Supporting Information

Silver-Mediated Fluorination of Aryl Silanes

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Materials and Methods

Reactions were carried out under ambient atmosphere unless otherwise specified. Solvents were dried by passage through alumina[1]. Except as indicated otherwise, reactions were 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. Flash chromatography was performed on Whatman Silica Gel 60 μm particle size using a forced flow of eluant at 0.3–0.5 bar pressure.[2] NMR spectra were recorded on either a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ^{1}H and ^{13}C acquisitions, respectively, or a Varian Mercury 400 spectrometer operating at 400 HMz and 375 MHz for ^{1}H and ^{19}F acquisitions, respectively. 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. Triethylamine were distilled over calcium hydride. Silver oxide was purchased from Strem. Acetone (CHROMASOLV® Plus, for HPLC, ≥ 99.9%), 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), tetraethyl orthosilicate, triethoxysilane, bis(acetonitrile)(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate were purchased from Aldrich and used as received. Commercially available aryl silanes (phenyltriethoxysilane, p-tolyltriethoxysilane, 4-chlorophenyltriethoxysilane, p-methoxyphenyltriethoxysilane, 4-trifluomethylphenyltriethoxysilane, ethyl 4-triethoxysilylbenzoate, 2-(3-triethoxylsilylphenyl)-1,3-dioxolane, 1-naphthyltriethoxylsilane) were purified by distillation prior to use. NMR spectroscopic data of known compounds correspond to the data given in the appropriate references. NMR spectra of new compounds are attached.

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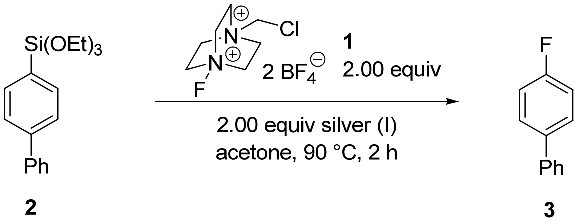
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

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

Experimental Data

Experimental Procedures and Compound Characterization

Evaluation of silver (I) source

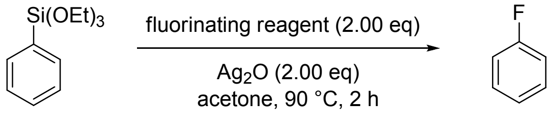


To 4-(biphenyl)triethoxysilane (**2**) (6.32 mg, 0.0200 mmol, 1.00 equiv) in acetone (0.4 mL) at 23 ºC, a silver salt (0.0400 mmol, 2.00 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (14.2 mg, 0.0400 mmol, 2.00 equiv) were added. The reaction mixture was stirred at 90 ºC for 2 h in a sealed vial, then cooled to 23 ºC. 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-*d*$_6$, 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)

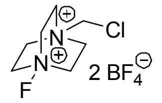
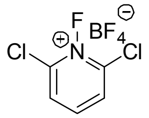
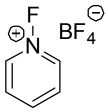
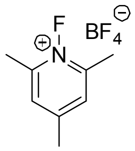
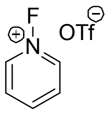
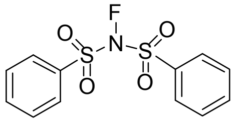
Silver salt	**Yield[%]** (^{19}F NMR)	**Silver salt**	**Yield[%]** (^{19}F NMR)
AgF	21	AgOCN	0
AgOAc	12	AgSCN	0
$AgBF_4$	11	AgOTf	6
$AgClO_4$	5	$AgPF_6$	10
$AgNO_3$	0	$AgSbF_6$	0
Ag_2CO_3	5	Ag_2O	69
AgCN	0	None	0

Evaluation of commercially available fluorinating reagents

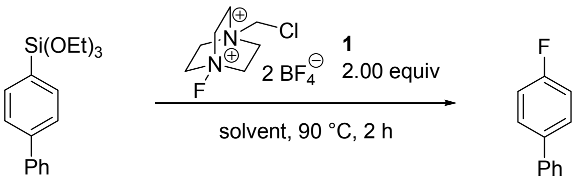


To phenyltriethoxysilane (4.80 mg, 0.0200 mmol, 1.00 equiv) in acetone (0.4 mL) at 23 ºC, silver oxide (9.28 mg, 0.0400 mmol, 2.00 equiv) and fluorinating reagent (0.0400 mmol, 2.00 equiv) were added. The reaction mixture was stirred at 90 ºC for 2 h in a sealed vial, then cooled to 23 ºC. To the reaction 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-d_6, 23 ºC) resonance of fluorobenzene (–115.0 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S2.

Table S2: Evaluate the commercially available fluorinating reagents

Fluorinating reagent	Yield [%] (^{19}F NMR)	Fluorinating reagent	Yield [%] (^{19}F NMR)
	81		0
	0		0
	0		0

Evaluation of fluorination in the absence of silver salt



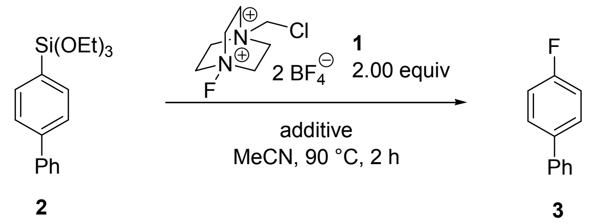
2 **3**

To 4-(biphenyl)triethoxysilane (**2**) (6.32 mg, 0.0200 mmol, 1.00 equiv) in solvent (0.4 mL) at 23 ºC, 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (14.2 mg, 0.0400 mmol, 2.00 equiv) was added. The reaction mixture was stirred at 90 ºC for 2 h in a sealed vial, then cooled to 23 ºC. 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-d_6, 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: Evaluation of fluorination in the absence of silver salt

Solvent	**Yield[%]** (^{19}F NMR)
acetone	0
MeCN	3
DMF	0
THF	0
toluene	0
1,4-dioxane	0
$CHCl_3$	0

Evaluation of fluorination in the presence of additives and in the absence of silver salts

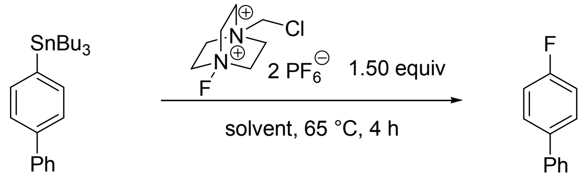


To 4-(biphenyl)triethoxysilane (**2**) (6.32 mg, 0.0200 mmol, 1.00 equiv) in MeCN (0.4 mL) at 23 ºC, an additive (0.00200 mmol, 0.100equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (14.2 mg, 0.0400 mmol, 2.00 equiv) were added. The reaction mixture was stirred at 90 ºC for 2 h in a sealed vial, then cooled to 23 ºC. 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-d_6, 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: Evaluation of fluorination in the presence of additives without silver salt

Additive	**Yield[%]** (^{19}F NMR)
KF	2
TBAF	2
BaO	2
K_3PO_4	2
$NaHCO_3$	3
NaOH	2
$Ba(OH)_2$	2

Evaluation of fluorination in the absence of silver salt for arylstannane fluorination

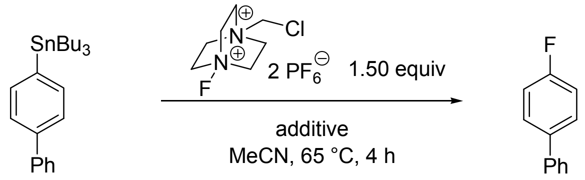


To 4-(biphenyl)tributylstannane (8.9 mg, 0.020 mmol, 1.0 equiv) in solvent (0.4 mL) at 23 ºC was added 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (14 mg, 0.030 mmol, 1.5 equiv). The reaction mixture was stirred at 65 ºC for 4 hr in a sealed vial and subsequently cooled to 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-d_6, 23 ºC) resonance of 4-fluorobiphenyl (–118.1 ppm) with that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S5.

Table S5: Evaluation of fluorination in the absence of silver salt for arylsatannane

Solvent	**Yield[%]** (^{19}F NMR)
acetone	4
MeCN	28
DMF	0
THF	0
toluene	0
$CHCl_3$	0

Evaluation of fluorination in the absence of silver salt in the presence of additives for arylstannane fluorination

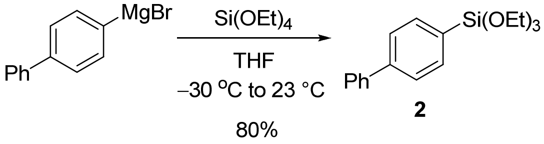


To 4-(biphenyl)tributylstannane (8.9 mg, 0.020 mmol, 1.0 equiv) in MeCN (0.4 mL) at 23 ºC was added additive (0.0020 mmol, 0.10 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(hexafluorophosphate) (14 mg, 0.030 mmol, 1.5 equiv). The reaction mixture was stirred at 65 ºC for 4 hr in a sealed vial and subsequently cooled to 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-d_6, 23 ºC) resonance of 4-fluorobiphenyl (–118.1 ppm) with that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S6.

Table S6: Evaluation of additives without silver salt

Additive	**Yield[%]** (^{19}F NMR)
KF	22
TBAF	23
BaO	28
K_3PO_4	20
$NaHCO_3$	30
NaOH	25
K_2CO_3	23

(4-Biphenyl)triethoxysilane[3] (2)



To tetraethyl orthosilicate (6.70 mL, 30.0 mmol, 3.00 equiv) in 20 mL of THF at –30 ºC was added biphenylmagnesium bromide solution (0.50 M in THF, 20 mL, 10 mmol, 1.0 equiv) dropwise over 10 min. After stirring at –30 ºC for 1 h, the reaction mixture was warmed to 23 ºC and was stirred for 12 h. The reaction mixture was poured onto 100 mL of pentane, washed three times with water (3 × 20 mL), and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. Bulb-to-bulb distillation (125 ºC, 0.5 Torr) afforded 2.52 g of the title compound as a colorless oil (80% yield).

$R_f = 0.50$ (hexanes). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.75 (d, $J = 8.0$ Hz, 2H), 7.62–7.60 (m, 4H), 7.45 (d, $J = 7.5$ Hz, 2H), 7.36 (t, $J = 7.5$ Hz, 1H), 3.90 (q, $J = 7.0$ Hz, 6H), 1.27 (t, $J = 7.0$ Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 142.96, 140.95, 135.28, 129.59, 128.76, 127.50, 127.17, 126.56, 58.76, 18.23.

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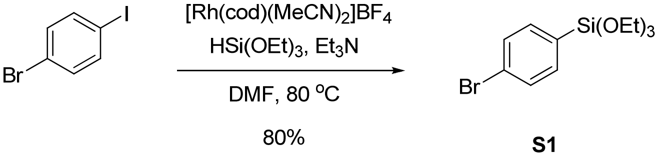
[3] Hargrave, J. D.; Herbert, J.; Bish, G.; Frost, C. G. *Org. Biomol. Chem.*, **2006**, *4*, 3235–3241.

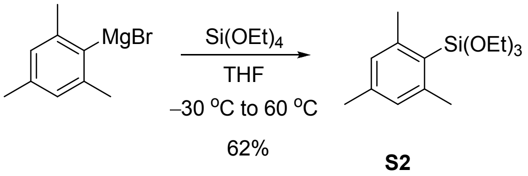
(4-Bromophenyl)triethoxysilane[4] (S1)



$[Rh(cod)(MeCN)_2]BF_4$ (22.0 mg, 0.0600 mmol, 0.0300 equiv) and 1-bromo-4-iodobenzene (563 mg, 2.00 mmol, 1.00 equiv) were charged in 20 mL vial capped with a rubber septum. The vial was evacuated and backfilled with nitrogen. To this vial, DMF (8 mL), triethylamine (0.830 mL, 6.00 mmol, 3.00 equiv) and triethoxysilane (0.730 mL, 4.00 mmol, 2.00 equiv) were added. The reaction mixture was stirred at 80 ºC for 2 h, then cooled to 23 ºC. The mixture was diluted with ether (100 mL) and washed three times with water (3 × 40 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by Kugelrohr distillation to give 508 mg of the title compound as a colorless oil (80% yield).

R_f = 0.63 (hexanes). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.53–7.52 (m, 4H), 3.85 (q, *J* = 7.0 Hz, 6H), 1.24 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ):136.34, 131.04, 129.86, 125.33, 58.77, 18.16.

(2, 4, 6-Trimethylphenyl)triethoxysilane[5] (S2)



To tetraethyl orthosilicate (3.30 mL, 15.0 mmol, 3.00 equiv) in 10 mL of THF at –30 ºC was added 2,4,6-trimethylphenylmagnesium bromide solution (1.0 M in THF, 5.0 mL, 5.0 mmol, 1.0 equiv) dropwise over 10 min. After stirring at –30 ºC for 1 h, the reaction mixture was warmed to 23 ºC and was further stirred for 12 h. The reaction mixture was poured onto 100 mL of pentane, and was washed three times with water (3 × 20 mL) and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure. Bulb-to-bulb distillation (125 ºC, 0.5 Torr) afforded 0.87 g of the title compound as a colorless oil (62% yield).

R_f = 0.14 (hexanes). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 6.80 (s, 2H), 3.83 (q, *J* = 7.0 Hz, 6H), 2.51 (s, 6H), 2.26 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 145.92, 139.79, 128.81, 124.99, 58.10, 23.73, 21.08, 18.15.

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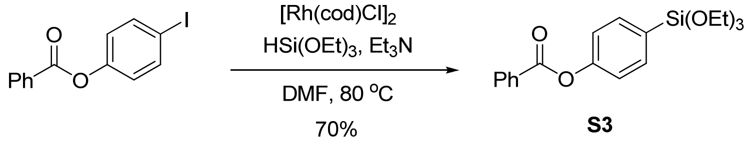
[4] Maegawa, Y.; Nagano, T.; Yabuno, T.; Nakagawa, H.; Shimada, T. *Tetrahedron*, **2007**, *63*, 11467–11474.

[5] Gilman, H.; Smart, G. N. R. *J. Org. Chem.* **1950**, *15*, 720–740.

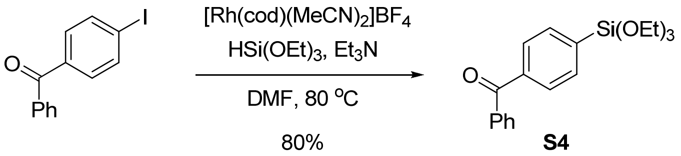
4-(Triethoxysilyl)phenylbenzoate (S3)



$[Rh(cod)Cl]_2$ (15.0 mg, 0.0300 mmol, 0.0300 equiv) and 4-iodophenyl benzoate (323 mg, 1.00 mmol, 1.00 equiv) were charged in 10 mL vial capped with a rubber septum. The vial was evacuated and backfilled with nitrogen. To this vial, DMF (4 mL), triethylamine (0.420 mL, 3.00 mmol, 3.00 equiv) and triethoxysilane (0.360 mL, 2.00 mmol, 2.00 equiv) were added. The reaction mixture was stirred at 80 ºC for 2 h, then cooled to 23 ºC. The mixture was diluted with ether (50 mL) and washed three times with water (3 × 20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by Kugelrohr distillation to give 252 mg of the title compound as a colorless oil (70% yield).

R_f = 0.30 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.24–8.21 (m, 2H), 7.78–7.75 (m, 2H), 7.68–7.64 (m, 1H), 7.56–7.52 (m, 2H), 7.28–7.25 (m, 2H), 3.90 (q, *J* = 7.0 Hz, 6H), 1.27 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 164.93, 152.82, 136.25, 133.63, 130.19, 129.52, 128.63, 128.58, 121.22, 58.78. 18.22. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + Na]^+$, 378.17313. Found, 378.17314.

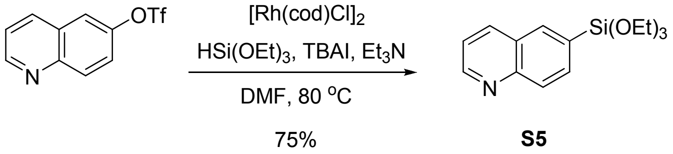
4-(Triethoxysilyl)benzophenone (S4)



$[Rh(cod)(MeCN)_2]BF_4$ (11.0 mg, 0.0300 mmol, 0.0300 equiv) and 4-iodobenzophenone (307 mg, 1.00 mmol, 1.00 equiv) were charged in 10 mL vial capped with a rubber septum. The vial was evacuated and backfilled with nitrogen. To this vial, DMF (4 mL), triethylamine (0.420 mL, 3.00 mmol, 3.00 equiv) and triethoxysilane (0.360 mL, 2.00 mmol, 2.00 equiv) were added. The reaction mixture was stirred at 80 ºC for 2 h, then cooled to 23 ºC. The mixture was diluted with ether (50 mL) and washed three times with water (3 × 20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by Kugelrohr distillation to give 275 mg of the title compound as a colorless oil (80% yield).

R_f = 0.45 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.82–7.77 (m, 6H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.48 (dd, *J* = 7.5 Hz, 7.5 Hz, 2H), 3.90 (q, *J* = 7.0 Hz, 6H), 1.27 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 196.84, 139.05, 137.29, 136.34, 134.66, 132.54, 130.11, 129.00, 128.28, 58.91, 18.21. Mass Spectrometry: HRMS-FIA (m/z): Calcd for $[M + Na]^+$, 367.13361. Found, 367.13347.

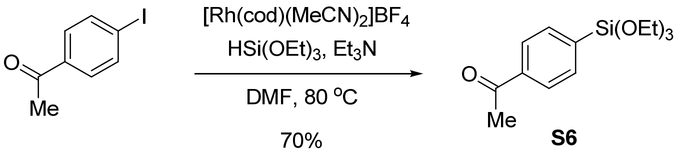
6-(Quinolinyl)triethoxysilane (S5)



$[Rh(cod)Cl]_2$ (15.0 mg, 0.0300 mmol, 0.0300 equiv), 6-(quinolinyl)trifluoromethanesulfonate (307 mg, 1.00 mmol, 1.00 equiv) and tetra-*n*-butylammonium iodide (369 mg, 1.00 mmol, 1.00 equiv) were charged in 10 mL vial capped with a rubber septum. The vial was evacuated and backfilled with nitrogen. To this vial, DMF (4 mL), triethylamine (0.420 mL, 3.00 mmol, 3.00 equiv) and triethoxysilane (0.360 mL, 2.00 mmol, 2.00 equiv) were added. The reaction mixture was stirred at 80 ºC for 2 h, then cooled to 23 ºC. The mixture was diluted with ether (50 mL) and washed three times with water (3 × 20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by Kugelrohr distillation to give 218 mg of the title compound as a colorless oil (75% yield).

R_f = 0.50 (hexanes/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.94 (dd, *J* = 4.0, *J* = 1.5 Hz, 1H), 8.19–8.18 (m, 2H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.41 (dd, *J* = 8.5, 4.5 Hz, 1 H), 3.92 (q, *J* = 7.0 Hz, 6H), 1.27 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 151.26, 149.18, 136.46, 136.18, 134.11, 129.87, 128.67, 127.69, 121.21, 58.91. 18.23.

4-(Triethoxysilyl)acetophenone[6] (S6)



$[Rh(cod)(MeCN)_2]BF_4$ (11.0 mg, 0.0300 mmol, 0.0300 equiv) and 4-iodoacetonphenone (246 mg, 1.00 mmol, 1.00 equiv) were charged in 10 mL vial capped with a rubber septum. The vial was evacuated and backfilled with nitrogen. To this vial, DMF (4 mL), triethylamine (0.420 mL, 3.00 mmol, 3.00 equiv) and triethoxysilane (0.360 mL, 2.00 mmol, 2.00 equiv) were added. The reaction mixture was stirred at 80 ºC for 2 h, then cooled to 23 ºC. The mixture was diluted with ether (50 mL) and washed three times with water (3 × 20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by Kugelrohr distillation to give 197 mg of the title compound as a colorless oil (70% yield).

R_f = 0.56 (hexanes). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.93 (dd, *J* = 6.5,

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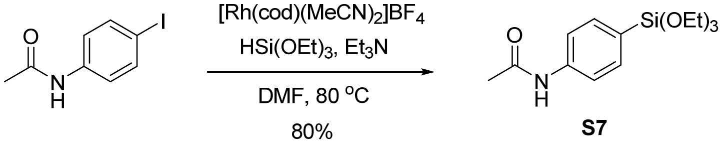
[6] Murata, M.; Yamasaki, H.; Ueta, T.; Nagata, M.; Ishikura, M.; Watanabe, S.; Masuda, Y. *Tetrahedron,* **2007**, *63*, 4087–4094.

