Electronic Supporting Information

Rhodium-Catalyzed Asymmetric Enyne Cycloisomerization of Terminal Alkynes and Formal Total Synthesis of (–)-Platensimycin

K. C. Nicolaou, Ang Li, Shelby P. Ellery, and David J. Edmonds*

Department of Chemistry and The Skaggs Institute for Chemical Biology, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, California 92037, and Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, California 92093

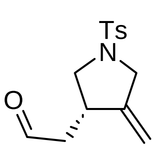
Email : kcn@scripps.edu

General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), methanol, triethylamine (Et_3N), and methylene chloride (CH_2Cl_2) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Dimethylsulfoxide (DMSO) and ethanol (EtOH) were purchased in anhydrous form and used without further purification. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on S-2 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and ethanolic *p*-anisaldehyde, aqueous ammonium cerium nitrate/ammonium molybdate, or basic aqueous potassium permanganate as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. Preparative thin layer chromatography separations were carried out on 0.25 or 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker AV-400, DRX-500 or DRX-600 instruments and calibrated using residual undeuterated chloroform (δ_H = 7.26 ppm) or $CDCl_3$ (δ_C = 77.0 ppm) as an internal reference. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quint = quintet, br = broad. IR spectra were recorded on a Perkin–Elmer Spectrum 100 FT-IR spectrometer. Melting points (m.p.) are uncorrected and were recorded on a Thomas Hoover Uni-Melt apparatus. High-resolution mass spectra (HRMS) were recorded on an Agilent ESITOF (time of flight) mass spectrometer at a 4000 V emitter voltage.

Preparation of catalyst [Rh((*S*)-BINAP)]SbF_6. The [Rh((*S*)-BINAP)]SbF_6 catalyst was freshly prepared according to the procedure reported by Wender et al.[1] and used within days. $[Rh(cod)Cl]_2$ (25.1 mg, 0.0509 mol) and $AgSbF_6$ (35.0 mg, 0.1019 mol) were weighed out in a flame-dried 25 mL round-bottom flask filled with argon. Acetone (2.5 mL) was added, and a white precipitate formed immediately. After stirring at 23 °C for 20 min, the yellow suspension was filtered under argon into a flask containing (*S*)-BINAP (63.4 mg, 0.1018 mol). The resulting acetone solution was stirred for 20 min and could be directly used for entries 5, 8 and 9 in Table 2. Acetone was then carefully removed under bubbling argon and finally under vacuum. The residue was dissolved in 1,2-dichloroethane (DCE, 2.5 mL) and the resulting solution was stirred at 23 °C for 5 min until homogeneous. The catalyst in both acetone and DCE kept at 4 °C for 5 days gave the same efficiency and optical activity in the cycloisomerization reaction as tested with substrates **1** and **6** (entries 1 and 6, Table 2).

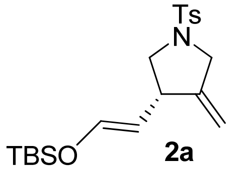
General procedure for Rh-catalyzed cycloisomerization. To a vial containing 0.08 mmol of the 1,6-enyne substrate under argon was added [Rh((*S*)-BINAP)]SbF_6 solution (0.20 mL, 0.04 M in DCE or acetone). The resulting mixture was stirred at 23 °C for 12–16 h. After removal of the solvent by a stream of argon, the residue was purified by flash column chromatography using EtOAc/hexanes (1:3–1:1) as eluent.

Measurement of enantiomeric excess (ee). Racemic and optically active aldehydes were prepared with [Rh((±)-BINAP)]SbF_6 and [Rh((*S*)-BINAP)]SbF_6 employing the general procedure described below, respectively. Cyclized products were reduced with $NaBH_4$ (**1a**, **2a**, **4a**, **7a**, **9a** and **10a**) or $LiBH_4$ (**5a** and **8a**) and ee's were measured after derivatization to the corresponding *p*-bromobenzoate esters[2] (Table 2, entries 1 and 2, by chiral HPLC, OD-H column) or to Mosher esters[2] (Table 2, entries 3–5 and 7–10, by ^1H and ^{19}F NMR spectroscopic analysis). Compounds **6a** and **11a** were converted to the corresponding ethylene glycol acetals ($TMSOCH_2CH_2OTMS$, TMSOTf) and the ee's were measured by chiral HPLC (OD-H column).

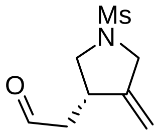

1a

1a: 19.2 mg, 86 %, >99 % ee (chiral HPLC analysis of the corresponding *p*-bromobenzoate ester,[2] OD-H column, see graph). $R_f = 0.17$ (silica, EtOAc:hexanes 3:7); $[\alpha]_D^{20} = -43.1$ ($c = 1.86$ in $CHCl_3$); IR (film): $\nu_{max} = 2841, 2729, 1721, 1667, 1597, 1494, 1402, 1343, 1304, 1160, 1094, 1044, 901, 816, 709, 663\ cm^{-1}$; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 9.75$ (s, 1 H), 7.70 (d, $J = 8.2$ Hz, 2 H), 7.34 (d, $J = 8.5$ Hz, 2 H), 4.97 (dd, $J = 3.9, 1.9$ Hz, 1 H), 4.89 (dd, $J = 4.4, 2.1$ Hz, 1 H), 3.87–3.77 (m, 2 H), 3.54 (dd, $J = 9.7, 7.4$ Hz, 1 H), 3.20–2.95 (m, 1 H), 2.91 (dd, $J = 9.7, 6.5$ Hz, 1 H), 2.70 (ddd, $J = 18.4, 4.9, 0.8$ Hz, 1 H), 2.54 (ddd, $J = 18.4, 8.7, 0.8$ Hz, 1 H), 2.44 (s, 3 H) ppm;

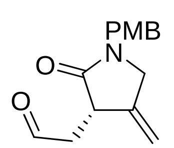
^{13}C NMR (151 MHz, CDCl$_3$): δ = 199.80, 146.70, 143.83, 132.40, 129.74, 127.83, 107.63, 53.25, 51.77, 46.74, 36.72, 21.55 ppm; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{14}H_{18}NO_3S^+$ 280.1002, found 280.1001.


2a

2a: 28.3 mg, 90 %, 97 % ee (chiral HPLC analysis of the corresponding *p*-bromobenzoate ester,[2] OD-H column, see graph). R$_f$ = 0.58 (silica, EtOAc:hexanes 3:7); $[\alpha]_D^{20}$ = –28.2 (*c* = 0.57 in CHCl$_3$); IR (film): ν_{max} = 2930, 2858, 1661, 1598, 1472, 1349, 1305, 1254, 1162, 1095, 1052, 929, 839, 814, 783, 708, 663 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.70 (d, *J* = 8.2 Hz, 2 H), 7.33 (d, *J* = 7.9 Hz , 2 H), 6.28 (d, *J* = 12.0 Hz, 1 H), 4.93 (dd, *J* = 4.4, 2.1 Hz, 1 H), 4.86 (dd, *J* = 4.9, 2.4 Hz, 1 H), 4.63 (dd, *J* = 11.9, 9.3 Hz, 1 H), 4.04 (dt, *J* = 14.2, 2.9 Hz, 1 H), 3.67–3.59 (m, 2 H), 3.17–3.09 (m, 1 H), 2.66 (t, *J* = 9.7 Hz, 1 H), 2.44 (s, 3 H), 0.90 (s, 9 H), 0.13 (s, 6 H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$): δ =147.87, 143.62, 143.54, 132.71, 129.67, 127.79, 108.28, 107.74, 54.03, 51.78, 42.52, 25.60, 21.54, 18.33, –5.30, –5.31 ppm; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{20}H_{32}NO_3SSi^+$ 394.1867, found 394.1868.


4a

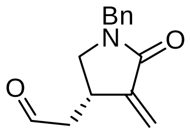
4a: 13.8 mg, 85 %, > 98 % ee (Mosher ester[2] analysis, see ^{1}H NMR spectrum). R$_f$ = 0.26 (silica, EtOAc:hexanes 1:1); $[\alpha]_D^{20}$ = –28.9 (*c* = 0.45 in CHCl$_3$); IR (film): ν_{max} = 2933, 1718, 1386, 1325, 1264, 1217, 1148, 1108, 1048, 961, 897, 822, 789, 749, 701, 659 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.83–9.81 (m, 1 H), 5.09 (dd, *J* = 4.2, 2.0 Hz, 1 H), 5.00 (dd, *J* = 4.4, 2.1 Hz, 1 H), 4.00 (dd, *J* = 3.6, 2.1 Hz, 2 H), 3.74 (dd, *J* = 9.8, 7.5 Hz, 1 H), 3.31–3.22 (m, 1 H), 3.06 (dd, *J* = 9.8, 7.0 Hz, 1 H), 2.86 (s, 3 H), 2.86–2.80 (m, 1 H), 2.67 (ddd, *J* = 18.5, 8.4, 0.9 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ = 199.73, 146.79, 108.05, 53.24, 51.86, 46.59, 37.30, 35.22 ppm; HRMS (*m/z*): [M + Na]$^+$ calcd for $C_8H_{13}NNaO_3S^+$ 226.0508, found 226.0501.


5a

5a: 15.6 mg, 75 %, 98 % ee (Mosher ester[2] analysis, see ^{19}F NMR spectrum). R$_f$ = 0.40 (silica, EtOAc:hexanes 3:2); $[\alpha]_D^{20}$ = –29.0 (*c* = 0.10 in CHCl$_3$); IR (film): ν_{max} = 3275, 2923, 2850, 1721, 1692, 1662, 1610, 1513, 1458, 1442, 1246, 1176, 1110, 1092, 1032, 800 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 9.81 (s, 1 H), 7.19 (d, *J* = 8.5 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 5.03–5.01 (m, 1 H), 4.98–4.95 (m, 1 H), 4.47 (dd, *J* = 34.5, 14.6 Hz, 2 H), 3.93–3.82

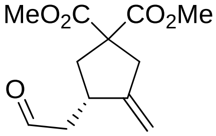
(m, 2 H), 3.80 (s, 3 H), 3.55–3.47 (m, 1 H), 3.10–3.03 (m, 1 H), 2.93 (dd, *J* = 18.4, 6.5 Hz, 1 H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$): δ = 199.50, 173.39, 159.19, 141.18, 129.58, 127.89, 114.12, 108.95, 55.30, 51.09, 45.93, 44.53, 41.11 ppm; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{15}H_{18}NO_3^+$ 260.1281, found 260.1269.

6a: 16.3 mg, 89 %, 93 % ee (chiral HPLC analysis of the corresponding ethylene glycol acetal, OD-H column, see graph). R$_f$ = 0.38 (silica, EtOAc:hexanes 3:2); $[\alpha]_D^{20}$ = –68.9 (*c* = 0.35 in CHCl$_3$); IR (film): ν_{max} = 2923, 2853, 1720, 1685, 1656, 1494, 1440, 1358, 1314, 1198, 1080, 1030, 930, 808, 748, 701 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 9.78 (s, 1 H), 7.35–7.27 (m, 3 H), 7.26–7.22 (m, 2 H), 6.11 (d, *J* = 2.8 Hz, 1 H), 5.34 (d, *J* = 2.4 Hz, 1 H), 4.54 (s, 2 H), 3.60 (dd, *J* = 10.3, 8.3 Hz, 1 H), 3.39–3.33 (m, 1 H), 2.91–2.82 (m, 2 H), 2.63 (dd, *J* = 18.7, 9.3 Hz, 1 H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$): δ = 199.73, 167.00, 142.95, 135.93, 128.77, 128.30, 127.77, 116.25, 50.11, 49.00, 47.09, 29.84 ppm; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{14}H_{16}NO_2^+$ 230.1175, found 230.1174.



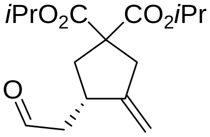
6a

7a: 15.0 mg, 78 %, 97 % ee (Mosher ester[2] analysis, see ^{19}F NMR spectrum). R$_f$ = 0.34 (silica, EtOAc:hexanes 3:7); $[\alpha]_D^{20}$ = –45.6 (*c* = 0.75 in CHCl$_3$); IR (film): ν_{max} = 2992, 2956, 2840, 2724, 1730, 1658, 1435, 1255, 1199, 1162, 1071, 1031, 890 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 9.80 (s, 1 H), 5.01–4.98 (m, 1 H), 4.82–4.78 (m, 1 H), 3.74 (s, 3 H), 3.72 (s, 3 H), 3.14–2.92 (m, 3 H), 2.72 (ddd, *J* = 21.2, 15.6, 6.7 Hz, 2 H), 2.52 (dd, *J* = 17.3, 8.0 Hz, 1 H), 1.88 (dd, *J* = 13.1, 10.4 Hz, 1 H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$): δ = 201.09, 171.94, 171.89, 150.40, 107.09, 58.30, 52.92, 52.86, 47.95, 40.58, 39.83, 36.44 ppm; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{12}H_{17}O_5^+$ 241.1070, found 241.1068.



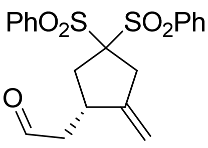
7a

8a: 19.9 mg, 84 %, > 98 % ee (Mosher ester[2] analysis, see ^{1}H NMR spectrum). R$_f$ = 0.43 (silica, EtOAc:hexanes 3:7); $[\alpha]_D^{20}$ = –49.5 (*c* = 0.96 in CHCl$_3$); IR (film): ν_{max} = 2982, 2931, 1725, 1467, 1375, 1257, 1191, 1106, 893, 827 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 9.80 (s, 1 H), 5.08–4.99 (m, 2 H), 4.98–4.96 (m, 1 H), 4.80–4.77 (m, 1 H), 3.08–



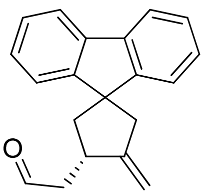
8a

3.04 (m, 1 H), 3.04–2.99 (m, 1 H), 2.91 (ddd, *J* = 16.9, 4.3, 2.1 Hz, 1 H), 2.73 (ddd, *J* = 17.4, 5.2, 1.6 Hz, 1 H), 2.63 (ddd, *J* = 12.9, 8.0, 0.7 Hz, 1 H), 2.52 (ddd, *J* = 17.4, 8.3, 1.8 Hz, 1H), 1.84 (dd, *J* = 13.1, 10.1 Hz, 1 H), 1.25–1.20 (m, 12 H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$): δ = 201.27, 171.01, 170.99, 150.82, 106.76, 69.01, 68.98, 58.41, 47.96, 40.39, 39.61, 36.49, 21.50 ppm; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{16}H_{25}O_5^+$ 297.1696, found 297.1695.



9a

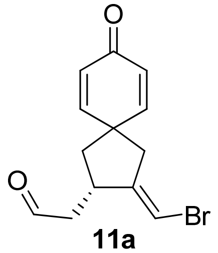
9a: 29.8 mg, 92 %, 87 % ee (Mosher ester[2] analysis, see ^{19}F NMR spectrum). R$_f$ = 0.54 (silica, EtOAc:hexanes 1:1); $[\alpha]_D^{20}$ = –29.1 (*c* = 0.95 in CHCl$_3$); IR (film): ν_{max} = 3066, 1719, 1663, 1583, 1478, 1447, 1426, 1326, 1308, 1215, 1141, 1075, 1024, 998, 895, 750, 730, 718, 685, 666 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 9.78 (s, 1 H), 8.13–7.98 (m, 4 H), 7.75–7.71 (m, 2 H), 7.64–7.58 (m, 4 H), 4.93–4.89 (d, *J* = 2.1 Hz, 1 H), 4.77–4.73 (m, 1 H), 3.29 (s, 2 H), 3.24–3.14 (m, 1 H), 2.94 (dd, *J* = 15.1, 8.6 Hz, 1 H), 2.80 (dd, *J* = 18.1, 4.7 Hz, 1 H), 2.57 (dd, *J* = 18.1, 8.7 Hz, 1 H), 2.31 (dd, *J* = 15.1, 10.0 Hz, 1 H) ppm; ^{13}C NMR (151 MHz, CDCl$_3$): δ = 200.13, 148.07, 136.40, 135.81, 134.79, 134.70, 131.27, 131.15, 128.84, 128.77, 107.53, 91.14, 47.48, 38.13, 37.18, 36.85 ppm; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{20}H_{21}O_5S_2^+$ 405.0825, found 405.0818.



10a

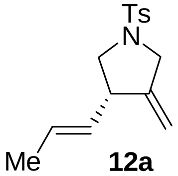
10a: 18.7 mg, 85 %, > 98 % ee (Mosher ester[2] analysis, see ^{19}F NMR spectrum). R$_f$ = 0.64 (silica, EtOAc:hexanes 1:3); $[\alpha]_D^{20}$ = –21.7 (*c* = 0.86 in CHCl$_3$); IR (film): ν_{max} = 3065, 2916, 2721, 1721, 1654, 1476, 1447, 1308, 1219, 1155, 1101, 1031, 1008, 935, 885, 759, 732, 666 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.88 (t, *J* = 1.7 Hz, 1 H), 7.75–7.68 (m, 2 H), 7.50 (d, *J* = 7.5 Hz, 1 H), 7.45–7.41 (m, 1 H), 7.39–7.25 (m, 4 H), 5.16 (dd, *J* = 4.1, 2.2 Hz, 1 H), 5.08 (dd, *J* = 4.3, 2.3 Hz, 1 H), 3.65–3.55 (m, 1 H), 3.07 (ddd, *J* = 16.2, 4.9, 2.4 Hz, 1 H), 2.98 (ddd, *J* = 17.2, 5.1, 1.7 Hz, 1 H), 2.79–2.73 (m, 1 H), 2.73–2.64 (m, 1 H), 2.27 (ddd, *J* = 13.0, 8.2, 1.4 Hz, 1 H), 2.08 (dd, *J* = 13.0, 10.7 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, CDCl$_3$): δ = 201.55, 154.33, 152.81, 150.99, 140.02, 139.42, 127.62, 127.58, 127.38, 127.31, 123.22, 122.66, 119.92, 119.86, 107.52, 55.61, 49.55, 45.86, 45.18, 37.87 ppm; GC/MS (*m/z*): [M]$^+$ calcd for $C_{20}H_{18}O^+$ 274, found 274.

11a: 20.7 mg, 92 %, > 99 % ee (chiral HPLC analysis of the corresponding ethylene glycol acetal, OD-H column, see graph). R_f = 0.09 (silica, EtOAc:hexanes 3:7); $[\alpha]_D^{20}$ = –95.0 (*c* = 0.28 in $CHCl_3$); IR (film): ν_{max} = 3073, 2916, 2850, 2724, 1720, 1662, 1623, 1407, 1256, 1183, 1016, 860 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 9.82 (s, 1 H), 6.96 (dd, *J* = 10.1, 3.0 Hz, 1 H), 6.78 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.33–6.23 (m, 2 H), 6.11 (dd, *J* = 5.0, 2.4 Hz, 1 H), 3.39–3.32 (m, 1 H), 2.90 (dd, *J* = 18.3, 5.3 Hz, 1 H), 2.70 (dd, *J* = 17.9, 7.0 Hz, 1 H), 2.67–2.59 (m, 2 H), 2.21 (ddd, *J* = 12.8, 7.4, 1.5 Hz, 1 H), 1.80 (dd, *J* = 12.7, 11.4 Hz, 1 H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 199.64, 185.64, 153.59, 151.14, 148.14, 129.31, 127.88, 101.25, 48.61, 46.17, 44.58, 44.13, 37.02 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{13}H_{14}BrO_2^+$ 280.0172, found 280.0172.



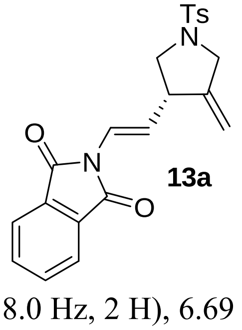
11a

12a: 22.2 mg, 93 %, > 98 % ee (Mosher ester[2] analysis, see ^1H NMR spectrum). R_f = 0.36 (silica, EtOAc:hexanes 1:4); $[\alpha]_D^{20}$ = –31.1 (*c* = 1.13 in $CHCl_3$); IR (film): ν_{max} = 2920, 2855, 1665, 1597, 1494, 1450, 1380, 1345, 1306, 1290, 1215, 1159, 1093, 1049, 1017, 997, 965, 896, 813, 708, 661 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.3 Hz, 2 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 5.52 (dqd, *J* = 15.1, 6.5, 0.7 Hz, 1 H), 5.10 (dddd, *J* = 15.2, 8.2, 3.2, 1.6 Hz, 1 H), 4.95–4.92 (m, 1 H), 4.85–4.82 (m, 1 H), 3.99 (ddd, *J* = 14.1, 3.4, 2.2 Hz, 1H), 3.69 (ddd, *J* = 14.1, 4.1, 2.0 Hz, 1H), 3.59 (dd, *J* = 9.4, 7.9 Hz, 1H), 3.22–3.14 (m, 1 H), 2.79 (t, *J* = 9.3 Hz, 1H), 2.44 (s, 3H), 1.65 (dd, *J* = 6.5, 1.6 Hz, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.39, 143.62, 132.76, 129.67, 129.16, 128.24, 127.81, 107.80, 53.52, 51.86, 46.76, 21.55, 17.88 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{15}H_{20}NO_2S^+$ 278.1209, found 278.1207.



12a

13a: 27.0 mg, 83 %, 94 % ee (chiral HPLC analysis of the corresponding *p*-bromobenzoate ester,[2] OD-H column, see graph). R_f = 0.50 (silica, EtOAc:hexanes 1:1); $[\alpha]_D^{20}$ = –65.9 (*c* = 0.39 in $CHCl_3$); IR (film): ν_{max} = 2923, 2850, 1781, 1719, 1663, 1597, 1468, 1383, 1346, 1306, 1162, 1094, 1048, 957, 884, 816, 716, 663 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.89–7.84 (m, 2 H), 7.77–7.74 (m, 2 H), 7.72 (d, *J* = 8.2 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 6.69 (d, *J* = 14.6 Hz, 1 H), 6.32 (dd, *J* = 14.7, 9.0 Hz, 1 H), 5.04–5.01 (m, 1 H), 4.94–4.91



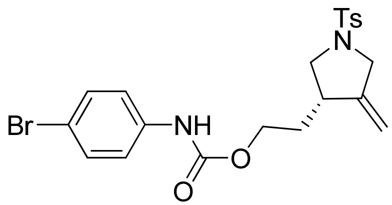
13a

(m, 1 H), 4.11–4.05 (m, 1 H), 3.76–3.70 (m, 2 H), 3.35–3.28 (m, 1 H), 2.88 (t, *J* = 9.5 Hz, 1 H), 2.44 (s, 3 H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.30, 146.47, 143.83, 134.58, 132.52, 131.48, 129.79, 127.83, 123.68, 120.41, 118.15, 108.94, 53.63, 51.88, 45.69, 21.55 ppm; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{22}H_{20}N_2NaO_4S^+$ 431.1036, found 431.1034.

