Electronic Supplementary Material (ESI) for Chemical Communications

takneNi(ClO_4)$_2$-Catalysed Regio- and Diastereoselctive [3+2] Cycloadditon of Indoles and Aryl Oxiranyl-dicarboxylates/Diketones: A Facile Access to Furo[3,4-b]indoles.

*Jieming Zhang, Zuliang Chen, Haihong Wu * and Junliang Zhang **

[a]*Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 N. Zhongshan Road, Shanghai 200062*

Fax:(+86)-021-6223-5039; e-mail : hhwu@chem.ecnu.edu.cn jlzhang@chem.ecnu.edu.cn

Supporting information

Electronic Supplementary Material (ESI) for Chemical Communications

Contents

General information.

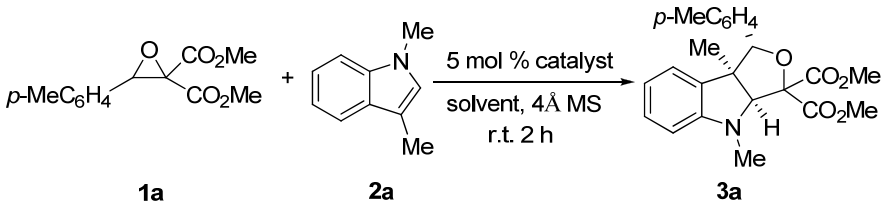
Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. ^{1}H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform-d_3. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. $ClCH_2CH_2Cl$ (DCE) and CH_2Cl_2 were freshly distilled from CaH_2; toluene was freshly distilled from sodium metal prior to use. Solid indoles were used directly. Lewis-acid purchased from Alfa, Acros or Aldrich were used directly. 4 Å molecular sieves purchased from Sinopharm Chemical Reagent Co.,Ltd were powdered and dried at 300 ºC in muffle furnace for 8-10 hours prior to use.

Oxiranes are prepared according to the literature (R. Antonioletti, P. Bovicelli, S. Malancona, *Tetrahedron* **2002**, *58*, 589; E. Hasegawa, K. Ishiyama, T. Horaguchi, T. Shimizu, *J. Org. Chem*. **1991**, *56*, 1631.)

Indoles are prepared according to the procedure of the work reported (M. Amat, S. Hadida, S. Sathyanarayana, and J. Bosch, *Org. Syn.* **1998**, *9*, 417; M. B. Johansen and M. A. Kerr, *Org. Lett.* **2010**, *12*, 4965; F. Bellina, F. Benelli, and R. Rossi, *J. Org. Chem*. **2008**, *73*, 5529. A. K. Verma, J. Singh, R. C. Larock, *Tetrahedron* **2009**, *65,* 8434.)

Typical procedure for $Ni(ClO_4)_2•6H_2O$ catalyzed [3+2] cycloaddition reaction.

1. Synthesis of 3a.

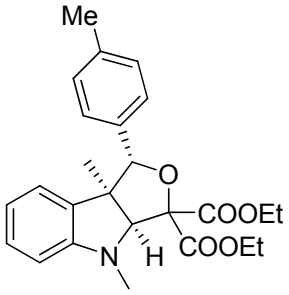


1a **2a** **3a**

In an inert atmosphere glovebox, a flame-dried vial was charged with 5 mol % $Ni(ClO_4)_2•6H_2O$, 60.0 mg of activated 4Å molecular sieves (M.S.), and a magnetic stir

bar. Outside of the glovebox, the vial was placed under an N_2 atmosphere and charged with 1 mL of CH_2Cl_2 followed by the indole **2a** (65.3 mg, 0.45 mmol). Afterwards, **1a** (75.0 mg, 0.3 mmol) and 2 mL of CH_2Cl_2 were added. The reaction was stirred at room temperature for 2 hour. The reaction mixture was then passed over a short column of silica with 25 mL of Et_2O. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography, eluting with (hexanes:AcOEt = 10:1) to afford 110 mg (92%) of **3a** (exo:endo = 19:1), ***exo***, white solid. M.p.: 168-170oC. IR (neat) 2917, 1765, 1742, 1603, 1082, 1052, 1014, 955, 779 cm-1. ^{1}H NMR (400 MHz, CDCl3): δ 1.00 (3H, s), 2.36 (3H, s), 2.87 (3H, s), 3.78 (3H, s), 3.92 (3H, s), 4.63 (1H, s), 5.24 (1H, s), 6.61 (1H, d, *J* = 8.0 Hz), 6.72-6.87 (2H, m), 7.09-7.30 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.3, 21.1, 38.6, 52.4, 53.2, 56.6, 87.1, 90.0, 90.3, 109.7, 118.9, 122.8, 126.4, 128.6, 132.7, 133.3, 137.4, 152.4, 168.3, 168.5. MS (EI) m/z(%): 395[M^+] (4.25), 144(100.00). HRMS (EI): calcd for $C_{23}H_{25}NO_5$ 395.1733, found 395.1734.

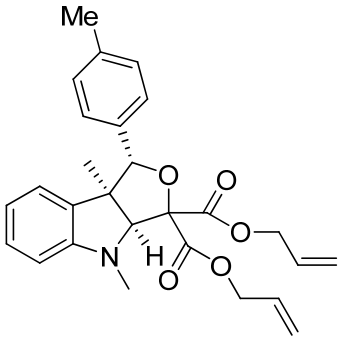
2. Synthesis of 3b.



The reaction of **1b** (83.5 mg, 0.3 mmol), **2a** (65.3 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 2 hours to afford 100.0 mg (79%) of **3b** (exo:endo = 18:1), ***exo***, white solid. M.p.: 103-104 ^{o}C. IR (neat) 2980, 2862, 2810, 1761, 1739, 1600, 1516, 1486, 1464, 1370, 1279, 1254, 1218, 1152, 1134, 1109, 1076, 1051, 1000, 772, 753 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (3H, s), 1.25 (3H, t, *J* = 6.4 Hz), 1.38 (3H, t, *J* = 6.4 Hz), 2.35 (3H, s), 2.88 (3H, s), 4.10-4.20 (1H, m), 4.25-4.50 (3H, m), 4.65 (1H, s), 5.28 (1H, s), 6.59 (1H, d, *J* = 7.6 Hz), 6.77 (1H, t, *J* = 6.4 Hz), 6.85

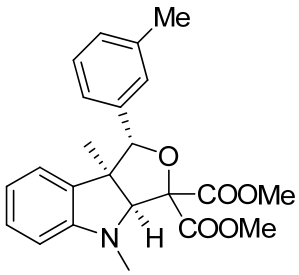
(1H, d, J = 6.4 Hz), 6.95-7.30 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 20.5, 21.1, 38.6, 56.5, 61.6, 62.2, 86.8, 90.0, 90.2, 109.5, 118.8, 122.7, 126.4, 128.48, 128.51, 132.8, 133.5, 137.3, 152.4, 167.8, 168.0. MS (EI) m/z(%): 423[M^+] (1.49), 144(100.00). HRMS (EI): calcd for $C_{25}H_{29}NO_5$ 423.2046, found 423.2045.

3. Synthesis of 3c.



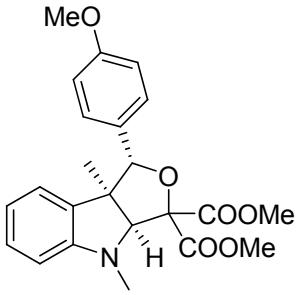
The reaction of **1c** (90.7 mg, 0.3 mmol), **2a** (65.3 mg, 0.45mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 2 hours to afford 105.9 mg (79%) of **3c** (exo:endo = 20:1), ***exo***, colourless oil. IR (neat) 2966, 2256, 1744, 1649, 1607, 1514, 1487, 1452, 1296, 1274, 1252, 1136, 1075, 1051, 991, 753, 730 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (3H, s), 2.35 (3H, s), 2.86 (3H, s), 4.58 (1H, d, J = 13.2 Hz), 4.66 (1H, s), 4.70-4.91 (3H, m), 5.20 (1H, d, J = 10.0 Hz), 5.25-5.39 (3H, m), 5.43 (1H, d, J = 17.2 Hz), 5.79-5.90 (1H, m), 5.90-6.05 (1H, m), 6.59 (1H, d, J = 7.6 Hz), 6.71-6.82 (1H, m), 6.82-6.91 (1H, m), 7.09-7.33 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 21.1, 38.7, 56.6, 66.1, 66.5, 86.9, 90.1, 90.3, 109.6, 118.6, 118.7, 118.8, 122.7, 126.4, 128.5, 128.9, 131.2, 132.7, 133.4, 137.4, 152.4, 167.4, 167.6. MS (EI) m/z(%): 447[M^+] (1.48), 39(100.00). HRMS (EI): calcd for $C_{27}H_{29}NO_5$ 447.2046, found 447.2047.

4. Synthesis of 3d.



The reaction of **1d** (75.0 mg, 0.3 mmol), **2a** (65.3 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 16 hours to afford 79.4 mg (68%) of **3d** (exo:endo = 14:1), ***exo***, white solid. M.p.: 157-159 ^oC. IR (neat) 2951, 1766, 1739, 1608, 1486, 1433, 1299, 1222, 1137, 1053, 992, 954, 750 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ 1.01 (3H, s), 2.36 (3H, s), 2.88 (3H, s), 3.78 (3H, s), 3.94 (3H, s), 4.65 (1H, s), 5.25 (1H, s), 6.62 (1H, d, *J* = 8.0 Hz), 6.72-6.92 (3H, m), 7.01-7.35 (5H, m). ^{13}C NMR (100MHz, $CDCl_3$): δ 20.3, 21.5, 38.6, 52.4, 53.3, 56.6, 87.1, 90.0, 90.4, 109.7, 118.9, 122.8, 123.6, 127.0, 127.8, 128.6, 132.6, 136.2, 137.5, 152.5, 168.3, 168.4. MS (EI) m/z(%): 395[M^+] (4.76), 144(100.00). HRMS (EI): calcd for $C_{23}H_{25}NO_5$ 395.1733, found 395.1735.

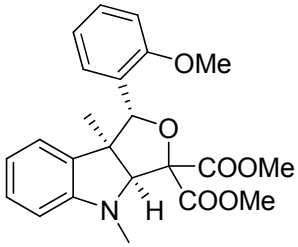
5. Synthesis of 3e.



The reaction of **1e** (78.3 mg, 0.29 mmol), **2a** (64.6 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 45 mins to afford 78.6 mg (65%) of **3e** (exo:endo = 18:1), ***exo***, white solid. M.p.: 165-167 ^oC. IR (neat) 2952, 1765, 1742, 1605, 1284, 1097, 1081, 1054, 1035, 1081, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.00 (3H, s), 2.87 (3H, s), 3.78 (3H, s), 3.81 (3H, s), 3.92 (3H, s), 4.64 (1H, s), 5.21 (1H, s), 6.61 (1H, d, *J* = 7.2 Hz), 6.70-6.87 (2H, m), 6.89 (2H, d, *J* = 7.2 Hz), 7.15-7.29 (3H, m).

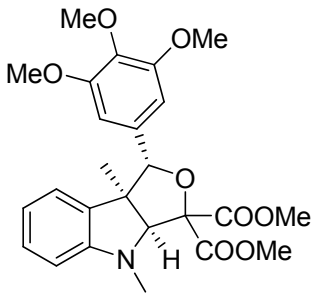
^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2, 38.6, 52.4, 53.3, 55.1, 56.6, 87.0, 89.9, 90.3, 109.7, 113.3, 118.9, 122.7, 127.7, 128.3, 128.5, 132.7, 152.4, 159.3, 168.3, 168.4. MS (EI) m/z(%): 411[M^+] (2.65), 144(100.00). HRMS (EI): calcd for $C_{23}H_{25}NO_6$ 411.1682, found 411.1680.

6. Synthesis of 3f.



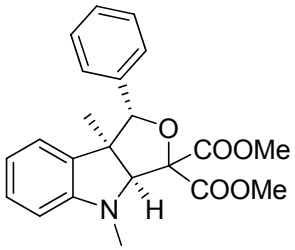
The reaction of **1f** (79.8 mg, 0.3 mmol), **2a** (65.3 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 24 hours to afford 64.9 mg (53%) of **3f** (exo:endo = 10:1), ***exo***, white solid. M.p.: 132-133 ^oC. IR (neat) 2954, 1770, 1746, 1603, 1485, 1462, 1435, 1299, 1280, 1252, 1221, 1140, 1113, 1096, 1079, 1048, 1024, 993, 944, 794, 768 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (3H, s), 2.91 (3H, s), 3.64 (3H, s), 3.68 (3H, s), 3.92 (3H, s), 4.57 (1H, s), 5.86 (1H, s), 6.54 (1H, d, J = 7.2 Hz), 6.72 (1H, t, J = 6.8 Hz), 6.82-7.03 (3H, m), 7.15 (1H, t, 7.2 Hz), 7.22-7.35 (1H, m), 7.48 (1H, d, J = 7.2 Hz) . ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 37.4, 52.4, 53.2, 54.5, 56.7, 84.9, 86.3, 90.0, 108.4, 109.9, 118.0, 120.1, 124.0, 125.6, 128.2, 128.2, 128.7, 133.6, 151.6, 156.3, 168.7, 168.8. MS (EI) m/z(%) 411 [M^+] (1.97), 144(100.00) . HRMS (EI): calcd for $C_{23}H_{25}NO_6$ 411.1682, found 411.1681.

7. Synthesis of 3g.



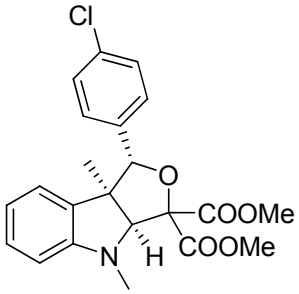
The reaction of **1g** (97.3 mg, 0.3 mmol), **2a** (65.3 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 30 mins to afford 97.4 mg (69%) of **3g** (exo:endo = 21:1), ***exo***, white solid. M.p.: 170-172 ^oC. IR (neat) 2953, 1745, 1591, 1237, 1124, 1075, 1064, 1016, 1000, 957, 754 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.05 (3H, s), 2.88 (3H, s), 3.81 (3H, s), 3.84 (6H, s), 3.86 (3H, s), 3.94 (3H, s), 4.64 (1H, s), 5.20 (1H, s), 6.53 (2H, s), 6.64 (1H, d, J = 7.6 Hz), 6.75-6.85 (1H, m), 6.92 (1H, d, J = 6.8 Hz), 7.18-7.25 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.9, 38.6, 52.4, 53.2, 56.0, 56.6, 60.7, 87.0, 89.8, 90.2, 103.6, 109.8, 118.6, 122.7, 128.7, 131.8, 132.3, 137.5, 152.5, 152.8, 168.1, 168.2. MS (EI) m/z(%): 471[M^+] (2.96), 144(100.00). HRMS (EI): calcd for $C_{25}H_{29}NO_8$ 471.1893, found 471.1891.

8. Synthesis of 3h.



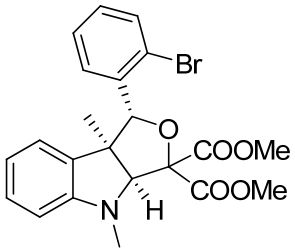
The reaction of **1h** (70.9 mg, 0.3 mmol), **2a** (65.3 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 10 mol % $Ni(ClO_4)_2$•$6H_2O$ (0. 03 mmol, 11.0 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 38 hours to afford 80.8 mg (71%) of **3h** (exo:endo = 20:1), ***exo***, white solid. M.p.: 167-169 ^oC. IR (neat) 2959, 1765, 1746, 1605, 1485, 1454, 1434, 1297, 1261, 1225, 1137, 1081, 1060, 1021, 758, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.00 (3H, s), 2.88 (3H, s), 3.79 (3H, s), 3.93 (3H, s), 4.65 (1H, s), 5.28 (1H, s), 6.62 (1H, d, J = 8 Hz), 6.76-6.90 (2H, m), 7.21 (1H, t, J = 7.2 Hz), 7.28-7.45 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.3, 38.6, 52.5, 53.3, 56.6, 87.0, 90.0, 90.4, 109.7, 118.9, 122.8, 126.5, 127.9, 127.9, 128.6, 132.5, 136.3, 152.4, 168.3, 168.4. MS (ESI) m/z(%): 382[$M+H^+$] (100.00). HRMS (ESI): calcd for $C_{22}H_{24}NO_5$ [$M+H^+$]382.1649, found 382.1646.

9. Synthesis of 3i.



The reaction of **1i** (81.2 mg, 0.3 mmol), **2a** (65.3 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 10 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.03 mmol, 11.0 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 48 hours to afford 88.5 mg (71%) of **3i** (exo:endo = 12:1), ***exo***, white solid. M.p.: 185-187 ^oC. IR (neat) 2910, 1766, 1743, 1604, 1485, 1331, 1290, 1253, 1152, 1084, 1053, 1015, 996, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.99 (3H, s), 2.87 (3H, s), 3.80 (3H, s), 3.93 (3H, s), 4.65 (3H, s), 5.24 (1H, s), 5.62 (1H, d, *J* = 7.6 Hz), 6.75-6.88 (2H, m), 7.18-7.40 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.0, 38.6, 52.5, 53.3, 56.6, 87.0, 89.3, 90.4, 109.9, 119.0, 122.6, 127.8, 128.1, 128.8, 132.1, 133.6, 134.9, 152.4, 168.1, 168.2. MS (EI) m/z(%): 417[M^++2] (0.58), 415[M^+] (1.75), 144(100.00). HRMS (EI): calcd for $C_{22}H_{22}ClNO_5$ 415.1187, found 415.1187.

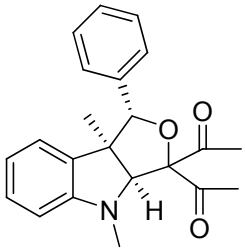
10. Synthesis of 3j.



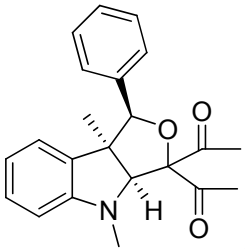
The reaction of **1j**(99.3 mg, 0.3 mmol), **2a** (65.3 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 20 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.06 mmol, 22.0 mg) in CH_2Cl_2 (3 mL) was carried out in a sealed tube at 60 ^oC. for 4 days to afford an inseparable mixture 96.5 mg (69%) of **3j (**exo:endo = 10:1**)**, colourless oil. IR (neat) 2954, 1744, 1607, 1487, 1372, 1273, 1250, 1152, 1078, 1023, 995, 955, 910, 751, 730, 682 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.12 (3H, s), 2.91 (3H, s), 2.35 (3H, s), 3.71 (3H, s), 3.91 (3H, s), 4.61 (1H, s), 5.91 (1H, s), 6.55 (1H, d, *J* = 8.0 Hz), 6.73 (1H, t, *J* = 6.4

Hz), 6.99 (1H, d, J = 6.8 Hz), 7.10-7.23 (2H, m), 7.34 (1H, t, J = 7.2 Hz), 7.54 (2H, d, J = 5.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 37.5, 52.5, 53.3, 57.0, 86.1, 88.0, 89.8, 108.7, 118.5, 122.8, 124.3, 126.8, 128.6, 129.5, 130.0, 132.2, 133.0, 136.1, 151.5, 168.2, 168.4. MS (EI) m/z(%): 461[M^++2] (14.49), 459[M^+] (15.01), 158(100.00). HRMS (EI): calcd for $C_{22}H_{22}BrNO_5$ 459.0681, found 459.0682.

11. Synthesis of 3k.



3k



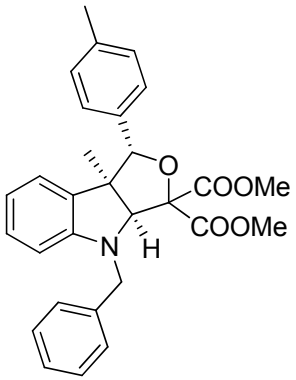
3k'

The reaction of **1k** (61.3 mg, 0.3 mmol), **2a** (65.3 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 24 hours to afford 53.3 mg (51%) of **3k** and 19.0 mg (18%) of **3k'**. **3k, *exo***, white solid. M.p.: 137-138 ^{o}C IR (neat) 2970, 2868, 1729, 1701, 1607, 1484, 1452, 1348, 1296, 1253, 1206, 1153, 1129, 1081, 1053, 1021, 903, 883, 747, 697 cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ 0.87 (3H, s), 2.37 (3H, s), 2.42 (3H, s), 2.72 (3H, s), 4.57 (1H, s), 5.26 (1H, s), 6.66 (1H, d, J = 7.6 Hz), 6.82 (1H, t, J = 6.8Hz), 6.87 (1H, d, J = 7.2 Hz), 7.20-7.32 (3H, m), 7.32-7.48 (3H, m). ^{13}C NMR (100MHz, $CDCl_3$): δ 18.4, 26.2, 27.5, 38.3, 56.2, 86.0, 90.6, 98.1, 110.2, 119.1, 122.8, 126.2, 128.1, 128.2, 128.8, 132.6, 136.7, 152.3, 201.1, 207.5. MS (EI) m/z(%): 349[M^+] (22.33), 158(100.00). HRMS (EI): calcd for $C_{22}H_{23}NO_3$ 349.1678, found 349.1679.

3k', ***endo***, colourless oil. IR (neat) 2961, 2869, 1726, 1707, 1603, 1489, 1454, 1353, 1300, 1200, 1154, 1132, 1068, 1025, 911, 887, 755, 732, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44 (3H, s), 2.20 (3H, s), 2.36 (3H, s), 2.75 (3H, s), 4.62 (2H, s),5.58 (1H, d, J = 7.2 Hz), 6.31 (1H, t, J = 7.2 Hz), 6.46 (1H, d, J = 7.6 Hz), 7.02 (1H, t, J = 7.6 Hz), 7.15 (2H, d, J = 6.4 Hz), 7.25-7.35 (3H, m). ^{13}C NMR (100 MHz,

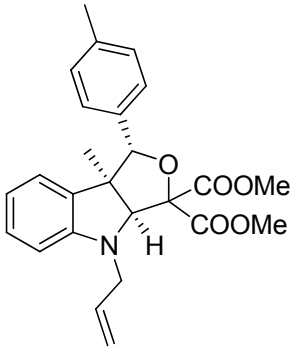
$CDCl_3$): δ 25.4, 25.9, 38.4, 58.9, 81.6, 90.0, 98.1, 108.3, 117.9, 125.4, 126.9, 127.9, 128.3, 128.4, 131.0, 136.4, 152.9, 203.7, 206.4. MS (EI) m/z(%): 349[M^+] (13.12), 158(100.00). HRMS (EI): calcd for $C_{22}H_{23}NO_3$ 349.1678, found 349.1681.

12. Synthesis of 3m.



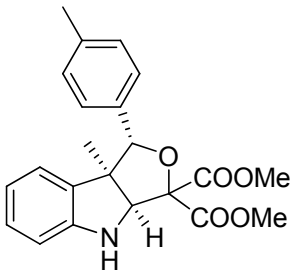
The reaction of **1a** (75.0 mg, 0.3 mmol), **2b** (77.0 mg, 0.33 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 2 hours to afford 110.2 mg (77%) of **3m** (exo:endo = 20:1), ***exo***, white solid. M.p.: 137-139 ^oC. IR (neat) 2951, 1767, 1742, 1605, 1515, 1486, 1453, 1437, 1310, 1294, 1217, 1150, 1085, 1056, 751, 736, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.94 (3H, s), 2.36 (3H, s), 3.43 (3H, s), 3.91 (3H, s), 4.32 (1H, d, *J* = 16.0 Hz), 4.64 (1H, d, *J* = 16.0 Hz), 4.91 (1H, s), 5.42 (1H, s), 6.48 (1H, d, *J* = 7.6 Hz), 6.78 (1H, t, *J* = 6.8 Hz), 6.86 (1H, d, *J* = 6.4 Hz), 7.10 (1H, t, 7.2 Hz), 7.15-7.40 (9H, m). ^{13}C NMR (100MHz, $CDCl_3$): δ 20.3, 21.2, 52.7, 53.3, 55.0, 56.6, 84.5, 90.0, 90.3, 110.4, 119.1, 122.8, 126.5, 126.9, 127.3, 128.4, 128.5, 128.6, 133.2, 133.4, 137.5, 138.0, 151.6, 168.4, 168.5. MS (ESI) m/z(%): 472[M+H^+](100.00). HRMS (ESI): calcd for $C_{29}H_{29}NO_5Na$ [M+Na^+] 494.1938, found 494.1939.

