Supporting Information

Silver-Mediated Fluorination of Functionalized Aryl Stannanes

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Materials and Methods

All reactions were carried out under an inert nitrogen atmosphere unless otherwise indicated. Solvents were dried by passage through alumina[1]. Except as indicated otherwise, reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using EMD TLC plates pre-coated with 250 µm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. In addition, TLC plates were stained using ceric ammonium molybdate or potassium permanganate stain. Flash chromatography was performed on Dynamic Adsorbents Silica Gel 40–63 µm particle size using a forced flow of eluant at 0.3–0.5 bar pressure.[2] Concentration under reduced pressure was performed by rotary evaporation at 25–30 ºC at appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). NMR spectra were recorded on a Varian Mercury 400 (400 MHz for ^{1}H, 100 MHz for ^{13}C, 375 MHz for ^{19}F, and 126 MHz for ^{31}P acquisitions), Unity/Inova 500 (500 MHz for ^{1}H, 125 MHz for ^{13}C acquisitions), or Unity/Inova 600 (600 MHz for ^{1}H acquisitions) spectrometer. ^{13}C NMR spectra are recorded ^{1}H decoupled. ^{19}F NMR spectra are recorded ^{1}H coupled. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. Data is reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad; coupling constants in Hz; integration. High-resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers at the Harvard University Mass Spectrometry Facilities. Pyridine and triethylamine were distilled over calcium hydride. *n*-Butyllithium, *tert*-butyllithium, isopropylmagnesium chloride, tetrakis(triphenyl-phosphine)palladium, lithium chloride, 4-(dimethylamino)pyridine, di-*tert*-butyl dicarbonate, trifluoromethanesulfonic anhydride, pyridine, bis(tributyltin), sodium hydride, ethanethiol, 2,4,6-colidine, N-phenylbis(trifluoromethanesulfonimide), acetone (CHROMASOLV® Plus, for HPLC, ≥ 99.9%), and silver triflate were purchased from Aldrich. 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), ammonium hexafluoro-phosphate, and tributyltin chloride were purchased from Alfa Aesar and used as received. NMR spectroscopic data of known compounds correspond to the data given in the appropriate references. NMR spectra of new compounds are attached. Freshly prepared arylstannanes and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) were used for fluorination reactions.

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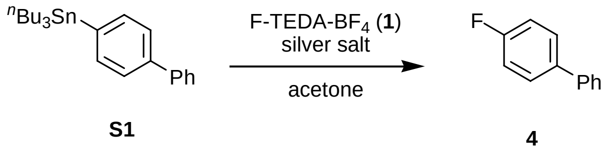
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

[2] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2925–2927.

Experimental Data

Identification of optimal silver(I) Salt



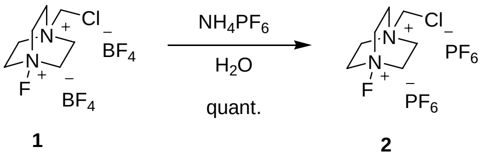
Under ambient atmosphere, to 4-(biphenyl)tributylstannane (**S1**) (8.9 mg, 0.020 mmol, 1.0 equiv) in acetone (0.4 mL) at 23 ºC was added silver salt (0.040 mmol, 2.0 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**1**) (8.5 mg, 0.024 mmol, 1.2 equiv). The reaction mixture was stirred at 23 ºC for 20 min. To the reaction mixture was added 3-nitrofluorobenzene (2.00 µL, 0.0188 mmol). The yields were determined by comparing integration of the ^{19}F NMR (375 MHz, acetone, 23 ºC) resonance of 4-fluorobiphenyl (–118.1 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S1.

Table S1: Identification of optimal silver(I) salt

Silver salt	**Yield [%]** (^{19}F NMR)	**Silver salt**	**Yield [%]** (^{19}F NMR)
AgF	51	AgCl	0
AgOAc	20	AgOBz	1
Ag(TFA)	0	AgOTf	63
$AgBF_4$	40	$AgPF_6$	55
$AgClO_4$	49	$AgSbF_6$	5
$AgNO_3$	11	$AgNO_2$	29
Ag_2CO_3	9	Ag_3PO_4	27
AgCN	4	none	0

Experimental Procedures and Compound Characterization

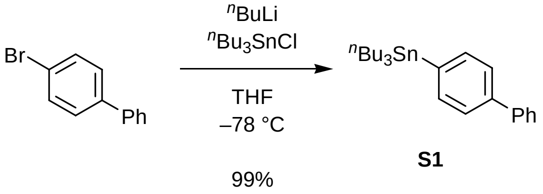
1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (2)



To 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (1.06 g, 3.00 mmol, 1.00 equiv) in H_2O (9.0 mL) at 23 ºC was added ammonium hexafluorophosphate (2.93 g, 18.0 mmol, 6.00 equiv). After stirring for 1 h, the suspension was filtered off and washed with H_2O (5 × 5 mL) and Et_2O (10 mL) to afford 1.43 g of the title compound as a colorless solid (quantitative yield).

NMR Spectroscopy: ^{1}H NMR (400 MHz, acetonitrile-*d*3, 23 ºC, δ): 5.27 (s, 2H), 4.70 (dt, J_{HF} = 7.6 Hz, 7.2 Hz, 6H), 4.24 (t, *J* = 7.2, 6H). ^{13}C NMR (125 MHz, acetonitrile-*d*6, 23 ºC, δ): 70.08, 58.18 (d, J_{CF} = 15.3 Hz), 54.67. ^{19}F NMR (375 MHz, acetonitrile-*d*3, 23 ºC, δ): 47.61 (s, 1F), –72.89 (d, J_{FP} = 710 Hz, 6F). ^{31}P NMR (162 MHz, acetonitrile-*d*3, 23 ºC, δ): –143.5 (h, J_{FP} = 710 Hz). Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M – PF_6]^+$, 325.04659. Found, 325.04664.

(4-Biphenyl)tributylstannane[3] (S1)



To 4-bromobiphenyl (2.00 g, 8.58 mmol, 1.00 equiv) in THF (20 mL) at –78 ºC was added ^{n}BuLi (2.5 M in hexane, 3.43 mL, 8.6 mmol, 1.0 equiv). The reaction mixture was stirred at –78 ºC for 30 min before the addition of $^nBu_3SnCl$ (2.79 g, 8.58 mmol, 1.00 equiv). After stirring for 1.0 hr at –78 ºC, the reaction mixture was warmed to 23 ºC and the solvent was removed in vacuo. The residue was dissolved in 20 mL of Et_2O and filtered through a plug of neutral alumina. The filtrate was concentrated in vacuo to afford 3.76 g of the title compound as a colorless oil (99% yield).

R_f = 0.58 (hexanes). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.61 (d, *J* = 8.4 Hz, 2H), 7.58–7.51 (m, 4H), 7.44 (dd, *J* = 7.8 Hz, 7.8 Hz, 2H), 7.34 (t, *J* = 8.4 Hz, 1H), 1.62–1.54 (m, 6H), 1.38–1.32 (m, 6H), 1.15–1.03 (m, 6H), 0.91 (t, *J* = 6.0 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 141.31, 140.76, 136.89, 128.71, 127.14, 127.08, 126.96, 126.63, 29.16, 27.44, 13.71, 9.62.

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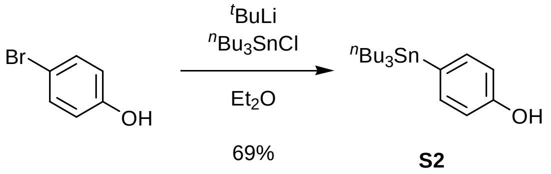
[3] Dienes, Y.; Durben, S.; Kárpáti, T.; Neumann, T.; Englert, U.; Nyulászi, L.; Baumgartner, T. *Chem. —Eur. J.* **2007**, *13*, 7487–7500.

Tributyl(4-hydroxyphenyl)stannane[4] (S2)

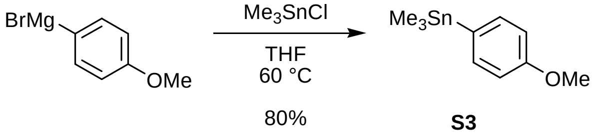


S2

To 4-bromophenol (346 mg, 2.00 mmol, 1.00 equiv) in Et_2O (10 mL) at –78 ºC was added ^{t}BuLi (1.7 M in pentane, 3.65 mL, 6.2 mmol, 3.1 equiv). The reaction mixture was stirred at –78 ºC for 2.0 hr before the addition of ^{n}Bu$_3$SnCl (780 mg, 2.40 mmol, 1.20 equiv). After stirring for 2.0 hr at –78 ºC, the reaction mixture was warmed to 23 ºC and quenched with saturated aqueous NH_4Cl (10 mL). The phases were separated and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phases were washed with brine (30 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 19:1 (v/v) to afford 530 mg of the title compound as a colorless oil (69% yield).

R_f = 0.68 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.32 (d, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 2H), 4.62 (s, 1H), 1.56–1.46 (m, 6H), 1.36–1.28 (m, 6H), 1.08–0.96 (m, 6H), 0.88 (t, *J* = 6.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 155.67, 137.65, 132.06, 115.29, 29.07, 27.35, 13.57, 9.58.

(4-Methoxyphenyl)trimethylstannane[4] (S3)



S3

To trimethyltin chloride (1.71 g, 8.58 mmol, 1.00 equiv) in THF (50 mL) at 23 ºC was added 4-methoxyphenylmagnesium bromide (0.50 M in THF, 34.3 mL, 17 mmol, 2.0 equiv). After stirring for 1.0 hr at 60 ºC, the reaction mixture was cooled to 0 ºC and quenched with saturated aqueous NH_4Cl (50 mL), and Et_2O (50 mL) was added. The phases were separated and the aqueous phase was extracted with Et_2O (2 × 50 mL). The combined organic phases were washed with brine (100 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by fractional distillation to afford 1.86 g of the title compound as a colorless oil (80% yield).

R_f = 0.14 (hexanes). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.47 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H), 0.38–0.29 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 159.86,

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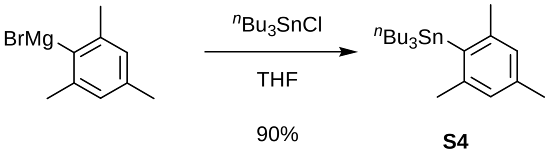
[4] Elguero, J.; Jaramillo, C.; Pardo, C. *Synthesis* **1997**, 563–566.

136.85, 132.34, 113.97, 55.00, –9.54.

Tributyl(2,4,6-trimethylphenyl)stannane[5] (S4)

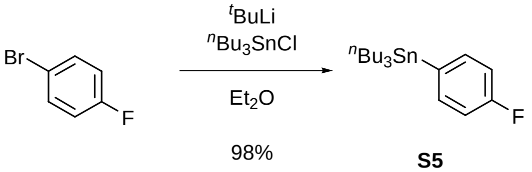


S4

To 2,4,6-trimethylphenylmagnesium bromide (1.0 M in THF, 10.0 mL, 10 mmol, 1.0 equiv) in THF (30 mL) at –78 ºC was added ^{n}Bu$_3$SnCl (3.25 g, 10.0 mmol, 1.00 equiv). After stirring for 1.0 hr at 23 ºC, the solvent was removed in vacuo and the residue was purified by fractional distillation to afford 3.68 g of the title compound as a colorless oil (90% yield).

R$_f$ = 0.76 (hexanes). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$, 23 ºC, δ): 6.88 (s, 2H), 2.37 (s, 6H), 2.31 (s, 3H), 1.55–1.46 (m, 6H), 1.39–1.30 (m, 6H), 1.11–1.07 (m, 6H), 0.92 (t, J = 6.0 Hz, 9H). ^{13}C NMR (125 MHz, CDCl$_3$, 23 ºC, δ): 145.18, 138.32, 137.83, 127.59, 29.18, 27.44, 25.54, 20.91, 13.62, 12.49.

Tributyl(4-fluorophenyl)stannane[6] (S5)



S5

To 1-bromo-4-fluorobenzene (1.75 g, 10.0 mmol, 1.00 equiv) in Et$_2$O (25 mL) at –78 ºC was added ^{t}BuLi (1.7 M in pentane, 11.8 mL, 20 mmol, 2.0 equiv). The reaction mixture was stirred at –78 ºC for 30 min before the addition of ^{n}Bu$_3$SnCl (3.26 g, 10.0 mmol, 1.00 equiv). The reaction mixture was warmed to 23 ºC and stirred for 1.0 hr before being filtered through a plug of neutral alumina. The filtrate was concentrated in vacuo to afford 3.76 g of the title compound as a colorless oil (98% yield).

R$_f$ = 0.63 (hexanes). NMR Spectroscopy: ^{1}H NMR (600 MHz, CDCl$_3$, 23 ºC, δ): 7.41 (dd, J = 8.4 Hz, 6.6 Hz, 2H), 7.04 (dd, J = 9.6 Hz, 8.4 Hz, 2H), 1.59–1.46 (m, 6H), 1.36–1.30 (m, 6H), 1.11–1.09 (m, 6H), 0.89 (t, J = 6.0 Hz, 9H). ^{13}C NMR (100 MHz, CDCl$_3$, 23 ºC, δ): 163.24 (d, J = 245 Hz), 137.83 (d, J = 6.9 Hz), 136.65 (d, J = 4.6 Hz), 115.11 (d, J = 19.0 Hz), 29.07, 27.38, 13.66, 9.65. ^{19}F NMR (375 MHz, CDCl$_3$, 23 ºC, δ): –114.1.

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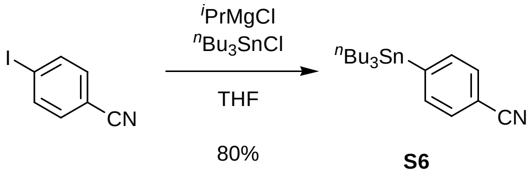
[5] Littke, A. F.; Schwarz, L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6343–6348.
[6] Justicia, J.; Oltra, J. E.; Querva, J. M. *J. Org. Chem.* **2004**, *69*, 5803–5806.

Tributyl(4-cyanophenyl)stannane[7] (S6)

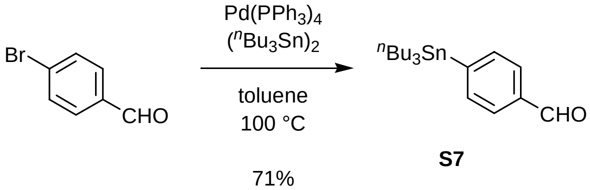


S6

To 4-iodobenzonitrile (2.29 g, 10.0 mmol, 1.00 equiv) in THF (30 mL) at –40 ºC was added ^{i}PrMgCl (2.0 M in Et_2O, 5.50 mL, 11 mmol, 1.1 equiv). The reaction mixture was stirred for 1.0 hr at –40 ºC before the addition of ^{n}Bu$_3$SnCl (3.91 g, 12.0 mmol, 1.20 equiv). After stirring for 1.0 hr at –40 ºC, the reaction mixture was warmed to 23 ºC and quenched with saturated aqueous NH_4Cl (30 mL), and Et_2O (20 mL) was added. The phases were separated and the aqueous phase was extracted with Et_2O (2 × 20 mL). The combined organic phases were washed with brine (50 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes to afford 3.14 g of the title compound as a colorless oil (80% yield).

R_f = 0.25 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.56–7.55 (m, 4H), 1.57–1.49 (m, 6H), 1.34–1.30 (m, 6H), 1.11–1.07 (m, 6H), 0.89 (t, J = 6.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 150.27, 136.83, 130.65, 119.17, 111.51, 28.92, 27.24, 13.58, 9.68.

Tributyl(4-formylphenyl)stannane[8] (S7)



S7

To 4-bromobenzaldehyde (185 mg, 1.00 mmol, 1.00 equiv) in toluene (10 mL) at 23 ºC was added tetrakis(triphenylphosphine)palladium (58.0 mg, 0.0500 mmol, 5.00 mol%) and bis(tri-*n*-butyltin) (1.01 mL, 2.00 mmol, 2.00 equiv). After stirring for 24 hr at 100 ºC, the reaction mixture was cooled to 23 ºC and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes to afford 280 mg of the title compound as a colorless oil (71% yield).

R_f = 0.50 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 9.99 (s, 1H), 7.79 (d, J = 7.8 Hz, 2H), 7.66 (d, J = 7.8 Hz, 2H), 1.58–1.42 (m, 6H), 1.36–1.26 (m, 6H), 1.12–0.98

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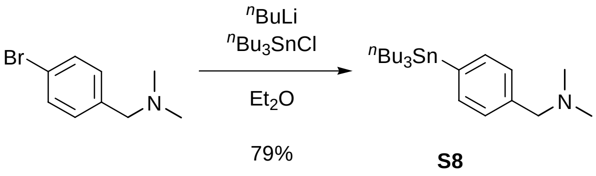
[7] Kosugi, M.; Ohya, T.; Migita, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3855–3856.

[8] Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704–714.

(m, 6H), 0.88 (t, *J* = 6.0 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 192.89, 152.61, 136.94, 135.87, 128.45, 29.00, 27.30, 13.63, 9.69.

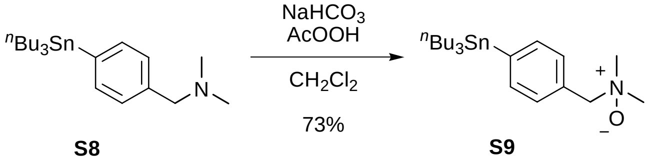
Tributyl[{(4-dimethylamino)methyl}phenyl]stannane (S8)



To (4-bromobenzyl)dimethylamine[9] (2.14 g, 10.0 mmol, 1.00 equiv) in Et_2O (25 mL) at 23 ºC was added ^{n}BuLi (2.4 M in hexane, 4.17 mL, 10 mmol, 1.0 equiv). The reaction mixture was warmed to 23 ºC and stirred for 2.0 hr before the addition of $^{n}Bu_3SnCl$ (3.25 g, 10.0 mmol, 1.00 equiv) at –78 ºC. After stirring for 1.0 hr at 23 ºC, the reaction mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:1 (v/v) to afford 3.35 g of the title compound as a colorless oil (79% yield).

R_f = 0.20 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.42 (d, *J* = 6.5 Hz, 2H), 7.27 (d, *J* = 6.5 Hz, 2H), 3.41 (s, 2H), 2.26 (s, 6H), 1.64–1.48 (m, 6H), 1.40–1.30 (m, 6H), 1.15–0.99 (m, 6H), 0.90 (t, *J* = 6.0 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 140.30, 138.40, 136.36, 128.72, 64.40, 45.36, 29.07, 27.35, 13.64, 9.52. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + H]^+$, 426.21772. Found, 426.21651.

Tributyl[{(4-dimethylamino)methyl}phenyl]stannane *N*-oxide (S9)



To tributyl[{4-dimethylamino}methyl]phenyl]stannane (**S8**) (42.4 mg, 0.100 mmol, 1.00 equiv) in CH_2Cl_2 (1.0 mL) at 0 ºC was added sodium bicarbonate (16.8 mg, 0.200 mmol, 2.00 equiv) and peracetic acid (21.0 µL, 32 wt. % in dilute acetic acid, 0.10 mmol, 1.0 equiv). The reaction mixture was warmed to 23 ºC and stirred for 10 min before being filtered through a plug of basic alumina. The filtrate was concentrated in vacuo and purified by preparative TLC eluting with CH_2Cl_2/MeOH 9:1 (v/v) to afford 32.9 mg of the title compound as a light orange solid (73% yield).

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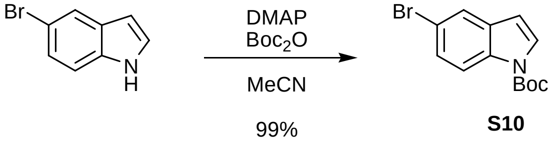
[9] Nielsen, S. F.; Larsen, M.; Boesen, T.; Schønning, K.; Kromann, H. *J.Med.Chem.* **2005**, *48*, 2667–2677.

R$_f$ = 0.15 (CH$_2$Cl$_2$/MeOH 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$, 23 ºC, δ): 7.50 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 4.38 (s, 2H), 3.11 (s, 6H), 1.58–1.42 (m, 6H), 1.36–1.27 (m, 6H), 1.12–0.97 (m, 6H), 0.86 (t, *J* = 6.0 Hz, 9H). ^{13}C NMR (100 MHz, CDCl$_3$, 23 ºC, δ): 144.77, 136.84, 131.20, 130.06, 76.76, 57.72, 28.97, 27.27, 13.60, 9.56. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [M + H]$^+$, 442.21264. Found, 442.21307.

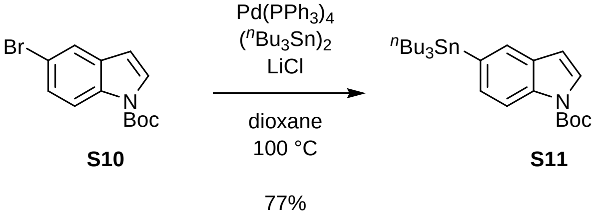
N-Boc-5-bromoindole[10] (S10)



To 5-bromoindole (196 mg, 1.00 mmol, 1.00 equiv) in acetonitrile (2.0 mL) at 23 ºC was added di-*tert*-butyl dicarbonate (276 mL, 1.20 mmol, 1.20 equiv) and 4-dimethylaminopyridine (12.0 mg, 0.100 mmol, 10.0 mol%). After stirring for 30 min at 23 ºC, the reaction mixture was concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 30:1 (v/v) to afford 293 mg of the title compound as a colorless solid (99% yield).

R$_f$ = 0.35 (hexanes/EtOAc 30:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, CDCl$_3$, 23 ºC, δ): 8.02 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.58 (d, *J* = 3.6 Hz, 1H), 7.39 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 6.50 (d, *J* = 3.6 Hz, 1H), 1.67 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$, 23 ºC, δ)[11]: 149.40, 133.90, 132.22, 127.00, 123.51, 116.54, 115.94, 106.45, 84.12, 28.14.

N-Boc-5-(tributylstannyl)indole (S11)



To N-Boc-5-bromoindole (**S10**) (285 mg, 0.962 mmol, 1.00 equiv) in dioxane (2.5 mL) at 23 ºC was added lithium chloride (203 mg, 4.81 mmol, 5.00 equiv), tetrakis(triphenylphosphine)palladium (55.6 mg, 0.0481 mmol, 5.00 mol%) and bis(tri-*n*-butyltin) (0.972 mL, 1.92 mmol, 2.00 equiv). After stirring for 6.0

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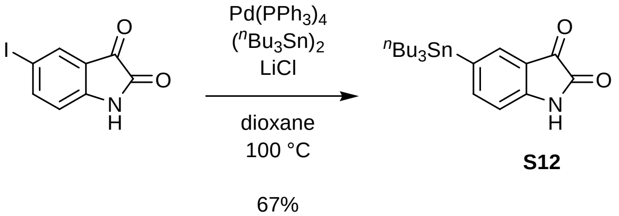
[10] Witulski, B.; Buschmann, N.; Bergsträßer, U. *Tetrahedron* **2000**, *56*, 8473–8480.

[11] Only ten peaks were observed probably due to accidental overlap of two peaks.

hr at 100 ºC, the reaction mixture was cooled to 23 ºC and concentrated in vacuo. The residue was dissolved in 10 mL hexanes and filtered through a plug of celite. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 50:1 (v/v) to afford 376 mg of the title compound as a colorless oil (77% yield).

R_f = 0.22 (hexanes/EtOAc 50:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.15 (d, *J* = 7.0 Hz, 1H), 7.70 (s, 1H), 7.60 (d, *J* = 3.5 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 3.5 Hz, 1H), 1.70 (s, 9H), 1.67–1.55 (m, 6H), 1.43–1.35 (m, 6H), 1.20–1.06 (m, 6H) 0.96 (t, *J* = 6.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 149.84, 135.24, 134.56, 131.88, 130.68, 129.00, 125.38, 114.77, 107.09, 83.48, 29.12, 28.18, 27.38, 13.67, 9.66. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + H]^+$, 508.22320. Found, 508.22257.

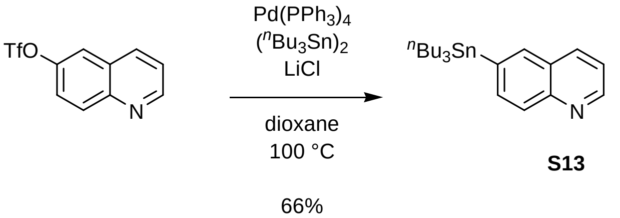
5-(Tributylstannyl)isatin (S12)



To 5-iodoisatin (273 mg, 1.00 mmol, 1.00 equiv) in dioxane (10 mL) at 23 ºC was added lithium chloride (212 mg, 5.00 mmol, 5.00 equiv), tetrakis(triphenylphosphine)palladium (58.0 mg, 0.0500 mmol, 5.00 mol%) and bis(tri-*n*-butyltin) (1.01 mL, 2.00 mmol, 2.00 equiv). After stirring for 5 hr at 100 ºC, the reaction mixture was cooled to 23 ºC and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 4:1 (v/v) to afford 289 mg of the title compound as a colorless oil (67% yield).

R_f = 0.73 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.10 (s br, 1H), 7.67 (s, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 1.58–1.42 (m, 6H), 1.36–1.26 (m, 6H), 1.12–0.98 (m, 6H), 0.88 (t, *J* = 6.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 183.85, 159.82, 149.35, 146.72, 137.41, 133.00, 117.81, 112.48, 29.02, 27.26, 13.60, 9.73. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + H]^+$, 438.14495. Found, 438.14536.

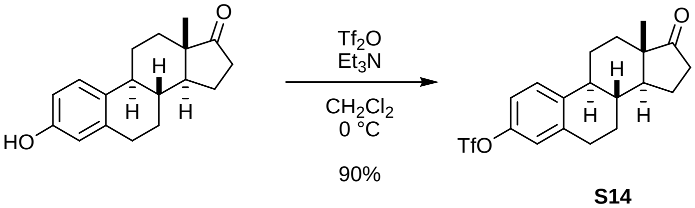
6-(Quinolinyl)tributylstannane (S13)



To 6-quinolinyl trifluoromethanesulfonate (277 mg, 1.00 mmol, 1.00 equiv) in dioxane (10 mL) at 23 ºC was added lithium chloride (212 mg, 5.00 mmol, 5.00 equiv), tetrakis(triphenylphosphine)palladium (58.0 mg, 0.0500 mmol, 5.00 mol%) and bis(tri-*n*-butyltin) (1.01 mL, 2.00 mmol, 2.00 equiv). After stirring for 5 hr at 100 ºC, the reaction mixture was cooled to 23 ºC and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 9:1 (v/v) to afford 275 mg of the title compound as colorless oil (66% yield).

R_f = 0.61 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.89 (d, *J* = 4.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 1.66–1.50 (m, 6H), 1.42–1.28 (m, 6H), 1.22–1.06 (m, 6H), 0.90 (t, *J* = 6.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 150.46, 148.51, 141.45, 137.06, 136.52, 135.91, 128.45, 128.34, 121.18, 29.38, 27.60, 13.91, 10.00. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + H]^+$, 420.17077. Found, 420.17191.

3-(Trifluoromethanesulfonyl)estrone[12] (S14)



S14

To estrone (1.00 g, 3.70 mmol, 1.00 equiv) in CH_2Cl_2 (19 mL) at 0 ºC was added triethylamine (1.03 mL, 7.40 mmol, 2.00 equiv) and trifluoromethanesulfonic anhydride (684 µL, 4.07 mmol, 1.10 equiv). The reaction mixture was stirred at 0 ºC for 20 min before the addition of saturated aqueous $NaHCO_3$ (20 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic phases are washed with brine (40 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 4:1 (v/v) to afford 1.34 g of the title compound as a colorless oil (90% yield).

R_f = 0.60 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.34 (d, *J* = 9.0 Hz, 1H), 7.03 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 6.99 (d, *J* = 2.5 Hz, 1H), 2.97–2.92 (m, 2H), 2.51 (dd, *J* = 19.0 Hz, 8.5 Hz, 1H), 2.43–2.37 (m, 1H), 2.33–2.26 (m, 1H), 2.20–1.95 (m, 4H), 1.68–1.42 (m, 6H), 0.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 220.59, 147.83, 140.53, 139.55, 127.43, 121.47, 118.99 (q, *J* = 320 Hz), 118.53, 50.63, 48.09, 44.34, 38.00, 36.03, 31.73, 29.62, 26.33, 25.92, 21.80, 14.03. ^{19}F NMR (375 MHz, $CDCl_3$, δ): –73.36.

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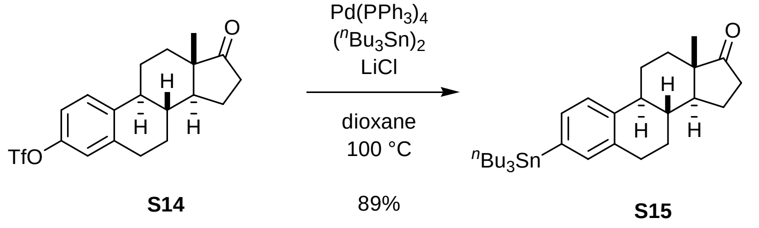
[12] Horwitz, J. P.; Iyer, V. K.; Vardhan, H. B.; Corombos, J.; Brooks, S. C. *J. Med. Chem.* **1986**, *29*, 692–698.

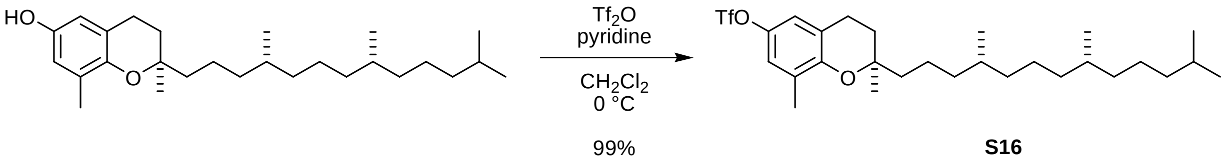
3-Deoxy-3-(tributystannyl)estrone (S15)



To 3-(trifluoromethanesulfonyl)estrone (**S14**) (402 mg, 1.00 mmol, 1.00 equiv) in dioxane (10 mL) at 23 ºC was added lithium chloride (212 mg, 5.00 mmol, 5.00 equiv), tetrakis(triphenylphosphine)palladium (58.0 mg, 0.0500 mmol, 5.00 mol%) and bis(tri-*n*-butyltin) (1.01 mL, 2.00 mmol, 2.00 equiv). After stirring for 14 hr at 100 ºC, the reaction mixture was cooled to 23 ºC and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 19:1 (v/v) to afford 484 mg of the title compound as a colorless oil (89% yield).

R_f = 0.48 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.30–7.12 (m, 3H), 2.94–2.90 (m, 2H), 2.52 (dd, *J* = 19.0 Hz, 8.5 Hz, 1H), 2.45–2.40 (m, 1H), 2.36–2.30 (m, 1H), 2.18–1.95 (m, 4H), 1.68–1.42 (m, 12H), 1.38–1.28 (m, 6H), 1.06–0.96 (m, 6H), 0.95–0.87 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 220.84, 139.47, 138.70, 137.30, 135.88, 133.95, 124.82, 50.56, 47.98, 44.47, 38.07, 35.82, 31.61, 29.35, 29.08, 27.38, 26.55, 25.50, 21.55, 13.82, 13.65, 9.48. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + H]^+$, 545.27999. Found, 545.28035.

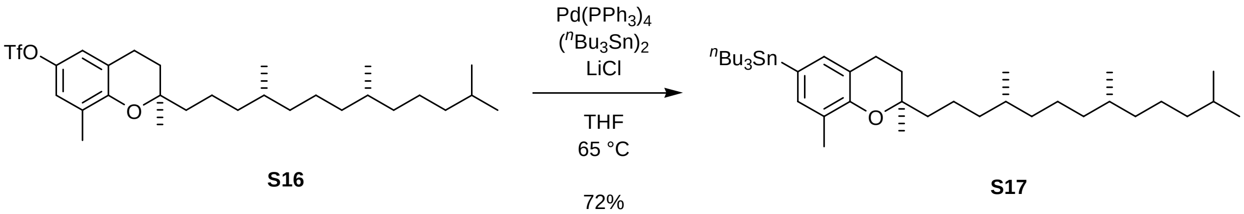
6-(Trifluoromethanesulfonyl)-δ-tocopherol (S16)



To δ-tocopherol (805 mg, 2.00 mmol, 1.00 equiv) in CH_2Cl_2 (10 mL) at 0 ºC was added pyridine (484 μL, 6.00 mmol, 3.00 equiv) and trifluoromethanesulfonic anhydride (404 μL, 2.40 mmol, 1.20 equiv). The reaction mixture was stirred at 0 ºC for 15 min before the addition of saturated aqueous $NaHCO_3$ (10 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases are washed with brine (20 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes to afford 1.06 g of the title compound as a colorless oil (99% yield).

