Supporting Information for

Dual behavior of isatin-based cyclic ketimines with dicarbomethoxy carbene: An expedient synthesis of highly functionalized spirooxindolyl oxazolidines and pyrrolines

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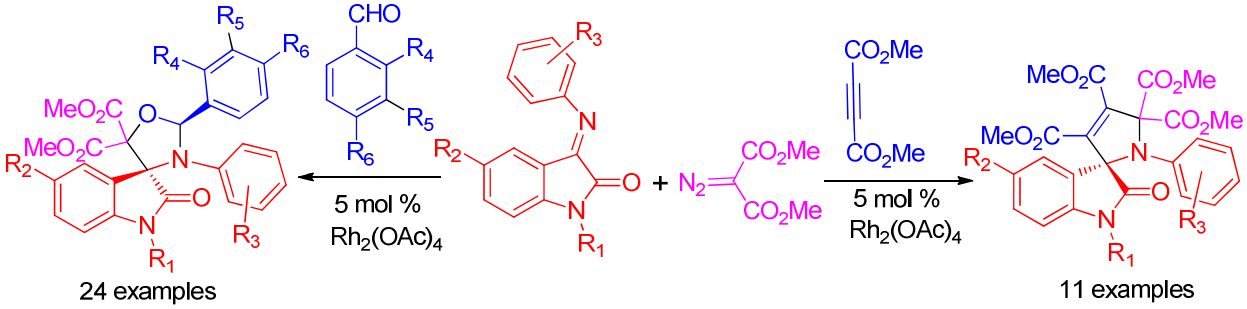

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1. General Information

Unless otherwise noted, reactions were performed in flame-dried glassware under an atmosphere of dry argon. Benzene was dried over Na prior to use. ^{1}H NMR spectra were recorded at 500 MHz, 300 MHz and ^{13}C NMR at 100 MHz. For ^{1}H NMR, tetramethylsilane (TMS) was used as internal standard (δ = 0) and the values are reported as follows: chemical shift, multiplicity, integration (s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet, dd = doublet of doublet), and the coupling constants in Hz. For ^{13}C NMR, $CDCl_3$ (δ = 77.00) was used as internal standard and spectra were obtained with complete proton decoupling. Low-resolution MS and HRMS data were obtained using ESI ionization. IR spectra were recorded on FT-IR spectrometer (KBr) and reported in reciprocal centimeters (cm-1). Melting points were measured on micro melting point apparatus. The dimethyl diazomalonate[1], isatin-3-arylimines[2] and epoxide[3] were prepared according to previously reported procedures.

General procedure for the three-component coupling of dimethyl diazomalonate, aldehyde and ketimine (3CC): To a solution of isatin-3-arylimine (1.2 equiv), aldehyde (1.0 equiv) and dimethyl diazomalonate (1.0 equiv) in dry benzene was added 5 mol % of $Rh_2(OAc)_4$ and the mixture was allowed to stir at 80 ^{o}C for about 20 min under argon atmosphere. After complete consumption of diazomalonate, the solvent was removed under reduced pressure and the resulting mixture was directly charged on silica gel column and eluted with *n*-hexane:ethyl acetate to afford the pure product.

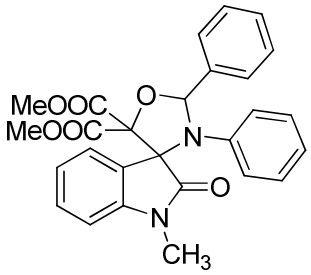
References

1. Tullis, J.S.; Helquist, P. *Org. Syn*. **1997**, *74*, 229.

2. Rajopadhye, M.; Popp, F. D. *J. Heterocycl. Chem*. **1987**, *24*, 1637.

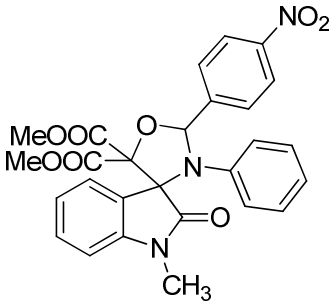
3. Russell, A. E.; Brekan, J.; Gronenberg, L.; Doyle, M. P. *J. Org. Chem*. **2004**, *69*, 5269.

Dimethyl 1-methyl-2-oxo-2',3'-diphenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxy-late (4a):



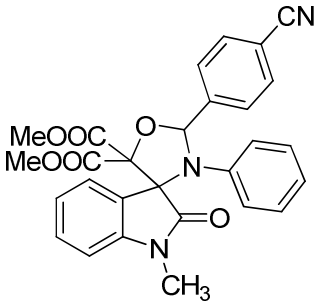
Colourless solid. mp: 188–189 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84-7.78 (m, 2H), 7,47 (d, 1H, *J* = 7.6 Hz), 7.39-7.27 (m, 4H), 7.11 (t, 1H, *J* = 7.6 Hz), 7.07 (s, 1H), 6.91 (t, 2H, *J* = 7.7 Hz), 6.85-6.67 (m, 4H), 3.78 (s, 3H), 3.67 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 167.3, 167.1, 144.7, 140.5, 136.4, 130.7, 129.4, 129.1, 128.3, 128.1 125.1, 124.3, 123.8, 122.5, 108.8, 94.1, 89.9, 75.4, 53.0, 52.8, 25.9; IR (neat) ν_{max} 3064, 2952, 2892, 1766, 1748, 1708, 1611, 1494, 1292, 1119, 766, 699 cm^{-1}; ESI-MS *m/z* 473 $(M+H)^+$; HRMS (ESI) calcd for $C_{27}H_{25}N_2O_6$, 473.1712 $(M+H)^+$; Found, 473.1731.

Dimethyl 1-methyl-2'-(4-nitrophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5', 5'-dicarboxylate (4b):



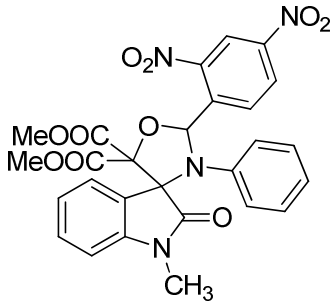
Colourless solid. mp: 201−202 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, 2H, *J* = 8.3 Hz), 8.03 (d, 2H, *J* = 9.0 Hz), 7.45-7.32 (m, 2H), 7.14 (s, 1H), 7.11 (d, 1H, *J* = 9Hz), 6.99-6.86 (m, 3H), 6.79-6.72 (m, 3H), 3.79 (s, 3H), 3.71 (s, 3H), 3.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 167.1, 166.9, 148.5, 144.9, 143.7, 139.4, 131.0., 130.1, 128.6, 125.6, 125.0, 125.0, 123.1, 122.9, 122.5, 108.9, 92.4, 89.7, 75.5, 53.1, 52.9, 25.8; IR (neat) ν_{max} 3060, 2953, 1742, 1707, 1609, 1523, 1493, 1346, 1299, 1237, 1123, 1049, 769, 701 cm^{-1}; ESI-MS *m/z* 518 $(M+H)^+$; HRMS (ESI) calcd for $C_{27}H_{24}O_8N_3$ = 518.1557 $(M+H)^+$; Found, 518.1543.

Dimethyl 2'-(4-cyanophenyl)-1-methyl-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4c):



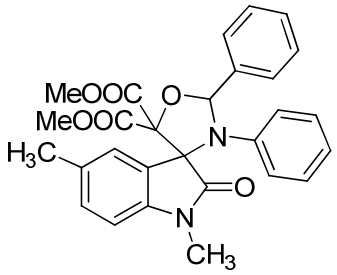
Colourless solid. mp: 196−197 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, 2H, *J* = 8.3 Hz), 7.60 (d, 2H, *J* = 8.1 Hz), 7.44-7.32 (m, 2H), 7.13 (d, 1H, *J* = 7.6 Hz), 7.09 (s, 1H), 6.98-6.86 (m, 3H), 6.77-6.71 (m, 3H), 3.79 (s, 3H), 3.70 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 167.1, 167.0, 144.9, 141.8, 139.5, 131.9, 131.0, 129.9, 128.6, 125.5, 125.1, 124.9, 123.1, 122.6, 113.1, 109.0, 92.9, 89.7, 75.6, 53.1, 53.0, 25.9; IR (neat) ν_{max} 3067, 2948, 2239, 1771, 1750, 1709, 1495, 1372, 1124, 1048, 765, 700 cm^{-1}; ESI-MS *m/z* 498 $(M+H)^+$; HRMS (ESI) calcd for $C_{28}H_{23}O_6N_3Na$ = 520.14791 $(M+Na)^+$; Found, 520.14727.

Dimethyl 2'-(2,4-dinitrophenyl)-1-methyl-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4d):



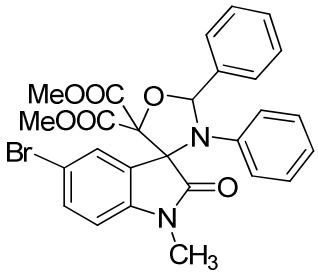
Colourless solid. mp: 123−124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (d, 1H, *J* = 8.7 Hz), 8.66 (d, 1H, *J* = 2.1 Hz), 8.45 (dd, 1H, *J* = 8.7, 2.1 Hz), 7.77 (s, 1H), 7.41-7.35 (m, 2H), 7.12 (t, 1H, *J* =7.5 Hz), 7.01-6.90 (m, 3H), 6.79-6.72 (m, 3H), 3.80 (s, 3H), 3.66 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 167.2, 166.5, 150.4, 148.1, 145.1, 139.1, 138.0, 133.4, 131.3, 129.0, 126.9, 125.8, 124.9, 124.5, 122.7, 122.6, 119.4, 109.2, 90.1, 86.9, 75.3, 53.4, 53.1, 26.1; IR (neat) ν_{max} 3062, 2953, 1743, 1708, 1610, 1523, 1347, 1237, 1124, 769 cm^{-1}; ESI-MS *m/z* 563 $(M+H)^+$; HRMS (ESI) calcd for $C_{27}H_{22}O_{10}N_4Na$ = 585.1228 $(M+H)^+$; Found, 585.1219.

Dimethyl 1,5-dimethyl-2-oxo-2',3'-diphenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4e):



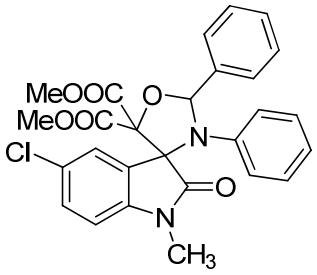
Colourless solid. mp: 151−152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.82 (dd, 2H, *J* = 1.9, 7.7 Hz), 7.37-7.27 (m, 4H), 7.16 (d, 1H, *J* = 7.9 Hz), 7.06 (s, 1H), 6.91 (t, 2H, *J* = 7.9 Hz), 6.81 (t, 1H, *J* = 7.2 Hz), 6.66 (t, 3H, J = 7.6 Hz), 3.78 (s, 3H), 3.67 (s, 3H), 3.03 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 167.2, 167.1, 142.3, 140.5, 136.3, 131.9, 130.9, 129.3, 128.9, 128.2, 128.0, 125.6, 124.1, 124.0, 123.5, 108.5, 93.9, 89.7, 75.3, 52.9, 52.7, 25.9, 20.97; IR (neat) ν_{max} 2952, 1747, 1710, 1601, 1501, 1433, 1232, 1118, 1046, 696 cm^{-1}; ESI-MS *m/z* 487 $(M+H)^+$; HRMS (ESI) calcd for $C_{28}H_{27}O_6N_2$, 487.1863 $(M+H)^+$; Found, 487.1846.

Dimethyl 5-bromo-1-methyl-2-oxo-2',3'-diphenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4f):



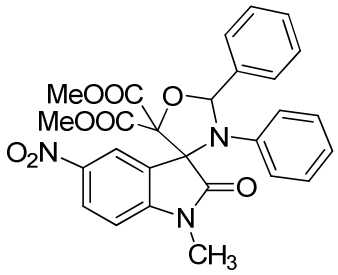
Colourless solid. mp: 152−153 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, 2H, *J* = 8.3, 2.3 Hz), 7.58 (d, 1H, *J* = 1.5 Hz), 7.47 (dd, 1H, *J* = 8.3, 2.3 Hz), 7.36-7.28 (m, 3H), 7.05 (s, 1H), 6.96 (t, 2H, *J* = 7.5 Hz), 6.88 (d, 1H, *J* = 7.5 Hz), 6.75 (d, 2H, *J* =7.5 Hz), 6.61 (d, 1H, *J* = 8.3 Hz), 3.78 (s, 3H), 3.74 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 167.1, 167.0, 143.8, 140.0, 136.0, 133.4, 129.5, 129.1, 128.5, 128.3, 128.1, 126.0, 125.0, 124.5, 115.0, 110.3, 94.3, 89.8, 75.3, 53.1, 53.0, 26.0; IR (neat) ν_{max} 3066, 2950, 1768, 1747, 1720, 1607, 1491, 1291, 1118, 1048, 736, 698 cm^{-1}; ESI-MS *m/z* 573 $(M+Na)^+$; HRMS (ESI) calcd for $C_{27}H_{23}O_6N_2BrNa$ = 573.0631 $(M+Na)^+$; Found, 573.0613.

Dimethyl 5-chloro-1-methyl-2-oxo-2',3'-diphenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4g):



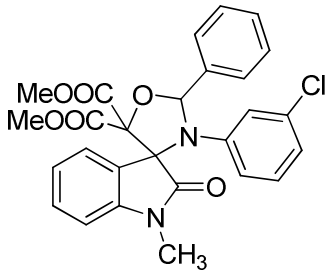
Colourless solid. mp: 157−158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (dd 2H, *J* = 2.3, 7.9 Hz), 7.45 (d, 1H, *J* = 2.1 Hz), 7.35-7.28 (m, 4H), 7.05 (s, 1H), 6.95 (t, 2H, *J* = 7.7 Hz), 6.85 (t, 1H, *J* = 7.4 Hz), 6.75 (d, 2H, *J* = 7.4 Hz), 6.66 (d, 1H, *J* = 8.5 Hz), 3.78 (s, 3H), 3.73 (s, 3H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 167.1, 166.9, 143.3, 140.0, 136.0, 130.5, 129.4, 129.0, 128.4, 128.1, 127.8, 125.4, 124.9, 124.4, 109.8, 94.2, 89.7, 75.2, 53.0, 52.9, 25.9; IR (neat) ν_{max} 3034, 2892, 1764, 1742, 1712, 1611, 1473, 1230, 1117, 1047, 767, 696 cm^{-1}; ESI-MS *m/z* 507 $(M+H)^+$; HRMS (ESI) calcd for $C_{27}H_{24}O_6N_2Cl$ = 507.13174 $(M+H)^+$; Found, 507.12988.

Dimethyl 1-methyl-5-nitro-2-oxo-2',3'-diphenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4h):



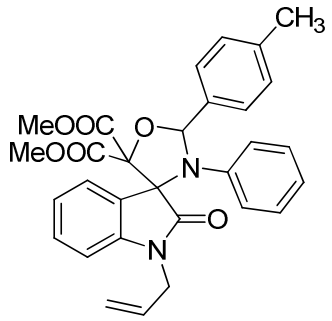
Colourless solid. mp: 178−179 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36-8.28 (m, 2H), 7.82 (dd, 2H, *J* = 2.3, 8.3 Hz), 7.36-7.28 (m, 3H), 7.07 (s, 1H), 6.99-6.88 (m, 3H), 6.83-6.78 (m, 3H), 3.82 (s, 3H), 3.79 (s, 3H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 167.2, 167.0, 150.3, 143.3, 139.4, 135.6, 129.7, 129.2, 128.7, 128.2, 127.6, 125.9, 125.4, 124.6, 121.1, 108.5, 94.5, 89.8, 74.9, 53.3, 53.2, 26.3; IR (neat) ν_{max} 3066, 2887, 1767, 1745, 1721, 1615, 1522, 1495, 1344, 1295, 1231, 1120, 1046, 760, 738, 696 cm^{-1}; ESI-MS *m/z* 518 $(M+H)^+$; HRMS (ESI) calcd for $C_{27}H_{24}O_8N_3$ = 518.15579 $(M+H)^+$; Found, 518.15445.

Dimethyl 3'-(3-chlorophenyl)-1-methyl-2'-(4-nitrophenyl)-2-oxospiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4i):



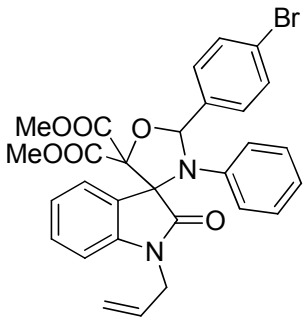
Colourless solid. mp: 193−194 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.47-7.33 (m, 5H), 7.16-7.11 (m, 1H), 7.02 (s, 1H), 6.88-6.75 (m, 3H), 6.55-6.48 (m, 2H), 3.79 (s, 3H), 3.62 (s, 3H), 3.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 166.8, 166.4, 144.4, 142.1, 133.7, 130.8, 129.5, 129.3, 128.7, 128.2, 124.8, 123.5, 122.7, 122.3, 120.2, 108.9, 93.8, 89.9, 74.8, 52.9, 52.7, 26.0; IR (neat) ν_{max} 3367, 2955, 1764, 1742, 1712, 1612 1590, 1474, 1233, 1116, 1047, 767, 696 cm^{-1}; ESI-MS *m/z* 507 $(M+H)^+$; HRMS (ESI) calcd for $C_{27}H_{23}O_6N_2ClNa$ = 529.1136 $(M+Na)^+$; Found, 529.1128.

Dimethyl 1-allyl-2-oxo-3'-phenyl-2'-(*p*-tolyl)spiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4j):



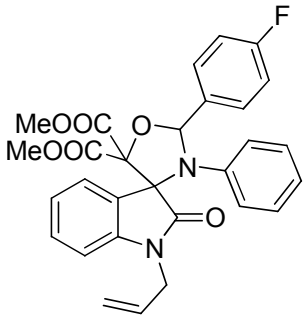
Colourless solid. mp: 147−148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, 2H, *J* = 8 Hz), 7.45 (d, 1H, *J* = 8 Hz), 7.28 (t, 1H, *J* = 7 Hz), 7.11-7.04 (m, 3H), 6.98 (s, 1H), 6.89 (t, 2H, *J* = 8 Hz), 6.79 (t, 1H, *J* = 8Hz), 6.65 (t, 3H, *J* = 7 Hz), 5.61-5.47 (m, 1H), 4.98 (d, 1H, *J* = 11Hz), 4.74 (d, 1H, *J* = 17.4 Hz), 4.22 (dd, 1H, *J* = 5, 17 Hz), 4.08 (dd, 1H, *J* = 5, 17 Hz), 3.76 (s, 3H), 3.67 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 167.3, 167.1, 144.0, 140.5, 139.1, 130.5, 130.4, 129.0, 128.8, 128.3, 124.0, 122.4, 117.0, 109.8, 93.7, 89.7, 75.4, 53.0, 52.8, 42.0, 21.2; IR (neat) ν_{max} 2950, 1748, 1720, 1610, 1496, 1240, 1121, 1047, 753, 697 cm^{-1}; ESI-MS *m/z* 513 $(M+H)^+$; HRMS (ESI) calcd for $C_{30}H_{29}O_6N_2$ = 513.2020 $(M+H)^+$; Found, 513.1997.

Dimethyl 1-allyl-2'-(4-bromophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4k):



Colourless solid. mp: 197−198 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, 2H, *J* = 8.3Hz), 7.48-7.42 (m, 3H), 7.31 (t, 1H, *J* = 7.6 Hz), 7.11 (t, 1H, *J* = 7.6 Hz), 7.06 (s, 1H), 6.96-6.84 (m, 3H), 6.75-6.67 (m, 3H), 5.58-5.44 (m, 1H), 4.95 (d, 1H, *J* = 10.6 Hz), 4.63 (d, 1H, *J* = 17.4 Hz), 4.27 (dd, 1H, *J* = 4.5, 18.9 Hz), 4.06 (dd, 1H, *J* = 4.5, 16.6 Hz), 3.78 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 167.21, 167.16, 144.1, 144.1, 139.9, 135.6, 131.3, 131.0, 130.7, 130.3, 128.5, 125.2, 125.1, 124.8, 123.7, 123.6, 122.5, 117.1, 109.9, 93.1, 89.6, 75.5, 53.1, 53.0, 42.0; IR (neat) ν_{max} 2952, 2902, 1742, 1699, 1608, 1491, 1370, 1303, 1236, 1122, 1049, 783 cm^{-1}; ESI-MS *m/z* 577 $(M+H)^+$; HRMS (ESI) calcd for $C_{29}H_{26}O_6N_2Br$ = 577.09688 $(M+H)^+$; Found, 577.09543.

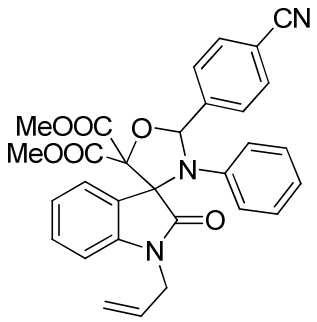
Dimethyl 1-allyl-2'-(4-fluorophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4l):



Colourless solid. mp: 146−147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (dd, 2H, *J*= 5, 8 Hz), 7.43 (d, 1H, *J* = 7 Hz), 7.27 (t, 1H, *J* = 8 Hz), 7.06 (t, 1H, *J* = 8 Hz), 7.00 (s, 1H), 7.10-6.81 (m, 6H), 6.71-6.62 (m, 3H), 5.58-5.45 (m, 1H), 4.96 (d, *J* = 10 Hz), 4.68 (d, 1H, *J* = 17 Hz), 4.22 (dd, 1H, *J* = 5, 17 Hz), 4.06 (dd, 1H, *J* = 5, 17 Hz), 3.77 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 167.4, 167.3, 164.7, 162.2, 144.2, 140.1, 131.3, 131.2, 130.7, 130.4, 128.5,

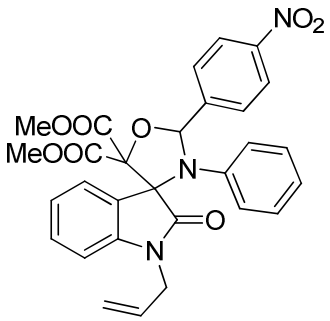
125.3, 125.0, 122.5, 117.1, 115.3, 115.0, 109.9, 93.1, 89.5, 75.6, 53.1, 53.0, 42.0; IR (neat) ν_{max} 2954, 1747, 1711, 1608, 1493, 1369, 1301, 1232, 1114, 788, 701 cm^{-1}; ESI-MS *m/z* 517 $(M+H)^+$; HRMS (ESI) calcd for $C_{29}H_{26}O_6N_2F$ = 517.1769 $(M+H)^+$; Found, 517.1751.

Dimethyl 1-allyl-2'-(4-cyanophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4m):



Colourless solid. mp: 181−182 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, 2H, *J* = 8.3 Hz), 7.60 (d, 2H, *J* = 8.3 Hz), 7.44 (d, 1H, *J* = 7.7 Hz), 7.31 (t, 1H, *J* = 8.5 Hz), 7.14-09 (m, 2H), 6.98-6.87 (m, 3H), 6.75 (d, 2H, *J* = 8.3 Hz), 6.69 (d, 1H, *J* = 7.7 Hz), 5.58-5.45 (m, 1H), 4.96 (d, *J* = 10 Hz), 4.64 (d, 1H, *J* = 18 Hz), 4.27 (dd, 1H, *J* = 5, 17 Hz), 4.06 (dd, 1H, *J* = 5, 17 Hz), 3.78 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 167.2, 166.9, 144.2, 141.7, 139.4, 131.9, 130.9, 130.2, 130.0, 128.6, 125.6, 125.1, 123.1, 122.5, 118.5, 117.1, 113.1, 110.0, 92.6, 89.6, 75.6, 53.1, 53.0, 41.9; IR (neat) ν_{max} 3068, 2955, 2229, 1747, 1702, 1611, 1305, 1238, 1120, 782 cm^{-1}; ESI-MS *m/z* 524 $(M+H)^+$; HRMS (ESI) calcd for $C_{30}H_{25}O_6N_3Na$ = 546.16356 $(M+Na)^+$; Found, 546.16252.

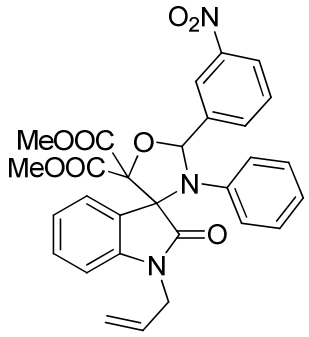
Dimethyl 1-allyl-2'-(4-nitrophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4n):



Colourless solid. mp: 179−180 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, 2H, *J* = 9 Hz), 8.04 (d, 2H, *J* = 9 Hz), 7.46 (d, 1H, *J* = 8 Hz), 7.32 (t, 1H, *J* = 8Hz), 7.17 (s, 1H), 7.12 (t, 1H, *J* = 8

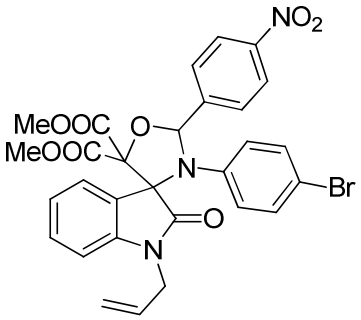
Hz), 6.98-6.89 (m, 3H), 6.77 (d, 2H, *J* = 7 Hz), 6.69 (d, 1H, *J* = 7.7 Hz), 5.58-5.45 (m, 1H), 4.96 (d, *J* = 10 Hz), 4.63 (d, 1H, *J* = 17 Hz), 4.27 (dd, 1H, *J* = 5, 17 Hz), 4.06 (dd, 1H, *J* = 5, 17 Hz), 3.79 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 167.2, 167.0, 148.6, 144.2, 143.6, 139.3, 130.3, 130.2, 128.6, 125.3 125.2, 123.3, 122.6, 117.1, 110.0, 92.3, 89.6, 75.7, 53.2, 53.1, 42.0; IR (neat) ν_{max} 3010, 2957, 1760, 1752, 1713, 1608, 1537, 1347, 1240, 1119, 1061, 786, 697 cm^{-1}; ESI-MS *m/z* 544 $(M+H)^+$; HRMS (ESI) calcd for $C_{29}H_{25}O_8N_3Na$ = 566.1533 $(M+Na)^+$; Found, 566.1521.

Dimethyl 1-allyl-2'-(3-nitrophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4o):



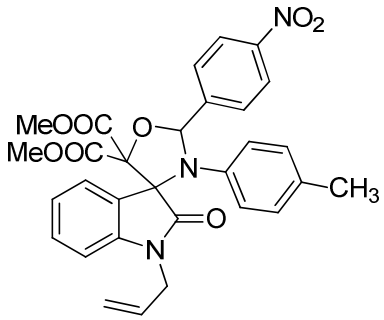
Colourless solid. mp: 167−168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (s, 1H), 8.13 (d, 1H, *J* = 8 Hz), 8.09 (d, 1H, *J* = 8 Hz), 7.46 (t, 2H, *J* = 8 Hz), 7.28 (t, 1H, *J* = 7 Hz), 7.11 (s, 1H), 7.09 (d, 1H, *J* = 8 Hz), 6.95-6.86 (m, 3H), 6.79 (d, 2H, *J* = 8 Hz), 6.64 (d, 1H, *J* = 7.7 Hz), 5.54-5.47 (m, 1H). 4.96 (d, 1H, *J* = 11 Hz), 4.66 (d, 1H, *J* = 17 Hz), 4.21 (dd, 1H, *J* = 5, 16 Hz), 4.06 (dd, 1H, *J* = 5, 17 Hz), 3.79 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 167.1, 166.7, 148.0, 144.0, 139.0, 138.7, 135.3, 130.7, 130.0, 128.9, 128.4, 125.7, 125.3, 125.0, 124.2, 124.1, 122.5, 122.4, 116.8, 109.8, 92.1, 89.3, 75.5, 52.9, 52.9, 41.6; IR (neat) ν_{max} 3110, 2957, 1767, 1746, 1713, 1608, 1537, 1347, 1240, 1119, 1061, 786, 697 cm^{-1}; ESI-MS *m/z* 544 $(M+H)^+$; HRMS (ESI) calcd for $C_{29}H_{26}O_8N_3$ = 544.17144 $(M+H)^+$; Found, 544.17072.

Dimethyl 1-allyl-3'-(4-bromophenyl)-2'-(4-nitrophenyl)-2-oxospiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4p):



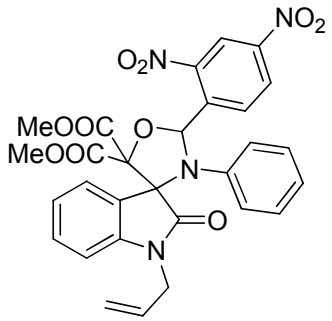
Colourless solid. mp: 207-208 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, 2H, *J* = 9 Hz), 8.02 (d, 2H, *J* = 9 Hz), 7.44 (d, 1H, *J* = 7Hz), 7.35 (1H, *J* = 8 Hz), 7.16-7.06 (m, 4H), 6.73 (d, 1H, *J* = 8 Hz), 6.64 (d, 2H, *J* = 9 Hz), 5.64-5.51 (m, 1H), 5.04 (d, 1H, *J* = 11Hz), 4.17 (d, 1H, *J* = 17 Hz), 4.30-4.08 (m, 2H), 3.79 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 167.0, 166.8, 148.7, 144.2, 143.2, 138.6, 131.8, 131.2, 130.3, 130.2, 126.7, 125.1, 123.4, 122.7, 119.2, 117.3, 110.2, 92.2, 89.6, 75.5, 53.3, 53.1, 42.0; IR (neat) ν_{max} 3082, 3002, 2953, 1750, 1705, 1611, 1525, 1346, 1243, 1120, 822, 761 cm^{-1}; ESI-MS *m/z* 622 $(M+H)^+$; HRMS (ESI) calcd for $C_{29}H_{25}BrN_3O_8$, 622.08195 $(M+H)^+$; Found, 622.0811.

Dimethyl 1-allyl-2'-(4-nitrophenyl)-2-oxo-3'-(*p*-tolyl)spiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4q):



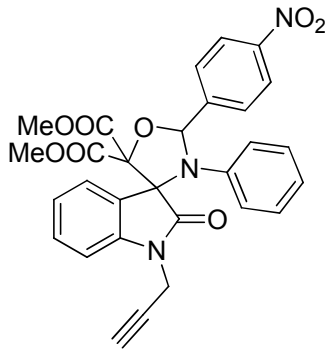
Colourless solid. mp: 196−197°C ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, 2H, J= 9Hz), 8.01 (d, 2H, J= 9Hz), 7.40 (d, 1H, J= 7Hz), 7.27 (t, 1H, 8Hz), 7.10-7.04 (m, 2H), 6.74-6.62 (m, 5H), 5.62-5.48 (m, 1H), 4.96 (d, 1H, J= 9Hz), 4.64 (d, 1H, J= 17Hz), 4.25-4.05 (m,2H), 3.78 (s, 3H), 3.72 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 167.3, 167.1, 144.0, 140.5, 139.1, 130.5, 130.4, 129.0, 128.8, 128.3, 124.0, 122.4, 117.0, 109.8, 93.7, 89.7, 75.4, 53.0, 52.8, 42.0, 21.2; IR (neat) ν_{max} 3010, 2950, 1762, 1750, 1710, 1608, 1537, 1347, 1240, 1119, 1061, 786, 697 cm^{-1}; ESI-MS *m/z* 558 $(M+H)^+$; HRMS (ESI) calcd for $C_{30}H_{28}O_8N_3$ = 558.18709 $(M+H)^+$; Found, 558.18494.

Dimethyl 1-allyl-2'-(2,4-dinitrophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4r):



Colourless solid. mp: 167−168°C ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.93 (d, 1H, *J* = 8.7 Hz), 8.59 (d, 1H, *J* = 2.3 Hz), 8.44 (dd, 1H, *J* = 2.1, 8.7 Hz), 7.69 (s, 1H), 7.37 (d, 1H, *J* = 7.6 Hz), 7.28 (t, 1H, *J* = 7.7 Hz), 7.06 (t, 1H, *J* = 7 Hz), 6.76-6.62 (m, 6H), 5.62-5.49 (m, 1H), 4.97 (d, 1H, *J* = 10.4 Hz), 4.68 (d, 1H, *J* = 17.8 Hz), 4.25-4.06 (m, 2H), 3.80 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 167.2, 166.4, 150.5, 148.0, 144.4, 137.9, 133.4, 131.1, 130.2, 128.9, 126.9, 125.9, 125.0, 124.8, 122.5, 119.3, 117.3, 110.2, 89.9, 86.5, 75.4, 53.3, 53.1, 42.1; IR (neat) ν_{max} 3110, 2957, 1749, 1714, 1608, 1537, 1349, 1241, 1120, 697 cm^{-1}; ESI-MS *m/z* 589 $(M+H)^+$; HRMS (ESI) calcd for $C_{29}H_{24}O_{10}N_4Na$ = 611.1384 $(M+Na)^+$; Found, 611.1372.

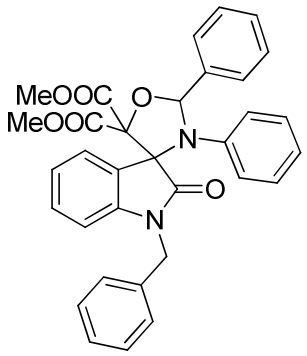
Dimethyl 2'-(4-nitrophenyl)-2-oxo-3'-phenyl-1-(prop-2-yn-1-yl)spiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (4s):



Colourless solid. mp: 188−189 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, 2H, *J* = 9 Hz), 8.02 (d, 2H, *J* = 9 Hz), 7.45 (d, 1H, *J* = 8 Hz), 7.38 (t, 1H, *J* = 7 Hz), 7.16 (t, 1H, *J* = 7Hz), 7.12 (s, 1H), 6.97-6.86 (m, 4H), 6.74 (d, 2H, *J* = 8 Hz), 4.41-4.27 (m, 2H), 3.79 (s, 3H), 3.72 (s, 3H), 2.12 (t, 1H, *J* = 3Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 167.1, 166.8, 148.6, 143.6, 143.0, 139.1, 131.0, 130.3, 128.7, 125.8, 125.3, 125.0, 123.4, 123.1, 123.0, 110.0, 92.5, 89.5, 75.9, 75.5,

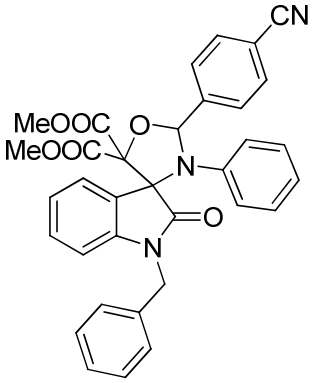
72.2, 53.3, 53.2, 28.9; IR (neat) ν_{max} 3072, 2956, 1751, 1711, 1610, 1527, 1347, 1304, 1242, 1121, 1056, 782 cm^{-1}; ESI-MS *m/z* 542 $(M+H)^+$; HRMS (ESI) calcd for $C_{29}H_{24}O_8N_3$ = 542.15579 $(M+H)^+$; Found, 542.15339.

Dimethyl 1-benzyl-2-oxo-2',3'-diphenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxy- late (compound 4t):



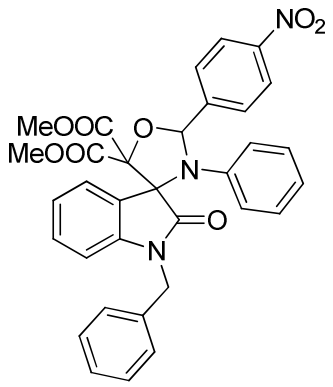
Colourless solid. mp: 169−170 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, 2H, *J* = 7 Hz), 7.51 (d, 1H, *J* = 7 Hz), 7.34-7.27 (m, 3H), 7.22-7.07 (m, 6H), 6.95-6.88 (m, 3H), 6.76 (d, 2H, *J* = 7 Hz), 6.73 (d, 2H, *J* = 7 Hz), 6.53 (d, 2H, *J* = 8 Hz), 5.01 (d, 1H, *J* = 16 Hz), 4.55 (d, 1H, *J* = 16 Hz), 3.77 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 167.3, 167.0, 143.9, 140.4, 136.2, 134.7, 130.6, 129.4, 129.1, 128.5, 128.4, 128.1, 127.1, 126.6, 125.1, 124.3, 123.9, 122.5, 110.0, 93.8, 89.9, 75.5, 53.0, 52.8, 43.5; IR (neat) ν_{max} 3063, 2953, 1762, 1740, 1711, 1607, 1493, 1233, 1106, 765 696 cm^{-1}; ESI-MS *m/z* 549 $(M+H)^+$; HRMS (ESI) calcd for $C_{33}H_{29}O_6N_2$ = 549.2020 $(M+H)^+$; Found, 549.2013.

Dimethyl 1-benzyl-2'-(4-cyanophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (compound 4u):



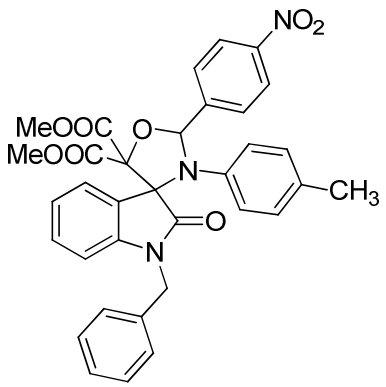
Colourless solid. mp: 170−171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, 2H, *J* = 8 Hz), 7.61 (d, 2H, *J* = 9 Hz), 7.47 (d, 1H, *J* = 8 Hz), 7.23-7.08 (m, 7H), 6.98-6.96 (m, 3H), 6.76-6.76 (m, 2H), 6.71 (d, 2H, *J* = 8 Hz), 6.52 (d, 1H, *J* = 8 Hz), 5.01 (d, 1H, *J* = 16 Hz), 4.52 (d, 1H, *J* = 16Hz), 3.78 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 167.0, 166.9, 144.0, 141.5, 139.5, 134.4, 131.9, 130.9, 129.9, 128.7, 128.4, 127.1, 126.4, 125.4, 125.0, 124.8, 123.0, 122.5, 118.4, 112.9, 110.1, 92.5, 89.6, 75.6, 53.1, 53.0, 43.3; IR (neat) ν_{max} 2952, 2916, 2229, 1746, 1710, 1611, 1366, 1253, 1122, 747, 696 cm^{-1}; ESI-MS *m/z* 574 $(M+H)^+$; HRMS (ESI) calcd for $C_{34}H_{28}O_6N_3$ = 574.19726 $(M+H)^+$; Found, 574.19582.

