CH), 4.31 (d, *J* = 7.2 Hz, 1H, CH), 3.92-3.80 (m, 2H, ArH), 2.28 (s, 3H, CH_3), 1.34 (t, *J* = 7.2 Hz, 3H, CH_3), 0.96 (t, *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.9, 163.3, 141.1, 139.0, 136.2, 135.7, 134.9, 131.9, 131.6, 130.7, 130.1, 129.3, 128.6, 128.5, 127.5, 127.2, 126.8, 123.8, 123.6, 121.4, 1120.0, 111.0, 109.4, 77.3, 77.2, 76.7, 72.6, 61.7, 60.5, 43.7, 21.3, 14.4, 13.5 ppm; IR (KBr) υ: 3424, 1739, 1715, 1676, 1609, 1592, 1558, 1509, 1486, 1468, 1375, 1351, 1325, 1245, 1209, 1183, 1118, 1082, 1022, 974, 857, 807, 763 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{33}N_3NaO_5$ ([M+Na]$^{+}$): 634.2313, Found: 634.2294.



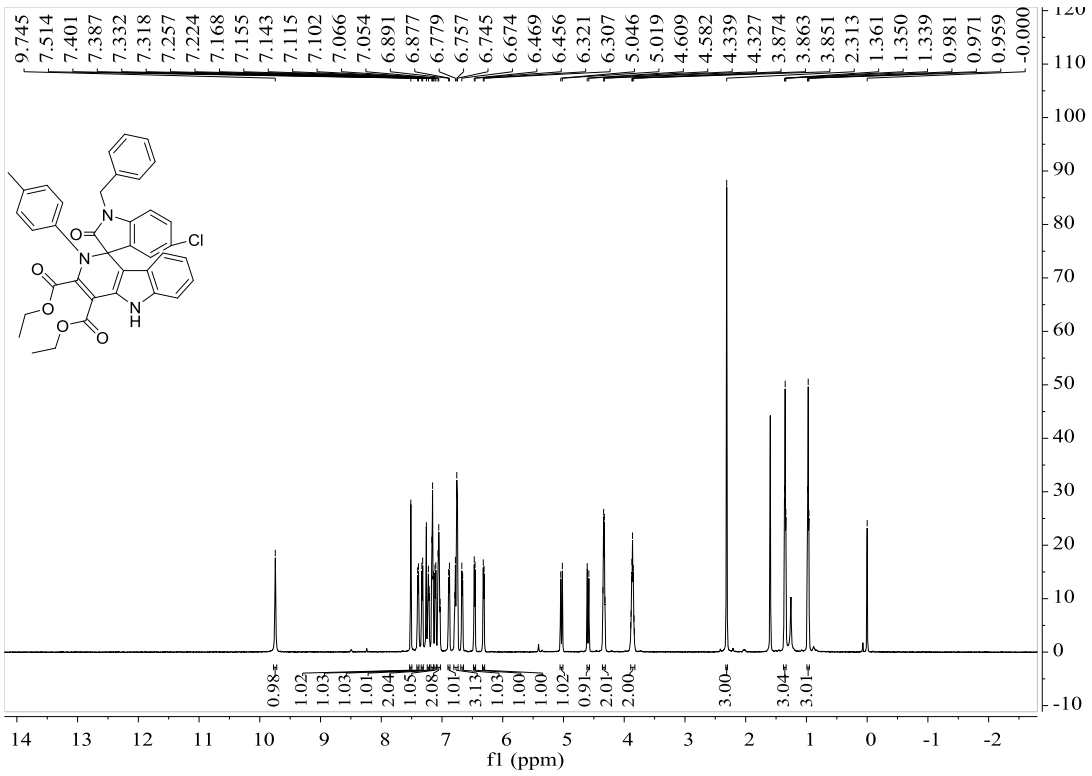
^{1}H NMR (400 MHz, $CDCl_3$)



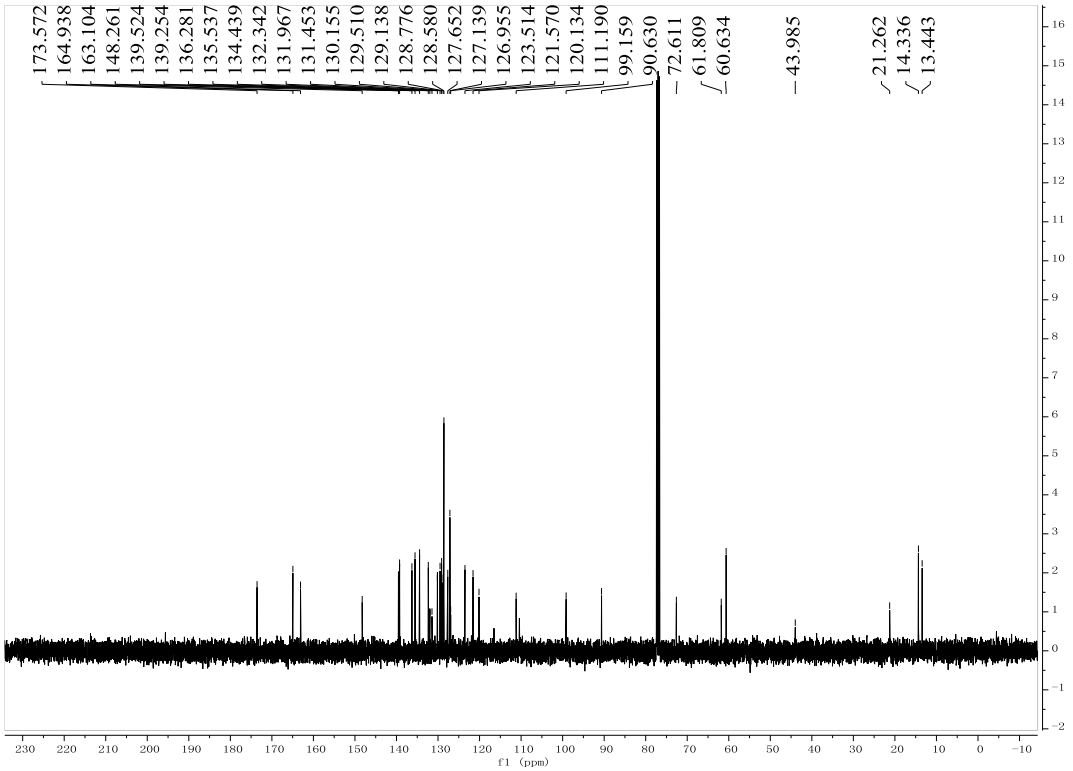
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



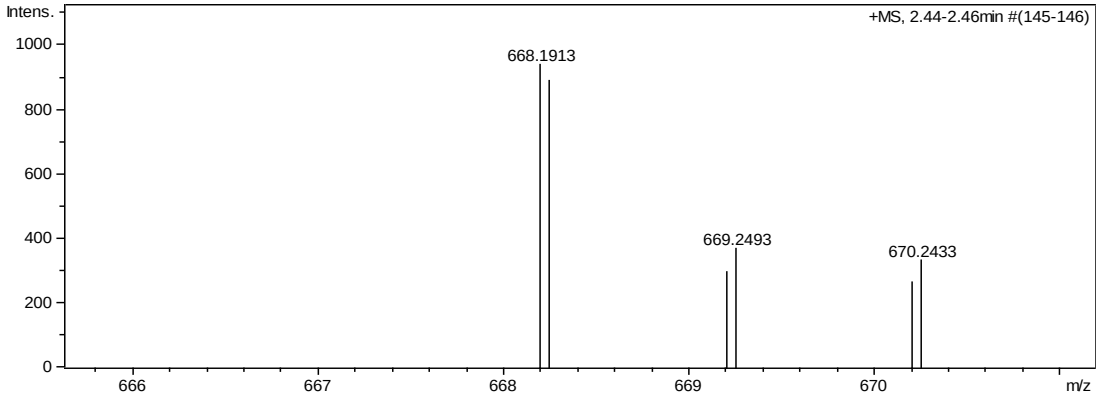
Diethyl 1-benzyl-5-chloro-2-oxo-2'-(*p*-tolyl)-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*] indole]-3',4'-dicarboxylate (4f): yellow solid, 57%, m.p. 228-232°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.75 (s, 1H, NH),7.51 (s, 1H, ArH), 7.39 (d, *J* = 8.4 Hz, 1H, ArH), 7.33 (d, *J* = 8.4 Hz, 1H, ArH), 7.22-7.21 (m 1H, ArH), 7.17-7.14 (m, 2H, ArH), 7.11 (d, *J* = 7.8 Hz, 1H, ArH), 7.07-7.03 (m, 2H, ArH), 6.88 (d, *J* = 8.4 Hz, 1H, ArH), 6.79-6.75 (m, 3H, ArH), 6.67 (d, *J* = 8.4 Hz, 1H, ArH), 6.46 (d, *J* = 7.8 Hz, 1H, ArH), 6.31 (d, *J* = 8.4 Hz, 1H, ArH), 5.03 (d, *J* = 16.2 Hz, 1H, CH), 4.60 (d, *J* = 16.2 Hz, 1H, CH), 4.35-4.32 (m, 2H, CH), 3.89-3.83 (m, 2H, CH), 2.31 (s, 3H, CH_3), 1.35 (t, *J* = 6.6 Hz, 3H, CH_3), 0.97 (t, *J* = 6.6 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.6, 164.9, 163.1, 148.3, 139.5, 139.3, 136.3, 135.5, 134.4, 132.3, 132.0, 131.5, 130.2, 129.5, 129.1, 128.8, 128.6, 127.7, 127.1, 127.0, 123.5, 121.6, 120.1, 111.2, 99.2, 90.6, 77.3, 77.0, 76.7, 72.6, 61.8, 60.6, 44.0, 21.3, 14.3, 13.4 ppm; IR (KBr) υ: 3469, 3264, 3061, 1729, 1548, 1477, 1310, 1210, 1088, 976 , 924 , 890, 860, 845, 818, 773 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{32}ClN_3NaO_5$ ([M+Na]$^+$): 668.1923, Found: 668.1913.



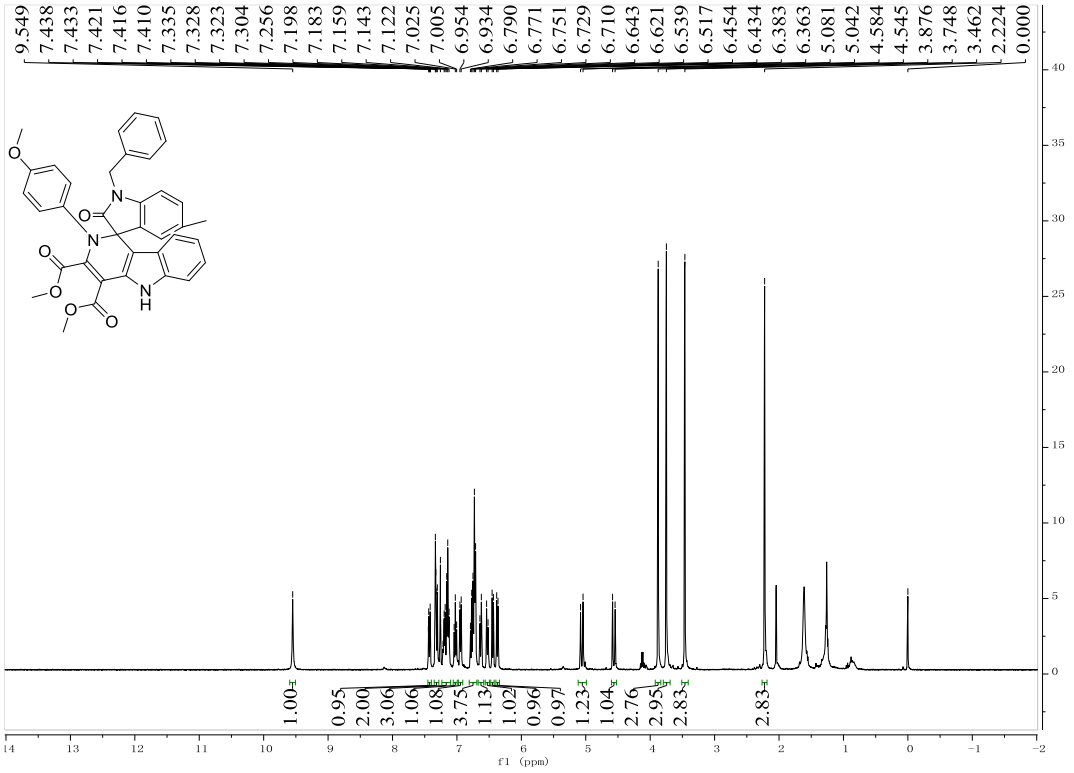
^{1}H NMR (600 MHz, $CDCl_3$)



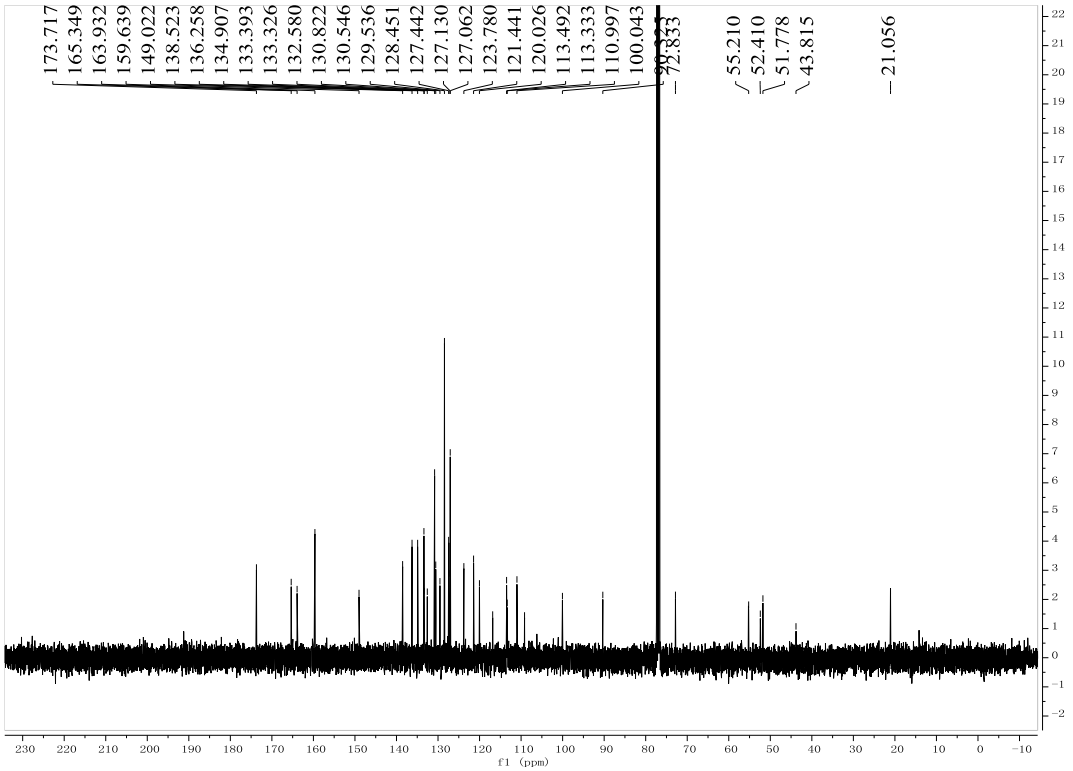
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



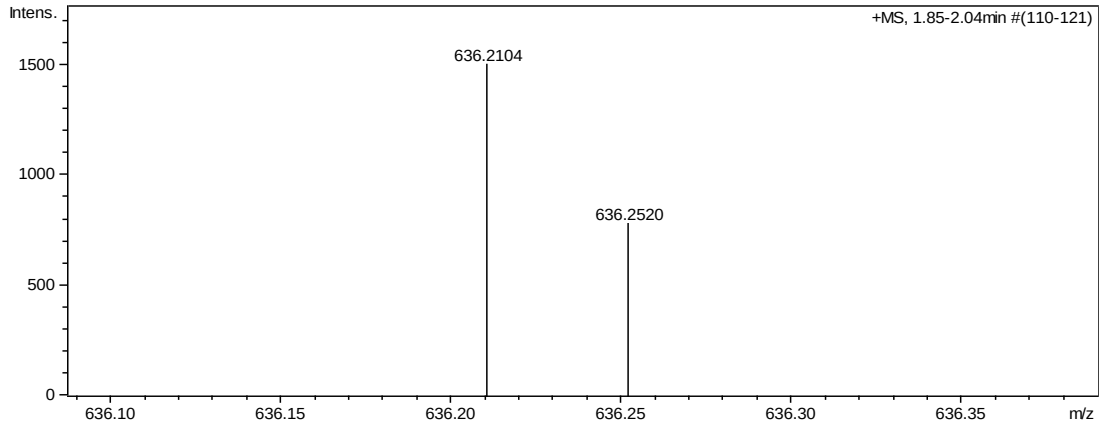
Dimethyl 1-benzyl-2'-(4-methoxyphenyl)-5-methyl-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (4g): yellow solid, 59%, m.p. 280-284 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.55 (s, 1H, NH), 7.44-7.41 (m, 1H, ArH), 7.34-7.30 (m, 2H, ArH), 7.22-7.12 (m, 3H, ArH), 7.03 (d, *J* = 7.6 Hz, 1H, ArH), 6.94 (d, *J* = 8.0 Hz, 1H, ArH), 6.79-6.71 (m, 4H, ArH), 6.63 (d, *J* = 8.8 Hz, 1H, ArH), 6.44 (d, *J* = 8.0 Hz, 1H, ArH), 6.37 (d, *J* = 8.0 Hz, 1H, ArH), 5.06 (d, *J* = 15.6 Hz, 1H, CH), 4.56 (d, *J* = 15.6 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 2.22 (s, 3H, CH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.7, 165.4, 163.9, 159.6, 149.0, 138.5, 136.3, 134.9, 133.4, 133.3, 132.6, 130.8, 130.6, 129.5, 128.5, 127.4, 127.1, 127.1, 123.8, 121.4, 120.0, 116.8, 113.5, 113.3, 111.0, 109.2, 100.0, 90.3, 77.3, 77.0, 76.7, 72.8, 55.2, 52.4, 51.8, 43.8, 21.1 ppm; IR (KBr) υ: 3420, 3063, 2836, 1729, 1603, 1569, 1508, 1422, 1385, 1316, 1177, 1092, 955, 878, 837, 813, 772 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{37}H_{31}N_3NaO_6$ ([M+Na]$^{+}$): 636.2106, Found: 636.2104.



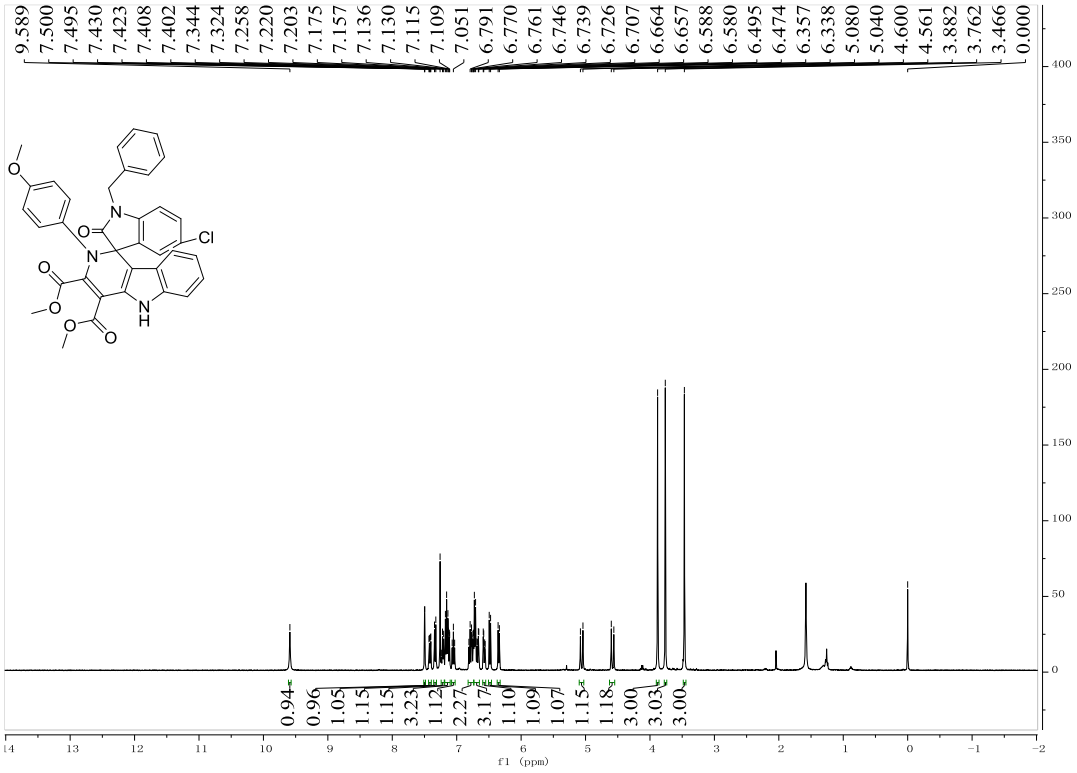
^{1}H NMR (400 MHz, $CDCl_3$)



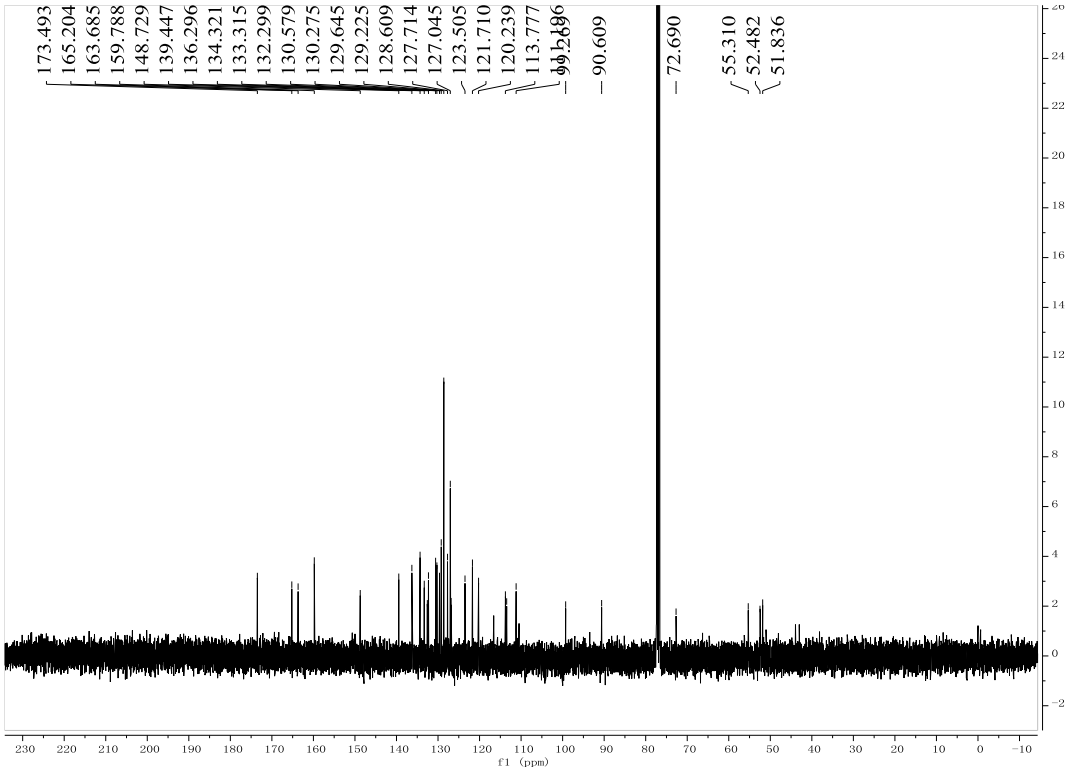
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



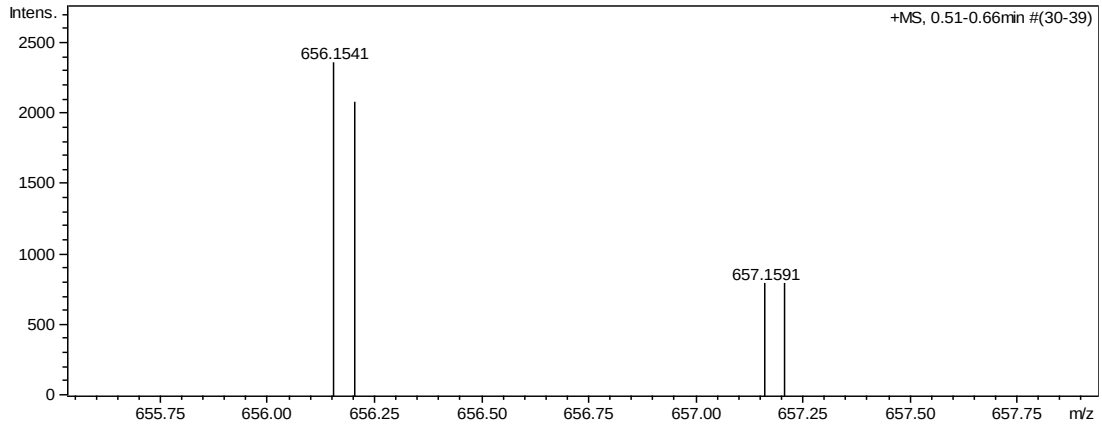
Dimethyl 1-benzyl-5-chloro-2'-(4-methoxyphenyl)-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (4h): yellow solid, 60%, m.p. 244-248 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.59 (s, 1H, NH), 7.50 (d, J = 2.0 Hz, 1H, ArH), 7.41 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 7.33 (d, J = 8.0 Hz, 1H, ArH), 7.24-7.20 (m, 1H, ArH), 7.17-7.11 (m, 3H, ArH), 7.05 (t, J = 7.6 Hz, 1H, ArH), 6.81-6.74 (m, 2H, ArH), 6.73-6.66 (m, 3H, ArH), 6.57 (dd, J_1 = 8.8 Hz, J_2 = 3.2 Hz, 1H, ArH), 6.48 (d, J = 8.4 Hz, 1H, ArH), 6.35 (d, J = 7.6 Hz, 1H, ArH), 5.06 (d, J = 16.0 Hz, 1H, CH), 4.58 (d, J = 15.6 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3) , 3.47 (s, 3H, OCH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.5, 165.2, 163.7, 159.8, 148.7, 139.5, 136.3, 134.3, 133.3, 132.6, 132.3, 130.6, 130.3, 129.6, 129.2, 128.6, 127.7, 127.1, 126.8, 123.5, 121.7, 120.2, 113.8, 113.5, 111.2, 99.3, 90.6, 72.7, 55.3, 52.5, 51.8 ppm; IR (KBr) υ: 3423, 1732, 1605, 1585, 1569, 1508, 1480, 1432, 1315, 1223, 1176, 1120, 1082, 1028, 909, 812, 776 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{28}ClN_3NaO_6$ ([M+Na]$^{+}$): 656.1559, Found: 656.1541.



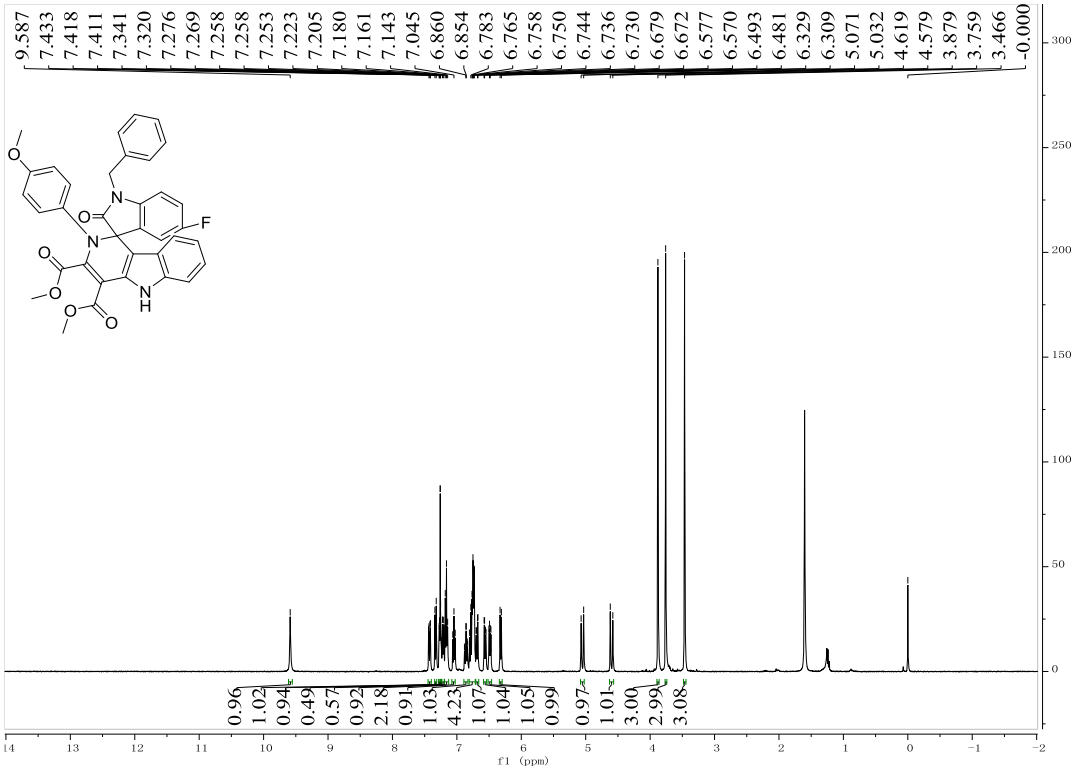
^{1}H NMR (400 MHz, $CDCl_3$)



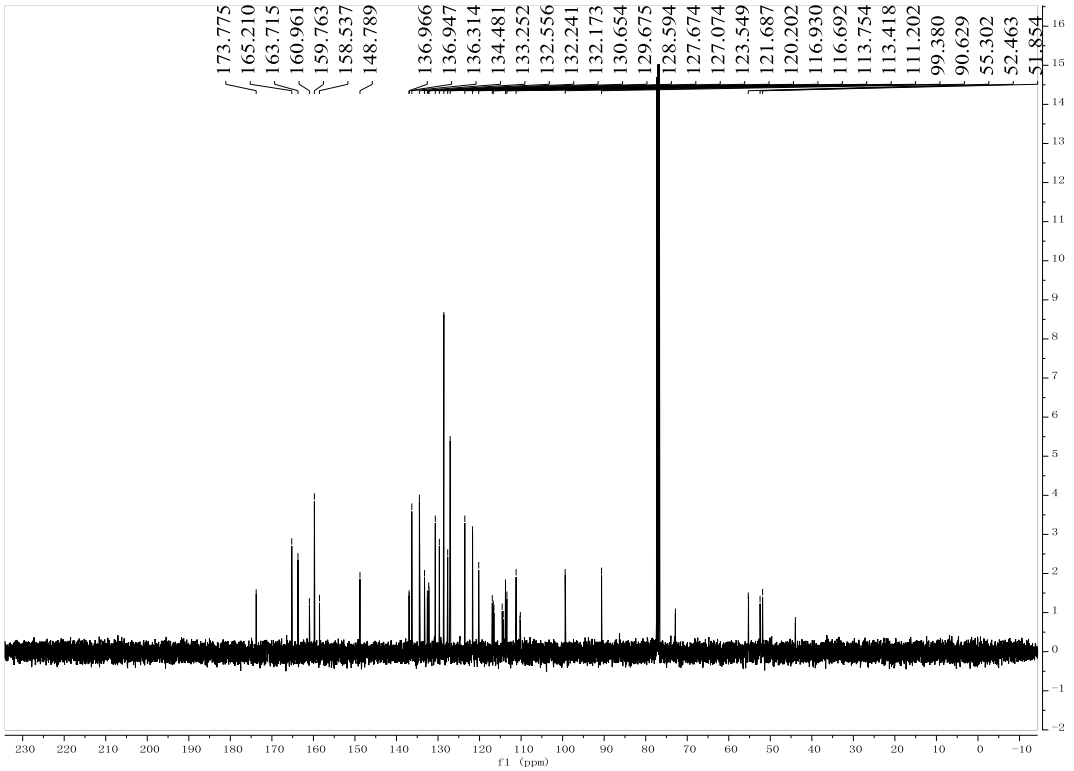
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



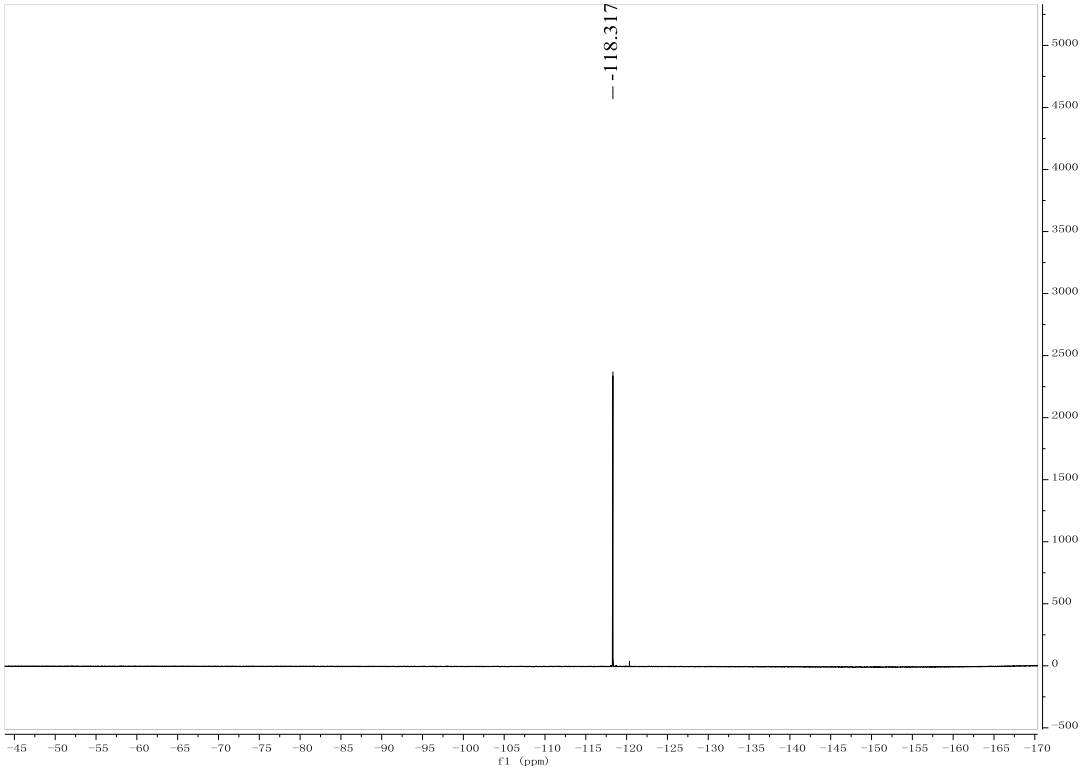
Dimethyl 1-benzyl-5-fluoro-2'-(4-methoxyphenyl)-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (4i): yellow solid, 60%, m.p. 233-236 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.59 (s, 1H, NH), 7.43 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 7.33 (d, J = 8.4 Hz, 1H, ArH), 7.28-7.24 (m, 1H, ArH), 7.21 (d, J = 7.2 Hz, 1H, ArH), 7.16 (t, J = 7.6 Hz, 2H, ArH), 7.05 (t, J = 7.6 Hz, 1H, ArH), 6.86 (td, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.80-6.73 (m, 4H, ArH), 6.69 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.56 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 6.49 (dd, J_1 = 8.8 Hz, J_2 = 4.0 Hz, 1H, ArH), 5.05 (d, J = 15.6 Hz, 1H, CH), 4.60 (d, J = 16.0 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.8, 165.2, 163.7, 161.0, 159.7 (d, J = 242.4 Hz), 148.8, 136.9 (d, J = 1.9 Hz), 136.3, 134.5, 133.3, 132.6, 132.2 (d, J = 6.8 Hz), 130.7, 129.7, 128.6, 127.7, 127.1, 123.6, 121.7, 120.2, 116.8 (d, J = 23.8 Hz), 114.4 (d, J = 25.0 Hz), 113.8, 113.4, 111.2,110.2 (d, J = 9.0 Hz), 99.4, 90.6, 77.4, 77.0, 76.7, 72.9, 55.3, 52.5, 51.9, 44.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -118.3 ppm; IR (KBr) υ: 3441, 1727, 1672, 1589, 1551, 1489, 1453, 1326, 1259, 1178, 1111, 1081, 1029, 944, 839, 826, 814, 789 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{28}FN_3NaO_6$ ([M+Na]$^{+}$): 640.1855, Found: 640.1838.



