Electronic Supplementary Material (ESI) for ChemComm.

Stereoselective Synthesis of 2,3-Disubstituted Indoline, Pyrrolidine and Cyclic Ether-Fused 1,2-Dihydroquinoline Derivatives using Alkyne Iminium Ion Cyclization of Vinylogous Carbamates: Switch of Regioselectivity using Internal Hydroxy Group as Nucleophile

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General experimental:

Melting points are recorded using Sigma melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on JASCO FT-IR 8300 and Nicolet 6700 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 spectrometer. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Bruker Avance 500 spectrometer. 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) was determined by recording the DEPT 135 experiment and is given in parentheses. High-resolution mass measurements were carried out using Micromass Q-ToF (Waters) or maXis impact (Bruker) instrument using direct inlet mode. X-ray diffraction studies were carried out using Bruker Single Crystal Kappa Apex II. 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 sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F245 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. All small-scale dry reactions were carried out using standard syringe septum technique. Dry dichloromethane and dry DMF were prepared by distilling over calcium hydride. Triethylamine was obtained by distillation over KOH and stored over KOH. $BF_3 \cdot OEt_2$ was obtained from Aldrich. All the commercial reagents were used as such without further purification.

General procedure for the preparation of vinylogous carbamate from the amine:

To a stirred solution of *N*-protected aniline or homopropargyl amine derivatives (1 equiv.) in dry CH_2Cl_2, was added DABCO (0.1 equiv.) and ethyl propiolate (1.1 equiv.) at r.t. and stirred for *ca.* 8 h (TLC). The reaction mixture was then concentrated under reduced pressure and residue was purified by silica gel column chromatography using EtOAc/petroleum ether as the eluent to yield the vinylogous carbamate.

General procedure for the synthesis of alkynyl vinylgous carbamate:

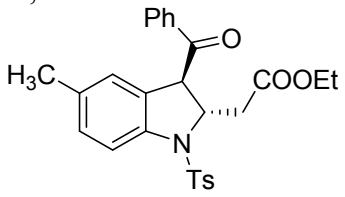
A solution of $[PdCl_2(PPh_3)_2]$ (2 mol%), CuI (2 mol%), alkyne (1.1 equiv.), *o*-iodo *N* protected aniline or aryl iodide (1.0 equiv.) in Et_3N as solvent was stirred at rt for 5 h under N_2 or in a sealed reaction tube. Reaction was monitored by TLC. After completion of the reaction, the

reaction mixture was concentrated under reduced pressure and residue was purified by silica gel column chromatography using EtOAc/petroleum ether as the eluent to yield the alkynyl vinylgous carbamate.

(Note: In the cases where diastereomeric mixture of products was obtained, the data for the major isomer is mentioned).

Ethyl 2-((2*S,3*R**)-3-benzoyl-5-methyl-1-tosylindolin-2-yl)acetate (1a):**

To a cold (0 °C) magnetically stirred solution of the vinylogous carbonate **2a** (100 mg, 0.217 mmol) in dry CH_2Cl_2 (3.0 mL) was added drop wise TMSOTf (45 μL, 0.239 mmol) at 0 °C and the resulting mixture was slowly warmed up to rt and stirred for completion (TLC control).The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (10 mL), extracted with CH_2Cl_2 (3 × 15 mL) and combined organic layer was washed with brine sol. and dried (*anhyd.* Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using EtOAc:petroleum ether (1:19) as an eluent furnished 2,3-disubstituted indoline **1a** (76 mg, 73%) as a white solid.



Physical appearance: white solid.

m.p.: 117-119 °C.

R*f*: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 3057, 2983, 2957, 2926, 2858, 1729, 1688, 1598, 1489, 1448, 1420, 1353, 1324, 1291, 1265, 1210, 1166, 1114, 1092, 1060, 1036, 964, 883, 817, 740, 703, 666, 621, 589, 568 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* =8.1, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.1Hz, 1H), 7.00 (d, *J* = 8.4, 1H), 6.59 (s, 1H), 5.18 (dt, *J* = 6.8, 3.6 Hz, 1H), 4.94 (d, *J* = 4.0 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.40 (ABX, *J* = 16.4, 3.6 Hz, 1H), 2.98 (ABX, *J* = 16.4, 10.4 Hz, 1H), 2.40 (s, 3H), 2.12 (s, 3H), 1.13 (t, *J*=7.2 Hz, 3H).

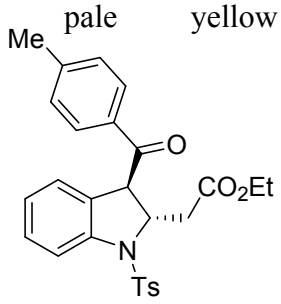
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ196.01 (C), 170.84 (C), 144.21 (C), 139.21 (C), 136.09 (C), 134.28 (C), 133.71 (CH), 129.84 (CH), 129.66 (2 × CH), 129.22 (2 × CH), 129.0 (C), 128.97 (2 × CH), 128.83 (C), 128.09 (2 × CH), 125.81 (CH), 115.47 (CH), 61.46 (CH), 60.96 (CH_2), 54.11 (CH), 41.78 (CH_2), 21.77 (CH_3), 20.96 (CH_3), 14.14 (CH_3).

LRMS (ESI, M+H$^+$): m/z 478.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{27}H_{28}NO_5S$ 478.1688, found 478.1693.

Ethyl 2-((2*S,3*R**)-3-(4-methylbenzoyl)-1-tosylindolin-2-yl)acetate (1b):**

Reaction of the vinylogous carbonate **2b** (156 mg, 0.339 mmol) with TMSOTf (68 μL, 0.373 mmol) in dry CH_2Cl_2 (5.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1b** (114 mg, 70%) as a pale yellow liquid.



Physical appearance: pale yellow liquid.

R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 2979, 1731, 1683, 1605, 1479, 1354, 1237, 1166, 1042, 754, 665, 576 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.79 (m, 4H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 4H), 720-7.15 (m, 1H), 6.85-6.80 (m, 2H), 5.23 (dt, *J* = 10.4, 3.6 Hz, 1H), 4.94 (d, *J* = 3.6 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.39 (ABX, *J* = 16.4, 3.6 Hz, 1H), 2.93 (ABX, *J* = 16.4, 10.4 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H).

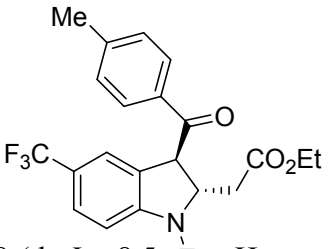
^{13}C NMR (100 MHz, $CDCl_3$, DEPT):δ 195.3 (C), 170.8 (C), 144.7 (C), 144.3 (C), 141.5 (C), 134.4 (C), 133.5 (C), 129.6 (3 × CH), 129.7 (2 × CH), 129.4 (2 × CH), 129.1 (C), 128.8 (C), 128.1 (2 × CH), 125.3 (CH), 123.8 (CH), 115.5 (CH), 61.3 (CH), 60.9 (CH_2), 54.1 (CH), 41.8 (CH_2), 21.8 (CH_3), 21.7 (CH_3), 14.2 (CH_3).

LRMS (ESI, M+Na^+): m/z 500.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{27}H_{27}NNaO_5S$ 500.1502, found 500.1504.

Ethyl 2-((2*S,3*R**)-3-(4-methylbenzoyl)-1-tosyl-5-(trifluoromethyl)indolin-2-yl)acetate (1c):**

Reaction of the vinylogous carbonate **2c** (75 mg, 0.142 mmol) with TMSOTf (30 μL, 0.178 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1c** (48 mg, 62%) as a pale yellow liquid.



Physical appearance: pale yellow liquid.

R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 2929, 1729, 1687, 1607, 1359, 1331, 1170, 1121, 963, 667 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 8.0, 4.0 Hz, 4H), 7.68 (d, *J* = 8.5 Hz,

1H), 7.44 (t, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 4H), 7.04 (bs, 1H), 5.24 (dt, J = 10.5, 3.5 Hz, 1H), 4.99 (d, J = 3.5 Hz, 1H), 4.05 (q, J = 7.0 Hz, 2H), 3.37 (ABX, J = 16.5, 3.5 Hz, 1H), 2.95 (ABX, J = 16.5, 10.5 Hz, 1H), 2.44 (s, 3H), 2.40 (s, 3H), 1.13 (t, J = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 194.9 (C), 170.5 (C), 145.3 (C), 144.9 (C), 144.6 (C), 134.1 (C), 132.9 (C), 129.9 (4 × CH), 129.6 (2 × CH), 129.4 (2 × CH), 128.8 (CH), 126.7 (CH), 122.6 (CH), 122.5 (CH), 115.0 (CH), 62.1 (CH), 61.2 (CH_2), 53.4 (CH), 41.5 (CH_2), 21.9 (CH_3), 21.8 (CH_3), 14.1 (CH_3).

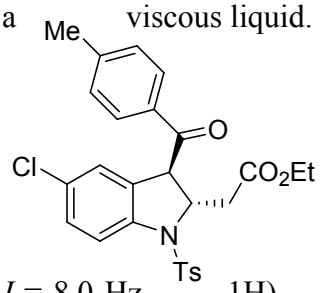
^{19}F NMR (470 MHz, $CDCl_3$): δ = – 61.8 ppm.

LRMS (ESI, M+Na$^+$): m/z 568.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{28}H_{26}F_3NNaO_5S$ 568.1376 found 568.1374.

Ethyl 2-((2S*,3R*)-5-chloro-3-(4-methylbenzoyl)-1-tosylindolin-2-yl)acetate (1d):

Reaction of the vinylogous carbonate **2d** (70 mg, 0.149 mmol) with TMSOTf (35 μL, 0.178 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1d** (48 mg, 65%) as a viscous liquid.



Physical appearance: viscous liquid.

R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 2928, 1728, 1685, 1473, 1356, 1238, 1165, 963, 818, 755, 667, 586 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 8.0 Hz, 4H), 7.55 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 4H), 7.15 (dd, J = 8.4, 2.5 Hz, 1H), 6.75 (d, J = 1.0, 1H), 5.19 (dt, J = 10.5, 3.5 Hz, 1H), 4.93 (d, J = 4.0 Hz, 1H), 4.04 (q, J = 7.0 Hz, 2H), 3.34 (ABX, J = 16.5, 3.5 Hz, 1H), 2.93 (ABX, J = 16.5, 10.5 Hz, 1H), 2.44 (s, 3H), 2.40 (s, 3H), 1.13 (t, J = 7.0 Hz, 3H).

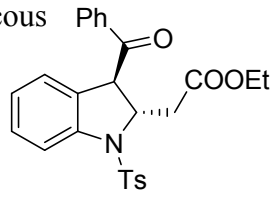
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 194.7 (C), 170.6 (C), 145.1 (C), 144.6 (C), 140.4 (C), 134.0 (C), 133.1(C), 130.8 (C), 129.9 (2 × CH), 129.8 (2 × CH), 129.4 (2 × CH), 129.2 (CH), 129.0 (C), 128.1 (2 × CH), 125.4 (CH), 116.5 (CH), 61.8 (CH), 61.1. (CH_2), 53.6 (CH), 41.6 (CH_2), 21.9 (CH_3), 21.8 (CH_3), 14.1 (CH_3).

LRMS (ESI, M+Na$^+$): m/z 534.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{27}H_{26}ClNNaO_5S$ 534.1112, found 534.1114.

Ethyl 2-((2*S, 3*R**)-3-benzoyl-1-tosylindolin-2-yl)acetate (1e)**

Reaction of the vinylogous carbonate **2e** (80 mg, 0.179 mmol) with TMSOTf (42 μL, 0.233 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1e** (58 mg, 70%) as a viscous liquid.



Physical appearance: viscous liquid.

R_f: 0.2 (1:9, EtOAc: Petroleum ether).

IR (neat): 3061, 2982, 2960, 2927, 2871, 2855, 1727, 1687, 1597, 1580, 1478, 1448, 1400, 1324, 1167, 1111, 1028, 962, 899, 813, 758, 705, 663 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.64-7.58 (m, 2H), 7.49(*J* = 8, 7.6 Hz, 2H), 7.26 (d, *J =8,* 2H*),* 7.18 (t, *J* = 8 Hz, 1H) 6.85-6.77 (m, 2H), 5.22 (dt, *J* = 3.6, 2.8 Hz, 1H), 4.97 (d, *J* = 3.6 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.40 (ABX, *J* = 16.4, 3.6 Hz, 1H), 2.92 (ABX, *J* = 16.4, 10.4 Hz, 1H), 2.38 (s, 3H), 2.39 (s, 3H). 1.13 (t, *J* = 7.2 Hz, 3H).

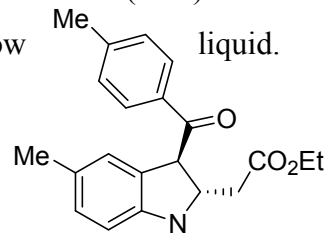
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 195.76 (C), 170.77 (C), 144.29 (C), 141.62 (C), 136.19 (C), 134.55 (C), 133.65 (CH), 129.67 (2 × CH), 129.21 (2 × CH), 128.96 (2 × CH), 128.66 (C), 128.08 (2 × CH), 125.36 (CH), 123.86 (CH), 115.64 (CH), 61.25 (CH), 60.96 (CH_2), 54.27 (CH), 41.74 (CH_2), 21.71 (CH_3), 14.13 (CH_3).

LRMS (ESI, M+Na^+): m/z 486.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{29}H_{25}NNaNO_5S$ 486.1346 found 486.1352.

Ethyl 2-((2*S,3*R**)-5-methyl-3-(4-methylbenzoyl)-1-tosylindolin-2-yl)acetate (1f):**

Reaction of the vinylogous carbonate **2f** (71 mg, 0.149 mmol) with TMSOTf (30 μL, 0.164 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using EtOAc-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1f** (55 mg, 74%) as a yellow liquid.



Physical appearance: yellow liquid.

R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 2923, 1729, 1684, 1489, 1354, 1183, 1165, 912, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 8.4, 4.4 Hz, 4H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.60 (bs, 1H), 5.14 (dt, *J* = 7.6, 4.0 Hz, 1H), 4.90 (d, *J* = 4.0 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.36 (ABX, *J*

= 16.4, 4.4 Hz, 1H), 2.91 (ABX, *J* = 16.4, 4.4 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H). 2.12 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H).

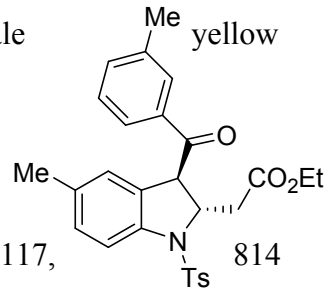
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 194.6 (C), 170.8 (C), 144.7 (C), 144.2 (C), 139.2 (C), 134.3 (C), 133.6 (C), 133.5 (CH), 129.7 (CH), 129.6 (2 × CH), 129.5 (C), 129.3 (2 × CH), 129.04 (C), 128.1 (2 × CH), 125.8 (CH), 115.3 (CH), 61.6 (CH), 60.9. (CH_2), 53.9 (CH), 41.8 (CH_2), 21.8 (CH_3), 21.7 (CH_3), 20.9 (CH_3), 14.1 (CH_3).

LRMS (ESI, M+H$^+$): m/z 492.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{28}H_{30}NO_5S$ 492.1845, found 492.1824.

Ethyl 2-((2*S,3*R**)-5-methyl-3-(3-methylbenzoyl)-1-tosylindolin-2-yl)acetate (1g):**

Reaction of the vinylogous carbonate **2g** (71 mg, 0.149 mmol) with TMSOTf (30 μL, 0.164 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using EtOAc-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1g** (57 mg, 76%) as a pale yellow liquid.



Physical appearance: pale yellow liquid.

R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 2924, 1730, 1693, 1600, 1489, 1354, 1324, 1255, 1164, 1117, 814 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.70 (s, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.43-7.35 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.58 (s, 1H), 5.16 (dt, *J* = 10.4, 3.6 Hz, 1H), 4.91 (d, *J* = 3.6 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 1H), 3.37 (ABX, *J* = 16.4, 3.6 Hz, 1H), 2.91 (ABX, *J* = 16.4, 10.4 Hz,1H), 2.41 (s, 3H), 2.39 (s, 3H), 2.11 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H).

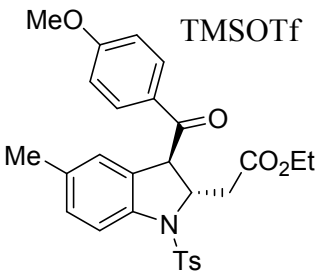
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 196.2 (C), 170.8 (C), 144.16 (C), 139.2 (C), 138.8 (C), 136.1 (C), 134.5 (CH), 134.3 (C), 133.6 (C), 129.8 (CH), 129.7 (CH), 129.6 (2 × CH), 128.9 (C), 128.8 (CH), 128.1 (2 × CH), 126.4 (CH), 125.8 (CH), 115.4 (CH), 61.5 (CH), 60.9. (CH_2), 54.0 (CH), 41.8 (CH_2), 21.8 (CH_3), 21.5 (CH_3), 20.9 (CH_3), 14.1 (CH_3).

LRMS (ESI, M+H$^+$): m/z 492.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{28}H_{30}NO_5S$ 492.1845, found 492.1824.

Ethyl 2-((2*S, 3*R**)-3-(4-methoxybenzoyl)-5-methyl-1-tosylindolin-2-yl)acetate (1h)**

Reaction of the vinylogous carbonate **2h** (121 mg, 0.24 mmol) with TMSOTf



(50 μL, 0.27 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using EtOAc-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1h** (62 mg, 51%) as a pale yellow liquid.

Physical appearance: pale yellow liquid.

R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 2927, 2854, 1732, 1676, 1599, 1579, 1491, 1354, 1333, 1250, 1244, 1225, 1165, 1101, 1030, 818, 673, 665 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.99-6.95 (m, 3H), 6.61 (bs, 1H), 5.14 (dt, *J* = 10.4, 4 Hz, 1H), 4.88 (d, *J* = 4 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 2H),3.89 (s, 3H), 3.36 (ABX, *J* = 16.4, 3.6 Hz, 1H), 2.90 (ABX, *J* = 16.4, 10.4 Hz, 1H),2.38 (s, 3H),2.11 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 194.56 (C), 170.83 (C), 164.09 (C), 144.18 (C), 139.28 (C), 134.35 (C), 133.62 (C), 131.62 (CH), 131.59 (CH), 129.73 (2 × CH), 129.65 (2 × CH), 129.26 (C), 128.95 (C), 128.14 (2 × CH), 125.71 (CH), 115.34 (CH), 114.20 (2 × CH), 61.72 (CH), 60.94. (CH_2), 55.67 (CH), 53.76 (CH_3), 41.92 (CH_2), 21.76 (CH_3), 20.96 (CH_3), 14.14 (CH_3).

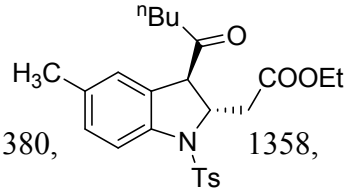
LRMS (ESI, M+H$^+$): m/z 508.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{28}H_{30}NO_6S$ 508.1794, found 508.1798.

Ethyl 2-((2*S, 3*R**)-5-methyl-3-pentanoyl-1-tosylindolin-2-yl)acetate (1j):**

Reaction of the vinylogous carbonate **2j** (54 mg, 0.12 mmol) with TMSOTf (25 μL, 0.13 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using EtOAc-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1j** (20 mg, 35%) as a pale yellow liquid.

Physical appearance: pale yellow liquid.



R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 2959, 2929, 2867, 2255, 1725, 1599, 1487, 1468, 1380, 1358, 1167, 1093, 909, 737, 651, 589 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.92 (bs, 1H), 4.85 (dt, *J* = 10.4, 3.6 Hz, 1H), 4.15-4.08 (m, 2H), 3.76 (d, *J* = 3.6 Hz, 1H), 3.22 (ABX, *J* = 16.8, 3.6 Hz, 1H), 2.73 (ABX, *J* = 16.8, 10.8

Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 2.17-1.98 (m, 2H), 1.33-1.20 (m, 5H), 1.09 -1.03 (m, 2H). 0.79 (t, *J*=7.2 Hz, 3H).

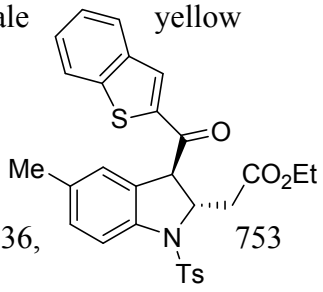
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 205.65 (C), 170.83 (C), 144.36 (C), 139.09 (C), 135.25 (C), 134.24 (C), 130.08 (CH), 129.75 (2 × CH), 128.50 (C), 127.74 (2 × CH), 126.02 (CH), 116.10 (CH), 61.0 (CH_2), 60.57 (CH), 60.17 (CH), 41.50 (CH_2), 39.53 (CH_2), 25.49 (CH_2), 22.17 (CH_2), 21.68 (CH_3), 21.09 (CH_3), 14.25 (CH_3), 13.97 (CH_3).

LRMS (ESI, M+Na$^+$): m/z 480.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{25}H_{31}NNaO_5S$ 480.1815, found 480.1823.

Ethyl 2-((2*S,3*R**)-3-(benzo[b]thiophene-2-carbonyl)-5-methyl-1-tosylindolin-2-yl)acetate (1k):**

Reaction of the vinylogous carbonate **2k** (75 mg, 0.146 mmol) with TMSOTf (30 μL, 0.160 mmol) in dry CH_2Cl_2, (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using EtOAc-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1k** (49 mg, 63%) as a pale yellow liquid.



Physical appearance: pale yellow liquid.

R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 2931, 1730, 1670, 1509, 1490, 1353, 1324, 1184, 1164, 1036, 753 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 5.10 (dt, *J* = 10.5, 4.0 Hz, 1H), 4.82 (d, *J* = 4.0 Hz, 1H), 4.03 (q, *J* = 7.5 Hz, 2H), 3.41 (ABX, *J* = 16.5, 4.0 Hz, 1H), 2.91 (ABX, *J* = 17.0, 10.5 Hz,1H), 2.36 (s, 3H), 2.11 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H).

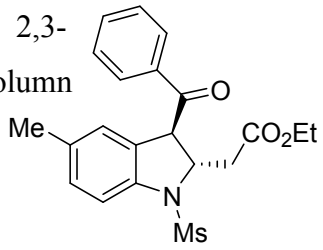
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 190.5 (C), 170.8 (C), 144.4 (C), 143.2 (C), 143.0 (C), 139.4 (C), 139.2 (C), 134.0 (C), 133.9 (C), 130.5 (CH), 130.1 (CH), 129.8 (2 × CH), 128.6 (C), 128.1 (2 × CH), 127.9 (CH), 126.4 (CH), 125.8 (CH), 125.3 (CH), 123.1 (CH), 115.5 (CH), 61.7 (CH), 61.0 (CH_2), 55.6 (CH), 41.9 (CH_2), 21.8 (CH_3), 21.0 (CH_3), 14.1 (CH_3).

LRMS (ESI, M+Na$^+$): m/z 556.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{29}H_{27}NNaO_5S_2$ 556.1223, found 556.1223.

Ethyl 2-((2*S,3*R**)-3-benzoyl-5-methyl-1-(methylsulfonyl)indolin-2-yl)acetate (1l):**

Reaction of the vinylogous carbonate **2l** (75 mg, 0.195 mmol) with TMSOTf (39 μL, 0.21 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using EtOAc-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1l** (54 mg, 68%) as a pale yellow liquid.



Physical appearance: pale yellow liquid.

R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 2932, 1730, 1679, 1489, 1351, 1329, 1161, 1139, 975, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$ δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 2H), 6.70 (s, 1H), 5.12 (dt, *J* = 10.8, 3.2 Hz, 1H), 5.03 (d, *J* = 2.8 Hz, 1H), 4.05 (q, *J* = 8.0 Hz, 2H), 3.17 (ABX, *J* = 16.8, 3.6 Hz, 1H), 3.06 (s, 3H), 2.79 (ABX, *J* = 16.8, 10.8 Hz, 1H), 2.17 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 197.5 (C), 170.8 (C), 139.3 (C), 135.7 (C), 134.4 (C), 134.2 (CH), 130.2 (CH), 129.4 (2 × CH, C), 129.2 (2 × CH), 126.0 (CH), 115.8 (CH), 61.7 (CH), 61.0 (CH_2), 53.8 (CH), 41.4 (CH_2), 35.9 (CH_3), 20.9 (CH_3), 14.1 (CH_3).

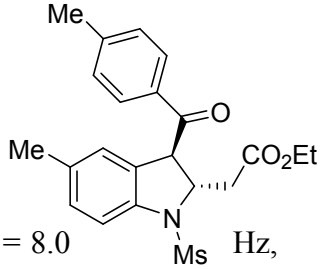
LRMS (ESI, M+Na^+): m/z 424.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{21}H_{23}NNaO_5S$ 424.1200, found 424.1195.

Ethyl 2-((2*S,3*R**)-5-methyl-3-(4-methylbenzoyl)-1-(methylsulfonyl)indolin-2-yl)acetate (1m):**

Reaction of the vinylogous carbonate **2m** (85 mg, 0.214 mmol) with TMSOTf (50 μL, 0.256 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using EtOAc-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1m** (61 mg, 69%) as a pale yellow liquid.

Physical appearance: pale yellow liquid.



R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 2981, 1731, 1678, 1489, 1350, 1160, 1037, 1111, 1037, 975, 823, 756, 566 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.74 (s, 1H), 5.10 (dt, *J* = 10.4, 3.6 Hz, 1H), 5.0 (d, *J* = 2.8 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.15 (ABX, *J* = 16.8, 3.6 Hz, 1H), 3.08 (s, 3H), 2.82 (ABX, *J* = 16.4, 10.8 Hz, 1H), 2.48 (s, 3H), 2.17 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H).

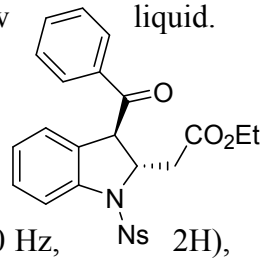
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 196.9 (C), 170.7 (C), 145.3 (C), 139.2 (C), 134.4 (C), 133.2 (C), 133.1 (C), 130.0 (CH), 129.9 (CH), 129.6 (C), 129.5 (2 × CH), 125.9 (CH), 115.8 (CH), 61.8 (CH), 60.9 (CH_2), 53.6 (CH), 41.4 (CH_2), 35.9 (CH_3), 21.9 (CH_3), 20.9 (CH_3), 14.1 (CH_3).

LRMS (ESI, M+Na^+): m/z 438.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{22}H_{25}NNaO_5S$ 438.1346, found 438.1350.

Ethyl 2-((2*S,3*R**)-3-benzoyl-1-(2-nitrophenylsulfonyl)indolin-2-yl)acetate (1n):**

Reaction of the vinylogous carbonate **2n** (75 mg, 0.157 mmol) with TMSOTf (35 μL, 0.189 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C as described for the 2,3-disubstituted indoline **1a** followed by purification on a silica gel column using EtOAc-petroleum ether (1:19) as eluent furnished the 2,3-disubstituted indoline **1n** (35 mg, 45%) as a pale yellow liquid.



Physical appearance: pale yellow liquid.

R_f: 0.2 (1:9, EtOAc:Petroleum ether).

IR (neat): 3315, 2986, 2342, 1727, 1543, 1367, 1175, 914, 759 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.65-7.60 (m, 4H), 7.53 (t, *J* = 8.0, 2H), 7.18 (t, *J* = 8 Hz, 1H) 7.28 (s, 1H), 6.97-6.94 (m, 2H), 5.37 (dt, *J* = 10.5, 3.0 Hz, 1H), 5.06 (d, *J* = 3.0 Hz, 1H), 4.05 (q, *J* = 7.0 Hz, 2H), 3.31 (ABX, *J* = 16.5, 3.5 Hz, 1H), 2.92 (ABX, *J* = 16.5, 10.5 Hz, 1H), 1.63 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 196.2 (C), 170.6 (C), 144.2 (C), 135.7 (C), 134.1 (C), 133.9 (CH), 131.8 (CH), 131.0 (C), 130.1 (CH), 129.6 (CH), 129.2 (2 × CH, C), 129.1 (2 × CH), 128.5 (C), 125.7 (CH), 124.6 (CH), 124.2 (CH), 116.2 (CH), 61.2 (CH), 61.1 (CH_2), 54.0 (CH), 40.8 (CH_2), 14.1 (CH_3).

LRMS (ESI, M+H^+): m/z 495.

HRMS (ESI, M+H^+): m/z calcd. for $C_{25}H_{23}N_2O_7S$ 495.1242 found 495.1226.

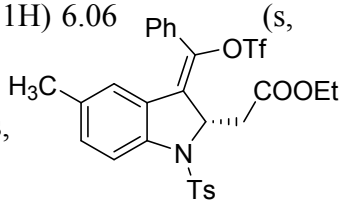
(*S,Z)-ethyl 2-(5-methyl-3-(phenyl(trifluoromethylsulfonyloxy)methylene)-1-tosylindolin-2-yl)acetate (5a):**

m.p.: 117-119 °C.

IR (neat): 3024, 2931, 1777, 1740, 1415, 1365, 1220, 1170, 961, 845 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.65-7.60 (m, 4H), 7.63 (d, *J* = 8.0, 1H), 7.57 (d, *J* = 8.0, 2H), 7.52 (t, *J* = 8.0,

1H*),* 7.45 (t, *J* = 8.0*,* 2H*),* 7.25 (t, *J* = 8.0*,* 4H*),* 7.09 (d, *J* = 8 Hz, 1H) 6.06 (s, 1H), 5.36 (t, *J* = 5.0 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.50 (ABX, *J* = 15.0, 6.0 Hz, 1H), 3.09 (ABX, *J* = 15.0, 5.0 Hz, 1H), 2.24 (s, 3H), 2.03 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 3H).



^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 169.3 (C), 144.5 (C), 142.9 (C), 139.2 (C), 134.9 (C), 133.4 (C), 132.0 (CH), 131.9 (C), 131.2 (CH), 130.2 (2 × CH, C), 129.9 (2 × CH), 129.3 (2 × CH), 127.6 (2 × CH), 126.8 (C), 124.0 (CH), 118.4 (CH), 62.8 (CH), 61.1 (CH_2), 40.1 (CH_2), 21.7 (CH_3), 21.2 (CH_3), 14.1 (CH_3).

^{19}F NMR (470 MHz, $CDCl_3$): δ = – 74.4 ppm.

LRMS (ESI, M+Na^+): m/z 632.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{28}H_{26}F_3NNaO_7S_2$ 632.0995 found 632.0998.

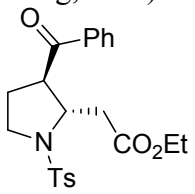
Typical procedure for the 'One pot' synthesis of 2,3-disubstituted indolines.

A reaction tube with a magnetic stirring bar was charged with ethyl propiolate (1.1 mmol), protected *o*-iodoaniline (1.0 mmol), DABCO (0.10 mmol) and CH_2Cl_2 (3.0 mL). The reaction mixture was stirred for 4 h at r.t. and then the solvent was evaporated under reduced pressure followed by terminal alkyne (1.1 mmol), [$PdCl_2(PPh_3)_2$] (2 mol%), CuI (2 mol%) and Et_3N (8 mL) were added and the reaction mixture was stirred for *ca.* 5 h at rt. then Et_3N was evaporated under reduced pressure and dry CH_2Cl_2 (4.0 mL) was added to the reaction tube, which was followed by drop-wise addition of TMSOTf (3 equiv.) at °C to rt. The reaction mixture was stirred at rt for *ca.* 5 h (TLC). The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (10 mL), extracted with CH_2Cl_2 (2 × 10 mL) and 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 EtOAc/petroleum ether (1:4) as eluent furnished 2,3-disubstituted indolines in good yield.

Ethyl 2-((2*S,3*R**)-3-benzoyl-1-tosylpyrrolidin-2-yl)acetate (1q):**

To a cold (0 °C) solution of the vinylogous carbamate **2q** (105 mg, 0.26 mmol) in dry CH_2Cl_2 (4.0 mL) was added TMSOTf (53 µL, 0.29 mmol) and the resulting mixture was slowly warmed up to rt. The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (10 mL), extracted with CH_2Cl_2 (2 × 10 mL) and 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 EtOAc/petroleum ether (1:4) as eluent furnished pyrrolidine **1q** (68 mg, 65%) as a pale yellow liquid.



Physical appearance: pale yellow liquid.

R_f: 0.5 (1:19, Ethylacetate-Petroleum ether).

IR (neat): 2983, 2959, 1731, 1683, 1449, 1160, 1095, 1017, 1002, 700, 663 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.74 (t, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.40 (dt, *J* = 9.0, 4.0 Hz, 1H), 4.07 (q, *J* = 7.5 Hz, 2H), 4.05-4.01 (m, 1H), 3.57-3.54 (m, 1H), 3.32-3.27 (m. 1H), 3.11 (ABX, *J* = 16.0, 4.0 Hz, 1H), 2.76 (ABX, *J* = 16.0, 9.0 Hz, 1H), 2.45 (s, 3H), 2.21-2.15 (m, 1H), 1.72-1.64 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H).

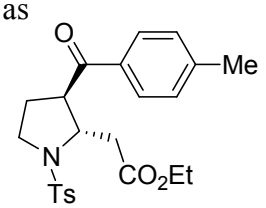
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 198.3 (C), 171.2 (C), 143.7 (C), 135.5 (C), 134.1 (C), 133.5 (CH), 129.8 (2 × CH), 128.7 (2 × CH), 128.6 (2 × CH), 127.9 (2 × CH), 60.8 (CH_2), 58.7 (CH), 50.9 (CH), 48.53 (CH_2), 41.1 (CH_2), 28.8 (CH_2), 21.7 (CH_3), 14.2 (CH_3).

LRMS (ESI, M+Na^+): m/z 438.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{22}H_{25}NNaO_5S$ 438.1346, found 438.1347.

Ethyl 2-((2*S,3*R**)-3-(4-methylbenzoyl)-1-tosylpyrrolidin-2-yl)acetate (1r):**

Reaction of the vinylogous carbamate **2r** (80.0 mg, 0.19 mmol) with TMSOTf (40 μL, 0.21 mmol) in dry CH_2Cl_2 (4.0 mL) at 0 °C, as described for the pyrrolidine **1q** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished pyrrolidine **1r** (50 mg, 61%) as a viscous liquid.



Physical appearance: viscous liquid.

R_f: 0.5 (1:19, Ethylacetate-Petroleum ether).

IR (neat): 2965, 1734, 1677, 1600, 1452, 1237, 1159, 1015, 816, 788, 663, 589 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.38 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.07 (q, *J* = 7.5 Hz, 2H), 4.02-4.01 (m, 1H), 3.58-3.53 (m, 1H), 3.31-3.28 (m. 1H), 3.10 (ABX, *J* = 16.0, 3.6 Hz, 1H), 2.76 (ABX, *J* = 16.0, 9.2 Hz, 1H), 2.45 (s, 3H), 2.38 (s, 3H), 2.20-2.12 (m, 1H), 1.71-1.69 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 197.9 (C), 171.1 (C), 144.4 (C), 143.7 (C), 134.2 (C), 132.9 (C), 129.8 (2 × CH), 129.4 (2 × CH), 128.7 (2 × CH), 128.0 (2 × CH), 60.8 (CH_2),

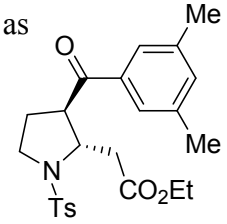
58.8 (CH), 50.9 (CH), 48.6 (CH_2), 41.1 (CH_2), 28.9 (CH_2), 21.7 (CH_3), 21.8 (CH_3), 14.2 (CH_3).

LRMS (ESI, M+Na$^+$): m/z 452.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{23}H_{27}NNaO_5S$ 452.1502, found 452.1503.

Ethyl 2-((2*S,3*R**)-3-(3,5-dimethylbenzoyl)-1-tosylpyrrolidin-2-yl)acetate (1s):**

Reaction of the vinylogous carbamate **2s** (100 mg, 0.23 mmol) with TMSOTf (46 µL, 0.25 mmol) in dry CH_2Cl_2 (4.0 mL) at 0 °C, as described for the pyrrolidine **1q** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished pyrrolidine **1s** (62 mg, 64 %) as a viscous liquid.



Physical appearance: viscous liquid.

R$_f$: 0.5 (Ethylacetate-Petroleum ether).

IR (neat): 2930, 1732, 1682, 1600, 1345, 1308, 1160, 1098, 1027, 757 cm^{-1}.

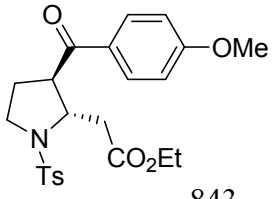
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.37 (s, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (s, 1H), 4.39 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 4.03-3.98 (m, 1H), 3.58-3.53 (m, 1H), 3.31-3.25 (m. 1H), 3.10 (ABX, *J* = 16.0, 3.6 Hz, 1H), 2.78 (ABX, *J* = 16.0, 9.6 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 6H), 2.20-2.15 (m, 1H), 1.70-1.62 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 198.7 (C), 171.1 (C), 143.7 (C), 138.4 (2 × C), 135.6 (C), 135.2 (CH), 134.2 (C), 129.8 (2 × CH), 128.0 (2 × CH), 126.3 (2 × CH), 60.8 (CH_2), 58.7 (CH), 51.1 (CH), 48.6 (CH_2), 41.1 (CH_2), 29.0 (CH_2), 21.8 (CH_3), 21.3 (2 × CH_3), 14.2 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{24}H_{29}NNaO_5S$ 446.1659, found 446.1658.

Ethyl 2-((2*S,3*R**)-3-(4-methoxybenzoyl)-1-tosylpyrrolidin-2-yl)acetate (1t):**

Reaction of the vinylogous carbamate **2t** (90 mg, 0.21 mmol) with TMSOTf (42 µL, 0.23 mmol) in dry CH_2Cl_2 (4.0 mL) at 0 °C, as described for the pyrrolidine **1q** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished pyrrolidine **1t** (52 mg, 56 %) as a viscous liquid.



Physical appearance: viscous liquid.

R$_f$: 0.5 (1:19, EtOAc:Petroleum ether).

IR (neat): 2939, 1731, 1677, 1601, 1354, 1261, 1261, 1239, 1161, 1030, 843, 663 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.74 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 4.38 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 4.0-3.95 (m, 1H), 3.86 (s, 3H), 3.57-3.52 (m, 1H), 3.34-3.28 (m, 1H), 3.09 (ABX, *J* = 16.0, 3.6 Hz, 1H), 2.76 (ABX, *J* = 16.0, 9.6 Hz, 1H), 2.44 (s, 3H), 2.17-2.10 (m, 1H), 1.71-1.65 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 196.7 (C), 171.1 (C), 163.9 (C), 143.6 (C), 134.2 (C), 130.9 (2 × CH), 129.7 (2 × CH), 128.4 (C), 127.9 (2 × CH), 113.9 (2 × CH), 60.8 (CH_2), 58.9 (CH), 55.6 (CH_3), 50.6 (CH), 48.6 (CH_2), 41.1 (CH_2), 28.9 (CH_2), 21.7 (CH_3), 14.2 (CH_3).

LRMS (ESI, M+H$^+$): m/z 446.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{23}H_{28}NO_6S$ 446.1637, found 446.1639.

Ethyl 2-((2*S,3*R**)-)-3-(3-methoxybenzoyl)-1-tosylpyrrolidin-2-yl)acetate (1u):**

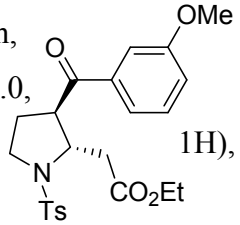
Reaction of the vinylogous carbamate **2u** (87 mg, 0.20 mmol) with TMSOTf (40 μL, 0.22 mmol) in dry CH_2Cl_2 (4.0 mL) at 0 °C, as described for the pyrrolidine **1q** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished pyrrolidine **1u** (48 mg, 53 %) as a viscous liquid.

Physical appearance: viscous liquid.

R_f: 0.5 (1:19, EtOAc/petroleum ether).

IR (neat): 2961, 1731, 1683, 1597, 1486, 1260, 1161, 1094, 1029, 814, 662 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.40-7.30 (m, 5H), 7.10-7.05 (m, 1H), 4.38 (dt, *J* = 9.6, 3.6 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 4.05-3.98 (m, 1H), 3.82 (s, 3H), 3.58-3.53 (m, 1H), 3.33-3.27 (m, 1H), 3.11 (ABX, *J* = 16.0, 3.6 Hz, 1H), 2.76 (ABX, *J* = 16.0, 9.6 Hz, 1H), 2.45 (s, 3H), 2.21-2.13 (m, 1H), 1.73-1.65 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H).



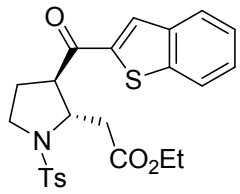
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 198.2 (C), 171.2 (C), 160.0 (C), 143.7 (C), 136.9 (C), 134.2 (C), 129.8 (2 × CH), 129.7 (CH), 127.9 (2 × CH), 121.1 (CH), 119.8 (CH), 113.2 (CH), 60.8 (CH_2), 58.8 (CH), 55.6 (CH_3), 51.1 (CH), 48.5 (CH_2), 41.1 (CH_2), 28.9 (CH_2), 21.7 (CH_3), 14.2 (CH_3).

LRMS (ESI, M+Na$^+$): m/z 468.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{23}H_{27}NNaO_6S$ 468.1451, found 468.1449.

Ethyl 2-((2*S,3*R**)-3-(benzo[b]thiophene-2-carbonyl)-1-tosylpyrrolidin-2-yl)acetate (1v).**

Reaction of the vinylogous carbamate **2v** (56 mg, 0.12 mmol) with TMSOTf (25 μL, 0.14 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C, as described for the pyrrolidine **1q** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished pyrrolidine **1v** (37 mg, 62 %) as a viscous liquid.



Physical appearance: viscous liquid.

R_f: 0.5 (1:19, EtOAc:Petroleum ether).

IR (neat): 3185, 1730, 1663, 1345, 1159, 1022, 757 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.47 (td, *J* = 8.0, 1.0 Hz, 1H), 7.41 (td, *J* = 8.0, 1.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.41 (dt, *J* = 9.5, 3.5 Hz, 1H), 4.12-4.08 (m, 2H), 4.0 (dt, *J* = 6.5, 5.0 Hz, 1H), 3.62-3.57 (m, 1H), 3.42-3.37 (m. 1H), 3.15 (ABX, *J* = 16.0, 3.5 Hz, 1H), 2.80 (ABX, *J* = 16.5, 9.5 Hz, 1H), 2.45 (s, 3H), 2.23-2.17 (m, 1H), 1.85-1.81 (m,1H), 1.22 (t, *J* = 7.0 Hz, 3H).

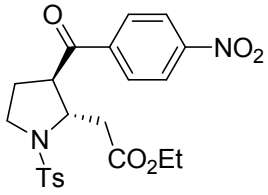
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 192.8 (C), 171.2 (C), 143.9 (C), 142.8 (C), 142.4 (C), 139.1 (C), 134.0 (C), 130.1 (CH), 129.8 (2 × CH), 127.9 (CH), 127.8 (2 × CH), 126.3 (CH), 125.2 (CH), 123.0 (CH), 60.9 (CH_2), 59.2 (CH), 51.9 (CH), 48.6 (CH_2), 41.1 (CH_2), 29.0 (CH_2), 21.7 (CH_3), 14.2 (CH_3).