R_f = 0.75 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 6.85 (d, *J* = 3.0 Hz, 1H), 6.81 (d, *J* = 3.0 Hz, 1H), 2.80–2.70 (m, 2H), 2.16 (s, 3H), 1.84–1.72 (m, 2H), 1.60–0.80 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 151.68, 141.46, 128.36, 121.67, 120.72, 119.06, 118.77 (q, *J* = 319 Hz), 76.82, 40.12, 39.38, 37.44, 37.39, 37.37, 37.28, 32.80, 32.66, 30.63, 27.98, 24.81, 24.44, 24.12, 22.70, 22.61, 22.41, 20.91, 19.73, 19.62, 16.16. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –73.45. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + Na]^+$, 557.28829. Found, 557.28842.

6-Deoxy-6-(tributylstannyl)-δ-tocopherol (S17)

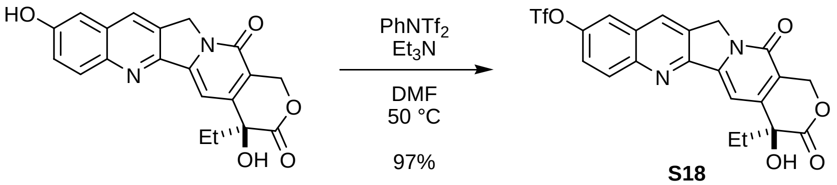


To trifluoromethanesulfonyl-δ-tocopherol (**S16**) (230 mg, 0.430 mmol, 1.00 equiv) in THF (4.3 mL) at 23 ºC was added lithium chloride (91.1 mg, 2.15 mmol, 5.00 equiv), tetrakis(triphenylphosphine)palladium (24.9 mg, 0.0215 mmol, 5.00 mol%) and bis(tri-*n*-butyltin) (434 µL, 0.860 mmol, 2.00 equiv). After stirring for 21 hr at 65 ºC, the reaction mixture was cooled to 23 ºC and concentrated in vacuo. The residue was dissolved in MeCN (3 mL) and was extracted with hexanes (3 × 3 mL). The combined hexanes phase were concentrated in vacuo and the excess bis(tri-*n*-butyltin) was removed by distillation (50 Torr, 170 ºC). The residue was dissolved in hexanes/Et_3N 19:1 (v/v) and passed through a plug of basic alumina. The filtrate was concentrated in vacuo to afford 210 mg of the title compound as a colorless oil (72% yield).

No R_f value available due to the instability of the title compound on silica gel. NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.00 (s, 1H), 6.94 (s, 1H), 2.80–2.70 (m, 2H), 2.17 (s, 3H), 1.87–1.81 (m, 1H), 1.79–1.73 (m, 1H), 1.60–0.84 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 152.49, 136.20, 135.13, 129.52, 125.91, 120.31, 75.91, 40.45, 39.37, 37.44, 37.27, 32.79, 32.70, 31.18, 30.63, 29.13, 27.97, 27.44, 24.80, 24.44, 24.37, 22.72, 22.63, 22.22, 21.00, 19.74, 19.65, 16.05, 13.69, 9.53.

Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + Na]^+$, 699.44973. Found, 699.44992.

10-(Trifluoromethanesulfonyloxy)camptothecin[13] (S18)



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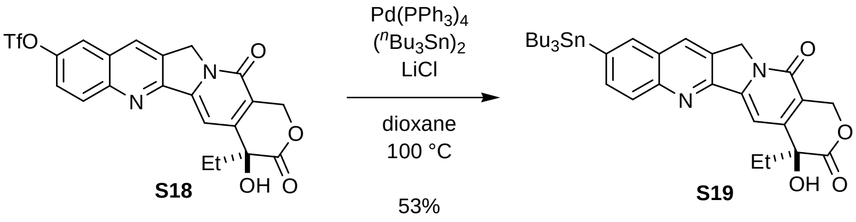
[13] Kingsbury, W. D.; Boehm, J. C.; Jakas, D. R.; Holden, K. G.; Hecht, S. M.; Gallagher, G.; Jo Caranfa, M.; McCabe, F. L.; Faucette, L. F.; Johnson, R. K.; Hertzberg, R. R. *J. Med. Chem.* **1991**, *34*, 98–107.

To 10-hydroxycamptothecin (200 mg, 0.549 mmol, 1.00 equiv) in DMF (5.0 mL) at 23 ºC was added triethylamine (153 μL, 1.10 mmol, 2.00 equiv) and N-phenylbis(trifluoromethanesulfonimide) (294 mg, 0.824 mmol, 1.50 equiv) and the reaction mixture was stirred for 3 hr at 50 ºC. The reaction mixture was cooled to 23 ºC and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 3:7 (v/v) to afford 265 mg of the title compound as a colorless solid (97% yield).

R_f = 0.25 (hexanes/EtOAc 3:7 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$, 23 ºC, δ): 8.44 (s, 1H), 8.33 (d, *J* = 9.6 Hz, 1H), 7.86 (d, *J* = 2.4 Hz, 1H), 7.71 (s, 1H), 7.70 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 5.74 (d, *J* = 16.8 Hz, 1H), 5.33 (s, 2H), 5.31 (d, *J* = 16.8 Hz, 1H), 3.94 (s, 1H), 2.00–1.81 (m, 2H), 1.04 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 173.72, 157.48, 153.96, 150.10, 147.79, 147.59, 145.54, 132.63, 131.17, 129.99, 128.12, 124.25, 119.58, 119.56, 118.73 (q, *J* = 319 Hz), 98.70, 72.69, 66.25, 49.97, 31.61, 7.79. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –72.99.

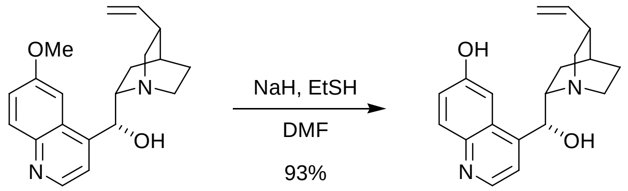
10-(Tributylstannyl)camptothecin (S19)



To 10-(trifluoromethanesulfonyloxy)camptothecin (**S18**) (170 mg, 0.342 mmol, 1.00 equiv) in dioxane (6.8 mL) at 23 ºC was added lithium chloride (72.0 mg, 1.71 mmol, 5.00 equiv), tetrakis(triphenylphosphine)palladium (20.0 mg, 0.0171 mmol, 5.00 mol%) and bis(tri-*n*-butyltin) (346 μL, 0.685 mmol, 2.00 equiv). After stirring for 24 hr at 100 ºC, the reaction mixture was cooled to 23 ºC and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with EtOAc/hexanes 1:1 (v/v) to afford 115 mg of the title compound as a light yellow solid (53% yield).

R_f = 0.77 (EtOAc). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.34 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.00 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.73 (s, 1H), 5.73 (d, *J* = 16.0 Hz, 1H), 5.30 (d, *J* = 16.0 Hz, 1H), 5.29 (s, 2H), 4.05 (s, 1H), 1.97–1.82 (m, 2H), 1.66–1.50 (m, 6H), 1.40–1.09 (m, 12H), 1.03 (t, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 173.83, 157.64, 151.97, 150.16, 148.83, 146.41, 143.91, 137.88, 136.37, 130.59, 128.36, 128.28, 127.63, 118.53, 98.26, 72.84, 66.21, 50.06, 31.55, 29.03, 27.29, 13.62, 9.79, 7.77. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + H]^+$, 639.22393. Found, 639.22374.

Cupreine[14] (S20)

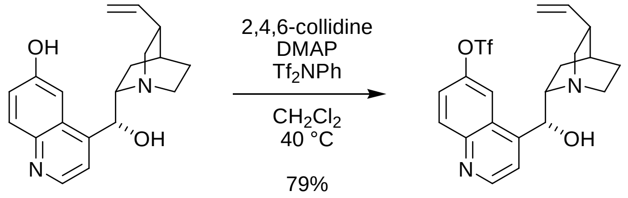


S20

NaH (60% in mineral oil, 800 mg, 20.0 mmol, 10.0 equiv) was washed with hexane, dried, and suspended in DMF (20 mL). To this suspension at 0 ºC was added ethanethiol (2.96 mL, 40.0 mmol, 20.0 equiv) dropwise over 5 min. The reaction mixture was stirred at 23 ºC for 10 min before the addition of quinine (649 mg, 2.00 mmol, 1.00 equiv) in DMF (10 mL) and further stirred for 13 hr at 100 ºC. The reaction mixture was cooled to 23 ºC and neutralized with aqueous 1N HCl. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were washed with brine (50 mL) and dried (K_2CO_3). The filtrate was concentrated in vacuo and the residue was triturated with Et_2O to afford 580 mg of the title compound as a colorless solid (93% yield).

R_f = 0.25 (CH_2Cl_2/MeOH 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3OD, 23 ºC, δ): 8.56 (d, *J* = 4.5 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.60 (d, *J* = 5.0 Hz, 1H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.28 (s, 1H), 5.72–5.67 (m, 1H), 5.53 (d, *J* = 2.5 Hz, 1H), 4.95 (d, *J* = 17.0 Hz, 1H), 4.86 (d, *J* = 10.0 Hz, 1H), 3.70 (s br, 1H), 3.09–3.02 (m, 2H), 2.73–2.61 (m, 2H), 2.31 (s br, 1H), 1.90–1.80 (m, 2H), 1.75 (s br, 1H), 1.55 (s br, 1H), 1.46–1.37 (m, 1H). ^{13}C NMR (125 MHz, CD_3OD, 23 ºC, δ): 158.10, 149.70, 147.33, 143.88, 142.52, 131.42, 128.37, 123.43, 119.78, 115.01, 105.13, 72.05, 60.90, 57.47, 44.20, 40.78, 29.16, 28.04, 21.62.

6-(Trifluoromethanesulfonyl)cupreine (S21)



S20 **S21**

To cupreine (**S20**) (310 mg, 1.00 mmol, 1.00 equiv) in CH_2Cl_2 (5 mL) at 23 ºC was added 2,4,6-collidine (132 μL, 1.00 mmol, 1.00 equiv), 4-(dimethylamino)pyridine (14.6 mg, 0.120 mmol, 0.120 equiv) and N-phenylbis(trifluoromethanesulfonimide) (357 mg, 1.00 mmol, 1.00 equiv) and the reaction mixture was stirred for 24 hr at 40 ºC. The reaction mixture was concentrated in vacuo and the residue was purified by

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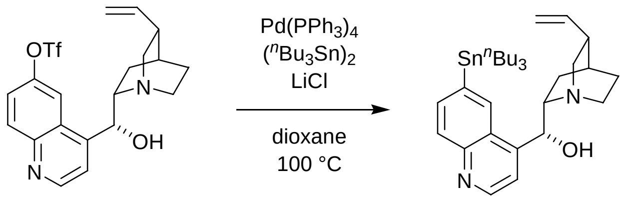
[14] Li, H.; Wang, Y.; Tang, L.; Deng, L. *J. Am. Chem. Soc.* **2004**, *126*, 9906–9907.

chromatography on silica gel eluting with CH_2Cl_2/MeOH 47:3 (v/v) to afford 350 mg of the title compound as a colorless solid (79% yield).

R_f = 0.25 (EtOAc/MeOH 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, CD_3OD, 23 ºC, δ): 8.90 (d, *J* = 4.5 Hz, 1H), 8.36 (d, *J* = 3.0 Hz, 1H), 8.19 (d, *J* = 9.5 Hz, 1H), 7.77 (d, *J* = 4.5 Hz, 1H), 7.74 (dd, *J* = 9.5 Hz, 3.0 Hz, 1H), 5.82–5.74 (m, 1H), 5.45 (d, *J* = 5.0 Hz, 1H), 4.96 (d, *J* = 17.0 Hz, 1H), 4.91 (d, *J* = 10.0 Hz, 1H), 3.51 (s br, 1H), 3.13 (s br, 1H), 3.03 (dd, *J* = 14.0 Hz, 11.0 Hz, 1H), 2.67–2.59 (m, 2H), 2.32 (s br, 1H), 1.87–1.77 (m, 3H), 1.63–1.53 (m, 2H). ^{13}C NMR (125 MHz, CD_3OD, 23 ºC, δ)[15]: 152.54, 148.54, 148.00, 142.66, 133.19, 127.47, 124.14, 121.66, 120.26 (q, *J* = 319 Hz), 117.86, 114.90, 73.27, 61.88, 57.32, 43.63, 40.82, 29.11, 28.22, 23.15. ^{19}F NMR (375 MHz, CD_3OD, 23 ºC, δ): –74.90. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + H]^+$, 443.12469. Found, 443.12970.

6-Demethoxy-6-(tributylstannyl)quinine (S22)



S21 **S22**

To 6-(trifluoromethanesulfonyl)cupreine (**S21**) (221 mg, 0.500 mmol, 1.00 equiv) in dioxane (5.0 mL) at 23 ºC was added lithium chloride (106 mg, 2.50 mmol, 5.00 equiv), tetrakis(triphenylphosphine)-palladium (29.0 mg, 0.0250 mmol, 5.00 mol%) and bis(tri-*n*-butyltin) (504 µL, 1.00 mmol, 2.00 equiv). After stirring for 24 hr at 100 ºC, the reaction mixture was cooled to 23 ºC and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with EtOAc/MeOH 19:1 (v/v) to afford 146 mg of the title compound as colorless oil (50% yield).

R_f = 0.25 (EtOAc/MeOH 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.86 (d, *J* = 4.5 Hz, 1H), 8.07 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 4.5 Hz, 1H), 6.26 (s br, 1H), 5.62–5.53 (m, 1H), 5.03 (d, *J* = 17.0 Hz, 1H), 5.01 (d, *J* = 10.0 Hz, 1H), 4.27 (s br, 1H), 3.54–3.45 (m, 2H), 3.20 (dd, *J* = 10.0 Hz, 10.0 Hz, 1H), 3.10 (d, *J* = 13 Hz, 1H), 2.65 (s br, 1H), 2.10–1.97 (m, 3H), 1.80 (s br, 1H), 1.66–1.47 (m, 6H), 1.44–1.12 (m, 13H), 0.87 (t, *J* = 6.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 149.87, 148.03, 144.62, 143.43, 137.94, 136.88, 130.22, 129.02, 124.47, 118.43, 117.01, 68.14, 60.84, 55.61, 44.72, 37.69, 29.09, 27.28, 26.83, 25.01, 19.67, 13.65, 9.86. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + H]^+$, 585.28669. Found, 585.28610.

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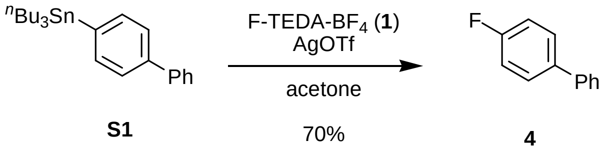
[15] Only nineteen peaks were observed probably due to accidental overlap of two peaks.

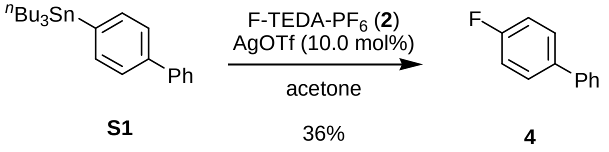
Fluorination of arylstannanes with F-TEDA-BF_4



To 4-(biphenyl)tributylstannane (**S1**) (44.3 mg, 0.100 mmol, 1.00 equiv) in acetone (2.0 mL) at 23 ºC was added silver triflate (51.4 mg, 0.0400 mmol, 2.00 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**1**) (42.5 mg, 0.120 mmol, 1.20 equiv). The reaction mixture was stirred for 20 min at 23 ºC and then concentrated in vacuo. The residue was purified by preparative TLC eluting with hexane to afford 12.0 mg of the title compound as colorless solid (70% yield).

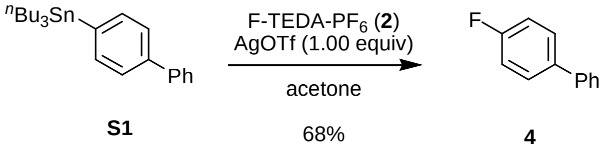
Fluorination of arylstannanes with F-TEDA-PF_6

With 10.0 mol% of AgOTf



To 4-(biphenyl)tributylstannane (**S1**) (44.3 mg, 0.100 mmol, 1.00 equiv) in acetone (2.0 mL) at 23 ºC was added silver triflate (2.57 mg, 0.0100 mmol, 10.0 mol%) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (**2**) (56.5 mg, 0.120 mmol, 1.20 equiv). The reaction mixture was stirred for 24 hr at 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (10.0 µL, 0.0939 mmol). The yield was determined to be 36% by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d6*, 23 ºC) resonance of 4-fluorobiphenyl (–118.1 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm).

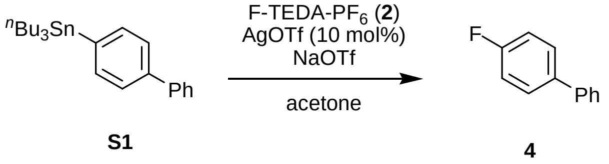
With 1.00 equivalent of AgOTf



To 4-(biphenyl)tributylstannane (**S1**) (44.3 mg, 0.100 mmol, 1.00 equiv) in acetone (2.0 mL) at 23 ºC was added silver triflate (25.7 mg, 0.100 mmol, 1.00 equiv) and 1-chloromethyl-4-fluoro-1,4-

diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (**2**) (56.5 mg, 0.120 mmol, 1.20 equiv). The reaction mixture was stirred for 12 hr at 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (10.0 μL, 0.0939 mmol). The yield was determined to be 68% by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d6*, 23 ºC) resonance of 4-fluorobiphenyl (–118.1 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm).

Effect of NaOTf

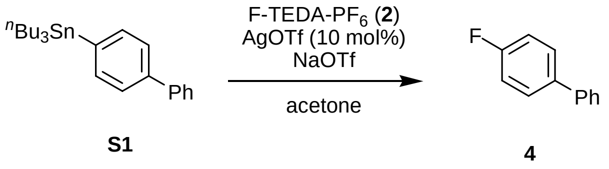


To 4-(biphenyl)tributylstannane (**S1**) (8.9 mg, 0.020 mmol, 1.0 equiv) in acetone (0.6 mL) at 23 ºC was added silver triflate (0.51 mg, 0.0020 mmol, 10 mol%), sodium triflate and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (**2**) (11 mg, 0.024 mmol, 1.2 equiv). The reaction mixture was stirred for 24 hr at 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (2.00 μL, 0.0188 mmol). The yield was determined by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d6*, 23 ºC) resonance of 4-fluorobiphenyl (–118.1 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S2.

Table S2: Effect of NaOTf

NaOTf	**Yield [%]** (^{19}F NMR)
none	36
2.0 equiv	50
5.0 equiv	49
10 equiv	48

Effect of slow addition of arylstannanes

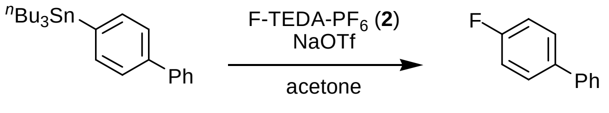


To silver triflate (0.51 mg, 0.0020 mmol, 10 mol%), sodium triflate (6.9 mg, 0.020 mmol, 2.0 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (**2**) (11 mg, 0.024 mmol, 1.2 equiv) in acetone (0.6 mL) at 23 ºC was added 4-(biphenyl)tributylstannane (**S1**) (8.9 mg, 0.020 mmol, 1.0 equiv). The reaction mixture was stirred for 24 hr at 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (2.00 μL, 0.0188 mmol). The yield was determined by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d6*, 23 ºC) resonance of 4-fluorobiphenyl (–118.1 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S3.

Table S3: Effect of slow addition

Manner of addition	**Yield [%]** (^{19}F NMR)
One portion	50
0.10 equiv every 10 min	53
0.10 equiv every 30 min	49

Background reaction without AgOTf



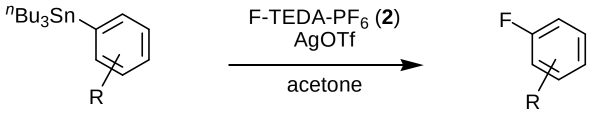
S1 **4**

To 4-(biphenyl)tributylstannane (**S1**) (8.9 mg, 0.020 mmol, 1.0 equiv) in acetone (0.6 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (**2**) (11 mg, 0.024 mmol, 1.2 equiv) and sodium triflate. The reaction mixture was stirred for 24 hr at 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (2.00 μL, 0.0188 mmol). The yield was determined by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d6*, 23 ºC) resonance of 4-fluorobiphenyl (–118.1 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S4.

Table S4: Background reaction without AgOTf

NaOTf	**Yield [%]** (^{19}F NMR)
none	0
2.0 equiv	0

Optimized conditions, General procedure A: for volatile compounds

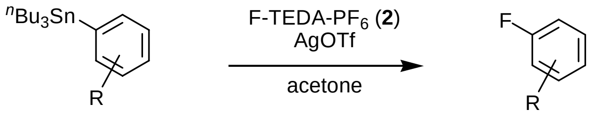


To the arylstannane (0.100 mmol, 1.00 equiv) in acetone (2.0 mL) at 23 ºC was added silver triflate (51.4 mg, 0.200 mmol, 2.00 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (**2**) (56.5 mg, 0.120 mmol, 1.20 equiv). The reaction mixture was stirred for 20 min at 23 ºC and to the reaction mixture was added 3-nitrofluorobenzene (10.0 µL, 0.0939 mmol). The yields were determined by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d6*, 23 ºC) resonance of arylfluoride and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S5.

Table S5: Synthesis of volatile arylfluorides

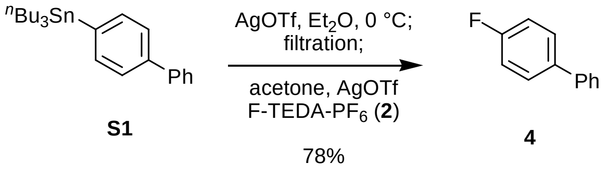
R	**^{19}F chemical shift**	**Yield [%]** (^{19}F NMR)
H	–115.3 ppm	82
4-CN	–105.0 ppm	76
4-F	–121.6 ppm	73
4-OMe	–126.8 ppm	76
2,4,6-Trimethyl	–129.7 ppm	73

Optimized conditions, General procedure B: for non-volatile compounds



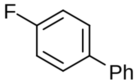
To the arylstannane (0.100 mmol, 1.00 equiv)) in acetone (2.0 mL) at 23 ºC was added silver triflate (51.4 mg, 0.0400 mmol, 2.00 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (**2**) (56.5 mg, 0.120 mmol, 1.20 equiv). The reaction mixture was stirred for 20 min at 23 ºC and then concentrated in vacuo. The residue was purified by chromatography on silica gel or preparative TLC.

Large-scale fluorination of 4-(biphenyl)tributylstannane



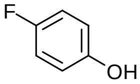
To 4-(biphenyl)tributylstannane (**S1**) (2.22 g, 5.00 mmol, 1.00 equiv) in Et_2O (25 mL) at 0 ºC was added silver triflate (2.57 g, 10.0 mmol, 2.00 equiv). The reaction mixture was stirred for 1.0 hr at 0 ºC before the addition of cold hexane (100 mL). The precipitate was filtered off and washed with cold hexane (3 × 30 mL). The red solid was transferred to another flask equipped with silver triflate (643 mg, 2.50 mmol, 0.500 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (**2**) (2.47 g, 5.25 mmol, 1.05 equiv) in acetone (50 mL). After stirring for 30 min at 23 ºC, the reaction mixture was concentrated in vacuo. The residue was dissolved in hexanes and filtered through a plug of celite. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes to afford 671 mg of 4-fluorobiphenyl as a colorless solid (78% yield).

4-Fluorobiphenyl[16] (4)



Yield: 14.3 mg (83%). R_f = 0.60 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.60–7.54 (m, 4H), 7.47 (dd, *J* = 7.5 Hz, 7.0 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.14 (dd, *J* = 8.0 Hz, 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 162.44 (d, *J* = 244 Hz), 140.24, 137.30, 129.0, 128.75 (d, *J* = 8.5 Hz), 127.24, 127.00, 115.59 (d, *J* = 21 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –116.2.

4-Fluorophenol[16] (5)



Yield: 8.1 mg (72%). R_f = 0.60 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 6.95–6.95 (dd, *J* = 8.0 Hz, 7.5 Hz, 2H), 6.80–6.76 (m, 2H), 5.41 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 157.32 (d, *J* = 237 Hz), 151.17, 116.25 (d, *J* = 8.0 Hz), 116.01 (d, *J* = 21

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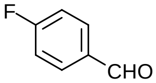
[16] Furuya, T.; Kaiser, H. M.; Ritter, T. *Angew. Chem. Int. Ed.* **2008**, *47*, 5993–5996.

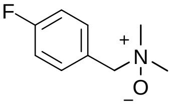
Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –124.3.

4-Fluorobenzaldehyde[16] (10)



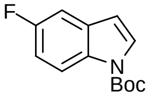
Yield: 9.6 mg (77%). R_f = 0.77 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.95 (s, 1H), 7.92–7.88 (m, 2H), 7.22–7.18 (dd, *J* = 8.0 Hz, 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 190.43, 166.42 (d, *J* = 255 Hz), 132.89, 132.14 (d, *J* = 9.9 Hz), 116.25 (d, *J* = 22 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –102.9.

(4-Fluorobenzyl)dimethylamine *N*-oxide (11)



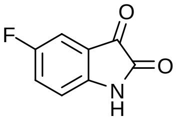
Yield: 10.6 mg (63%). R_f = 0.05 (CH_2Cl_2/MeOH 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$, 23 ºC, δ): 7.50 (dd, *J* = 7.2 Hz, 6.4 Hz, 2H), 7.08 (dd, *J* = 8.4 Hz, 7.2 Hz, 2H), 4.34 (s, 2H), 3.10 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 163.56 (d, *J* = 249 Hz), 133.94 (d, *J* = 8.1 Hz), 126.49 (d, *J* = 2.9 Hz), 115.74 (d, *J* = 22 Hz), 74.95, 58.03. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –111.5. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + Na]^+$, 192.07951. Found, 192.07923.

N-Boc-5-fluoroindole[16] (12)



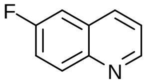
Yield: 17.6 mg (75%). R_f = 0.75 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.08 (br, 1H), 7.62 (d, *J* = 4.0 Hz, 1H), 7.20 (dd, *J* = 6.5 Hz, 2.0 Hz, 1H), 7.03 (ddd, *J* = 7.0 Hz, 6.5 Hz, 2.0 Hz, 1H), 6.52 (d, *J* = 4.0 Hz, 1H), 1.68 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 159.27 (d, *J* = 238 Hz), 149.51, 131.60, 131.38 (d, *J* = 10 Hz), 127.51, 116.08 (d, *J* = 9.1 Hz), 112.00 (d, *J* = 24 Hz), 107.01, 106.27 (d, *J* = 24 Hz), 83.9, 28.2. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –121.7.

5-Fluoroisatin (13)



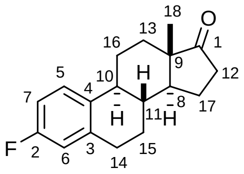
Yield: 11.9 mg (72%). R_f = 0.55 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, acetone-*d6*, 23 ºC, δ): 10.01 (br, 1H), 7.03 (ddd, *J* = 9.0 Hz, 9.0 Hz, 3.0 Hz, 1H), 7.31 (dd, *J* = 6.6 Hz, 2.4 Hz, 1H), 7.20 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H). ^{13}C NMR (100 MHz, acetone-*d6*, 23 ºC, δ): 184.18, 159.68, 159.49 (d, *J* = 241 Hz), 147.66, 125.26 (d, *J* = 24 Hz), 119.41 (d, *J* = 6.8 Hz), 114.33 (d, *J* = 6.8 Hz), 111.74 (d, *J* = 24 Hz). ^{19}F NMR (375 MHz, acetone-*d6*, 23 ºC, δ): –122.1. These spectroscopic data correspond to those of an authentic sample purchased from Alfa Aesar.

6-Fluoroquinoline[17] (14)



Yield: 11.6 mg (79%). R_f = 0.47 (EtOAc). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.91 (dd, *J* = 4.5 Hz, 1.5 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.15 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H), 7.53 (ddd, *J* = 9.0 Hz, 8.5 Hz, 2.0 Hz, 1H), 7.50–7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 160.43 (d, *J* = 247 Hz), 149.56, 145.11, 135.70 (d, *J* = 5.3 Hz), 131.80 (d, *J* = 9.1 Hz), 128.86, 121.79, 119.94 (d, *J* = 26 Hz), 110.74 (d, *J* = 21 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –113.0.

3-Deoxy-3-fluoroestrone[18] (15)



Yield: 23.2 mg (85%). R_f = 0.33 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 7.23 (dd, *J* = 8.4 Hz, *J* = 6.0 Hz, 1H, H-5), 6.83 (ddd, *J* = 9.6 Hz, 8.4 Hz, 3.0 Hz, 1H, H-7), 7.03 (dd, *J* = 9.6 Hz, 3.0 Hz, 1H, H-6), 2.92–2.88 (m, 2H, H-14), 2.51 (dd, *J* = 19.2 Hz, 8.4 Hz, 1H, H-12a), 2.42–2.38 (m, 1H, H-16a), 2.29–2.23 (m, 1H, H-10), 2.18–1.94 (m, 4H, H-12b, H-17a, H-15a, H-

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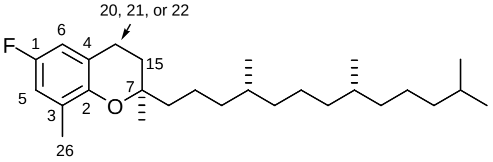
[17] Sveinbjornsson, A.; Bradlow, H. L.; Oae, S.; Vanderwerf, C. A. *J. Org. Chem.* **1951**, 16, 1450–1457.

[18] Morrow, D. F.; Hofer, R. M. *J. Med. Chem.* **1966**, 9, 249– 251.

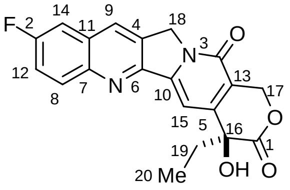
13a), 1.67–1.41 (m, 6H, H-17b, H-11, H-8, H-16b, H-15b, H-13b), 0.91 (s, 3H, H-18). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 220.67 (C-1), 161.01 (d, *J* = 243 Hz, C-2), 138.65 (d, *J* = 6.4 Hz, C-3), 135.33 (C-4), 126.78 (d, *J* = 8.3 Hz, C-5), 115.11 (d, *J* = 20 Hz, C-6), 112.48 (d, *J* = 20 Hz, C-7), 50.39 (C-8), 47.92 (C-9), 43.99 (C-10), 38.11 (C-11), 35.82 (C-12), 31.53 (C-13), 29.45 (C-14), 26.30 (C-15), 25.89 (C-16), 21.57 (C-17), 13.81 (C-18). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –118.5.

6-Deoxy-6-fluoro-δ-tocopherol (16)



Yield: 27.9 mg (69%). R_f = 0.46 (hexanes). NMR Spectroscopy[19]: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 6.67 (dd, *J* = 9.0 Hz, 1.8 Hz, 1H, H-5), 6.59 (dd, *J* = 9.0 Hz, *J* = 1.8 Hz, 1H, H-6), 2.77–2.66 (m, 2H, H-20, 21 or 22), 2.14 (s, 3H, H-26), 1.82–1.70 (m, 2H, H-15), 1.60–0.83 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 155.73 (d, *J* = 235 Hz, C-1), 147.88 (C-2), 127.71 (d, *J* = 8.1 Hz, C-3), 121.32 (d, *J* = 7.2 Hz, C-4), 114.84 (d, *J* = 23 Hz, C-5), 112.21 (d, *J* = 23 Hz, C-6), 75.91 (C-7), 39.90 (C-8), 39.36 (C-9), 37.43 (C-10), 37.40 (C-11), 37.27 (C-12), 32.79 (C-13), 32.65 (C-14), 31.07 (C-15), 27.97 (C-16), 24.79 (C-17), 24.43 (C-18), 24.07 (C-19), 22.71 (C-20), 22.61 (C-21), 22.54 (C-22), 20.92 (C-23), 19.74 (C-24), 19.64 (C-25), 16.11 (C-26). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –126.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + H]^+$, 404.34544. Found, 404.34647.

10-Fluorocamptothecin[20] (17)



Yield: 25.6 mg (70%). R_f = 0.35 (EtOAc). NMR Spectroscopy: ^{1}H NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.35 (s, 1H, H-9), 8.24 (dd, *J* = 9.0 Hz, 4.8 Hz, 1H, H-8), 7.66 (s, 1H, H-15), 7.61 (ddd, *J* = 7.6 Hz, 6.4 Hz, 3.0 Hz, 1H, H-12), 7.56 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H, H-14), 5.75 (d, *J* = 16.2 Hz, 1H, H-17a), 5.31 (d,

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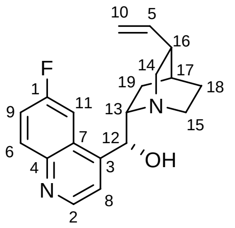
[19] Due to the overlap of peaks, further assignment has been difficult.