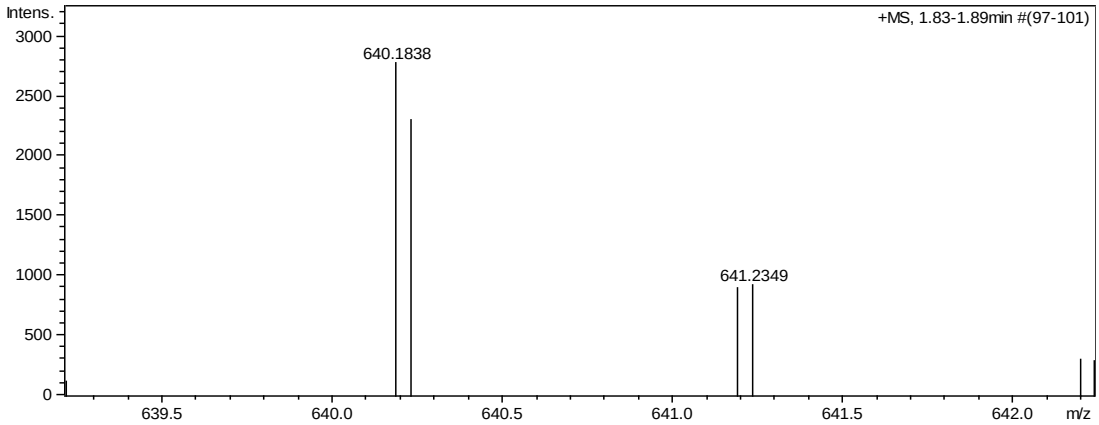
^{1}H NMR (400 MHz, $CDCl_3$)



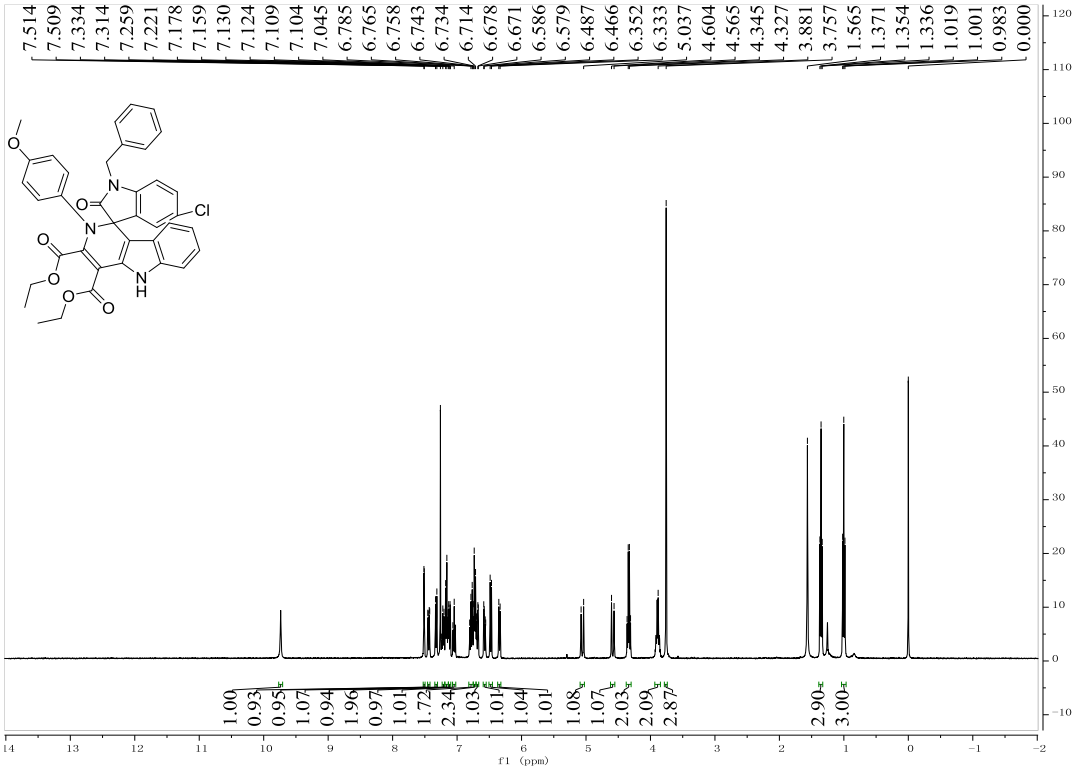
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



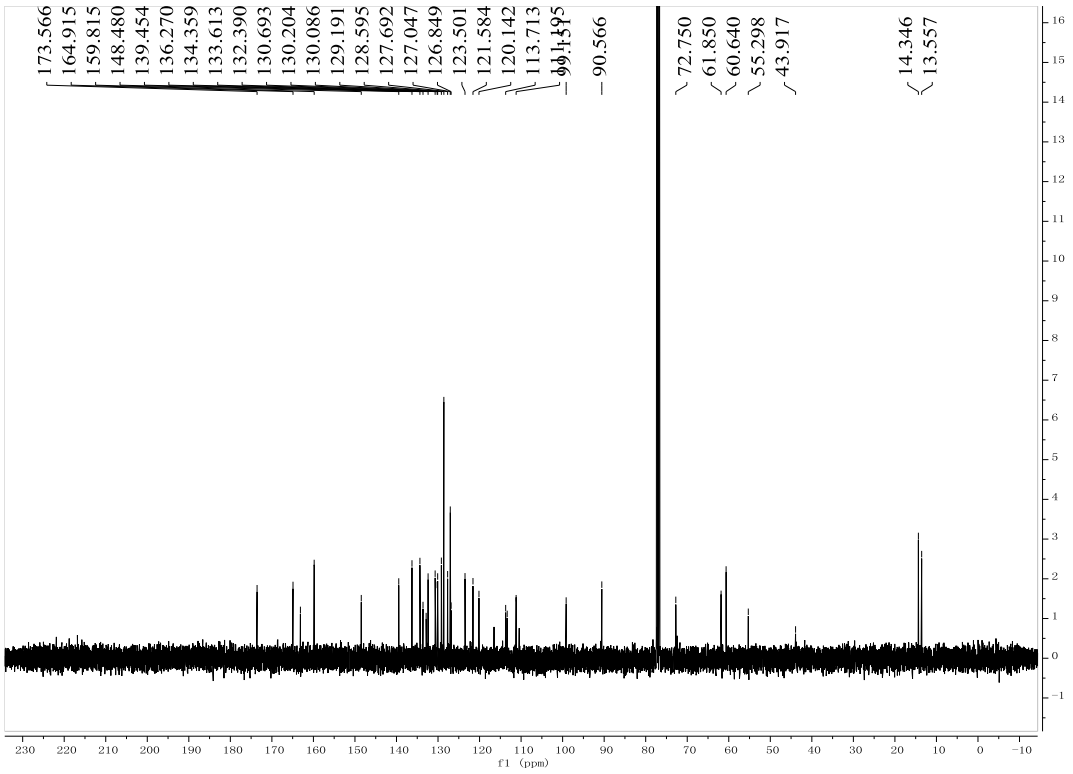
^{19}F NMR (376 MHz, $CDCl_3$)


Intens.
+MS, 1.83-1.89min #(97-101)
3000
2500
2000
1500
1000
500
0
640.1838
641.2349
639.5
640.0
640.5
641.0
641.5
642.0
m/z

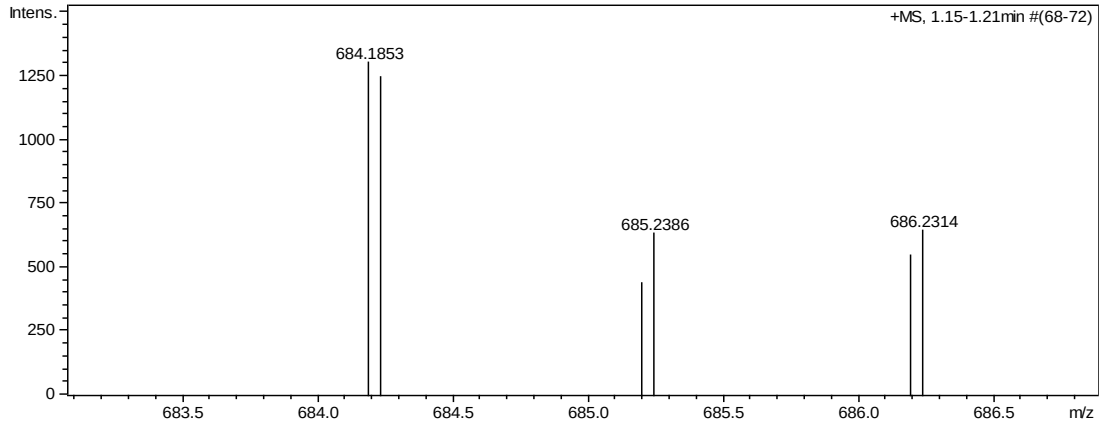
Diethyl 1-benzyl-5-chloro-2'-(4-methoxyphenyl)-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (4j): yellow solid, 59%, m.p. 218-223°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.74 (s, 1H, NH),7.51 (d, *J* = 2.0 Hz, 1H, ArH), 7.44 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 7.32 (d, *J* = 8.4 Hz, 1H, ArH), 7.22-7.20 (m, 1H, ArH), 7.18-7.14 (m, 2H, ArH), 7.12 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.06-7.02 (m, 1H, ArH), 6.80-6.74 (m, 2H, ArH), 6.72 (d, *J* = 7.2 Hz, 2H, ArH), 6.69 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 6.57 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 6.48 (d, *J* = 8.4 Hz, 1H, ArH), 6.34 (d, *J* = 8.0 Hz, 1H, ArH), 5.05 (d, *J* = 16.0 Hz, 1H, CH), 4.58 (d, *J* = 16.0 Hz, 1H, CH), 4.35 (d, *J* = 7.2 Hz, 1H, CH), 4.32 (d, *J* = 7.2 Hz, 1H, CH), 3.93-3.85 (m, 2H, CH), 3.75 (s, 3H, OCH_3), 1.35 (t, *J* = 7.2 Hz, 3H, CH_3), 1.00 (t, *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.6, 164.9, 163.1, 159.8, 148.5, 139.5, 136.3, 134.4, 133.6, 132.9, 132.4, 130.7, 130.2, 130.1, 129.2, 128.6, 127.7, 127.1, 126.9, 123.5, 121.6, 120.1, 113.7, 113.3, 111.2, 99.2, 90.6, 77.3, 77.0, 76.7, 72.8, 61.9, 60.6, 55.3, 43.9, 14.4, 13.6 ppm; IR (KBr) υ: 3441, 1727, 1672, 1589, 1551, 1489, 1453, 1326, 1259, 1178, 1111, 1081, 1029, 944, 839, 826, 814, 789, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{32}ClN_3NaO_6$ ($[M+Na]^+$): 684.1872, Found: 684.1853.



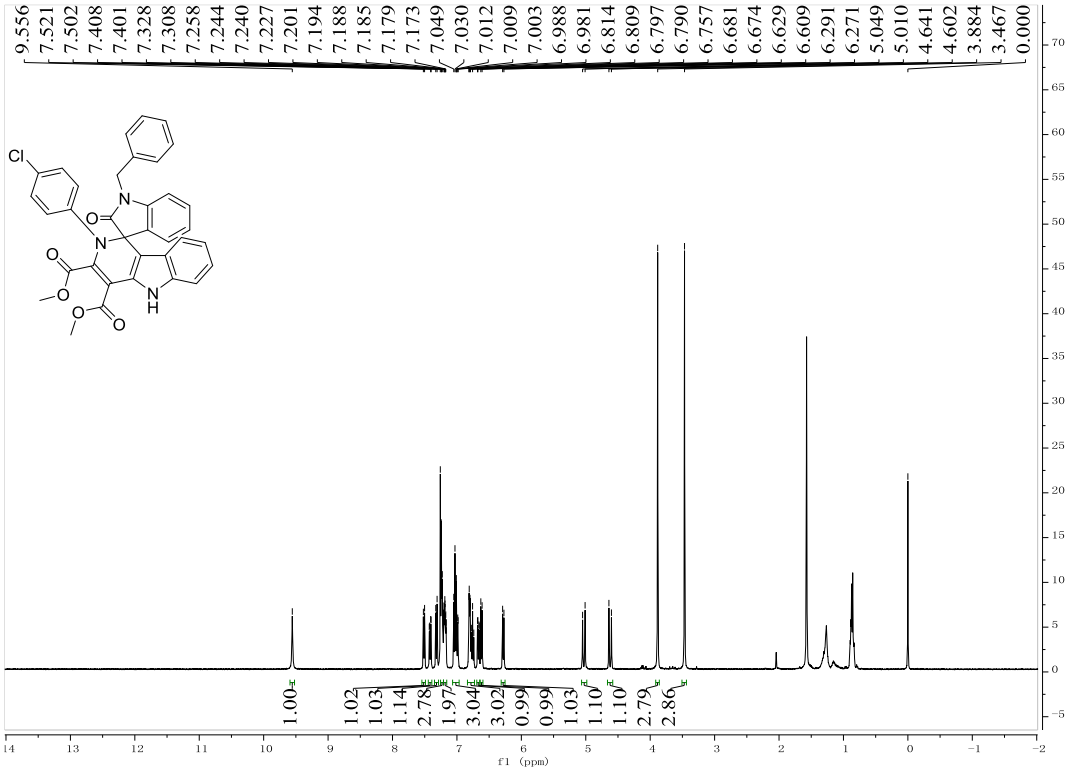
^{1}H NMR (400 MHz, $CDCl_3$)



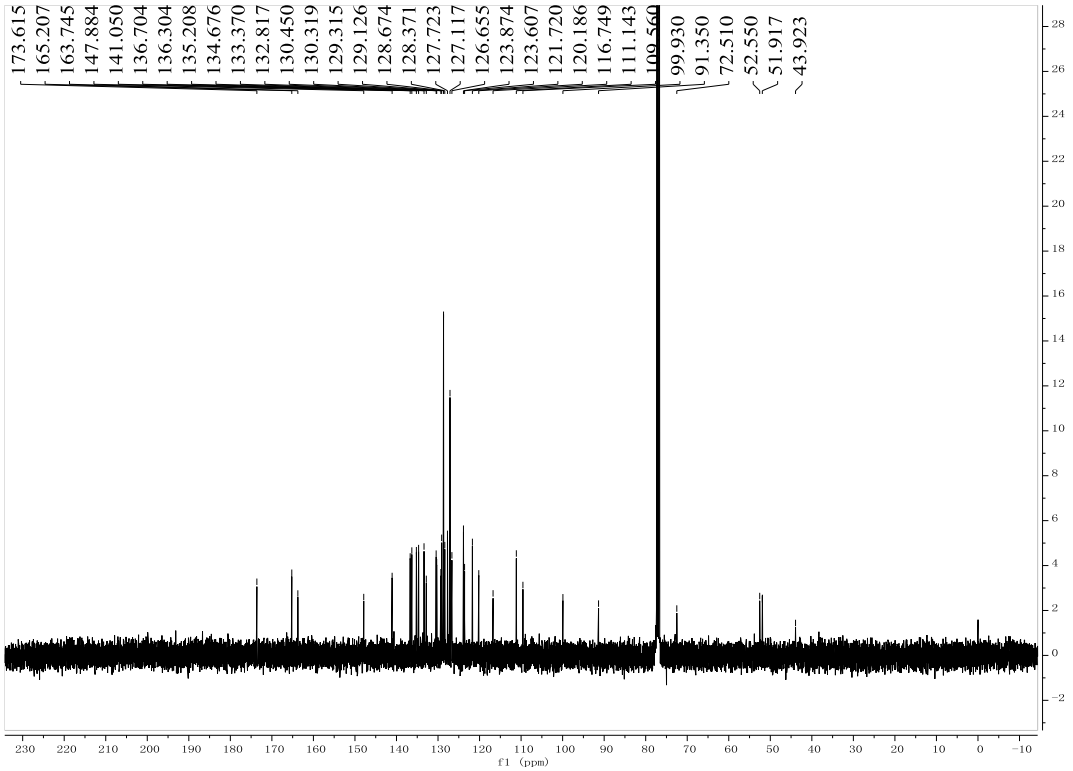
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



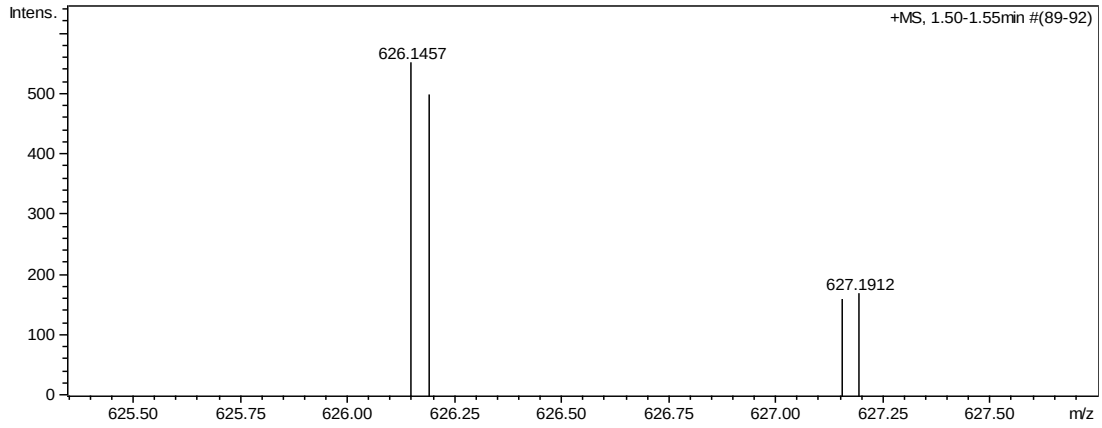
Dimethyl 1-benzyl-2'-(4-chlorophenyl)-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*] indole]-3',4'-dicarboxylate (4k): yellow solid, 58%, m.p. 265-268 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.56 (s, 1H, NH), 7.51 (d, J = 7.6 Hz, 1H, ArH), 7.42 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.32 (d, J = 8.0 Hz, 1H, ArH), 7.24-7.23 (m, 3H, ArH), 7.21-7.17 (m, 2H, ArH), 7.05-6.98 (m, 3H, ArH), 6.81-6.74(m, 3H, ArH), 6.62 (d, J = 8.0 Hz, 1H, ArH), 5.03 (d, J = 15.6 Hz, 1H, CH), 4.62 (d, J = 15.6 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.6, 165.2, 163.7, 147.9, 141.1, 136.7, 136.3, 135.2, 134.7, 133.4, 132.8, 130.5, 130.3, 129.3, 129.1, 128.7, 128.4, 127.7, 127.1, 126.7, 123.9, 123.6, 121.7, 120.2, 116.2, 111.1, 109.6, 100.0, 91.4, 77.3, 77.0, 76.7, 72.5, 52.6, 51.9, 43.9 ppm; IR (KBr) υ: 3416, 1732, 1711, 1618, 1584 , 1551, 1488, 1465, 1434, 1330, 1315, 1227, 1177, 1121, 1091, 1015, 962, 814, 783 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{35}H_{26}ClN_3NaO_5$ ([M+Na]$^{+}$): 626.1454, Found: 626.1457.



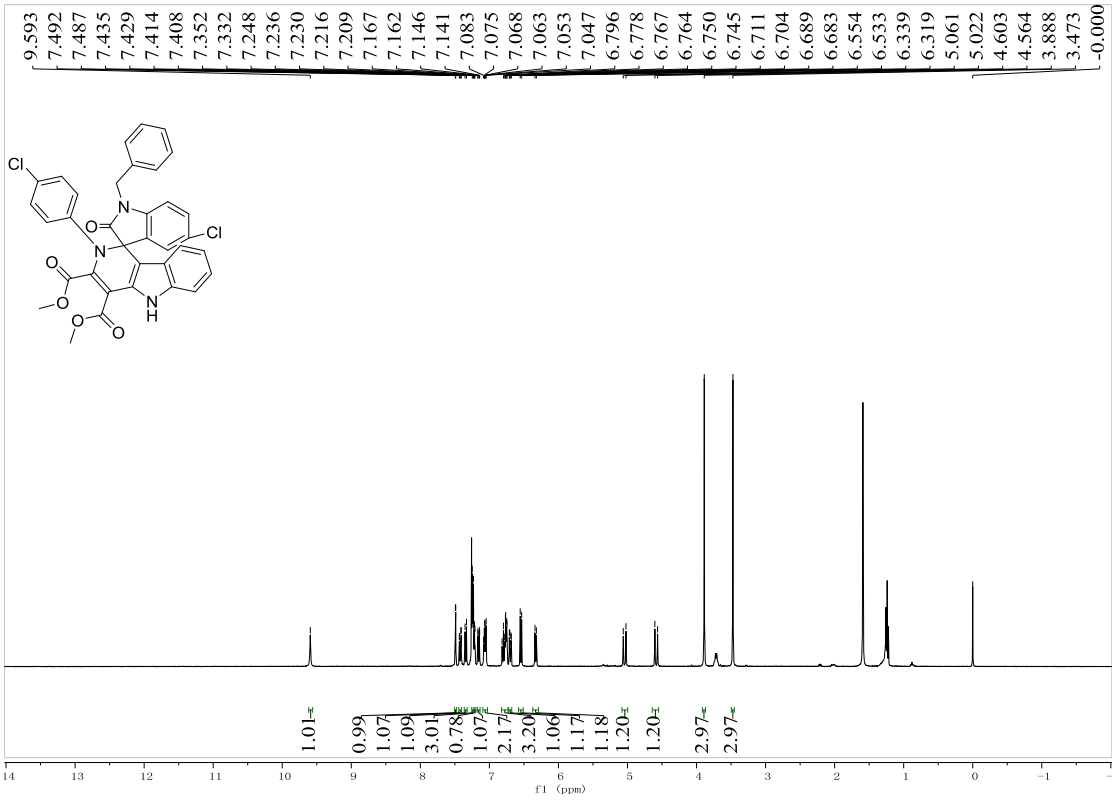
^{1}H NMR (400 MHz, $CDCl_3$)



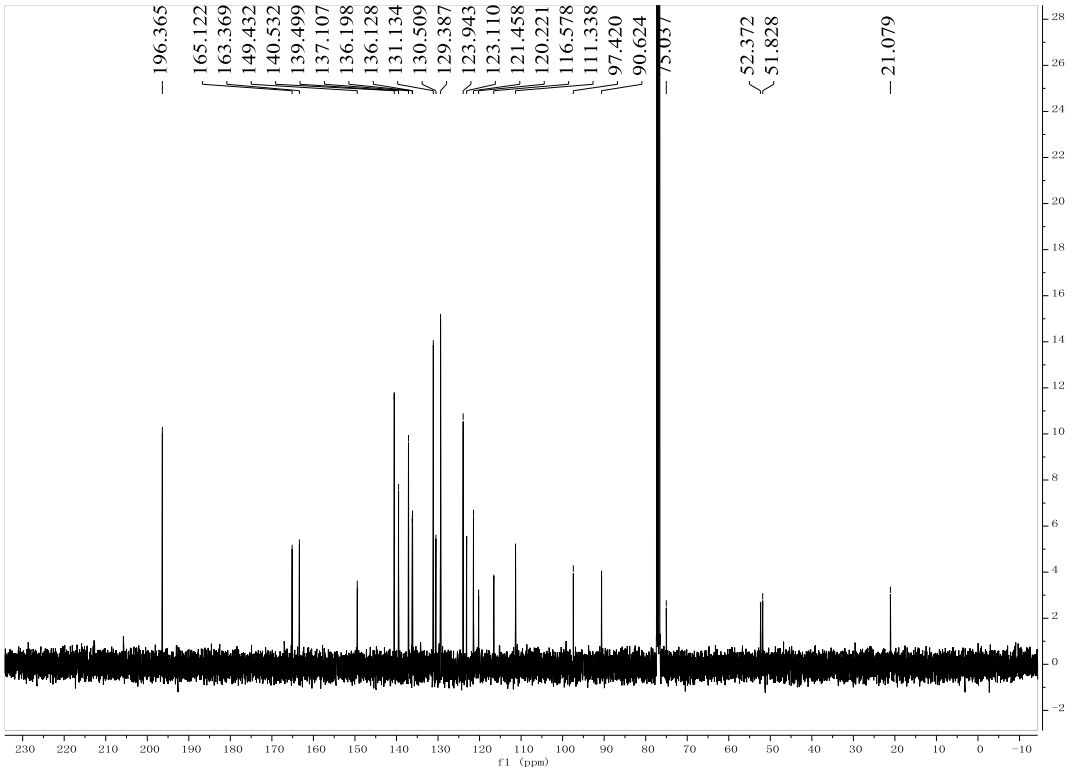
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



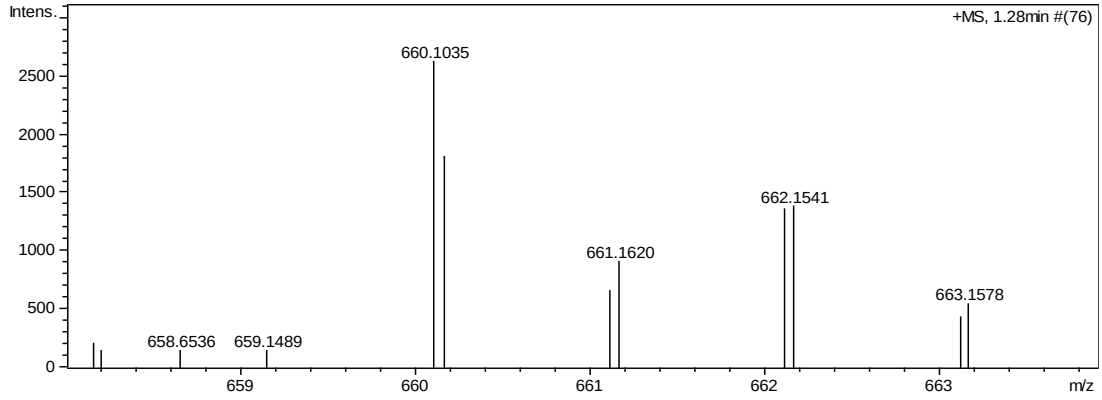
Dimethyl 1-benzyl-5-chloro-2'-(4-chlorophenyl)-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (4l): yellow solid, 62%, m.p. 191-195 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.59 (s, 1H, NH), 7.49 (d, J = 2.0 Hz, 1H, ArH), 7.42 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.34 (d, J = 8.0 Hz, 1H, ArH), 7.25-7.22 (m, 3H, ArH), 7.21 (d, J = 2.8 Hz, 1H, ArH), 7.15 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H, ArH), 7.08-7.05 (m, 2H, ArH), 6.82-6.75 (m, 3H, ArH), 6.70 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 6.54 (d, J = 8.4 Hz, 1H, ArH), 6.33 (d, J = 8.0 Hz, 1H, ArH), 5.04 (d, J = 15.6 Hz, 1H, CH), 4.58 (d, J = 15.6 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 196.4, 165.1, 163.4, 149.4, 140.5, 139.5, 137.1, 136.2, 136.1, 131.1, 130.5, 129.4, 123.9, 123.1, 121.5, 120.2, 116., 111.3, 97.4, 90.6, 77.3, 77.0, 76.7, 75.0, 52.4, 51.8, 21.1 ppm; IR (KBr) υ: 3424, 1729, 1620, 1589, 1571, 1485, 1427, 1383, 1316, 1178, 1126, 1092, 1012, 998, 955, 817, 773 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{35}H_{25}Cl_2N_3NaO_5$ ([M+Na]$^{+}$): 660.1064, Found: 660.1035.



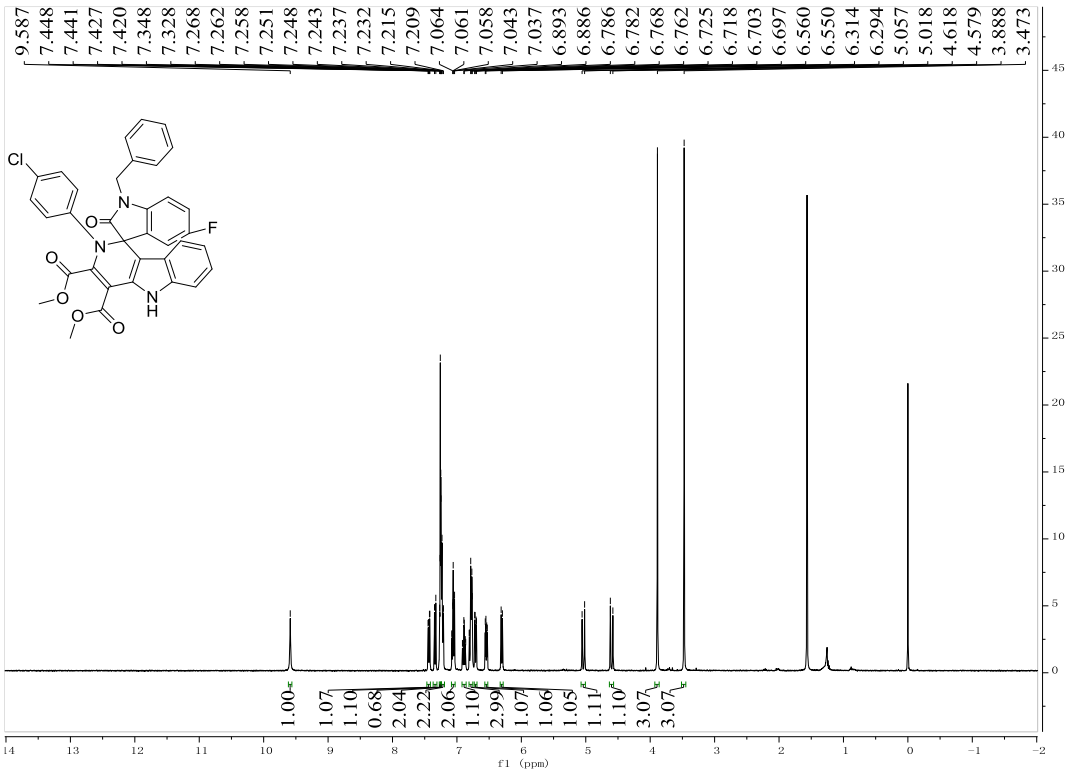
^{1}H NMR (400 MHz, $CDCl_3$)



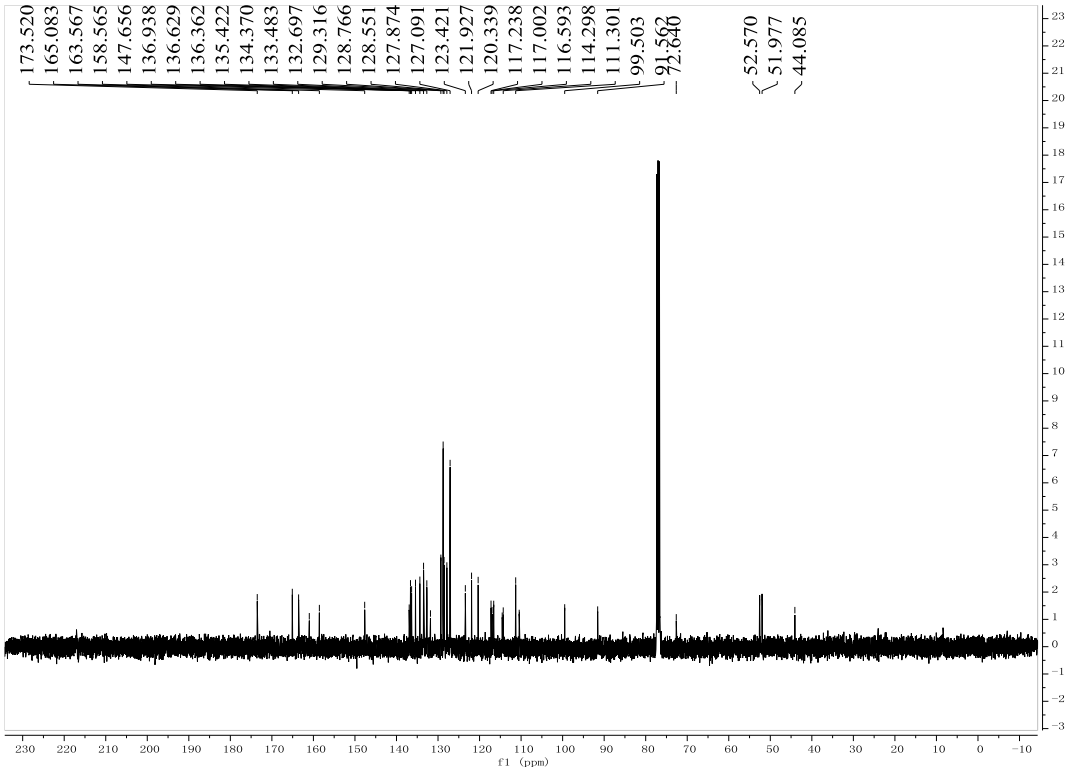
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



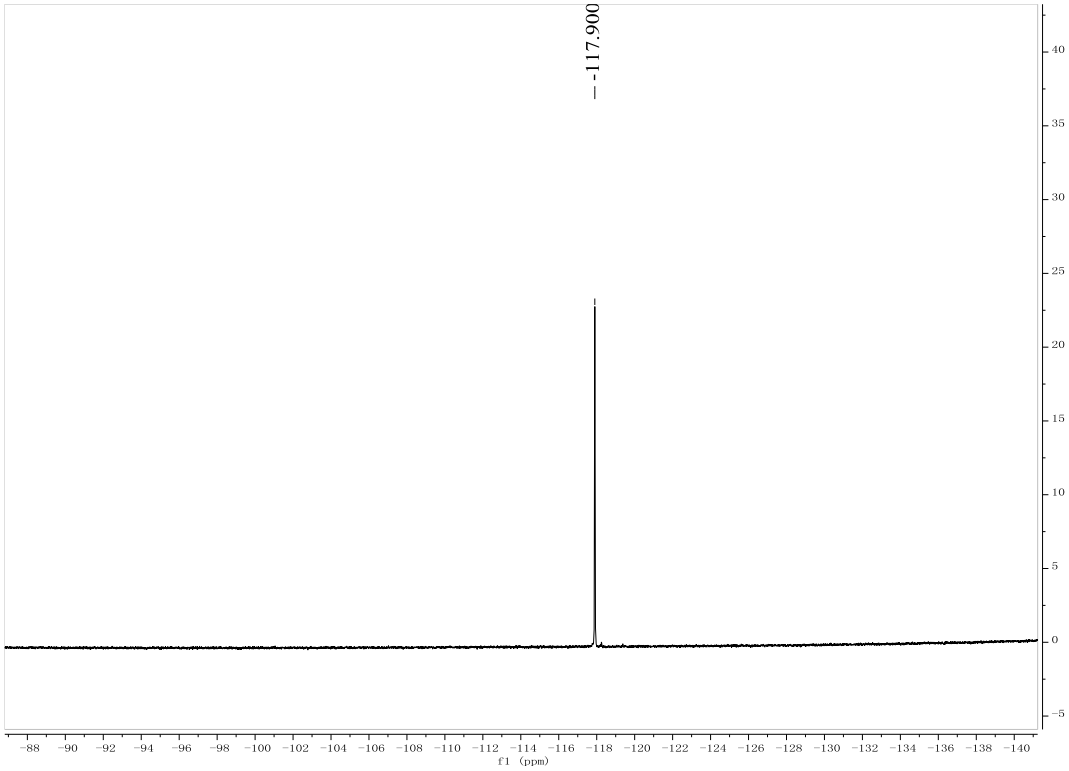
Dimethyl 1-benzyl-2'-(4-chlorophenyl)-5-fluoro-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (4m): yellow solid, 62%, m.p. 282-287 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.59 (s, 1H, NH), 7.43 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H, ArH), 7.34 (d, J = 8.0 Hz, 1H, ArH), 7.27-7.24 (m, 3H, ArH), 7.24-7.21 (m, 2H, ArH), 7.08-7.04 (m, 2H, ArH), 6.91-6.86(m, 1H, ArH), 6.81-6.76(m, 3H, ArH), 6.71 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 6.54 (dd, J_1 = 8.8 Hz, J_2 = 4.0 Hz, 1H, ArH), 6.30 (d, J = 8.0 Hz, 1H, ArH), 5.04 (d, J = 15.6 Hz, 1H, CH), 4.60 (d, J = 15.6 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.5, 165.1, 163.6, 159.8 (d, J = 242.6 Hz), 147.7, 136.9, 136.5, 135.4, 134.4, 133.5, 132.7, 131.8, 129.3, 128.8, 128.6, 127.9, 127.1, 123.4, 121.9, 120.3, 117.1 (d, J = 23.6 Hz), 116.8, 114.4 (d, J = 24.9 Hz), 111.3, 110.5, 110.4 (d, J = 6.1 Hz), 99.5, 91.6, 77.4, 77.1, 76.7, 72.6, 52.6, 52.0, 44.1 ppm; ^{19}F NMR (564 MHz, $CDCl_3$) δ: -117.9 ppm; IR (KBr) υ: 3427, 1729, 1618, 1592, 1570, 1488, 1453, 1434, 1360, 1315, 1217, 1178, 1121, 1089, 1029, 1015, 971, 909, 881, 839, 818, 786 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{35}H_{25}ClFN_3NaO_5$ ([M+Na]$^{+}$): 644.1359, Found: 644.1337.