LRMS (ESI, M+Na^+): m/z 494.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{24}H_{25}NNaO_5S_2$ 494.1066, found 494.1067

Ethyl 2-((2*S,3*R**)-3-(4-nitrobenzoyl)-1-tosylpyrrolidin-2-yl)acetate (1w):**

Reaction of the vinylogous carbamate **2w** (55 mg, 0.124 mmol) with TMSOTf (35 μL, 0.18 mmol) in dry CH_2Cl_2 (4.0 mL) at 0 °C, as described for the pyrrolidine **1q** followed by purification on a silica gel column using EtOAc/petroleum ether (3:7) as eluent furnished pyrrolidine **1w** (17 mg, 30%) as a viscous liquid.



Physical appearance: viscous liquid.

R_f: 0.4 (30:70, Ethylacetate-Petroleum ether).

IR (neat): 2939, 1730, 1601, 1527, 1348, 1218, 1161, 764 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.38 (dt, *J* = 10.0, 3.5 Hz, 1H), 4.07 (q, *J* = 7.5 Hz, 2H), 4.02-4.0 (m, 1H), 3.61-3.56 (m, 1H), 3.36-3.31 (m. 1H), 3.18 (ABX, *J* = 16.0, 3.5 Hz, 1H), 2.75 (ABX, *J* = 16.0, 10.0 Hz, 1H), 2.47 (s, 3H), 2.24-2.17 (m, 1H), 1.77-1.72 (m, 1H), 1.14 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 197.2 (C), 171.4 (C), 150.6 (C), 143.9 (C), 140.0 (C), 134.2 (C), 129.9 (2 × CH), 129.7 (2 × CH), 127.9 (2 × CH), 123.9 (2 × CH), 60.1 (CH_2), 58.6 (CH), 51.5 (CH), 48.3 (CH_2), 40.9 (CH_2), 28.4 (CH_2), 21.8 (CH_3), 14.3 (CH_3).

LRMS (ESI, M+H$^+$): m/z 461.

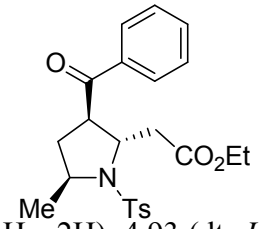
HRMS (ESI, M+H$^+$): m/z calcd. for $C_{22}H_{25}N_2O_7S$ 461.1382, found 461.1387.

Ethyl 2-((2*S*,3*R*,5*S*)-3-benzoyl-5-methyl-1-tosylpyrrolidin-2-yl)acetate (1x):

Reaction of the vinylogous carbamate **2x** (56 mg, 0.13 mmol) with TMSOTf (30 μL, 0.14 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 °C, as described for the pyrrolidine **1q** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished pyrrolidine **1x** (36 mg, 62 %) as a white solid.

m.p.: 102-104 ^oC.

Physical appearance: white solid.



R_f: 0.5 (1:4, Ethylacetate-Petroleum ether).

IR (neat): 2957, 1733, 1597, 1449, 1334, 1157, 758, 604 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.89 (t, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.93 (dt, *J* = 10.0, 3.0 Hz, 1H), 4.12-4.07 (m, 3H), 3.93 (dt, *J* = 8.0, 4.0 Hz, 1H), 3.33 (ABX, *J* = 16.0, 4.0 Hz, 1H), 2.73 (ABX, *J* = 16.0, 10.0 Hz, 1H), 2.64 (ABX, *J* = 16.0, 4.0 Hz, 1H), 2.44 (s, 3H), 1.86 (dt, *J* = 13.0, 4.0 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.07 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 199.1 (C), 171.2 (C), 143.1 (C), 140.1 (C), 135.6 (C), 133.4 (CH), 129.6 (2 × CH), 128.8 (2 × CH), 128.7 (2 × CH), 127.2 (2 × CH), 60.8 (CH_2), 59.3 (CH_2), 56.1 (CH), 50.4 (CH), 40.0 (CH_2), 36.3 (CH), 21.6 (CH_3), 19.9 (CH_3), 14.2 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{23}H_{27}NNaO_5S$ 452.1502, found 452.1505.

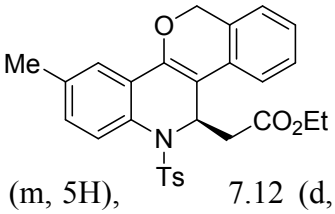
LRMS (ESI, M+Na$^+$): m/z 452.

(*R)-Ethyl 2-(3-methyl-12-tosyl-11,12-dihydro-6H-isochromeno[4,3-c]quinolin-11-yl)acetate (8a) :**

To a stirred solution of the alkynyl vinylogous carbamate **7a** (azeotrophic dry with toluene) (140 mg, 0.285 mmol) in dry CH_2Cl_2 (6 mL) was added TMSOTf (77 μL, 0.427 mmol) drop wise at 0 °C and the resulting mixture was slowly warmed up to r.t and stirred for completion (TLC control).The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (10 mL), extracted with CH_2Cl_2 (3 × 15 mL) and combined organic layer was washed with brine

solution and dried (*anhyd.* Na_2SO_4). Solvent was evaporated under vacuum and purification of the residue was carried out by silica gel column chromatography using EtOAc:petroleum ether(1:19) as an eluent to furnish dihydroquinoline **8a** (85 mg, 61%) as a pale yellow liquid.

Physical appearance: pale yellow liquid.



R_f: 0.2 (1:19, EtOAc:Petroleum ether).

IR (neat): 2927, 1735, 11352, 1167, 754 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.38-7.20 (m, 5H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 7.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 5.88 (t, *J* = 7.0 Hz, 1H), 4.91 (t, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 2.48-2.18 (m, 2H), 2.40 (s, 3H), 2.20 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 169.1 (C), 145.8 (C), 143.7 (C), 137.1 (C), 135.1 (C), 130.7 (C), 130.3 (CH), 129.2 (C), 128.8 (2 × CH), 128.6 (C), 127.9 (CH), 127.4 (2 × CH), 125.2 (C), 124.1 (CH), 123.1 (CH), 120.0 (CH), 109.8 (C), 68.4 (CH_2), 61.1 (CH_2), 51.6 (CH), 38.5 (CH_2), 21.5 (CH_3), 21.4 (CH_3), 14.3 (CH_3).

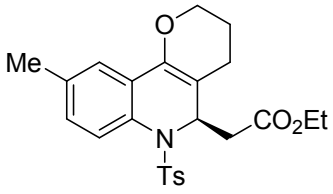
LRMS (ESI, M+Na^+): m/z 512.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{28}H_{27}NNaO_5S$ 512.1508, found 512.1528.

(*R)-Ethyl 2-(9-methyl-6-tosyl-3,4,5,6-tetrahydro-2H-pyrano[3,2-c]quinolin-5-yl)acetate (8b):**

Reaction of the vinylogous carbamate **7b** (75 mg, 0.169 mmol) with TMSOTf (46 μL, 0.254 mmol) in dry CH_2Cl_2, (5.0 mL) at 0 °C, as described for dihydroquinoline **8a** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished dihyroquioline **8b** (36 mg, 48%) as a yellow liquid.

Physical appearance: yellow liquid.



R_f: 0.2 (1:19, EtOAc:Petroleum ether).

IR (neat): 2930, 1737, 1469, 1372, 1168, 916, 981, 732, 704 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15-7.08 (m, 4H), 4.91 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.23-4.10 (m, 2H), 3.85-3.80 (m, 1H), 3.54-3.50 (m, 1H), 2.36-2.33 (m, 8H), 2.05-1.62 (m, 4H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.3 (C), 143.9 (C), 143.4 (C), 136.9 (C), 136.0 (C), 129.9 (C), 129.1 (3 × CH), 128.3 (CH), 126.9 (2 × CH), 126.1 (C), 121.8 (CH), 107.1 (C), 65.9

(CH_2), 61.0 (CH_2), 56.3 (CH), 38.5 (CH_2), 23.6 (CH_2), 22.1 (CH_2), 21.6 (CH_3), 21.4 (CH_3), 14.4 (CH_3).

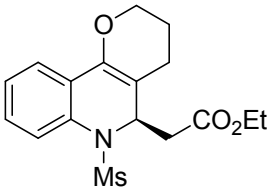
LRMS (ESI, M+Na$^+$): m/z 464.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{24}H_{27}NNaO_5S$, 464.1502, found 464.1508.

(*R)-Ethyl 2-(6-(methylsulfonyl)-3,4,5,6-tetrahydro-2H-pyrano[3,2-c]quinolin-5-yl)acetate (8c):**

Reaction of the vinylogous carbamate **7c** (140 mg, 0.398 mmol) with TMSOTf (108 µL, 0.597 mmol) in dry CH_2Cl_2 (5.0 mL) at 0 °C, as described porcedure for dihydroquinoline **8a** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished dihyroquioline **8c** (56 mg, 40%) as a white solid which was crystallized from EtOH.

Physical appearance: white solid.



m.p.: 115-117 °C.

R$_f$: 0.2 (1:19, EtOAc:Petroleum ether).

IR (neat): 2933, 1732, 1708, 1632, 1493, 1347, 1158, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.48 (m, 2H), 7.29-7.26 (m, 2H), 5.03 (dd, *J* = 9.2, 5.2 Hz, 1H), 4.18-4.10 (m, 2H), 2.65 (s, 3H), 2.46 (ABX, *J* = 14.4, 5.2 Hz, 1H), 2.38 (ABX, *J* = 14.4, 5.2 Hz, 1H), 2.27-2.20 (m, 2H), 2.01-1.96 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.2 (C), 144.2 (C), 132.4 (C), 128.7 (CH), 127.5 (CH), 127.0 (CH), 125.7 (C), 121.9 (CH), 107.9 (C), 66.5 (CH_2), 60.1 (CH_2), 56.3 (CH), 38.5 (CH_2), 37.7 (CH_3), 23.3 (CH_2), 22.3 (CH_2), 14.3 (CH_3).

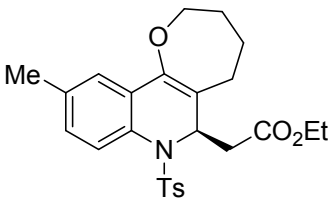
LRMS (ESI, M+Na$^+$): m/z 374.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{17}H_{21}NNaO_5S$ 374.1038, found 374.1037.

(*R)-Ethyl 2-(10-methyl-7-tosyl-2,3,4,5,6,7-hexahydrooxepino[3,2-c]quinolin-6-yl)acetate.(8d):**

Reaction of the vinylogous carbamate **7d** (80 mg, 0.175 mmol) with TMSOTf (48 µL, 0.263 mmol) in dry CH_2Cl_2, (5.0 mL) at 0 °C, as described porcedure for dihydroquinoline **8a** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished dihydroquinoline **8d** (34 mg, 45%) as a pale yellow liquid.

Physical appearance: pale yellow liquid.



R$_f$: 0.2 (1:19, EtOAc:Petroleum ether).

IR (neat): 2928, 1737, 1492, 1352, 1305, 1236, 1168, 1044, 815, 681 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (s, 1H), 7.08 (t, *J* = 8.0 Hz, 3H), 4.99 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.21-4.12 (m, 2H), 3.69 (ABXY, *J* = 11.2, 7.2, 3.6 Hz, 1H), 3.29 (ABXY, *J* = 11.2, 7.2, 3.6 Hz, 1H), 2.37 (bs, 5H), 2.32 (s, 3H), 2.17-2.12 (m, 1H), 2.00-1.94 (m, 1H), 1.76-1.69 (m, 2H), 1.65-1.42 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H).

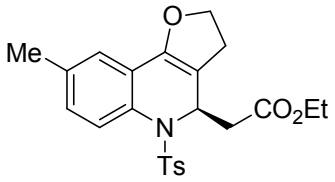
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.0 (C), 149.4 (C), 143.4 (C), 136.8 (C), 136.1 (C), 129.5 (C), 129.1 (2 × CH), 128.9 (CH), 127.8 (CH), 127.6 (C), 127.2 (2 × CH), 122.3 (CH), 119.3 (C), 72.1 (CH_2), 61.0 (CH_2), 58.1 (CH), 38.3 (CH_2), 31.3 (CH_2), 31.2 (CH_2), 24.3 (CH_2), 21.5 (CH_3), 21.4 (CH_3), 14.4 (CH_3).

LRMS (ESI, M+Na^+): m/z 478.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{25}H_{29}NNaO_5S$ 478.1659 found 478.1664.

(*R)-Ethyl 2-(8-methyl-5-tosyl-2,3,4,5-tetrahydrofuro[3,2-c]quinolin-4-yl)acetate (8e):**

Reaction of the vinylogous carbamate **7e** (78 mg, 0.182 mmol) with TMSOTf (50 μL, 0.273 mmol) in dry CH_2Cl_2, (5.0 mL) at 0 °C, as described porcedure for dihydroquinoline **8a** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished dihydroquinoline **8e** (7 mg, 8%) as a viscous liquid.



Physical appearance: viscous liquid.

R_f: 0.6 (1:9, EtOAc:Petroleum ether).

IR (neat): 2930, 1737, 1469, 1372, 1168, 916, 81, 732, 04 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.29 (dd, *J* = 10.4, 2.4 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 4.15-1.10 (m, 1H), 3.85-3.80 (m, 1H), 3.13-3.08 (m, 2H), 2.98 (ABX, *J* = 15.6, 2.8 Hz, 1H), 2.61 (ABX, *J* = 15.6, 10.4 Hz, 1H), 2.57 (s, 3H), 2.39 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

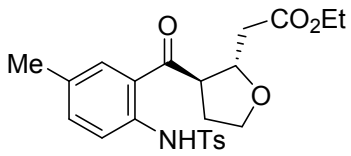
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.3 (C), 143.9 (C), 143.4 (C), 136.9 (C), 136.0 (C), 129.9 (C), 129.1 (2 × CH), 128.3 (CH), 126.9 (2 × CH), 126.1 (C), 121.8 (CH), 107.1 (C), 65.9 (CH_2), 61.0 (CH_2), 56.3 (CH), 38.5 (CH_2), 23.5 (CH_2), 22.1 (CH_2), 21.6 (CH_3), 21.4 (CH_3), 14.4 (CH_3).

LRMS (ESI, M+Na^+): m/z 450.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{23}H_{25}NNaO_5S$ 450.1346, found 450.1339.

Further elution furnished (48 mg, 52%) THF **9e** derivatives as a white solid.

Ethyl 2-((2*S,3*R**)-3-(5-methyl-2-(4-methylphenylsulfonamido)benzoyl)tetrahydrofuran-2-yl)acetate (9e):**



m.p.: 100-102 °C.

Physical appearance: white solid.

R_f: 0.4 (20:80, EtOAc:Petroleum ether).

IR (neat): 3152, 2981 1732, 1647, 1496, 1184, 1091, 899 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.1 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.50 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.87 (q, *J* = 7.0 Hz, 1H), 4.15-1.10 (m, 1H), 4.09-4.03 (m, 2H), 3.98-3.93 (m, 1H), 3.82-3.76 (m, 2H), 2.57 (ABX, *J* = 15.0, 6.5 Hz, 1H), 2.51 (ABX, *J* = 15.0, 6.5 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 1.85-1.81 (m,1H), 1.29 (t, *J* = 7.2 Hz, 3H).

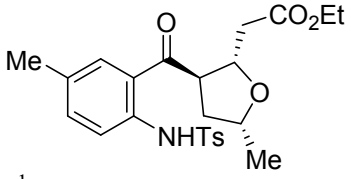
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 203.8 (C), 170.7 (C), 143.9 (C), 137.8 (C), 136.7 (C), 135.9 (CH), 132.9 (C), 131.2 (CH), 129.7 (2 × CH), 127.3 (2 × CH), 126.7 (C), 120.6 (CH), 76.9 (CH), 67.7 (CH_2), 60.8 (CH_2), 51.3 (CH_2), 39.3 (CH_2), 32.0 (CH_2), 21.6 (CH_3), 20.9 (CH_3), 14.2 (CH_3).

LRMS (ESI, M+Na^+): m/z 468.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{23}H_{27}NNaO_6S$ 468.1457, found 468.1448.

Ethyl 2-((2*S,3*R**,5*R**)-5-methyl-3-(5-methyl-2-(4-methylphenylsulfonamido)benzoyl)tetrahydrofuran-2-yl)acetate (9f);**

Reaction of the vinylogous carbamate **7f** (102 mg, 0.231 mmol) with TMSOTf (85 μL, 0.462 mmol) in dry CH_2Cl_2 (5.0 mL) at 0 °C, as described porcedure for dihydroquinoline **8a** followed by purification on a silica gel column using EtOAc/petroleum ether (1:19) as eluent furnished THF derivatives **9f** (67 mg, 63%) as a viscous liquid.



Physical appearance: viscous liquid.

R_f: 0.5 (10:90, EtOAc:Petroleum ether).

IR (neat): 2977, 2933, 1732, 1650, 1496, 1185, 1165, 1092, 909 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.01 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.53 (s, 1H), 7.29 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.44 (q, *J* = 13.0, 6.0 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.01-3.97 (m, 1H), 3.86-3.82 (m, 1H), 2.61 (ABX, *J* = 15.0, 6.5 Hz, 1H), 2.52 (ABX, *J* = 15.0, 6.5 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 1.83-1.76 (m, 2H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 204.3 (C), 170.7 (C), 143.9 (C), 137.9 (C), 136.8 (C), 135.8 (CH), 132.8 (C), 131.2 (CH), 129.7 (2 × CH), 127.4 (2 × CH), 122.7 (C), 120.7 (CH), 75.1 (CH), 75.1 (CH), 60.8 (CH_2), 51.5 (CH), 39.6 (CH_2), 39.3 (CH_2), 21.6 (CH_3), 20.9 (CH_3), 20.7 (CH_3), 14.2 (CH_3).

LRMS (ESI, M+Na$^+$): m/z 482.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{24}H_{29}NNaO_6S$ 482.1608, found 482.1611.

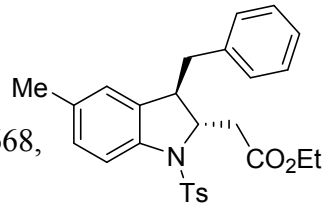
One Pot procedure for alkyne iminium reductive cyclization.

Ethyl 2-((2*S,3*R**)-)-3-benzyl-5-methyl-1-tosylindolin-2-yl)acetate (18):**

To a stirred solution of the alkynyl vinylgous carbamatae **7c** (80.0 mg, 0.17 mmol) in dry CH_2Cl_2 (3 mL) was added TMSOTf (48 µL, 0.34 mmol) drop wise at 0 °C and the resulting mixture was slowly warmed up to r.t monitor by TLC, then added excess Et_3SiH (111 µL, 0.68 mmol) stirred for completion 6h (TLC control). The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (10 mL), extracted with CH_2Cl_2 (3 × 15 mL) and combined organic layer was washed with brine solution and dried (*anhyd.* Na_2SO_4). Solvent was evaporated under vacuum and purification of the residue was carried out by silica gel column chromatography using ethyl acetate- petroleum ether (1:19) as an eluent to furnished dihydroindoline **18** (43 mg, 54%) as a white solid, which was crystallized from CH_3CN.

m.p.: 90-92 ^{o}C.

Physical appearance: white solid.



R_f: 0.6 (1:9, EtOAc:Petroleum ether).

IR (neat): 3026, 2980, 1732, 1598, 1488, 1357, 1167, 1032, 816, 668, 590 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.24-7.18 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.20 (s, 1H), 4.18 (ABXY, *J* = 10.0, 4.0, 2.0 Hz, 1H), 4.06-3.95 (m. 2H), 3.03 (t, *J* = 8.0 Hz, 1H), 2.85 (ABX, *J* = 16.0, 4.0 Hz, 1H), 2.60 (ABX, *J* = 15.0, 10.0 Hz, 1H), 2.38 (s, 3H), 2.25 (ABX, *J* = 15.0, 14.0 Hz, 1H), 2.15 (s, 3H), 1.62 (ABX, *J* = 14.0, 10.0 Hz, 1H), 1.46 (t, *J* = 7.0 Hz, 3H).

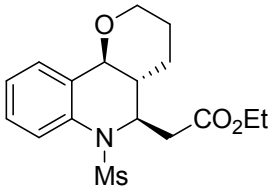
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 170.7 (C), 144.3 (C), 138.3 (C), 138.3 (C),134.9 (C), 134.0 (C), 133.9 (C), 129.8 (2 × CH), 129.4 (2 × CH), 129.1 (CH), 128.4 (2 × CH), 127.3 (2 × CH), 126.6 (CH), 126.5 (CH), 116.5 (CH), 64.5 (CH), 60.7 (CH_2), 48.9 (CH), 42.7 (CH_2), 41.4 (CH_2), 21.7 (CH_3), 21.0 (CH_3), 14.2 (CH_3).

LRMS (ESI, M+H$^+$): m/z 464.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{27}H_{30}NO_4S$, 464.1896 found 464.1893.

Ethyl 2-((4a*R,5*R**,10b*S**)-6-(methylsulfonyl)-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinolin-5-yl)acetate (17):**

To a stirred solution of the alkynyl vinylgous carbamatae **7c** (60.0 mg, 0.164 mmol) in dry CH_2Cl_2 (3 mL) was added TMSOTf (60 µL, 0.328 mmol) drop wise at 0 °C and the resulting mixture was slowly warmed up to r.t monitor by TLC, then added excess Et_3SiH (78 µL, 0.486 mmol) stirred for completion 5h (TLC control). The reaction mixture was then quenched with saturated aq. $NaHCO_3$ (10 mL), extracted with CH_2Cl_2 (3 × 15 mL) and combined organic layer was washed with brine solution and dried (*anhyd.* Na_2SO_4). Solvent was evaporated under vacuum and purification of the residue was carried out by silica gel column chromatography using ethyl acetate- petroleum ether (1:19) as an eluent to furnished THP fused quinoline **17** (17 mg, 28%) as a viscous liquid.



Physical appearance: viscous liquid.

R$_f$: 0.2 (1:19, EtOAc:Petroleum ether).

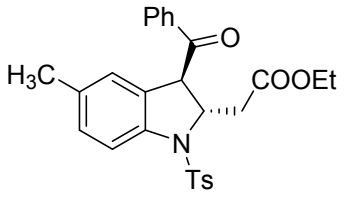
IR (neat): 2945, 1735, 1712, 1632, 1493, 1347, 1155, 1100, 752 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6): δ 7.35-7.65 (m, 2H), 7.05-7.03 (m, 2H), 4.14 (dt, *J* = 9.0, 5.5 Hz, 1H), 3.89 (q, *J* = 7.0 Hz, 2H), 3.88-3.86 (m, 2H), 3.18-3.13 (m, 1H), 2.48 (ABX, *J* = 15.0, 5.5 Hz, 1H), 2.43 (ABX, *J* = 15.0, 5.5 Hz, 1H), 2.19 (s, 3H), 1.65-1.44 (m, 2H), 1.37-1.05 (m, 3H), 0.92 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, C_6D_6, DEPT): δ 170.2 (C), 136.9 (C), 134.4 (C), 127.4 (CH), 126.8 (CH), 126.2 (CH), 122.9 (C), 75.0 (CH), 67.8 (CH_2), 60.6 (CH_2), 58.1 (CH), 46.7 (CH), 41.3 (CH_2), 38.0 (CH), 38.0 (CH), 29.4 (CH_2), 25.6 (CH_2), 14.1 (CH_3).

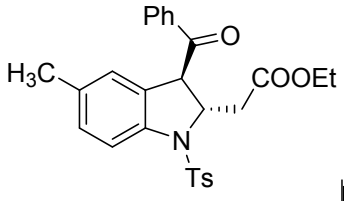
LRMS (ESI, M+Na$^+$): m/z 376.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{17}H_{23}NNaO_5S$ 376.1189, found 376.1175.