Dimethyl 1-benzyl-2'-(4-nitrophenyl)-2-oxo-3'-phenylspiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (compound 4v):



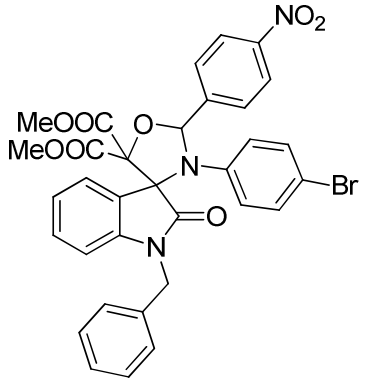
Colourless solid. mp: 206−207 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, 2H, *J* = 8.3 Hz), 8.03 (d, 1H, *J* = 8.3 Hz), 7.44 (d, 1H, *J* = 7.6 Hz), 7.23-7.04 (m, 6H), 6.94-6.98 (m, 3H), 6.78-6.67 (m, 4H), 6.47 (d, 1H, *J* = 7.6 Hz), 4.95 (d, 1H, *J* = 15.9 Hz), 4.53 (d, 1H, *J* = 15.9 Hz), 3.78 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 167.2, 167.0, 148.6, 144.2, 143.6, 139.5, 134.5, 131.0, 130.4, 128.9, 128.6, 127.3, 126.5, 125.7, 125.2, 125.1, 123.4, 123.0, 122.7, 110.3, 92.3, 89.8, 75.8, 53.3, 53.2, 43.5; IR (neat) ν_{max} 3033, 2955, 1749, 1721, 1610, 1521, 1347, 1233, 1121, 744, 697 cm^{-1}; ESI-MS *m/z* 594 $(M+H)^+$; HRMS (ESI) calcd for $C_{33}H_{28}O_8N_3$ = 594.18709 $(M+H)^+$; Found, 594.18700

Dimethyl 1-benzyl-2'-(4-nitrophenyl)-2-oxo-3'-(p-tolyl)spiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (compound 4w):



Colourless solid. mp: 200−201 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, 2H, *J* = 8.9 Hz), 8.07 (d, 2H, *J* = 8.9 Hz), 7.48 (d, 1H, *J* = 7.5 Hz), 7.24-7.06 (m, 6H), 6.49 (d, 1H, *J* = 7.7 Hz), 5.07 (d, 1H, *J* = 16.2 Hz), 4.49 (d, 1H, *J* = 16.1Hz), 3.79 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 174.2, 167.4, 167.2, 148.6, 144.3, 143.7, 135.7, 134.6, 130.9, 130.4, 129.5, 128.4, 127.3, 126.6, 125.6, 125.3, 123.3, 122.6, 110.3, 92.4, 89.7, 75.9, 53.3, 53.2,, 43.5, 20.8; IR (neat) ν_{max} 3031, 2956, 1752, 1723, 1610, 1517, 1346, 1253, 1122, 754 cm^{-1}; ESI-MS *m/z* 608 $(M+H)^+$; HRMS (ESI) calcd for $C_{34}H_{30}O_8N_3$ = 608.20274 $(M+H)^+$; Found, 608.20291.

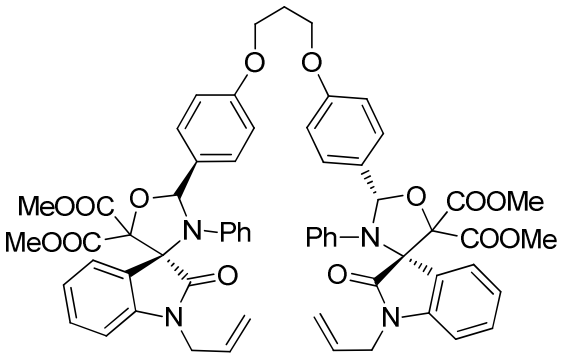
Dimethyl 1-benzyl-3'-(4-bromophenyl)-2'-(4-nitrophenyl)-2-oxospiro[indoline-3,4'-oxazolidine]-5',5'-dicarboxylate (compound 4x):



Colourless solid. mp: 198−199 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, 2H, *J* = 8.3 Hz), 8.04 (d, 2H, *J* = 9 Hz), 7.47 (d, 1H, *J* = 9 Hz), 7.29-7.05 (m, 8H), 6.74-6.69 (m, 2H), 6.65 (d, 2H, *J* = 9 Hz), 6.57 (d, 1H, *J* = 7.6 Hz), 5.06 (d, 1H, *J* = 16.6 Hz), 4.51 (d, 1H, *J* = 15.9 Hz), 3.79 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 167.1, 166.9, 148.7, 144.2, 143.1, 138.7, 134.4, 131.9, 131.3, 130.3, 128.6, 127.5, 126.6, 126.5, 125.2, 123.4, 122.8, 122.7, 119.2, 110.4, 92.2, 89.8, 75.6, 53.3, 53.2, 43.6; IR (neat) ν_{max} 3066, 2955, 1755, 1721, 1608, 1524, 1492,

1347, 1262, 1119, 749 cm^{-1}; ESI-MS *m/z* 694 $(M+Na)^+$; HRMS (ESI) calcd for $C_{33}H_{26}O_8N_3BrNa$ = 694.07955 $(M+Na)^+$; Found, 694.07982.

Bis adduct: (compound 6)

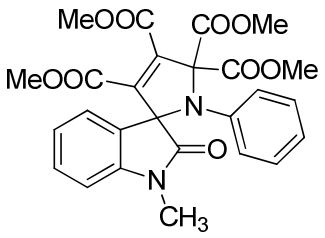


Colourless solid. mp: 140−141 °C ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, 2H, *J* = 8 Hz), 7.48 (d, 1H, *J* = 8 Hz), 7.10 (t, 1H, *J* = 8 Hz), 7.04 (s, 1H), 6.94-6.8 (m, 5H), 6.69 (d, 3H, *J* = 8 Hz), 5.58-5.45 (m, 1H), 4.96 (d, *J* = 10 Hz), 4.68 (d, 1H, *J* = 17 Hz), 4.26 (dd, 1H, *J* = 5, 17 Hz), 4.11-4.02 (m, 3H), 3.77 (s, 3H), 3.69 (s, 3H), 2.16 (t, 1H, *J* = 6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 167.4, 167.3, 159.7, 144.0, 140.4, 130.6, 130.4, 128.4, 125.2, 124.6, 124.4, 124.2, 122.5, 117.0, 114.1, 109.8, 93.6, 89.5, 75.4, 64.2, 53.1, 53.0, 41.9, 29.0; IR (neat) ν_{max} 2950, 1748, 1720, 1610, 1496, 1240, 1121, 1047, 753, 697 cm^{-1}; ESI-MS *m/z* 1069 $(M+H)^+$; HRMS (ESI) calcd for $C_{61}H_{57}O_{14}N_4$ = 1069.38658 $(M+Na)^+$; Found, 1069.38305.

Three-component coupling of dimethyl diazomalonate, ketimine and DMAD:

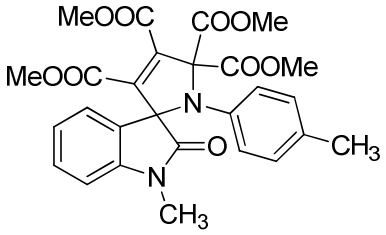
General procedure: To a solution of isatin-3-arylimine (1.2 equiv), dimethyl acetylenedicarboxylate (1.2 equiv) and dimethyl diazomalonate (1.0 equiv) in dry benzene was added 5 mol % of $Rh_2(OAc)_4$ and the resulting mixture was stirred at 80 ^oC for about 15 min under argon atmosphere. After complete consumption of diazomalonate, the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel using *n*-hexane-ethyl acetate as eluent to afford the pure product.

Tetramethyl 1-methyl-2-oxo-1'-phenylspiro[indoline-3,2'-pyrrole]-3',4',5',5'(1'*H*)-tetracarboxylate (10a):



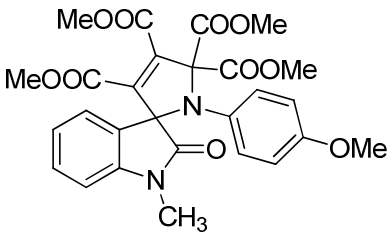
Colourless solid. mp: 162−163 °C ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, 1H, *J* = 8 Hz), 7.30 (t, 1H, *J* = 8 Hz), 7.01 - 6.94 (m, 3H), 6.83 (d, 1H, *J* = 8 Hz), 6.72 (t, 1H, *J* = 7 Hz), 6.34 (d, 2H, *J* = 8 Hz), 3.96 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.54 (s, 3H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ; 172.6, 168.0, 166.4, 162.1, 160.5, 143.5, 140.7, 138.6, 137.7, 130.5, 128.6, 125.3, 124.8, 123.4, 120.6, 116.4, 108.5, 80.8, 77.6, 53.9, 53.3, 52.8, 52.5, 26.8; IR (neat) ν_{max} 3021, 2961, 1757, 1732, 1606, 1319, 1241, 1037, 753 cm^{-1}; ESI-MS *m/z* 509 $(M+H)^+$; HRMS (ESI) calcd for $C_{26}H_{25}O_9N_2$ = 509.15546 $(M+H)^+$; Found, 509.15402.

Tetramethyl 1-methyl-2-oxo-1'-(*p*-tolyl)spiro[indoline-3,2'-pyrrole]-3',4',5',5'(1'*H*)-tetracarboxylate (10b):



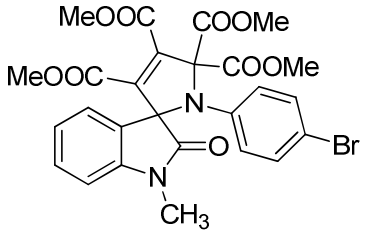
Colourless solid. mp: 198−199°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, 1H, *J* = 7.2 Hz), 7.31 (d, 1H, *J* = 7.7 Hz), 7.00 (t, 1H, *J* = 7.4 Hz), 6.82 (t, 3H, *J* = 8.3, 7.6 Hz), 6.41 (d, 2H, *J* = 8.5 Hz), 3.95 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.53 (s, 3H), 3.29 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 168.1, 166.5, 162.0, 160.5, 143.5, 138.7, 137.9, 137.8, 130.3, 129.0, 125.2, 124.9, 123.1, 118.3, 108.3, 80.9, 77.7, 53.6, 52.7, 52.6, 52.3, 26.5, 20.1; IR (neat) ν_{max} 3018, 2961, 1756, 1730, 1605, 1320, 1241, 1037, 753 cm^{-1}; ESI-MS *m/z* 523 $(M+H)^+$; HRMS (ESI) calcd for $C_{27}H_{27}O_9N_2$ = 523.17111 $(M+H)^+$; Found, 523.16937.

Tetramethyl 1'-(4-methoxyphenyl)-1-methyl-2-oxospiro[indoline-3,2'-pyrrole]-3',4',5',5'(1'*H*)-tetracarboxylate 10c):



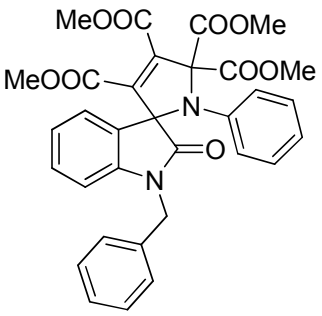
Colourless solid. mp: 174−175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, 1H, *J* = 7.2 Hz), 7.25 (t, 1H, *J* = 8.8 Hz), 7.02 (t, 1H, *J* = 7.4 Hz), 6.79 (d, 2H, *J* = 9 Hz), 6.71 (d, 1H, *J* = 7.9 Hz), 6.58 (d, 2H, *J* = 9 Hz) 3.91 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.65 (s, 3H), 3.54 (s, 3H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 168.5, 167.2, 162.3, 160.9, 156.3, 143.8, 139.1, 138.8, 132.9, 130.3, 126.7, 125.5, 123.0, 113.7, 108.2, 81.9, 78.9, 55.1, 53.6, 52.9, 52.7, 52.5, 26.5; IR (neat) ν_{max} 3020, 2961, 1757, 1732, 1606, 1319, 1241, 1037, 753, 685 cm^{-1}; ESI-MS *m/z* 539 $(M+H)^+$; HRMS (ESI) calcd for $C_{27}H_{27}O_{10}N_2$ = 539.16602 $(M+H)^+$; Found, 539.16467.

Tetramethyl 1'-(4-bromophenyl)-1-methyl-2-oxospiro[indoline-3,2'-pyrrole]-3',4',5',5'(1'*H*)-tetracarboxylate (10d):



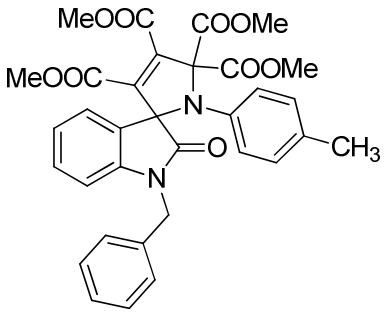
Colourless solid. mp: 179−180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, 1H, *J* = 6. 8 Hz), 7.35 (t, 1H, *J* = 7.5 Hz), 7.10 (d, 2H, *J* = 9 Hz), 7.03 (t, 1H, *J* = 7.6 Hz), 6.89 (d, 1H, *J* = 7.6Hz), 6.28 (d, 2H, *J* = 9 Hz), 3.97 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 3.54 (s, 3H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ; 172.3, 167.8, 166.2, 162.0, 160.5, 143.5, 139.9, 138.4, 137.6, 131.5, 130.8, 125.4, 124.4, 123.6, 118.4, 113.0, 108.7, 80.9, 77.7, 54.1, 53.5, 52.9, 52.7, 26.9; IR (neat) ν_{max} 3020, 2961, 1757, 1732, 1606, 1319, 1241, 1037, 753, 685 cm^{-1}; ESI-MS *m/z* 587 $(M+H)^+$; HRMS (ESI) calcd for $C_{26}H_{24}O_9N_2Br$ = 587.06597 $(M+H)^+$; Found, 587.06512.

Tetramethyl 1-benzyl-2-oxo-1'-phenylspiro[indoline-3,2'-pyrrole]-3',4',5',5'(1'*H*)-tetracarboxylate (10e):



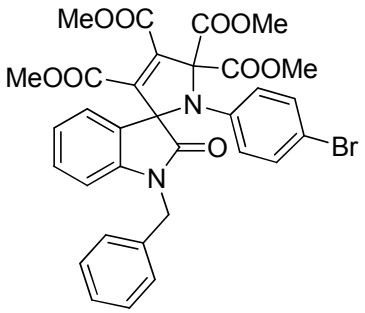
Colourless solid. mp: 150−151 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.19 (m, 7H), 7.00-6.93 (m, 3H), 6.83 - 6.74 (m, 2H), 6.46 (d, 2H, *J* = 8.3 Hz), 5.14 (d, 1H, *J* = 15 Hz), 4.82 (d, 1H, *J* = 15 Hz), 3.97 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 168.0, 166.4, 162.1, 160.6, 142.8, 140.5, 138.6, 138.0, 135.3, 130.4, 128.7, 128.6, 128.1, 127.8, 125.4, 125.1, 123.4, 120.6, 117.6, 109.4, 80.9, 77.6, 53.9, 53.3, 52.8, 52.4, 44.7; IR (neat) ν_{max} 2955, 1731, 1605, 1313, 1240, 1183, 754 cm^{-1}; ESI-MS *m/z* 585 $(M+H)^+$; HRMS (ESI) calcd for $C_{32}H_{29}O_9N_2$ = 585.18676 $(M+H)^+$; Found, 585.18606.

Tetramethyl 1-benzyl-2-oxo-1'-(*p*-tolyl)spiro[indoline-3,2'-pyrrole]-3',4',5',5'(1'*H*)-tetracarboxylate (10f):



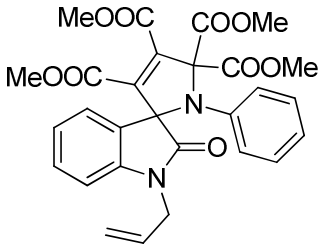
Colourless solid. mp: 168−169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, 1H, *J* = 7.6 Hz), 7.33-7.27 (m, 5H), 7.18 (t, 1H, *J* = 7.6 Hz) 6.97 (t, 1H, *J* = 7.6 Hz), 6.79 (d, 2H, *J* = 8.3 Hz), 6.72 (d, 1H, *J* = 8.3Hz), 6.50 (d, 2H, *J* = 8.3 Hz), 5.09 (d, 1H, *J* = 15 Hz), 4.79 (d, 1H, *J* = 15 Hz), 3.93 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 3.44 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 168.3, 166.7, 162.2, 160.7, 142.9, 138.8, 138.4, 137.8, 135.3, 131.4, 130.2, 129.2, 128.6, 127.9, 127.7, 125.5, 125.5, 123.3, 120.3, 109.3, 81.3, 78.1, 53.7, 53.2, 52.8, 52.4, 44.5, 20.4; IR (neat) ν_{max} 2950, 1738, 1679, 1607, 1501, 1327, 1292, 1265, 1236, 1201, 1176, 758 cm^{-1}; ESI-MS *m/z* 599 $(M+H)^+$; HRMS (ESI) calcd for $C_{33}H_{31}O_9N_2$ = 599.20241 $(M+H)^+$; Found, 599.20123

Tetramethyl 1-benzyl-1'-(4-bromophenyl)-2-oxospiro[indoline-3,2'-pyrrole]-3',4',5',5' (1'*H*)-tetracarboxylate (10g):



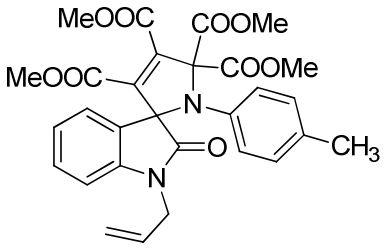
Colourless solid. mp: 151−152 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.31 (m, 6H), 7.22 (d, 1H, *J* = 7.7 Hz), 7.04 (d, 2H, *J* = 9 Hz), 6.98 (d, 2H, *J* = 7 Hz), 6.82 (d, 1H, *J* = 8 Hz), 6.34 (d, 2H, *J* = 9 Hz), 5.12 (d, 1H, *J* = 15.3Hz), 4.80 (d, 1H, *J* = 15.3Hz), 3.95 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 167.7, 166.1, 161.9, 160.3, 142.6, 139.6, 138.4, 137.7, 135.1, 131.3, 130.5, 128.6, 128.0, 127.8, 125.3, 124.4, 123.4, 119.3, 113.3, 109.5, 80.8, 77.6, 53.9, 53.3, 52.8, 52.4, 44.6; IR (neat) ν_{max} 2954, 1741, 1679, 1607, 1501, 1327, 1292, 1265, 1236, 1201, 1176, 758 cm^{-1}; ESI-MS *m/z* 663 $(M+H)^+$; HRMS (ESI) calcd for $C_{32}H_{28}O_9N_2Br$ = 663.09727 $(M+H)^+$; Found, 663.09747.

Tetramethyl 1-allyl-2-oxo-1'-phenylspiro[indoline-3,2'-pyrrole]-3',4',5',5'(1'*H*)-tetra-carboxylate (10h):



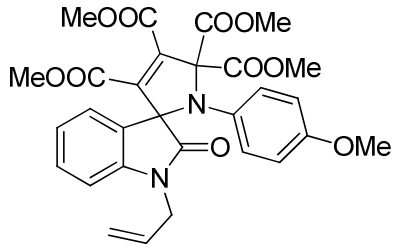
Colourless solid. mp: 142−143°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, 1H, *J* = 8 Hz), 7.28 (t, 1H, *J* = 8 Hz), 7.00 (t, 3H, *J* = 7.6 Hz), 6.88 (d, 1H, *J* = 8 Hz), 6.75 (t, 1H, *J* = 7 Hz), 6.47 (d, 2H, *J* = 8 Hz), 5.93- 5.86 (m, 1H), 5.37-5.27 (m, 2H), 4.43 (d, 2H, *J* = 4Hz), 3.95 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ; 172.3, 168.0, 166.5, 162.1, 160.6, 142.8, 140.6, 138.7, 137.9, 131.0, 130.3, 128.6, 125.5, 125.0, 123.3, 120.7, 118.5, 117.6, 109.4, 80.9, 77.7, 53.8, 53.3, 52.8, 52.5, 43.2; IR (neat) ν_{max} 2956, 1759, 1732, 1610, 1308, 1235, 1196, 774 cm^{-1}; ESI-MS *m/z* 535 $(M+H)^+$; HRMS (ESI) calcd for $C_{28}H_{27}O_9N_2$ = 535.17111 $(M+H)^+$; Found, 535.17006.

Tetramethyl 1-allyl-2-oxo-1'-(*p*-tolyl)spiro[indoline-3,2'-pyrrole]-3',4',5',5'(1'*H*)-tetra-carboxylate (10i):



Colourless solid. mp: 136−137 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, 1H, *J* = 7.4 Hz), 7.27 (t, 1H, *J* = 8 Hz), 7.00 (t, 1H, *J* = 7.5 Hz), 6.81 (d, 3H, *J* = 8.5 Hz), 6.48 (d, 2H, *J* = 8.7 Hz), 5.92-5.79 (m, 1H), 5.30-5.22 (m, 2H), 4.47-4.32 (m, 2H), 3.94 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H), 3.54 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ; 172.7, 168.2, 166.7, 162.2, 160.7, 142.9, 138.8, 138.2, 137.9, 131.2, 131.0, 130.2, 129.2, 125.5, 125.3, 123.2, 119.8, 118.3, 109.3, 81.2, 78.0, 53.8, 53.2, 52.8, 52.5, 43.0, 20.3; IR (neat) ν_{max} 2957, 1760, 1733, 1714, 1612, 1520, 1327, 1301, 1244, 1196, 1037, 804 cm^{-1}; ESI-MS *m/z* 549 $(M+H)^+$; HRMS (ESI) calcd for $C_{29}H_{29}O_9N_2$ = 549.18676 $(M+H)^+$; Found, 549.18579.

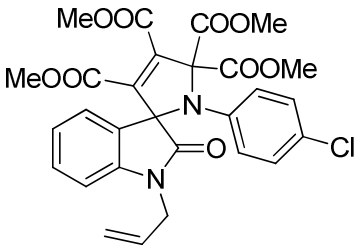
Tetramethyl 1-allyl-1'-(4-methoxyphenyl)-2-oxospiro[indoline-3,2'-pyrrole]-3',4',5',5' (1'*H*)-tetracarboxylate (10j):



Colourless solid. mp: 130 −131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, 1H, *J* = 6 Hz), 7.20 (t, 1H, *J* = 7.5 Hz), 7.01 (t, 1H, *J* = 7.6Hz), 6.86 (d, 2H, *J* = 9 Hz), 6.68 (d, 1H, *J* = 7.6 Hz), 6.57 (d, 2H, *J* = 9 Hz), 5.81-5.68 (m, 1H), 5.16-5.00 (dd, 2H, *J* = 11, 26 Hz), 4.39-4.20 (m, 2H), 3.90 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.65 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ; 173.4, 168.5, 167.3 162.3, 160.9 156.88 143.0, 139.1, 139.0, 132.6, 130.7, 130.1 128.3, 125.8, 125.6, 122.9, 117.6, 113.6, 109.1, 82.0, 79.0, 55.0, 53.5, 52.8, 52.7, 52.4, 42.6; IR (neat) ν_{max}

2959, 1729, 1605, 1513, 1315, 1242, 1192, 1032, 772 cm^{-1}; ESI-MS *m/z* 565 $(M+H)^+$; HRMS (ESI) calcd for $C_{29}H_{29}O_{10}N_2$ = 565.18167 $(M+H)^+$; Found, 565.18067.

Tetramethyl 1-allyl-1'-(4-chlorophenyl)-2-oxospiro[indoline-3,2'-pyrrole]-3',4',5',5' (1'*H*)-tetracarboxylate (107k):



Colourless solid. mp: 149−150 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, 1H, *J* = 7 Hz), 7.30 (t, 1H, *J* = 8 Hz), 7.02 (t, 1H, *J* = 7.6 Hz), 6.96 (d, 2H, *J* = 9 Hz), 6.87 (d, 1H, *J* = 8 Hz), 6.43 (d, 2H, *J* = 9 Hz), 5.95-5.81 (m, 1H), 5.37-5.28 (m, 2H), 4.42 (d, 2H, *J* = 6 Hz), 3.96 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ; 172.1, 167.9, 166.4, 162.0, 160.5, 142.8, 139.2, 138.6, 137.8, 130.9, 130.6, 128.6, 126.3 125.5, 124.6, 123.5, 119.5, 118.7, 109.5, 81.04, 77.8, 54.0, 53.4, 52.9, 52.6, 43.22; IR (neat) ν_{max} 2950, 1730, 1607, 1510, 1315, 1238, 1190, 1030, 758 cm^{-1}; ESI-MS *m/z* 569 $(M+H)^+$; HRMS (ESI) calcd for $C_{28}H_{26}O_9N_2Cl$ = 569.13213 $(M+H)^+$; Found, 569.13098.

5. X-ray crystal structures of product 4q and **10e**

The structure and stereochemistry of the product **4q** was confirmed by single crystal X-ray crystallography as shown in figure **1**. X-ray data was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 6946 reflections in the range of $2.31 < \theta < 25.20°$. Integration and scaling of intensity data was accomplished using SAINT program. The structure was solved by direct methods using SHELXS97 and refinement was carried out by full-matrix least-squares technique using SHELXL97. Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and $U_{iso}(H)$ = $1.5U_{eq}(C)$ for methyl H or $1.2U_{eq}(c)$ for other H atoms].

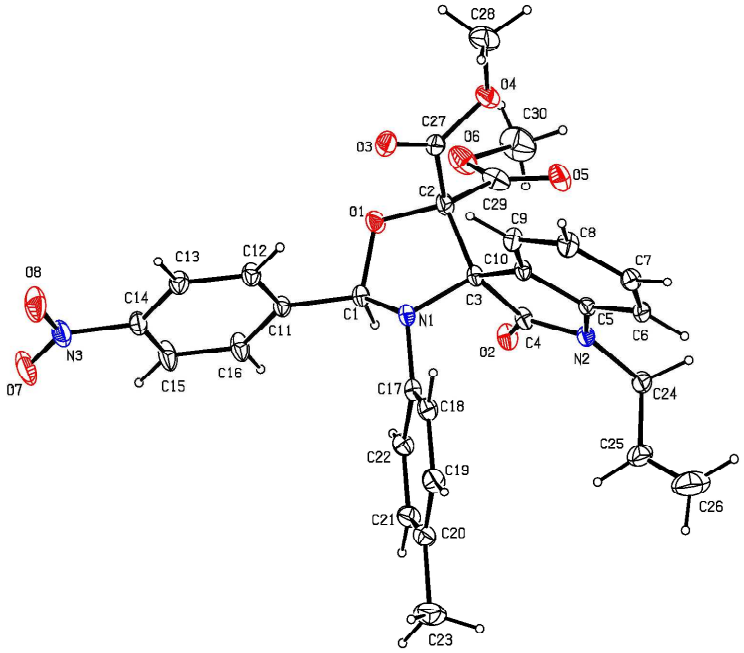
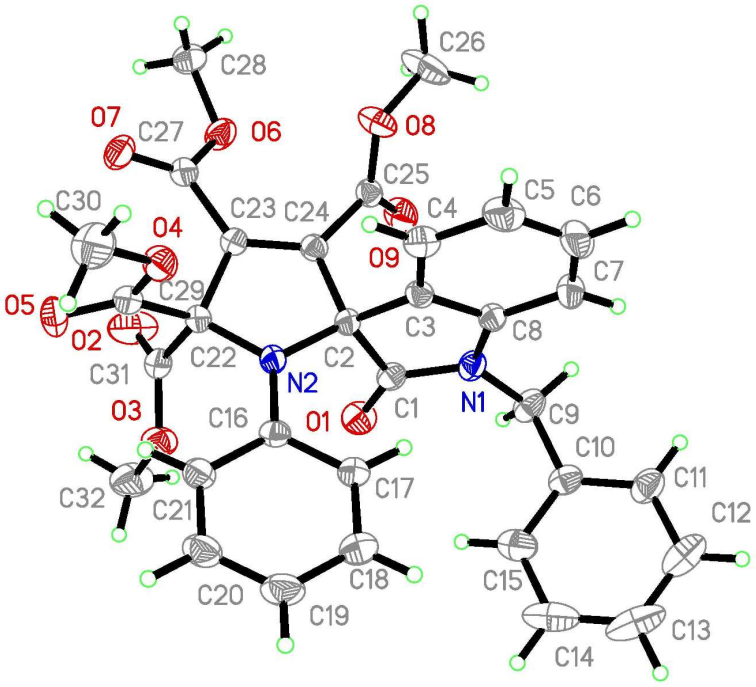
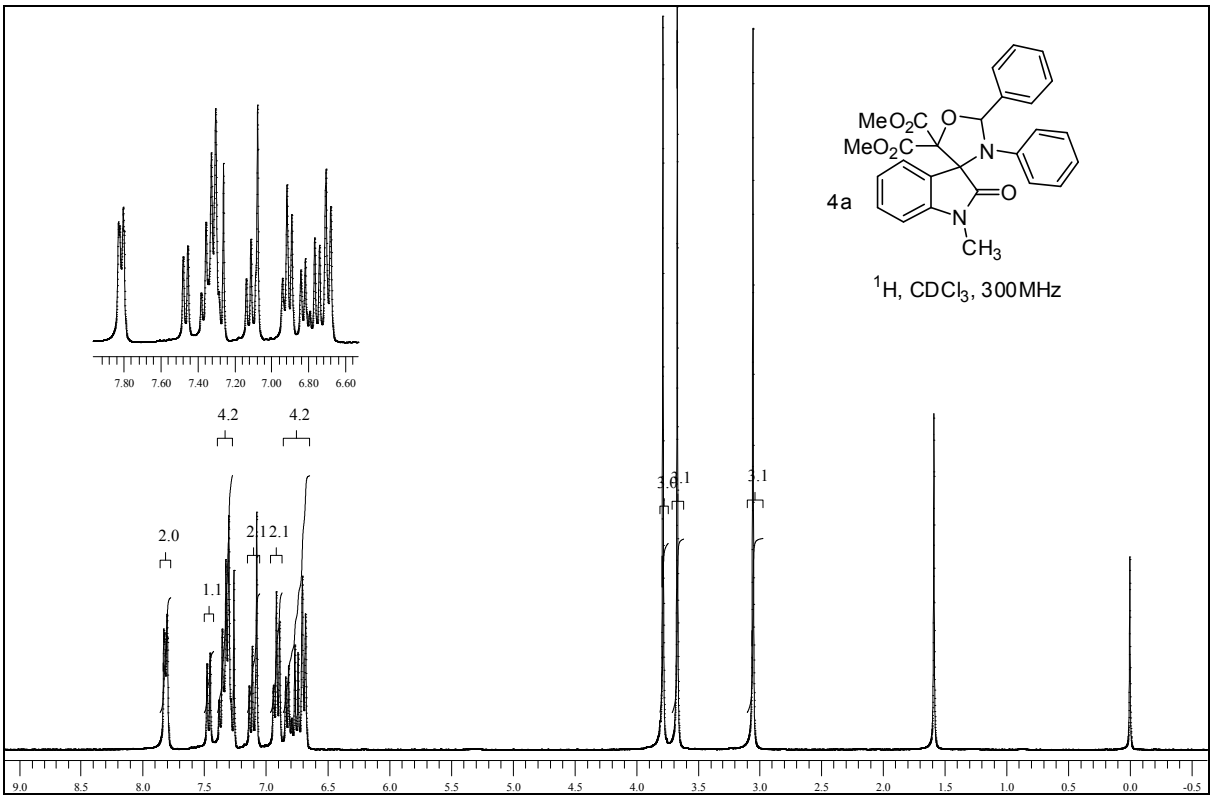


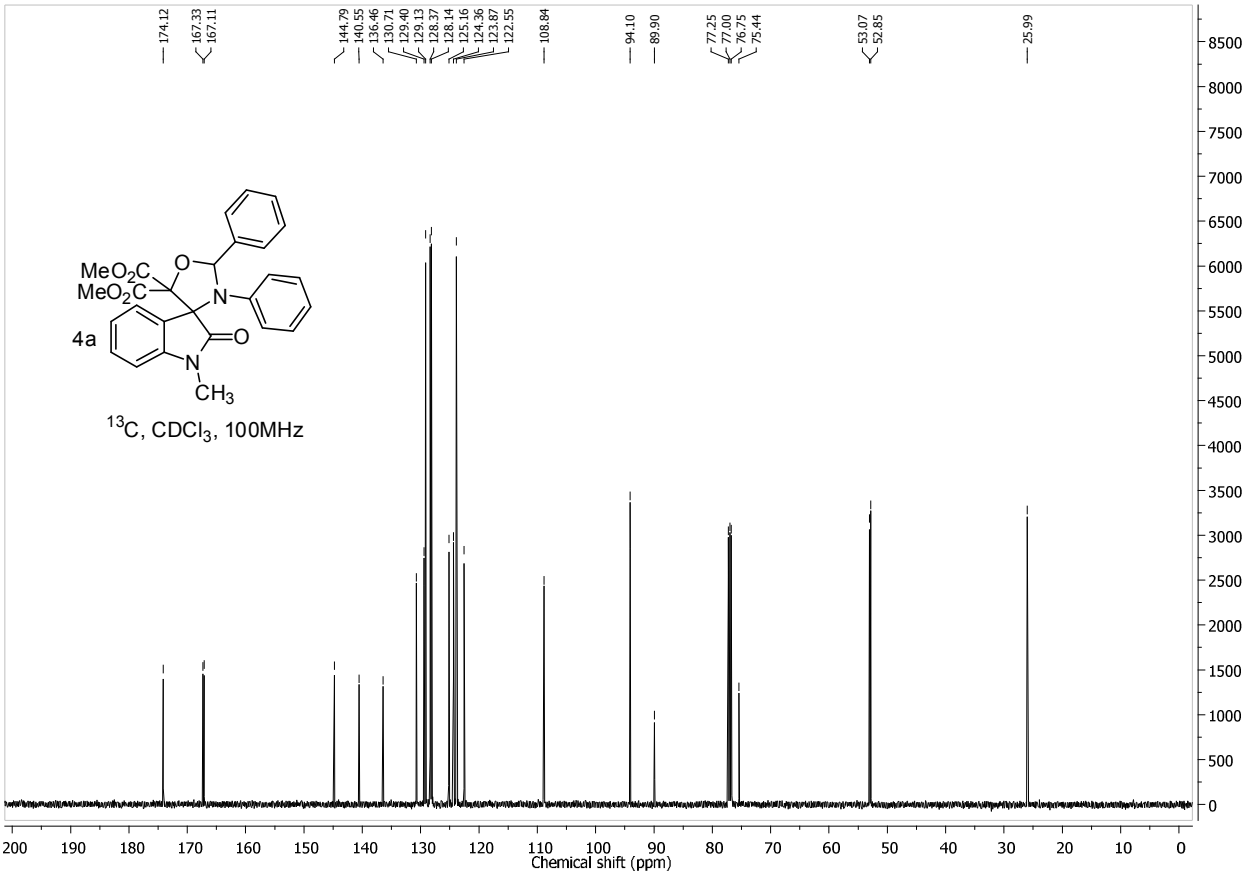
Figure 1

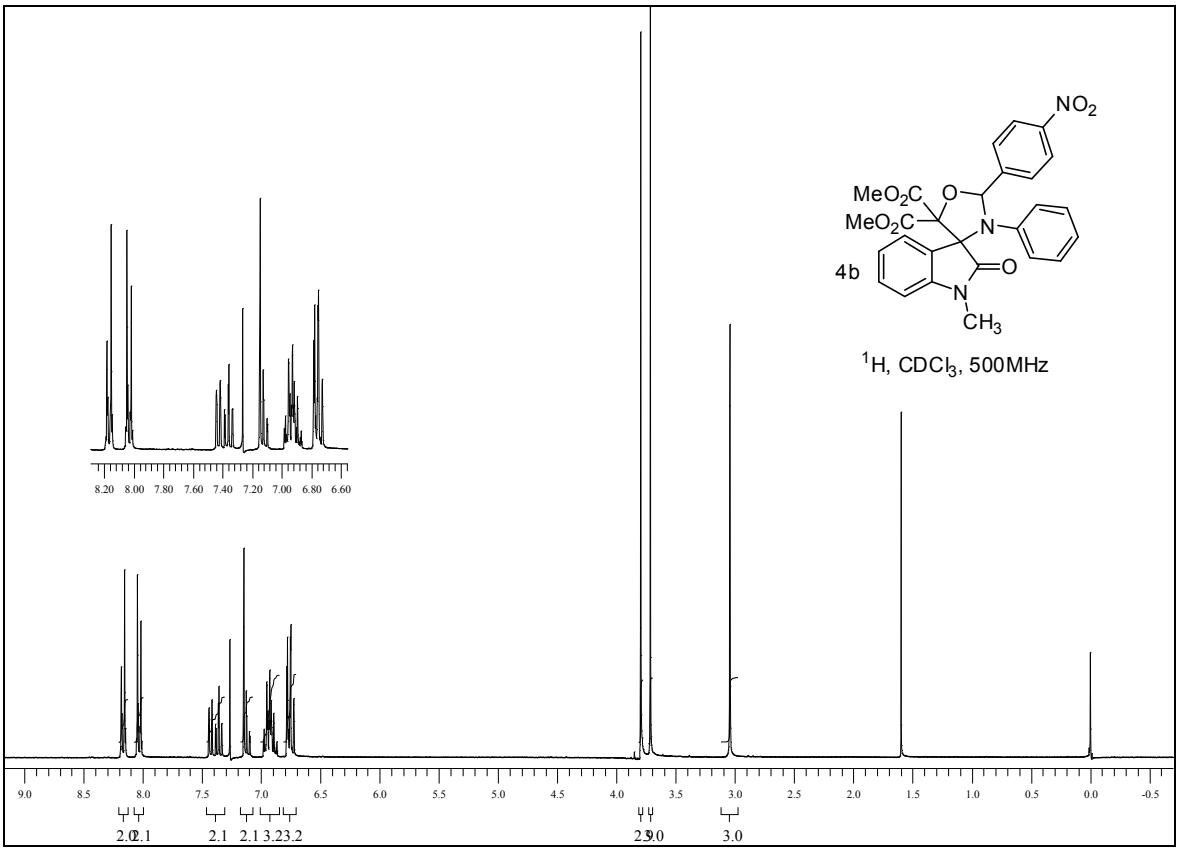
Crystal data: $C_{30}H_{27}N_3O_8$, M = 557.55, monoclinic, space group C2/c, a = 22.5171(11) Å, b = 13.1220(6) Å, c = 21.6558(10) Å, β = 118.366(1) °, V = 5630.3(5) $Å^3$, Z = 8, D_{calcd} = 1.315 mg m^{-3}, T = 294(2)K, μ = 0.097 mm^{-1}, F(000) = 2336, λ = 0.71073Å. Data collection yielded 26585 reflections resulting in 4955 unique, averaged reflection, 4001 with I>2σ(I). Full-matrix least-squares refinement led to a final R = 0.0704, wR = 0.2073 and GOF = 1.017. Intensity data were measured on Bruker Smart Apex with CCD area detector. CCDC 837874 contains supplementary Crystallographic data for the structure **4q**.

