Supporting information

Organocatalytic Diastereoselective Synthesis of Spirooxindols via [3+2] Cycloadditions of Azomethine Ylides with α,β-Unsaturated Esters

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General information

Microwave reactions were performed in a Microwave Synthesis Reactor Monowave 300 instrument (Anton Paar, IR sensor for temperature control, sealed vessel). The vibrational ball mill MM400 (Retsch, 20Hz) was used for solvent-free reactions. Flash chromatography was performed on silica gel 60A, 0.035–0.070 nm, from Fluka. Thin-layer chromatography was performed on Merck TLC plates silica gel 60, F-254.NMR spectra were recorded on a Varian NMR SystemTM 300(300 MHz for ^{1}H, 75MHz for ^{13}C). Chemical shifts (δ) are given in ppm relative to tetramethylsilane. 2D NMR experiments:^{1}H-^{1}H NOESY and TOCSY were recorded on a Varian NMR System 600 (600 MHz for ^{1}H). IR spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer. Enantiomer purity was determined by HPLC on a Chiralcel OD-H (Daicel Chemical Industries) column using hexane–*i*PrOH as a mobile phase and with UV detection. HRMS were measured on a Thermo Velos Pro Orbitrap instrument by electrospray ionisation (ESI). All the melting points were determined on a Kofler apparatus.

Starting materials as well as organocatalysts, which were not commercially available, were synthesized according to the literature procedures: 1-methylindoline-2,3-dione (**1b**),[1]1-benzylindoline-2,3-dione (**1c**),[2] 5-bromoindoline-2,3-dione (**1d**),[3] 5-bromo-1-methylindoline-2,3-dione (**1e**),[1,3] methyl cinnamate (**3a**),[4] *tert*-butyl cinnamate (**3b**),[5] dimethyl 2-benzylidenemalonate (**7a**), [6] dimethyl 2-(4-

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isopropylbenzylidene)malonate (**7b**)[6], 2-benzylidenemalononitrile (**11**)[7], catalyst **C1**,[8] catalyst **C2**,[9] catalyst **C3**,[10] catalyst **C4**,[11] catalyst **C5**,[12] catalyst **C6**,[13] catalyst **C7**,[13] catalyst **C8**,catalyst **C9**,[14] catalyst **C10**,[14] catalyst **C11**,[15] catalyst **C12**.[16]

Typical procedure for [3+2] cycloadditions of azomethine ylides with α,β-unsaturated esters

Isatin (0.310 mmol), ester/diester (0.465 mmol), $MgSO_4$ (120 mg) and catalyst (0.031 mmol) were dissolved in dry DCM (2 ml) and benzylamine (35 µl, 0.31 mmol) was then added. The reaction mixture was refluxed for 24 h. $MgSO_4$ was filtered out and solvent was evaporated under vacuum. The crude reaction mixture was separated by column chromatography on SiO_2 (hexanes/ethyl acetate 3:1, or 1:1 for **4a**, **4d** and **4k**). The products were obtained as white or pale yellow solids.

Characterization data for compounds 4

Methyl (3*R,3'*S**,4'*R**,5'*S**)-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4a)**

(52 mg, 30%, white solid)

m.p. 178−180 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (dd, *J* = 6.1, 2.6 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.28 (m, 1H), 7.20 (t, *J* = 6.2 Hz, 2H), 7.17–6.98 (m, 5H), 6.94 (s, 1H), 6.60 (dd, *J* = 7.0, 1.6 Hz, 1H), 5.60 (d, *J* = 10.6 Hz, 1H), 4.69–4.58 (m, 1H), 4.24 (d, *J* = 11.8 Hz, 1H), 3.08 (s, 3H), 2.59 (s, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.7, 171.7, 141.7, 140.6, 134.5, 129.8, 129.2, 128.1, 128.0, 127.9, 127.9, 127.7, 127.5, 124.2, 123.0, 109.5, 77.8, 60.9, 55.3, 51.5, 51.3 ppm.

IR: ν 3349, 3177, 3031, 2252, 1736, 1693, 1619, 1471, 1434, 1171, 909, 726, 699 cm^{-1}.

HRMS (ESI): calcd. for $C_{25}H_{22}N_2O_3$ $[M+H]^+$= 399.1703, found 399.1705.

Methyl (3*R,3'*S**,4'*R**,5'*S**)-1-methyl-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4b)**

(90 mg, 50 %, white solid)

m.p. 132−134 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 3H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.07 (m, 3H), 6.96 (m, 2H), 6.56 (d, *J* = 7.5 Hz, 1H), 5.63 (d, *J* = 10.6 Hz, 1H), 4.65 (t, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 11.8 Hz, 1H), 3.08 (s, 3H), 2.81 (s, 3H), 2.54 (s, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.0, 171.8, 143.6, 141.9, 134.4, 129.3, 129.2, 127.9, 127.9, 127.9, 177.8, 177.6, 127.4, 123.6, 122.9, 107.8, 72.9, 61.0, 55.5, 51.5, 51.3, 25.5 ppm.

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IR: ν 3335, 3057, 2984, 1733, 1704, 1613, 1470, 1342, 1254, 1088, 745, 696, 627cm^{-1}.
HRMS (ESI): calcd. for $C_{26}H_{24}N_2O_3$ $[M+H]^+$= 413.1860, found 413.1857.
HPLC: Chiralcel OD-H, *i*PrOH/hexane 10:90, 1.0 ml/min, λ = 254nm, t_R = 7.22 min, 8.17 min.

Methyl (3*R,3'*S**,4'*R**,5'*S**)-1-benzyl-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4c), mixture of diastereomers.**
(134 mg, 75 %, white solid)
m.p. 164–166 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 4.8 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 2H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.21 (m, 29H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 7.0 Hz, 2H), 6.35 (d, *J* = 8.5 Hz, 1H), 5.66 (d, *J* = 10.6 Hz, 1H), 5.28 (d, *J* = 6.2 Hz, 1H), 5.21 (s, 1H), 5.03 (m, 2H), 4.73 (m, 2H), 4.35 (d, *J* = 11.7 Hz, 1H), 4.22 (d, *J* = 16.0 Hz, 1H), 3.99 (d, *J* = 11.5 Hz, 1H), 3.89 (d, *J* = 10.2 Hz, 1H), 3.09 (s, 3H), 2.96 (s, 3H), 2.59 (s, 2H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.4, 179.0, 171.9, 170.2, 143.1, 142.5, 141.8, 140.5, 138.2, 135.6, 134.0, 134.6, 130.6, 129.3, 129.3, 129.3, 128.7, 128.6, 128.5, 128.4, 128.4, 128.2, 128.2, 127.9, 127.9, 127.7, 127.7, 127.6, 127.6, 127.2, 127.1, 127.1, 127.0, 126.4, 124.8, 123.8, 123.0, 122.9, 109.2, 109.0, 72.7, 68.7, 67.9, 61.1, 60.9, 55.9, 55.0, 51.6, 51.38, 44.0, 43.4 ppm.
IR: ν 3330, 3028, 1704, 1612, 1488, 1465, 1453, 1434, 1351, 1167, 748, 729, 696 cm^{-1}.
HRMS (ESI): calcd. for $C_{32}H_{28}N_2O_3$ $[M+H]^+$= 489.2173, found 489.2176.

Methyl 5-bromo-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4d)
(50 mg, 24 %, white solid)
m.p. 228−230 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 3 Hz, 1H), 7.61 (d, *J* = 3 Hz, 1H), 7.58 (s, 1H), 7.4–7,28 (m, 5H), 7,15–7.13 (m, 2H), 7.06–7,02 (m, 2H), 6.78 (s, 1H), 6.49 (d, *J* = 6 Hz, 1H), 5.61 (d, *J* = 9 Hz, 1H), 4.59 (t, *J* = 12 Hz, 1H), 4.21 (d, *J* = 12 Hz, 1H), 3.08 (s, 3H), 2.58 (br s, 1H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.3, 171.5, 141.3, 139.7, 132.1, 131.7, 128.3, 128.2, 128.1, 127.9, 127.9, 127.8, 127.7, 127.7, 127.4, 115.6, 111.6, 111.2, 72.9, 62.9, 60.9, 55.5, 51.6, 51.5, 51.3 ppm.
IR: ν 3725, 3698, 3359, 3288, 2949, 1724, 1709, 1619, 1476, 1435, 1171, 807, 751, 699, 669 cm^{-1}.
HRMS (ESI): calcd. for $C_{25}H_{21}BrN_2O_3$ $[M+H]^+$= 477.0808, found 477.0808.

Methyl (3*R,3'*S**,4'*R**,5'*S**)-5-bromo-1-methyl-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4e)**
(111 mg, 52 %, white solid)
m.p. 162−164 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 2.0 Hz, 1H), 7.63–7.56 (m, 2H), 7.41–7.33 (m, 3H), 7.29 (m, 1H), 7.09 (m, 3H), 6.98 (m, 2H), 6.43 (d, *J* = 8.2 Hz, 1H), 5.63 (d, *J* = 10.6 Hz, 1H), 4.66–4.54 (m, 1H), 4.18 (d, *J* = 11.7 Hz, 1H), 3.08 (s, 3H), 2.78 (s, 3H), 2.53 (br s, 1H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.5, 171.5, 142.7, 141.5, 134.0, 132.1, 131.6, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 126.8, 115.6, 109.3, 72.9, 61.0, 55.7, 51.4, 42.0, 25.6 ppm.
IR: ν 3340, 2945, 1739, 1712, 1606, 1489, 1430, 1266, 1159, 1094, 1010, 748, 701 cm^{-1}.
HRMS (ESI): calcd. for $C_{26}H_{23}BrN_2O_3$ $[M+H]^+$= 491.0965, found 491.0964.

Methyl (3*R,3'*S**,4'*R**,5'*S**)-1-methyl-2-oxo-3'-phenyl-5'-(*p*-tolyl)spiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4f)**
(76 mg, 41 %, white solid)
m.p. 161–163 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.30–7.11 (m, 4H), 7.06 (d, *J* = 21.4 Hz, 3H), 6.96 (d, *J* = 9.5 Hz, 2H), 6.55 (d, *J* = 7.4 Hz, 1H), 5.59 (d, *J* = 10.6 Hz, 1H), 4.69–4.58 (m, 1H), 4.20 (d, *J* = 11.9 Hz, 1H), 3.11 (s, 3H), 2.80 (s, 3H), 2.51 (s, 1H), 2.34 (s, 3H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.0, 171.9, 143.7, 138.87, 137.2, 134.6, 129.4, 129.2, 128.6, 127.9, 127.8, 127.8, 127.4, 123.6, 122.9, 107.8, 72.9, 60.9, 55.5, 51.5, 51.3, 25.5, 21.2 ppm.
IR: ν 3333, 2952, 1730, 1704, 1613, 1470, 1379, 1348, 1260, 1175, 1112, 754, 745, 699, 608 cm^{-1}.
HRMS (ESI): calcd. for $C_{27}H_{26}N_2O_3$ $[M+H]^+$= 427.2016, found 427.2015.

Methyl (3*R,3'*S**,4'*R**,5'*S**)-1-methyl-2-oxo-3'-phenyl-5'-(*o*-tolyl)spiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4g)**
(85 mg, 46 %, white solid)
m.p. 186−188 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 7.1 Hz, 1H), 7.33–6.94 (m, 10H), 6.57 (d, *J* = 7.9 Hz, 1H), 5.98 (d, *J* = 10.5 Hz, 1H), 4.54 (t, *J* = 10.8 Hz, 1H), 4.28 (d, *J* = 11.1 Hz, 1H), 3.03 (s, 3H), 2.82 (s, 3H), 2.50 (s, 3H), 2.40 (s, 1H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.0, 172.1, 143.7, 139.5, 136.2, 134.7, 129.7, 129.3, 129.2, 128.0, 127.9, 127.5, 127.4, 127.1, 125.7, 123.7, 122.9, 107.8, 72.8, 56.7, 56.0, 51.1, 50.9, 25.4, 19.6 ppm.
IR: ν 3332, 3029, 2946, 1730, 1702, 1612, 1491, 1465, 1254, 1168, 1087, 1004, 843, 756, 747, 698, 630 cm^{-1}.
HRMS (ESI): calcd. for $C_{27}H_{26}N_2O_3$ $[M+H]^+$= 427.2016, found 427.2016.

Methyl (3*R,3'*S**,4'*R**,5'*S**)-5'-(4-methoxyphenyl)-1-methyl-2-oxo-3'-phenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4h)**
(96 mg, 50 %, white solid)
m.p. 147−148 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 6.1 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.22 (m, 2H), 7.07 (m, 3H), 6.93 (m, 4H), 6.55 (d, *J* = 7.3 Hz, 1H), 5.59 (d, *J* = 10.5 Hz, 1H), 4.69–4.52 (m, 1H), 4.20 (d, *J* = 11.8 Hz, 1H), 3.81 (s, 3H), 3.13 (s, 3H), 2.80 (s, 3H), 2.51 (s, 1H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.0, 171.9, 159.0, 143.7, 134.6, 134.0, 129.4, 129.2, 129.0, 127.9, 127.8, 127.4, 123.5, 122.9, 107.8, 72.8, 60.5, 55.5, 55.3, 51.5, 51.3, 25.5 ppm.
IR: ν 3336, 1711, 1613, 1346, 1239, 1175, 1107, 1020, 845, 743, 696 cm^{-1}.
HRMS (ESI): calcd. for $C_{27}H_{26}N_2O_4$ $[M+H]^+$= 443.1965, found 443.1964.

Methyl (3*R,3'*S**,4'*R**,5'*S**)-5'-(4-fluorophenyl)-1-methyl-2-oxo-3'-phenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4i)**
(95 mg, 51%, white solid)
m.p. 202−203 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 6.0 Hz, 1H), 7.59 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.22 (m, 2H), 7.06 (m, 5H), 6.95 (m, 2H), 6.56 (d, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 7.3 Hz, 1H), 5.63 (d, *J* = 10.6 Hz, 1H), 4.67–4.55 (m, 1H), 4.19 (d, *J* = 11.8 Hz, 1H), 3.12 (s, 3H), 2.80 (s, 3H), 2.53 (s, 1H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = δ 178.9, 171.7, 143.6, 137.6, 134.3, 129.5, 129.4, 129.3, 129.1, 127.9, 127.8, 127.5, 123.5, 122.9, 114.8, 114.5, 107.9, 72.8, 60.2, 55.4, 51.3, 25.5 ppm.
^{19}F NMR (282 MHz, $CDCl_3$): δ = -115.11 (tt, *J* = 8.7, 5.5 Hz, 1F) ppm.
IR: ν3368, 3036, 2958, 1740, 1704, 1615, 1503, 1345, 1211, 1113, 1022, 844, 736, 696 cm^{-1}.
HRMS (ESI): calcd. for $C_{26}H_{23}FN_2O_3$ $[M+H]^+$= 431.1765, found 431.1766.

Methyl (3*R,3'*S**,4'*R**,5'*S**)-5'-(3-chlorophenyl)-1-methyl-2-oxo-3'-phenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4j)**

(85 mg, 44 %, white solid)

m.p. 175−176 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.3 Hz, 1H), 7.64 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.24 (m, 4H), 7.06 (m, 3H), 6.95 (m, 2H), 6.56 (d, *J* = 7.3 Hz, 1H), 5.60 (d, *J* = 10.6 Hz, 1H), 4.71–4.60 (m, 1H), 4.17 (d, *J* = 11.9 Hz, 1H), 3.16 (s, 3H), 2.80 (br s, 3H), 2.55 (s, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.9, 171.4, 144.2, 143.6, 134.1, 133.8, 129.3, 129.1, 129.1, 128.0, 127.9, 127.8, 127.7, 127.5, 126.1, 123.6, 123.0, 107.9, 72.8, 60.2, 55.3, 51.4, 51.3, 25.5 ppm.

IR: ν 3371, 3039, 2949, 1737, 1705, 1614, 1471, 1345, 1169, 1108, 1021, 785, 739, 746, 706, 697 cm^{-1}.

HRMS (ESI): calcd. for $C_{26}H_{23}ClN_2O_3$ $[M+H]^+$= 447.1470, found 447.1466.

***Tert*-butyl (3*R**,3'*S**,4'*R**,5'*S**)-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4k)**

(61 mg, 32 %, white solid)

m.p. 204−206 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.69 (m, 1H), 7.65–7.59 (m, 2H), 7.34 (m, 3H), 7.20 (m, 2H), 7.05 (m, 6H), 6.64–6.53 (m, 1H), 5.52 (d, *J* = 10.6 Hz, 1H), 4.61–4.46 (m, 1H), 4.20 (d, *J* = 11.9 Hz, 1H), 2.58 (s, 1H), 0.92 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.8, 170.2, 142.3, 140.7, 134.9, 130.0, 129.1, 128.6, 128.0, 128.0, 127.8, 127.6, 127.3, 124.1, 122.9, 109.5, 80.5, 72.6, 60.9, 55.8, 51.8, 27.6 ppm.

IR: ν 3327, 3059, 3029, 2972, 1727, 1697, 1618, 1488, 1470, 1247, 1151, 745, 697 cm^{-1}.

HRMS (ESI): calcd. for $C_{28}H_{28}N_2O_3$ $[M+H]^+$= 441.2173, found 441.2172.

***Tert*-butyl (3*R**,3'*S**,4'*R**,5'*S**)-1-methyl-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4l)**

(101 mg, 51 %, white solid)

m.p. 202−204 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.1 Hz, 2H), 7.34 (m, 3H), 7.19 (dm, 2H), 7.07 (m, 3H), 6.95 (m, 2H), 6.55 (d, *J* = 7.5 Hz, 1H), 5.55 (d, *J* = 10.6 Hz, 1H), 4.62–4.45 (m, 1H), 4.18 (d, *J* = 11.9 Hz, 1H), 2.80 (s, 3H), 2.54 (br s, 1H), 0.92 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.3, 170.4, 143.9, 142.7, 135.2, 129.8, 129.3, 128.8, 128.2, 128.0, 127.9, 127.8, 127.4, 123.7, 123.1, 108.0, 80.6, 72.9, 61.3, 56.3, 52.0, 27.6, 25.7 ppm.

IR: ν3343,2921,1720, 1702, 1616, 1471, 1366, 1256, 1149, 1108, 1082, 1018, 747, 697 cm^{-1}.

HRMS (ESI): calcd. for $C_{29}H_{30}N_2O_3$ $[M+H]^+$= 455.2329, found 455.2330.

***Tert*-butyl (3*R**,3'*S**,4'*R**,5'*S**)-1-benzyl-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4'-carboxylate (4m); mixture of diastereomers**

(81 mg, 35 %, white solid)

m.p. 150–151 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.22 (m, 36H), 6.45 (d, *J* = 7.0 Hz, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 5.58 (d, *J* = 10.6 Hz, 1H), 5.09–4.90 (m, 1H), 4.73–4.59 (m, 1H), 4.25 (m, 4H), 2.59 (s, 2H), 0.93 (s, 9H), 0.85 (s, 9H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.2, 173.7, 165.0, 163.3, 137.8, 137.1, 135.4, 133.2, 130.3, 129.8, 125.9, 124.3, 123.9, 123.5, 123.3, 123.2, 123.1, 123.0, 122.9, 122.8, 122.7, 122.4, 122.3, 122.2, 122.0,

121.7, 121.6, 121.1, 120.1, 118.4, 117.8, 117.7, 103.9, 103.6, 75.7, 75.2, 67.2, 63.4, 62.5, 55.8, 55.7, 50.9, 50.2, 46.5, 38.9, 38.0, 22.1 ppm.
IR: ν 3326, 3027, 2966, 2921, 1718, 1704, 1614, 1489, 1467, 1352, 1259, 1147, 750, 732, 695 cm^{-1}.
HRMS (ESI): calcd. for $C_{35}H_{34}N_2O_3$ $[M+H]^+$= 531.2642, found 531.2643.

Characterization data for compounds 8

Dimethyl (3*R,3'*R**,5'*R**)-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4',4'-dicarboxylate (8a)**
(43 mg, 27 %, pale yellow solid)
m.p. = 208–210 °C
^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.90–7.87 (m, 1H), 7.66–7.63 (m, 2H), 7.41–7.40 (m, 1H), 7.36–7.23 (m, 5H), 7.20–7.11 (m, 4H), 6.88 (s, 1H), 6.61–6.59 (m, 1H), 6.52 (s, 1H), 4.91 (s, 1H), 3.21 (s, 3H), 3.09 (s, 3H), 2.53 (br s, 1H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.8, 170.6, 169.4, 143.0, 140.5, 138.8, 135.1, 130.9, 130.5, 129.9, 129.4, 129.3, 128.9, 127.9, 127.9, 127.6, 127.5, 124.6, 123.1, 109.4, 71.7, 69.6, 66.4, 62.0, 52.7, 52.2, 51.7, 29.7 ppm.
IR ν 3318, 3063, 2921, 2850, 1726, 1698, 1338, 1256, 735, 702 cm^{-1}.
HRMS (ESI): calcd. for $C_{27}H_{24}N_2O_5[M+H]^+$ = 457.1763, found 457.1761.

Dimethyl (3*R,3'*R**,5'*R**)-1-methyl-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4',4'-dicarboxylate (8b)**
(94 mg, 65 %, pale yellow solid)
m.p. = 167–169 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 0.9, 7.2 Hz, 1H), 7.66–7.63 (m, 2H), 7.35–7.09 (m, 10H), 6.6 (s, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 4.91 (s, 1H), 3.23 (s, 3H), 3.06 (s, 3H), 2.87 (s, 3H), 2.5 (br s, 1H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.7, 170.7, 169.4, 143.5, 139.0, 135.0, 130.2, 129.8, 129.3, 127.9 (2), 127.7, 127.4, 124.0, 123.0, 107.7, 71.6, 69.5, 66.3, 61.9, 52.2, 51.7, 29.7, 25.7 ppm.
IR ν 3725, 3315, 2946, 1724, 1610, 1254, 1049, 740, 702 cm^{-1}.
HRMS (ESI): calcd. for $C_{28}H_{26}N_2O_5[MH]^+$ = 471.1920, found 471.1915
HPLC: Chiralcel OD-H, *i*PrOH/hexane 10:90, 0.8 ml/min, λ = 254 nm. t_R = 10.21 min, 13.05 min.

Dimethyl (3*R,3'*R**,5'*R**)-1-benzyl-2-oxo-3',5'-diphenylspiro[indoline-3,2'-pyrrolidine]-4',4'-dicarboxylate (8c)**
(60 mg, 39 %, pale yellow solid)
m.p. = 175–176 °C
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.93 (m, 1H), 7.68–7.65 (m, 2H), 7.36–7.04 (m, 16H), 6.60 (s, 1H), 6.52 (d, *J* = 6 Hz, 2H), 4.97 (s, 1H), 3.23 (s, 3H), 3.12 (s, 3H), 2.58 (br s, 1H) ppm.
^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.5, 170.8, 169.4, 142.7, 138.7, 135.3 (2), 130.5, 130.2, 129.3, 128.5, 128.0, 127.9, 127.6, 127.5, 127.1, 126.6, 124.3, 123.2, 108.8, 71.7, 69.8, 66.6, 62.1, 52.5, 52.3, 51.7, 43.3 ppm.
IR ν 3319, 3031, 2951, 1728, 1608, 1351, 1251, 1174, 1053, 745, 704, 696 cm^{-1}.
HRMS (ESI): calcd. for $C_{34}H_{30}N_2O_5[MH]^+$ = 547.2233, found 547.2228
HPLC: Chiralcel OD-H, *i*PrOH/hexane 10:90, 0.8 ml/min, λ = 254 nm. t_R = 11.84 min, 13.82 min.

Dimethyl (3*R,3'*R**,5'*R**)-3'-(4-isopropylphenyl)-1-methyl-2-oxo-5'-phenylspiro[indoline-3,2'-pyrrolidine]-4',4'-dicarboxylate (8d)**

(41 mg, 30 %, pale yellow solid)

m.p. = 152–154 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 0.9, 7.2 Hz, 1H), 7.65–7.62 (m, 2H), 7.35–7.13 (m, 6H), 6.98 (q, *J* = 8.4, 13.5 Hz, 3H), 6.59–6.57 (m, 2H), 4.89 (s, 1H), 3.20 (s, 3H), 3.05 (s, 3H), 2.88 (s, 3H), 2.77 (k, *J* = 6.9, 13.8, 20.7 Hz, 1H), 2.47 (s, 1H), 1.15 (d, *J* = 1.5 Hz, 3H), 1.12 (d, *J* = 1.5 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 179.0, 170.9, 169.7, 148.1, 143.8, 139.3, 132.5, 130.6, 129.9, 129.4, 128.1, 128.0, 127.9, 125.9, 124.2, 123.2, 107.8, 71.7, 69.9, 66.5, 61.8, 52.4, 51.9, 33.8, 31.1, 29.9, 25.9, 24.0 ppm.

IR: ν 3318, 2956, 2925, 1727, 1708, 1248, 1179, 752, 697 cm^{-1}.

HRMS (ESI): calcd. for $C_{31}H_{32}N_2O_5[MH]^+$ = 513.2389, found 513.2381.

Dimethyl (3*R,3'*R**,5'*R**)-1-benzyl-3'-(4-isopropylphenyl)-2-oxo-5'-phenylspiro[indoline-3,2'-pyrrolidine]-4',4'-dicarboxylate (8e)**

(184 mg, 67 %, pale yellow semisolid)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95–7.92 (m, 2H), 7.66–7.64 (m, 2H), 7.38–7.23 (m, 8H), 7.16–7.00 (m, 6H), 6.65–6.63 (m, 2H), 6.59 (s, 1H), 4.95 (s, 1H), 3.17 (s, 3H), 3.10 (s, 3H), 2.84–2.79 (m, 1H), 2.57 (br s, 1H), 1.19 (d, *J* = 2.4 Hz, 3H), 1.17 (d, *J* = 2.4 Hz, 3H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 178.7, 170.8, 169.4, 167.4, 164.7, 142.9, 130.2 (2), 129.7, 129.2, 128.5, 127.9, 127.6, 127.1, 126.7, 126.0, 124.2, 108.9, 71.5, 70.1, 66.5, 61.7, 52.6, 52.2, 51.6, 43.5, 34.1, 33.6, 24.0, 23.8, 23.7 ppm.