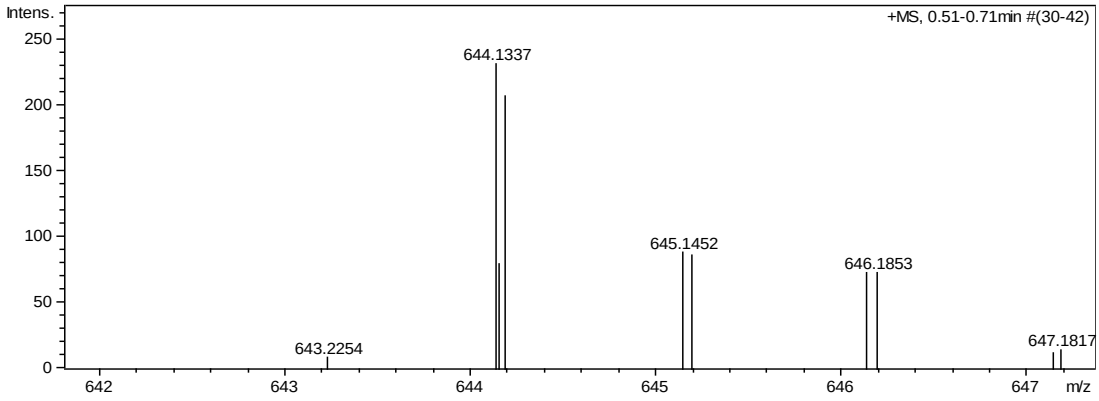
^{1}H NMR (400 MHz, $CDCl_3$)



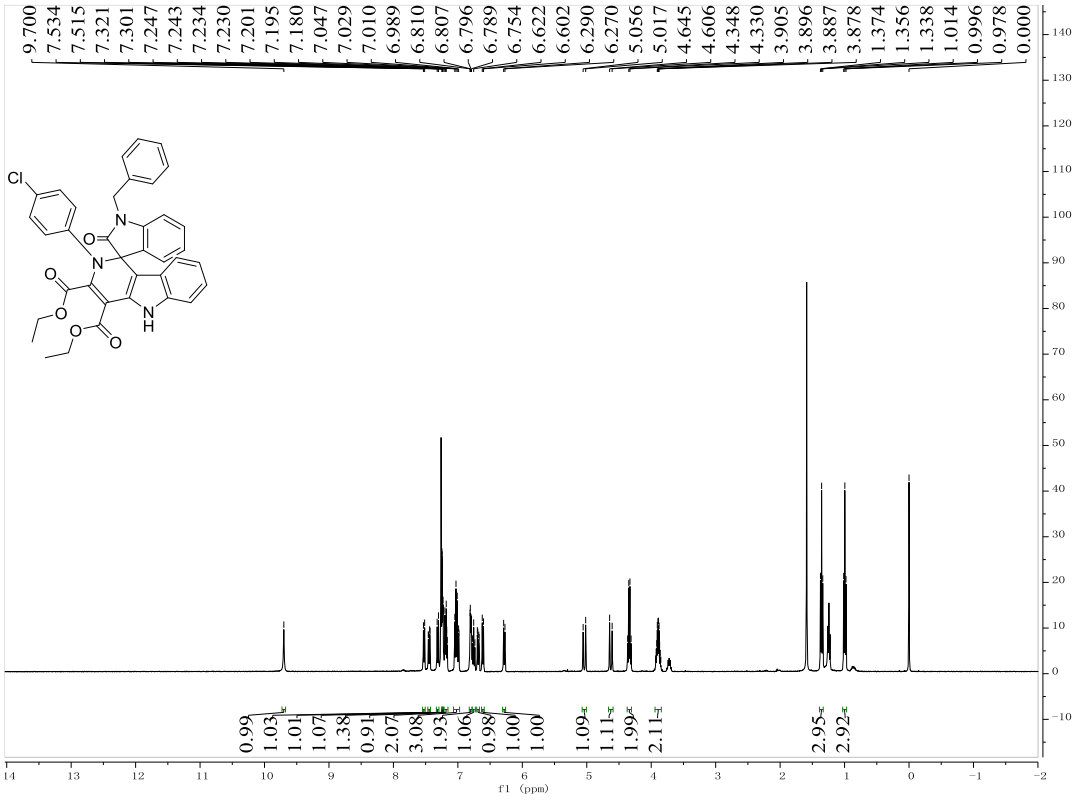
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



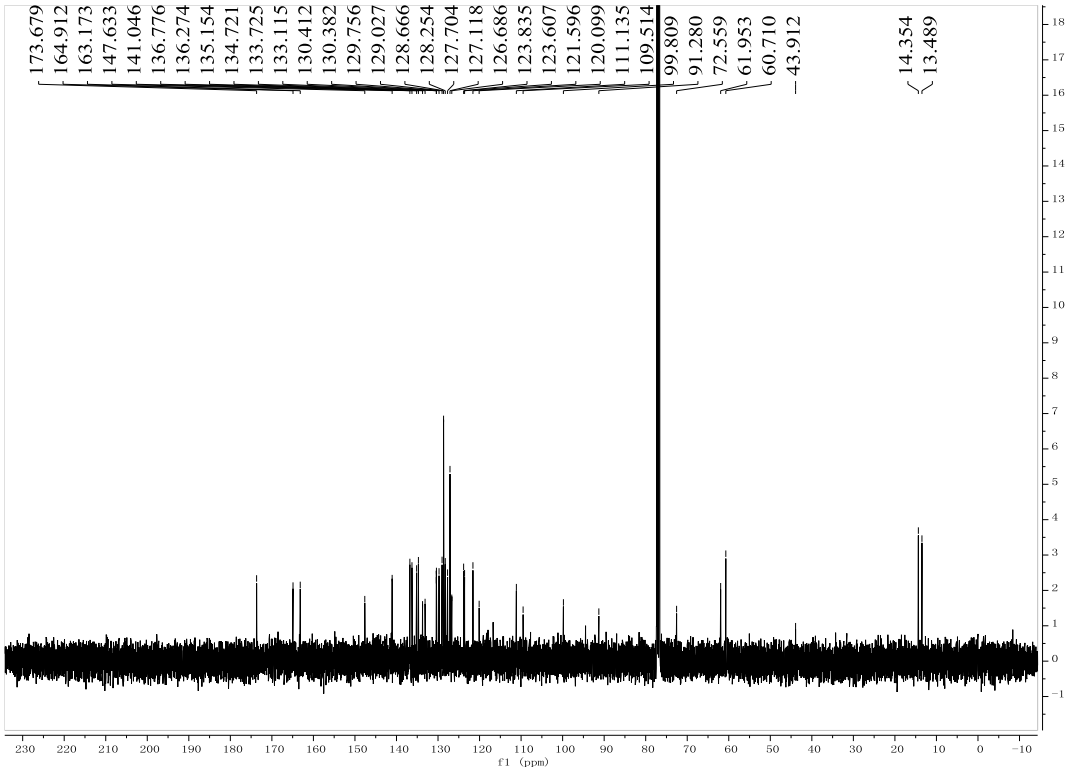
^{19}F NMR (564 MHz, $CDCl_3$)


Intens.
+MS, 0.51-0.71min #(30-42)
250
200
150
100
50
0
644.1337
645.1452
646.1853
643.2254
647.1817
642
643
644
645
646
647
m/z

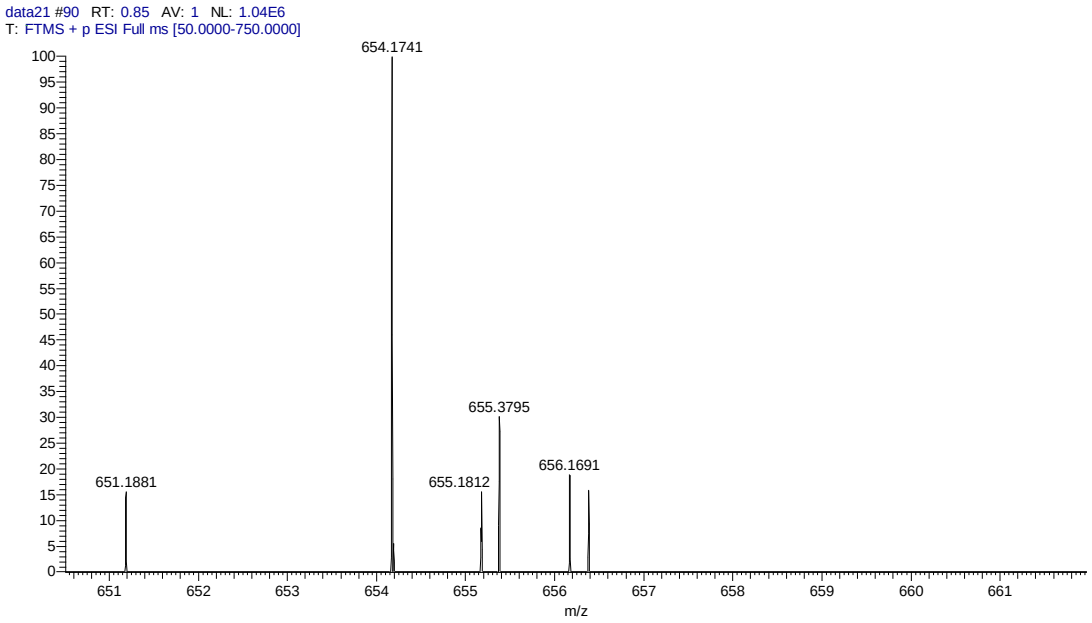
Diethyl 1-benzyl-2'-(4-chlorophenyl)-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*] indole]-3',4'-dicarboxylate (4n): yellow solid, 52%, m.p. 227-231 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.70 (s, 1H, NH), 7.52 (d, J = 7.6 Hz, 1H, ArH), 7.45 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.31 (d, J = 8.0 Hz, 1H, ArH), 7.25 (d, J = 1.6 Hz, 1H, ArH), 7.23 (d, J = 1.6 Hz, 1H, ArH), 7.20-7.16 (m, 2H, ArH), 7.05-6.98 (m, 3H, ArH), 6.81-6.79 (m, 2H, ArH), 6.77-6.74 (m, 1H, ArH), 6.68 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 6.61 (d, J = 8.0 Hz, 1H, ArH), 6.28 (d, J = 8.0 Hz, 1H, ArH), 5.04 (d, J = 15.6 Hz, 1H, CH), 4.63 (d, J = 15.6 Hz, 1H, CH), 4.36 (d, J = 7.2 Hz, 1H, CH), 4.32 (d, J = 7.2 Hz, 1H, CH), 3.93-3.85 (m, 2H, CH), 1.36 (t, J = 7.2 Hz, 3H, CH_3), 1.00 (t, J = 7.2 Hz, 3H, CH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.7, 164.9, 163.2, 147.6, 141.1, 136.8, 136.3, 135.2, 134.7, 133.7, 133.1, 130.4, 130.4, 129.8, 129.0, 128.7, 128.3, 127.7, 127.1, 126.7, 123.8, 123.6, 121.6, 120.1, 111.1, 109.5, 99.8, 91.3, 77.3, 77.0, 76.7, 72.6, 62.0, 60.7, 43.9, 14.4, 13.5 ppm; IR (KBr) υ: 3397, 1733, 1623, 1577, 1544, 1488, 1437, 1322, 1311, 1222, 11777, 1122, 1077, 1011, 966, 811, 778 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{37}H_{30}ClN_3NaO_5$ ([M+Na]$^{+}$): 654.1767, Found: 654.1741.



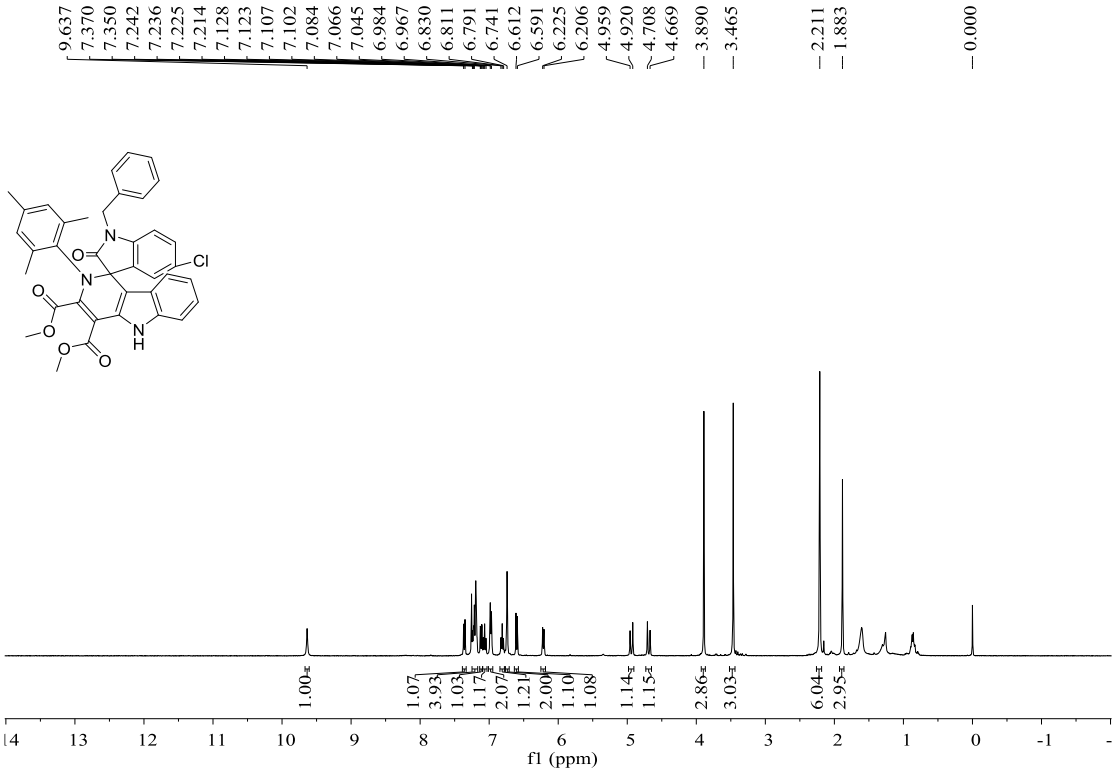
^{1}H NMR (400 MHz, $CDCl_3$)



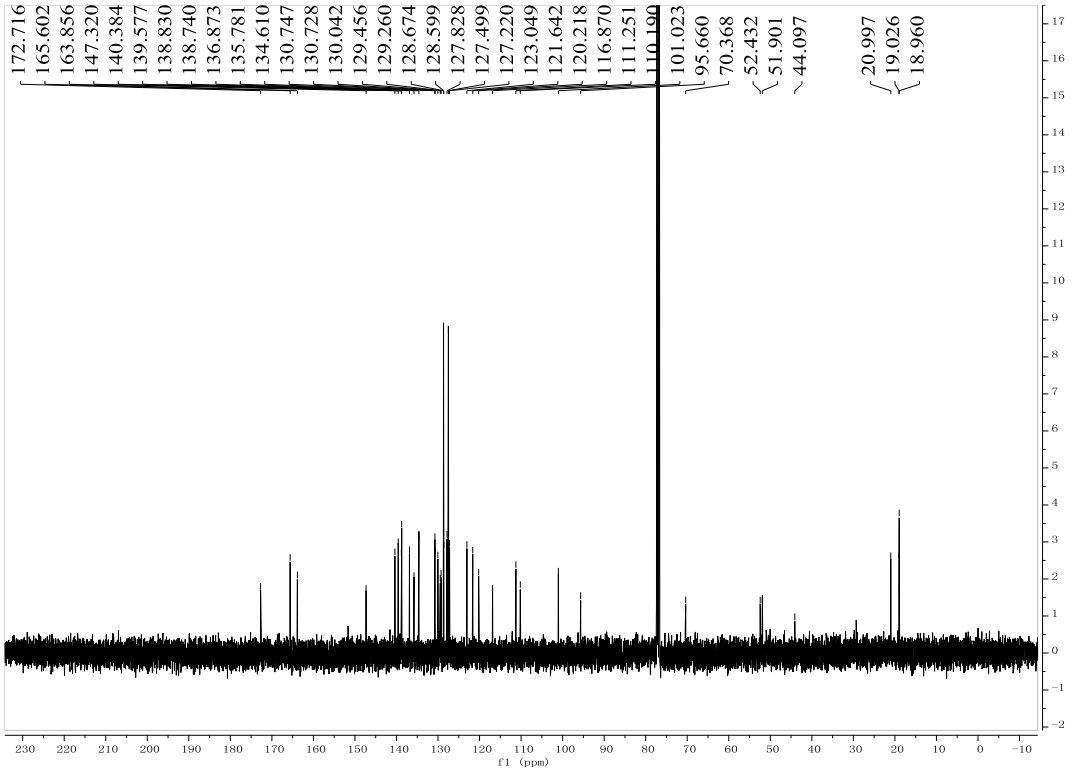
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



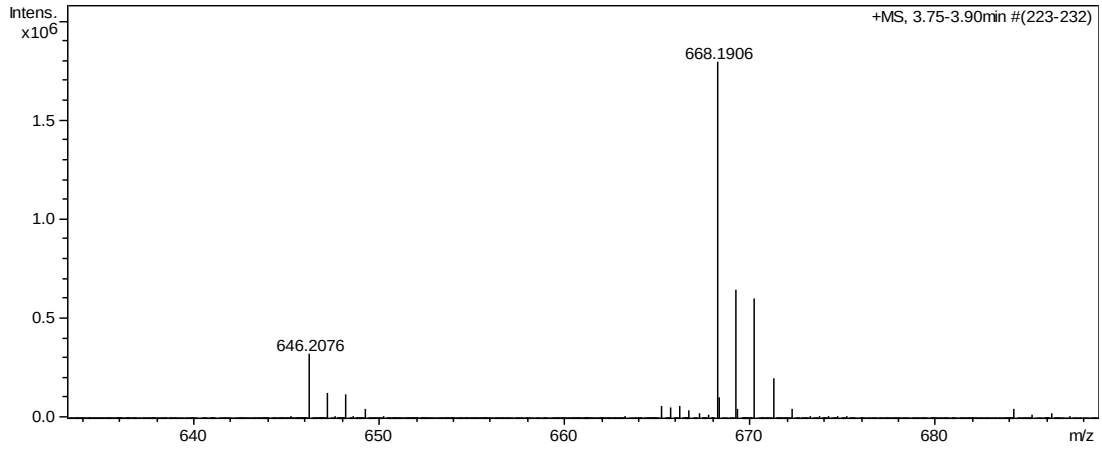
Dimethyl 1-benzyl-5-chloro-2'-mesityl-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*] indole]-3',4'-dicarboxylate (4o): yellow solid, 66%, m.p. 235-239 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.64 (s, 1H, NH), 7.36 (d, J = 8.0 Hz, 1H, ArH), 7.24-7.18 (m, 4H, ArH),7.12 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H, ArH), 7.09-7.05 (m, 1H, ArH), 6.98 (d, J = 6.8 Hz, 2H, ArH), 6.83-6.79 (m, 1H, ArH), 6.74 (s, 2H, ArH), 6.60 (d, J = 8.4 Hz, 1H, ArH), 6.22 (d, J = 7.6 Hz, 1H, ArH), 4.94 (d, J = 15.6 Hz, 1H, CH), 4.69 (d, J = 15.6 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 3.47 (s, 3H, OCH_3) , 2.21 (s, 6H, CH_3) , 1.89 (s, 3H, CH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 172.7, 165.6, 163.9, 147.3, 140.4, 139.6, 138.8, 138.7, 136.9, 135.8, 134.6, 130.8, 130.7, 130.0, 129.5, 129.3, 128.7, 128.6, 127.8, 127.5, 127.2, 123.1, 121.6, 120.2, 116.9, 111.3, 110.2, 101.0, 95.7, 77.3, 77.0, 76.7, 70.4, 52.4, 51.9, 44.1, 21.0, 19.1, 19.0 ppm; IR (KBr) υ: 3430, 1738, 1607, 1564, 1482, 1457, 1431, 1376, 1328, 1241, 1214, 1174, 1119, 1076, 1029, 946, 849, 814, 778 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{34}H_{28}N_2NaO_4$ ([M+Na]$^{+}$): 668.1923, Found: 668.1906.



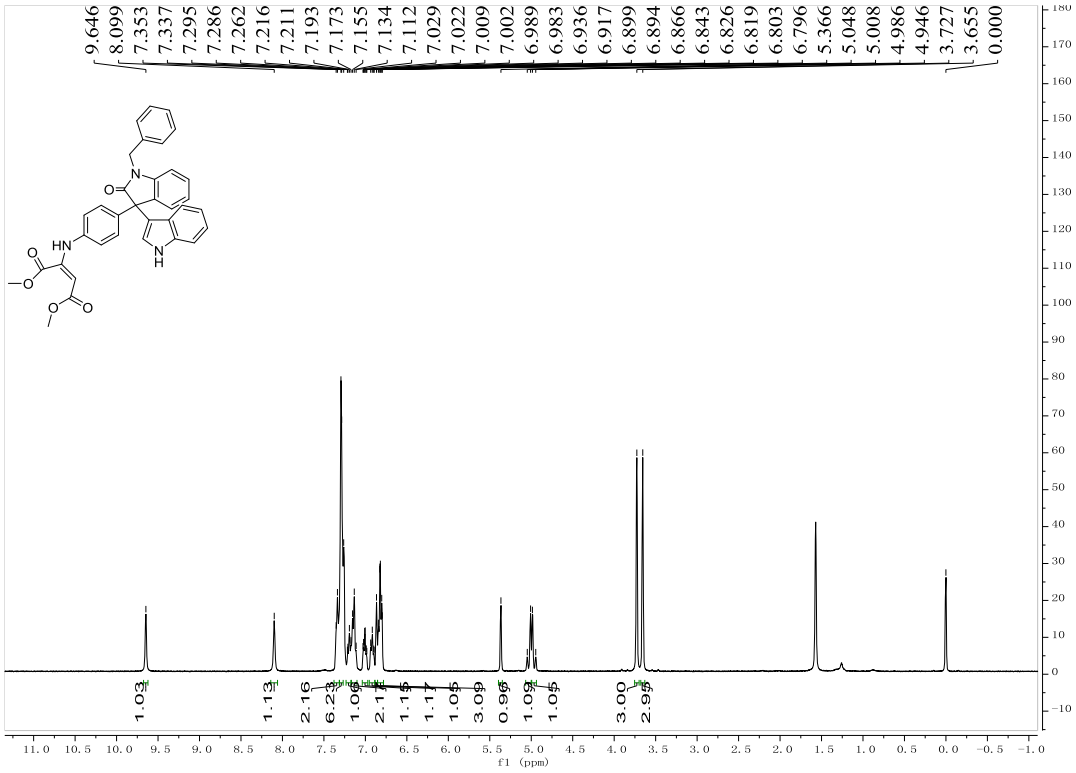
^{1}H NMR (400 MHz, $CDCl_3$)



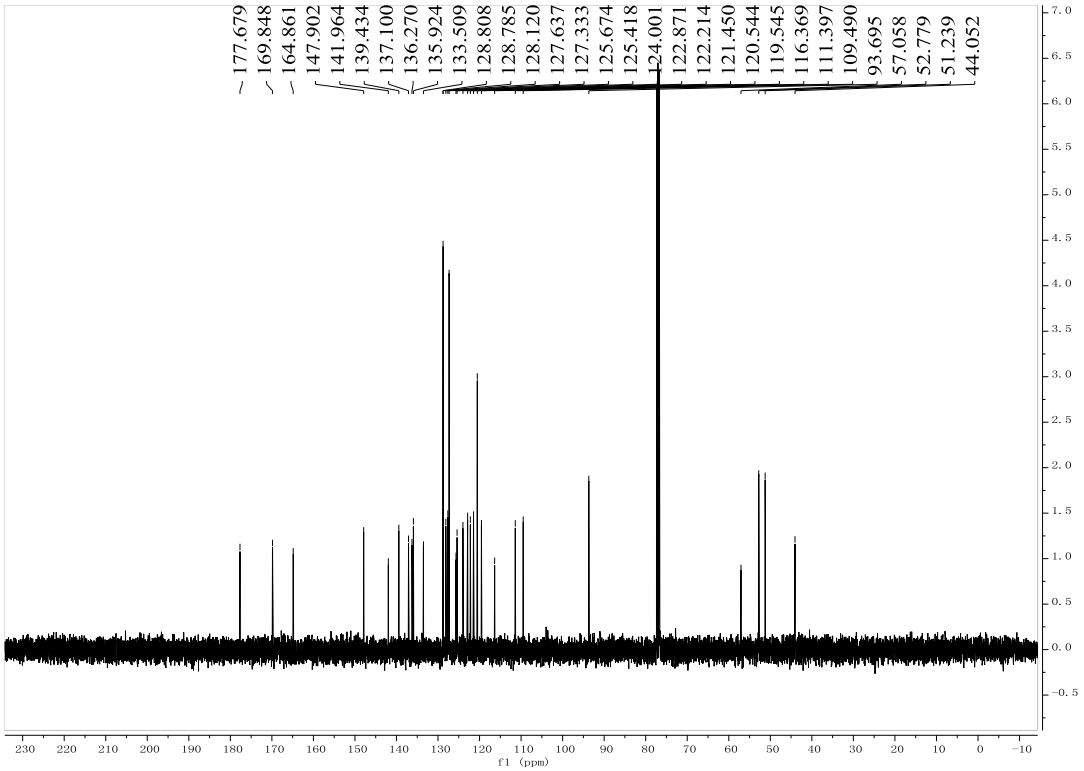
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



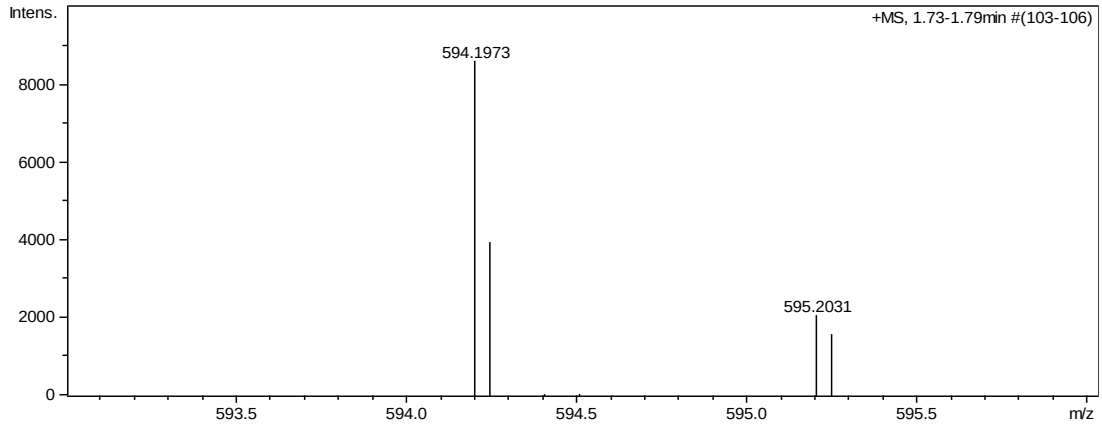
Dimethyl 2-((4-(1-benzyl-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)phenyl)amino)maleate (5a): yellow solid, 78%, m.p. 162-167 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.65 (s, 1H, NH), 8.10 (s, 1H, NH), 7.35-7.34 (m, 2H, ArH), 7.30-7.27 (m, 6H, ArH), 7.22-7.17 (m, 1H, ArH), 7.16-7.11 (m, 2H, ArH), 7.03-6.98 (m, 1H, ArH), 6.94-6.89 (m, 1H, ArH), 6.87 (s, 1H, ArH), 6.84-6.80 (m, 3H, ArH), 5.37 (s, 1H, CH), 5.03 (d, *J* = 16.0 Hz, 1H, CH), 4.97 (d, *J* = 16.0 Hz, 1H, CH), 3.73 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.7, 169.9, 164.9, 147.9, 142.0, 139.4, 137.1, 136.3, 135.9, 133.5, 128.8, 128.8, 128.1, 127.6, 127.3, 125.7, 125.4, 124.0, 122.9, 122.2, 121.5, 120.5, 119.6, 116.4, 111.4, 109.5, 93.7, 77.4, 77.1, 76.7, 57.1, 52.8, 51.2, 44.1 ppm; IR (KBr) υ: 3267, 3033, 2357, 1736, 1686, 1607, 1514, 1487, 1466, 1434, 1371, 1348, 1280, 1219, 1138, 1078, 1028, 934, 889, 815, 783 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{35}H_{29}N_3NaO_5$ ([M+Na]$^{+}$): 594.2000, Found: 594.1973.



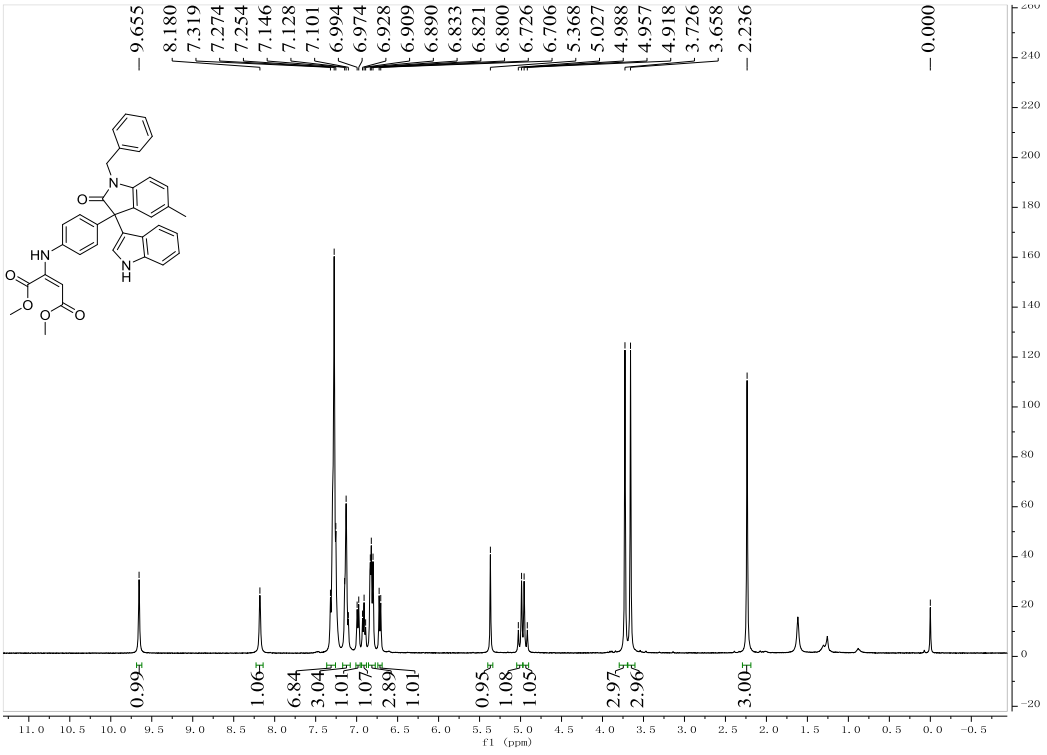
^{1}H NMR (400 MHz, $CDCl_3$)



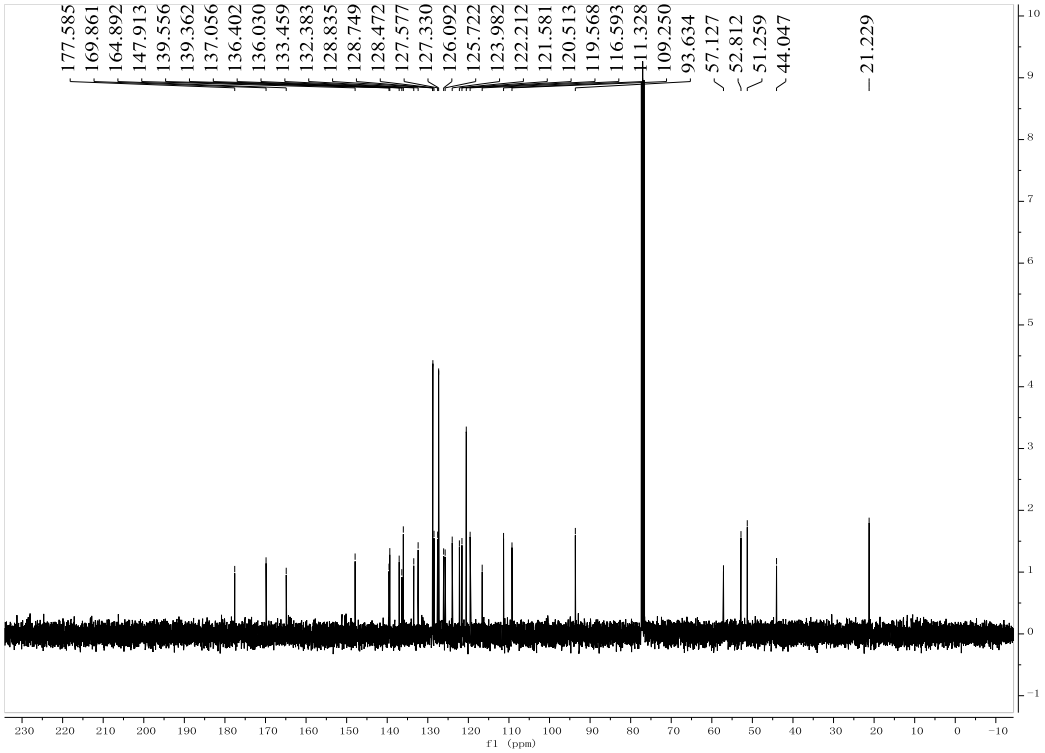
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



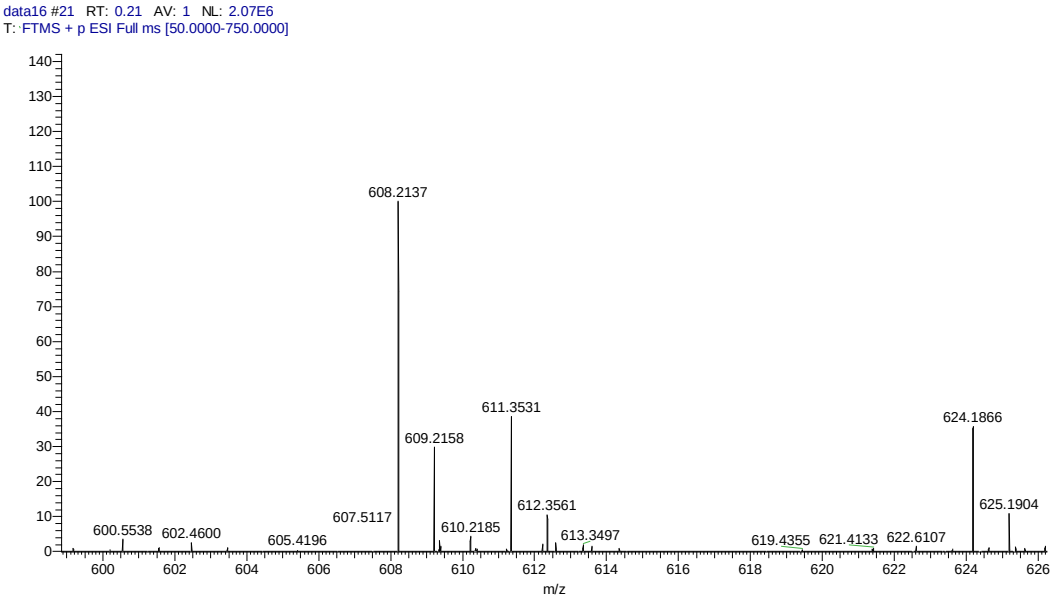
Dimethyl 2-((4-(1-benzyl-3-(1H-indol-3-yl)-5-methyl-2-oxoindolin-3-yl)phenyl)amino) maleate (5b): yellow solid, 67%, m.p. 189-194 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.66 (s, 1H, NH), 8.18 (s, 1H, NH), 7.32-7.27 (m, 7H, ArH), 7.15-7.10 (m, 1H, ArH), 6.98 (d, *J* = 8.0 Hz, 1H, ArH), 6.91 (t, *J* = 7.6 Hz, 1H, ArH), 6.83-6.80(m, 3H, ArH), 6.72 (d, *J* = 8.0 Hz, 1H, ArH), 5.37 (s, 1H, CH), 5.01 (d, *J* = 15.6 Hz, 1H, CH), 4.94 (d, *J* = 15.6 Hz, 1H, CH), 3.73 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 2.25 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.6, 169.9, 164.9, 147.9, 139.6, 139.4, 137.1, 136.4, 136.0, 133.5, 132.4, 128.8, 128.8, 128.5, 127.6, 127.3, 126.1, 125.7, 124.0, 122.2, 121.6, 120.5, 119.6, 116.6, 111.3, 109.3, 93.6, 77.4, 77.0, 76.7, 57.1, 52.8, 51.3, 44.1, 21.2 ppm; IR (KBr) υ: 3297, 1739, 1711, 1605, 1514, 1495, 1456, 1435, 1346, 1282, 1218, 1185, 1141, 1030, 810, 781 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{31}N_3NaO_5$ ([M+Na]$^{+}$): 608.2156, Found: 608.2137.