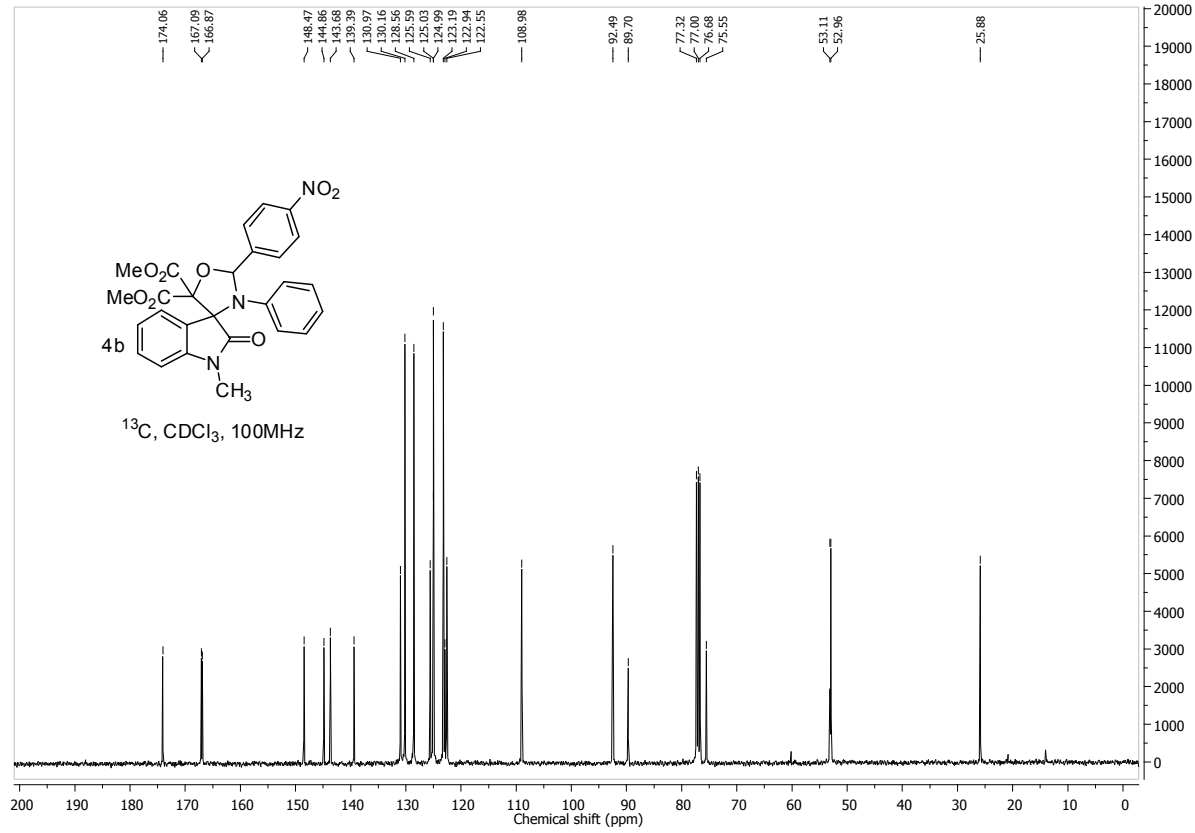


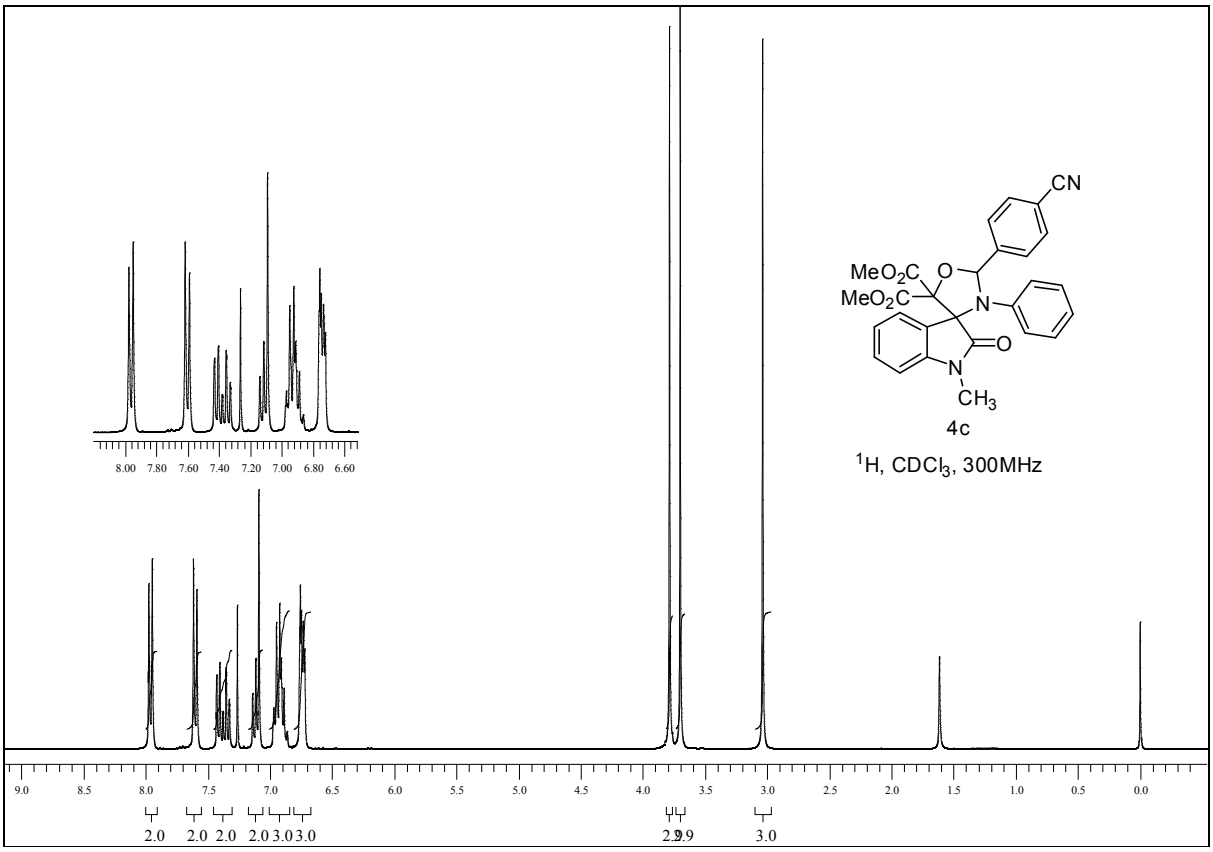
Crystal data for **10e**: $C_{32}H_{28}N_2O_9$, MW = 584.56, colorless block, 0.19 × 0.17 × 0.13 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 7.9805(11), b = 19.764(3), c = 17.862(3) Å, β = 99.901(2)°, V = 2775.4(7) $Å^3$, Z = 4, D_c = 1.399 g/cm^3, F_{000} = 1224, CCD Area Detector, MoKα radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 50.0º, 22205 reflections collected, 4878 unique (R_{int} = 0.0488). Final *GooF* = 1.070, *R1* = 0.0408, *wR2* = 0.0981, *R* indices based on 3520 reflections with I>2σ(I) (refinement on F^2), 392 parameters, 0 restraints, μ = 0.103 mm^{-1}. CCDC 901999 contains supplementary Crystallographic data for the structure

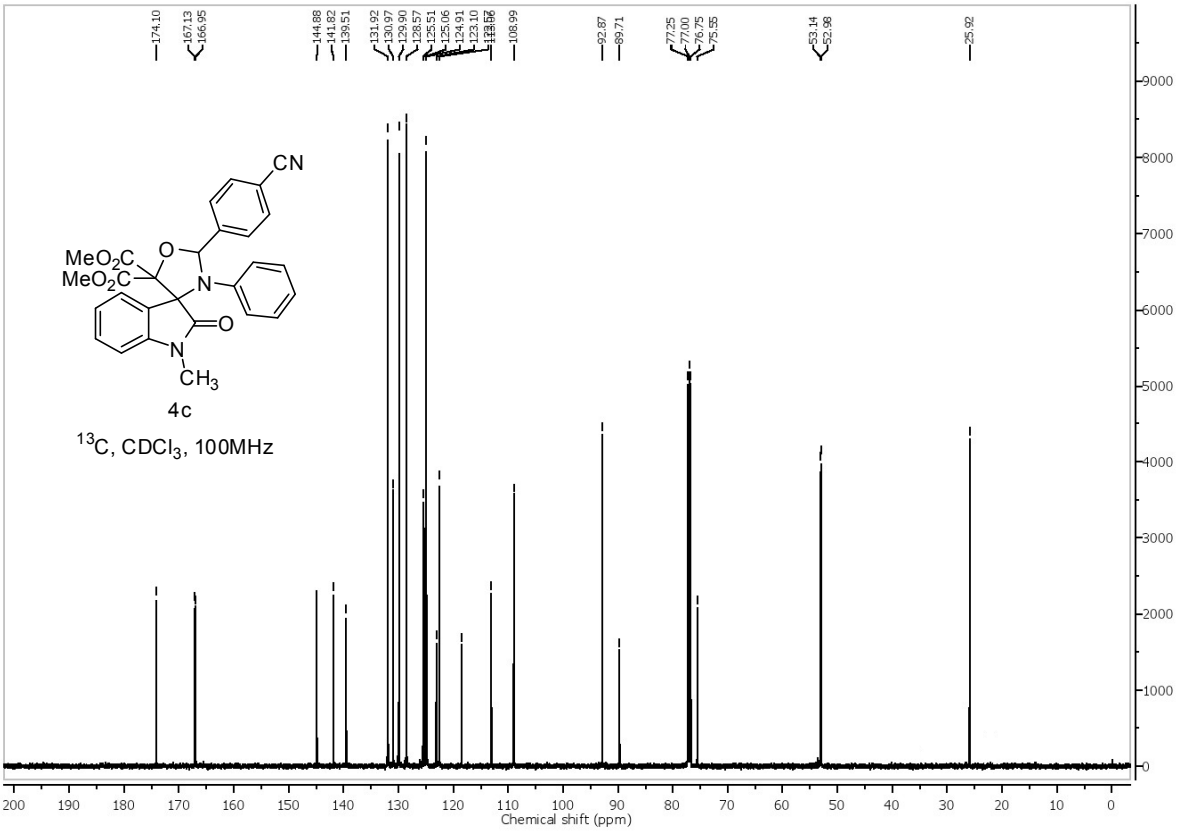

MeO2C
MeO2C
O
N
O
N
CH3
4a
1H, CDCl3, 300MHz
7.80 7.60 7.40 7.20 7.00 6.80 6.60
4.2
4.2
2.0
1.1
2.1
2.1
3.0
3.1
3.1
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

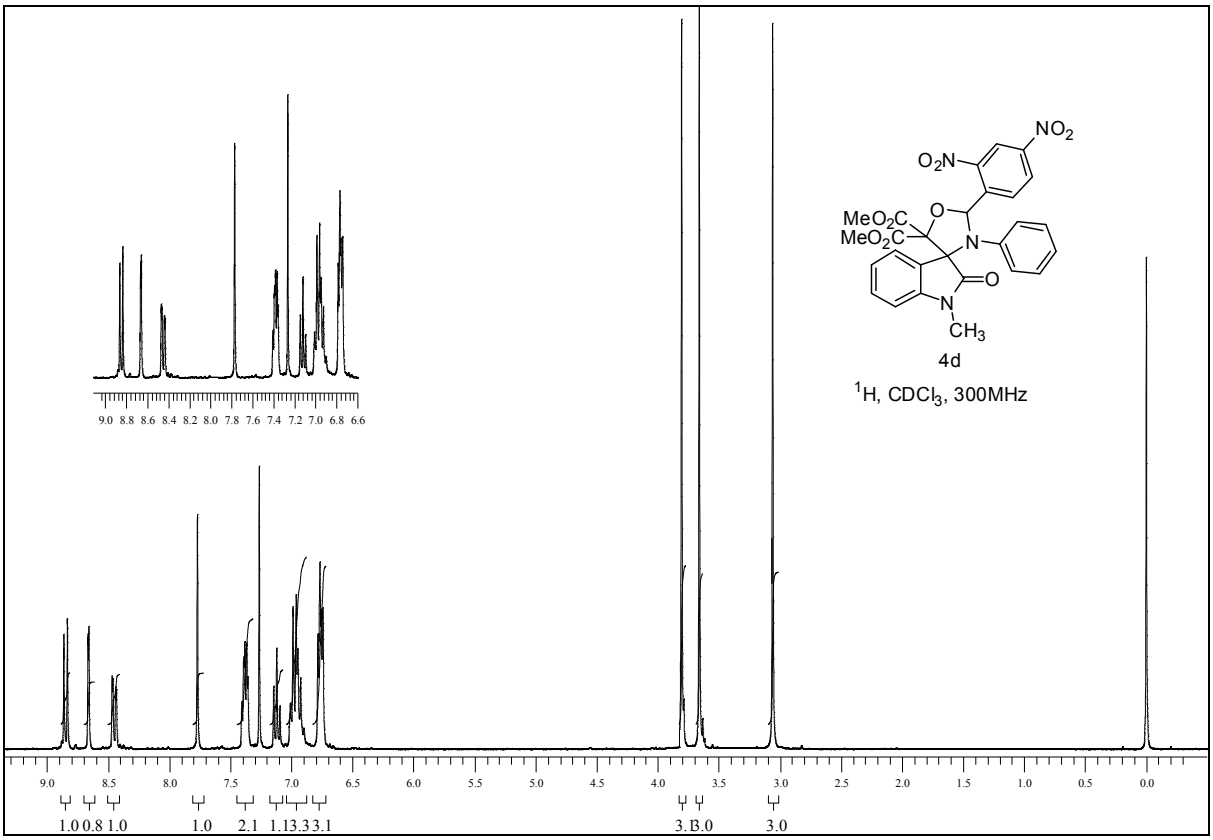

174.12
167.33
167.11
144.79
140.55
136.46
130.71
129.40
129.13
128.37
128.14
125.16
124.36
123.87
122.55
108.84
94.10
89.90
77.25
77.00
76.75
75.44
53.07
52.85
25.99
MeO2C
MeO2C
O
N
O
N
CH3
4a
13C, CDCl3, 100MHz
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

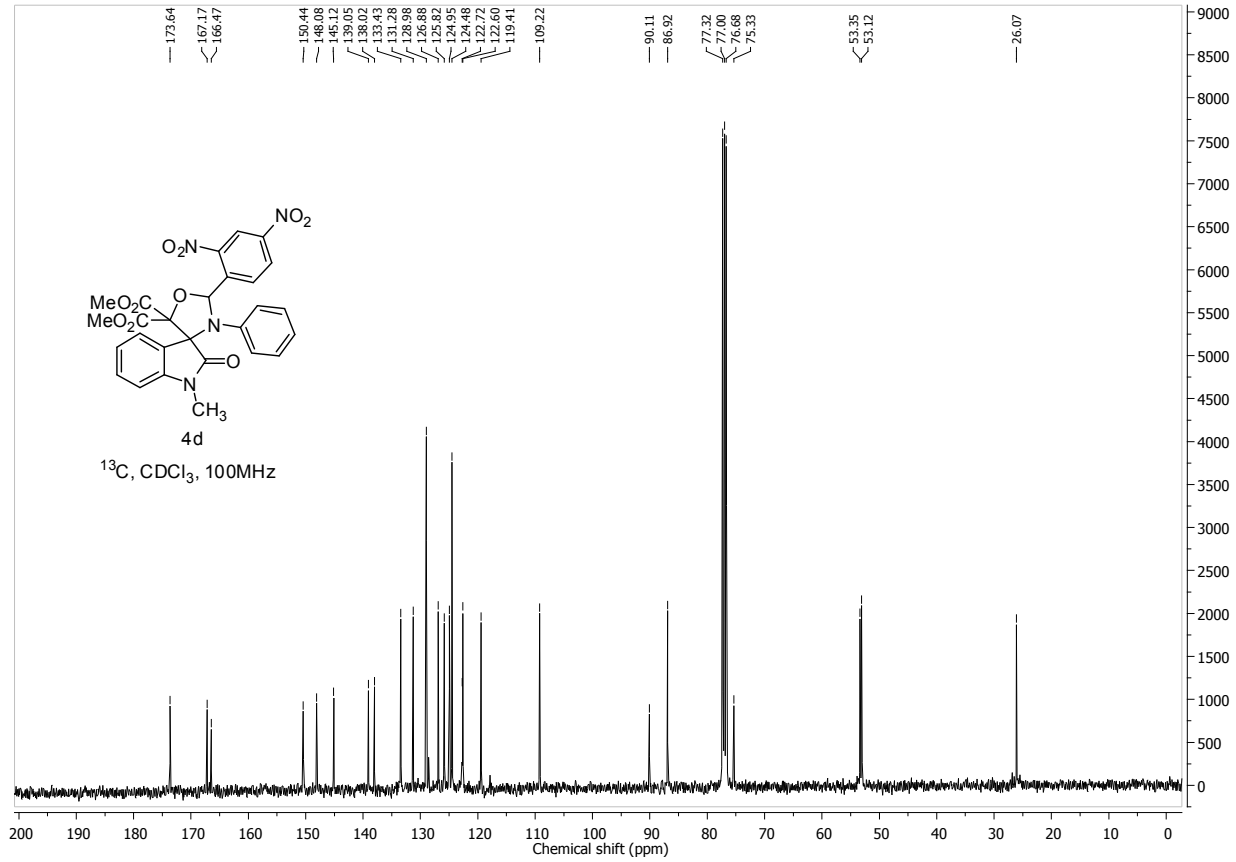

NO2
MeO2C
MeO2C
O
N
4b
O
N
CH3
1H, CDCl3, 500MHz

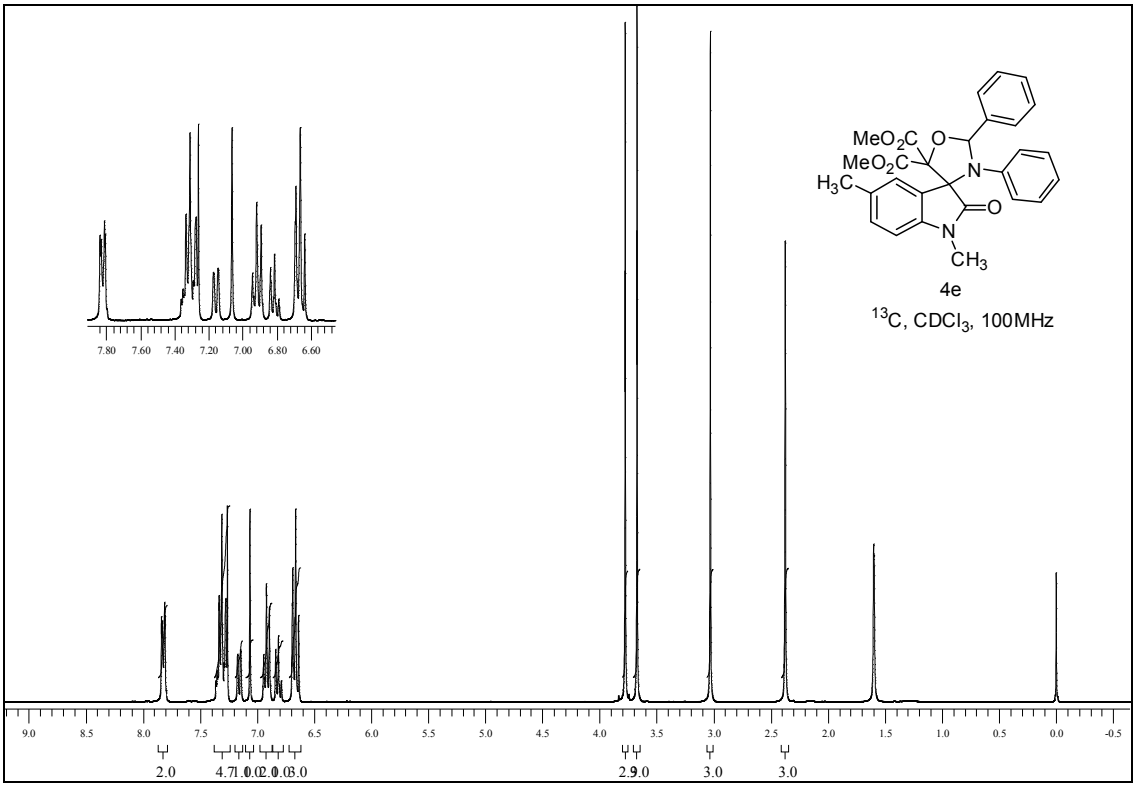

NO2
MeO2C
MeO2C
O
N
4b
O
N
CH3
13C, CDCl3, 100MHz
Chemical shift (ppm)

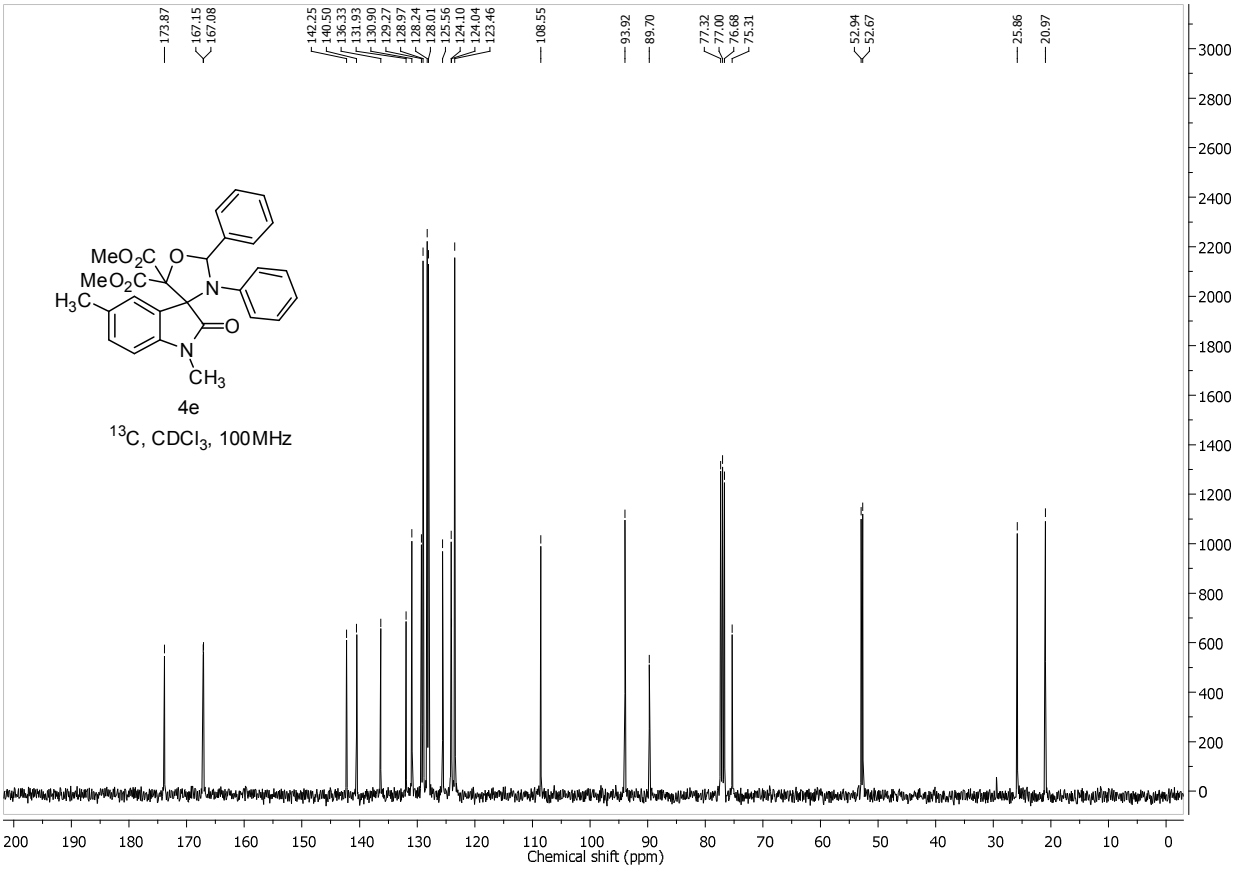

CN
MeO2C
MeO2C
O
N
O
N
CH3
4c
1H, CDCl3, 300MHz
8.00 7.80 7.60 7.40 7.20 7.00 6.80 6.60
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
2.0 2.0 2.0 2.0 3.0 3.0
3.0

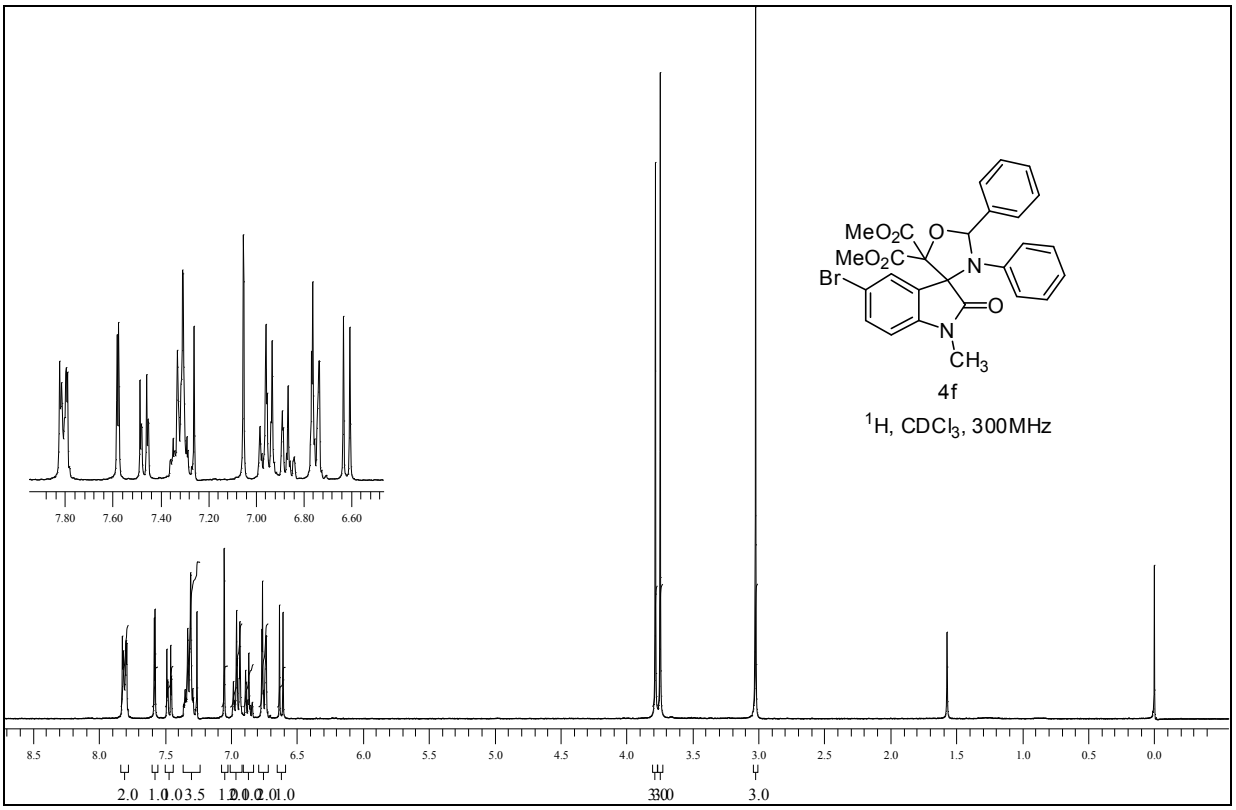

174.10
167.13
166.95
144.88
141.82
139.51
131.92
130.97
129.90
128.57
125.51
125.06
124.91
123.10
108.99
92.87
89.71
77.25
77.00
76.75
75.55
53.14
52.98
25.92
CN
MeO2C
MeO2C
O
N
O
N
CH3
4c
13C, CDCl3, 100MHz
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

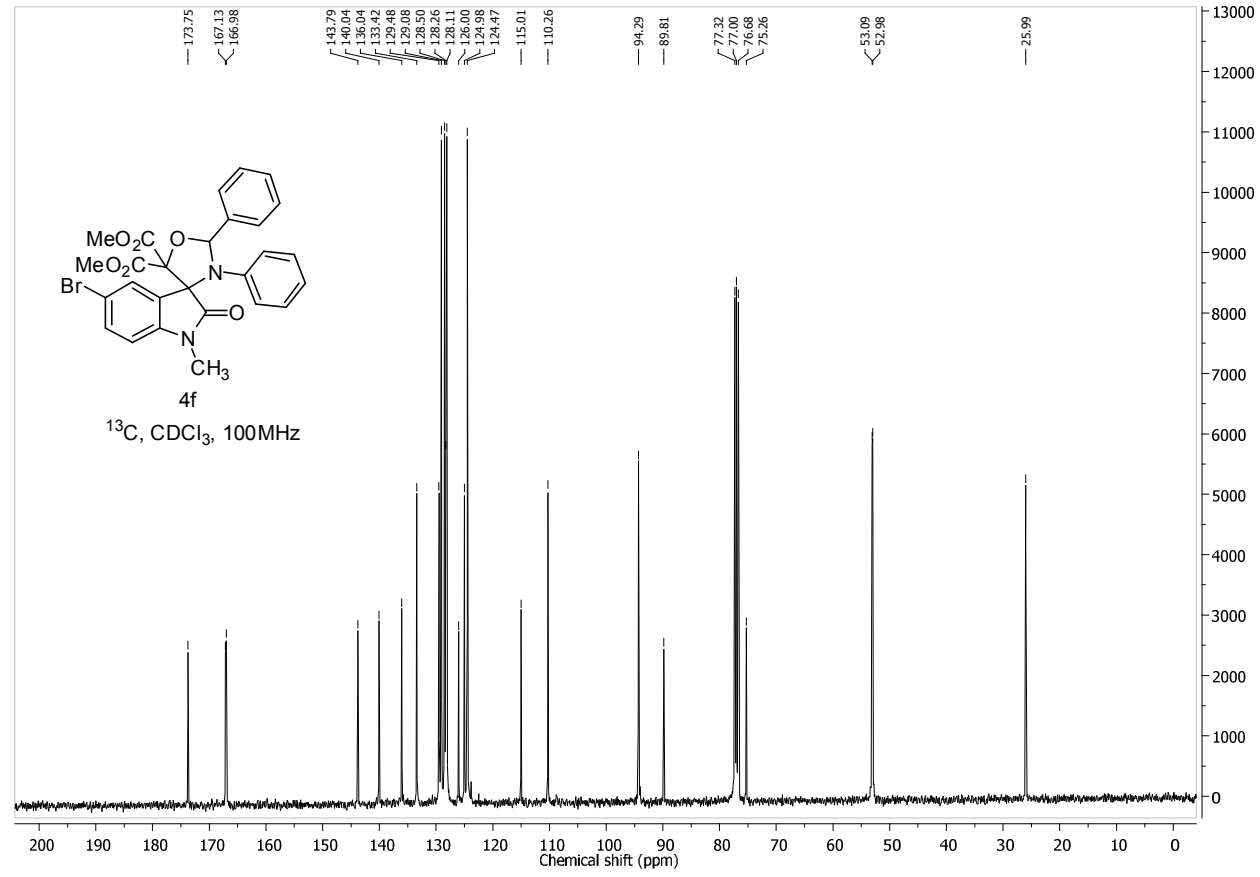

NO2
O2N
MeO2C
MeO2C
O
N
O
N
CH3
4d
1H, CDCl3, 300MHz

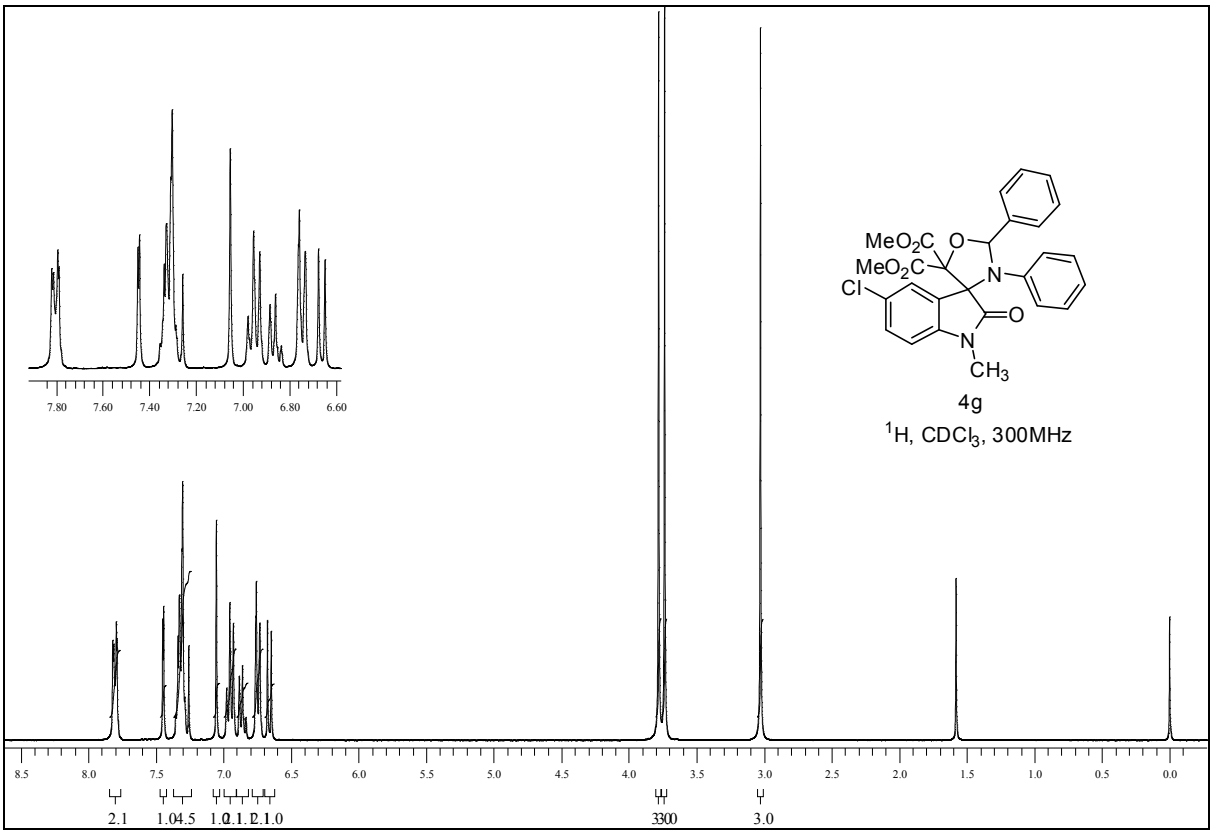

NO2
O2N
MeO2C
MeO2C
O
N
O
N
CH3
4d
13C, CDCl3, 100MHz
Chemical shift (ppm)

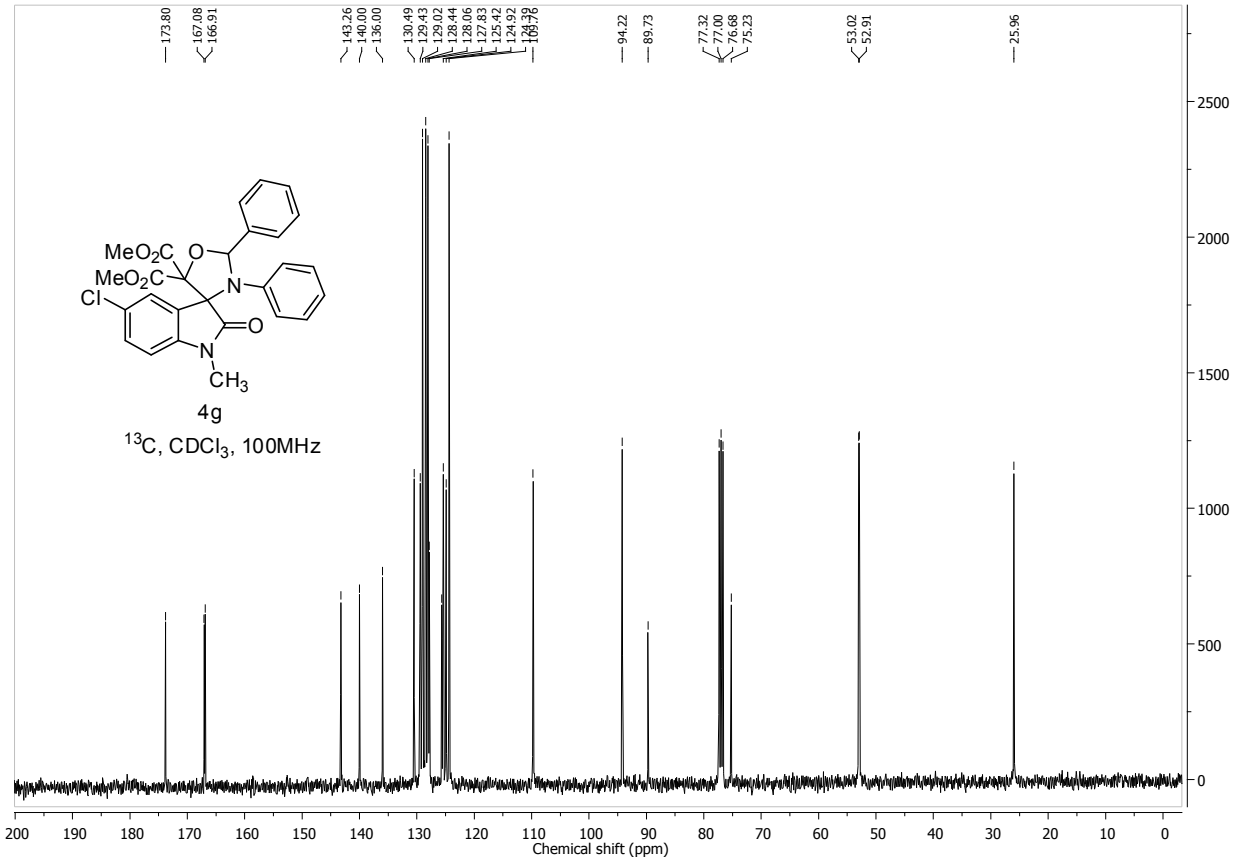

MeO2C
MeO2C
H3C
O
N
O
N
CH3
4e
13C, CDCl3, 100MHz

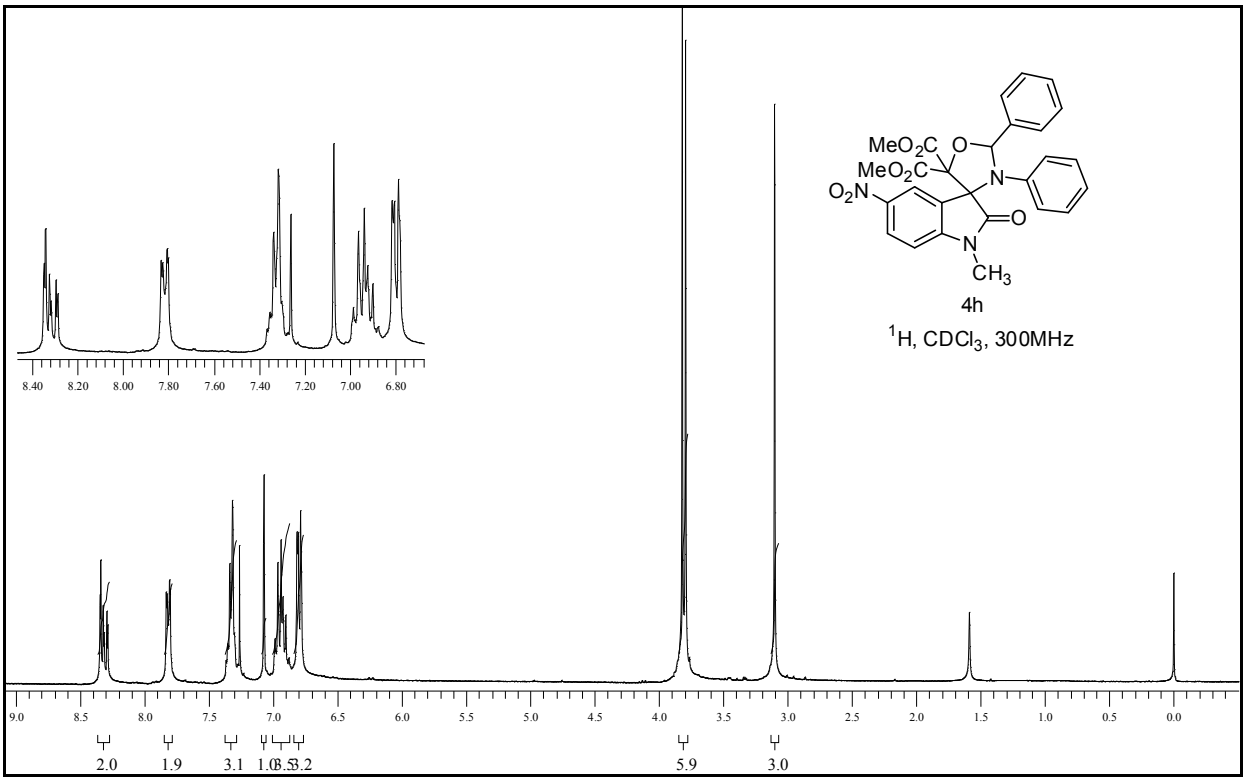

MeO2C
MeO2C
H3C
O
N
O
N
CH3
4e
13C, CDCl3, 100MHz
Chemical shift (ppm)