[20] Wall, M. E.; Wani, M. C.; Nicholas, A. W.; Manikumar, G.; Tele, C.; Moore, L.; Truesdale, A.; Leitner, P.; Besterman, J. M. *J. Med. Chem.* **1993**, *36*, 2689–2700.

J = 16.2 Hz, 1H, H-17b), 5.30 (s, 2H, H-18), 3.73 (s, 1H, OH), 1.96–1.84 (m, 2H, H-19), 1.05 (t, *J* = 7.2 Hz, 3H, H-20). ^{13}C NMR (100 MHz, $CDCl_3$, 23 ºC, δ): 173.88 (C-1), 161.29 (d, *J* = 240 Hz, C-2), 157.58 (C-3), 152.10 (C-4), 150.11 (C-5), 146.15 (C-6), 146.03 (C-7), 132.34 (d, *J* = 9.1 Hz, C-8), 130.31 (d, *J* = 6.0 Hz, C-9), 129.37 (C-10), 128.85 (d, *J* = 9.9 Hz, C-11), 121.09 (d, *J* = 26 Hz, C-12), 118.77 (C-13), 111.23 (d, *J* = 23 Hz, C-14), 97.98 (C-15), 72.71 (C-16), 66.33 (C-17), 49.99 (C-18), 31.59 (C-19), 7.80 (C-20). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –110.7.

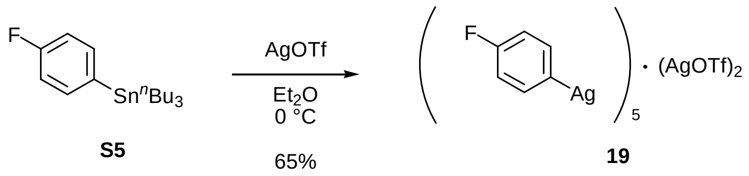
6-Demethoxy-6-fluoroquinine (18)



Yield: 22.8 mg (73%). R_f = 0.40 (CH_2Cl_2/MeOH 9:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (600 MHz, CD_3CN, 23 ºC, δ): 8.85 (d, *J* = 4.2 Hz, 1H, H-2), 8.10 (dd, *J* = 9.0 Hz, 5.4 Hz, 1H, H-6), 7.97 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H, H-11), 7.65 (d, *J* = 4.2 Hz, 1H, H-8), 7.54 (ddd, *J* = 9.0 Hz, 9.0 Hz, 3.0 Hz, 1H, H-9), 5.83 (d, *J* = 3.0 Hz, 1H, H-12), 5.78–5.72 (m, 1H, H-5), 5.06 (d, *J* = 17.4 Hz, 1H, H-10a), 4.99 (d, *J* = 10.2 Hz, 1H, H-10b), 3.92–3.86 (m, 1H, H-15a), 3.48–3.43 (m, 1H, H-13), 3.35 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H, H-14a), 3.06–3.00 (m, 2H, H-14b, H-15b), 2.68 (s br, 1H, H-16), 2.05–1.99 (m, 3H, H-17, H-18a, H-19a), 1.84–1.78 (m, 1H, H-18b), 1.65–1.58 (m, 1H, H-19b). ^{13}C NMR (100 MHz, CD_3CN, 23 ºC, δ): 161.48 (d, *J* = 244 Hz, C-1), 150.63 (C-2), 146.83 (d, *J* = 6.1 Hz, C-3), 146.45 (C-4), 139.78 (C-5), 133.81 (d, *J* = 9.9 Hz, C-6), 126.76 (d, *J* = 9.9 Hz, C-7), 120.78 (C-8), 120.18 (d, *J* = 26 Hz, C-9), 116.68 (C-10), 108.25 (d, *J* = 24 Hz, C-11), 68.99 (C-12), 61.30 (C-13), 55.61 (C-14), 44.78 (C-15), 38.38 (C-16), 27.87 (C-17), 25.32 (C-18), 20.44 (C-19). ^{19}F NMR (375 MHz, CD_3CN, 23 ºC, δ): –113.6. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + H]^+$, 313.17162. Found, 313.17160.

Synthesis of Arylsilver complexes

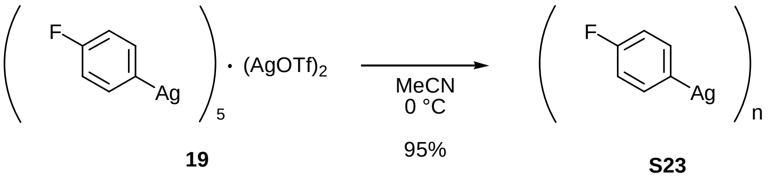
(4-Fluorophenyl)silver-silver triflate 5:2 complex (19)



To silver triflate (514 mg, 2.00 mmol, 2.00 equiv) in Et_2O (10 mL) at 0 ºC was added (4-fluorophenyl)tributylstannane (**S5**) (385 mg, 1.00 mmol, 1.00 equiv). The reaction mixture was stirred for 1.0 hr at 0 ºC and the solvent was decanted. The residue was washed with Et_2O (3 ×10 mL) and dried in vacuo at 0 ºC to afford 200 mg of the title compound as a yellow solid (65% yield).

NMR Spectroscopy: ^{1}H NMR (400 MHz, acetone-*d6*, –10 ºC, δ): 8.07 (dd, *J* = 7.2 Hz, 6.8 Hz, 2H), 7.10 (dd, *J* = 8.8 Hz, 7.2 Hz, 2H). ^{13}C NMR (100 MHz, acetone-*d6*, –10 ºC, δ): 166.79 (d, *J* = 251 Hz), 147.95 (d, *J* = 7.6 Hz), 139.86 (s br), 121.36 (q, *J* = 319 Hz), 116.46 (d, *J* = 18 Hz). ^{19}F NMR (375 MHz, acetone-*d6*, –10 ºC, δ): –78.40 (s, 6F), –107.71 (s br, 5F). Anal: calcd for $(C_6H_4AgF)_5(CAgF_3O_3S)_2$: C, 25.14; H, 1.32; found: C, 24.94; H, 1.19.

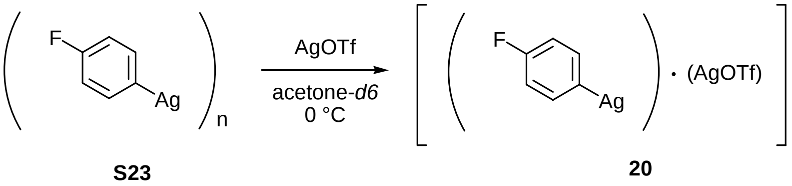
(4-Fluorophenyl)silver (S23)



To (4-fluorophenyl)silver-silver triflate 5:2 complex (**19**) (153 mg, 0.500 mmol, 1.00 equiv) was added MeCN (2.5 mL) at 0 ºC. The reaction mixture was stirred for 1 min at 0 ºC and the suspension was filtered off and washed with MeCN (2.5 mL) at 0 ºC to afford 96.0 mg of the title compound as an off-white solid (95% yield).

NMR Spectroscopy: ^{1}H NMR (400 MHz, $CDCl_3$, –10 ºC, δ): 7.76 (dd, *J* = 7.6 Hz, 7.6 Hz, 2H), 7.00 (dd, *J* = 7.6 Hz, 7.6 Hz, 2H). ^{19}F NMR (375 MHz, $CDCl_3$, –10 ºC, δ): –107.75 (s br). Due to the poor solubility and the thermal instability, the title compound was not amenable to further characterization.

(4-Fluorophenyl)silver-silver triflate 1:1 complex (20)

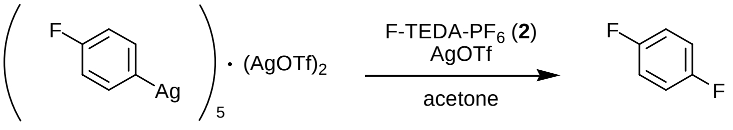


To (4-fluorophenyl)silver (**S23**) (10.2 mg, 0.0500 mmol, 1.00 equiv) in acetone-*d6* (0.6 mL) at 0 ºC was added silver triflate (12.8 mg, 0.0500 mmol, 1.00 equiv). The NMR spectroscopic data were obtained directly from the reaction mixture, but the product was neither isolated nor purified.

NMR Spectroscopy: ^{1}H NMR (400 MHz, acetone-*d6*, –10 ºC, δ): 8.07 (dd, *J* = 7.2 Hz, 6.8 Hz, 2H), 7.10 (dd, *J* = 8.8 Hz, 7.2 Hz, 2H). ^{19}F NMR (375 MHz, acetone-*d6*, –10 ºC, δ): –78.79 (s, 3F), –107.03 (s br, 1F).

Fluorination of Arylsilver complexes

Fluorination of (4-Fluorophenyl)silver-silver triflate complex with various amount of AgOTf



19

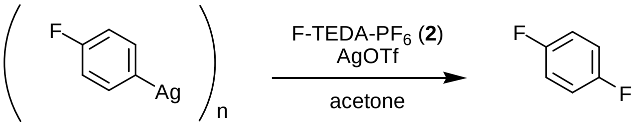
8

To (4-fluorophenyl)silver-silver triflate complex (**19**) (15.3 mg, 0.0500 mmol, 1.00 equiv) in acetone (1.0 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluoro-phosphate) (**2**) (28.3 mg, 0.120 mmol, 1.20 equiv) and various amount of silver triflate. The reaction mixture was stirred for 20 min at 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (5.0 µL, 0.047 mmol). The yields were determined by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d6*, 23 ºC) resonance of 1,4-difluorobenzne (–121.6 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S6.

Table S6: Fluorination of **19** with various amount of AgOTf

AgOTf	**Yield [%]** (^{19}F NMR)
none	45
0.6 equiv	83
1.0 equiv	80
2.0 equiv	81

Fluorination of (4-fluorophenyl)silver with various amount of AgOTf



S23

8

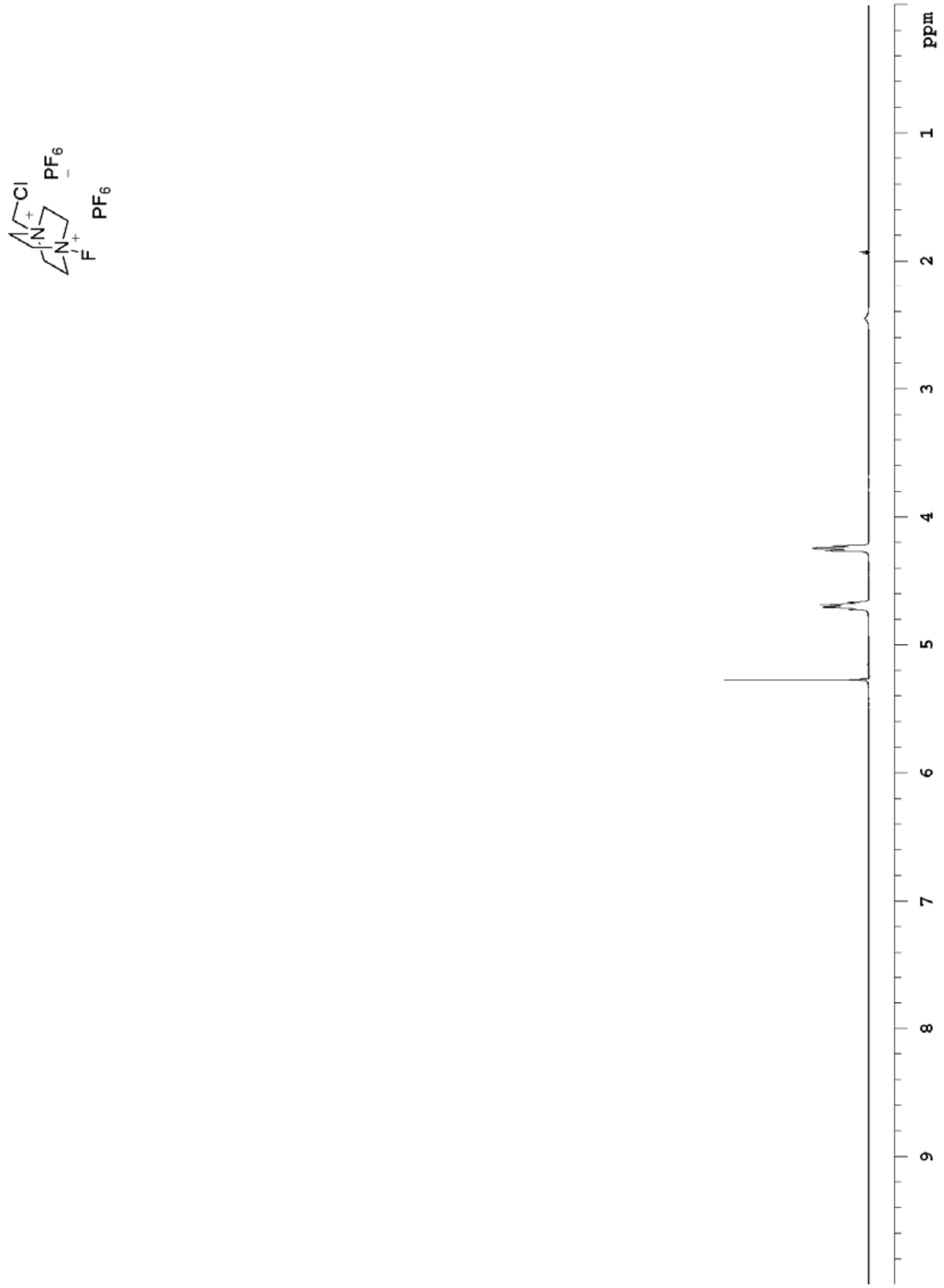
To (4-fluorophenyl)silver (**S23**) (10.2 mg, 0.0500 mmol, 1.00 equiv) in acetone (1.0 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (**2**) (28.3 mg, 0.120 mmol, 1.20 equiv) and various amount of silver triflate. The reaction mixture was stirred for 20 min at 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (5.0 µL, 0.047 mmol). The yields were determined by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d6*, 23 ºC) resonance of 1,4-difluorobenzne (–121.6 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S7.

Table S7: Fluorination of **S23** with various amount of AgOTf

AgOTf	**Yield [%]** (^{19}F NMR)
none	47
1.0 equiv	84
2.0 equiv	81

Spectroscopic Data

^{1}H NMR spectrum of



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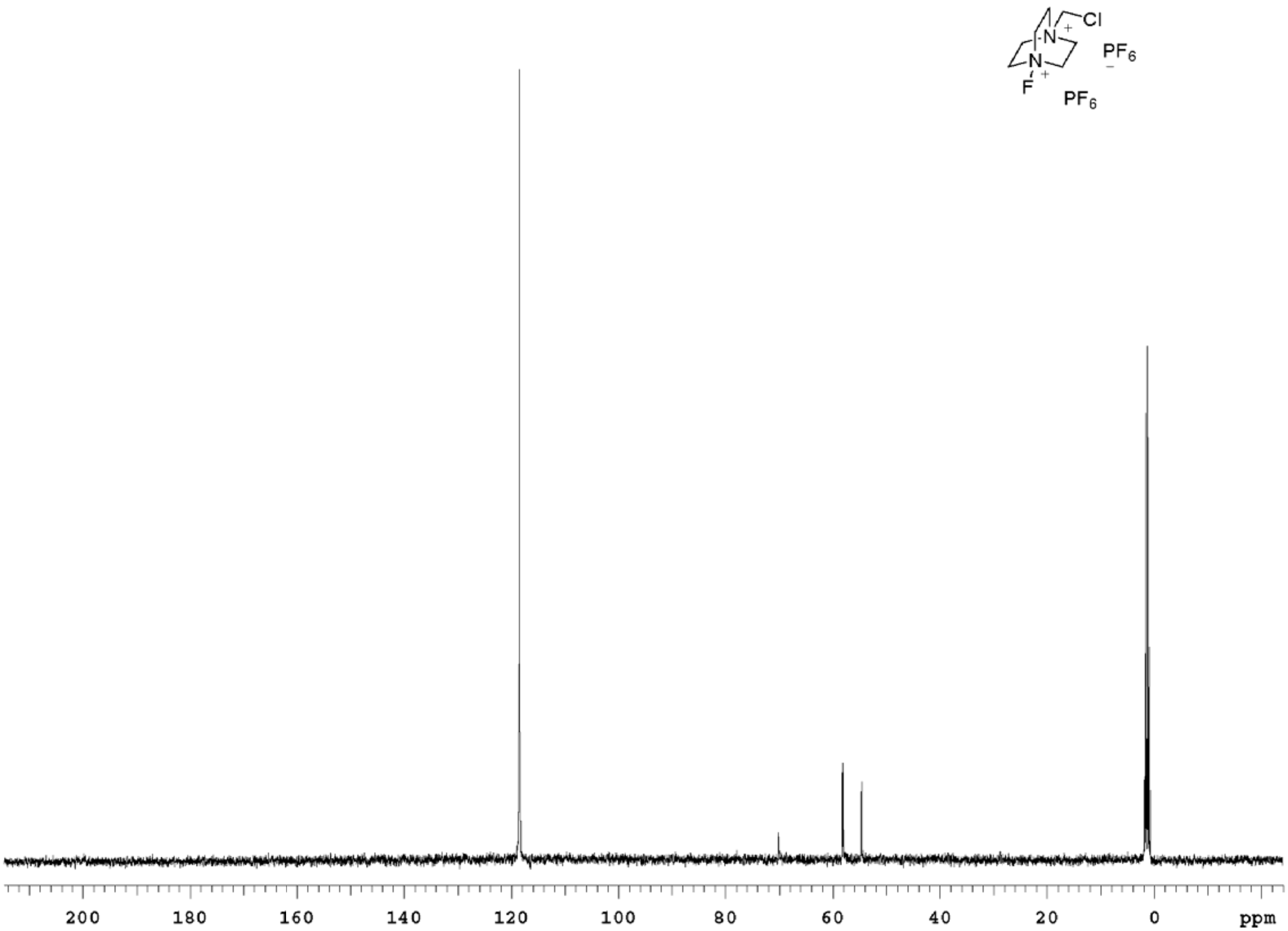

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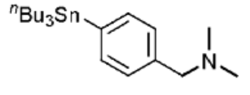

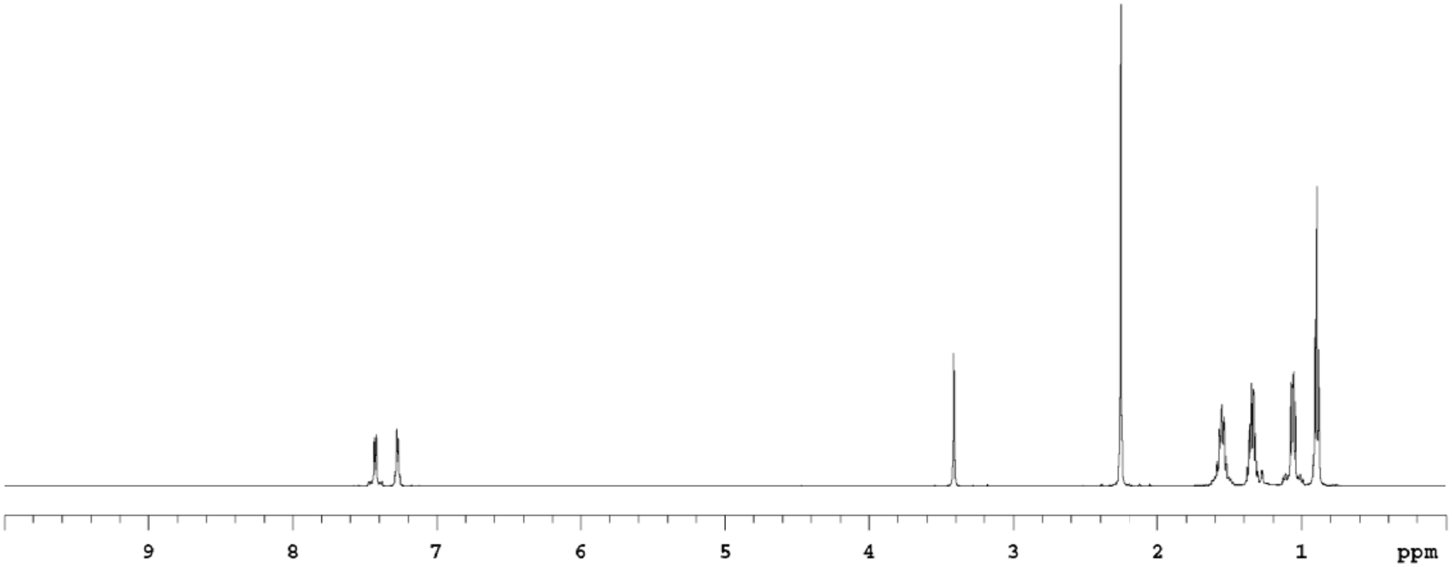

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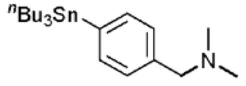

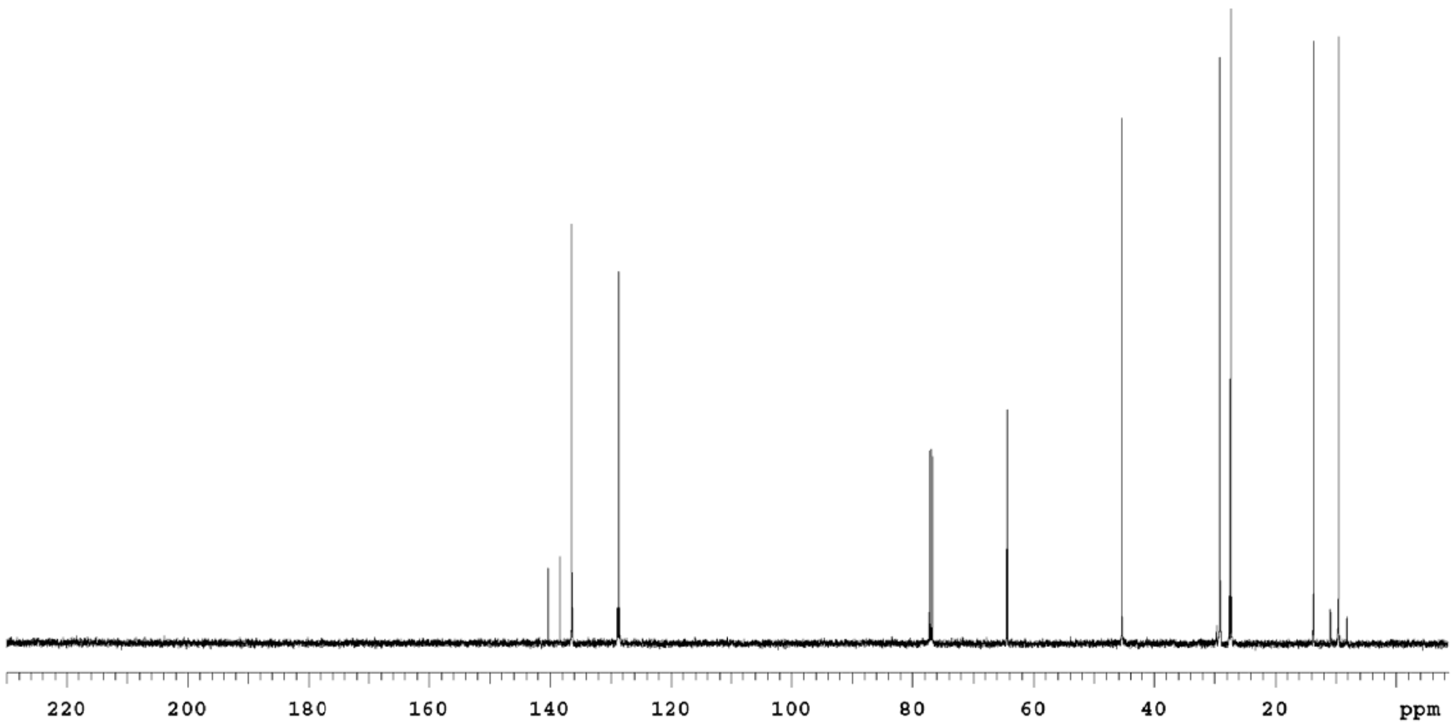

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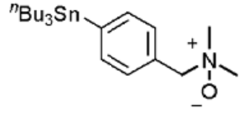

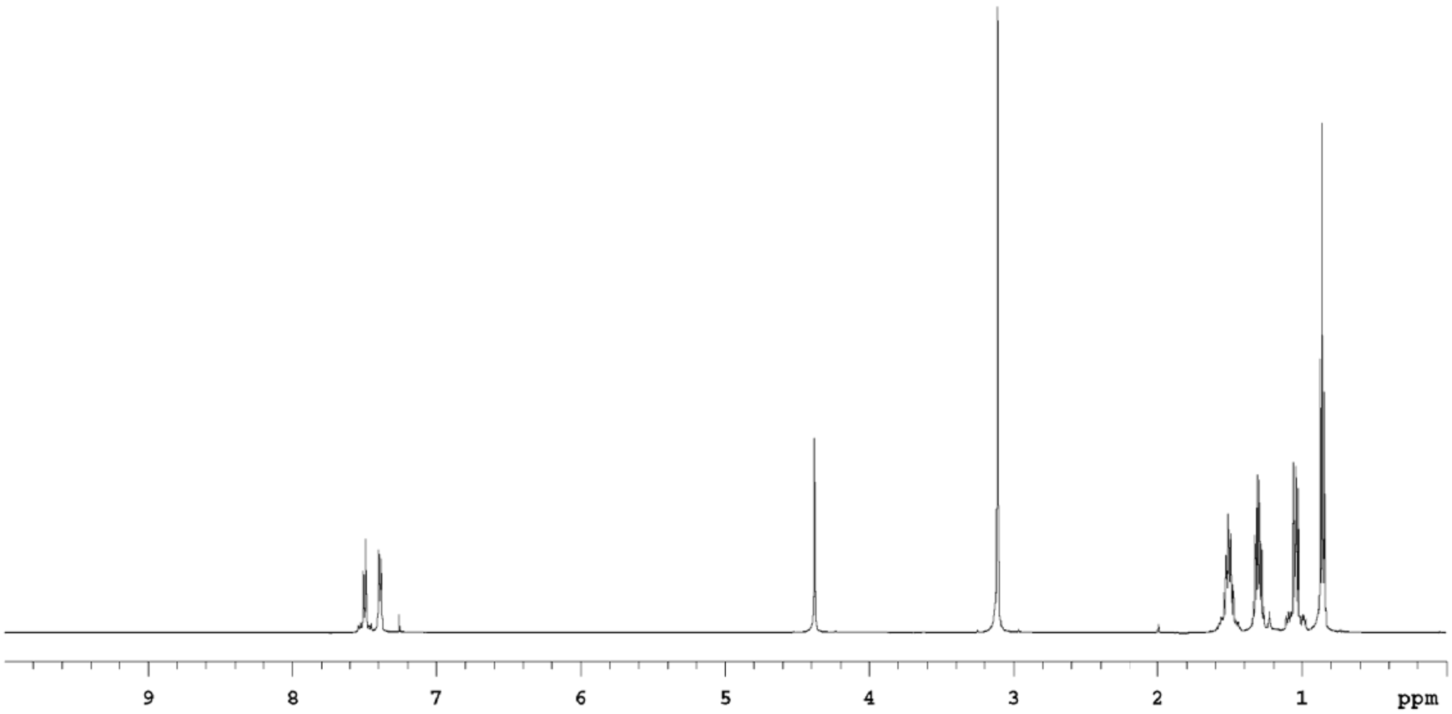

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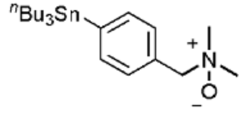

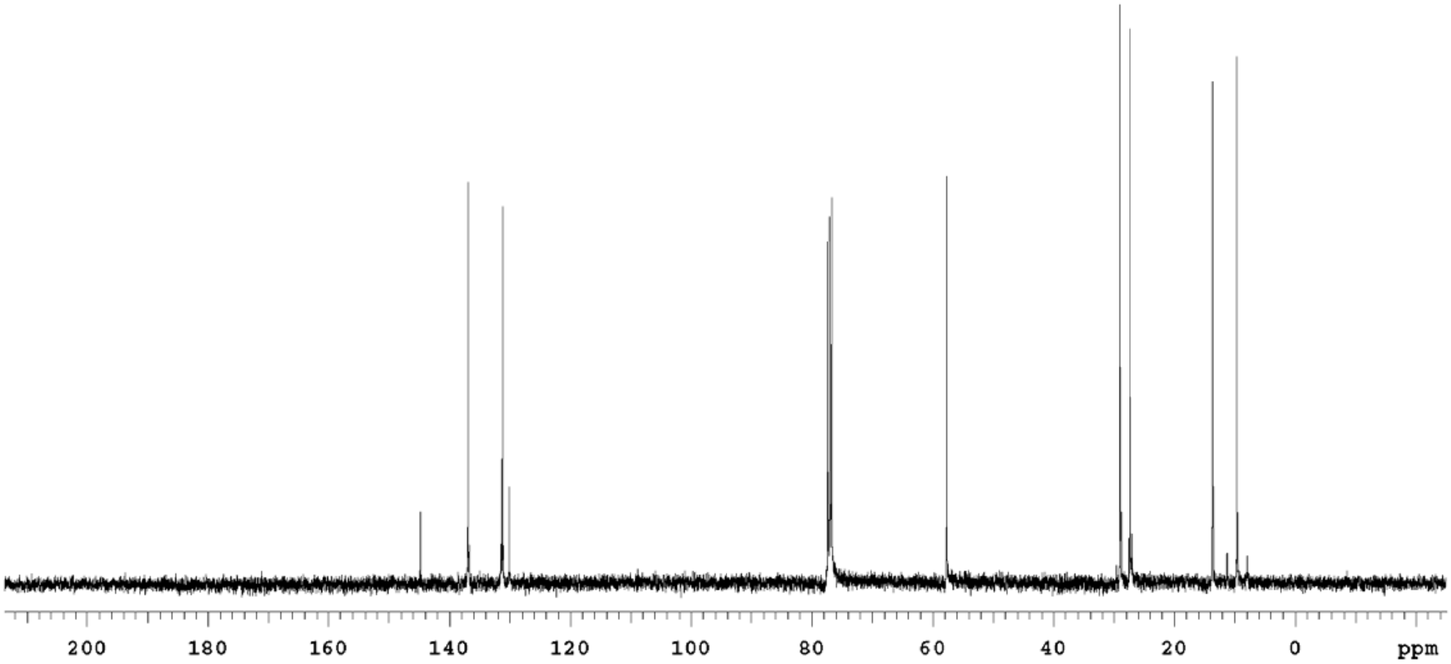

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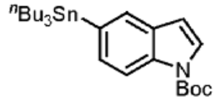