13. Synthesis of 3n.



The reaction of **1a** (75.0 mg, 0.3 mmol), **2c** (77.9 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 2 hours to afford 89.7 mg (70%) of **3n** (exo:endo = 20:1), ***exo***, white solid. M.p.: 89-90 ^oC. IR (neat) 2954, 1744, 1604, 1516, 1483, 1436, 1279, 1248, 1224, 1152, 1082, 1055, 1016, 911, 754, 731 cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ 0.98 (3H, s), 2.36 (3H, s), 3.66-3.73 (1H, m), 3.75 (3H, s), 3.91 (3H, s), 4.01 (1H, d, *J* = 16.4Hz), 4.87 (1H, s), 5.23 (1H, d, *J* = 11.2 Hz), 5.31 (1H, d, *J* = 6.4 Hz), 5.70-5.86 (1H, m), 6.69 (1H, d, *J* = 7.6 Hz), 6.72-6.81 (1H, m), 6.81-6.87 (1H, m), 7.09-7.30 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 21.2, 52.7, 53.0, 53.2, 56.4, 83.6, 90.1, 90.6, 110.4, 118.2, 119.0, 122.8, 126.4, 128.4, 128.6, 132.9, 133.3, 133.4, 137.4, 151.1, 168.4, 168.6. MS (EI) m/z(%): 421[M^+] (0.55), 139(100.00). HRMS (EI): calcd for $C_{25}H_{27}NO_5$ 421.1889, found 421.1885.

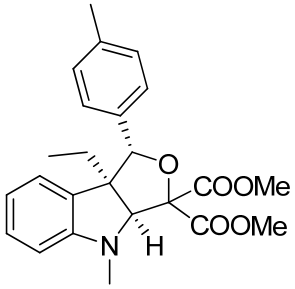
14. Synthesis of 3o.



The reaction of **1a** (75.0 mg, 0.3 mmol), **2d** (59.0 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 24 hours to afford 75.5 mg (66%) of **3o**, pale yellow solid. M.p.: 73-75 ^oC. IR (neat) 3362, 2953, 1744, 1610, 1516, 1485, 1436, 1279, 1250, 1226, 1136, 1079, 1041, 943, 751 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.02

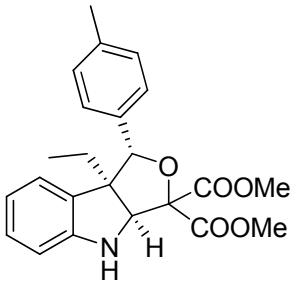
(3H, s), 2.35 (3H, s), 3.84 (3H, s), 3.90 (3H, s), 4.29 (1H, s), 5.10 (1H, d, J = 2.4 Hz), 5.16 (1H, s), 6.67 (1H, d, *J* = 7.6 Hz), 6.72-6.86 (2H, m), 7.09-7.20 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 21.2, 52.8, 53.4, 57.4, 78.9, 89.6, 90.3, 110.2, 119.2, 123.3, 126.3, 128.5, 128.6, 132.0, 133.2, 137.4, 148.8, 168.1, 168.7. MS (ESI) m/z(%): 404[M+Na^+] (93.00), 382(100.00). HRMS (ESI): calcd for $C_{22}H_{23}NO_5Na$ [M+Na^+] 404.1468, found 404.1467.

15. Synthesis of 3p.



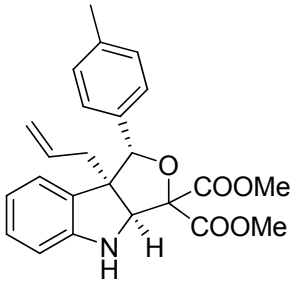
The reaction of **1a** (75.0 mg, 0.3 mmol), **2e** (77.9 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 2 hours to afford 98.2 mg (81%) of **3p** (exo:endo = 17:1), ***exo***, white solid. M.p.: 155-157 ^{o}C. IR (neat) 2963, 2919, 1767, 1743, 1607, 1486, 1460, 1440, 1294, 1250, 1221, 1128, 1114, 1084, 1054, 1022, 997, 952, 747, 671 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.60 (3H, t, *J* = 7.5 Hz), 1.07-1.43 (2H, m), 2.36 (3H, s), 2.87 (3H, s), 3.77 (3H, s), 3.92 (3H, s), 4.76 (1H, s), 5.31 (1H, s), 6.59 (1H, d, *J* = 8.1 Hz), 6.75-6.87 (2H, m), 7.09-7.21 (5H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.4, 21.2, 23.9, 38.5, 52.4, 53.2, 61.4, 82.0, 90.8, 90.9, 109.6, 118.9, 123.0, 126.6, 128.4, 128.6, 130.3, 133.3, 137.4, 153.1, 168.5, 168.6. MS (EI) m/z(%): 409[M^+] (29.52), 135(100.00). HRMS (EI): calcd for $C_{24}H_{27}NO_5$ 409.1888, found 409.1889.

16. Synthesis of 3q.



The reaction of **1a** (75.0 mg, 0.3 mmol), **2f** (65.3 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 38 hours to afford 88.8 mg (75%) of **3q**, pale brown solid. M.p.: 77-79 ^oC. IR (neat) 3375, 3055, 2928, 2852, 1769, 1730, 1610, 1517, 1485, 1466, 1436, 1284, 1245, 1221, 1113, 1076, 1042, 1019, 954, 921, 826, 751, 681 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.71 (3H, t, *J* = 7.5 Hz), 1.10-1.30 (1H, m), 1.30-1.52 (1H, m), 2.34 (3H, s), 3.84 (3H, s), 3.89 (3H, s), 4.25 (1H, d, *J* = 5.1 Hz), 5.20 (1H, s), 5.31 (1H, d, *J* = 5.1 Hz), 6.67 (1H, d, *J* = 7.8 Hz), 6.70-6.85 (2H, m), 7.00-7.21 (5H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.3, 21.1, 21.8, 52.6, 53.2, 62.2, 73.7, 90.4, 90.6, 110.0, 119.0, 123.3, 126.4, 128.3, 128.4, 129.4, 133.0, 137.3, 149.3, 168.1, 168.7. MS (EI) m/z(%): 395[M^+] (17.83), 135(100.00). HRMS (EI): calcd for $C_{23}H_{25}NO_5$ 395.1733, found 395.1735.

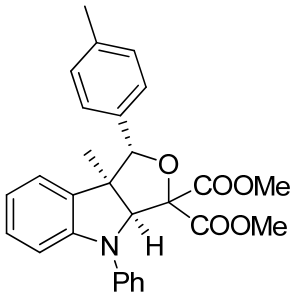
17. Synthesis of 3r.



The reaction of **1a** (75.0 mg, 0.3 mmol), **2g** (70.8 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 24 hours to afford 96.4 mg (79%) of **3r**, white solid. M.p.: 148-149 ^oC. IR (neat) 2959, 1773, 1738, 1642, 1607, 1253, 1111, 1076, 1017, 926, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.95-2.10 (1H, m), 2.10-2.20 (1H, m), 2.35 (3H, s), 3.83 (3H, s), 3.89 (3H, s), 4.23 (1H, d, *J* = 4.0 Hz), 4.91-5.10 (2H, m),

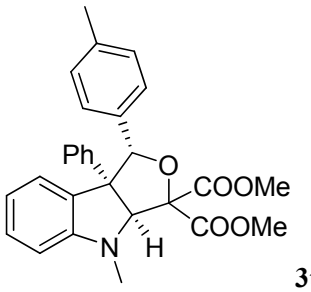
5.22 (1H, s), 5.29 (1H, d, J = 4.0 Hz), 5.36-5.49 (1H, m), 6.65 (1H, d, J = 7.6 Hz), 6.77 (1H, t, J = 7.2 Hz), 6.85 (1H, d, J = 7.2 Hz), 7.09-7.25 (5H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 34.2, 52.6, 53.2, 61.3, 74.3, 90.2, 90.7, 110.2, 118.5, 119.1, 123.5, 126.4, 128.5, 128.6, 129.3, 132.8, 134.3, 137.5, 149.2, 168.0, 168.6. MS (EI) m/z(%): 407[M^+] (19.61), 135(100.00). HRMS (EI): calcd for $C_{24}H_{25}NO_5$ 407.1733, found 407.1734.

18. Synthesis of 3s

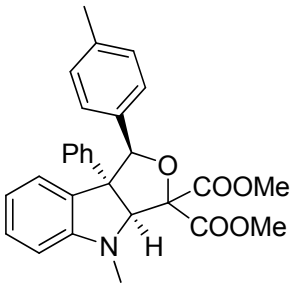


The reaction of **1a** (50.0 mg, 0.2 mmol), **2h** (61.7 mg, 0.3 mmol), 40.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2$•$6H_2O$ (0.01 mmol, 3.7 mg) in CH_2Cl_2 (2 mL) was carried out at r.t. for 8 hours to afford 61.2 mg (67%) of **3s** (exo:endo > 20:1), white solid. M.p.: 147-148 ^{o}C. IR (neat) 2971, 2878, 1743, 1595, 1499, 1480, 1453, 1435, 1271, 1245, 1137, 1088, 1072, 1047, 1021, 964, 765, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (3H, s), 2.37 (3H, s), 3.14 (3H, s), 3.90 (3H, s), 5.51 (1H, s), 5.73 (1H, s), 6.78-6.88 (2H, m), 6.92 (1H, d, J = 6.8 Hz), 7.07-7.25 (6H, m), 7.35-7.45 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 21.2, 51.9, 53.3, 56.3, 81.8, 89.0, 90.3, 108.9, 119.7, 123.1, 124.3, 126.5, 128.3, 128.6, 129.0, 132.5, 133.5, 137.6, 143.2, 148.4, 167.6, 168.5. MS (EI) m/z(%): 457[M^+] (39.51), 135(100.00). HRMS (EI): calcd for $C_{28}H_{27}NO_5$ 457.1889, found 457.1890.

19. Synthesis of 3t.



3t

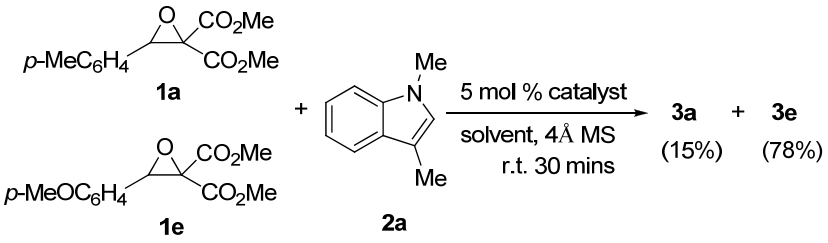


3t'

The reaction of **1a** (74.7 mg, 0.3 mmol), **2i** (93.2 mg, 0.45 mmol), 60.0 mg of activated 4Å M.S. and 5 mol % $Ni(ClO_4)_2 \cdot 6H_2O$ (0.015 mmol, 5.5 mg) in CH_2Cl_2 (3 mL) was carried out at r.t. for 48 hours to afford 52.5 mg (38%) of **3t** (exo : endo = 4:1), white solid. M.p.: 171-173 ^oC. IR (neat) 3030, 2897, 1752, 1607, 1556, 1493, 1438, 1405, 1372, 1336, 1231, 1219, 1170, 1107, 1022, 935, 808, 752, 703 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.36 (3H, s), 3.53 (3H, s), 3.55 (6H, s), 4.42 (1H, s), 6.01 (1H, s), 7.18 (3H, d, J = 8.4 Hz), 7.28-7.45 (9H, m), 7.67 (1H, d, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 31.2, 52.6, 52.7, 75.0, 76.2, 109.3, 119.92, 119.94, 121.0, 123.0, 126.0, 126.4, 126.7, 128.5, 129.2, 130.0, 130.9, 133.9, 136.1, 137.5, 138.0, 166.4, 167.1. MS (EI) m/z(%): 457[M^+] (65.36), 310(100.00). HRMS (EI): calcd for $C_{28}H_{27}NO_5$ 457.1889, found 457.1887.

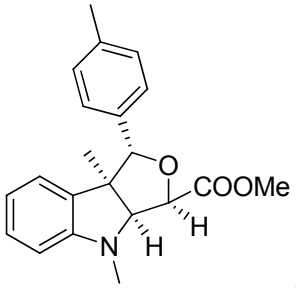
3t', ***endo***, 13.6 mg, white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 2.22 (3H, s), 2.94 (3H, s), 3.74 (3H, s), 3.96 (3H, s), 5.12 (1H, s), 5.71 (1H, s), 6.64 (1H, d, J = 8.0 Hz), 6.88 (1H, td, ^4J = 0.6 Hz, ^3J = 7.4 Hz), 6.94 (2H, d, J = 8.0 Hz), 7.04-7.19 (7H, m), 7.23-7.28 (1H, m), 7.34 (1H, d, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 37.6, 52.5, 53.5, 65.4, 87.4, 91.5, 92.2, 109.6, 118.6, 126.2, 126.4, 127.1, 127.6, 127.8, 128.2, 128.8, 130.0, 133.2, 137.0, 141.1, 152.3, 168.3, 168.5. MS (EI) m/z(%): 457[M^+] (10.91), 207(100.00). HRMS (EI): calcd for $C_{28}H_{27}NO_5$ 457.1889, found 457.1889.

Procedure for competing experiment using 1a versus 1e with 2a

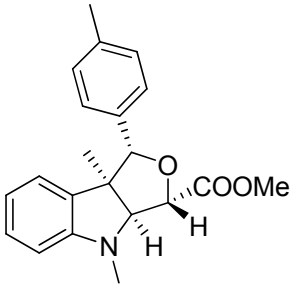


In an inert atmosphere glovebox, a flame-dried vial was charged with 5 mol % $Ni(ClO_4)_2 \cdot 6H_2O$, 60.0 mg of activated 4Å molecular sieves (M.S.), and a magnetic stir bar. Outside of the glovebox, the vial was placed under an N_2 atmosphere and charged with 1 mL of CH_2Cl_2 followed by the indole **2a** (43.8 mg, 0.3 mmol). Afterwards, **1a** (75.0 mg, 0.3 mmol), **1e** (79.6 mg, 0.3 mmol) and 2 mL of CH_2Cl_2 were added. The reaction was stirred at room temperature for 30 mins until **2a** disappeared monitored by TLC. After standard work-up, this experiment gave the products **3a** and **3e** in 15% and 78% ^1H NMR yield, respectively.

Procedure for demethoxycarboxylatiaon of 3a



5a



5a'

The solution of **3a** (79.1 mg, 0.2 mmol) and NaCl (14.7 mg, 0.25 mmol) in DMSO/H_2O (20:1) was heated to 160 ^oC under N_2. The mixture was allowed to cool to room temperature after 5 hours, then it was poured into 5 ml water, extracted with ethyl ether (3*5 mL), washed with water (2*5 mL). The solvent was removed in vacuo. The residue was purified by flash chromatography, eluting with (hexanes:AcOEt = 20:1) to afford 32.0 mg (45%) of **5a** (dr = 30:1). **5a**, colourless oil. IR (neat) 2953, 2867, 1759, 1735, 1608, 1486, 1451, 1376, 1301, 1200, 1117, 1087, 1038, 1020, 996, 858, 797, 741 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.98 (3H, s), 2.36 (3H, s), 2.90 (3H, s), 3.88 (4H, s),4.74 (1H, s), 4.88 (1H, s), 6.56 (1H, d, *J* = 7.6 Hz), 6.73 (1H, t, *J* = 7.2 Hz), 6.84 (1H, d, *J* = 7.2 Hz), 7.10-7.21 (3H, m), 7.24-7.35 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.7, 21.2, 34.3, 52.3, 55.6, 81.6, 86.2, 88.5, 107.4, 118.1, 123.0, 126.4, 128.5, 128.6, 132.4, 134.2, 137.2, 150.9, 171.6. MS (EI) m/z(%): 337[M^+] (28.24), 158(100.00). HRMS (EI): calcd for $C_{21}H_{23}NO_3$ 337.1678, found 337.1676.

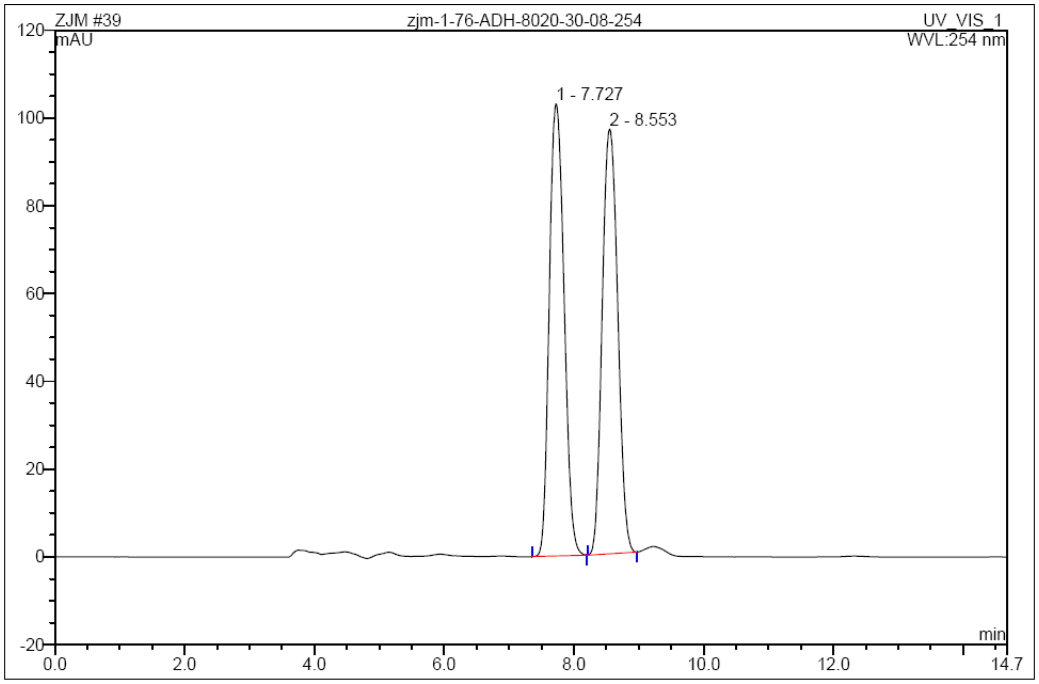
5a', ^1H NMR (400 MHz, $CDCl_3$): δ 1.02 (3H, s), 2.36 (3H, s), 2.82 (3H, s), 3.78 (3H, s),4.15(1H, d, *J* = 6.0 Hz), 5.06 (1H, s), 5.11 (1H, d, *J* = 6.0 Hz), 6.60 (1H, d, *J* = 7.6 Hz), 6.77 (1H, t, *J* = 7.2 Hz), 6.84 (1H, d, *J* = 7.2 Hz), 7.12-7.24 (5H, m). ^{13}C NMR (100MHz, $CDCl_3$): δ 19.8, 21.2, 38.2, 51.8, 56.8, 80.4, 84.4, 88.0, 109.4, 118.7, 122.9, 126.5, 128.5, 128.6, 132.4, 134.0, 137.3, 152.5, 171.4. MS (EI) m/z(%): 337[M^+] (27.67), 158(100.00). HRMS (EI): calcd for $C_{21}H_{23}NO_3$ 337.1678, found 337.1680.

Procedure for $Ni(ClO_4)_2•6H_2O$ /BOX catalyzed cycloaddition of oxirane 1a with 1,3-dimethyl-1H-indole 2d

In an inert atmosphere, a flame-dried vial was charged with a maganetic stir bar, 60.0 mg of activated 4Å molecular sieves (M.S.), $Ni(ClO_4)_2•6H_2O$ (8.1 mg, 5 mol%), BOX **4** (6.5 mg, 5.5 mol%) and 2.0 mL of DCM. The mixture was allowed to stir for 3 h at room temperature. Then, indole **2d** (69.8 mg, 0.52 mmol,) was added, followed by oxirane **1a** (110.5 mg, 0.44 mmol) and 1.0 mL of DCM. The mixture was continued to stir at room temperature for further 5 d. The products were obtained by flash chromatography providing isolated yield of 72%. The enantiomeric excess of product was determined by chiral HPLC. HPLC analysis: Chiralcel AD-H (hexane/*i*-PrOH = 80/20, 0.8 mL/min), t_{minor} = 7.66 min, t_{major} = 8.27 min, ee = 19%.