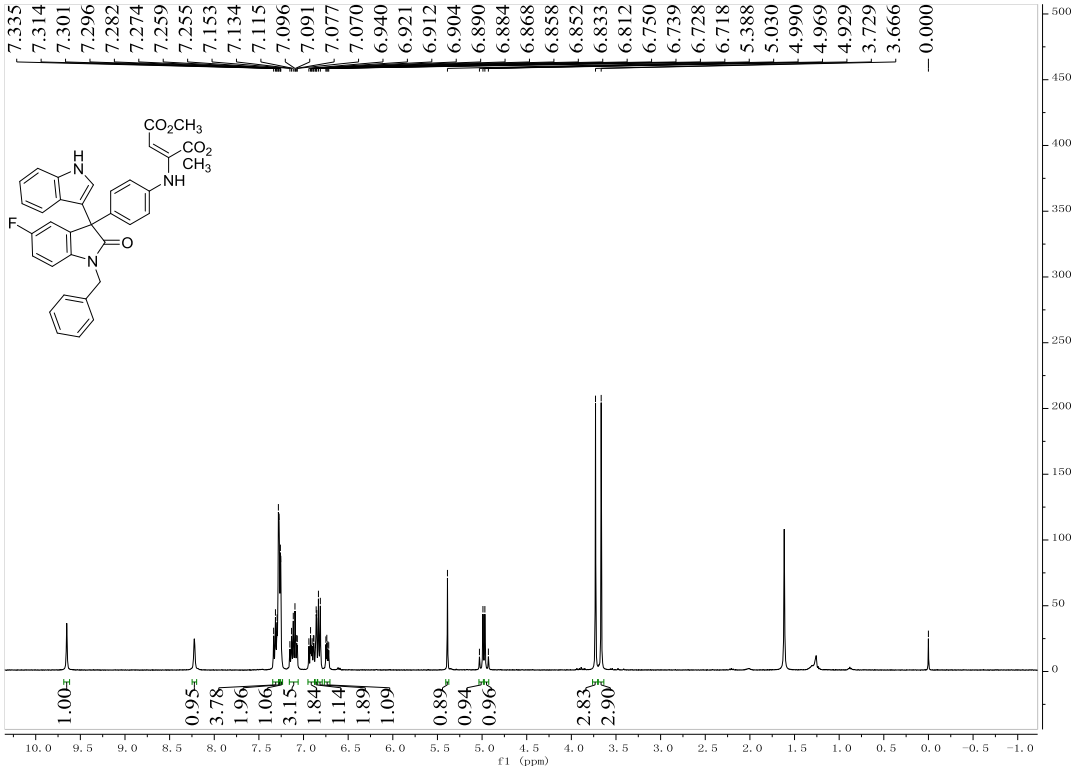
^{1}H NMR (400 MHz, $CDCl_3$)



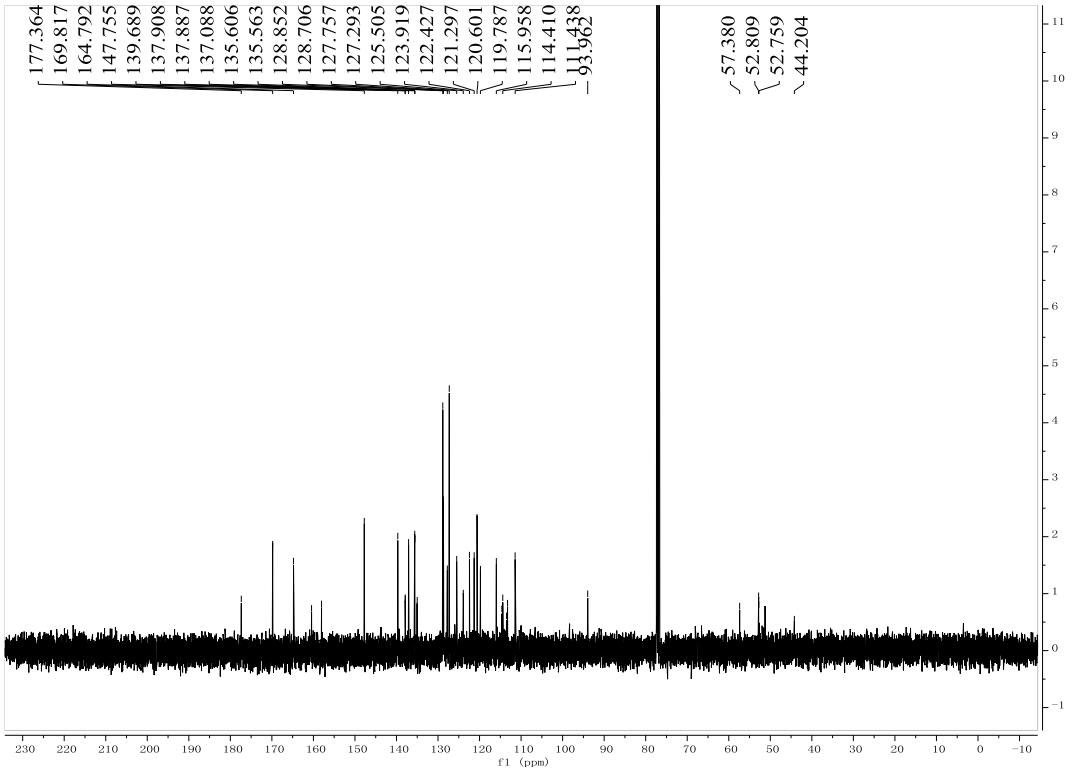
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



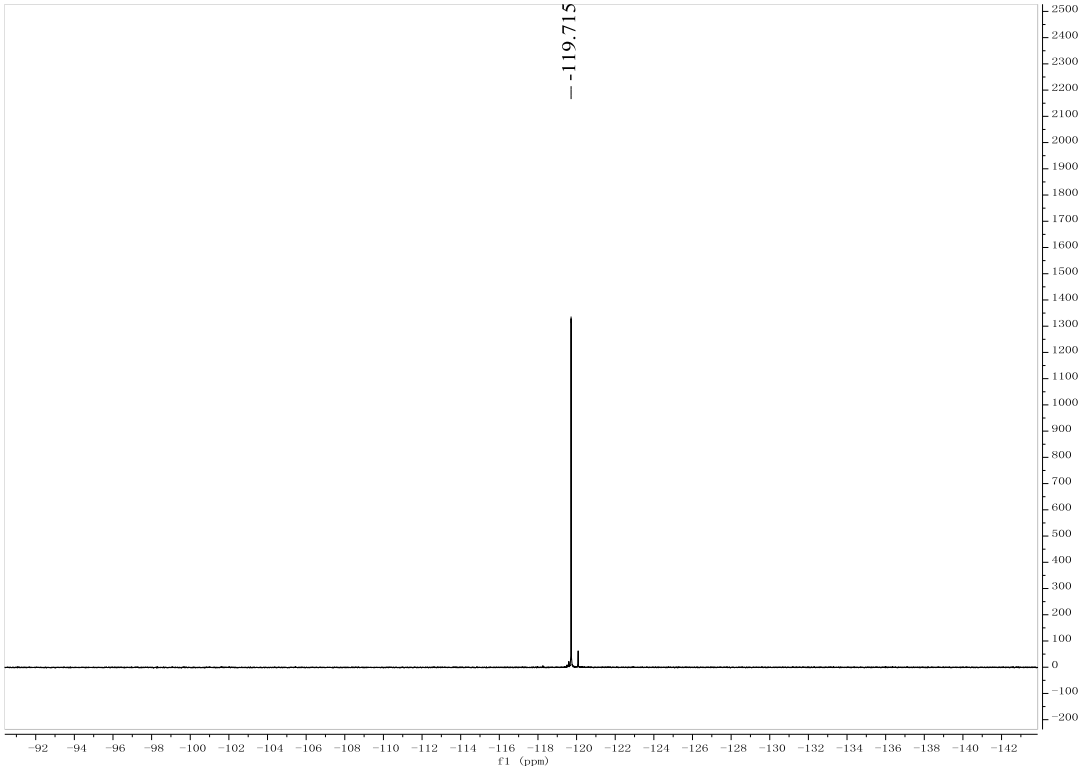
Dimethyl 2-((4-(1-benzyl-5-fluoro-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)phenyl)amino)maleate (5c): yellow solid, 73%, m.p. 172-176 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.65 (s, 1H, NH), 8.22 (s, 1H, NH), 7.34-7.28 (m, 4H, ArH), 7.27 (s, 2H, ArH), 7.25 (s, 1H, ArH), 7.15-7.07 (m, 3H, ArH), 6.94-6.88 (m, 2H, ArH), 6.87-6.85 (m, 1H, ArH), 6.82 (t, *J* = 8.4 Hz, 2H, ArH), 6.75-6.72 (m, 4H, ArH), 5.39 (s, 1H, CH), 5.01 (d, *J* = 16.0 Hz, 1H, CH), 4.95 (d, *J* = 16.0 Hz, 1H, CH), 3.73 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.4, 169.8, 164.8, 159.2 (d, *J* = 240.1 Hz), 147.8, 139.7, 137.9 (d, *J* = 2.1 Hz), 137.1, 135.6, 135.1 (d, *J* = 7.8 Hz), 128.9, 128.7, 127.8, 127.3, 125.5, 123.9, 122.4, 121.3, 120.6, 119.8, 116.0, 114.5 (d, *J* = 22.8 Hz), 113.4 (d, *J* = 24.5 Hz), 111.4, 94.0, 77.3, 77.0, 76.7, 57.4, 52.8, 52.7, 44.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -119.7 ppm; IR (KBr) υ: 3306, 3033, 2360, 1731, 1697, 1607, 1514, 1490, 1449, 1436, 1392, 1364, 1340, 1283, 1245, 1221, 1175, 1140, 1081, 1027, 982, 929, 889, 864, 842, 811, 785, 763 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{31}H_{24}N_2NaO_6$ ([M+Na]$^{+}$): 612.1906, Found: 612.1887.



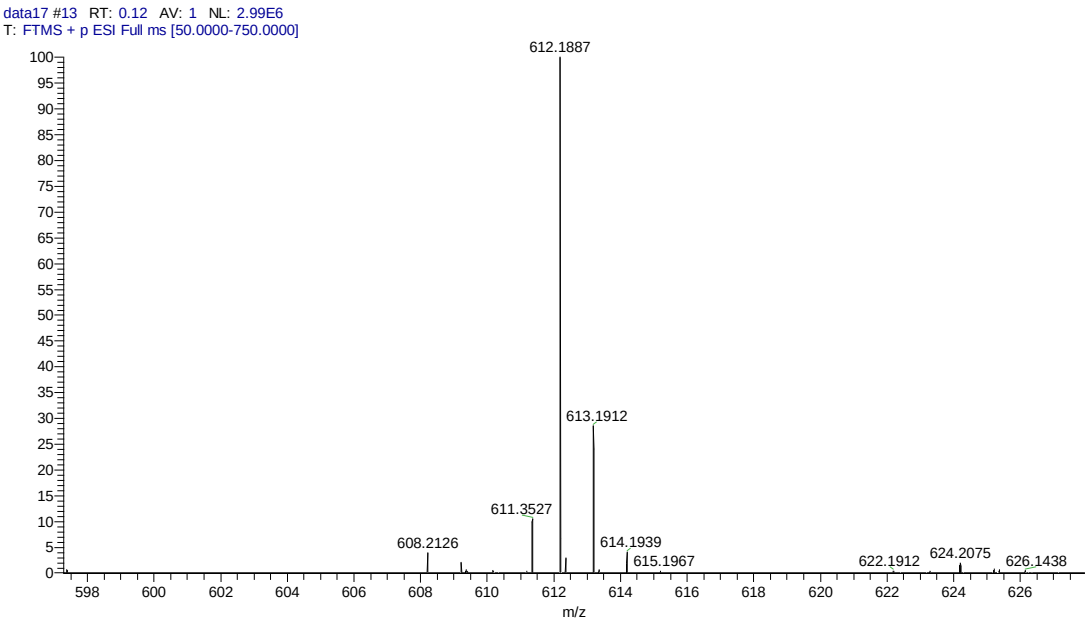
^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)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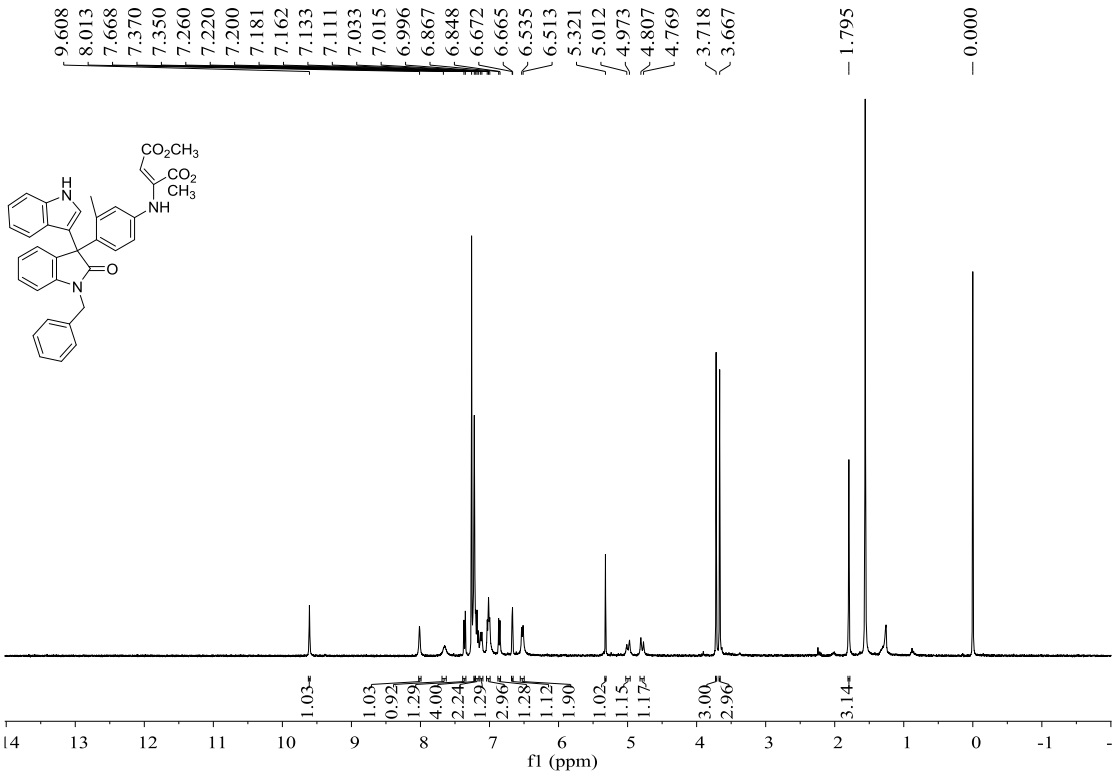
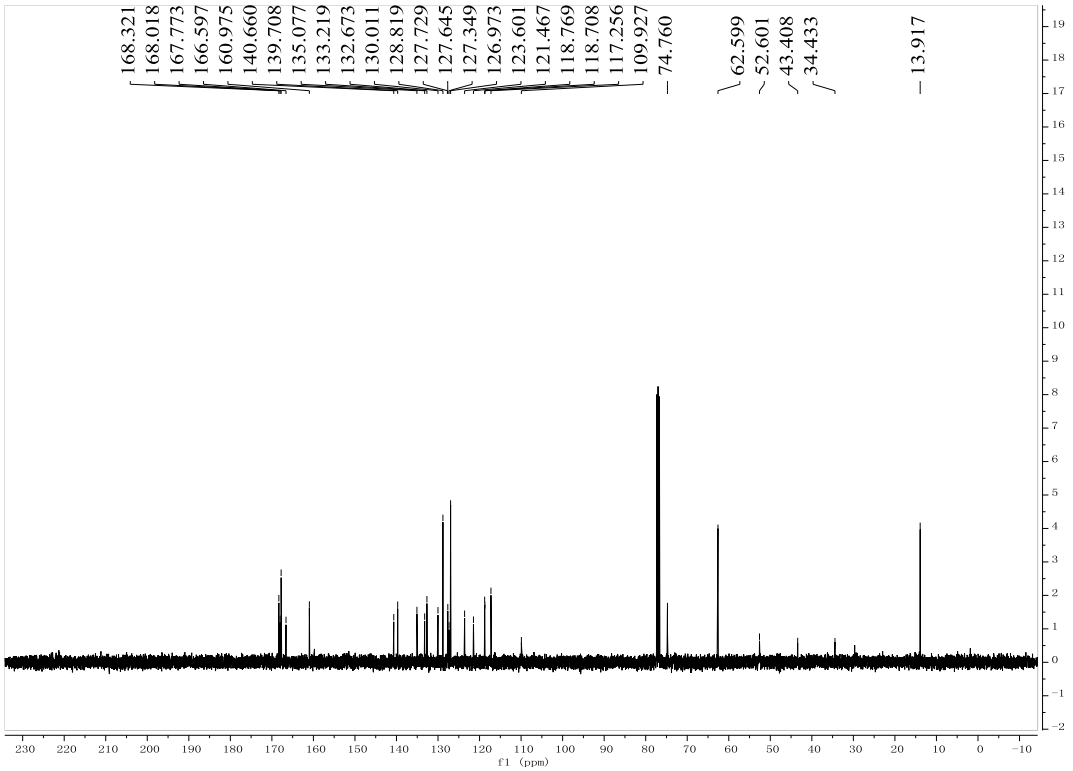
612.1887
613.1912
611.3527
608.2126
614.1939
615.1967
622.1912
624.2075
626.1438
m/z

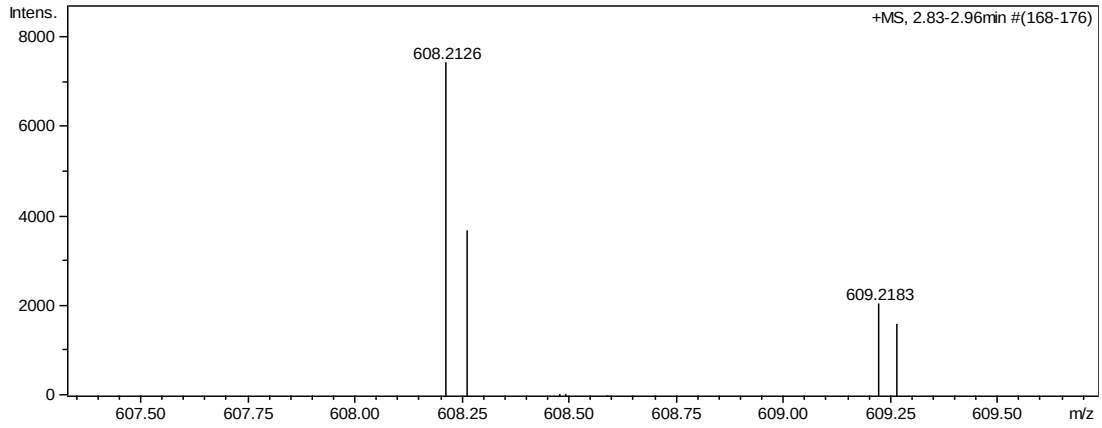
Dimethyl 2-((4-(1-benzyl-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-3-methylphenyl)amino) maleate (5d): yellow solid, 52%, m.p. 149-154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.61 (s, 1H, NH), 8.01 (s, 1H, NH), 7.67 (s, 1H, ArH), 7.36 (d, *J* = 8.0 Hz, 1H, ArH), 7.22 (s, 4H, ArH), 7.18 (t, *J* = 7.6 Hz, 2H, ArH), 7.12 (d, *J* = 8.8 Hz, 1H, ArH), 6.86 (d, *J* = 7.6 Hz, 1H, ArH), 6.67 (d, *J* = 2.8 Hz, 1H, ArH), 5.32 (s, 1H, CH), 4.99 (d, *J* = 15.6 Hz, 1H, CH), 4.79 (d, *J* =15.2 Hz, 1H, CH), 3.72 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 1.80 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.3, 168.0, 167.8, 166.6, 161.0, 140.7, 139.7, 135.1, 133.2, 132.7, 130.0, 128.8, 127.7, 127.6, 127.4, 127.0, 123.6, 121.5, 118.8, 118.7, 117.3, 110.0, 77.3, 77.0, 76.7, 74.8, 62.6, 52.6, 43.4, 34.4, 13.9 ppm; IR (KBr) υ: 3410, 1714, 1607, 1487, 1456, 1435, 1342, 1276, 1219, 1143, 1030, 811 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{32}H_{26}N_2NaO_6$ ($[M+Na]^+$): 608.2156, Found: 608.2126.



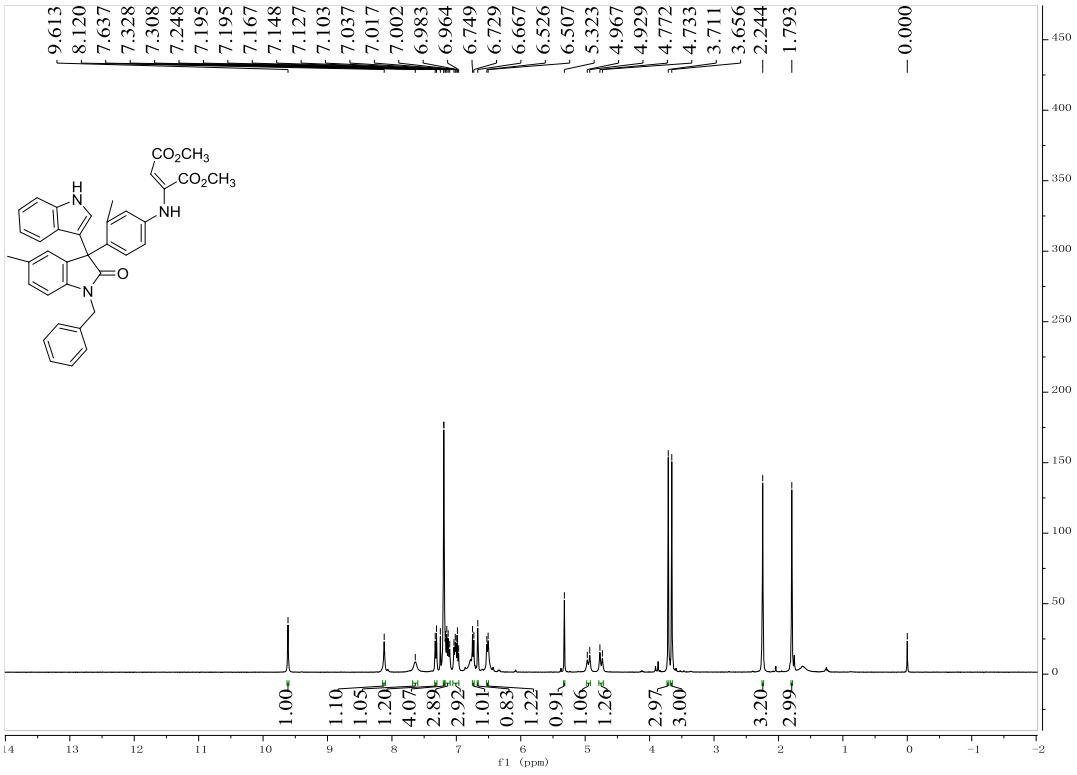
^{1}H NMR (400 MHz, $CDCl_3$)



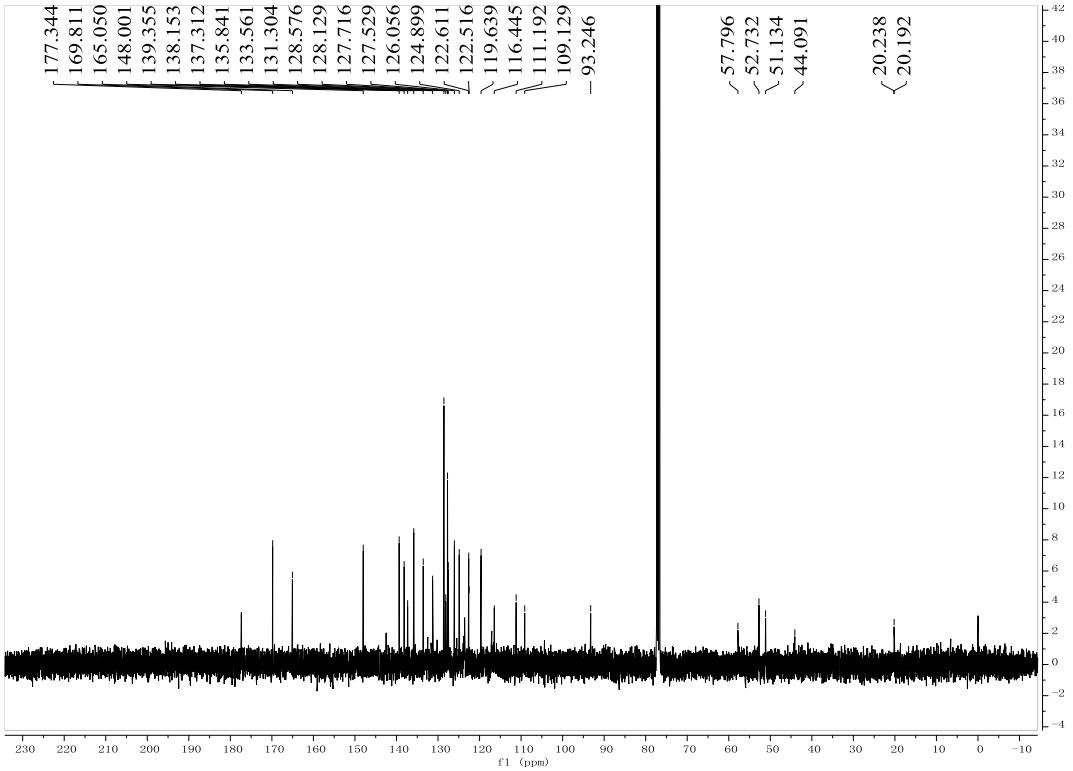
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



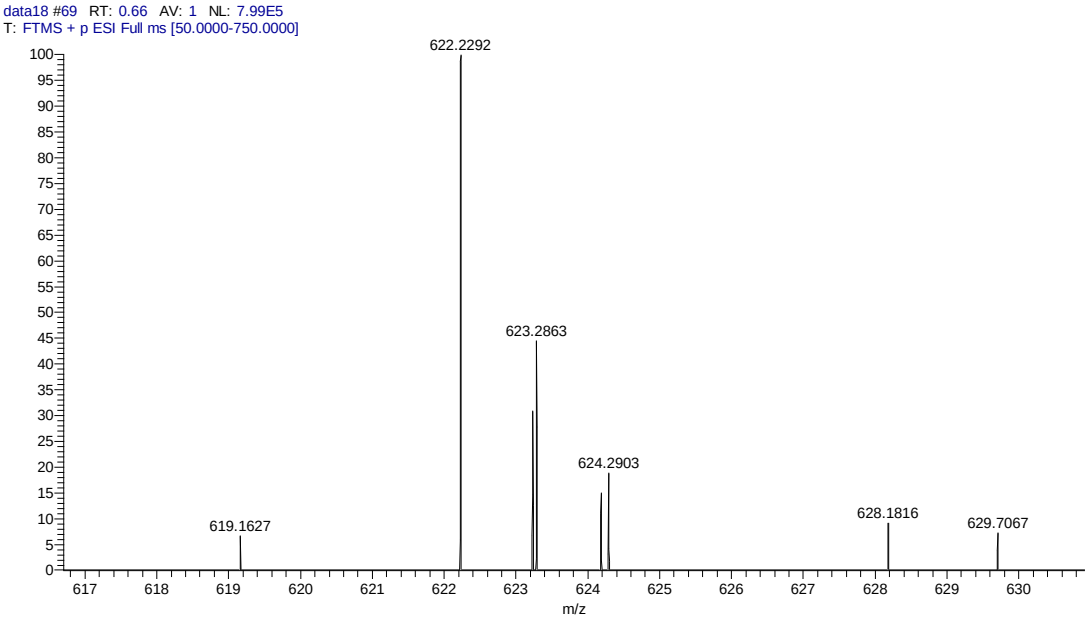
Dimethyl 2-((4-(1-benzyl-3-(1H-indol-3-yl)-5-methyl-2-oxoindolin-3-yl)-3-methylphenyl) amino)maleate (5e): yellow solid, 48%, m.p. 153-156 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.61 (s, 1H, NH), 8.12 (s, 1H, NH), 7.64 (s, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 1H, ArH), 7.20 (s, 4H, ArH), 7.17-7.10 (m, 3H, ArH), 7.04-6.96 (m, 3H, ArH), 6.74 (d, *J* = 8.0 Hz, 1H, ArH), 6.67 (s, 1H, ArH), 6.52 (d, *J* = 7.6 Hz, 1H, ArH), 5.32 (s, 1H, CH), 4.95 (d, *J* = 15.2 Hz, 1H, CH) , 4.75 (d, *J* =15.6 Hz, 1H, CH), 3.71 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 2.24 (s, 3H, CH_3), 1.79 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.3, 169.8, 165.1, 148.0, 139.4, 138.2, 137.3, 135.8, 133.6, 131.3, 128.6, 128.1, 127.7, 127.5, 126.1, 124.9, 122.6, 122.5, 119.6, 116.4, 111.2, 109.1, 93.3, 77.3, 77.0, 76.7, 57.8, 52.7, 51.1, 44.1, 20.3, 20.2 ppm; IR (KBr) υ: 3400, 1711, 1688, 1611, 1695, 1518, 1486, 1455, 1438, 1340, 1278, 1222, 1143, 1033, 933, 808, 778 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{31}H_{24}N_2NaO_7$ ([M+Na]$^{+}$): 622.2313, Found: 622.2292.



