Supporting information for

Pd-catalyzed Tandem sp^2-sp^3 Coupling Reactions of Chiral Stannolanes: an Efficient Preparation of Optically Active Tetrahydrobenz[f]isoindoles

Akio Kamimura,*[,1] Masahiro So,[1] Shingo Ishikawa,[1] and Hidemitsu Uno[2]

[1]*Department of Applied Molecular Science, Graduate School of Medicine, Yamaguchi University, Ube 755-8611, Japan,*

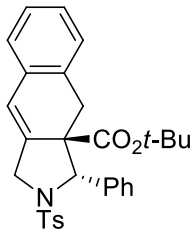
[2]*Department of Chemistry, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan*

Contents

General

All ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-ECA500 Delta2 (500 MHz for ^{1}H, 125 MHz for ^{13}C, and 186 MHz for ^{119}Sn) spectrometer. All the reactions in this paper were performed under nitrogen atmosphere unless otherwise mentioned. CH_2Cl_2 was dried over CaH_2, and distilled under nitrogen before use. Dry THF was purchased from Kanto Kagaku Co. Ltd. High resolution mass spectra (HRMS) were measured at Tokiwa Instrumentation Centre, Yamaguchi University, or Integrated Centre for Sciences, Ehime University, Matsuyama, Japan.

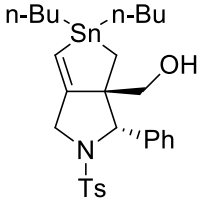
Preparation of (3*S*,3a*R*)-*tert*-butyl 3-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole-3a-carboxylate (2a)



A mixture of **1a** (134.9 mg, 0.21 mmol), Pd(*t*-$Bu_3P)_2$ (105.6 mg, 0.2 mmol), 1,2-dibromobenzene (0.02 mL, 0.20 mmol) and CsF (156.0 mg, 1.00 mmol) in dioxane (4 mL) was heated at 100 ºC for 24 h. After cooled the reaction mixture was filted through celite and the filtrate was concentrated. Obtained crude mixture was purified by flash chromatography (silica gel/hexane-EtOAc 4:1), giving **2a** in 41% yield (42.3 mg, 0.084 mmol). White solid; mp 105 – 106 ºC; $[\alpha]_D$ = +95.6 (c 0.57, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2 H), 7.21 (br, 3 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 7.06 (t, *J* = 7.4 Hz, 2 H), 6.99 (m, 3 H), 6.90 (d, *J* = 7.4 Hz, 1 H), 6.50 (s, 1 H), 5.30 (s, 1 H), 4.52 (dd, *J* = 14.0, 2.4 Hz, 1 H), 4.37 (dd, *J* = 14.0, 1.4 Hz, 1 H), 2.65 (d, *J* = 15.6 Hz, 1 H), 2.34 (s, 3 H), 2.10 (d, *J* = 15.5 Hz, 1 H), 1.19 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.24, 143.15, 139.01, 137.75, 135.84, 132.70, 132.57, 129.41 129.39 (2C), 128.53, 127.88 (2C), 127.87, 127.40 (2C), 127.38, 126.86 (2C), 126.03, 122.49, 82.13, 70.74, 58.28, 51.84, 34.96, 27.60 (3C), 21.52; IR ($CHCl_3$) ν 2976, 1717, 1343, 1153,

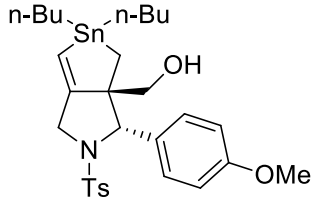
1094 cm^{-1}; Anal. Calcd. for $C_{30}H_{31}NO_4S$: C, 71.83; H, 6.23; N, 2.79. Found: C, 71.48; H, 6.31; N, 2.87.

Preparation of (*3S,3aS*)-5,5-dibutyl-3a-hydroxymethyl-3-phenyl-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole (3a)



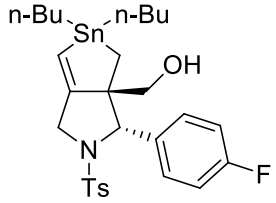
Under nitrogen atmosphere, DIBAL (1.0 M, 5.9 mL, 5.9 mmol, 3.0 eq) was added to a solution of **1a** (1.289 g, 1.957 mmol) in CH_2Cl_2 (10 mL) at –78°C, and the reaction mixture was stirred for 3 h at the same temperature. Then the reaction mixture was warmed to room temperature for an additional 30 min. Aqueous saturated Rochelle's salt (15 mL) was added to the reaction mixture, and the resulting solution was stirred for 3 h. The solution was extracted with EtOAc (30 mL x 3). The organic phase was combined, washed with brine (10 mL), and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 10:1 then 5:1) to give **3a** in 84% yield as a pale yellow oil (0.972 g, 1.65 mmol). $[\alpha]_D$ +1.60 (c 1.18, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.1 Hz, 2 H), 7.14 (d, J = 5.8 Hz, 3 H), 7.09 (d, J = 8.3 Hz, 2 H), 6.92 (s, 2 H), 6.46 (s, 1 H, J^{119}Sn–^{1}H = 111.8 Hz), 4.85 (s, 1 H), 4.23 (dd, J = 14.1, 2.1 Hz, 1 H), 4.05 (d, J =14.1 Hz, 1 H), 3.40 – 3.60 (br, 1H), 3.31 (t, J = 9.5 Hz, 1 H), 3.14 (dd, J = 10.5, 4.2 Hz, 1 H), 2.34 (s, 3 H), 1.75 (dd, J =8.0, 4.2 Hz, 1 H), 1.57 – 0.80 (m, 12 H), 0.84 (t, J = 7.3 Hz, 3 H), 0.74 (t, J =7.1 Hz, 3 H), 0.09 (d, J =12.9 Hz, 1 H, J^{119}Sn–^{1}H = 54.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 143.0, 140.4, 136.1, 129.3 (2C), 128.1(2C), 127.9, 127.3 (2C), 127.2 (2C), 127.0, 69.2, 68.1, 65.2, 50.4, 29.2, 28.8, 27.1, 27.0, 21.5, 13.7, 13.6, 13.5, 12.3, 12.0; ^{119}Sn NMR (186 MHz, $CDCl_3$) δ 134.5; IR (neat) ν 3501, 2922, 1337, 1157, 1098 cm^{-1}; HRMS (EI M+) m/z 589.1666. Calcd for $C_{28}H_{39}NO_3SSn$ m/z 589.1673.

Preparation of (*3S,3aS*)-5,5-dibutyl-3a-hydroxymethyl-3-(4-methoxyphenyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-*c*]pyrrole (3b)



Under nitrogen atmosphere, DIBAL (1.0 M, 6.9 mL, 6.9 mmol, 3.0 equiv) was added to a solution of (3*S*,3a*S*)-tert-butyl 5,5-dibutyl-3-(4-methoxyphenyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (1.578 g, 2.292 mmol) in CH_2Cl_2 (11 mL) at –78°C, and the reaction mixture was stirred for 3 h at the same temperature. Then the reaction mixture was warmed to room temperature for an additional 3 h. Aqueous saturated Rochelle's salt (15 mL) was added to the reaction mixture, and the resulting solution was stirred for 3 h. The solution was extracted with EtOAc (30 mL x 3). The organic phase was combined, washed with brine (10 mL), and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 10:1 then 5:1) to give **3b** in 92% yield as colorless oil (1.300 g, 2.103 mmol). $[\alpha]_D$ +8.0 (c 1.21, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.84 (br, 2H), 6.67 (d, *J* = 8.1 Hz, 2H), 6.46 (s, 1H, J^{119}Sn–^{1}H = 112.4 Hz), 4.79 (s, 1H), 4.21 (d, *J* = 13.9 Hz, 1H), 4.02 (d, *J* = 14.1 Hz, 1H), 3.76 (s, 3H), 3.40 – 3.60 (br, 1H), 3.30 (dd, *J* = 9.9, 9.0 Hz, 1H), 3.14 (dd, *J* = 10.8, 5.1 Hz, 1H), 2.35 (s, 3H), 1.54 – 1.44 (m, 4H), 1.30 – 1.01 (m, 8H), 0.85 (t, *J* = 7.3 Hz, 4H), 0.77 (t, *J* = 6.0 Hz, 3H), 0.16 (d, *J* = 12.9 Hz, 1H, J^{119}Sn–^{1}H = 57.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 158.9, 142.9, 136.1, 132.7, 129.2 (2C), 128.9(2C), 127.2 (2C), 126.9, 113.5 (2C), 69.2, 67.7, 65.2, 55.3, 50.3, 29.2 (J^{119}Sn–^{13}C = 21.8 Hz), 28.9 (J^{119}Sn–^{13}C = 22.2 Hz), 27.1 (J^{119}Sn–^{13}C = 54.4 Hz), 27.0 (J^{119}Sn–^{13}C = 56.7 Hz), 21.5, 13.7, 13.6, 13.5, 12.3, 12.0; ^{119}Sn NMR (186 MHz, $CDCl_3$) δ 134.4; IR (neat) *v* 3499, 2926, 1337, 1157, 1098 cm^{-1}; HRMS (EI M^+) *m/z* 619.1807. calcd for $C_{29}H_{41}NO_4SSn$ 619.1778.

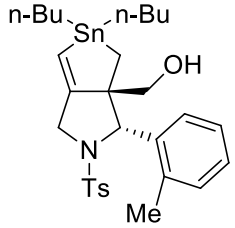
Preparation of (3*S*,3a*S*)-5,5-dibutyl-3-(4-fluorophenyl)-3a-hydroxymethyl-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-*c*]pyrrole (3c)



Under nitrogen atmosphere, DIBAL (1.0 M, 6.9 mL, 6.9 mmol, 3.0 equiv) was added to a solution of (3*S*,3a*S*)-*tert*-butyl 5,5-dibutyl-3-(4-fluorophenyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (1.551 g, 2.292 mmol) in CH_2Cl_2 (11 mL) at –78°C, and the reaction mixture was stirred for 3 h at the same temperature. Then the reaction mixture was warmed to room temperature for an additional 3 h Aqueous saturated Rochelle's salt (15 mL) was added to the reaction mixture, and the resulting solution was stirred for 3 h. The solution was extracted with EtOAc (30 mL x 3). The organic phase was combined, washed with brine (10 mL), and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 8:1 then 3:1) to give **3c** in 84% yield as colorless oil (1.161 g, 1.915 mmol). $[\alpha]_D$ +0.4 (c 1.04, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.96 – 6.87 (m, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.47 (s, 1H, J^{119}Sn–^{1}H = 112.3 Hz), 4.84 (s, 1H), 4.21 (dd, *J* = 14.0, 2.2 Hz, 1H), 4.05 (dd, *J* = 14.0, 1.5 Hz, 1H), 3.40 – 3.60 (br, 1H), 3.27 (dd, *J* = 10.8, 8.6 Hz, 1H), 3.11 (dd, *J* = 11.5, 4.9 Hz, 1H), 2.36 (s, 3H), 1.54 – 1.44 (m, 4H), 1.29 – 1.01 (m, 8H), 0.85 (t, *J* = 7.3 Hz, 3H), 0.76 (t, *J* = 7.0 Hz, 4H), 0.06 (d, *J* = 12.9 Hz, 1H, J^{119}Sn–^{1}H = 57.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, J^{19}F–^{13}C = 245.8 Hz), 159.9, 143.2, 136.5 (d, J^{19}F–^{13}C = 3.1 Hz), 135.99, 135.98, 129.3 (2C), 127.3 (2C, d, J^{19}F–^{13}C = 8.9 Hz), 127.2 (2C), 115.0 (2C, d, J^{19}F–^{13}C = 22.1 Hz), 68.9, 67.3, 65.3, 50.4, 29.1 (J^{119}Sn–^{13}C = 22.1 Hz), 28.9 (J^{119}Sn–^{13}C = 22.1 Hz), 27.1 (J^{119}Sn–^{13}C = 54.3 Hz), 27.0 (J^{119}Sn–^{13}C = 55.2 Hz), 21.5, 13.7, 13.6, 13.5, 12.3, 11.9; ^{119}Sn NMR (186 MHz, $CDCl_3$) δ 134.6; IR (neat) *v* 3512, 2922, 1337, 1225, 1157, 1096

cm^{-1}; HRMS (EI M^+) *m/z* 607.1601. calcd for $C_{28}H_{38}FNO_3SSn$ 607.1578.

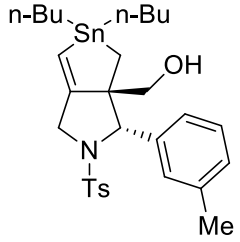
Preparation of (3S,3aS)-5,5-dibutyl-3a-hydroxymethyl-3-(o-tolyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole (3d)



Under nitrogen atmosphere, DIBAL (1.0 M, 9.2 mL, 9.2 mmol, 3.0 equiv) was added to a solution of (3*S*,3a*S*)-*tert*-butyl 5,5-dibutyl-3-(*o*-tolyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (2.054 g, 3.054 mmol) in CH_2Cl_2 (15 mL) at –78°C, and the reaction mixture was stirred for 3 h at the same temperature. Then the reaction mixture was warmed to room temperature for an additional 3 h. Aqueous saturated Rochelle's salt (15 mL) was added to the reaction mixture, and the resulting solution was stirred for 20 h. The solution was extracted with EtOAc (20 mL x 3). The organic phase was combined, washed with brine (10 mL), and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 8:1 then 5:1) to give **3d** in 81% yield as pale yellow oil (1.495 g, 2.481 mmol). $[\alpha]_D$ +24.4 (c 1.22, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.04 (dt, *J* = 14.4, 7.2 Hz, 2H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.46 (s, 1H, J^{119}Sn–^{1}H = 113.0 Hz), 5.23 (s, 1H), 4.22 (d, *J* = 14.0 Hz, 1H), 4.09 (d, *J* = 14.2 Hz, 1H), 3.25 (t, *J* = 8.0 Hz, 1H), 3.10 (dd, *J* = 10.5, 4.9 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 1.63 – 1.44 (m, 2H), 1.25 (dt, *J* = 14.8, 7.4 Hz, 3H), 1.29 – 0.99 (m, 8H), 0.89 – 0.81 (m, 4H), 0.73 (t, *J* = 7.0 Hz, 3H), 0.04 (d, *J* = 12.8 Hz, 1H, J^{119}Sn–^{1}H = 57.9 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 143.1, 139.0, 136.0, 135.9, 129.8, 129.3 (2C), 127.2 (2C), 127.1, 126.9, 126.6, 126.0, 69.0, 65.3, 63.3, 50.6, 29.2 (J^{119}Sn–^{13}C = 22.2 Hz), 28.7 (J^{119}Sn–^{13}C = 22.2 Hz), 27.1 (J^{119}Sn–^{13}C = 55.6 Hz), 27.0 (J^{119}Sn–^{13}C = 55.8

Hz), 21.5, 19.9, 13.7, 13.6, 13.5, 12.2, 11.0; ^{119}Sn NMR (186 MHz, $CDCl_3$) δ 136.1; IR (neat) *v* 3524, 2920, 1337, 1157, 1096 cm^{-1}; HRMS (EI M^+) *m/z* 603.1788. calcd for $C_{29}H_{41}NO_3SSn$ 603.1829.

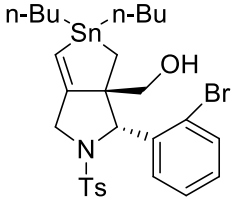
Preparation of (3S,3aS)-5,5-dibutyl-3a-hydroxymethyl-3-(m-tolyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole (3e)



Under nitrogen atmosphere, DIBAL (1.0 M, 7.1 mL, 7.1 mmol, 3.0 equiv) was added to a solution of (3S,3aS)-tert-butyl 5,5-dibutyl-3-(m-tolyl)-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (1.581 g, 2.351 mmol) in CH_2Cl_2 (12 mL) at –78°C, and the reaction mixture was stirred for 3 h at the same temperature. Then the reaction mixture was warmed to room temperature for an additional 3 h. Aqueous saturated Rochelle's salt (15 mL) was added to the reaction mixture, and the resulting solution was stirred for 2 h. The solution was extracted with EtOAc (20 mL x 3). The organic phase was combined, washed with brine (10 mL), and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 8:1 then 5:1) to give **3e** in 81% yield as pale yellow oil (1.259 g, 2.091 mmol). $[\alpha]_D$ –3.3 (c 1.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.03 (t, *J* = 6.7 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.70 – 6.77 (br, 1H), 6.60 – 6.65 (br, 1H), 6.46 (s, 1H, J^{119}Sn–^{1}H = 111.3 Hz), 4.78 (s, 1H), 4.23 (dd, *J* = 14.1, 2.1 Hz, 1H), 4.05 (d, J = 13.8 Hz, 1H), 3.31 (dd, *J* = 9.8, 8.8 Hz, 1H), 3.16 (dd, *J* = 10.6, 4.8 Hz, 1H), 2.35 (s, 3H), 2.17 (s, 3H), 1.60 – 1.43 (m, 4H), 1.31 – 1.00 (m, 8H), 0.92 – 0.81 (m, 4H), 0.75 (t, *J* = 7.2 Hz, 3H), 0.12 (d, *J* = 12.9 Hz, 1H, J^{119}Sn–^{1}H = 58.0 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 142.8, 140.1, 137.5, 136.1, 129.2 (2C), 128.1, 128.0, 127.9,

127.2 (2C), 126.8, 126.7, 69.2, 68.2, 65.2, 50.5, 29.2 (J^{119}Sn–^{13}C = 21.5 Hz), 28.7 (J^{119}Sn–^{13}C = 22.1 Hz), 27.1 (J^{119}Sn–^{13}C = 56.4 Hz), 27.0 (J^{119}Sn–^{13}C = 56.8 Hz), 21.5, 21.4, 13.7, 13.6, 13.5, 12.2, 12.0; ^{119}Sn NMR (186 MHz, $CDCl_3$) δ 134.5; IR (neat) *v* 3510, 2920, 1339, 1157, 1098 cm^{-1}; HRMS (EI M^+) *m/z* 603.1870. calcd for $C_{29}H_{41}NO_3SSn$ 603.1829.

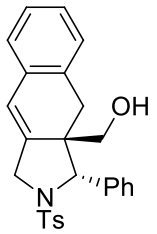
Preparation of (3S,3aS)-3-(2-bromophenyl)-5,5-dibutyl-3a-hydroxymethyl-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole (3f)



Under nitrogen atmosphere, DIBAL (1.0 M, 4.0 mL, 4.0 mmol, 3.0 equiv) was added to a solution of (3*S*,3a*S*)-*tert*-butyl 3-(2-bromophenyl)-5,5-dibutyl-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole-3a-carboxylate (0.971 g, 1.32 mmol) in CH_2Cl_2 (7 mL) at –78°C, and the reaction mixture was stirred for 3 h at the same temperature. Then the reaction mixture was warmed to room temperature for an additional 30 min. Aqueous saturated Rochelle's salt (15 mL) was added to the reaction mixture, and the resulting solution was stirred for 2 h. The solution was extracted with EtOAc (20 mL x 3). The organic phase was combined, washed with brine (10 mL), and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 8:1 then 5:1) to give **3f** in 55% yield as colorless oil (0.485 g, 0.726 mmol). $[\alpha]_D$ +56.8 (c 1.09, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.49 (s, 1H, J^{119}Sn–^{1}H = 110.2 Hz), 5.28 (s, 1H), 4.23 – 4.08 (m, 2H), 3.16 (t, *J* = 9.2 Hz, 1H), 2.94 (dd, *J* = 10.6, 4.1 Hz, 1H), 2.38 (s, 3H), 1.62 – 1.45 (m, 5H), 1.27 – 1.00 (m, 8 H), 0.89 (d, J = 13.2 Hz, 1H), 0.83 (t, *J* = 7.0 Hz, 3H), 0.72 (t, *J* = 7.0 Hz, 3H), 0.01 (d, *J* = 13.0 Hz, 1H, J^{119}Sn–^{1}H = 59.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ

158.9 (J^{117}Sn–^{13}C = 58.0 Hz, J^{119}Sn–^{13}C = 61.4 Hz), 143.6, 140.3, 135.1, 132.3, 129.6 (2C), 128.6, 128.0, 127.6, 127.5 (2C), 127.4, 124.1, 69.2, 66.7 (J^{119}Sn–^{13}C = 35.8 Hz), 65.4 (J^{119}Sn–^{13}C = 12.7 Hz), 51.0, 29.1 (J^{119}Sn–^{13}C = 22.3 Hz), 28.7 (J^{119}Sn–^{13}C = 57.2 Hz), 27.1 (J^{119}Sn–^{13}C = 35.8 Hz), 27.0 (J^{119}Sn–^{13}C = 55.3 Hz), 21.6, 14.3, 13.7, 13.5 (J^{117}Sn–^{13}C = 328.0 Hz, J^{119}Sn–^{13}C = 343.8.8 Hz), 12.2 (J^{117}Sn–^{13}C = 320.8 Hz, J^{119}Sn–^{13}C = 333.6 Hz), 11.7 (J^{117}Sn–^{13}C = 292.5 Hz, J^{119}Sn–^{13}C = 306.8 Hz); ^{119}Sn NMR (186 MHz, $CDCl_3$) δ 134.4; IR (neat) *v* 3526, 2922, 1341, 1157, 1096 cm^{-1}; HRMS (FAB+ M+H) *m/z* 668.0824. calcd for $C_{28}H_{39}NO_3BrSSn$ 668.0856.

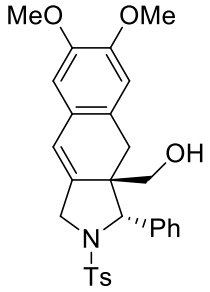
Preparation of ((*3S,3aR*)-3a-hydroxymethyl-3-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4a)



Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.015 g, 0.030 mmol), DABCO (0.096 g, 0.86 mmol) and 1,2-dibromobenzene (0.067 g, 0.28 mmol) in 1,4-dioxane (2.0 mL) was added to a solution of **3a** (0.168 g, 0.286 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 5:1 then 3:1) to give **4a** in 76% yield as viscose oil (0.094 g, 0.22 mmol). $[\alpha]_D$ +33.6. (c 1.83, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2 H), 7.18 (d, *J* = 4.2 Hz, 3 H), 7.14 (d, *J* = 8.1 Hz, 2 H), 7.07 (t, *J* = 7.4 Hz, 1 H), 7.11 – 6.98 (m, 2 H), 7.01 (t, *J* = 7.5 Hz, 1 H), 6.95 (d, *J* = 6.4 Hz, 1 H), 6.94 (d, *J* = 6.1 Hz, 1 H), 6.43 (s, 1 H), 5.29 (s, 1 H), 4.42 (dd, *J* = 15.1, 2.3 Hz, 1 H), 4.33 (dd, *J* = 15.1, 1.3 Hz, 1 H), 3.4 – 3.6 (br, 1H), 3.26 (d, *J* = 10.7 Hz, 1 H), 3.10 (d, *J* = 10.7 Hz, 1 H), 2.58 (d, *J* = 16.1 Hz, 1 H), 2.35 (s, 3 H), 2.08 (d, J = 16.0 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 139.9, 139.3, 135.7, 133.2, 132.3, 129.5 (2C), 128.8, 128.5 (2C), 127.5, 127.4, 127.3

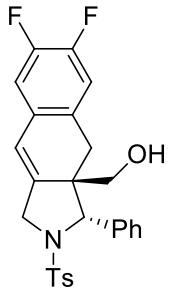
(2C), 126.8 (2C), 126.22, 126.21, 122.3, 69.1, 62.0, 53.0, 51.1, 31.8, 21.6; IR (neat) *v* 3512, 2924, 1339, 1157, 1096 cm^{-1}; HRMS (ESI+ M+Na) m/z 454.1447. Calcd for $C_{26}H_{25}NNaO_3S$ m/z 454.1453.

Preparation of (3S,3aR)-3a-hydroxymethyl-6,7-dimethoxy-3-phenyl-2-tosyl-2,3,3a,4,9,9a-hexahydro-1H-benzo[f]isoindole (4b)



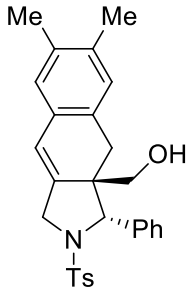
Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.010 g, 0.020 mmol), DABCO (0.066 g, 0.59 mmol) and 1,2-dibromo-4,5-dimethoxybenzene (0.058 g, 0.20 mmol) in 1,4-dioxane (2.0 mL) was added to a solution of **3a** (0.116 g, 0.197 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4b** in 73% yield as pale yellow oil (0.071g, 0.14 mmol). $[\alpha]_D$ –18.9 (c 1.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.17 (s, 3H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.04 (s, 2H), 6.51 (s, 1H), 6.50 (s, 1H), 6.34 (s, 1H), 5.26 (s, 1H), 4.39 (dd, *J* = 14.9, 2.3 Hz, 1H), 4.31 (dd, *J* = 15.0, 1.3 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.28 (d, *J* = 10.7 Hz, 1H), 3.09 (d, *J* = 10.7 Hz, 1H), 2.49 (d, *J* = 16.0 Hz, 1H), 2.35 (s, 3H), 2.10 – 2.40 (br, 1H), 2.02 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 147.4, 143.3, 140.0, 136.9, 135.7, 129.4 (2C), 129.3, 128.4 (2C), 127.4 (2C), 127.3 (2C), 125.6, 124.9, 121.8, 112.5, 110.0, 69.1, 61.8, 56.1, 55.9, 53.1, 50.9, 31.4, 21.6; IR (neat) *v* 3514, 2936, 1512, 1335, 1275, 1155, 1096cm^{-1}; HRMS (ESI+ M+Na) *m/z* 514.1664. calcd for $C_{28}H_{29}NNaO_5S$ 514.1664.

Preparation of (3S,3aR)-6,7-difluoro-3a-hydroxymethyl-3-phenyl-2-tosyl-2,3,3a,4,9,9a-hexahydro-1H-benzo[f]isoindole (4c)



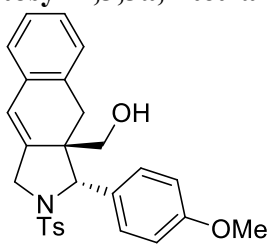
Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.092 g, 0.018 mmol), DABCO (0.061 g, 0.54 mmol) and 1,2-dibromo-4,5-difluorobenzene (0.049 g, 0.18 mmol) in 1,4-dioxane (2.0 mL) was added to a solution of **3a** (0.107 g, 0.182 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4c** in 78% yield as pale yellow oil (0.066g, 0.14 mmol). Pale yellow oil; $[\alpha]_D$ +30.2 (c 1.83, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.20 (s, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.03 (s, 2H), 6.80 – 6.72 (m, 2H), 6.33 (s, 1H), 5.25 (s, 1H), 4.42 (dd, *J* = 15.3, 2.2 Hz, 1H), 4.32 (d, *J* = 15.5 Hz, 1H), 3.23 (d, *J* = 10.6 Hz, 1H), 3.10 (d, *J* = 10.3 Hz, 1H), 2.51 (d, *J* = 16.1 Hz, 1H), 2.37 (s, 3H), 1.98 (d, *J* = 16.0 Hz, 1H), 1.67 – 1.75 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0 (dd, $J^{19}F–^{13}C$ = 248.4, 12.9 Hz), 148.8 (dd, $J^{19}F–^{13}C$ = 245.8, 12.8 Hz), 143.5, 140.3 (d, $J^{19}F–^{13}C$ = 2.6 Hz), 139.5, 135.6, 129.8 (t, $J^{19}F–^{13}C$ = 4.3 Hz), 129.5 (2C), 128.8 (dd, $J^{19}F–^{13}C$ = 8.2, 4.3 Hz), 128.6 (2C), 127.6 (2C), 127.5, 127.3 (2C), 120.6 (t, $J^{19}F–^{13}C$ = 1.5 Hz), 117.8 ($J^{19}F–^{13}C$ = 18.1 Hz), 114.7 ($J^{19}F–^{13}C$ = 17.8 Hz), 68.9, 61.6, 52.8, 50.8, 31.1, 21.6; IR (neat) *v* 3503, 2924, 1337, 1308, 1153, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 490.1251. calcd for $C_{26}H_{23}F_2NNaO_3S$ 490.1264.

Preparation of (3S,3aR)-3a-hydroxymethyl-6,7-dimethyl-3-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4d)



Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.099 g, 0.019 mmol), DABCO (0.069 g, 0.61 mmol) and 1,2-dibromo-4,5-dimethylbenzene (0.055 g, 0.21 mmol) in 1,4-dioxane (2.0 mL) was added to a solution of **3a** (0.121 g, 0.206 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4d** in 64% yield as white solid (0.061g, 0.13 mmol). mp 162.0 – 163.0 °C; $[\alpha]_D$ +1.2 (c 1.58, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.17 (s, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.04 (s, 2H), 6.73 (s, 1H), 6.72 (s, 1H), 6.37 (s, 1H), 5.22 (s, 1H), 4.39 (dd, *J* = 14.9, 2.3 Hz, 1H), 4.31 (dd, *J* = 15.0, 1.5 Hz, 1H), 3.45 – 3.63 (br, 1H), 3.27 (dd, J = 10.7, 4.5 Hz, 1H), 3.09 (dd, *J* = 10.4, 4.9 Hz, 1H), 2.45 (d, *J* = 16.1 Hz, 1H), 2.36 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 2.02 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 140.0, 137.9, 135.9, 135.8, 134.7, 130.4, 130.2 (2C), 129.9, 129.4 (2C), 128.4, 127.6 – 127.8 (br), 127.6 (2C), 127.4, 127.3 (2C), 122.1, 69.1, 62.2, 53.1, 50.9, 31.3, 21.6, 19.5, 19.3; IR (neat) *v* 3493, 2924, 1323, 1157, 1098 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 482.1757. calcd for $C_{28}H_{29}NNaO_3S$ 482.1766.

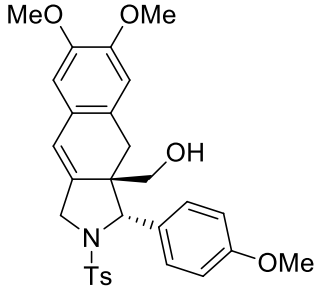
Preparation of (3S,3aR)-3a-hydroxymethyl-3-(4-methoxyphenyl)-6,7-dimethyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4e)



Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.097 g, 0.019 mmol), DABCO (0.065 g, 0.58

mmol) and 1,2-dibromobenzene (0.045 g, 0.19 mmol) in 1,4-dioxane (1.9 mL) was added to a solution of **3b** (0.118 g, 0.19 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4e** in 71% yield as pale yellow oil (0.063g, 0.14 mmol). $[\alpha]_D$ +8.5 (c 2.09, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.02 (td, *J* = 7.4, 1.3 Hz, 1H), 6.91 – 6.98 (m, 4H), 6.73 (br, 2H), 6.43 (s, 1H), 5.21 (s, 1H), 4.40 (dd, *J* = 15.1, 2.3 Hz, 1H), 4.30 (dd, *J* = 15.1, 1.5 Hz, 1H), 3.76 (s, 3H), 3.26 (d, *J* = 10.4 Hz, 1H), 3.10 (d, *J* = 10.5 Hz, 1H), 2.53 (d, *J* = 16.1 Hz, 1H), 2.37 (s, 3H), 2.15 (d, *J* = 15.9 Hz, 1H), 1.60 – 1.65 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 143.2, 139.4, 135.8, 133.2, 132.3, 132.0, 129.4 (2C), 128.6 – 129.1 (2C, br) 128.8, 127.5, 127.3 (2C), 126.8, 126.2, 122.3, 113.8 (2C), 68.7, 62.1, 55.3, 53.0, 50.8, 31.8, 21.6; IR (neat) *v* 3524, 2934, 1339, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 484.1549. calcd for $C_{27}H_{27}NNaO_4S$ 484.1558.