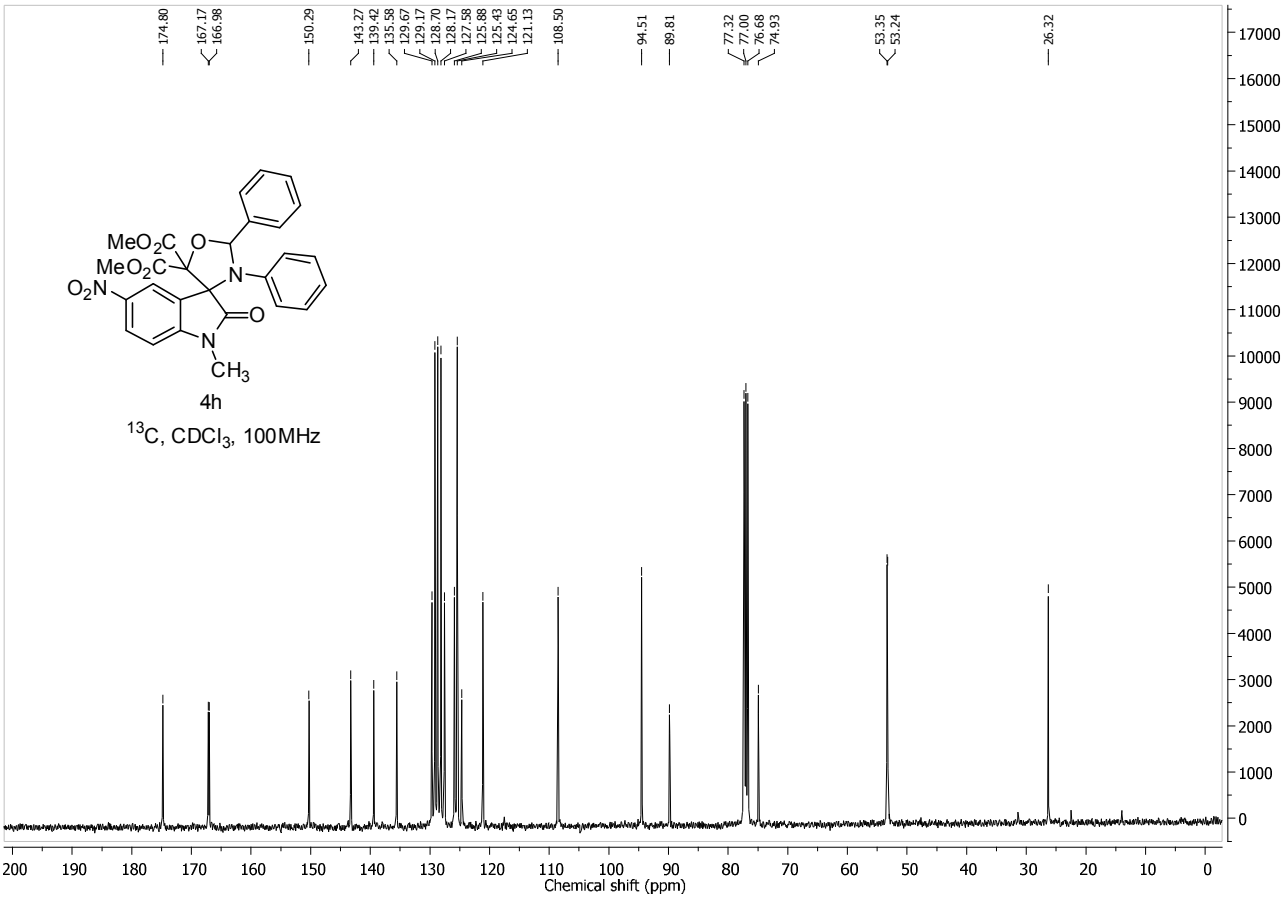

MeO2C
MeO2C
Br
O
N
O
N
CH3
4f
1H, CDCl3, 300MHz

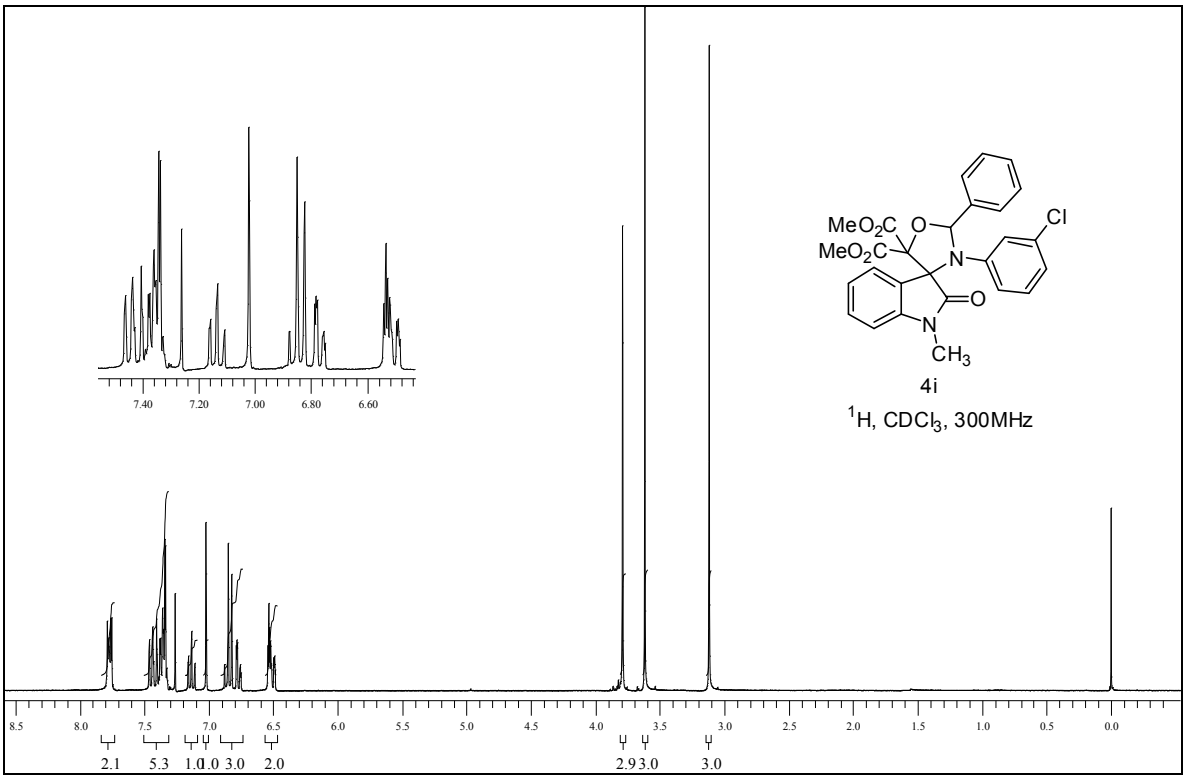

MeO2C
MeO2C
Br
O
N
O
N
CH3
4f
13C, CDCl3, 100MHz
Chemical shift (ppm)

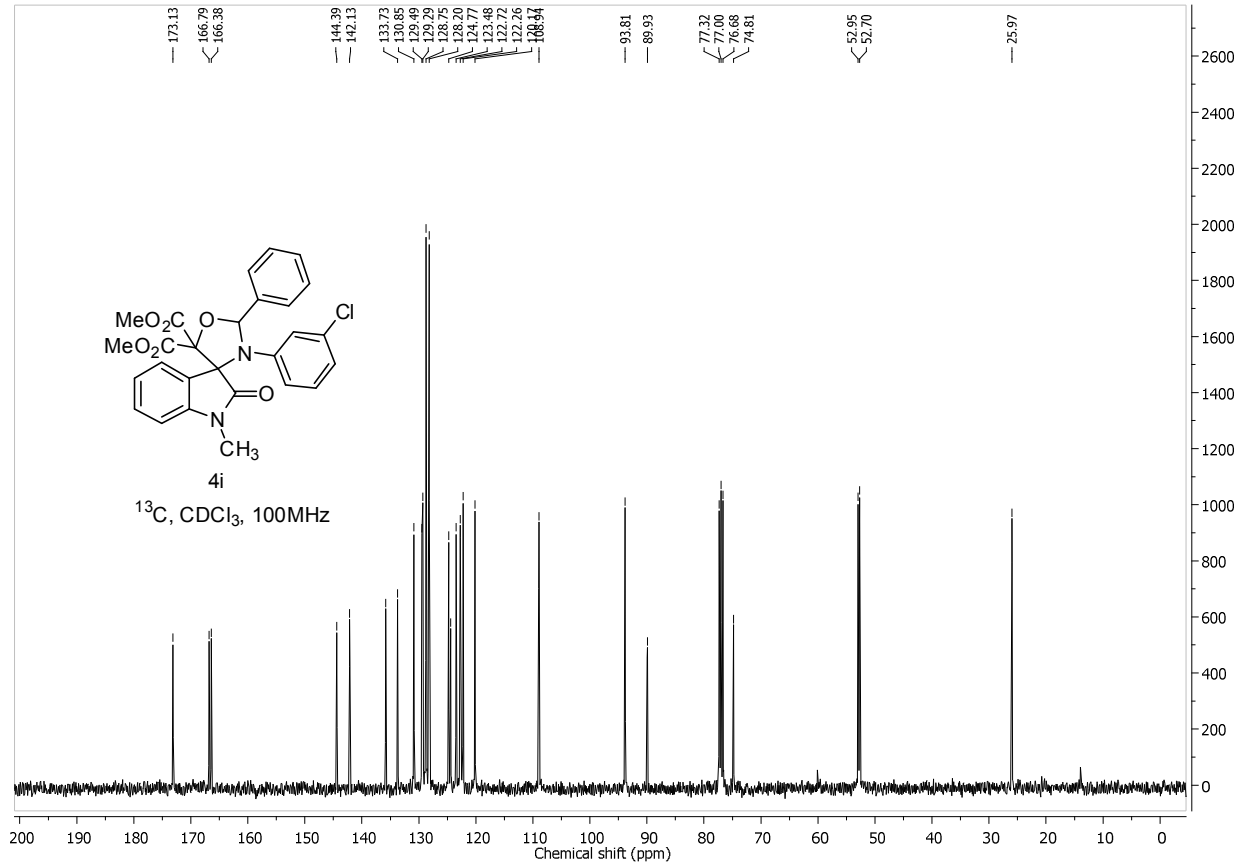

MeO2C
MeO2C
O
N
Cl
O
N
CH3
4g
1H, CDCl3, 300MHz

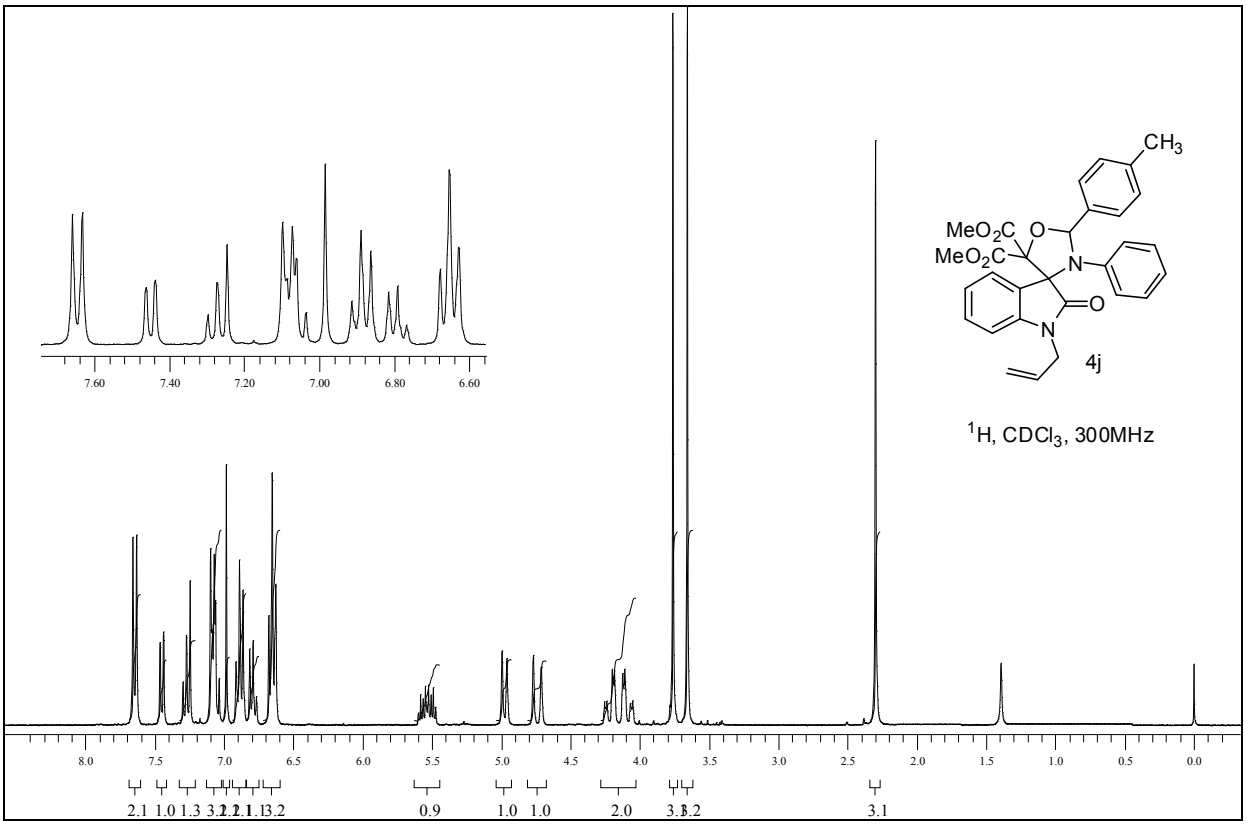

MeO2C
MeO2C
O
N
Cl
O
N
CH3
4g
13C, CDCl3, 100MHz
Chemical shift (ppm)

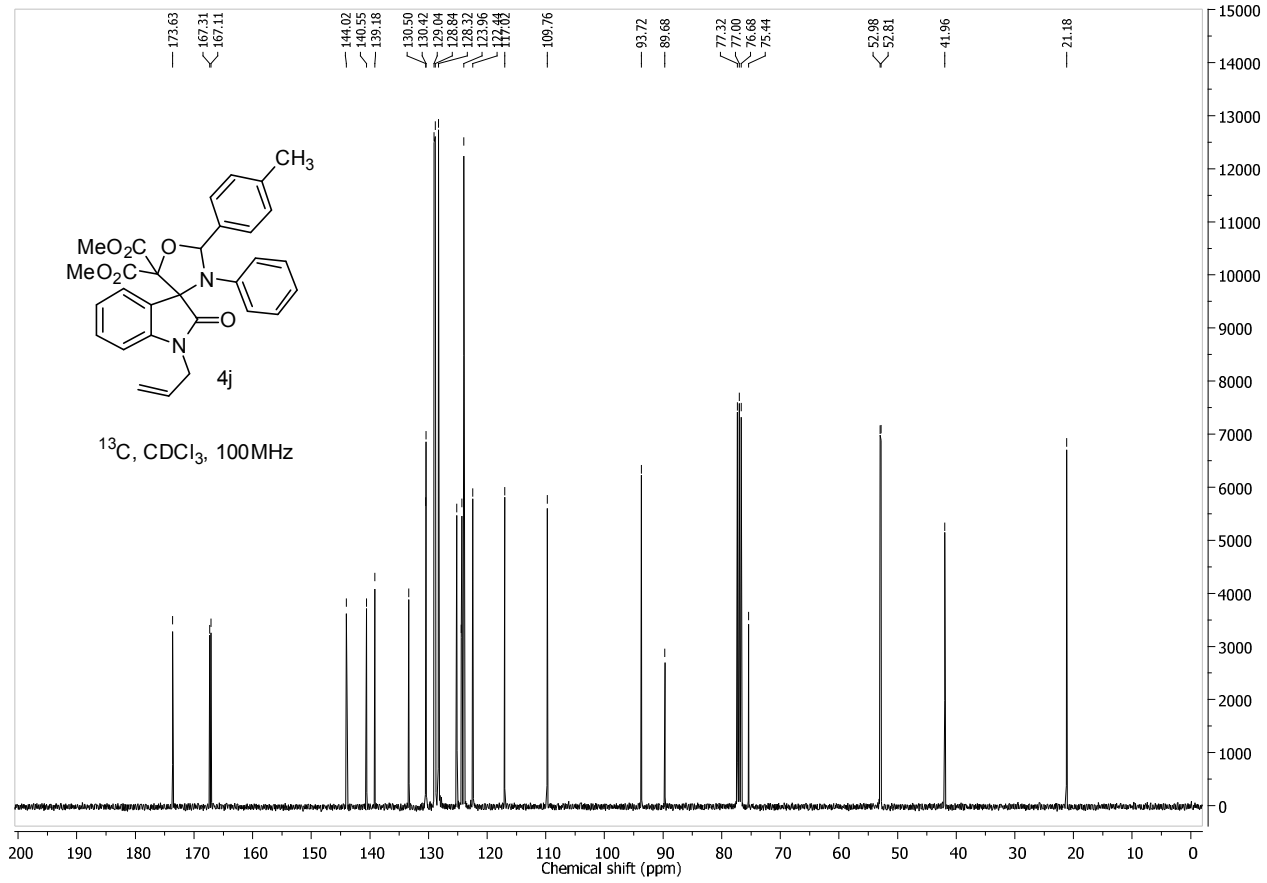

MeO2C
MeO2C
O2N
O
N
O
N
CH3
4h
1H, CDCl3, 300MHz
2.0
1.9
3.1
1.0
3.2
5.9
3.0

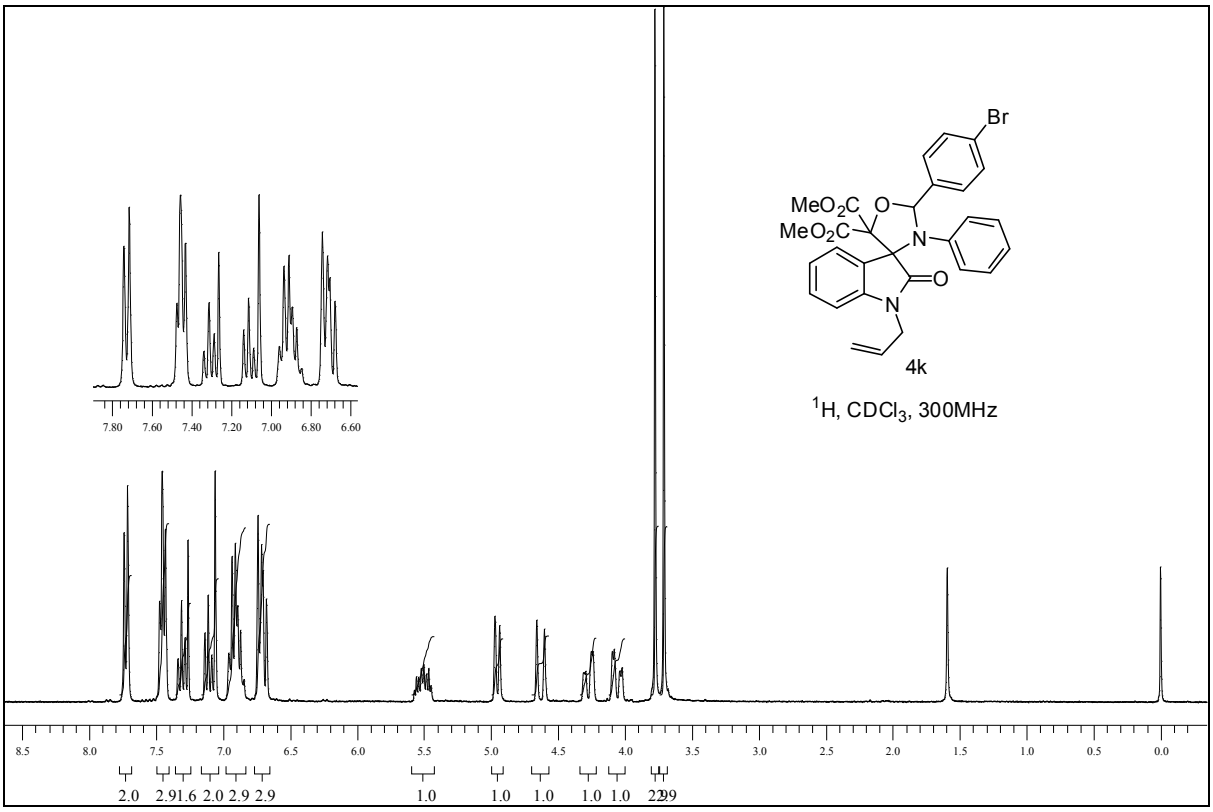

MeO2C
MeO2C
O2N
O
N
O
N
CH3
4h
13C, CDCl3, 100MHz
Chemical shift (ppm)

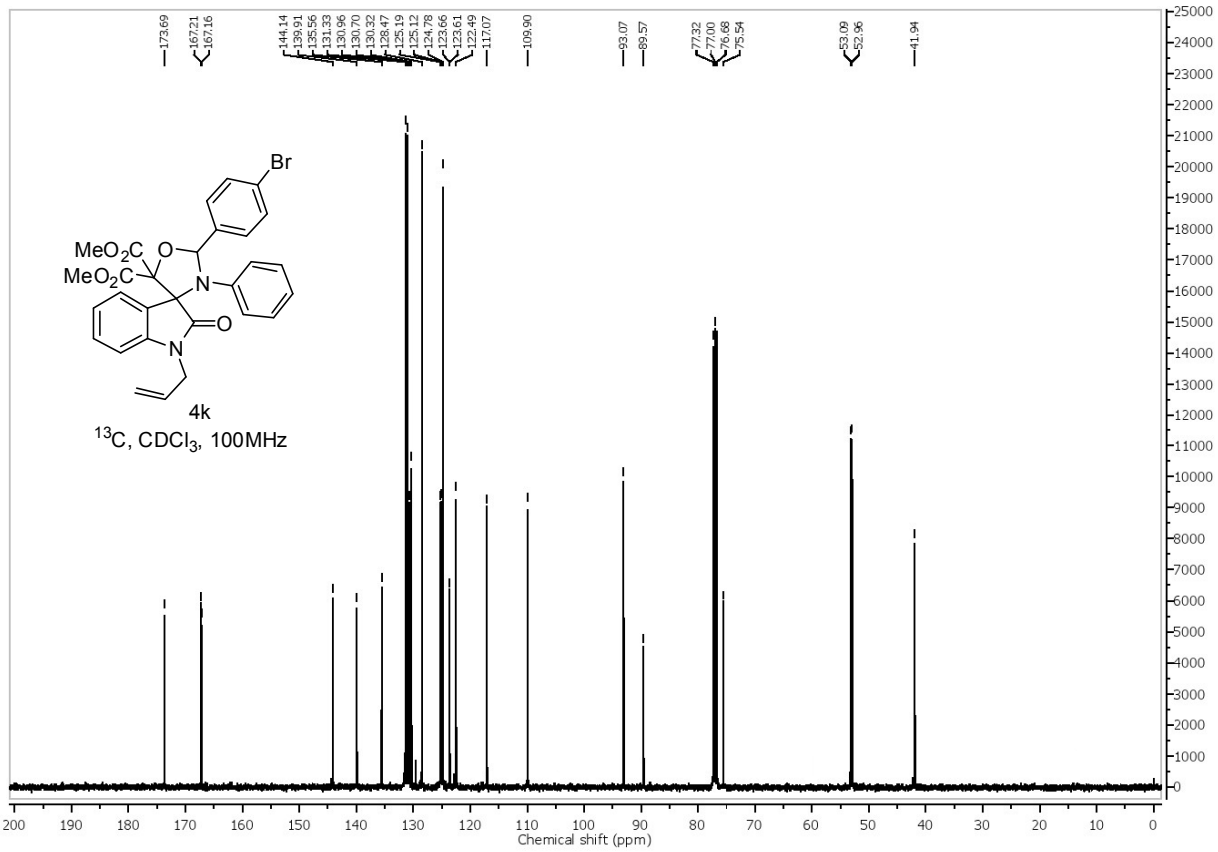

MeO2C
MeO2C
O
N
Cl
O
N
CH3
4i
1H, CDCl3, 300MHz

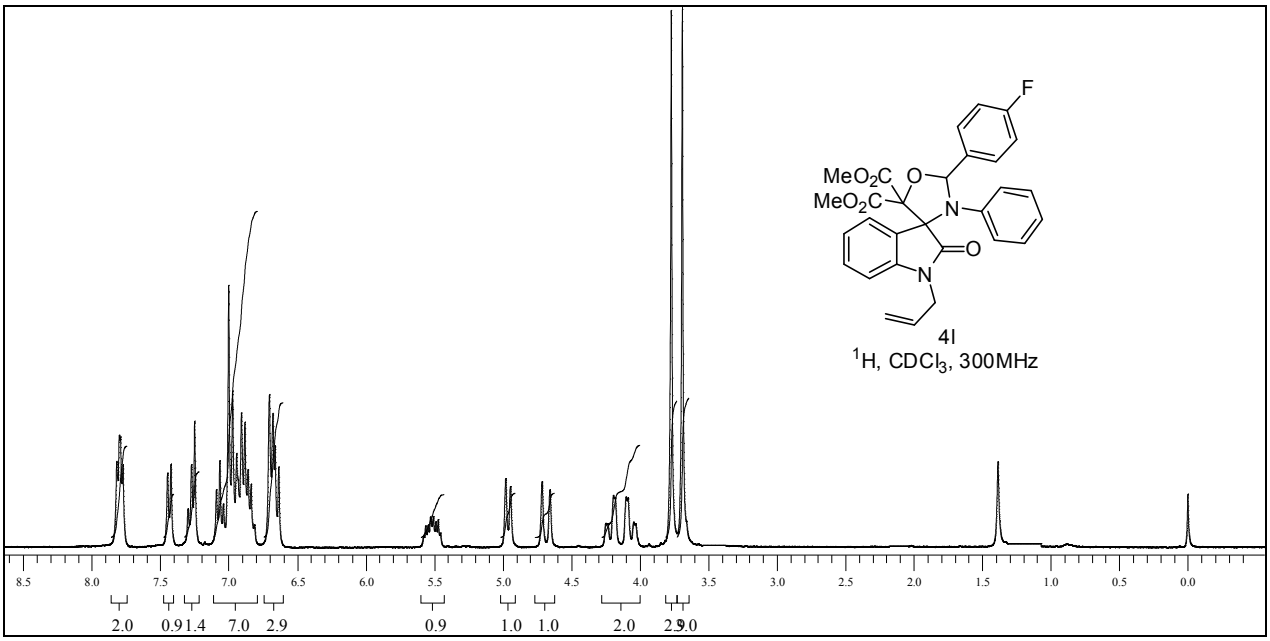

MeO2C
MeO2C
O
N
Cl
O
N
CH3
4i
13C, CDCl3, 100MHz
Chemical shift (ppm)

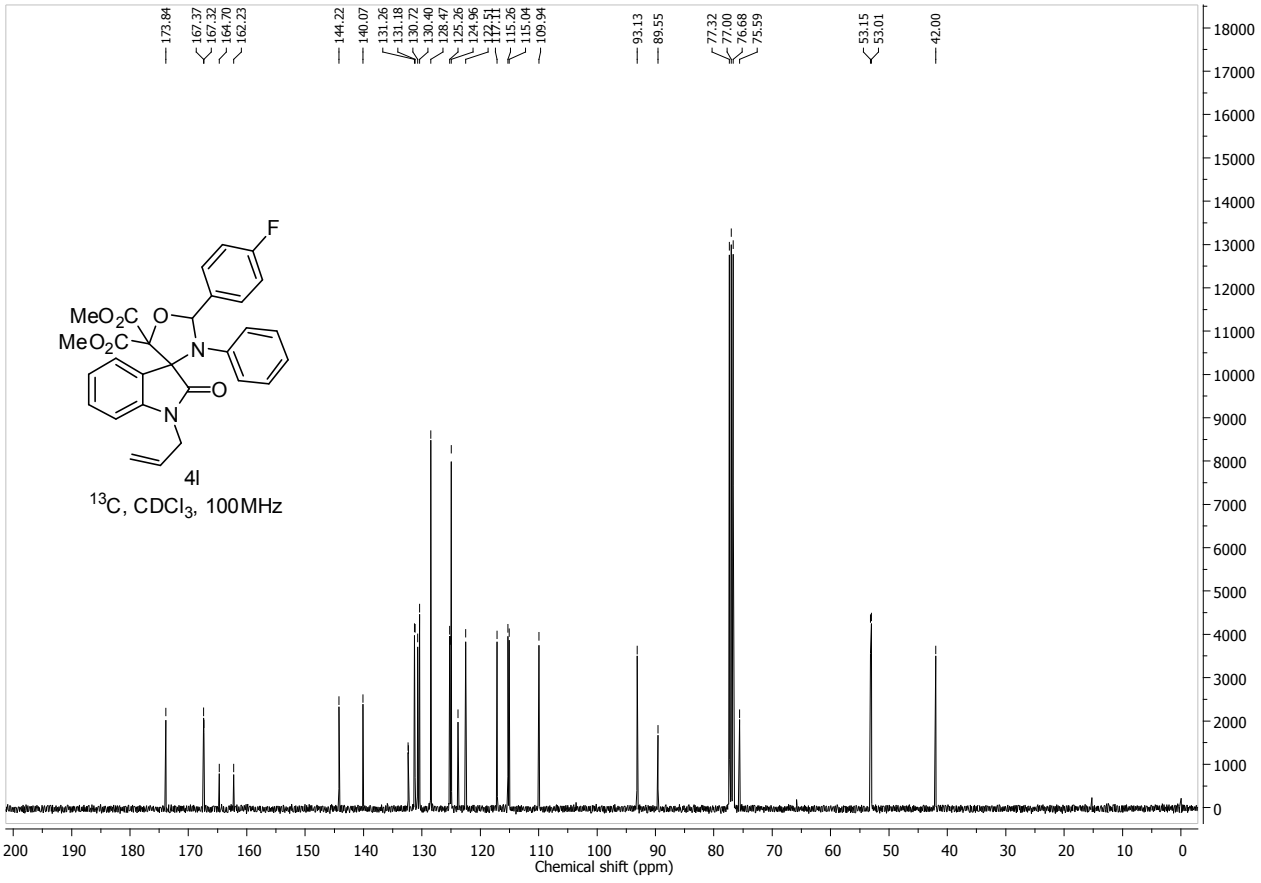

CH3
MeO2C
MeO2C
O
N
O
N
4j
1H, CDCl3, 300MHz

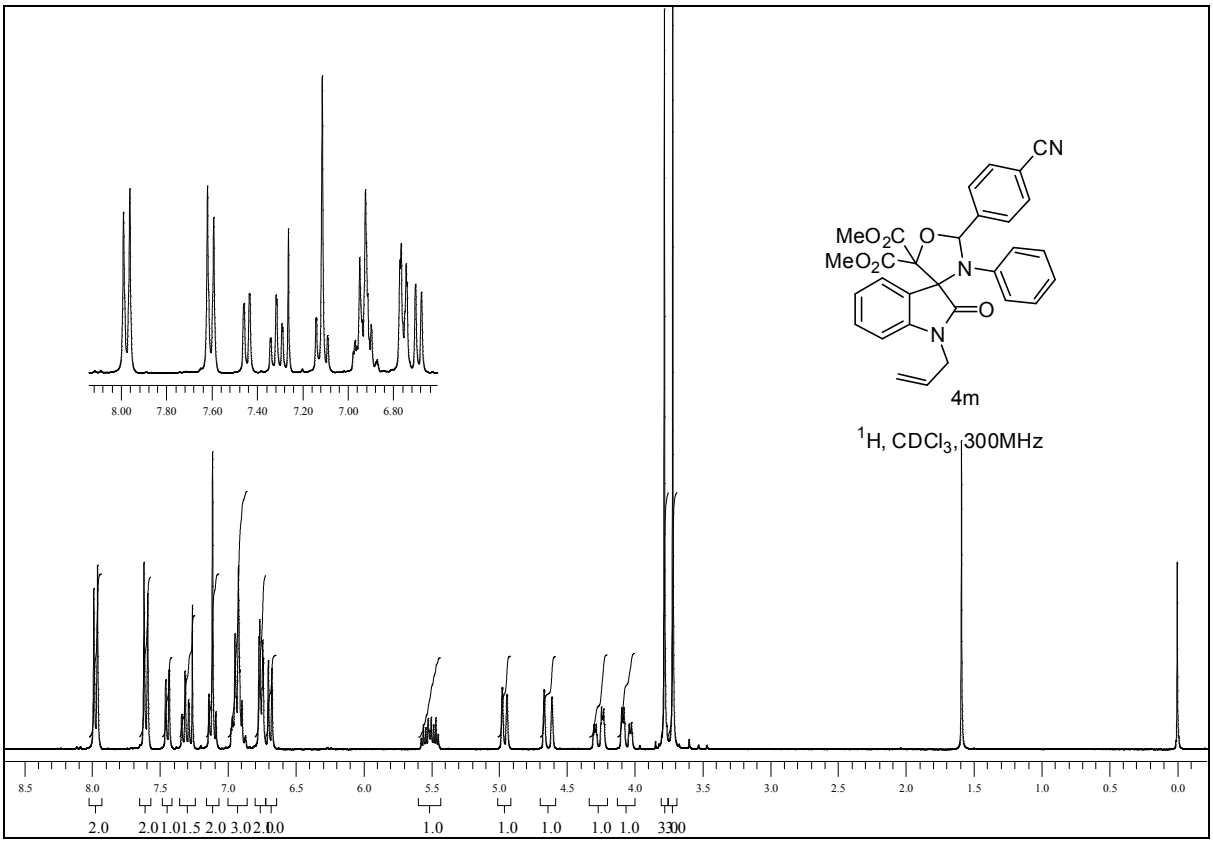

173.63
167.31
167.11
144.02
140.55
139.18
130.50
130.42
129.04
128.84
128.32
123.96
109.76
93.72
89.68
77.32
77.00
76.68
75.44
52.98
52.81
41.96
21.18
CH3
MeO2C
MeO2C
O
N
O
N
4j
13C, CDCl3, 100MHz
Chemical shift (ppm)

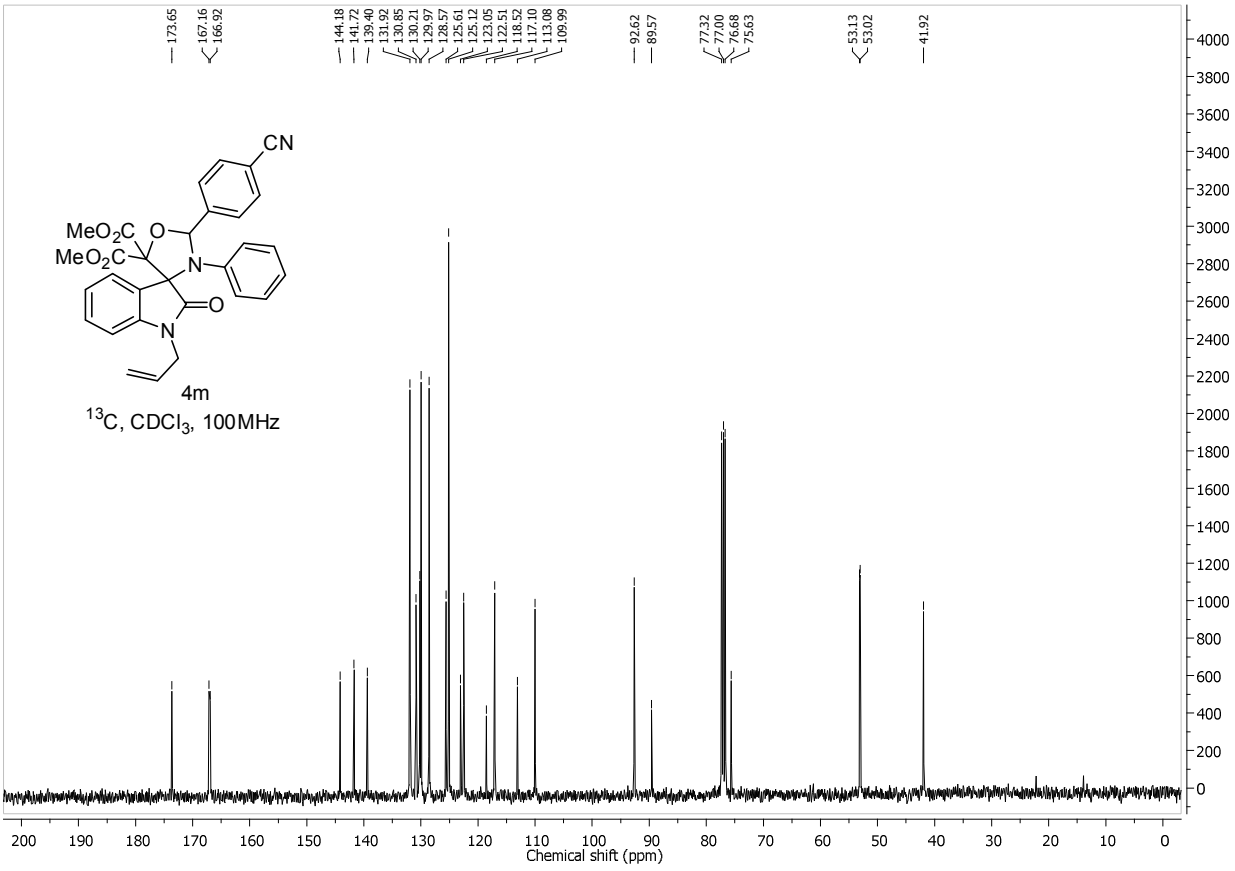

Br
MeO2C
MeO2C
O
N
O
N
4k
1H, CDCl3, 300MHz
7.80 7.60 7.40 7.20 7.00 6.80 6.60
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
2.0 2.91.6 2.0 2.9 2.9 1.0 1.0 1.0 1.0 1.0 2.9 2.9

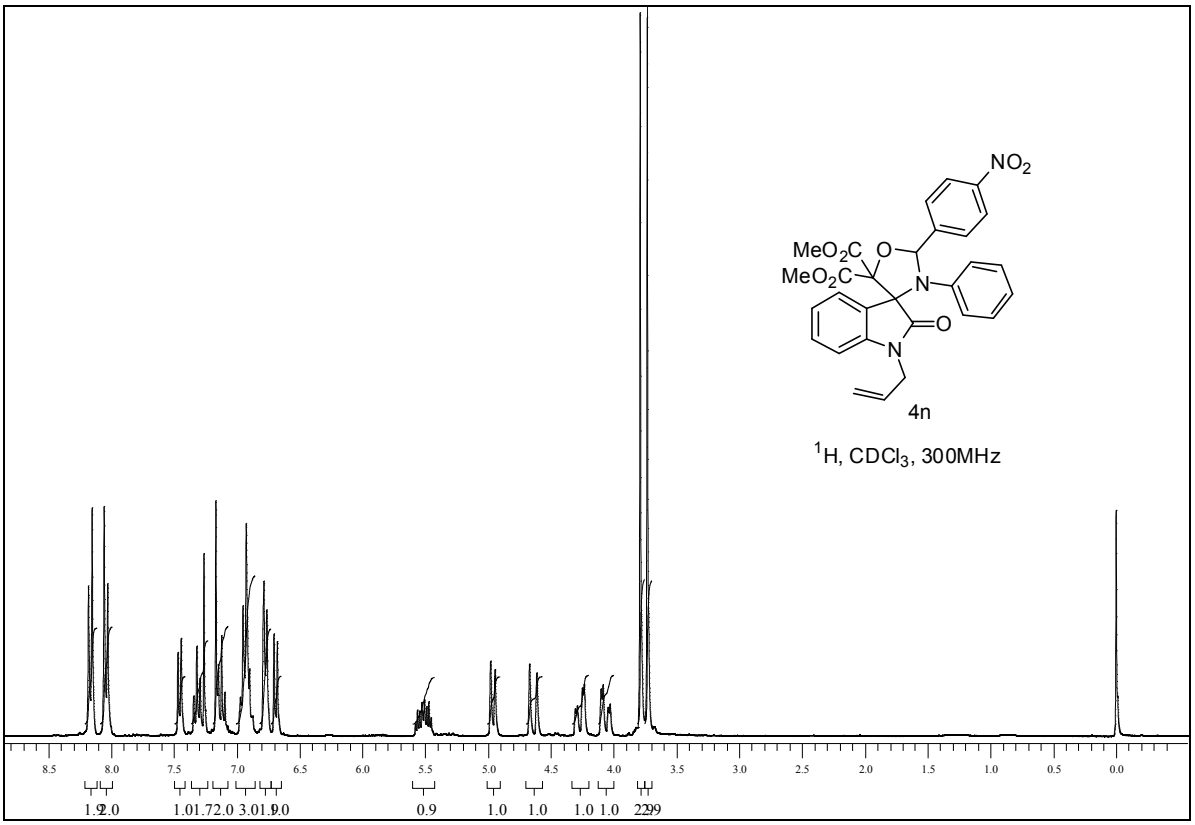

173.69
167.21
167.16
144.14
139.91
135.56
131.33
130.96
130.70
130.32
128.47
125.19
125.12
124.78
123.66
123.61
122.49
117.07
109.90
93.07
89.57
77.32
77.00
76.68
75.54
53.09
52.96
41.94
Br
MeO2C
MeO2C
O
N
O
N
4k
13C, CDCl3, 100MHz
Chemical shift (ppm)