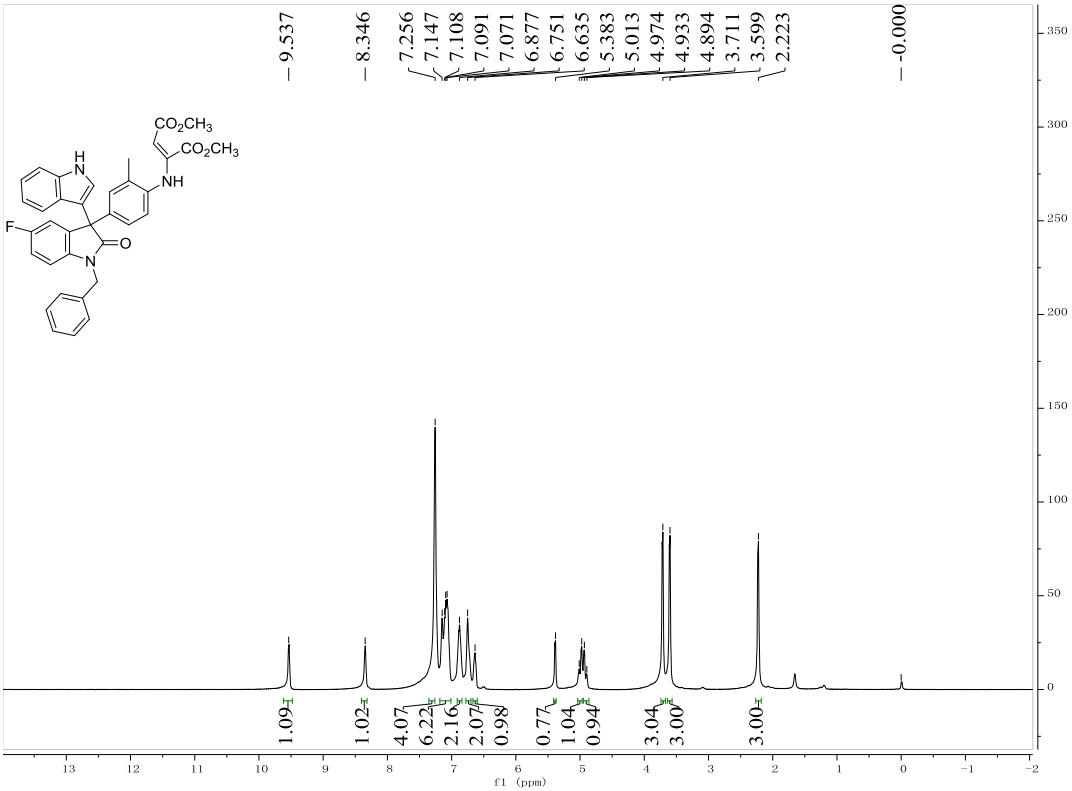
^{1}H NMR (400 MHz, $CDCl_3$)



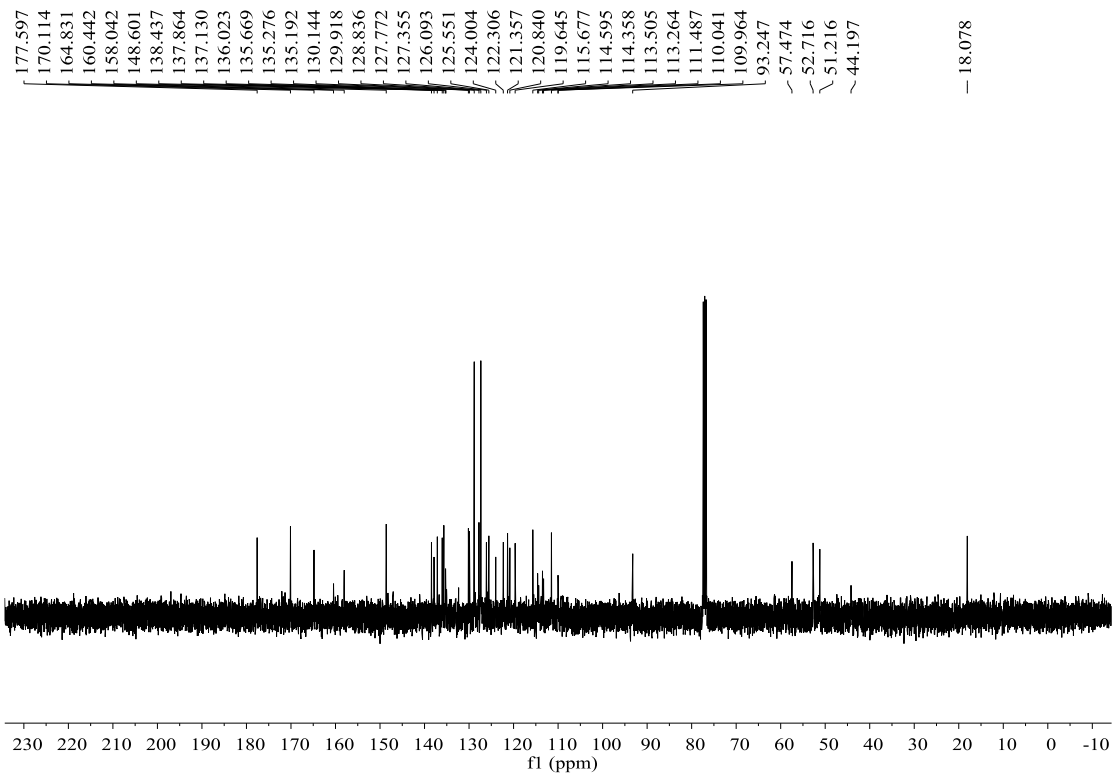
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



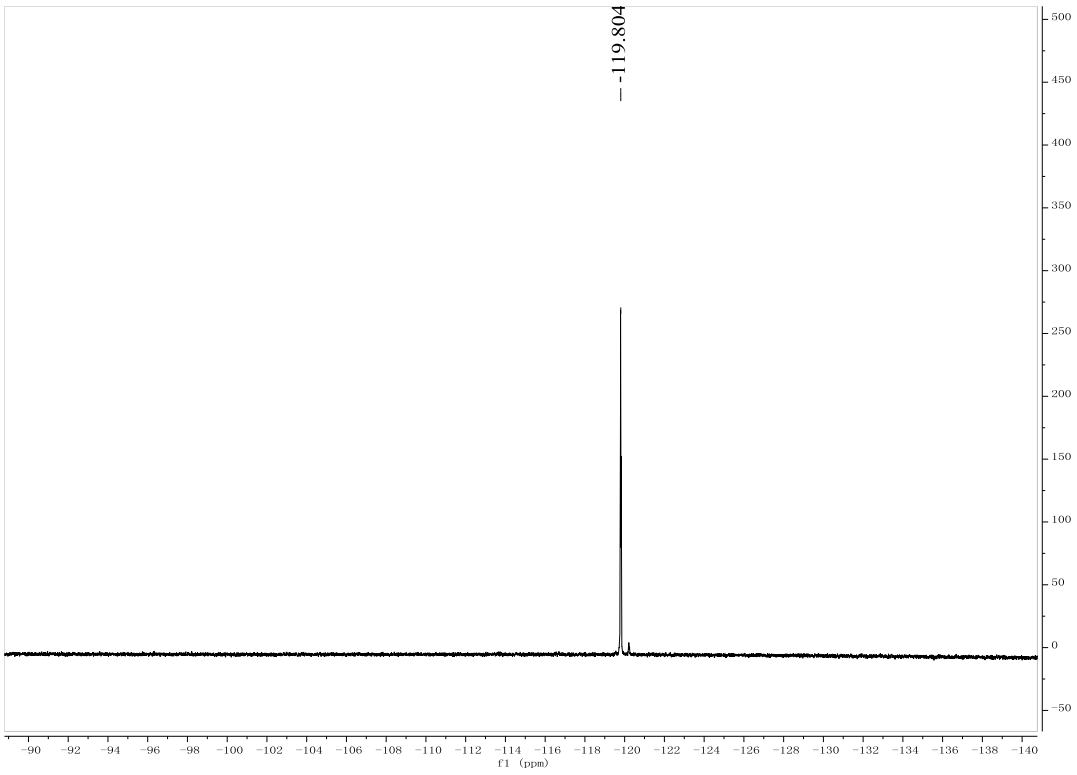
Dimethyl 2-((4-(1-benzyl-5-fluoro-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-2-methylphenyl) amino)maleate (5f): yellow solid, 66%, m.p. 195-199 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.54 (s, 1H, NH), 8.35 (s, 1H, NH), 7.26 (s, 4H, ArH), 7.15-7.07 (m, 6H, ArH), 6.888 (s, 2H, ArH), 6.75 (s, 2H, ArH), 6.64 (s, 1H, ArH), 5.38 (s, 1H, CH), 4.99 (d, *J* = 15.6 Hz, 1H, CH), 4.91 (d, *J* = 15.6 Hz, 1H, CH), 3.71 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 2.22 (s, 3H, CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ: 177.6, 170.1, 164.8, 159.2 (d, *J* = 240.0 Hz), 148.6, 138.4, 137.9, 137.1, 136.1, 135.7, 135.3(d, *J* = 8.4 Hz), 130.0, 128.8, 127.8, 127.4, 126.1, 125.6, 124.0, 122.3, 121.4, 120.8, 119.6, 115.7, 114.5 (d, *J* = 23.7 Hz) 113.4 (d, *J* = 24.1 Hz), 111.5, 110.0 (d, *J* = 7.7 Hz), 93.3, 77.4, 77.1, 76.8, 57.5, 52.7, 51.2, 44.2, 18.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -119.8 ppm; IR (KBr) υ: 3316, 1744, 1698, 1676, 1619, 1577, 1491, 1449, 1437, 1381, 1363, 1340, 1272, 1219, 1174, 1141, 1117, 1080, 1031, 845, 832, 810, 786, 762 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{32}H_{26}N_2NaO_7$ ([M+Na]$^{+}$): 626.2062, Found: 626.2039.



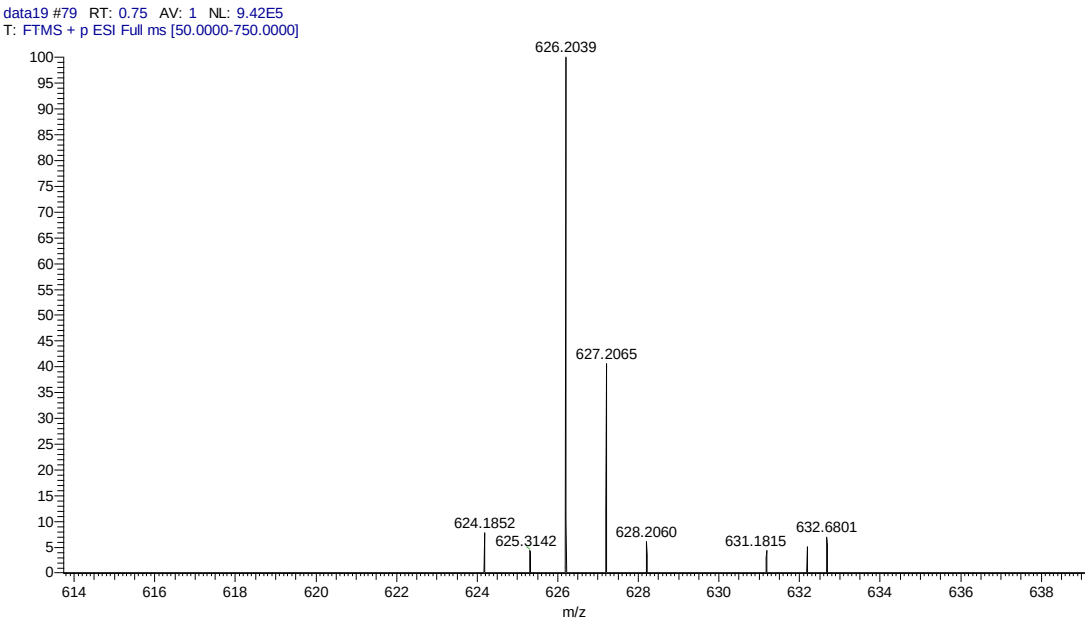
^{1}H NMR (400 MHz, $CDCl_3$)



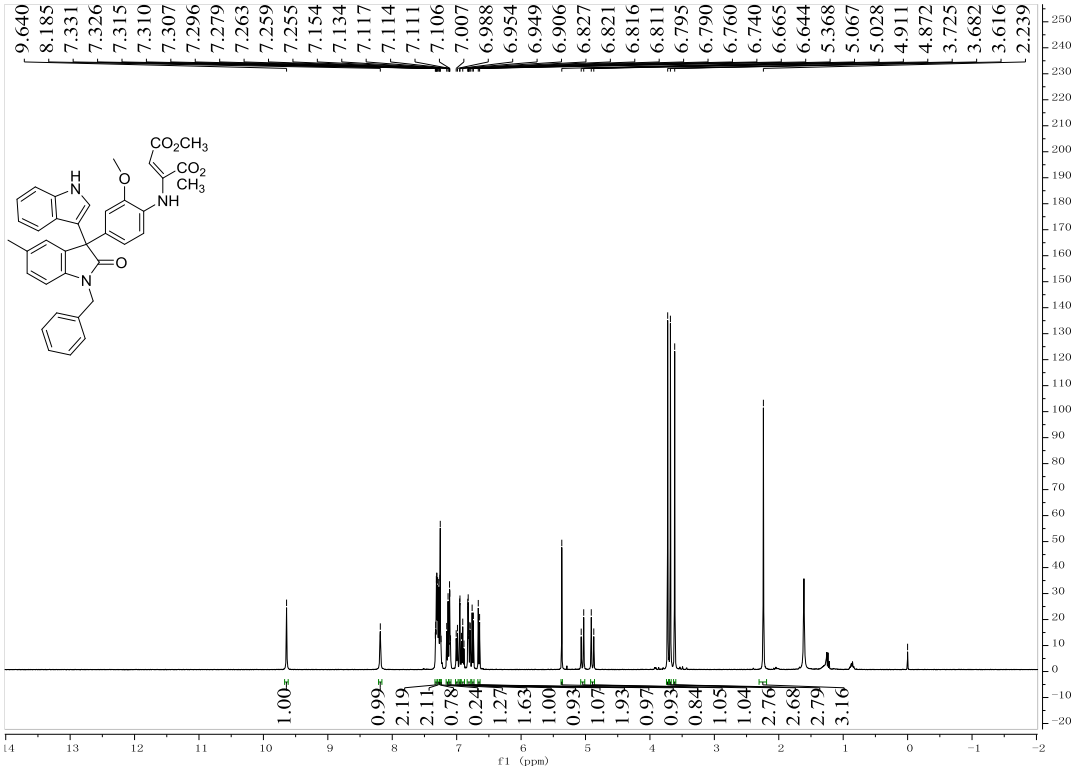
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



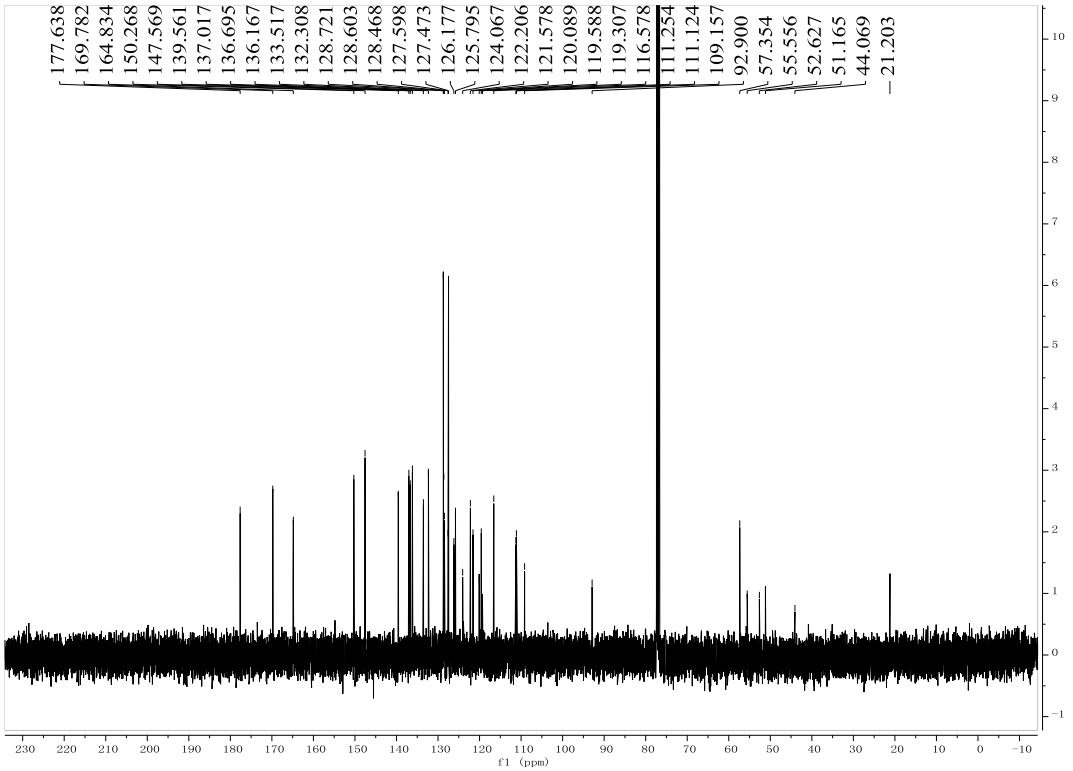
^{19}F NMR (376 MHz, $CDCl_3$)


data19 #79 RT: 0.75 AV: 1 NL: 9.42E5
T: FTMS + p ESI Full ms [50.0000-750.0000]
626.2039
627.2065
624.1852
625.3142
628.2060
631.1815
632.6801
m/z

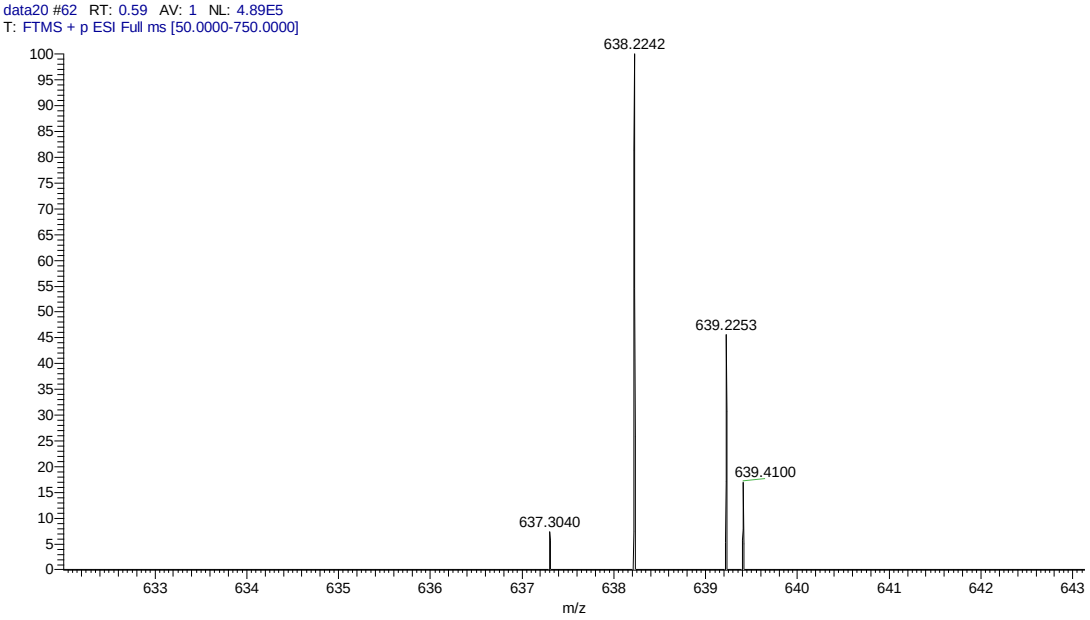
Dimethyl 0-2-((4-(1-benzyl-3-(1H-indol-3-yl)-5-methyl-2-oxoindolin-3-yl)-2-methoxyphenyl) amino)maleate (5g): yellow solid, 64%, m.p. 236-241 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.64 (s, 1H, NH), 8.19 (s, 1H, NH), 7.33-7.30 (m, 2H, ArH), 7.29 (d, *J* = 6.8 Hz, 2H, ArH), 7.26-7.24 (m, 1H, ArH), 7.15-7.13 (m, 1H, ArH), 7.12-7.10 (m, 1H, ArH), 7.00 (d, *J* = 7.6 Hz, 1H, ArH), 6.95 (d, *J* = 2.0 Hz, 1H, ArH), 6.91 (t, *J* = 7.6 Hz, 1H, ArH), 6.83-6.79 (m, 2H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 6.65 (d, *J* = 8.4 Hz, 1H, ArH), 5.37 (s, 1H, CH), 5.05 (d, *J* = 15.6 Hz, 1H, CH), 4.89 (d, *J* = 15.6 Hz, 1H, CH), 3.73 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 2.24 (s, 3H, CH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 177.6, 169.8, 164.8, 150.3, 147.6, 139.6, 137.0, 136.7, 136.2, 133.5, 132.3, 128.7, 128.6, 128.5, 127.6, 127.5, 126.2, 125.8, 124.1, 122.2, 121.6, 120.1, 119.,6 119.3, 116.6, 111.3, 111.1, 109.2, 92.9, 77.3, 77.0, 76.7, 57.4, 55.6, 52.6, 51.2, 44.1, 21.2 ppm; IR (KBr) υ: 3408, 3063, 3000, 2360, 1732, 1696, 1615, 1519, 1497, 1458, 1438, 1346, 1280, 1218, 1191, 1150, 1114, 1029, 891, 851, 813, 779 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{29}H_{19}ClN_2NaO_6$ ([M+Na]$^{+}$): 638.2262, Found: 638.2242.



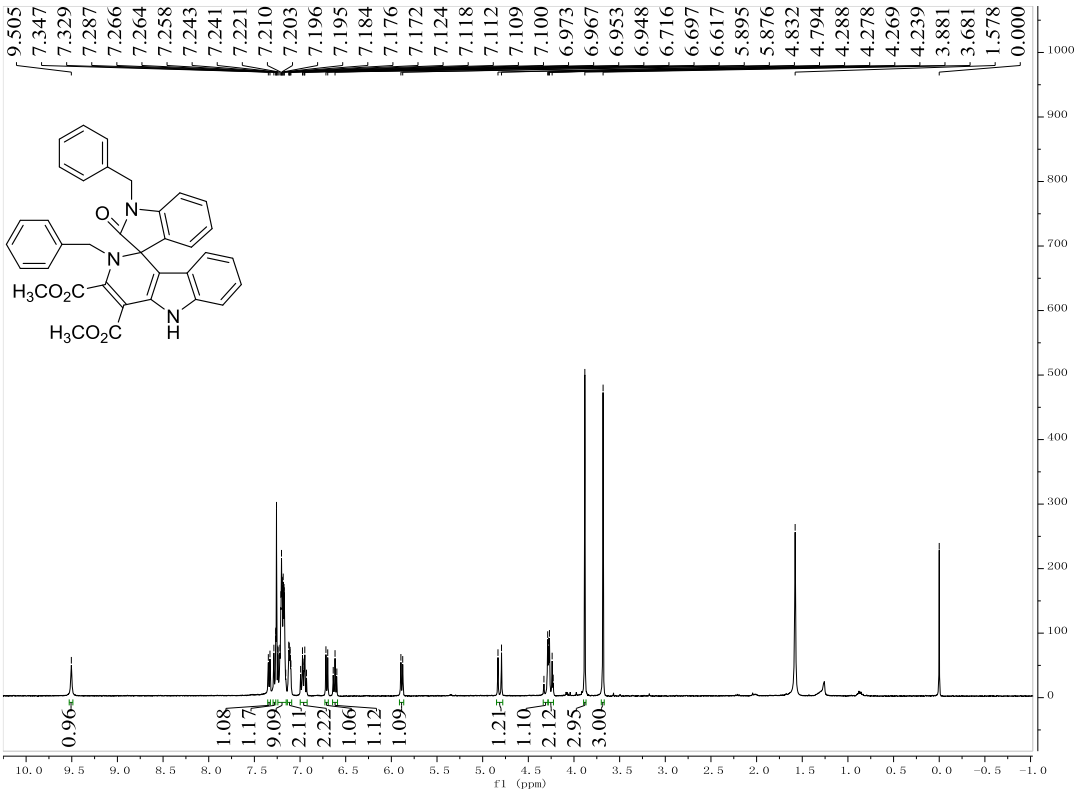
^{1}H NMR (400 MHz, $CDCl_3$)



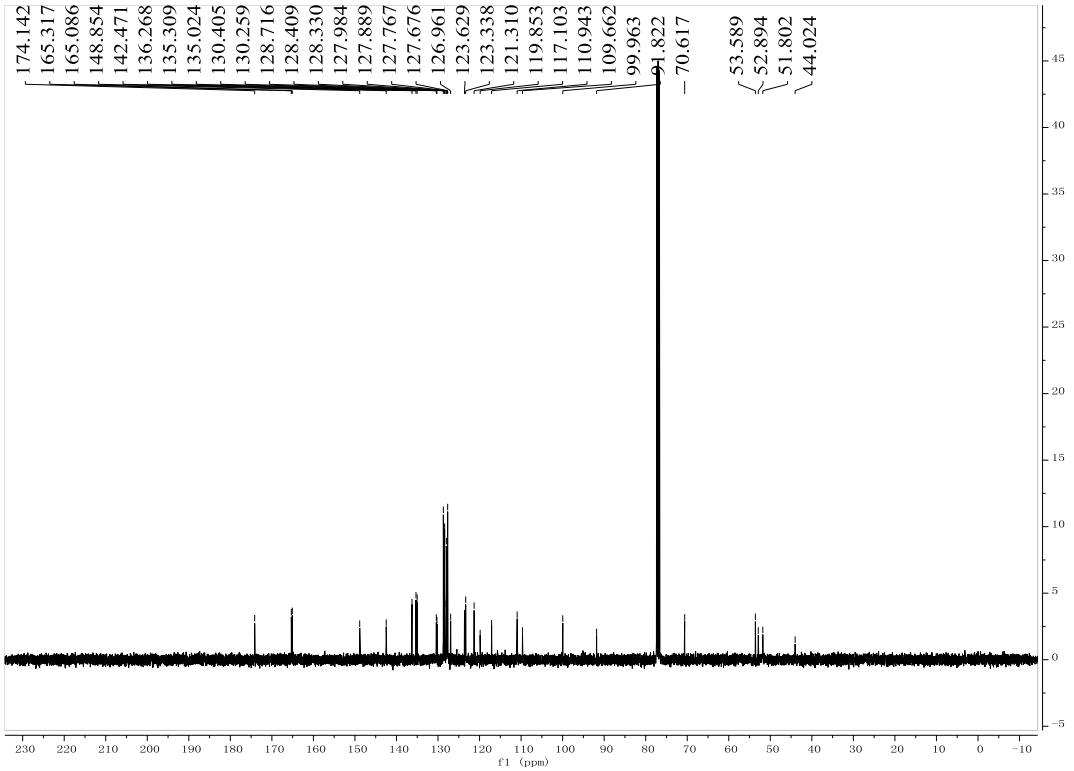
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



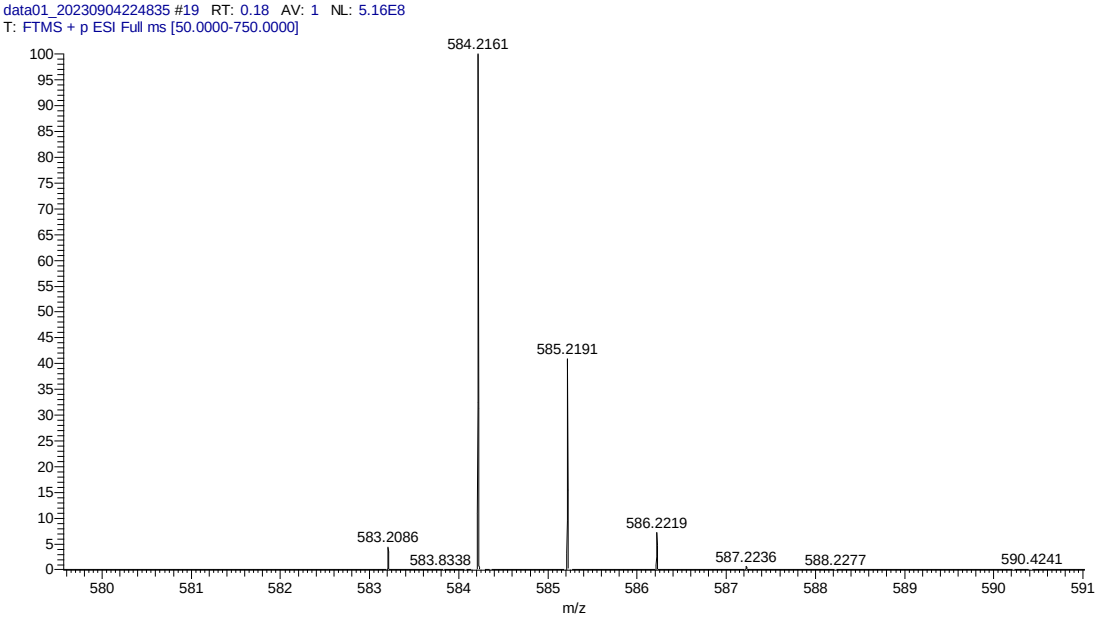
Dimethyl 1,2'-dibenzyl-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (6a): yellow solid, 63%, m.p. 192-198 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.51 (s, 1H, NH), 7.34 (d, *J* = 7.2 Hz, 1H, ArH), 7.28 (d, *J* = 8.4 Hz, 1H, ArH), 7.22-7.16 (m, 9H, ArH), 7.12-7.10 (m, 2H, ArH), 6.99-6.93 (m, 2H, ArH), 6.71 (d, *J* = 7.6 Hz, 1H, ArH), 6.62 (t, *J* = 8.0 Hz, 1H, ArH), 5.89 (d, *J* = 7.6 Hz, 1H, ArH), 4.81 (d, *J* = 15.2 Hz, 1H, CH), 4.31 (d, *J* = 15.6 Hz, 1H, CH), 4.28-4.23 (m, 2H, CH), 3.88 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.1, 165.3, 165.1, 148.9, 142.5, 136.3, 135.3, 135.0, 130.4, 130.3, 128.7, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.0, 123.6, 123.3, 121.3, 119.9, 117.1, 110.9, 109.7, 100.0, 91.8, 77.3, 77.0, 76.7, 70.6, 53.6, 52.9, 51.8, 44.0 ppm; IR (KBr) υ: 1740, 1722, 1682, 1568, 1540, 1489, 1468, 1433, 1399, 1362, 1177, 1081, 945 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{30}N_3NaO_5$ ([M+H]$^{+}$): 584.2180, Found: 584.2161.



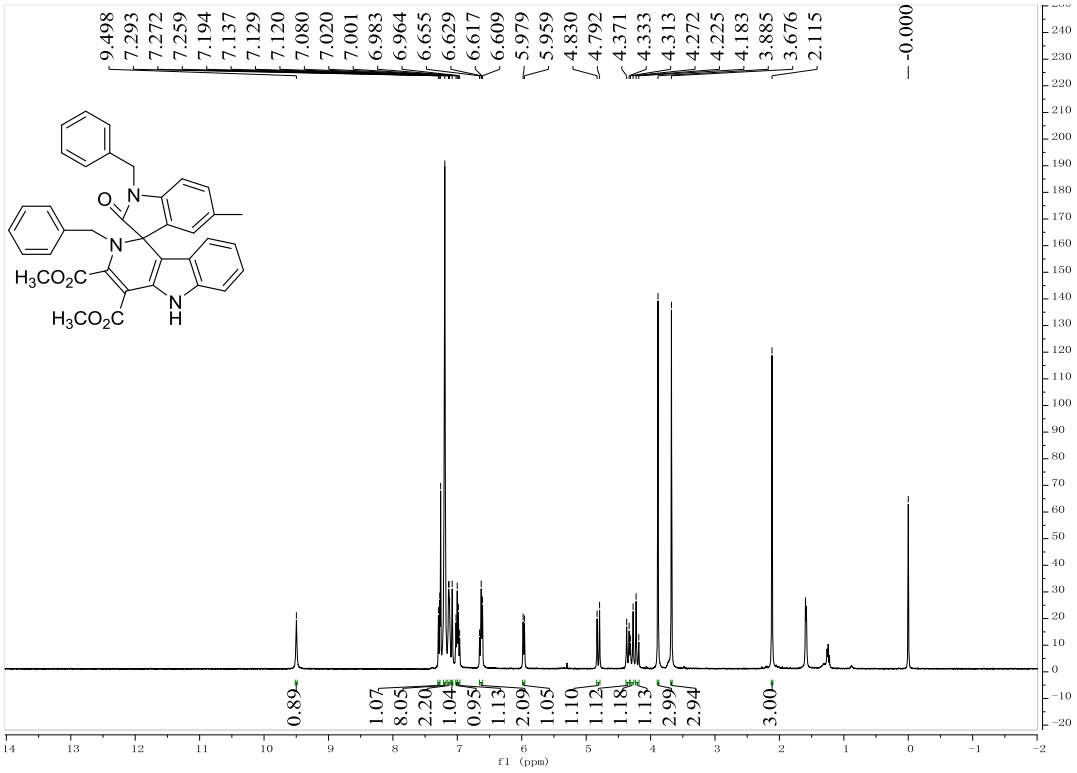
^{1}H NMR (400 MHz, $CDCl_3$)



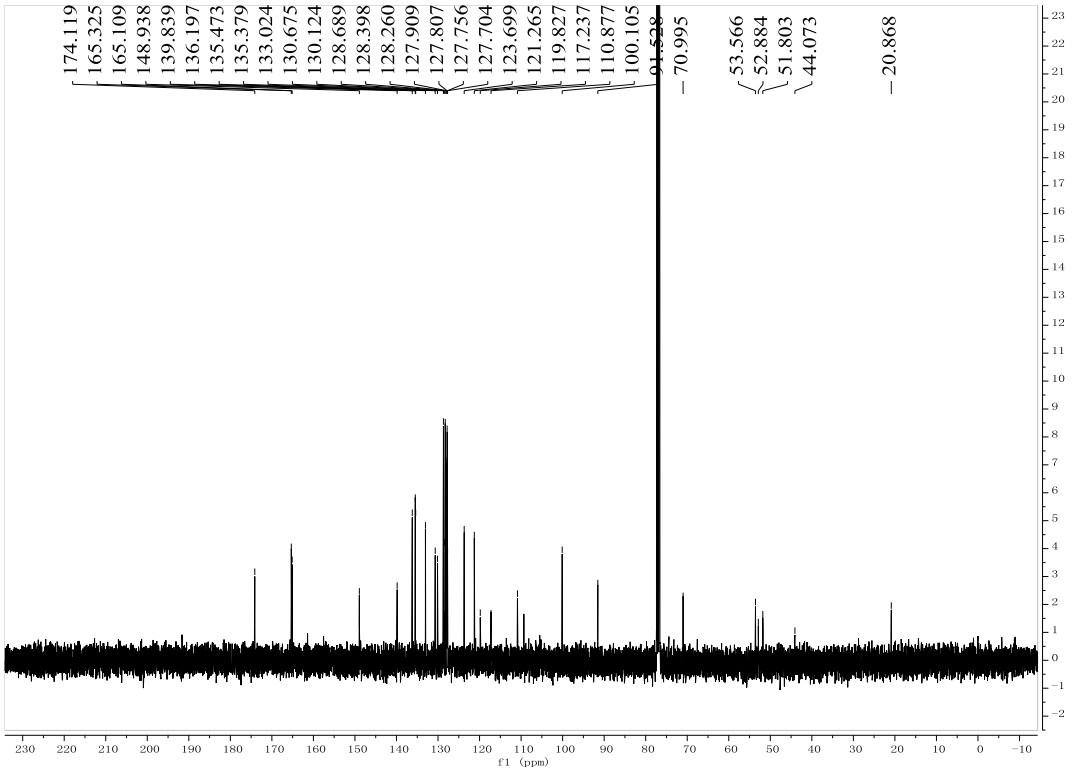
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



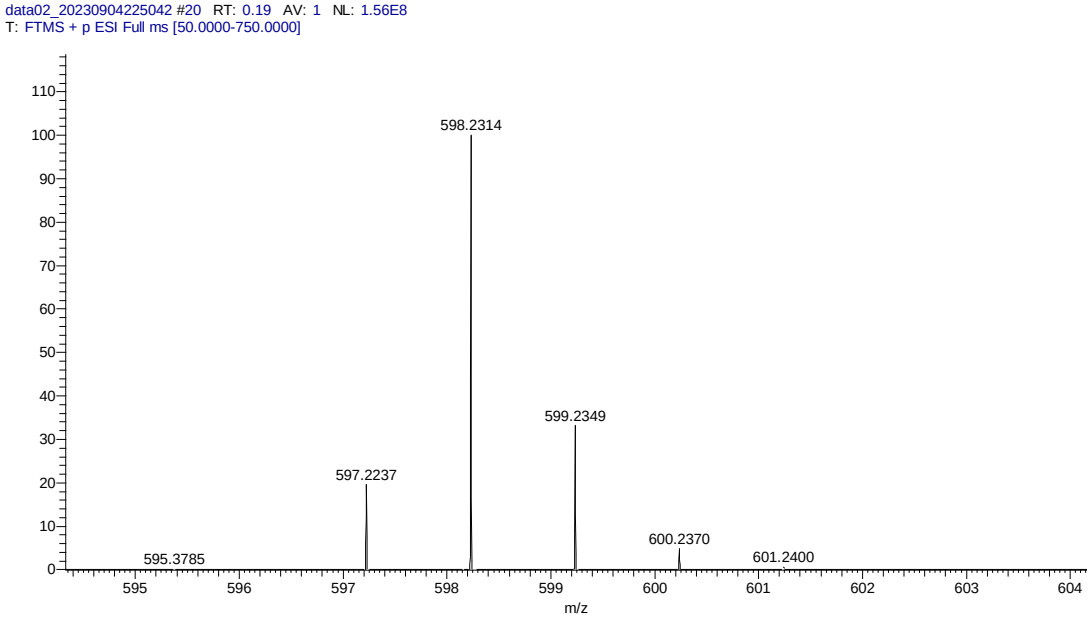
Dimethyl 1,2'-dibenzyl-5-methyl-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole] -3',4'-dicarboxylate (6b): yellow solid, 48%, m.p. 223-226 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.50 (s, 1H, NH), 7.28 (d, *J* = 8.4 Hz, 1H, ArH), 7.19 (s, 8H, ArH), 7.14-7.12 (m, 1H, ArH), 7.08 (s, 1H, ArH), 7.01 (d, *J* = 7.6 Hz, 1H, ArH), 6.98 (t, *J* = 7.6 Hz, 1H, ArH), 6.66-6.61 (m, 2H, ArH), 5.97 (d, *J* = 8.0 Hz, 1H, ArH), 4.81 (d, *J* = 15.2 Hz, 1H, CH), 4.35 (d, *J* = 15.2 Hz, 1H, CH), 4.29 (d, *J* = 15.6 Hz, 1H, CH), 4.20 (d, *J* = 15.2 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 2.12 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.1, 165.3, 165.1, 148.9, 139.8, 136.2, 135.5, 135.4, 133.0, 130.7, 130.1, 128.7, 128.4, 128.3, 127.9, 127.8, 127.7, 123.7, 121.3, 119.8, 117.2, 110.9, 100.1, 91.5, 77.3, 77.0, 76.7, 71.0, 53.6, 52.9, 51.8, 44.1, 20.9 ppm; IR (KBr) υ: 3447, 1738, 1718, 1663, 1590, 1571, 1544, 1495, 1427, 1404, 1374, 1358, 1326, 1270, 1230, 1170, 1125, 1080, 1013, 958, 916, 852, 809, 783, 758 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{37}H_{32}N_3O_5$ ($[M+H]^+$): 598.2337, Found: 598.2337.