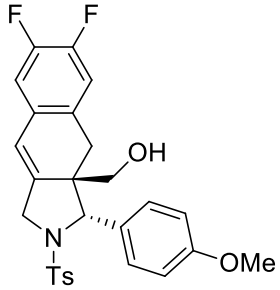
Preparation of (3S,3aR)-3a-hydroxymethyl-6,7-dimethoxy-3-(4-methoxyphenyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4f)



Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.010 g, 0.020 mmol), DABCO (0.067 g, 0.60 mmol) and 1,2-dibromo-4,5-dimethoxybenzene (0.059 g, 0.20 mmol) in 1,4-dioxane (2.0 mL) was added to a solution of **3b** (0.123 g, 0.199 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:3) to give **4f** in 64% yield as pale yellow oil

(0.066g, 0.13 mmol). $[\alpha]_D$ –32.7 (c 2.07, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.96 (br, 2H), 6.72 (br, 2H), 6.51 (s, 1H), 6.50 (s, 1H), 6.34 (s, 1H), 5.19 (s, 1H), 4.38 (dd, *J* = 14.9, 2.4 Hz, 1H), 4.28 (dd, *J* = 15.0, 1.5 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.28 (d, *J* = 10.4 Hz, 1H), 3.10 (d, *J* = 10.6 Hz, 1H), 2.45 (d, *J* = 16.0 Hz, 1H), 2.37 (s, 3H), 2.10 (d, *J* = 16.1 Hz, 1H), 1.55 – 1.62 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 148.1, 147.4, 143.2, 137.1, 135.8, 132.1, 129.4 (2C), 128.7 – 129.2 (2C, br), 127.3 (2C), 125.7, 124.9, 121.7, 112.5, 113.5 – 114.1 (2C, br), 110.0, 68.7, 61.9, 56.1, 55.9, 55.3, 53.0, 50.7, 31.4, 21.6; IR (neat) *v* 3503, 2936, 1335, 1157, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 544.1767. calcd for $C_{29}H_{31}NNaO_6S$ 544.1770.

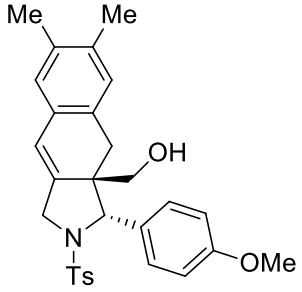
Preparation of (3S,3aR)-6,7-difluoro-3a-hydroxymethyl-3-(4-methoxyphenyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4g)



Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.010 g, 0.020 mmol), DABCO (0.065 g, 0.58 mmol) and 1,2-dibromo-4,5-difluorobenzene (0.053 g, 0.19 mmol) in 1,4-dioxane (1.9 mL) was added to a solution of **3b** (0.120 g, 0.193 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4g** in 70% yield as pale yellow oil (0.067g, 0.14 mmol). $[\alpha]_D$ +14.0 (c 2.17, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.93 (br, 2H), 6.79 – 6.75 (m, 2H), 6.70 – 6.80 (br, 2H), 6.33 (s, 1H), 5.20 (s, 1H), 4.39 (dd, *J* = 15.3, 2.1 Hz, 1H), 4.29 (d, *J* = 15.8 Hz, 1H), 3.76 (s, 3H), 3.22 (d, *J* = 10.6 Hz, 1H), 3.11 (d, *J* = 10.5 Hz, 1H), 2.50 (d, *J* = 16.2 Hz,

1H), 2.37 (s, 3H), 2.04 (d, J = 15.6 Hz, 1H), 1.67 – 1.72 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 149.1 (dd, $J^{19}F–^{13}C$ = 248.6, 12.7 Hz), 148.8 (dd, $J^{19}F–^{13}C$ = 245.7, 13.0 Hz), 143.4, 140.4 (d, $J^{19}F–^{13}C$ = 3.6 Hz), 135.7 (d, $J^{19}F–^{13}C$ = 1.3 Hz), 131.6, 129.9 (dd, $J^{19}F–^{13}C$ = 5.3, 4.2 Hz), 129.4 (2C), 128.9 (dd, $J^{19}F–^{13}C$ = 6.2, 3.3 Hz), 128.5 – 129.0 (2C, br), 127.3 (2C), 120.6, 117.8 (d, $J^{19}F–^{13}C$ = 18.0 Hz), 114.7 (d, $J^{19}F–^{13}C$ = 17.9 Hz), 113.7 – 114.2 (2C, br), 68.5, 61.7, 55.3, 52.8, 50.7, 31.1, 21.6; IR (neat) v 3505, 2932, 1339, 1306, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) m/z 520.1357. calcd for $C_{27}H_{25}F_2NNaO_4S$ 520.1370.

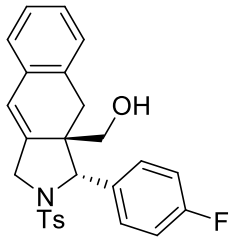
Preparation of (3S,3aR)-3a-hydroxymethyl-3-(4-methoxyphenyl)-6,7-dimethyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4h)



Under nitrogen atmosphere, Pd(t-Bu_3P)$_2$ (0.010 g, 0.019 mmol), DABCO (0.064 g, 0.57 mmol) and 1,2-dibromo-4,5-dimethylbenzene (0.050 g, 0.19 mmol) in 1,4-dioxane (1.9 mL) was added to a solution of **3b** (0.118 g, 0.190 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4h** in 75% yield as pale yellow oil (0.070g, 0.14 mmol). $[\alpha]_D$ –36.0 (c 1.86, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 6.90 – 7.00 (br, 2H), 6.73 (d, J = 6.1 Hz, 2H), 6.66 – 6.75 (br, 2 H), 6.37 (s, 1H), 5.17 (s, 1H), 4.37 (dd, J = 15.0, 2.3 Hz, 1H), 4.27 (d, J = 16.2 Hz, 1H), 3.75 (s, 3H), 3.40 – 3.60 (br, 1H), 3.26 (d, J = 10.6 Hz, 1H), 3.11 (d, J = 10.4 Hz, 1H), 2.45 (d, J = 16.1 Hz, 1H), 2.36 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.08 (d, J = 16.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 143.1, 138.0, 135.9, 135.8, 134.6, 132.1,

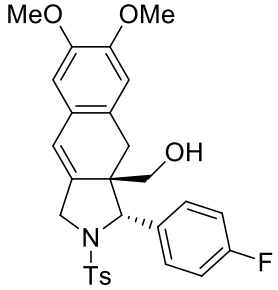
130.4, 130.2, 129.9, 129.4 (2C), 128.6 – 129.2 (2C, br), 127.6, 127.3 (2C), 122.1, 113.6 – 114.1 (2C, br), 68.7, 62.3, 55.3, 53.0, 50.8, 31.3, 21.6, 19.5, 19.3; IR (neat) *v* 3522, 2920, 1337, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 512.1864. calcd for $C_{29}H_{31}NNaO_4S$ 512.1871.

Preparation of (3S,3aR)-3-(4-fluorophenyl)-3a-hydroxymethyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4i)



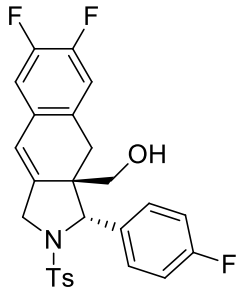
Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.010 g, 0.019 mmol), DABCO (0.067 g, 0.59 mmol) and 1,2-dibromobenzene (0.047 g, 0.20 mmol) in 1,4-dioxane (2.0 mL) was added to a solution of **3c** (0.120 g, 0.198 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4i** in 73% yield as pale yellow oil (0.065g, 0.15 mmol). $[\alpha]_D$ +41.9 (c 1.91, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 7.1 Hz, 1H), 7.00 – 7.10 (br, 2H), 6.96 (d, *J* = 6.1 Hz, 1H), 6.94 (d, *J* = 6.3 Hz, 1H), 6.85 – 6.93 (br, 2H), 6.44 (s, 1H), 5.25 (s, 1H), 4.40 (dd, *J* = 15.1, 2.0 Hz, 1H), 4.32 (d, *J* = 15.6 Hz, 1H), 3.26 (d, *J* = 10.6 Hz, 1H), 3.05 (d, *J* = 10.5 Hz, 1H), 2.53 (d, *J* = 16.0 Hz, 1H), 2.38 (s, 3H), 2.06 (d, *J* = 16.3 Hz, 1H), 1.60 – 1.70 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, $J^{19}F–^{13}C$ = 246.2 Hz), 143.6, 138.9, 135.8 (d, $J^{19}F–^{13}C$ = 3.4 Hz), 135.6, 132.9, 132.2, 129.5 (2C), 129.2 – 129.4 (2C, br), 128.8, 127.6, 127.3 (2C), 126.9, 126.3, 122.5, 115.3 (2C, d, $J^{19}F–^{13}C$ = 21.2 Hz), 68.4, 61.8, 53.0, 50.9, 31.8, 21.6; IR (neat) *v* 3516, 2924, 1337, 1225, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 472.1354. calcd for $C_{26}H_{24}FNNaO_3S$ 472.1359.

Preparation of (3S,3aR)-3-(4-fluorophenyl)-3a-hydroxymethyl-6,7-dimethoxy-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4j)



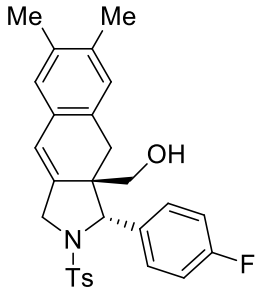
Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.0099 g, 0.019 mmol), DABCO (0.066 g, 0.59 mmol) and 1,2-dibromo-4,5-dimethoxybenzene (0.058 g, 0.19 mmol) in 1,4-dioxane (1.9 mL) was added to a solution of **3c** (0.118 g, 0.194 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4j** in 56% yield as pale yellow oil (0.055g, 0.11 mmol). $[\alpha]_D$ +3.5 (c 1.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.97 – 7.08 (br, 2H), 6.86 – 6.93 (br, 2H), 6.51 (s, 1H), 6.50 (s, 1H), 6.35 (s, 1H), 5.23 (s, 1H), 4.38 (dd, *J* = 14.9, 2.4 Hz, 1H), 4.30 (dd, *J* = 15.0, 1.5 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.28 (d, *J* = 10.0 Hz, 1H), 3.05 (d, *J* = 10.3 Hz, 1H), 2.45 (d, *J* = 16.0 Hz, 1H), 2.38 (s, 3H), 2.01 (d, *J* = 15.9 Hz, 1H), 1.66 – 1.70 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, $J^{19}F–^{13}C$ = 246.3 Hz), 148.2, 147.5, 143.5, 136.6, 135.9 (d, $J^{19}F–^{13}C$ = 3.3 Hz), 135.7, 129.5 (2C), 129.1 – 129.4 (2C, br), 127.3 (2C), 125.4, 124.8, 122.0, 115.1 – 115.5 (2C, br), 112.4, 110.1, 68.4, 61.7, 56.1, 56.0, 53.0, 50.8, 31.5, 21.6; IR (neat) *v* 3514, 2938, 1335, 1227, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 532.1558. calcd for $C_{28}H_{28}FNNaO_5S$ 532.1570.

Preparation of (3S,3aR)-6,7-difluoro-3-(4-fluorophenyl)-3a-hydroxymethyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4k)



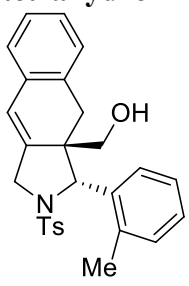
Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.0100 g, 0.020 mmol), DABCO (0.066 g, 0.59 mmol) and 1,2-dibromo-4,5-difluorobenzene (0.053 g, 0.20 mmol) in 1,4-dioxane (1.9 mL) was added to a solution of **3c** (0.118 g, 0.194 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4k** in 67% yield as pale yellow oil (0.063g, 0.13 mmol). $[\alpha]_D$ +41.7 (c 1.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.96 – 7.05 (br, 2H), 6.87 – 6.95 (br, 2H), 6.78 (d, *J* = 7.9 Hz, 1H) , 6.76 (d, *J* = 7.8 Hz, 1H), 6.34 (s, 1H), 5.24 (s, 1H), 4.39 (dd, *J* = 15.4, 2.2 Hz, 1H), 4.31 (d, *J* = 16.5 Hz, 1H), 3.22 (d, *J* = 10.5 Hz, 1H), 3.06 (dd, *J* = 10.5, 1.1 Hz, 1H), 2.50 (d, *J* = 16.1 Hz, 1H), 2.38 (s, 3H), 1.96 (d, *J* = 16.0 Hz, 1H), 1.69 – 1.82 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2 (d, $J^{19}F–^{13}C$ = 246.7), 149.8 (dd, $J^{19}F–^{13}C$ = 248.6, 12.7 Hz), 148.9 (dd, $J^{19}F–^{13}C$ = 246.1, 13.2 Hz), 143.7, 140.0 (d, $J^{19}F–^{13}C$ = 2.8 Hz), 135.5, 135.4 (d, $J^{19}F–^{13}C$ = 3.6 Hz), 129.5 (2C), 129.3, 129.0 – 129.4 (2C, br), 128.8 (dd, $J^{19}F–^{13}C$ = 6.3, 3.5 Hz), 127.3 (2C), 120.8, 117.8 (2C, d, $J^{19}F–^{13}C$ = 18.0 Hz), 115.5 (d, $J^{19}F–^{13}C$ = 23.4 Hz), 114.8, (d, $J^{19}F–^{13}C$ = 18.0 Hz), 68.2, 61.5, 52.7, 50.8, 31.1, 21.6; IR (neat) *v* 3522, 2924, 1339, 1308, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 508.1171. calcd for $C_{26}H_{22}F_3NNaO_3S$ 508.1170.

Preparation of (3S,3aR)-3-(4-fluorophenyl)-3a-hydroxymethyl-6,7-dimethyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4l)



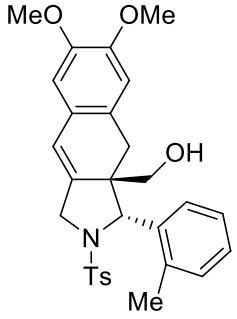
Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.0103 g, 0.020 mmol), DABCO (0.067 g, 0.60 mmol) and 1,2-dibromo-4,5-dimethylbenzene (0.053 g, 0.20 mmol) in 1,4-dioxane (2.0 mL) was added to a solution of **3c** (0.120 g, 0.199 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4l** in 76% yield as pale yellow oil (0.072g, 0.15 mmol). $[\alpha]_D$ +8.8 (c 2.03, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.96 – 7.07 (s, 2H), 6.86 – 6.92 (s, 2H), 6.73 (s, 1H), 6.72 (s, 1H), 6.38 (s, 1H), 5.22 (s, 1H), 4.37 (dd, *J* = 15.0, 2.2 Hz, 1H), 4.30 (d, *J* = 15.7 Hz, 1H), 3.42 – 3.56 (br, 1H), 3.26 (d, *J* = 10.6 Hz, 1H), 3.05 (d, *J* = 10.6 Hz, 1H), 2.45 (d, *J* = 16.0 Hz, 1H), 2.38 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 1.99 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, $J^{19}F-^{13}C$ = 246.0 Hz), 143.5, 137.5 136.0, 135.9 (d, $J^{19}F-^{13}C$ = 3.2 Hz), 135.7, 134.8, 130.2, 130.1, 129.8, 129.5 (2C), 129.1 – 129.4 (2C, br), 127.7, 127.3 (2C), 122.3, 115.3 (2C, d, $J^{19}F-^{13}C$ = 24.1 Hz), 68.4, 62.0, 53.0, 50.8, 31.3, 21.6, 19.5, 19.3; IR (neat) *v* 3507, 2922, 1339, 1225, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 500.1662. calcd for $C_{28}H_{28}FNNaO_3S$ 500.1672.

Preparation of (3S,3aR)-3a-hydroxymethyl-3-(o-tolyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4m)



Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.0102 g, 0.0199 mmol), DABCO (0.067 g, 0.60 mmol) and 1,2-dibromobenzene (0.048 g, 0.20 mmol) in 1,4-dioxane (2.0 mL) was added to a solution of **3d** (0.121 g, 0.200 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4m** in 73% yield as pale yellow oil (0.065g, 0.15 mmol). $[\alpha]_D$ +61.7 (c 1.88, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.09 – 6.98 (m, 3H), 6.97 – 6.88 (m, 3H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.44 (s, 1H), 5.63 (s, 1H), 4.44 (dd, *J* = 15.1, 2.0 Hz, 1H), 4.34 (d, *J* = 15.7 Hz, 1H), 3.29 (d, *J* = 10.5 Hz, 1H), 3.12 (d, *J* = 10.4 Hz, 1H), 2.61 (d, *J* = 16.0 Hz, 1H), 2.46 (s, 3H), 2.36 (s, 3H), 2.13 (d, *J* = 15.9 Hz, 1H), 1.68 – 1.75 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 139.3, 138.4, 135.9, 135.8, 133.1, 132.2, 130.4, 129.4 (2C), 128.8, 127.6, 127.5, 127.3 (2C), 127.1, 126.7, 126.2, 126.1, 122.5, 64.9, 62.1, 53.5, 51.0, 30.6, 21.6, 19.7; IR (neat) *v* 3526, 2924, 1337, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 468.1606. calcd for $C_{27}H_{27}NNaO_3S$ 468.1609.

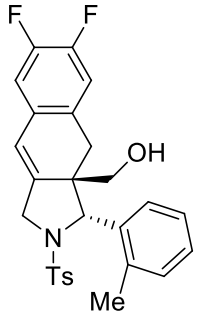
Preparation of (3S,3aR)-3a-hydroxymethyl-6,7-dimethoxy-3-(o-tolyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4n)



Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.0113 g, 0.0221 mmol), DABCO (0.074 g, 0.66 mmol) and 1,2-dibromo-4,5-dimethoxybenzene (0.066 g, 0.22 mmol) in 1,4-dioxane (2.2 mL) was added to a solution of **3d** (0.132 g, 0.220 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography

(silica gel/hexane-EtOAc 3:1 then 1:3) to give **4n** in 59% yield as pale yellow oil (0.065g, 0.13 mmol). $[\alpha]_D$ +22.8 (c 2.13, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.51 (s, *1*H), 6.49 (s, *1*H), 6.35 (s, 1H), 5.61 (s, 1H), 4.42 (dd, *J* = 15.0, 2.2 Hz, 1H), 4.32 (d, *J* = 15.8 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.30 (d, *J* = 10.4 Hz, 1H), 3.11 (d, *J* = 10.4 Hz, 1H), 2.54 (d, *J* = 15.9 Hz, 1H), 2.46 (s, 3H), 2.36 (s, 3H), 2.09 (d, *J* = 15.8 Hz, 1H), 1.68 – 1.72 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 147.4, 143.3, 138.4, 137.0, 135.9, 135.7, 130.4, 129.4 (2C), 127.7, 127.2 (2C), 127.1, 126.2, 125.5, 124.8, 121.9, 112.5, 110.0, 64.9, 61.9, 56.1, 55.9, 53.6, 51.0, 30.2, 21.6, 19.7; IR (neat) *v* 3520, 2936, 1335, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 528.1813. calcd for $C_{29}H_{31}NNaO_5S$ 528.1821.

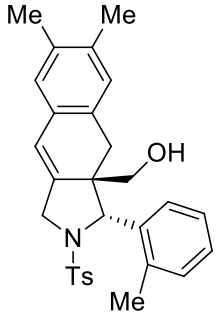
Preparation of (3S,3aR)-6,7-difluoro-3a-hydroxymethyl-3-(o-tolyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4o)



Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.0127 g, 0.0248 mmol), DABCO (0.083 g, 0.74 mmol) and 1,2-dibromo-4,5-difluorobenzene (0.067 g, 0.25 mmol) in 1,4-dioxane (2.5 mL) was added to a solution of **3d** (0.149 g, 0.248 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4o** in 70% yield as colorless oil (0.084g, 0.17 mmol). $[\alpha]_D$ +55.3 (c 2.78, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.5 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 10.5 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.73 – 6.78

(m, 1H), 6.34 (s, 1H), 5.62 (s, 1H), 4.43 (d, J = 15.4 Hz, 1H), 4.33 (d, J = 15.6 Hz, 1H), 3.24 (d, J = 10.4 Hz, 1H), 3.12 (d, J = 10.4 Hz, 1H), 2.58 (d, J = 16.0 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H), 2.03 (d, J = 15.8 Hz, 1H), 1.72 – 1.78 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0 (dd, $J^{19}F–^{13}C$ = 254.2, 12.8 Hz), 148.0 (dd, $J^{19}F–^{13}C$ = 245.7, 12.9 Hz), 143.7, 140.4 (d, J = 2.8 Hz), 138.0, 135.8, 135.7 (d, $J^{19}F–^{13}C$ = 8.0 Hz), 130.5, 129.7 (dd, $J^{19}F–^{13}C$ = 5.5, 4.2 Hz), 129.5 (2C), 128.8 (d, $J^{19}F–^{13}C$ = 6.2 Hz), 127.5, 127.3, 127.2 (2C), 126.3, 120.8, 117.8 (d, $J^{19}F–^{13}C$ = 18.1 Hz), 114.7 (d, $J^{19}F–^{13}C$ = 17.8 Hz), 64.7, 61.7, 53.3, 50.9, 29.9, 21.6, 19.6; IR (neat) v 3522, 2924, 1337, 1307, 1155, 1096 cm^{-1}; HRMS (ESI+ M+Na) m/z 504.1412. calcd for $C_{27}H_{25}F_2NNaO_3S$ 504.1421.

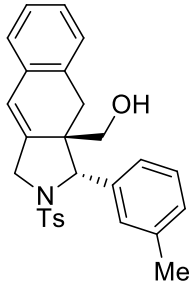
Preparation of (3S,3aR)-3a-hydroxymethyl-6,7-dimethyl-3-(o-tolyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4p)



Under nitrogen atmosphere, Pd(t-Bu_3P)$_2$ (0.0123 g, 0.0241 mmol), DABCO (0.082 g, 0.73 mmol) and 1,2-dibromo-4,5-dimethylbenzene (0.064 g, 0.24 mmol) in 1,4-dioxane (2.4 mL) was added to a solution of **3d** (0.146 g, 0.242 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4p** in 70% yield as colorless oil (0.080g, 0.17 mmol). $[\alpha]_D$ +36.2 (c 2.04, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.5 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 6.72 (s, 1H), 6.71 (s, 1H), 6.38 (s, 1H), 5.60 (s, 1H), 4.41 (dd, J = 15,0, 1,6 Hz, 1H), 4.32 (d, J = 15.2 Hz, 1H), 3.45 – 3.65 (br, 1H), 3.28 (d, J = 10.4 Hz, 1H), 3.10 (d, J = 10.4 Hz, 1H), 2.53 (d, J = 15.9 Hz, 1H),

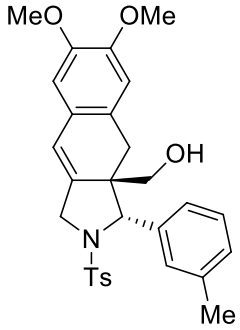
2.45 (s, 3H), 2.36 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 2.07 (d, J = 16.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 138.5, 138.0, 135.9, 135.8, 135.7, 134.6, 130.3, 130.3, 130.2, 129.8, 129.4 (2C), 127.7, 127.6, 127.3 (2C), 127.1, 126.1, 122.3, 64.9, 62.2, 53.6, 51.0, 30.1, 21.6, 19.7, 19.5, 19.3; IR (neat) v 3503, 2922, 1331, 1155, 1096 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 496.1908. calcd for $C_{29}H_{31}NNaO_3S$ 496.1922.

Preparation of (3S,3aR)-3a-hydroxymethyl-3-(m-tolyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4q)



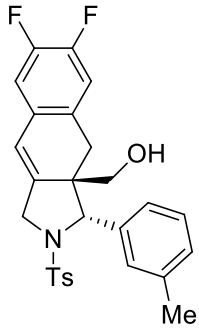
Under nitrogen atmosphere, Pd(t-Bu_3P)$_2$ (0.0102 g, 0.0199 mmol), DABCO (0.067 g, 0.60 mmol) and 1,2-dibromobenzene (0.047 g, 0.20 mmol) in 1,4-dioxane (2.0 mL) was added to a solution of **3e** (0.120 g, 0.199 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4q** in 66% yield as colorless oil (0.059g, 0.13 mmol). $[\alpha]_D$ +31.7 (c 1.63, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 7.11 – 6.92 (m, 6H), 6.80 – 6.90 (br, 2H), 6.44 (s, 1H), 5.21 (s, 1H), 4.43 (dd, J = 15.1, 2.2 Hz, 1H), 4.33 (d, J = 15.7 Hz, 1H), 3.40 – 3.60 (br, 1H), 3.27 (d, J = 10.6 Hz, 1H), 3.12 (d, J = 10.5 Hz, 1H), 2.53 (d, J = 16.1 Hz, 1H), 2.36 (s, 3H), 2.15 – 2.25 (br, 3H), 2.11 (d, J = 16.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 139.5, 139.4, 138.0, 135.8, 133.2, 132.3, 129.3 (2C), 128.0 – 129.0 (br), 128.8, 128.3, 128.2, 127.5, 127.3 (2C), 126.8, 126.2, 124.5 – 125.5 (br), 122.2, 69.2, 62.1, 53.0, 51.0, 31.8, 21.6, 21.5; IR (neat) v 3524, 2920, 1335, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 468.1607. calcd for $C_{27}H_{27}NNaO_3S$ 468.1609.

Preparation of (3S,3aR)-3a-hydroxymethyl-6,7-dimethoxy-3-(m-tolyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4r)



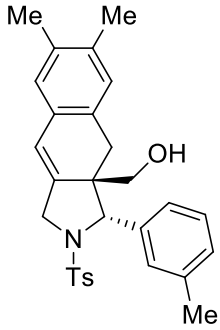
Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.0120 g, 0.0234 mmol), DABCO (0.077 g, 0.66 mmol) and 1,2-dibromo-4,5-dimethoxybenzene (0.066 g, 0.22 mmol) in 1,4-dioxane (2.2 mL) was added to a solution of **3e** (0.138 g, 0.230 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:3) to give **4r** in 65% yield as pale yellow oil (0.076g, 0.15 mmol). $[\alpha]_D$ -7.9 (c 2.18, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.01 – 7.11 (br, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.80 – 6.89 (br, 2H), 6.52 (s, 1H), 6.51 (s, 1H), 6.35 (s, 1H), 5.19 (s, 1H), 4.41 (dd, *J* = 15.0, 1.4 Hz, 1H), 4.31 (d, *J* = 15.2 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.40 – 3.60 (br, 1H), 3.29 (d, *J* = 10.5 Hz, 1H), 3.11 (d, *J* = 10.4 Hz, 1H), 2.45 (d, *J* = 16.0 Hz, 1H), 2.37 (s, 3H), 2.12 – 2.27 (br, 3H), 2.05 (d, *J* = 15.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 147.4, 143.2, 139.6, 137.9, 137.1, 135.8, 129.3 (2C), 128.3, 128.2, 127.6 – 128.9 (br), 127.3 (2C), 125.7, 125.0, 124.6 – 125.6 (br), 121.7, 112.5, 110.0, 69.2, 61.9, 56.1, 56.0, 53.0, 50.9, 31.5, 21.5, 21.5; IR (neat) *v* 3512, 2936, 1335, 1157, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 528.1814. calcd for $C_{29}H_{31}NNaO_5S$ 528.1821.

Preparation of (3S,3aR)-6,7-difluoro-3a-hydroxymethyl-3-(m-tolyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4s)



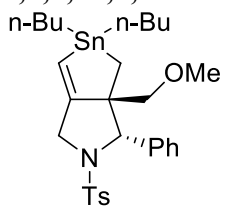
Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.0103 g, 0.0201 mmol), DABCO (0.066 g, 0.59 mmol) and 1,2-dibromo-4,5-difluorobenzene (0.055 g, 0.20 mmol) in 1,4-dioxane (2.0 mL) was added to a solution of **3e** (0.120 g, 0.199 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4s** in 73% yield as pale yellow oil (0.070g, 0.15 mmol). $[\alpha]_D$ +31.9 (c 2.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.05 – 7.15 (br, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.77 (dd, *J* = 8.0 Hz, 1H), 6.75 (dd, *J* = 7.8 Hz, 1H), 6.72 – 6.88 (br, 2H), 6.33 (s, 1H), 5.21 (s, 1H), 4.42 (d, *J* = 13.7 Hz, 1H), 4.32 (d, *J* = 15.3 Hz, 1H), 3.40 – 3.60 (br, 1H), 3.23 (d, *J* = 10.6 Hz, 1H), 3.12 (d, *J* = 10.5 Hz, 1H), 2.51 (d, *J* = 16.1 Hz, 1H), 2.36 (s, 3H), 2.10 - 2.30 (br, 3H), 2.00 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0 (dd, $J^{19}F–^{13}C$ = 248.4, 13.0 Hz), 148.8 (dd, $J^{19}F–^{13}C$ = 245.7, 13.0 Hz), 143.4, 140.4 (d, $J^{19}F–^{13}C$ = 2.8 Hz), 139.2, 138.1, 135.7, 129.8, 129.4 (2C), 128.9, 128.4, 128.3, 128.2 – 128.5 (br), 127.2 (2C), 124.5 – 125.2 (br), 120.6, 117.8 (d, $J^{19}F–^{13}C$ = 17.8 Hz), 114.7 (d, $J^{19}F–^{13}C$ = 17.8 Hz), 69.0, 61.7, 52.8, 50.9, 31.1, 21.5, 21.5; IR (neat) *v* 3509, 2920, 1335, 1155, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 504.1413. calcd for $C_{27}H_{25}F_2NNaO_3S$ 504.1421.

Preparation of (3S,3aR)-3a-hydroxymethyl-6,7-dimethyl-3-(m-tolyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (4t)



Under nitrogen atmosphere, Pd(*t*-$Bu_3P)_2$ (0.0113 g, 0.0221 mmol), DABCO (0.073 g, 0.65 mmol) and 1,2-dibromo-4,5-dimethylbenzene (0.058 g, 0.22 mmol) in 1,4-dioxane (2.2 mL) was added to a solution of **3e** (0.132 g, 0.220 mmol) and the reaction mixture was heated to refluxing temperature for 20 h. The solution was filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 then 1:1) to give **4t** in 74% yield as colorless oil (0.077g, 0.16 mmol). $[\alpha]_D$ -5.5 (c 2.56, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.04 – 7.12 (br, 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 6.82 – 6.90 (br, 2H), 6.73 (s, 1H), 6.72 (s, 1H), 6.38 (s, 1H), 5.18 (s, 1H), 4.40 (dd, *J* = 15.0, 1.6 Hz, 1H), 4.30 (d, *J* = 16.1 Hz, 1H), 3.40 – 3.60 (br, 1H), 3.27 (d, *J* = 10.6 Hz, 1H), 3.12 (d, *J* = 10.2 Hz, 1H), 2.45 (d, *J* = 16.1 Hz, 1H), 2.36 (s, 3H), 2.10 – 2.25 (br, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.04 (d, *J* = 16.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 139.6, 138.0, 137.9, 135.9, 135.8, 134.6, 130.4, 130.2, 129.9, 129.3 (2C), 128.3, 128.2, 128.0 – 128.5 (br), 127.6, 127.3 (2C), 124.8 – 125.5 (br), 122.1, 69.2, 62.3, 53.0, 51.0, 31.3, 21.5, 21.5, 19.5, 19.3; IR (neat) *v* 3503, 2992, 1321, 1157, 1096 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 496.1915. calcd for $C_{29}H_{31}NNaO_3S$ 496.1922.