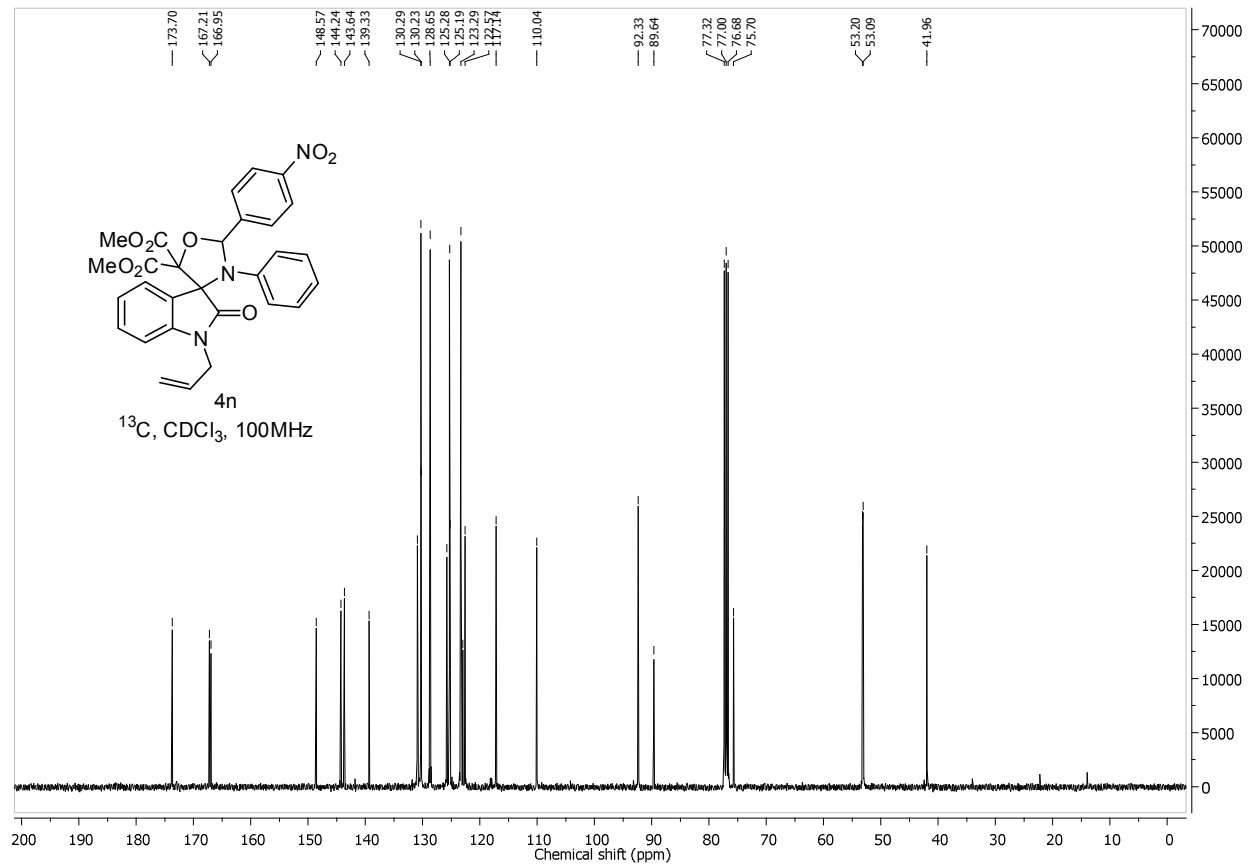

F
MeO2C
MeO2C
O
N
O
N
4l
1H, CDCl3, 300MHz
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
2.0 0.9 1.4 7.0 2.9 0.9 1.0 1.0 2.0 2.9 3.0

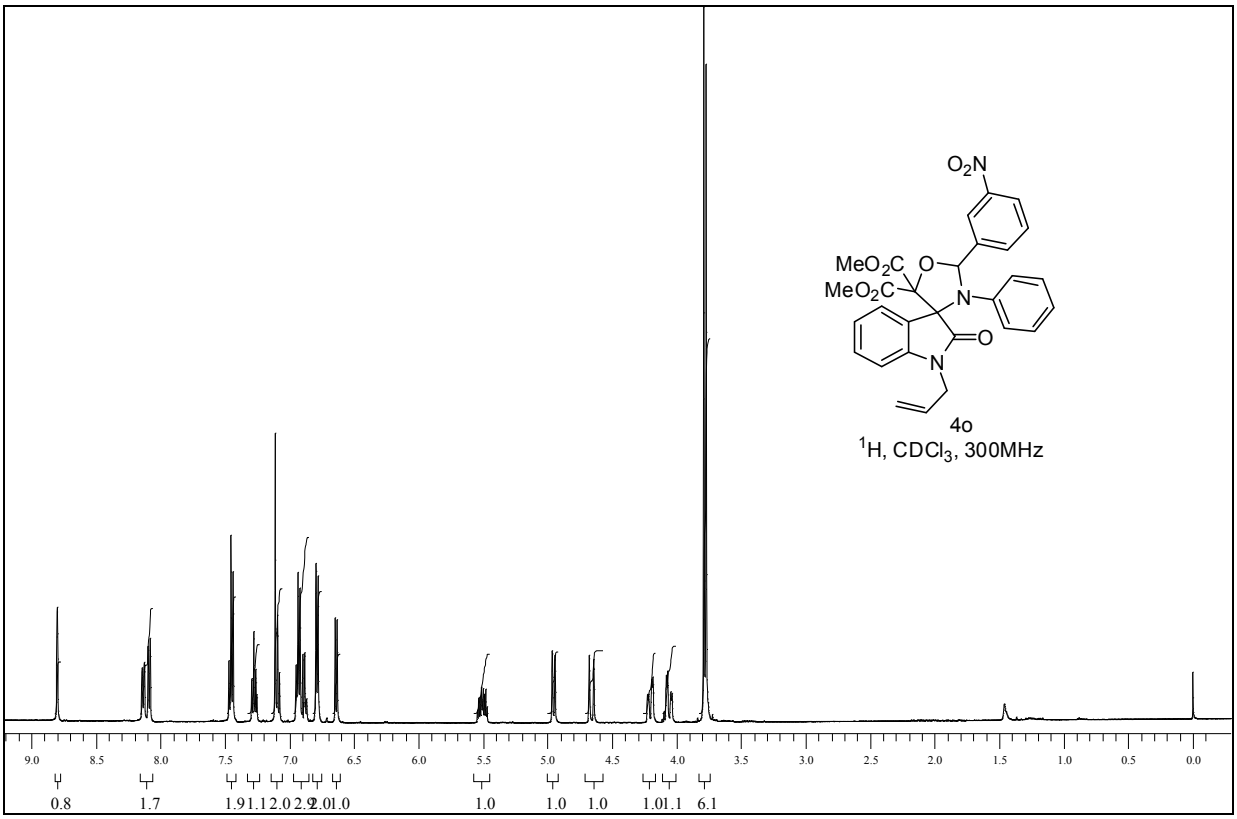

173.84
167.37
167.32
164.70
162.23
144.22
140.07
131.26
131.18
130.72
130.40
128.47
125.26
124.96
115.26
115.04
109.94
93.13
89.55
77.32
77.00
76.68
75.59
53.15
53.01
42.00
F
MeO2C
MeO2C
O
N
O
N
4l
13C, CDCl3, 100MHz
18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

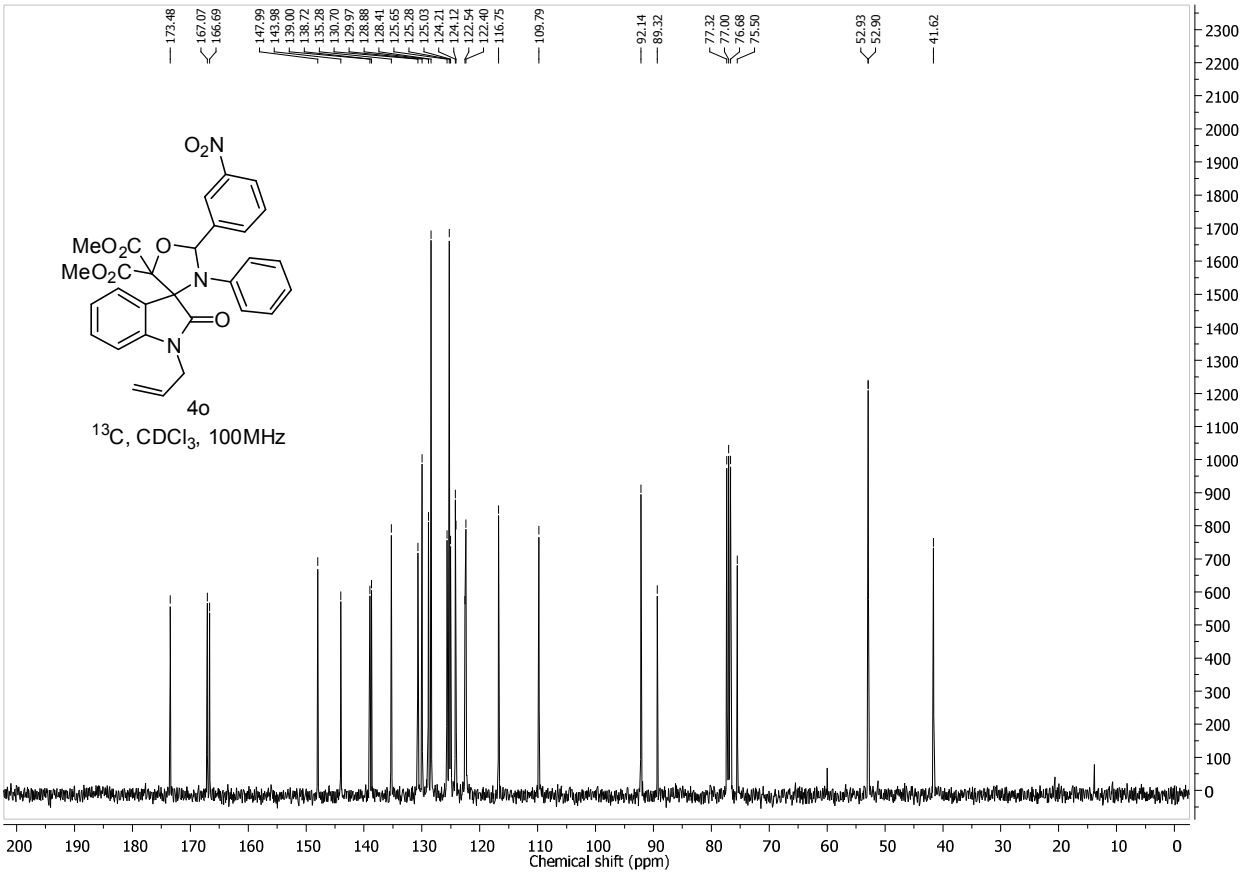

CN
MeO2C
MeO2C
O
N
O
N
4m
1H, CDCl3, 300MHz

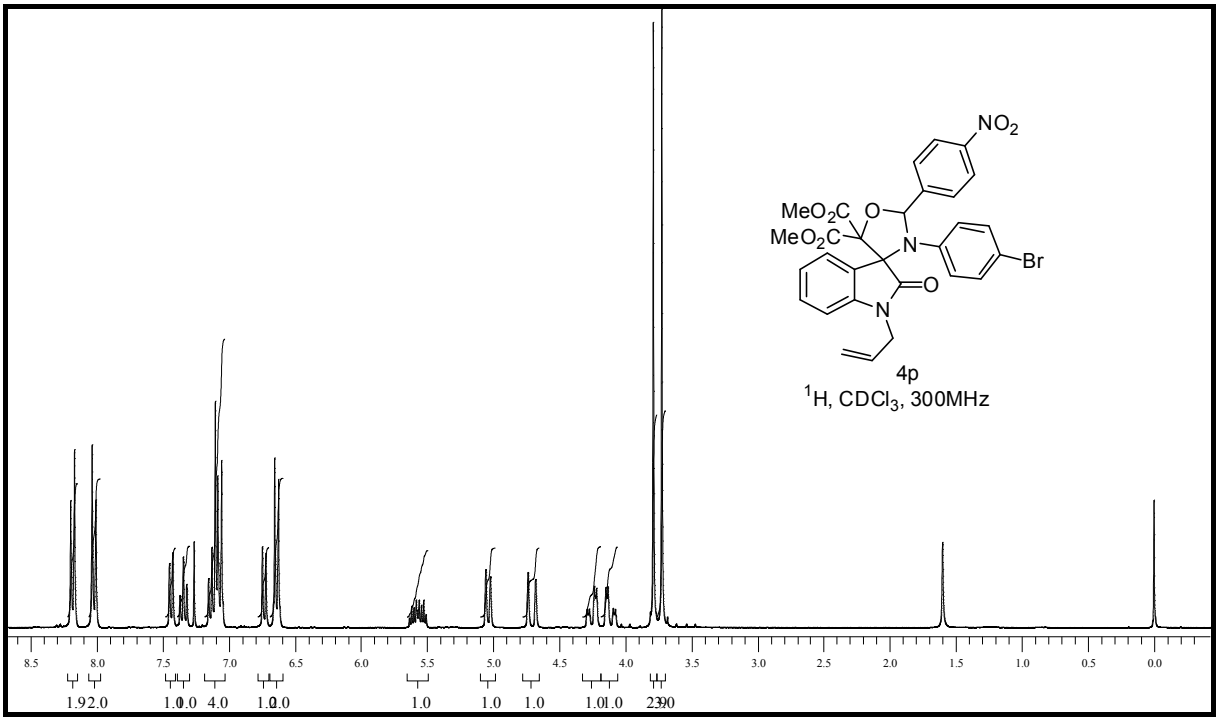

CN
MeO2C
MeO2C
O
N
O
N
4m
13C, CDCl3, 100MHz
Chemical shift (ppm)

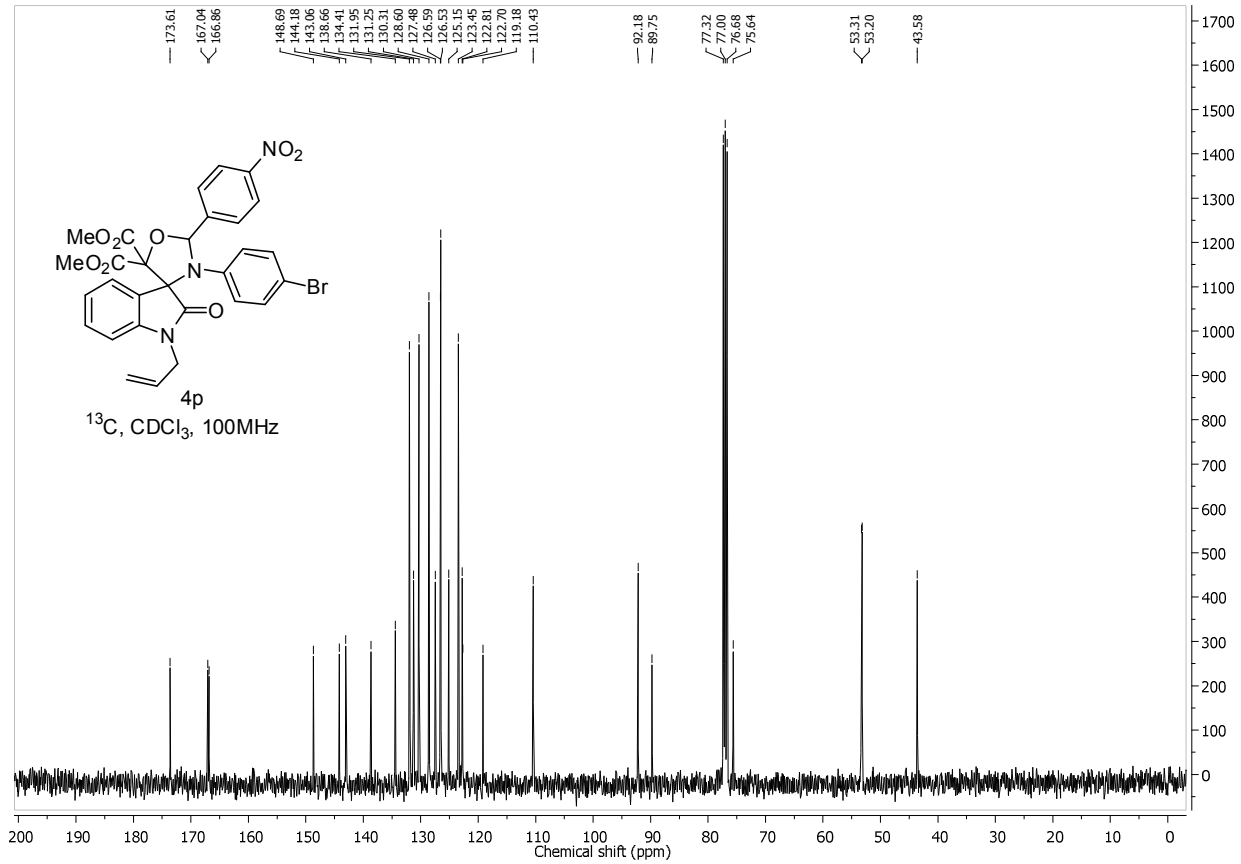

NO2
MeO2C
MeO2C
O
N
O
N
4n
1H, CDCl3, 300MHz

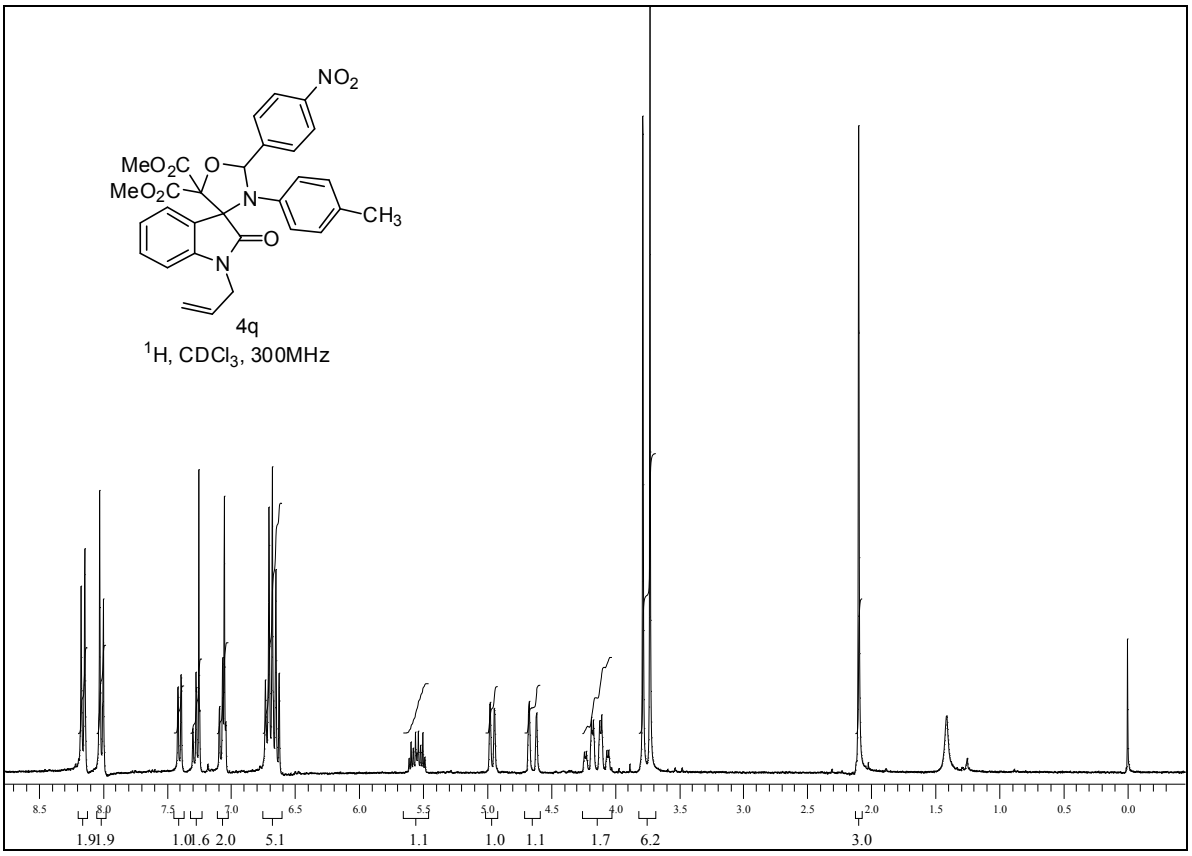

NO2
MeO2C
MeO2C
O
N
O
N
4n
13C, CDCl3, 100MHz
Chemical shift (ppm)

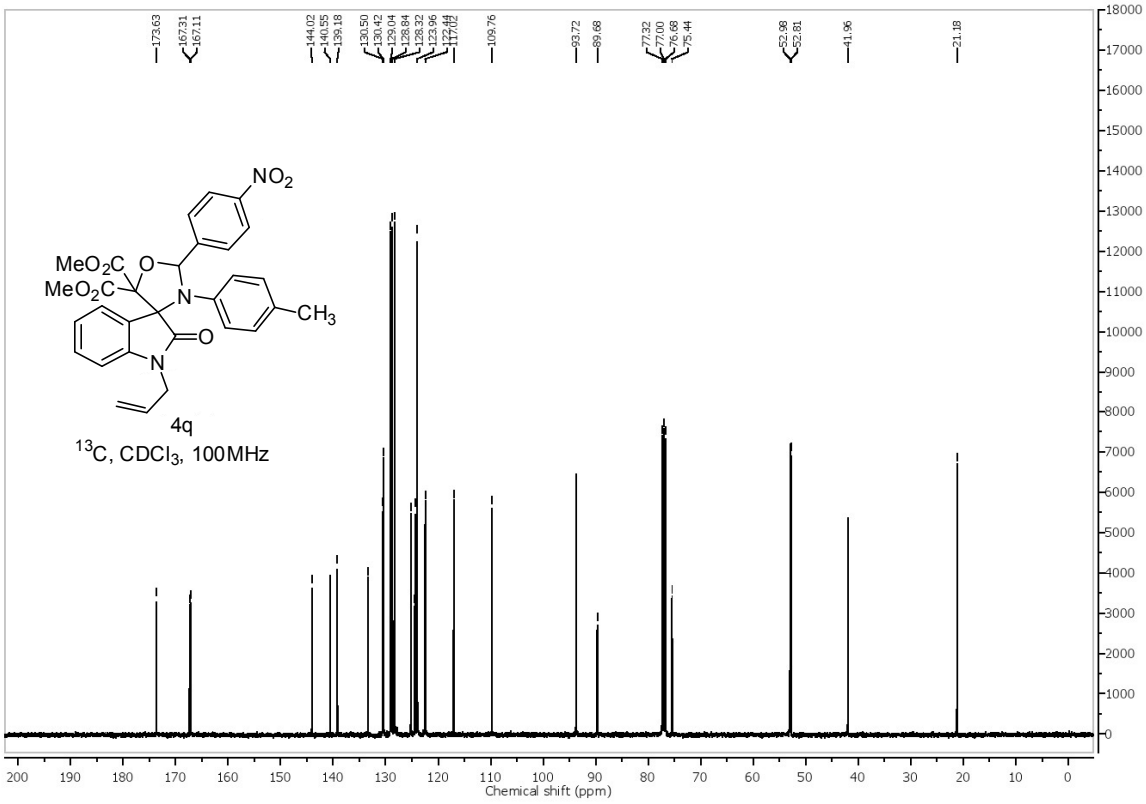

O2N
MeO2C
MeO2C
O
N
O
N
4o
1H, CDCl3, 300MHz
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0.8 1.7 1.9 1.1 2.0 2.2 2.0 1.0 1.0 1.0 1.0 1.0 1.1 6.1

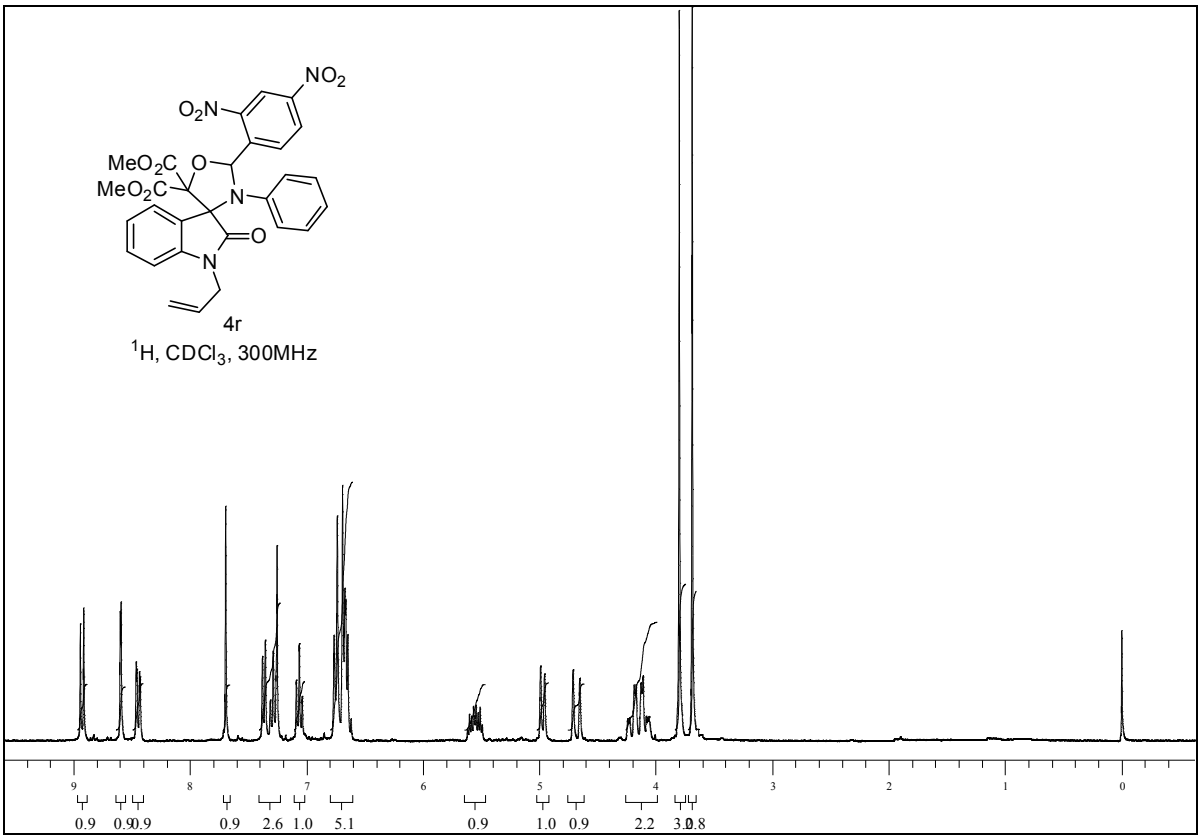

173.48
167.07
166.69
147.99
143.98
139.00
138.72
135.28
130.70
129.97
128.88
128.41
125.65
125.28
125.03
124.21
124.12
122.54
122.40
116.75
109.79
92.14
89.32
77.32
77.00
76.68
75.50
52.93
52.90
41.62
O2N
MeO2C
MeO2C
O
N
O
N
4o
13C, CDCl3, 100MHz
Chemical shift (ppm)

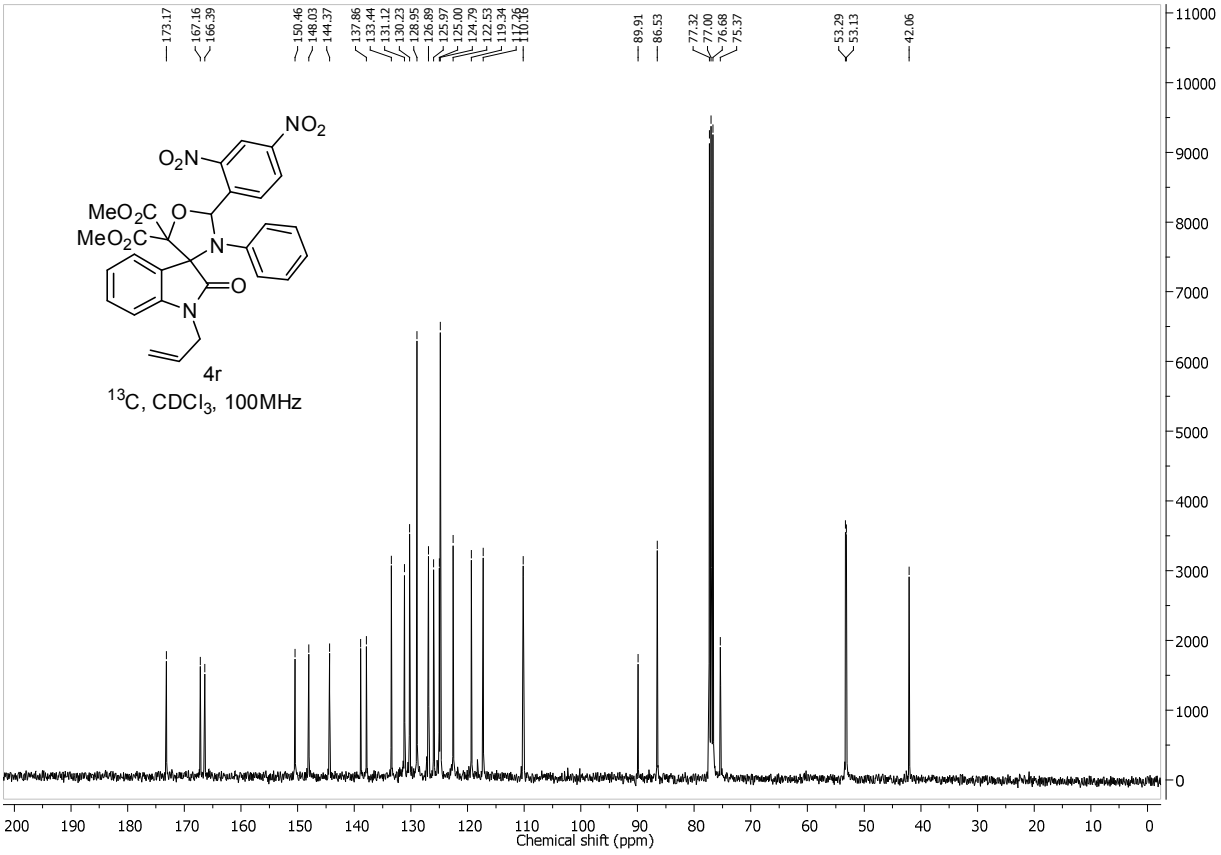

NO2
MeO2C
MeO2C
O
N
Br
O
N
4p
1H, CDCl3, 300MHz

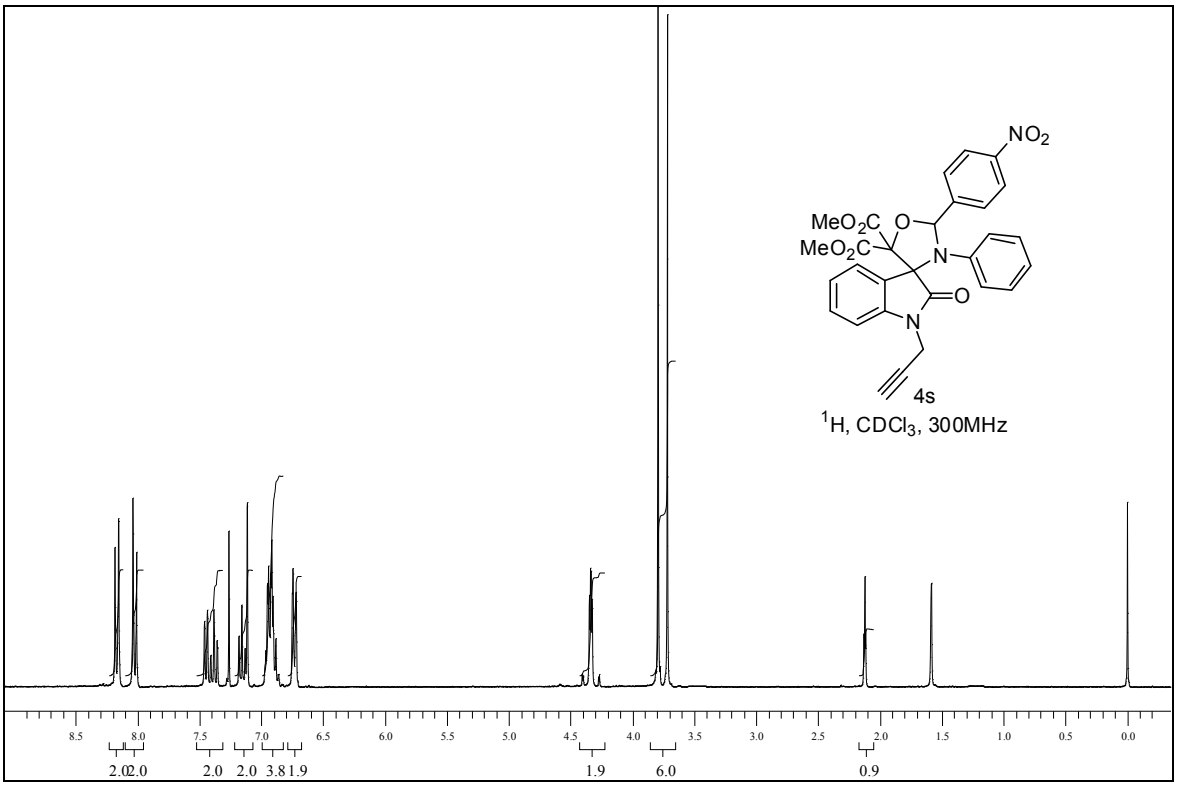

NO2
MeO2C
MeO2C
O
N
Br
O
N
4p
13C, CDCl3, 100MHz
Chemical shift (ppm)

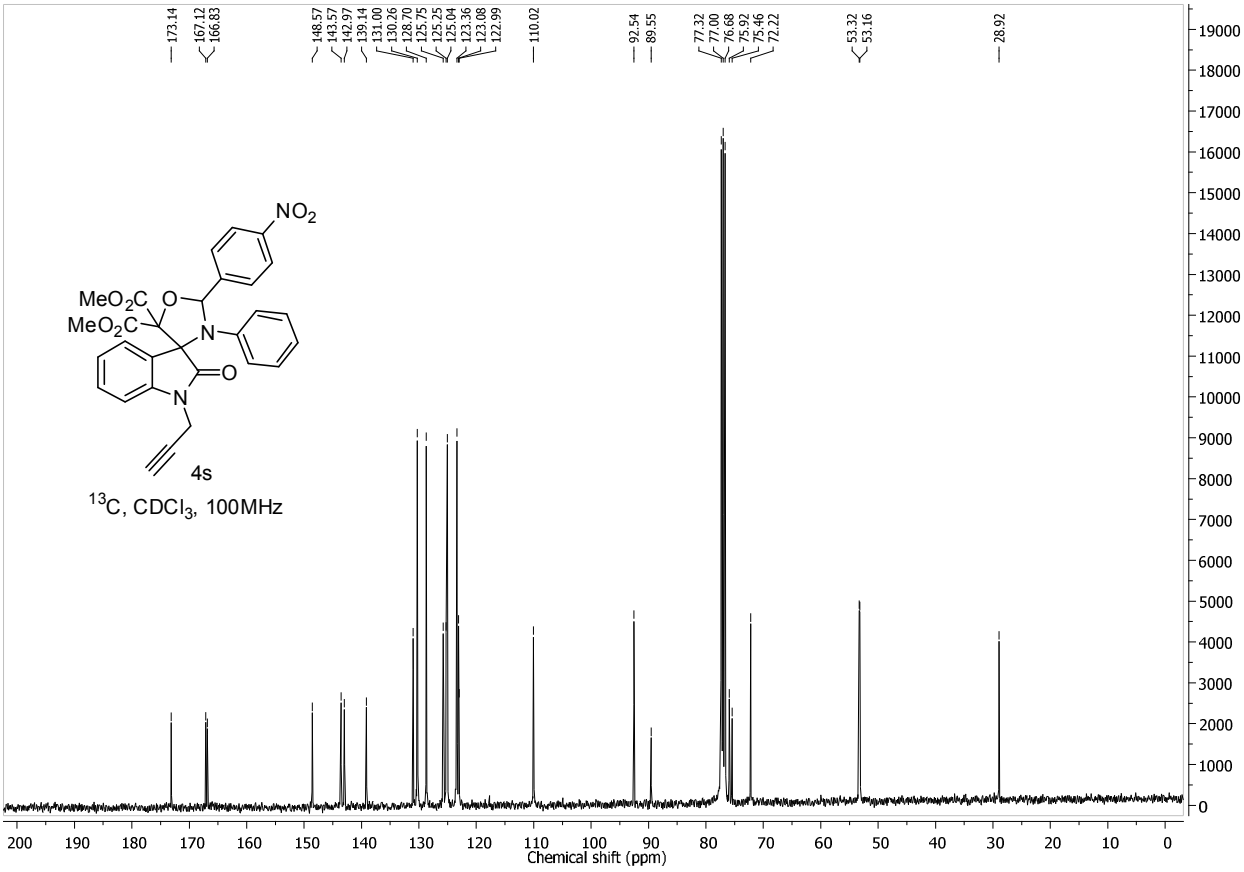

NO2
MeO2C
MeO2C
O
N
CH3
O
N
4q
1H, CDCl3, 300MHz
1.9 1.9 1.0 1.6 2.0 5.1 1.1 1.0 1.1 1.7 6.2 3.0