J = 1.5 Hz, 2H), 7.78 (dd, *J* = 6.5, *J* = 1.5 Hz, 2H), 3.88 (q, *J* = 7.0 Hz, 6H), 2.61 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (125 MHz, CDCl$_3$, 23 ºC, δ): 198.37, 138.33, 137.32, 135.02, 127.28, 58.88, 26.68, 18.19.

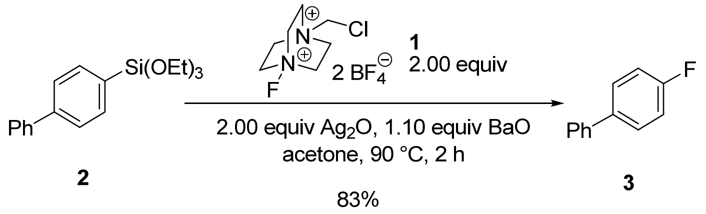
4-(Triethoxysilyl)acetanilide[7] (S7)



[Rh(cod)(MeCN)$_2$]BF$_4$ (11.0 mg, 0.0300 mmol, 0.0300 equiv) and 4-iodoacetanilide (260 mg, 1.00 mmol, 1.00 equiv) were charged in 10 mL vial capped with a rubber septum. The vial was evacuated and backfilled with nitrogen. To this vial, DMF (4 mL), triethylamine (0.420 mL, 3.00 mmol, 3.00 equiv) and triethoxysilane (0.360 mL, 2.00 mmol, 2.00 equiv) were added. The reaction mixture was stirred at 80 ºC for 2 h, then cooled to 23 ºC. The mixture was diluted with ether (50 mL) and washed three times with water (3 × 20 mL), dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The residue was purified by Kugelrohr distillation to give 238 mg of the title compound as a colorless oil (80% yield).

R$_f$ = 0.25 (hexanes/EtOAc 1:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$, 23 ºC, δ): 7.69 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.42 (br s, 1H), 3.85 (q, *J* = 7.0 Hz, 6H), 2.17 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (125 MHz, CDCl$_3$, 23 ºC, δ): 168.39, 139.79, 135.77, 126.28, 118.89, 58.69, 24.66, 18.18.

Fluorination of arylsilanes with F-TEDA-BF$_4$



To 4-(biphenyl)triethoxylsilane (**2**) (31.6 mg, 0.100 mmol, 1.00 equiv) in acetone (2.0 mL) at 23 ºC was added silver oxide (46.4 mg, 0.200 mmol, 2.00 equiv), barium oxide (17.2 mg, 0.110 mmol, 1.10 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (70.8 mg, 0.200 mmol, 2.00 equiv). The reaction mixture was stirred at 90 ºC for 2 h in a sealed vial. The reaction mixture was cooled to 23 ºC and concentrated under reduced pressure. To the residue was added CH$_2$Cl$_2$ (10 mL) and the mixture was filtered through

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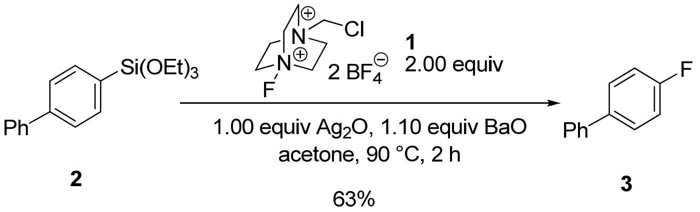
[7] Murata, M.; Suzuki, K.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62,* 8569–8571.

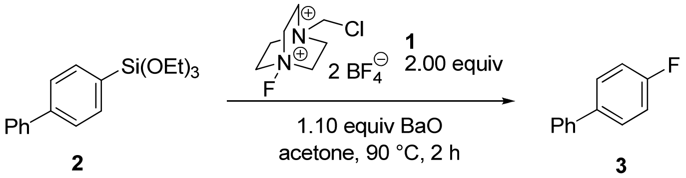
a pad of Celite eluting with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by chromatography on silica gel eluting with hexanes, to afford 14.3 mg of the title compound as a white solid (83% yield).

With 1.00 equivalent of Ag_2O



To 4-(biphenyl)triethoxylsilane (**2**) (31.6 mg, 0.100 mmol, 1.00 equiv) in acetone (2.0 mL) at 23 ºC was added silver oxide (23.2 mg, 0.100 mmol, 1.00 equiv), barium oxide (17.2 mg, 0.110 mmol, 1.10 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (70.8 mg, 0.200 mmol, 2.00 equiv). The reaction mixture was stirred at 90 ºC for 2 h in a sealed vial, then cooled to 23 ºC. To the reaction mixture was added 3-nitrofluorobenzene (2.00 µL, 0.0188 mmol). The yield was determined to be 63% by comparing the integration of the ^{19}F NMR (375 MHz, acetone-d_6, 23 ºC) resonance of 4-fluorobiphenyl (–118.1 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm).

Background reaction without Ag_2O

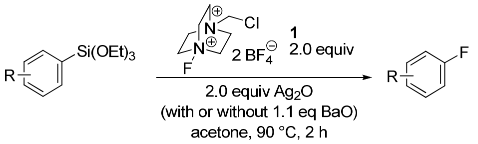


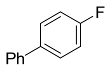
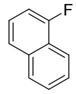
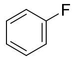
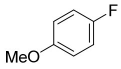
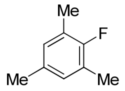
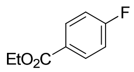
To 4-(biphenyl)triethoxylsilane (**2**) (6.32 mg, 0.0200 mmol, 1.00 equiv) in acetone (0.40 mL) at 23 ºC was added barium oxide and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (14.2 mg, 0.0400 mmol, 2.00 equiv). The reaction mixture was stirred at 90 ºC for 2 h in a sealed vial, then cooled to 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-d_6, 23 ºC) resonance of 4-fluorobiphenyl (–118.1 ppm) and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S7.

Table S7: Background reaction without Ag_2O

BaO	**Yield[%]** (^{19}F NMR)
None	0
1.1 equiv	0

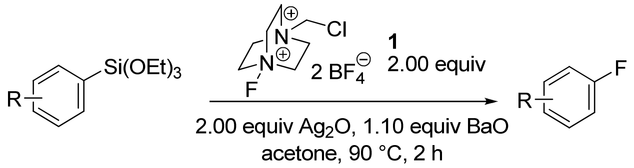
Reaction with or without BaO



substrate	with BaO	without BaO		with BaO	without BaO
 **3**	85%	75%	 **9**	67%	72%
 **7**	90%	81%	 **15**	78%	78%
 **8**	38%	55%	 **16**	85%	78%

To arylsilane (0.0200 mmol, 1.00 equiv) in acetone (0.40 mL) at 23 ºC was added silver oxide (9.28 mg, 0.400 mmol, 2.00 equiv), barium oxide and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (14.2 mg, 0.0400 mmol, 2.00 equiv). The reaction mixture was stirred at 90 ºC for 2 h in a sealed vial, then cooled to 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-d_6, 23 ºC) resonance of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S7.

General Procedure A (for volatile compounds)

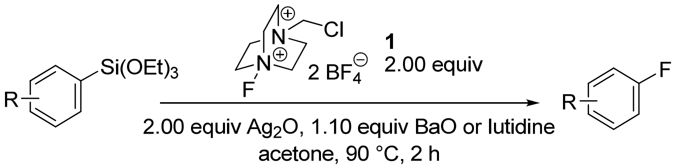


To arylsilane (0.100 mmol, 1.00 equiv) in acetone (2.0 mL) at 23 ºC was added silver oxide (46.4 mg, 0.200 mmol, 2.00 equiv), barium oxide (15.6 mg, 0.100 mmol, 1.00 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (**1**) (70.8 mg, 0.200 mmol, 2.00 equiv). The reaction mixture was stirred for 2 h at 90 ºC in a sealed vial, then cooled to 23 ºC. 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-d_6, 23 ºC) resonance of an arylfluoride and that of 3-nitrofluorobenzene (–112.0 ppm). Yields are reported in Table S8.

Table S8: Synthesis of volatile arylfluorides

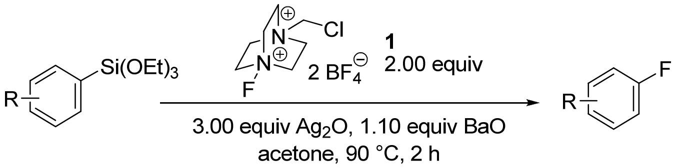
R	^{19}F chemical shift	Yield[%] (^{19}F NMR)
4-CF3 (**4**)	–109.2 ppm	90
4-Cl (**5**)	–117.6 ppm	86
4-Br (**6**)	–117.1 ppm	85
H (**7**)	–115.3 ppm	90
2,4,6-trimethyl (**8**)	–129.7 ppm	73
3-(1,3-dioxolane) (**10**)	–115.1 ppm	74
4-Me (**11**)	–120.5 ppm	79
4-OMe (**15**)	–126.8 ppm	76

General Procedure B (for non-volatile compounds)



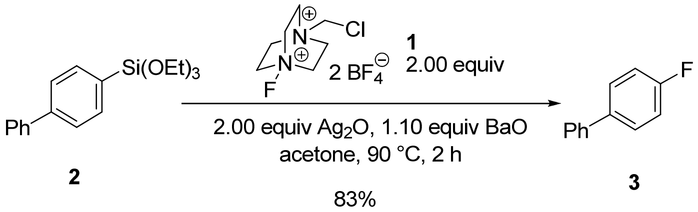
To arylsilane (0.100 mmol, 1.00 equiv) in acetone (2.0 mL) at 23 ºC was added silver oxide (46.4 mg, 0.200 mmol, 2.00 equiv), barium oxide (17.2 mg, 0.110 mmol, 1.10 equiv) or 2,6-lutidine (12.8 µL, 0.110 mmol, 1.10 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane bis(tetrafluoroborate) (**1**) (70.8 mg, 0.200 mmol, 2.00 equiv). The reaction mixture was stirred for 2 h at 90 ºC in a sealed vial. The reaction mixture was cooled to 23 ºC and concentrated under reduced pressure. To the residue was added CH_2Cl_2 and the mixture was filtered through a pad of Celite eluting with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by chromatography on silica gel or preparative TLC.

General Procedure C (for heterocyclic compounds)



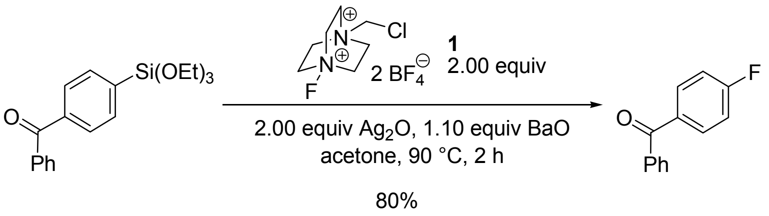
To arylsilane (0.100 mmol, 1.00 equiv) in acetone (2.0 mL) at 23 ºC was added silver oxide (69.6 mg, 0.300 mmol, 3.00 equiv), barium oxide (17.2 mg, 0.110 mmol, 1.10 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo-[2.2.2]octane bis(tetrafluoroborate) (**1**) (70.8 mg, 0.200 mmol, 2.00 equiv). The reaction mixture was stirred for 2 h at 90 ºC in a sealed vial. The reaction mixture was cooled to 23 ºC, passed through a pad of Celite and concentrated under reduced pressure. To the residue was added CH_2Cl_2 (20 mL) and a saturated aqueous solution of $NaHCO_3$ (20 mL). The organic phase was separated, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified on preparative TLC.

5-mmol-Scale fluorination of 4-(biphenyl)triethoxysilane



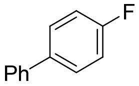
To 4-(biphenyl)triethoxylsilane (**2**) (1.58 g, 5.00 mmol, 1.00 equiv) in acetone (100 mL) at 23 ºC was added silver oxide (2.32 g, 10.0 mmol, 2.00 equiv), barium oxide (0.780 g, 5.00 mmol, 1.10 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]-octane bis(trifluoroborate) (**1**) (3.54 g, 10.0 mmol, 2.00 equiv). The reaction mixture was stirred at 90 ºC for 2 h in a 350 mL sealed vessel. The reaction mixture was cooled to 23 ºC and concentrated under reduced pressure. To the residue was added CH_2Cl_2 and the mixture was filtered through a pad of Celite eluting with CH_2Cl_2. The filtrate is concentrated under reduced pressure and the residue is purified by chromatography on silica gel eluting with hexane, to afford 714 mg of the title compound as a white solid (83% yield).

1-mmol-scale fluorination of 4-(triethoxysilyl)benzophenone



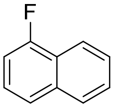
To 4-(triethoxysilyl)benzophenone (344 mg, 1.00 mmol, 1.00 equiv) in acetone (20 mL) at 23 ºC was added silver oxide (464 mg, 2.00 mmol, 2.00 equiv), barium oxide (168 mg, 1.10 mmol, 1.10 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]-octane bis(trifluoroborate) (**1**) (706 mg, 2.00 mmol, 2.00 equiv). The reaction mixture was stirred at 90 ºC for 2 h in a sealed vessel. The reaction mixture was cooled to 23 ºC and concentrated under reduced pressure. To the residue was added CH_2Cl_2 and the mixture was filtered through a pad of Celite eluting with CH_2Cl_2. The filtrate is concentrated under reduced pressure and the residue is purified by chromatography on silica gel eluting with hexanes/EtOAc 10:1 (v/v), to afford 160 mg of the title compound as a white solid (80% yield).

4-Fluorobiphenyl (3)



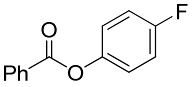
Yield: 14.3 mg (83%). R_f = 0.60 (hexanes/EtOAc 19:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$, 23 ºC, δ): 7.60–7.54 (m, 4H), 7.47 (dd, *J* = 7.5 Hz, 7.0 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.14 (dd, *J* = 8.0 Hz, 7.5 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$, 23 ºC, δ): 162.44 (d, *J* = 244 Hz), 140.25, 137.30, 128.80, 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): –117.2. These spectroscopic data correspond to previously reported data.[8]

1-Fluoronaphthalene (9)



Yield: 10.9 mg (75%). R_f = 0.40 (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$, 23 ºC, δ): 8.13–8.11 (m, 1H), 7.88–7.86 (m, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.56–7.53 (m, 1H), 7.43–7.38 (m, 1H), 7.17–7.13 (m, 1H). ^{13}C NMR (125 MHz, CDCl$_3$, 23 ºC, δ): 158.78 (d, *J* = 250 Hz), 134.87 (d, *J* = 4.5 Hz), 127.50 (d, *J* = 3.6 Hz), 126.80, 126.15 (d, *J* = 1.9 Hz), 125.58 (d, *J* = 9.1 Hz), 123.76, 123.62 (d, *J* = 3.6 Hz), 120.53 (d, *J* = 5.5 Hz), 109.39 (d, *J* = 20 Hz). ^{19}F NMR (375 MHz, CDCl$_3$, 23 ºC, δ): –125.6. These spectroscopic data correspond to previously reported data.[9]

4-Fluorophenyl benzoate (12)



Yield: 16.9 mg (78%). R_f = 0.20 (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, CDCl$_3$, 23 ºC, δ): 8.21–8.18 (m, 2H), 7.66–7.63 (m, 1H), 7.54–7.51 (m, 2H), 7.20–7.17 (m, 2H), 7.13–7.09 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$, 23 ºC, δ): 165.19, 160.30 (d, *J* = 242 Hz), 146.75 (d, *J* = 2.8 Hz), 133.71, 130.17, 129.29, 128.61, 123.10 (d, *J* = 9.0 Hz), 116.14 (d, *J* = 24 Hz). ^{19}F NMR (375 MHz, CDCl$_3$, 23 ºC, δ): –119.2. These spectroscopic data correspond to

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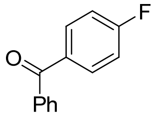
[8] Furuya, T.; Kaiser, H. M.; Ritter, T. *Angew. Chem. Int. Ed.* **2008**, *47*, 5993–5996.

[9] Yokoka, M.; Fujita, D.; Ichikawa, J. *Org. Lett.* **2007**, *22*, 4639–4642.

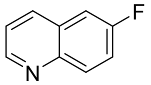
previously reported data.[10]

4-Fluorobenzophenone (13)



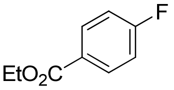
Yield: 17.0 mg (85%). R$_f$ = 0.50 (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.86–7.84 (m, 2H), 7.78–7.76 (m, 2H), 7.61–7.58 (m, 1H), 7.51–7.48 (m, 2H), 7.18–7.15 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 195.27, 165.39 (d, *J* = 252 Hz), 137.51, 133.79, 132.66 (d, *J* = 9.1 Hz), 132.45, 129.87, 128.35, 115.45 (d, *J* = 22 Hz). ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –108.7. These spectroscopic data correspond to previously reported data.[11]

6-Fluoroquinoline (14)



Yield: 8.8 mg (60%). 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 (125 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. These spectroscopic data correspond to previously reported data.[12]

Ethyl 4-fluorobenzoate (16)



Yield: 14.3 mg (85%). R$_f$ = 0.30 (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.06 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 2H), 7.10 (dd, *J* = 9.0 Hz, *J* = 8.5 Hz,

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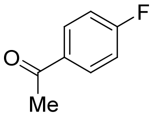
[10] Conte, L.; Napoli, M.; Gambaretto, G. P.; Guerrato, A. *J. Fluor. Chem.* **1994**, *67*, 41–45.

[11] Xing, D.; Guan, B.; Cai, G.; Fang, Z.; Yang, L.; Shi, Z. *Org. Lett.* **2006**, *8*, 693–696.

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

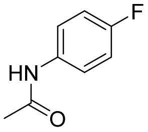
2H), 4.37 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 9.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 165.68 (d, J = 252 Hz), 165.65, 132.04 (d, J = 10 Hz), 126.72, 115.42 (d, J = 22 Hz), 61.07, 14.30. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –108.4. These spectroscopic data correspond to previously reported data.[13]

4-Fluoroacetophenone (17)



Yield: 11.3 mg (82%). R_f = 0.30 (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.99–7.96 (m, 2H), 7.14–7.11 (m, 2H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 196.68, 165.99 (d, J = 253 Hz), 133.84, 131.16 (d, J = 9.1 Hz), 115.88 (d, J = 22 Hz), 26.75. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –108.4. These spectroscopic data correspond to previously reported data.[14]

4-Fluoroacetanilide (18)



Yield: 10.7 mg (70%). R_f = 0.30 (hexane/EtOAc 3:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.99–7.96 (m, 2H), 7.14–7.11 (m, 2H), 2.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 168.43, 159.35 (d, J = 242 Hz), 133.83, 121.81 (d, J = 7.3 Hz), 115.56 (d, J = 23 Hz), 24.32. ^{19}F NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –121.4. These spectroscopic data correspond to previously reported data.[15]

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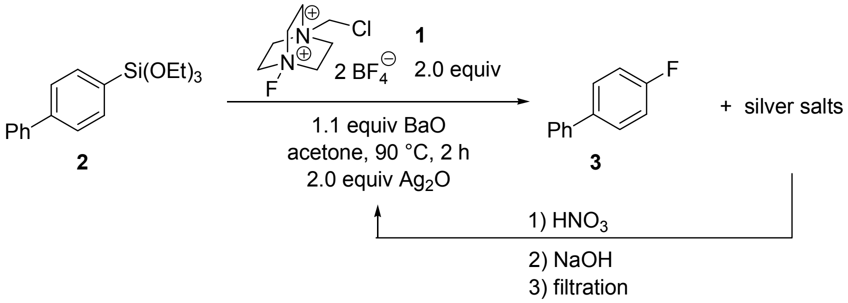
[13] Cai, C.; Rivera, N. R.; Balsells, J.; Sidler, R. R.; Mcwilliams, J. C.; Shultz, C. S.; Sun, Y. *Org. Lett.* **2006**, *8*, 5161–5164.

[14] Liu, S.; Berry, N.; Thomson, N.; Pettman, A.; Hyder, Z.; Mo, J.; Xiao, J. *J. Org. Chem.,* **2006**, *71*, 7467–7470.