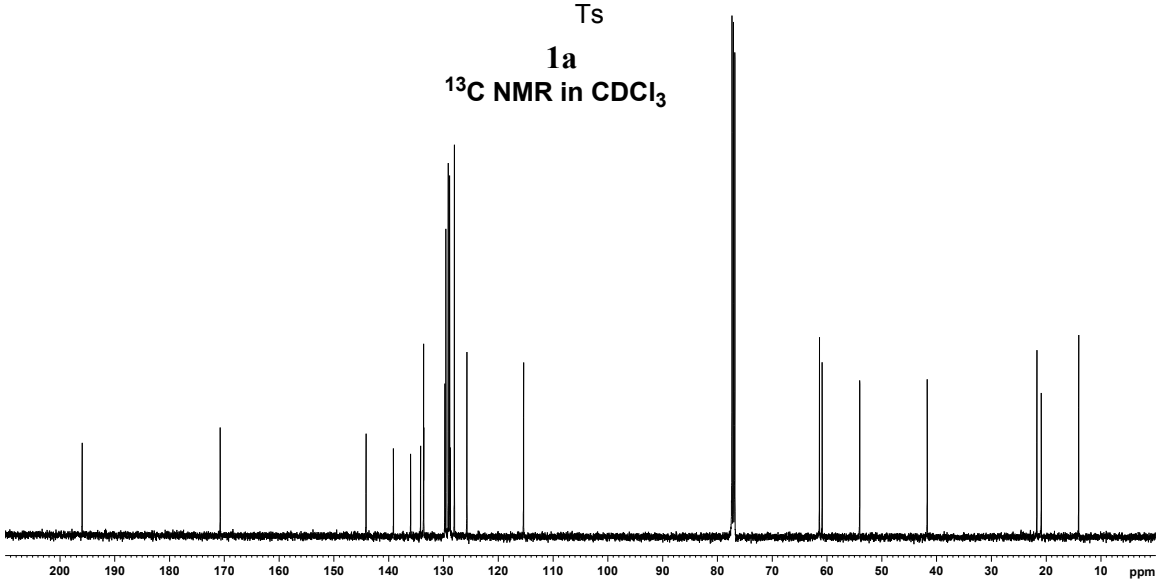
1a

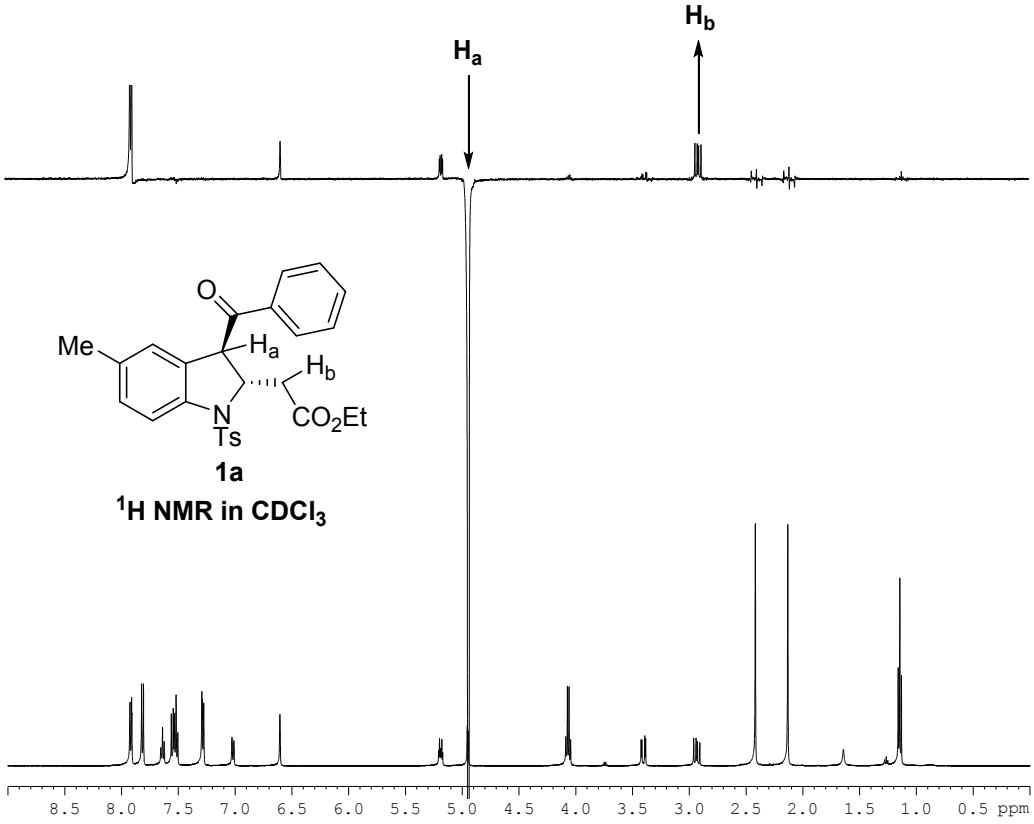
^{1}H NMR in $CDCl_3$



1a

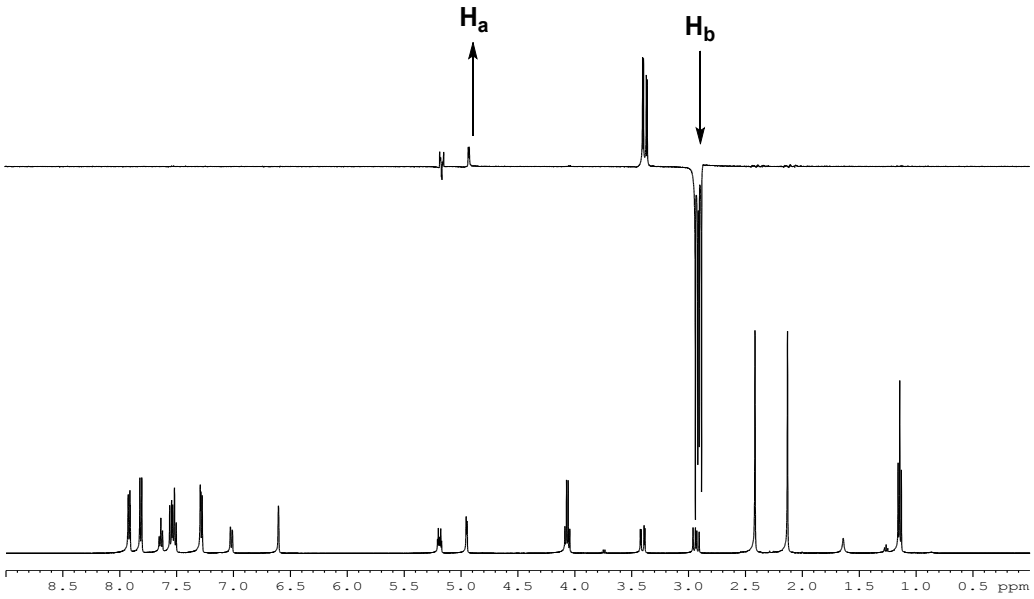
^{13}C NMR in $CDCl_3$

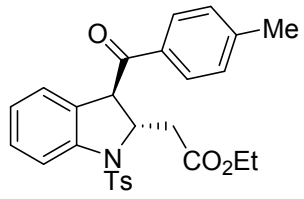




1a

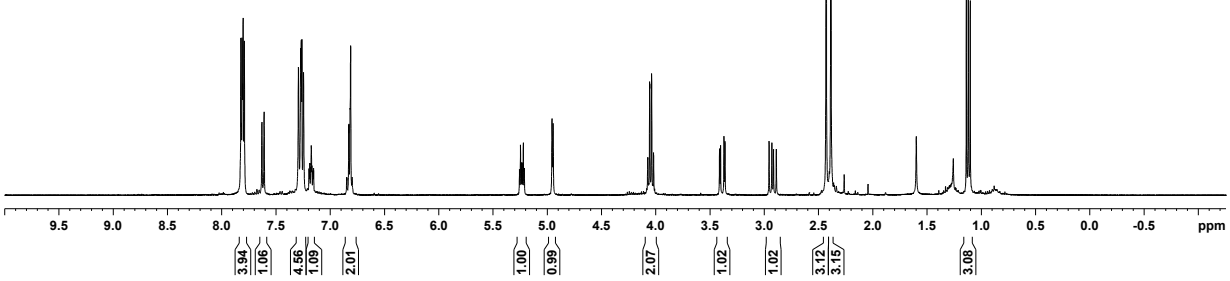
^{1}H NMR in $CDCl_3$

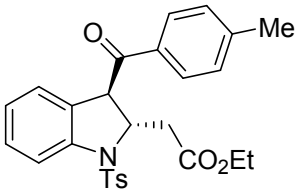




1b

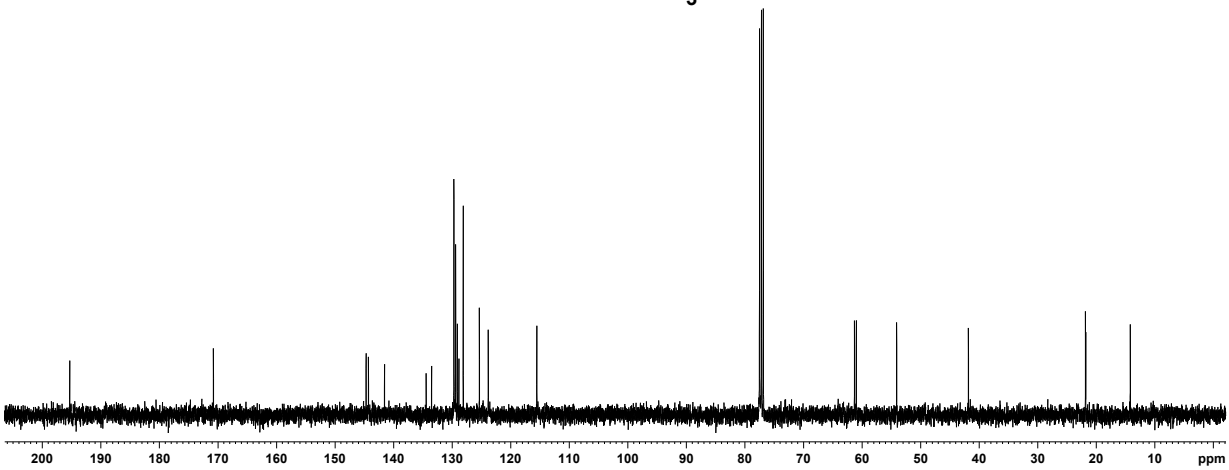
^{1}H NMR in $CDCl_3$

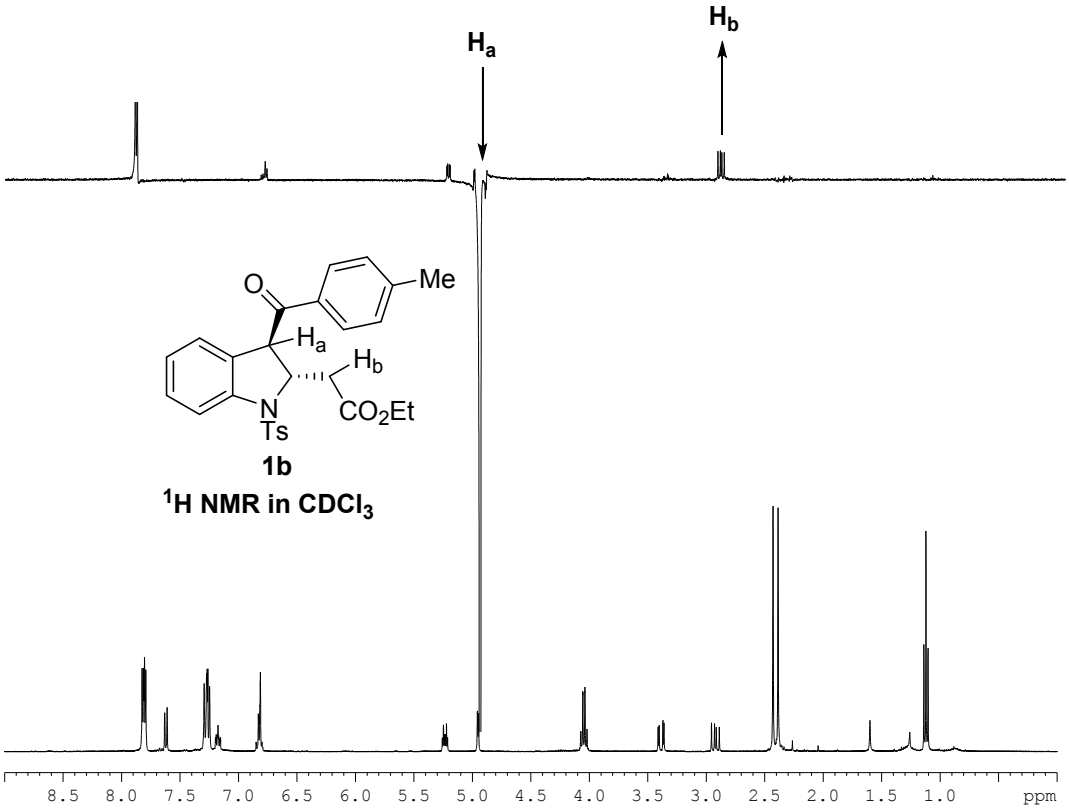




1b

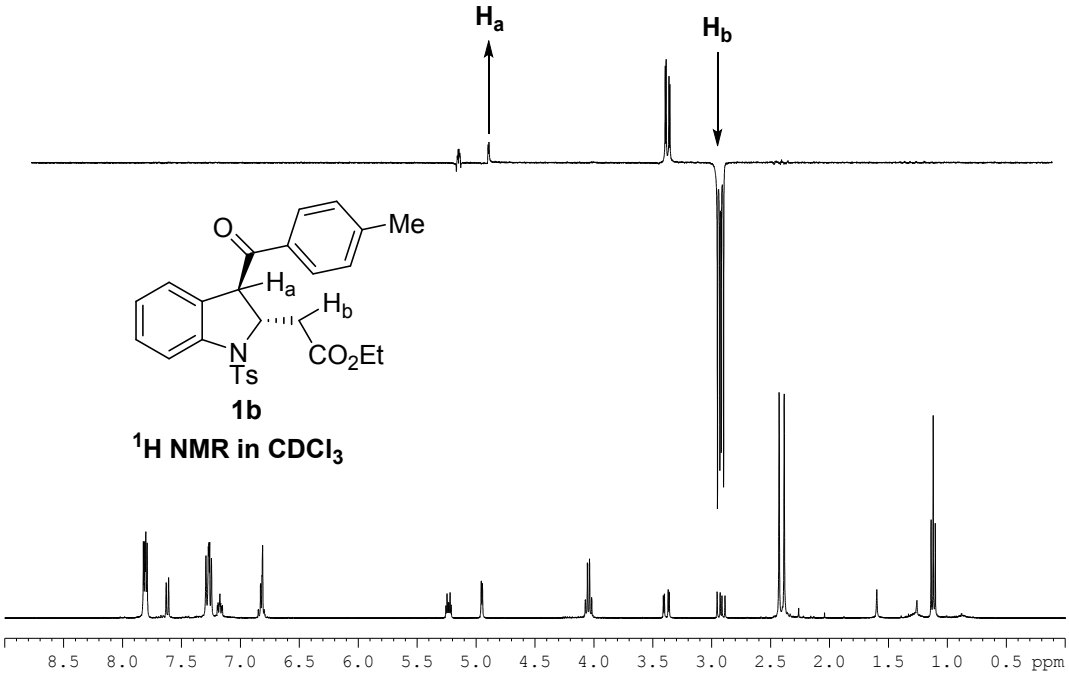
^{13}C NMR in $CDCl_3$





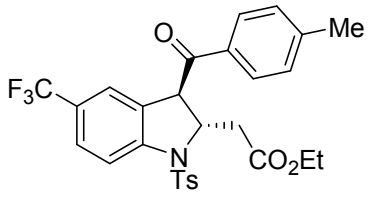
1b

^{1}H NMR in $CDCl_3$



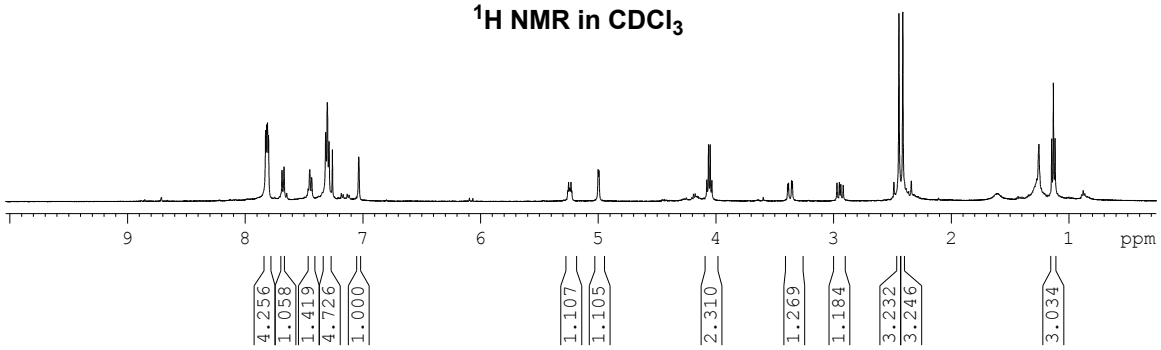
1b

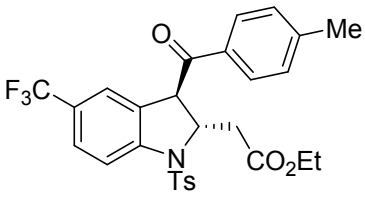
^{1}H NMR in $CDCl_3$



1c

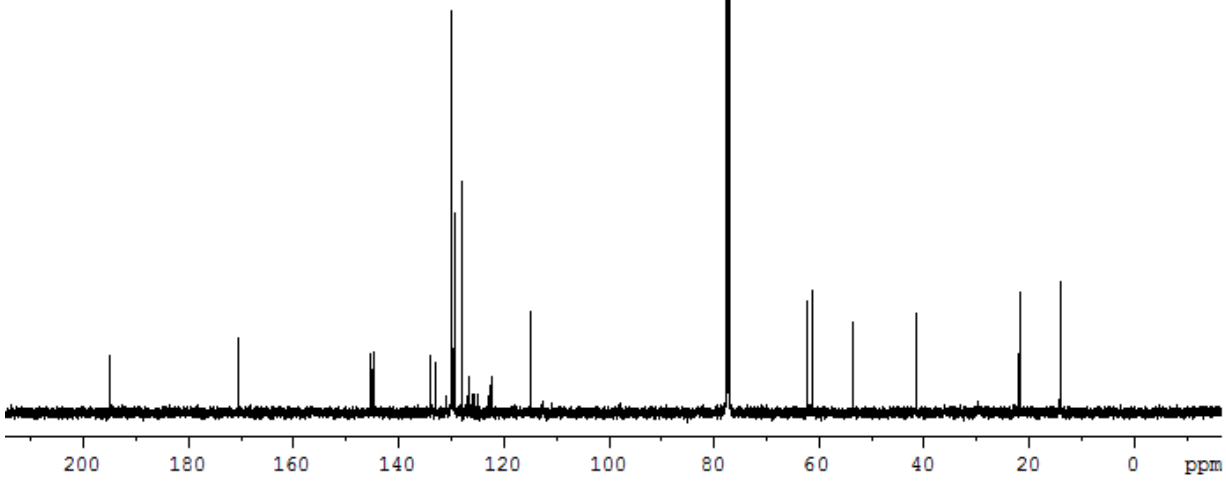
^{1}H NMR in $CDCl_3$

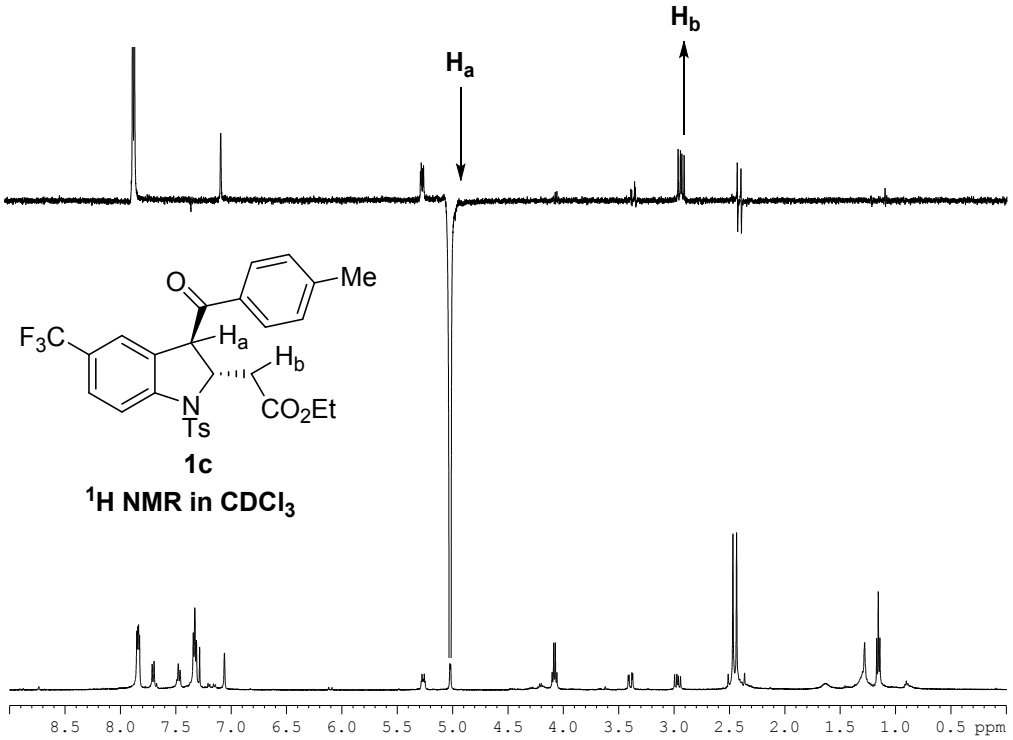




1c

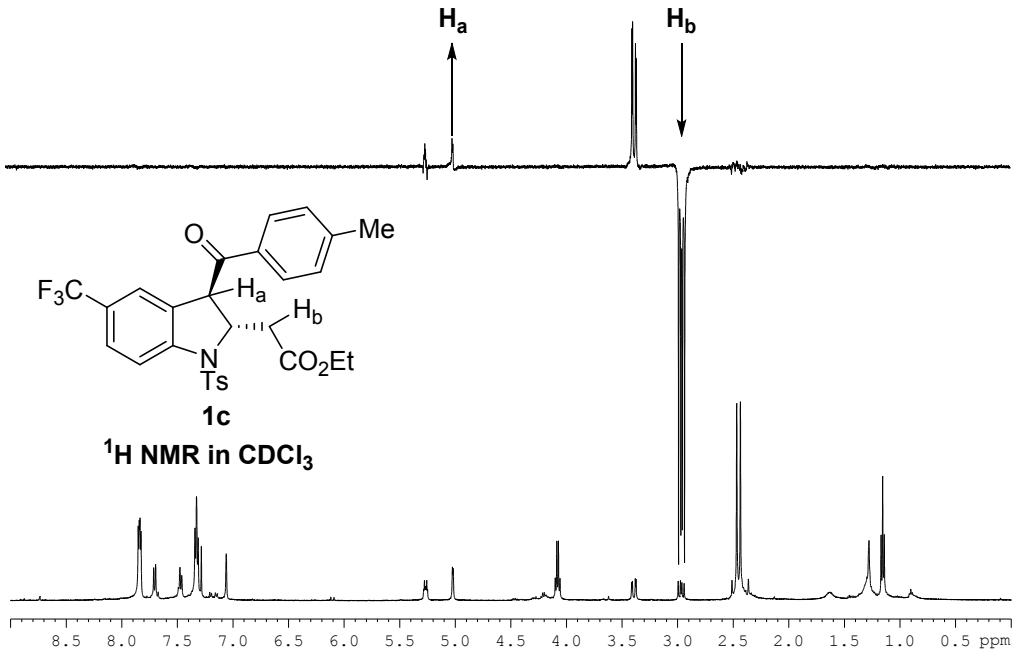
^{13}C NMR in $CDCl_3$





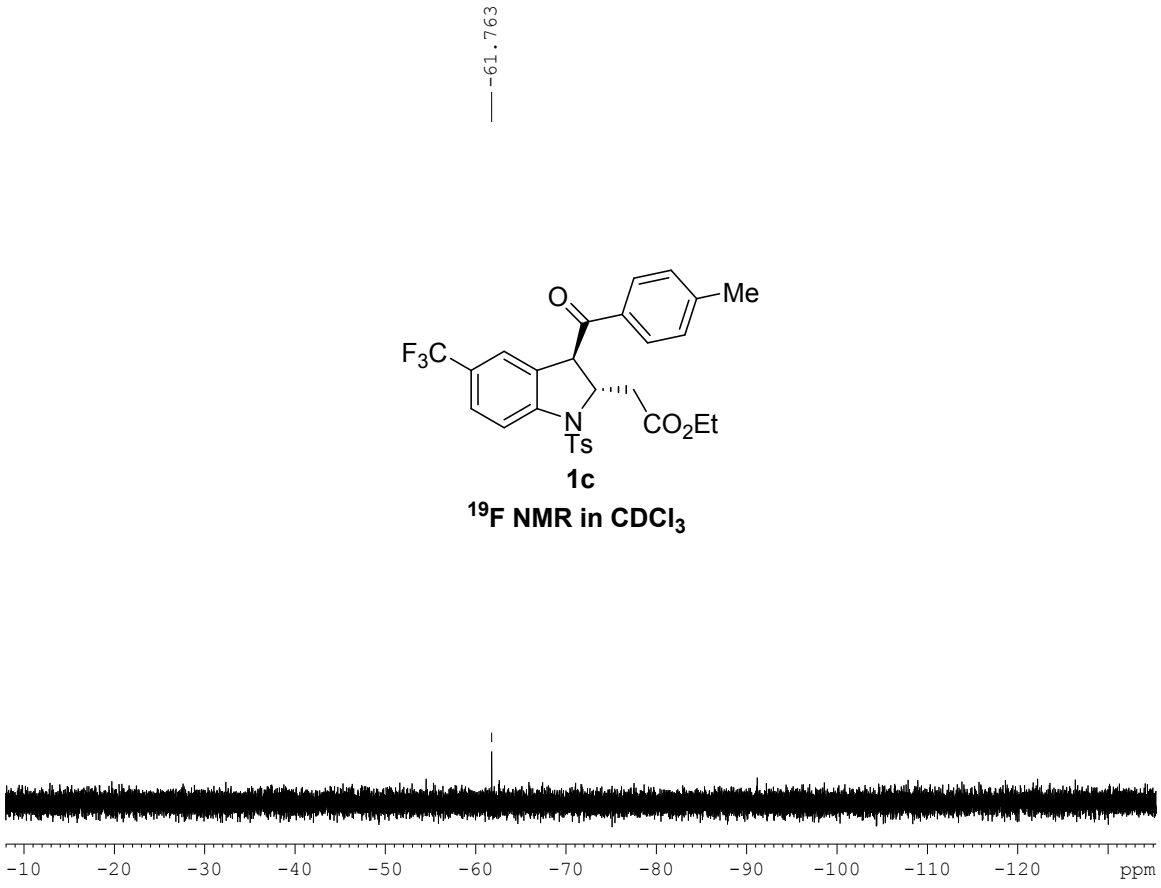
1c

^{1}H NMR in $CDCl_3$



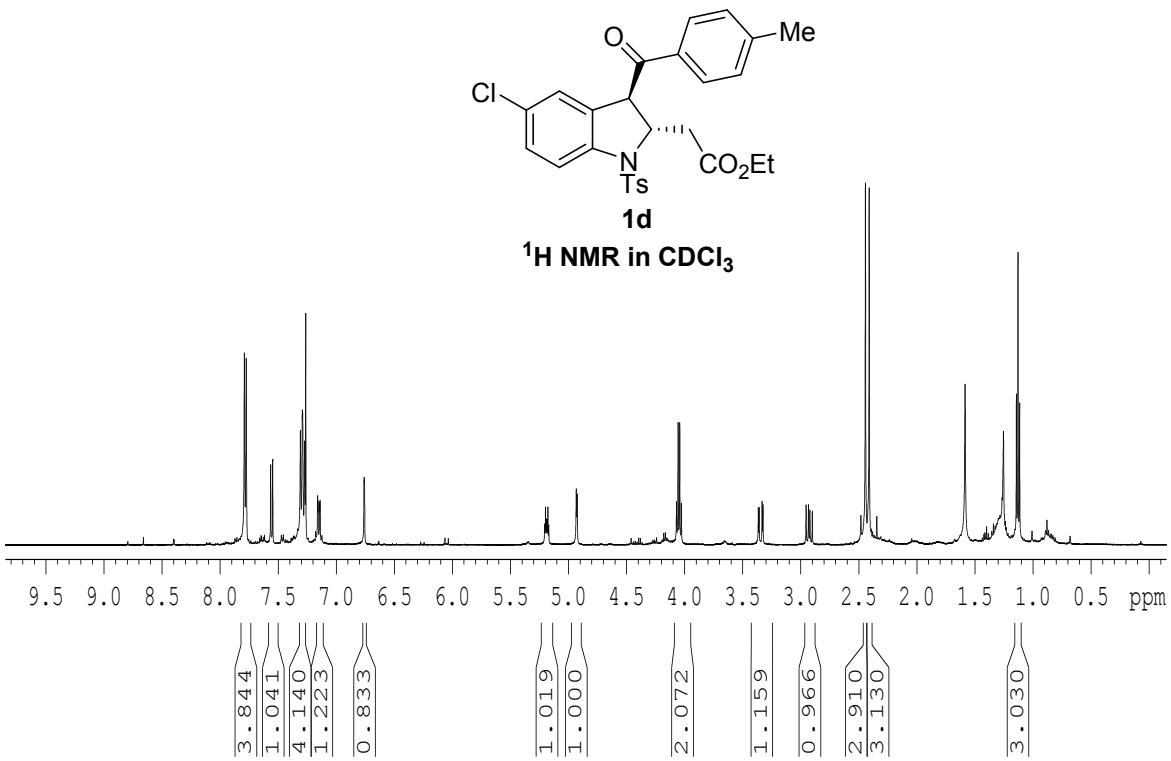
1c

^{1}H NMR in $CDCl_3$



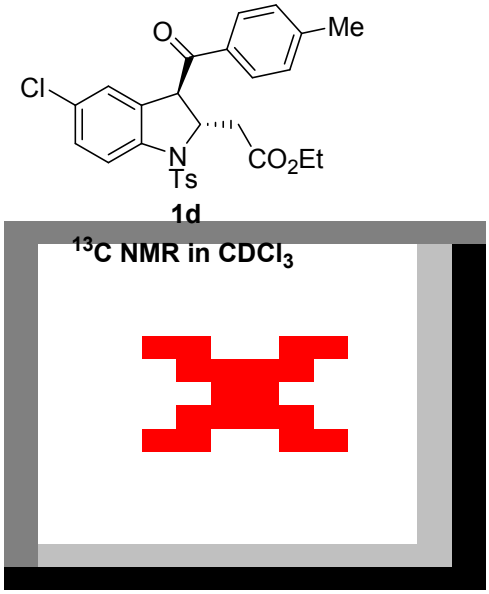
1c

^{19}F NMR in $CDCl_3$



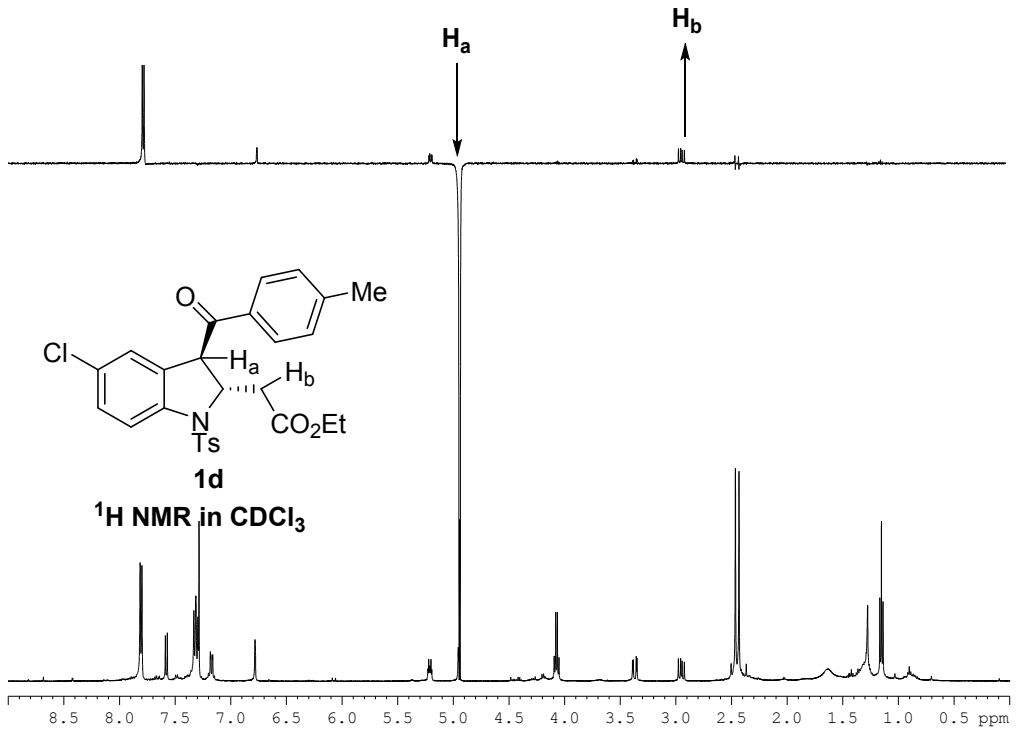
1d

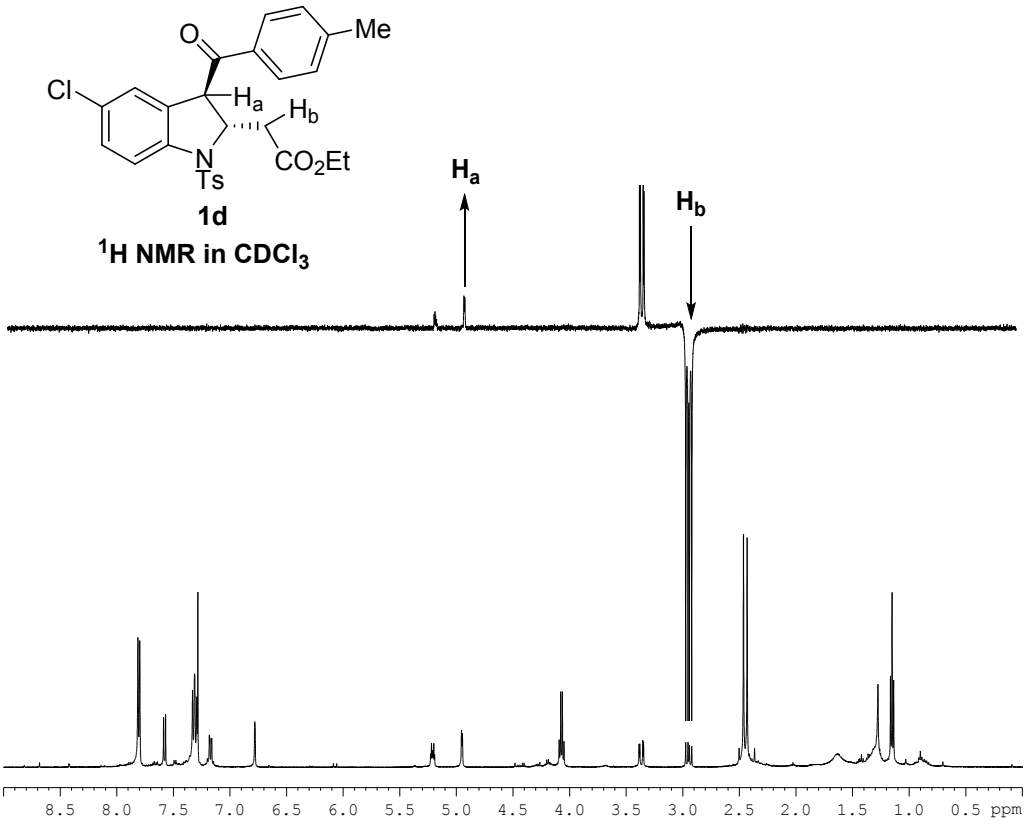
^{1}H NMR in $CDCl_3$

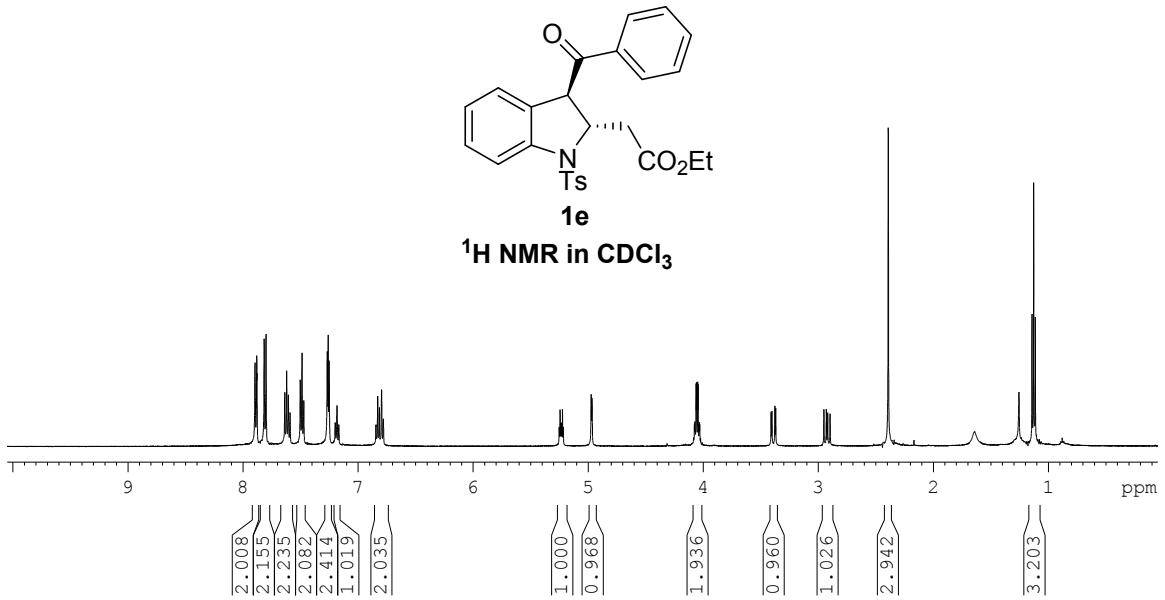


1d

^{13}C NMR in $CDCl_3$

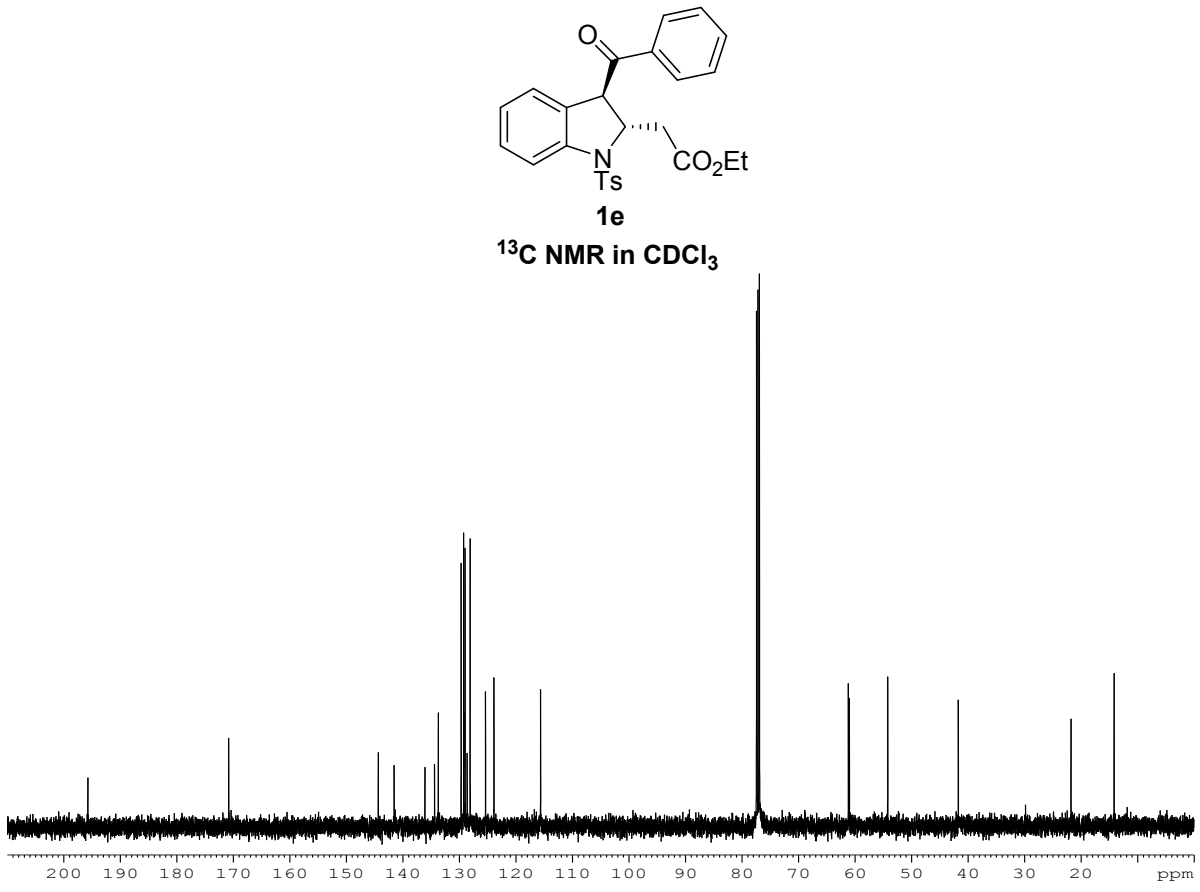

Ha
Hb
O
Me
Cl
Ha
Hb
N
Ts
CO2Et
1d
1H NMR in CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


O
Me
Cl
Ha
Hb
N
Ts
CO2Et
1d
1H NMR in CDCl3
Ha
Hb
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



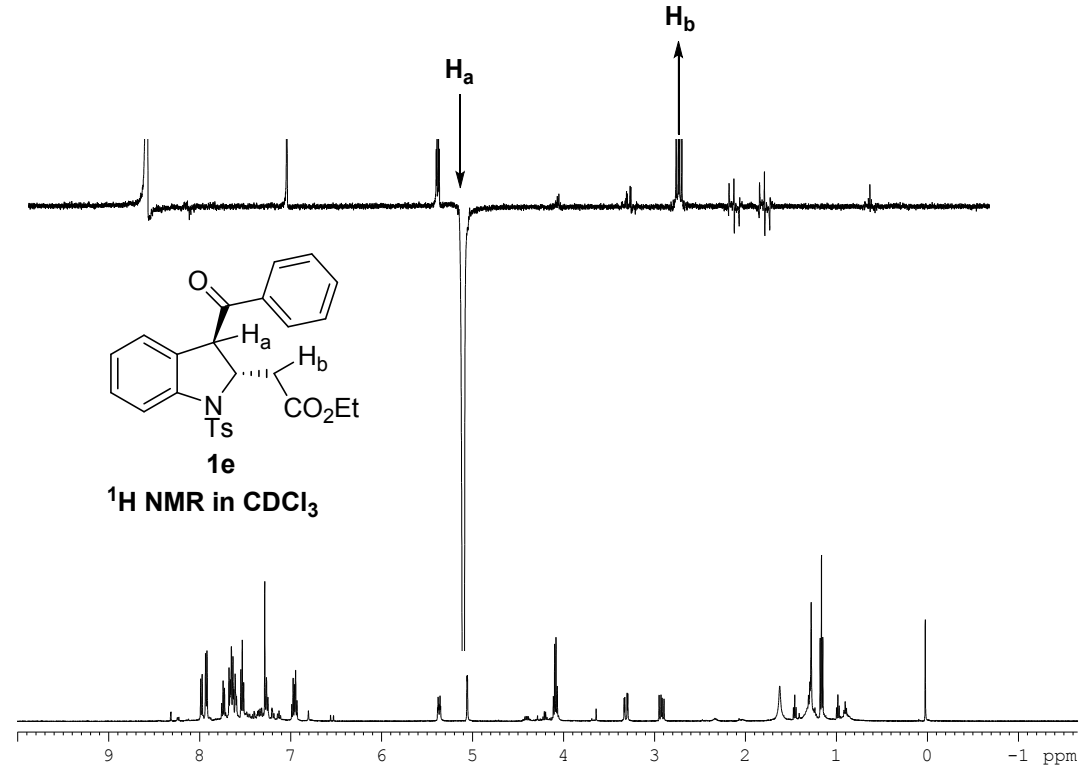
1e

^{1}H NMR in $CDCl_3$



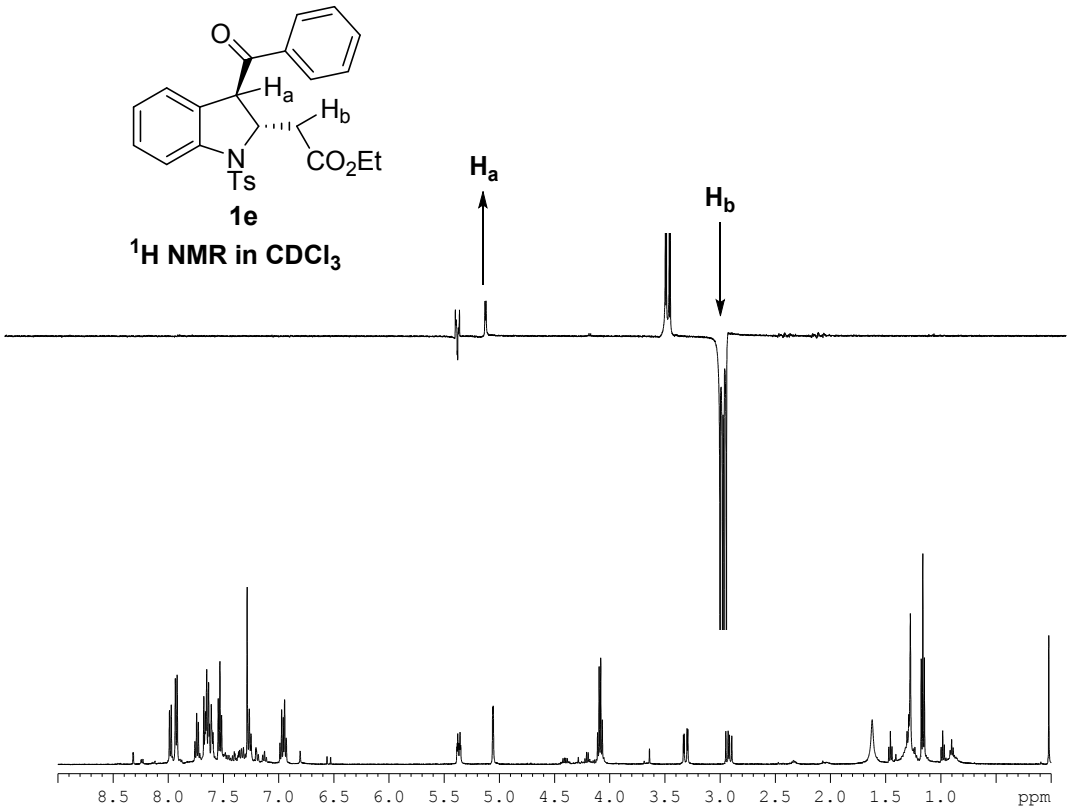
1e

^{13}C NMR in $CDCl_3$



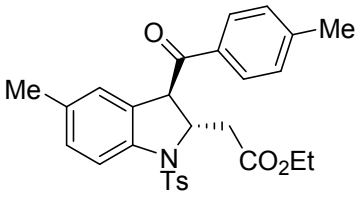
1e

^{1}H NMR in $CDCl_3$



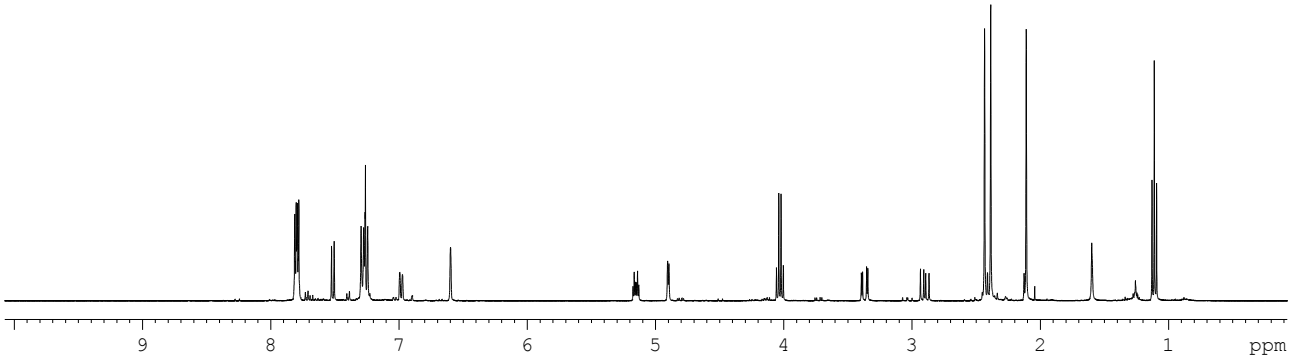
1e

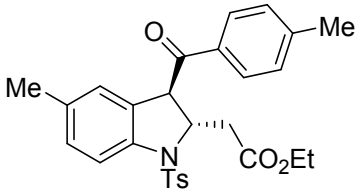
^{1}H NMR in $CDCl_3$



1f

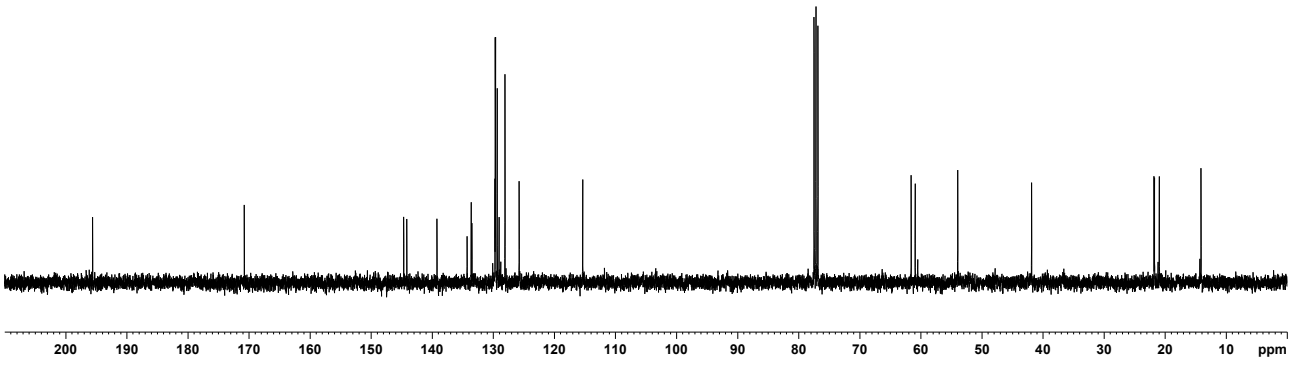
^{1}H NMR in $CDCl_3$

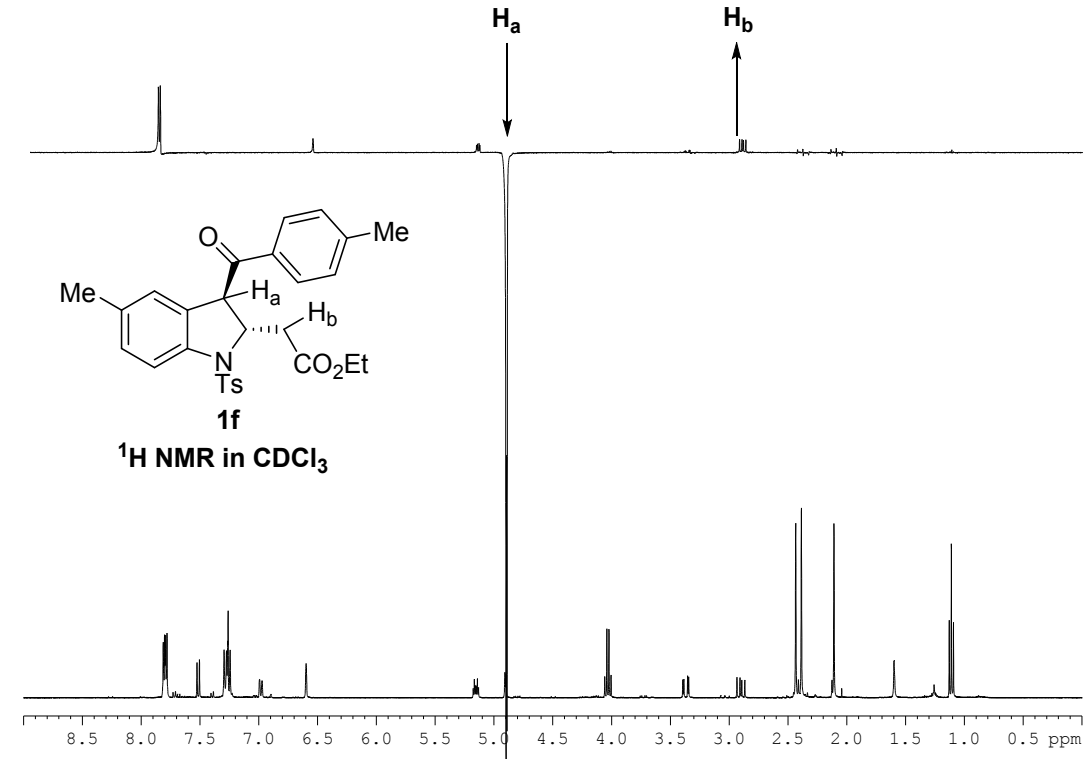




1f

^{13}C NMR in $CDCl_3$





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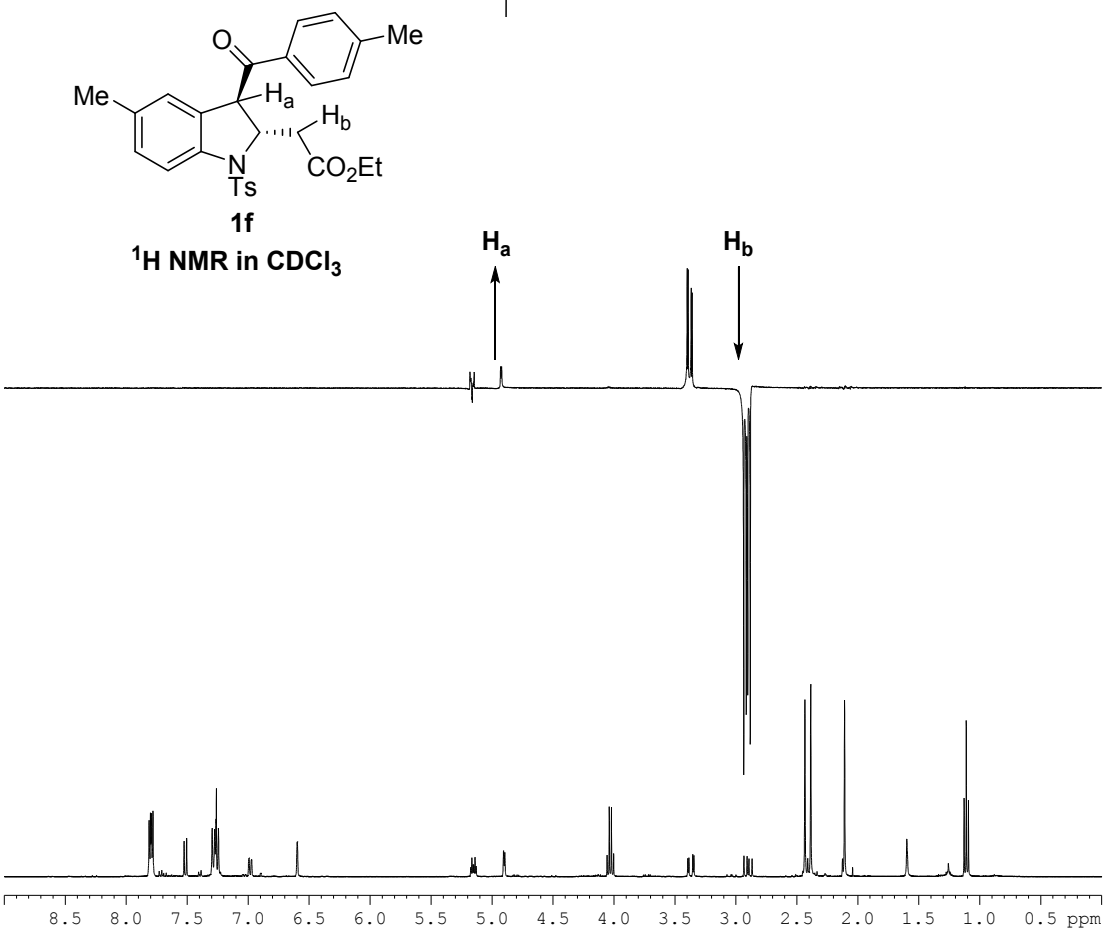
^{1}H NMR in $CDCl_3$



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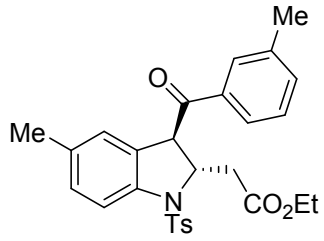
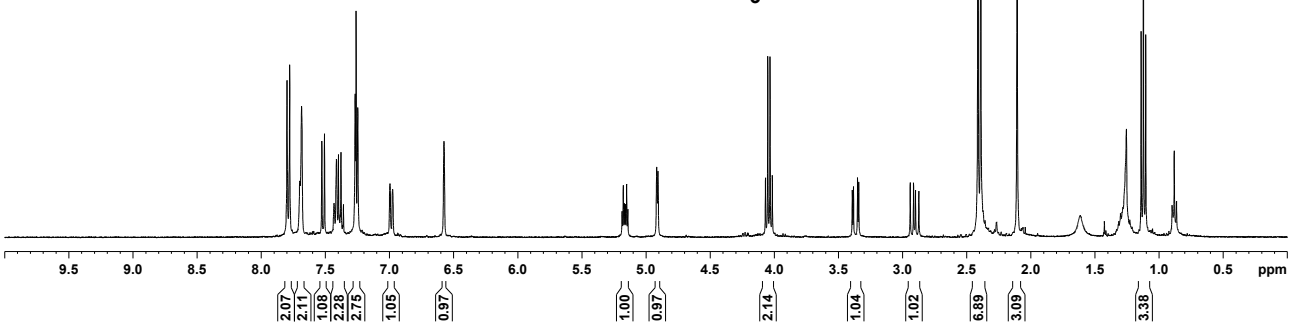
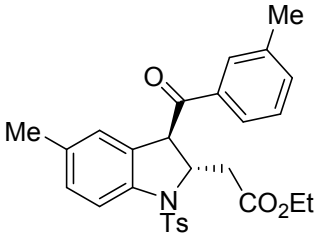
^{1}H NMR in $CDCl_3$