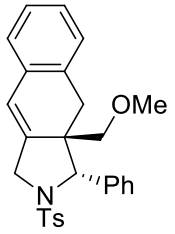
Preparation of (3S,3aS)-5,5-dibutyl-3a-(methoxymethyl)-3-phenyl-2-tosyl-1,2,3,3a,4,5-hexahydrostannolo[3,4-c]pyrrole (5a)



Under nitrogen atmosphere, NaH (0.050 g, 1.3 mmol, 3.2 equiv) was placed in a 30 mL

round flask and washed with hexane. A solution of **3a** (0.241 g, 0.410 mmol) in THF (3 mL) was added to NaH at 0°C and the resulting mixture was stirred for 15 min at 0°C. MeI (0.08 mL, 1.3 mmol) was added to the solution at 0°C and the reaction mixture was stirred for 18 hours at room temperature. Water (10 mL) was added to the mixture and the resulting solution was extracted with EtOAc (20 mL x 3). The organic phase was combined, washed with brine (10 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated in vacuo and the residue was purified through flash column chromatography (silica gel/hexane-EtOAc 10:1 to 8:1) to give **5a** in 90% yield as colorless liquid (0.223 g, 0.370 mmol). $[\alpha]_D$ +16.8 (c 0.82, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 8.2 Hz, 2H), 7.11 – 7.17 (br, 3H), 7.13 (d, J = 8.2 Hz, 2H), 6.90 – 6.98 (br, 2H), 6.43 (s, 1H, J^{119}Sn–^{1}H = 112.7 Hz), 4.89 (s, 1H), 4.21 (dd, J = 13.9, 1.9 Hz, 1H), 4.07 (d, J = 14.6 Hz, 1H), 3.17 (s, 3H), 2.93 (d, J = 8.5 Hz, 1H), 2.78 (d, J = 8.7 Hz, 1H), 2.35 (s, 3H), 1.47 (p, J = 7.6 Hz, 2H), 1.29 – 1.05 (m, 8H), 1.00 (t, J = 8.0 Hz, 2H), 0.84 (t, J = 7.3 Hz, 4H), 0.74 (t, J = 7.1 Hz, 3H), 0.04 (d, J = 12.8 Hz, 1H, J^{119}Sn–^{1}H = 57.1 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 142.8, 140.8, 136.1, 129.3 (2C), 128.1 (2C), 128.0 – 128.2 (br), 127.3 (2C), 127.2, 126.5 (2C), 79.0, 68.2, 64.0, 59.2, 50.5, 29.2 (J^{119}Sn–^{13}C = 22.1 Hz), 28.8 (J^{119}Sn–^{13}C = 22.6 Hz), 27.1, 27.0, 21.5, 13.7, 13.6, 13.4, 12.6, 12.2; ^{119}Sn NMR (186 MHz, $CDCl_3$) δ 132.5; IR (neat) ν 2922, 1346, 1161, 1098 cm^{-1}; HRMS (FAB+ M+H) m/z 604.1909. calcd for $C_{29}H_{42}NO_3SSn$ m/z 604.1907.

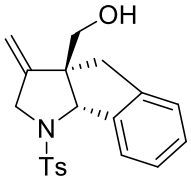
Preparation of (3*S*,3a*R*)-3a-(methoxymethyl)-3-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (6a)



Pd(t-Bu_3P)$_2$ (0.012 g, 0.024 mmol), DABCO (0.084 g, 0.75 mmol) and 1,2-dibromo

benzene (0.060 g, 0.25 mmol) were added to a solution of **5a** (0.151 g, 2.50 mmol) in 1,4-dioxane (2.5 mL) and the reaction mixture was heated to refluxing temperature for 20 hours. The reaction mixture was cooled and filtered. The filtrate was concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 8:1 to 5:1) to give **6a** in 48% yield as pale yellow oil (0.054 g, 0.12 mmol). $[\alpha]_D$ +50.9 (c 1.51, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.25 (m, 3 H), 7.07 – 7.14 (m, 2 H), 7.06 (t, *J* = 7.4 Hz, 1H), 7.01 (td, *J* = 7.4, 1.3 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.41 (s, 1H), 5.26 (s, 1H), 4.39 (dd, *J* = 15.1, 1.3 Hz, 1H), 4.34 (dd, *J* = 15.0, 2.3 Hz, 1H), 3.08 (s, 3H), 2.91 (d, *J* = 8.9 Hz, 1H), 2.59 (dd, *J* = 8.9, 1.3 Hz, 1H), 2.51 (d, *J* = 15.9 Hz, 1H), 2.38 (s, 3H), 1.98 (d, *J* = 15.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 140.4, 139.3, 135.6, 133.5, 132.2, 129.7, 129.5 (2C), 128.8, 128.4 (2C) , 127.5, 127.4 (2C), 127.4 (2C), 126.7, 126.1, 122.2, 71.2, 69.2, 59.0, 52.0, 51.1, 32.4, 21.6; IR (neat) *v* 2924, 1344, 1161, 1092 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 468.1601. calcd for $C_{27}H_{27}NNaO_3S$ 468.1609.

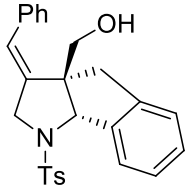
Preparation of (3aR,8bS)-3a-hydroxymethyl-3-methylene-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-b]pyrrole (7a)



$Pd(t\text{-}Bu_3P)_2$ (0.0102 g, 0.0199 mmol) and DABCO (0.067 g, 0.60 mmol) were added to a solution of **3f** (0.133 g, 0.199 mmol) in 1,4-dioxane (2.0 mL) and the reaction mixture was heated to refluxed temperature for 20 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 to 1:1) to give **7a** in 76% yield as white solid (0.054g, 0.15 mmol). mp 165.0 – 166.0 °C, $[\alpha]_D$ +15.8 (c 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.0

Hz, 2H), 7.28 – 7.20 (m, 2H), 7.11 (d, *J* = 6.6 Hz, 1H), 5.27 (s, 1H), 5.08 (t, J = 2.2 Hz, 1H), 5.04 (s, 1H), 4.15 (ddd, J = 15.1, 3.2, 1.5 Hz, 1H),3.96 (dd, *J* = 15.1, 0.9 Hz, 1H), 3.10 (d, *J* = 16.1 Hz, 1H), 3.10 (d, *J* = 11.1 Hz, 1H), 3.01 (d, *J* = 10.9 Hz, 1H), 2.99 (d, *J* = 16.2 Hz, 1H), 2.44 (s, 3H), 1.71 – 1.61 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 144.0, 141.3, 140.7, 135.6, 129.9 (2C), 128.6, 127.7 (2C), 127.5, 126.4, 124.7, 108.4, 70.8, 65.3, 59.9, 52.9, 39.1, 21.7; IR (neat) *v* 3528, 2866, 1339, 1306, 1157, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 378.1129. calcd for $C_{20}H_{21}NNaO_3S$ 378.1140.

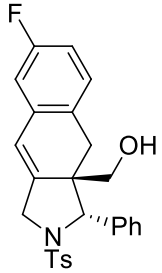
Preparation of ((3aR,8bS,E)-3-benzylidene-3a-hydroxymethyl-1-tosyl-1,2,3,3a,4,8b-hexahydroindeno[1,2-b]pyrrole (7b)



Pd(*t*-$Bu_3P)_2$ (0.0120 g, 0.0234 mmol), DABCO (0.079 g, 0.70 mmol), CsF (0.104 g, 0.69 mmol) and iodobenzene (0.047 g, 0.23 mmol) were added to a solution of **3f** (0.155 g, 0.232 mmol) in 1,4-dioxane (2.3 mL) and the reaction mixture was heated to refluxing temperature for 20 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 to 1:1) to give **7b** in 56% yield (0.056g, 0.13 mmol) along with **7a** in 7% yield (0.006 g, 0.017 mmol). Pale yellow solid; mp 113.0 – 114.0 ºC; $[\alpha]_D$ -33.4 (c 1.87, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.18 (m, 5H), 7.12 (d, *J* = 7.3 Hz, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.50 (s, 1H), 5.45 (s, 1H), 4.32 (dd, *J* = 15.1, 2.0 Hz, 1H), 4.11 (dd, *J* = 15.1, 1.9 Hz, 1H), 3.46 (dd, *J* = 11.3, 6.6 Hz, 1H), 3.13 (d, *J* = 16.5 Hz, 1H), 3.08 (dd, *J* = 11.2, 5.2 Hz, 1H), 2.84 (d, *J* = 16.5 Hz, 1H), 2.46 (s, 3H), 1.52 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 141.5, 141.2, 140.8, 136.0, 135.8, 129.8 (2C), 128.7 (2C), 128.6, 128.4 (2C), 127.9 (2C), 127.6, 127.4, 126.6, 124.9, 124.4, 72.9, 64.5, 59.5, 56.0, 38.3, 21.7; IR (neat) *v* 3524, 2924, 1339, 1155, 1092 cm^{-1}; HRMS

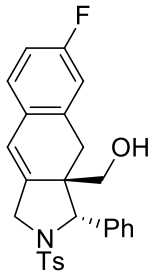
(ESI+ M+Na) *m/z* 454.1439. calcd for $C_{26}H_{25}NNaO_3S$ 454.1453.

Preparation of (3S,3aR)-7-fluoro-3a-(hydroxymethyl)-3-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (8)

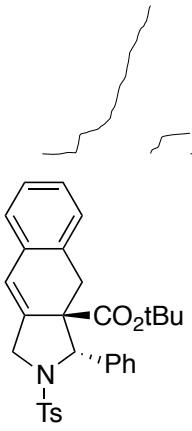


Pd(*t*-$Bu_3P)_2$ (0.0109 g, 0.021 mmol), DABCO (0.071 g, 0.63 mmol), CsF (0.096 g, 0.63 mmol) and 1-bromo-4-fluoro-2-iodobenzene (0.063 g, 0.21 mmol) were added to a solution of **3a** (0.124 g, 0.211 mmol) in 1,4-dioxane (2.1 mL) and the reaction mixture was heated to refluxing temperature for 20 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 to 1:1) to give **8** in 52% yield (0.049 g, 0.11 mmol). Pale yellow oil; $[\alpha]_D$ + 37.7 (c 0.48, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.09 – 6.95 (m, 2H), 6.88 (dd, *J* = 7.7, 5.9 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.66 (dd, *J* = 9.2, 2.6 Hz, 1H), 6.38 (s, 1H), 5.27 (s, 1H), 4.42 (dd, *J* = 15.4, 2.3 Hz, 1H), 4.33 (dd, *J* = 15.4, 1.5 Hz, 1H), 3.24 (d, *J* = 10.7 Hz, 1H), 3.09 (d, *J* = 10.6 Hz, 1H), 2.55 (d, *J* = 16.0 Hz, 1H), 2.35 (s, 3H), 2.15 – 2.04 (br, 1H), 1.99 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (d, $J^{19}F–^{13}C$ = 243.8 Hz), 143.5, 141.2, 139.8, 135.8, 134.1 (d, $J^{19}F–^{13}C$ = 8.1 Hz), 129.9 (d, $J^{19}F–^{13}C$ = 8.0 Hz), 129.6 (2C), 128.65, 128.61 (2C), 127.7 (2C), 127.4 (2C), 127.5 – 128.1 (br), 121.7 (d, $J^{19}F–^{13}C$ = 2.2 Hz), 113.7 (d, $J^{19}F–^{13}C$ = 21.1 Hz), 113.1 (d, $J^{19}F–^{13}C$ = 22.2 Hz), 69.1, 61.9, 53.3, 51.0, 31.1, 21.7; IR (neat) *v* 3528, 2926, 1339, 1159, 1096 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 472.1354. calcd for $C_{26}H_{24}FNNaO_3S$ 472.1359.

Preparation of (3S,3aR)-6-fluoro-3a-(hydroxymethyl)-3-phenyl-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole (9)



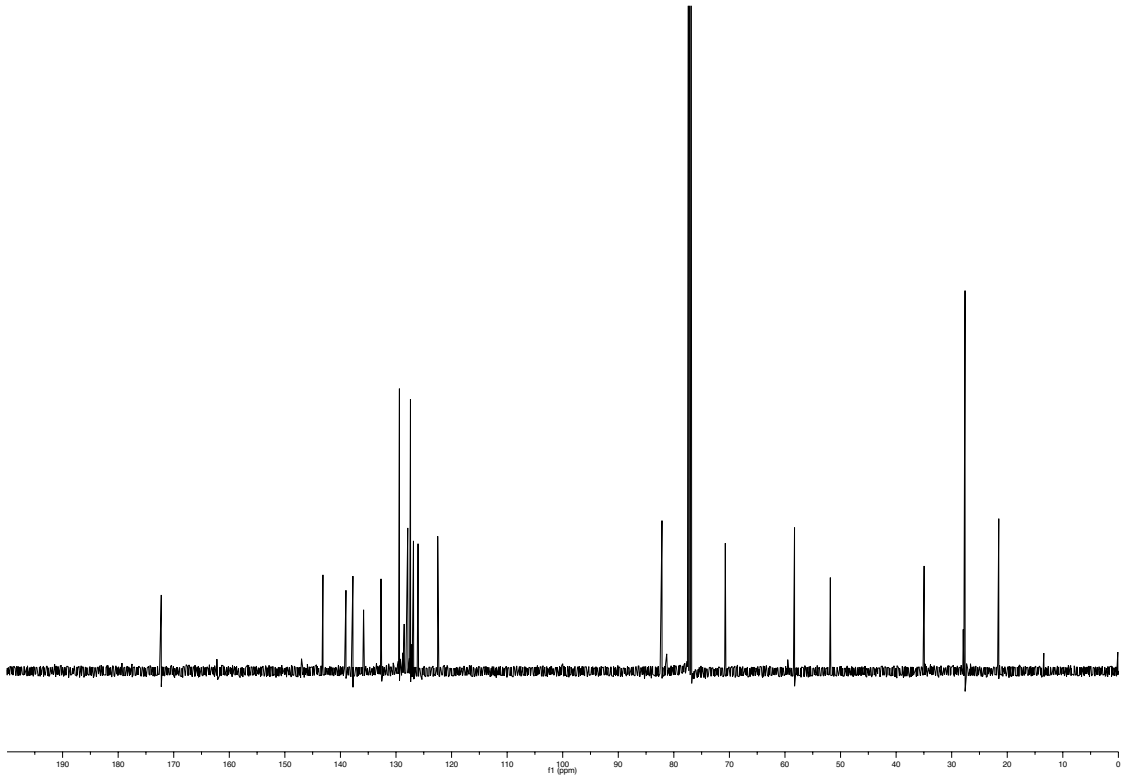
$Pd(t\text{-}Bu_3P)_2$ (0.0105 g, 0.0205 mmol), DABCO (0.069 g, 0.62 mmol), CsF (0.093 g, 0.61 mmol) and 2-bromo-4-fluoro-1-iodobenzene (0.062 g, 0.21 mmol) were added to a solution of **3a** (0.120 g, 0.204 mmol) in 1,4-dioxane (2.0 mL) and the reaction mixture was heated to refluxing temperature for 20 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel/hexane-EtOAc 3:1 to 1:1) to give **9** in 49% yield (0.045 g, 0.10 mmol). Pale yellow oil; $[\alpha]_D$ +35.4 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.24 – 7.17 (br, 3H), 7.15 (d, J = 7.9 Hz, 2H), 7.10 – 6.98 (br, 2H), 6.90 (dd, J = 8.3, 5.7 Hz, 1H), 6.75 (tdd, J = 8.5, 2.6, 0.9 Hz, 1H), 6.67 (dd, J = 8.9, 1.9 Hz, 1H), 6.40 (s, 1H), 5.26 (s, 1H), 4.41 (dd, J = 15.0, 2.2 Hz, 1H), 4.32 (dd, J = 15.1, 1.4 Hz, 1H), 3.24 (d, J = 10.7 Hz, 1H), 3.09 (dd, J = 10.6, 0.7 Hz, 1H), 2.55 (d, J = 16.2 Hz, 1H), 2.36 (s, 3H), 2.05 (d, J = 16.2 Hz, 1H), 2.02 – 1.92 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, $J^{19}F–^{13}C$ = 246.9 Hz), 143.5, 139.8, 138.7 (d, $J^{19}F–^{13}C$ = 2.5 Hz), 135.9 (d, $J^{19}F–^{13}C$ = 8.0 Hz), 135.8, 129.6 (2C), 128.6 (2C), 128.56 (d, $J^{19}F–^{13}C$ = 2.8 Hz), 128.19 – 127.29 (br), 127.7 (2C), 127.5 (d, $J^{19}F–^{13}C$ = 8.3 Hz), 127.4 (2C), 121.5, 116.19 (d, $J^{19}F–^{13}C$ = 22.2 Hz), 113.33 (d, $J^{19}F–^{13}C$ = 21.6 Hz), 69.1, 62.1, 52.8, 51.0, 32.1, 21.7; IR (neat) ν 3511, 2922, 1337, 1159, 1094 cm^{-1}; HRMS (ESI+ M+Na) *m/z* 472.1350. calcd for $C_{26}H_{24}FNNaO_3S$ 472.1359.

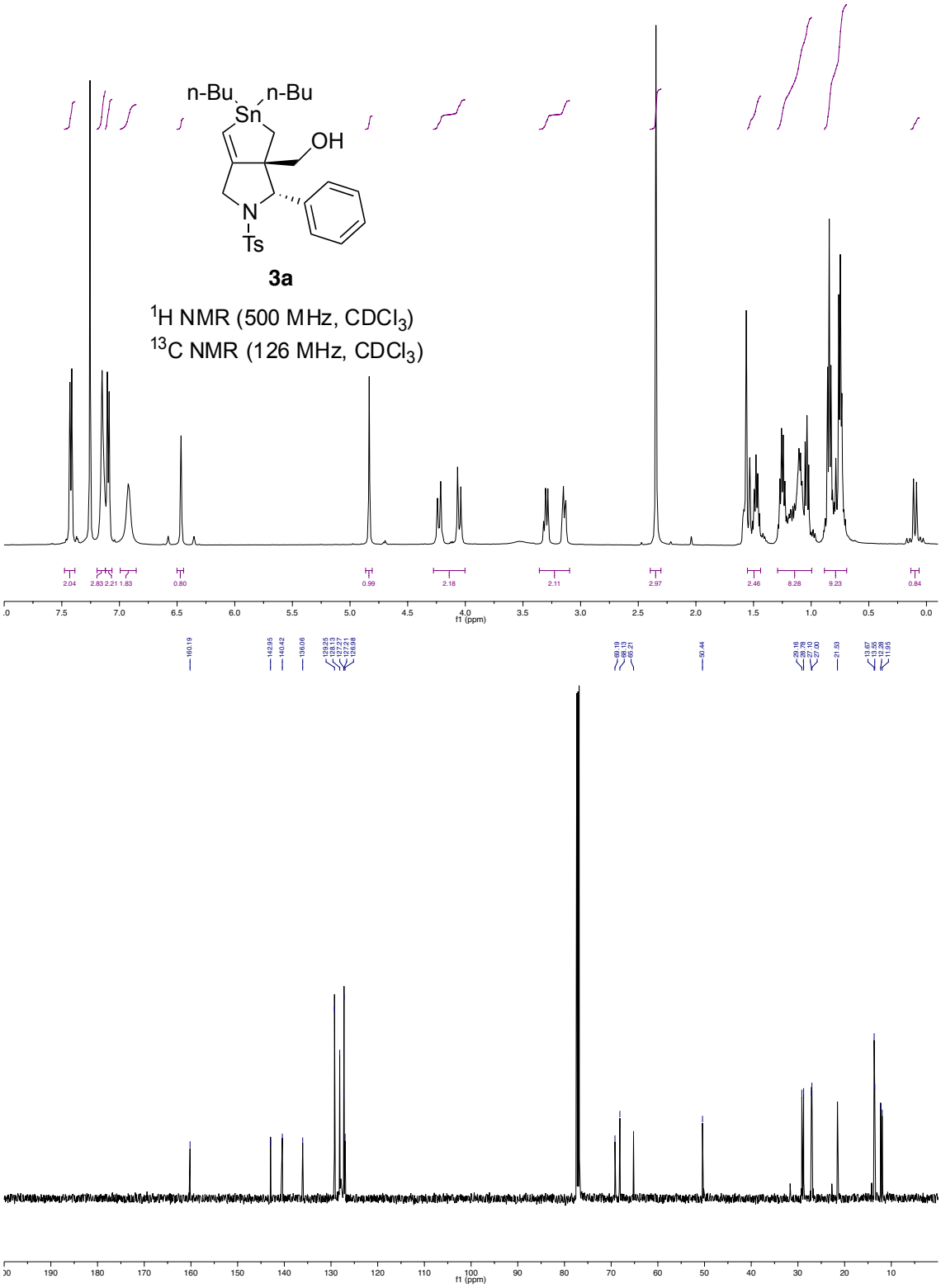


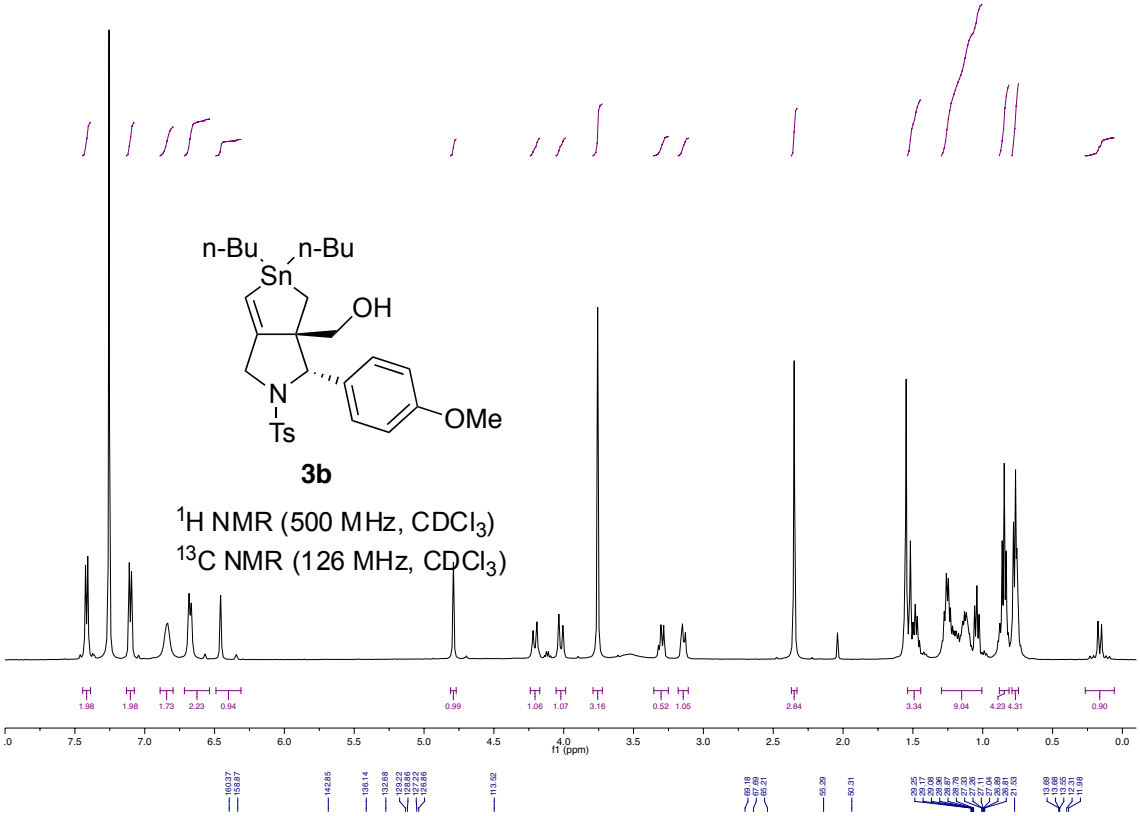
2a

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

^{13}C NMR (126 MHz, $CDCl_3$)



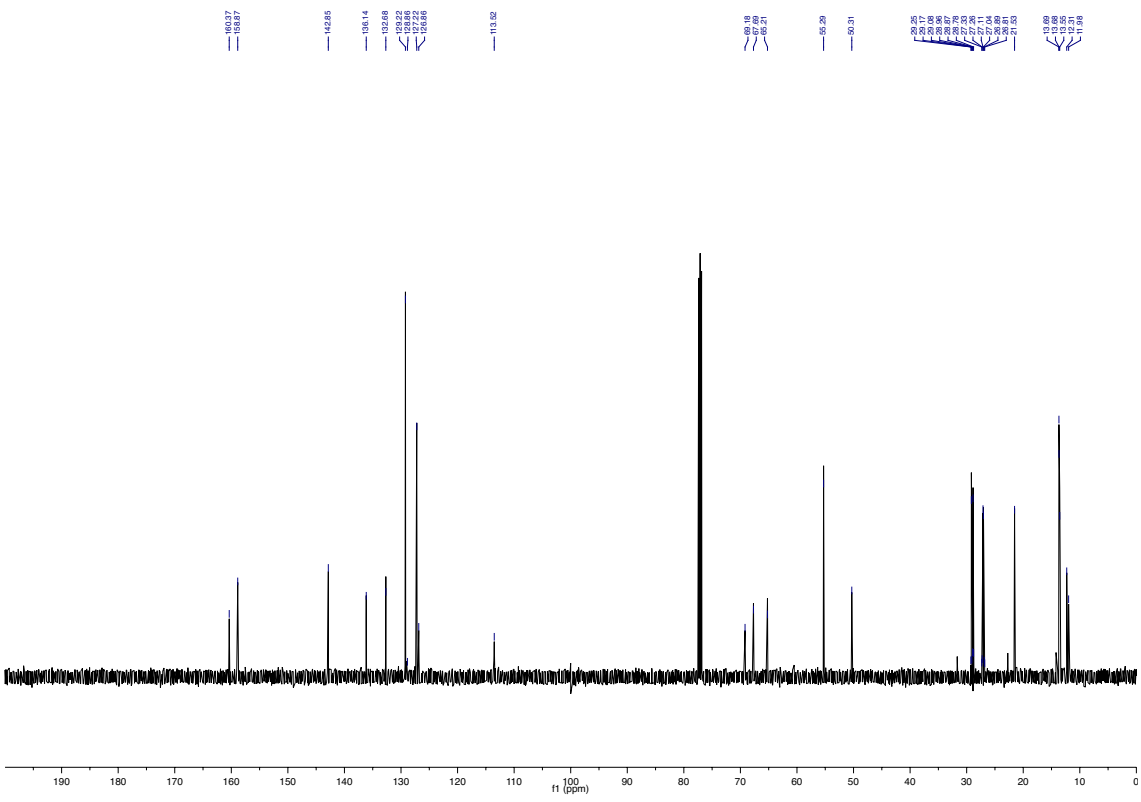

n-Bu
n-Bu
Sn
OH
N
Ts
3a
1H NMR (500 MHz, CDCl3)
13C NMR (126 MHz, CDCl3)
f1 (ppm)

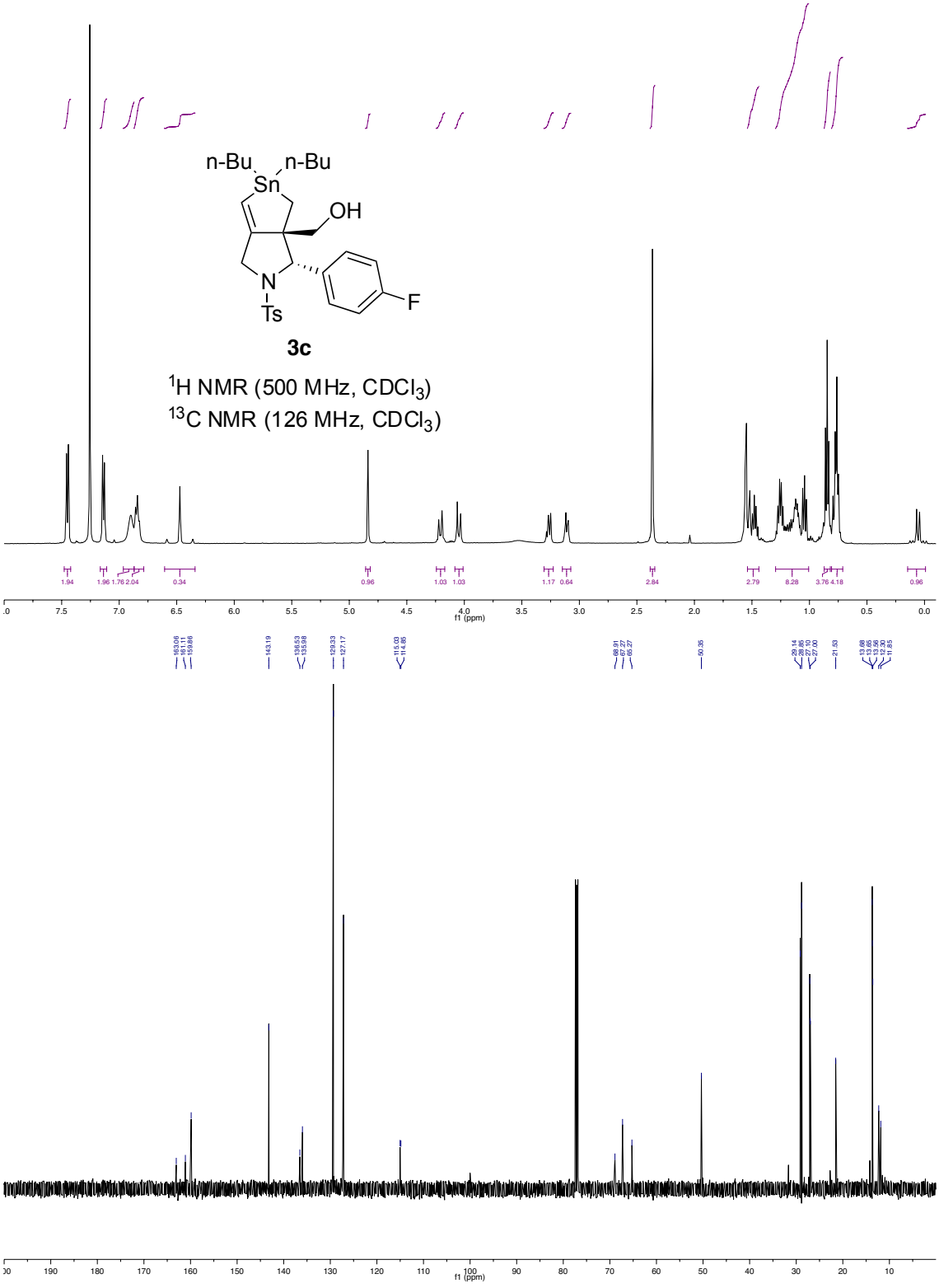


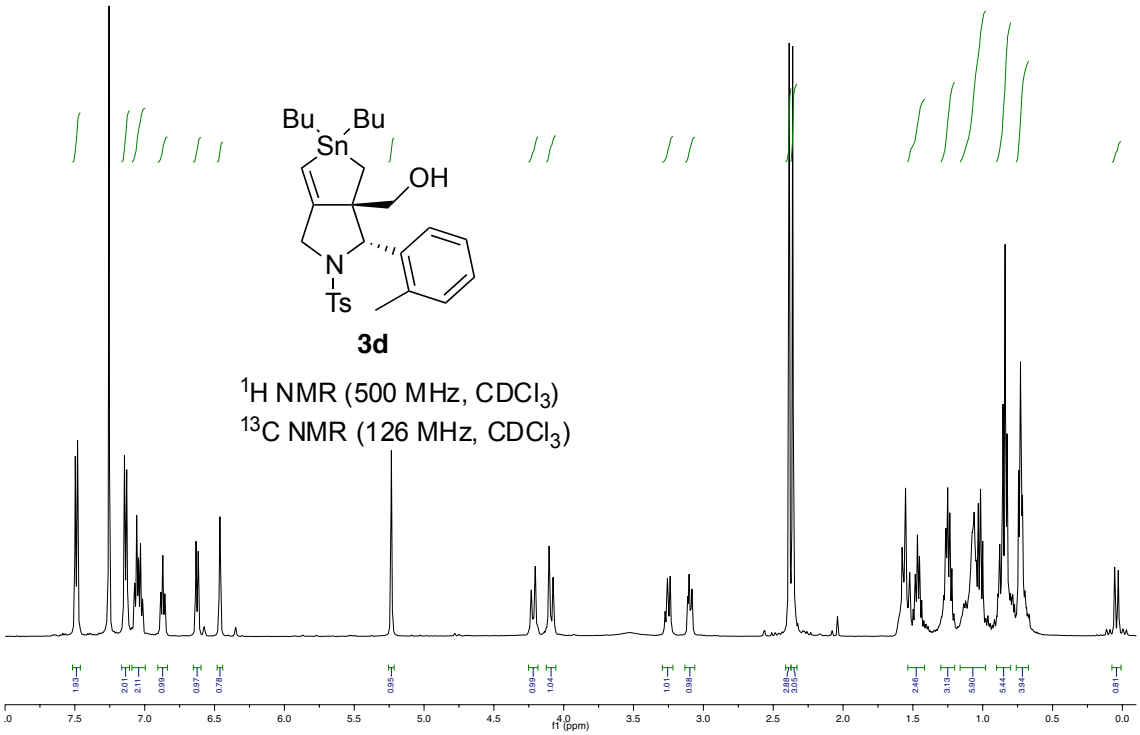
3b

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

^{13}C NMR (126 MHz, $CDCl_3$)