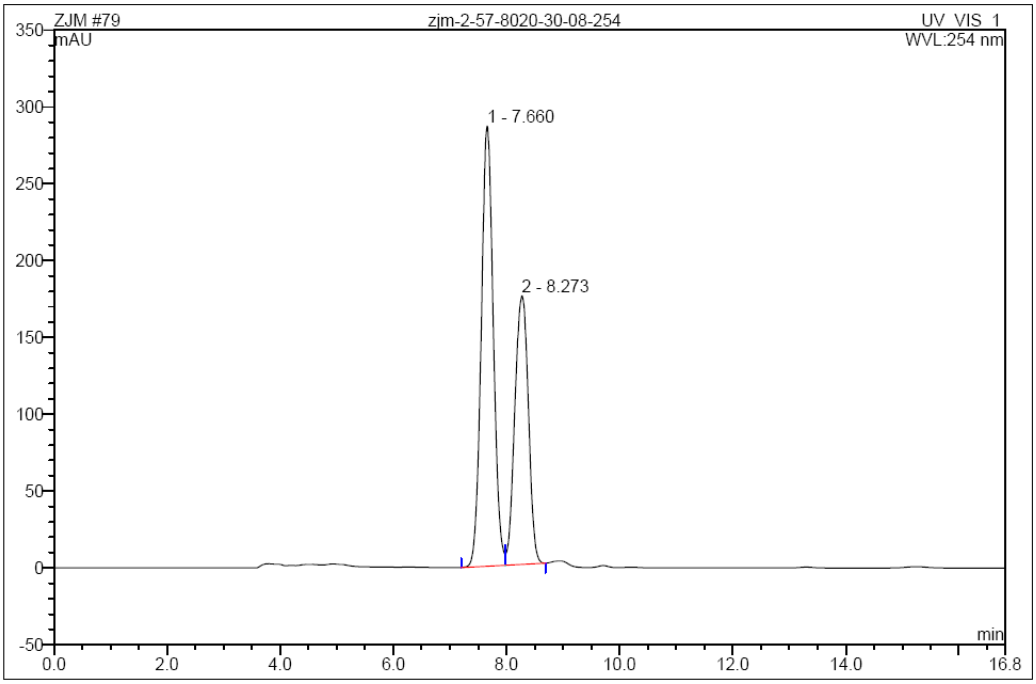
HPLC spectra

Racemic of product of **3o**



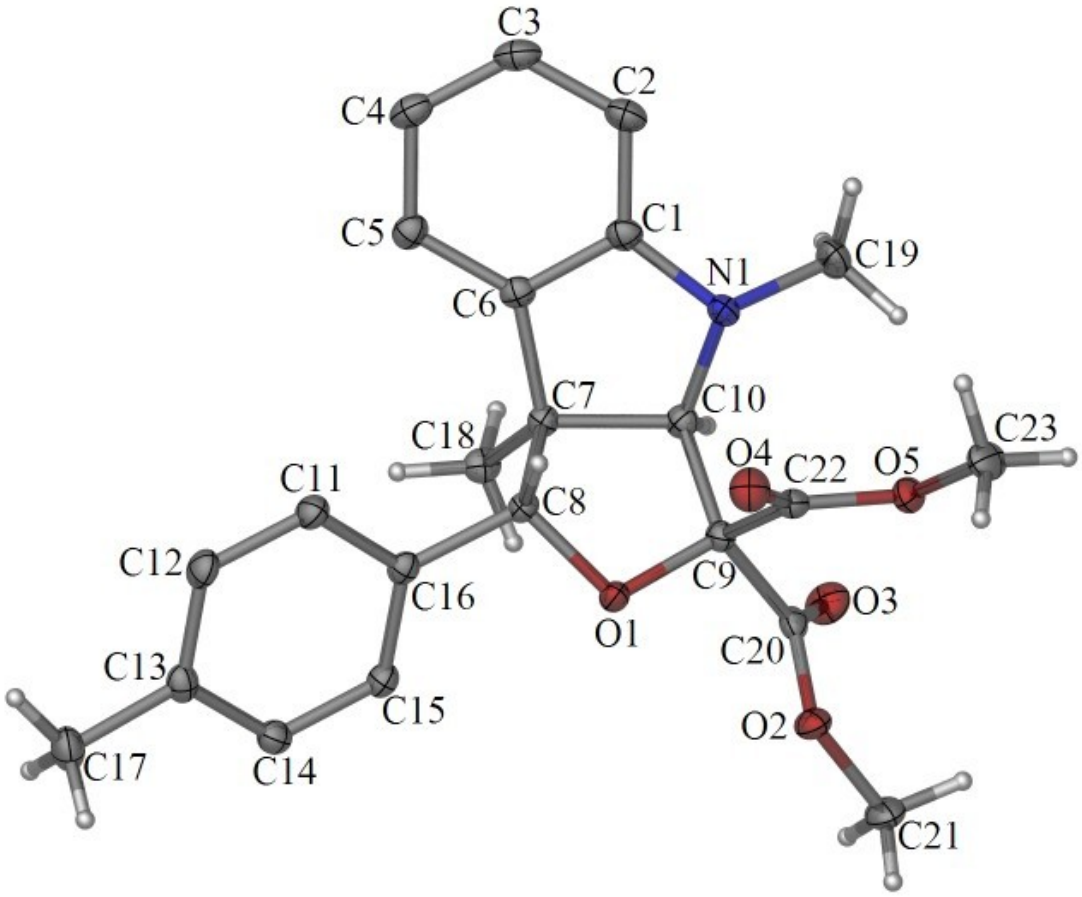
序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	7.73	n.a.		102.975	27.193	50.37	n.a.	BMB
2	8.55	n.a.		96.752	26.793	49.63	n.a.	BMB
总和:				199.728	53.986	100.00	0.000	

Enantioenriched product of **3o**

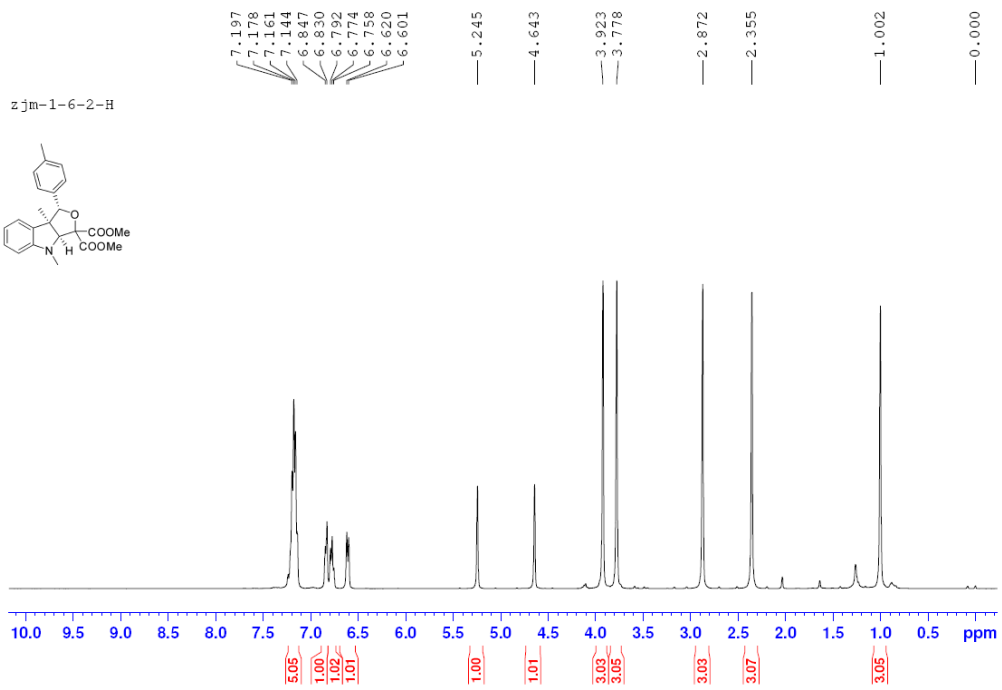


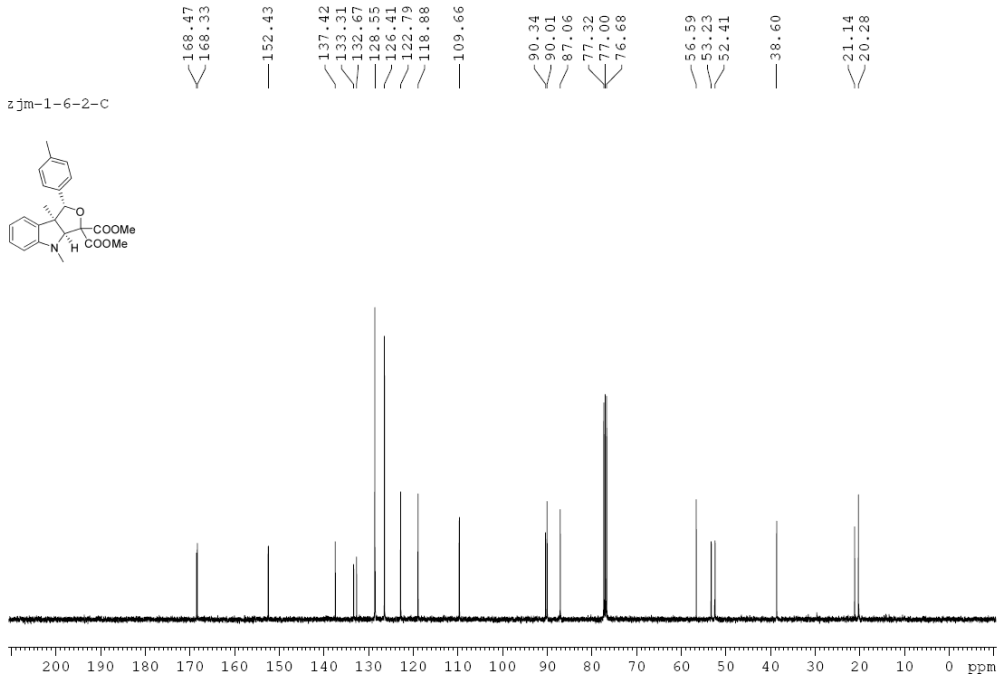
序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	7.66	n.a.		286.588	70.738	59.26	n.a.	BM
2	8.27	n.a.		174.709	48.631	40.74	n.a.	MB
总和:				461.296	119.369	100.00	0.000	

ORTEP view of cis-isomers of 3a.

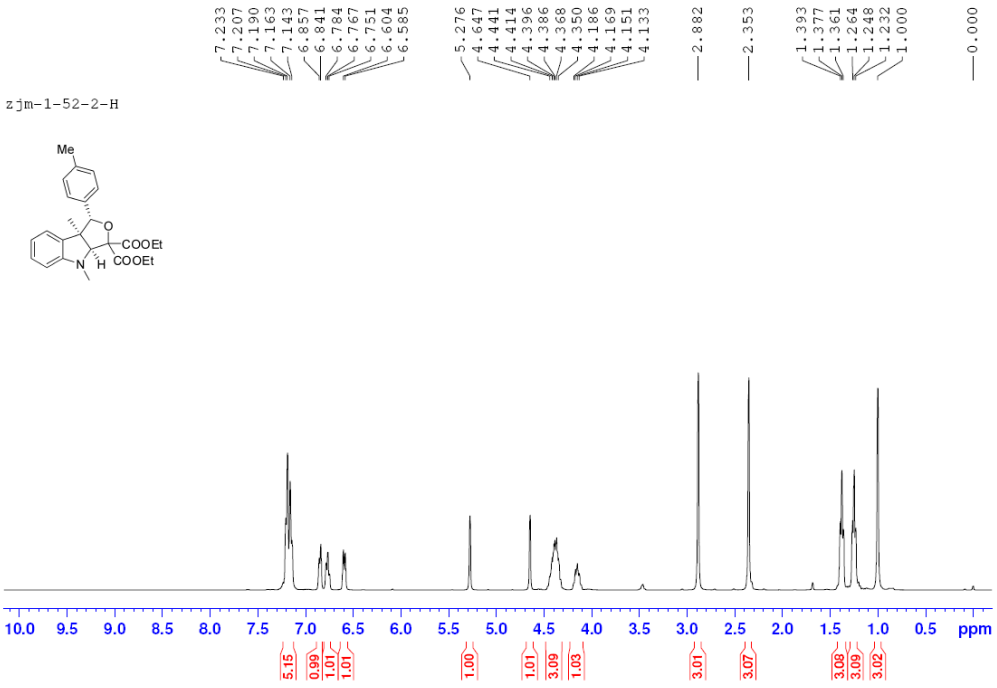


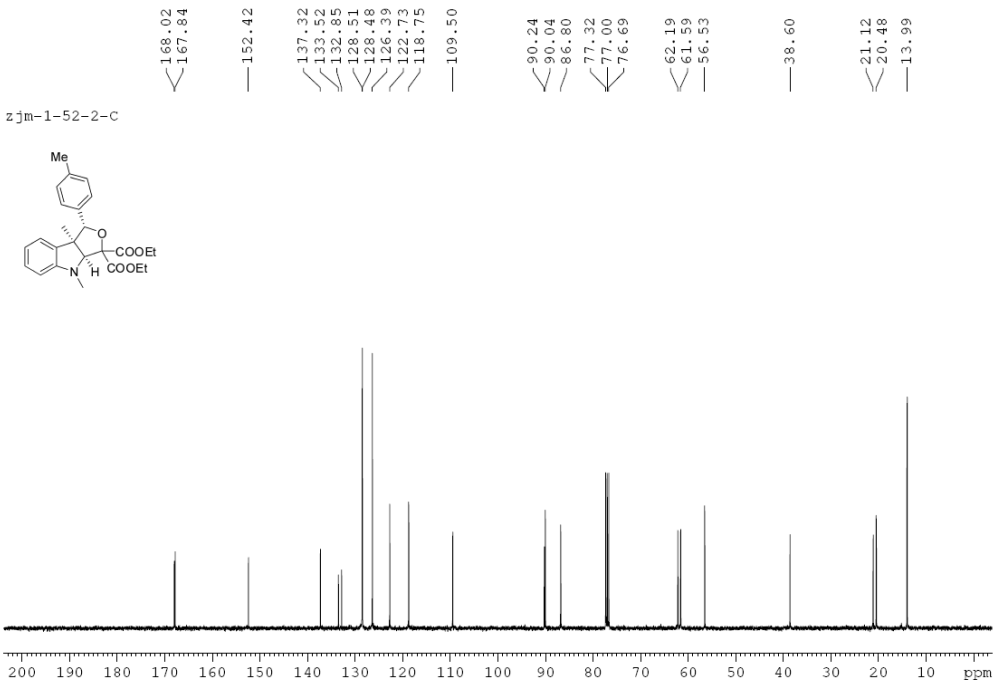
NMR spectra



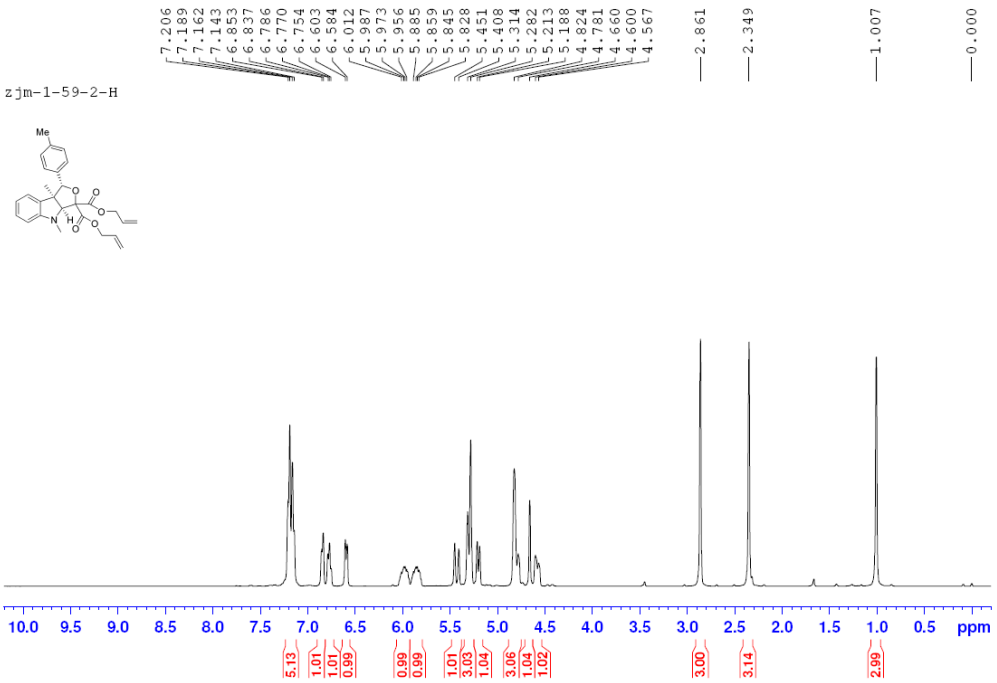


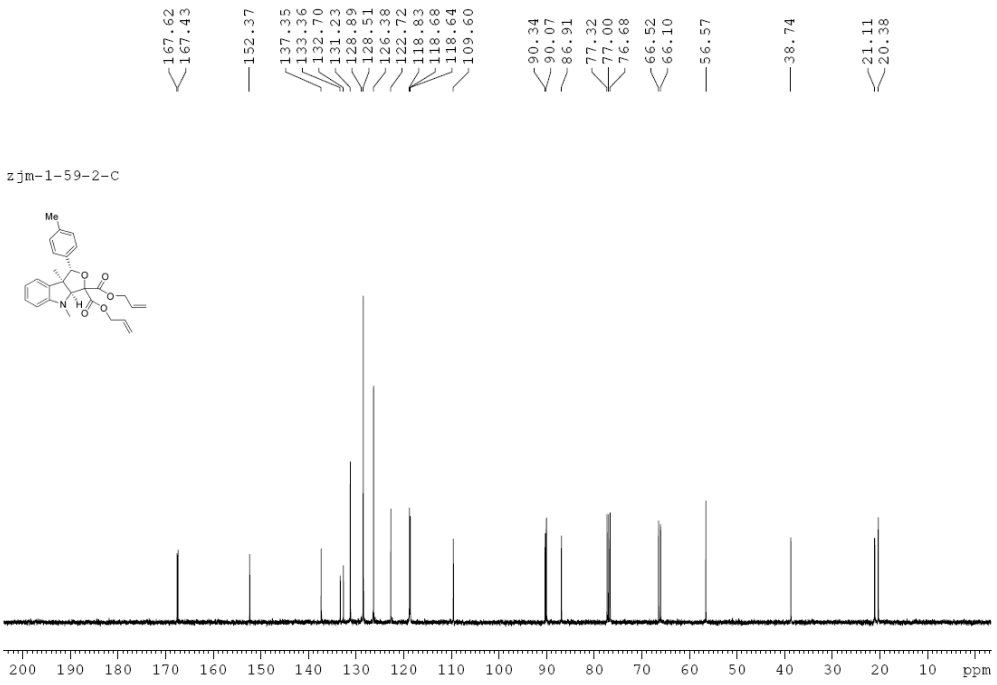
3a


7.233
7.207
7.190
7.163
7.143
6.857
6.841
6.784
6.767
6.751
6.604
6.585
5.276
4.647
4.441
4.414
4.396
4.386
4.368
4.350
4.186
4.169
4.151
4.133
2.882
2.353
1.393
1.377
1.361
1.264
1.248
1.232
1.000
0.000
zjm-1-52-2-H
Me
O
COOEt
COOEt
N
H
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.15
0.99
1.01
1.01
1.00
1.01
3.09
1.03
3.01
3.07
3.08
3.09
3.02

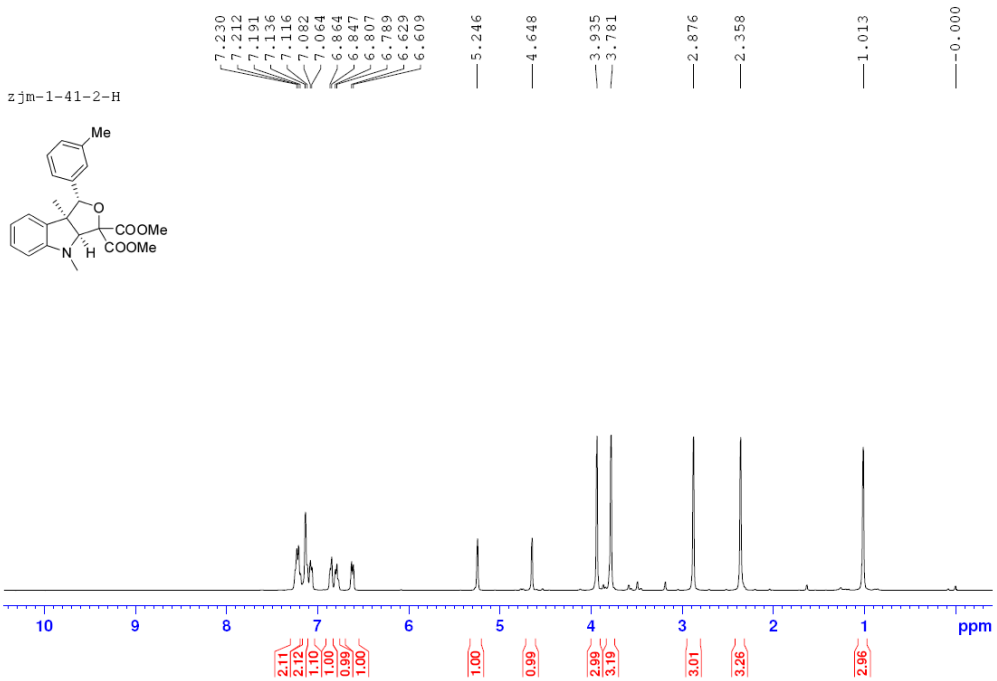

168.02
167.84
152.42
137.32
133.52
132.85
128.51
128.48
126.39
122.73
118.75
109.50
90.24
90.04
86.80
77.32
77.00
76.69
62.19
61.59
56.53
38.60
21.12
20.48
13.99
zjm-1-52-2-C
Me
O
COOEt
COOEt
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

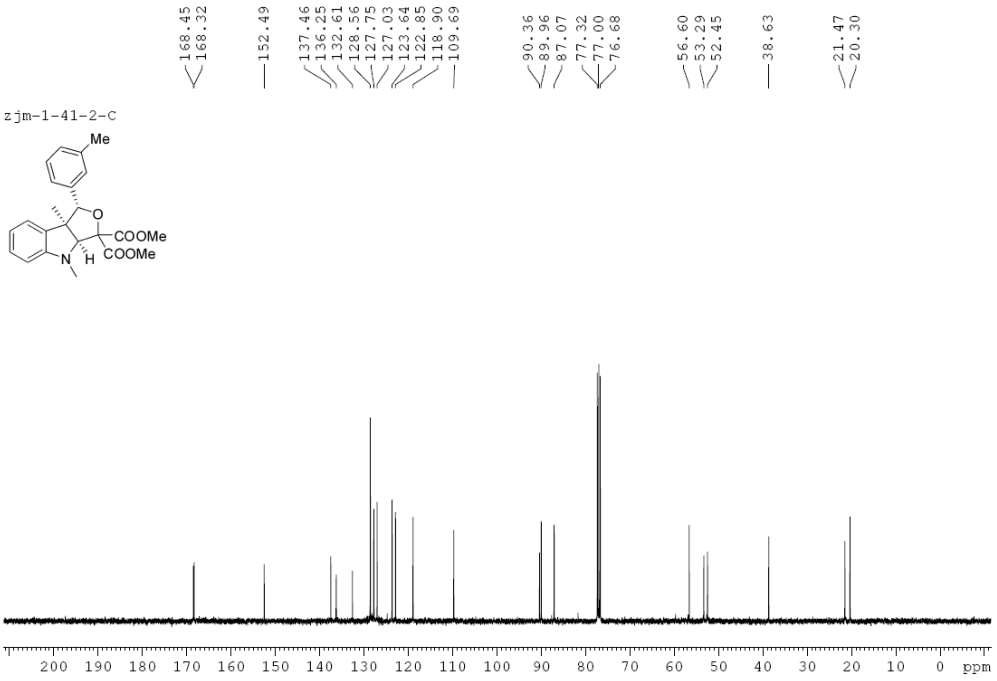
3b


7.206
7.189
7.162
7.143
6.853
6.837
6.786
6.770
6.754
6.603
6.584
6.012
5.987
5.973
5.956
5.885
5.859
5.845
5.828
5.451
5.408
5.314
5.282
5.213
5.188
4.824
4.781
4.660
4.600
4.567
2.861
2.349
1.007
0.000
zjm-1-59-2-H
Me
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.13
1.01
1.01
0.99
0.99
0.99
1.01
3.03
1.04
3.06
1.04
1.02
3.00
3.14
2.99

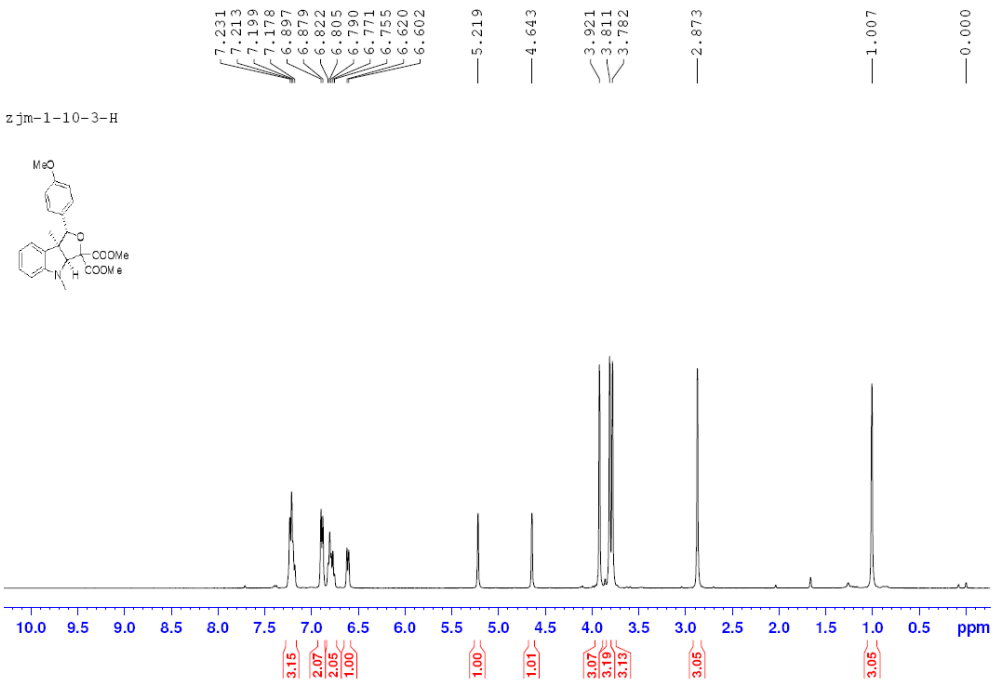

167.62
167.43
152.37
137.35
133.36
132.70
131.23
128.89
128.51
126.38
122.72
118.83
118.68
118.64
109.60
90.34
90.07
86.91
77.32
77.00
76.68
66.52
66.10
56.57
38.74
21.11
20.38
zjm-1-59-2-C
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