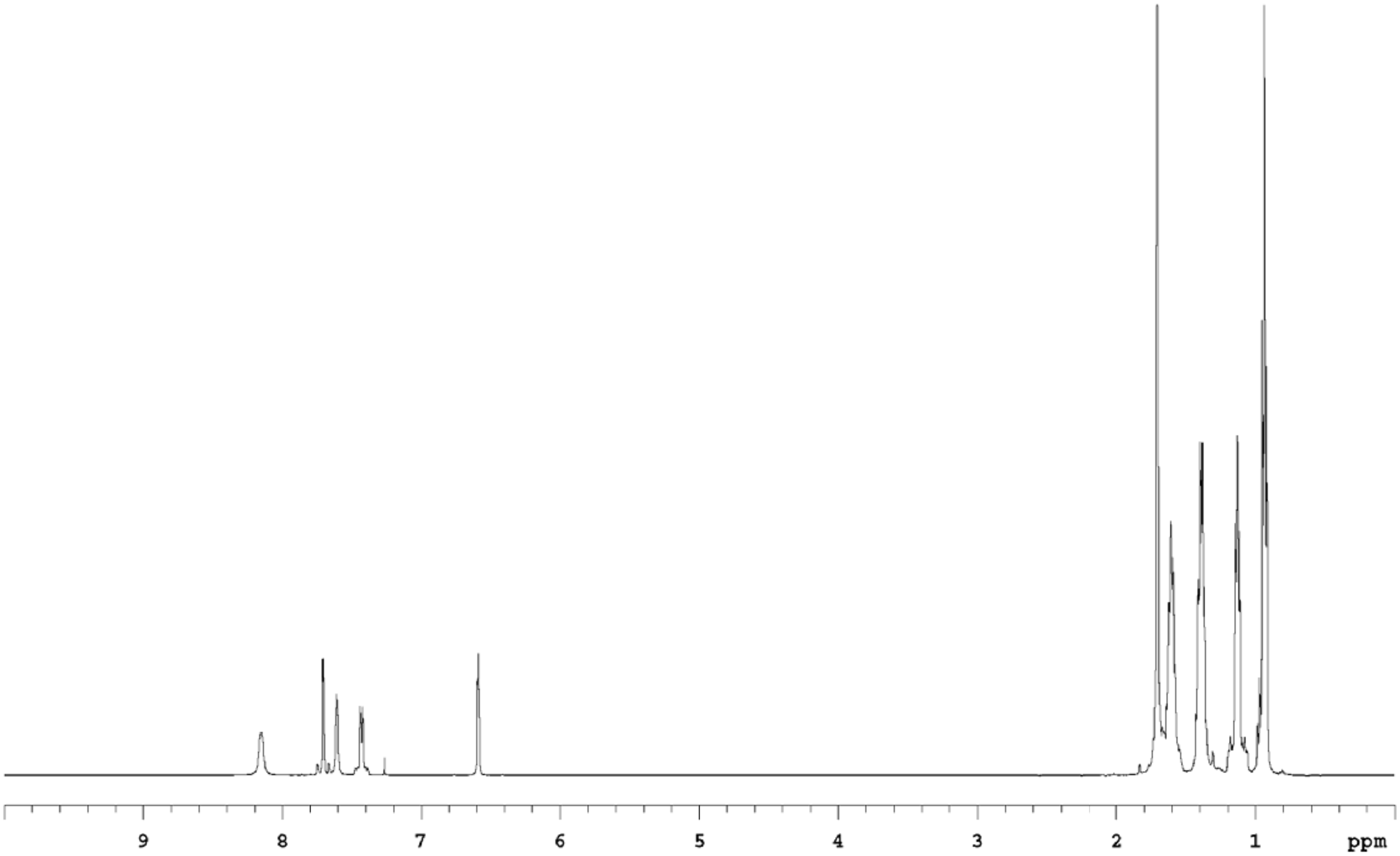

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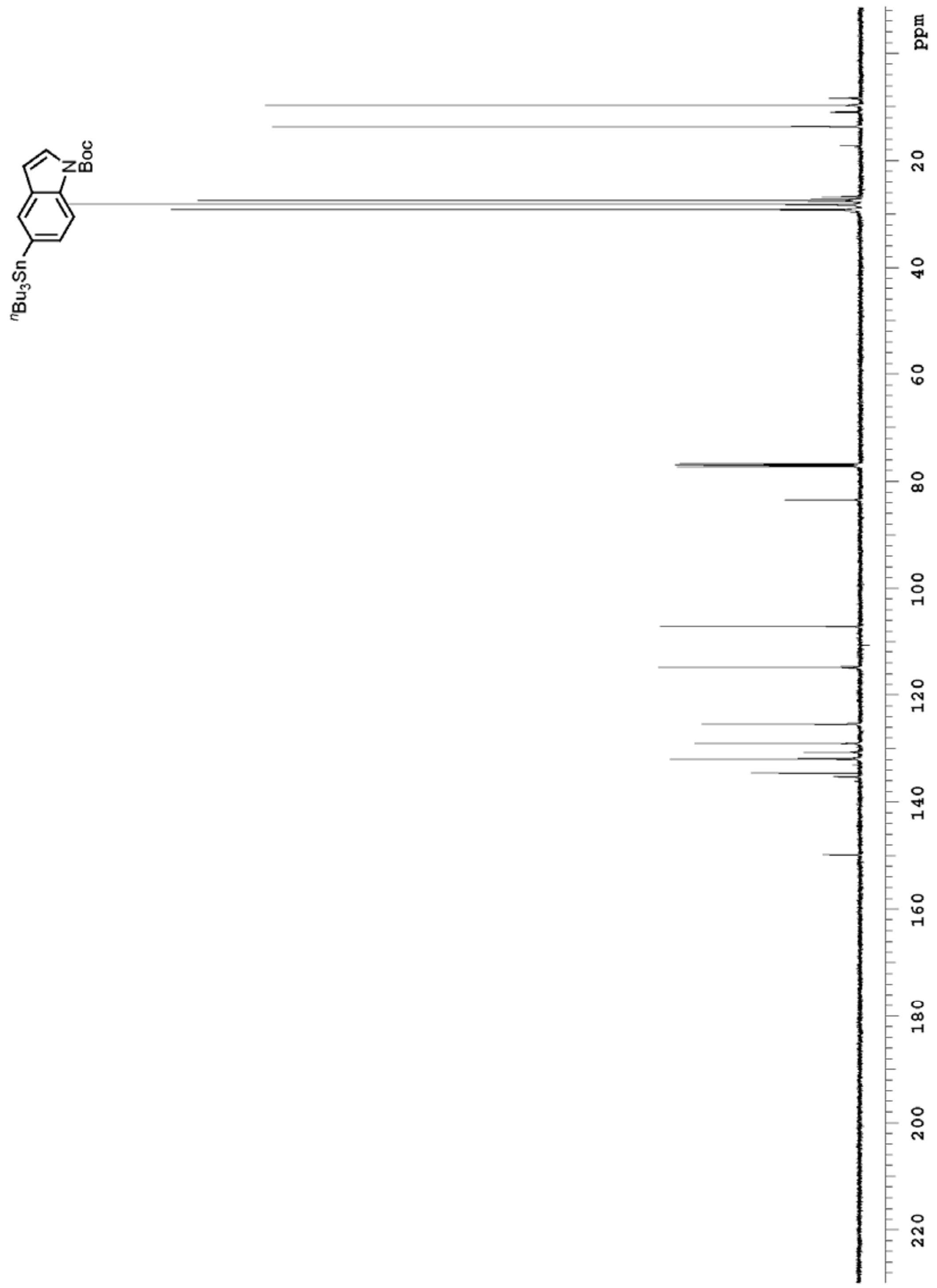

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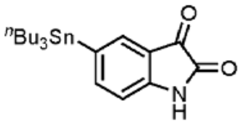

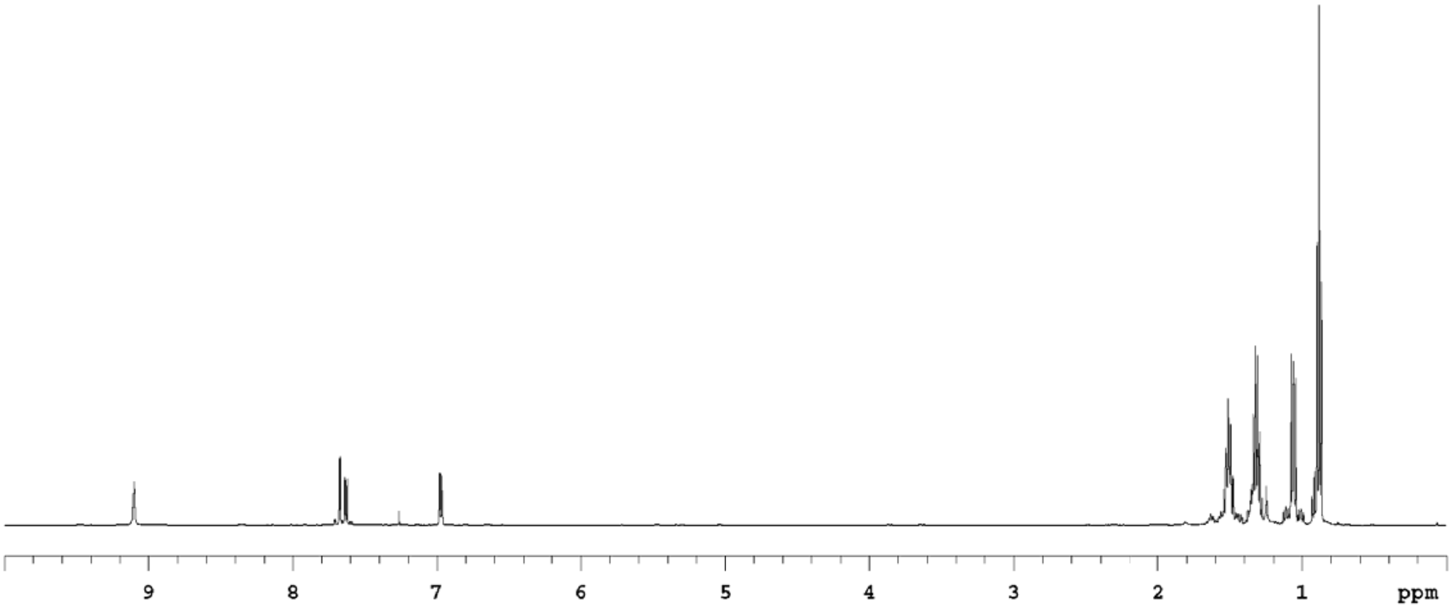

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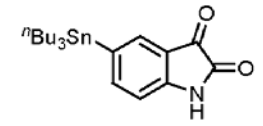

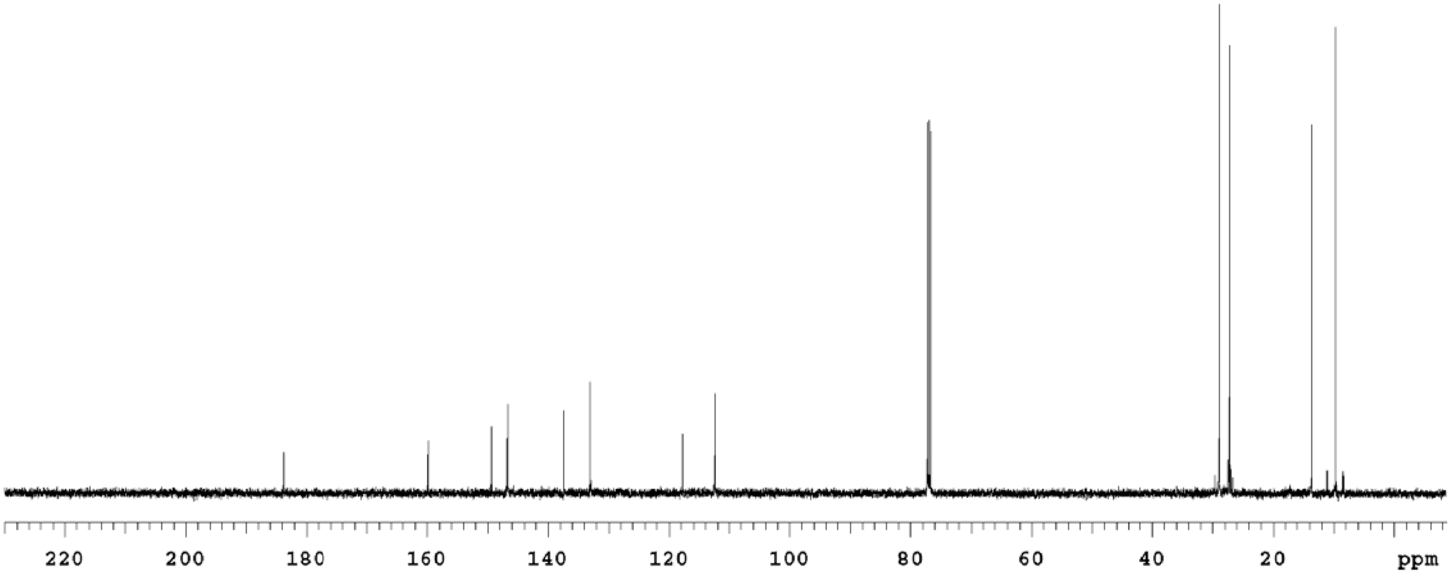

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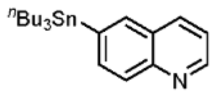

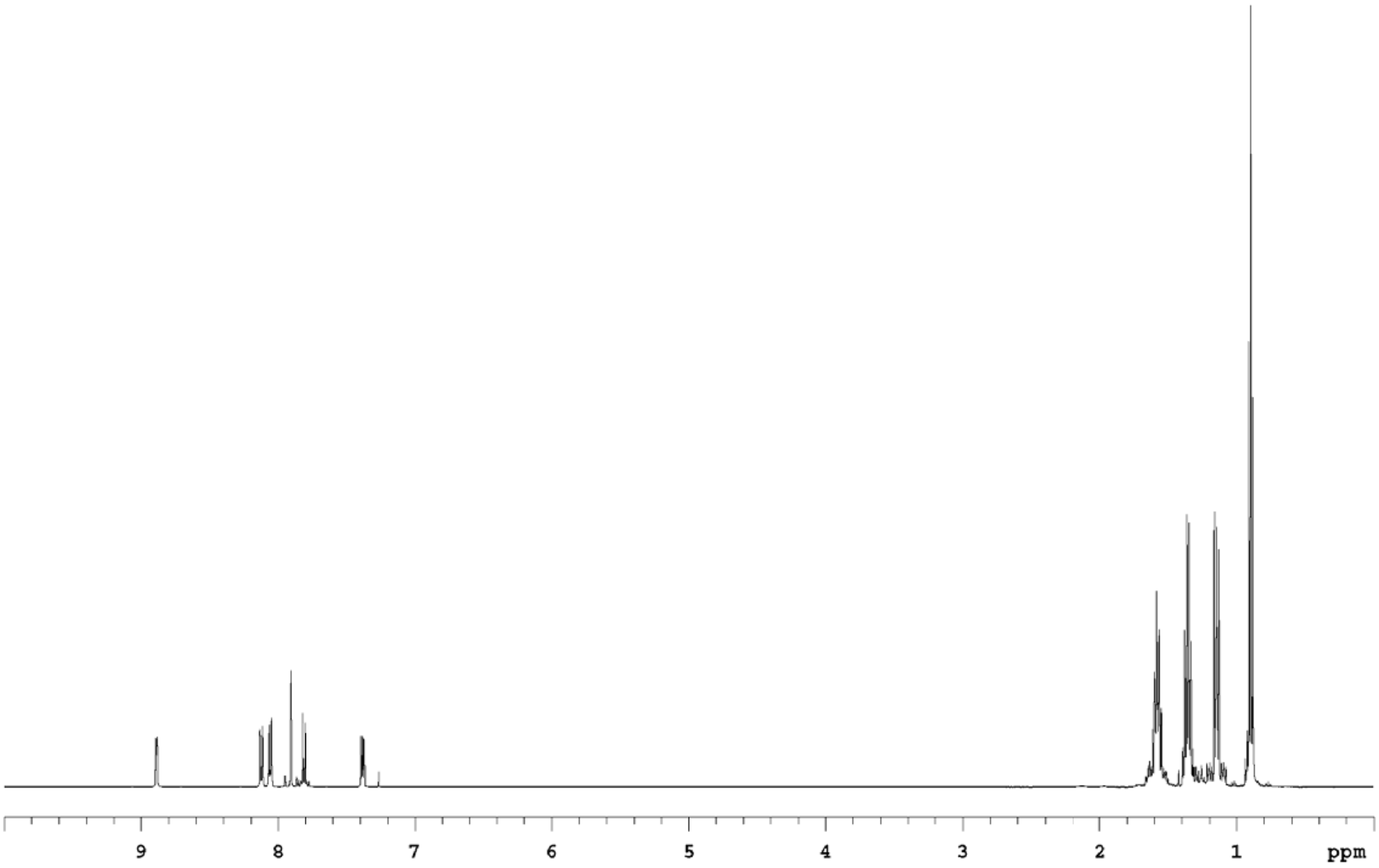

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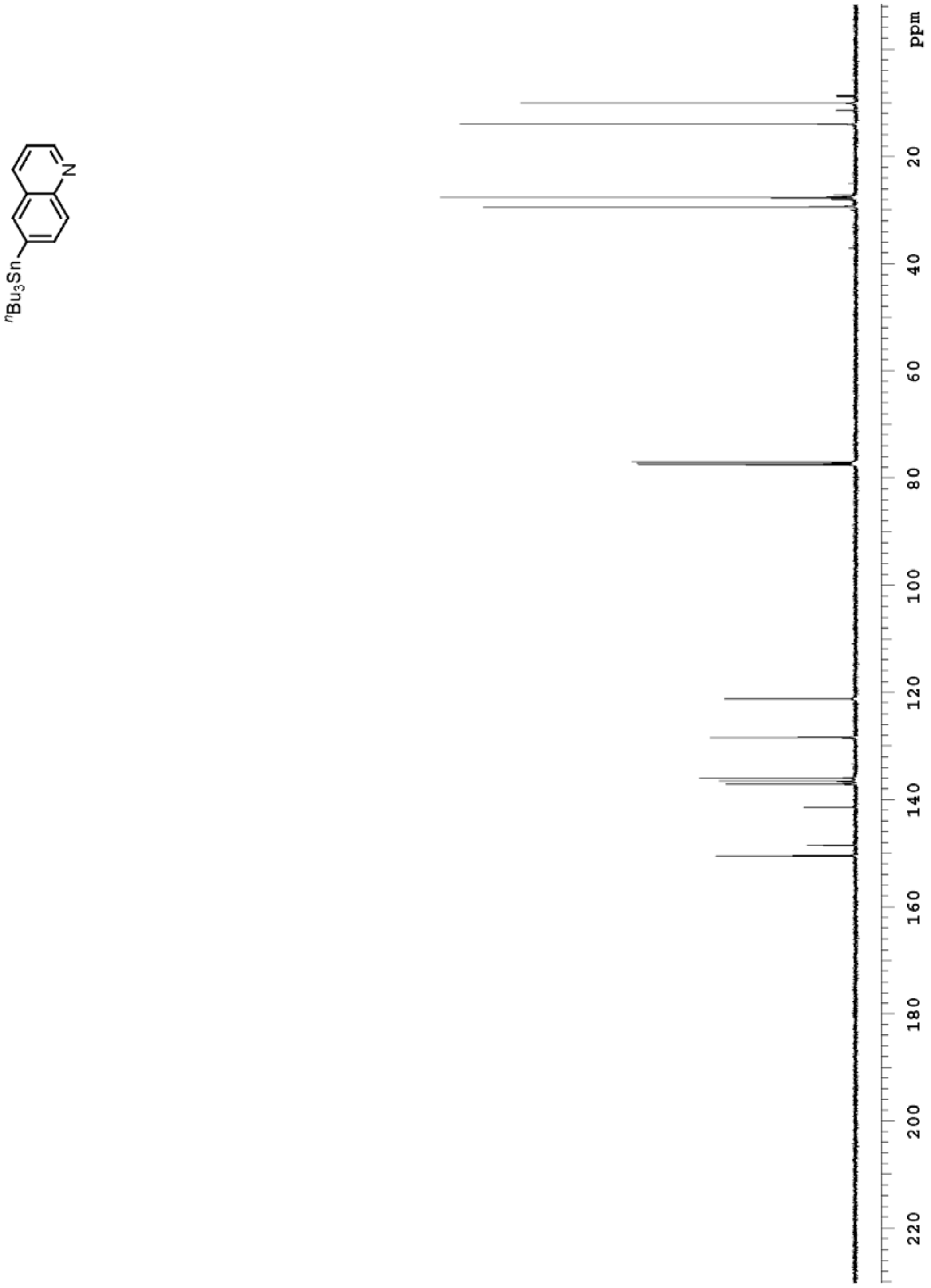

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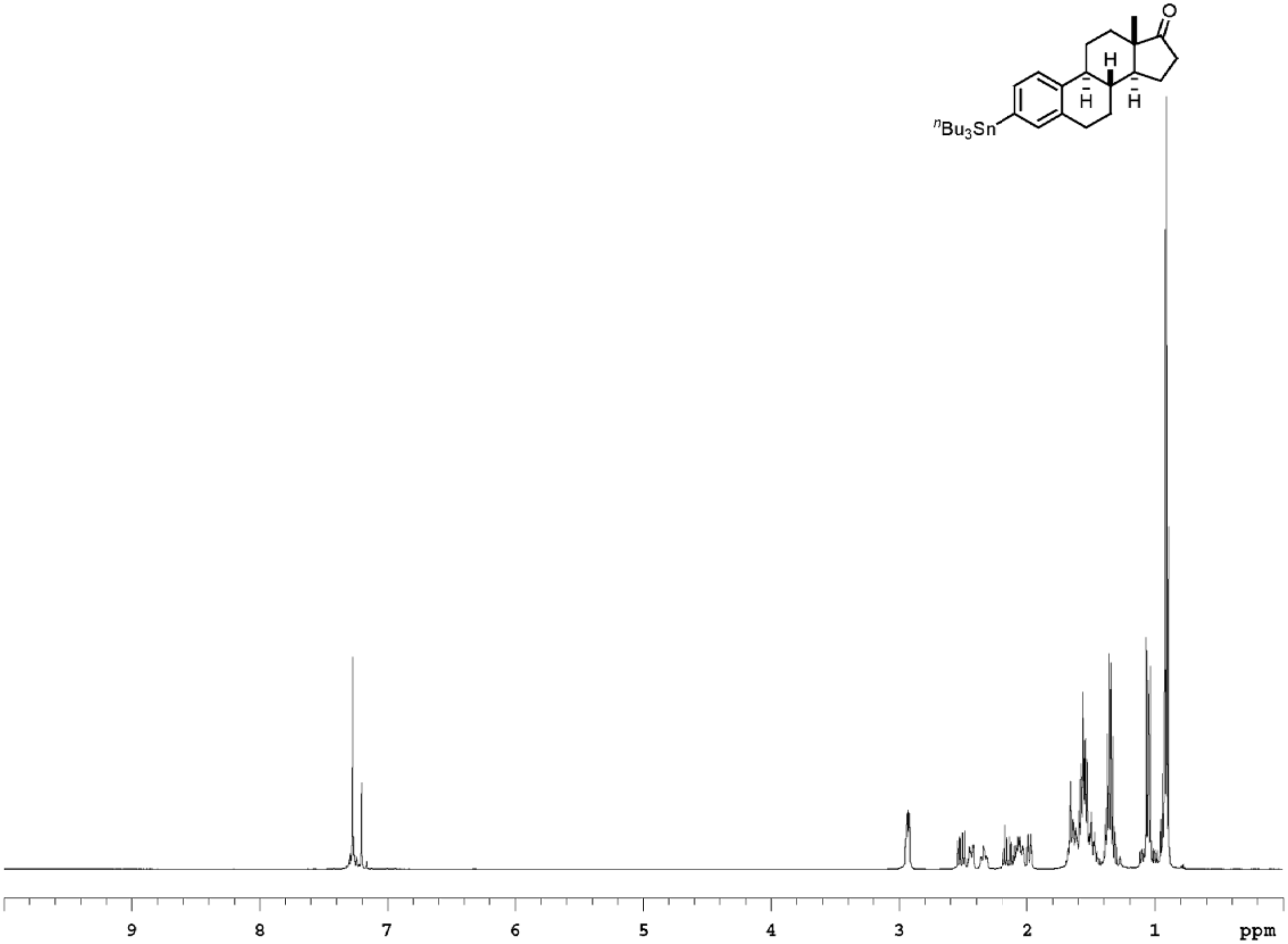

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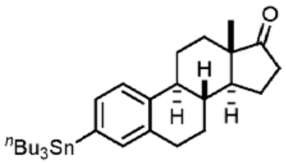

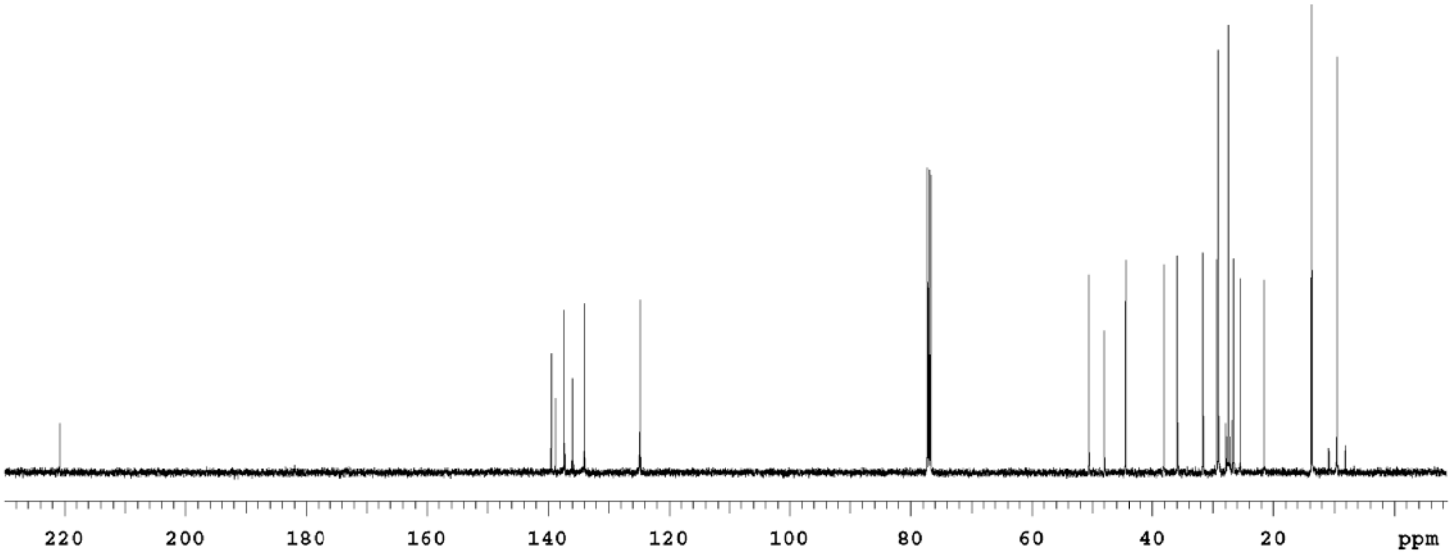

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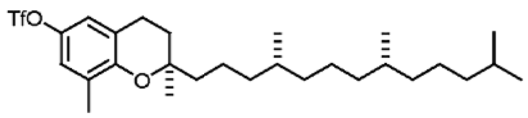

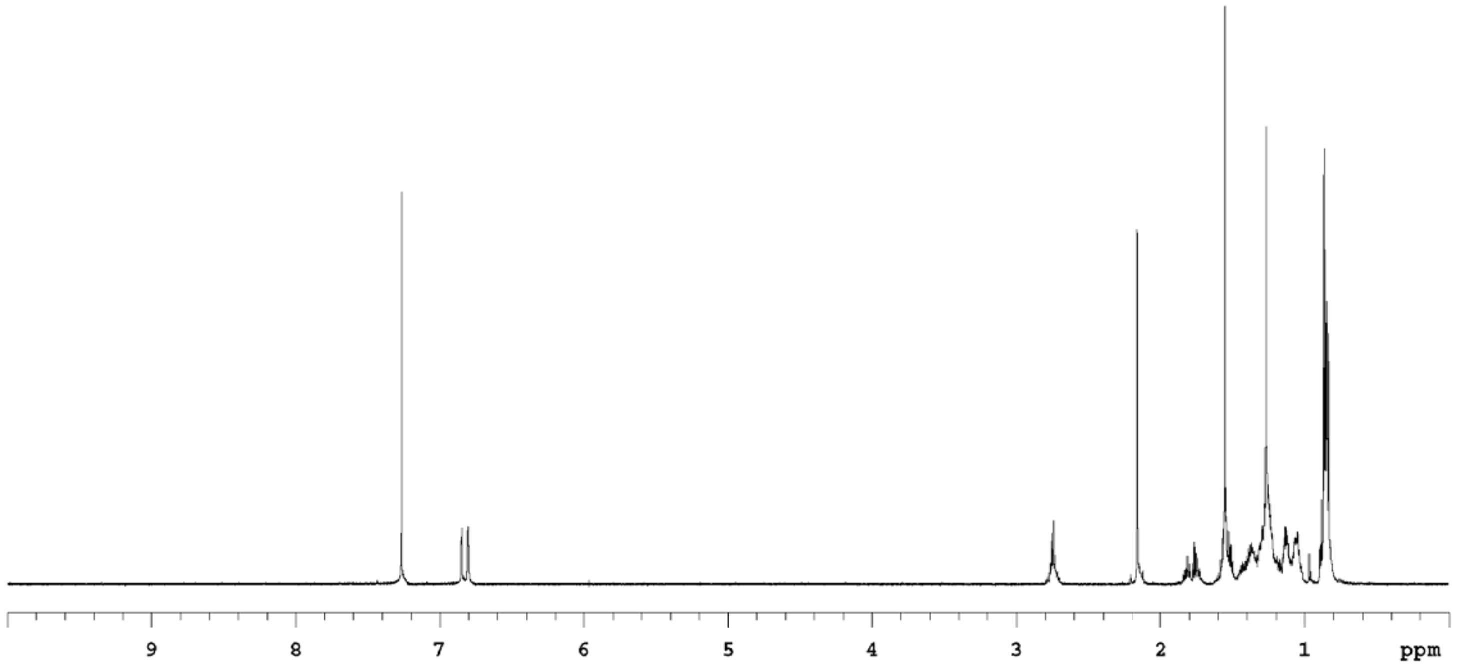

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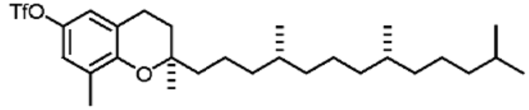

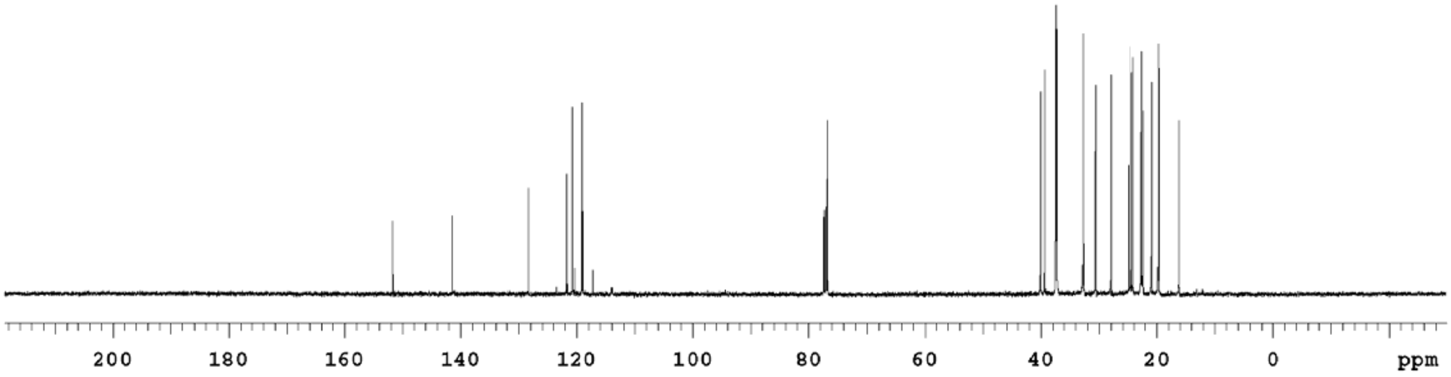

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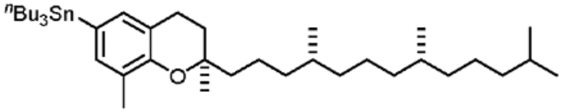

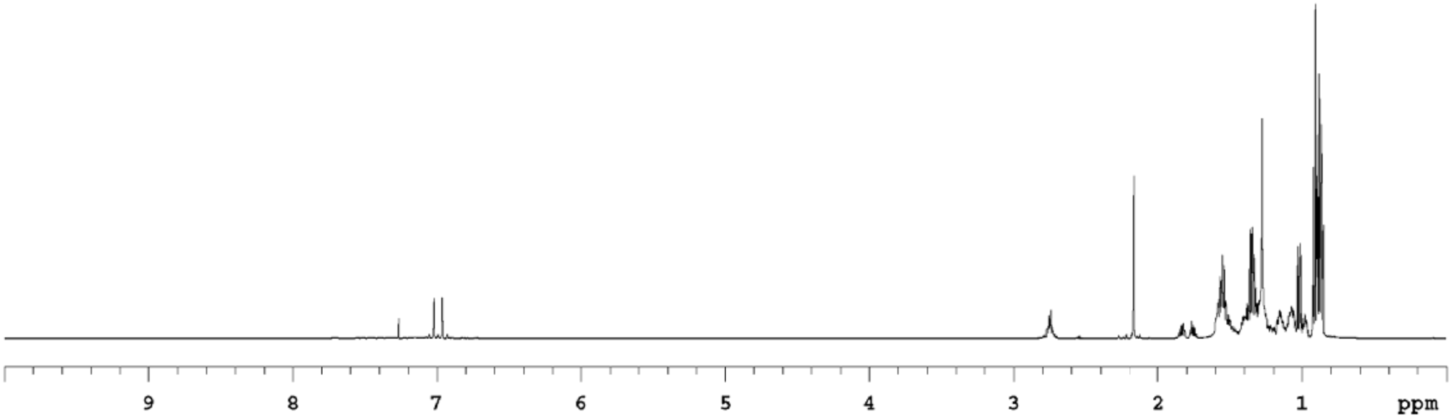

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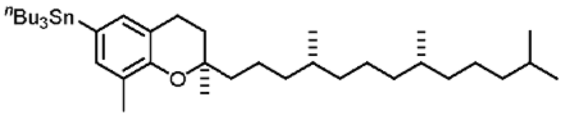