IR: ν 3334, 2956, 1724, 1257, 1206, 1178, 1067, 754, 695 cm^{-1}.

HRMS (ESI): calcd. for $C_{37}H_{36}N_2O_5[MH]^+$ = 589.2702, found 589.2698.

Dimethyl (3*R,3'*R**,5'*R**)-5'-(4-methoxyphenyl)-1-methyl-2-oxo-3'-phenylspiro[indoline-3,2'-pyrrolidine]-4',4'-dicarboxylate (8f)**

(100 mg, 46 %, white solid)

m.p. 92−93 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.3 Hz, 1H), 7.55 (d, J = 8.7 Hz, 2H), 7.10 (m, 7H), 6.86 (d, J = 8.8 Hz, 2H), 6.56 (d, J = 11.3 Hz, 2H), 4.89 (s, 1H), 3.80 (s, 3H), 3.22 (s, 3H), 3.14 (s, 3H), 2.86 (s, 3H), 2.48 (br s, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.7, 170.8, 169.5, 159.3, 143.5, 135.1, 131.0, 130.2, 129.8, 129.2, 128.8, 127.7, 127.3, 123.9, 123.0, 113.3, 107.6, 71.5, 69.3, 66.0, 61.9, 55.2, 52.4, 51.7, 25.6 ppm.

IR: ν 3325, 2945, 1724, 1610, 1510, 1470, 1345, 1246, 1210, 1180, 1061, 1034, 840, 751, 703, 617 cm^{-1}.

HRMS (ESI): calcd. for $C_{27}H_{26}N_2O_4$ $[M+H]^+$= 501.2020, found 501.2020.

Dimethyl (3*R,3'*R**,5'*R**)-5'-(3-chlorophenyl)-1-methyl-2-oxo-3'-phenylspiro[indoline-3,2'-pyrrolidine]-4',4'-dicarboxylate (8g)**

(87 mg, 55 %, pale yellow solid)

m.p. = 154–156 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 3 Hz, 1H), 7.64 (s, 1H), 7.57–7.55 (m, 1H), 7.28–7.23 (m, 3H), 7.18–7.16 (m, 1H), 7.12–7.11 (m, 3H), 7.08–7.06 (m, 2H), 6.58–6.57 (m, 2H), 4.91 (s, 1H), 3.23 (s, 3H), 3.14 (s, 3H), 2.86 (s, 3H), 2.45 (br s, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 178.7, 170.3, 169.2, 143.4, 141.4, 134.8, 133.9, 130.0, 129.8, 129.4, 129.2, 128.0, 127.9, 127.7 (3), 127.6, 127.5, 126.3, 124.1, 123.1, 107.7, 71.4, 69.2, 65.6, 61.6, 52.3, 51.8, 29.7, 25.7 ppm.
IR ν 3930, 2951, 1726, 1612, 1250, 1087, 746, 701 cm^{-1}.
HRMS (ESI): calcd. for $C_{28}H_{25}ClN_2O_5[MH]^+$ = 505.1525, found 505.1526.

Characterization data for compounds 10 and 12

(1*E*,2*E*)-*N*-benzyl-3-phenylprop-2-en-1-imine (10)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16–8.14 (m, 1H), 7.48–7.28 (m, 10H), 6.98–6.96 (m, 2H), 4.72 (s, 2H) ppm. ^{1}H NMR spectrum corresponds with data described in literature.[17]

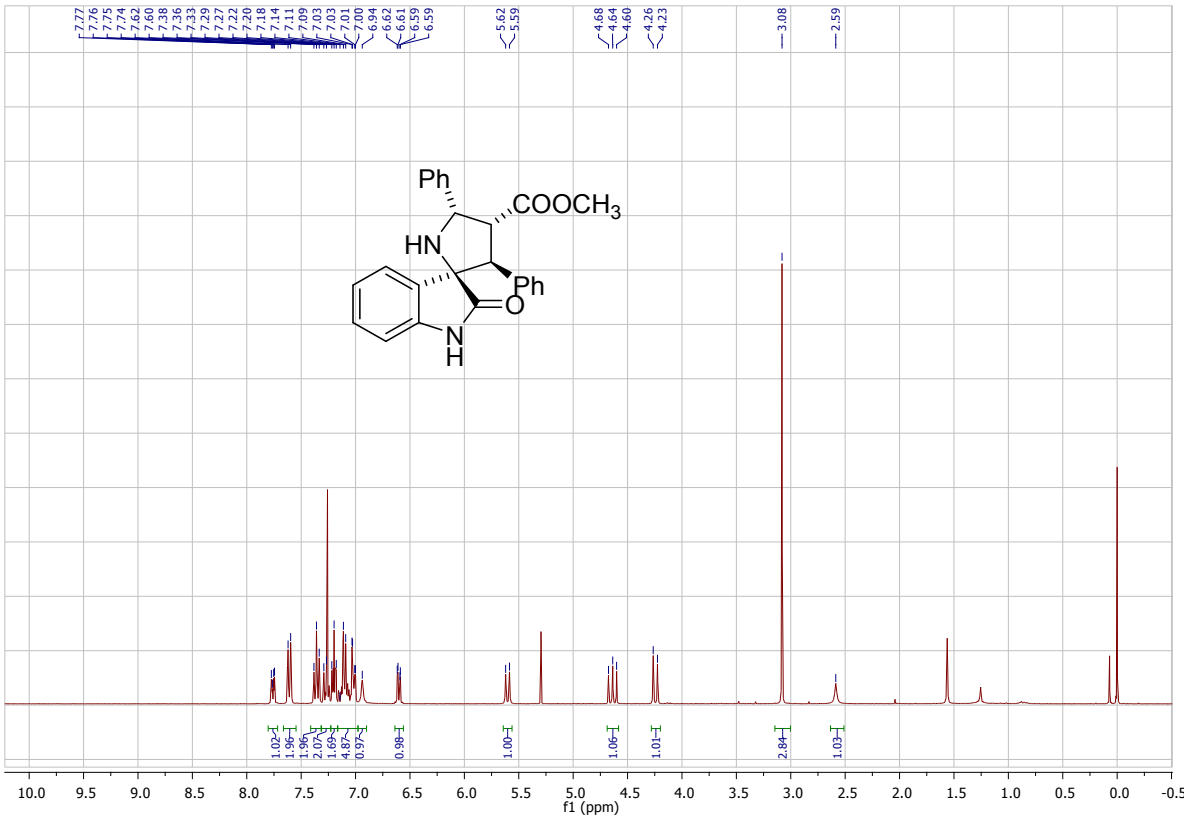
2-(1-methyl-2-oxoindolin-3-ylidene)malononitrile (12)

m.p. = 233–236 °C (234–238 °C[18])
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 9 Hz, 1H), 7.58 (dt, *J* = 15.6; 7.8; 1.2 Hz, 1H), 7.15 (t, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 3.25 (s, 3H) ppm. ^{1}H NMR spectrum corresponds with data described in literature.[19]

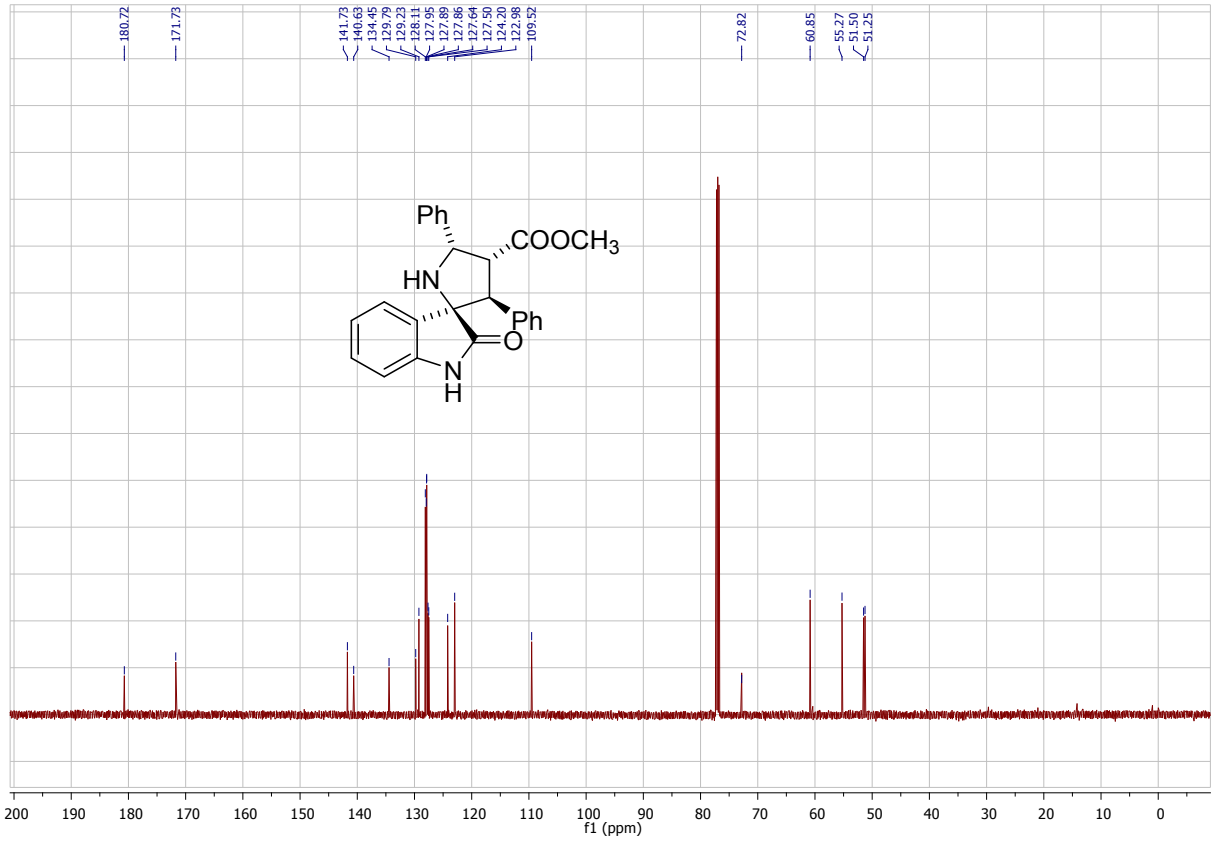
[17]Colby, D. A.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 3645–3651.
[18]Abdelhamid, I. A.; Mohamed, M. H.; Abdelmoniem, A. M.; Ghozlan, S.A.S.*Tetrahedron* **2009**, *65*, 10069-10073.
[19] Deng, H.-P.; Wei, Y.; Shi, M. *Org. Lett.* **2011,** *13,* 3348–3351.