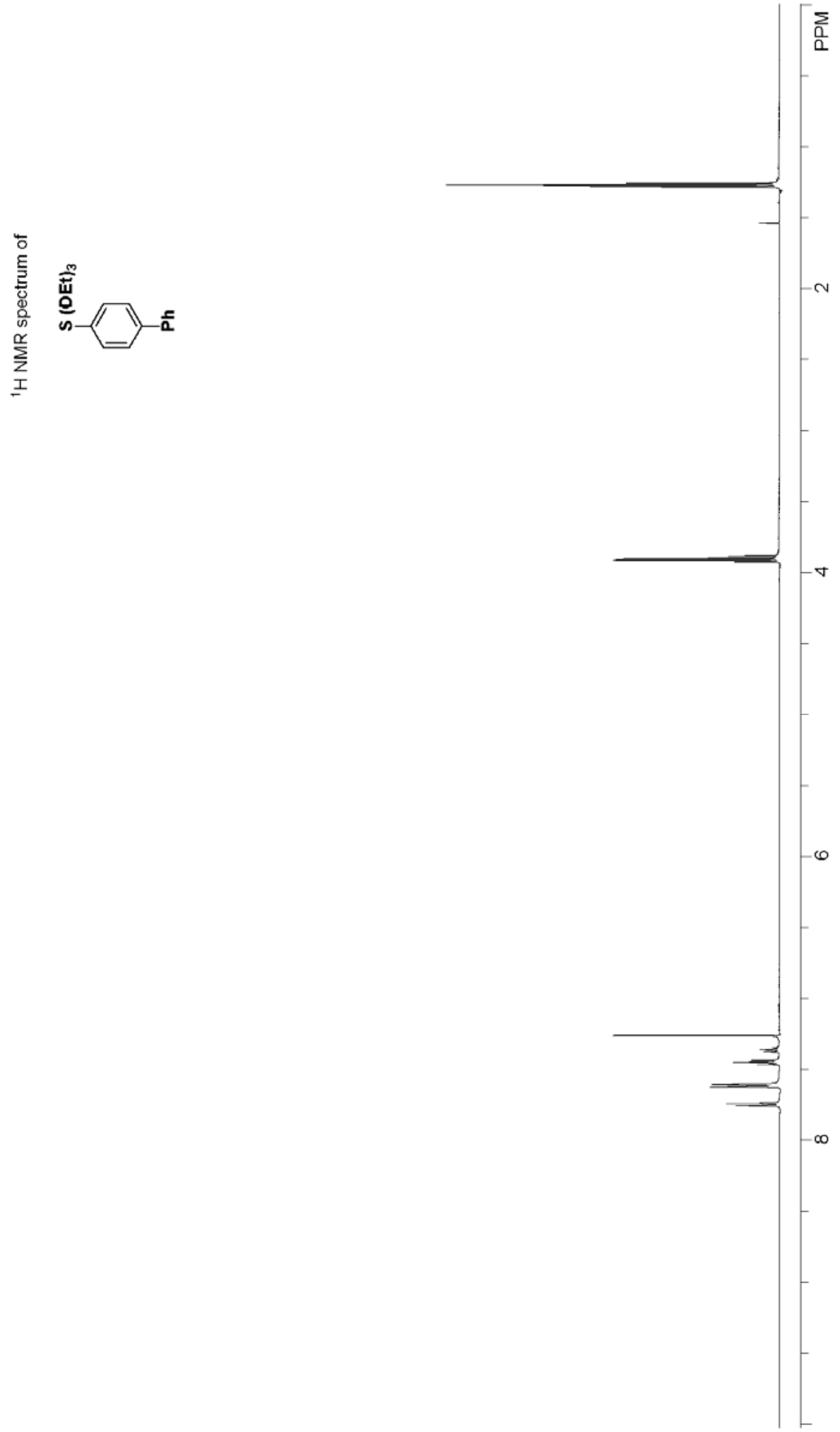
[15] Furuya, T.; Ritter, T. *Org. Lett.* **2009**, *11*, 2860–2863.

Regeneration of Ag_2O

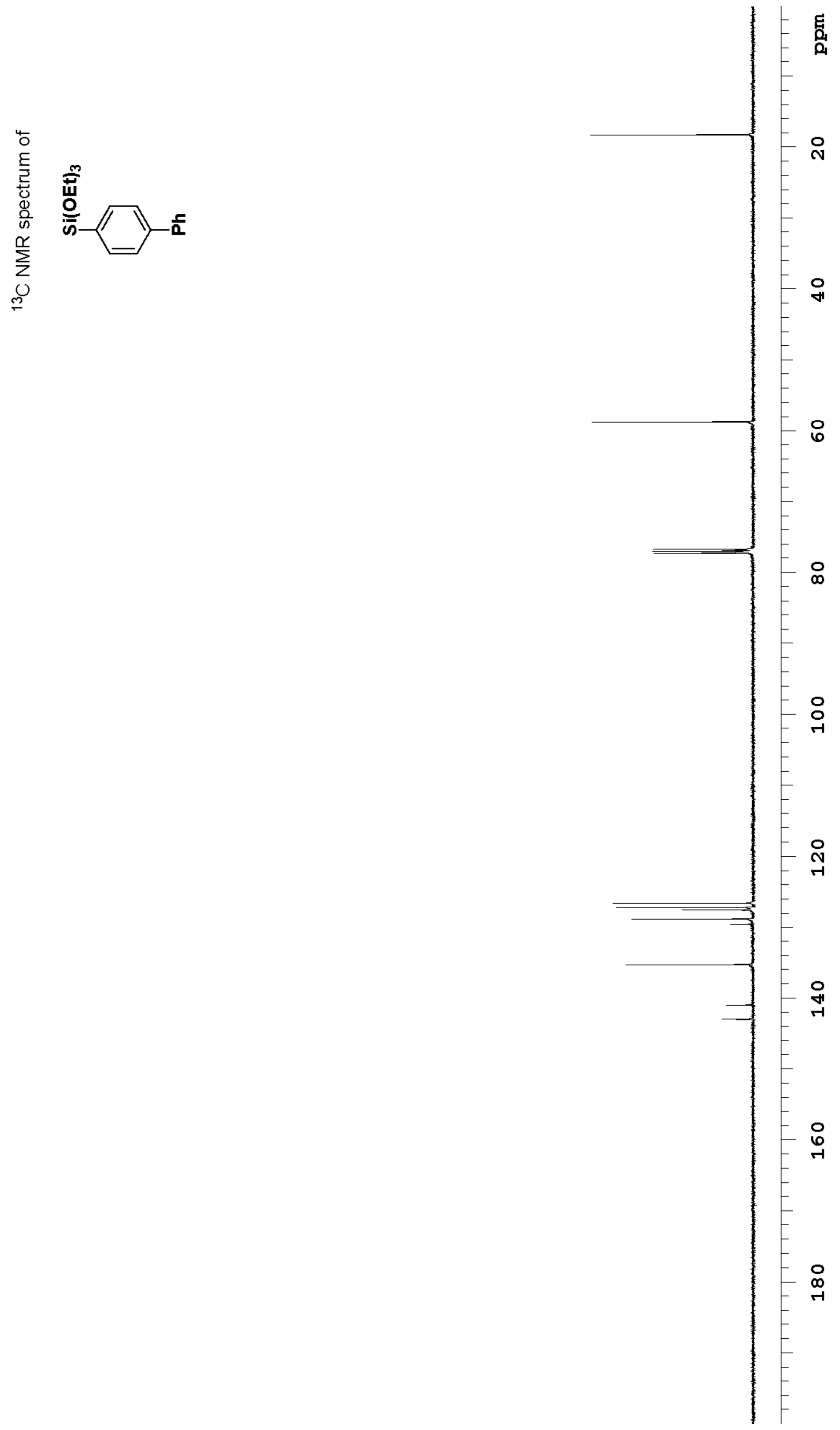


To 4-(biphenyl)triethoxylsilane (**2**) (1.58 g, 5.00 mmol, 1.00 equiv) in acetone (100 mL) at 23 ºC was added silver oxide (2.32 g, 10.0 mmol, 2.00 equiv), barium oxide (0.780 g, 5.00 mmol, 1.10 equiv) and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]-octane bis(trifluoroborate) (**1**) (3.54 g, 10.0 mmol, 2.00 equiv). The reaction mixture was stirred at 90 ºC for 2 h in a 350 mL sealed vessel. The reaction mixture was cooled to 23 ºC and concentrated under reduced pressure. The residue was washed with CH_2Cl_2 (3 × 20 mL) and the solid was dissolved in 250 mL HNO_3 (10%, v/v in H_2O). After stirring for 30 min at 23 ºC, the reaction mixture was filtered. To the filtrate was added NaOH (10%, v/v in H_2O, 250 mL). The suspention was filtered and the solid residue washed with water (3 × 20 mL) to afford 1.86 g Ag_2O (80%) as a brown powder.

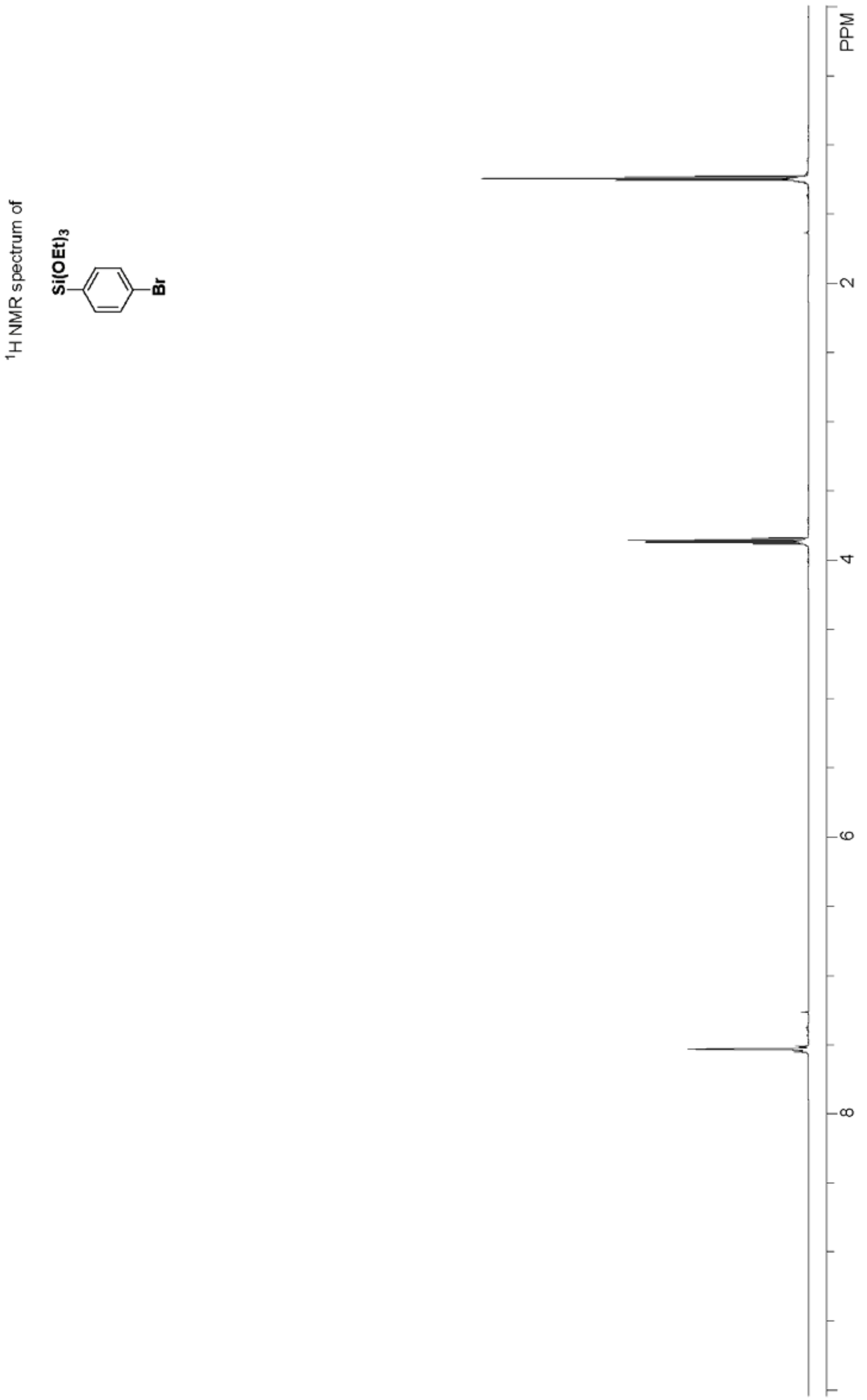
Spectroscopic Data



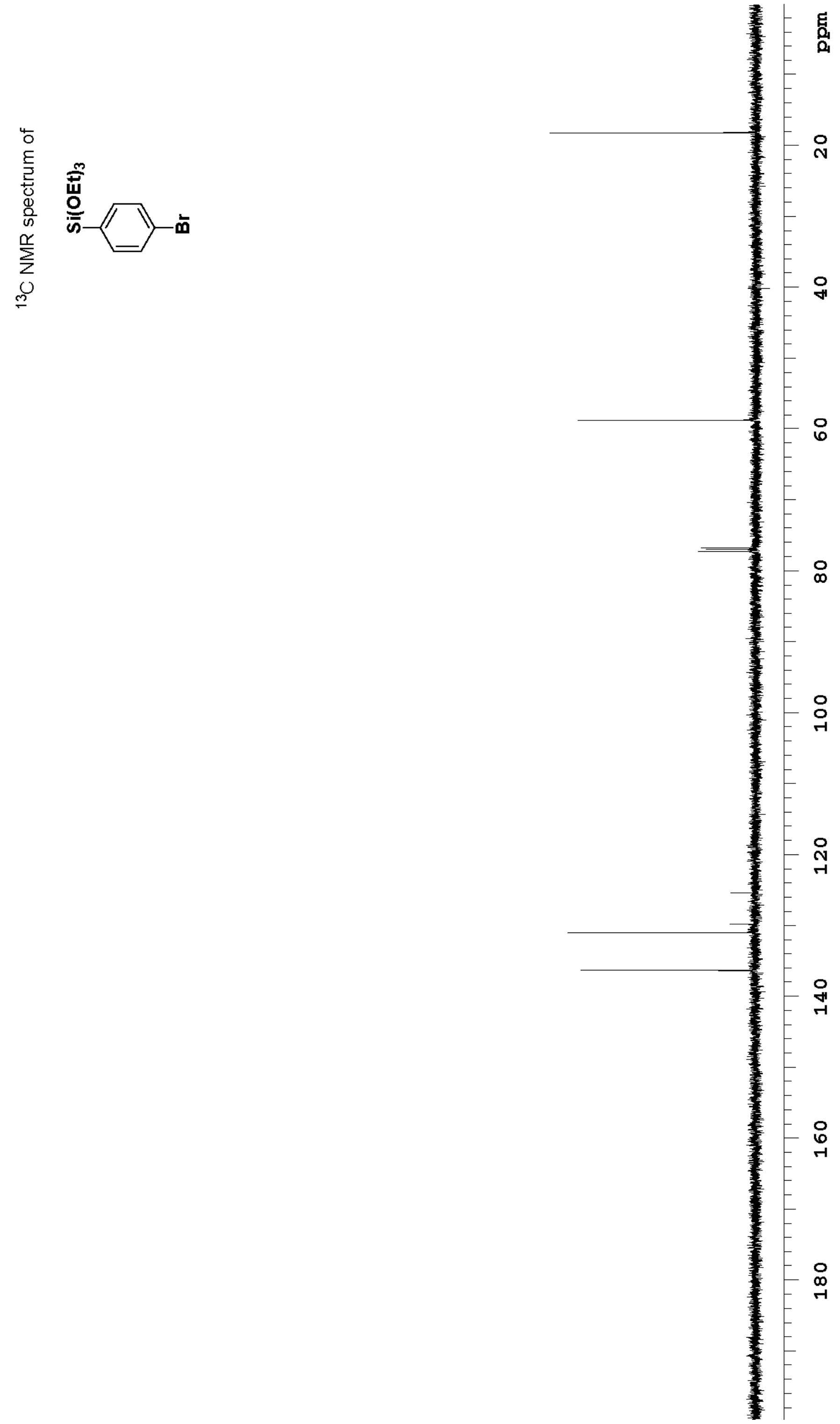
^{1}H NMR spectrum (500 MHz, CDCl$_3$, 23 ºC) of **2**



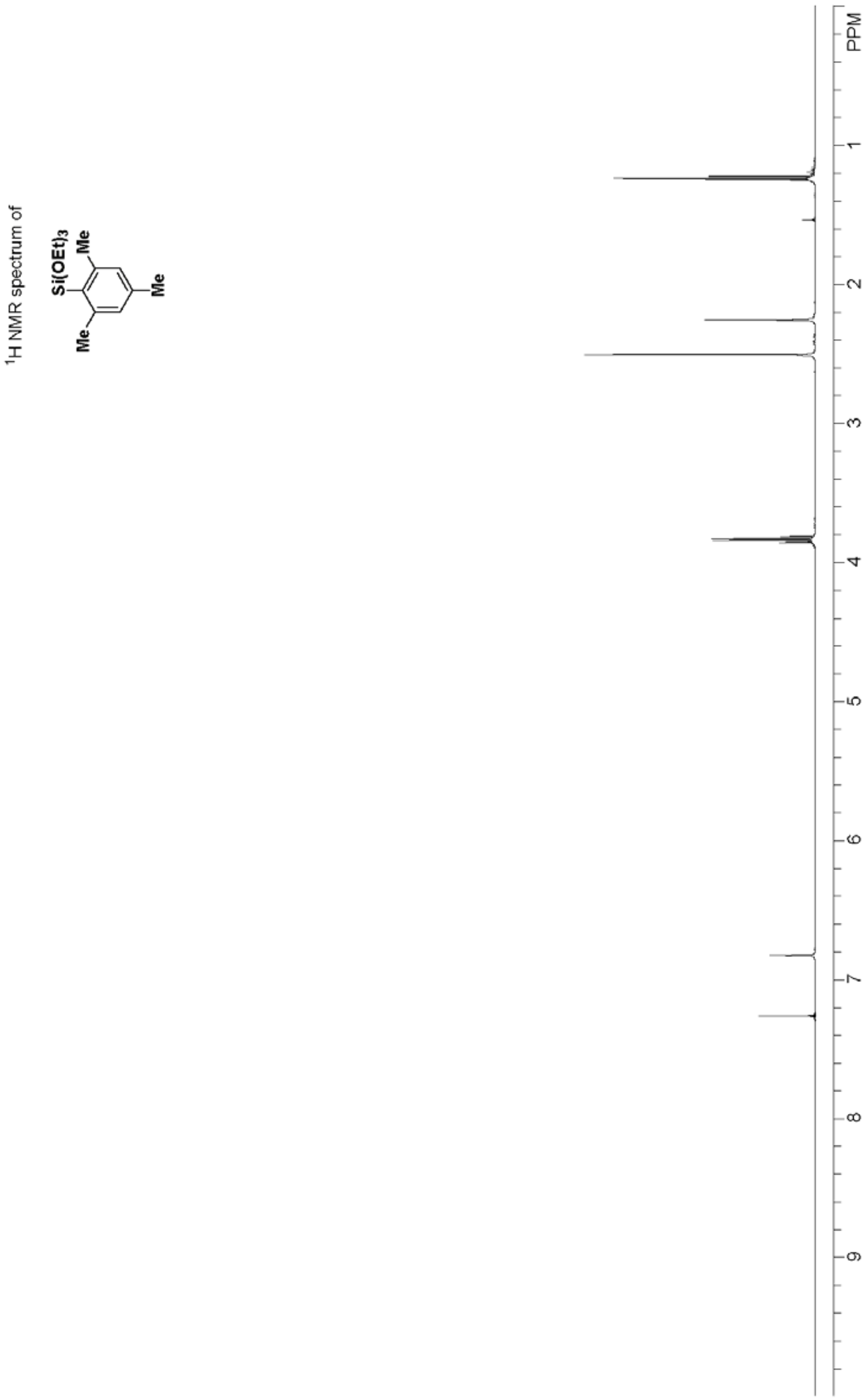
^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23 ºC) of **2**