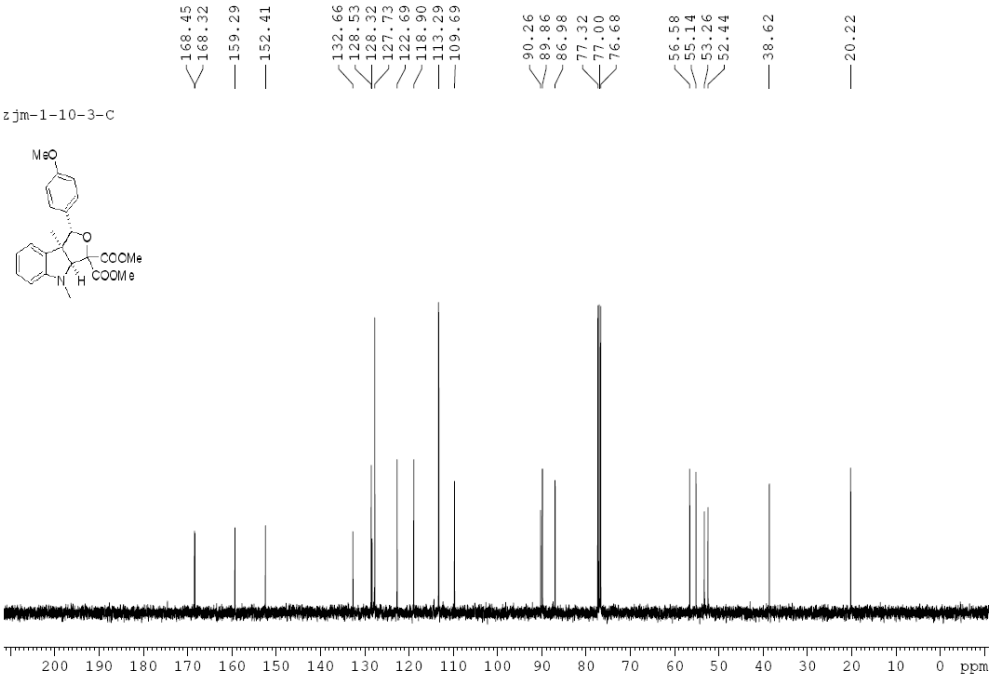
3c


7.230
7.212
7.191
7.136
7.116
7.082
7.064
6.864
6.847
6.807
6.789
6.629
6.609
5.246
4.648
3.935
3.781
2.876
2.358
1.013
0.000
zjm-1-41-2-H
Me
O
COOMe
COOMe
N
H
10
9
8
7
6
5
4
3
2
1
ppm
2.11
2.12
1.10
1.00
0.99
1.00
1.00
0.99
2.99
3.19
3.01
3.26
2.96

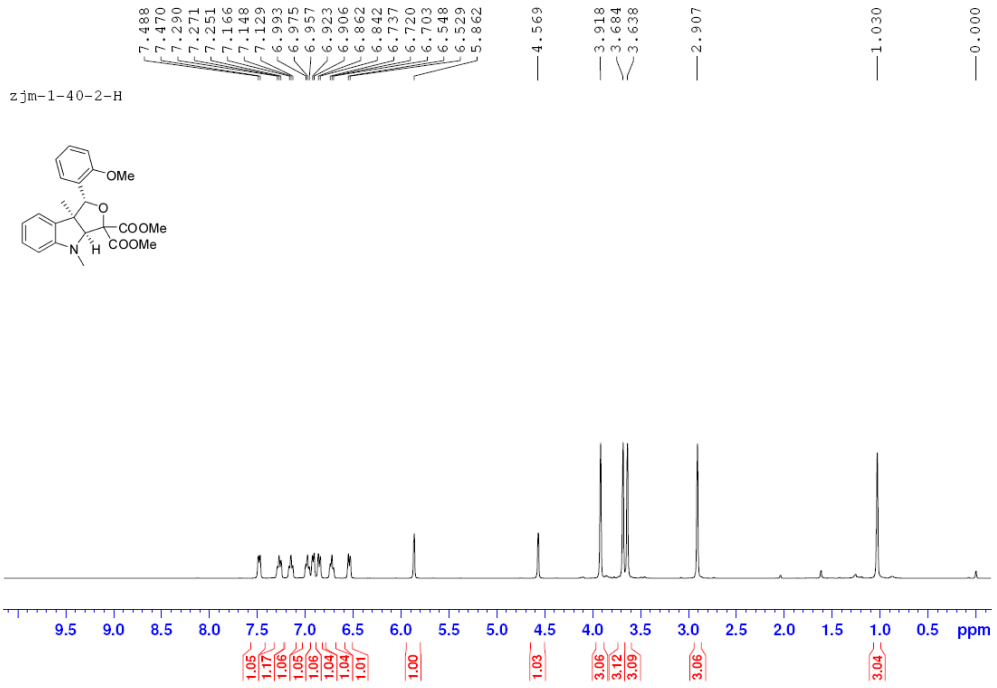

168.45
168.32
152.49
137.46
136.25
132.61
128.56
127.75
127.03
123.64
122.85
118.90
109.69
90.36
89.96
87.07
77.32
77.00
76.68
56.60
53.29
52.45
38.63
21.47
20.30
zjm-1-41-2-C
Me
O
COOMe
COOMe
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

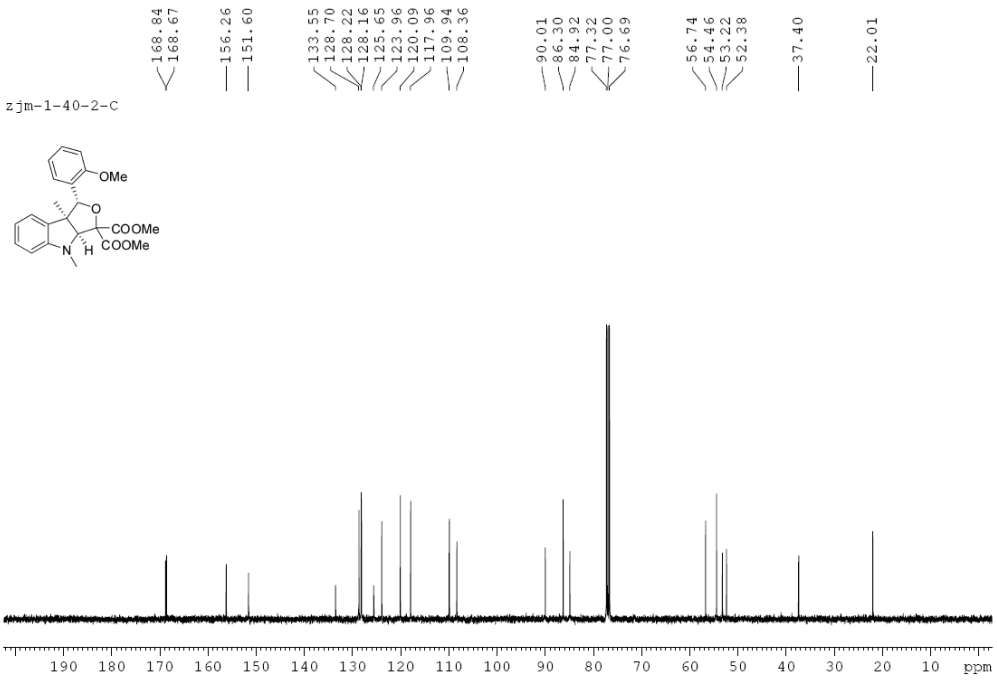
3d


7.231
7.213
7.199
7.178
6.897
6.879
6.822
6.805
6.790
6.771
6.755
6.620
6.602
5.219
4.643
3.921
3.811
3.782
2.873
1.007
0.000
zjm-1-10-3-H
MeO
COOMe
COOMe
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.15
2.07
2.05
1.00
1.00
1.01
3.07
3.19
3.13
3.05
3.05

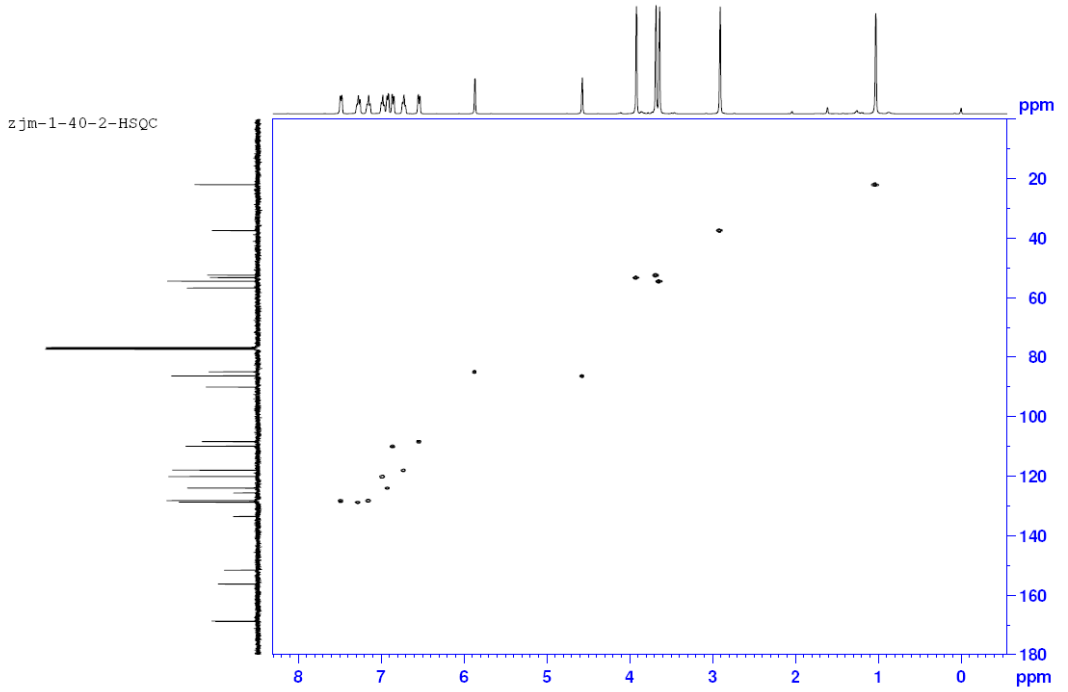

168.45
168.32
159.29
152.41
132.66
128.53
128.32
127.73
122.69
118.90
113.29
109.69
90.26
89.86
86.98
77.32
77.00
76.68
56.58
55.14
53.26
52.44
38.62
20.22
zjm-1-10-3-C
MeO
COOMe
COOMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

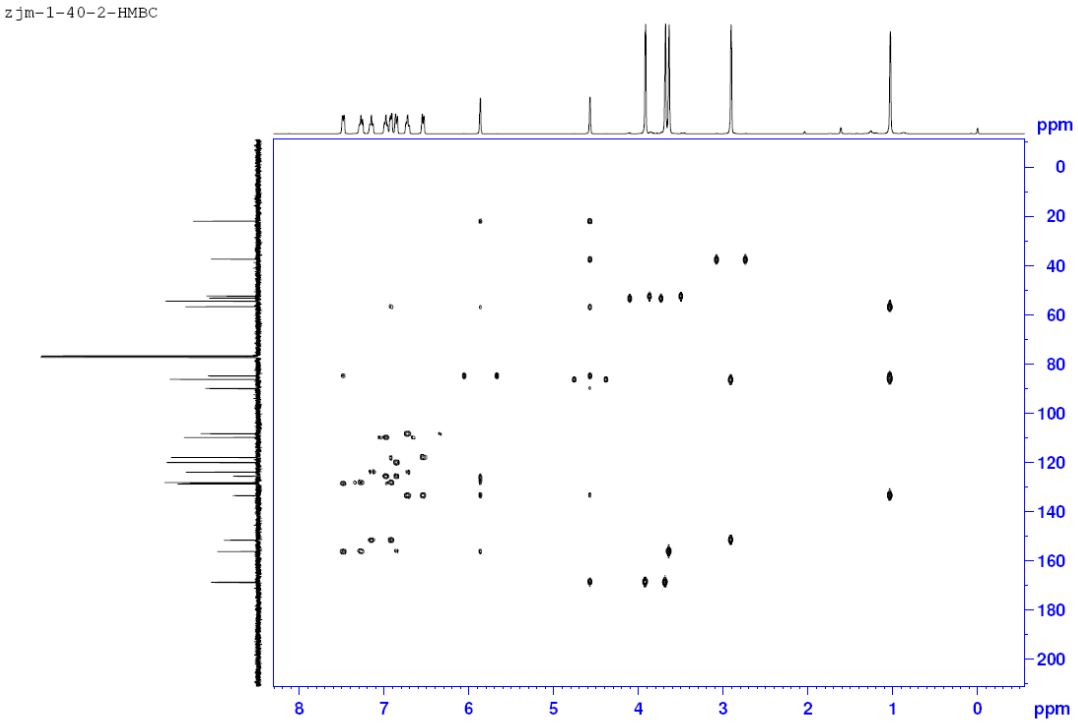
3e


7.488
7.470
7.290
7.271
7.251
7.166
7.148
7.129
6.993
6.975
6.957
6.923
6.906
6.862
6.842
6.737
6.720
6.703
6.548
6.529
5.862
4.569
3.918
3.684
3.638
2.907
1.030
0.000
zjm-1-40-2-H
OMe
O
COOMe
COOMe
N
H
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.05
1.17
1.06
1.05
1.06
1.04
1.04
1.01
1.00
1.03
3.06
3.12
3.09
3.06
3.04

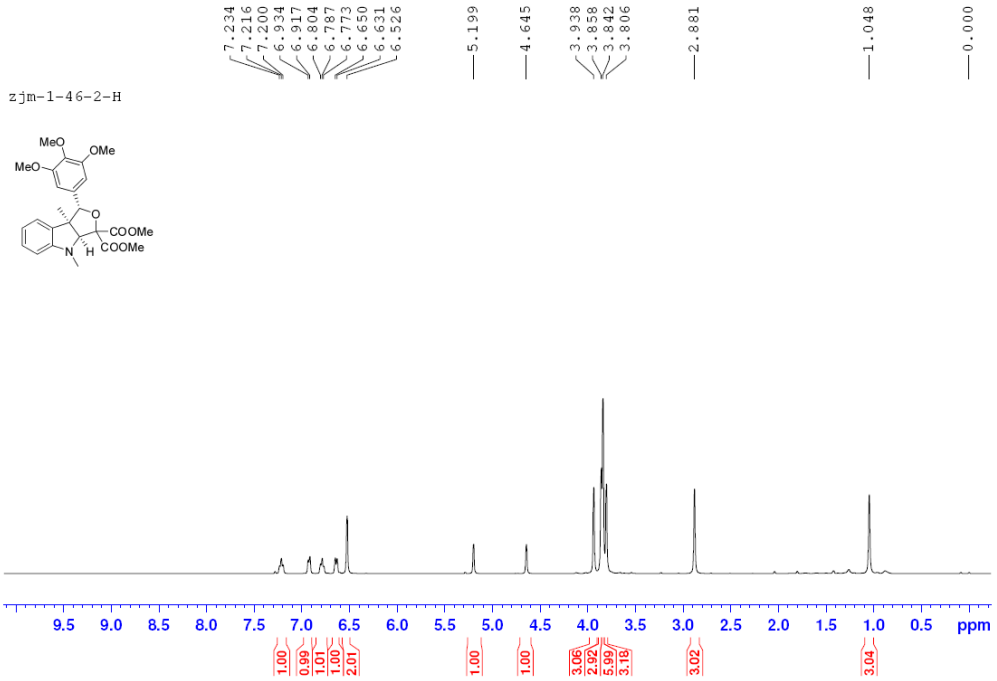

168.84
168.67
156.26
151.60
133.55
128.70
128.22
128.16
125.65
123.96
120.09
117.96
109.94
108.36
90.01
86.30
84.92
77.32
77.00
76.69
56.74
54.46
53.22
52.38
37.40
22.01
zjm-1-40-2-C
OMe
O
COOMe
COOMe
N
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

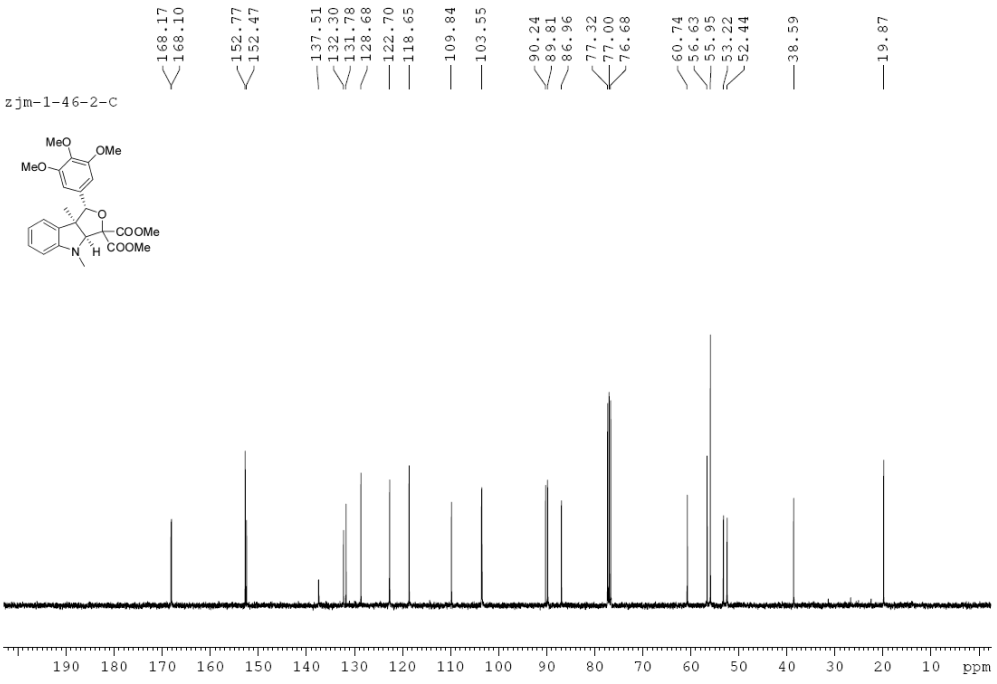
3f


zjm-1-40-2-HSQC
ppm
20
40
60
80
100
120
140
160
180
8
7
6
5
4
3
2
1
0
ppm

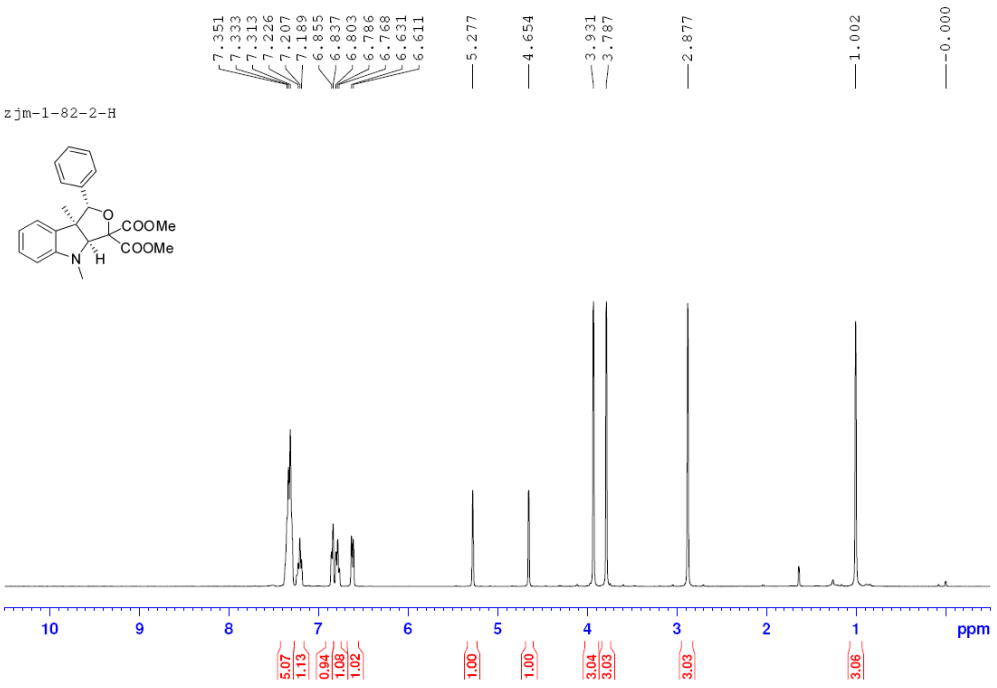

zjm-1-40-2-HMBC
ppm
0
20
40
60
80
100
120
140
160
180
200
8
7
6
5
4
3
2
1
0
ppm

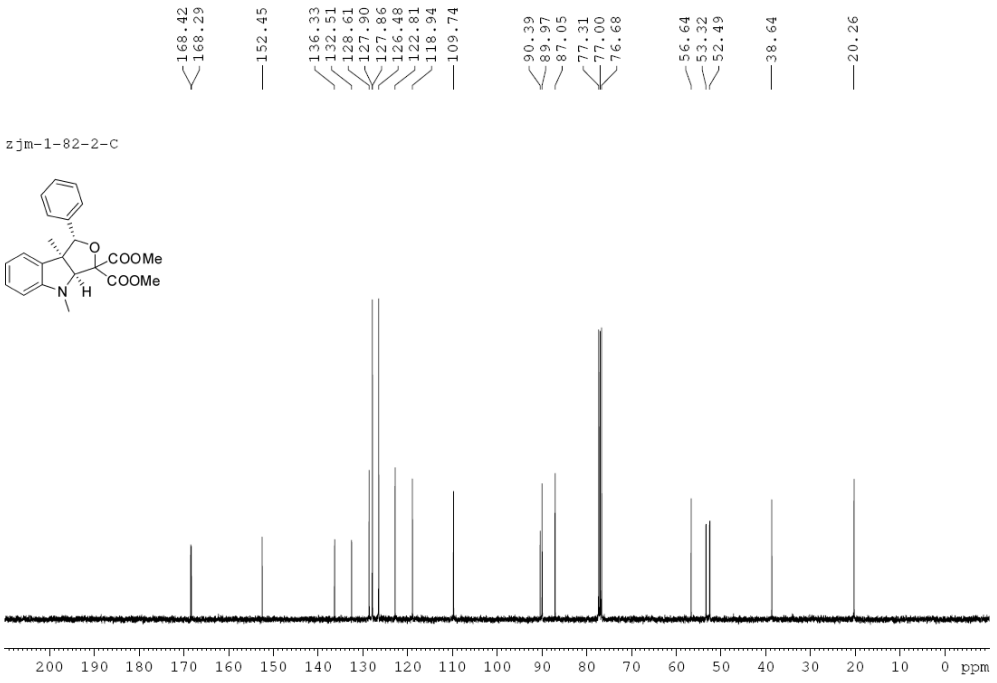
3f


7.234
7.216
7.200
6.934
6.917
6.804
6.787
6.773
6.650
6.631
6.526
5.199
4.645
3.938
3.858
3.842
3.806
2.881
1.048
0.000
zjm-1-46-2-H
MeO
OMe
MeO
O
COOMe
N
H
COOMe
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.99
1.01
1.00
2.01
1.00
1.00
3.06
2.92
5.99
3.18
3.02
3.04