1g

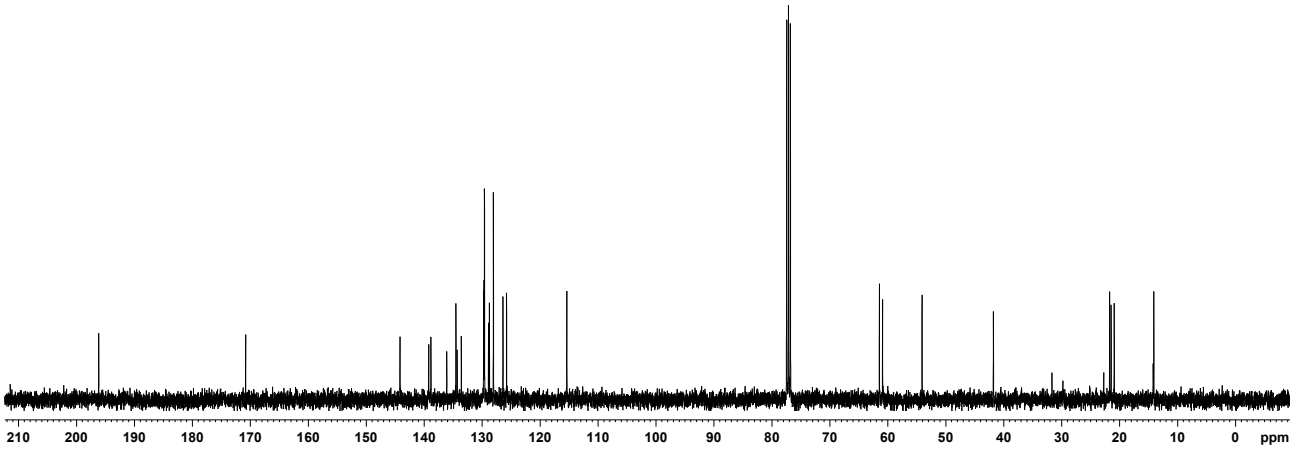
^{1}H NMR in $CDCl_3$

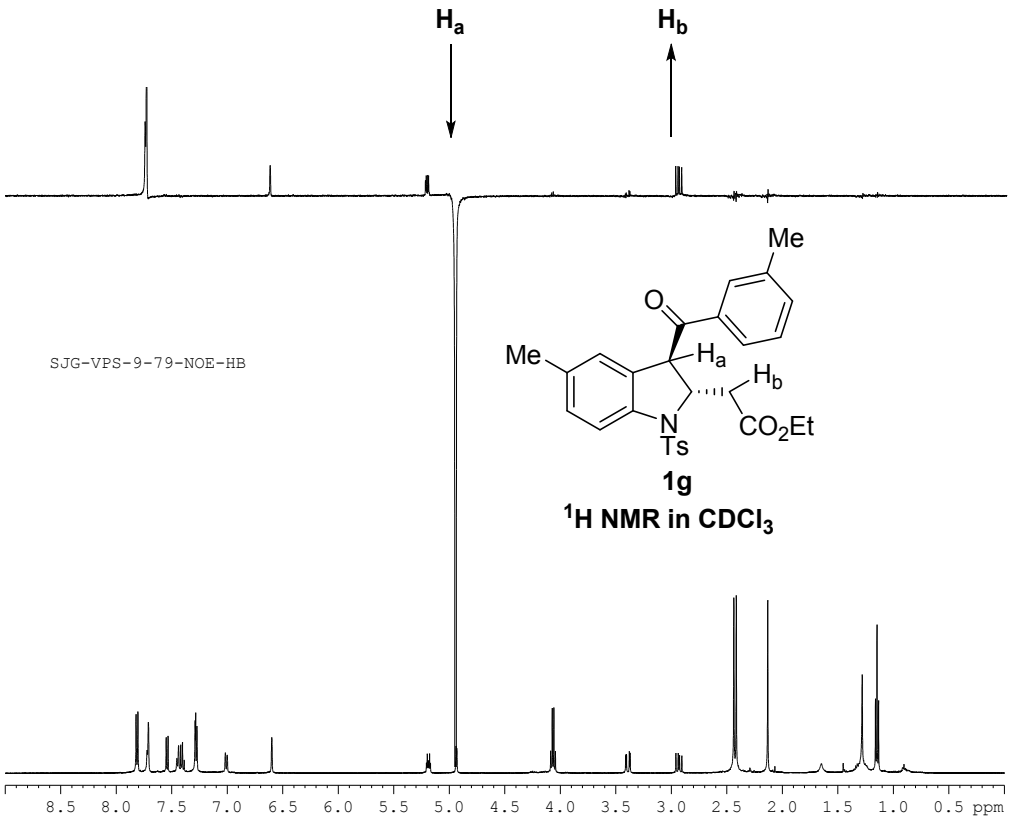


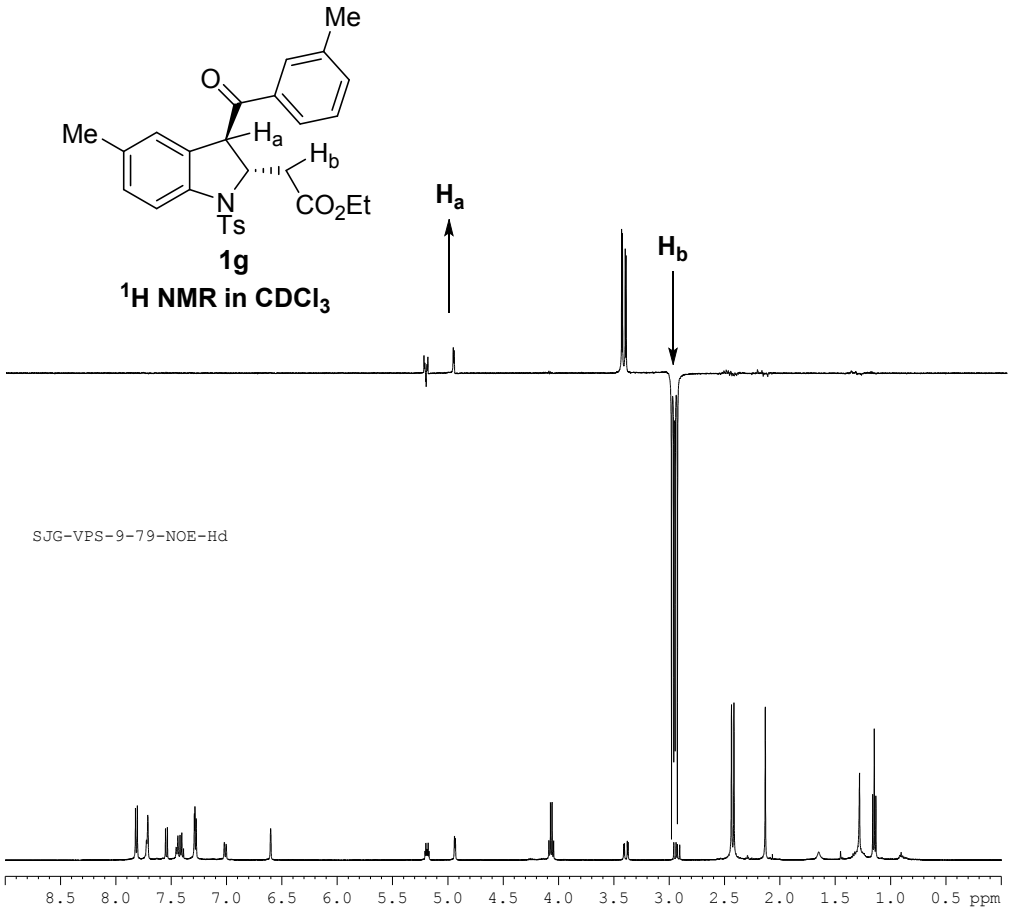


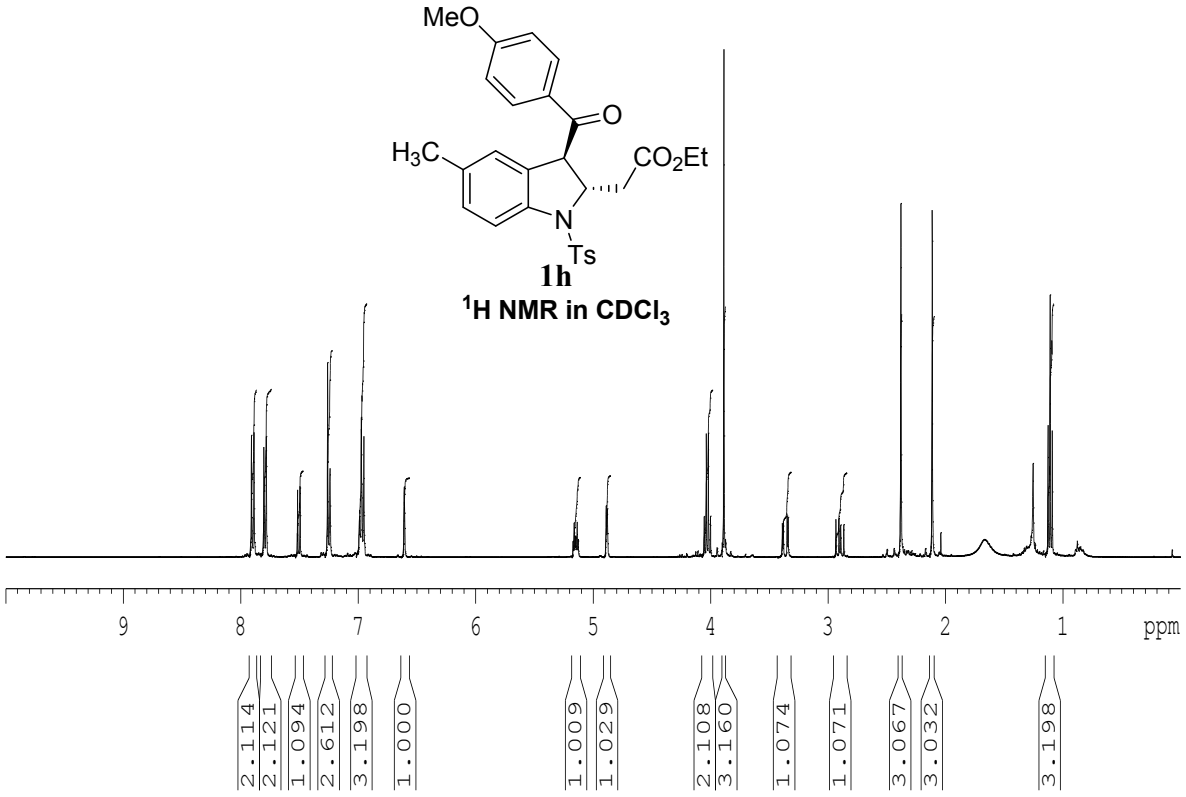
1g

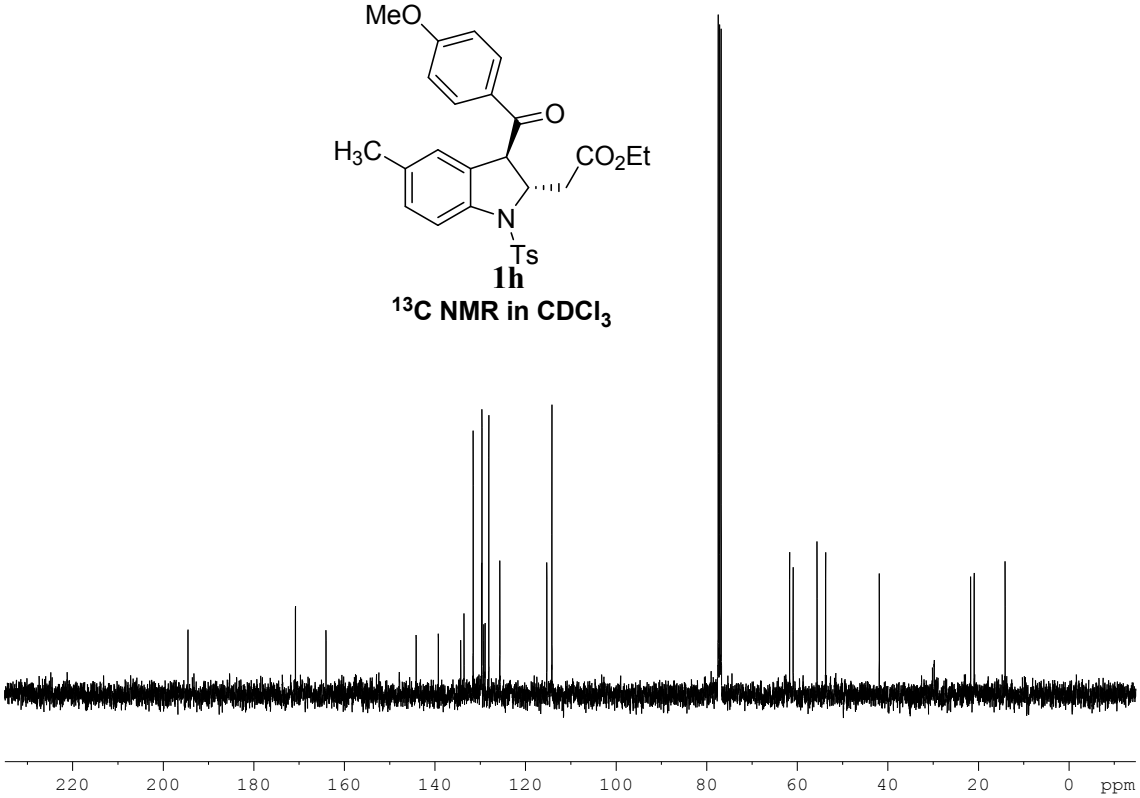
^{13}C NMR in $CDCl_3$

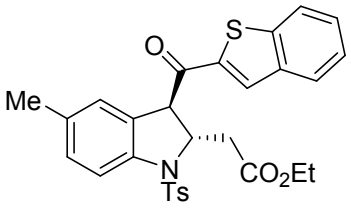



Ha
Hb
SJG-VPS-9-79-NOE-HB
Me
O
Me
Ha
Hb
N
Ts
CO2Et
1g
1H NMR in CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


Me
O
Me
Ha
Hb
N
Ts
CO2Et
1g
1H NMR in CDCl3
Ha
Hb
SJG-VPS-9-79-NOE-Hd
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

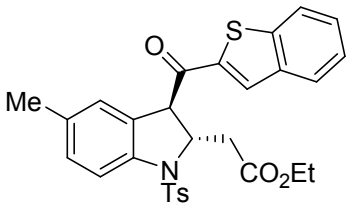

MeO
O
H3C
CO2Et
N
Ts
1h
1H NMR in CDCl3
9
8
7
6
5
4
3
2
1
ppm
2.114
2.121
1.094
2.612
3.198
1.000
1.009
1.029
2.108
3.160
1.074
1.071
3.067
3.032
3.198


MeO
O
H3C
CO2Et
N
Ts
1h
13C NMR in CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm