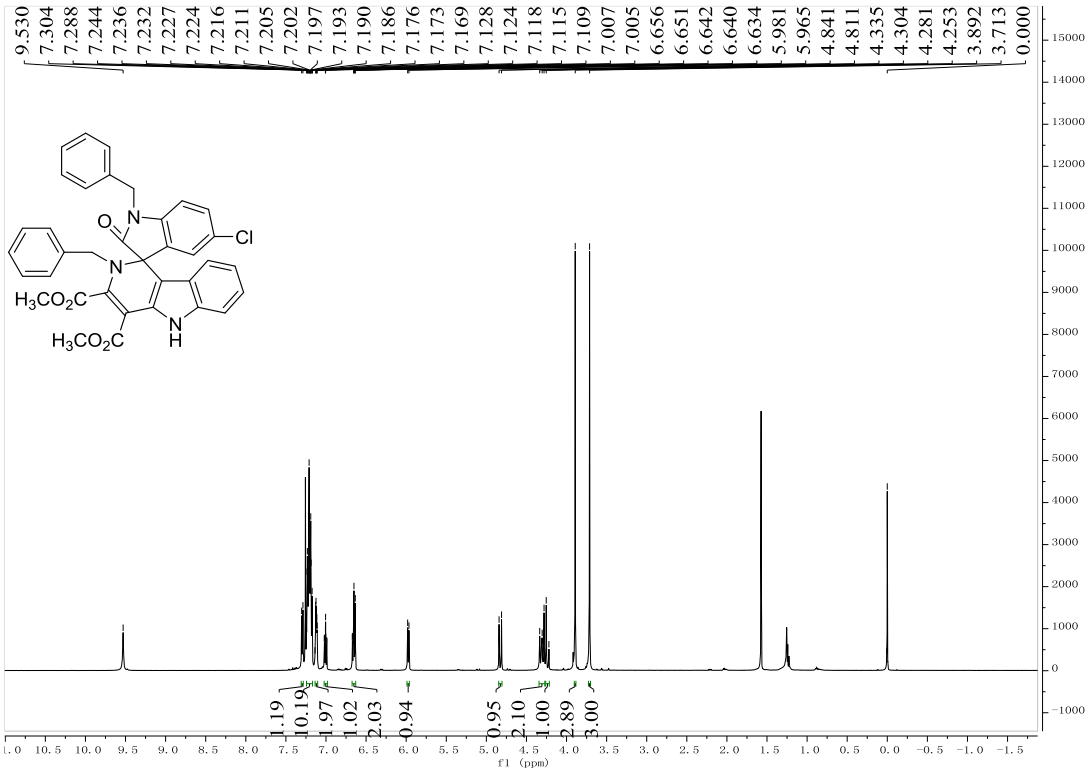
^{1}H NMR (400 MHz, $CDCl_3$)



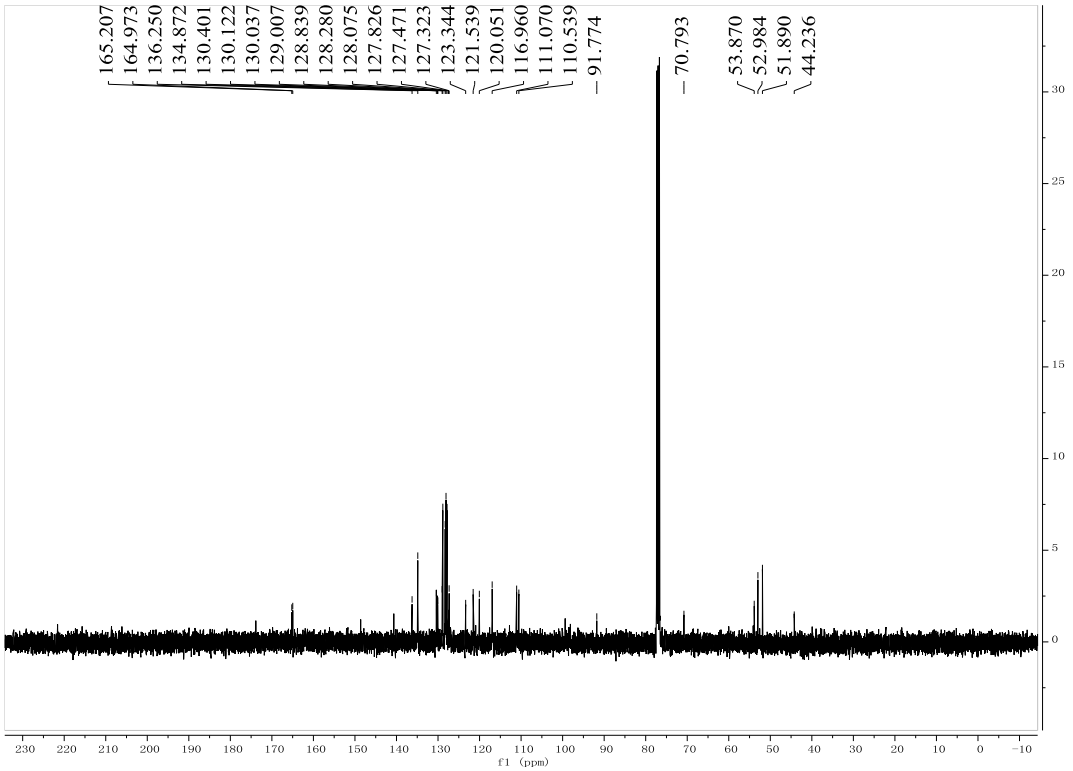
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



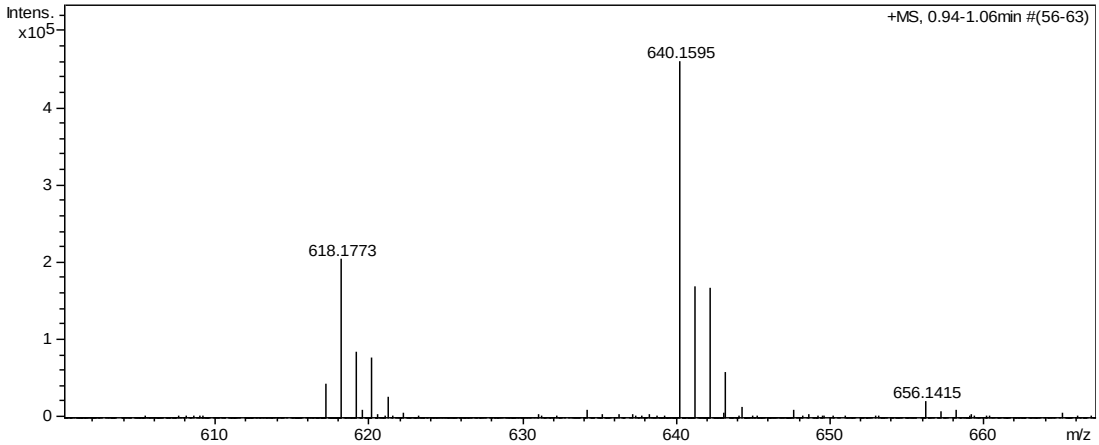
Dimethyl 1,2'-dibenzyl-5-chloro-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (6c): yellow solid, 43%, m.p. 277-283 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.53 (s, 1H, NH), 7.30 (d, *J* = 8.0 Hz, 1H, ArH), 7.24-7.17 (m, 10H, ArH), 7.13-7.11 (m, 2H, ArH), 7.02-6.99 (m, 1H, ArH), 6.67-6.63 (m, 2H, ArH), 5.97 (d, *J* = 8.0 Hz, 1H, ArH), 4.83 (d, *J* = 15.0 Hz, 1H, CH), 4.33-4.29 (m, 2H, CH), 4.24 (d, *J* = 16.5 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 165.0, 136.3, 134.9, 130.4, 130.1, 130.0, 129.0, 128.8, 128.3, 128.1, 127.8, 127.5, 127.3, 123.3, 121.5, 120.1, 117.0, 111.1, 110.5, 91.8, 70.8, 53.9, 53.0, 51.9, 44.2 ppm; IR (KBr) υ: 1734, 1613, 1585, 1566, 1544, 1489, 1453, 1393, 1311, 1174, 1077, 1015, 932, 816, 780 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{28}ClN_3NaO_5$ ([M+Na]$^{+}$): 640.1610, Found: 640.1595.



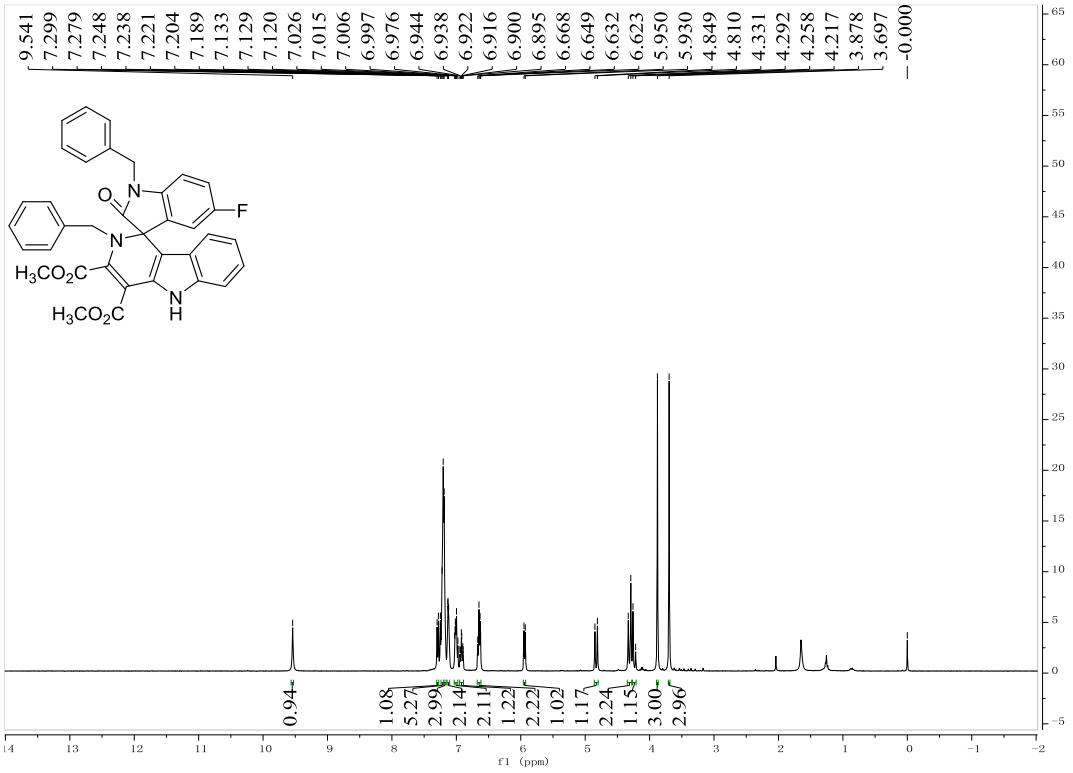
^{1}H NMR (500 MHz, $CDCl_3$)



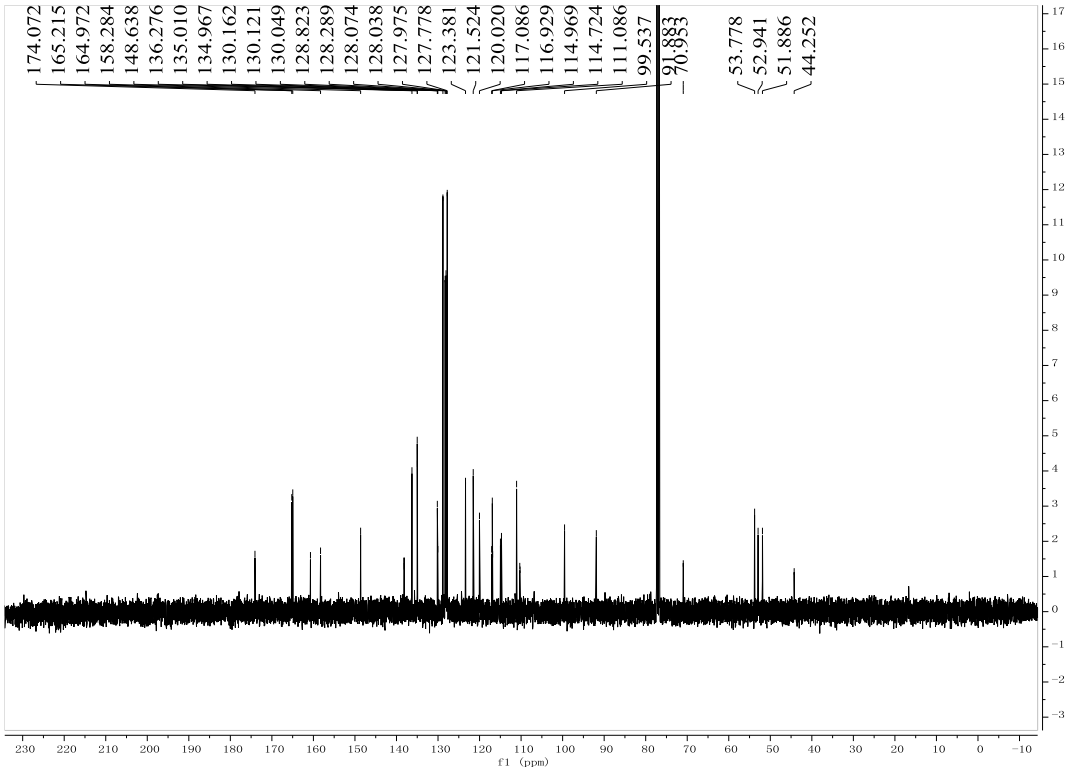
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



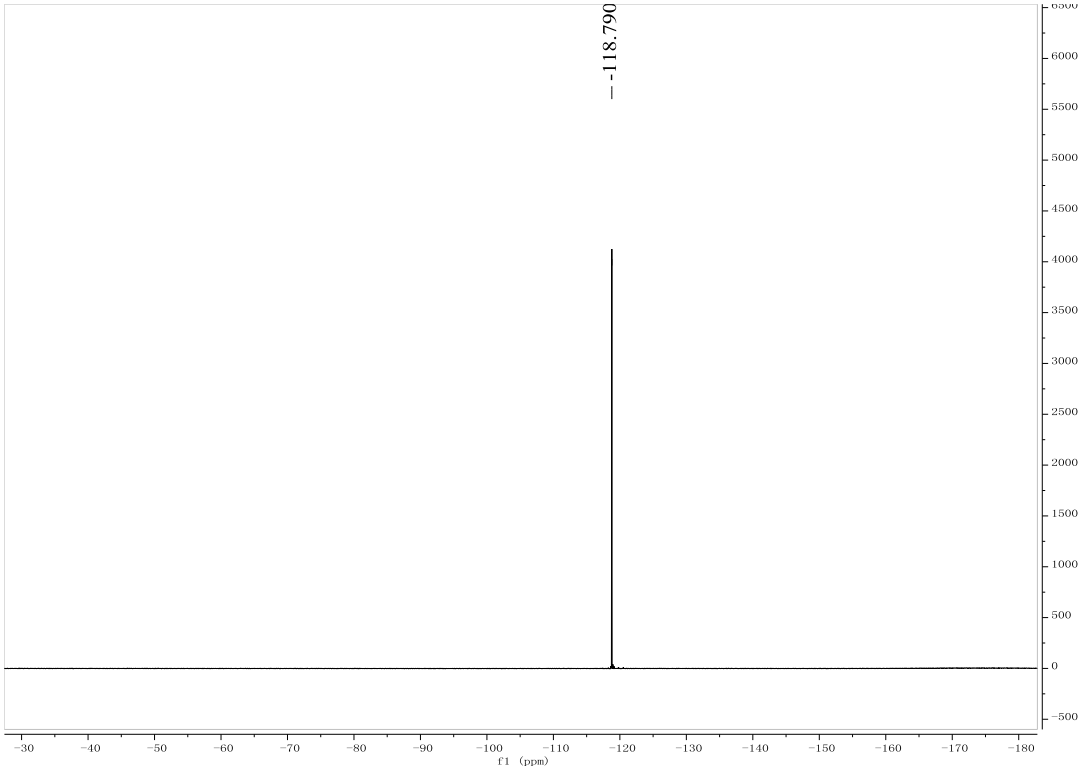
Dimethyl 1,2'-dibenzyl-5-fluoro-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*] indole]-3',4'-dicarboxylate (6d): yellow solid, 52%, m.p. 178-182 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ:9.54 (s, 1H, NH), 7.29 (d, *J* = 8.0 Hz, 1H, ArH), 7.24-7.20 (m, 5H, ArH), 7.19 (s, 3H, ArH),7.13-7.12 (m, 2H, ArH), 7.03-6.98 (m, 2H, ArH), 6.94-6.90 (m, 1H, ArH), 6.67-6.62 (m, 2H, ArH), 5.94 (d, *J* = 8.0 Hz, 1H, ArH), 4.83 (d, *J* = 15.6 Hz, 1H, CH), 4.31(d, *J* =15.6 Hz, 2H, CH), 4.24 (d, *J* =16.4 Hz, 1H, CH), 3.88 (s, 3H, NCH_3), 3.70 (s, 3H, OCH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.1, 165.2, 165.0, 159.5 (d, *J* = 242.6 Hz), 148.6, 138.2, 136.3, 135.0, 135.0, 130.2, 130.1 (d, *J* = 7.2 Hz), 128.8, 128.3, 128.1, 128.0, 128.0, 127.9, 123.4, 121.5, 120.2, 117.0 (d, *J* = 23.4 Hz), 116.8, 114.8 (d, *J* = 24.5 Hz), 111.1, 110.3 (d, *J* = 7.7 Hz), 99.5, 91.9, 77.4, 77.0, 76.7, 71.0, 53.8, 52.9, 51.9, 44.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -118.8 ppm; IR (KBr) υ: 1732, 1616, 1586, 1568, 1547, 1489, 1454, 1398, 1313, 1264, 1175, 1079, 1017, 933, 816, 787 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{29}FN_3O_5$ ([M+H]$^{+}$): 602.2086, Found: 602.2064.



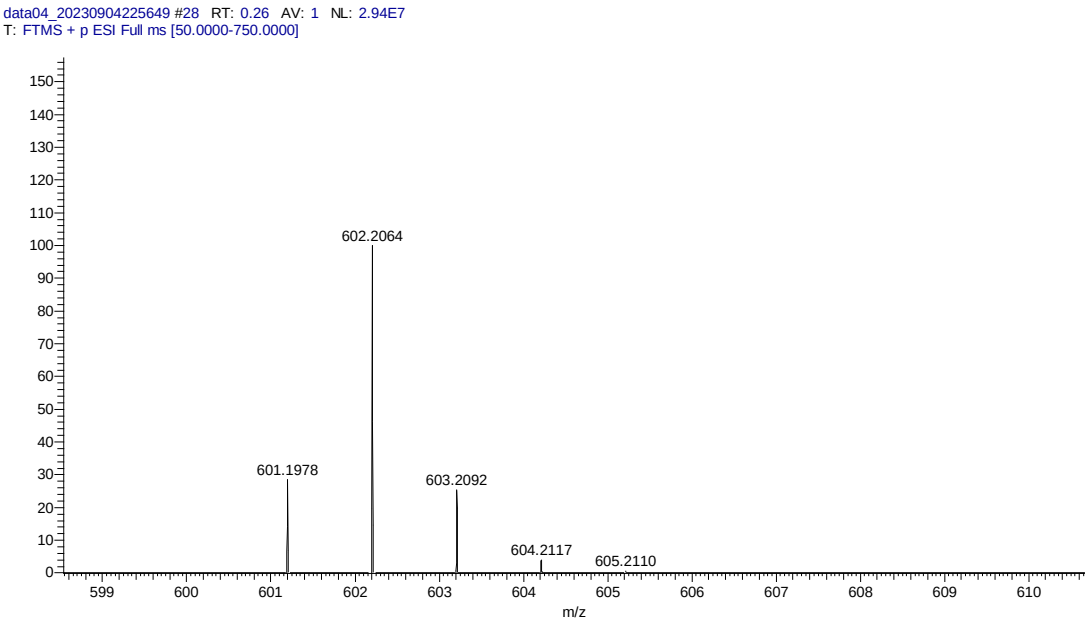
^{1}H NMR (400 MHz, $CDCl_3$)



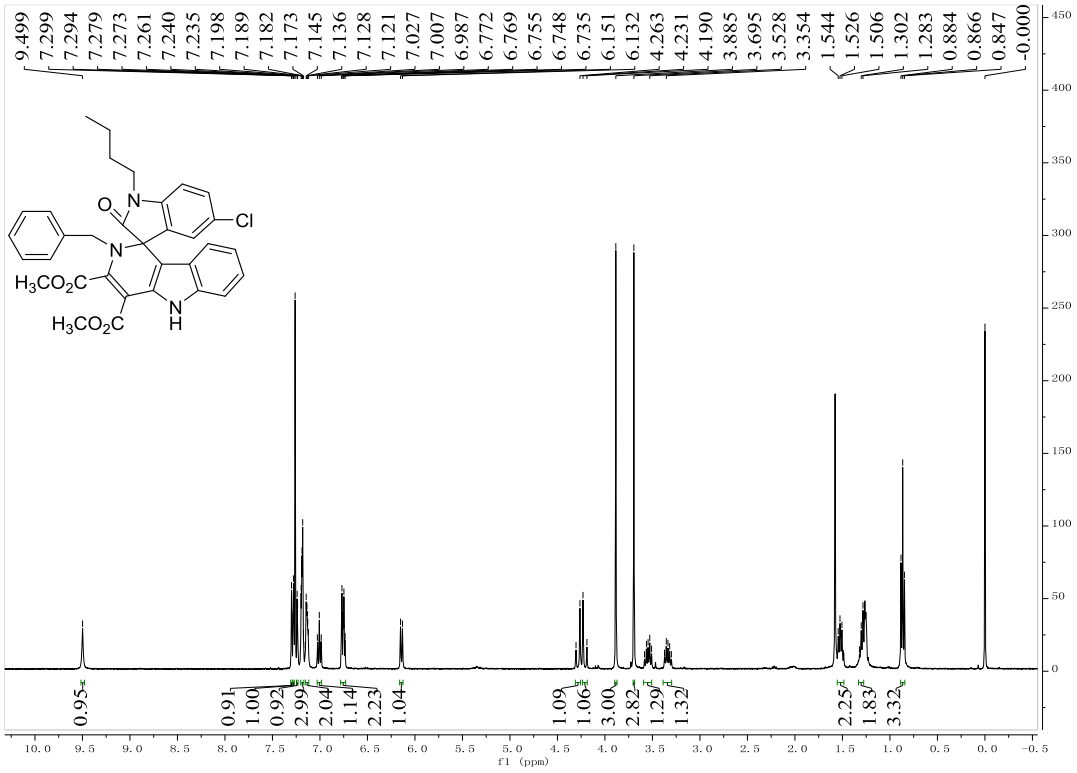
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



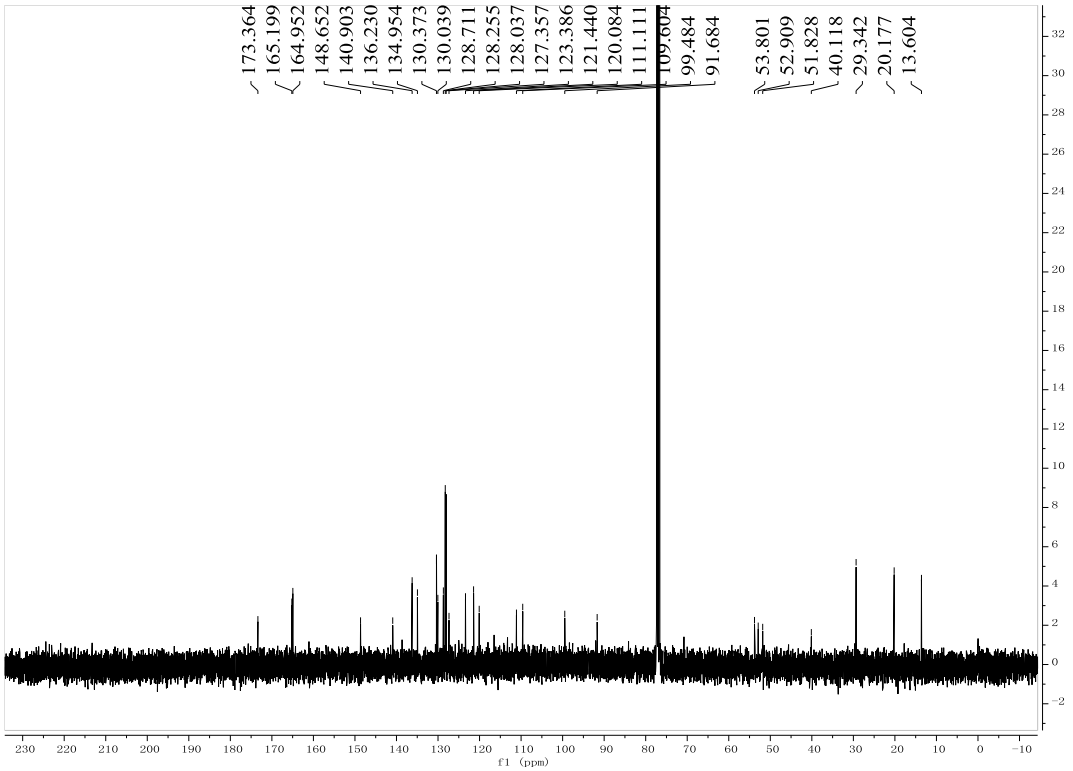
^{19}F NMR (376 MHz, $CDCl_3$)


data04_20230904225649 #28 RT: 0.26 AV: 1 NL: 2.94E7
T: FTMS + p ESI Full ms [50.0000-750.0000]
602.2064
601.1978
603.2092
604.2117
605.2110
m/z

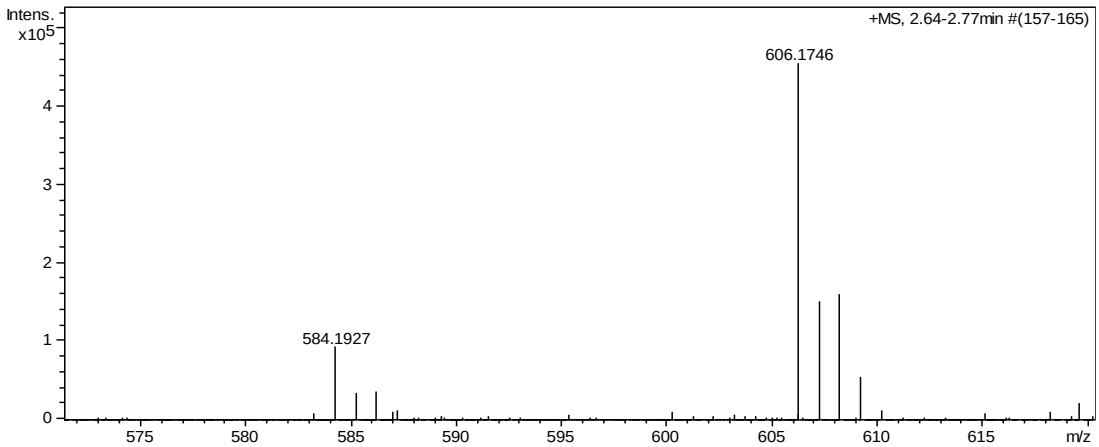
Dimethyl 2'-benzyl-1-butyl-5-chloro-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole]-3',4'-dicarboxylate (6e): yellow solid, 57%, m.p. 223-228 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.50 (s, 1H, NH), 7.30 (d, *J* = 2.0 Hz, 1H, ArH), 7.28 (d, *J* = 1.6 Hz, 1H, ArH), 7.24 (d, *J* = 2.0 Hz, 1H, ArH), 7.20-7.17 (m, 3H, ArH), 7.15-7.12 (m, 2H, ArH), 7.01 (t, *J* = 8.0 Hz, 1H, ArH), 6.77-6.74 (m, 2H, ArH), 6.14 (d, *J* = 7.6 Hz, 1H, ArH), 4.28 (d, *J* = 8.4 Hz, 1H, CH), 4.21 (d, *J* = 8.4 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 3.70 (s, 3H, CH_3), 3.58-3.51 (m, 1H, CH), 3.37-3.30 (m, 1H, CH), 1.54-1.49 (m, 2H, CH), 1.32-1.28 (m, 2H, CH), 0.87 (t, *J* = 7.6 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.4, 165.2, 165.0, 148.7, 140.9, 136.2, 135.0, 130.4, 130.0, 128.7, 128.3, 128.0, 127.4, 123.4, 121.4, 120.1, 111.1, 109.6, 99.5, 91.7, 77.3, 77.0, 76.7, 53.8, 52.9, 51.8, 40.1, 29.3, 20.2, 13.6 ppm; IR (KBr) υ: 1748, 1715, 1682, 1647, 1568, 1540, 1489, 1362, 1179 , 919 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{33}H_{30}ClN_3NaO_5$ ([M+Na]$^{+}$): 606.1767, Found: 606.1746.