Conversion of diene 12a to the corresponding Mosher ester. To a stirred solution of diene **l2a** (5.5 mg, 0.02 mmol) and NMO (2.8 mg, 0.024 mmol) in acetone/water (4:1, 0.5 mL) was added $K_2OsO_4 \cdot 2H_2O$ (1.5 mg, 0.004 mmol) at 23 °C. The resulting mixture was stirred at that temperature for 4 h before it was quenched with saturated aq. $Na_2S_2O_4$ solution (2 mL). The mixture was extracted with EtOAc (5 × 2 mL), and the combined organic phase was dried over $MgSO_4$. After filtration and evaporation of the solvent, the residue was dissolved in EtOH/water (1:1, 0.5 mL). To the resulting solution was added $NaIO_4$ (12.8 mg, 0.06 mmol) in one portion at 0 °C. The reaction mixture was stirred at that temperature for 5 min before $NaBH_4$ (2.3 mg, 0.06 mmol) was added. The resulting mixture was stirred at 0 °C for 15 min before it was quenched with saturated aq. NH_4Cl solution (2 mL). After extraction with EtOAc (5 × 2 mL), the combined organic phase was dried over $MgSO_4$ and filtered. The solvent was evaporated and the resulting crude alcohol was subjected to Mosher ester formation according to the general procedure.[2]

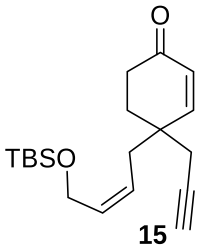
Conversion of imide 13a to the corresponding *p*-bromobenzoate ester. To a vial containing imide **l3a** (8.2 mg, 0.02 mmol) in THF (0.3 mL) was added aq. HCl solution (3.0 M, 0.3 mL). The vial was sealed and heated at 85 °C for 5 h before the reaction was quenched with saturated aq. $NaHCO_3$ solution (2 mL). The resulting mixture was extracted with EtOAc (5 × 2 mL), and the combined organic phase was dried over $MgSO_4$. After filtration and evaporation of the solvent, the residue was dissolved in EtOH (0.5 mL). To the resulting solution was added $NaBH_4$ (1.1 mg, 0.03 mmol) at 0 °C and the mixture was stirred at that temperature for 15 min before it was quenched with saturated aq. $NaHCO_3$ solution (1 mL). The resulting mixture was extracted with EtOAc (5 × 2 mL), and the combined organic phase was dried over $MgSO_4$. After filtration and evaporation of the solvent, the resulting crude alcohol was subjected to *p*-bromobenzoate ester formation according to the general procedure.[2]

***p*-Bromophenyl carbamate 1b:** To a stirred solution of aldehyde **1a** (10.0 mg, 0.0358 mmol) in ethanol (0.30 mL) at 0 °C was added $NaBH_4$ (2.0 mg, 0.0537 mmol). The resulting mixture was stirred at 0 °C for 15 min before saturated aq. $NaHCO_3$ solution (1 mL) was slowly added. The mixture was diluted with brine (1 mL) and extracted with EtOAc (5 × 2 mL). The combined organic phase was dried over $MgSO_4$ and filtered. After removal of the solvent under vacuum, the residue was purified by column chromatography with EtOAc/hexanes (2:1), giving the corresponding alcohol as a colorless oil. To a stirred solution of this alcohol in CH_2Cl_2 (0.20 mL) at 0 °C was sequentially added Et_3N (3.5 mg, 0.0346 mmol) and *p*-bromophenyl isocyanate (6.8 mg, 0.0343 mmol), and the resulting mixture was stirred for 1 h at 0 °C before it was quenched with saturated aq. $NaHCO_3$ solution (1.0 mL). The resulting mixture was extracted with EtOAc (5 × 2 mL), and the combined organic phase was dried over $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography with EtOAc/hexanes (1:3), giving carbamate **1b** as a white amorphous solid (12.4 mg, 72 % overall). **1b**: $R_f = 0.23$ (silica, EtOAc:hexanes 3:7); $[\alpha]_D^{20} = -30.2$ ($c = 0.42$ in $CHCl_3$); IR (film): ν_{max} = 3340, 2956, 2924, 2850, 1731, 1594, 1532, 1491, 1400, 1342, 1307, 1219, 1160, 1094, 1075, 1008, 898, 817, 768, 708, 664 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.1 Hz, 2 H), 7.42 (d, J = 8.8 Hz, 2 H), 7.34–7.28 (d, J = 8.2 Hz, 4 H), 6.82–6.69 (br, 1 H), 4.98 (d, J = 1.9 Hz, 1 H), 4.92 (d, J = 2.1 Hz, 1 H), 4.22–4.14 (m, 2 H), 3.88–3.76 (m, 2 H), 3.45 (dd, J = 9.4, 7.3 Hz, 1 H), 3.03 (dd, J = 9.2, 6.3 Hz, 1 H), 2.78–2.69 (m, 1 H), 2.42 (s, 3 H), 1.93 (dt, J = 20.9, 6.2 Hz, 1 H), 1.67 (ddt, J = 14.7, 8.6, 6.1 Hz, 2 H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$): δ = 153.09, 146.99, 143.79, 136.90, 132.55, 132.01, 129.73, 127.77, 120.15, 116.00, 107.56, 63.14, 53.22, 51.83, 40.15, 31.45, 21.55 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{21}H_{24}BrN_2O_4S$ 479.0635, found 479.0630.



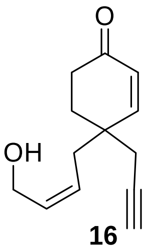
1b

Enone 15: To a stirred solution of β-ethoxy enone **14** (3.80 g, 10.48 mmol) in THF (30 mL) was added DIBAL-H (12.0 mL, 1.0 M in hexanes) at −78 °C. The resulting solution was warmed up to −20 °C over a period of 30 min before aq. HCl solution (2.0 M, 30 mL) was slowly added. The mixture was stirred at 0 °C for 30 min and then quickly extracted with EtOAc (3 × 50 mL). The combined organic phase was washed with saturated aq. $NaHCO_3$ solution (2 × 20 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography with EtOAc/hexanes (1:8–1:4), giving enone **15** as a pale yellow oil (2.94 g, 88 %). **15**: $R_f = 0.41$ (silica, EtOAc:hexanes 3:7); IR (film): $\nu_{max} = 3310$, 2953, 2929, 2856, 1680, 1471, 1463, 1388, 1361, 1252, 1168, 1081, 1005, 938, 834, 774, 663 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): $\delta = 6.80$ (d, $J = 10.2$ Hz, 1 H), 6.01 (d, $J = 10.2$ Hz, 1 H), 5.79–5.72 (m, 1 H), 5.49–5.42 (m, 1 H), 4.26 (dd, $J = 6.2$, 1.0 Hz, 2 H), 2.49–2.45 (m, 2H), 2.44–2.30 (m, 4H), 2.09 (t, $J = 2.6$ Hz, 1 H), 2.06–1.96 (m, 2 H), 0.92 (s, 9 H), 0.09 (s, 6 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 198.68$, 155.34, 133.85, 129.13, 124.32, 80.07, 71.50, 59.23, 38.72, 35.08, 33.85, 31.12, 27.72, 25.90, 18.31, –5.17 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{19}H_{31}O_2Si^+$ 319.2088, found 319.2086.



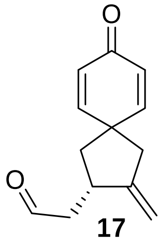
15

Bis-enone alcohol 16: To a stirred solution of enone **15** (2.94 g, 9.23 mmol) and Et_3N (1.40 g, 13.85 mmol) in CH_2Cl_2 (20 mL) was slowly added TMSOTf (2.27 g, 10.2 mmol) at 0 °C. After stirring for 30 min at that temperature, the reaction mixture was quenched with saturated aq. $NaHCO_3$ solution (100 mL). The resulting mixture was extracted with ether (3 × 100 mL) and the combined organic phase was washed with brine (50 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, a solution of IBX (3.07 g, 11.0 mmol) and MPO (1.38 g, 11.0 mmol) in DMSO (18 mL) was slowly added to the residue, and the mixture was stirred for 1 h at 23 °C before it was quenched with saturated aq. $NaHCO_3$ solution (100 mL). The resulting mixture was extracted with EtOAc (3 × 100 mL). The combined organic phase was dried over $MgSO_4$ and filtered. After removal of the solvent under vacuum, the residue was purified by flash column chromatography with EtOAc/hexanes (1:6–1:3), giving the TBS bis-enone as a pale yellow oil. This compound was dissolved in THF (20 mL), and to this solution was added aq. HCl solution (1.0 M, 20 mL) at 0 °C. The resulting mixture was vigorously stirred at 0 °C for 1 h before it was quenched with saturated aq. $NaHCO_3$ solution (30 mL). After extraction with EtOAc (3 × 50 mL), the combined organic phase was dried over $MgSO_4$, filtered, and evaporated under vacuum. The residue was purified



16

by flash column chromatography with EtOAc/hexanes (1:1), giving enone alcohol **16** as a colorless oil (1.27 g, 68 % over three steps). **16**: R_f = 0.11 (silica, EtOAc:hexanes 1:1); IR (film): ν_{max} = 3417, 3920, 3019, 2908, 2860, 1658, 1619, 1429, 1405, 1262, 1176, 1102, 1013, 858, 769, 728, 708 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.87–6.79 (m, 2 H), 6.34–6.27 (m, 2 H), 5.73–5.65 (m, 1 H), 5.32–5.24 (m, 1 H), 4.18–4.10 (m, 2 H), 2.54–2.49 (m, 2 H), 2.43 (d, *J* = 2.7 Hz, 2 H), 2.12 (t, *J* = 2.7 Hz, 1 H), 2.11 (br, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 185.75, 152.23, 132.68, 130.16, 124.94, 78.50, 72.37, 58.13, 43.96, 35.07, 28.20 ppm; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{13}H_{14}NaO_2^+$ 225.0886, found 225.0893.



17

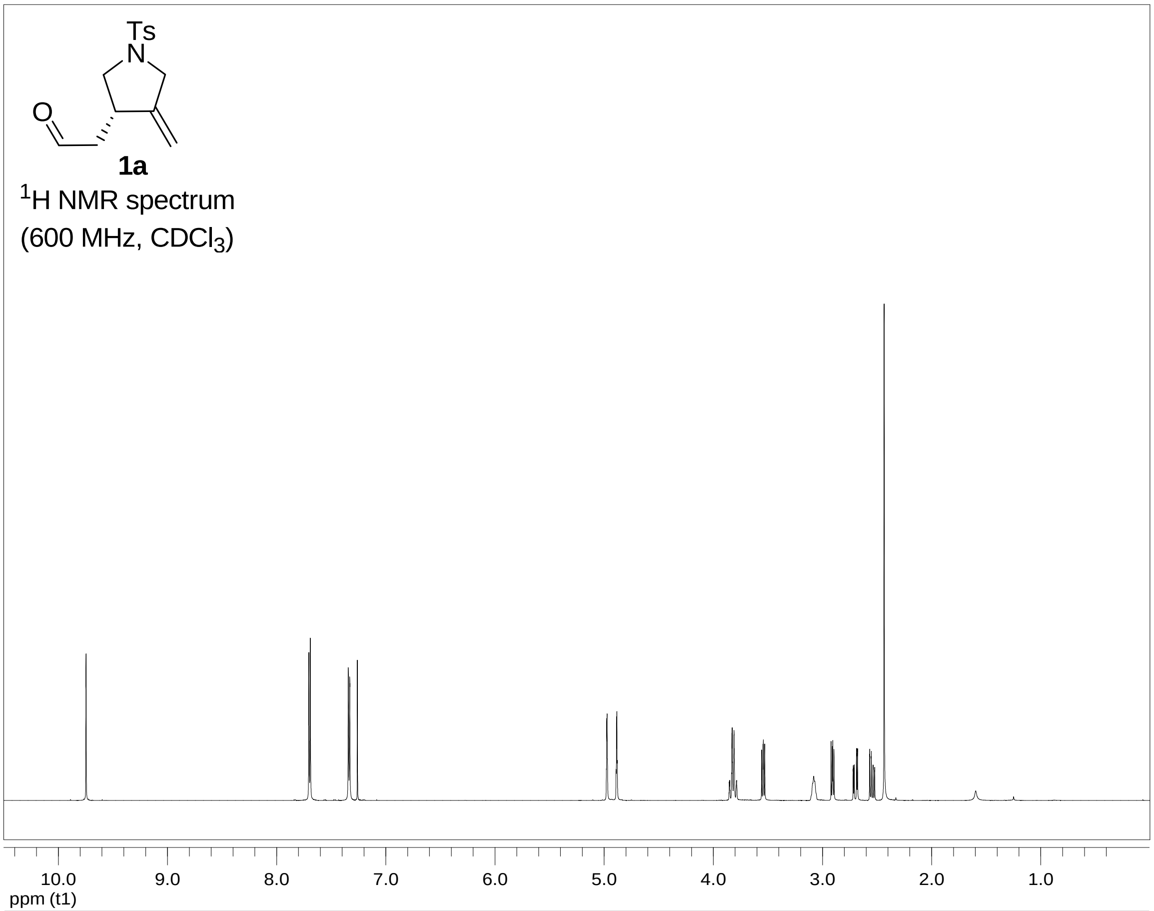
Bis-enone aldehyde 17: To a flame-dried flask containing enyne **16** (1.27 g, 6.28 mmol) under argon was quickly added [Rh((*S*)-BINAP)]SbF_6 solution prepared freshly as described above (7.85 mL, 0.04 M in DCE). The resulting solution was stirred under argon at 23 °C for 12 h before the solvent was removed under vacuum. The residue was purified by flash column chromatography with EtOAc/hexanes (1:2), giving bis-enone aldehyde **17** as a pale yellow oil (1.09 g, 86 %, > 99 % ee, chiral HPLC analysis of the corresponding ethylene glycol acetal, OD-H column, see graph). **17**: R_f = 0.31 (silica, EtOAc/hexane 1:1); $[\alpha]_D^{20}$ = –68.4 (*c* = 0.75 in $CHCl_3$); IR (film): ν_{max} = 2831, 2725, 1718, 1657, 1621, 1406, 1284, 1259, 1180, 1090, 1059, 1023, 888, 858, 706 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 9.83 (t, *J* = 1.3 Hz, 1 H), 6.98–6.95 (m, 1 H), 6.79–6.76 (m, 1 H), 6.27–6.23 (m, 2 H), 5.11–5.09 (m, 1 H), 4.99–4.97 (m, 1 H), 3.31–3.23 (m, 1 H), 2.85 (ddd, *J* = 17.9, 4.9, 1.2 Hz, 1 H), 2.68 (dq, *J* = 16.0, 2.4 Hz, 1 H), 2.64 (ddd, *J* = 17.8, 8.3, 1.4 Hz, 1 H), 2.47 (dd, *J* = 16.0, 1.6 Hz, 1 H), 2.15 (ddd, *J* = 13.0, 8.0, 1.6 Hz, 1 H), 1.69 (dd, *J* = 13.0, 10.3 Hz, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.5, 185.8, 154.2, 152.1, 151.2, 128.7, 127.7, 108.5, 49.2, 46.8, 44.4, 43.7, 36.2 ppm; HRMS (*m/z*): [M + H]$^+$ calcd for $C_{13}H_{15}O_2$ [M + H]$^+$: 203.1067; found 203.1067.

References

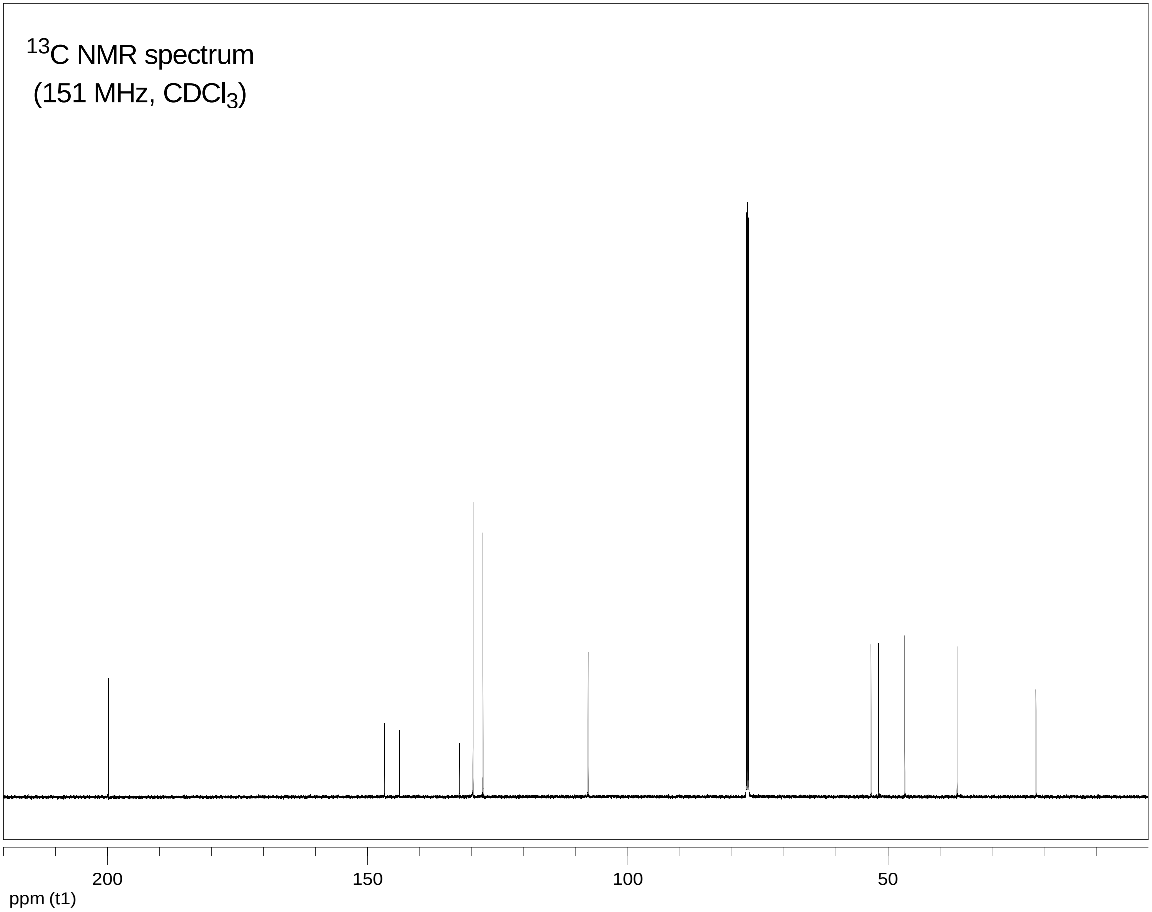
[1] P. A. Wender, L. J. Haustedt, J. A. Love, T. J. Williams, J. Y. Yoon, *J. Am. Chem. Soc.* **2006**, *128*, 6302–6303.

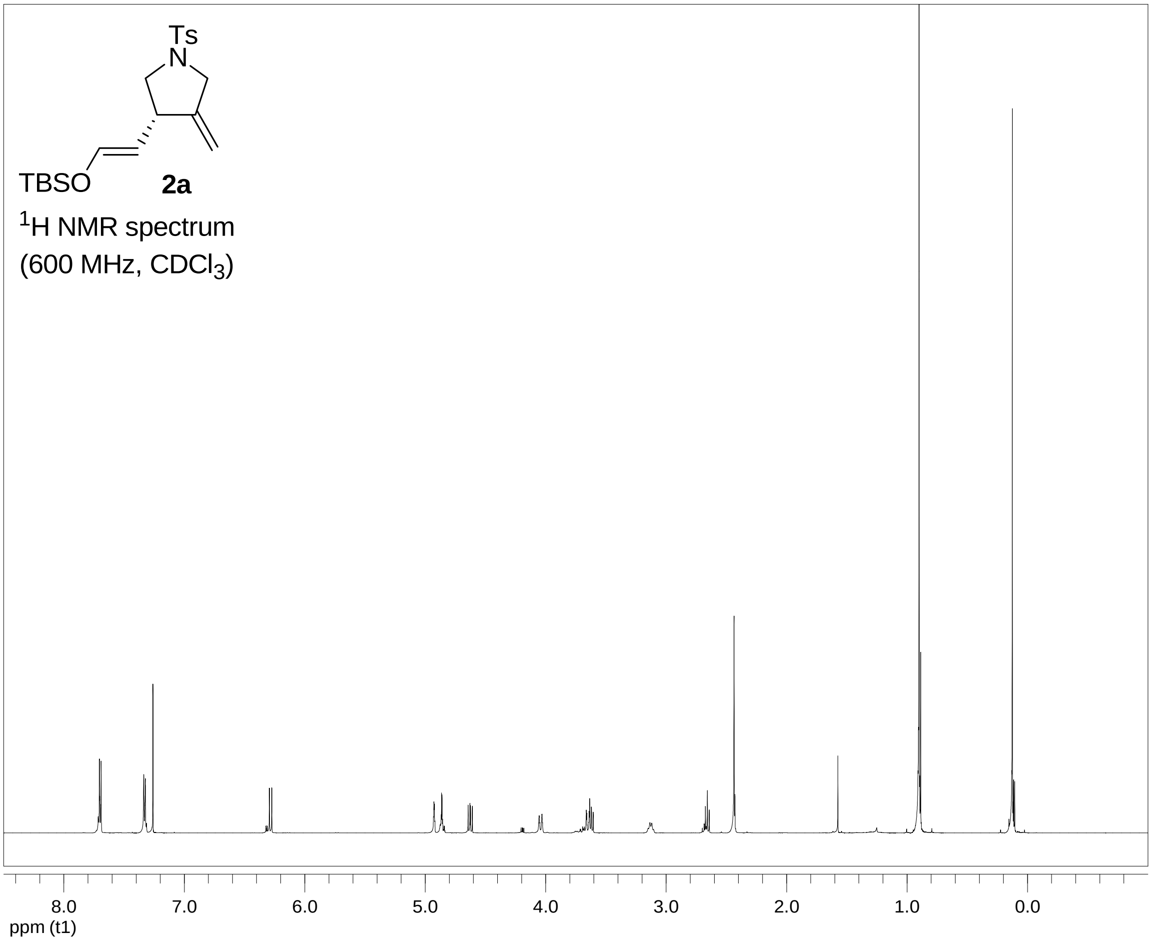
[2] General procedure for the preparation of Mosher esters: To a stirred solution of the alcohol (0.02 mmol) derived from the corresponding aldehyde in CH_2Cl_2 (0.20 mL) at 0 °C was sequentially added DMAP (0.2 mg, 0.002 mmol), Et_3N (4.0 mg, 0.04 mmol) and Mosher acid chloride (7.6 mg, 0.03 mmol). After stirring at 0 °C for 30 min, the reaction mixture was directly purified by flash column chromatography with EtOAc/hexanes (1:6–1:3). Longer reaction times (i. e. 1 h) had no effect on the *de* value of the resulting Mosher ester, confirming that there was no kinetic resolution of the 30 min period. *p*-Bromobenzoate esters were also prepared in this procedure using *p*-bromobenzoyl chloride as acylating reagent.