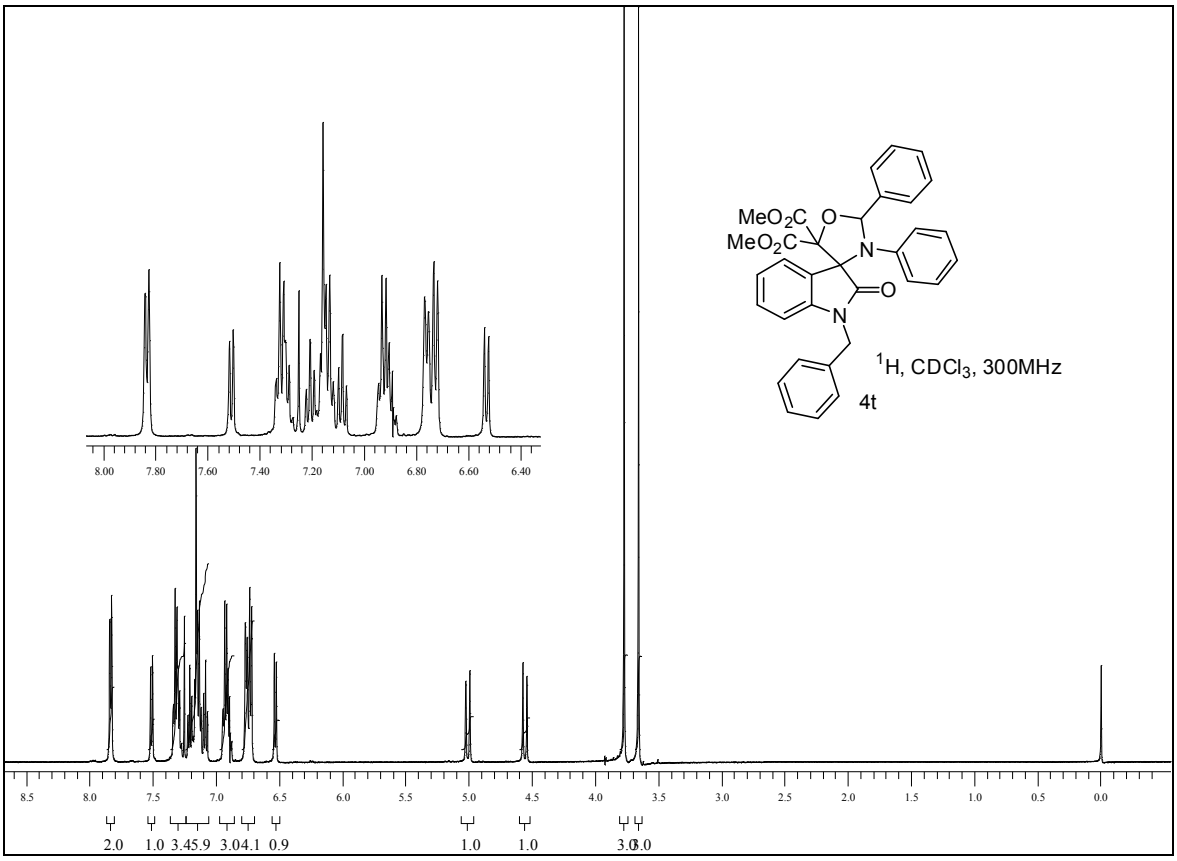

NO2
MeO2C
MeO2C
O
N
CH3
O
N
4q
13C, CDCl3, 100MHz
Chemical shift (ppm)

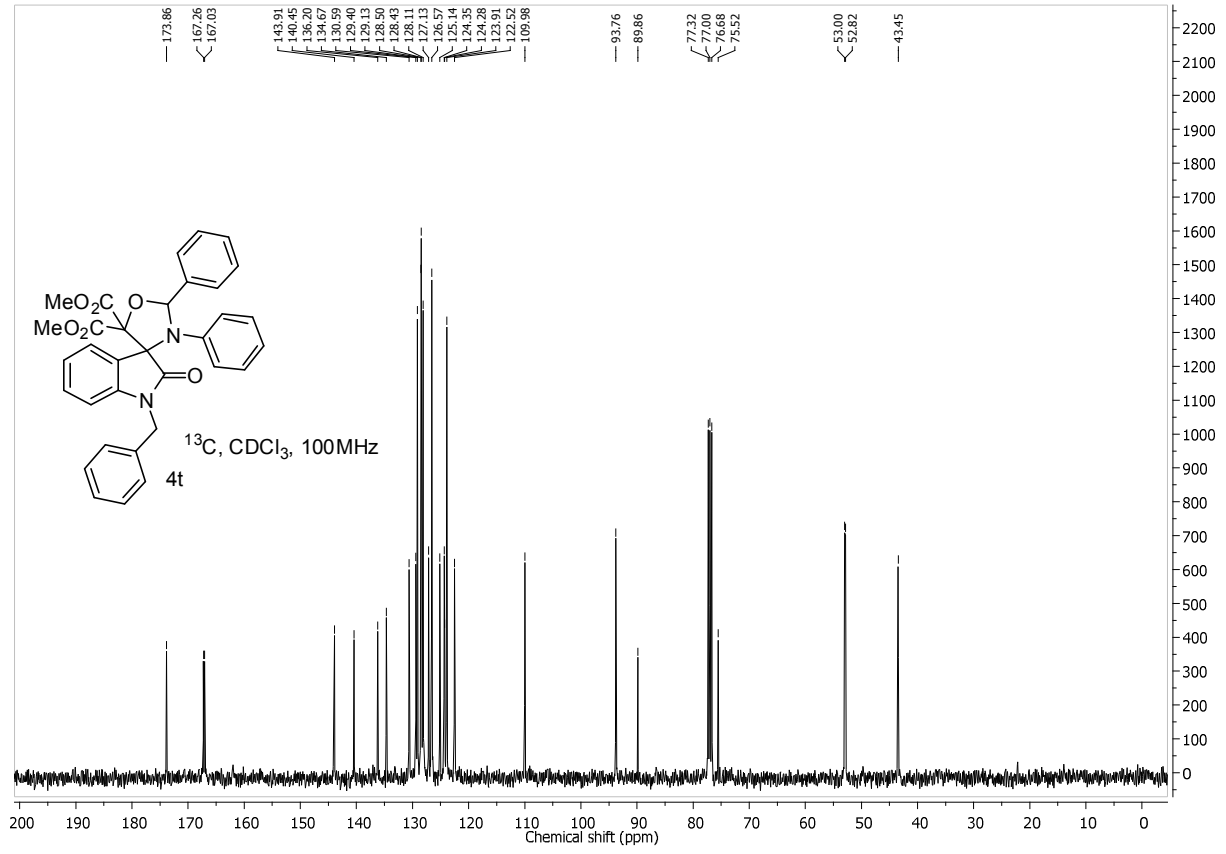

NO2
O2N
MeO2C
MeO2C
O
N
O
N
4r
1H, CDCl3, 300MHz
9
8
7
6
5
4
3
2
1
0
0.9
0.9
0.9
0.9
2.6
1.0
5.1
0.9
1.0
0.9
2.2
3.0
0.8

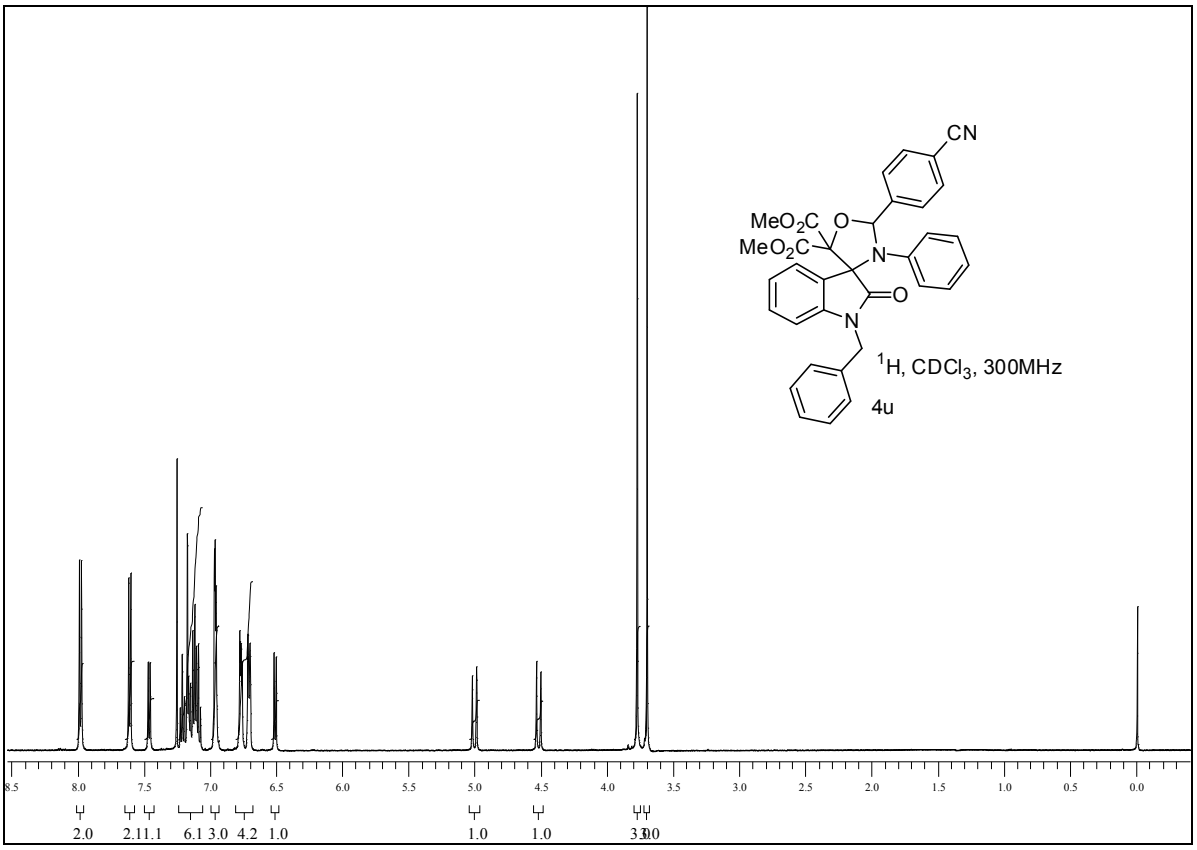

173.17
167.16
166.39
150.46
148.03
144.37
137.86
133.44
131.12
130.23
128.95
126.89
125.97
125.00
124.79
122.53
119.34
89.91
86.53
77.32
77.00
76.68
75.37
53.29
53.13
42.06
NO2
O2N
MeO2C
MeO2C
O
N
O
N
4r
13C, CDCl3, 100MHz
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

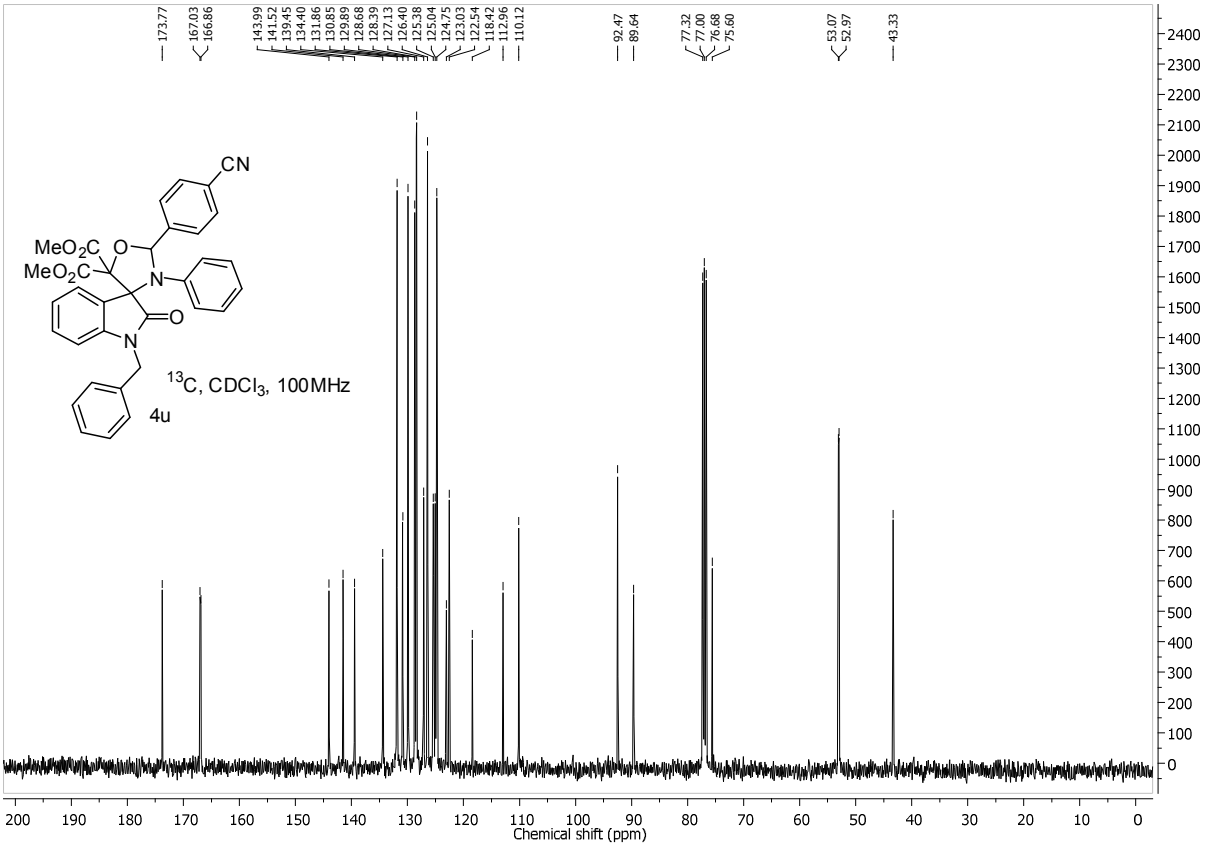

NO2
MeO2C
MeO2C
O
N
O
N
4s
1H, CDCl3, 300MHz
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.0
2.0
2.0
2.0
3.8
1.9
1.9
6.0
0.9

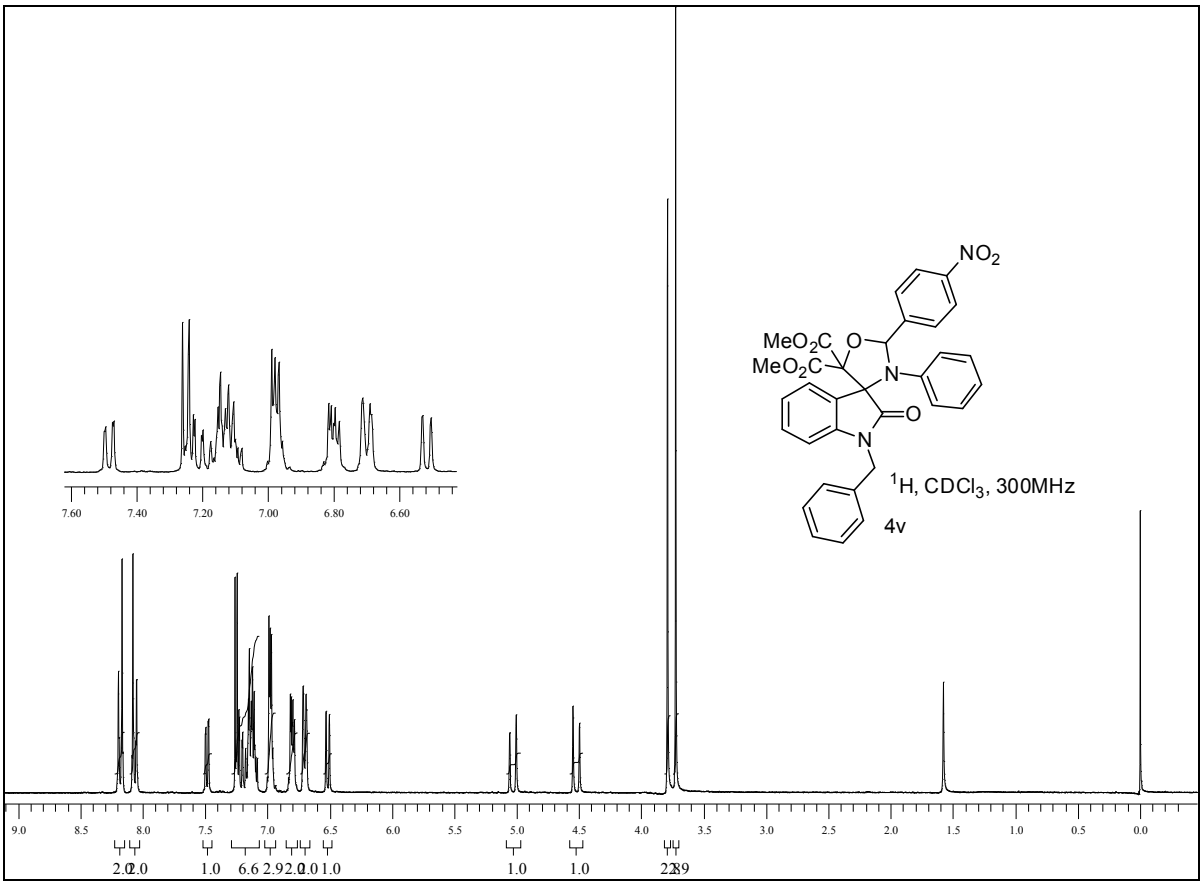

173.14
167.12
166.83
148.57
143.57
142.97
139.14
131.00
130.26
128.70
125.75
125.25
125.04
123.36
123.08
122.99
110.02
92.54
89.55
77.32
77.00
76.68
75.92
75.46
72.22
53.32
53.16
28.92
NO2
MeO2C
MeO2C
O
N
O
N
4s
13C, CDCl3, 100MHz
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical shift (ppm)

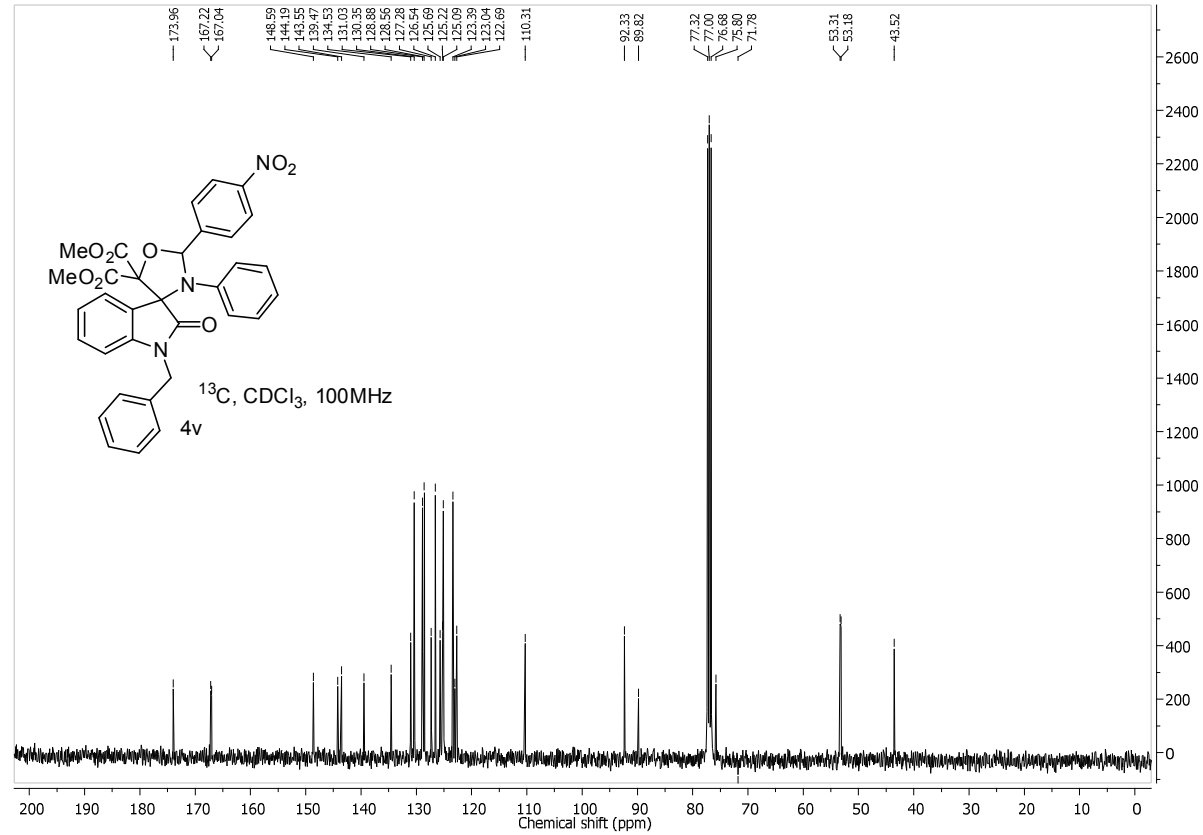

MeO2C
MeO2C
O
N
O
N
1H, CDCl3, 300MHz
4t
8.00 7.80 7.60 7.40 7.20 7.00 6.80 6.60 6.40
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
2.0 1.0 3.45.9 3.04.1 0.9 1.0 1.0 3.06.0

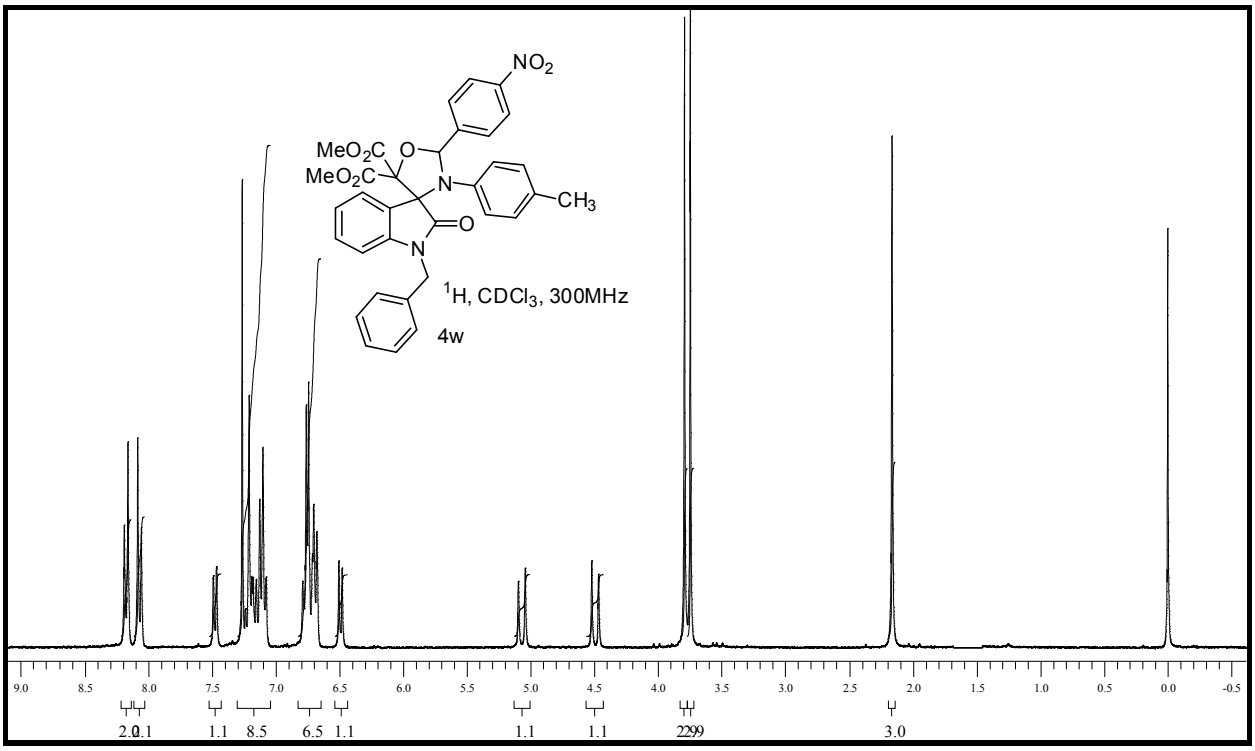

173.86
167.26
167.03
143.91
140.45
136.20
134.67
130.59
129.40
129.13
128.50
128.43
128.11
127.13
126.57
125.14
124.35
124.28
123.91
122.52
109.98
93.76
89.86
77.32
77.00
76.68
75.52
53.00
52.82
43.45
MeO2C
MeO2C
O
N
O
N
13C, CDCl3, 100MHz
4t
Chemical shift (ppm)

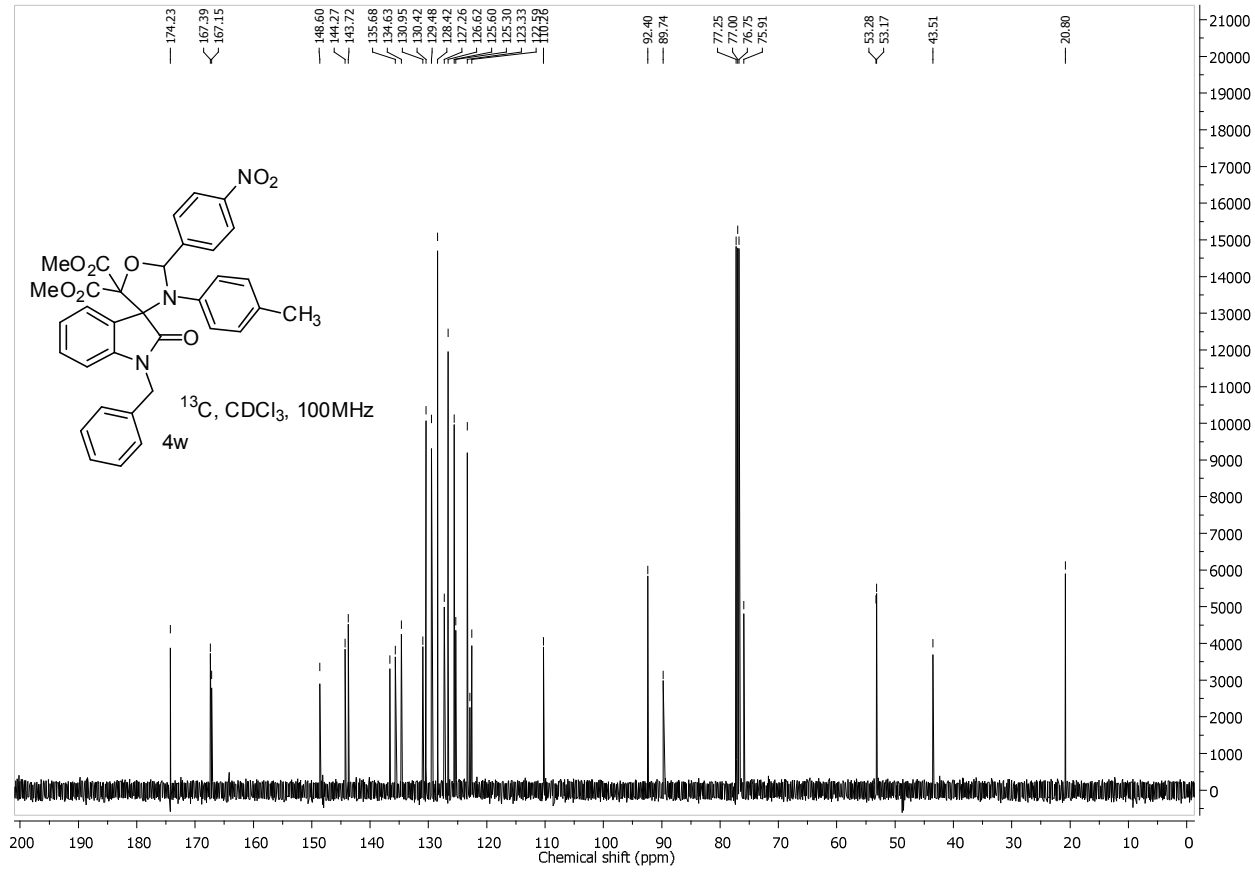

CN
MeO2C
MeO2C
O
N
O
N
1H, CDCl3, 300MHz
4u
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
2.0 2.1 1.1 6.1 3.0 4.2 1.0 1.0 1.0 3.0

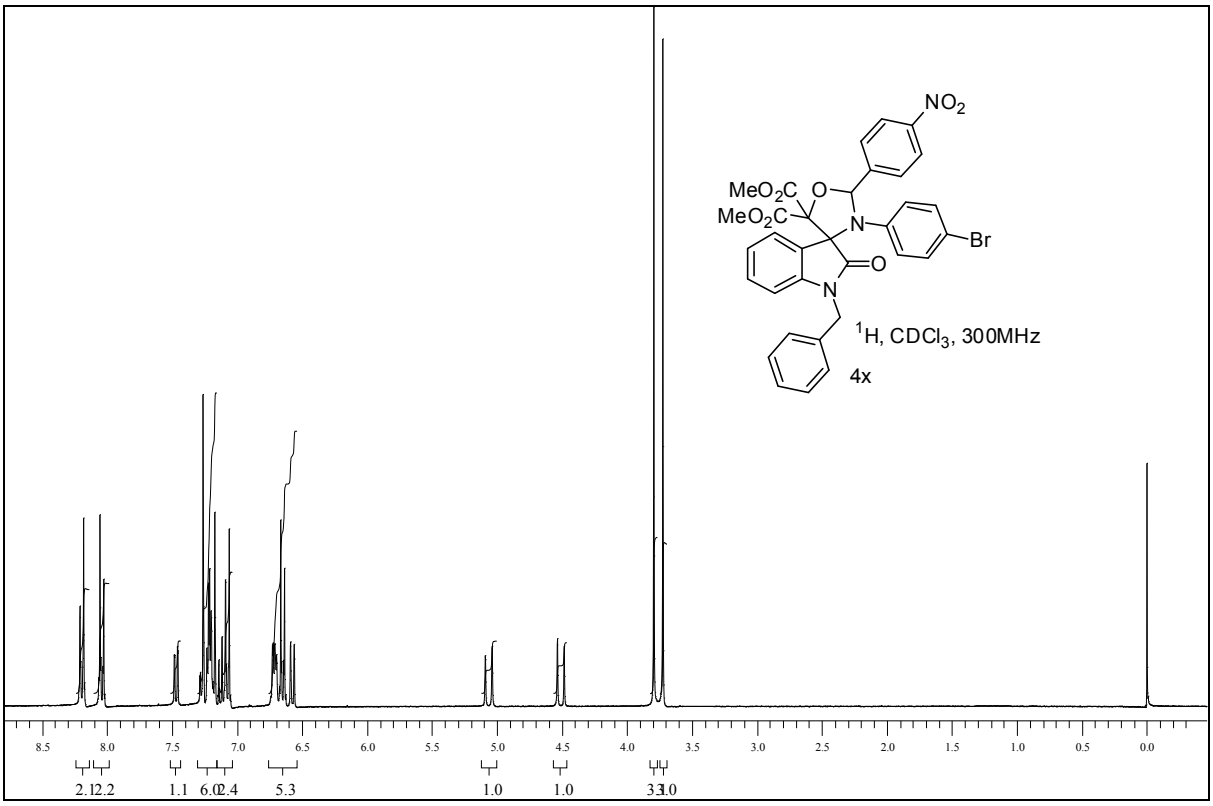

173.77
167.03
166.86
143.99
141.52
139.45
134.40
131.86
130.85
129.89
128.68
128.39
127.13
126.40
125.38
125.04
124.75
123.03
122.54
118.42
112.96
110.12
92.47
89.64
77.32
77.00
76.68
75.60
53.07
52.97
43.33
CN
MeO2C
MeO2C
O
N
O
N
13C, CDCl3, 100MHz
4u
Chemical shift (ppm)

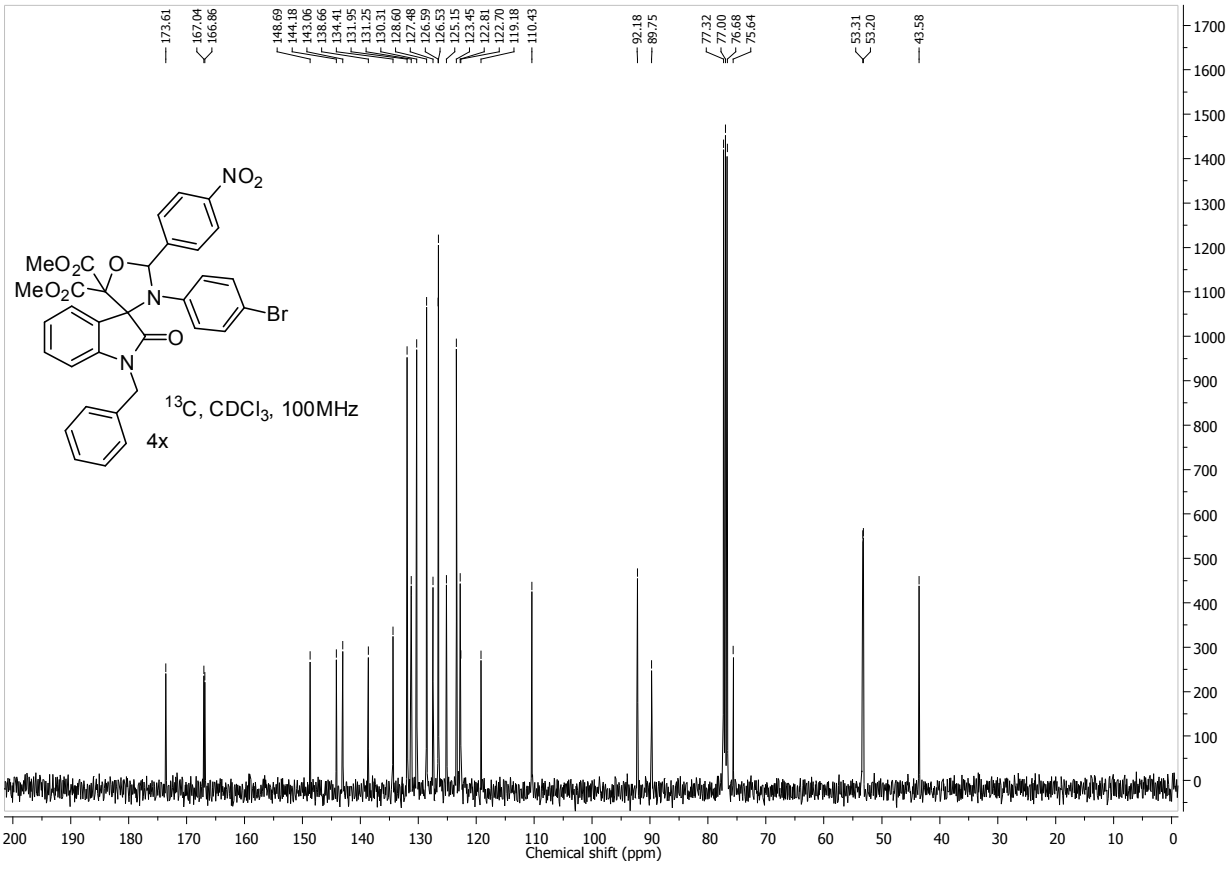

NO2
MeO2C
MeO2C
O
N
O
N
1H, CDCl3, 300MHz
4v

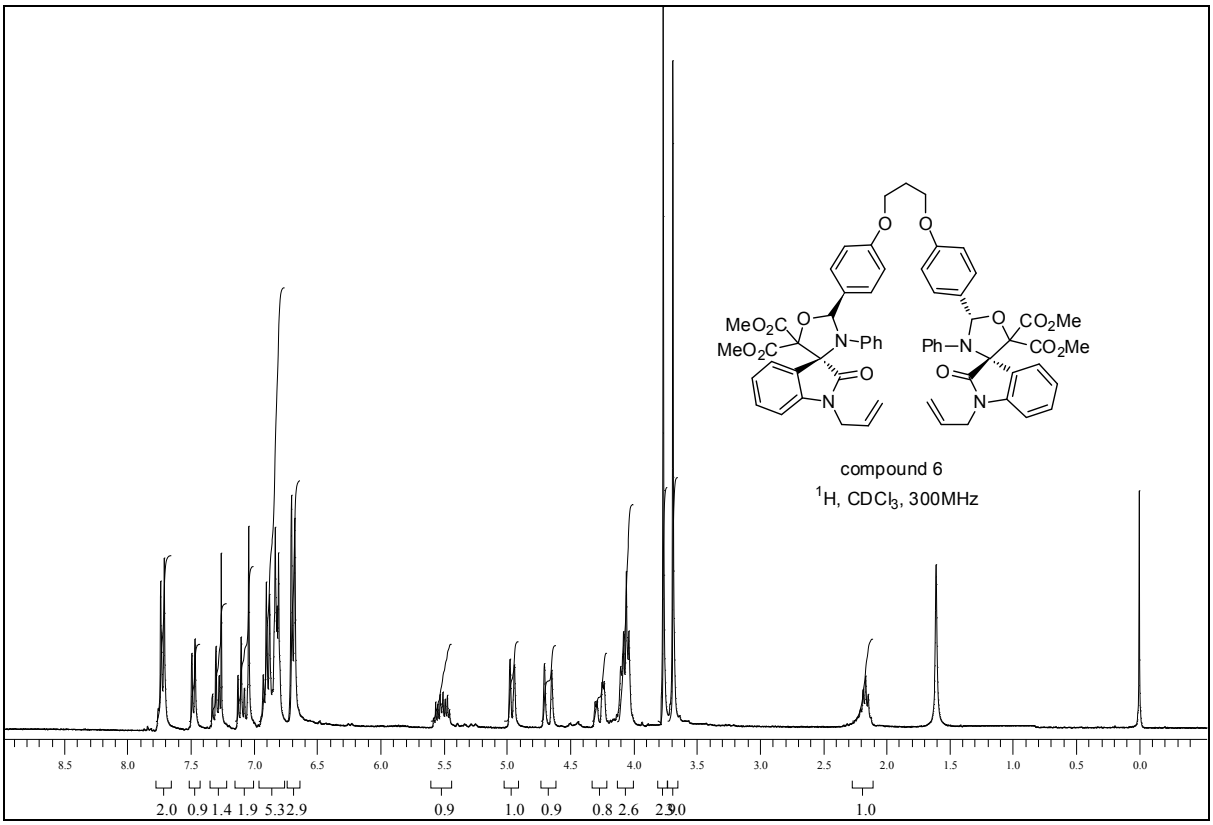

NO2
MeO2C
MeO2C
O
N
O
N
13C, CDCl3, 100MHz
4v
Chemical shift (ppm)

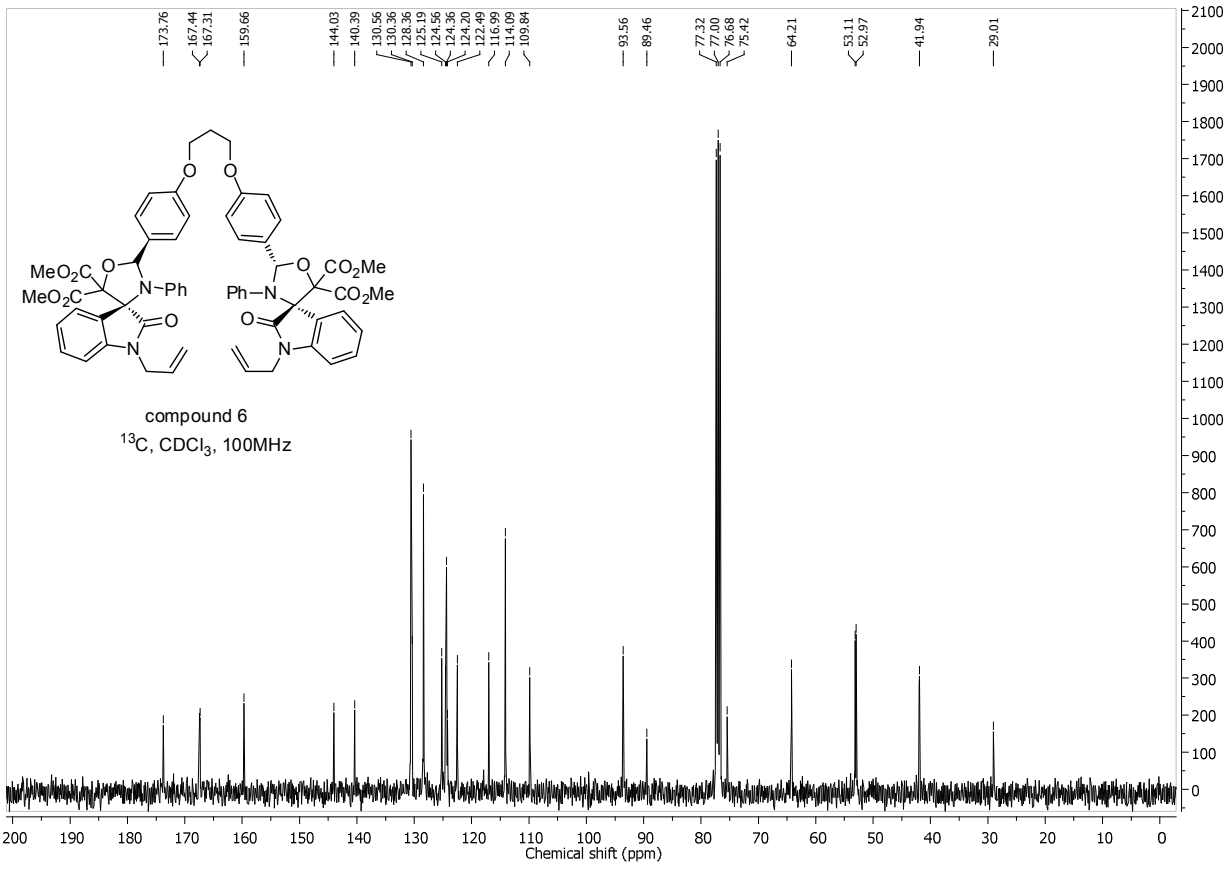

NO2
MeO2C
MeO2C
O
N
CH3
O
N
1H, CDCl3, 300MHz
4w
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
2.0 1.1 1.1 8.5 6.5 1.1 1.1 1.1 2.9 3.0