Pictures of ^{1}H and ^{13}C NMR spectra

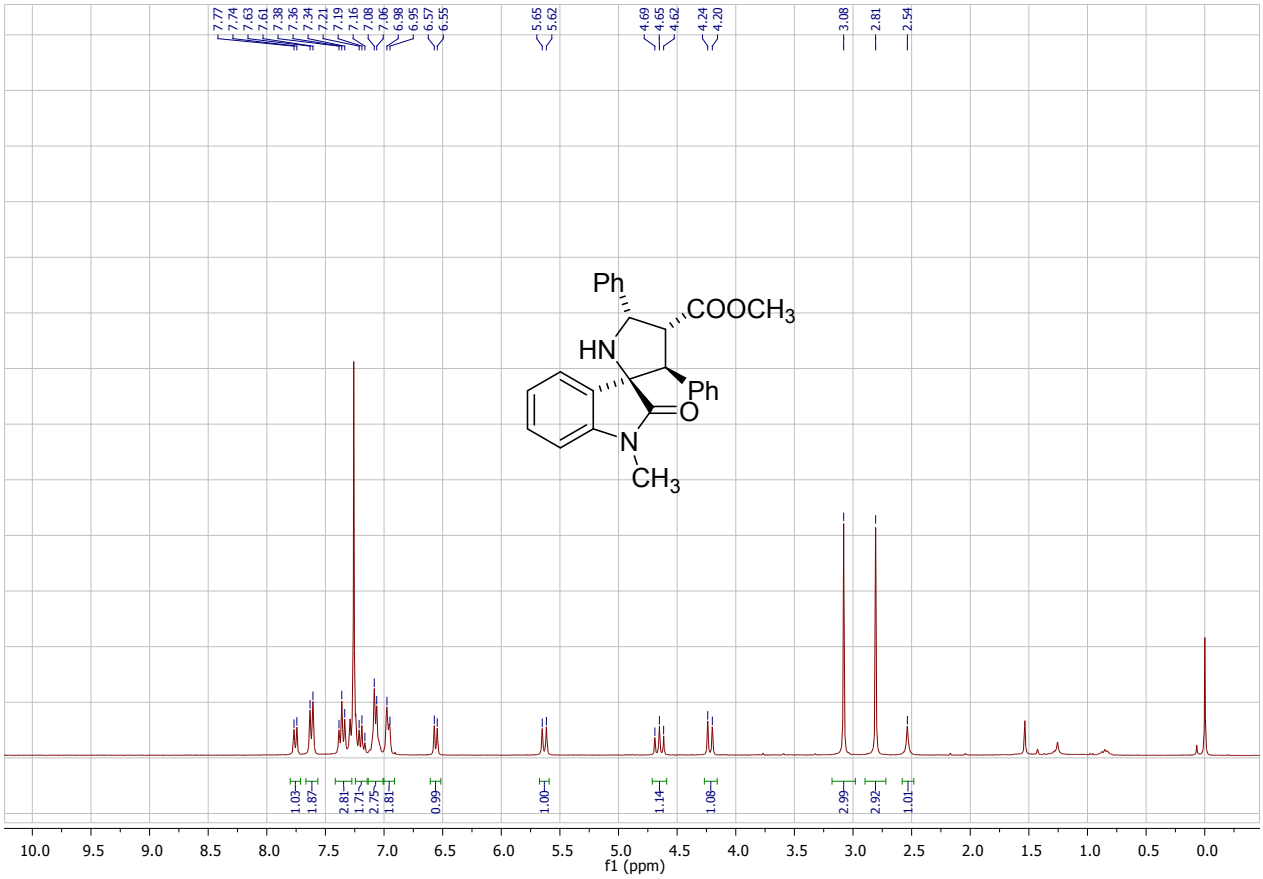
^{1}H NMR of **4a**



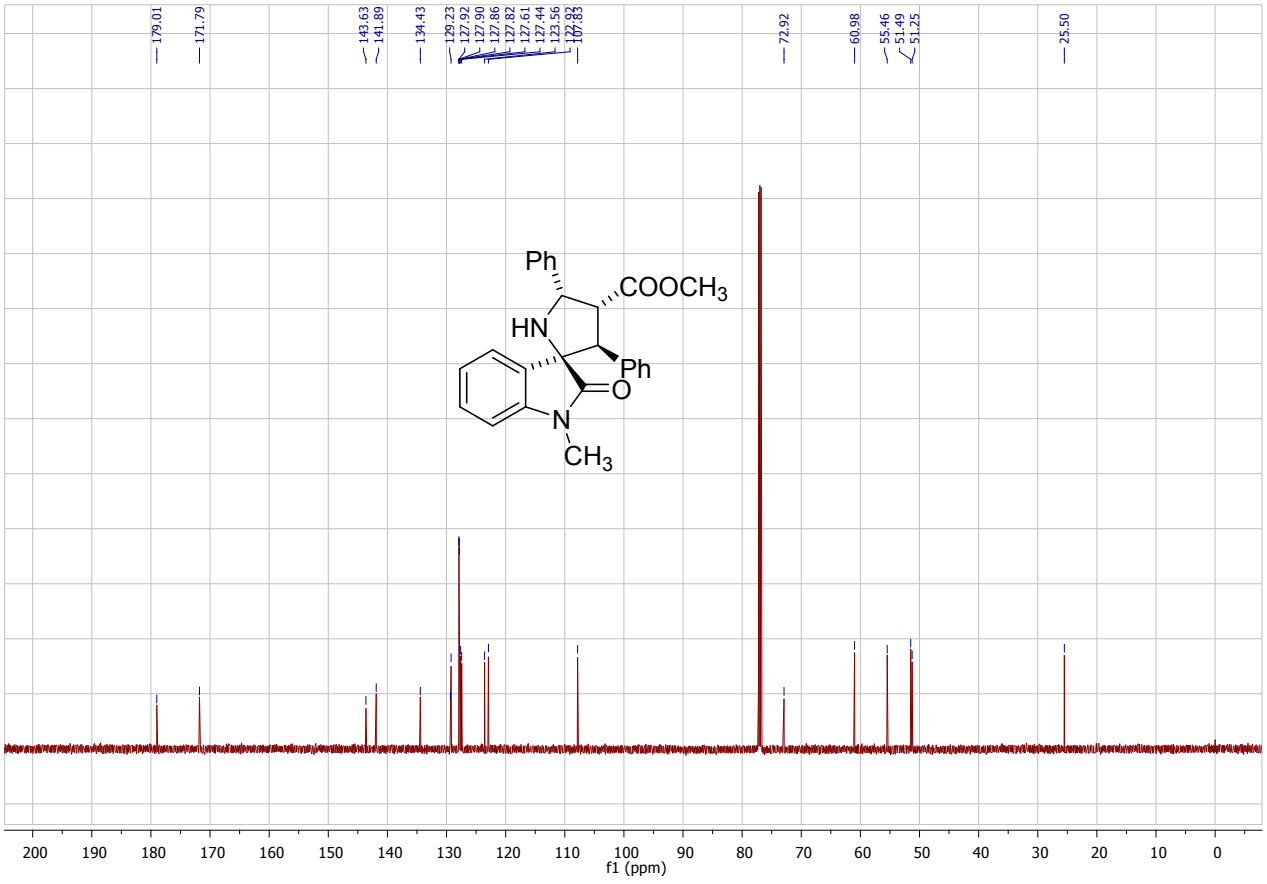
^{13}C NMR of **4a**



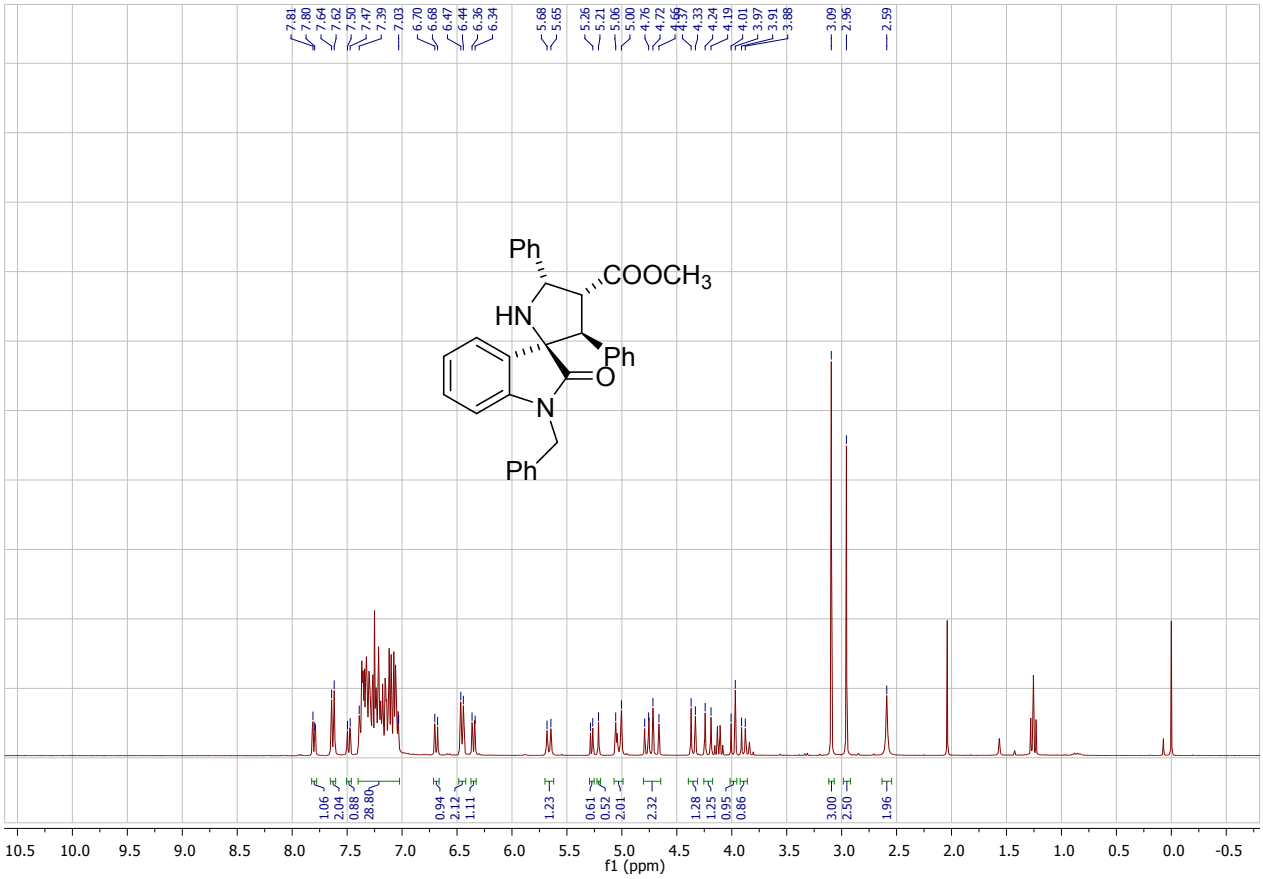
^{1}H NMR of **4b**



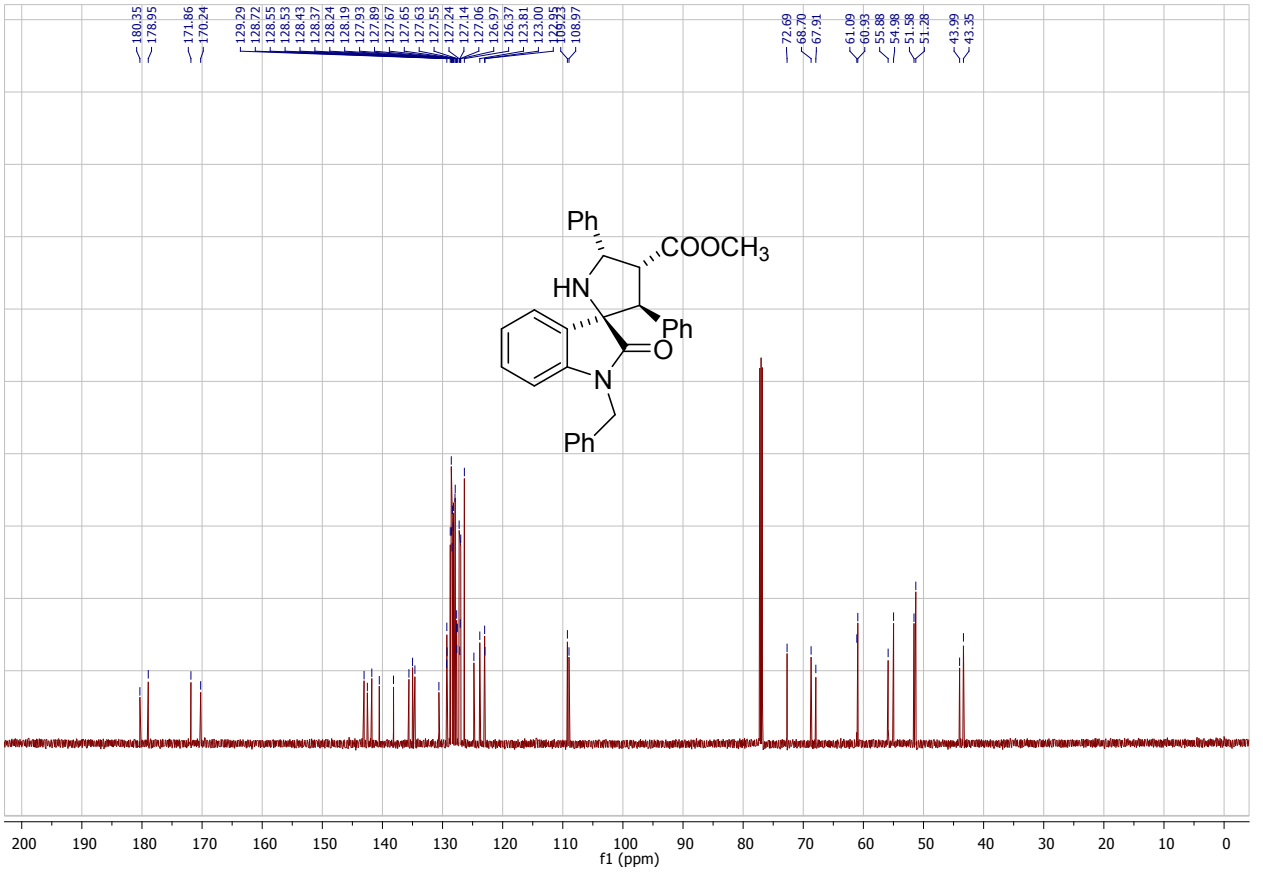
^{13}C NMR of **4b**



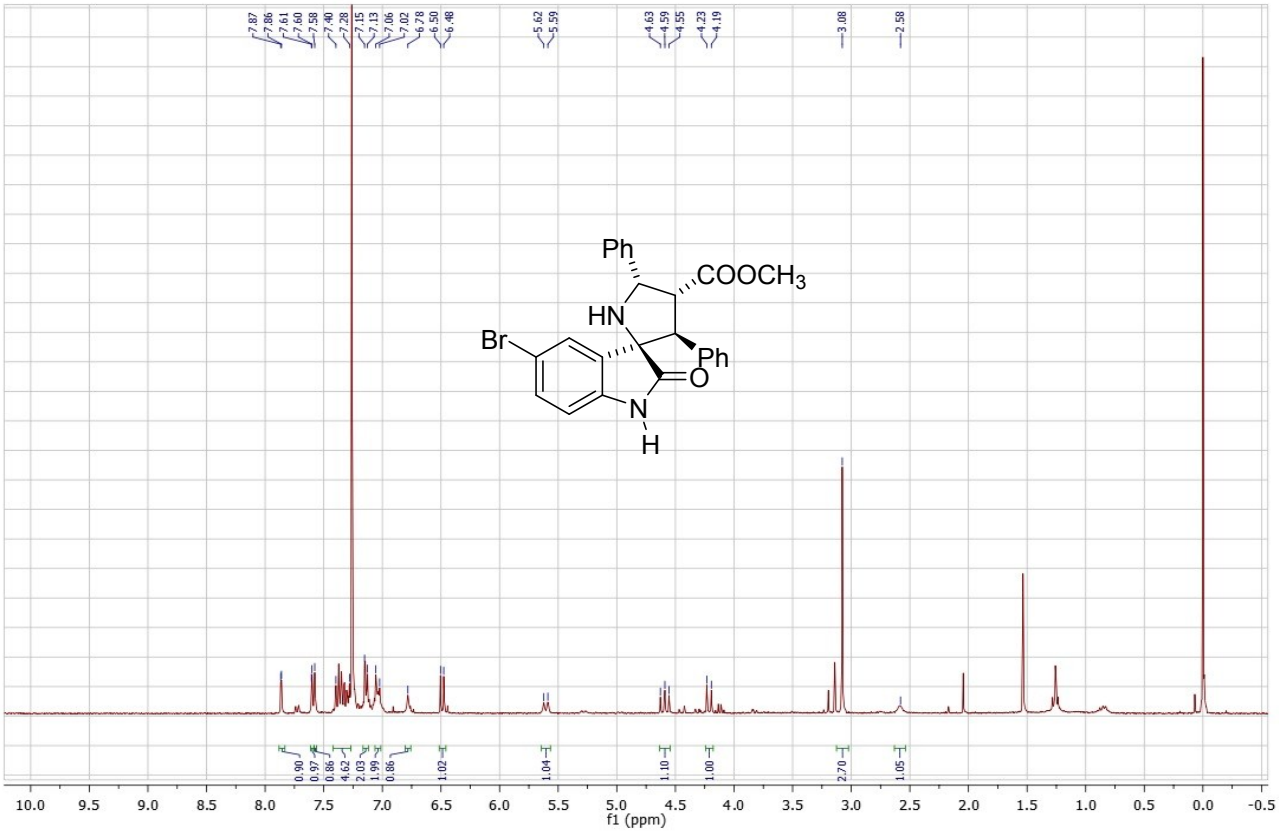
^{1}H NMR of **4c**



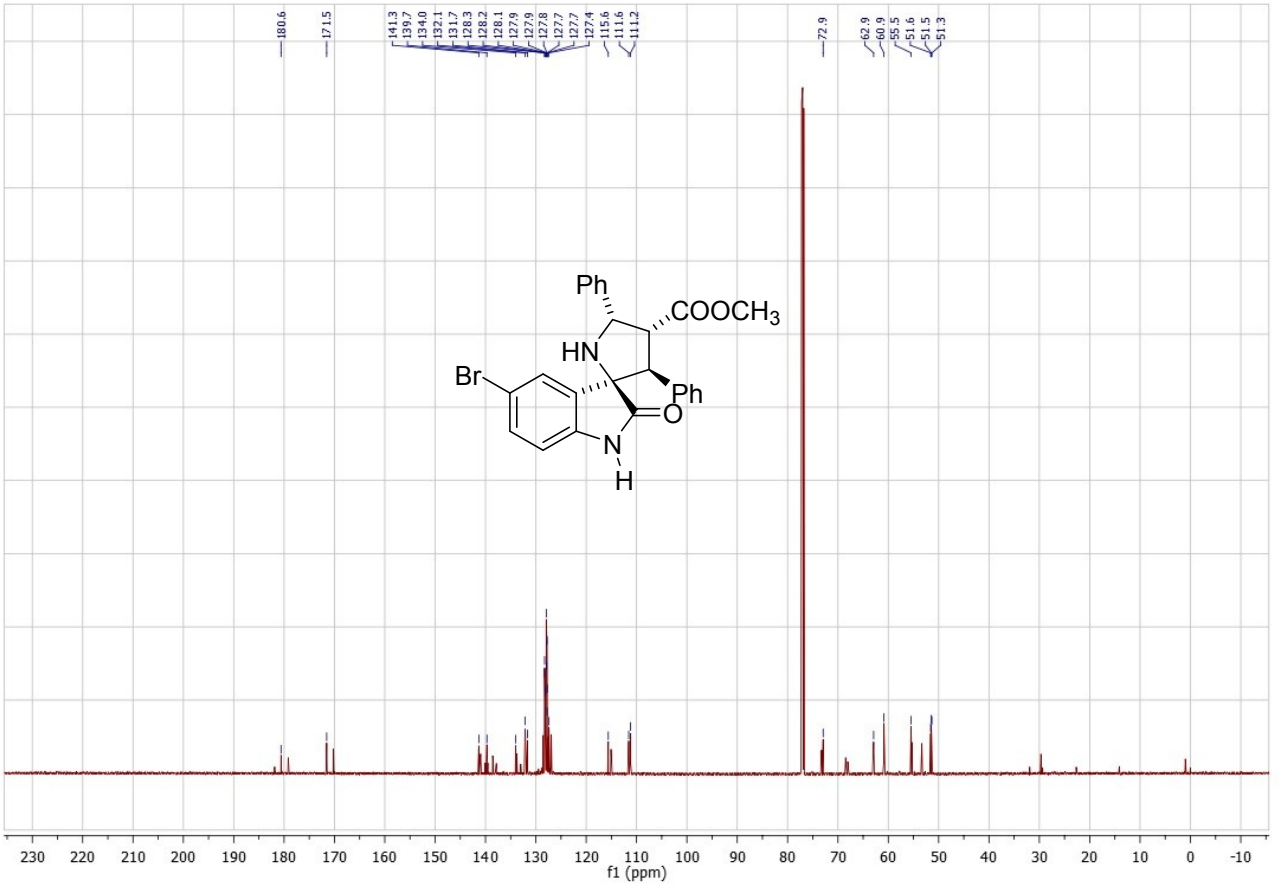
^{13}C NMR of **4c**



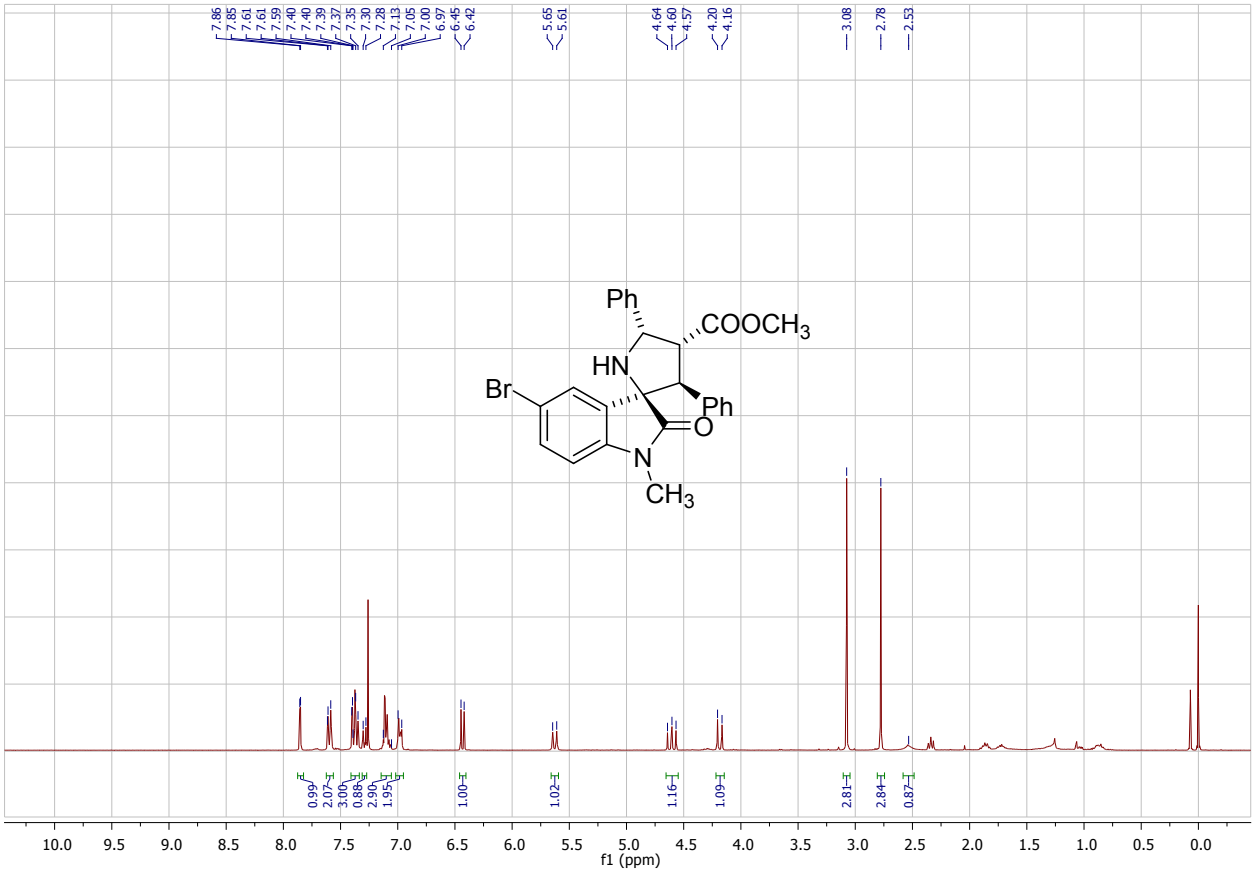
^{1}H NMR of **4d**



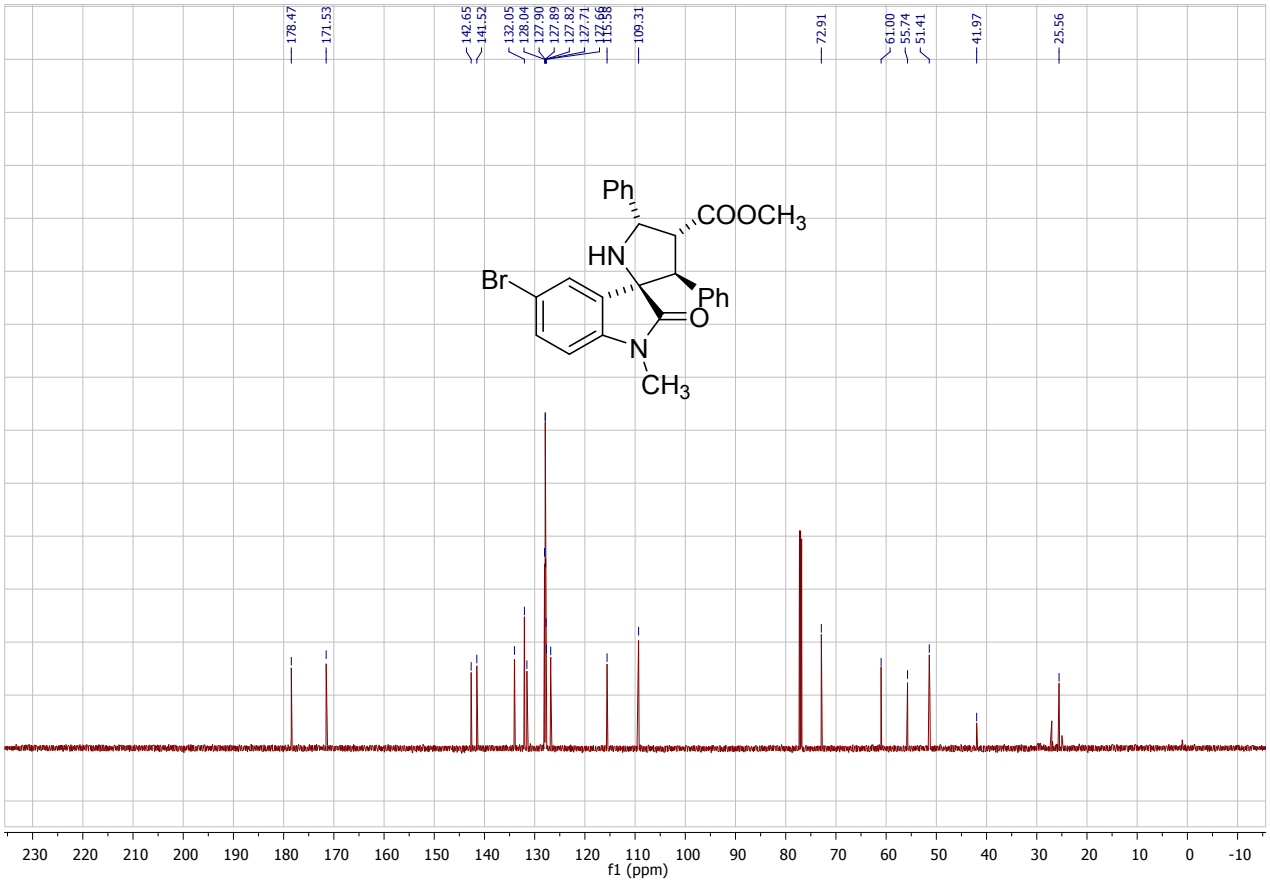
^{13}C NMR of **4d**



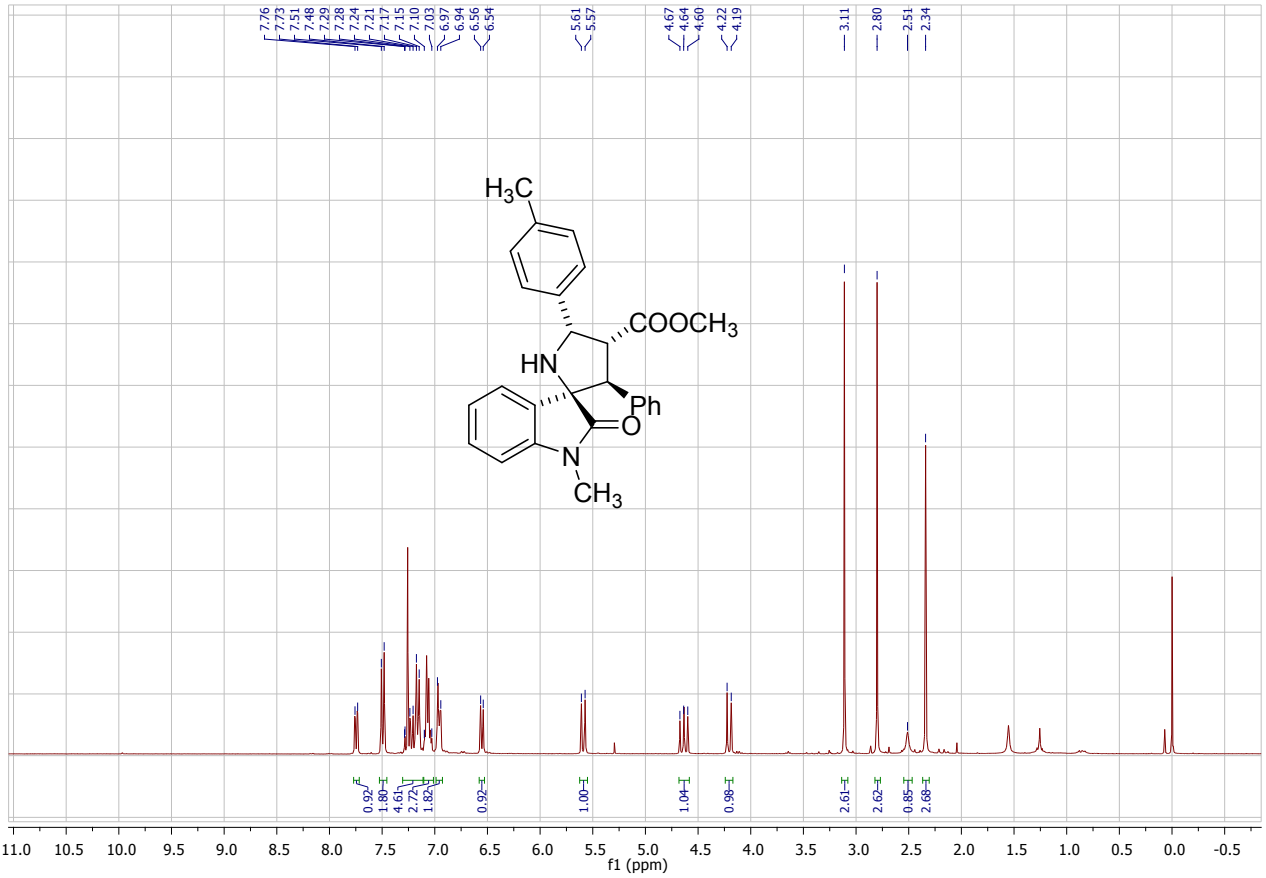
^{1}H NMR of **4e**



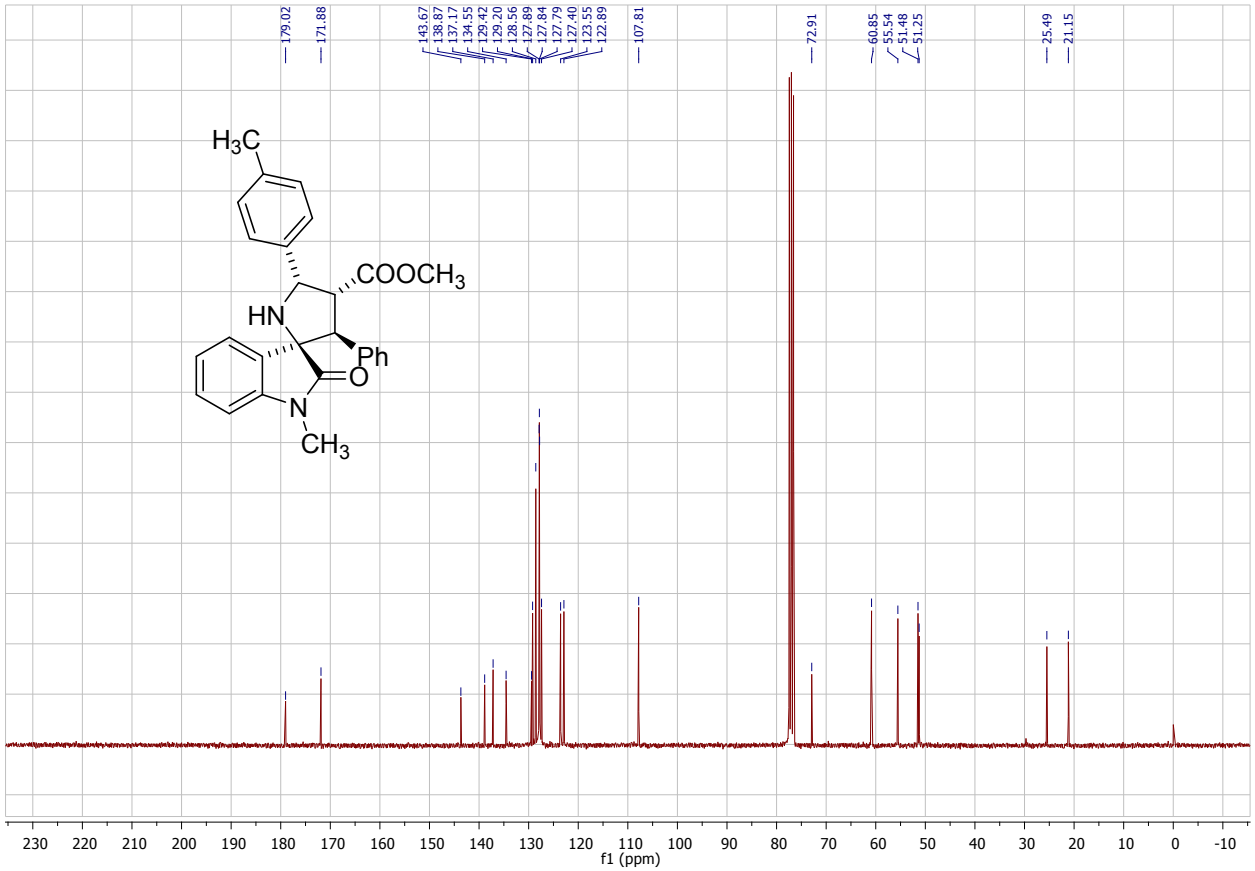
^{13}C NMR of **4e**



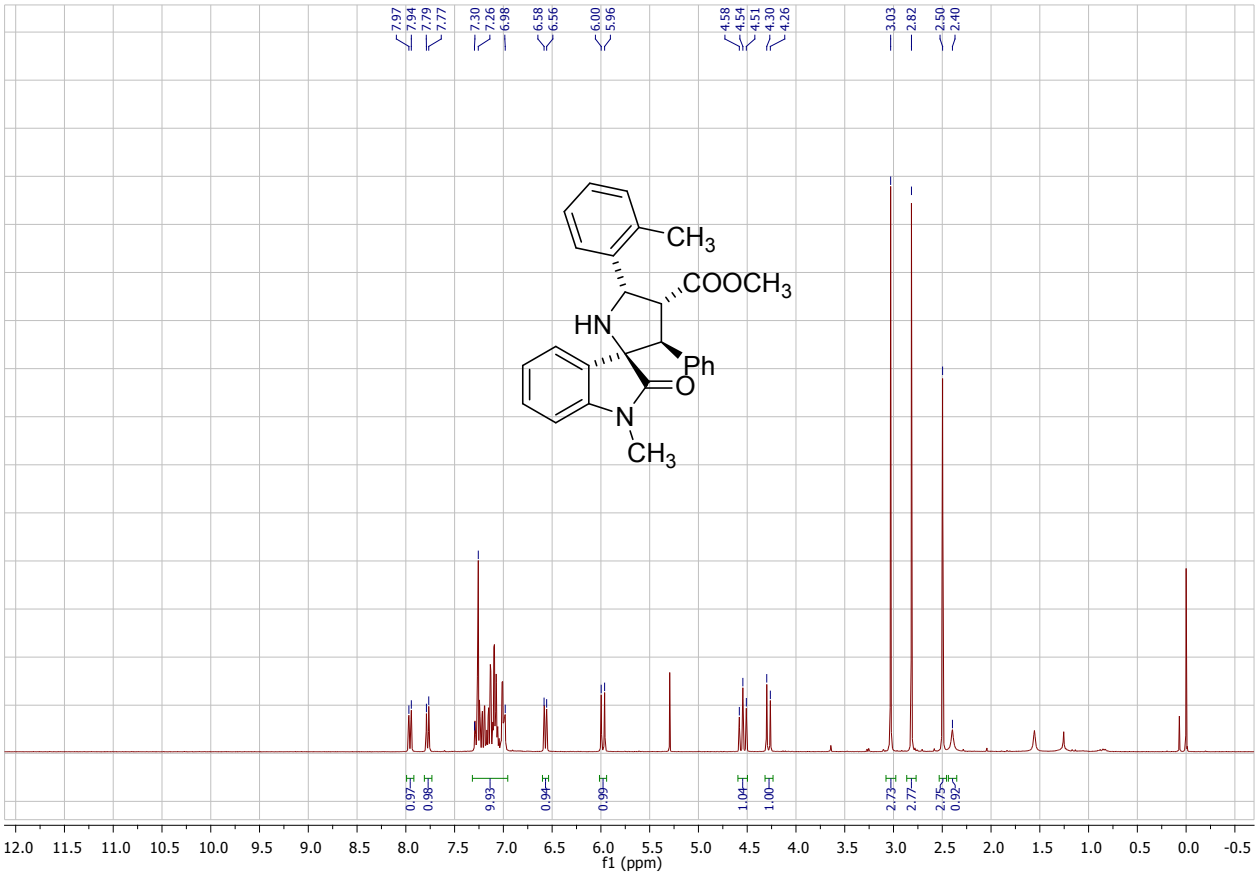