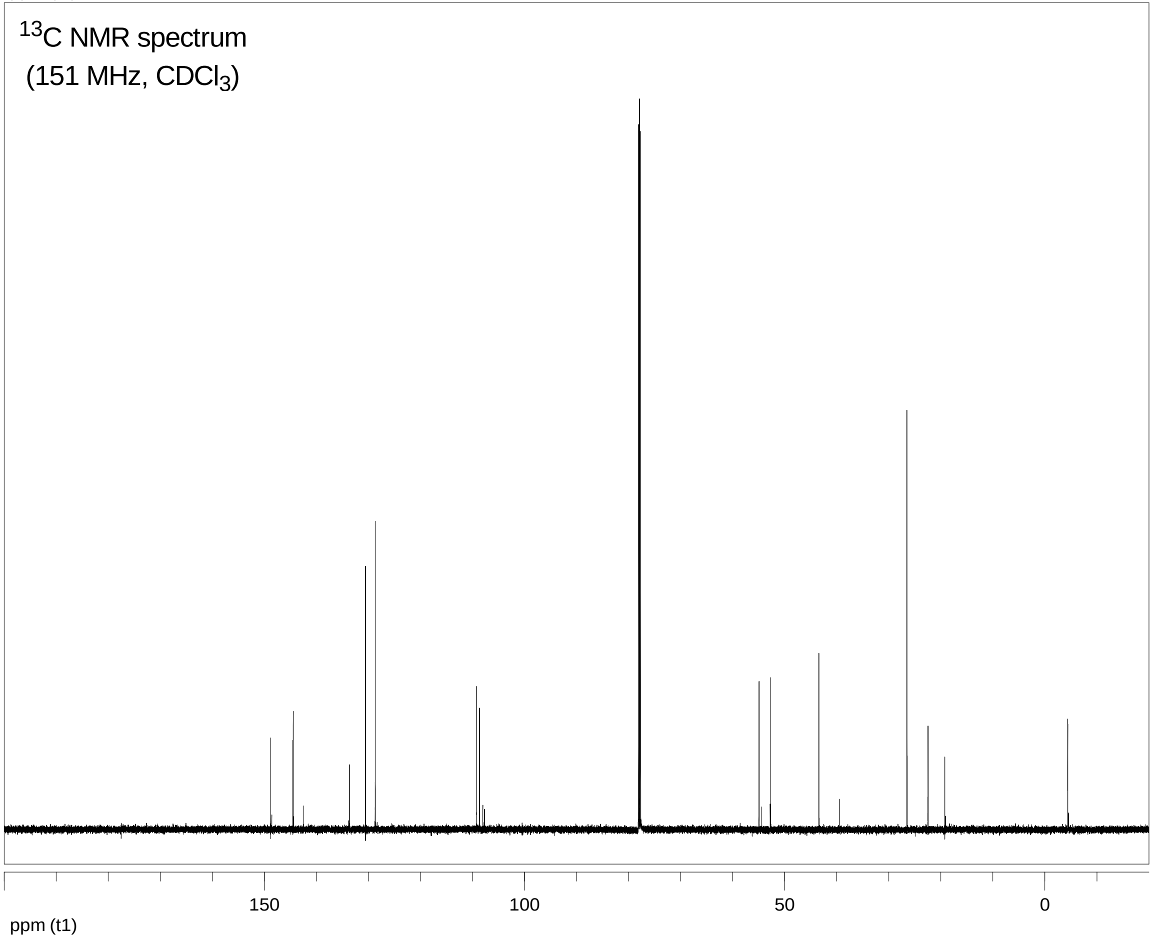
^{1}H and ^{13}C NMR spectra

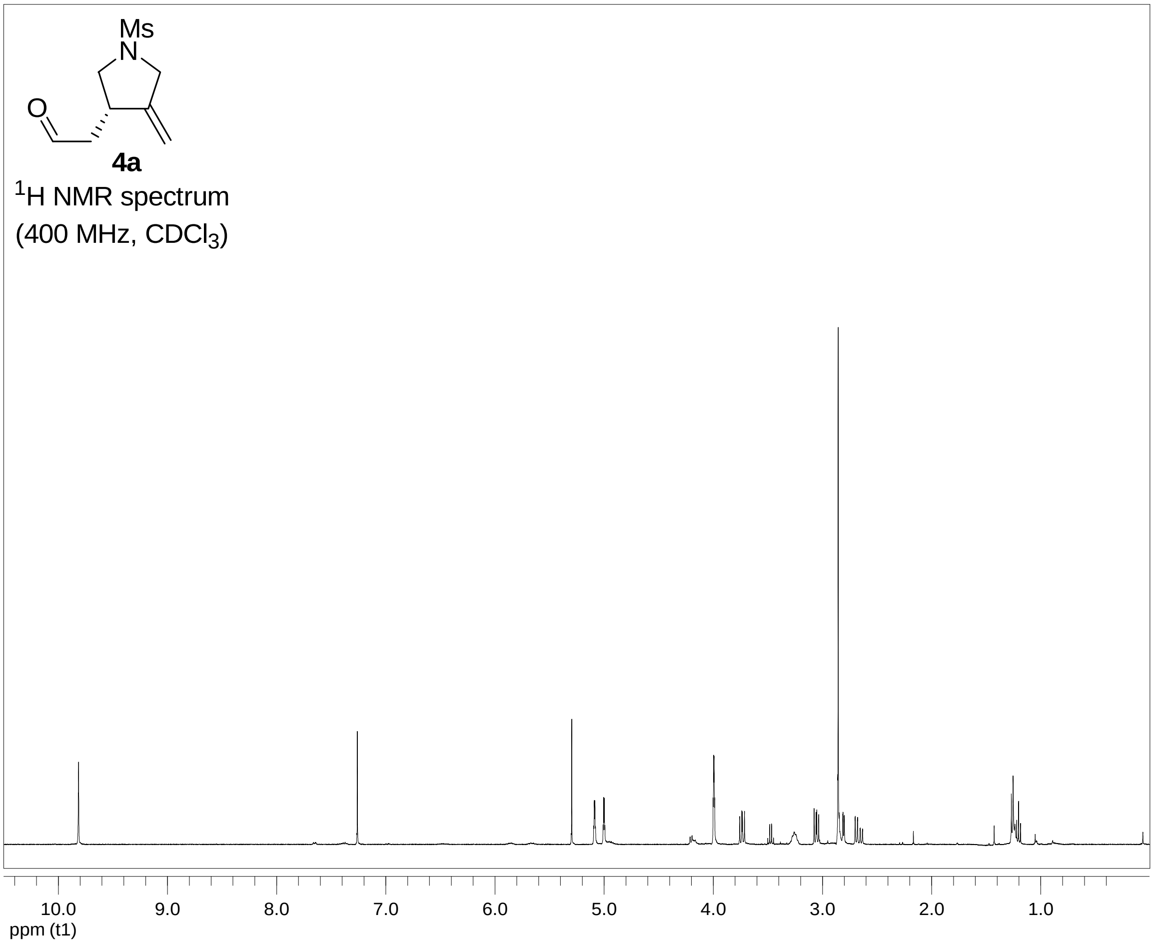


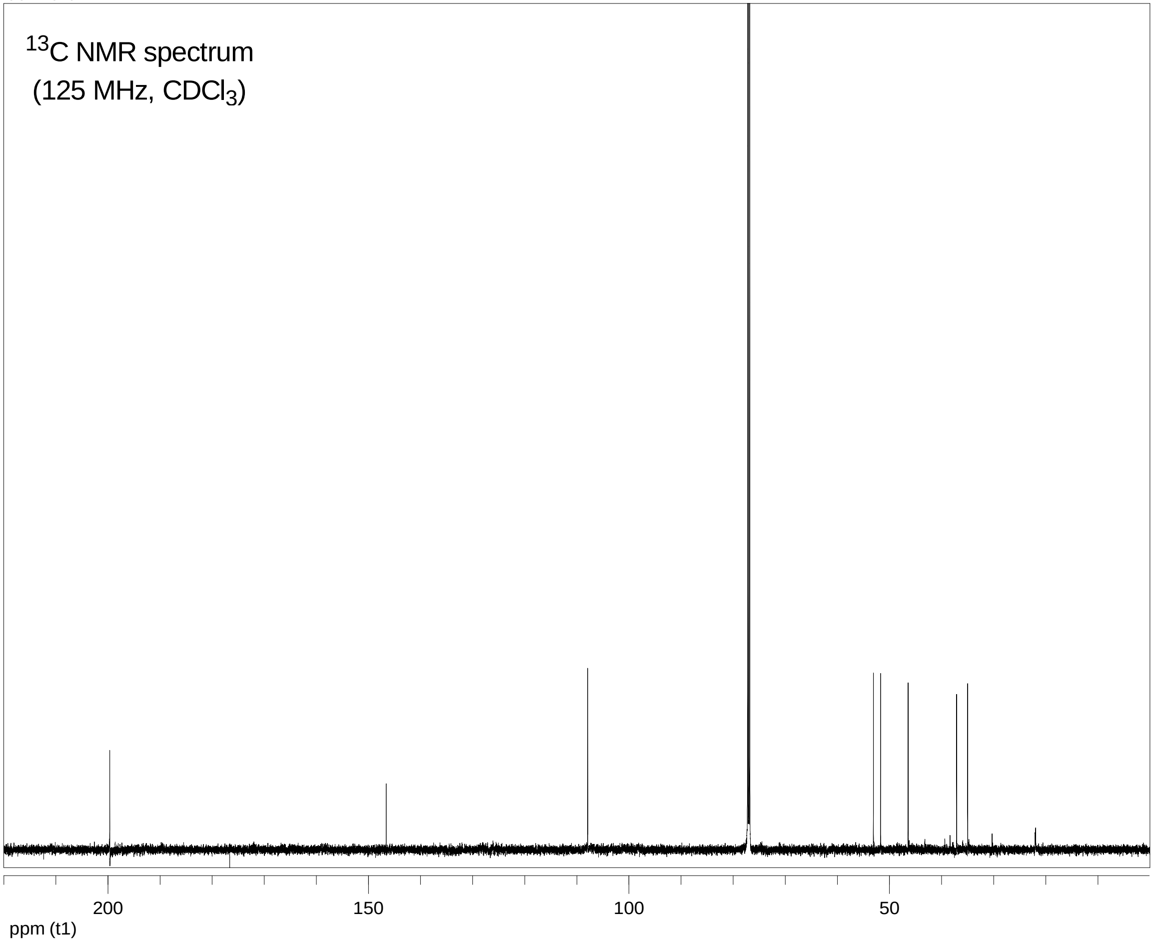
1a

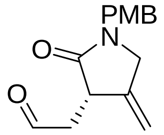



Ts
N
TBSO
2a
^{1}H NMR spectrum
(600 MHz, $CDCl_3$)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

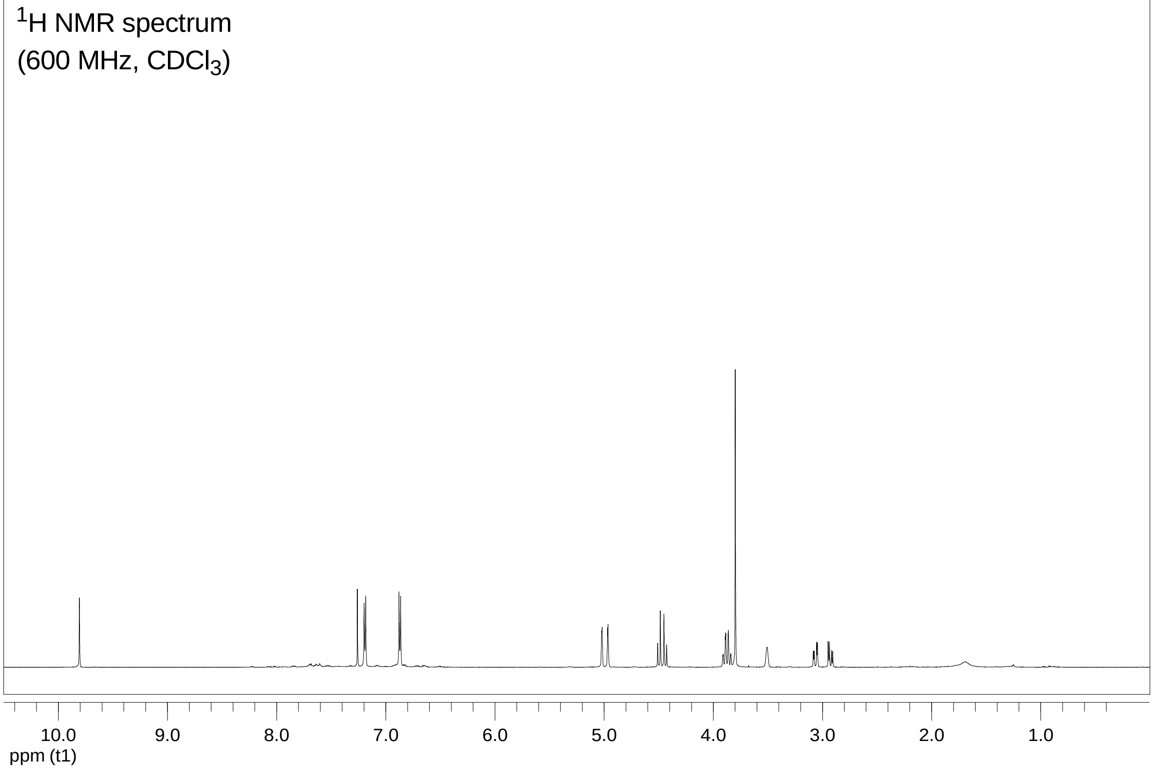

^{13}C NMR spectrum
(151 MHz, $CDCl_3$)
150
100
50
0
ppm (t1)


Ms
N
O
4a
^{1}H NMR spectrum
(400 MHz, $CDCl_3$)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


^{13}C NMR spectrum
(125 MHz, $CDCl_3$)
200
150
100
50
ppm (t1)


PMB
N
O
O

5a


^{1}H NMR spectrum
(600 MHz, $CDCl_3$)
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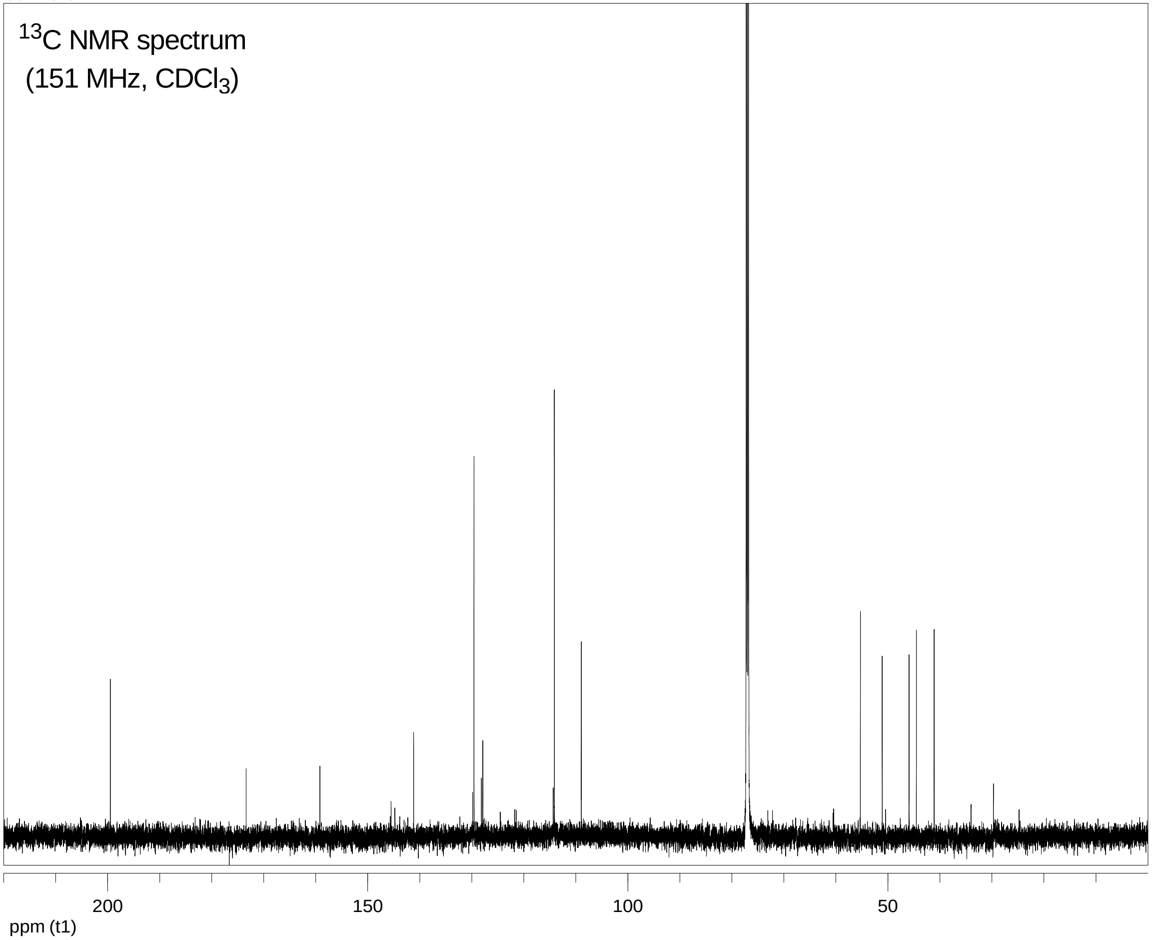
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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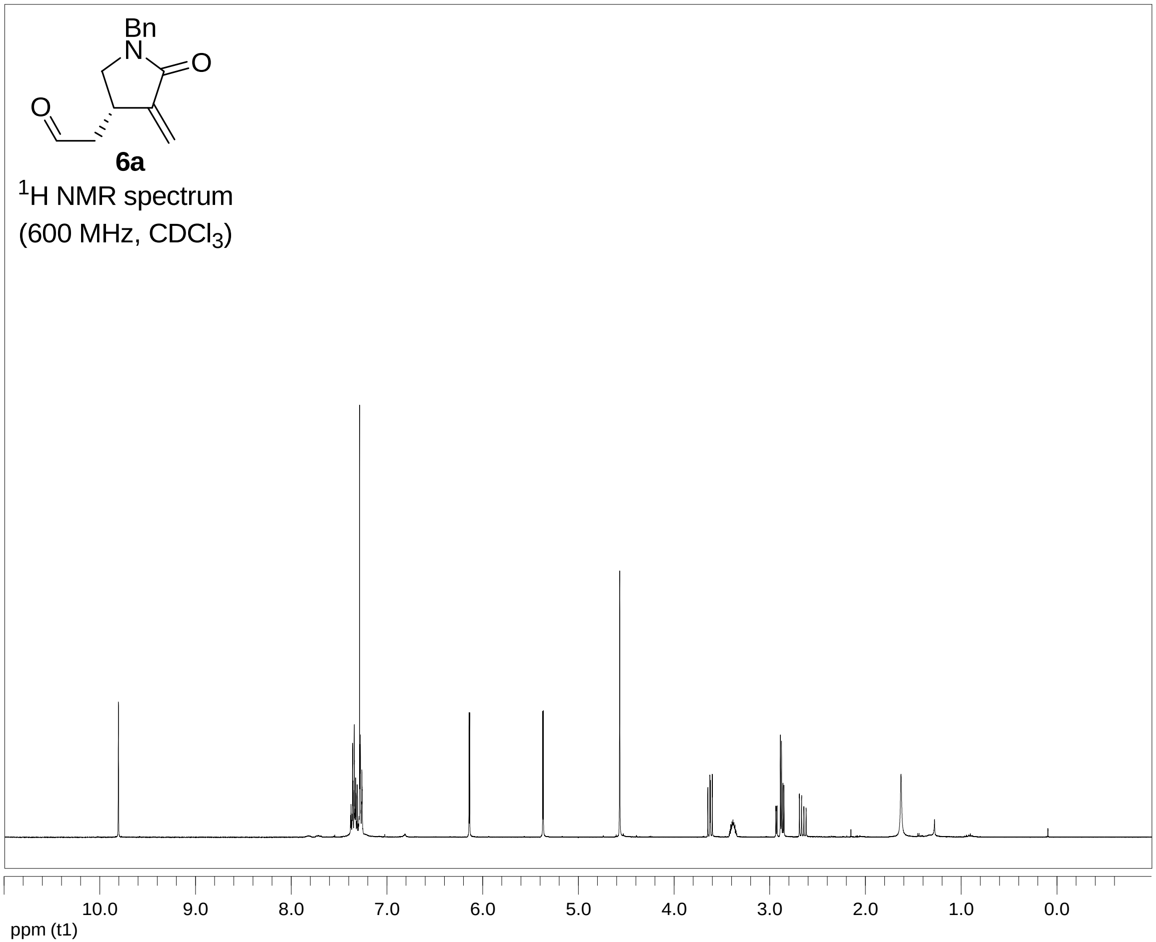
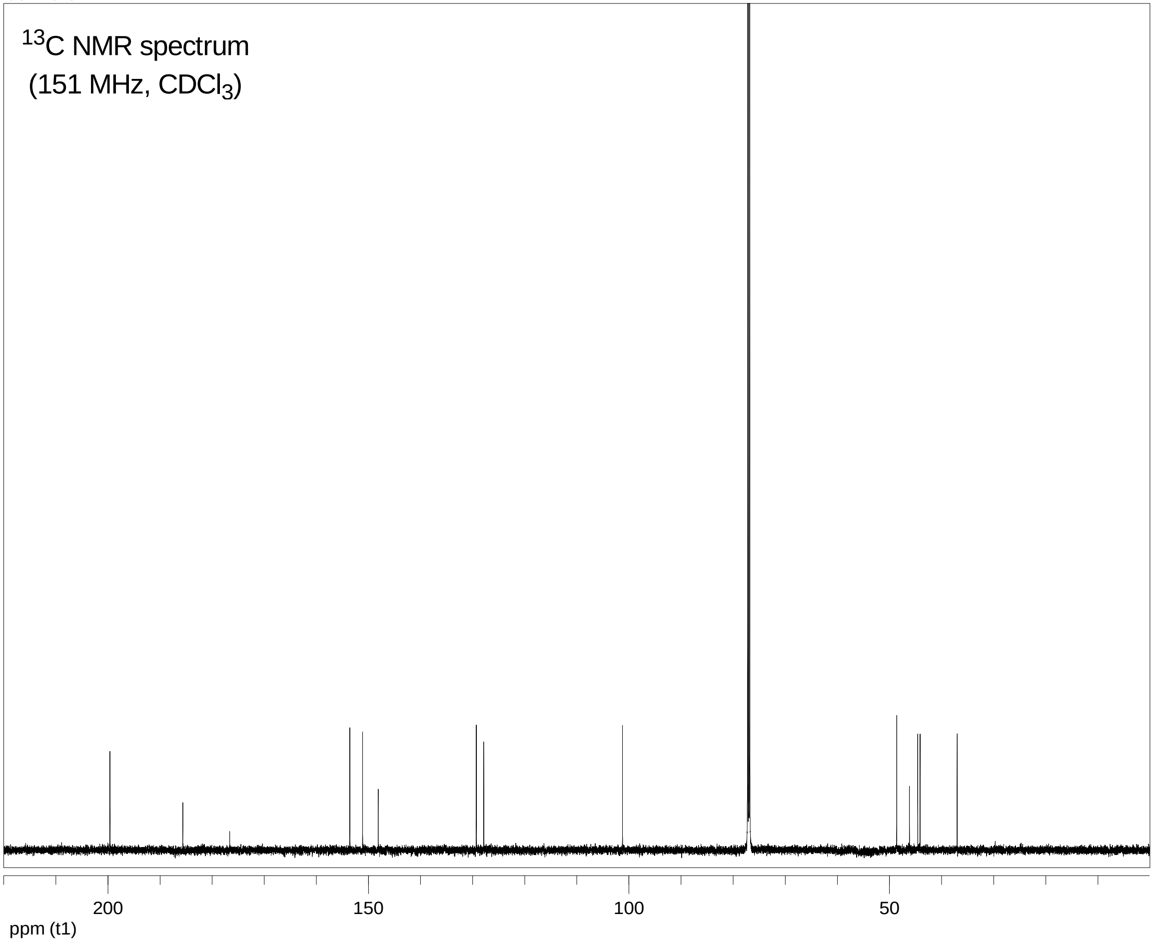
(151 MHz, $CDCl_3$)
200
150
100
50
ppm (t1)