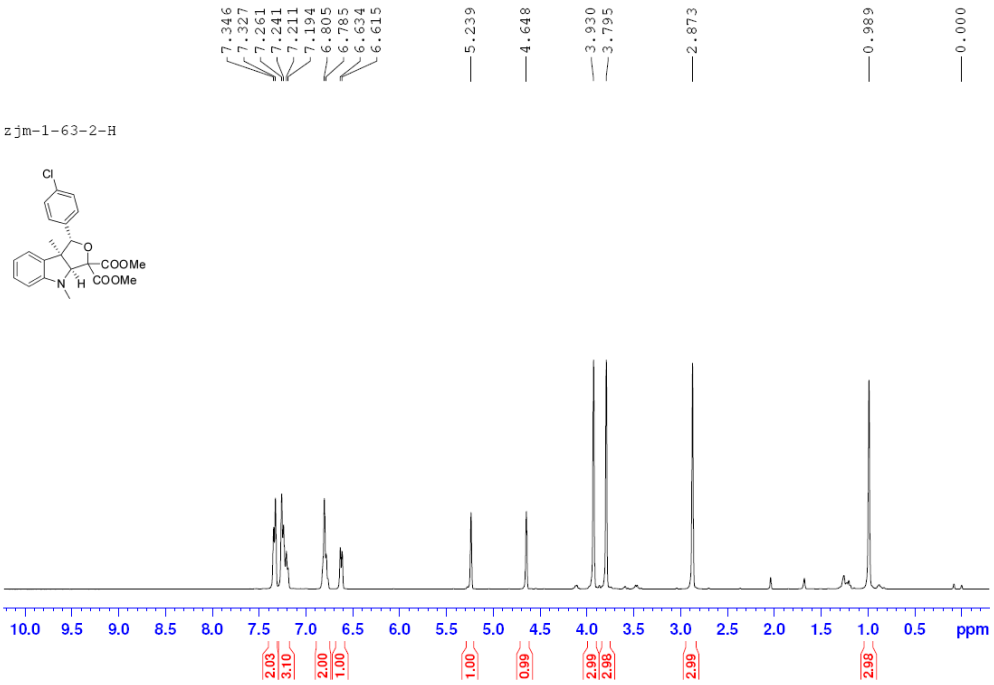

168.17
168.10
152.77
152.47
137.51
132.30
131.78
128.68
122.70
118.65
109.84
103.55
90.24
89.81
86.96
77.32
77.00
76.68
60.74
56.63
55.95
53.22
52.44
38.59
19.87
zjm-1-46-2-C
MeO
OMe
MeO
O
COOMe
N
H
COOMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

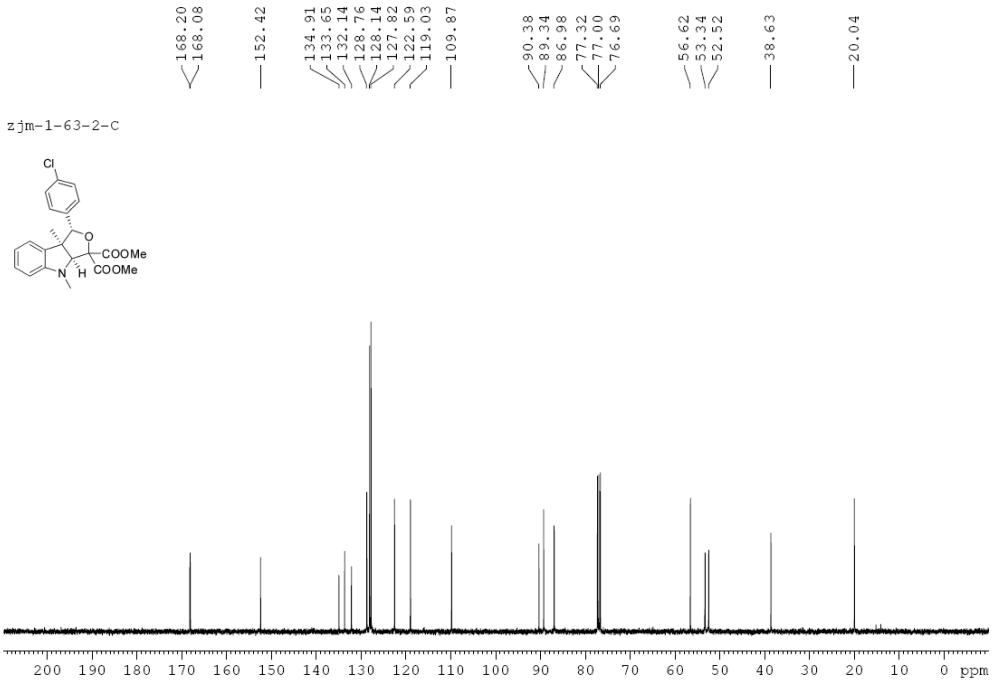
3g


7.351
7.333
7.313
7.226
7.207
7.189
6.855
6.837
6.803
6.786
6.768
6.631
6.611
5.277
4.654
3.931
3.787
2.877
1.002
0.000
zjm-1-82-2-H
COOMe
COOMe
N
H
10
9
8
7
6
5
4
3
2
1
ppm
5.07
1.13
0.94
1.08
1.02
1.00
1.00
3.04
3.03
3.03
3.06

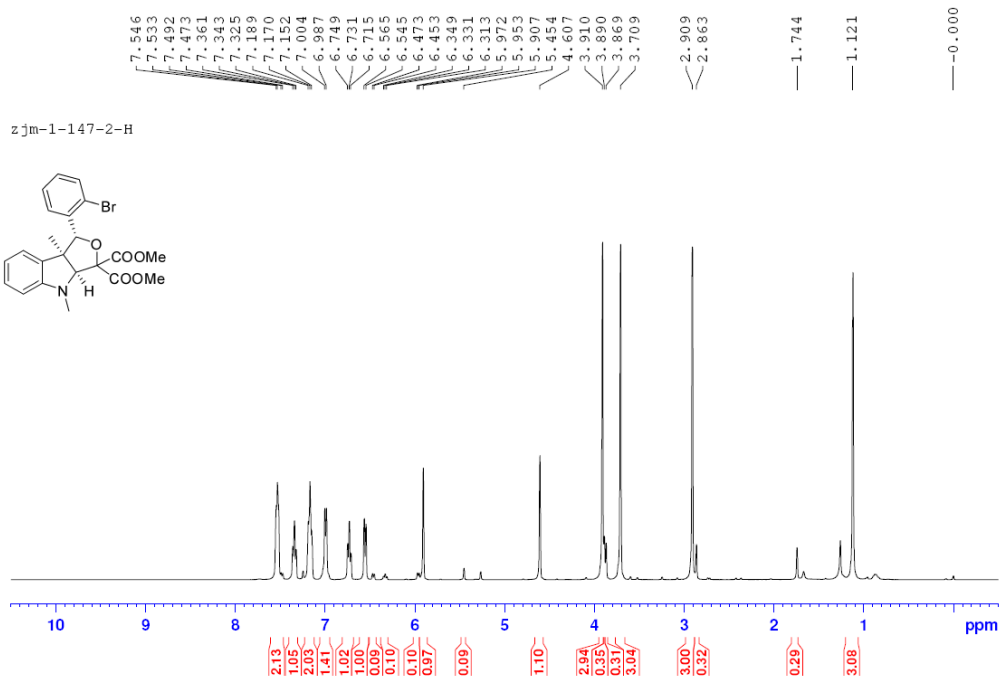

168.42
168.29
152.45
136.33
132.51
128.61
127.90
127.86
126.48
122.81
118.94
109.74
90.39
89.97
87.05
77.31
77.00
76.68
56.64
53.32
52.49
38.64
20.26
zjm-1-82-2-C
COOMe
COOMe
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

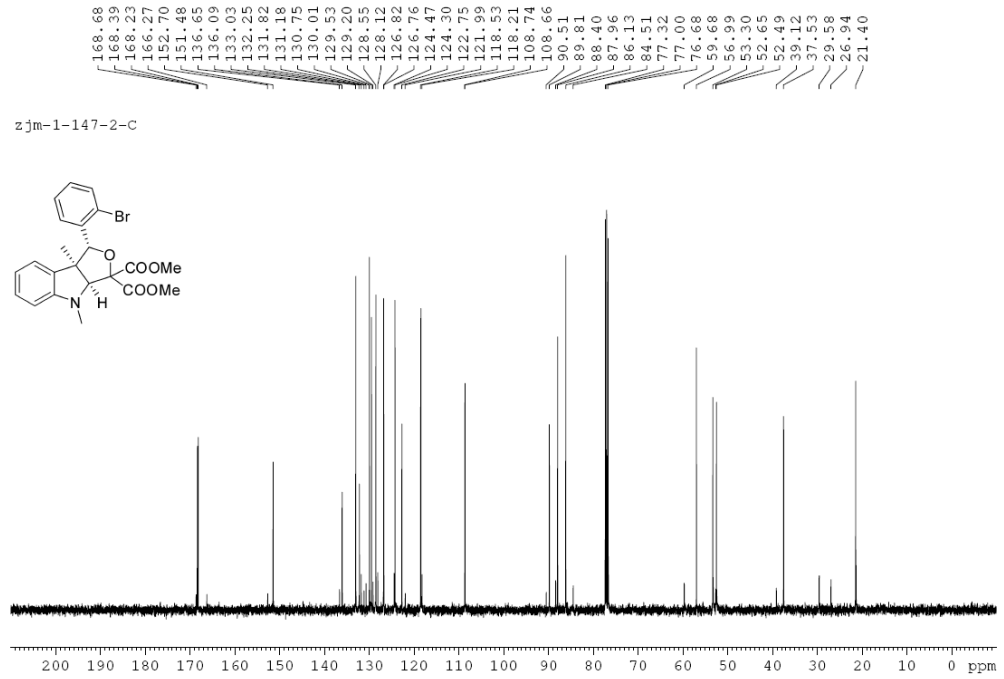
3h


7.346
7.327
7.261
7.241
7.211
7.194
6.805
6.785
6.634
6.615
5.239
4.648
3.930
3.795
2.873
0.989
0.000
zjm-1-63-2-H
Cl
O
COOMe
COOMe
N
H
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.03
3.10
2.00
1.00
1.00
0.99
2.99
2.98
2.99
2.98

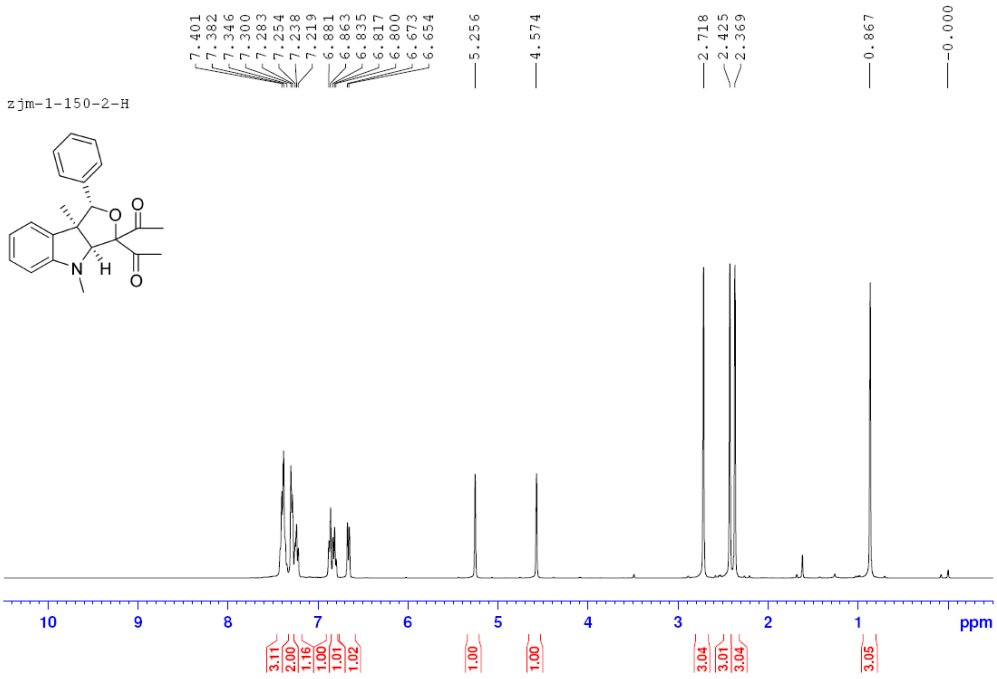

168.20
168.08
152.42
134.91
133.65
132.14
128.76
128.14
127.82
122.59
119.03
109.87
90.38
89.34
86.98
77.32
77.00
76.69
56.62
53.34
52.52
38.63
20.04
zjm-1-63-2-C
Cl
O
COOMe
COOMe
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

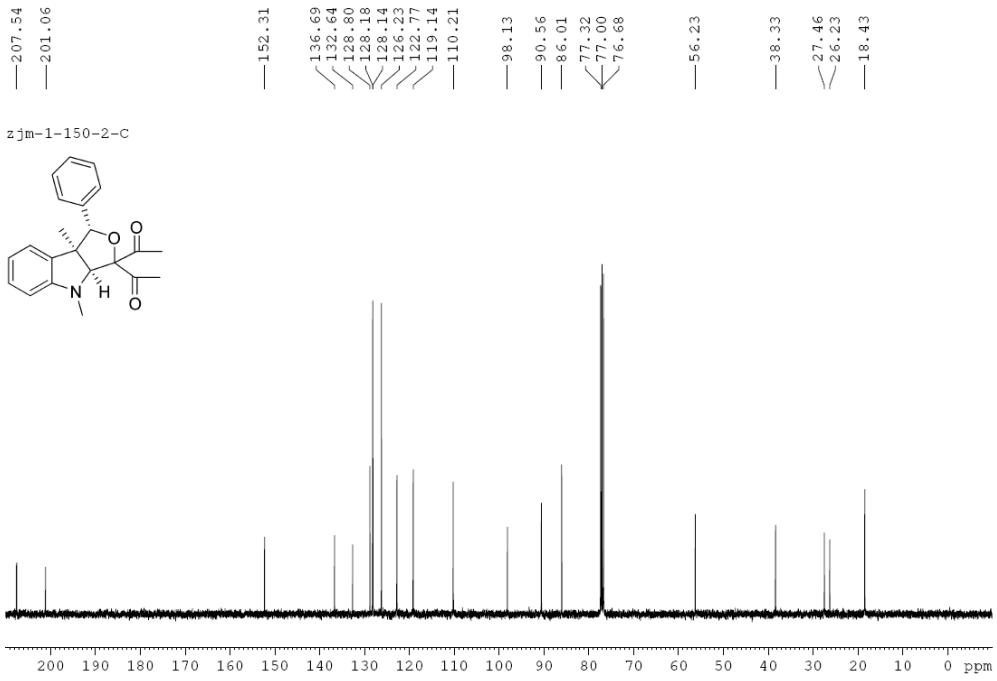
3i


7.546
7.533
7.492
7.473
7.361
7.343
7.325
7.189
7.170
7.152
7.004
6.987
6.749
6.731
6.715
6.565
6.545
6.473
6.453
6.349
6.331
6.313
5.972
5.953
5.907
5.454
4.607
3.910
3.890
3.869
3.709
2.909
2.863
1.744
1.121
-0.000
zjm-1-147-2-H
Br
O
COOMe
COOMe
N
H
10
9
8
7
6
5
4
3
2
1
ppm
2.13
1.05
2.03
1.41
1.02
1.00
0.09
0.10
0.10
0.07
0.09
1.10
2.94
0.35
0.31
3.04
3.00
0.32
0.29
3.08

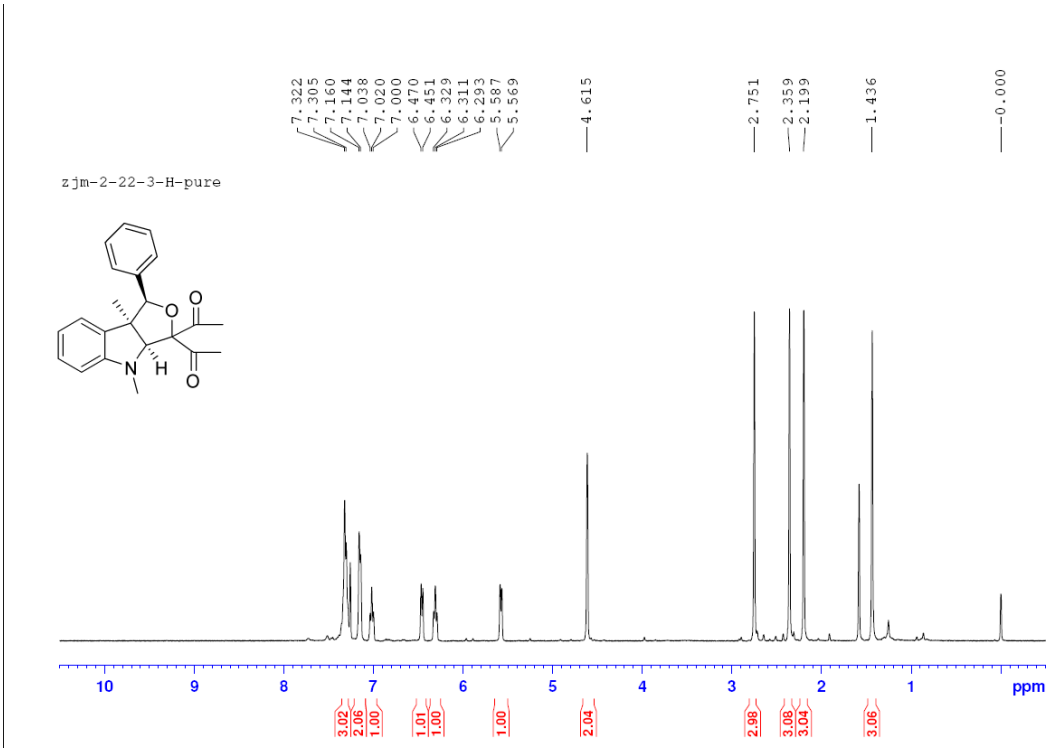

168.68
168.39
168.23
166.27
152.70
151.48
136.65
136.09
133.03
132.25
131.82
131.18
130.75
130.01
129.53
129.20
128.55
128.12
126.82
126.76
124.47
124.30
122.75
121.99
118.53
118.21
108.74
108.66
90.51
89.81
88.40
87.96
86.13
84.51
77.32
77.00
76.68
59.68
56.99
53.30
52.65
52.49
39.12
37.53
29.58
26.94
21.40
zjm-1-147-2-C
Br
O
COOMe
COOMe
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

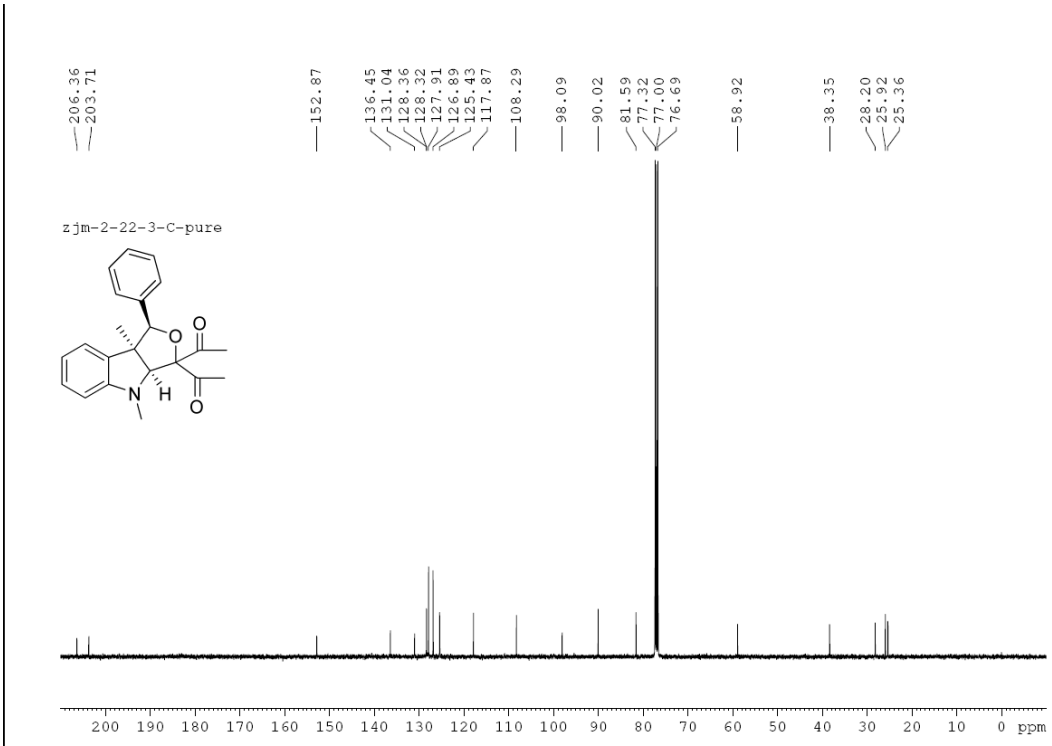
3j


7.401
7.382
7.346
7.300
7.283
7.254
7.238
7.219
6.881
6.863
6.835
6.817
6.800
6.673
6.654
5.256
4.574
2.718
2.425
2.369
0.867
-0.000
zjm-1-150-2-H
O
O
N
H
O
10
9
8
7
6
5
4
3
2
1
ppm
3.11
2.00
1.16
1.00
1.01
1.02
1.00
1.00
3.04
3.01
3.04
3.05

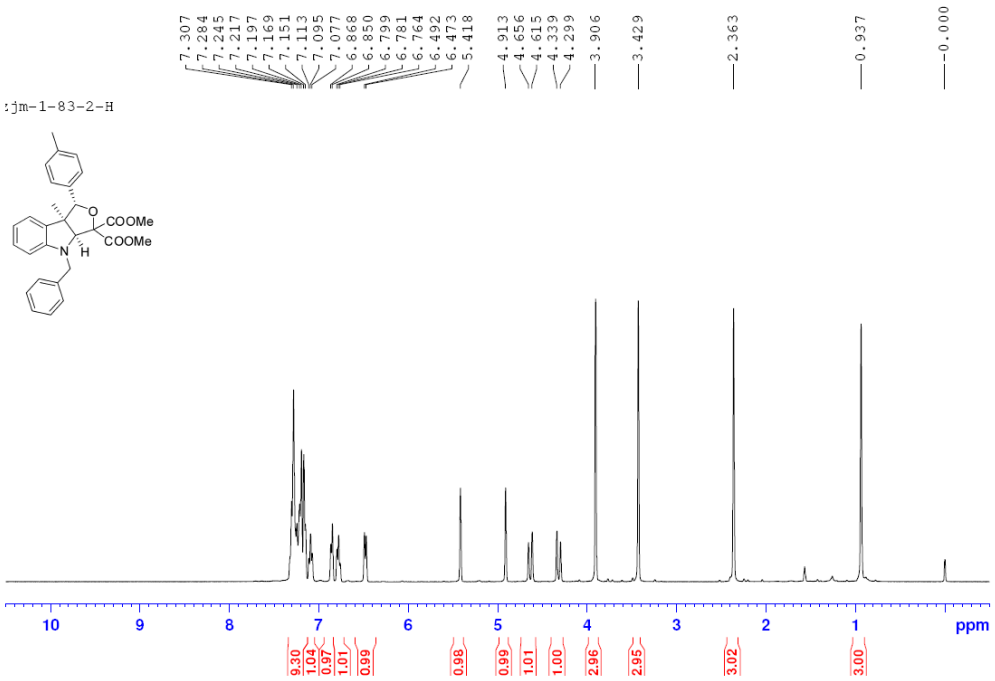

207.54
201.06
152.31
136.69
132.64
128.80
128.18
128.14
126.23
122.77
119.14
110.21
98.13
90.56
86.01
77.32
77.00
76.68
56.23
38.33
27.46
26.23
18.43
zjm-1-150-2-C
O
O
N
H
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

