

Supporting Information

Fluorination of Boronic Acids Mediated by Silver(I) Triflate

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Materials and Methods

All reactions were carried out under an inert nitrogen atmosphere unless otherwise indicated. Solvents other than methanol were dried by passage through alumina¹. 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 °C 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 ^1H , 100 MHz for ^{13}C , 375 MHz for ^{19}F , and 126 MHz for ^{31}P acquisitions), Unity/Inova 500 (500 MHz for ^1H , 125 MHz for ^{13}C acquisitions), or Unity/Inova 600 (600 MHz for ^1H acquisitions) spectrometer. ^{13}C NMR spectra were recorded ^1H decoupled. ^{19}F NMR spectra were recorded ^1H coupled. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. Data are 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. Sodium hydroxide was purchased from Mallinckrodt chemicals, Molecular sieves 3Å was purchased from EMD chemicals and finely grinded and dried at 130 °C overnight prior to use. Silver triflate, Dichloro[1,1'-bis(diphenylphosphino)-ferrocene] palladium(II) dichloromethane adduct were purchased from Strem. Acetone (CHROMASOLV[®] Plus, for HPLC, $\geq 99.9\%$), 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), bis(pinacolato)diboron, (1,5-Cyclooctadiene)(methoxy)iridium(I) dimer, 5-bromoindazole, 4-(dimethylamino)pyridine, di-*tert*-butyl dicarbonate, *N*-Boc-5-bromoindole, 6-bromoquinoxaline, 4,4'-di-*tert*-butyl-2,2'-dipyridyl were purchased from Aldrich. *m*-Toluic acid methyl ester was purchased from Alfa Aesar. Bis(neopentyl-glycolato)diboron was purchased from Frontier Scientific. Boronic acids were purchased from either Aldrich, Alfar, Frontier Scientific, Beta Pharma, Matrix Scientific, Boron Molecular, or CombiPhos Catalysts and used as received. NMR spectroscopic data of known compounds correspond to the data given in the appropriate references.

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

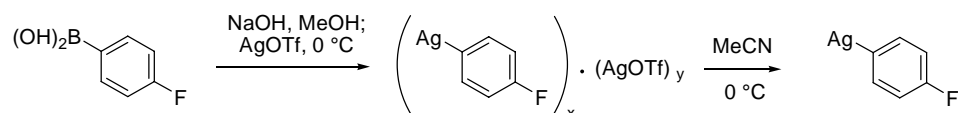
² Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2925–2927.

Experimental Data

Experimental Procedures and Compound Characterization

Synthesis of Arylsilver complexes

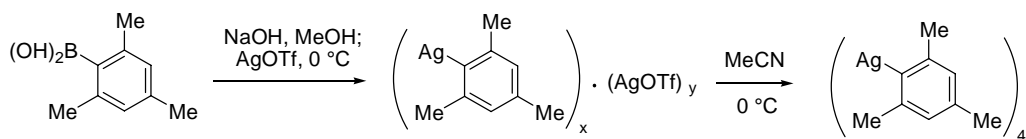
(4-Fluorophenyl)silver³ (2)



To NaOH (40.0 mg, 1.00 mmol, 1.00 equiv) in MeOH (1.0 mL) at 23 °C was added 4-fluorophenylboronic acid (140 mg, 1.00 mmol, 1.00 equiv). After stirring for 15 min at 23 °C, the reaction mixture was cooled to 0 °C and to the reaction mixture was added AgOTf (514 mg, 2.00 mmol, 2.00 equiv). After stirring for 30 min at 0 °C, to the reaction mixture was added Et₂O (5 mL) and hexanes (10 mL) to precipitate an arylsilver complex. This precipitate contains variable amount of AgOTf and the arylsilver to AgOTf ratio was irreproducible. Thus, the precipitate was filtered off and washed with MeCN (2 × 2 mL) to remove AgOTf and subsequently washed with Et₂O (2 × 2 mL) at 0 °C to afford 101 mg of the title compound as a colorless solid (50% yield).

NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃, -10 °C, δ): 7.76 (dd, *J* = 7.6 Hz, 7.6 Hz, 2H), 7.00 (dd, *J* = 7.6 Hz, 7.6 Hz, 2H). ¹⁹F NMR (375 MHz, CDCl₃, -10 °C, δ): -107.75 (s br). Due to the low solubility and the thermal instability, the title compound was not amenable to further characterization.

(2,4,6-Trimethylphenyl)silver, tetramer⁴ (S1)



To NaOH (40.0 mg, 1.00 mmol, 1.00 equiv) in MeOH (1.0 mL) at 23 °C was added 2,4,6-trimethylphenylboronic acid (164 mg, 1.00 mmol, 1.00 equiv). After stirring for 15 min at 23 °C, the reaction mixture was cooled to 0 °C and to the reaction mixture was added AgOTf (514 mg, 2.00 mmol, 2.00 equiv). After stirring for 30 min at 0 °C, to the reaction mixture was added MeCN (3 mL) to precipitate an arylsilver complex. The precipitate was filtered off and washed with MeCN (2 × 1 mL) and

³ Furuya, T.; Strom, A. E.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 1662–1663.

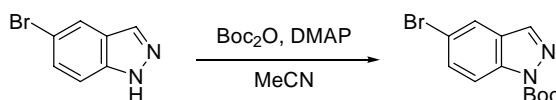
⁴ Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067–1079

subsequently washed with Et₂O (2 × 1 mL) at 0 °C to afford 152 mg of the title compound as a colorless solid (67% yield).

NMR Spectroscopy: ¹H NMR (400 MHz, CDCl₃, 23 °C, δ): 6.91 (s, 2H), 2.73 (s, 6H), 2.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, 23 °C, δ): 154.59, 140.75, 126.88, 125.65, 29.74, 21.18.

Synthesis of boronic acid derivatives

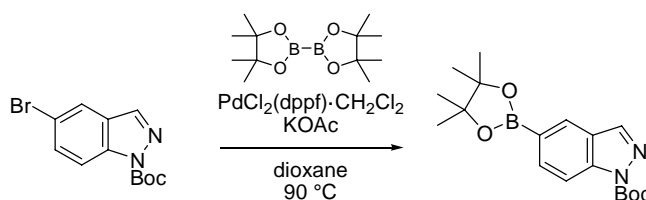
N-Boc-5-bromoindazole (S2)



To 5-bromoindazole (394 mg, 2.00 mmol, 1.00 equiv) in MeCN (4.0 mL) at 23 °C was added Boc₂O (436 mg, 2.00 mmol, 1.00 equiv) and 4-(dimethylamino)pyridine (24.4 mg, 0.200 mmol, 0.100 equiv). After stirring for 15 min at 23 °C, the reaction mixture was concentrated in vacuo. The residue was filtered through a plug of silica gel eluting with hexanes/EtOAc 7:3 (v/v) to afford 588 mg of the title compound as a pale yellow oil (99% yield).

R_f = 0.65 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy⁵: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 8.57 (s, 1H_B), 8.11 (s, 1H_A), 8.09 (d, *J* = 9.0 Hz, 1H_A), 7.88 (s, 1H_A), 7.81 (s, 1H_B), 7.66–7.60 (m, 1H_A, 1H_B), 7.36 (d, *J* = 9.0 Hz, 1H_B) 1.72 (s, 9H_A, 9H_B). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 148.96, 148.85, 147.80, 138.47, 138.35, 132.69, 131.88, 127.31, 123.67, 123.55, 123.04, 122.71, 120.89, 117.60, 116.79, 115.95, 87.11, 85.33, 28.09, 27.83. Mass Spectrometry: HRMS-FIA (*m/z*): Calcd for [M + Na]⁺, 319.00526. Found, 319.00530.

N-Boc-indazole-5-boronic acid, pinacol ester (S3)



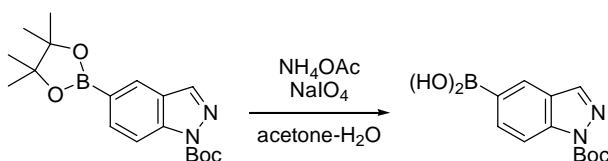
To *N*-Boc-5-bromoindazole (**S2**) (594 mg, 2.00 mmol, 1.00 equiv) in dioxane (10 mL) at 23 °C was added PdCl₂(dppf)·CH₂Cl₂ (163 mg, 0.200 mmol, 0.100 equiv), bis(pinacolato)diboron (559 mg, 2.20 mmol,

⁵ NMR spectroscopy showed the product was a mixture of two rotamers around *N*-Boc moiety. The ratio of rotamers was 1 to 0.7. Peaks of the major and minor isomers are shown with a subscript A and B respectively.

1.10 equiv), and KOAc (392 mg, 4.00 mmol, 2.00 equiv). After stirring for 9.0 hr at 90 °C, the reaction mixture was cooled to 23 °C and concentrated in vacuo. The residue was dissolved in CH₂Cl₂ and filtered through a plug of celite. After removal of CH₂Cl₂, the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 9:1 (v/v) to afford 500 mg of the title compound as a pale yellow oil (73% yield).

R_f = 0.55 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ¹H NMR (600 MHz, CDCl₃, 23 °C, δ): 8.23 (s, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.16 (s, 1H), 7.95 (d, J = 8.4 Hz, 1H), 1.73 (s, 9H), 1.37 (s, 12H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 149.09, 141.27, 139.83, 134.67, 128.66, 125.56, 124.16 (br), 113.71, 84.80, 83.90, 28.07, 24.80. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [M + Na]⁺, 367.17996. Found, 367.18018.

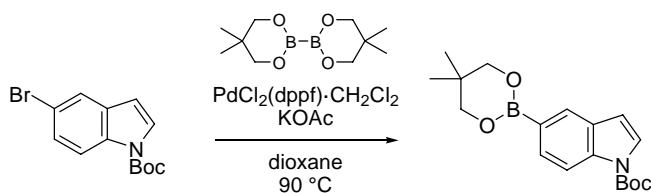
***N*-Boc-indazole-5-boronic acid (S4)**



To *N*-Boc-indazole-5-boronic acid pinacol ester (**S3**) (390 mg, 1.13 mmol, 1.00 equiv) in acetone/H₂O (5.0 mL/5.0 mL) at 23 °C was added NH₄OAc (436 mg, 5.65 mmol, 5.00 equiv) and NaIO₄ (1.21 g, 5.65 mmol, 5.00 equiv). After stirring for 48 hr at 23 °C, the reaction mixture was concentrated in vacuo to remove acetone. To the residual solution was added EtOAc (5 mL) and the phases were separated. The aqueous phase was extracted with EtOAc (2 × 5 mL). The combined organic phases were washed with brine (10 mL) and dried (Na₂SO₄). The filtrate was concentrated in vacuo and the residue was triturated with Et₂O to afford 200 mg of the title compound as a colorless solid (68% yield).

R_f = 0.20 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ¹H NMR (400 MHz, DMSO-*d*₆, 23 °C, δ): 8.42 (s, 1H), 8.29 (s, 1H), 8.18 (s, 2H), 8.03 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 1.64 (s, 9H). ¹³C NMR (100 MHz, DMSO-*d*₆, 23 °C, δ): 148.60, 140.28, 140.13, 134.57, 129.38 (br), 128.06, 125.45, 112.88, 84.38, 27.69. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [M + Na]⁺, 285.10171. Found, 285.10191.

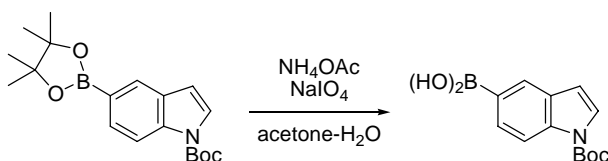
***N*-Boc-indole-5-boronic acid, neopentylglycol ester (28b)**



To *N*-Boc-5-bromoindole (592 mg, 2.00 mmol, 1.00 equiv) in dioxane (10 mL) at 23 °C was added PdCl₂(dppf)·CH₂Cl₂ (163 mg, 0.200 mmol, 0.100 equiv), bis(neopentylglycolato)diboron (497 mg, 2.20 mmol, 1.10 equiv), and KOAc (392 mg, 4.00 mmol, 2.00 equiv). After stirring for 6.0 hr at 90 °C, the reaction mixture was cooled to 23 °C and concentrated in vacuo. The residue was dissolved in CH₂Cl₂ and filtered through a plug of celite. After removal of CH₂Cl₂, the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 97:3 (v/v) to afford 609 mg of the title compound as a colorless solid (92% yield).

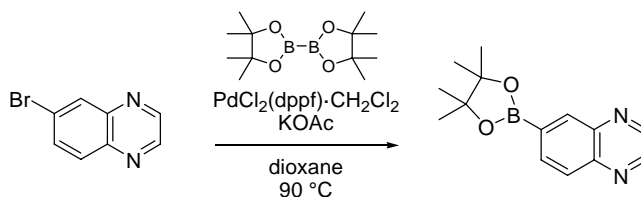
R_f = 0.45 (hexanes/EtOAc 9:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 8.16 (d, J = 7.5 Hz, 1H), 8.08 (s, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.59 (d, J = 3.5 Hz, 1H), 6.60 (d, J = 3.5 Hz, 1H), 3.81 (s, 4H), 1.69 (s, 9H), 1.05 (s, 6H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 149.69, 136.96, 130.09, 129.72, 127.17, 126.10 (br), 125.61, 114.22, 107.59, 83.50, 72.25, 31.83, 28.11, 21.83. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [M + H]⁺, 330.18712. Found, 330.18650.

***N*-Boc-indole-5-boronic acid (28a)**



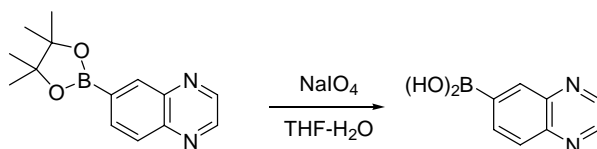
To *N*-Boc-indole-5-boronic acid pinacol ester (172 mg, 0.500 mmol, 1.00 equiv) in acetone/H₂O (5.0 mL/5.0 mL) at 23 °C was added NH₄OAc (193 mg, 2.50 mmol, 5.00 equiv) and NaIO₄ (428 mg, 2.00 mmol, 4.00 equiv). After stirring for 24 hr at 23 °C, the reaction mixture was concentrated in vacuo to remove acetone. To the residual solution was added EtOAc (5 mL) and the phases were separated. The aqueous phase was extracted with EtOAc (2 × 5 mL). The combined organic phases were washed with brine (10 mL) and dried (Na₂SO₄). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 1:1 (v/v) to afford 70.0 mg of the title compound as a colorless solid (54% yield).

R_f = 0.50 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ¹H NMR (500 MHz, CDCl₃, 23 °C, δ): 8.56 (s, 1H), 8.31–8.23 (m, 2H), 7.67 (d, J = 3.0 Hz, 1H), 6.75 (d, J = 3.5 Hz, 1H), 1.72 (s, 9H). ¹³C NMR (125 MHz, CDCl₃, 23 °C, δ): 149.71, 138.05, 131.31, 130.42, 129.41, 126.19, 124.31 (br), 114.69, 107.76, 83.91, 28.21. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [M + Na]⁺, 284.10646. Found, 284.10767.

6-Quinoxaline boronic acid, pinacol ester (S5)

To 6-bromoquinoxaline (418 mg, 2.00 mmol, 1.00 equiv) in dioxane (10 mL) at 23°C was added $\text{PdCl}_2(\text{dppf}) \cdot \text{CH}_2\text{Cl}_2$ (163 mg, 0.200 mmol, 0.100 equiv), bis(pinacolato)diboron (610 mg, 2.40 mmol, 1.20 equiv), and KOAc (392 mg, 4.00 mmol, 2.00 equiv). After stirring for 1.5 hr at 90°C , the reaction mixture was cooled to 23°C and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and filtered through a plug of celite. After removal of CH_2Cl_2 , the residue was purified by chromatography on silica gel eluting with hexanes/ EtOAc 4:1 (v/v) to afford 500 mg of the title compound as a colorless solid (98% yield).

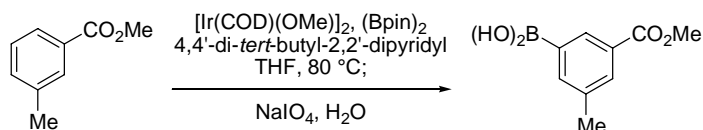
$R_f = 0.45$ (hexanes/ EtOAc 1:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23°C , δ): 8.86–8.82 (m, 2H), 8.59 (s, 1H), 8.12 (dd, $J = 8.0$ Hz, 2.0 Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 1.37 (s, 12H). ^{13}C NMR (125 MHz, CDCl_3 , 23°C , δ): 145.53, 145.03, 144.37, 142.41, 137.31, 134.75, 131.90 (br), 128.44, 84.36, 24.86. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[\text{M} + \text{H}]^+$, 257.14558. Found, 257.14440.

6-Quinoxaline boronic acid (S6)

To 6-quinoxaline boronic acid pinacol ester (S4) (256 mg, 1.00 mmol, 1.00 equiv) in THF (2.0 mL) at 23°C was added H_2O (8.0 mL) and NaIO_4 (321 mg, 1.50 mmol, 1.50 equiv). After stirring for 1.0 hr at 23°C , to the reaction mixture was added 1N HCl aq (20 mL) and the reaction mixture was further stirred for 1.0 hr. To the reaction mixture was added EtOAc (20 mL) and the phases were separated. The aqueous phase was extracted with EtOAc (2×20 mL). The combined organic phases were washed with brine (20 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was triturated with Et_2O to afford 121 mg of the title compound as a colorless solid (70% yield).

$R_f = 0.10$ (hexanes/ EtOAc 1:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, $\text{DMSO-}d_6$, 23°C , δ): 8.96–8.93 (m, 2H), 8.55 (s, 1H), 8.47 (s, 2H), 8.18 (d, $J = 8.0$ Hz, 1H), 8.04 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, 23°C , δ): 146.08, 145.66, 143.21, 141.73, 136.61 (br), 135.82, 134.73, 127.77. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[\text{M} + \text{H}]^+$, 175.06733. Found, 176.06705.

3-Methoxycarbonyl-5-methylphenyl boronic acid⁶ (S7)

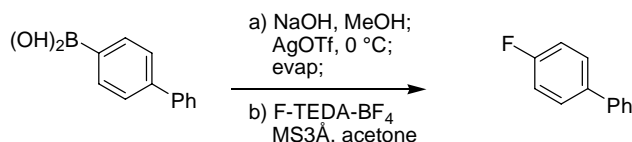


To *m*-toluic acid methyl ester (451 mg, 3.00 mmol, 1.00 equiv) in THF (6.0 mL) at 23 °C was added [Ir(COD)(OMe)]₂ (10 mg, 0.015 mmol, 0.50 mol%), 4,4'-di-*tert*-butyl-2,2'-dipyridyl (8.0 mg, 0.030 mmol, 1.0 mol%) and bis(pinacolato)diboron (610 mg, 2.40 mmol, 0.800 equiv). After stirring for 24 hr at 80 °C, to the reaction mixture was added H₂O (6.0 mL) and NaIO₄ (3.21 g, 15.0 mmol, 5.00 equiv). After stirring for 8.0 hr at 23 °C, to the reaction mixture was added 1N HCl aq (10 mL) and the reaction mixture was further stirred for 1.0 hr. To the reaction mixture was added EtOAc (20 mL) and the phases were separated. The aqueous phase was extracted with EtOAc (2 × 20 mL). The combined organic phases were washed with brine (20 mL) and dried (Na₂SO₄). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/EtOAc 7:3 (v/v) to afford 466 mg of the title compound as a colorless solid (80% yield).

R_f = 0.15 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ¹H NMR (400 MHz, DMSO-*d*₆, 23 °C, δ): 8.20 (m, 3H), 7.84 (s, 1H), 7.79 (s, 1H), 3.83 (s, 3H), 2.35 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆, 23 °C, δ): 166.71, 139.65, 136.97, 134.70 (br), 132.24, 131.14, 128.83, 51.99, 20.82.

Fluorination of arylboronic acids

Large-scale fluorination of 4-biphenylboronic acid

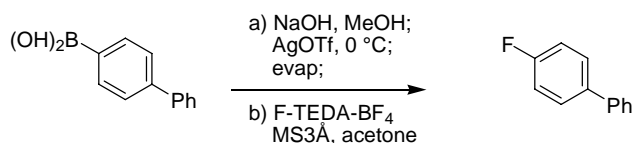


To NaOH (480 mg, 12.0 mmol, 1.20 equiv) in MeOH (20 mL) at 23 °C was added 4-biphenylboronic acid (1.98 g, 10.0 mmol, 1.00 equiv). After stirring for 15 min at 23 °C, the reaction mixture was cooled to 0 °C and to the reaction mixture was added AgOTf (7.71 g, 30.0 mmol, 3.00 equiv). After stirring for 30 min at 0 °C, the solvent was removed under reduced pressure at 0 °C and the residual MeOH was removed by co-evaporation with acetone (20 mL × 2). To the residue was added acetone (50 mL), MS3Å (5.0 g), and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**3**) (3.72 g, 10.5 mmol, 1.05 equiv) and the reaction mixture was stirred for 30 min and concentrated in vacuo. The residue was dissolved in CH₂Cl₂ and filtered through a plug of celite. After removal of CH₂Cl₂, H₂O (30

⁶ Murphy, J. M.; Tzschucke, C. C.; Hartwig, J. F. *Org. Lett.*, **2007**, 9, 757–760.

mL) and Et₂O (30 mL) were added to the residue and the phases were separated. The aqueous phase was extracted with Et₂O (2 × 20 mL). The combined organic phases were washed with brine (30 mL) and dried (Na₂SO₄). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes to afford 1.62 g of 4-fluorobiphenyl as a colorless solid (94% yield).

Dependence of fluorination on NaOH and AgOTf

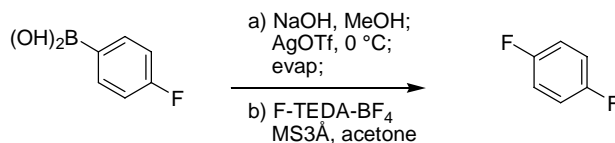


To NaOH (1.0–1.5 equiv) in MeOH (0.50 mL) at 23 °C was added a 4-biphenylboronic acid (19.8 mg, 0.100 mmol, 1.00 equiv). After stirring for 15 min at 23 °C, the reaction mixture was cooled to 0 °C and to the reaction mixture was added AgOTf (0–3.0 equiv). After stirring for 30 min at 0 °C, the solvent was removed under reduced pressure at 0 °C and the residual MeOH was removed by co-evaporation with acetone (0.5 mL × 2). To the residue was added acetone-*d*₆ (0.5 mL), MS3Å (50 mg), and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**3**) (37.2 mg, 0.105 mmol, 1.05 equiv) and the reaction mixture was stirred for 1.0 hr. The yields were determined by comparing the integration of the ¹⁹F NMR (375 MHz, acetone-*d*₆, 23 °C) resonance of 4-biphenylfluoride (−116.2 ppm) and that of 3-nitrofluorobenzene (−112.0 ppm). The results are summarized in Table S1.