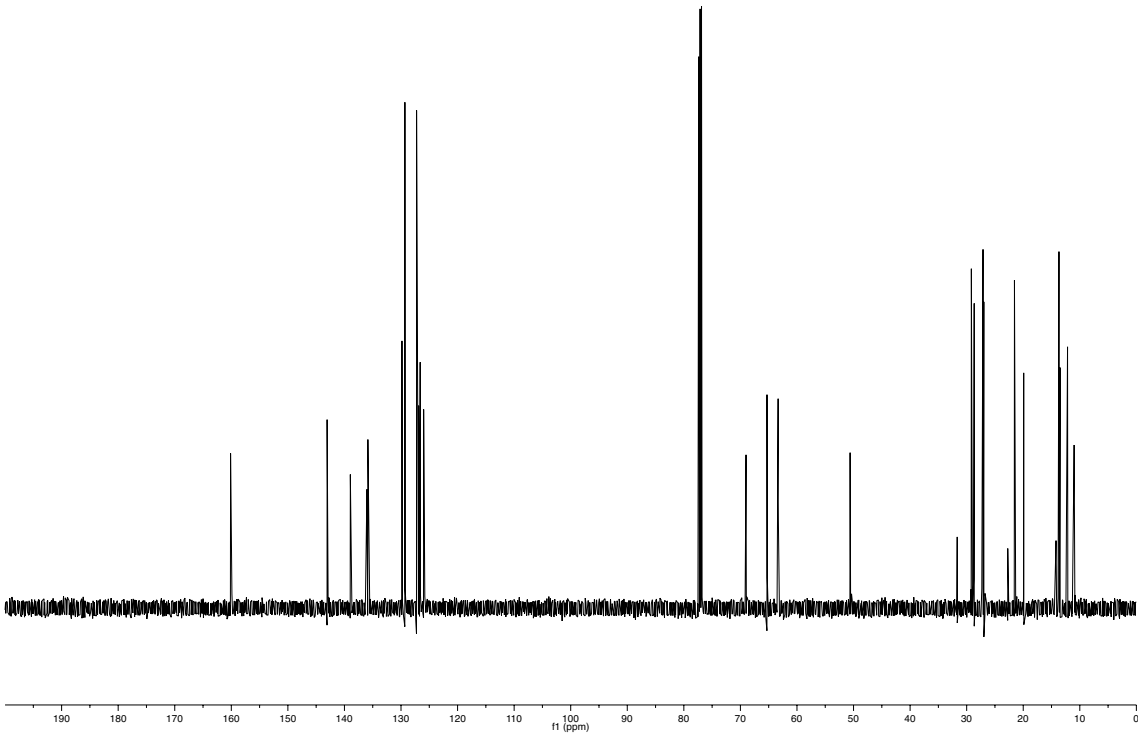

n-Bu
n-Bu
Sn
OH
N
Ts
F
3c
^{1}H NMR (500 MHz, $CDCl_3$)
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

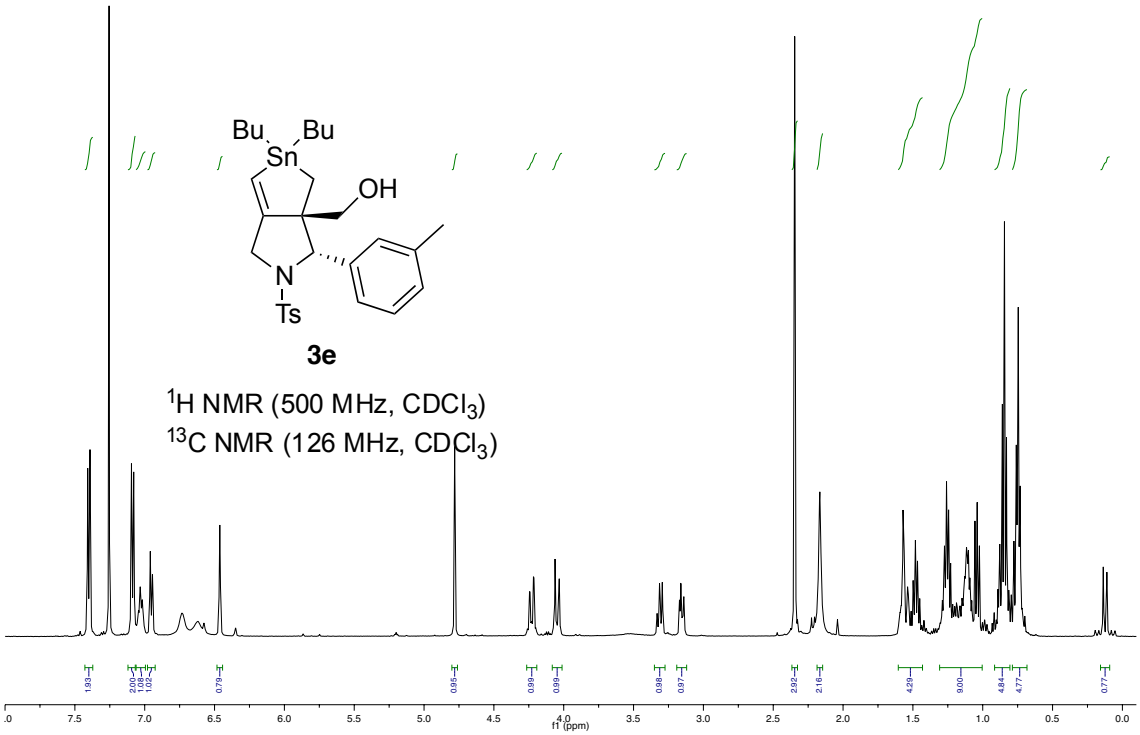


3d

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

^{13}C NMR (126 MHz, $CDCl_3$)

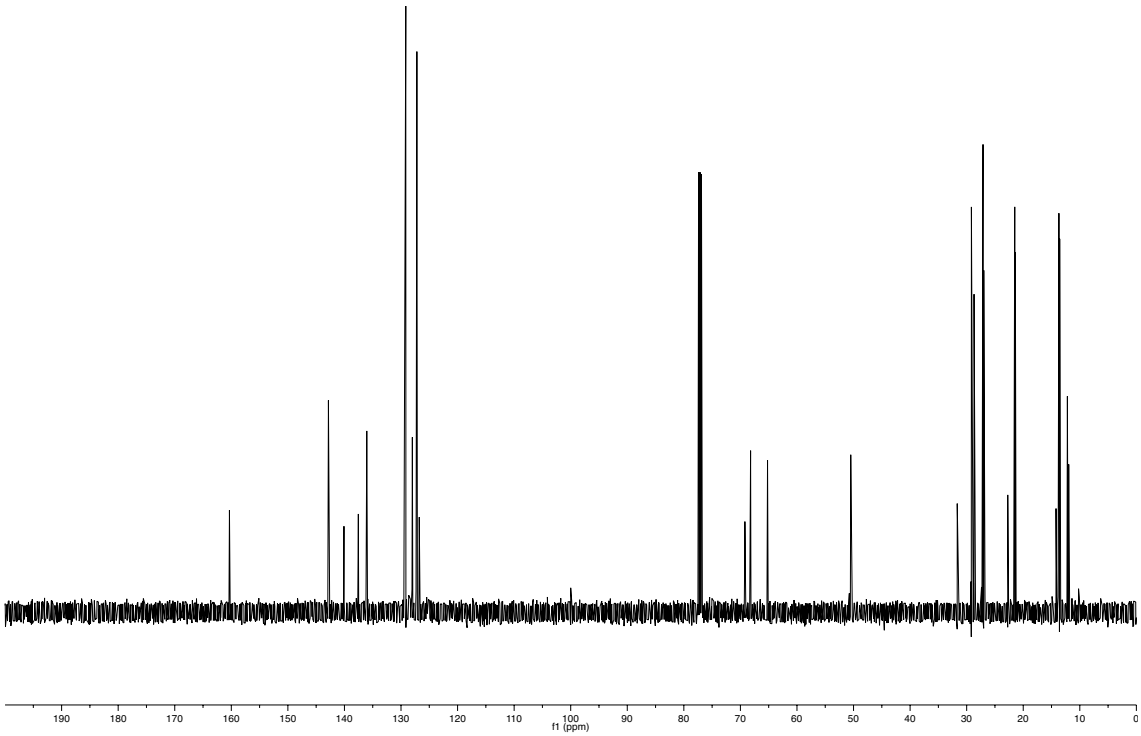


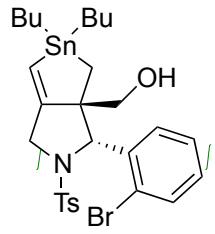


3e

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

^{13}C NMR (126 MHz, $CDCl_3$)

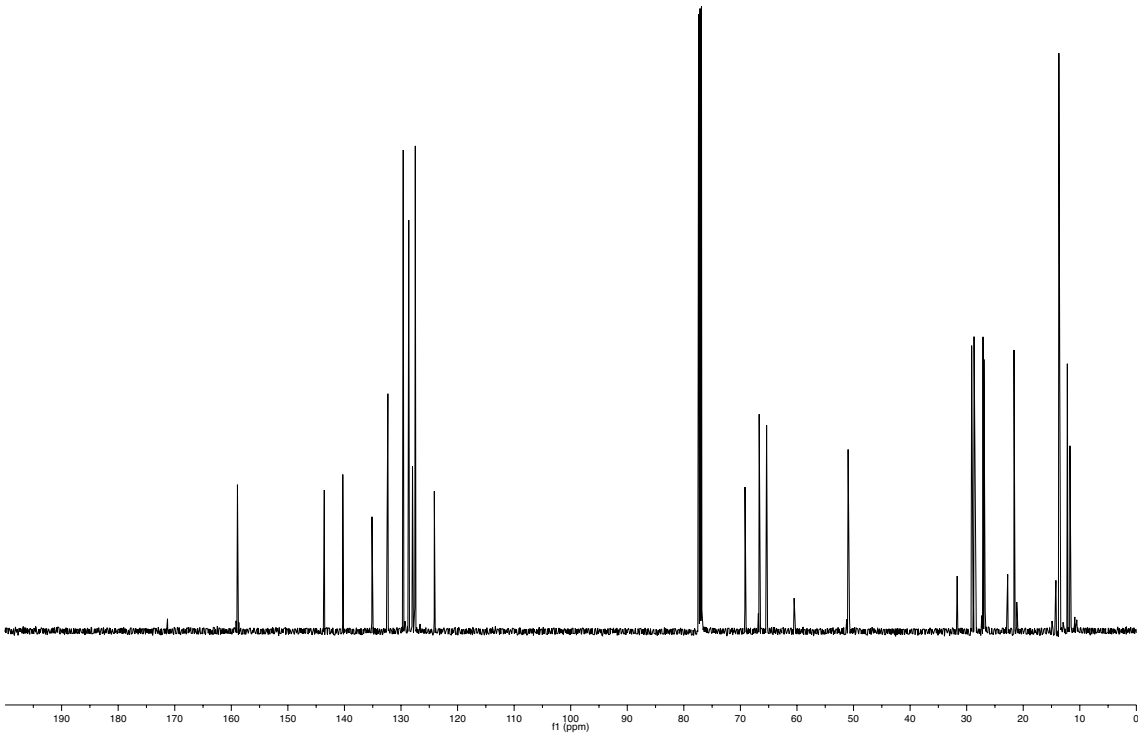


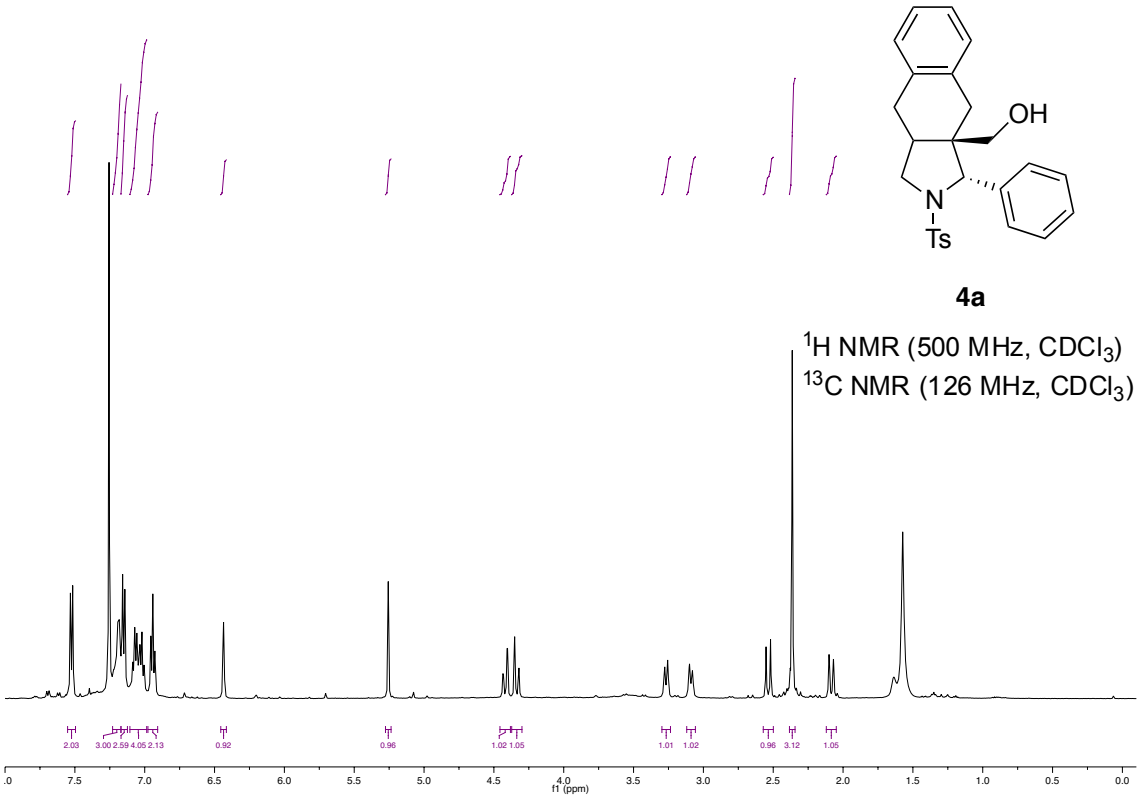


3f

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

^{13}C NMR (126 MHz, $CDCl_3$)

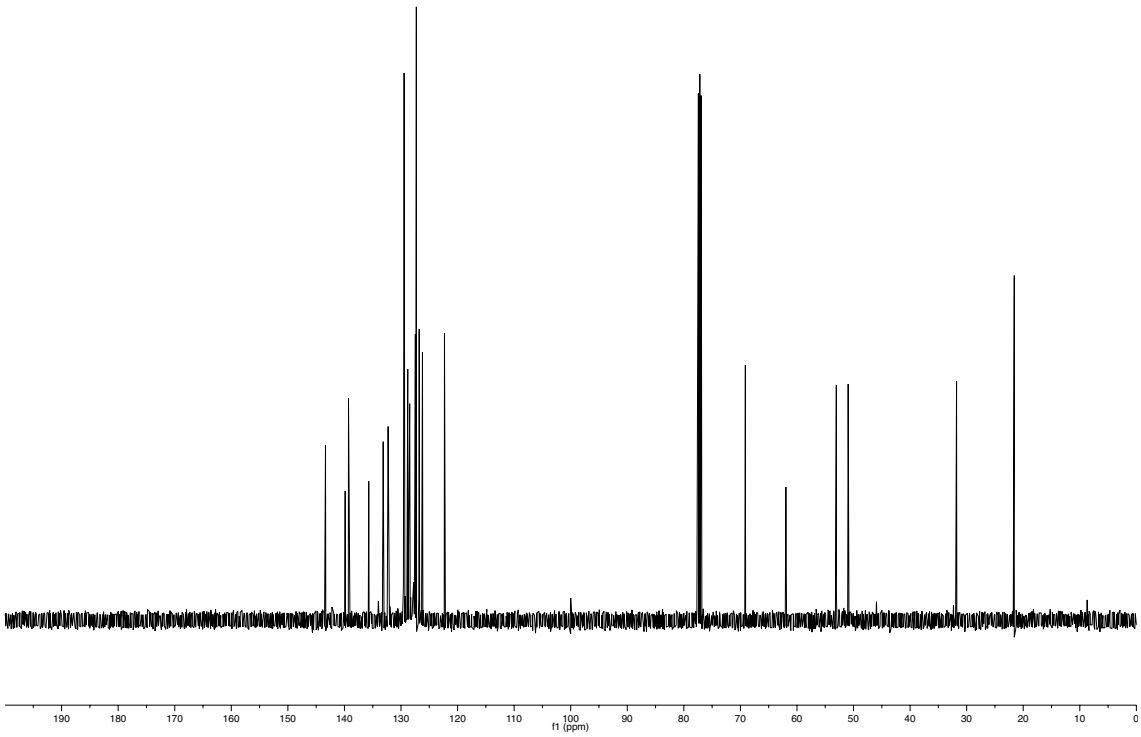


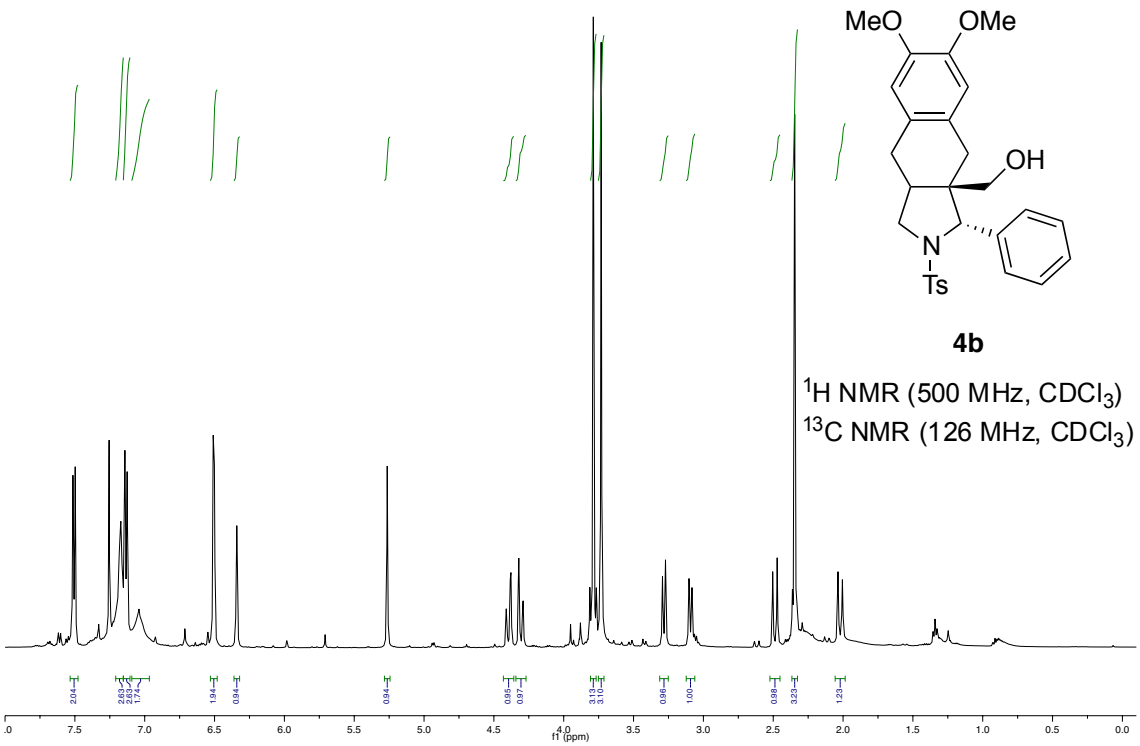


4a

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

^{13}C NMR (126 MHz, $CDCl_3$)

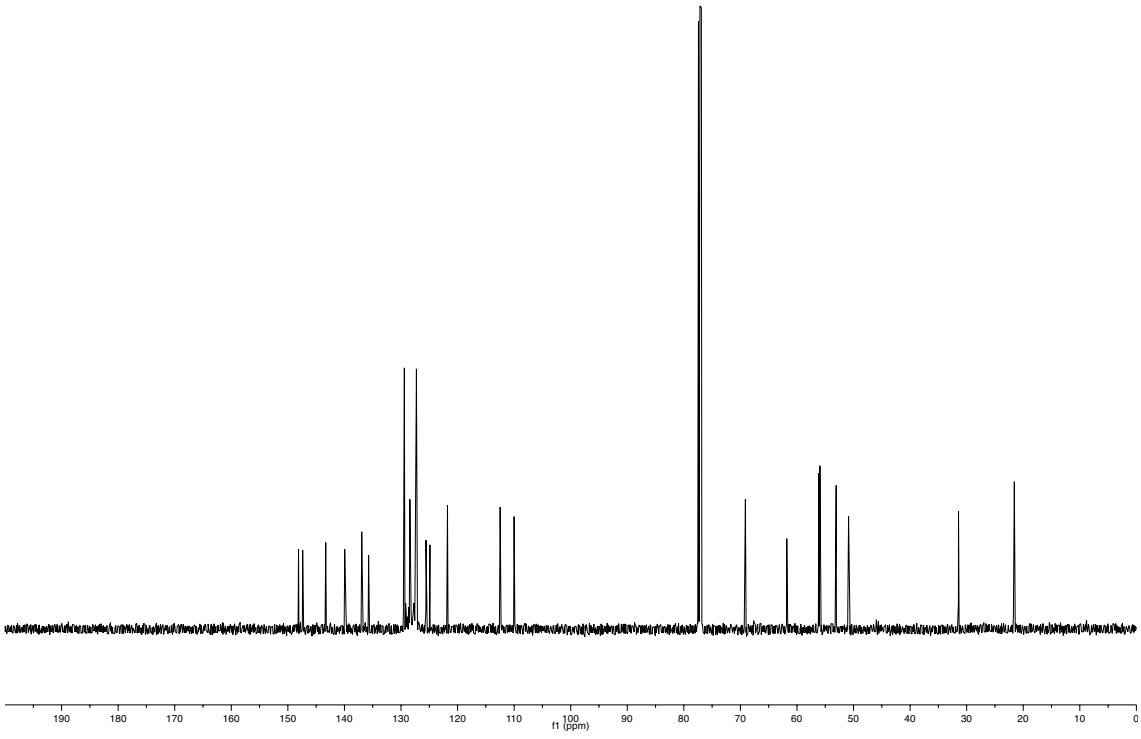


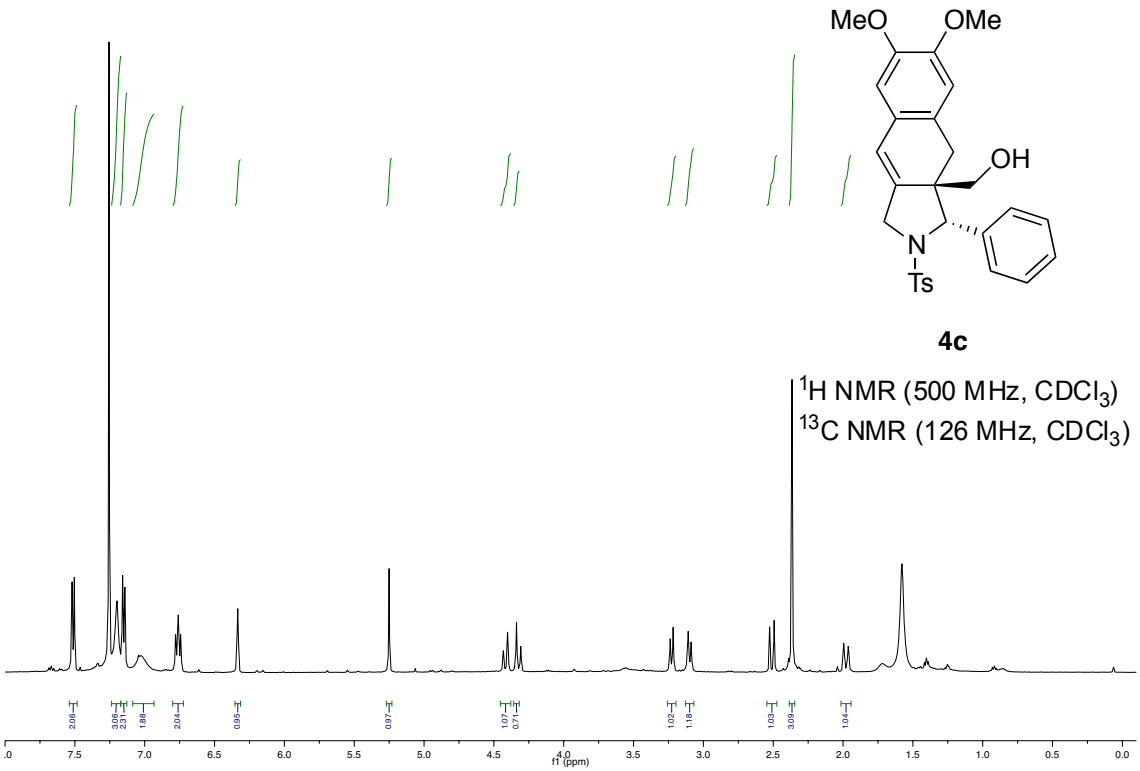


4b

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

^{13}C NMR (126 MHz, $CDCl_3$)