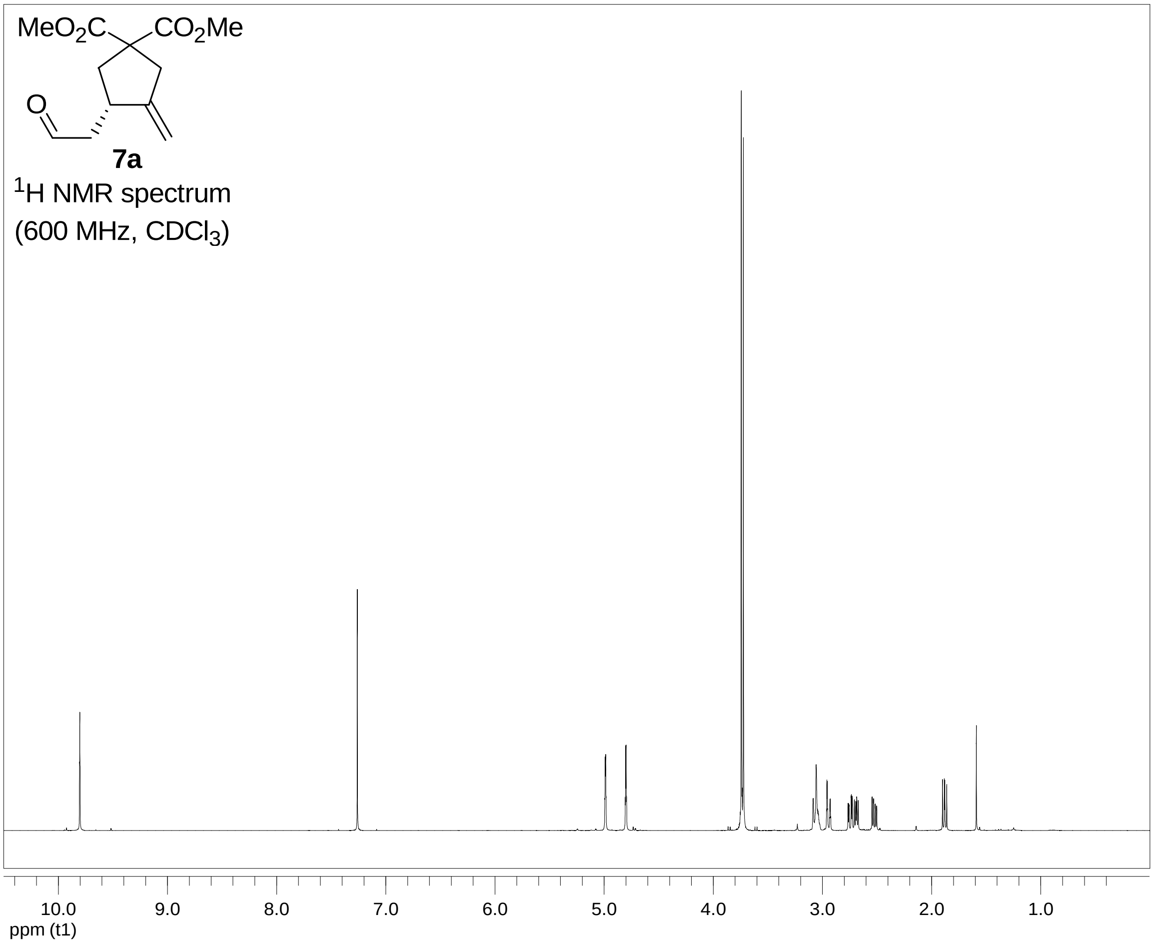


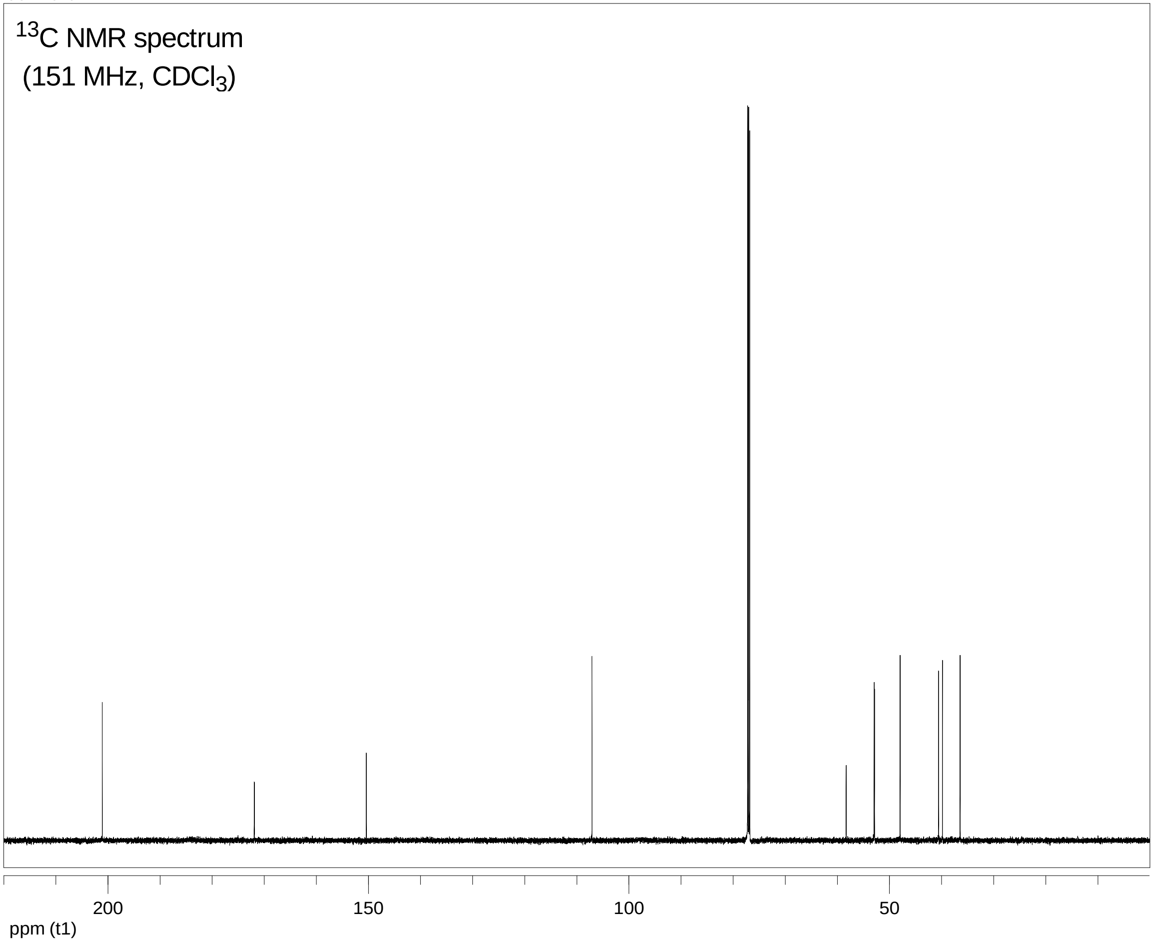
6a

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



^{13}C NMR spectrum
(151 MHz, $CDCl_3$)


MeO2C
CO2Me
O
7a
1H NMR spectrum
(600 MHz, CDCl3)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


13C NMR spectrum
(151 MHz, CDCl3)
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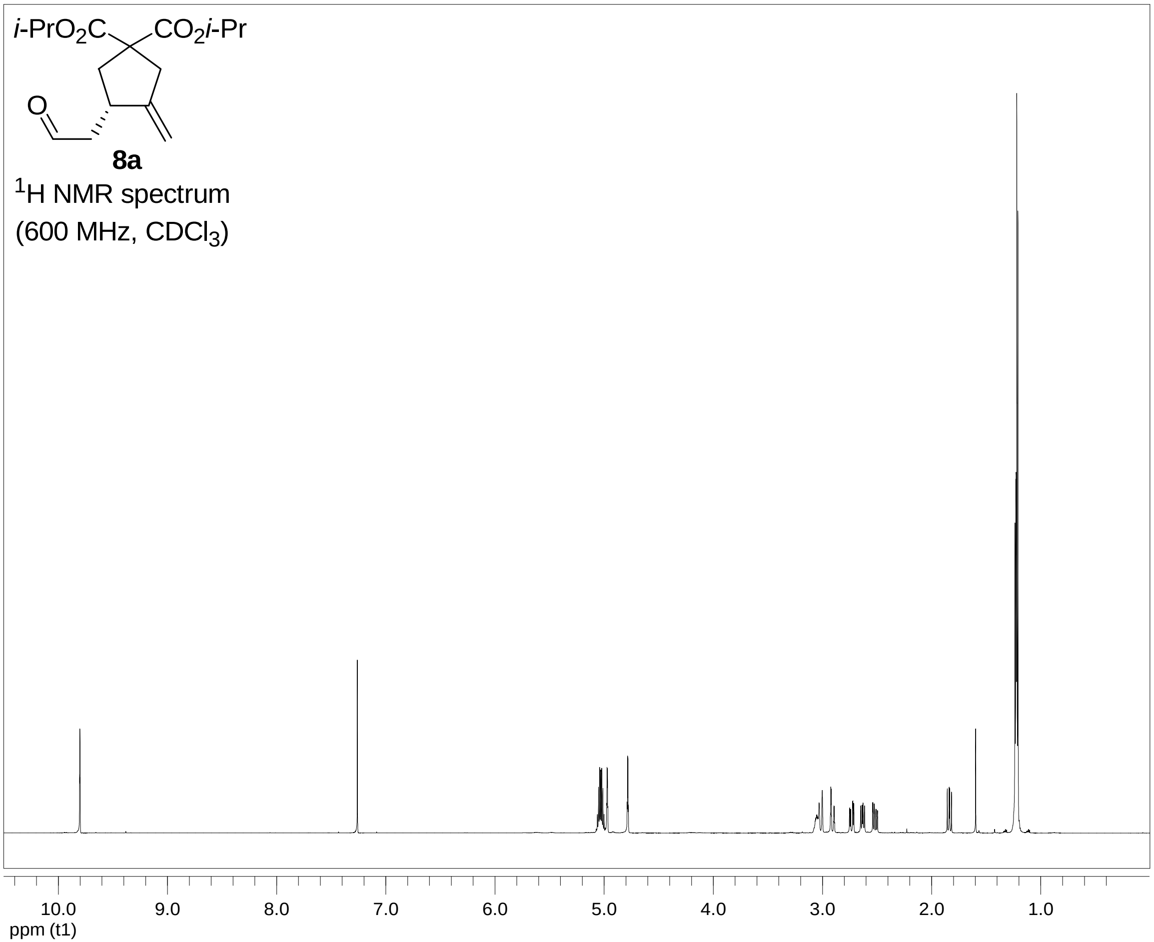
150
100
50
ppm (t1)



i-PrO$_2$C
CO$_2$$i$-Pr
O
8a
^{1}H NMR spectrum
(600 MHz, CDCl$_3$)
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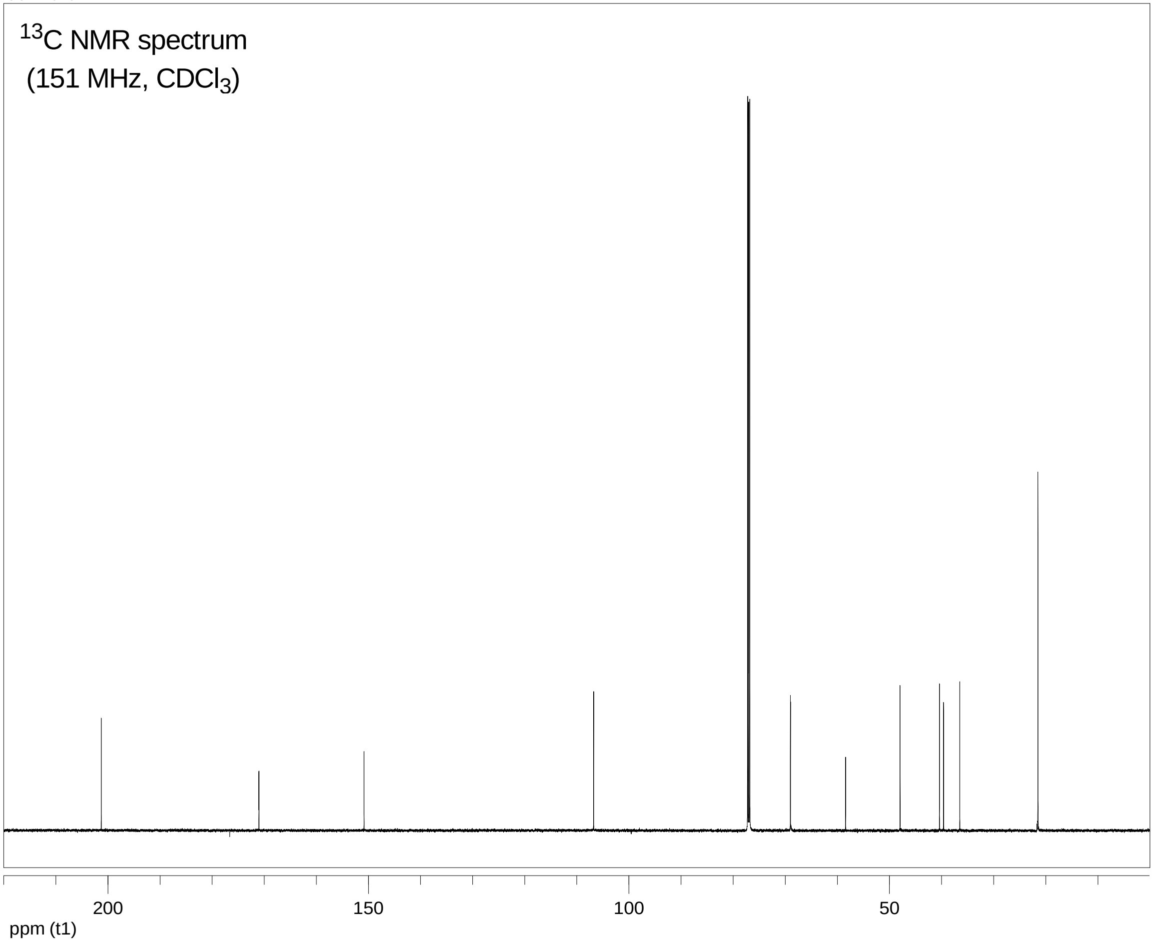
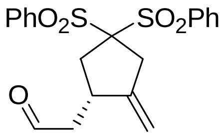
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)



^{13}C NMR spectrum
(151 MHz, CDCl$_3$)
200
150
100
50
ppm (t1)



9a

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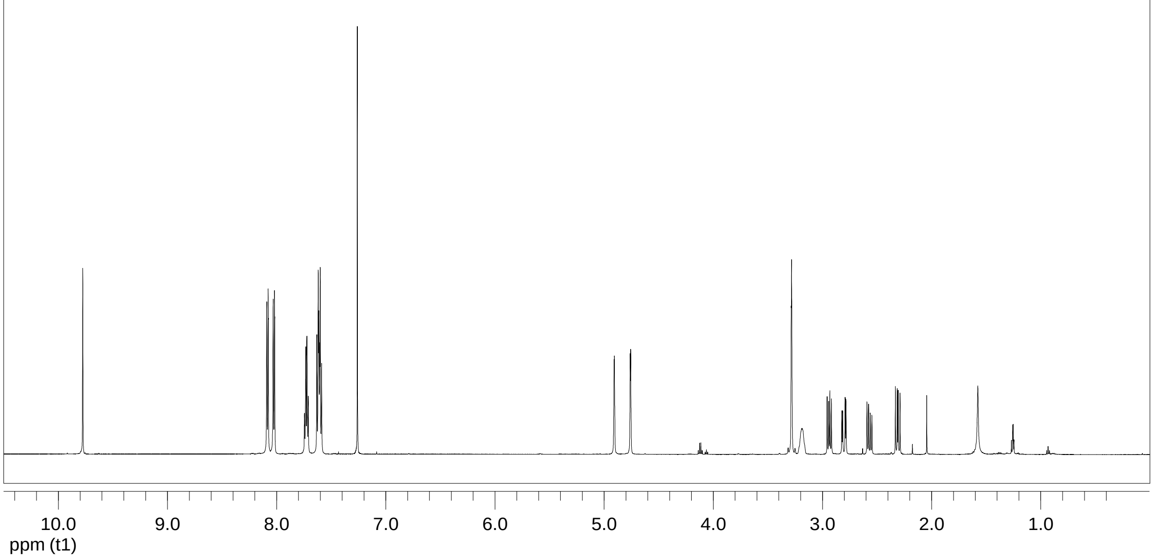
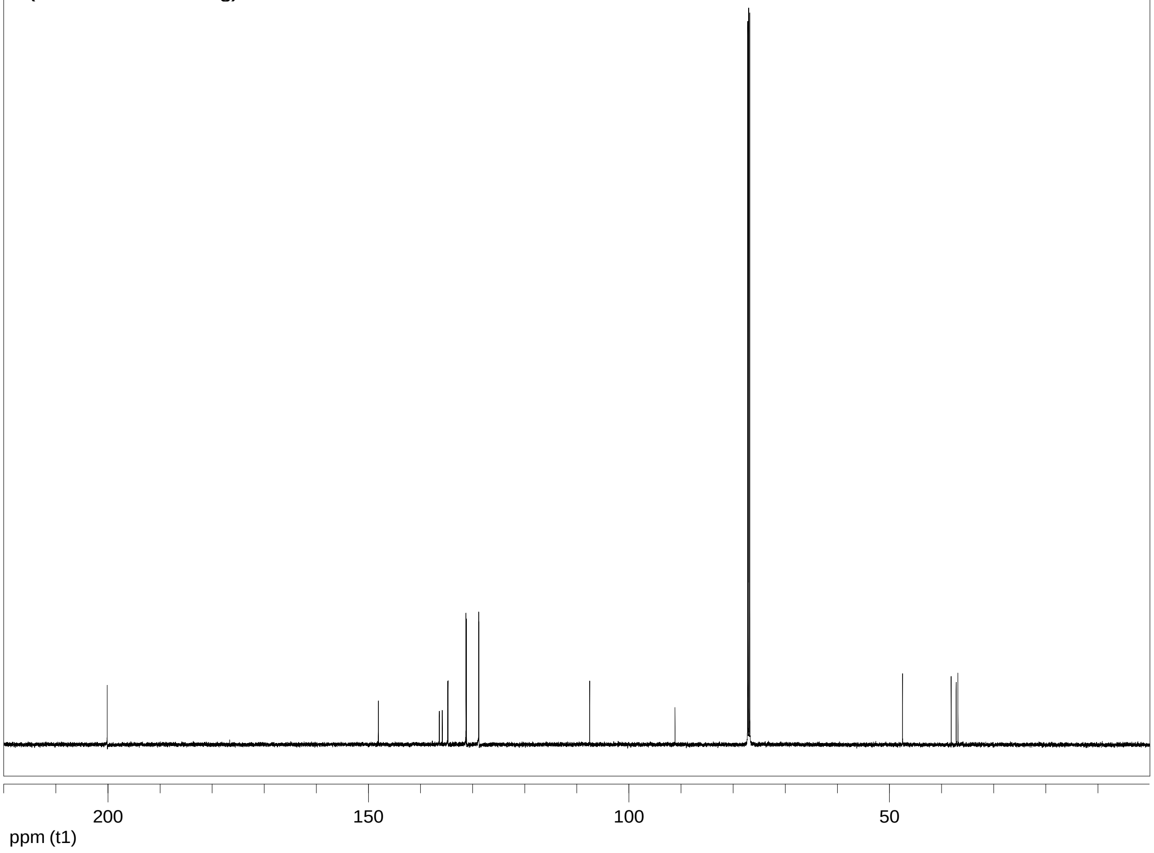
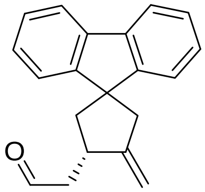
(600 MHz, $CDCl_3$)

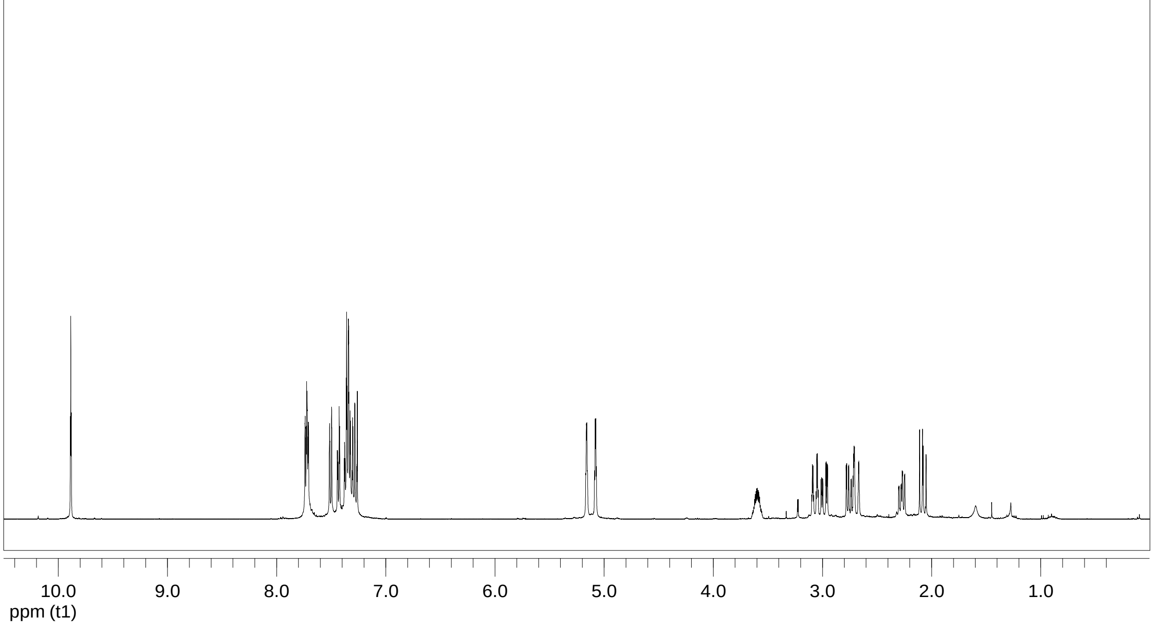


^{13}C NMR spectrum
(151 MHz, $CDCl_3$)





10a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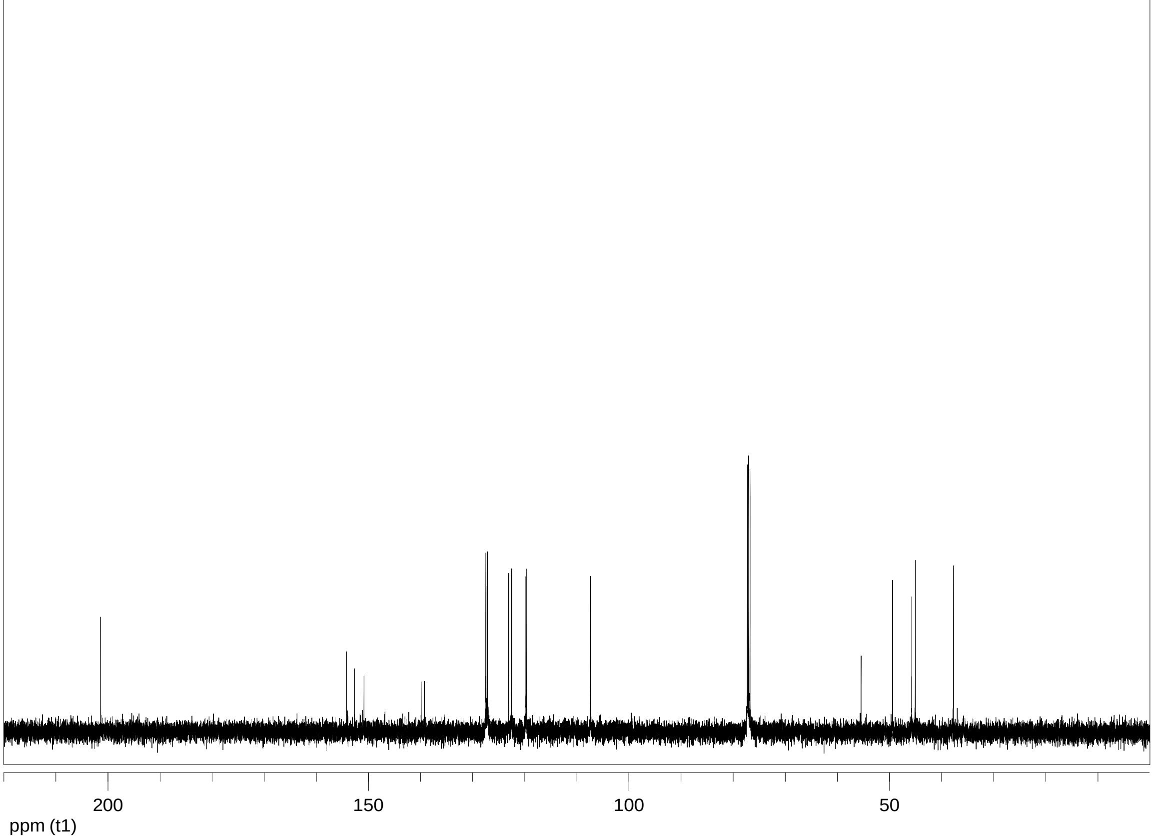
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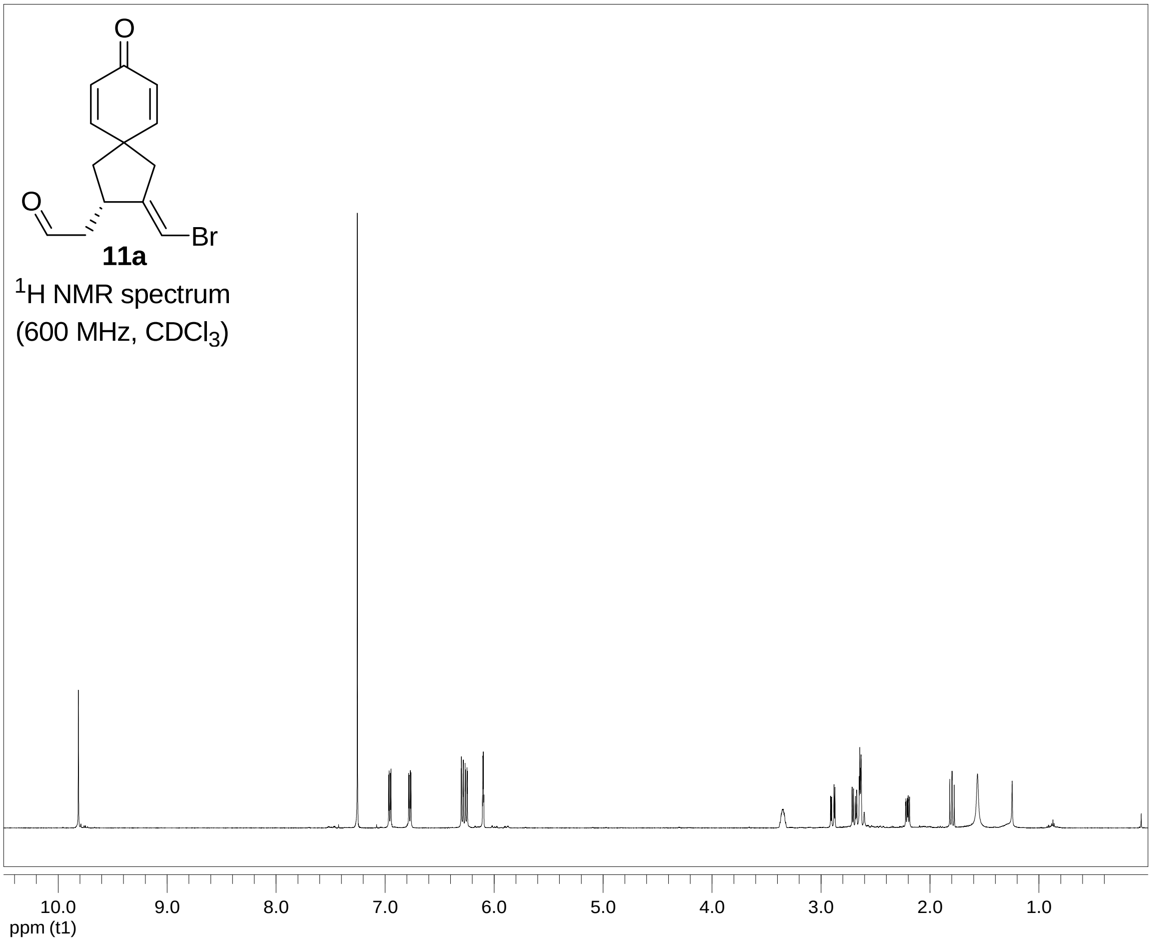
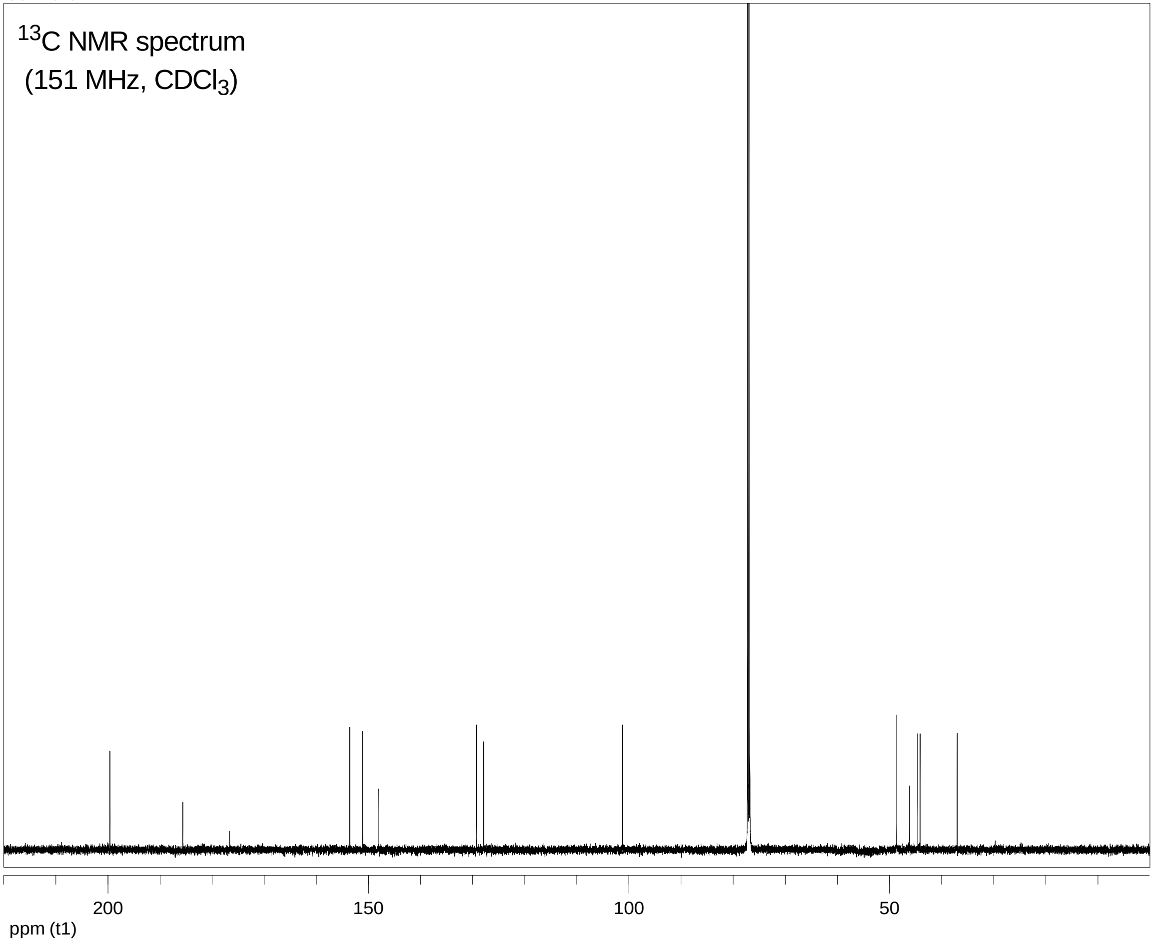
(125 MHz, $CDCl_3$)