Table S1: Fluorination with various amounts of NaOH and AgOTf

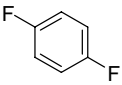
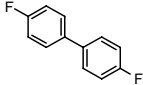
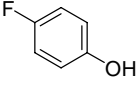
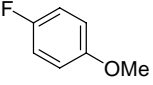
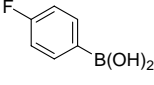
Entry	AgOTf (equiv)	NaOH (equiv)	Yield (%)
1	0	1.0	0
2	1.0	1.0	43
3	2.0	1.0	82
4	2.0	1.2	78
5	2.0	1.5	63
6	3.0	1.0	90
7	3.0	1.2	95
8	3.0	1.5	83

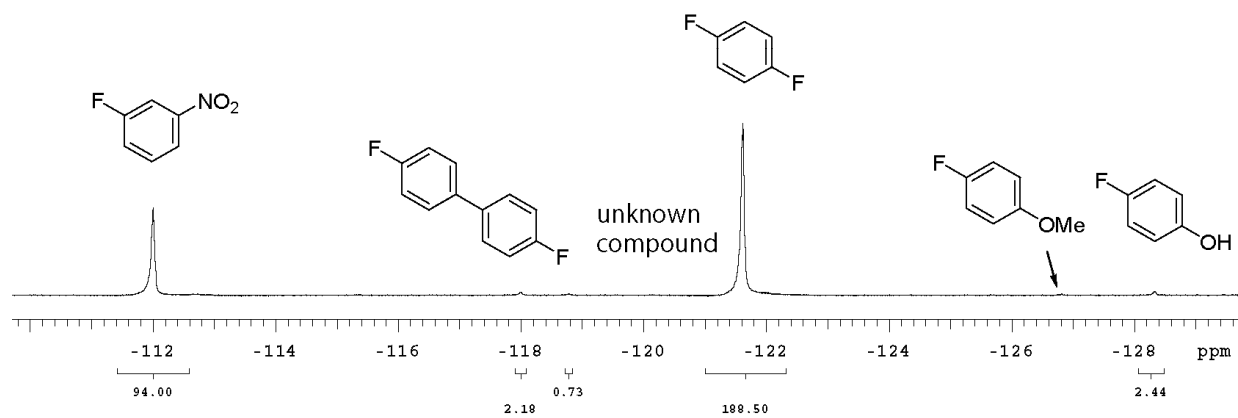
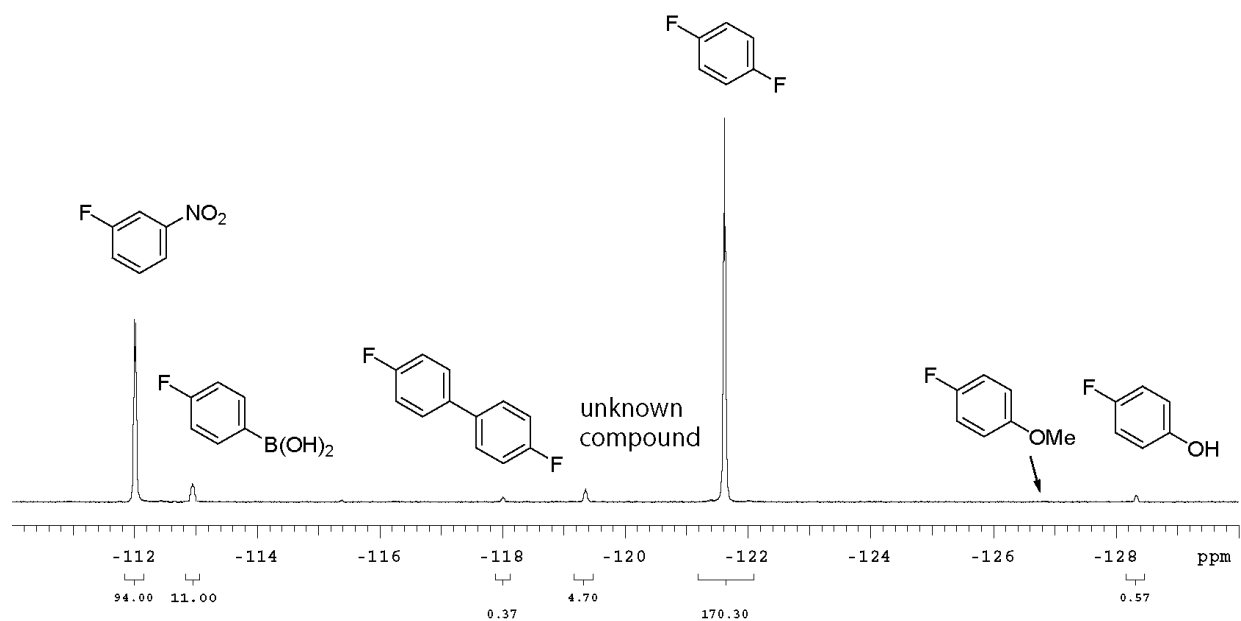
Identification of byproducts by ^{19}F NMR



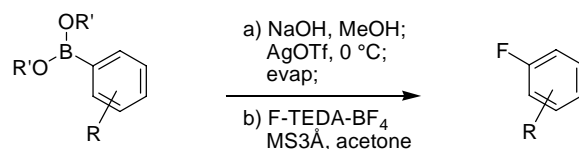
To NaOH (1.0 or 1.2 equiv) in MeOH (0.50 mL) at 23 °C was added a 4-fluorophenylboronic acid (14.0 mg, 0.100 mmol, 1.00 equiv). After stirring for 15 min at 23 °C, the reaction mixture was cooled to 0 °C and to the reaction mixture was added AgOTf (2.0 or 3.0 equiv). After stirring for 30 min at 0 °C, the solvent was removed under reduced pressure at 0 °C and the residual MeOH was removed by co-evaporation with acetone (0.5 mL \times 2). To the residue was added acetone-*d*₆ (0.5 mL), MS3Å (50 mg), and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**3**) (37.2 mg, 0.105 mmol, 1.05 equiv) and the reaction mixture was stirred for 1.0 hr. To the crude reaction mixture was added 1N HCl (0.05 mL) and the yield for each product was determined by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d*₆, 23 °C) resonance of byproducts and that of 3-nitrofluorobenzene (–112.0 ppm). The results are summarized in Table S2 and the crude ^{19}F NMR spectrum is shown on the next page.

Table S2: Identification of byproducts

conditions		products				
AgOTf (equiv)	NaOH (equiv)					
2.0	1.0	85%	<1%	1%	<1%	11%
3.0	1.2	94%	1%	2%	<1%	<1%



Comparison of boronic acid and boronic ester fluorination

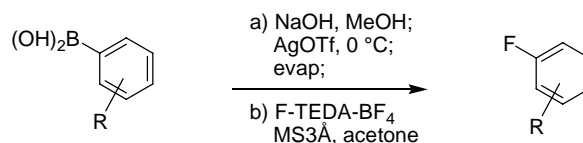


To NaOH (4.8 mg, 0.12 mmol, 1.2 equiv) in MeOH (0.50 mL) at 23 °C was added a boronic acid derivative (0.100 mmol, 1.00 equiv). After stirring for 15 min at 23 °C, the reaction mixture was cooled to 0 °C and to the reaction mixture was added AgOTf (77.1 mg, 0.300 mmol, 3.00 equiv). After stirring for 30 min at 0 °C, the solvent was removed under reduced pressure at 0 °C and the residual MeOH was removed by co-evaporation with acetone (0.5 mL × 2). To the residue was added acetone-*d*₆ (0.5 mL), MS3A (50 mg), and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**3**) (37.2 mg, 0.105 mmol, 1.05 equiv) and the reaction mixture was stirred for 1.0 hr. The yields were determined by comparing the integration of the ¹⁹F NMR (375 MHz, acetone-*d*₆, 23 °C) resonance of the product arylfluoride and that of 3-nitrofluorobenzene (−112.0 ppm). The results are summarized in Table S3.

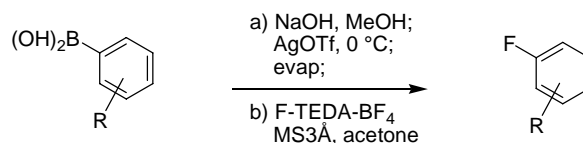
Boronic acids, neopentylglycol ester, and pinacol esters were fluorinated with decreasing yields in this order. The yield of fluorination for boronic esters can vary significantly depending on the substrate.

Table S3: Comparison of boronic acid and esters in yield of fluorination.

Substrate	Yield (%)	Substrate	Yield (%)
	97		95
	81		76
	70		36

General procedure A: Yield determined by ^{19}F NMR, 2.0 equiv AgOTf

To NaOH (4.0 mg, 0.10 mmol, 1.0 equiv) in MeOH (0.50 mL) at 23 °C was added a boronic acid (0.100 mmol, 1.00 equiv). After stirring for 15 min at 23 °C, the reaction mixture was cooled to 0 °C and to the reaction mixture was added AgOTf (51.4 mg, 0.200 mmol, 2.00 equiv). After stirring for 30 min at 0 °C, the solvent was removed under reduced pressure at 0 °C and the residual MeOH was removed by co-evaporation with acetone (0.5 mL \times 2). To the residue was added acetone-*d*₆ (0.5 mL), MS3Å (50 mg), and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**3**) (37.2 mg, 0.105 mmol, 1.05 equiv) and the reaction mixture was stirred for 1.0 hr. The yields were determined by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d*₆, 23 °C) resonance of the product arylfluoride and that of 3-nitrofluorobenzene (−112.0 ppm). The average yields of two runs are reported in Table S4.

General procedure B: Yield determined by ^{19}F NMR, 3.0 equiv AgOTf

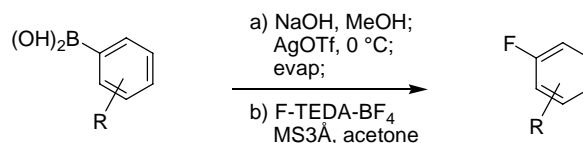
To NaOH (4.8 mg, 0.12 mmol, 1.2 equiv) in MeOH (1.0 mL) at 23 °C was added a boronic acid (0.100 mmol, 1.00 equiv). After stirring for 15 min at 23 °C, the reaction mixture was cooled to 0 °C and to the reaction mixture was added AgOTf (77.1 mg, 0.300 mmol, 3.00 equiv). After stirring for 30 min at 0 °C, the solvent was removed under reduced pressure at 0 °C and the residual MeOH was removed by co-evaporation with acetone (0.5 mL \times 2). To the residue was added acetone-*d*₆ (0.5 mL), MS3Å (50 mg), and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**3**) (37.2 mg, 0.105 mmol, 1.05 equiv) and the reaction mixture was stirred for 1.0 hr. The yields were determined by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d*₆, 23 °C) resonance of the product arylfluoride and that of 3-nitrofluorobenzene (−112.0 ppm). The average yields of two runs are reported in Table S4.⁷

⁷ ^{19}F NMR chemical shifts given in Table S4 correspond to those of authentic samples purchased from Aldrich, Alfa, or TCI, or those of data given in appropriate references.

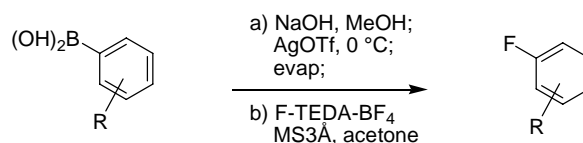
Table S4: NMR yield of fluorination

R	¹⁹F chemical shift [ppm] in acetone-<i>d</i>₆	NMR Yield [%] with 2.0 equiv AgOTf	NMR Yield [%] with 3.0 equiv AgOTf
4-F (4)	−121.6	85	91
4-Ph (6)	−118.1	82	95
H (7)	−115.3	83	95
4-OH (8)	−128.2	58	70
4- ^{<i>i</i>} Bu ⁸ (9)	−120.8	82	90
4-OMe (10)	−126.8	84	98
2,4,6-Trimethyl ³ (11)	−129.7	73	73
4-CO ₂ Me (12)	−109.5	76	92
4-CN ³ (13)	−105.0	61	77
4-CHO (14)	−105.9	71	71
4-Br (15)	−117.4	73	93
4-NHAc (16)	−114.4	79	89
4-CF ₃ (17)	−109.5	67	86
3,5-Dimethyl (18)	−117.6	78	88
1-Naphthyl (19)	−125.9	86	95
<i>N</i> -Boc-5-Indazolyl ⁹ (20)	−120.0	74	95
<i>N</i> -Boc-5-Indolyl ³ (21)	−123.2	81	97
6-Quinoxaliny ¹⁰ (22)	−107.1	65	79
6-Quinoliny ³ (23)	−113.8	63	80
3-Pyridyl (24)	−125.6	59	72
<i>trans</i> -2-Phenylvinyl ¹¹ (25)	−132.2	74	90
<i>trans</i> -1-Octen-1-yl (26)	−132.4	85	92
1-Cyclohexyl ¹² (27)	−102.5	65	83

⁸ Furuya, T.; Ritter, T. *J. Am. Chem. Soc.* **2008**, *130*, 10060–10061.⁹ Isolated and characterized in this paper.¹⁰ Zhang, L.; Qiu, B.; Li, X.; Wang, X.; Li, J.; Zhang, Y.; Liu, J.; Li, J.; Shen, J. *Molecules* **2006**, *11*, 988–999.

General procedure C: Isolated yield, 2.0 equiv AgOTf

To NaOH (20.0 mg, 0.500 mmol, 1.00 equiv) in MeOH (2.5 mL) at $23\text{ }^\circ\text{C}$ was added a boronic acid (0.500 mmol, 1.00 equiv). After stirring for 15 min at $23\text{ }^\circ\text{C}$, the reaction mixture was cooled to $0\text{ }^\circ\text{C}$ and to the reaction mixture was added AgOTf (257 mg, 1.00 mmol, 2.00 equiv). After stirring for 30 min at $0\text{ }^\circ\text{C}$, the solvent was removed under reduced pressure at $0\text{ }^\circ\text{C}$ and the residual MeOH was removed by co-evaporation with acetone ($2.5\text{ mL} \times 2$). To the residue was added acetone (5.0 mL), MS3A (250 mg), and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**3**) (186 mg, 0.525 mmol, 1.05 equiv). The reaction mixture was stirred for 1.0 hr and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and filtered through a plug of celite. After removal of CH_2Cl_2 , to the residue was added H_2O (5 mL) and EtOAc (5 mL) and the phases were separated. The aqueous phase was extracted with EtOAc ($2 \times 3\text{ mL}$). The combined organic phases were washed with brine (5 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel or preparative TLC.

General procedure D: Isolated yield, 3.0 equiv AgOTf

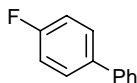
To NaOH (24.0 mg, 0.600 mmol, 1.20 equiv) in MeOH (2.5 mL) at $23\text{ }^\circ\text{C}$ was added a boronic acid (0.500 mmol, 1.00 equiv). After stirring for 15 min at $23\text{ }^\circ\text{C}$, the reaction mixture was cooled to $0\text{ }^\circ\text{C}$ and to the reaction mixture was added AgOTf (385 mg, 1.50 mmol, 3.00 equiv). After stirring for 30 min at $0\text{ }^\circ\text{C}$, the solvent was removed under reduced pressure at $0\text{ }^\circ\text{C}$ and the residual MeOH was completely removed by co-evaporation with acetone ($2.5\text{ mL} \times 2$). To the residue was added acetone (5.0 mL), MS3A (250 mg), and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**3**) (186 mg, 0.525 mmol, 1.05 equiv). The reaction mixture was stirred for 1.0 hr and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and filtered through a plug of celite. After removal of CH_2Cl_2 , to the residue was added H_2O (5 mL) and EtOAc (5 mL) and the phases were separated. The aqueous phase was

¹¹ Goumans, T. P. M.; van Alem, K.; Lodder, G. *Eur. J. Org. Chem.* **2008**, 435–443.

¹² Hudlicky, M. *J. Fluorine Chem.*, **1986**, 32, 441–445.

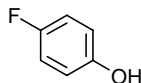
extracted with EtOAc (2×3 mL). The combined organic phases were washed with brine (5 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel or preparative TLC.

4-Fluorobiphenyl¹³ (6)



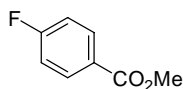
(General Procedure C) Yield: 70.6 mg (82%). $R_f = 0.60$ (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 7.60–7.54 (m, 4H), 7.47 (dd, $J = 7.5$ Hz, 7.0 Hz, 2H), 7.36 (t, $J = 7.5$ Hz, 1H), 7.14 (dd, $J = 8.0$ Hz, 7.5 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 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 °C, δ): –116.2.

4-Fluorophenol¹³ (8)



(General Procedure D) Yield: 39.0 mg (70%). $R_f = 0.58$ (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, 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 °C, δ): 157.32 (d, $J = 237$ Hz), 151.17, 116.25 (d, $J = 8.0$ Hz), 116.01 (d, $J = 21$ Hz). ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): –124.3.

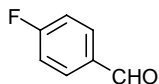
Methyl 4-fluorobenzoate¹⁴ (12)



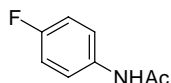
(General Procedure C) Yield: 58.6 mg (76%). $R_f = 0.85$ (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, CDCl_3 , 23 °C, δ): 8.05 (dd, $J = 8.8$ Hz, 6.4 Hz, 2H), 7.11 (dd, $J = 8.8$ Hz, 8.8 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 166.13, 165.74 (d, $J = 253$ Hz), 132.09 (d, $J = 9.1$ Hz), 126.41, 115.49 (d, $J = 22$ Hz), 52.2. ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): –106.2.

¹³ Furuya, T.; Kaiser, H. M.; Ritter, T. *Angew. Chem. Int. Ed.* **2008**, 47, 5993–5996.

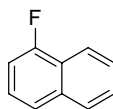
¹⁴ NMR spectroscopic data correspond to the authentic samples purchased from Aldrich

4-Fluorobenzaldehyde¹³ (14)

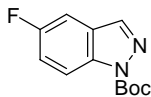
(General Procedure C) Yield: 37.8 mg (61%). R_f = 0.77 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 9.95 (s, 1H), 7.92–7.88 (m, 2H), 7.22–7.18 (dd, J = 8.0 Hz, 7.5 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 190.43, 166.42 (d, J = 255 Hz), 132.89, 132.14 (d, J = 9.9 Hz), 116.25 (d, J = 22 Hz). ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): –102.9.

4-Fluoroacetanilide¹⁴ (16)

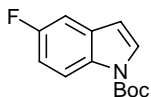
(General Procedure C) Yield: 59.0 mg (77%). R_f = 0.25 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 7.51 (br s, 1H), 7.44 (dd, J = 9.5 Hz, 5.0 Hz, 2H), 6.99 (dd, J = 8.0 Hz, 7.5 Hz, 2H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 23 °C, δ): 168.43, 159.34 (d, J = 243 Hz), 133.84, 121.80 (d, J = 7.3 Hz), 115.56 (d, J = 23 Hz), 24.33. ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): –118.4.

1-Fluoronaphthalene¹⁴ (19)

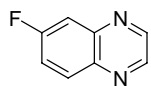
(General Procedure C) Yield: 60.0 mg (82%). R_f = 0.50 (hexanes). NMR Spectroscopy: ^1H NMR (400 MHz, CDCl_3 , 23 °C, δ): 8.14–8.09 (m, 1H), 7.89–7.84 (m, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.58–7.52 (m, 2H), 7.40 (ddd, J = 8.8 Hz, 8.8 Hz, 4.8 Hz, 1H), 7.15 (dd, J = 11.2 Hz, 8.0 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, δ): 158.78 (d, J = 250 Hz), 134.87, 127.51 (d, J = 3.6 Hz), 126.81, 126.15, 125.58 (d, J = 8.3 Hz), 123.68 (d, J = 18 Hz), 123.64, 120.53 (d, J = 5.5 Hz), 109.39 (d, J = 20 Hz). ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): –123.8.

***N*-Boc-5-fluoroindazole (20)**

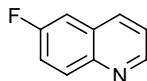
(General Procedure C) Yield: 88.6 mg (75%). R_f = 0.60 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, CDCl_3 , 23 °C, δ): 8.15 (dd, J = 8.8 Hz, 4.0 Hz, 1H), 8.12 (s, 1H), 7.35 (dd, J = 8.4 Hz, 3.0 Hz, 1H), 7.27 (ddd, J = 11.2 Hz, 8.8 Hz, 2.0 Hz, 1H), 1.72 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3 , 23 °C, δ): 159.20 (d, J = 240 Hz), 148.96, 138.91, 136.44, 126.24 (d, J = 10 Hz), 117.72 (d, J = 26 Hz), 115.81 (d, J = 9.1 Hz), 105.66 (d, J = 24 Hz), 85.12, 28.10. ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): -119.6. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[\text{M} + \text{Na}]^+$, 259.08533. Found, 259.08550.

***N*-Boc-5-fluoroindole¹³ (21)**

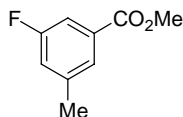
(General Procedure C) Yield: 88.2 mg (75%). R_f = 0.75 (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, δ): 8.08 (br, 1H), 7.62 (d, J = 4.0 Hz, 1H), 7.20 (dd, J = 6.5 Hz, 2.0 Hz, 1H), 7.03 (ddd, J = 7.0 Hz, 6.5 Hz, 2.0 Hz, 1H), 6.52 (d, J = 4.0 Hz, 1H), 1.68 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3 , 23 °C, 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 °C, δ): -121.7.

6-Fluoroquinoxaline¹⁰ (22)

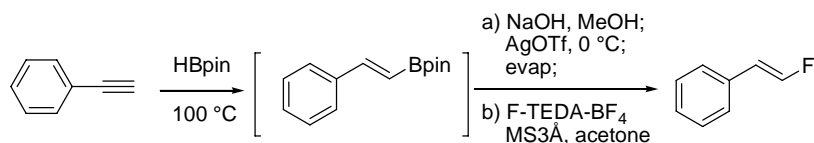
(General Procedure D) Yield: 52.6 mg (71%). NMR Spectroscopy: ^1H NMR (400 MHz, CDCl_3 , 23 °C, δ): 8.84 (d, J = 4.0 Hz, 1H), 8.81 (d, J = 4.0 Hz, 1H), 8.11 (dd, J = 9.2 Hz, 6.0 Hz, 1H), 7.72 (dd, J = 9.2 Hz, 3.5 Hz, 1H), 7.56 (ddd, J = 9.2 Hz, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3 , 23 °C, δ): 163.00 (d, J = 249 Hz), 145.98, 145.25 (d, J = 6.4 Hz), 144.57, 144.10 (d, J = 14 Hz), 131.96 (d, J = 10 Hz), 120.93 (d, J = 26 Hz), 113.27 (d, J = 21 Hz). ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): -107.0.

6-Fluoroquinoline³ (23)

(General Procedure D) Yield: 55.2 mg (75%). $R_f = 0.47$ (EtOAc). NMR Spectroscopy: ^1H NMR (500 MHz, CDCl_3 , 23 °C, 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 °C, 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 °C, δ): –113.0.

Methyl 3-fluoro-5-methylbenzoate (29)

(General Procedure D) Yield: 60.5 mg (72%). $R_f = 0.70$ (hexanes/EtOAc 7:3 (v/v)). NMR Spectroscopy: ^1H NMR (400 MHz, CDCl_3 , 23 °C, δ): 7.65 (s, 1H), 7.51 (d, $J = 8.8$ Hz, 1H), 7.07 (d, $J = 8.8$ Hz, 1H), 3.91 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3 , 23 °C, δ): 166.14, 162.46 (d, $J = 245$ Hz), 140.60 (d, $J = 7.3$ Hz), 131.84 (d, $J = 8.0$ Hz), 125.96 (d, $J = 2.9$ Hz), 120.53 (d, $J = 21$ Hz), 113.50 (d, $J = 23$ Hz), 52.28, 21.19. ^{19}F NMR (375 MHz, CDCl_3 , 23 °C, δ): –114.0. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[\text{M} + \text{H}]^+$, 169.06938. Found, 169.06993.

One-pot hydrofluorination of phenylacetylene

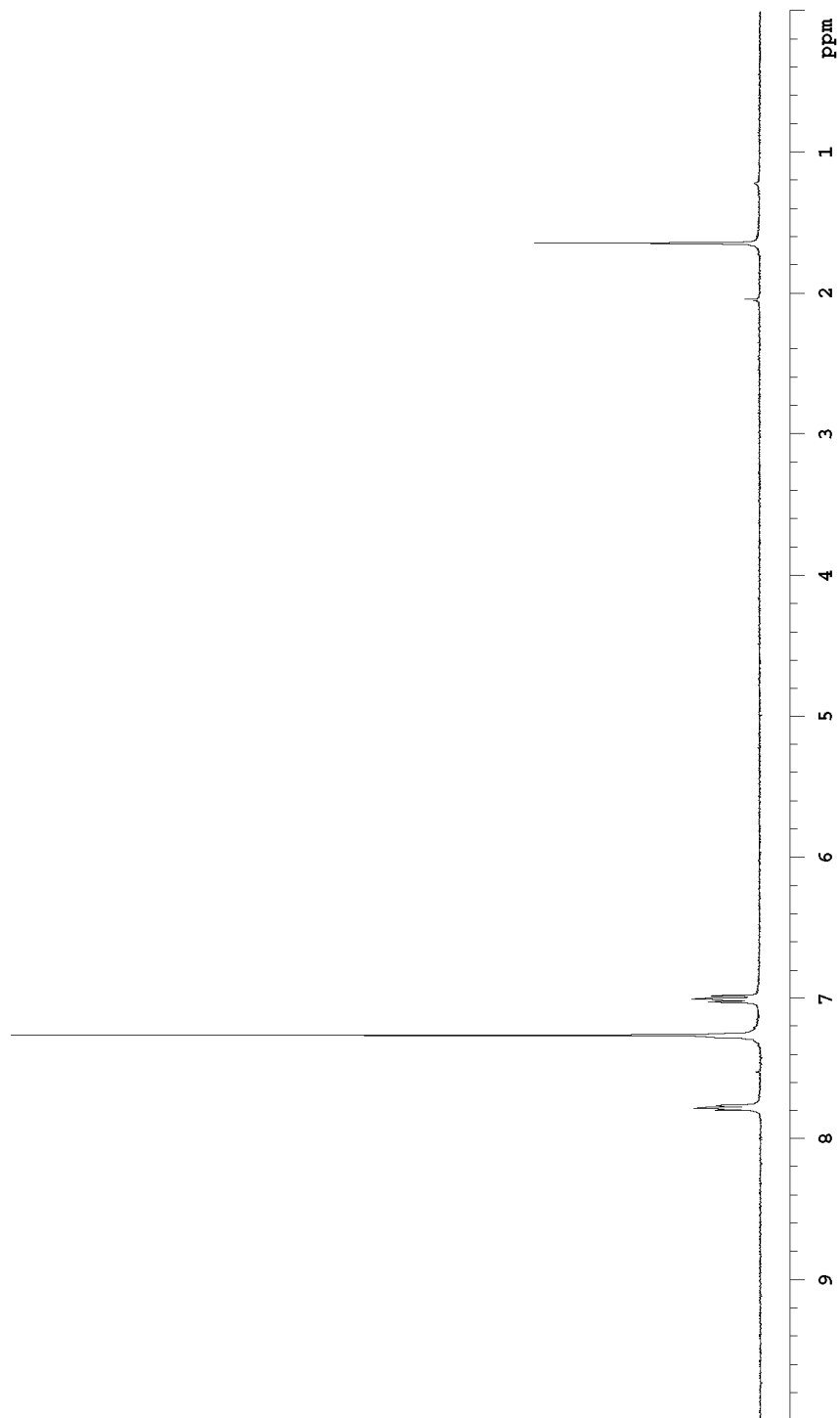
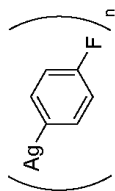
To phenylacetylene (**30**) (10.2 mg, 0.100 mmol, 1.00 equiv) at 23 °C was added pinacolborane (32.0 mg, 0.250 mmol, 2.50 equiv). The reaction mixture was heated to 100 °C and stirred for 36 hr before being cooled to 23 °C. To the residue was added NaOH (4.8 mg, 0.12 mmol, 1.2 equiv) in MeOH (0.50 mL). After stirring for 15 min at 23 °C, the reaction mixture was cooled to 0 °C and added to AgOTf (77.1 mg, 0.300 mmol, 3.00 equiv). After stirring for 30 min at 0 °C, the solvent was removed under reduced pressure at 0 °C and the residual MeOH was removed by co-evaporation with acetone (0.5 mL \times 2). To the residue was added acetone- d_6 (0.5 mL), MS3Å (50 mg), and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(trifluoroborate) (**3**) (37.2 mg, 0.105 mmol, 1.05 equiv) and the reaction

mixture was stirred for 1.0 hr. The yield was determined to be 76% by comparing the integration of the ^{19}F NMR (375 MHz, acetone-*d*₆, 23 °C) resonance of β -fluorostyrene (−132.2 ppm) and that of 3-nitrofluorobenzene (−112.0 ppm).

