Stereoselective Synthesis and Applications of Nitrogen Substituted Donor-Acceptor Cyclopropanes (N-DACs) in the Divergent Synthesis of Azacycles

Santosh J. Gharpure,*[a] U. Vijayasree[a] and S. Raja Bhushan Reddy[a]

Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600036, India

General methods:

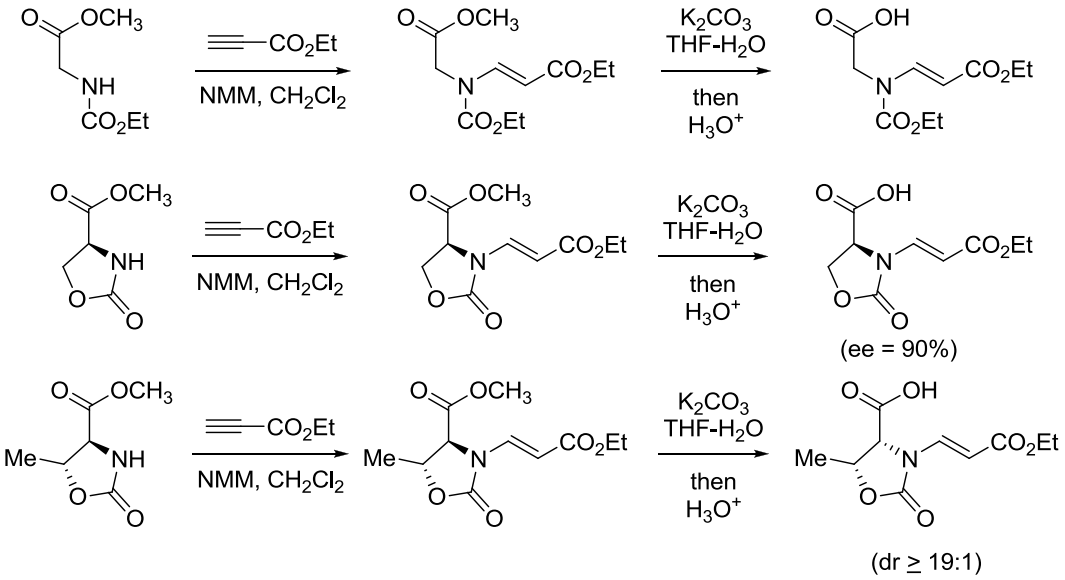
Melting points are recorded using Sigma melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 spectrophotometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane or residual $CHCl_3$ (7.26 ppm for ^{1}H) or the central line (77.16 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) were determined by recording the DEPT-135 experiment, and are given in parentheses. High resolution mass measurements were carried out using Micromass Q-ToF instrument using direct inlet mode. Optical rotations were measured using a Rudolph digital polarimeter and $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. Analytical thin-layer chromatographies (TLC) were performed on glass plates (7.5 × 2.5 and 9 × 5.0 cm) coated with Merck or Acme's silica gel G containing 13% calcium sulphate as binder or on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates and various combinations of ethyl acetate and hexanes were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour or $KMnO_4$ stain. Acme's silica gel (100-200 mesh) was used for column chromatography (approximately 15-20 g per 1 g of the crude product). All small-scale dry reactions were carried out using standard syringe septum technique.

Low temperature reactions were conducted in a bath made of acetone and liquid nitrogen. Dry THF and dry ether were obtained by distillation over sodium-benzophenone ketyl. Dry dichloromethane and dry benzene were prepared by distilling over calcium hydride. N-nitroso-N-methylurea was prepared according to literature procedures. LAH, *m*-CPBA, DBU, 1,2-ethanedithiol and n-Bu_3SnH were obtained from Aldrich. All the α-amino acids were obtained from Spectrochem. AIBN obtained from Spectrochem was

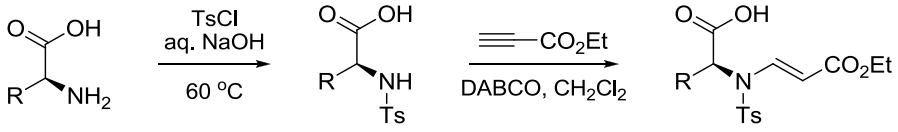
recrystallized from methanol and stored in dark. All the commercial reagents were used as such without further purification.

General synthesis of acids 3:

A) Synthesis of *N*-carbamate protected acid precursors:



B) Synthesis of *N*-tosyl protected acid precursors:



R= H, CH_3, $PhCH_2$, $TsOC_6H_4CH_2$, $(CH_3)_2CHCH_2$,$C_2H_5(CH_3)CH$, $(CH_3)_2CH$

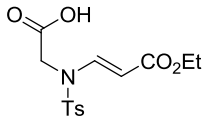
Synthesis of cyclopropapyrrolidinone 1:

To a magnetically stirred solution of the acid **3a** (248 mg, 0.76 mmol) in dry CH_2Cl_2 (1 mL) was added oxalyl chloride (328 µL, 3.82 mmol) and the reaction mixture was stirred for 2 h at rt. Evaporation of CH_2Cl_2 and the excess oxalyl chloride under reduced pressure furnished the acid chloride, which was immediately used for the preparation of the diazo ketone **2a**. To the acid chloride obtained above, was added a cold solution of diazomethane (15 mL, prepared from 1.5 g of N-nitroso-N-methylurea and 22.5 mL of 60% aq. KOH solution) at 0 °C. The reaction mixture was slowly warmed up to rt, stirred for 2h and the excess diazomethane and ether were carefully evaporated on a water bath. . Rapid purification by filtration of the crude product through a silica gel column using ethyl acetate/hexanes (1:9) as eluent furnished the diazoketone **2a** (189 mg, 70%) as a pale yellow solid.

A solution of the diazo ketone **2a** (38 mg, 0.11 mmol) and $Cu(acac)_2$ (3 mg, 0.01 mmol) in CH_2Cl_2 (5 mL) was vigorously refluxed for 3 h. Reaction mass was washed with 5% aq. ammonia (3 x 5 mL), layers were separated and extraction with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexanes (1:9) as eluent furnished the cyclopropapyrrolidinone **1a** (24 mg, 69%) as a white solid.

***(E)-2-(N-(3-Ethoxy-3-oxoprop-1-enyl)-4-methylphenylsulfonamido)aceticacid* (3a):**

Physical appearance: white solid.



m.p.: 138-140°C.

IR (neat): 2982, 1724, 1697, 1625, 1479, 1442, 1416, 1377, 1364, 1314, 1294, 1265, 1250, 1164, 1116, 1091, 1075, 1034, 993, 966, 875, 897, 835, 811, 735, 704 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 14.0 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.63 (br s, 1H), 4.97 (d, *J* = 14.0 Hz, 1H), 4.26 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

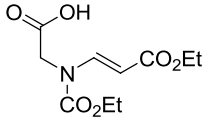
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.14 (CO), 167.53 (CO), 145.45 (C), 141.62 (CH), 134.87 (C), 130.26 (2 × CH), 127.65 (2 × CH), 98.76 (CH), 60.83 (CH_2), 46.52 (CH_2), 21.76 (CH_3), 14.40 (CH_3).

LRMS (ESI, M+H^+): m/z 328.

HRMS (ESI, M+H^+): m/z calcd. for $C_{14}H_{18}NO_6S$ 328.0855, found 328.0859.

***(E)-2-((3-Ethoxy-3-oxoprop-1-enyl)(ethoxycarbonyl)amino)acetic acid* (3b):**

Physical appearance: cream coloured solid.



m.p.: 92-94 °C.

IR (neat): 2986, 1747, 1716, 1673, 1619, 1476, 1450, 1422, 1386, 1372, 1333, 1289, 1235, 1176, 1026, 1002, 975, 928, 871, 848, 768, 700 cm^{-1}.

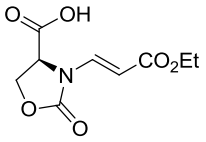
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (br s, 1H), 7.68 (br s, 1H), 5.11 (d, *J* = 14.2 Hz, 1H), 4.37 (br s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.34 (br t, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.98 (CO), 167.71 (CO), 153.28 (CO), 141.96 (CH), 98.87 (CH), 64.26 (CH_2), 60.63 (CH_2), 45.62 (CH_2), 14.40 (2 x CH_3).

LRMS (ESI, M+Na^+): m/z 268.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{10}H_{15}NO_6Na$ 268.0797, found 268.0795.

***(S,E)-3-(3-Ethoxy-3-oxoprop-1-enyl)-2-oxooxazolidine-4-carboxylic acid* (3c)**



Physical appearance: white solid.

m.p.: 68-70 °C.

$[\alpha]_D^{24}$: – 77.85 (c 1.00, $CHCl_3$).

IR (neat): 3469, 2984, 1765, 1694, 1631, 1431, 1375, 1349, 1324, 1302, 1252, 1180, 1104, 1066, 1026, 966, 899, 841, 795, 757 cm^{-1}.

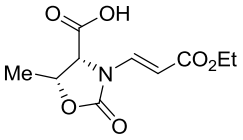
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 14.3 Hz, 1H), 5.28 (d, *J* = 14.3 Hz, 1H), 4.66 (m, 1H), 4.57 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 1H), 2.71 (br s, 1H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 169.71 (CO), 168.15 (CO), 154.22 (CO), 138.13 (CH), 101.29 (CH), 65.84 (CH_2), 61.38 (CH_2), 55.59 (CH), 14.33 (CH_3).

LRMS (ESI, M+H$^+$): m/z 230.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_9H_{12}NO_6$ 230.0665, found 230.0665.

***(4S,5R)-3-((E)-3-Ethoxy-3-oxoprop-1-enyl)-5-methyl-2-oxooxazolidine-4-carboxylic acid* (3d):**



Physical appearance: pale yellow oil.

$[\alpha]_D^{24}$: – 44.1 (c 1.00, $CHCl_3$).

IR (neat): 3476, 2984, 2930, 1759, 1696, 1636, 1415, 1388, 1367, 1342, 1296, 1265, 1180, 1101, 1039, 968, 860, 835, 757, 703 cm^{-1}.

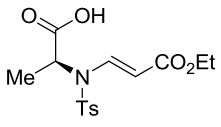
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (br s, 1H), 7.91 (d, *J* = 14.3 Hz, 1H), 5.22 (d, *J* = 14.3 Hz, 1H), 4.80 (dq, *J* = 6.0, 4.0 Hz, 1H), 4.20 (d, *J* = 7.1 Hz, 2H), 4.14 (d, *J* = 4.0 Hz, 1H), 1.57 (d, *J* = 6.0 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 169.41 (CO), 168.35 (CO), 153.74 (CO), 138.45 (CH), 100.83 (CH), 74.97 (CH), 62.02 (CH), 61.43 (CH_2), 21.45 (CH_3), 14.26 (CH_3).

HRMS (ESI, M+H$^+$): m/z 244.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{10}H_{14}NO_6$ 244.0812, found 244.0812.

***(S,E)-2-(N-(3-Ethoxy-3-oxoprop-1-enyl)-4-methylphenylsulfonamido)propanoic acid* (3e):**



Physical appearance: sticky solid.

$[\alpha]_D^{32}$: 16.2 (c 1.00, $CHCl_3$).

IR (neat): 2982, 2939, 1734, 1703, 1620, 1494, 1455, 1360, 1307, 1238, 1154, 1084, 1043, 993, 938, 814, 756, 706 cm^{-1}.

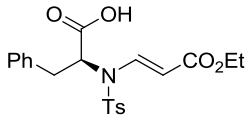
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 14.8 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.07 (bs, OH), 5.08 (d, *J* = 14.8 Hz, 1H), 4.93 (q, *J* = 7.2 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.46 (d, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.97 (CO), 168.08 (CO), 145.28 (C), 139.61 (CH), 134.93 (C), 130.16 (2 × CH), 127.80 (2 × CH), 99.23 (CH), 60.88 (CH_2), 54.43 (CH), 21.78 (CH_3), 14.41 (CH_3), 13.87 (CH_3).

HRMS (ESI, M+Na^+): m/z 364.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{15}H_{19}NO_6NaS$ 364.0831, found 364.0832.

***(S,E)-2-(N-(3-Ethoxy-3-oxoprop-1-enyl)-4-methylphenylsulfonamido)-3-phenyl propanoic acid* (3f):**



Physical appearance: sticky solid.

$[\alpha]_D^{23}$: –58.9 (c 1.00, $CHCl_3$).

IR (neat): 2982, 1712, 1624, 1451, 1366, 1310, 1164, 1087, 1052, 892, 820, 748, 697 cm^{-1}.

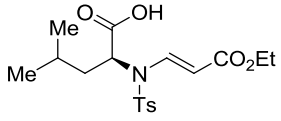
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 14.3 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.20-7.00 (m, 7H), 5.26 (d, *J* = 14.3 Hz, 1H), 5.11 (dd, *J* = 8.7, 5.9 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.44 (ABX, *J* = 14.4, 5.9 Hz, 1H), 3.04 (ABX, *J* = 14.4, 8.7 Hz, 1H), 2.28 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.47 (CO), 168.19 (CO), 144.99 (C), 140.18 (CH), 136.77 (C), 134.85 (C), 129.98 (2 × CH), 129.50 (2 × CH), 128.74 (2 × CH), 127.90 (2 × CH), 127.14 (CH), 100.17 (CH), 61.06 (CH), 60.98 (CH_2), 34.39 (CH_2), 21.69 (CH_3), 14.38 (CH_3).

LRMS (ESI, M+H^+): m/z 418.

HRMS (ESI, M+H^+): m/z calcd. for $C_{21}H_{24}NO_6S$ 418.1324, found 418.1314.

***(S,E)-2-(N-(3-Ethoxy-3-oxoprop-1-enyl)-4-methylphenylsulfonamido)-4-methylpentanoic acid* (3h):**



Physical appearance: pale yellow sticky solid.

$[\alpha]_D^{27}$: – 40.6 (c 1.8, $CHCl_3$).

IR (neat): 3509, 2983, 2924, 1753, 1384, 1290, 1202, 1043, 773 cm^{-1}.

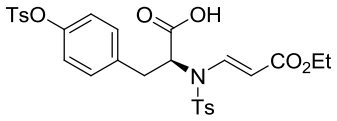
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 14.4 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 5.19 (d, *J* = 14.4 Hz, 1H), 4.94 (d, *J* = 6.4 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 1.95-1.85 (m, 1H), 1.80-1.60 (m, 2H), 1.25 (t, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.2 Hz, 3H), 1.89 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 172.12 (CO), 167.87 (CO), 145.12 (C), 139.93 (CH), 135.01 (C), 129.91 (2 × CH), 127.95 (2 × CH), 100.38 (CH), 60.75 (CH_2), 57.62 (CH), 37.27 (CH_2), 25.19 (CH), 22.83 (CH_3), 21.68 (2 × CH), 14.34 (CH_3).

HRMS (ESI, M+H^+): m/z 384.

HRMS (ESI, M+H^+): m/z calcd. for $C_{18}H_{26}NO_6S$ 384.1481, found 384.1483.

***(S,E)-2-(N-(3-Ethoxy-3-oxoprop-1-enyl)-4-methylphenylsulfonamido)-3-(4-(tosyloxy)phenyl)propanoic acid* (3g):**



Physical appearance: sticky solid.

$[\alpha]_D^{24}$: –63.0 (c 1.00, $CHCl_3$).

IR (neat): 2980, 1709, 1622, 1504, 1446, 1368, 1306, 1149, 1090, 1044, 1019, 905, 864, 842, 812, 727, 705 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 14.4 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 5.28 (d, *J* = 14.4 Hz, 1H), 5.08 (dd, *J* = 8.9, 5.5 Hz, 1H), 4.71 (br s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.45 (ABX, *J* = 14.5, 5.5 Hz, 1H), 3.12 (ABX, *J* = 14.4, 8.9 Hz, 1H), 2.43 (s, 3H), 2.40 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.79 (CO), 168.08 (CO), 148.79 (C), 145.47 (C), 145.22 (CH), 140.06 (C), 135.77 (C), 134.76 (C), 132.10 (C), 130.65 (2 x CH), 129.97 (2 x CH), 129.88 (2 x CH), 128.62 (2 x CH), 127.77 (2 x CH), 122.61 (2 x CH), 99.99 (CH), 61.03 (CH), 60.73 (CH_2), 33.43 (CH_2), 21.77 (CH_3), 21.65 (CH_3),14.32 (CH_3).

LRMS (ESI, M+H^+): m/z 588.

HRMS (ESI, M+H^+): m/z calcd. for $C_{28}H_{30}NO_9S_2$ 588.1362, found 588.1378.

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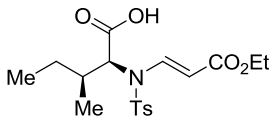
***(2S,3S)-2-(N-((E)-3-Ethoxy-3-oxoprop-1-enyl)-4-methylphenylsulfonamido)-3-methylpentanoic acid* (3i):**



Physical appearance: pale yellow sticky solid.

$[\alpha]_D^{27}$: – 40.6 (c 1.8, $CHCl_3$).

IR (neat): 3509, 2983, 2924, 1753, 1384, 1290, 1202, 1043, 773 cm^{-1}.

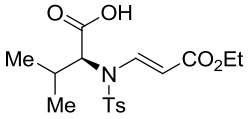
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 14.4 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 5.19 (d, *J* = 14.4 Hz, 1H), 4.94 (d, *J* = 6.4 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 2.39 (s, 3H), 1.95-1.85 (m, 1H), 1.80-1.60 (m, 2H), 1.25 (t, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.2 Hz, 3H), 1.89 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 172.12 (CO), 167.87 (CO), 145.12 (C), 139.93 (CH), 135.01 (C), 129.91 (2 × CH), 127.95 (2 × CH), 100.38 (CH), 60.75 (CH_2), 57.62 (CH), 37.27 (CH_2), 25.19 (CH), 22.83 (CH_3), 21.68 (2 × CH), 14.34 (CH_3).

LRMS (ESI, M+H^+): m/z 384.

HRMS (ESI, M+H^+): m/z calcd. for $C_{18}H_{26}NO_6S$ 384.1481, found 384.1483.

***(S,E)-2-(N-(3-Ethoxy-3-oxoprop-1-enyl)-4-methylphenylsulfonamido)-3-methylbutanoic acid* (3j):**



Physical appearance: sticky solid.

$[\alpha]_D^{24}$: – 61.0 (c 2.00, $CHCl_3$).

IR (neat): 3402, 3257, 2973, 2930, 2872, 1738, 1713, 1624, 1466, 1366, 1311, 1166, 1090, 1045, 891, 840, 818, 703 cm^{-1}.

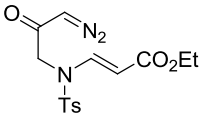
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 14.0 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.32 (br s, 1H), 5.46 (d, *J* = 14.0 Hz, 1H), 4.53 (d, *J* = 10.2 Hz, 1H), 4.12 (q, *J* = 3.4 Hz, 2H), 2.50-2.40 (m, 1H), 2.39 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.11 (d, *J* = 6.3 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.92 (CO), 167.87 (CO), 145.10 (C), 140.12 (CH), 135.07 (C), 129.90 (2 × CH), 128.06 (2 × CH), 100.48 (CH), 65.28 (CH), 60.64 (CH_2), 27.36 (CH), 21.70 (CH_3), 20.98 (CH_3), 19.11 (CH_3), 14.36 (CH_3).

LRMS (ESI, M+H^+): m/z 370.1318.

HRMS (ESI, M+H^+): m/z calcd. for $C_{17}H_{23}NO_6S$ 370.1324, found 370.1318.

***(E)-Ethyl 3-(N-(3-diazo-2-oxopropyl)-4-methylphenylsulfonamido)acrylate* (2a):**



Physical appearance: pale yellow solid.

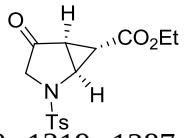
IR (neat): 3084, 2985, 2103, 1698, 1653, 1625, 1491, 1449, 1373, 1355, 1321, 1266, 1159, 1084, 1052, 1032, 969, 941, 921, 858, 812, 783, 729, 703 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 14.0 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 5.60 (s, 1H), 5.04 (d, *J* = 14.0 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.02 (s, 2H), 2.44 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 188.10 (CO), 166.61 (CO), 145.70 (C), 141.17 (CH), 134.44 (C), 130.52 (2 x CH), 127.44 (2 x CH), 100.25 (CH), 60.56 (CH_2), 54.58 (CH), 52.97 (CH_2), 21.80 (CH_3), 14.42 (CH_3).

***(1S*,5S*,6S*)-ethyl 4-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-6-carboxylate (*1a):**

Physical appearance: white solid.



m.p.: 92-94 °C.

IR (neat): 3080, 2991, 2909, 1757, 1718, 1596, 1475, 1429, 1408, 1349, 1319, 1287, 1265, 1164, 1140, 1092, 1060, 1036, 1012, 956, 907, 855, 805, 727, 706 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.30 (d, *J* = 5.2 Hz, 1H), 4.20-4.00 (m, 2H), 3.75 (AB, *J* = 17.9 Hz, 1H), 3.22 (AB, *J* = 17.9 Hz, 1H), 2.61 (dd, *J* = 4.4, 4.2 Hz, 1H), 2.47 (s, 3H), 1.61 (dd, *J* = 2.9, 2.2 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H).

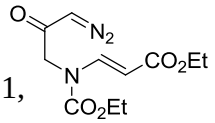
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 200.17 (CO), 167.38 (CO), 145.22 (C), 131.97 (C), 130.38 (2 × CH), 128.36 (2 × CH), 61.91 (CH_2), 51.34 (CH_2), 46.10 (CH), 32.50 (CH), 25.19 (CH), 21.79 (CH_3), 14.28 (CH_3).

LRMS (ESI, M+H^+): m/z 324.

HRMS (ESI, M+H^+): m/z calcd. for $C_{15}H_{18}NO_5S$ 324.0906; found 324.0902.

***(E)-Ethyl 3-((3-diazo-2-oxopropyl)(ethoxycarbonyl)amino)acrylate* (2b):**

Physical appearance: pale yellow oil.



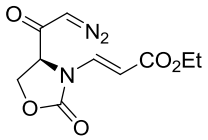
IR (neat): 3096, 2983, 2938, 2108, 1727, 1702, 1626, 1532, 1466, 1411, 1375, 1324, 1305, 1269, 1216, 1151, 1093, 1037, 1019, 956, 905, 866, 831, 771, 734 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 14.2 Hz, 1H), 5.32 (s, 1H), 5.11 (d, *J* = 14.2 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 3H), 4.30 (br s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 188.05 (CO), 167.07 (CO), 153.25 (CO), 141.80 (CH), 99.49 (CH), 64.15 (CH_2), 60.28 (CH_2), 53.84 (CH), 51.53 (CH_2), 14.35 (2× CH_3).

***(S, Z)-Ethyl 3-(4-(2-diazoacetyl)-2-oxooxazolidin-3-yl)acrylate* (2c):**

Physical appearance: pale yellow solid.

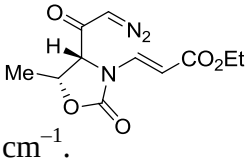


IR (neat): 3097, 2979, 2918, 2114, 1760, 1711, 1639, 1619, 1479, 1466, 1423, 1389, 1371, 1354, 1330, 1297, 1270, 1205, 1156, 1094, 1065, 1021, 970, 910, 881, 857, 836, 787, 758, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 14.3 Hz, 1H), 5.49 (s, 1H), 5.19 (d, *J* = 14.3 Hz, 1H), 4.65 (m, *J* = 11.5, 4.1 Hz, 1H), 4.44 (m, *J* = 11.5, 3.7 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 188.64 (CO), 166.16 (CO), 154.18 (CO), 137.14 (CH), 102.39 (CH), 66.68 (CH_2), 60.75 (CH_2), 59.84 (CH), 55.05 (CH), 14.40 (CH_3).

***(Z)-Ethyl 3-((4S,5S)-4-(2-diazoacetyl)-5-methyl-2-oxooxazolidin-3-yl)acrylate* (2d)**



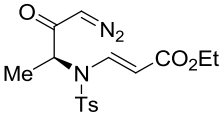
Physical appearance: pale yellow solid

IR (neat): 3090, 2984, 2110, 1770, 1704, 1635, 1389, 1364, 1334, 1262, 1205, 1174, 1087, 1043, 968, 911, 834, 798, 758, 732, 702, 663 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 14.3 Hz, 1H), 5.47 (s, 1H), 5.11 (d, *J* = 14.3 Hz, 1H), 5.00-4.85 (m, 1H), 4.40 (d, *J* = 8.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 187.18 (CO), 166.29 (CO), 153.84 (CO), 137.15 (CH), 102.04 (CH), 74.19 (CH), 63.77 (CH), 60.69 (CH_2), 56.36 (CH), 15.71 (CH_3), 14.39 (CH_3).

***(S,E)-Ethyl 3-(N-(4-diazo-3-oxobutan-2-yl)-4-methylphenylsulfonamido)acrylate* (2e):**



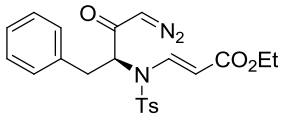
Physical appearance: pale yellow solid.

IR (neat): 3089, 2981, 2108, 1700, 1621, 1451, 1352, 1301, 1162, 1080, 1041, 1003, 967, 933, 892, 835, 815, 744, 712 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 14.6 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 5.61 (s, 1H), 5.08 (d, *J* = 14.6 Hz, 1H), 4.73 (d, *J* = 7.0 Hz, 1H), 4.16 (dq, *J* = 7.1, 2.9 Hz, 2H), 2.45 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.10 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 190.39 (CO), 166.89 (CO), 145.69 (C), 138.20 (CH), 135.05 (C), 130.53 (2 x CH), 127.57 (2 x CH), 100.52 (CH), 60.45 (CH_2), 58.96 (CH), 54.67 (CH), 21.78 (CH_3), 14.41(CH_3), 10.84 (CH_3).

***(S,E)-Ethyl 3-(N-(4-diazo-3-oxobutan-2-yl)-4-methylphenylsulfonamido)acrylate* (2f):**



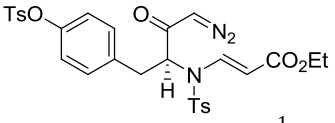
Physical appearance: pale yellow solid.

IR (neat): 3112, 3062, 2985, 2937, 2361, 2341, 2115, 1708, 1628, 1495, 1454, 1362, 1309, 1267, 1163, 1089, 1049, 976, 906, 840, 814, 740, 705 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 14.4 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.20-7.10 (m, 5H), 6.91 (d, *J* = 6.9 Hz, 2H), 5.69 (s, 1H), 5.34 (d, *J* = 14.4 Hz, 1H), 5.00 (t, *J* = 6.8 Hz, 1H), 4.25-4.15 (m, 2H), 3.61 (ABX, *J* = 14.4, 6.8 Hz, 1H), 2.64 (ABX, *J* = 14.4, 6.8 Hz, 1H), 2.42 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 189.81 (CO), 166.99 (CO), 145.42 (C), 138.71 (CH), 137.47 (C), 134.38 (C), 130.36 (2 × CH), 129.34 (2 × CH), 128.76 (2 × CH), 127.80 (2 × CH), 126.84 (CH), 101.11 (CH), 65.48 (CH), 60.59 (CH_2), 55.41 (CH), 32.40 (CH_2), 21.78 (CH_3), 14.44 (CH_3).

***(S,E)-Ethyl 3-(N-(4-diazo-3-oxo-1-(4-(tosyloxy)phenyl)butan-2-yl)-4-methylphenyl sulfonamido)acrylate* (2g):**



Physical appearance: pale yellow solid.

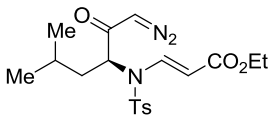
IR (neat): 2925, 2115, 1708, 1626, 1502, 1361, 1154, 1092, 1047, 909, 864, 706 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 14.4 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 5.61 (s, 1H), 5.26 (d, *J* = 14.4 Hz, 1H), 4.86 (t, *J* = 6.6 Hz, 1H), 4.25-4.10 (m, 2H), 3.54 (ABX, *J* = 14.5, 6.3 Hz, 1H), 2.62 (ABX, *J* = 14.5, 7.3 Hz, 1H), 2.44 (s, 6H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 189.48 (CO), 166.83 (CO), 148.61 (C), 145.83 (C), 145.57 (C), 138.62 (CH), 136.45 (C), 134.45 (C), 132.42 (C), 130.49 (2 × CH), 130.46 (2 × CH), 129.92 (2 × CH), 128.55 (2 × CH), 127.62 (2 × CH), 122.49 (2 × CH), 101.03 (CH), 65.24 (CH), 60.60 (CH_2), 55.43 (CH), 31.69 (CH_2), 21.81 (CH_3), 21.76 (CH_3), 14.29 (CH_3).

***(S,E)-Ethyl 3-(N-(1-diazo-5-methyl-2-oxohexan-3-yl)-4-methylphenylsulfonamido) acrylate* (2h):**

Physical appearance: pale yellow oil.

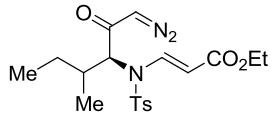


IR (neat): 2960, 2111, 1802, 1708, 1622, 1466, 1349, 1315, 1265, 1155, 1088, 1044, 958, 900, 814, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 14.4 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 5.55 (S, 1H), 5.21 (d, *J* = 14.4 Hz, 1H), 4.63 (t, *J* = 0.0 Hz, 1H), 4.15 (q, *J* = 6.5 Hz, 2H), 2.44 (s, 3H), 2.13 (dt, *J* = 6.8, 13.7 Hz, 1H), 1.40-1.25 (m, 1H), 1.26 (t, *J* = 6.8 Hz, 3H), 1.04 (dt, *J* = 6.8, 13.7 Hz, 1H), 0.80 (d, *J* = 6.0 Hz, 3H), 0.67 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 190.12 (CO), 167.04 (CO), 145.63 (C), 138.87 (CH), 135.16 (C), 130.34 (2 × CH), 127.76 (2 × CH), 100.94 (CH), 61.95 (CH), 60.46 (CH_2), 55.12 (CH), 35.67 (CH_2), 26.01 (CH), 22.37 (CH_3), 21.78 (2 × CH_3), 14.41 (CH_3).

***(E)-Ethyl 3-(N-((3S,4S)-1-diazo-4-methyl-2-oxohexan-3-yl)-4-methylphenylsulfonamido)acrylate* (2i):**



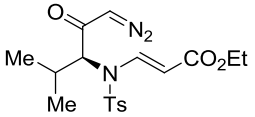
Physical appearance: pale yellow solid.

IR (neat): 2972, 2929, 2109, 1708, 1628, 1458, 1359, 1316, 1247, 1161, 1093, 1044, 962, 819, 753 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 14.4 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 5.51 (d, *J* = 14.4 Hz, 1H), 5.45 (s, 1H), 4.26 (d, *J* = 10.8 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 2.25-2.20 (m, 1H), 1.25-1.15 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H), 0.85-0.75 (m, 1H), 0.68 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 189.33 (CO), 167.21 (CO), 145.41 (C), 139.16 (CH), 135.02 (C), 130.09 (2 × CH), 127.86 (2 × CH), 101.39 (CH), 67.85 (CH), 60.25 (CH_2), 56.03 (CH), 31.98 (CH), 24.44 (CH_2), 21.68 (CH_3), 17.09 (CH_3), 14.30 (CH_3), 11.09 (CH_3).

***(S,E)-Ethyl 3-(N-(1-diazo-4-methyl-2-oxopentan-3-yl)-4- ethylphenylsulfonamido) acrylate* (2j):**



Physical appearance: pale yellow solid.

IR (neat): 3108, 2974, 2159, 2107, 2035, 1704, 1621, 1467, 1358, 1317, 1220, 1146, 1088, 1041, 951, 904, 837, 814, 766, 708 cm^{-1}.

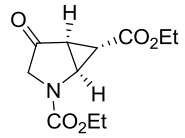
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 14.4 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 5.53 (s, 1H), 5.51 (d, *J* = 14.4 Hz, 1H), 4.22 (d, *J* = 10.4 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.60-2.50 (m, 1H), 2.41 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 6.3 Hz, 3H), 0.42 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 189.37 (CO), 167.20 (CO), 145.54 (C), 139.12 (CH), 135.17 (C), 130.22 (2 x CH), 127.89 (2 x CH), 101.06 (CH), 68.62 (CH), 60.26 (CH_2), 55.96 (CH), 25.71 (CH), 21.69 (CH_3), 21.13 (CH_3), 18.51 (CH_3), 14.34 (CH_3).

***(1R*,5R*,6R*)-Diethyl 4-oxo-2-azabicyclo[3.1.0]hexane-2,6-dicarboxylate* (1b):**

Physical appearance: colourless liquid.

IR (neat): 3074, 2984, 1801, 1711, 1418, 1372, 1336, 1266, 1182, 1116, 1096, 1015, 851 769 cm^{-1}.



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

At 25 °C temperature:

δ 4.50-4.35 (br d, 1H), 4.30-4.10 (m, 4H), 3.91 (AB, *J* = 19.0 Hz, 1H), 3.66 (AB, *J* = 19.0 Hz, 1H), 2.65 (t, *J* = 3.8 Hz, 1H), 2.22 (bs, 1H), 1.20 - 1.30 (m, 6H).

At -25 °C temperature: Rotamer 1:

δ 4.50 (d, *J* = 5.4 Hz, 1H), 4.30 - 4.20 (m, 4H), 3.93 (AB, *J* = 19.5 Hz, 1H), 3.64 (AB, *J* = 19.5 Hz, 1H), 2.69 (br s, 1H), 2.26 (br s, 1H), 1.26 (t, *J* = 7.2 Hz, 6H).

At -25 °C temperature: Rotamer 2:

δ 4.41 (d, *J* = 5.5 Hz, 1H), 4.20 - 4.00 (m, 4H), 3.96 (AB, *J* = 8.9 Hz, 1H), 3.63 (AB, *J* = 19.8 Hz, 1H), 2.69 (br s, 1H), 2.24 (br s, 1H), 1.31 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT):

At 25 °C temperature:

δ 203.00 (CO), 168.16 (CO), 154.74 (CO), 62.38 (CH_2), 61.89 (CH_2), 51.99 (CH_2), 45.13 (CH), 29.82 (CH), 28.22 (CH), 14.76 (CH_3), 4.23 (CH_3).

At -25 °C temperature: Rotamer 1:

δ 203.32 (CO), 168.45 (CO), 154.67 (CO), 62.42 (CH_2), 62.04 (CH_2), 51.87 (CH_2), 45.14 (CH), 33.63 (CH), 28.01 (CH), 14.75 (CH_3), 14.16 (CH_3).

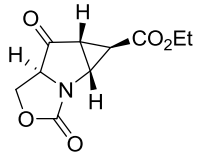
At -25 °C temperature: Rotamer 2:

δ 202.87 (CO), 168.23 (CO), 154.36 (CO), 62.37 (CH_2), 61.96 (CH_2), 51.75 (CH_2), 44.89 (CH), 32.93 (CH), 28.01(CH_3), 14.70 (CH_3), 14.16 (CH_3).

LRMS (ESI, M+H$^+$): m/z found 242.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{11}H_{16}NO_5$ 242.1028, found 242.1032.

***N-DAC* (1c):**



Physical appearance: white crystalline solid.

m.p.: 134-136 °C.

[α]$_D^{33}$: 139.1 (c 1.00, $CHCl_3$).

IR (neat): 2992, 2922, 1770, 1741, 1715, 1640, 1466, 1417, 1388, 1304, 1277, 1256, 1222, 1183, 1169, 1119, 1078, 1043, 1006, 984, 926, 904, 863, 837, 796, 766, 743, 717, 698 cm^{-1}.

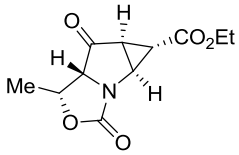
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69 (dd, *J* = 4.5, 3.0 Hz, 1H), 4.56 (ABX, *J* = 9.6, 0.0 Hz, 1H), 4.40 (ABX, *J* = 9.6, 4.2 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.87 (dd, *J* = 9.6, 4.2 Hz, 1H), 2.57 (t, *J* = 3.0 Hz, 1H), 2.43 (dd, *J* = 4.5, 3.0 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 205.20 (CO), 167.49 (CO), 160.32 (CO), 65.31 (CH_2), 62.31 (CH_2), 58.70 (CH), 48.21 (CH), 29.71 (CH), 27.63 (CH), 14.22 (CH_3).

LRMS (ESI, M+Na$^+$): m/z found 248.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{10}H_{11}NO_5Na$ 248.0535, found 248.0530.

***N-DAC* (1d):**



Physical appearance: colourless oil.

[α]$_D^{31}$: –97.8 (c 0.50, $CHCl_3$).

IR (neat): 3081, 2983, 1726, 1641, 1446, 1386, 1347, 1256, 1221, 1180, 1106, 1042, 998, 962, 936, 903, 867, 840, 813, 770, 733 cm^{-1}.

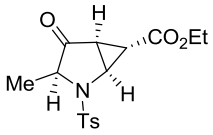
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.66 (dd, *J* = 3.5, 0.0 Hz, 1H), 4.64 (quint, *J* = 5.2 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.44 (d, *J* = 5.2 Hz, 1H), 2.50 (dd, *J* = 3.5, 0.0 Hz, 1H), 2.45 (t, *J* = 3.5, 0.0 Hz, 1H), 1.54 (d, *J* = 5.2 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 204.74 (CO), 167.53 (CO), 159.83 (CO), 75.07 (CH), 65.24 (CH), 62.28 (CH_2), 47.93 (CH), 30.36 (CH), 27.57 (CH), 21.97 (CH_3), 14.22 (CH_3).

LRMS (ESI, M+H$^+$): m/z found 240.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{11}H_{14}NO_5$ 240.0872, found 240.0871.

***(1S,3S,5S,6S)-Ethyl 3-methyl-4-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-6-carboxylate* (1e):**



Physical appearance: fluffy cream colour solid.

m.p.: 144-146 °C.

[α]$_D^{34}$: –35.5 (c 1.00, $CHCl_3$).

IR (neat): 2992, 2943, 1752, 1714, 1597, 1467, 1445, 1411, 1384, 1350, 1328, 1306, 1271, 1186, 1161, 1094, 1060, 1039, 1006, 968, 918, 872, 852, 813, 710 cm^{-1}.

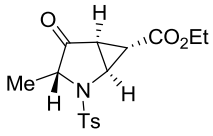
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.42 (dd, *J* = 5.5, 2.0 Hz, 1H), 4.25-4.10 (m, 2H), 3.78 (qd, *J* = 7.2, 1.5 Hz, 1H), 2.52 (ddd, *J* = 5.5, 3.4, 1.5 Hz, 1H), 2.45 (s, 3H), 2.12 (dd, *J* = 3.4, 2.0 Hz, 1H), 1.37 (d, *J* = 7.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 204.72 (CO), 167.88 (CO), 144.76 (C), 134.80 (C), 130.36 (2 × CH), 127.57 (2 × CH), 62.12 (CH_2), 62.02 (CH), 47.16 (CH), 31.67 (CH), 27.70 (CH), 21.73 (CH_3), 19.64 (CH_3), 14.27 (CH_3).

LRMS (ESI, M+Na$^+$): m/z found 360.0883.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{16}H_{19}NO_5NaS$ 360.0882, found 360.0883.

***(1S,3R,5S,6S)-Ethyl 3-methyl-4-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-6-carboxylate* (1e'):**



Physical appearance: white solid.

m.p.: 84-86 °C.

[α]$_D^{32}$: 30.4 (c 1.00, $CHCl_3$).

IR (neat): 2936, 1753, 1714, 1594, 1447, 1417, 1353, 1306, 1266, 1197, 1168, 1139, 1082, 1055, 999, 967, 907, 871, 848, 806, 761, 708 cm^{-1}.

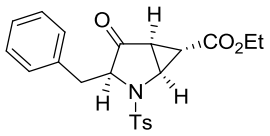
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 4.23 (d, *J* = 5.2 Hz, 1H), 4.25-4.05 (m, 2H), 3.17 (q, *J* = 6.8 Hz, 1H), 2.62 (dd, *J* = 5.8, 3.5 Hz, 1H), 2.48 (s, 3H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.44 (dd, *J* = 3.5, 2.1 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 203.18 (CO), 167.48 (CO), 145.14 (C), 132.41 (C), 130.36 (2 × CH), 128.52 (2 × CH), 61.87 (CH_2), 57.69 (CH), 44.90 (CH), 31.29 (CH), 25.31 (CH), 21.84 (CH_3), 17.88 (CH_3), 14.34 (CH_3).

LRMS (ESI, M+H$^+$): m/z found 338.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{16}H_{20}NO_5S$ 338.1062, found 338.1060.

***(1S,3S,5S,6S)-Ethyl 3-benzyl-4-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-6-carboxylate* (1f):**



Physical appearance: white solid.

m.p.: 92-96 °C.

$[\alpha]_D^{24}$: –8.8 (c 4.51, $CHCl_3$).

IR (neat): 3074, 3025, 2920, 2853, 1738, 1725, 1592, 1459, 1410, 1362, 1267, 1211, 1169, 1089, 1029, 921, 858, 767, 711 cm^{-1}.

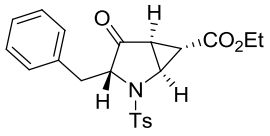
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.35-7.25 (m, 3H), 7.20-7.15 (m, 2H), 4.17 (dd, *J* = 5.6, 2.0 Hz, 1H), 4.05-3.95 (m, 2H), 3.87 (ddd, *J* = 4.9, 3.1, 1.6 Hz, 1H), 3.21 (dd, *J* = 8.0, 5.4 Hz, 2H), 2.47 (s, 3H), 2.19 (ddd, *J* = 5.2, 3.4, 1.6 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.54 (dd, *J* = 3.4, 2.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 203.92 (CO), 168.17 (CO), 145.03 (C), 135.44 (C), 133.36 (C), 130.84 (2 × CH), 130.51 (2 × CH), 128.88 (2 × CH), 127.77 (CH), 127.70 (2 × CH), 68.40 (CH), 61.79 (CH_2), 47.40 (CH), 36.99 (CH_2), 31.39 (CH), 23.52 (CH), 21.77 (CH_3), 14.10 (CH_3).

LRMS (ESI, M+H$^+$): m/z 414.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{22}H_{24}NO_5S$ 414.1375, found 414.1373.

***(1S,3R,5S,6S)-Ethyl 3-benzyl-4-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-6-carboxylate* (1f'):**



Physical appearance: white solid.

m.p.: 110-112 °C.

$[\alpha]_D^{24}$: –22.5 (c 1.00, $CHCl_3$).

IR (neat): 3070, 3035, 2983, 2927, 2861, 1749, 1728, 1599, 1452, 1403, 1347, 1308, 1267, 1166, 1089, 1046, 928, 850, 802, 739 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.30-7.20 (m, 5H), 4.20-4.00 (m, 2H), 3.91 (dt, *J* = 5.7, 1.5 Hz, 1H), 3.55 (br d, *J* = 3.7 Hz,

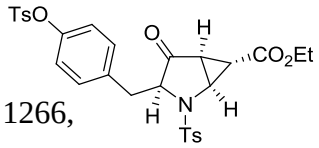
1H), 3.41 (ABX, *J* = 13.8, 5.8 Hz, 1H), 3.19 (ABX, *J* = 13.8, 2.5 Hz, 1H), 2.48 (s, 3H), 2.29 (dd, *J* = 5.7, 3.6 Hz, 1H), 1.31 (dd, *J* = 3.6, 1.5 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 203.21 (CO), 167.25 (CO), 145.20 (C), 134.88 (C), 132.57 (C), 130.93 (2 × CH), 130.40 (2 × CH), 128.47 (2 × CH), 128.38 (2 × CH), 127.13 (CH), 63.41 (CH), 61.79 (CH_2), 45.03 (CH), 37.45 (CH_2), 32.00 (CH), 25.08 (CH_3), 21.84 (CH), 14.29 (CH_3).

LRMS (ESI, M+H$^+$): m/z 414.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{22}H_{24}NO_5S$ 414.1375, found 414.1370.

***(1S,3S,5S,6S)-Ethyl 4-oxo-2-tosyl-3-(4-(tosyloxy)benzyl)-2-azabicyclo[3.1.0]hexane-6-carboxylate* (1g):**



Physical appearance: brownish liquid.

IR (KBr): 3070, 2976, 2918, 1761, 1719, 1595, 1501, 1311, 1266, 1188, 1062, 982, 944, 861, 824, 798 cm^{-1}.

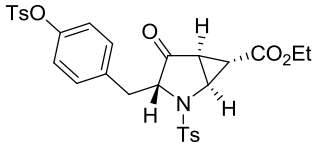
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.20 (dd, *J* = 5.4 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 3.45-3.80 (m, 1H), 3.22 (ABX, *J* = 12.2, 6.0 Hz, 1H), 3.13 (ABX, *J* = 12.2, 2.8 Hz, 1H), 2.47 (s, 6H), 2.24 (ddd, *J* = 1.8, 3.3, 5.4 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.70 (dd, *J* = 3.3, 1.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 203.33 (CO), 167.86 (CO), 149.16 (C), 145.56 (C), 145.17 (C), 134.56 (C), 132.96 (C), 132.53 (C), 132.03 (2 × CH), 130.51 (2 × CH), 129.91 (2 × CH), 128.63 (2 × CH), 128.71 (2 × CH), 128.81 (2 × CH), 68.22 (CH), 62.06 (CH_2), 47.26 (CH), 36.06 (CH_2), 31.26 (CH), 23.93 (CH), 21.81 (CH_3), 21.70 (CH_3), 14.09 (CH_3).

LRMS (ESI, M+Na$^+$): m/z 606.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{29}H_{29}NO_8NaS_2$ 606.1232, found 606.1241.

***(1S,3R,5S,6S)-Ethyl 4-oxo-2-tosyl-3-(4-(tosyloxy)benzyl)-2-azabicyclo[3.1.0]hexane-6-carboxylate* (1g'):**



Physical appearance: white solid.

m.p.: 140-142 °C.

$[\alpha]_D^{30}$: – 8.6 (c 1.00, $CHCl_3$).

IR (KBr): 3077, 2988, 2924, 1755, 1727, 1596, 1499, 1359, 1309, 1278, 1186, 1093, 1066, 1036, 982, 944, 861, 823, 797, 786, 736 cm^{-1}.