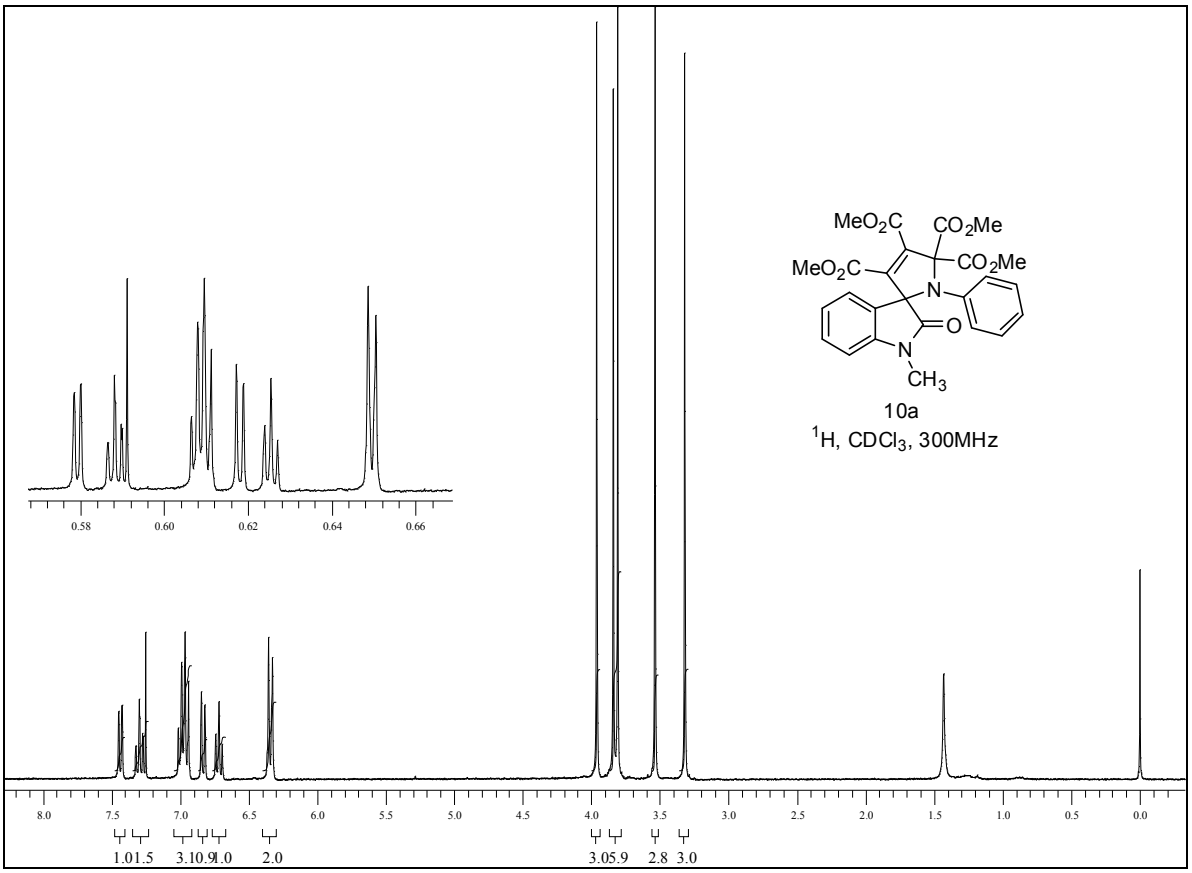

174.23
167.39
167.15
148.60
144.27
143.72
135.68
134.63
130.95
130.42
129.48
128.42
127.26
126.62
125.60
125.30
123.33
122.59
110.26
92.40
89.74
77.25
77.00
76.75
75.91
53.28
53.17
43.51
20.80
NO2
MeO2C
MeO2C
O
N
CH3
O
N
13C, CDCl3, 100MHz
4w
21000 20000 19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

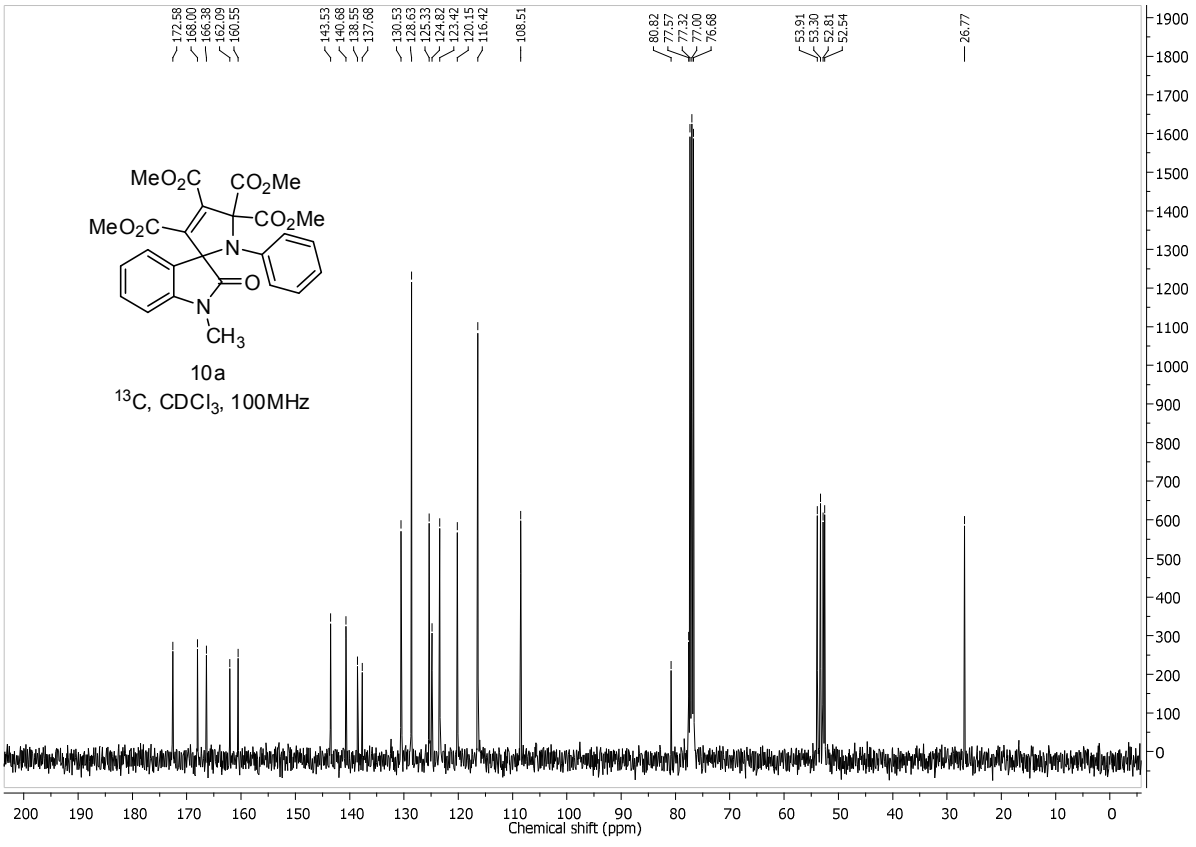

NO2
MeO2C
MeO2C
O
N
Br
O
N
1H, CDCl3, 300MHz
4x
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
2.1 2.2 1.1 6.0 2.4 5.3 1.0 1.0 3.3 3.0

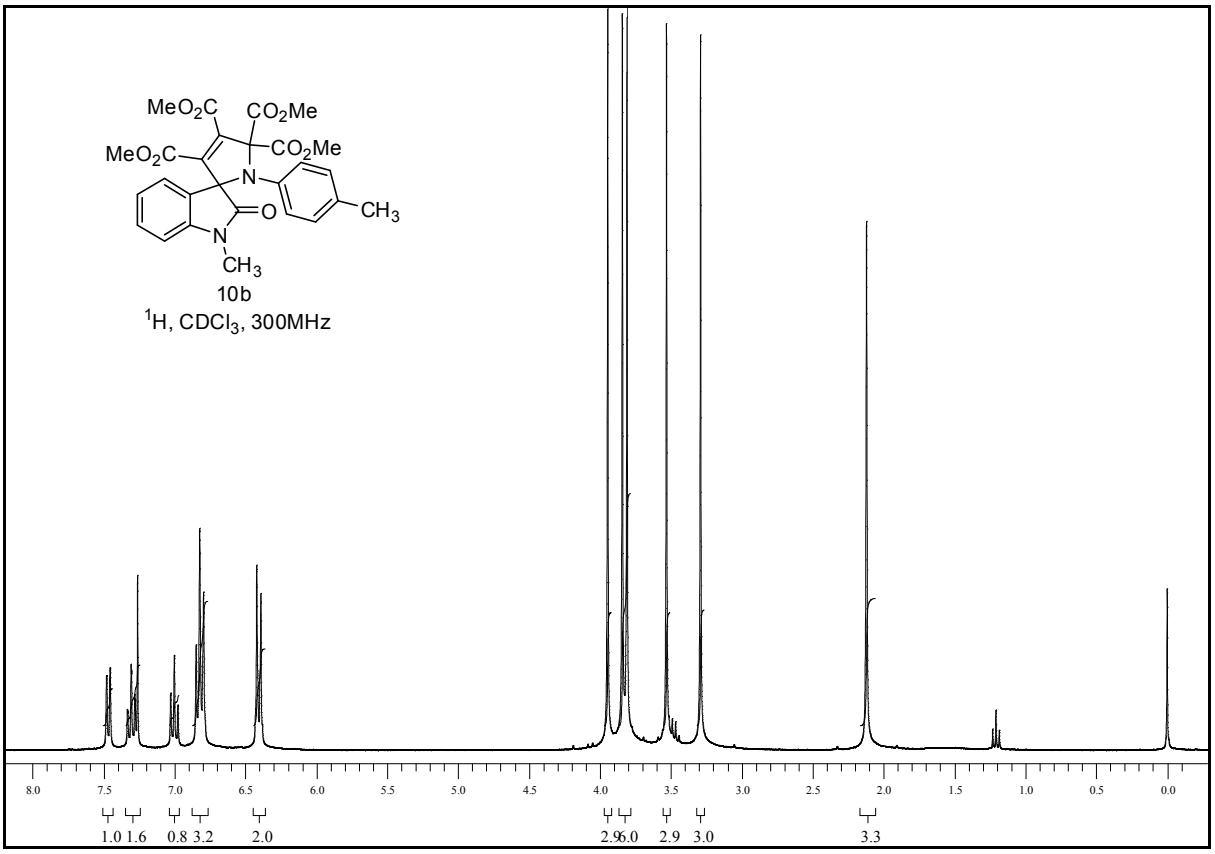

173.61
167.04
166.86
148.69
144.18
143.06
138.66
134.41
131.95
131.25
130.31
128.60
127.48
126.59
126.53
125.15
123.45
122.81
122.70
119.18
110.43
92.18
89.75
77.32
77.00
76.68
75.64
53.31
53.20
43.58
NO2
MeO2C
MeO2C
O
N
Br
O
N
13C, CDCl3, 100MHz
4x
1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

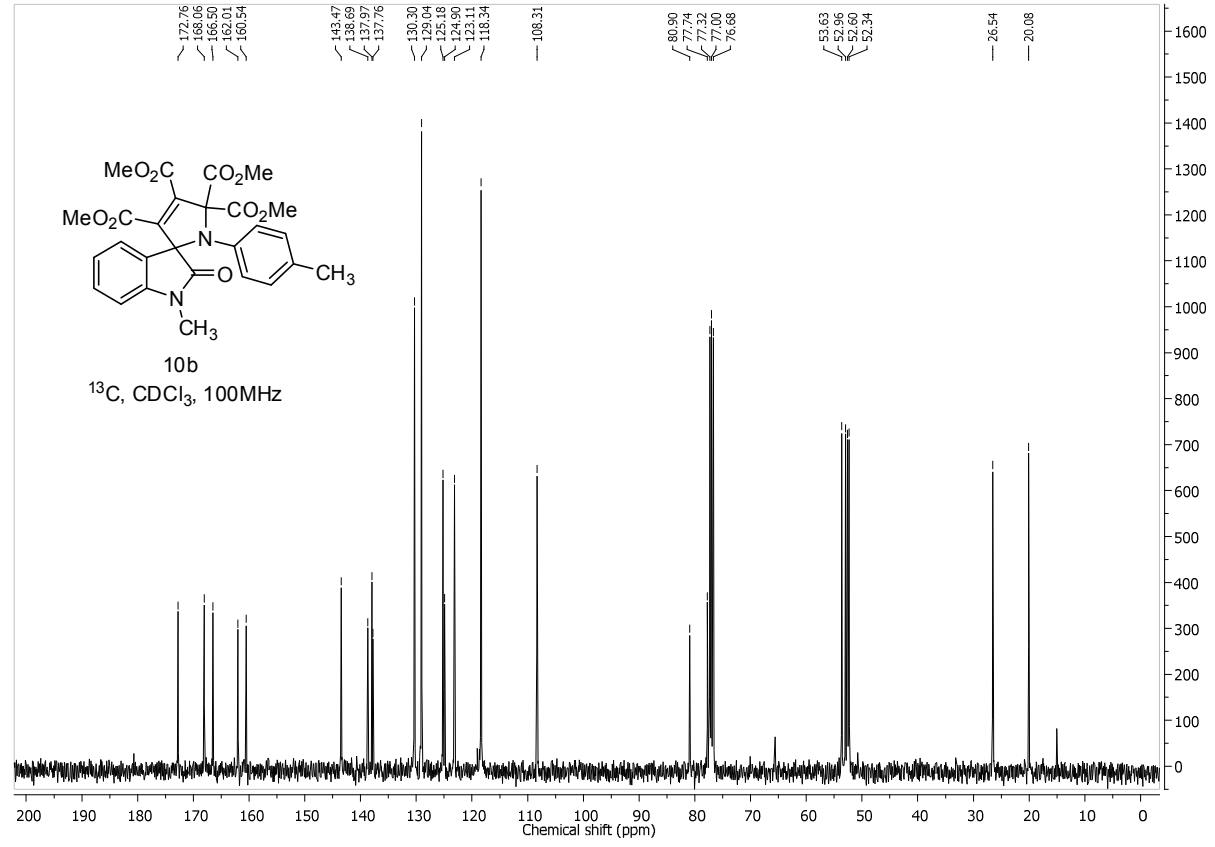

compound 6
^{1}H, $CDCl_3$, 300MHz

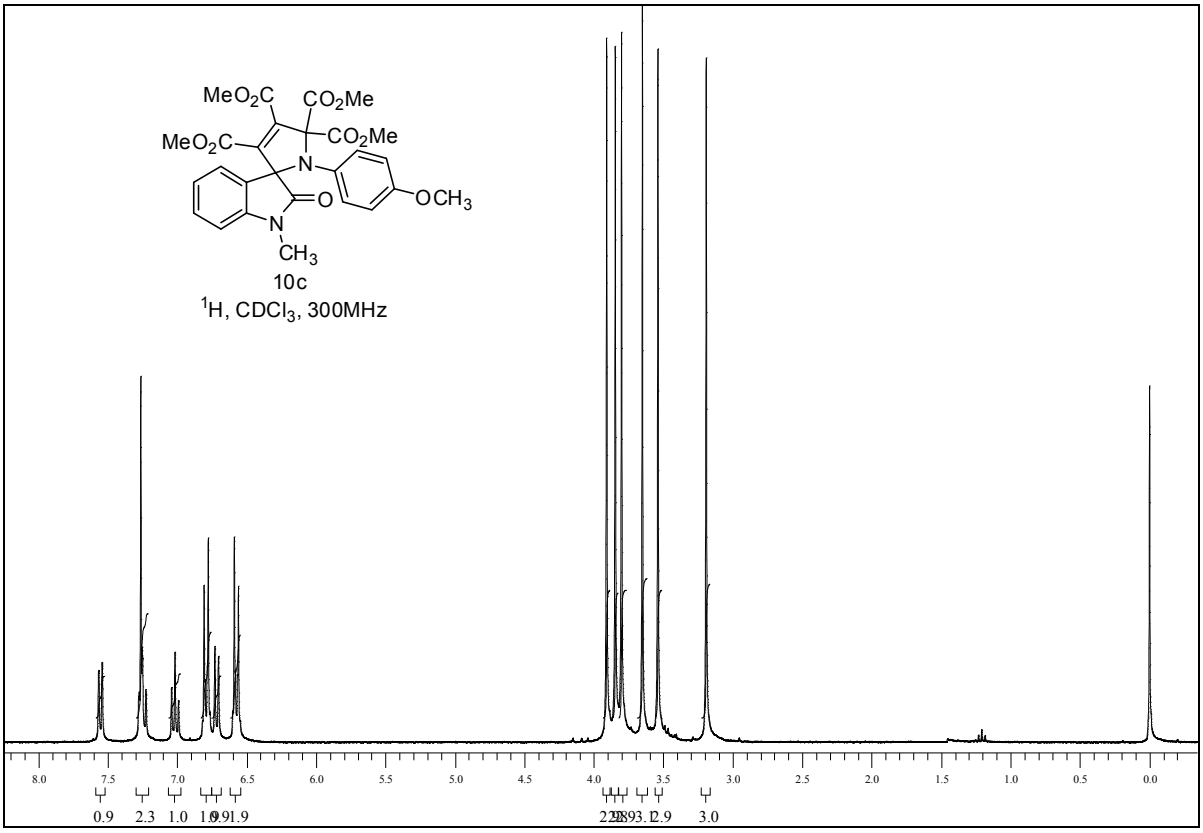

compound 6
^{13}C, $CDCl_3$, 100MHz
Chemical shift (ppm)

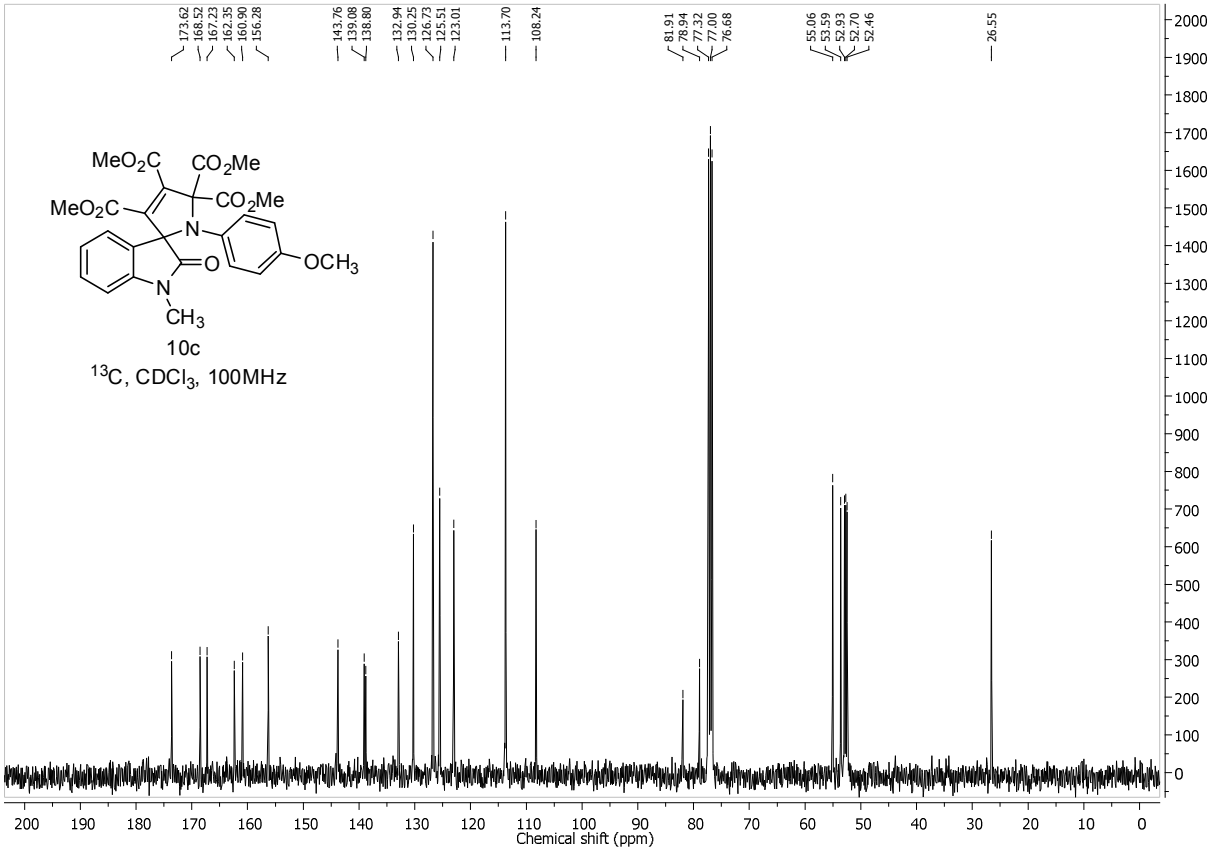

MeO2C
CO2Me
MeO2C
CO2Me
N
O
N
CH3
10a
1H, CDCl3, 300MHz

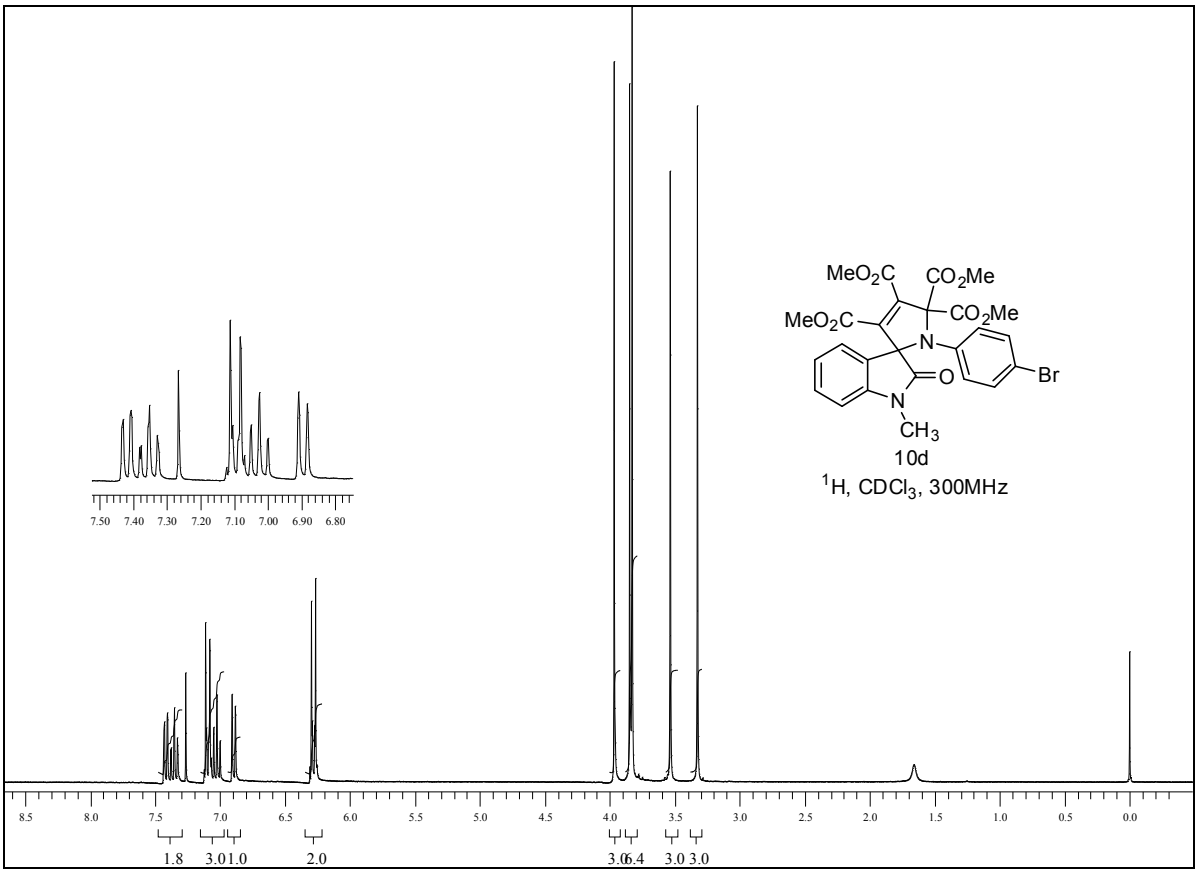

MeO2C
CO2Me
MeO2C
CO2Me
N
O
N
CH3
10a
13C, CDCl3, 100MHz
Chemical shift (ppm)

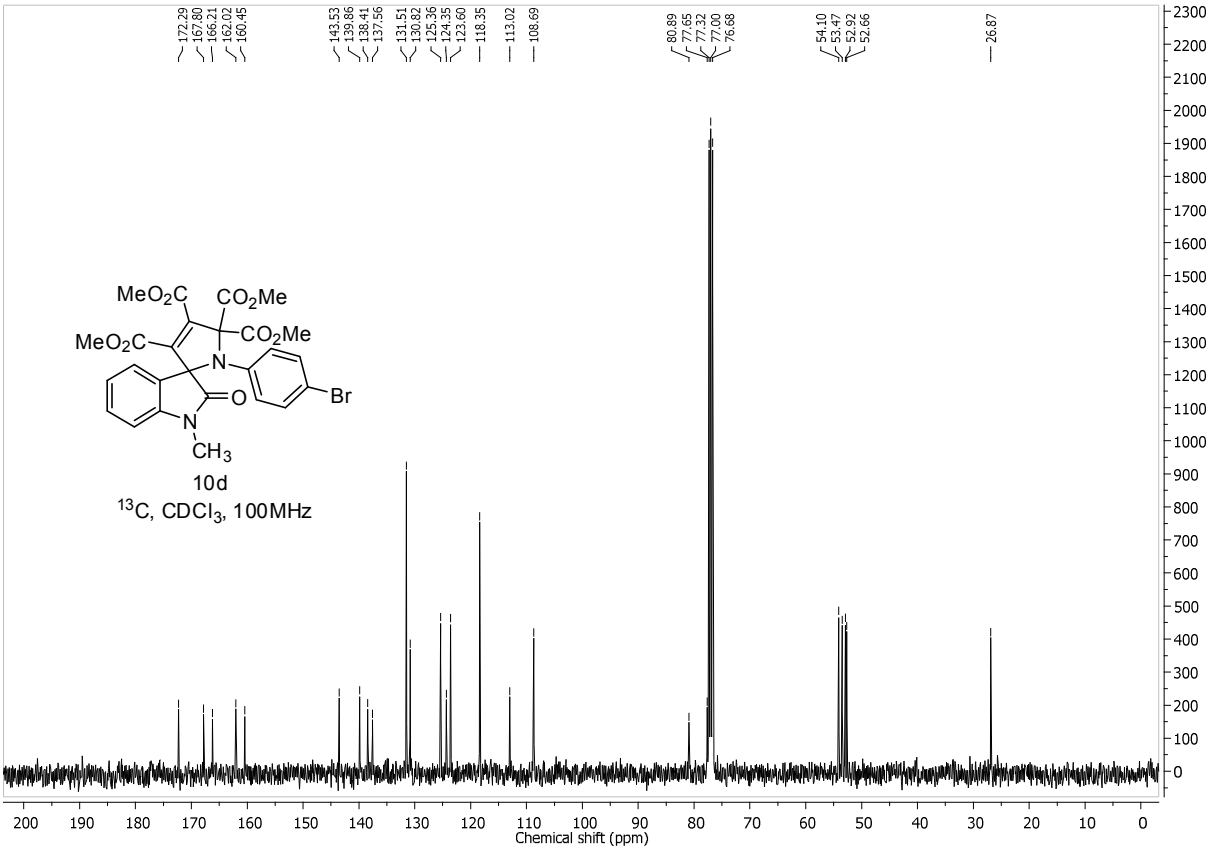

MeO2C
CO2Me
MeO2C
CO2Me
N
O
CH3
N
CH3
10b
1H, CDCl3, 300MHz
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1.0 1.6 0.8 3.2 2.0 2.9 6.0 2.9 3.0 3.3

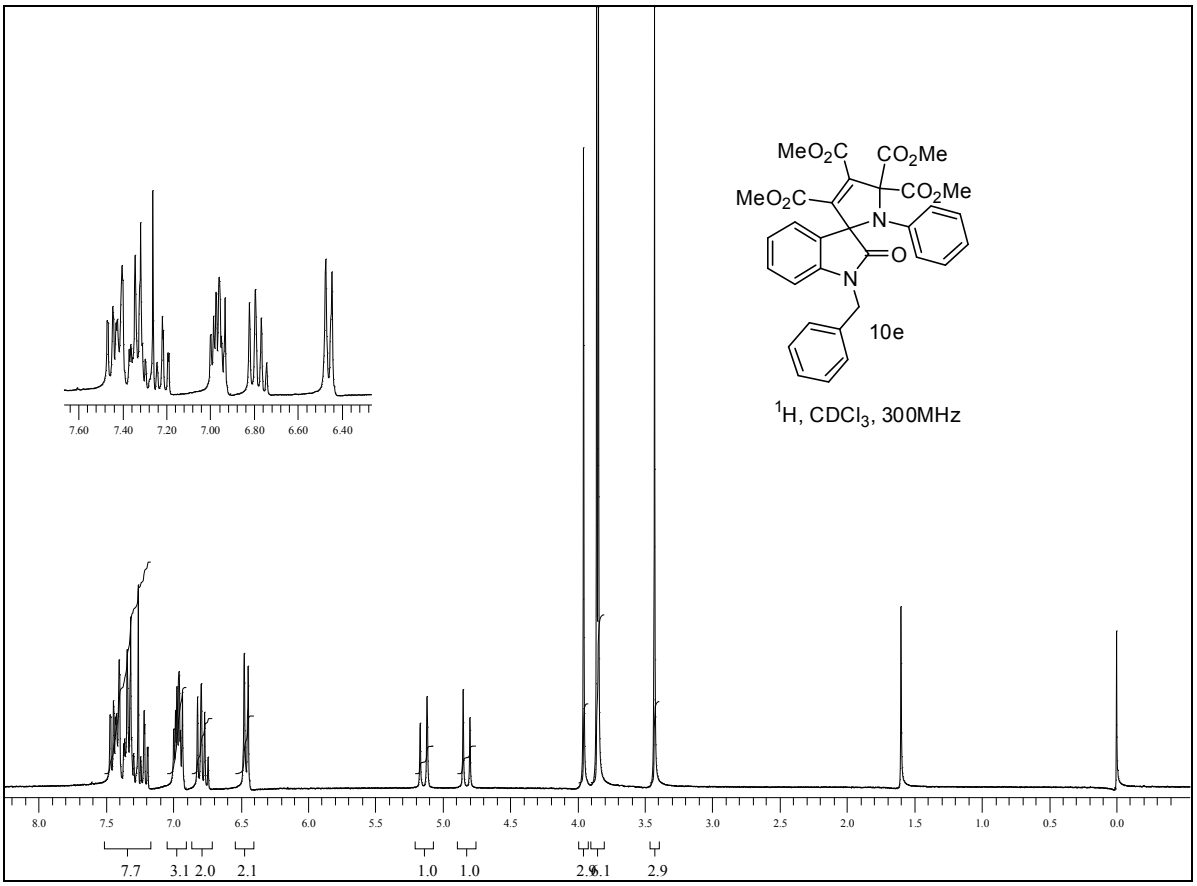

172.76 168.06 166.50 162.01 160.54 143.47 138.69 137.97 137.76 130.30 129.04 125.18 124.90 123.11 118.34 108.31 80.90 77.74 77.32 77.00 76.68 53.63 52.96 52.60 52.34 26.54 20.08
MeO2C
CO2Me
MeO2C
CO2Me
N
O
CH3
N
CH3
10b
13C, CDCl3, 100MHz
Chemical shift (ppm)

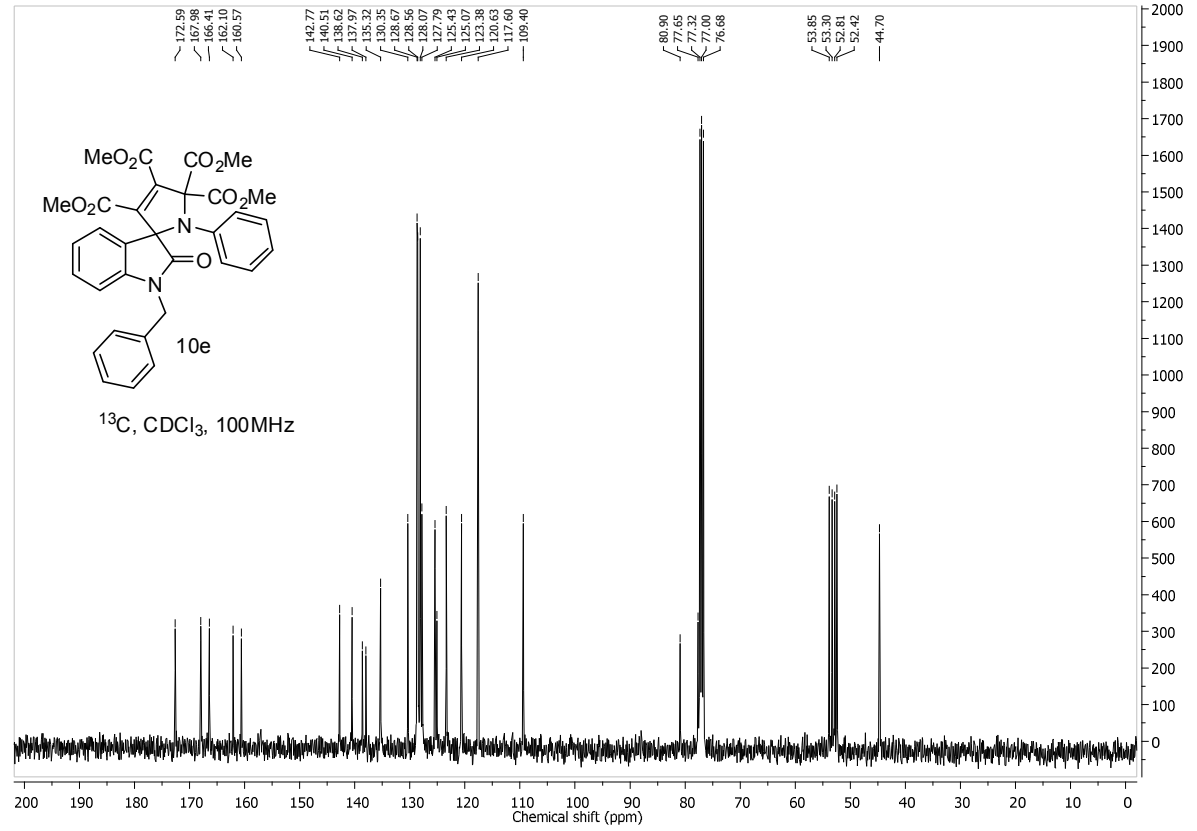

MeO2C
CO2Me
MeO2C
CO2Me
N
O
OCH3
N
CH3
10c
1H, CDCl3, 300MHz

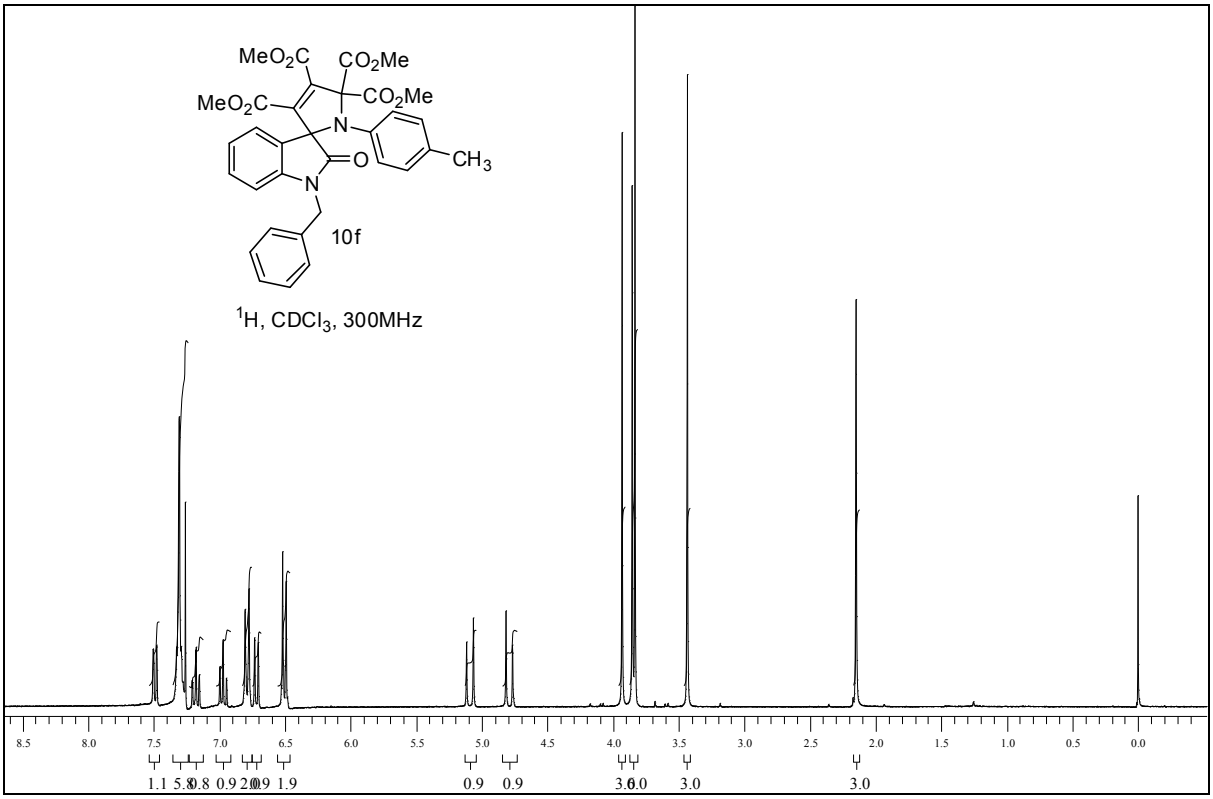

MeO2C
CO2Me
MeO2C
CO2Me
N
O
OCH3
N
CH3
10c
13C, CDCl3, 100MHz
Chemical shift (ppm)