Spectroscopic Data

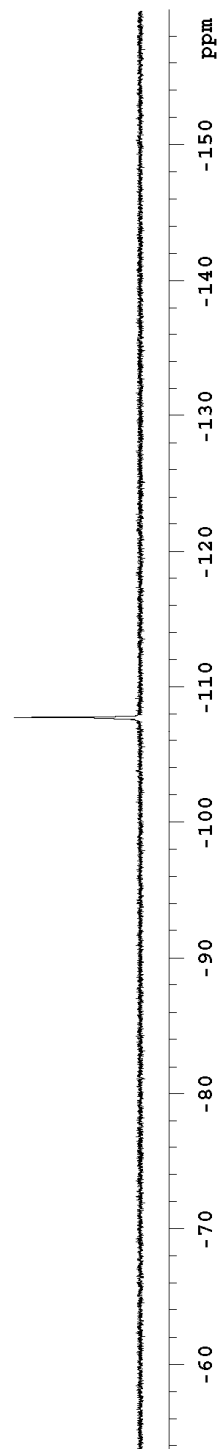
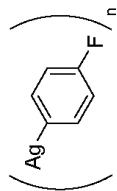
^1H NMR (CDCl_3 , 23 °C) of **2**

^1H NMR spectrum of

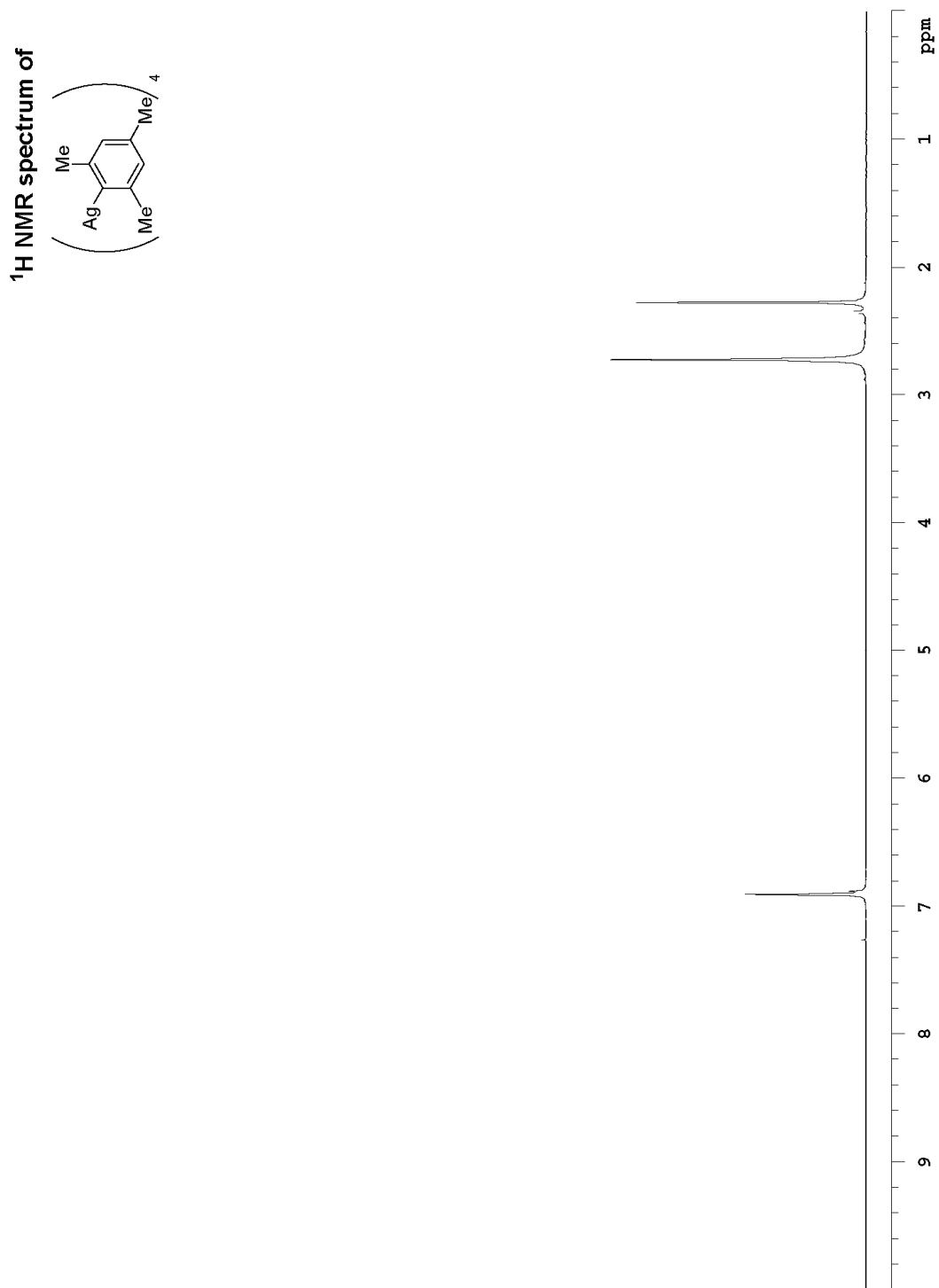


^{19}F NMR (CDCl_3 , 23 °C) of **2**

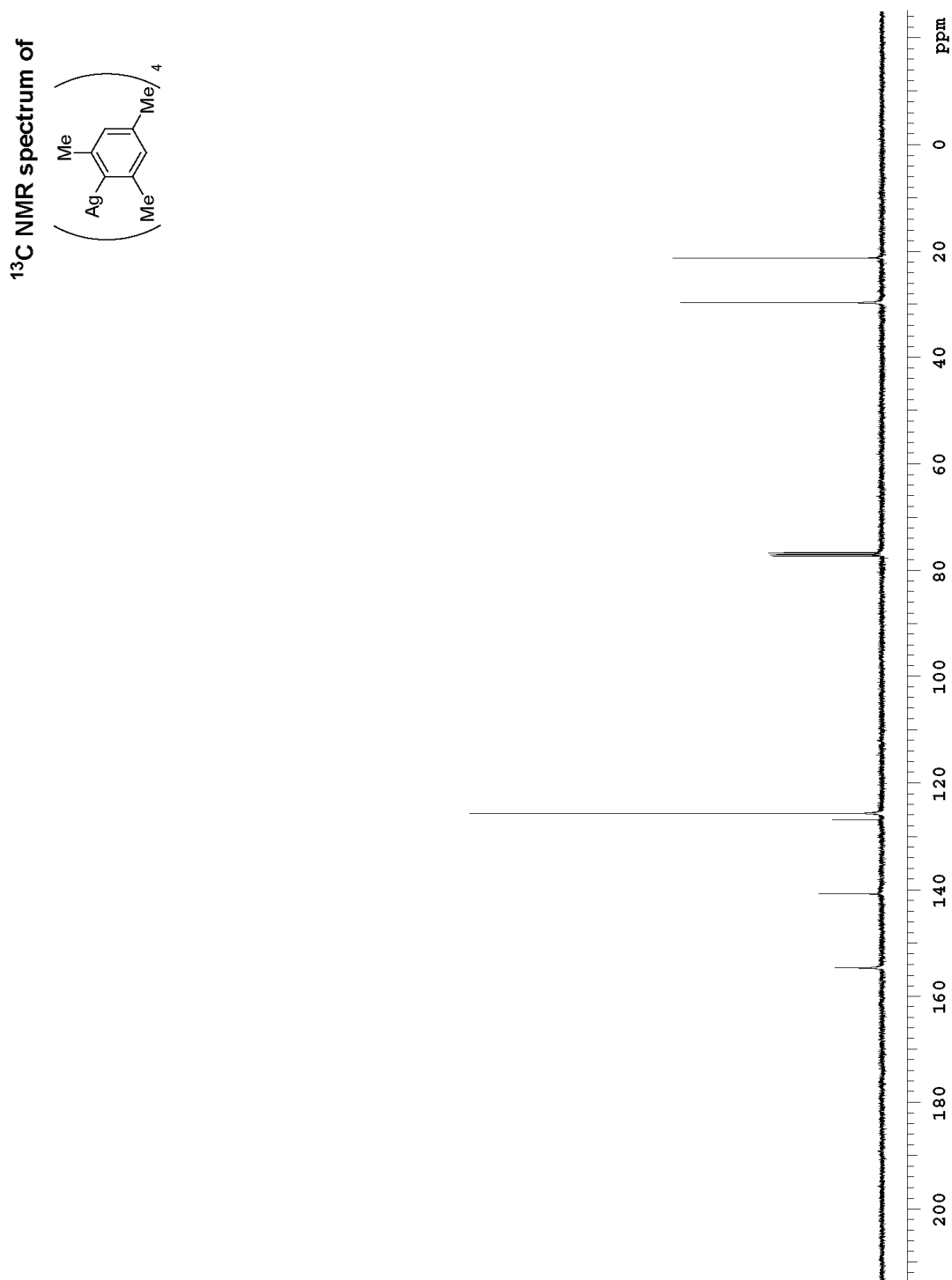
^{19}F NMR spectrum of



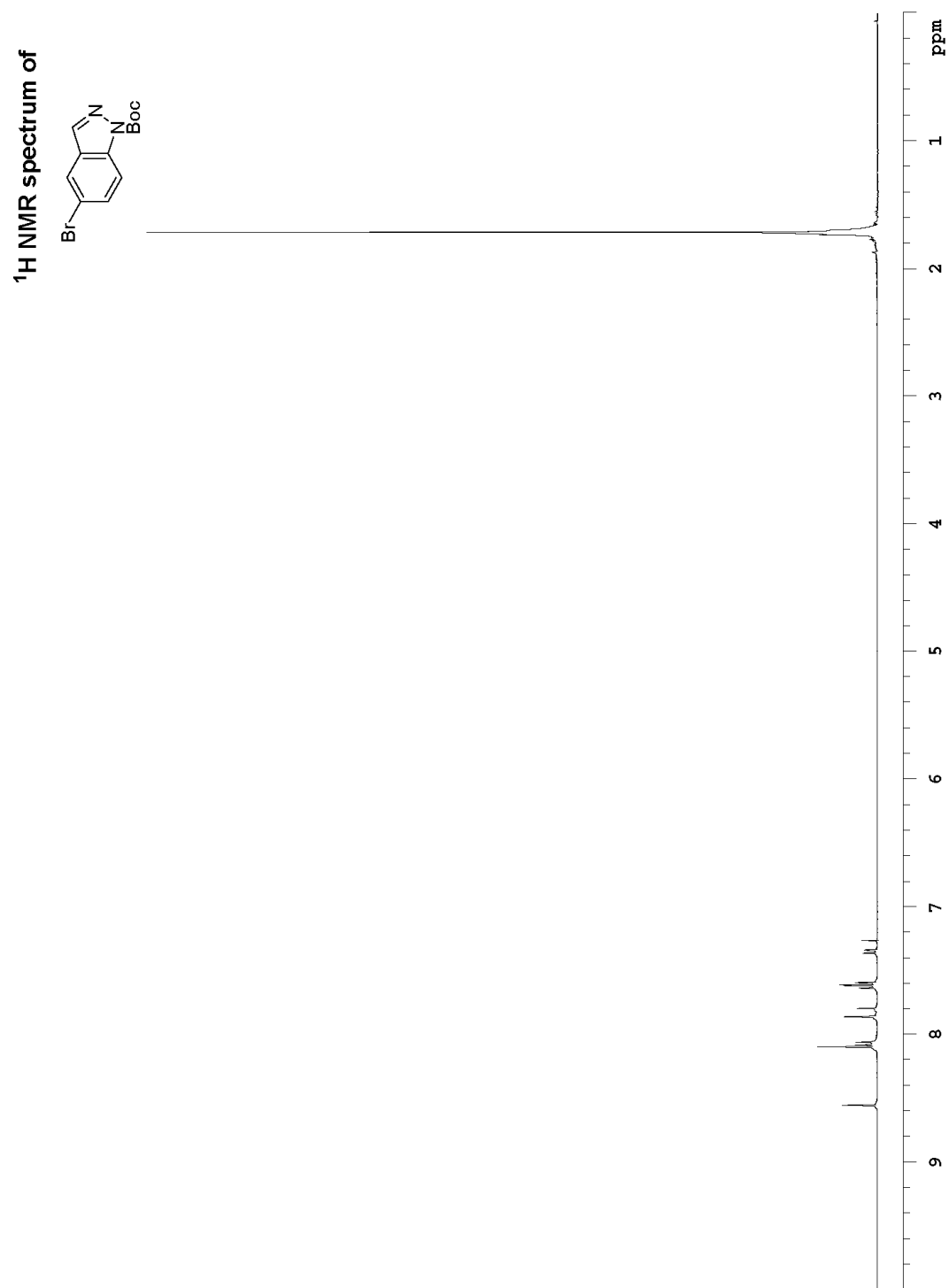
^1H NMR (CDCl_3 , 23 °C) of **S1**



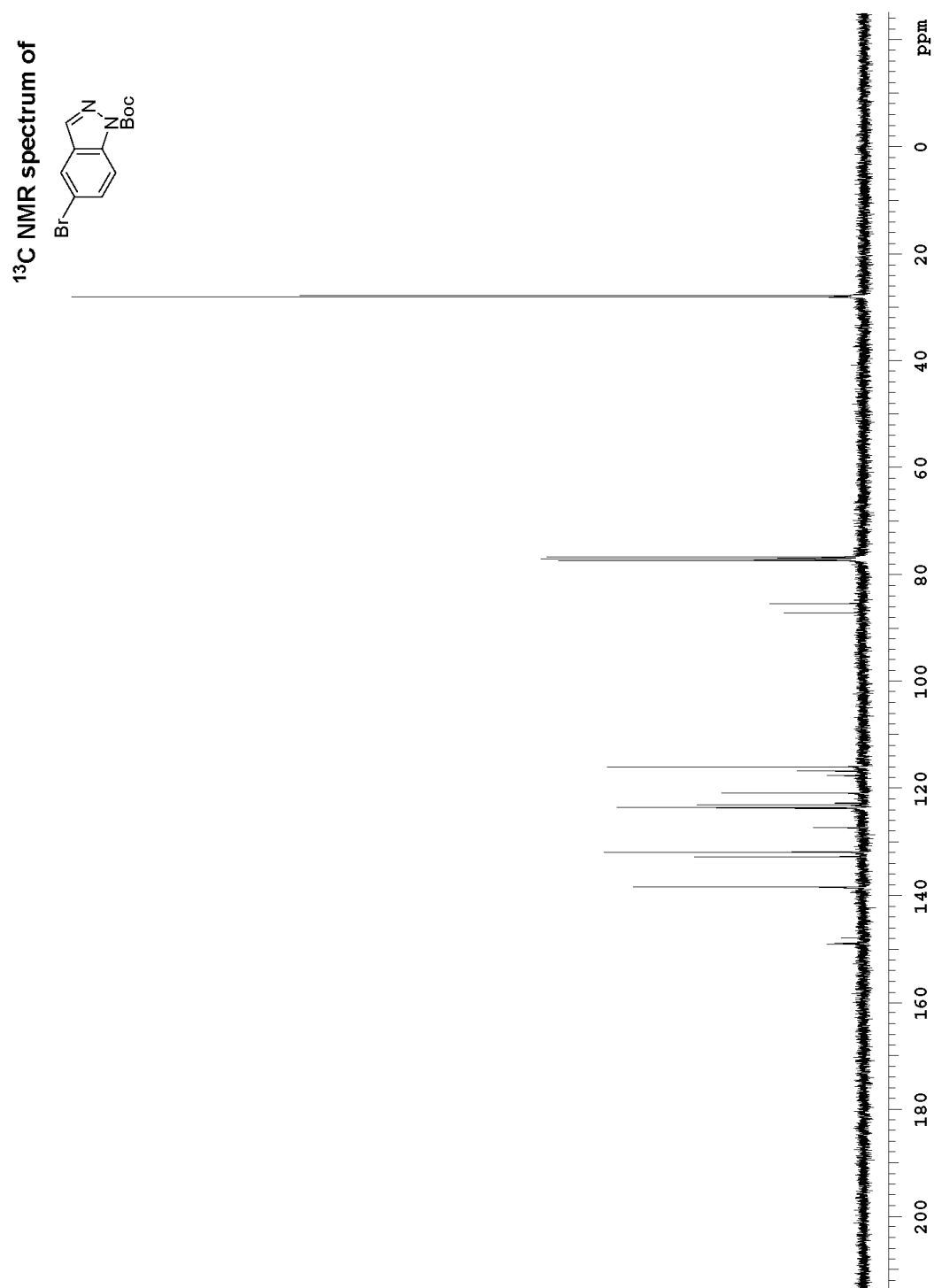
^{13}C NMR (CDCl_3 , 23 °C) of **S1**



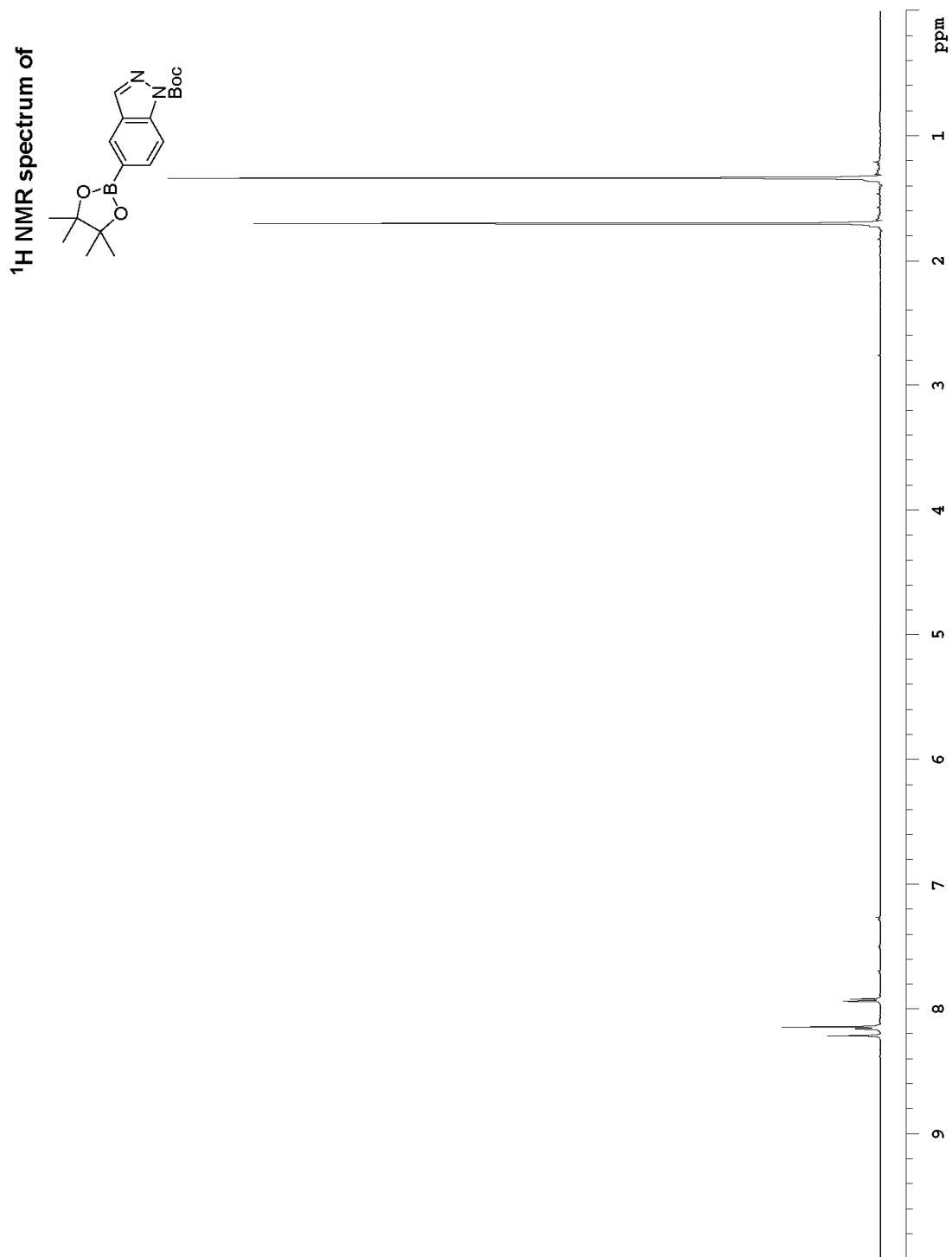
^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **S2**