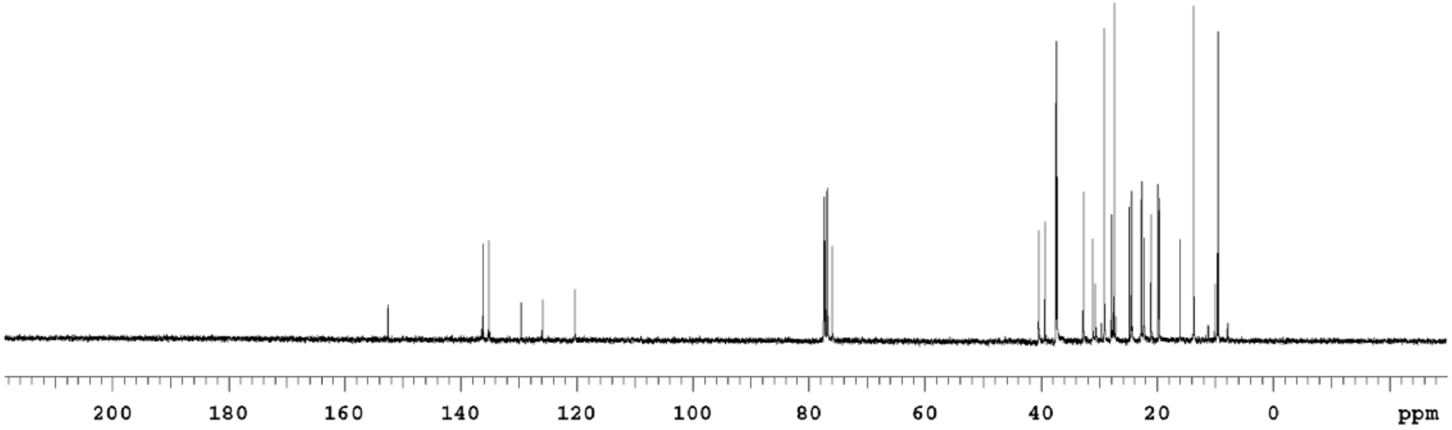

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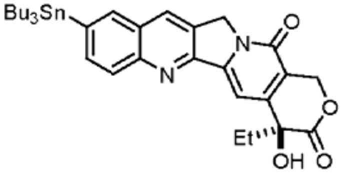

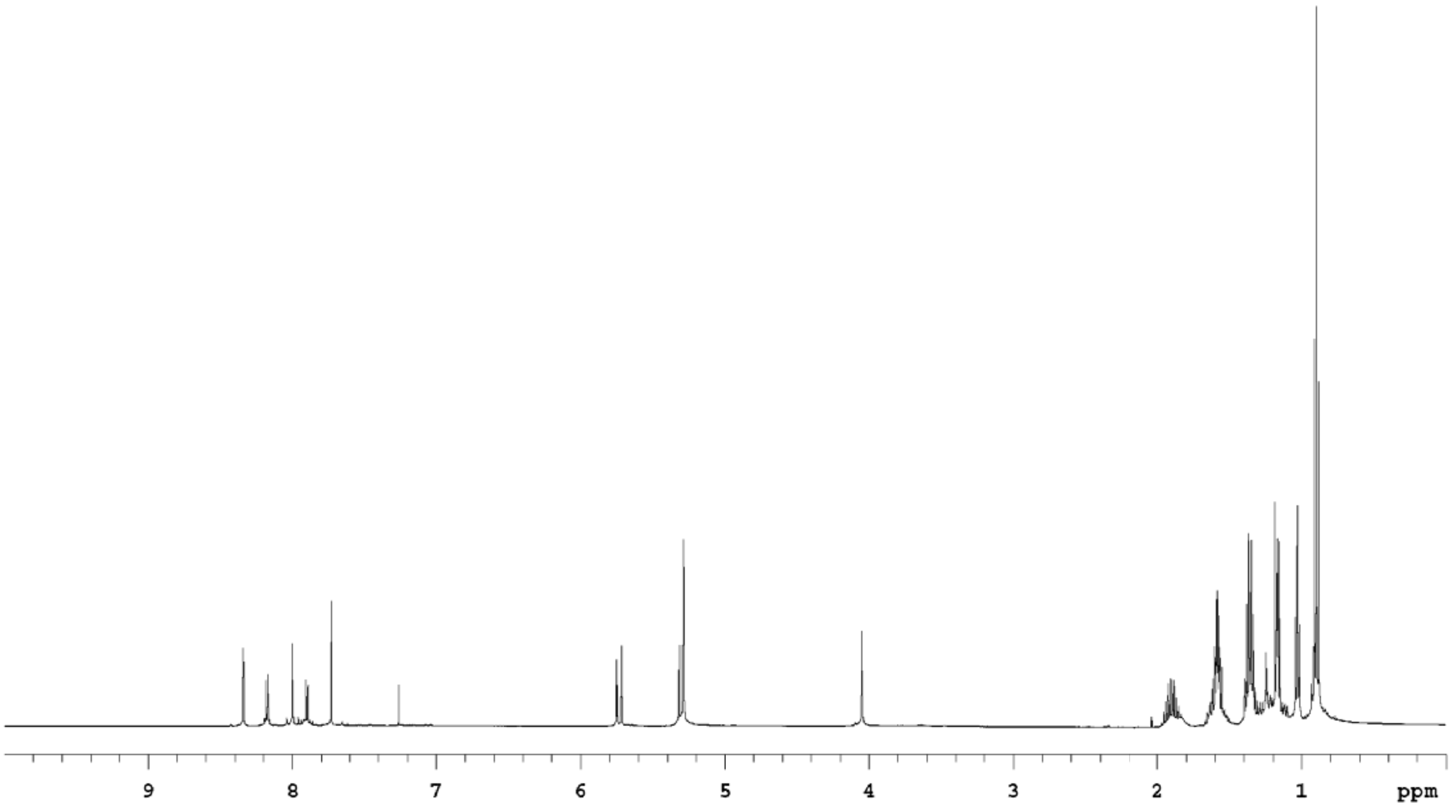

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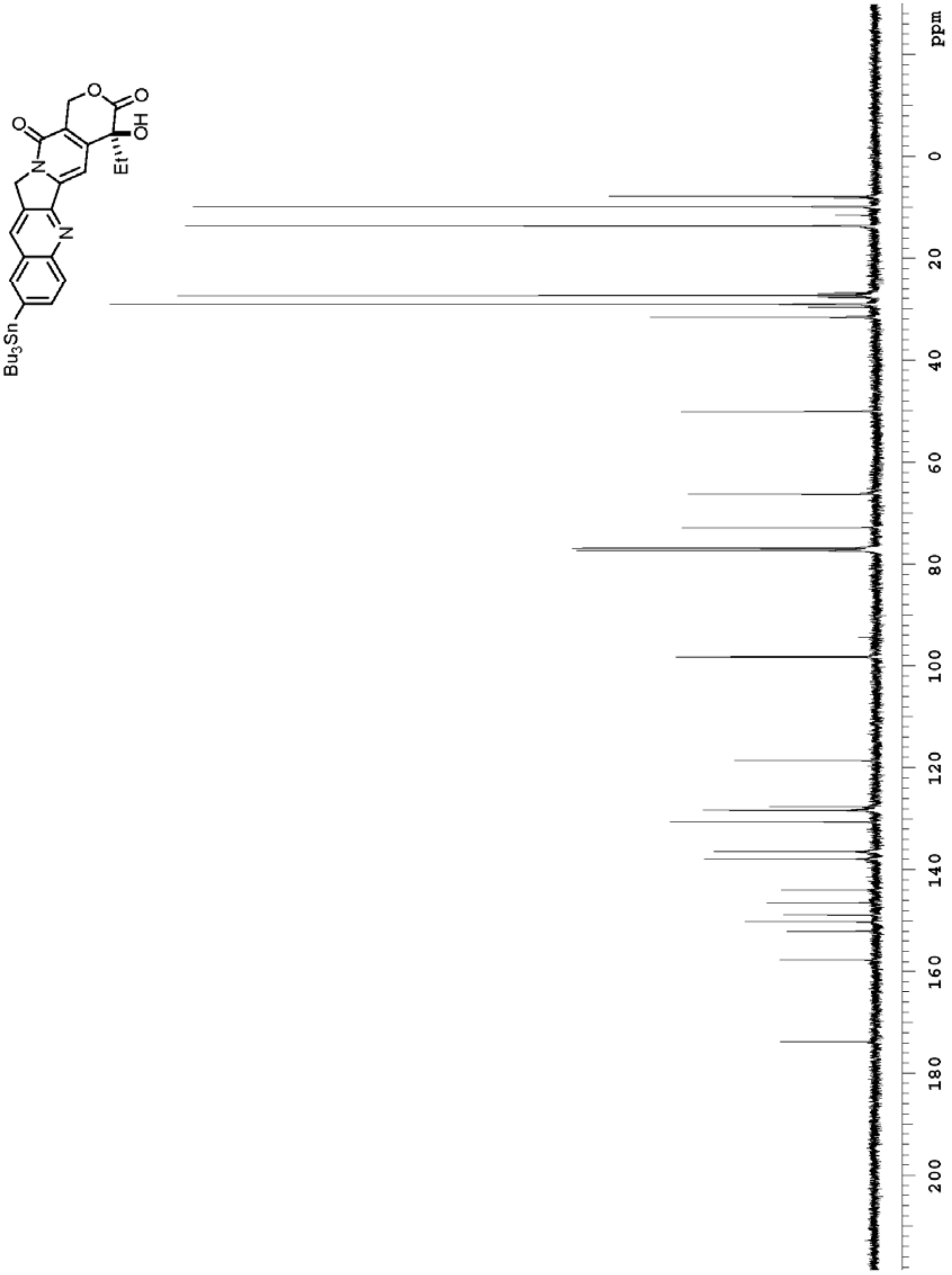
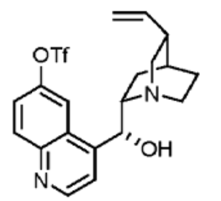
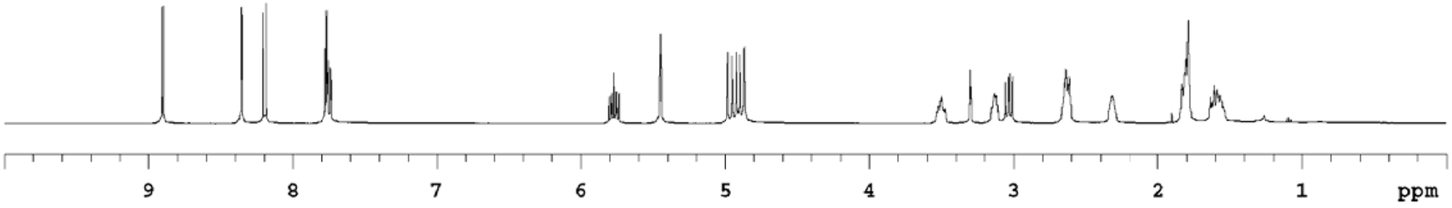
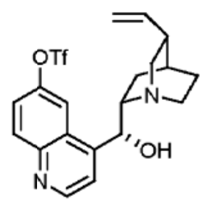