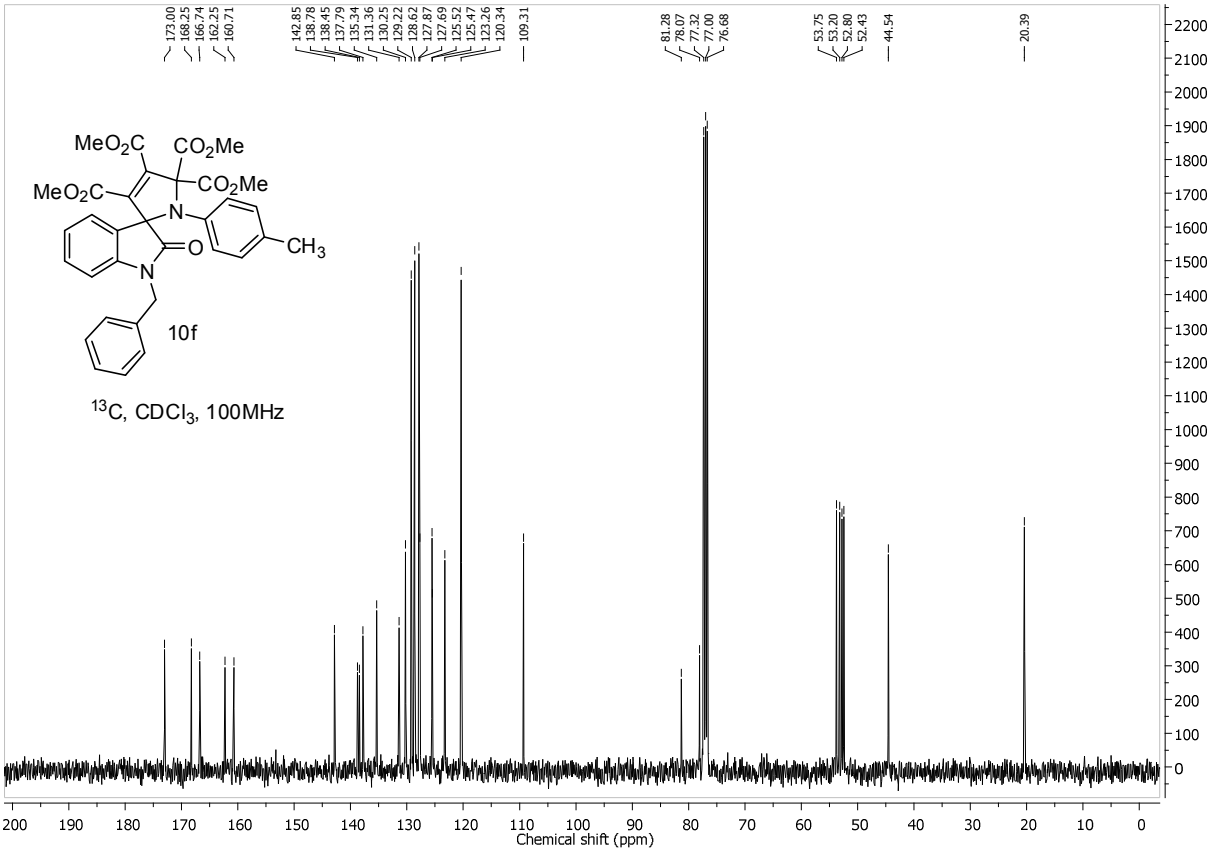

MeO2C
CO2Me
MeO2C
CO2Me
N
O
Br
N
CH3
10d
1H, CDCl3, 300MHz
7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1.8 3.0 1.0 2.0 3.0 6.4 3.0 3.0

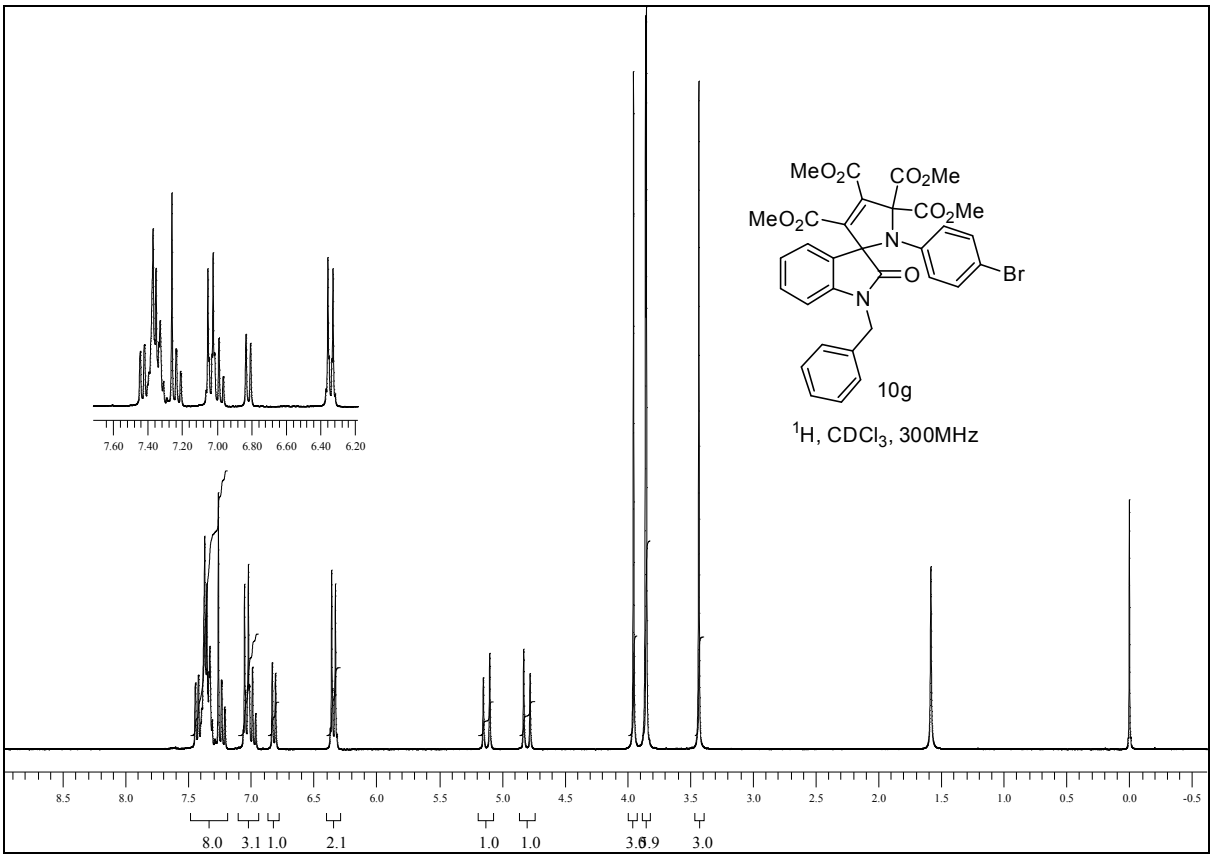

172.29
167.80
166.21
162.02
160.45
143.53
139.86
138.41
137.56
131.51
130.82
125.36
124.35
123.60
118.35
113.02
108.69
80.89
77.65
77.32
77.00
76.68
54.10
53.47
52.92
52.66
26.87
MeO2C
CO2Me
MeO2C
CO2Me
N
O
Br
N
CH3
10d
13C, CDCl3, 100MHz
Chemical shift (ppm)

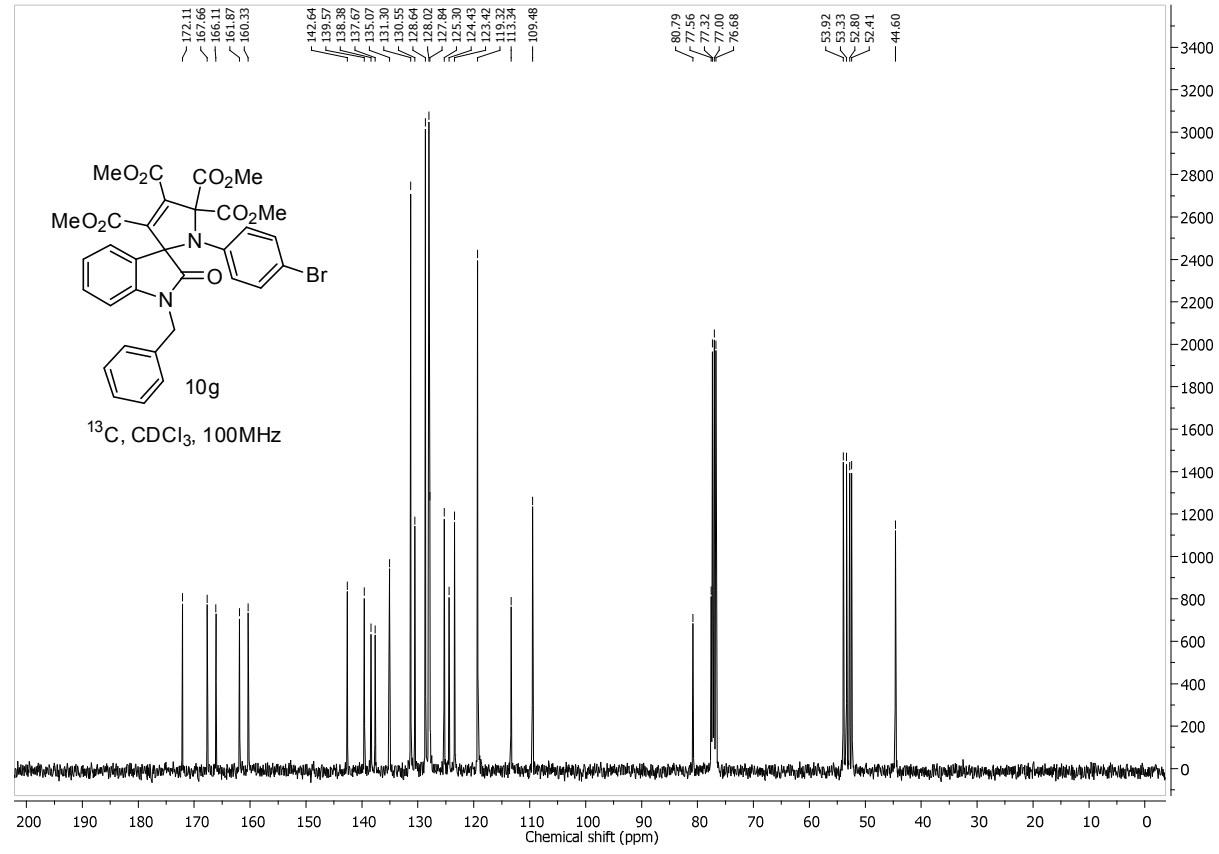

MeO2C
CO2Me
MeO2C
CO2Me
N
O
N
10e
1H, CDCl3, 300MHz
7.60 7.40 7.20 7.00 6.80 6.60 6.40
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
7.7 3.1 2.0 2.1 1.0 1.0 2.9 2.9

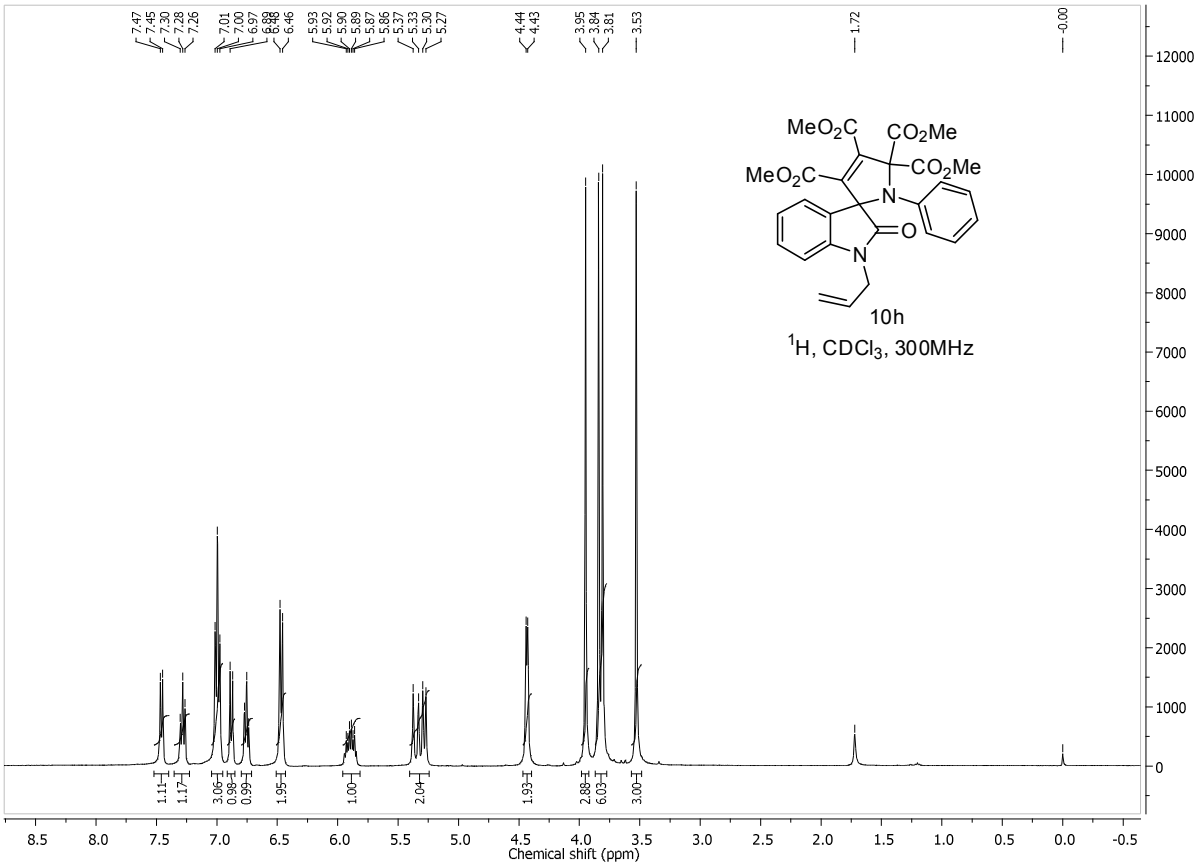

172.59 167.98 166.41 162.10 160.57
142.77 140.51 138.62 137.97 135.32 130.35 128.67 128.56 128.07 127.79 125.43 125.07 123.38 120.63 117.60 109.40
80.90 77.65 77.32 77.00 76.68
53.85 53.30 52.81 52.42 44.70
MeO2C
CO2Me
MeO2C
CO2Me
N
O
N
10e
13C, CDCl3, 100MHz
Chemical shift (ppm)

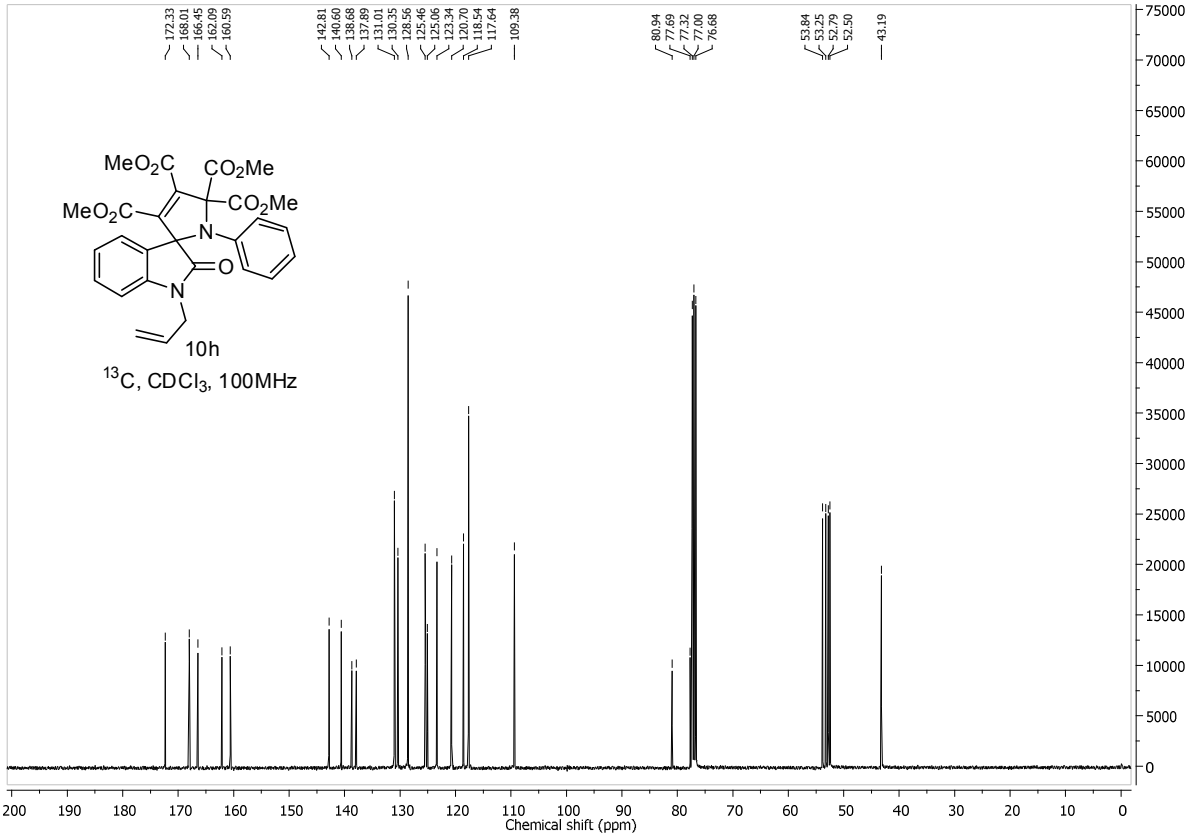

MeO2C
CO2Me
MeO2C
CO2Me
N
O
CH3
N
10f
1H, CDCl3, 300MHz
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1.1 5.8 0.8 0.9 2.0 0.9 1.9 0.9 0.9 3.0 6.0 3.0 3.0

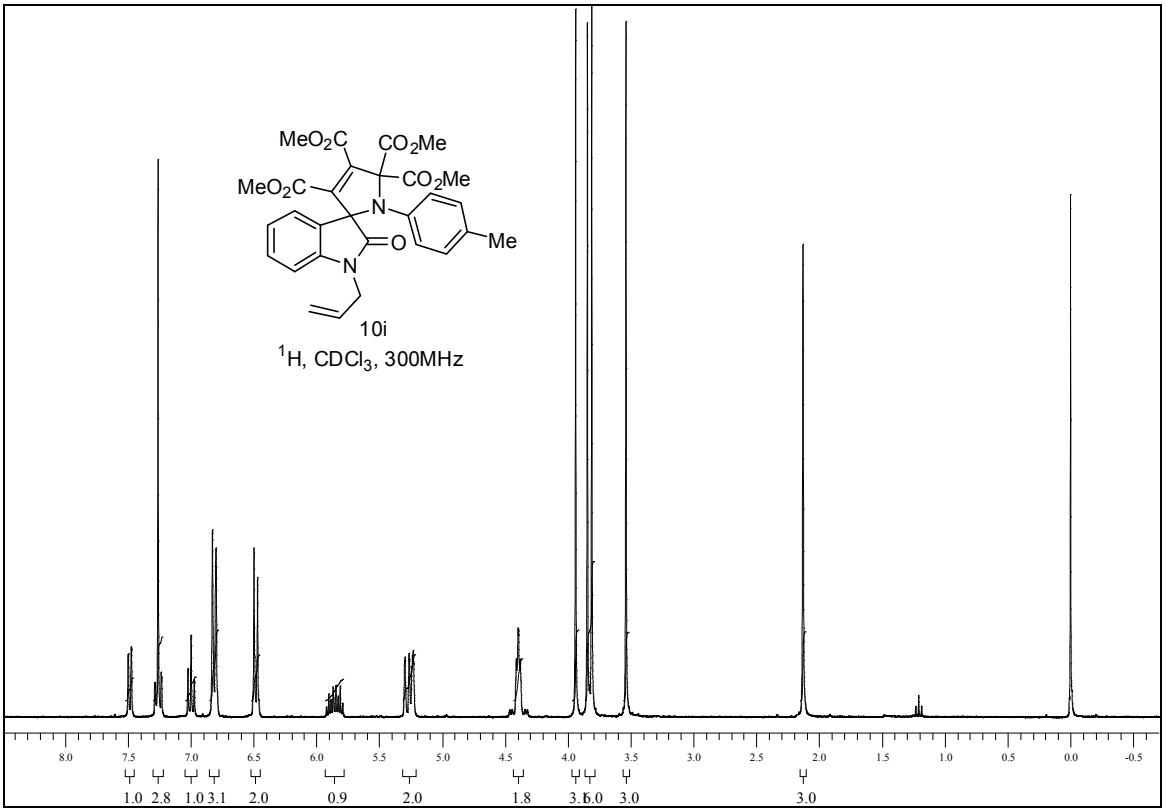

173.00
168.25
166.74
162.25
160.71
142.85
138.78
138.45
137.79
135.34
131.36
130.25
129.22
128.62
127.87
127.69
125.52
125.47
123.26
120.34
109.31
81.28
78.07
77.32
77.00
76.68
53.75
53.20
52.80
52.43
44.54
20.39
MeO2C
CO2Me
MeO2C
CO2Me
N
O
CH3
N
10f
13C, CDCl3, 100MHz
2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)

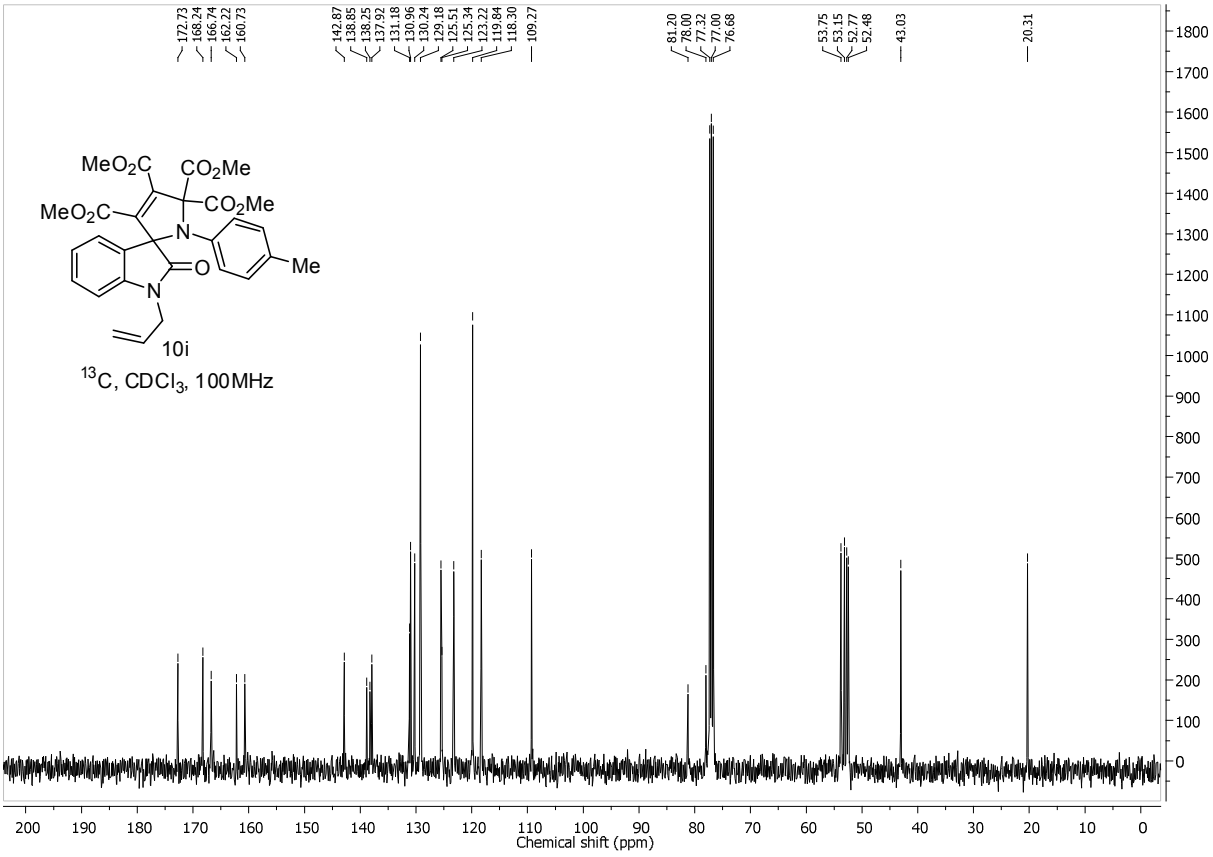

MeO2C
CO2Me
MeO2C
CO2Me
N
O
N
Br
10g
1H, CDCl3, 300MHz
8.0
3.1
1.0
2.1
1.0
1.0
3.0

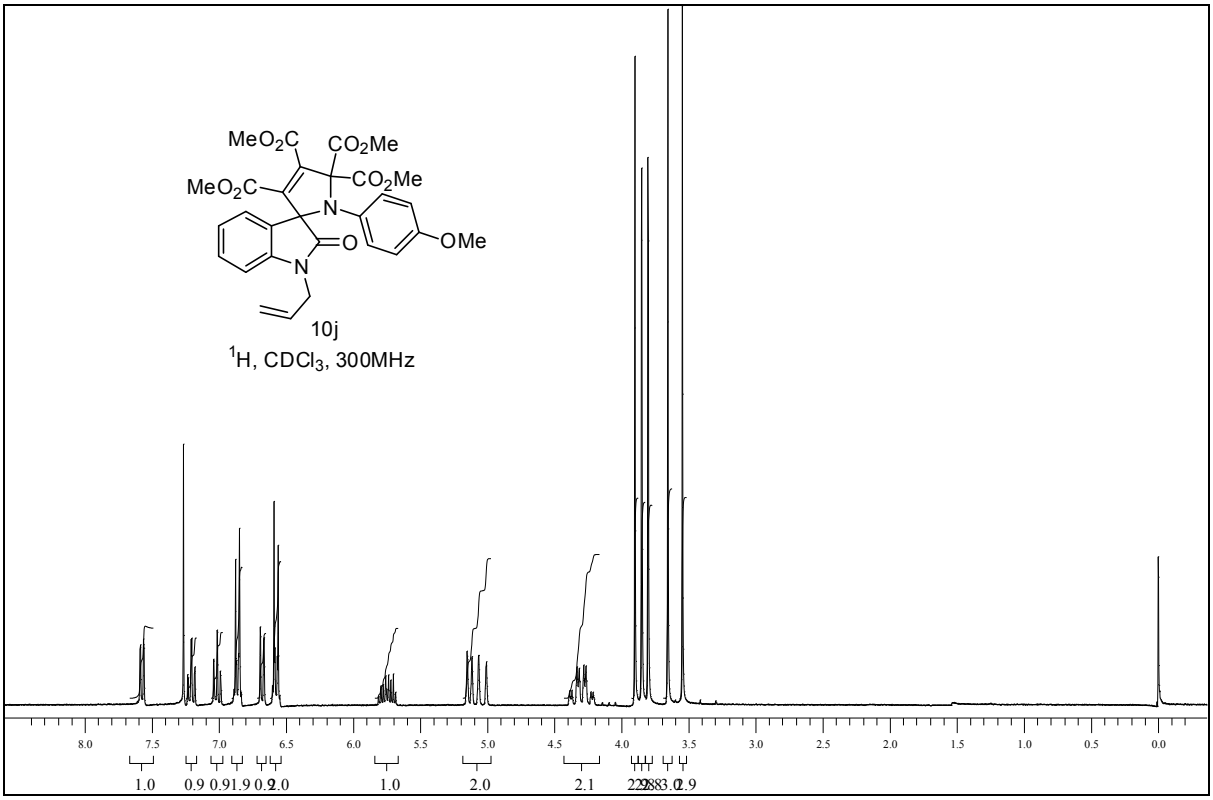

MeO2C
CO2Me
MeO2C
CO2Me
N
O
N
Br
10g
13C, CDCl3, 100MHz
Chemical shift (ppm)

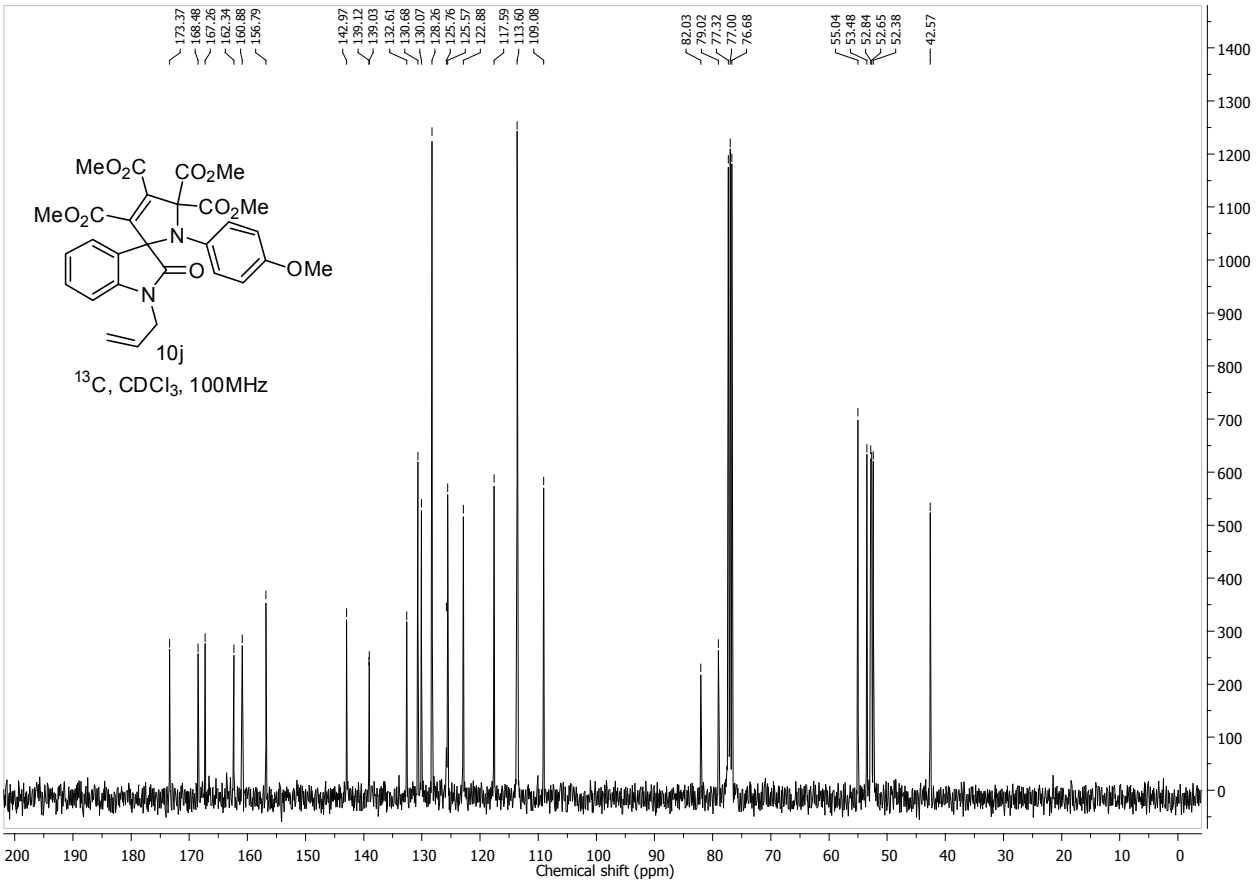

MeO2C
CO2Me
MeO2C
CO2Me
N
O
N
10h
1H, CDCl3, 300MHz
Chemical shift (ppm)

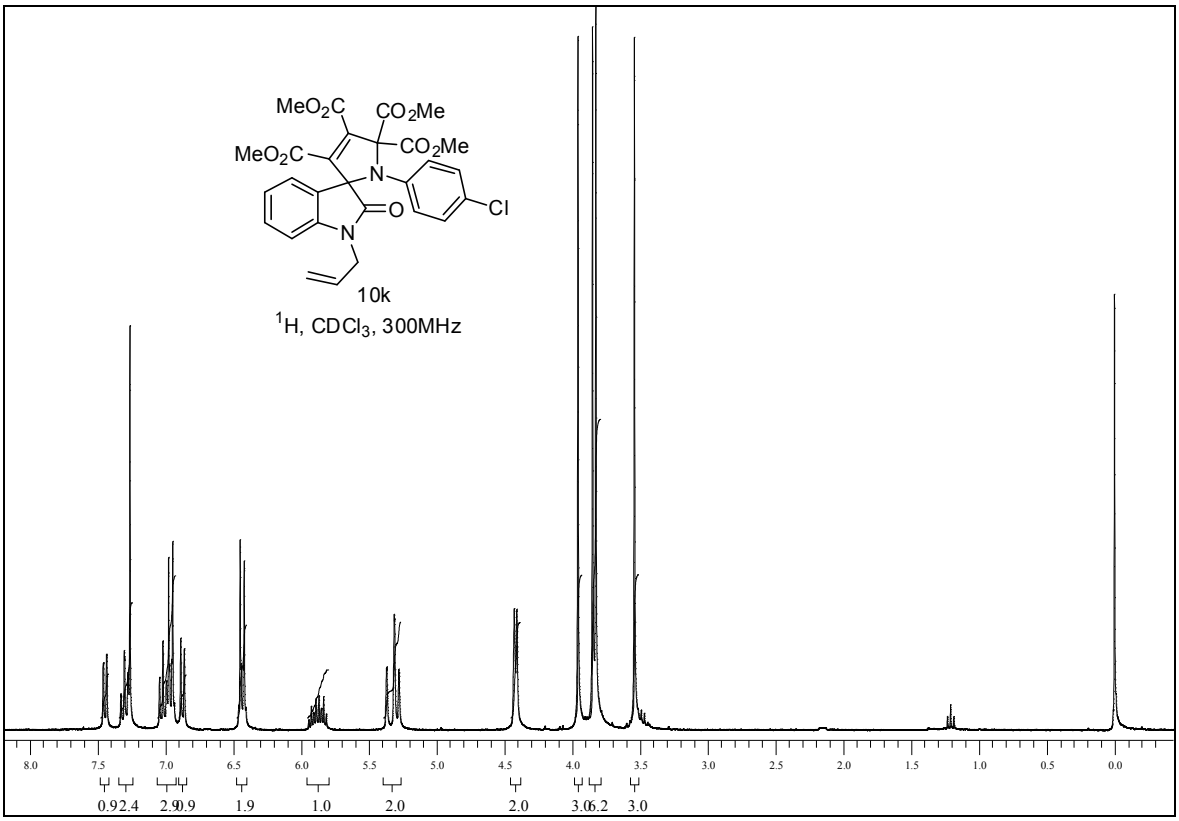

MeO2C
CO2Me
MeO2C
CO2Me
N
O
N
10h
13C, CDCl3, 100MHz
Chemical shift (ppm)

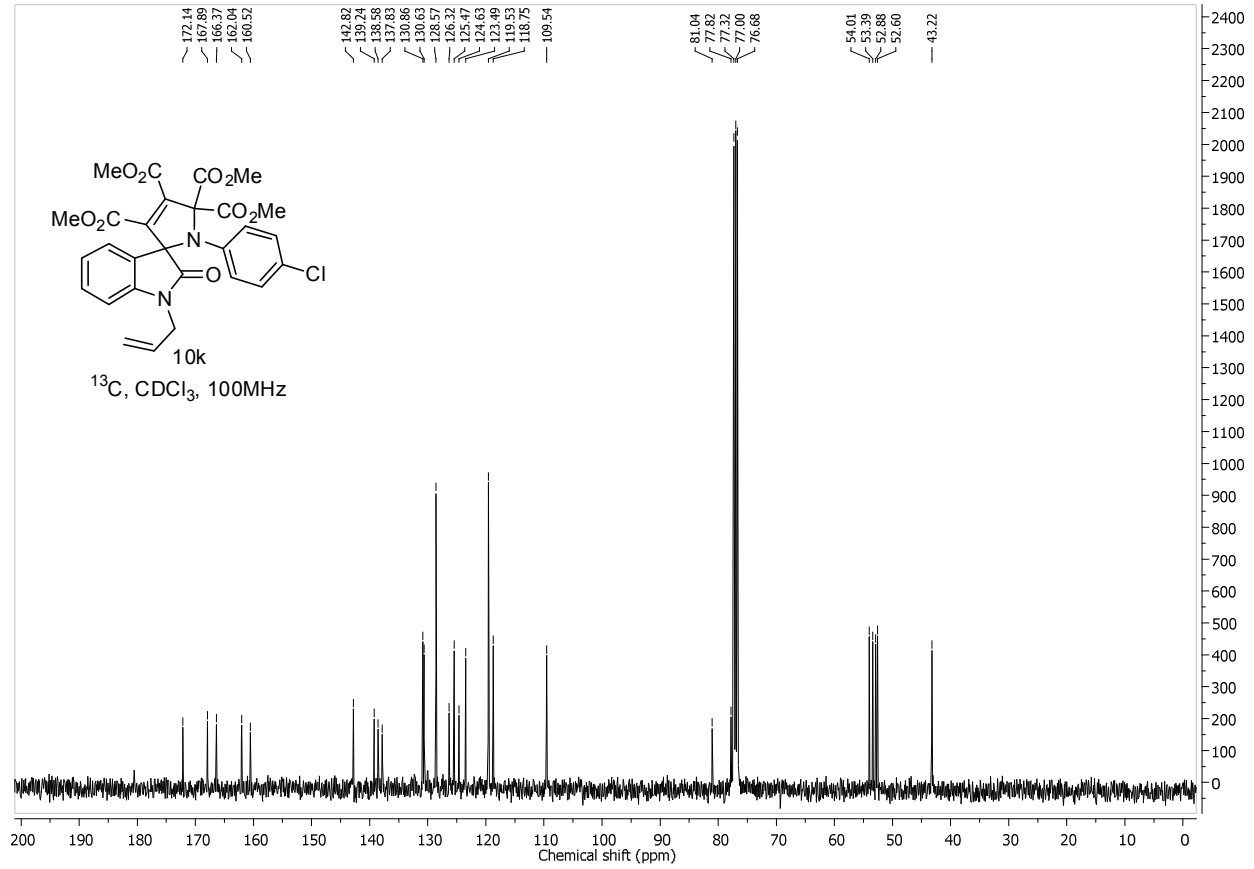

MeO2C
CO2Me
MeO2C
CO2Me
N
O
Me
N
10i
1H, CDCl3, 300MHz
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
1.0 2.8 1.0 3.1 2.0 0.9 2.0 1.8 3.6 3.0 3.0


172.73
168.24
166.74
162.22
160.73
142.87
138.85
138.25
137.92
131.18
130.96
130.24
129.18
125.51
125.34
123.22
119.84
118.30
109.27
81.20
78.00
77.32
77.00
76.68
53.75
53.15
52.77
52.48
43.03
20.31
MeO2C
CO2Me
MeO2C
CO2Me
N
O
Me
N
10i
13C, CDCl3, 100MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)


MeO2C
CO2Me
MeO2C
CO2Me
N
O
OMe
N
10j
1H, CDCl3, 300MHz
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
1.0 0.9 0.9 1.9 0.9 2.0 1.0 2.0 2.1 2.2 2.8 3.0 1.9


173.37
168.48
167.26
162.34
160.88
156.79
142.97
139.12
139.03
132.61
130.68
130.07
128.26
125.76
125.57
122.88
117.59
113.60
109.08
82.03
79.02
77.32
77.00
76.68
55.04
53.48
52.84
52.65
52.38
42.57
MeO2C
CO2Me
MeO2C
CO2Me
N
O
OMe
N
10j
13C, CDCl3, 100MHz
1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift (ppm)


MeO2C
CO2Me
MeO2C
CO2Me
N
O
N
Cl
10k
1H, CDCl3, 300MHz
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
0.9 2.4 2.9 0.9 1.9 1.0 2.0 2.0 3.0 6.2 3.0


172.14
167.89
166.37
162.04
160.52
142.82
139.24
138.58
137.83
130.86
130.63
128.57
126.32
125.47
124.63
123.49
119.53
118.75
109.54
81.04
77.82
77.32
77.00
76.68
54.01
53.39
52.88
52.60
43.22
MeO2C
CO2Me
MeO2C
CO2Me
N
O
N
Cl
10k
13C, CDCl3, 100MHz
Chemical shift (ppm)