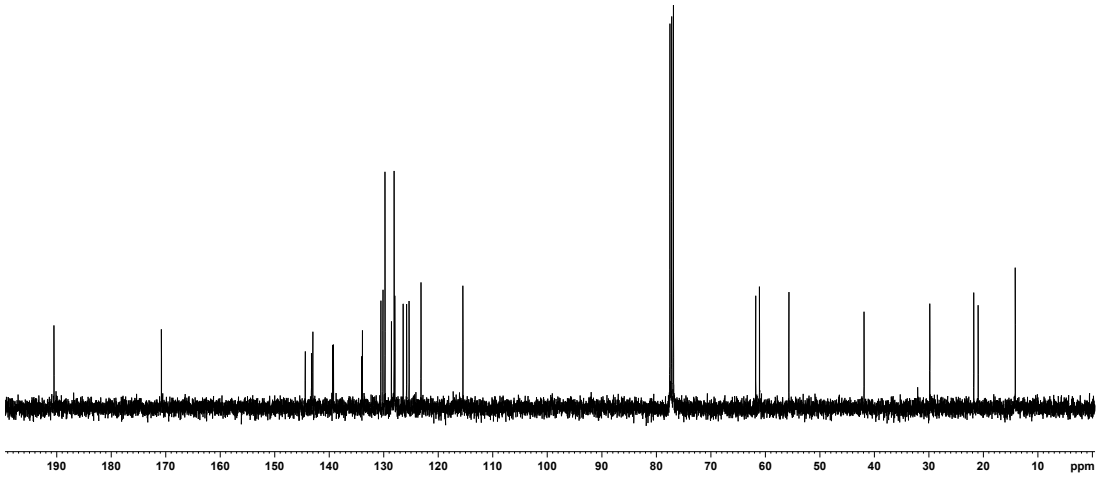
1k

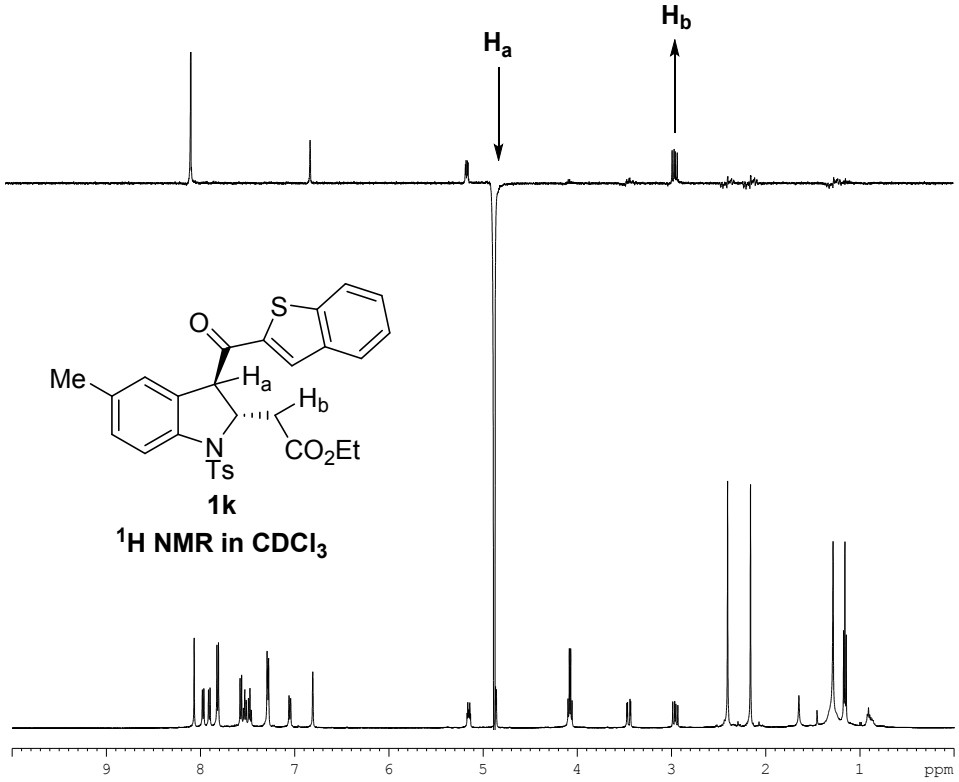
^{1}H NMR in $CDCl_3$



1k

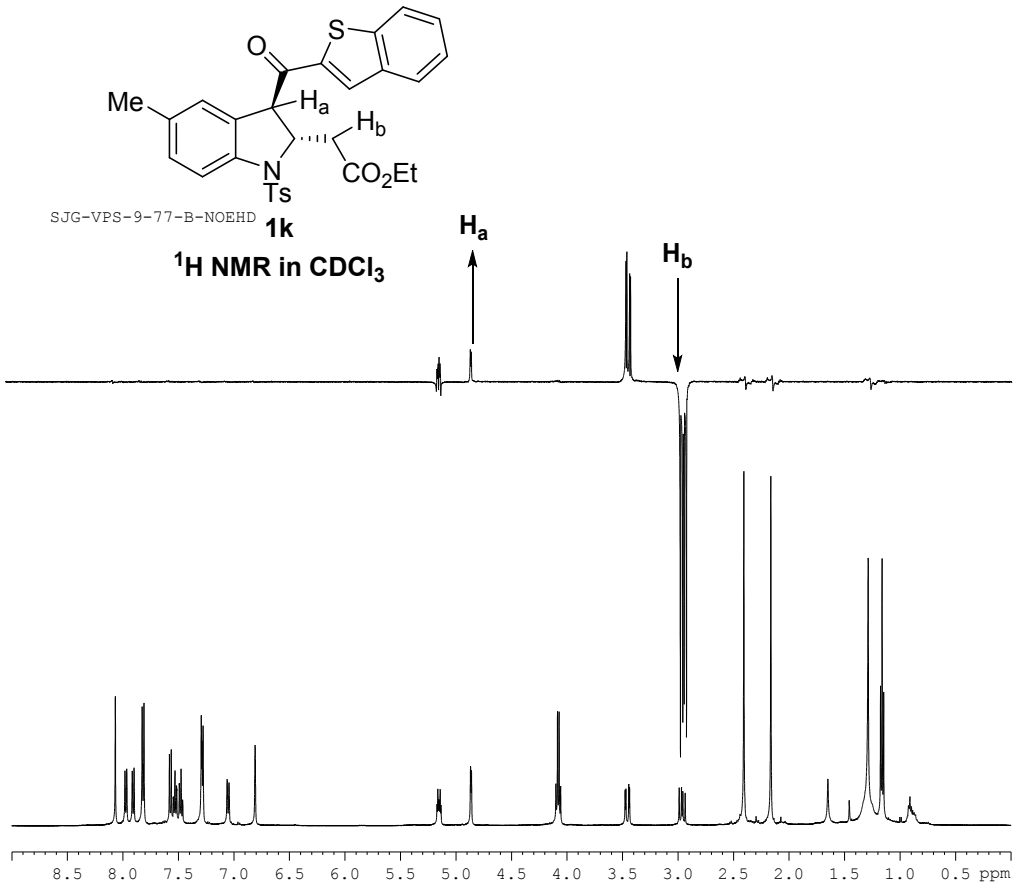
^{13}C NMR in $CDCl_3$





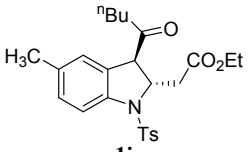
1k

^{1}H NMR in $CDCl_3$



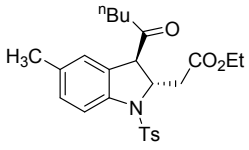
1k

^{1}H NMR in $CDCl_3$



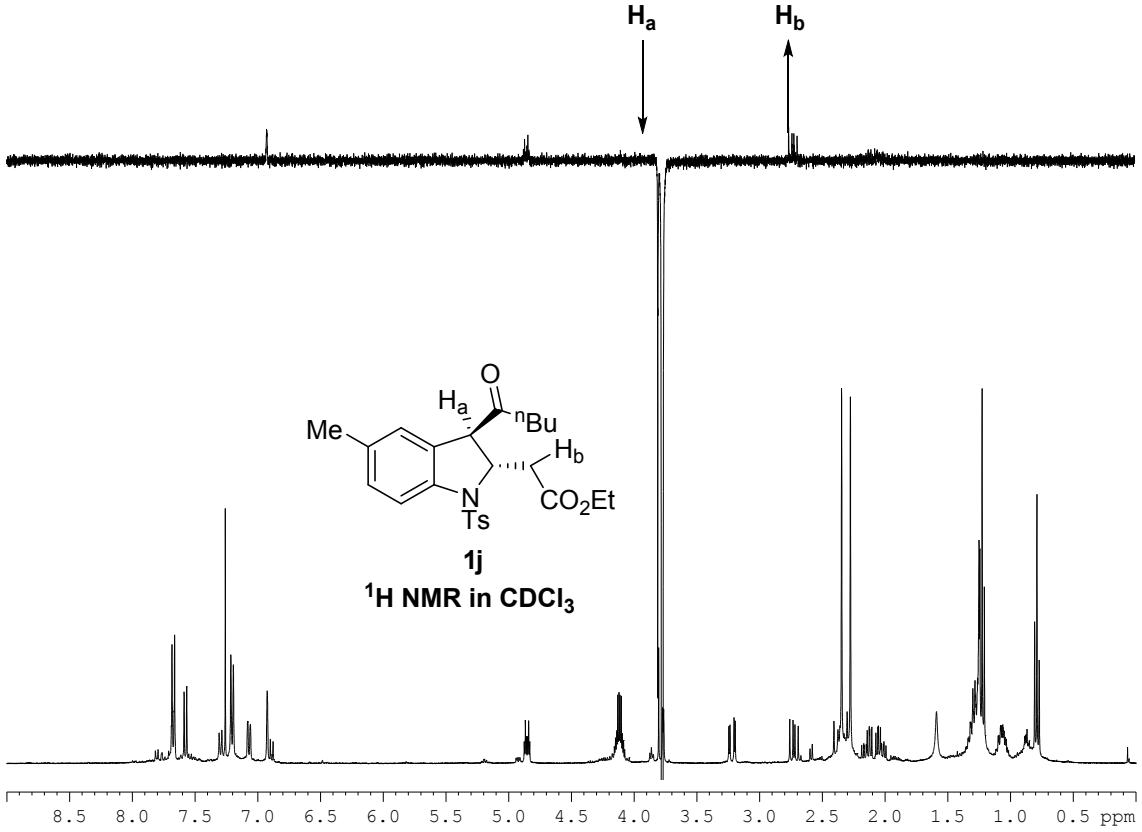
1j

^{1}H NMR in $CDCl_3$



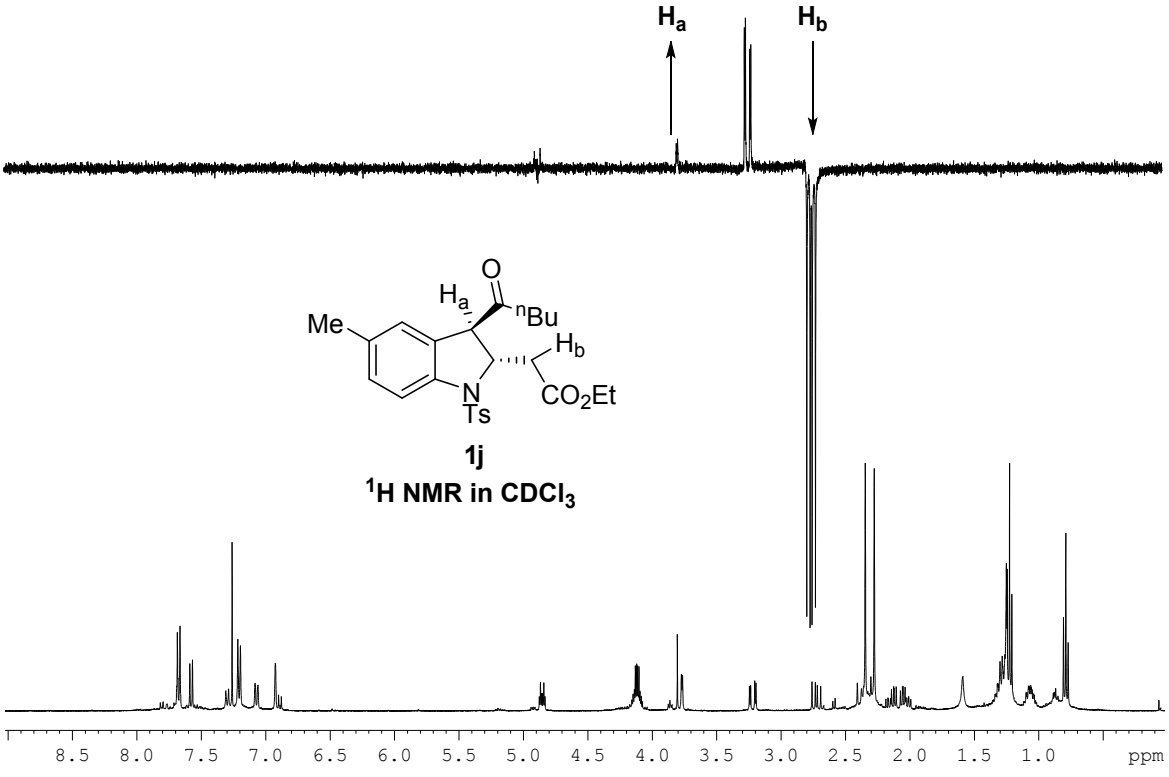
1j

^{13}C NMR in $CDCl_3$



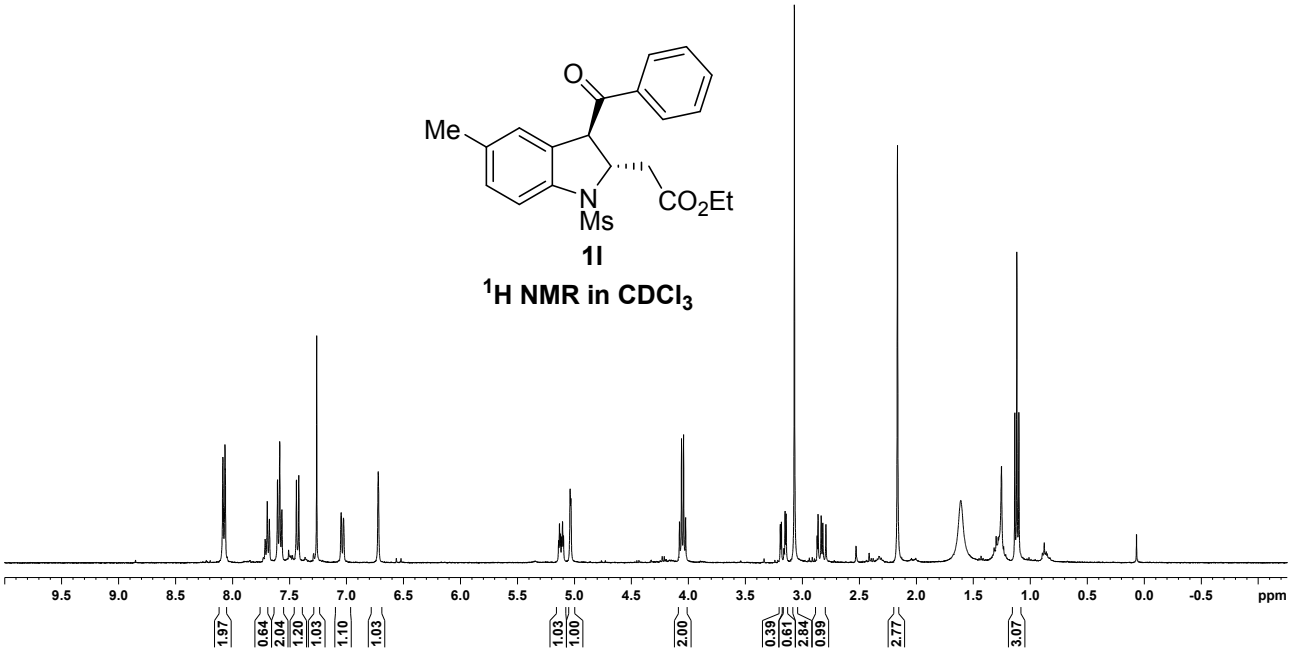
1j

^{1}H NMR in $CDCl_3$



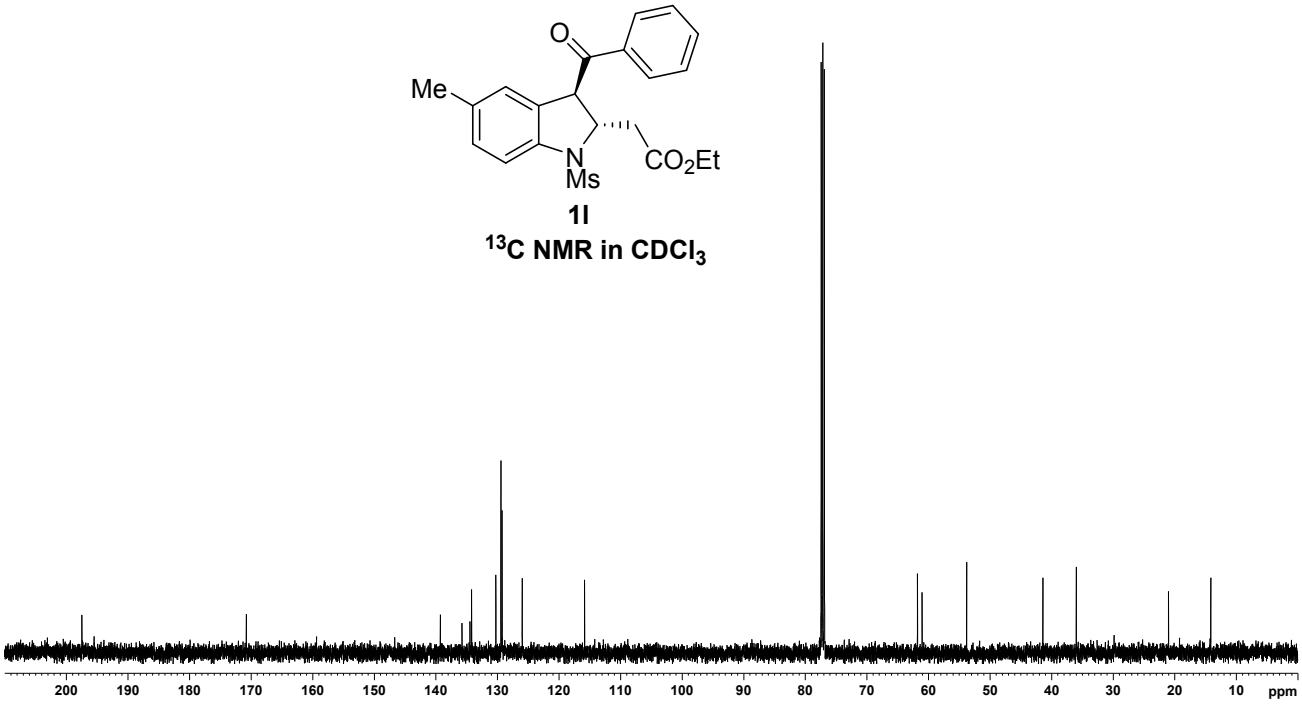
1j

^{1}H NMR in $CDCl_3$



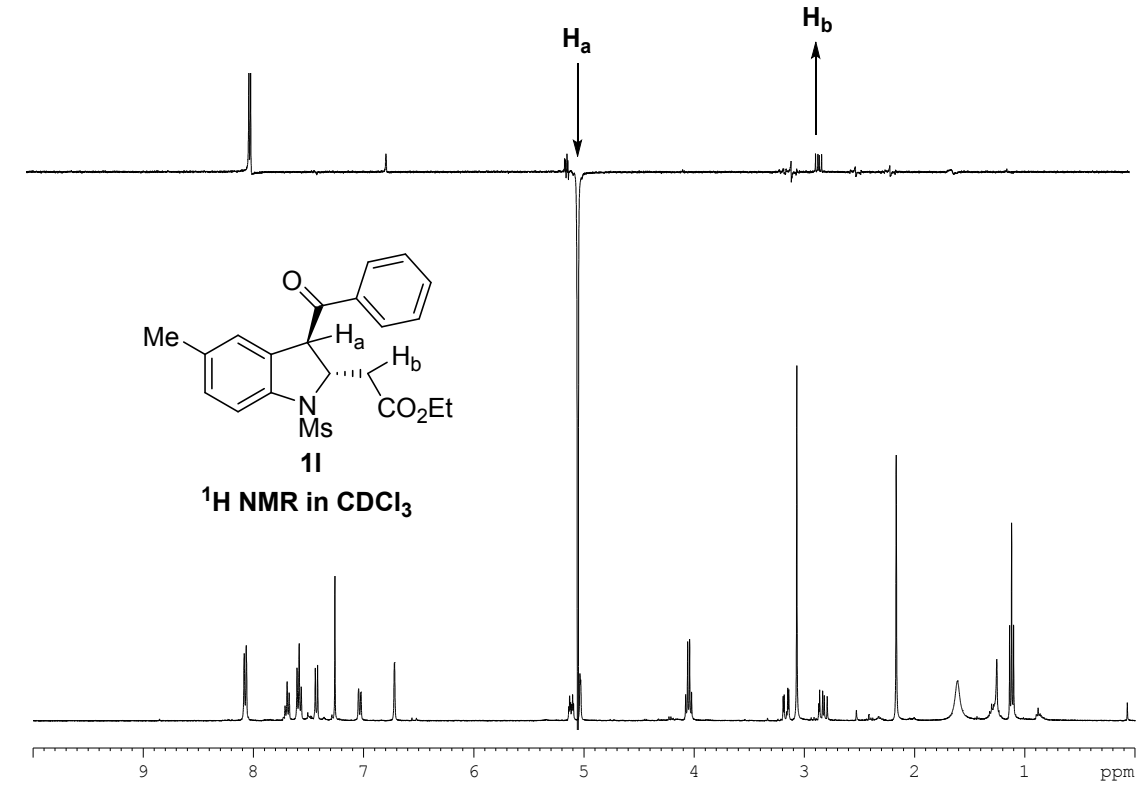
1l

^{1}H NMR in $CDCl_3$



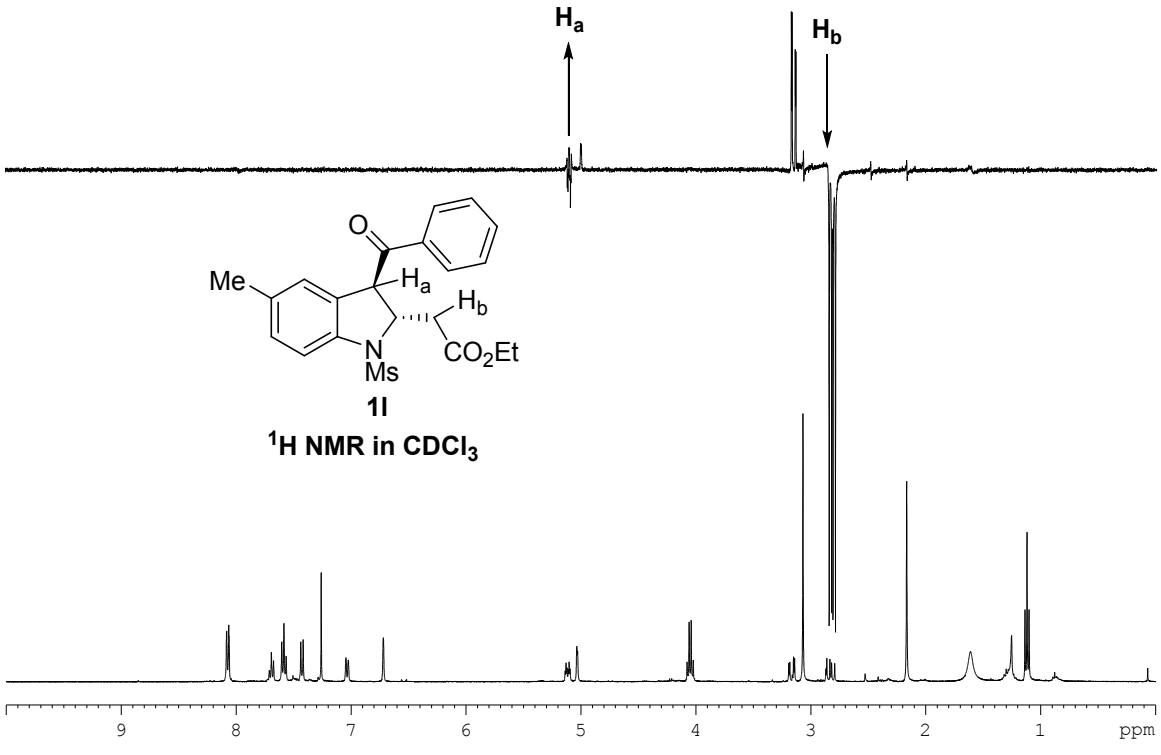
1l

^{13}C NMR in $CDCl_3$



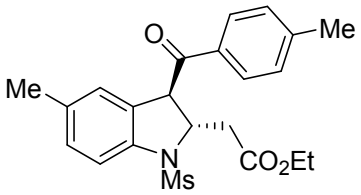
1l

^{1}H NMR in $CDCl_3$



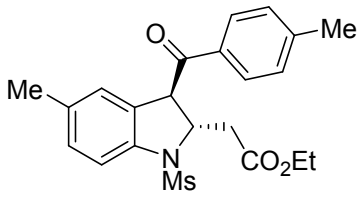
1l

^{1}H NMR in $CDCl_3$



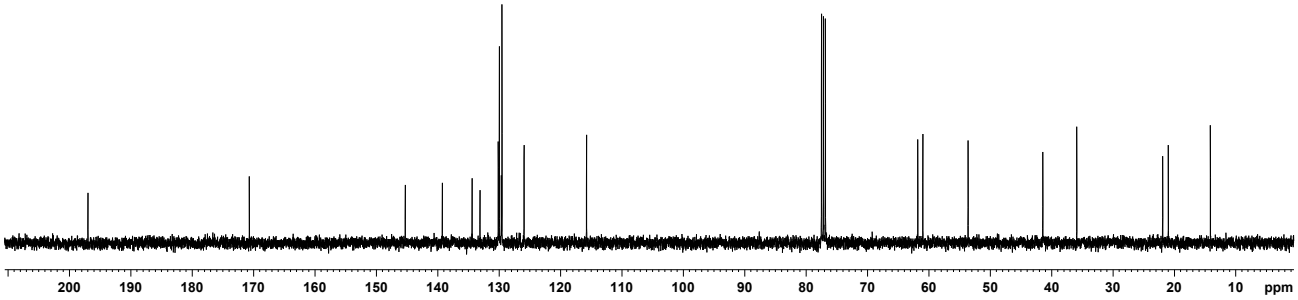
1m

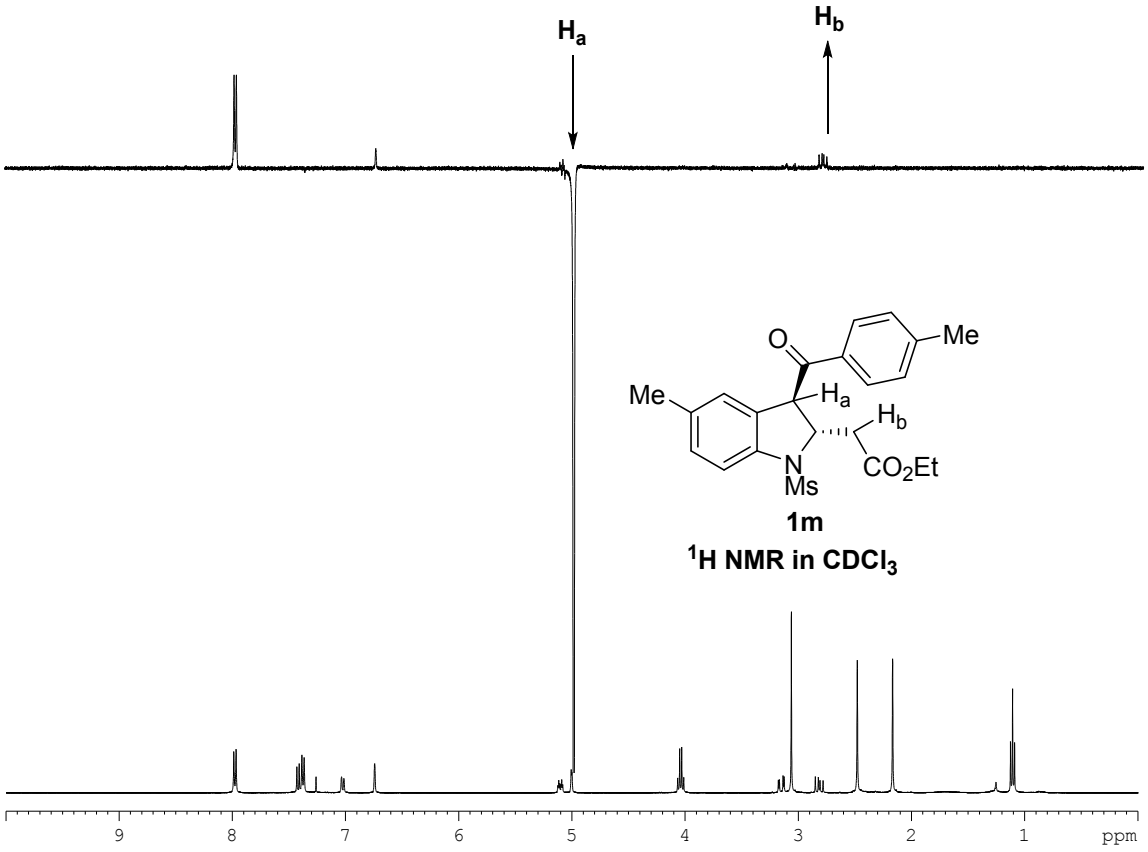
^{1}H NMR in $CDCl_3$



1m

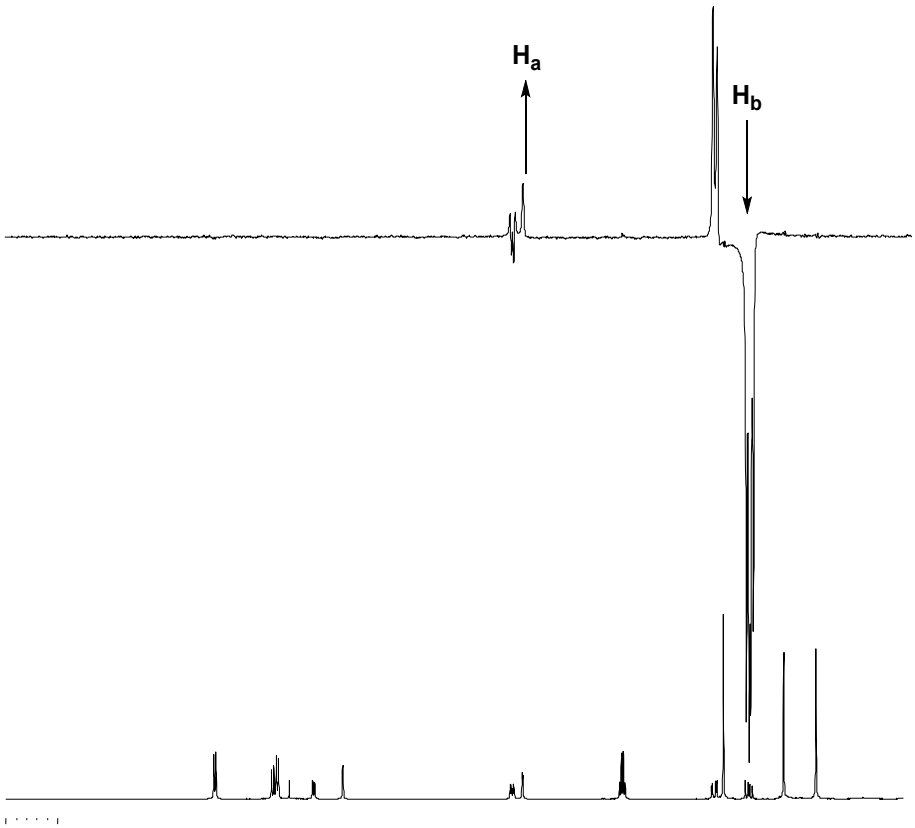
^{13}C NMR in $CDCl_3$

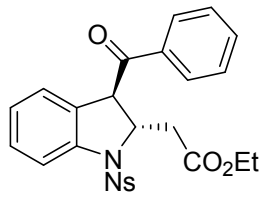




1m

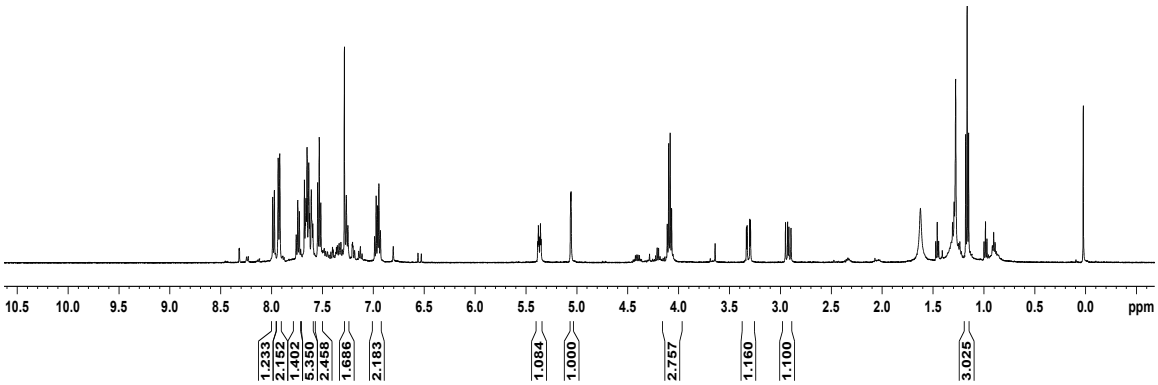
^{1}H NMR in $CDCl_3$

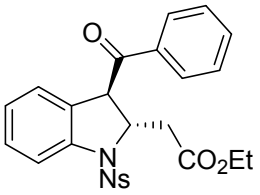




1n

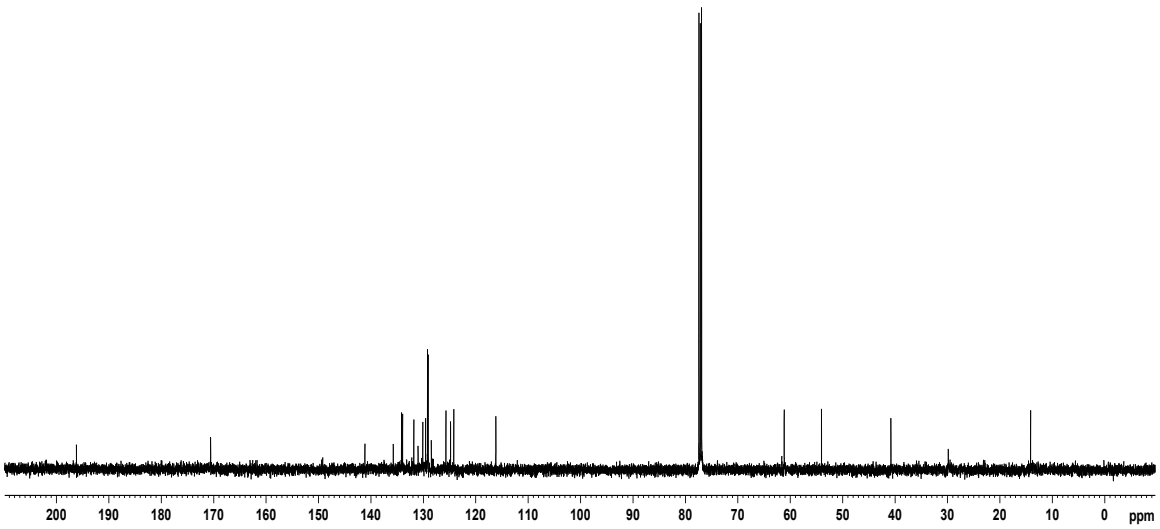
^{1}H NMR in $CDCl_3$

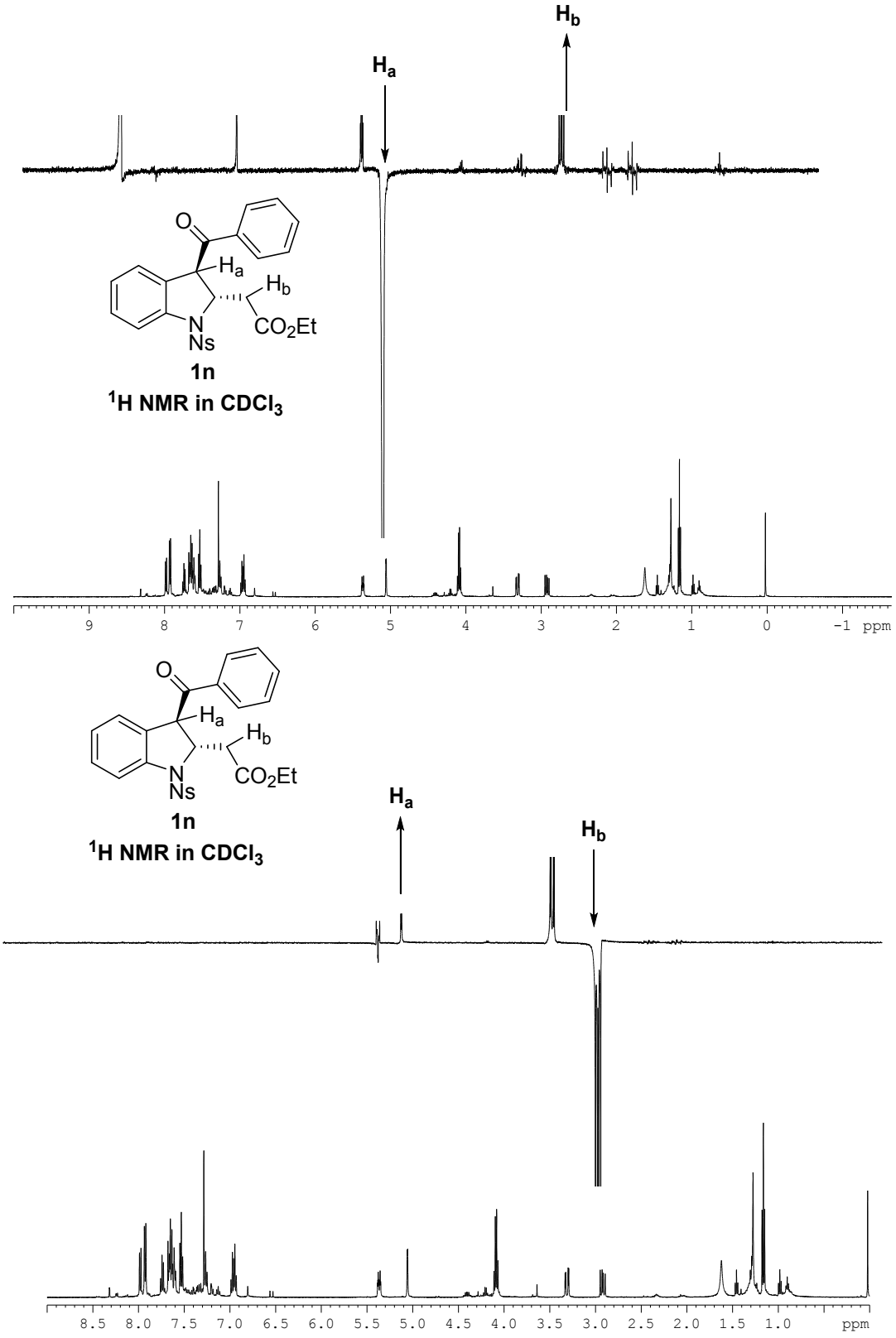


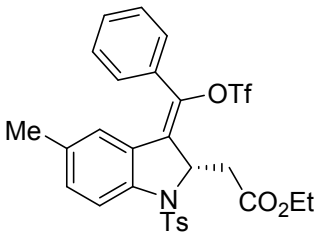


1n

^{13}C NMR in $CDCl_3$

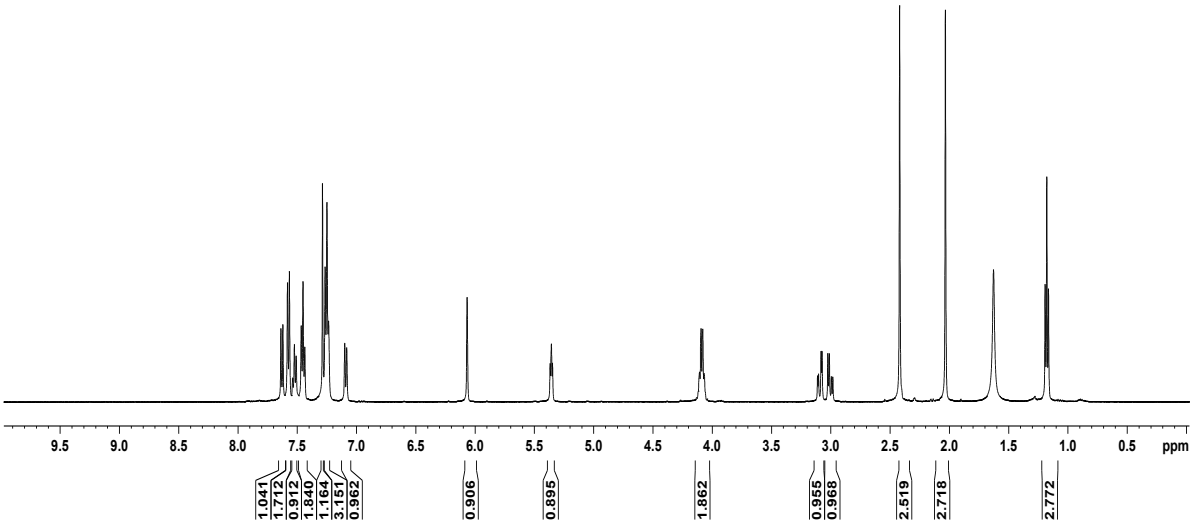


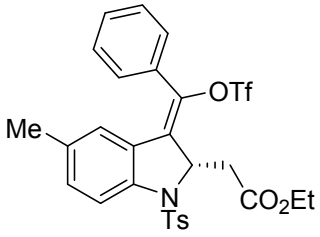

Ha
Hb
O
Ha
Hb
N
Ns
CO2Et
1n
1H NMR in CDCl3
9 8 7 6 5 4 3 2 1 0 -1 ppm
O
Ha
Hb
N
Ns
CO2Et
1n
1H NMR in CDCl3
Ha
Hb
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm



5a

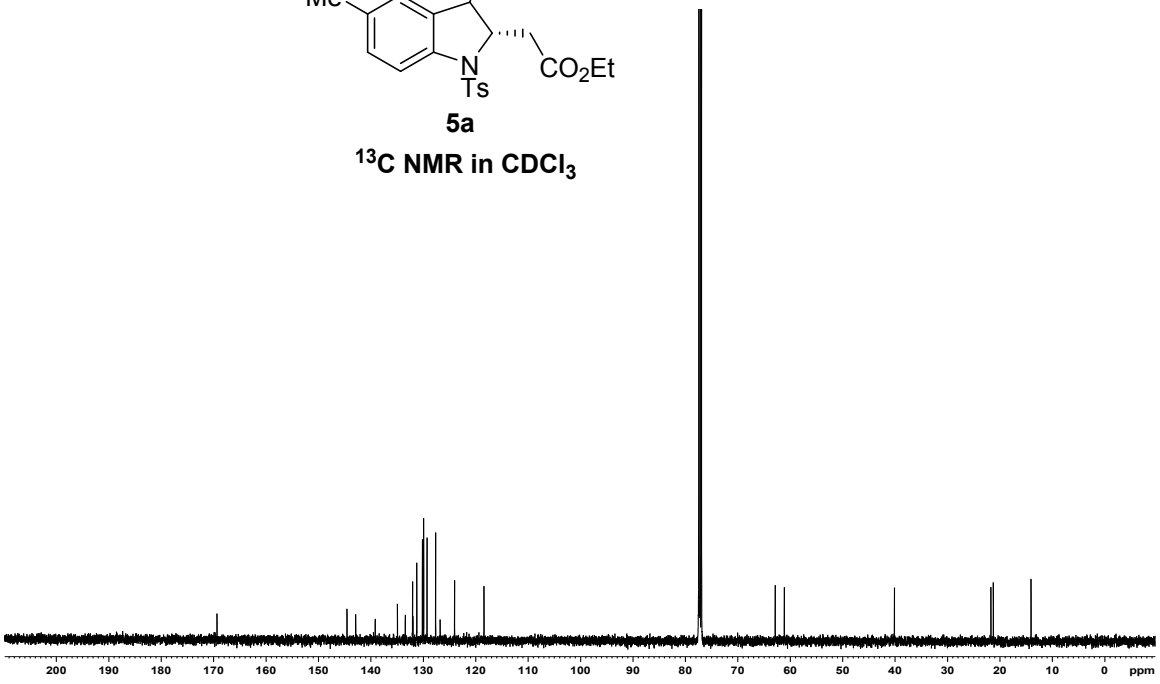
^{1}H NMR in $CDCl_3$

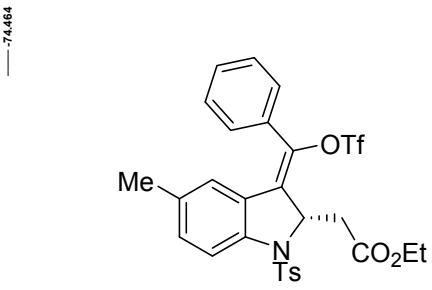




5a

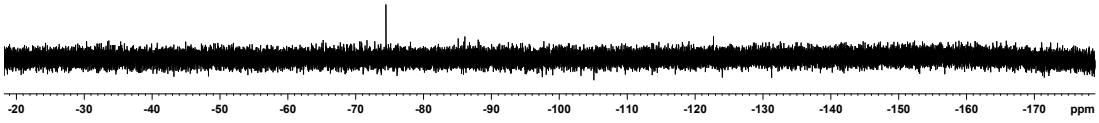
^{13}C NMR in $CDCl_3$

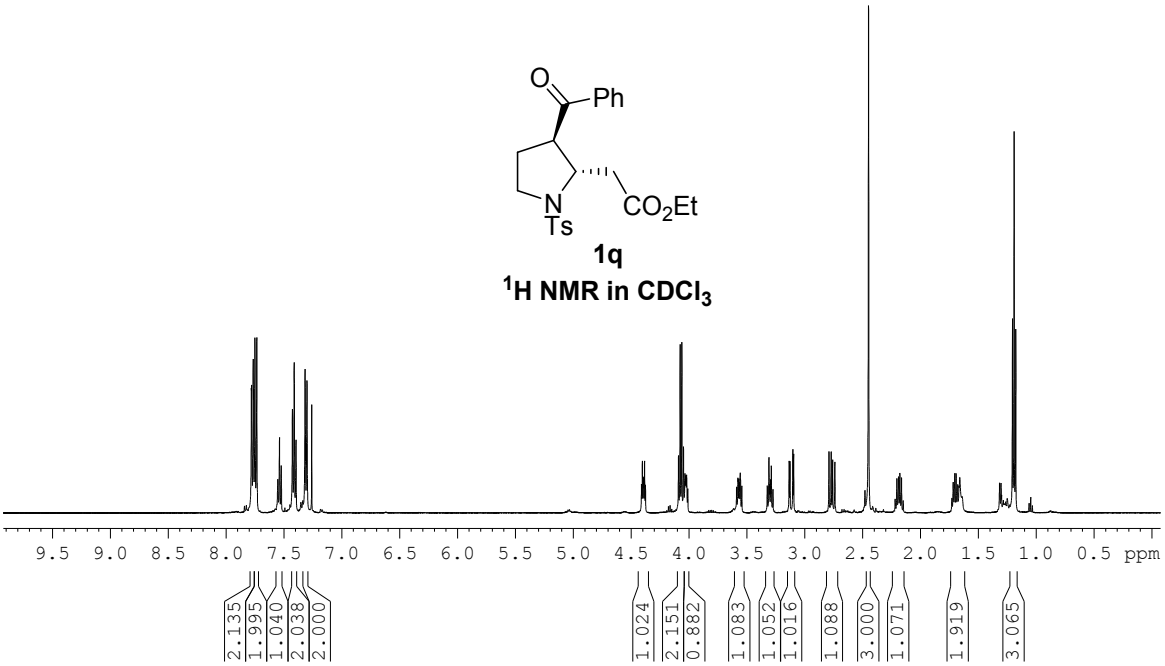




5a

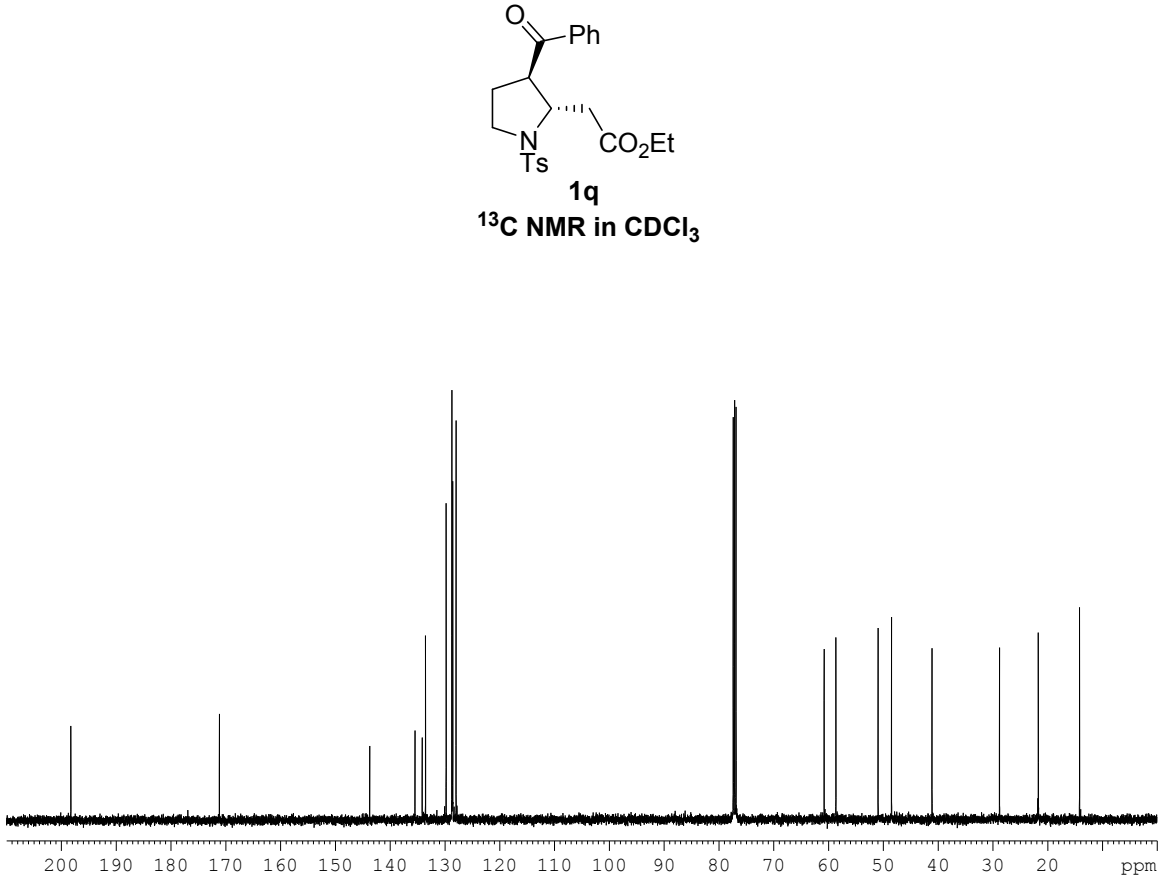
^{19}F NMR in $CDCl_3$





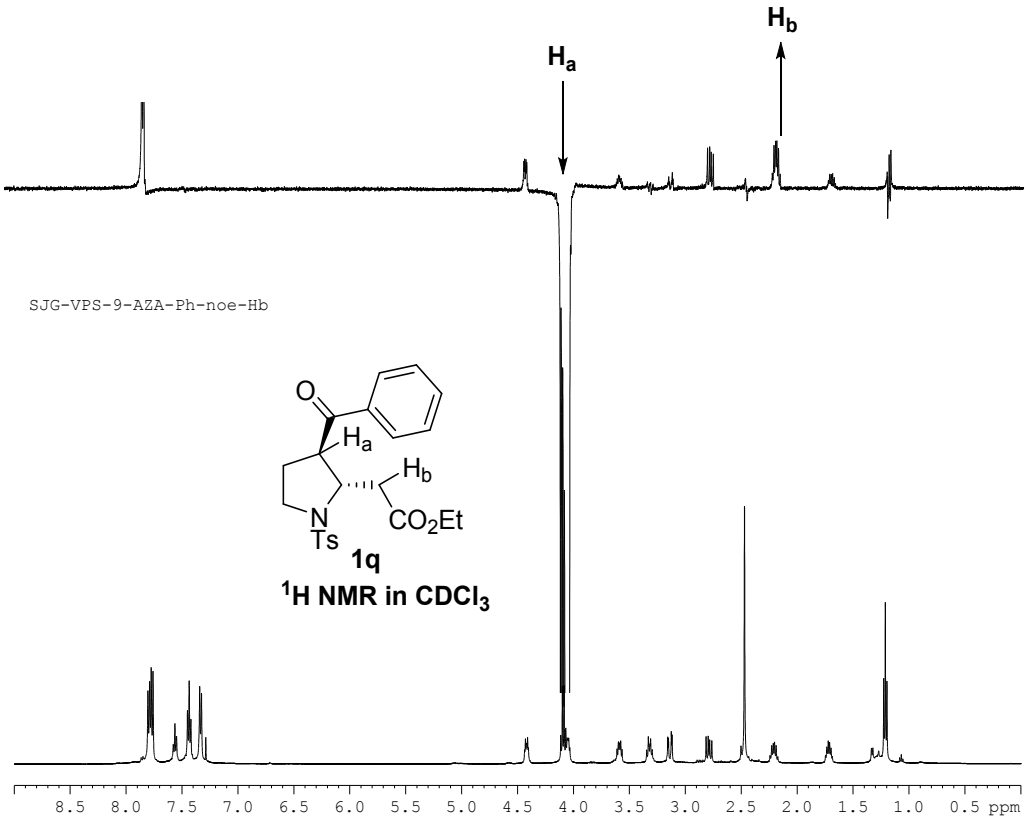
1q

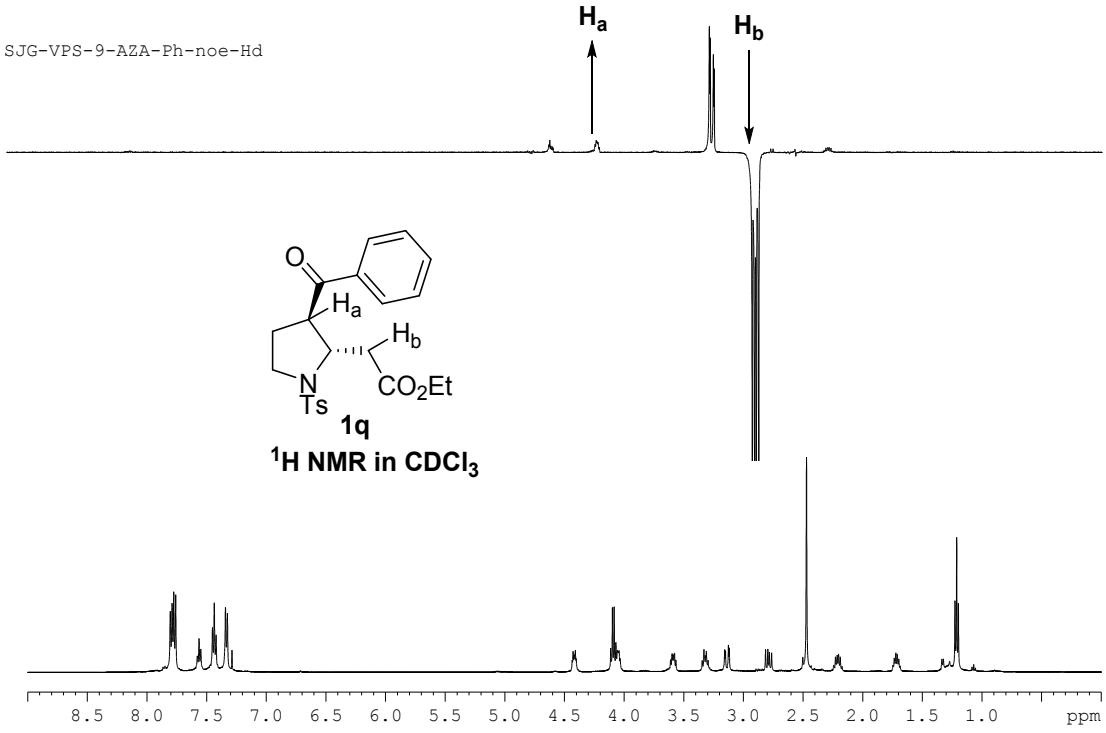
^{1}H NMR in $CDCl_3$

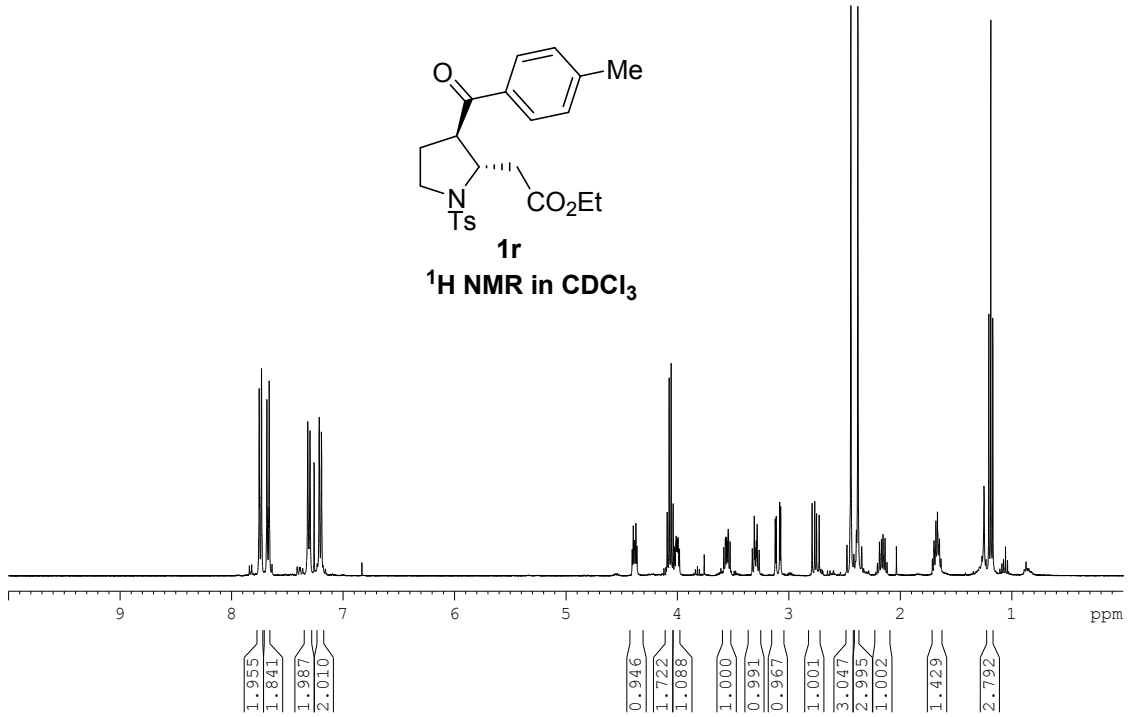


1q

^{13}C NMR in $CDCl_3$

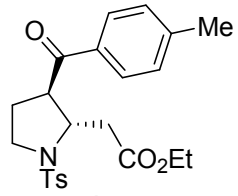

H_a
H_b
SJG-VPS-9-AZA-Ph-noe-Hb
O
H_a
H_b
N
Ts
CO2Et
1q
1H NMR in CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


SJG-VPS-9-AZA-Ph-noe-Hd
H_a
H_b
O
H_a
H_b
N
Ts
CO2Et
1q
1H NMR in CDCl3
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 ppm



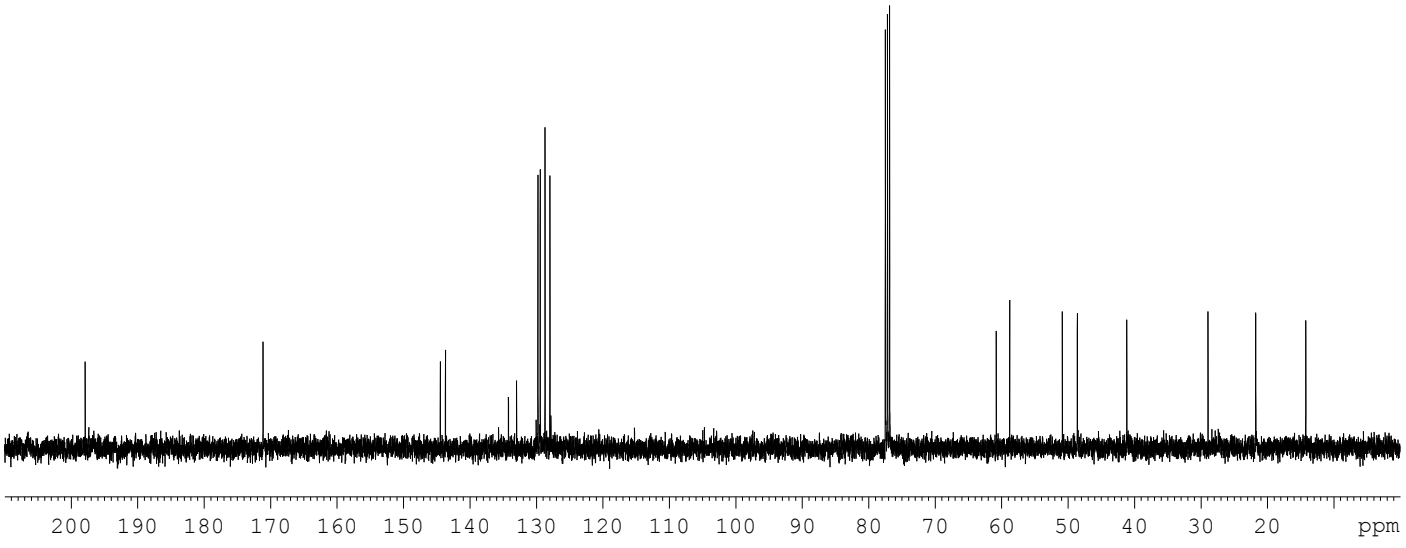
1r

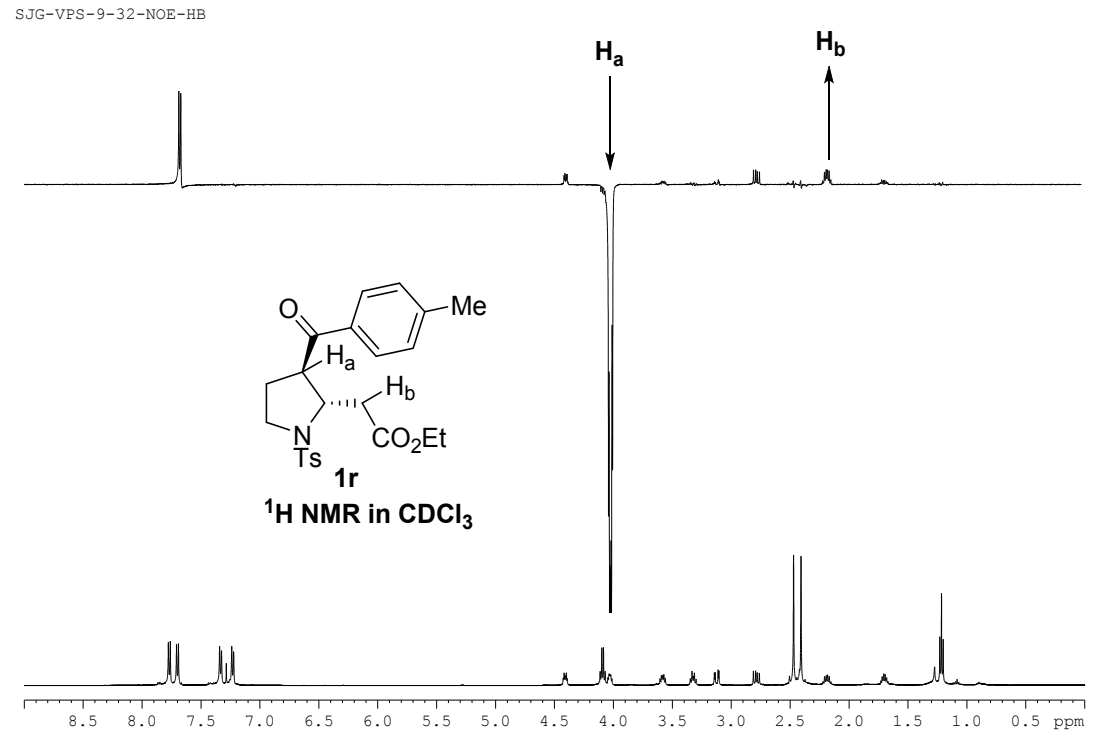
^{1}H NMR in $CDCl_3$

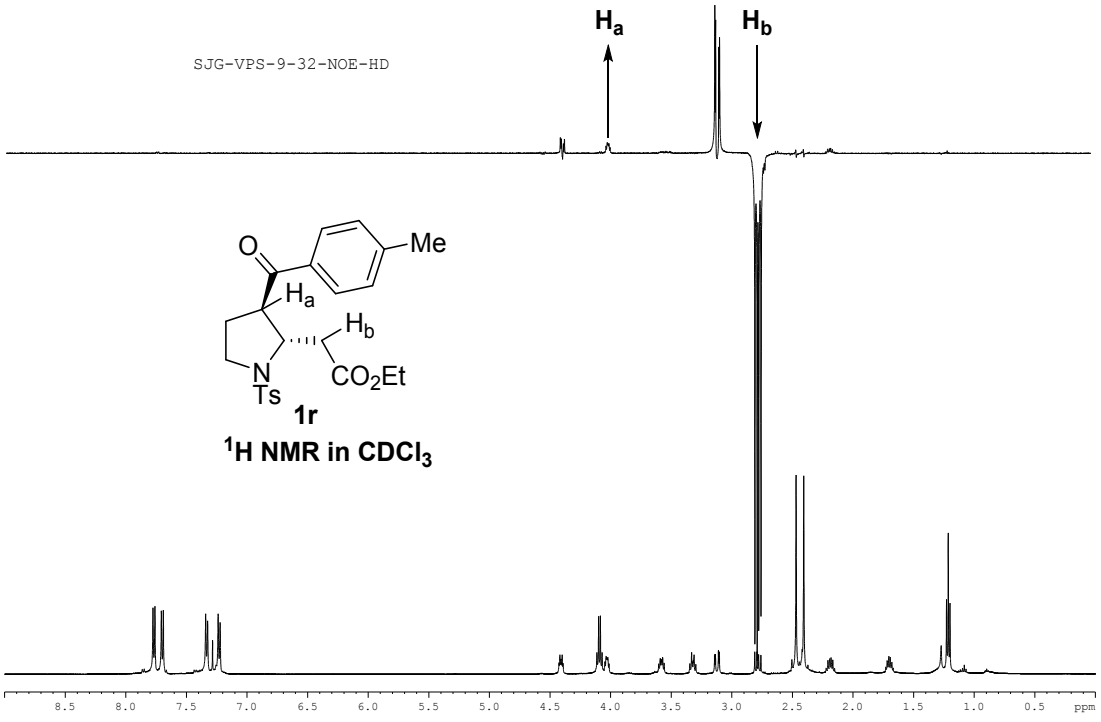


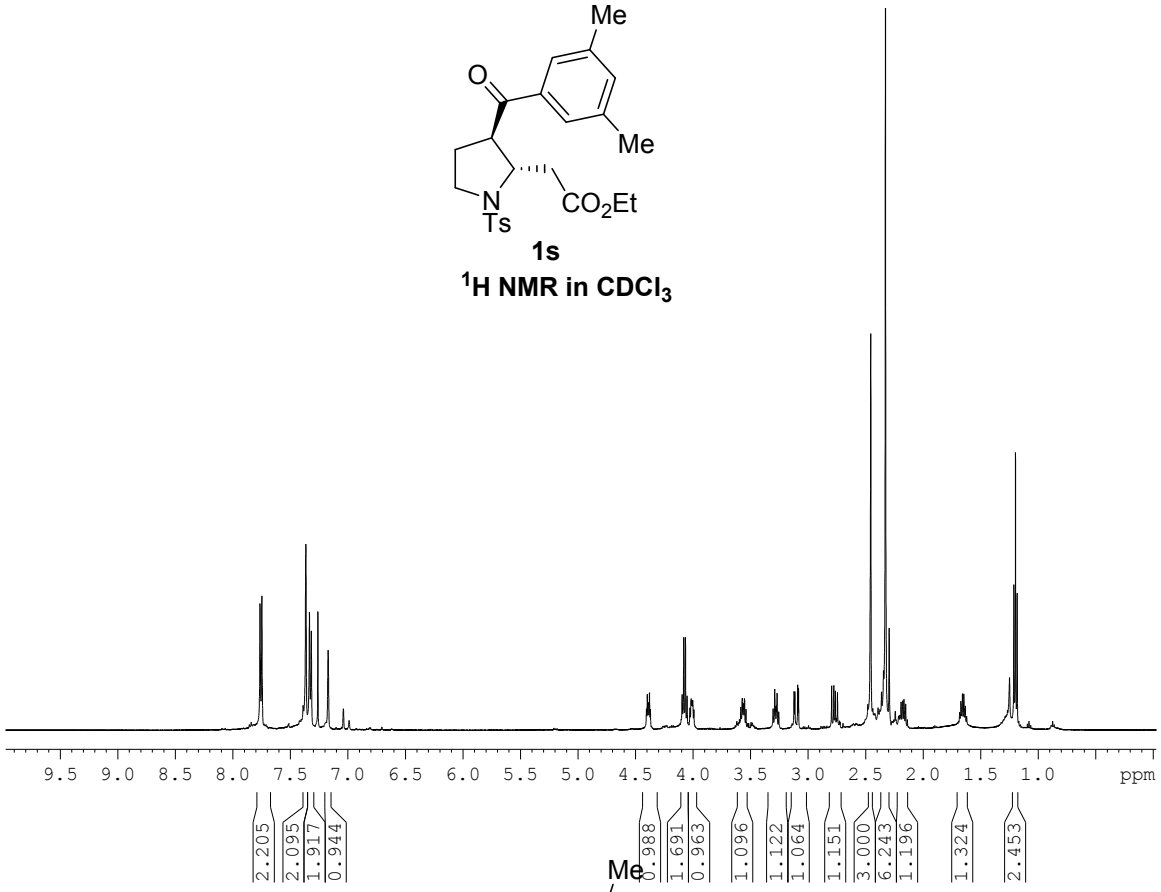
1r

^{13}C NMR in $CDCl_3$



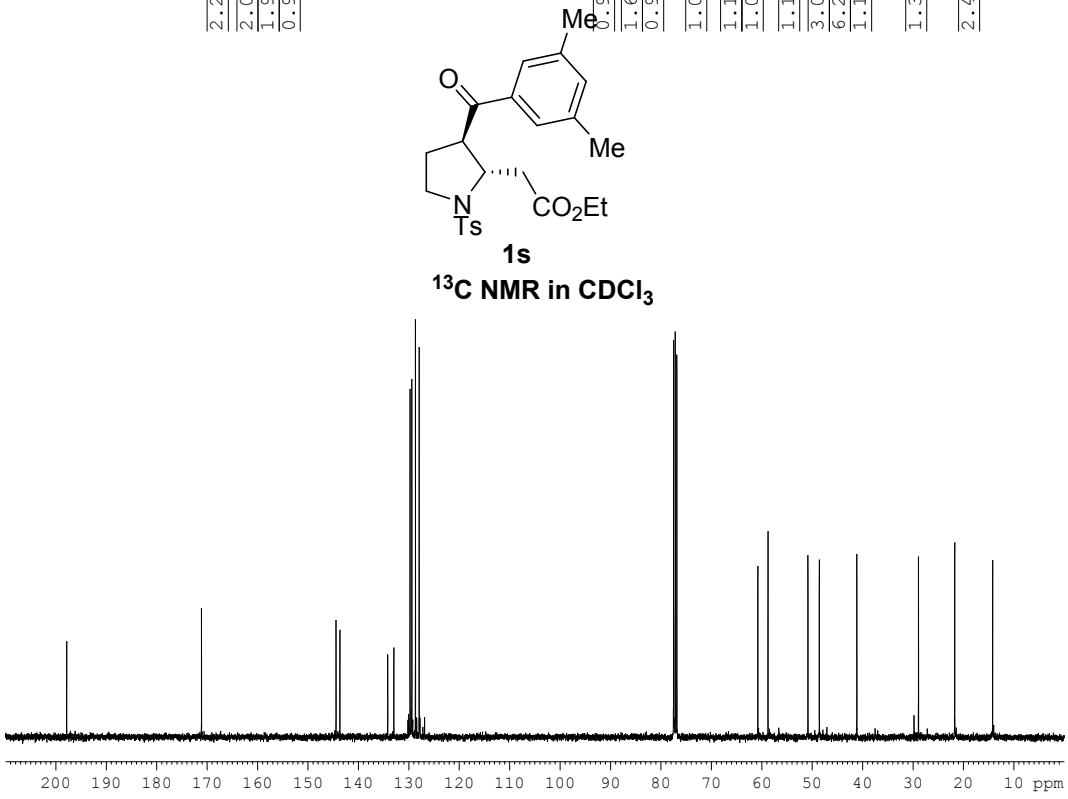

SJG-VPS-9-32-NOE-HB
Ha
Hb
O
Me
Ha
Hb
N
Ts
CO2Et
1r
1H NMR in CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


SJG-VPS-9-32-NOE-HD
Ha
Hb
O
Me
Ha
Hb
N
Ts
CO2Et
1r
1H NMR in CDCl3
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