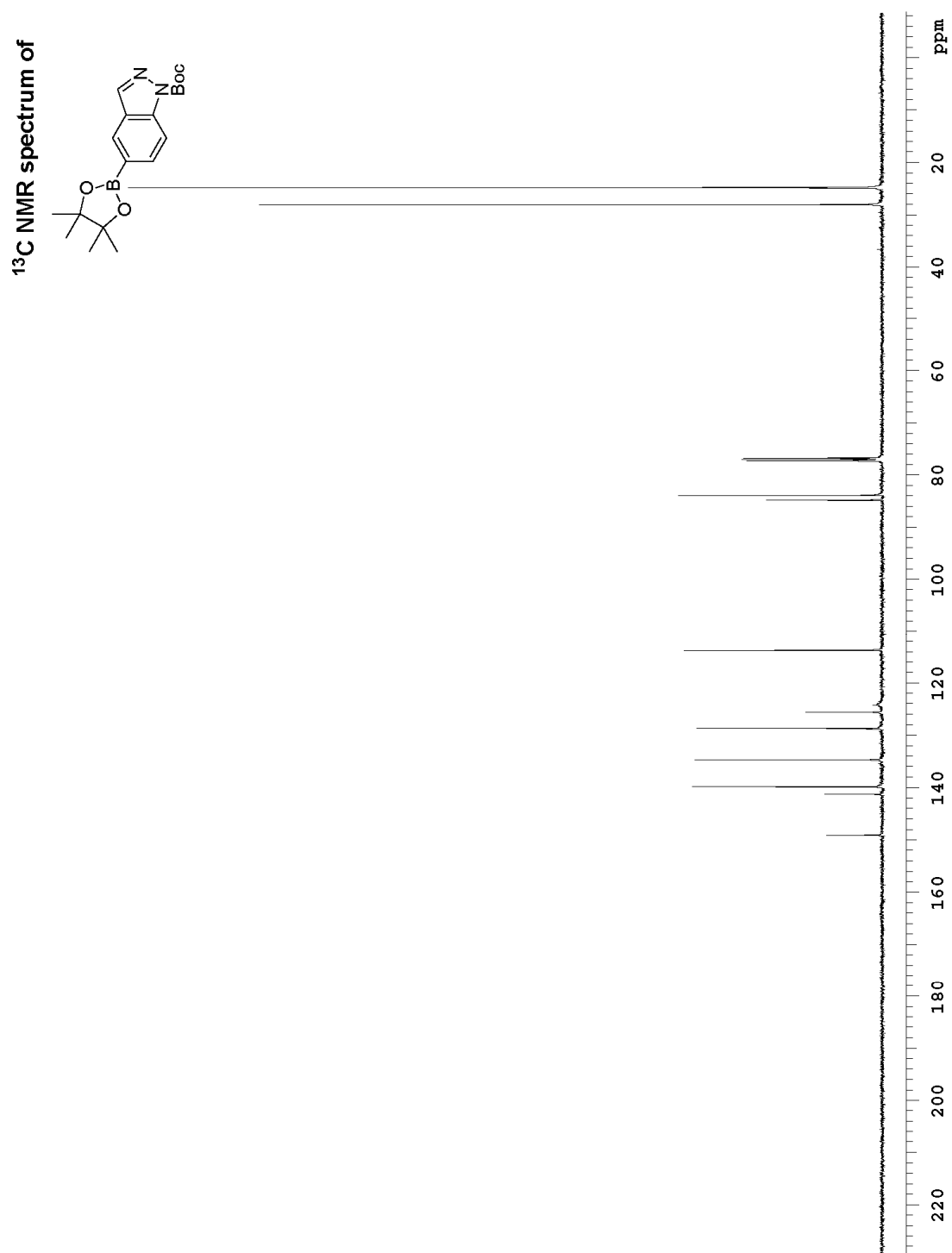


^{13}C NMR (CDCl_3 , 23 °C) of **S2**

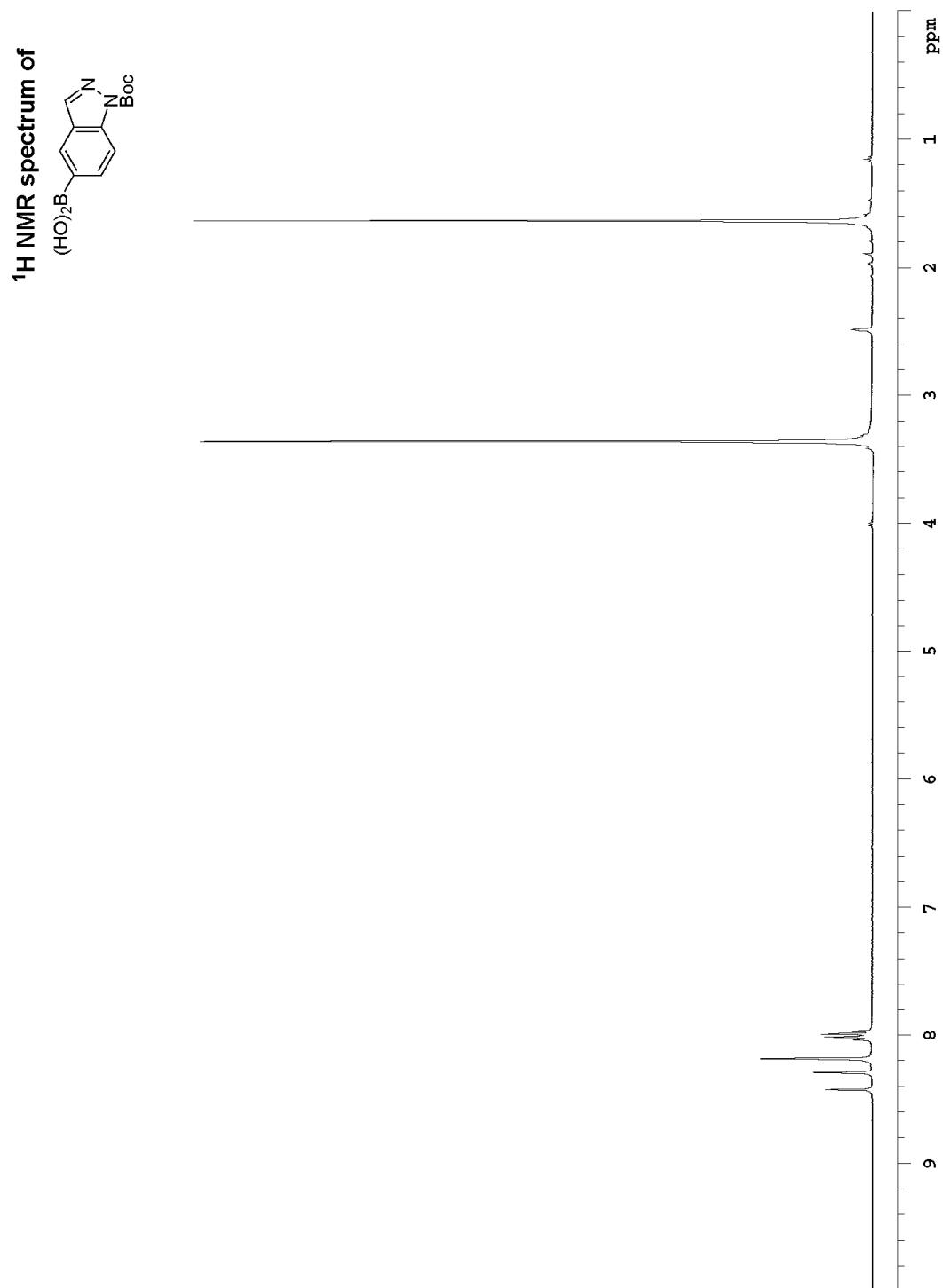


^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **S3**

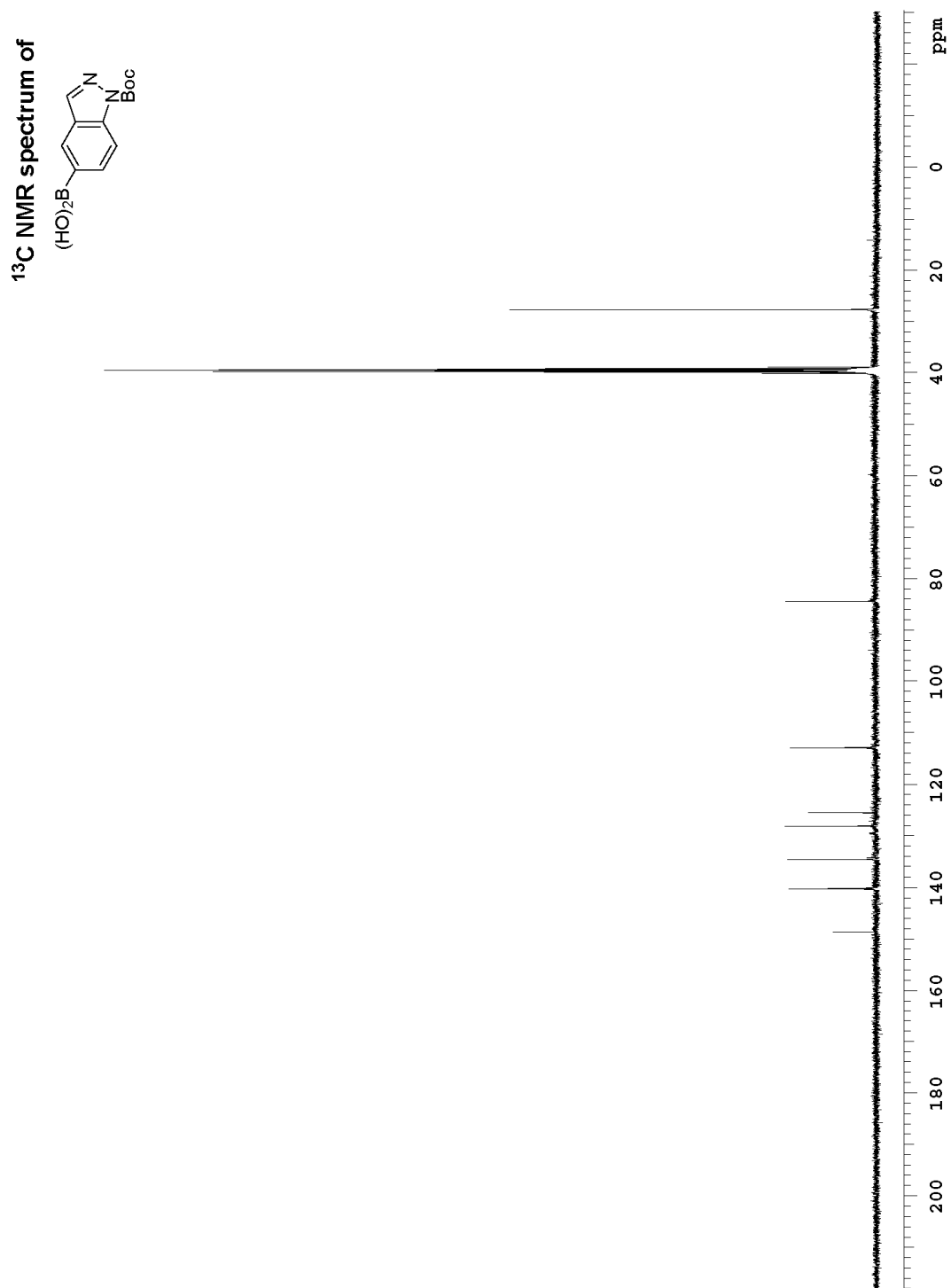




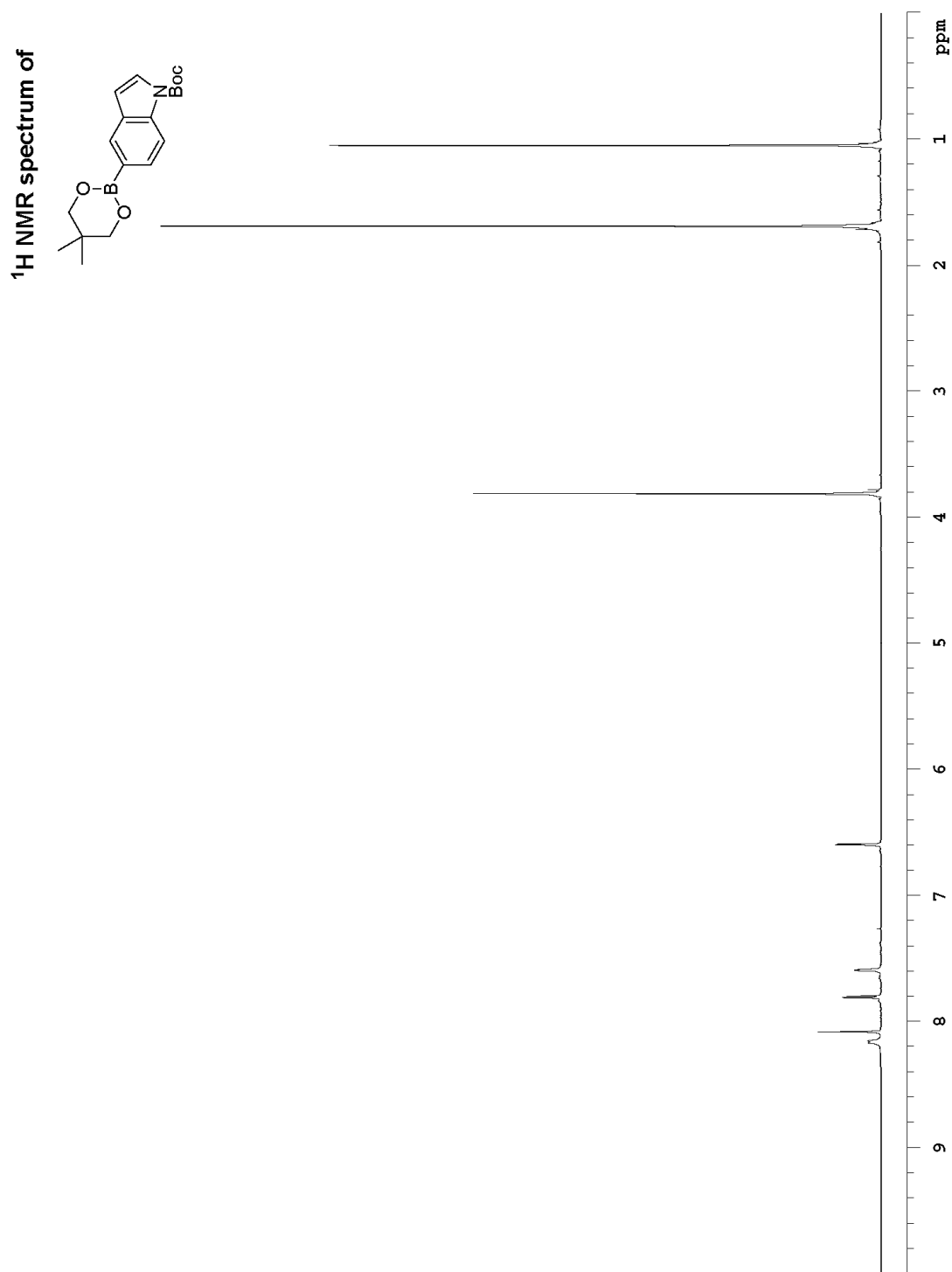
^1H NMR (DMSO- d_6 , 23 °C) of **S4**



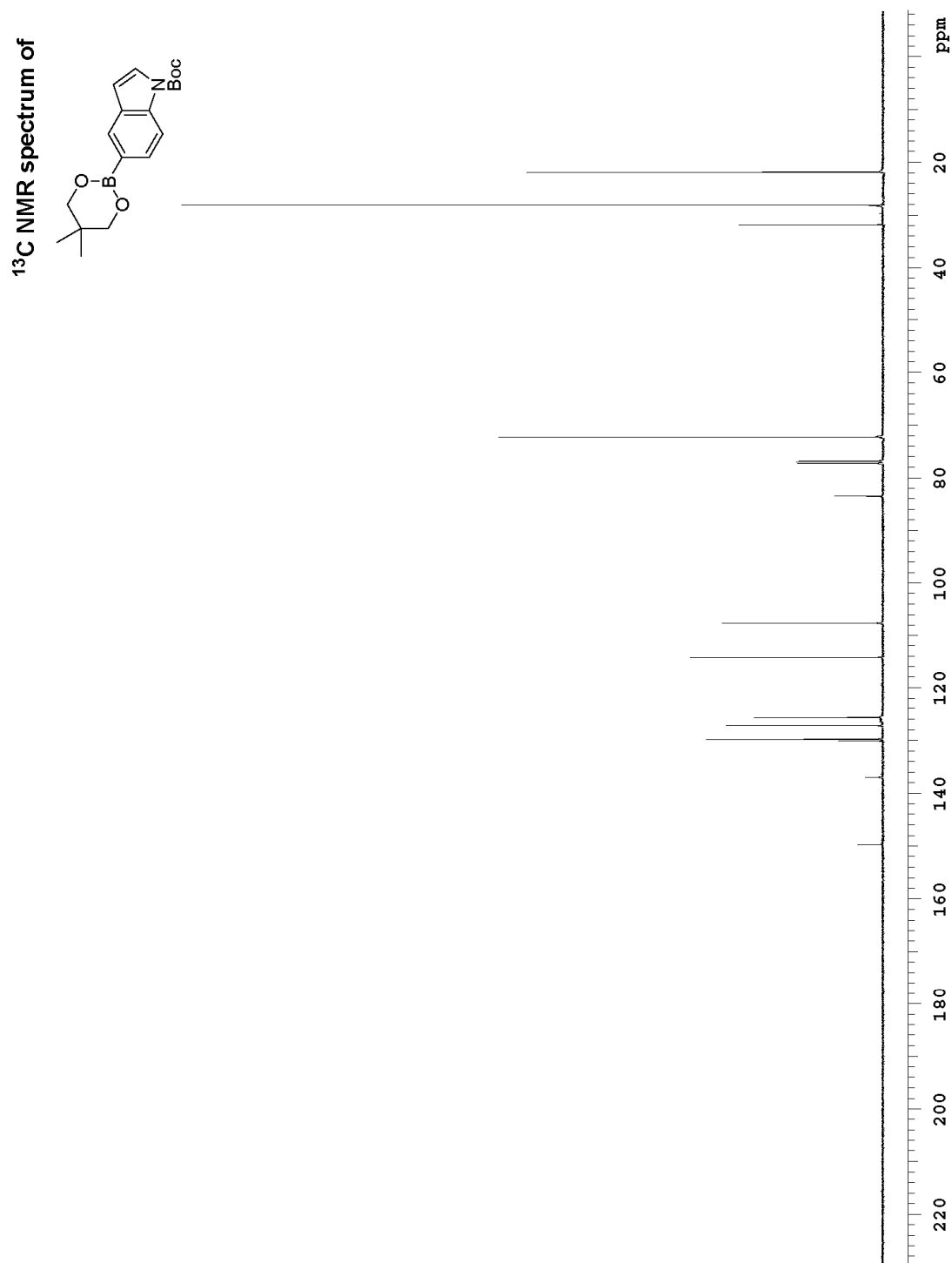
^{13}C NMR (DMSO- d_6 , 23 °C) of **S4**



^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **28b**

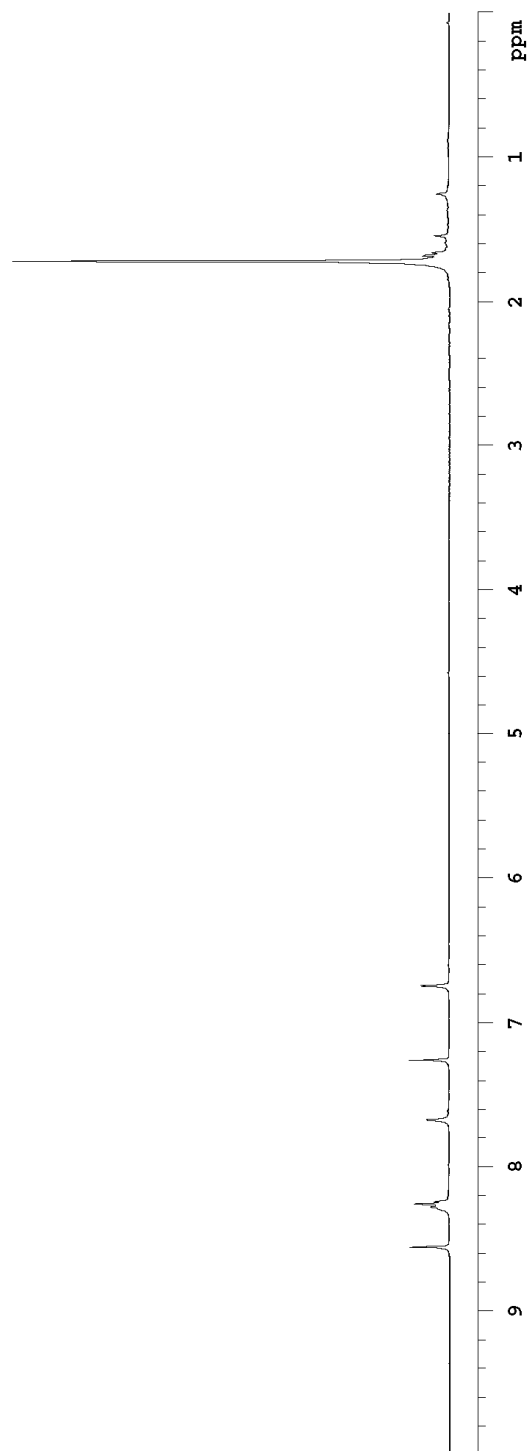
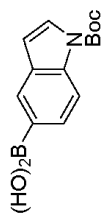