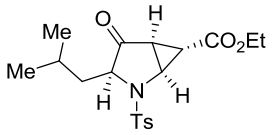
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.20-4.05 (m, 2H), 3.86 (d, *J* = 5.7 Hz, 1H), 3.48 (d, *J* = 5.0 Hz, 1H), 3.37 (ABX, *J* = 13.8, 5.0 Hz, 1H), 3.13 (ABX, *J* = 13.8, 0.0 Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H), 2.25 (dd, *J* = 5.3, 3.8 Hz, 1H), 1.30 (dd, *J* = 3.8, 2.0 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 202.72 (CO), 167.12 (CO), 148.84 (C), 145.56 (C), 145.37 (C), 133.97 (C), 132.32 (C), 132.23 (C), 132.12 (2 × CH), 130.45 (2 × CH), 129.85 (2 × CH), 128.62 (2 × CH), 128.43 (2 × CH), 122.21 (2 × CH), 63.04 (CH), 61.87 (CH_2), 44.95 (CH), 36.55 (CH_2), 31.82 (CH), 24.97 (CH), 21.82 (2 × CH_3), 14.28 (CH_3).

LRMS (ESI, M+H$^+$): m/z 584.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{29}H_{30}NO_8S_2$ 584.1413, found 584.1416.

***(1S,3S,5S,6S)-Ethyl 3-isobutyl-4-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-6-carboxylate* (1h):**



Physical appearance: white solid.

m.p.: 64-68 °C.

$[\alpha]_D^{24}$: – 6.2 (c 0.64, $CHCl_3$).

IR (neat): 2958, 1729, 1596, 1359, 1271, 1169, 1095, 1047, 813 cm^{-1}.

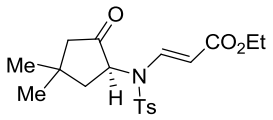
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.45 (dd, *J* = 5.2, 2.1 Hz, 1H), 4.17 (dq, *J* = 7.1, 3.1 Hz, 2H), 3.64 (dd, *J* = 6.6, 1.4 Hz, 1H), 2.44 (s, 3H), 2.38 (ddd, *J* = 5.1, 3.4, 1.5 Hz, 1H), 2.25 (dd, *J* = 3.3, 2.5 Hz, 1H), 1.93 (quint, *J* = 7.1 Hz, 1H), 1.60 (ABX, *J* = 13.8, 7.5 Hz, 1H), 1.45 (ABX, *J* = 7.5, 6.8 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 204.96 (CO), 168.02 (CO), 144.89 (C), 133.89 (C), 130.42 (2 x CH), 127.68 (2 x CH), 63.85 (CH), 62.15 (CH_2), 47.80 (CH), 44.20 (CH_2), 31.57 (CH), 26.71 (CH), 24.74 (CH), 22.66 (CH_3), 22.06 (CH_3), 21.73 (CH_3), 14.25 (CH_3).

LRMS (ESI, M+H$^+$): m/z 380.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{19}H_{26}NO_5S$ 380.1532, found 380.1520.

***(S,E)-Ethyl3-(N-(4,4-dimethyl-2-oxocyclopentyl)-4-methylphenylsulfonamido) acrylate* (4):**



Physical appearance: colourless liquid.

$[\alpha]_D^{24}$: 23.4 (c 1.09, $CHCl_3$).

IR (neat): 2928, 1758, 1709, 1626, 1462, 1364, 1255, 1166, 1090, 1054, 963, 819, 754, 703 cm^{-1}.

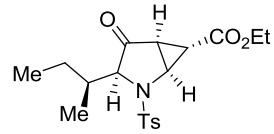
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 14.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.80 (d, *J* = 14.2 Hz, 1H), 4.58 (dd, *J* = 12.2, 8.9 Hz, 1H), 2.44 (s, 3H), 2.35-2.10 (m, 3H), 2.06 (ABX, *J* = 21.2, 8.9 Hz, 1H), 1.25 (d, *J* = 7.2 Hz, 6H), 1.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 210.54 (CO), 166.64 (CO), 145.25 (C), 140.05 (CH), 135.40 (C), 130.16 (2 × CH), 127.87 (2 × CH), 99.67 (CH), 62.84 (CH), 60.42 (CH_2), 50.90 (CH_2), 39.39 (CH_2), 32.65 (C), 30.17 (CH_3), 28.36 (CH_3), 21.81 (CH_3), 14.48 (CH_3).

LRMS (ESI, M+H^+): m/z 380.

HRMS (ESI, M+H^+): m/z calcd. for $C_{19}H_{26}NO_5S$ 380.1532, found 380.1538.

***(1S,3R,5S,6S)-Ethyl 3-sec-butyl-4-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-6-carboxylate* (1i):**



Physical appearance: low melting solid.

IR (KBr): 2967, 1728, 1625, 1597, 1578, 1524, 1462, 1361, 1290, 1269, 1166, 1092, 1044, 1017, 926, 815, 707 cm^{-1}.

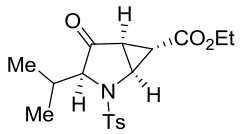
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.33 (dd, *J* = 5.6, 2.0 Hz, 1H), 4.15-4.10 (m, 2H), 3.52 (dd, *J* = 5.6, 1.5 Hz, 1H), 2.39 (s, 3H), 2.31 (dd, *J* = 5.4, 3.2 Hz, 1H), 2.28 (dt, *J* = 3.2, 1.6 Hz, 1H), 1.90-1.80 (m, 1H), 1.64 (ABX, *J* = 13.6, 6.4 Hz, 1H), 1.35 (ABX, *J* = 14.0, 8.0 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.80 (d, *J* = 3.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 204.14 (CO), 168.02 (CO), 144.81 (C), 133.35 (C), 130.29 (2 × CH), 127.70 (2 × CH), 70.14 (CH), 62.00 (CH_2), 47.44 (CH), 38.53 (CH), 32.11 (CH), 26.14 (CH_2), 25.40 (CH), 21.63 (CH_3), 15.45 (CH_3), 14.14 (CH_3), 11.93 (CH_3).

LRMS (ESI, M+H^+): m/z 380.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{19}H_{26}NO_5S$ 380.1532, found 380.1526.

***(1S,3S,5S,6S)-Ethyl 3-isopropyl-4-oxo-2-tosyl-2-azabicyclo[3.1.0]hexane-6-carboxylate* (1j):**



Physical appearance: white solid.

m.p.: 72-74 °C.

[α]$_D^{29}$: –26.5 (c 1.00, $CHCl_3$).

IR (KBr): 2973, 2931, 2878, 1753, 1718, 1627, 1596, 1462, 1406, 1388, 1350, 1294, 1269, 1182, 1161, 1125, 1091, 1062, 1020, 1007, 961, 919, 855, 810, 750, 709, 666, 628 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 4.39 (dd, *J* = 5.5, 2.1 Hz, 1H), 4.17 (dq, *J* = 7.1, 2.4 Hz, 2H), 3.35 (dd, *J* = 6.5, 1.5 Hz, 1H), 2.45 (s, 3H), 2.37 (dd, *J* = 3.0, 2.3 Hz, 1H), 2.35-2.30 (m, 1H), 2.00-2.10 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 6.6 Hz, 3H).

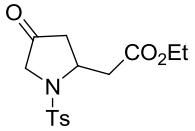
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 204.26 (CO), 168.12 (CO), 144.95 (C), 133.44 (C), 130.42 (2 x CH), 127.82 (2 x CH), 71.36 (CH), 62.14 (CH_2), 47.66 (CH), 32.40 (CH), 31.88 (CH), 25.67 (CH), 21.76 (CH_3), 20.08 (CH_3), 18.66 (CH_3), 14.25 (CH_3).

HRMS (ESI, M+H$^+$): m/z 366.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{18}H_{24}NO_5S$ 366.1375, found 366.1371.

***(S*)-Ethyl 2-(4-oxo-1-tosylpyrrolidin-2-yl)acetate* (5a):**

To a magnetically stirred solution of the cyclopropapyrrolidinone **1a** (38 mg, 0.12 mmol) and AIBN (6 mg, 0.036 mmol) in dry benzene (5 mL) was added n-Bu_3SnH (97 μL, 0.36 mmol) and the resulting mixture was refluxed for 2h. Reaction mixture was then cooled, diluted with ethyl acetate (15 mL) and washed with aq. ammonia (2 × 5 mL) and brine and the organic layer was dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexanes (1:9) as eluent gave the pyrrolidone **5a** (36 mg, 92%) as a white solid.



Physical appearance: white solid.

m.p.: 58-60 °C.

IR (neat): 2985, 2926, 1754, 1725, 1598, 1492, 1455, 1427, 1377, 1398, 1350, 1336, 1304, 1261, 1240, 1187, 1155, 1127, 1089, 1064, 1021, 1100, 960, 893, 874, 833, 812, 771, 706 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 4.50-4.40 (m, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.79 (d, *J* = 18.0 Hz, 1H), 3.66 (d, *J* = 18.0 Hz, 1H), 2.85 (dd, *J* = 7.1, 4.0 Hz, 1H), 2.55-2.30 (m, 5H), 1.23 (t, *J* = 7.0 Hz, 3H).

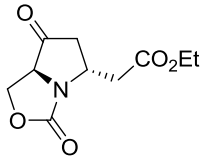
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 208.16 (CO), 170.72 (CO), 144.53 (C), 134.56 (C), 130.28 (2 x CH), 127.50 (2 x CH), 61.10 (CH_2), 53.87 (CH_2), 53.73 (CH), 42.67 (CH_2), 40.49 (CH_2), 21.68 (CH_3), 14.23 (CH_3).

LRMS (ESI, M+H$^+$): m/z 326.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{15}H_{20}NO_5S$ 326.1062, found 326.1071.

***Ethyl 2-((5R,7aS)-3,7-dioxohexahydropyrrolo[1,2-c]oxazol-5-yl)acetate* (5c):**

Reaction of the cyclopropapyrrolidinone **1c** (72 mg, 0.32 mmol) with n-Bu_3SnH (86 μL, 0.70 mmol) and AIBN (15 mg, 0.09 mmol) in dry benzene (5 mL) as described for the ketone **5a** followed by purification of the residue on a silica gel column using ethyl acetate-hexanes (1:2) as eluent furnished the pyrrolidone **5c** (69 mg, 95%) as a colourless liquid.



Physical appearance: colourless liquid.

$[\alpha]_D^{27}$: 46.1 (c 1.40, $CHCl_3$).

IR (neat): 2983, 2924, 1745, 1724, 1477, 1381, 1349, 1289, 1196, 1025, 976, 850, 773 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.75-4.65 (m, 1H), 4.52 (ABX, *J* = 9.5, 0.0 Hz, 1H), 4.36 (ABX, *J* = 9.2, 4.1 Hz, 1H), 4.19 (ABX, *J* = 9.8, 4.2 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 2.80 (ABX, *J* = 15.2, 6.3 Hz, 1H), 2.76 (ABX, *J* = 15.2, 6.3 Hz, 1H), 2.73 (ABX, *J* = 14.6, 5.5 Hz, 1H), 2.56 (ABX, *J* = 16.5, 2.9 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H).

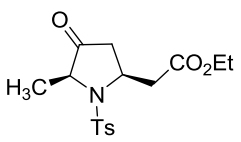
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 211.74 (CO), 170.60 (CO), 161.51 (CO), 65.15 (CH_2), 61.28 (CH_2), 60.62 (CH), 53.17 (CH), 41.74 (CH_2), 39.70 (CH_2), 14.26 (CH_3).

LRMS (ESI, M+Na$^+$): m/z 250.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{10}H_{13}NO_5Na$ 250.0691, found 250.0699.

***Ethyl 2-((2S,5S)-5-methyl-4-oxo-1-tosylpyrrolidin-2-yl)acetate* (5e):**

Reaction of the cyclopropapyrrolidinone **1e** (40 mg 0.12 mmol) with n-Bu_3SnH (70 μL, 0.26 mmol) and AIBN (9 mg, 0.06 mmol) in dry benzene (5 mL) as described for the ketone **5a** followed by purification of the residue on a silica gel column using ethyl



acetate-hexanes (1:9) as eluent furnished the pyrrolidone **5e** (37 mg, 90%) as a colourless liquid.

Physical appearance: colourless liquid.

$[\alpha]_D^{24}$: 59.1 (c 1.00, $CHCl_3$).

IR (neat): 2983, 2934, 1757, 1729, 1599, 1451, 1406, 1378, 1343, 1262, 1200, 1164, 1094, 1028, 982, 894, 848, 810, 709 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.45-4.35 (m, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.65 (q, *J* = 7.0 Hz, 1H), 2.96 (ABX, *J* = 16.7, 3.7 Hz, 1H), 2.69 (ABX, *J* = 16.7, 8.6 Hz, 1H), 2.45 (ABX, *J* = 18.3, 9.8 Hz, 1H), 2.43 (s, 3H), 2.35 (ABX, *J* = 18.3, 3.3 Hz, 1H), 1.46 (d, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

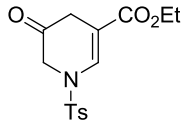
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 210.78 (CO), 170.59 (CO), 144.56 (C), 134.05 (C), 130.28 (2 × CH), 127.62 (2 × CH), 61.05 (CH_2), 60.22 (CH), 52.72 (CH), 42.25 (CH_2), 41.69 (CH_2), 21.69 (CH_3), 19.43 (CH_3), 14.27 (CH_3).

LRMS (ESI, M+H^+): m/z 340.

HRMS (ESI, M+H^+): m/z calcd. for $C_{16}H_{22}NO_5S$ 340.1219, found 340.1220.

***Ethyl 5-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-3-carboxylate* (6a):**

To a magnetically stirred solution of cyclopropapyrrolidinone **1a** (36 mg, 0.11 mmol) and 2,6-lutidine (28 μL, 0.24 mmol) in CH_2Cl_2 (2 mL) at −78 ^oC was added TMSOTf (43 μL, 0.24 mmol) and the resulting mixture was stirred for 50 min. The reaction mixture was quenched with saturated aq. $NaHCO_3$ (3 mL) and extracted with CH_2Cl_2 (3 × 10 mL), combined organic layer was washed with brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexanes (1:9) as eluent gave the dihydropiperidone **6a** (27 mg, 76%) as a colourless liquid.



Physical appearance: colourless liquid.

IR (neat): 3026, 2984, 2930, 1730, 1703, 1642, 1532, 1441, 1379, 1301, 1247, 1219, 1172, 1100, 1025, 930, 858, 807, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (t, *J* = 1.5 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.87 (br s, 2H), 3.12 (br s, 2H), 2.45 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

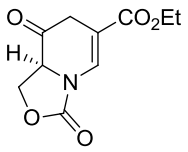
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 199.80 (CO), 165.84 (CO), 145.67 (C), 134.74 (CH), 133.38 (C), 130.54 (2 × CH), 127.56 (2 × CH), 105.12 (C), 61.02 (CH_2), 51.94 (CH_2), 35.66 (CH_2), 21.79 (CH_3), 14.47 (CH_3).

LRMS (ESI, M+H$^+$): m/z 324.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{15}H_{18}NO_5S$ 324.0906, found 324.0904.

(S)-Ethyl 3,8-dioxo-3,7,8,8a-tetrahydro-1H-oxazolo[3,4-a]pyridine-6-carboxylate **(6c):**

Reaction of the cyclopropapyrrolidinone **1e** (60 mg, 0.26 mmol) in dry CH_2Cl_2 (2.5 mL) with 2,6-lutidine (66 μL, 0.57 mmol) and TMSOTf (110 μL, 0.59 mmol) as described for **6a** followed by purification of the residue on a silica gel column using ethyl acetate-hexanes (1:2) as eluent gave the dihydropiperidinone **6c** (49 mg, 82%) as a yellow liquid.



Physical appearance: yellow liquid.

[α]$_D^{24}$: –20.02 (c 3.10, $CHCl_3$).

IR (neat): 2984, 1723, 1704, 1641, 1416, 1391, 1372, 1205, 1093, 1022, 899, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 4.65 (ABX, *J* = 18.5, 1.3 Hz, 2H), 4.58 (ABX, *J* = 18.5, 1.3 Hz, 2H), 4.41 (t, *J* = 2.1 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.47 (AB, *J* = 21.3 Hz, 1H), 3.21 (AB, *J* = 21.3 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H).

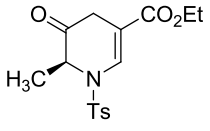
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 197.90 (CO), 165.18 (CO), 152.94 (CO), 131.14 (CH), 109.34 (C), 63.79 (CH_2), 61.22 (CH_2), 58.09 (CH), 37.53 (CH_2), 14.36 (CH_3).

LRMS (ESI, M+H$^+$): m/z 226.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{10}H1_2NO_5$ 226.0715, found 226.0722.

(S)-Ethyl 6-methyl-5-oxo-1-tosyl-1,4,5,6-tetrahydropyridine-3-carboxylate **(6e):**

Reaction of the cyclopropapyrrolidinone **1e** (50 mg, 0.15 mmol) in dry CH_2Cl_2 (2 mL) with 2,6-lutidine (38 μL, 0.33 mmol) and TMSOTf (63 μL, 0.35 mmol) at –78 ^{o}C as described for **6a** followed by purification of the residue on a silica gel column using ethyl acetate-hexanes (1:9) as eluent gave the dihydropiperidone **6e** (40 mg, 80%) as a colourless liquid.



Physical appearance: colourless liquid.

[α]$_D^{29}$: 32.7 (c 1.00, $CHCl_3$).

IR (neat): 3026, 2981, 2926, 1727, 1700, 1635, 1522, 1451, 1369, 1291, 1216, 1168, 1110, 1086, 1045, 1008, 926, 896, 766 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (br s, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 4.30-4.15 (m, 3H), 3.28 (ABXY, *J* = 22.5, 1.3, 0.0 Hz, 2H), 2.89 (ABXY, *J* = 22.5, 3.4, 1.7 Hz, 1H), 2.42 (s, 3H), 1.38 (d, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

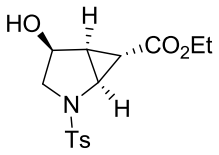
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 202.34 (CO), 165.63 (CO), 145.30 (C), 135.37 (C), 133.66 (CH), 130.48 (2 × CH), 127.08 (2 × CH), 105.77 (C), 61.06 (CH_2), 59.25 (CH), 34.01 (CH_2), 21.78 (CH_3), 18.55 (CH_3), 14.47 (CH_3).

LRMS (ESI, M+H^+): m/z 338.

HRMS (ESI, M+H^+): m/z calcd. for $C_{16}H_{20}NO_5S$ 338.1062, found 338.1057.

***(1R*,4R*,5R*,6R*)-ethyl 4-hydroxy-2-tosyl-2-azabicyclo[3.1.0]hexane-6-carboxylate* (7):**

To a cold (–78 °C), magnetically stirred solution of the cyclopropapyrrolidinone **1a** (39 mg, 0.24 mmol) in THF (2 mL) was added LAH (10 mg, 0.24 mmol) in one portion. The reaction mixture was stirred at the same temperature for 30 min., quenched carefully with a saturated aq. Na_2SO_4 and then stirred for additional 30 min. The solids were filtered and the filtrate was dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexanes (1:4) as eluent gave the alcohol **7** (29 mg, 75%) (dr = *ca.* 19:1) as a white solid.



Physical appearance: white solid.

m.p.: 146-148 °C.

IR (KBr): 3470, 3060, 2987, 2941, 2885, 1690, 1596, 1462, 1410, 1346, 1290, 1168, 1094, 1056, 1020, 979, 926, 846, 817, 715 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 4.80-4.70 (m, 1H), 4.20-4.00 (m, 2H), 3.77 (d, *J* = 6.5 Hz, 1H), 3.69 (ABX, *J* = 10.3, 8.3 Hz, 1H), 2.47 (s, 3H), 2.35 (dd, *J* = 9.5, 4.1 Hz, 1H), 2.19 (ABX, *J* = 10.3, 7.9 Hz, 1H), 1.42 (dd, *J* = 4.1, 1.5 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H).

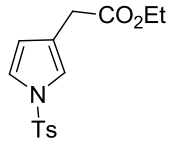
^{13}C NMR (100 MHz, CDCl3, DEPT): δ 170.01 (CO), 144.59 (C), 131.51 (C), 130.00 (2 × CH), 128.51 (2 × CH), 69.43 (CH), 61.02 (CH_2), 50.35 (CH_2), 45.31 (CH), 29.28 (CH), 21.79 (CH), 19.13 (CH_3), 14.37 (CH_3).

LRMS (ESI, M+H^+): m/z 326.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{15}H_{20}NO_5S$ 326.1062, found 326.1061.

***Ethyl 2-(1-tosyl-1H-pyrrol-3-yl)acetate* (8):**

To a cold (−10 °C), magnetically stirred solution of the alcohol **7** (29 mg, 0.09 mmol) in EtOH (3 mL) was added conc. H_2SO_4 (400 μL) and the reaction mixture was stirred for 24h (TLC control). Solvent was removed under reduced pressure and residue was diluted with ethyl acetate and cooled to (0 °C). It was then neutralized with saturated aq. $NaHCO_3$ and extracted with ethyl acetate (3 × 5 mL), the combined organic layer was washed with brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexanes (1:9) as eluent gave the pyrrole derivative **8** (18 mg, 64%) as a colourless liquid.



Physical appearance: colourless liquid.

IR (neat): 3022, 2979, 2931, 2861, 1725, 1599, 1469, 1448, 1371, 1217, 1172, 1097, 1062, 1028, 930, 866, 810, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.10-7.05 (m, 2H), 6.25 (dd, *J* = 3.1, 1.6 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.40 (s, 2H), 2.40 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

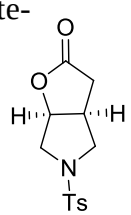
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 171.23 (CO), 145.09 (C), 136.27 (C), 130.12 (2 × CH), 127.04 (2 × CH), 121.27 (C), 121.09 (CH), 119.04 (CH), 114.90 (CH), 61.00 (CH_2), 32.89 (CH_2), 21.74 (CH_3), 14.28 (CH_3).

LRMS (ESI, M+H$^+$): m/z 308.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{15}H_{18}NO_4S$ 308.0957, found 308.0953.

***(3aS*,6aS*)-5-Tosylhexahydro-2H-furo[2,3-c]pyrrol-2-one* (9):**

To a magnetically stirred solution of the alcohol **7** (30 mg, 0.09 mmol) and triethylsilane (45 μL, 0.28 mmol) in dry CH_2Cl_2 (2 mL) at −10 ^{o}C was added TMSOTf (37 μL, 0.21 mmol) and the resulting mixture was stirred for 2h. The reaction mixture was quenched with saturated aq. $NaHCO_3$ (3 mL) and extracted with CH_2Cl_2 (3 × 5 mL), combined organic layer was washed with brine and dried over (anhydr. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexanes (2:3) as eluent furnished the lactone **9** (24 mg, 92%) as a white solid.



Physical appearance: white solid.

m.p.: 122-124 °C.

IR (KBr): 2977, 2927, 1774, 1627, 1599, 1459, 1427, 1339, 1298, 1238, 1157, 1101, 1024, 930, 846, 807, 709 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.96 (t, *J* = 6.2 Hz, 1H), 3.57 (d, *J* = 11.7 Hz, 1H), 3.25-3.10 (m, 3H), 3.10-3.00 (m, 1H), 2.80 (ABX, *J* = 18.4, 10.0 Hz, 1H), 2.45 (ABX, *J* = 18.4, 3.4 Hz, 1H), 2.44 (s, 3H).

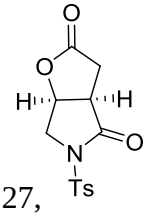
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 175.47 (CO), 144.58 (C), 131.64 (C), 130.05 (2 × CH), 128.09 (2 × CH), 81.87 (CH), 54.09 (CH_2), 53.73 (CH_2), 37.58 (CH), 34.04 (CH_2), 21.71 (CH_3).

LRMS (ESI, M+H^+): m/z 282.

HRMS (ESI, M+H^+): m/z calcd. for $C_{13}H_{16}NO_4S$ 282.0800, found 282.0797.

***(3aR*,6aS*)-5-Tosyltetrahydro-2H-furo[2,3-c]pyrrole-2,4(5H)-dione* (10):**

To a cold (−10 °C), magnetically stirred solution of the alcohol **7** (28 mg, 0.09 mmol) and *m*-CPBA (44 mg, 77% by wt., 0.26 mmol) in dry CH_2Cl_2 (2 mL) was added TMSOTf (34 μL, 0.19 mmol) and the resulting mixture was stirred for 1.5h. The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (3 mL), extracted with ethyl acetate (3 × 5 mL), combined organic layer was washed with saturated thio solution followed by brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexanes (2:3) as eluent gave the lactone **10** (19 mg, 74%) as a white solid.



Physical appearance: white solid.

m.p.: 162-164 °C.

IR (KBr): 2924, 2852, 1779, 1729, 1626, 1598, 1427, 1360, 1317, 1288, 1227, 1196, 1168, 1143, 1082, 1033, 1011, 944, 887, 816, 706 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 5.07 (dd, *J* = 6.3, 4.7 Hz, 1H), 4.25 (ABX, *J* = 12.5, 0.0 Hz, 1H), 4.17 (ABX, *J* = 12.5, 4.7 Hz, 1H), 3.39 (q, *J* = 6.3 Hz, 1H), 2.81 (d, *J* = 6.3 Hz, 2H), 2.45 (s, 3H).

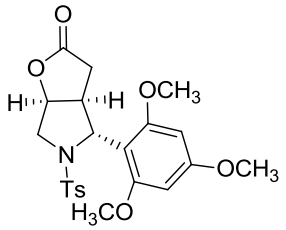
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 173.35 (CO), 170.99 (CO), 146.26 (C), 134.34 (C), 130.13 (2 × CH), 128.29 (2 × CH), 74.56 (CH), 51.81 (CH_2), 43.78 (CH), 30.83 (CH_2), 21.89 (CH_3).

LRMS (ESI, M+H^+): m/z 296.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{13}H_{14}NO_5S$ 296.0593, found 296.0602.

***(3aS*,4S*,6aS*)-5-Tosyl-4-(2,4,6-trimethoxyphenyl)hexahydro-2H-furo[2,3-c]pyrrol-2-one* (12):**

To a cold (−10 °C), magnetically stirred solution of the alcohol **7** (16 mg, 0.05 mmol) and 1,3,5-trimethoxybenzene **11** (25 mg, 0.15 mmol) in dry CH_2Cl_2 (2 mL) was added TMSOTf (22 μL, 0.12 mmol) and the resulting mixture was stirred for 1h. The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (3 mL), extracted with ethyl acetate (3 × 5 mL), combined organic layer was washed with saturated thio solution followed by brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexanes (1:2) as eluent gave the lactone **12** (20 mg, 91%) as a white solid.



Physical appearance: white solid.

m.p.: 192-194 °C.

IR (neat): 3056, 2926, 1781, 1596, 1464, 1423, 1341, 1266, 1205, 1158, 1122, 1018, 897, 815, 740, 706 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.06 (br s, 2H), 5.15 (d, *J* = 5.8 Hz, 1H), 4.94 (dd, *J* = 5.9, 4.2 Hz, 2H), 4.07 (ABX, *J* = 12.5, 0.0 Hz, 1H), 3.90 (ABX, *J* = 12.5, 4.2 Hz, 1H), 3.80 (s, 3H), 3.80-3.75 (br s, 6H), 3.19 (dddd, *J* = 5.9 Hz, 1H), 3.25-3.15 (m, 1H), 2.58 (ABX, *J* = 18.1, 8.6 Hz, 1H), 2.40 (s, 3H), 2.39 (ABX, *J* = 18.1, 1.9 Hz, 1H).

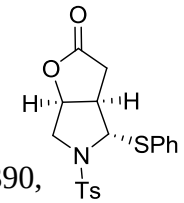
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 175.36 (CO), 161.36 (C), 158.82 (2 × C), 143.20 (C), 135.42 (C), 129.30 (2 × CH), 127.36 (2 × CH), 108.89 (C), 91.11 (2 × CH), 83.81 (CH), 59.92 (CH), 55.89 (2 × CH_3), 55.50 (CH), 54.92 (CH_2), 46.20 (CH), 35.18 (CH_2), 21.61 (CH_3).

LRMS (ESI, M+H$^+$): m/z 448.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{22}H_{26}NO_7S$ 448.1430, found 448.1421.

***(3aR*,4R*,6aS*)-4-(phenylthio)-5-Tosylhexahydro-2H-furo[2,3-c]pyrrol-2-one* (14):**

To a cold (−10 °C), magnetically stirred solution of the alcohol **7** (10 mg, 0.03 mmol) and thiophenol (**13**) (10 μL, 0.10 mmol) in dry CH_2Cl_2 (2 mL) was added TMSOTf (15 μL, 0.08 mmol) and the resulting mixture was stirred for 2h. The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (3 mL), extracted with ethyl acetate (3 × 5 mL), combined organic layer was washed with saturated thio solution followed by brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexanes (1:2) as eluent gave the lactone **14** (11 mg, 91%) as a white solid.



Physical appearance: white solid.

m.p.: 138-140 °C.

IR (neat): 2924, 2883, 2855, 1925, 1780, 1695, 1595, 1511, 1444, 1390, 1344, 1256, 1162, 1127, 1093, 1071, 1019, 858, 814, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.45-7.40 (m, 2H), 7.40-7.30 (m, 3H), 7.30-7.25 (m, 2H), 5.33 (s, 1H), 4.97 (dd, *J* = 7.1, 5.1 Hz, 1H), 3.84 (ABX, *J* = 12.8, 0.0 Hz, 1H), 3.61 (ABX, *J* = 12.8, 5.1 Hz, 1H), 3.25-3.15 (m, 1H), 2.74 (ABX, *J* = 18.7, 10.6 Hz, 1H), 2.42 (s, 3H), 2.38 (ABX, *J* = 13.6, 5.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 174.49 (CO), 144.55 (C), 135.77 (C), 134.91 (2 × CH), 131.41 (C), 129.99 (2 × CH), 129.54 (2 × CH), 129.21 (CH), 127.69 (2 × CH), 82.09 (CH), 73.90 (CH), 52.77 (CH_2), 46.96 (CH), 33.60 (CH_2), 21.72 (CH_3).

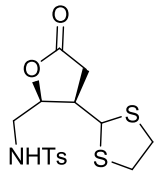
LRMS (ESI, M+H$^+$): m/z 390.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{19}H_{20}NO_4S_2$ 390.0834, found 390.0839.

***N*-(((2S*,3R*)-3-(1,3-dithiolan-2-yl)-5-Oxotetrahydrofuran-2-yl)methyl)-4-methylbenzenesulfonamide* (16):**

To a cold (−10 °C), magnetically stirred solution of the alcohol **7** (20 mg, 0.06 mmol) and 1,2-ethanedithiol (**15**) (16 μL, 0.15 mmol) in dry CH_2Cl_2 (2 mL) was added TMSOTf (28 μL, 0.15 mmol) and the resulting mixture was stirred for 2h. The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (3 mL), extracted with ethyl acetate (3 × 5 mL), combined organic layer was washed with saturated thio solution followed by brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on

a silica gel column using ethyl acetate-hexanes (2:3) as eluent gave the lactone **16** (16 mg, 70%) as a white solid.



Physical appearance: white solid.

m.p.: 136-138 °C.

IR (neat): 3270, 3058, 2924, 2856, 1778, 1597, 1526, 1423, 1331, 1269, 1160, 1122, 1091, 1038, 973, 938, 851, 814, 740, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.09 (dd, *J* = 7.9, 5.7 Hz, 1H), 4.66 (d, *J* = 8.5 Hz, 1H), 4.59 (dt, *J* = 11.1, 7.3, 3.7 Hz, 1H), 3.35 (ddd, *J* = 13.7, 7.9, 6.0 Hz, 1H), 3.30-3.25 (m, 5H), 2.97 (quint, *J* = 8.1 Hz, 1H), 2.67 (ABX, *J* = 17.7, 8.1 Hz, 1H), 2.60 (ABX, *J* = 17.7, 9.9 Hz, 1H), 2.43 (s, 3H).

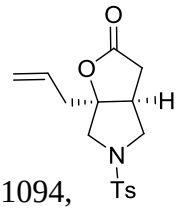
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 174.89 (CO), 144.12 (C), 136.43 (C), 130.10 (2 × CH), 127.26 (2 × CH), 79.92 (CH), 51.57 (CH), 45.52 (CH), 43.74 (CH_2), 39.32 (CH_2), 38.99 (CH_2), 33.63 (CH_2), 21.70 (CH_3).

LRMS (ESI, M+Na^+): m/z 396.

HRMS (ESI, M+ Na^+): m/z calcd. for $C_{15}H_{19}NO_4S_3Na$ 396.0374, found 396.0380.

(3aS*,6aS*)-6a-Allyl-5-tosylhexahydro-2H-furo[2,3-c]pyrrol-2-one **(17):**

To a magnetically stirred solution of the cyclopropapyrrolidinone **1a** (13 mg, 0.04 mmol) and triethylsilane (17 μL, 0.11 mmol) in CH_2Cl_2 (2 mL) at –10 °C was added TMSOTf (14 μL, 0.08 mmol) and the resulting mixture was stirred at the same temperature till starting material consumed (TLC control). Then further TMSOTf (14 μL, 0.08 mmol) and allyltributylstanane (20 μL, 0.11 mmol) were added and stirred at the same temperature. After complete consumption of alcohol, the reaction mixture was quenched with saturated aq. $NaHCO_3$ (3 mL) and extracted with CH_2Cl_2 (3 × 5 mL), combined organic layer was washed with brine and dried (anhyd. Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate-hexanes (1:7) as eluent furnished the lactone **17** (8.6 mg, 67%) as a white solid.



Physical appearance: white solid.

m.p.: 84-86 °C.

IR (neat): 3022, 2923, 2853, 1776, 1639, 1598, 1417, 1350, 1214, 1161, 1094, 1033, 1016, 957, 931, 814, 762 cm^{-1}.

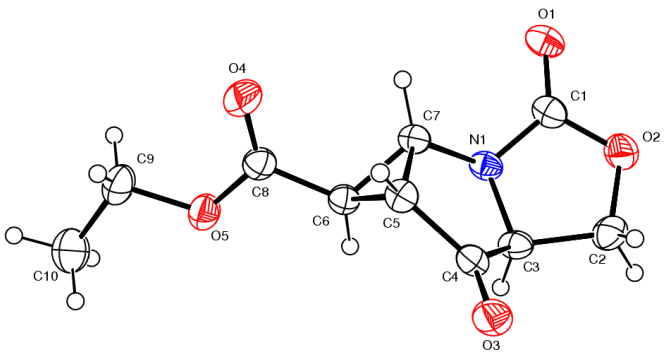
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 5.75-5.60 (m, 1H), 5.19 (d, *J* = 9.3 Hz, 1H), 5.17 (d, *J* = 17.0 Hz, 1H), 3.45 (AB, *J* = 11.2 Hz, 1H), 3.33 (ABX, *J* = 10.1, 7.5 Hz, 1H), 3.07 (AB, *J* = 11.2 Hz, 1H), 3.05 (ABX, *J* = 10.1, 4.0 Hz, 1H), 2.85-2.70 (m, 2H), 2.55-2.25 (m, 3H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 174.94 (CO), 144.60 (CO), 131.74 (C), 130.46 (C), 130.06 (2 × CH), 128.11 (2 × CH), 121.23 (CH_2), 92.99 (C), 57.67 (CH_2), 54.32 (CH_2), 41.73 (CH_2), 41.25 (CH), 34.93 (CH_2), 21.73 (CH_3).

LRMS (ESI, M+H$^+$): m/z 322.

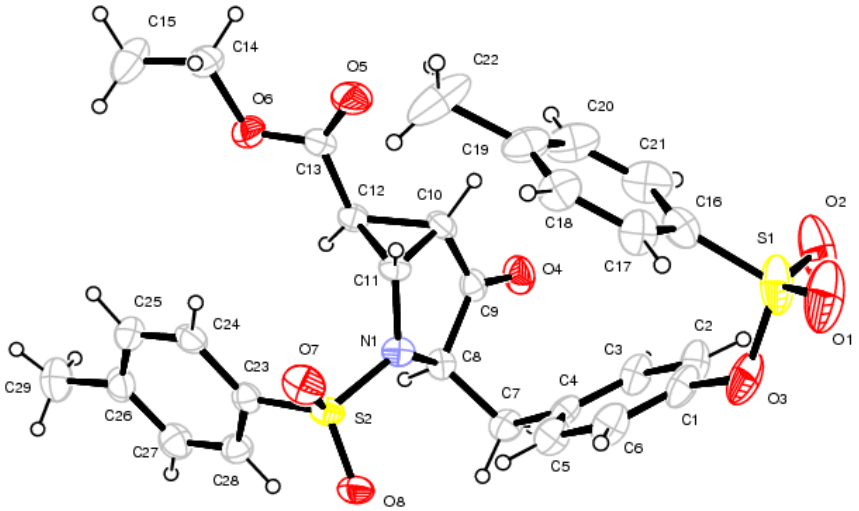
HRMS (ESI, M+H$^+$): m/z calcd. for $C_{16}H_{20}NO_4S$ 322.1113, found 322.1115.

Crystal structural refinement parameters for 1c

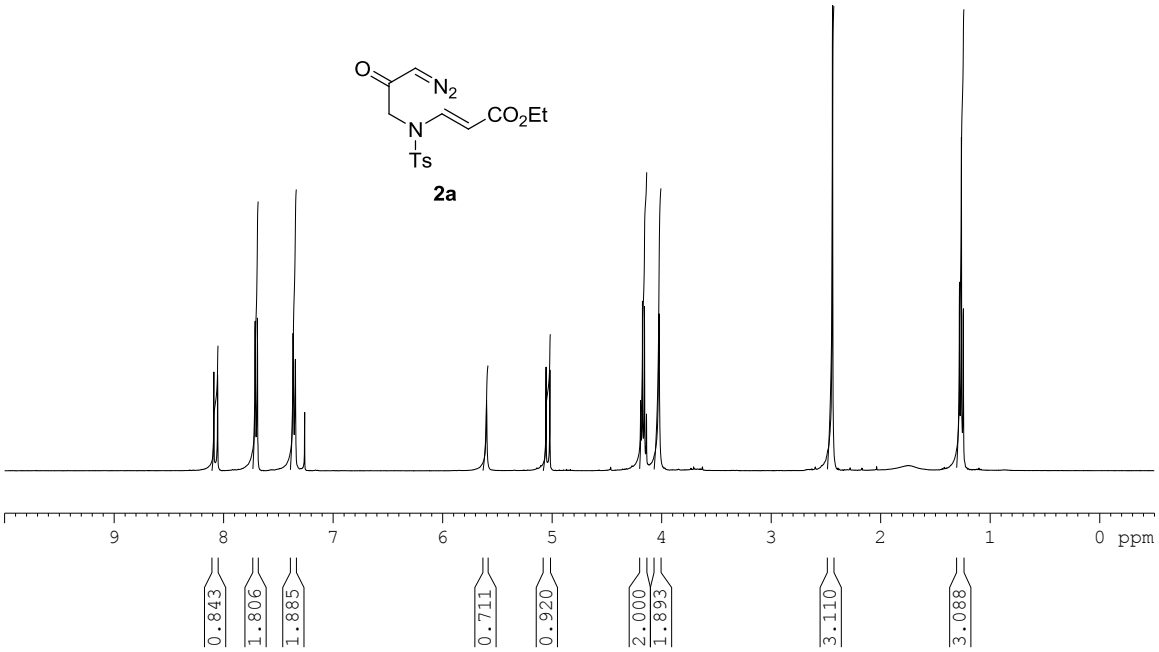


Identification code	**CCDC 826028**
Empirical formula	C10 H11 N O5
Formula weight	225.20
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P21212
Unit cell dimensions	a = 16.4826(6) A alpha = 90 deg. b = 6.8123(3) A beta = 90 deg. c = 9.0139(4) A gamma = 90 deg.
Volume	1012.12(7) A^3
Z, Calculated density	4, 1.478 Mg/m^3
Absorption coefficient	0.120 mm^-1
F(000)	472
Crystal size	0.35 x 0.32 x 0.30 mm
Theta range for data collection	2.26 to 28.29 deg.
Limiting indices	-21<=h<=18, -7<=k<=8, -12<=l<=12
Reflections collected / unique	7263 / 2478 [R(int) = 0.0169]
Completeness to theta = 25.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9712 and 0.9222
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2478 / 0 / 147
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0332, wR2 = 0.0847
R indices (all data)	R1 = 0.0390, wR2 = 0.0889
Absolute structure parameter	1.3(10)
Extinction coefficient	0.006(3)
Largest diff. peak and hole	0.210 and -0.177 e.A^-3

Crystal structural refinement parameters for 1g'



Identification code	**CCDC 826029**
Empirical formula	C29 H29 N O8 S2
Formula weight	583.65
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P1
Unit cell dimensions	a = 7.9762(6) A alpha = 83.948(3) deg. b = 8.4759(5) A beta = 80.632(3) deg. c = 11.3641(9) A gamma = 73.019(2) deg.
Volume	723.61(9) A^3
Z, Calculated density	1,1.339 Mg/m^3
Absorption coefficient	0.234 mm^-1
F(000)	306
Crystal size	0.32 x 0.20 x 0.19 mm
Theta range for data collection	3.01 to 25.23 deg.
Limiting indices	-9<=h<=9, -10<=k<=9, -13<=l<=13
Reflections collected / unique	7682 / 3873 [R(int) = 0.0240]
Completeness to theta = 25.00	96.5 %
Absorption correction	None
Max. and min. transmission	0.9568 and 0.9288
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3873 / 3 / 364
Goodness-of-fit on F^2	1.088
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1148
R indices (all data)	R1 = 0.0585, wR2 = 0.1249
Absolute structure parameter	0.07(9)
Largest diff. peak and hole	0.383 and -0.376 e.A^-3


O
N2
CO2Et
N
Ts
2a
9
8
7
6
5
4
3
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0 ppm
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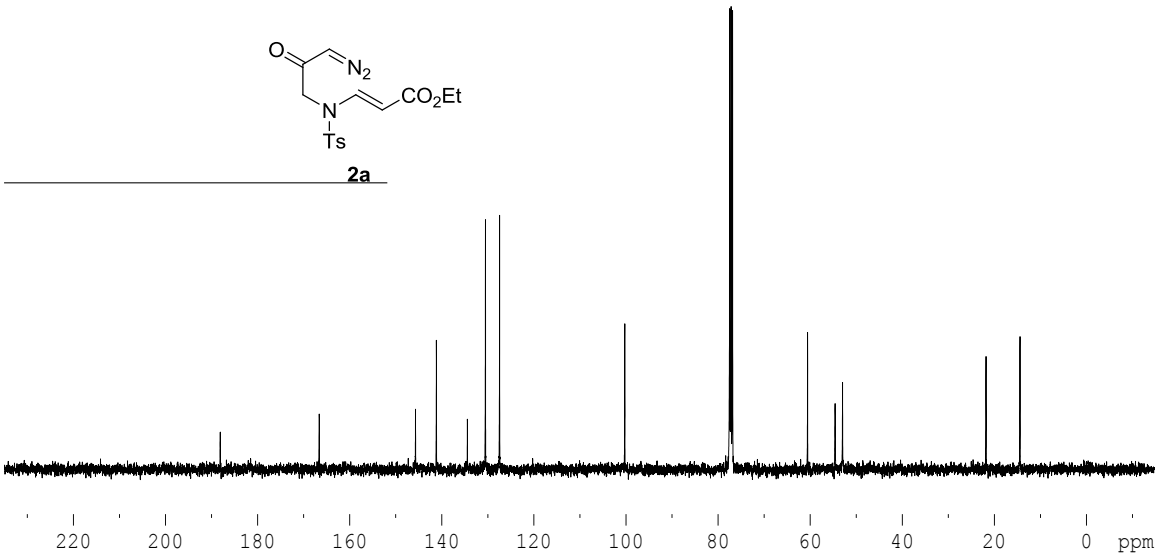
1.885
0.711
0.920
2.000
1.893
3.110
3.088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CO2Et
N
Ts
2a
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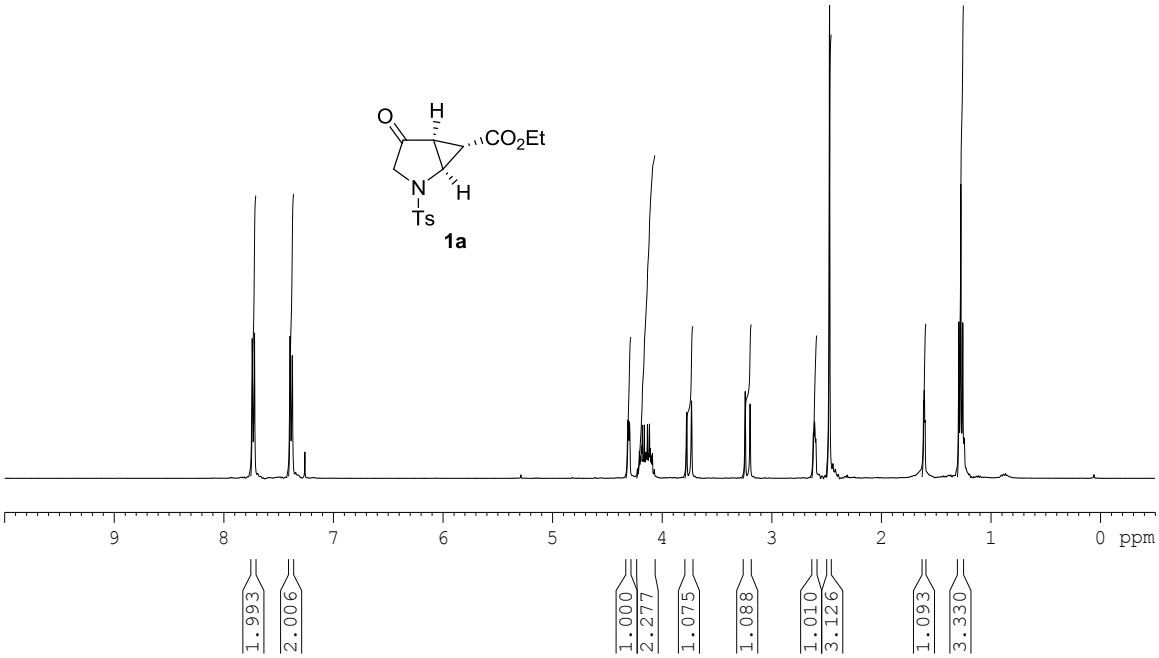
200
180
160
140
120
100
80
60
40
20
0 ppm