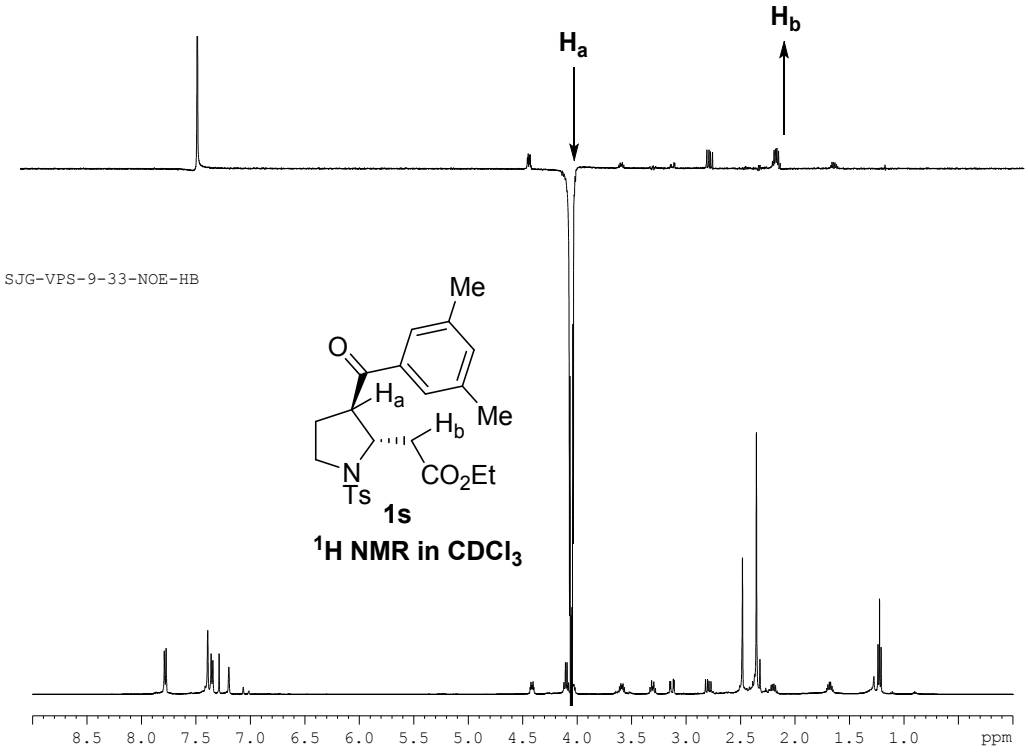
1s

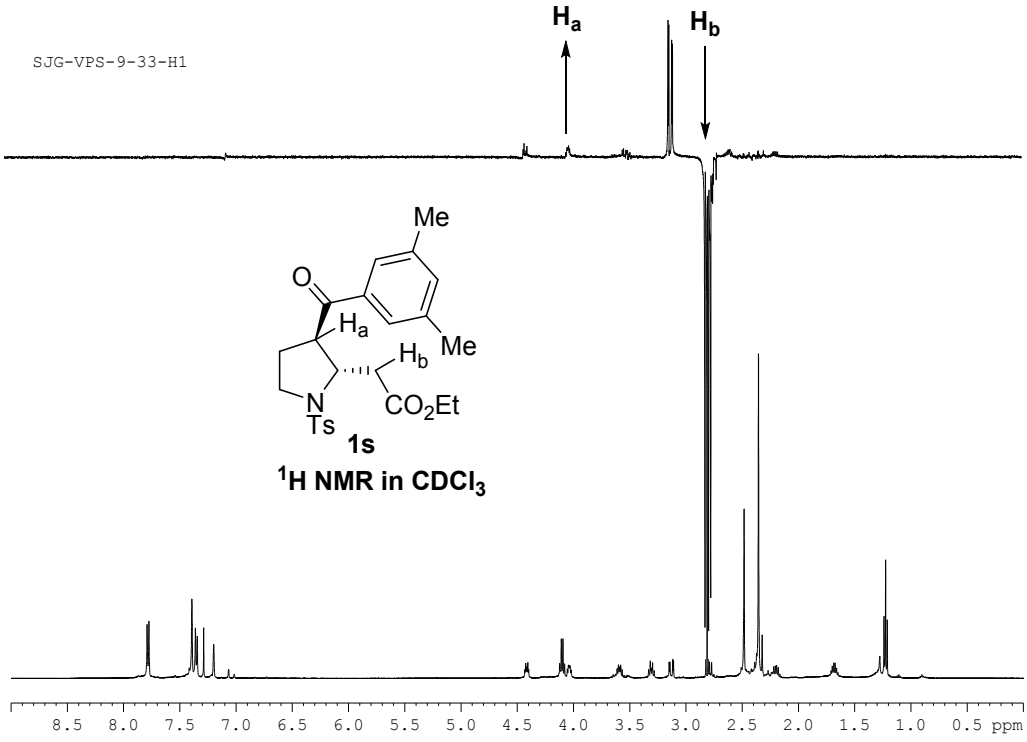
^{1}H NMR in $CDCl_3$

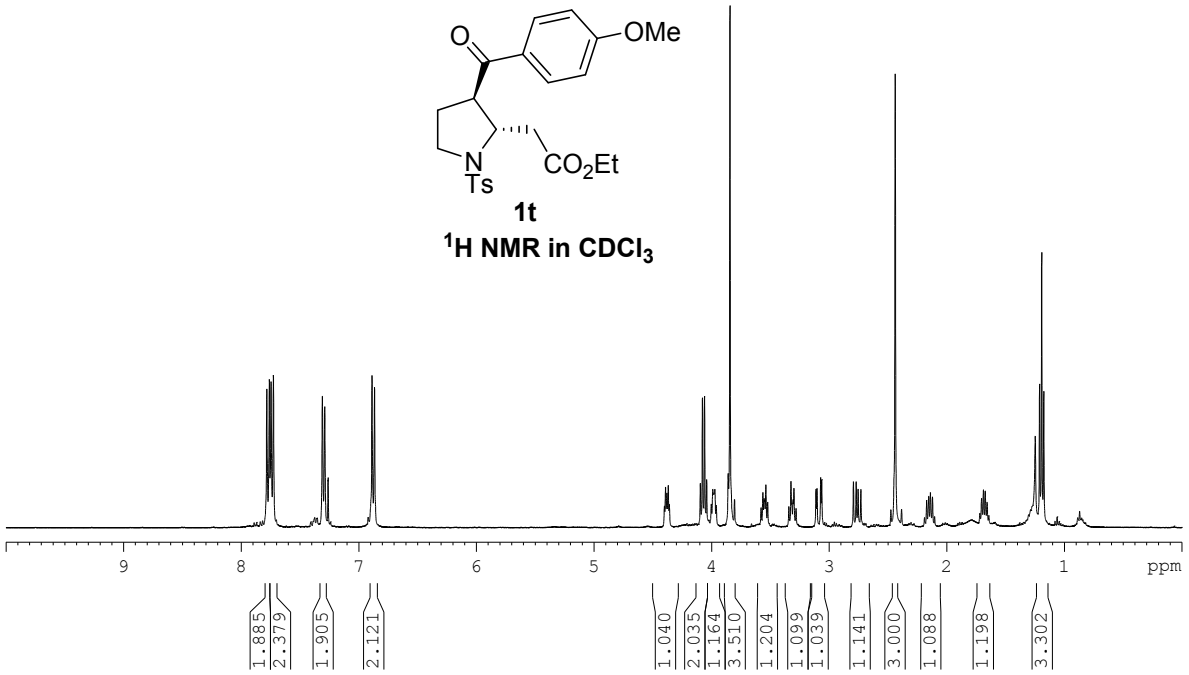


1s

^{13}C NMR in $CDCl_3$

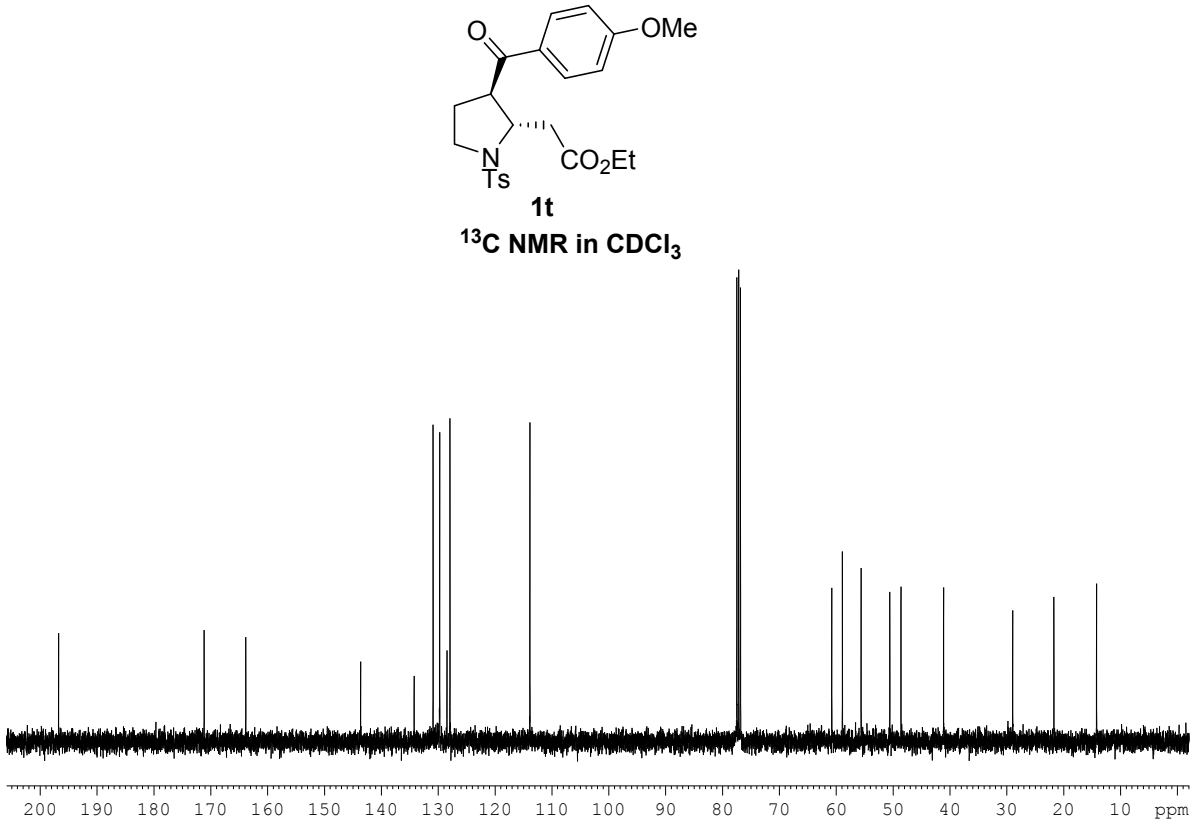

H_a
H_b
SJG-VPS-9-33-NOE-HB
Me
O
H_a
Me
H_b
N
Ts
CO2Et
1s
1H NMR in CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


H_a
H_b
SJG-VPS-9-33-H1
Me
O
H_a
Me
H_b
N
Ts
CO2Et
1s
1H NMR in CDCl3
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



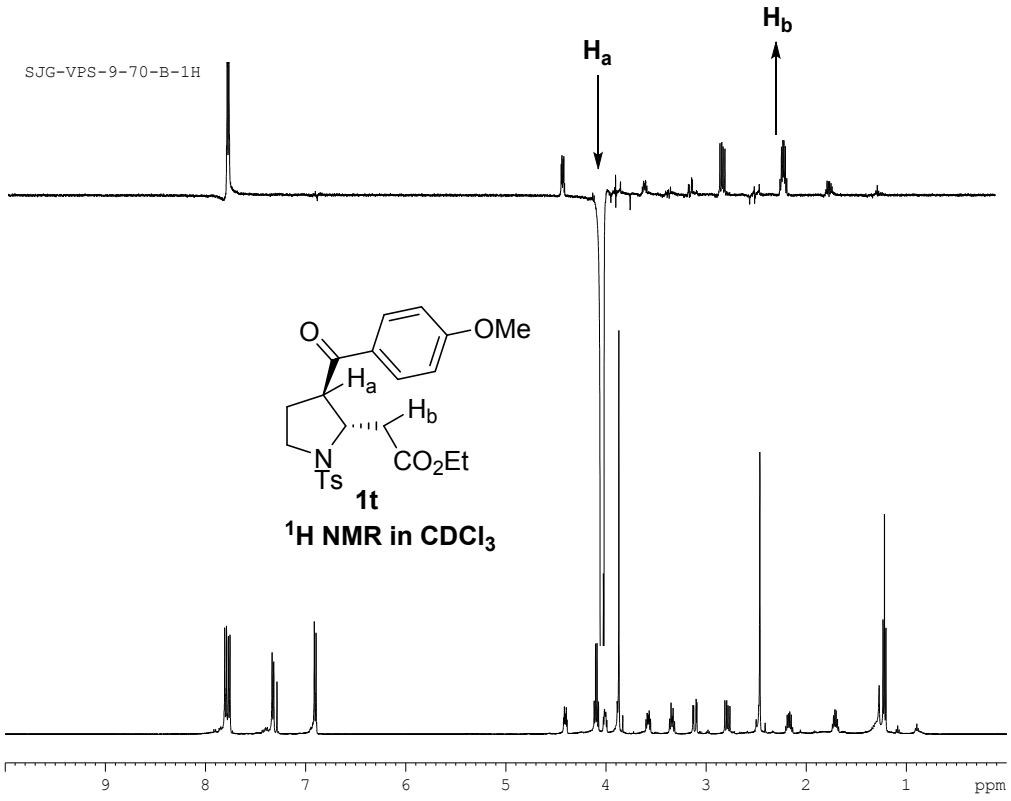
1t

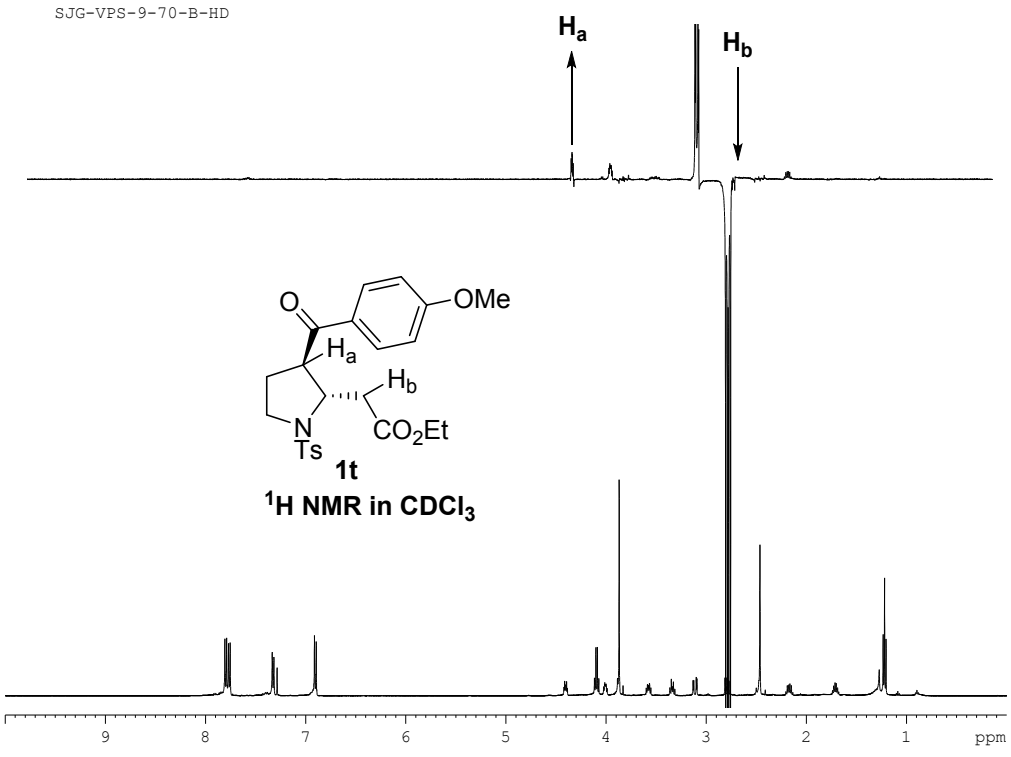
^{1}H NMR in $CDCl_3$

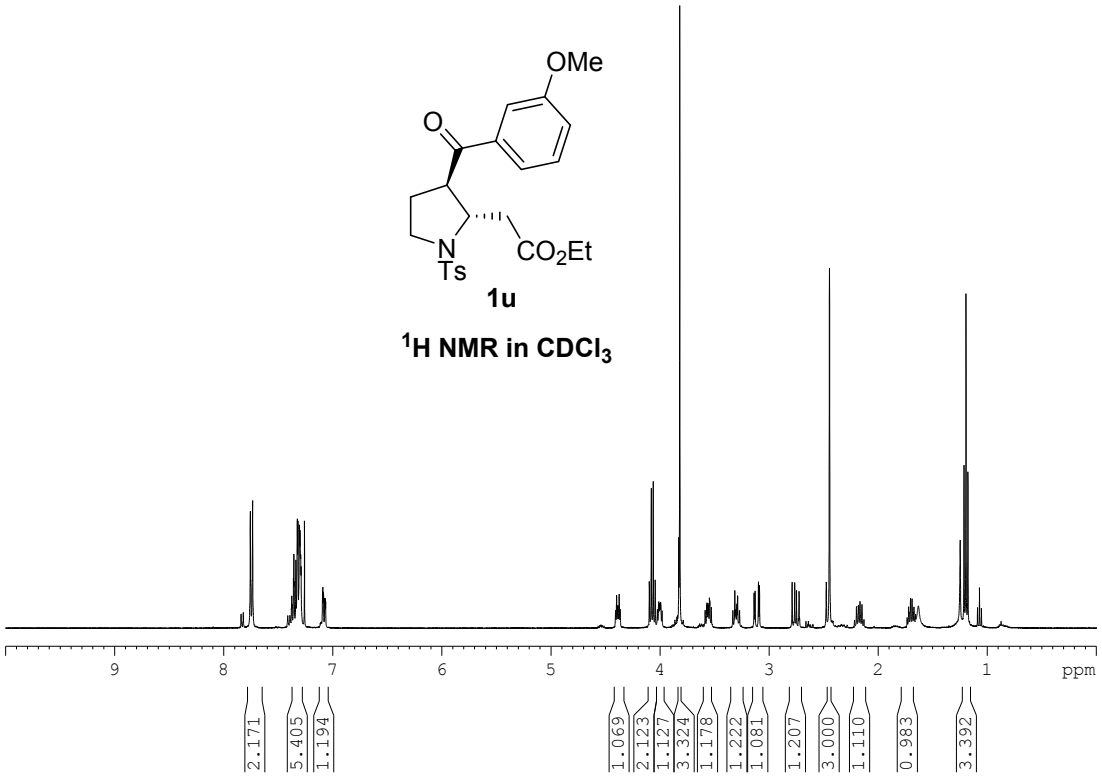


1t

^{13}C NMR in $CDCl_3$

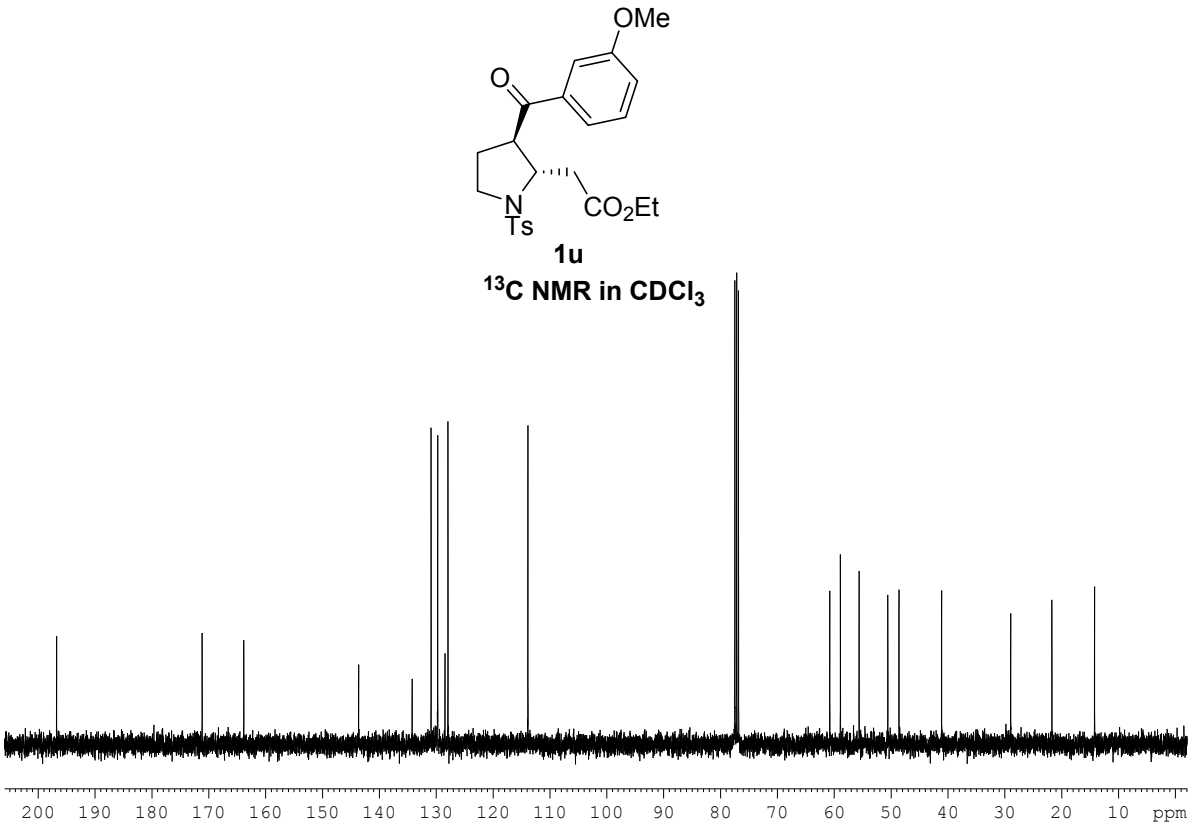

SJG-VPS-9-70-B-1H
Ha
Hb
O
OMe
Ha
Hb
N
Ts
CO2Et
1t
1H NMR in CDCl3
9
8
7
6
5
4
3
2
1
ppm


SJG-VPS-9-70-B-HD
Ha
Hb
O
OMe
Ha
Hb
N
Ts
CO2Et
1t
1H NMR in CDCl3
9
8
7
6
5
4
3
2
1
ppm



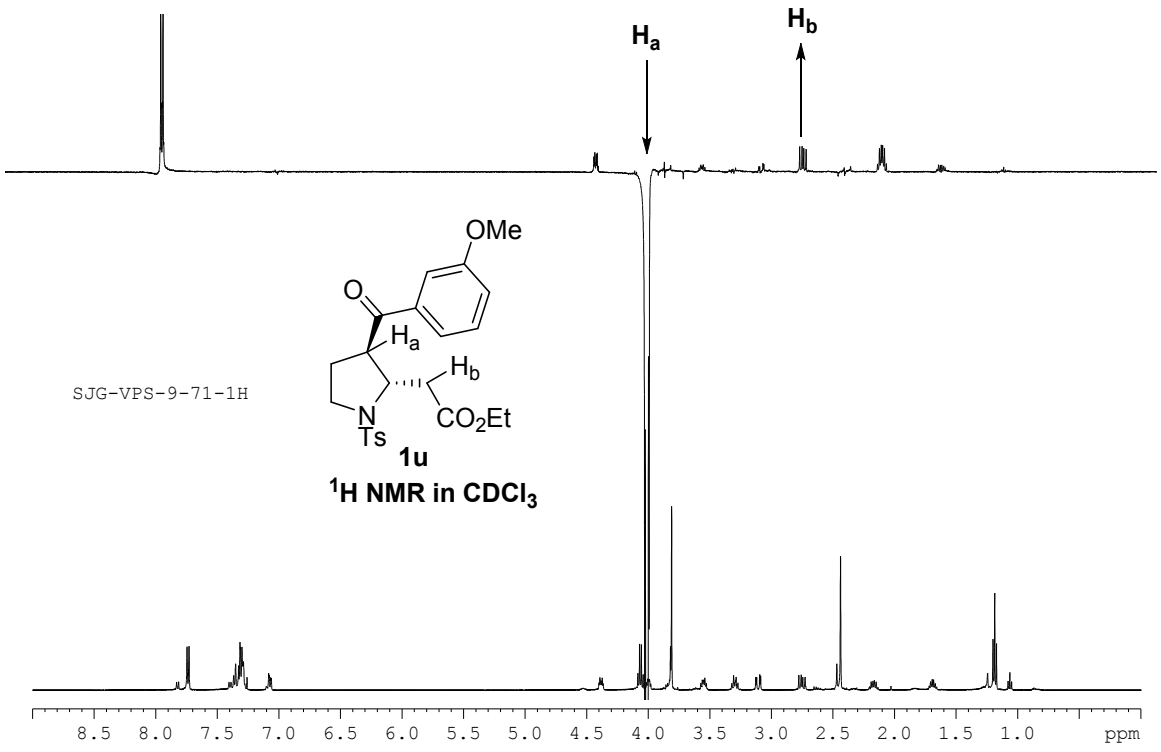
1u

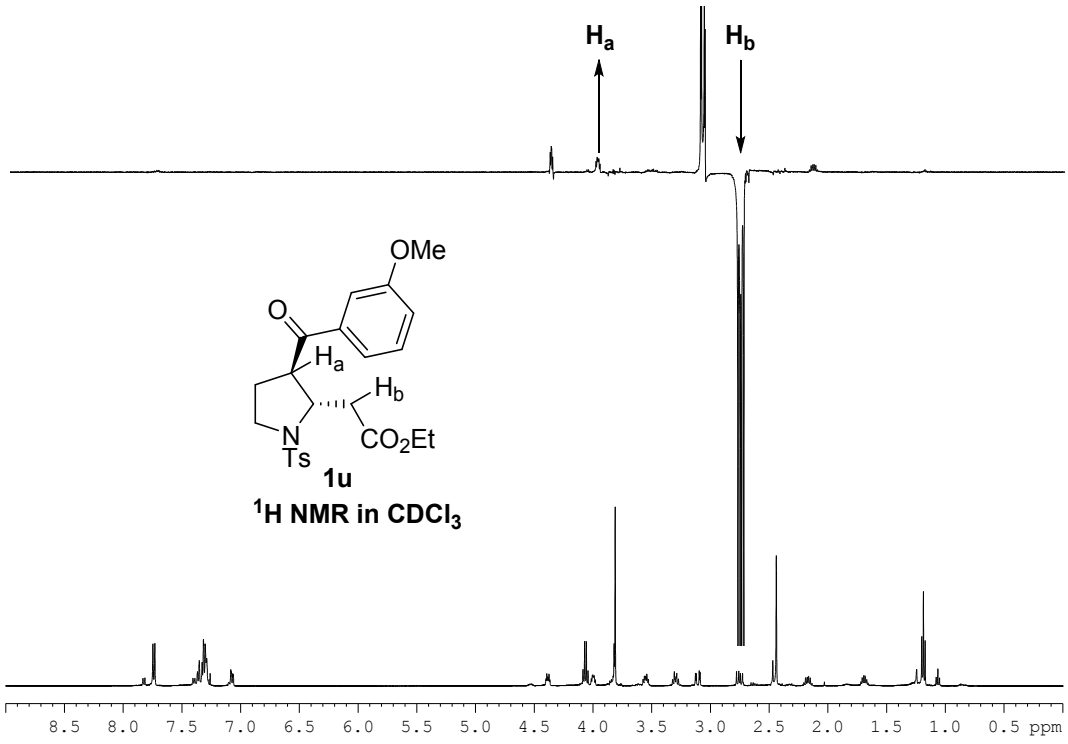
^{1}H NMR in $CDCl_3$

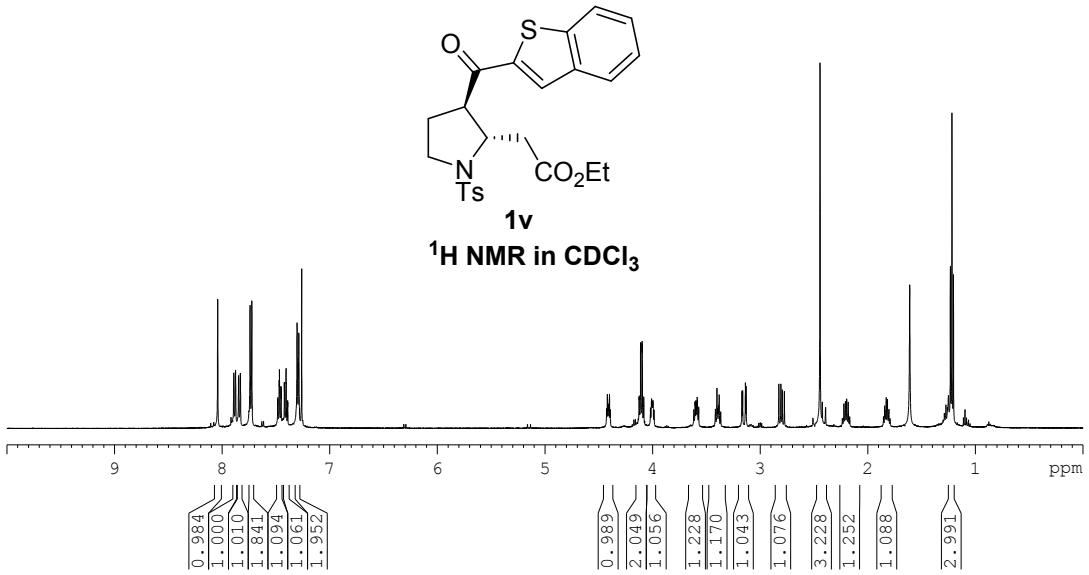


1u

^{13}C NMR in $CDCl_3$

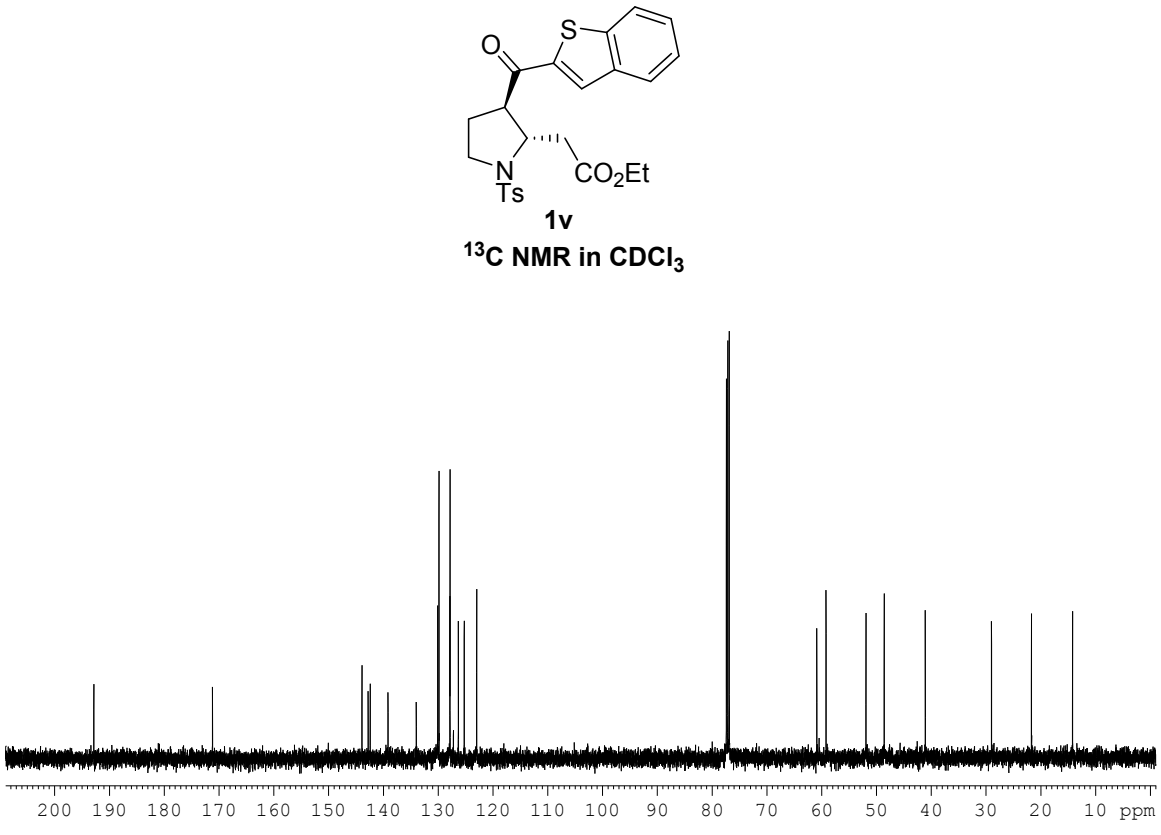

Ha
Hb
OMe
O
Ha
Hb
N
Ts
CO2Et
SJG-VPS-9-71-1H
1u
1H NMR in CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm


Ha
Hb
OMe
O
Ha
Hb
N
Ts
CO2Et
1u
1H NMR in CDCl3
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



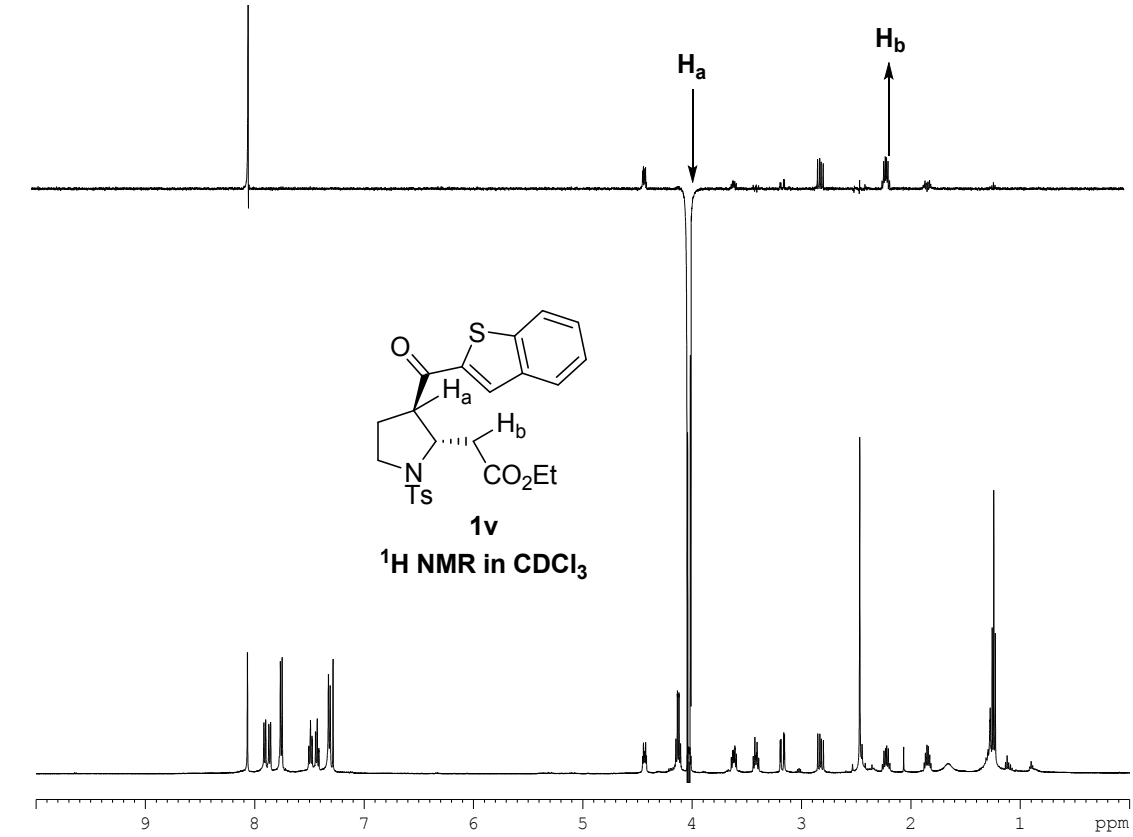
1v

^{1}H NMR in $CDCl_3$



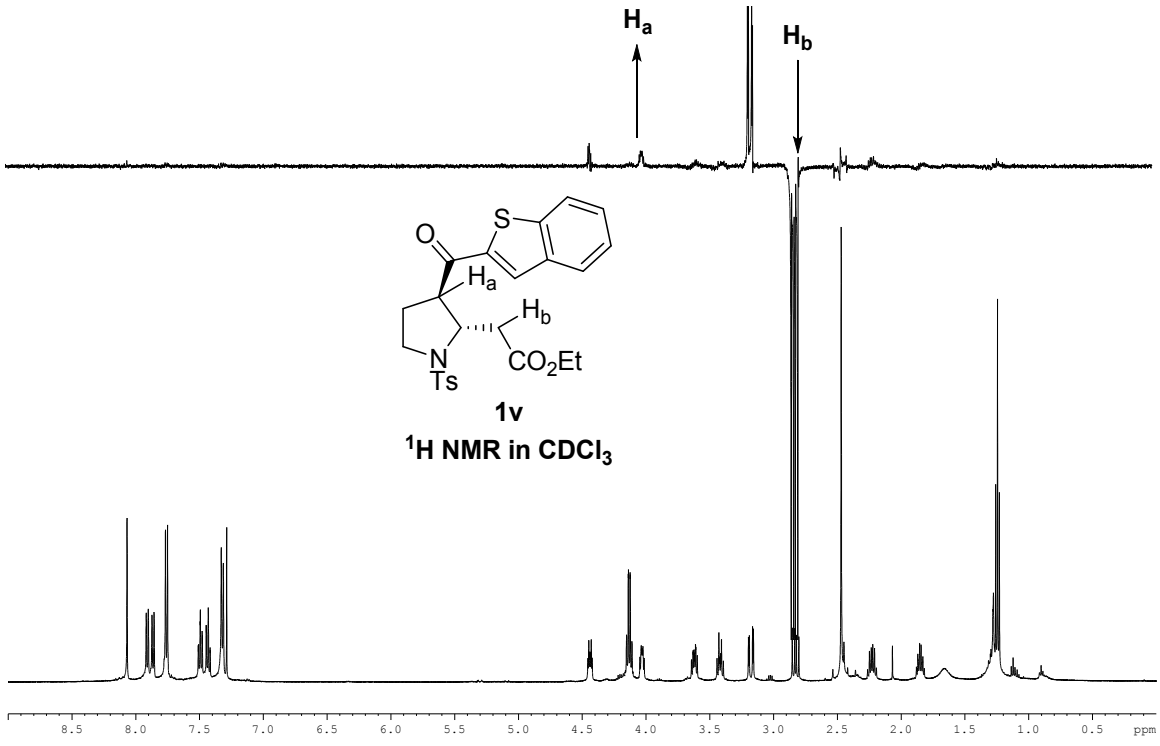
1v

^{13}C NMR in $CDCl_3$



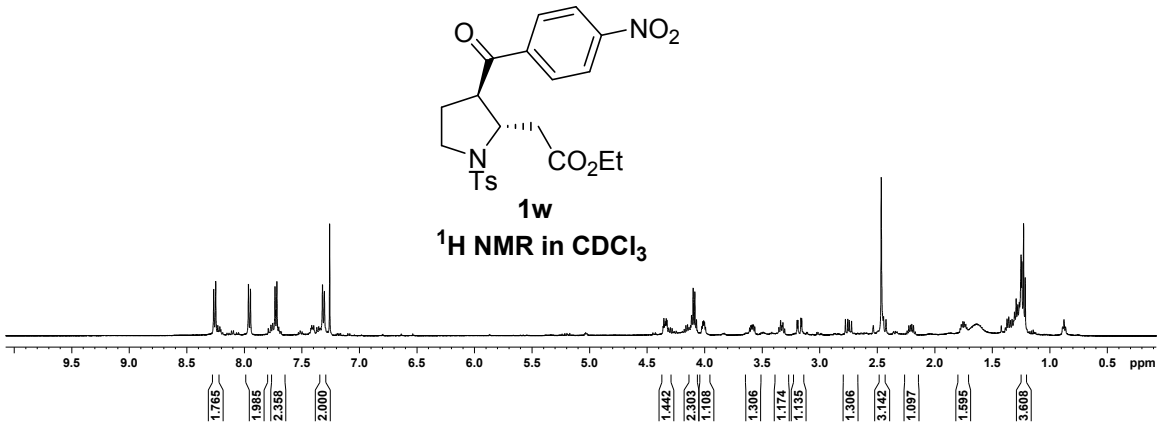
1v

^{1}H NMR in $CDCl_3$



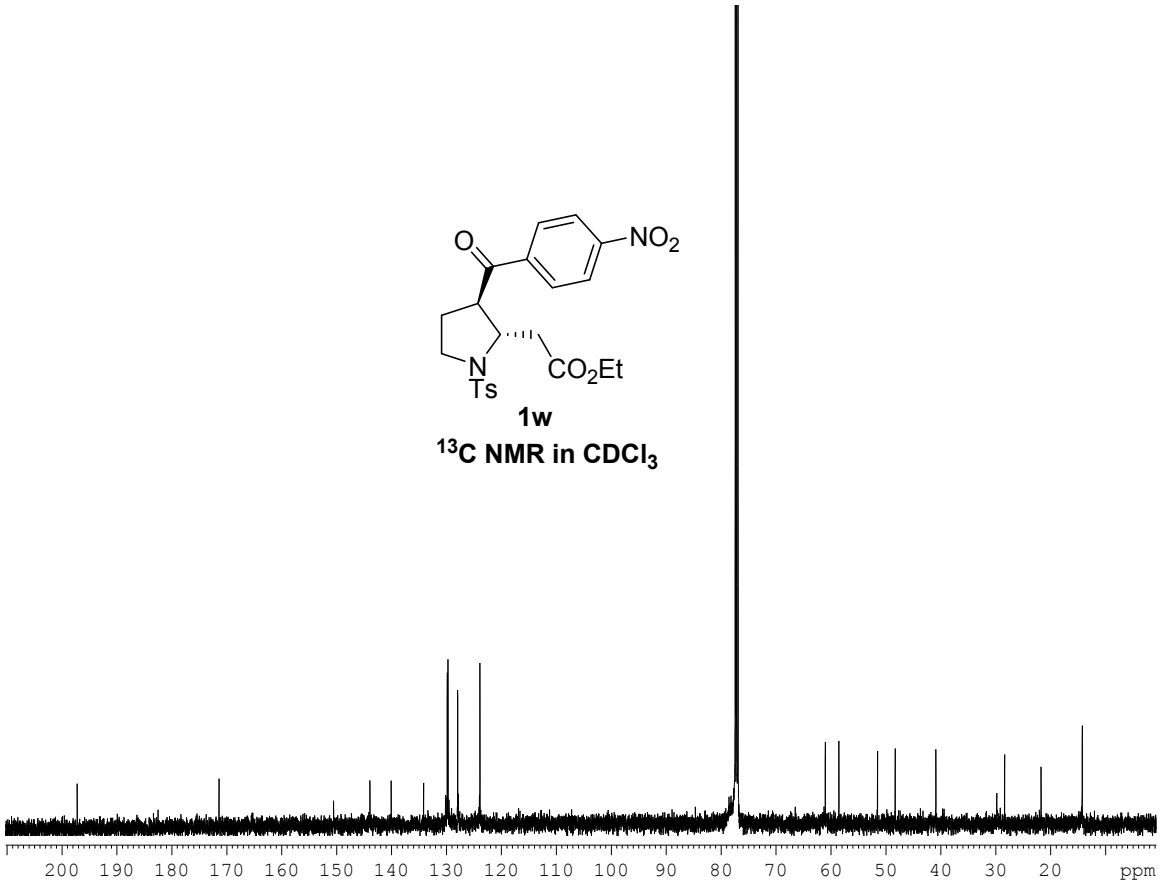
1v

^{1}H NMR in $CDCl_3$



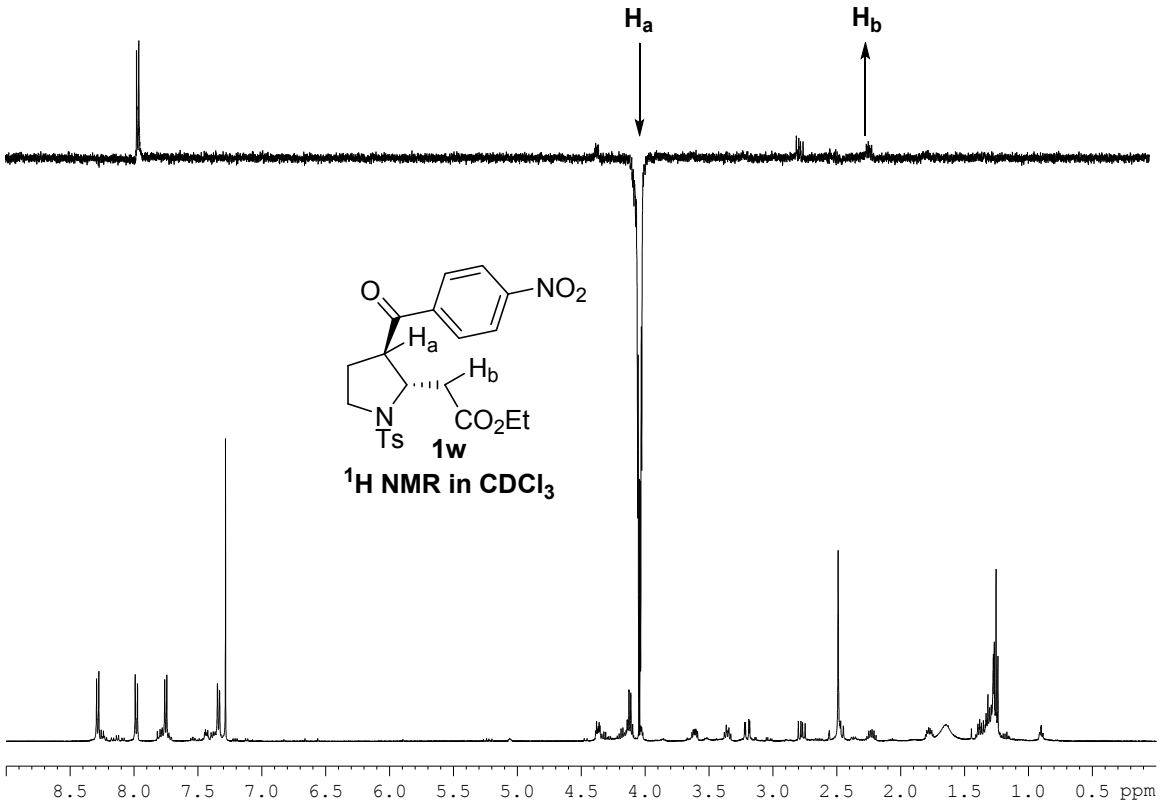
1w

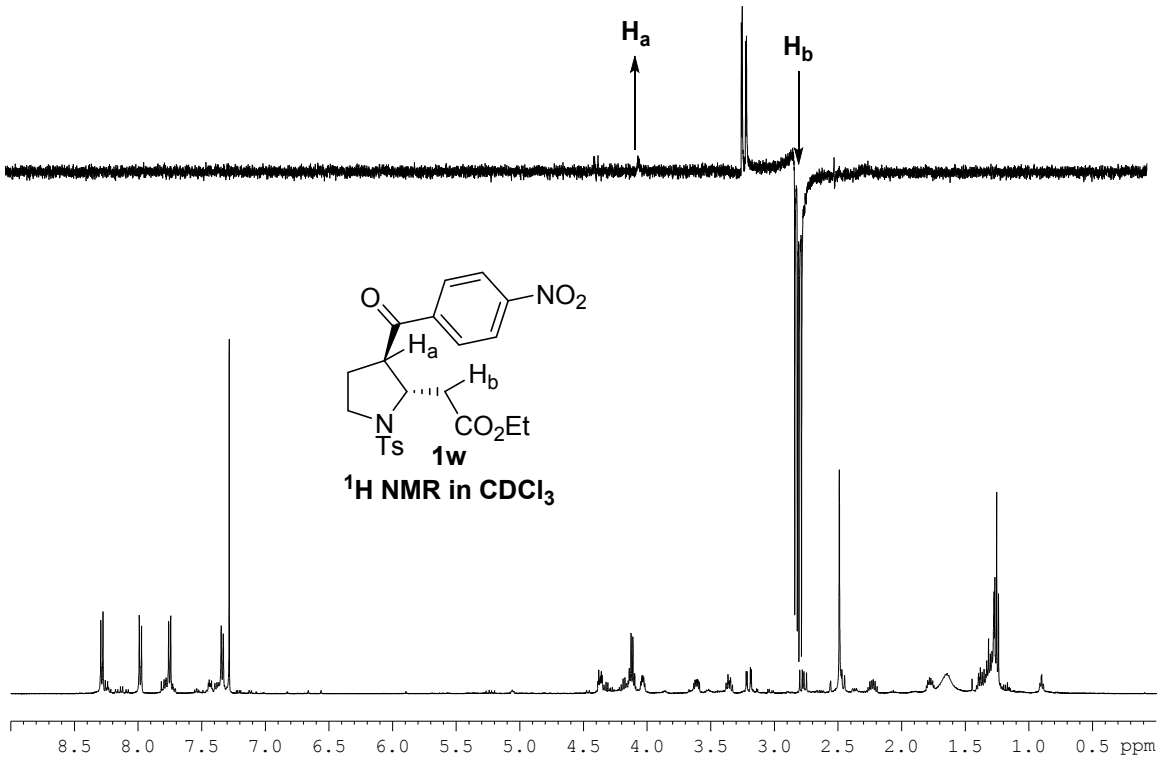
^{1}H NMR in $CDCl_3$

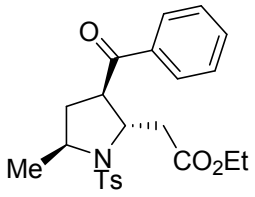


1w

^{13}C NMR in $CDCl_3$

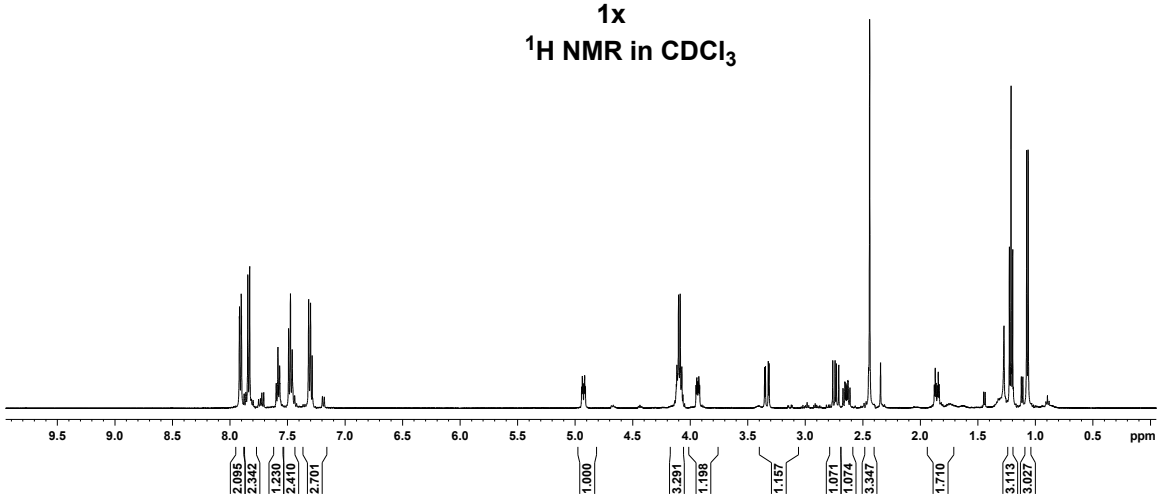

Ha
Hb
O
NO2
Ha
Hb
N
Ts
CO2Et
1w
1H NMR in CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