^{1}H NMR of **4f**



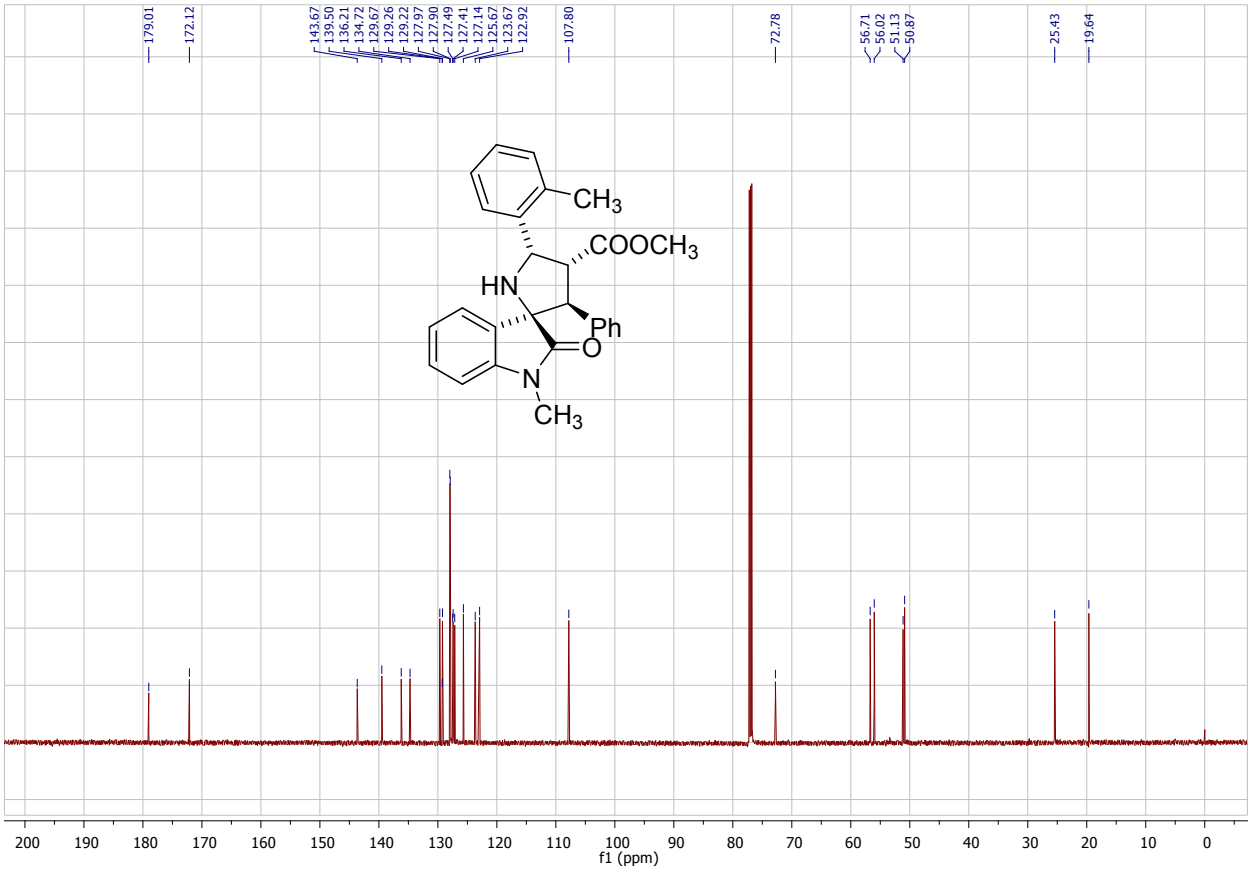
^{13}C NMR of **4f**



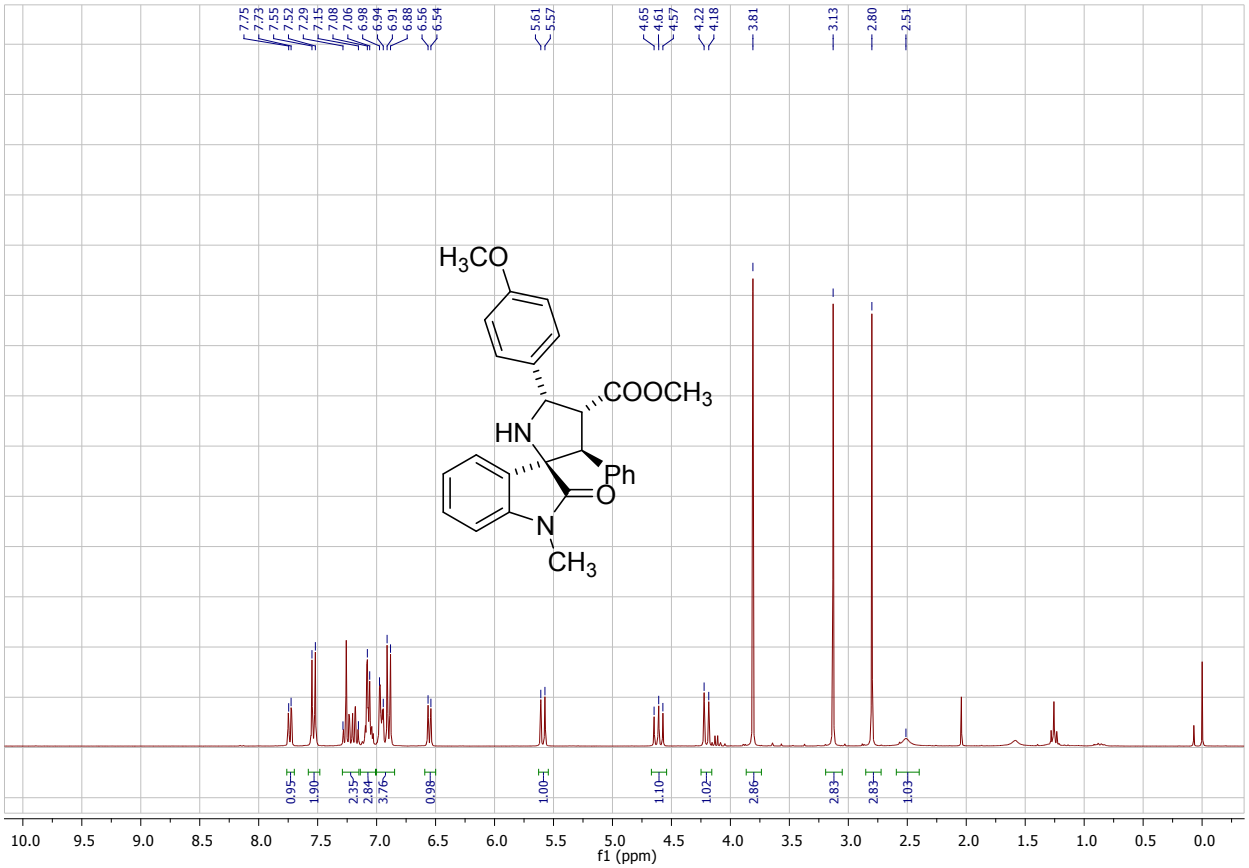
^{1}H NMR of **4g**



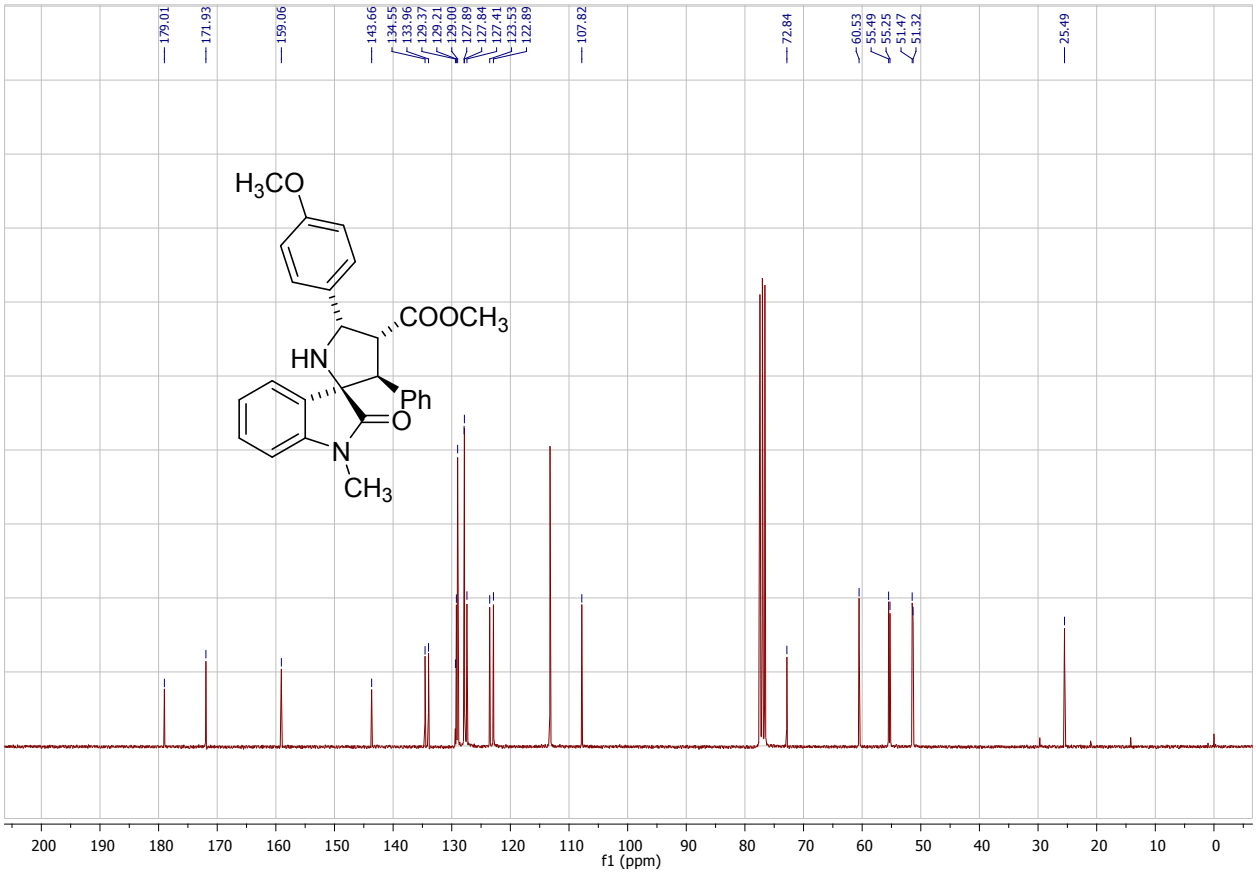
^{13}C NMR of **4g**



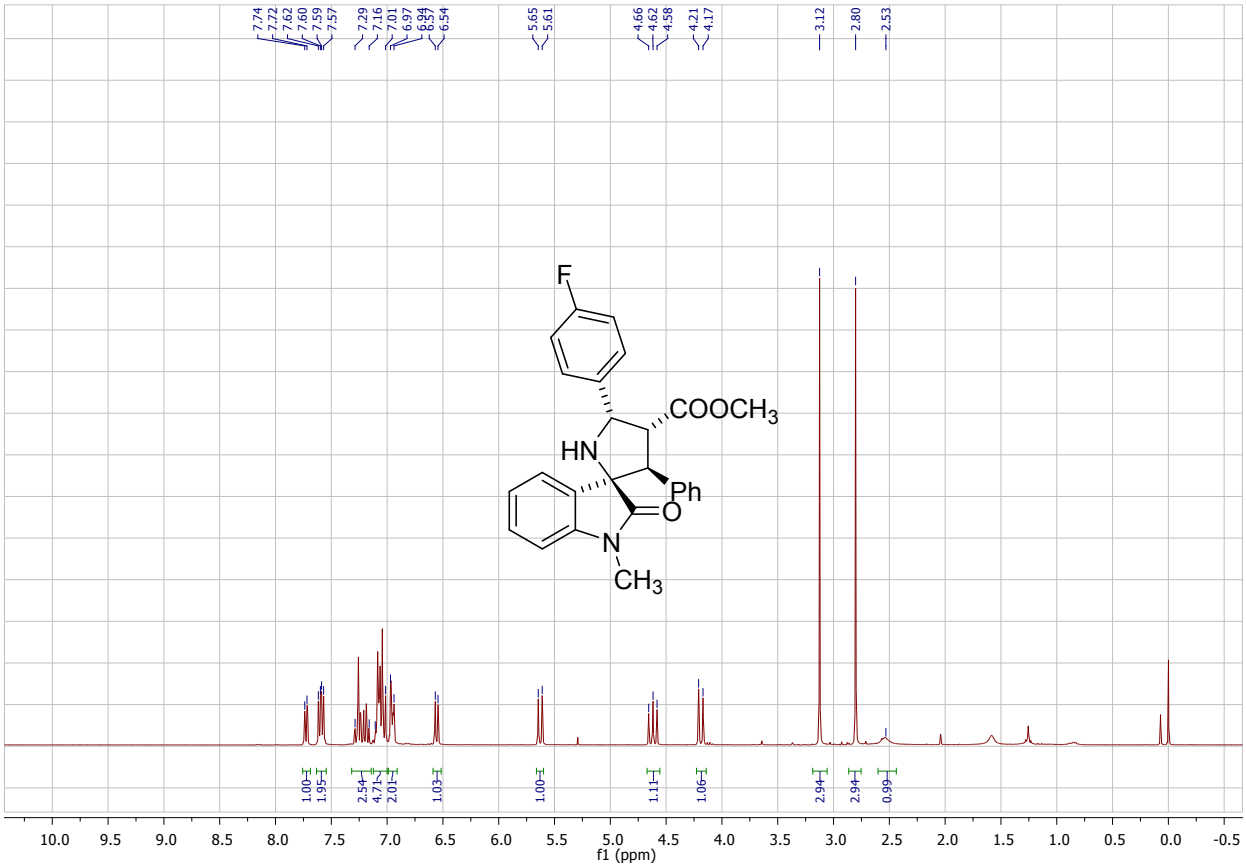
^{1}H NMR of **4h**



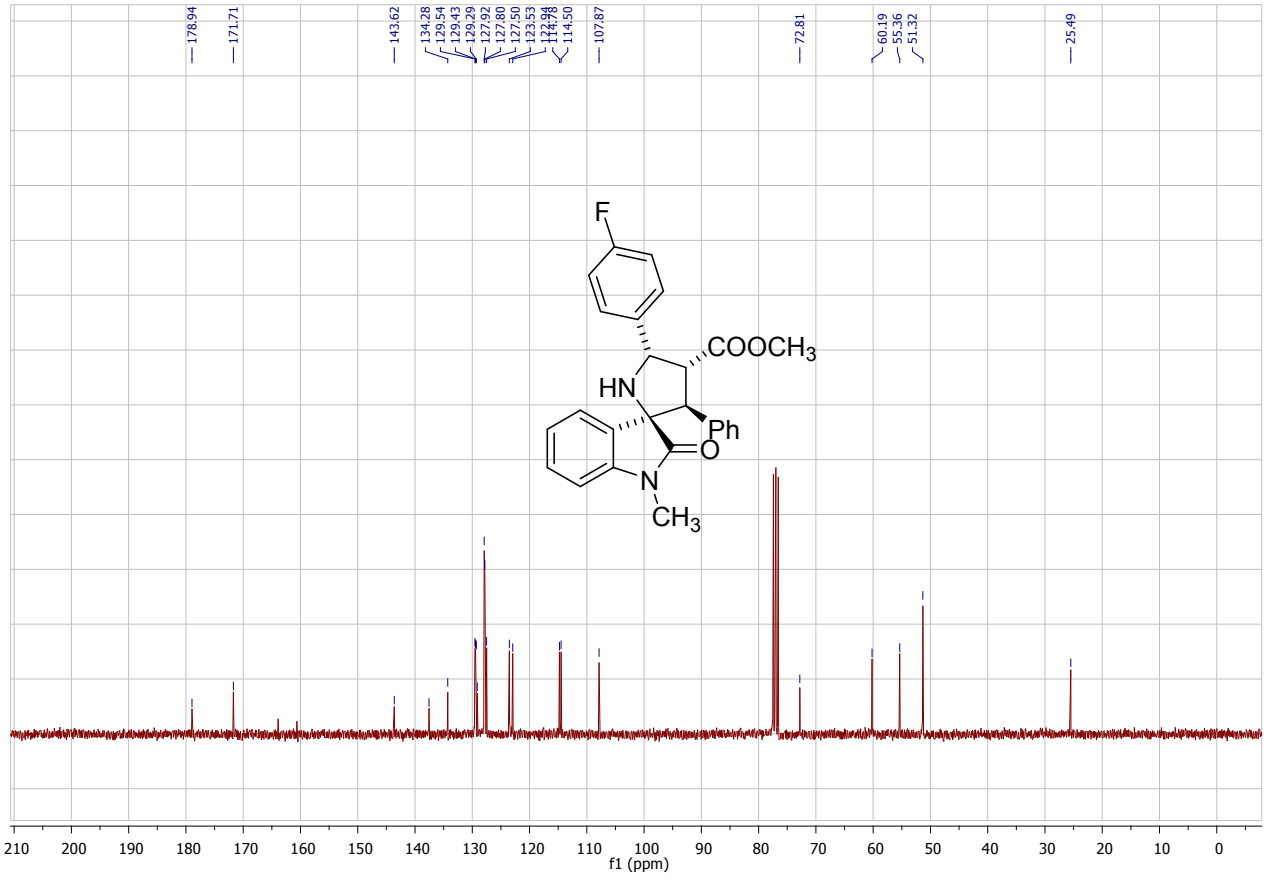
^{13}C NMR of **4h**



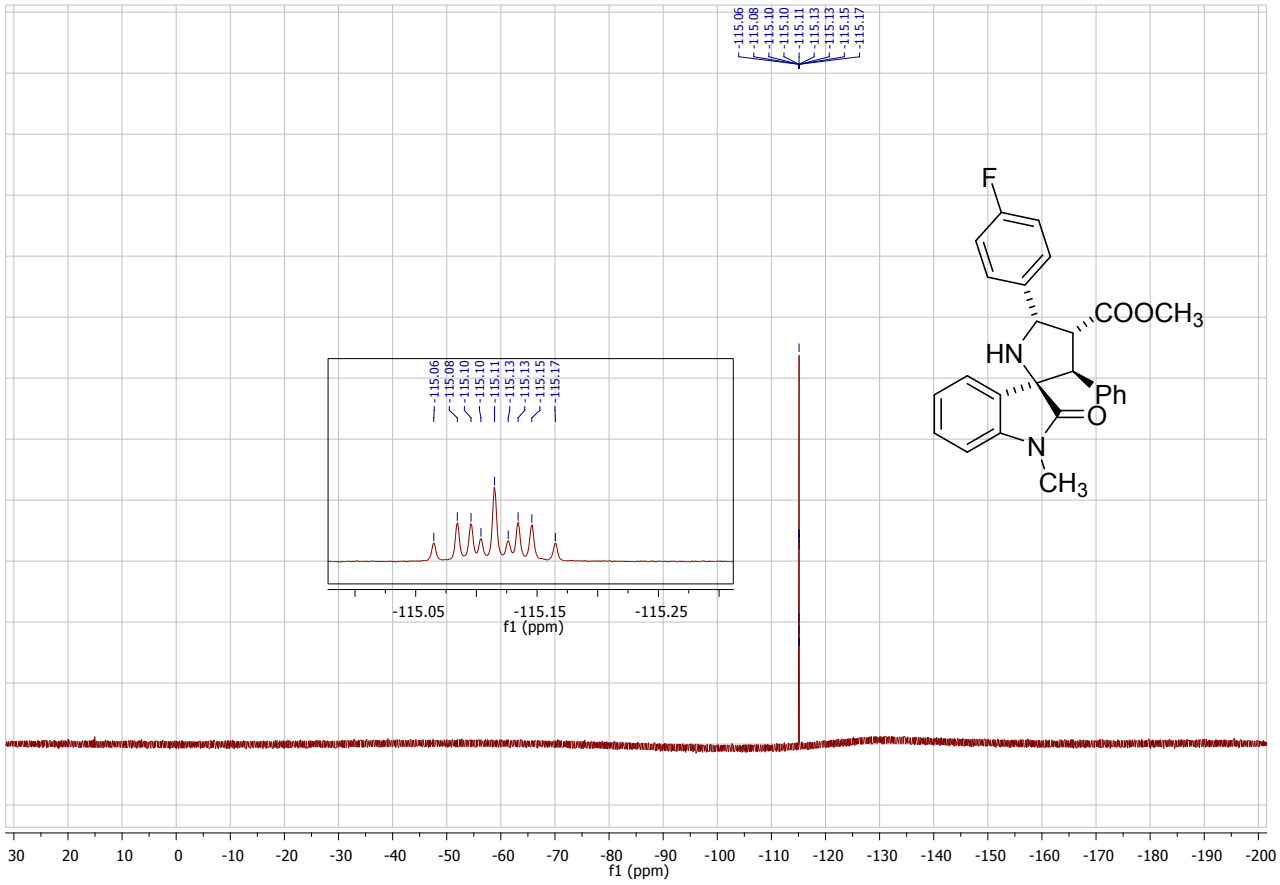
^{1}H NMR of **4i**



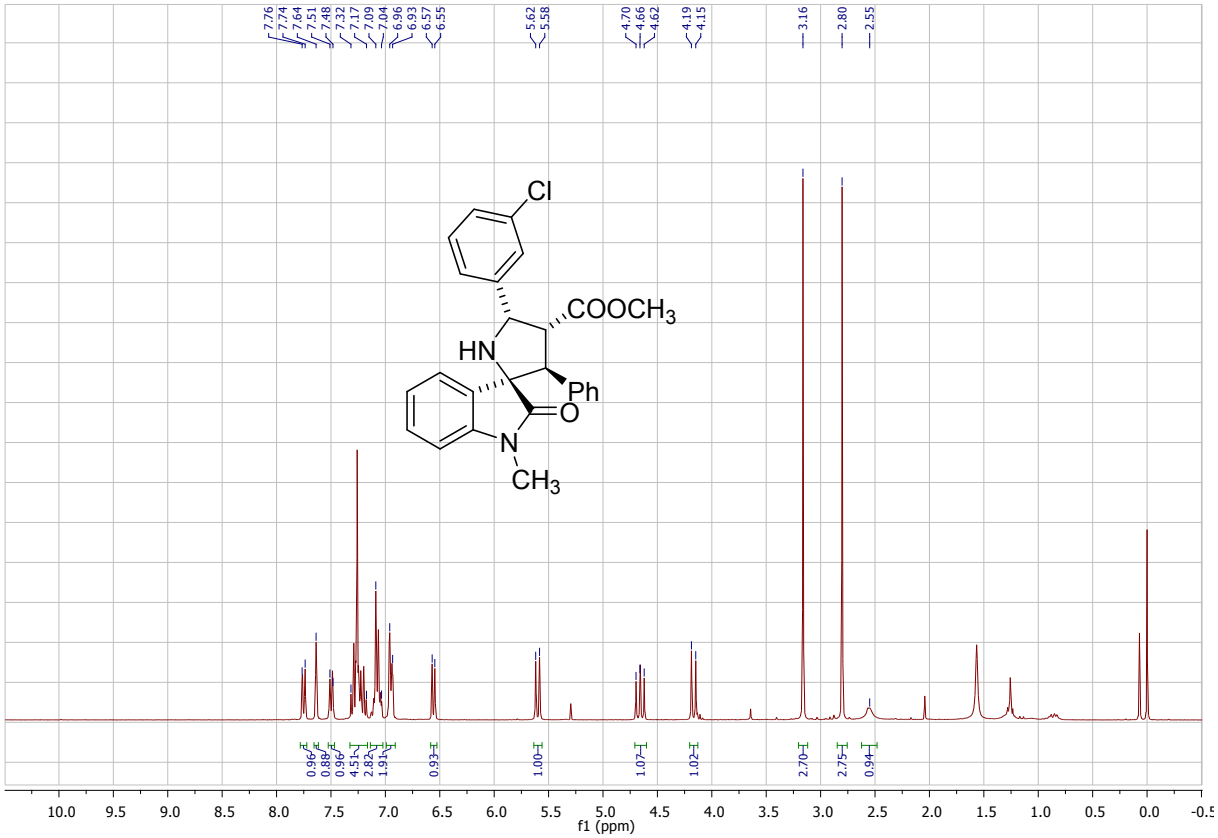
^{13}C NMR of **4i**



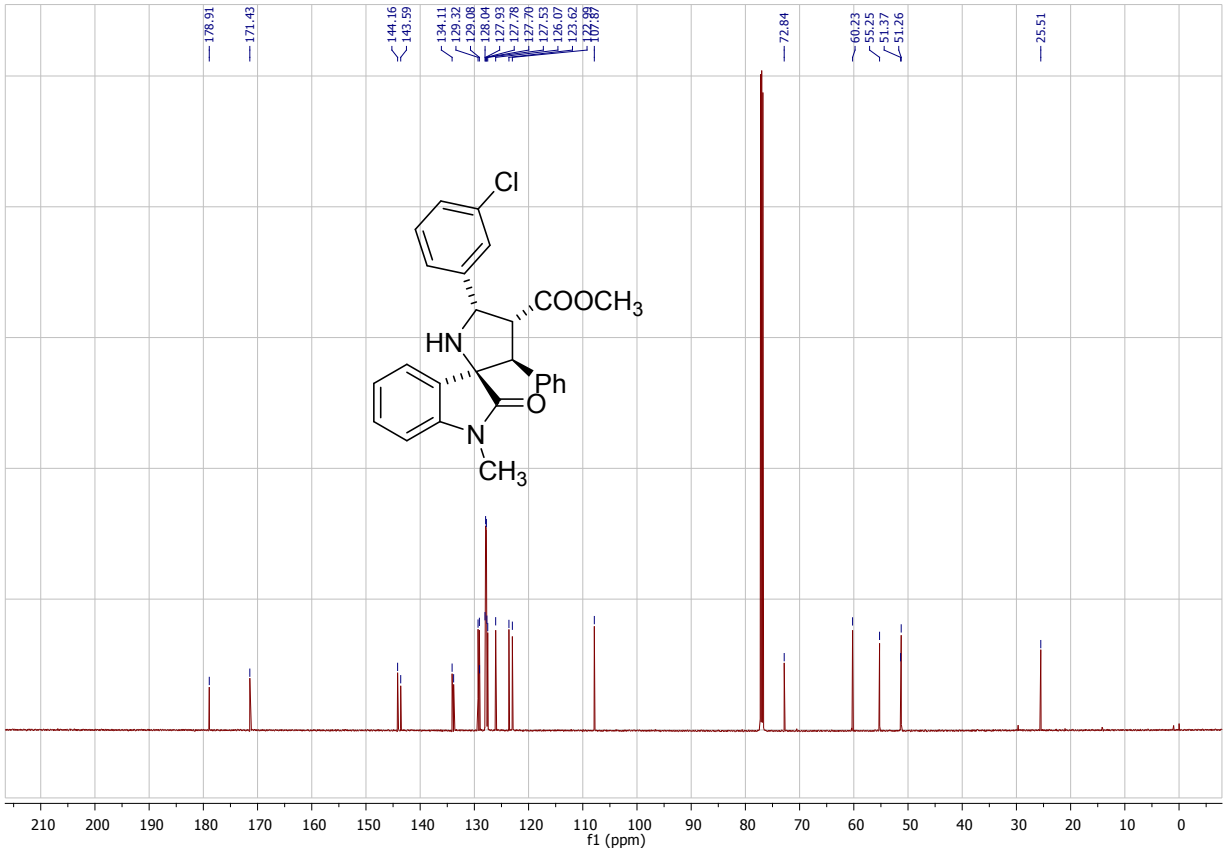
^{19}F NMR of **4i**


-115.06
-115.08
-115.10
-115.10
-115.11
-115.13
-115.13
-115.15
-115.17
F
COOCH3
HN
Ph
O
N
CH3
-115.05
-115.15
-115.25
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