O
H
CO2Et
N
H
Ts
1a
9
8
7
6
5
4
3
2
1
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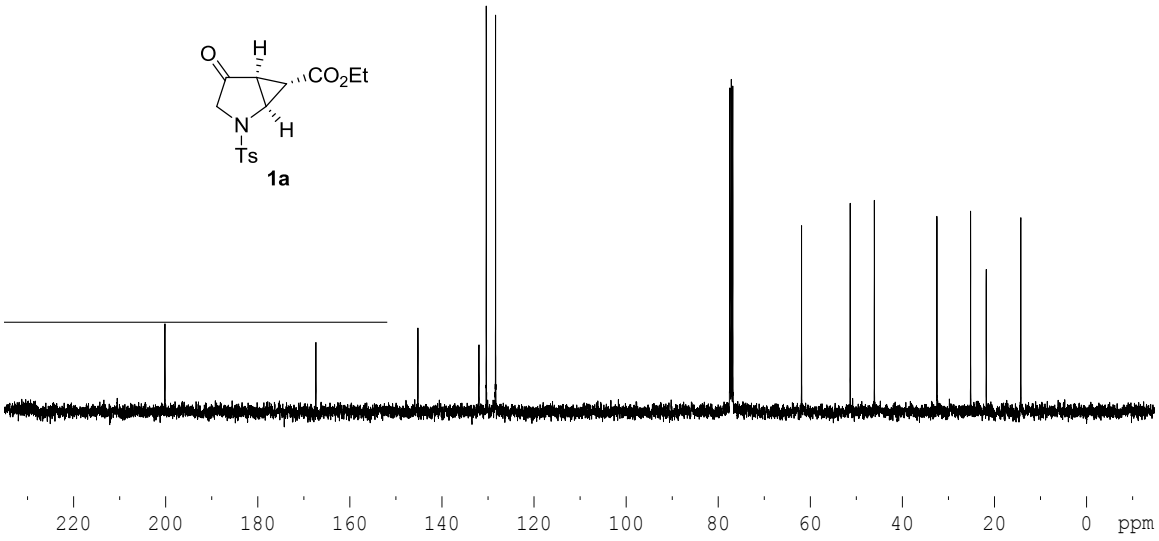
1.000
2.277
1.075
1.088
1.010
3.126
1.093
3.330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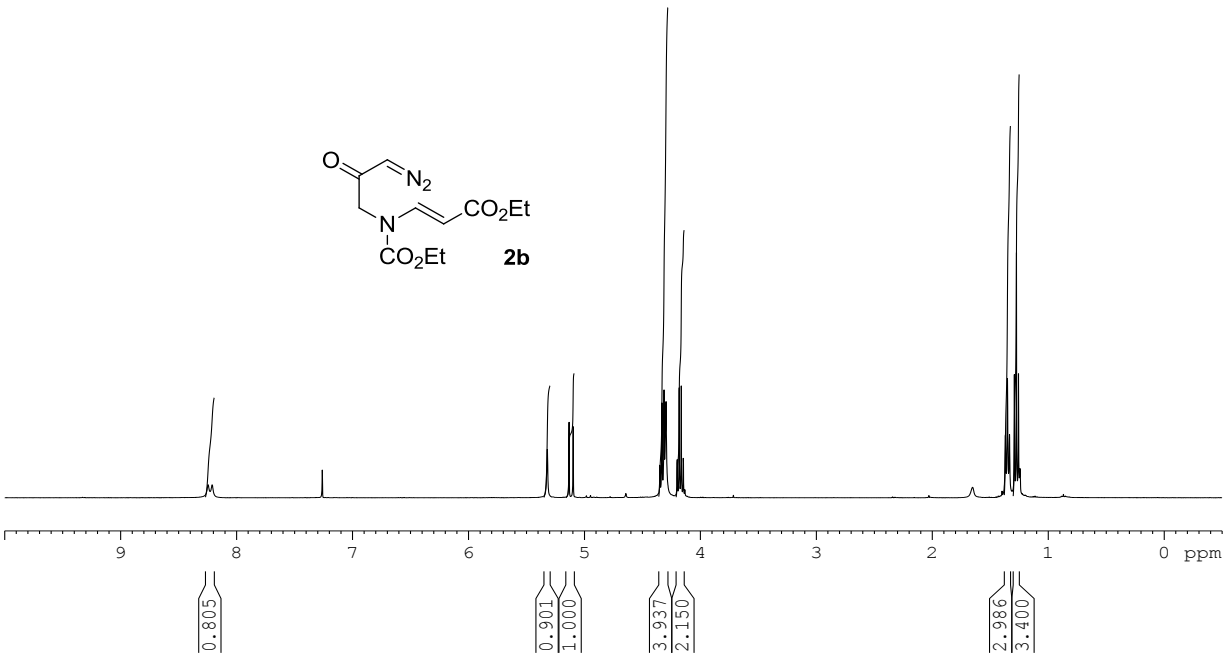
H
CO2Et
N
H
Ts
1a
220
200
180
160
140
120
100
80
60
40
20
0 ppm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N2
CO2Et
N
CO2Et
2b
9
8
7
6
5
4
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1
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1.000
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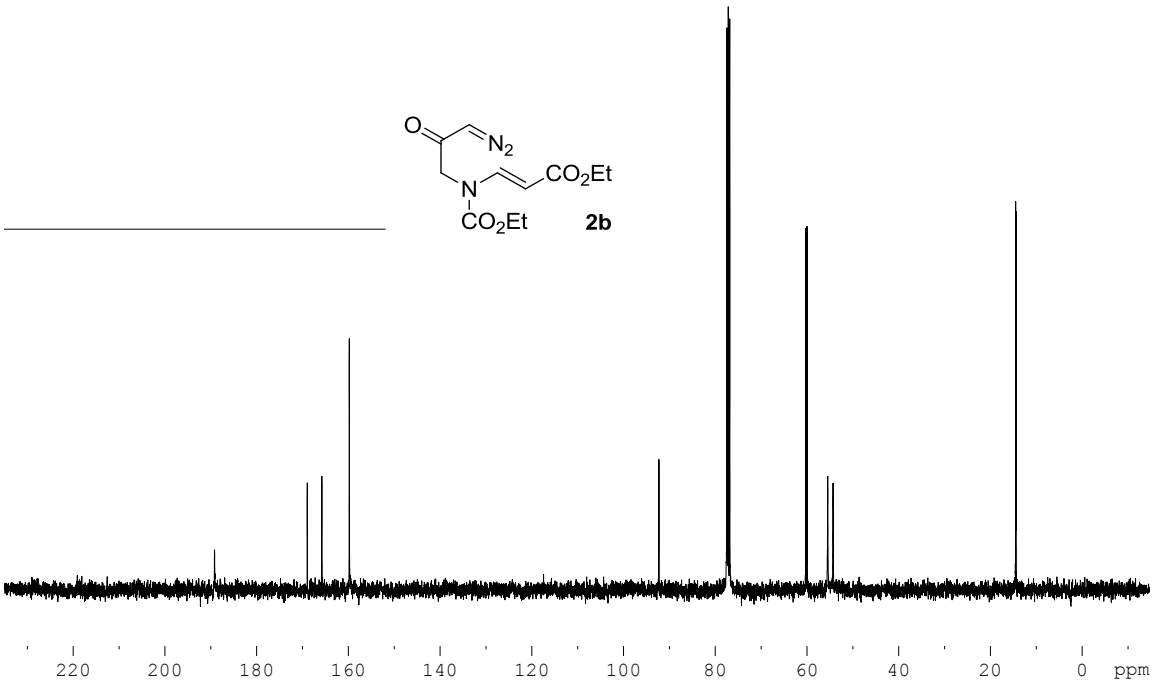
2.986
3.400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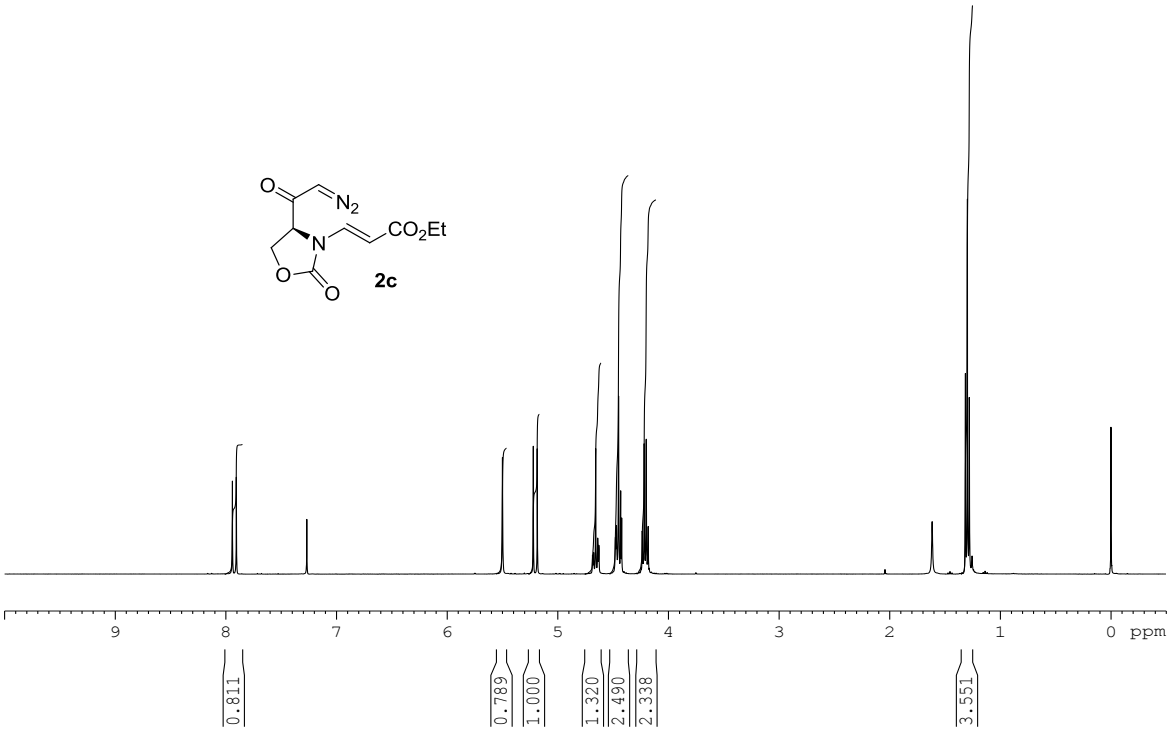
N2
CO2Et
N
CO2Et
2b
220
200
180
160
140
120
100
80
60
40
20
0 ppm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N2
CO2Et
N
O
O
2c
9
8
7
6
5
4
3
2
1
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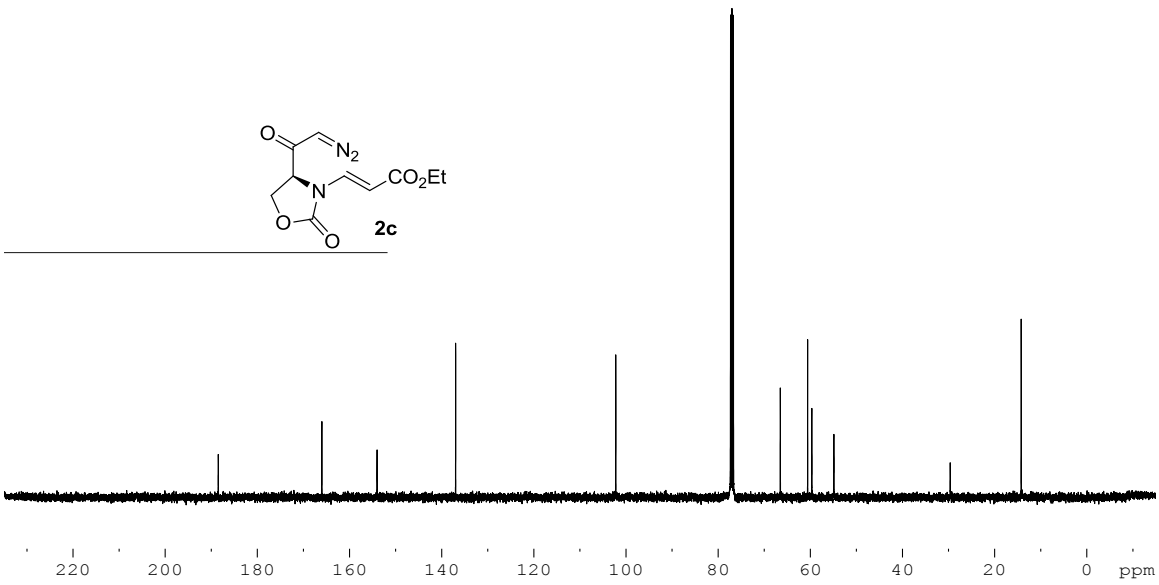
0.789
1.000
1.320
2.490
2.338
3.551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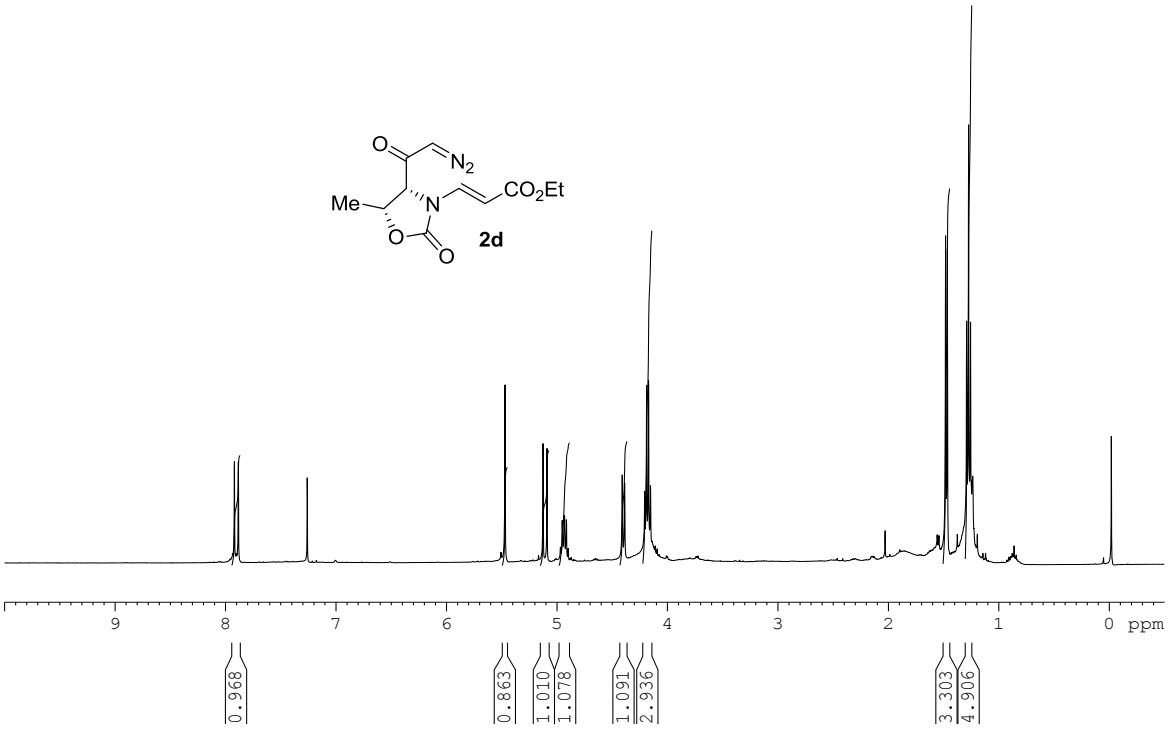
N2
CO2Et
N
O
O
2c
220
200
180
160
140
120
100
80
60
40
20
0 ppm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N2
Me
N
CO2Et
O
O
2d
9
8
7
6
5
4
3
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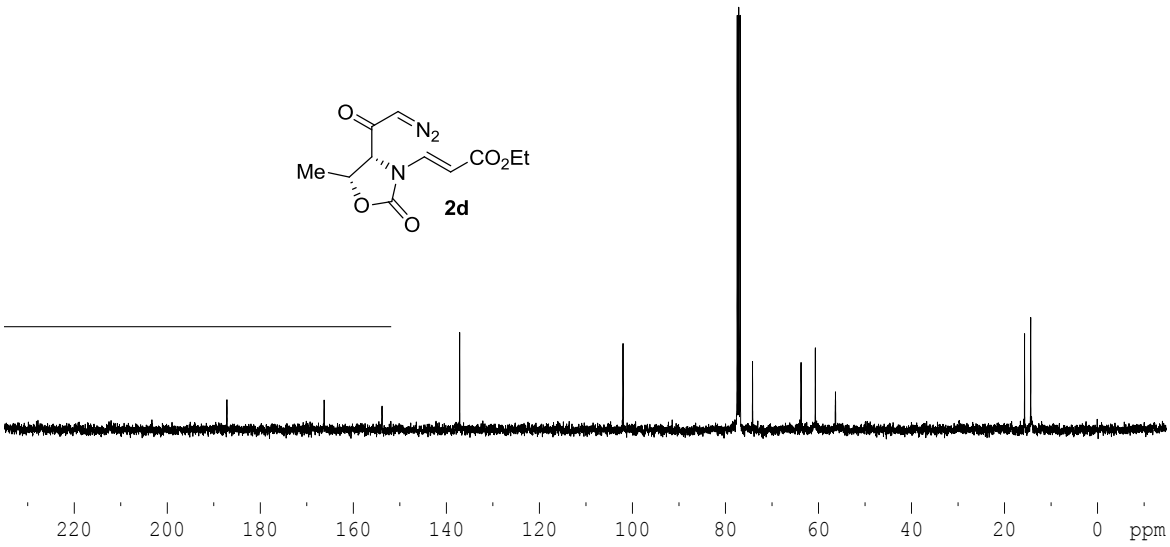
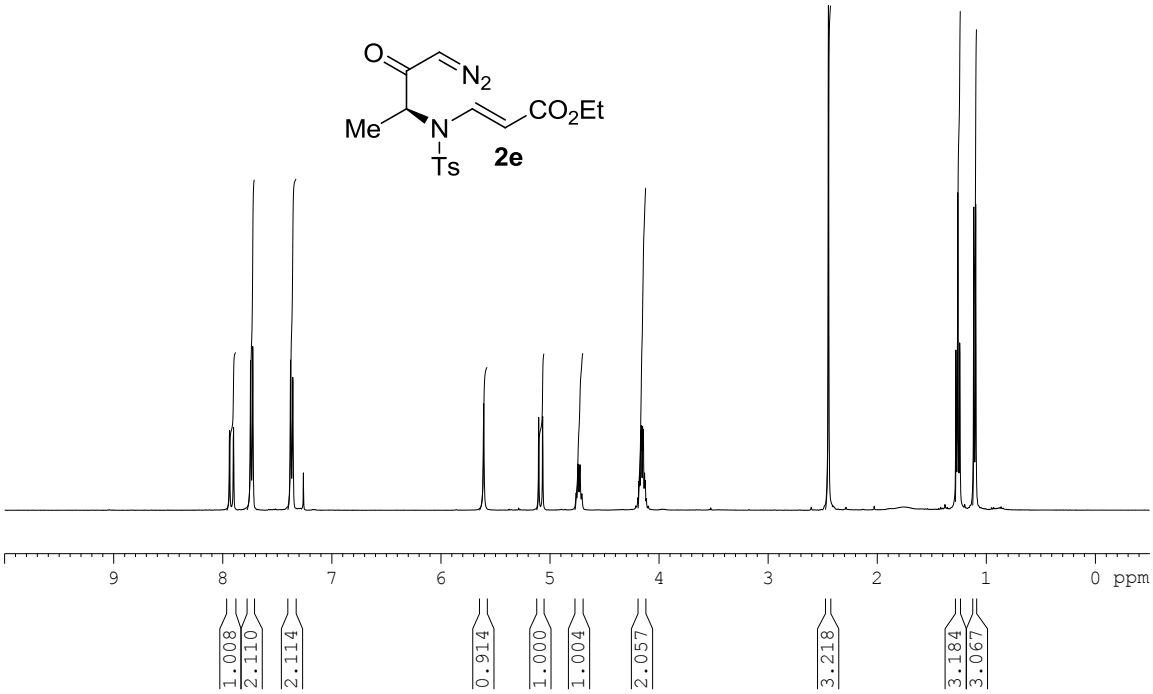
1.078
1.091
2.936
3.303
4.906


O
N2
Me
N
CO2Et
O
O
2d
220
200
180
160
140
120
100
80
60
40
20
0 ppm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N2
Me
N
CO2Et
Ts
2e
9
8
7
6
5
4
3
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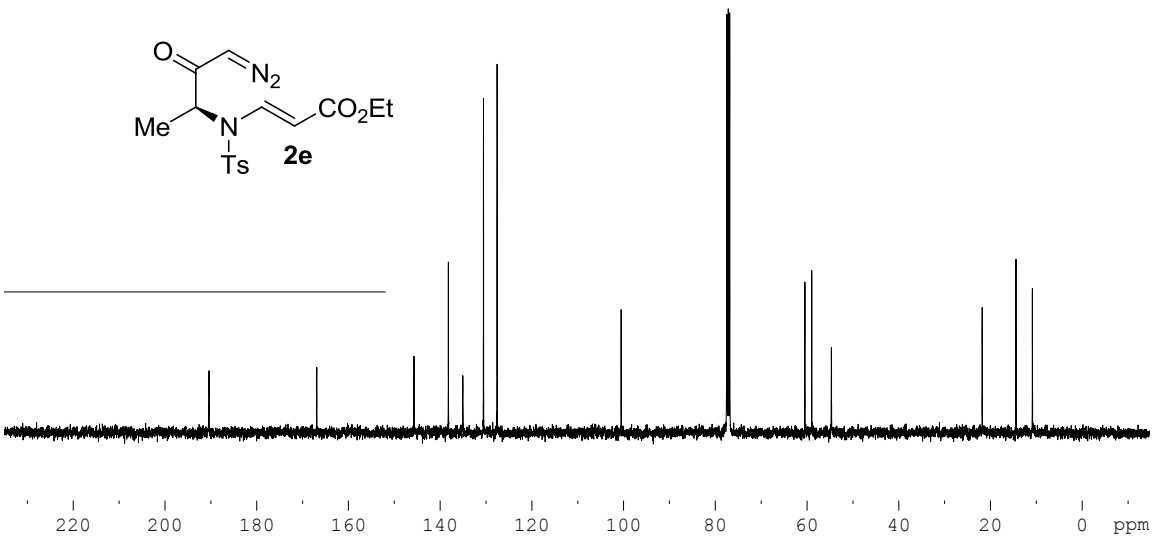
1.004
2.057
3.218
3.184
3.067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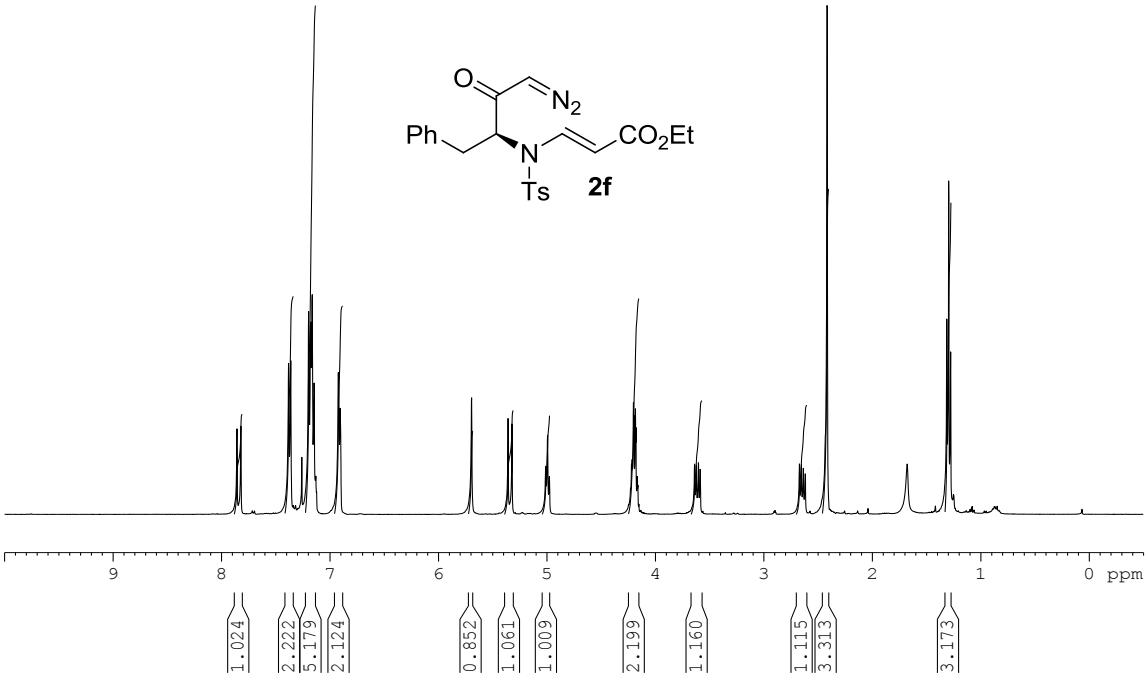
N2
Me
N
CO2Et
Ts
2e
220
200
180
160
140
120
100
80
60
40
20
0 ppm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N2
Ph
CO2Et
N
Ts
2f
9
8
7
6
5
4
3
2
1
0 ppm
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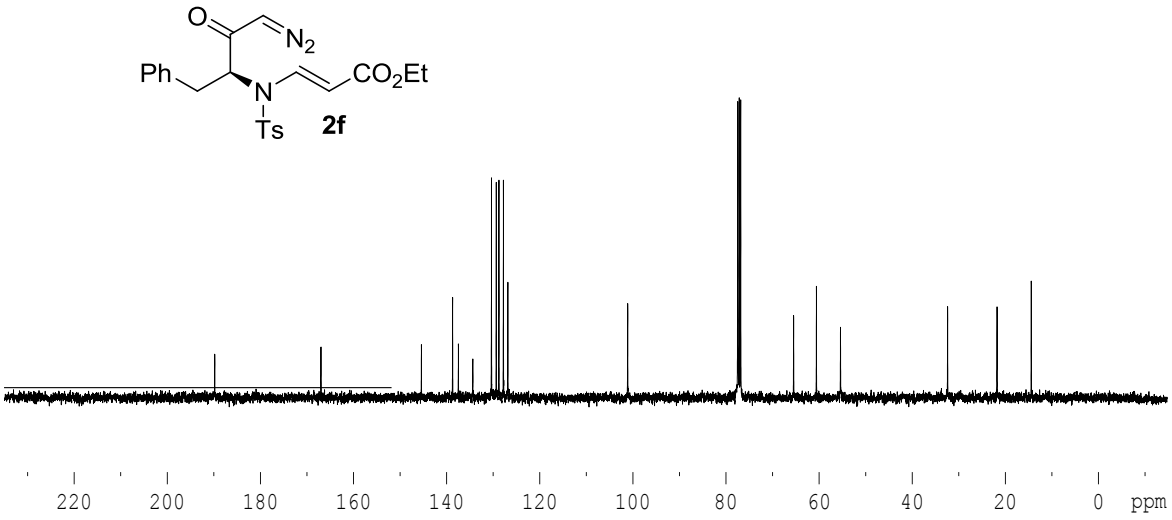
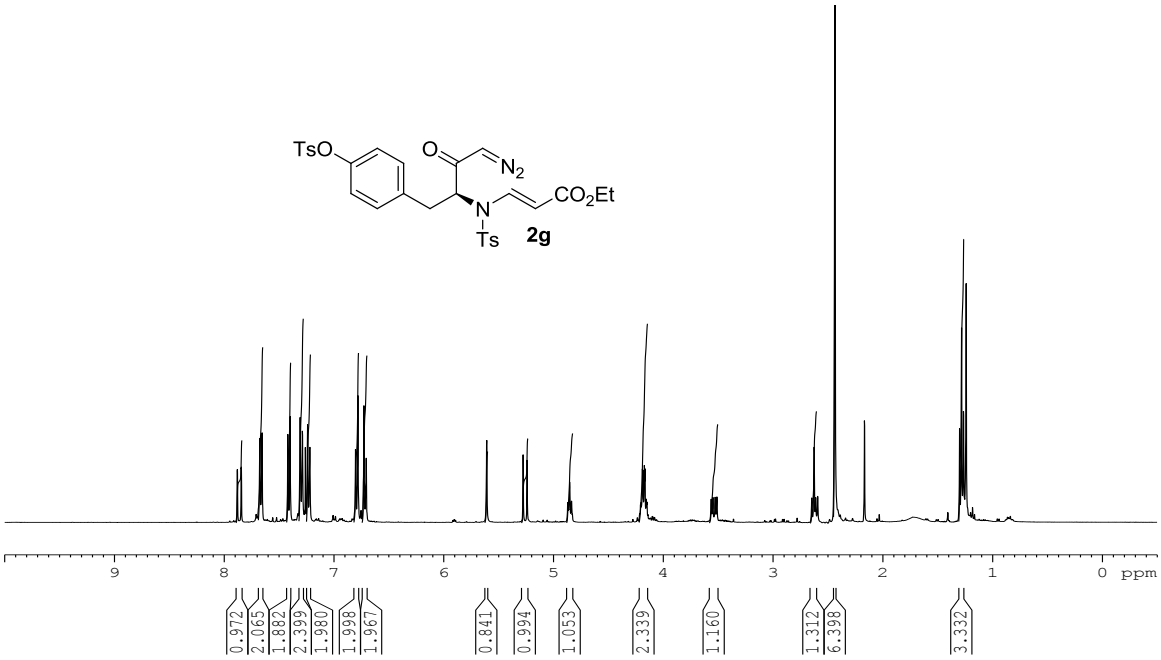
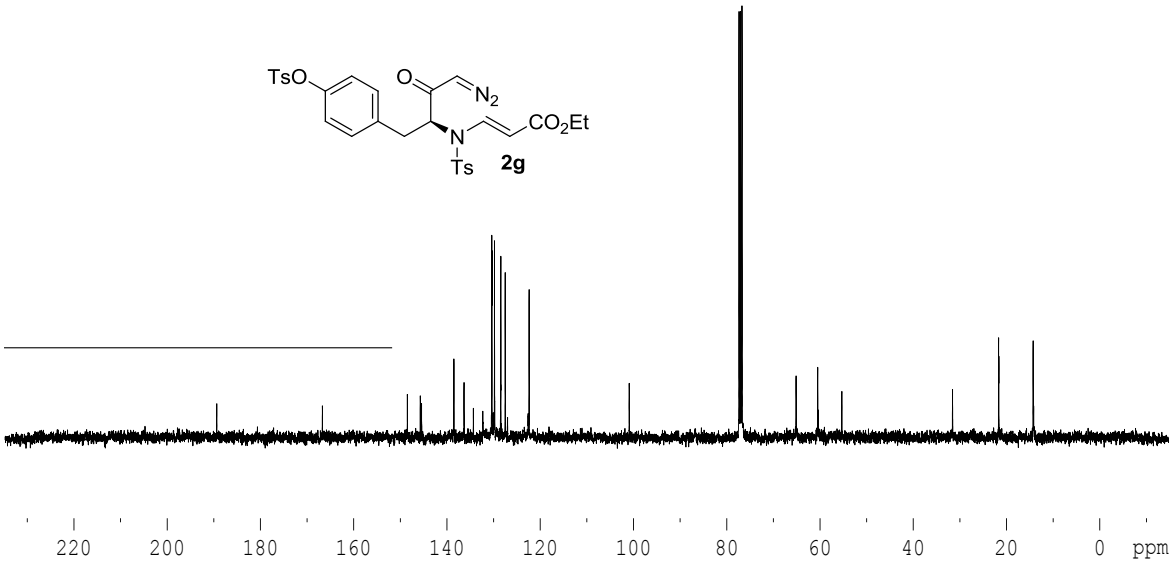
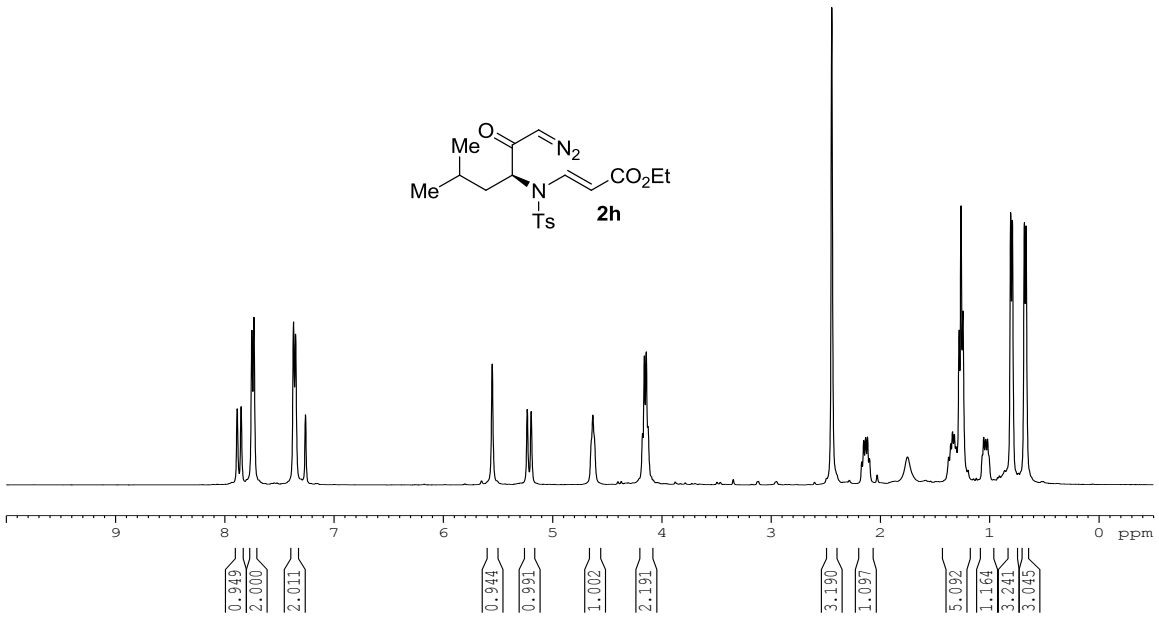
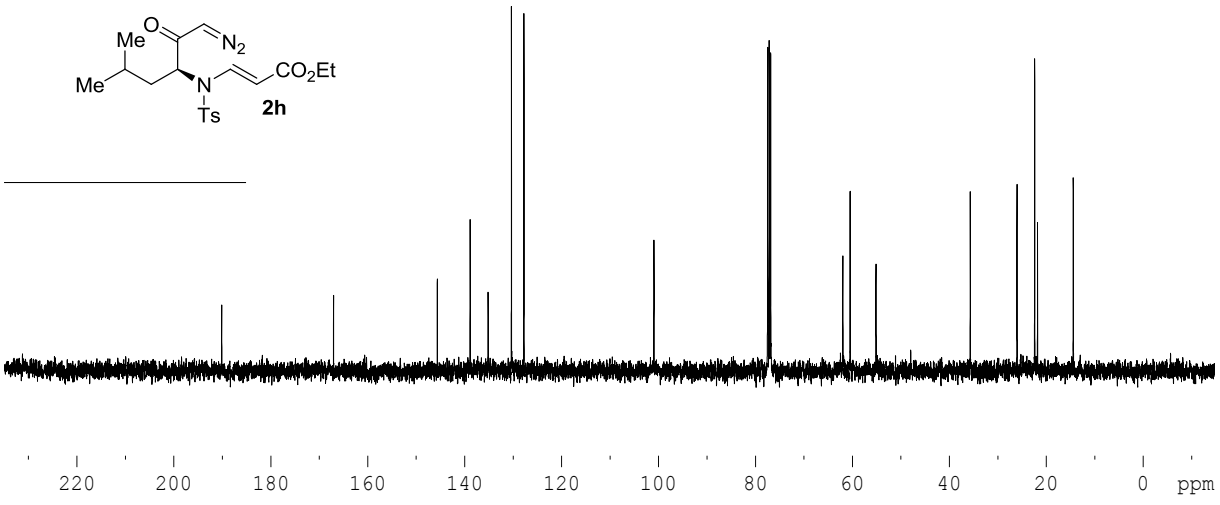
2.124
0.852
1.061
1.009
2.199
1.160
1.115
3.313
3.173

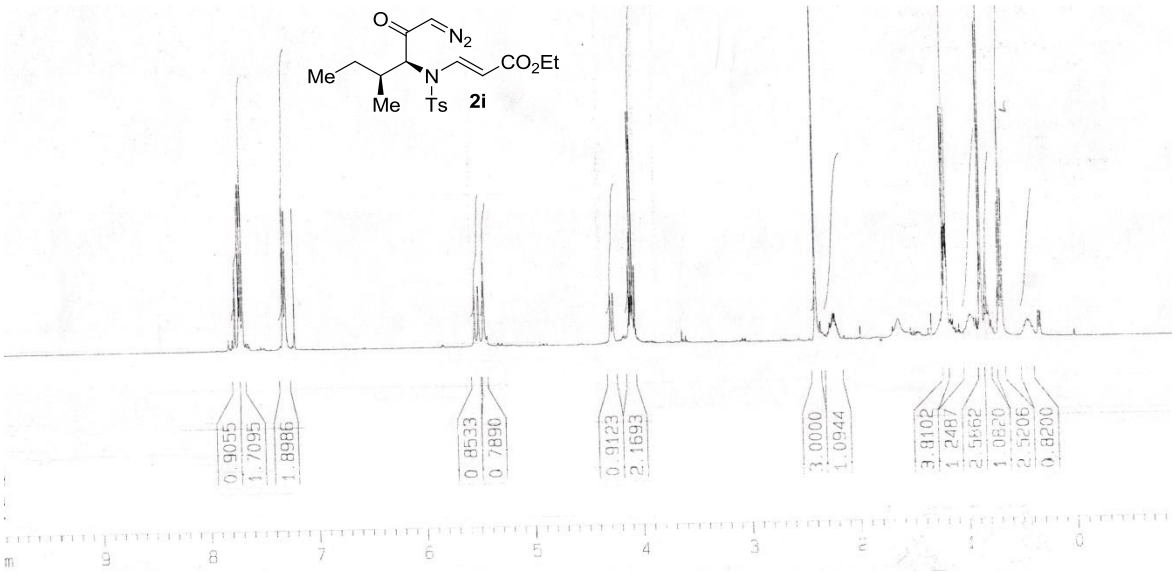

O
N2
Ph
CO2Et
N
Ts
2f
220
200
180
160
140
120
100
80
60
40
20
0 ppm

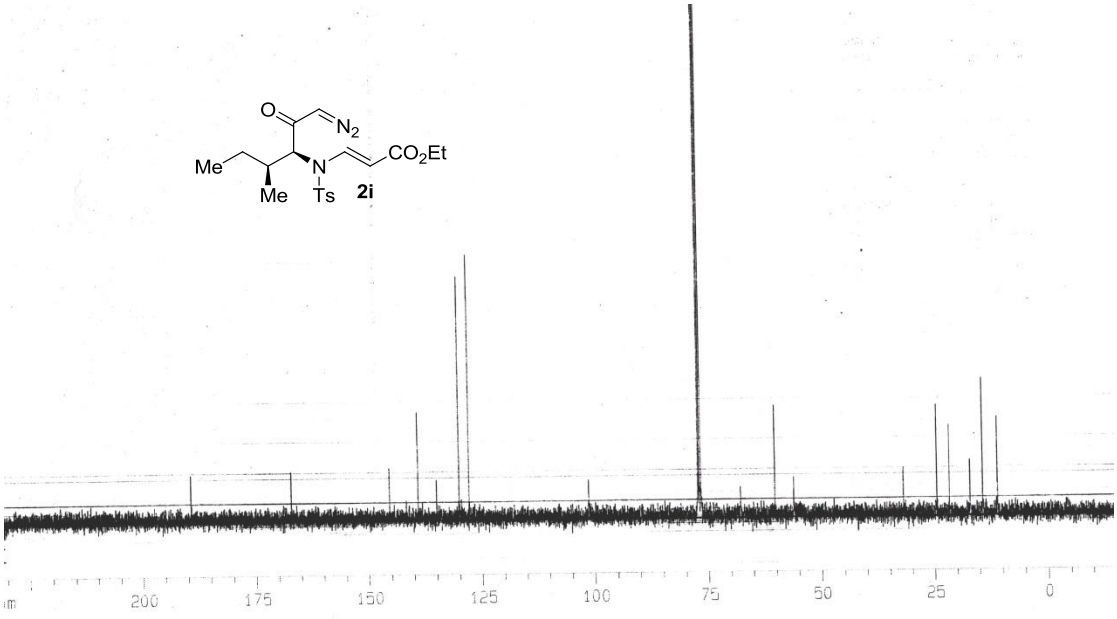

TsO
O
N2
CO2Et
N
Ts
2g
9
8
7
6
5
4
3
2
1
0 ppm
0.972
2.065
1.882
2.399
1.980
1.998
1.967
0.841
0.994
1.053
2.339
1.160
1.312
6.398
3.332

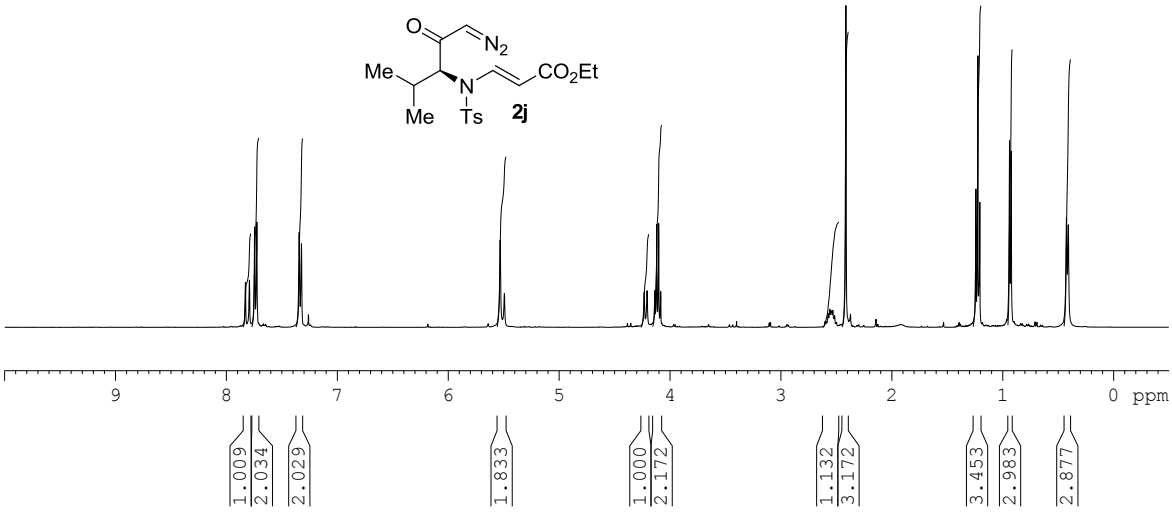

TsO
O
N2
CO2Et
N
Ts
2g
220
200
180
160
140
120
100
80
60
40
20
0 ppm

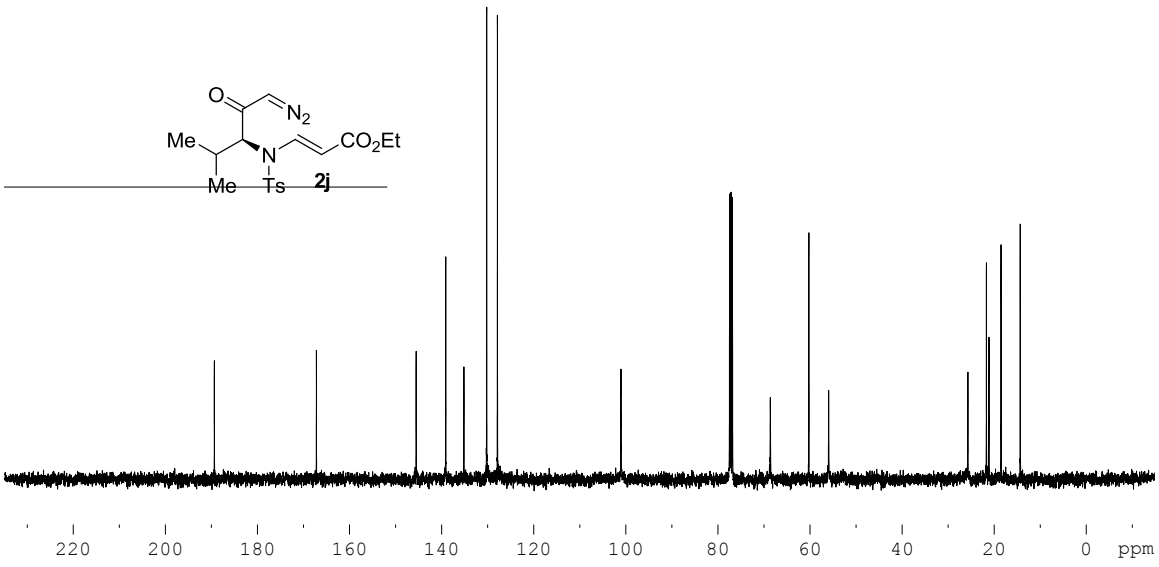

Me
O
N2
Me
N
CO2Et
Ts
2h
9
8
7
6
5
4
3
2
1
0 ppm
0.949
2.000
2.011
0.944
0.991
1.002
2.191
3.190
1.097
5.092
1.164
3.241
3.045