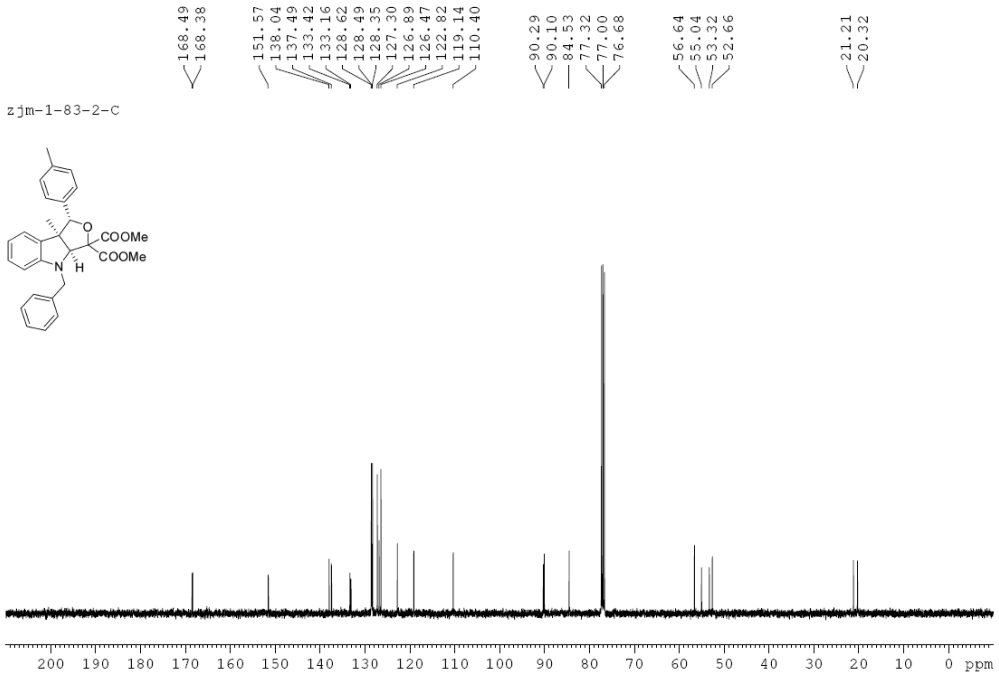
3k


7.322
7.305
7.160
7.144
7.038
7.020
7.000
6.470
6.451
6.329
6.311
6.293
5.587
5.569
4.615
2.751
2.359
2.199
1.436
0.000
zjm-2-22-3-H-pure
O
O
N
H
O
10
9
8
7
6
5
4
3
2
1
ppm
3.02
2.06
1.00
1.01
1.00
1.00
2.04
2.98
3.08
3.04
3.06

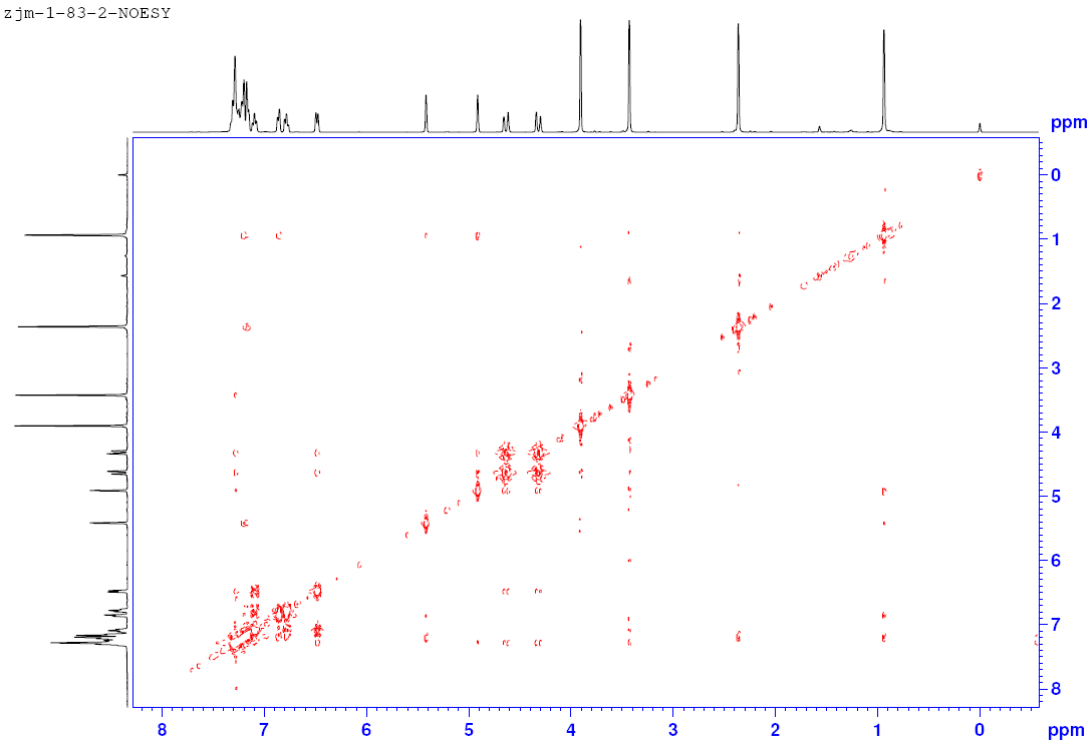

206.36
203.71
152.87
136.45
131.04
128.36
128.32
127.91
126.89
125.43
117.87
108.29
98.09
90.02
81.59
77.32
77.00
76.69
58.92
38.35
28.20
25.92
25.36
zjm-2-22-3-C-pure
O
O
N
H
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

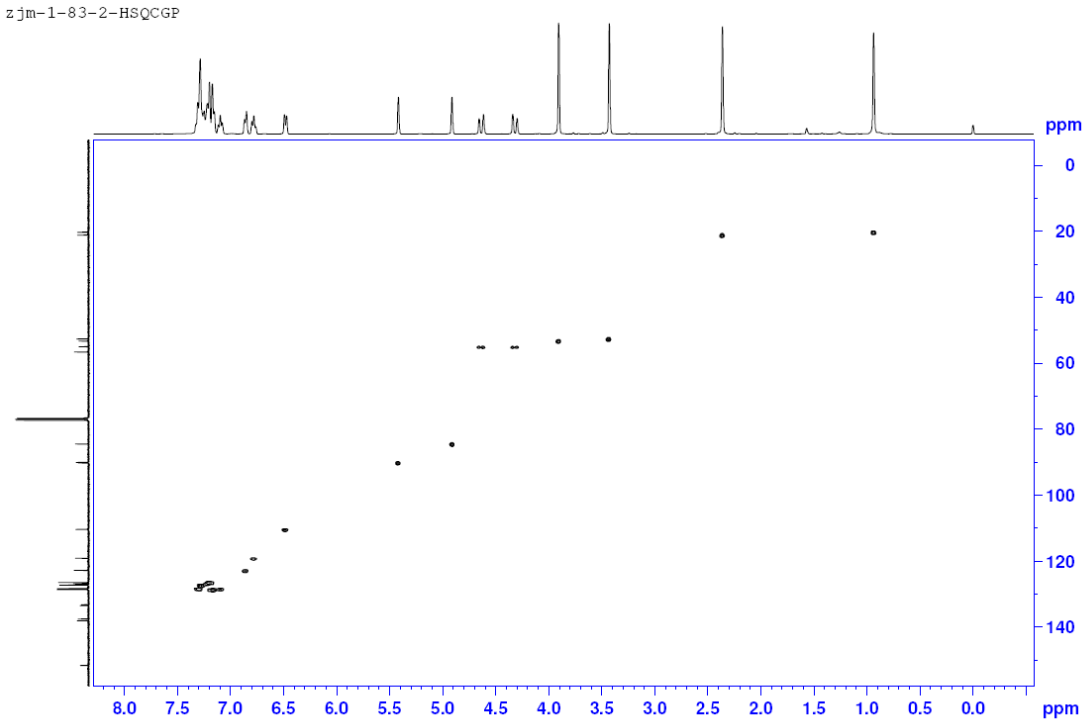
3k'


7.307
7.284
7.245
7.217
7.197
7.169
7.151
7.113
7.095
7.077
6.868
6.850
6.799
6.781
6.764
6.492
6.473
5.418
4.913
4.656
4.615
4.339
4.299
3.906
3.429
2.363
0.937
0.000
jm-1-83-2-H
COOMe
COOMe
N
H
O
10
9
8
7
6
5
4
3
2
1
ppm
9.30
1.04
0.97
1.01
0.99
0.98
0.99
1.01
1.00
2.96
2.95
3.02
3.00

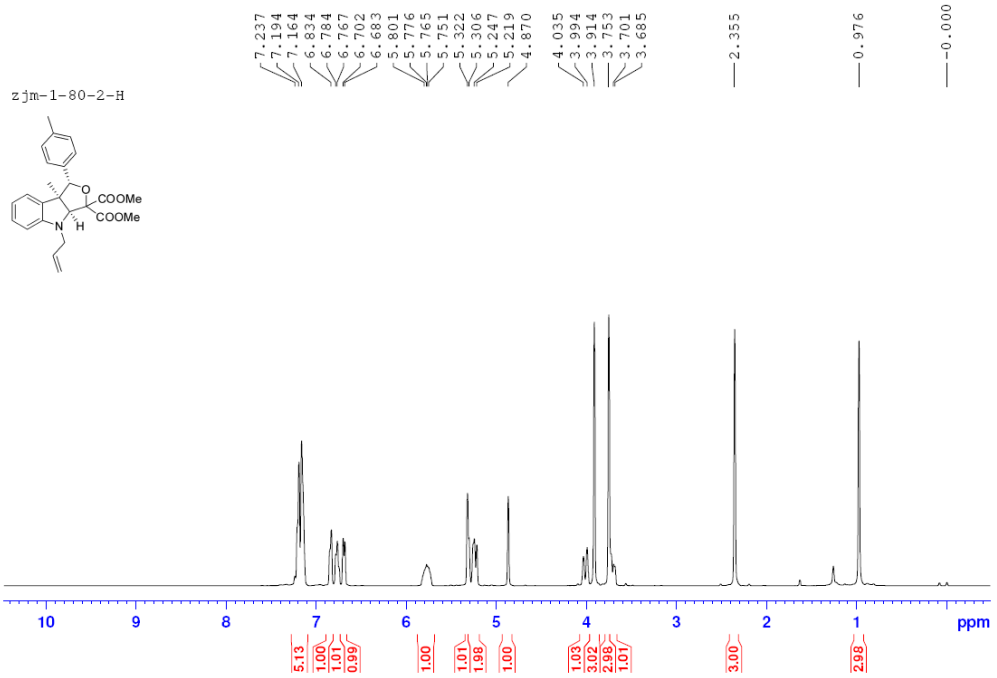

168.49
168.38
151.57
138.04
137.49
133.42
133.16
128.62
128.49
128.35
127.30
126.89
126.47
122.82
119.14
110.40
90.29
90.10
84.53
77.32
77.00
76.68
56.64
55.04
53.32
52.66
21.21
20.32
zjm-1-83-2-C
COOMe
COOMe
N
H
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

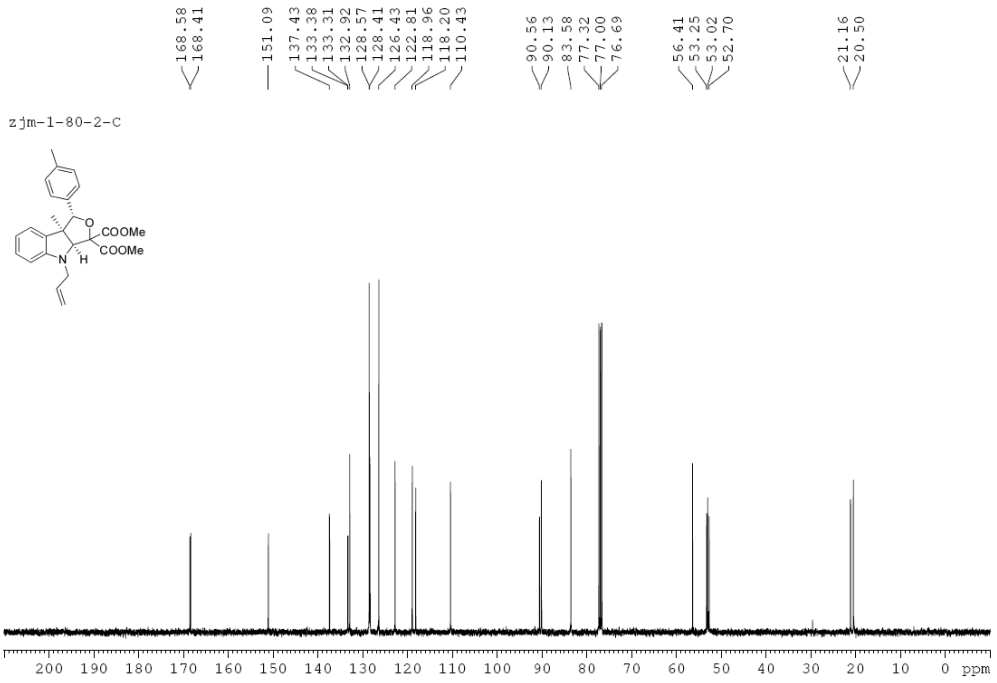
3m


zjm-1-83-2-NOESY
ppm
0
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
0
ppm

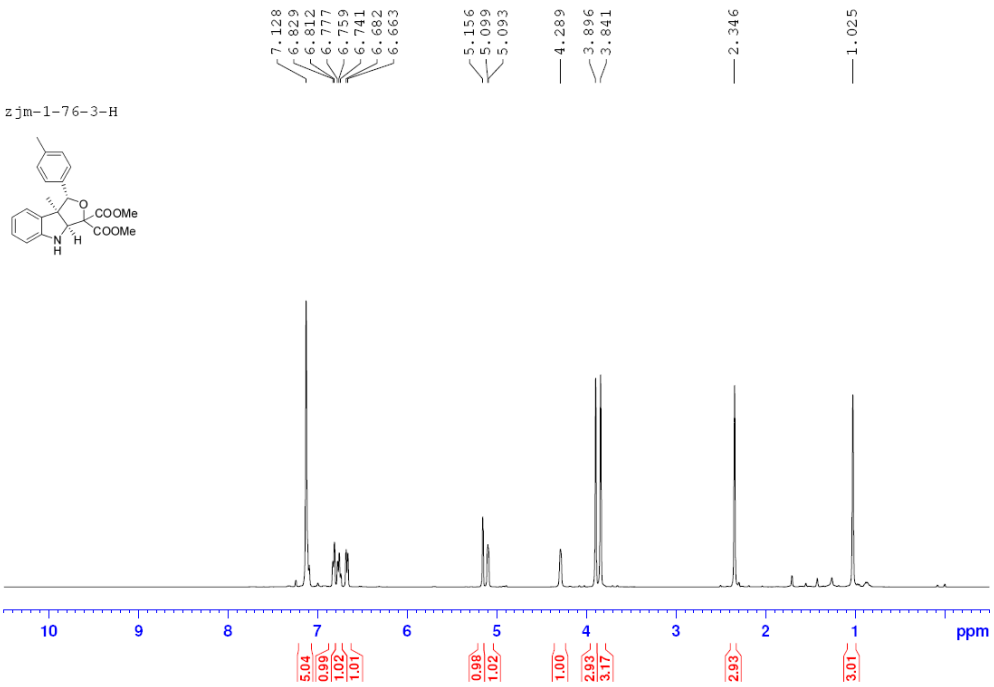

zjm-1-83-2-HSQCGP
ppm
0
20
40
60
80
100
120
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

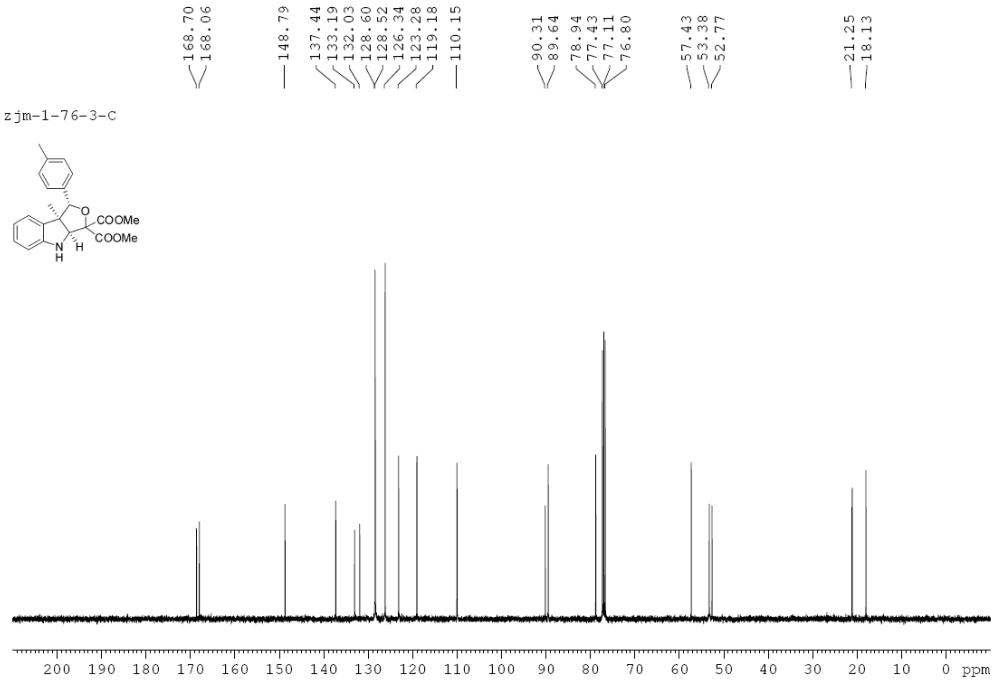
3m


zjm-1-80-2-H
7.237
7.194
7.164
6.834
6.784
6.767
6.702
6.683
5.801
5.776
5.765
5.751
5.322
5.306
5.247
5.219
4.870
4.035
3.994
3.914
3.753
3.701
3.685
2.355
0.976
-0.000
COOMe
COOMe
10
9
8
7
6
5
4
3
2
1
ppm
5.13
1.00
1.01
0.99
1.00
1.01
1.98
1.00
1.03
3.02
2.98
1.01
3.00
2.98

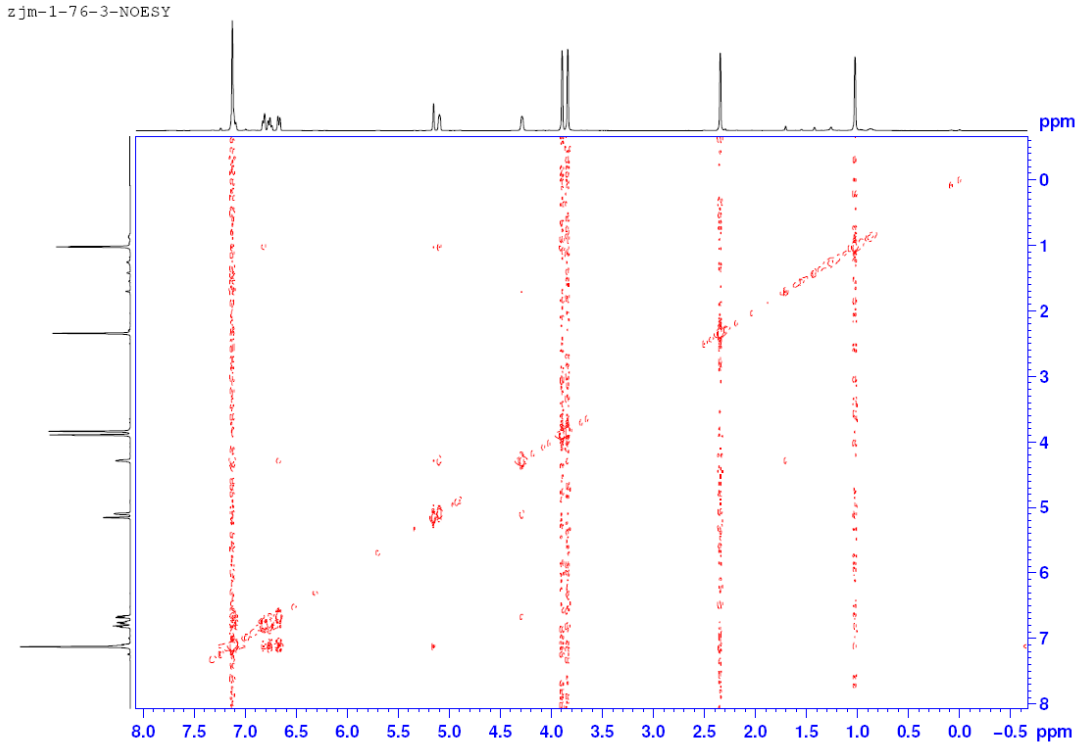

zjm-1-80-2-C
168.58
168.41
151.09
137.43
133.38
133.31
132.92
128.57
128.41
126.43
122.81
118.96
118.20
110.43
90.56
90.13
83.58
77.32
77.00
76.69
56.41
53.25
53.02
52.70
21.16
20.50
COOMe
COOMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

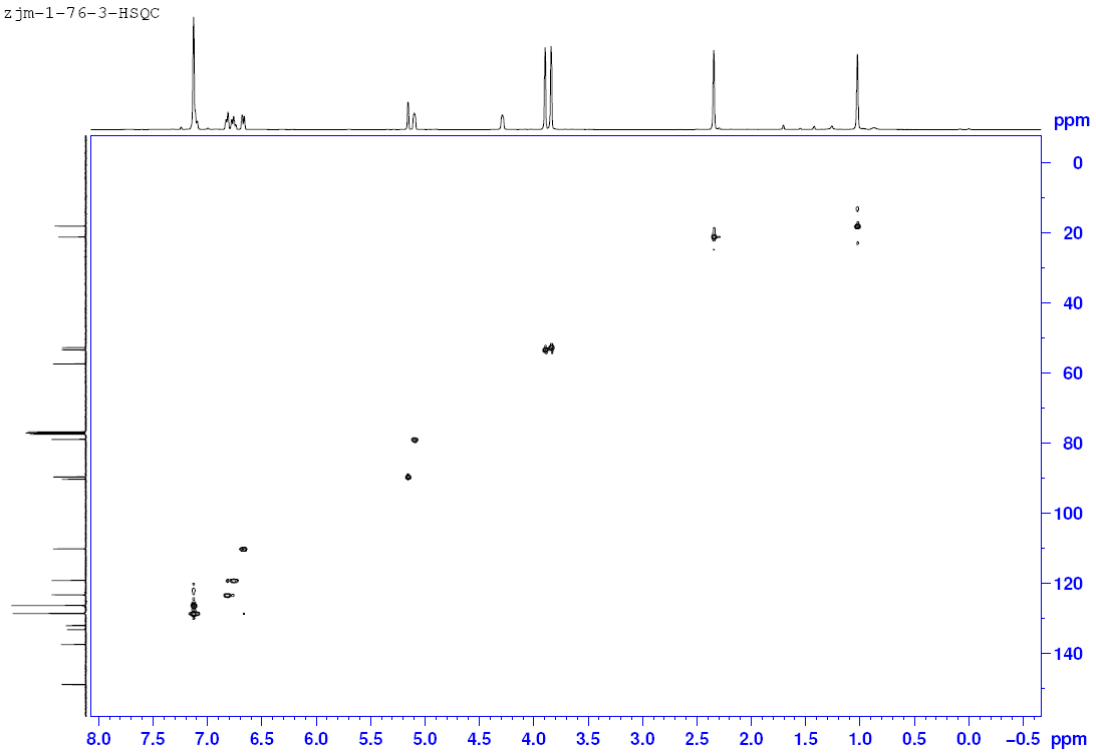
3n

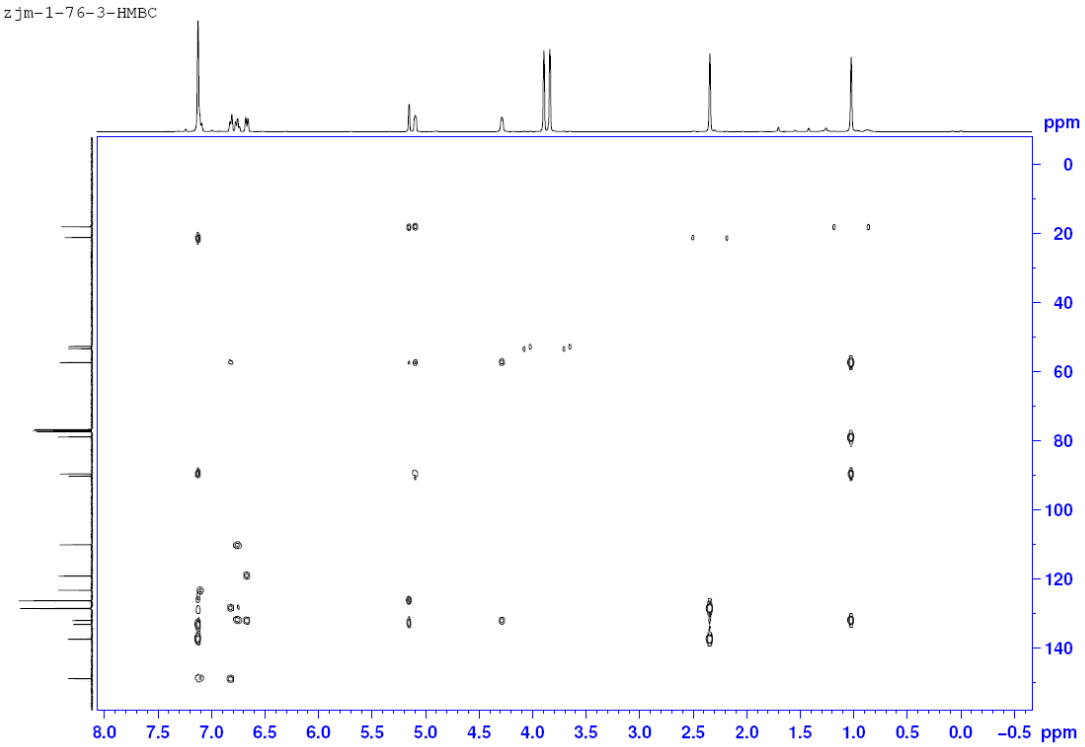

7.128
6.829
6.812
6.777
6.759
6.741
6.682
6.663
5.156
5.099
5.093
4.289
3.896
3.841
2.346
1.025
zjm-1-76-3-H
COOMe
COOMe
10
9
8
7
6
5
4
3
2
1
ppm
5.04
0.99
1.02
1.01
0.98
1.02
1.00
2.03
3.17
2.93
3.01