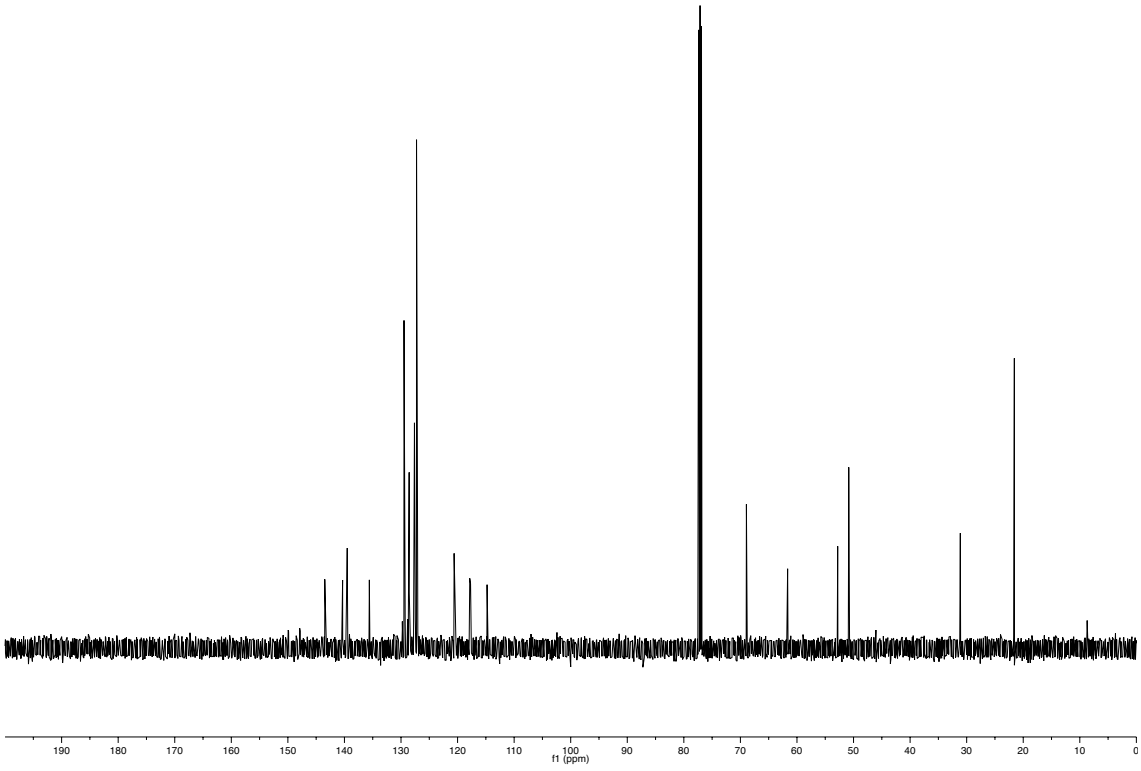


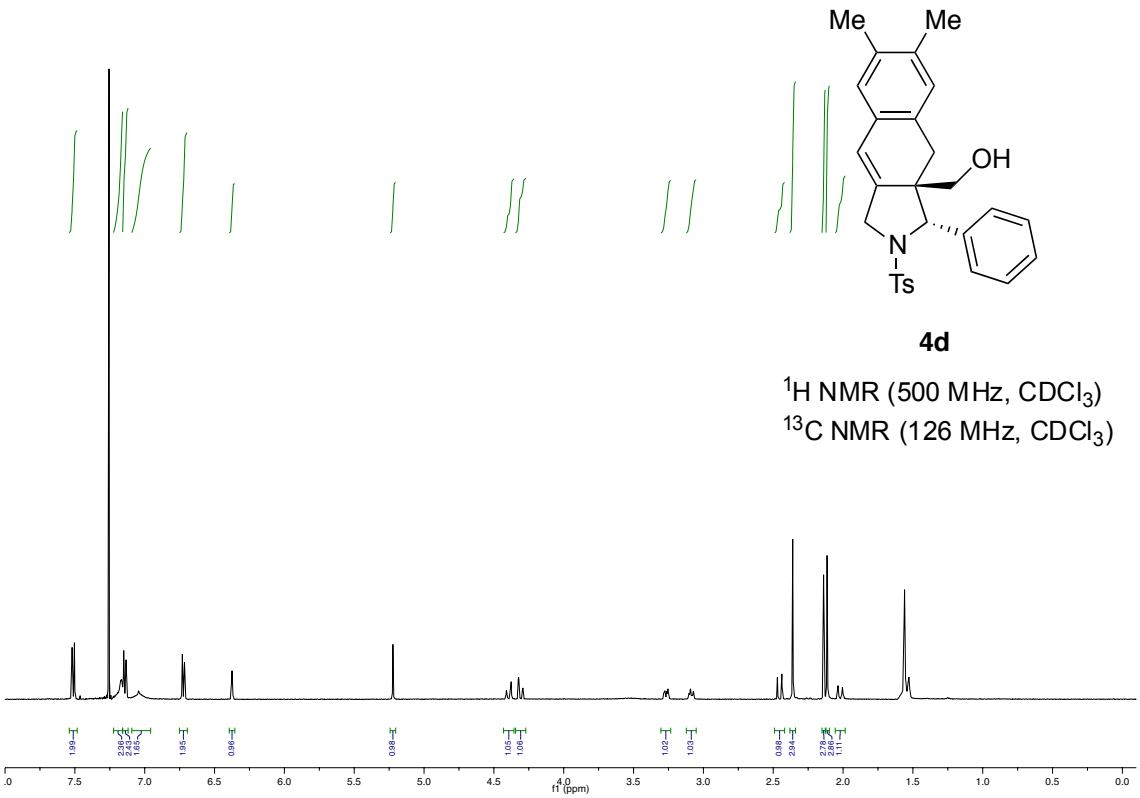


4c

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

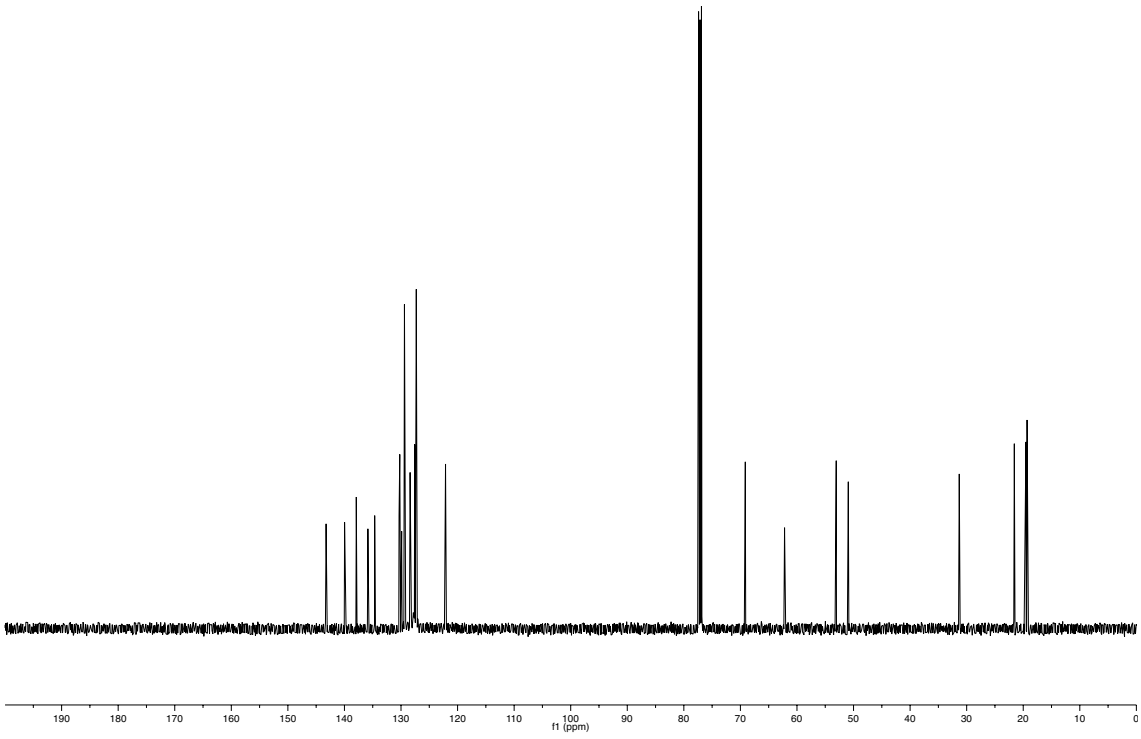
^{13}C NMR (126 MHz, $CDCl_3$)

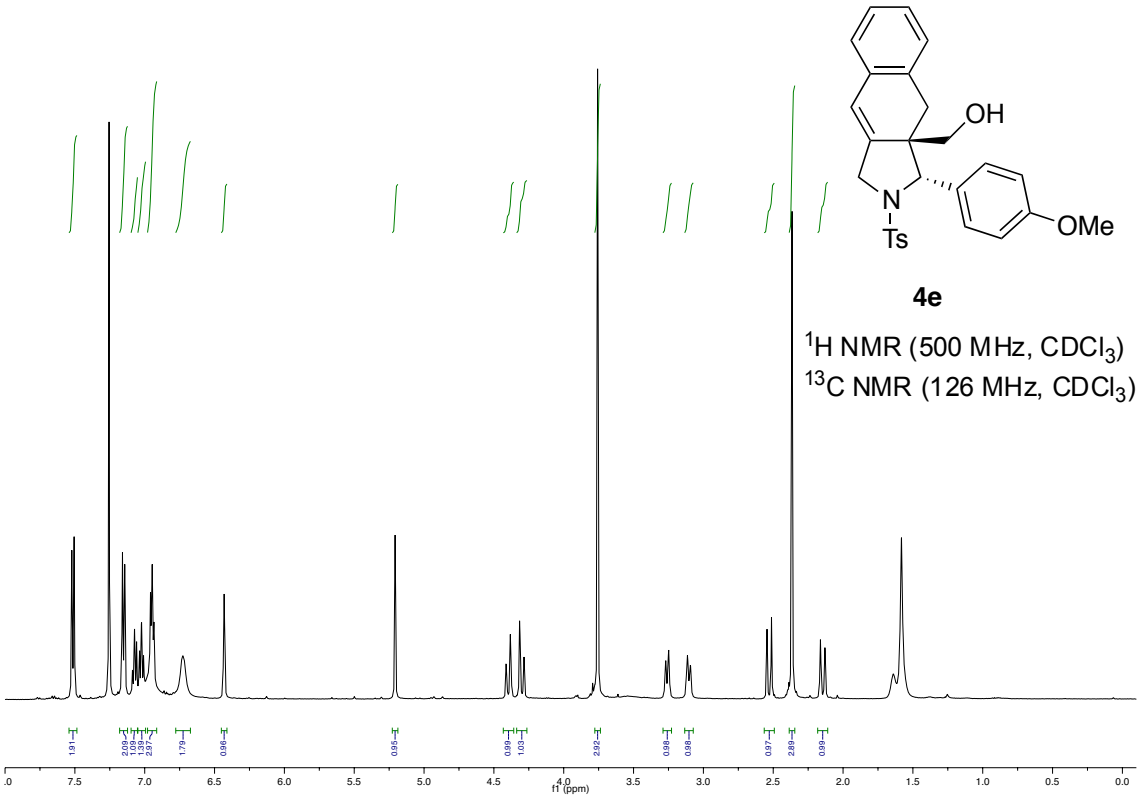




4d

^{1}H NMR (500 MHz, $CDCl_3$)
^{13}C NMR (126 MHz, $CDCl_3$)

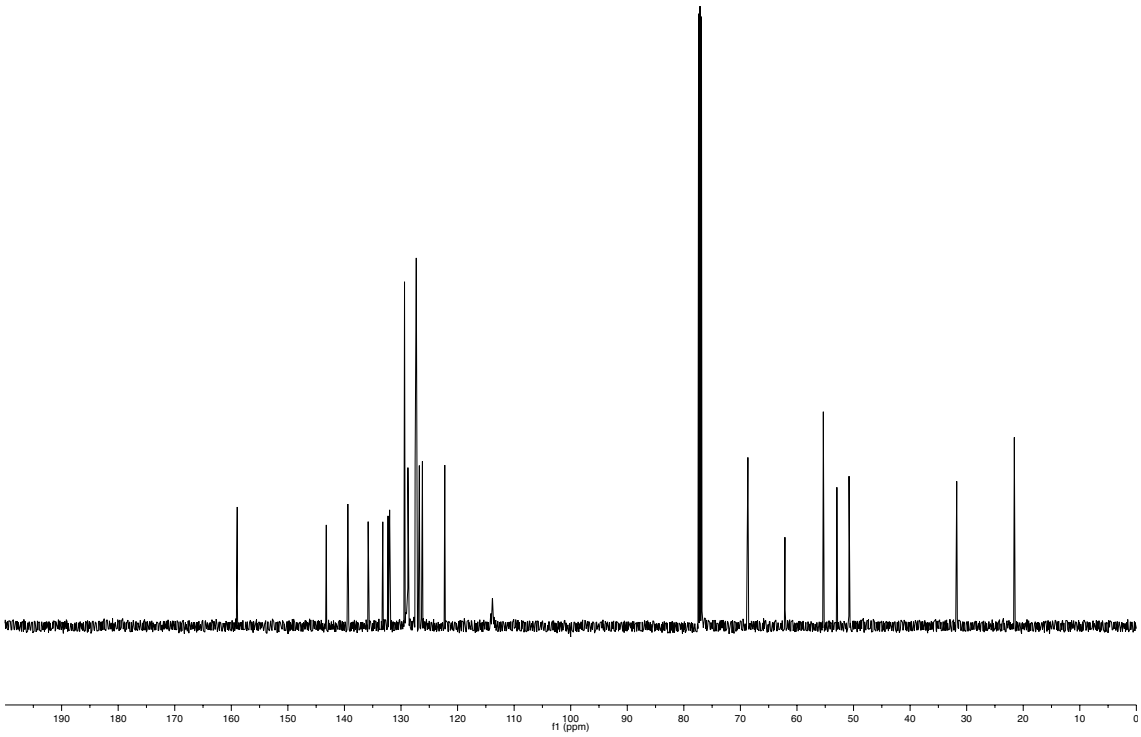


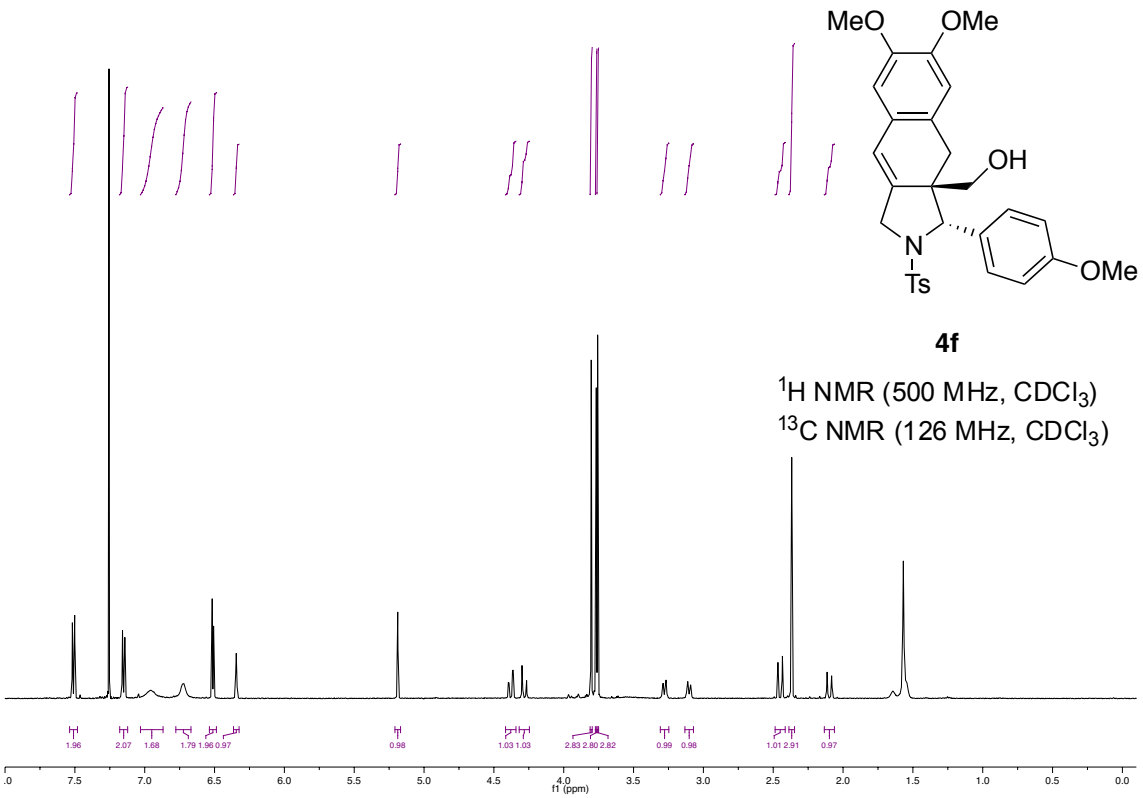


4e

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

^{13}C NMR (126 MHz, $CDCl_3$)

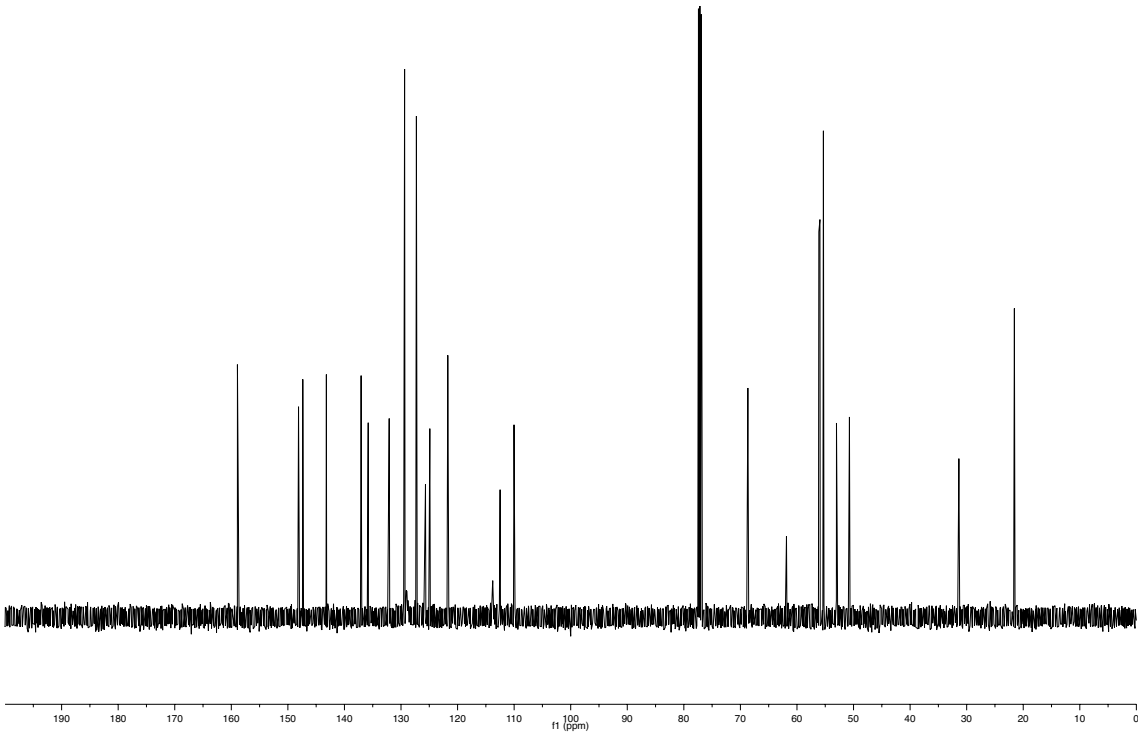


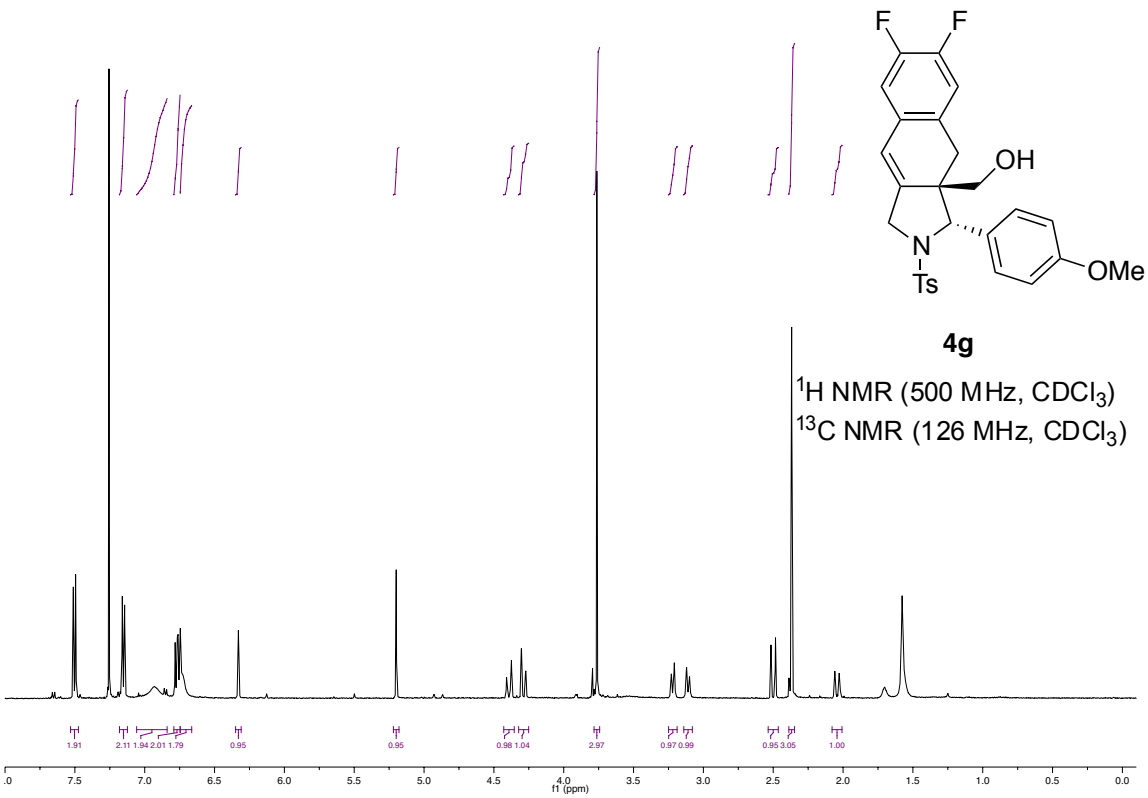


4f

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

^{13}C NMR (126 MHz, $CDCl_3$)

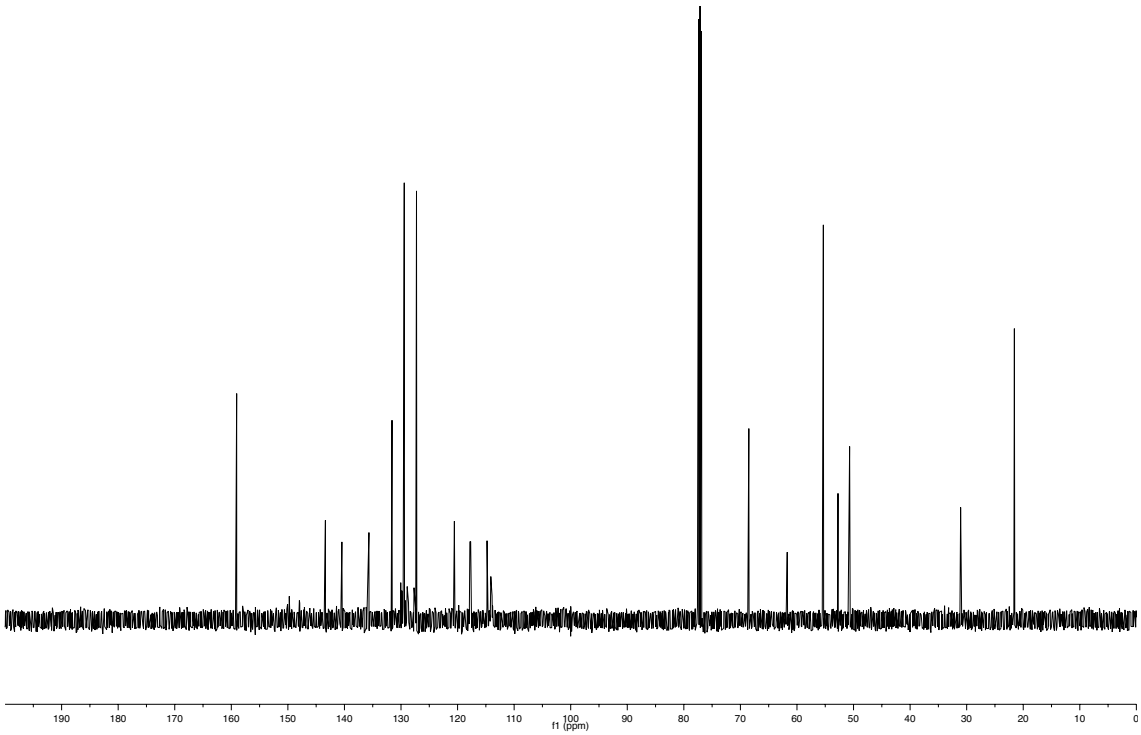


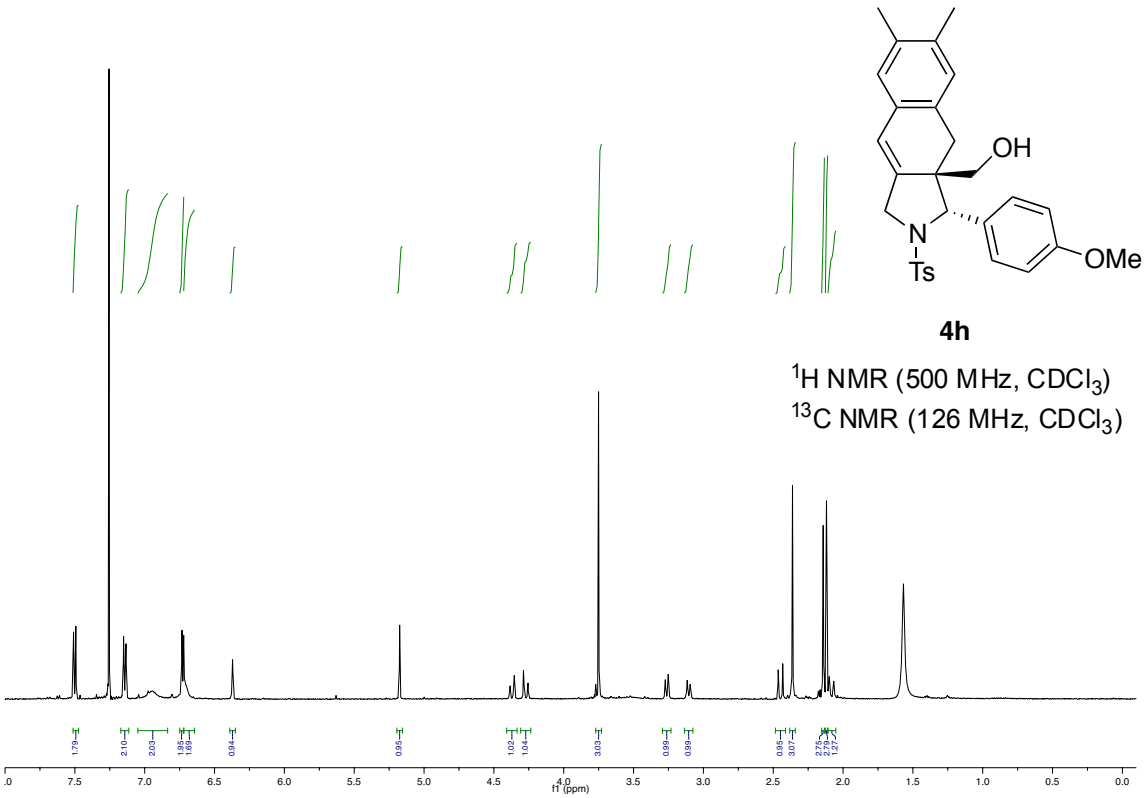


4g

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

^{13}C NMR (126 MHz, $CDCl_3$)

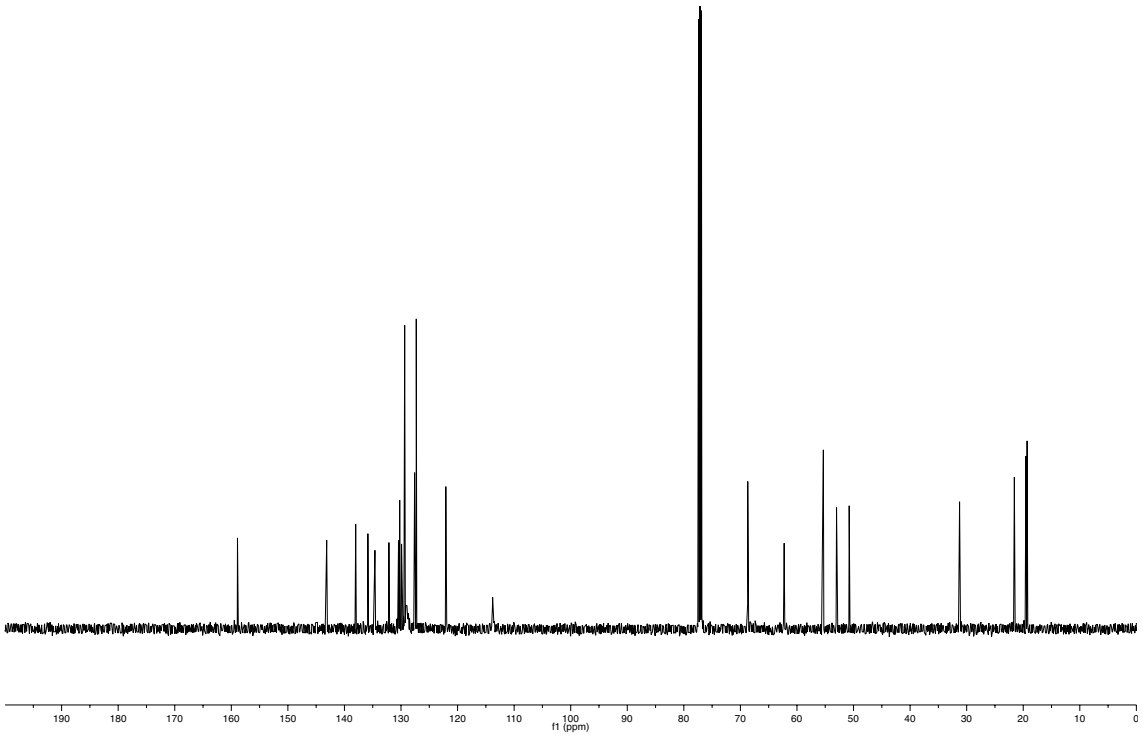


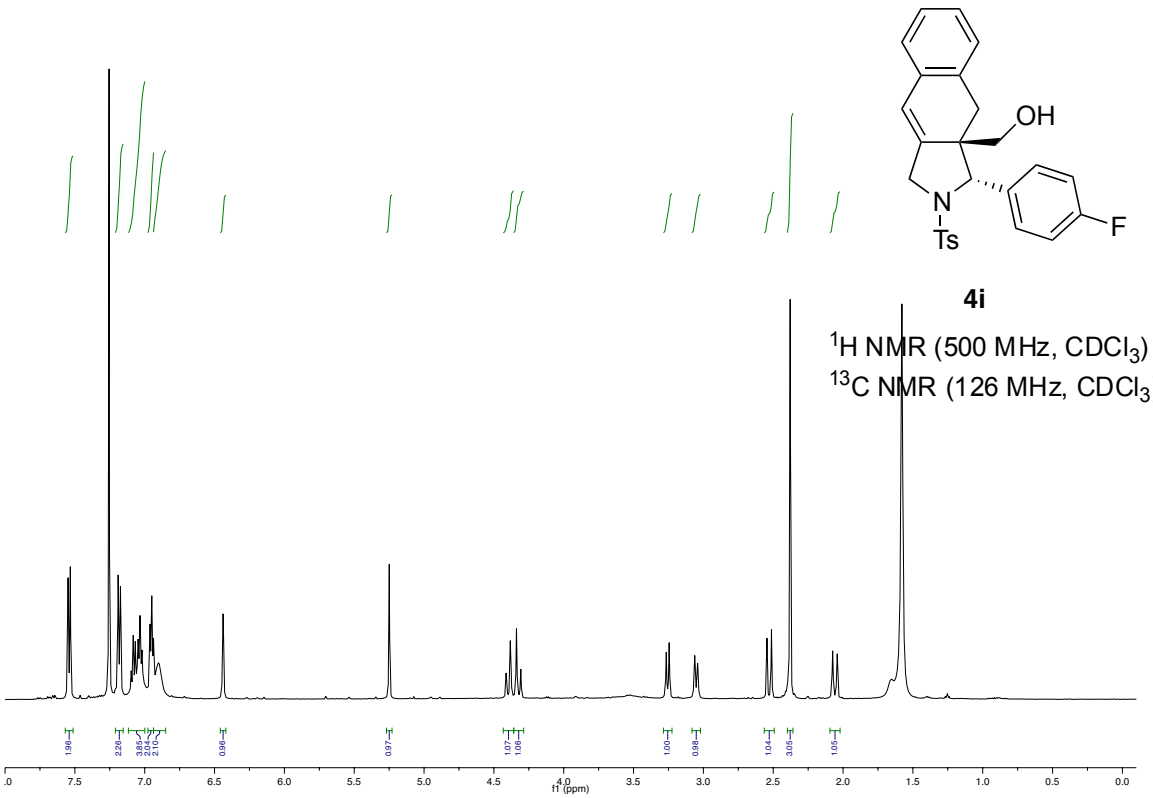


4h

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

^{13}C NMR (126 MHz, $CDCl_3$)