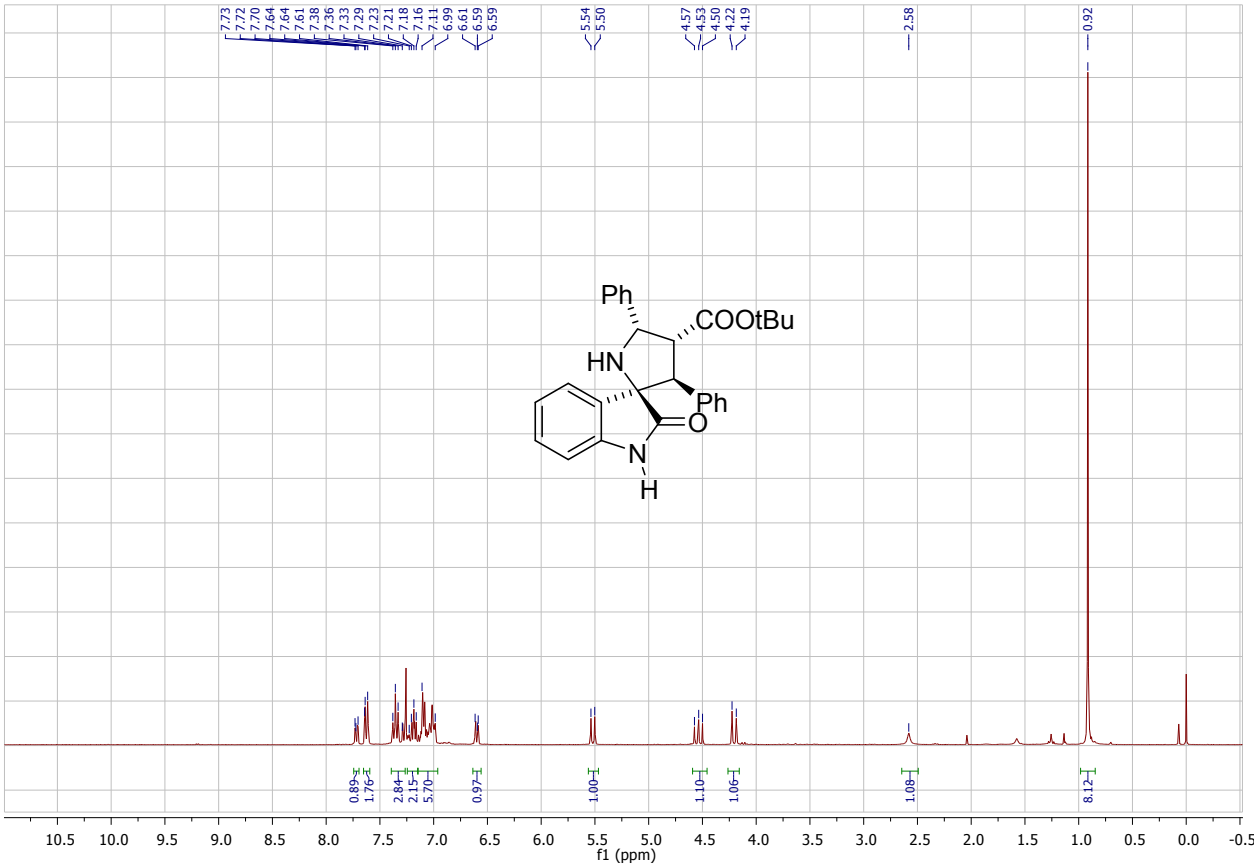
^{1}H NMR of **4j**



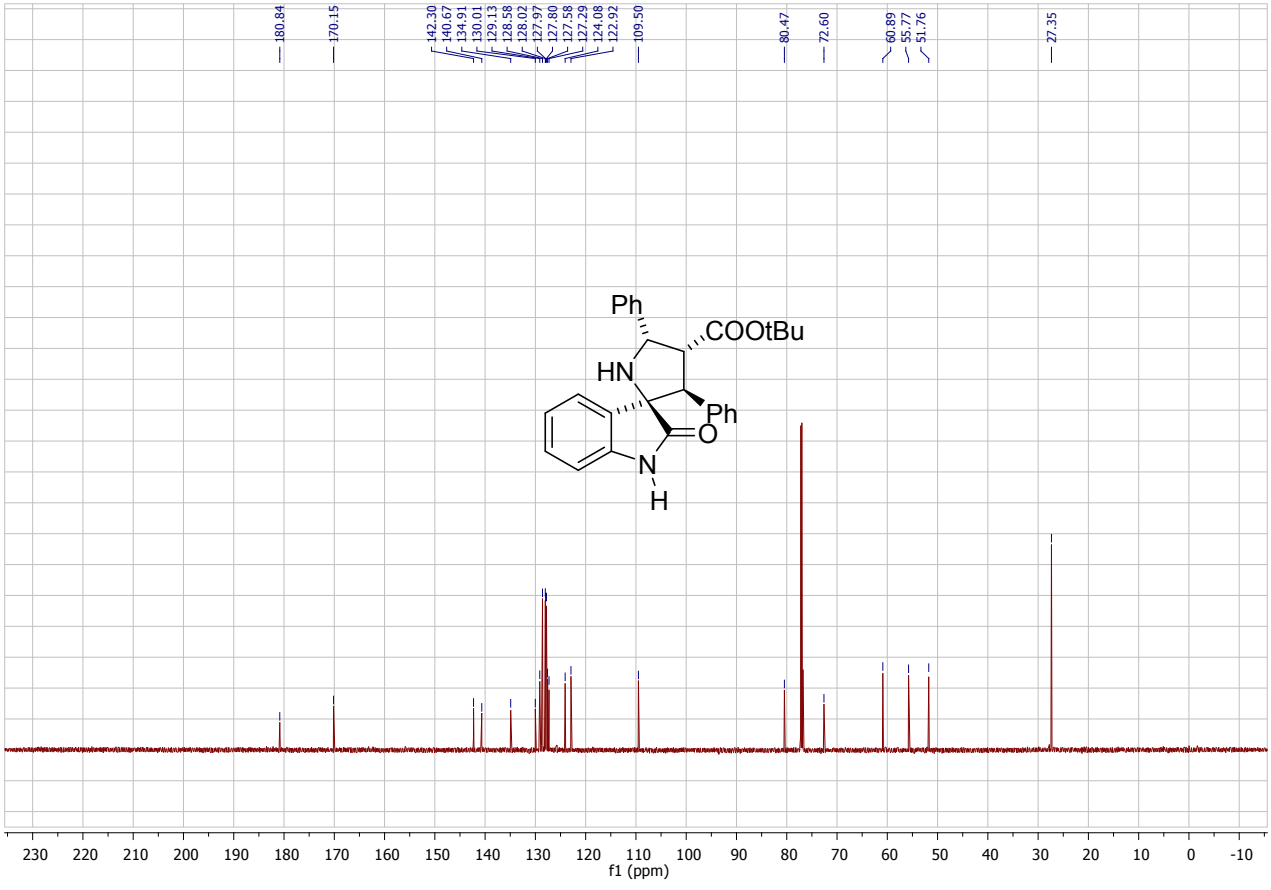
^{13}C NMR of **4j**



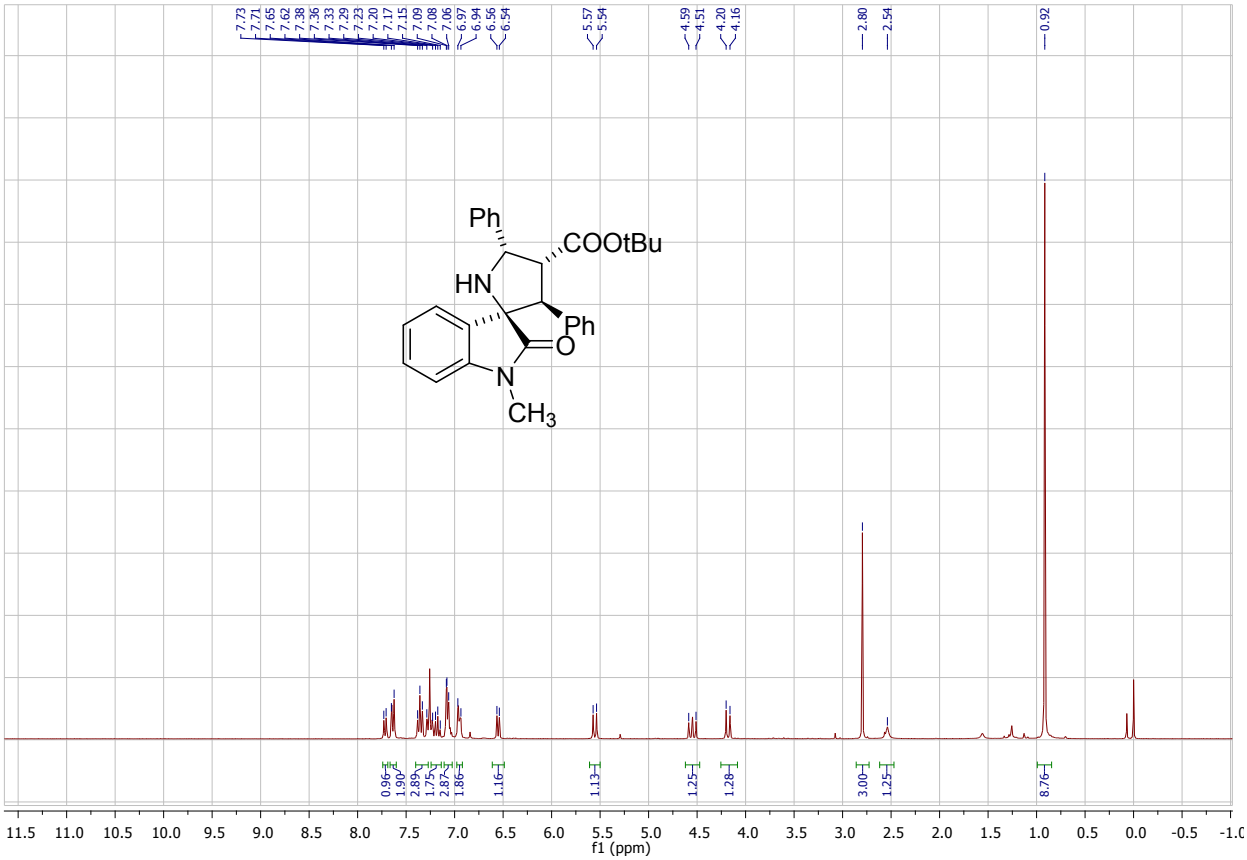
^{1}H NMR of **4k**



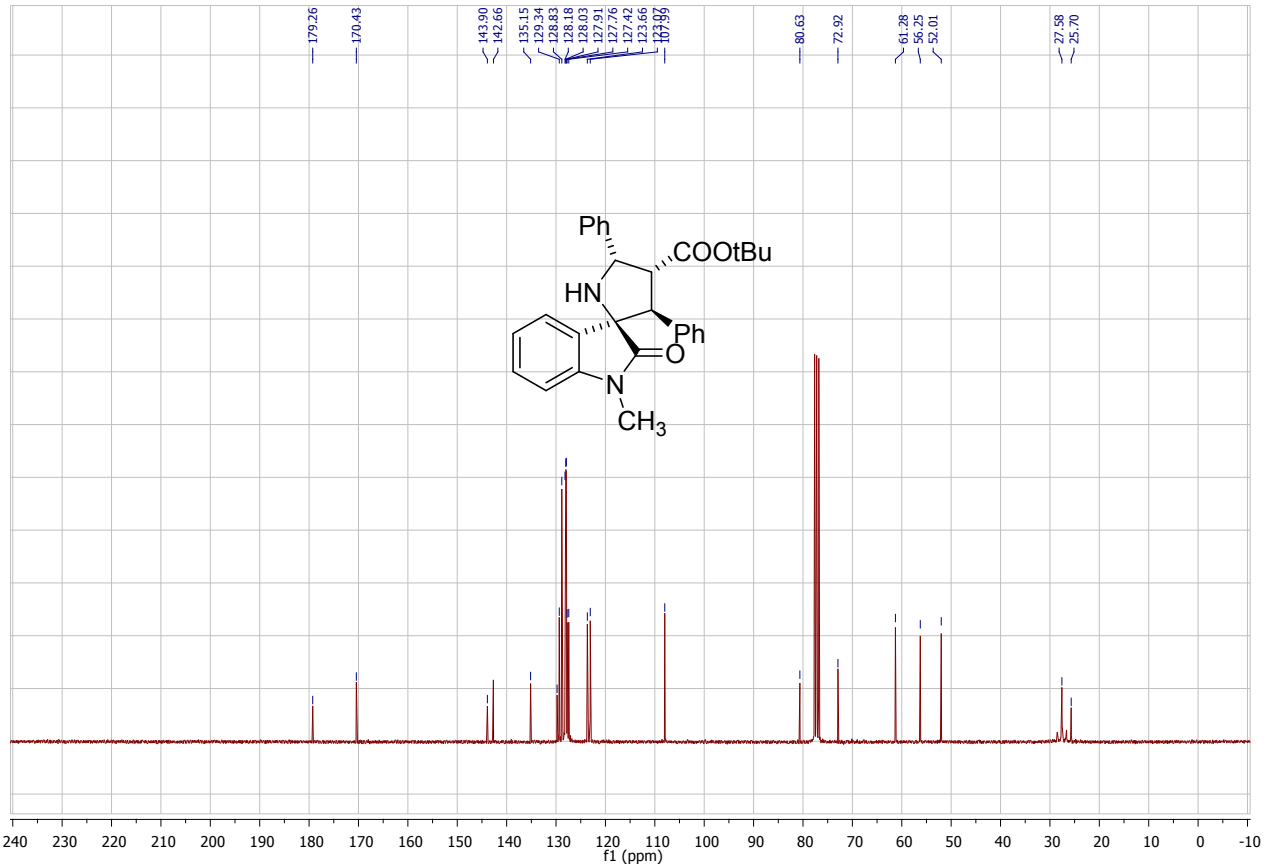
^{13}C NMR of **4k**



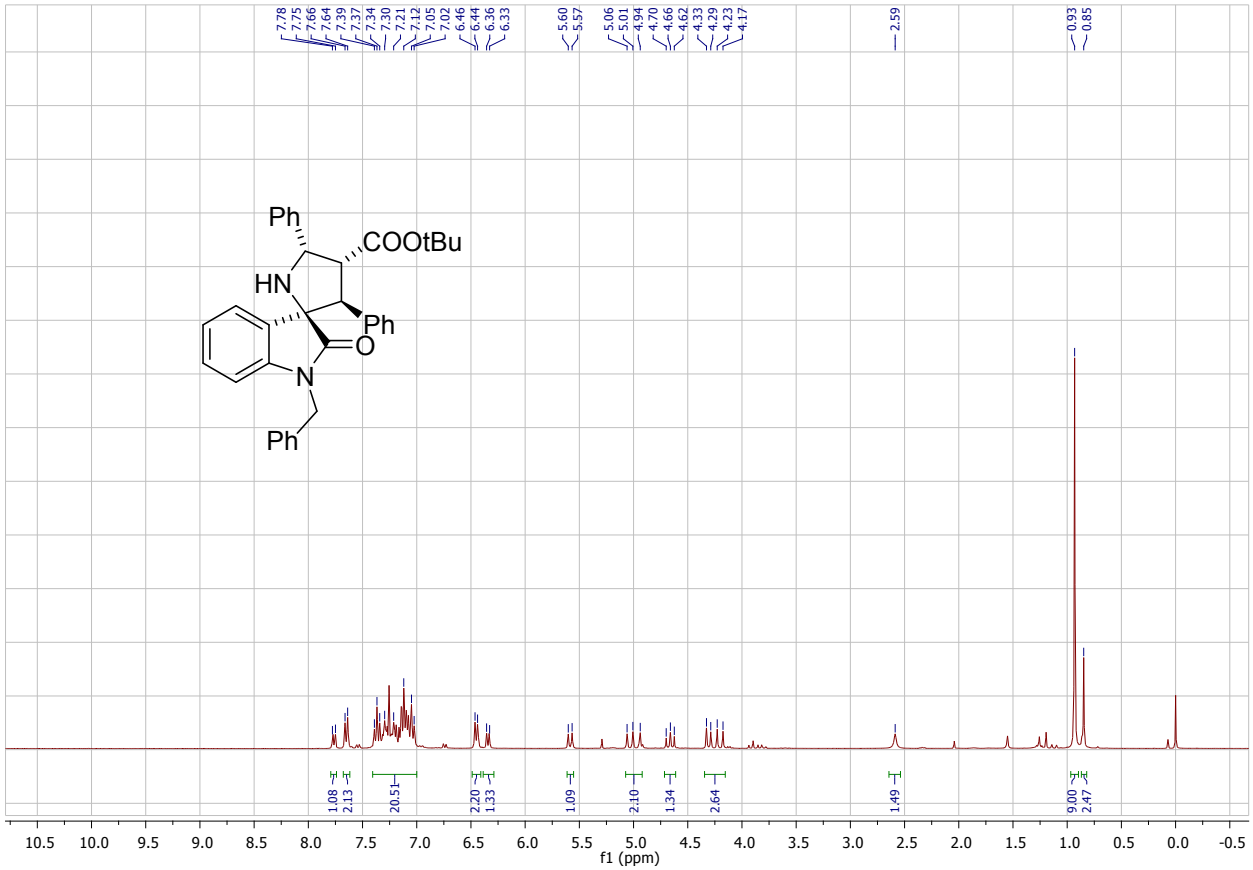
^{1}H NMR of **4l**



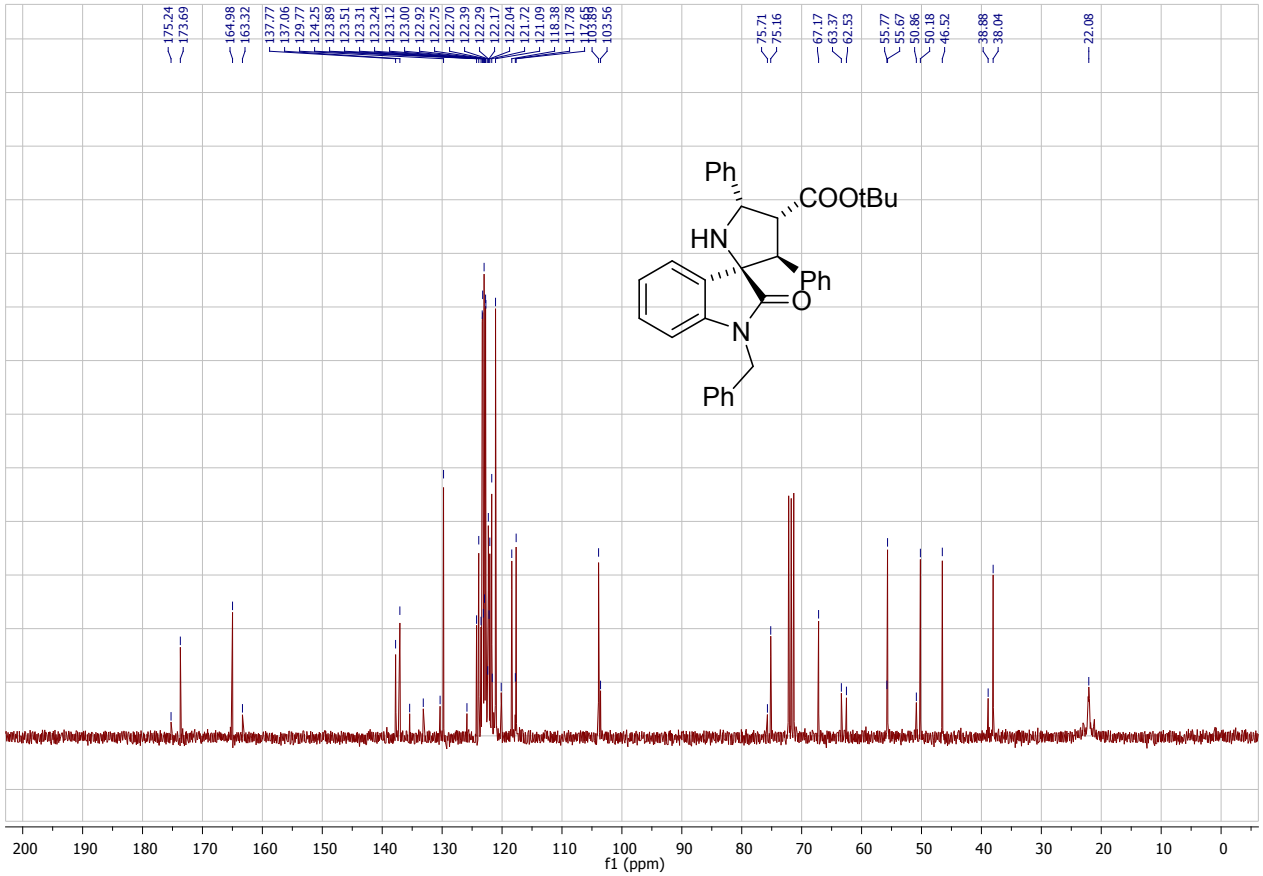
^{13}C NMR of **4l**



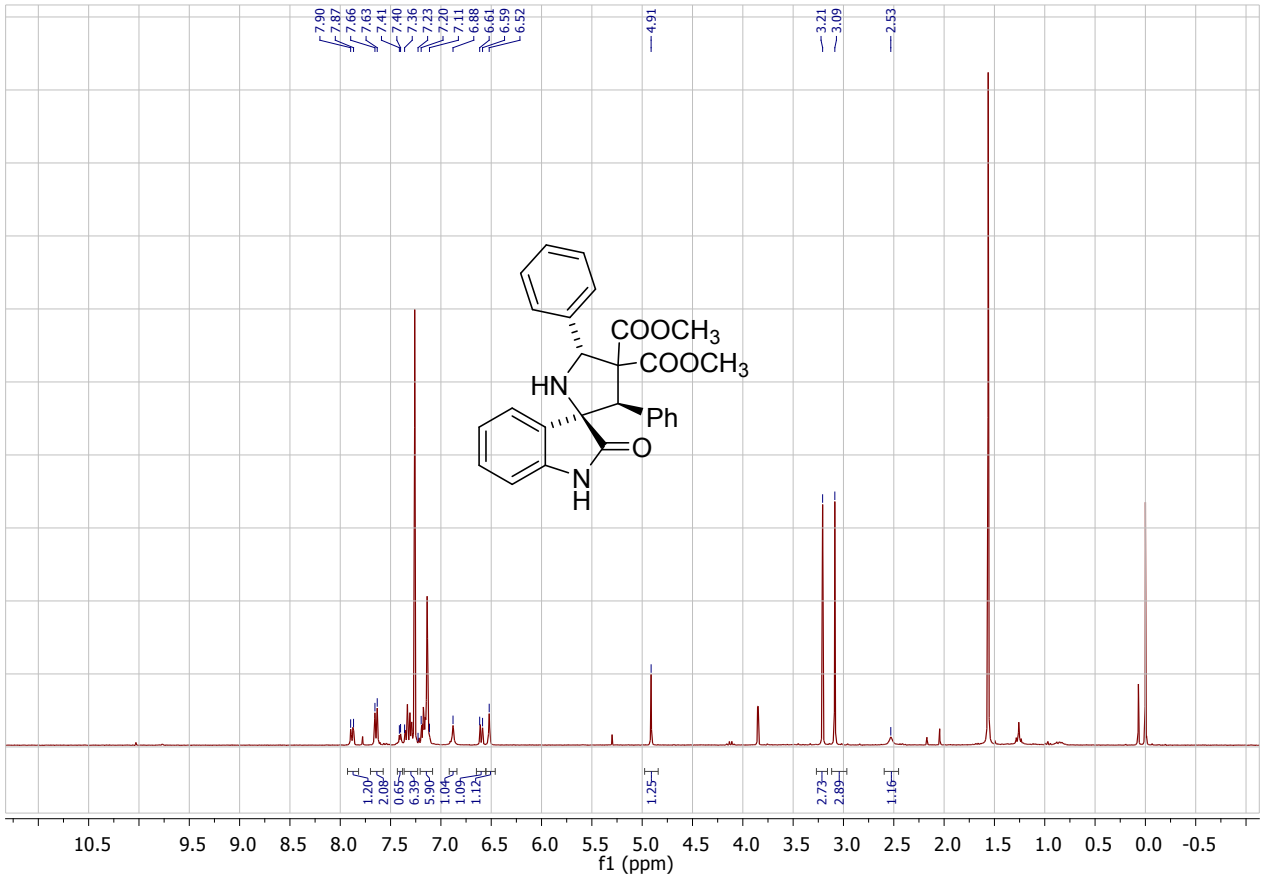
^{1}H NMR of **4m**



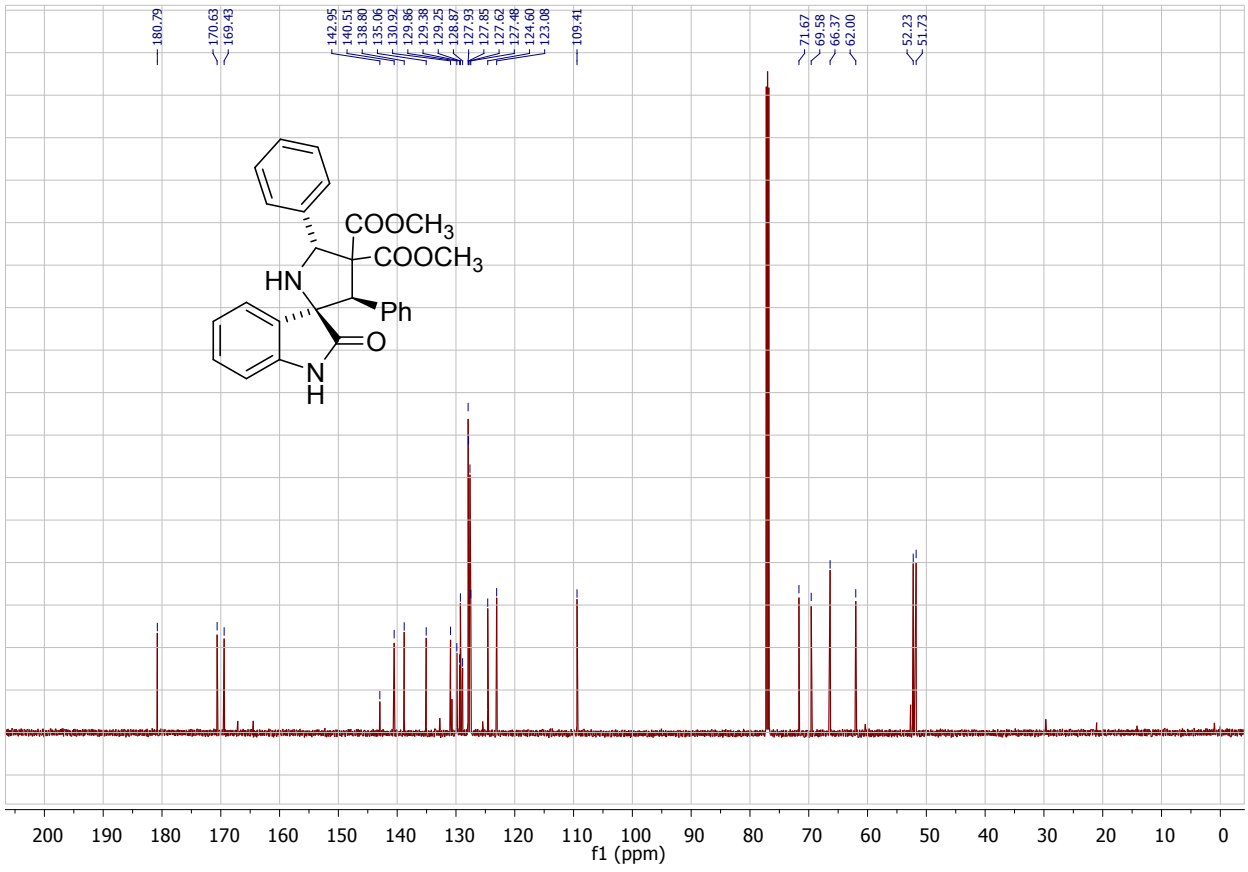
^{13}C NMR of **4m**