^{13}C NMR (CDCl_3 , 23 $^\circ\text{C}$) of **28b**

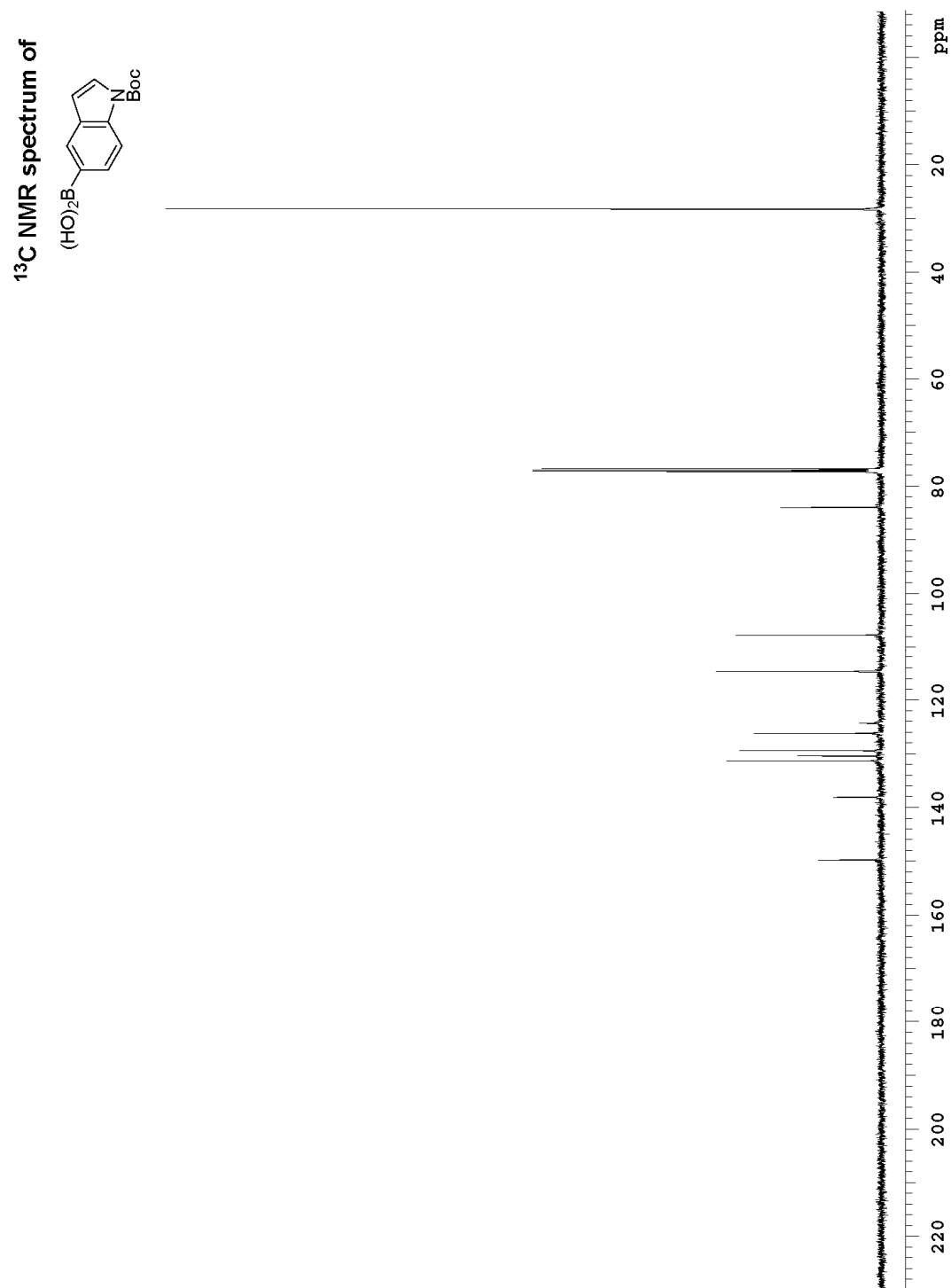


^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **28a**

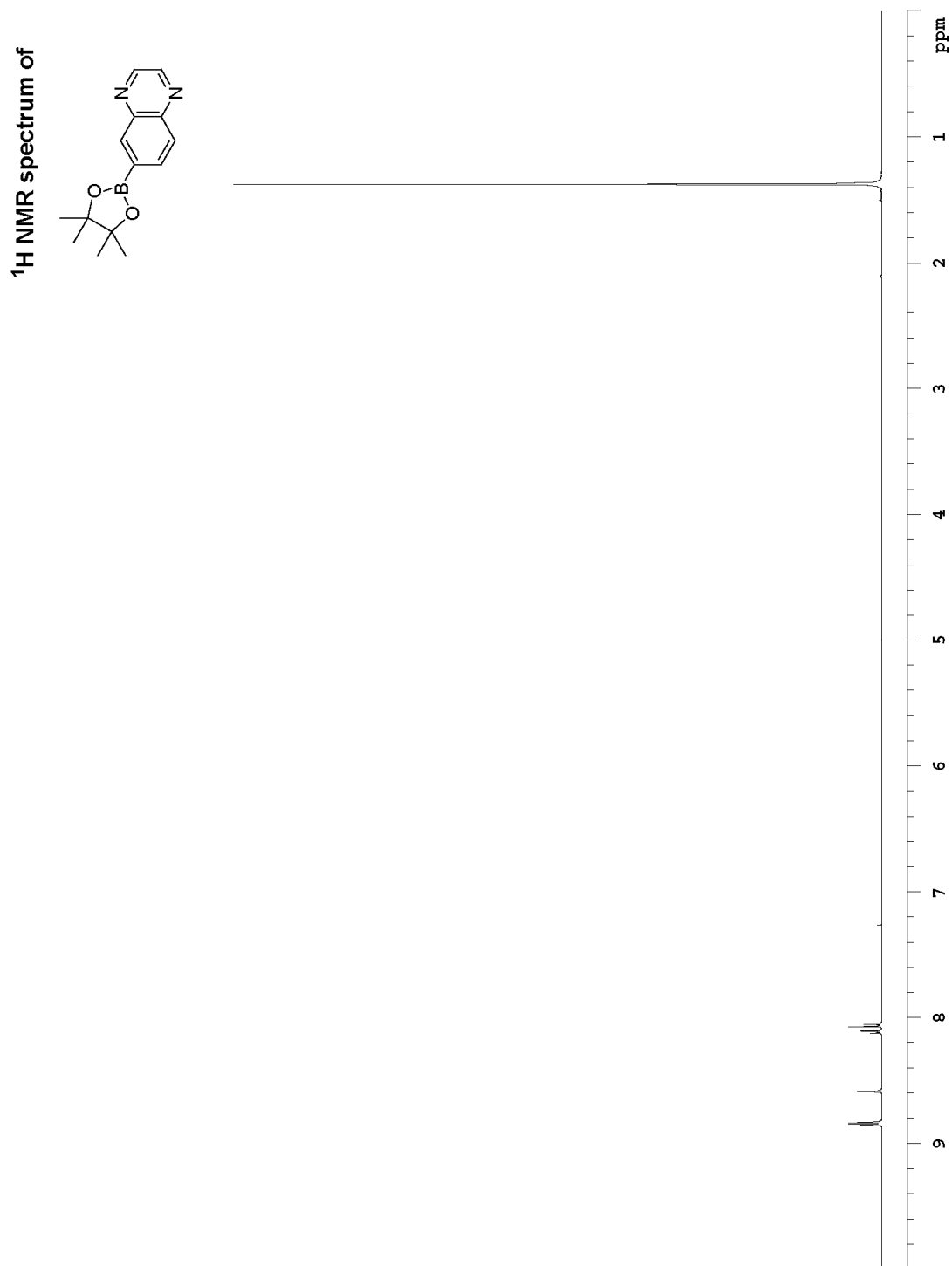
^1H NMR spectrum of



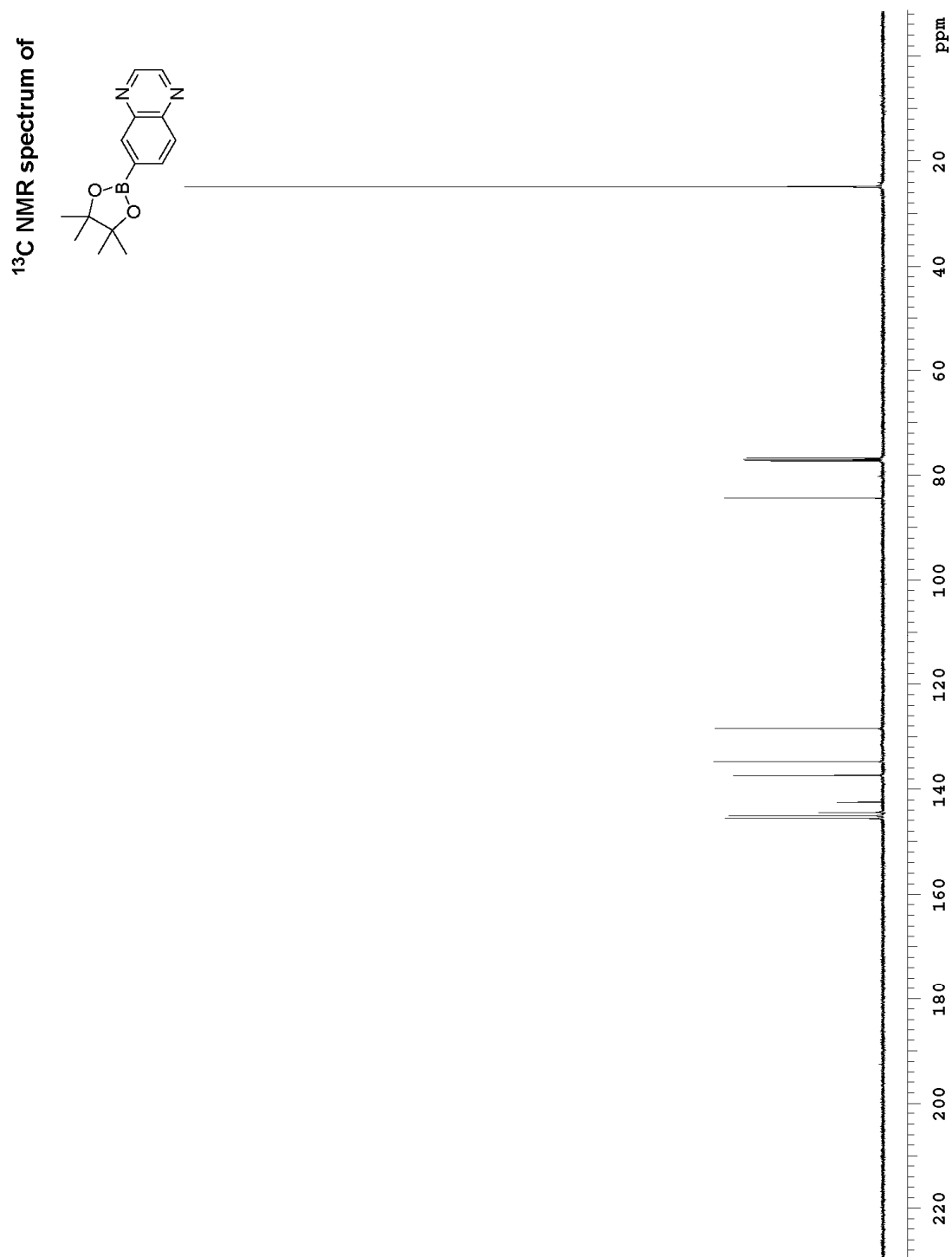
^{13}C NMR (CDCl_3 , 23 °C) of **28a**



^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **S5**

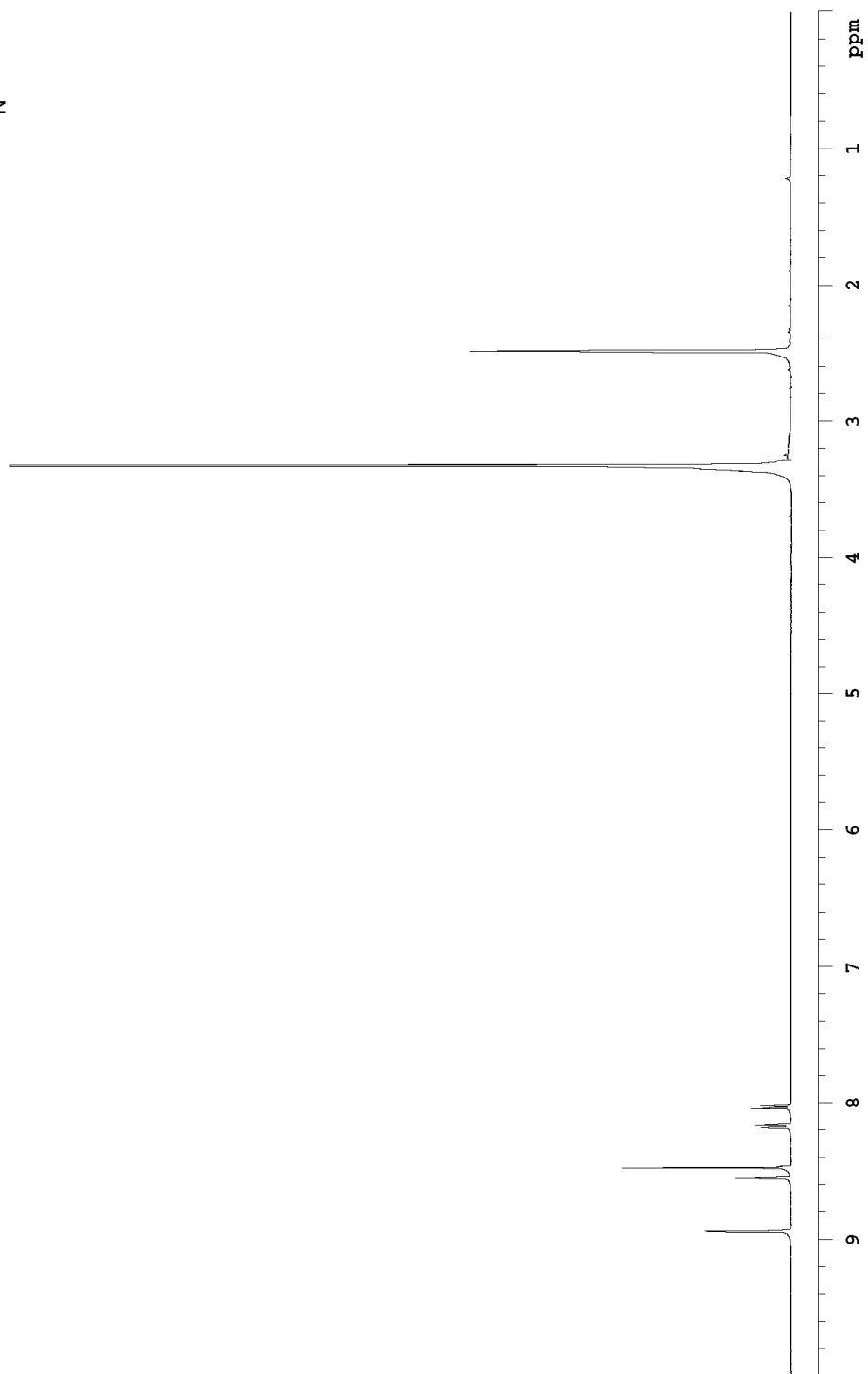
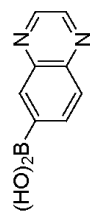


^{13}C NMR (CDCl_3 , 23 °C) of **S5**

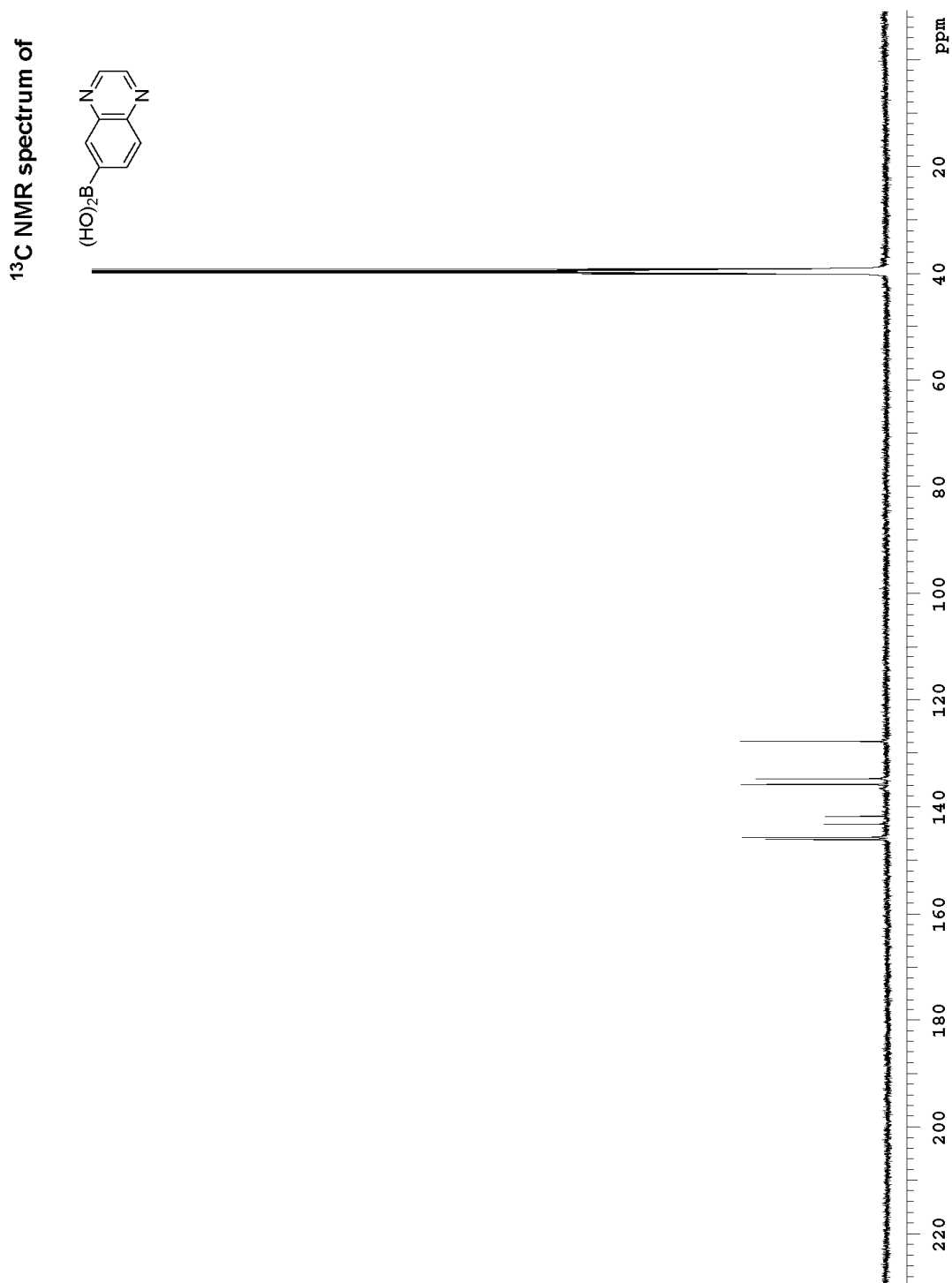


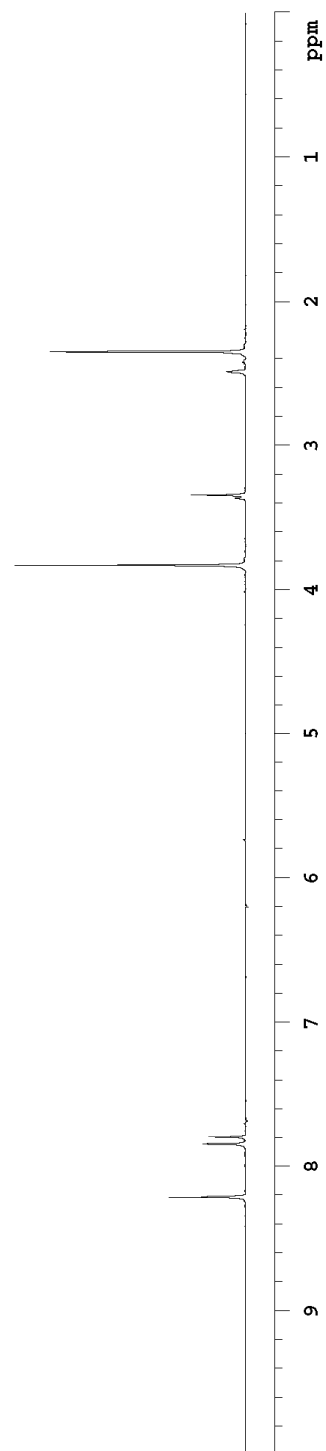
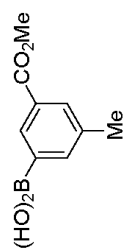
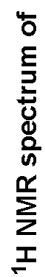
^1H NMR (DMSO- d_6 , 23 °C) of **S6**

^1H NMR spectrum of

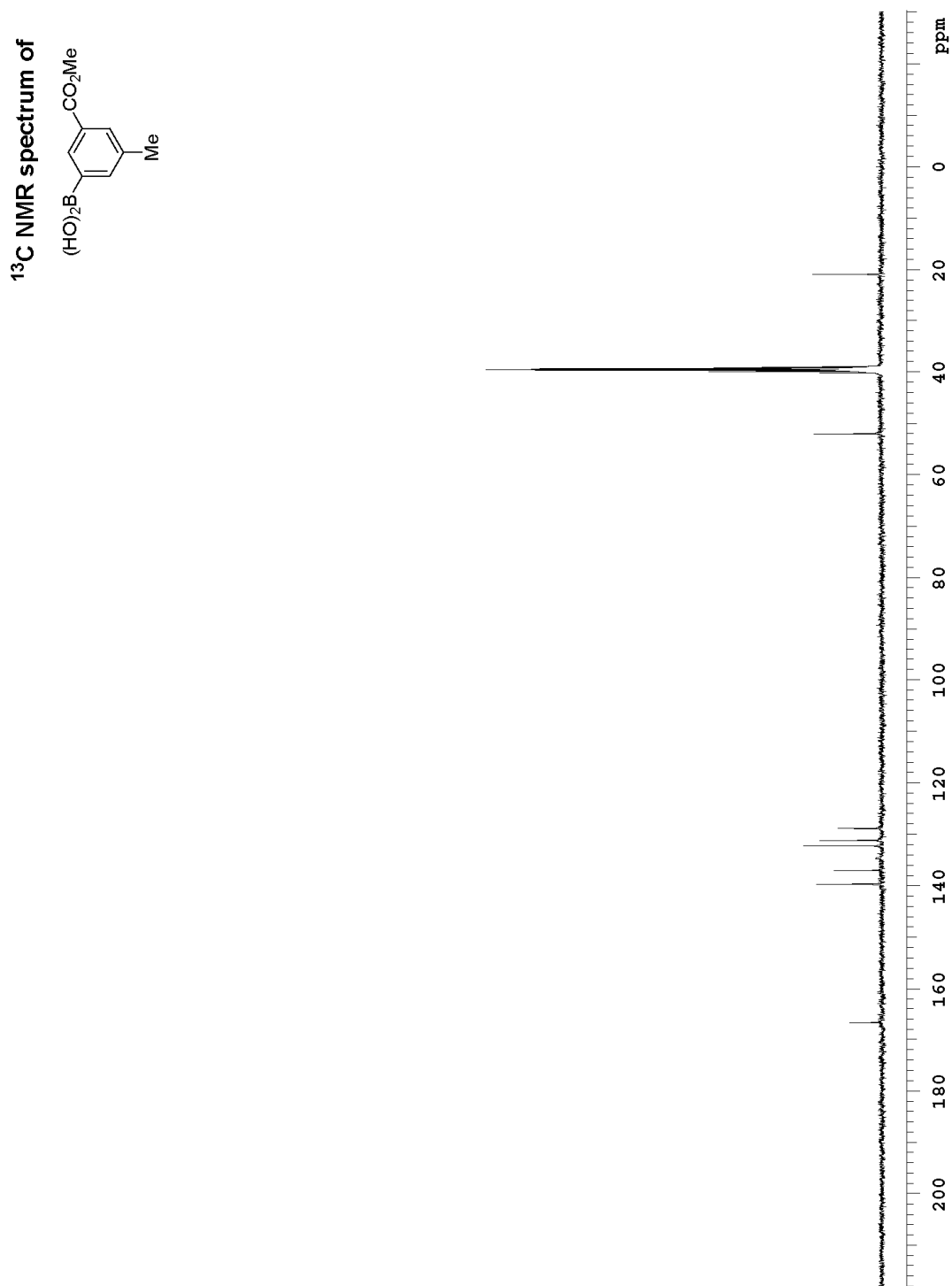


^{13}C NMR (DMSO- d_6 , 23 °C) of **S6**



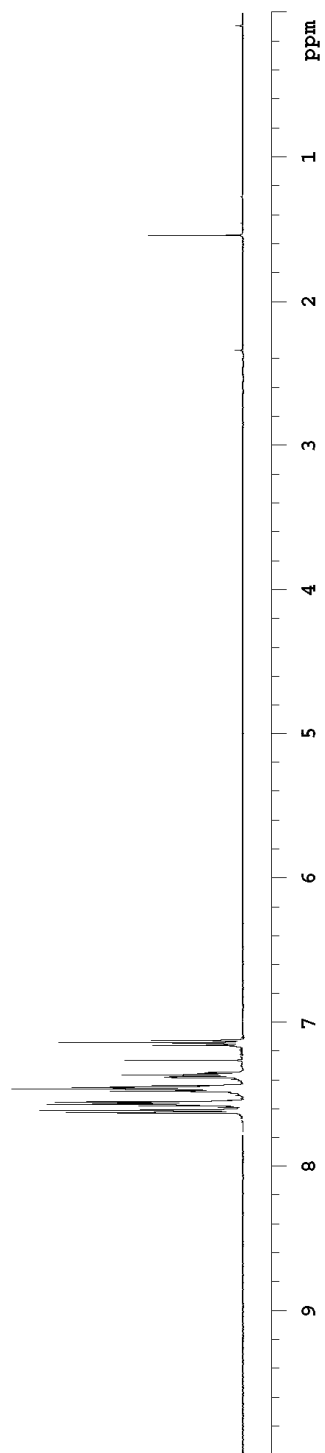
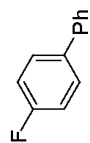


^{13}C NMR (DMSO- d_6 , 23 °C) of **S7**



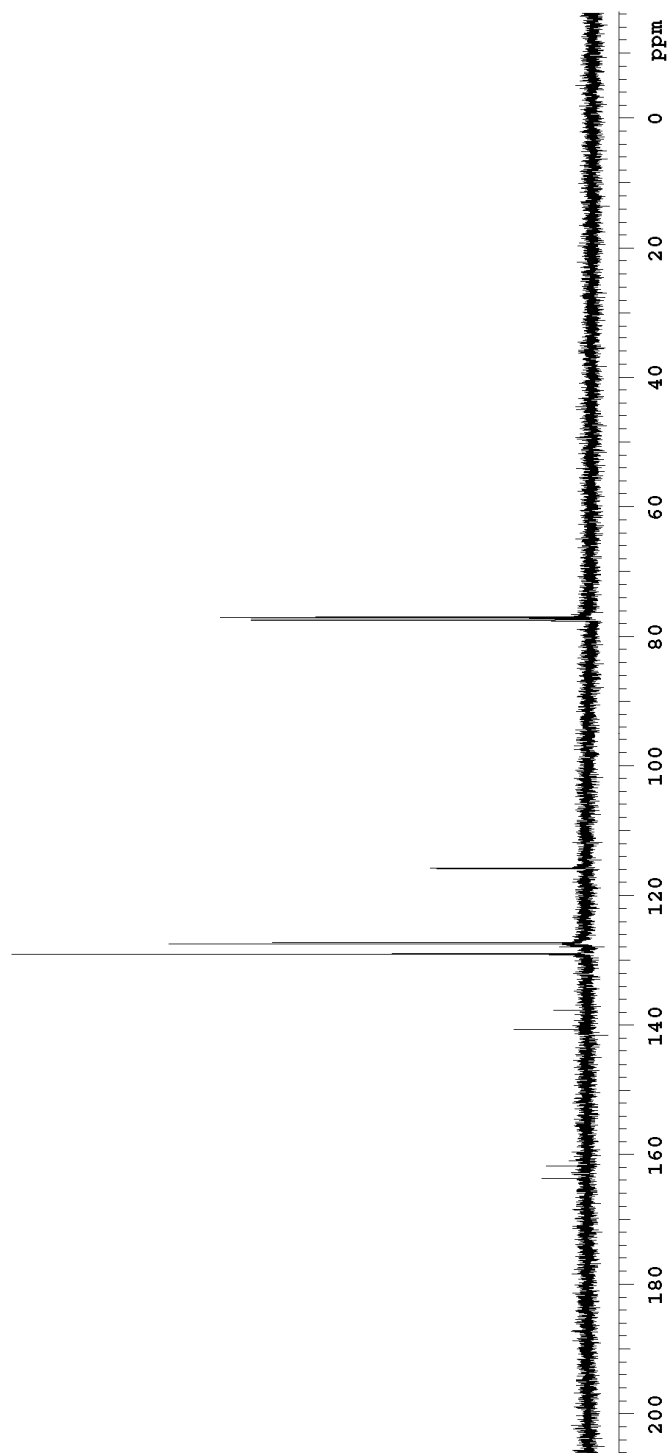
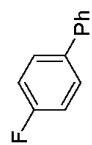
^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **6**