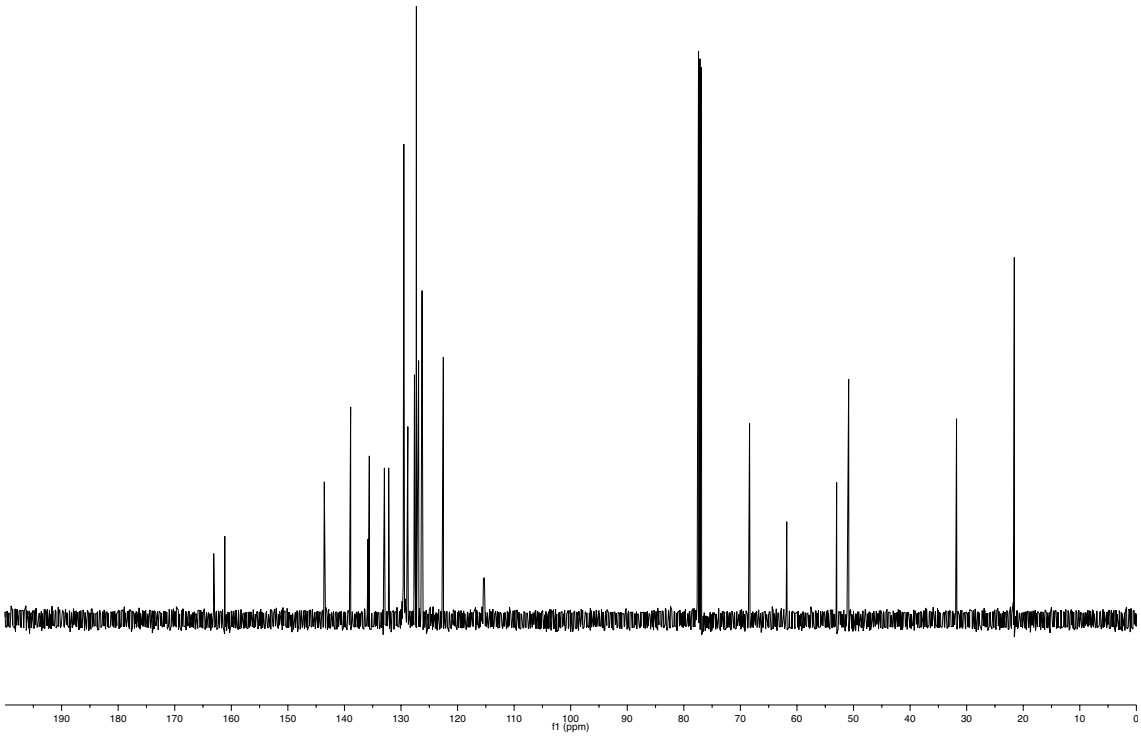


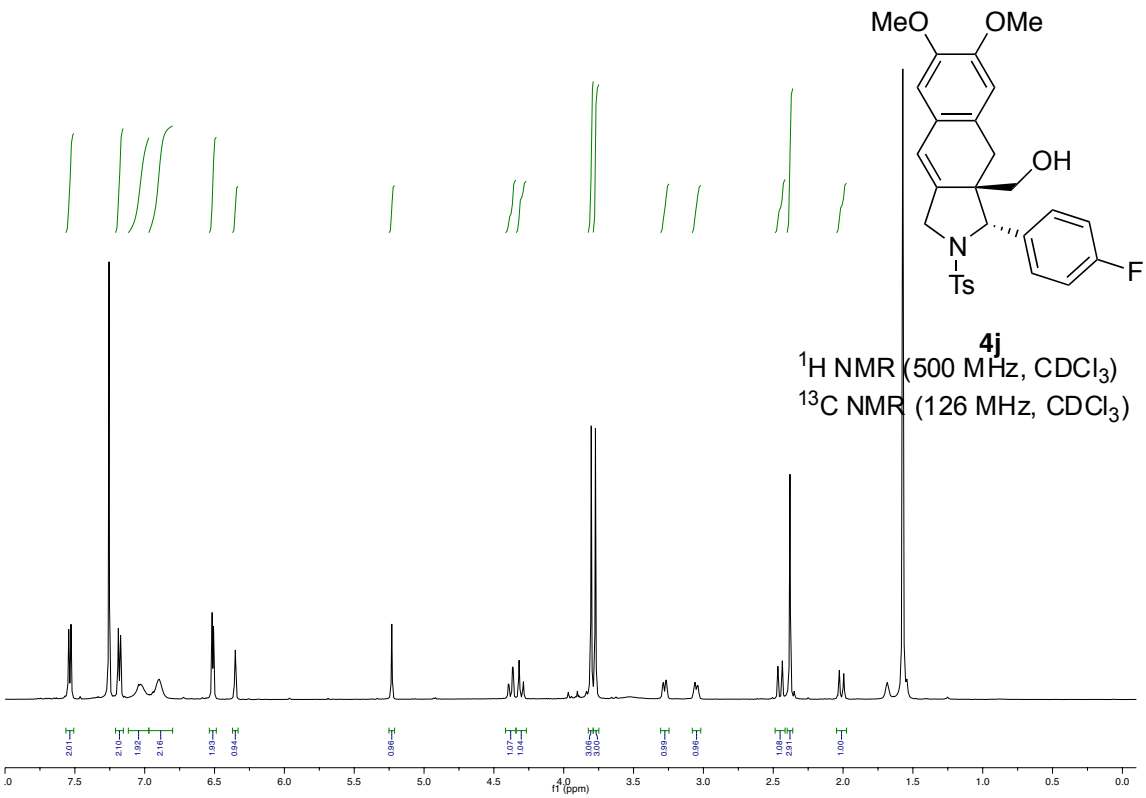


4i

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

^{13}C NMR (126 MHz, $CDCl_3$)

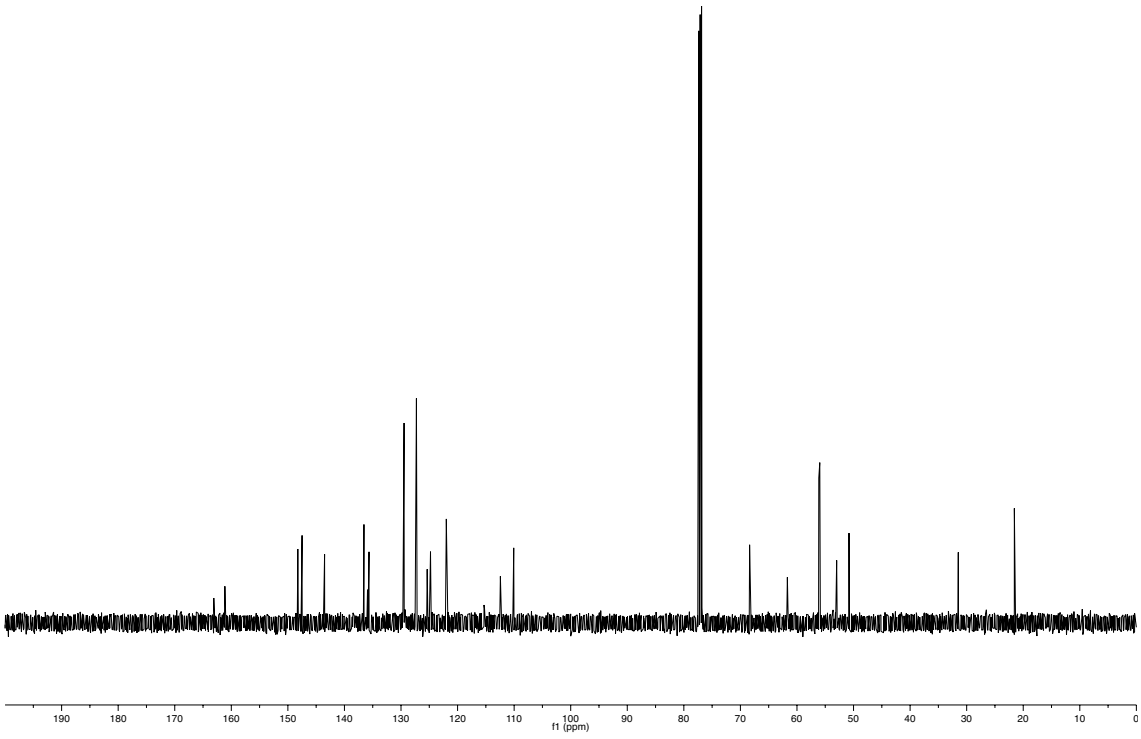


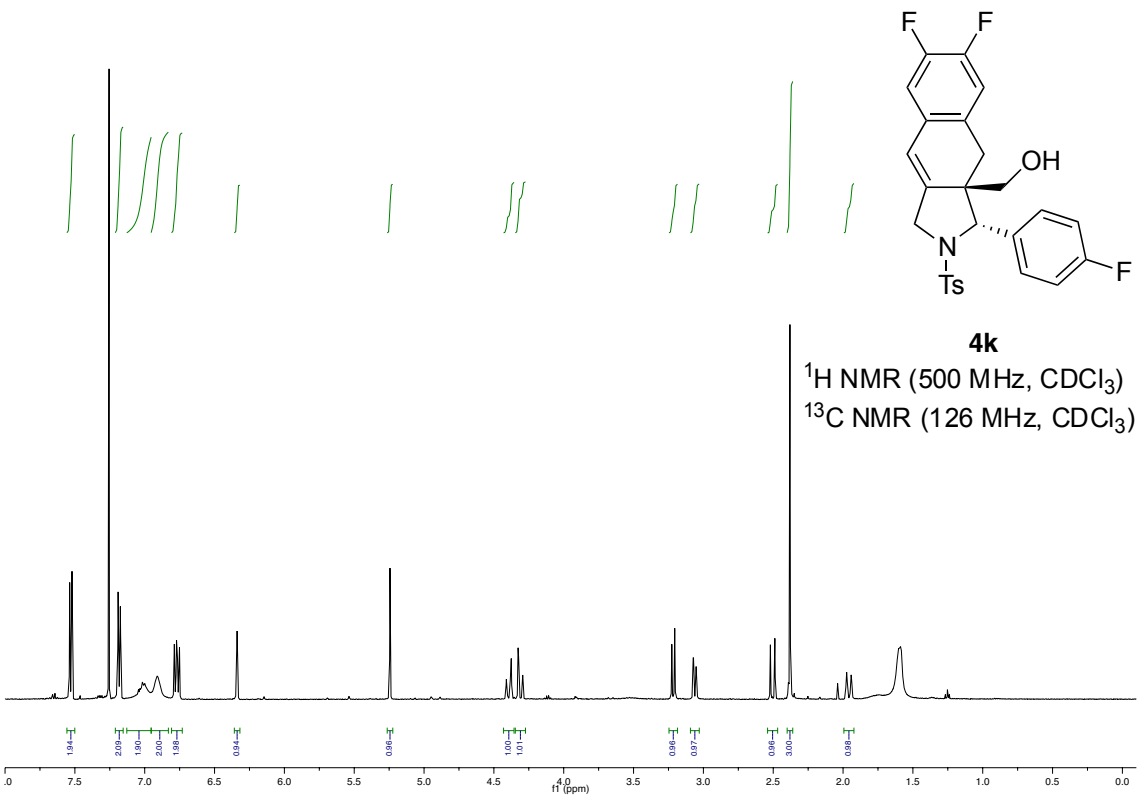


4j

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

^{13}C NMR (126 MHz, $CDCl_3$)

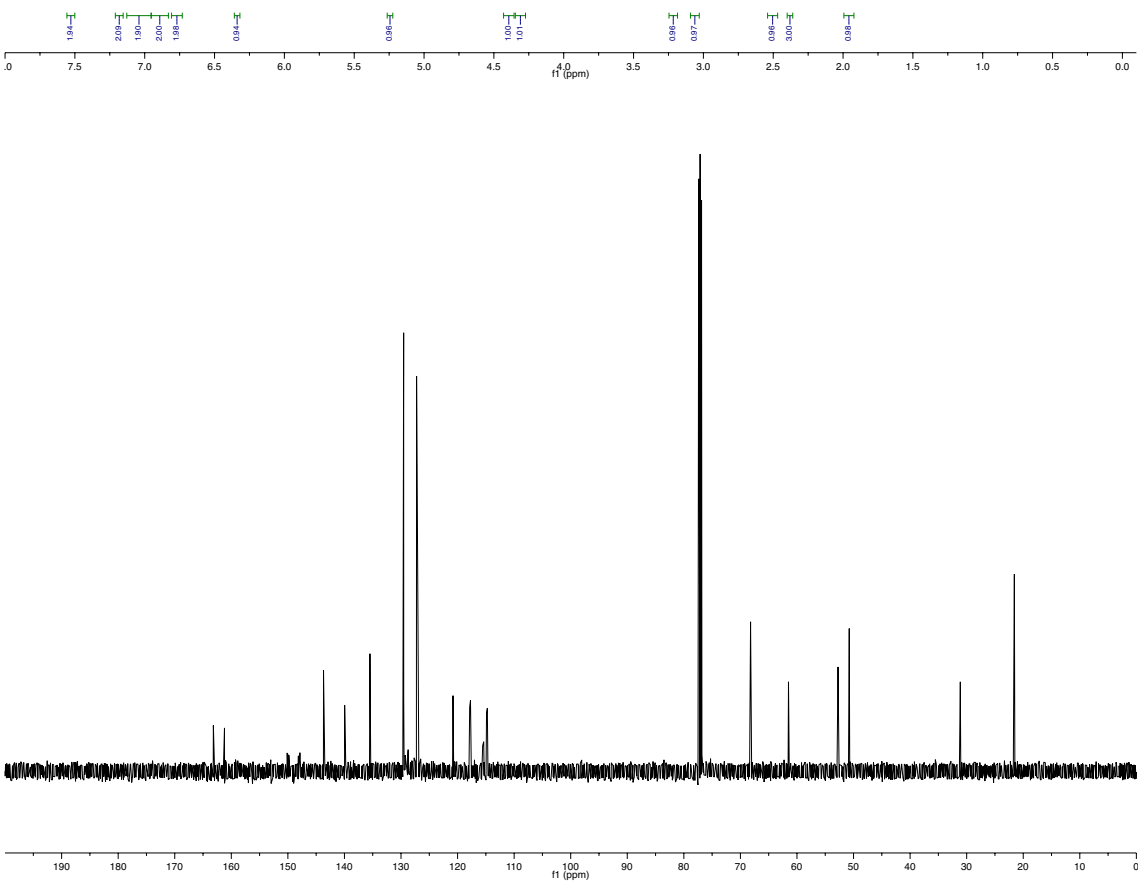


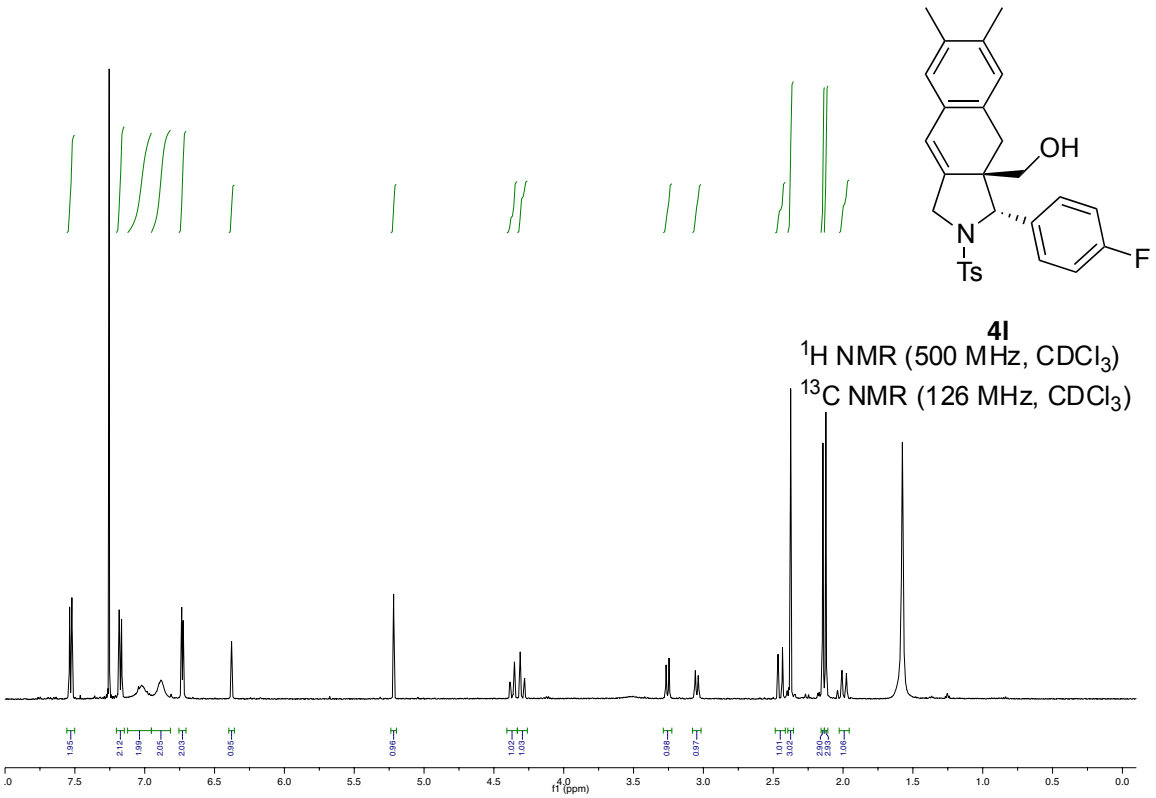


4k

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

^{13}C NMR (126 MHz, $CDCl_3$)

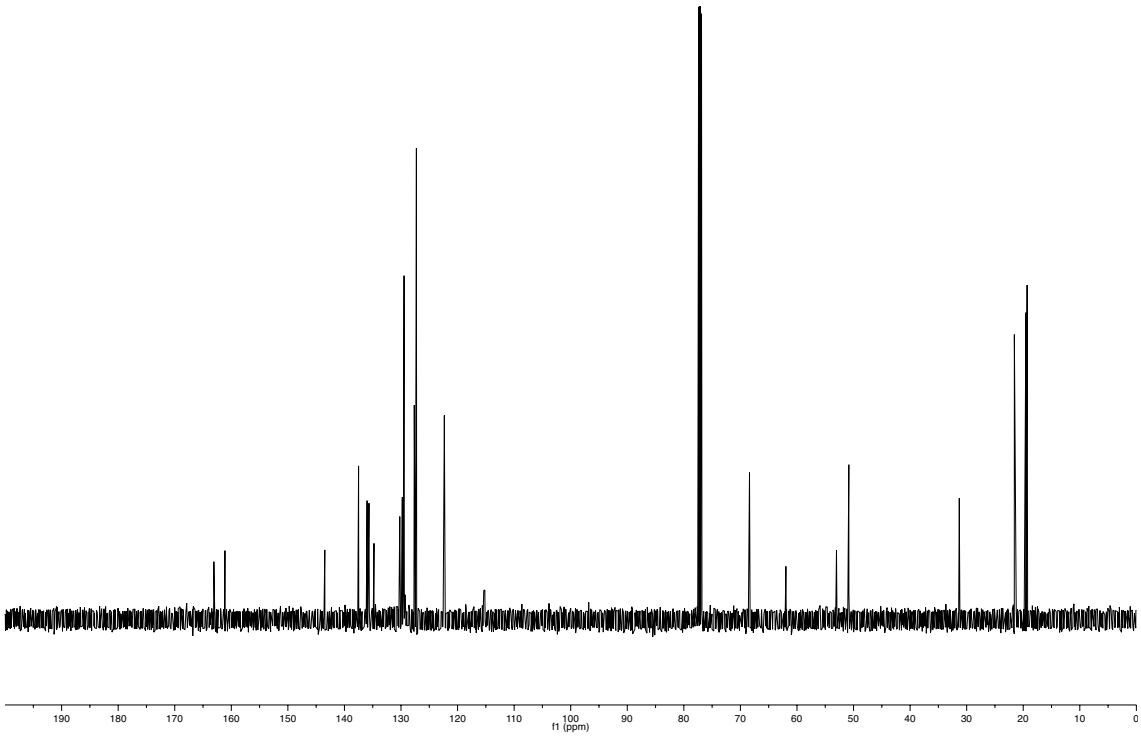


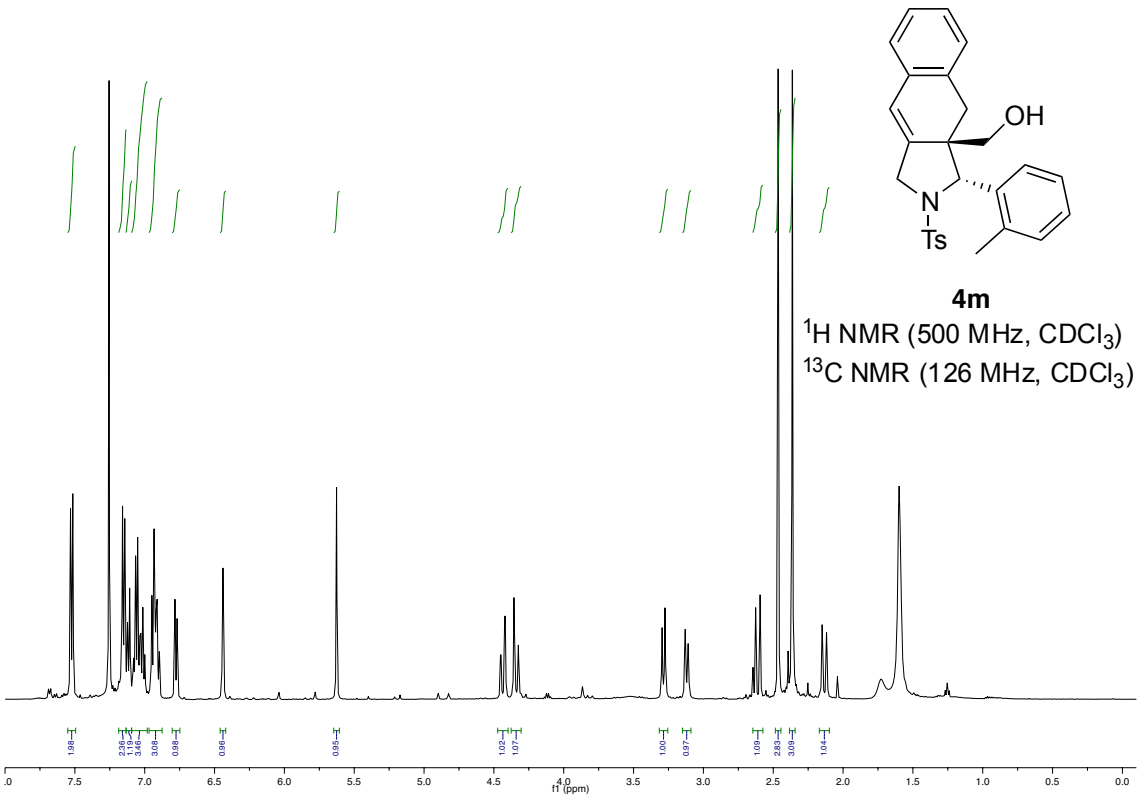


4l

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

^{13}C NMR (126 MHz, $CDCl_3$)

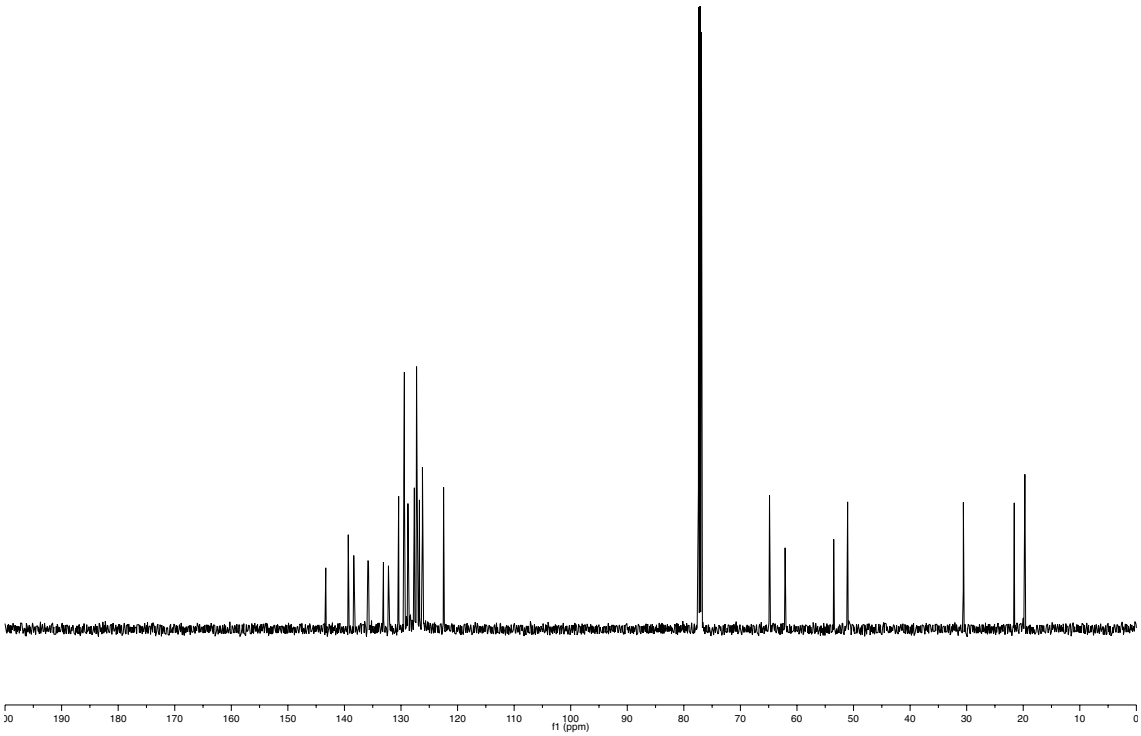


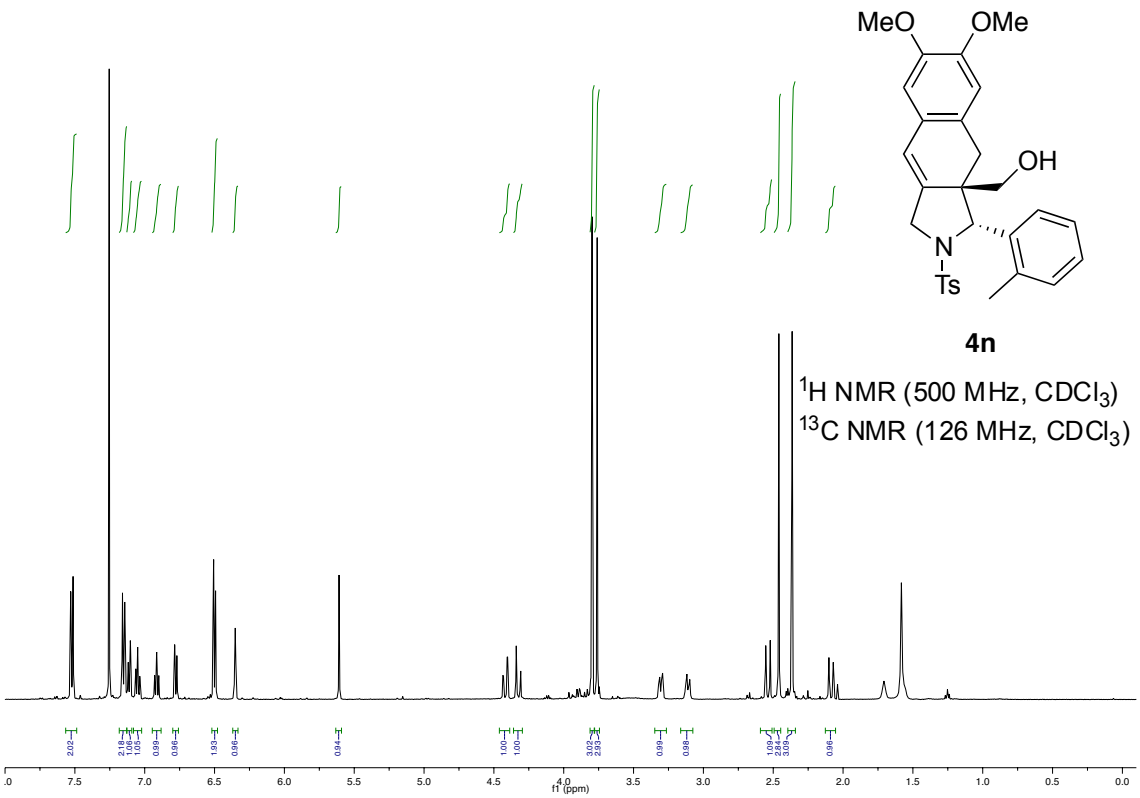


4m

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

^{13}C NMR (126 MHz, $CDCl_3$)