168.70
168.06
148.79
137.44
133.19
132.03
128.60
128.52
126.34
123.28
119.18
110.15
90.31
89.64
78.94
77.43
77.11
76.80
57.43
53.38
52.77
21.25
18.13
zjm-1-76-3-C
COOMe
COOMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

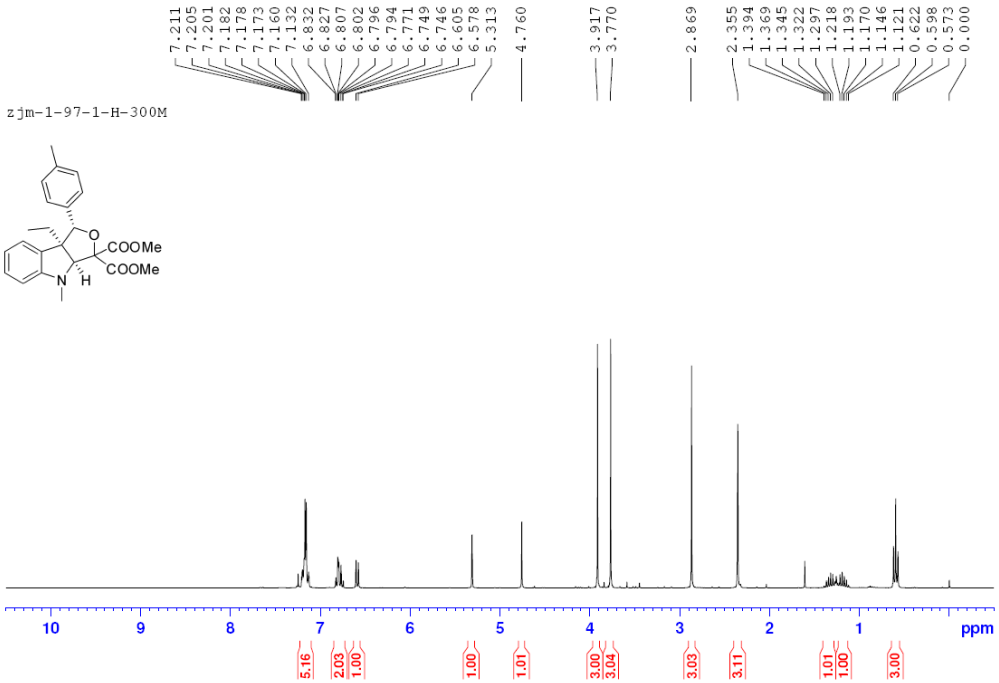
3o

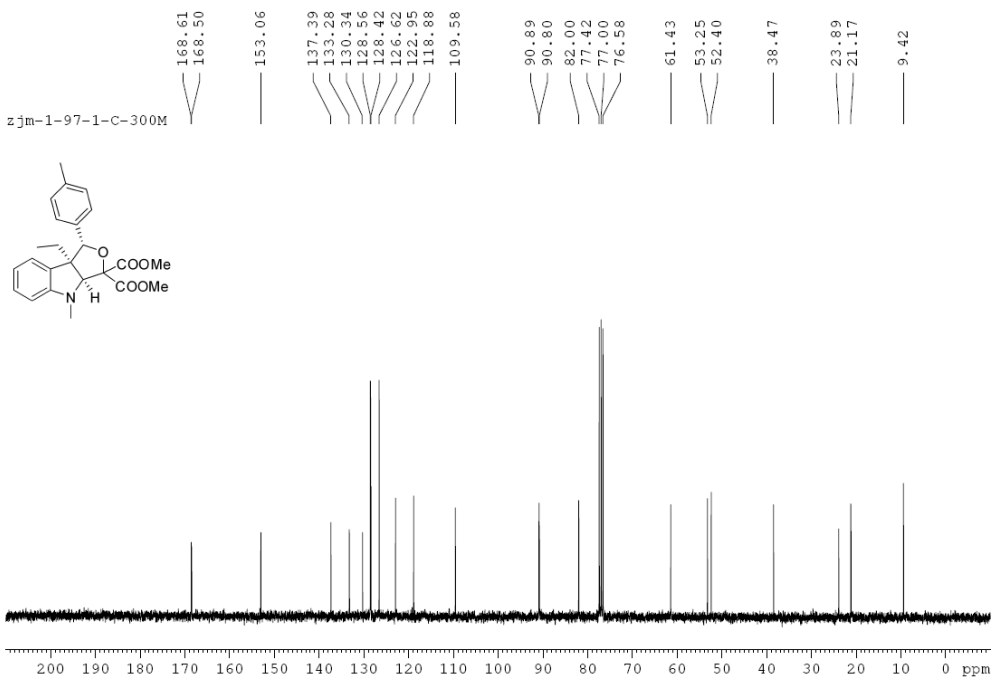




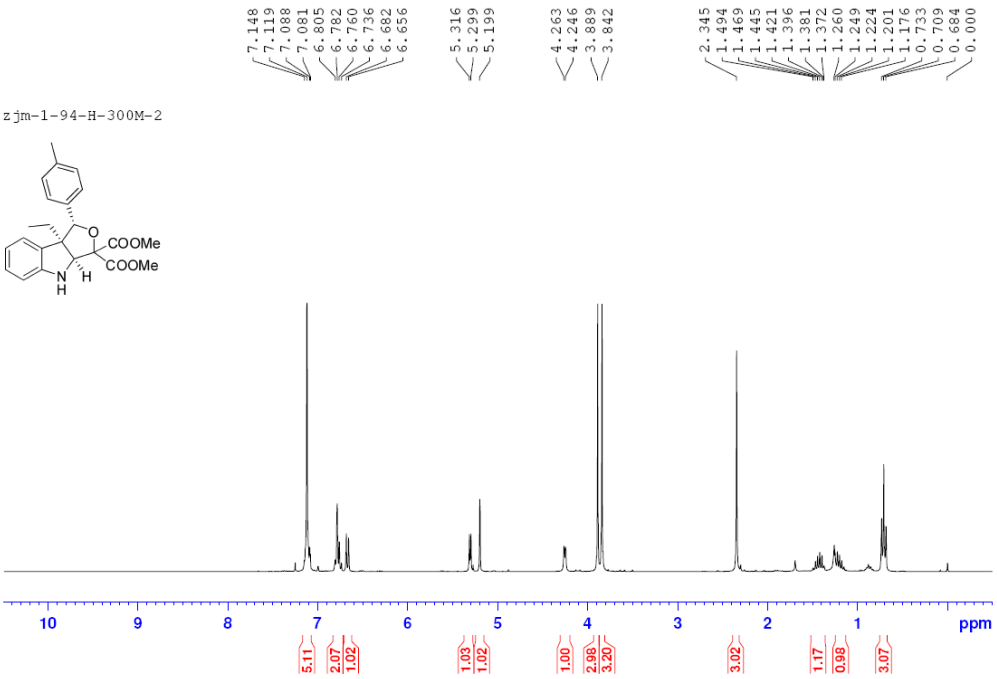

zjm-1-76-3-HMBC
ppm
0
20
40
60
80
100
120
140
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm

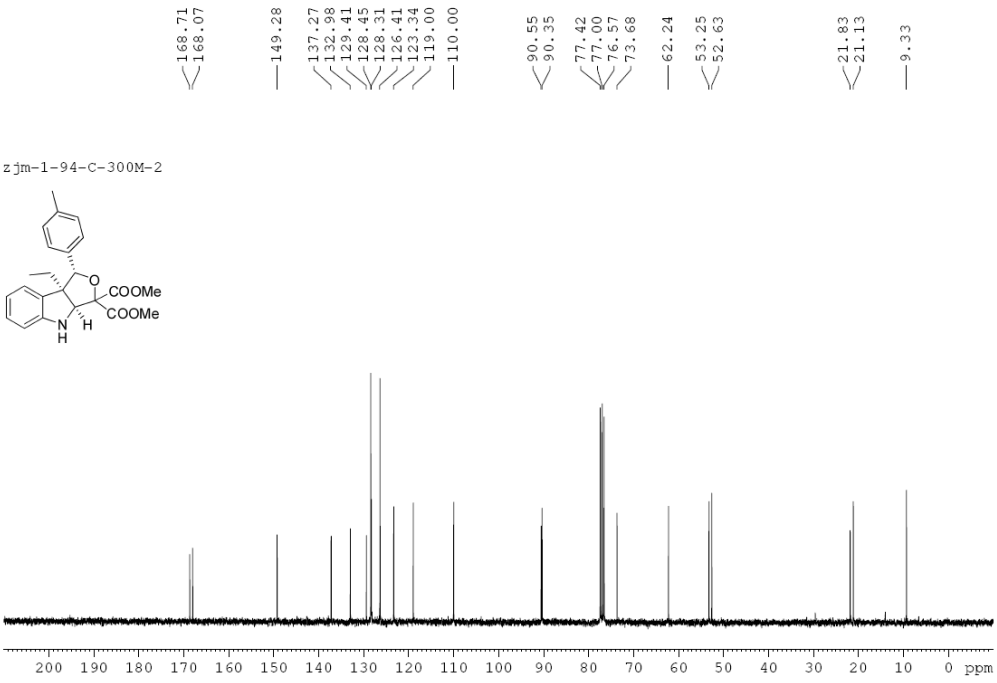
3o


7.211
7.205
7.201
7.182
7.178
7.173
7.160
7.132
6.832
6.827
6.807
6.802
6.796
6.794
6.771
6.749
6.746
6.605
6.578
5.313
4.760
3.917
3.770
2.869
2.355
1.394
1.369
1.345
1.322
1.297
1.218
1.193
1.170
1.146
1.121
0.622
0.598
0.573
0.000
zjm-1-97-1-H-300M
COOMe
COOMe
O
N
H
10
9
8
7
6
5
4
3
2
1
ppm
5.16
2.03
1.00
1.00
1.01
3.00
3.04
3.03
3.11
1.01
1.00
3.00

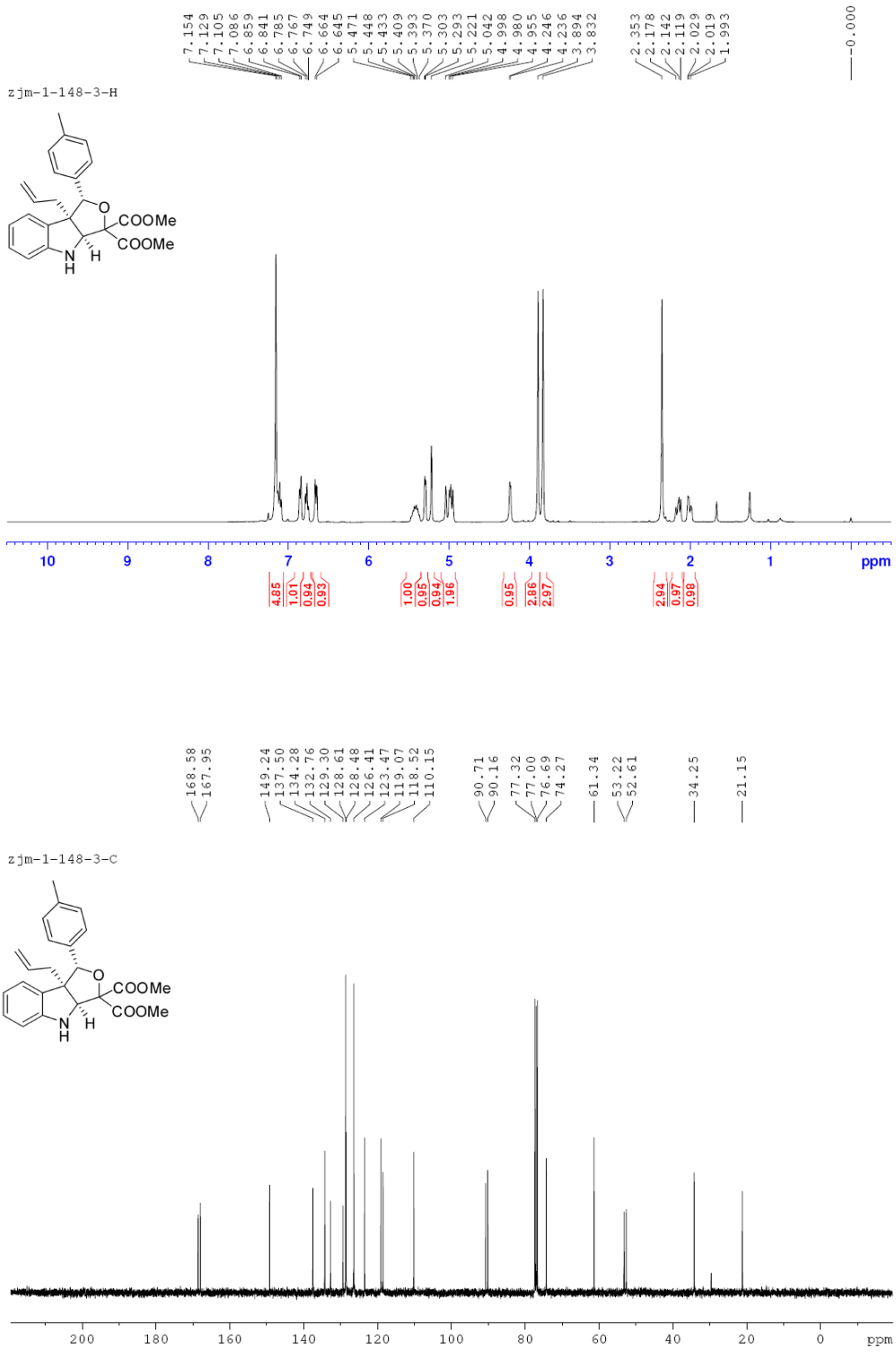

168.61
168.50
153.06
137.39
133.28
130.34
128.56
128.42
126.62
122.95
118.88
109.58
90.89
90.80
82.00
77.42
77.00
76.58
61.43
53.25
52.40
38.47
23.89
21.17
9.42
zjm-1-97-1-C-300M
COOMe
COOMe
O
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3p

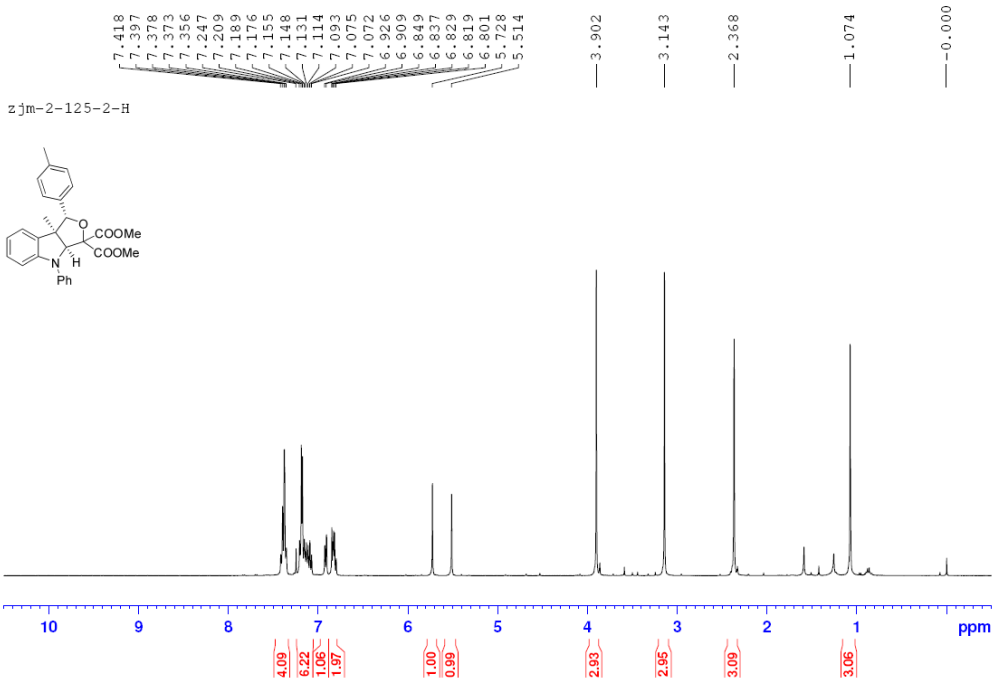

7.148
7.119
7.088
7.081
6.805
6.782
6.760
6.736
6.682
6.656
5.316
5.299
5.199
4.263
4.246
3.889
3.842
2.345
1.494
1.469
1.445
1.421
1.396
1.381
1.372
1.260
1.249
1.224
1.201
1.176
0.733
0.709
0.684
0.000
zjm-1-94-H-300M-2
COOMe
COOMe
N
H
H
10
9
8
7
6
5
4
3
2
1
ppm
5.11
2.07
1.02
1.03
1.02
1.00
2.98
3.20
3.02
1.17
0.98
3.07

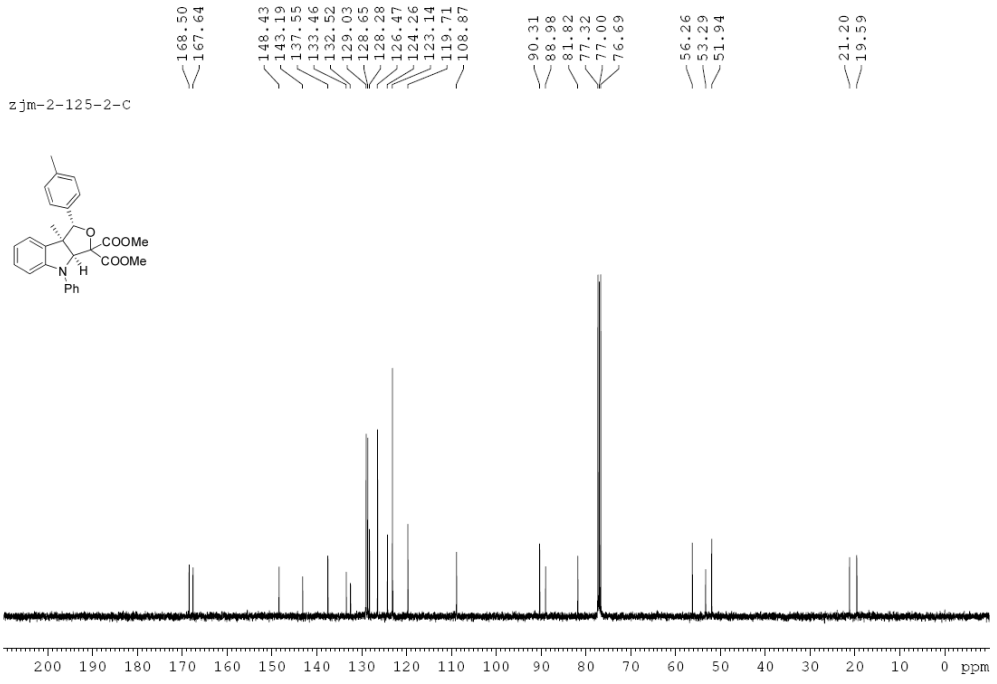

168.71
168.07
149.28
137.27
132.98
129.41
128.45
128.31
126.41
123.34
119.00
110.00
90.55
90.35
77.42
77.00
76.57
73.68
62.24
53.25
52.63
21.83
21.13
9.33
zjm-1-94-C-300M-2
COOMe
COOMe
N
H
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3q

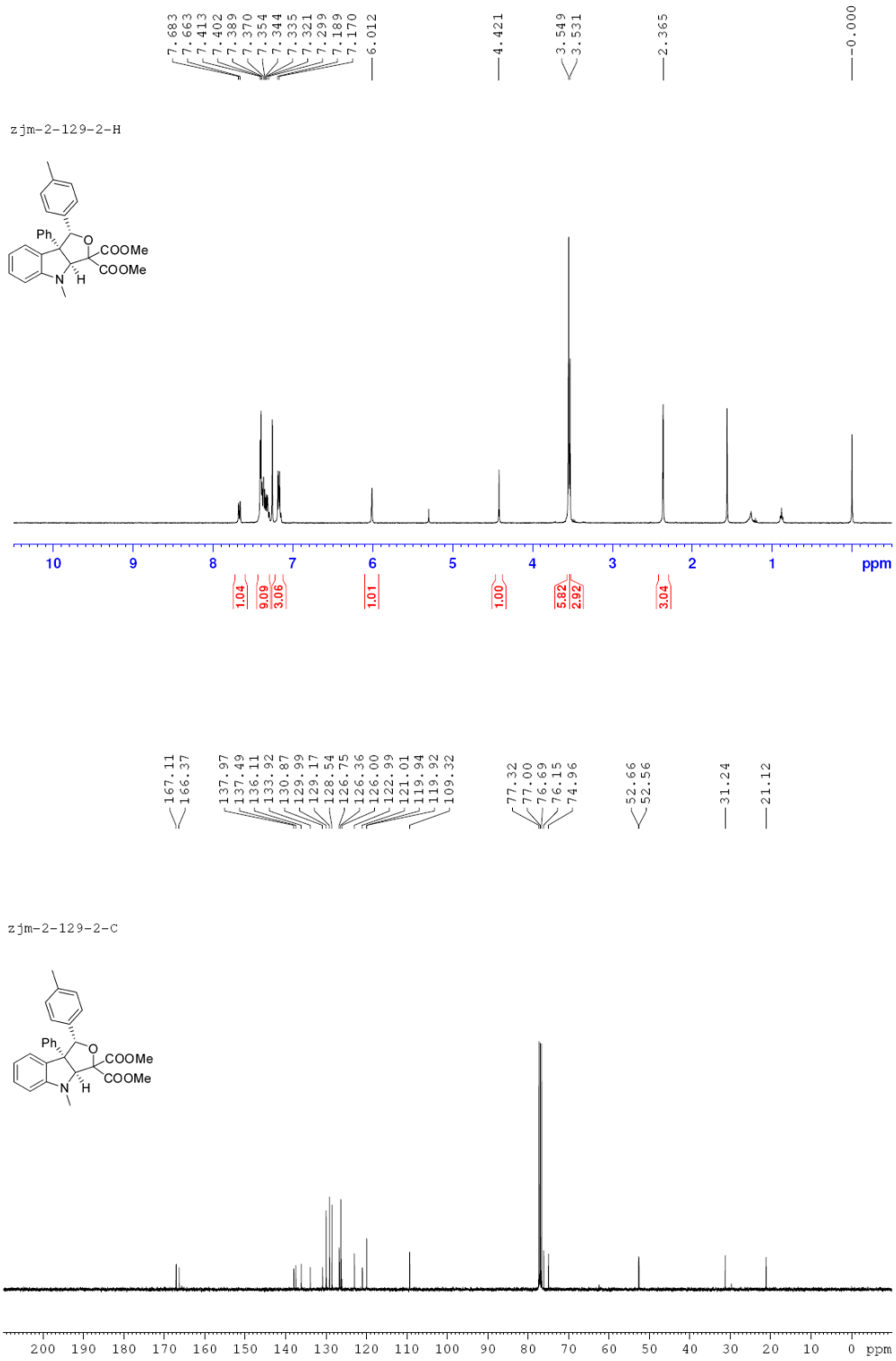

7.154
7.129
7.105
7.086
6.859
6.841
6.785
6.767
6.749
6.664
6.645
5.471
5.448
5.433
5.409
5.393
5.370
5.303
5.293
5.221
5.042
4.998
4.980
4.955
4.246
4.236
3.894
3.832
2.353
2.178
2.142
2.119
2.029
2.019
1.993
0.000
zjm-1-148-3-H
COOMe
COOMe
N H
O
10
9
8
7
6
5
4
3
2
1
ppm
4.85
1.01
0.84
0.93
1.00
0.95
0.94
1.96
0.95
2.66
2.97
2.94
0.97
0.98
168.58
167.95
149.24
137.50
134.28
132.76
129.30
128.61
128.48
126.41
123.47
119.07
118.52
110.15
90.71
90.16
77.32
77.00
76.69
74.27
61.34
53.22
52.61
34.25
21.15
zjm-1-148-3-C
COOMe
COOMe
N H
O
200
180
160
140
120
100
80
60
40
20
0
ppm