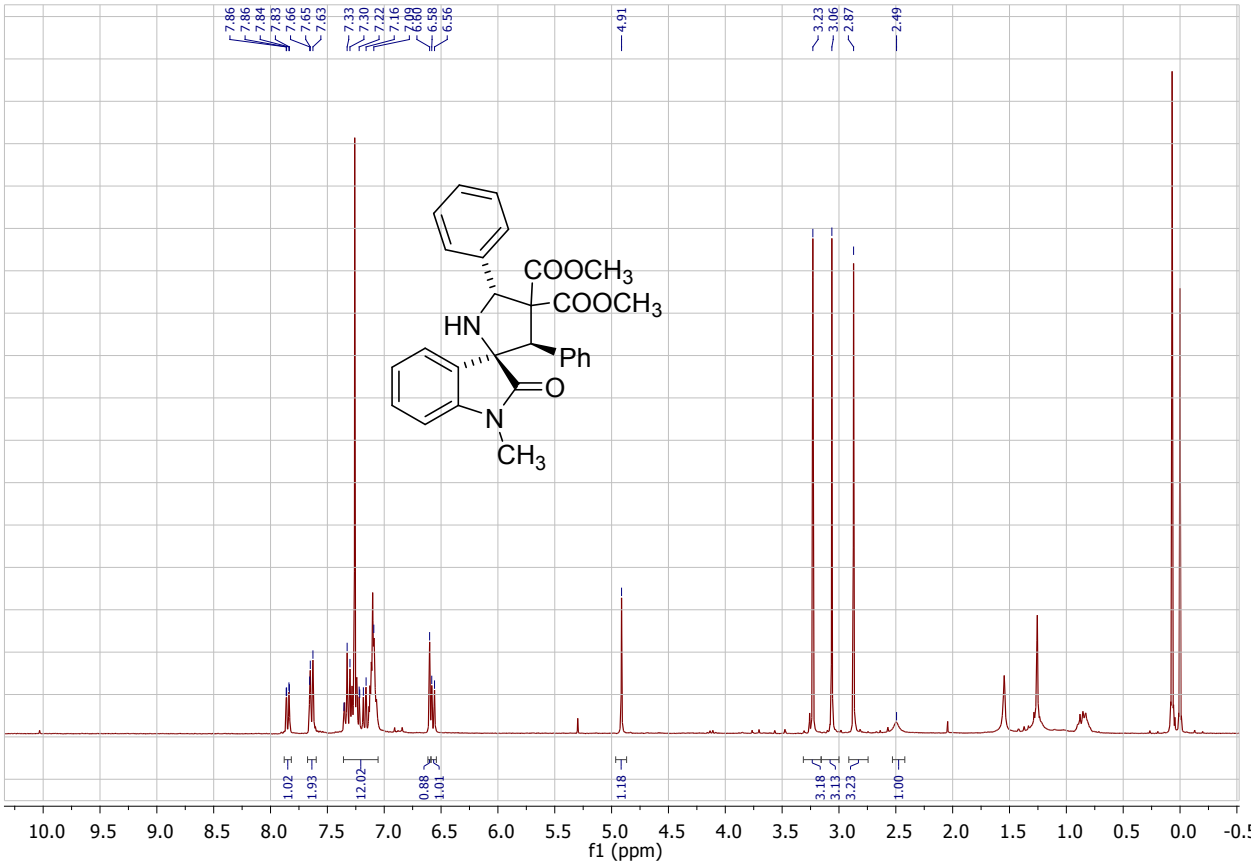
^{1}H NMR of **8a**



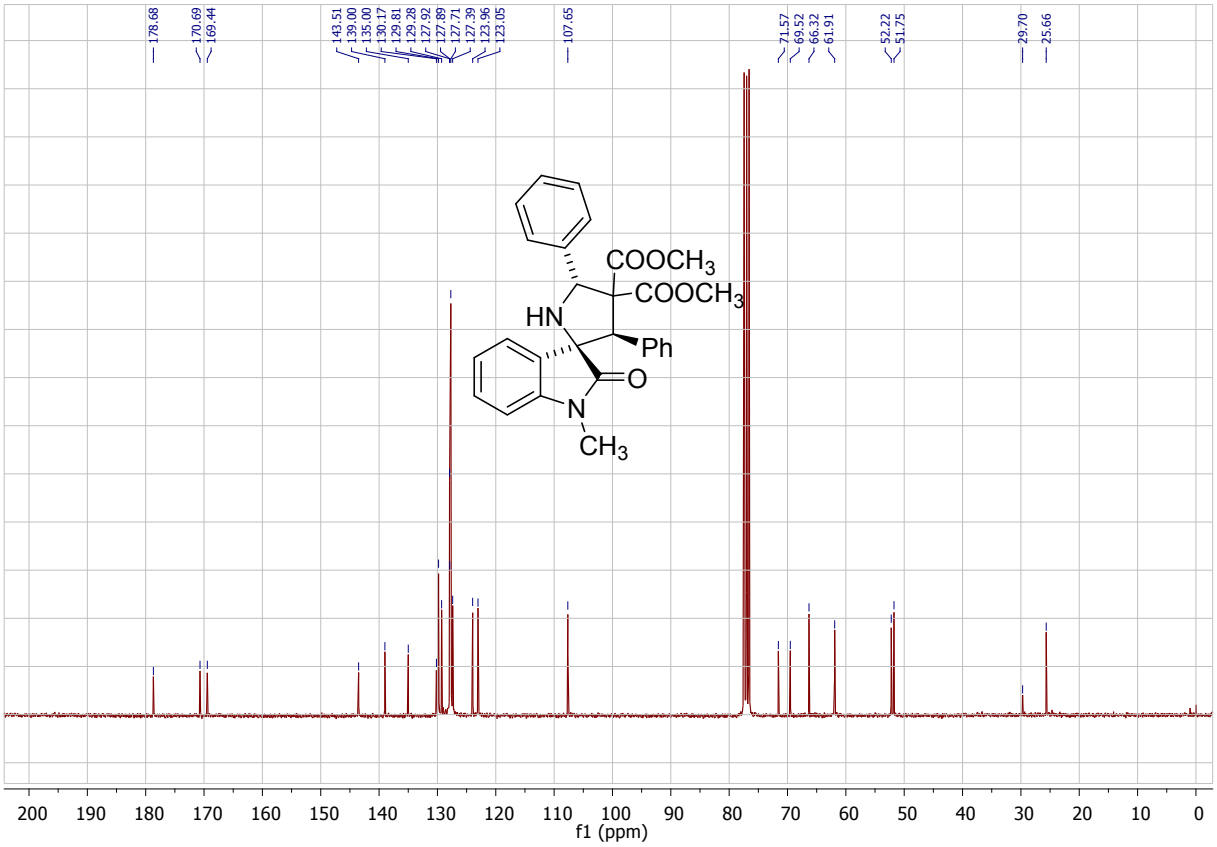
^{13}C NMR of **8a**



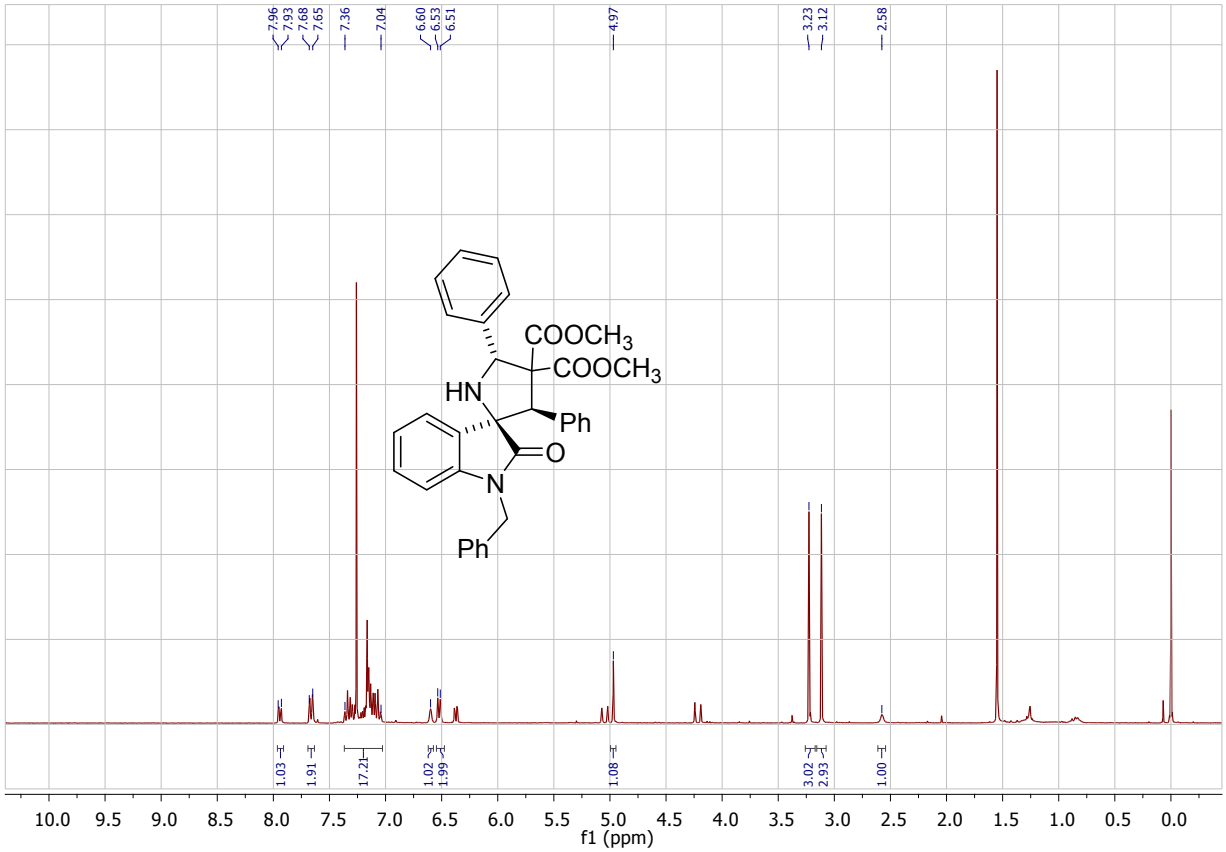
^{1}H NMR of **8b**



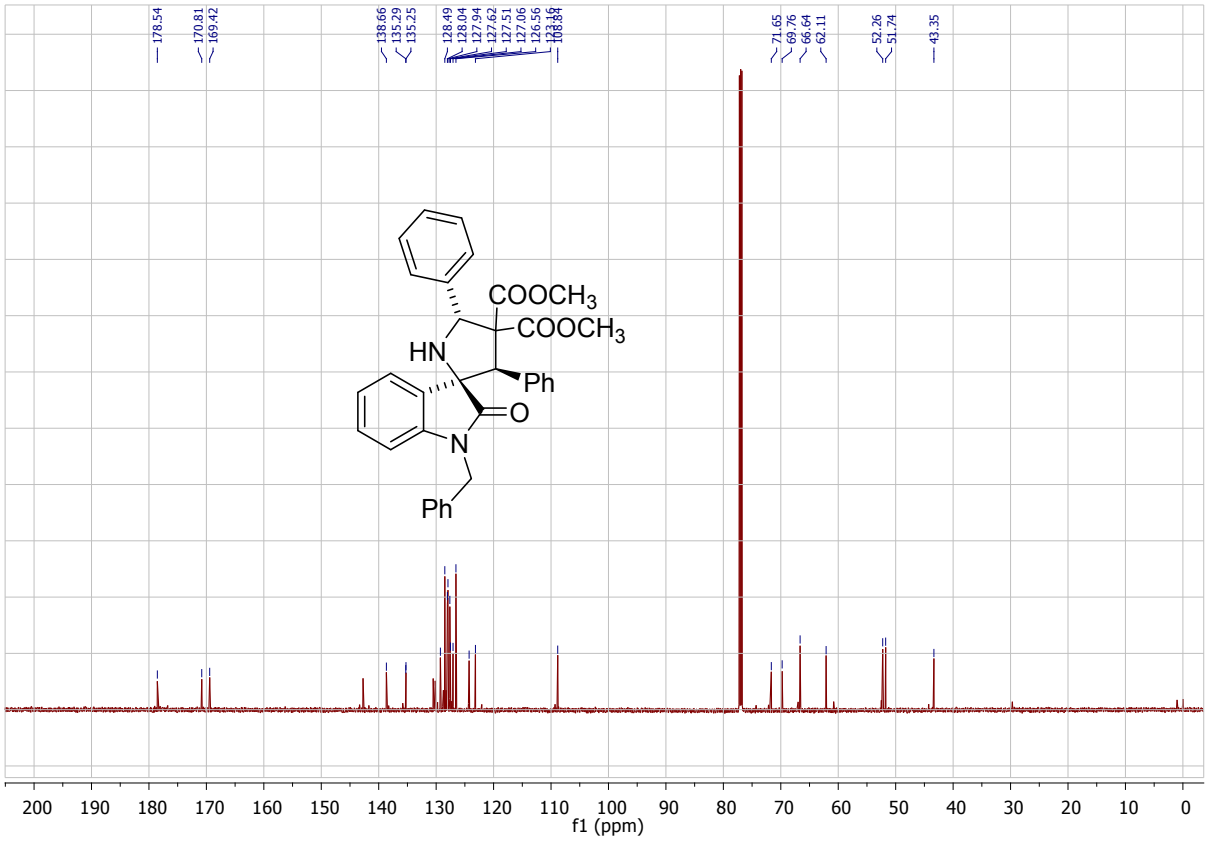
^{13}C NMR of **8b**



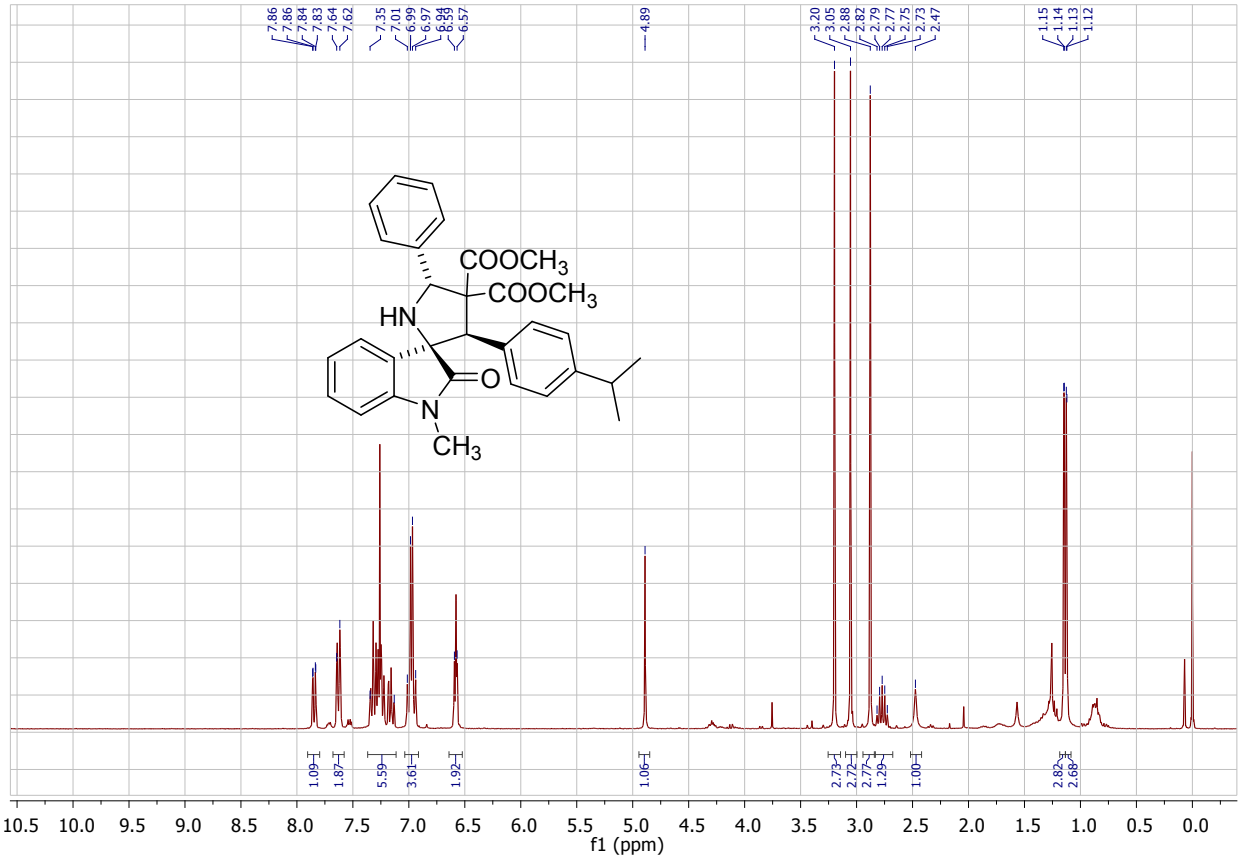
^{1}H NMR of **8c**



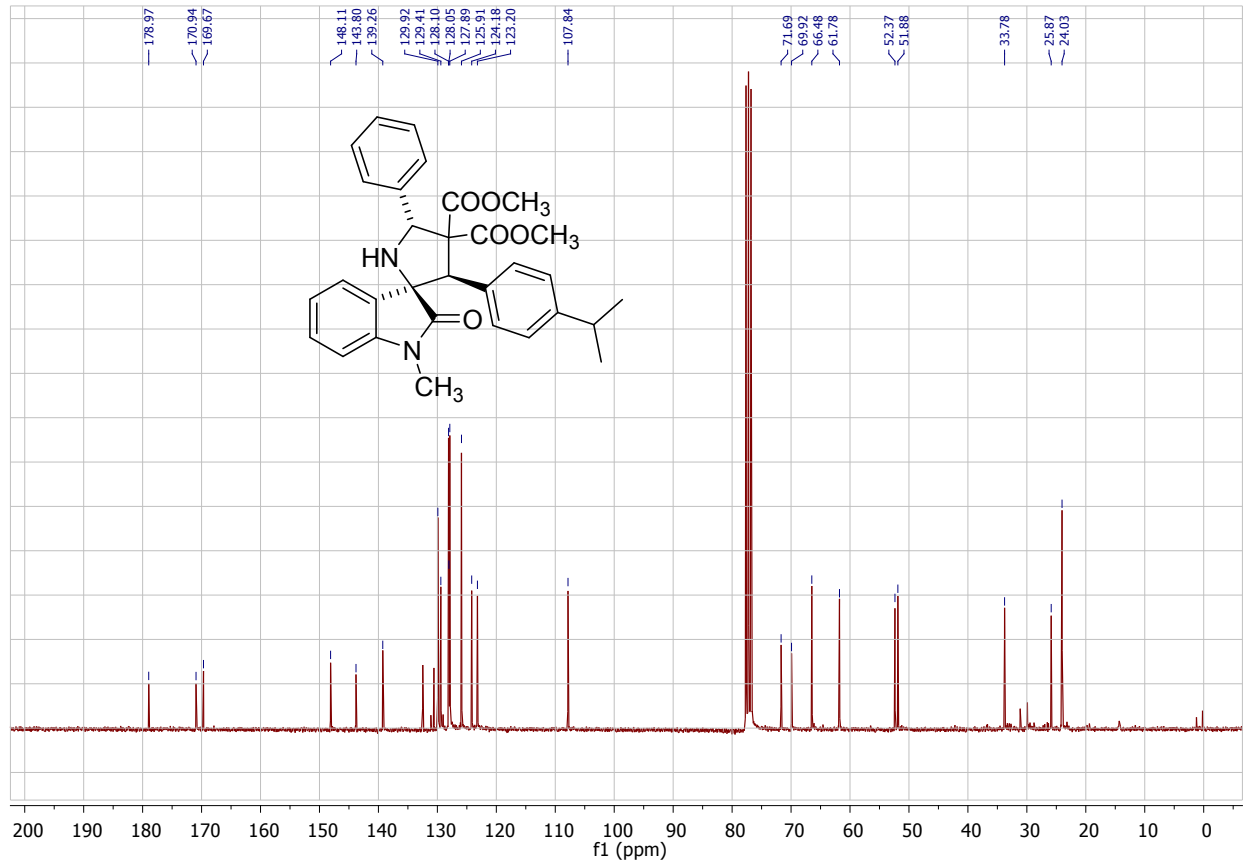
^{13}C NMR of **8c**



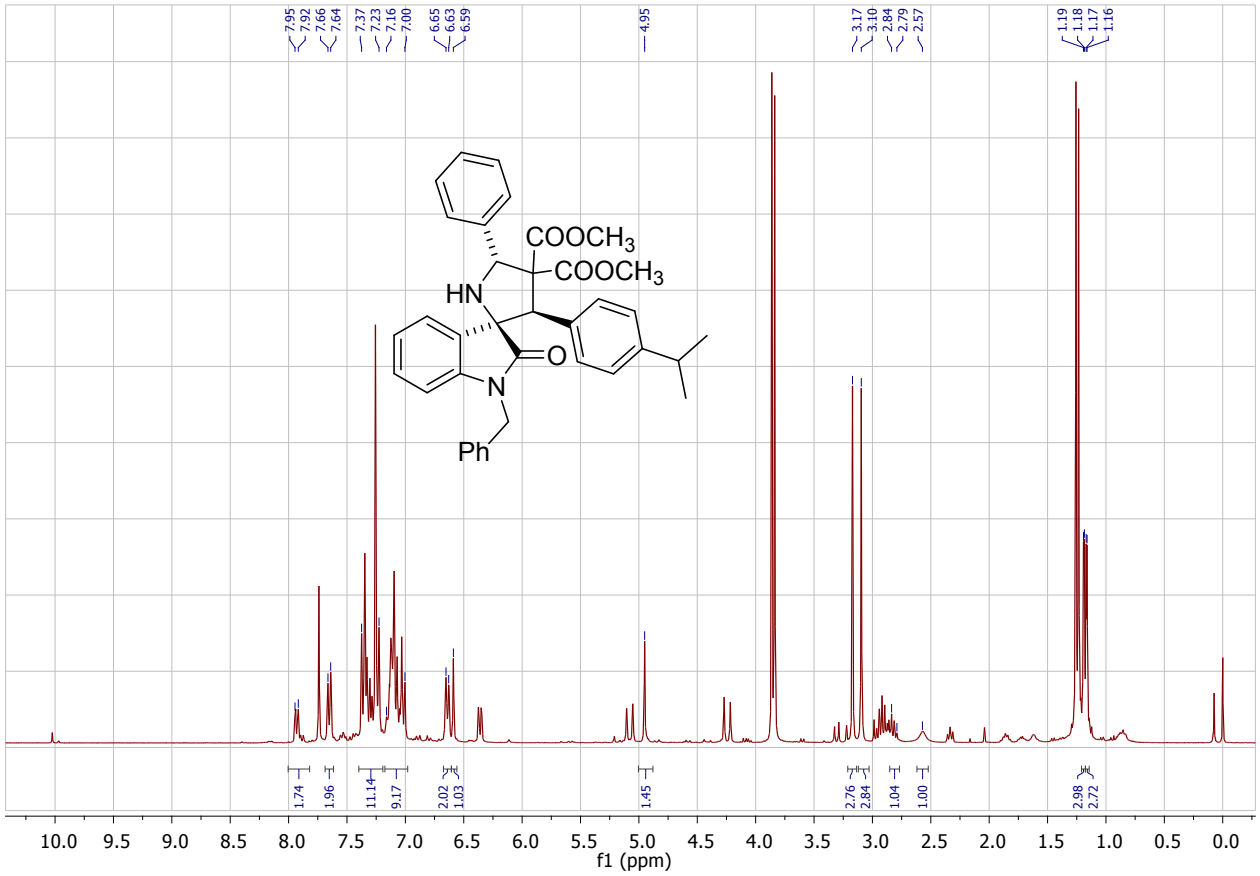
^{1}H NMR of **8d**



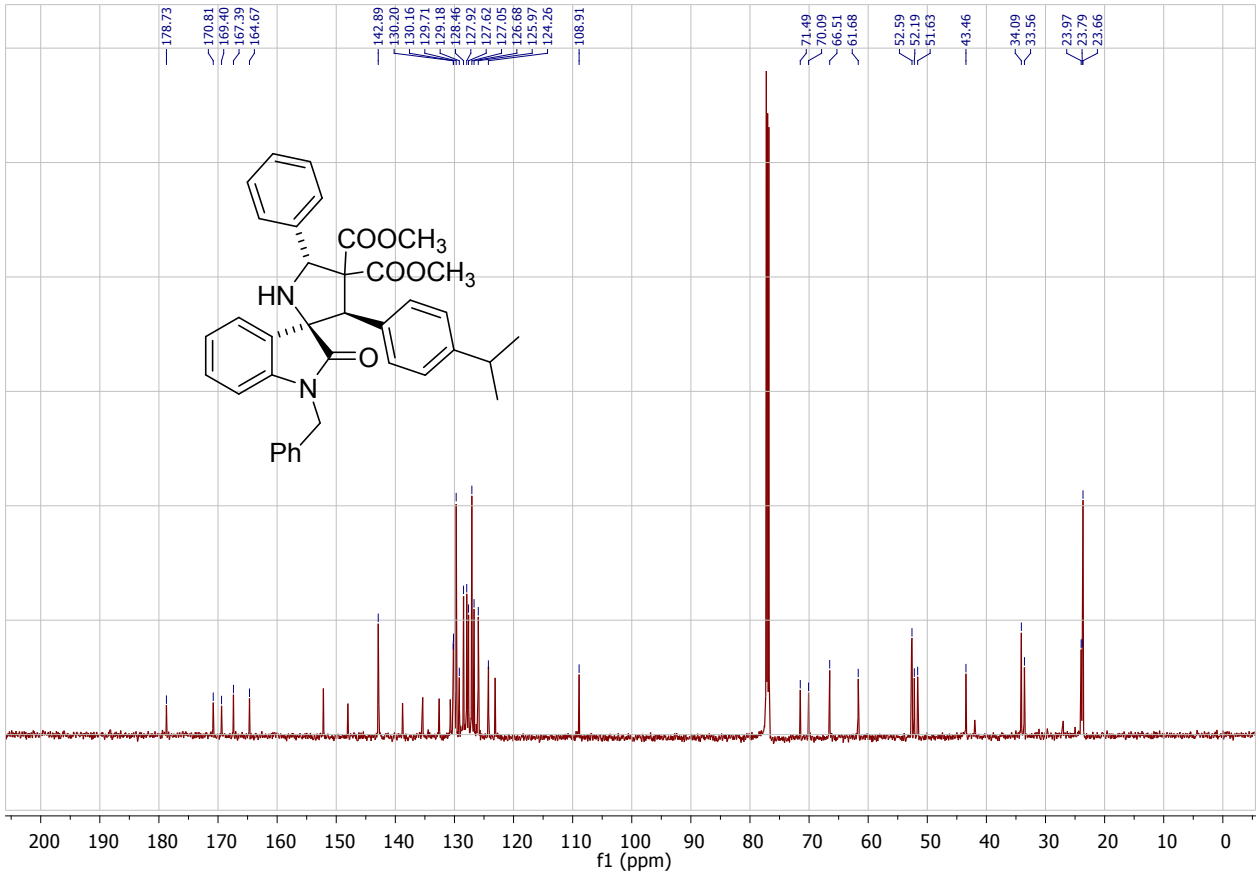
^{13}C NMR of **8d**