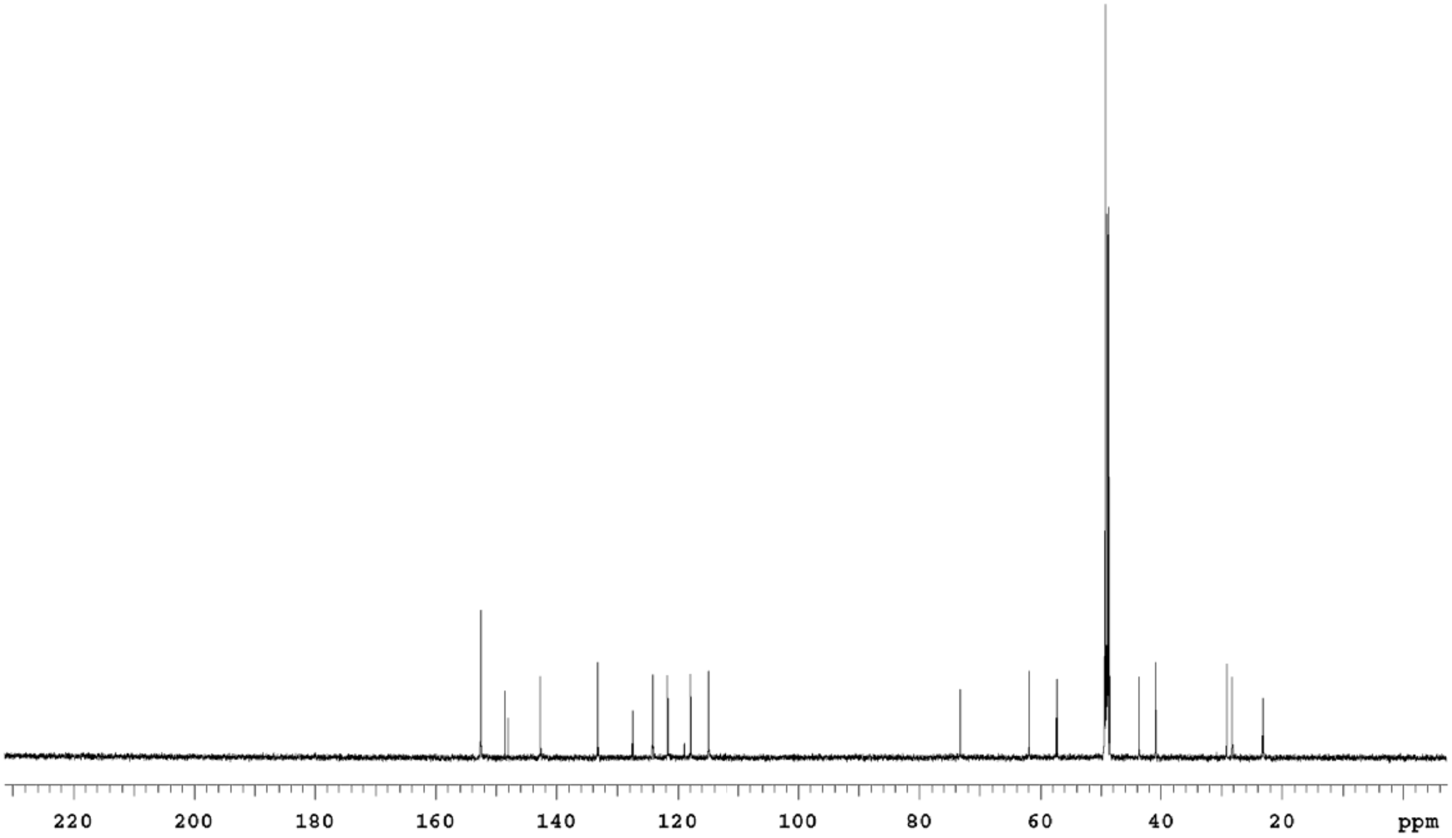
^{1}H NMR spectrum of



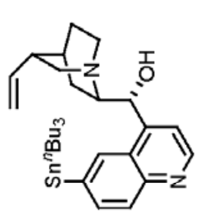


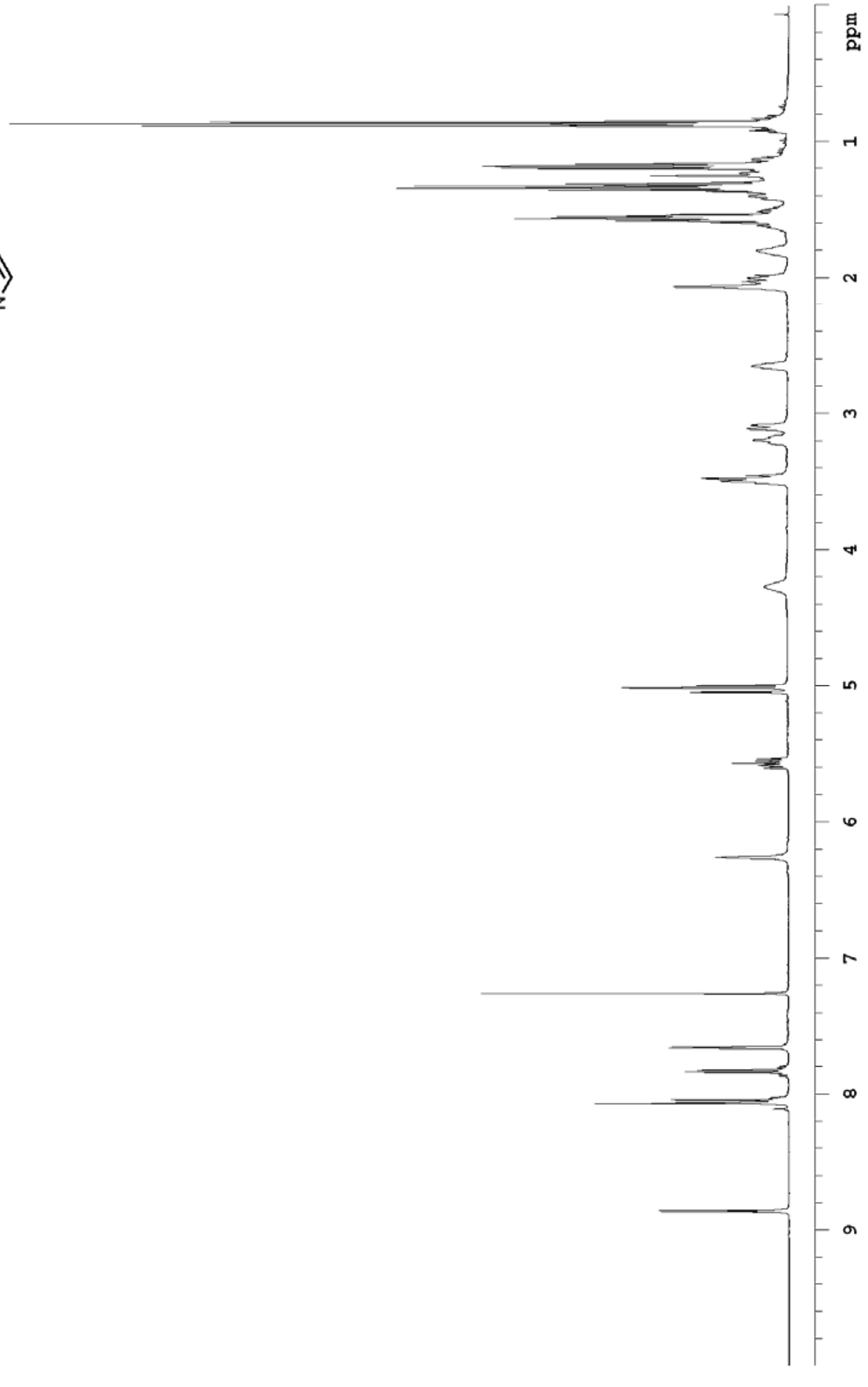
^{13}C NMR spectrum of



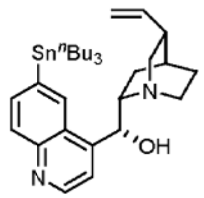


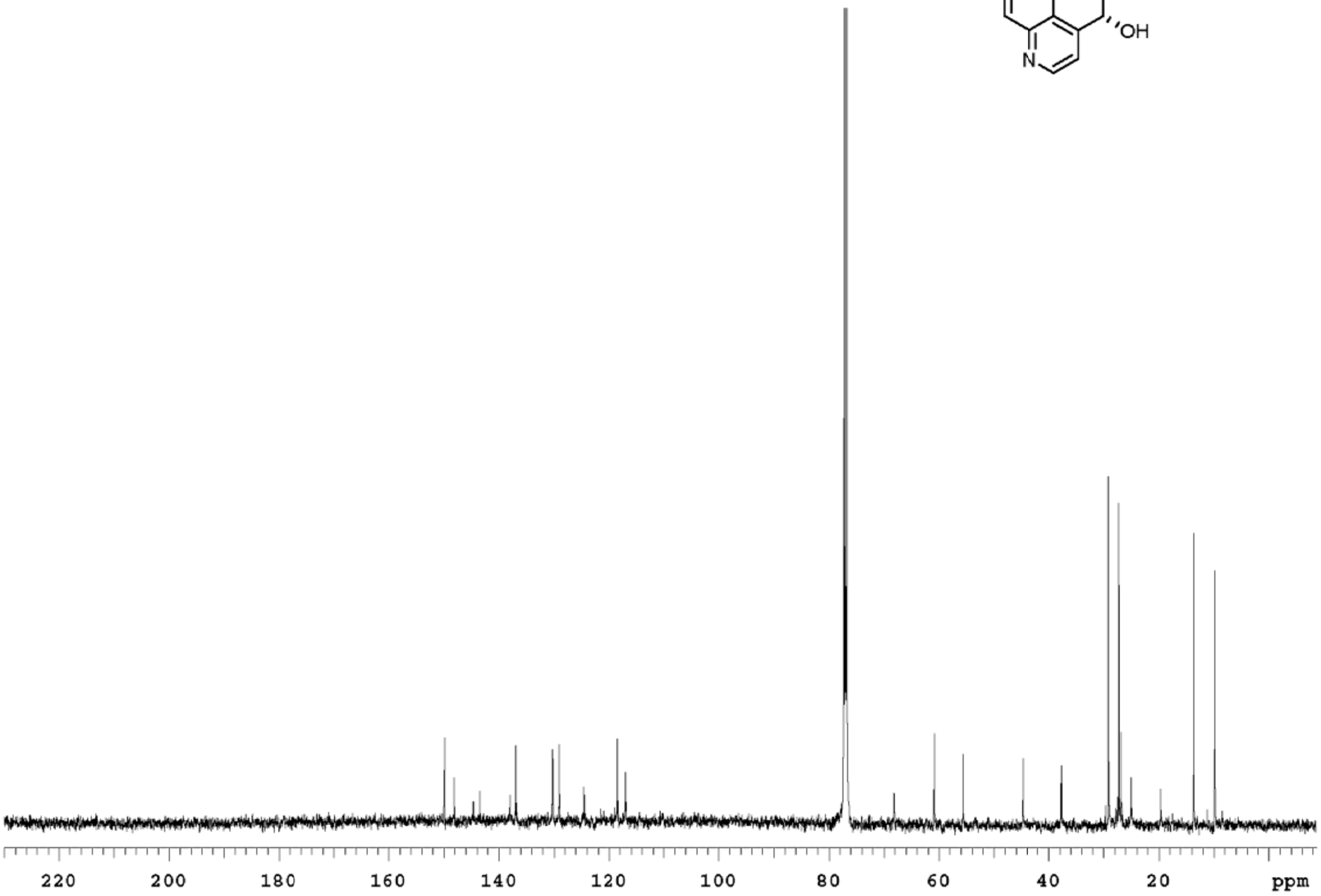
^{1}H NMR spectrum of



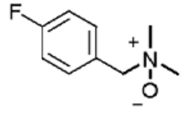


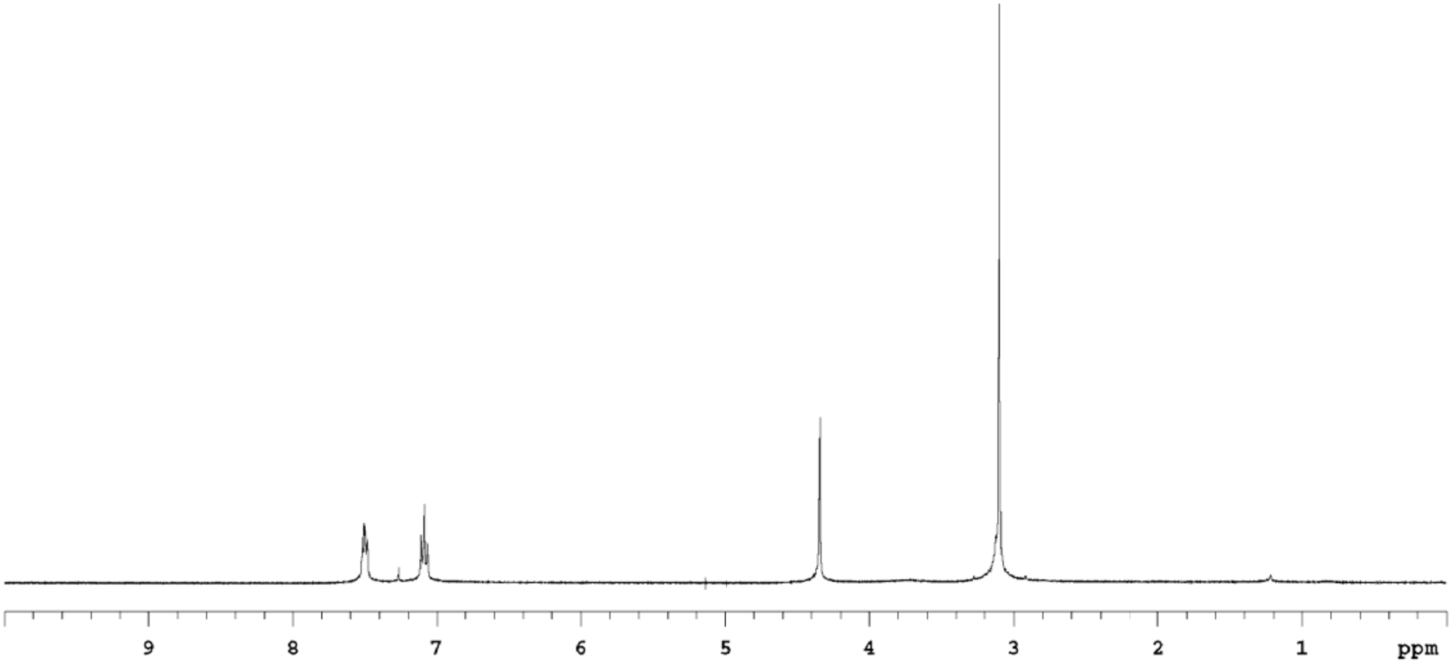
^{13}C NMR spectrum of



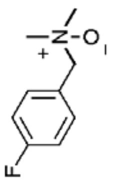


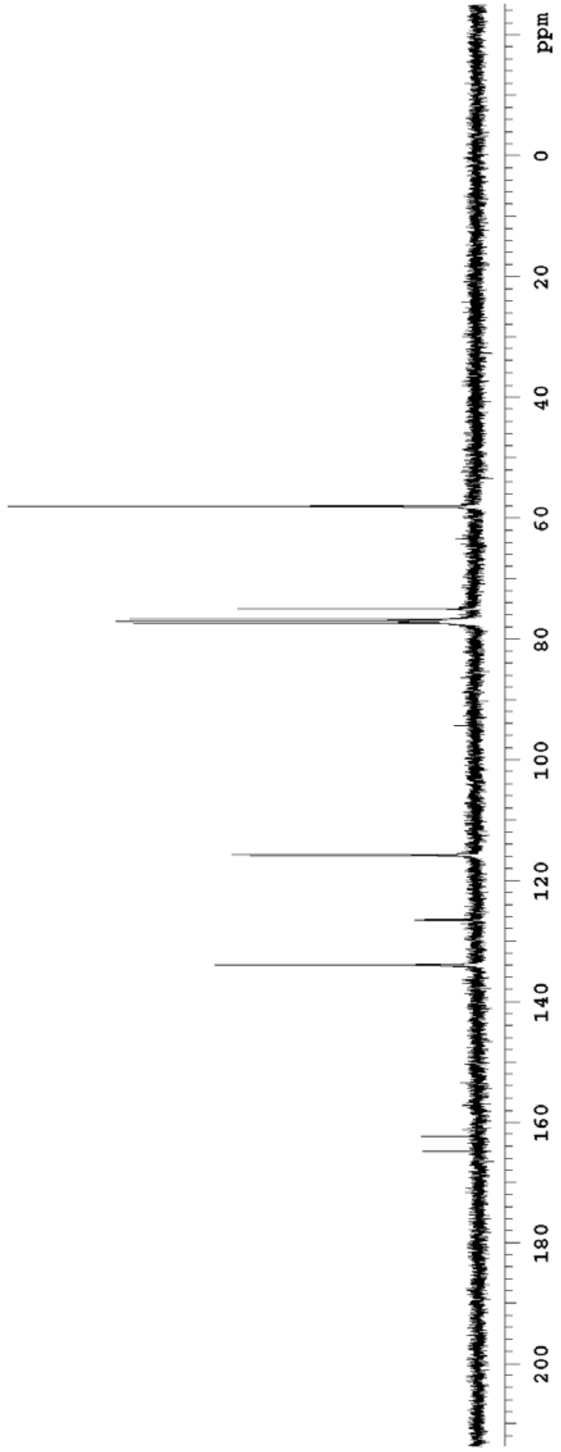
^{1}H NMR spectrum of



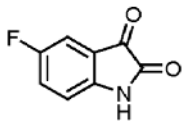


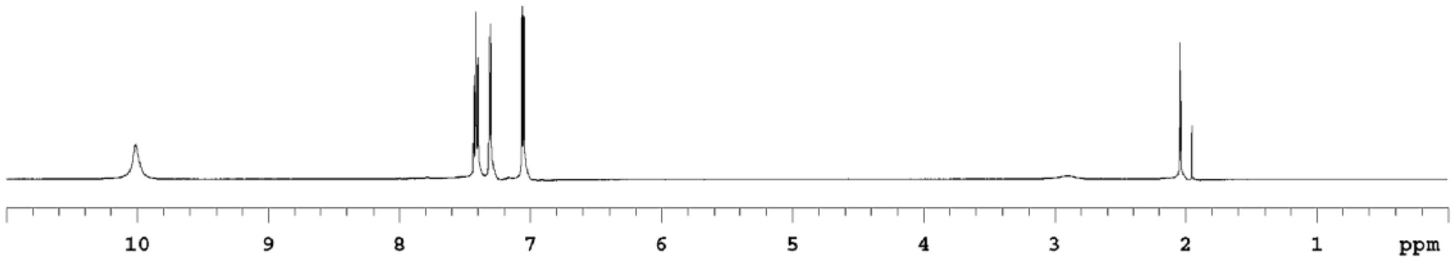
^{13}C NMR spectrum of



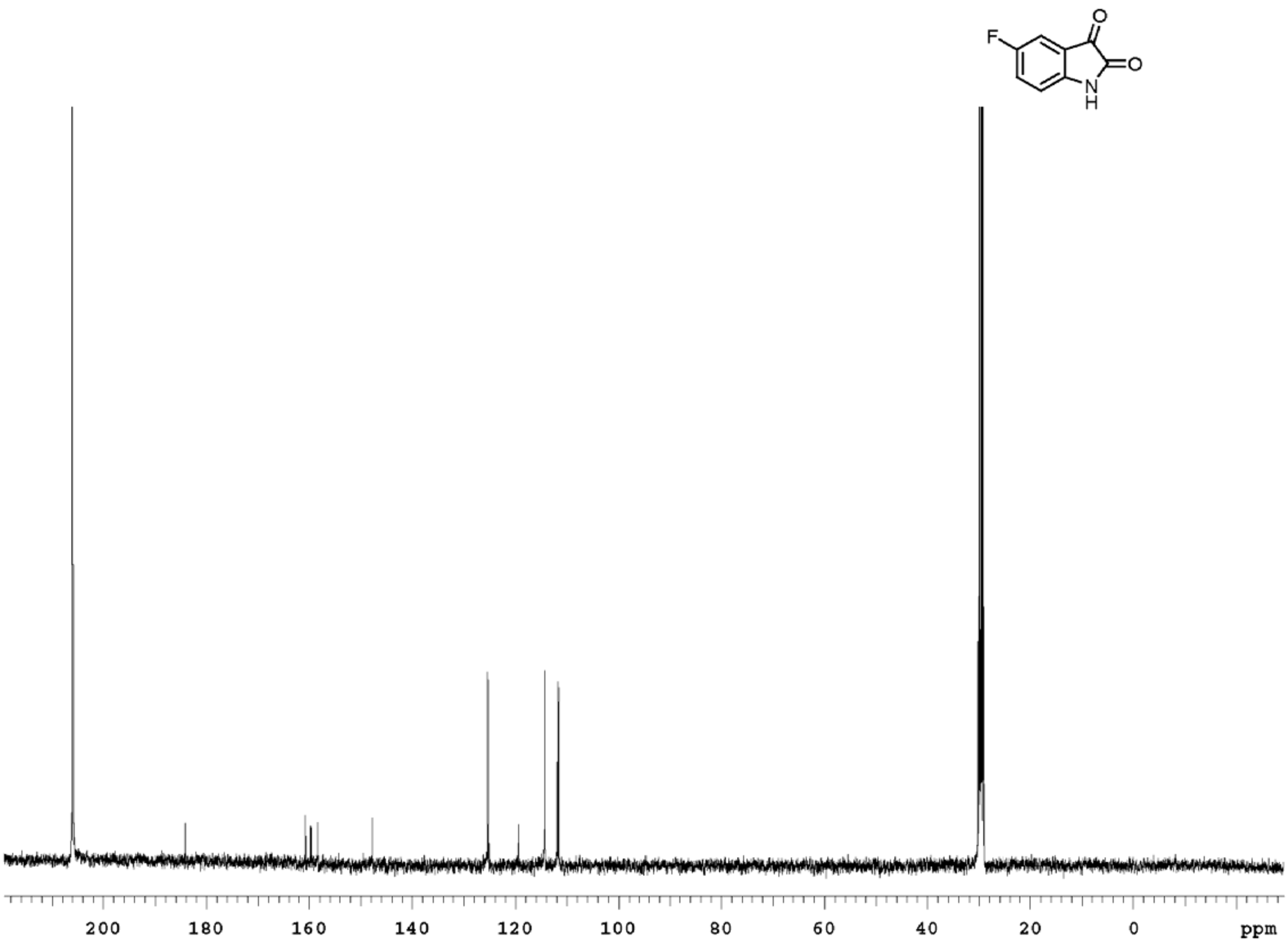


^{1}H NMR spectrum of

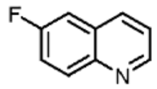


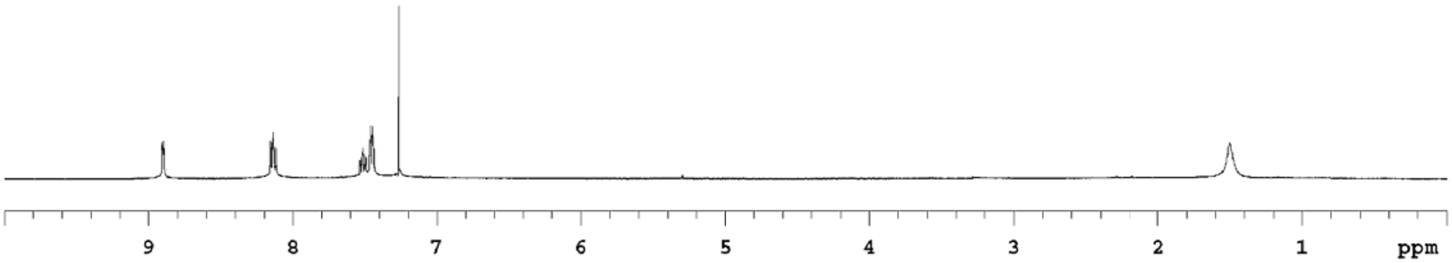


^{13}C NMR spectrum of

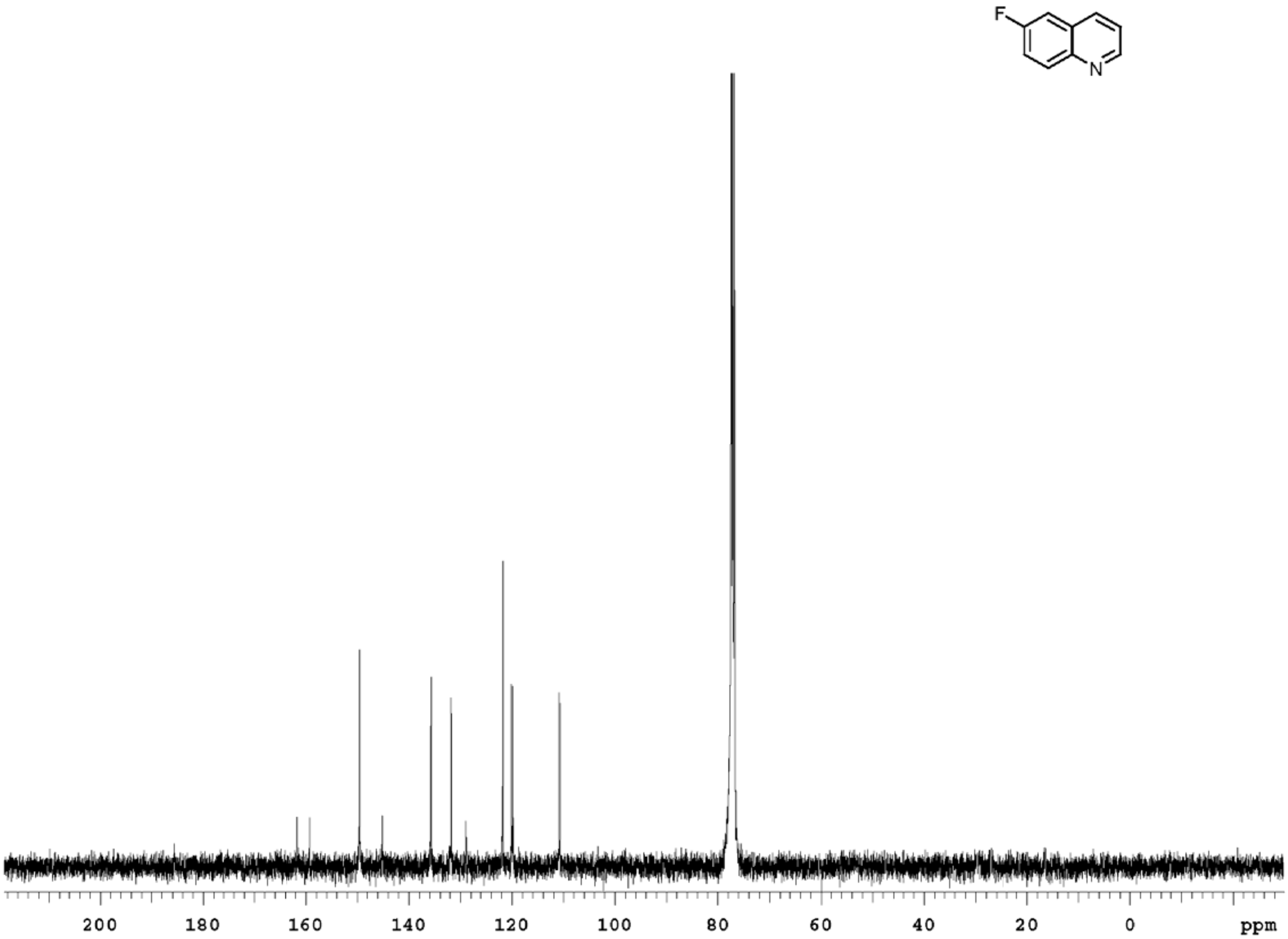


^{1}H NMR spectrum of

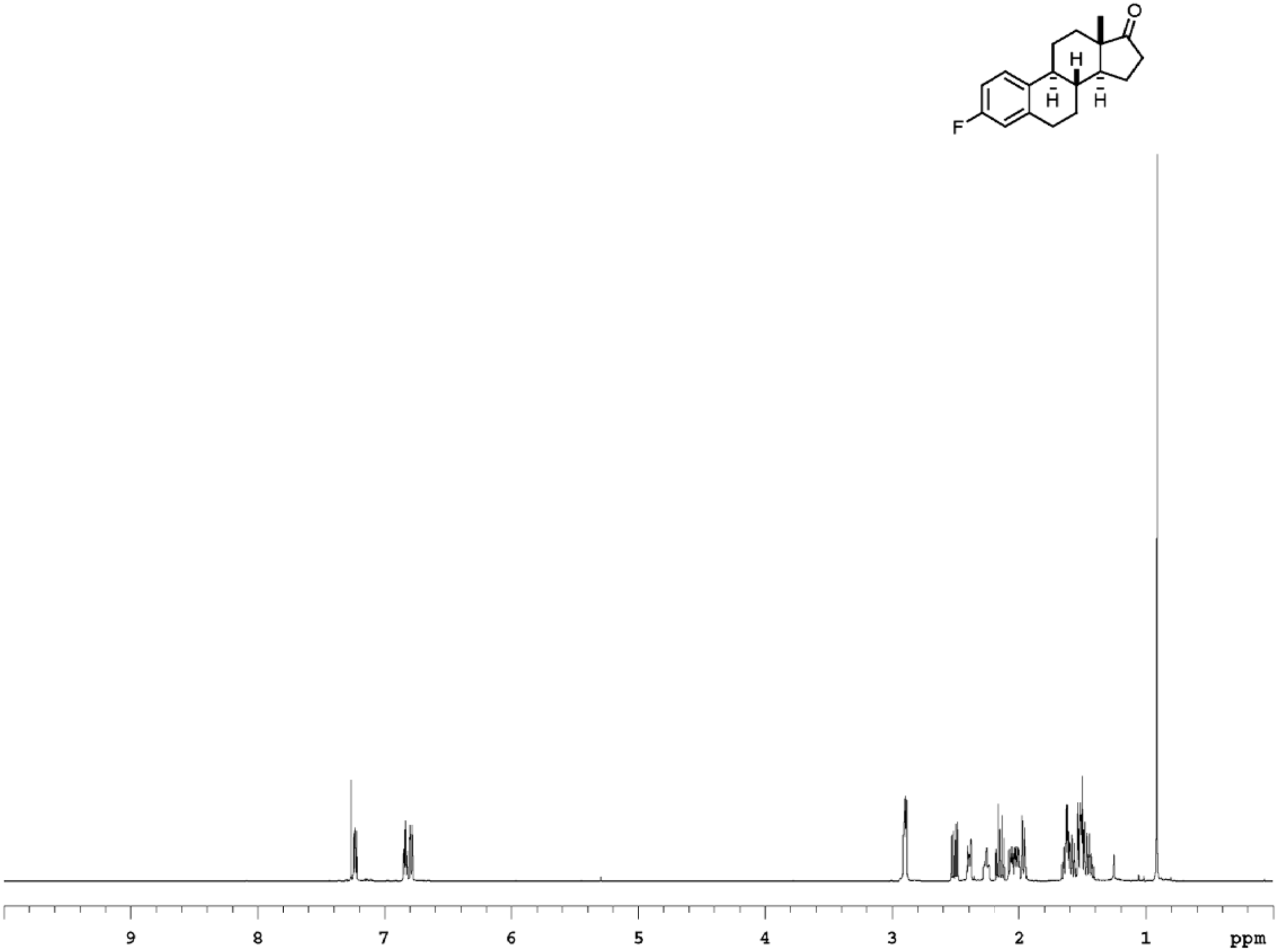




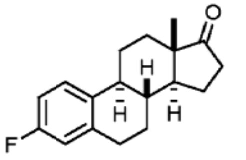
^{13}C NMR spectrum of

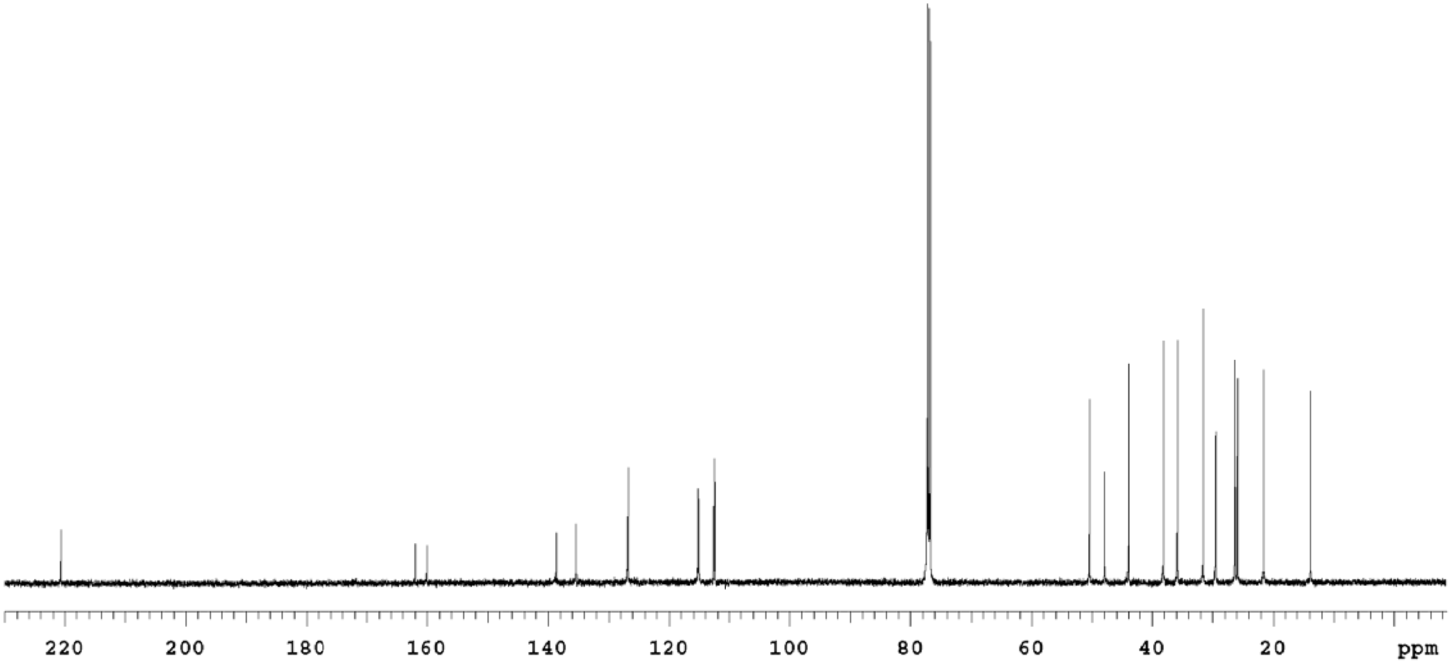


^{1}H NMR spectrum of

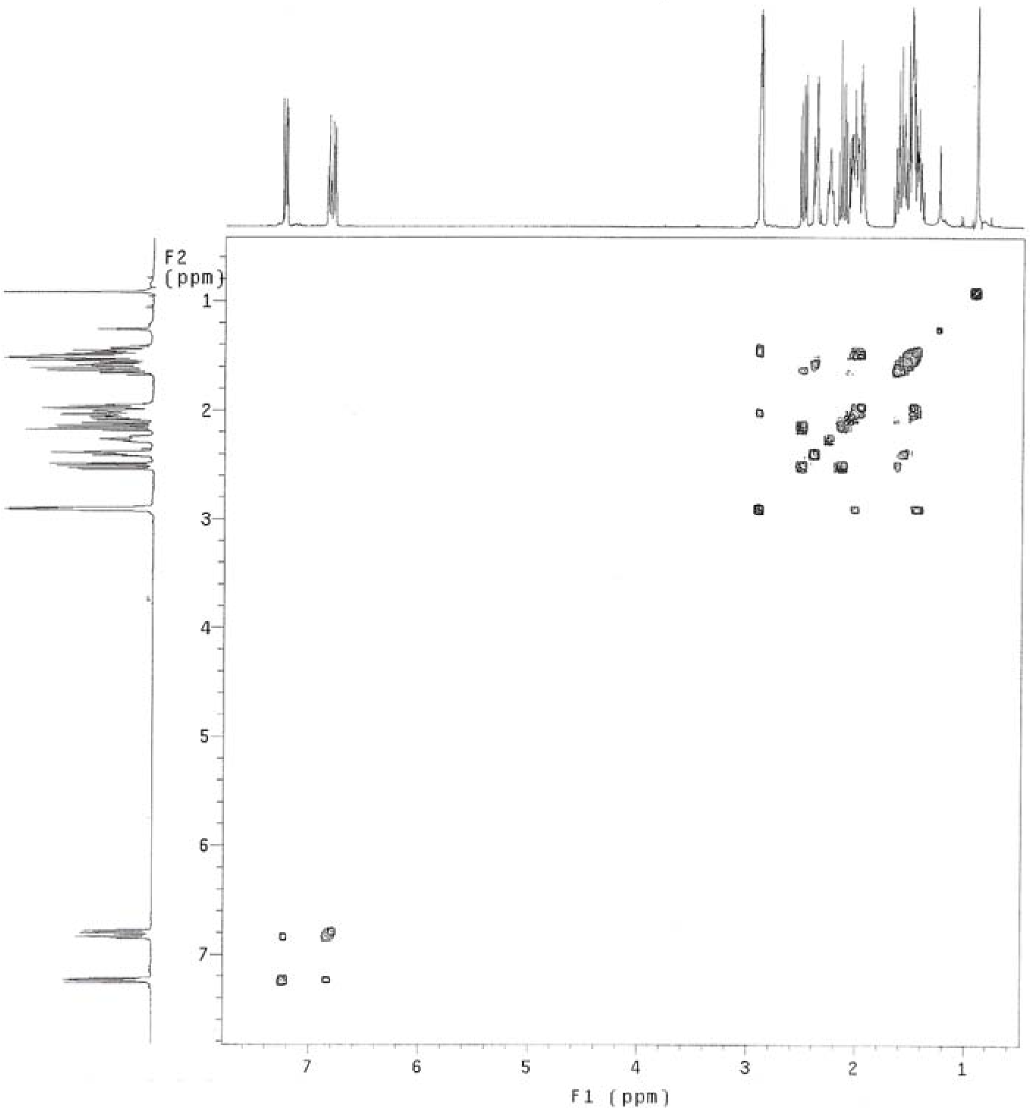


^{13}C NMR spectrum of

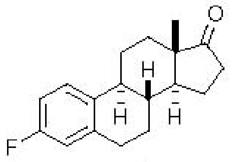




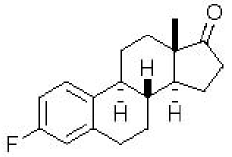
```
Pulse Sequence: gCOSY
 Solvent: CDCl3
 Temp. 23.0 C / 296.1 K
INOVA-500  "inova500b"

 Relax. delay 1.000 sec
 Acq. time 0.128 sec
 Width     8000.0 Hz
 2D Width 8000.0 Hz
 Single scan
 128 increments
OBSERVE   H1, 500.1739479 MHz
DATA PROCESSING
 Sq. sine bell 0.064 sec
F1 DATA PROCESSING
 Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 2 min, 45 sec
```



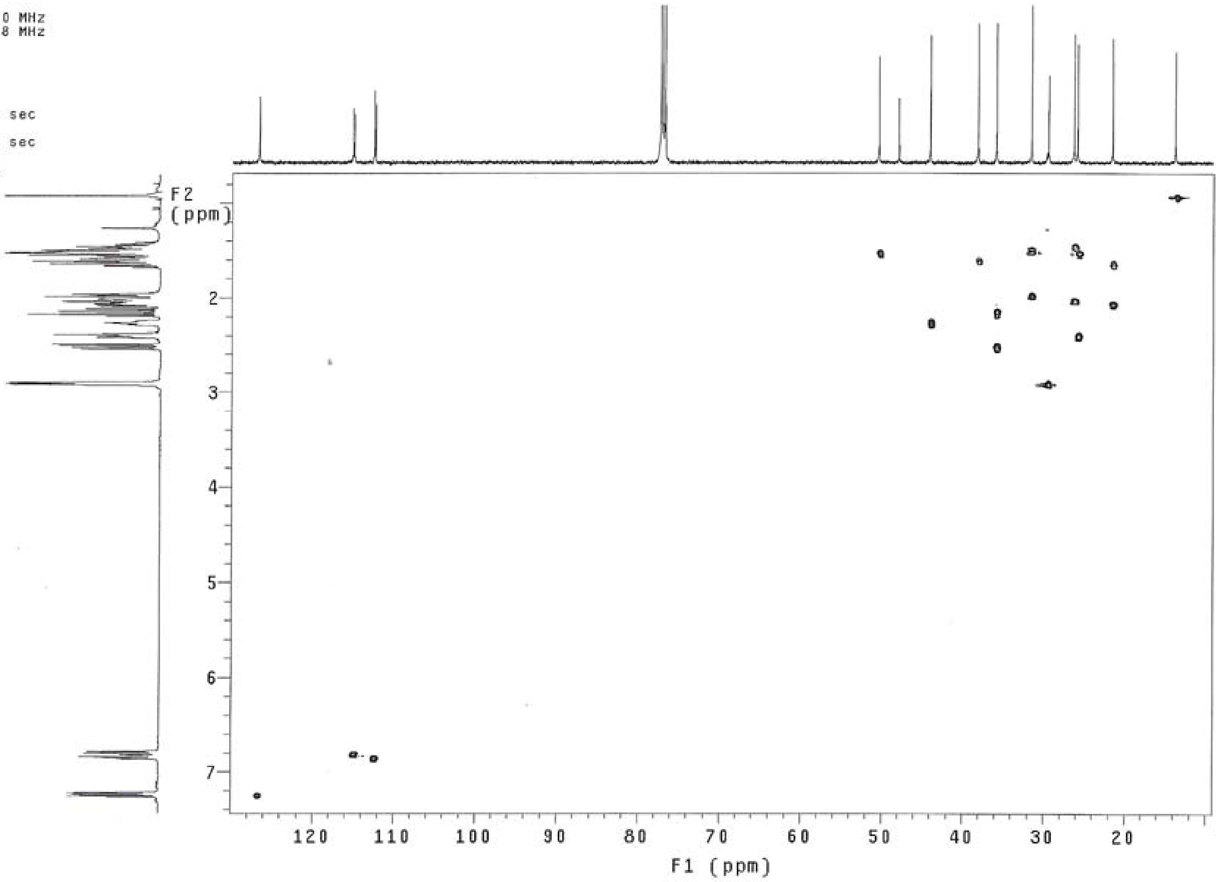
^1H-^1H COSY spectrum of



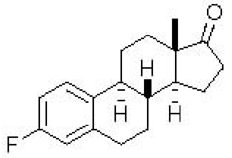
^{1}H - ^{13}C HSQC spectrum of



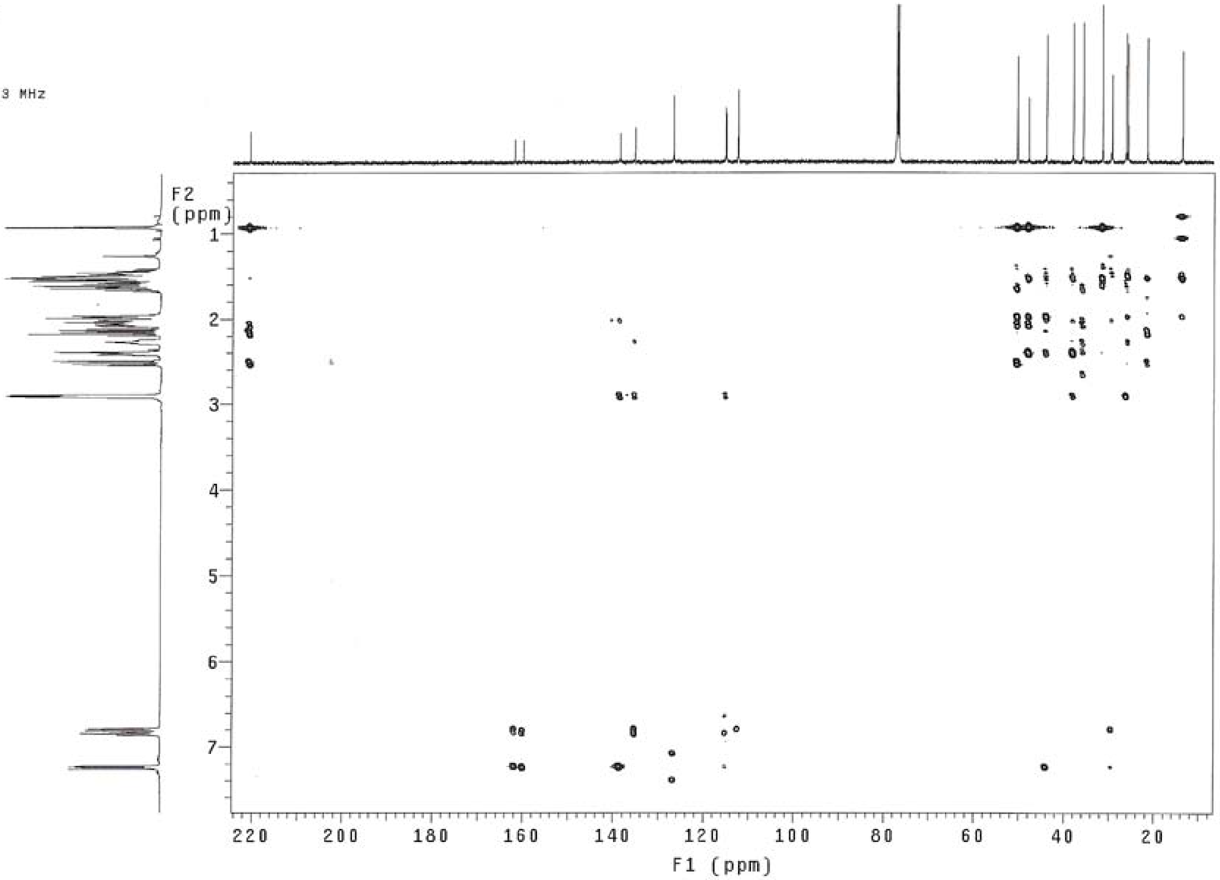
```
Pulse Sequence: gHSQC

 Solvent: CDCl3
 Temp. 23.0 C / 296.1 K
User:  1-14-87
File: F-estrone_HSQC
INOVA-500  "nmrsun"

 Relax. delay 1.000 sec
 Acq. time 0.128 sec
 Width    8000.0 Hz
 2D Width 21378.9 Hz
 4 repetitions
 2 x 128 increments
OBSERVE   H1, 500.1739390 MHz
DECOUPLE C13, 125.7782418 MHz
 Power 45 dB
 on during acquisition
 off during delay
 GARP-1 modulated
DATA PROCESSING
 Gauss apodization 0.059 sec
F1 DATA PROCESSING
 Gauss apodization 0.011 sec
FT size 2048 x 2048
Total time 21 min, 6 sec
```



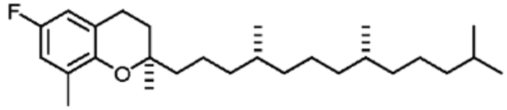
^{1}H - ^{13}C HMBC spectrum of

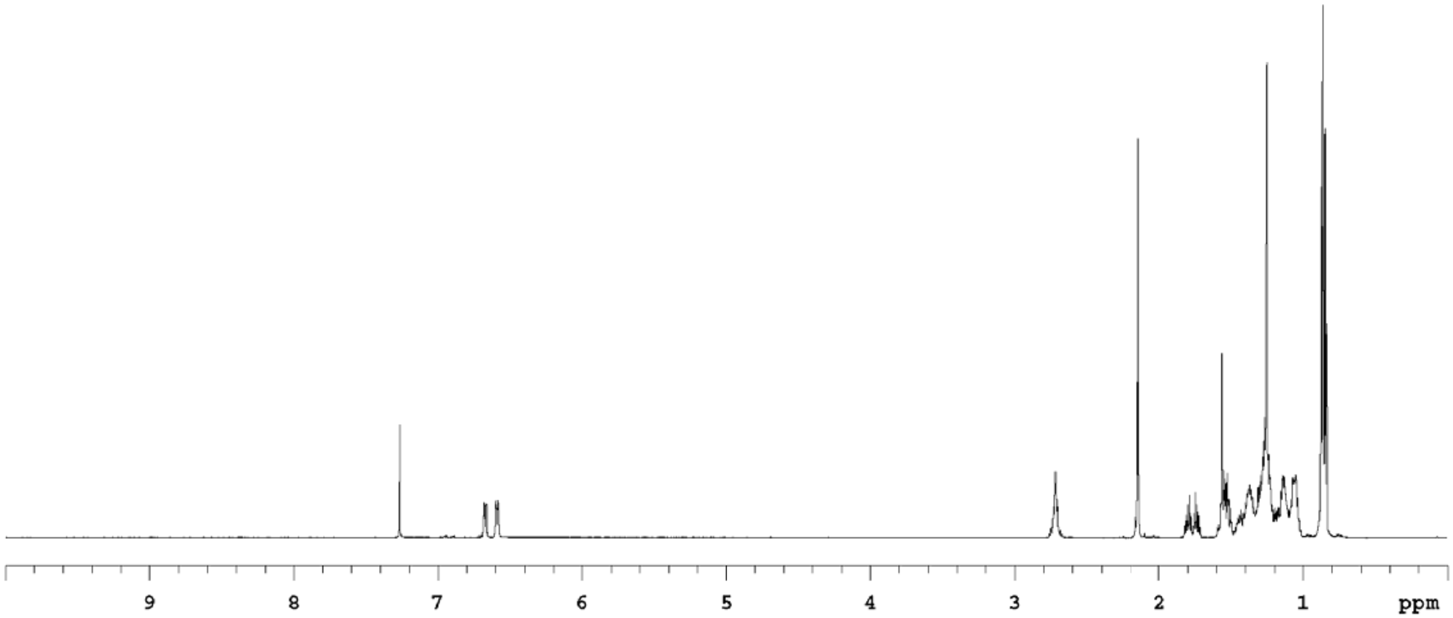


```
 Data Collected on:
   nmrsun2-inova500
 Archive directory:
   /export/home/ds2/vnmrsys/data
 Sample directory:

 File: F-estrone_HMBC

Pulse Sequence: gHMBC
Solvent: CDCl3

 Temp. 23.0 C / 296.1 K
User:  1-14-87

 Relax. delay 1.000 sec
 Acq. time 0.128 sec
 Width     8000.0 Hz
 2D Width 30188.7 Hz
 8 repetitions
 400 increments
OBSERVE   H1, 500.1739493 MHz
DATA PROCESSING
 Sine bell 0.064 sec
F1 DATA PROCESSING
 Sine bell 0.007 sec
FT size 2048 x 2048
Total time 1 hr, 5 min
```