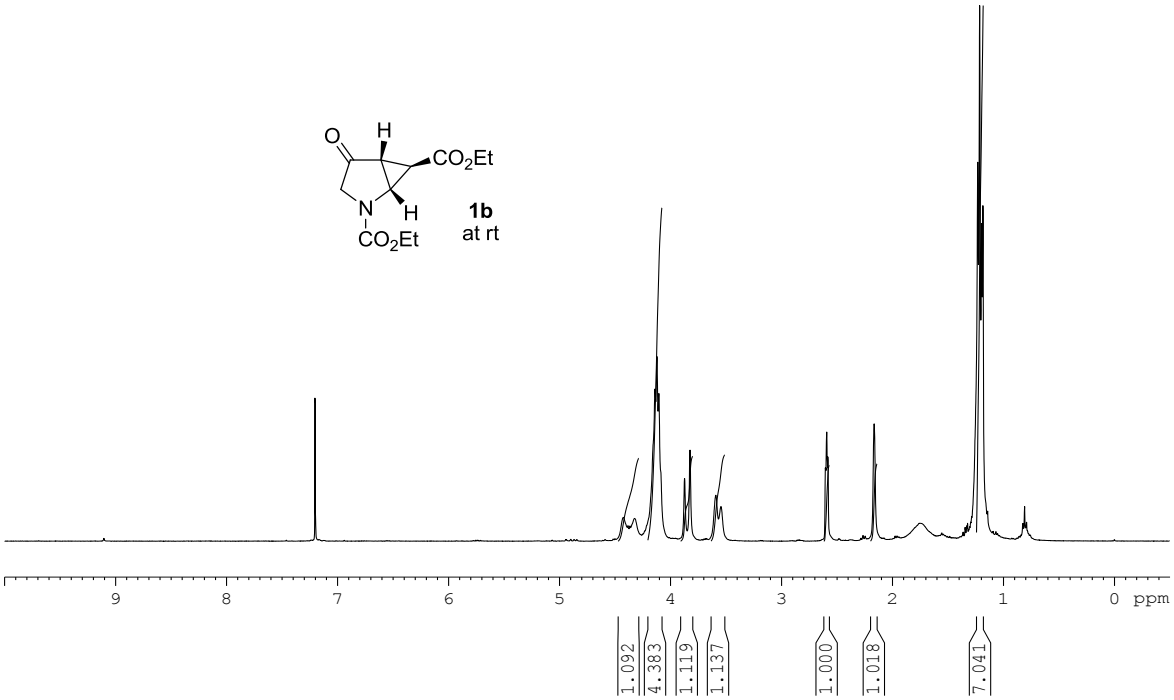

Me
O
N2
Me
N
CO2Et
Ts
2h
220
200
180
160
140
120
100
80
60
40
20
0 ppm

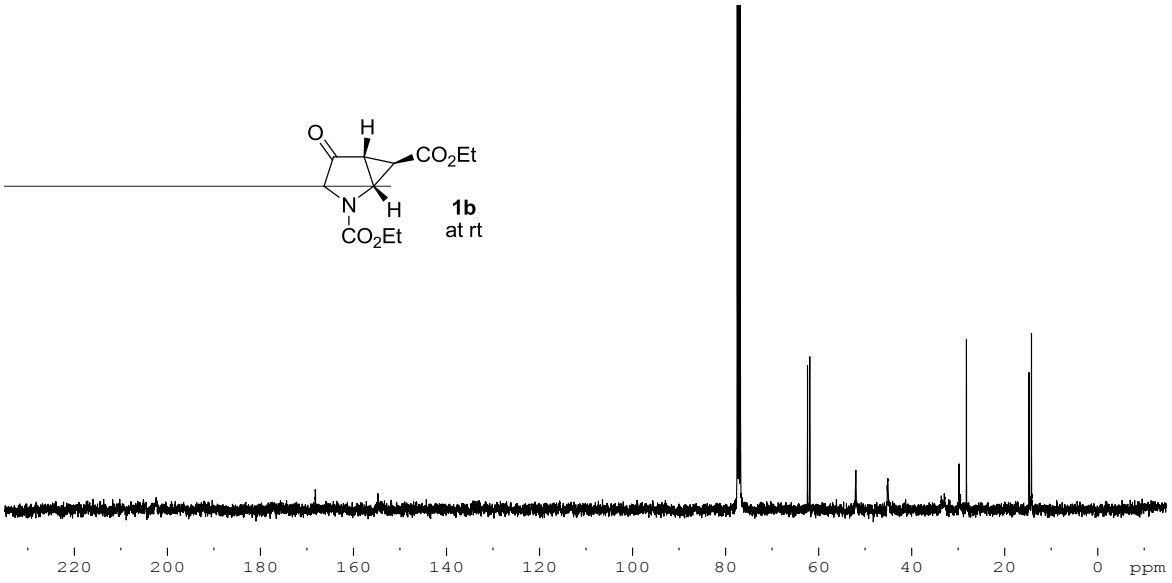

O
N2
Me
N
CO2Et
Me
Ts
2i
0.9055
1.7095
1.8986
0.8533
0.7890
0.9123
2.1693
3.0000
1.0944
3.9102
1.2487
2.5662
1.0820
2.5206
0.8200
9
8
7
6
5
4
3
2
1
0

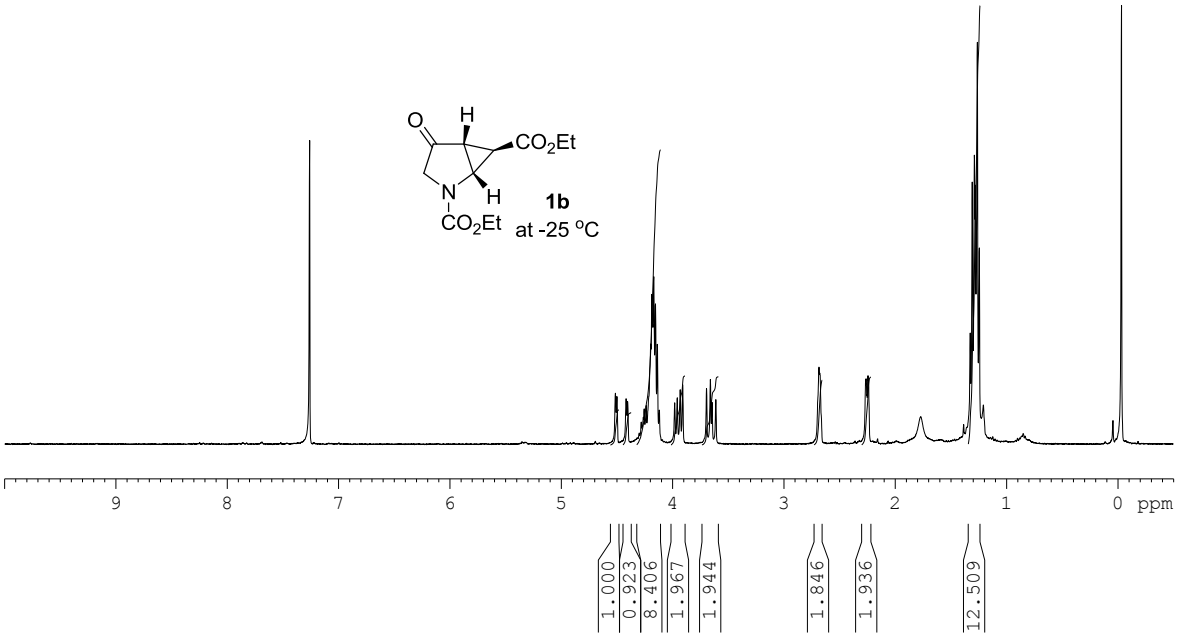

O
N2
Me
N
CO2Et
Me
Ts
2i
200
175
150
125
100
75
50
25
0

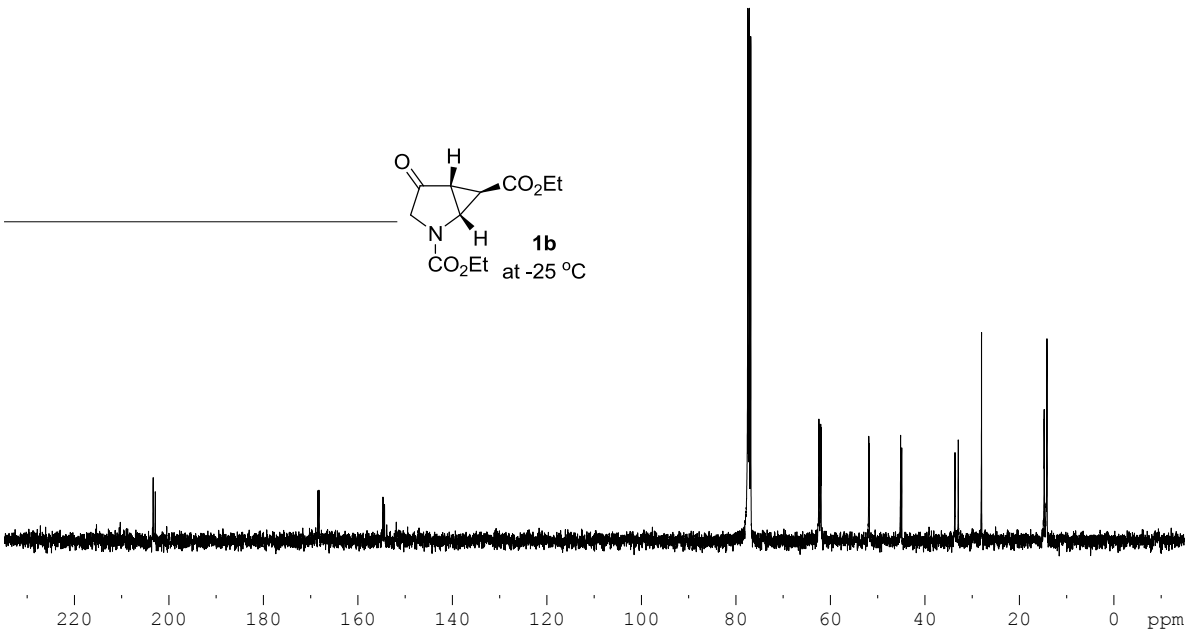

O
N2
Me
CO2Et
N
Me
Ts
2j
9
8
7
6
5
4
3
2
1
0 ppm
1.009
2.034
2.029
1.833
1.000
2.172
1.132
3.172
3.453
2.983
2.877

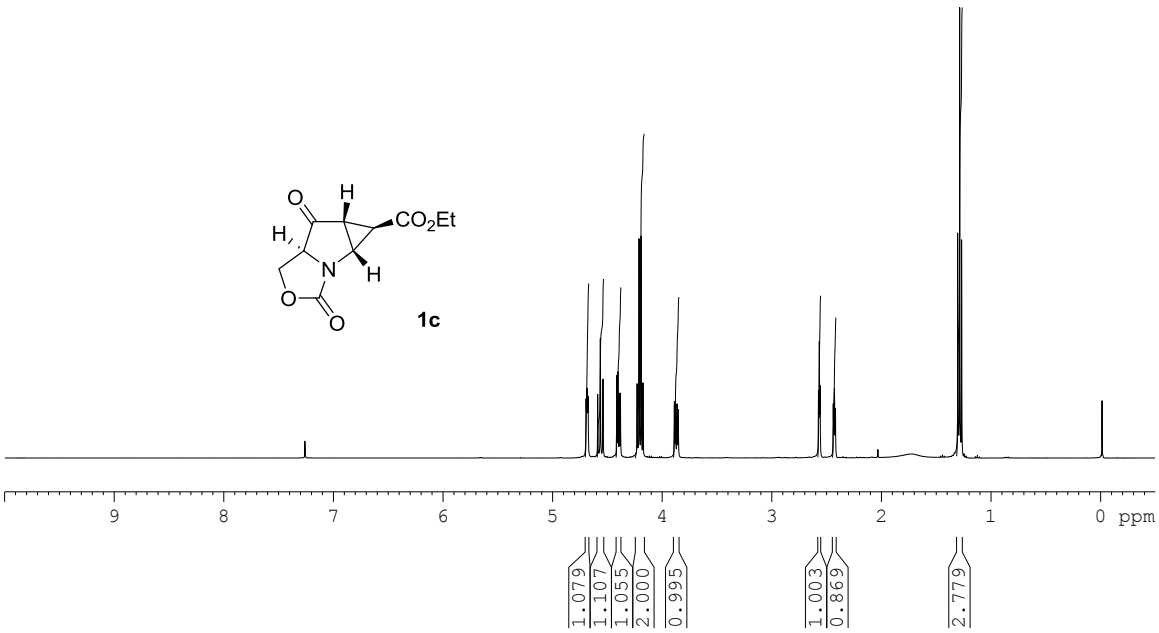

O
N2
Me
CO2Et
N
Me
Ts
2j
220
200
180
160
140
120
100
80
60
40
20
0 ppm

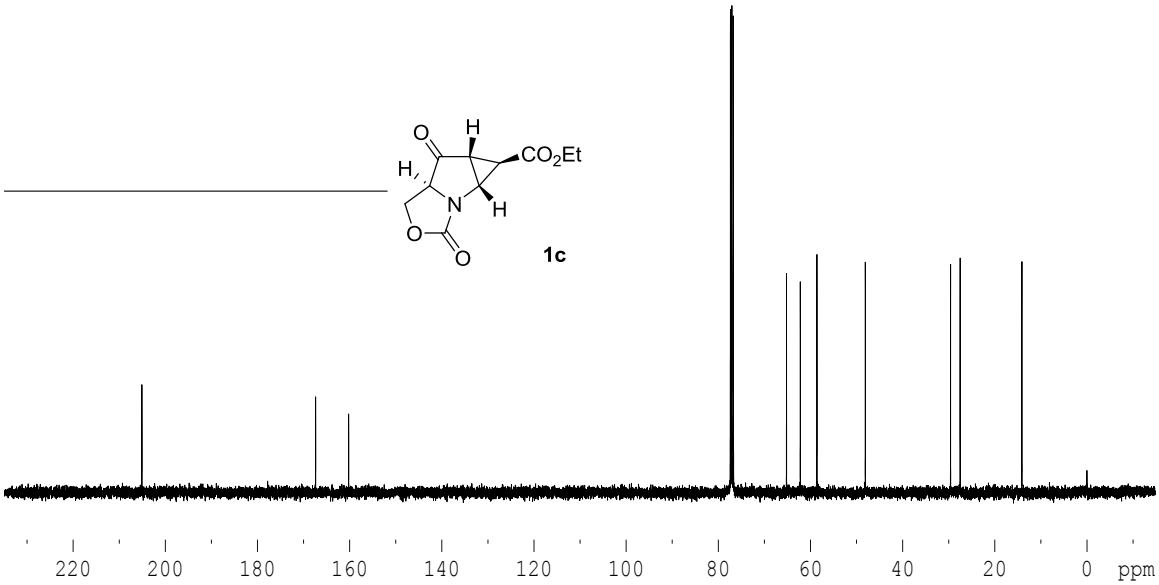

O
H
CO2Et
N
H
CO2Et
1b
at rt
9
8
7
6
5
4
3
2
1
0 ppm
1.092
4.383
1.119
1.137
1.000
1.018
7.041

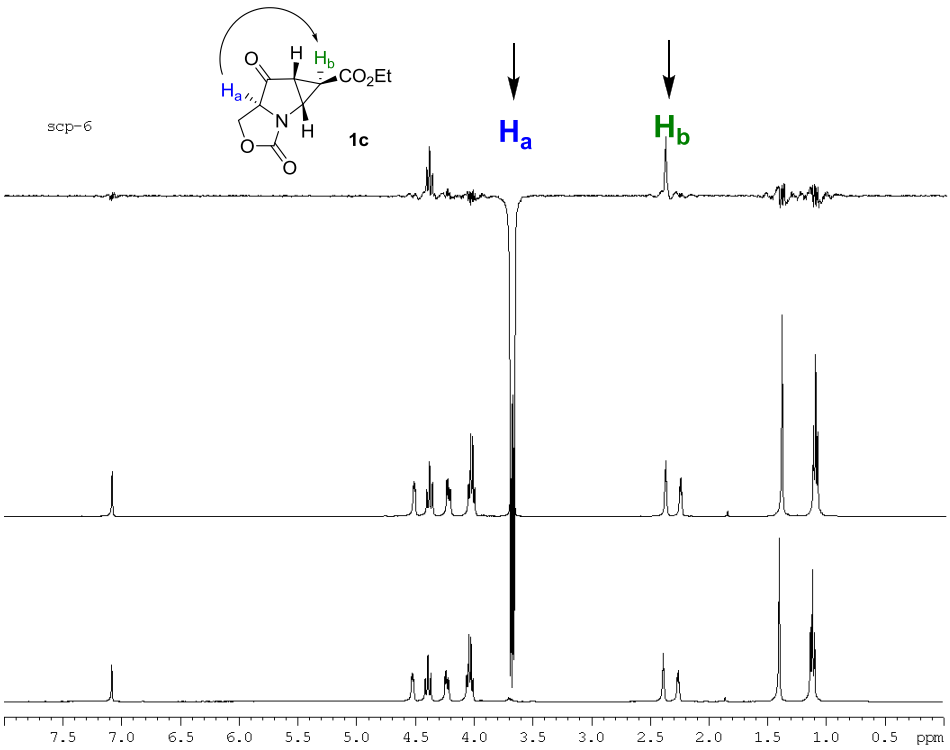

O
H
CO2Et
N
H
CO2Et
1b
at rt
220
200
180
160
140
120
100
80
60
40
20
0 ppm

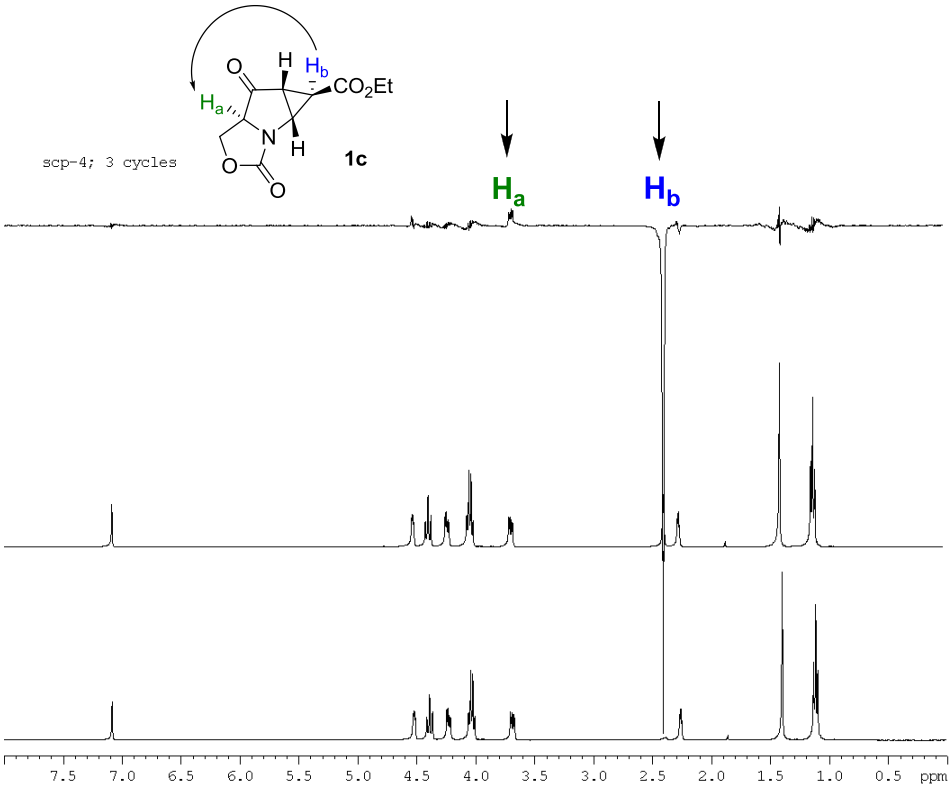

O
H
CO2Et
N
H
CO2Et
1b
at -25 °C
9
8
7
6
5
4
3
2
1
0 ppm
1.000
0.923
8.406
1.967
1.944
1.846
1.936
12.509

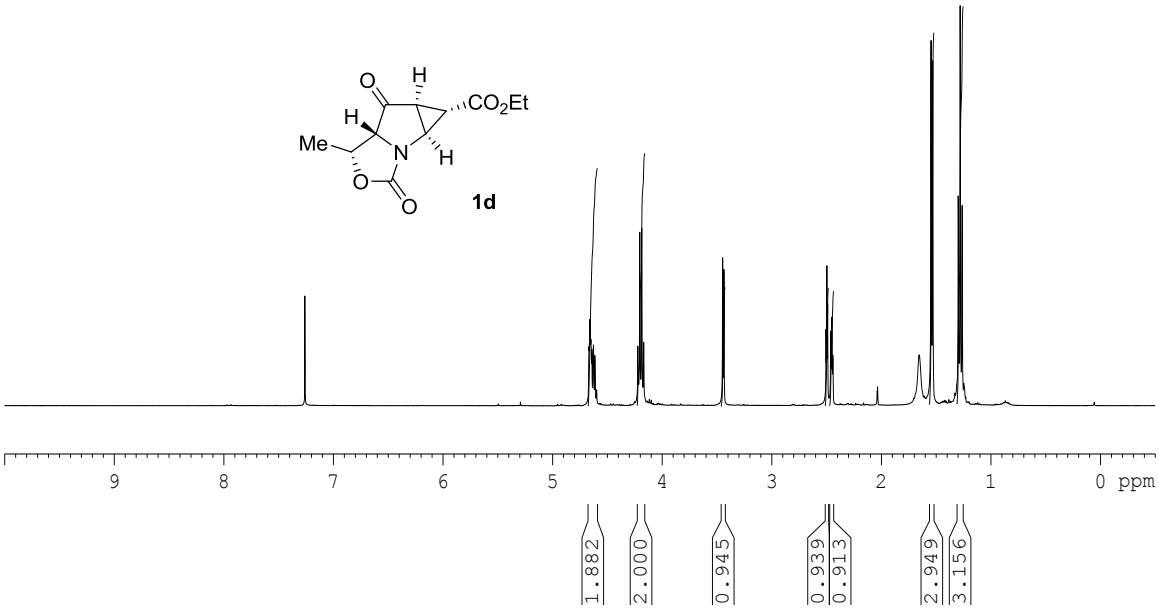

O
H
CO2Et
N
H
CO2Et
1b
at -25 °C
220
200
180
160
140
120
100
80
60
40
20
0 ppm

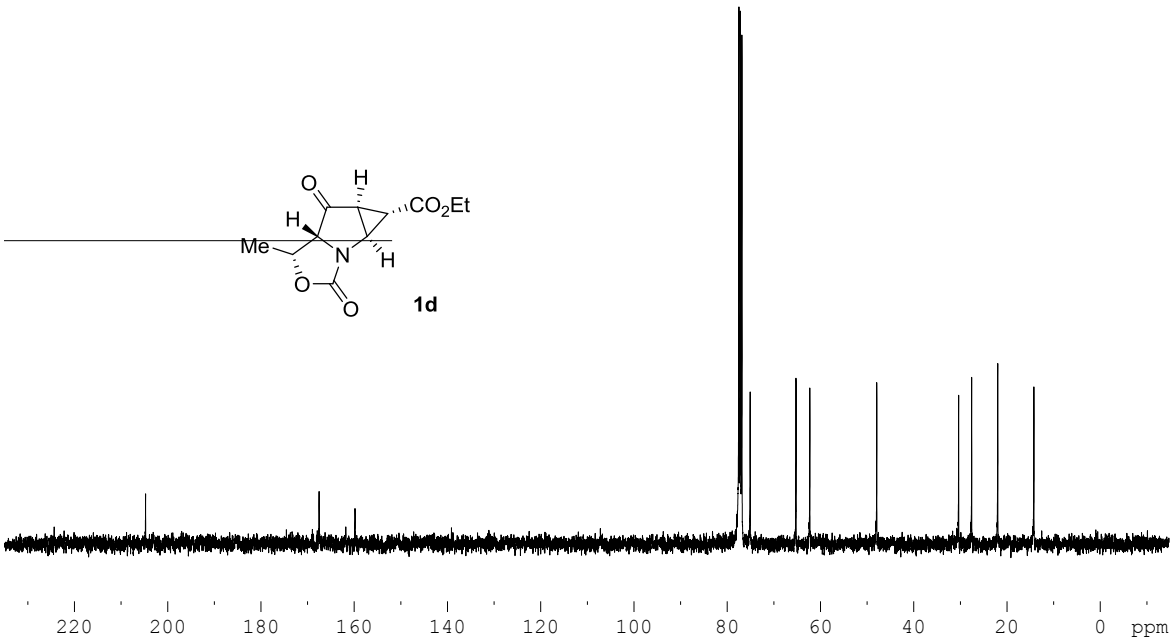

O
H
CO2Et
H
N
H
O
O
1c
9
8
7
6
5
4
3
2
1
0 ppm
1.079
1.107
1.055
2.000
0.995
1.003
0.869
2.779

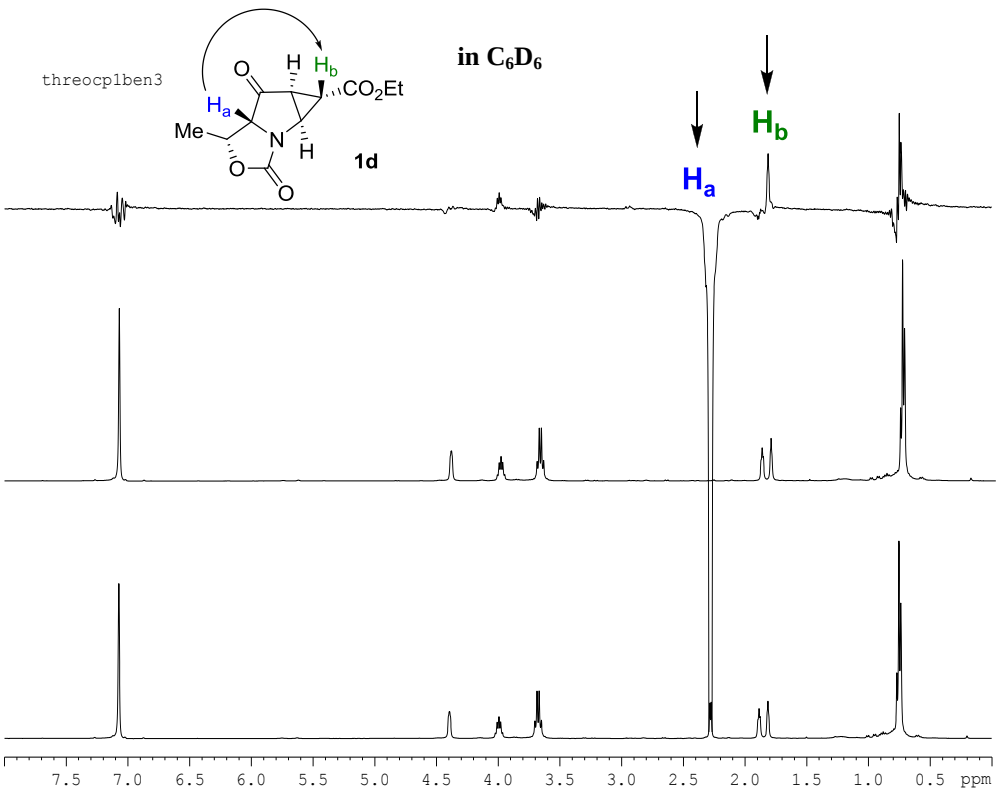

O
H
CO2Et
H
N
H
O
O
1c
220
200
180
160
140
120
100
80
60
40
20
0 ppm

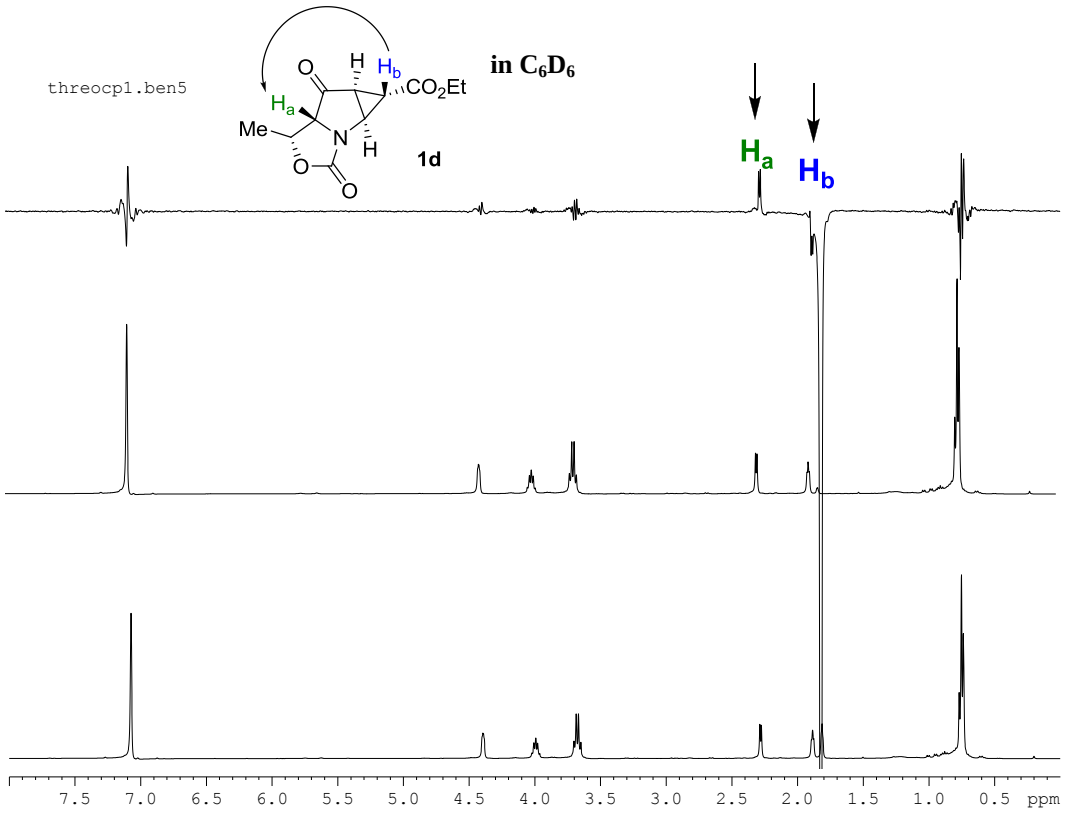

scp-6
1c
H_a
H_b
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

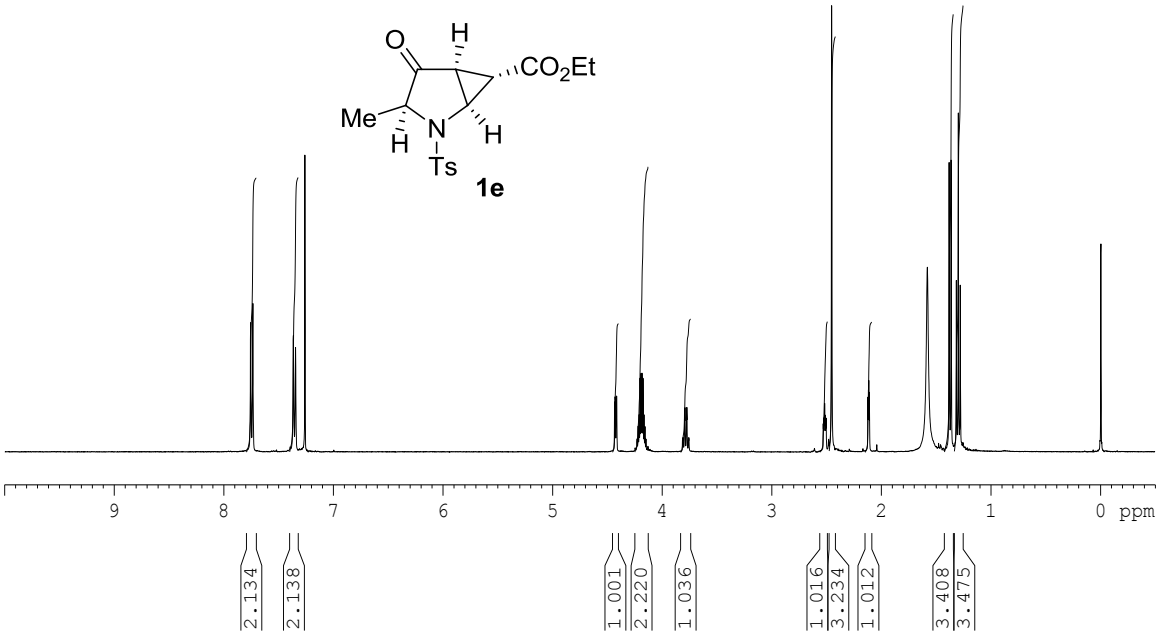

scp-4; 3 cycles
1c
H_a
H_b
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

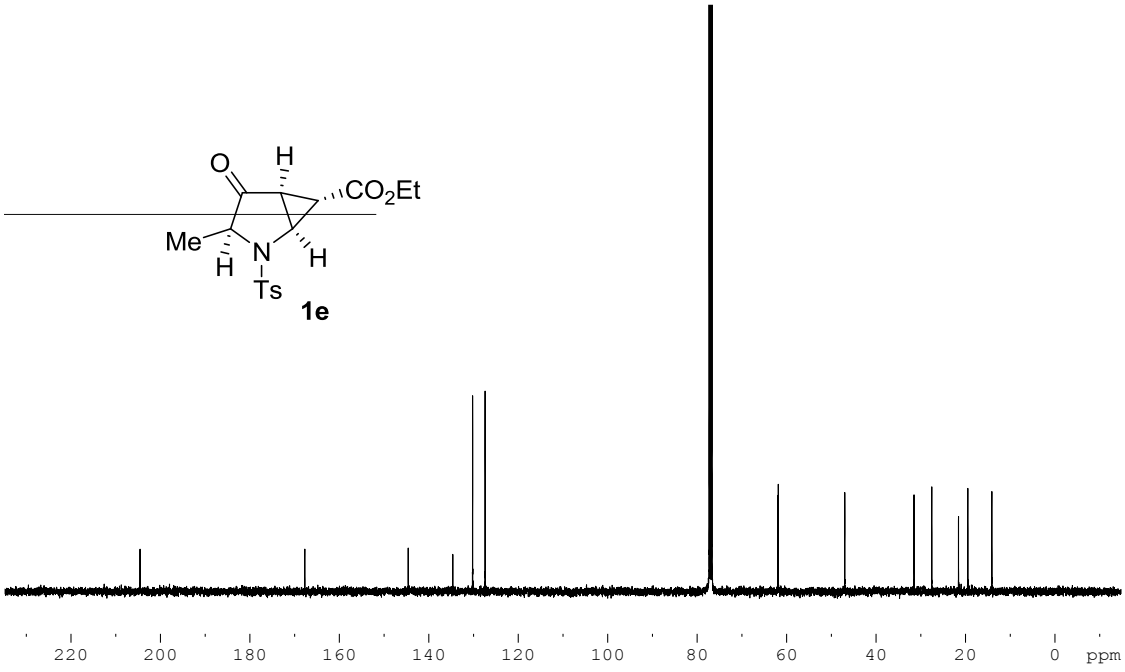

O
H
CO2Et
H
Me
N
H
O
O
1d
9
8
7
6
5
4
3
2
1
0 ppm
1.882
2.000
0.945
0.939
0.913
2.949
3.156

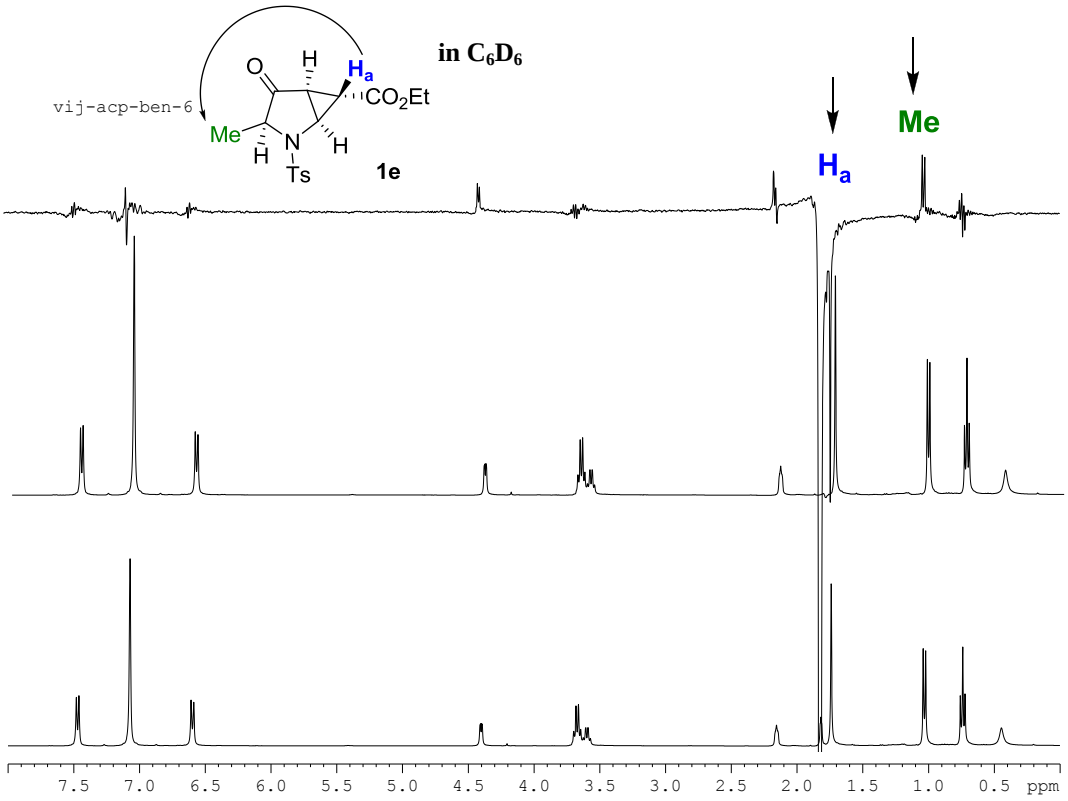

O
H
CO2Et
H
Me
N
H
O
O
1d
220
200
180
160
140
120
100
80
60
40
20
0 ppm

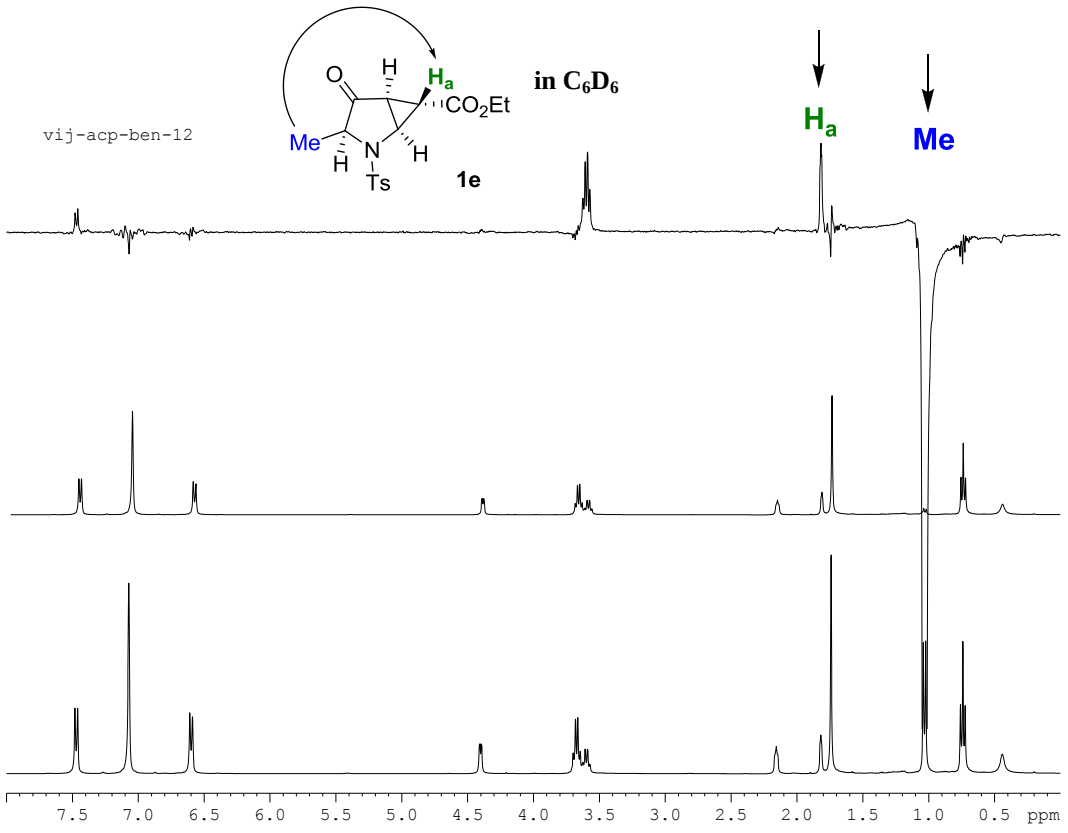

threocp1ben3
in C6D6
Ha
Hb
1d
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

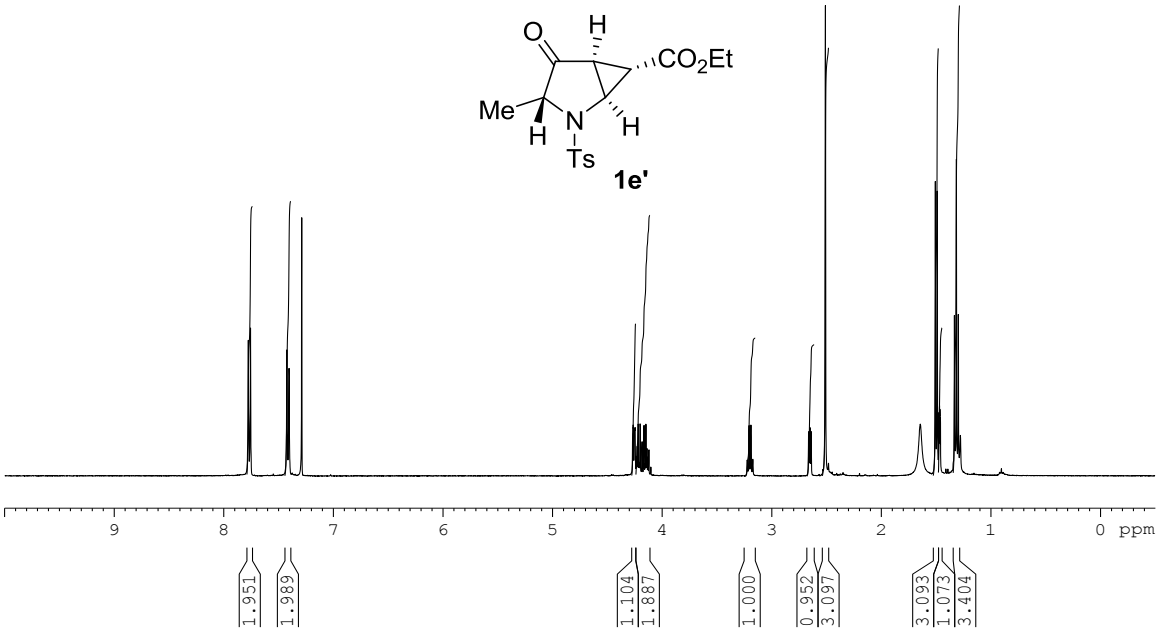

threocp1.ben5
in C6D6
Ha
Hb
1d
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

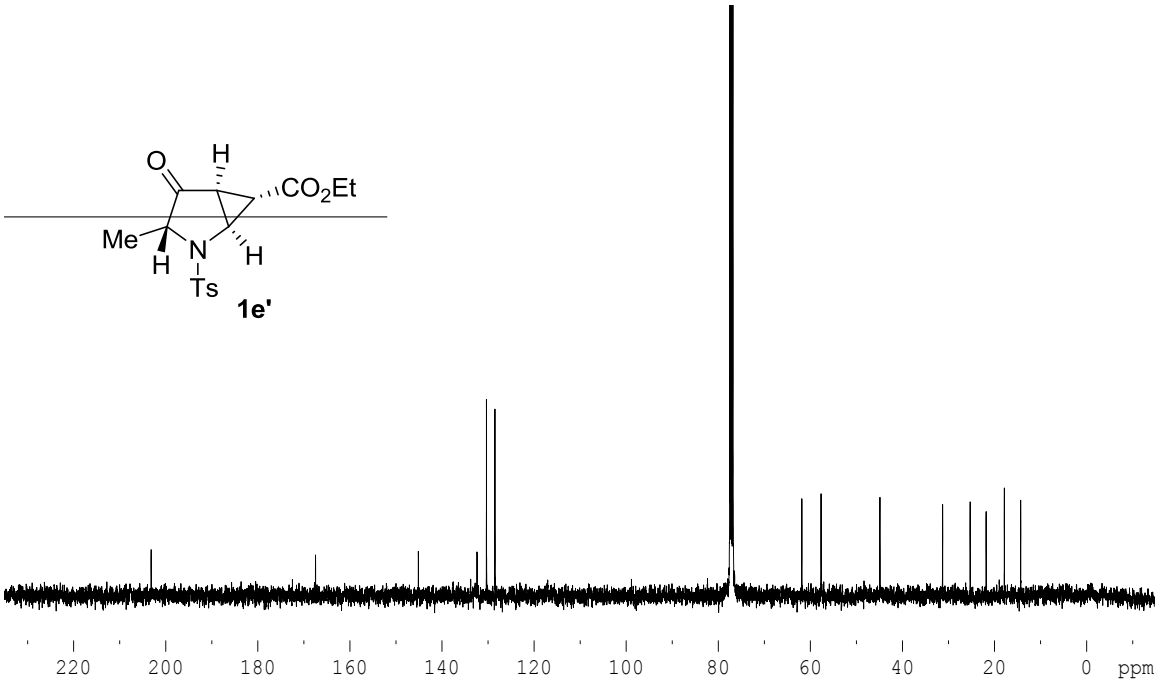

O
H
CO2Et
Me
H
N
H
Ts
1e
9
8
7
6
5
4
3
2
1
0 ppm
2.134
2.138
1.001
2.220
1.036
1.016
3.234
1.012
3.408
3.475