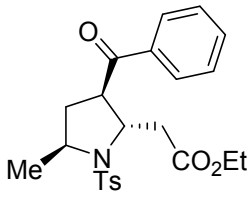

Ha
Hb
O
NO2
Ha
Hb
N
Ts
CO2Et
1w
1H NMR in CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



1x

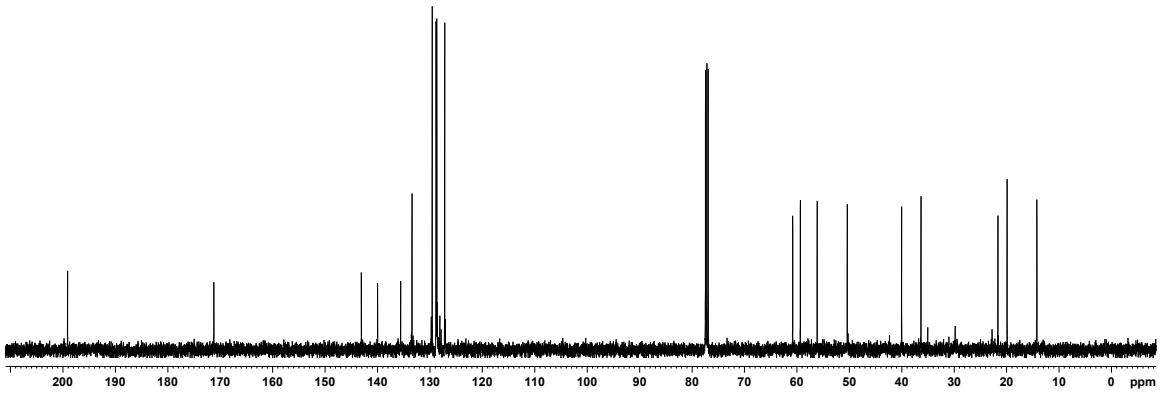
^{1}H NMR in $CDCl_3$

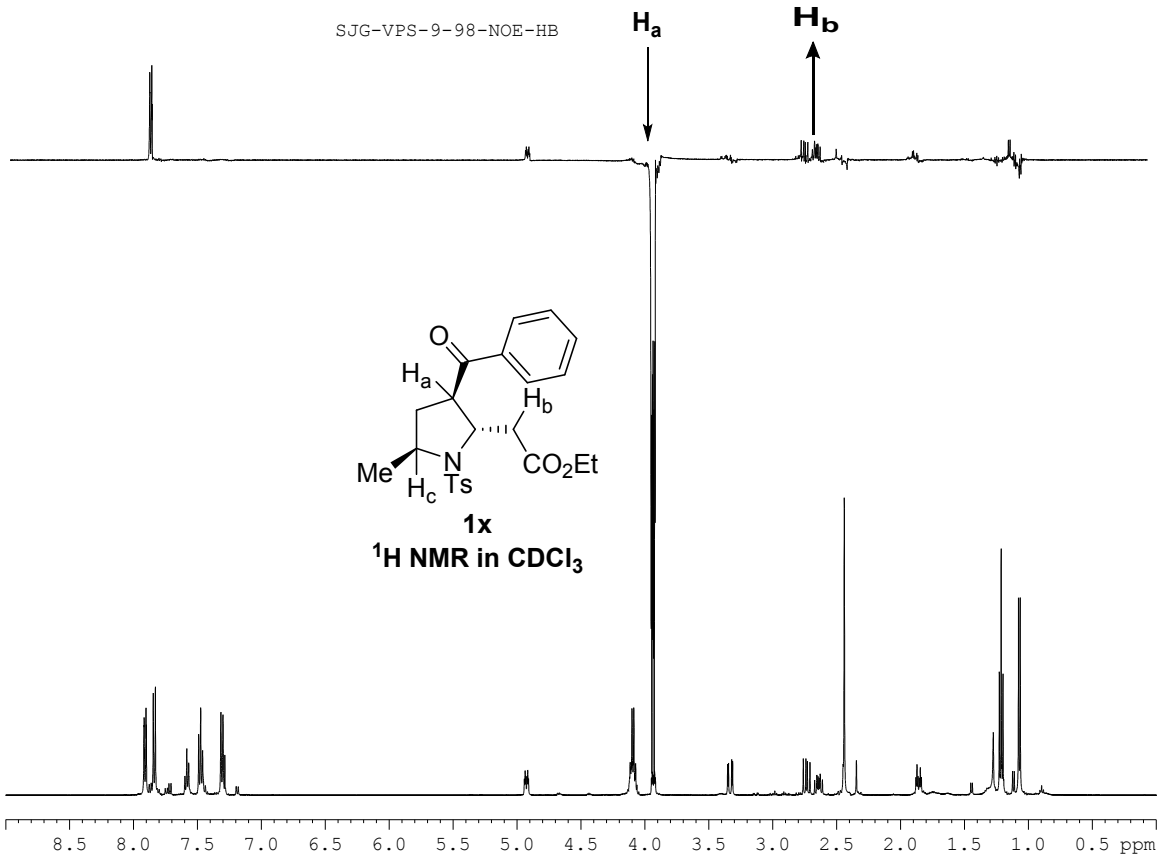




1x

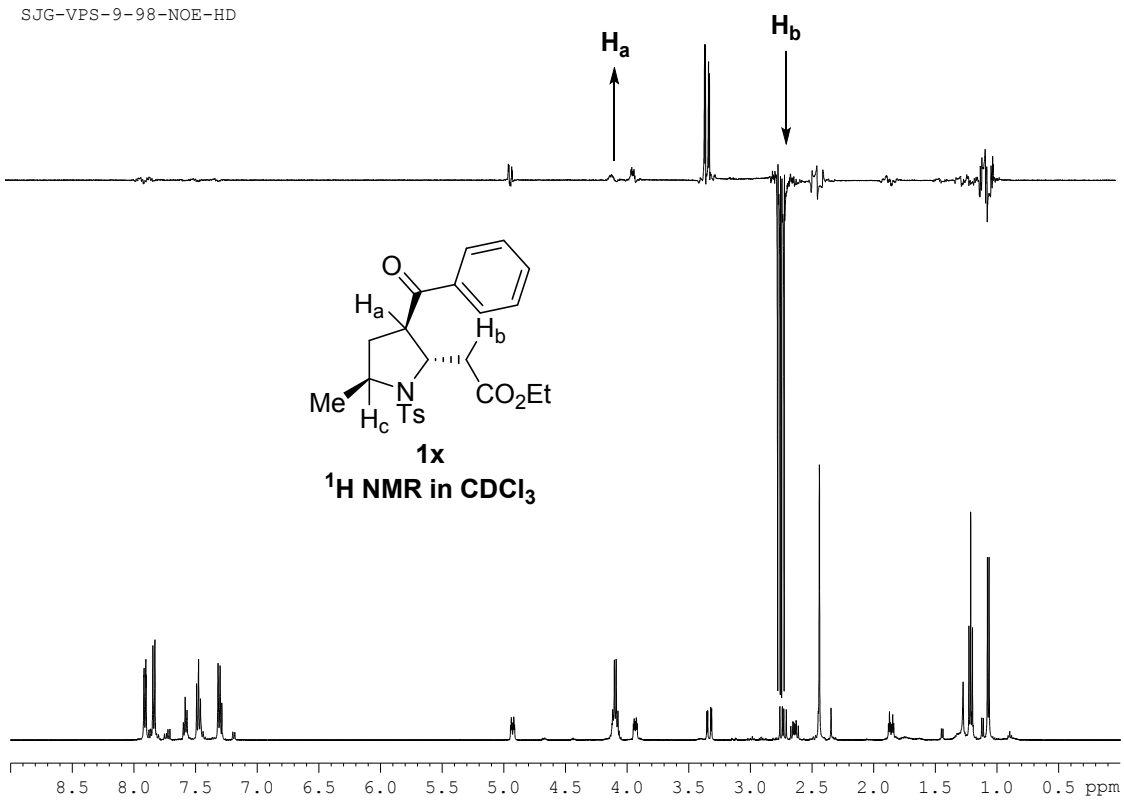
^{13}C NMR in $CDCl_3$





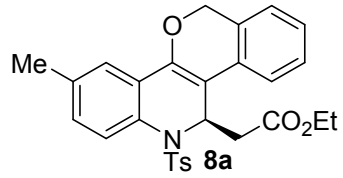
1x

^{1}H NMR in $CDCl_3$



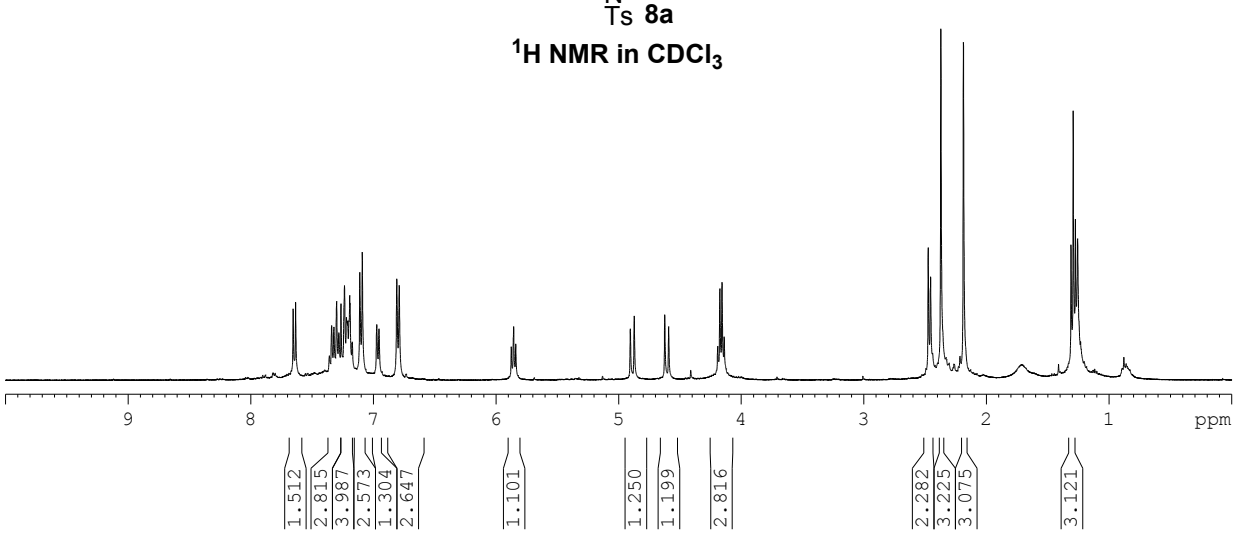
1x

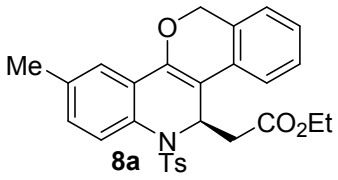
^{1}H NMR in $CDCl_3$



8a

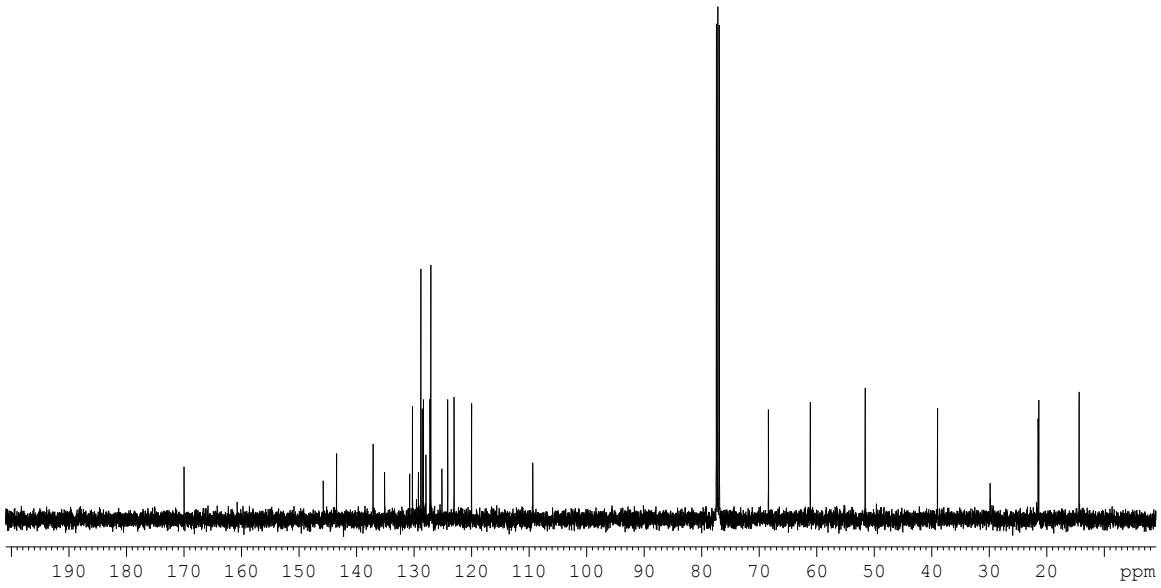
^{1}H NMR in $CDCl_3$

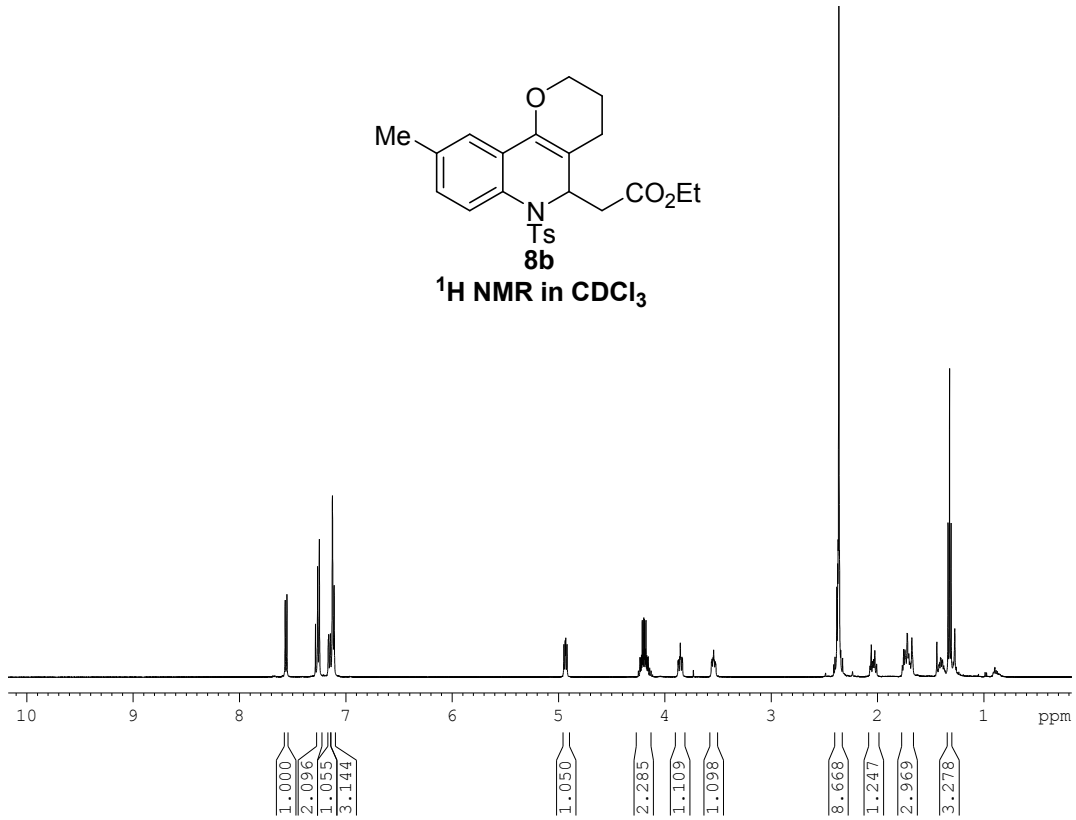




8a

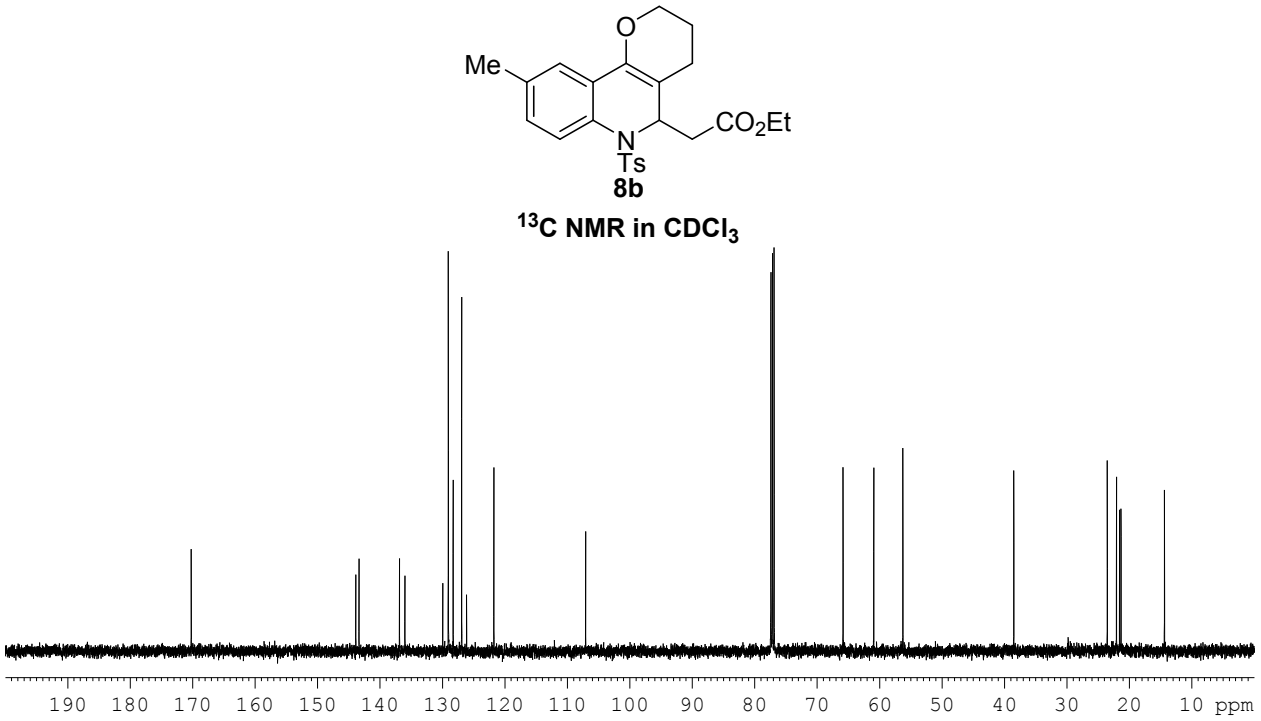
^{13}C NMR in $CDCl_3$





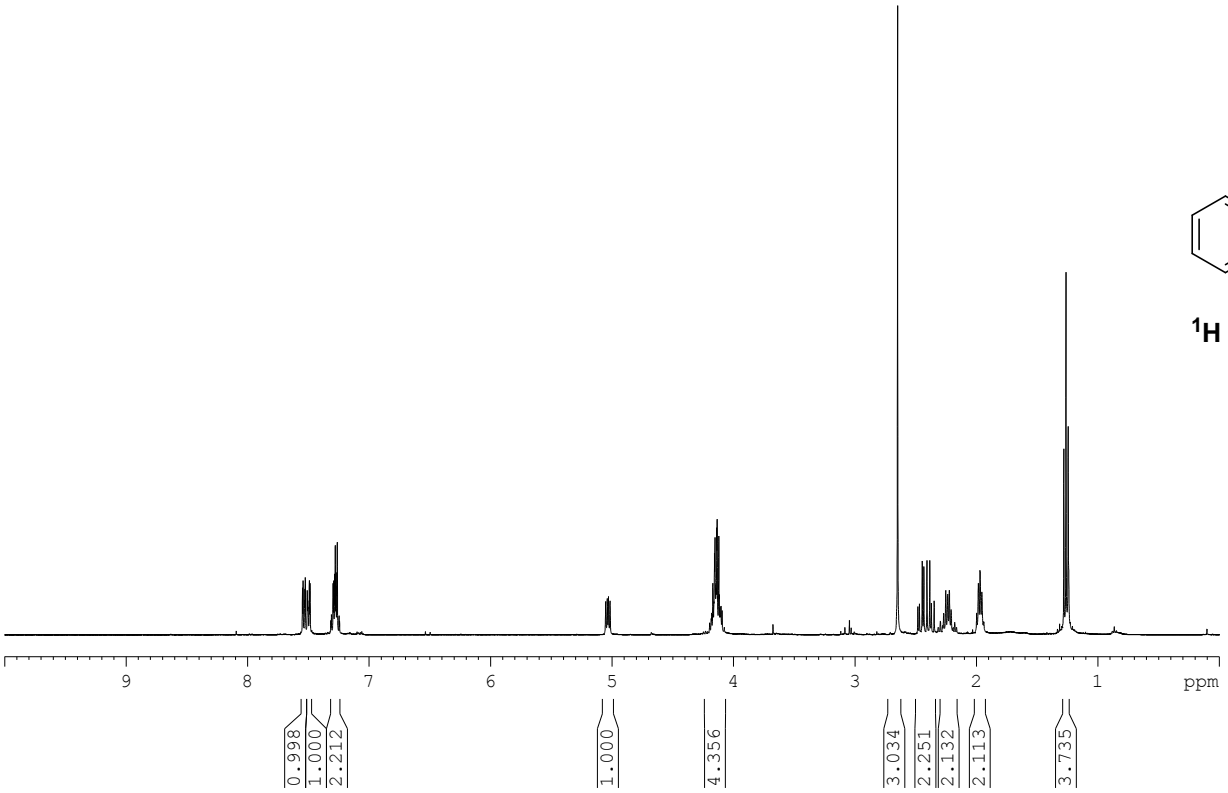
8b

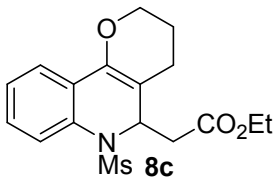
^{1}H NMR in $CDCl_3$



8b

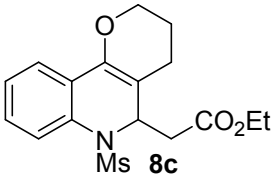
^{13}C NMR in $CDCl_3$





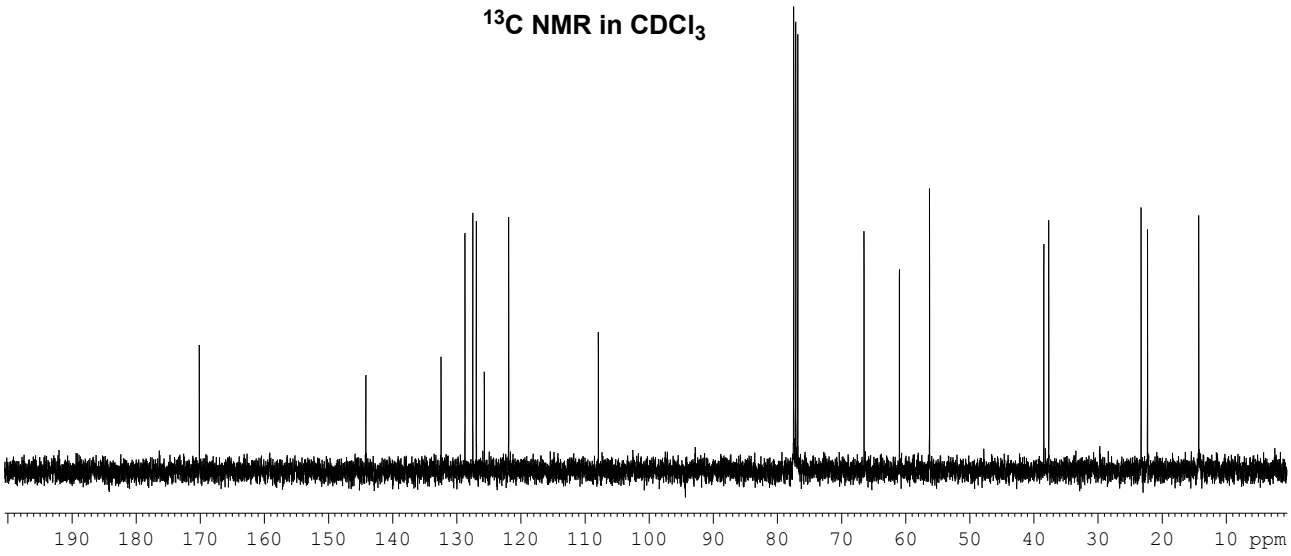
8c

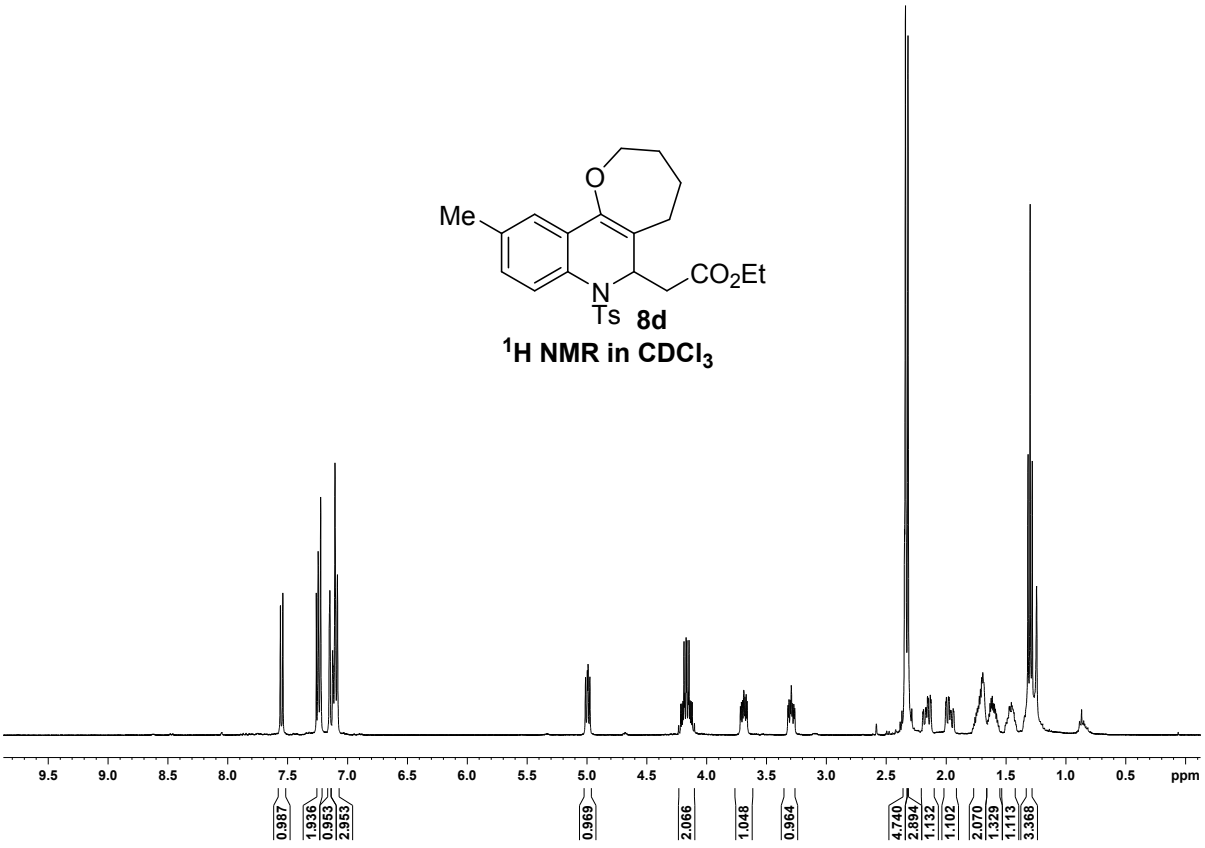
^{1}H NMR in $CDCl_3$



8c

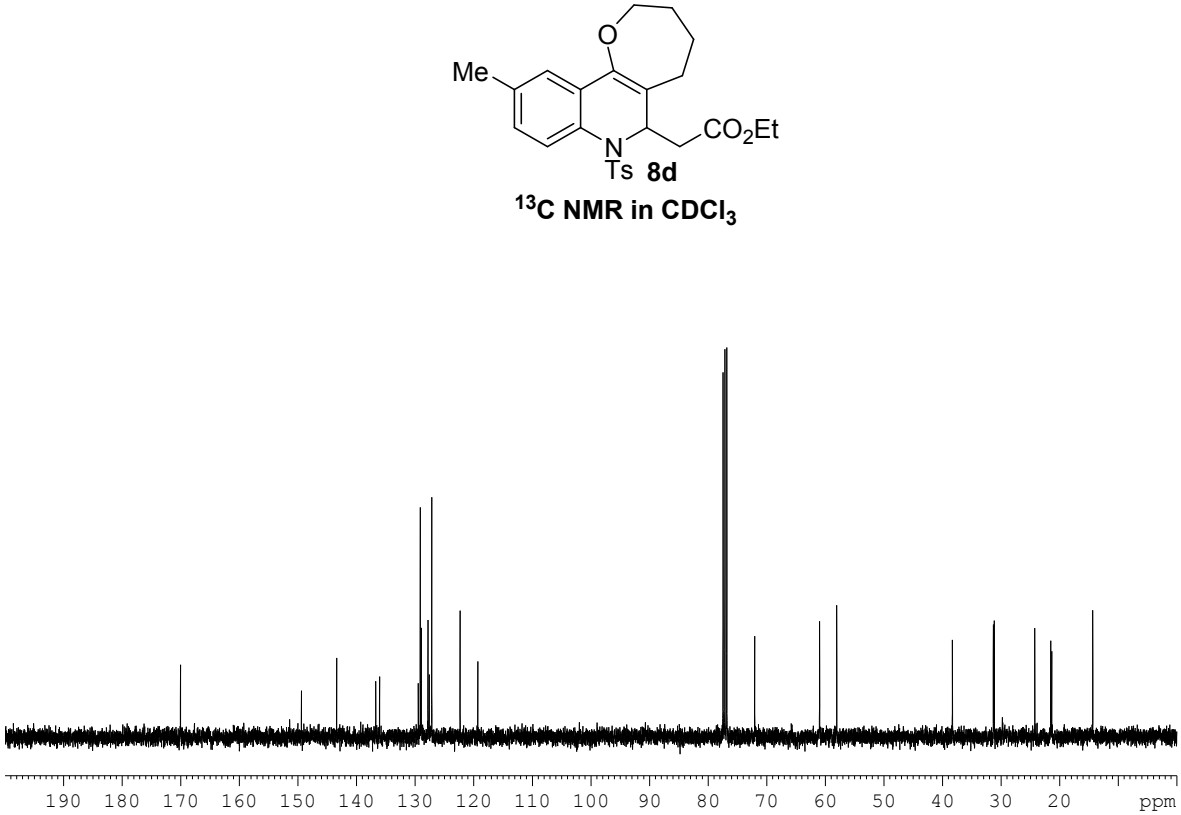
^{13}C NMR in $CDCl_3$





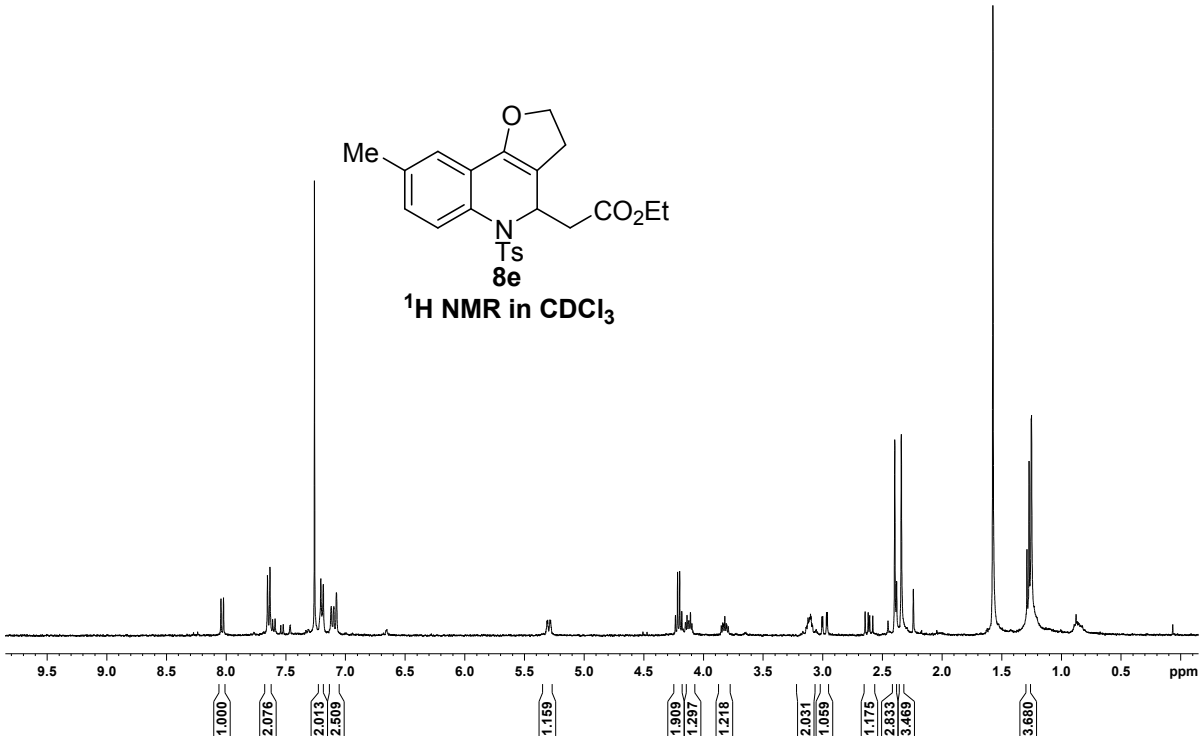
8d

^{1}H NMR in $CDCl_3$



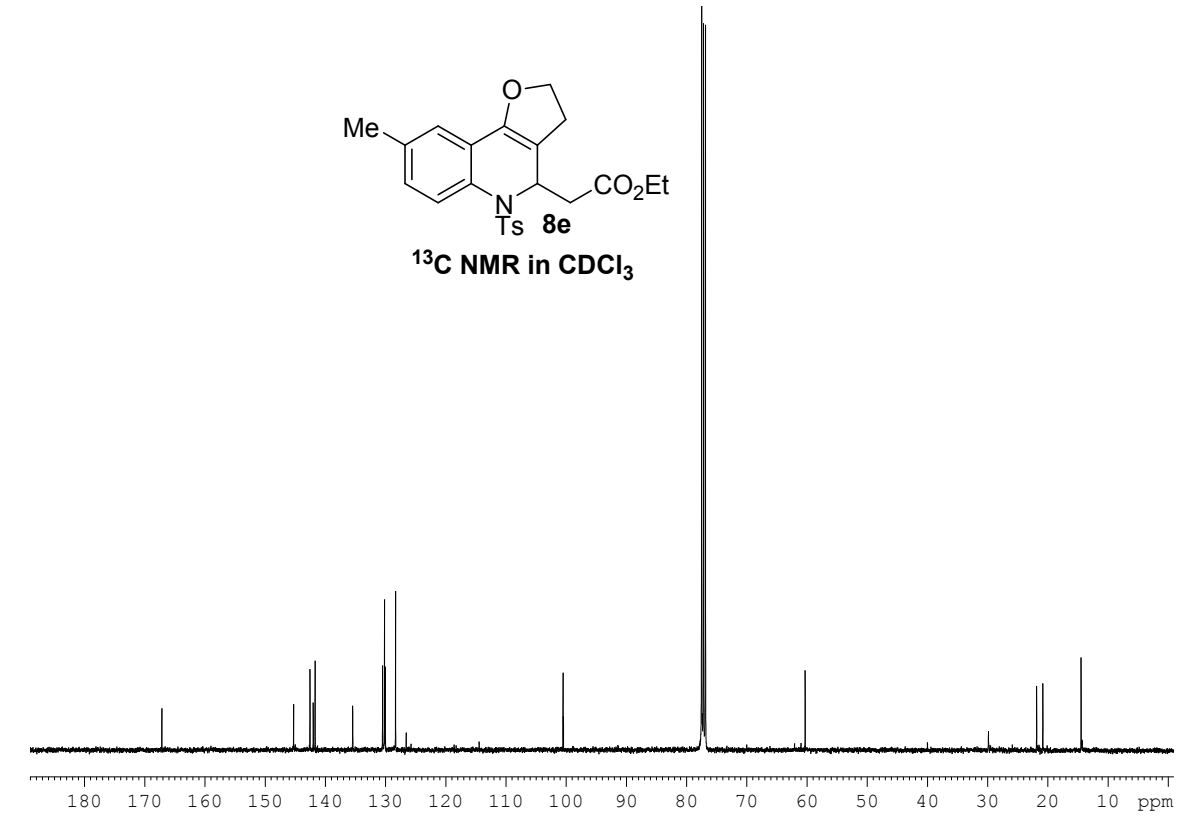
8d

^{13}C NMR in $CDCl_3$



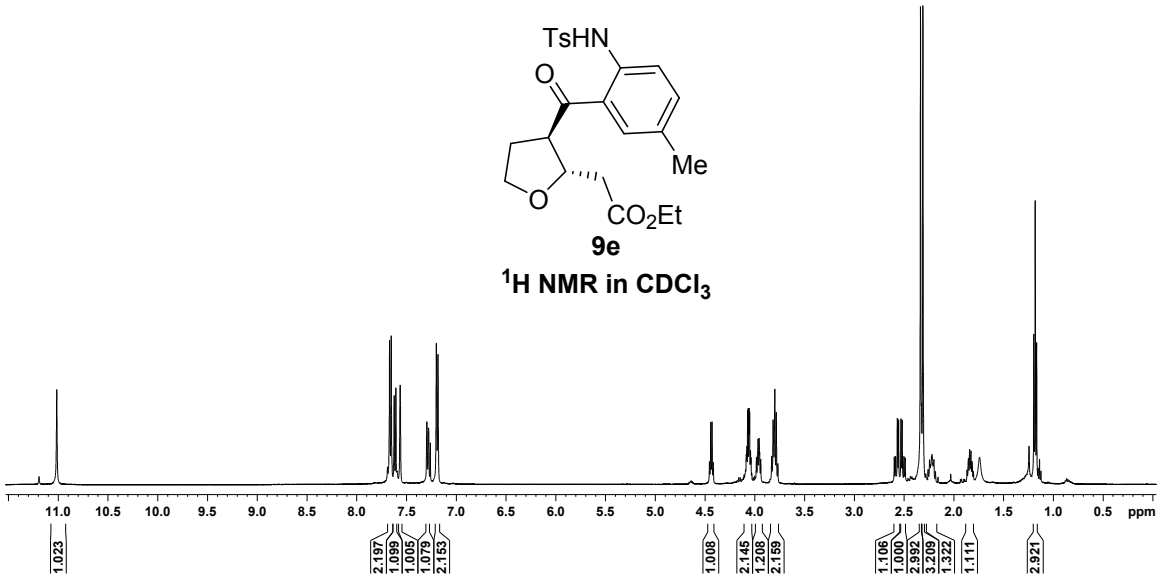
8e

^{1}H NMR in $CDCl_3$



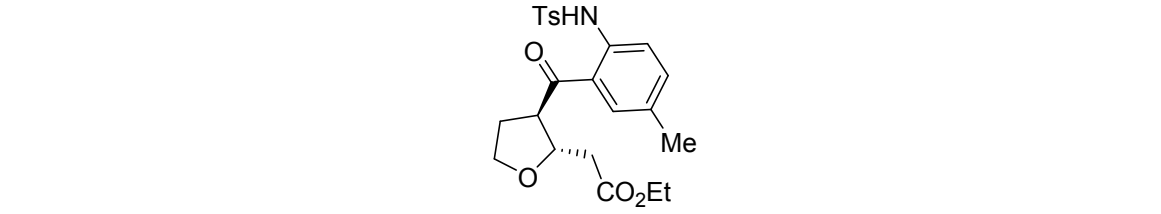
8e

^{13}C NMR in $CDCl_3$



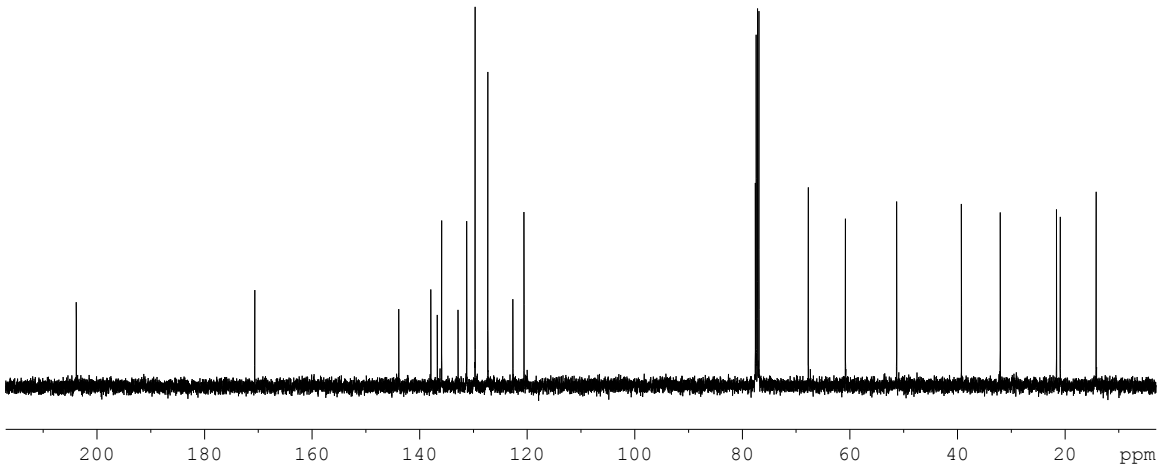
9e

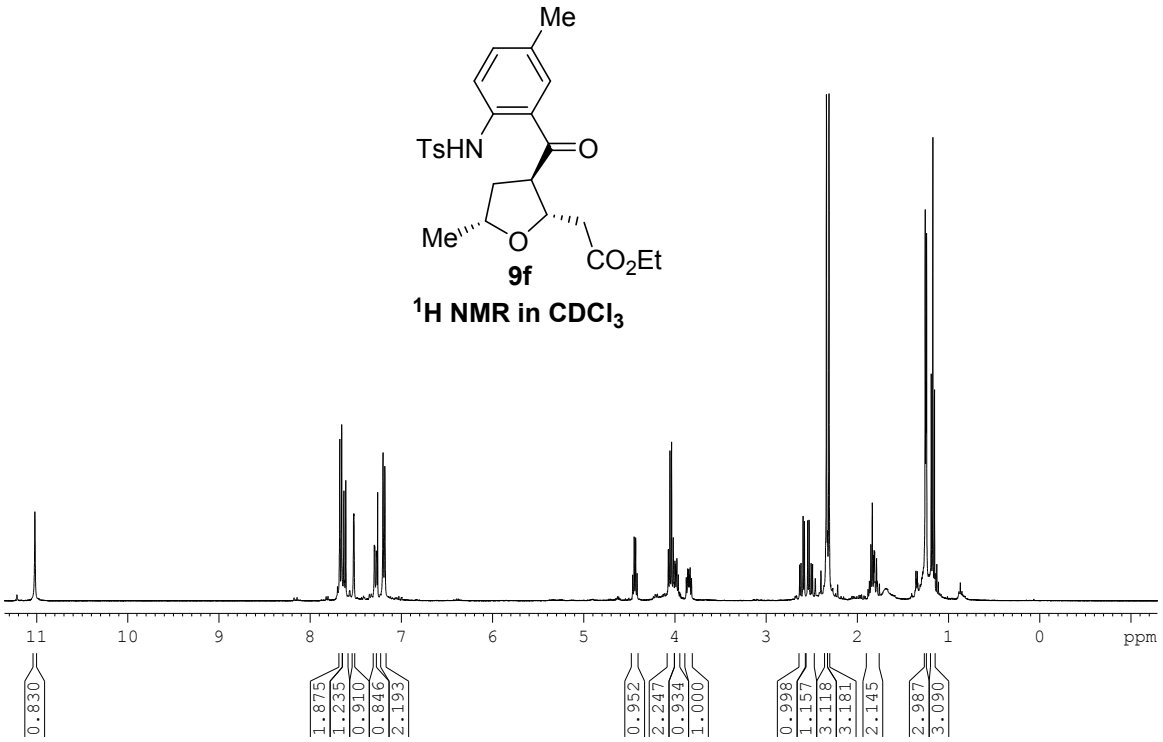
^{1}H NMR in $CDCl_3$

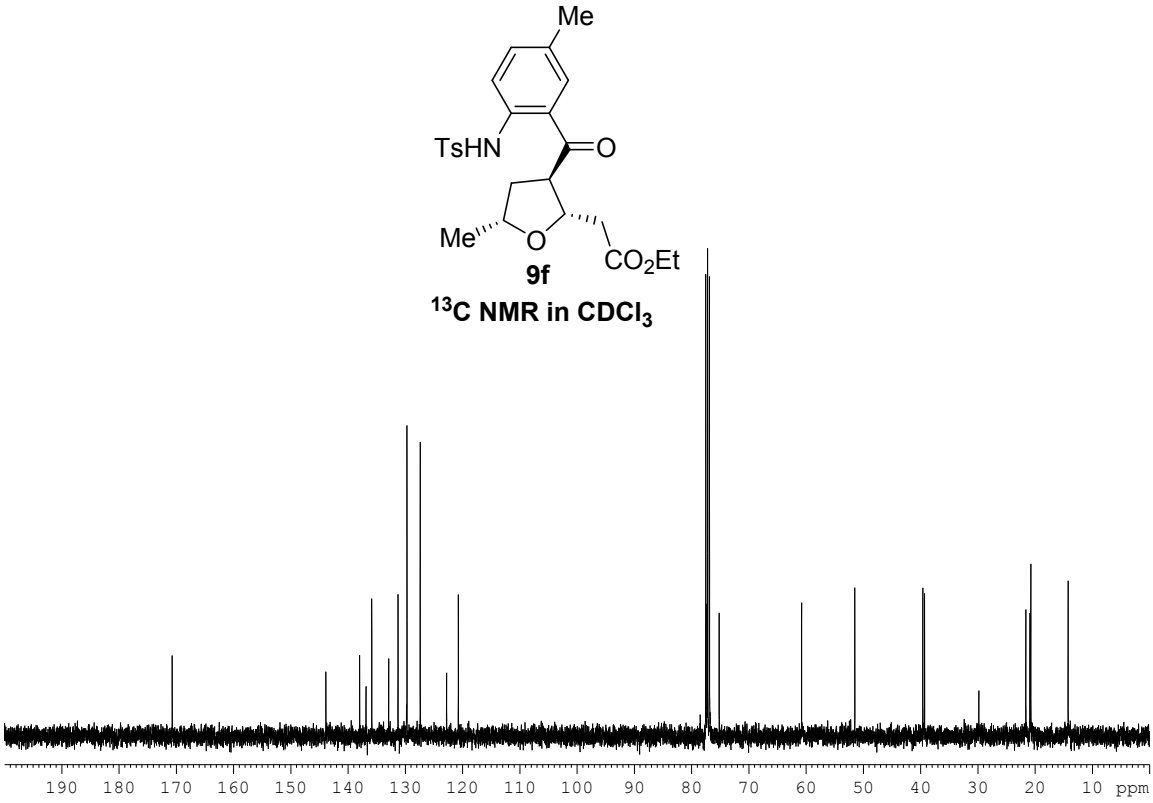


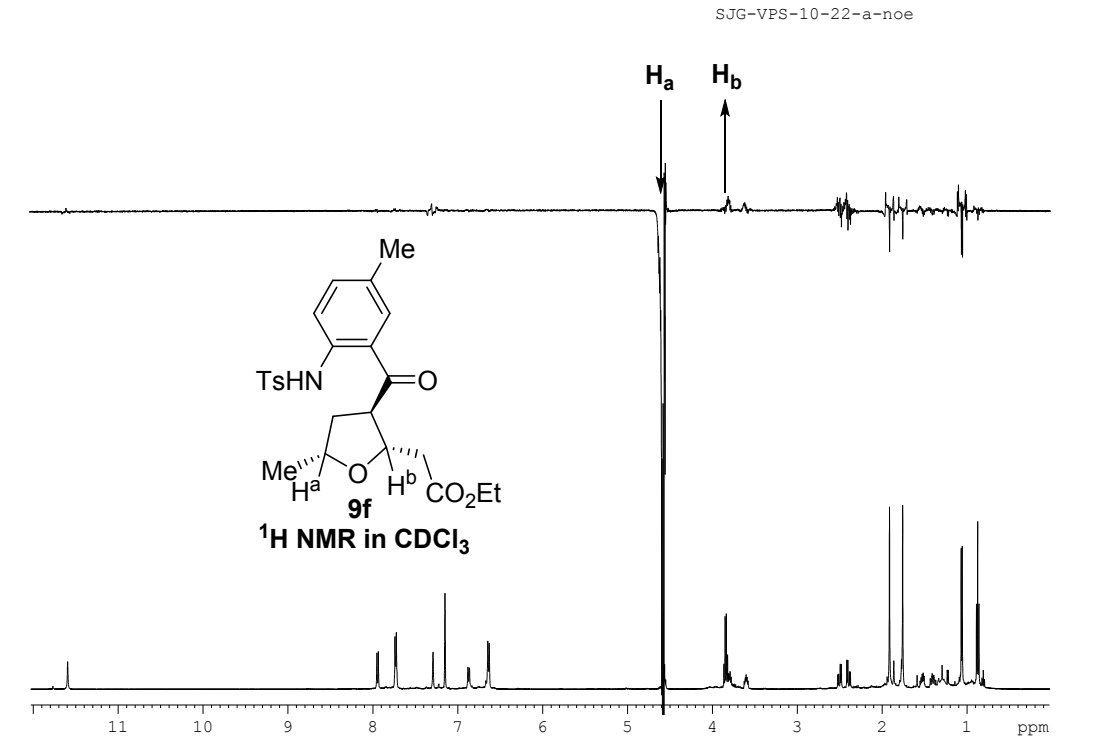
9e

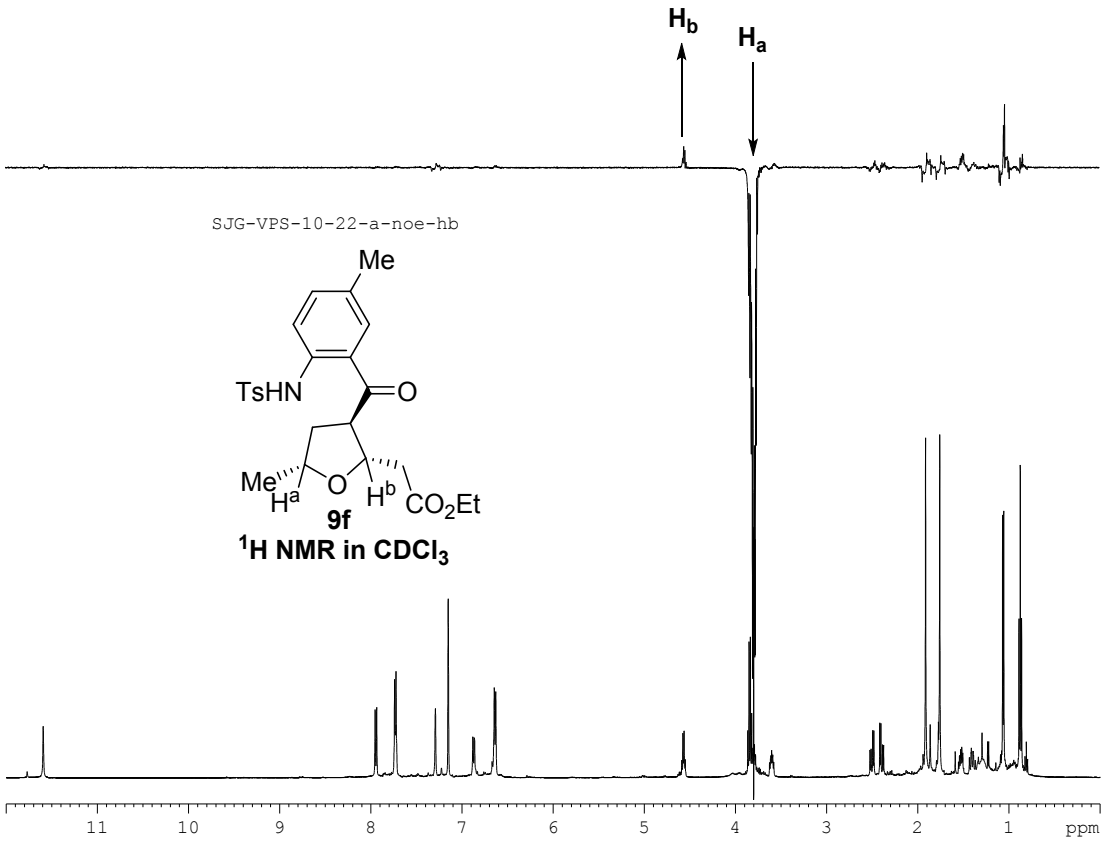
^{13}C NMR in $CDCl_3$

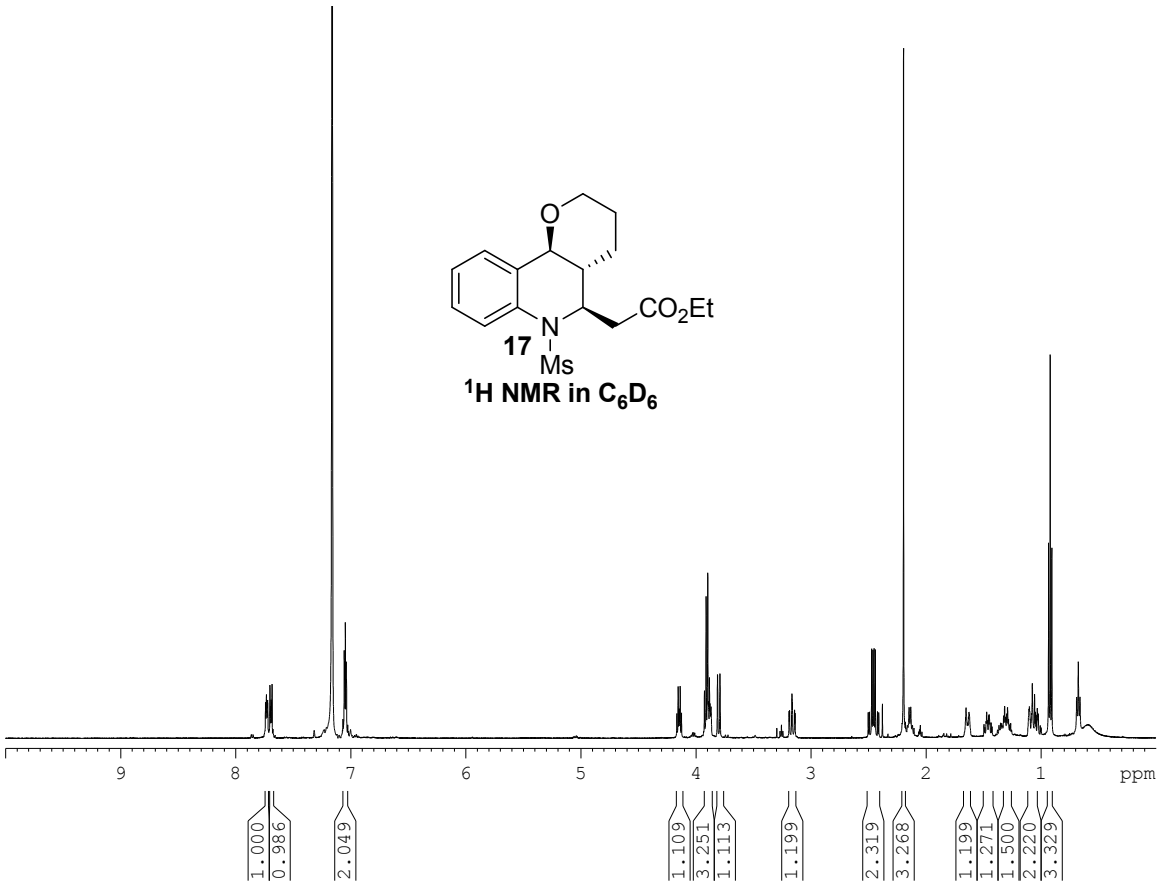



Me
TsHN
O
Me
O
CO2Et
9f
1H NMR in CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.830
1.875
1.235
0.910
0.846
2.193
0.952
2.247
0.934
1.000
0.998
1.157
3.118
3.181
2.145
2.987
3.090


Me
TsHN
O
Me
O
CO2Et
9f
13C NMR in CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

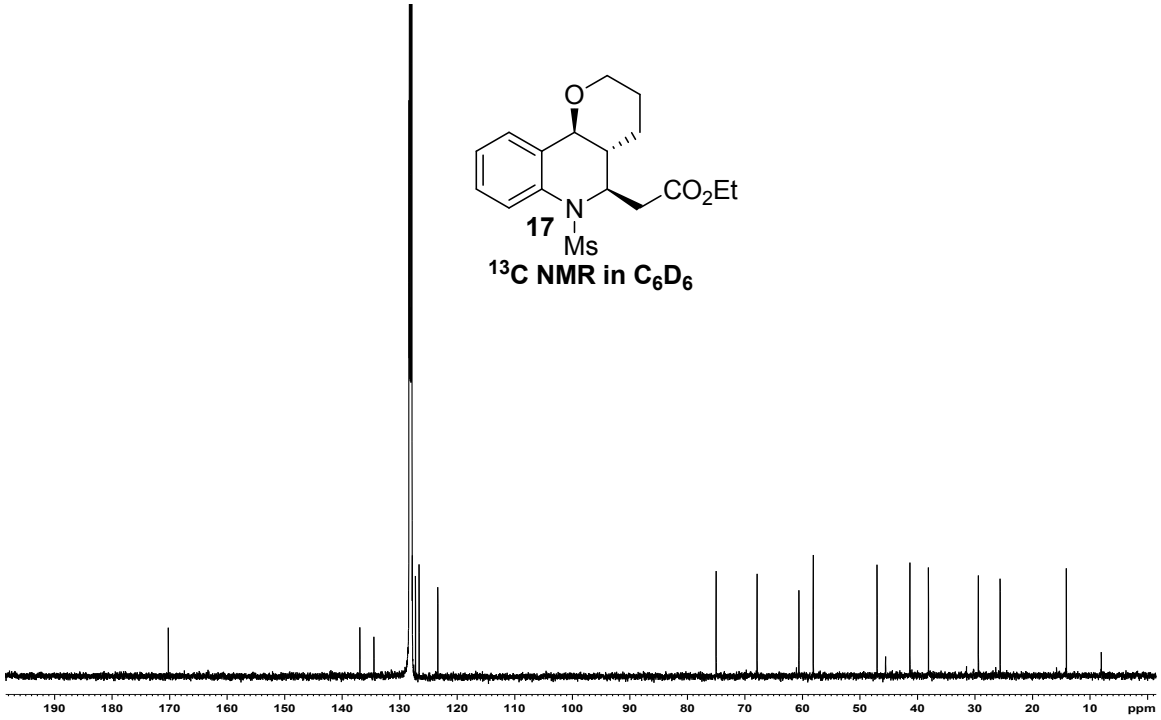

SJG-VPS-10-22-a-noe
Ha
Hb
Me
TsHN
O
Me
Ha
O
Hb
CO2Et
9f
1H NMR in CDCl3
11
10
9
8
7
6
5
4
3
2
1
ppm


Hb
Ha
SJG-VPS-10-22-a-noe-hb
Me
TsHN
O
Me
Ha
O
Hb
CO2Et
9f
1H NMR in CDCl3
11
10
9
8
7
6
5
4
3
2
1
ppm



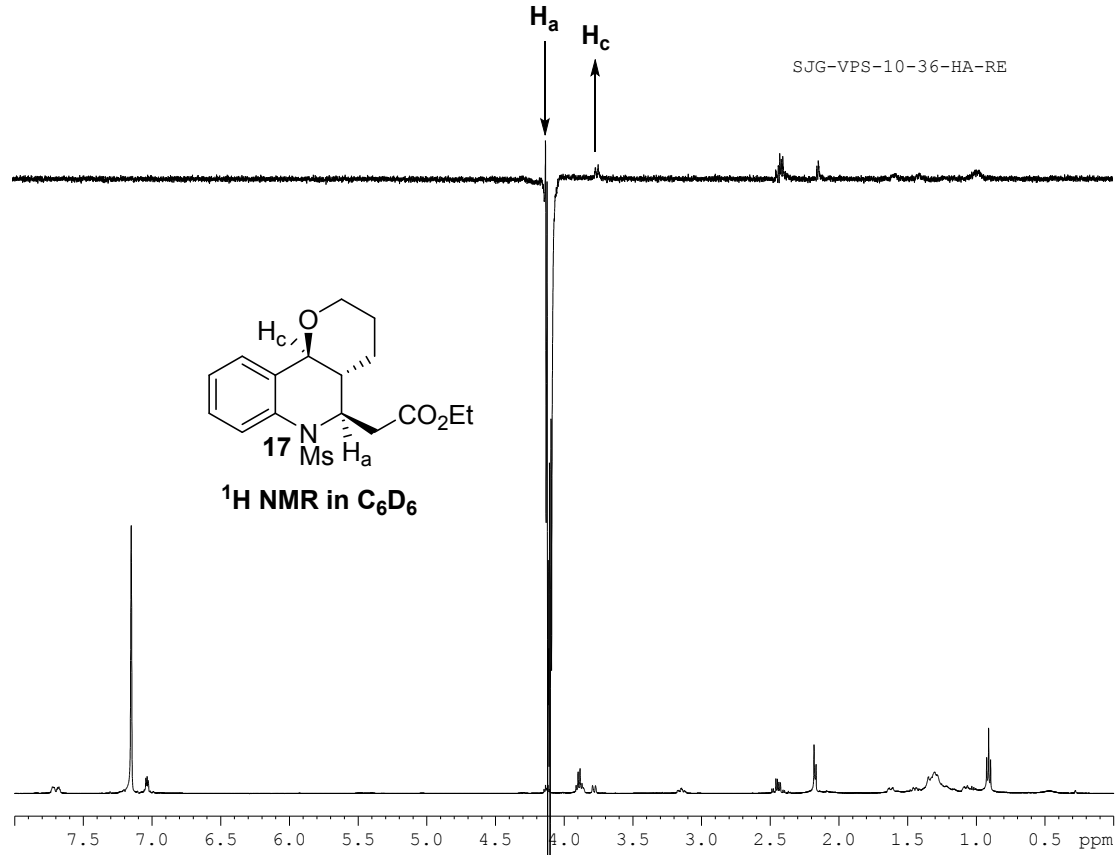
17

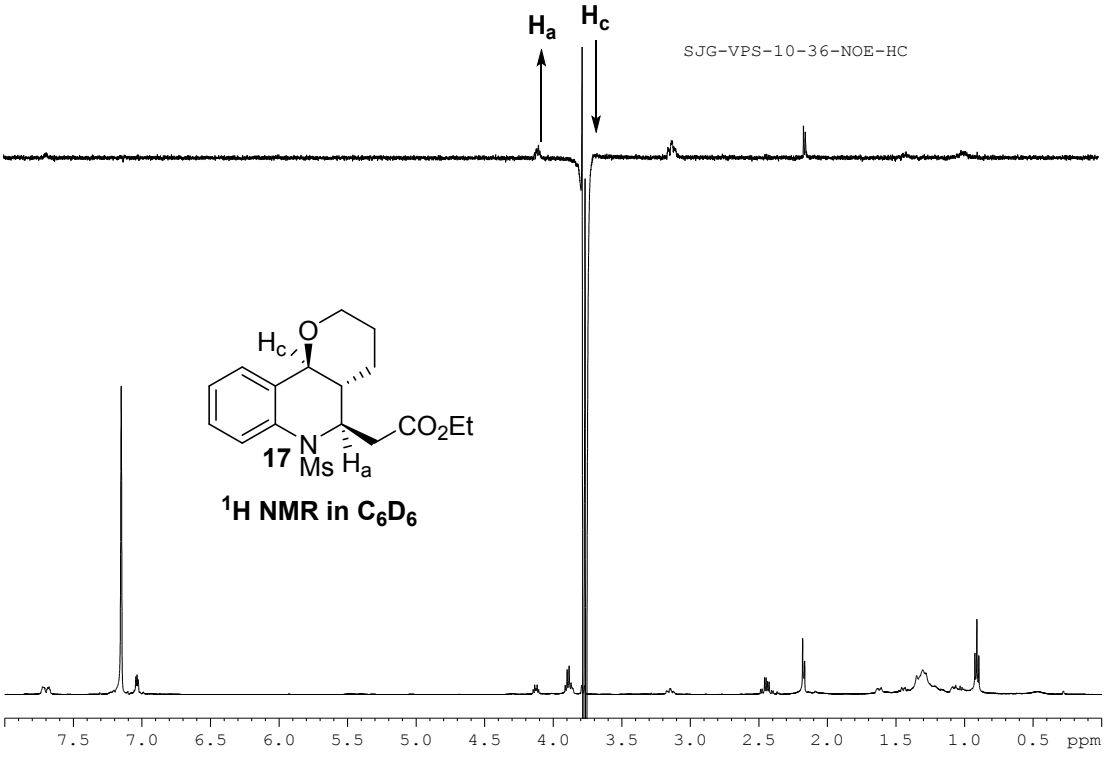
^{1}H NMR in C_6D_6

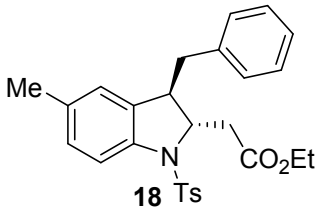


17

^{13}C NMR in C_6D_6

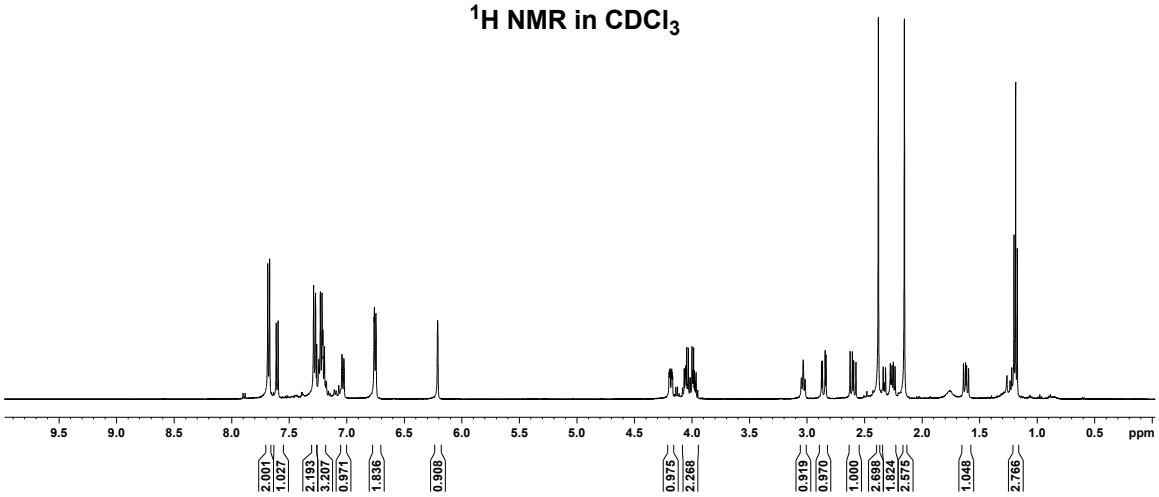

Ha
Hc
SJG-VPS-10-36-HA-RE
Hc
O
CO2Et
17
N
Ms
Ha
1H NMR in C6D6
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

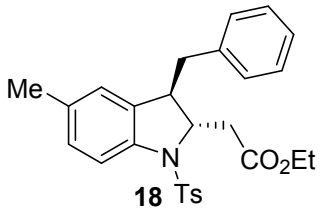

Ha
Hc
SJG-VPS-10-36-NOE-HC
Hc
O
CO2Et
17
N
Ms
Ha
1H NMR in C6D6
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



18

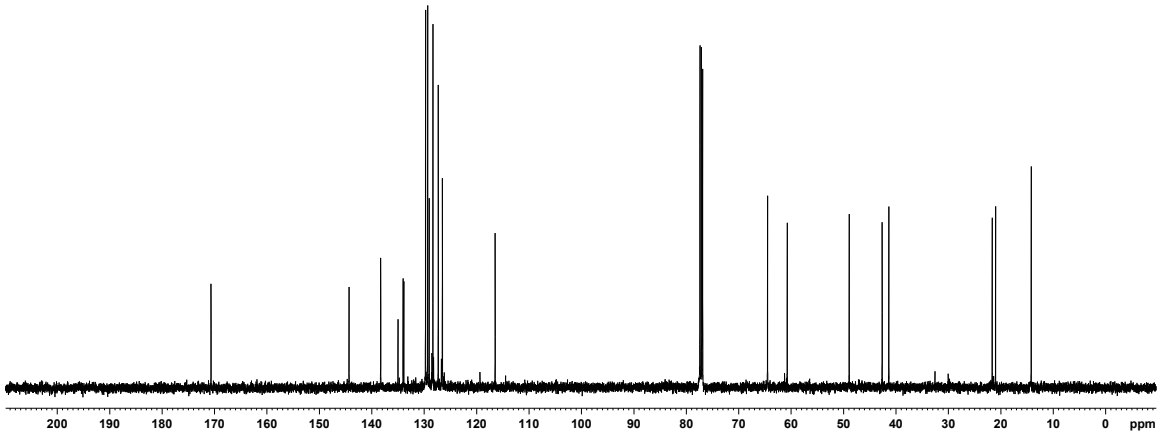
^{1}H NMR in $CDCl_3$



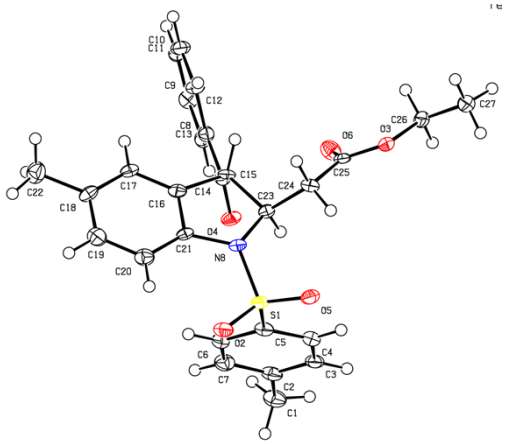


18

^{13}C NMR in $CDCl_3$



Crystal data and structure refinement for 1a



Identification code	**1a**
Solvent	CH_3CN
CCDC	1408685

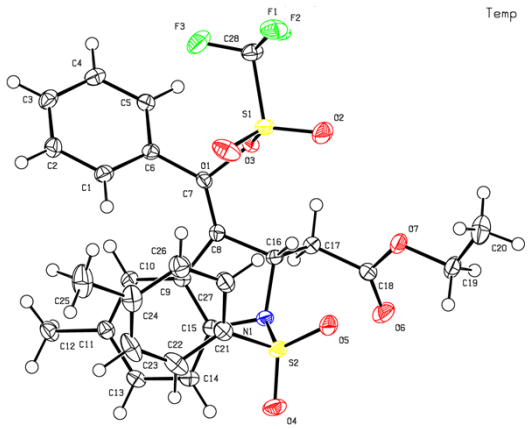
Bond precision: C-C = 0.0056 A Wavelength = 1.54187

Cell: A = 9.687(13) B = 10.731(8) C = 12.624(12)
Alpha = 99.142(9) Beta = 109.67(4) Gamma = 102.46(2)
Temperature: 100 K

	Calculated	Reported
Volume	1168(2)	1168(3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C27 H27 N O5 S	C27 H27 N O5 S
Sum formula	C27 H27 N O5 S	C27 H27 N O5 S
Mr	477.56	477.57
Dx,g cm-3	1.358	1.358
Z	2	2
Mu (mm-1)	1.560	1.561
F000	504.0	504.0
F000'	506.14	
h,k,lmax	11,12,14	11,12,14
Nref	3972	3835
Tmin,Tmax	0.768,0.732	0.489,0.732
Tmin'	0.697	

Correction method = # Reported T Limits: Tmin = 0.489 Tmax = 0.732
AbsCorr = NUMERICAL
Data completeness = 0.966 Theta (max) = 65.000
R (reflections) = 0.0524 (2759) wR2 (reflections) = 0.1549(3834)
S = 0.986 Npar= 307

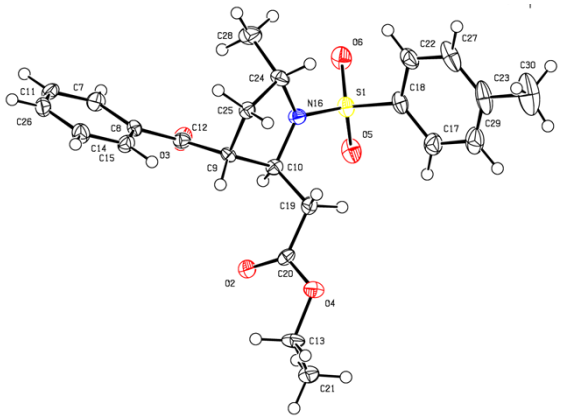
Crystal data and structure refinement for 5a



Identification code	**5a**		
Solvent	CH_3CN		
CCDC	1408686		
Bond precision:	C-C = 0.0027 A	Wavelength = 1.54190	
Cell:	A = 10.689 (5)	B = 16.049 (6)	C = 16.697 (7)
	Alpha = 90	Beta = 103.962 (9)	Gamma = 90
Temperature:	100 K		
	Calculated	Reported	