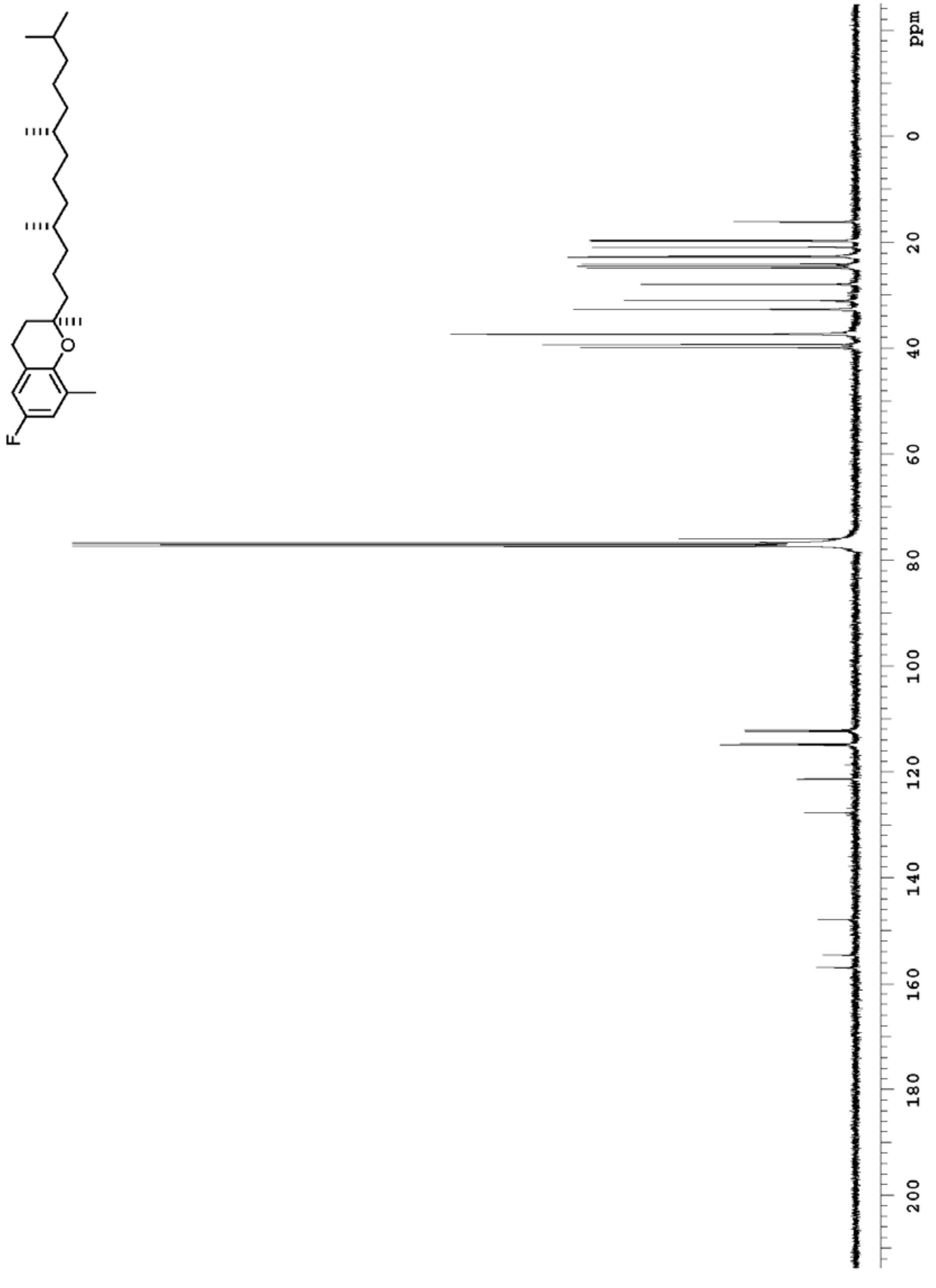


^{1}H NMR spectrum of

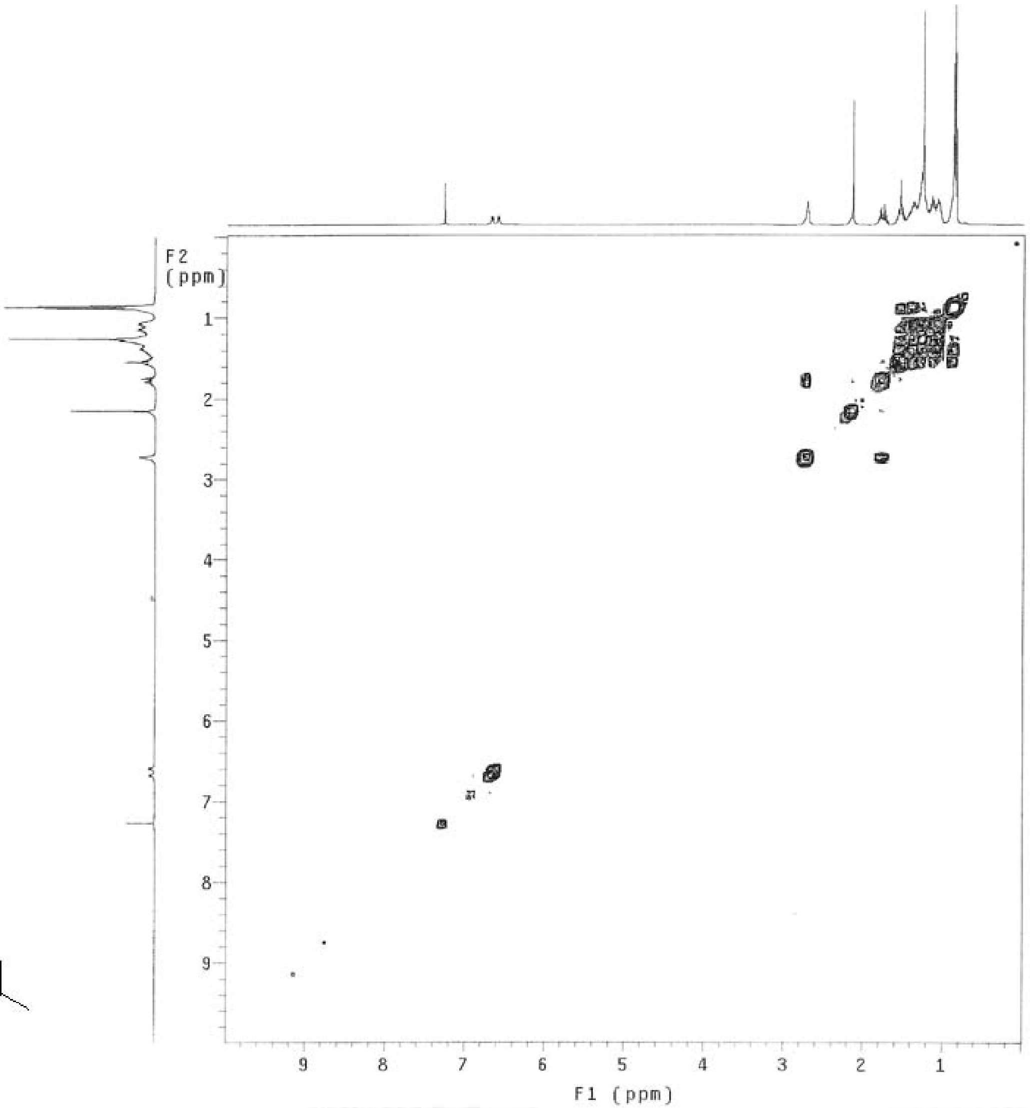




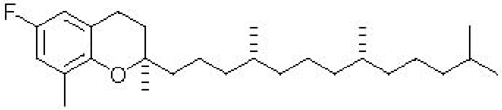
^{13}C NMR spectrum of



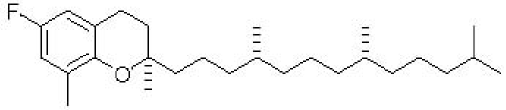
```
Pulse Sequence: gCOSY

 Solvent: CDCl3
 Temp. 23.0 C / 296.1 K
INOVA-500  "inova500b"

 Relax. delay 1.000 sec
 Acq. time 0.128 sec
 Width     8000.0 Hz
 2D Width 8000.0 Hz
 Single scan
 128 increments
OBSERVE   H1, 500.1739479 MHz
DATA PROCESSING
 Sq. sine bell 0.064 sec
F1 DATA PROCESSING
 Sq. sine bell 0.016 sec
FT size 2048 x 2048
Total time 2 min, 45 sec
```



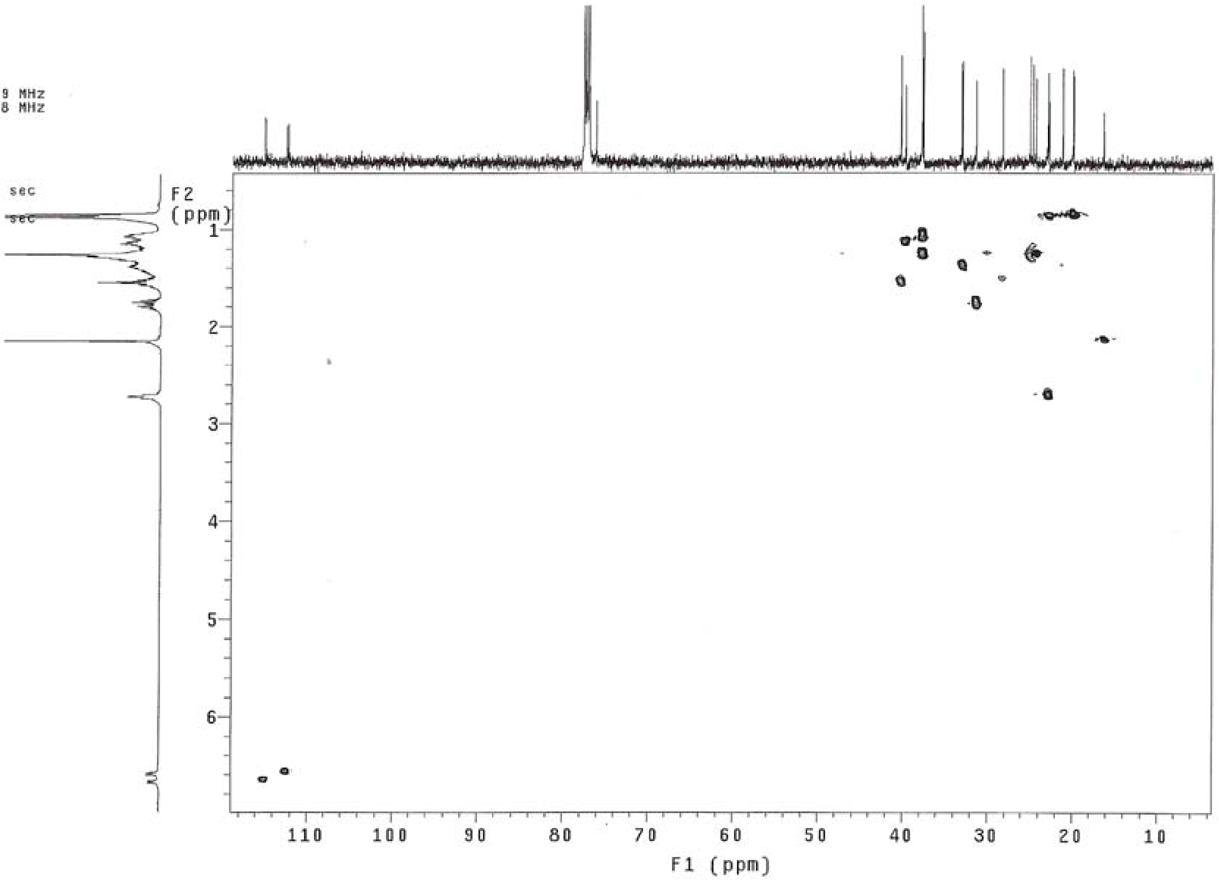
^{1}H -^{1}H COSY spectrum of



^{1}H - ^{13}C HSQC spectrum of

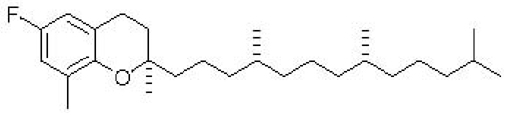


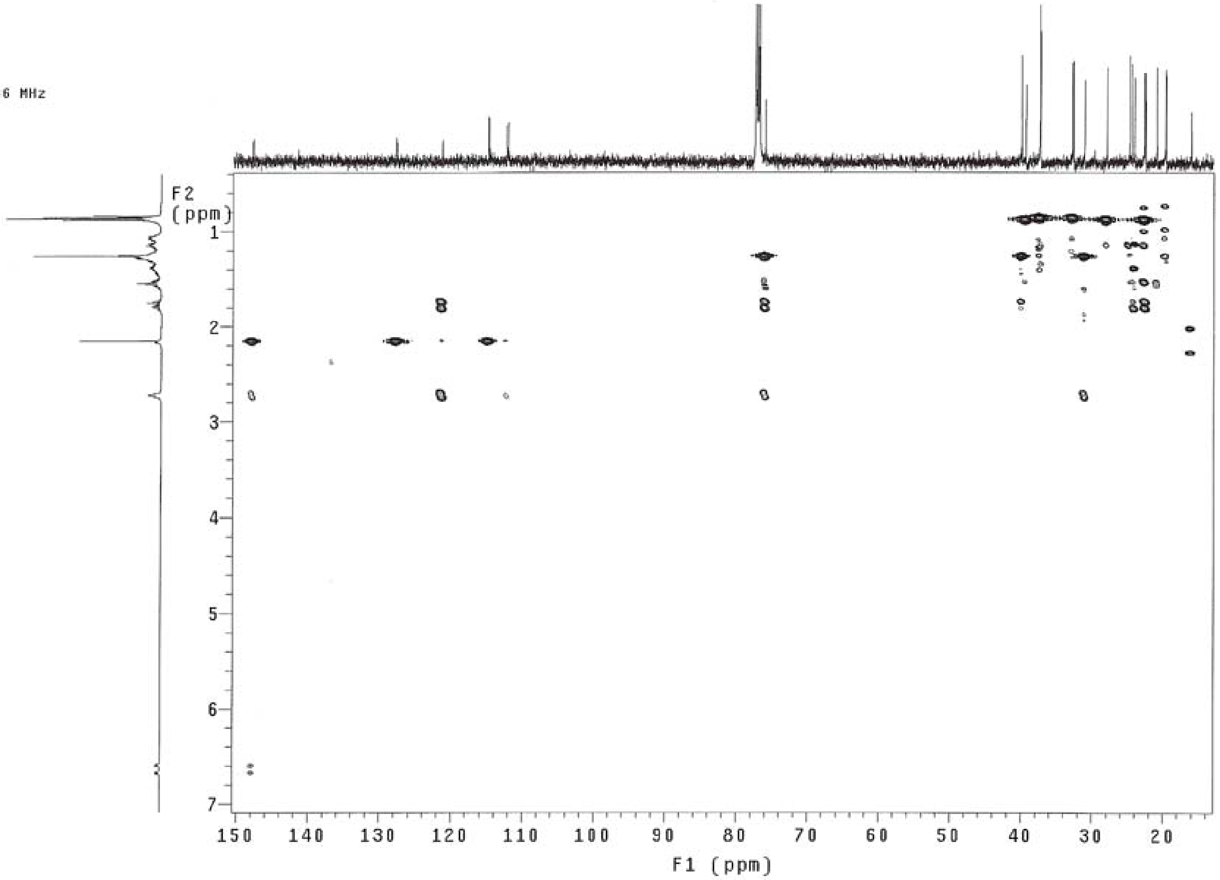
```
 Data Collected on:
   nmrsun2-inova500
 Archive directory:
   /export/home/ds2/vnmrsys/data
 Sample directory:

 File: F-tocopherol_HSQC

Pulse Sequence: gHSQC
Solvent: CDCl3

 Temp. 23.0 C / 296.1 K
User:  1-14-87

 Relax. delay 1.000 sec
 Acq. time 0.128 sec
 Width    8000.0 Hz
 2D Width 21378.9 Hz
 4 repetitions
 2 x 128 increments
OBSERVE   H1, 500.1739609 MHz
DECOUPLE C13, 125.7782418 MHz
 Power 45 dB
 on during acquisition
 off during delay
 GARP-1 modulated
DATA PROCESSING
 Gauss apodization 0.059 sec
F1 DATA PROCESSING
 Gauss apodization 0.011 sec
FT size 2048 x 2048
Total time 21 min
```



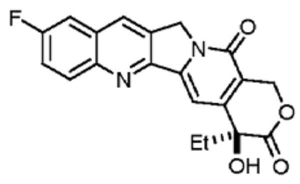
```
 Data Collected on:
   nmrsun2-inova500
 Archive directory:
   /export/home/ds2/vnmrsys/data
 Sample directory:

 File: F-tocopherol_HMBC

Pulse Sequence: gHMBC
Solvent: CDCl3

 Temp. 23.0 C / 296.1 K
User:  1-14-87

 Relax. delay 1.000 sec
 Acq. time 0.128 sec
 Width    8000.0 Hz
 2D Width 30188.7 Hz
 8 repetitions
 400 increments
OBSERVE   H1, 500.1739496 MHz
DATA PROCESSING
 Sine bell 0.064 sec
F1 DATA PROCESSING
 Sine bell 0.007 sec
FT size 2048 x 2048
Total time 1 hr, 5 min
```

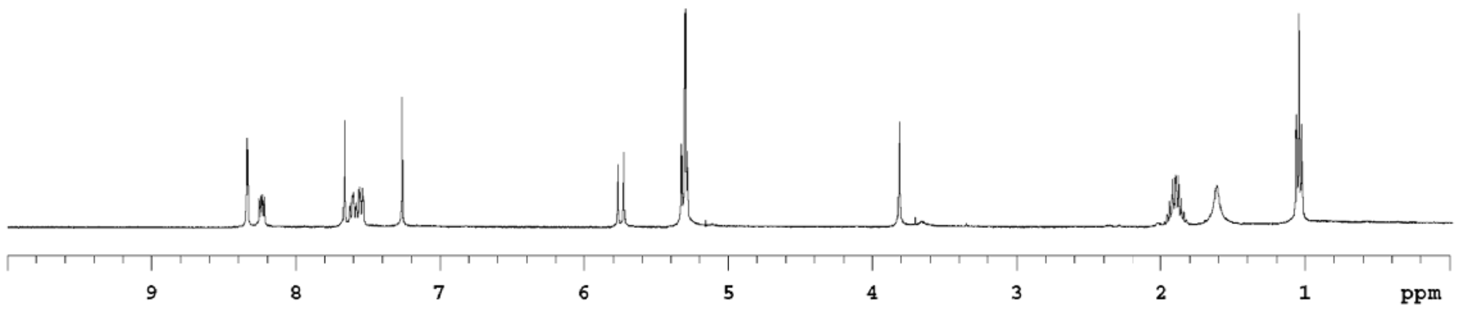
^{1}H - ^{13}C HMBC spectrum of



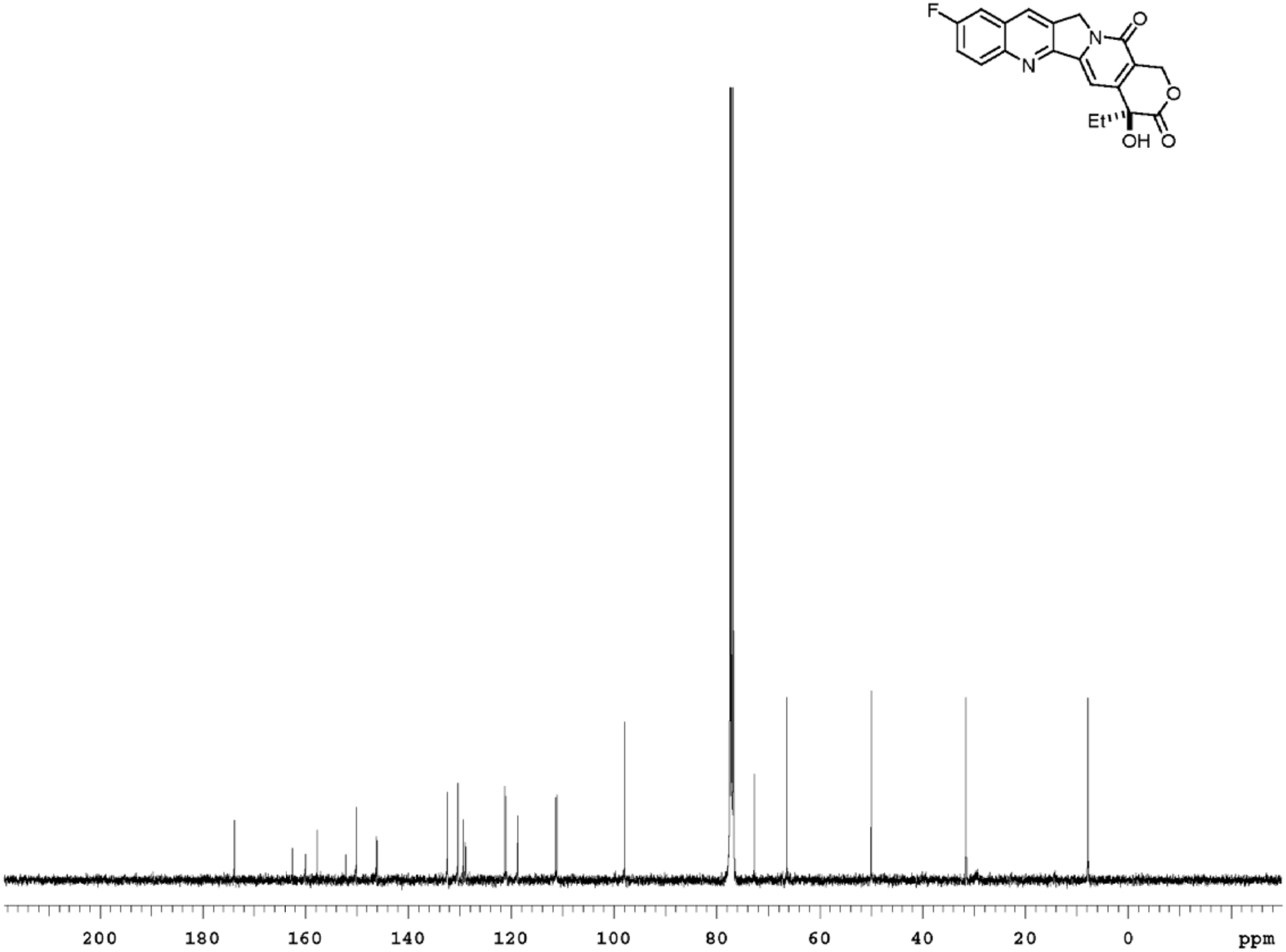


^{1}H NMR spectrum of

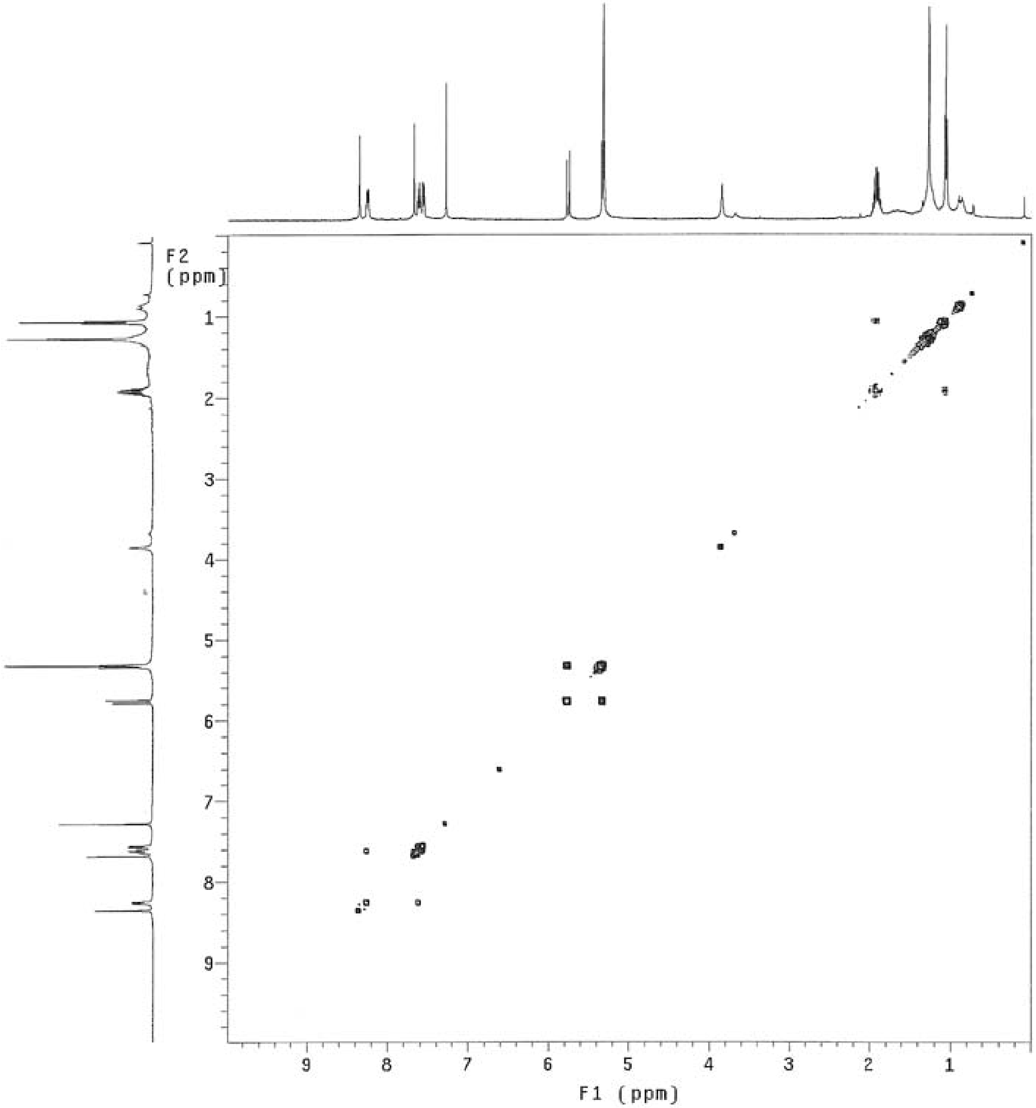




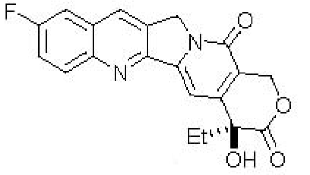
^{13}C NMR spectrum of



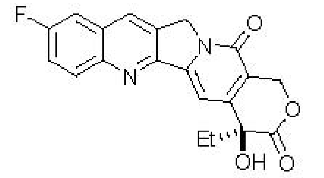
```
Pulse Sequence: gCOSY
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
INOVA-500  "inova500c"

 Relax. delay 1.000 sec
 Acq. time 0.136 sec
 Width     7509.6 Hz
 2D Width 7509.6 Hz
 Single scan
 128 increments
OBSERVE   H1, 499.8716820 MHz
DATA PROCESSING
 Sq. sine bell 0.068 sec
F1 DATA PROCESSING
 Sq. sine bell 0.017 sec
FT size 2048 x 2048
Total time 2 min, 46 sec
```



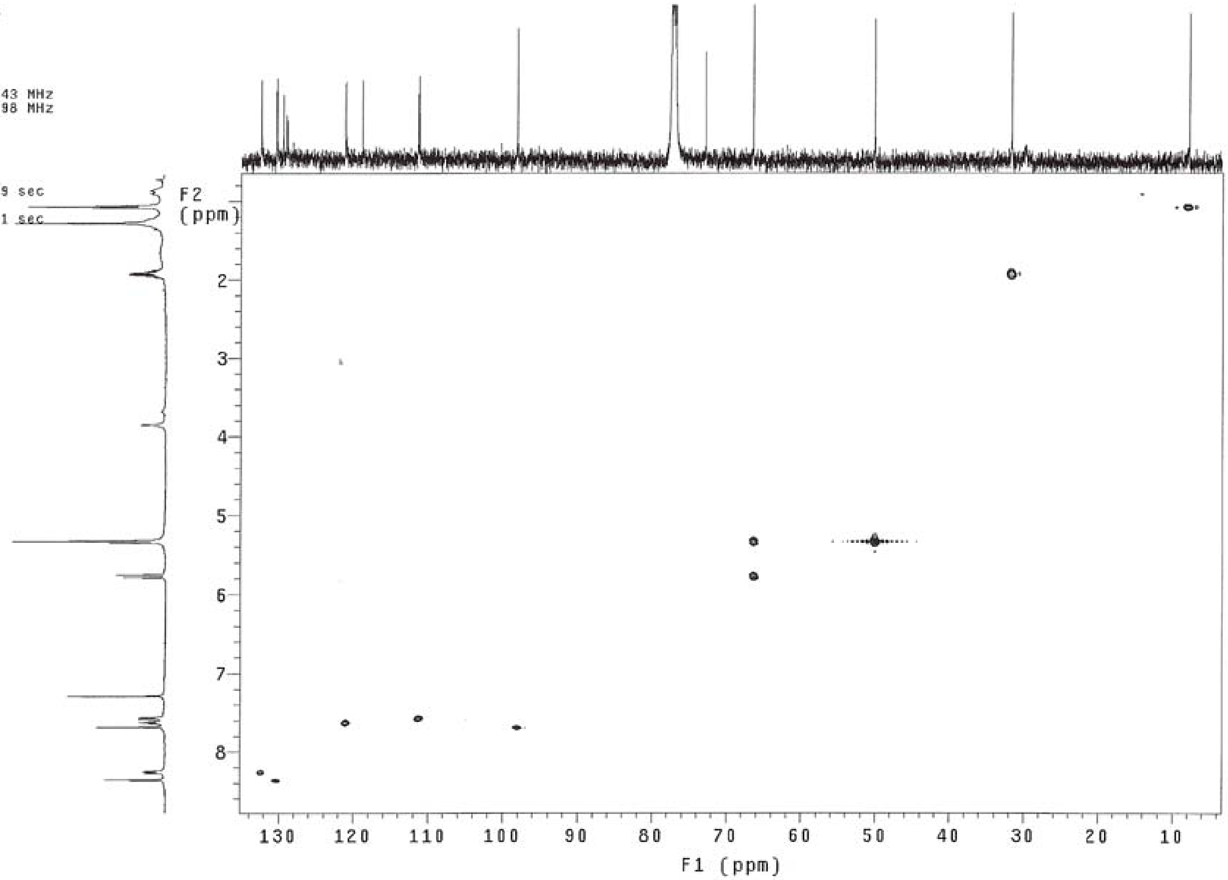
^{1}H - ^{1}H COSY spectrum of



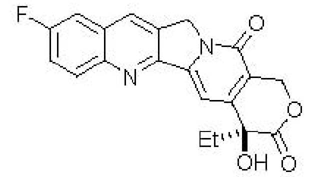
^{1}H - ^{13}C HSQC spectrum of



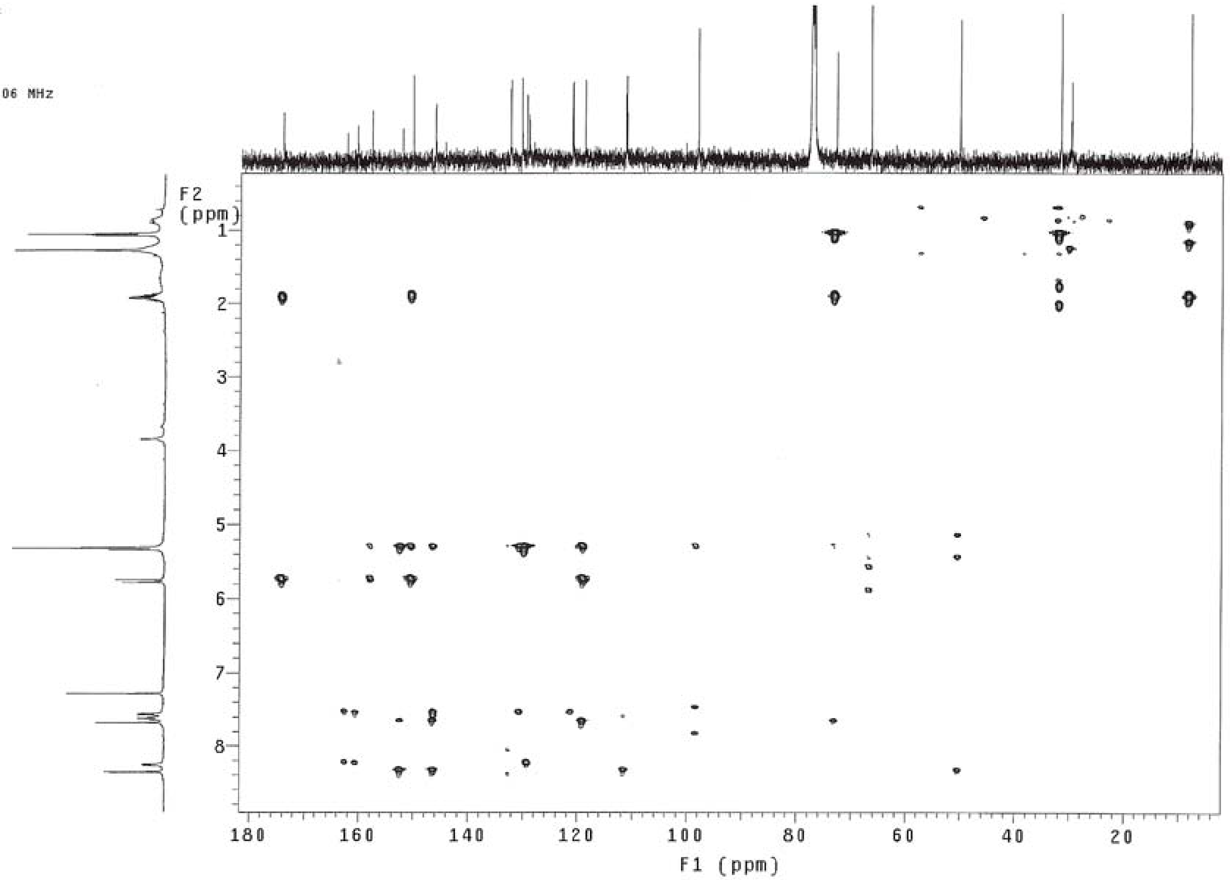
```
 Data Collected on:
   nmrsun2-inova500
 Archive directory:
   /export/home/ds2/vnmrsys/data
 Sample directory:

 File: F-camptothecin_HSQC

Pulse Sequence: gHSQC
Solvent: CDCl3

 Temp. 23.0 C / 296.1 K
User:  1-14-87

 Relax. delay 1.000 sec
 Acq. time 0.128 sec
 Width     8000.0 Hz
 2D Width 21356.1 Hz
 24 repetitions
 2 x 128 increments
OBSERVE   H1, 499.6084943 MHz
DECOUPLE C13, 125.6360498 MHz
 Power 42 dB
 on during acquisition
 off during delay
 GARP-1 modulated
DATA PROCESSING
 Gauss apodization 0.059 sec
F1 DATA PROCESSING
 Gauss apodization 0.011 sec
FT size 2048 x 2048
Total time 2 hr, 3 min
```