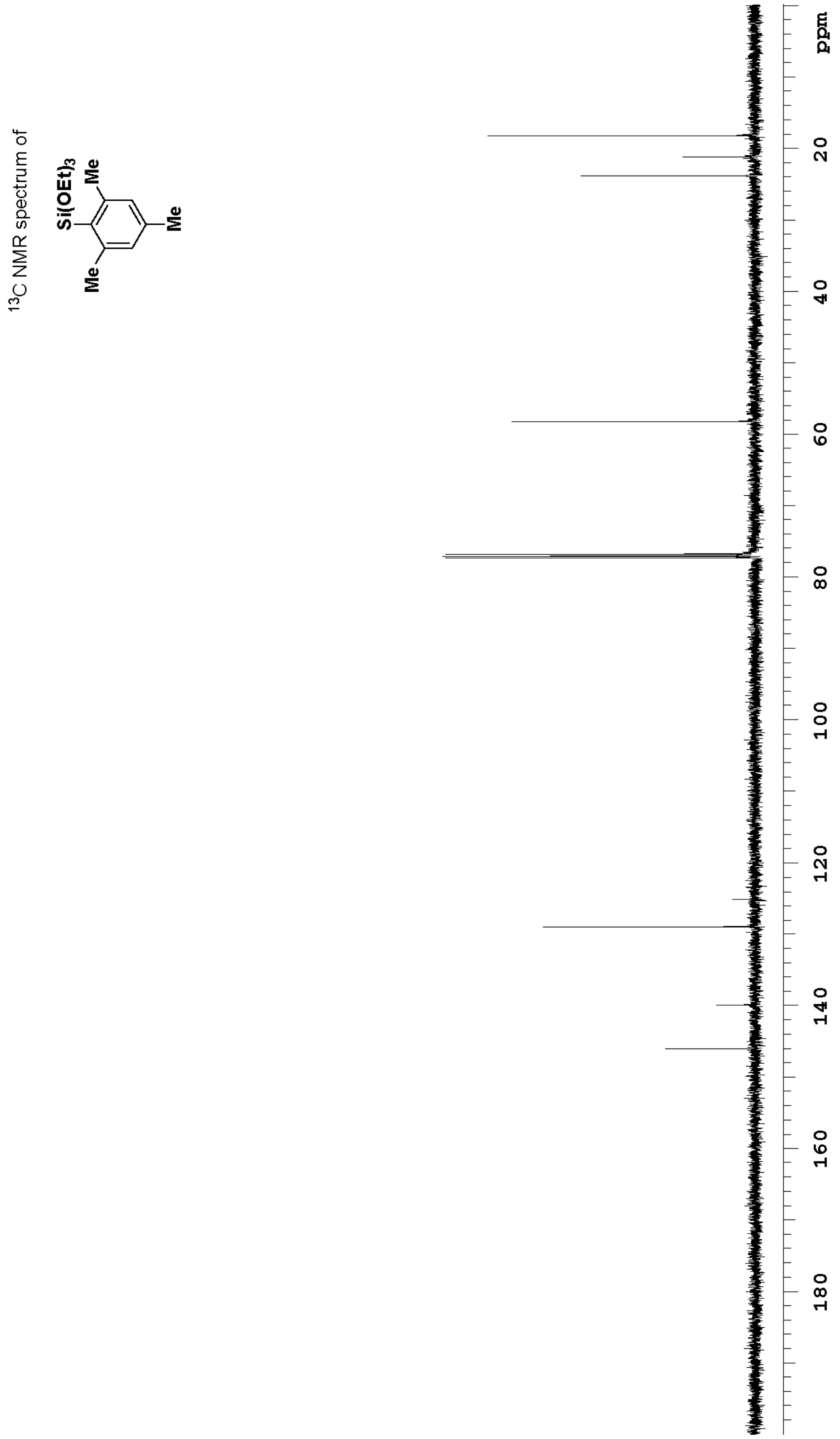
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **S1**



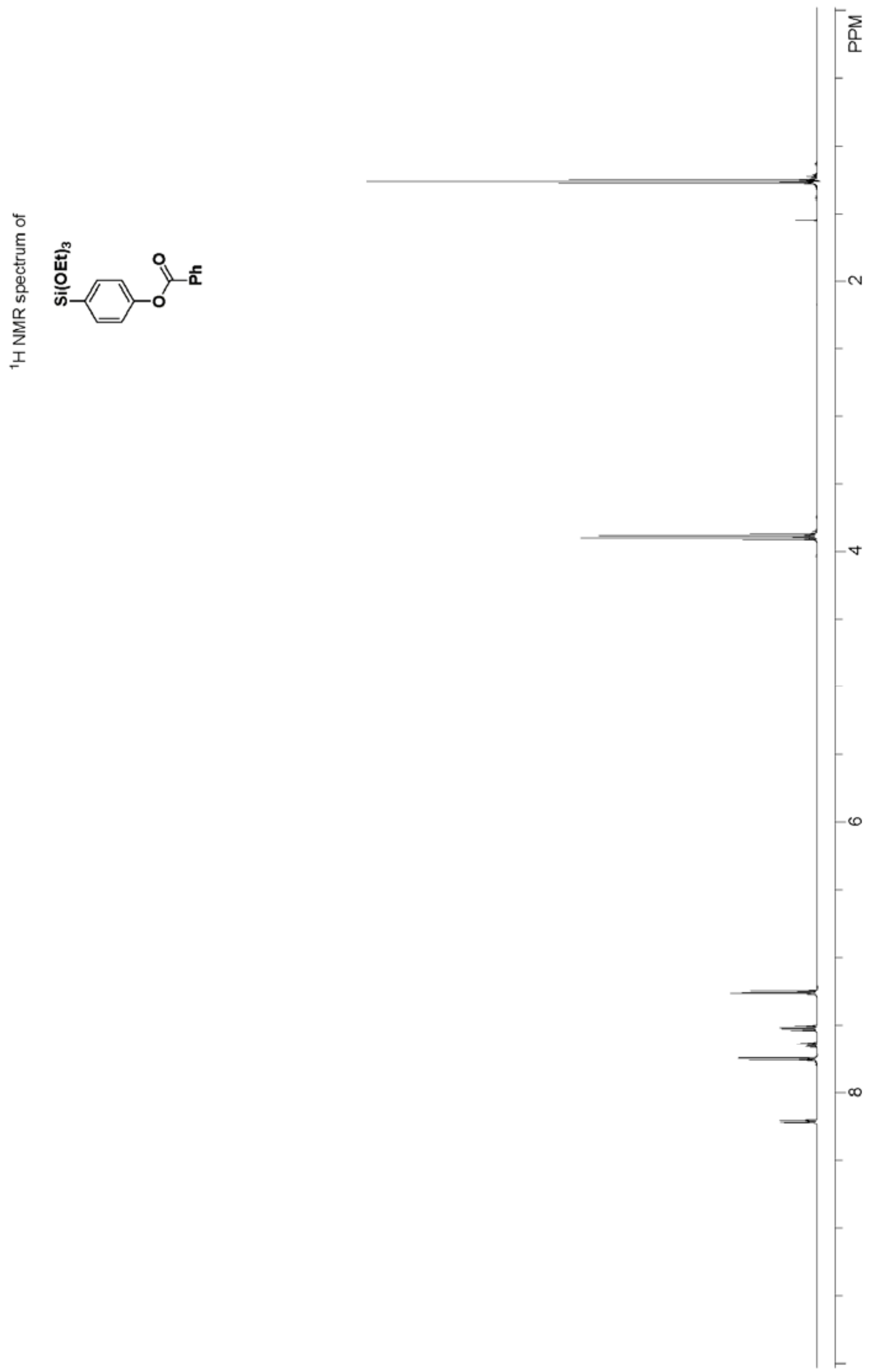
^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23 ºC) of **S1**



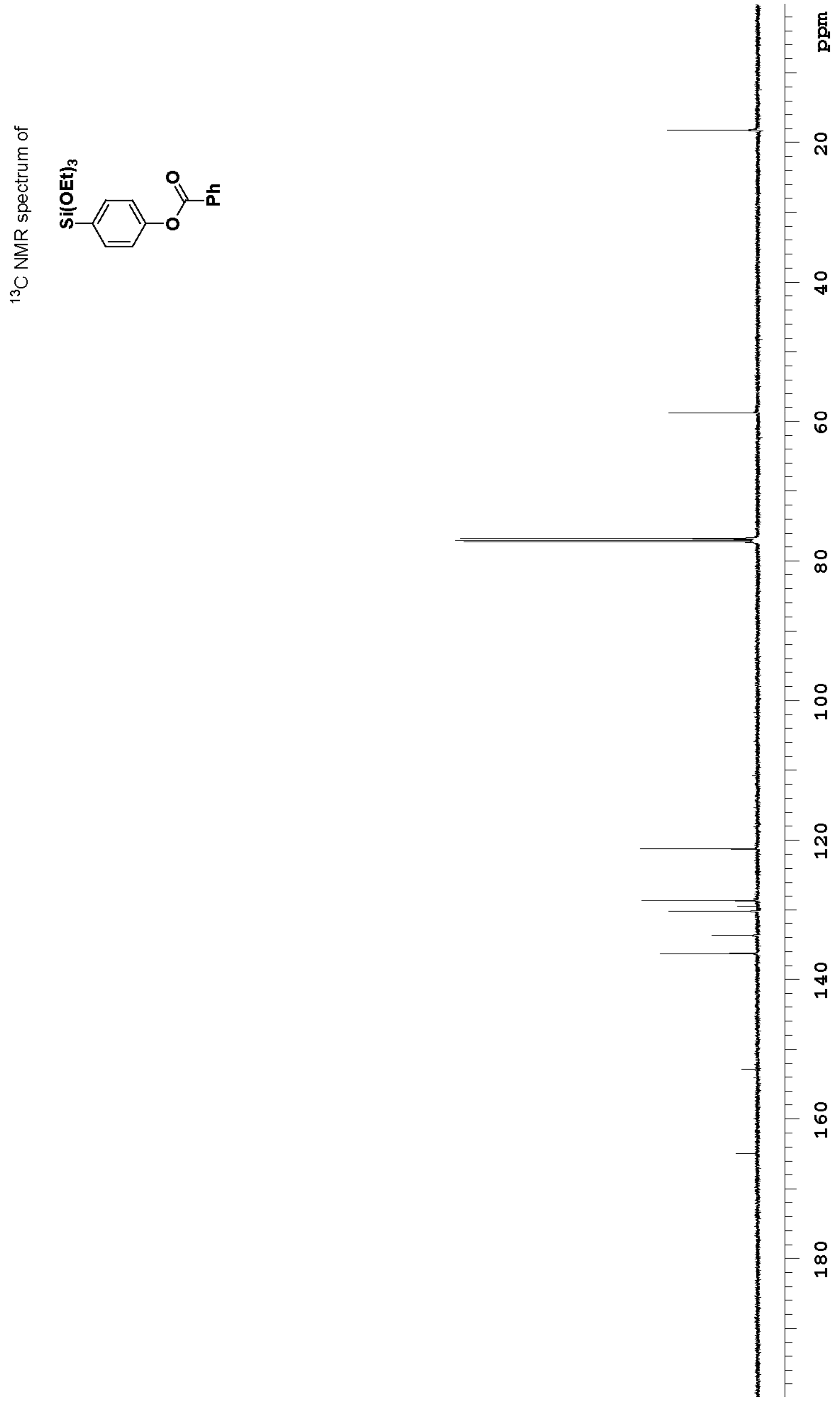
^{1}H NMR spectrum (500 MHz, CDCl$_3$, 23 ºC) of **S2**



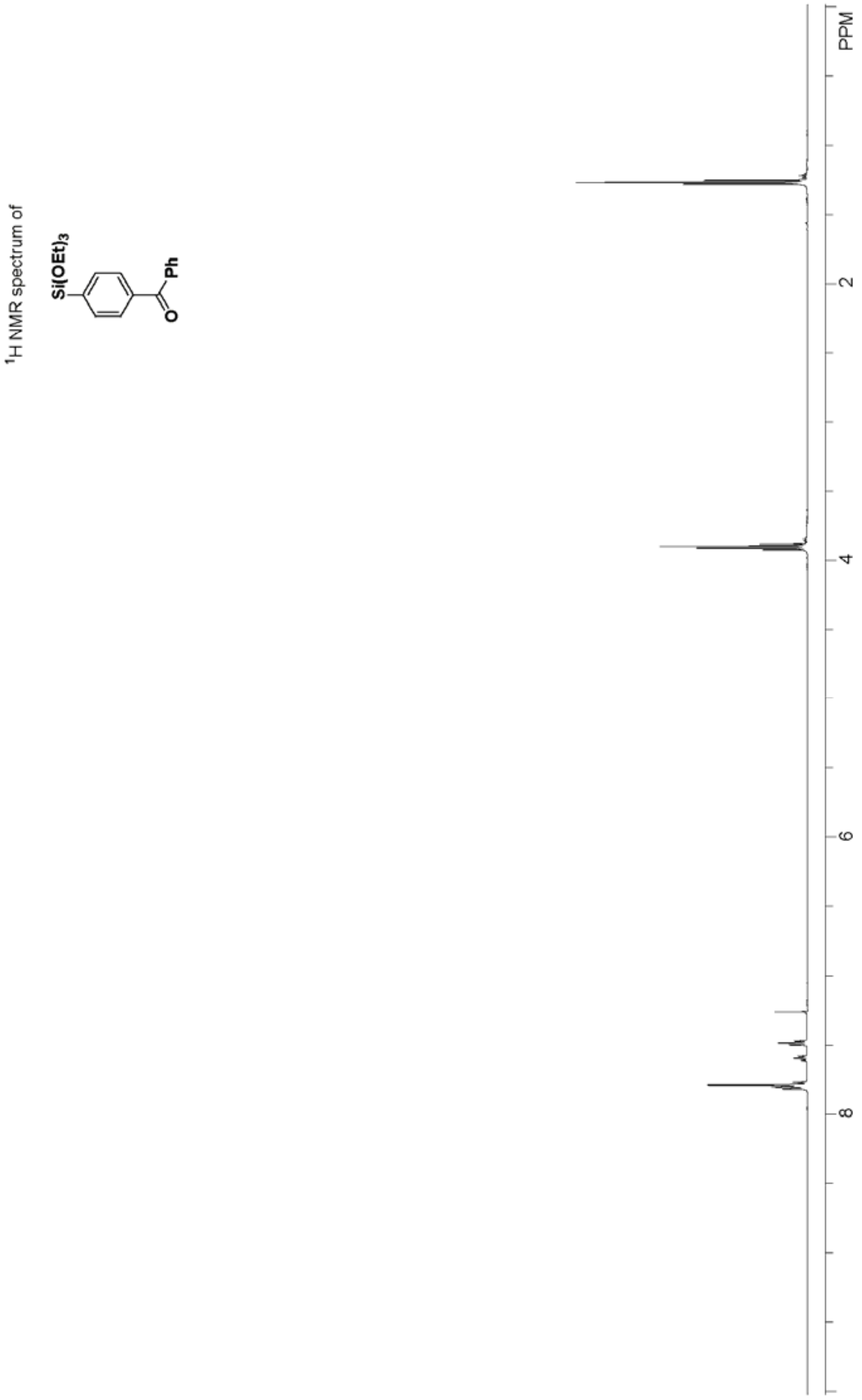
^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23 ºC) of **S2**



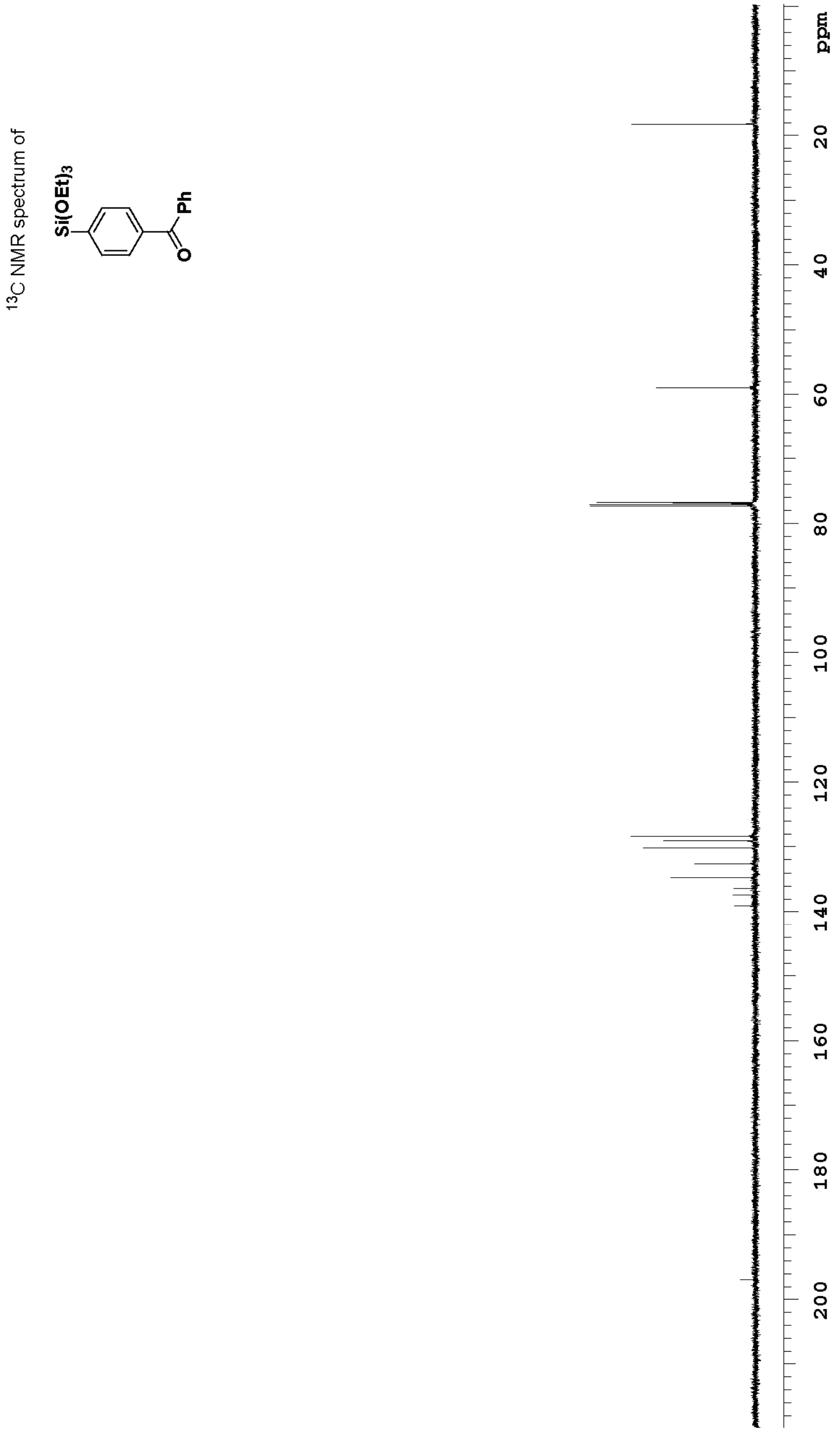
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **S3**



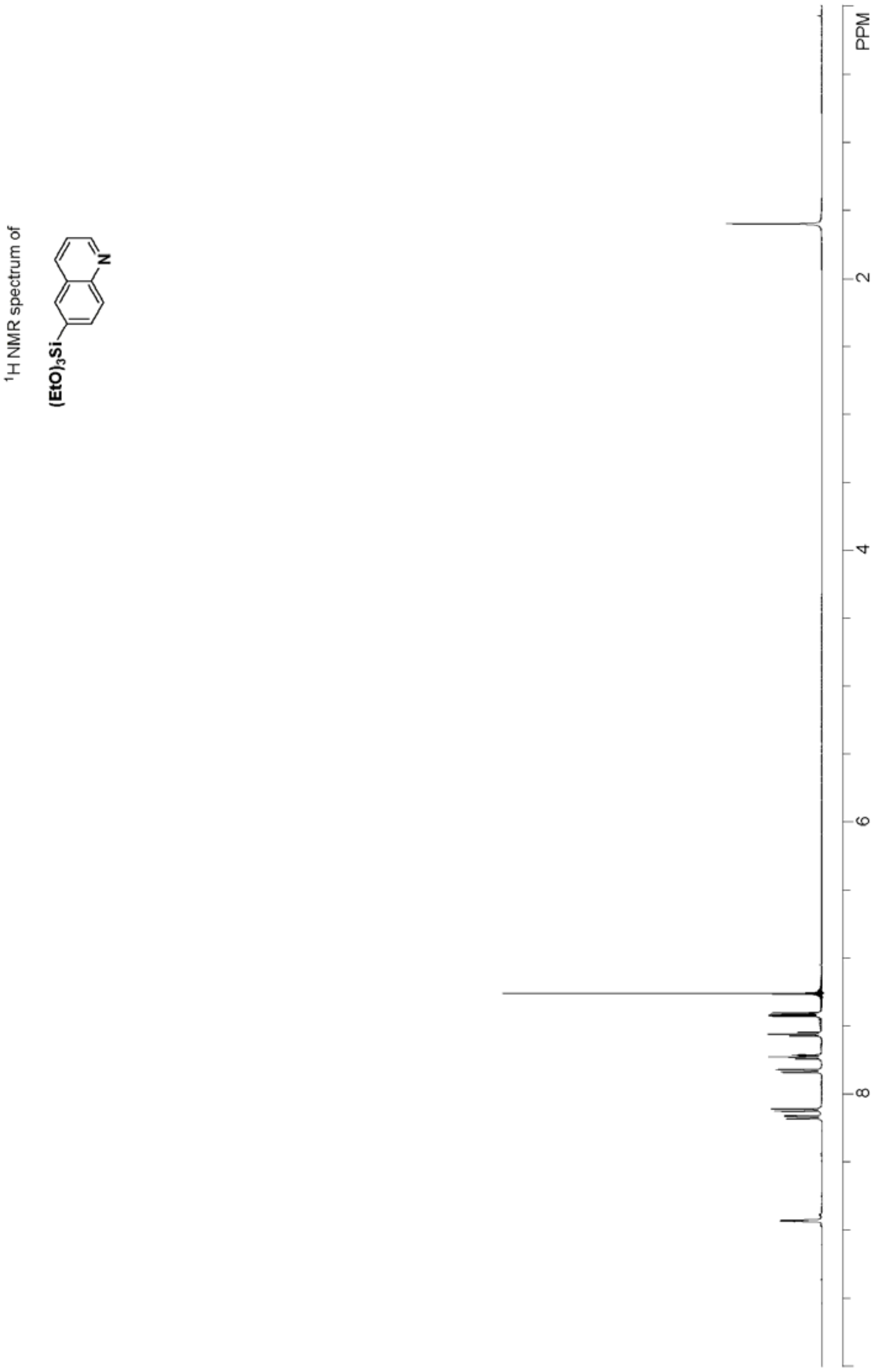
^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23 ºC) of **S3**