^1H NMR spectrum of



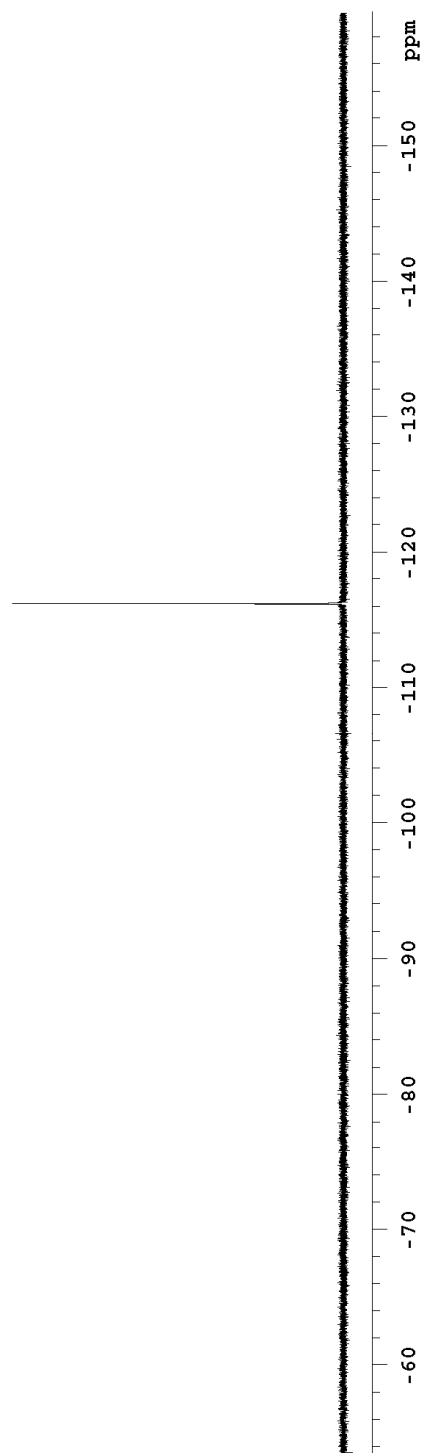
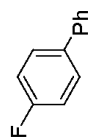
^{13}C NMR (CDCl_3 , 23 $^\circ\text{C}$) of **6**

^{13}C NMR spectrum of



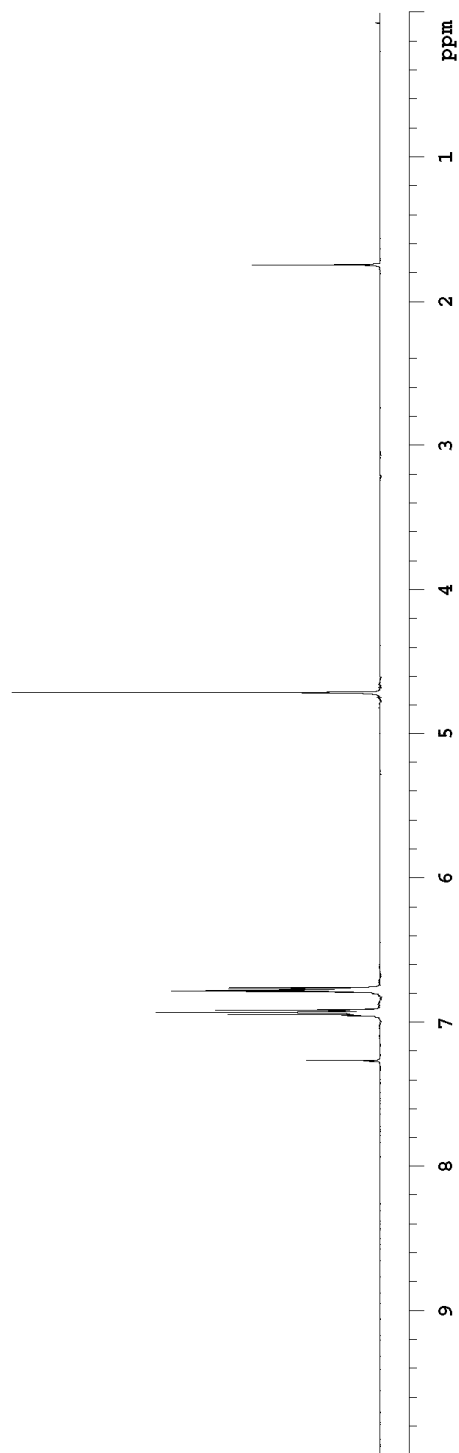
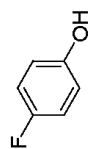
^{19}F NMR (CDCl_3 , 23 $^\circ\text{C}$) of **6**

^{19}F NMR spectrum of



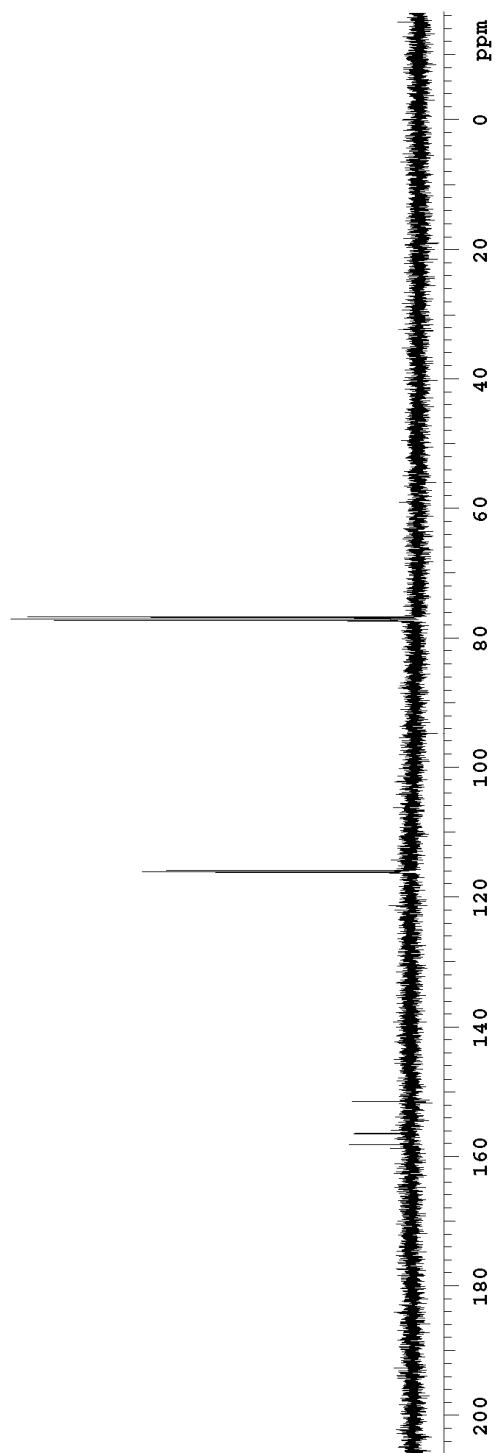
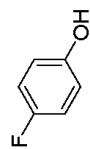
^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **8**

^1H NMR spectrum of



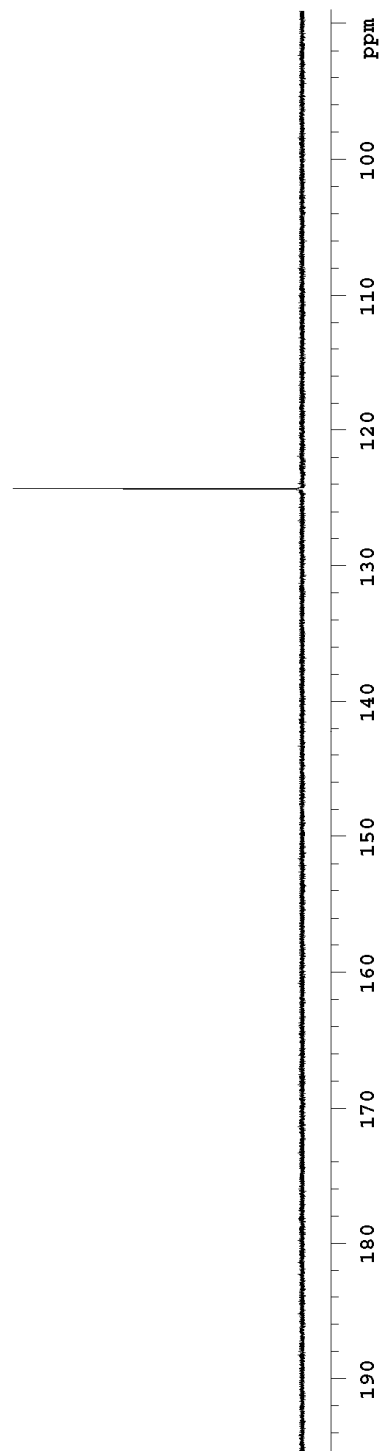
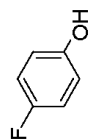
^{13}C NMR (CDCl_3 , 23 °C) of **8**

^{13}C NMR spectrum of



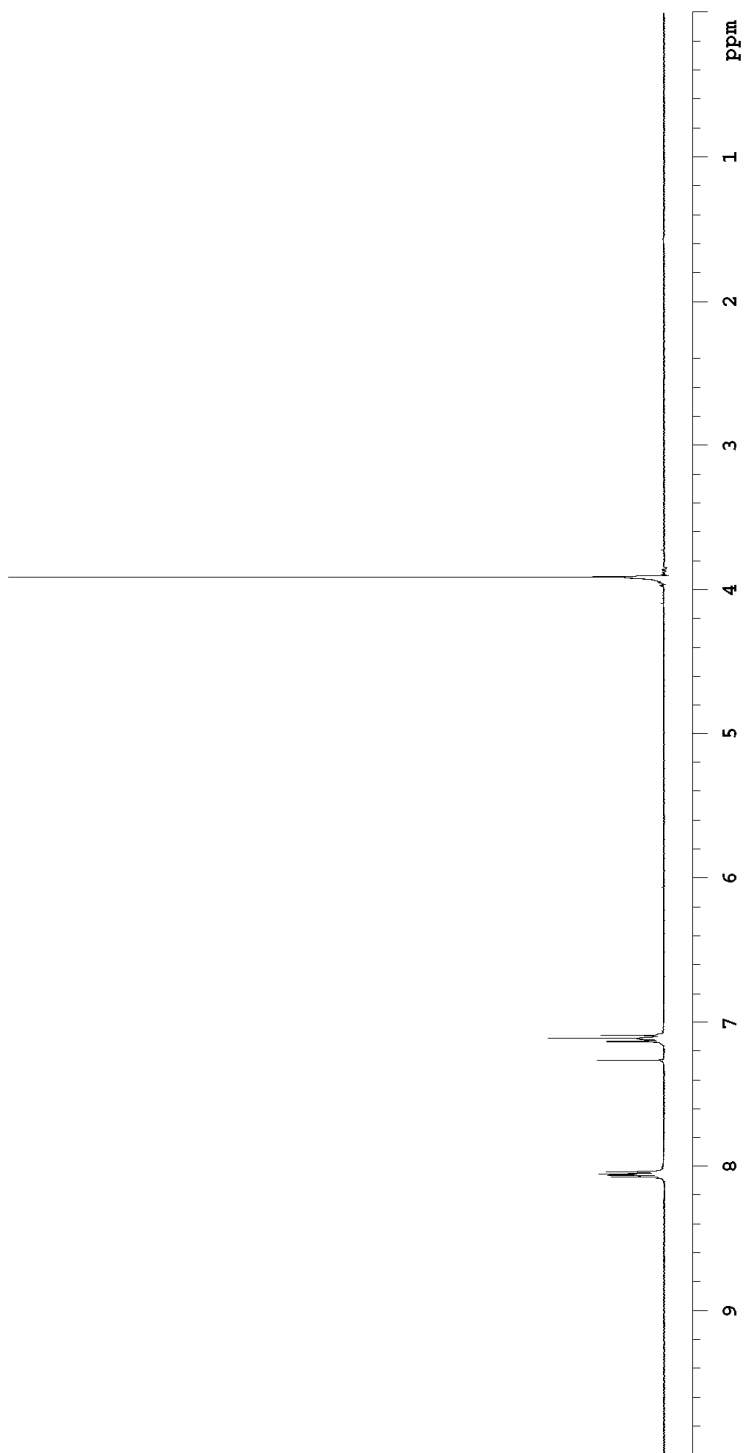
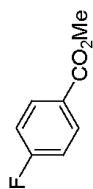
^{19}F NMR (CDCl_3 , 23 $^\circ\text{C}$) of **8**

^{19}F NMR spectrum of



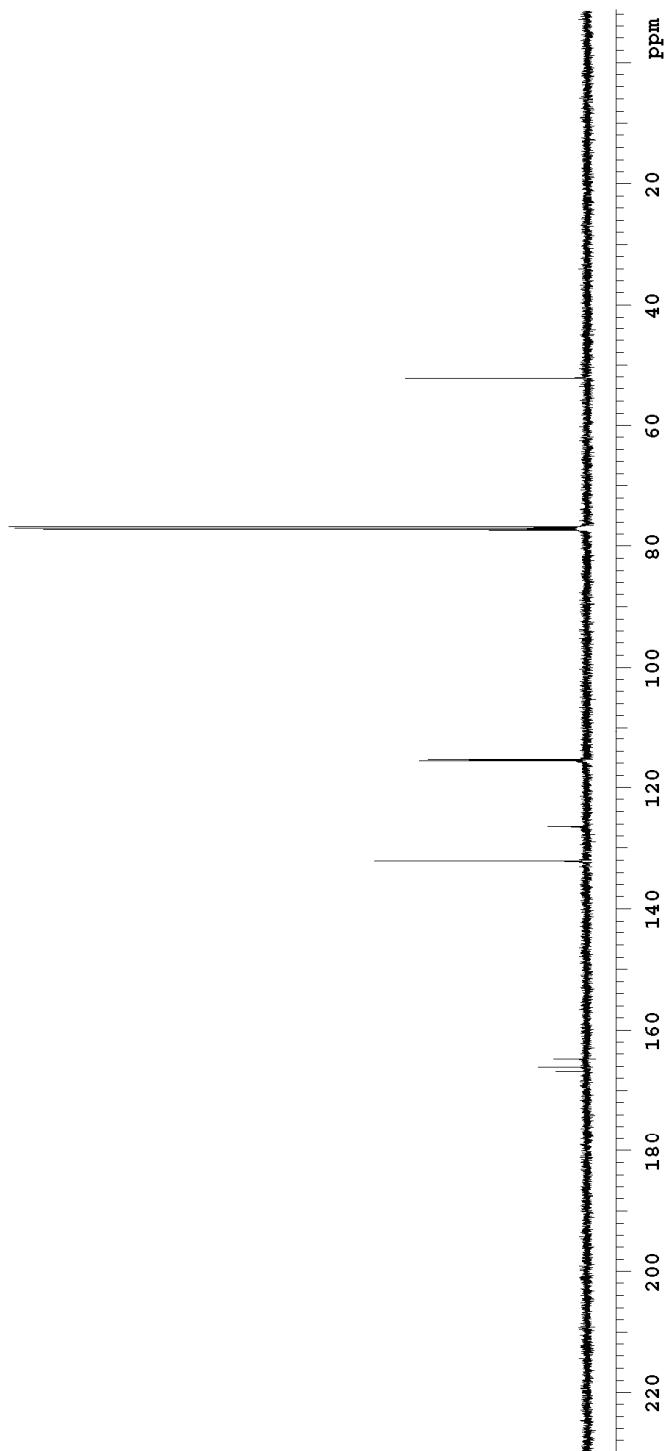
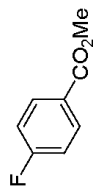
^1H NMR (CDCl_3 , 23 °C) of **12**

^1H NMR spectrum of

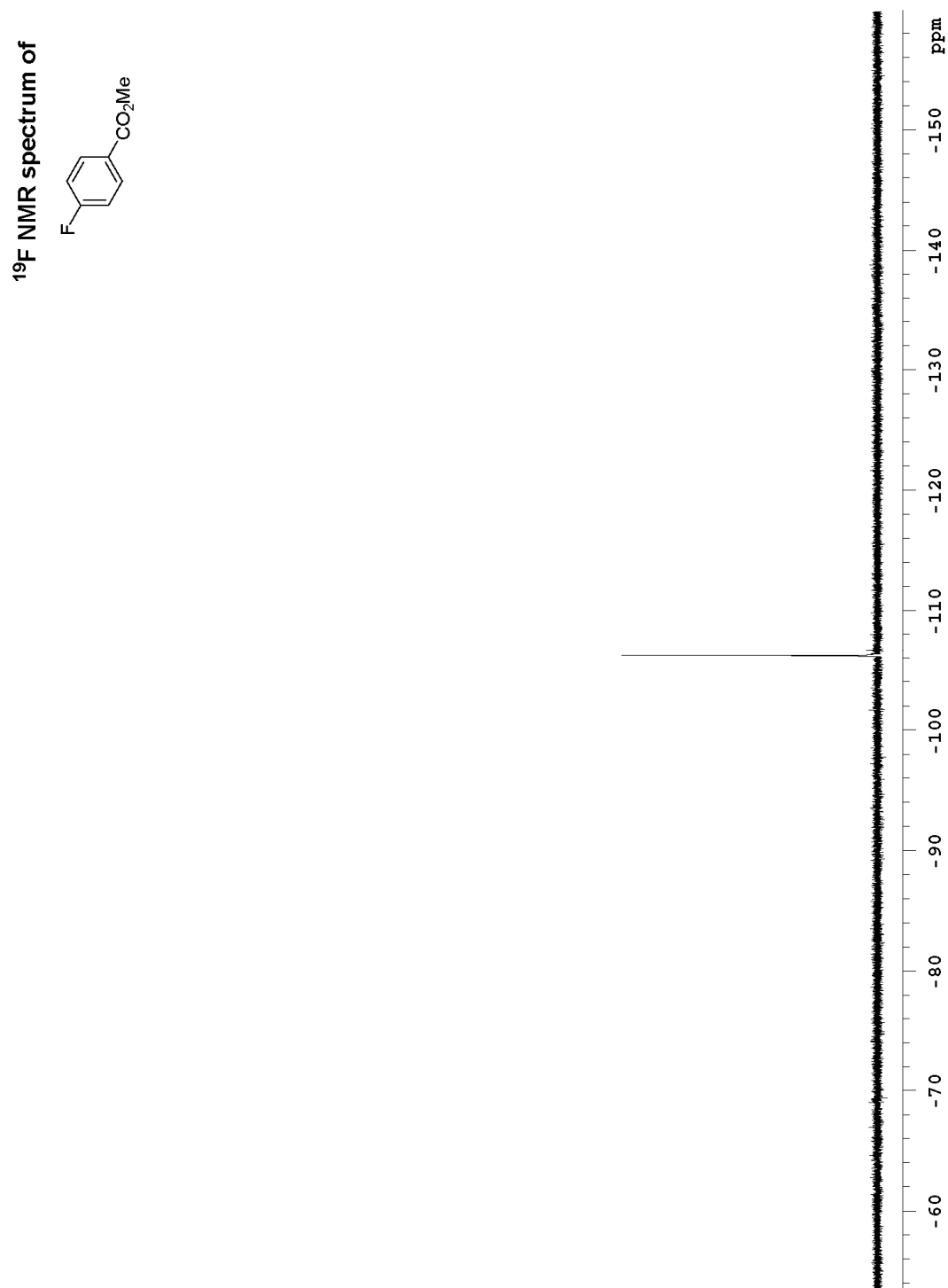


^{13}C NMR (CDCl_3 , 23 °C) of **12**

^{13}C NMR spectrum of

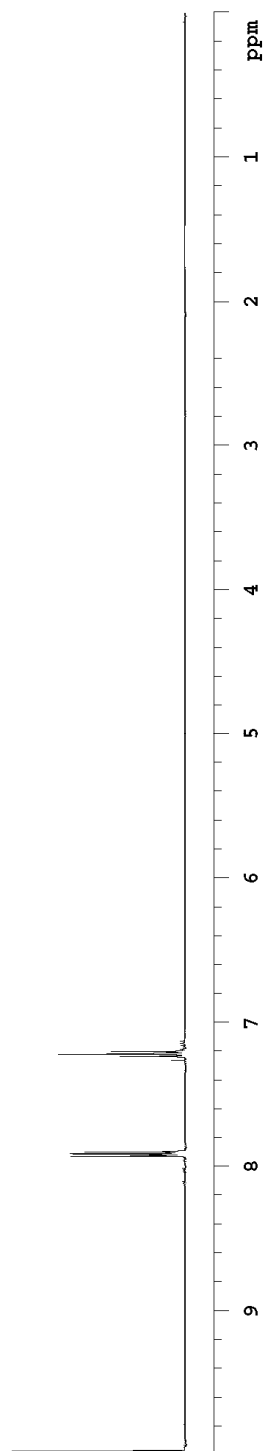
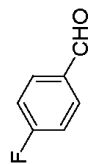


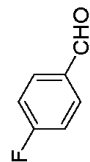
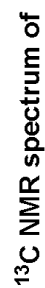
^{19}F NMR (CDCl_3 , 23 °C) of **12**



^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **14**

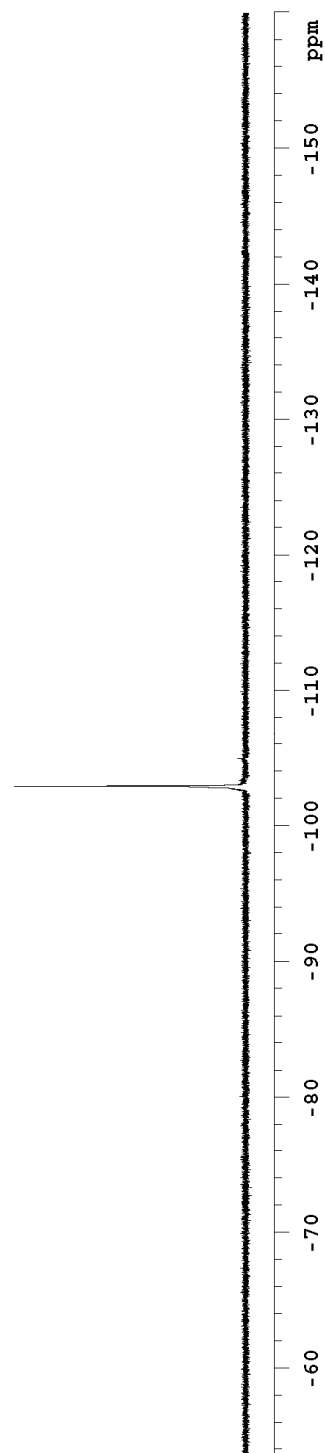
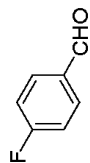
^1H NMR spectrum of





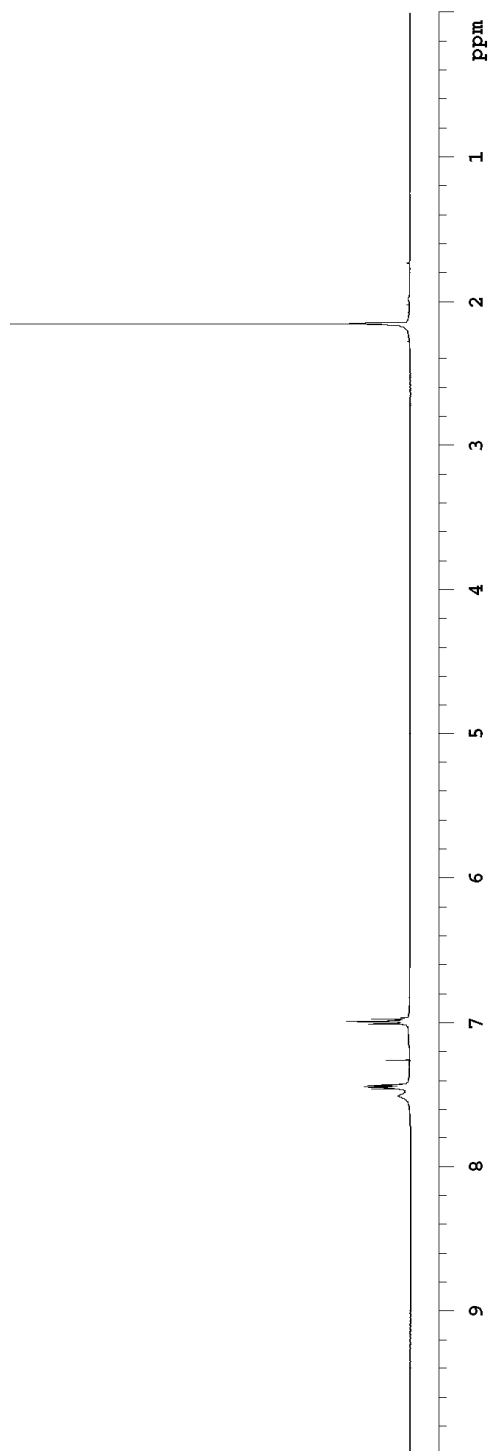
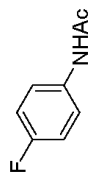
^{19}F NMR (CDCl_3 , 23 °C) of **14**