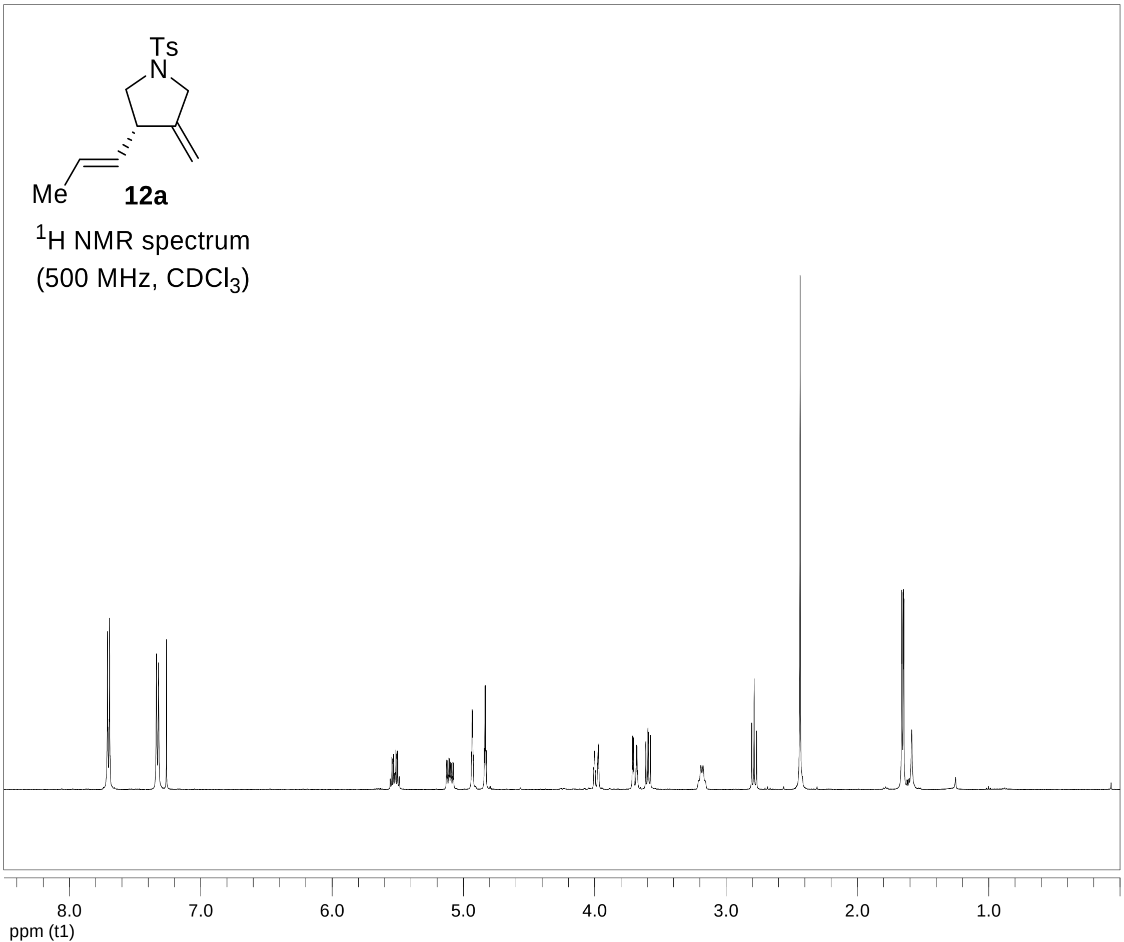

11a

^{1}H NMR spectrum

(600 MHz, $CDCl_3$)

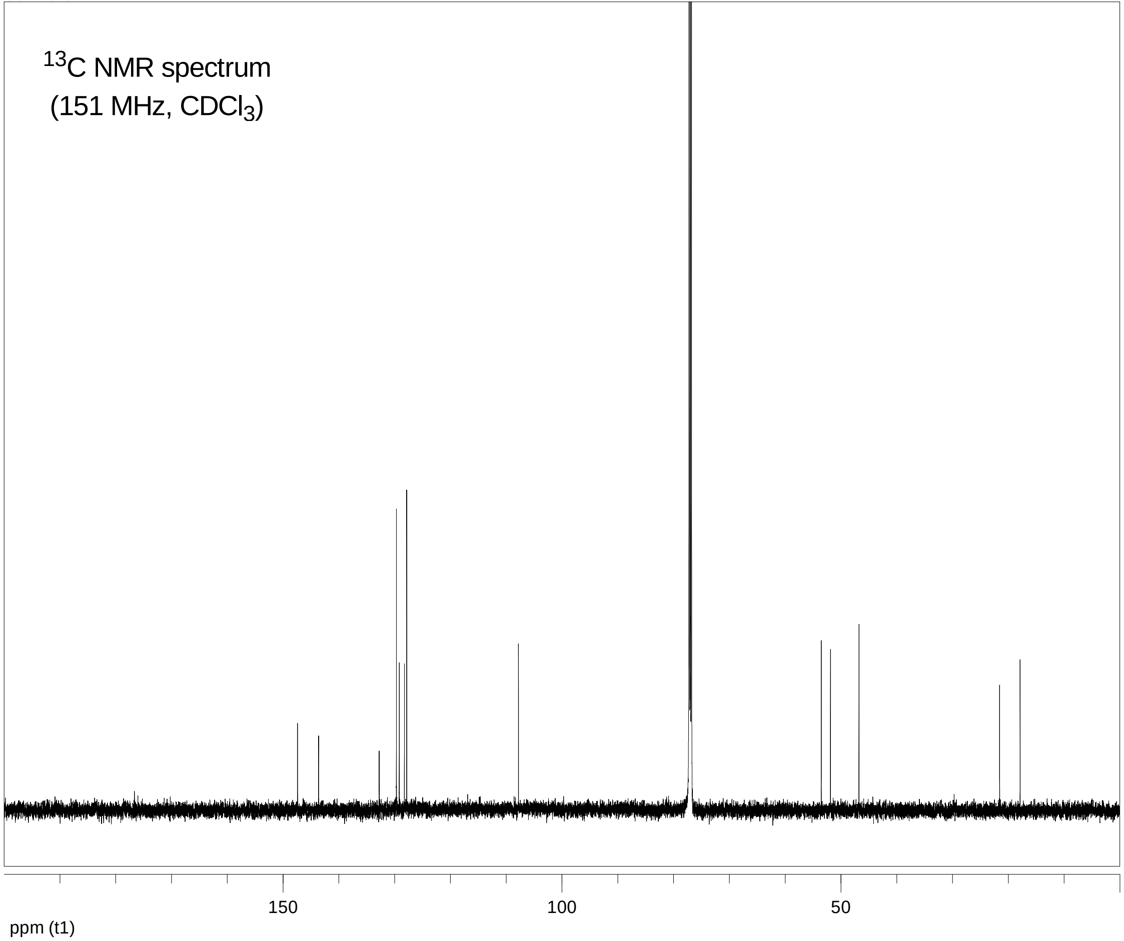

^{13}C NMR spectrum

(151 MHz, $CDCl_3$)

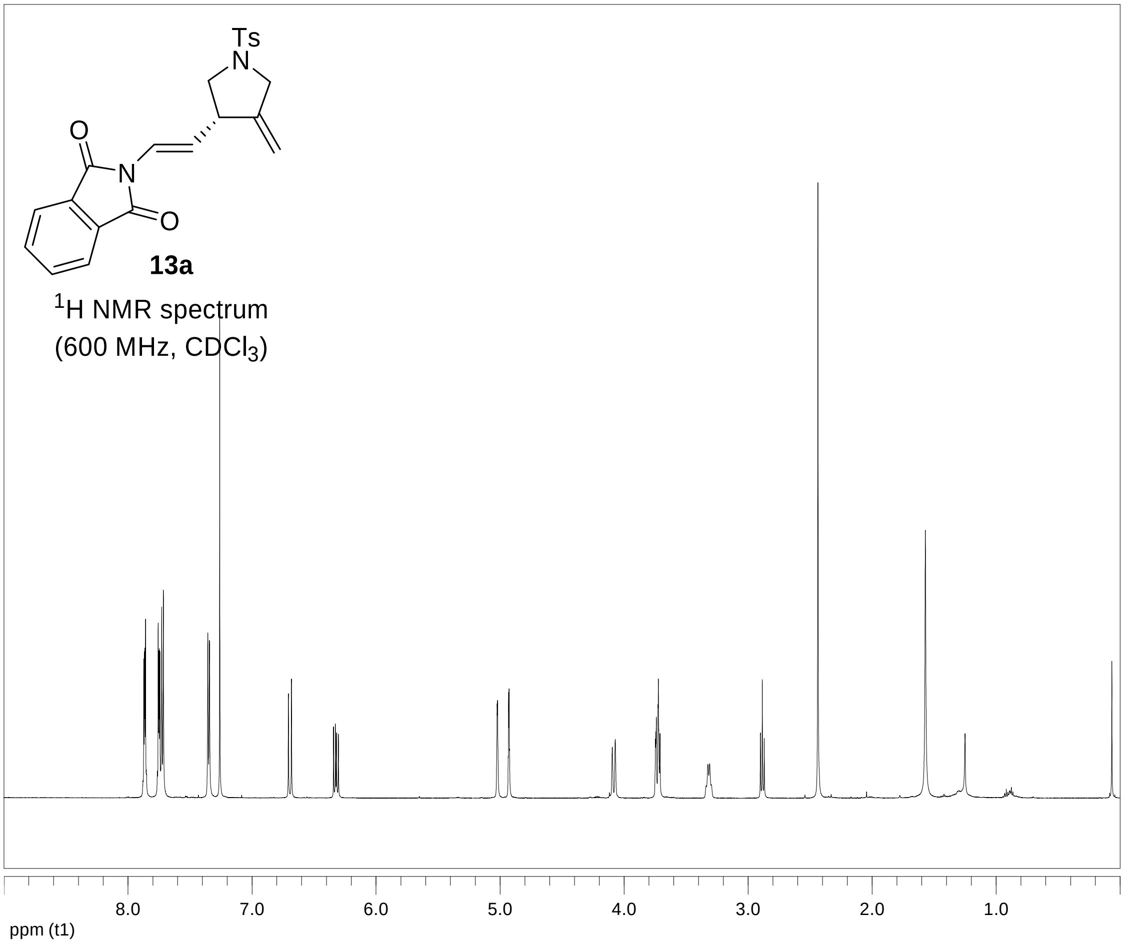


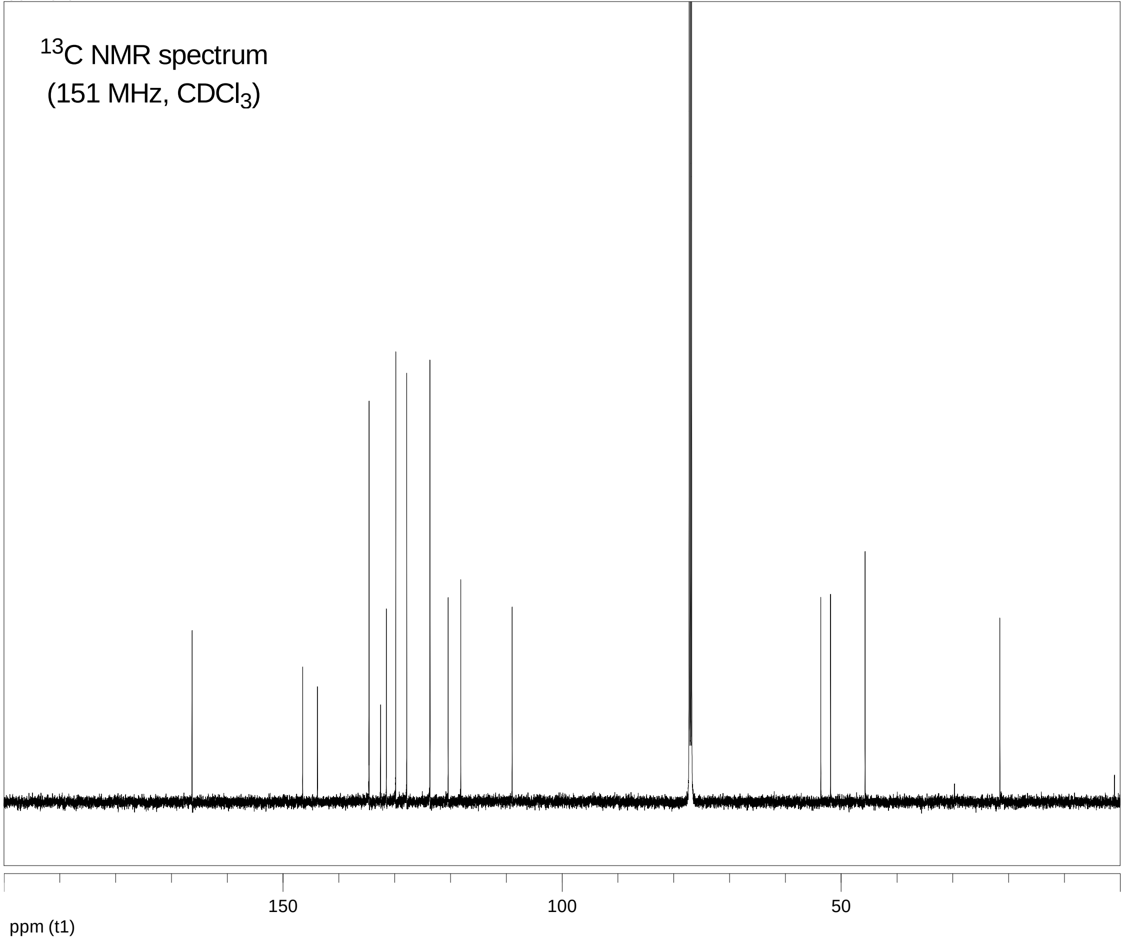
12a

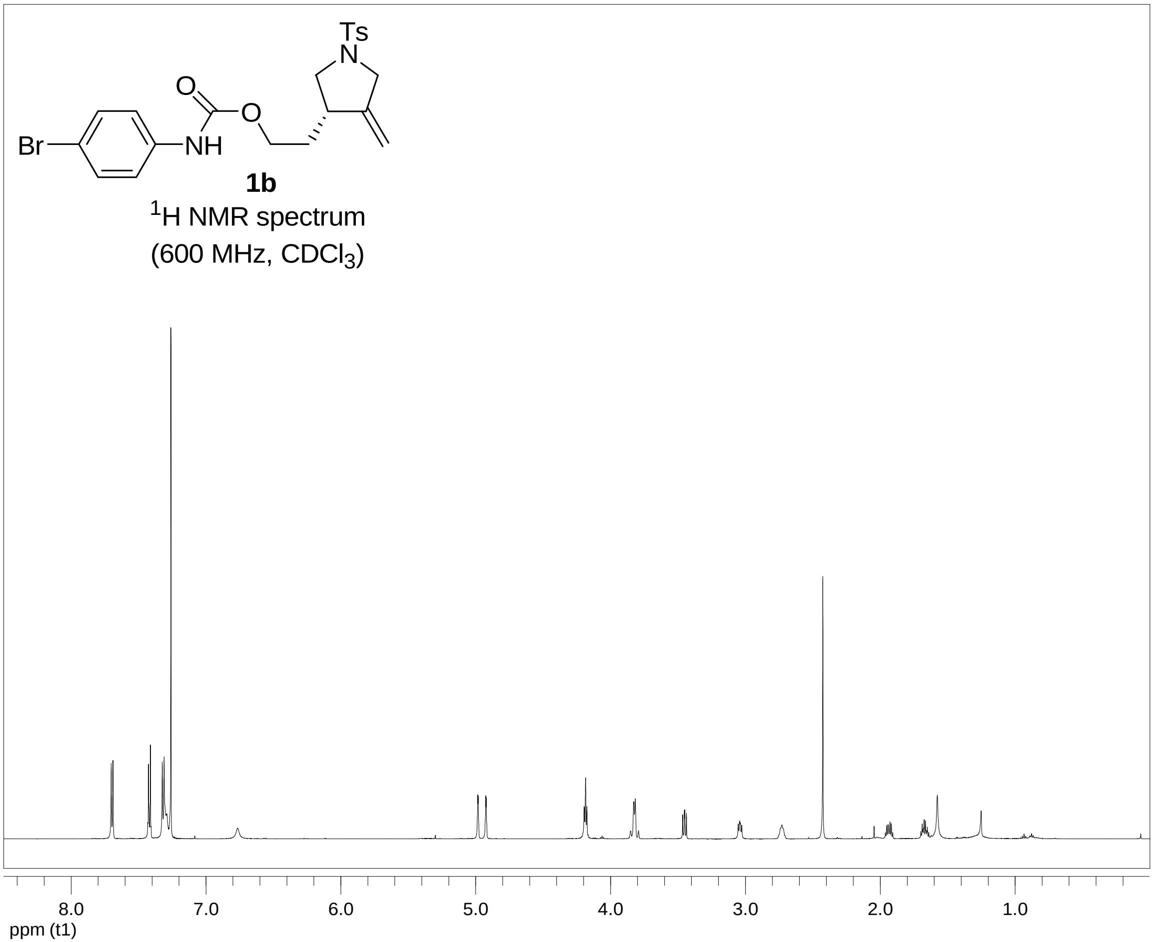
^{1}H NMR spectrum
(500 MHz, $CDCl_3$)