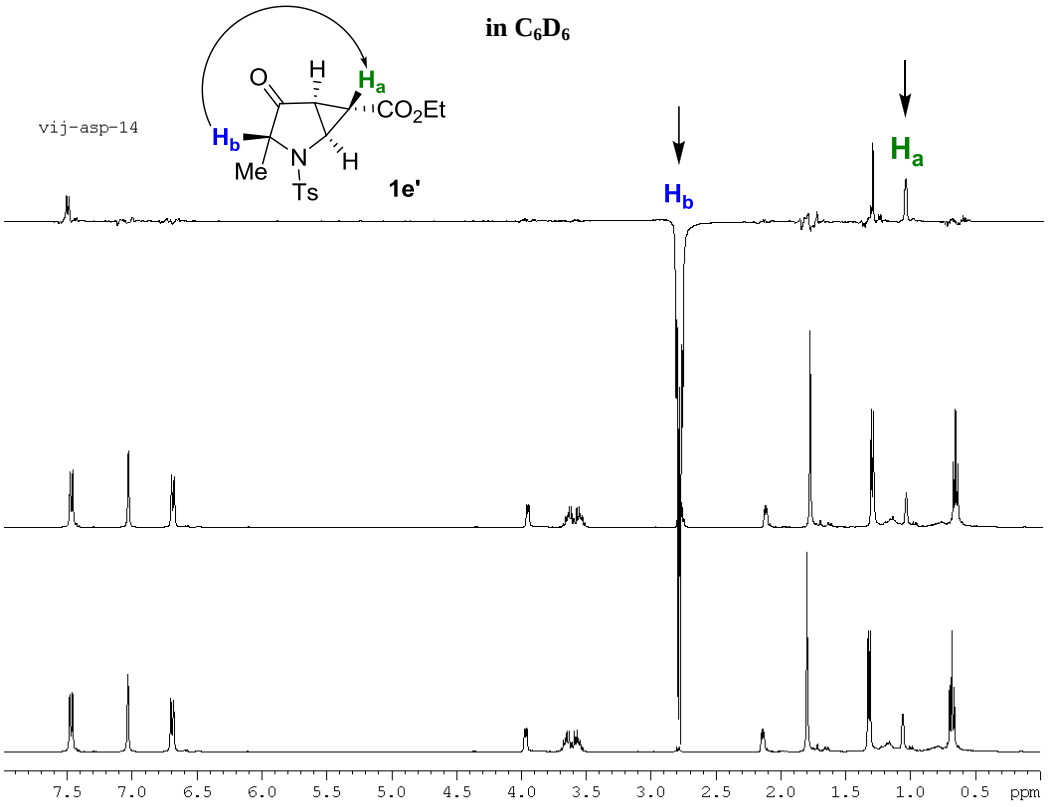

O
H
CO2Et
Me
H
N
H
Ts
1e
220
200
180
160
140
120
100
80
60
40
20
0 ppm

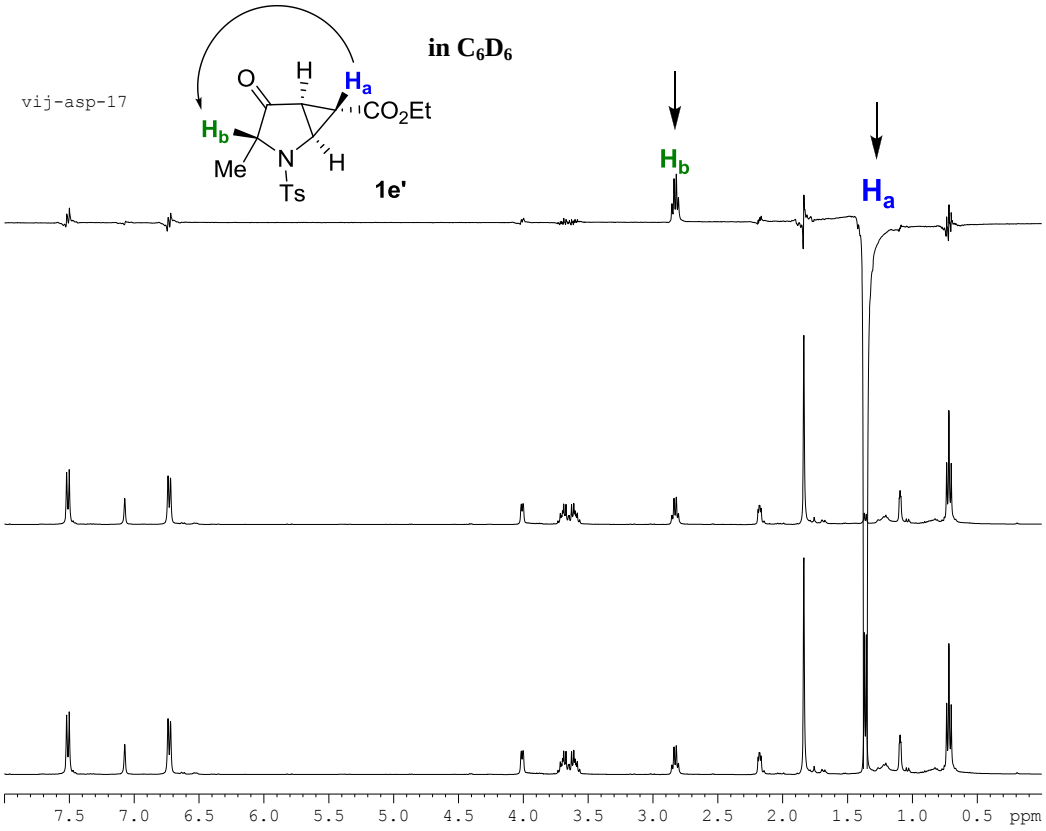

vij-acp-ben-6
in C6D6
Ha
CO2Et
Me
N
H
H
Ts
1e
Ha
Me
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

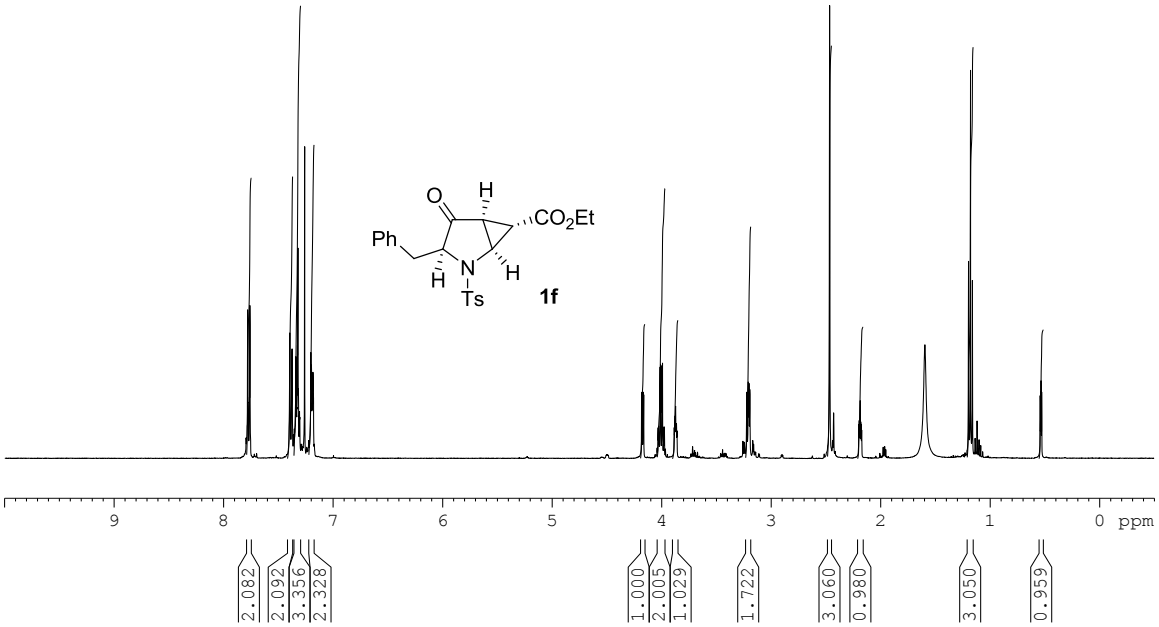

vij-acp-ben-12
in C6D6
Ha
CO2Et
Me
N
H
H
Ts
1e
Ha
Me
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

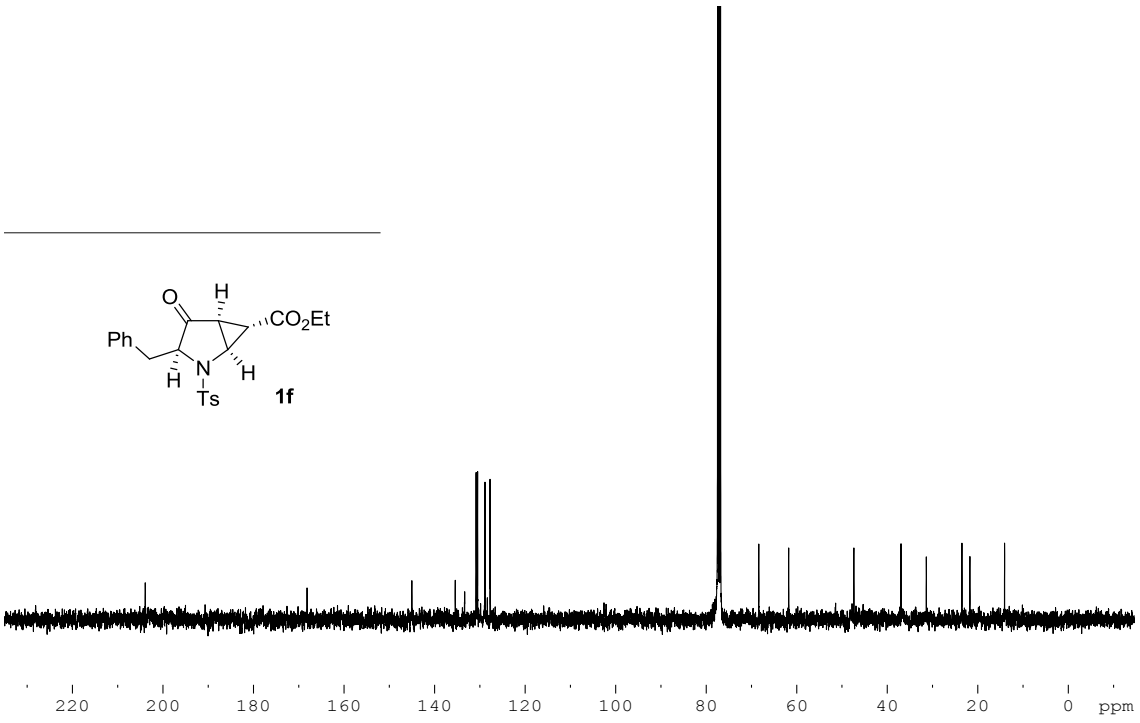

O
H
CO2Et
Me
H
N
H
Ts
1e'
9
8
7
6
5
4
3
2
1
0 ppm
1.951
1.989
1.104
1.887
1.000
0.952
3.097
3.093
1.073
3.404

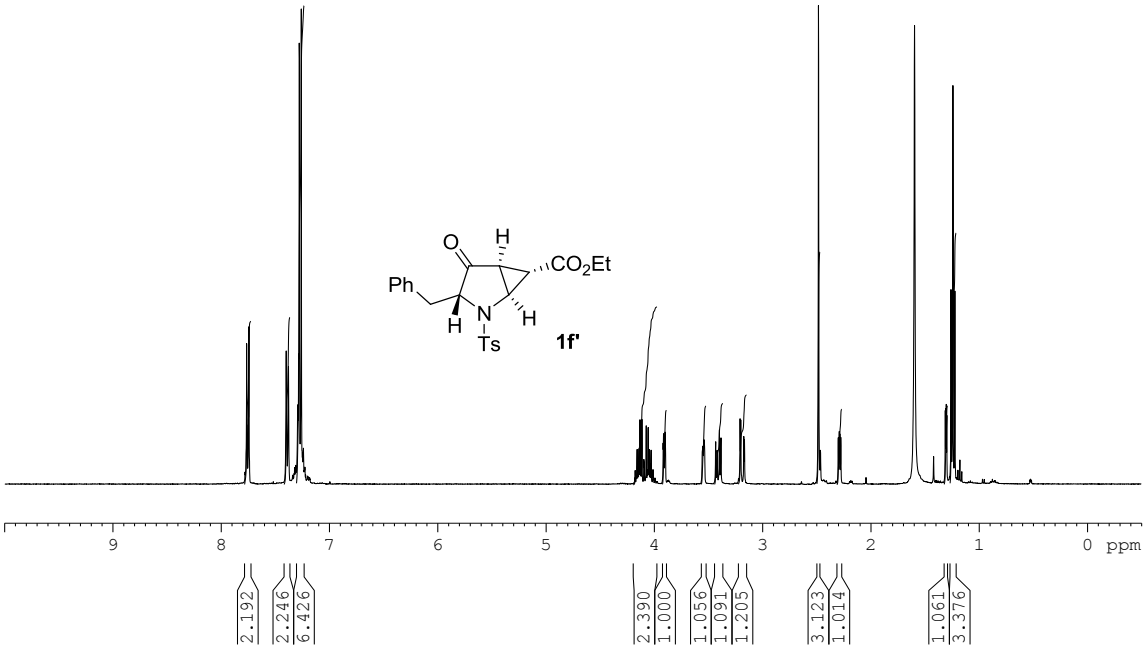

O
H
CO2Et
Me
H
N
H
Ts
1e'
220
200
180
160
140
120
100
80
60
40
20
0 ppm

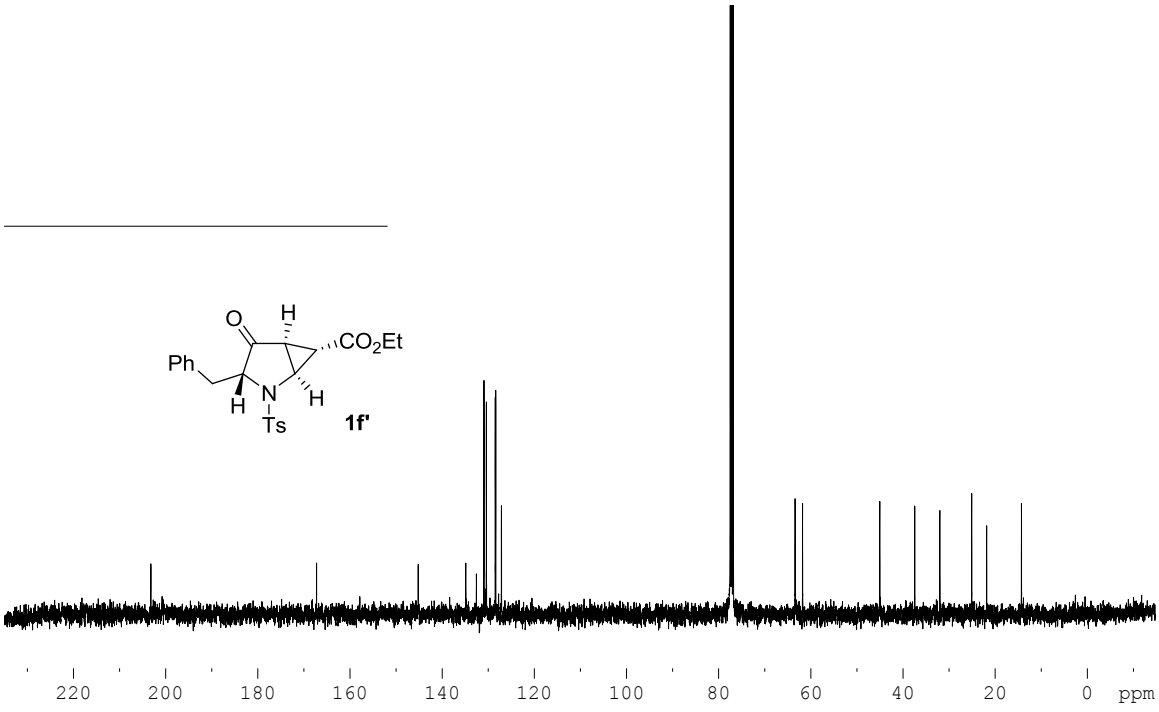

in C6D6
vij-asp-14
O
H
Ha
CO2Et
Hb
Me
N
H
Ts
1e'
Hb
Ha
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

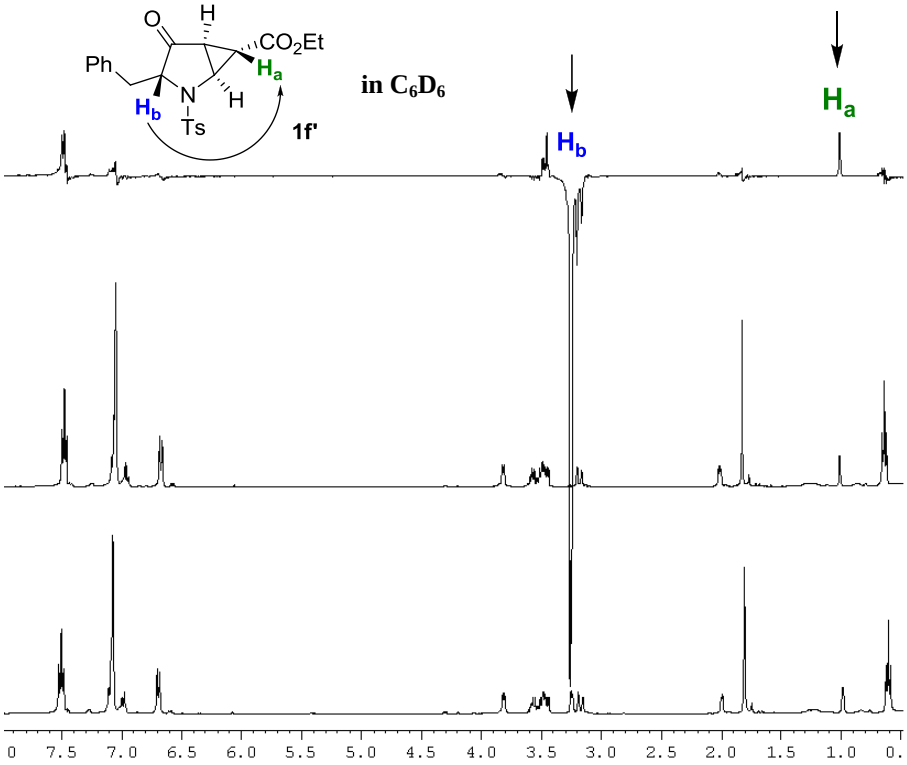

in C6D6
vij-asp-17
O
H
Ha
CO2Et
Hb
Me
N
H
Ts
1e'
Hb
Ha
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

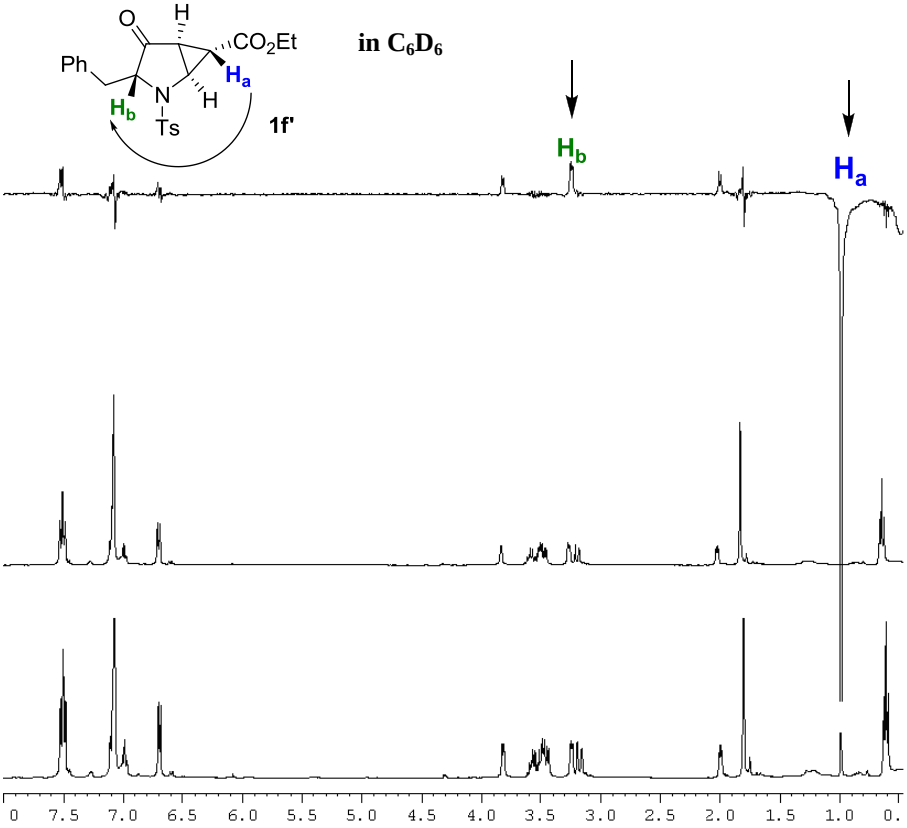

O
H
CO2Et
Ph
H
N
H
Ts
1f
9
8
7
6
5
4
3
2
1
0 ppm
2.082
2.092
3.356
2.328
1.000
2.005
1.029
1.722
3.060
0.980
3.050
0.959

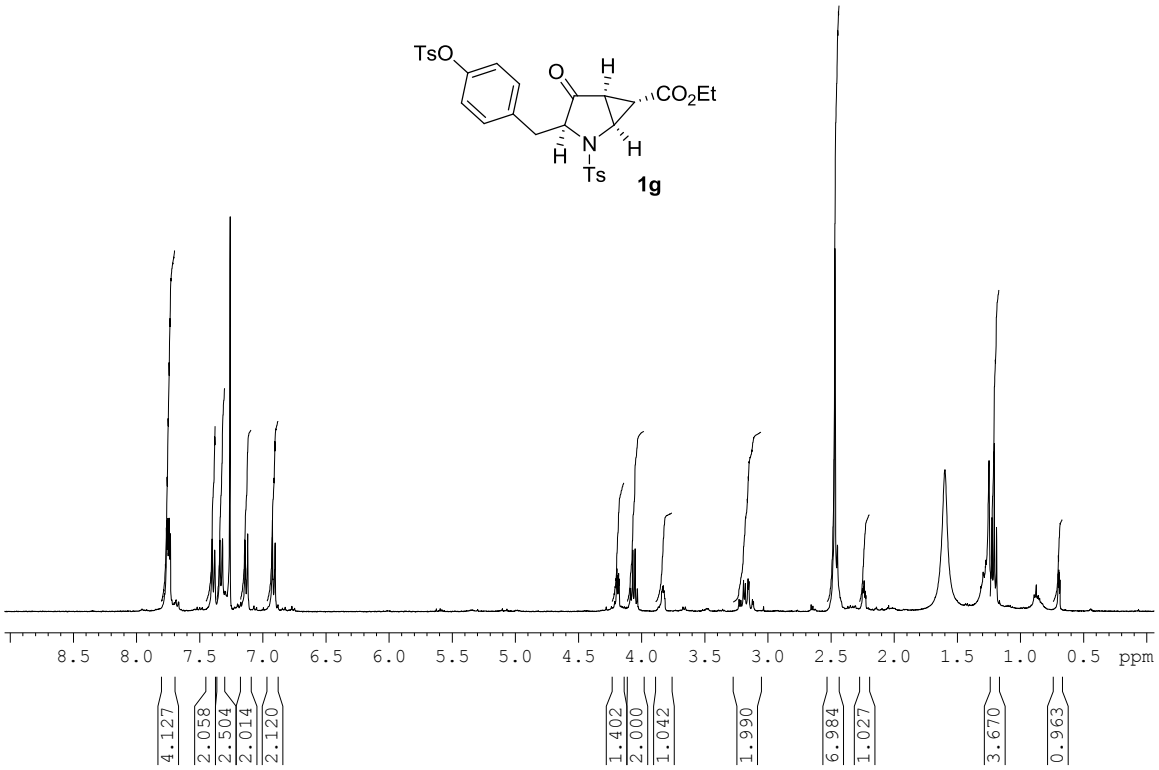

O
H
CO2Et
Ph
H
N
H
Ts
1f
220
200
180
160
140
120
100
80
60
40
20
0 ppm

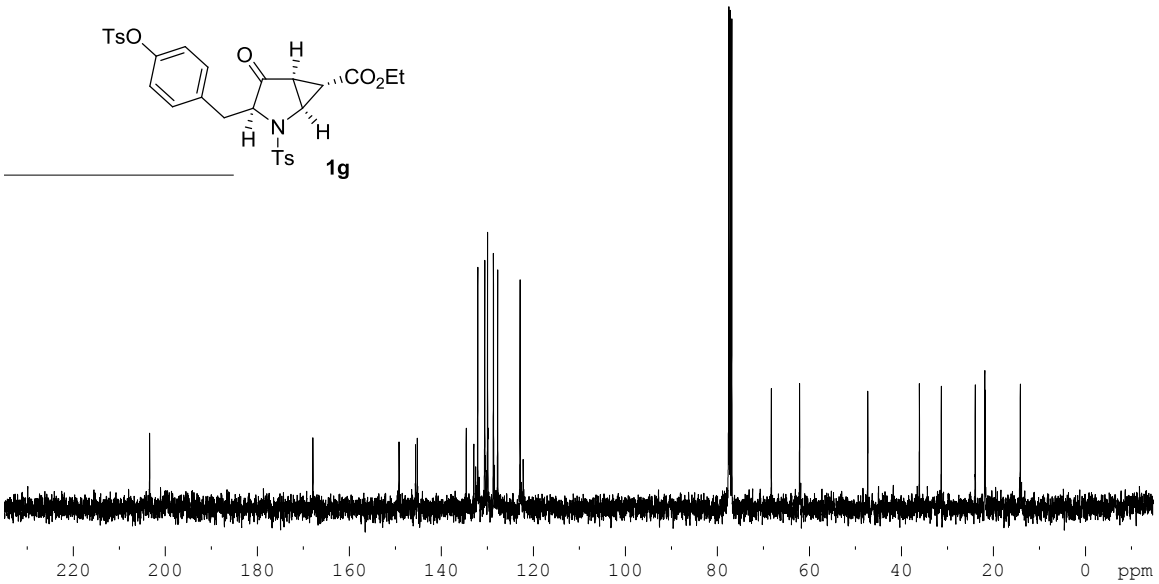

O
H
CO2Et
Ph
H
N
H
Ts
1f'
9
8
7
6
5
4
3
2
1
0 ppm
2.192
2.246
6.426
2.390
1.000
1.056
1.091
1.205
3.123
1.014
1.061
3.376

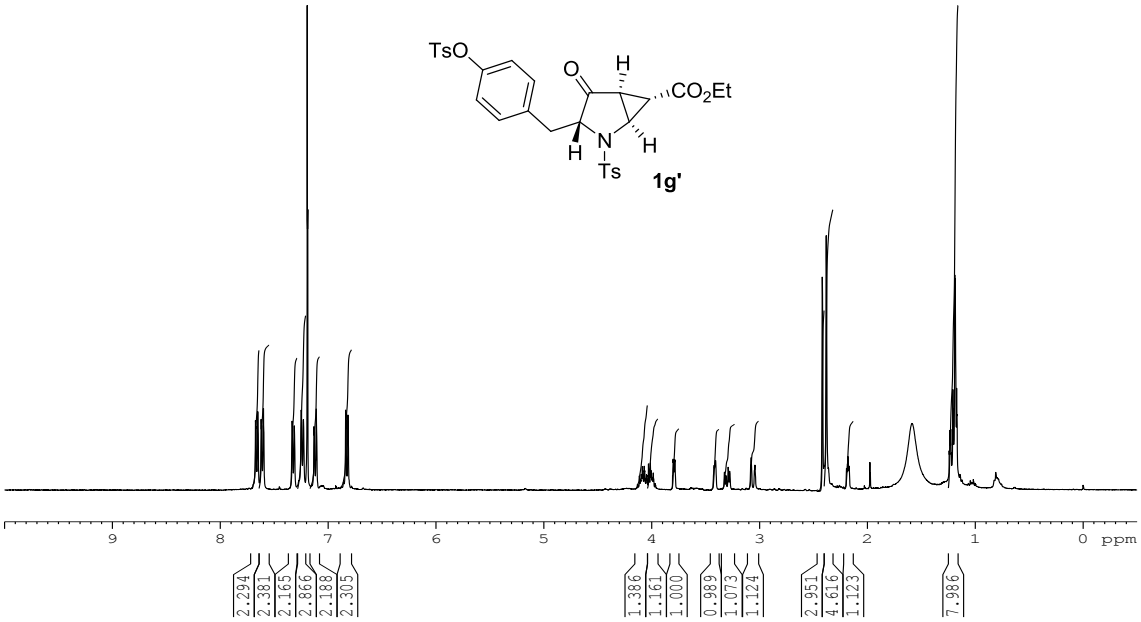

O
H
CO2Et
Ph
H
N
H
Ts
1f'
220
200
180
160
140
120
100
80
60
40
20
0 ppm

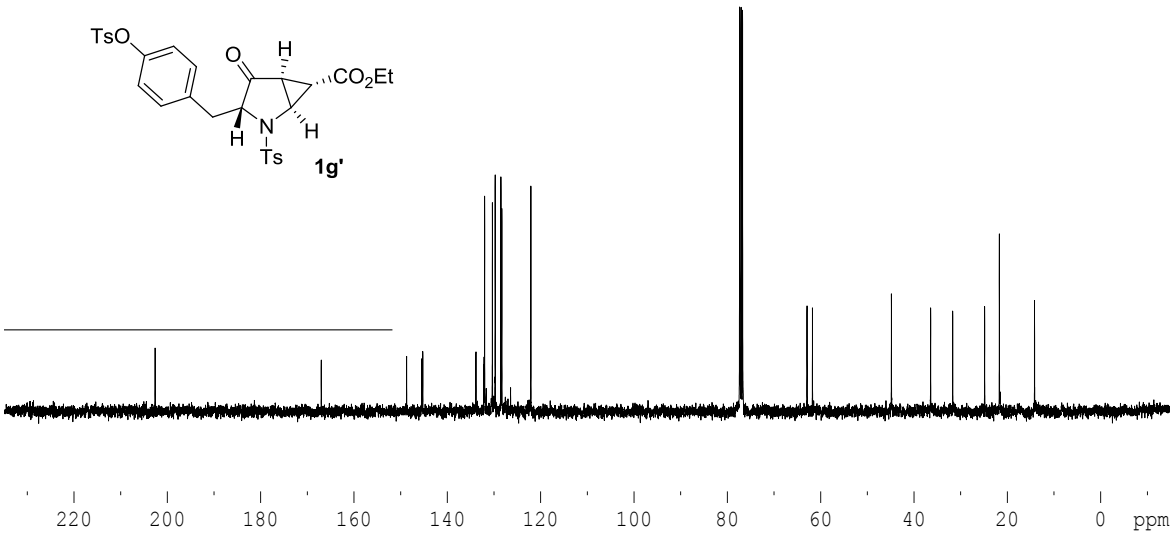

O
H
CO2Et
Ph
Ha
N
H
Hb
Ts
1f'
in C6D6
Hb
Ha
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.

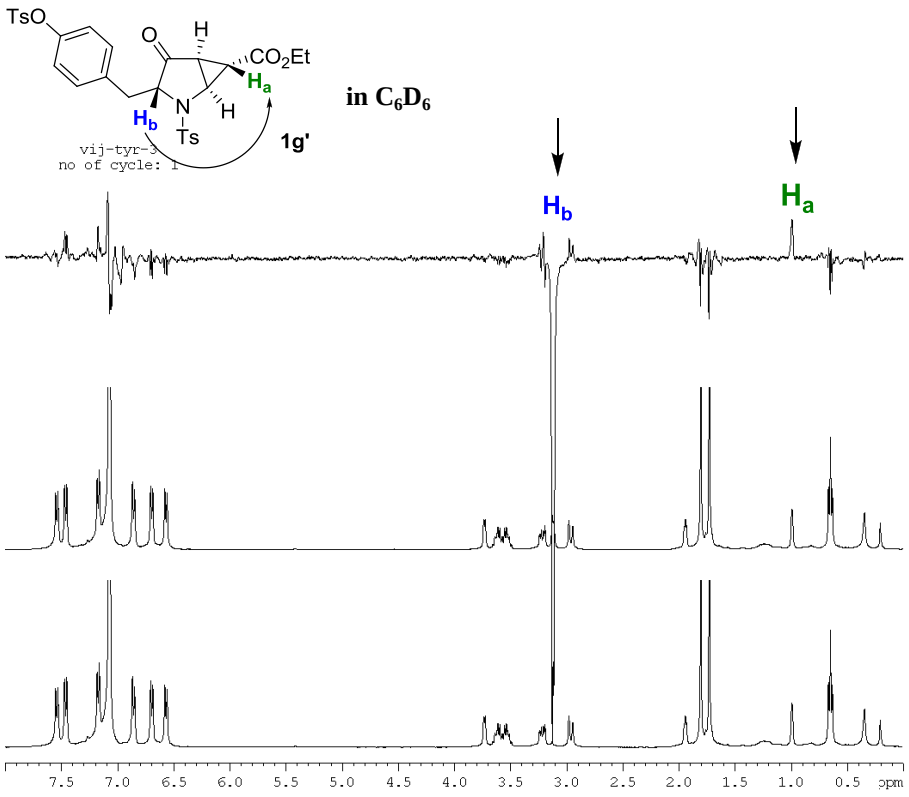

O
H
CO2Et
Ph
Ha
N
H
Hb
Ts
1f'
in C6D6
Hb
Ha
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.

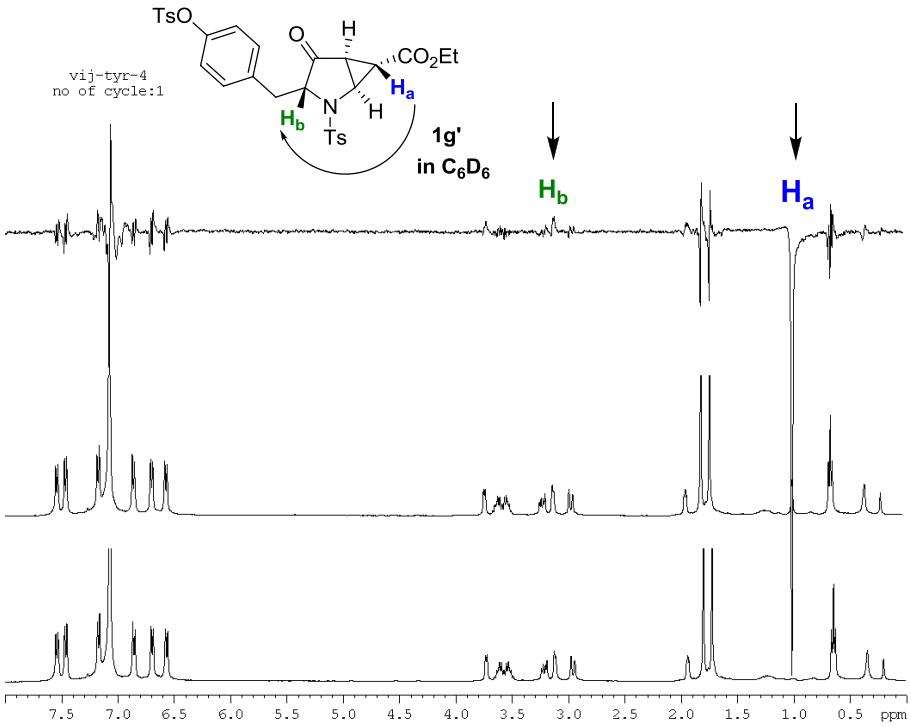

TsO
O
H
CO2Et
H
N
H
Ts
1g
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.127
2.058
2.504
2.014
2.120
1.402
2.000
1.042
1.990
6.984
1.027
3.670
0.963

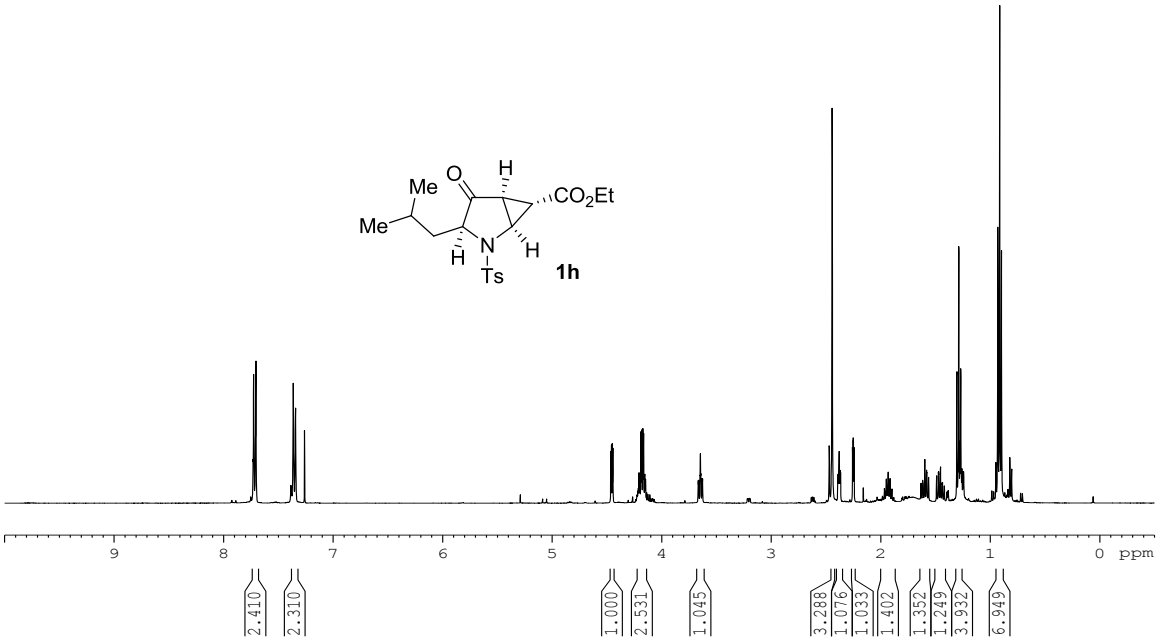

TsO
O
H
CO2Et
H
N
H
Ts
1g
220 200 180 160 140 120 100 80 60 40 20 0 ppm

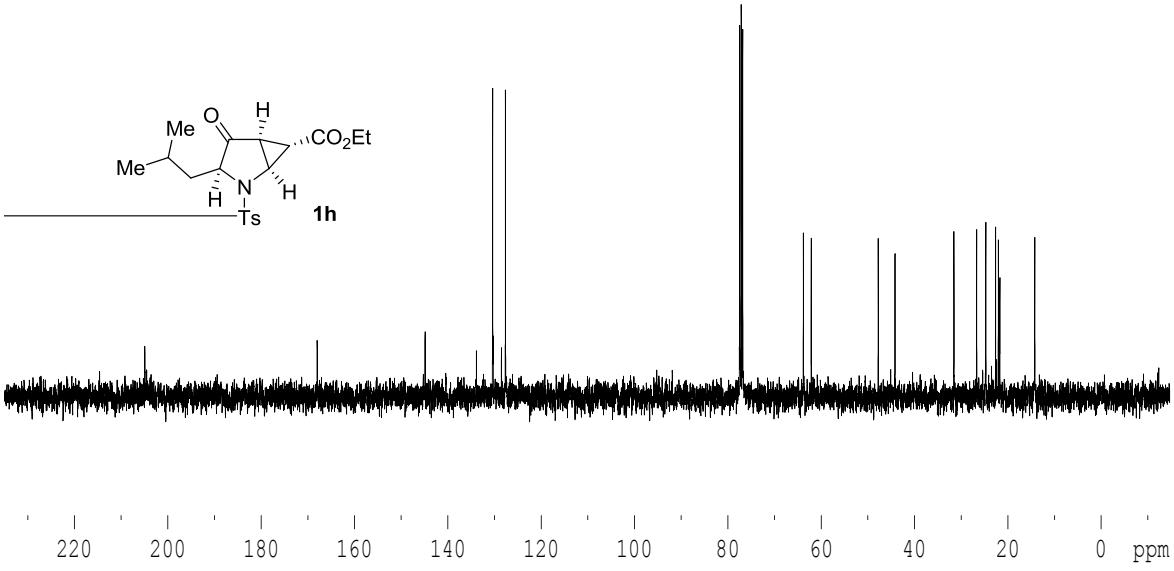

TsO
O
H
CO2Et
H
N
H
Ts
1g'
9
8
7
6
5
4
3
2
1
0 ppm
2.294
2.381
2.165
2.866
2.188
2.305
1.386
1.161
1.000
0.989
1.073
1.124
2.951
4.616
1.123
7.986

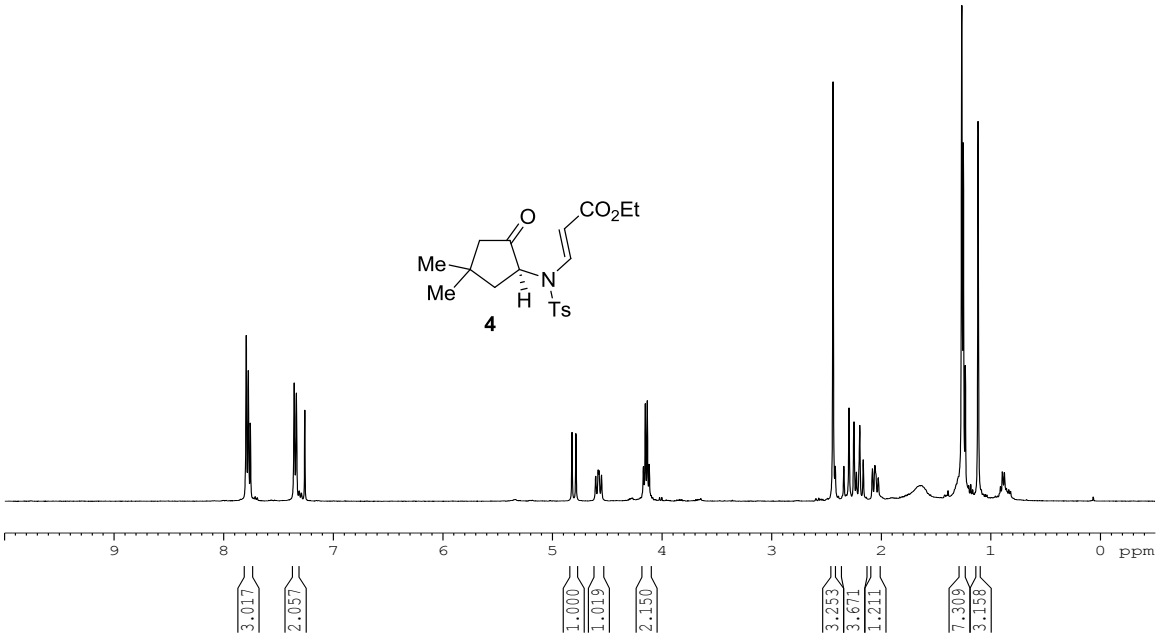

TsO
O
H
CO2Et
H
N
H
Ts
1g'
220
200
180
160
140
120
100
80
60
40
20
0 ppm

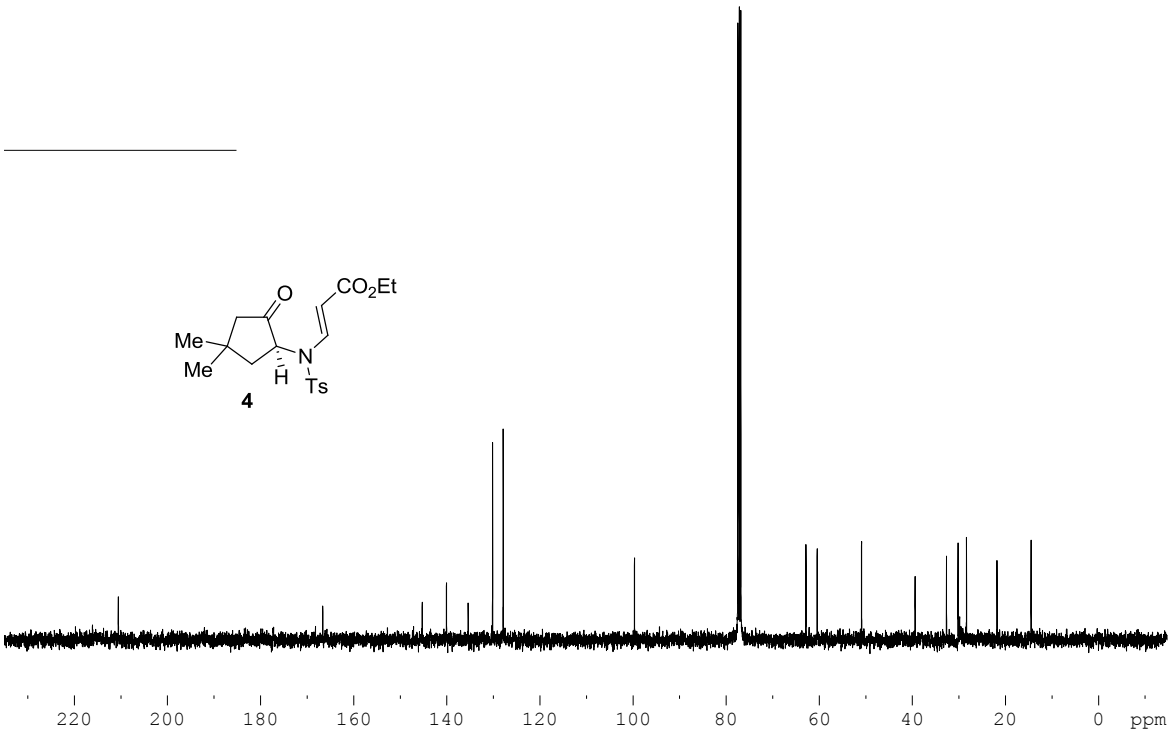

TsO
O
H
CO2Et
Ha
Hb
N
Ts
H
1g'
in C6D6
vij-tyr-3
no of cycle: 1
Hb
Ha
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

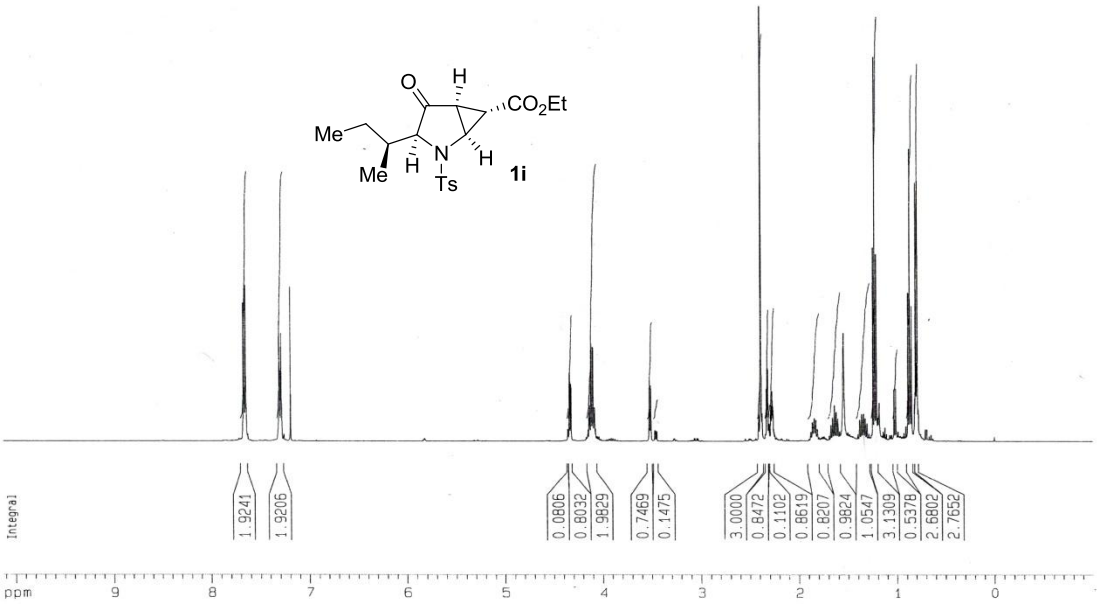

TsO
O
H
CO2Et
Ha
Hb
N
Ts
H
1g'
in C6D6
vij-tyr-4
no of cycle:1
Hb
Ha
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