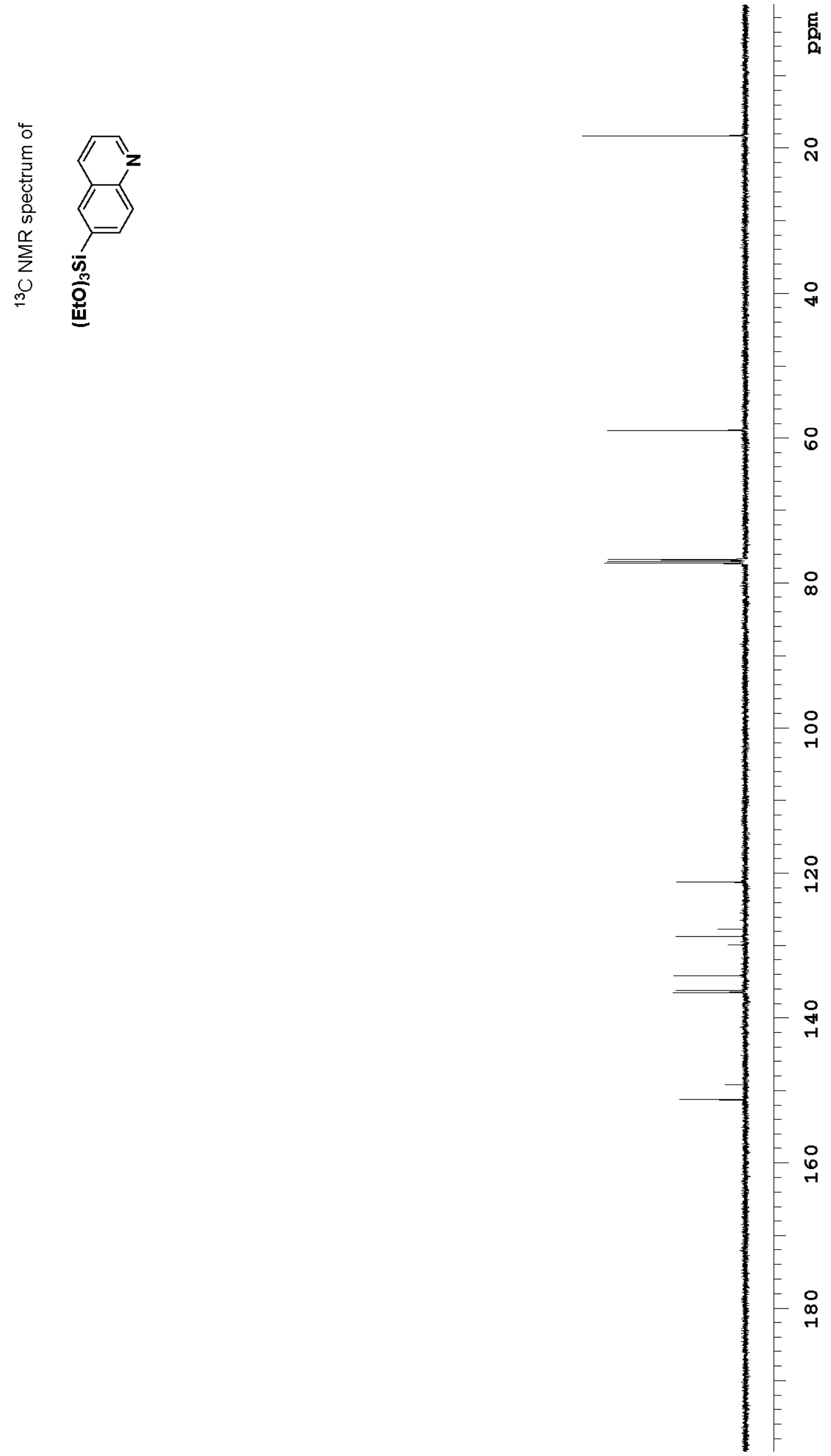
^{1}H NMR spectrum (500 MHz, CDCl$_3$, 23 ºC) of **S4**



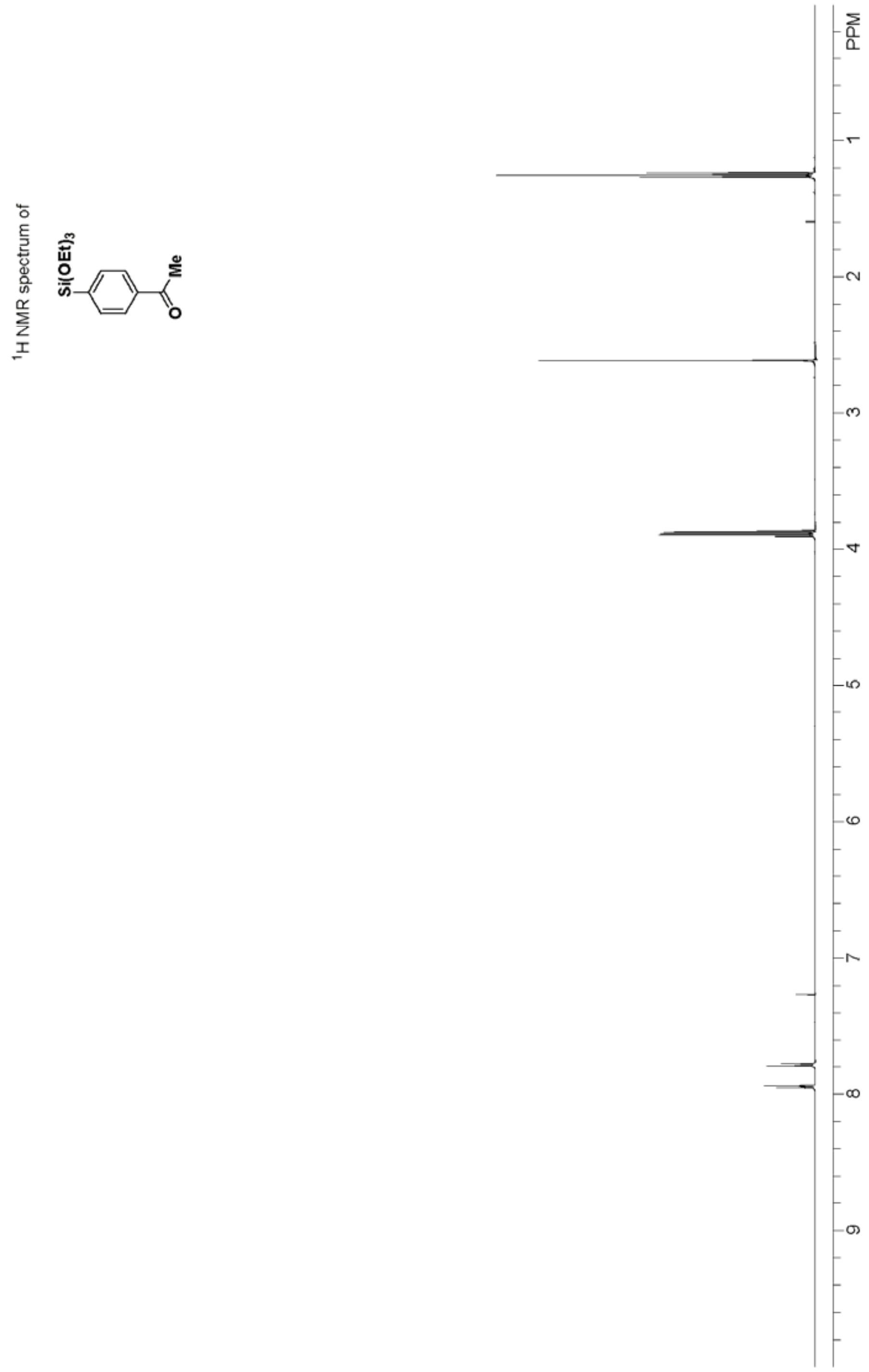
^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23 ºC) of **S4**



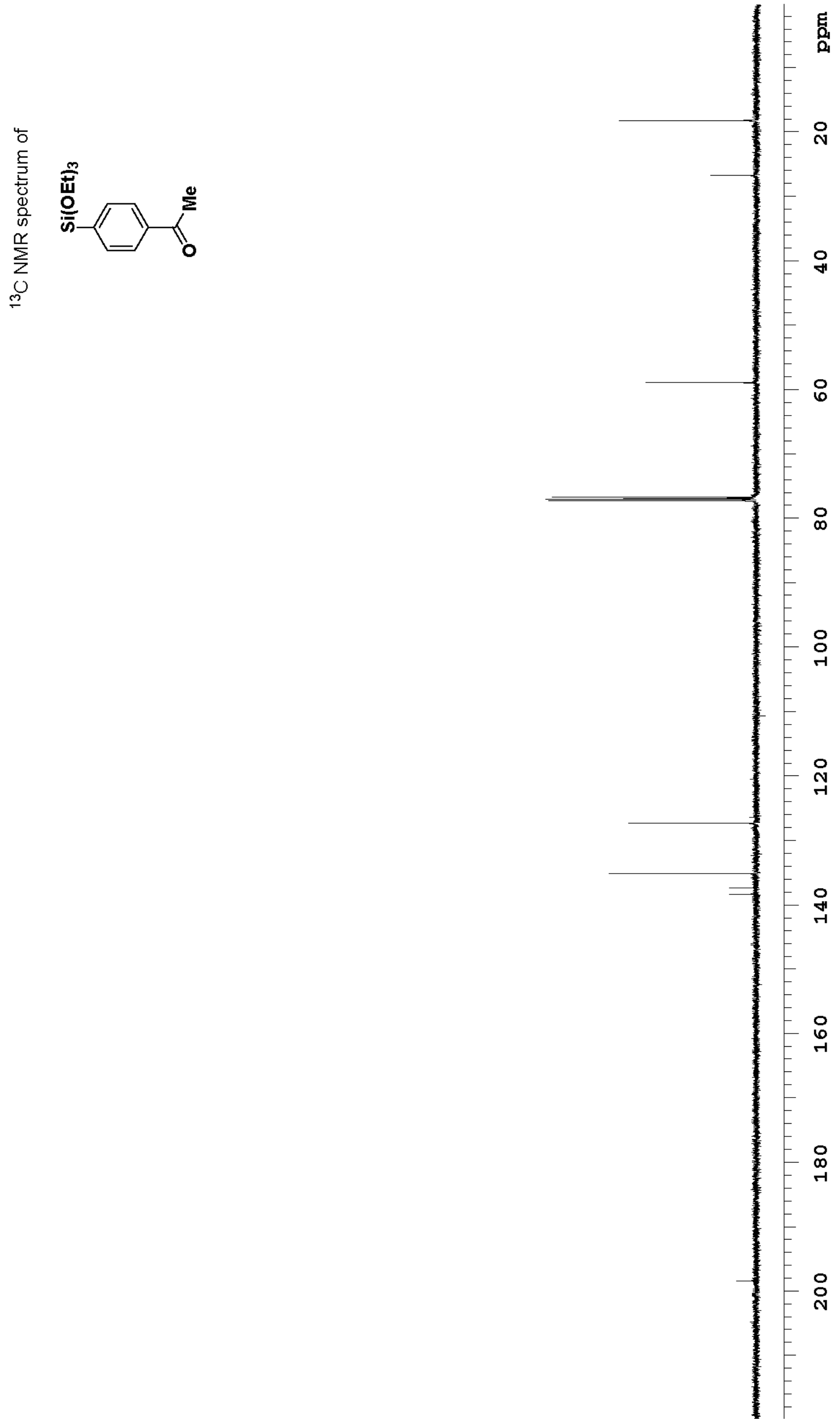
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **S5**



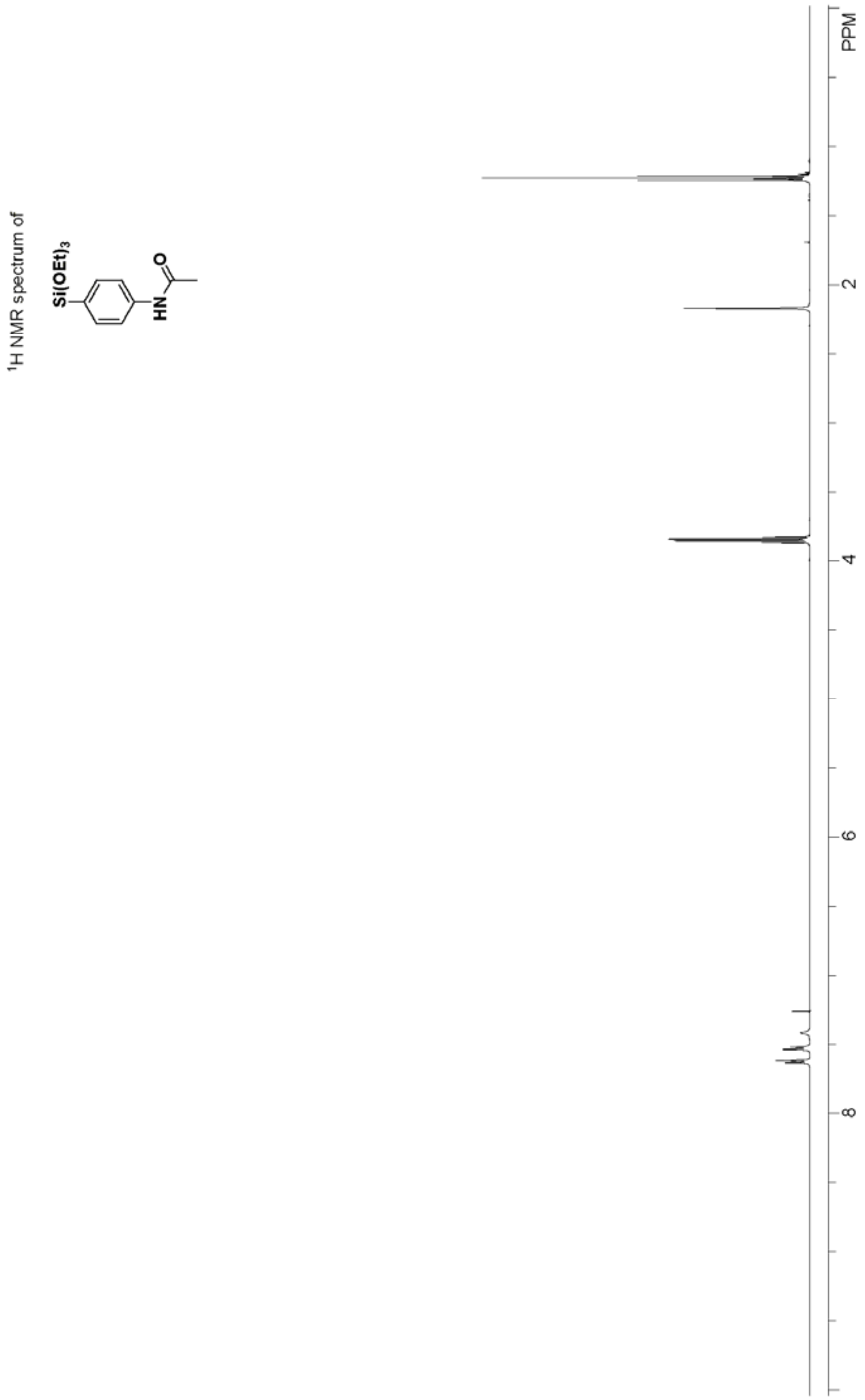
^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23 ºC) of **S5**



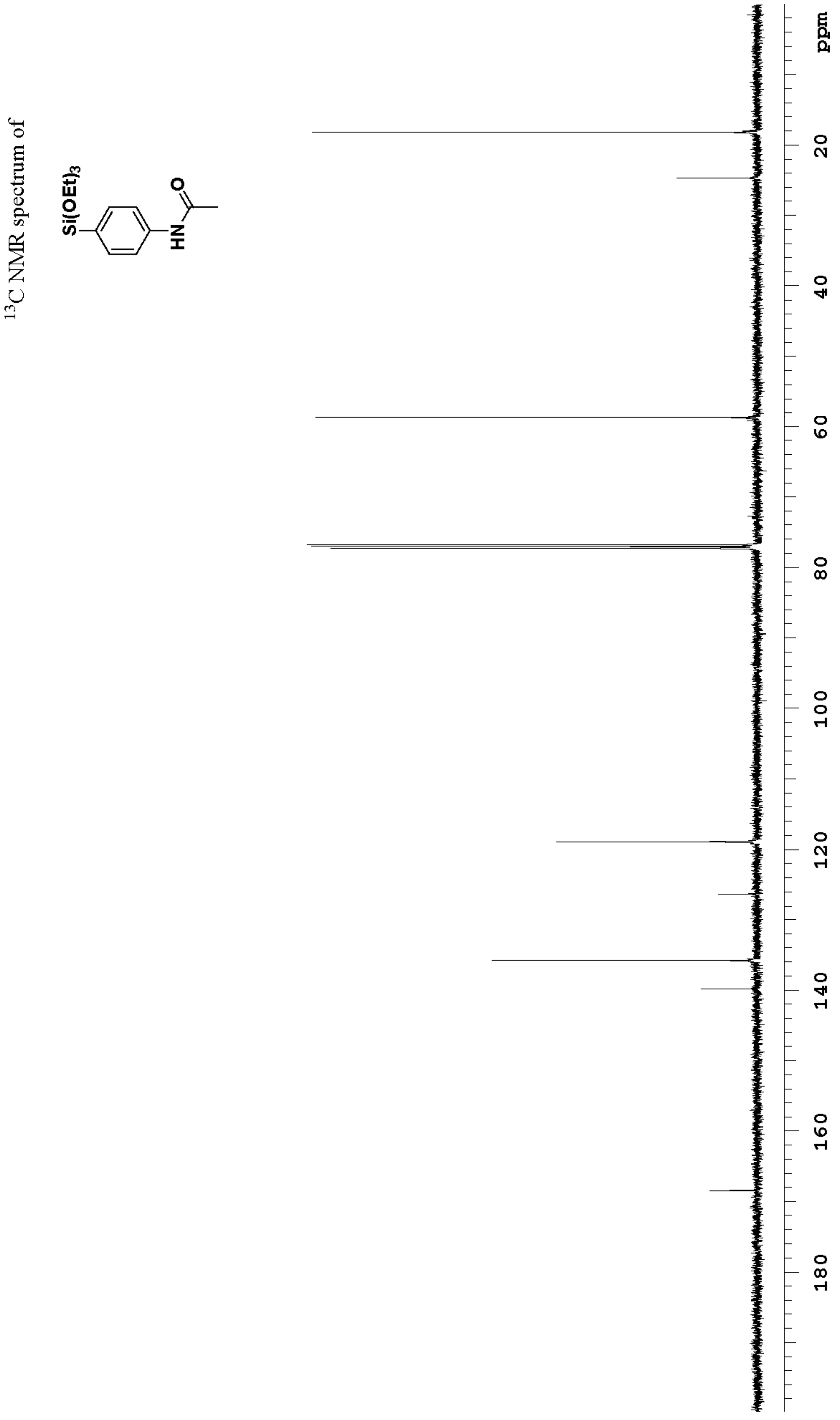
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **S6**