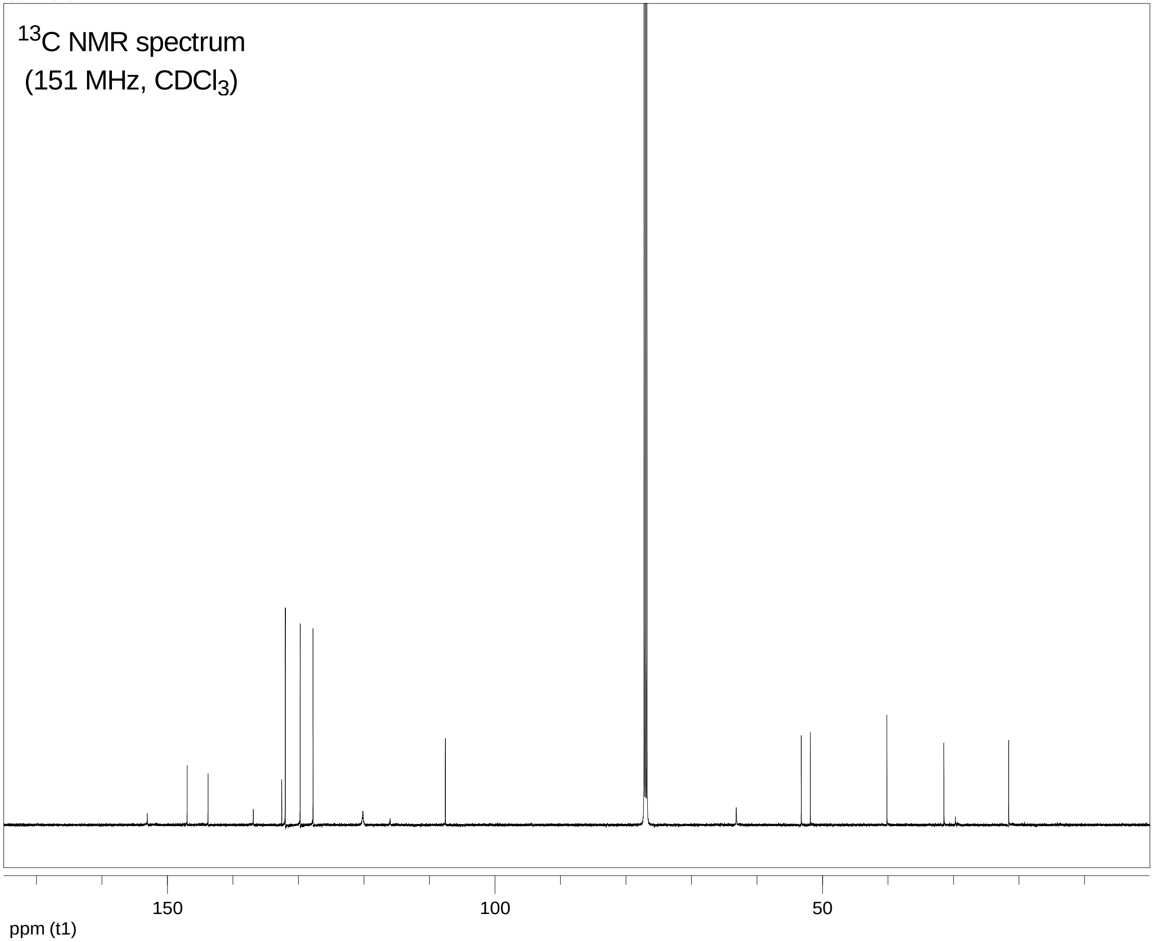


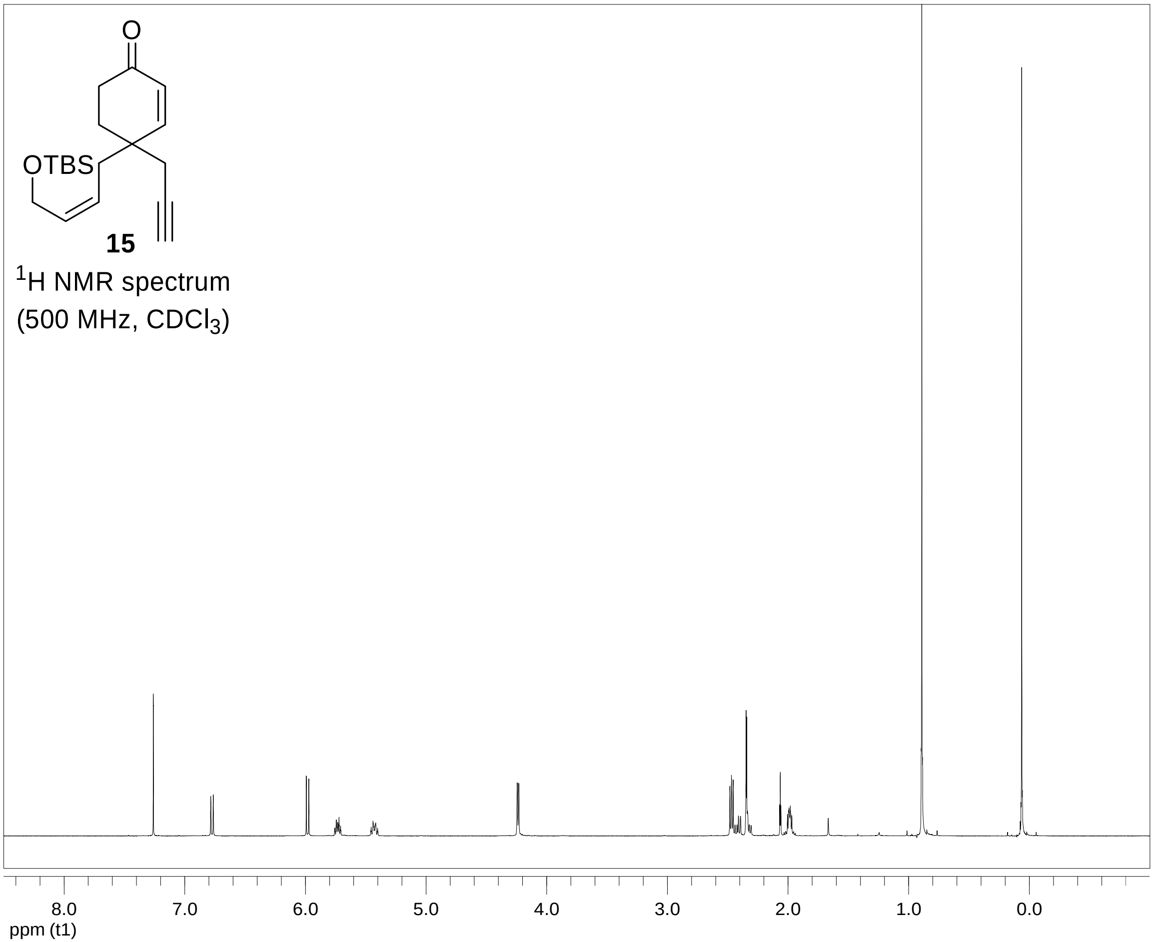
^{13}C NMR spectrum
(151 MHz, $CDCl_3$)

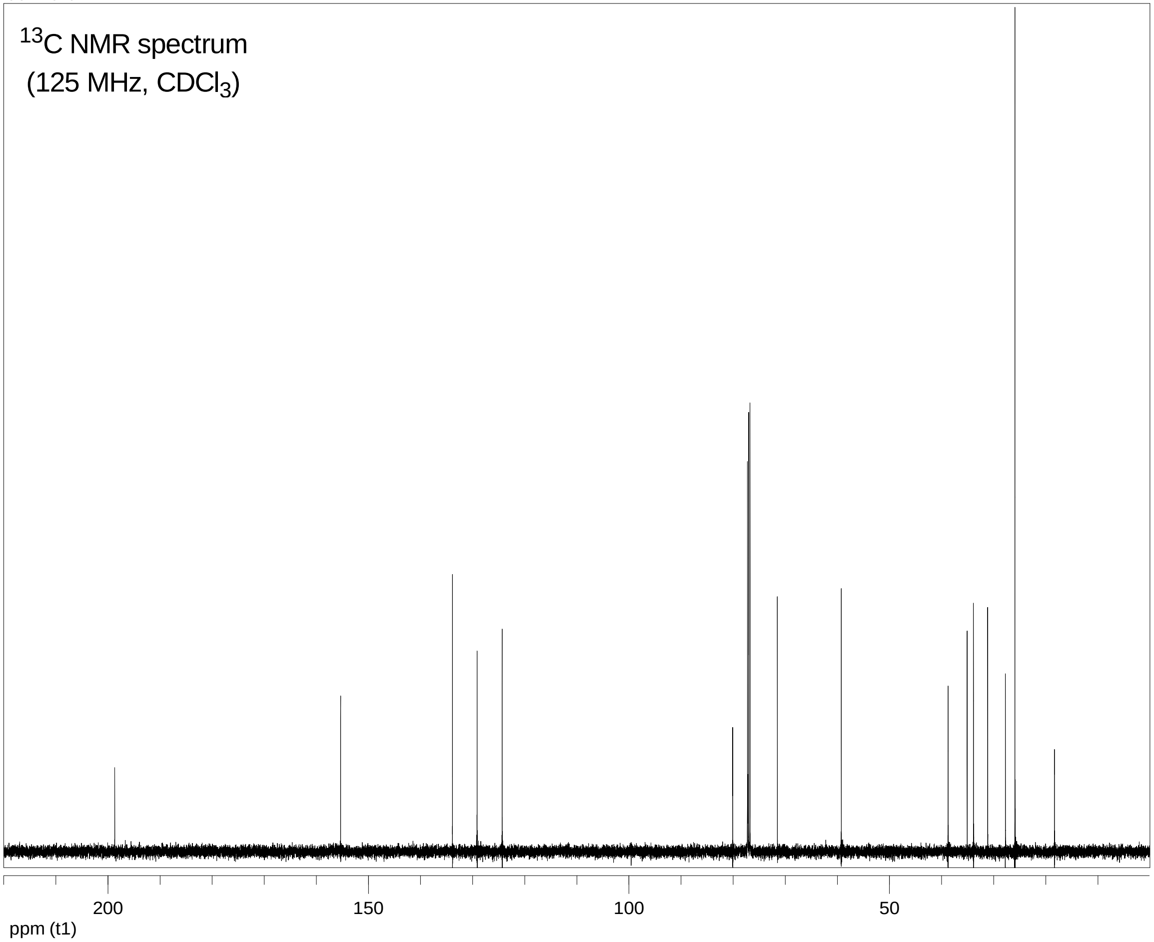

Ts
N
O
N
O
13a
^{1}H NMR spectrum
(600 MHz, $CDCl_3$)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

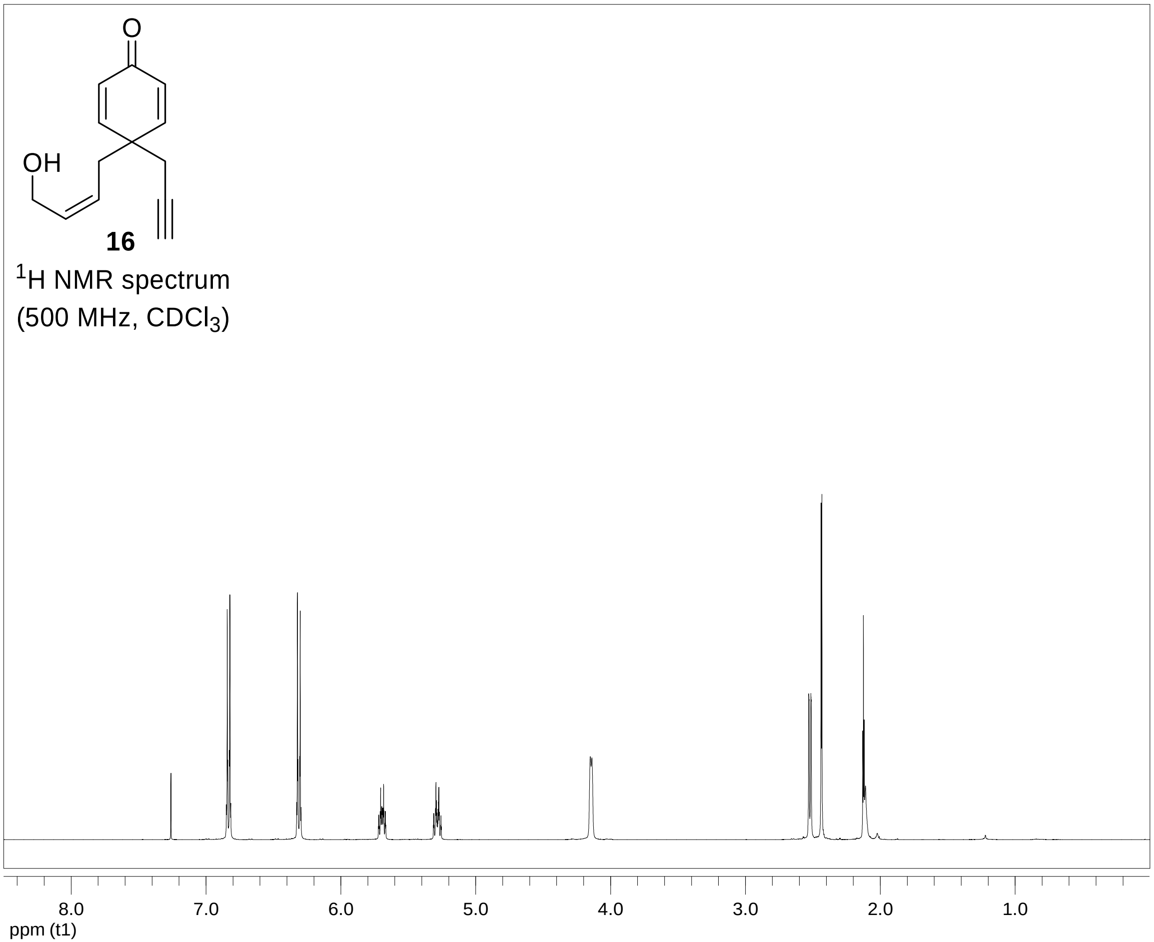

^{13}C NMR spectrum
(151 MHz, $CDCl_3$)
150
100
50
ppm (t1)


Ts
N
O
O
Br
NH
1b
^{1}H NMR spectrum
(600 MHz, CDCl$_3$)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


^{13}C NMR spectrum
(151 MHz, CDCl$_3$)
150
100
50
ppm (t1)

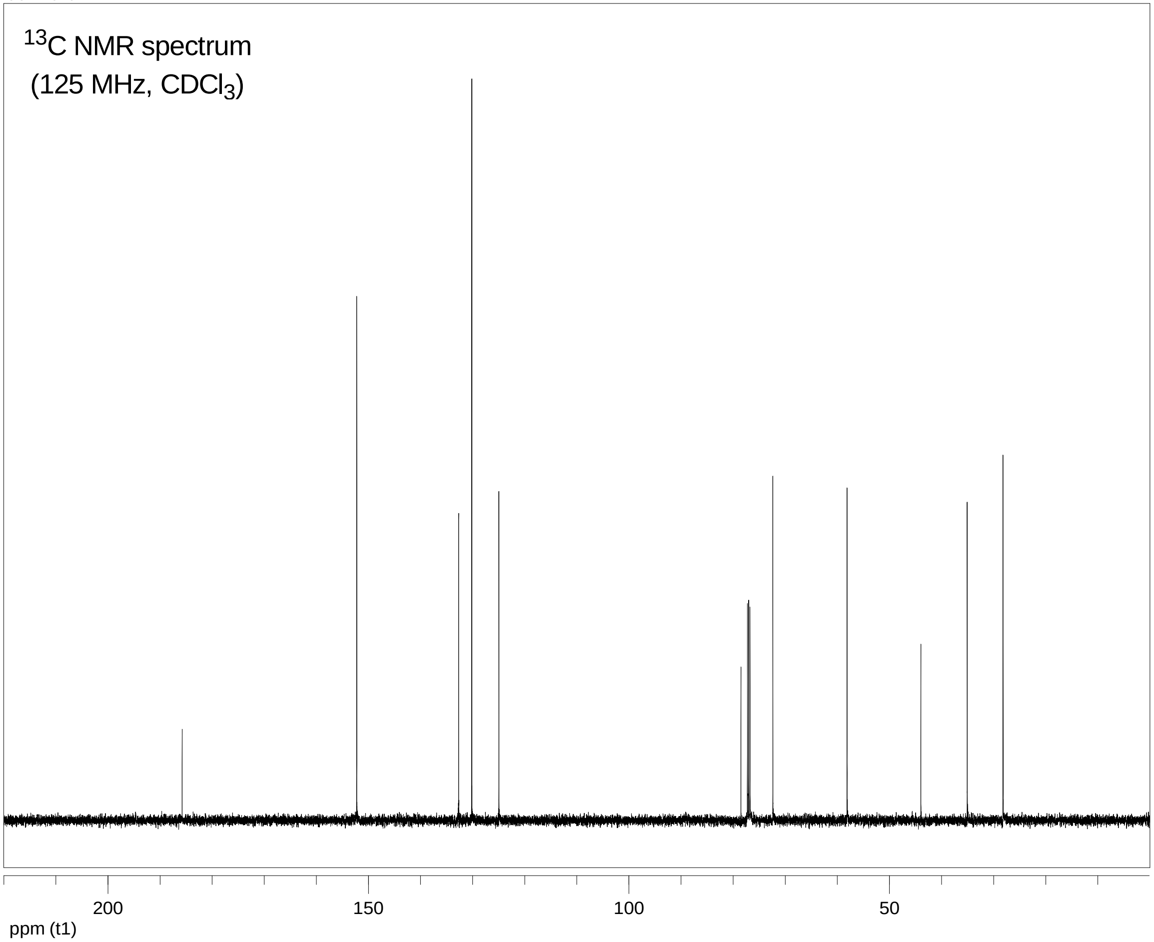

O
OTBS
15
^{1}H NMR spectrum
(500 MHz, $CDCl_3$)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


^{13}C NMR spectrum
(125 MHz, $CDCl_3$)
200
150
100
50
ppm (t1)

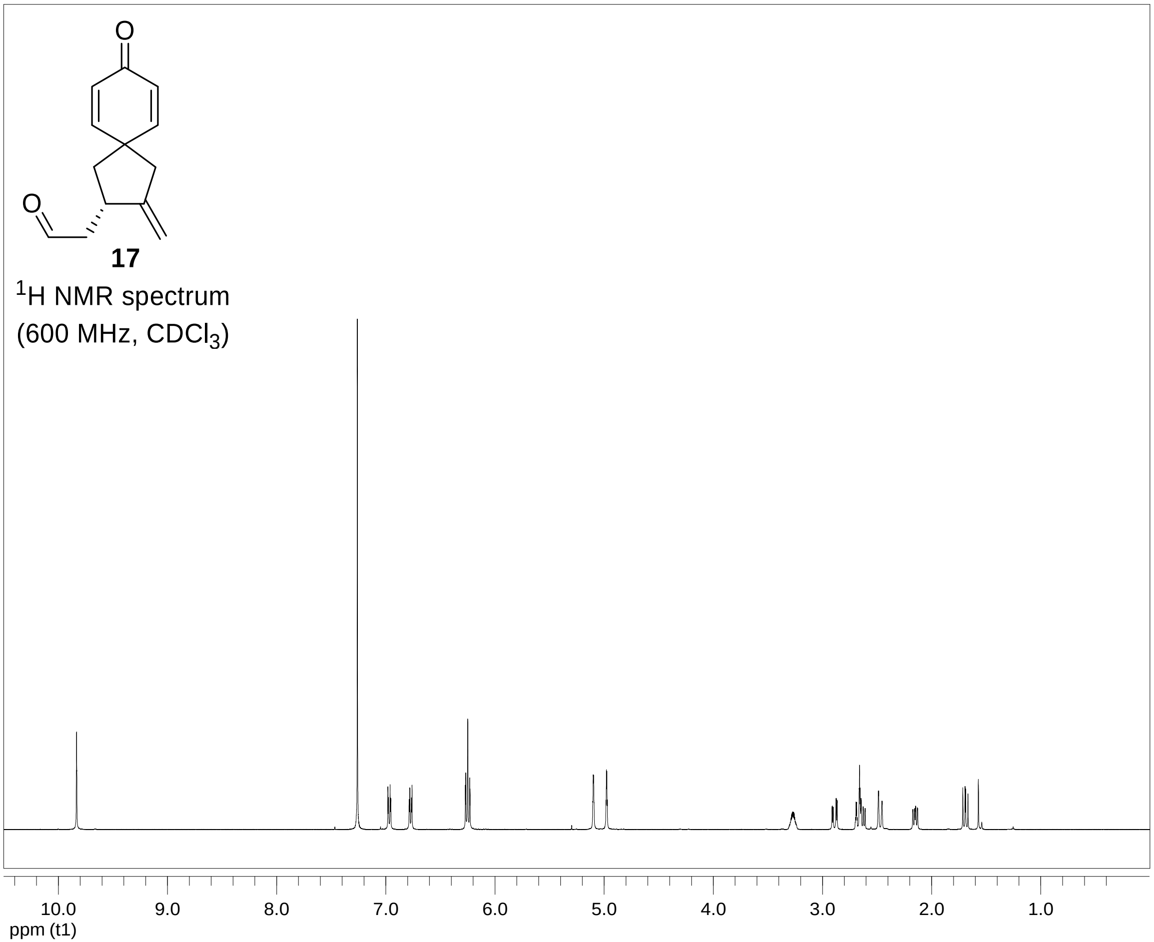


16

^{1}H NMR spectrum
(500 MHz, $CDCl_3$)

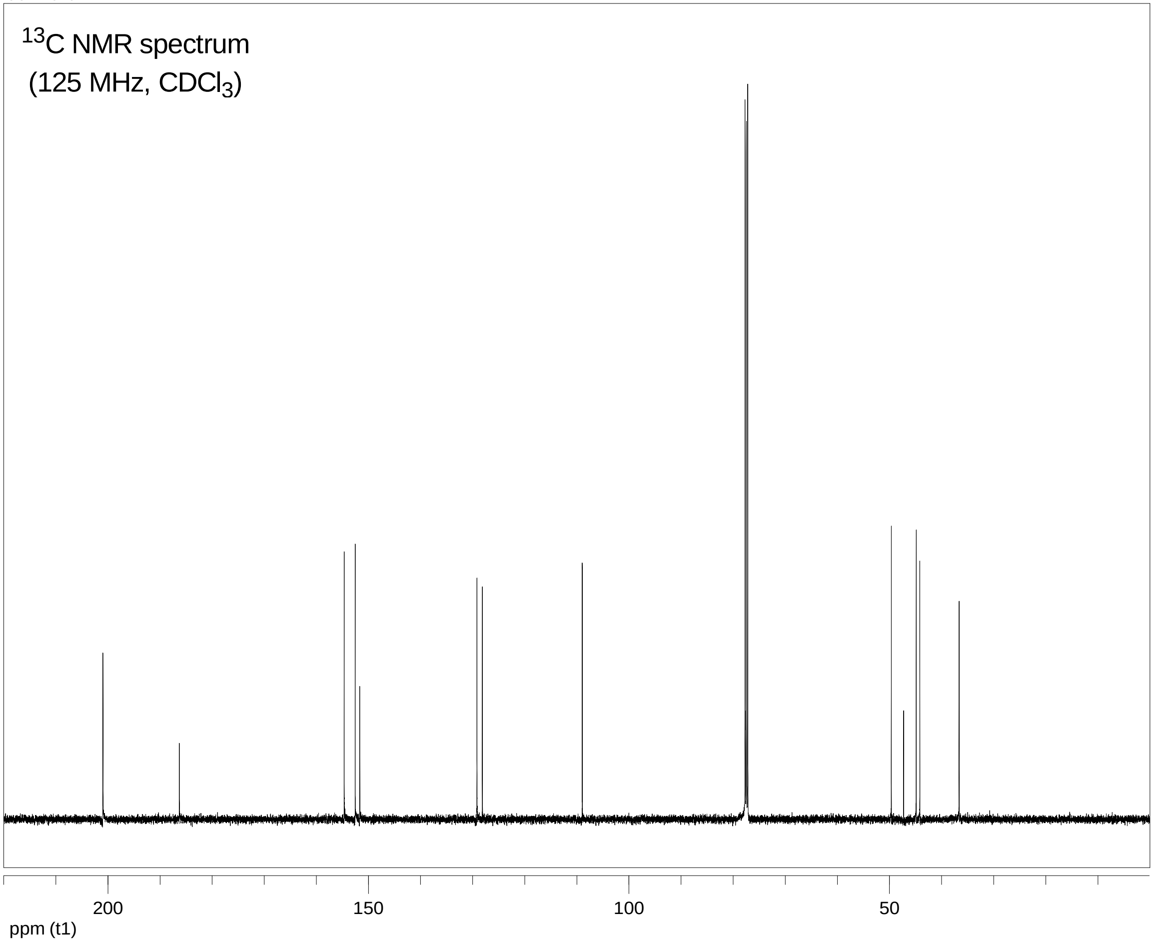


^{13}C NMR spectrum
(125 MHz, $CDCl_3$)



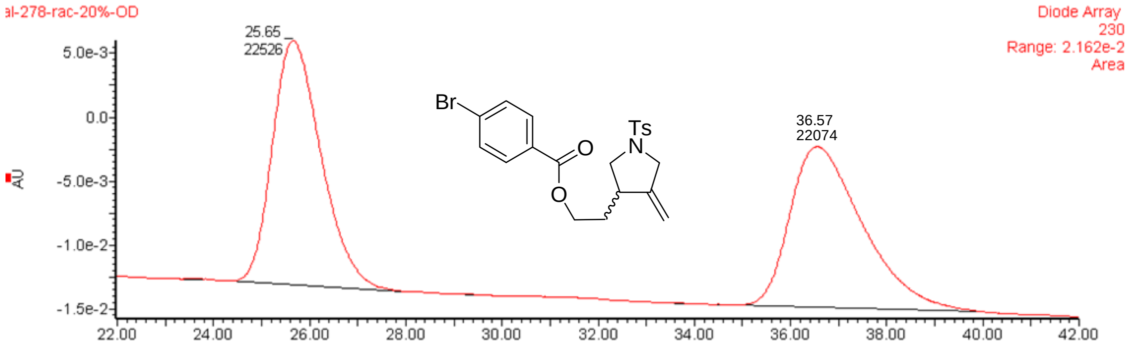
17

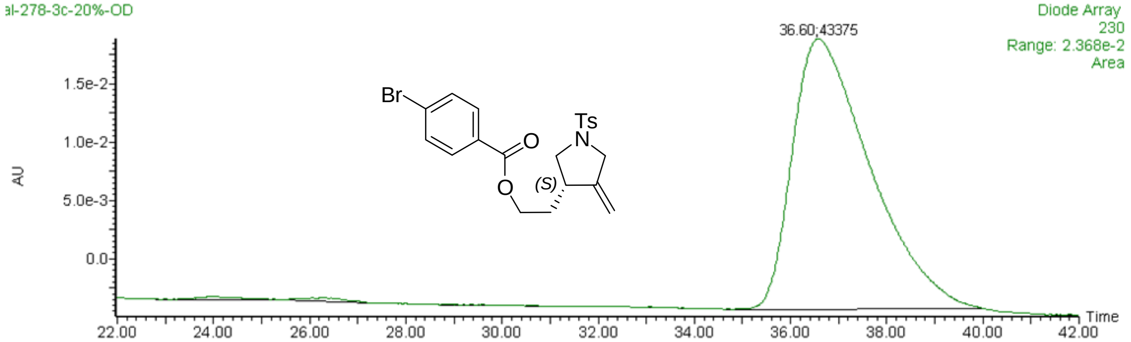
^{1}H NMR spectrum (600 MHz, $CDCl_3$)



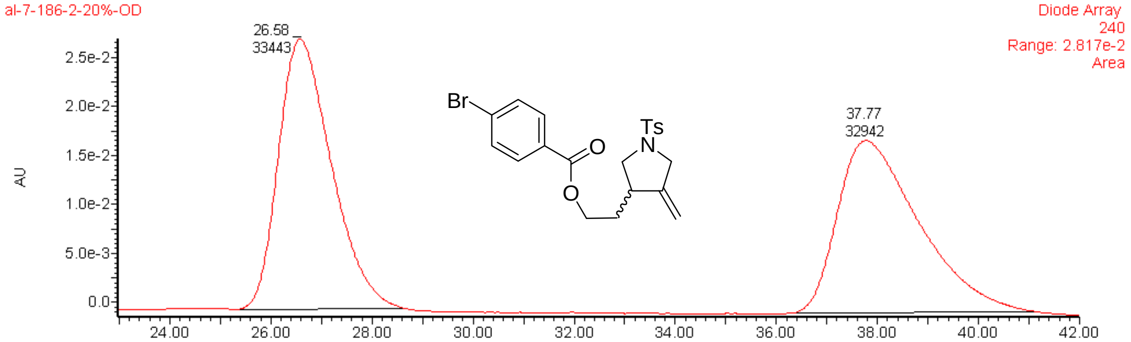
^{13}C NMR spectrum (125 MHz, $CDCl_3$)

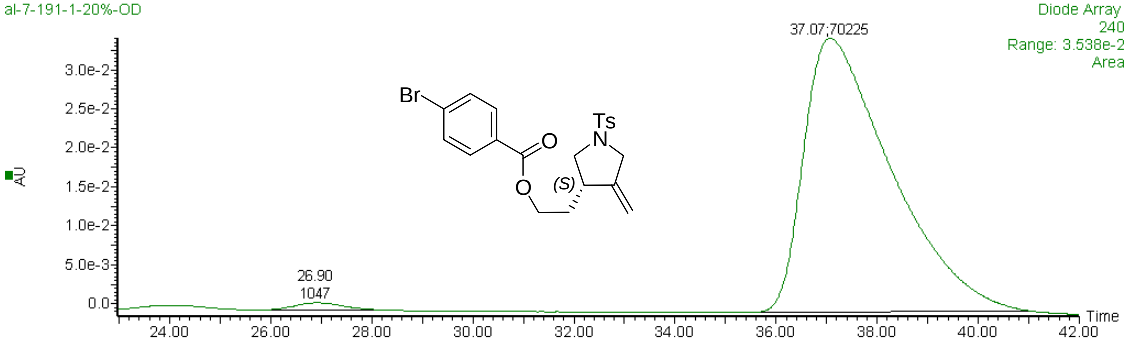
HPLC Traces. Racemic and optically active *p*-bromobenzoate esters (Table 2, entries 1 and 2) or ethylene glycol acetals (Table 2, entries 6 and 11, and compound **15**) were analyzed with chiral HPLC (OD-H column, 1 mL/min) to determine retention time and enantiomeric excesses.