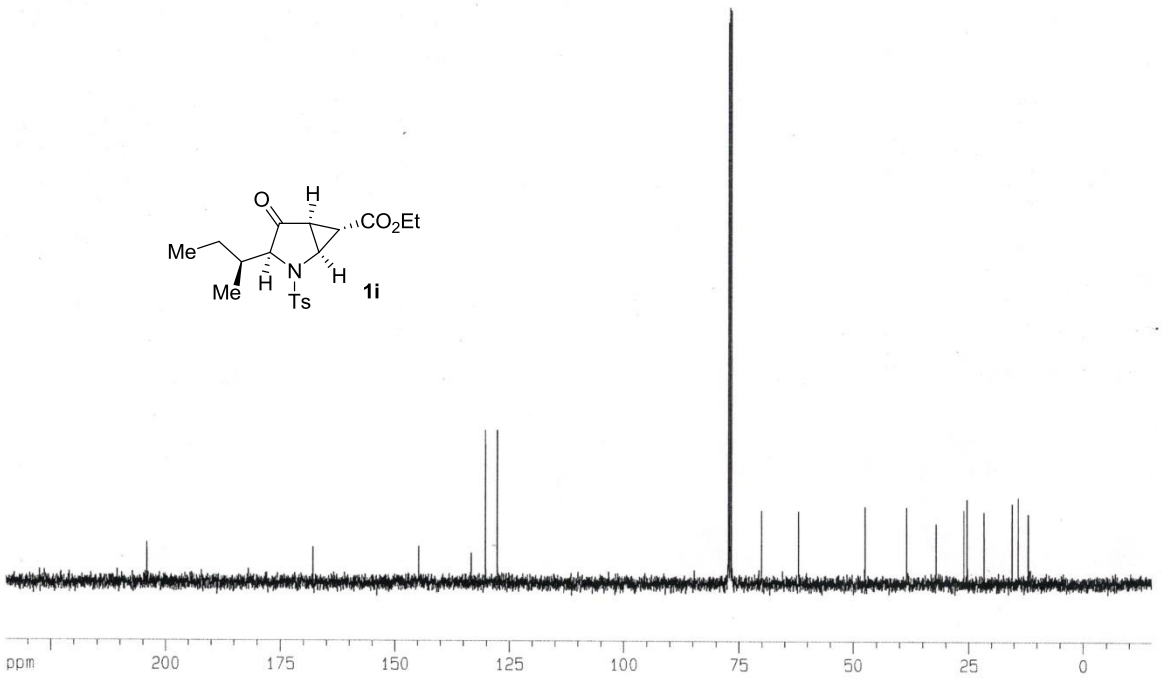

Me
O
H
CO2Et
Me
N
H
H
Ts
1h
9
8
7
6
5
4
3
2
1
0 ppm
2.410
2.310
1.000
2.531
1.045
3.288
1.076
1.033
1.402
1.352
1.249
3.932
6.949

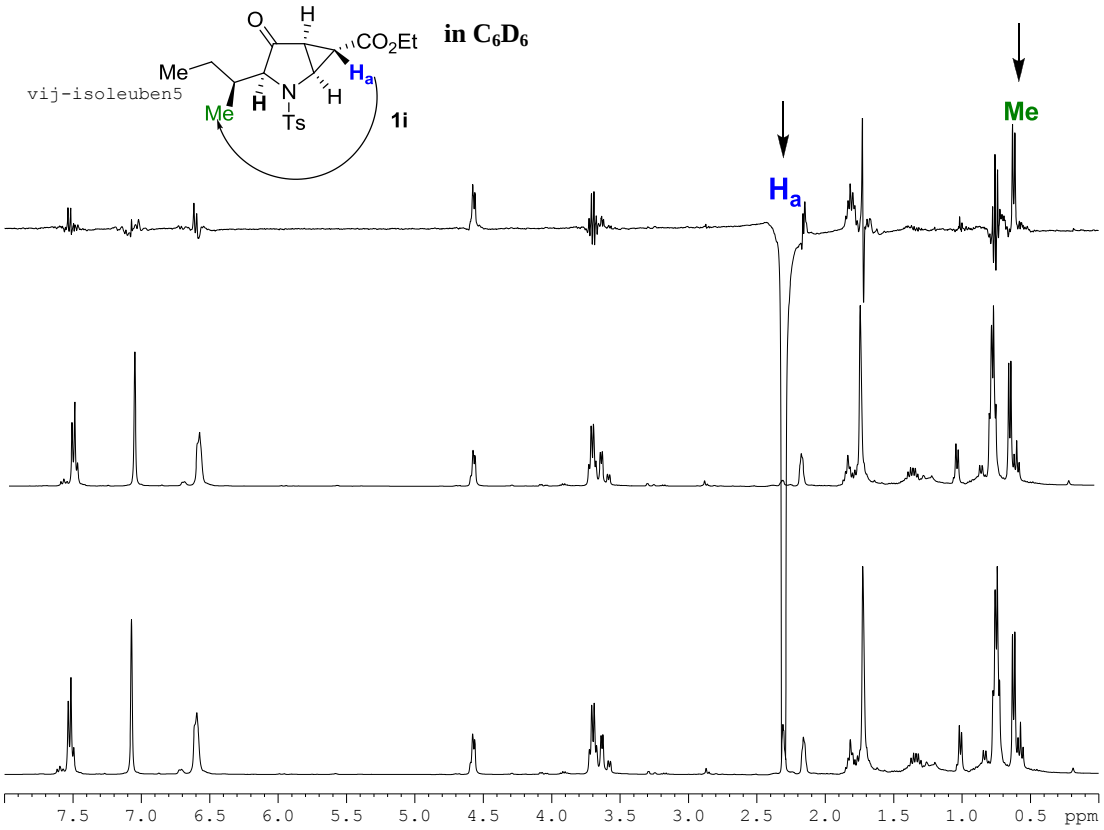

Me
O
H
CO2Et
Me
N
H
H
Ts
1h
220
200
180
160
140
120
100
80
60
40
20
0 ppm

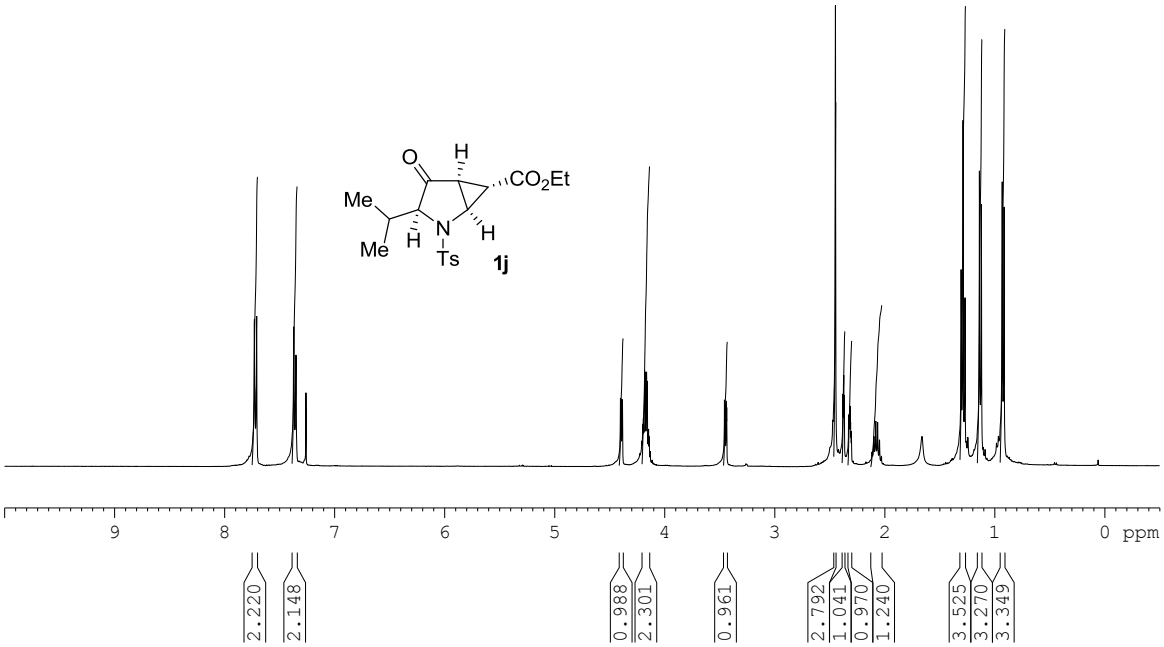

O
CO2Et
Me
Me
N
H
Ts
4
9
8
7
6
5
4
3
2
1
0 ppm
3.017
2.057
1.000
1.019
2.150
3.253
3.671
1.211
7.309
3.158

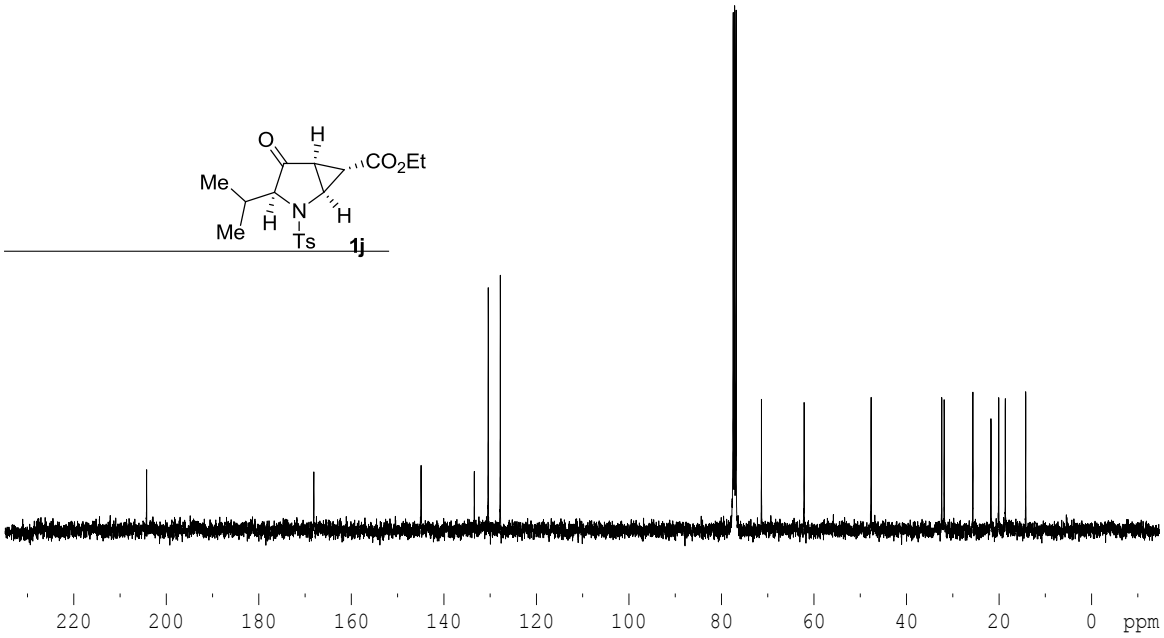

O
CO2Et
Me
Me
N
H
Ts
4
220
200
180
160
140
120
100
80
60
40
20
0 ppm

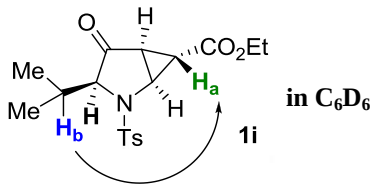

O
H
CO2Et
Me
H
N
H
Me
Ts
1i
Integral
1.9241
1.9206
0.0806
0.8032
1.9829
0.7469
0.1475
3.0000
0.8472
0.1102
0.8619
0.8207
0.9824
1.0547
3.1309
0.5378
2.6802
2.7652
ppm
9
8
7
6
5
4
3
2
1
0


O
H
CO2Et
Me
H
N
H
Me
Ts
1i
ppm
200
175
150
125
100
75
50
25
0

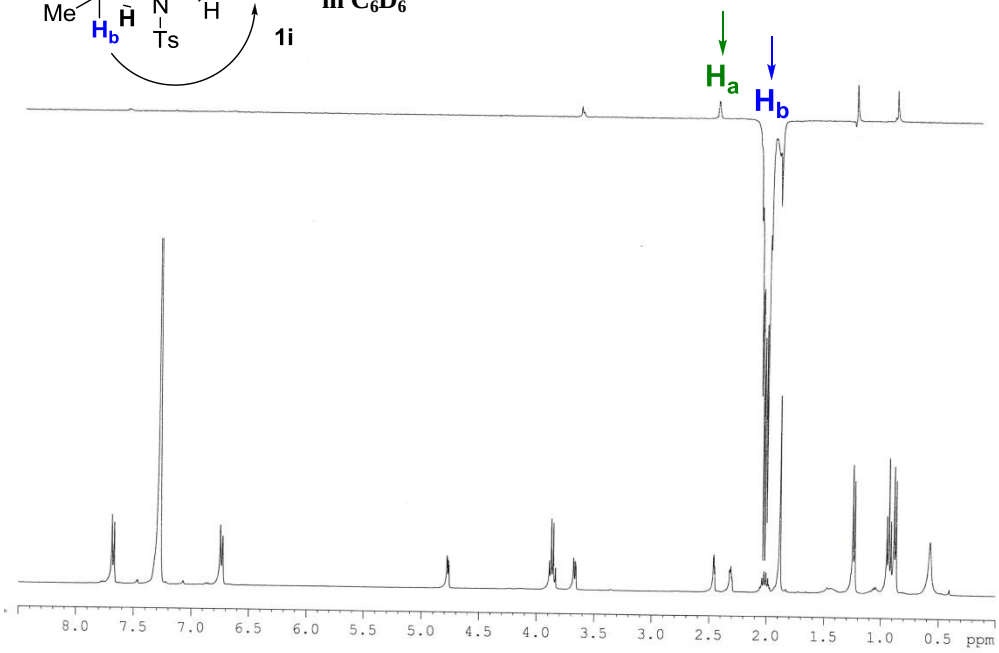

vij-isoleuben5
in C6D6
1i
Ha
Me
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

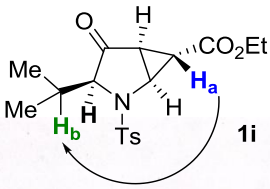

O
H
CO2Et
Me
Me
H
N
Ts
H
1j
9
8
7
6
5
4
3
2
1
0 ppm
2.220
2.148
0.988
2.301
0.961
2.792
1.041
0.970
1.240
3.525
3.270
3.349


O
H
CO2Et
Me
Me
H
N
Ts
H
1j
220
200
180
160
140
120
100
80
60
40
20
0 ppm

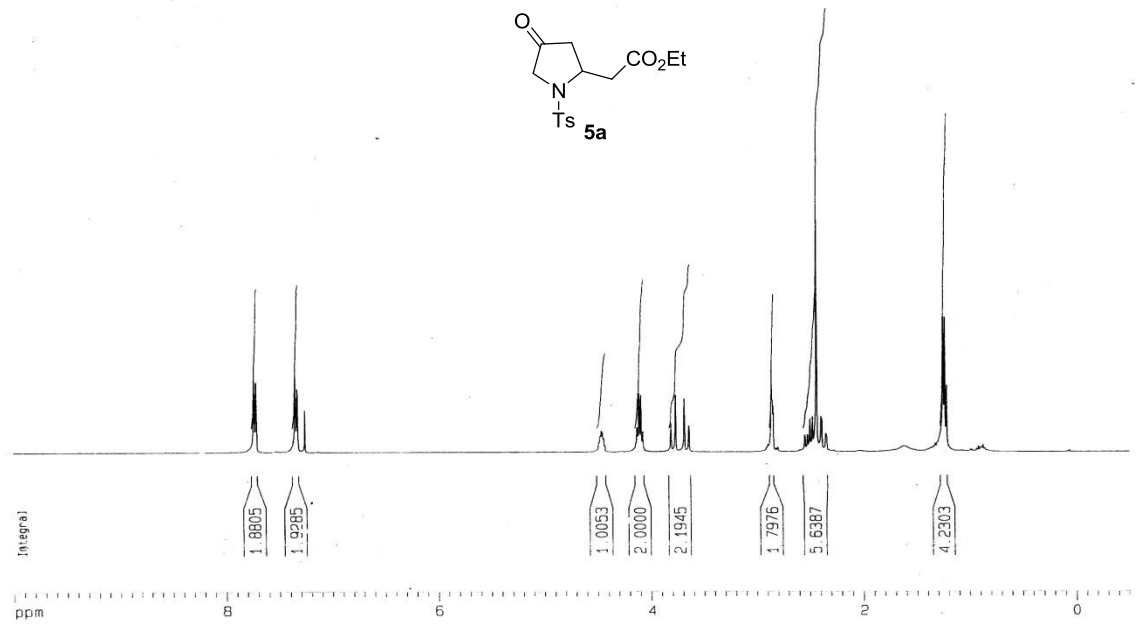


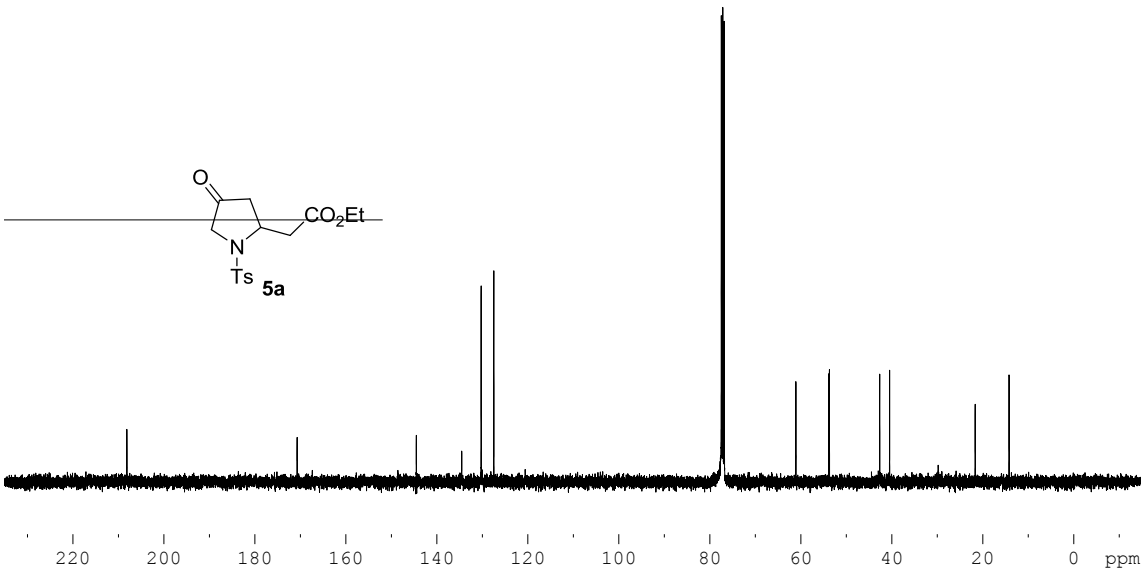
1i **in C_6D_6**

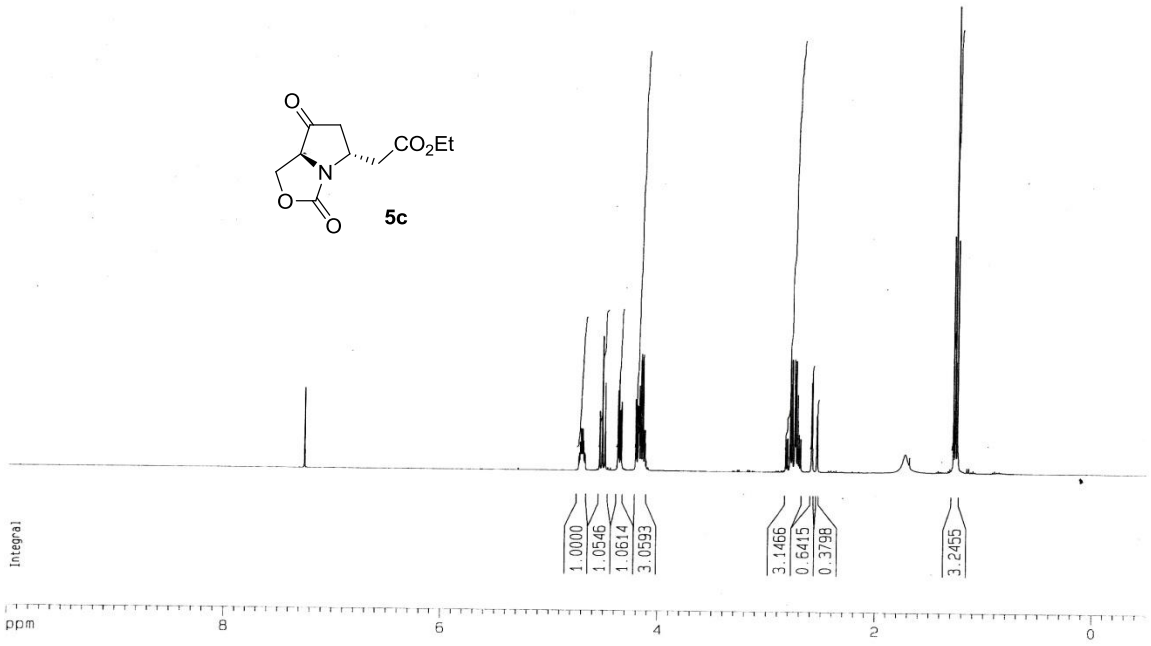


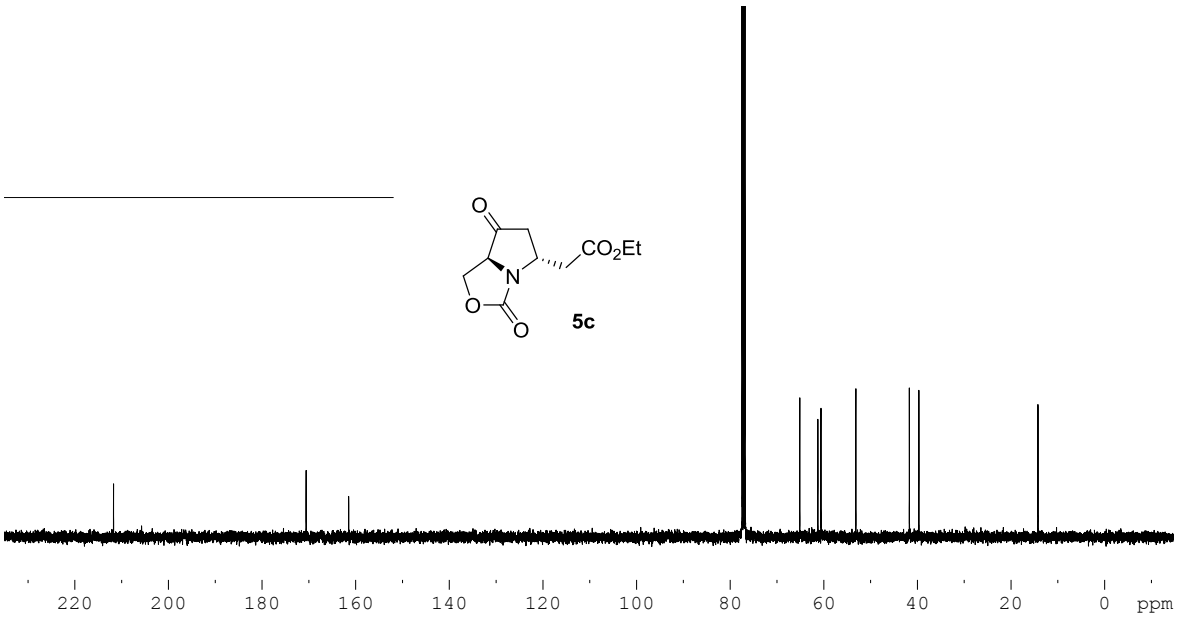


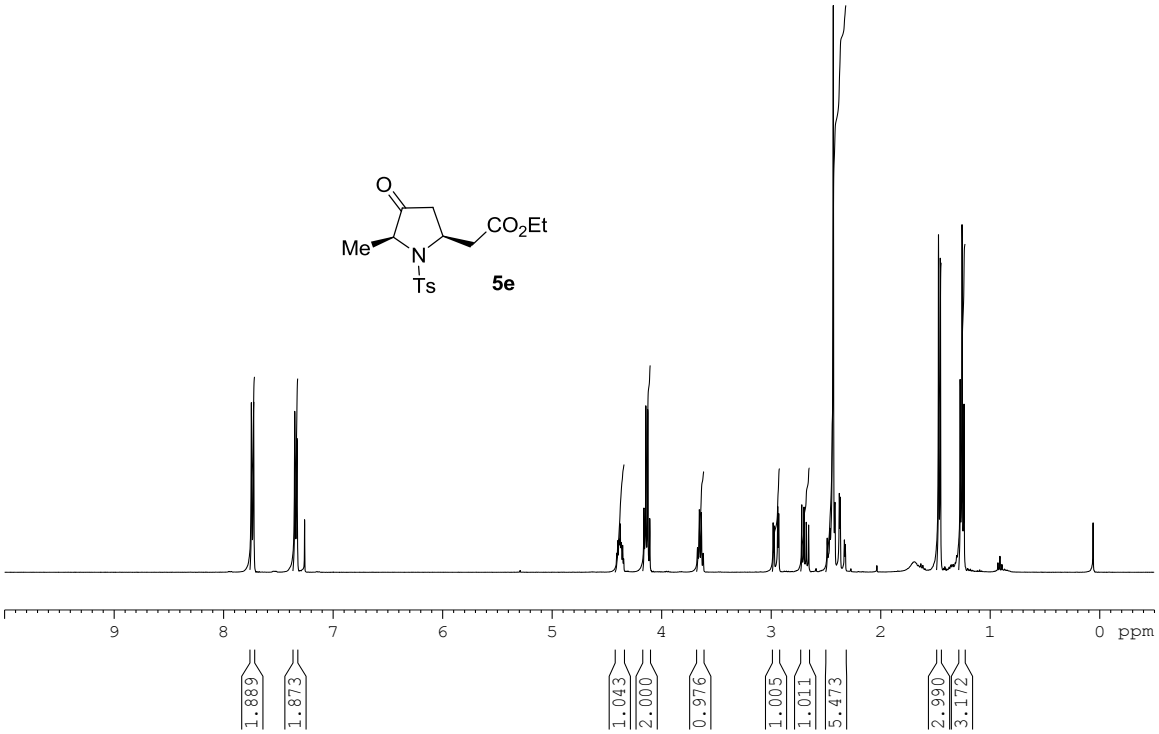
1i **in C_6D_6**

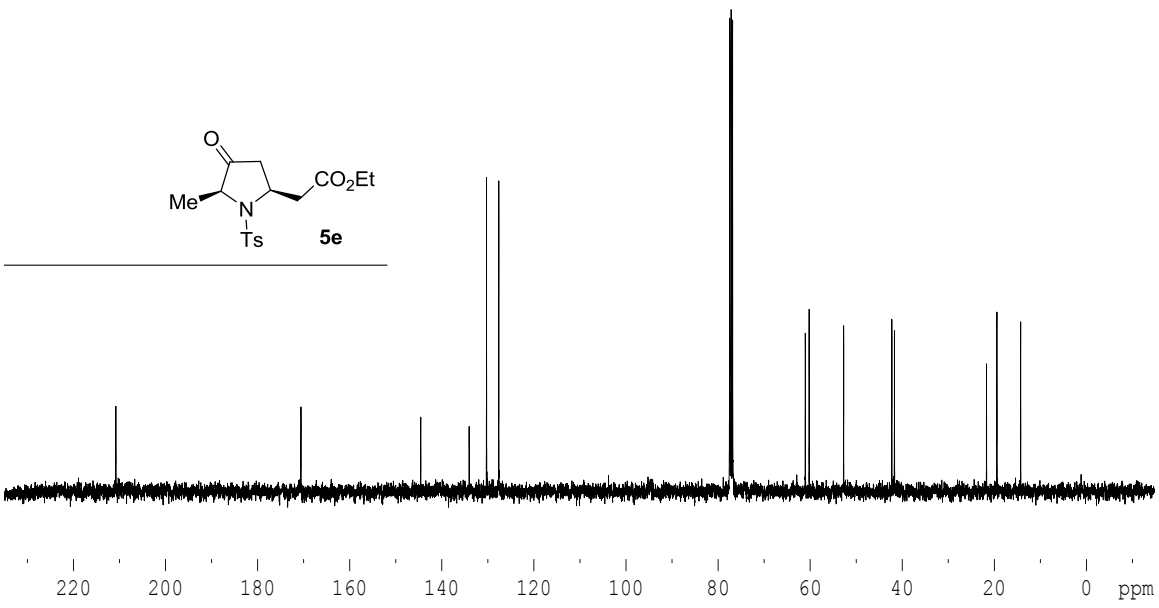

O
CO2Et
N
Ts
5a
Integral
1.0805
1.9285
1.0053
2.0000
2.1945
1.7976
5.6387
4.2303
ppm
8
6
4
2
0

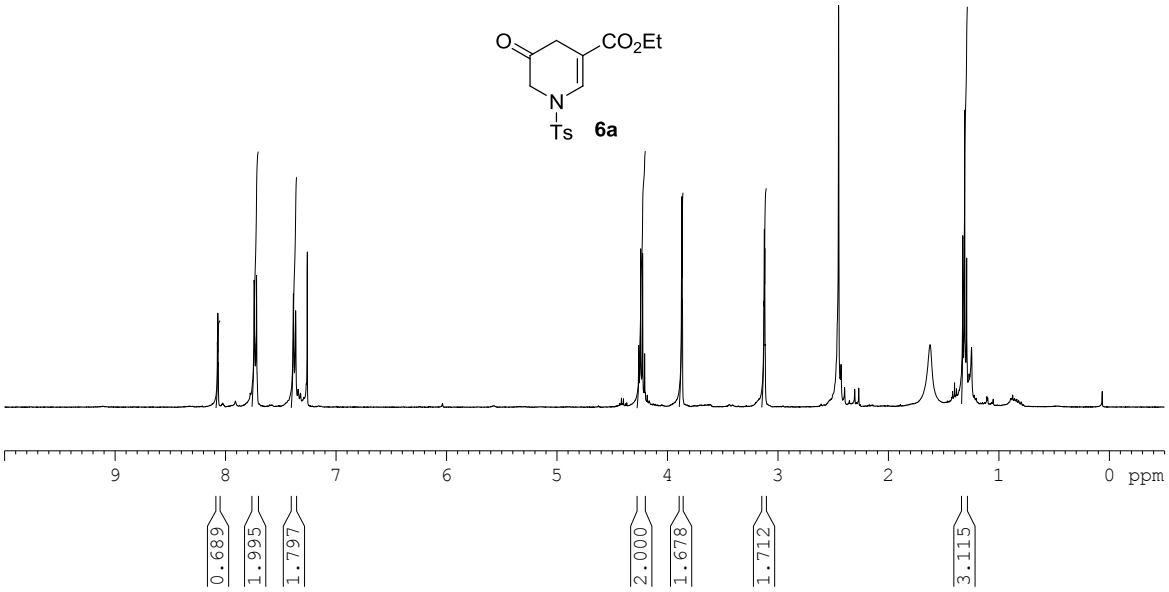

O
CO2Et
N
Ts
5a
220
200
180
160
140
120
100
80
60
40
20
0
ppm

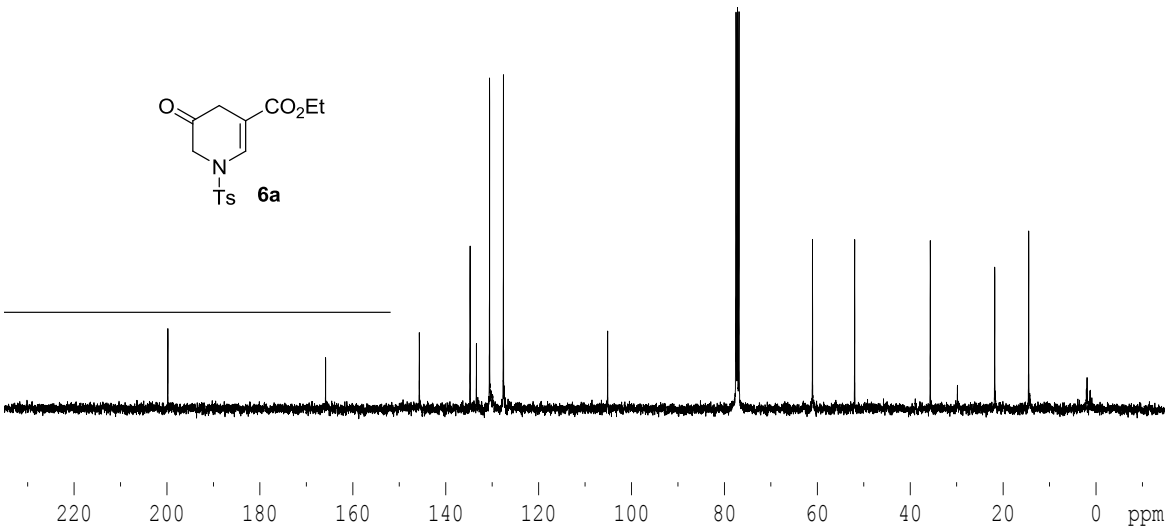

O
CO2Et
N
O
O
5c
Integral
1.0000
1.0546
1.0614
3.0593
3.1466
0.6415
0.3798
3.2455
ppm
8
6
4
2
0

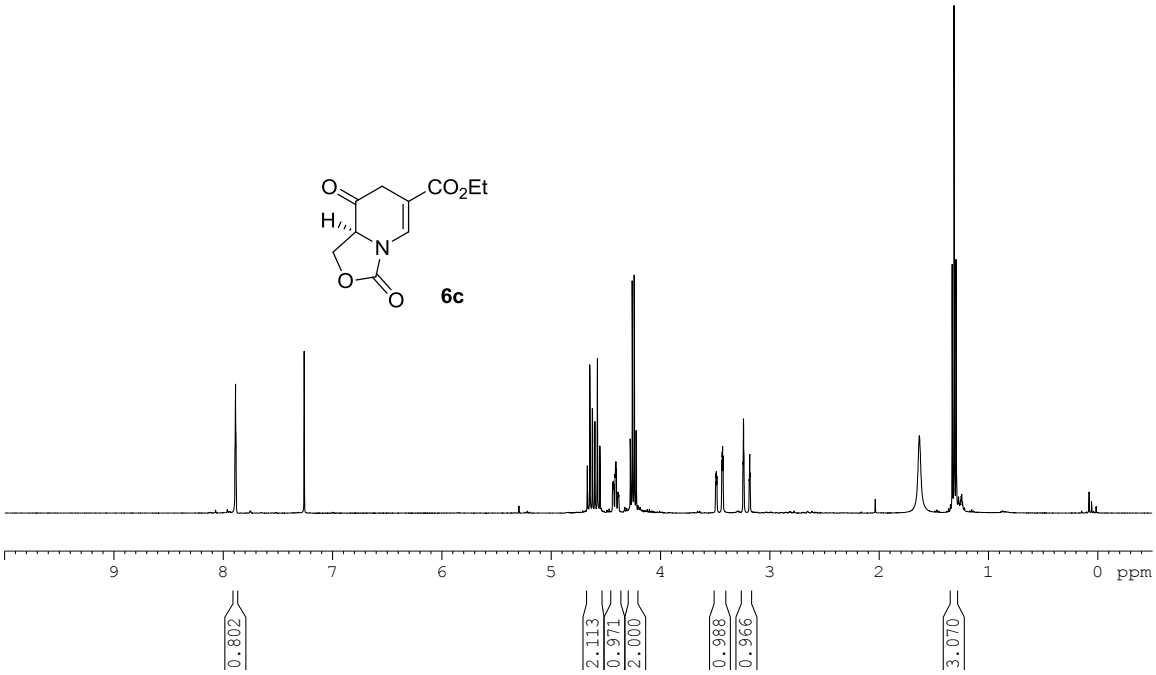

O
CO2Et
N
O
O
5c
220
200
180
160
140
120
100
80
60
40
20
0
ppm

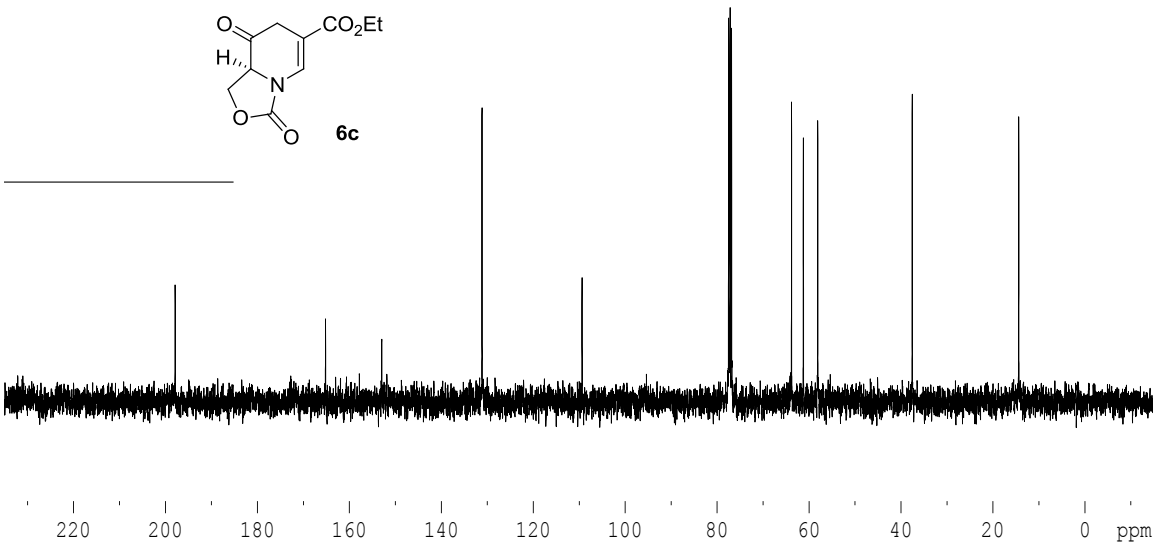

O
CO2Et
Me
N
Ts
5e
9
8
7
6
5
4
3
2
1
0 ppm
1.889
1.873
1.043
2.000
0.976
1.005
1.011
5.473
2.990
3.172

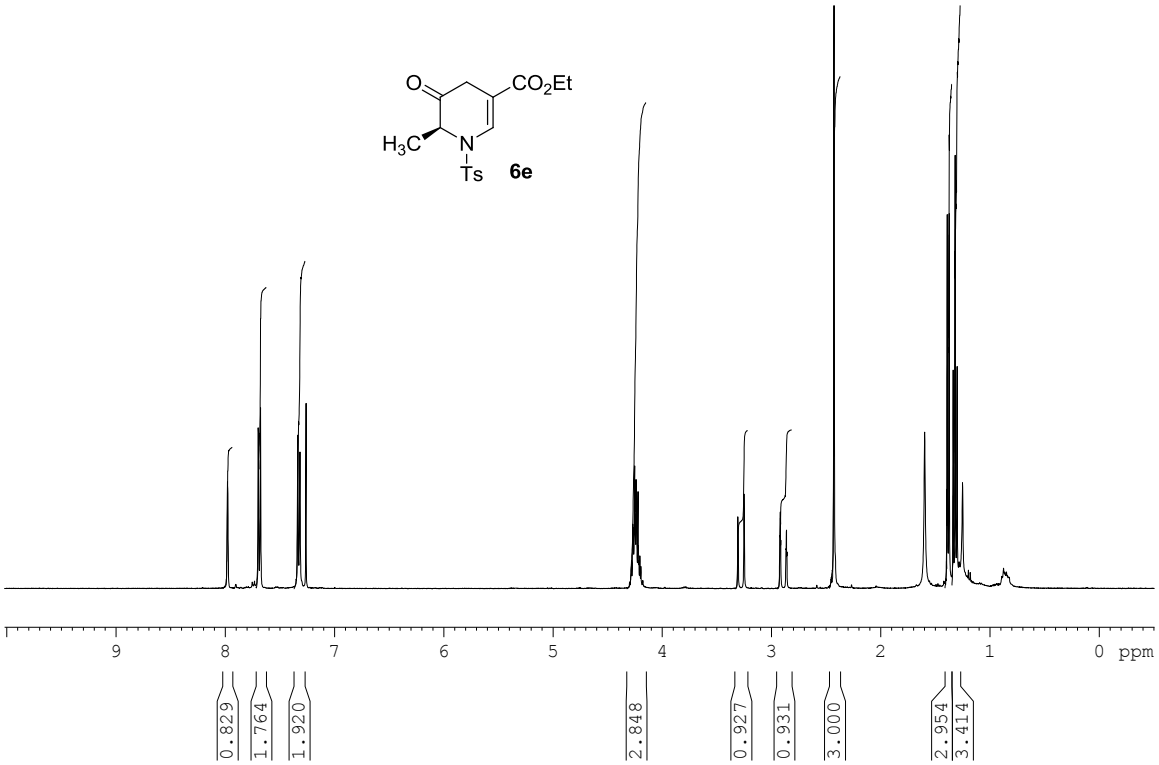

O
CO2Et
Me
N
Ts
5e
220
200
180
160
140
120
100
80
60
40
20
0 ppm

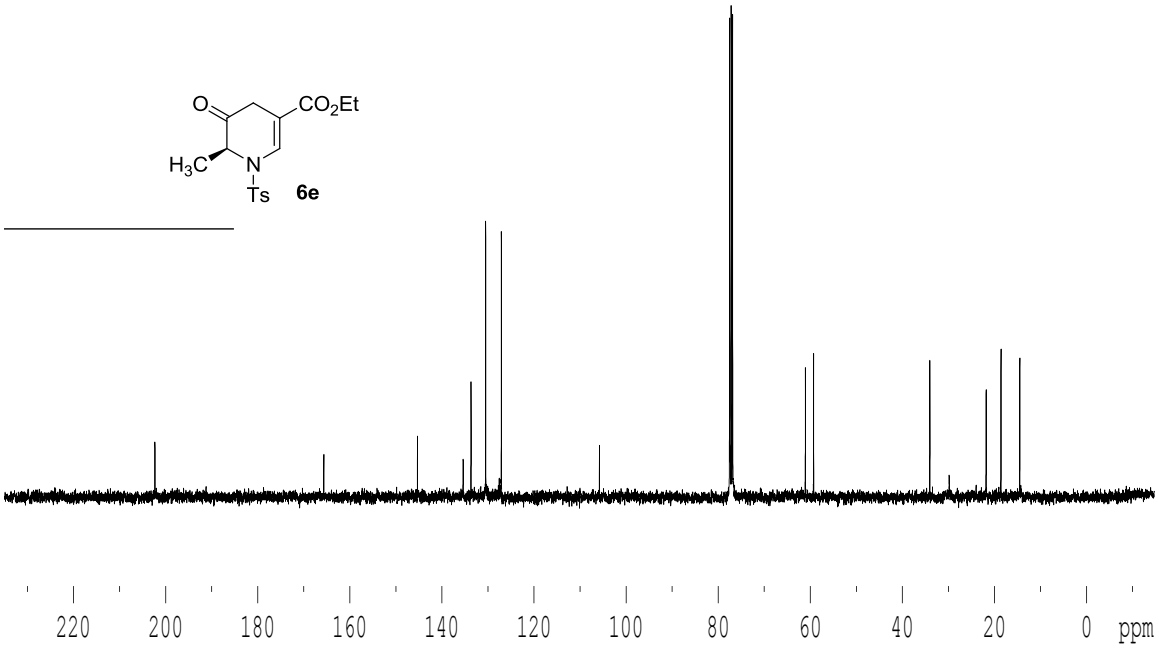

O
CO2Et
N
Ts
6a
9
8
7
6
5
4
3
2
1
0 ppm
0.689
1.995
1.797
2.000
1.678
1.712
3.115