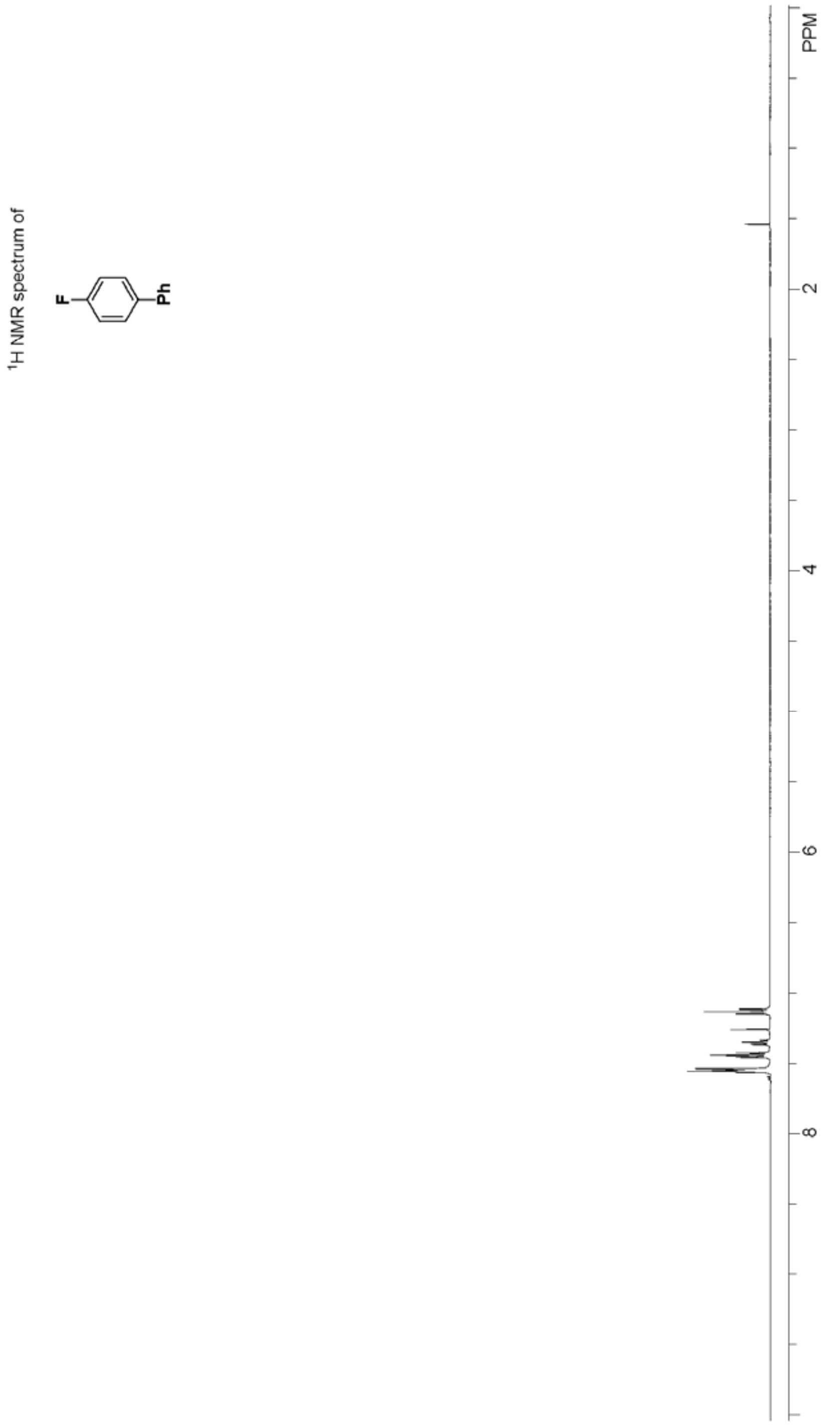
^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23 ºC) of **S6**



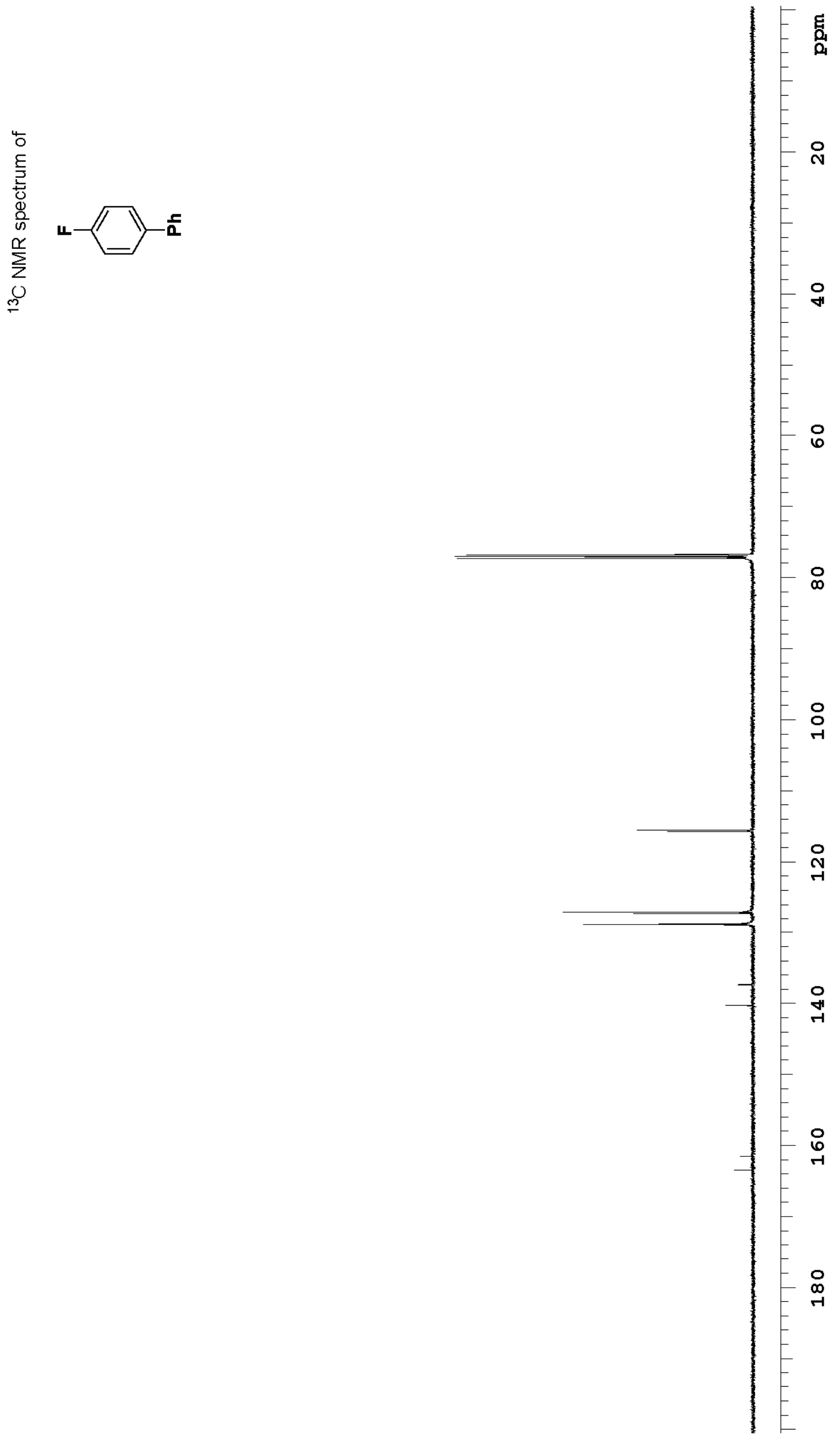
^{1}H NMR spectrum (500 MHz, CDCl$_3$, 23 ºC) of **S7**



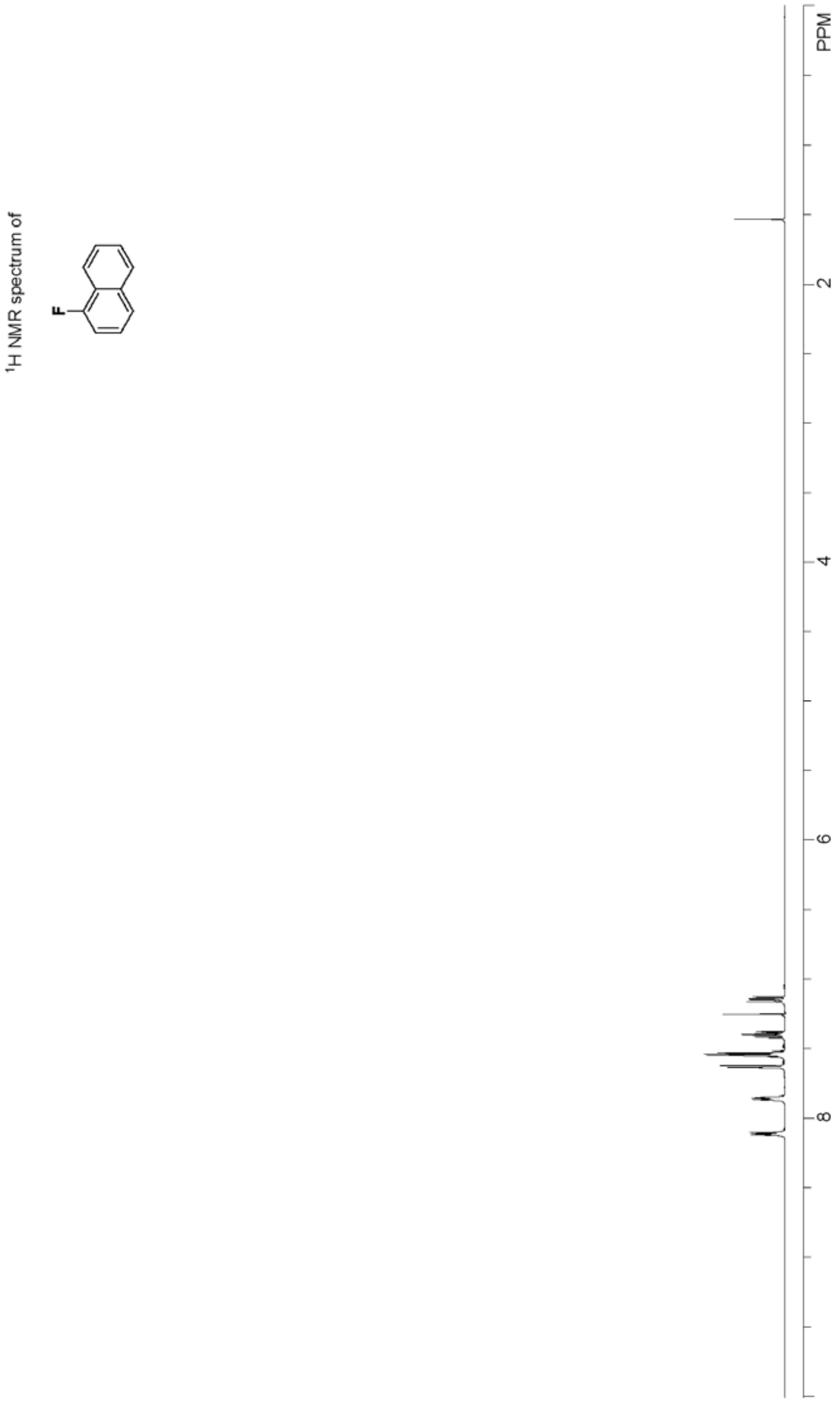
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **S7**



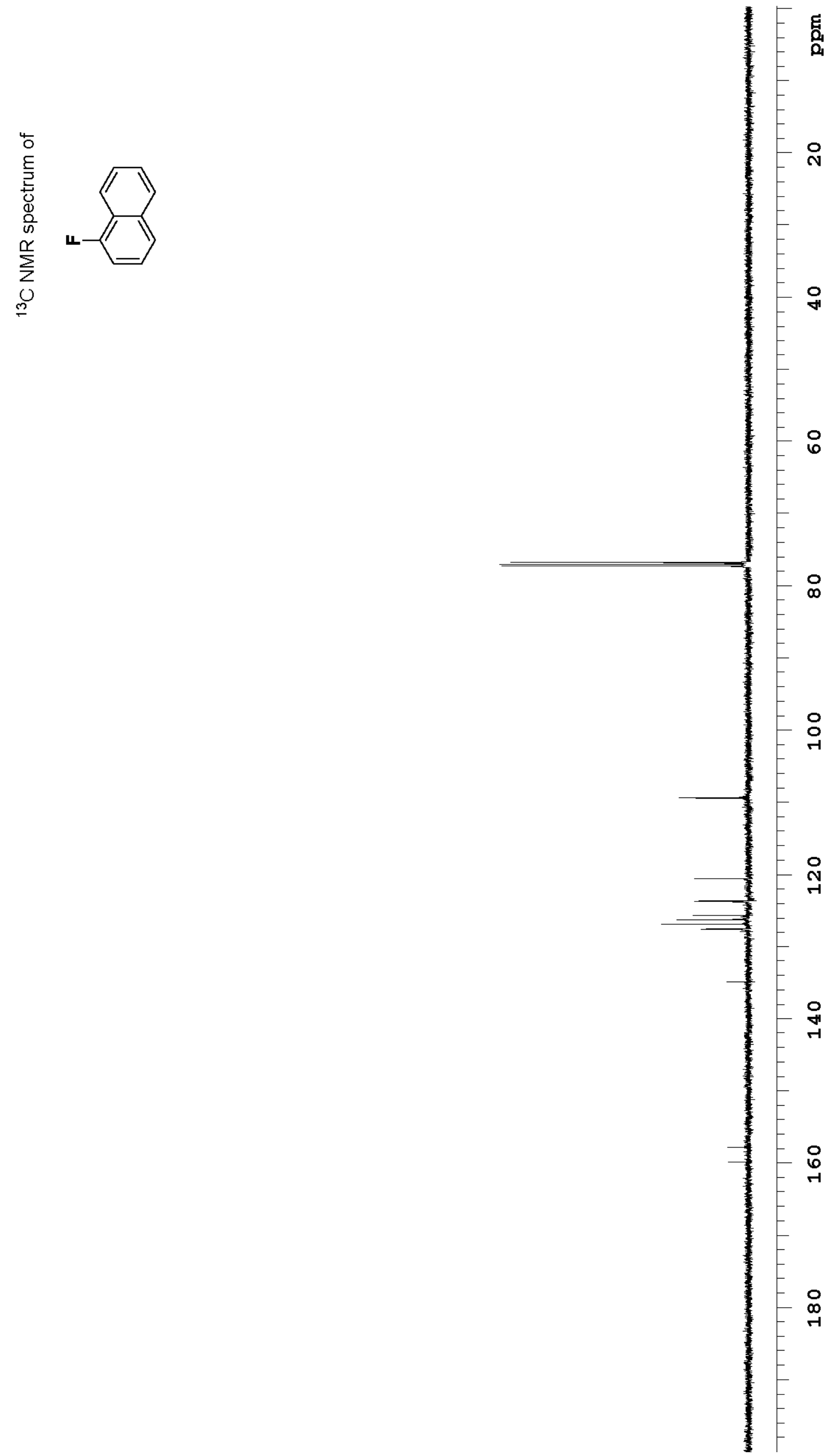
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **3**



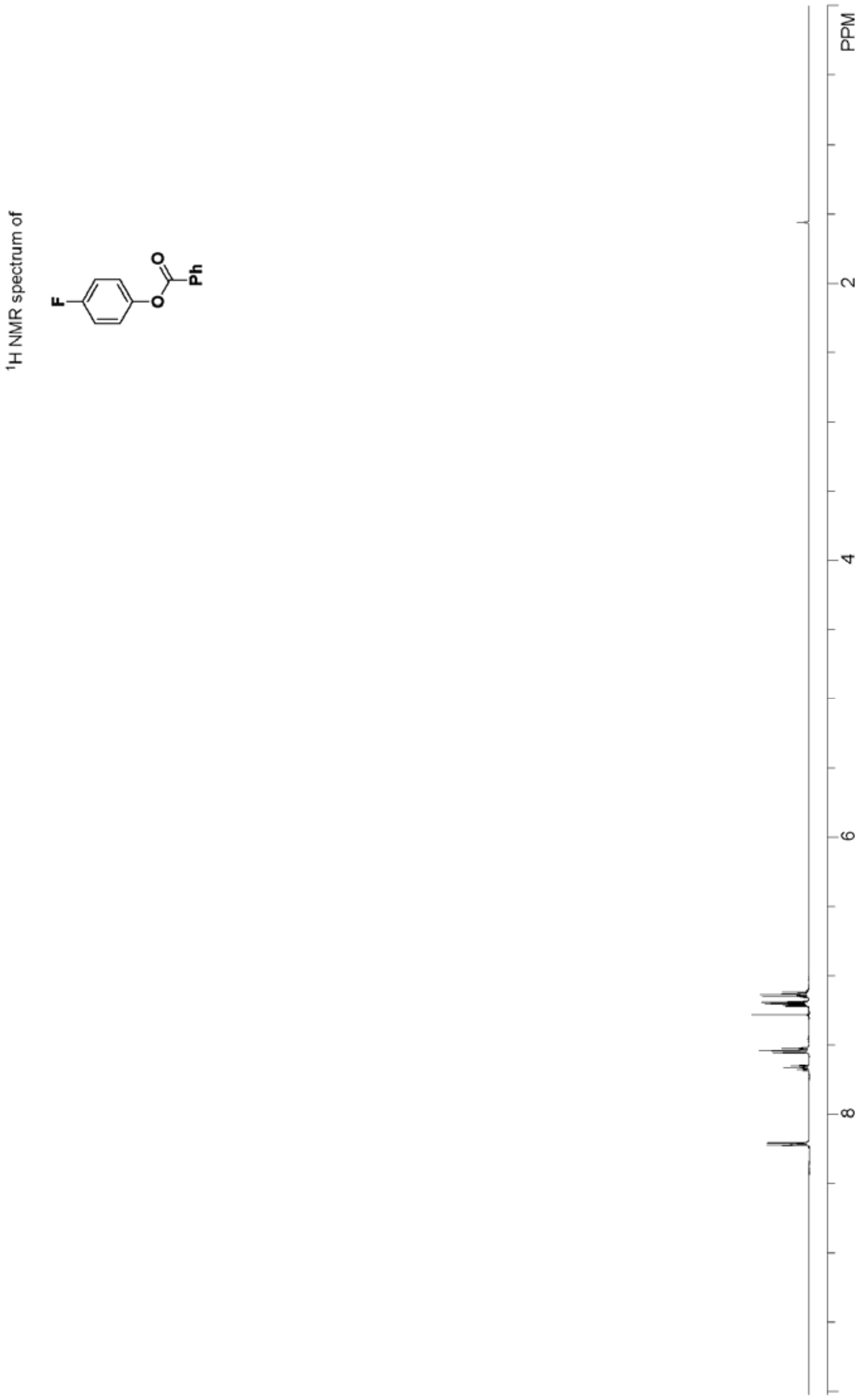
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **3**