^{19}F NMR spectrum of



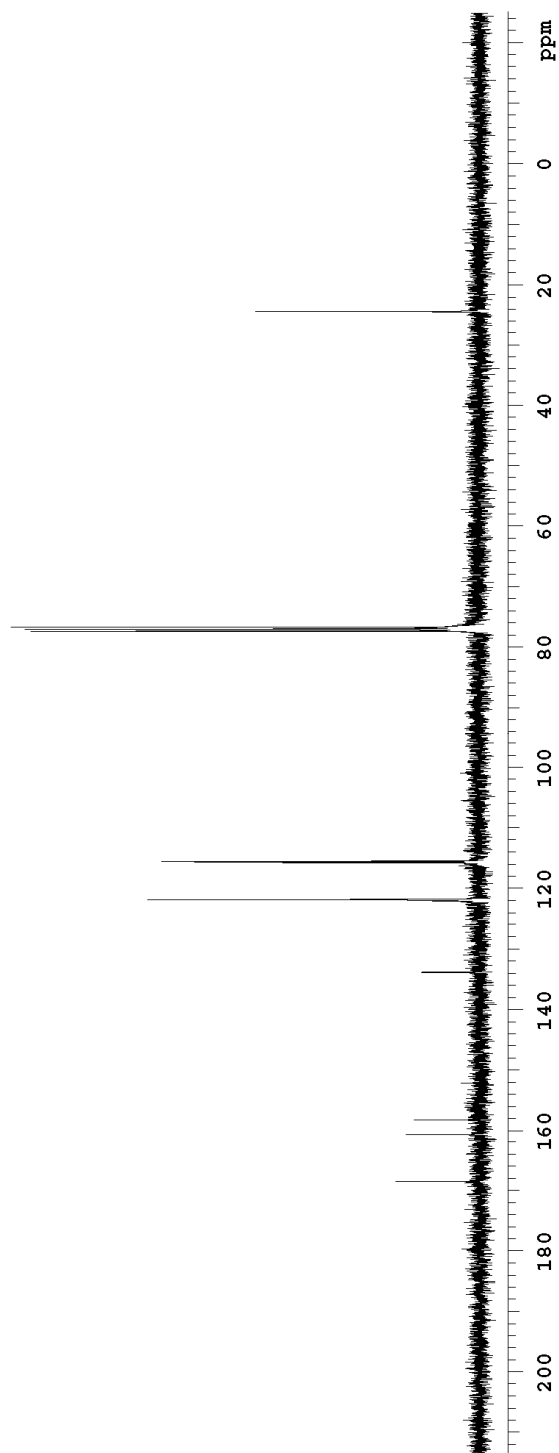
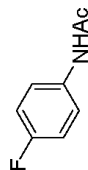
^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **16**

^1H NMR spectrum of



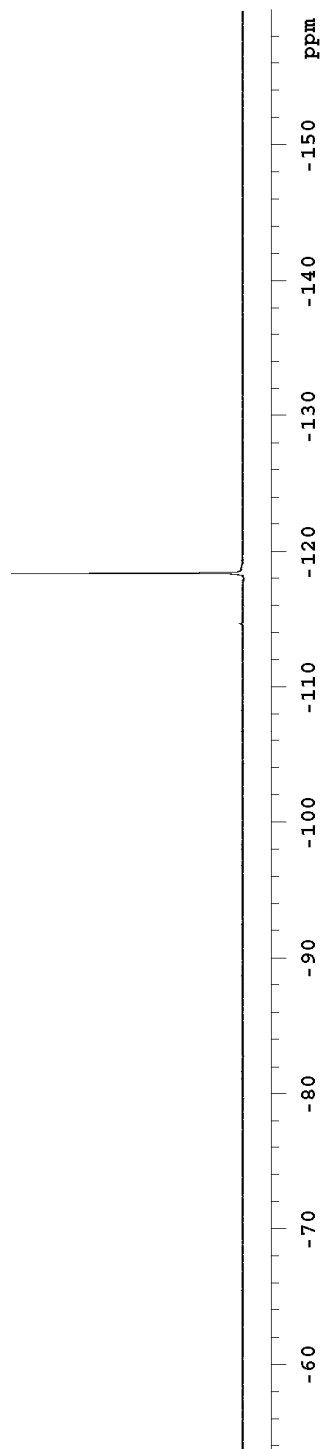
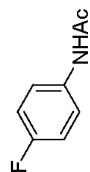
^{13}C NMR (CDCl_3 , 23 °C) of **16**

^{13}C NMR spectrum of



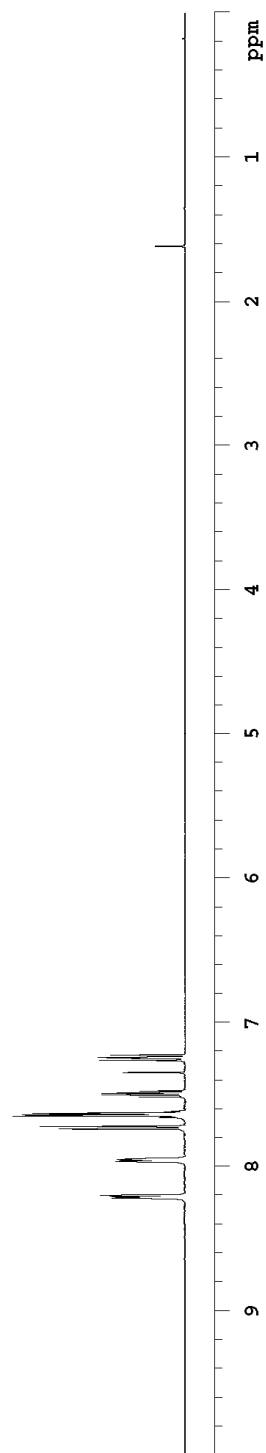
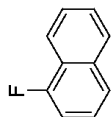
^{19}F NMR (CDCl_3 , 23 °C) of **16**

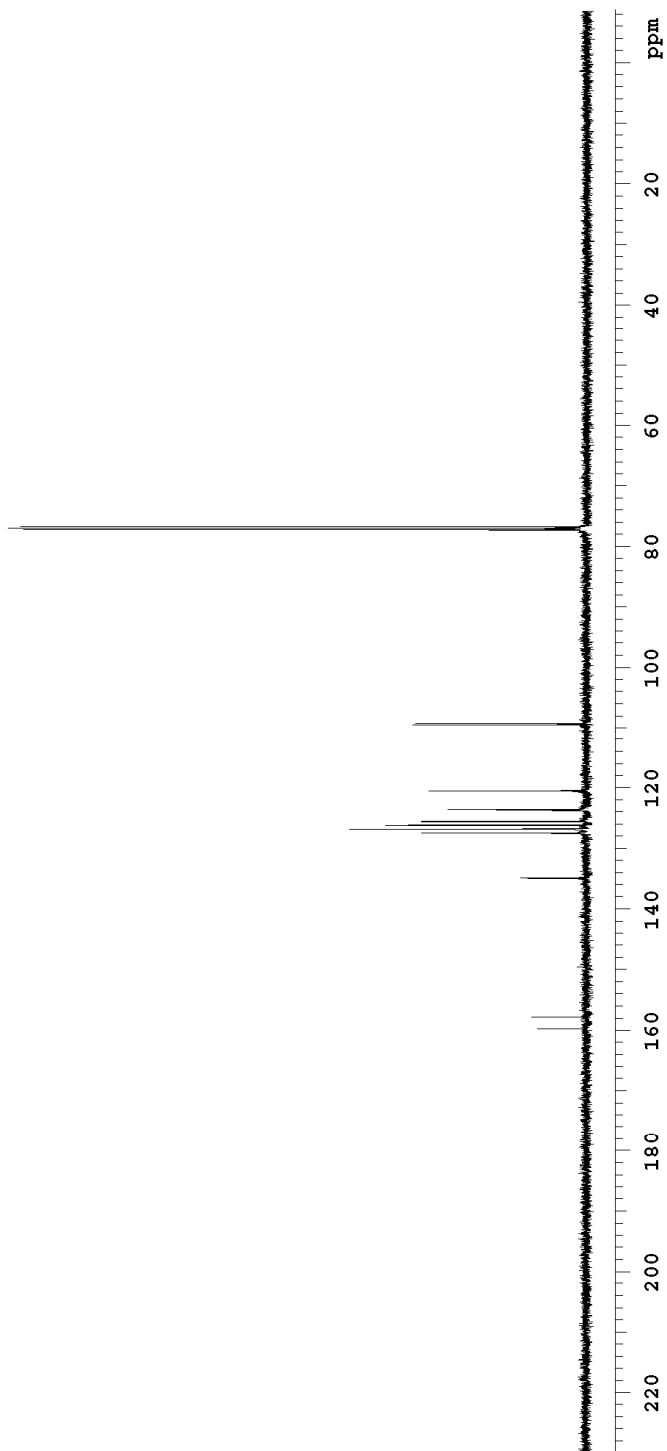
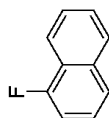
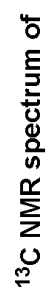
^{19}F NMR spectrum of



^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **19**

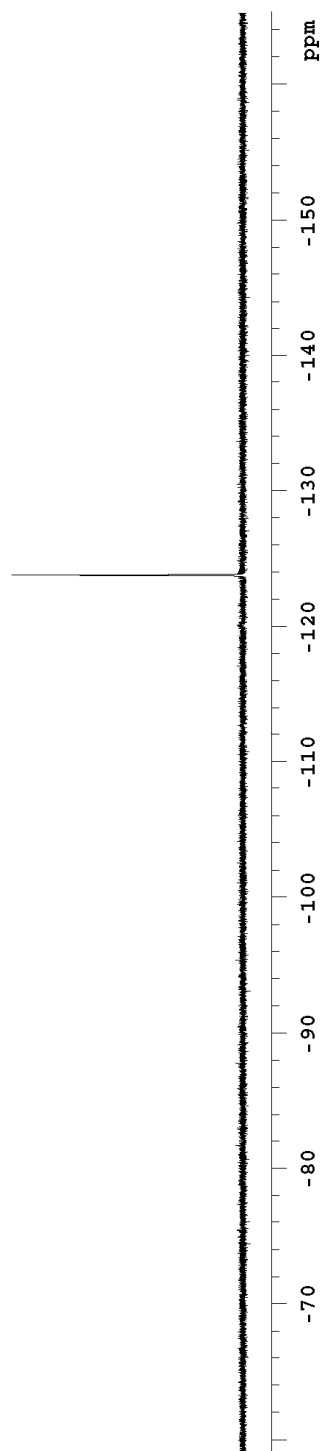
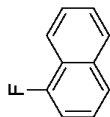
^1H NMR spectrum of



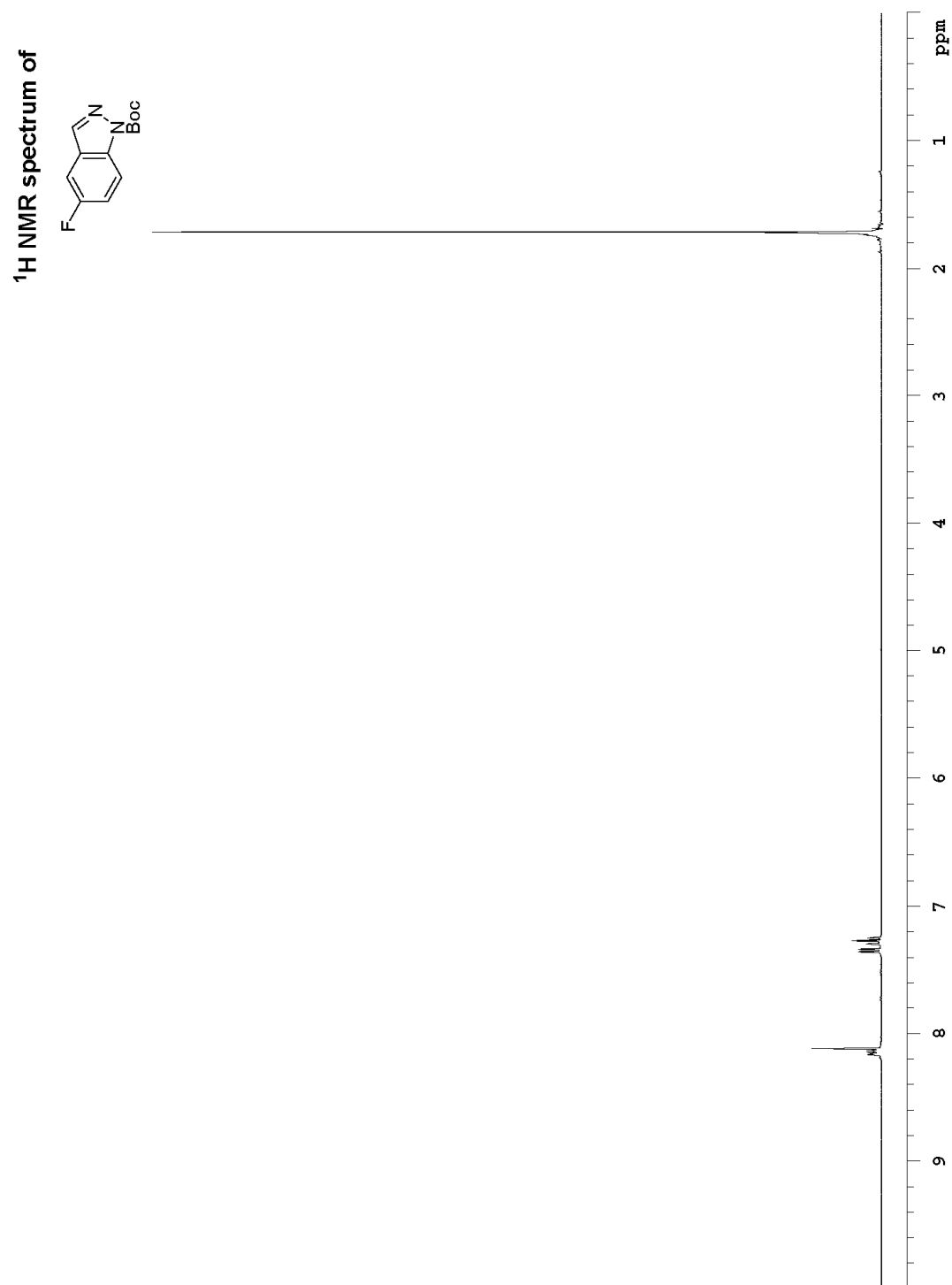


^{19}F NMR (CDCl_3 , 23 °C) of **19**

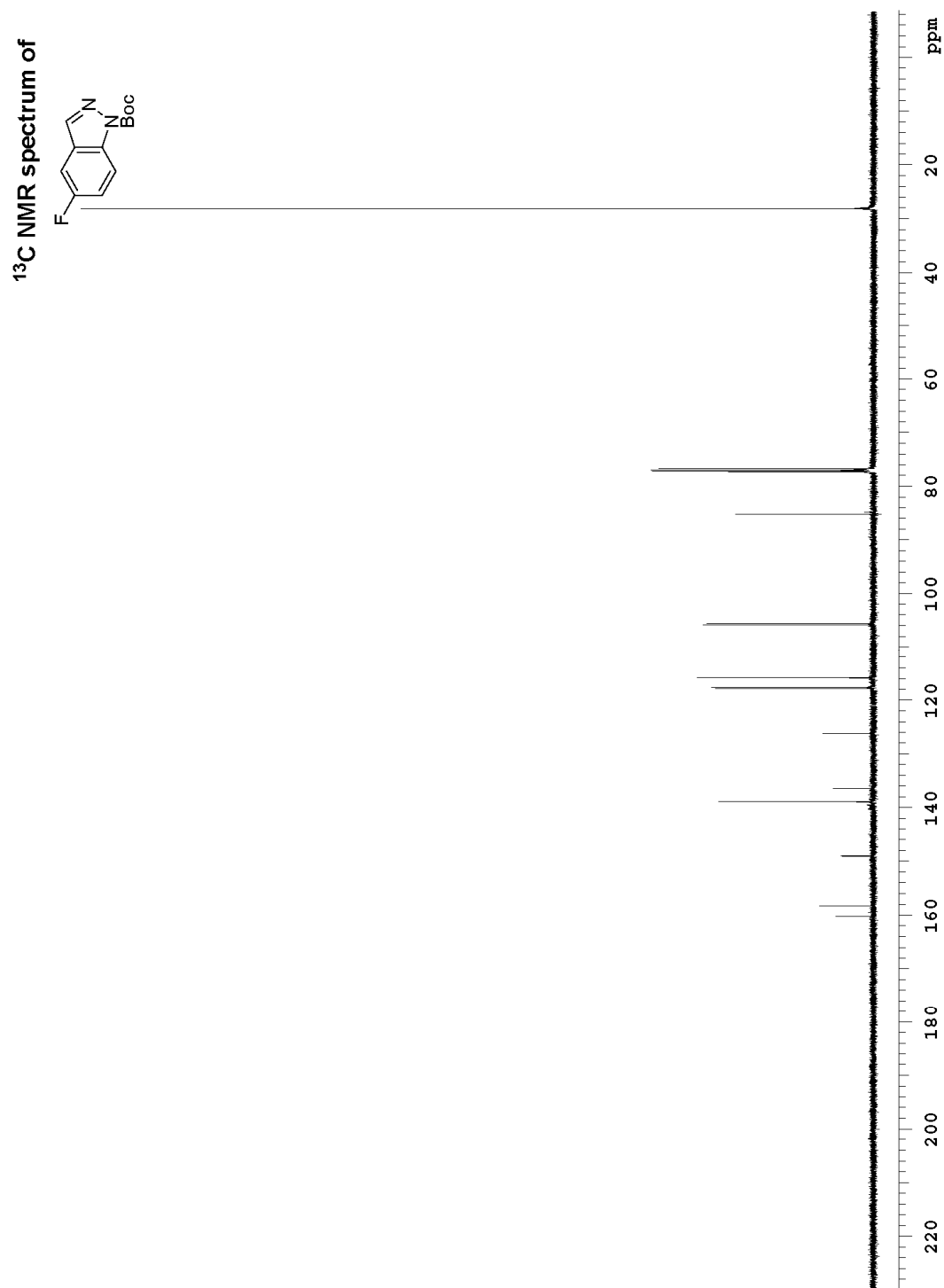
^{19}F NMR spectrum of



^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **20**

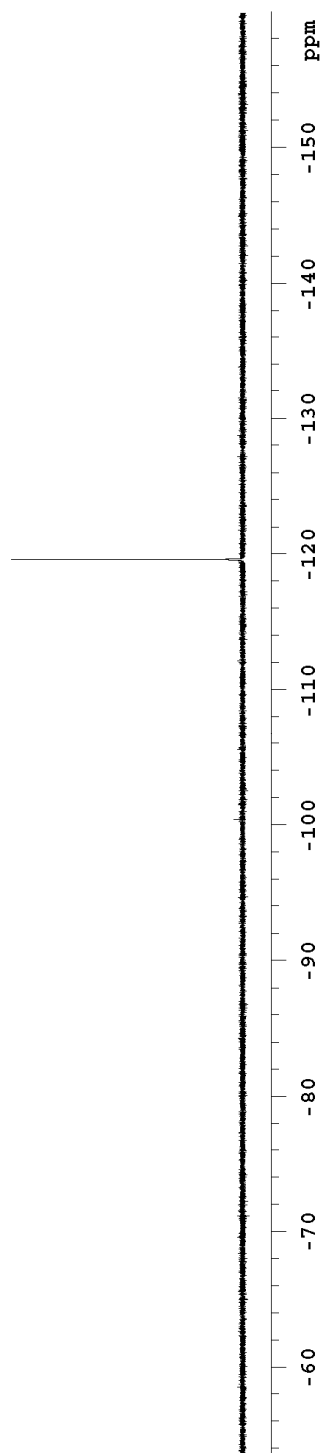
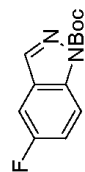


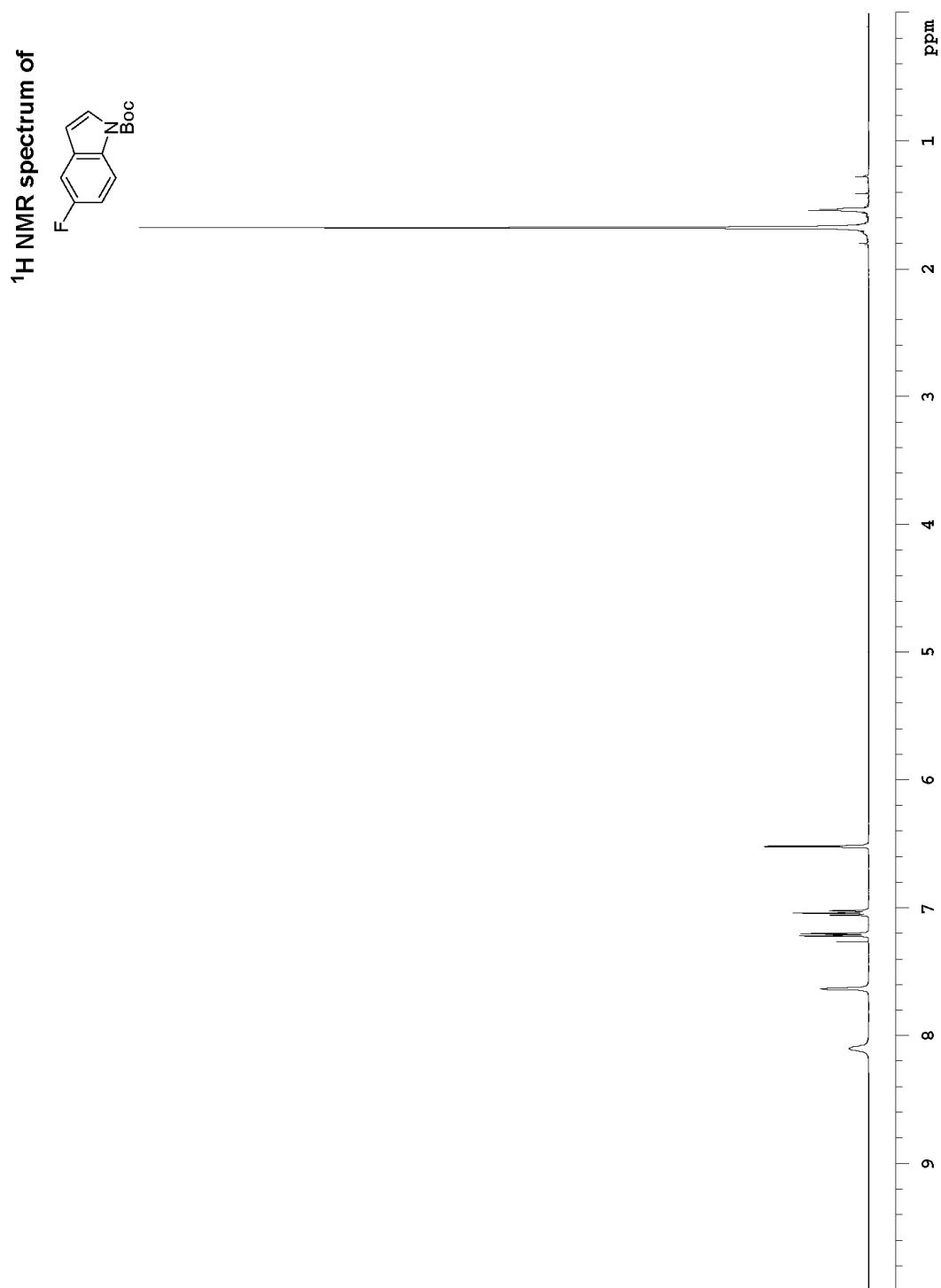
^{13}C NMR (CDCl_3 , 23 $^\circ\text{C}$) of **20**



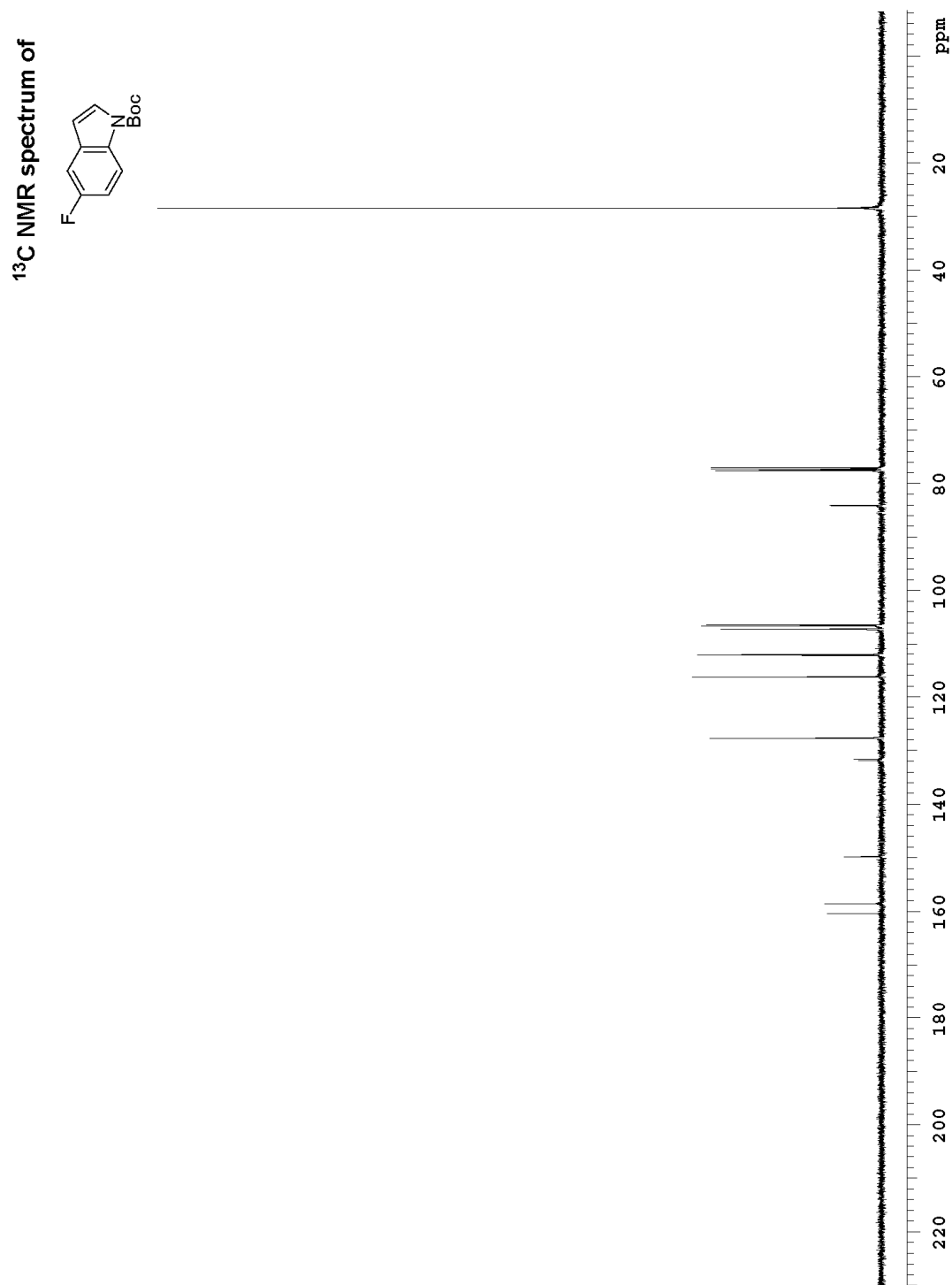
^{19}F NMR (CDCl_3 , 23 $^\circ\text{C}$) of **20**