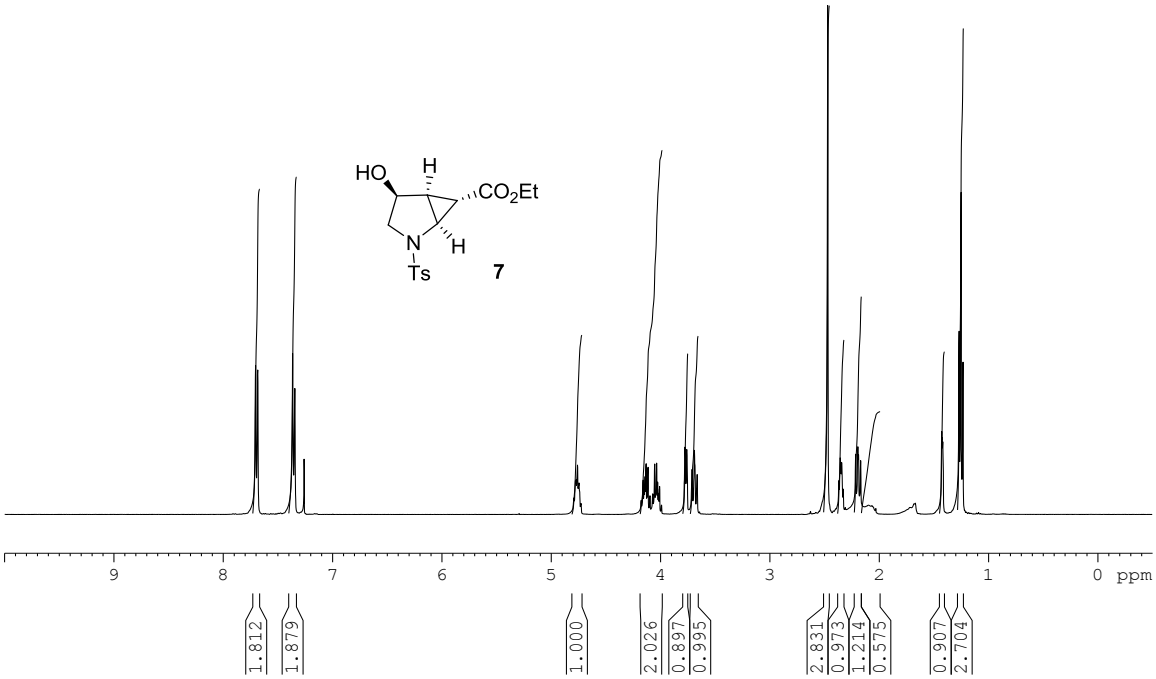

O
CO2Et
N
Ts
6a
220
200
180
160
140
120
100
80
60
40
20
0 ppm

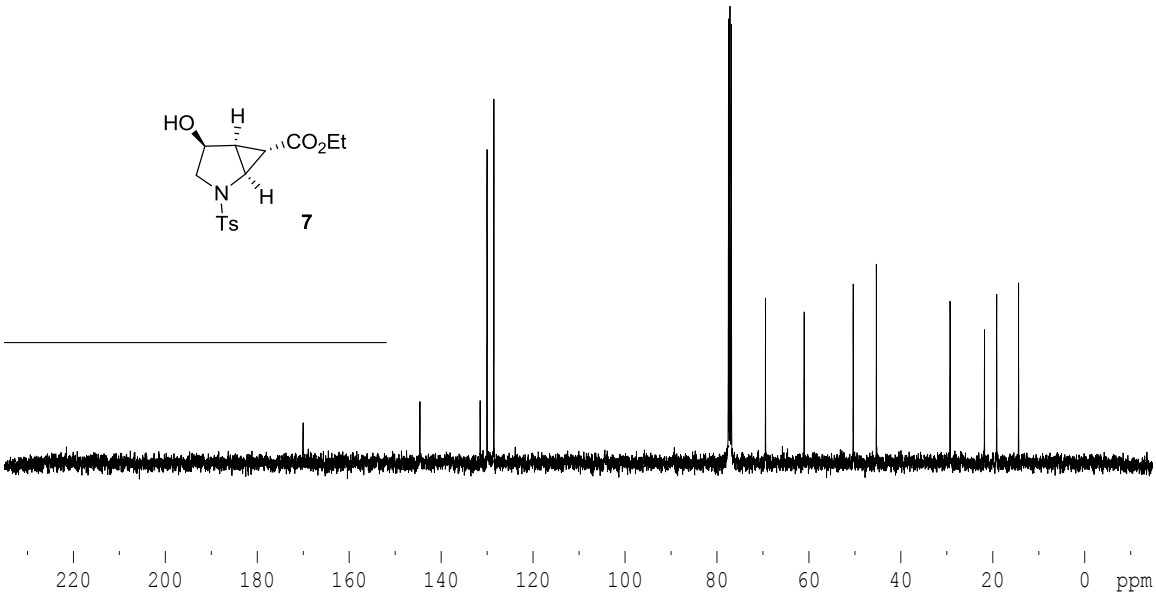

O
CO2Et
H
N
O
O
6c
9
8
7
6
5
4
3
2
1
0 ppm
0.802
2.113
0.971
2.000
0.988
0.966
3.070

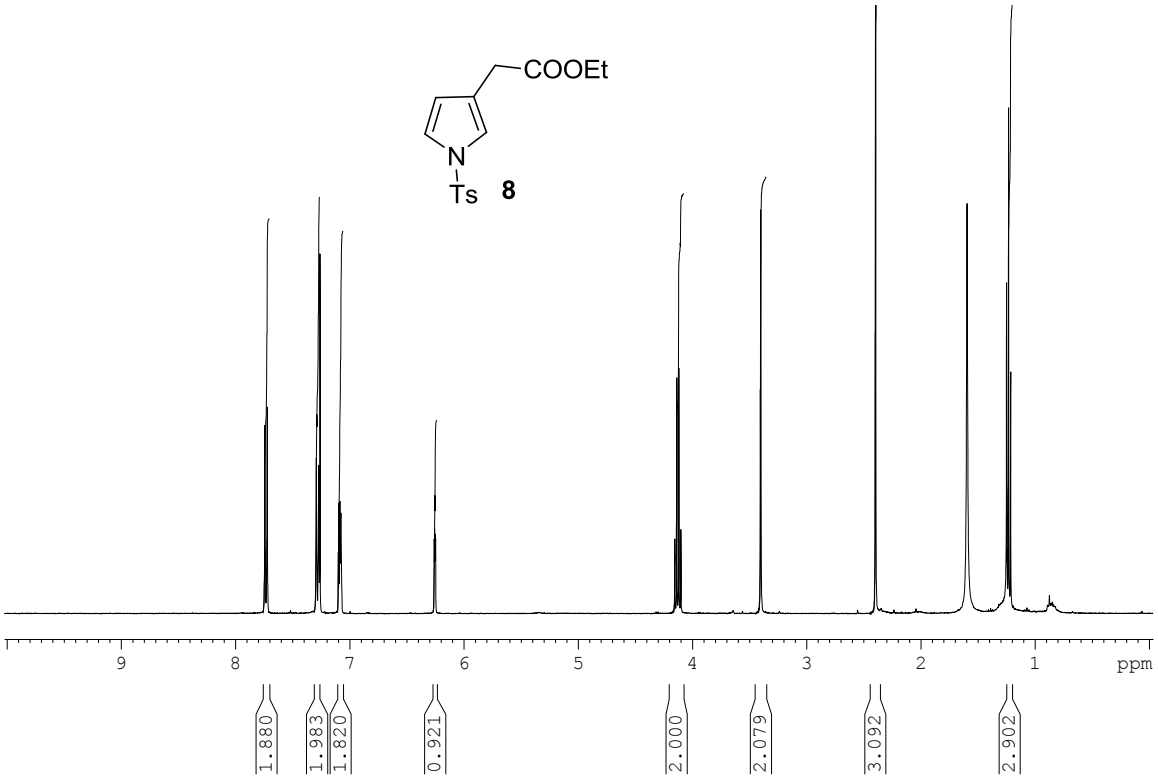

O
CO2Et
H
N
O
O
6c
220
200
180
160
140
120
100
80
60
40
20
0 ppm

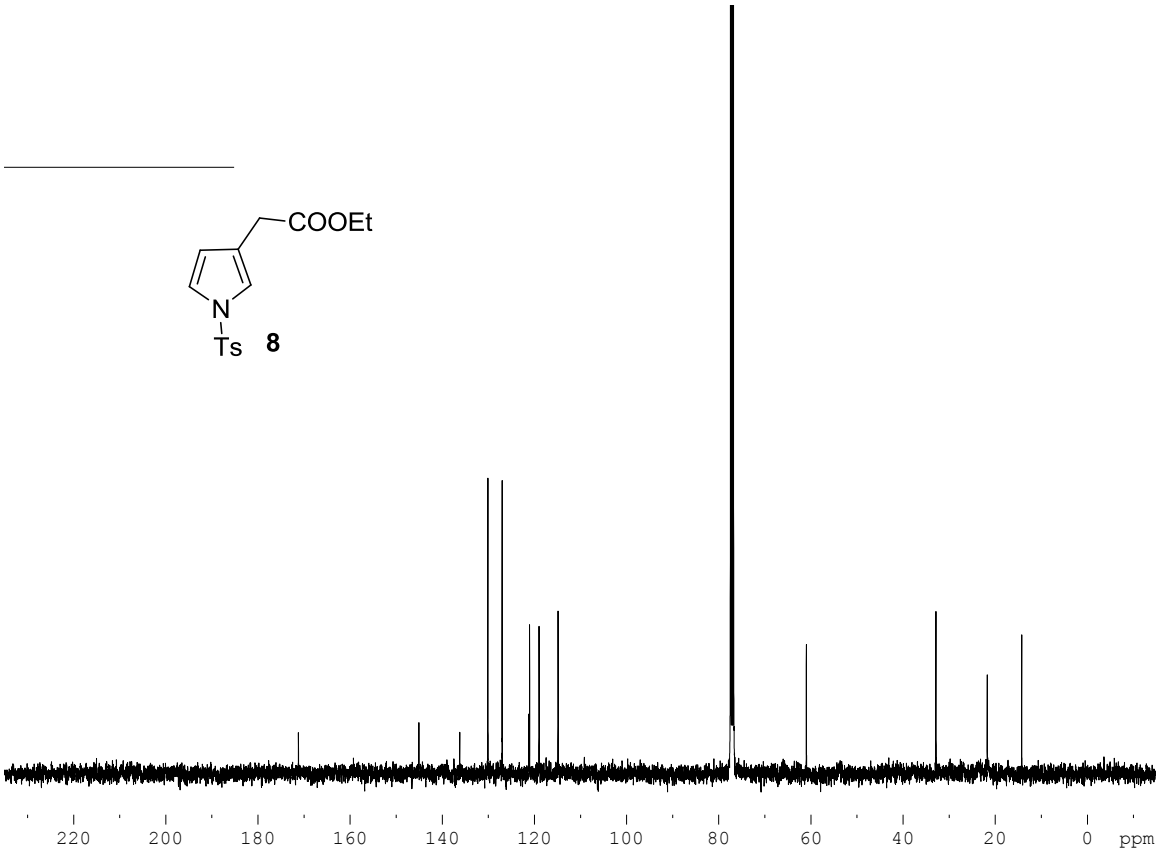

O
CO2Et
H3C
N
Ts
6e
9
8
7
6
5
4
3
2
1
0 ppm
0.829
1.764
1.920
2.848
0.927
0.931
3.000
2.954
3.414

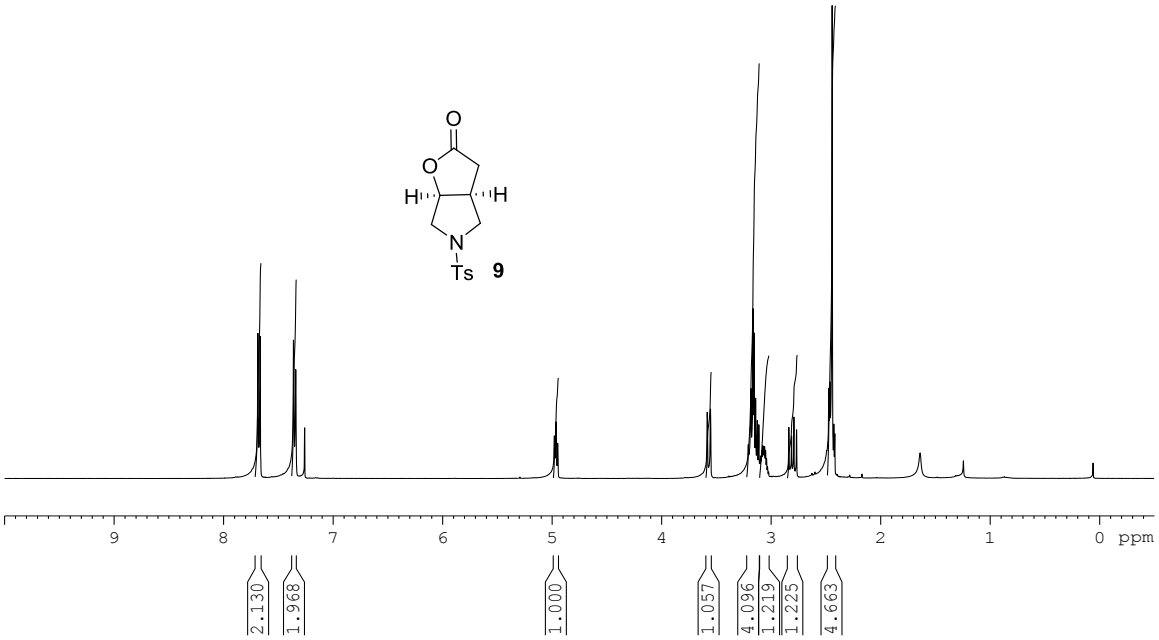

O
CO2Et
H3C
N
Ts
6e
220
200
180
160
140
120
100
80
60
40
20
0 ppm

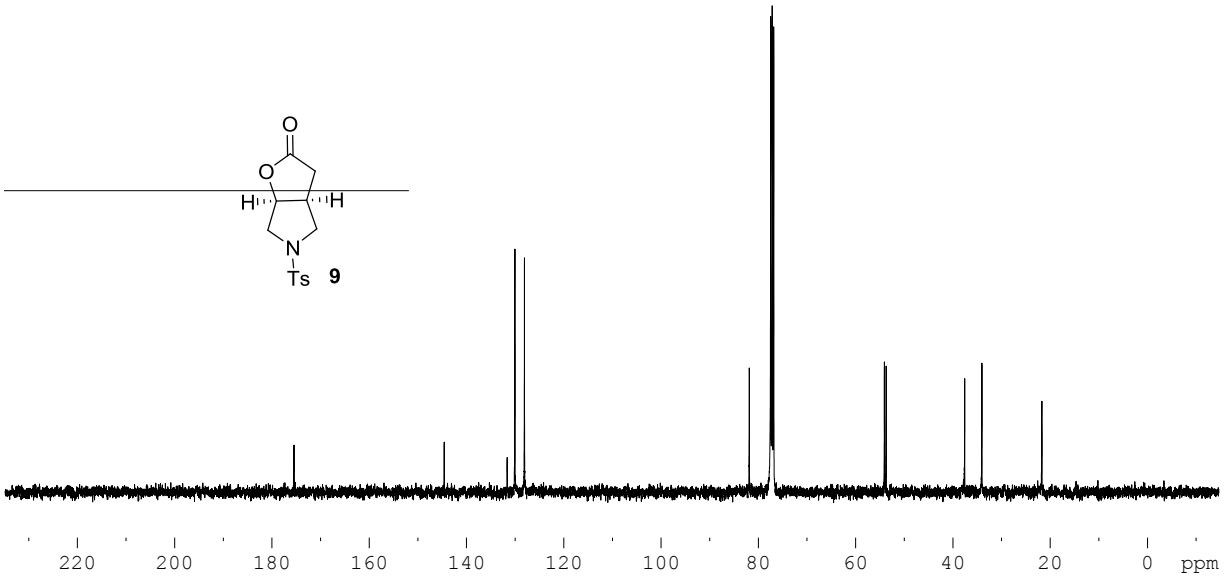

HO
H
CO2Et
N
H
Ts
7
9
8
7
6
5
4
3
2
1
0 ppm
1.812
1.879
1.000
2.026
0.897
0.995
2.831
0.973
1.214
0.575
0.907
2.704

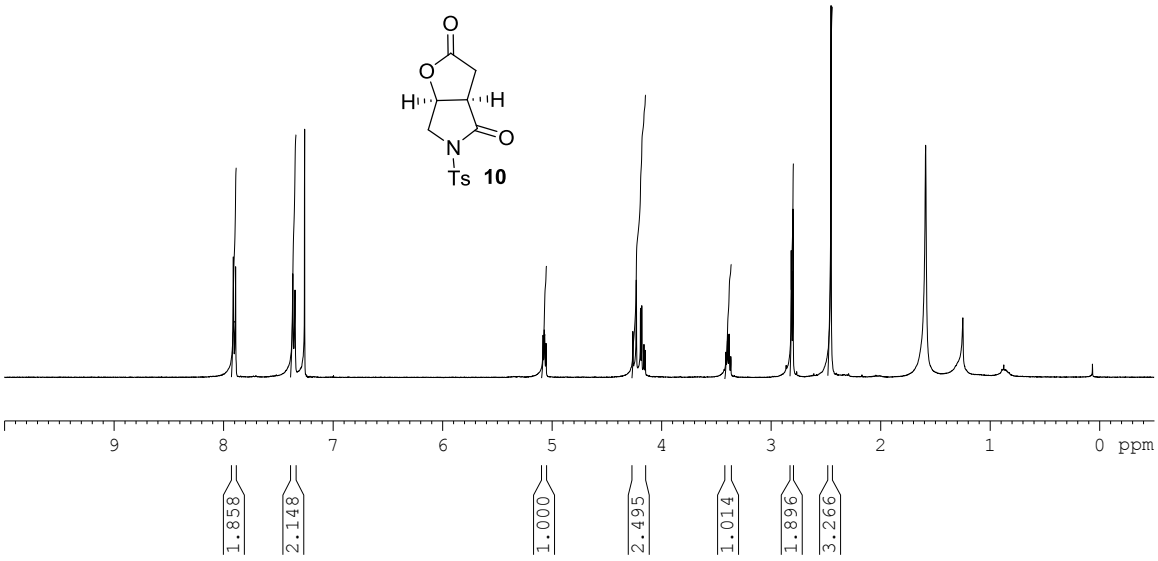

HO
H
CO2Et
N
H
Ts
7
220
200
180
160
140
120
100
80
60
40
20
0 ppm

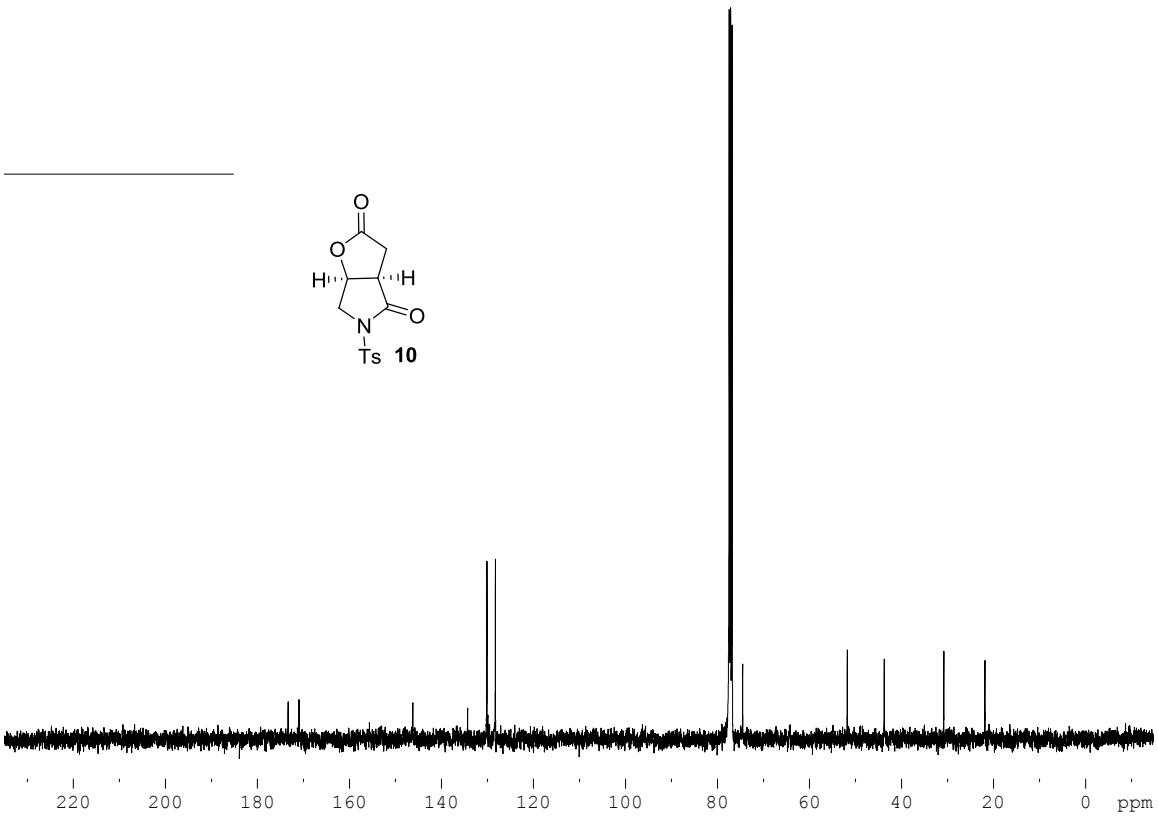

COOEt
N
Ts 8
9
8
7
6
5
4
3
2
1
ppm
1.880
1.983
1.820
0.921
2.000
2.079
3.092
2.902

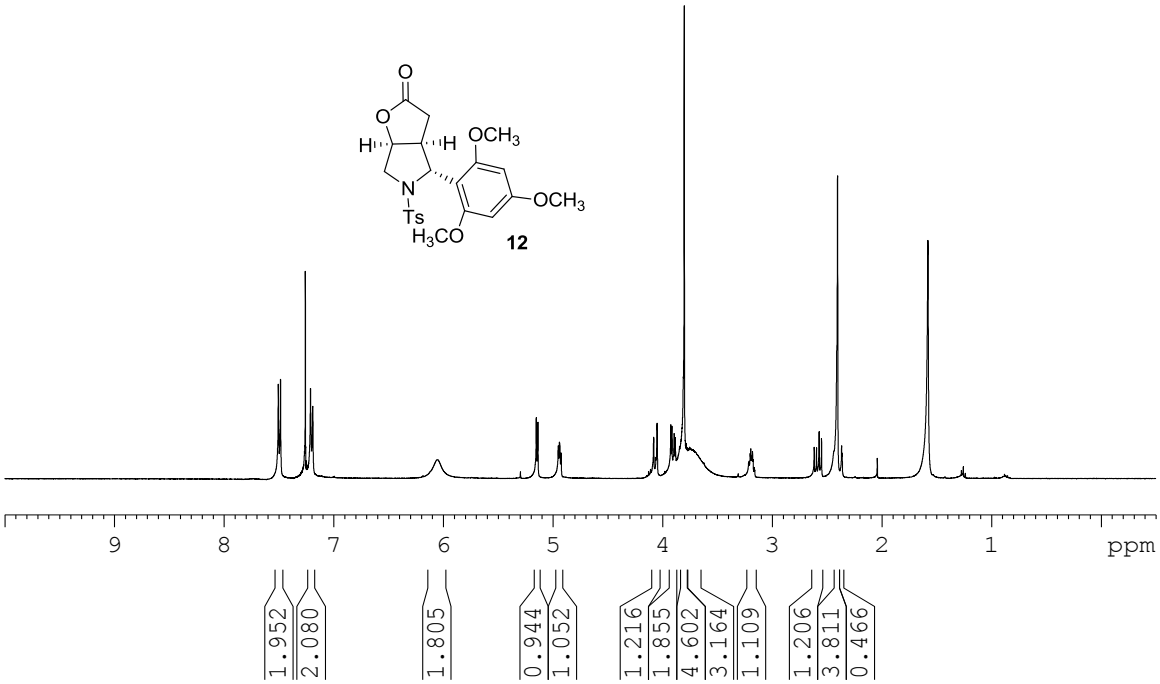

COOEt
N
Ts 8
220
200
180
160
140
120
100
80
60
40
20
0
ppm

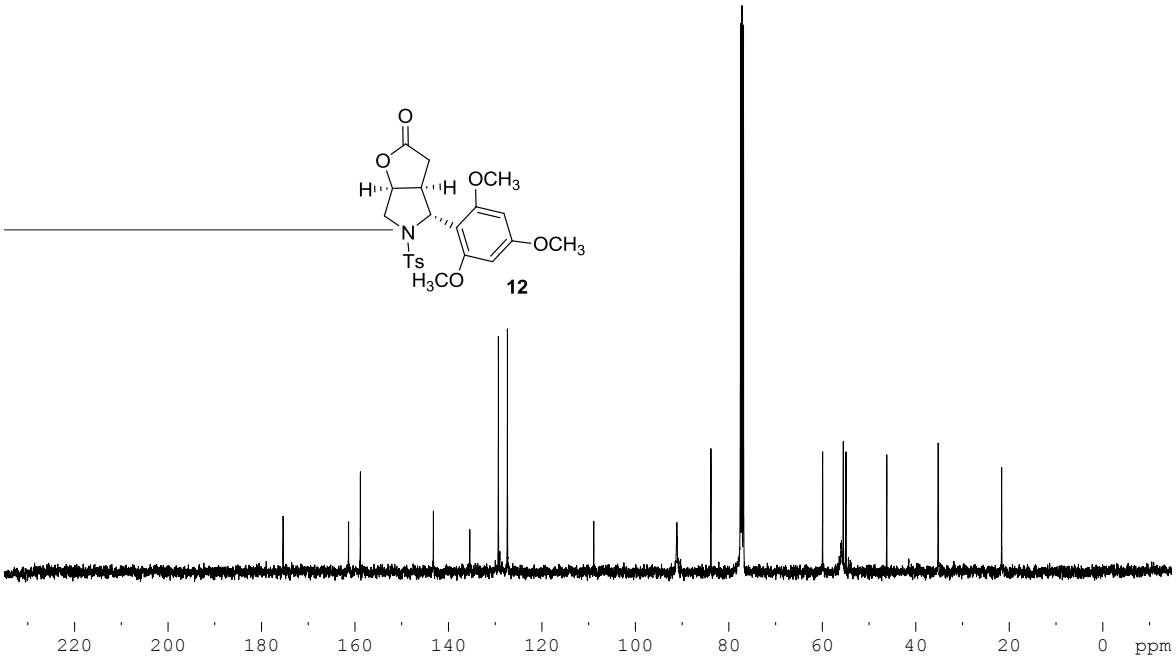

O
O
H
H
N
Ts 9
9 8 7 6 5 4 3 2 1 0 ppm
2.130
1.968
1.000
1.057
4.096
1.219
1.225
4.663

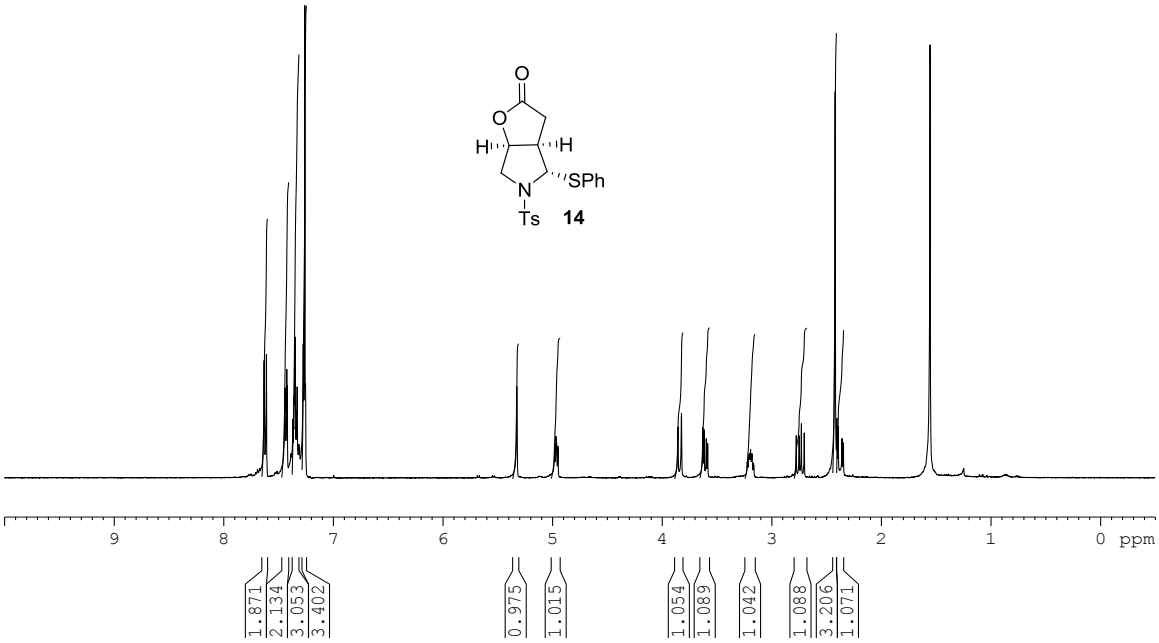

O
O
H
H
N
Ts 9
220 200 180 160 140 120 100 80 60 40 20 0 ppm

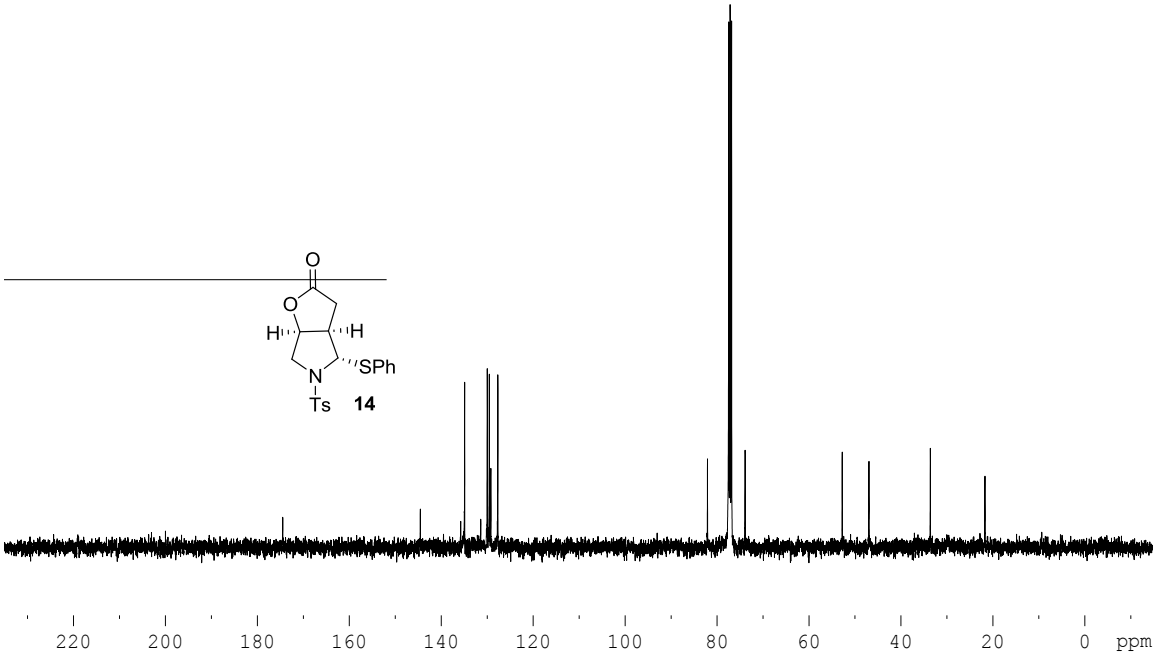

O
O
H
H
O
N
Ts 10
9
8
7
6
5
4
3
2
1
0 ppm
1.858
2.148
1.000
2.495
1.014
1.896
3.266

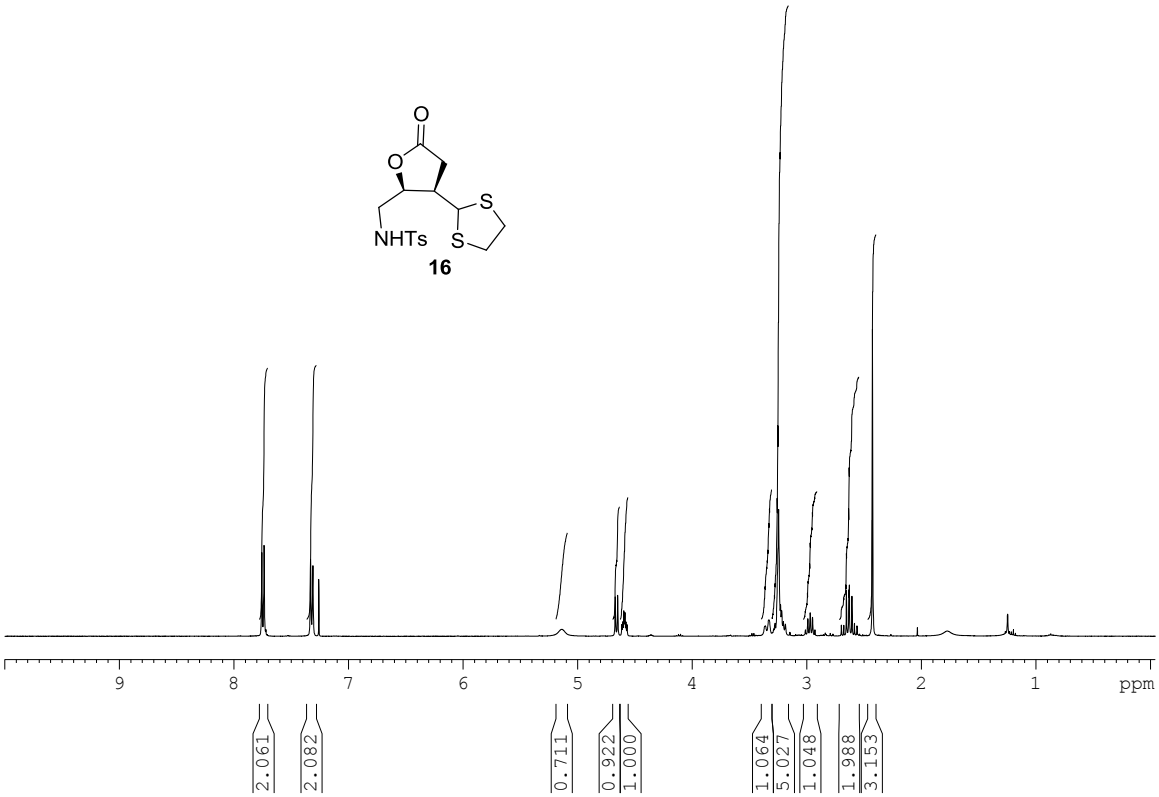

O
O
H
H
O
N
Ts 10
220
200
180
160
140
120
100
80
60
40
20
0 ppm

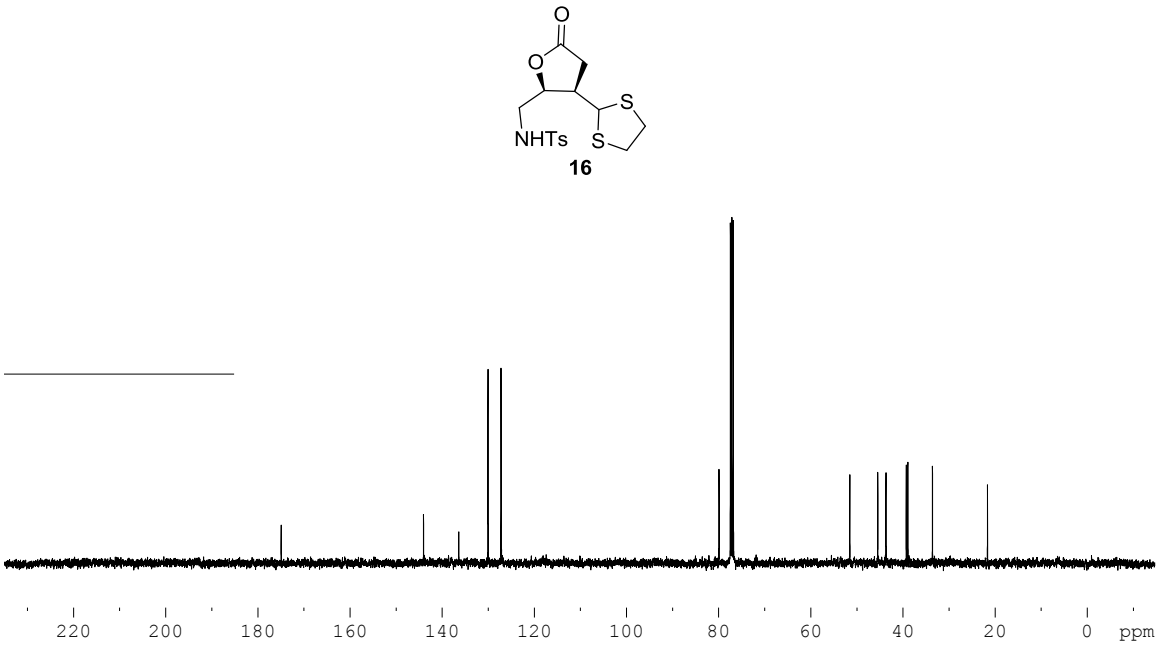

O
O
H
H
OCH3
N
Ts
H3CO
OCH3
12
9
8
7
6
5
4
3
2
1
ppm
1.952
2.080
1.805
0.944
1.052
1.216
1.855
4.602
3.164
1.109
1.206
3.811
0.466

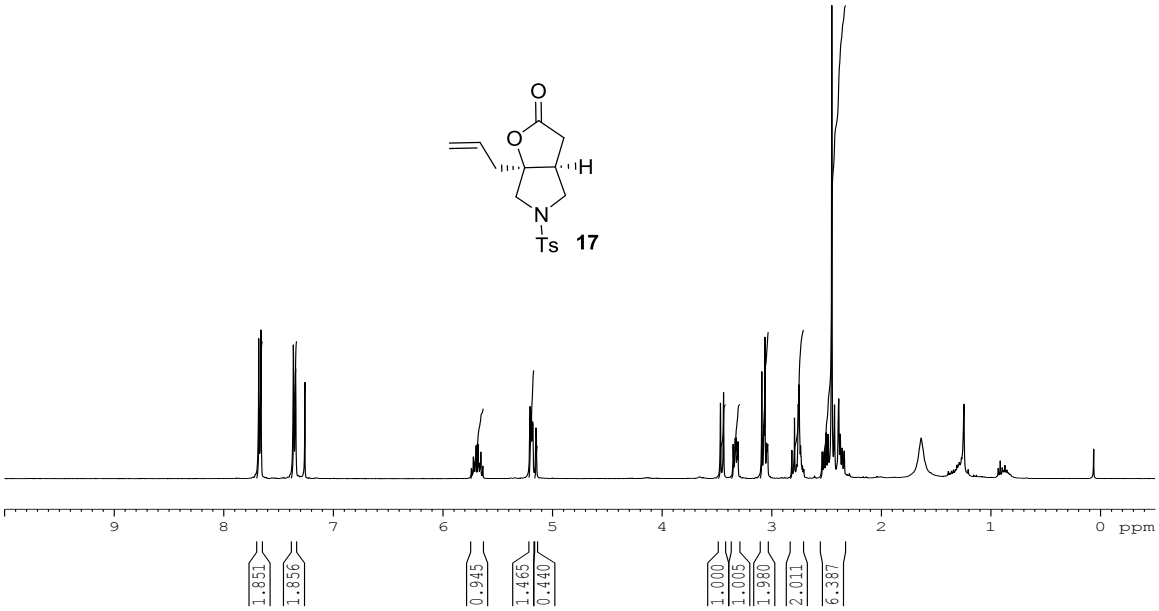

O
O
H
H
OCH3
N
Ts
H3CO
OCH3
12
220
200
180
160
140
120
100
80
60
40
20
0
ppm

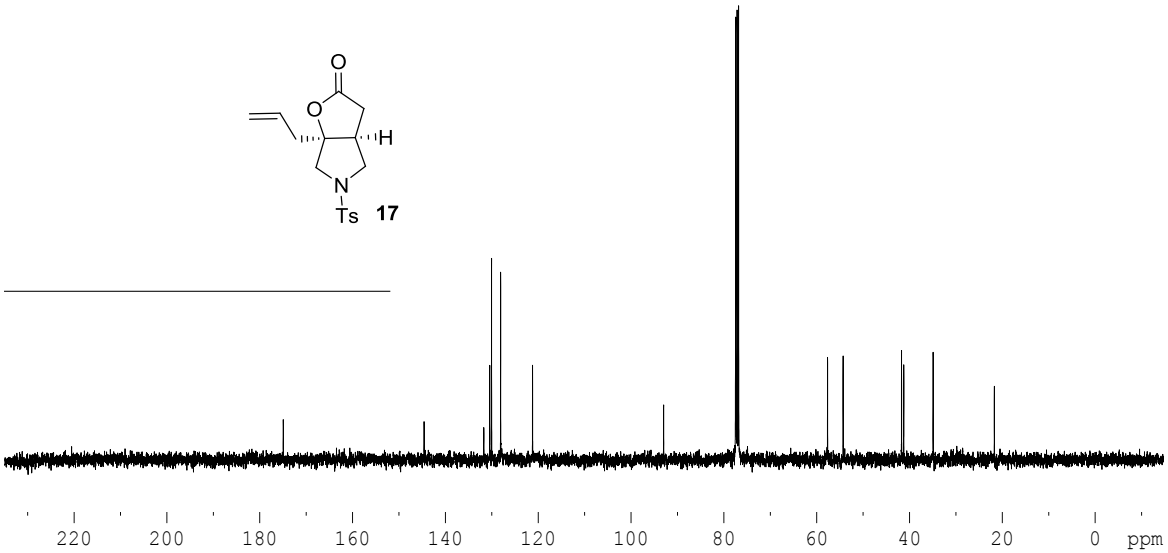

O
O
H
H
SPh
N
Ts
14
9
8
7
6
5
4
3
2
1
0 ppm
1.871
2.134
3.053
3.402
0.975
1.015
1.054
1.089
1.042
1.088
3.206
1.071

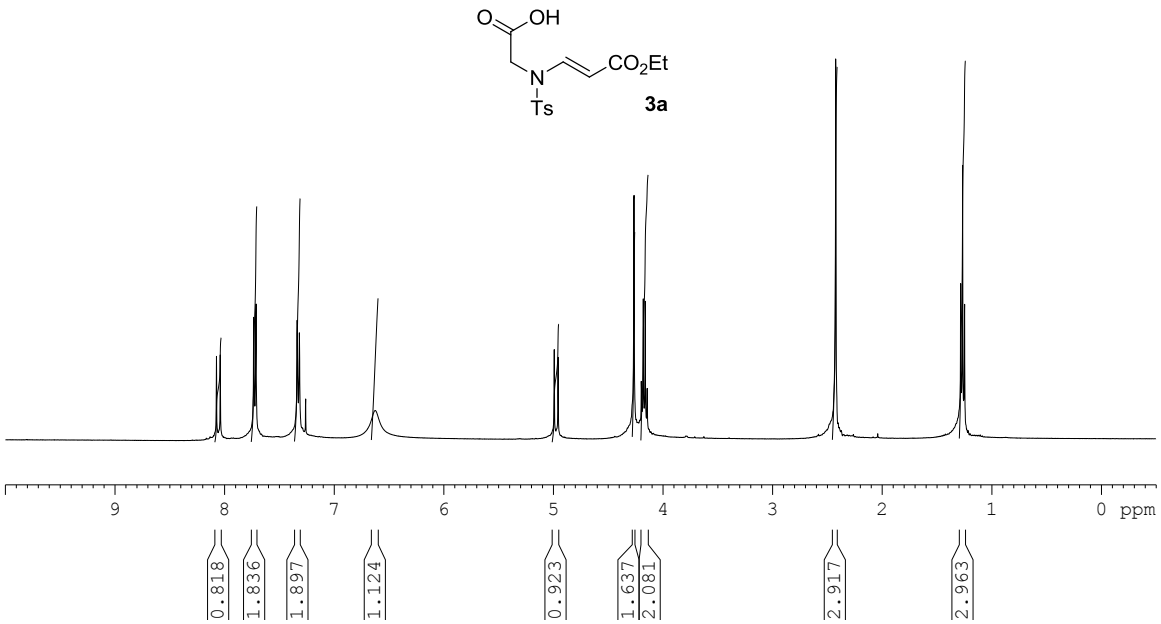

O
O
H
H
SPh
N
Ts
14
220
200
180
160
140
120
100
80
60
40
20
0 ppm

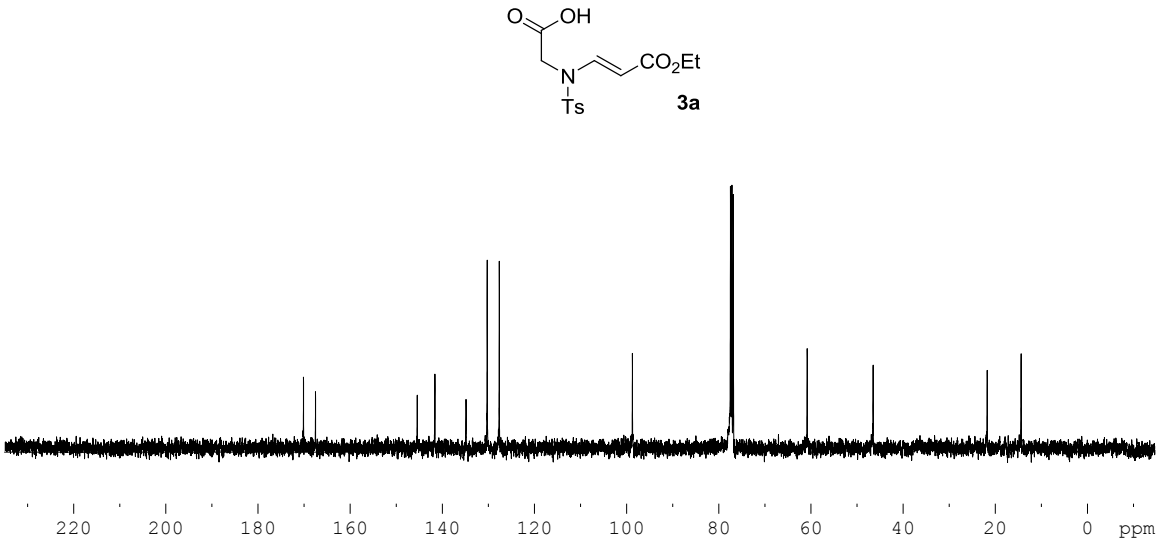

O
O
S
S
NHTs
16
9
8
7
6
5
4
3
2
1
ppm
2.061
2.082
0.711
0.922
1.000
1.064
5.027
1.048
1.988
3.153