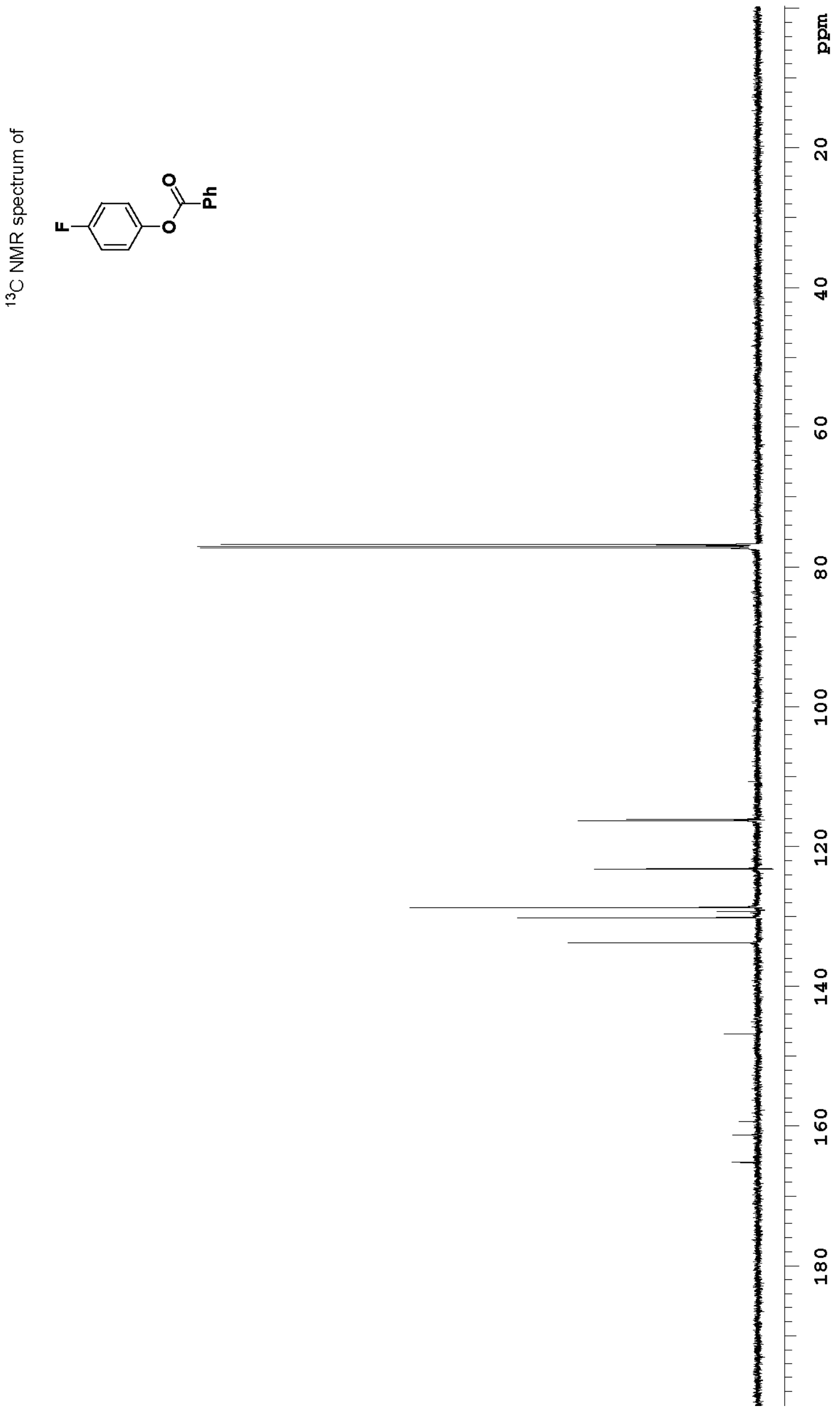
^{1}H NMR spectrum (500 MHz, CDCl$_3$, 23 ºC) of **9**



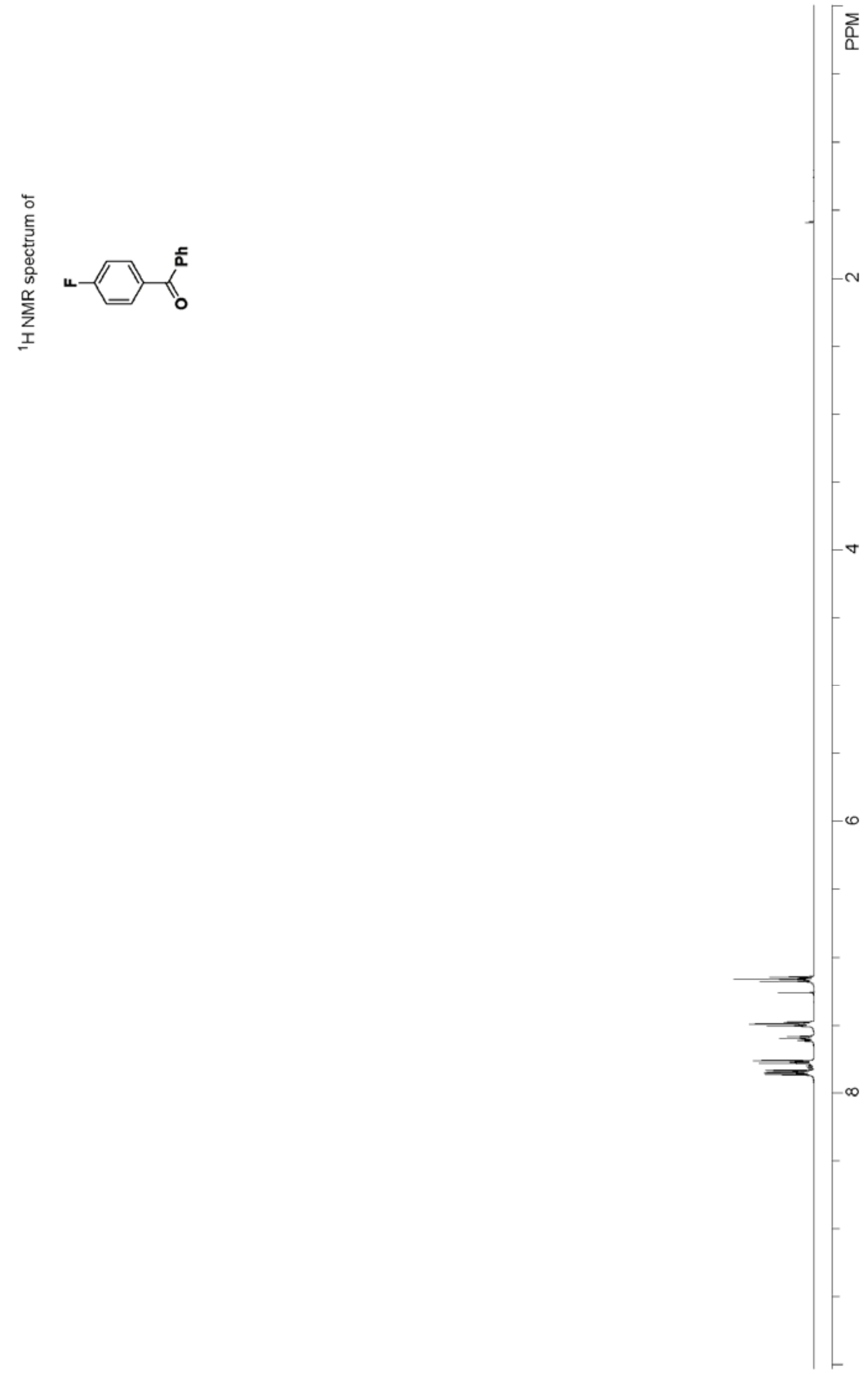
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **9**



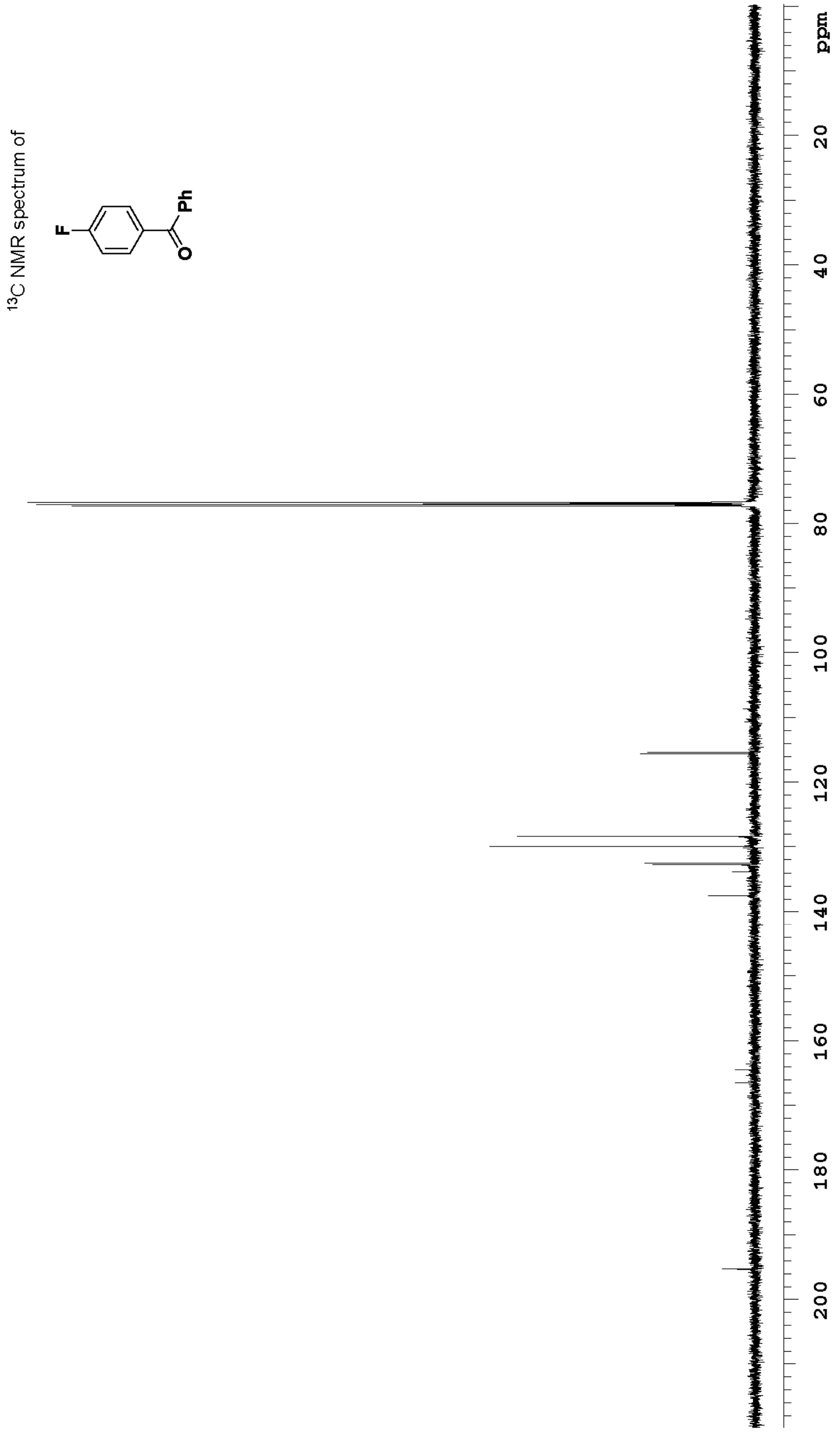
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **12**



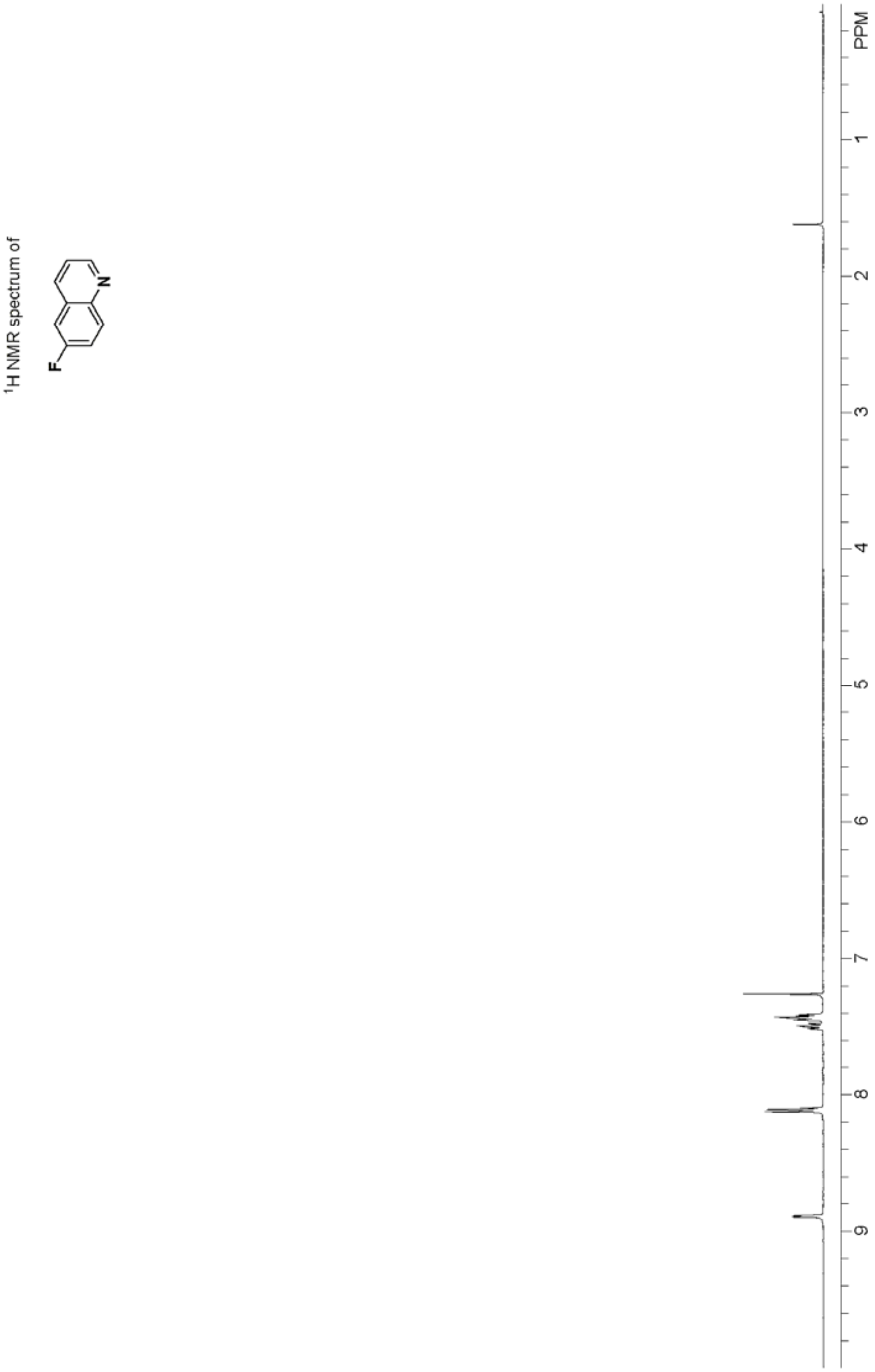
^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23 °C) of **12**



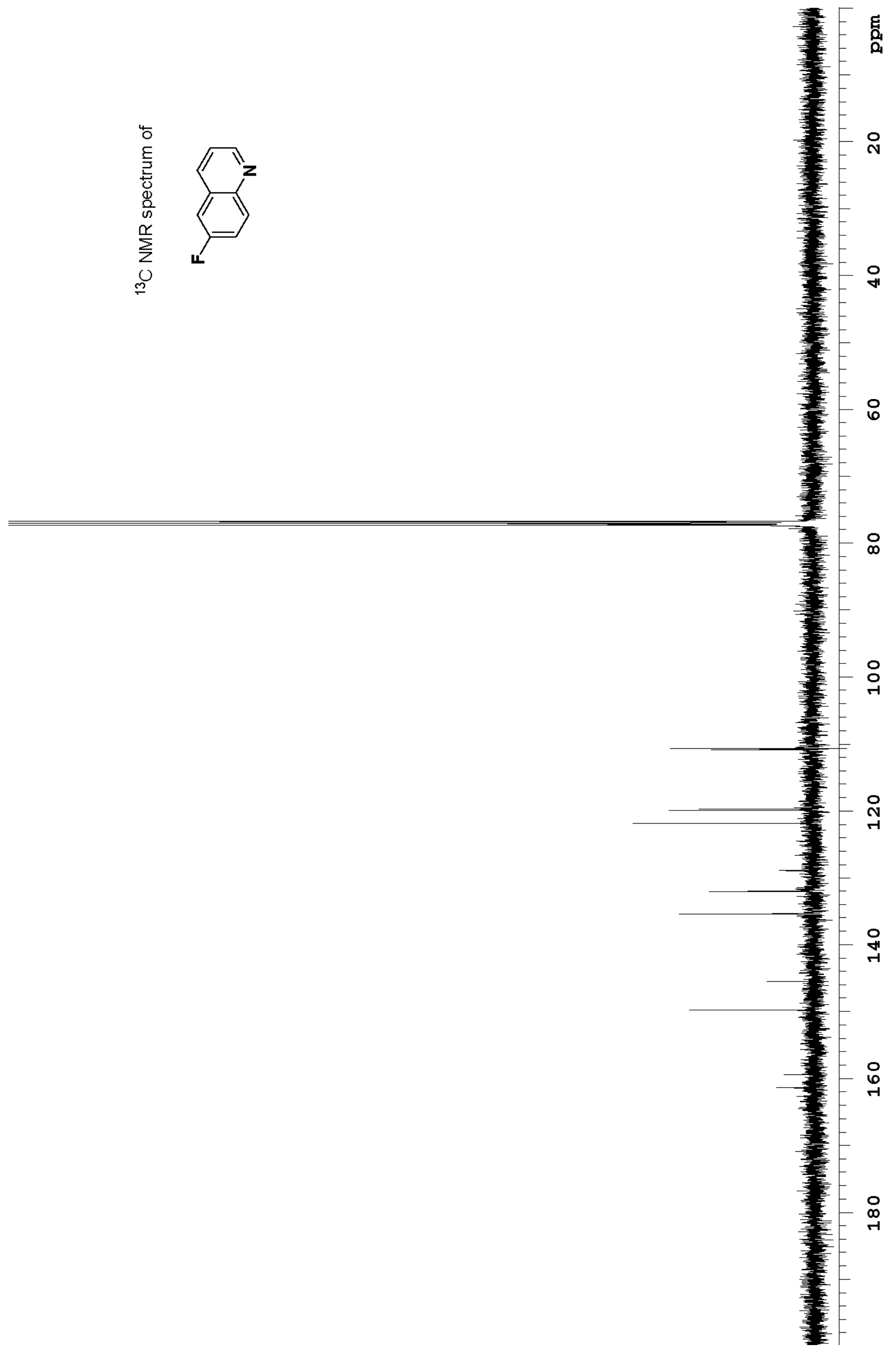
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **13**



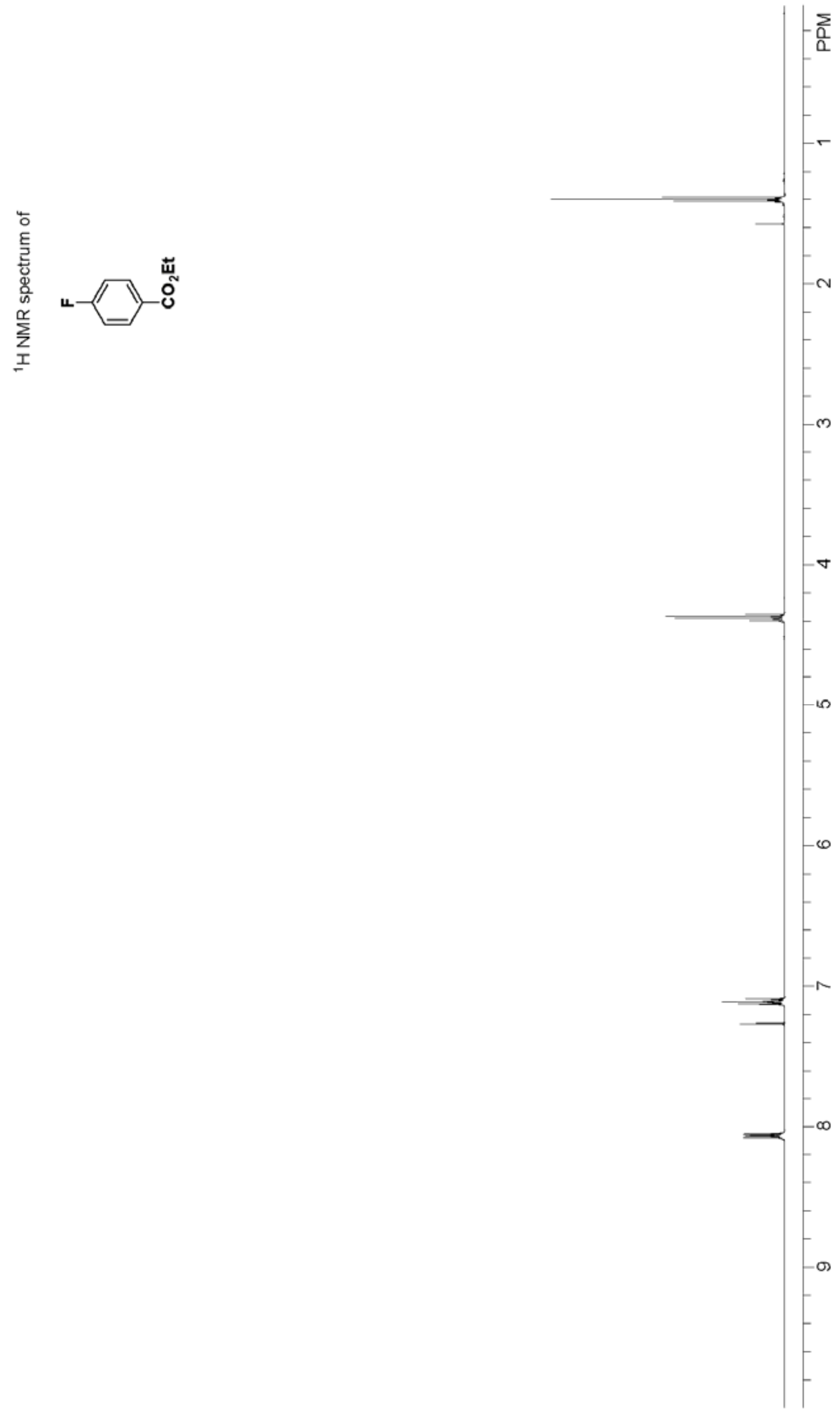
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **13**