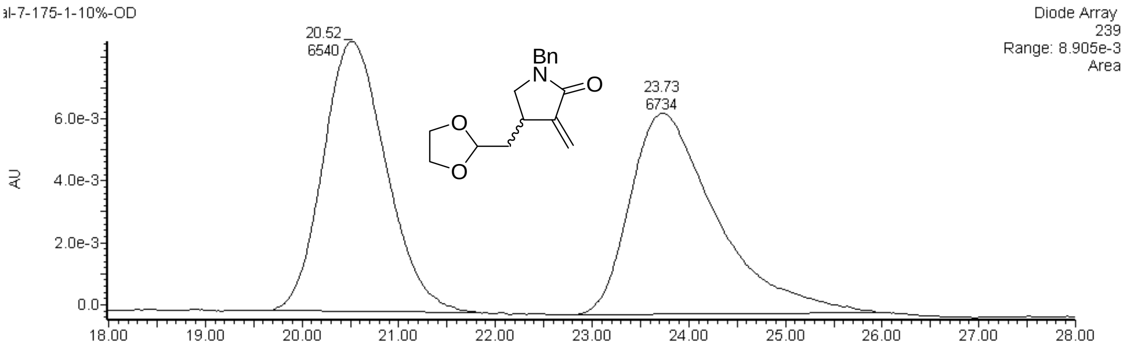


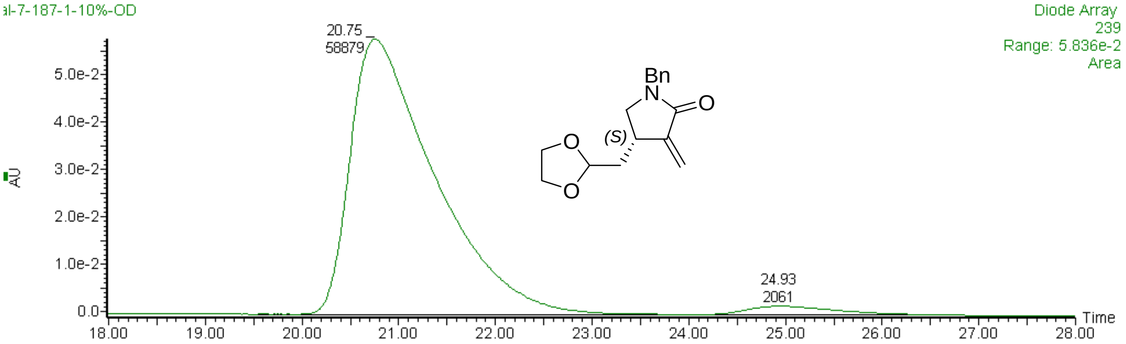
entry 1	mobile phase	t_r (*R*)	t_r (*S*)	*ee* (%)
(±)	*i*-PrOH:hexanes (20:80)	25.65 min	36.57 min	-
(*S*)	*i*-PrOH:hexanes (20:80)	-	36.60 min	>99



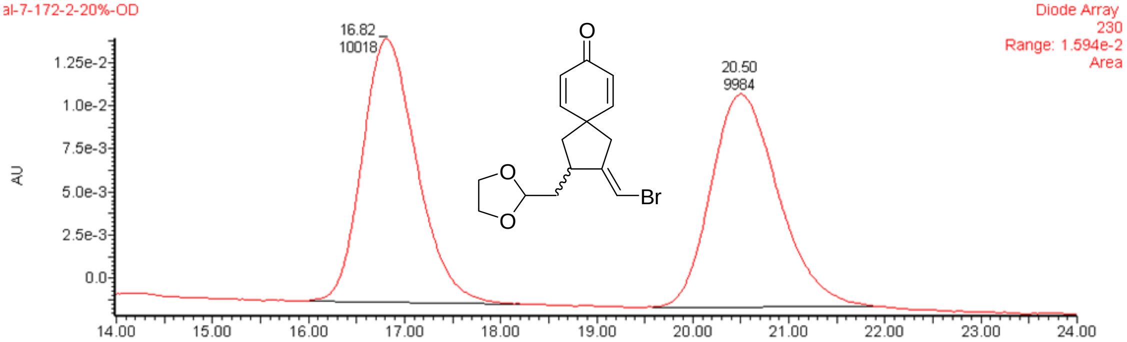


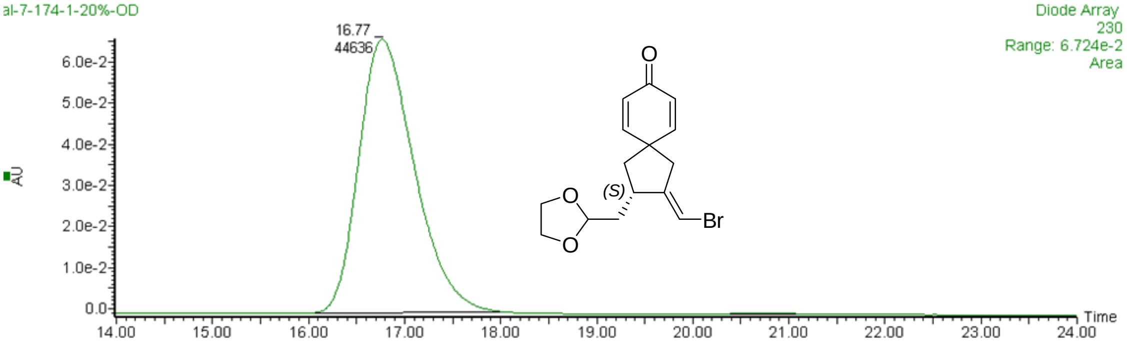
entry 2	mobile phase	t_r (*R*)	t_r (*S*)	*ee* (%)
(±)	*i*-PrOH:hexanes (20:80)	26.58 min	37.77 min	-
(*S*)	*i*-PrOH:hexanes (20:80)	26.90 min	37.07 min	97



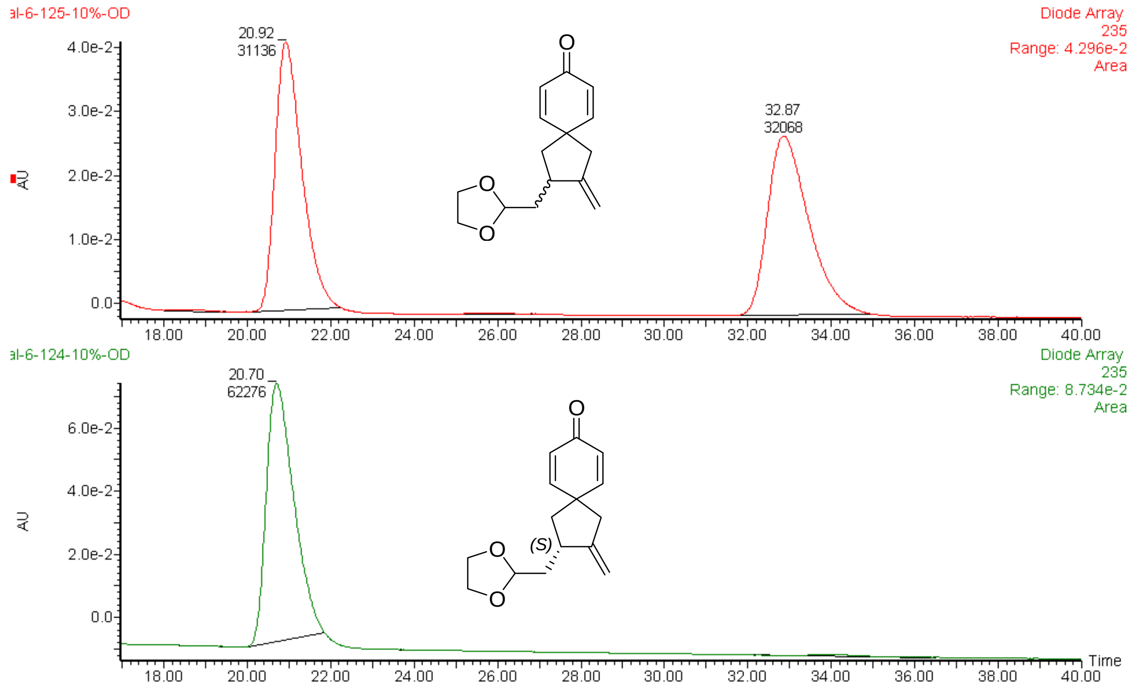


entry 6	mobile phase	t_r (*S*)	t_r (*R*)	*ee* (%)
(±)	*i*-PrOH:hexanes (10:90)	20.52 min	23.73 min	-
(*S*)	*i*-PrOH:hexanes (10:90)	20.75 min	24.93 min	93

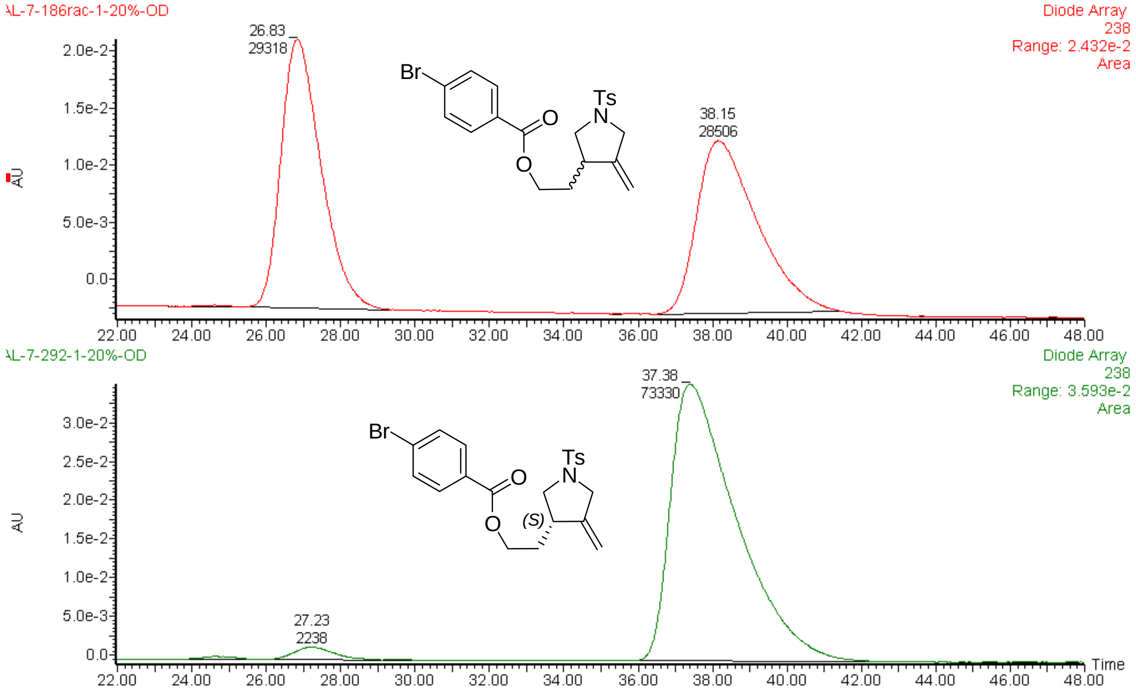




entry 11	mobile phase	t_r (*S*)	t_r (*R*)	*ee* (%)
(±)	*i*-PrOH:hexanes (20:80)	16.82 min	20.50 min	-
(*S*)	*i*-PrOH:hexanes (20:80)	16.77 min	-	>99

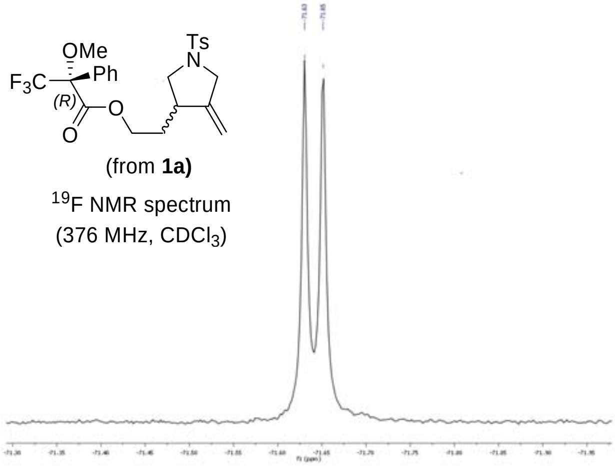


17	mobile phase	t_r (*S*)	t_r (*R*)	*ee* (%)
(±)	*i*-PrOH:hexanes (10:90)	20.92 min	32.87 min	-
(*S*)	*i*-PrOH:hexanes (10:90)	20.70 min	-	>99



Entry 13	mobile phase	t_r (*R*)	t_r (*S*)	*ee* (%)
(±)	*i*-PrOH:hexanes (10:90)	26.83 min	38.15 min	-
(*S*)	*i*-PrOH:hexanes (10:90)	27.23 min	37.38 min	94

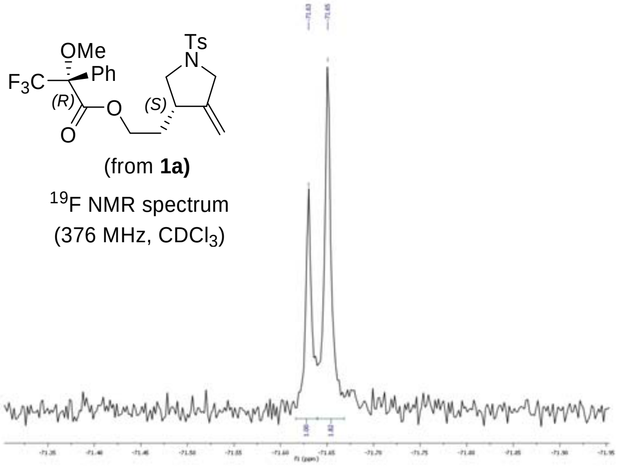
^{19}F and ^{1}H NMR spectroscopic analysis. For entries 3–5 and 7–10 in Table 2, enantiomeric excesses were determined by ^{19}F or ^{1}H NMR spectroscopic analysis of the Mosher esters derived from corresponding racemic and optically active aldehydes.



(from **1a)**

^{19}F NMR spectrum

(376 MHz, CDCl$_3$)

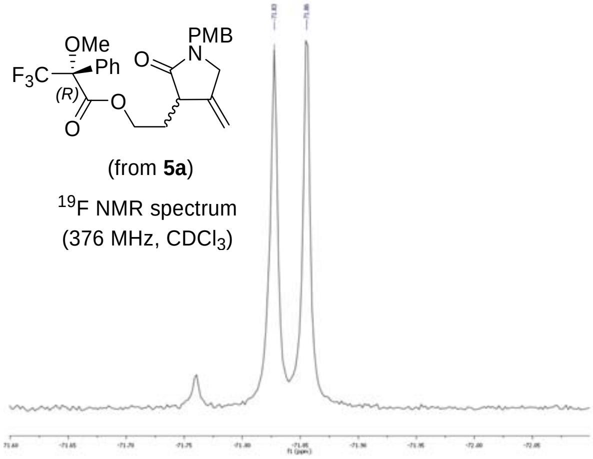


(from **1a)**

^{19}F NMR spectrum

(376 MHz, CDCl$_3$)

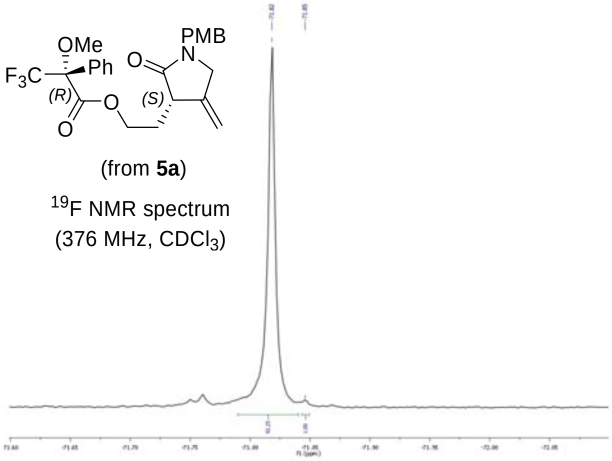
entry 3	chemical shift (*R*, *S*)	chemical shift (*R*, *R*)	*ee* (%)
(*R*, *S*) and (*R*, *R*)	–71.65 ppm	–71.63 ppm	-
(*R*, *S*)	–71.65 ppm	–71.63 ppm	29



(from **5a**)

^{19}F NMR spectrum

(376 MHz, CDCl$_3$)

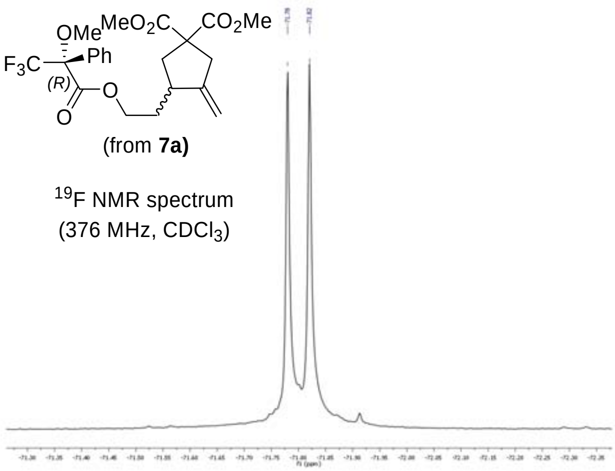


(from **5a**)

^{19}F NMR spectrum

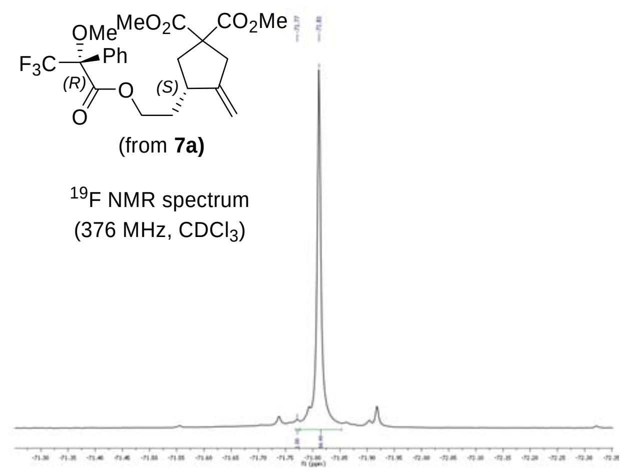
(376 MHz, CDCl$_3$)

entry 5	chemical shift (*R*, *S*)	chemical shift (*R*, *R*)	*ee* (%)
(*R*, *S*) and (*R*, *R*)	–71.83 ppm	–71.86 ppm	-
(*R*, *S*)	–71.82 ppm	–71.85 ppm	98



(from **7a**)

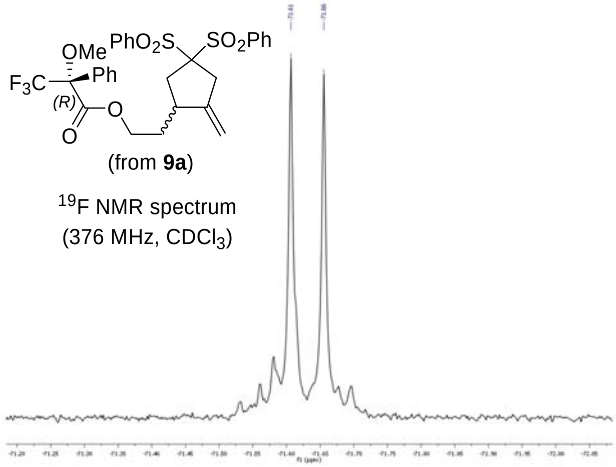
^{19}F NMR spectrum
(376 MHz, CDCl$_3$)



(from **7a**)

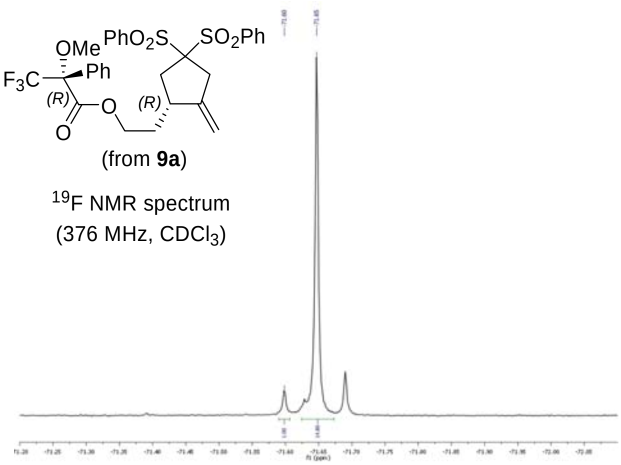
^{19}F NMR spectrum
(376 MHz, CDCl$_3$)

entry 7	chemical shift (*R*, *S*)	chemical shift (*R*, *R*)	*ee* (%)
(*R*, *S*) and (*R*, *R*)	–71.82 ppm	–71.78 ppm	-
(*R*, *S*)	–71.81 ppm	–71.77 ppm	97



(from **9a**)