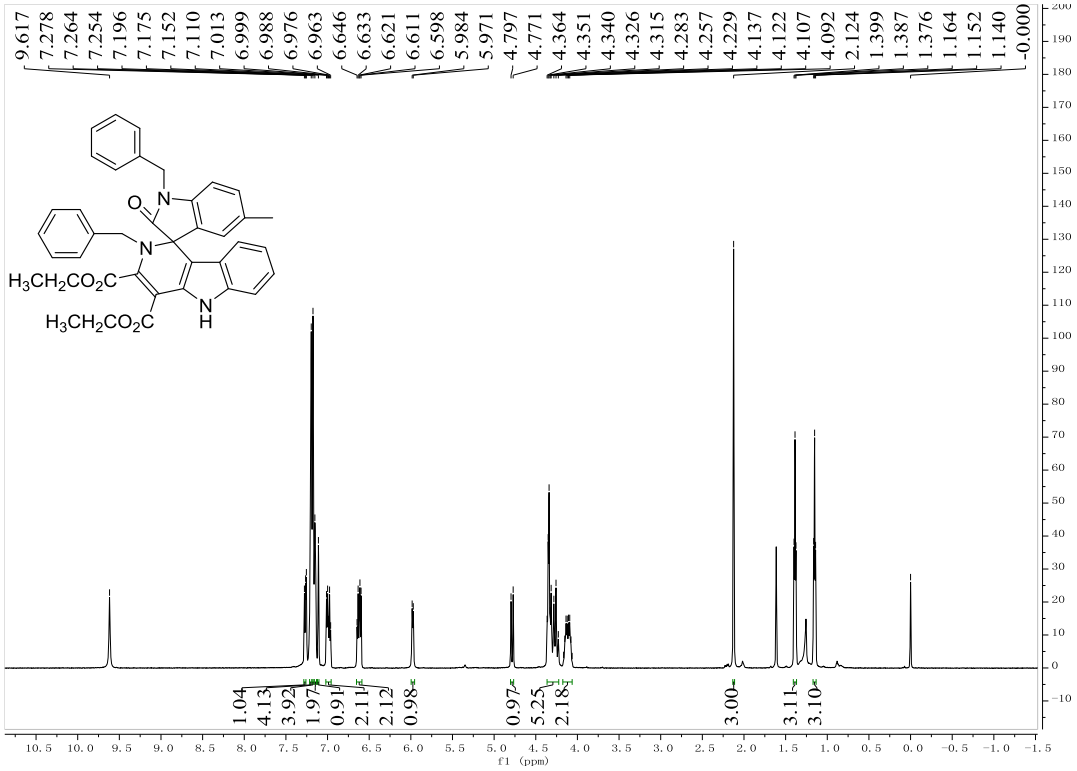
^{1}H NMR (400 MHz, $CDCl_3$)



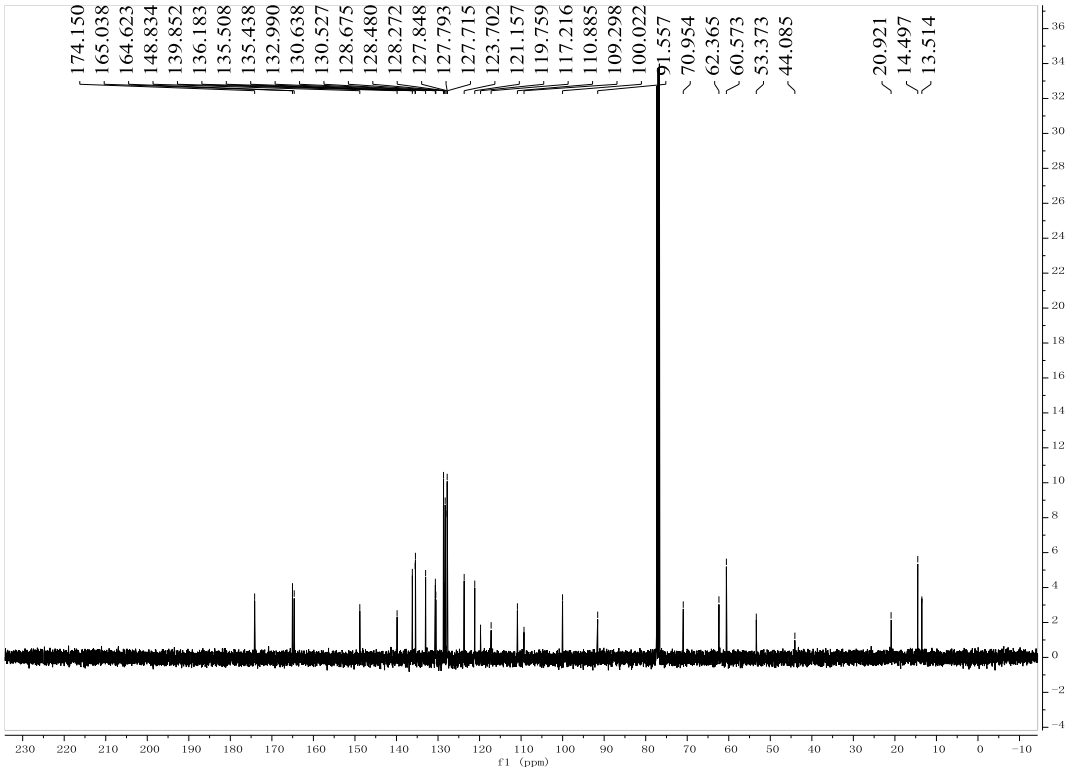
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



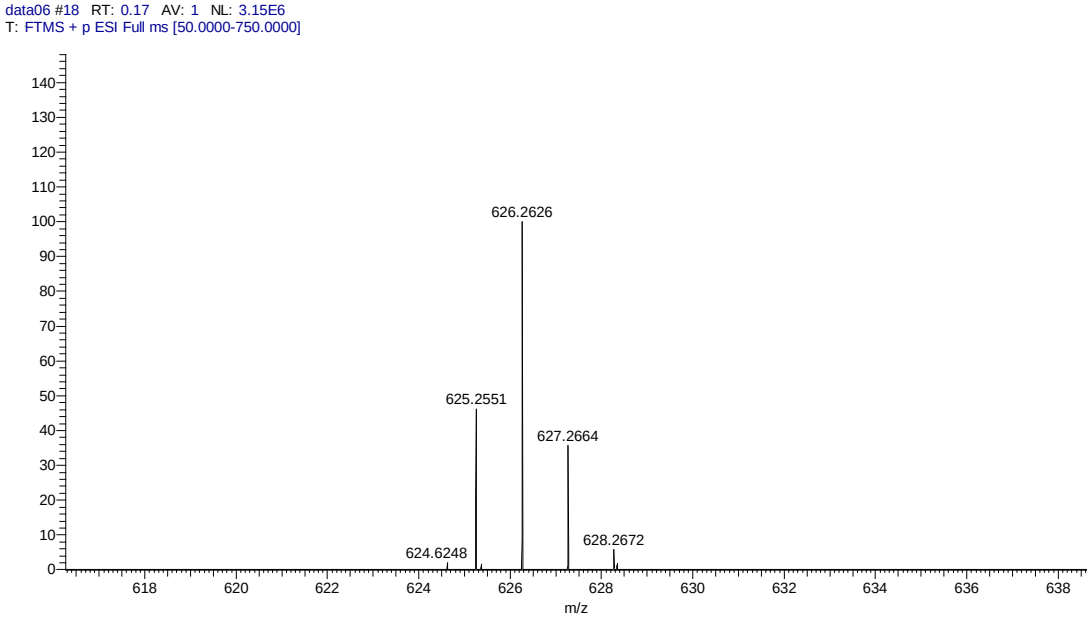
Diethyl 1,2'-dibenzyl-5-methyl-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole] -3',4'-dicarboxylate (6f): yellow solid, 53%, m.p. 223-229 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.62 (s, 1H, NH), 7.27 (d, *J* = 8.4 Hz, 1H, ArH), 7.20 (s, 4H, ArH), 7.18 (s, 4H, ArH), 7.15 (s, 2H, ArH), 7.11 (s, 1H, ArH), 7.01 (d, *J* = 8.4 Hz, 1H, ArH), 6.98 (t, *J* = 7.8 Hz, 1H, ArH), 6.63 (t, *J* = 7.8 Hz, 1H, ArH), 6.60 (d, *J* = 7.2 Hz, 1H, ArH), 5.98 (d, *J* = 8.0 Hz, 1H, ArH), 4.78 (d, *J* = 15.6 Hz, 1H, CH), 4.36-4.33 (m, 2H, CH), 4.33 (d, J_1 = 15.6 Hz, 2H, CH), 4.29 (d, *J* = 16.8 Hz, 1H, CH), 4.24 (d, *J* = 16.8 Hz, 1H, CH), 4.17-4.06 (m, 2H, CH), 2.12 (s, 3H, CH_3), 1.39 (t, *J* = 7.2 Hz, 3H, CH_3), 1.15 (t, *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 165.0, 164.6, 148.8, 139.6, 136.2, 135.5, 135.4, 133.0, 130.6, 130.5, 128.7, 128.5, 128.3, 127.9, 127.8, 127.7, 123.7, 121.2, 119.8, 117.2, 110.9, 109.3, 100.0, 91.6, 77.3, 77.0, 76.7, 71.0, 62.4, 60.6, 53.4, 44.1, 20.9, 14.5, 13.5 ppm; IR (KBr) υ: 3433, 1734, 1716, 1662, 1568, 1543, 1493, 1402, 1356, 1323, 1227, 1163, 1124, 1077, 1014, 955 918, 852, 808, 782 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{39}H_{36}N_3O_5$ ([M+H]$^+$): 626.2650, Found: 626.2626.



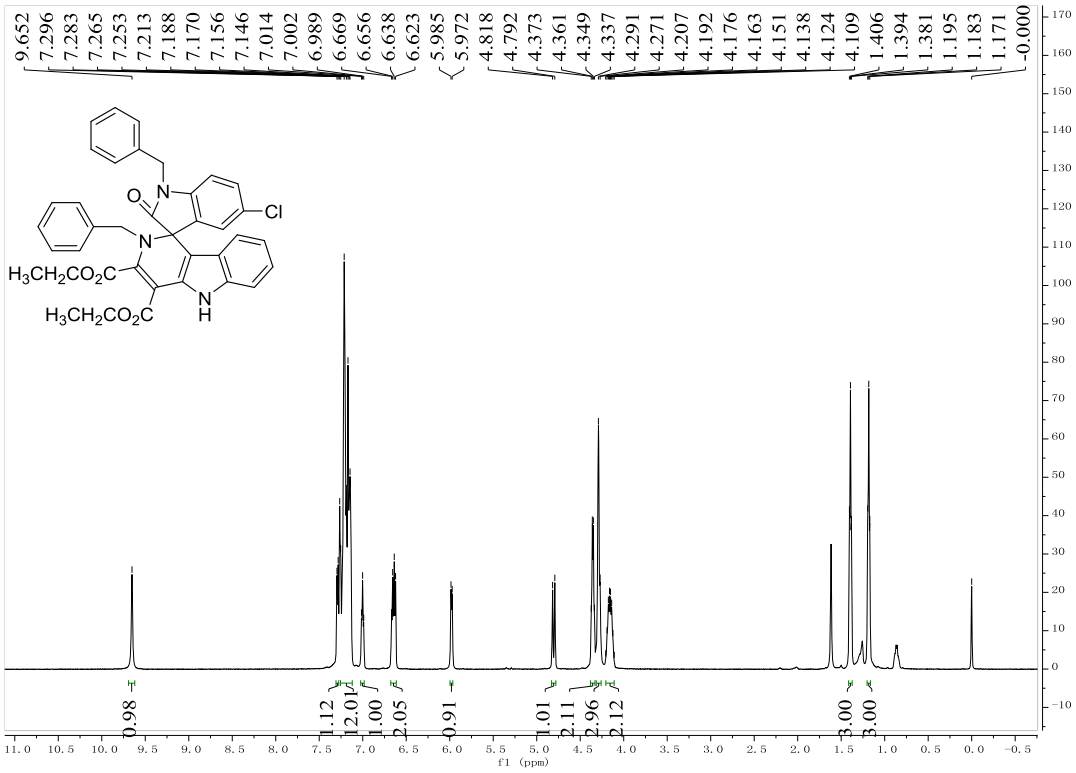
^{1}H NMR (600 MHz, $CDCl_3$)



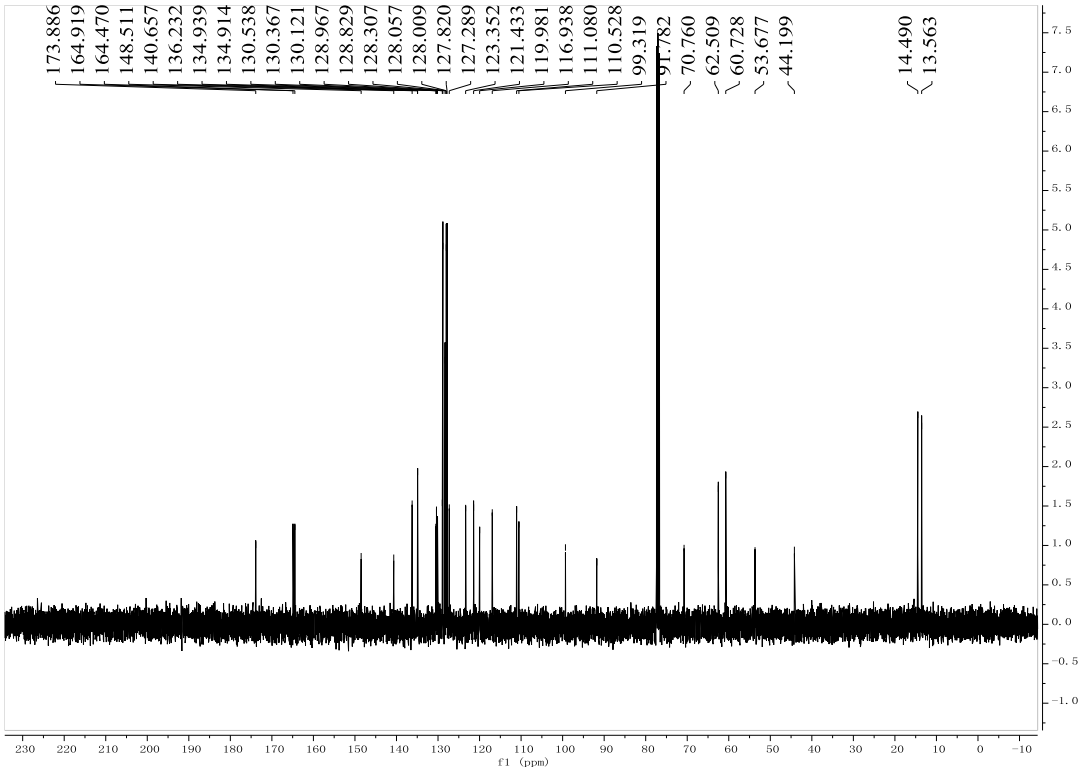
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



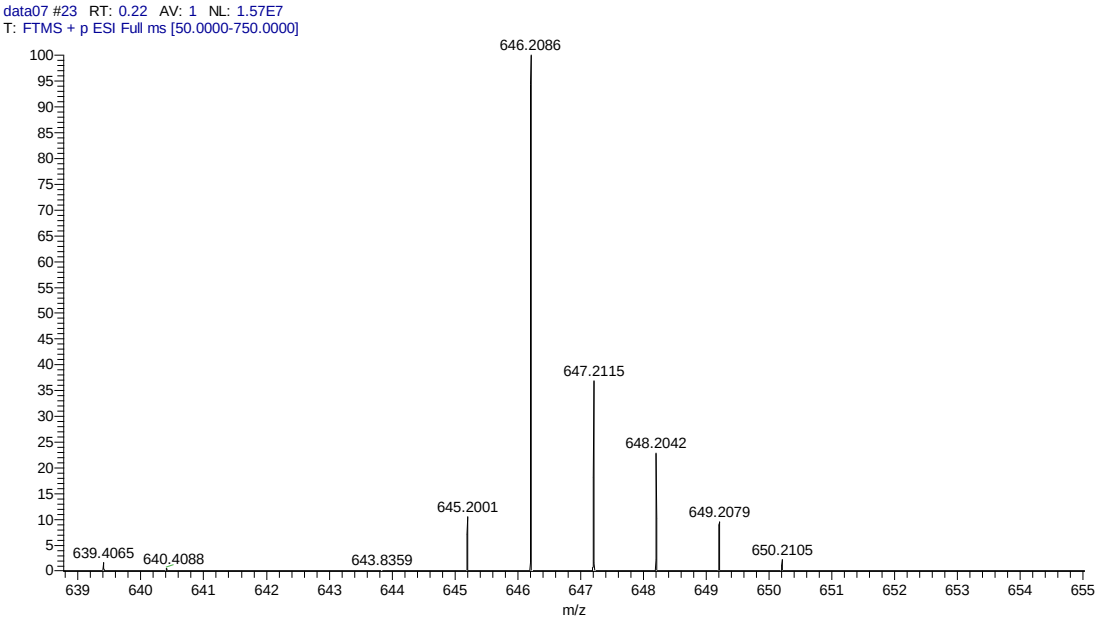
Diethyl 1,2'-dibenzyl-5-chloro-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido[4,3-*b*]indole] -3',4'-dicarboxylate (6g): yellow solid, 62%, ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.65 (s, 1H, NH), 7.29 (d, *J* = 7.8 Hz, 1H, ArH), 7.25-7.15 (m, 12H, ArH), 7.00 (d, *J* = 7.8 Hz, 1H, ArH), 6.67-6.62 (m, 2H, ArH), 5.98 (d, *J* = 7.8 Hz, 1H, ArH), 4.81 (d, *J* = 15.6 Hz, 1H, CH), 4.36 (dd, J_1 = 14.4 Hz, J_2 = 7.2Hz, 2H, CH), 4.28 (m, 3H, ArH), 4.21-4.11 (m, 2H, CH), 1.39 (t, J = 7.2 Hz, 3H, CH_3), 1.18 (t, J = 7.2 Hz, 3H, CH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.9, 164.9, 164.5, 148.5, 140.7, 136.2, 134.9, 134.9, 130.5, 130.4, 130.1, 129.0, 128.8, 128.3, 128.1, 128.0, 127.8, 127.3, 123.4, 121.4, 120.0, 116.9, 111.1, 110.5, 99.3, 91.8, 77.4, 77.1, 76.7, 70.8, 62.5, 60.7, 44.2, 14.5, 13.6 ppm; IR (KBr) υ: 1737, 1664, 1618, 1585, 1563, 1547, 1477, 1466, 1388, 1310, 1188, 1066, 1013, 928, 815, 781 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{33}ClN_3O_5$ ([M+H]$^{+}$): 646.2104, Found: 646.2086.



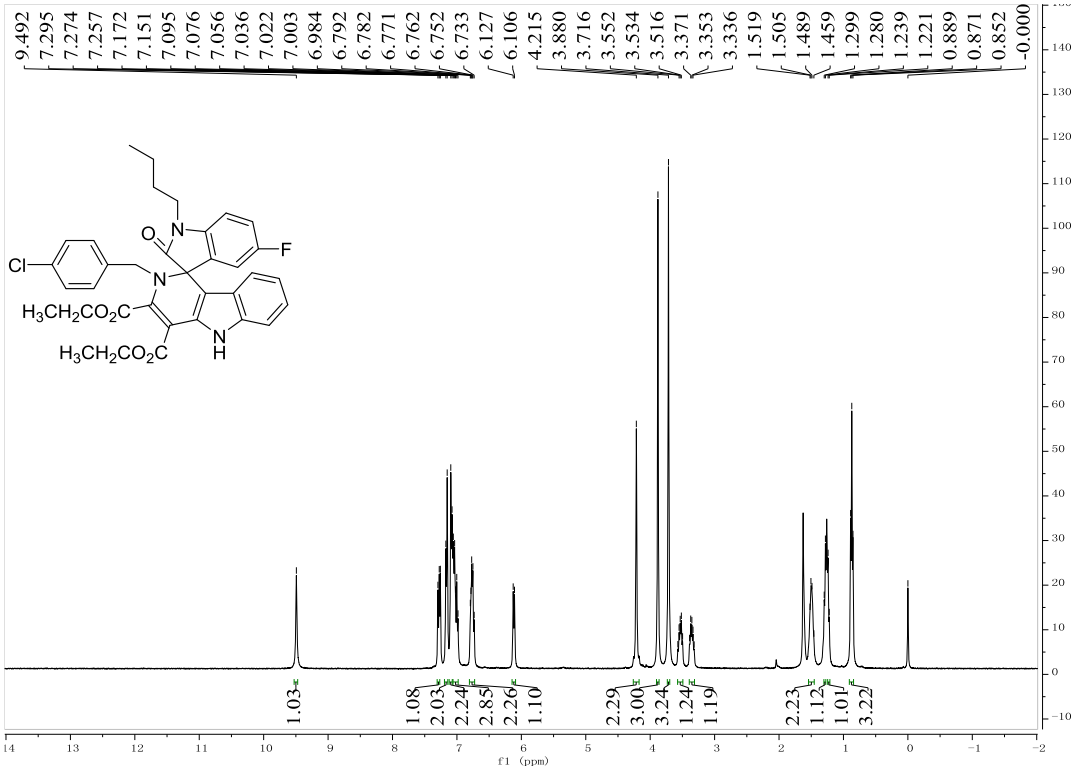
^{1}H NMR (600 MHz, $CDCl_3$)



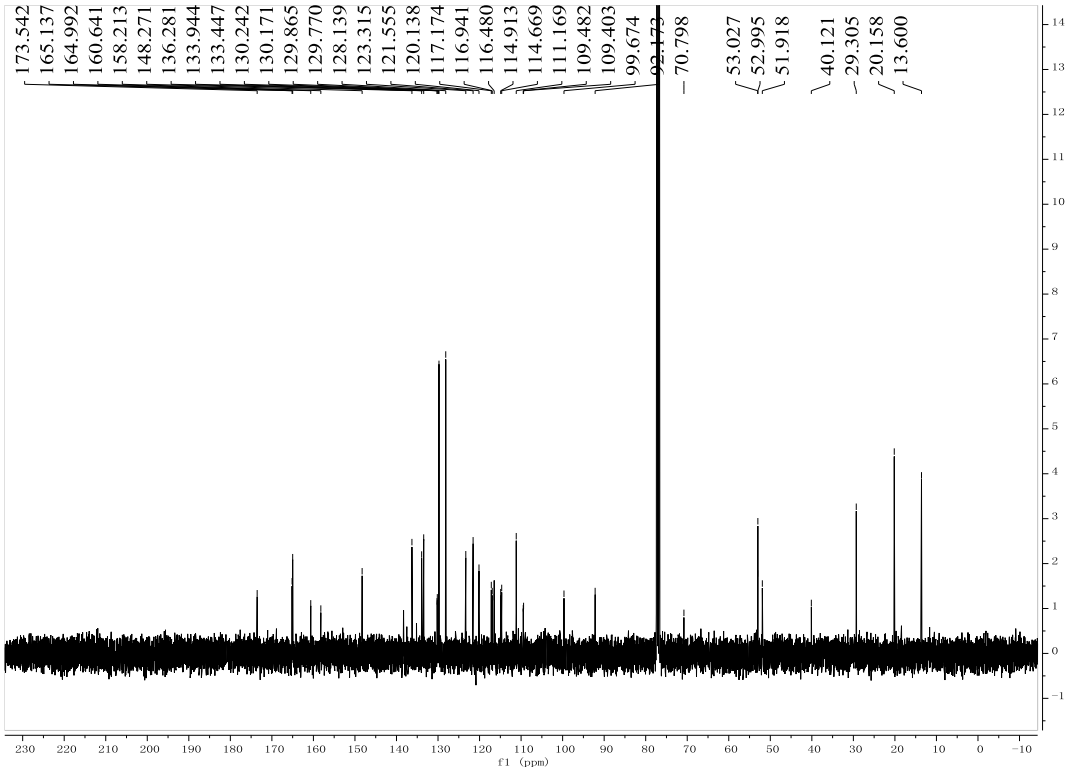
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



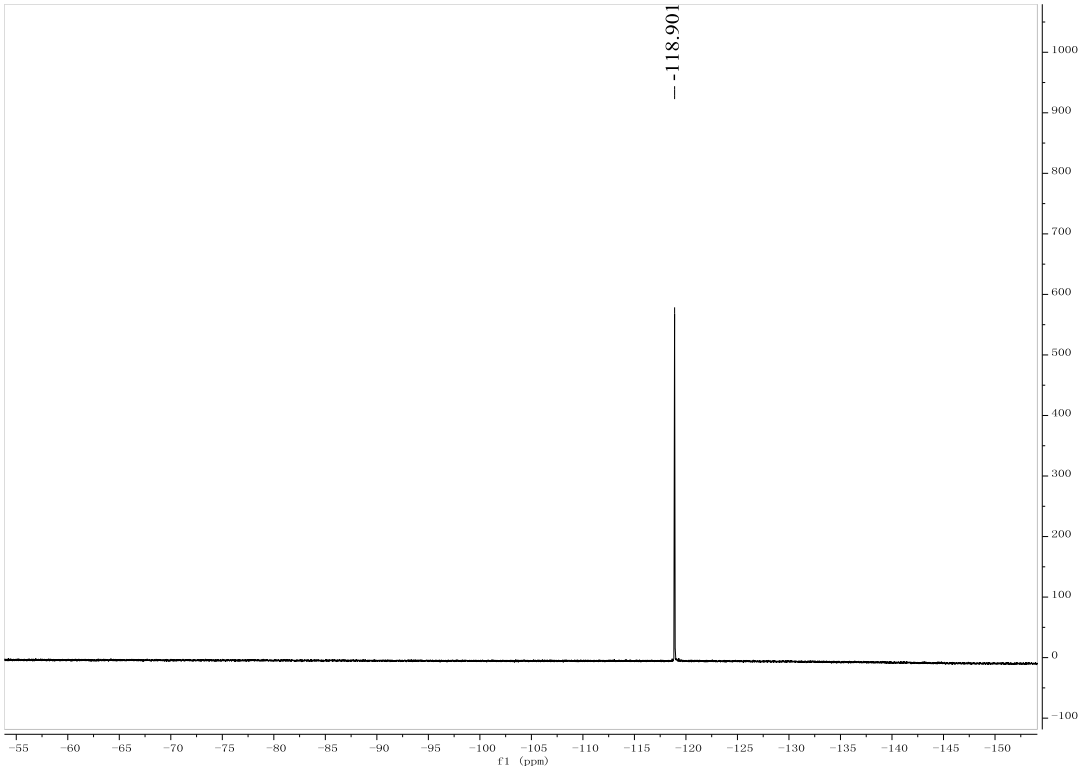
Diethyl 1-butyl-2'-(4-chlorobenzyl)-5-fluoro-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido [4,3-*b*]indole]-3',*4*'-dicarboxylate (6h): yellow solid, 53%, m.p. 249-255 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.49 (s, 1H, NH), 7.28 (d, *J* = 8.4 Hz, 1H, ArH), 7.16 (d, *J* = 8.4 Hz, 1H, ArH), 7.09 (d, *J* = 7.6 Hz, 2H, ArH), 7.06-6.98 (m, 3H, ArH), 6.79-6.73 (m, 2H, ArH), 6.12 (d, *J* = 8.4 Hz, 1H, ArH), 4.22 (s, 2H, CH), 3.88 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.57-3.50 (m, 1H, CH), 3.39-3.32 (m, 1H, CH), 1.52-1.46 (m, 2H, CH), 1.29 (d, *J* = 7.6 Hz, 1H, CH), 1.23 (d, *J* = 8.2 Hz, 1H, CH), 0.87 (t, *J* = 7.6 Hz, 3H, CH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 173.5, 165.1, 165.0, 159.4 (d, *J* = 242.8 Hz), 148.3, 136.3, 133.9, 133. 5, 130.2 (d, *J* = 7.1 Hz), 129.9, 129.8, 128.1, 123.3, 121.6, 120.1, 117.1 (d, *J* = 23.3 Hz), 116.5, 114.8 (d, *J* = 24.4 Hz), 111.2, 109.4 (d, *J* = 7.9 Hz), 99.7, 92.2, 77.3, 77.0, 76.7, 70.8, 53.0, 53.0, 51.9, 40.1, 29.3, 20.2, 13.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -118.9 ppm; IR (KBr) υ: 1748, 1715, 1698, 1682, 1647, 1568, 1540, 1489, 1362, 1179, 920 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{35}H_{34}ClFN_3O_5$ ($[M+H]^+$): 602.1853, Found: 602.1824.



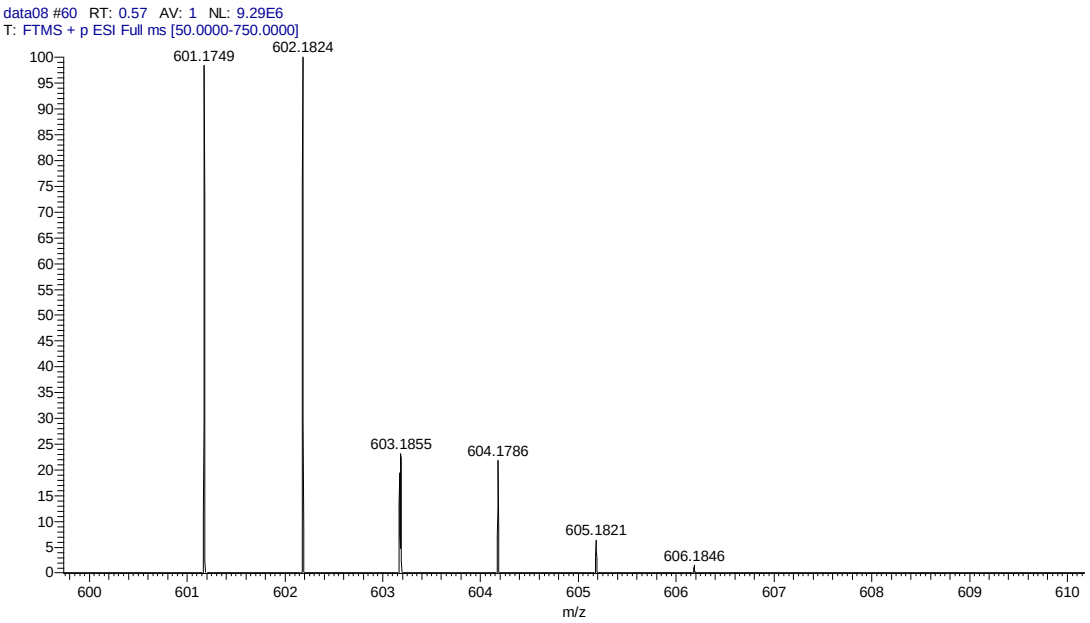
^{1}H NMR (400 MHz, $CDCl_3$)



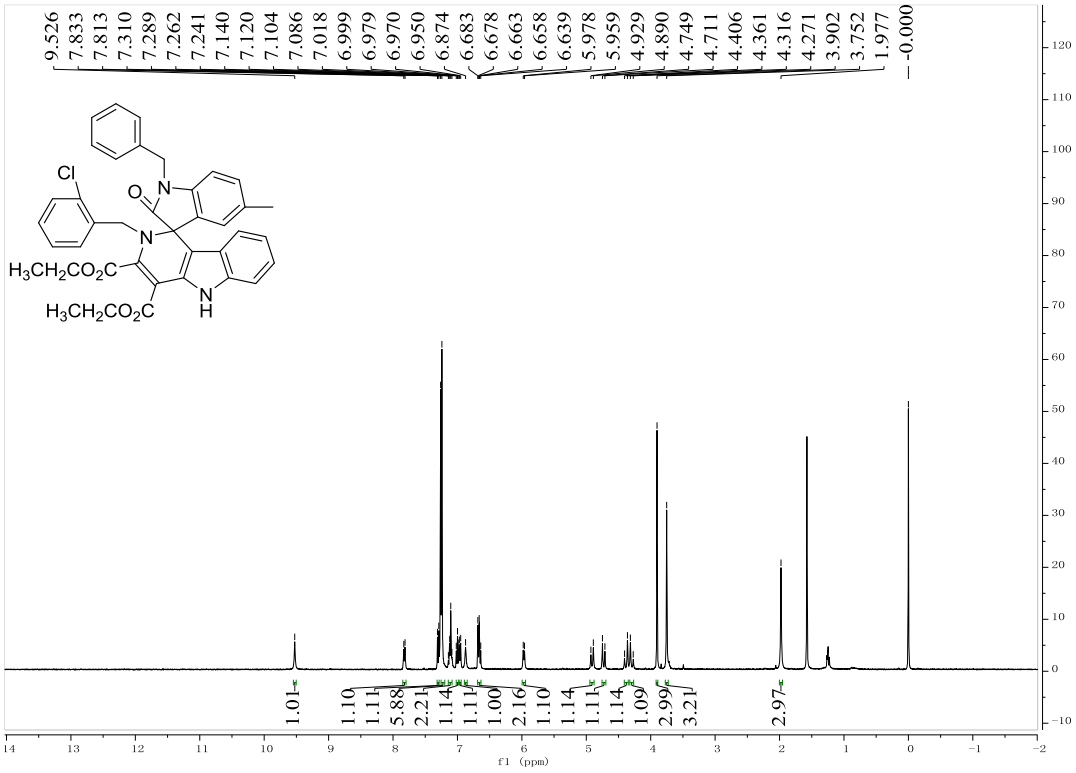
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



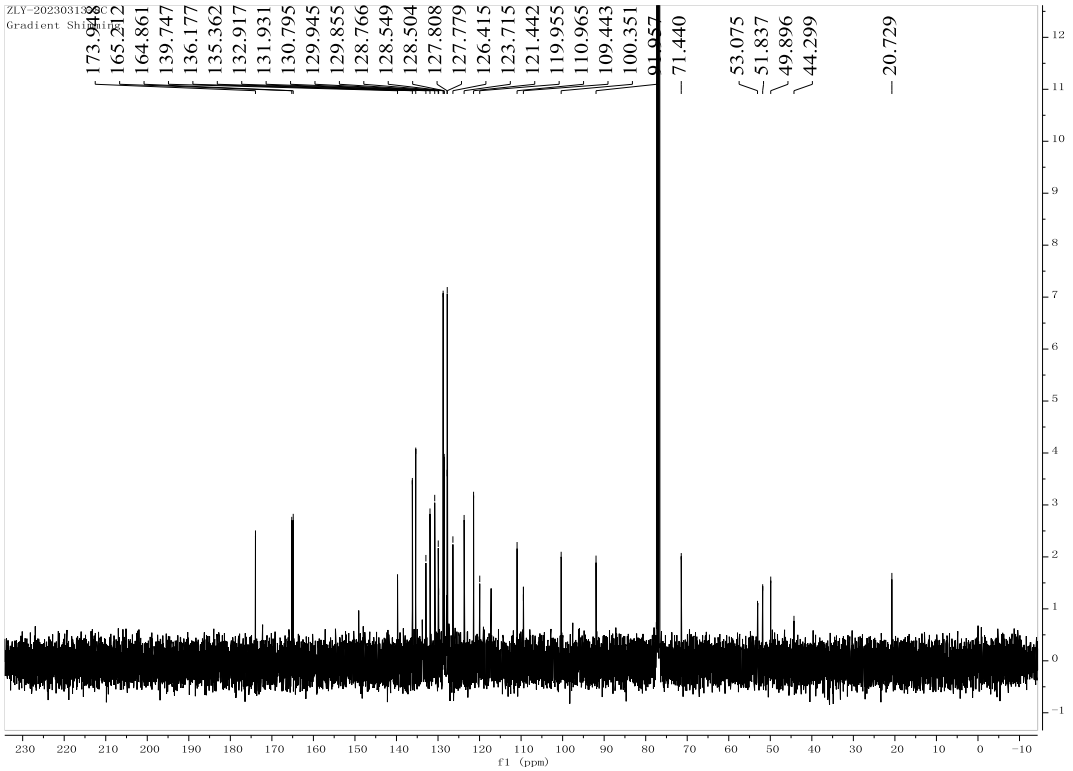
^{19}F NMR (376 MHz, $CDCl_3$)


data08 #60 RT: 0.57 AV: 1 NL: 9.29E6
T: FTMS + p ESI Full ms [50.0000-750.0000]
601.1749
602.1824
603.1855
604.1786
605.1821
606.1846
m/z

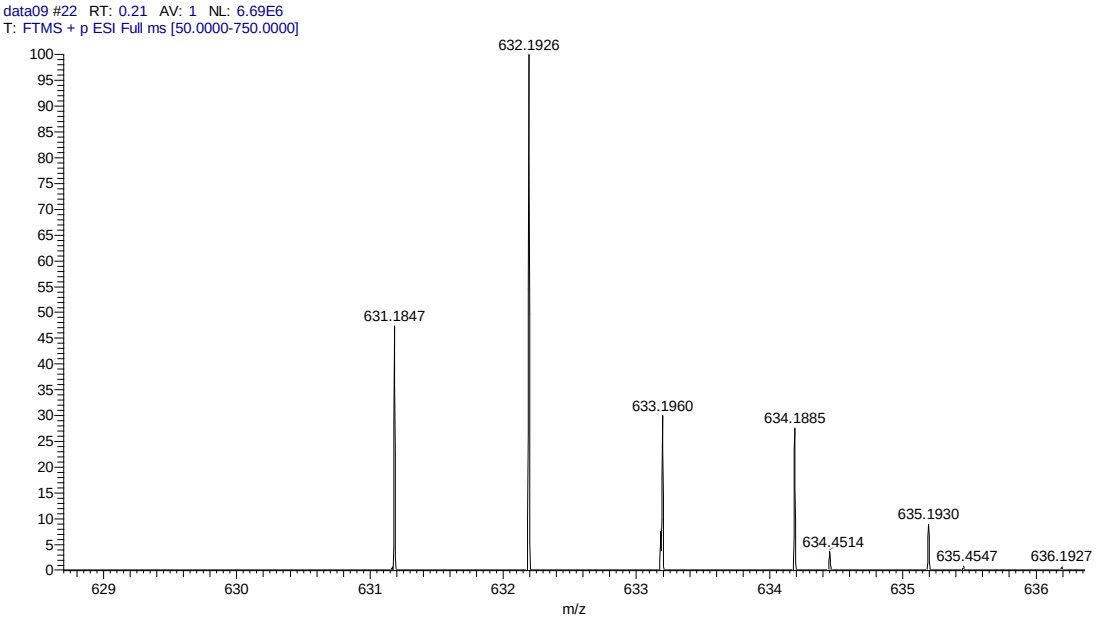
Diethyl 1-benzyl-2'-(2-chlorobenzyl)-5-methyl-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido [4,3-*b*]indole]-3',*4*'-dicarboxylate (6i): yellow solid, 57%, m.p. 275-281 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.53 (s, 1H, NH), 7.82 (t, *J* = 8.0 Hz, 1H, ArH), 7.30 (d, *J* = 8.4 Hz, 1H, ArH), 7.24 (s, 6H, ArH), 7.14-7.09 (m, 2H, ArH), 7.00 (t, *J* = 8.0 Hz, 1H, ArH), 6.96 (d, *J* = 8.0 Hz, 1H, ArH), 6.87 (s, 1H, ArH), 6.67 (d, *J* = 8.0 Hz, 1H, ArH), 6.66 (t, *J* = 8.0 Hz, 1H, ArH), 5.97 (d, *J* = 7.6 Hz, 1H, ArH), 4.91 (d, *J* = 15.6 Hz, 1H, CH), 4.73 (d, *J* = 15.2 Hz, 1H, CH), 4.38 (d, *J* = 18.0 Hz, 1H, CH), 4.29 (d, *J* = 18.0 Hz, 1H, CH), 3.90 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3) ppm, 1.98 (s, 3H, CH_3); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 174.0, 165.2, 164.9, 139.8, 136.2, 135.4, 132.9, 131.9, 130.8, 129.9, 129.8, 128.8, 128.6, 128.5, 127.9, 127. 8, 126.4, 123.7, 121.4, 120.0,111.0, 109.4, 100.4, 92.0, 77.3, 77.0, 76.7, 71.4, 53.1, 51.8, 49.9, 44.3, 20.7 ppm; IR (KBr) υ: 3445, 1737, 1716, 1664, 1592, 1547, 1495, 1442, 1401, 1327, 1283, 1231, 1171, 1082, 916, 810, 783 cm^{-1};MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{37}H_{31}ClN_3O_5$ ([M+H]$^{+}$): 632.1947, Found: 632.1926.