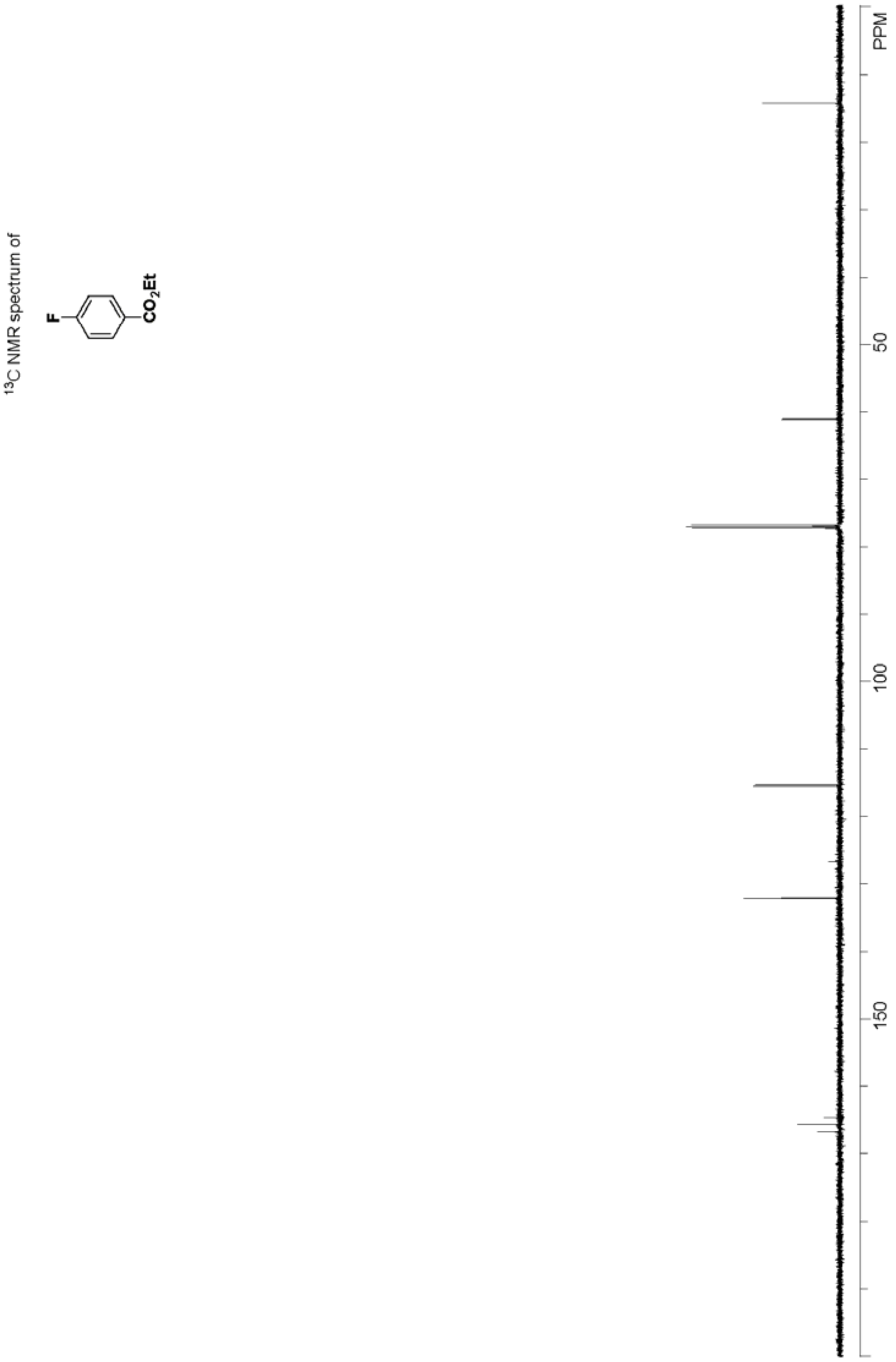
^{1}H NMR spectrum (500 MHz, $CDCl_3$, 23 ºC) of **14**



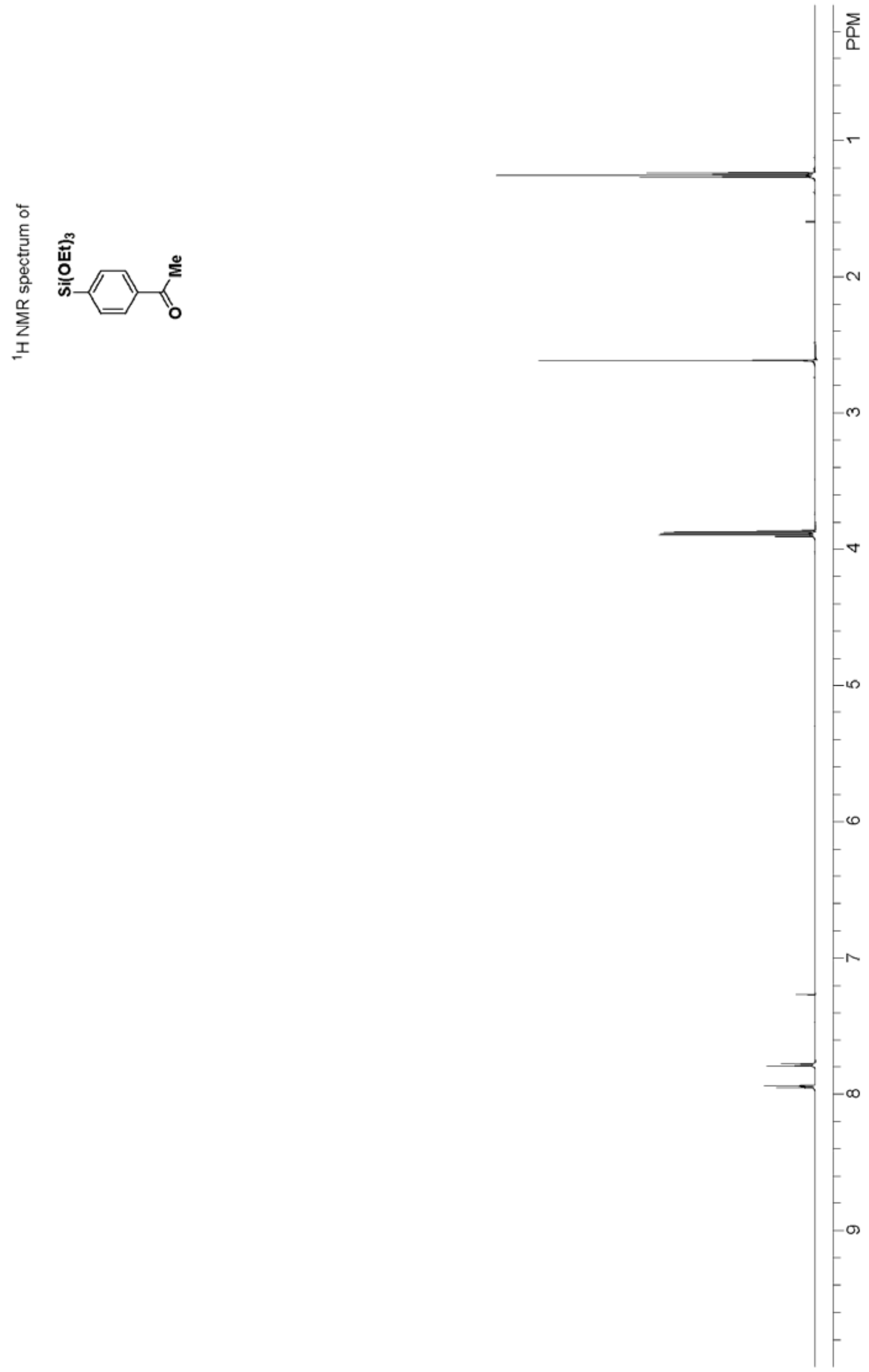
^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 ºC) of **14**



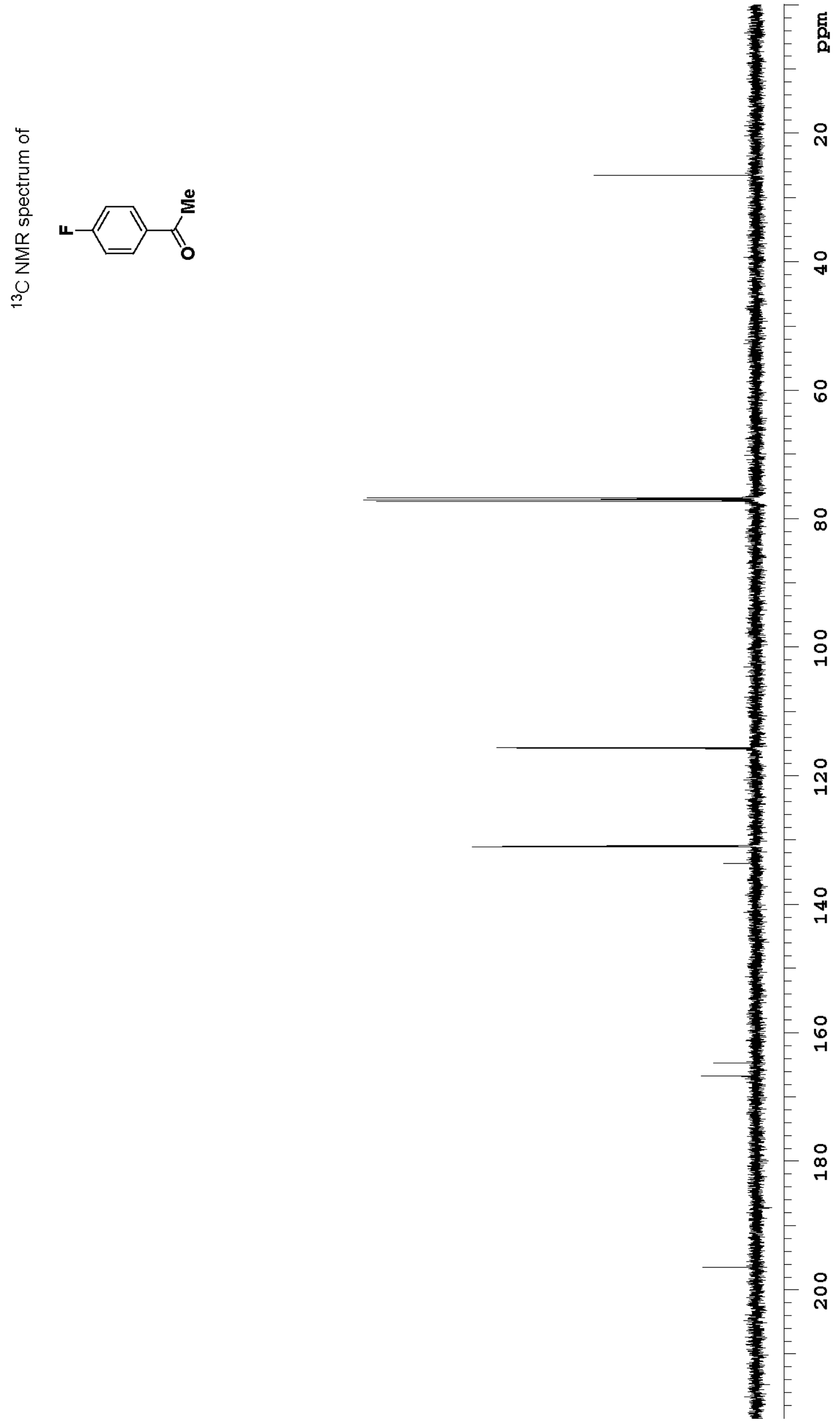
^{1}H NMR spectrum (500 MHz, CDCl$_3$, 23 ºC) of **16**



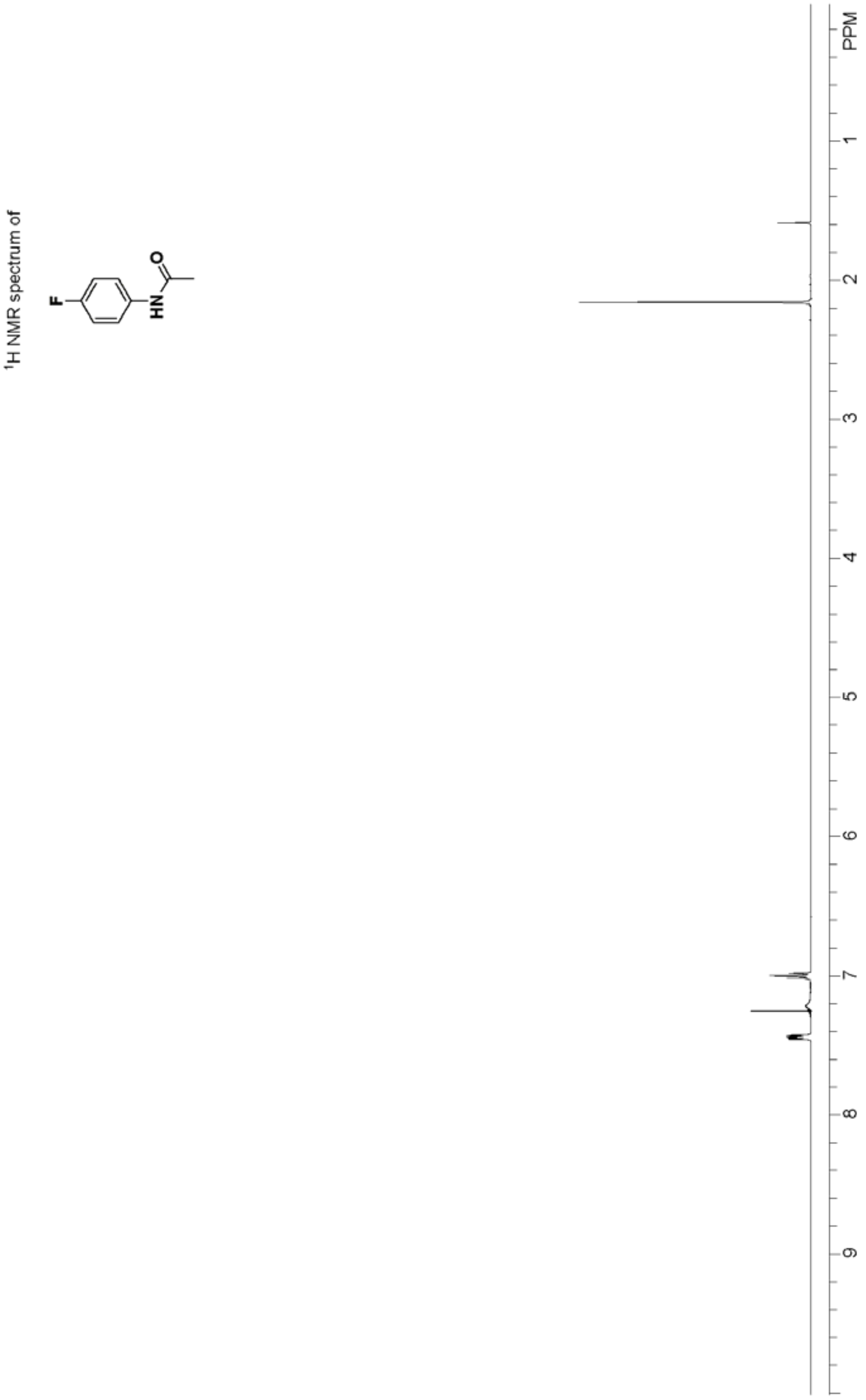
^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23 ºC) of **16**



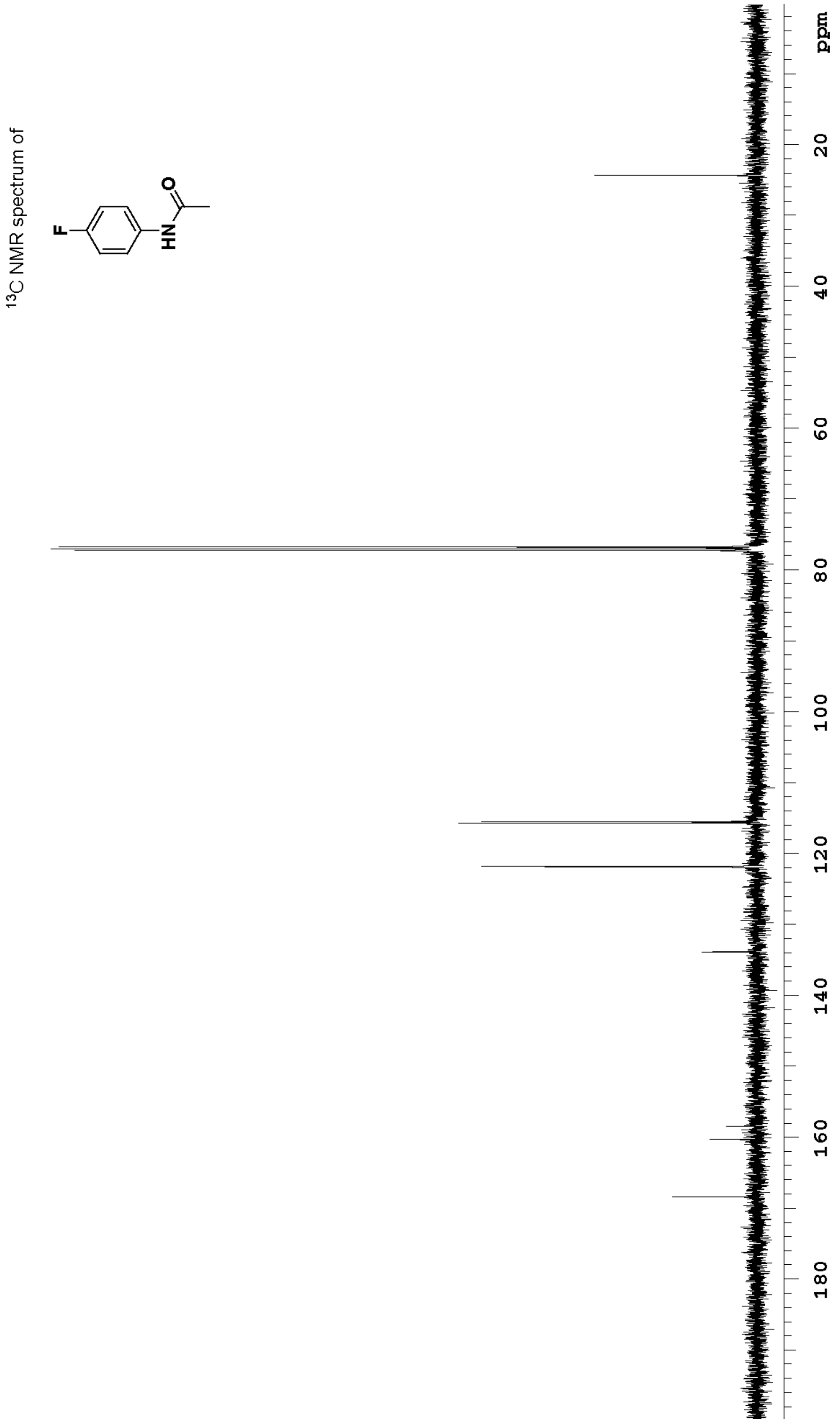
^{1}H NMR spectrum (500 MHz, CDCl$_3$, 23 ºC) of **17**



^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23 ºC) of **17**



^{1}H NMR spectrum (500 MHz, CDCl$_3$, 23 ºC) of **18**



^{13}C NMR spectrum (125 MHz, $CDCl_3$, 23 °C) of **18**