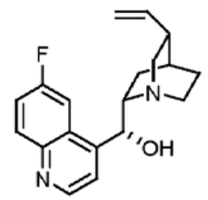
^{1}H - ^{13}C HMBC spectrum of

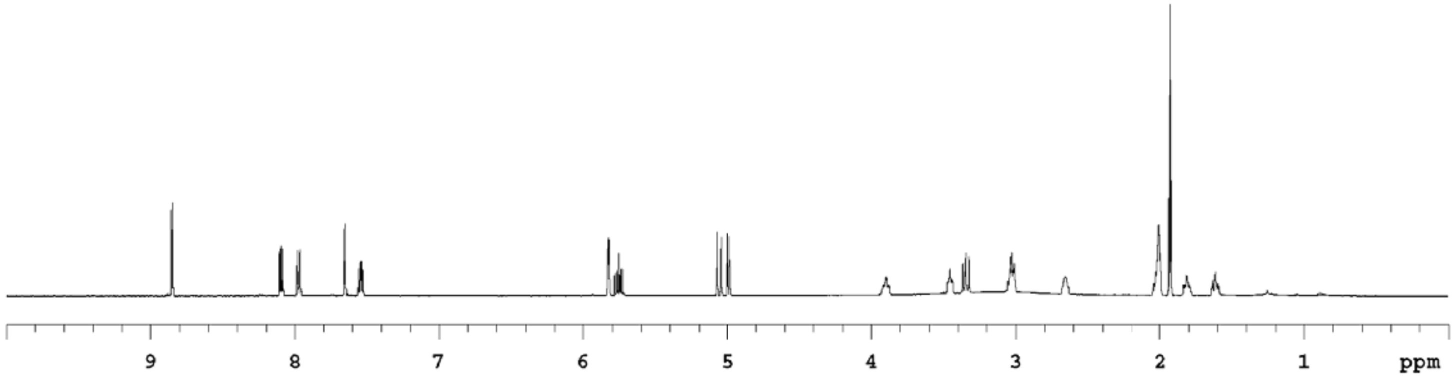


```
 Data Collected on:
   nmrsun2-inova500
 Archive directory:
   /export/home/ds2/vnmrsys/data
 Sample directory:

 File: F-camptothecin_HMBC

Pulse Sequence: gHMBC
Solvent: CDC13

 Temp. 23.0 C / 296.1 K
User:  1-14-87

 Relax. delay 1.000 sec
 Acq. time 0.128 sec
 Width     8000.0 Hz
 2D Width 30154.5 Hz
 48 repetitions
 400 increments
OBSERVE   H1, 499.6085206 MHz
DATA PROCESSING
 Sine bell 0.064 sec
F1 DATA PROCESSING
 Sine bell 0.007 sec
FT size 2048 x 2048
Total time 6 hr, 29 min
```

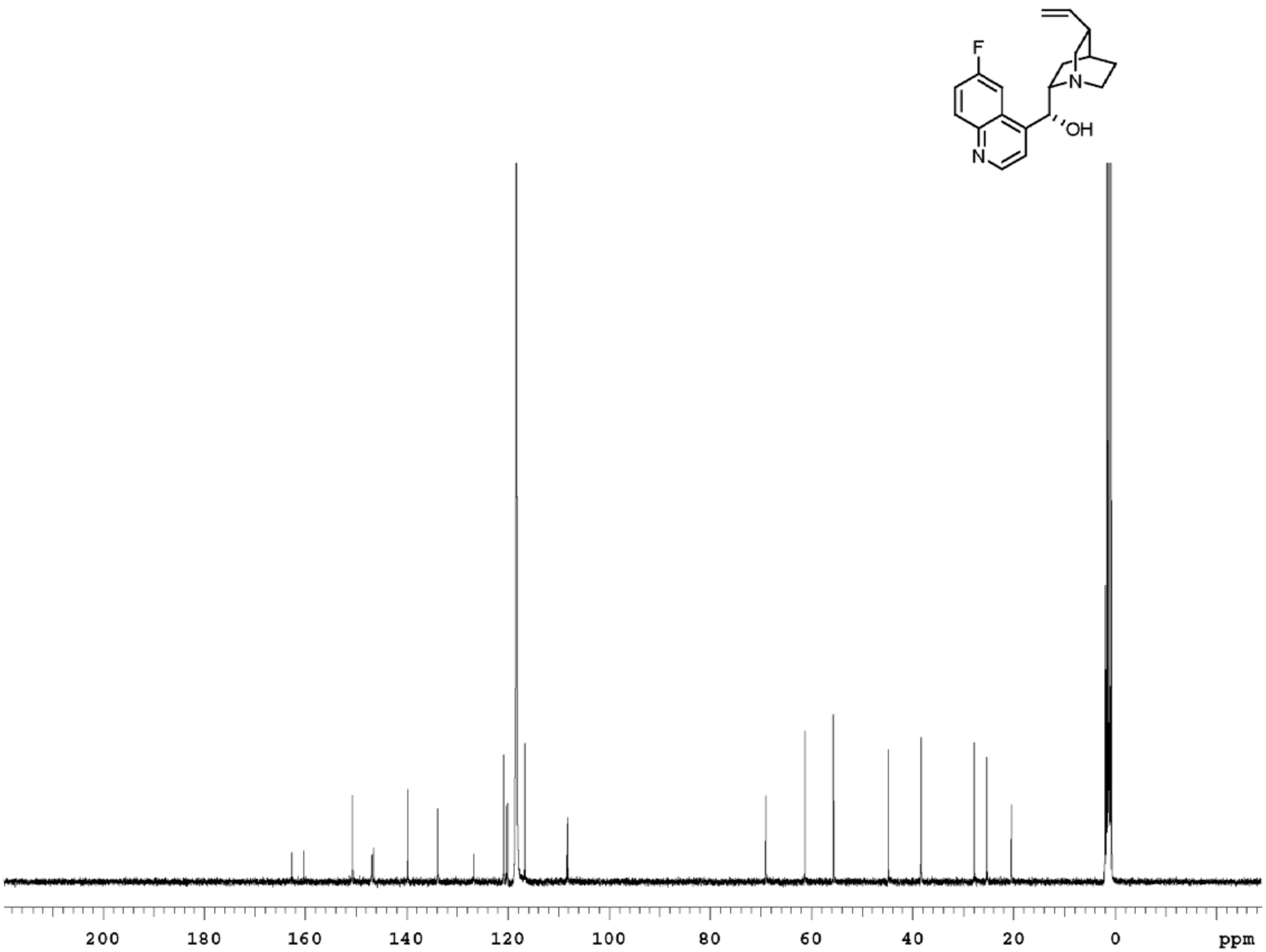


^{1}H NMR spectrum of

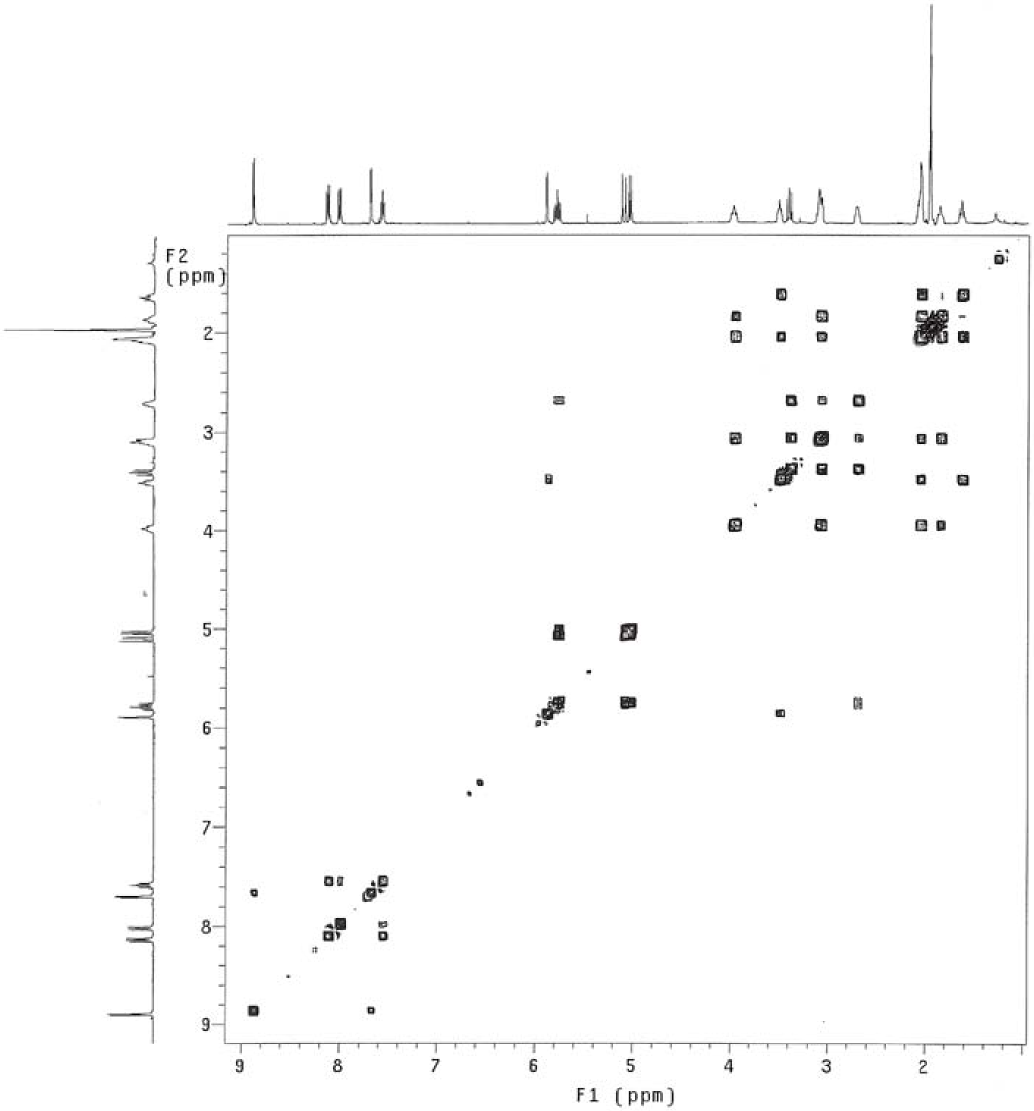




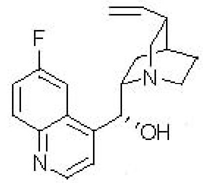
^{13}C NMR spectrum of



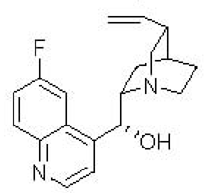
```
 Data Collected on:
   nmrsun2-inova500
 Archive directory:
   /export/home/ds2/vnmrsys/data
 Sample directory:

 File: F-quinine-COSY

Pulse Sequence: gCOSY
Solvent: CD3CN
 Temp. 22.0 C / 295.1 K

 Relax. delay 1.000 sec
 Acq. time 0.136 sec
 Width    7509.6 Hz
 2D Width 7509.6 Hz
 Single scan
 128 increments
OBSERVE   H1, 499.8743519 MHz
DATA PROCESSING
 Sq. sine bell 0.068 sec
F1 DATA PROCESSING
 Sq. sine bell 0.017 sec
FT size 2048 x 2048
Total time 2 min
```



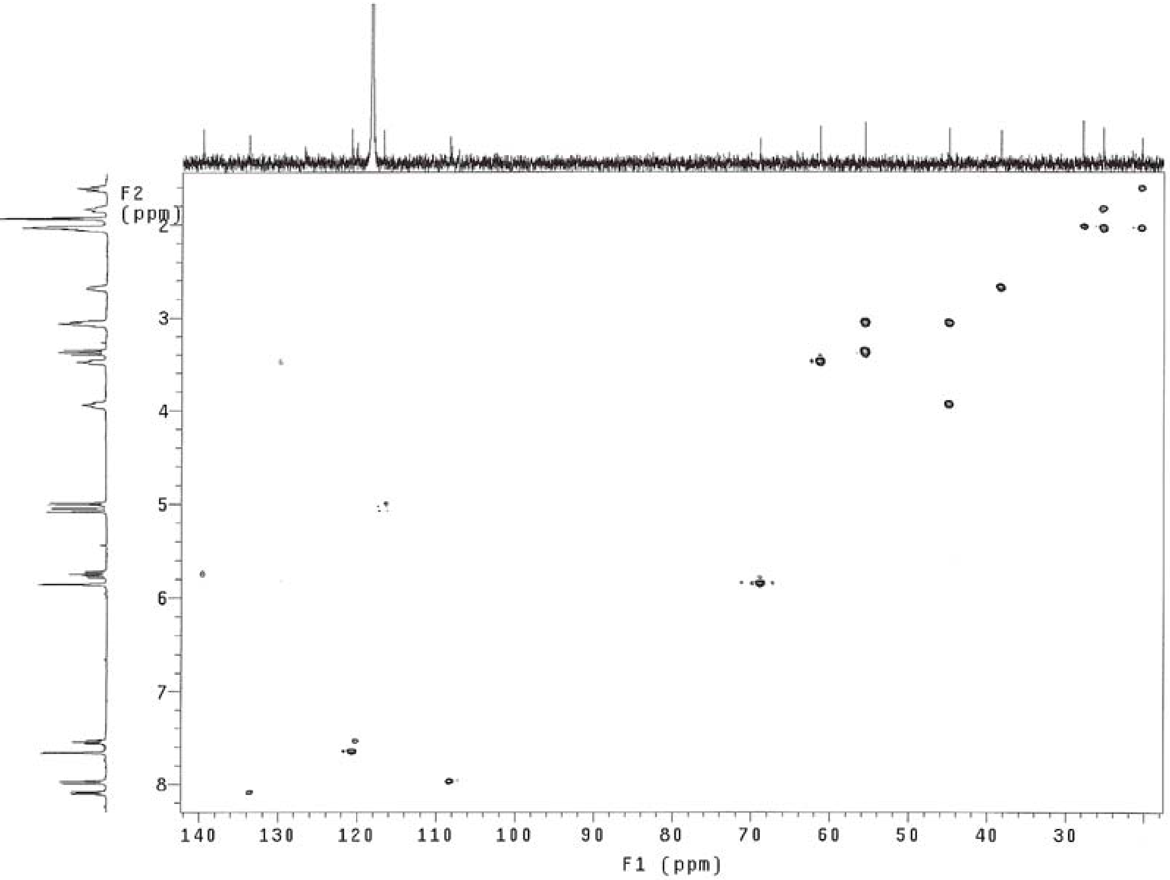
^{1}H - ^{1}H COSY spectrum of



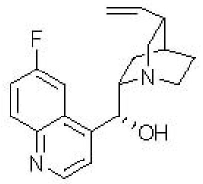
^{1}H -^{13}C HSQC spectrum of



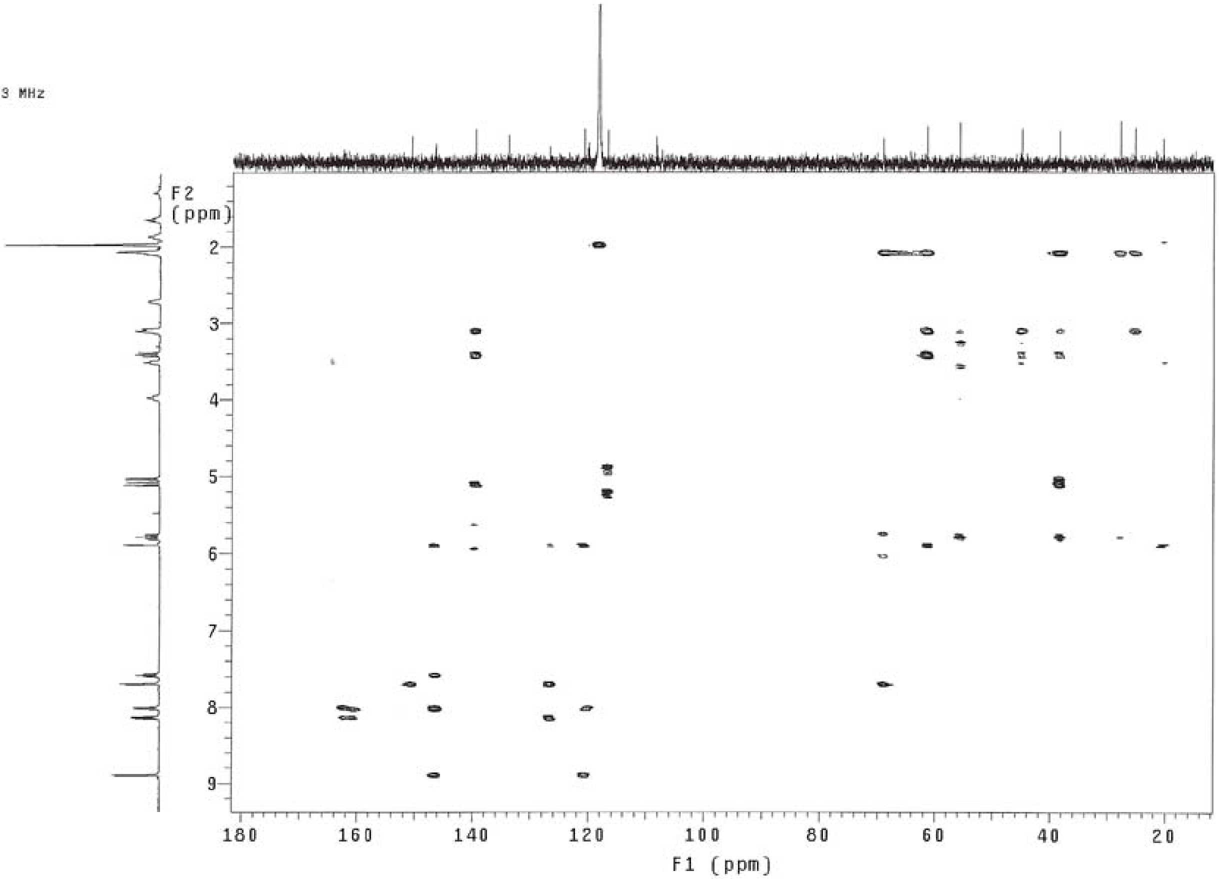
```
  Data Collected on:
    nmrsun2-inova500
  Archive directory:
    /export/home/ds2/vnmrsys/data
  Sample directory:

  File: F-quinine-HSQC

 Pulse Sequence: gHSQC
 Solvent: CD3CN

  Temp. 26.0 C / 299.1 K
 User:  1-14-87

  Relax. delay 1.000 sec
  Acq. time 0.128 sec
  Width     8000.0 Hz
  2D Width 21378.9 Hz
  4 repetitions
  2 x 128 increments
 OBSERVE   H1, 500.1766222 MHz
 DECOUPLE C13, 125.7789073 MHz
  Power 45 dB
  on during acquisition
  off during delay
  GARP-1 modulated
 DATA PROCESSING
  Gauss apodization 0.041 sec
 F1 DATA PROCESSING
  Gauss apodization 0.011 sec
 FT size 2048 x 2048
 Total time 20 min
```



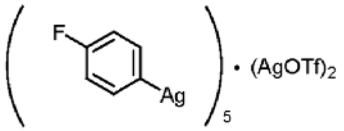
^{1}H - ^{13}C HMBC spectrum of

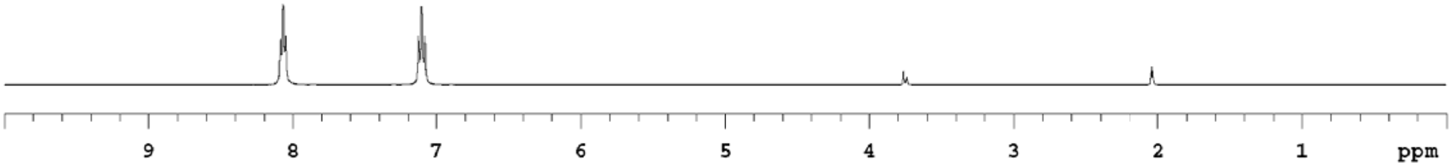


```
Data Collected on:
  nmrsun2-inova500
Archive directory:
  /export/home/ds2/vnmrsys/data
Sample directory:

File: F-quinine_HMBC

Pulse Sequence: gHMBC
Solvent: CD3CN

Temp. 23.0 C / 296.1 K
User:  1-14-87

Relax. delay 1.000 sec
Acq. time 0.128 sec
Width    8000.0 Hz
2D Width 30188.7 Hz
16 repetitions
200 increments
OBSERVE   H1, 500.1765933 MHz
DATA PROCESSING
 Sine bell 0.064 sec
F1 DATA PROCESSING
 Sine bell 0.007 sec
FT size 2048 x 2048
Total time 1 hr, 5 min
```

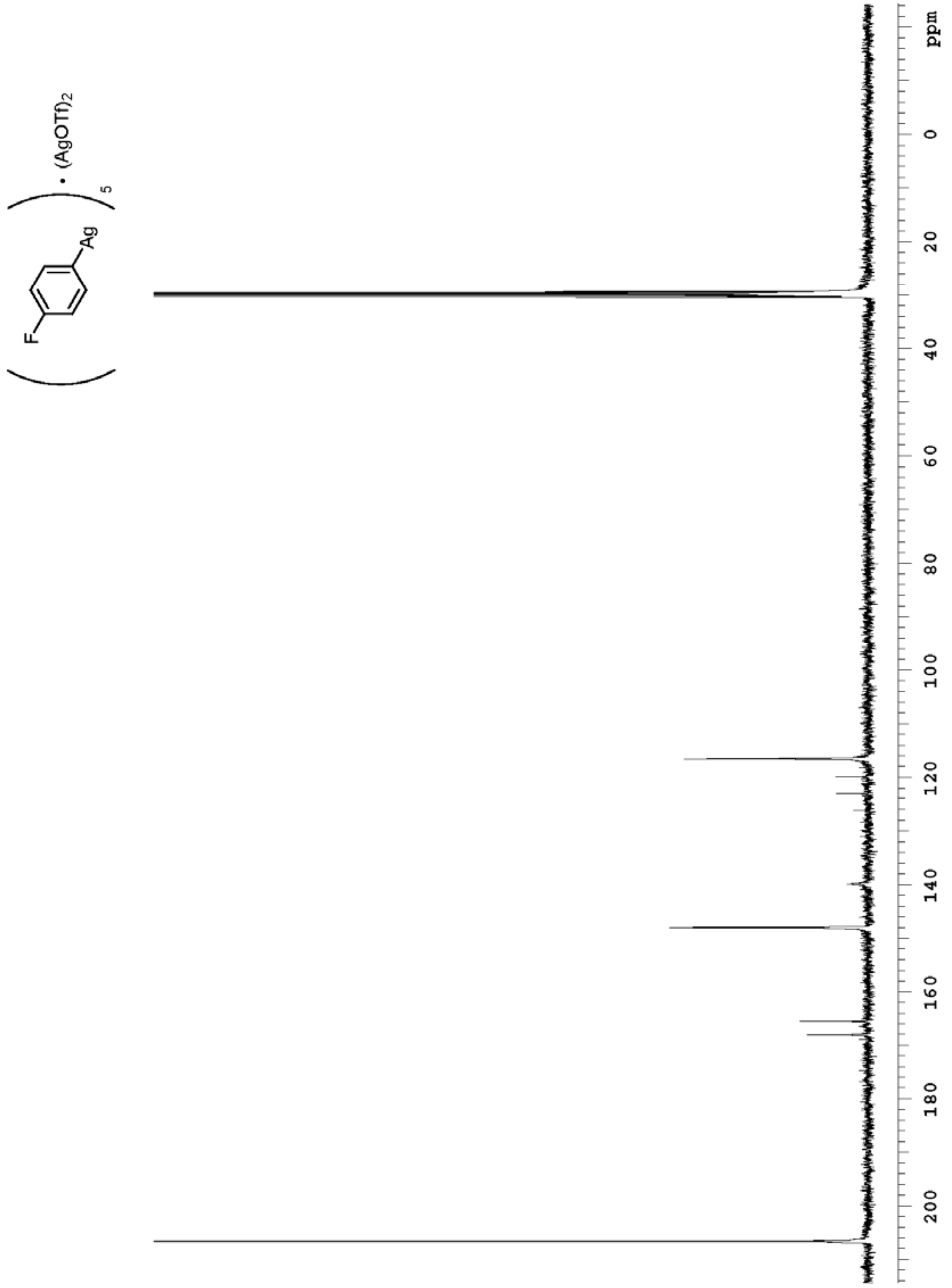


^{1}H NMR spectrum of

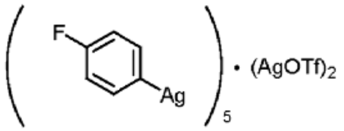


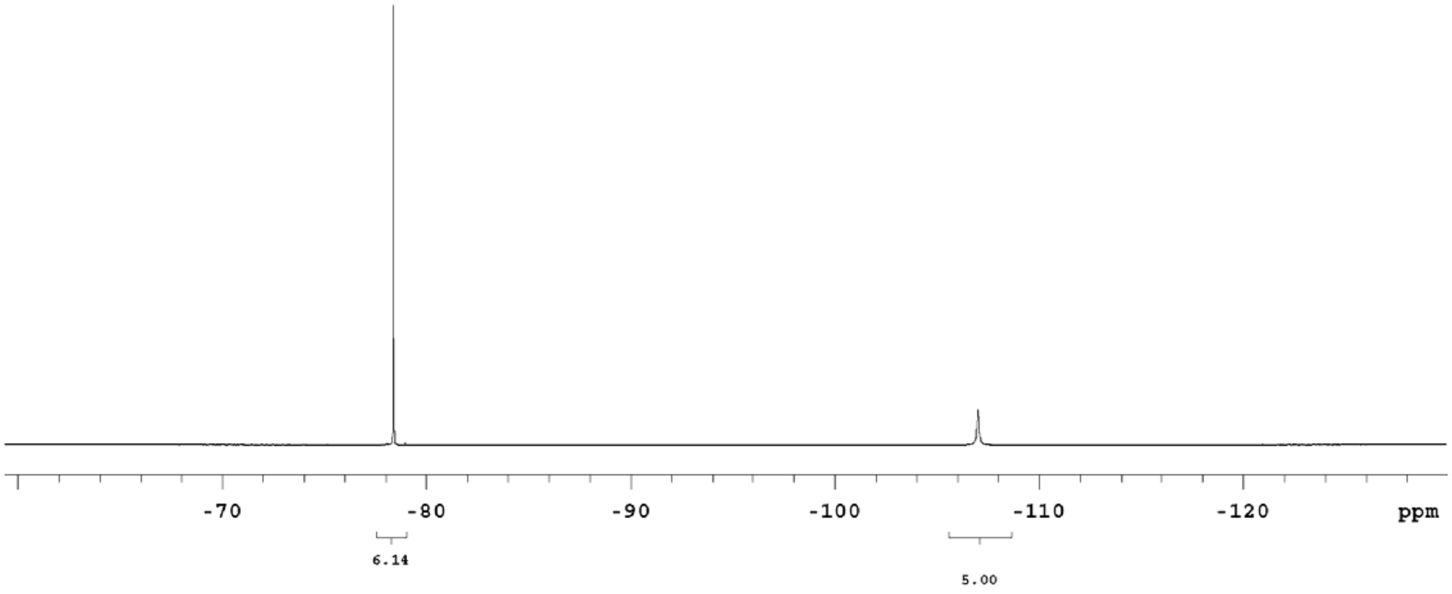


^{13}C NMR spectrum of

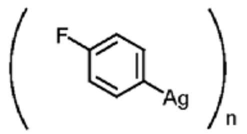


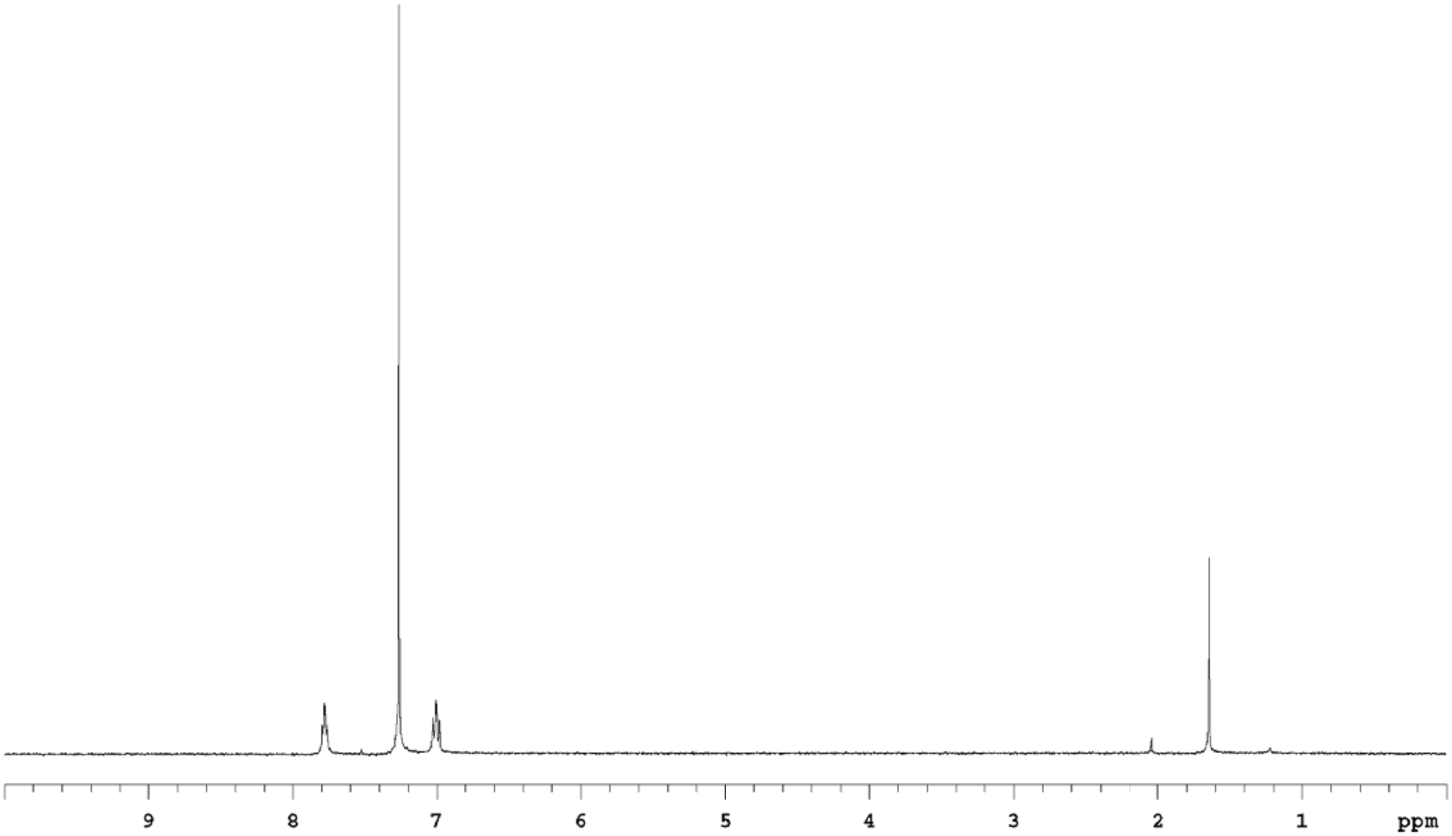
^{19}F NMR spectrum of



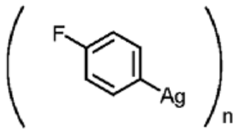


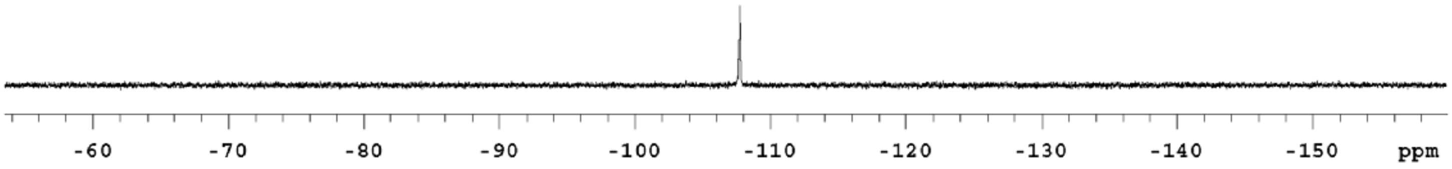
^{1}H NMR spectrum of





^{19}F NMR spectrum of





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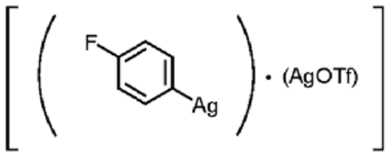

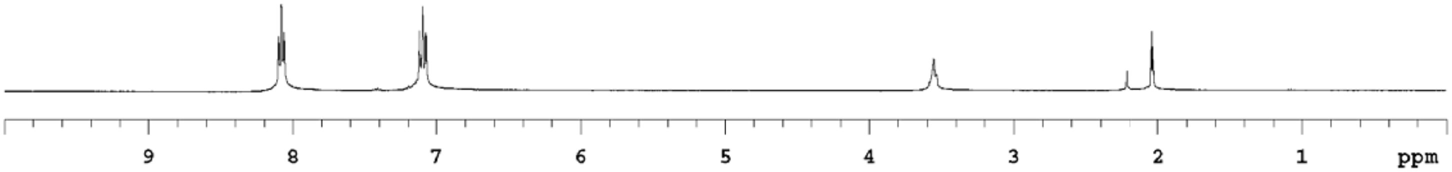

^{19}F NMR spectrum of