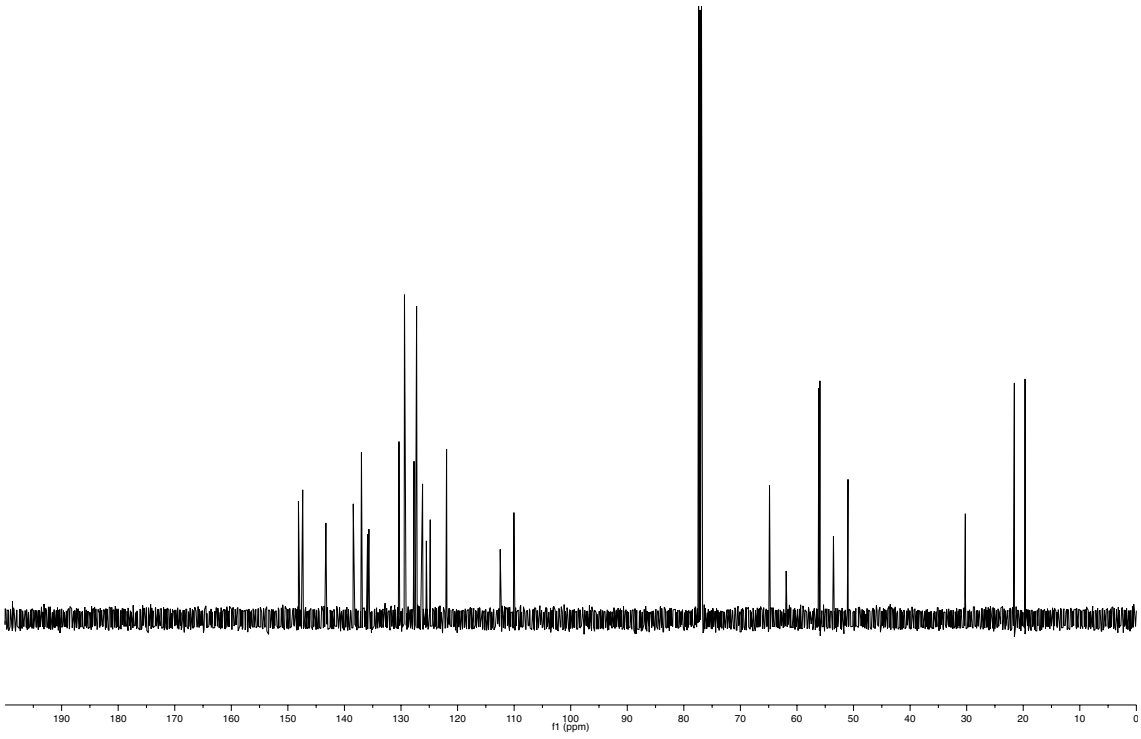


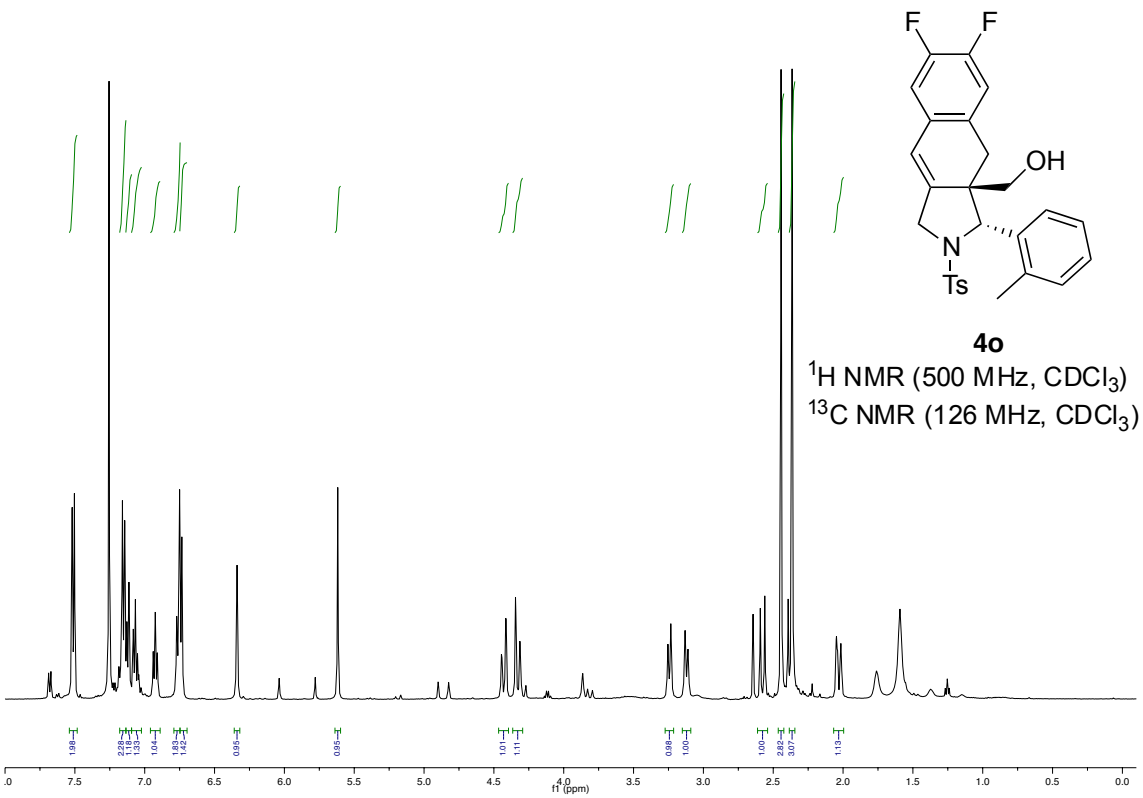


4n

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

^{13}C NMR (126 MHz, $CDCl_3$)

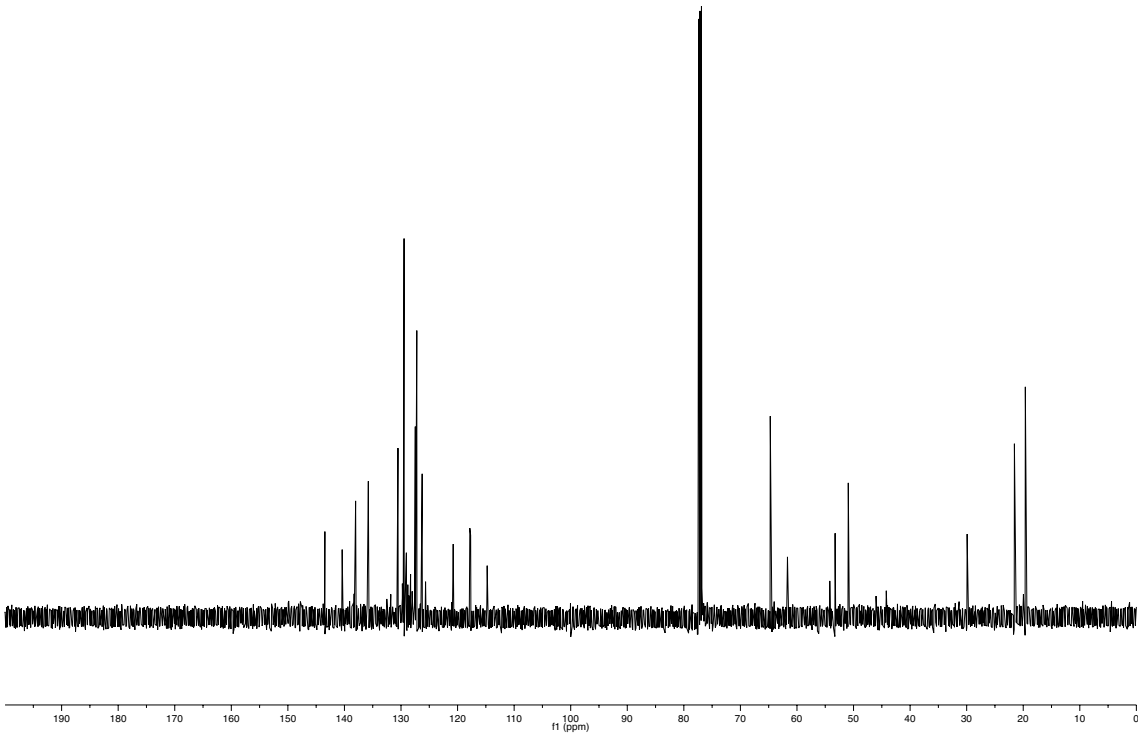


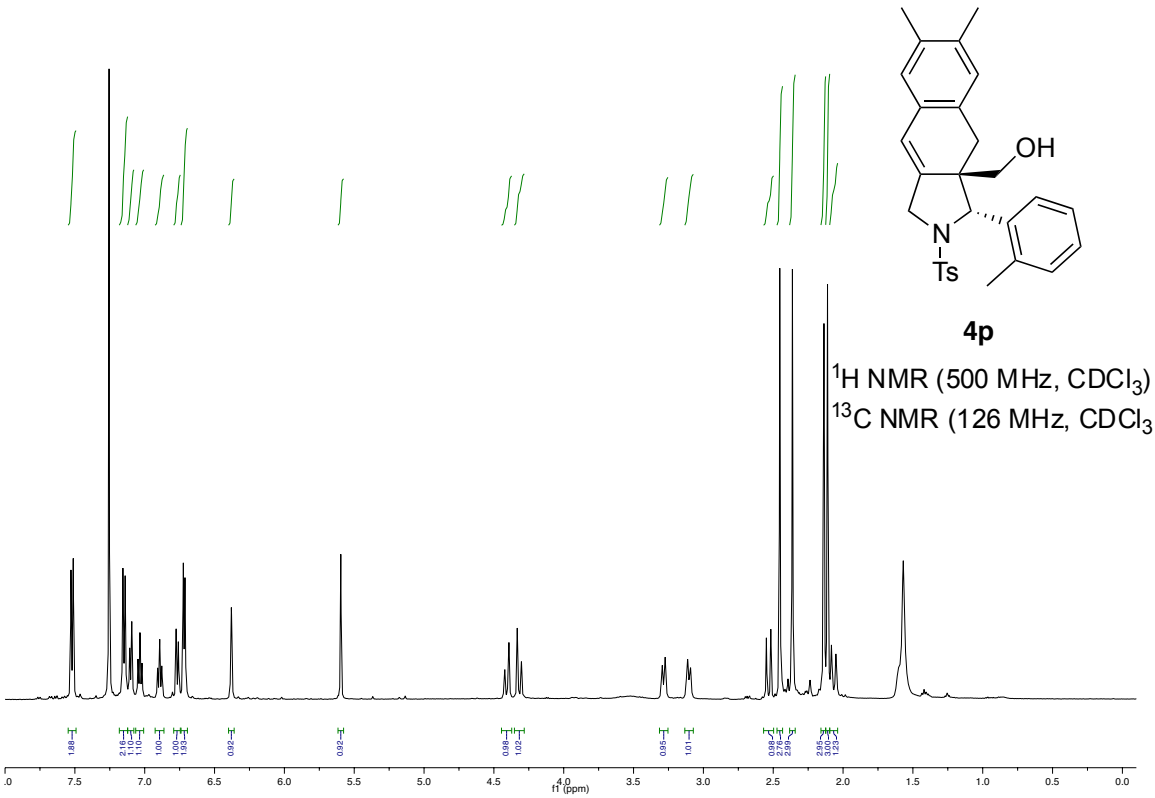


4o

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

^{13}C NMR (126 MHz, $CDCl_3$)

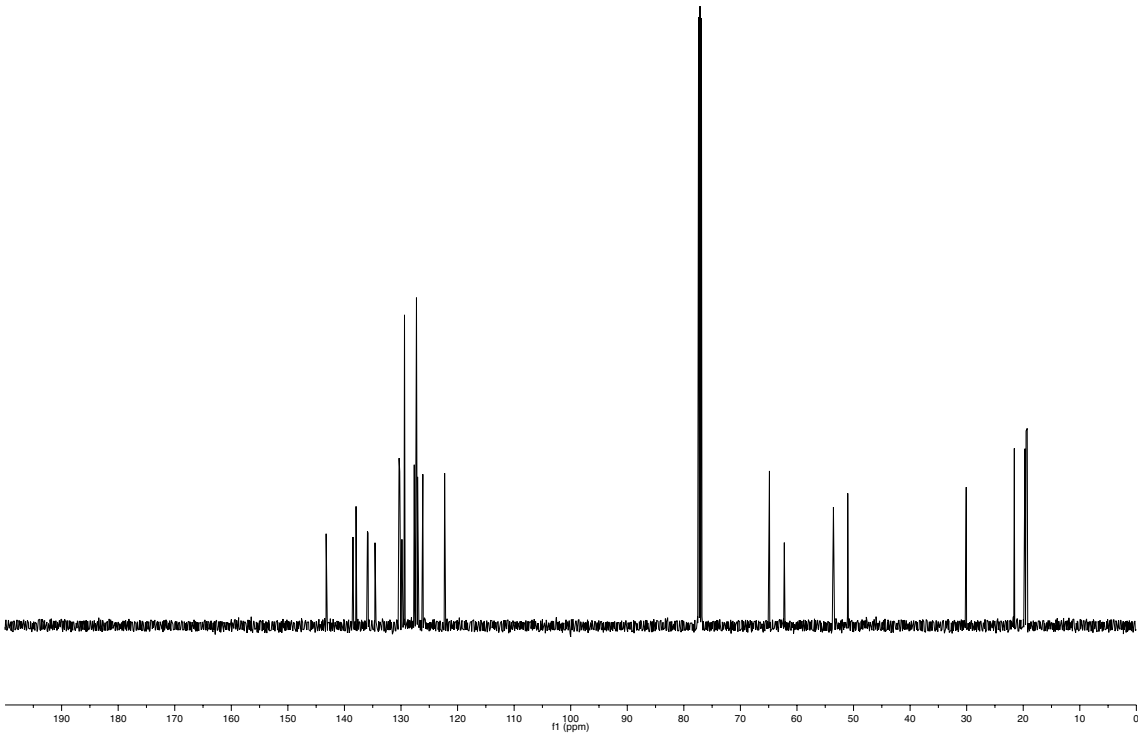


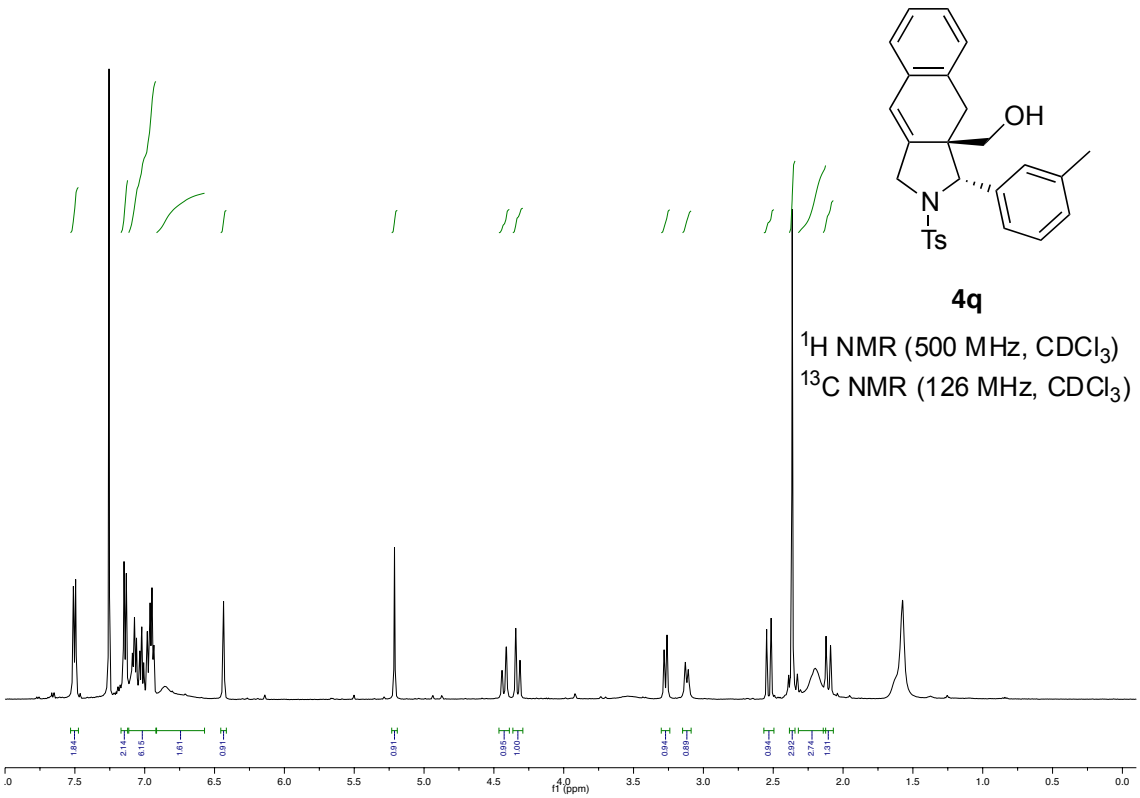


4p

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

^{13}C NMR (126 MHz, $CDCl_3$)

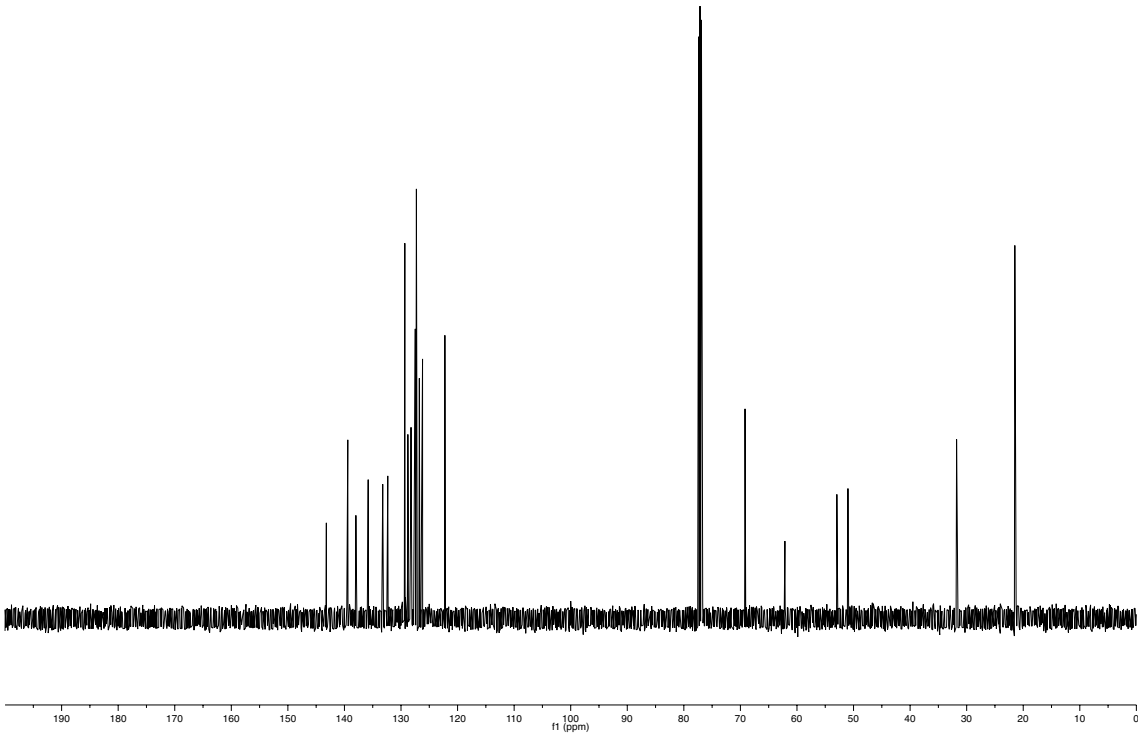


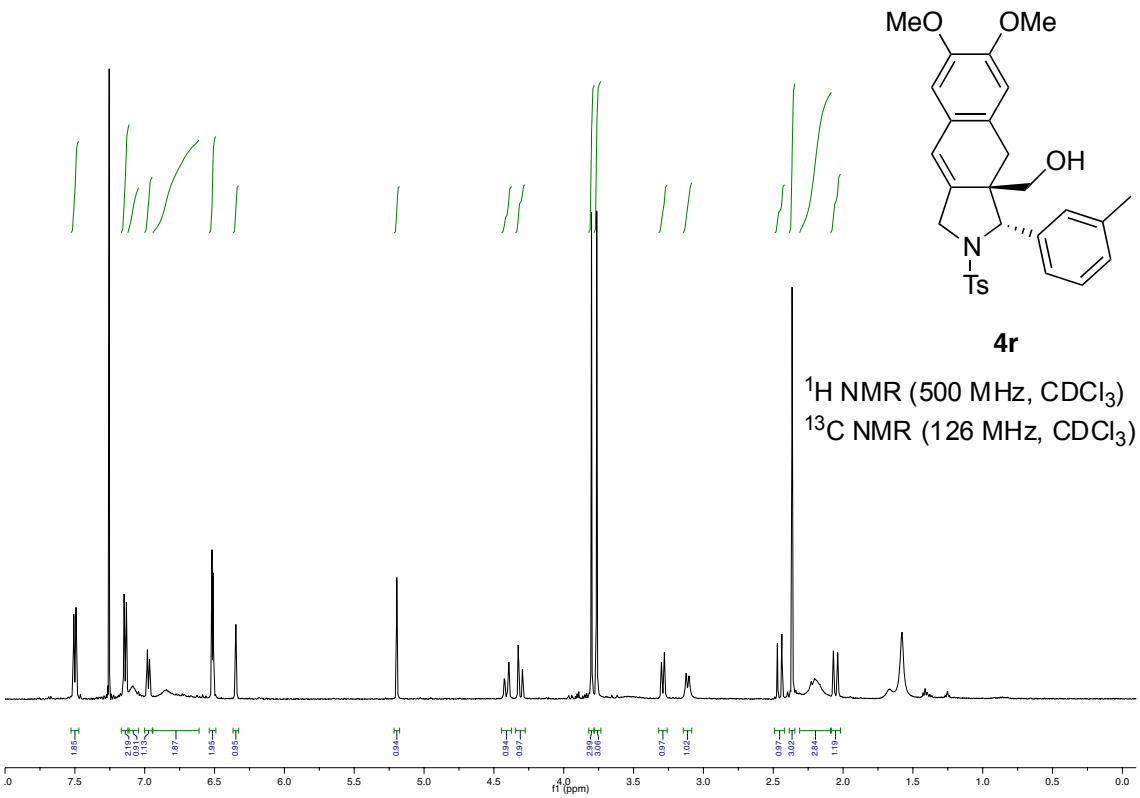


4q

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

^{13}C NMR (126 MHz, $CDCl_3$)

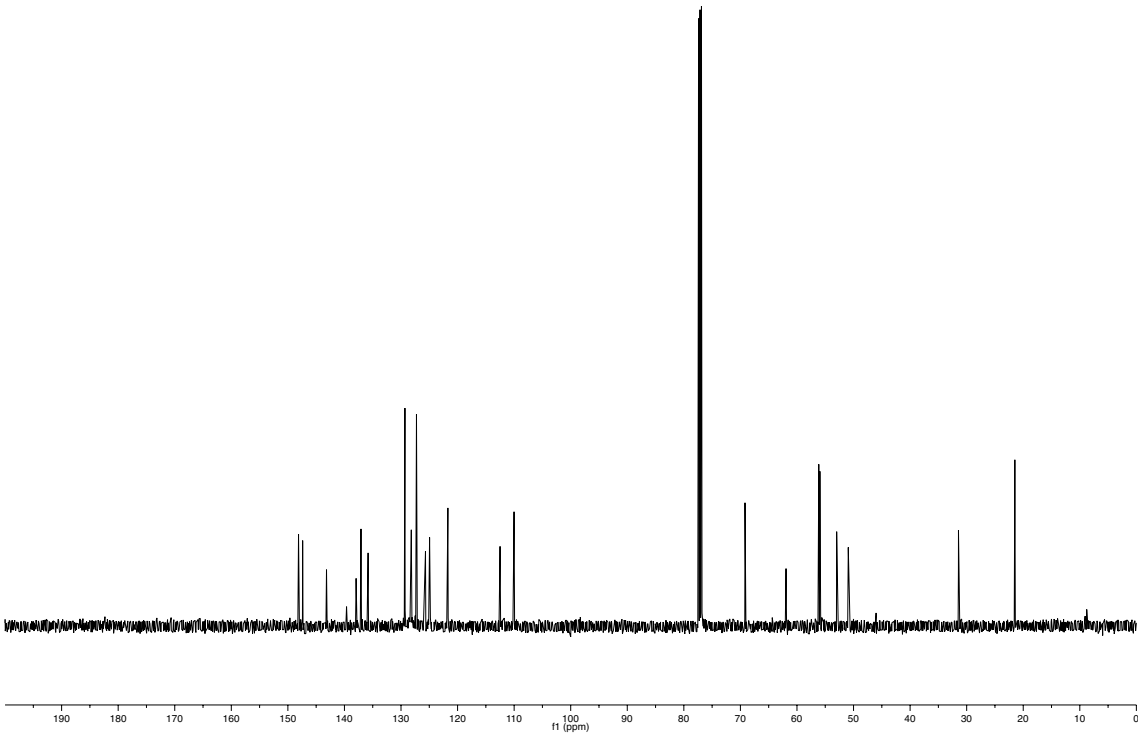


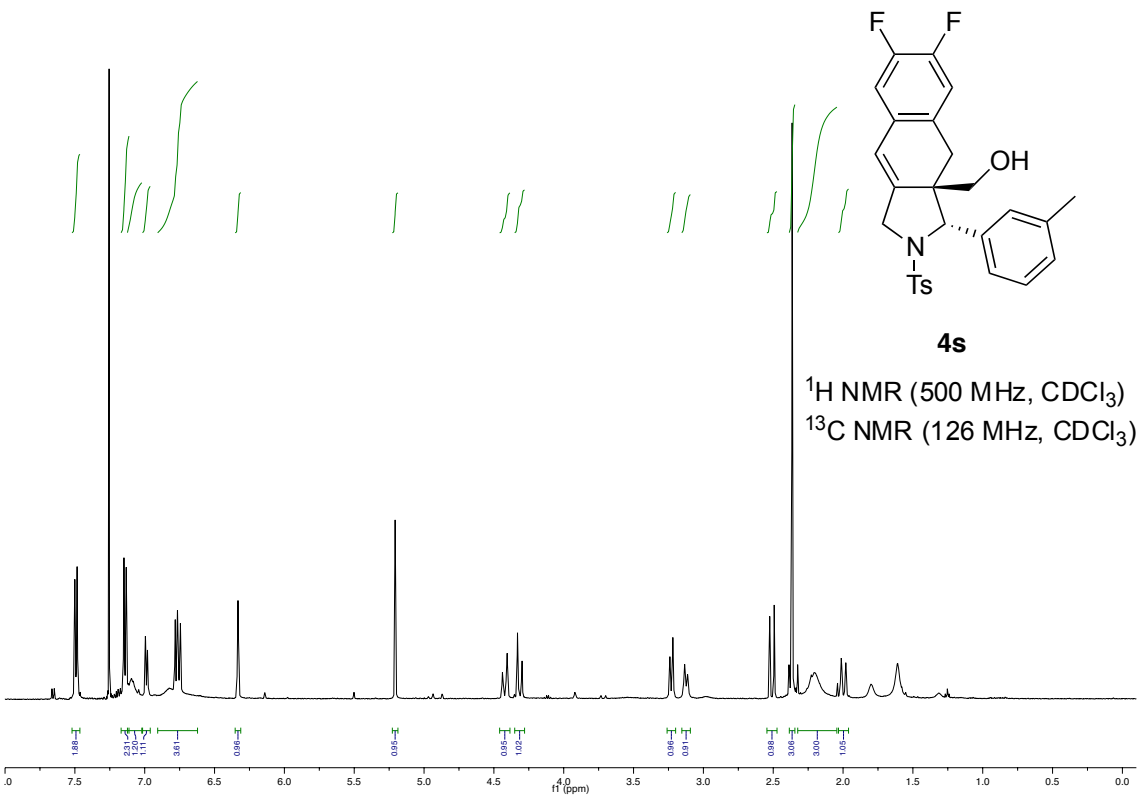


4r

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

^{13}C NMR (126 MHz, $CDCl_3$)

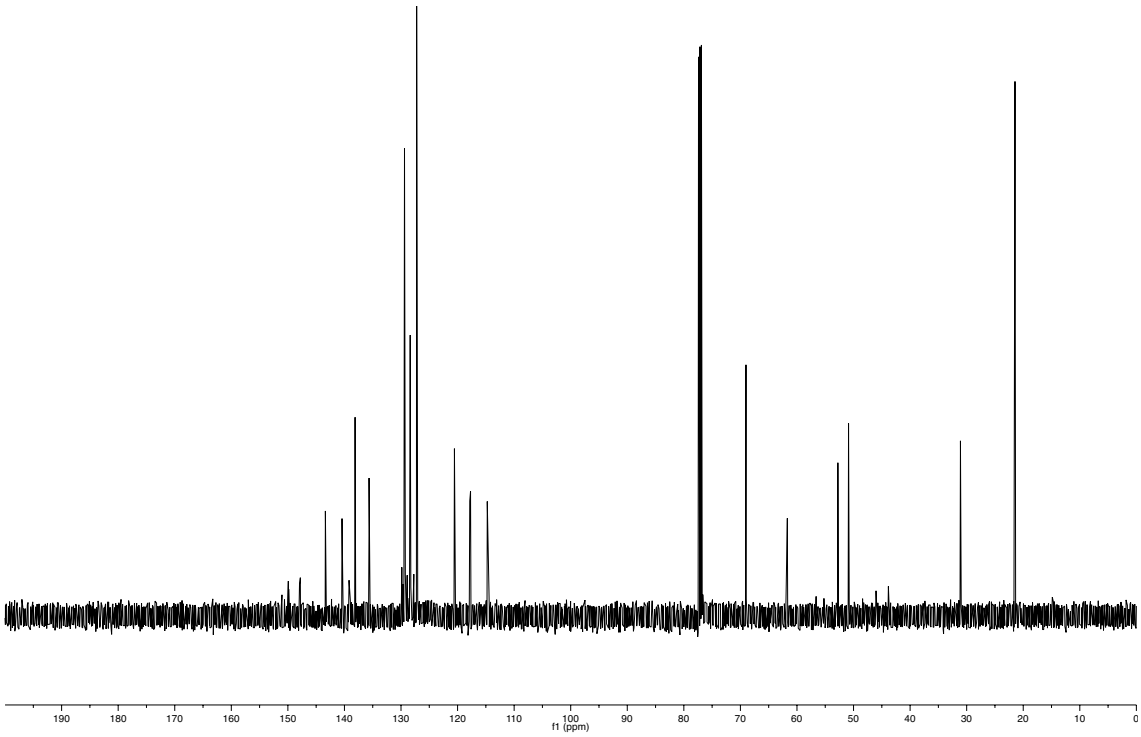


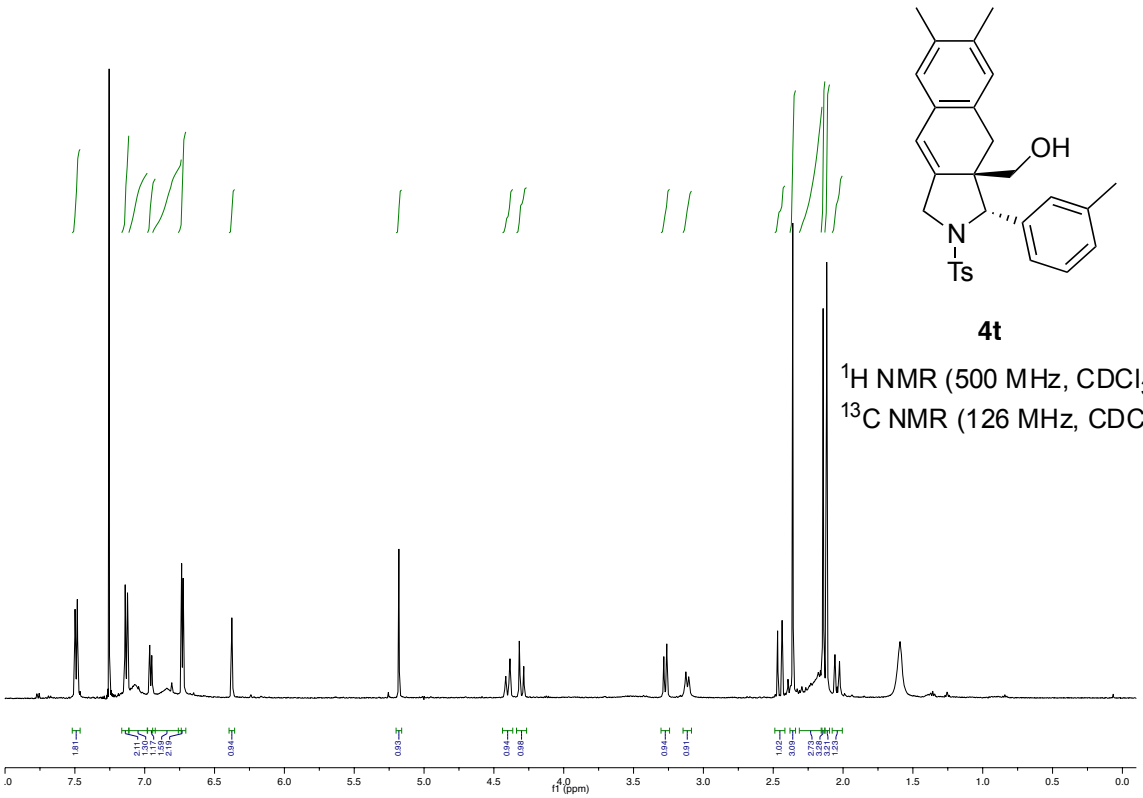


4s

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

^{13}C NMR (126 MHz, $CDCl_3$)