^{19}F NMR spectrum of



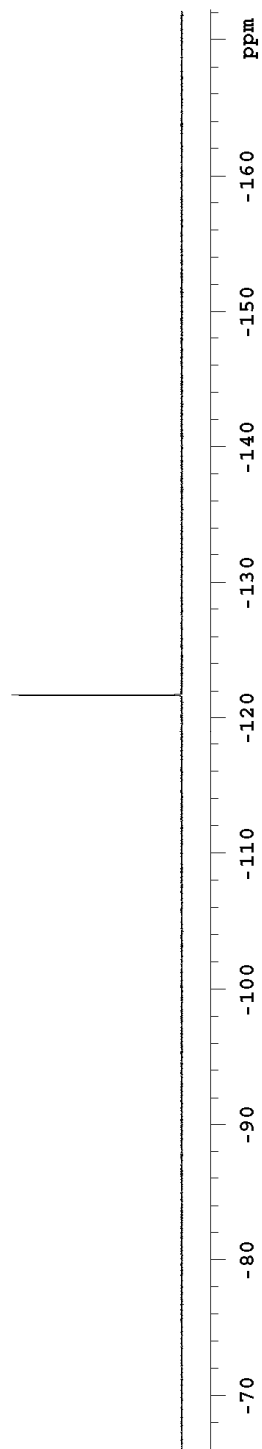
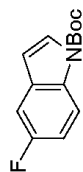


^{13}C NMR (CDCl_3 , 23 $^\circ\text{C}$) of **21**



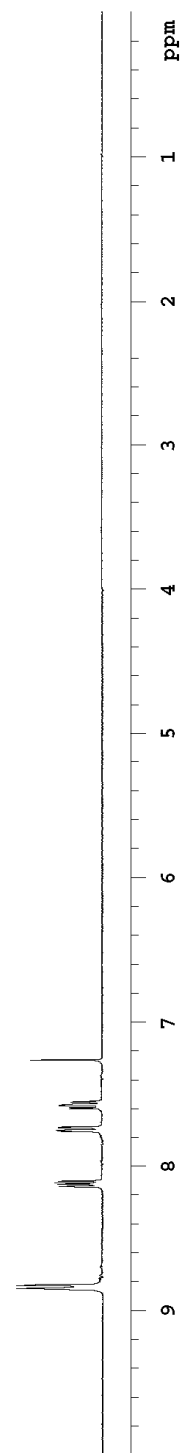
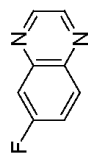
^{19}F NMR (CDCl_3 , 23 °C) of **21**

^{19}F NMR spectrum of



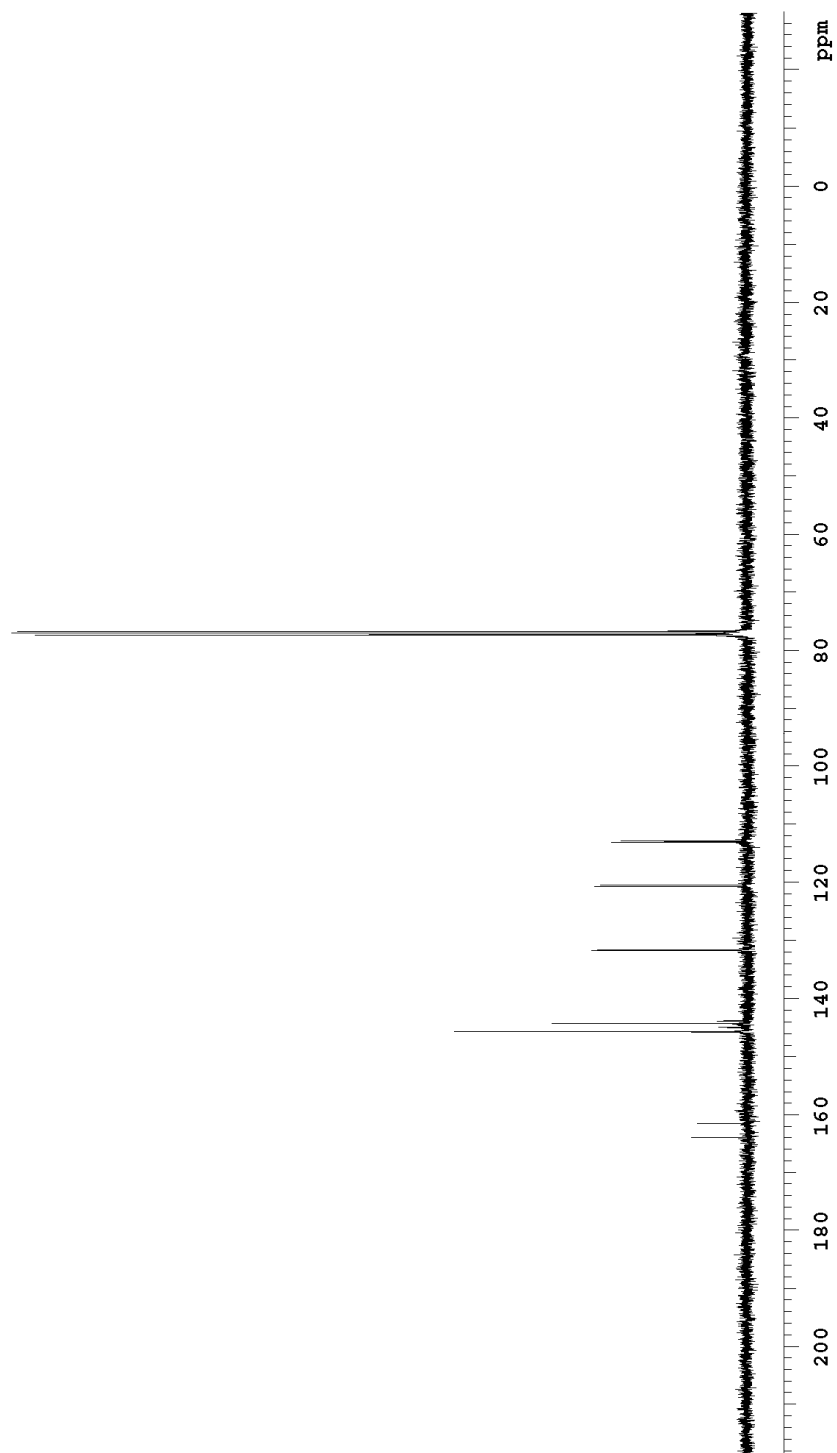
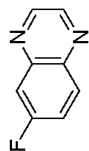
^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **22**

^1H NMR spectrum of



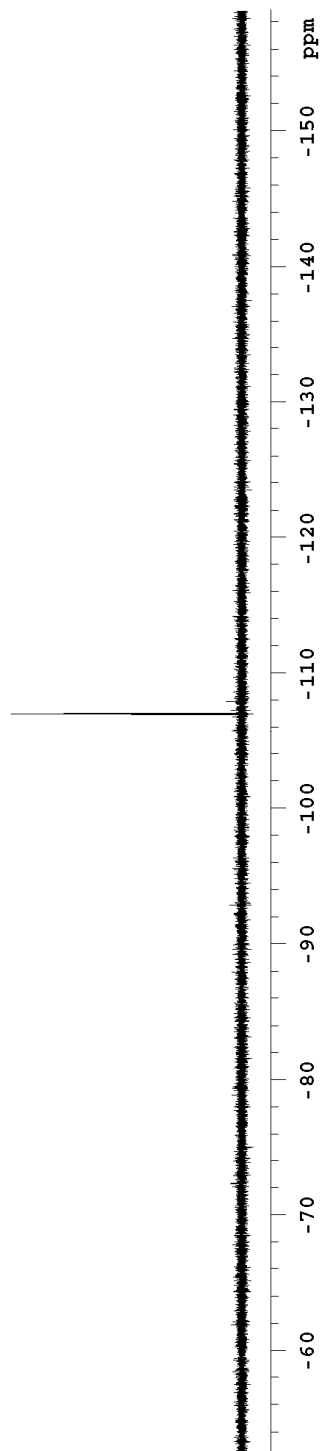
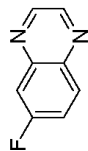
^{13}C NMR (CDCl_3 , 23 $^\circ\text{C}$) of **22**

^{13}C NMR spectrum of



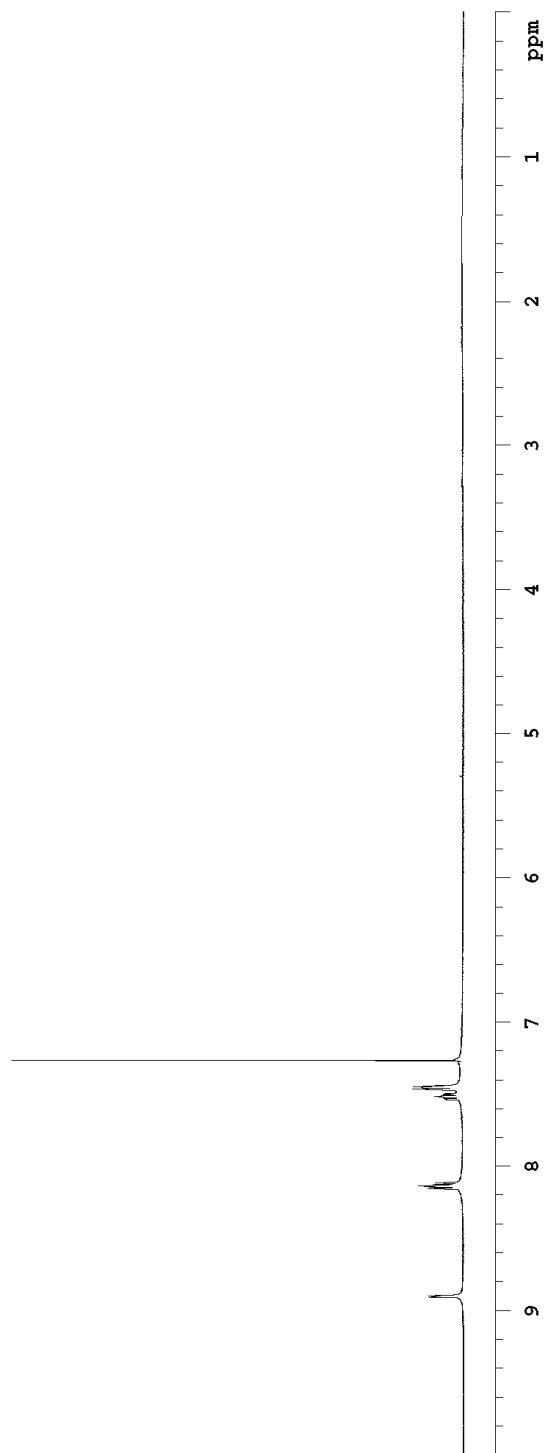
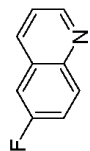
^{19}F NMR (CDCl_3 , 23 $^\circ\text{C}$) of **22**

^{19}F NMR spectrum of



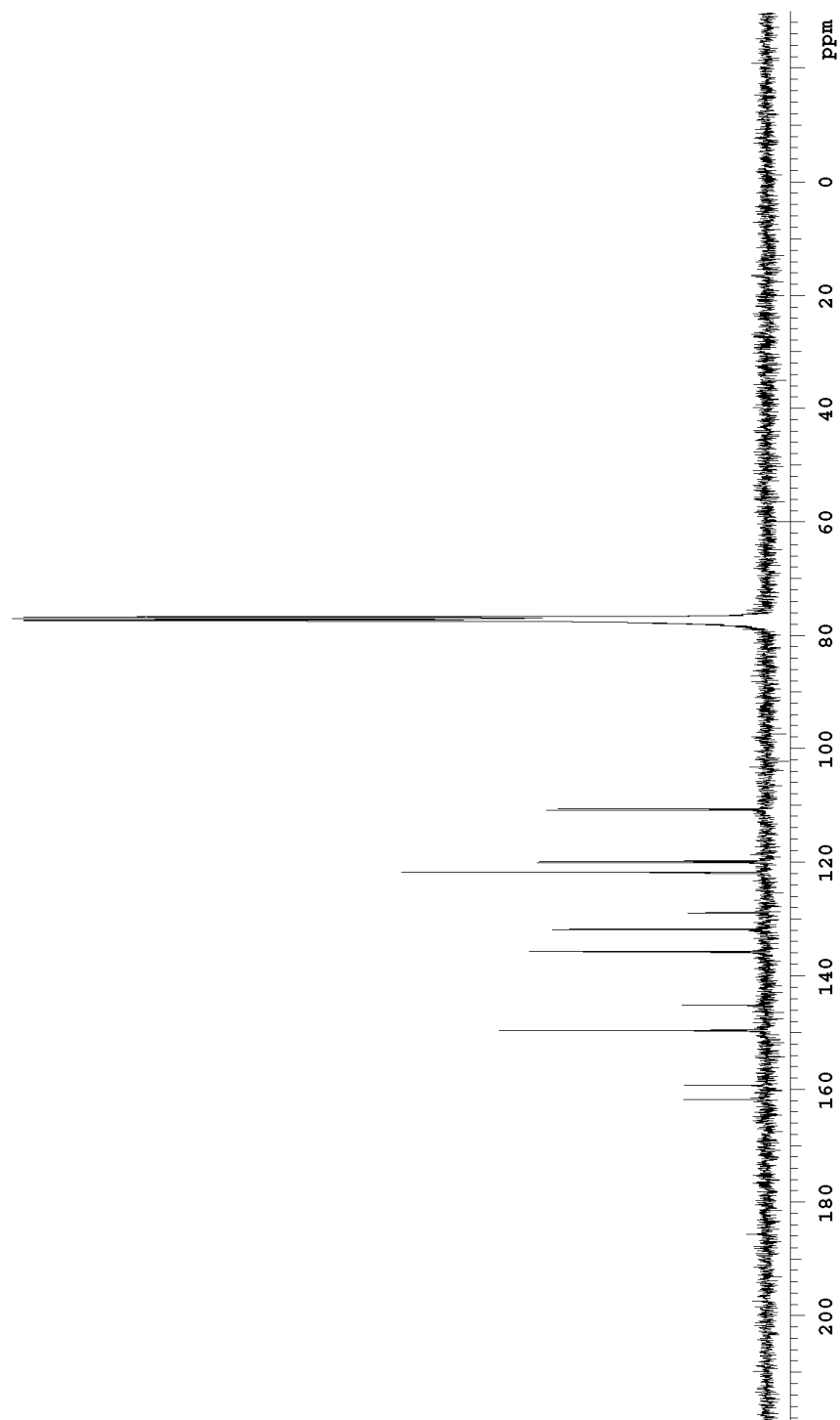
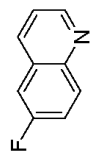
^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **23**

^1H NMR spectrum of



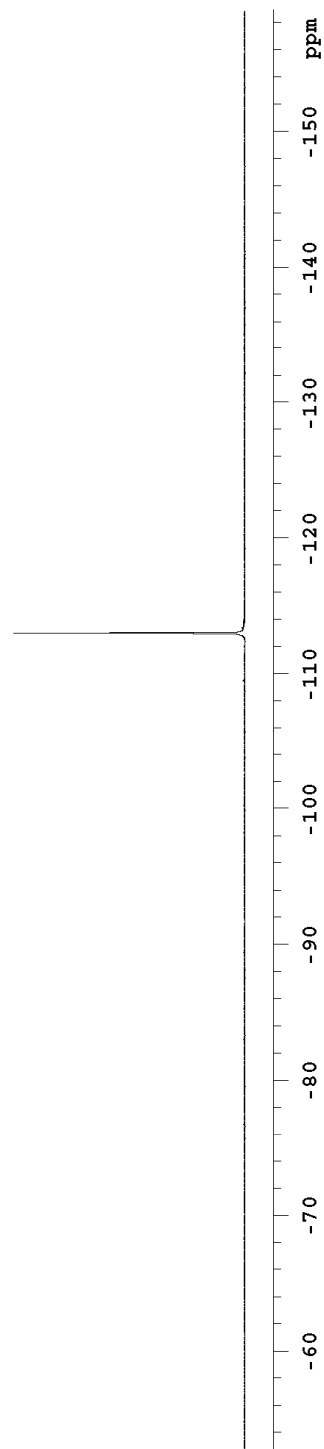
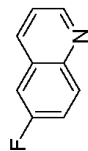
^{13}C NMR (CDCl_3 , 23 $^\circ\text{C}$) of **23**

^{13}C NMR spectrum of



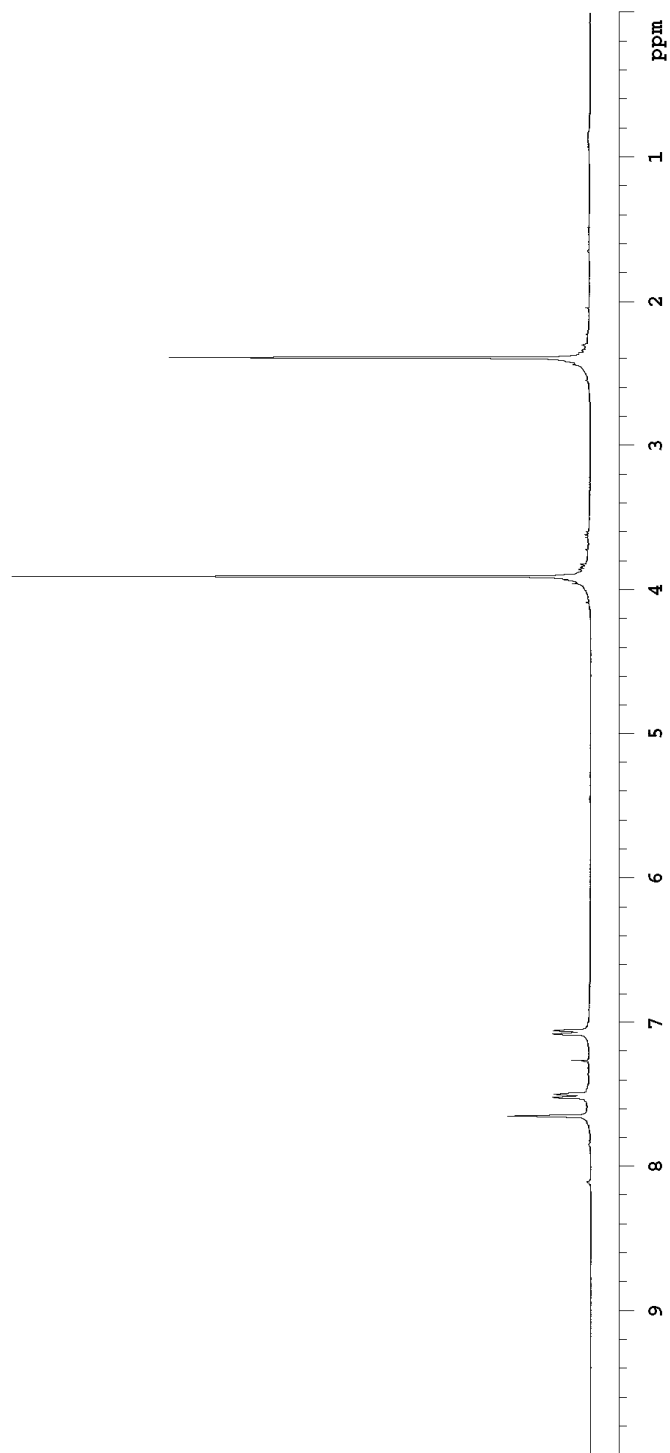
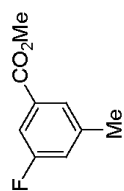
^{19}F NMR (CDCl_3 , 23 $^\circ\text{C}$) of **23**

^{19}F NMR spectrum of



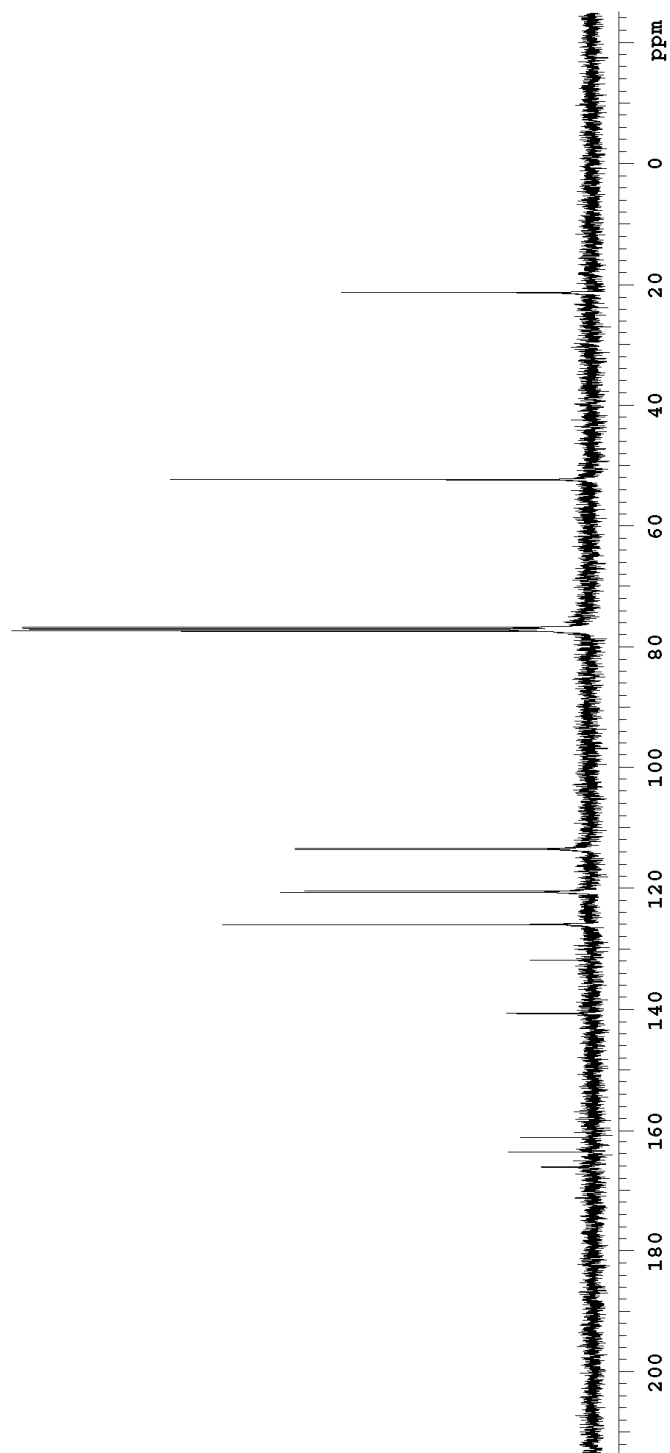
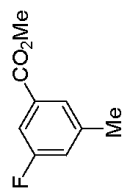
^1H NMR (CDCl_3 , 23 $^\circ\text{C}$) of **29**

^1H NMR spectrum of



^{13}C NMR (CDCl_3 , 23 $^\circ\text{C}$) of **29**

^{13}C NMR spectrum of



^{19}F NMR (CDCl_3 , 23 $^\circ\text{C}$) of **29**

^{19}F NMR spectrum of