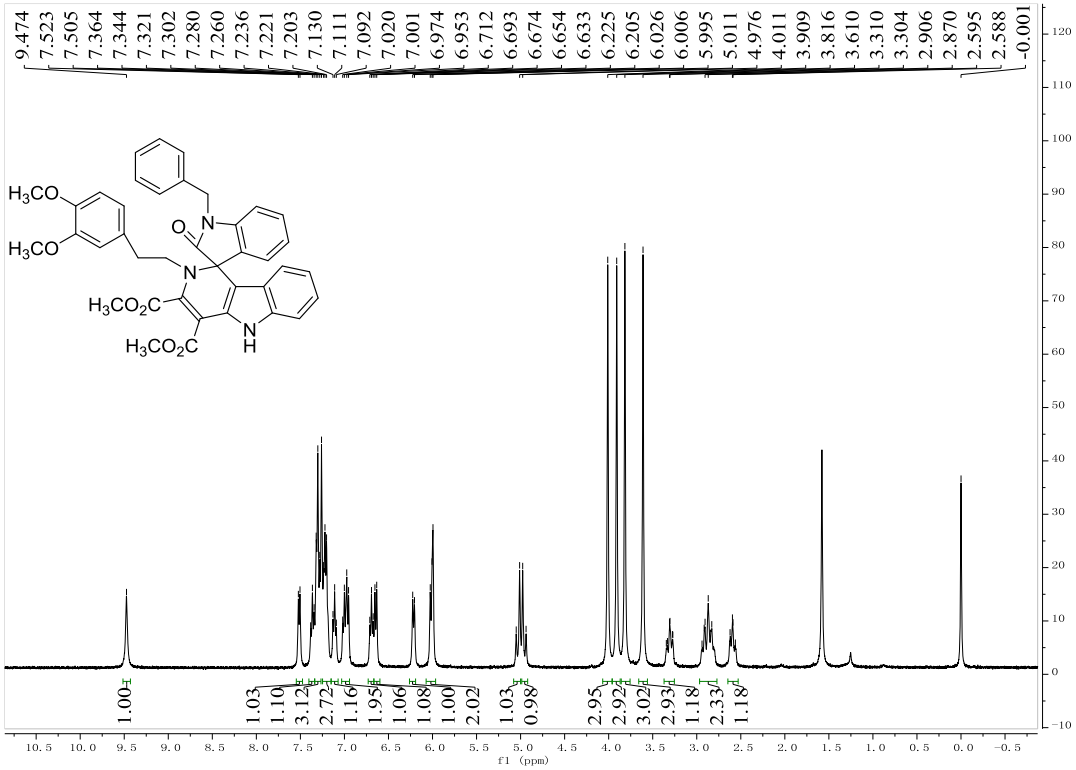
^{1}H NMR (400 MHz, $CDCl_3$)



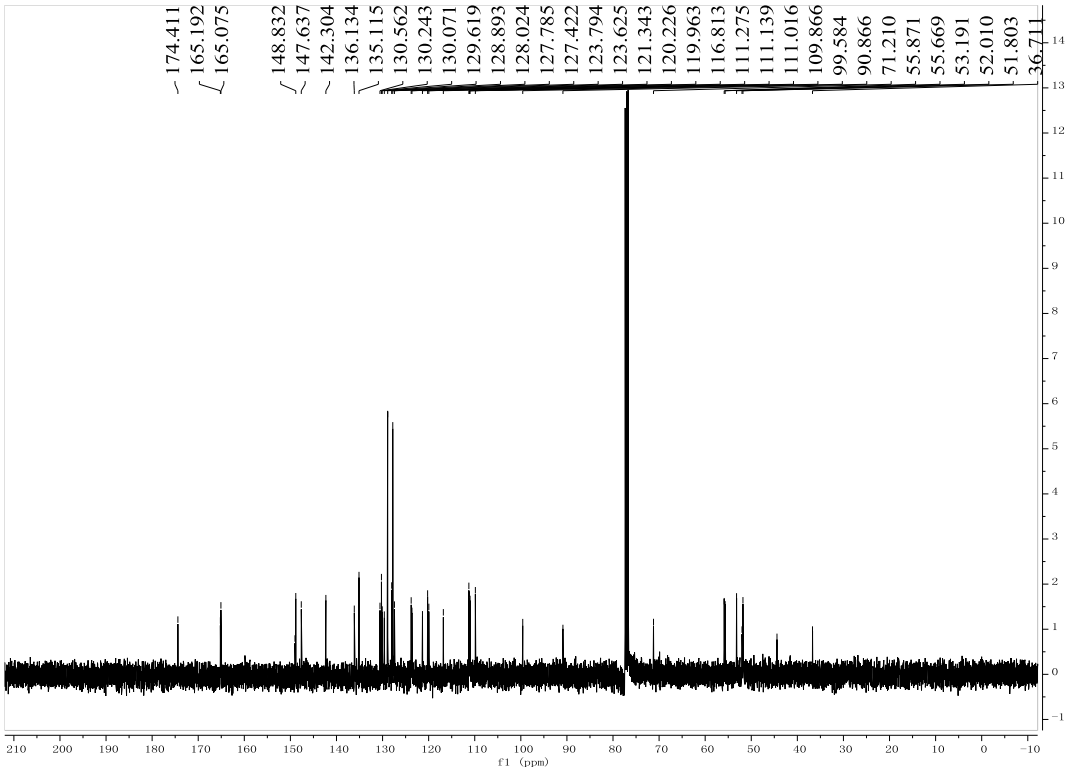
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



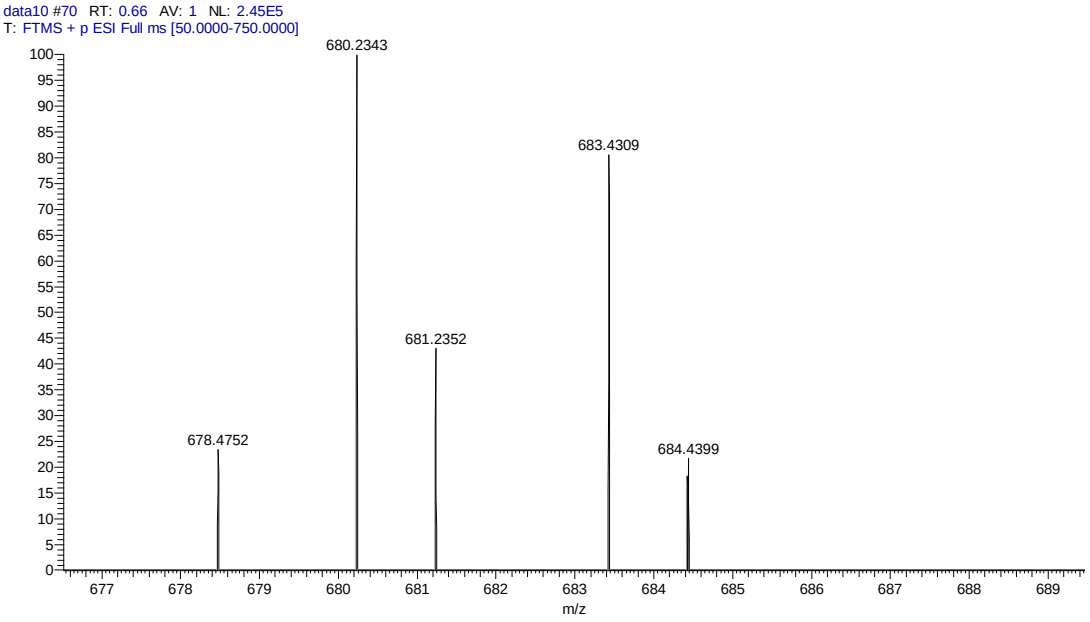
Diethyl 1-benzyl-2'-(3,4-dimethoxyphenethyl)-2-oxo-2',5'-dihydrospiro[indoline-3,1'-pyrido [4,3-*b*]indole]-3',*4*'-dicarboxylate (6j): yellow solid, 50%, m.p. 178-183 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.47 (s, 1H, NH), 7.51 (d, *J* = 7.2 Hz, 1H, ArH), 7.36 (t, *J* = 8.0 Hz, 1H, ArH), 7.30 (t, *J* = 7.6 Hz, 3H, ArH), 7.24-7.20 (m, 3H, ArH), 7.11 (t, *J* = 7.6 Hz, 1H, ArH), 6.99 (dd, J_1 = 18.4 Hz, J_2 = 7.6 Hz, 2H, ArH), 6.69 (t, *J* = 7.6 Hz, 1H, ArH), 6.64 (d, *J* = 8.4 Hz, 1H, ArH), 6.62 (d, *J* = 8.0 Hz, 1H, ArH), 6.03-6.00 (m, 2H, ArH), 5.03 (d, *J* = 15.6 Hz, 1H, CH), 4.96 (d, *J* = 15.2 Hz, 1H, CH), 4.01 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 3.35-3.27 (m, 1H, CH), 2.94-2.83 (m, 2H, CH), 2.62-2.56 (m, 1H, CH) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 174.4, 165.2, 165.1, 149.0, 148.8, 147.6, 142.3, 136.1, 135.1, 130.6, 130.2, 130.1, 129.6, 128.9, 128.0, 127.8, 127.4, 123.8, 123.6, 121.3, 120.3, 120.0, 116.8, 111.3, 111.1, 111.0, 109.9, 99.6, 90.9, 77.4, 77.0, 76.7, 71.2, 55.9, 55.7, 53.2, 52.0, 51.8, 44.4, 36.7 ppm; IR (KBr) υ: 3418, 1736, 1717, 1696, 1608, 1568, 1548, 1515, 1465, 1408, 1317, 1259, 1240, 1177, 1084, 1026, 799, 764 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{41}H_{39}N_3NaO_7$ ([M+Na]$^{+}$): 680.2368, Found: 680.2343.



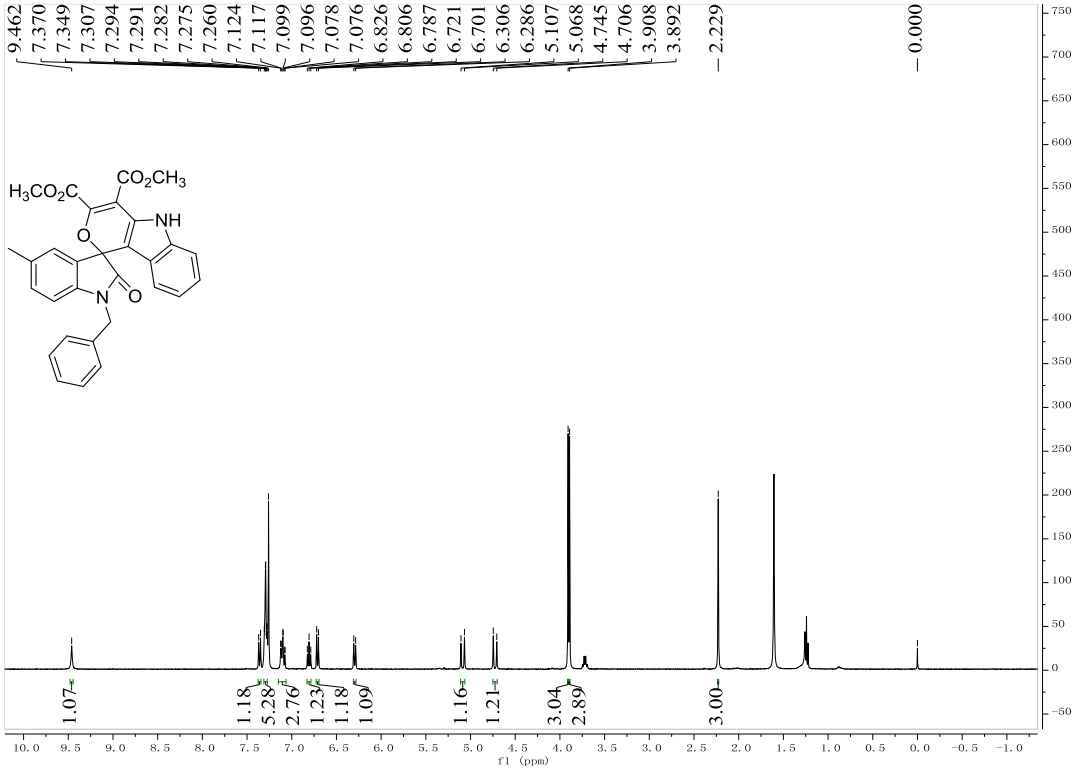
^{1}H NMR (400 MHz, $CDCl_3$)



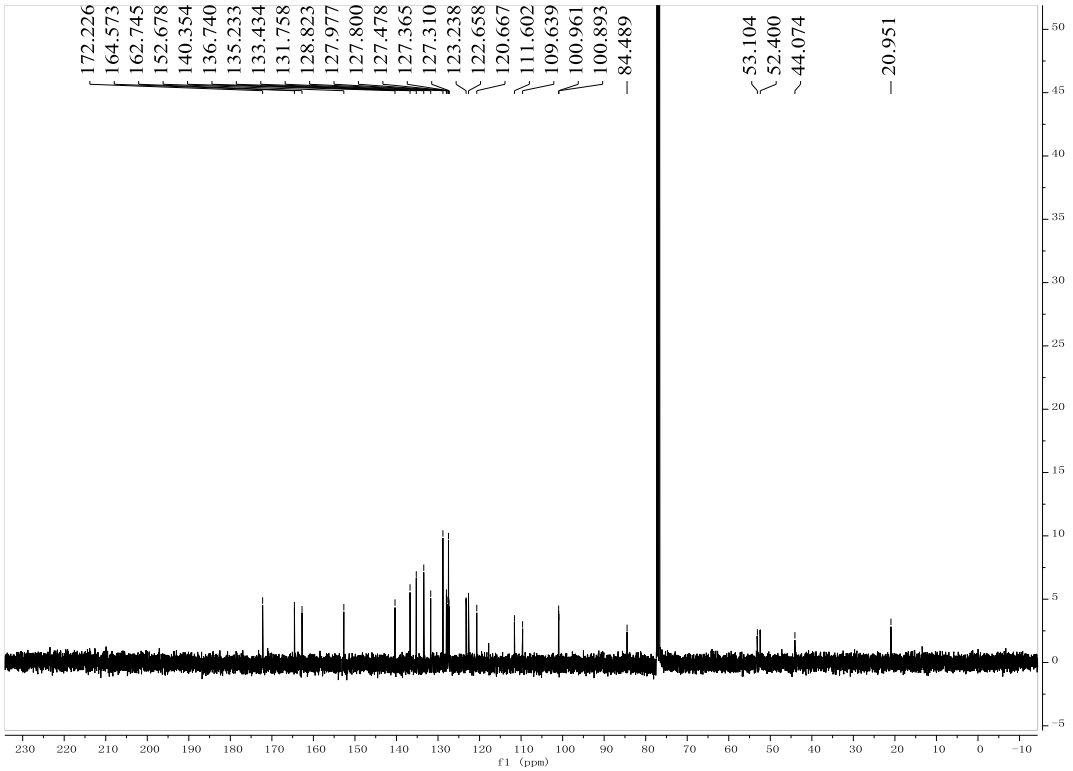
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



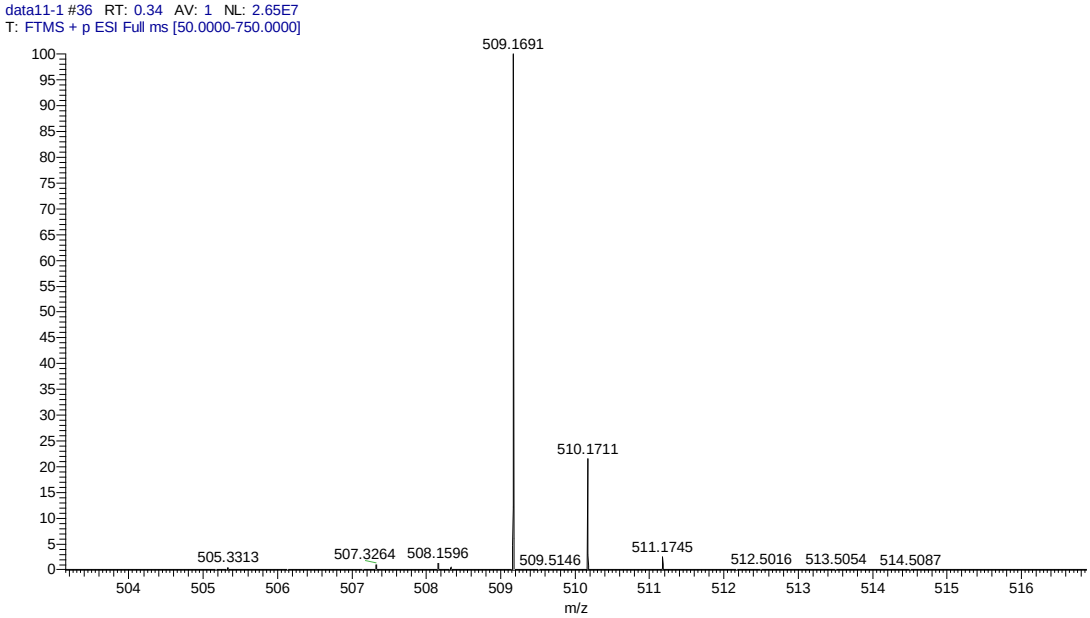
Dimethyl 1-benzyl-5-methyl-2-oxo-5'H-spiro[indoline-3,1'-pyrano[4,3-*b*]indole]-3',4'-dicarboxylate (7a): yellow solid, 22%, m.p. 200-208 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.46 (s, 1H, NH), 7.36 (d, *J* = 8.4 Hz, 1H, ArH), 7.31-7.28 (m, 5H, ArH), 7.12-7.08 (m, 3H, ArH), 6.81 (t, *J* = 8.0 Hz, 1H, ArH), 6.71 (d, *J* = 8.0 Hz, 1H, ArH), 6.30 (d, *J* = 8.0 Hz, 1H, ArH), 5.09 (d, *J* = 15.6 Hz, 1H, CH), 4.73 (d, *J* = 15.6 Hz, 1H, CH), 3.91 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 2.23 (s, 3H, CH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 172.2, 164.6, 162.7, 152.7, 140.4, 136.7, 135.2, 133.4, 131.8, 128.8, 128.0, 127.8, 127.5, 127.4, 127.3, 123.2, 122.7, 120.7, 111.6, 109.6, 101.0, 100.9, 84.5, 53.1, 52.4, 44.1, 21.0 ppm; IR (KBr) υ: 3368, 3030, 2922, 2851, 1723, 1622, 1604, 1496, 1435, 1287, 1242, 1193, 1162, 1119, 1076, 1019, 982, 909, 812, 784 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{30}H_{24}N_2O_6$ ([M+H]$^{+}$): 509.1708, Found: 509.1691.



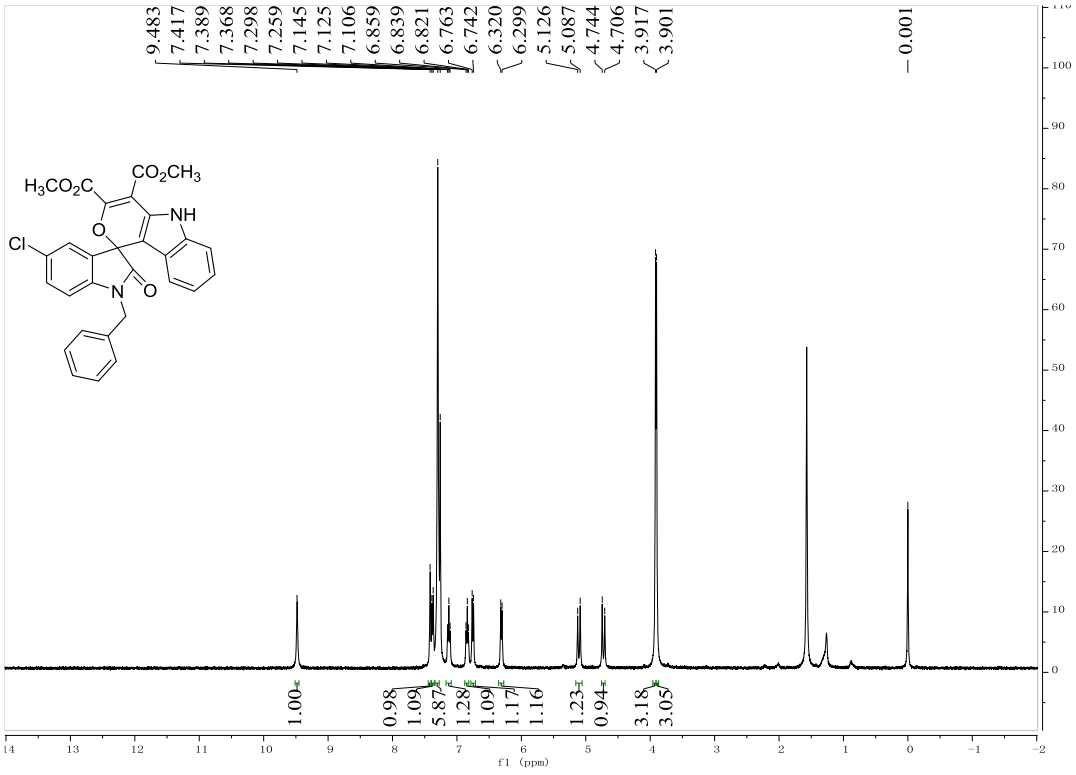
^{1}H NMR (400 MHz, $CDCl_3$)



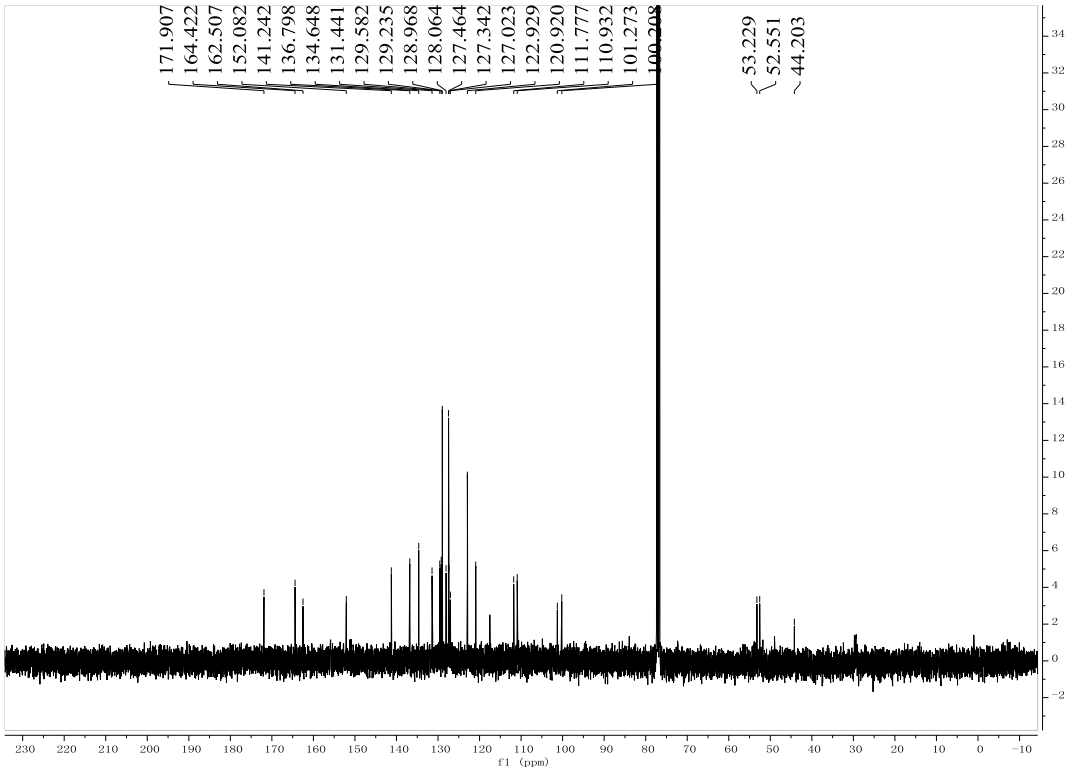
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



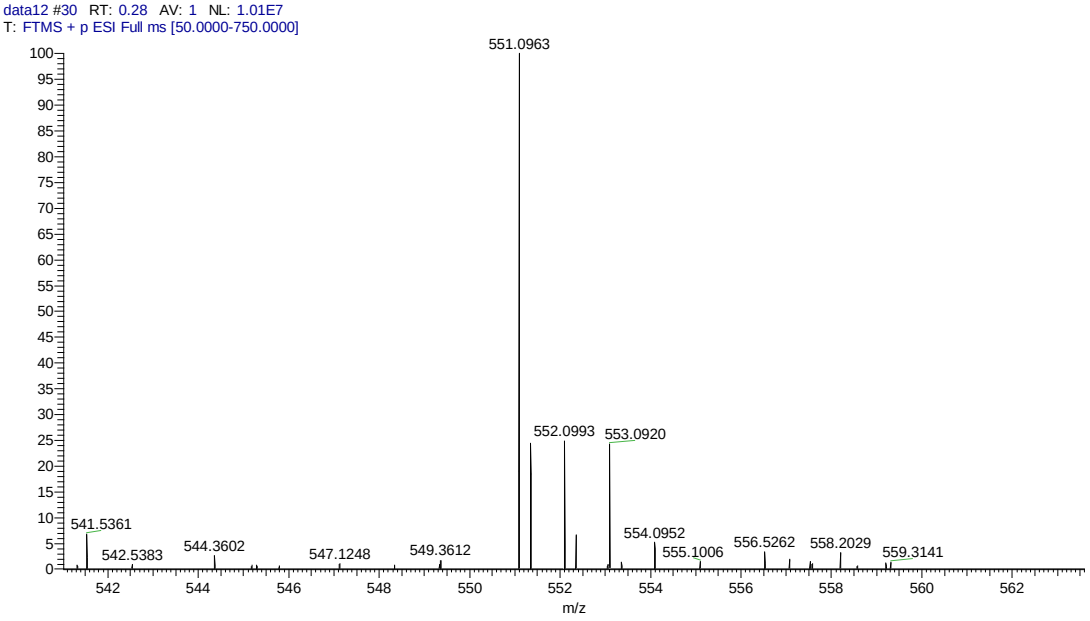
Dimethyl 1-benzyl-5-chloro-2-oxo-5'H-spiro[indoline-3,1'-pyrano[4,3-*b*]indole]-3',4'-dicarboxylate (7b): yellow solid, 20%, m.p. 192-196 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.48 (s, 1H, NH), 7.42 (s, 1H, ArH), 7.38 (d, *J* = 8.4 Hz, 1H, ArH), 7.30 (s, 6H, ArH), 7.13 (t, *J* = 8.0 Hz, 1H, ArH), 6.84 (t, *J* = 8.0 Hz, 1H, ArH), 6.75 (d, *J* = 8.4 Hz, 1H, ArH), 6.31 (d, *J* = 8.4 Hz, 1H, ArH), 5.11 (d, *J* = 15.6 Hz, 1H, CH), 4.73 (d, *J* = 15.2 Hz, 1H, CH), 3.92 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 171.9, 164.4, 162.5, 152.1, 141.2, 136.8, 134.7, 131.4, 129.6, 129.2, 129.0, 128.1, 127.5, 127.3, 127.0, 122.9, 120.9, 111.8, 110.9, 101.3, 100.2, 77.3, 77.0, 76.7, 53.2, 52.6, 44.2 ppm; IR (KBr) υ: 3328, 2852, 1721, 1612, 1484, 1455, 1433, 1317, 1289, 1259, 1235, 1171.10, 1145, 1119, 1077, 1027, 945, 879 ,841 ,822, 782, 764 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{29}H_{21}ClN_2NaO_6$ ([M+Na]$^{+}$): 551.0981, Found: 551.0963.



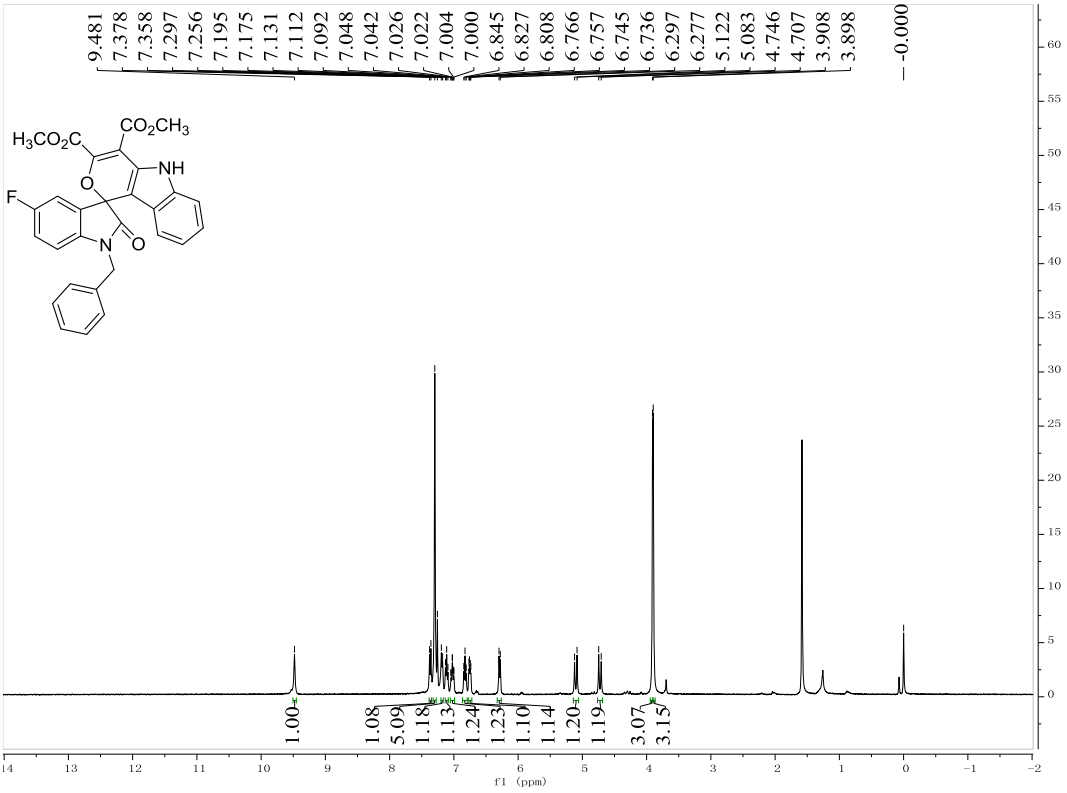
^{1}H NMR (400 MHz, $CDCl_3$)



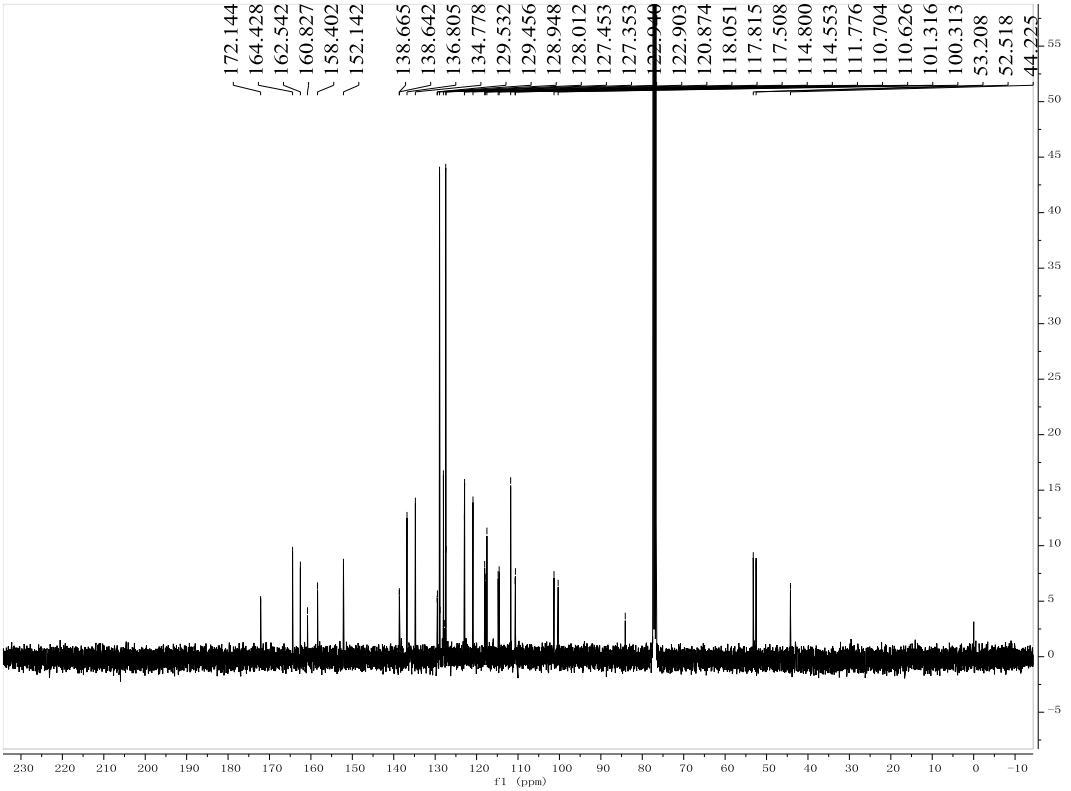
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)



Dimethyl 1-benzyl-5-fluoro-2-oxo-5'H-spiro[indoline-3,1'-pyrano[4,3-*b*]indole]-3',4'-dicarboxylate (7c): yellow solid, 16%, m.p. 192-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.48 (s, 1H, NH), 7.37 (d, *J* = 8.0 Hz, 1H, ArH), 7.30 (s, 5H, ArH), 7.19 (d, *J* = 8.0 Hz, 1H, ArH), 7.11 (t, *J* = 8.0 Hz, 1H, ArH), 7.05-.00 (m, 1H, ArH), 6.83 (t, *J* = 7.6 Hz, 1H, ArH), 6.75 (dd, J_1 = 8.4 Hz, J_2 = 3.6 Hz, 1H, ArH), 6.29 (d, *J* = 8.0 Hz, 1H, ArH), 5.10 (d, *J* = 15.6 Hz, 1H, CH), 4.73 (d, *J* = 15.6 Hz, 1H, CH), 3.91 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3) ppm; ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 172.1, 164.4, 162.5, 160.8, 158.4, 152.1, 138.7, 138.6, 136.8, 134.8, 129.5, 129.5, 129.0, 128.8, 128.0, 127.8, 127.5, 127.4, 123.0, 122.90, 120.8, 118.1, 117.8, 117.5, 114.8, 114.6, 111.8, 110.7, 110.6, 101.3, 100.3, 84.1, 77.3, 77.2, 77.0, 76.7, 53.2, 52.5, 44.2 ppm; IR (KBr) υ: 3354, 3031, 2850, 1727, 1606, 1491, 1455, 1290, 1163, 1120, 1077, 1019, 935, 875, 819, 789 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{29}H_{22}FN_2O_6$ ([M+H]$^+$): 513.1457, Found: 513.1441.



^{1}H NMR (400 MHz, $CDCl_3$)



$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$)