3r

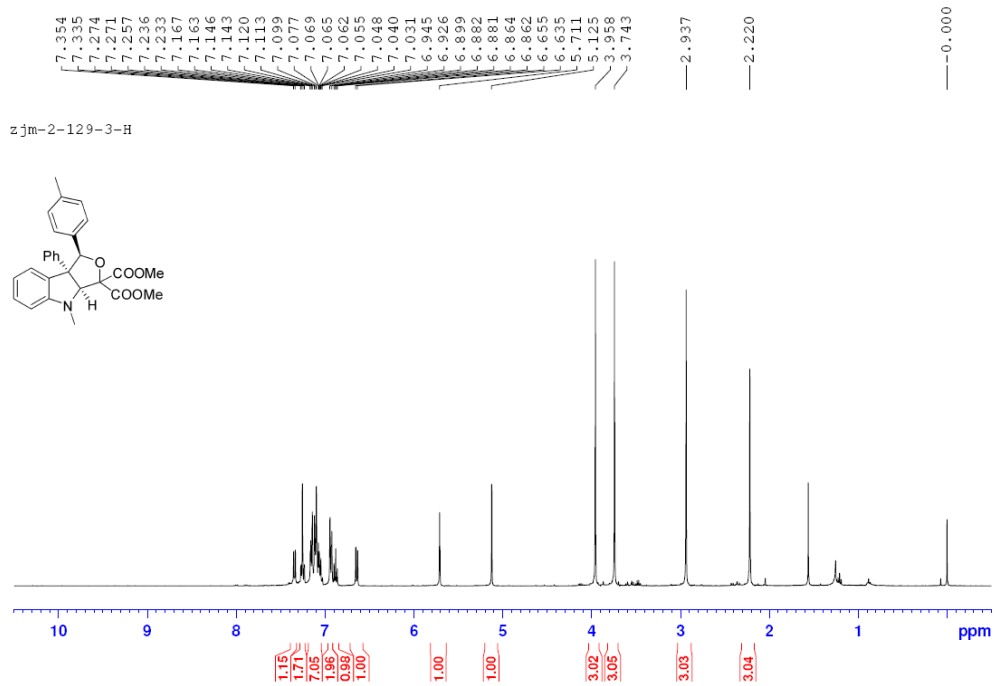

7.418
7.397
7.378
7.373
7.356
7.247
7.209
7.189
7.176
7.155
7.148
7.131
7.114
7.093
7.075
7.072
6.926
6.909
6.849
6.837
6.829
6.819
6.801
5.728
5.514
3.902
3.143
2.368
1.074
0.000
zjm-2-125-2-H
COOMe
COOMe
N H
Ph
10
9
8
7
6
5
4
3
2
1
ppm
4.09
6.22
1.06
1.97
1.00
0.99
2.93
2.95
3.09
3.06

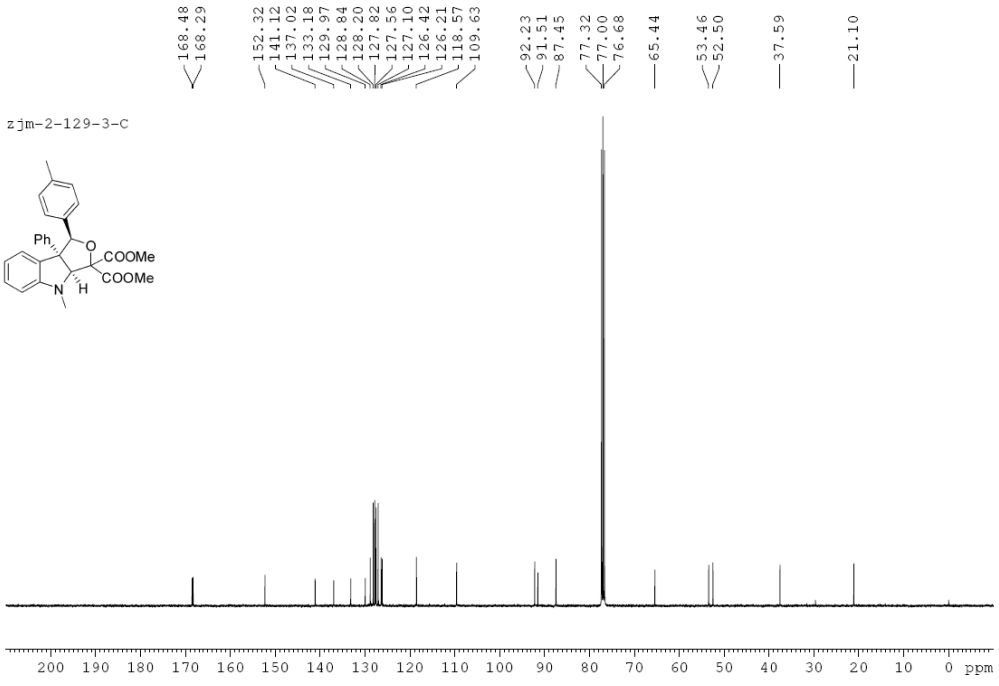

168.50
167.64
148.43
143.19
137.55
133.46
132.52
129.03
128.65
128.28
126.47
124.26
123.14
119.71
108.87
90.31
88.98
81.82
77.32
77.00
76.69
56.26
53.29
51.94
21.20
19.59
zjm-2-125-2-C
COOMe
COOMe
N H
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

3s

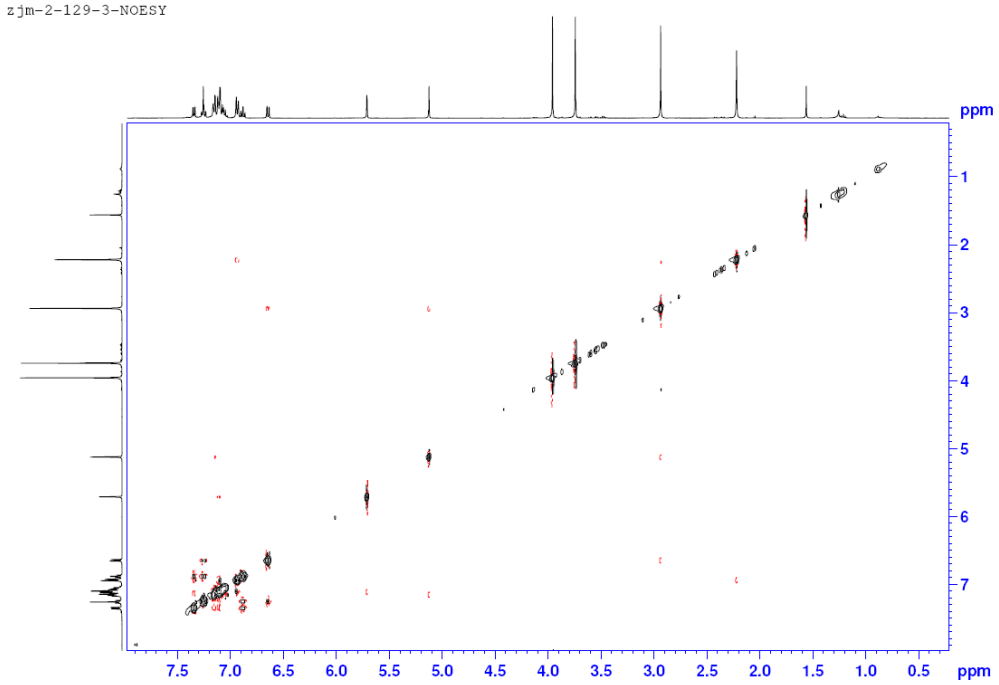

7.683
7.663
7.413
7.402
7.389
7.370
7.354
7.344
7.335
7.321
7.299
7.189
7.170
6.012
4.421
3.549
3.531
2.365
0.000
zjm-2-129-2-H
Ph
O
COOMe
COOMe
N
H
10
9
8
7
6
5
4
3
2
1
ppm
1.04
9.09
3.06
1.01
1.00
5.82
2.92
3.04
167.11
166.37
137.97
137.49
136.11
133.92
130.87
129.99
129.17
128.54
126.75
126.36
126.00
122.99
121.01
119.94
119.92
109.32
77.32
77.00
76.69
76.15
74.96
52.66
52.56
31.24
21.12
zjm-2-129-2-C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

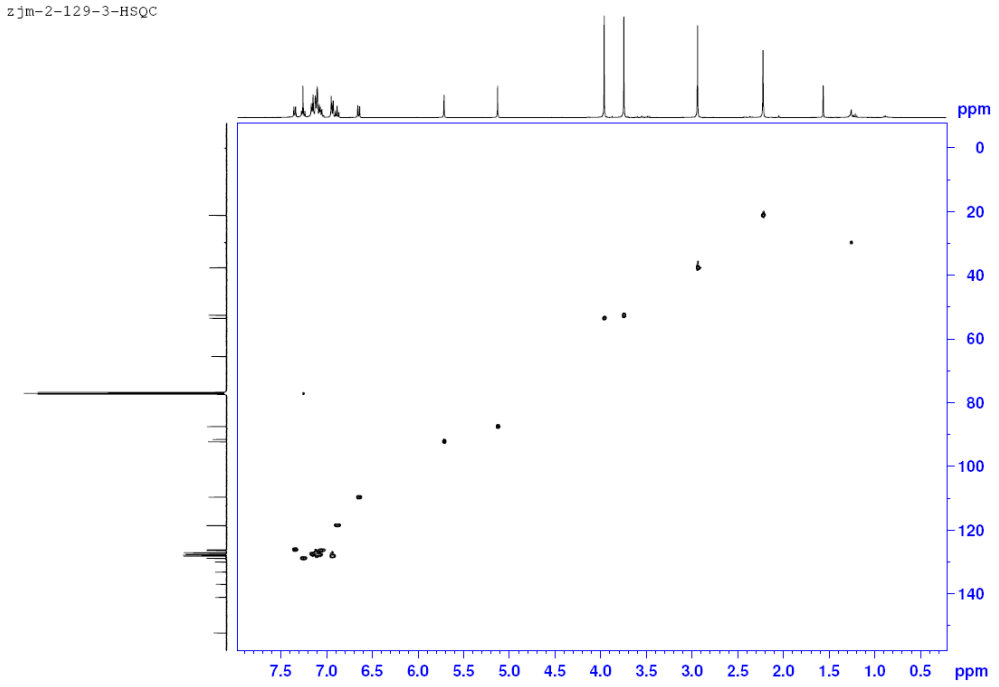
3t


7.354
7.335
7.274
7.271
7.257
7.236
7.233
7.167
7.163
7.146
7.143
7.120
7.113
7.099
7.077
7.069
7.065
7.062
7.055
7.048
7.040
7.031
6.945
6.926
6.899
6.882
6.881
6.864
6.862
6.655
6.635
5.711
5.125
3.958
3.743
2.937
2.220
0.000
zjm-2-129-3-H
Ph
O
COOMe
COOMe
N
H
10
9
8
7
6
5
4
3
2
1
ppm
1.15
1.71
7.05
1.96
0.98
1.00
1.00
1.00
3.02
3.05
3.03
3.04

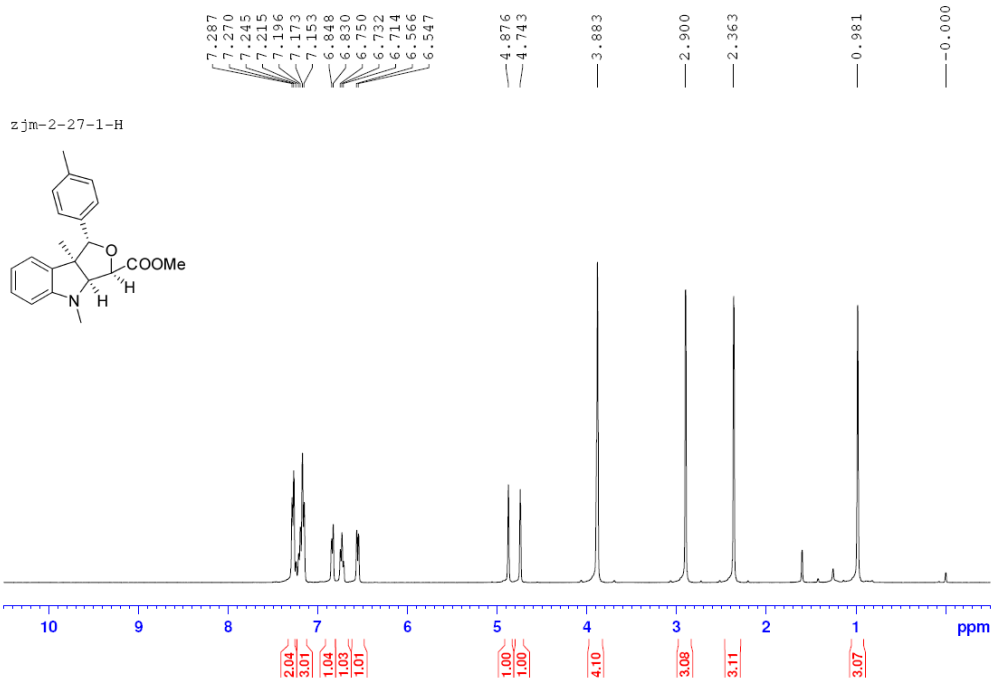

168.48
168.29
152.32
141.12
137.02
133.18
129.97
128.84
128.20
127.82
127.56
127.10
126.42
126.21
118.57
109.63
92.23
91.51
87.45
77.32
77.00
76.68
65.44
53.46
52.50
37.59
21.10
zjm-2-129-3-C
Ph
O
COOMe
COOMe
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

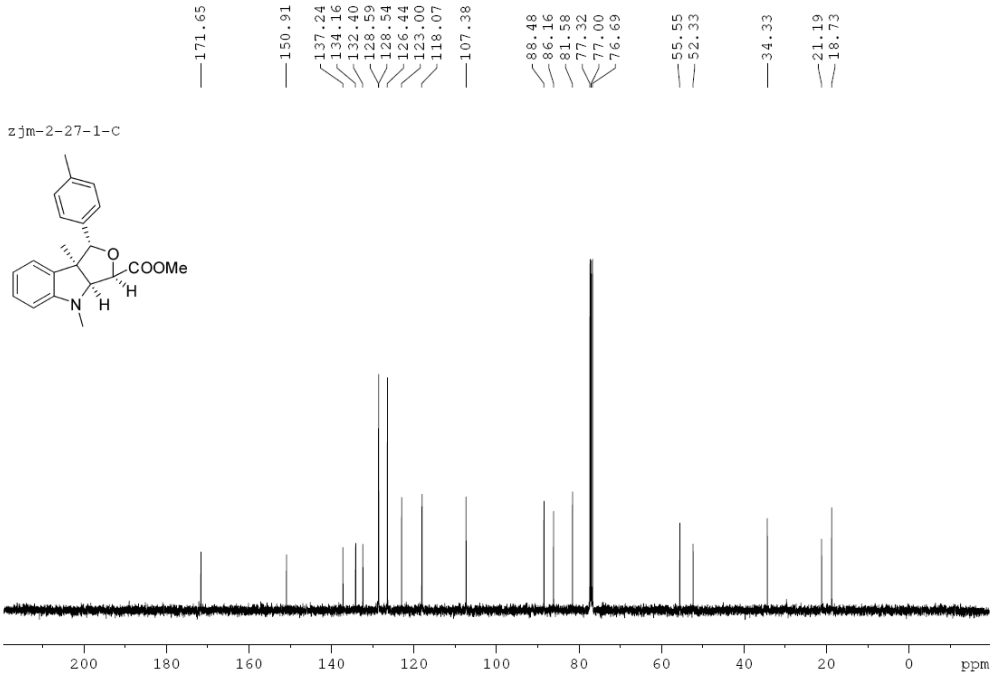
3t'


zjm-2-129-3-NOESY
ppm
1
2
3
4
5
6
7
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

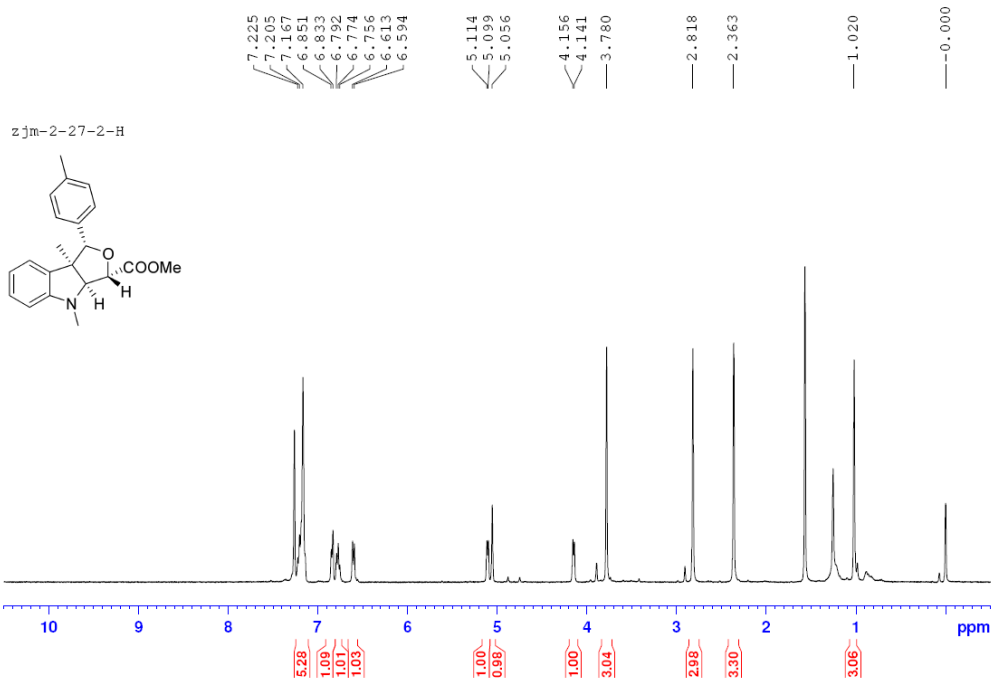

zjm-2-129-3-HSQC
ppm
0
20
40
60
80
100
120
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

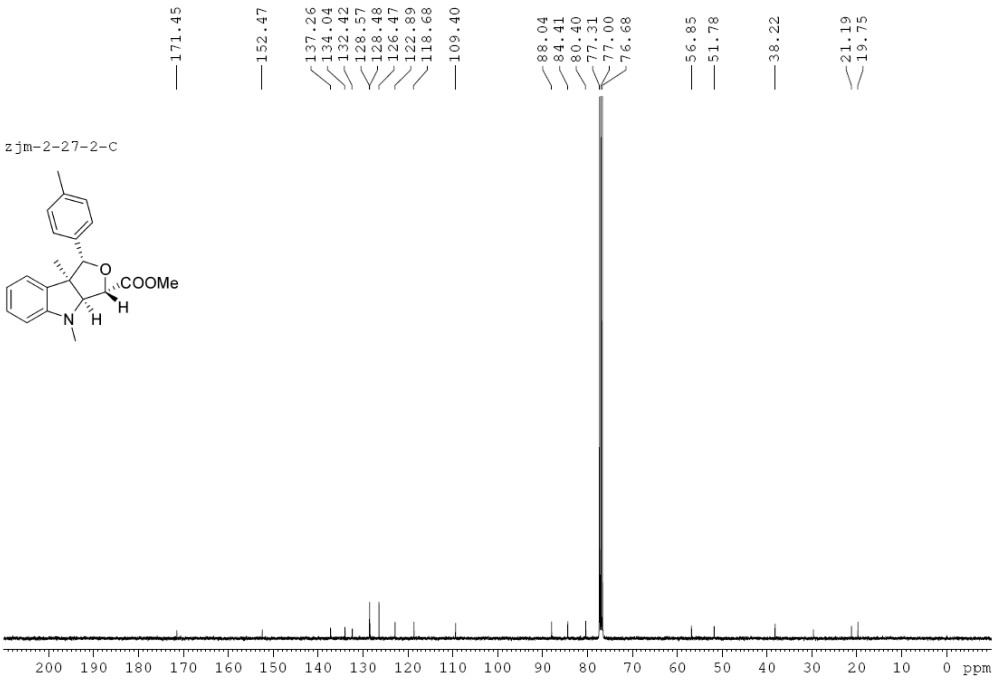
3t'


7.287
7.270
7.245
7.215
7.196
7.173
7.153
6.848
6.830
6.750
6.732
6.714
6.566
6.547
4.876
4.743
3.883
2.900
2.363
0.981
0.000
zjm-2-27-1-H
COOMe
H
N
H
10
9
8
7
6
5
4
3
2
1
ppm
2.04
3.01
1.04
1.03
1.01
1.00
1.00
4.10
3.08
3.11
3.07


171.65
150.91
137.24
134.16
132.40
128.59
128.54
126.44
123.00
118.07
107.38
88.48
86.16
81.58
77.32
77.00
76.69
55.55
52.33
34.33
21.19
18.73
zjm-2-27-1-C
COOMe
H
N
H
200
180
160
140
120
100
80
60
40
20
0
ppm

5a


7.225
7.205
7.167
6.851
6.833
6.792
6.774
6.756
6.613
6.594
5.114
5.099
5.056
4.156
4.141
3.780
2.818
2.363
1.020
0.000
zjm-2-27-2-H
COOMe
H
N
H
10
9
8
7
6
5
4
3
2
1
ppm
5.28
1.09
1.01
1.03
1.00
0.98
1.00
3.04
2.98
3.30
3.06


171.45
152.47
137.26
134.04
132.42
128.57
128.48
126.47
122.89
118.68
109.40
88.04
84.41
80.40
77.31
77.00
76.68
56.85
51.78
38.22
21.19
19.75
zjm-2-27-2-C
COOMe
H
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

5a'