Volume	2780(2)	2780(2)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C28 H26 F3 N O7 S2	C28 H26 F3 N O7 S2	
Sum formula	C28 H26 F3 N O7 S2	C28 H26 F3 N O7 S2	
Mr	609.62	609.63	
Dx,g cm-3	1.457	1.457	
Z	4	4	
Mu (mm-1)	2.341	2.342	
F000	1264.0	1264.0	
F000'	1270.94		
h,k,lmax	12,19,20	12,19,20	
Nref	5125	4989	
Tmin,Tmax	0.508,0.656	0.461,0.656	
Tmin'	0.461		

Correction method = # Reported T Limits: Tmin = 0.461 Tmax = 0.656
AbsCorr = NUMERICAL
Data completeness = 0.973 Theta (max) = 68.510
R (reflections) = 0.0358 (4440) wR2 (reflections) = 0.1013(4989)
S = 1.078 Npar = 370

Crystal data and structure refinement for 1x

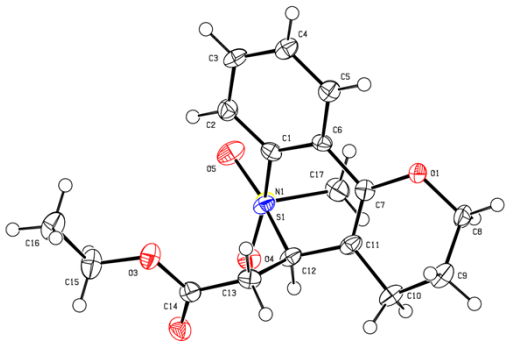


Identification code	**1x**
Solvent	CH_3CN
CCDC	1408687

Bond precision:	C-C = 0.0045 A	Wavelength=1.54190	
Cell:	A = 7.466(8)	B = 13.997(9)	C = 20.362(12)
	Alpha = 90	Beta = 90	Gamma = 90
Temperature:	100 K		
	Calculated	Reported	
Volume	2128(3)	2128(3)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C23 H27 N O5 S	C23 H27 N O5 S	
Sum formula	C23 H27 N O5 S	C23 H27 N O5 S	
Mr	429.52	429.53	
Dx,g cm-3	1.341	1.341	
Z	4	4	
Mu (mm-1)	1.644	1.646	
F000	912.0	912.0	
F000’	916.00		
h,k,lmax	8,16,24	8,16,24	
Nref	3881[2234]	3788	
Tmin,Tmax	0.604,0.936	0.713,0.936	
Tmin’	0.510		

Correction method = # Reported T Limits: Tmin = 0.713 Tmax = 0.936
AbsCorr = NUMERICAL
Data completeness = 1.70/0.98 Theta (max) = 68.180
R (reflections) = 0.0351(3359) wR2 (reflections) = 0.1143(3788)
S = 1.119 Npar = 271

Crystal data and structure refinement for 8c



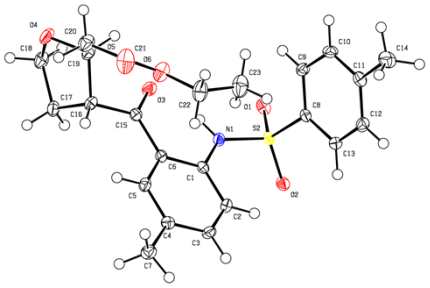
Identification code	**8c**
Solvent	CH_3CN and EtOH
CCDC	1408688

Bond precision:	C-C = 0.0061 A	Wavelength = 1.54190	
Cell:	A =13.648(5)	B = 8.763(3)	C = 14.280(6)
	Alpha = 90	Beta = 91.288(11)	Gamma = 90
Temperature:	100 K		
	Calculated	Reported	
Volume	1707.4(11)	1707.4(12)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C17 H21 N O5 S	C17 H21 N O5 S	
Sum formula	C17 H21 N O5 S	C17 H21 N O5 S	
Mr	351.41	351.42	
Dx,g cm-3	1.367	1.367	
Z	4	4	
Mu (mm-1)	1.922	1.923	
F000	744.0	744.0	
F000’	747.59		
h,k,lmax	16,10,17	16,10,17	
Nref	3148	3113	
Tmin,Tmax	0.741,0.908	0.715,0.908	
Tmin’	0.721		

Correction method= # Reported T Limits: Tmin = 0.715 Tmax=0.908
AbsCorr = NUMERICAL

Data completeness = 0.989	Theta (max) = 68.470
R(reflections)= 0.0578(2145)	wR2 (reflections) = 0.2492(3113)
S = 1.174 Npar = 217	

Crystal data and structure refinement for 9e

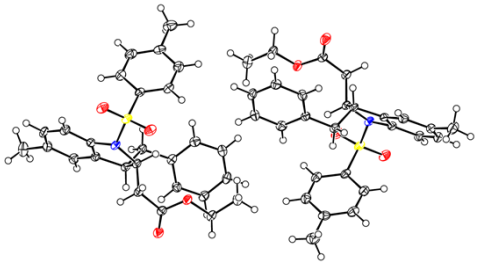


Identification code	**9e**
Solvent	CH_3CN
CCDC	1408689

Bond precision:	C-C = 0.0030 A		Wavelength = 0.71070
Cell:	A = 8.2174(11)	b=25.204(4)	C = 10.5671(16
	Alpha = 90	Beta = 95.161(3)	Gamma = 90
Temperature:	100 K		
	Calculated	Reported	
Volume	2179.7(6)	2179.7(6)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C23 H27 N O6 S	C23 H27 N O6 S	
Sum formula	C23 H27 N O6 S	C23 H27 N O6 S	
Mr	445.52	445.51	
Dx,g cm-3	1.358	1.358	
Z	4	4	
Mu (mm-1)	0.189	0.189	
F000	944.0	944.0	
F000’	944.97		
h,k,lmax	9,29,12	9,29,12	
Nref	3844	3827	
Tmin,Tmax	0.975,0.983	0.968,0.983	
Tmin’	0.972		

Correction method = # Reported T Limits: Tmin = 0.968 Tmax = 0.983
AbsCorr = NUMERICAL
Data completeness = 0.996 Theta (max)= 24.997
R(reflections) = 0.0476 (3531) wR2(reflections) = 0.1246(3827)
S = 1.039 Npar = 280

Crystal data and structure refinement for 18



Identification code	**18**
Solvent	CH_3CN
CCDC	1408690

Bond precision:	C-C = 0.0030 A	Wavelength = 0.71070	
Cell:	A = 8.050(2)	B =16.385(4)	C = 18.274(5)
	Alpha = 94.603(4)	Beta = 93.801(5)	Gamma = 94.487(4)
Temperature:	100 K		

	Calculated	Reported
Volume	2388.8(11)	2388.8(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C27 H29 N O4 S	C27 H29 N O4 S
Sum formula	C27 H29 N O4 S	C27 H29 N O4 S
Mr	463.57	463.59
Dx,g cm-3	1.289	1.289
Z	4	4
Mu (mm-1)	0.169	0.169
F000	984.0	984.0
F000’	984.92	
h,k,lmax	9,19,21	9,19,21
Nref	8424	8391
Tmin,Tmax	0.976,0.990	0.970,0.990
Tmin’	0.973	

Correction method = NUMERICAL	
Data completeness = 0.996	Theta (max) = 25.000
R(reflections) = 0.0475(6888)	wR2 (reflections) = 0.1255(8391)
S = 0.993 Npar = 595	