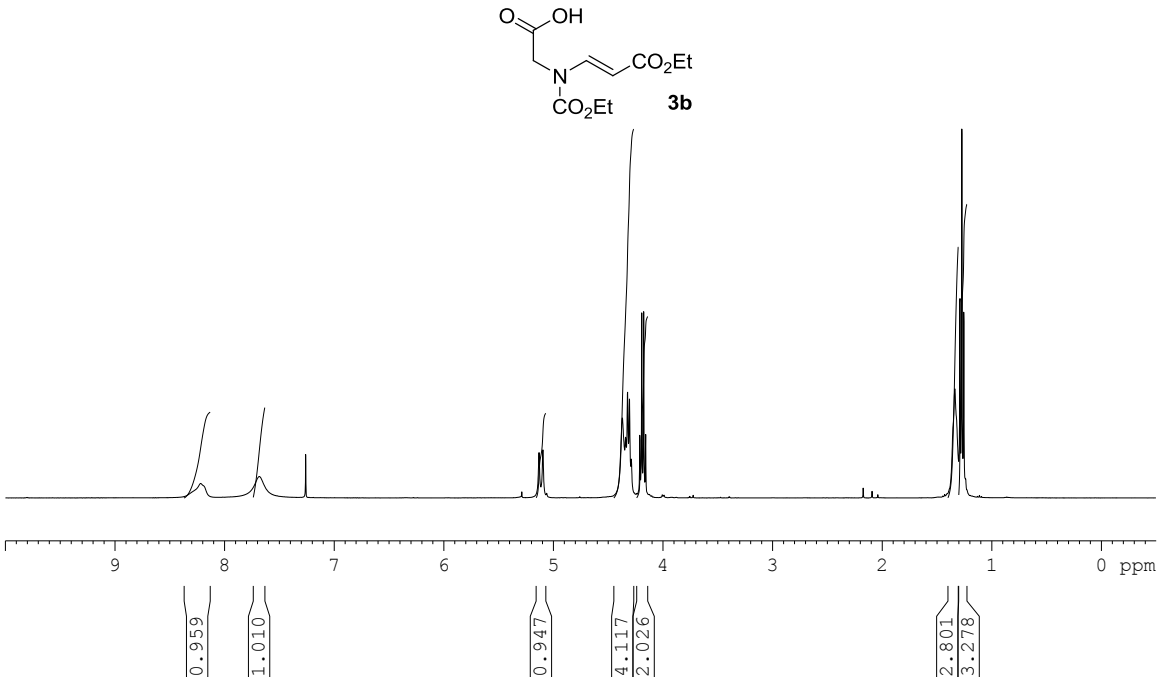

O
O
S
S
NHTs
16
220
200
180
160
140
120
100
80
60
40
20
0
ppm

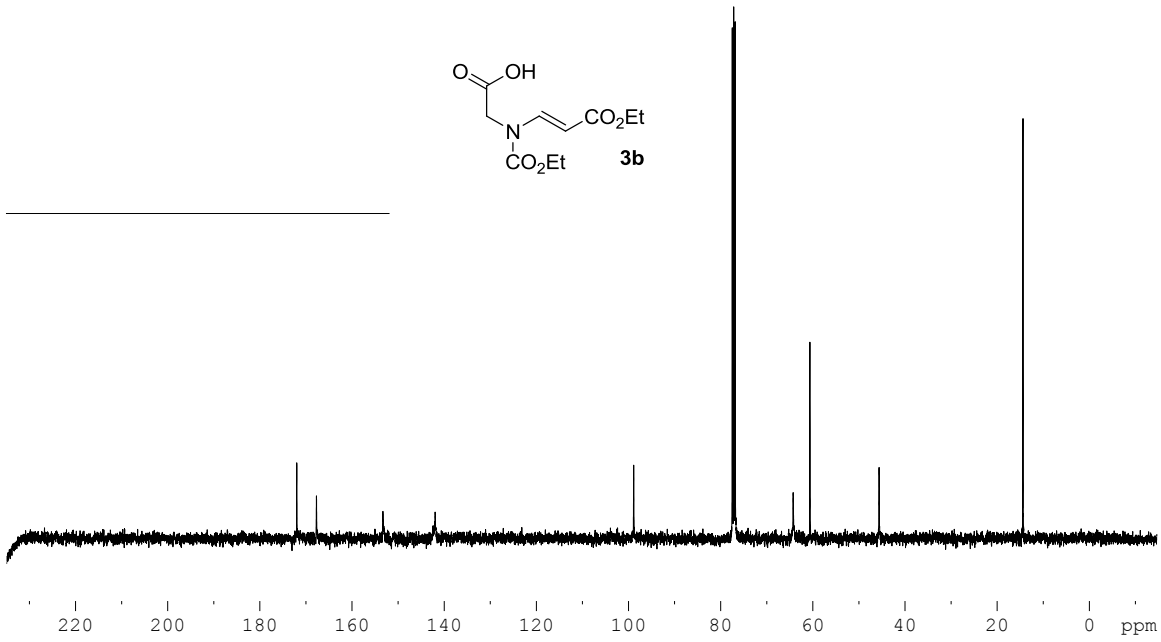

O
O
H
N
Ts
17
9
8
7
6
5
4
3
2
1
0 ppm
1.851
1.856
0.945
1.465
0.440
1.000
1.005
1.980
2.011
6.387

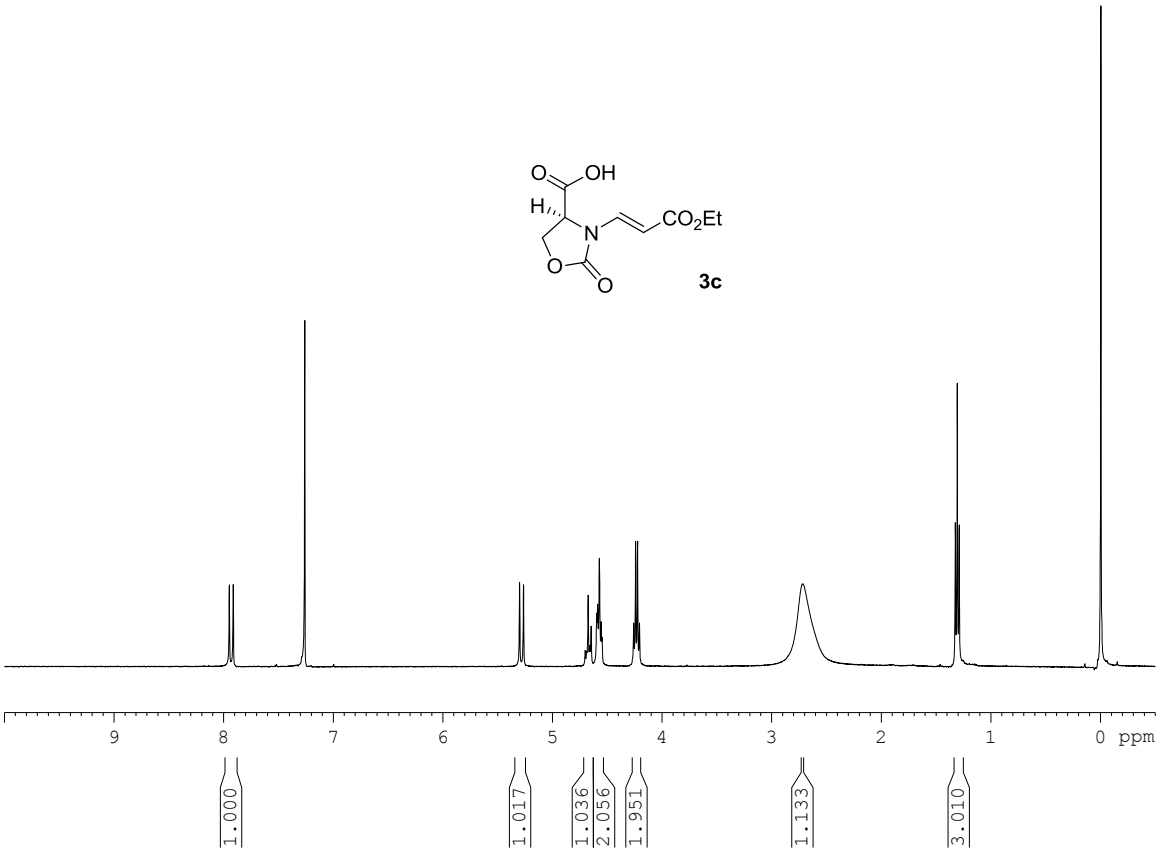

O
O
H
N
Ts
17
220
200
180
160
140
120
100
80
60
40
20
0 ppm

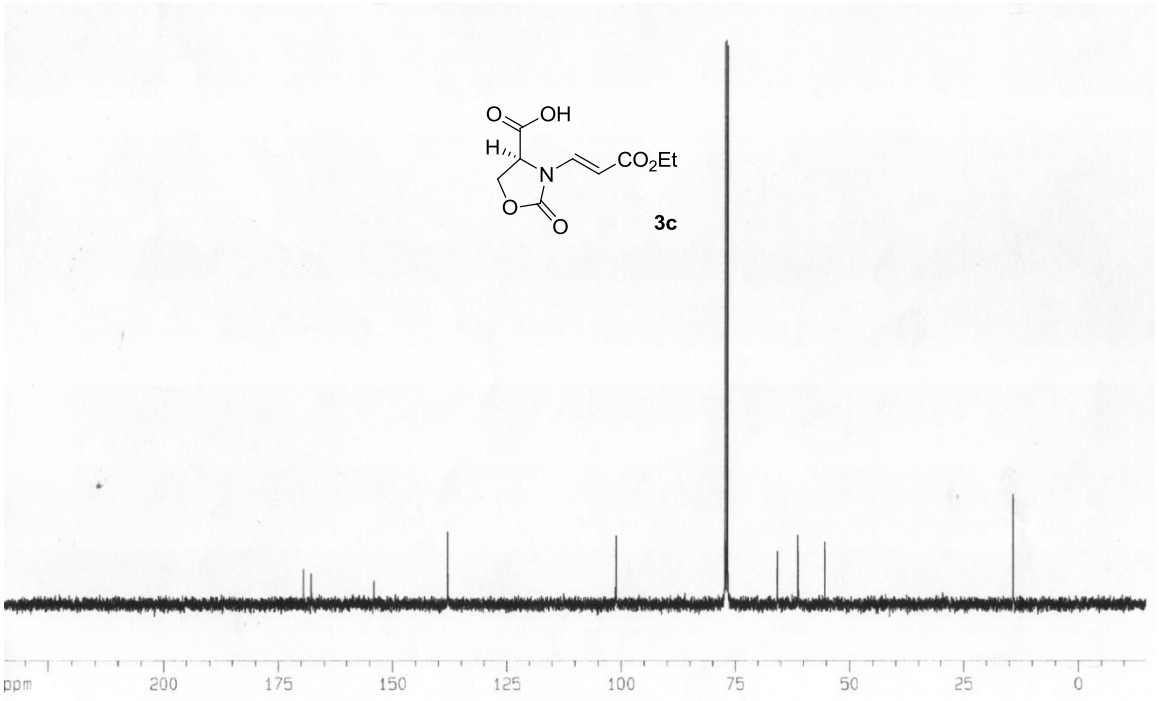

O
OH
CO2Et
N
Ts
3a
9
8
7
6
5
4
3
2
1
0 ppm
0.818
1.836
1.897
1.124
0.923
1.637
2.081
2.917
2.963

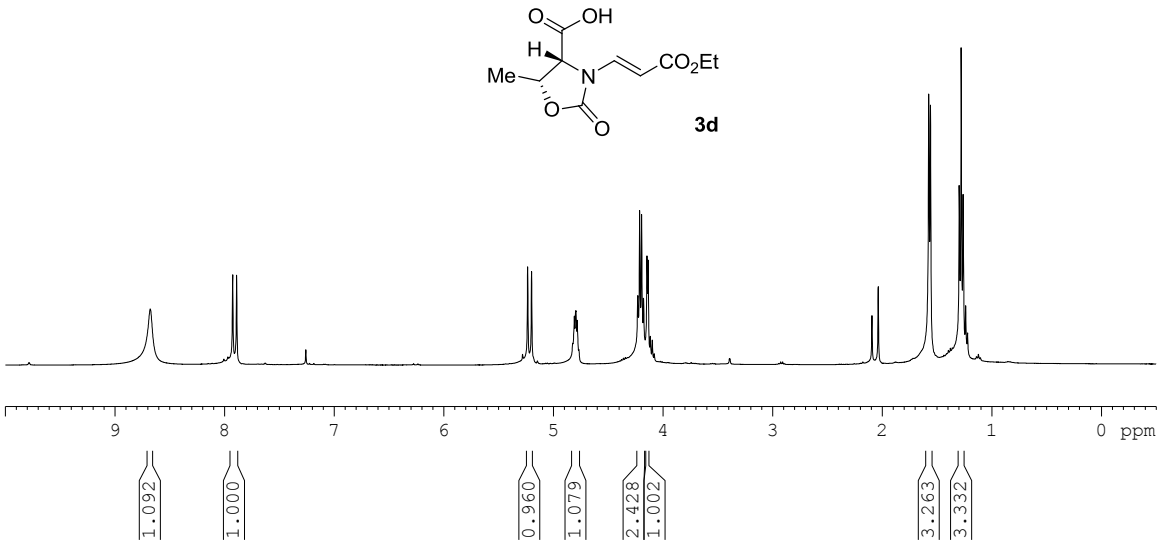

O
OH
CO2Et
N
Ts
3a
220
200
180
160
140
120
100
80
60
40
20
0 ppm

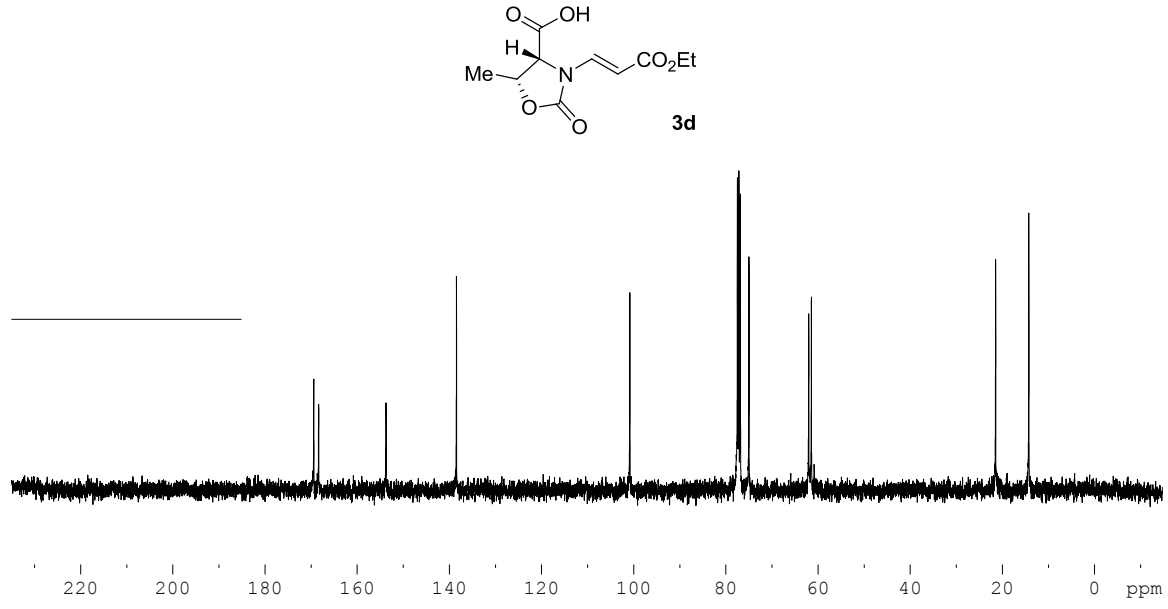

O
OH
N
CO2Et
CO2Et
CO2Et
3b
9
8
7
6
5
4
3
2
1
0 ppm
0.959
1.010
0.947
4.117
2.026
2.801
3.278

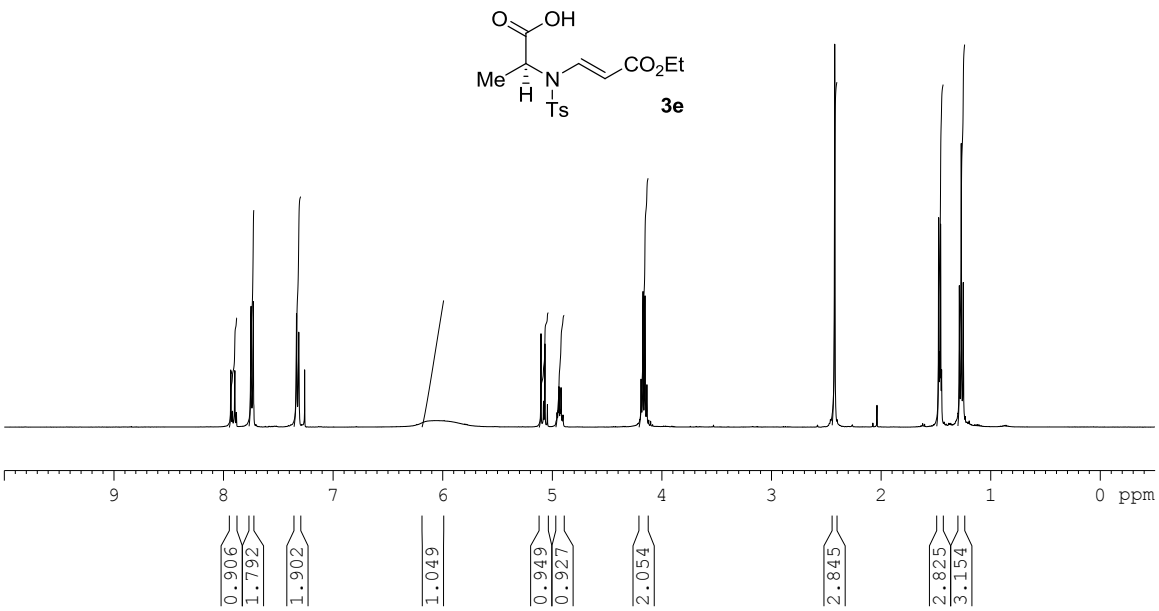

O
OH
N
CO2Et
CO2Et
CO2Et
3b
220
200
180
160
140
120
100
80
60
40
20
0 ppm

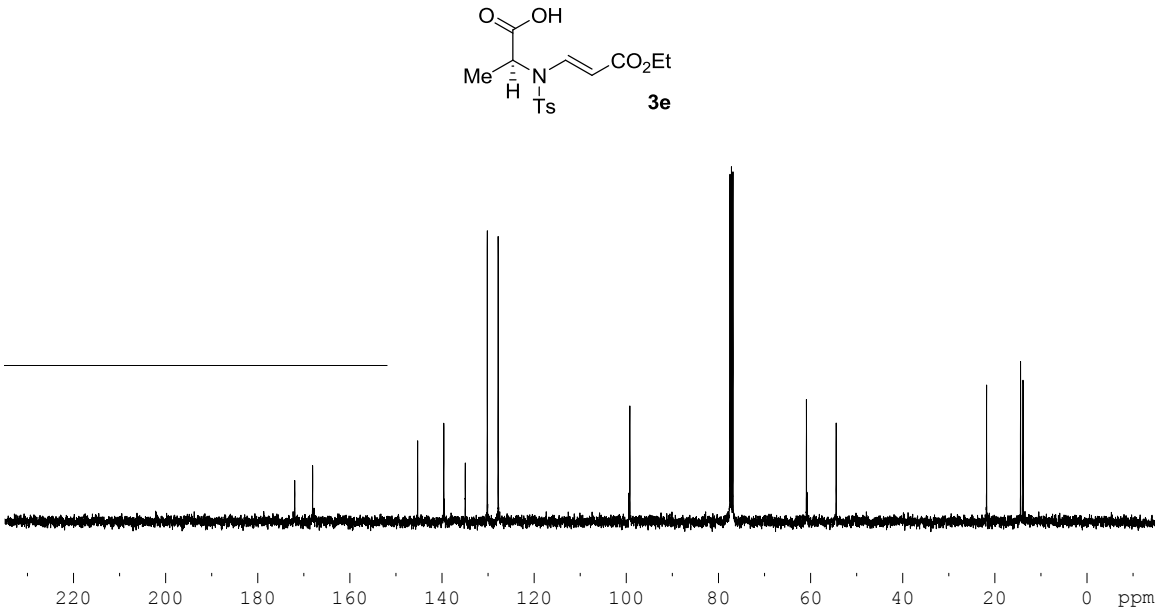

O
OH
H
N
CO2Et
O
O
3c
9
8
7
6
5
4
3
2
1
0 ppm
1.000
1.017
1.036
2.056
1.951
1.133
3.010

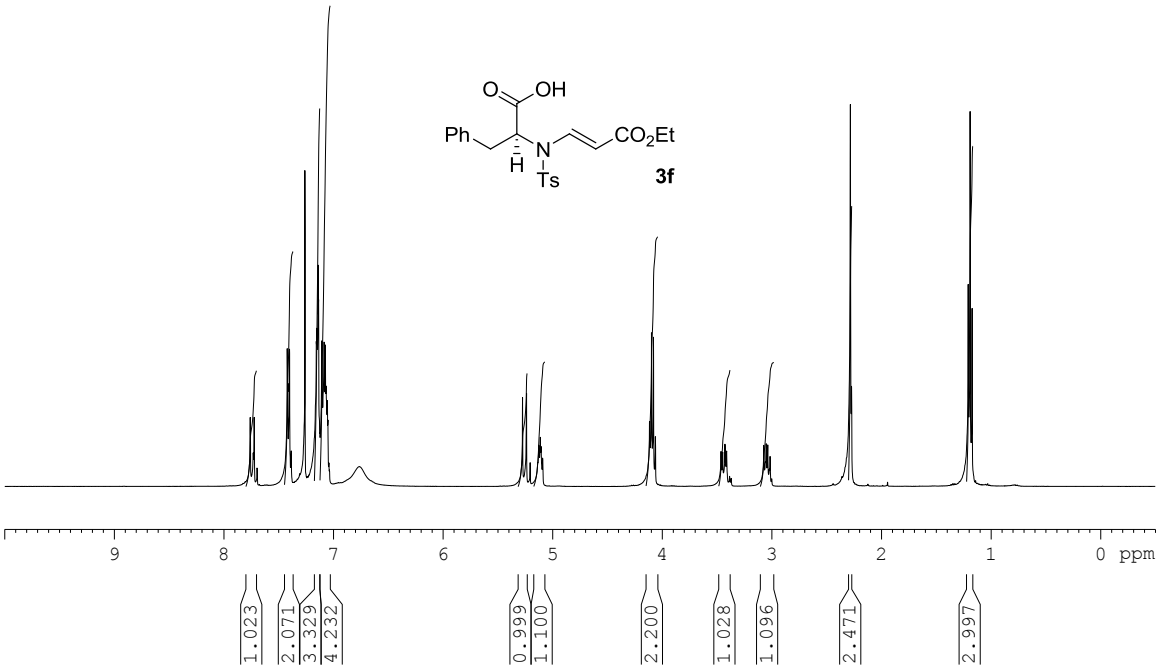

O
OH
H
N
CO2Et
O
O
3c
ppm
200
175
150
125
100
75
50
25
0

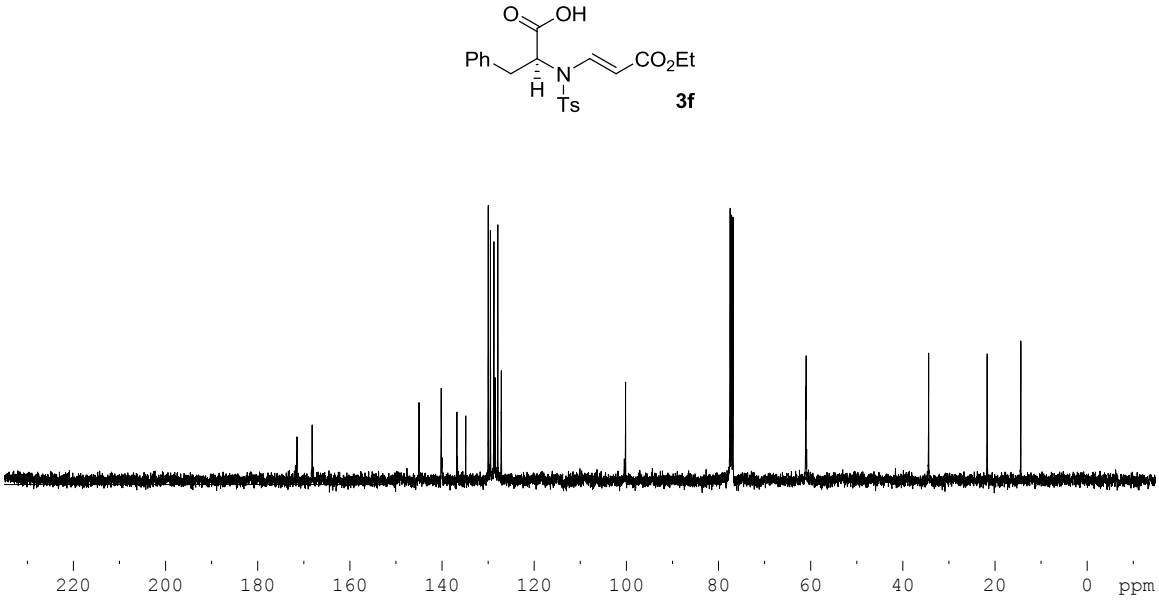

O
OH
H
Me
N
CO2Et
O
O
3d
9
8
7
6
5
4
3
2
1
0 ppm
1.092
1.000
0.960
1.079
2.428
1.002
3.263
3.332

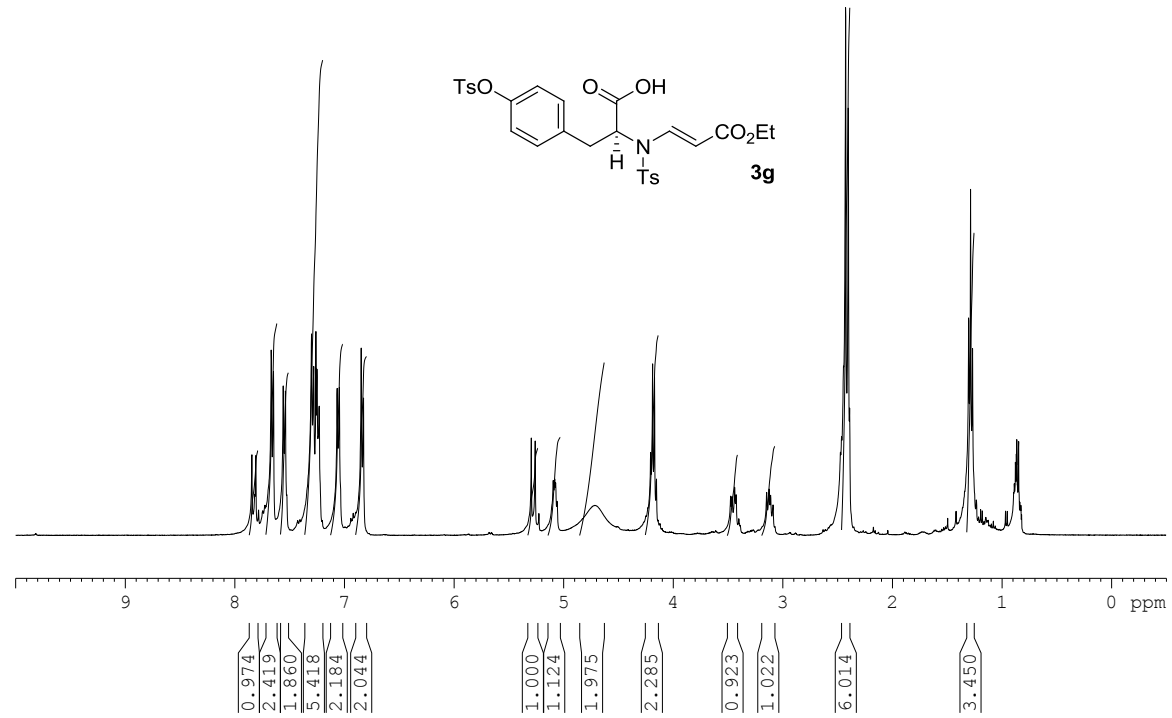

O
OH
H
Me
N
CO2Et
O
O
3d
220
200
180
160
140
120
100
80
60
40
20
0 ppm

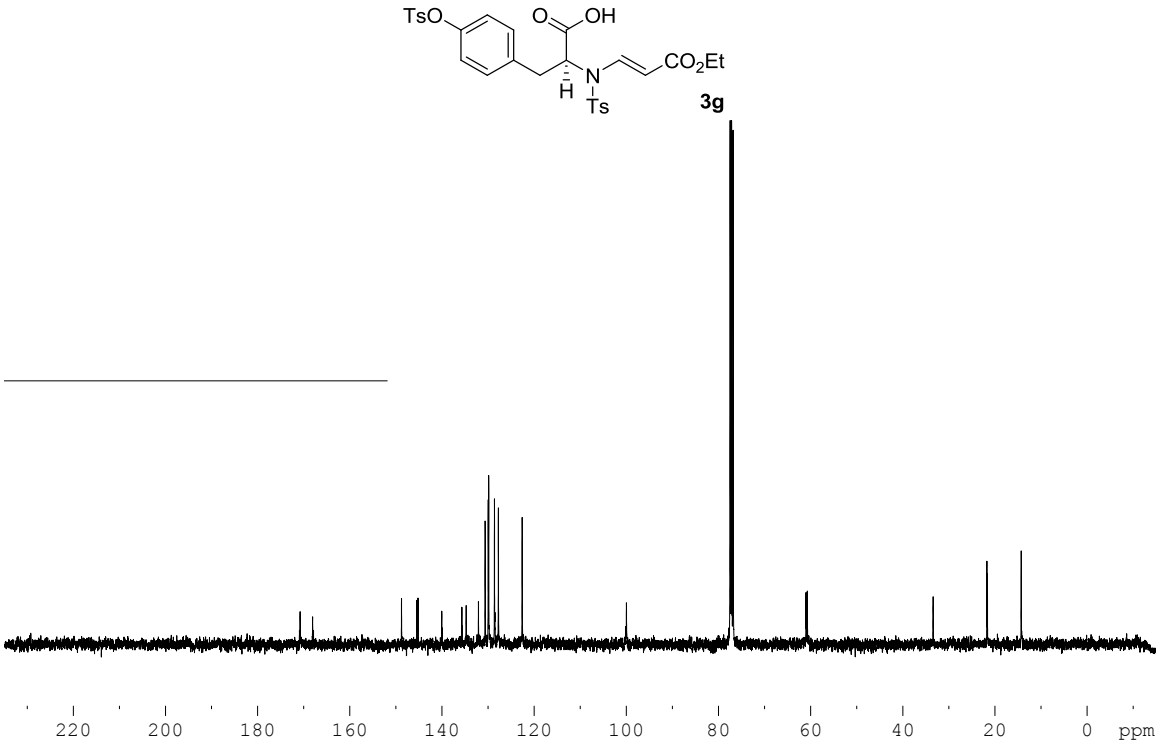

O
OH
Me
H
N
Ts
CO2Et
3e
9
8
7
6
5
4
3
2
1
0 ppm
0.906
1.792
1.902
1.049
0.949
0.927
2.054
2.845
2.825
3.154

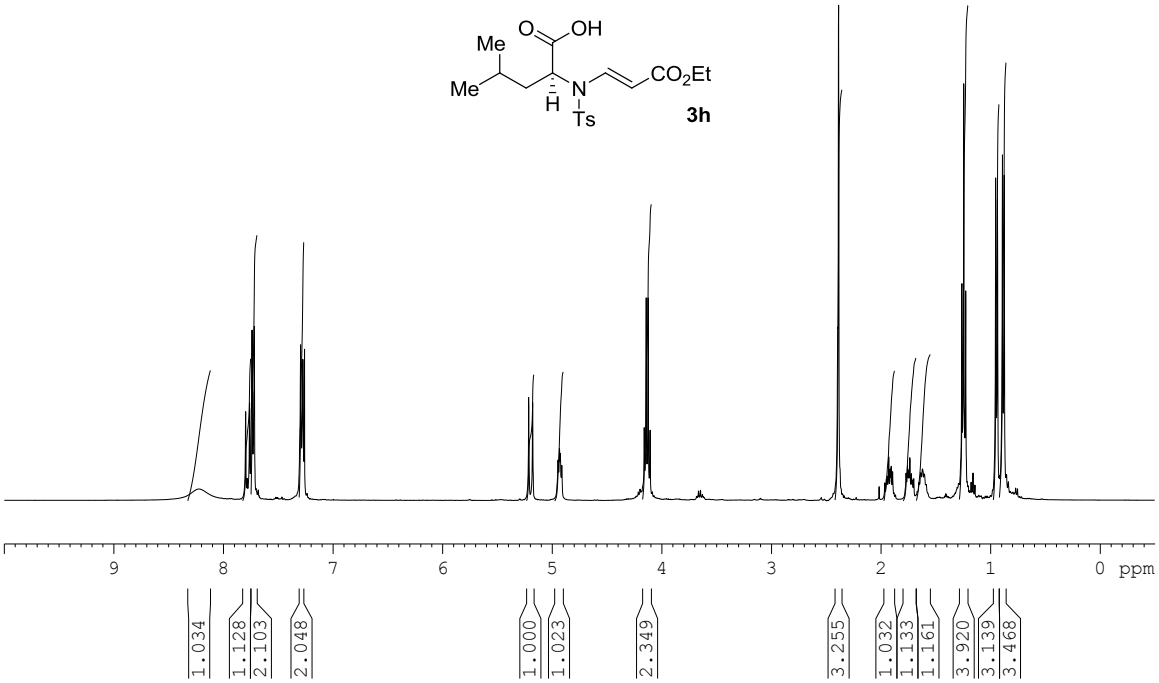

O
OH
Me
H
N
Ts
CO2Et
3e
220
200
180
160
140
120
100
80
60
40
20
0 ppm

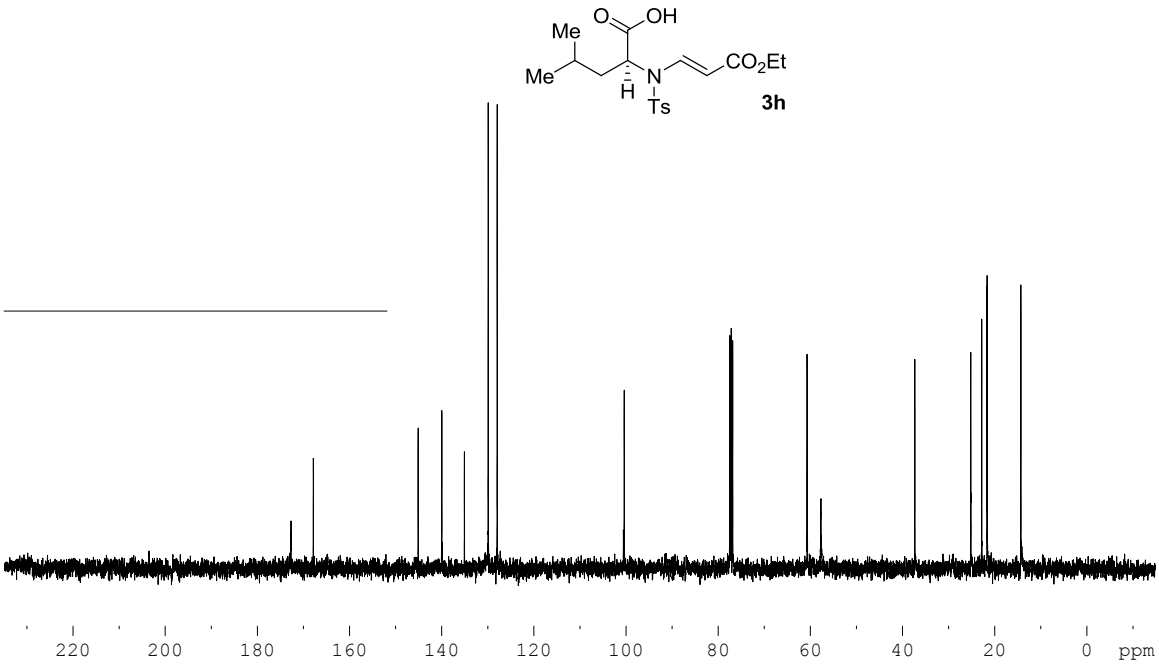

O
OH
Ph
N
H
Ts
CO2Et
3f
9
8
7
6
5
4
3
2
1
0 ppm
1.023
2.071
3.329
4.232
0.999
1.100
2.200
1.028
1.096
2.471
2.997

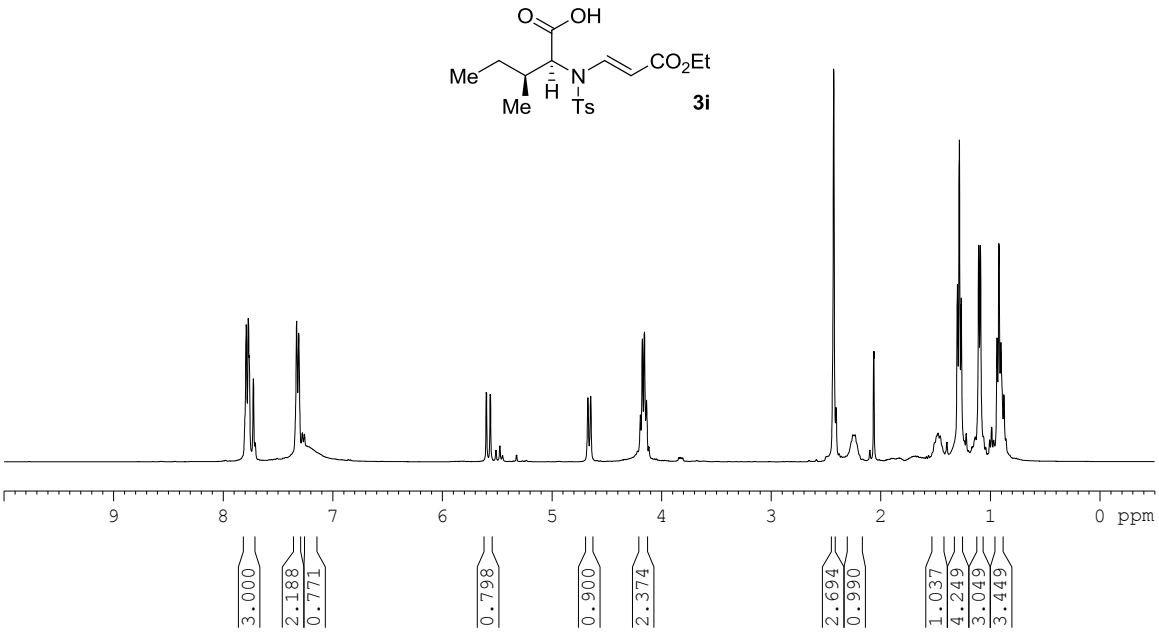

O
OH
Ph
N
H
Ts
CO2Et
3f
220
200
180
160
140
120
100
80
60
40
20
0 ppm

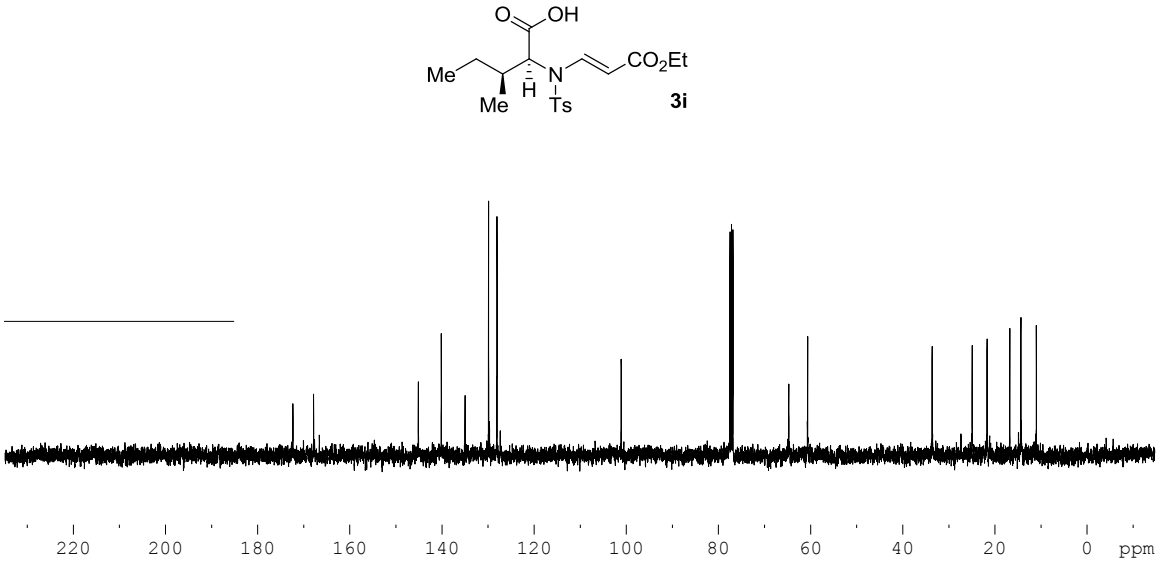

TsO
O
OH
CO2Et
N
H
Ts
3g
9
8
7
6
5
4
3
2
1
0 ppm
0.974
2.419
1.860
5.418
2.184
2.044
1.000
1.124
1.975
2.285
0.923
1.022
6.014
3.450

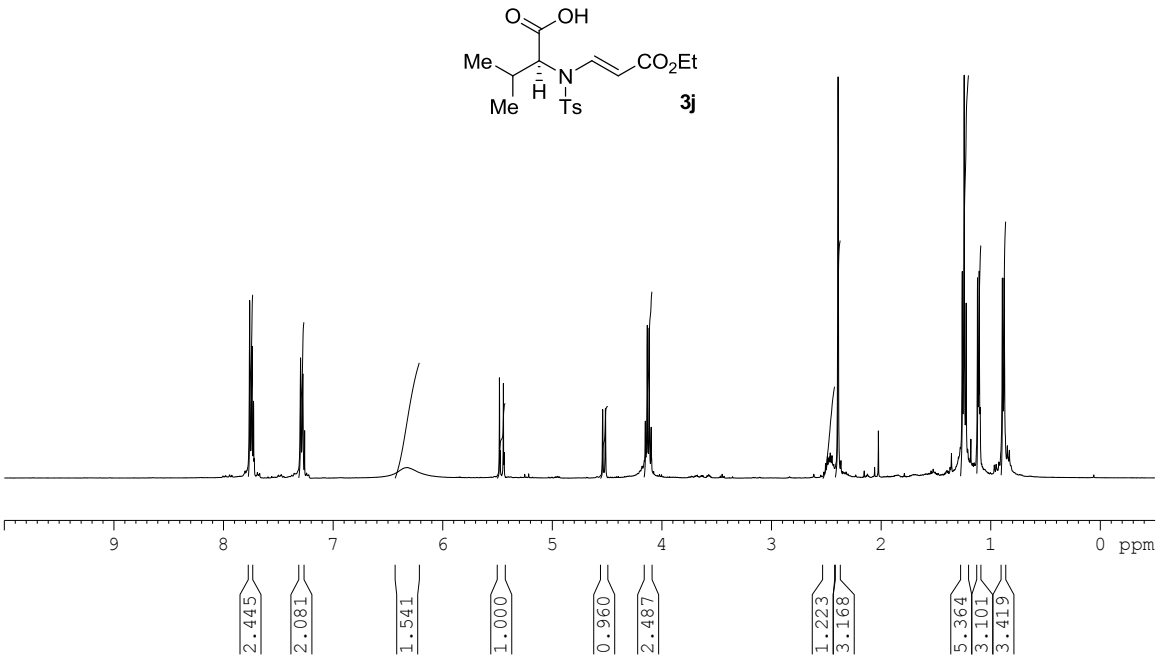

TsO
O
OH
CO2Et
N
H
Ts
3g
220
200
180
160
140
120
100
80
60
40
20
0 ppm

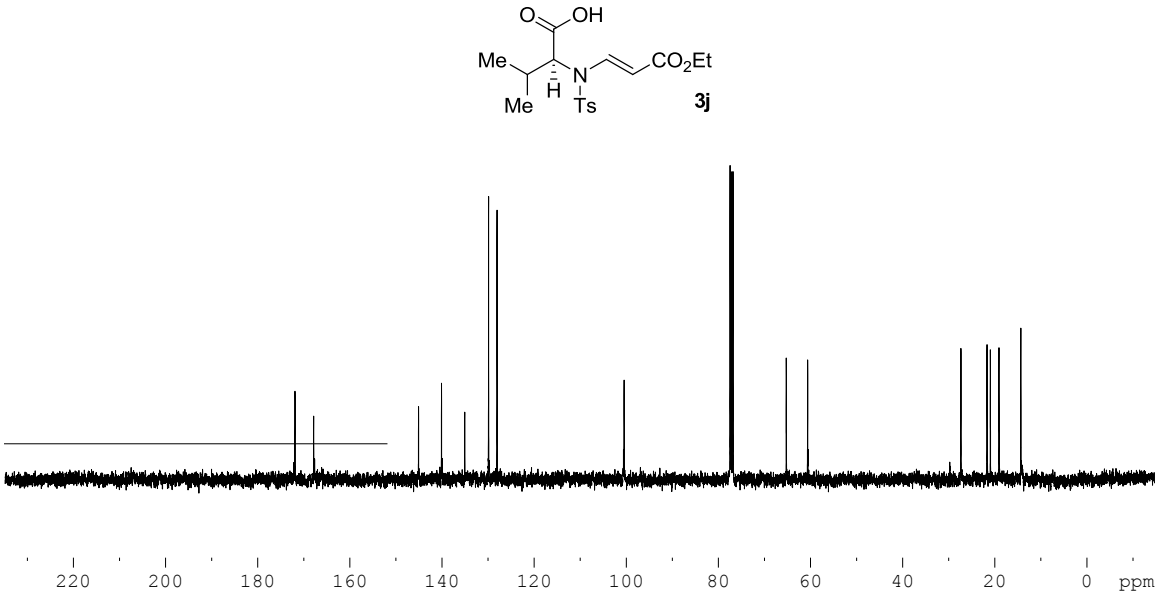

O
OH
Me
Me
N
H
Ts
CO2Et
3h
9
8
7
6
5
4
3
2
1
0 ppm
1.034
1.128
2.103
2.048
1.000
1.023
2.349
3.255
1.032
1.133
1.161
3.920
3.139
3.468


O
OH
Me
Me
N
H
Ts
CO2Et
3h
220
200
180
160
140
120
100
80
60
40
20
0 ppm


O
OH
Me
H
N
CO2Et
Me
Ts
3i
9
8
7
6
5
4
3
2
1
0 ppm
3.000
2.188
0.771
0.798
0.900
2.374
2.694
0.990
1.037
4.249
3.049
3.449


O
OH
Me
H
N
CO2Et
Me
Ts
3i
220
200
180
160
140
120
100
80
60
40
20
0 ppm


O
OH
Me
CO2Et
N
H
Me
Ts
3j
9
8
7
6
5
4
3
2
1
0 ppm
2.445
2.081
1.541
1.000
0.960
2.487
1.223
3.168
5.364
3.101
3.419


O
OH
Me
CO2Et
N
H
Me
Ts
3j
220
200
180
160
140
120
100
80
60
40
20
0 ppm