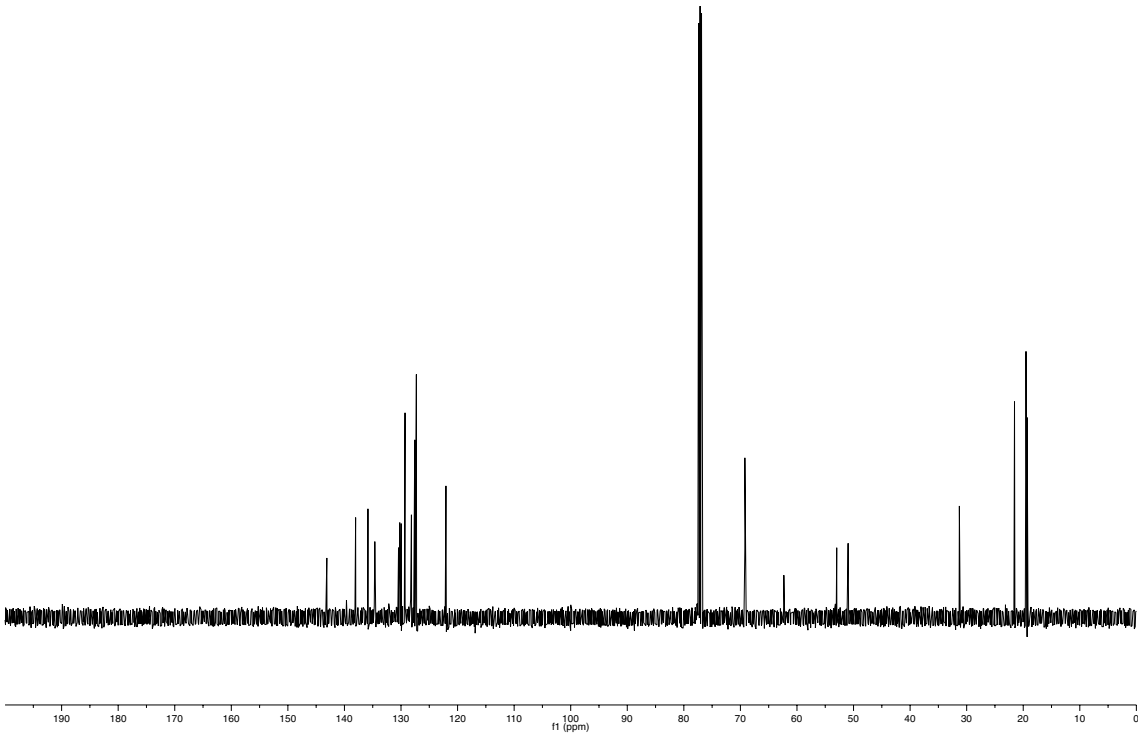


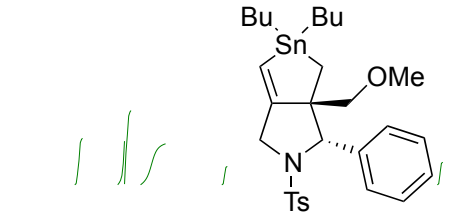


4t

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

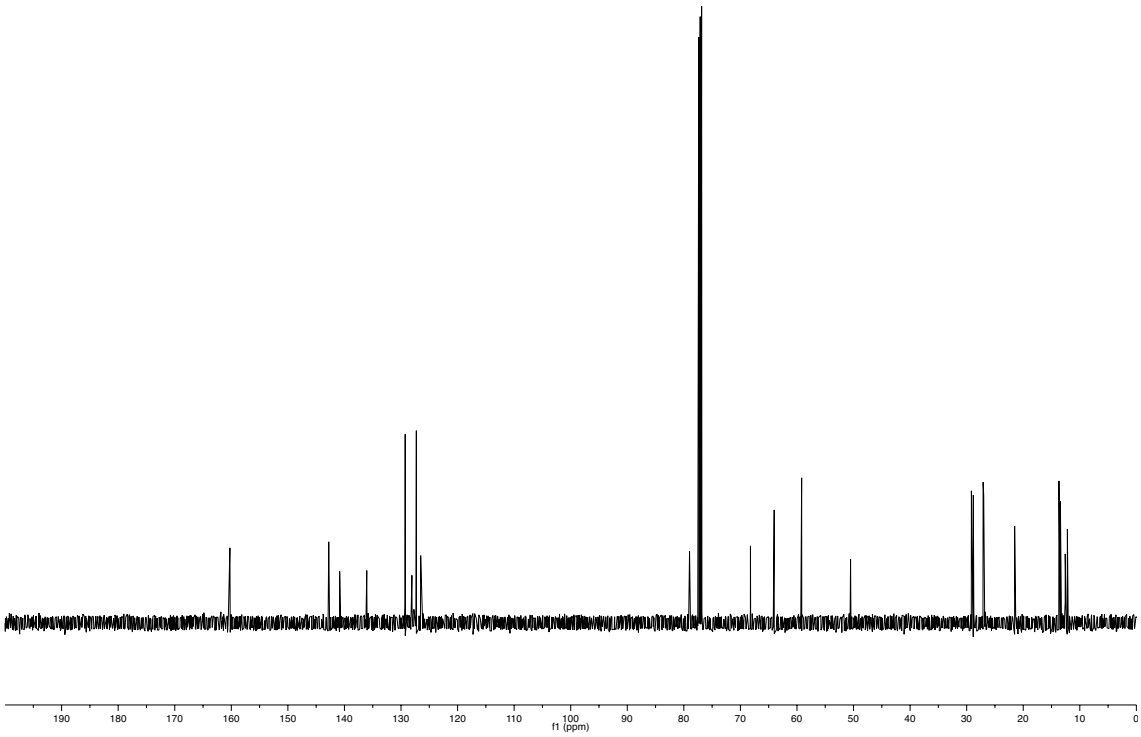
^{13}C NMR (126 MHz, $CDCl_3$)

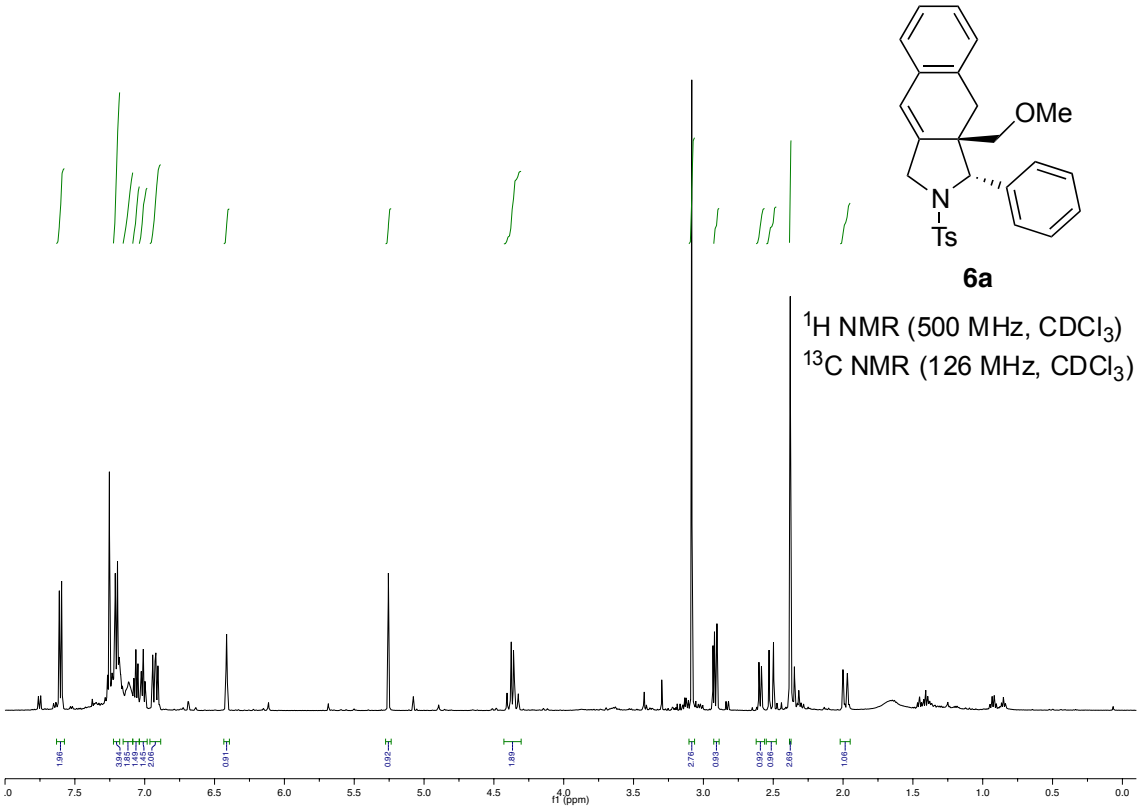




5a

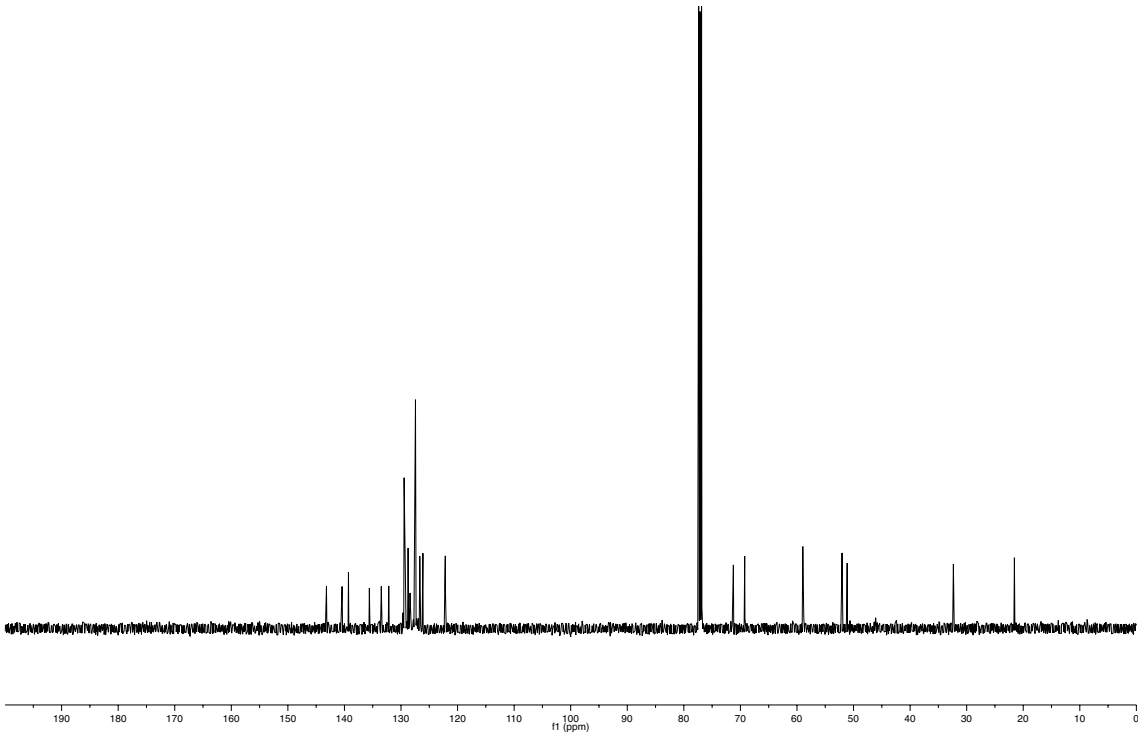
^{1}H NMR (500 MHz, $CDCl_3$)
^{13}C NMR (126 MHz, $CDCl_3$)

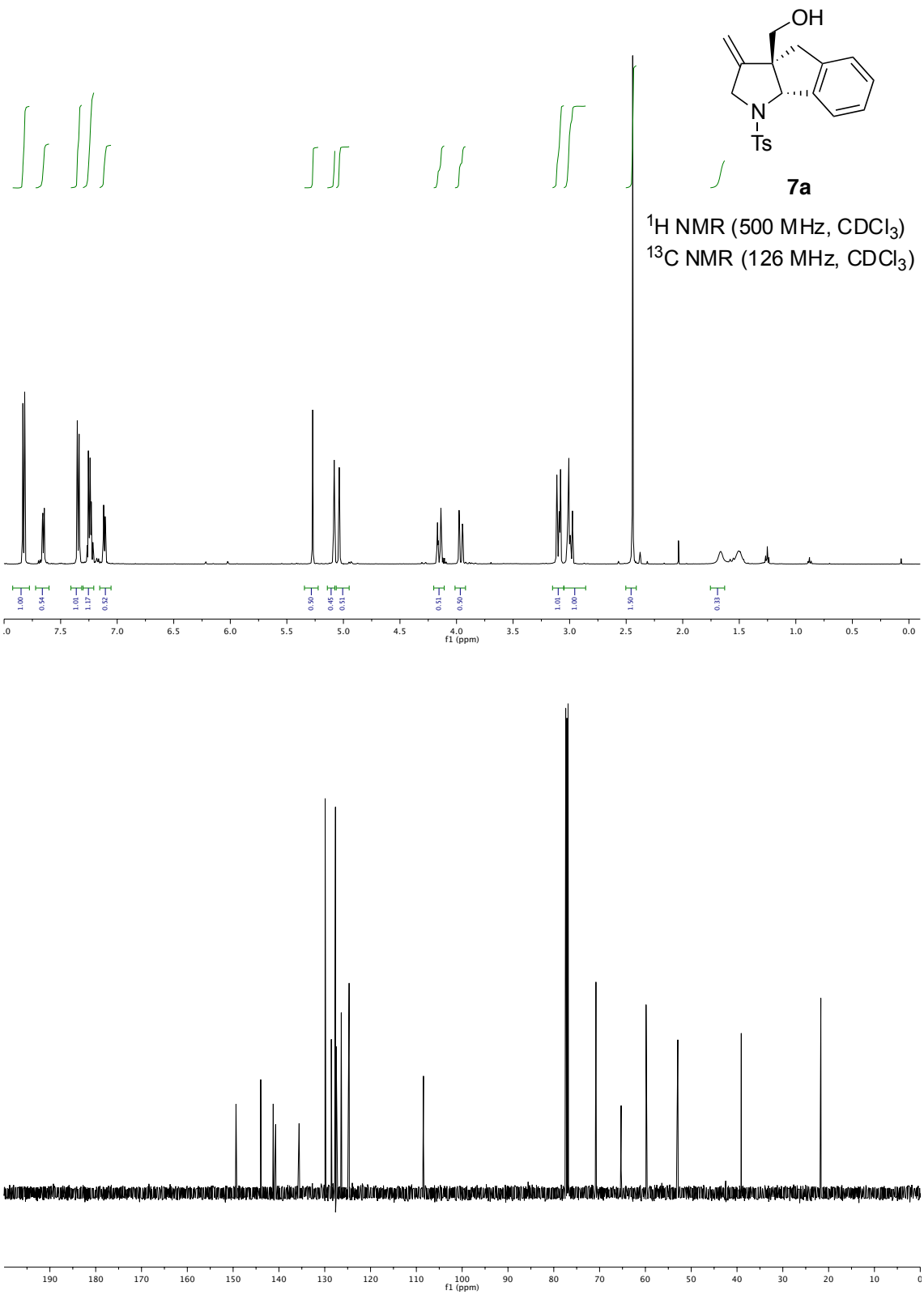


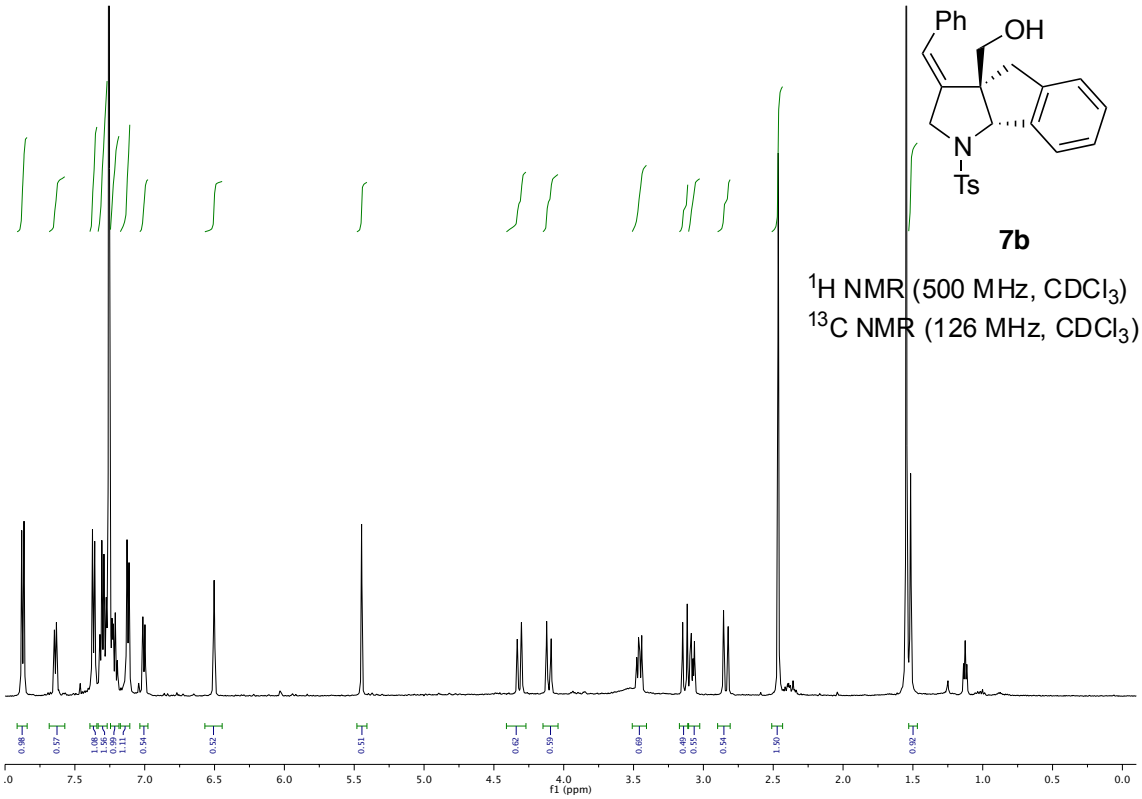


6a

^{1}H NMR (500 MHz, $CDCl_3$)
^{13}C NMR (126 MHz, $CDCl_3$)

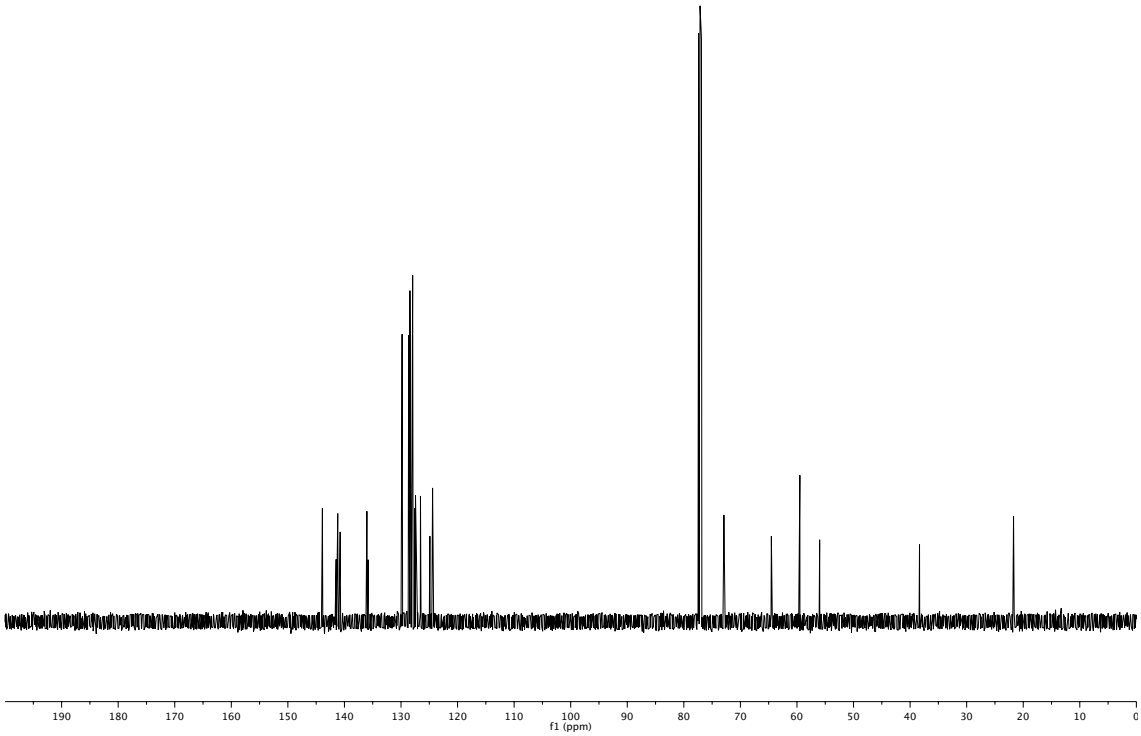


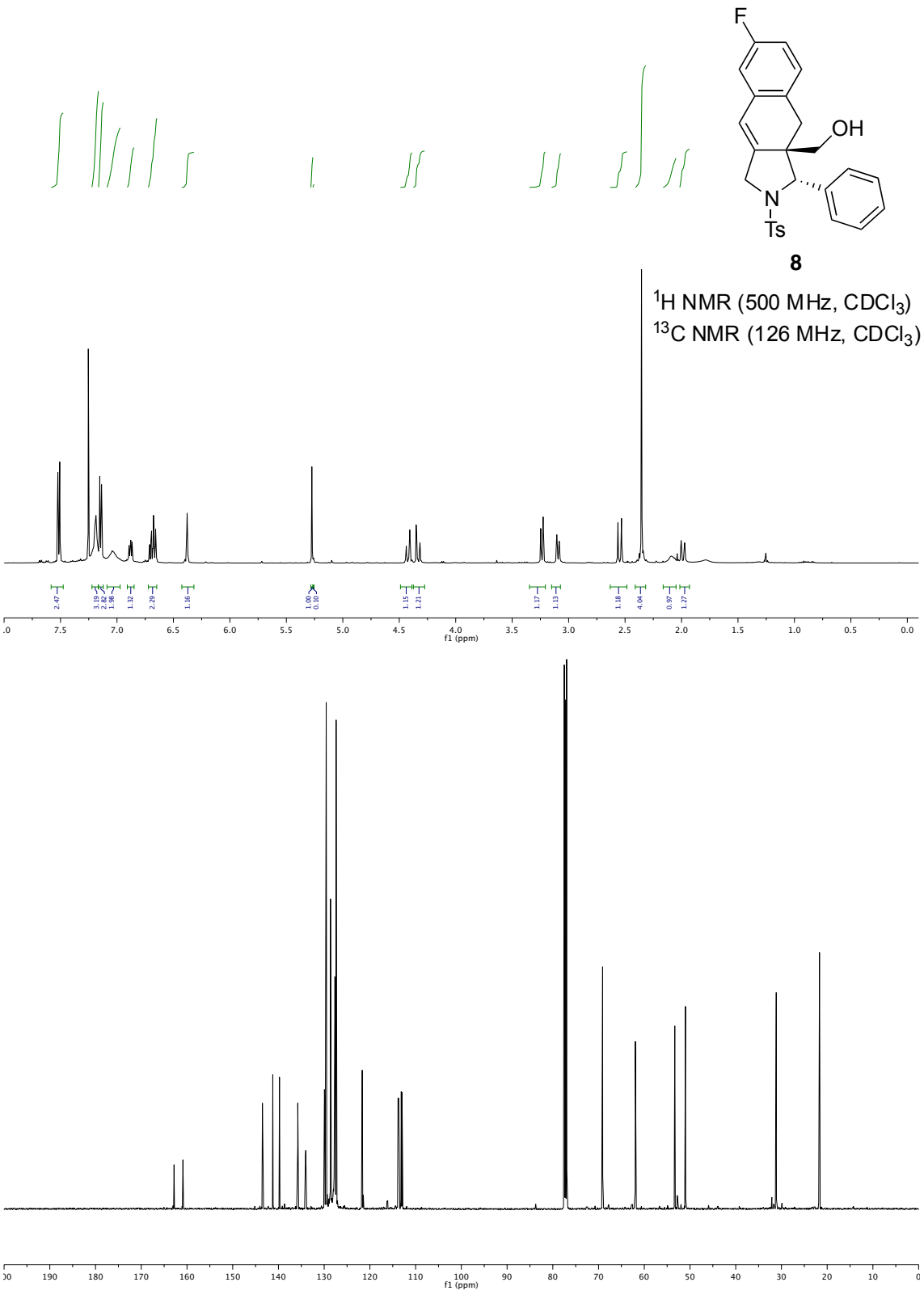

OH
N
Ts
7a
1H NMR (500 MHz, CDCl3)
13C NMR (126 MHz, CDCl3)
f1 (ppm)
f1 (ppm)

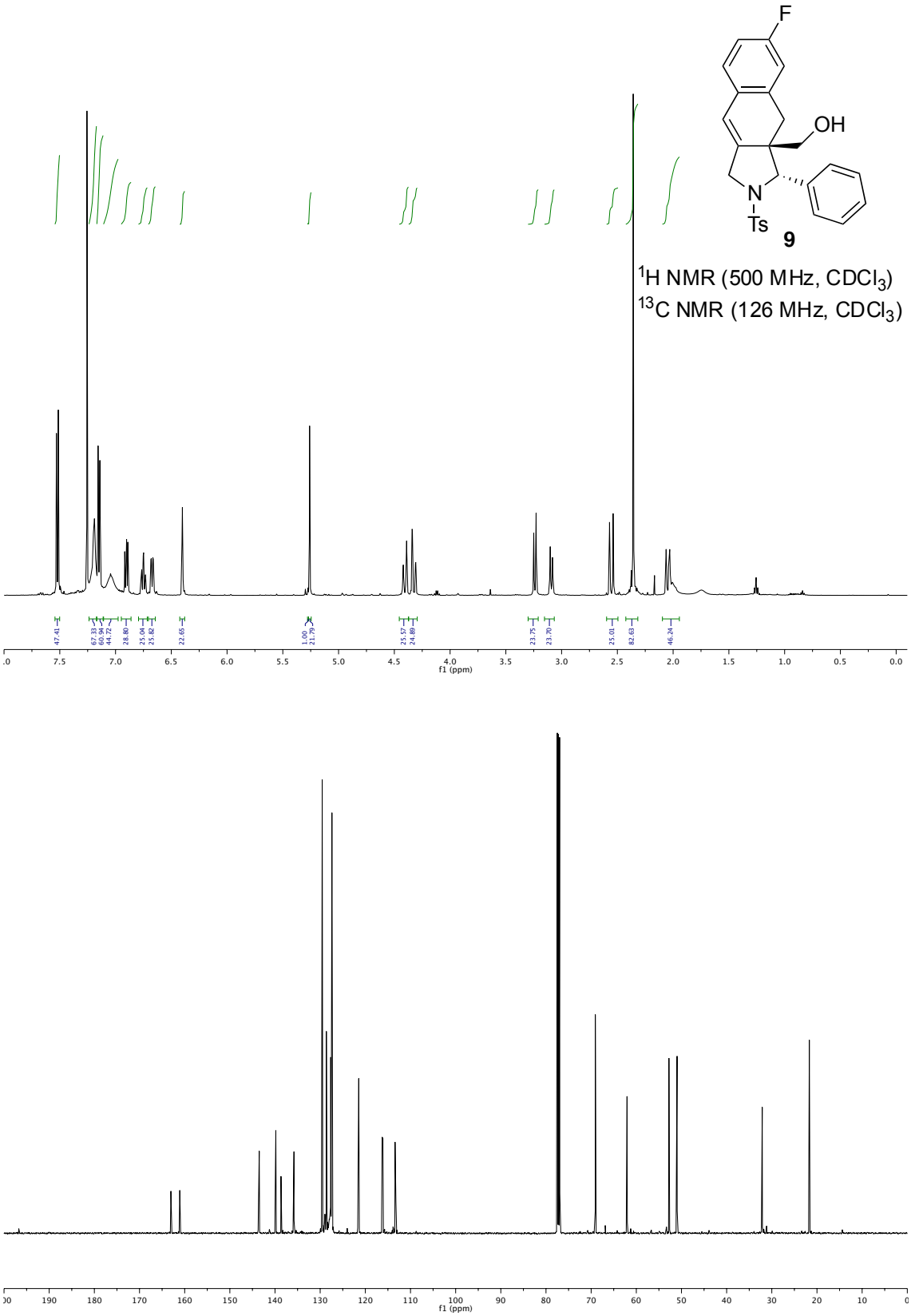


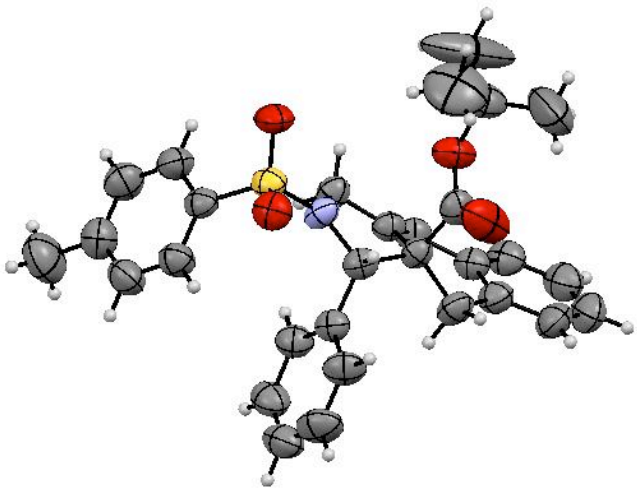
7b

^{1}H NMR (500 MHz, $CDCl_3$)
^{13}C NMR (126 MHz, $CDCl_3$)

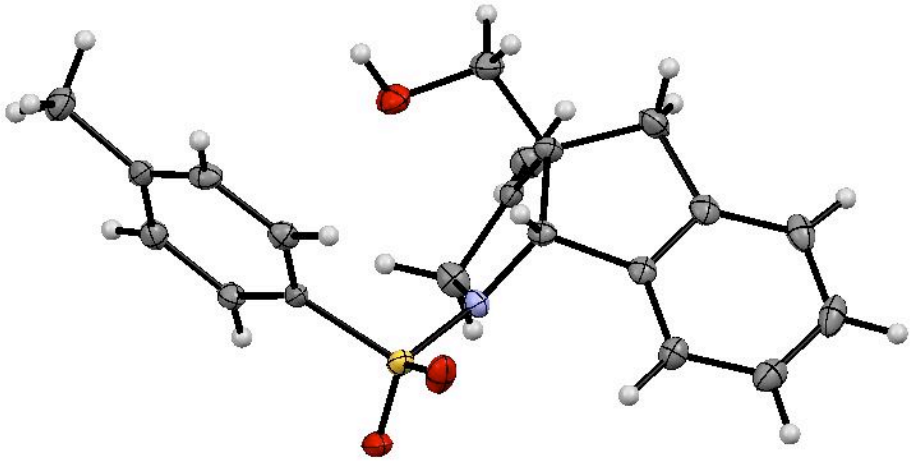



F
OH
N
Ts
8
^{1}H NMR (500 MHz, $CDCl_3$)
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)
f1 (ppm)


F
OH
N
Ts
9
^{1}H NMR (500 MHz, $CDCl_3$)
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)
f1 (ppm)



ORTEP chart for compound **2a.**



ORTEP chart for compound **7a.**