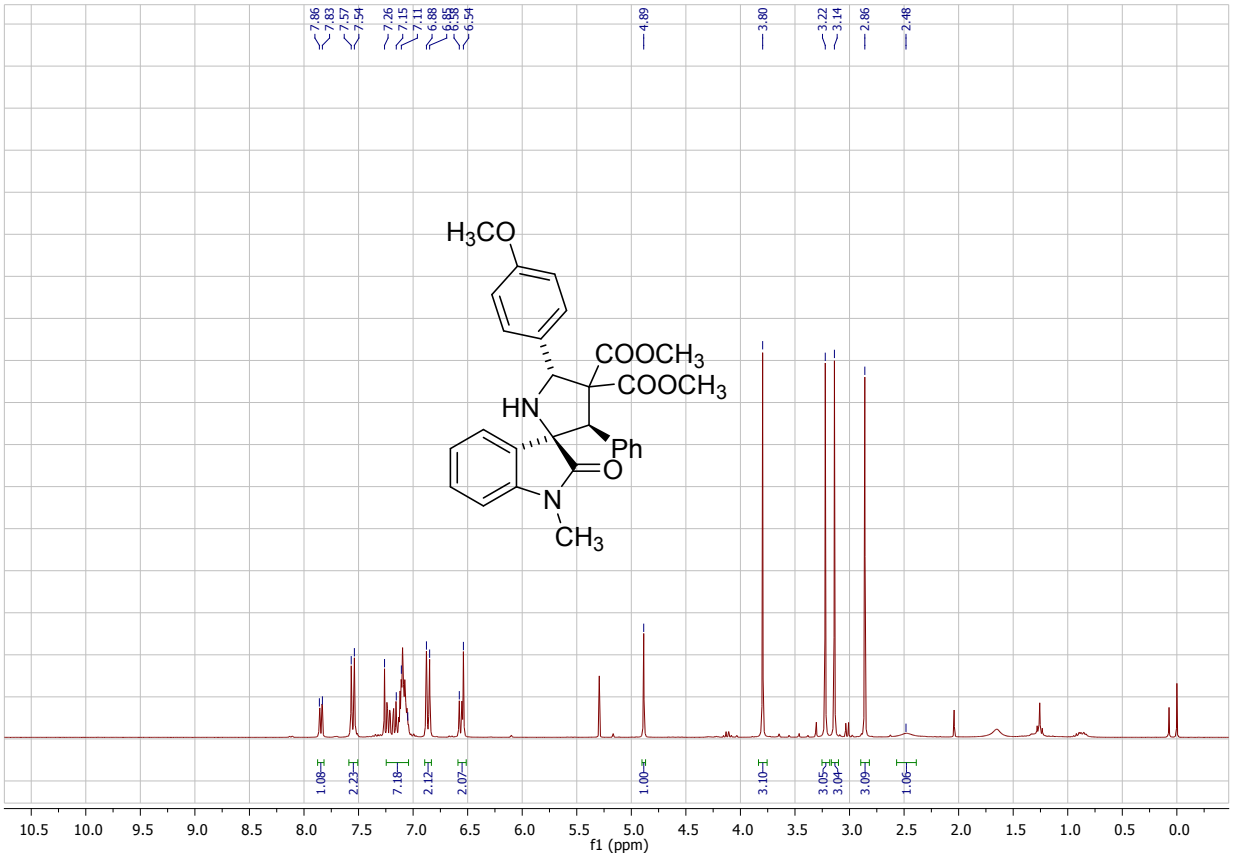
^{1}H NMR of **8e**



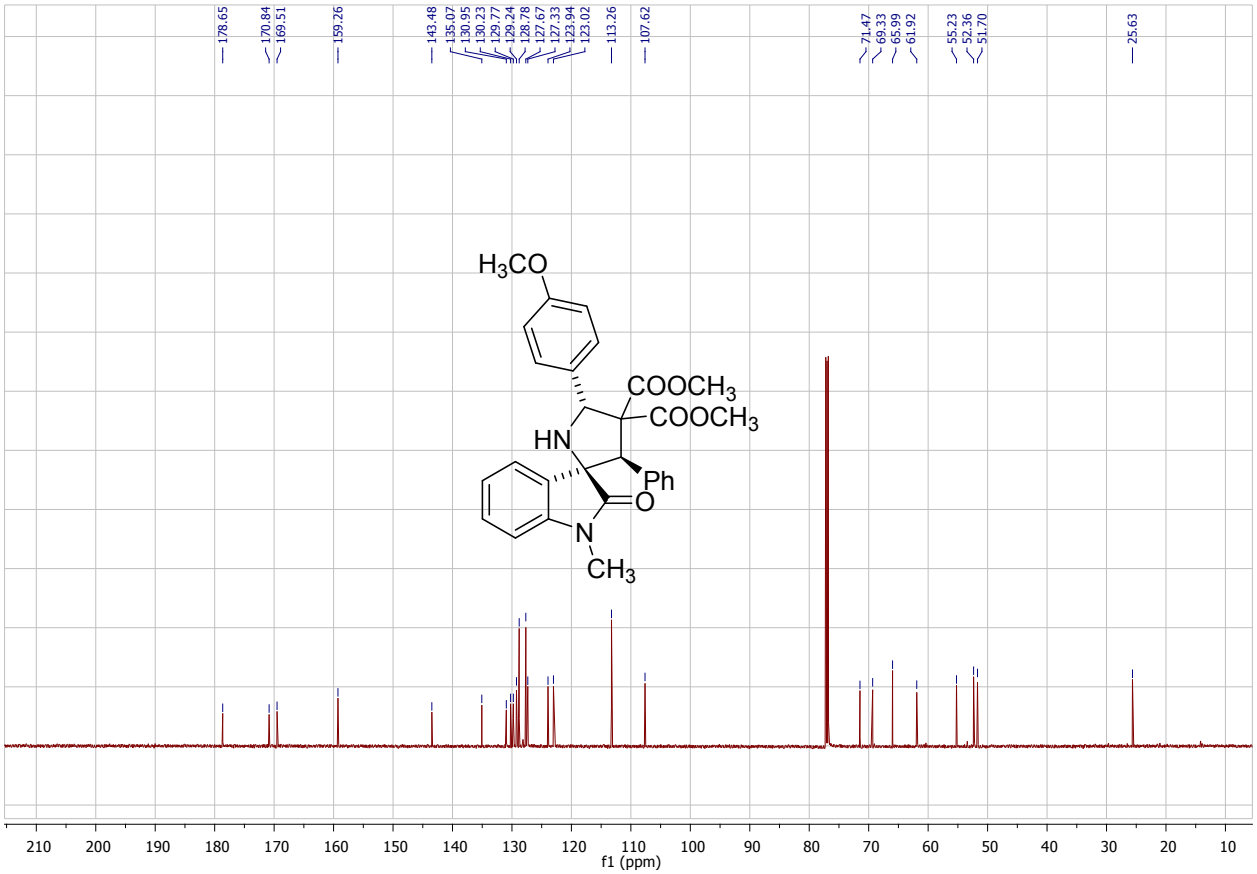
^{13}C NMR of **8e**



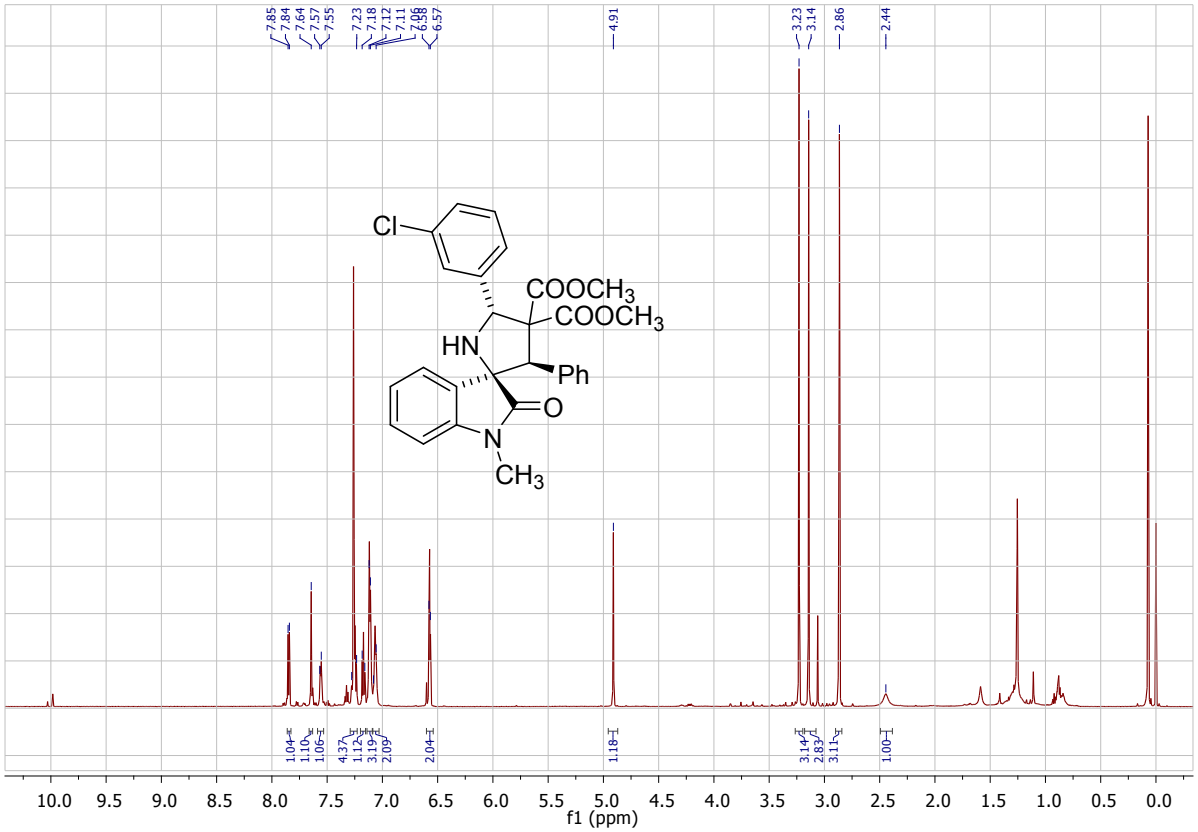
^{1}H NMR of **8f**



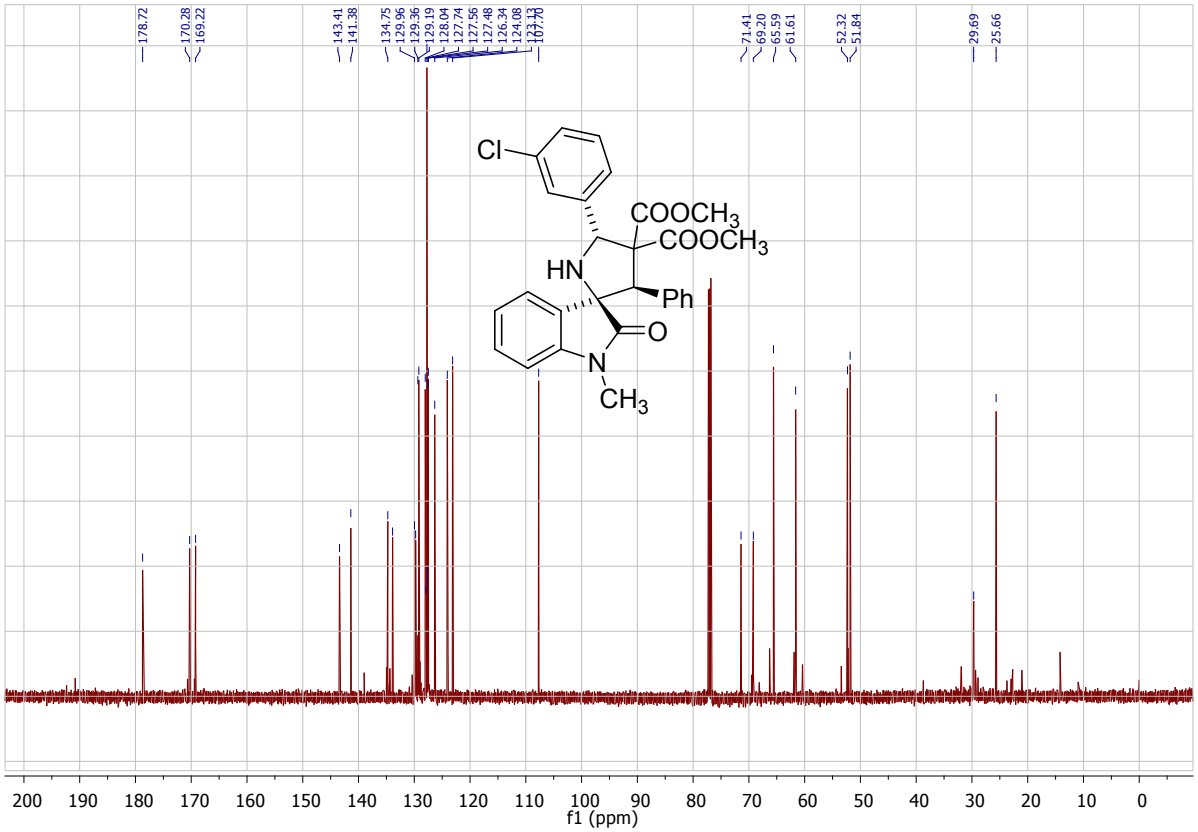
^{13}C NMR of **8f**



^{1}H NMR of **8g**

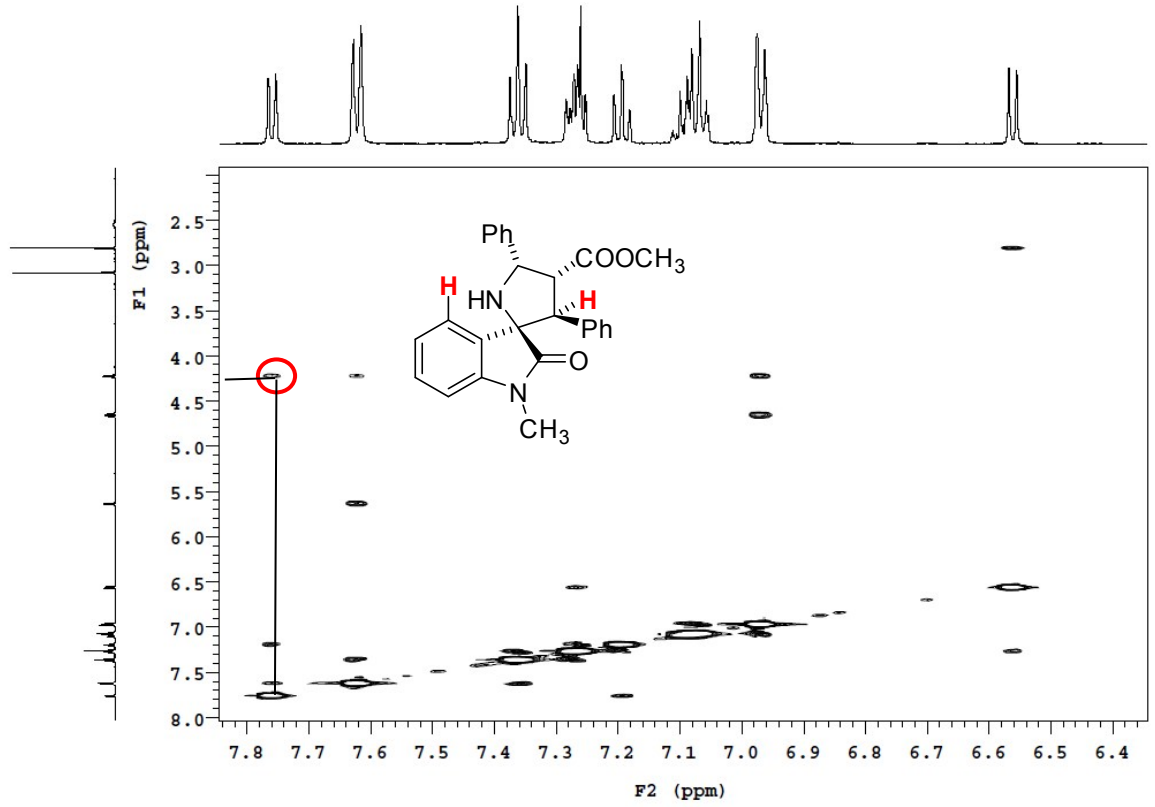


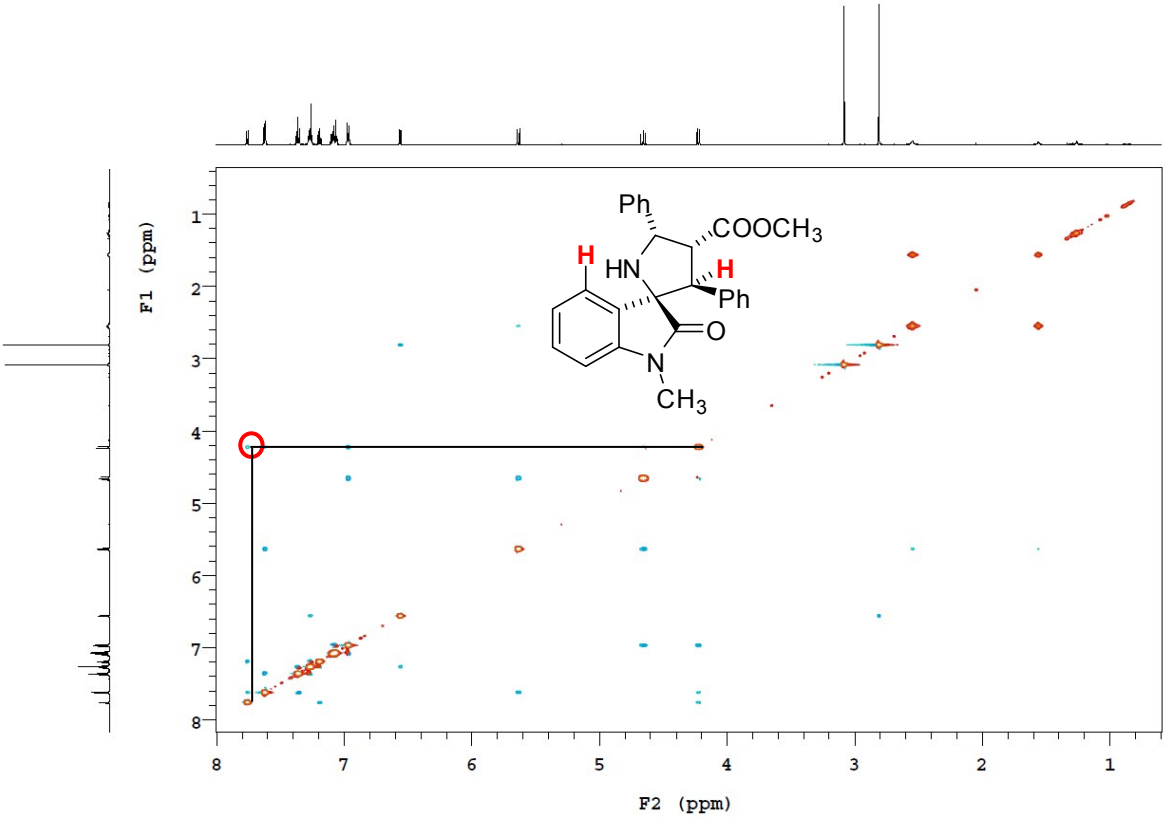
^{13}C NMR of **8g**



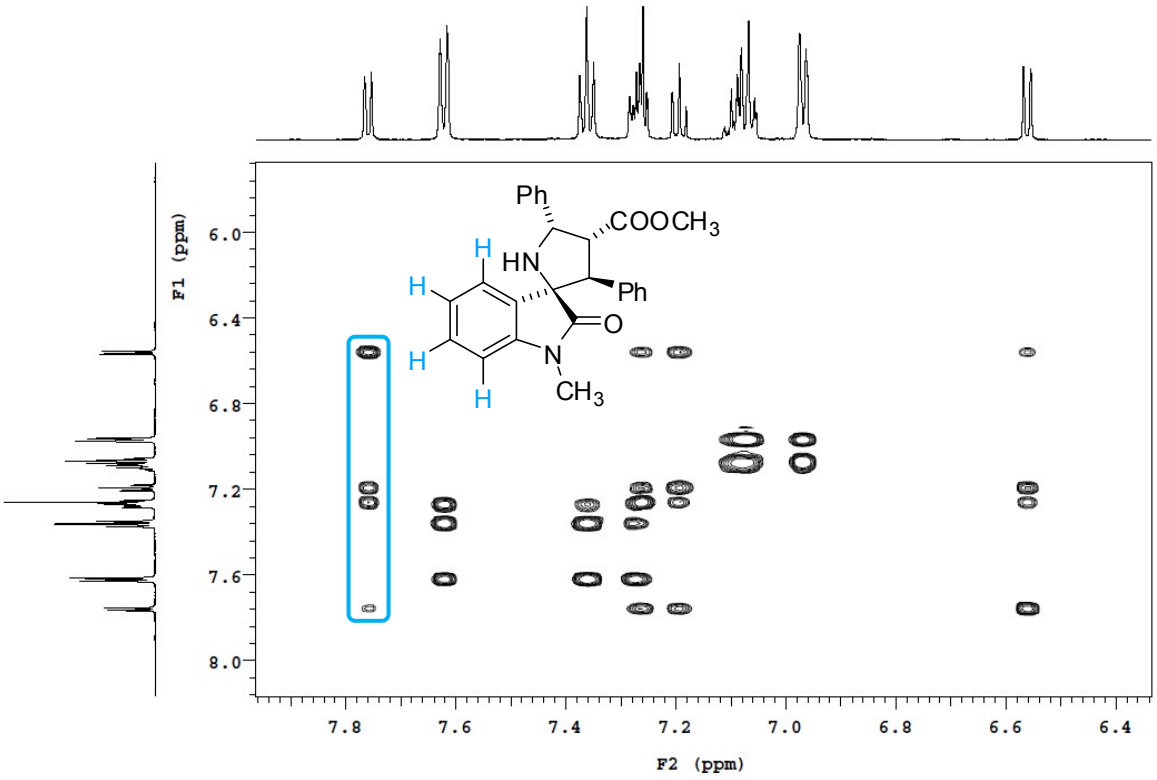
NMR data for the determination of relative configuration of compound 4b and 8b