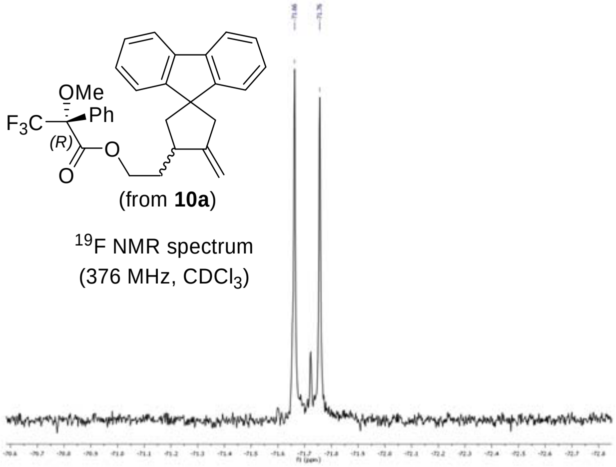
^{19}F NMR spectrum
(376 MHz, CDCl$_3$)



(from **9a**)

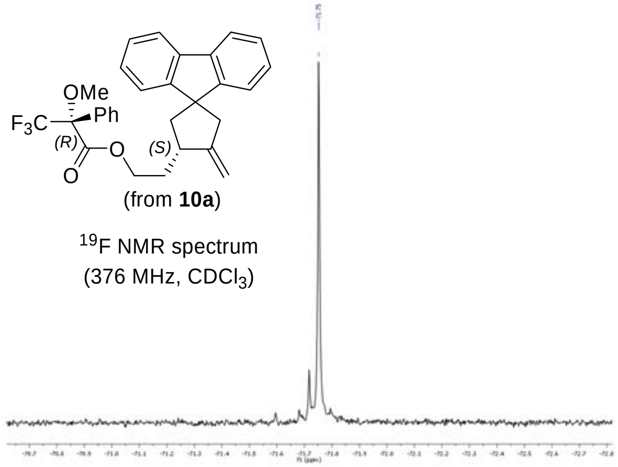
^{19}F NMR spectrum
(376 MHz, CDCl$_3$)

entry 9	chemical shift (*R*, *R*)	chemical shift (*R*, *S*)	*ee* (%)
(*R*, *R*) and (*R*, *S*)	–71.66 ppm	–71.61 ppm	-
(*R*, *R*)	–71.65 ppm	–71.60 ppm	87



(from **10a**)

^{19}F NMR spectrum
(376 MHz, CDCl$_3$)

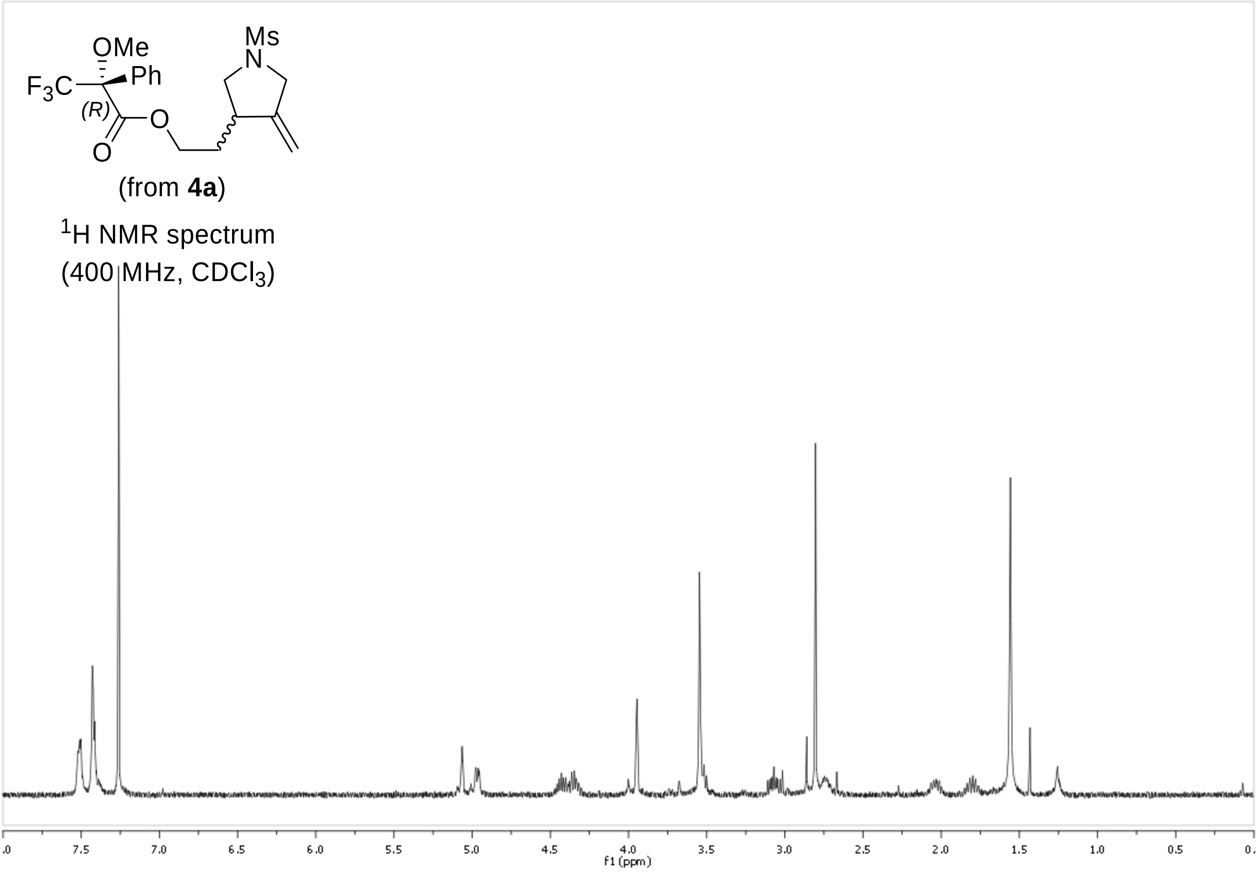


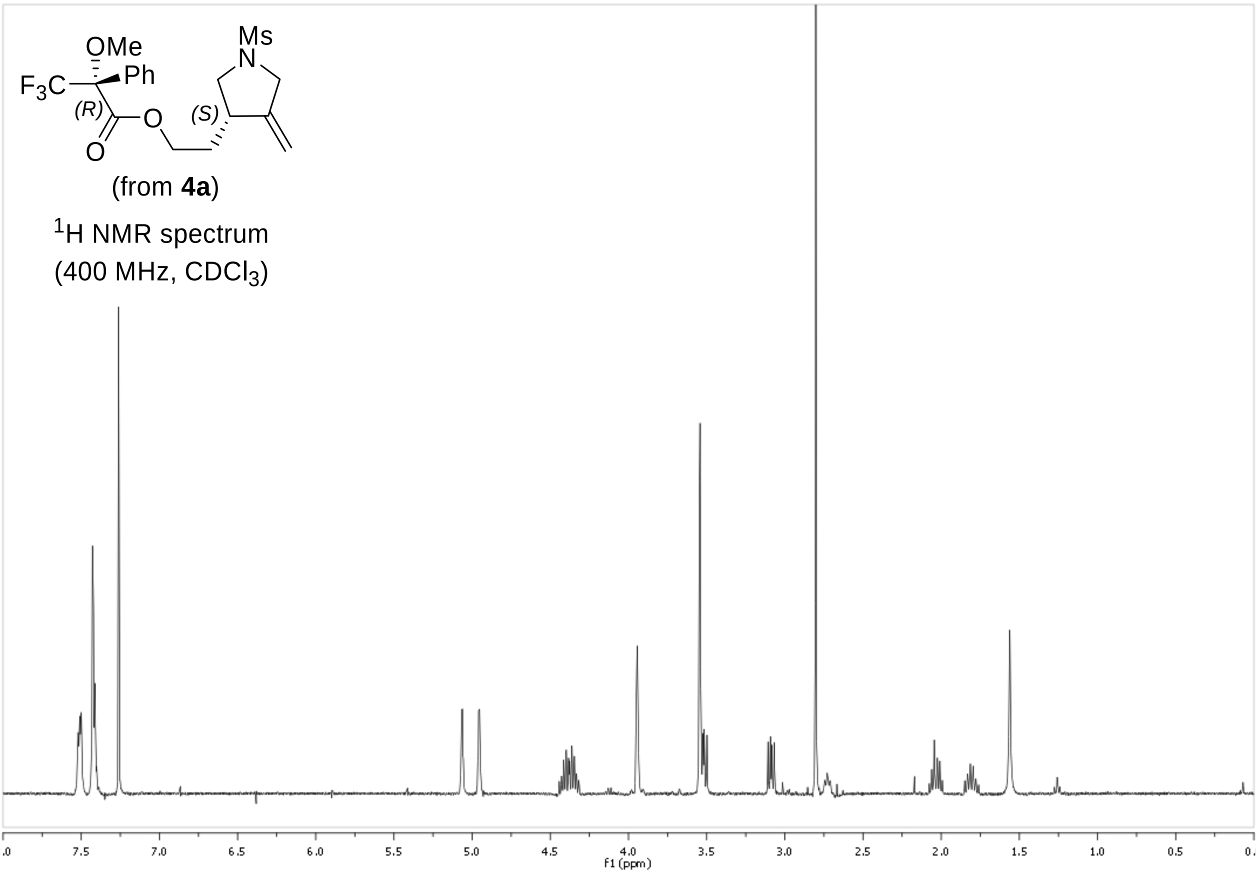
(from **10a**)

^{19}F NMR spectrum
(376 MHz, CDCl$_3$)

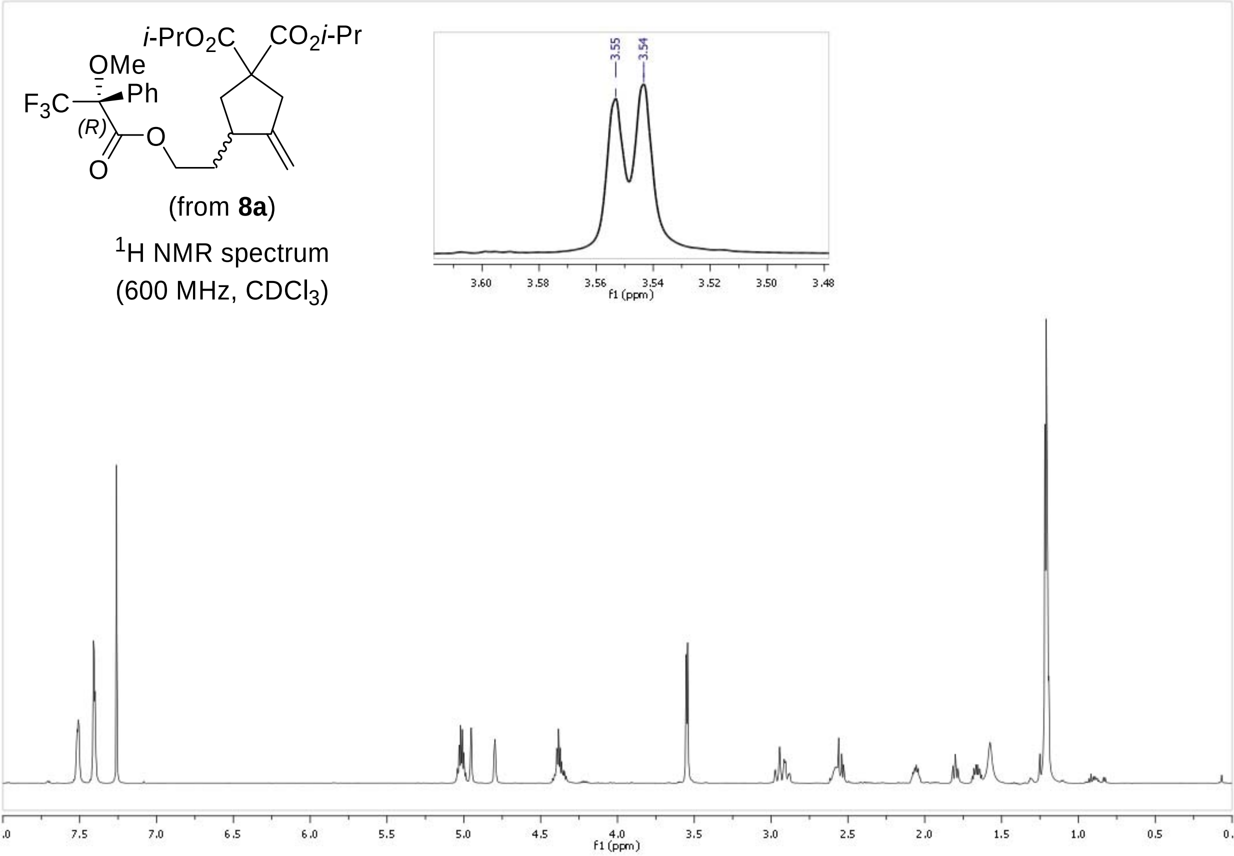
entry 10	chemical shift (*R*, *R*)	chemical shift (*R*, *S*)	*ee* (%)
(*R*, *R*) and (*R*, *S*)	–71.66 ppm	–71.76 ppm	-
(*R*, *S*)	-	–71.75 ppm	>98

Entry 4

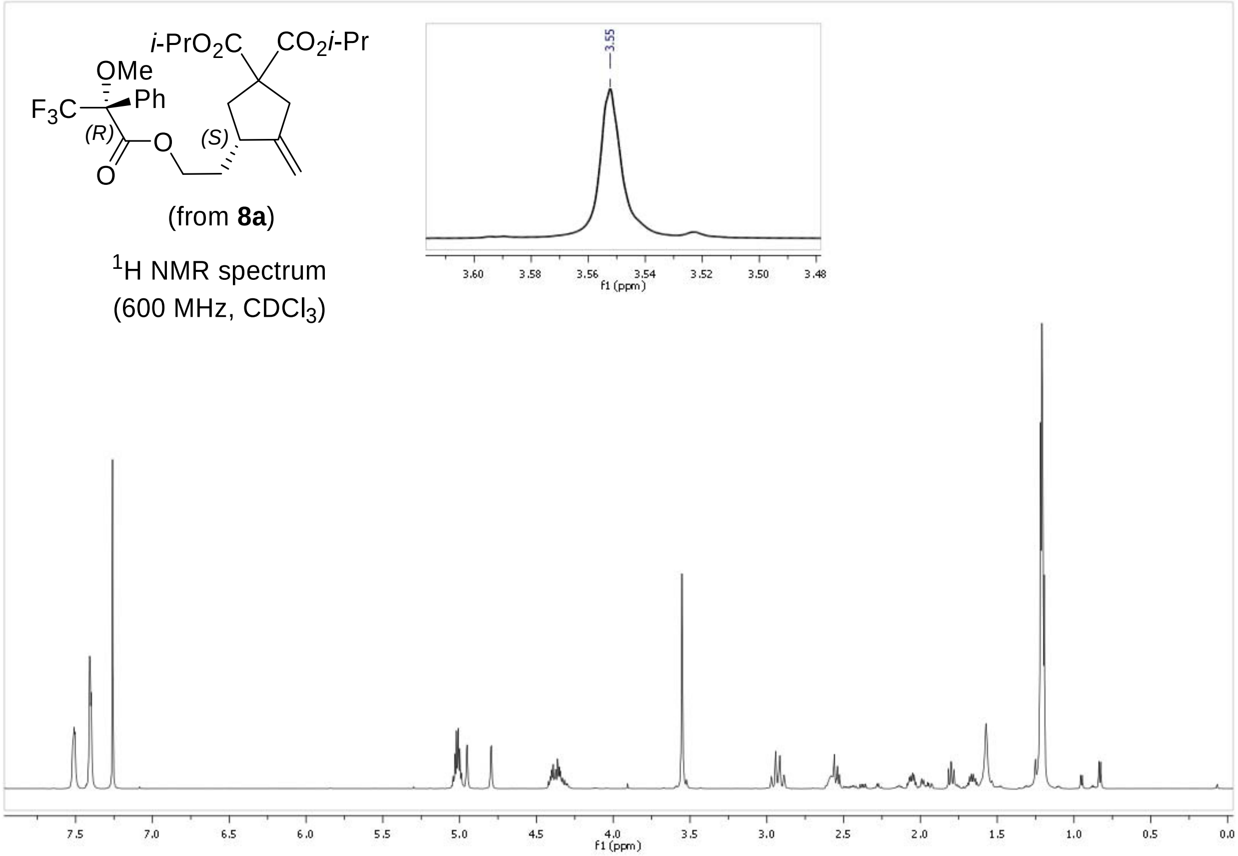

OMe
Ph
F3C
(R)
O
O
Ms
N
(from 4a)
1H NMR spectrum
(400 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OMe
Ph
F3C
(R)
O
O
(S)
Ms
N
(from 4a)
1H NMR spectrum
(400 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Entry 8

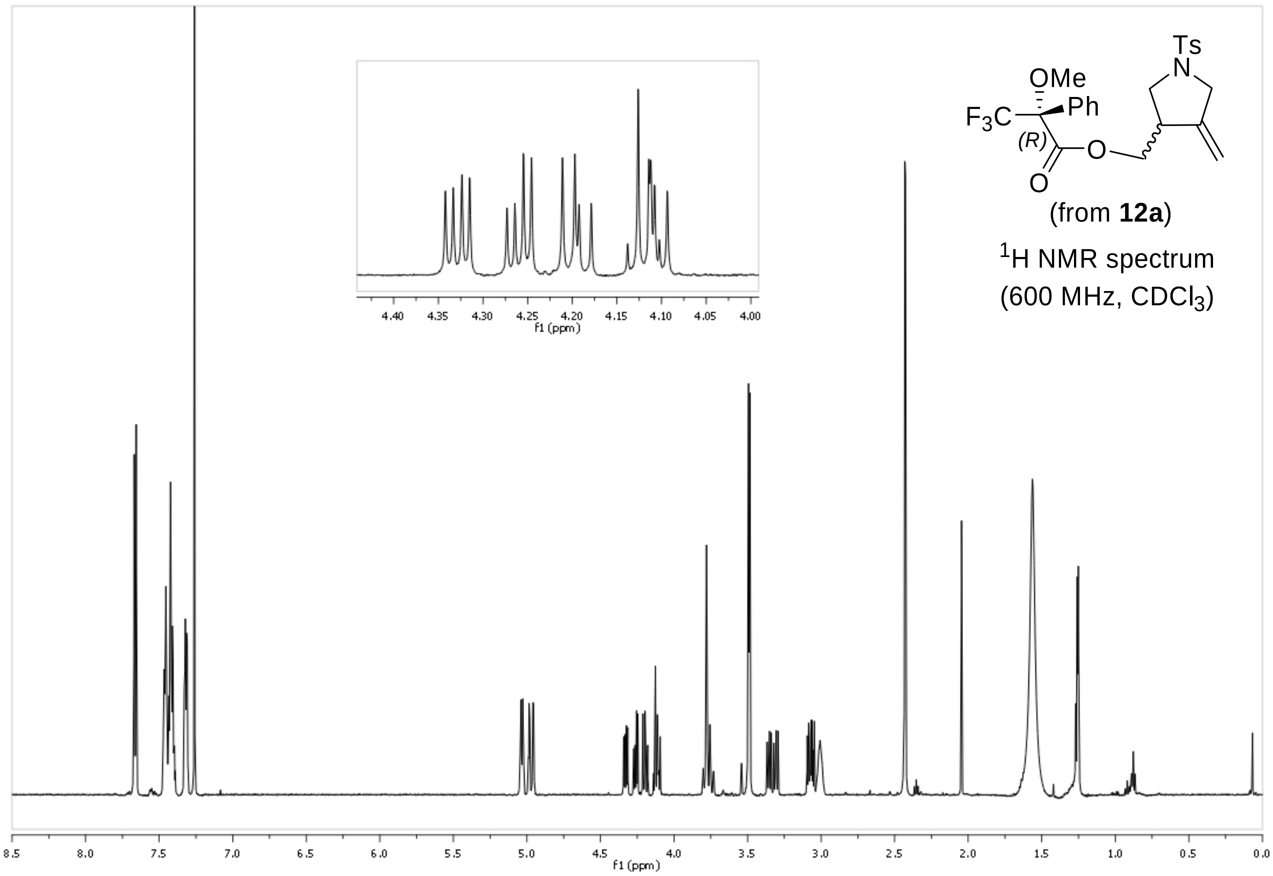


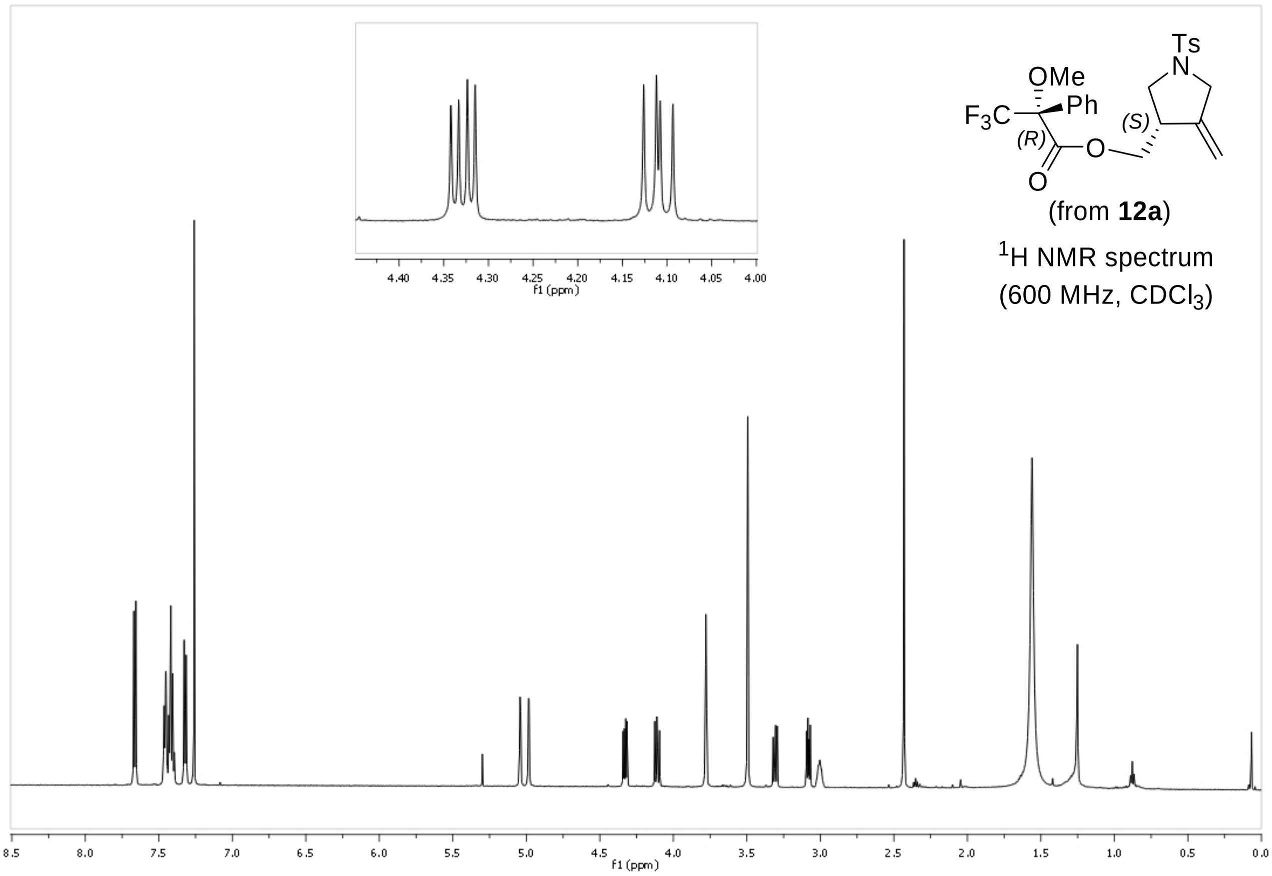
i-PrO₂C
CO₂i-Pr
OMe
Ph
F₃C
(R)
O
O
(from **8a**)
¹H NMR spectrum
(600 MHz, CDCl₃)
3.55
3.54
3.60
3.58
3.56
3.54
3.52
3.50
3.48
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



i-PrO₂C
CO₂i-Pr
OMe
Ph
F₃C
(R)
(S)
O
O
(from **8a**)
¹H NMR spectrum
(600 MHz, CDCl₃)
3.55
3.60
3.58
3.56
3.54
3.52
3.50
3.48
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Entry 12


Ts
N
OMe
Ph
F_3C
(R)
O
O
(from **12a**)
^1H NMR spectrum
(600 MHz, $CDCl_3$)
4.40
4.35
4.30
4.25
4.20
4.15
4.10
4.05
4.00
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ts
N
OMe
Ph
F_3C
(R)
(S)
O
O
(from **12a**)
^1H NMR spectrum
(600 MHz, $CDCl_3$)
4.40
4.35
4.30
4.25
4.20
4.15
4.10
4.05
4.00
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)