2D NMR ^{1}H-^{1}H NOESY (**4b**)

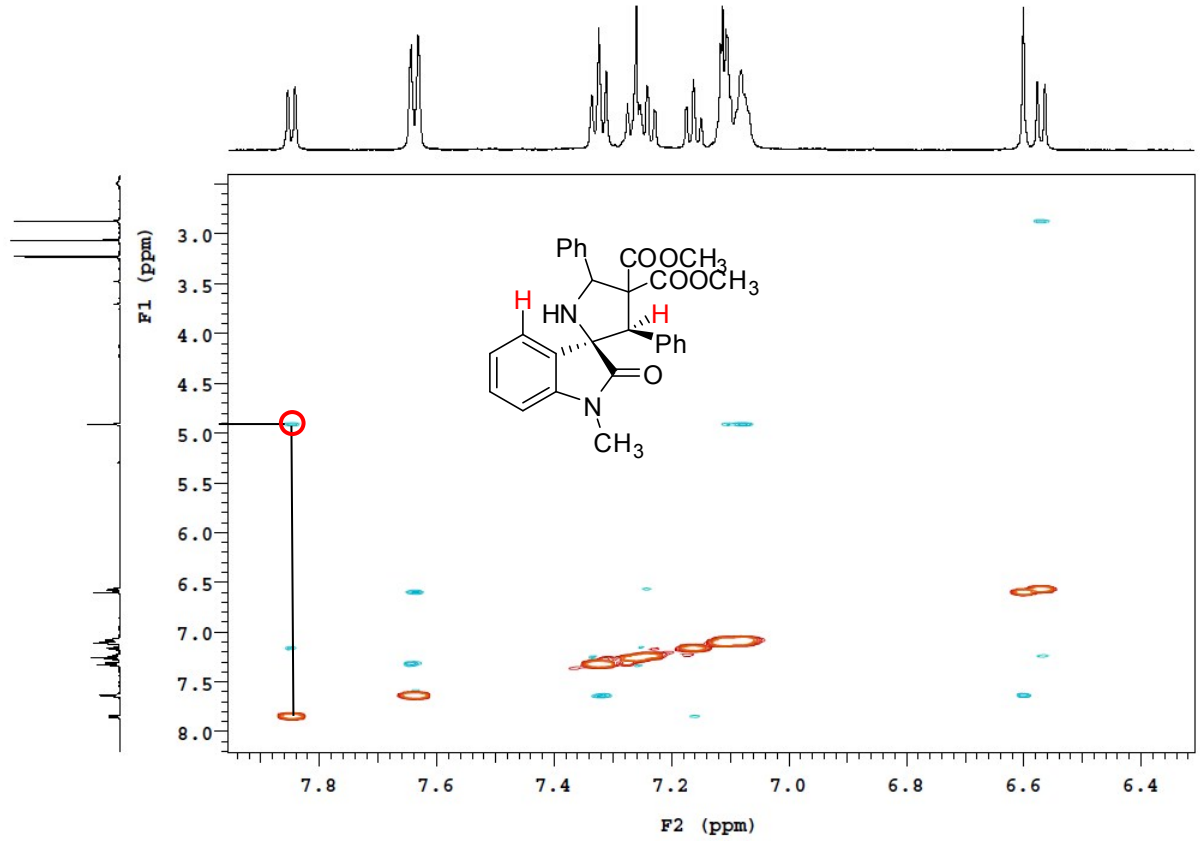


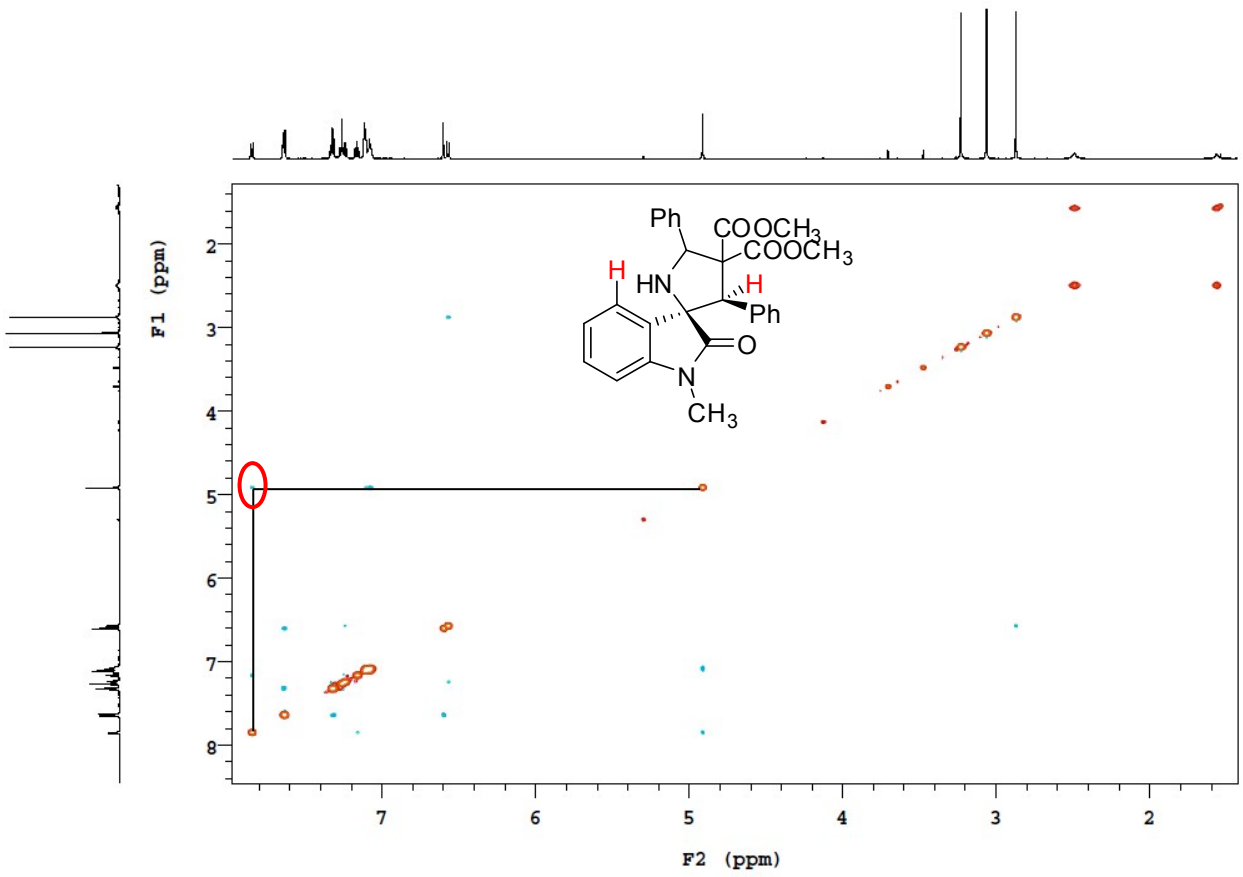


2D NMR ^{1}H-^{1}H TOCSY (**4b**)



2D NMR ^{1}H-^{1}H NOESY (**8b**)

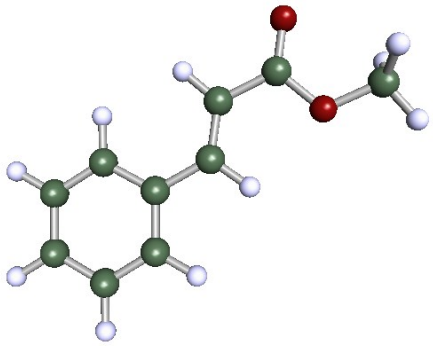




Computational details

Structures were fully geometrically optimized using dispersion corrected DFT calculations at the B3LYP-D3(BJ)/def2-SVP level of theory[20] using Turbomole 7.0 program.[21]

Methyl cinnamate



Cartesian coordinates

C	0.08613255	-0.43581106	2.16239627
C	0.24444464	-1.77485143	7.31896823
C	0.31886877	1.42152109	4.05394959
C	-0.06490633	-2.98797640	2.91447223
C	0.01325285	-3.64630006	5.46094892
C	0.39738095	0.76290609	6.60651476
C	0.01040808	0.36308304	-0.48639952
C	-0.21336564	-1.13118492	-2.53665164
C	-0.28628963	-0.18997663	-5.16175935
O	-0.50734669	-1.53978236	-6.99649493
O	-0.08359083	2.35279955	-5.32732564
C	-0.15423994	3.37790074	-7.81431759
H	-0.36774752	-3.18496042	-2.40355525
H	-0.24508408	-4.46937204	1.48975342
H	-0.10624886	-5.63406307	6.00794953
H	0.30467292	-2.29881852	9.31556550
H	0.57809203	2.23474594	8.04388705
H	0.43780404	3.40829507	3.49915910
H	0.14993852	2.40008020	-0.81285772
H	-1.95150508	2.91775865	-8.75749155

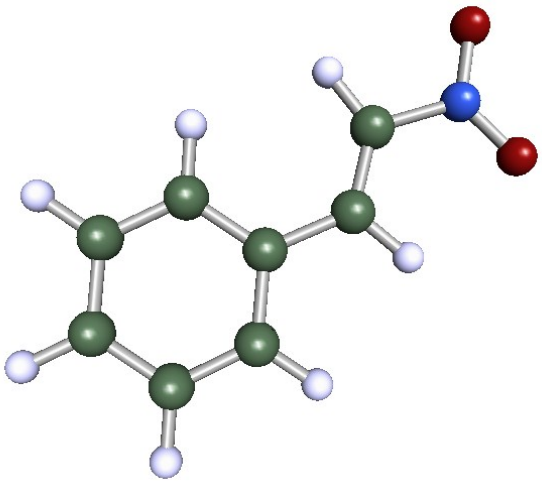
[20] DFT-D3(BJ): a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys*. **2010**, *132*, 154104; b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem*. **2011**, *32*, 1456-1465; B3LYP: Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648-5652; Lee, C.; Yang, W.; R.G. Parr *Phys. Rev. B* **1988**, *37*, 785-789; (1) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem*. **1994**, *98*, 11623-11627; Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys*. **1980**, *58*, 1200-1211; DFT implenetation and basis set in Turbomole: Treutler, O.; Ahlrichs, R. *J. Chem. Phys*. **1995**, *102*, 346-354; Von Arnim, M.; Ahlrichs, R. *J. Comp. Chem*. **1998**, *19*, 1746-1757; Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. Chem. Phys. Lett. 1995, 242, 652-660; Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. Theor. Chem. Acc. 1997, 97, 119-124.

[21] TURBOMOLE V7.0 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

H	1.39921410	2.62264092	-8.97486920
H	0.03992619	5.43155459	-7.60184222

There are no imaginary frequencies.
SCF energy: -536.8623018 hartree
zero-point correction: +0.176887 hartree
enthalpy correction: +0.188899 hartree
free energy correction: +0.138554 hartree

Nitrostyrene

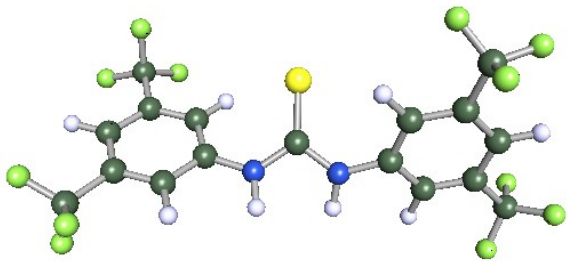


Cartesian coordinates

C	0.13530405	-0.42923195	0.15722932
C	0.20334717	-1.14968388	5.42742430
C	0.79455087	-2.78602098	1.20372782
C	-0.48831852	1.56720278	1.80971907
C	-0.45305415	1.20730561	4.41479875
C	0.82733541	-3.14540672	3.81531021
C	0.12680656	-0.16392690	-2.58958502
C	-0.48487070	1.90586649	-3.92010915
N	-0.40163497	1.86910251	-6.67224744
O	0.24359988	-0.06553998	-7.75792793
O	-1.00473361	3.84351284	-7.71757661
H	-1.08036283	3.73629304	-3.19772827
H	0.67037545	-1.82011957	-3.70215051
H	1.28240440	-4.34510657	-0.06015407
H	-1.00176113	3.41504584	1.04874927
H	-0.93836412	2.77147932	5.67210618
H	1.34139228	-4.98694259	4.59420902
H	0.22779499	-1.42382926	7.47401610

There are no imaginary frequencies.
SCF energy: -513.5218704 hartree
zero-point correction: + 0.137006 hartree
enthalpy correction: + 0.147007 hartree
free energy correction: + 0.101333 hartree

Schreiner´s thiourea



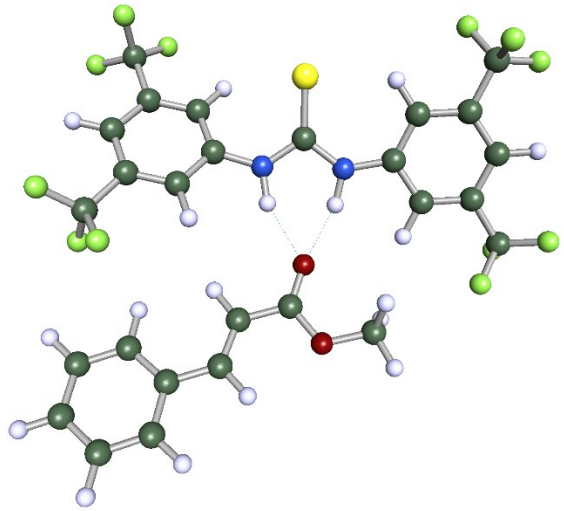
Cartesian coordinates

C	-4.65272272	6.99681652	-1.36431635
C	-1.50004298	6.15186315	2.74655116
C	-3.57331393	4.61407524	-1.02976631
C	-4.19674471	8.96297373	0.33833847
C	-2.62432408	8.51247818	2.40602871
C	-1.97003431	4.18522449	1.03695540
N	-0.88457018	1.81605912	1.54944373
C	0.02822855	0.02686789	-0.11974308
S	0.33894830	0.44340876	-3.20715641
N	0.64173176	-2.15981668	1.16839297
C	1.85766049	-4.34805248	0.27832542
C	4.28003211	-8.85053758	-1.18285695
C	3.83156597	-4.28039222	-1.48726458
C	1.10871357	-6.67424832	1.30227626
C	2.31576250	-8.90184618	0.57701504
C	5.01848383	-6.52801962	-2.19432227
C	7.24136828	-6.40458407	-3.98019374
C	1.39562814	-11.39918178	1.60020983
C	-6.29663603	7.45963187	-3.65255657
C	-2.20406846	10.54805478	4.35729349
F	9.38431367	-5.83974789	-2.72907011
F	6.92197082	-4.62310454	-5.75398879
F	7.62359059	-8.61826805	-5.16042662
F	3.28780003	-13.07018070	1.84291268
F	-0.33525723	-12.44374662	0.06009664
F	0.30379140	-11.13205793	3.88038409
F	-4.90292869	8.10744787	-5.67369053
F	-7.95660447	9.33746489	-3.24989408
F	-7.61871400	5.38703509	-4.28577949
F	-3.88489667	10.35829886	6.25833778
F	-2.44652104	12.86838654	3.36861404
F	0.10953045	10.38222068	5.39662561
H	-5.06046100	10.81178196	0.06294673
H	-0.23662071	5.84656876	4.34996208
H	-3.97799137	3.10049267	-2.35862824

H	-0.34785763	1.58372696	3.37720464
H	-0.24236949	-2.39401301	2.85574985
H	4.43031725	-2.49238847	-2.30425621
H	5.22378157	-10.58890054	-1.75501067
H	-0.43016163	-6.75141342	2.67506742

There are no imaginary frequencies.
SCF energy: -2356.0724040 hartree
zero-point correction: + 0.242808 hartree
enthalpy correction: + 0.271832 hartree
free energy correction: + 0.177305 hartree

Schreiner´s thiourea + cinnamate



Cartesian coordinates

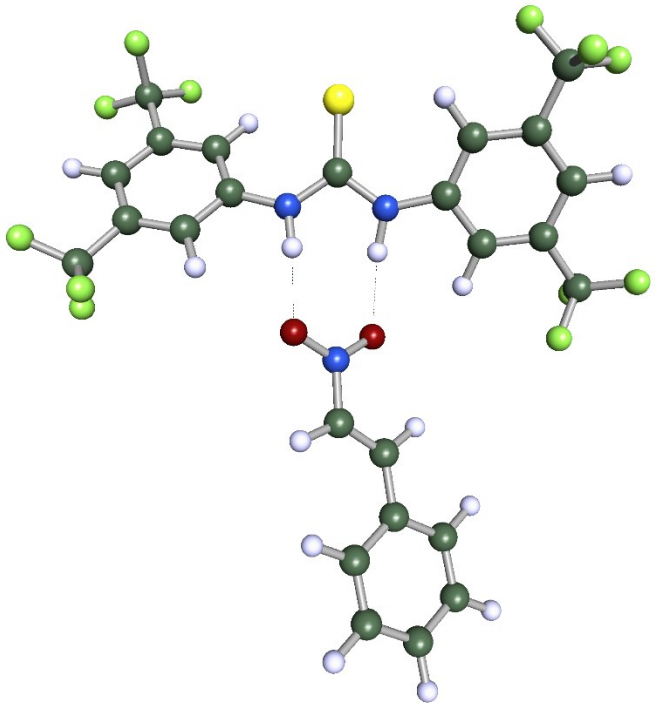
C	-2.02064002	8.63882117	-2.80141752
C	-0.61570334	5.04074404	0.74828112
C	-1.44043936	6.19481263	-3.60040324
C	-1.93952285	9.31351827	-0.24940297
C	-1.24590375	7.48405413	1.51868983
C	-0.71756773	4.36394763	-1.81740380
N	-0.18371786	1.84875370	-2.42889333
C	0.89833992	0.83636374	-4.57814919
S	1.95303332	2.53388718	-7.01063971
N	0.99996501	-1.74883216	-4.35987433
C	2.00790370	-3.65247892	-5.88118748
C	3.94044959	-7.86681023	-8.53946871
C	3.28002307	-3.31076531	-8.18519323
C	1.70156234	-6.12593555	-4.94745840
C	2.65706615	-8.19591532	-6.25473067
C	4.22707025	-5.41525406	-9.47007917
C	5.70629340	-4.98601589	-11.87302364
C	2.18964668	-10.80864333	-5.22400439

C	-2.68316429	10.62671206	-4.73962158
C	-1.26406466	8.12595368	4.29193612
F	8.13689874	-4.43136767	-11.36711957
F	4.76750762	-3.05957640	-13.22875578
F	5.70605831	-7.04694546	-13.35849581
F	3.92795385	-12.47227878	-6.01477711
F	-0.08433695	-11.70118907	-5.92617891
F	2.21988502	-10.82603312	-2.66626836
F	-0.63747077	11.97542306	-5.41273206
F	-4.39091372	12.27635647	-3.82883129
F	-3.64679051	9.61139181	-6.85285523
F	-3.57304505	7.69280766	5.32279903
F	-0.72324598	10.56054916	4.71990624
F	0.38732080	6.71702642	5.61303562
H	-2.41229407	11.22721125	0.34629954
H	-0.00590799	3.65209845	2.14492187
H	-1.54459629	5.70222386	-5.59058448
H	-0.48322389	0.59642279	-0.98737373
H	0.27060895	-2.44450009	-2.71633038
H	3.51102522	-1.41682522	-8.94703916
H	4.69577604	-9.48193598	-9.56814130
H	0.70406931	-6.40864977	-3.16754894
C	-2.09935549	0.19173615	9.32344429
C	-3.23102205	3.66764393	13.18413304
C	-1.75632327	-0.45587831	11.88349928
C	-3.03651829	2.61663868	8.73895207
C	-3.58574068	4.33805281	10.64750567
C	-2.32043878	1.26502323	13.79845478
C	-1.43116081	-1.64800268	7.38179282
C	-1.57173454	-1.30864609	4.85366250
C	-0.77102617	-3.18321533	2.98575296
O	-0.10843083	-5.41795127	3.93757478
C	0.75034945	-7.31559881	2.21345885
O	-0.69770047	-2.73174611	0.70863016
H	-2.26435513	0.44998210	4.03009000
H	-3.33252324	3.17724951	6.78033594
H	-4.27967456	6.21483763	10.14470424
H	-3.66283615	5.02417510	14.68012751
H	-2.04145208	0.73544506	15.77428640
H	-1.02937023	-2.33004483	12.36086857
H	-0.71530698	-3.46601423	8.06041131
H	1.29166523	-8.94278860	3.37467005
H	2.38535991	-6.64206435	1.12250953
H	-0.76887997	-7.85871628	0.90324930

There are no imaginary frequencies.
SCF energy: -2892.9738001 hartree
zero-point correction: + 0.422026 hartree

enthalpy correction: + 0.463826 hartree
free energy correction: + 0.336433 hartree

Schreiner´s thiourea + nitrostyrene



Cartesian coordinates

C	-4.49172386	8.09174777	-6.33735102
C	-2.01761394	7.04207564	-1.83334855
C	-3.29822560	5.75905387	-6.03452232
C	-4.48470488	9.90849114	-4.42471860
C	-3.24682478	9.34862270	-2.16237236
C	-2.02727561	5.21865068	-3.76817581
N	-0.84023323	2.91781992	-3.23725341
C	0.10062111	1.07093568	-4.81848897
S	0.39950956	1.34310863	-7.93956518
N	0.75707086	-1.01904058	-3.41316386
C	1.97174519	-3.27819007	-4.04533116
C	4.36672895	-7.98265937	-4.86682569
C	3.36946746	-3.70180271	-6.26509657
C	1.80947511	-5.22906769	-2.24623771
C	2.99042153	-7.54485882	-2.66052644
C	4.54288109	-6.03460923	-6.63953392
C	6.15881952	-6.42581700	-8.95877739
C	2.65668586	-9.60942880	-0.72917782
C	-5.74797253	8.67617223	-8.83038881
C	-3.33351659	11.20335143	-0.00178603
F	8.59869873	-5.87902569	-8.47662486
F	5.43195410	-4.96097408	-10.89331691
F	6.08800225	-8.84125338	-9.74955509

F	4.43274717	-11.40679182	-0.93494019
F	0.39623567	-10.75357171	-0.96266055
F	2.76372867	-8.69379921	1.65038504
F	-4.08460710	9.60874196	-10.51104444
F	-7.59146552	10.40665844	-8.56877227
F	-6.78165835	6.60594356	-9.87380121
F	-5.28515618	10.71461798	1.56149058
F	-3.61074525	13.59156884	-0.81292777
F	-1.22267245	11.11157466	1.41298702
H	-5.43112803	11.71764582	-4.68594865
H	-1.04370518	6.64422088	-0.05921988
H	-3.34535756	4.36735808	-7.54306857
H	-0.43773617	2.69239487	-1.36321597
H	0.07764632	-1.03088886	-1.60712482
H	3.50628847	-2.22501270	-7.68519374
H	5.28325076	-9.79637952	-5.19552311
H	0.75752381	-4.91858234	-0.50090579
C	0.02460013	-2.60395961	9.77721752
C	0.40058237	-3.88747217	14.91499927
C	-0.27271927	-5.13053278	10.57479577
C	0.51402077	-0.72643979	11.61056066
C	0.69847853	-1.36723209	14.15187149
C	-0.08432943	-5.76708109	13.12361865
C	-0.19045636	-2.05435065	7.09751816
C	0.10016049	0.21705596	5.97513402
N	-0.15847537	0.45182169	3.28840032
O	-0.78385690	-1.39027574	2.01184654
O	0.27442945	2.54675775	2.37407733
H	0.56615240	2.00919950	6.86622491
H	-0.62573608	-3.64365374	5.84872121
H	-0.65034979	-6.59427486	9.16757101
H	0.74556138	1.24369832	11.04355531
H	1.07451327	0.09846543	15.55584868
H	-0.31641841	-7.73056435	13.71503306
H	0.54685243	-4.37997400	16.91481786

There are no imaginary frequencies.
SCF energy: -2869.6275285 hartree
zero-point correction: + 0.381689 hartree
enthalpy correction: + 0.420778 hartree
free energy correction: + 0.299659 hartree